

Universidad de Oviedo

Departamento de Química Orgánica e Inorgánica

**Activación de N-heterociclos
aromáticos coordinados a fragmentos
organometálicos**

Tesis Doctoral

Programa de Doctorado: Síntesis y Reactividad Química

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Artículo I (Capítulo 2)

Título: Re-mediated C-C Coupling of Pyridines and Imidazoles

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Índice de impacto (2012): 10.677

En esta comunicación se describe la síntesis de ligandos 2,2'-piridilimidazol por acoplamiento de dos ligandos monodentados coordinados a un fragmento *fac*-tricarbonílico de renio (I). Se trata de un nuevo método, radicalmente diferente a los conocidos, para efectuar este tipo de acoplamientos, en el que la coordinación al metal es la única prefuncionalización requerida. El trabajo experimental de esta comunicación fue llevado a cabo prácticamente en su totalidad por Maialen Espinal. En estudios previos a que Maialen comenzara su tesis doctoral, Miguel A. Huertos había obtenido inesperadamente uno de estos productos de acoplamiento. Maialen fue la encargada de racionalizar el método de síntesis, así como de extenderlo a los otros derivados incluidos en esta comunicación, demostrando, por tanto, la generalidad de este método.

Artículo II (Capítulo 2)

Título: C-C Coupling of N-heterocycles at the *fac*-{Re(CO)₃} fragment: synthesis of pyridylimidazole and bipyridine ligands.

Publicado en: *Chem. Eur. J.* **2014**, *20*, 5732-5740.

Índice de impacto (2013): 5.696

Este artículo constituye el *Full Paper* de la comunicación anterior. En el mismo se extienden los estudios previamente realizados a otros ligandos N-heterocíclicos monodentados, teniendo una especial relevancia la síntesis de 2,2'-bipiridinas a partir de dos piridinas coordinadas, pues este tipo de ligandos son de los más empleados dentro de la Química de Coordinación. La contribución de Maialen en este artículo ha sido fundamental, pues no sólo ha llevado a cabo el trabajo experimental en su totalidad, sino que además ha contribuido al desarrollo de los resultados aportando ideas de gran valía, como por ejemplo el empleo de ligandos piridínicos diferentes para obtener 2,2'-bipiridinas asimétricas, cuya síntesis es, de otra manera, muy problemática.

Artículo III (Capítulo 3)

Título: Influence of the N-N Coligand: C-C Coupling Instead of Formation of Imidazol-2-yl Complexes at {Mo(η^3 -allyl)(CO)₂} Fragments. Theoretical and Experimental Studies

Publicado en: *Inorg. Chem.* **2015**, Article ASAP. DOI: 10.1021/ic502729z.

Índice de impacto (2013): 4.794

En este artículo Maialen Espinal completó y extendió los resultados preliminares obtenidos por Andrea Cebollada, en La Universidad de Zaragoza, bajo la dirección de la Dra. Riera. Estos estudios se centran en la variación de la naturaleza de un ligando diimina coordinado al fragmento {Mo(η^3 -alilo)(CO)₂} para lograr una reactividad diferente de los mismos. La aportación experimental de Maialen se podría cuantificar en, aproximadamente, el 80 %. Asimismo, ha participado aportando ideas, sugiriendo mecanismos de reacción alternativos y relacionando los estudios teóricos con los experimentales, en la colaboración establecida con los Dres. Ramón López (Universidad de Oviedo) y Jesús Díaz (Universidad de Extremadura) para llevar a cabo un estudio computacional sobre la reactividad de los complejos estudiados. El trabajo realizado por Maialen en este artículo lo consideramos, por tanto, imprescindible para la publicación del mismo.

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Lista de abreviaturas empleadas

$\eta^3\text{-C}_4\text{H}_7$	2-metilalilo
Ar	arilo
Ar ^f	3,5-bis(trifluorometil)fenilo
bipy	2,2'-bipiridina
bipy- ^t Bu	4,4'-di- <i>terc</i> -butil-2,2'-bipiridina
bipy-NMe ₂	4,4'-bis(dimetilamino)-2,2'-bipiridina
bipy-OMe	4,4'-dimetoxi-2,2'-bipiridina
^t Bu	<i>terc</i> -butilo
DMAD	acetilendicarboxilato de dimetilo
DMAP	4-dimetilaminopiridina
DMSO	dimetilsulfóxido
Et	etilo
fc	ferrocenilo
HDN	hidrodesnitrogenación
HetAr	heteroarilo aromático
IR	infrarrojo
Me	metilo
Mes	2,4,6-trimetilfenilo (mesitilo)
neo	2,6-dimetil-1,10-fenantrolina (neocuproina)
neo-Et	2-metil-9-etil-1,10-fenantrolina
NMe ₂	dimetilamino
N-MeIm	N-metilimidazol
N-MesIm	N-mesitilimidazol
N-N	ligando bidentado quelato
N-RIm	N-alkilimidazol
OMe	metoxi
OTf	Triflato, trifluorometilsulfonato
Ph	fenilo
phen	1,10-fenantrolina
pimH	2,2'-piridil-1H-imidazol
pimMe	2,2'-piridil-1-metilimidazol
pimR	2,2'-piridil-1-alkilimidazol

py	piridina
py-OMe	4-metoxipiridina
py-R	piridina sustituida en la posición 4
RMN	resonancia magnética nuclear
THF	tetrahidrofurano
TMS	tetrametilsilano
X	ligando aniónico

Abreviaturas empleadas para RMN

δ	desplazamiento químico
d	doblete
dd	doblete de dobletes
Hz	hertzios
<i>J</i>	constante de acoplamiento
m	multiplete
ppm	partes por millón
q	cuatriplete
s	singulete
s_{br}	singulete ancho
t	triplete

INTRODUCCIÓN

Los imidazoles son heterociclos aromáticos que presentan una elevada estabilidad y, debido a la presencia de un átomo de nitrógeno con un par de electrones no deslocalizado, se comportan como buenos ligandos frente a gran variedad de centros metálicos (Figura 1.a), incluyendo fragmentos organometálicos en los que el metal se encuentra en un bajo estado de oxidación. La química de coordinación de estas especies ha sido extensamente estudiada,¹ así como la de los ligandos imidazol-2-ilidenos (carbenos N-heterocíclicos, NHCs),² que se basan igualmente en el esqueleto del imidazol (Figura 1.b). En las últimas dos décadas, los carbenos NHC han experimentado un gran auge dentro de la Química Organometálica debido a la posibilidad de aislarlos como especies libres y a las excelentes prestaciones que poseen muchos de sus complejos metálicos en procesos de catálisis homogénea.³

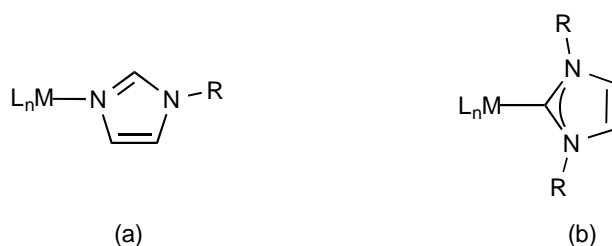


Figura 1. Ligando *N*-alquilimidazol (a) o carbeno *N*-heterocíclico (b) coordinado a un fragmento metálico

¹ (a) R. J. Sundberg, R. B. Martin, *Chem. Rev.* **1974**, *74*, 471. (b) J. Reedijk, In *Comprehensive Coordination Chemistry*; G. Wilkinson, Ed.; Pergamon: Oxford, **1987**, Vol. 2, 73. (c) M. Haga, In *Comprehensive Coordination Chemistry*; J. A. McCleverty, T. J. Meyer, Ed.; Elsevier Pergamon: Amsterdam, **2004**, Vol. 1, 125.

² Revisiones seleccionadas: (a) W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162. (b) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122. (c) O. Kühl, *Coord. Chem. Rev.* **2009**, *253*, 2481.

³ Revisiones seleccionadas: (a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. (b) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992. (c) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612. (d) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445.

Los carbenos NHC fueron propuestos por primera vez en 1960,⁴ y unos años más tarde, en 1968, Wanzlick⁵ y Öfele⁶ en trabajos independientes, consiguieron aislar los primeros complejos de mercurio y cromo con un ligando de este tipo. En 1991, mediante el empleo de sustituyentes lo suficientemente voluminosos (grupos adamantilo) en los átomos de nitrógeno, Arduengo fue capaz de aislar y caracterizar completamente, incluyendo su estructura de rayos X, uno de estos carbenos (Figura 2).⁷ Este hecho supuso una novedad considerable, puesto que, hasta entonces, se consideraba a los carbenos especies intrínsecamente inestables, que podían, como mucho, ser interceptadas en medios de reacción o detectadas espectroscópicamente a baja temperatura. Además de la protección estérica procedente de los sustituyentes voluminosos, en estas especies el carácter electrofílico del carbono carbénico, que en general es lo que convierte a los carbenos en especies muy reactivas, se encuentra atenuado como consecuencia de la deslocalización de los pares no enlazantes que se encuentran sobre los dos átomos de nitrógeno adyacentes.

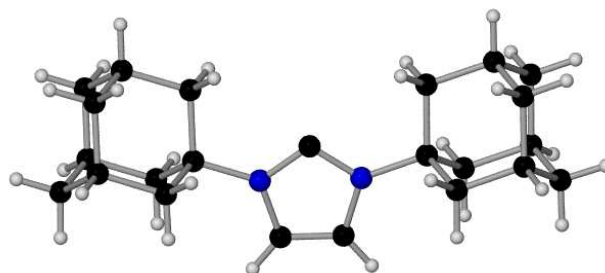


Figura 2. Estructura de rayos X de un NHC

Además del interés en sí mismo suscitado por la caracterización de una especie carbénica estable, pronto se comprobó que los NHC eran excelentes ligandos para una gran variedad de fragmentos metálicos de los elementos de los bloques d y f.⁸ Dado que se trata de ligandos fuertemente dadores y voluminosos, los NHC se han considerado comparables, en sus propiedades como ligandos, a las trialkil- o triarilfosfinas, que son ligandos de gran importancia, en buena parte porque se encuentran presentes en la mayoría de los complejos metálicos con actividad catalítica. No obstante, en algunos tipos de catálisis de reacciones orgánicas, los carbenos NHC

⁴ (a) H. W. Wanzlick, E. Schikora, *Angew. Chem.* **1960**, *72*, 494. (b) H. W. Wanzlick, H. J. Kleiner, *Angew. Chem.* **1961**, *73*, 493. (c) H. W. Wanzlick, *Angew. Chem. Int. Ed.* **1962**, *1*, 75.

⁵ H. W. Wanzlick, H. J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141.

⁶ K. Öfele, *J. Organomet. Chem.* **1968**, *12*, 42.

⁷ A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.

⁸ (a) W. A. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2023. (b) W. A. Hermann, C. Kocher, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (c) D. S. McGuinness, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **1999**, *18*, 1596. (d) S. Grundemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485. (e) R. W. Simms, M. J. Drewitt, M. C. Baird, *Organometallics* **2002**, *21*, 2958.

son en la actualidad los ligandos que han dado lugar a mejores resultados, como por ejemplo en la reacción de Heck,⁹ en las reacciones de acoplamiento cruzado (como las reacciones de Suzuki-Miyaura),^{3a,10} metátesis de olefinas,¹¹ etc. Por otra parte, también han mostrado gran aplicabilidad como organocatalizadores.¹²

Teniendo en cuenta la relación existente entre los complejos con ligandos N-alkilimidazol (N-RIm) y los complejos con ligandos NHC (Figura 3), resulta llamativa la escasa atención que se ha dado a los procesos de interconversión entre ambos tipos de complejos, extensamente estudiados de manera independiente, como acabamos de comentar. En este contexto, Sini, Eisenstein y Crabtree han llevado a cabo un estudio teórico sobre la preferencia de un ligando imidazol a coordinarse por el átomo de nitrógeno (Figura 3.a) o por el átomo de carbono central (Figura 3.b), encontrando que el modo de coordinación depende de la naturaleza del fragmento metálico.¹³

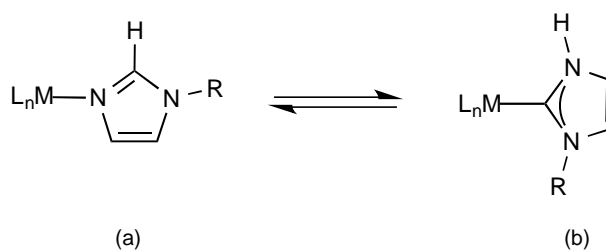


Figura 3 Tautomerización de un ligando imidazol a NH-NHC

Los procesos de tautomerización mostrados en la Figura 3 son, por tanto, muy raros, y, hasta donde sabemos sólo se conocen los ejemplos publicados por Sundberg en 1974,^{1a} en los que en medio ácido se produce la tautomerización de un ligando imidazol a NHC en un fragmento de Ru(II), y mucho más recientemente el trabajo de Bergman y colaboradores en el que consiguen la tautomerización de derivados de benzimidazol, de N- a C- coordinados, empleando complejos de Rh(I) (Esquema 1).¹⁴ Este tipo de procesos son igualmente muy poco habituales para otros

⁹ (a) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741. (b) M. B. Andrus, C. Song, J. Zhang, *Org. Lett.* **2002**, *4*, 2079. (c) M. Poyatos, F. Marquez, E. Peris, C. Claver, E. Fernandez, *New J. Chem.* **2003**, *27*, 425. (d) W. A. Hermann, K. Ofële, D. Von Preysing, S. K. Schneider, *J. Organomet. Chem.* **2003**, *687*, 229. (e) H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu, P. Y. Cheng, *Tetrahedron* **2004**, *60*, 5807.

¹⁰ (a) A. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, S. P. Nolan, *J. Organomet. Chem.* **2002**, *653*, 69. (b) M. S. Viciu, R. F. Germaneau, O. Navarro-Fernández, E. D. Stevens, S. P. Nolan, *Organometallics* **2002**, *21*, 5470.

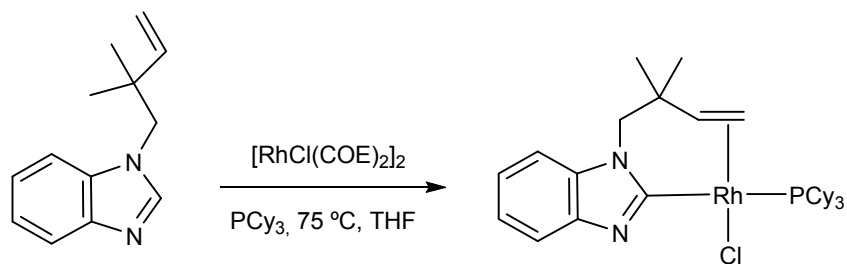
¹¹ (a) J. Huang, E. D. Stevens, S. P. Nolan *Organometallics* **2000**, *19*, 1194. (b) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Cat.* **2002**, *344*, 749. (c) F. Courchay, J. C. Sworen, K. B. Wagener, *Macromolecules*, **2003**, *36*, 8231. (d) T.-L. Choi, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2003**, *42*, 1743. (e) Q. Yao, A. Rodríguez-Mota, *Tetrahedron Lett.* **2004**, *45*, 2447.

¹² N. Marion, S. Gonzalez-Díez, S. P. Nolan, *Angew. Chem Int. Ed.* **2007**, *46*, 2.

¹³ G. Sini, O. Eisenstein, R. H. Crabtree *Inorg. Chem.* **2002**, *41*, 602.

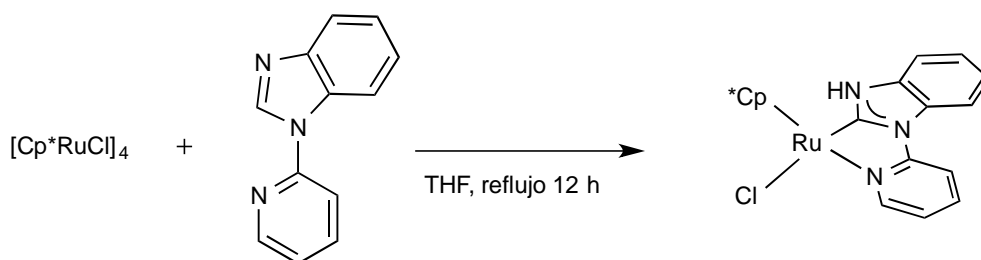
¹⁴ K. L. Tan, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2002**, *124*, 3202.

heterociclos aromáticos, como las piridinas y sus derivados.¹⁵



Esquema 1. Tautomerización de un derivado de benzimidazol mediada por un complejo de Rh(I).

Se conocen, no obstante, los estudios de Kuwata¹⁶ y Grotjahn¹⁷ con rutenio e iridio respectivamente, en los que la tautomerización de un imidazol a NHC está favorecida por la formación de un anillo quelato. A modo de ejemplo, se muestra en el Esquema 2 el caso de los complejos de Ru(II) estudiados por Kuwata y colaboradores.



Esquema 2. Tautomerización de un derivado de benzimidazol favorecida por la formación de un quelato de Ru(II)

Los trabajos publicados por los grupos de Whittlesey¹⁸ y Li¹⁹ describen los escasos ejemplos en los que se produce el proceso inverso de tautomerización, de carbenos N-heterocíclicos a ligandos imidazol, mediados por complejos de rutenio e iridio, respectivamente. En el Esquema 3 se muestra la transformación de un complejo NHC de Ru(II) en su especie tautomérica con un

¹⁵ (a) S. H. Wiedeman, J. C. Lewis, J. A. Ellman, R. G. Bergman, *J. Am. Chem. Soc.* **2006**, *128*, 2452. (b) M. A. Esteruelas, F. J. Fernández-Alvarez, E. Oñate, *J. Am. Chem. Soc.* **2006**, *128*, 13044. (c) E. Álvarez, S. Conejero, J. A. López, P. Lara, M. Paneque, A. Petronilho, M. L. Poveda, D. del Río, O. Serrano, E. Carmona, *J. Am. Chem. Soc.* **2007**, *129*, 14130. (d) M. L. Buil, M. A. Esteruelas, K. Garcés, M. Oliván, E. Oñate, *J. Am. Chem. Soc.* **2007**, *129*, 10998. (e) M. A. Esteruelas, F. J. Fernández-Alvarez, E. Oñate, *Organometallics* **2007**, *26*, 5239. (f) S. Conejero, P. Lara, M. Paneque, A. Petronilho, M. L. Poveda, O. Serrano, F. Vattier, E. Álvarez, C. Maya, V. Salazar, E. Carmona, *Angew. Chem. Int. Ed.* **2008**, *47*, 4380. (g) G. Song, Y. Li, S. Chen, X. Li, *Chem Commun.* **2008**, 3558. (h) M. Paneque, M. L. Poveda, F. Vattier, E. Alvarez, E. Carmona, *Chem. Commun.* **2009**, 5561. (i) G. Song, Y. Su, R. A. Periana, R. H. Crabtree, K. Han, H. Zhang, X. Li, *Angew. Chem. Int. Ed.* **2010**, *49*, 912.

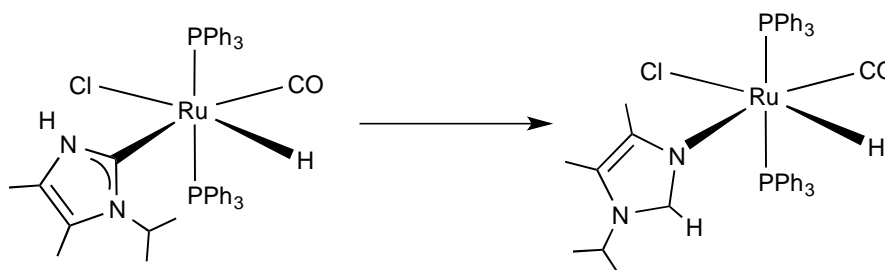
¹⁶ K. Araki, S. Kuwata, T. Ikariya, *Organometallics*, **2008**, *27*, 2176.

¹⁷ V. Miranda-Soto, D. B. Grotjahn, A. G. Dipasquale, A. L. Rheingold, *J. Am. Chem. Soc.* **2008**, *130*, 13200.

¹⁸ S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 13702.

¹⁹ X. Wang, H. Chen, X. Li, *Organometallics* **2007**, *26*, 4684.

ligando N-alquilimidazol.



Esquema 3. Tautomerización de un ligando NH-NHC a N-RIm en un complejo de Ru (II)

Por otra parte, es interesante notar la analogía que se puede establecer entre un complejo catiónico con un ligando N-alquilimidazol coordinado y una sal de imidazolio, pudiendo considerar a los primeros como sales de imidazolio N-metaladas, es decir que presentan un fragmento metálico como sustituyente de uno de sus átomos de nitrógeno (Figura 4). Teniendo en cuenta que la desprotonación de sales de imidazolio es el método más común para preparar carbenos NHC,² resulta interesante considerar lo que ocurriría al desprotonar el grupo CH central de un imidazol coordinado a un fragmento metálico.

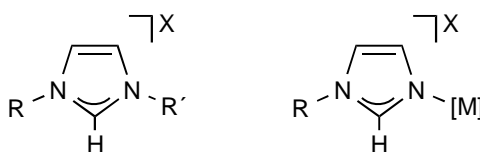


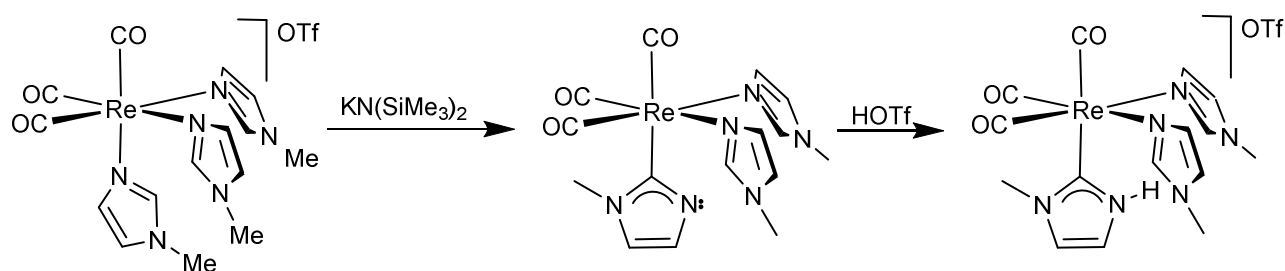
Figura 4. Analogía entre una sal de imidazolio y un complejo metálico catiónico con un ligando N-RIm

En los últimos años una línea de investigación de nuestro grupo se ha centrado precisamente en el estudio de las reacciones de desprotonación de compuestos con ligandos N-alquilimidazol coordinados a fragmentos organometálicos, encontrando una rica y variada reactividad que iremos comentando, en parte, a lo largo de la presente Memoria. En particular, hemos encontrado que la acción de una base externa, seguida de la adición de un ácido puede originar, en determinados casos, la tautomerización de un ligando N-alquilimidazol a NHC,²⁰ tal y como se muestra en el Esquema 4, para un complejo tris(imidazol) de renio (I). Esta reacción, que sólo contaba con un precedente bibliográfico para un compuesto carbonílico de Mn(I),²¹ se ha extendido recientemente

²⁰ (a) M. A. Huertos, J. Pérez, L. Riera, A. Menéndez-Velazquez, *J. Am. Chem. Soc.* **2008**, *130*, 13530. (b) M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Chem. Eur. J.* **2010**, *16*, 8495. (c) M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Angew. Chem. Int. Ed.* **2010**, *49*, 6409. (d) M. A. Huertos, J. Pérez, L. Riera *Chem. Eur. J.* **2012**, *18*, 9530.

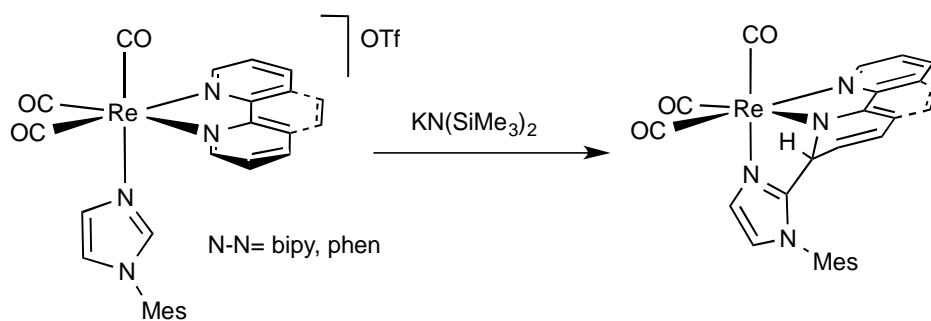
²¹ J. Ruiz, B. F. Perandones *J. Am. Chem. Soc.* **2007**, *129*, 9298.

a otros fragmentos metálicos.²²



Esquema 4. Reactividad del complejo $[Re(CO)_3(N-MeIm)_3]OTf$ frente a $KN(SiMe_3)_2$ y $HOTf$

Otro tipo general de reactividad que hemos encontrado al estudiar la evolución de los productos resultantes de desprotonar el grupo CH central de un ligando N-alquilimidazol coordinado a un fragmento metálico, son reacciones de acoplamiento carbono-carbono con otros ligandos coordinados al mismo metal en disposición *cis* al imidazol.^{20b,23} Así por ejemplo, la reacción de desprotonación de los compuestos $[Re(CO)_3(N-MesIm)(N-N)]OTf$ (N-N= 2,2'-bipiridina, bipy; 1,10-fenantrolina, phen; N-MesIm= N-mesitilimidazol) dio lugar a los productos de acoplamiento C-C, con la consecuente desaromatización del anillo piridínico involucrado (Esquema 5).^{23a} Los resultados obtenidos permiten proponer que el átomo de carbono central del imidazol (C2) una vez desprotonado atacaría actuando como un nucleófilo a uno de los carbonos *orto* de la bipy, originando así la formación de un nuevo enlace C-C y la desaromatización de la α -diimina.



Esquema 5. Desprotonación de los complejos $[Re(CO)_3(N-MesIm)(N-N)]OTf$

Cabe destacar que los complejos $[ReX(CO)_3(N-N)]$ han sido objeto de amplios y numerosos

²² (a) C. Hsieh, R. Pulukkody, M. Y. Darensbourg, *Chem Comm.* **2013**, 49, 9326. (b) F. He, P. Braunstein, M. Wesolek, A. A. Danopoulos, *Chem. Commun.* **2015**, 51, 2814.

²³ (a) M. A. Huertos, J. Pérez, L. Riera *J. Am. Chem. Soc.* **2008**, 130, 5662. (b) M. Espinal Viguri, M. A. Huertos, J. Pérez, L. Riera, *Chem. Eur. J.* **2013**, 19, 12974.

estudios, debido a sus propiedades fotofísicas y fotoquímicas,²⁴ así como a su participación en procesos de activación catalítica de CO₂,²⁵ mostrando una elevada estabilidad (siendo, en su mayoría, estables en condiciones atmosféricas, compatibles con medio acuoso y considerablemente inertes frente a la sustitución de ligandos). Dado lo regular de su geometría octaédrica han sido ampliamente empleados en Química Supramolecular,²⁶ y en los últimos años se han comenzado a estudiar sus aplicaciones como agentes anticancerígenos.²⁷ Por otra parte, heterociclos aromáticos que contienen átomos de nitrógeno, como bipy, phen o sus derivados, han sido extensamente empleados como ligandos en Química de Coordinación y Organometálica,²⁸ y también en catálisis homogénea.²⁹ La presencia de los átomos de nitrógeno, con hibridación sp², hace que se trate de compuestos con una gran capacidad dadora, y en presencia de fragmentos metálicos se coordinan, casi sin excepciones,^{15f} como ligandos bidentados quelato. Entre las propiedades de estos ligandos destacan lo inertes que son y su elevada robustez.

La activación de este tipo de ligandos despierta un considerable interés también por su relevancia en biología.³⁰ De hecho, no existen muchos ejemplos de activación de N-heterociclos coordinados a fragmentos metálicos, y en los pocos ejemplos que se conocen, suelen participar metales de los primeros grupos de transición, muy electrófilos y, por tanto, muy reactivos.

Así por ejemplo, la activación de un enlace C-H de una piridina mediada por un metal de los primeros grupos de transición suele dar lugar a un aducto κ²-(N,C)-piridilo. En el Esquema 6 se muestra uno de los primeros ejemplos de la formación de un compuesto de esta clase en el que Jordan y colaboradores emplean un compuesto de circonio altamente reactivo.³¹

²⁴ (a) A. Lees, *J. Chem. Rev.* **1987**, *87*, 711. (b) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163. (c) K. S. Schance, D. B. MacQueen, T. B. Perkins, L. A. Caban, *Coord. Chem. Rev.* **1993**, *122*, 63. (d) D. J. Stufkens, A. Vlcek Jr., *Coord. Chem. Rev.* **1998**, *177*, 127. (e) I. R. Farrel, A. Vlcek Jr., *Coord. Chem. Rev.* **2000**, *208*, 87. (f) D. R. Striplin, G. A. Crosby, *Coord. Chem. Rev.* **2001**, *211*, 163.

²⁵ (a) J. P. Collins, J. P. Sauvage, *Coord. Chem. Rev.* **1989**, *93*, 245. (b) P. Christensen, A. Hamnett, A. V. G. Muir, J. A. Timney, *J. Chem. Soc., Dalton Trans.* **1992**, 1455. (c) G. J. Stor, F. Hartl, J. W. van Outerstep, D. J. Stufkens, *Organometallics* **1995**, *14*, 1115. (d) F. P. A. Johnson, M. W. George, F. Hartl, J. J. Turner, *Organometallics* **1996**, *15*, 3374. (e) B. R. Rossenaar, F. Hartl, D. J. Stufkens, *Inorg. Chem.* **1996**, *35*, 6194. (f) T. Scheiring, A. Klein, W. Kaim, *J. Chem. Soc., Perkin Trans. 2* **1997**, 2569.

²⁶ (a) R. V. Slone, D. I. Yoon, R. M. Calhoun, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 11813. (b) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759. (c) R. V. Slone, J. T. Hupp, *Inorg. Chem.* **1997**, *36*, 5422.

²⁷ A. Laonodiva, G. Gasser *ACS Chem. Biol.* **2014**, *9*, 2180.

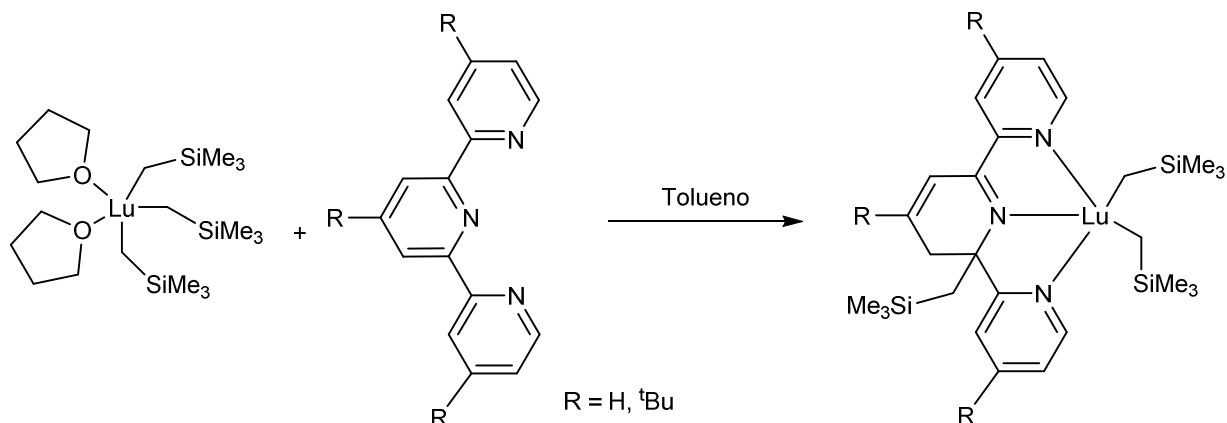
²⁸ (a) E. C. Constable, *Adv. Inorg. Chem. Radiochem.* **1989**, *34*, 1. (b) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**. (c) A. P. Smith, C. L. Fraser, *Comprehensive Coordination Chemistry II, Vol. 1*, Pergamon, Oxford, **2004**.

²⁹ (a) T. M. Boller, J. M. Murphy, M. Hapke, T. Ishiyama, N. Miyaura, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 14263. (b) J. M. McFarland, M. B. Francis, *J. Am. Chem. Soc.* **2005**, *127*, 13490.

³⁰ (a) A. R. Katritzky, C. W. Rees, E. F. V. Scriven, *Comprehensive Heterocyclic Chemistry II*, Pergamon, Oxford, **1996**. (b) T. L. Gilchrist, G. W. Gribble, *Advances in Heterocyclic Chemistry, Vol. 11*, Pergamon, Oxford, **1999**. (c) J. A. Joule, K. Mills, *Heterocyclic Chemistry*, Blackwell Science, Oxford, **2000**. (d) A. R. Katritzky, A. F. Pozharskii, *Handbook of Heterocyclic Chemistry*, Pergamon, Oxford, **2003**.

³¹ R. F. Jordan, S. A. Guran, *Organometallics* **1990**, *9*, 2116.

En este caso, la migración 1,3 de uno de los grupos trimetilsililo, unido inicialmente al átomo metálico, da lugar a la pérdida de aromaticidad de la terpy (Esquema 9).

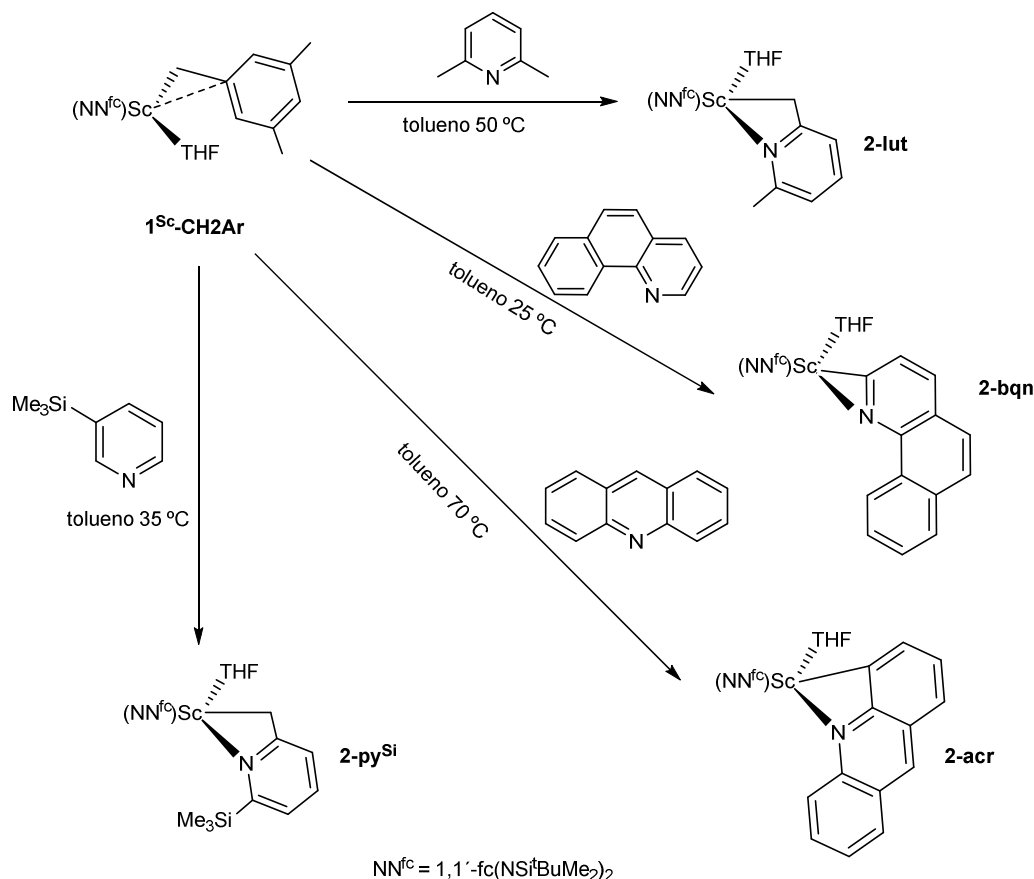


Esquema 9. Activación y desaromatización de una terpiridina.

En los últimos años cabe destacar la aportación en este área realizada por Diaconescu y colaboradores, que en el estudio de la reactividad de complejos alquilo de metales del grupo 3 han encontrado una gran variedad de activaciones de N-heterociclos aromáticos.³⁵ Así por ejemplo, en muchos casos han logrado la activación de piridinas (y ligandos relacionados) en los que obtienen aductos κ^2 -(N,C)-piridilo (Esquema 10).

³⁴ K. C. Jantunen, B. L. Scoot, P. J. Hay, J. C. Gordon, J. L. Kiplinger, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 6322.

³⁵ P. L. Diaconescu *Acc. Chem. Res.* **2010**, *43*, 1352 y referencias allí citadas.



Esquema 10. Activación de grupos piridilo empleando un complejo de Sc(III)

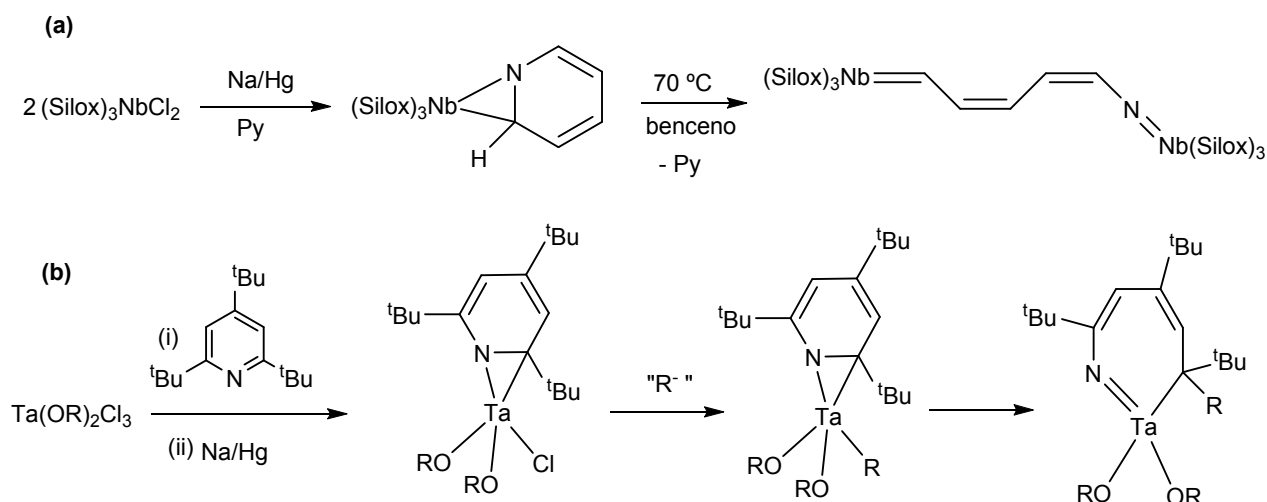
Estos fragmentos metálicos de los primeros grupos de transición en estado de oxidación alto, y por tanto muy electrofílicos, no sólo son capaces de activar enlaces CH de heterociclos aromáticos, sino que, en algunas ocasiones, también son capaces de activar enlaces C-N de los mismos. Estas reacciones de activación de enlaces C-N de heterociclos aromáticos presentan un interés adicional dada su relación con los procesos de hidrodensnitración (HDN).³⁶

La HDN es uno de los muchos procesos catalíticos de hidrogenación que se realiza en las refinerías modernas. Su principal objetivo es eliminar el nitrógeno de los combustibles, en forma de NH_3 , para evitar o reducir al máximo las emisiones de óxidos de nitrógeno a la atmósfera. Para ello los N-heterociclos presentes en fueles y petróleos son catalíticamente convertidos en NH_3 y productos hidrocarbonados que no contienen nitrógeno. En la industria la catálisis es heterogénea y se emplean elevadas presiones y temperaturas, de manera que la naturaleza de los procesos elementales que ocurren sobre la superficie del catalizador aún no está clara. Por tanto, estudiar y comprender el mecanismo por el cual enlaces C-N fuertes de sustratos aromáticos, como la

³⁶ (a) J. R. Katzer, R. Sivasubramanian, *Catal. Rev.-Sci. Eng.* **1979**, *20*, 155. (b) T. C. Ho, *Catal. Rev.-Sci. Eng.* **1988**, *30*, 117. (c) G. Perot, *Catal. Today* **1991**, *10*, 447. (d) R. Prins, In *A Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knözinger, J. Weitkamp, Eds. VCH Verlagsgesellschaft, Weinheim, Germany, **1997**. (e) T. Kabe, A. Ishikawa, W. Qian, *Hydrodesulfurization and Hydrodenitrogenation*, Wiley-VCH, Chichester, UK, **1999**. (f) E. Furimsky, F. E. Massoth, *Catal. Rev.-Sci. Eng.* **2005**, *47*, 297, and references therein. (g) P. L. Diaconescu, *Curr. Org. Chem.* **2008**, *12*, 1388.

piridina, se pueden romper en condiciones homogéneas constituye una excelente oportunidad para mejorar o sintetizar más catalizadores eficaces para los procesos de HDN.

Dada la fortaleza del enlace C-N de heterociclos aromáticos (133 kcal/mol para la piridina), no es de extrañar que existan muy pocos ejemplos de ruptura de este enlace mediada por un metal de transición. Básicamente el trabajo de Wolczanski³⁷ y el de Wigley³⁸ constituyen la mayoría de los escasos ejemplos bien determinados en los que, en condiciones suaves y fase homogénea, tiene lugar la ruptura de un enlace C-N de anillo piridínico (Esquema 11).



Esquema 11. Apertura de anillos piridínicos por ruptura de enlaces C-N

Un paso común en ambos trabajos es la coordinación κ^2 -(N,C) del sustrato piridínico a un centro metálico del grupo 5. La posterior reducción (Esquema 11.a) o migración de un grupo alquilo (Esquema 11.b) da lugar a la apertura del anillo N-heterocíclico.

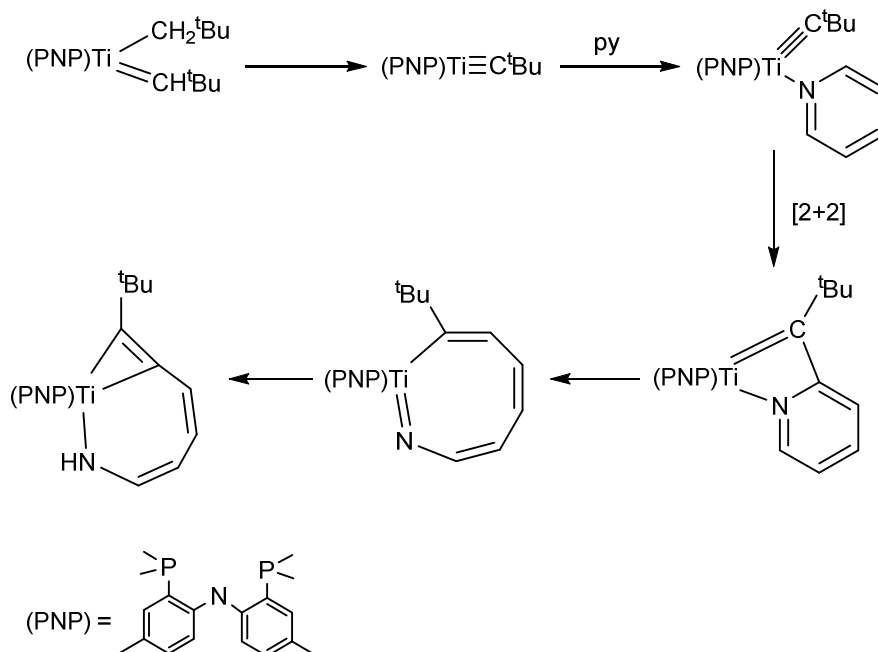
En el año 2006 Mindiola y colaboradores encontraron un ejemplo en el que se produce la activación y ruptura de un enlace C-N de una piridina en un medio no reductor y a temperatura ambiente (Esquema 12).³⁹ Estos autores, basándose en los resultados experimentales y en cálculos teóricos, proponen que la apertura de la piridina se promueve por la formación de un intermedio alquilideno de titanio, altamente reactivo. En este proceso se ve involucrada una cicloadición [2 + 2] de un enlace C=N aromático y del enlace triple Ti-C del alquilideno metálico. Un año más tarde,

³⁷ (a) D. R. Neirhamer, L. Parkanyi, J. F. Mitchel, P. T. Wolczansky, *J. Am. Chem. Soc.* **1988**, *110*, 4421. (b) T. S. Kleckley, J. L. Bennet, P. T. Wolczansky, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1997**, *119*, 247. (c) K. J. Covert, D. R. Neirhamer, M. C. Zonneville, R. E. Lapointe, C. P. Schaller, P. T. Wolczansky, *Inorg. Chem.* **1999**, *30*, 2494. (d) J. B. Bonanno, A. S. Veige, P. T. Wolczansky, E. B. Lobkovsky, *Inorg. Chim. Acta* **2003**, *345*, 173.

³⁸ (a) S. D. Gray, D. P. Smith, M. A. Bruck, D. E. Wigley, *J. Am. Chem. Soc.* **1992**, *114*, 5462. (b) S. D. Gray, K. J. Weller, M. A. Bruck, P. M. Brigs, D. E. Wigley, *J. Am. Chem. Soc.* **1995**, *117*, 10678. (c) K. J. Weller, S. D. Gray, P. M. Brigs, D. E. Wigley, *Organometallics* **1995**, *14*, 5588. (d) K. D. Allen, M. A. Bruck, S. D. Gray, R. P. Kinsborough, D. P. Smith, K. J. Weller, D. E. Wigley, *Polyhedron* **1995**, *14*, 3315. (e) K. J. Weller, I. Filippov, P. M. Brigs, D. E. Wigley, *J. Organomet. Chem.* **1997**, *528*, 225. (f) K. J. Weller, I. Filippov, P. M. Brigs, D. E. Wigley, *Organometallics* **1998**, *17*, 322.

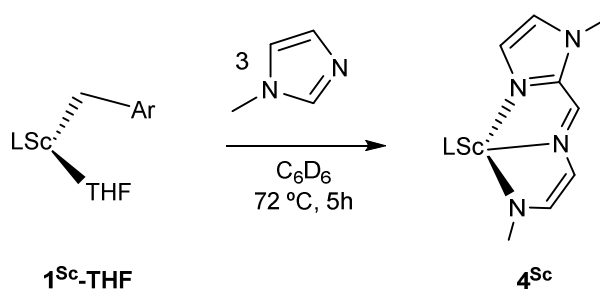
³⁹ (a) B. C. Baley, H. Fan, J. C. Huffman, M. Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2006**, *128*, 6798.

consiguen la desnitrogenación de la piridina en estos complejos de titanio mediante la adición de un electrófilo, dando lugar a derivados de fenilo, y más recientemente, basándose en estudios teóricos y experimentales, proponen un mecanismo para este proceso.⁴⁰



Esquema 12. Reactividad de complejos de titanio estudiada por Mindiola

En el año 2008, Diaconescu publicó el primer ejemplo de apertura de un N-metilimidazol mediada por un complejo metálico en condiciones homogéneas (Esquema 13).⁴¹ En este caso la activación y ruptura de enlaces carbono-nitrógeno del heterociclo aromático está mediada por un fragmento metálico de Sc(III) que, al igual que los casos comentados previamente, se caracteriza por su elevada reactividad y electrofilia.



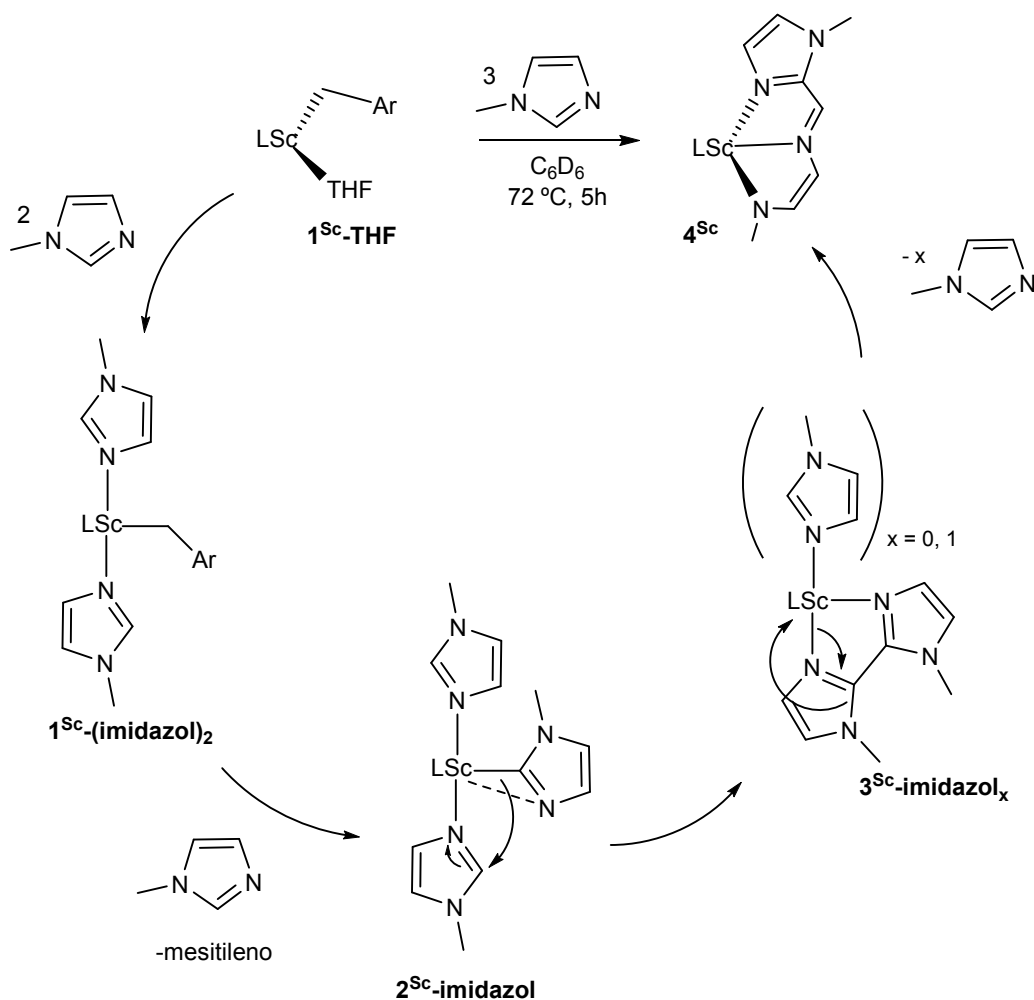
Esquema 13. Apertura de un anillo de N-metilimidazol mediada por un compuesto de Sc(III)

⁴⁰ (a) A. R. Fout, B. C. Bailey, J. Tomaszewsky, D. J. Mindiola, *J. Am. Chem. Soc.* **2007**, *129*, 12640. (b) A. R. Fout, B. C. Bailey, D. M. Buck, H. Fan, J. C. Huffman, M-H. Baik, D. J. Mindiola, *Organometallics* **2010**, *29*, 5409.

⁴¹ C. T. Carver, P. L. Diaconescu *J. Am. Chem. Soc.* **2008**, *130*, 7558.

En concreto, la reacción de 1^{Sc}-THF ($L = \text{fc}[\text{NSi}^t\text{BuMe}_2]$, $\text{fc} =$ ferrocenilo, $\text{Ar} = 3,5\text{-dimetilfenilo}$) con 3 equivalentes de N-metilimidazol, da lugar, al cabo de 5 horas y 72°C a la formación de 4^{Sc} , en el que se ha producido la activación y ruptura de un enlace C-N de un imidazol, originando así el producto de apertura heterocíclica.

La extensión de estos estudios a compuestos análogos de Y, La, Lu (III) o de U (IV) con dos ligandos alquilo en *cis*, han mostrado la generalidad de este comportamiento, no sólo con N-metilimidazol, sino también con N-metilbenzimidazol.³⁵ Basándose en este conjunto de resultados experimentales, estos autores propusieron para la reacción de acoplamiento C-C y apertura del anillo heterocíclico, el mecanismo que se muestra en el Esquema 14, para el caso concreto de la formación del complejo de Sc (III).



Esquema 14 Mecanismo propuesto por Diaconescu y colaboradores para la ruptura de un enlace C-N de un ligando N-MeIm

En primer lugar el compuesto **1^{Sc}-THF** reacciona con dos equivalentes de metilimidazol, que pasan a formar parte de la primera esfera de coordinación del metal, aumentando en una unidad el índice de coordinación del Sc en el compuesto **1^{Sc}-(imidazol)₂**. En un segundo paso, el tercer metilimidazol provoca la eliminación del grupo arilo (mesitileno) y la formación de la especie **2^{Sc}-imidazol**, que es un producto de activación C-H, en el que el imidazol se coordina κ^2 -(N,C). A continuación, se forma el producto de acoplamiento C-C (**3^{Sc}-imidazol_x**), que finalmente da lugar a la formación del producto de apertura **4^{Sc}** (Figura 5.a).

Este mecanismo, se propuso basándose en estudios de RMN y de difracción de rayos X de monocristal, pues la determinación estructural del intermedio de Y análogo a **2^{Sc}-imidazol**, con un ligando metilimidazol coordinado κ^2 -(N,C) al metal (Figura 5.b), supuso un gran apoyo a esta propuesta. Posteriormente, el mecanismo se confirmó mediante cálculos computacionales (DFT).⁴²

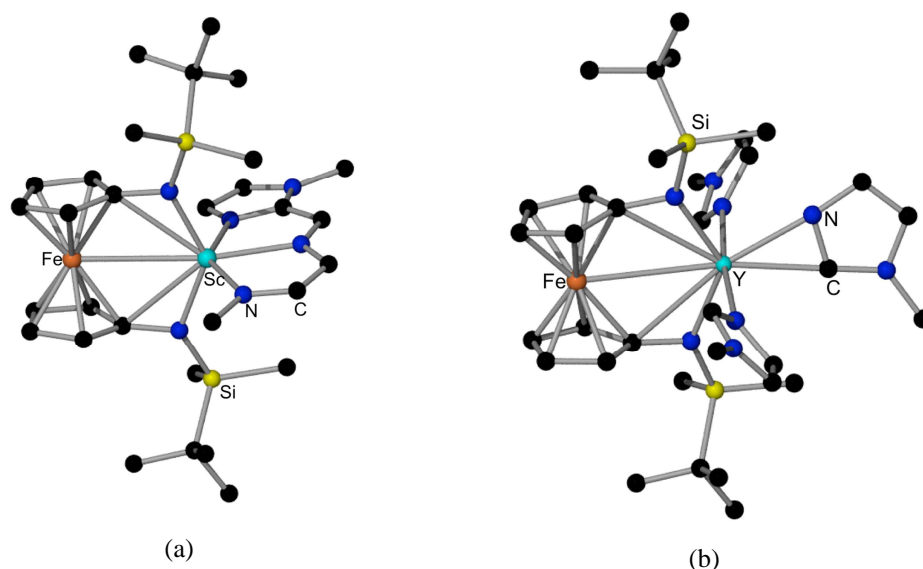


Figura 5. Estructuras en estado sólido de (a) complejo **4^{Sc}** y (b) intermedio de Y análogo a **2^{Sc}-imidazol**

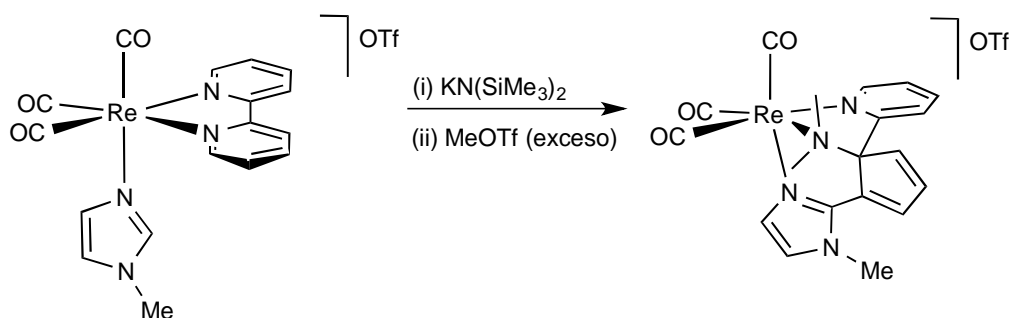
Estos resultados constituyen el primer ejemplo en el que en la ruptura de un enlace C-N de un heterociclo aromático sólo se ven implicados enlaces σ metal-elemento.⁴³ Hasta entonces sólo se conocía algún ejemplo en que complejos metálicos, que únicamente empleaban enlaces σ , eran capaces de producir apertura de heterociclos aromáticos que contenían átomos de oxígeno o azufre.⁴⁴ Por el contrario, en los escasos ejemplos que se conocían de ruptura de enlaces C-N de heterociclos aromáticos, siempre se habían visto involucrados enlaces múltiples M-elemento.

⁴² C. T. Carver, D. Benitez, K. L. Miller, B. N. Williams, E. Tkatchouk, W. A. Goddard III, P. L. Diaconescu, *J. Am. Chem. Soc.* **2009**, *131*, 10269.

⁴³ Recientemente se han publicado resultados análogos empleando complejos alquilo de Y(III): (a) W. Yi, J. Zhang, S. Huang, L. Weng, X. Zhou, *Chem. Eur. J.* **2014**, *20*, 867. (b) Y. Zhang, J. Zhan, J. Hong, F. Zhang, L. Weng, X. Zhou, *Organometallics* **2014**, *33*, 705.

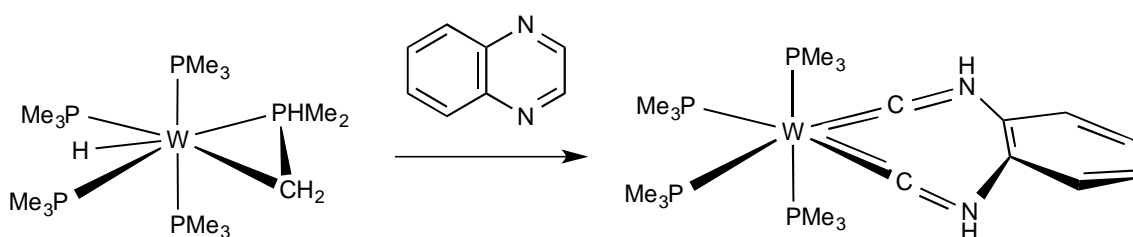
⁴⁴ J. Hitzbleck, J. Okuda, *Organometallics* **2007**, *26*, 3227 y referencias allí citadas.

En este contexto, hay que mencionar que en nuestros estudios previos obtuvimos un ejemplo en el que se producía la ruptura de un anillo piridínico de un ligando 2,2'-bipiridina coordinado al fragmento $\{\text{Re}(\text{CO})_3\}$,^{23a} como se muestra en el Esquema 15. Si bien esta reacción en concreto la discutiremos más detalladamente en la Introducción del Capítulo 1 de la presente Memoria, cabe señalar que éste constituye el primer ejemplo en el que se logra la activación y ruptura de un enlace C-N de un grupo piridilo mediada por un fragmento organometálico, en el que el metal se encuentra en un bajo estado de oxidación y empleando condiciones suaves de reacción.



Esquema 15. Ruptura de un anillo piridínico del ligando 2,2'-bipiridina coordinado al fragmento $\{\text{Re}(\text{CO})_3\}$

Como hemos comentado previamente los ejemplos de ruptura de enlaces C-N de heterociclos aromáticos son reacciones que no se producen habitualmente, sin embargo aún más difícil es la ruptura de un enlace C-C aromático.⁴⁵ Un ejemplo de un proceso de este tipo, que no contaba con precedentes en la bibliografía, es el encontrado por Parkin y Sattler e implica la participación de un fragmento de wolframio en bajo estado de oxidación. Los autores proponen que la ruptura de un enlace C-C aromático de un ligando quinoxalina se produce debido a la inserción del wolframio en el anillo heterocíclico (Esquema 16).



Esquema 16. Ruptura de un enlace C-C de un heterociclo aromático

⁴⁵ A. Sattler, G. Parkin, *Nature*, **2010**, *463*, 523.

OBJETIVOS

El interés de los resultados obtenidos hasta el momento por nuestro grupo de investigación sobre el estudio de la reactividad de compuestos organometálicos con ligandos N-alquilimidazol frente a bases fuertes, nos ha llevado a plantearnos los siguientes objetivos.

1. Estudiar el efecto de los sustituyentes del ligando 2,2'-bipiridina en la reactividad de los complejos $[\text{Re}(\text{CO})_3(4,4'\text{-R}'_2\text{-}2,2'\text{-bipy})(\text{N-RIm})]\text{OTf}$ frente a la base $\text{KN}(\text{SiMe}_3)_2$, dado que se había comprobado en estudios previos que esta reactividad es muy sensible a pequeñas modificaciones en el fragmento metálico.
2. Estudiar el acoplamiento oxidativo entre ligandos monodentados N- heterocíclicos, como piridinas e imidazoles, coordinados al mismo fragmento *fac*-tricarbonílico de renio(I) para dar lugar a ligandos biheterocíclicos aromáticos. Esto podría lograrse mediante la acción consecutiva de una base y de una agente oxidante.
3. Extender los estudios encontrados previamente para los complejos $[\text{Mo}(\eta^3\text{-alilo})(\text{CO})_2(\text{bipy})(\text{N-MeIm})]\text{OTf}$ a complejos análogos con un ligando diimina diferente de la 2, 2'-bipiridina, como pueden ser 2-piridiliminas. Con esta modificación del entorno de coordinación del átomo de molibdeno se pretende obtener una reactividad diferente a la encontrada para los complejos con bipy.

CAPÍTULO 1

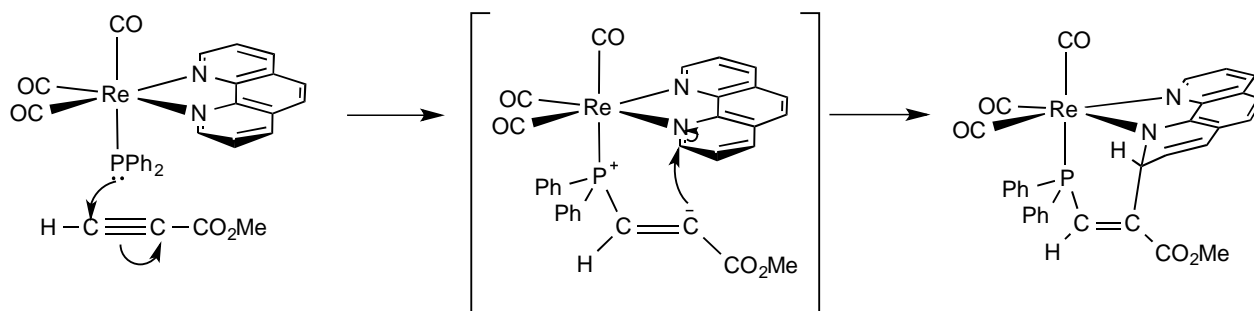
Introducción

Como hemos comentado brevemente en la Introducción de esta Memoria, en los últimos años una de las líneas de investigación de nuestro grupo se ha centrado en el estudio de las reacciones de desprotonación de ligandos N-alquilimidazol (N-RIm) coordinados a fragmentos organometálicos.^{20,23} Consideramos, en primer lugar, los compuestos $[\text{Re}(\text{CO})_3(\text{N-N})(\text{N-RIm})]\text{OTf}$ (N-N= bipy, phen, R= Me, Mes), que al ser catiónicos facilitarían la reacción de desprotonación (en comparación con complejos análogos neutros) y que, en principio, no poseen ningún ligando susceptible de experimentar una reacción de desprotonación más fácilmente que el grupo CH central del N-alquilimidazol. La elección de este fragmento de Re(I) se basó principalmente en la experiencia que nuestro grupo había adquirido previamente al estudiar la reactividad de los complejos $[\text{ReX}(\text{CO})_3(\text{N-N})]$ (X= Br, OTf). Estos estudios, centrados sobre todo en la sustitución del ligando X por ligandos aniónicos (alcóxidos, amiduros, fosfuros, etc.) y la reactividad de estos últimos frente a electrófilos orgánicos insaturados,^{46,47} habían mostrado la gran estabilidad de este fragmento. De hecho, sólo se encontró un ejemplo, que no contaba con precedentes, en el que la reactividad de un compuesto de fórmula $[\text{ReX}(\text{CO})_3(\text{N-N})]$ (N-N= bipy, phen) daba lugar a la activación del ligando bipy o phen y, consecuentemente, a su desaromatización.⁴⁷ En este caso, el complejo $[\text{Re}(\text{PPh}_2)(\text{CO})_3(\text{phen})]$ reacciona con acetilenos activados, generando, presumiblemente, un zwitterion cuyo extremo negativo es un carbanión

⁴⁶ (a) E. Hevia, J. Pérez, V. Riera, D. Miguel, D. *Inorg. Chem.* **2002**, *41*, 4673. (b) E. Hevia, J. Pérez, V. Riera, D. Miguel, D. *Chem. Commun.* **2002**, 1814. (c) E. Hevia, J. Pérez, V. Riera, V. D. Miguel, *Organometallics* **2002**, *21*, 5312. (d) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Angew. Chem., Int. Ed.* **2002**, *41*, 3858. (e) E. Hevia, J. Pérez, L. Riera, V. Riera, D. Miguel, *Organometallics* **2002**, *21*, 1750. (f) E. Hevia, J. Pérez, L. Riera, V. Riera, I. del Río, S. García-Granda, D. Miguel, *Chem. Eur. J.* **2002**, *8*, 4510. (g) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2002**, *21*, 1966. (h) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2003**, *22*, 257. (i) E. Hevia, J. Pérez, V. Riera, D. Miguel, D. Campomanes, P.; Menéndez, M. I.; Sordo, T.; García-Granda, S. *J. Am. Chem. Soc.* **2003**, *125*, 3706. (j) L. Cuesta, D. C. Gerbino, E. Hevia, D. Morales, M. E. Navarro-Clemente, J. Pérez, L. Riera, V. Riera, D. Miguel, I. del Río, S. García-Granda, *Chem. Eur. J.* **2004**, *10*, 1765. (k) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2006**, *25*, 1717. (l) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2006**, *25*, 4909. (m) L. Cuesta, M. A. Huertos, D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, A. Menéndez-Velázquez, S. García-Granda, *Inorg. Chem.* **2007**, *46*, 2836.

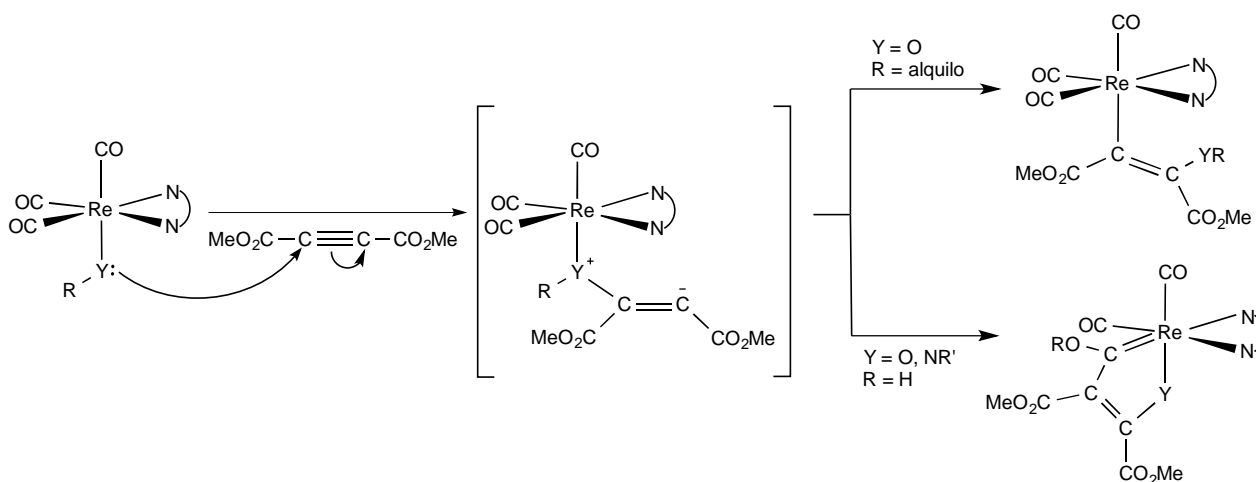
⁴⁷ (a) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, M. Seitz, D. Miguel, *Organometallics* **2005**, *24*, 1772. (b) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, E. Rodríguez, D. Miguel, *Chem. Commun.* **2005**, 116.

muy reactivo, que tras atacar a uno de los carbonos en posición *orto* de la phen, da lugar a su desaromatización. En el Esquema 1.1 se muestra, a modo de ejemplo, la reacción con propiolato de metilo.



Esquema 1.1 Reacción del complejo $[Re(PPh_2)(CO)_3(phen)]$ con propiolato de metilo

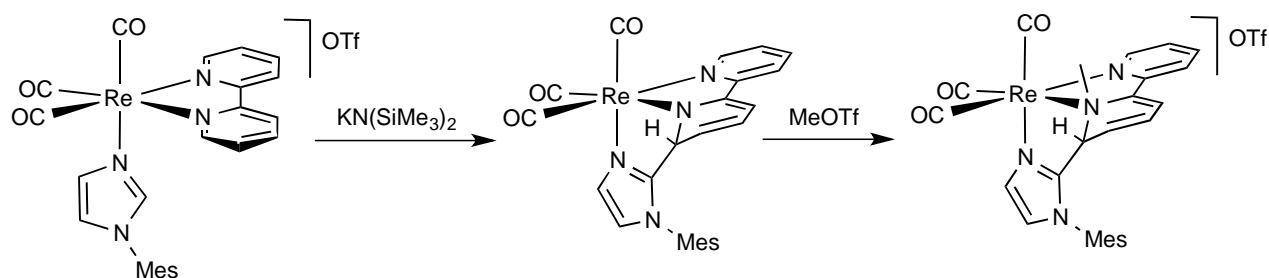
Cabe mencionar que en las reacciones análogas de los compuestos alcóxido o amiduro $[ReY(CO)_3(N-N)]$ ($Y = OR, NR_2$) con electrófilos insaturados, como acetilendicarboxilato de dimetilo (DMAD) o propiolato de metilo, no se produce la desaromatización de la diimina, sino que tiene lugar la reacción de inserción del electrófilo en el enlace $Re-Y$,^{46e} o la activación de un ligando carbonilo^{46h} (Esquema 1.2). Este hecho se ha atribuido a la menor nucleofilia de los ligandos alcoxo o amiduro con respecto al fosforo.



Esquema 1.2 Reacciones de $[ReY(CO)_3(N-N)]$ ($Y = OR, NR_2$) con DMAD

Al estudiar la reactividad de los compuestos $[Re(CO)_3(N-N)(N-RIm)]OTf$ frente a bases fuertes se encontró, en primer lugar, que la reactividad podía variar en función del sustituyente del ligando imidazol.^{23a} Así, la reacción del derivado con mesitilimidazol con la cantidad estequiométrica de base da lugar a la desprotonación del grupo CH central del imidazol. La especie carbénica resultante presenta una elevada nucleofilia, y ataca a uno de los carbonos *orto*

de la bipy (o phen), dando lugar a la formación del producto de acoplamiento carbono-carbono (Esquema 1.3). Como consecuencia el anillo piridínico involucrado resulta desaromatizado, y el nitrógeno imínico pasa ahora a ser de tipo amido. Esta especie neutra resultó ser lo suficientemente estable para ser aislada y caracterizada, pero presenta igualmente reactividad frente a electrófilos. Así por ejemplo, la reacción con MeOTf da lugar a la metilación del nitrógeno antes mencionado para dar lugar al complejo catiónico correspondiente (Esquema 1.3).



Esquema 1.3 Reactividad de los compuestos $[Re(CO)_3(N-N)(N-MesIm)]OTf$

Nótese que en el único precedente en el que se producía la desaromatización de una α -diimina en un compuesto derivado del fragmento $\{Re(CO)_3\}$, se trataba del ligando fenantrolina.⁴⁷ Las reacciones análogas empleando el complejo $[Re(PPh_2)(CO)_3(bipy)]$ dieron lugar a productos cuya escasa estabilidad no permitió su caracterización. Esta diferencia de comportamiento entre la bipy y la phen se atribuyó a que, al producirse el ataque nucleófilo a uno de los anillos de la diimina, en el caso de la phen, la desestabilización debida a la pérdida de aromaticidad se minimiza al conjugarse los dos dobles enlaces restantes con el resto del sistema π a través del anillo central. Por el contrario, en el caso de la bipy esto no es posible y se produce la pérdida total de aromaticidad (Figura 1.1).

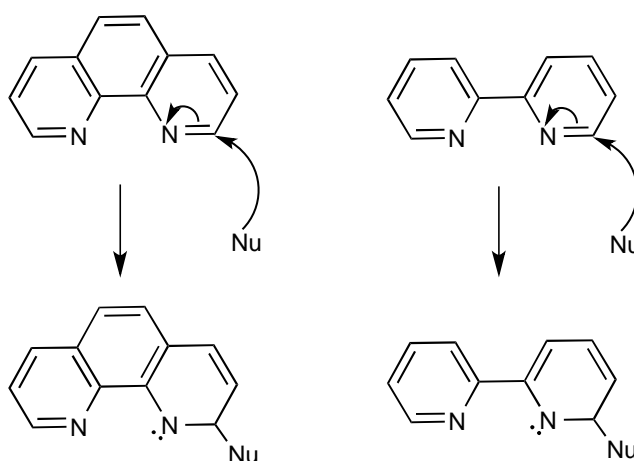
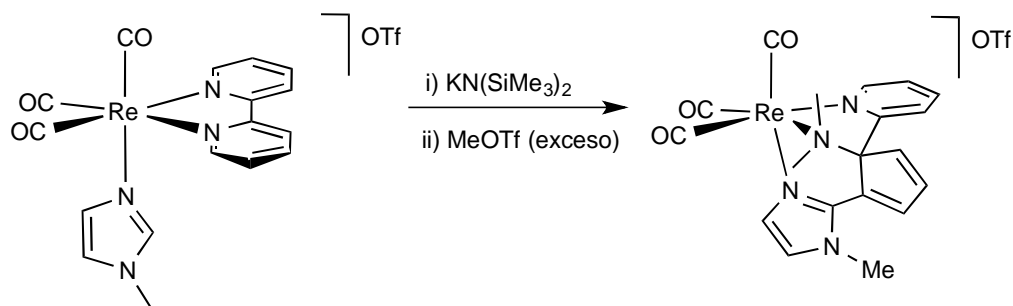


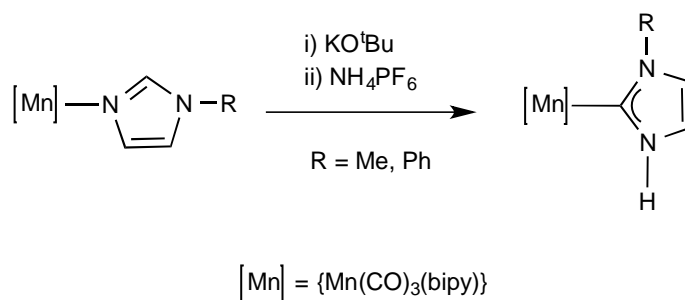
Figura 1.1 Desaromatización de los ligandos bipy y phen por un ataque nucleófilo

El compuesto análogo con metilimidazol, $[\text{Re}(\text{CO})_3(\text{bipy})(\text{N-MeIm})]\text{OTf}$ presenta una mayor reactividad, y el producto neutro resultante de su desprotonación no pudo ser caracterizado debido a su elevada inestabilidad. La adición de triflato de metilo al medio de reacción dio lugar a la formación de un producto estable, que resultó ser un producto de apertura de uno de los anillos piridínicos (Esquema 1.4). En ausencia de estudios mecanísticos, se podría proponer que el N-MeIm una vez desprotonado atacaría a un *Corto* de la bipy, de manera análoga al derivado con N-MesIm, y la doble metilación del nitrógeno de tipo amiduro daría lugar a la extrusión del mismo del anillo, con la consecuente formación del grupo ciclopentadienilo. Éste constituye uno de los escasos ejemplos en los que se produce la apertura de un ligando N-heterocíclico mediada por un metal de transición en condiciones suaves. Difiere de los ejemplos que se conocían hasta el momento en que se trata de un compuesto estable, bien definido y en el que el metal se encuentra en un bajo estado de oxidación, mientras que aquéllos eran compuestos de los primeros grupos de transición, en altos estados de oxidación y por lo tanto, muy electrofílicos (véase Introducción).



Esquema 1.4 Reactividad del compuesto $[\text{Re}(\text{CO})_3(\text{bipy})(\text{N-MeIm})]\text{OTf}$

La reactividad de los compuestos de renio con ligandos N-alquilimidazol, que acabamos de comentar, y que da lugar a la formación de productos de acoplamiento C-C, contrasta con la que poco antes se había encontrado para los compuestos análogos de Mn(I).²¹ Así, la desprotonación de los compuestos $[\text{Re}(\text{CO})_3(\text{N-N})(\text{N-RIm})]\text{OTf}$ (R= Me, Ph), seguida por una reacción de protonación, da lugar a la formación de complejos con un ligando carbeno N-heterocíclico (Esquema 1.5).



Esquema 1.5 Reactividad de los compuestos $[\text{Mn}(\text{CO})_3(\text{bipy})(\text{N-RIm})]\text{OTf}$ (R= Me, Ph)

Esta diferencia en el comportamiento al pasar de los compuestos de manganeso a los de renio podría atribuirse, en principio, a la mayor fortaleza del enlace metal-nitrógeno del ligando imidazol en el caso del renio, de manera que, una vez que se ha producido la desprotonación, en el caso del renio resulta más favorable el ataque intramolecular al ligando bipyridina contiguo que la ruptura del enlace Re-N.

Teniendo en cuenta la gran diferencia encontrada en la reactividad de los compuestos $[M(CO)_3(N-N)(N-RIm)]OTf$ frente a bases fuertes dependiendo de la naturaleza del centro metálico, así como del sustituyente del ligando N-alkylimidazol, nos planteamos extender este estudio a los compuestos análogos de renio con ligandos 2,2'-bipyridina con sustituyentes en las posiciones 4,4'.⁴⁸ Este estudio nos permitirá establecer si los patrones de reactividad encontrados previamente poseen una cierta generalidad, o si por el contrario la modificación electrónica del ligando bipy es suficiente para variar la reactividad de los complejos.

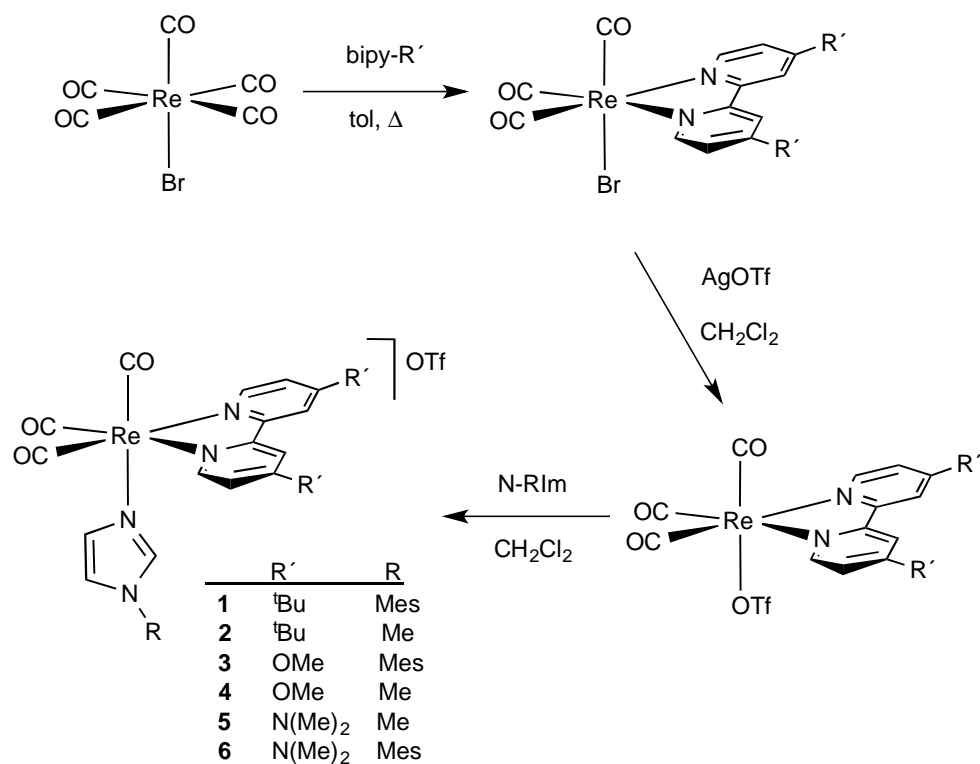
⁴⁸ M. Espinal Viguri, J. Pérez, L. Riera, *Angew. Chem. Int. Ed.* **2015**, enviado para su publicación.

Resultados y discusión

Comenzamos entonces el estudio de la reactividad de complejos tricarbónicos de renio con ligandos bipyridina funcionalizados en las posiciones 4, 4' frente a bases fuertes. El empleo de grupos dadores de densidad electrónica, tales como los grupos *terc*-butilo (^tBu), metoxi (OMe) o dimetilamino (NMe₂), podrían hacer que el ataque nucleófilo sobre la bipy esté desfavorecido, de manera que la reactividad de estas especies se vería forzada a seguir un curso diferente al encontrado en los estudios precedentes con 2,2'-bipyridina, en los que se obtenían los productos de acoplamiento C-C.

Parte de los resultados obtenidos en este Capítulo se encuentran recogidos en una comunicación que ha sido enviada para su publicación. Los resultados restantes se encuentran sin publicar, y constituirán el Artículo Completo (*Full Paper*) de la comunicación enviada. Por este motivo, los resultados incluidos en este Capítulo se discutirán más detalladamente que si estuvieran publicados en su totalidad.

La síntesis de los complejos de partida se llevó a cabo de manera análoga a la descrita previamente en la literatura,^{23a} partiendo de [Re(CO)₅Br]. En primer lugar se produce una sustitución térmica de dos ligandos carbonilo por el ligando bidentado correspondiente, para después desplazar el ligando aniónico bromuro por triflato. En un último paso, se añade el correspondiente imidazol que sustituye el triflato de la esfera de coordinación del renio, pasando entonces de complejos neutros, a complejos catiónicos (Esquema 1.6). Los compuestos formados se obtienen como sólidos amarillos y en buen rendimiento.



Esquema 1.6 Síntesis de los compuestos $[Re(CO)_3(bipy-R')(N-RIm)]OTf$ (**1-6**)

Los compuestos **1-6** así obtenidos se caracterizaron espectroscópicamente en disolución (IR y RMN). Los espectros de IR en disolución de los nuevos compuestos **1-6** muestran, para los ligandos carbonilo, las bandas típicas correspondientes a especies *fac*-tricarbonílicas, a frecuencias coherentes con su naturaleza catiónica. Por otro lado, en los espectros de 1H y ^{13}C RMN se observa claramente la presencia de un plano de simetría que hace equivalentes los dos anillos piridínicos de la bipy, así como a dos ligandos carbonilo. A modo de ejemplo, en la Figura 1.2 se muestra el espectro de 1H RMN en CD_2Cl_2 del compuesto **1**, en el que se observa el patrón típico de señales para una bipy simétrica, así como las señales correspondientes al ligando N-MesIm.

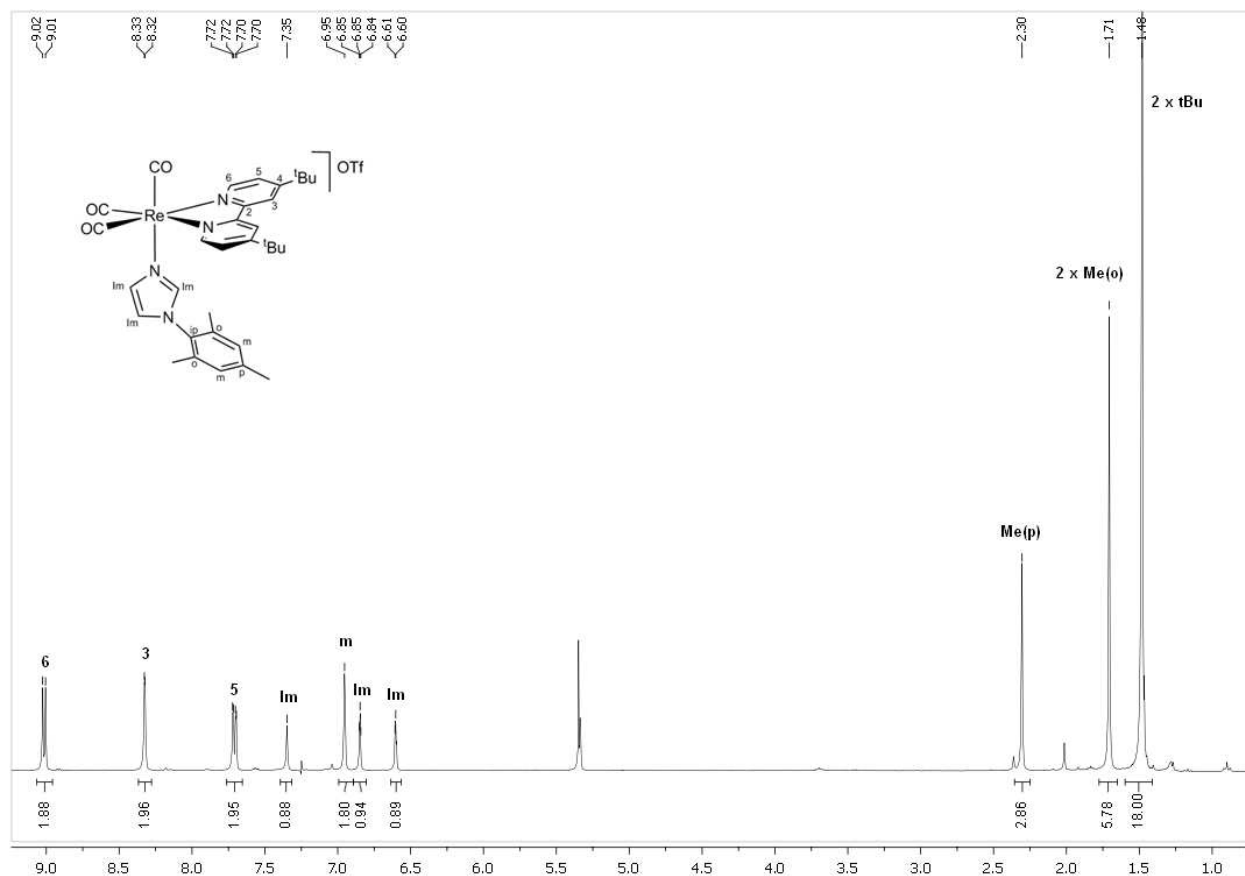


Figura 1.2 Espectro de ^1H RMN del compuesto **1** en CD_2Cl_2

El espectro de ^{13}C RMN del compuesto **1** (Figura 1.3) es consistente con la geometría propuesta, observándose, por ejemplo, sólo dos señales para los carbonilos (a 196.1 y 191.8 ppm) y cinco para los dos anillos piridínicos equivalentes que constituyen la bipy- ^tBu . Igualmente, los dos sustituyentes *tert*-butilo son equivalentes. Los compuestos **2-6** son análogos y muestran datos espectroscópicos similares.

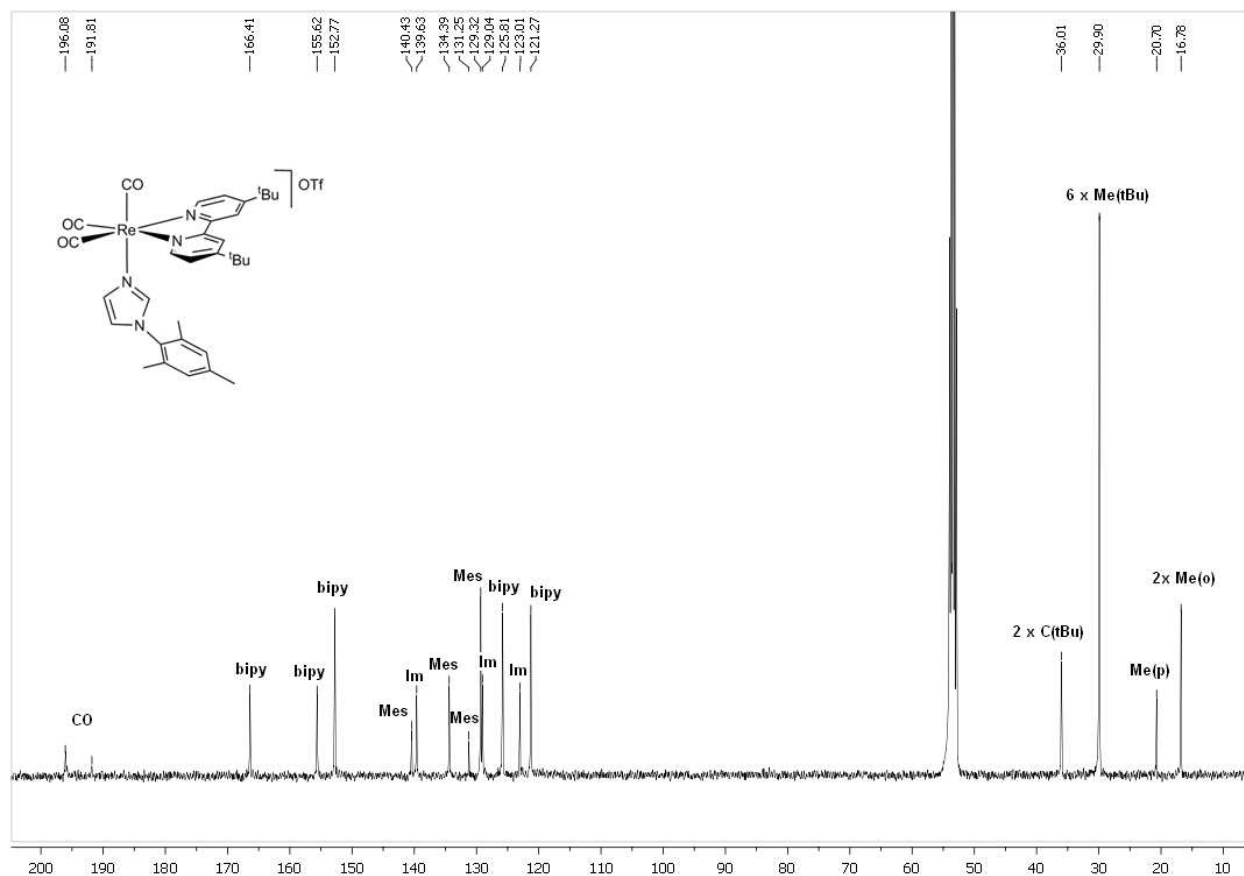


Figura 1.3 Espectro de ^{13}C RMN del compuesto **1** en CD_2Cl_2

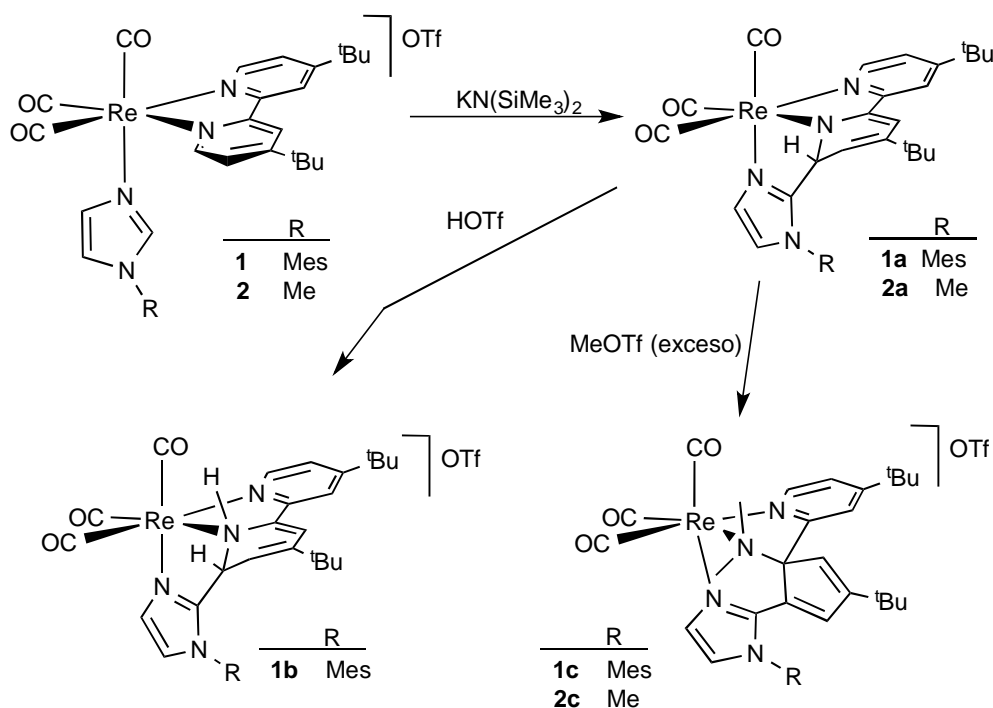
A continuación se procedió al estudio de la reactividad de los compuestos **1-6** frente a la base $\text{KN}(\text{SiMe}_3)_2$. En concreto, se eligió esta base debido a que se puede manipular fácilmente, es comercial, de bajo coste, poco nucleófila, y su ácido conjugado es la amina $\text{HN}(\text{SiMe}_3)_2$, la cual se puede lavar fácilmente con hexano, disolvente en el que, en la mayor parte de los casos, nuestros complejos no son solubles. Por otra parte, en los estudios previos de nuestro grupo de investigación, había dado lugar a mejores resultados que otras bases fuertes empleadas.

La adición de un ligero exceso de $\text{KN}(\text{SiMe}_3)_2$ a una disolución de los complejos **1** ó **2** en THF a $-78\text{ }^\circ\text{C}$ origina un llamativo cambio de color de amarillo a rojo intenso en ambos casos. Las bandas de IR correspondientes a los carbonilos se observan a frecuencias considerablemente más bajas, lo que es consistente con que haya tenido lugar una desprotonación y se hayan formado complejos neutros a partir de los derivados catiónicos. Los complejos resultantes **1a** y **2a** respectivamente (Esquema 1.7) presentan una elevada inestabilidad, de manera que no pudieron ser aislados. Únicamente en el caso del complejo **2a** fue posible caracterizar esta especie mediante un espectro de ^1H RMN en tolueno- d_8 del crudo de reacción.

La información más relevante de este espectro es, por un lado, la pérdida de simetría con respecto al complejo precursor, observándose una señal para cada hidrógeno aromático, así como la no equivalencia de los grupos ^tBu de la bipy- ^tBu . Por otro lado, sólo se observan dos señales

para los grupos CH del imidazol, lo que sugiere que ha sido uno de estos grupos el que ha sufrido la desprotonación. Además, las señales correspondientes a los hidrógenos de uno de los anillos piridínicos del ligando bipy-^tBu aparecen a campos inusualmente altos (5.70, 5.54 y 4.92 ppm), lo que se podría atribuir a la desaromatización del mismo como consecuencia del acoplamiento C-C entre el carbono central del imidazol y uno de los carbonos *orto* de la bipy-^tBu. Esta reactividad es análoga a la encontrada anteriormente para los compuestos [Re(CO)₃(bipy)(N-RIm)]OTf.^{23a}

Dada la inestabilidad de los complejos neutros **1a** y **2a**, decidimos hacerlos reaccionar *in situ* con electrófilos, intentando así que los productos finales de reacción fueran más estables y permitieran su caracterización. De esta forma, la adición de la cantidad equimolar de HOTf al crudo de reacción de **1a** en CH₂Cl₂, dio lugar a la formación del compuesto **1b** como único producto de reacción y en buen rendimiento (Esquema 1.7).



Esquema 1.7 Reactividad de los compuestos **1** y **2**

El compuesto **1b**, que efectivamente presentó una mayor estabilidad, se caracterizó espectroscópicamente en disolución, y mediante difracción de rayos X de monocristal en estado sólido. En la Figura 1.4 se muestra el espectro de ¹H RMN del mismo. En él podemos apreciar la ausencia de simetría, ya que cada grupo CH aromático se corresponde con una señal que integra por un hidrógeno. También se observan dos señales a campos altos, que integran por un hidrógeno cada una y que corresponden al anillo piridínico desaromatizado, en concreto, al hidrógeno unido al carbono que ha sufrido el acoplamiento, que ha pasado de hibridación sp² a sp³, y al hidrógeno del carbono contiguo al mismo. Se aprecia un singulete para cada grupo ^tBu, y un singulete para cada grupo CH₃ del mesitilo. Otra característica a destacar en este espectro es un singulete ancho a

8.11 ppm que corresponde al grupo NH formado como consecuencia de la protonación del átomo de nitrógeno del anillo piridínico desaromatizado.

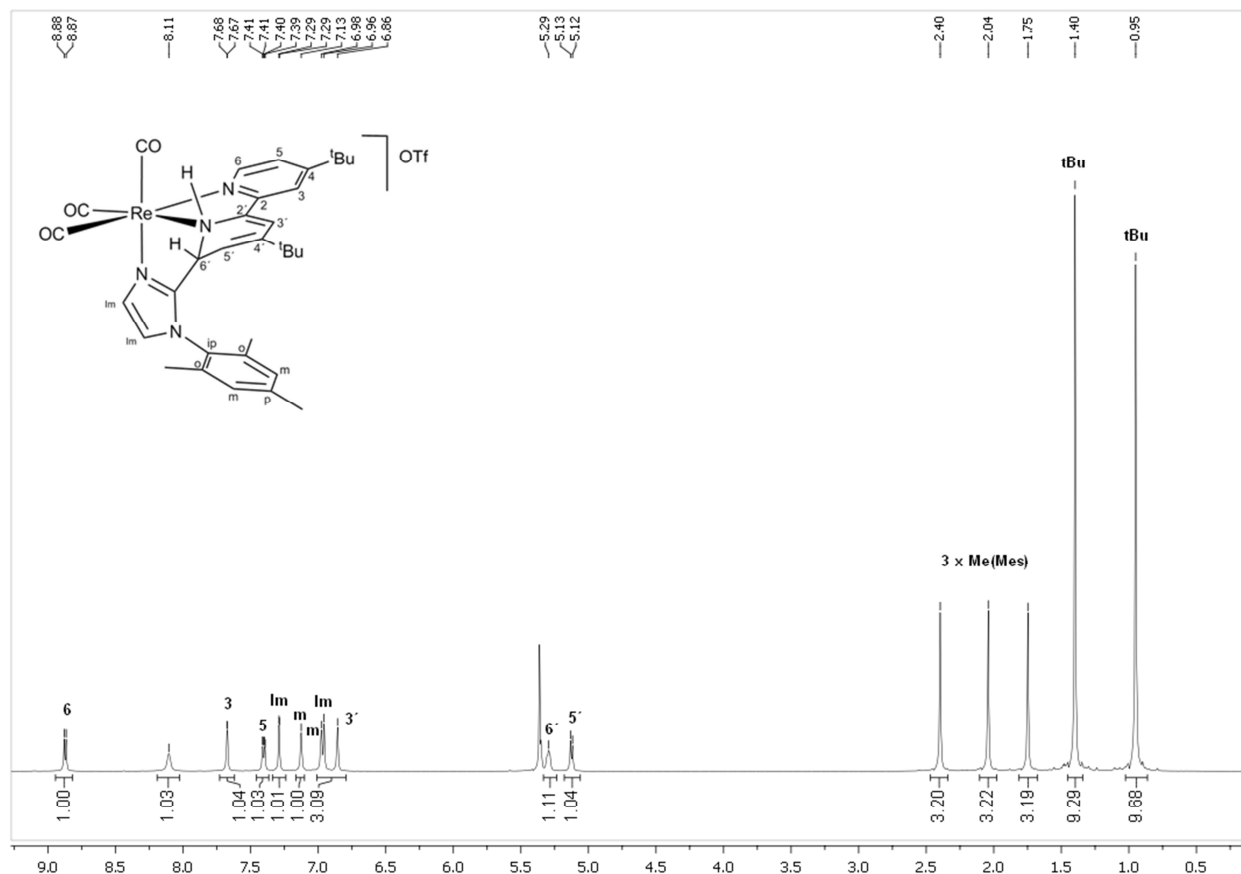


Figura 1.4 Espectro de ^1H RMN del compuesto **1b** en CD_2Cl_2

El espectro de ^{13}C RMN de **1b** es consistente con el acoplamiento y desaromatización del producto resultante, observándose la ausencia de simetría en la molécula. Significativamente, se observa una señal a 58.1 ppm que asignamos al carbono en posición *orto* del anillo piridínico que ha sufrido el acoplamiento, consistente con que haya pasado de hibridación sp^2 a sp^3 .

La estructura cristalina en estado sólido del compuesto **1b** está de acuerdo con la deducida a partir de sus datos espectroscópicos en disolución. Como se observa en la Figura 1.5 el catión de **1b** consta de un fragmento tricarbónico de renio en disposición facial, y un ligando tridentado resultante del acoplamiento entre el carbono C22 del imidazol y uno de los carbonos en posición *orto* de la bipy-^tBu (C6). Como consecuencia, esta última resulta desaromatizada, tal y como evidencian las distancias y ángulos de enlace en torno a dicho carbono, así como la pérdida de planicidad del anillo piridínico afectado. La distancia C6-C22, de 1.513(5) Å, muestra la formación de un enlace sencillo entre estos dos átomos y las distancias de enlace N1-C6 (de 1.490(5) Å) y C6-C5 (de 1.495(6) Å) son consistentes con la desaromatización del anillo piridínico, permitiendo proponer un enlace sencillo entre los mismos. También se observa que los

ángulos en torno al carbono C6 indican que su geometría es aproximadamente tetraédrica, es decir, presenta hibridación sp^3 , en lugar de sp^2 , como correspondería a un carbono aromático. Por otro lado, el átomo de nitrógeno del anillo piridínico activado, como consecuencia de la protonación, ha pasado de pertenecer a un ligando de tipo imina a pertenecer a un grupo amino. Esta reactividad es análoga a la encontrada anteriormente para los compuestos $[\text{Re}(\text{CO})_3(\text{N-N})(\text{N-MesIm})]\text{OTf}$ (siendo N-N= bipy, phen).^{23a}

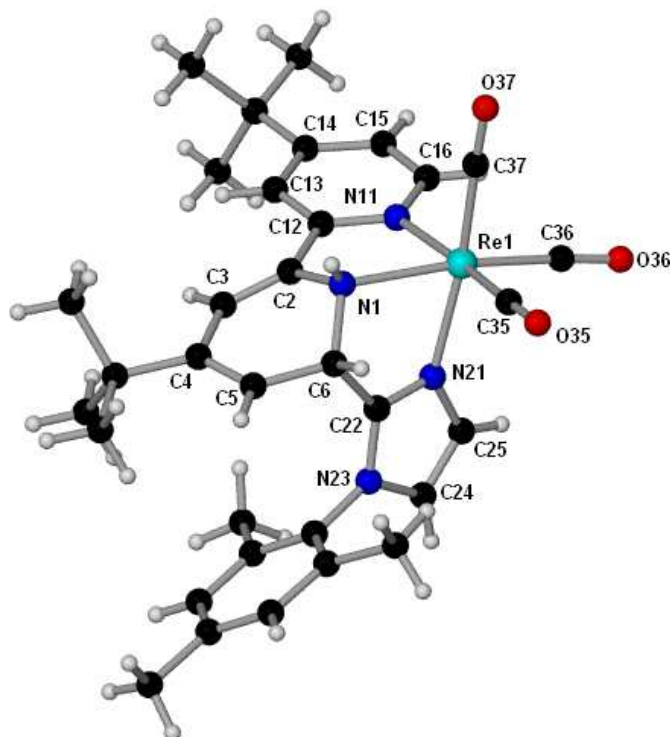


Figura 1.5 Estructura en estado sólido del catión presente en **1b**

En vista de la estructura de **1b** podemos proponer que la inestabilidad de los intermedios neutros **1a** y **2a** puede deberse, al menos en parte, a que una vez que se ha producido la desaromatización del grupo piridilo, éste pasa de ser un ligando imínico neutro a ser un amiduro aniónico. El par de electrones no compartido de ese nitrógeno es el responsable de la elevada reactividad de estos compuestos, y al añadir el HOTf es este átomo de nitrógeno el que resulta protonado formando un grupo amino, mucho más estable.

La reacción de los compuestos **1a** y **2a** con triflato de metilo presenta alguna diferencia con respecto a la adición de HOTf, pues se encontró que era necesario el empleo de exceso de este reactivo (aproximadamente el doble de la cantidad equimolar) para que la reacción se completara (Esquema 1.7). Se obtuvieron así los compuestos **1c** y **2c** respectivamente, como únicos productos de reacción, y se caracterizaron espectroscópicamente en disolución y, en el caso de **1c**, en estado sólido mediante difracción de rayos X de monocristal.

Como se muestra en la Figura 1.6, el catión presente en el compuesto **1c** consta de un fragmento metálico en el que el átomo de renio se encuentra en un entorno de coordinación aproximadamente octaédrico, con tres ligandos carbonilo en disposición facial y situados en posición *trans*, cada uno de ellos, a un átomo de nitrógeno de un ligando tridentado. Este ligando puede describirse como un ciclopentadienilo central del que salen tres grupos nitrógeno-dadores distintos: un grupo 2-piridilo, un grupo dimetilamino y un N-MesIm. La formación de este ligando implica el acoplamiento C-C entre el N-MesIm y la bipy-^tBu, y la ruptura del enlace C-N del anillo piridínico que sufre el ataque nucleófilo. Se observa también que el átomo de nitrógeno que sufre la ruptura está doblemente metilado, formando el grupo dimetilamino anteriormente mencionado. Las distancias de enlace de los carbonos que forman el ciclopentadienilo muestran que no hay deslocalización electrónica, siendo C2-C3 (1.528(11) Å), C2-C6 (1.533(13) Å) y C4-C5 (1.499(12) Å) características de enlaces sencillos, mientras que las distancias C3-C4 y C5-C6 (1.314(11) Å y 1.347(13) Å respectivamente) son típicas de enlaces dobles.

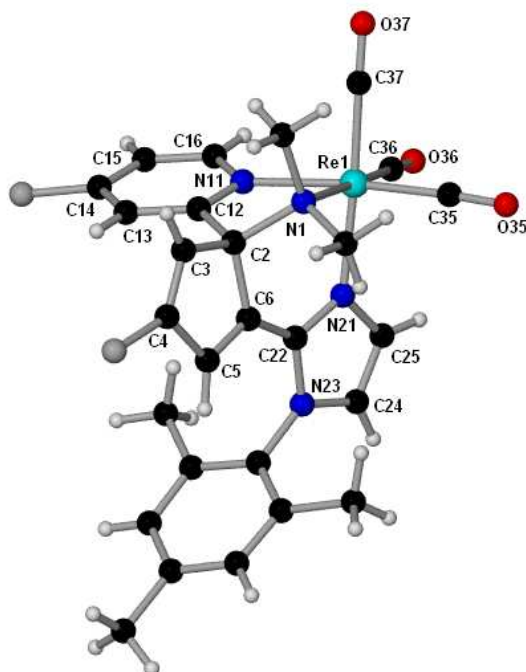


Figura 1.6 Estructura en estado sólido del catión presente en **1c**

El espectro de ¹H RMN del compuesto **1c** en CD₂Cl₂ se muestra en la Figura 1.7, y es coherente con la estructura encontrada en estado sólido. En primer lugar se observa la asimetría de la molécula, y además de las señales que corresponden al N-MesIm acoplado, se observan 3 señales correspondientes a un anillo piridínico y dos dobletes con la misma constante, a campos algo más altos que los hidrógenos aromáticos, que asignamos a los dos grupos CH del ciclopentadienilo. En la zona de hidrógenos alifáticos se observan, además de las señales de los

grupos ^tBu y mesitilo, dos singuletes que integran por 3 hidrógenos cada uno que asignamos a los dos grupos metilo del nitrógeno que ha experimentado la extrusión.

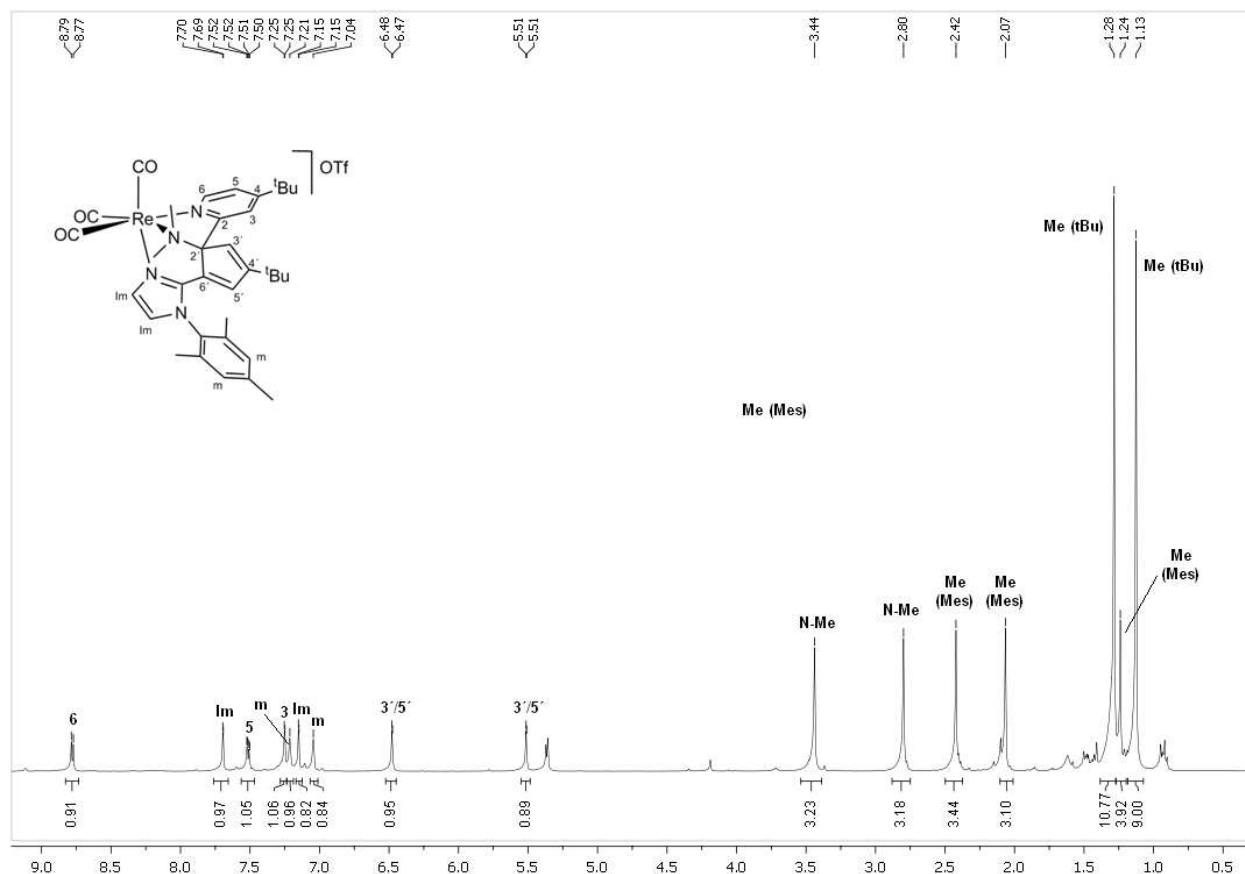
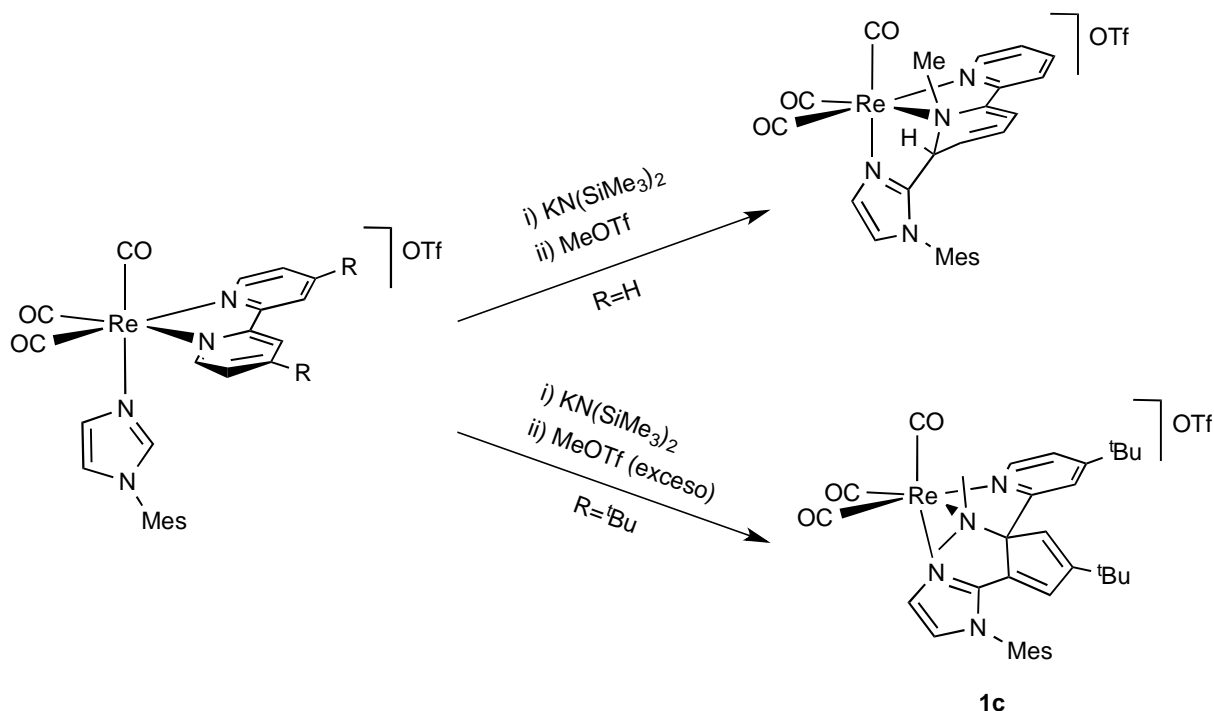


Figura 1.7 Espectro ¹H RMN del compuesto **1c** en CD₂Cl₂

Los datos espectroscópicos del compuesto **2c** son similares a los que acabamos de comentar para **1c**, lo que nos permite proponer que su naturaleza es análoga.

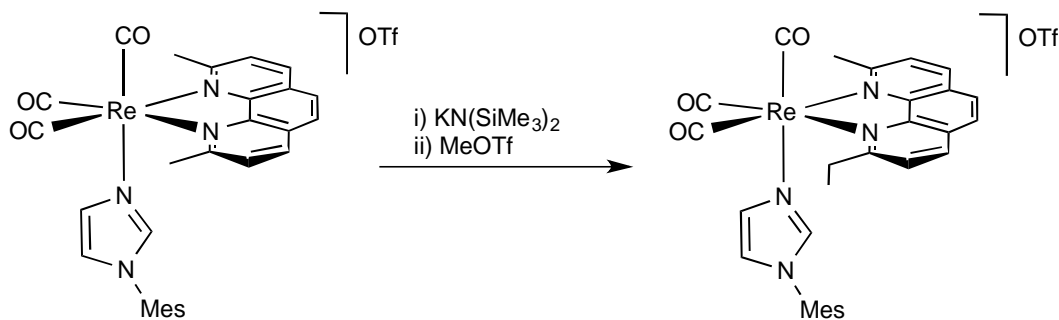
En los estudios previos con el ligando 2,2'-bipiridina sin sustituir esta reactividad se había observado únicamente para el compuesto [Re(CO)₃(bipy)(N-MeIm)]OTf, mientras que para el complejo análogo con mesitilimidazol [Re(CO)₃(bipy)(N-MesIm)]OTf, se había obtenido el producto de acoplamiento monometilado en el nitrógeno, sin que llegara a producirse la ruptura del enlace C-N (Esquema 1.8). Esto parece indicar que la presencia de los sustituyentes ^tBu en las posiciones 4 y 4' de la bipy no sólo no evita el ataque nucleófilo del imidazolilo al carbono *orto* de la bipiridina, sino que confieren una reactividad adicional a los compuestos. Esto puede atribuirse a que, una vez se ha producido el acoplamiento C-C, el carácter σ -dador del grupo ^tBu hace al grupo piridilo desaromatizado más reactivo frente al MeOTf, de manera que el N-MesIm, que es menos rico electrónicamente que el N-MeIm, es también capaz, en este caso, de producir la apertura del heterociclo.



Esquema 1.8 Diferencia entre la reactividad de los compuestos $[Re(CO)_3(bipy)(N-MesIm)]OTf$ y **1**

La reactividad de los compuestos **1** y **2**, que incluye dos nuevos ejemplos de apertura de un anillo piridínico en condiciones suaves, confiere una cierta generalidad a la previamente encontrada para los compuestos con bipy.

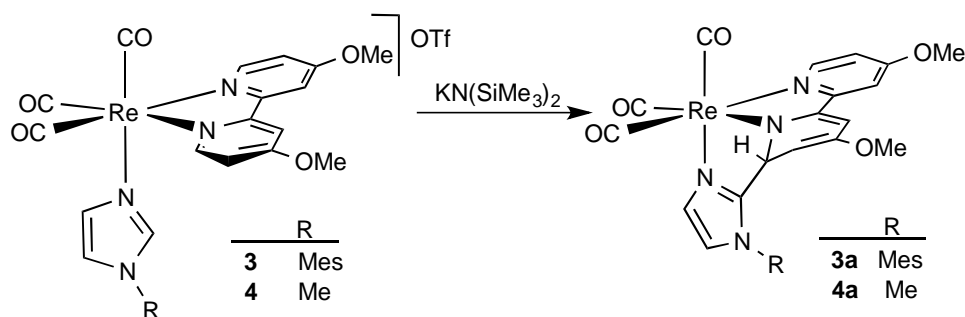
Ante estos resultados, se decidió utilizar un ligando bidentado con las posiciones *orto* sustituidas para, por impedimento estérico, dirigir el ataque nucleófilo hacia otras posiciones de la molécula. Se preparó el compuesto análogo a **1** con el ligando 2,9-dimetil-1,10-fenantrolina (neocuproina) siguiendo la misma estrategia sintética que para los compuestos **1-6** (ver Parte Experimental de este Capítulo). El compuesto $[Re(CO)_3(neo)(N-MesIm)]OTf$ (neo= neocuproina) reaccionó con un equivalente de la base $KN(SiMe_3)_2$, y a continuación con MeOTf para dar lugar a la formación del compuesto $[Re(CO)_3(neo-Et)(N-MesIm)]OTf$ (neo-Et= 2-etil-9-metil-1,10-fenantrolina), como se muestra en el Esquema 1.9.



Esquema 1.9 Reactividad del compuesto $[Re(CO)_3(neo)(MesIm)]OTf$

Tanto la caracterización en disolución como en estado sólido del complejo $[\text{Re}(\text{CO})_3(\text{neo-Et})(\text{N-MesIm})]\text{OTf}$ muestran la formación de un grupo etilo como sustituyente de uno de los carbonos *orto* de la diimina. La formación del mismo se produce por la desprotonación de uno de los grupos metilo de la neocuproina, y posterior metilación del grupo CH_2 resultante.

Continuamos entonces nuestro estudio empleando sustituyentes más dadores en las posiciones 4 y 4' de la bipy. La reacción de desprotonación de los compuestos **3** y **4**, con el ligando 4,4'-dimetoxi-2,2'-bipiridina (bipy-OMe) tiene lugar de manera prácticamente instantánea, observándose un cambio de color de amarillo a rojo oscuro en ambos casos, y la disminución de la frecuencia de las bandas ν_{CO} en los espectros de IR, lo que es coherente con la formación de los compuestos neutros **3a** y **4a** respectivamente (Esquema 1.10).



Esquema 1.10 Reacción de los compuestos **3** y **4** con $\text{KN}(\text{SiMe}_3)_2$

Si bien los compuestos **3a** y **4a** resultaron ser bastante inestables, el derivado con N-MesIm, **3a**, pudo ser caracterizado espectroscópicamente en disolución. En la Figura 1.8 se muestra el espectro de ^1H RMN de **3a** en CD_2Cl_2 .

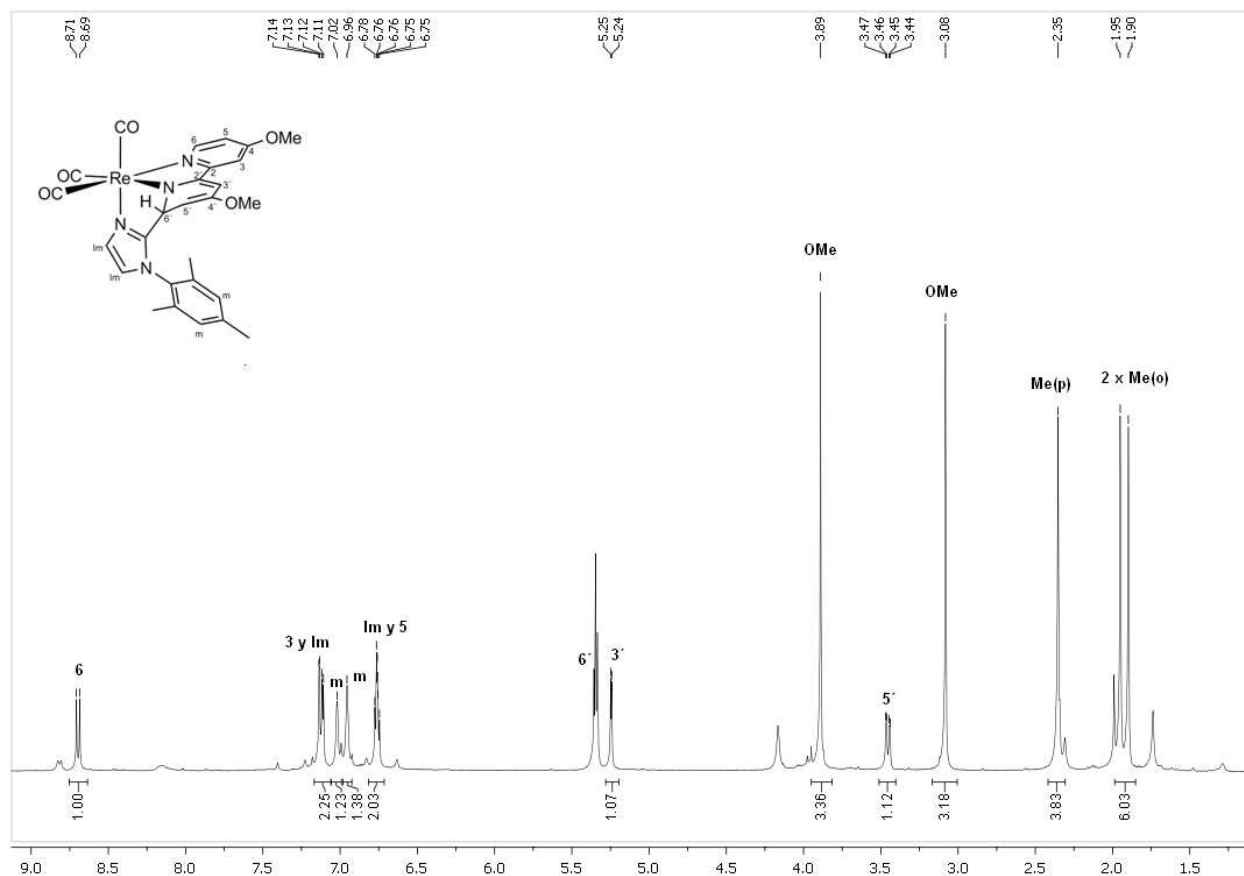


Figura 1.8 Espectro ^1H RMN del complejo **3a**

En primer lugar, resulta sorprendente que el compuesto **3a** presenta un patrón de señales en el espectro de ^1H RMN considerablemente diferente al encontrado para el derivado análogo **2a**, comentado anteriormente. Coincide con aquél en la pérdida del plano de simetría presente en los compuestos de partida; sin embargo, en las señales correspondientes al anillo piridínico desaromatizado se observa una clara diferencia. Dos de las señales aparecen a desplazamientos químicos similares a los encontrados para **2a** (5.25 y la otra señal, asignada con la ayuda de los experimentos bidimensionales HSQC y COSY, está enmascarada bajo la señal residual del disolvente), sin embargo la tercera se encuentra a campo excepcionalmente alto, a 3.45 ppm. De hecho, la señal de ^{13}C correspondiente a este grupo CH se observa, basándonos en el experimento bidimensional de HSQC, a 64.5 ppm, un desplazamiento químico típico para carbonos no aromáticos.

La reacción de **3a** y **4a** con ácido tríflico, dio lugar, selectivamente y en buen rendimiento, a los nuevos productos **3b** y **4b**, respectivamente (Esquema 1.11). La difusión lenta de hexano en una disolución concentrada de **3b** en CH_2Cl_2 a $-20\text{ }^\circ\text{C}$ dio lugar a cristales de color rojo, uno de los cuales se empleó para la determinación estructural en estado sólido mediante difracción de rayos X de monocristal. La representación grafica del catión se muestra en la Figura 1.9 y en la Tabla 1.1 se recogen las distancias y ángulos de enlace más representativos.

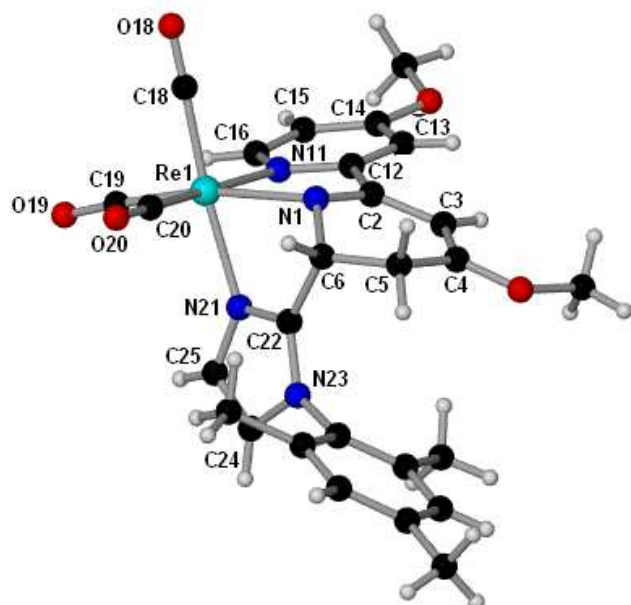


Figura 1.9 Estructura en estado sólido del catión presente en el compuesto **3b**.

Distancias de enlace (Å)			
Re(1)-C(18)	1.923(5)	C(6)-C(22)	1.526(6)
Re(1)-C(19)	1.912(6)	C(6)-C(5)	1.516(6)
Re(1)-C(20)	1.940(6)	C(5)-C(4)	1.491(6)
Re(1)-N(1)	2.148(4)	C(4)-C(3)	1.348(7)
Re(1)-N(11)	2.193(4)	C(3)-C(2)	1.433(6)
Re(1)-N(21)	2.202(4)	C(2)-C(12)	1.488(6)
N(1)-C(2)	1.308(6)	C(12)-C(13)	1.375(7)
N(1)-C(6)	1.489(6)	C(13)-C(14)	1.401(7)
N(11)-C(16)	1.331(6)	C(14)-C(15)	1.381(7)
N(11)-C(12)	1.357(6)	C(15)-C(16)	1.385(7)

Ángulos de enlace (°)			
O(18)-C(18)-Re(1)	178.4(5)	N(1)-C(6)-C(22)	99.3(3)
O(19)-C(19)-Re(1)	176.9(5)	C(5)-C(6)-C(22)	118.2(4)
O(20)-C(20)-Re(1)	178.5(5)	C(6)-N(1)-Re(1)	111.4(3)
N(1)-Re(1)-N(11)	73.6(1)	C(2)-N(1)-Re(1)	119.8(3)
N(11)-Re(1)-N(21)	91.8(2)	C(6)-C(22)-N(21)	117.9(4)
N(1)-Re(1)-N(21)	70.1(1)	C(6)-C(22)-N(23)	132.4(4)
C(6)-N(1)-C(2)	115.9(4)	Re(1)-N(21)-C(22)	113.9(3)
N(1)-C(6)-C(5)	114.0(4)	C(5)-C(4)-C(3)	121.3(4)
C(6)-C(5)-C(4)	111.6(4)	C(4)-C(3)-C(2)	118.9(4)

Tabla 1.1 Ángulos y distancias de enlace seleccionados del compuesto **3b**

Como se puede observar, el catión de **3b** consiste en un fragmento *fac*-{Re(CO)₃} enlazado a un ligando tridentado N-dador, que es el resultado del acoplamiento C-C entre el átomo de carbono central del imidazol (C22) y uno de los grupos CH en posición *orto* del ligando bipy-OMe (C6). Aunque este tipo de reactividad puede resultar similar a la comentada anteriormente para el compuesto **1b**, existe una diferencia sorprendente, ya que en este caso, la protonación se ha producido en el carbono C5 del anillo desaromatizado y no en el nitrógeno (N1), lo que da lugar a la formación de un grupo dihidropiridilo. Las distancias C5-C6 y C4-C5 de 1.516(6) Å y 1.491(6) Å corresponden a enlaces simples, mientras que N1-C2 (1.308(6) Å) y C3-C4 (1.348(7) Å) son distancias típicas para enlaces dobles. Además, el ángulo diedro entre los planos definidos por C4-C5-C6 y C2-C3-C4, de 23.0°, refleja la desviación del átomo C5 del plano del anillo aromático.

Los datos espectroscópicos en disolución de **3b** y **4b** están de acuerdo con la estructura encontrada en estado sólido para **3b**. Como ejemplo, en la Figura 1.10 se muestra el espectro de ¹H RMN del compuesto **3b**. Cabe destacar que se observan 3 señales para el anillo de bipy-OMe que no ha sufrido el ataque y, a campos considerablemente más bajos, cuatro señales que corresponden al anillo desaromatizado. Las dos señales de este anillo que se observan a un desplazamiento químico extraordinariamente bajo (3.07 y 1.99 ppm) correlacionan fuertemente entre sí en el espectro bidimensional de COSY, lo que conjuntamente con el espectro de HSQC, nos permite proponer que ambos hidrógenos se encuentran unidos al mismo átomo de carbono (a 28.1 ppm en el espectro de ¹³C RMN). Un experimento DEPT-135 confirmó que este grupo es un CH₂, al observarse en antifase al resto de las señales del espectro (grupos CH y CH₃).

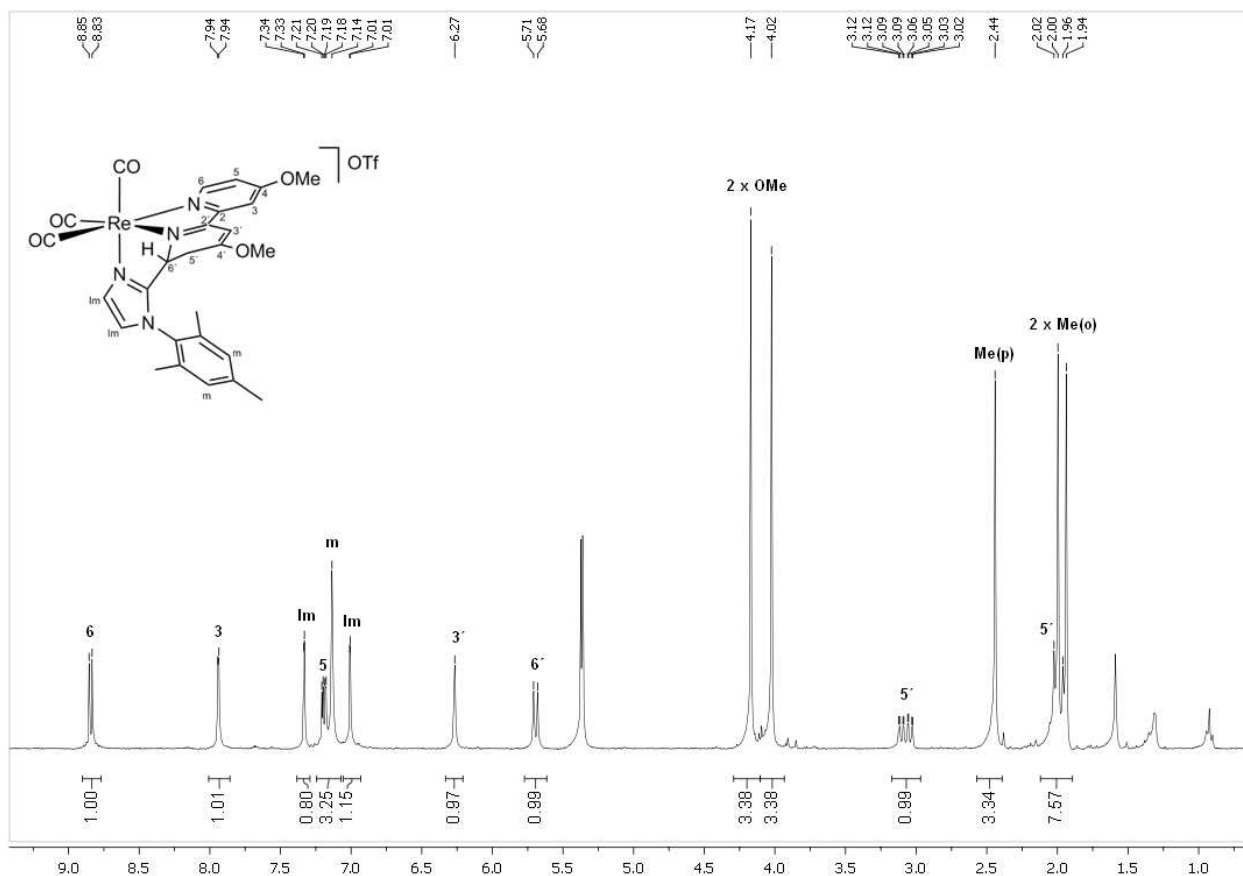
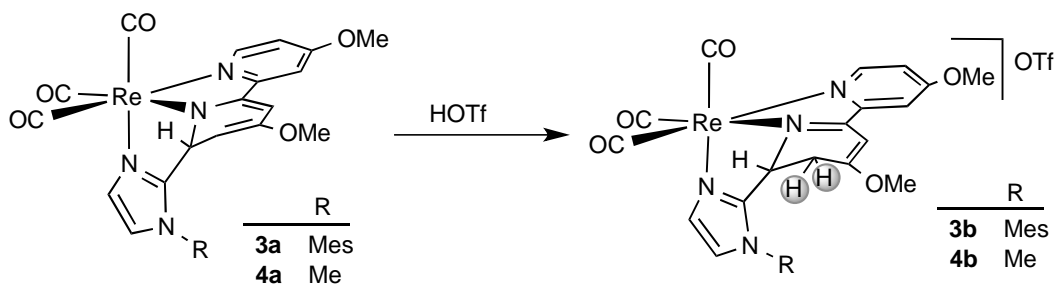


Figura 1.10 Espectro de ^1H RMN en CD_2Cl_2 del compuesto **3b**

Los datos espectroscópicos en disolución del compuesto **4b** son análogos a los que acabamos de comentar para **3b**, lo que nos permite proponer que se trata de un compuesto isoestructural a **3b** (Esquema 1.11).

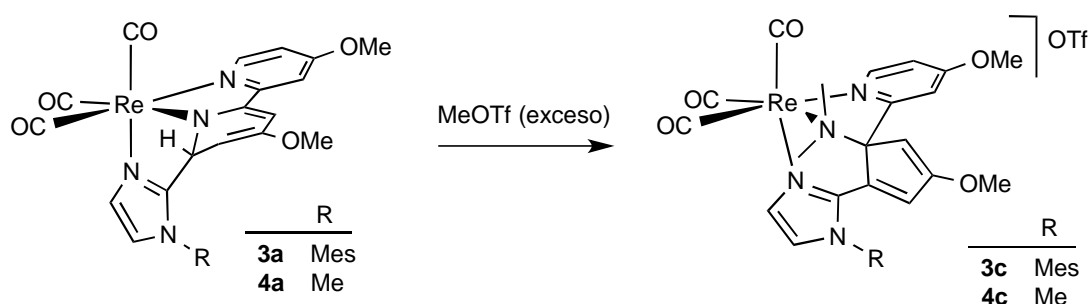


Esquema 1.11 Reactividad frente a la adición de HOTf de **3a** y **4a**

Es sorprendente que, en este caso, la protonación no tiene lugar en el átomo de nitrógeno del anillo desaromatizado, sino que se produce sobre el carbono contiguo al que sufre el acoplamiento (C5) para dar lugar a la formación de un grupo dihidropiridilo. Este resultado tan novedoso, que, hasta donde sabemos, carecía de precedentes en la bibliografía, podría considerarse un paso

crucial en la ruptura de un enlace C-C aromático, reacción que juega un papel muy importante para la síntesis de moléculas orgánicas partiendo de materias primas del petróleo.^{45,49}

Los compuestos neutros **3a** y **4a** reaccionan con triflato de metilo en exceso para dar lugar a la formación, como únicos productos de reacción, de los compuestos de doble metilación y apertura del anillo piridínico **3c** y **4c**, respectivamente (Esquema 1.12).



Esquema 1.12 Reacción de los compuestos **3a** y **4a** con exceso de MeOTf

Los espectros de ¹H RMN de **3c** y **4c** muestran que ambos compuestos son análogos a los compuestos ya descritos **1c** y **2c**, siendo lo más significativo de los mismos la doble metilación del átomo de nitrógeno del anillo piridínico desaromatizado originando, por tanto, su extrusión y la formación de un grupo ciclopentadienilo. Es interesante notar que, al igual que ocurría con los derivados con sustituyentes ^tBu, la reacción de apertura se produce con el N-MeIm, pero también con el N-MesIm.

Como se observa en la Figura 1.11, la estructura en estado sólido del catión presente en **4c** coincide con la propuesta a partir de sus datos espectroscópicos en disolución. Como en el caso de los compuestos análogos **1c** y **2c**, el catión consta de un átomo de renio central en un entorno de coordinación pseudo-octaédrico con los tres ligandos carbonilo en disposición facial y un ligando tridentado N-dador ocupando la cara opuesta, que resulta del acoplamiento C-C entre el carbono central del imidazol y el carbono en posición *orto* de la bipy-OMe, y la posterior ruptura del enlace C-N del anillo piridínico que ha sido atacado.

⁴⁹ (a) R. H. Crabtree, *Chem. Rev.* **1985**, 85, 245. (b) W. D. Jones, *Nature*, **1993**, 364, 676. (c) B. Rybtchinski, D. Milstein, *Angew. Chem. Int. Edn Engl.* **1999**, 38, 870. (d) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, 103, 1759. (e) C. H. Jun, *Chem. Soc. Rev.* **2004**, 33, 610. (f) W. D. Jones in *Comprehensive Organometallic Chemistry III*, Vol. 1, Ch. 1.25, R. H. Crabtree, D. M. P. Mingos, eds.; Elsevier, **2006**.

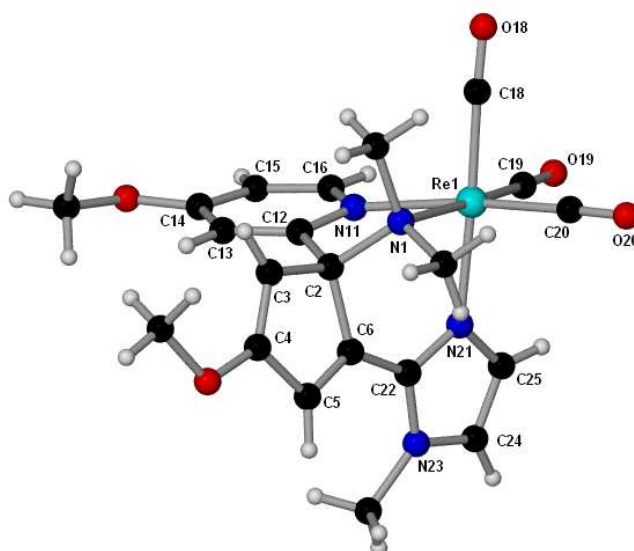
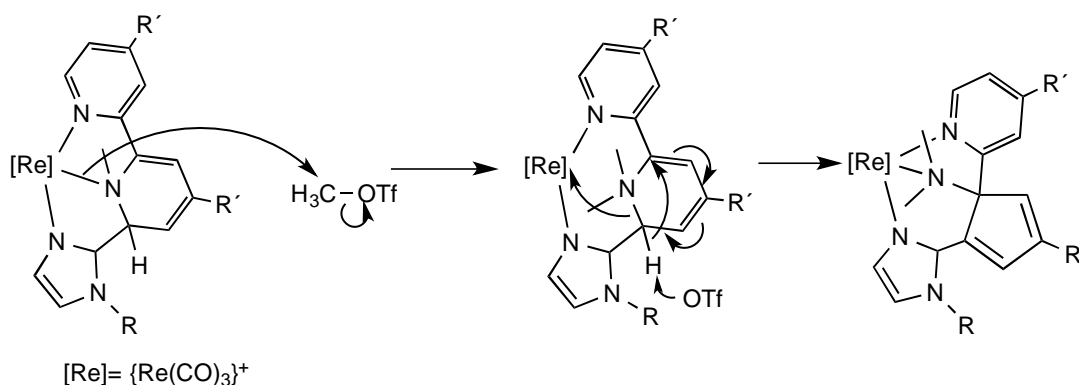


Figura 1.11 Estructura en estado sólido del catión presente en **4c**

Estos resultados muestran que la reacción de acoplamiento C-C y ruptura de un enlace C-N por adición de MeOTf a los productos de desprotonación de los compuestos $[\text{Re}(\text{CO})_3(\text{bipy-R}')(\text{N-RIm})]\text{OTf}$ tiene una cierta generalidad y establece un nuevo tipo de activación y ruptura de enlaces C-N en sistemas piridínicos, pues en los escasos ejemplos que se conocen con metales de los primeros grupos de transición, la coordinación $\kappa^2\text{-(C,N)}$ de la piridina es la que genera la pérdida de aromaticidad, para posteriormente evolucionar hasta el producto final.^{31-33,35}

Como se ha comentado anteriormente, el estudio de esta misma reactividad en complejos análogos de tipo $[\text{Re}(\text{CO})_3(\text{N-N})(\text{N-MesIm})]\text{OTf}$ (siendo N-N= bipy o phen), dio lugar a los productos de acoplamiento y metilación en el nitrógeno. En ausencia de estudios mecanísticos, esto nos permite proponer que en la formación de los productos doblemente metilados **1c-4c** en primer lugar se obtienen los productos resultantes de una sola metilación. A continuación, una segunda metilación de los mismos originaría la ruptura del enlace C-N y formación del grupo ciclopentadienilo (Esquema 1.13).



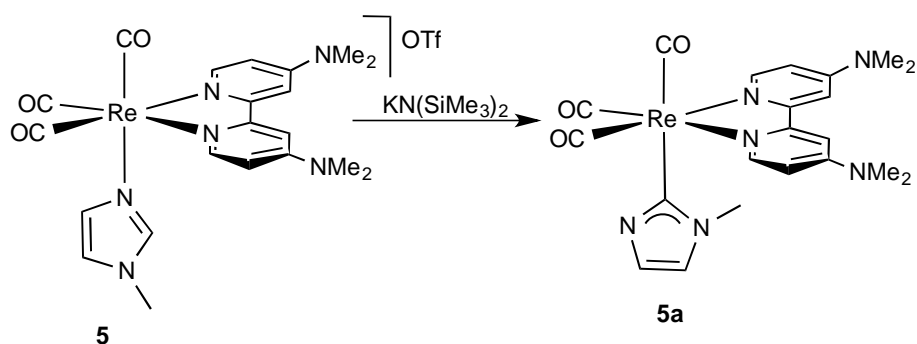
Esquema 1.13 Mecanismo propuesto para la formación de los compuestos **1c-4c**.

Finalmente pasamos a estudiar la reactividad de los compuestos $[\text{Re}(\text{CO})_3(\text{bipy-NMe}_2)(\text{N-RIm})\text{OTf}]$ ($\text{R} = \text{Me}$, **5**; Mes , **6**) frente a bases fuertes, en los que los sustituyentes en las posiciones 4, 4' de la bipy son grupos dimetilamino (NMe_2), muy dadores de densidad electrónica.

La adición de $\text{KN}(\text{SiMe}_3)_2$ a una disolución del compuesto **5** en THF a -78°C da lugar a la formación del complejo imidazol-2-ilo **5a** (Esquema 1.14). En el espectro de IR del nuevo complejo **5a** la frecuencia de las bandas para los carbonilos es considerablemente menor que en el espectro de IR de **5**, lo que es consistente con la formación de un complejo neutro a partir de uno catiónico.

En el espectro de ^1H RMN de **5a** se observa que la molécula sigue manteniendo un plano de simetría, que hace a los dos anillos del ligando bipy- NMe_2 equivalentes. Por otro lado, se aprecia la ausencia de una de las señales correspondientes a un grupo CH del imidazol, lo que confirma que la desprotonación ha tenido lugar. La señal más significativa en el espectro de ^{13}C RMN de **5a** es una señal de baja intensidad, a 178.5 ppm, que es característica de un enlace Re-C .²⁰ Los datos espectroscópicos en disolución nos permiten proponer, por tanto, que en el caso del compuesto **5**, la evolución del producto resultante de la desprotonación da lugar a la formación de un complejo 2-imidazolilo, coordinado al renio por el átomo de carbono. Características espectroscópicas similares se encontraron en el complejo resultante de desprotonar el grupo CH central de un imidazol en el compuesto $[\text{Re}(\text{CO})_3(\text{N-MeIm})_3]\text{OTf}$, cuya estructura cristalina confirmó que se trataba de un complejo 2-imidazolilo.^{20a}

Esta clase de complejos, que contienen un ligando imidazolilo, con un átomo de nitrógeno sin sustituyentes son escasos en la bibliografía,^{50,20} tienden a ser muy inestables y han sido propuestos como intermedios de reacción en la tautomerización de ligandos N-alquilimidazol a carbenos NHC.⁵¹

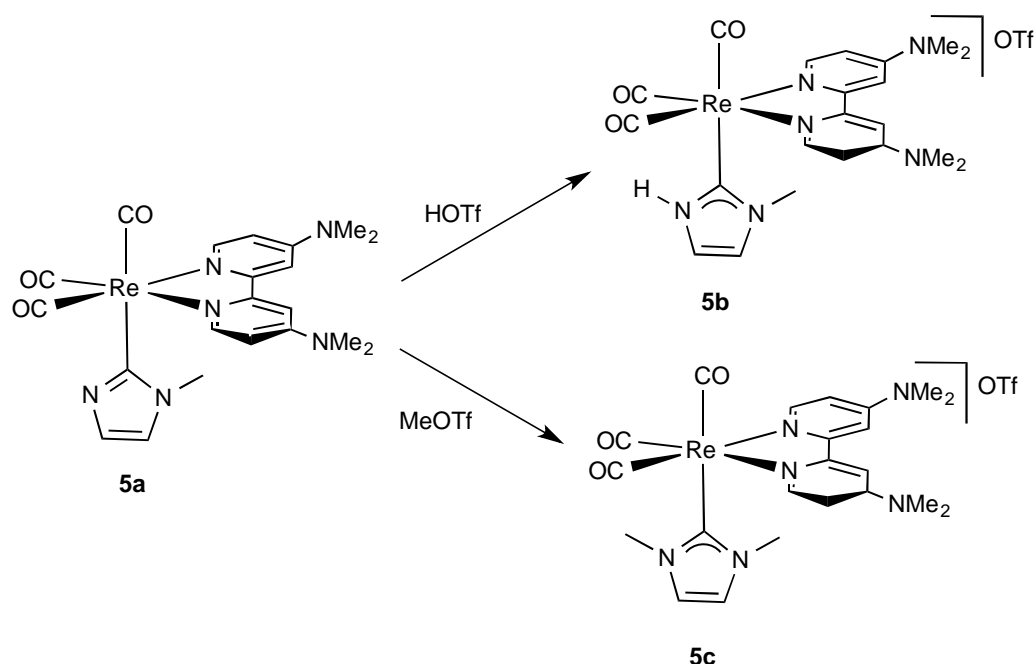


Esquema 1.14 Reacción del complejo **5** con $\text{KN}(\text{SiMe}_3)_2$

⁵⁰ (a) A. Wacker, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 843. (b) D. Vagedes, G. Kehr, D. König, K. Wedeking, R. Fröhlich, G. Erker, C. Mück-Lichtenfeld, S. Grimme, *Eur. J. Inorg. Chem.* **2002**, 2015. (c) A. Kaufhold, T. Stasch, A. Pape, P. G. Hepp, P. D. Edwards, O. Newman, F. E. Hahn, *J. Am. Chem. Soc.* **2009**, *131*, 306. (d) J. Ruiz, A. Berros, B. F. Perandones, M. Vivanco, *Dalton Trans.* **2009**, 6999. (e) T. Kösterke, J. Kösters, E.-U. Würthwein, C. Mück-Lichtenfeld, C. Schulte to Brinke, F. Lahoz, F. E. Hanh, *Chem. Eur. J.* **2012**, *18*, 14594. (f) D. Brackemeyer, A. Hervé, C. Schulte to Brinke, M. C. Jahnke, F. E. Hahn, *J. Am. Chem. Soc.* **2014**, *136*, 7841.

⁵¹ R. J. Sundberg, R. F. Bryan, I. F. Taylor Jr, H. Taube, *J. Am. Chem. Soc.* **1974**, *96*, 381. Ver también referencias 14, 16, 17 y 22b.

La reacción del compuesto **5** con MeOTf ó HOTf dio lugar a la formación de los compuestos **5b** y **5c** respectivamente (Esquema 1.15), cuyas estructuras se determinaron mediante difracción de rayos X de monocristal.



Esquema 1.15 Adición de HOTf y MeOTf al complejo **5a**. Obtención de **5b** y **5c**.

Los datos resultantes de la determinación estructural del complejo **5b** mostraron que el cristal elegido estaba maclado, de manera que la calidad de los mismos no es suficiente para poder llevar a cabo un análisis detallado de sus ángulos y distancias de enlace. No obstante se puede determinar inequívocamente su conectividad, encontrando que se trata de un complejo con un ligando NH-NHC. Este tipo de ligandos son mucho menos habituales que los ligandos NHC disustituidos, pues su síntesis no es accesible por el método más común de desprotonación de una sal de imidazolío.

En la Figura 1.12 se muestra el catión presente en el compuesto **5c**, que contiene tres carbonilos en disposición facial, un ligando bipyridina quelato y un ligando carbeno NHC simétrico, con sustituyentes metilo en ambos nitrógenos del imidazol, uno de los cuales procede de la metilación con MeOTf. El ligando NHC se coordina al renio por el átomo de carbono central con una distancia Re-C(22) de 2.192 Å, relativamente corta, como es de esperar para un ligando muy σ -dador como es el ligando NHC.

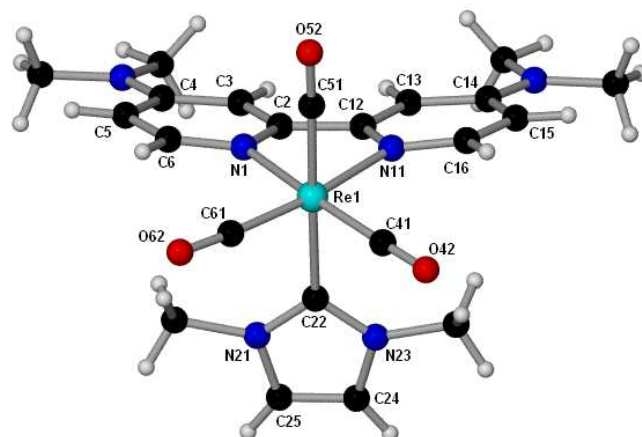


Figura 1.12 Estructura en estado sólido del catión de **5c**.

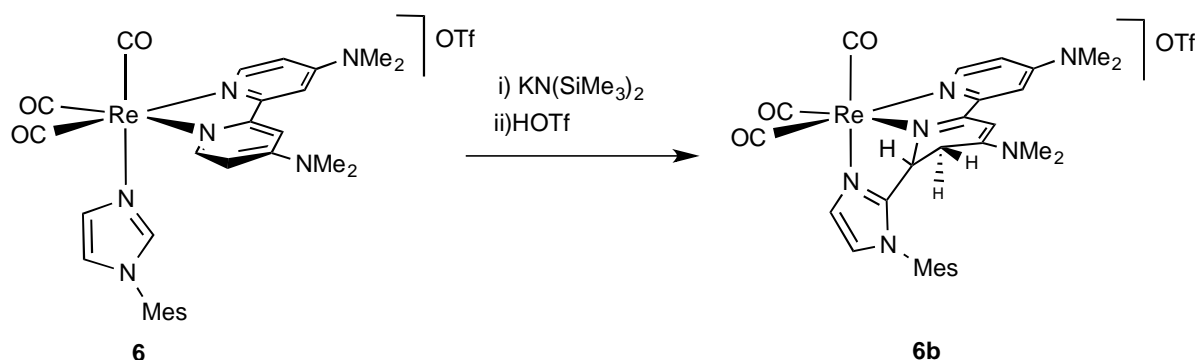
Los datos espectroscópicos en disolución de ambos compuestos, **5b** y **5c**, son coherentes con la formación de los complejos NHC catiónicos encontrados en estado sólido. Así, por ejemplo, el espectro de ^1H RMN de **5b** muestra el patrón de señales típico para una bipy-NMe₂ simétrica, dos señales que integran por un hidrógeno cada una a 6.91 y 6.86 ppm, que corresponden a los dos grupos CH del NHC (en el caso del compuesto **5c**, estos dos grupos son equivalentes), y un singlete a 3.95 ppm que asignamos al grupo metilo. Lo más significativo en los espectros de ^{13}C RMN es la señal que corresponde al carbono carbénico unido al átomo de renio, por ejemplo, a 177.1 ppm para el compuesto **5c**.

El efecto electrónico de los sustituyentes NMe₂ en posición 4 y 4' del ligando bipy-NMe₂ es, por tanto, lo suficientemente acusado como para evitar el ataque nucleófilo del imidazolilo al carbono *orto* de uno de los anillos del ligando bidentado. En su lugar, el ataque se produce sobre el átomo metálico, de manera que el imidazolilo cambia su modo de coordinación de N- a C-coordinado. La posterior metilación o protonación del nitrógeno no sustituido da lugar a la formación del correspondiente carbeno NHC. Esta reactividad es reminiscente de la encontrada para los complejos de fórmula $[\text{Mn}(\text{CO})_3(\text{bipy})(\text{N-RIm})]^+$ comentada en la Introducción de este Capítulo.

Estudiamos a continuación la reactividad del compuesto $[\text{Re}(\text{CO})_3(\text{bipy-NMe}_2)(\text{N-MesIm})]\text{OTf}$ (**6**) encontrando, en este caso, una diferencia sustancial al cambiar el ligando N-MeIm (en **5**) por N-MesIm. La desprotonación del compuesto **6** dio lugar al complejo neutro **6a**, que resultó demasiado inestable y no pudo ser aislado ni caracterizado en disolución.

La adición de ácido trifílico al crudo de reacción de **6a** condujo a la formación del compuesto **6b** (Esquema 1.16). Análogamente a lo que ocurría para los compuestos **3b** y **4b**, la caracterización en disolución de **6b** (ver Parte Experimental de este Capítulo) muestra que se ha producido, por un lado, un acoplamiento C-C entre el N-MesIm y el ligando bipy-NMe₂ con la consecuente desaromatización del anillo piridínico implicado, y por otro, la formación de un

grupo CH₂ contiguo al carbono piridínico acoplado. Las señales más características en el espectro de ¹H RMN son dos multipletes que corresponden a un hidrógeno cada uno, a desplazamientos químicos bajos y que correlacionan fuertemente en el espectro de COSY. Estas señales se asignan a los hidrógenos del grupo CH₂ formado por la reacción de protonación, cuya señal en el espectro de ¹³C RMN se observa a 27.1 ppm. Este desplazamiento químico es típico para un carbono sp³, mientras que el carbono que ha sufrido el acoplamiento, ahora también con hibridación sp³, aparece a menor campo, a 64.2 ppm, como consecuencia de estar unido directamente a un átomo de nitrógeno.



Esquema 1.16 Reactividad del compuesto **6**

La estructura en estado sólido del compuesto **6b** (Figura 1.13) muestra claramente la formación de un nuevo enlace carbono-carbono (C22-C6) y la desaromatización del anillo aromático formando un grupo dihidropiridilo como consecuencia de la protonación del carbono C5. Como en el complejo análogo **3b**, los enlaces en torno a este carbono, C5-C6 y C5-C4 (de 1.517(9) Å y 1.493(9) Å respectivamente), son característicos de enlaces sencillos, al igual el nuevo enlace formado C6-C22 (1.511(9) Å). Los ángulos en torno a C5 y C6 confirman que el entorno es prácticamente tetraédrico, como corresponde a carbonos con hibridación sp³, y además, se puede observar claramente como ambos carbonos se desvían significativamente del plano que originalmente contenía a ese grupo piridilo.

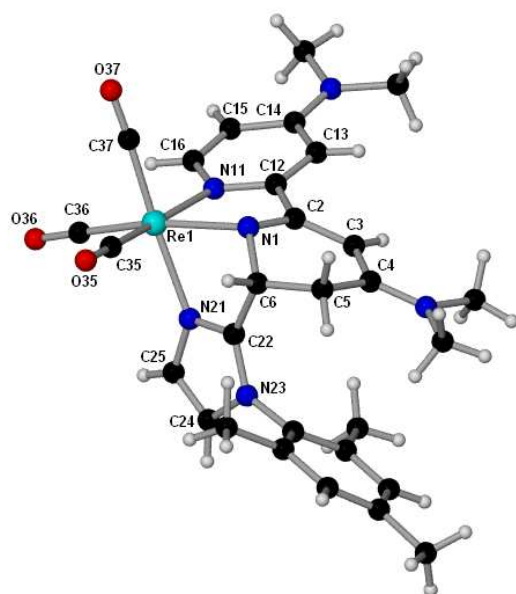
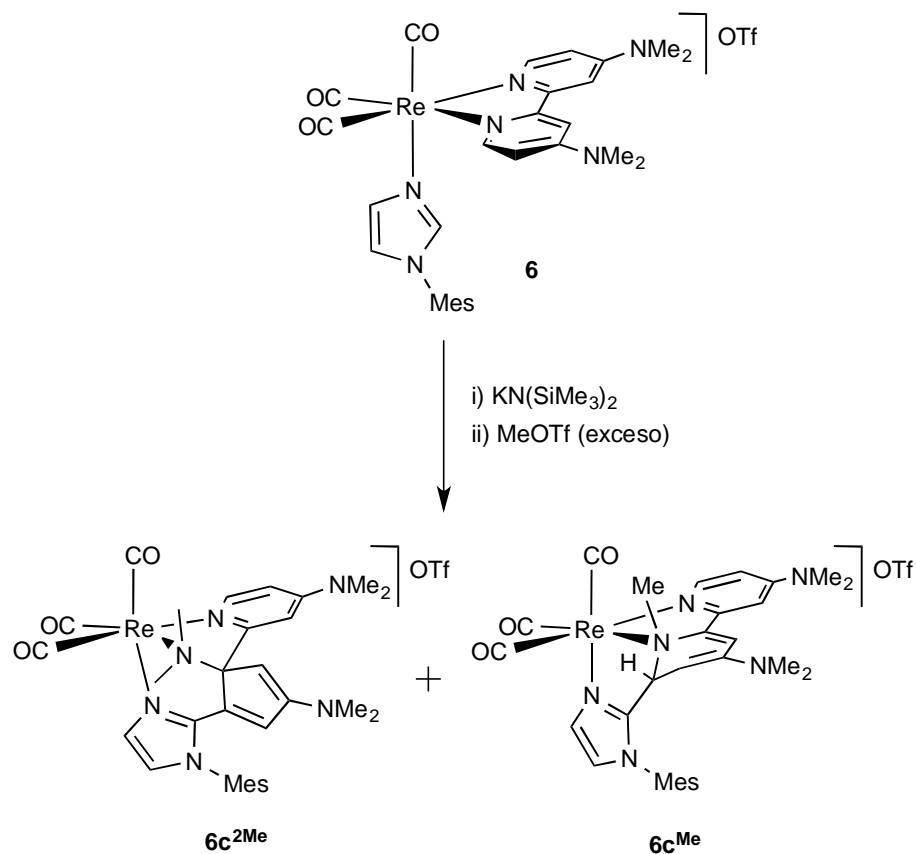


Figura 1.13 Estructura en estado sólido del compuesto 6b

La reacción del compuesto **6** con base y posteriormente con exceso de triflato de metilo dio lugar a una mezcla de dos compuestos **6c^{Me}** y **6c^{2Me}** (Esquema 1.17), que pudieron ser separados por cristalización fraccionada y caracterizados individualmente. Ambos productos resultan del acoplamiento y desaromatización de la biperidina, siendo **6c^{Me}** el producto metilado solamente una vez en el nitrógeno, y **6c^{2Me}** el producto de doble metilación y apertura del anillo piridínico. Los intentos de obtener solamente un producto fueron infructuosos.



Esquema 1.17 Reactividad del compuesto **6** frente a KN(SiMe₂)₃ y MeOTf.

Los datos de RMN en disolución (¹H, ¹³C RMN, COSY y HSQC, ver Parte Experimental) del compuesto doblemente metilado **6c^{2Me}** confirman inequívocamente la geometría mostrada en el Esquema 1.17, siendo completamente análogos a los de los compuestos isoestructurales **1c-4c** comentados previamente.

Por otra parte, los espectros de RMN del compuesto **6c^{Me}** muestran claramente la asimetría de la molécula, la desaromatización de un anillo de la bipy-NMe₂ y la incorporación de un grupo CH₃ (Figura 1.14). La señal más característica en el espectro de ¹³C RMN corresponde al carbono *orto* del ligando bipy-NMe₂ que ha sufrido el ataque nucleófilo, a 67.9 ppm, que ha pasado de ser sp² a ser sp³, además de una nueva señal a 47.2 ppm que asignamos al grupo metilo coordinado al nitrógeno del anillo piridínico desaromatizado.

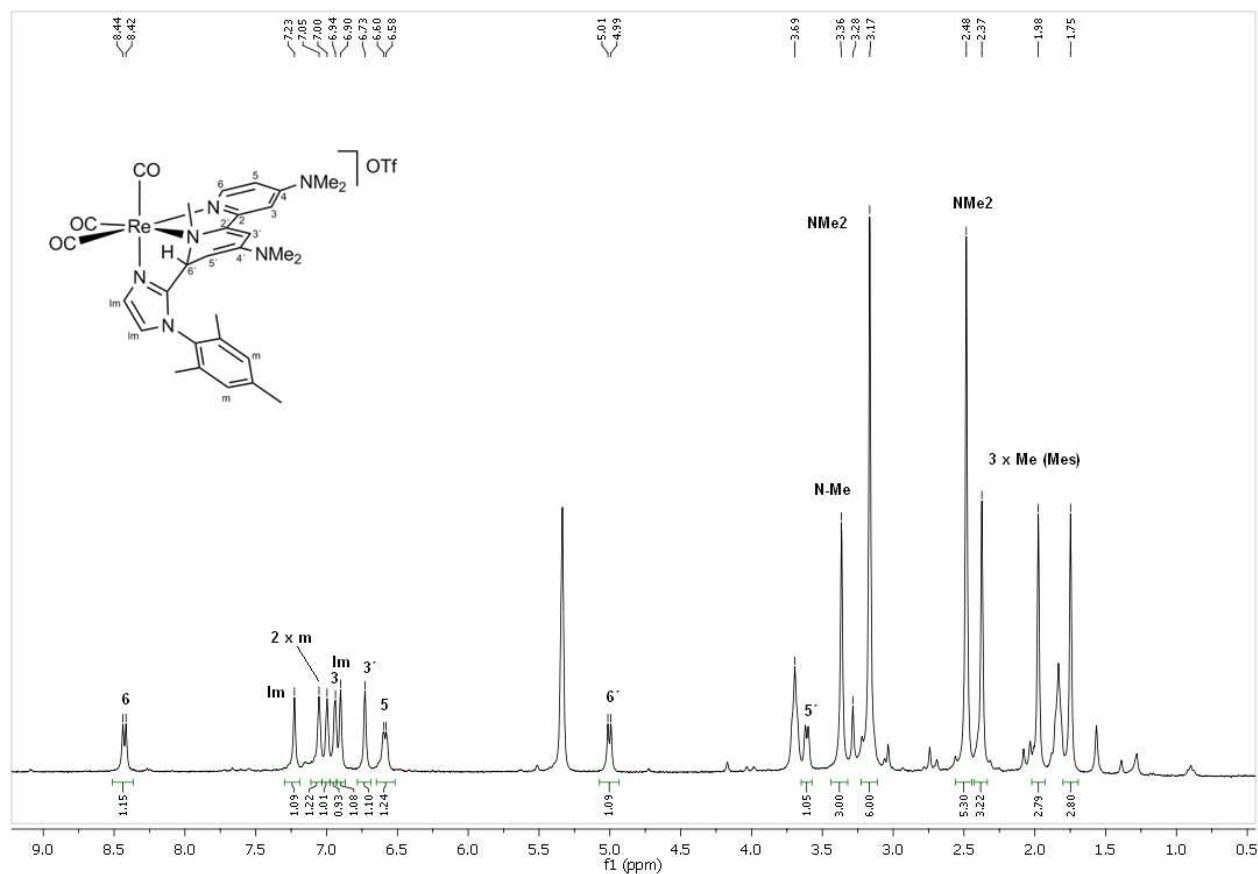


Figura 1.14 Espectro de ^1H RMN en CD_2Cl_2 del compuesto- 6c^{Me} .

La estructura molecular del catión metálico presente en compuesto 6c^{Me} se muestra en la Figura 1.15. Aunque la calidad del cristal no resultó suficiente para poder discutir las distancias y ángulos de enlace, no hay duda de que la conectividad es la propuesta mediante sus datos espectroscópicos en disolución, observándose que se ha producido el acoplamiento entre el imidazol y uno de los anillos piridínicos de la bipy- NMe_2 y como consecuencia éste se ha desaromatizado. Se puede apreciar también como se ha incorporado un grupo metilo en el nitrógeno del anillo que sufre el ataque.

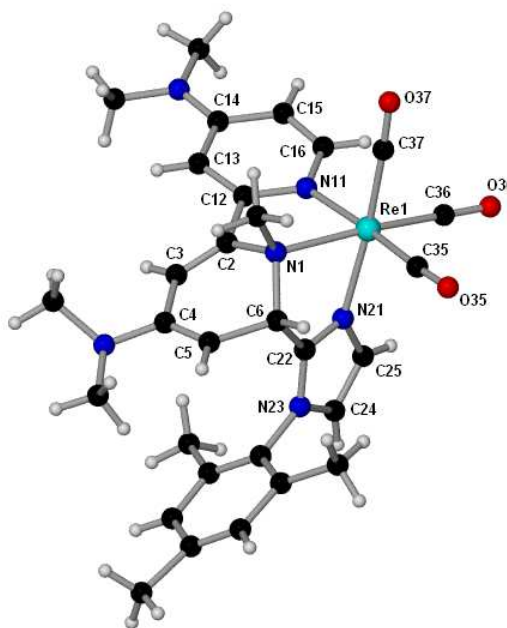


Figura 1.15 Estructura en estado sólido del compuesto $6c^{Me}$

Los resultados encontrados para el compuesto **6**, de formación de productos de acoplamiento C-C y desaromatización de la bipy-NMe₂, contrastan con la reactividad encontrada para el compuesto análogo **5** en el que el imidazol, una vez desprotonado, ataca al centro metálico, dando lugar a la formación de un ligando imidazol-2-ilo coordinado al átomo de renio por el carbono. En ausencia de estudios teóricos, podemos proponer que al ser el ligando bipy-NMe₂ muy rico en densidad electrónica, la naturaleza del nucleófilo es determinante para obtener uno u otro tipo de reactividad. Esto es, cuando el nucleófilo es el ligando N-MeIm desprotonado, el ataque sobre la bipy se encuentra tan desfavorecido que la reactividad sobre el centro metálico es la preferida. Por el contrario, para el ligando N-MesIm desprotonado, con menor carácter nucleófilo debido al sustituyente arilo del nitrógeno, el ataque sobre el ligando bipy-NMe₂ está, a pesar de los sustituyentes dimetilamino, más favorecido que la formación del imidazolilo. Esto puede deberse a que los sustituyentes de la bipy no sólo afectan a las características electrónicas de este ligando, sino que la bipy transfiere, en gran medida, parte de esa densidad electrónica al metal, haciéndolo más rico y desfavoreciendo, por tanto, la formación de complejos de tipo imidazol-2-ilo. Esto estaría en concordancia con los estudio teóricos realizados por Cundari y colaboradores sobre la reactividad de complejos alquilo de Rh(III) frente a nucleófilos, encontrando que efectivamente los sustituyentes de la bipy pueden determinar que el nucleófilo ataque sobre el metal o sobre el grupo metilo.⁵²

⁵² D. R. Palhs, J. T. Groves, T. B. Gunnoe, T. R. Cundari, *Organometallics*, **2014**, *33*, 1936.

Parte Experimental

Condiciones generales de reacción.

Todas las reacciones que se describen en este apartado han sido efectuadas en atmósfera de nitrógeno, empleando matraces de Schlenk, líneas de vacío convencionales y agitación magnética. Todas las filtraciones se han llevado a cabo en atmósfera de nitrógeno, empleando tierra de diatomeas y silicagel en columnas entre 15 y 40 cm de altura y 1-2 cm de diámetro, o con papel de filtro en el extremo de una cánula de acero a través de la cual se ha hecho pasar la disolución empleando presión de nitrógeno. El diclorometano ha sido destilado sobre CaH₂, el tetrahidrofurano y el éter dietílico sobre Na/benzofenona, la acetona sobre CaSO₄ y el hexano y el tolueno sobre Na. La destilación de los disolventes se ha llevado a cabo, en todos los casos, bajo atmósfera de nitrógeno. Todos los reactivos han sido obtenidos de fuentes comerciales, excepto los compuestos de partida [ReBr(CO)₅],⁵³ [Re(OTf)(CO)₃(bipy-R¹)],^{46f} y N-MesIm,⁵⁴ que se han preparado de acuerdo con los métodos bibliográficos descritos.

Técnicas empleadas para la caracterización de compuestos.

Espectroscopia de infrarrojo (IR).

Los espectros de infrarrojo han sido obtenidos en un espectro Perkin Elmer FT1720-X con una resolución de 2 cm⁻¹, empleando celdas de CaF₂ de 0.1 mm de espesor y se ha restado en cada caso el espectro del disolvente puro correspondiente para descontar las bandas debidas al mismo.

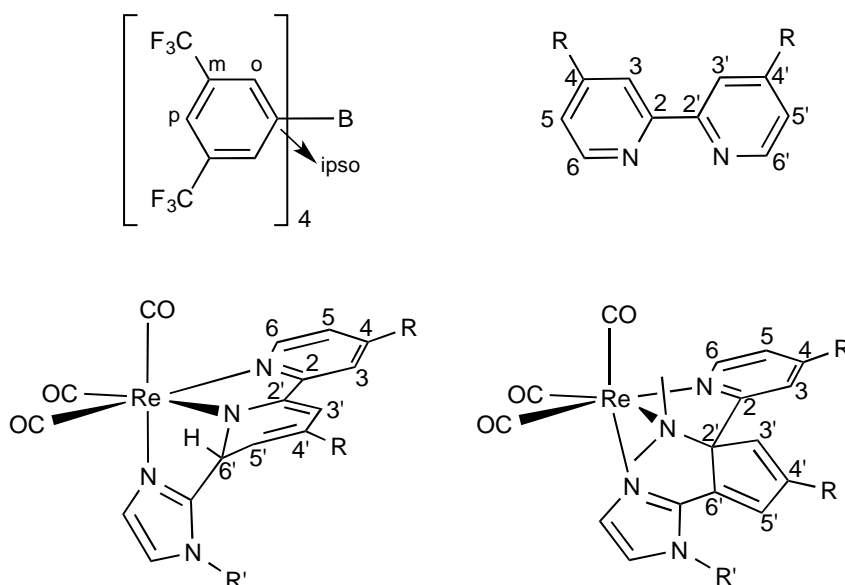
Espectroscopia de resonancia magnética nuclear (RMN).

La resonancia magnética nuclear de ¹H y ¹³C{H} ha sido obtenida en espectrómetros Bruker DPX-300, Bruker AV-400, Bruker AV-300 y Bruker NAV-400. En todos los casos se han empleado tubos de 5 mm y la señal de deuterio del disolvente para el mantenimiento y

⁵³ S. P. Schmidt, W. C. Trogler, F. Basolo, *Inorg. Synth.* **1990**, 28, 160.

⁵⁴ A. A. Gridnev, I. M. Mihaltseva, *Synth. Commun.* **1994**, 24, 1547.

homogeneidad del campo magnético. El disolvente empleado ha sido CD_2Cl_2 previamente desoxigenado y guardado protegido de la luz en tubos Young sobre tamices moleculares de 4 Å. Los valores de los desplazamientos químicos (δ) se expresan en partes por millón (ppm), tomando como referencia TMS (^1H y ^{13}C). Las constantes de acoplamiento (J) se dan entre paréntesis, expresadas en hertzios (Hz). Los espectros de ^{13}C se obtuvieron con desacoplamiento total de protón y se expresan como ^{13}C RMN $\{^1\text{H}\}$. Las notaciones empleadas para la asignación de señales en los espectros de ^1H y ^{13}C RMN han sido:



Notaciones empleadas

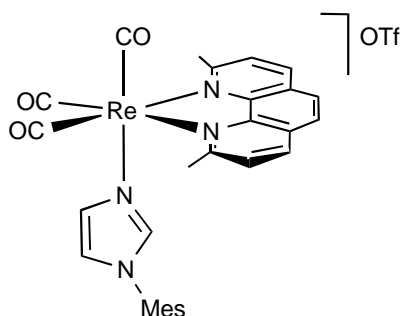
Análisis elemental.

El análisis elemental (C, H, N) de los compuestos incluidos en esta Memoria ha sido realizado por el servicio de Análisis Elemental de la Universidad de Vigo, empleando un microanalizador Fisons EA-1108.

Estudios de difracción de rayos X.

La toma de datos de los compuestos determinados mediante difracción de rayos X de monocristal ha sido llevada a cabo por la Unidad de Difracción de Rayos X de Monocristal de los Servicios Científico-Técnicos de la Universidad de Oviedo y la Unidad de Rayos X de la Universidad de Santiago de Compostela. La resolución de las estructuras ha sido llevada a cabo por la Dra. Lucía Riera (CSIC-Universidad de Zaragoza). Los datos cristalográficos se recogen en las tablas del Apéndice.

Síntesis de $[\text{Re}(\text{CO})_3(\text{neo})(\text{N-MesIm})]\text{OTf}$.



Una mezcla de $[\text{ReBr}(\text{CO})_5]$ (200 mg, 0.49 mmol) y neocuproina (113 mg, 0.54 mmol) se calienta a reflujo en tolueno (20 mL) durante 3 horas. La disolución resultante se evapora a sequedad, obteniéndose el compuesto $[\text{ReBr}(\text{CO})_3(\text{neo})]$ como un sólido amarillo que se lava con hexano (2×15 mL), éter dietílico (1×15 mL) y se seca a vacío. A continuación se añade CH_2Cl_2 (20 mL) y AgOTf (152 mg, 0.59 mmol) y la mezcla se agita en ausencia de luz durante toda la noche. Transcurrido ese tiempo la disolución se filtra para eliminar el AgBr formado, y la disolución amarilla resultante se evapora a sequedad obteniéndose el complejo $[\text{Re}(\text{OTf})(\text{CO})_3(\text{neo})]$ como un sólido amarillo que se lava con hexano (2×15 mL) y éter dietílico (1×15 mL).

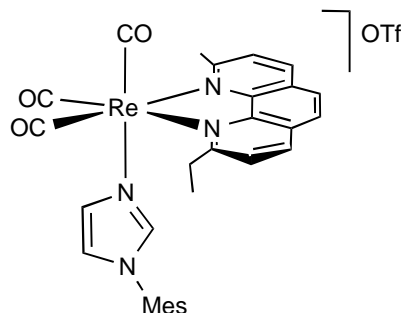
Una mezcla de $[\text{Re}(\text{OTf})(\text{CO})_3(\text{neo})]$ (100 mg, 0.16 mmol), y N-mesitilimidazol (33 mg, 0.18 mmol) en CH_2Cl_2 (25 mL) se agita a temperatura ambiente 3 días. Transcurrido ese tiempo, el disolvente se evapora a vacío hasta un volumen aproximado de 3 mL. La adición de hexano (15 mL) causa la precipitación de un sólido amarillo que se lava con hexano (3×15 mL).

IR (CD_2Cl_2 , cm^{-1}) 2033, 1930 (ν_{CO})

$^1\text{H-NMR}$ (CD_2Cl_2) δ 8.60 (d, $J = 8.4$ Hz, 2H, H_4, H_4' neocup); 8.02 (s, 2H, H_7, H_7' neocup); 7.98 (d, $J = 8.4$ Hz, 2H, H_5, H_5' neocup); 6.88 (s, 2H, H_m Mes); 6.82, 6.63, 6.36 (m, 1H, N-Im); 3.38 (s, 6H, CH_3 neocup); 2.26 (s, 3H, $\text{CH}_3(\text{p})$ Mes); 1.46 (s, 6H, $\text{CH}_3(\text{o})$ Mes).

$^{13}\text{C RMN} \{^1\text{H}\}$ (CD_2Cl_2) δ 195.7 (2CO); 192.0 (CO); 164.9, 147.6, 140.9, 140.6, 139.8, 134.7, 131.3, 130.2, 129.8, 129.6, 127.6, 127.5, 123.4 (neocup y N-MesIm); 31.3 ($2 \times \text{CH}_3$ neocup); 21.1 ($\text{CH}_3(\text{p})$ Mes); 16.9 ($2 \times \text{CH}_3(\text{o})$ Mes).

**Reacción de [Re(CO)₃(neo)(N-MesIm)]OTf con KN(SiMe₃)₂ y posterior adición de MeOTf.
Síntesis de [Re(CO)₃(neo-Et)(N-MesIm)] OTf**



Se añade KN(SiMe₃)₂ (0.14 mL de una disolución 0.7 M en tolueno, 0.09 mmol) a una disolución de [Re(CO)₃(neo)(N-MesIm)]OTf (70 mg, 0.09 mmol) en THF (20 mL) a -78°C, produciéndose un cambio de color instantáneo de amarillo a rojo. El disolvente se evapora a vacío, al residuo sólido así obtenido se le añade una disolución preparada previamente de MeOTf (10 µL, 0.09 mmol) en CH₂Cl₂ (20 mL) y se deja con agitación a temperatura ambiente durante media hora. La mez-

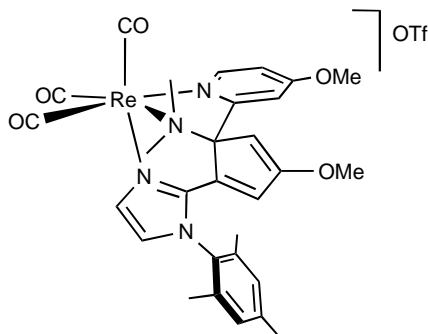
cla se filtra utilizando una cánula y presión positiva de nitrógeno y la disolución resultante se concentra, evaporando el disolvente a vacío hasta un volumen aproximado de 3 mL. La adición de hexano provoca la precipitación de un sólido amarillo que se lava con hexano (3x 15mL) y se seca a vacío.

IR (CD₂Cl₂, cm⁻¹) 2033, 1930 (ν_{CO})

¹H-NMR (CD₂Cl₂) δ 8.69 (m, 1H, H₄/H_{4'} neocup); 8.63 (m, 1H, H₄/H_{4'} neocup); 8.03 (m, 4H, H₇, H_{7'}, H₅, H_{5'} neocup); 6.90 (s, 2H, H_m Mes); 6.82, 6.65, 6.35 (m, 1H, N-Im); 3.69 (q, *J*= 7.5 Hz, 2H, CH₂ neocup); 3.39 (s, 3H, CH₃ neocup); 2.28 (s, 3H, CH₃(p) Mes); 1.64 (t, *J*= 7.5 Hz, 3H, CH₃ neocup); 1.50, 1.48 (s, 3H, CH₃(o) Mes).

¹³C RMN {¹H} (CD₂Cl₂) δ 195.7, 195.3, 192.2 (CO); 169.6, 164.9, 147.7, 147.4, 140.9, 140.6, 139.7, 134.7, 131.3, 130.1, 130.0, 129.6, 129.0, 127.6, 125.7, 123.4 (neocup y N-MesIm); 37.0 (CH₂ neocup) 31.2 (CH₃ neocup); 21.1 (CH₃(p) Mes); 16.9 (2×CH₃(o) Mes); 14.8 (CH₃ neocup).

Reacción de [Re(CO)₃(bipy-OMe)(N-MesIm)]OTf con KN(SiMe₃)₂ y posterior reacción con exceso de MeOTf Síntesis de 3b.

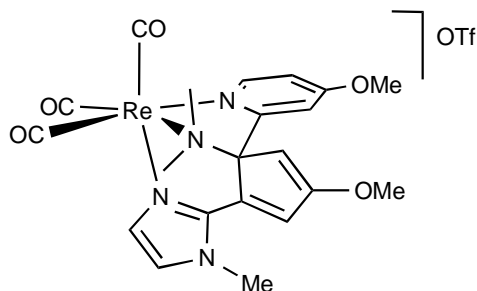


Al compuesto **3** (75 mg, 0.09 mmol) se le añade KN(SiMe₃)₂ (0.14 mL de una disolución 0.7 M en tolueno, 0.10 mmol) en THF (15 mL) a -78 °C observándose un cambio de color en la disolución de amarillo a rojo intenso. El disolvente se evapora a vacío y el residuo se redissuelve en CH₂Cl₂ (20 mL) y se añade MeOTf (21.0 μL, 0.19 mmol). La mezcla se deja con agitación media hora a temperatura ambiente y a continuación se filtra con cánula. La disolución se concentra a presión reducida hasta un volumen aproximado de 5 mL, y

se añade hexano (20 mL), lo que provoca la precipitación de un sólido marrón claro que se lava con hexano (3x15 mL).

<u>Rendimiento</u>	31 mg (52%)
IR (CH ₂ Cl ₂ , cm ⁻¹)	2032, 1923 (ν _{CO})
¹H RMN (CD ₂ Cl ₂)	δ 8.66 (d, <i>J</i> = 6.4 Hz, 1H, H ₆); 7.70 (d, <i>J</i> = 1.6 Hz, 1H, N-Im); 7.15 (bs, 1H, H _m); 7.10 (d, <i>J</i> = 1.6 Hz, 1H, N-Im); 7.07 (d, <i>J</i> = 2.6 Hz, 1H, H ₃); 7.04 (m, 2H, H _m y H ₅); 5.68 (d, <i>J</i> = 1.7 Hz, 1H, H ₅ /H ₃); 5.40 (d, <i>J</i> = 1.7 Hz, 1H, H ₅ /H ₃); 3.97 (s, 3H, OMe); 3.95 (s, 3H, OMe); 3.37 (s, 3H, NMe); 2.79 (s, 3H, NMe); 2.40, 2.03, 1.35 (s, 3H, CH ₃ de N-MesIm).
¹³C RMN {¹H} (CD ₂ Cl ₂)	δ 196.5, 195.6, 195.0 (CO); 169.3, 167.0, 160.8 (C ₄ , C ₄ , C ₂); 155.5 (C ₆); 141.88 (C _p Mes); 139.4 (NCN N-Im); 135.3 (CH N-Im); 134.8, 134.7 (C _o Mes); 134.4 (C ₆); 132.3 (C _{ipso} Mes); 130.9, 130.6 (C _m Mes); 129.9 (C ₅ /C ₃); 125.3 (CH N-Im); 112.9 (C ₅); 110.7 (C ₃); 96.8 (C ₅ /C ₃); 86.9 (C ₂); 58.9 (OCH ₃); 57.5 (NCH ₃); 57.3 (OCH ₃); 47.3 (NCH ₃); 21.3 (CH ₃ (p) Mes); 17.8, 16.6 (CH ₃ (o) Mes).

Reacción de [Re(CO)₃(bipy-OMe)(N-MeIm)]OTf con KN(SiMe₃)₂ y posterior reacción con exceso de MeOTf. Síntesis de 4b.



Se sintetiza de manera análoga al compuesto **3b** partiendo de **4** (70 mg, 0.10 mmol), KN(SiMe₃)₂ (0.15 mL de una disolución 0.7 M en tolueno, 0.11 mmol) y MeOTf (23 μL, 0.20 mmol).

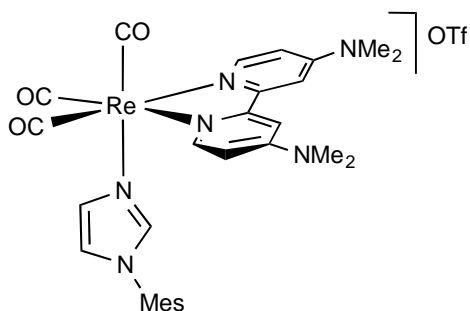
Rendimiento 27 mg (53 %)

IR (CH₂Cl₂, cm⁻¹) 2032, 1925 (ν_{CO})

¹H RMN (CD₂Cl₂) δ 8.58 (d, *J*= 6.5 Hz, 1H, H₆); 7.45, 7.20 (d, *J*= 1.5 Hz, 1H, N-Im); 7.10 (d, *J*= 2.7 Hz, 1H, H₃); 6.95 (dd, *J*= 6.5 Hz, *J*= 2.7 Hz, 1H, H₅); 6.82 (d, *J*= 1.6 Hz, 1H, H₅/H₃); 5.58 (d, *J*= 1.6 Hz, 1H, H₅/H₃); 4.04, 3.95 (s, 3H, OCH₃); 3.85 (s, 3H, CH₃ N-MeIm); 3.31, 2.76 (s, 3H, NMe).

¹³C RMN {¹H} (CD₂Cl₂) δ 196.6, 195.9, 195.1 (CO); 169.3, 167.3, 160.6 (C₄, C₄', C₂); 155.4 (C₆); 139.6 (NCN N-Im); 134.9 (C₆); 133.7 (CH N-Im); 130.6 (C₅); 127.1 (CH N-Im); 112.8 (C₅); 111.2 (C₃); 95.9 (C₃); 87.0 (C₂); 59.0 (OCH₃), 57.4 (NCH₃), 57.1(OCH₃), 47.3 (NCH₃), 37.9 (CH₃ N-MeIm).

Síntesis de [Re(CO)₃(bipy-NMe₂)(N-MesIm)]OTf (6).



El compuesto **6** se prepara de manera análoga a la descrita para preparar [Re(CO)₃(neo)(N-MesIm)]OTf empleando para ello [ReBr(CO)₅] (200 mg, 0.49 mmol), 4,4'-dimetilamino-2,2'-bipiridina (132 mg, 0.54 mmol) y AgOTf (152 mg, 0.59 mmol). Para preparar el complejo **6** desde [Re(OTf)(CO)₃(bipy-NMe₂)₂] (105 mg, 0.16 mmol), y N-mesitilimidazol (32 mg, 0.17 mmol) se necesita dejar la mezcla con agitación en CH₂Cl₂ (25 mL)

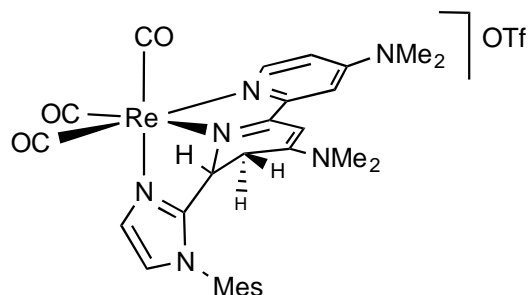
durante una noche. Transcurrido este tiempo, el disolvente se evapora a vacío y el sólido amarillo resultante se lava con hexano (3×15 mL).

IR (CD₂Cl₂, cm⁻¹) 2024, 1913 (ν_{CO})

¹H-NMR (CD₂Cl₂) δ 8.48 (d, *J*= 6.8 Hz, 2H, H₆, H_{6'} bipy-NMe₂); 7.45 (d, *J*= 2.7 Hz, 2H, H₃, H_{3'} bipy-NMe₂); 7.20, 6.84, 6.75 (m, 1H, N-Im); 6.98 (s, 2H, H_m Mes); 6.65 (dd, *J*= 6.8 Hz, *J*= 2.7 Hz, 2H, H₅, H_{5'} bipy-NMe₂); 3.25 (s, 12H, CH₃ bipy-NMe₂); 2.33 (s, 3H, CH₃(p) Mes); 1.77 (s, 6H, CH₃(o) Mes).

¹³C RMN {¹H} (CD₂Cl₂) δ 197.5 (2CO); 194.1 (CO); 156.2, 155.4 (C₄, C_{4'}, C₂, C_{2'} bipy-NMe₂); 151.4 (C₆, C_{6'} bipy-NMe₂); 140.2 (C_{ipso} Mes); 139.2 (CH N-Im); 134.6 (C_o Mes); 131.5 (C_p Mes); 129.5 (CH N-Im); 129.3 (C_m Mes); 122.4 (CH N-Im); 108.8 (C₃, C_{3'} bipy-NMe₂); 105.4 (C₅, C_{5'} bipy-NMe₂); 39.8 (2×N(CH₃)₂ bipy-NMe₂); 20.7 (CH₃(p) Mes); 16.8 (2×CH₃(o) Mes).

Reacción de [Re(CO)₃(bipy-NMe₂)(N-MesIm)]OTf con KN(SiMe₃)₂ y posterior adición de HOTf. Síntesis de 6c.



A una disolución del compuesto [Re(CO)₃(bipy-NMe₂)₂(N-MesIm)]OTf (**6**) (72 mg, 0.08 mmol) en THF (20 mL), previamente enfriada a -78° C, se le añade KN(SiMe₃)₂ (0.15 mL de una disolución 0.5 M en tolueno, 0.10 mmol). El color de la disolución se oscurece notablemente conforme la mezcla va alcanzando la temperatura ambiente pasando de amarillo a rojo oscuro.

Transcurridos 15 minutos el THF se evapora a vacío y se añade, mediante una cánula y presión positiva de nitrógeno, una disolución previamente preparada de HOTf (9 µL, 0.10 mmol) en CH₂Cl₂ (20 mL). Se obtiene así una disolución amarilla que se filtra con una cánula y presión positiva de nitrógeno, para luego evaporar el diclorometano hasta un volumen aproximado de 3 mL y se precipita mediante la adición de hexano (15 mL). El compuesto **6c** se obtuvo como un sólido de color amarillo.

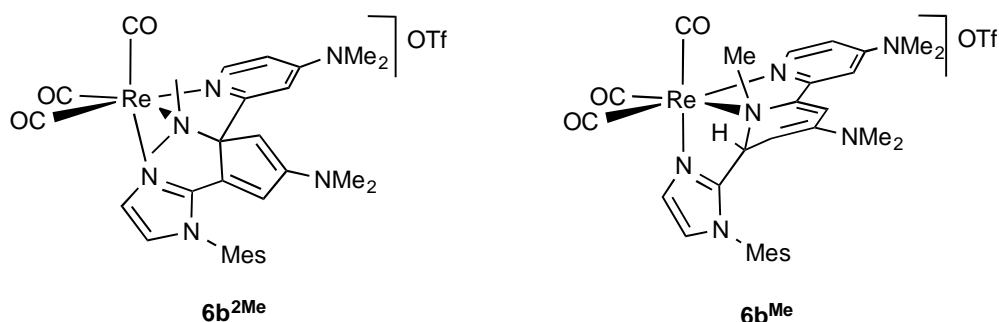
IR (CD₂Cl₂, cm⁻¹) 2019, 1906 (ν_{CO})

¹H-NMR (CD₂Cl₂) δ 8.46 (d, *J*= 6.8 Hz, 1H, H₆); 7.29, 6.92 (d, *J*= 1.5 Hz, 1H, N-Im); 7.16, 7.15 (s, 1H, H_m Mes); 7.08 (d, *J*= 2.7 Hz, 1H, H₃); 6.64 (dd, *J*= 6.8 Hz, *J*= 2.7 Hz, 1H, H₅); 5.53 (s, 1H, H_{3'}); 5.43 (d, *J*= 6.7 Hz, 1H, H_{6'}); 3.18 (s, 6H, NMe₂); 3.15 (s, 3H, CH₃ NMe₂); 2.89 (m, 1H, H_{5'}); 2.58 (s, 3H, CH₃ NMe₂); 2.42 (s, 3H, CH₃(p) Mes); 2.33 (m, 1H, H_{5'}); 2.05, 1.90 (s, 3H, CH₃(o) Mes).

¹³C RMN {¹H} (CD₂Cl₂) δ 198.8, 196.5, 195.1 (CO); 159.8, 158.8, 155.6, 152.5 (C₂, C_{2'}, C₄, C_{4'}); 152.4 (C₆); 141.6 (C_p Mes); 135.7, 135.6, 135.1 (C_o Mes y NCN N-Im); 131.3 (C_{ipso} Mes); 130.4, 130.3, 130.1 (C_m Mes y CH de N-Im); 123.4 (CH de N-Im); 109.5 (C₅); 107.3 (C₃); 91.0 (C_{3'}); 64.2 (C_{6'}); 41.0 (NCH₃); 40.1 (N(CH₃)₂); 39.9 (NCH₃); 27.1 (C_{5'}); 21.2 (CH₃(p) N-MesIm); 17.4, 17.2 (CH₃(o) N-MesIm).

Reacción de $[\text{Re}(\text{CO})_3(\text{bipy-NMe}_2)(\text{N-MesIm})]\text{OTf}$ con $\text{KN}(\text{SiMe}_3)_2$ y posterior adición de MeOTf . Síntesis de $6\text{b}^{2\text{Me}}$ y 6b^{Me} .

Se añade $\text{KN}(\text{SiMe}_3)_2$ (0.13 mL de una disolución 0.7 M en tolueno, 0.09 mmol) a una disolución de $[\text{Re}(\text{CO})_3(\text{bipy-NMe}_2)_2(\text{N-MesIm})]\text{OTf}$ (**6**) (72 mg, 0.08 mmol) en THF (20 mL), previamente enfriada a -78°C observándose un cambio de color inmediato de amarillo a rojo oscuro. La disolución resultante se evapora a presión reducida, y se le añade una disolución previamente preparada de MeOTf (21 μL , 0.19 mmol) en CH_2Cl_2 (20 mL) a temperatura ambiente. La mezcla se agita durante 20 minutos lo que provoca un cambio de color de rojo a amarillo. El residuo se filtra utilizando una cánula y presión positiva de nitrógeno. Se evapora el disolvente hasta 5 mL y la adición de hexano (15 mL) provoca la precipitación de un sólido amarillo que resulto ser una mezcla de compuestos que pudieron separarse mediante cristalización.



Caracterización de $6^{2\text{Me}}$

IR (CD_2Cl_2 , cm^{-1}) 2027, 1915 (ν_{CO})

$^1\text{H-NMR}$ (CD_2Cl_2) δ 8.28 (d, $J=6.7$ Hz, 1H, H_6); 7.68 (d, $J=1.5$ Hz, 1H, N-Im); 7.17 (s, 1H, H_m Mes); 7.09 (d, $J=1.5$ Hz, 1H, N-Im); 7.06 (s, 1H, H_m Mes); 6.65 (d, $J=2.9$ Hz, 1H, H_3); 6.51 (dd, $J=6.7$ Hz, $J=2.9$ Hz, 1H, H_5); 5.53 (d, $J=1.6$ Hz, 1H, H_5/H_3); 4.75 (d, $J=1.6$ Hz, 1H, H_5/H_3); 3.24 (s, 3H, NMe); 3.06, 2.76 (s, 6H, NMe_2); 2.71 (s, 3H, NMe); 2.40 (s, 3H, $\text{CH}_3(\text{p})$ Mes); 2.05, 1.41 (s, 3H, $\text{CH}_3(\text{o})$ Mes).

$^{13}\text{C RMN } \{^1\text{H}\}$
(CD_2Cl_2) δ 196.9, 196.0, 195.3 (CO); 159.2, 156.8, 155.6 (C_2 , C_4 , C_4'); 152.4 (C_6); 141.4 (C_p Mes); 139.7 (NCN N-Im); 135.4 (C_6'); 134.6 (C_o Mes); 134.5 (CH N-Im); 134.4 (C_o Mes); 132.3 (C_{ipso} Mes); 130.5, 129.9 (C_m Mes); 127.6 (C_5'/C_3'); 124.1 (CH N-Im); 107.9 (C_5); 104.7 (C_3); 90.1 (C_5'/C_3'); 87.6 (C_2'); 56.2, 46.4 (NCH₃); 39.7, 39.6 (N(CH₃)₂); 20.8 (CH₃(p) Mes); 17.5, 16.3 (CH₃(o) Mes).

Caracterización de 6^{Me}

IR (CD_2Cl_2 , cm^{-1}) 2027, 1915 (ν_{CO})

$^1\text{H-NMR}$
(CD_2Cl_2) δ 8.45 (d, $J=6.8$ Hz, 1H, H_6); 7.25 (d, $J=1.5$ Hz, 1H, N-Im); 7.07, 7.02 (s, 1H, H_m Mes); 6.95 (d, $J=2.8$ Hz, 1H, H_3); 6.92 (d, $J=1.5$ Hz, 1H, N-Im); 6.74 (s, 1H, H_3'); 6.61 (dd, $J=6.8$ Hz, $J=2.8$ Hz, 1H, H_5); 5.03 (d, $J=6.4$ Hz, 1H, H_6'); 3.63 (d, $J=6.4$ Hz, 1H, H_5'); 3.38 (s, 3H, NMe); 3.18, 2.50 (s, 6H, NMe₂); 2.39 (s, 3H, CH₃(p) Mes); 1.99, 1.77 (s, 3H, CH₃(o) Mes).

$^{13}\text{C RMN } \{^1\text{H}\}$
(CD_2Cl_2) δ 196.4, 196.1, 195.5 (CO); 155.6, 154.7 (C_2 y C_2'); 152.3 (C_6); 150.4, 148.0 (C_4 y C_4'); 143.2 (C_p Mes); 140.9 (NCN N-Im); 135.4, 134.9, 131.9 (C_{ipso} y $2\times\text{C}_o$ Mes); 129.8 (C_m Mes); 129.6 (CH N-Im); 129.5 (C_m Mes); 124.6 (CH N-Im); 119.6 (C_3'); 109.0 (C_5); 104.9 (C_3); 85.8 (C_5'); 67.9 (C_6'); 47.2 (NCH₃); 40.0, ($2\times\text{N}(\text{CH}_3)_2$); 21.2 (CH₃(p) Mes); 17.8, 17.3 (CH₃(o) Mes).

Datos cristalográficos de los compuestos

Datos cristalográficos del compuesto **1b**

Fórmula	$C_{35}H_{38}Cl_2F_3N_4O_6ReS$
Peso molecular ($g \cdot mol^{-1}$)	956.85
Sistema cristalino	Monoclínico
Grupo espacial	P21/n
a (Å)	14.853
b (Å)	12.0156(2)
c (Å)	21.8740(4)
α (°)	90
β (°)	98.56
γ (°)	90
V (Å ³)	3860.30(10)
Z	4
$F(000)$	1904
D_{calcd} ($g \cdot cm^{-3}$)	1.646
Dimensiones del cristal (mm)	0.18 x 0.13 x 0.09
μ (mm^{-1})	8.479
Temperatura (K)	293(2)
Radiación (Å)	1.54180
Rango de toma de datos, θ (°)	3.88 a 69.32
Relación datos/parámetros	7112 / 557
R_1 (F, $I > 2\sigma(I)$)	0.0336
wR_2 (F ²), todos los datos	0.0856

Datos cristalográficos del compuesto 1c

Fórmula	$C_{36}H_{33}F_3N_4O_6ReS$
Peso molecular ($g \cdot mol^{-1}$)	892.92
Sistema cristalino	Ortorrómbico
Grupo espacial	P212121
a (Å)	9.620(5)
b (Å)	19.622(5)
c (Å)	20.558(5)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	3881(2)
Z	4
$F(000)$	1772
D_{calcd} ($g \cdot cm^{-3}$)	1.528
Dimensiones del cristal (mm)	0.10 x 0.09 x 0.03
μ (mm^{-1})	3.246
Temperatura (K)	293(2)
Radiación (Å)	0.71073
Rango de toma de datos, θ (°)	1.43 a 26.37
Relación datos/parámetros	7929 / 454
R_1 (F, $I > 2\sigma(I)$)	0.0529
wR_2 (F ²), todos los datos	0.1171

Datos cristalográficos del compuesto 3b

Fórmula	$C_{29}H_{28}Cl_2F_3N_4O_8ReS$
Peso molecular ($g \cdot mol^{-1}$)	906.71
Sistema cristalino	Triclínico
Grupo espacial	P-1
a (Å)	10.6877(4)
b (Å)	11.3894(5)
c (Å)	15.5194(7)
α (°)	99.974(4)
β (°)	108.769(4)
γ (°)	102.369(3)
V (Å ³)	1686.21(12)
Z	2
$F(000)$	892
D_{calcd} ($g \cdot cm^{-3}$)	1.786
Dimensiones del cristal (mm)	0.02 x 0.04 x 0.02
μ (mm^{-1})	9.713
Temperatura (K)	293(2)
Radiación (Å)	1.54180
Rango de toma de datos, θ (°)	3.12 a 69.28
Relación datos/parámetros	6195 / 433
R_1 (F, $I > 2\sigma(I)$)	0.0463
wR_2 (F ²), todos los datos	0.1320

Datos cristalográficos del compuesto [Re(CO)₃(neo-Et)(N-MesIm)]

Fórmula	C ₃₅ H ₂₈ C ₁₀ F ₃ N ₄ O ₆ ReS
Peso molecular (g.mol ⁻¹)	875.87
Sistema cristalino	Monoclínico
Grupo espacial	P21/c
a (Å)	8.904(5)
b (Å)	16.986(5)
c (Å)	22.883(5)
α (°)	90
β (°)	99.141(5)
γ (°)	90
V (Å ³)	3417(2)
Z	4
F(000)	1728
D _{calcd} (g.cm ⁻³)	1.703
Dimensiones del cristal (mm)	0.43 x 0.05 x 0.04
μ (mm ⁻¹)	3.685
Temperatura (K)	293(2)
Radiación (Å)	0.71073
Rango de toma de datos, θ (°)	1.50 a 26.02
Relación datos/parámetros	6682 / 431
R ₁ (F, I>2σ(I))	0.0735
wR ₂ (F ²), todos los datos	0.1642

Datos cristalográficos del compuesto 5c

Fórmula	$C_{23}H_{26}F_3N_6O_6ReS$
Peso molecular ($g \cdot mol^{-1}$)	757.76
Sistema cristalino	Monoclínico
Grupo espacial	P21/c
a (Å)	13.3520(3)
b (Å)	17.3530(4)
c (Å)	15.2838(4)
α (°)	90
β (°)	110.9660(10)
γ (°)	90
V (Å ³)	3306.76(14)
Z	4
$F(000)$	1488
D_{calcd} ($g \cdot cm^{-3}$)	1.522
Dimensiones del cristal (mm)	0.41 x 0.16 x 0.06
μ (mm^{-1})	3.796
Temperatura (K)	100(2)
Radiación (Å)	0.71073
Rango de toma de datos, θ (°)	2.74 a 27.17
Relación datos/parámetros	131983 / 368
R_1 (F, $I > 2\sigma(I)$)	0.0533
wR_2 (F ²), todos los datos	0.1063

Datos cristalográficos del compuesto 4c

Fórmula	C ₂₂ H ₂₂ F ₃ N ₄ O ₈ ReS
Peso molecular (g.mol ⁻¹)	745.70
Sistema cristalino	Monoclínico
Grupo espacial	P21/c
a (Å)	13.150(5)
b (Å)	13.426(5)
c (Å)	14.500(5)
α (°)	90
β (°)	97.644(5)
γ (°)	90
V (Å ³)	2537.3(16)
Z	4
F(000)	1456
D _{calcd} (g.cm ⁻³)	1.952
Dimensiones del cristal (mm)	0.12 x 0.09 x 0.06
μ (mm ⁻¹)	4.949
Temperatura (K)	293(2)
Radiación (Å)	0.71073
Rango de toma de datos, θ (°)	2.08 a 25.59
Relación datos/parámetros	4672 / 352
R ₁ (F, I>2σ(I))	0.0307
wR ₂ (F ²), todos los datos	0.0866

Datos cristalográficos del compuesto 6b

Fórmula	$C_{30}H_{32}F_3N_6O_6ReS$
Peso molecular ($g \cdot mol^{-1}$)	847.88
Sistema cristalino	Triclínico
Grupo espacial	P-1
a (Å)	9.844(5)
b (Å)	11.002(5)
c (Å)	17.019(5)
α (°)	100.826(5)
β (°)	104.168(5)
γ (°)	97.310(5)
V (Å ³)	1726.1(13)
Z	2
$F(000)$	840
D_{calcd} ($g \cdot cm^{-3}$)	1.631
Dimensiones del cristal (mm)	0.28 x 0.14 x 0.06
μ (mm^{-1})	3.646
Temperatura (K)	293(2)
Radiación (Å)	0.71073
Rango de toma de datos, θ (°)	1.92 a 30.57
Relación datos/parámetros	10507 / 274
R_1 (F, $I > 2\sigma(I)$)	0.0611
wR_2 (F ²), todos los datos	0.1766

ARTÍCULO

Reactivity of $[\text{Re}(\text{CO})_3(4,4'\text{-R}_2\text{-2,2'\text{-bipy})(\text{N-RIm})]\text{OTf}$ compounds: control by the bipy substituents

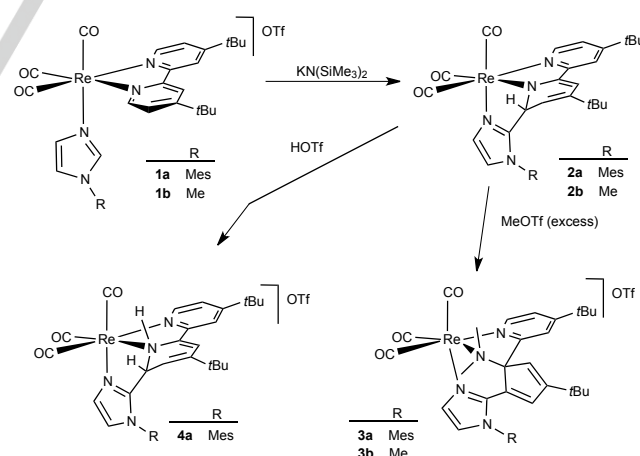
Maialen Espinal Viguri,^[b] Julio Pérez,^[a,b] and Lucía Riera^{*[a]}

Abstract: The reactivity of $[\text{Re}(\text{CO})_3(4,4'\text{-R}_2\text{-2,2'\text{-bipy})(\text{N-RIm})]\text{OTf}$ [$\text{R} = t\text{Bu}, \text{OMe}, \text{NMe}_2$; $\text{R}' = \text{Me}, \text{Mes}$ (2,4,6-trimethylphenyl)] compounds towards the strong base $\text{KN}(\text{SiMe}_3)_2$ has shown a dramatic dependence on the nature of the substituents at 4 and 4' positions of the 2,2'-bipyridine ligand. C-C coupling, pyridine ring-opening, formation of a *N*-heterocyclic carbene (NHC) or protonation of an aromatic CH group to afford a novel type of dihydropyridine ring of a bipy ligand are obtained.

Dearomatization of pyridines and other six-membered *N*-heterocycles is a challenging task that can provide a route to the synthesis of functionalized molecules present in many natural products and pharmaceuticals.^[1] In particular, dihydropyridines have a broad natural occurrence and are used to treat a great variety of medical diseases.^[2] In some cases the harsh conditions employed, along with the instability of the dearomatized products, lead to ring-opening reactions that usually imply a C-N bond cleavage.^[3] These reactions are particularly interesting since they are related to the very important yet mechanistically poorly understood hydrodenitrogenation (HDN) process.^[4] In the last years some examples of metal-mediated dearomatization and ring-opening of aromatic *N*-heterocycles have been described, mainly based on highly reactive early-transition and rare-earth metal complexes.^[5-6] In our previous studies, focused on the deprotonation of *N*-alkylimidazole (*N*-RIm) ligands coordinated to organometallic fragments, we achieved the dearomatization and ring-opening of one pyridine ring of a 2,2'-bipyridine (bipy) ligand coordinated to the *fac*- $\{\text{Re}(\text{CO})_3\}$ fragment.^[7] It is interesting to note that complexes containing $\{\text{Re}(\text{CO})_3(\text{bipy})\}$ fragment are remarkably stable, and have been used in many areas of chemistry,^[8] and, in particular, 2,2'-bipyridine has been found to be a very robust ligand that forms complexes with the vast majority of metals.^[9] The reactivity of $[\text{Re}(\text{CO})_3(4,4'\text{-R}_2\text{-2,2'\text{-bipy})(\text{N-RIm})]\text{OTf}$ ($\text{R} = t\text{Bu}, \text{OMe}, \text{NMe}_2$; $\text{R}' = \text{Me}, \text{Mes}$ (2,4,6-trimethylphenyl)) compounds towards an external base and the reaction of the products with electrophilic reagents are reported herein, showing that the remote substituents of the bipy ligand (at 4, 4' positions) are crucial to determine the reaction pattern

and the nature of the product. C-C coupling, ring-opening, formation of a *N*-heterocyclic carbene (NHC) or protonation of an aromatic CH group to afford a novel type of dihydropyridine ring of a bipy ligand are obtained, demonstrating the rich reactivity showed by this family of compounds, previously regarded as chemically inert.

Starting cationic imidazole complexes were prepared by simple substitution of the triflate ligand by the *N*-alkylimidazole.^[10] The reaction of the *tert*-butyl derivatives $[\text{Re}(\text{CO})_3(4,4'\text{-}t\text{Bu}_2\text{-2,2'\text{-bipy})(\text{N-R'Im})]\text{OTf}$ ($\text{R}' = \text{Mes}$, **1a**; Me **1b**) with the equimolar amount of $\text{KN}(\text{SiMe}_3)_2$ afforded immediately, as indicated by the IR ν_{CO} values, neutral species which, in the case of **1b** could be spectroscopically characterized in solution by means of ¹H NMR. This spectrum showed the signals of one pyridyl ring very upfield shifted (at 5.70, 5.54 and 4.92 ppm), so we can propose that complex **2b** results from the intramolecular nucleophilic attack at a bipy *C*_{ortho} atom by the deprotonated imidazole, which generates a new C-C bond with consequent dearomatization of the involved pyridyl ring. The addition of an excess of MeOTf in CH_2Cl_2 to the neutral intermediates **2a,b** led to two successive methylations, and cleave of the C-N bond of the dearomatized ring, resulting in formation of ring-opening products, **3a,b** respectively (Scheme 1). The new compounds, that display an *N*-ligated cyclopentadienyldimethylamine group, were spectroscopically characterized in solution, and, for **3a**, by X-ray diffraction (Figure 1a).



Scheme 1. Reactivity of compounds **1a,b**.

Note that although this reactivity is reminiscent of that found for $[\text{Re}(\text{CO})_3(\text{bipy})(\text{N-RIm})]\text{OTf}$ compounds, in that case the *N*-mesitylimidazole derivative did not afford the pyridine ring-opening; rather, just C-C coupling and monomethylation product was obtained instead.^[7a] A product of this latter type, **4a**, was obtained from the reaction of **2a** with HOTf (Scheme 1), which was fully characterized.

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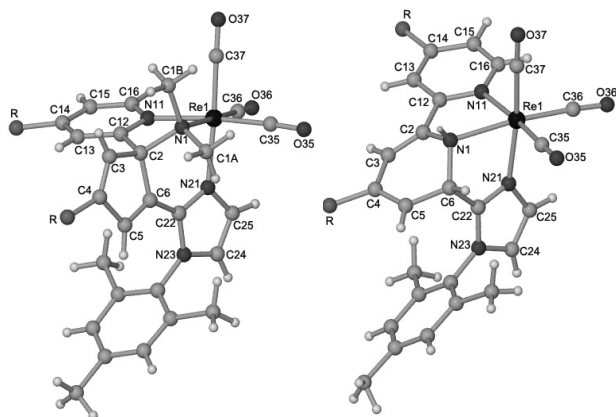


Figure 1. a) Molecular structure of the cation of **3a**; b) Molecular structure of the cation of **4a**. *Tert*-butyl groups (R) have been omitted for clarity.

As shown in Figure 1b, the central imidazole C atom (C22) is bonded to an *ortho* bipy C atom (C6), dearomatization of that pyridyl ring is maintained, and the protonation has occurred on the nitrogen atom of the dearomatized ring (N1), transforming it from an amido, in **2a**, to an amino-like N in **4a**.

It is remarkable that the *tert*-butyl substituents not only do not prevent the nucleophilic attack on the bipy ligand by the 2-imidazolyl group formed upon deprotonation reaction, but in fact enhance the reactivity of the complex, as for the 4,4'-*t*Bu-2,2'-bipy complexes the less nucleophilic *N*-MesIm ligand is able to generate the ring-opening process too. Presumably, the 4,4'-location of the *tert*-butyl substituents deprive them of steric influence on the attack at *C*_{ortho}, while their electron-releasing power makes the product of the C-C coupling more reactive towards the MeOTf electrophile. These results, that highlight the wider generality of this type of ring-opening process, prompted us to investigate the effect of other substituents at 4,4' positions of the 2,2'-bipyridine ligand.^[11]

The addition of KN(SiMe₃)₂ to previously cooled (-78 °C) THF solutions of [Re(CO)₃(4,4'-(OMe)₂-2,2'-bipy)(*N*-R'Im)]OTf (R' = Mes, **5a**; Me **5b**) afforded the corresponding neutral species, as evidenced by a large shift to lower wavenumbers of the ν_{CO} bands in the IR spectra (from 2031, 1925 cm⁻¹ to 2006, 1890 cm⁻¹ for **5a**, for example). Electrophilic interception of these species was achieved by addition of the equimolar amount, in each case, of HOTf to afford stable cationic compounds **7a** and **7b** respectively (see Scheme 2), which were spectroscopically characterized in solution, and for **7a** the solid-state structure was determined by X-ray diffraction (Figure 2). The cation of **7a** consists of a *fac*-{Re(CO)₃} fragment bonded to a tridentate *N*-donor ligand that results from the C-C coupling between the central C atom of the *N*-mesitylimidazole and one of the *ortho* CH (C6) groups of the 4,4'-OMe-2,2'-bipy ligand. Although this type of reactivity resembles that described above for compound **4a**, a dramatic difference exists, as the site of protonation for **7a** is the C5-H group of the dearomatized ring rather than the amido nitrogen, affording as a result a dihydropyridyl group. The C5-C6 and C4-C5 bond distances of 1.516(6) Å and 1.491(6) Å respectively correspond to single bonds, whereas the N1-C2 (1.308(6) Å) and C3-C4 (1.348(7) Å) bond distances are typical

of double bonds. In addition, the dihedral angle between the planes defined by C4-C5-C6 and C2-C3-C4, of 23.0°, undoubtedly reflects the large deviation of the C5 atom from the original aromatic plane.

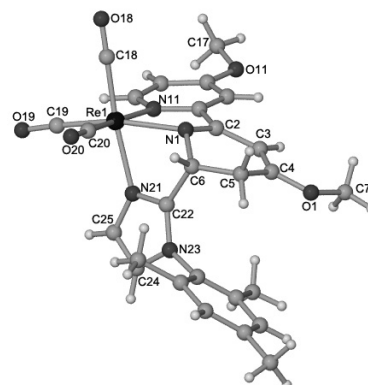
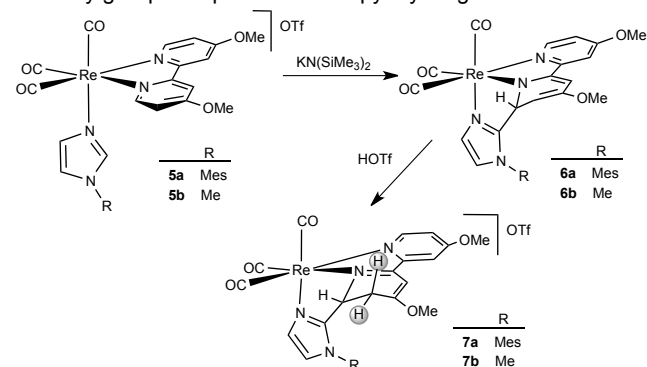


Figure 2. Molecular structure of the cation of **7a**

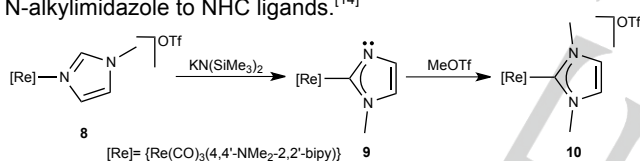
The spectroscopic data in solution of compound **7a** supported this novel structure as the ¹H NMR spectrum in CD₂Cl₂ shows an asymmetric dearomatized 4,4'-disubstituted-2,2'-bipyridine, and a 2D ¹H-¹H correlation spectroscopic (COSY) study clearly established that the two multiplets at 3.07 and 1.99 ppm correspond to the methylenic hydrogen atoms. Accordingly, a 2D HSQC showed that these two signals correspond to the same peak at 28.1 ppm in the ¹³C NMR spectrum, its CH₂ nature being confirmed by a DEPT-135 experiment (in which all other carbon atoms of **7a** were found to be quaternary, methine or methyl groups). The spectroscopic data of **7b** are analogous to those of **7a**, reflecting the isostructurality between the two complexes. It has to be noted that in the ¹H NMR spectrum of the neutral mesityl derivative (**6a**), that results from the deprotonation of [Re(CO)₃(4,4'-(OMe)₂-2,2'-bipy)(*N*-MesIm)]OTf (**5a**), the signal of the C5-H group is very upfield shifted, at 3.46 ppm. This fact can be attributed to the resonant effect of the methoxy group at 4-position of the pyridyl ring.



Scheme 2. Reactivity of compounds **5a,b**

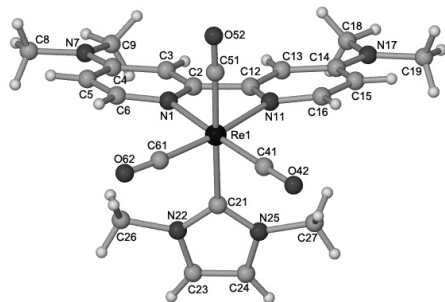
Although the reactions do not end in ring-opening, the sequence shown in Scheme 2, transforming **5a-b** into their isomers **7a-b**, weakens the C4-C5 and C5-C6 bonds of the pyridyl ring (that are single bonds in the products, as mentioned above).^[12] The strong electron-releasing effect of the OMe groups is undoubtedly one of the factors that make protonation at C preferred over protonation at the pyridyl N atom in the transformation from **6a-b** to **7a-b**.

Finally, we studied the effect of an even stronger donor substituent (dimethylamine) at 4,4' positions in the bipy ligand. The deprotonation of $[\text{Re}(\text{CO})_3(4,4'-(\text{NMe}_2)_2-2,2'\text{-bipy})(\text{N-Melm})]\text{OTf}$ (**8**) in THF at low temperature (-78°C) led to the formation of a neutral complex, **9**, as indicated by its ν_{CO} IR bands (at 2000, 1884 and 1878 cm^{-1}). The ^1H NMR of **9** in CD_2Cl_2 clearly showed that the outcome of this reaction was different from those described above since no dearomatization features were observed. Instead, a symmetric 4,4'-(NMe_2)₂-2,2'-bipy was observed, and, in agreement with the deprotonation of the imidazole central CH group, only two signals at 6.90 and 6.86 ppm for this ligand could be found. Furthermore, the ^{13}C NMR spectrum of **9** showed a low intensity signal at 178.5 ppm attributable to a Re-bonded C atom. Thus, it seems that the dimethylamino substituents at 4 and 4' positions make the bipy ligand so electron rich that the nucleophilic attack is directed to the rhenium atom instead, affording an imidazol-2-yl complex (Scheme 3). Complexes featuring C-bonded imidazol-2-yl ligands with a non-coordinated N atom are very rare,^[7b,13] and have been proposed as intermediates in the tautomerization of N-alkylimidazole to NHC ligands.^[14]



Scheme 3. Reactivity of compounds **5a,b**

Addition of the equimolar amount of MeOTf to a solution of imidazol-2-yl complex **9** in CH_2Cl_2 , led to the methylation of the non-substituted nitrogen atom and the corresponding NHC compound (**10**) was obtained. Figure 3 shows the molecular structure of the cation of **10** confirming its carbene nature. The Re-C(21) bond distance of 2.192(8) Å is similar to those of other NHC complexes with the $\{\text{Re}(\text{CO})_3\}$ fragment,^[7b,15] and the low



Molecular structure of the cation of 10

intensity signal at 171.1 ppm in the ^{13}C NMR spectrum is clearly indicative of a rhenium-bonded NHC ligand.^[16]

Figure 3.

In summary, the presence of electron-donating substituents on the backbone (4,4'-positions) of a 2,2'-bipyridine ligand determine the deprotonation reaction pathway in rhenium tricarbonyl complexes containing N-alkylimidazole ligands. With *tert*-butyl or methoxy groups, C-C coupling (between the imidazole C2 and bipy C6) and pyridyl dearomatization results, while for dimethylamino, the product is an imidazol-2-yl ligand, which, by methylation, generates a NHC ligand. The dearomatized products react with electrophiles: protonation with HOTf and methylation (MeOTf) of the *t*Bu-substituted complexes occur at the Re-bonded, amido-type nitrogen in the dearomatized ring, but with excess of MeOTf, ring-cleavage, nitrogen extrusion products result. The protonation of the OMe-substituted products follows a novel reaction pattern affording a dihydropyridine ring.

Acknowledgements

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Keywords: bipyridine • dearomatization • NHC • organometallic compounds • rhenium

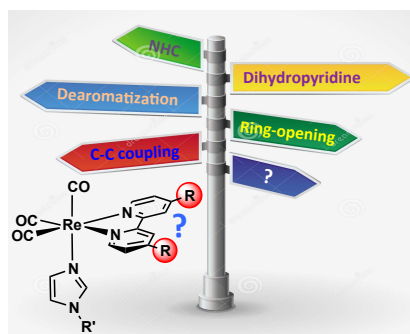
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- [16] CCDC-1050350 (**3a**), CCDC-1050351 (**4a**), CCDC-1050352 (**7a**), and CCDC-1050353 (**10**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Entry for the Table of Contents

COMMUNICATION

The nature of the substituents on the backbone of the 2,2'-bipyridine ligand determines the reaction pathway of rhenium tricarbonyl complexes containing N-alkylimidazole ligands once have been deprotonated



Maialen Espinal Viguri, Julio Pérez,
Lucía Riera*

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Reactivity of $[\text{Re}(\text{CO})_3(4,4'\text{-R}_2\text{-2,2'\text{-bipy})(\text{N-Rim})]\text{OTf}$ compounds:
control by the bipy substituents

Supporting Information

Reactivity of [Re(CO)₃(4,4'-R₂-2,2'-bipy)(N-R₁m)]OTf compounds: control by the bipy substituents.

Maialen Espinal Viguri, Julio Pérez and Lucía Riera*

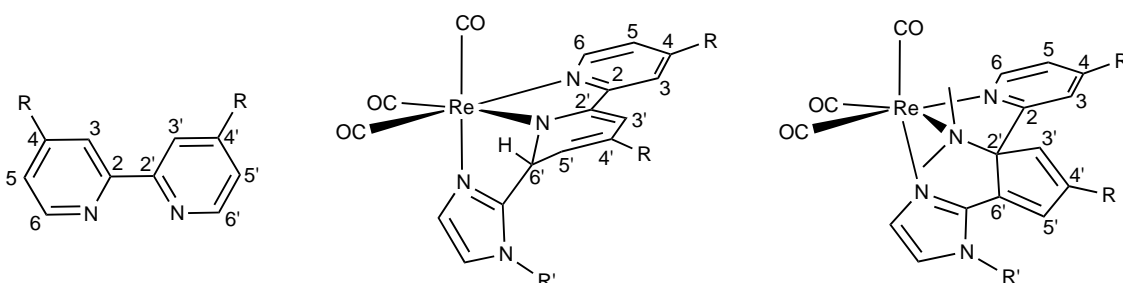
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Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were distilled from Na (toluene and hexanes), Na/benzophenone (thf) and CaH_2 (CH_2Cl_2). Compounds *N*-mesitylimidazole,¹ $[\text{Re}(\text{OTf})(\text{CO})_3(4,4'\text{-}t\text{Bu}_2\text{-}2,2'\text{-bipy})]^2$ and $[\text{ReBr}(\text{CO})_3(4,4'\text{-(OMe)}_2\text{-}2,2'\text{-bipy})]^3$ were prepared as previously reported. Deuterated dichloromethane and toluene (Cambridge Isotope Laboratories, Inc.) were stored under nitrogen in a Young tube and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400, Bruker Avance 300 or DPX-300 spectrometer. NMR spectra are referred to the internal residual solvent peak for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm. CaF_2 cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich.

NMR Labelling Schemes:



Synthesis of $[\text{ReBr}(\text{CO})_3(4,4'\text{-}t\text{Bu}_2\text{-}2,2'\text{-bipy})]$. The synthesis of this complex has been described previously as a microwave reaction.⁴ 4,4'-di-*tert*-butyl-2,2'-bipyridine (165 mg, 0.677 mmol) was added to a solution of $[\text{ReBr}(\text{CO})_5]$ (250 mg, 0.616 mmol) in toluene (20 mL), and the mixture was refluxed for 3 h. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a yellow solid that was washed with hexane (2×20 mL), diethylether (2×20 mL) and dried under vacuum. Yield: 336 mg (88 %). IR (CH_2Cl_2 , cm^{-1}): 2021, 1922, 1894 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.93 (d ($J = 5.9$ Hz), 2H, $\text{H}_{6,6'}$), 8.18 (d ($J = 1.8$ Hz), 2H, $\text{H}_{3,3'}$), 6.61 (dd ($J = 5.9, 1.8$ Hz), 2H, $\text{H}_{5,5'}$), 1.47 (s, 18H CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 197.8 (2CO), 189.7 (CO), 164.4, 155.9, 153.1, 124.9, 120.3 (4,4'-*t*Bu₂-2,2'-bipy), 30.4 (CH_3). Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{BrN}_2\text{O}_3\text{Re}$: C 40.78, H 3.91, N 4.53. Found: C 41.11, H 3.72, N 4.46.

Synthesis of $[\text{ReBr}(\text{CO})_3(4,4'\text{-(NMe}_2)_2\text{-}2,2'\text{-bipy})]$. 4,4'-bis(*N,N'*-dimethylamino)-2,2'-bipyridine (131 mg, 0.542 mmol) was added to a solution of $[\text{ReBr}(\text{CO})_5]$ (200 mg, 0.492 mmol) in toluene (20 mL), and the mixture was refluxed for 4 h. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of an orange solid that was washed with hexane (2×20 mL), diethylether (1×20 mL) and dried under vacuum. Yield: 243 mg (83 %). IR (CH_2Cl_2 , cm^{-1}): 2022, 1919, 1896 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.47 (d ($J = 6.7$ Hz), 2H, $\text{H}_{6,6'}$), 7.18 (d ($J = 2.6$ Hz), 2H, $\text{H}_{3,3'}$), 6.61 (dd ($J = 6.7, 2.6$ Hz), 2H, $\text{H}_{5,5'}$), 3.18 (s, 12H CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 156.6, 155.3, 152.3, 108.8, 104.5 (4,4'-(NMe_2)₂-2,2'-bipy), 39.9

(CH₃ *t*Bu). Anal. Calcd. for C₁₇H₁₈BrN₄O₃Re: C 34.46, H 3.06, N 9.46. Found: C 34.96, H 2.91, N 9.40.

Synthesis of [Re(OTf)(CO)₃(4,4'-(OMe)₂-2,2'-bipy)]. AgOTf (109 mg, 0.424 mmol) was added to a solution of [ReBr(CO)₃(4,4'-(OMe)₂-2,2'-bipy)] (200 mg, 0.353 mmol) in CH₂Cl₂ (20 mL), and the mixture was stirred in the dark at room temperature for 4 h. The reaction mixture was filtered through diatomaceous earth, and the resulting yellow solution was evaporated under reduced pressure to a volume of 7-10 mL. Addition of hexane (20 mL) caused the precipitation of a yellow solid that was washed with hexane (2 × 20 mL), diethylether (1 × 20 mL) and dried under vacuum. Yield: 175 mg (78 %). IR (CH₂Cl₂, cm⁻¹): 2033, 1930, 1909 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.86 (d (*J*= 6.5 Hz), 2H, H_{6,6'}), 7.64 (d (*J*= 2.6 Hz), 2H, H_{3,3'}), 7.09 (dd (*J*= 6.5, 2.6 Hz), 2H, H_{5,5'}), 4.06 (s, 6H OCH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.6 (2CO), 192.7 (CO), 168.8, 157.9, 155.5, 112.7, 110.7 (4,4'-(OMe)₂-2,2'-bipy), 57.2 (OCH₃). Anal. Calcd. for C₁₆H₁₂F₃N₂O₈ReS: C 30.24, H 1.90, N 4.41. Found: C 30.89, H 1.34, N 4.41.

Synthesis of [Re(OTf)(CO)₃(4,4'-(NMe)₂-2,2'-bipy)]. This compound was prepared as described above for [Re(OTf)(CO)₃(4,4'-(OMe)₂-2,2'-bipy)] starting from [ReBr(CO)₃(4,4'-(NMe)₂-2,2'-bipy)] (200 mg, 0.337 mmol) and AgOTf (104 mg, 0.405 mmol). [Re(OTf)(CO)₃(4,4'-(NMe)₂-2,2'-bipy)] was obtained as an orange solid. Yield: 172 mg (77 %). IR (CH₂Cl₂, cm⁻¹): 2027, 1921, 1901 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.51 (d (*J*= 6.7 Hz), 2H, H_{6,6'}), 7.19 (d (*J*= 2.2 Hz), 2H, H_{3,3'}), 6.65 (dd (*J*= 6.7, 2.2 Hz), 2H, H_{5,5'}), 3.21 (s, 12H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 197.3 (2CO), 193.8 (CO), 156.5, 155.2, 152.4, 108.3, 103.8 (4,4'-(NMe)₂-2,2'-bipy), 39.5 (CH₃). Anal. Calcd. for C₁₈H₁₈F₃N₂O₈ReS: C 32.68, H 2.74, N 8.47. Found: C 33.13, H 2.81, N 7.88.

Synthesis of [Re(CO)₃(*N*-MesIm)(4,4'-*t*Bu₂-2,2'-bipy)]OTf (1a). *N*-mesitylimidazol (22 mg, 0.120 mmol) was added to a solution of [Re(OTf)(CO)₃(4,4'-*t*Bu₂-2,2'-bipy)] (75 mg, 0.109 mmol) in CH₂Cl₂ (20 mL). The mixture was stirred at room temperature for two days. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a yellow solid. Compound **1a** was washed with hexane (3 × 20 mL) and dried under vacuum. Yield: 81 mg (85 %). IR (CH₂Cl₂, cm⁻¹): 2032, 1927 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.01 (d (*J*= 5.9 Hz), 2H, H_{6,6'}), 8.32 (d (*J*= 1.5 Hz), 2H, H_{3,3'}), 7.70 (dd (*J*= 5.9, 1.5 Hz), 2H, H_{5,5'}), 7.35 (s, 1H, NCHN *N*-MesIm), 6.95 (s, 2H, *N*-MesIm), 6.84, 6.60 (s_{br}, 1H each, CH *N*-MesIm), 2.30 (s, 3H, CH₃ *N*-MesIm), 1.71 (s, 6H, CH₃ *N*-MesIm), 1.48 (s, 18H, CH₃ *t*Bu). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.1 (2CO), 191.9 (CO), 166.4, 155.6, 152.8, 125.8, 121.3 (4,4'-*t*Bu₂-2,2'-bipy), 140.4, 134.4, 131.2, 129.3 (Mes), 139.6, 129.0, 123.0 (CH *N*-MesIm), 36.0 (C(CH₃)₃), 29.9 (CH₃, *t*Bu), 20.7 (CH₃ *N*-MesIm), 16.8 (2CH₃ *N*-MesIm). Anal. Calcd. for C₃₄H₃₈F₃N₄O₆ReS: C 46.73, H 4.38, N 6.41. Found: C 47.05, H 4.22, N 6.42.

Synthesis of [Re(CO)₃(*N*-Melm)(4,4'-*t*Bu₂-2,2'-bipy)]OTf (1b). Compound **1b** was prepared as described above for the synthesis of **1a** starting from [Re(OTf)(CO)₃(4,4'-*t*Bu₂-2,2'-bipy)] (75 mg, 0.109 mmol) and *N*-methylimidazol (10 μL, 0.120 mmol). Compound **1b** was obtained as a yellow microcrystalline solid. Yield: 77 mg (91 %). IR (CH₂Cl₂, cm⁻¹): 2030, 1921 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.98 (m, 2H, H_{6,6'}), 8.35 (s_{br}, 2H, H_{3,3'}), 7.72 (m, 2H, H_{5,5'}), 7.42 (s, 1H, NCHN *N*-Melm), 6.89, 6.60 (s, 1H each, CH *N*-Melm), 3.63 (s, 3H CH₃ *N*-Melm), 1.51 (s, 18H, CH₃ *t*Bu).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 196.2 (2CO), 192.2 (CO), 165.8, 155.6, 152.7, 125.7, 121.4 (4,4'-*t*Bu₂-2,2'-bipy), 140.0, 129.3, 122.5 (CH *N*-Melm), 35.9 ($\text{C}(\text{CH}_3)_3$), 34.5 (CH_3 , *N*-Melm), 29.9 (CH_3 , *t*Bu). Anal. Calcd. for $\text{C}_{26}\text{H}_{30}\text{F}_3\text{N}_4\text{O}_6\text{ReS}$: C 40.57, H 3.93, N 7.28. Found: C 40.94, H 4.13, N 7.21.

Reaction of $[\text{Re}(\text{CO})_3(\text{N-Melm})(4,4'\text{-tBu}_2\text{-2,2'\text{-bipy}})]\text{OTf}$ (1b**) with $\text{KN}(\text{SiMe}_3)_2$.**
Spectroscopic characterization of 2b. $\text{KN}(\text{SiMe}_3)_2$ (0.14 mL of a 0.7 M solution in toluene, 0.100 mmol) was added to a solution of $[\text{Re}(\text{N-Melm})(\text{CO})_3(4,4'\text{-tBu}_2\text{-2,2'\text{-bipy}})]$ (**1b**) (70 mg, 0.091 mmol) in THF (20 mL) previously cooled to $-78\text{ }^\circ\text{C}$, affording immediately change in the color of the solution from yellow to red. The solvent was evaporated to dryness under reduced pressure. The residue was washed with hexane ($3 \times 15\text{ mL}$) and dried in vacuo. IR (CH_2Cl_2 , cm^{-1}): 2004, 1890, 1883 (ν_{CO}). ^1H NMR (toluene- d_8): δ 8.63 (*s*_{br}, 1H, H_6), 7.40 (*s*_{br}, 1H, H_5), 6.71 (*s*_{br}, 1H, CH *N*-Melm), 6.37 (*s*_{br}, 1H, H_3), 5.74 (*s*_{br}, 1H, CH *N*-Melm), 5.70 (*s*_{br}, 1H, H_3), 5.54, 4.92 (*s*_{br}, 1H each, H_5 and H_6), 2.83 (*s*, 3H, CH_3 *N*-Melm), 1.22, 0.87 (*s*, 9H each, CH_3 *t*Bu). Unfortunately, compound **2b** decomposed in unidentified products over the acquisition time of a ^{13}C NMR spectrum.

Reaction of $[\text{Re}(\text{CO})_3(\text{N-MesIm})(4,4'\text{-tBu}_2\text{-2,2'\text{-bipy}})]\text{OTf}$ (1a**) with $\text{KN}(\text{SiMe}_3)_2$ and MeOTf (excess). Synthesis of 3a.** $\text{KN}(\text{SiMe}_3)_2$ (0.13 mL of a 0.7 M solution in toluene, 0.091 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{N-MesIm})(4,4'\text{-tBu}_2\text{-2,2'\text{-bipy}})]\text{OTf}$ (**1a**) (75 mg, 0.086 mmol) in THF (20 mL) previously cooled to $-78\text{ }^\circ\text{C}$. The solvent was evaporated to dryness under reduced pressure, the residue redissolved in CH_2Cl_2 (20 mL) and MeOTf (21 μL , 0.189 mmol) was added. The mixture was stirred at room temperature for 30 min., filtered via canula and evaporated to dryness. The resulting yellow solid was washed with hexane ($3 \times 15\text{ mL}$) and dried in vacuo. Yield: 54 mg (69 %). IR (CH_2Cl_2 , cm^{-1}): 2033, 1928, 1922 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.78 (*d* ($J= 5.9\text{ Hz}$), 1H, H_6), 7.69 (*d* ($J= 1.5\text{ Hz}$), 1H, CH *N*-MesIm), 7.51 (*dd* ($J= 6.0, 2.0\text{ Hz}$), 1H, H_5), 7.25 (*d* ($J= 2.0\text{ Hz}$), 1H, H_3), 7.21 (*s*_{br}, 1H, *N*-MesIm), 7.15 (*d* ($J= 1.5\text{ Hz}$), 1H, CH *N*-MesIm), 7.04 (*s*_{br}, 1H, *N*-MesIm), 6.51 (*d* ($J= 1.6\text{ Hz}$), 1H, H_3/H_5), 6.48 (*d* ($J= 1.6\text{ Hz}$), 1H, H_3/H_5), 3.44, 2.80 (*s*, 3H each, *N*- CH_3), 2.42, 2.07 (*s*, 3H each, CH_3 *N*-MesIm), 1.28 (*s*, 9H, CH_3 *t*Bu), 1.24 (*s*, 3H, CH_3 *N*-MesIm), 1.13 (*s*, 9H, CH_3 *t*Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 195.9, 195.0, 194.3 (CO), 166.8, 166.1, 158.4 (4,4'-*t*Bu₂-2,2'-bipy), 153.6 (C_6), 141.8, 139.4, 135.3, 134.7, 133.9, 132.0, 130.2, 130.1 (4,4'-*t*Bu₂-2,2'-bipy and *N*-MesIm), 134.8, 124.6 (CH *N*-MesIm), 131.8, 123.4 (C_3 and C_5), 124.3 (C_5), 119.4 (C_3), 88.0 (C_6), 57.2, 47.4 (*N*- CH_3), 35.7, 33.1 ($\text{C}(\text{CH}_3)_3$), 29.7, 28.3 (3 CH_3 *t*Bu), 20.9, 17.4, 16.1 (CH_3 *N*-MesIm). Anal. Calcd. for $\text{C}_{36}\text{H}_{43}\text{F}_3\text{N}_4\text{O}_6\text{ReS}$: C 47.88, H 4.80, N 6.20. Found: C 47.52, H 4.75, N 6.57.

Reaction of $[\text{Re}(\text{CO})_3(\text{N-Melm})(4,4'\text{-tBu}_2\text{-2,2'\text{-bipy}})]\text{OTf}$ (1b**) with $\text{KN}(\text{SiMe}_3)_2$ and MeOTf (excess). Synthesis of 3b.** Compound **3b** was prepared as described above for the synthesis of **3a** starting from $[\text{Re}(\text{CO})_3(\text{N-Melm})(4,4'\text{-tBu}_2\text{-2,2'\text{-bipy}})]\text{OTf}$ (**1b**) (70 mg, 0.091 mmol), $\text{KN}(\text{SiMe}_3)_2$ (0.14 mL of a 0.7 M solution in toluene, 0.100 mmol) and MeOTf (22 μL , 0.200 mmol). Compound **5b** was obtained as a yellow solid. Yield: 45 mg (62 %). IR (CH_2Cl_2 , cm^{-1}): 2032, 1924 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.69 (*d* ($J= 6.0\text{ Hz}$), 1H, H_6), 7.45 (*m*, 2H, H_5 and CH *N*-Melm), 7.29, 7.24 (*m*, 1H each, H_3 and CH *N*-Melm), 7.11 (*d* ($J= 1.4\text{ Hz}$), H_3/H_5), 6.42 (*d* ($J=$

1.4 Hz), H₃/H₅), 3.94 (s, 3H, CH₃ *N*-Melm), 3.36, 2.75 (s, 3H each, N-CH₃), 1.40, 1.28 (s, 9H each, CH₃ *t*Bu). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.4, 195.8, 194.9 (CO), 167.0, 166.8, 158.7 (4,4'-*t*Bu₂-2,2'-bipy), 153.8 (C₆), 140.1, 136.0, 133.7, 127.1 (4,4'-*t*Bu₂-2,2'-bipy and *N*-Melm), 132.9, 123.2 (C₃' and C₅'), 124.8 (C₅), 120.3 (C₃), 88.4 (C₆'), 57.6, 47.4 (N-CH₃), 38.2, 36.0, 33.8 (C(CH₃)₃ and CH₃ *N*-Melm), 30.1, 29.1 (3CH₃ *t*Bu). Anal. Calcd. for C₂₈H₃₅F₃N₄O₆ReS: C 42.10, H 4.42, N 7.01. Found: C 41.87, H 4.51, N 7.30.

Reaction of [Re(CO)₃(*N*-MesIm)(4,4'-*t*Bu₂-2,2'-bipy)]OTf (1a) with KN(SiMe₃)₂ and HOTf.

Synthesis of 4a. KN(SiMe₃)₂ (0.13 mL of a 0.7 M solution in toluene, 0.094 mmol) was added to a solution of [Re(CO)₃(*N*-MesIm)(4,4'-*t*Bu₂-2,2'-bipy)](1a) (75 mg, 0.086 mmol) in THF (20 mL) previously cooled to -78 °C. The solvent was evaporated to dryness under reduced pressure, the residue redissolved in CH₂Cl₂ (20 mL) and HOTf (9 μL, 0.095 mmol) was then added. The mixture was stirred at room temperature for 10 min., filtered via canula and evaporated to dryness. The resulting yellow solid was washed with hexane (3 × 15 mL) and dried in vacuo. Yield: 54 mg (70 %). IR (CH₂Cl₂, cm⁻¹): 2032, 1928, 1916 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.87 (d (*J*= 6.0 Hz), 1H, H₆), 8.11 (s_{br}, 1H, NH), 7.67 (d (*J*= 1.4 Hz), 1H, H₃), 7.40 (dd (*J*= 6.0, 1.4 Hz), 1H, H₅), 7.29 (d (*J*= 1.4 Hz), 1H, CH *N*-MesIm), 7.13, 6.98 (s_{br}, 1H each, *N*-MesIm), 6.96 (d (*J*= 1.4 Hz), 1H, CH *N*-MesIm), 6.86 (s_{br}, 1H, H₃'), 5.29 (m, 1H, H₆'), 5.12 (m, 1H, H₅'), 2.40, 2.04, 1.75 (s, 3H each, CH₃ *N*-MesIm), 1.40, 0.95 (s, 9H, CH₃ *t*Bu). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.5, 194.9, 194.4 (CO), 164.7, 157.0 (4,4'-*t*Bu₂-2,2'-bipy), 152.9 (C₆), 149.5, 145.3, 141.3, 139.6, 135.3, 134.8, 131.6, 130.0, 129.8 (4,4'-*t*Bu₂-2,2'-bipy and *N*-MesIm), 130.2, 124.4 (CH *N*-MesIm), 124.3 (C₃'), 123.4 (C₅'), 118.9 (C₃), 118.1 (C₃'), 58.1 (C₆'), 35.9, 34.3 (C(CH₃)₃), 30.2, 28.3 (3CH₃ *t*Bu), 21.1, 18.5, 17.2 (CH₃ *N*-MesIm). Anal. Calcd. for C₃₄H₃₈F₃N₄O₆ReS: C 46.73, H 4.38, N 6.41. Found: C 46.98, H 4.44, N 6.07.

Synthesis of [Re(CO)₃(*N*-MesIm)(4,4'-(OMe)₂-2,2'-bipy)]OTf (5a). *N*-mesitylimidazol (32 mg, 0.173 mmol) was added to a solution of [Re(OTf)(CO)₃(4,4'-(OMe)₂-2,2'-bipy)] (175 mg, 0.275 mmol) in CH₂Cl₂ (20 mL). The mixture was stirred at room temperature for 24 h. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a yellow solid. Compound 5a was washed with hexane (3 × 20 mL) and dried under vacuum. Yield: 201 mg (89 %). IR (CH₂Cl₂, cm⁻¹): 2031, 1925 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.83 (d (*J*= 6.4 Hz), 2H, H_{6,6}'), 8.12 (d (*J*= 2.5 Hz), 2H, H_{3,3}'), 7.24 (s, 1H, NCHN *N*-MesIm), 7.15 (dd (*J*= 6.4, 2.5 Hz), 2H, H_{5,5}'), 6.96 (s, 2H, *N*-MesIm), 6.83, 6.64 (s, 1H each, CH *N*-MesIm), 4.16 (s, 6H, OCH₃), 2.31 (s, 6H, CH₃ *N*-MesIm), 1.74 (s, 6H, CH₃ *N*-MesIm). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.8 (2CO), 192.9 (CO), 169.5, 158.2, 154.0, 115.5, 111.0 (4,4'-(OMe)₂-2,2'-bipy), 140.7, 139.8, 134.9, 131.7, 129.7, 129.6, 123.2 (*N*-MesIm), 58.04 (OCH₃), 21.1 (CH₃ *N*-MesIm), 17.1 (2CH₃ *N*-MesIm). Anal. Calcd. for C₂₈H₂₆F₃N₄O₈ReS: C 40.92, H 3.19, N 6.82. Found: C 41.15, H 3.19, N 6.86.

Synthesis of [Re(CO)₃(*N*-Melm)(4,4'-(OMe)₂-2,2'-bipy)]OTf (5b). Compound 5b was prepared as described above for the synthesis of 5a starting from *N*-methylimidazol (21 μL, 0.260 mmol) and [Re(OTf)(CO)₃(4,4'-(OMe)₂-2,2'-bipy)] (150 mg, 0.236 mmol). Compound 5b was obtained as a yellow solid. Yield: 142 mg (84 %). IR (CH₂Cl₂, cm⁻¹): 2028, 1919 (ν_{CO}). ¹H NMR (CD₂Cl₂):

δ 8.78 (d ($J= 6.5$ Hz), 2H, H_{6,6'}), 8.01 (d ($J= 2.6$ Hz), 2H, H_{3,3'}), 7.18 (s, 1H, NCHN *N*-Melm), 7.12 (dd ($J= 6.5, 2.6$ Hz), 2H, H_{5,5'}), 6.81, 6.65 (s, 1H each, CH *N*-Melm), 4.15 (s, 6H, OCH₃), 3.59 (s, 3H, CH₃ *N*-Melm). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.9 (2CO), 193.1 (CO), 169.1, 158.0, 154.1, 115.1, 111.3 (4,4'-(OMe)₂-2,2'-bipy), 139.8, 130.1, 122.7 (CH *N*-Melm), 57.6 (OCH₃), 34.9 (CH₃ *N*-Melm). Anal. Calcd. for C₂₀H₁₈F₃N₄O₈ReS: C 33.47, H 2.53, N 7.81. Found: C 33.45, H 2.50, N 7.83.

Reaction of [Re(CO)₃(*N*-MesIm)(4,4'-(OMe)₂-2,2'-bipy)]OTf (5a) with KN(SiMe₃)₂. Synthesis of 6a. KN(SiMe₃)₂ (0.14 mL of a 0.7 M solution in toluene, 0.100 mmol) was added to a solution of [Re(*N*-MesIm)(CO)₃(4,4'-(OMe)₂-2,2'-bipy)]OTf (5a) (75 mg, 0.091 mmol) in THF (20 mL) previously cooled to -78 °C, affording a change in the color of the solution from yellow to red. The solvent was evaporated to dryness under reduced pressure. The residue was redissolved in CH₂Cl₂ (20 mL), filtered via canula and evaporated to dryness. The resulting red solid was washed with hexane (3 × 15 mL) and dried in vacuo. Yield: 51 mg (76 %). IR (CH₂Cl₂, cm⁻¹): 2005, 1891, 1886 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.70 (d ($J= 6.4$ Hz), 1H, H₆), 7.12 (m, 2H, CH *N*-MesIm and H₃), 7.02, 6.96 (s_{br}, 1H each, *N*-MesIm), 6.77 (m, 2H, CH *N*-MesIm and H₅), 6.96 (s, 2H, *N*-MesIm), 6.83, 6.64 (s, 1H each, CH *N*-MesIm), 5.24 (d ($J= 2.1$ Hz), 1H, H_{5'}), 3.89 (s, 3H, OCH₃), 3.45 (dd ($J= 6.4, 2.1$ Hz), 1H, H_{6'}), 3.08 (s, 3H, OCH₃), 2.35, 1.95, 1.90 (s, 3H each, CH₃ *N*-MesIm). The signal of H_{3'} is overlapped with the solvent residual peak, however the HSQC experiment showed unequivocally a strong correlation between the overlapped signal with those corresponding to H_{5'} and H_{6'}. ¹³C{¹H} NMR (CD₂Cl₂, 193K): δ 201.0, 199.3, 199.0 (CO), 166.4, 163.7, 159.2, 158.6, 154.8, 153.3, 139.5, 135.7, 135.1, 132.2128.9, 128.6, 128.33, 121.6, 112.0, 105.6 (4,4'-(OMe)₂-2,2'-bipy and *N*-MesIm), 96.5 (C₅), 81.4 (C₃), 64.5 (C_{6'}), 56.5 (OCH₃), 21.5, 17.5, 17.3 (CH₃ *N*-MesIm). One of the methoxy signals is overlapped with the solvent residual peak.

Reaction of 6a with HOTf. Synthesis of 7a. To a solution of compound 6a (75 mg, 0.091 mmol) in CH₂Cl₂ (15 mL), HOTf (9 μ L, 0.100 mmol) was added, and the reaction mixture was stirred at room temperature for 10 min. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a brownish solid that was washed with hexane (3 × 15 mL). Slow diffusion of hexane (25 mL) into a concentrated solution of 7a in CH₂Cl₂ (5-7 mL) afforded crystals, one of which was employed for an X-ray structure determination. Yield: 48 mg (63 %). IR (CH₂Cl₂, cm⁻¹): 2028, 1921 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.83 (d ($J= 6.4$ Hz), 1H, H₆), 7.94 (d ($J= 2.7$ Hz), 1H, H₃), 7.34 (d ($J= 1.5$ Hz), 1H, CH *N*-MesIm), 7.19 (dd ($J= 6.4, 2.7$ Hz), 1H, H₅), 7.14 (s, 2H, *N*-MesIm), 7.01 (d ($J= 1.5$ Hz), 1H, CH *N*-MesIm), 6.27 (s_{br}, 1H, H_{3'}), 5.69 (d ($J= 8.9$ Hz), 1H H_{6'}), 4.17, 4.02 (s, 3H each, OCH₃), 3.07 (ddd ($J= 19.0, 8.9, 1.8$ Hz), 1H, H_{5'}), 2.44, 2.00, 1.94 (s, 3H each, CH₃ *N*-MesIm), 1.99 (d ($J= 19.0$ Hz), H_{5'}). ¹³C{¹H} NMR (CD₂Cl₂): δ 197.8, 195.2, 192.4 (CO), 177.5, 173.1, 169.2, 159.1, 154.4, 151.6, 141.9, 135.1, 135.0, 130.7, 130.5, 130.3, 130.2, 124.2 (4,4'-(OMe)₂-2,2'-bipy and *N*-MesIm), 116.3 (C₅), 113.7 (C₃), 94.3 (C₃), 65.7 (C_{6'}), 59.0, 58.0 (OCH₃), 28.1 (CH₂, C_{5'}), 21.3, 17.2, 17.1 (CH₃ *N*-MesIm). Anal. Calcd. for C₂₈H₂₆F₃N₄O₈ReS: C 40.92, H 3.19, N 6.82. Found: C 40.55, H 3.49, N 7.00.

Reaction of [Re(CO)₃(*N*-Melm)(4,4'-OMe-2,2'-bipy)]OTf (5b**) with KN(SiMe₃)₂, and HOTf.**

Synthesis of 7b. KN(SiMe₃)₂ (0.15 mL of a 0.7 M solution in toluene, 0.107 mmol) was added to a solution of [Re(*N*-Melm)(CO)₃(4,4'-(OMe)₂-2,2'-bipy)]OTf (**5b**) (70 mg, 0.098 mmol) in THF (20 mL) previously cooled to -78 °C, affording immediately a change in the color of the solution from yellow to red. The solvent was evaporated to dryness under reduced pressure. The residue was redissolved in CH₂Cl₂ (20 mL) and filtered via canula. HOTf (10 μL, 0.107 mmol) was added, and the reaction mixture was stirred at room temperature for 30 min. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a brown solid that was washed with hexane (3 × 15 mL). Yield: 41 mg (59 %). IR (CH₂Cl₂, cm⁻¹): 2027, 1916 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.81 (d (*J*= 6.4 Hz), 2H, H₆), 7.78 (d (*J*= 2.6 Hz), 2H, H₃), 7.21 (dd (*J*= 6.4, 2.6 Hz), 2H, H₅), 7.03, 6.91 (d (*J*= 1.2 Hz), 1H each, *CH N*-Melm), 6.16 (s_{br}, 1H, H_{3'}), 5.68 (dd (*J*= 9.3, 4.7 Hz), 1H, H_{6'}), 4.10, 3.94 (s, 3H each, OCH₃), 3.76 (s, 3H, CH₃ *N*-Melm), 3.19 (dd (*J*= 17.6, 9.3 Hz), 2H, H₅), 2.68 (dd (*J*= 17.6, 4.7 Hz), 2H, H₅). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.3, 195.6, 191.1 (CO), 172.6, 170.0, 169.1, 157.0, 144.0 (4,4'-(OMe)₂-2,2'-bipy and *N*-Melm), 155.8 (C₆), 127.8, 123.7 (CH *N*-Melm), 115.5 (C₃), 114.4 (C₅), 90.5 (C₃), 60.0 (C₆), 57.7, 57.6 (OCH₃), 33.4 (CH₃ *N*-Melm), 32.5 (CH₂, C₅). Anal. Calcd. for C₂₀H₁₈F₃N₄O₈ReS: C 33.47, H 2.53, N 7.81. Found: C 33.63, H 2.47, N 7.86.

Synthesis of [Re(CO)₃(*N*-Melm)(4,4'-(NMe₂)₂-2,2'-bipy)]OTf (8**).** *N*-methylimidazol (23 μL, 0.291 mmol) was added to a solution of [Re(OTf)(CO)₃(4,4'-(NMe₂)₂-2,2'-bipy)] (175 mg, 0.264 mmol) in CH₂Cl₂ (20 mL). The mixture was stirred at room temperature for 24 h. The solvent was evaporated under vacuum to a volume of 5 mL, and addition of hexane (20 mL) caused the precipitation of a yellow solid. Compound **8** was washed with hexane (3 × 20 mL) and dried under vacuum. Yield: 163 mg (83 %). IR (CH₂Cl₂, cm⁻¹): 2022, 1911 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.42 (d (*J*= 6.7 Hz), 2H, H_{6,6'}), 7.43 (d (*J*= 2.5 Hz), 2H, H_{3,3'}), 7.15 (s, 1H, NCHN *N*-Melm), 6.82 (s, 1H, *CH N*-Melm), 6.63 (dd (*J*= 6.7, 2.5 Hz), 2H, H_{5,5'}), 6.60 (s, 1H, *CH N*-Melm), 3.59 (s, 3H, CH₃ *N*-Melm), 3.22 (s, 12H, CH₃ NMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 197.9 (2CO), 194.7 (CO), 156.4, 155.7, 151.9, 109.2, 105.9 (4,4'-(NMe₂)₂-2,2'-bipy), 139.6, 130.0, 122.4 (CH *N*-Melm), 40.1 (CH₃ NMe₂), 34.9 (CH₃ *N*-Melm). Anal. Calcd. for C₂₂H₂₄F₃N₆O₆ReS: C 35.53, H 3.25, N 11.30. Found: C 35.57, H 2.86, N 10.92.

Reaction of [Re(CO)₃(*N*-Melm)(4,4'-(NMe₂)₂-2,2'-bipy)]OTf (8**) with KN(SiMe₃)₂. Synthesis of**

compound 9. KN(SiMe₃)₂ (0.14 mL of a 0.7 M solution in toluene, 0.096 mmol) was added to a solution of [Re(*N*-Melm)(CO)₃(4,4'-(NMe₂)₂-2,2'-bipy)] (**8**) (65 mg, 0.087 mmol) in THF (20 mL) previously cooled to -78 °C. The color of the solution changed from yellow to red, and the solvent was evaporated to dryness under reduced pressure. The residue was redissolved in toluene (20 mL), filtered via canula and evaporated to dryness. The resulting red solid was washed with hexane (3 × 15 mL) and dried in vacuo. Yield: 47 mg (73 %). IR (THF, cm⁻¹): 2000, 1884, 1878 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.35 (d (*J*= 6.6 Hz), 2H, H_{6,6'}), 7.27 (d (*J*= 2.5 Hz), 2H, H_{3,3'}), 6.72 (s, 1H, *CH N*-Melm), 6.48 (dd (*J*= 6.6, 2.5 Hz), 2H, H_{5,5'}), 6.45 (s, 1H, *CH N*-Melm), 3.79 (s, 3H, CH₃ *N*-Melm), 3.14 (s, 12H, CH₃ NMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 202.4 (2CO), 196.1 (CO), 178.5 (Re-C), 157.3, 154.8, 151.9, 108.3, 104.3 (4,4'-(NMe₂)₂-2,2'-bipy), 128.1,

120.2 (CH *N*-MeIm), 39.8 (CH₃ NMe₂), 33.5 (CH₃ *N*-MeIm).

Reaction of [Re(CO)₃(*N*-MeIm)(4,4'-(NMe₂)₂-2,2'-bipy)]OTf (8**) with KN(SiMe₃)₂ and MeOTf.**

Synthesis of compound 10. KN(SiMe₃)₂ (0.14 mL of a 0.7 M solution in toluene, 0.096 mmol) was added to a solution of [Re(*N*-MeIm)(CO)₃(4,4'-(NMe₂)₂-2,2'-bipy)]OTf (**8**) (65 mg, 0.087 mmol) in THF (20 mL) previously cooled to -78 °C. The color of the solution changed from yellow to red, and the solvent was evaporated to dryness under reduced pressure. The residue was redissolved in CH₂Cl₂ (20 mL), filtered via canula and MeOTf (11 μL, 0.096 mmol) was added. The solution was stirred for 15 min. at room temperature, and then evaporated to dryness. The resulting red solid was washed with hexane (3 × 15 mL) and dried in vacuo. Yield: 40 mg (61 %). IR (CH₂Cl₂, cm⁻¹): 2020, 1914, 1899 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.58 (d (*J*= 6.8 Hz), 2H, H_{6,6'}), 7.28 (d (*J*= 2.7 Hz), 2H, H_{3,3'}), 6.80 (s, 2H, *CH N*-MeIm), 6.60 (dd (*J*= 6.8, 2.7 Hz), 2H, H_{5,5'}), 3.53 (s, 6H, *CH*₃ *N*-MeIm), 3.20 (s, 12H, *CH*₃ NMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 197.4 (2CO), 192.9 (CO), 171.1 (Re-C), 156.9, 155.5, 153.2, 108.5, 105.5 (4,4'-(NMe₂)₂-2,2'-bipy), 123.5 (CH *N*-MeIm), 40.1 (CH₃ NMe₂), 39.3 (CH₃ *N*-MeIm). Anal. Calcd. for C₂₃H₂₆F₃N₆O₆ReS: C 34.46, H 3.46, N 11.10. Found: C 34.25, H 3.16, N 10.84.

X-ray structures of 3a, 4a, 7a and 10.

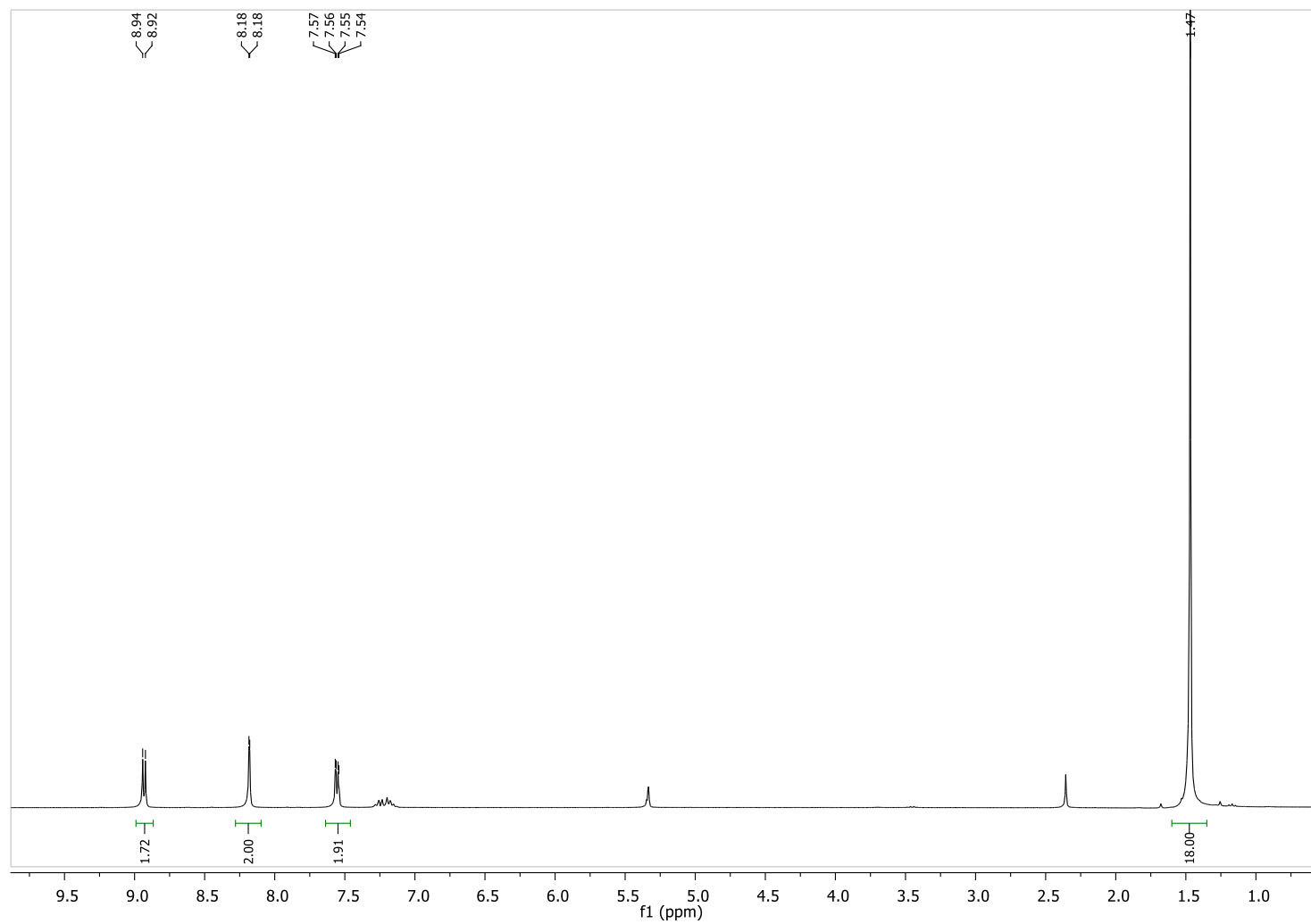
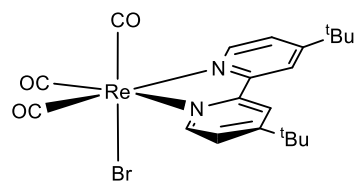
General Description: For Compounds **3a** and **10**. Crystal data were collected on a Bruker APPEX II diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focus sealed tube source at 100 K. Computing data and reduction were made with the APPEX II software.⁵ In all cases empirical absorption corrections were applied using SADABS.⁶ For compounds **4a** and **7a**: data collection was performed at 150 K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4-16 s). Data collection strategy was calculated with the program CrysAlis^{Pro} CCD.⁷ Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.⁷ An empirical absorption correction was applied using the SCALE3 ABSPACK.⁷ In all cases the structures were solved using SIR92⁸ and finally refined by full-matrix, least-squares based on F^2 by SHELXL.⁹

References

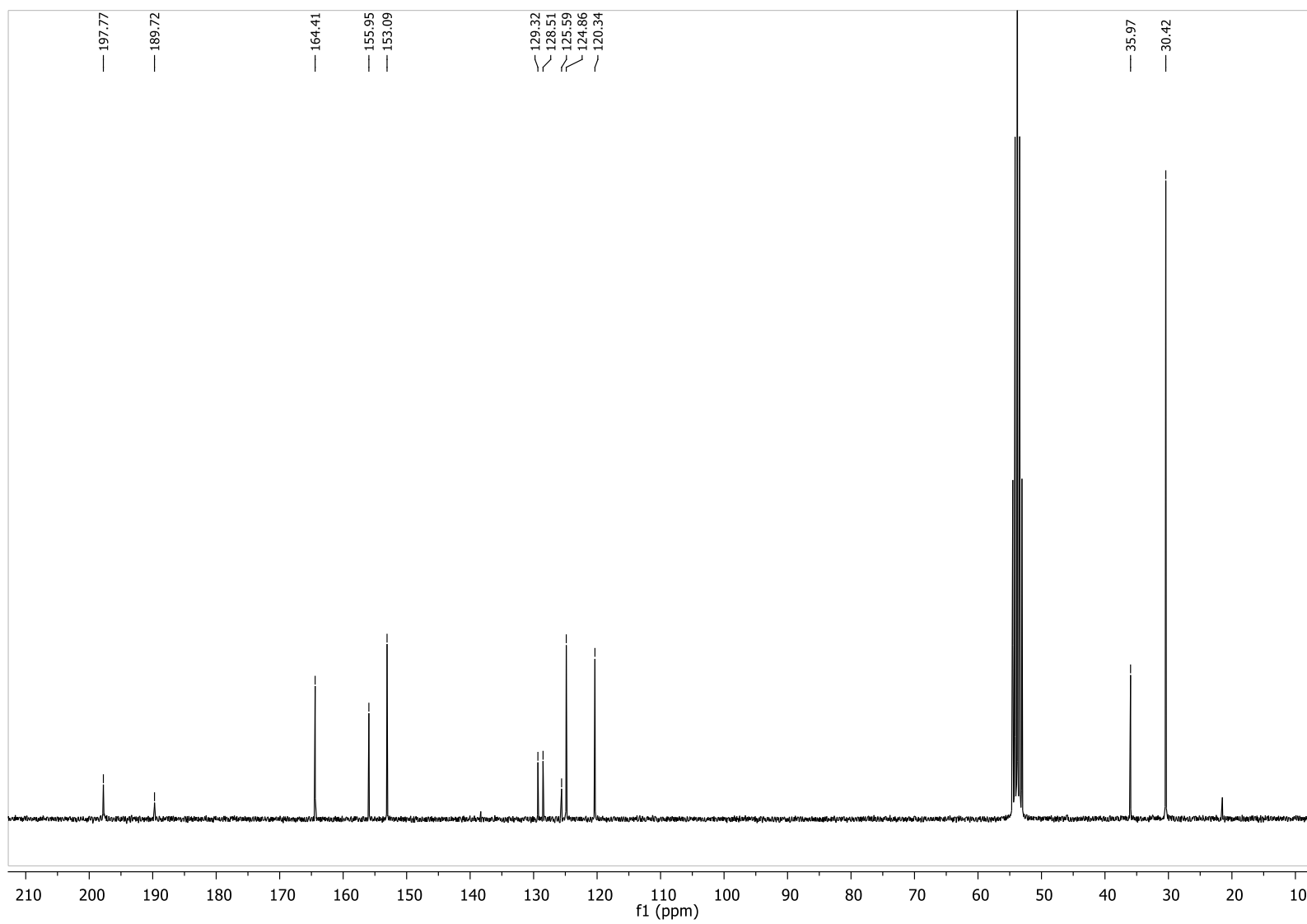
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[Re(Br)(CO)₃(4,4'-^tBu-2,2'-bipy)]

¹H-RMN (CD₂Cl₂)

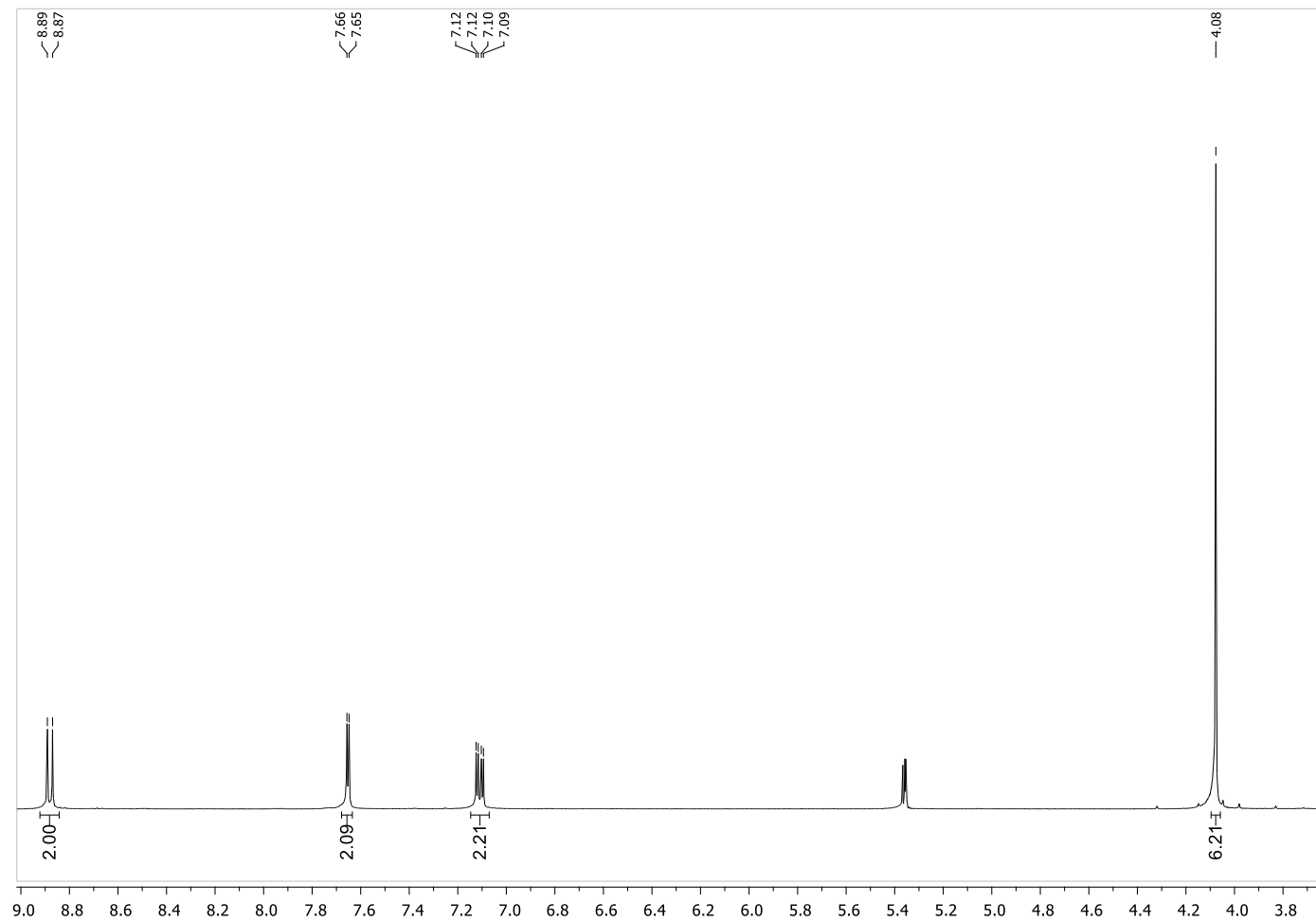
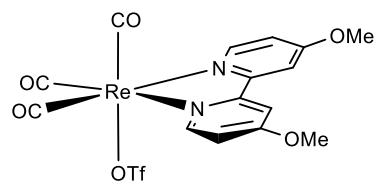


¹³C-RMN (CD₂Cl₂)

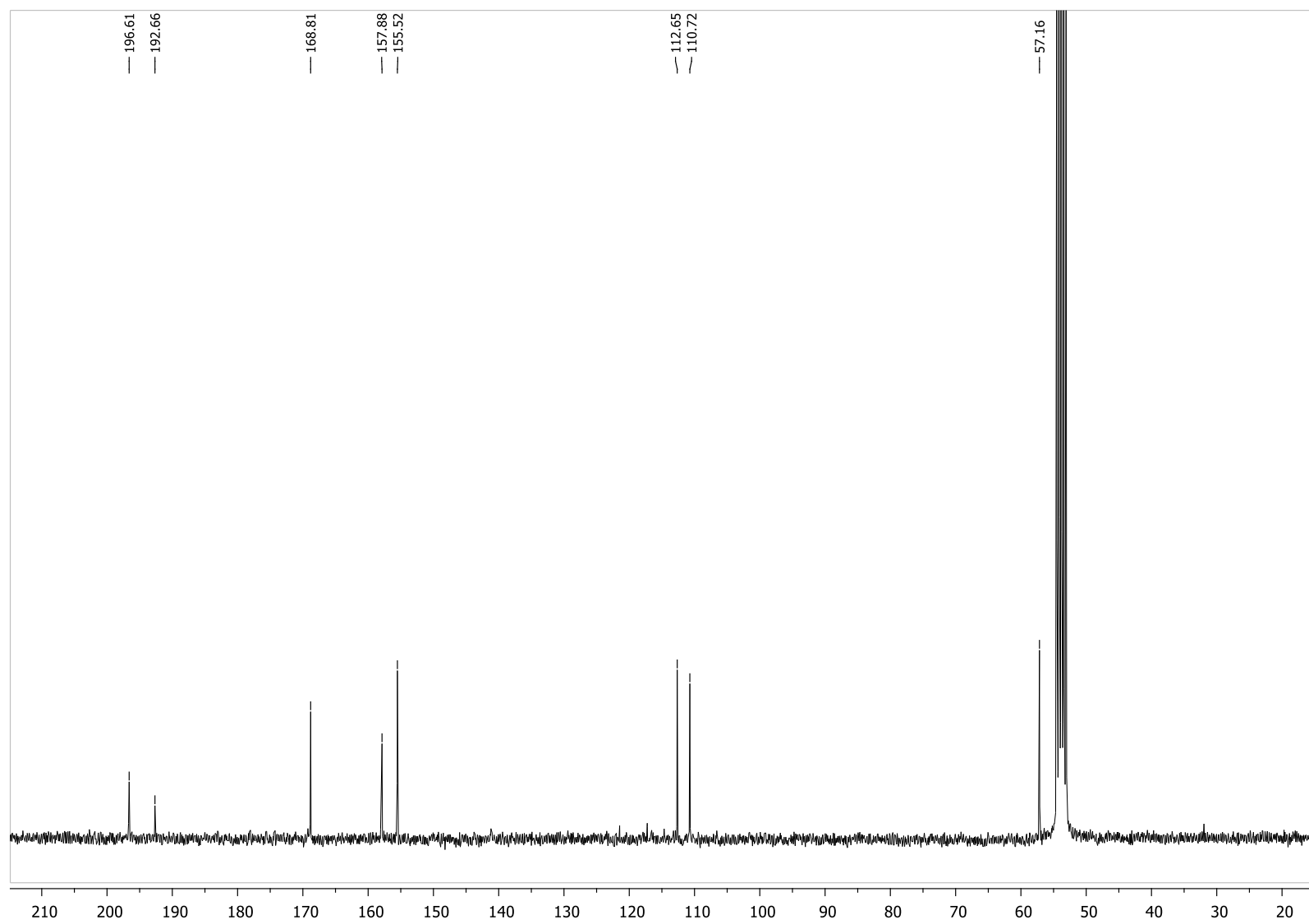


[Re(OTf)(CO)₃((4,4'-OMe-2,2'-bipy))]

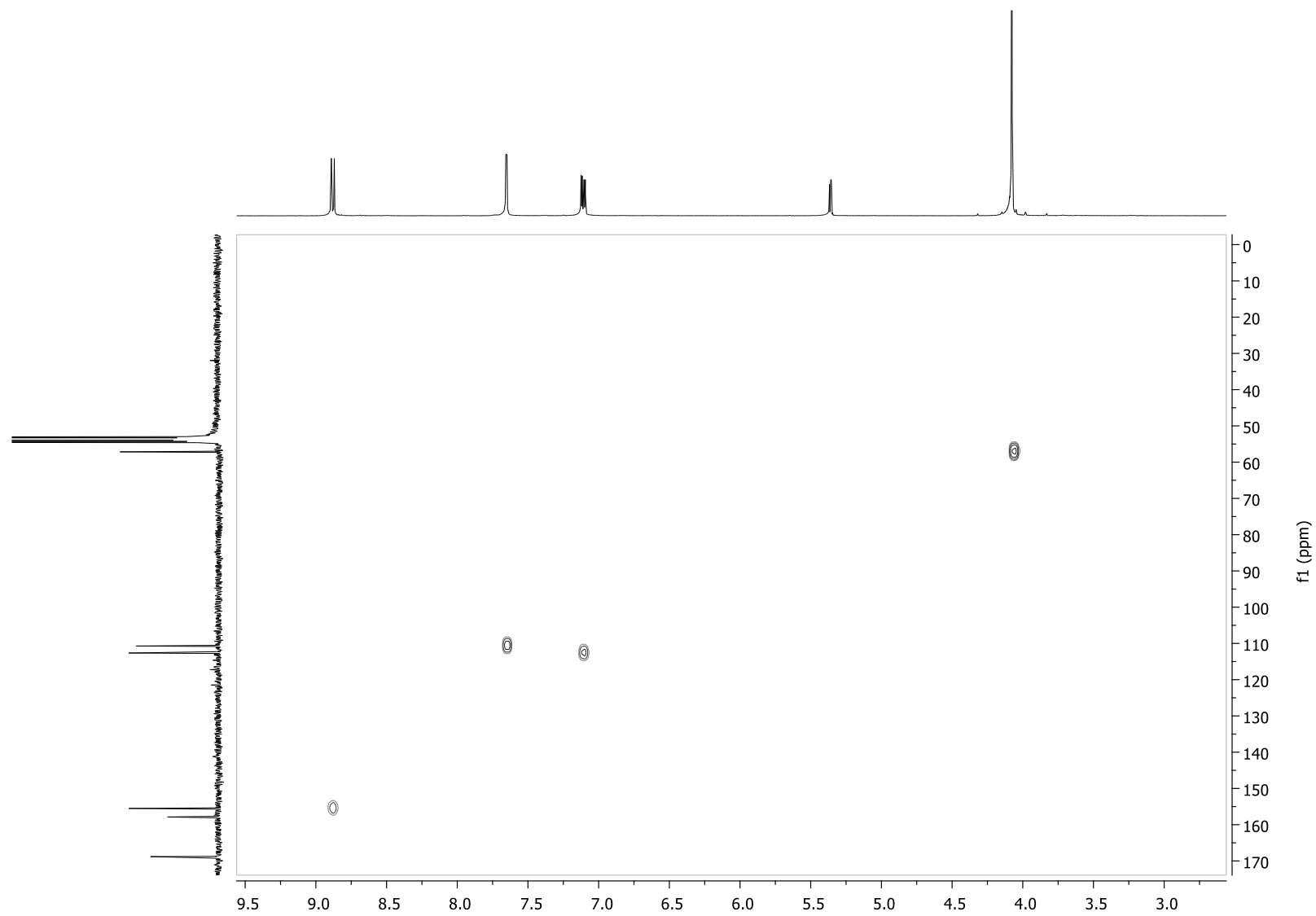
¹H-RMN (CD₂Cl₂)



^{13}C -RMN (CD_2Cl_2)

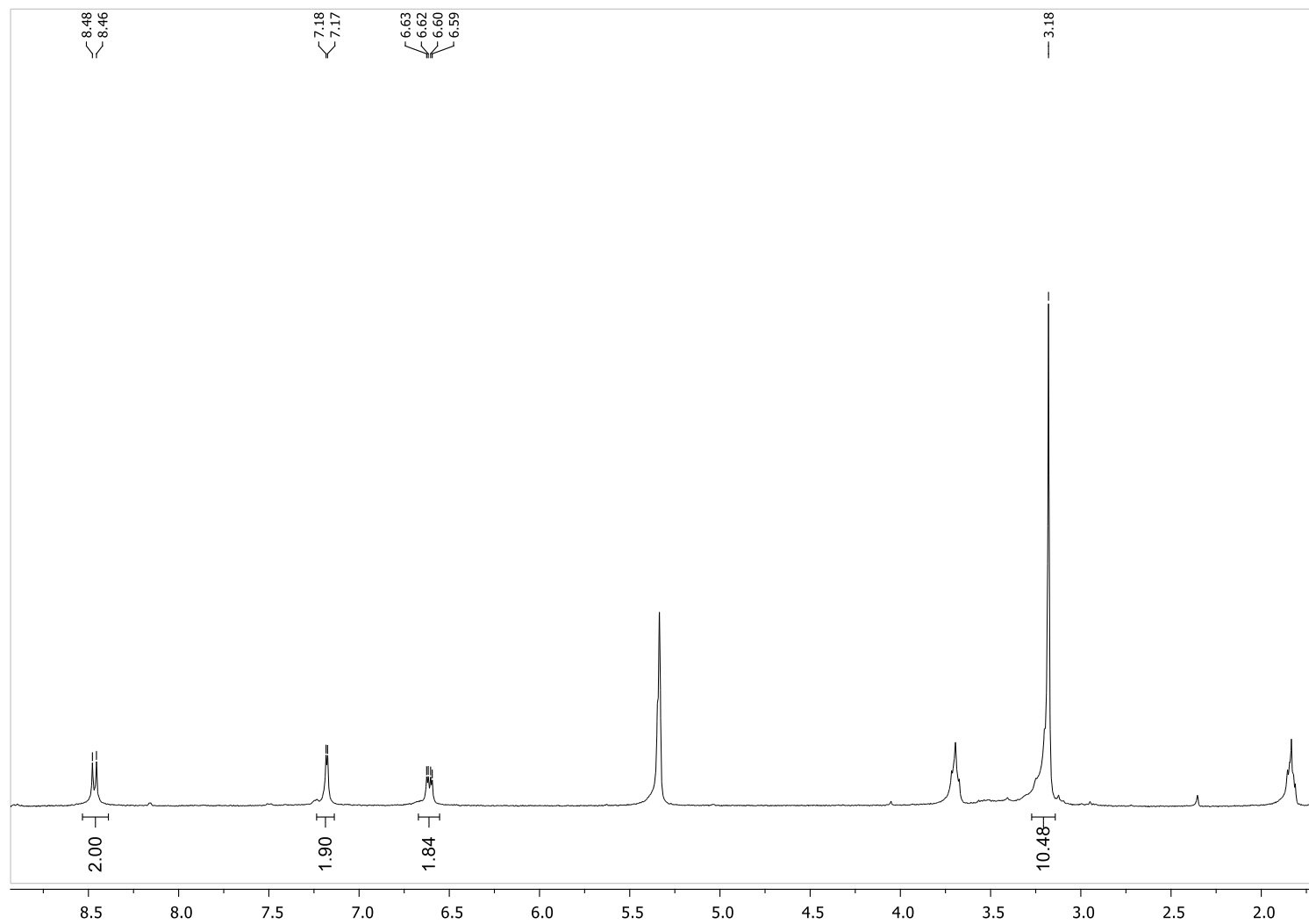
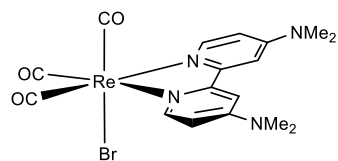


HSQC (CD₂Cl₂)

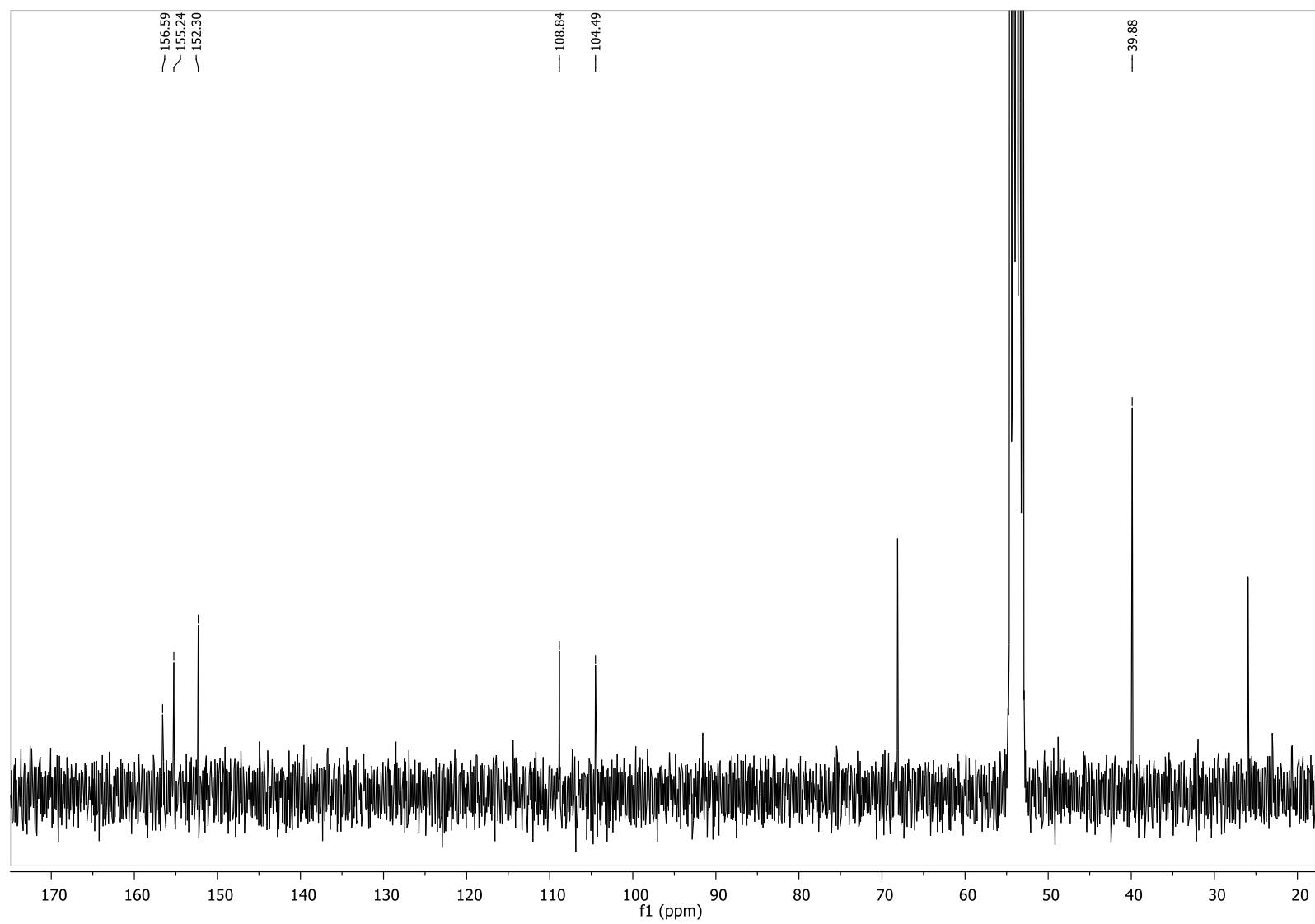


[Re(Br)(CO)₃((4,4'-NMe₂-2,2'-bipy))]

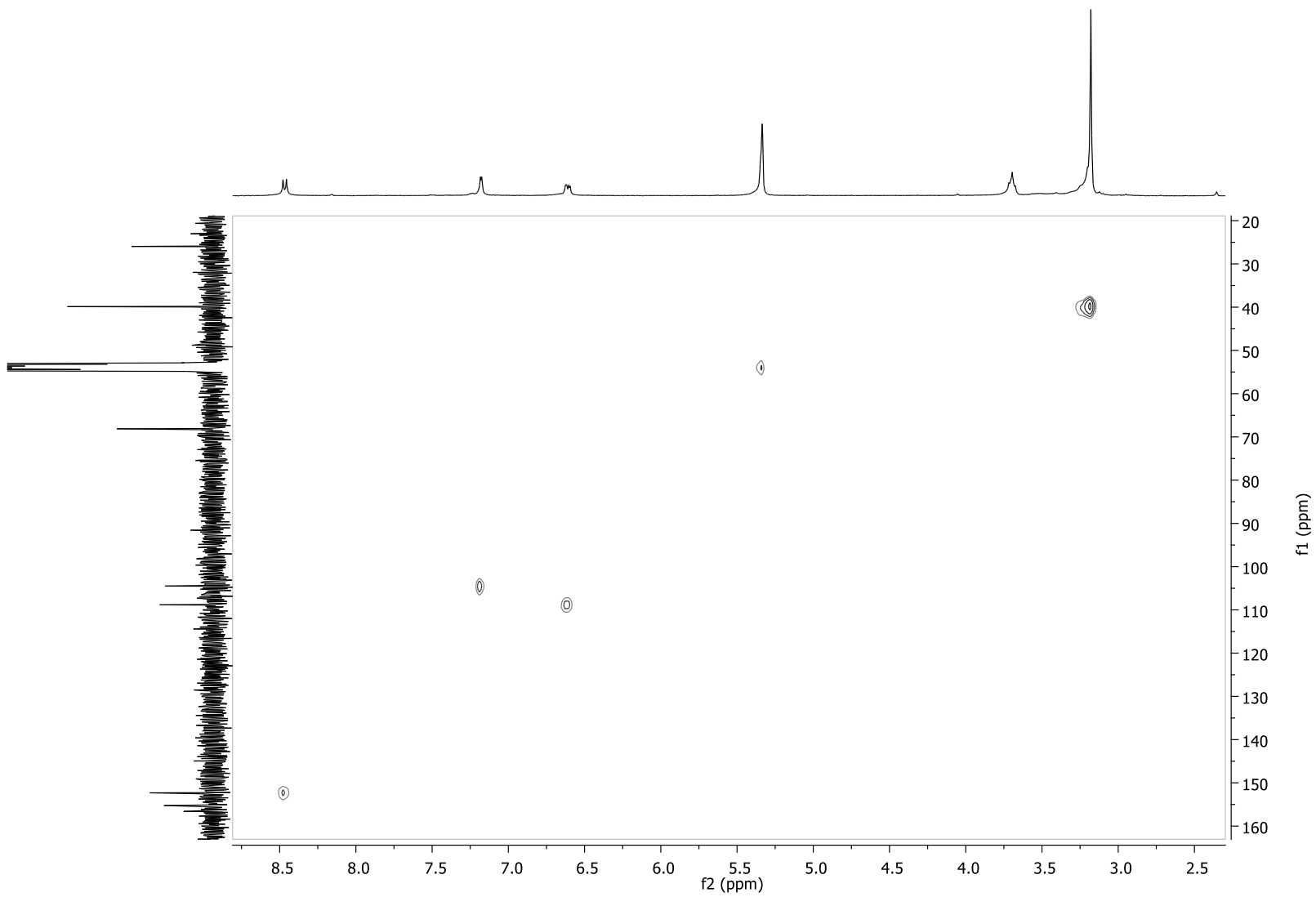
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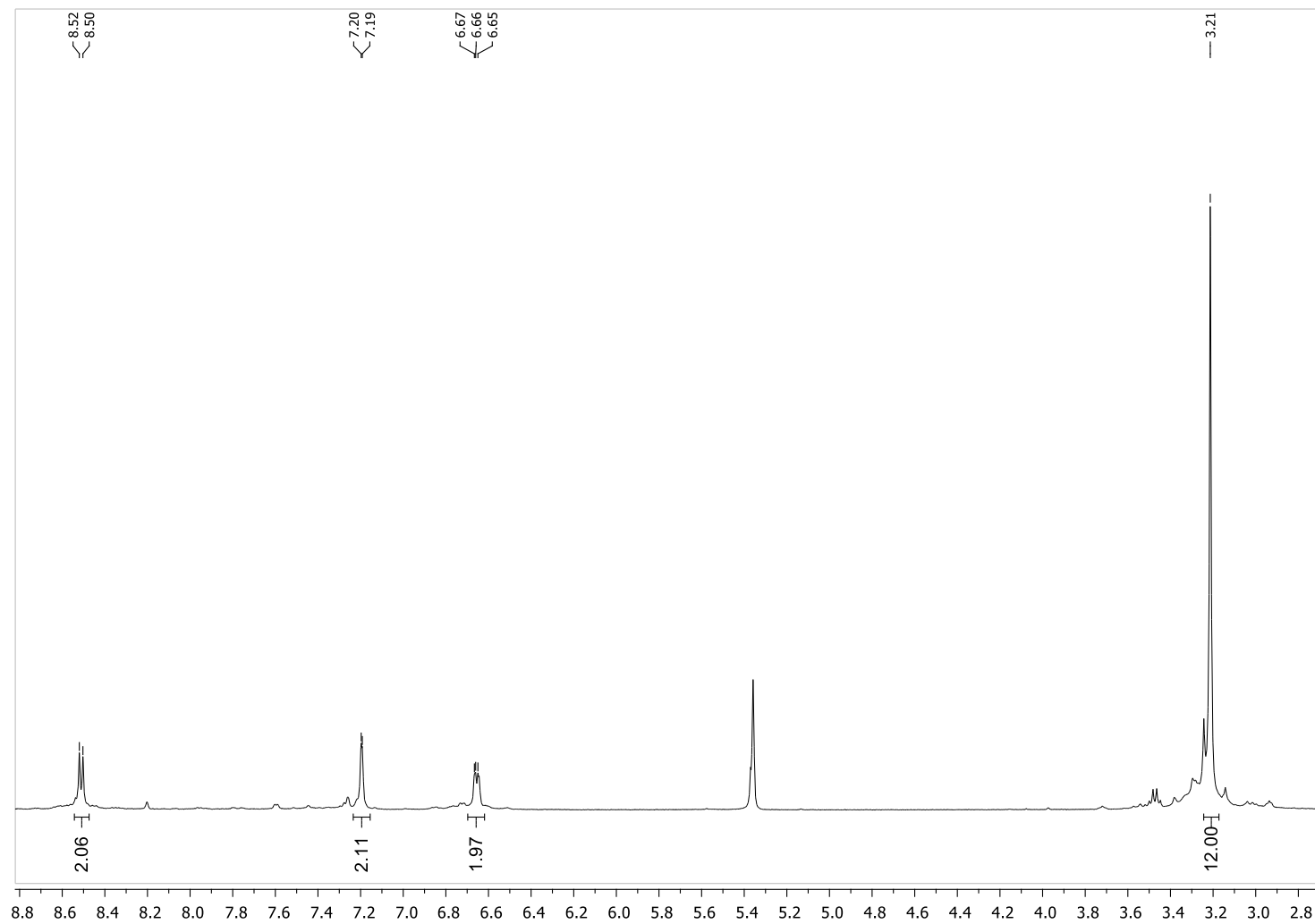
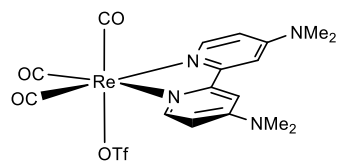


HSQC (CD₂Cl₂)

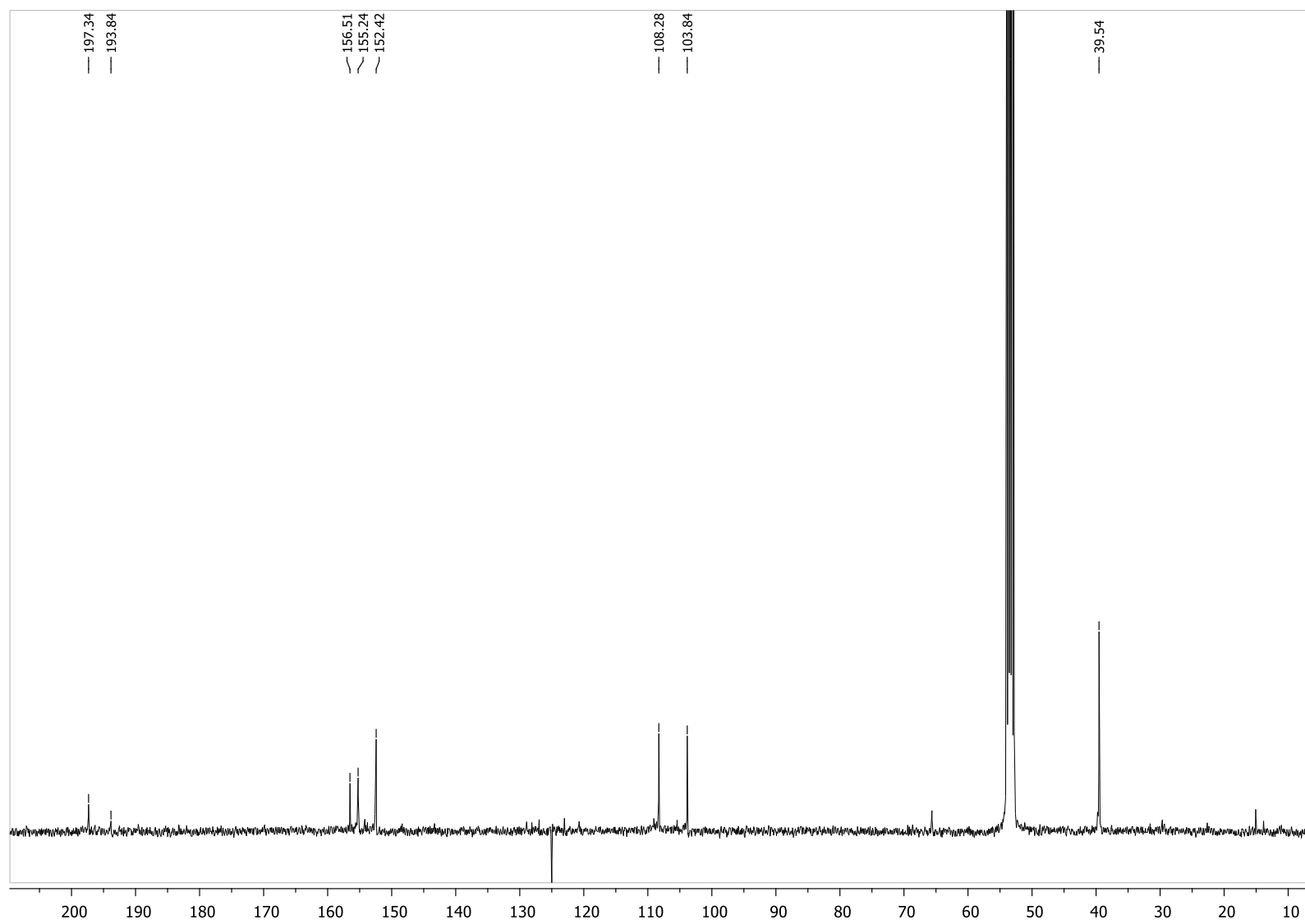


[Re(OTf)(CO)₃((4,4'-NMe₂-2,2'-bipy)]

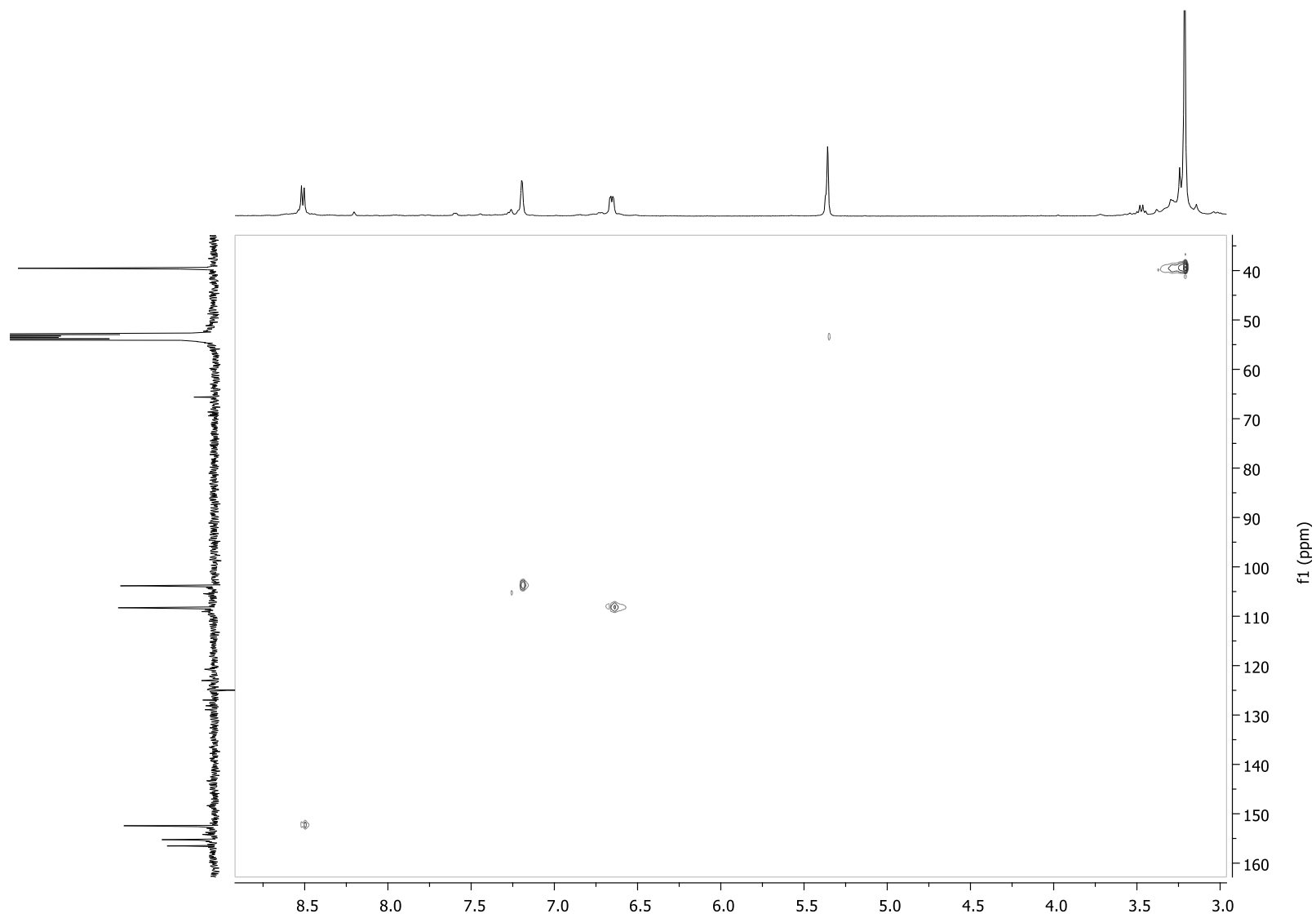
¹H-RMN (CD₂Cl₂)



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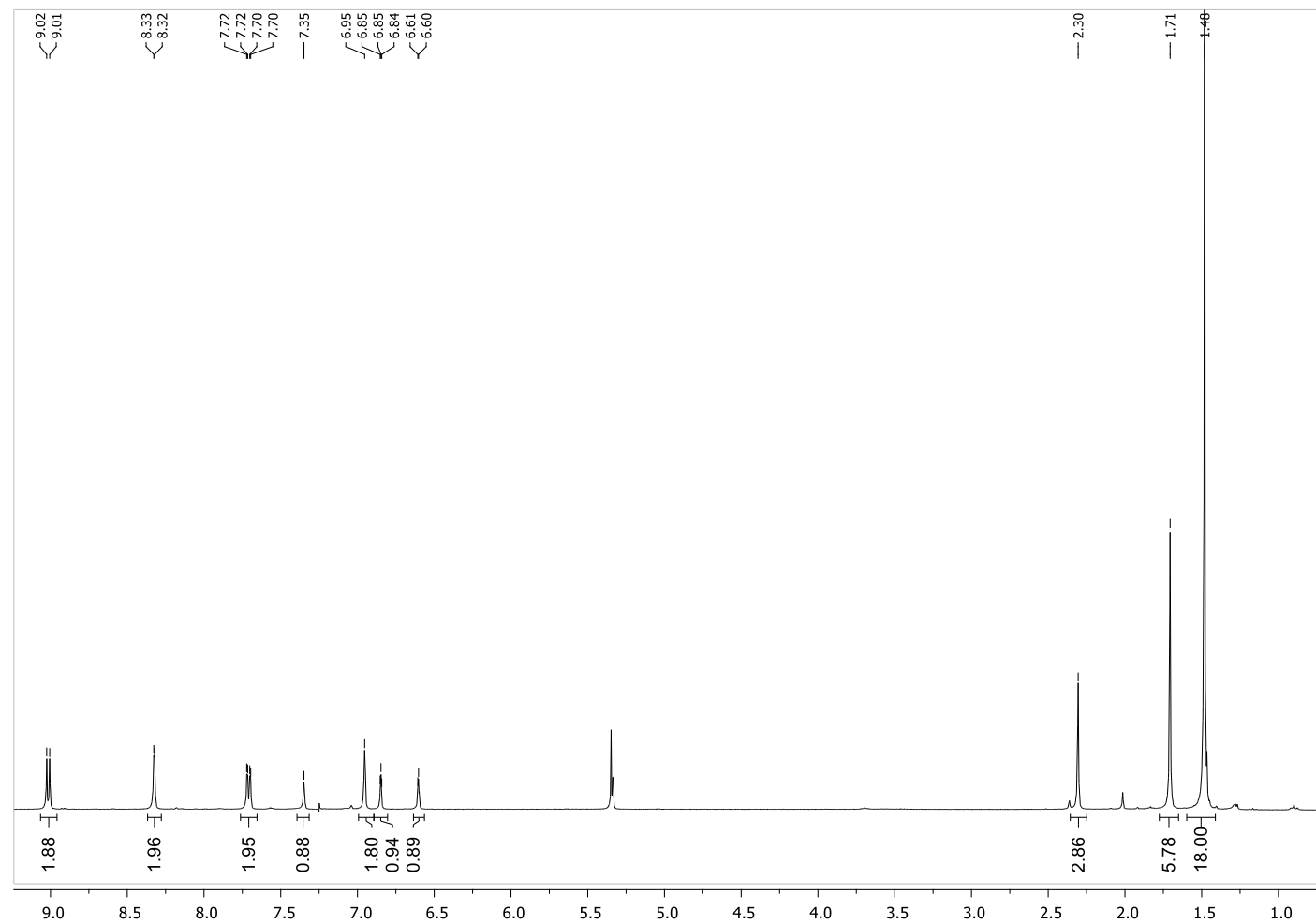
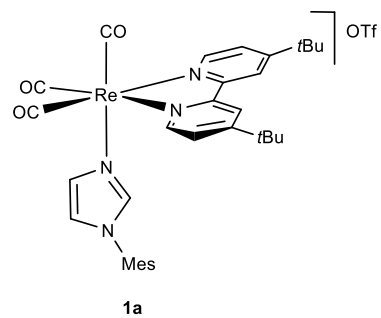


HSQC (CD₂Cl₂)

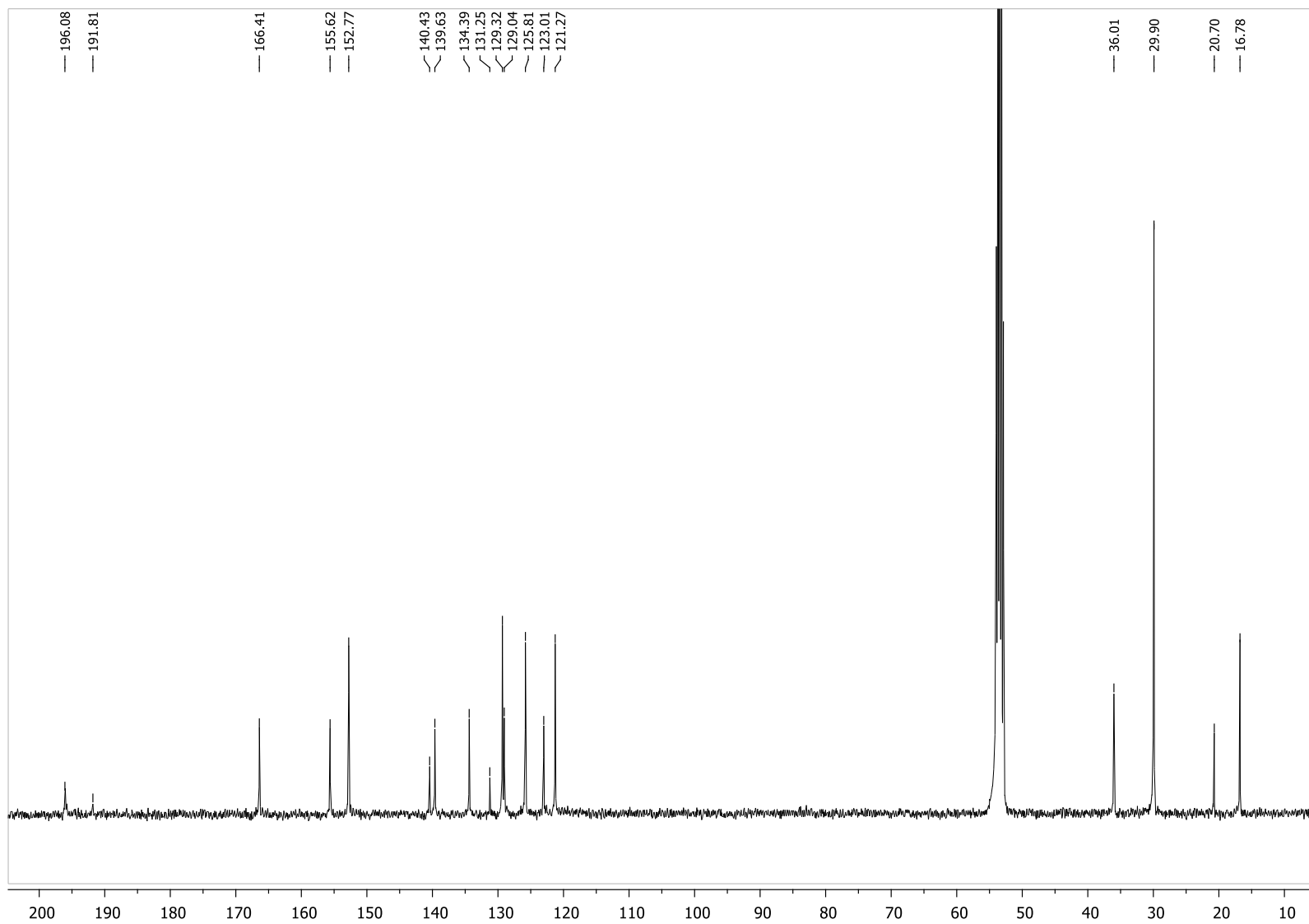


COMPOUND 1a

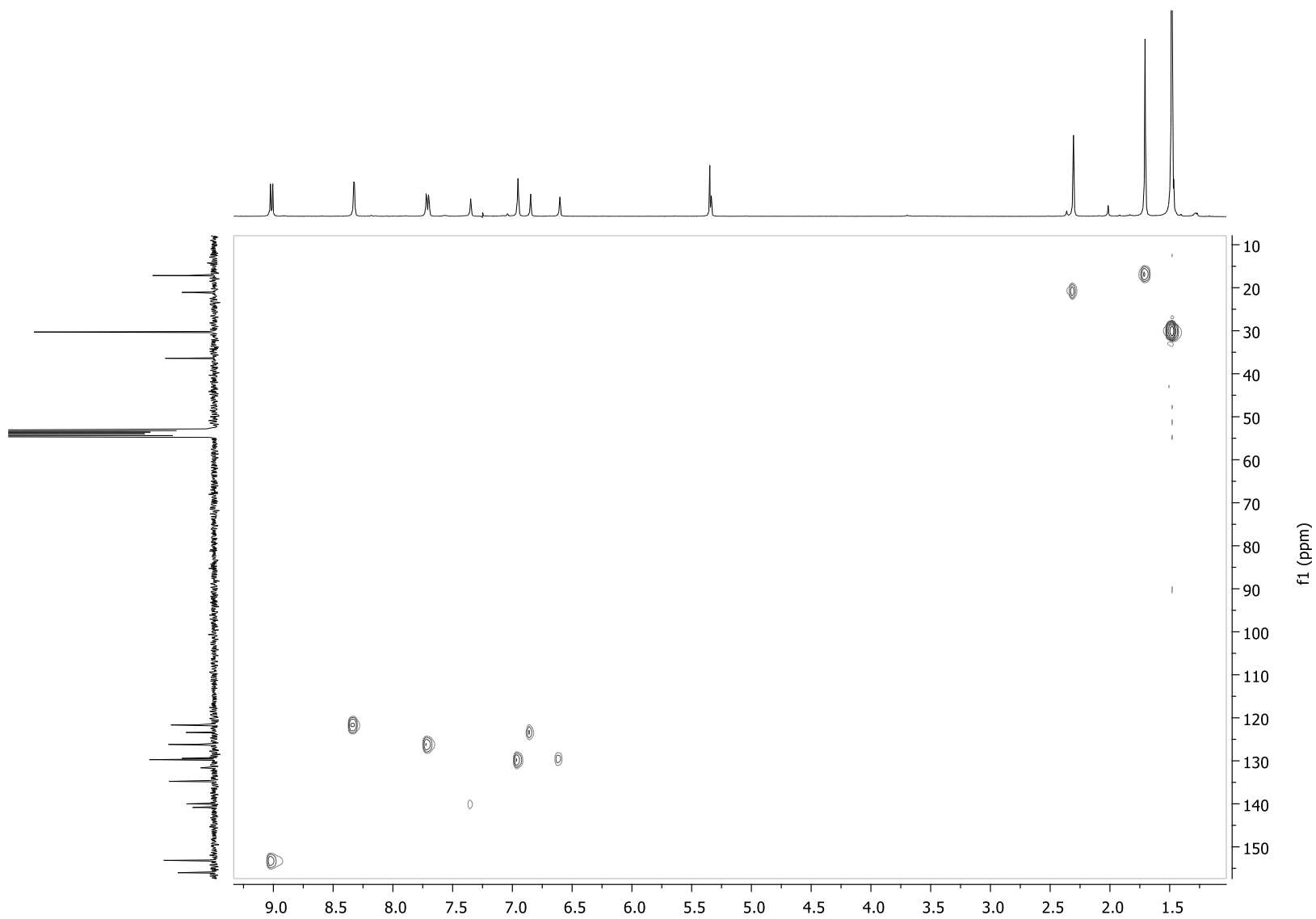
$^1\text{H-RMN}$ (CD_2Cl_2)



^{13}C -RMN
(CD_2Cl_2)

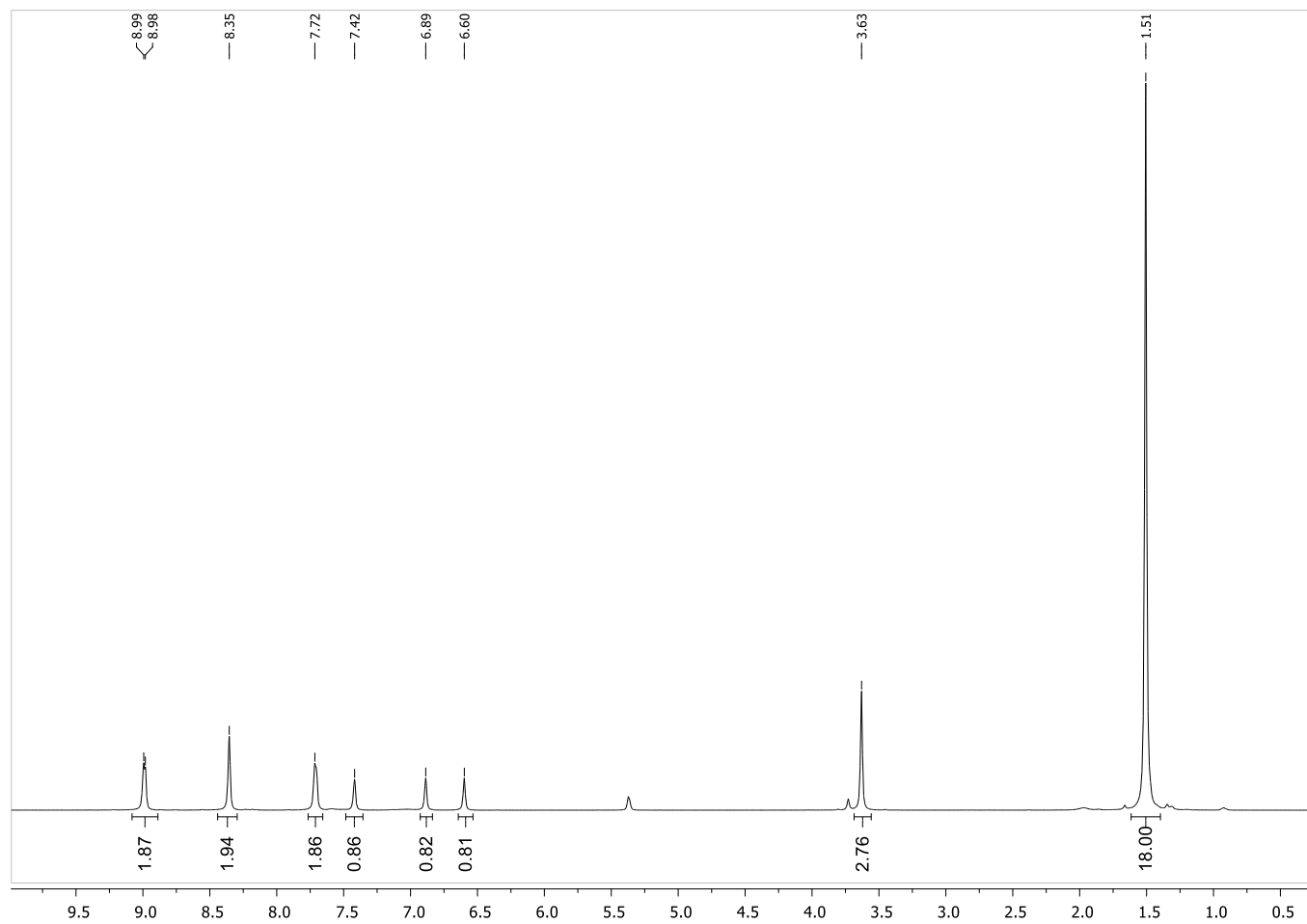
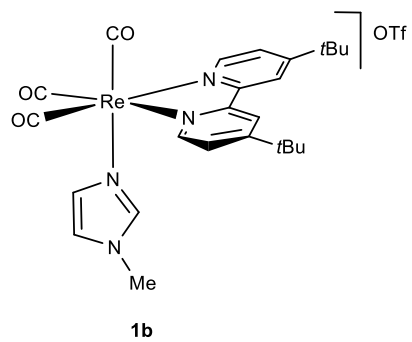


HSQC (CD₂Cl₂)

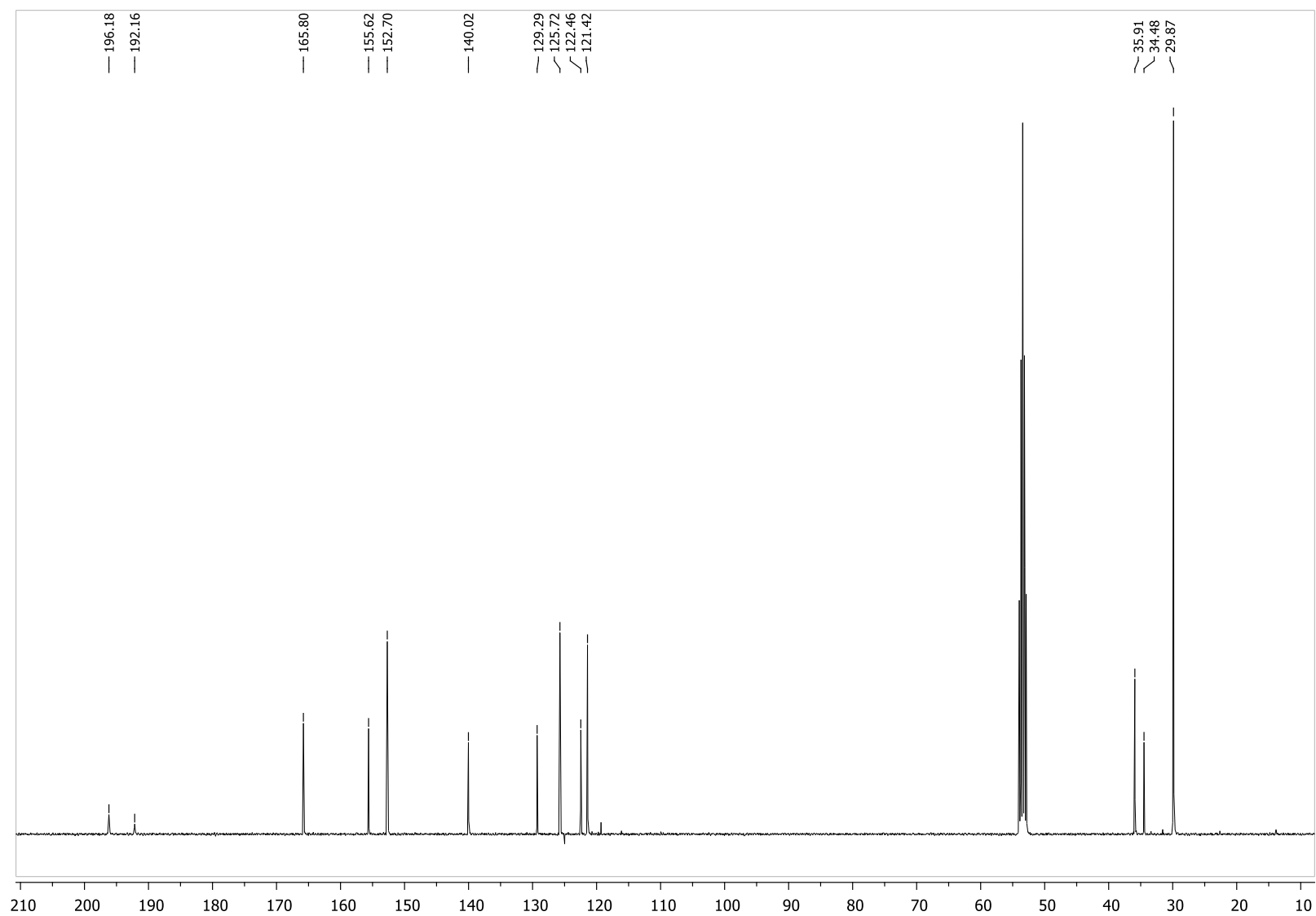


COMPOUND **1b**

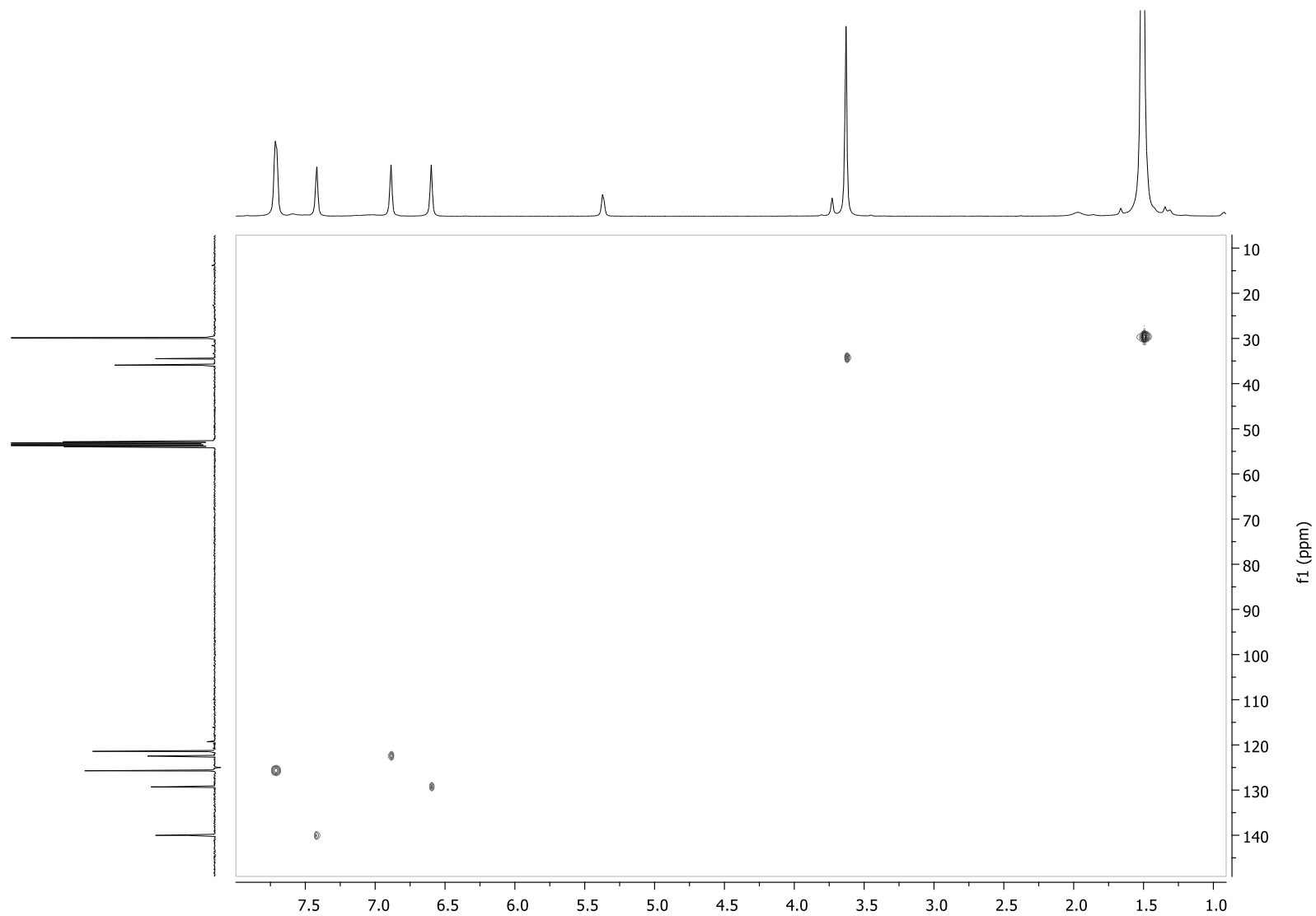
$^1\text{H-RMN}$ (CD_2Cl_2)



^{13}C -RMN (CD_2Cl_2)

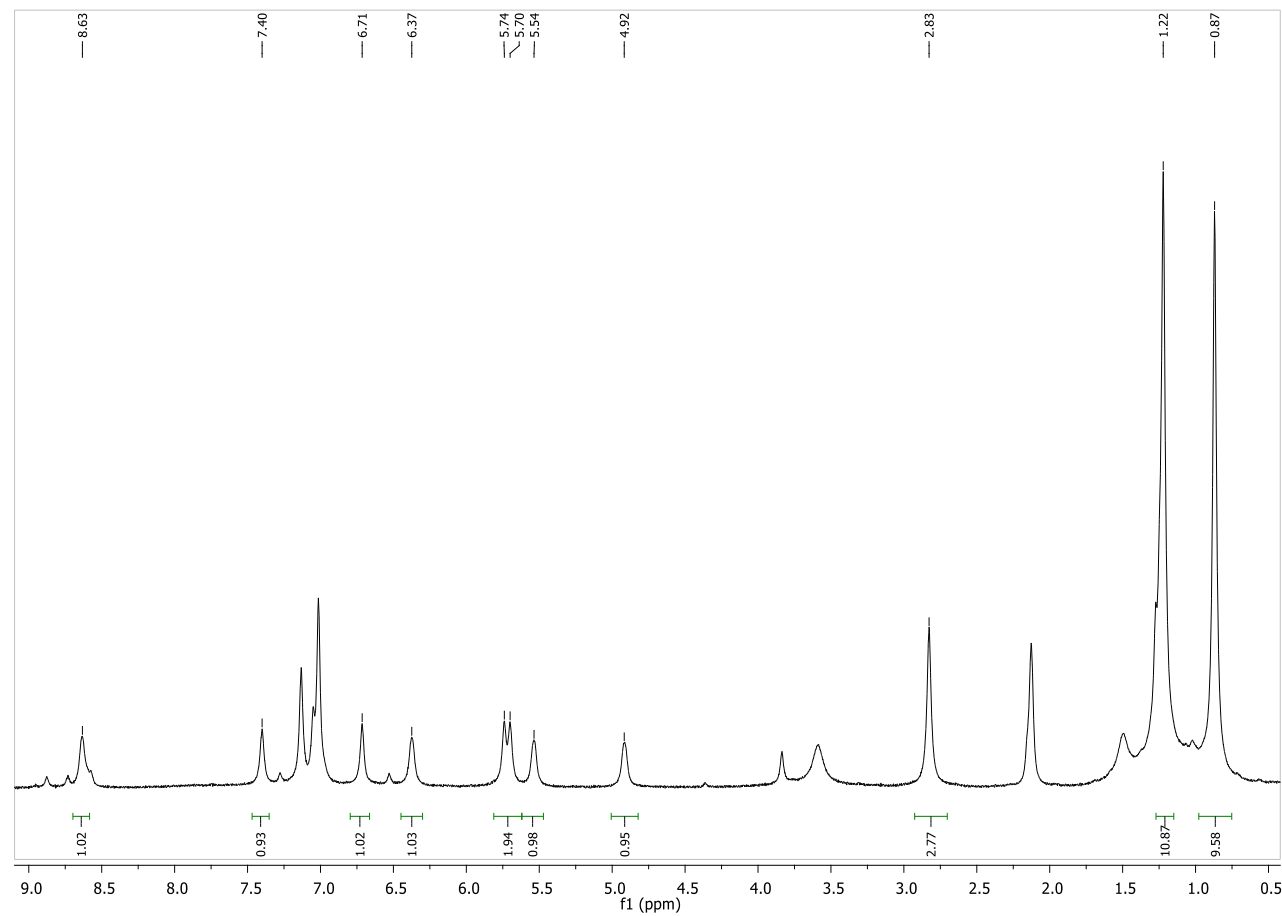
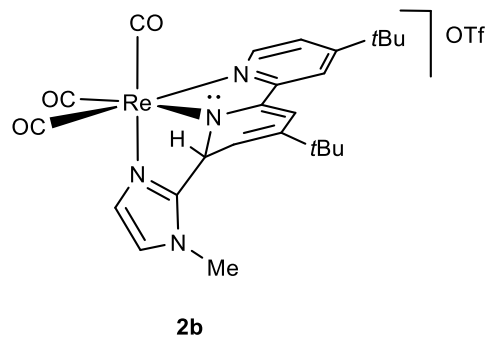


HSQC (CD₂Cl₂)

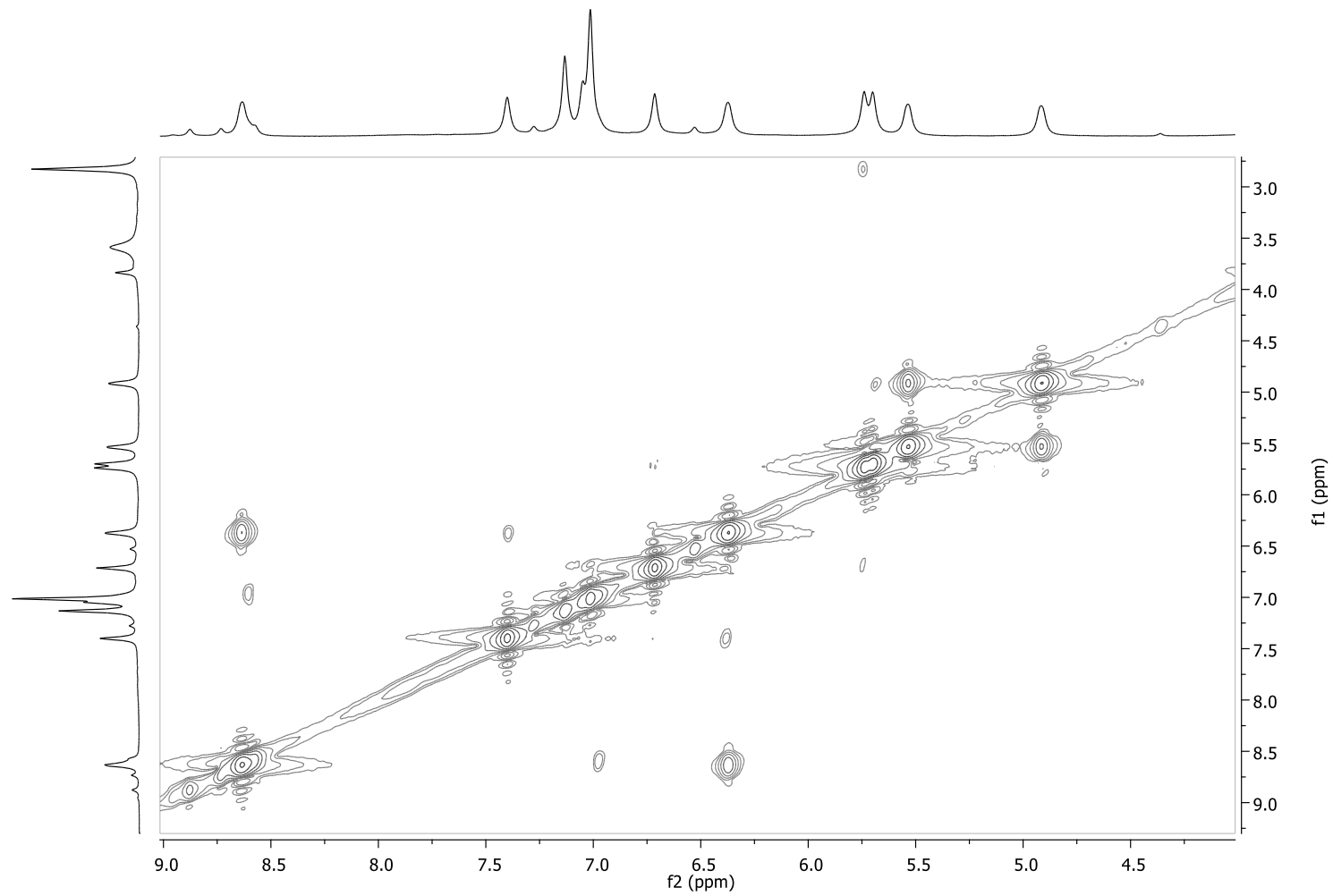


COMPOUND 2b

¹H-RMN (toluene-d8)

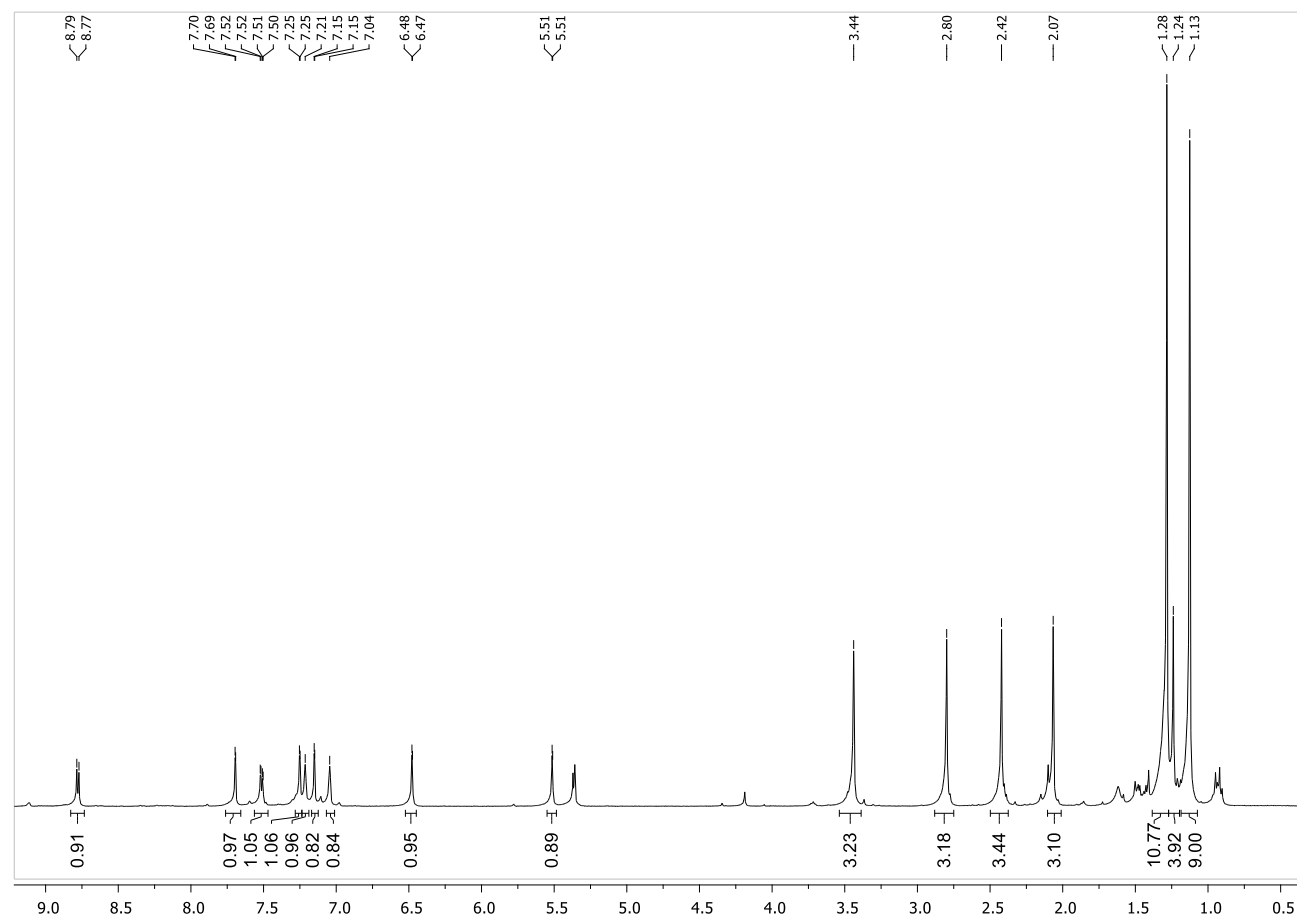
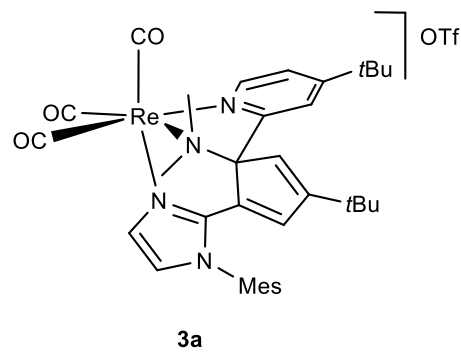


COSY (CD₂Cl₂)

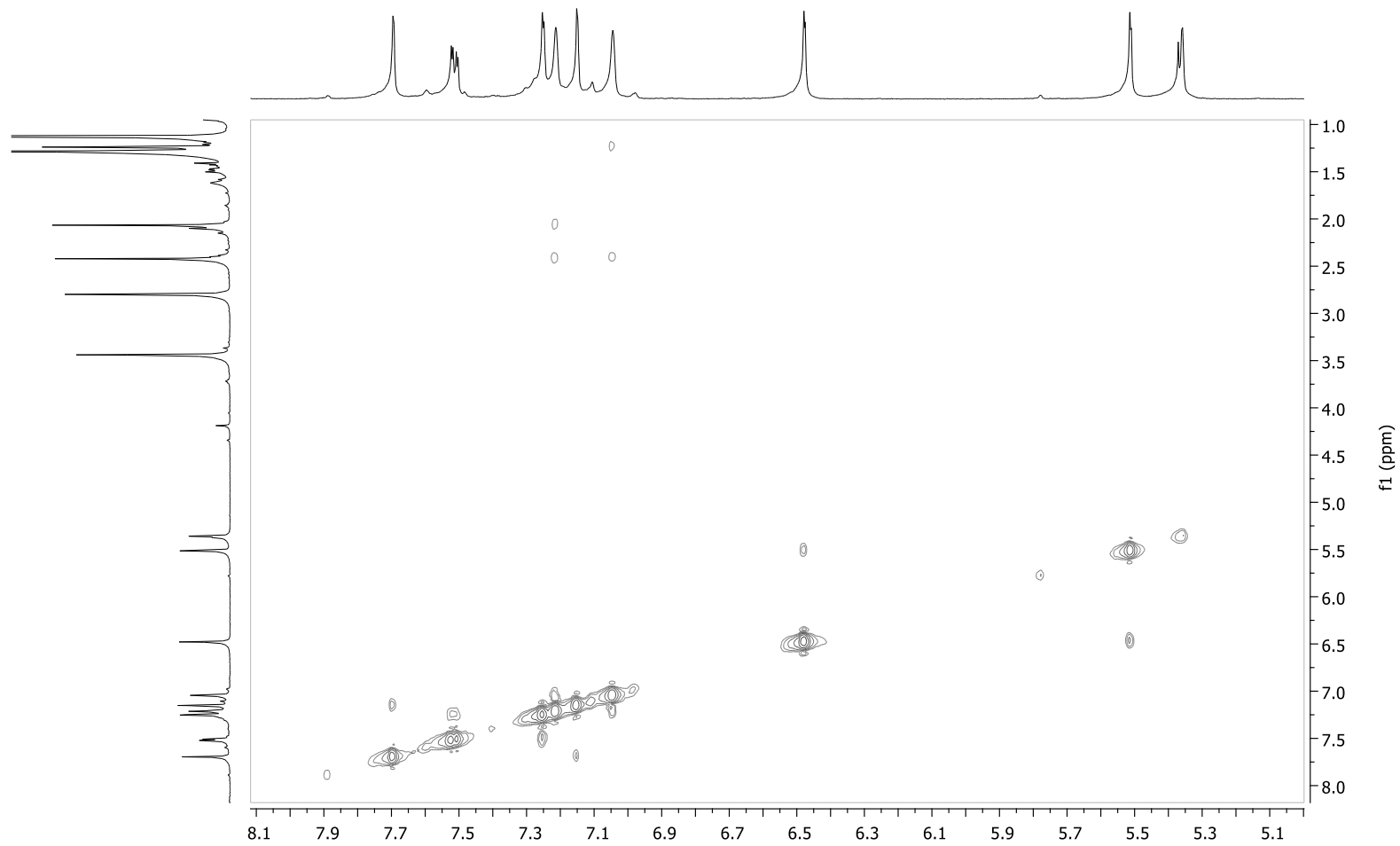


COMPOUND 3a

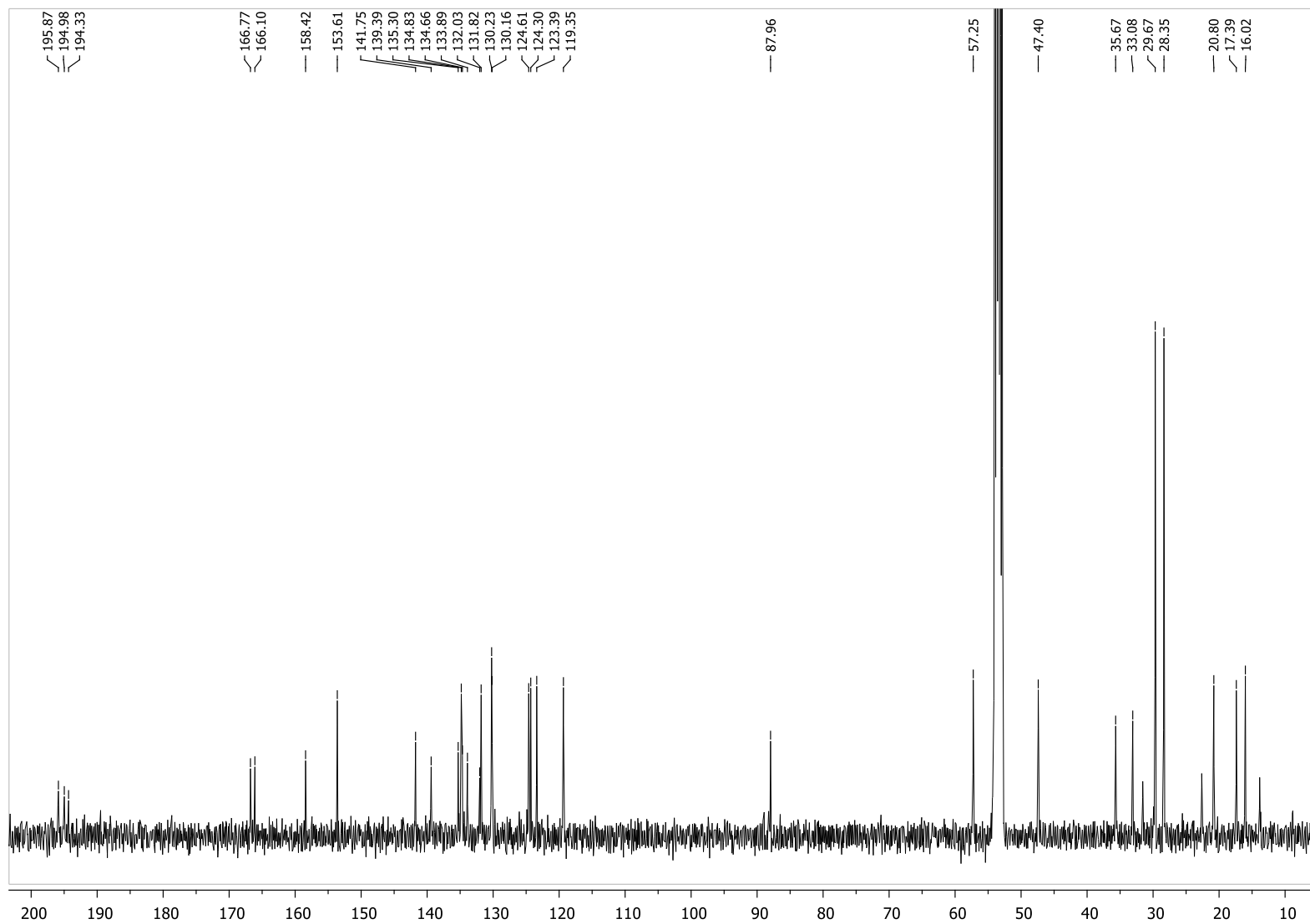
¹H-RMN (CD₂Cl₂)



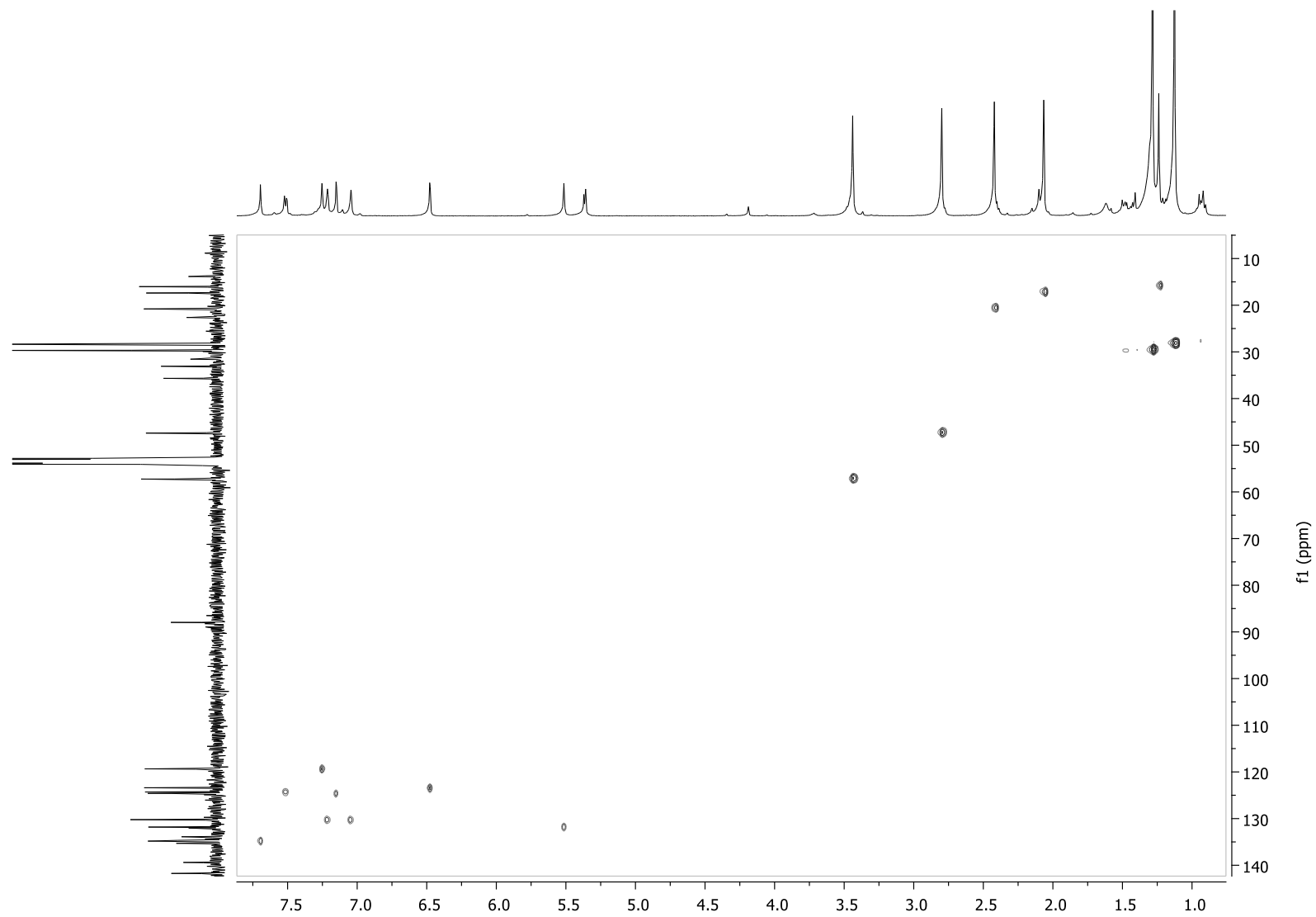
COSY (CD₂Cl₂)



^{13}C -RMN (CD_2Cl_2)

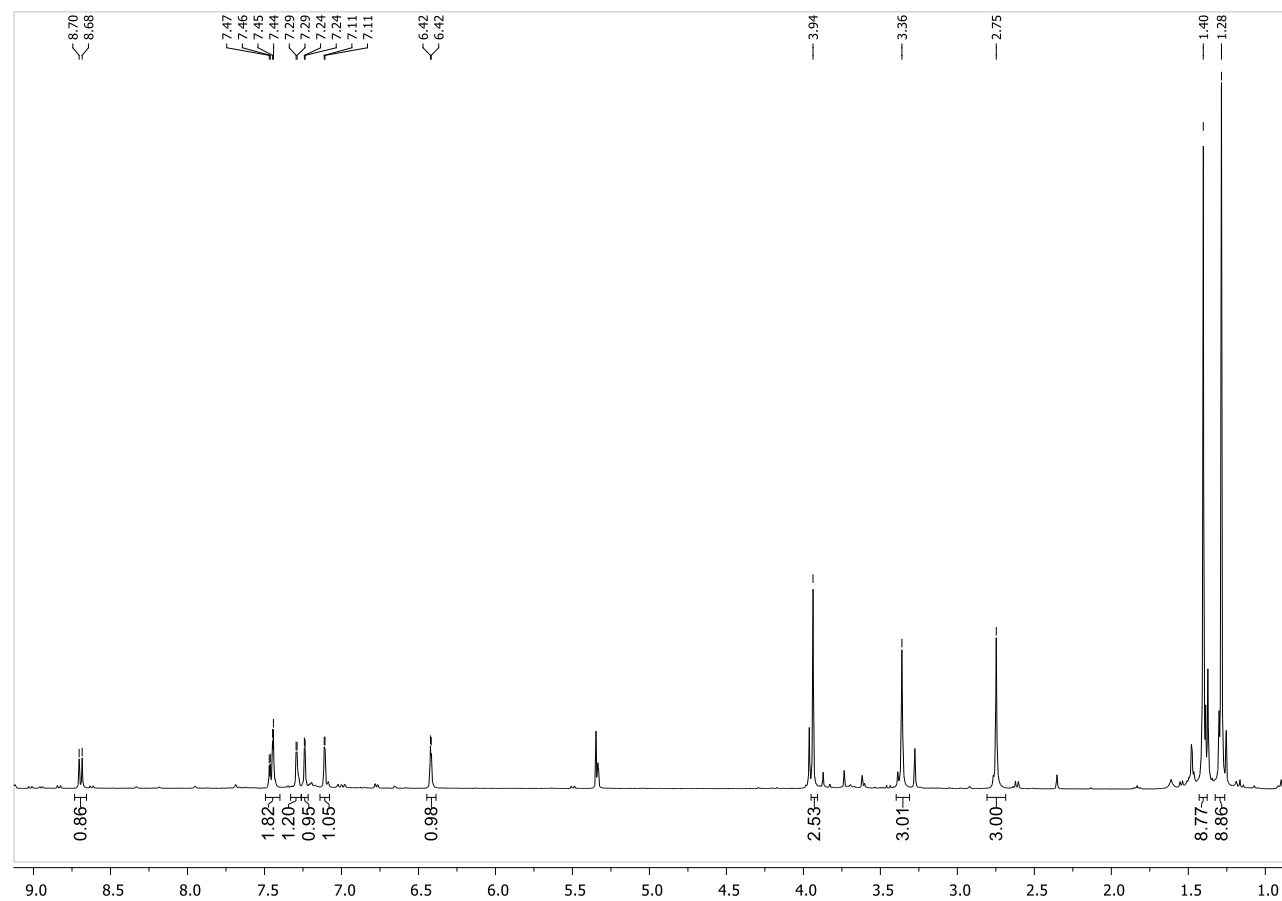
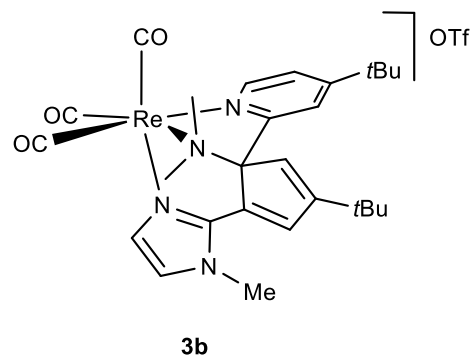


HSQC (CD₂Cl₂)

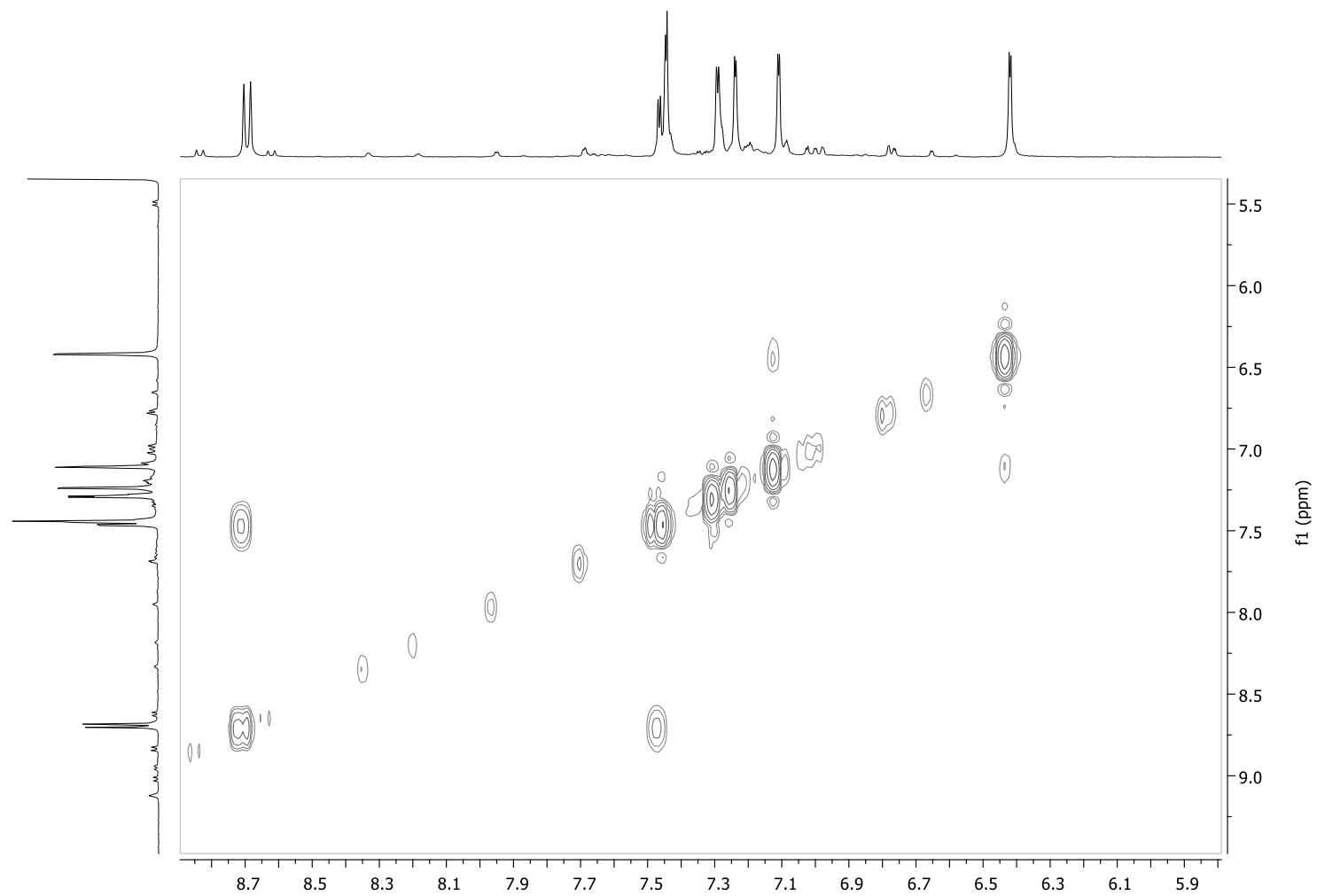


COMPOUND 3b

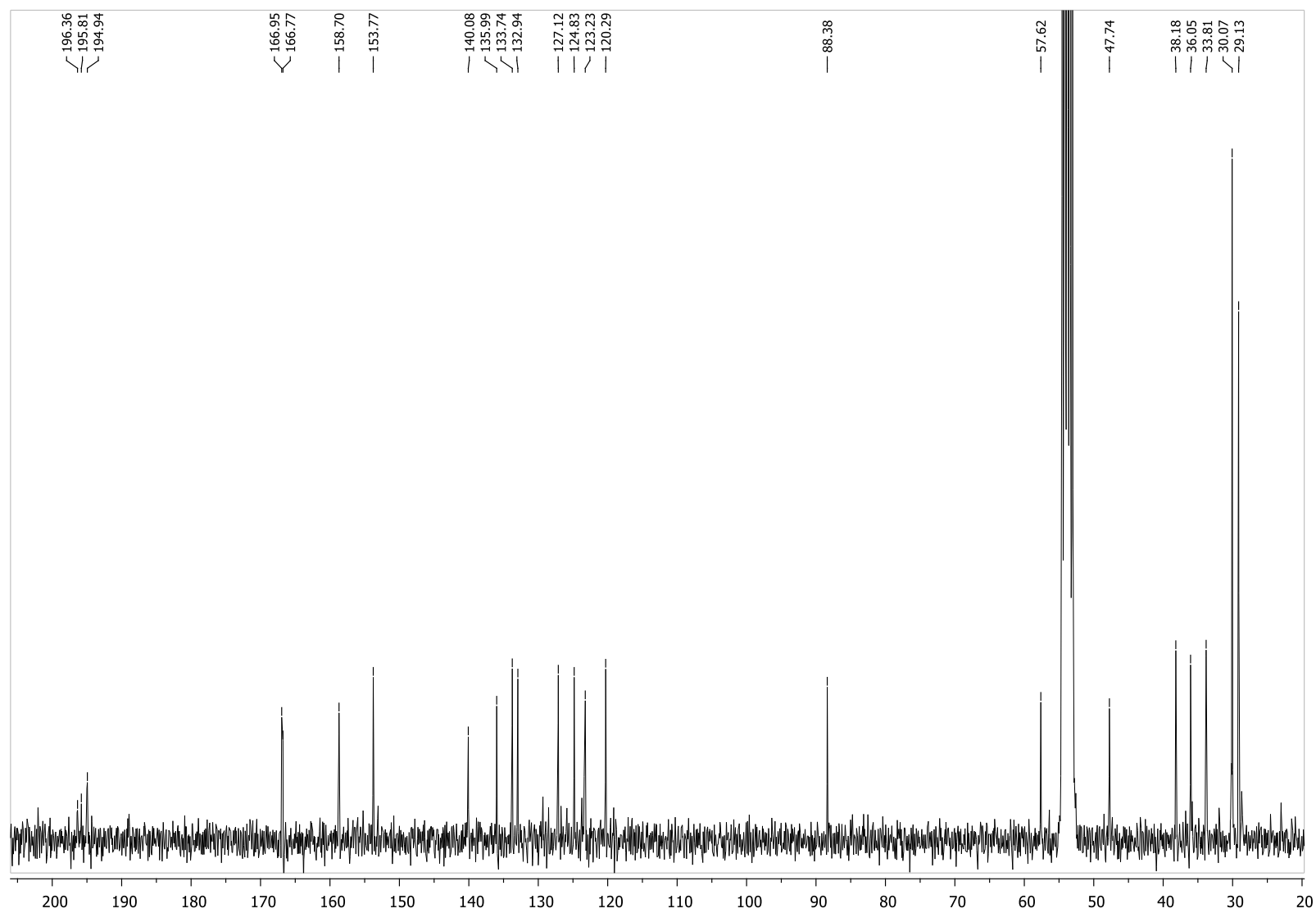
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COSY (CD₂Cl₂)

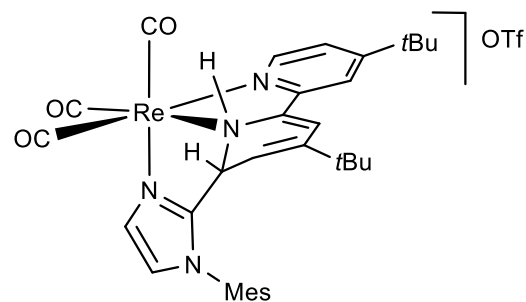


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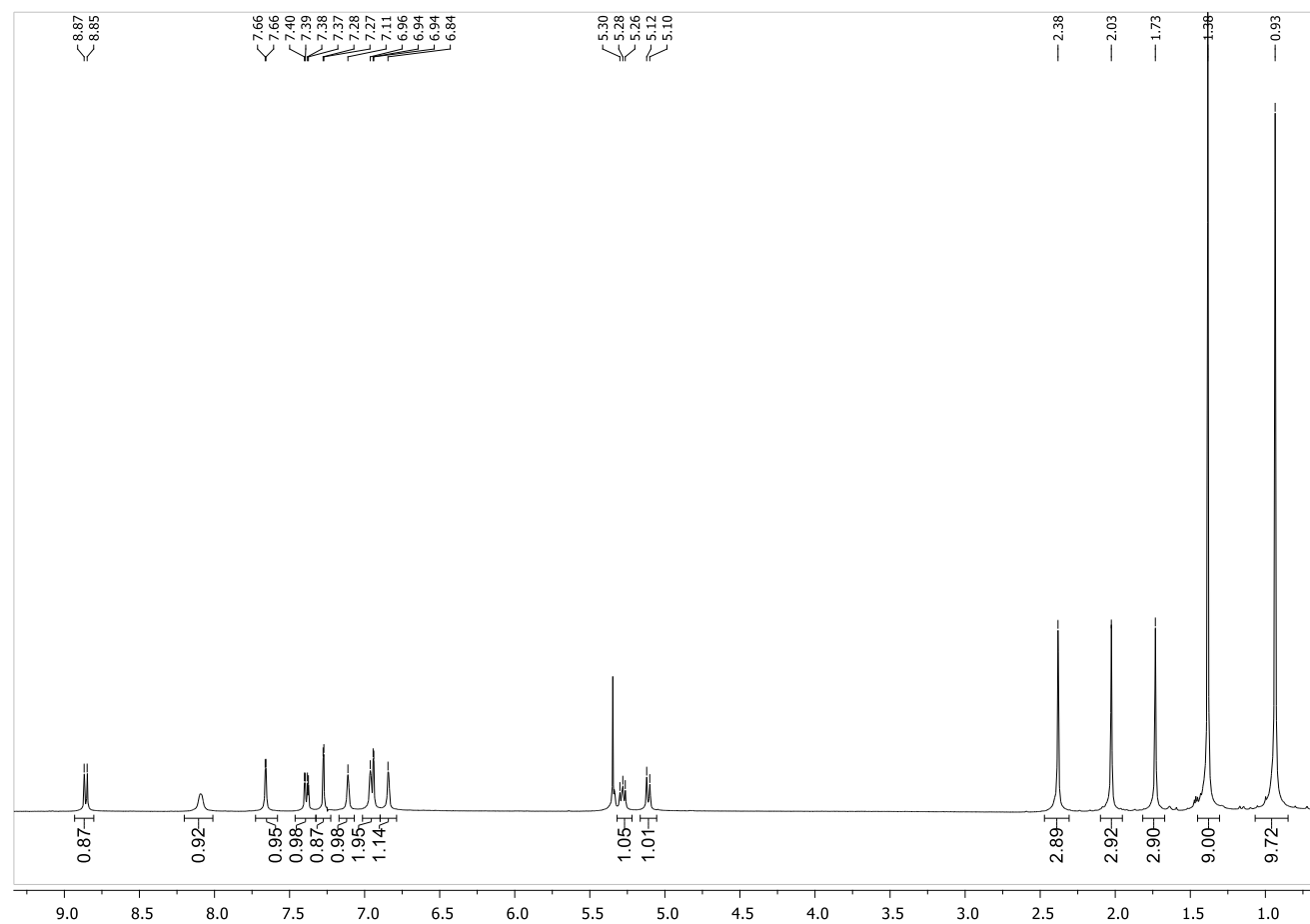


COMPOUND 4a

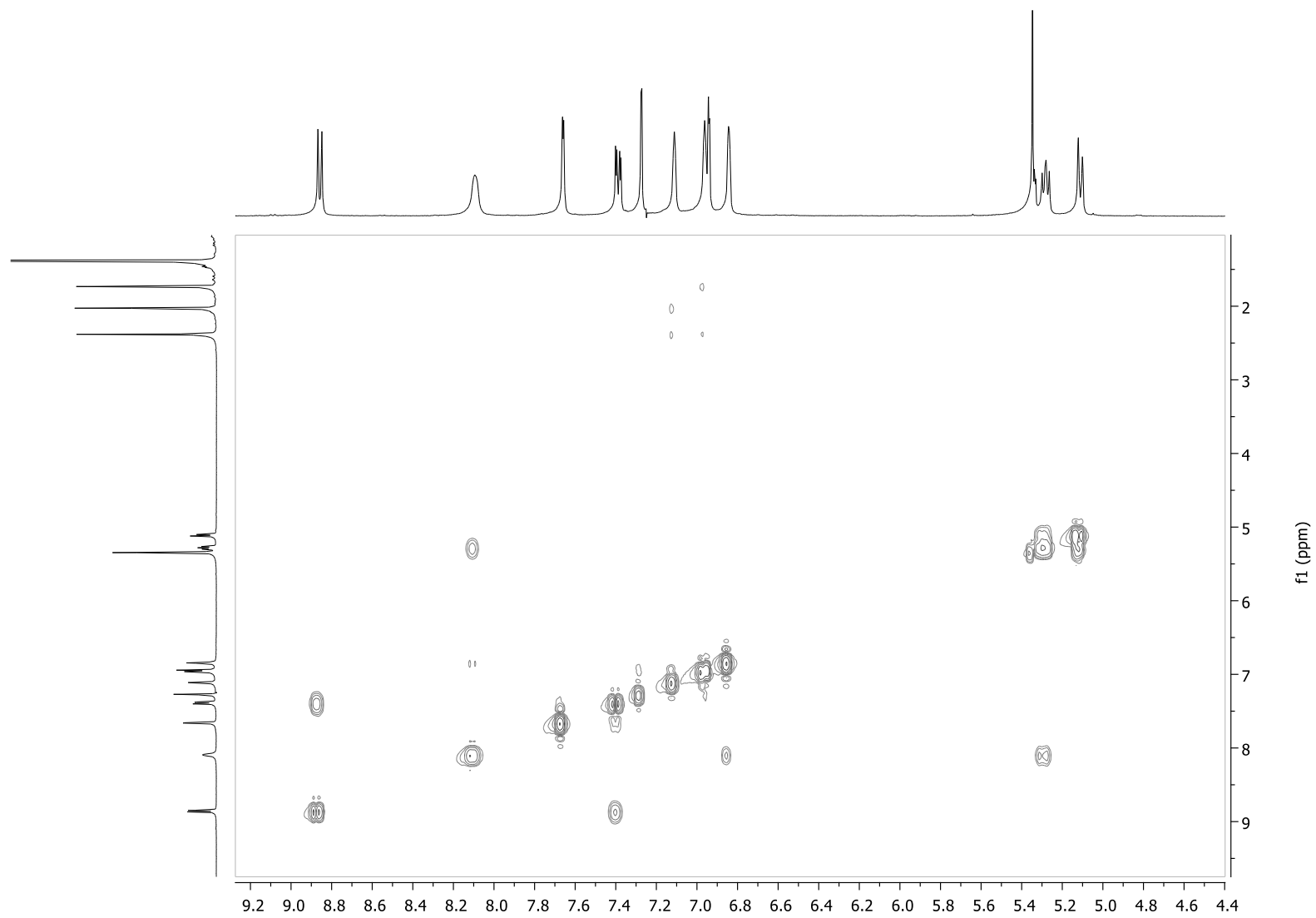
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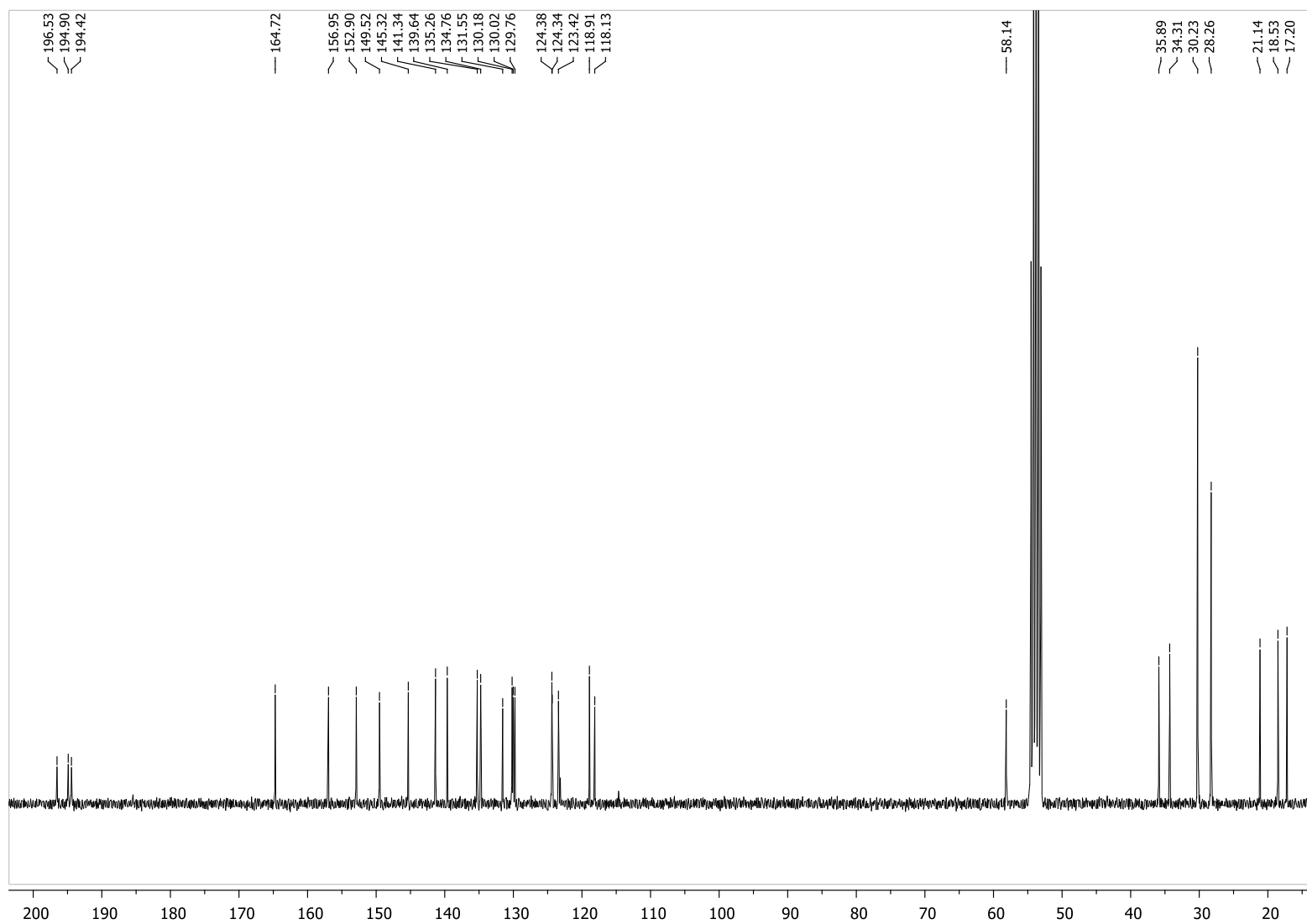
4a



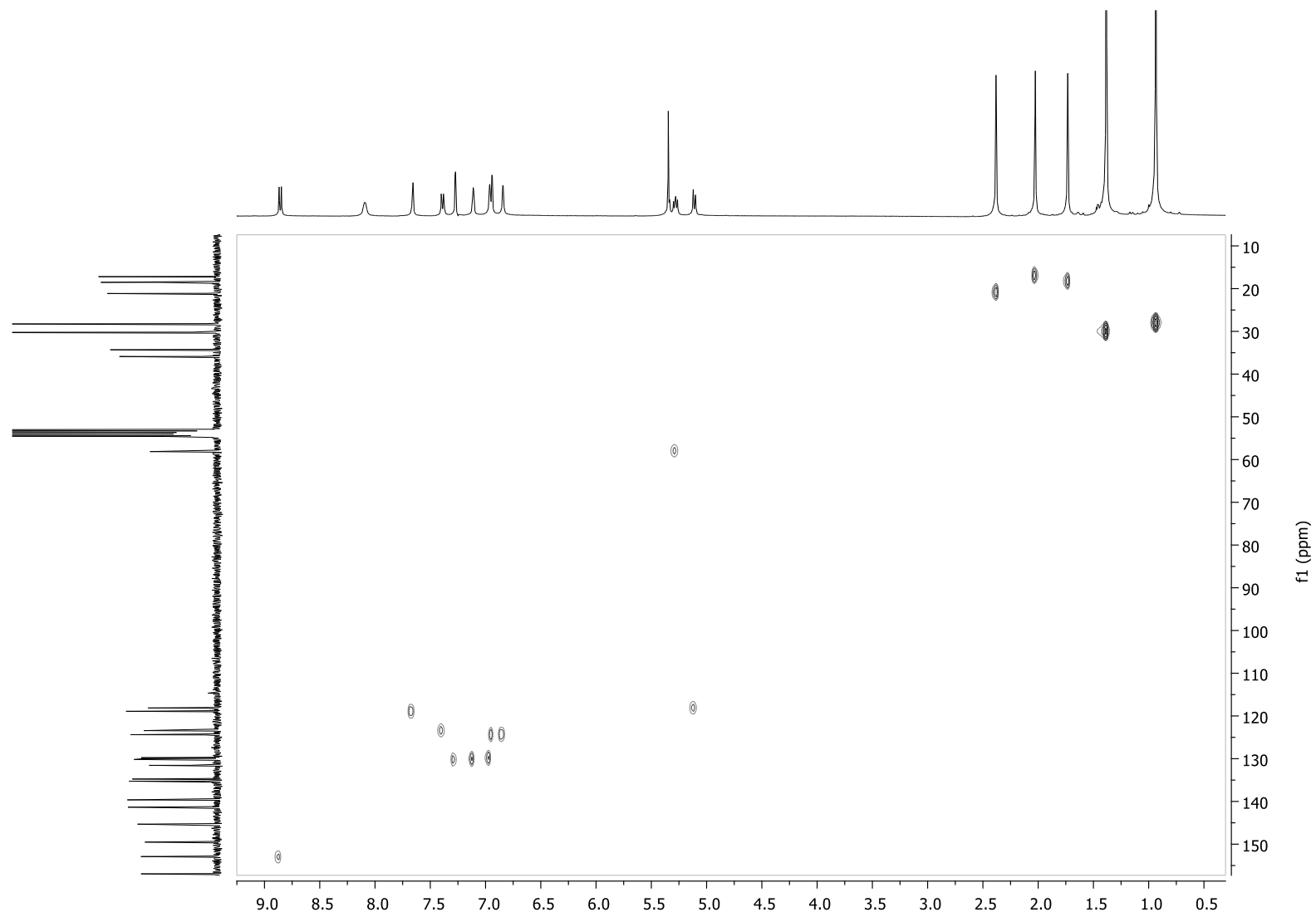
COSY (CD₂Cl₂)



^{13}C -RMN (CD_2Cl_2)

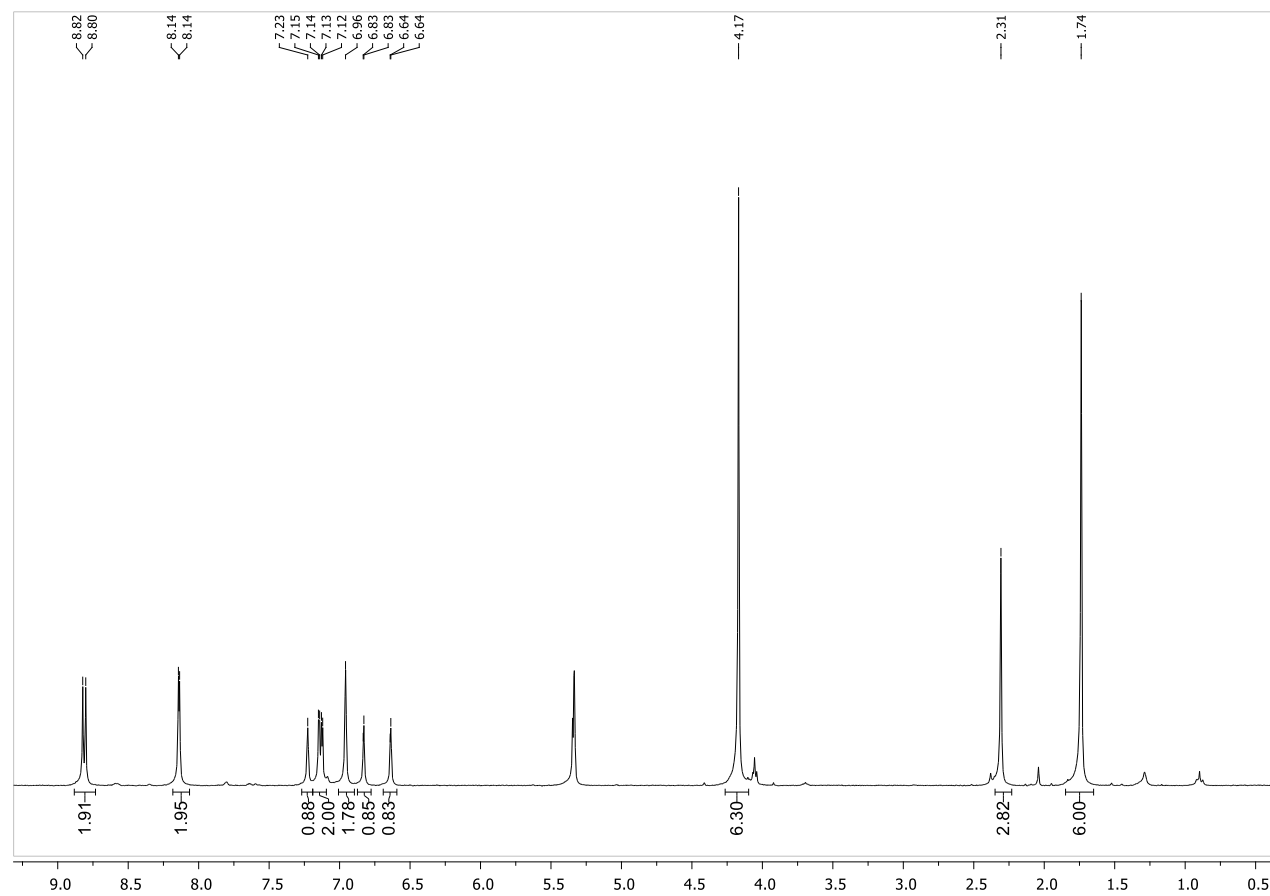
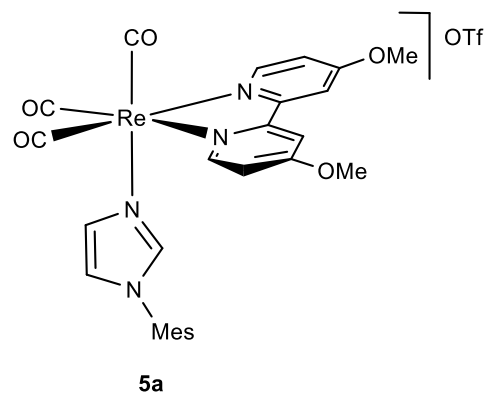


HSQC (CD₂Cl₂)

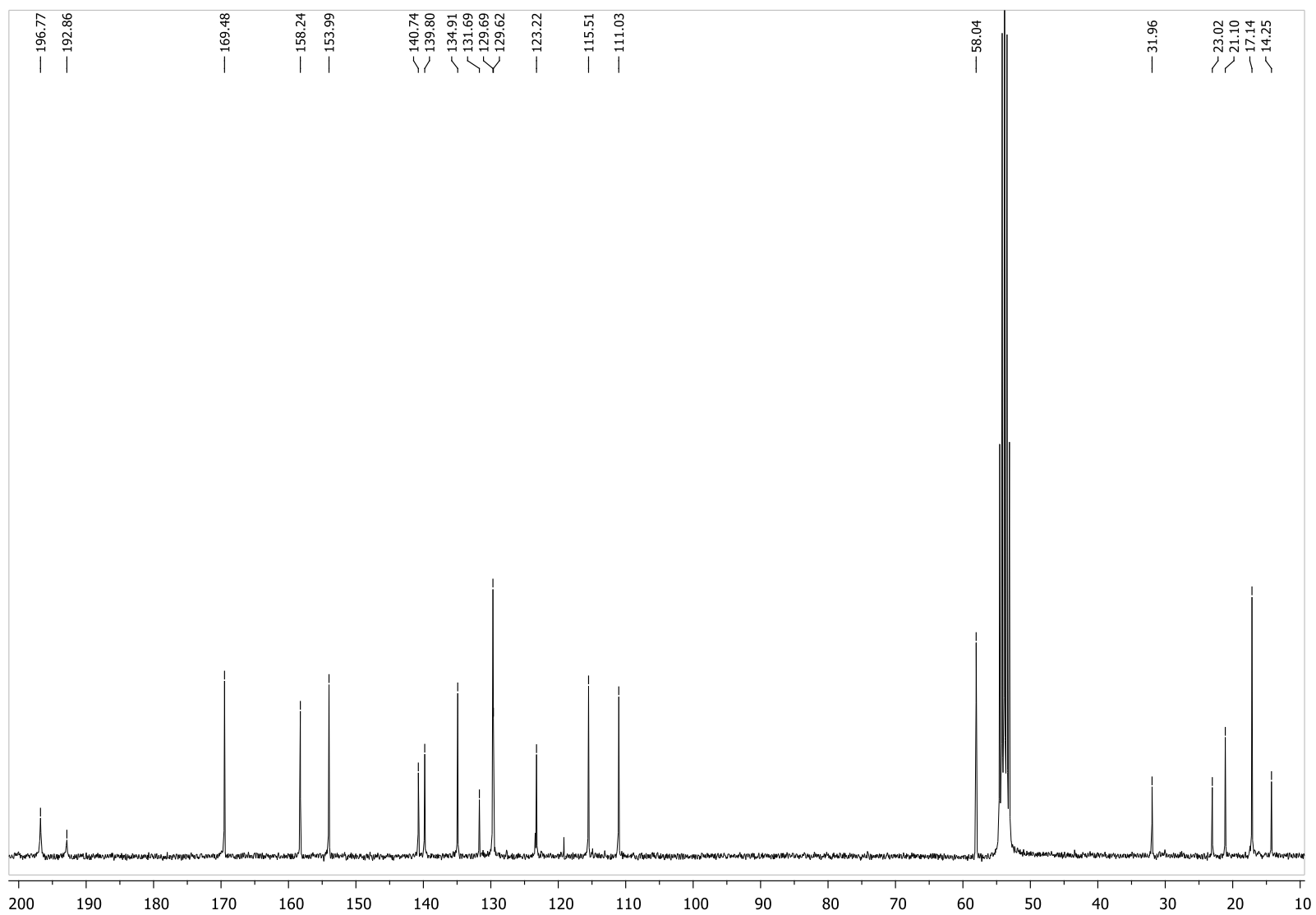


COMPOUND 5a

$^1\text{H-RMN}$ (CD_2Cl_2)

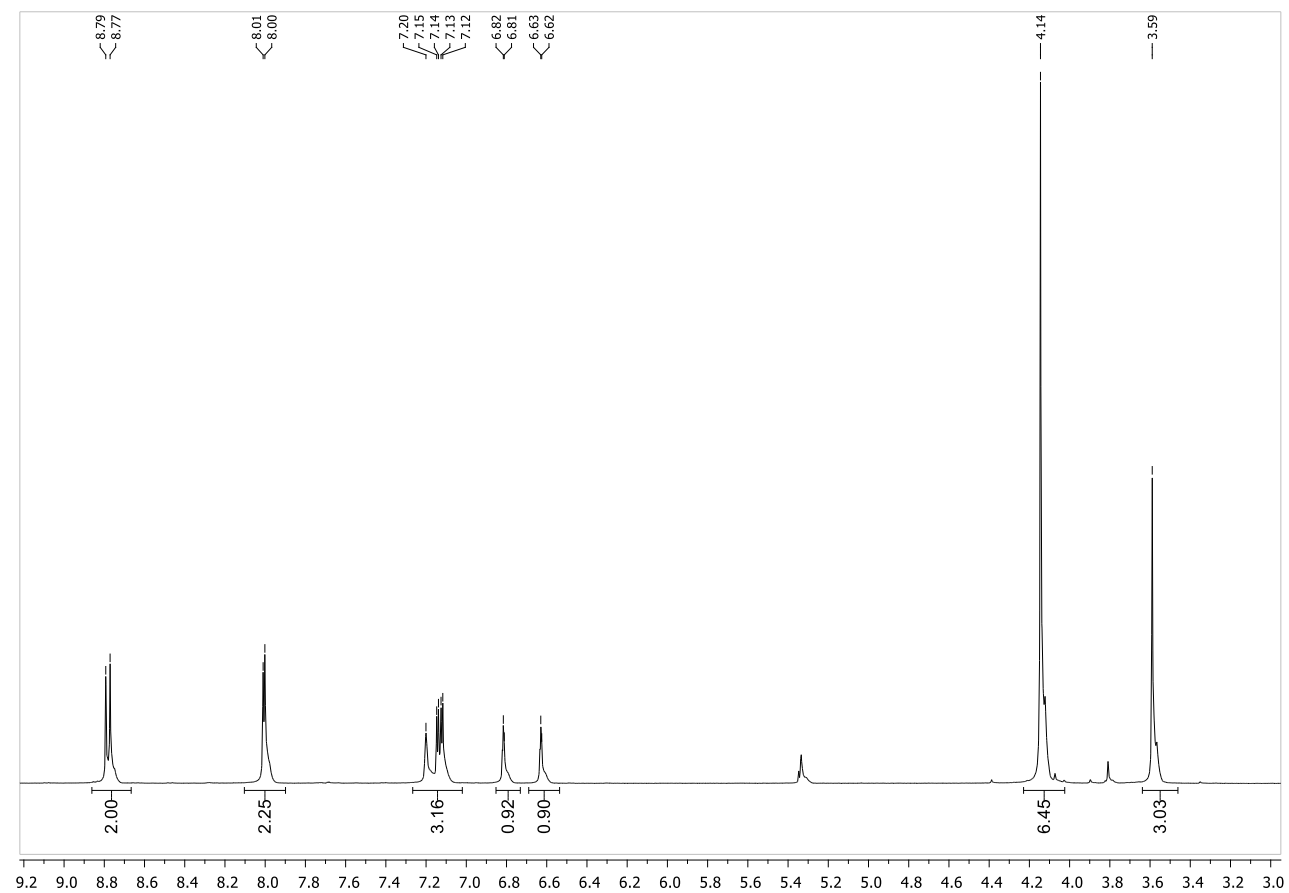
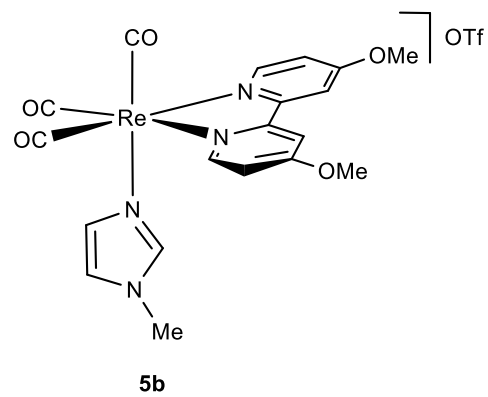


^{13}C -RMN (CD_2Cl_2)

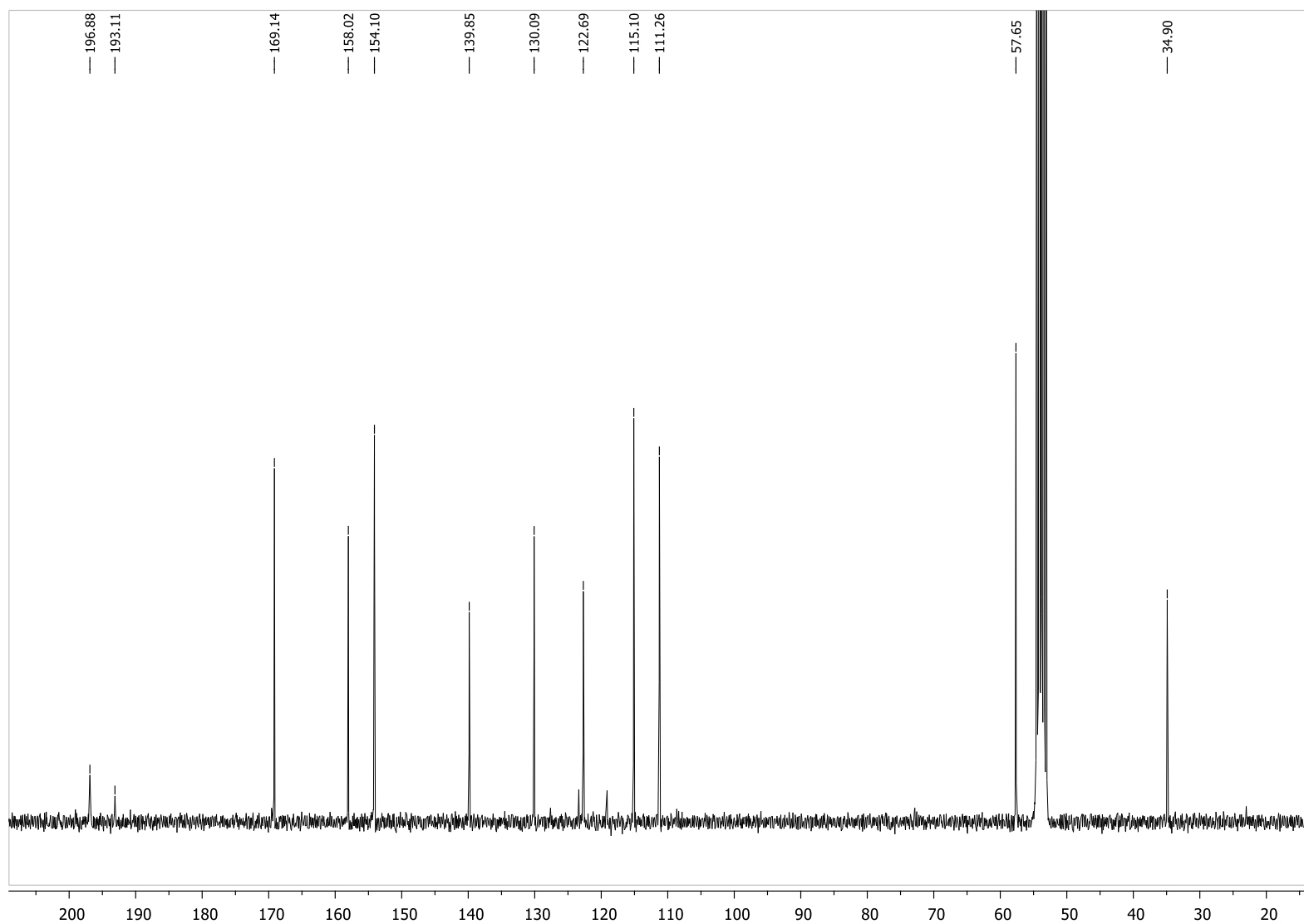


COMPOUND 5b

$^1\text{H-RMN}$ (CD_2Cl_2)

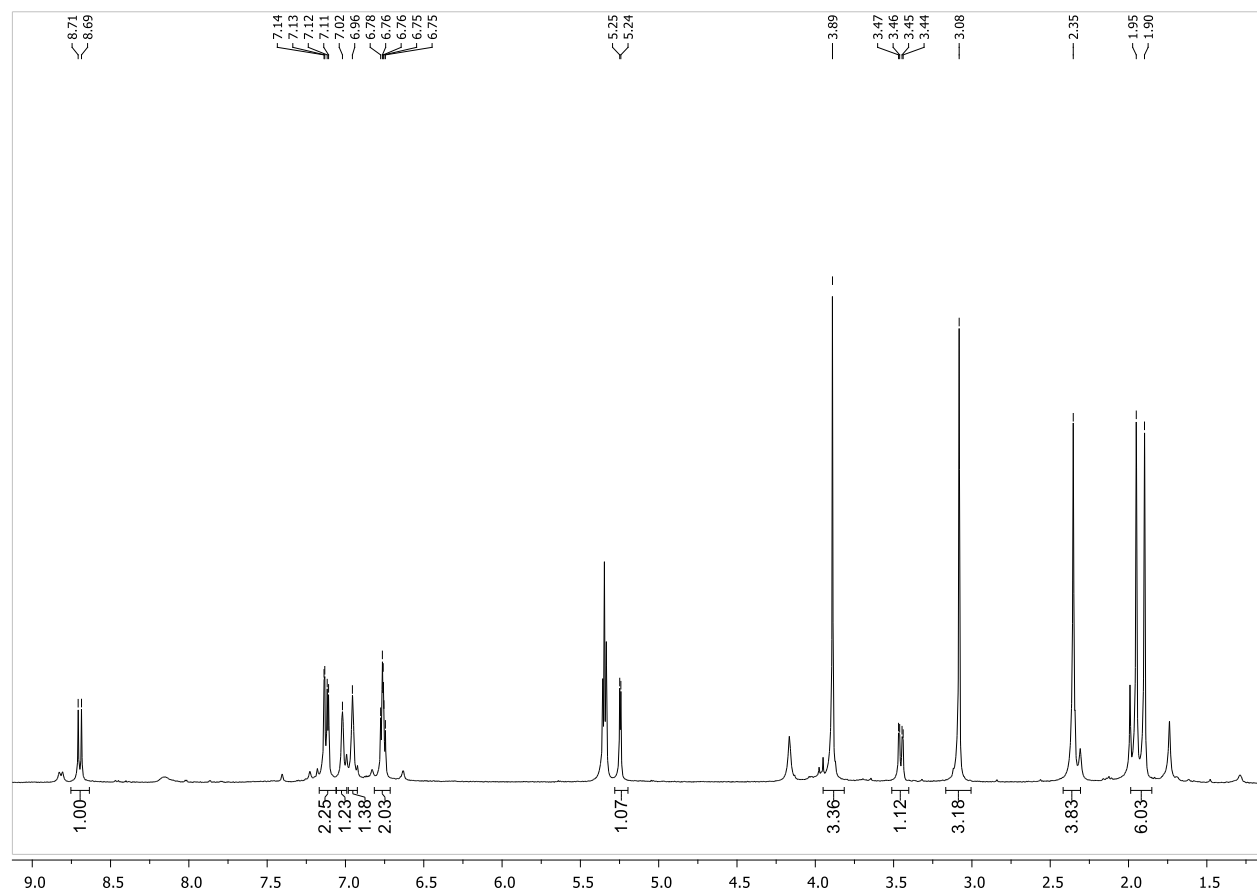
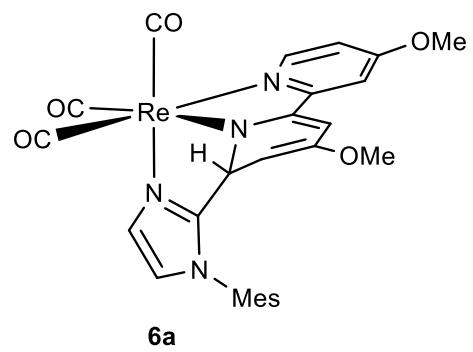


^{13}C -RMN (CD_2Cl_2)

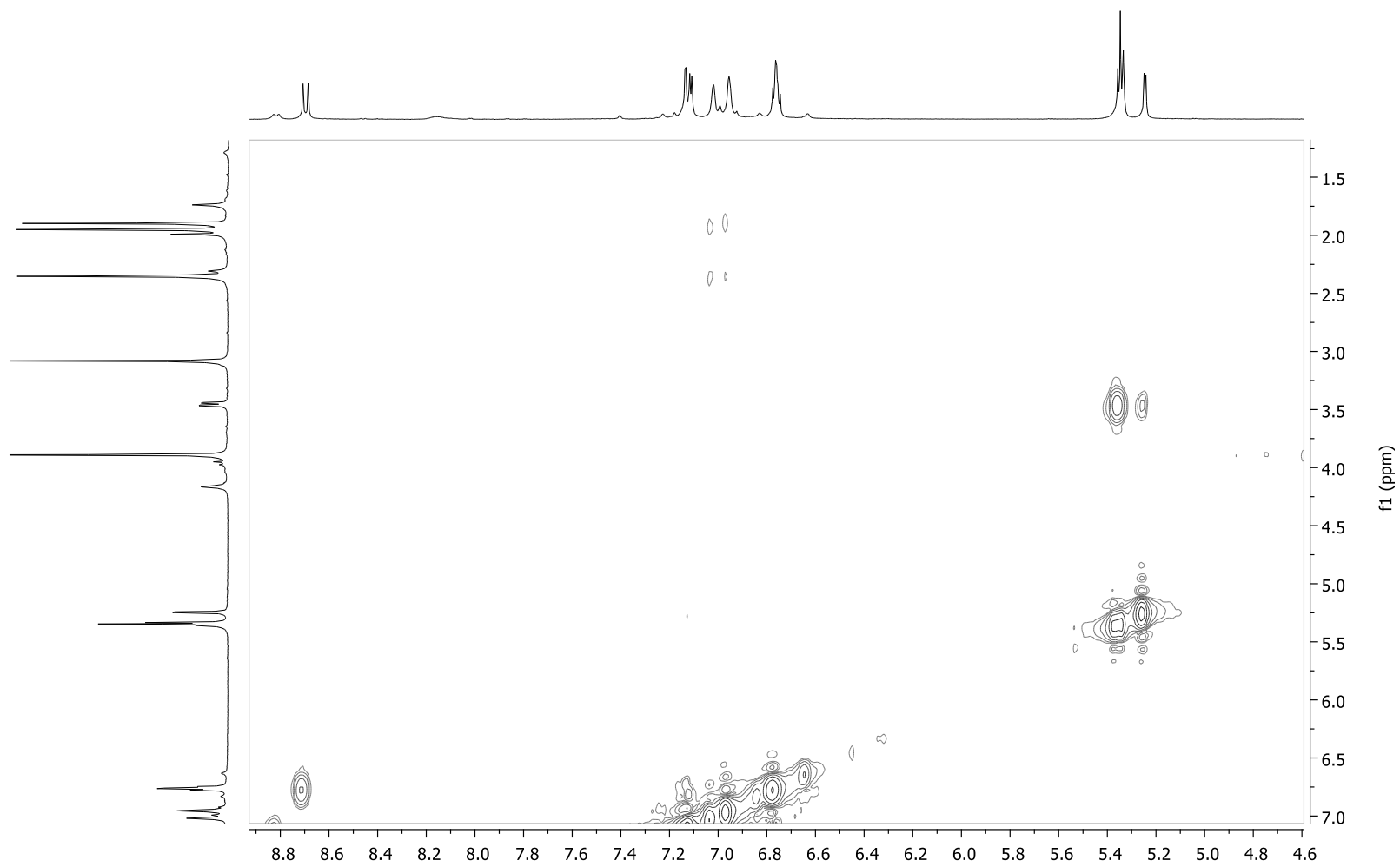


COMPOUND 6a

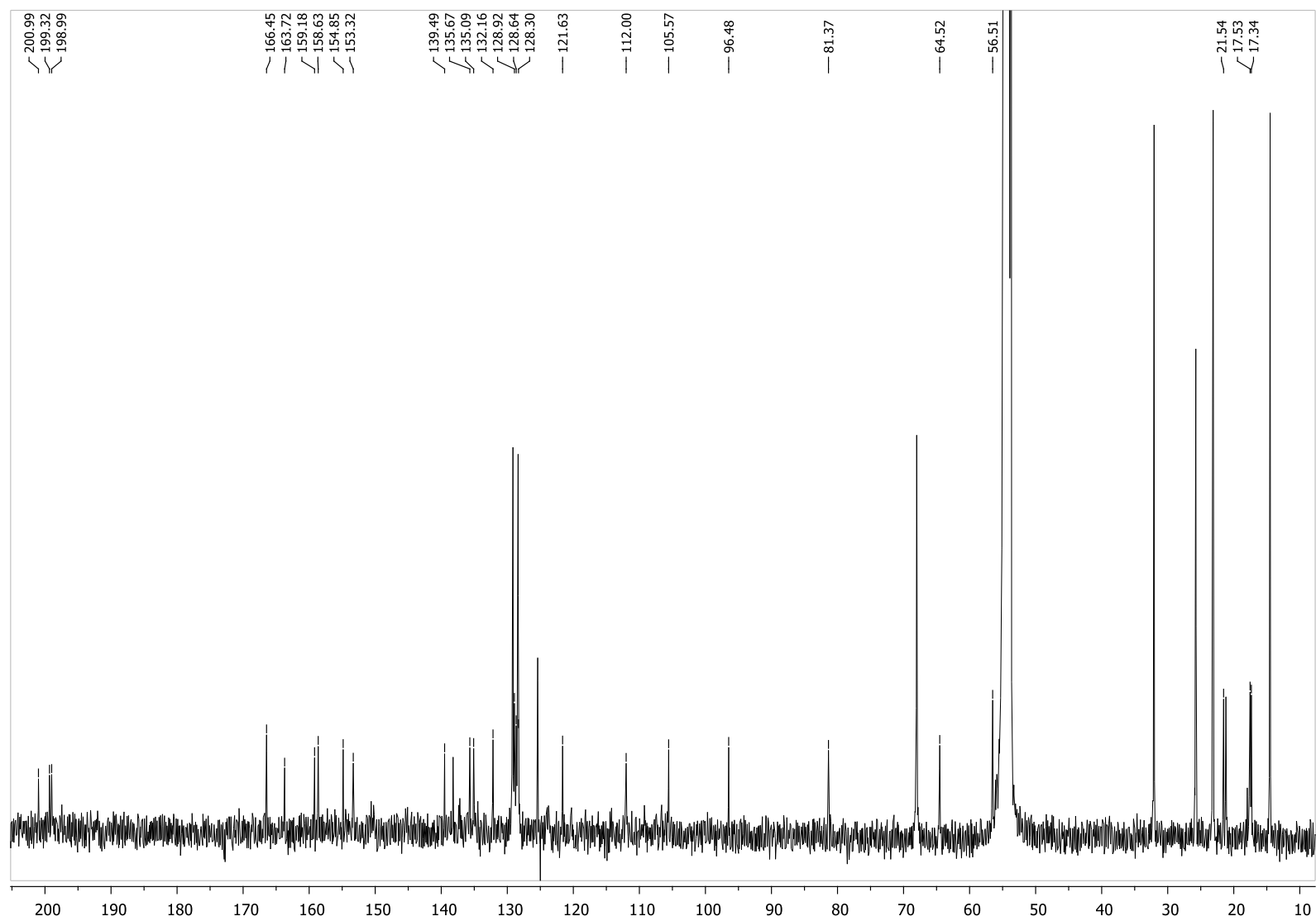
$^1\text{H-RMN}$ (CD_2Cl_2)



COSY (CD₂Cl₂)

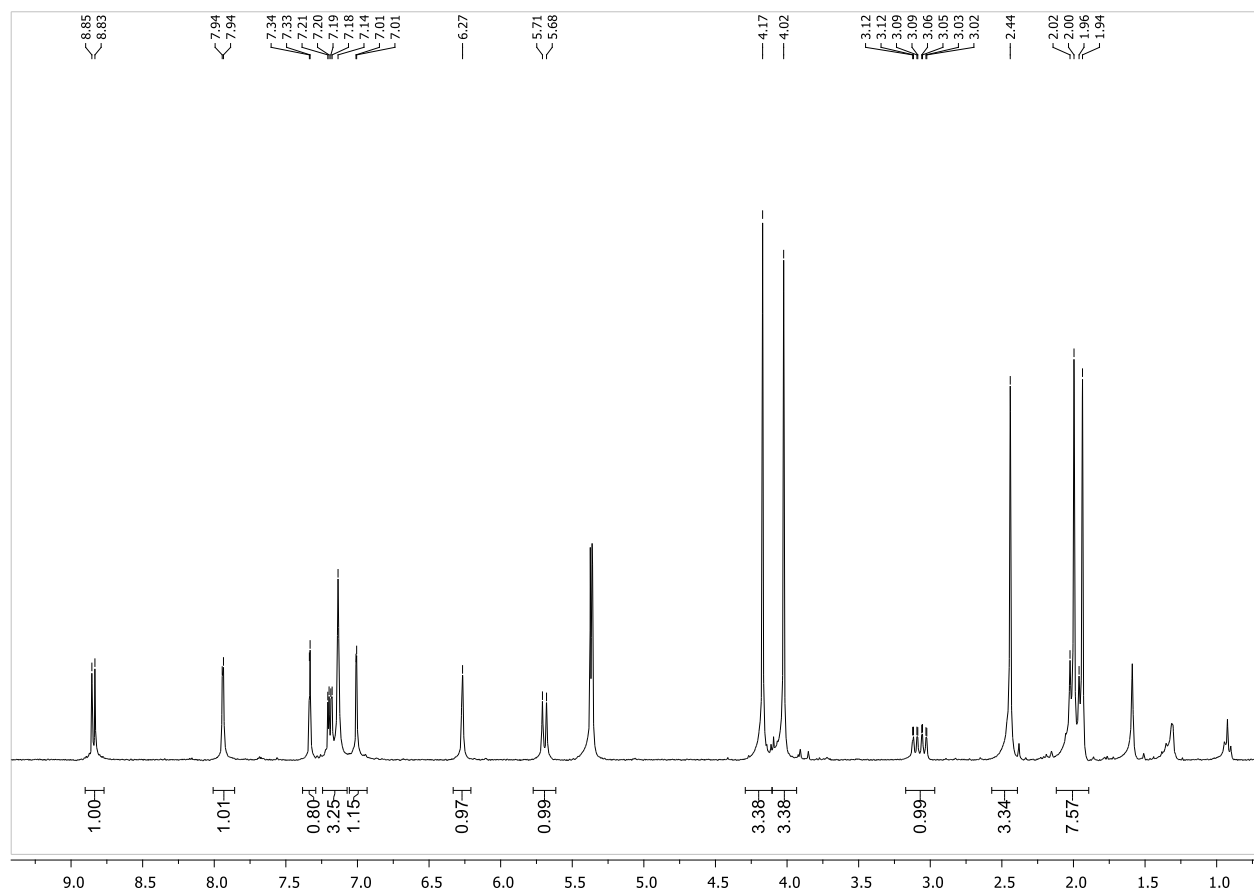
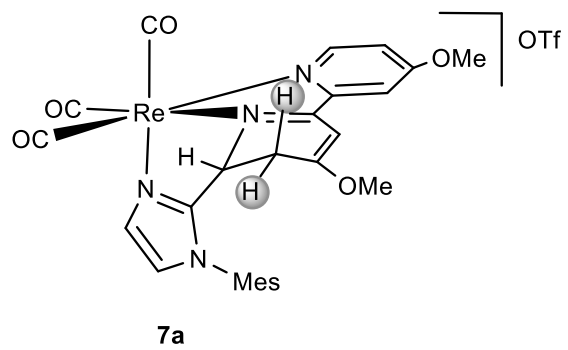


^{13}C -RMN (CD_2Cl_2)

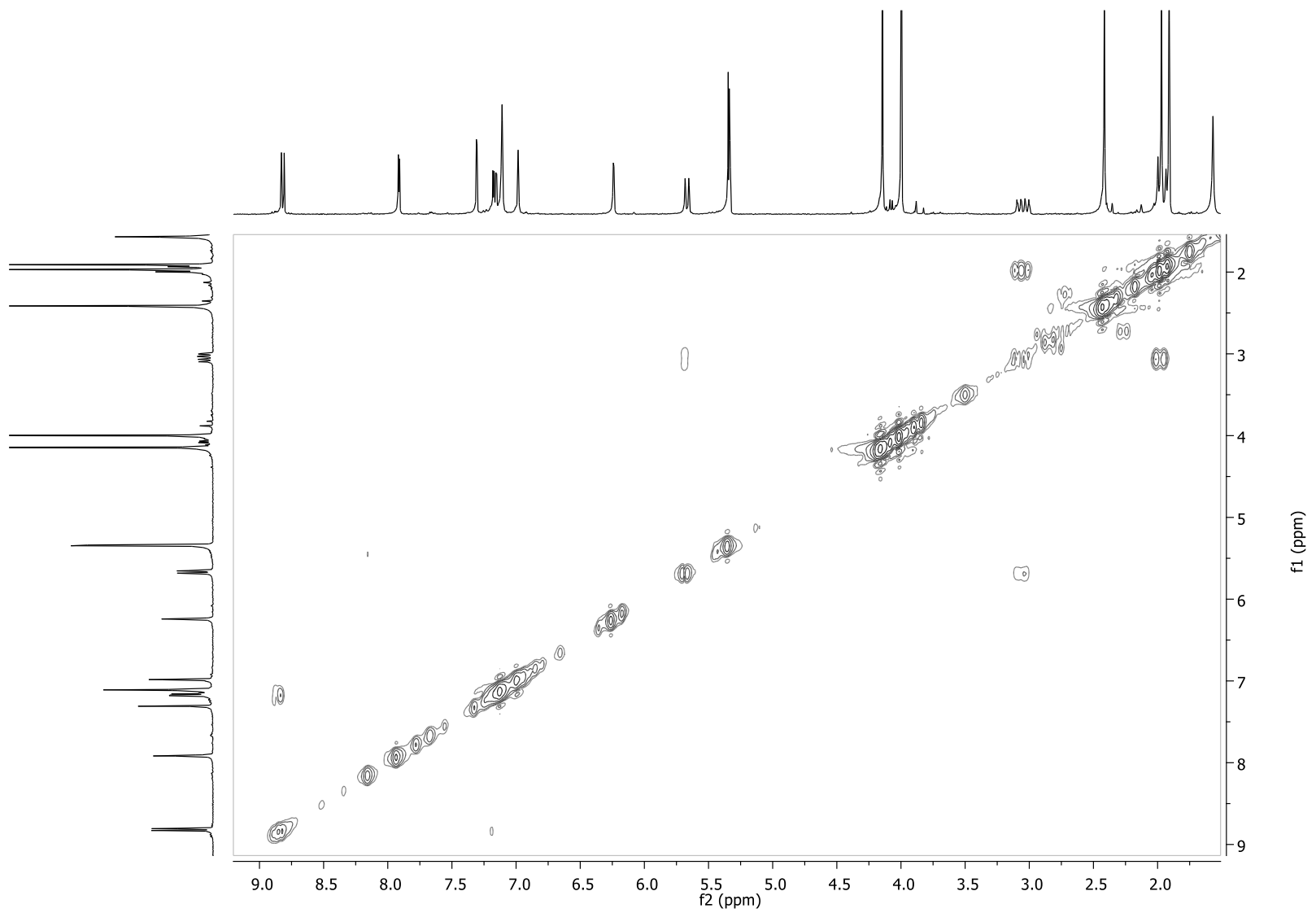


COMPOUND 7a

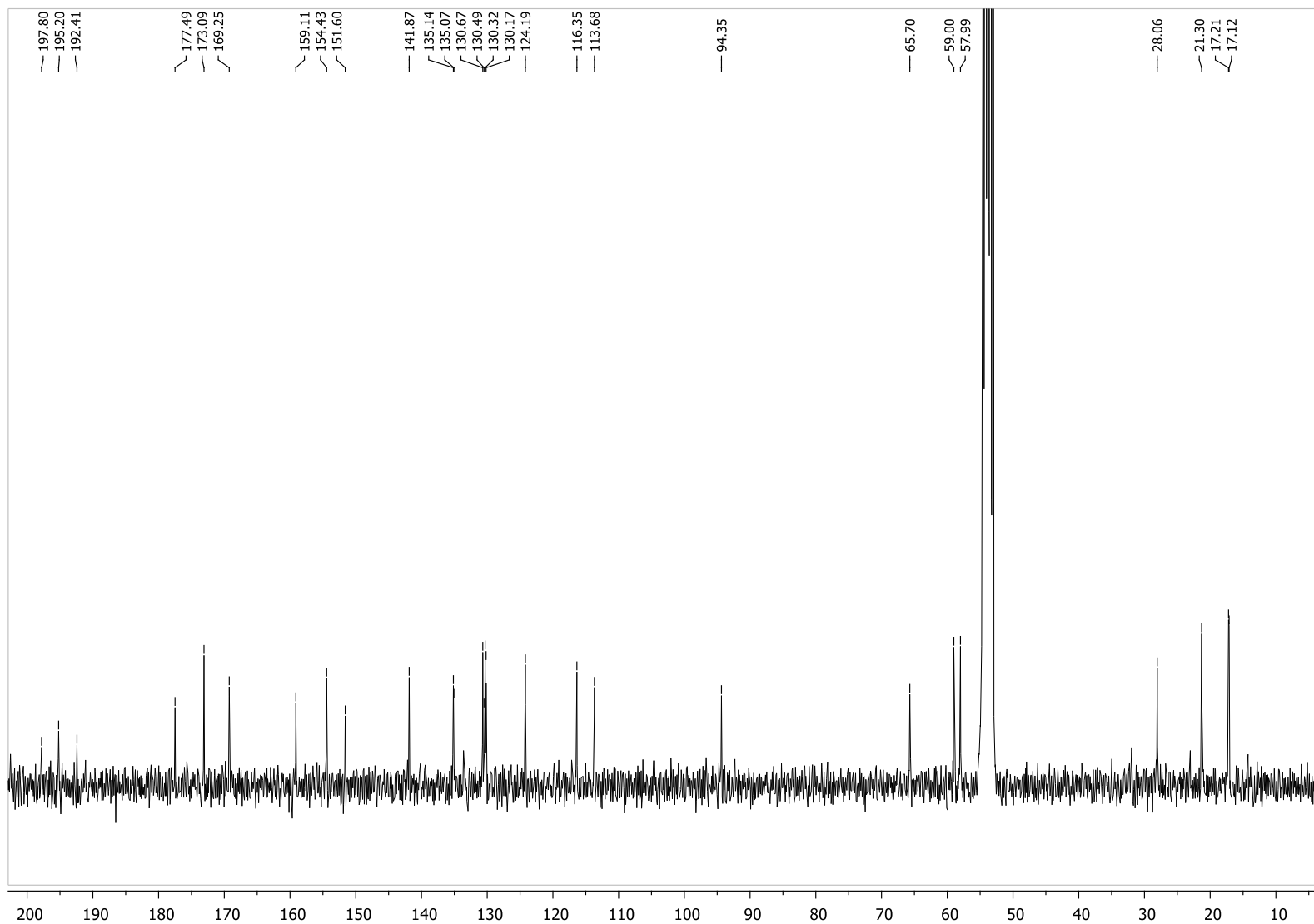
$^1\text{H-RMN}$ (CD_2Cl_2)



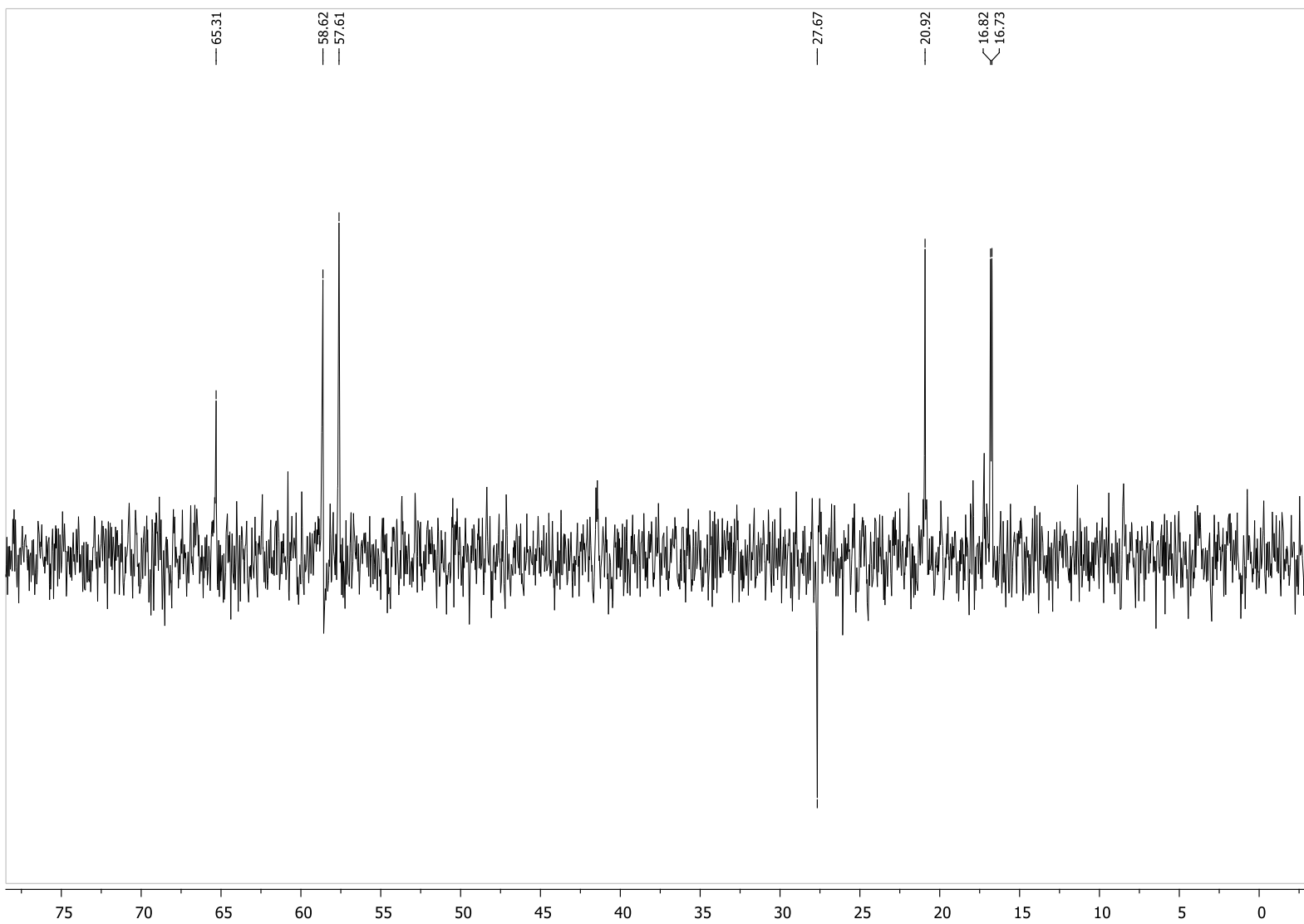
COSY (CD₂Cl₂)



¹³C-RMN (CD₂Cl₂)

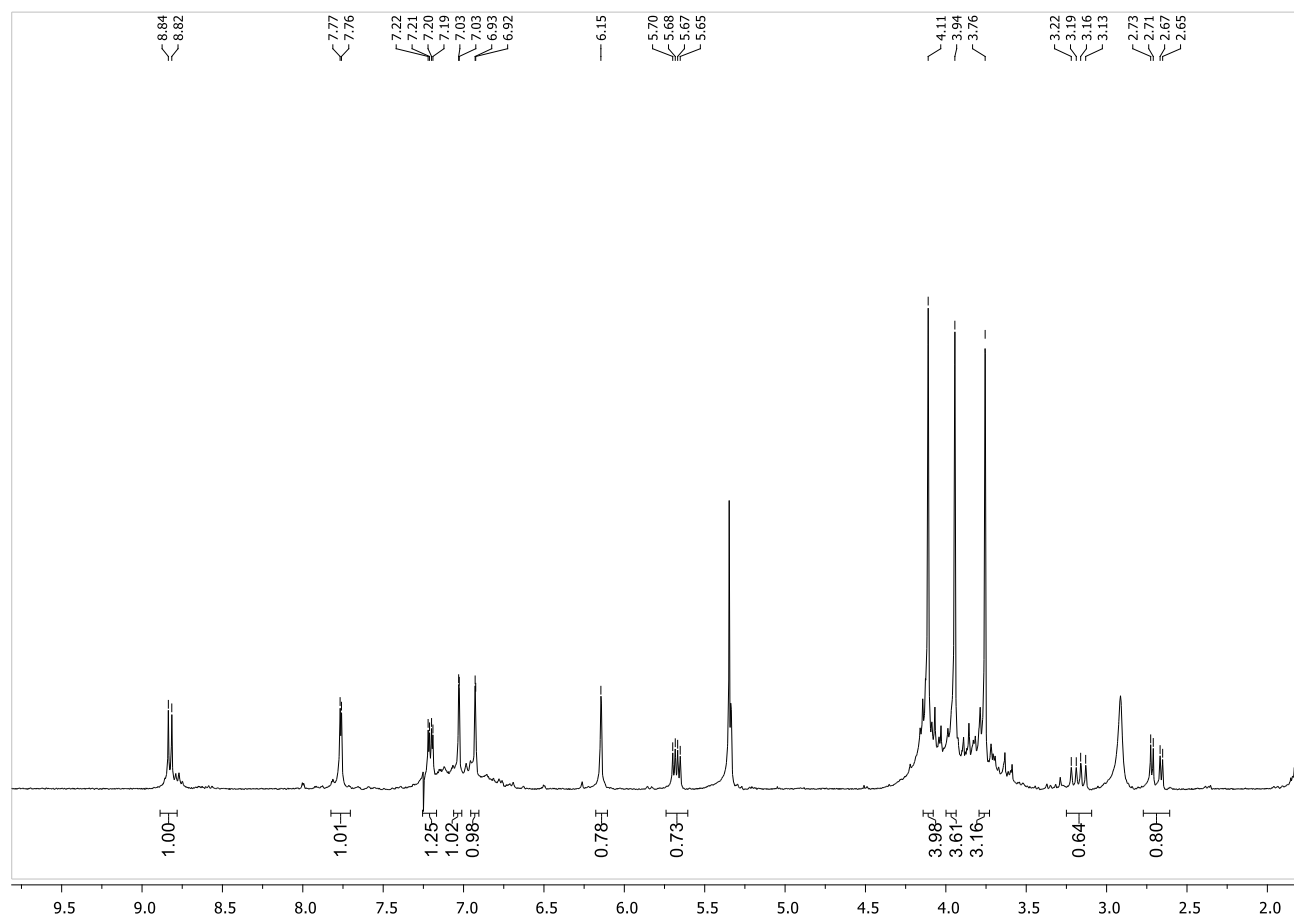
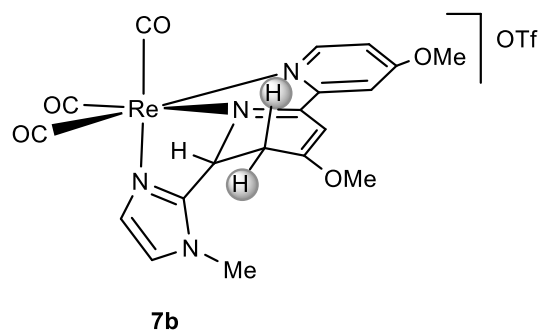


^{13}C -DEP135
(CD_2Cl_2)

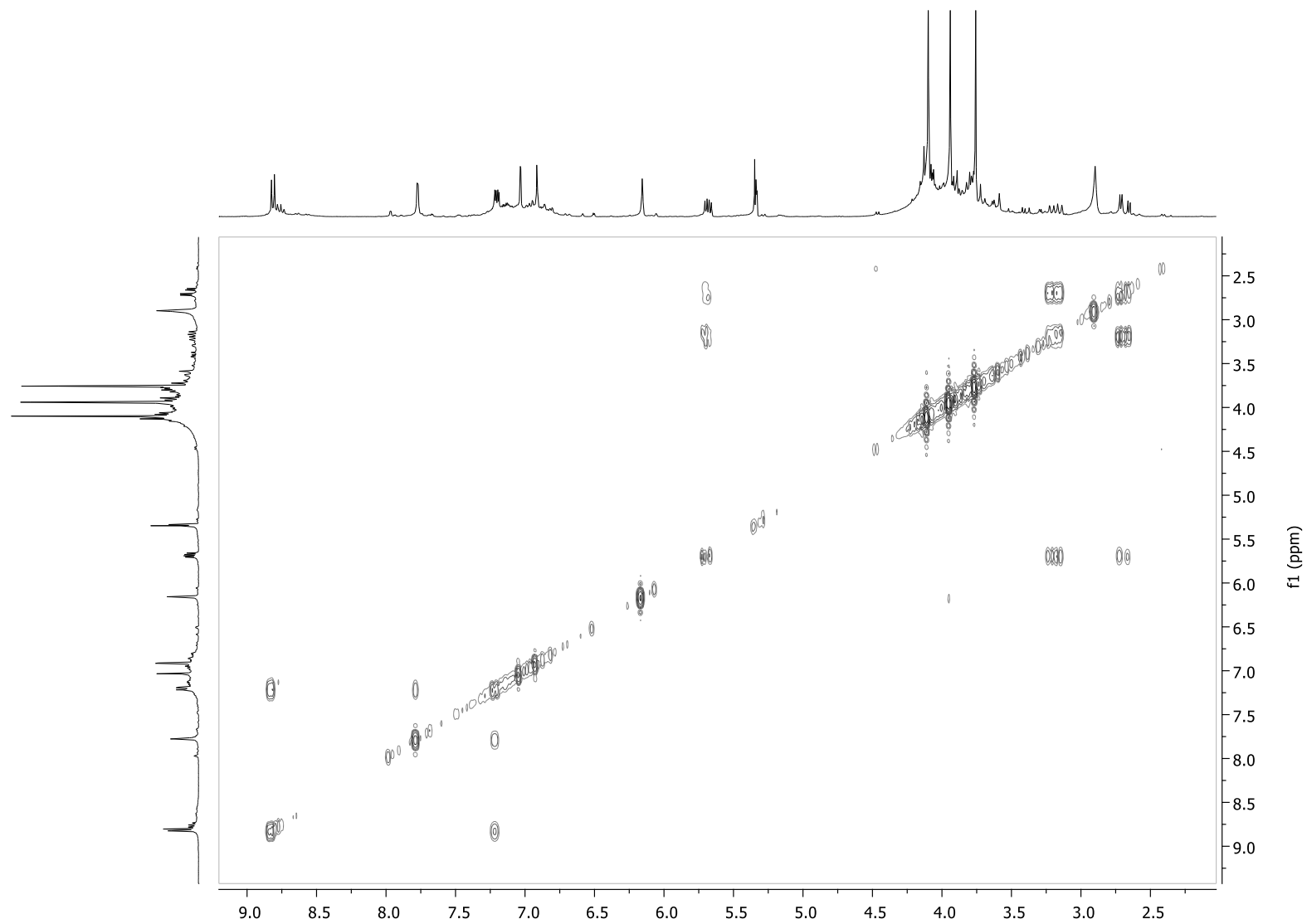


COMPOUND 7b

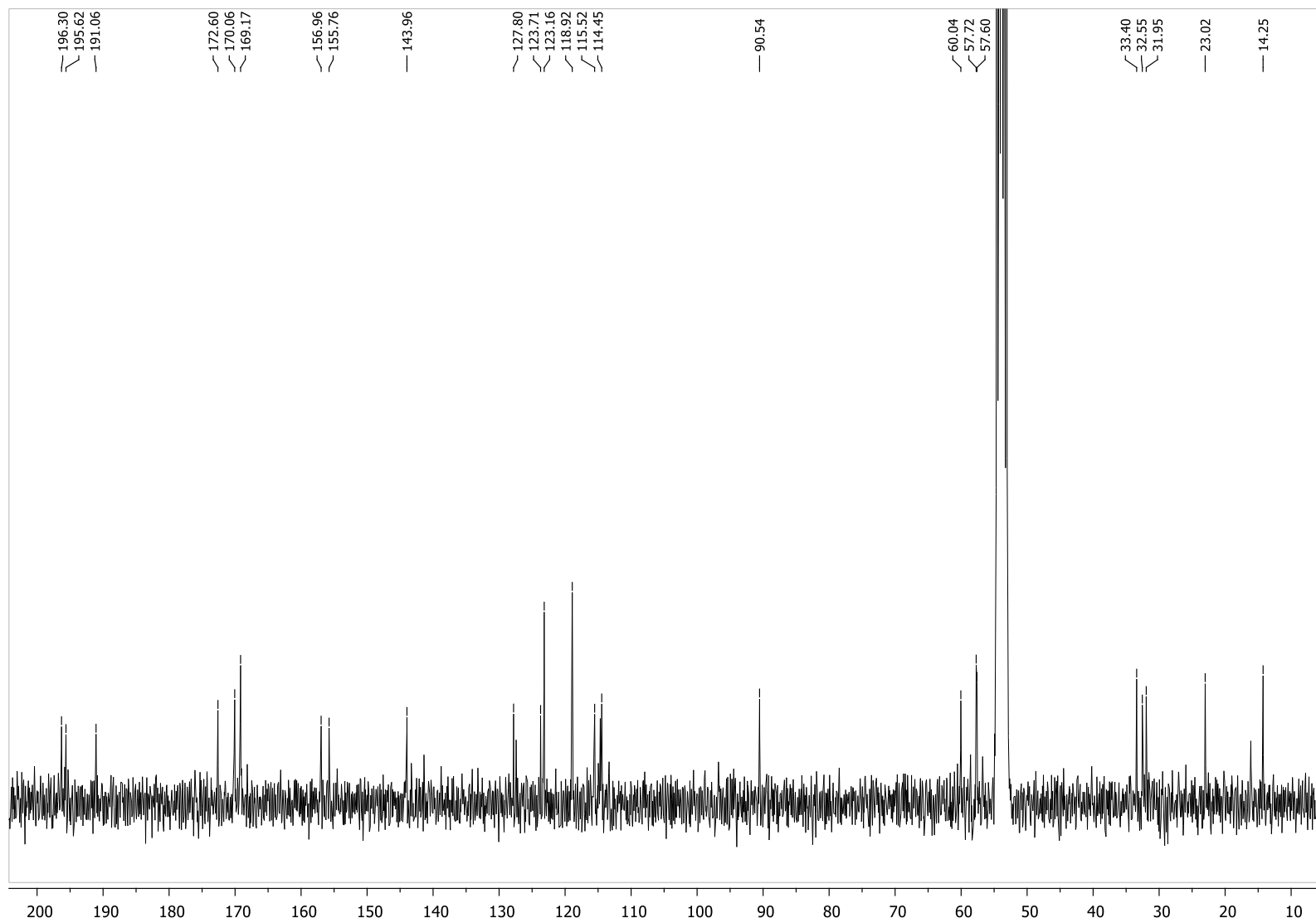
$^1\text{H-RMN}$ (CD_2Cl_2)



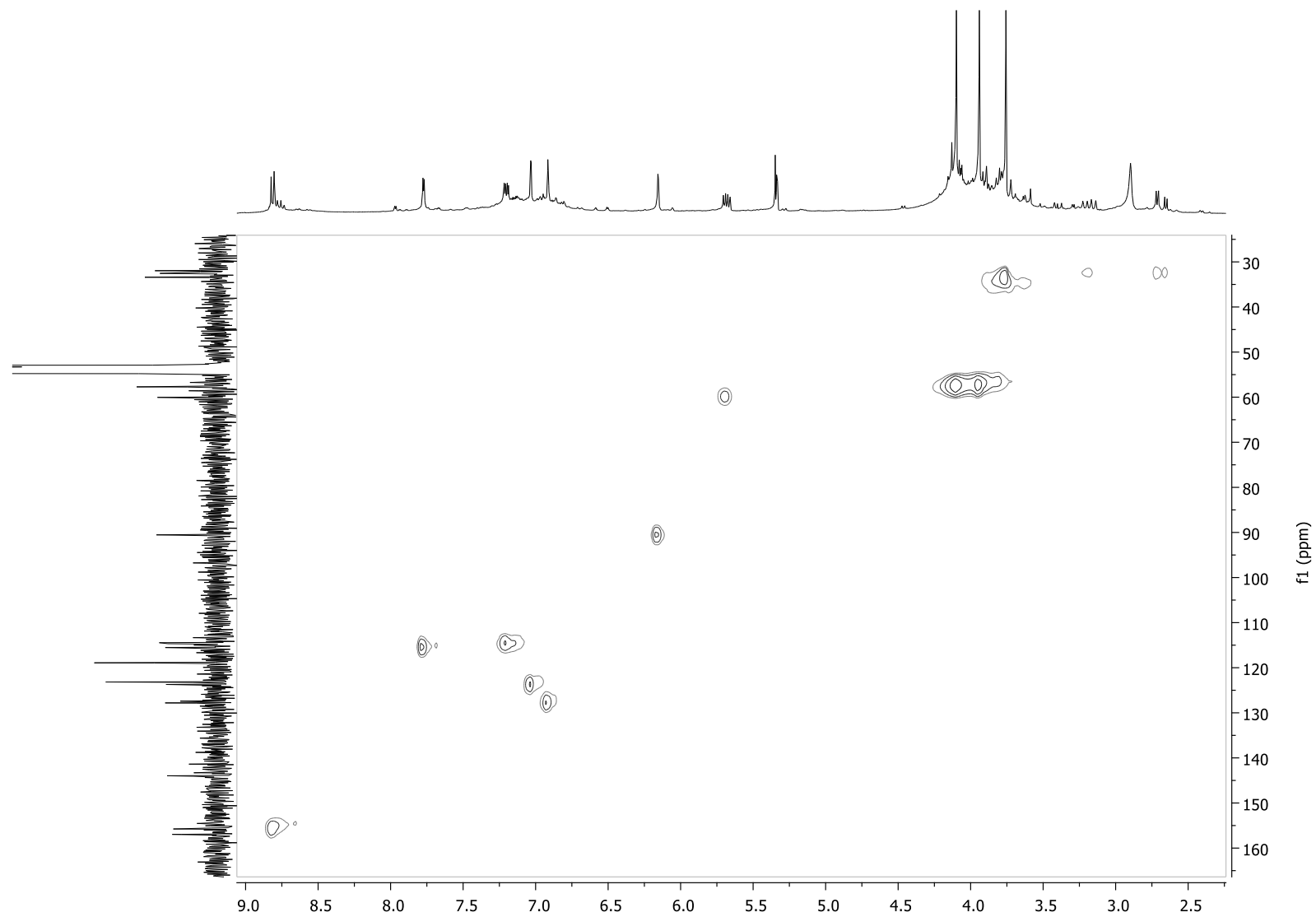
COSY (CD₂Cl₂)



^{13}C -RMN (CD_2Cl_2)

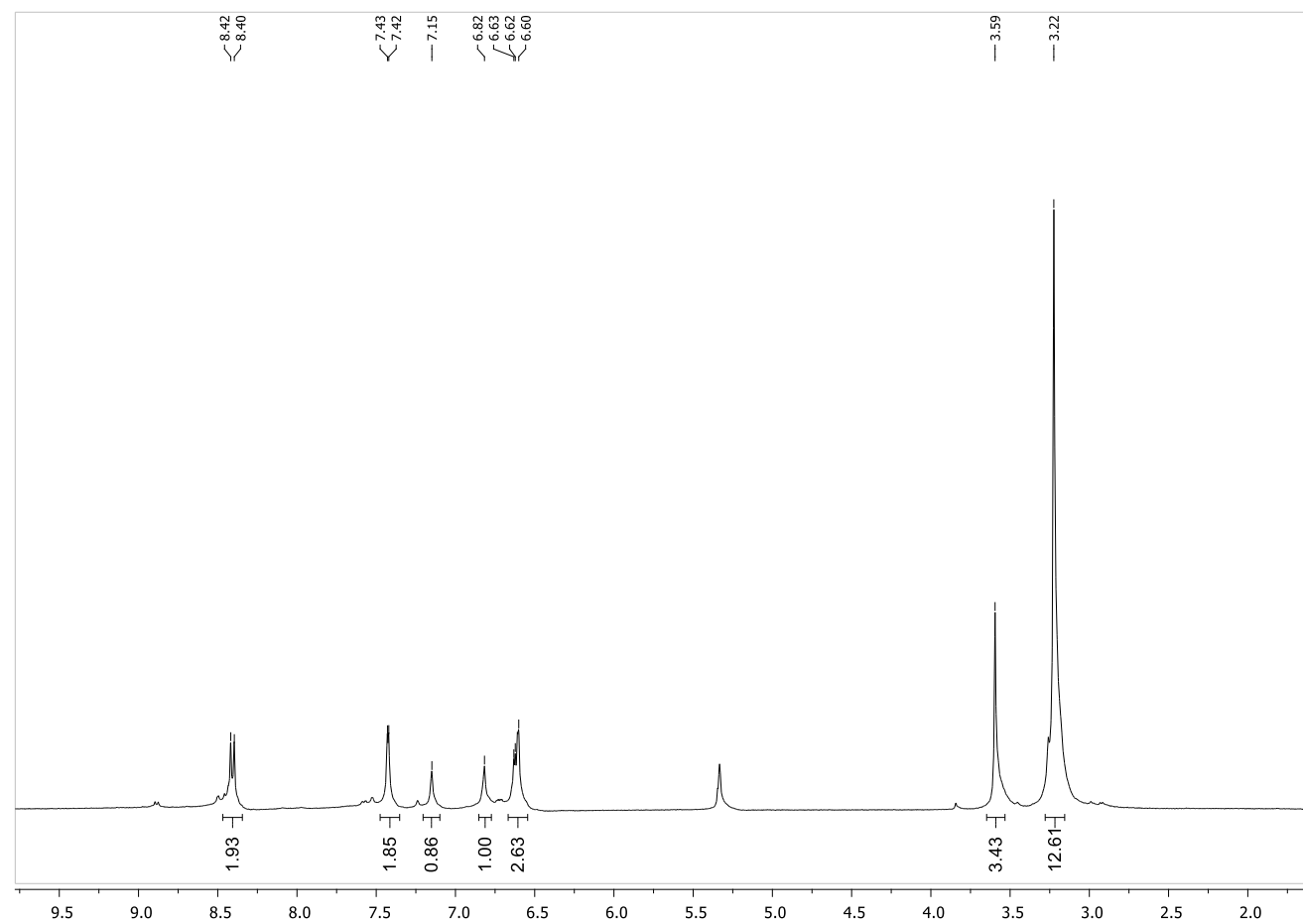
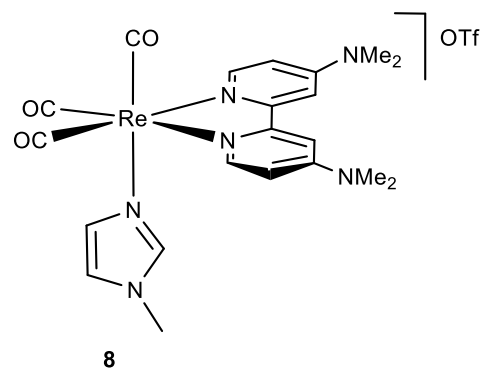


HSQC (CD₂Cl₂)

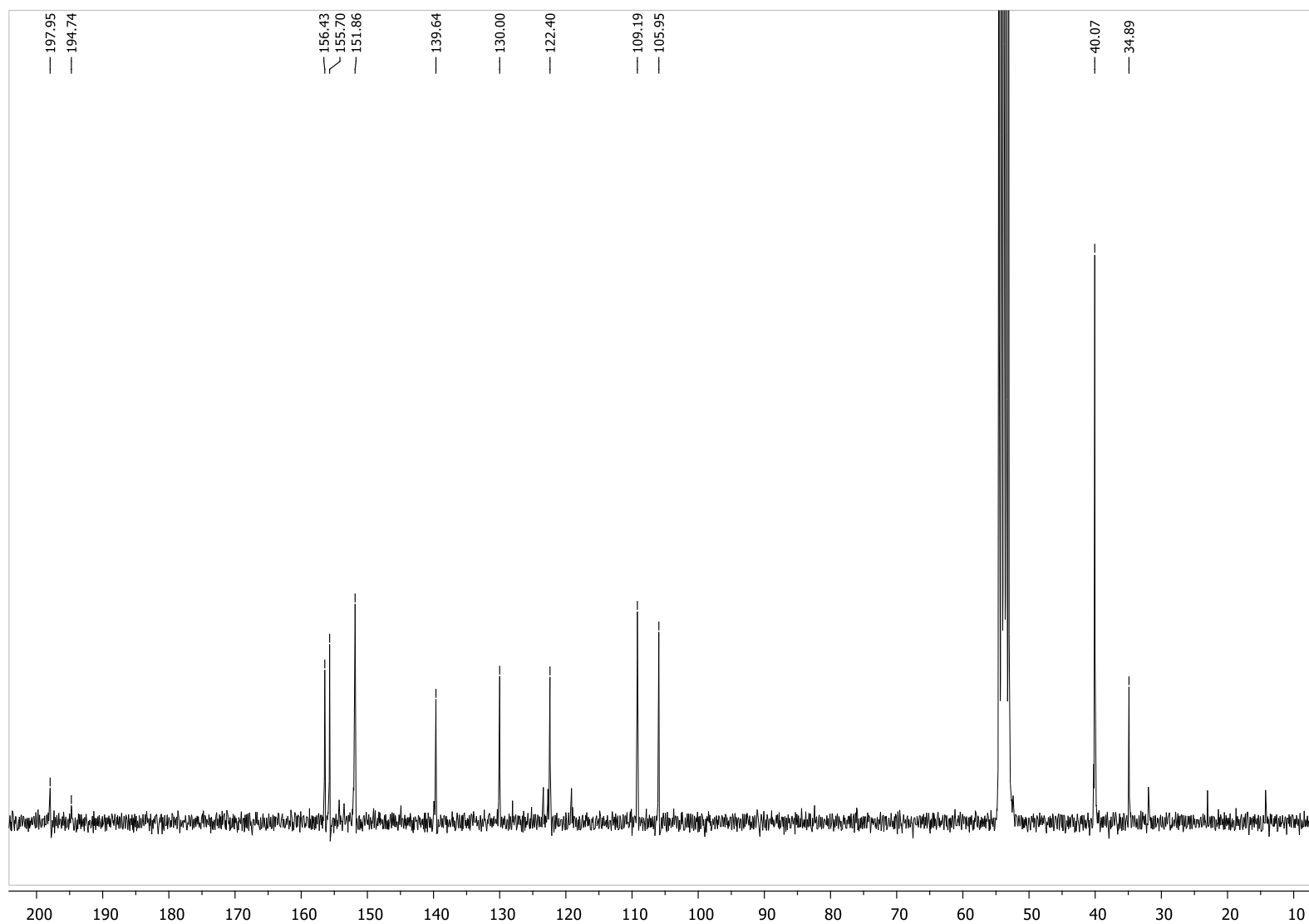


COMPOUND 8

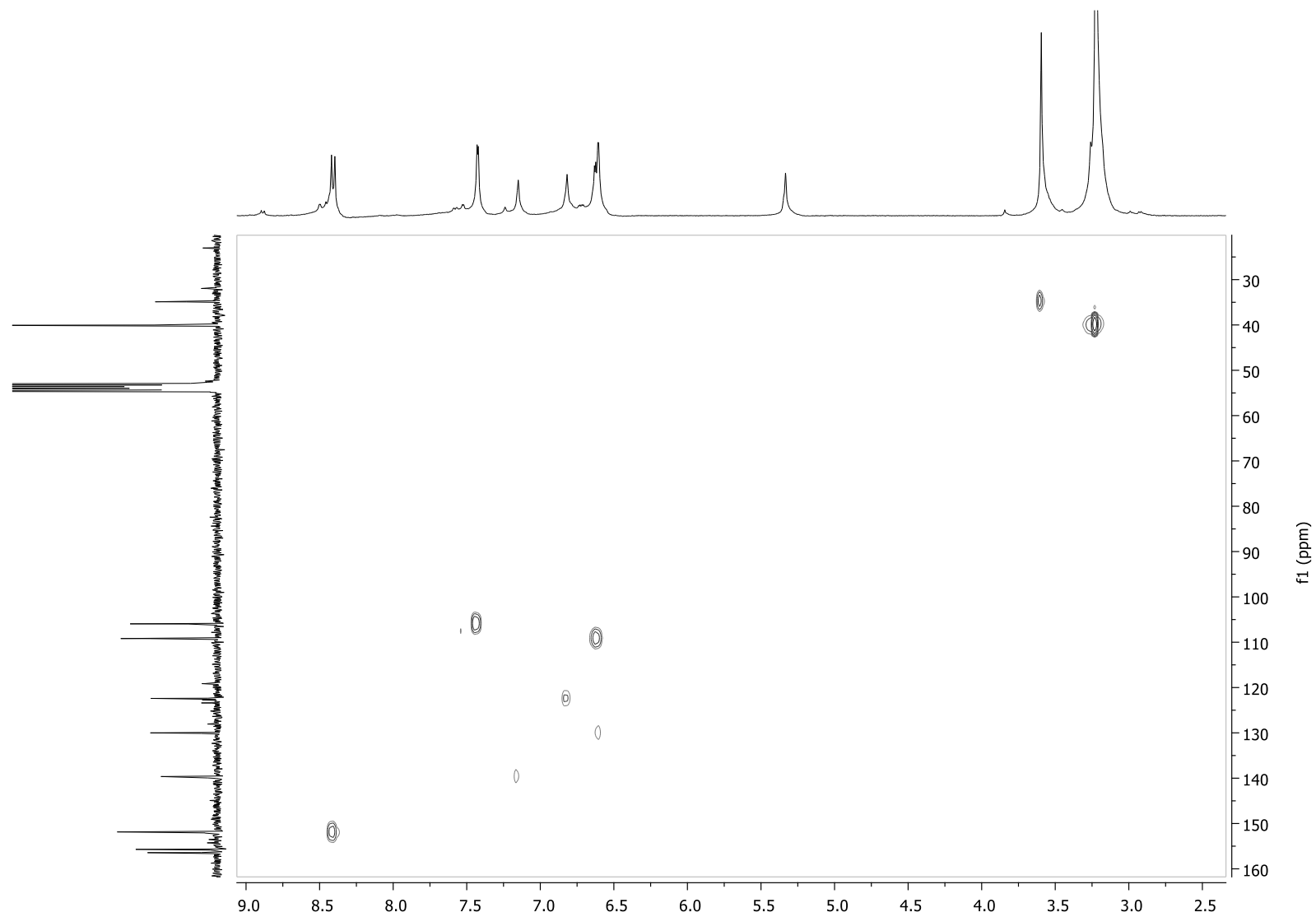
$^1\text{H-RMN}$ (CD_2Cl_2)



^{13}C -RMN (CD_2Cl_2)

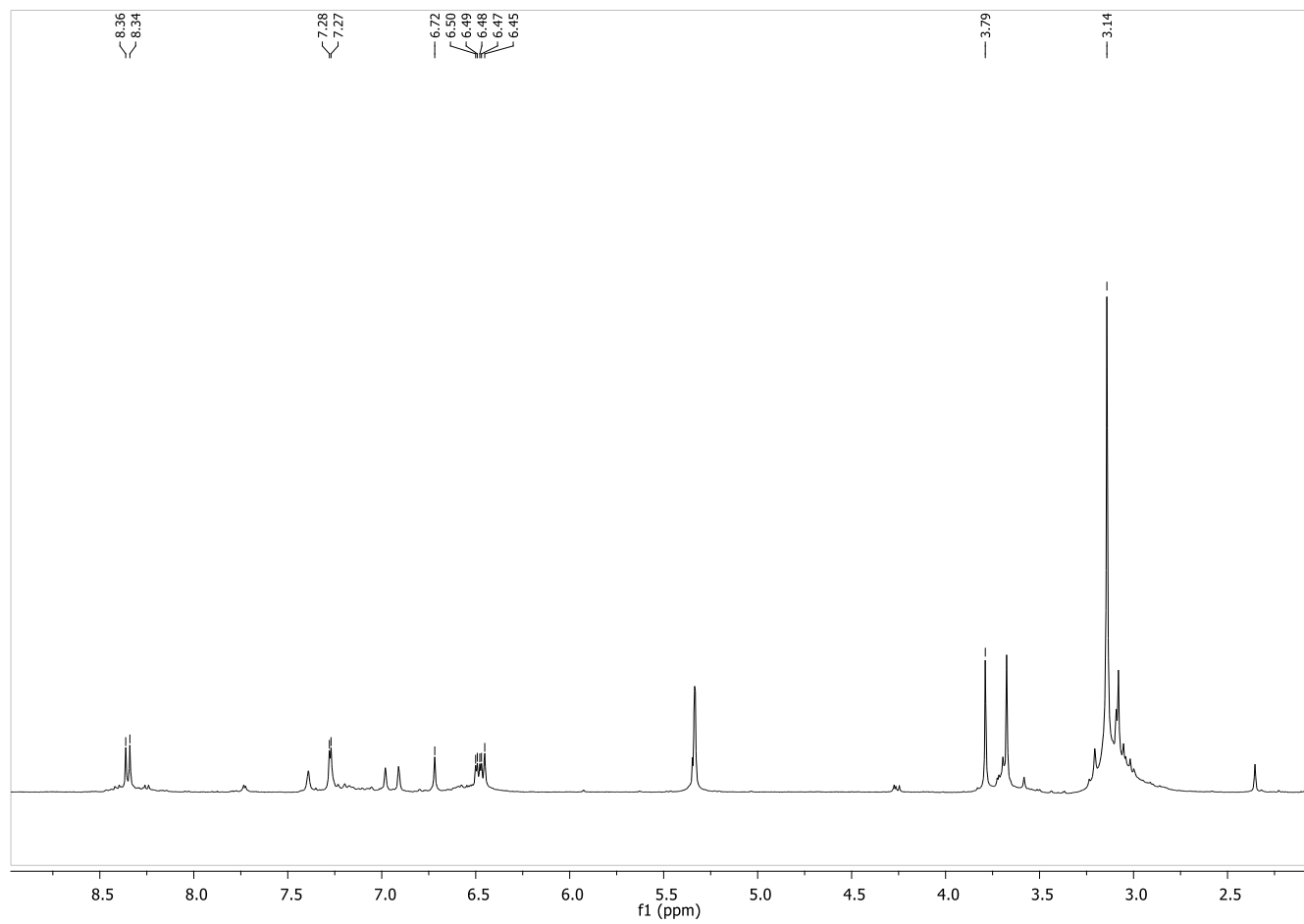
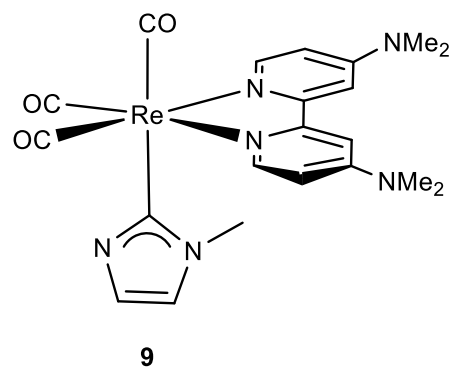


HSQC (CD₂Cl₂)

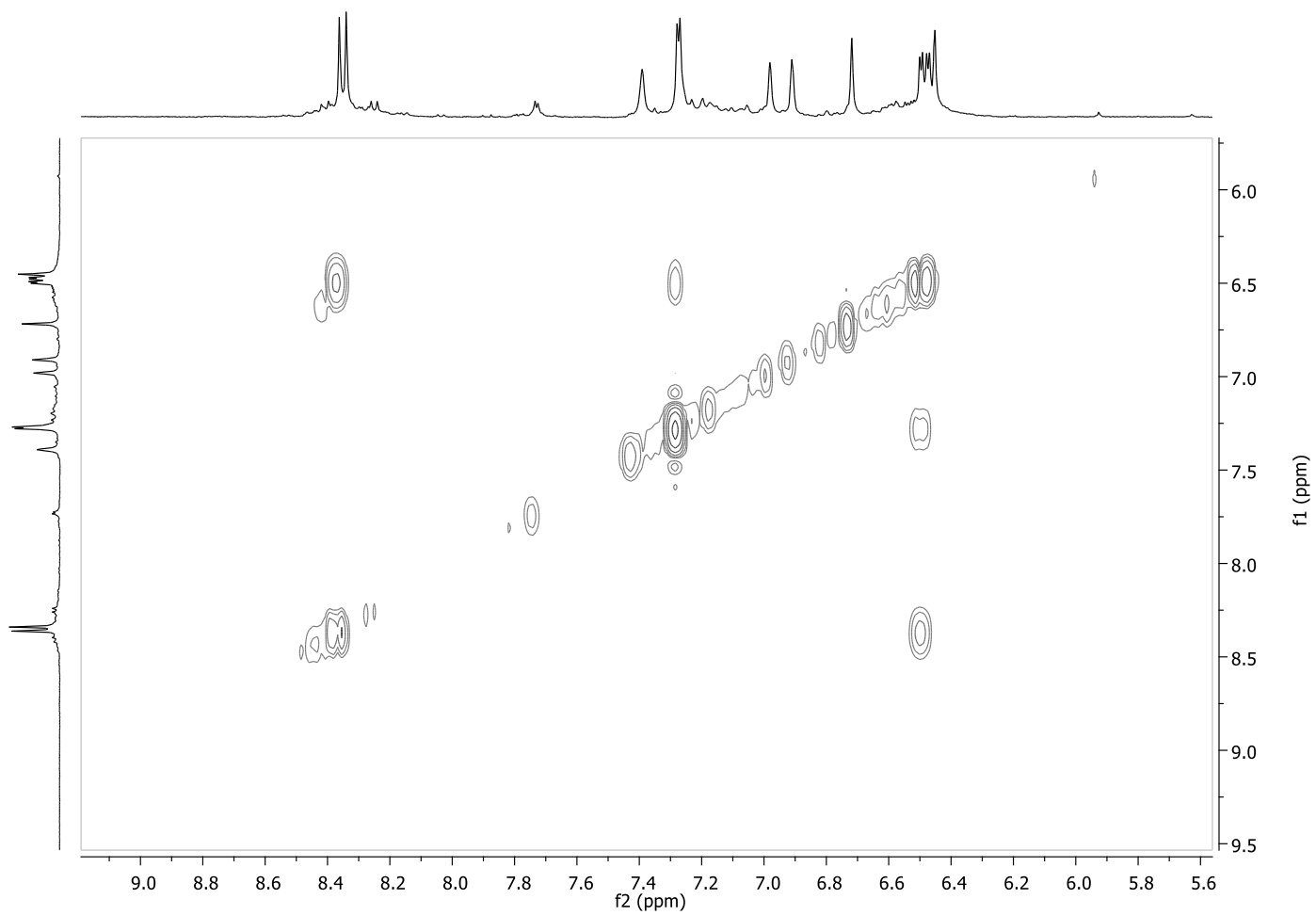


COMPOUND 9

$^1\text{H-RMN}$ (CD_2Cl_2)

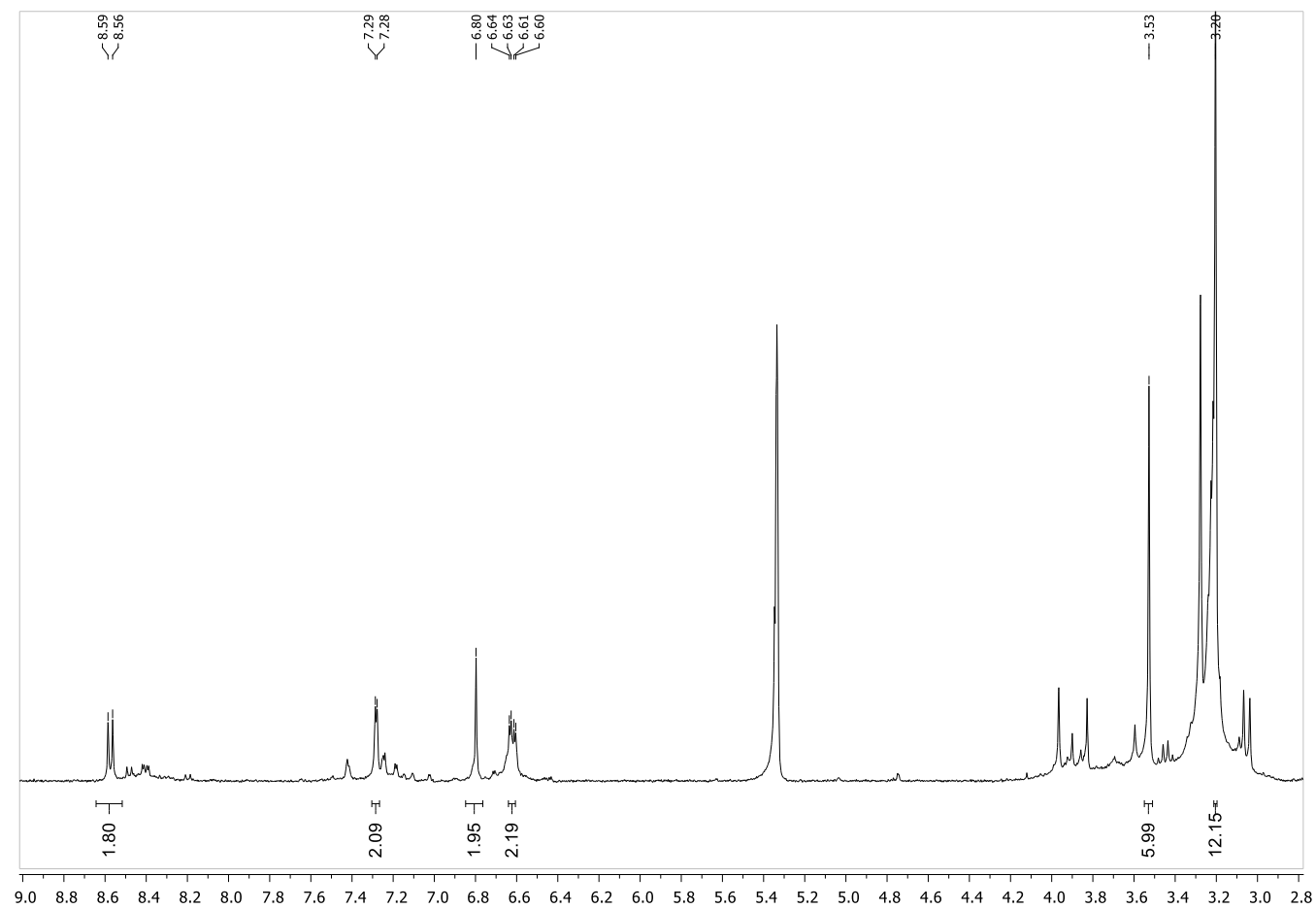
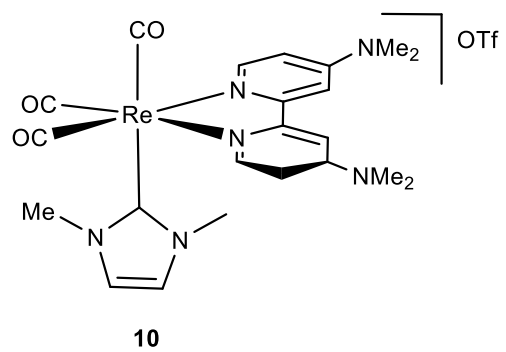


COSY (CD₂Cl₂)

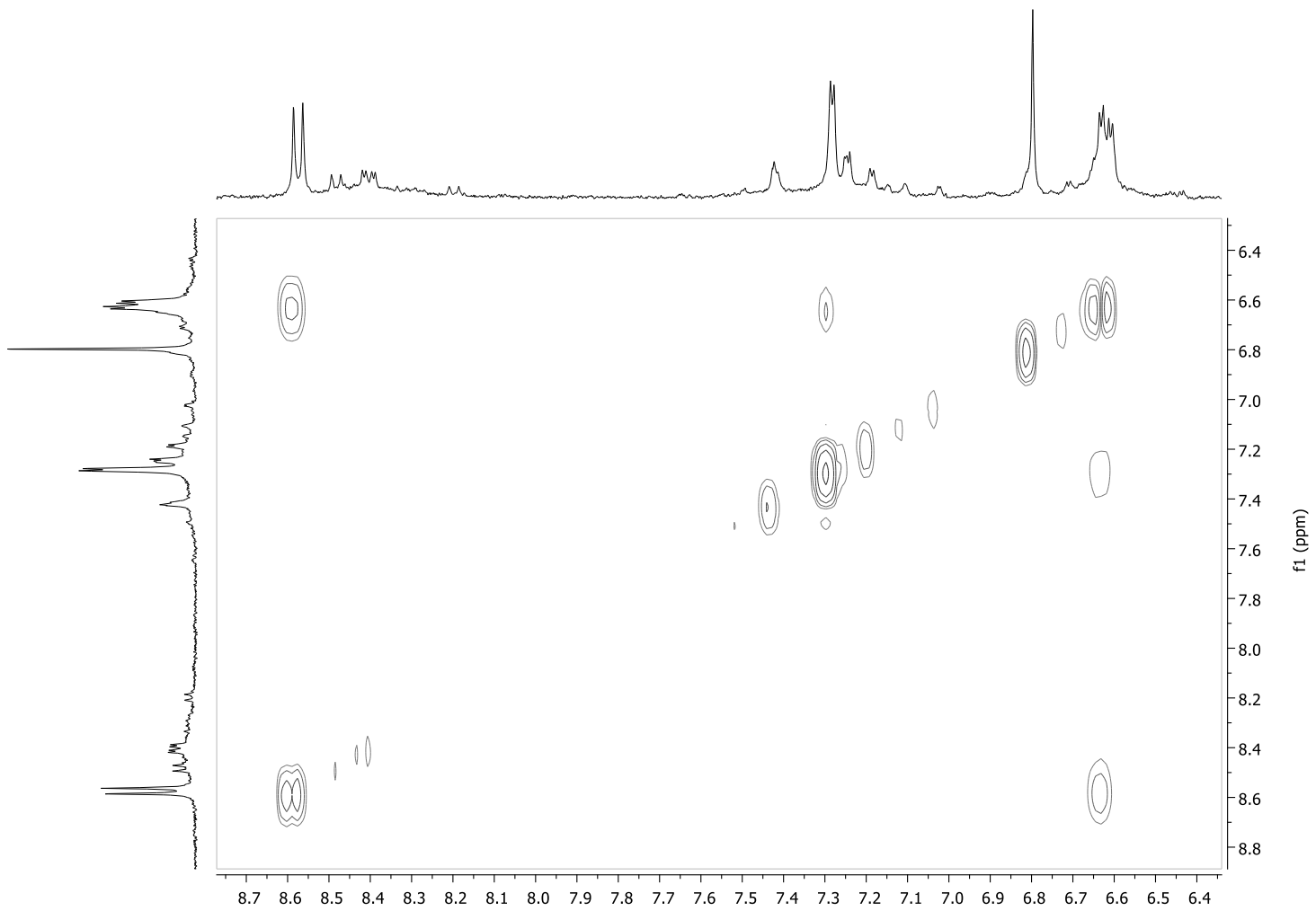


COMPOUND 10

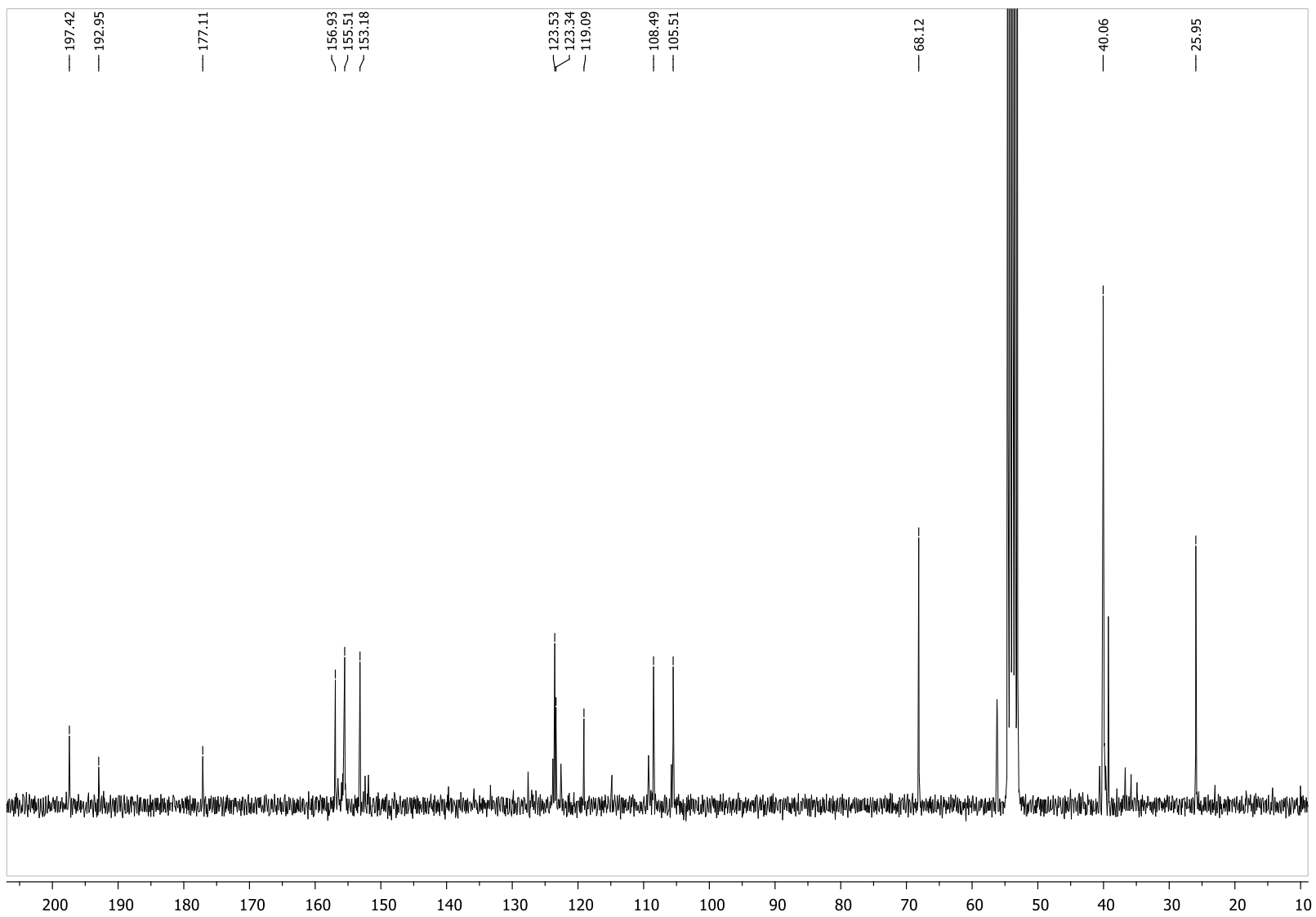
$^1\text{H-RMN}$ (CD_2Cl_2)



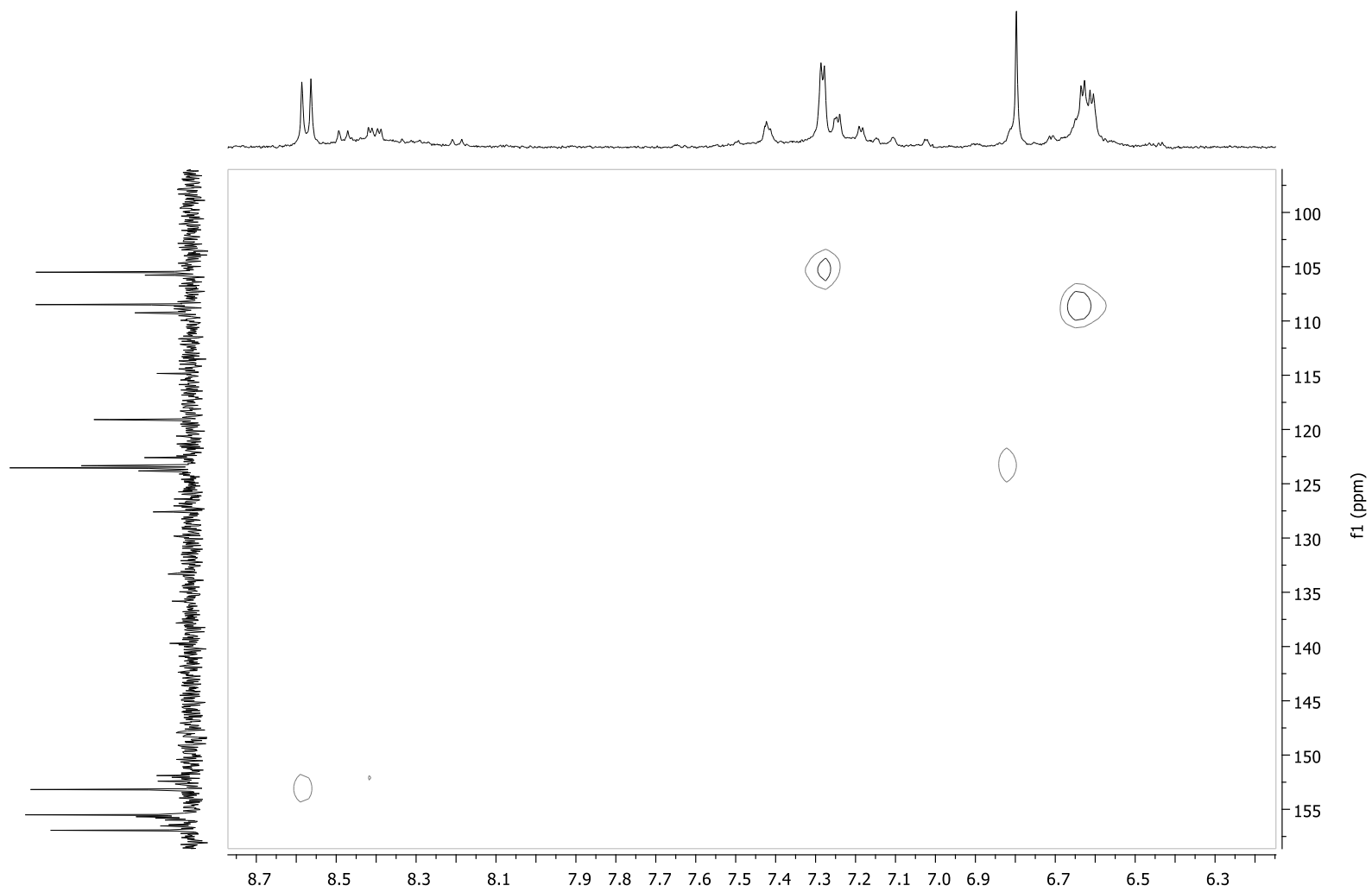
COSY (CD₂Cl₂)



^{13}C -RMN
(CD_2Cl_2)



HSQC (CD₂Cl₂)

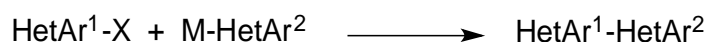


CAPÍTULO 2

Introducción

La formación de enlaces carbono-carbono ha sido, y continúa siendo en la actualidad, uno de los principales objetivos de la síntesis orgánica. Entre una gran variedad de transformaciones sintéticas, las reacciones de acoplamiento catalizadas por metales de transición constituyen uno de los métodos más eficaces para lograr la formación de enlaces C-C. Este tipo de metodología sintética no ha encontrado, sin embargo, una gran aplicación en la formación de enlaces heteroarilo-heteroarilo.⁵⁵

Desde un punto de vista orgánico, las reacciones de acoplamiento de un haluro de heteroarilo con un heteroarilo metálico catalizadas por un metal de transición (del tipo de las reacciones de Negishi y Suzuki, Esquema 2.1) constituyen uno de los principales métodos para sintetizar bi(heteroarilos) simétricos.⁵⁶



Esquema 2.1. Método de acoplamiento cruzado tradicional

Sin embargo, los ejemplos de formación de enlaces heteroarilo-heteroarilo empleando este método son escasos, debido, principalmente, a que gran parte de los derivados organometálicos de heteroarilo, así como los haluros o pseudohaluros de heteroarilo, son difíciles de preparar y frecuentemente muy inestables.⁵⁷

⁵⁵ Una revisión reciente centrada en la síntesis de biheteroarilos por acoplamiento de dos heteroareños se puede encontrar en: D. Zhao, J. You, C. Hu, *Chem. Eur. J.* **2011**, *17*, 5466.

⁵⁶ (a) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359. (b) M. Hapke, L. Brandt, A. Lutzen, *Chem. Soc. Rev.* **2008**, *37*, 2782.

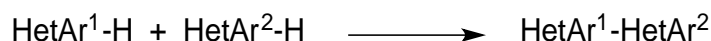
⁵⁷ T. Kinzel, Y. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.* **2010**, *132*, 14073 y referencias allí citadas.

Como consecuencia de ello, gran parte de los esfuerzos de este área se han centrado en el estudio de las reacciones de heteroarilación directa de un enlace Csp²-H de un heteroareno con un haluro o pseudohaluro de heteroarilo (Esquema 2.2). De esta forma sólo es necesaria la prefuncionalización de uno de los dos sustratos que van a experimentar el acoplamiento.⁵⁸



Esquema 2.2. Método de acoplamiento cruzado directo

Finalmente, y llevando esta metodología un paso más allá, en los últimos años se ha conseguido lograr el acoplamiento oxidante de dos heteroarenos sin funcionalizar mediante la activación de dos enlaces CH (Esquema 2.3). Estas reacciones se pueden llevar a cabo en condiciones aeróbicas, o bien empleando un oxidante.⁵⁹



Esquema 2.3. Método de acoplamiento cruzado deshidrogenativo

Si bien esta estrategia sintética sería la ideal para llevar a cabo la síntesis de biheteroarilos asimétricos por acoplamiento cruzado, lo cierto es que continúa siendo objeto de estudio en la actualidad debido a su falta de selectividad, encontrando una gran tendencia al homoacoplamiento cuando los sustratos empleados son muy similares, como por ejemplo, diferentes azoles.⁶⁰

Nos planteamos entonces emplear la coordinación de heterociclos aromáticos a fragmentos metálicos como única prefuncionalización para facilitar el acoplamiento de los mismos. Por un lado, la coordinación al fragmento metálico puede aumentar la acidez de los grupos α-CH haciendo más fácil su desprotonación.⁶¹ Esto daría lugar al sustrato con carácter nucleófilo necesario para llevar a cabo el acoplamiento C-C (sería el equivalente del compuesto organometálico, M-C, en las reacciones clásicas de acoplamiento cruzado). Por otro lado, la coordinación de heterociclos aromáticos puede incrementar su carácter electrófilo, haciéndolos

⁵⁸ Revisiones recientes de este tema son, por ejemplo: (a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174. (b) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (c) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677.

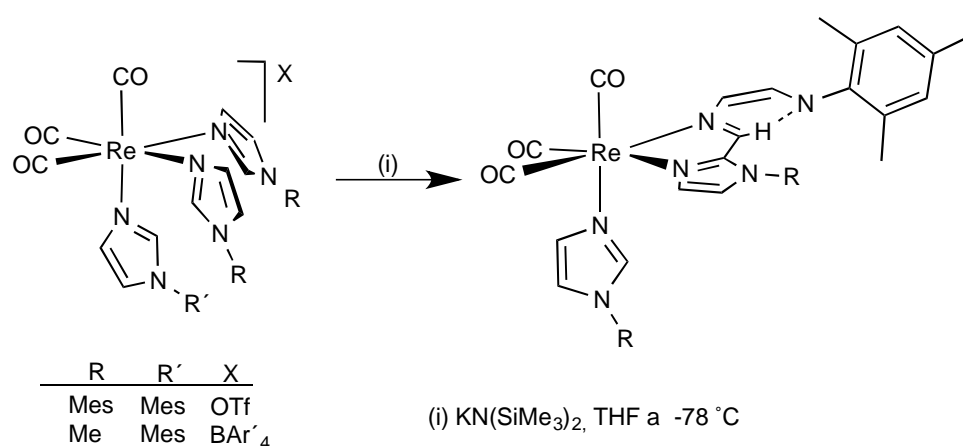
⁵⁹ (a) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 11904. (b) D. R. Stuart, K. Fagnou, *Science* **2007**, *316*, 1172. (c) D. R. Stuart, E. Villemure, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 12072. (d) B. Li, S. L. Tian, Z. Fang, Z. J. Shi, *Angew. Chem. Int. Ed.* **2008**, *47*, 1115. (e) S. J. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254. (f) W. Han, P. Mayer, A. R. Ofial, *Angew. Chem. Int. Ed.* **2011**, *50*, 2178. (g) X. Bugaut, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 7479 y referencias allí citadas.

⁶⁰ (a) Y. Li, J. Jin, W. Qian, W. Bao, *Org. Biomol. Chem.* **2010**, *8*, 326. (b) T. Truong, J. Alvarado, L. D. Tran, O. Daugulis, *Org. Lett.* **2010**, *12*, 1200. (c) D. Monguchi, A. Yamamura, T. Fujiwara, T. Omete, A. Mori, *Tetrahedron Lett.* **2010**, *51*, 850.

⁶¹ E. Buncel, O. Clement, I. Onyido, *J. Am. Chem. Soc.* **1994**, *116*, 2679.

susceptibles de experimentar ataques nucleófilos,⁶² y ejerciendo, por tanto, el papel de los haluros de heterociclo en las reacciones de acoplamiento C-C.

Hay que señalar que ya habíamos notado con anterioridad ambos efectos al estudiar la reactividad de los complejos $[\text{Re}(\text{CO})_3(\text{bipy})(\text{N-RIm})]^+$ (Capítulo 1),^{23a} y también de los complejos $[\text{Re}(\text{CO})_3(\text{N-RIm})_3]^+$ frente a bases fuertes.^{20a,b} Estos últimos merecen una especial atención dado que presentan tres ligandos N-heterocíclicos monodentados coordinados al mismo centro metálico, de manera que el acoplamiento de dos de ellos podría dar lugar a la formación de un biheteroarilo. Sin embargo, esta reactividad no fue la encontrada. La adición de la cantidad equimolar de la base $\text{KN}(\text{SiMe}_3)_2$ a una disolución del compuesto con tres ligandos N-mesitilimidazol da lugar a la desprotonación del grupo C-H central de uno de ellos. Se genera así un carbono muy nucleófilo que ataca al grupo C-H central de otro ligando N-MesIm en disposición *cis*, dando lugar a la formación de un enlace C-C, y a la apertura del anillo heterocíclico que ha sido atacado (Esquema 2.4). Esta reactividad tiene lugar siempre que haya al menos un ligando N-MesIm (que es el que actúa como electrófilo) coordinado al átomo de renio. En el caso del complejo con tres ligandos N-MeIm, como se ha comentado en el Capítulo 1, la reactividad sigue un curso diferente y se obtiene la formación del complejo imidazol-2-ilo.^{20a}

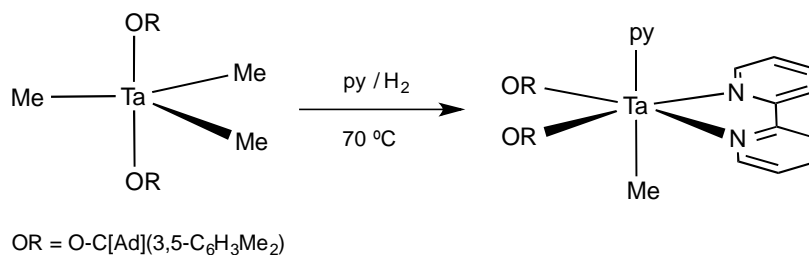


Esquema 2.4. Desprotonación de los complejos $[\text{Re}(\text{CO})_3(\text{N-RIm})_2(\text{N-R}'\text{Im})]\text{X}$

Uno de los escasos ejemplos conocidos de acoplamiento de dos heteroarilos en la esfera de coordinación de un metal es el publicado por Cummins, en el que un complejo de Ta(V) reacciona a elevada temperatura con piridina en un medio reductor (H_2), para dar lugar, al cabo de 5 días, a la formación, en bajo rendimiento, de un complejo de Ta(III) con un ligando bipyridina (Esquema 2.5).⁶³

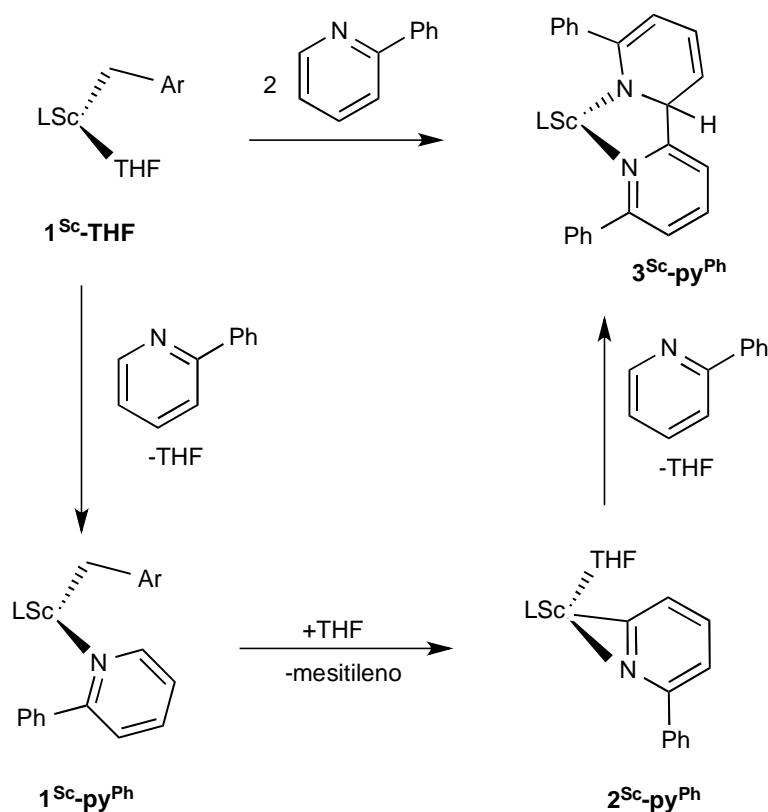
⁶² D. Tzalis, Y. Tor, *Angew. Chem. Int. Ed.* **1997**, 36, 2666.

⁶³ H. S. Soo, P. L. Diaconescu, C. Cummins *Organometallics* **2004**, 23, 498.



Esquema 2.5 Acoplamiento de piridinas estudiado por Cummins

En este contexto hay que mencionar los estudios realizados por Diaconescu y colaboradores en los que logra el acoplamiento de dos unidades de 2-fenilpiridina (2-Phpy) mediado por un complejo de Sc(III).⁴¹ En el Esquema 2.6 se muestra el mecanismo propuesto para esta reacción, que comienza con la activación de un ligando 2-Phpy dando lugar a un complejo de Sc(III) con un ligando $\kappa^2(N,C)$ -piridilo. Cuando esta especie se calienta en presencia de 2-Phpy (1-2 equivalentes) se obtiene el producto de acoplamiento de los dos anillos piridínicos, obteniéndose uno de ellos desaromatizado en el producto final.



Esquema 2.6 Acoplamiento de 2-fenilpiridina mediada por un complejo de Sc(III)

La extensión de estos estudios a otros N-heterociclos aromáticos, como quinolina e isoquinolina, y a complejos análogos de ytrio y lutecio dieron lugar a resultados análogos a los que acabamos de comentar.⁴²

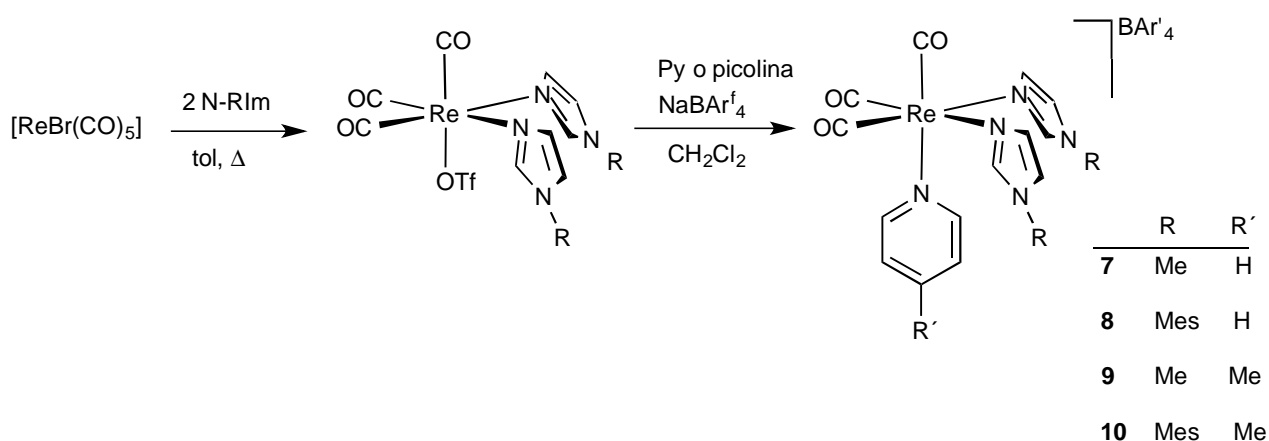
En este Capítulo se recogen los resultados obtenidos al estudiar la reactividad frente a bases fuertes de complejos *fac*-tricarbonílicos de renio con tres ligandos N-heterocíclicos monodentados, siendo al menos uno de ellos un ligando piridínico. El acoplamiento de dos de estos ligandos monodentados podría dar lugar a la formación de biheterociclos desaromatizados en la esfera de coordinación del metal, de manera análoga a los ejemplos publicados por Diaconescu. Nos planteamos entonces, que la acción de un reactivo oxidante podría rearomatizar el ligando bidentado obtenido generando así reacciones de acoplamiento de dos heterociclos aromáticos mediada por un fragmento organometálico.⁶⁴

⁶⁴ (a) M. Espinal Viguri, M. A. Huertos, J. Pérez, L. Riera, I. Ara, *J. Am. Chem. Soc.* **2012**, *134*, 20326. (b) M. Espinal Viguri, J. Pérez, L. Riera, *Chem. Eur. J.* **2014**, *20*, 5732.

Resultados y discusión

En el Capítulo 1 de esta Memoria hemos estudiado la reactividad de los compuestos $[\text{Re}(\text{CO})_3(\text{bipy-R})(\text{N-RIm})]\text{OTf}$ frente a bases fuertes. Decidimos extender este estudio a complejos catiónicos derivados del fragmento $\{\text{Re}(\text{CO})_3\}$ con dos ligandos monodentados (en lugar de bipy) además del N-RIm cuya desprotonación se quiere llevar a cabo. Dado que la reactividad de los compuestos tris(N-alkylimidazol) ya la habíamos llevado a cabo, nos pareció interesante incluir en nuestros derivados, al menos, un ligando piridina.

Los compuestos $[\text{Re}(\text{CO})_3(\text{N-RIm})_2(\text{py-R}')] \text{BAR}^f_4$, ($\text{R} = \text{Me, Mes}$; $\text{R}' = \text{H, Me}$; $\text{Ar}^f = 3,5$ -bis(trifluorometil)fenil) se prepararon mediante sencillas reacciones de sustitución a partir de compuestos fácilmente accesibles como se muestra en el Esquema 2.7. El empleo del tetraarilborato de sodio, NaBAR^f_4 , fue necesario para favorecer la sustitución del ligando triflato por el ligando piridina o picolina (4-metilpiridina).

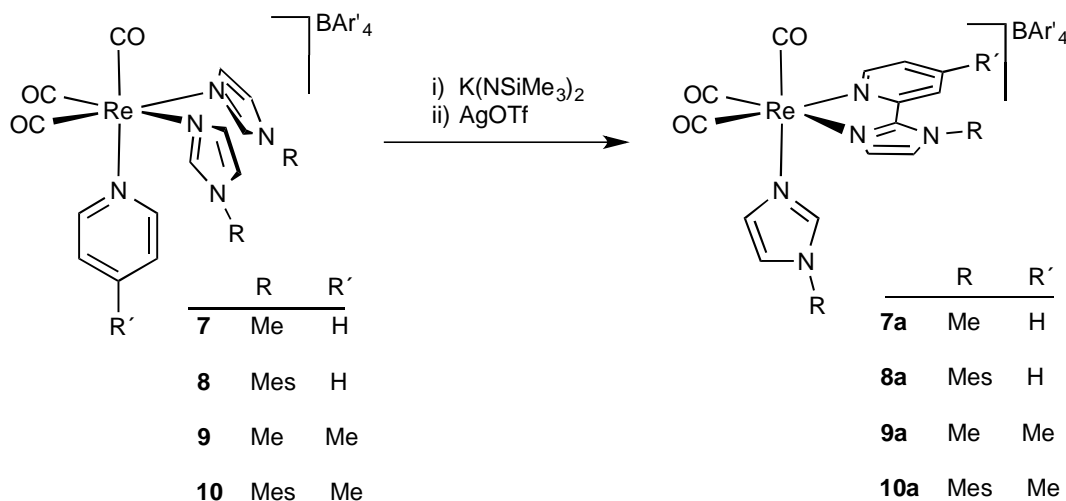


Esquema 2.7 Síntesis de los precursores $[\text{Re}(\text{CO})_3(\text{N-RIm})_2(\text{pyR}')] \text{BAR}^f_4$ (7-10).

Los nuevos compuestos **7-10** se caracterizaron espectroscópicamente en disolución, mostrando en los espectros de IR el patrón típico para un fragmento *fac*-tricarbonílico catiónico de Re(I). Los espectros de ^1H y ^{13}C RMN son consistentes con la estequiometría y geometría propuestas. Así, para todos ellos, la integración de la señales del espectro de ^1H RMN confirma la presencia de un ligando piridínico y de un tetraarilborato por fragmento $\{\text{Re}(\text{CO})_3(\text{N-RIm})_2\}$. Los compuestos **7-10** presentan, además, un plano de simetría que hace equivalentes los dos ligandos N-alquilimidazol y dos de los ligandos carbonilo.

La reacción de los compuestos **7-10** con la base $\text{KN}(\text{SiMe}_3)_2$ en THF a -78°C originó llamativos cambios en el color de las disoluciones, pasando de incoloro a amarillo intenso en todos los casos. El seguimiento de la reacción por espectroscopia IR en la zona de carbonilos muestra que las reacciones tienen lugar de manera prácticamente instantánea, ya que las bandas ν_{CO} aparecen a frecuencias considerablemente menores, lo que resulta coherente con la formación de complejos neutros a partir de catiónicos.

Los compuestos neutros formados resultaron muy inestables para su caracterización en disolución, por lo que se decidió añadir un agente oxidante (AgOTf) para que, en caso de que hubiera tenido lugar una reacción de acoplamiento C-C, se produjera una rearomatización del ligando bidentado formado. La caracterización espectroscópica en disolución de los productos finales (**7a-10a**, Esquema 2.8) mostró que se había producido, en todos los casos, la formación de un ligando 2,2'-piridilimidazol.

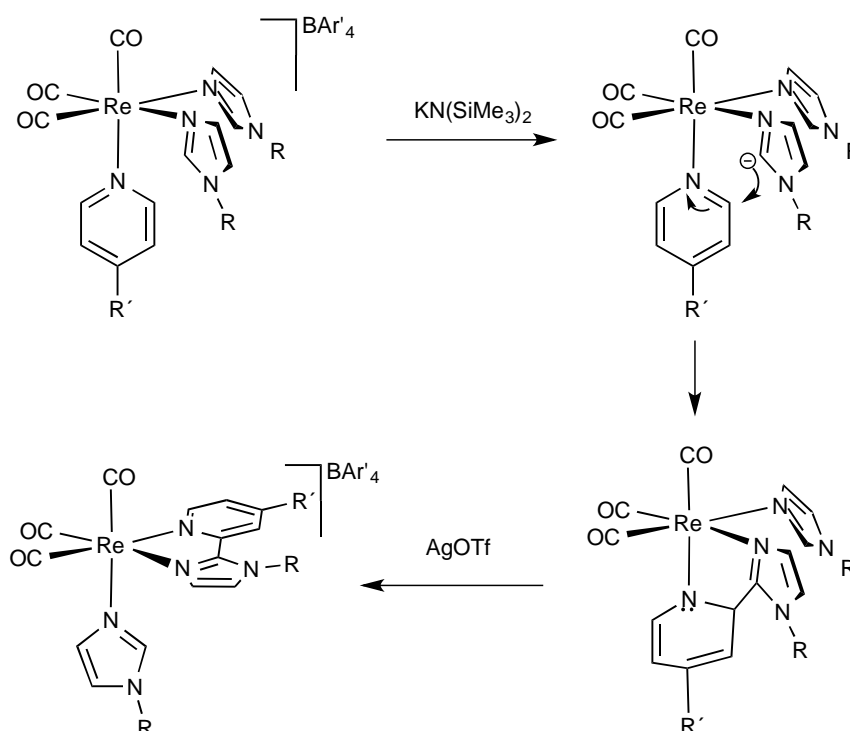


Esquema 2.8 Reactividad de los complejos $[\text{Re}(\text{CO})_3(\text{N-RIm})_2(\text{py-R}')]\text{BAR}'_4$ (**7-10**). Síntesis de los complejos 2,2'-piridilimidazol **7a-10a**

Las estructuras en estado sólido de los compuestos **7a** y **9a** se determinaron mediante difracción de rayos X de monocristal, siendo consistentes con las deducidas a partir de los datos espectroscópicos en disolución. En ellas se observa la presencia de un ligando 2,2'-piridilimidazol aromático, que se forma por el acoplamiento oxidativo del carbono central de imidazol y uno de los carbonos *orto* del ligando piridínico.

Es interesante notar que los compuestos **9** y **10** que contienen un ligando picolina dan lugar a la misma reactividad, no observándose los productos de desprotonación de los grupos metilo a pesar de la conocida acidez del mismo. Es importante comentar también que, para estos compuestos, las características estéricas y electrónicas debidas al sustituyente del imidazol (metilo o mesitilo) no afectan a la naturaleza de los productos de reacción, de manera que se obtiene el mismo patrón de reactividad en todos los casos.

En ausencia de estudios mecanísticos y en vista de los productos resultantes, en el Esquema 2.9 se propone una secuencia de reacciones que explicaría las transformaciones observadas. El primer paso del mecanismo propuesto comprendería la desprotonación del grupo CH central de uno de los ligandos imidazol (pasando de un complejo catiónico a uno neutro, como reflejan los valores ν_{CO} en el espectro de IR) y el ataque nucleofílico del mismo al carbono *orto* de la piridina, resultando así un intermedio en el que se ha producido la formación de un enlace C-C y el ligando piridínico ha perdido su aromaticidad. Esta reactividad sería análoga a la ya comentada en el Capítulo 1 con bipy-R, pero en este caso la elevada inestabilidad de los complejos resultantes no permitió su caracterización en ningún caso. Esta inestabilidad puede que se deba, en parte, a que el ligando que sufre el acoplamiento es una piridina monodentada, que es un ligando menos robusto, y más lábil en comparación con las 2,2'-bipiridinas empleadas en el Capítulo 1. Un segundo paso consistiría entonces en la oxidación del ligando quelato, produciéndose la rearomatización del anillo piridínico para dar lugar a la formación de un ligando bidentado 2,2'-piridilimidazol.



Esquema 2.9 Mecanismo de reacción propuesto para la formación de los compuestos **7a-10a**

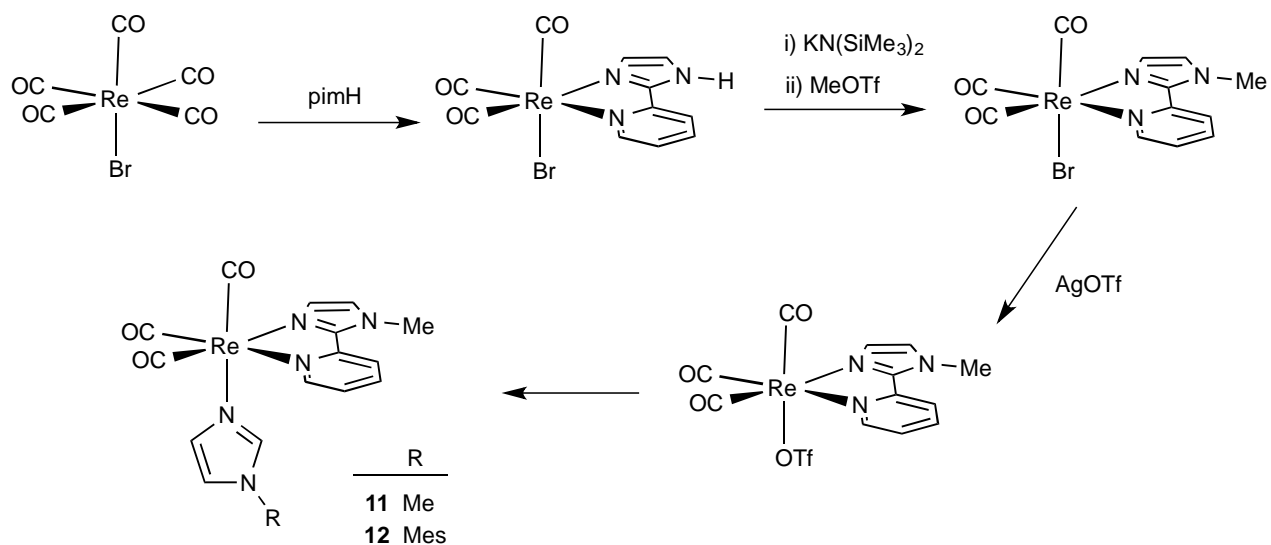
Los compuestos **7a-10a** se obtienen como productos únicos de reacción, no observándose en ningún caso la formación de los productos resultantes del homoacoplamiento (complejos con ligandos 2,2'-biimidazol). Esta reactividad resulta muy interesante, ya que se ha conseguido el acoplamiento cruzado de dos heterociclos aromáticos de forma selectiva con la única prefuncionalización de coordinarlos a un centro metálico. Hasta donde sabemos no existían precedentes de la síntesis de ligandos 2,2'-piridilimidazol mediada por un fragmento metálico, y, de hecho, sólo se conocen unos pocos ejemplos de síntesis de ligandos bidentados por acoplamiento de dos ligandos monodentados.⁶⁵

Por otra parte, los compuestos **7a-10a** presentan ciertas similitudes con los compuestos $[\text{Re}(\text{CO})_3(\text{bipy})(\text{N-RIm})]\text{OTf}$, ya que ambos tipos de compuestos contienen un ligando imidazol y una diimina coordinada en forma quelato al mismo centro metálico, ocupando conjuntamente una disposición facial. Se trata en ambos casos, además, de complejos catiónicos con el fragmento $\{\text{Re}(\text{CO})_3\}$. Nos planteamos entonces comprobar si los compuestos **7a-10a** se comportan frente a una base fuerte de manera análoga a la encontrada para los derivados con bipy.

Si bien habíamos obtenido los compuestos con ligandos 2,2'-piridilimidazol mediante una reacción de acoplamiento cruzado entre un ligando piridina y un imidazol, para el estudio de su reactividad preparamos de manera alternativa los compuestos derivados del 2-(2'-piridil)-1-Me-imidazol (pimMe) de fórmula $[\text{Re}(\text{CO})_3(\text{N-RIm})(\text{pimMe})]\text{OTf}$ (R= Me, **11**; Mes, **12**) a partir del ligando comercial 2-(2'-piridil)-1H-imidazol (pimH), como se muestra en el Esquema 2.10.⁶⁶ Para el compuesto $[\text{Re}(\text{CO})_3(\text{N-MesIm})(\text{pimMes})]\text{BAr}_4^f$ (**8a**), del que también estudiaremos su reactividad, no encontramos, en cambio, una síntesis alternativa mejor, pues no es sencillo realizar la sustitución del hidrógeno por el grupo mesitilo en el pimH.

⁶⁵ D. Lorcy, M. Guerro, P. Pellon, R. Carlier, *Chem. Commun.* **2004**, 212. C. T. Carver, B. N. Williams, K. R. Ogilby, P. L. Diaconescu, *Organometallics* **2010**, *29*, 835. Refs 64, 42, 35.

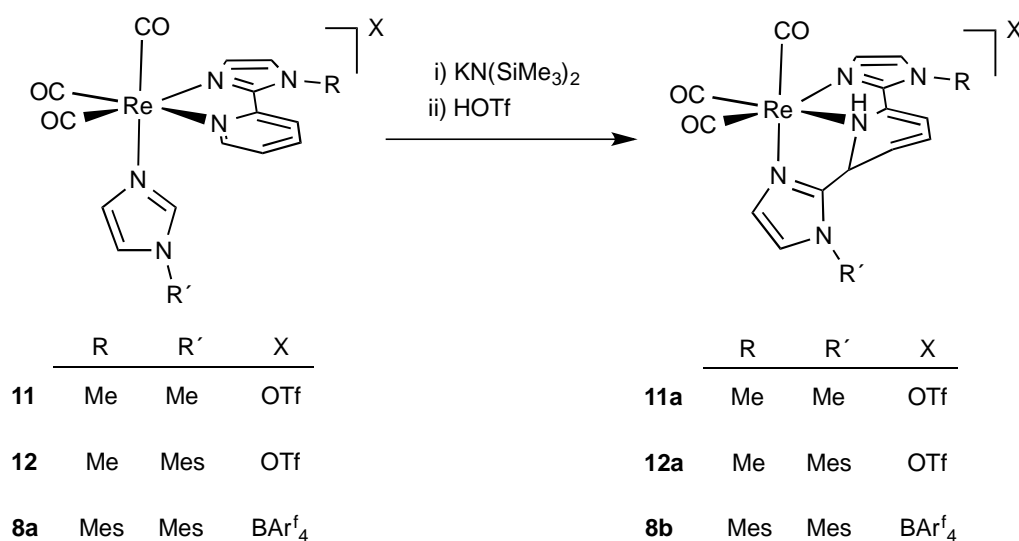
⁶⁶ El procedimiento descrito para la síntesis de 2-(2'-piridil)-1-metilimidazol presenta algunos inconvenientes, como es la necesidad de mantener la temperatura alta durante tiempo prolongado, purificar mediante destilación y rendimiento moderado. Ver T. I. A. Gerber, E. Hosten, P. Mayer, Z. R. Tshentu, *J. Coord. Chem.* **2006**, *59*, 243.



Esquema 2.10 Preparación de los complejos **11** y **12**

Cuando se hizo reaccionar los compuestos **8a**, **11** y **12** en THF a -78°C con $\text{KN}(\text{SiMe}_3)_2$ se observó que las bandas de IR en la zona de los carbonilos disminuían considerablemente, lo que es consistente con la desprotonación de los mismos.

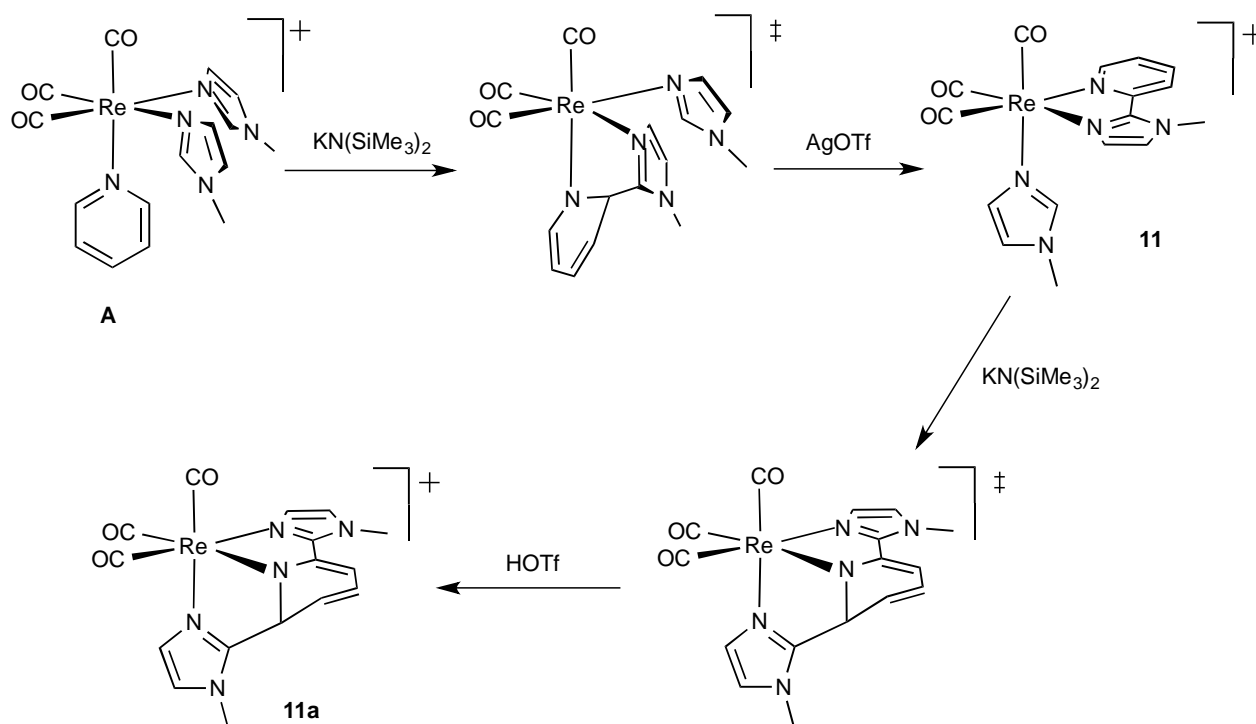
La baja estabilidad de estos derivados neutros sólo resultó suficiente para caracterizar en disolución mediante ^1H RMN y ^{13}C RMN el complejo **12*** (complejo **12** desprotonado), encontrándose que el anillo piridínico del ligando piridilimidazol se ha desaromatizado, lo que se atribuye al acoplamiento C-C entre el carbono central del imidazol y el anillo piridínico. La posterior adición de HOTf dio lugar a un aumento en el número de ondas de las bandas ν_{CO} en el infrarrojo consistente con la protonación de los derivados neutros (Esquema 2.11).



Esquema 2.11 Síntesis de los compuestos **11a**, **12a** y **8b**

Los datos espectroscópicos en disolución de los nuevos compuestos **8b**, **11a** y **12a** permiten proponer que, una vez desprotonado el grupo CH central del imidazol, este ataca al carbono *orto* del anillo piridínico del 2,2'-piridilimidazol dando lugar al producto de acoplamiento C-C y desaromatización. En la etapa posterior, el átomo de nitrógeno inicialmente piridínico sería protonado por el ácido trifílico dando lugar a la formación de los complejos finales, catiónicos y más estables.

La reactividad de los compuestos de fórmula general $[\text{Re}(\text{CO})_3(\text{N-RIm})(\text{pim-R}')]\text{X}$ es por tanto análoga a la de los compuestos $[\text{Re}(\text{CO})_3(\text{N-N})(\text{N-MesIm})]\text{OTf}$ (N-N= bipy, bipy-^tBu o phen). Si bien podría pensarse que el ataque a la piridina está más favorecido por ser un grupo con menos densidad electrónica que el imidazol, el ataque a este último ya se había observado para el complejo $[\text{Re}(\text{CO})_3(\text{N-MesIm})_3]^+$ en el que, como ya hemos comentado, se produce el ataque del imidazol desprotonado sobre otro de los ligandos N-MesIm, para dar lugar al producto de apertura del heterociclo.^{20a} No se observa tampoco en este tipo de complejos el ataque del imidazol desprotonado al metal para dar lugar a la formación de complejos 2-imidazolilo.



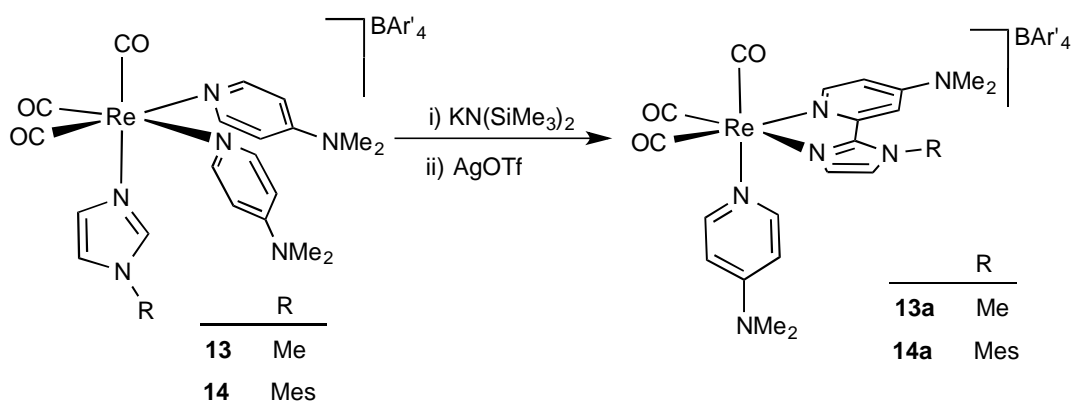
Esquema 2.12 Síntesis del compuesto **11a** a partir del derivado catiónico $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{py})]^+$

Es interesante considerar, como se muestra en el Esquema 2.12, la reacción completa de formación del compuesto **11a** a partir del complejo catiónico con tres ligandos N-heterocíclicos monodentados $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{py})]^+$ (**A**). En una primera etapa, hasta la formación del complejo con el ligando 2,2'-piridilimidazol (**11**), se produce la activación de un enlace $\text{C}_{\text{orto}}\text{-H}$ de un ligando piridina sin funcionalizar. La segunda parte de la reacción consiste en activar el segundo grupo $\text{C}_{\text{orto}}\text{-H}$ del mismo ligando piridina, lo que bajo nuestro punto de vista es aun más

interesante. Es decir, si se considera la formación del compuesto **11a** a partir de **A** se puede apreciar claramente que se ha conseguido, en condiciones suaves, la activación consecutiva de los dos hidrógenos *orto* de un ligando piridina.

Se extendió a continuación el estudio de este tipo de reactividad a los compuestos análogos derivados del fragmento *fac*-{Re(CO)₃} con dos ligandos piridínicos y un imidazol. Para evitar que los ligandos imidazol desplazaran de la esfera de coordinación del renio a los ligandos piridínicos (considerablemente más lábiles), fue necesario emplear la 4-dimetilaminopiridina (DMAP). Los compuestos [Re(CO)₃(DMAP)₂(N-RIm)]BAR'₄, (R= Me (**13**) y Mes (**14**)) se prepararon análogamente a como se ha descrito para los compuestos con dos ligandos imidazol y un ligando piridina (**7-10**, Esquema 2.8).

La reacción de **13** y **14** con la cantidad estequiométrica de KN(SiMe₃)₂ y, seguidamente, el tratamiento de las especies neutras resultantes con AgOTf, dio lugar a la formación de los compuestos **13a** y **14a**, respectivamente, con ligandos 2,2'-piridilimidazol (Esquema 2.13).



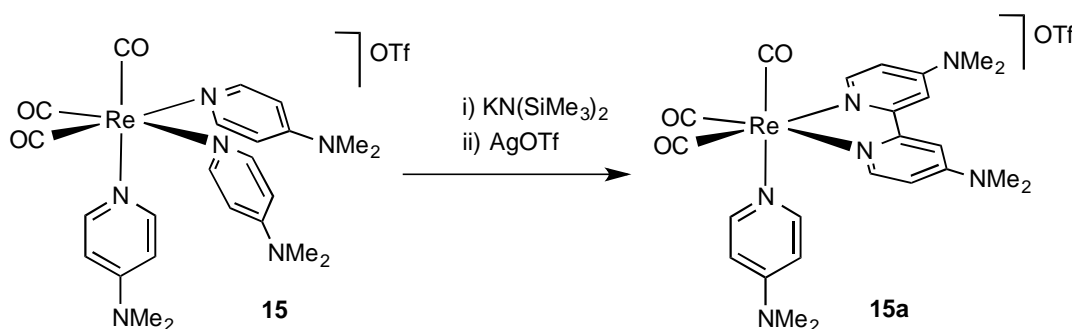
Esquema 2.13 Reactividad de los compuestos [Re(CO)₃(DMAP)₂(N-RIm)]BAR'₄ (**13** y **14**).

Se puede concluir, por tanto, que, independientemente de la composición de los complejos empleados (dos imidazoles y una piridina, o bien dos piridinas y un imidazol), se produce la desprotonación selectiva de un ligando imidazol como resultado de la mayor acidez del grupo CH central del mismo. Además, el 2-imidazolilo así formado ataca también de manera selectiva a una piridina, lo que muestra el mayor carácter electrófilo de las mismas con respecto a los imidazoles. Este patrón de reactividad se mantiene empleando distintos imidazoles (N-MeIm, N-MesIm) y diferentes piridinas, lo que indica que tiene cierta generalidad.

Teniendo en cuenta los resultados comentados hasta ahora en este Capítulo, se consideró interesante extender esta reactividad a los compuestos con tres ligandos piridínicos [Re(CO)₃(py-R')₃]OTf que, de comportarse de forma análoga a los anteriores, darían lugar a una síntesis alternativa de ligandos bipyridina (pudiendo éstas estar sustituidas en diferentes posiciones de sus anillos aromáticos). En principio cabría esperar que la desprotonación inicial fuera más difícil que

en el caso de un ligando N-RIm, debido a la menor acidez de los grupos CH de la piridina,⁶⁷ y a que son ligandos mucho más lábiles, lo que podría dar lugar a reacciones secundarias no deseadas.

En primer lugar, empleamos como compuesto de partida el derivado con tres ligandos DMAP, pues esta piridina ya había mostrado ser lo suficientemente inerte a la sustitución para este tipo de reacciones. La adición de un ligero exceso de $\text{KN}(\text{SiMe}_3)_2$ a una disolución del compuesto $[\text{Re}(\text{CO})_3(\text{DMAP})_3]\text{OTf}$ (**15**),⁶⁸ en THF a baja temperatura origina un cambio de color de incoloro a morado intenso. La posterior adición de AgOTf al crudo de reacción origina un único complejo catiónico, **15a**, como queda reflejado en el aumento del número de ondas de las bandas en la zona de carbonilos del espectro IR. Los datos espectroscópicos en disolución de **15a** indican que se ha producido una reacción de acoplamiento C-C y la posterior rearomatización del ligando bidentado quelato formado (Esquema 2.14). Así, en los espectros de ^1H y ^{13}C RMN se observa claramente la presencia de un ligando 4,4'-dimetilamino-2,2'-bipiridina simétrico, además de un ligando DMAP que permanece inalterado.



Esquema 2.14 Reactividad del compuesto $[\text{Re}(\text{CO})_3(\text{DMAP})_3]\text{OTf}$ (**15**)

La formación del ligando 2,2'-bipiridina en la esfera de coordinación del renio se confirmó al determinar la estructura en estado sólido de **15a** mediante difracción de rayos X de monocristal. Una representación gráfica de la estructura del catión del compuesto **15a** se muestra en la Figura 2.1, y en la Tabla 2.1 están recogidas las distancias y ángulos de enlace más significativos.

⁶⁷ K. Shen, Y. Fu, J. N. Li, L. Liu, Q. X. Guo, *Tetrahedron* **2007**, 63, 1568.

⁶⁸ Sintetizado por reacción de $[\text{Re}(\text{OTf})(\text{CO})_5]$ y DMAP en tolueno a reflujo durante 4 h.

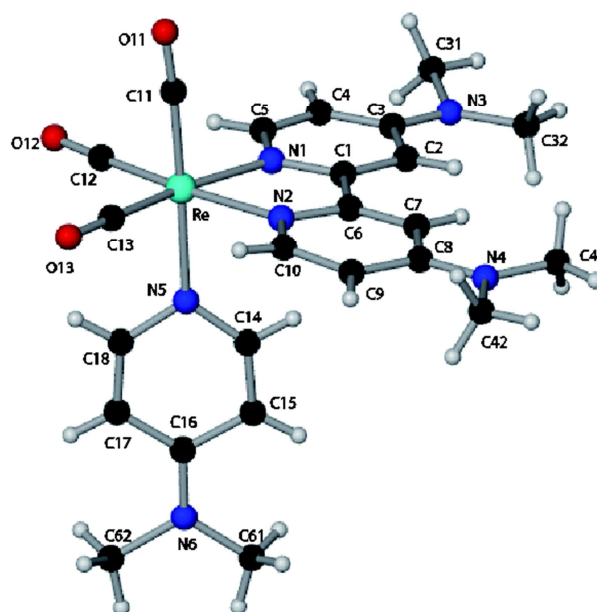


Figura 2.1 Estructura en estado sólido del catión presente en el compuesto **15a**

Distancias de enlace (Å)			
Re(01)-C(13)	1.89(2)	C(6)-C(1)	1.52(2)
Re(01)-C(12)	1.90(2)	C(10)-C(9)	1.32(2)
Re(01)-C(11)	1.88(2)	C(9)-C(8)	1.36(2)
Re(01)-N(1)	2.13(1)	C(8)-C(7)	1.50(2)
Re(01)-N(2)	2.13(1)	C(7)-C(6)	1.38(2)
Re(01)-N(5)	2.20(1)	C(5)-C(4)	1.41(2)
N(2)-C(10)	1.38(2)	C(4)-C(3)	1.38(2)
N(2)-C(6)	1.35(2)	C(3)-C(2)	1.40(2)
N(1)-C(1)	1.36(2)	C(2)-C(1)	1.37(2)
N(1)-C(5)	1.39(2)		

Ángulos de enlace (°)			
O(13)-C(13)-Re(01)	177(2)	C(1)-N(1)-C(5)	115.1(3)
O(12)-C(12)-Re(01)	179(2)	C(1)-N(1)-Re(01)	120.2(9)
O(11)-C(11)-Re(01)	175(1)	C(5)-N(1)-Re(01)	125(1)
N(1)-Re(01)-N(2)	73.8(4)	N(2)-C(6)-C(1)	112(1)
N(1)-Re(01)-N(5)	86.3(4)	C(7)-C(6)-C(1)	122(1)
N(2)-Re(01)-N(5)	86.6(4)	N(2)-C(6)-C(7)	126(1)
N(1)-C(1)-C(2)	124(1)	C(6)-N(2)-C(10)	114(1)
N(1)-C(1)-C(6)	113(1)	C(6)-N(2)-Re(01)	121.0(9)
C(2)-C(1)-C(6)	123(1)	C(10)-N(2)-Re(01)	125(1)

Tabla 2.1 Distancias (Å) y ángulos (°) de enlace seleccionados del compuesto **15a**

Como se observa en la Figura 2.1 el complejo catiónico presente en **15a** está constituido por un fragmento *fac*-{Re(CO)₃} al que se encuentran coordinados dos ligandos aromáticos N-dadores: un ligando DMAP monodentado coordinado de la forma más habitual, a través del átomo de nitrógeno piridínico, y un ligando bidentado quelato, que es una 2,2'-bipiridina. Esta última resulta del acoplamiento de dos anillos piridínicos y posterior rearomatización de uno de los mismos. El acoplamiento tiene lugar entre dos carbonos *orto*, siendo la distancia C1-C6 característica de un enlace sencillo.

Aunque la desprotonación de la posición *orto* de una piridina es una reacción conocida, presenta algunos problemas fundamentales, pues los reactivos empleados como bases pueden adicionarse a la posición *orto* del anillo de piridina. En particular, la desprotonación de DMAP libre es especialmente difícil y no se consiguió llevar a cabo hasta 2002,⁶⁹ aunque es interesante notar que previamente se había conseguido la desprotonación de DMAP coordinada a BF₃.⁷⁰ Por otro lado, Davies y Shipton demostraron que la coordinación κ^6 de piridina a un fragmento Cr(CO)₃ permite una desprotonación selectiva de la posición *orto* de la misma,⁷¹ y grupos como los de Harman,⁷² Diaconescu y Carmona han encontrado que la coordinación κ^2 -(C,N) de derivados piridínicos a fragmentos metálicos pobres en densidad electrónica activa el anillo

⁶⁹ D. Cuperly, P. Gros, Y. Fort, *J. Org. Chem.* **2002**, *67*, 238.

⁷⁰ T. Sammakia, T. Hurley, *J. Org. Chem.* **1999**, *64*, 4652.

⁷¹ S. G. Davies, M. R. Shipton, *J. Chem. Soc. Perkin Trans 1* **1991**, 501.

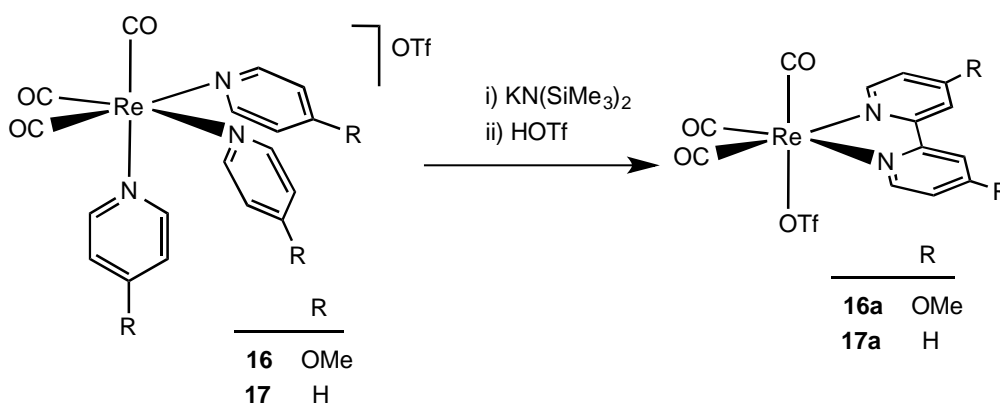
⁷² D. P. Harrison, V. E. Zottig, G. W. Kosturko, K. D. Welch, M. Sabat, W. H. Myers, W. D. Harman, *Organometallics* **2009**, *28*, 5682.

respecto del ataque nucleófilo sobre la posición *orto*. Sin embargo, la desprotonación de piridinas coordinadas a centros metálicos en el modo “normal” κ^1 -(*N*) carecía de precedentes.

Extendimos a continuación el estudio a otros derivados tris(piridilo) del fragmento *fac*-{Re(CO)₃}. Decidimos emplear para ello piridina y 4-metoxipiridina (py-OMe) como ligandos, la primera por el interés intrínseco de desprotonar una piridina simple, sin sustituir y por ser un ligando tan ampliamente empleado, y la segunda por poseer propiedades electrónicas intermedias entre DMAP y piridina.

La síntesis de los compuestos [Re(CO)₃(py-R)₃]OTf (R= OMe, **16**; H, **17**) se llevó a cabo siguiendo el método descrito previamente en la bibliografía para este tipo de derivados, por sustitución de los ligandos dimetilsulfóxido (DMSO) en el complejo [Re(CO)₃(DMSO)₃]OTf.⁷³

La reactividad de los compuestos **16** y **17** con el amiduro de potasio y HOTf da lugar a la formación de los complejos bipyridina **16a** y **17a**, en buen rendimiento y como únicos productos de reacción (Esquema 2.15).⁷⁴



Esquema 2.15 Reactividad de los compuestos [Re(CO)₃(py-R)₃]OTf (**16** y **17**)

Para estos compuestos el ligando piridina o 4-metoxipiridina que no participa en la reacción de acoplamiento se ve desplazado por el ligando triflato de la esfera de coordinación del renio. Esto puede deberse a la labilidad de estos ligandos monodentados, y podría ser también el factor responsable de que en estos ejemplos el ácido triflico haya dado lugar a resultados más satisfactorios que el empleo de otros agentes oxidantes (yodo, tetrafluoroborato de ferricinio, triflato de plata o “*azul mágico*”).

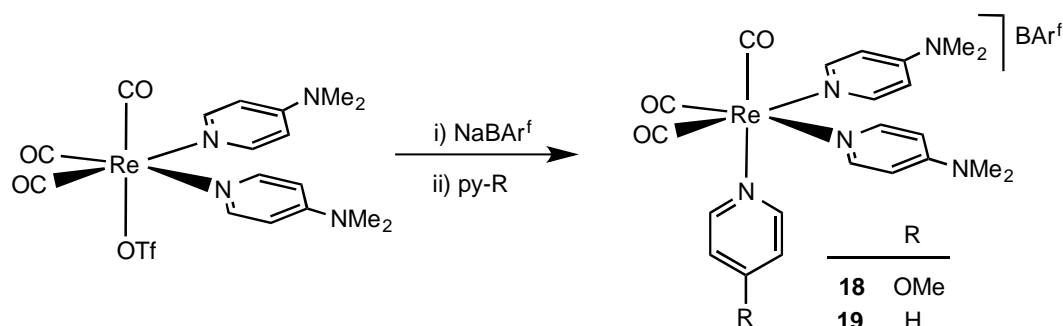
Finalmente nos planteamos la síntesis de un ligando 2,2'-bipiridina 4,4'-disustituido asimétrico por acoplamiento de dos ligandos piridínicos de diferente naturaleza, es decir, nos propusimos

⁷³ M. Casanova, E. Zangrando, F. Munini, E. Iengo, E. Alessio, *Dalton Trans.* **2006**, 5033.

⁷⁴ El compuesto [Re(OTf)(CO)₃(bipy)] es bien conocido, y sus datos espectroscópicos en disolución coinciden con los previamente publicados: ver ref. 46f.

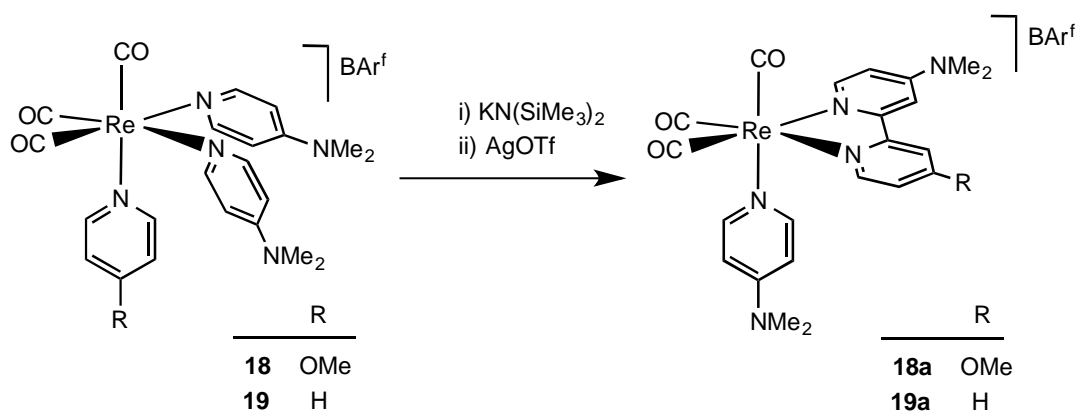
aplicar la reactividad discutida hasta ahora para lograr el acoplamiento cruzado selectivo de dos ligandos piridilo coordinados al fragmento *fac*-{Re(CO)₃}.

La síntesis de estos compuestos con más de un tipo de ligando piridínico coordinado al mismo fragmento metálico se llevó a cabo a partir del complejo [Re(OTf)(CO)₃(DMAP)₂] mediante la sustitución del triflato, en presencia de la sal NaBAR^f₄, por el ligando piridínico correspondiente (Esquema 2.16).



Esquema 2.16 Síntesis de los compuestos [Re(CO)₃(DMAP)₂(py-R)]BAR^f₄ (**18**, **19**)

De manera análoga a la reactividad descrita previamente, llevamos a cabo el acoplamiento oxidante de dos ligandos piridínicos mediante el tratamiento de los compuestos mixtos **18** y **19** con KN(SiMe₃)₂, y a continuación con AgOTf. Los nuevos compuestos, **18a** y **19a**, respectivamente, se obtienen como únicos productos de la reacción y en buen rendimiento (Esquema 2.17).



Esquema 2.17 Síntesis del compuesto **18a** y **19a**

El primer aspecto a destacar de los espectros de ¹H RMN y ¹³C RMN de ambos compuestos es que muestran la pérdida de la simetría existente en los complejos de partida, lo que claramente indica que el acoplamiento ha tenido lugar entre dos ligandos piridínicos diferentes, dando lugar a la formación de un ligando 2,2'-bipiridina asimétrico.

Es interesante notar que la formación de estos compuestos implica que ha tenido lugar una reacción de acoplamiento cruzado entre dos ligandos piridina de manera selectiva, no observándose la formación de productos de homoacoplamiento (serían los complejos con un ligando 4,4'-bis(dimetilamino)-2,2'-bipiridina).

Debe notarse que entre las principales aplicaciones de los piridilimidazoles y las 2,2'-bipiridinas se encuentra su empleo como ligandos, y que entre las familias de complejos de elementos de transición con ligandos aromáticos bidentados N-dadores, los que contienen el fragmento *fac*-{Re(CO)₃} son de los que más se emplean en diferentes áreas de la química de coordinación, por su propiedades de luminiscencia y su aplicación en química supramolecular, química bioinorgánica y catálisis.⁷⁵ Justamente son éstos los complejos con los que hemos llevado a cabo las reacciones de acoplamiento. Por ello, aunque la desmetalación de los ligandos resultantes del acoplamiento será, previsiblemente, muy difícil, dado que se trata de quelatos muy robustos, la obtención de los complejos de renio posee un interés sintético claro.

⁷⁵ Ver, por ejemplo, refs 24e, 24f, 25d, 25e, 26a, 26c

ARTÍCULOS

Re-Mediated C–C Coupling of Pyridines and Imidazoles

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Supporting Information

ABSTRACT: Rhenium tricarbonyl complexes with three *N*-heterocyclic ligands (*N*-alkylimidazoles or pyridines) undergo deprotonation with KN(SiMe₃)₂ and then oxidation with AgOTf to afford complexes with pyridylimidazole or bipyridine bidentate ligands resulting from deprotonation, C–C coupling and rearomatization.

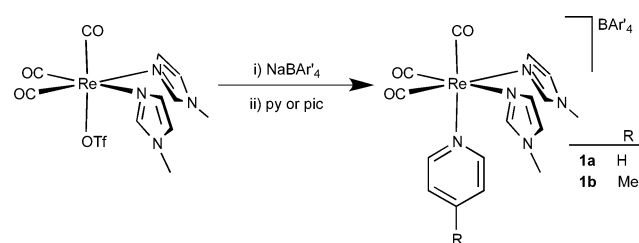
Heteroaromatic biaryls are important structural motifs found in many natural products, pharmaceuticals, agrochemicals, and functional materials.¹ Classical palladium-catalyzed cross-coupling methods require previously activated substrates, a heteroaryl halide and an organometallic species.² In the last years, catalytic direct arylations have emerged which avoid the introduction of functional groups by C–H activation prior to cross-coupling of at least one of the two coupling partners.³ This strategy is especially useful for heteroaromatic substrates as their prefunctionalizations are often difficult (organometallic derivatives are often troublesome to prepare and unstable).⁴ Recently, this concept has been developed one step further designing dehydrogenative cross-coupling of two heteroarenes.⁵ However, to date, efficient C–H/C–H cross-coupling between very similar partners remains a challenge because of their tendency to undergo homocoupling.⁶

Herein, we report the metal-templated synthesis of (a) pyridylimidazole complexes by selective cross-coupling of pyridines and imidazoles, and (b) 2,2'-bipyridine complexes by C–C coupling of two pyridyl ligands. In both cases, coordination to the same organometallic fragment is the only previous functionalization.

Metal coordination of *N*-heterocycles can increase the acidity of their α -CH groups,⁷ and make them more electrophilic.⁸ We decided to explore if the combination of both features could be used to effect C–C coupling between two *N*-heterocyclic ligands coordinated to the same metal fragment.

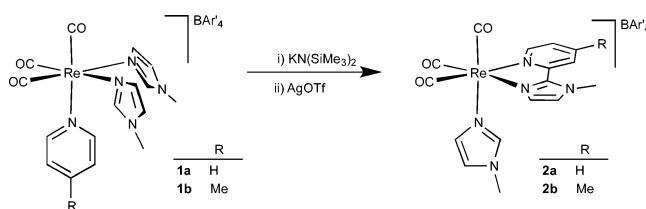
The reaction of [Re(OTf)(CO)₃(*N*-MeIm)₂] (*N*-MeIm = *N*-methylimidazole) with the equimolar amount of NaBAR'₄ (Ar' = 3, 5-bis(trifluoromethyl)phenyl)⁹ and either pyridine (py) or γ -picoline (pic) afforded the new compounds [Re(CO)₃(*N*-MeIm)₂(pyR)]BAR'₄ (R = H, **1a**; Me, **1b**; see Scheme 1), which were characterized by IR, and NMR.¹⁰ The IR spectra showed the typical two intense ν_{CO} bands pattern for *fac*-{Re(CO)₃} complexes (e.g., at 2028 and 1914 cm⁻¹ for **1a**). ¹H and ¹³C NMR spectra indicate the incorporation of one pyridinic ligand per rhenium fragment.

Scheme 1. Synthesis of [Re(CO)₃(*N*-MeIm)₂(pyR)]BAR'₄ Compounds



When compound **1a** was treated with KN(SiMe₃)₂ in THF at –78 °C, a neutral product was formed, as shown by a large shift to lower wavenumbers of the ν_{CO} IR (to 2004, 1890, and 1877 cm⁻¹), which was too unstable for isolation. Addition of silver trifluoromethanesulfonate afforded compound **2a** along with metallic silver (Scheme 2).

Scheme 2. Reactivity of [Re(CO)₃(*N*-MeIm)₂(pyR)]BAR'₄ Compounds



The solid-state structure of **2a**, determined by X-ray diffraction (see Figure 1a),¹¹ despite its low quality, shows that the cationic complex consists of a *fac*-{Re^I(CO)₃} fragment bonded to *N*-MeIm, and 2-pyridylimidazole ligands. The latter results from the C–C coupling of the imidazole C2, once deprotonated, and one pyridine C_{ortho} followed by oxidative rearomatization. Pyridylimidazoles, usually synthesized via de novo construction of the imidazole ring,¹² are used as ligands in the preparation of luminescent complexes, including two rhenium tricarbonyl examples.¹³ The γ -picoline derivative **1b** afforded, under the same reaction conditions, complex **2b**, which was fully characterized, including an X-ray structure determination (Figure 1b),¹⁴ that confirms the formation of the bidentate ligand. No side reactions affecting the methyl group

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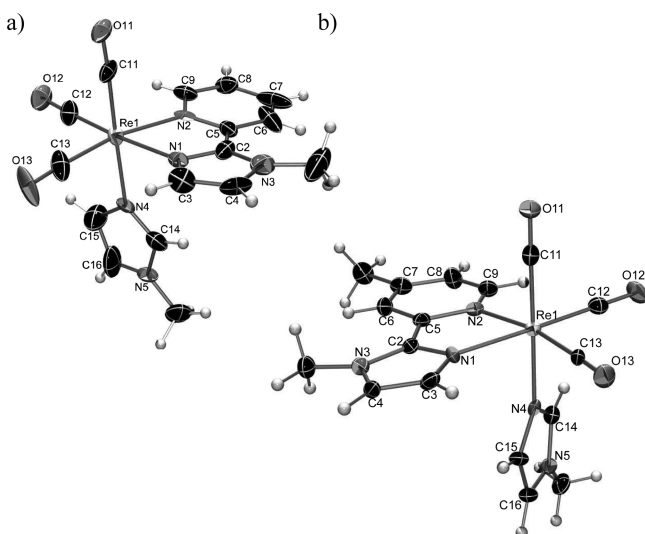


Figure 1. (a) Molecular structure of the cationic complex of **2a**; (b) molecular structure of the cation in **2b**.

of the γ -picoline unit were detected. The pyridine and imidazole rings are planar, as expected, and nearly coplanar, with a dihedral angle of $4.1(0.4)^\circ$. The Re–N(1) [2.180(6) Å] is longer than the Re–N(2) bond distance [2.132(5) Å], reflecting the stronger basicity of the imidazole and both distances are virtually identical to those found for the only pyridylimidazole rhenium(I) compound structurally characterized.^{13a}

A growing number of pyridylimidazole complexes are known; however, their chemistry remains somewhat underdeveloped as a result of synthetic difficulties.¹⁵ No precedent of their metal-templated synthesis has been reported, and the synthesis of bidentate ligands via C–C coupling of monodentate ligands remains rare.¹⁶ The highly reactive Sc(III) complex [(NN^{fc})Sc(η^2 -N,C-1-methylimidazolyl)(N-MeIm)] (NN^{fc} = fc-(NSi^tBuMe₂)₂, fc = 1,1'-ferrocenylene) does not react with pyridines, but does react with 2,2'-bipyridine to yield the coupled product which does not undergo further transformation (rearomatization or ring-opening) even upon prolonged heating.^{16c}

To test the generality of the reaction, we extended our study to the bis(pyridyl) complex [Re(CO)₃(dmap)₂(N-MeIm)]-BAR'₄ (dmap = 4-dimethylaminopyridine, **3**).¹⁰ Treatment of **3** with the stoichiometric amount of KN(SiMe₃)₂ in THF at -78°C followed by reaction with AgOTf yielded the cationic pyridylimidazole complex **4**, analogously to the formation of **2a** and **2b**. This shows that the employment of the more electron-rich dmap ligand did not prevent the proposed (see below) nucleophilic attack of the imidazol-2-yl, and the formation of pyridylimidazole ligand.

Note that, regardless of the particular composition of the cationic complex (two imidazoles and one pyridine, as in **1a,b** or one imidazole and two pyridines, as in **3**), no homocoupling products (containing biimidazole or bipyridine chelates) have been detected, suggesting a clear-cut difference between the two type of ligands in that *N*-methylimidazole is significantly more acidic, and pyridines are more electrophilic.

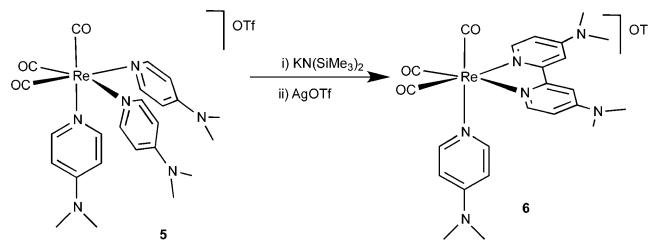
In the absence of mechanistic studies, we speculate that the formation of the pyridylimidazole complexes occurs via deprotonation of the imidazole C2–H, nucleophilic attack of the deprotonated carbon onto a pyridine *ortho* carbon to afford

a dearomatized intermediate,¹⁷ which then would be oxidized by Ag⁺,^{18,19} the latter step encouraged by the restoration of the aromaticity and the conjugation between the two adjacent aromatic cycles.²⁰ We have encountered that 2 equiv of AgOTf are needed for the reactions to reach completion. This could be an indication of two 1e[−] oxidations: the neutral C–C coupled product would undergo one electron oxidation to a radical cation, followed by deprotonation to a radical, and oxidation to the observed product. The base for the second deprotonation (only 1 equiv of KN(SiMe₃)₂ was used) would be HN(SiMe₃)₂ formed in the first deprotonation step.²¹ An alternative mechanism involving initial 2e[−] oxidation of Re(I) to Re(III) by Ag(I), and subsequent deprotonation of the 2-pyridyl group, which would rearomatize the ligand and return the metal oxidation state to (I) could not be ruled out.

Finally, we wondered if this reactivity could be extended to tris(pyridyl) derivatives to get, after the dehydrogenative C–C coupling reaction, bipyridine (bipy) ligands. There are obvious difficulties: (1) as for the site of the deprotonation, pyridines are less acidic than *N*-alkylimidazoles;²² and (2) monodentate pyridines could be more problematic electrophiles because of their lability that could promote attack to the metal instead. 2,2'-bipyridines are one of the most versatile bidentate ligands in organometallic and inorganic chemistry.²³ Heterogeneous catalytic pyridine homocoupling is not applicable to 4-substituted pyridines,²⁴ and the other major method to prepare bips, transition-metal catalyzed cross-coupling reactions require prefunctionalization of the substrates.^{23,25}

Compound [Re(CO)₃(dmap)₃]OTf (**5**), prepared straightforwardly by thermal substitution from [Re(OTf)(CO)₅] and dmap, reacted with the strong base KN(SiMe₃)₂ and AgOTf to afford the coupling product [Re(CO)₃(bipy')(dmap)]OTf (bipy' = 4,4'-bis(dimethylamino)-2,2'-bipyridine, **6**; see Scheme 3).

Scheme 3. Formation of the Bipyridine Derivative **6**



The new compound **6** (Figure 2) displays a 2,2'-bipyridine ligand showing that the deprotonation of an *ortho* C–H group of a pyridyl ligand has been achieved, a reaction that, as far as we know, lacks precedents. In fact, there are just a few examples of metal-mediated coupling of pyridines, restricted to alkali or very reactive early transition metals.^{16a,26} Coordination of metals fragments in the rare κ^2 and κ^6 coordination modes have been employed for enhancing the reactivity of pyridines.²⁷ In the majority of its metal complexes, pyridines are $\kappa^1(\text{N})$ coordinated. Nucleophilic attack to nonfunctionalized pyridine in such complexes has been the subject of a long-standing controversy,²⁸ and clear-cut evidence remains scarce.

In summary, unprecedented intramolecular C–C coupling via deprotonation/oxidation sequences allowed the synthesis of complexes of pyridylimidazole chelates from complexes containing monodentate, nonfunctionalized pyridine and imidazole ligands. Extension of this methodology to tris-

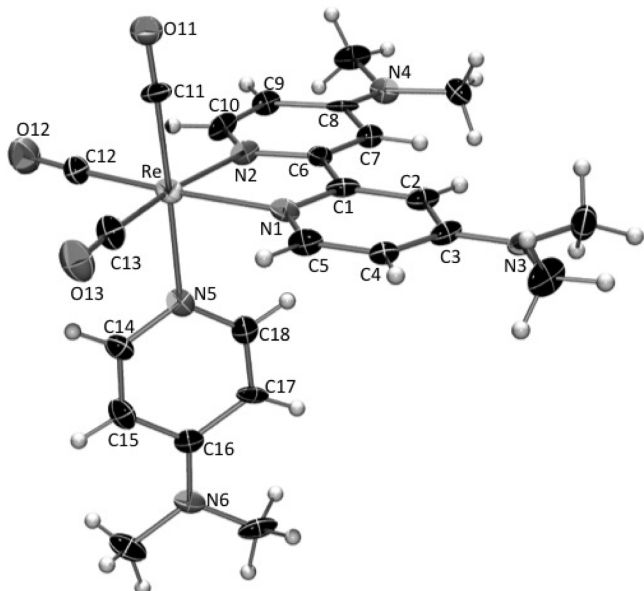


Figure 2. Molecular structure of the cationic complex of **6**.²⁹

(pyridyl) species afforded a 4,4'-disubstituted 2,2'-bipyridine, which synthesis is not well established nowadays.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information of compounds **2a**, **2b**, **I** and **6**, and experimental details for the synthesis of **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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- (10) See Supporting Information for complete experimental details.
- (11) Selected crystallographic data for **2a**: $C_{48}H_{27}BF_2N_5O_3Re$, $M = 1374.76$, orthorhombic, *Prn2*(1), $a = 17.071(2)$ Å, $b = 15.982(2)$ Å, $c = 18.311(1)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, 100(2) K, $V = 4995.8(11)$ Å³, $Z = 8$. 11278 reflections measured, 7715 independent ($R_{int} = 0.0543$). $R_1 = 0.00531$, $wR_2 = 0.1211$ (all data).

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(29) Selected crystallographic data for **6**: C₂₅H₂₈F₃N₆O₆ReS, *M* = 783.79, triclinic, *P* $\bar{1}$, *a* = 13.6164(8) Å, *b* = 15.5341(9) Å, *c* = 16.0883(11) Å, α = 89.142(4)°, β = 77.599(4)°, γ = 77.534(3)°, 150.0(1) K, *V* = 3243.5(3) Å³, *Z* = 4. 1993 reflections used. *R*₁ = 0.0976, *wR*₂ = 0.2418 (all data).

Supporting Information

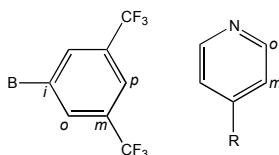
Re-mediated C-C coupling of pyridines and imidazoles

Maialen Espinal Viguri, Miguel A. Huertos, Julio Pérez, Lucía Riera and Irene Ara

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and DPX 300 spectrometers. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer. Compounds $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-RIm})_2]$ ($\text{R} = \text{Me}$, Mes),^[1] $N\text{-MesIm}$,^[2] and NaBAR'_4 ^[3] were prepared following the reported procedures.

Labelling scheme for BAR'_4 and pyridinic ligands:



Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{py})]\text{BAR}'_4$ (1a**).** NaBAR'_4 (0.134 g, 0.151 mmol) and pyridine (0.012 mL, 0.151 mmol) were added to a solution of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (0.080 g, 0.137 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 2 h. at room temperature. The solution was filtered off the white solid via canula, concentrated under reduced pressure to a volume of 5 mL, and addition of hexane (15 mL) caused the precipitation of a white solid, which was washed with hexane (3×15 mL) and dried in vacuum. Yield: 168 mg (87 %). IR (THF, cm^{-1}): 2028, 1914 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.40 (m, 2H, H_o py), 7.99 (m, 1H, H_p py), 7.73 (s_{br}, 8H, H_o BAR'_4), 7.60 (s, 2H, NCHN $N\text{-MeIm}$), 7.58 (s_{br}, 4H, H_p BAR'_4), 7.46 (m, 2H, H_m py), 7.01, 6.71 (s, 2H each, CH $N\text{-MeIm}$), 3.73 (s, 6H, CH_3 $N\text{-MeIm}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 194.8 ($2 \times \text{CO}$), 194.5 (CO), 162.2 (q ($J = 49.6$ Hz), C_i BAR'_4), 153.5 (C_o py), 141.5 (NCHN, $N\text{-MeIm}$), 140.2 (C_p py), 135.2 (C_o BAR'_4), 130.4 (CH, $N\text{-MeIm}$), 129.3 (q ($J = 31.4$ Hz), C_m BAR'_4), 127.1 (C_m py), 125.0 (q ($J = 272.3$ Hz), CF_3), 123.4 (CH, $N\text{-MeIm}$), 117.9 (C_p BAR'_4), 35.0 ($2 \times \text{CH}_3$ $N\text{-MeIm}$). Anal. Calcd. for $\text{C}_{48}\text{H}_{29}\text{BF}_6\text{N}_5\text{O}_3\text{Re}$: C 41.87, H 2.12, N 5.09. Found: C 41.49, H 2.31, N 4.85.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{pic})]\text{BAR}'_4$ (1b**).** Compound **1b** was prepared as described above for **1a** starting from $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (0.100 g, 0.171 mmol), NaBAR'_4 (0.153 g, 0.173 mmol) and γ -picoline (0.017 mL, 0.171 mmol). Compound **3** was obtained as white solid that was washed with hexane (2×20 mL) and dried under reduced pressure. Yield: 190 mg (80 %). IR (THF, cm^{-1}): 2031, 1917 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.23 (d ($J = 5.5$ Hz), 2H, pic), 7.77 (s_{br}, 8H, H_o BAR'_4), 7.60 (s_{br}, 4H, H_p BAR'_4), 7.58 (s, 2H, NCHN $N\text{-MeIm}$), 7.25 (d ($J = 5.5$ Hz), 2H, pic), 6.97, 6.73 (m, 2H each, CH $N\text{-MeIm}$), 3.69 (s, 6H, CH_3 $N\text{-MeIm}$), 2.39 (s, 3H, CH_3 pic). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 194.9 ($2 \times \text{CO}$), 194.7 (CO), 162.1 (q ($J = 50.0$ Hz), C_i BAR'_4), 153.5 (C_p pic), 152.8 (C_p pic), 141.5 (NCHN, $N\text{-MeIm}$), 135.2 (C_o BAR'_4), 130.4 (CH, $N\text{-MeIm}$), 129.3 (q ($J = 31.3$ Hz), C_m BAR'_4), 127.9 (C_m pic), 125.0 (q ($J = 272.3$ Hz), CF_3), 123.3 (CH, $N\text{-MeIm}$), 117.9 (C_p BAR'_4), 35.1 ($2 \times \text{CH}_3$ $N\text{-MeIm}$), 21.3 (CH_3 pic). Anal. Calcd. for $\text{C}_{49}\text{H}_{31}\text{BF}_6\text{N}_5\text{O}_3\text{Re}$: C 42.32, H 2.25, N 5.04. Found: C 42.73, H 2.41, N 5.11.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})(\text{pyimMe})]\text{BAR}'_4$ (2a**).** $\text{KN}(\text{SiMe}_3)_2$ (0.100 mL of a 0.5 M solution in toluene, 0.050 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{py})]\text{BAR}'_4$ (**1a**) (0.055 g, 0.040 mmol) in THF (20 mL) previously cooled to -78 °C. The colour of the solution changed immediately from colourless to bright yellow. The mixture was allowed to reach room temperature, AgOTf (0.021 g, 0.082 mmol) was added and the mixture was stirred for 5 min. The solvent was evaporated to dryness under reduced pressure, diethyl ether (25 mL) was added and the suspension was decanted for 12 h. at -20 °C. The reaction crude was then filtered via cannula and the solvent was evaporated in vacuum. The residue was extracted with CH_2Cl_2 (20 mL), filtered through silica gel and the solvent was evaporated under reduced pressure to a volume of 5 mL. Addition of

hexane (20 mL) caused the precipitation of a yellow solid that was washed with hexane (3 × 15 mL). Slow diffusion of hexane (15 mL) in a concentrated solution of **2a** in CH₂Cl₂ (5 mL) at -20 °C afforded yellow crystals, one of which was used for an X-ray structure determination. Yield: 26 mg (47 %). IR (THF, cm⁻¹): 2032, 1926, 1920 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.12 (m, 1H, *pyimMe*), 8.13 (m, 1H, *pyimMe*), 7.98 (m, 1H, *pyimMe*), 7.76 (s_{br}, 8H, H_o BAR'₄), 7.61 (m, 1H, *pyimMe*), 7.59 (s_{br}, 4H, H_p BAR'₄), 7.52 (d (*J* = 1.4 Hz), 1H, *CH pyimMe*), 7.30 (s, 1H, *NCHN N-MeIm*), 7.26 (d (*J* = 1.4 Hz), 1H, *CH pyimMe*), 6.75, 6.39 (m, 1H each, *CH N-MeIm*), 4.11 (s, 3H, *CH₃ pyimMe*), 3.56 (s, 3H, *CH₃ N-MeIm*). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.1, 194.9, 190.9 (CO), 162.2 (q (*J* = 49.8 Hz), C_i BAR'₄), 154.5 (*pyimMe*), 147.7, 146.9, 140.6, 139.5, 130.2, 127.0, 122.3, 122.0 (*pyimMe* and *N-MeIm*), 135.2 (C_o BAR'₄), 129.3 (q (*J* = 30.5 Hz), C_m BAR'₄), 125.0 (q (*J* = 271.7 Hz), CF₃), 117.9 (C_p BAR'₄), 37.0, 34.4 (CH₃ *pyimMe*), 34.4 (CH₃ *N-MeIm*). Anal. Calcd. for C₄₈H₂₇BF₂₄N₅O₃Re: C 41.94, H 1.98, N 5.09. Found: C 42.20, H 2.09, N 4.78.

Synthesis of [Re(CO)₃(N-MeIm)(picimMe)]BAR'₄ (2b). Compound **2b** was prepared as described above for **2a** starting from [Re(CO)₃(N-MeIm)₂(pic)]BAR'₄ (**1b**) (0.100 g, 0.072 mmol), KN(SiMe₃)₂ (0.170 mL of a 0.5 M solution in toluene, 0.085 mmol) and AgOTf (0.038 g, 0.148 mmol). Slow diffusion of hexane (15 mL) into a concentrated solution of **2b** in CH₂Cl₂ (5 mL) at -20 °C afforded orange crystals, one of which was used for an X-ray structure determination. Yield: 55 mg (56 %). IR (THF, cm⁻¹): 20321 1910 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.94 (d (*J* = 5.7 Hz), 1H, *picimMe*), 7.76 (s_{br}, 9H, H_o BAR'₄ and 1H *picimMe*), 7.60 (s_{br}, 4H, H_p BAR'₄), 7.49 (d (*J* = 1.3 Hz), 1H, *CH picimMe*), 7.41 (d (*J* = 5.7 Hz), 1H, *picimMe*), 7.29 (s, 1H, *NCHN N-MeIm*), 7.23 (d (*J* = 1.3 Hz), 1H, *CH picimMe*), 6.73, 6.28 (m, 1H each, *CH N-MeIm*), 4.11 (s, 3H, *CH₃ picimMe*), 3.55 (s, 3H, *CH₃ N-MeIm*), 2.56 (s, *CH₃ picimMe*). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.6, 195.5, 191.7 (CO), 162.1 (q (*J* = 49.9 Hz), C_i BAR'₄), 154.3, 154.1 (C_o *picimMe*), 148.2 (NCN *picimMe*), 147.0 (C_p *picimMe*), 139.9 (NCHN *N-MeIm*), 135.2 (C_o BAR'₄), 130.5, 128.6 (CH *picimMe*), 129.2, 122.6 (CH *N-MeIm*), 129.1 (q (*J* = 30.6 Hz), C_m BAR'₄), 128.2, 123.3 (C_m *picimMe*), 125.0 (q (*J* = 271.7 Hz), CF₃), 117.9 (C_p BAR'₄), 37.5 (CH₃ *picimMe*), 34.8 (CH₃ *N-MeIm*), 22.0 (CH₃ *picimMe*). Anal. Calcd. for C₄₉H₂₉BF₂₄N₅O₃Re: C 42.38, H 2.10, N 5.04. Found: C 42.56, H 2.21, N 5.28.

Synthesis of [Re(CO)₃(dmap)₂(N-MeIm)]BAR'₄ (3). A mixture of [ReBr(CO)₅] (0.069 g, 0.170 mmol) and dmap (0.044 g, 0.357 mmol) were refluxed in toluene for 2 h. The solvent was evaporated to dryness, the white residue redissolved in CH₂Cl₂ (20 mL), AgOTf (0.053 g, 0.206 mmol) was added and the mixture was stirred in the dark for 2 h. The solution was then filtered off the white solid (AgBr), the solvent evaporated to dryness and the residue was washed with hexane (2 × 15 mL), and diethylether (2 × 15 mL). Slow diffusion of hexane (20 mL) into a concentrated solution in CH₂Cl₂ (5 mL) afforded colorless crystals of [Re(OTf)(CO)₃(dmpa)₂] (**I**), one of which was employed for an X-ray structure determination. NaBAR'₄ (0.147 g, 0.166 mmol) and *N-MeIm* (0.013 mL, 0.166 mmol) were added to a solution of triflate compound **I** (0.100 g, 0.151 mmol) in CH₂Cl₂ (25 mL), and the reaction mixture was stirred for 3 h. at room temperature. Then the solution was filtered via canula, concentrated under reduced pressure to a volume of 5 mL, and addition of hexane (15 mL) caused the precipitation of a white solid, that was washed with hexane (2 × 15 mL) and dried in vacuum. Yield: 198 mg (90 %). IR (THF, cm⁻¹): 2024, 1909 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.87 (d (*J* = 5.9 Hz), 4H, dmap), 7.80 (s_{br}, 8H, H_o BAR'₄), 7.62 (s_{br}, 4H, H_p BAR'₄), 7.60 (s, 1H, *NCHN N-MeIm*), 6.98, 6.90 (m, 1H each, *CH N-MeIm*), 6.49 (d (*J* = 5.9 Hz), 2H, dmap), 3.69 (s, 3H, *CH₃ N-MeIm*), 3.01 (s, 12H, *CH₃ dmap*). ¹³C{¹H} NMR (CD₂Cl₂): δ 195.8 (s_{br} CO), 162.2 (q (*J* = 50.4 Hz), C_i BAR'₄), 155.2 (C_p dmap), 152.2 (C_o dmap), 141.2 (NCHN, *N-MeIm*), 135.2 (C_o BAR'₄), 130.5 (CH, *N-MeIm*), 129.3 (q (*J* = 31.0 Hz), C_m BAR'₄), 125.0 (q (*J* = 272.0 Hz), CF₃), 122.9 (CH, *N-MeIm*), 117.9 (C_p BAR'₄), 108.5 (C_m dmap), 39.2 (4×CH₃ dmap), 34.9 (CH₃ *N-MeIm*). Anal. Calcd. for C₅₃H₃₈BF₂₄N₆O₃Re: C 43.60, H 2.62, N 5.76. Found: C 43.81, H 2.69, N 5.61.

Synthesis of [Re(CO)₃(dmap)(dmapimMe)]BAR'₄ (4). Compound **4** was prepared as described above for **2a** starting from [Re(CO)₃(dmap)₂(*N*-MeIm)]BAR'₄ (**3**) (0.088 g, 0.060 mmol), KN(SiMe₃)₂ (0.150 mL of a 0.5 M solution in toluene, 0.075 mmol) and AgOTf (0.032 g, 0.124 mmol). Compound **4** was obtained a yellow microcrystalline solid. Yield: 35 mg (40 %). IR (THF, cm⁻¹): 2024, 1913 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.55 (d (*J*= 6.9 Hz), 1H, *dmapimMe*), 7.78 (s_{br}, 8H, H_o BAR'₄), 7.67 (d (*J*= 6.1 Hz), 2H, *dmap*), 7.60 (s_{br}, 4H, H_p BAR'₄), 7.46 (d (*J*= 1.2 Hz), 1H, *CH dmapimMe*), 7.11 (d (*J*= 1.2 Hz), 1H, *CH dmapimMe*), 6.90 (d (*J*= 2.6 Hz), 1H, *dmapimMe*), 6.64 (dd (*J*= 6.9 Hz, *J*= 2.6 Hz), 1H, *dmapimMe*), 6.29 (d (*J*= 6.1 Hz), 2H, *dmap*), 4.00 (s, 3H, *CH*₃ *dmapimMe*), 3.10, 2.87 (s, 6H each, *CH*₃ *dmapimMe* and *dmap*). ¹³C{¹H} NMR (CD₂Cl₂): δ 197.6, 196.5, 192.9 (CO), 162.2 (q (*J*= 50.4 Hz), C_i BAR'₄), 155.4, 154.8, 153.0, 150.7, 149.2, 147.0, 129.7, 128.0, 108.5, 108.1, 104.6 (*dmap* and *dmapimMe*), 135.2 (C_o BAR'₄), 129.3 (q (*J*= 31.4 Hz), C_m BAR'₄), 125.0 (q (*J*= 272.5 Hz), CF₃), 117.9 (C_p BAR'₄), 39.8, 39.1 (2×CH₃ each, *dmapimMe* and *dmap*), 37.1 (CH₃ *dmapimMe*). Anal. Calcd. for C₅₃H₃₆BF₂₄N₆O₃Re: C 43.66, H 2.49, N 5.76. Found: C 43.97, H 2.62, N 5.45.

Synthesis of [Re(CO)₃(dmap)₃]OTf (5). 4-dimethylaminopyridine (0.186 g, 1.53 mmol) was added to a suspension of [Re(OTf)(CO)₅] (0.200 g, 0.49 mmol) in toluene (25 mL), and the mixture was refluxed for 4 hours. The resulting colourless solution was evaporated to dryness under reduced pressure. The white solid was washed with hexane (2 × 15 mL), diethyl ether (1 × 20 mL), and dried under vacuum. Yield: 334 mg (90 %). IR (THF, cm⁻¹): 2022, 1906 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.88 (d (*J*= 7.3 Hz), 6H, *dmap*), 6.52 (d (*J*= 7.3 Hz), 6H, *dmap*), 3.08 (s, 18H, *CH*₃ *dmap*). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.4 (3×CO), 155.2, 152.1, 108.7 (*dmap*), 39.6 (CH₃ *dmap*). Anal. Calcd. for C₂₅H₃₀F₃N₆O₆ReS: C 38.21, H 3.85, N 10.69. Found: C 38.10, H 4.06, N 10.97.

Synthesis of [Re(CO)₃(bipy')(dmap)]OTf (6). Compound **5** was prepared as described above for **2a** starting from [Re(CO)₃(dmap)₃]OTf (**5**) (0.055 g, 0.07 mmol), KN(SiMe₃)₂ (0.15 mL of a 0.5 M solution in toluene, 0.08 mmol) and AgOTf (0.043 g, 0.16 mmol). Compound **6** was obtained an orange microcrystalline solid. Slow diffusion of hexane (15 mL) into a concentrated solution of **6** in CH₂Cl₂ (5 mL) at -20 °C afforded orange crystals, one of which was used for an X-ray structure determination. Yield: 29 mg (55 %). IR (THF, cm⁻¹): 2021, 1908 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.46 (d (*J*= 6.8 Hz), 2H, *bipy'*), 7.60 (d (*J*= 7.3 Hz), 2H, *dmap*), 7.35 (d (*J*= 2.4 Hz), 2H, *bipy'*), 6.64 (dd (*J*= 6.8, 2.4 Hz), 2H, *bipy'*), 6.31 (d (*J*= 7.3 Hz), 2H, *dmap*), 3.22 (s, 12H, *CH*₃ *bipy'*), 2.96 (s, 6H, *CH*₃ *dmap*). ¹³C{¹H} NMR (CD₂Cl₂): δ 198.2 (2×CO), 194.5 (CO), 156.5, 155.8, 154.9, 151.7, 150.6, 109.3, 108.2, 105.7 (*bipy'* and *dmap*), 39.3 (CH₃ *dmap*) Anal. Calcd. for C₂₅H₂₈F₃N₆O₆ReS: C 38.31, H 3.60, N 10.72. Found: C 38.02, H 3.78, N 11.01.

Crystal Structure Determination.

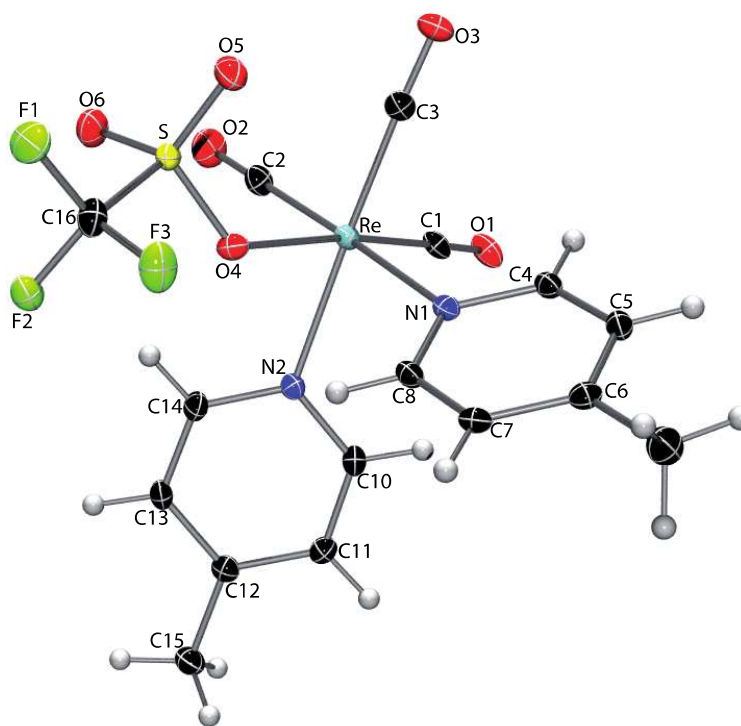
For Compound 6. Data collection was performed at 150(2) K on a Nonius KappaCCD single crystal diffractometer, using Mo-Kα radiation (λ= 0.71073 Å). Images were collected at a 29 mm fixed crystal-detector distance, using the oscillation method, with 2° oscillation and 40 s exposure time per image. Data collection strategy was calculated with the program Collect.⁴ Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.⁵ A semi-empirical absorption correction was applied using the program SORTAV.⁶

For Compounds 2a, 2b and I. Data collection was performed at 100(2) K on a Bruker Smart Apex CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 6.0 cm. Unit cell dimensions were determined on the basis of the positions of 1287 (**2a**), 5379 (**2b**) or 8962 (**I**) reflections from the main dataset.

In all cases, a sphere of data based on 3 ω -scan runs (starting $\omega = -28^\circ$) at values $\phi = 0, 120$ and 240 with the detector at $2\theta = 28^\circ$ was collected. At each of these runs, 606 frames were collected at 0.3° intervals and 30 s per frame. The diffraction frames were integrated using the SAINT package⁷ and corrected for absorption with SADABS.⁸ Lorentz and polarization corrections were applied.

Crystal structures were solved by direct methods, using the program SIR-92.⁹ Non-hydrogen atoms were assigned anisotropic displacement parameters. H atoms were added at calculated positions with equivalent isotropic displacement parameters set equal to 1.2 or 1.5 times those of the corresponding parent atoms. Anisotropic least-squares refinement was carried out with SHELXL-97.¹⁰

Figure S1. Molecular Structure of compound I.



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N Ligands

C–C Coupling of N-Heterocycles at the *fac*-Re(CO)₃ Fragment: Synthesis of Pyridylimidazole and Bipyridine LigandsMaialen Espinal Viguri,^[b] Julio Pérez,^{*,[a, b]} and Lucía Riera^{*,[a]}

Abstract: A new family of cationic rhenium tricarbonyl complexes with either two N-alkylimidazole (N-RIm) and one pyridine (Py) ligand, or two pyridine and one N-RIm ligand, [Re(CO)₃(N-RIm)_(3-x)(Py)_x]⁺, has been prepared. The reaction of these complexes with a strong base, followed by an oxidant, selectively afforded 2,2'-pyridylimidazole complexes as the result of intramolecular dehydrogenative C–C coupling reactions. For tris(pyridine) complexes [Re(CO)₃(Py)₃]⁺ the re-

action pattern upon a deprotonation/oxidation sequence is maintained, which allows the generation of complexes with 2,2'-bipyridine ligands. In the particular combination of two different types of pyridine ligand in the cationic *fac*-Re(CO)₃ complexes only the cross-coupling products with asymmetric 2,2'-bipyridine ligands were obtained; the homocoupling products were not observed.

Introduction

Aromatic heterobiaryls are ubiquitous motifs in many natural products and bioactive compounds, pharmaceutical agents, and functional materials.^[1] Classical transition-metal-catalyzed methods for the synthesis of biaryls require functionalized substrates to link two heteroarenes with a C–C bond (Figure 1 A).^[2]

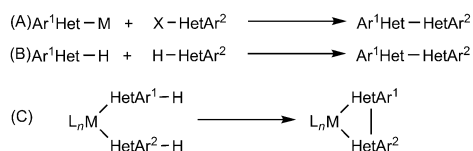


Figure 1. Synthesis of aromatic heterobiaryl compounds.

Oxidative cross-coupling between two heteroarenes by two-fold C–H activation would be the ideal route to heterobiaryls because it would avoid tedious prefunctionalization (Figure 1 B).^[3] In this context some important achievements have been reported in recent years,^[4] however, the heteroarylation of pyridine and related azines still remains a challenge.^[5] Whereas significant progress in the arylation of pyridines by

C–H/C–X coupling reactions has been achieved,^[6] examples of heteroarylation of pyridines are scarce, and only very recently You et al.^[7] have reported, for the first time, a selective methodology for the direct C2 heteroarylation of pyridines with a wide range of heteroarenes.

On the other hand, despite the significant progress made, the transition-metal-catalyzed oxidative cross-coupling between two partners with similar structure and electronic characteristics faces significant hurdles because homocoupled products are frequently found along with the desired products of heterocoupling.^[8]

We have found that coordination to a transition organometallic fragment can suffice as the only prefunctionalization required to selectively obtain cross-coupled heterobiaryl ligands from precursors that contain monodentate heteroarenes.^[9] Coordination of two different aromatic N-heterocycles to the same metal fragment can result in enhancement of the nucleophilicity of one (the α -CH groups become more acidic)^[10] and the electrophilicity of the other,^[11,12] which generates the appropriate counterparts to undergo an intramolecular cross-coupling reaction (Figure 1 C).

By this strategy we have accomplished the cross-coupling of pyridine (Py) and N-alkylimidazole (N-RIm) ligands to afford 2,2'-pyridylimidazole (Pyim) complexes and, in a similar way, even more interestingly, 2,2'-bipyridines by oxidative coupling of two pyridyl ligands. For the latter the selective cross-coupling of two different pyridyl ligands to afford asymmetric 2,2'-bipyridine complexes has been achieved and the homocoupling products were not observed.

Synthetic routes to aromatic N,N'-chelating ligands remain a challenge and often lead to low yields, thus limiting access to metal derivatives of interest. Among such complexes, *fac*-Re(CO)₃ derivatives are widely employed in several areas of chemical research. Currently available synthetic routes invariably rely on substitution reactions from precursors such as

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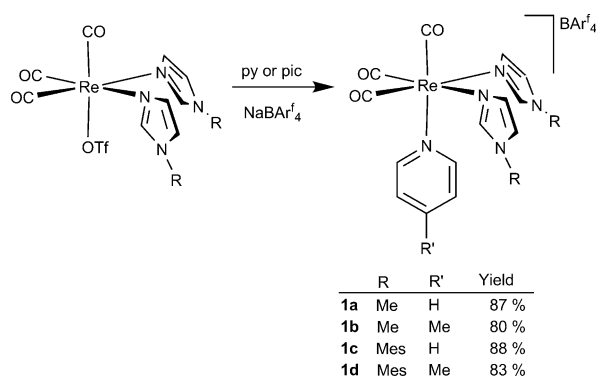
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[ReX(CO)₅] (X = Cl, Br), which employ preformed chelates. Herein, we propose an alternative based on at-the-metal modular synthesis of the chelate. Our route begins with the synthesis of a complex with the monodentate building blocks (readily available compounds), followed by a deprotonation/oxidation sequence in which a C–C bond is created between two of the monodentate ligands and results in the formation of the metal-bonded chelate. A clear advantage of this method is that it allows access to derivatives that contain difficult-to-synthesize chelates, such as asymmetric 2,2'-bipyridines.

Results and Discussion

Compounds [Re(CO)₃(N-Rlm)₂(Py-R')]BAr^f₄ (**1 a–d**; R = Me, mesityl (Mes); R' = H, Me; Ar^f = 3,5-bis(trifluoromethyl)phenyl) with both pyridyl and imidazole ligands were prepared by reaction of the triflate bis(imidazole) complexes [Re(CO)₃(N-Rlm)₂(OTf)] (in turn, synthesized from [Re(CO)₅(OTf)] and N-alkylimidazoles)^[10e] with a slight excess of pyridine or γ -picoline (pic) in the presence of NaBAr^f₄ (Scheme 1). The new cationic complexes were obtained in good yields and characterized by IR



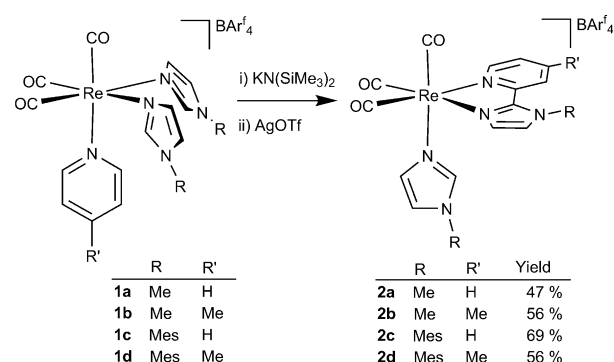
Scheme 1. Synthesis of complexes [Re(CO)₃(N-Rlm)₂(Py-R')]BAr^f₄ (**1 a–d**).

and NMR spectroscopy in solution. The IR $\tilde{\nu}_{\text{CO}}$ bands of **1 a–d** showed the typical pattern for cationic Re^I *fac*-tricarbonyl complexes and the ¹H and ¹³C NMR spectra were in agreement with the stoichiometry and geometry shown in Scheme 1.

In contrast to traditional prefunctionalized N-heterocycles,^[13] compounds **1 a–d** are easy to prepare on a half-gram scale, are relatively stable, and can be kept for weeks under nitrogen atmosphere at room temperature.

The reaction of compounds **1 a–d** with KN(SiMe₃)₂ (1 equiv) in THF at –78 °C led immediately to neutral species (evidenced by large shifts of the $\tilde{\nu}_{\text{CO}}$ bands in the IR spectra to lower wavenumbers) that were unstable for isolation. Addition of silver trifluoromethanesulfonate as an oxidant afforded the formation of cationic compounds **2 a–d** (Scheme 2).

The solid-state structures of **2 a** and **2 b**, derived from bis(*N*-methylimidazole) complexes, were determined by X-ray diffraction and confirmed the reactivity pattern depicted in Scheme 2.^[9] The spectroscopic data of compounds **2 c** and **2 d** in solution were in accordance with the formation of 2,2'-pyri-



Scheme 2. Synthesis of 2,2'-pyridylimidazole complexes **2 a–d**.

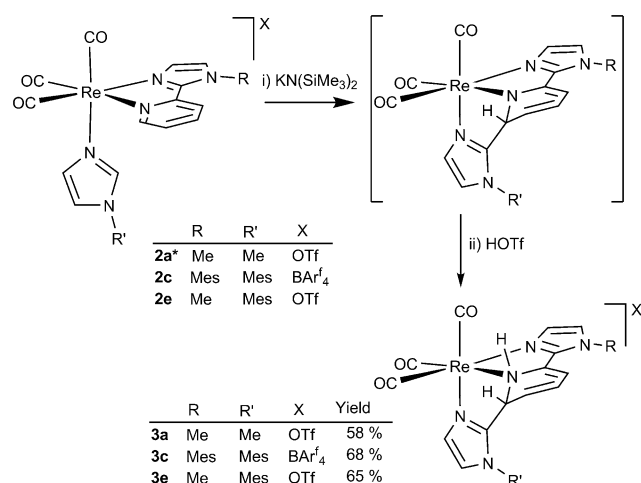
dylimidazole ligands, and showed the presence of an intact *N*-Meslm ligand coordinated to the *fac*-Re(CO)₃ unit, which indicates that in this reaction the imidazole substituent is not crucial to determine the reaction product.^[14] No side reactions were detected, not even of the methyl group of the γ -picoline ligand, despite its acidic character.

Pyridylimidazoles are usually synthesized by the de novo construction of the imidazole ring^[15] and a growing number of pyridylimidazole complexes are known. There is no precedent for their metal-templated synthesis; in fact, the synthesis of bidentate ligands by C–C coupling of monodentate ligands remains rare.^[16]

It is interesting to note that the presence of an intact imidazole ligand (which, because of the positive charge of the complex, could be deprotonated) in compounds **2 a–d** *cis* to the pyridylimidazole chelate (the potential electrophile) could permit a second, base-triggered C–C-coupling reaction. Unlike in the first reaction (see above), the *fac* disposition of the ligands would prevent planarity and, hence, rearomatization. Therefore, we decided to further study the deprotonation reaction of the imidazole-pyridylimidazole species.

The treatment of compound **2 a***^[17] with the strong base KN(SiMe₃)₂ instantaneously produced a neutral species, evidenced by shifts of the bands in the IR spectra to lower wavenumbers ($\tilde{\nu}_{\text{CO}}$ = 2026, 1915 to 2004, 1885 cm^{–1}), which was too unstable for isolation. The addition of HOTf (1 equiv) afforded compound **3 a**, in which the nitrogen atom adjacent to the attacked carbon atom (on the pyridine ring) is protonated, as the only product of the reaction (Scheme 3).

Compound **3 a** was fully characterized and the X-ray structure was determined (Figure 2a).^[18] The cationic complex consists of a *fac*-Re^I(CO)₃ fragment bonded to a tridentate N-donor ligand. The latter results from C–C coupling between the central carbon atom of the *N*-Melm ligand and the *ortho*-carbon atom of the pyridyl ring of the bidentate ligand. As a consequence of the formation of this new single C2–C6 bond, the pyridyl group is dearomatized, evidenced by the bond lengths C6–C7 = 1.53(2) Å, C6–N2 = 1.49(1) Å, and N2–C10 = 1.49(1) Å, which are clearly longer than those expected for an aromatic ring. The C6 atom is, therefore, sp³ hybridized, and shows angles consistent with an approximately tetrahedral geometry (C2–C6–N2 = 105.5(10)°, C2–C6–C7 = 109.2(9)°, C7–C6–



Scheme 3. Reactivity of 2,2'-pyridylimidazole complexes.

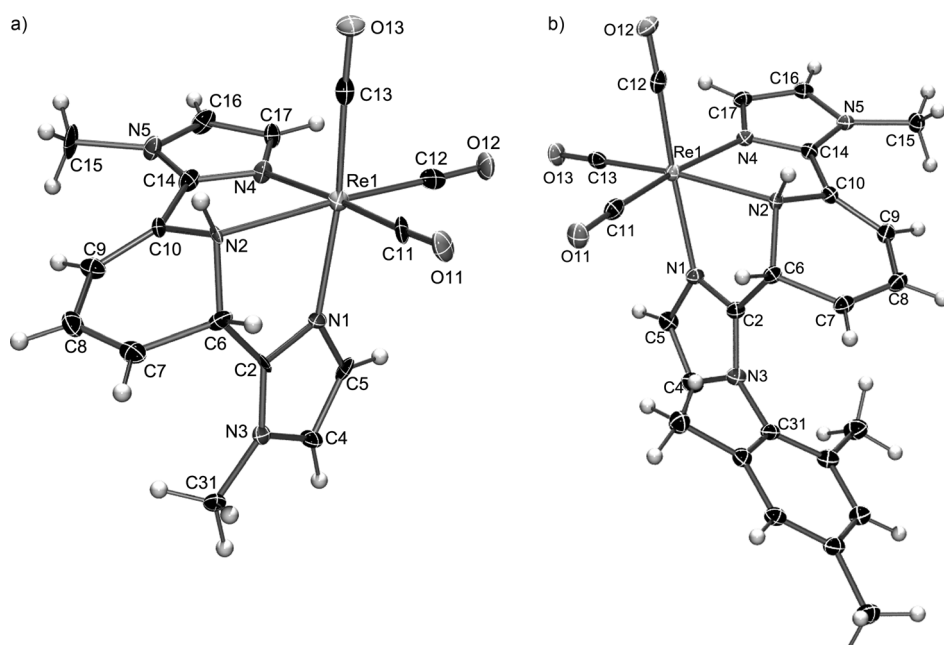


Figure 2. a) Molecular structure of the cation of complex **3a**. b) Molecular structure of the cation complex of **3e**.

$N2 = 114.9(11)^\circ$. The angles around the N2 nitrogen atom ($107.8(6)$, $110.1(6)$, and $110.6(9)^\circ$) are also in agreement with an almost tetrahedral geometry. In solution, evidence of dearomatization is provided by the presence of a multiplet at $\delta 5.42$ ppm in the ^1H NMR spectrum and a signal at $\delta 56.4$ ppm in the ^{13}C NMR spectrum for the pyridine CH group that underwent the nucleophilic attack to give an sp^3 center.

In an attempt to isolate the neutral intermediate species produced by deprotonation of the pyridylimidazole compound **2a***, we synthesized the analogous *N*-MesIm compound (**2e**) because we have found previously that the products derived from this imidazole are often noticeably more stable than the *N*-Melm derivatives.^[10c] The deprotonation of $[\text{Re}(\text{CO})_3(\text{N-MesIm})(\text{Pyim-Me})]\text{OTf}$ (**2e**) afforded complex **IIe** (between brackets in Scheme 3), which was not stable enough for isola-

tion, but could be characterized spectroscopically in solution. The IR data for **IIe** ($\nu_{\text{CO}} = 2004, 1885 \text{ cm}^{-1}$) agree with its neutral nature and the ^1H NMR spectrum in $[\text{D}_8]\text{THF}$ is consistent with dearomatization of the pyridine ring (two multiplets at $\delta = 4.18$ and 5.77 ppm and two doublets at $\delta = 5.23$ and 5.30 ppm for this group). The addition of HOTf (1 equiv) to a solution of **IIe** in CH_2Cl_2 led to the formation of the protonated compound **3e** (Scheme 3). The solid-state structure of **3e** was determined by X-ray diffraction (Figure 2b)^[19] and, like that of the *N*-Melm derivative **3a** (Figure 2a), shows the formation of a C–C bond between the central imidazole carbon atom and the *ortho*-carbon atom of the pyridyl group, and the subsequent dearomatization of the pyridyl group.^[20] The isolation of **IIe** allows us to propose that the addition of a strong base to $[\text{Re}(\text{CO})_3(\text{N-RIm})(\text{Pyim-Me})]\text{OTf}$ compounds deprotonates the central CH group of the *N*-RIm ligand to generate a nucleophilic *N*-coordinated imidazol-2-yl ligand that attacks

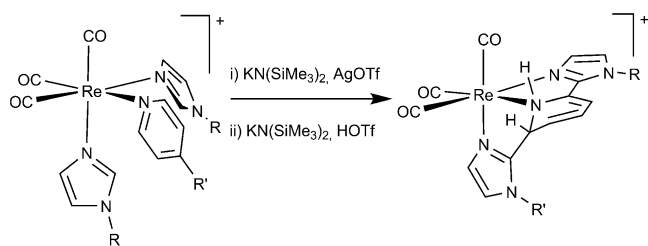
the *ortho* CH group of the pyridyl ring and results in dearomatization. The reaction is selective and attack onto the imidazole backbone of the pyridylimidazole ligand is not observed.

Finally, we studied the deprotonation/protonation reaction sequence of $[\text{Re}(\text{CO})_3(\text{N-MesIm})(\text{Pyim-Mes})]\text{BAr}_4^f$ (**2c**)^[21] and found the same reactivity pattern discussed above for the *Pyim-Me* derivatives. It is interesting to note that the synthesis of $[\text{Re}(\text{CO})_3(\text{N-RIm})(\text{Pyim-R})]^+$ complexes from the corresponding bis(imidazole) compounds (Scheme 2) implies the activation of an *ortho*-CH group of a monodentate pyridyl ligand, and the formation of the dearomatized products from the pyridylimidazole complexes implies the activation of the remaining *ortho*-CH group of the same pyridine

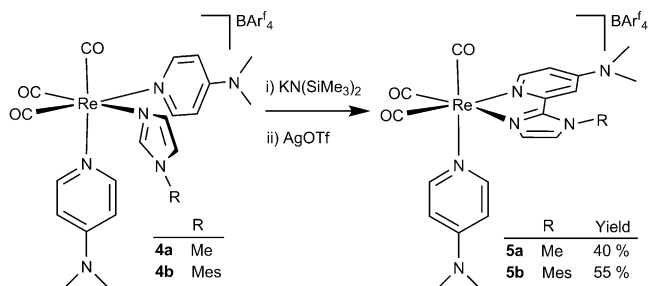
ligand (Scheme 3). Overall, the two *ortho* C–H groups of a monodentate pyridine ligand have been easily activated (Scheme 4), a reaction that, as far as we know, lacks any precedent.

To continue with our initial study of oxidative coupling of monodentate *N*-heterocyclic ligands to afford bis(heteroaromatic) ligands, we extended our results from complexes with two imidazole and one pyridine ligand to compounds with one imidazole and two pyridine ligands, $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{N-RIm})]\text{BAr}_4^f$ (**4a**, $\text{R} = \text{Me}$; **4b**, $\text{R} = \text{Mes}$; $\text{dmap} = 4$ -dimethylamino-pyridine).^[22] Treatment of **4a** or **4b** with $\text{KN}(\text{SiMe}_3)_2$ (1 equiv) in THF at -78°C followed by reaction with AgOTf yielded the cationic pyridylimidazole complexes **5a** and **5b**, respectively (Scheme 5).

The NMR spectroscopic data of **5a** and **5b** in solution in CD_2Cl_2 show the asymmetry of the rhenium complexes. We ob-



Scheme 4. Activation of the two *ortho*-CH groups of a pyridine ligand.



Scheme 5. Reactivity of compounds **4a** and **4b**.

served three signals for the three carbonyl ligands in the ^{13}C NMR spectra and two sets of signals for the two different dmap groups (coupled and intact) in the ^1H NMR spectra. Significantly, the ^1H NMR spectra show only two signals for the imidazole ring CH groups, which indicated that the deprotonation occurred at this ligand. The molecular structure of the cation of compound **5b**, determined by X-ray diffraction,^[23] is depicted in Figure 3 and is in agreement with the spectroscopic data in solution. The *fac*- $\text{Re}(\text{CO})_3$ fragment displays a dmap ligand and a pyridylimidazole chelate formed by coupling of the *N*-MesIm central carbon atom (C2) and a C_{ortho} atom of the other dmap ligand (C6). The bidentate ligand formed is aromatic, evidenced by the angles and bond lengths found for both rings, which are virtually in the same plane.

This reaction shows that employment of the more electron-rich dmap ligand does not prevent the proposed (see below)

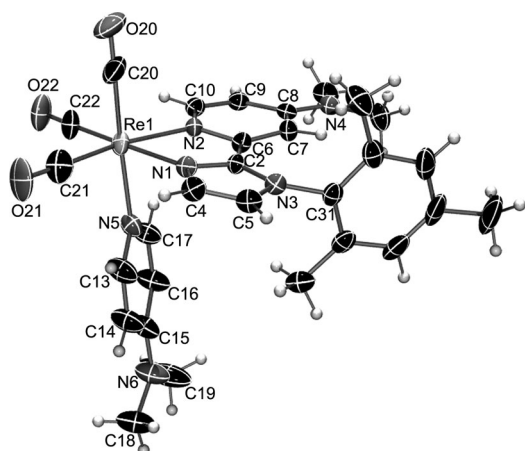


Figure 3. Molecular structure of the cation of **5b**.

nucleophilic attack of the imidazol-2-yl group, and the formation of the pyridylimidazole ligand.

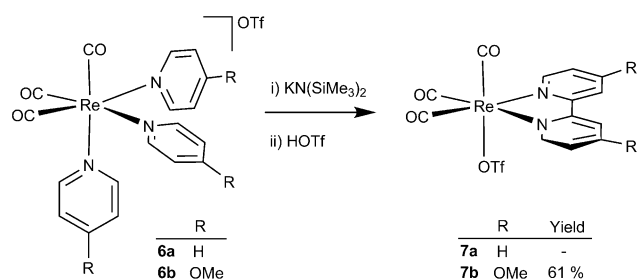
Note that, regardless of the particular composition of the cationic complex (two imidazole and one pyridine ligand, as in **1a–d**, or one imidazole and two pyridine ligands, as in **4a** and **4b**), no homocoupling products (with 2,2'-biimidazole or 2,2'-bipyridine chelates) have been detected, which suggests a clear-cut difference between the two types of ligands, in that *N*-alkylimidazoles are significantly more acidic and pyridines are more electrophilic.

In the absence of mechanistic studies, we speculate that the formation of the pyridylimidazole complexes occurs by deprotonation of the imidazole C2–H, nucleophilic attack of the deprotonated carbon atom onto a pyridine *ortho*-carbon atom to afford a dearomatized intermediate, which then would be oxidized by Ag^+ ,^[24,25] the latter step encouraged by restoration of aromaticity and conjugation between the two adjacent aromatic rings.^[26] We have encountered that two equivalents of AgOTf are required for the reactions to reach completion. This could be an indication of two consecutive one-electron oxidations: the neutral C–C coupled product would undergo a one-electron oxidation to give a radical cation, followed by deprotonation to give a radical, then oxidation to the observed product. The base for the second deprotonation (only one equivalent of $\text{KN}(\text{SiMe}_3)_2$ is used) would be $\text{HN}(\text{SiMe}_3)_2$ formed in the first deprotonation step.^[27]

We extended this reactivity to tris(2-pyridyl) derivatives in an attempt to obtain 2,2'-bipyridine (bipy) ligands after the dehydrogenative C–C coupling reaction. A more difficult deprotonation was anticipated because pyridines are less acidic than *N*-alkylimidazoles.^[28] 2,2'-Bipyridines are one of the most versatile and widely used type of bidentate ligand in organometallic and inorganic chemistry.^[29] Heterogeneous catalytic pyridine homocoupling is not applicable to 4-substituted pyridines,^[30] and the other major method to prepare the bipy moiety—transition-metal catalyzed cross-coupling reactions—requires prefunctionalization of the substrates.^[31]

The reaction of $[\text{Re}(\text{CO})_3(\text{dmap})_3]\text{OTf}$, first with $\text{KN}(\text{SiMe}_3)_2$, then with AgOTf, afforded the coupling product $[\text{Re}(2,2'\text{-bipy-4,4'}\text{-NMe}_2)(\text{CO})_3(\text{dmap})]\text{OTf}$, which was fully characterized, including a solid-state X-ray structure determination.^[9] Tris(2-pyridyl) compounds $[\text{Re}(\text{CO})_3(\text{Py-R})_3]\text{OTf}$ (**6a**, R = H; **6b**, OMe) were prepared by thermal substitution of the DMSO ligands of the known compound $[\text{Re}(\text{CO})_3(\text{dmsO})_3]\text{OTf}$ ^[32] by pyridine or 4-methoxypyridine, respectively.^[22] The reaction of **6a** with $\text{KN}(\text{SiMe}_3)_2$ in THF at -78°C , followed by oxidation with HOTf, led to the formation of **7a** (Scheme 6). The known bipy complex $[\text{Re}(2,2'\text{-bipy})(\text{CO})_3(\text{OTf})]$ ^[33] was prepared independently from $[\text{Re}(\text{CO})_5(\text{OTf})]$ and 2,2'-bipy heated at reflux in toluene. Its spectroscopic data in solution are identical to those of **7a**, which confirms the composition of the latter.

The analogous deprotonation of **6b**, followed by addition of HOTf (1 equiv), afforded the triflate complex $[\text{Re}(2,2'\text{-bipy-4,4'}\text{-OMe})(\text{CO})_3(\text{OTf})]$ (**7b**). The reaction was followed by IR spectroscopy, which showed that the addition of the base afforded a neutral species ($\tilde{\nu}_{\text{CO}} = 2029, 1917\text{ cm}^{-1}$ replaced by $\tilde{\nu}_{\text{CO}} = 1993, 1882, 1865\text{ cm}^{-1}$) and that, upon HOTf addition, oxidative



Scheme 6. Reactivity of tris(pyridyl) compounds **6a** and **6b**.

rearomatization occurred (upfield shift to $\tilde{\nu}_{\text{CO}}=2032, 1931, 1909 \text{ cm}^{-1}$). In accordance, the $^1\text{H NMR}$ spectrum of **7b** showed the typical pattern for a symmetric 4,4'-disubstituted-2,2'-bipyridine ligand and in the $^{13}\text{C NMR}$ spectrum only two signals, one twice the intensity of the other, are found for the three carbonyl ligands, which indicates the presence of a molecular mirror plane. The molecular structure of compound **7b**, determined by X-ray diffraction^[34] (Figure 4) confirmed the

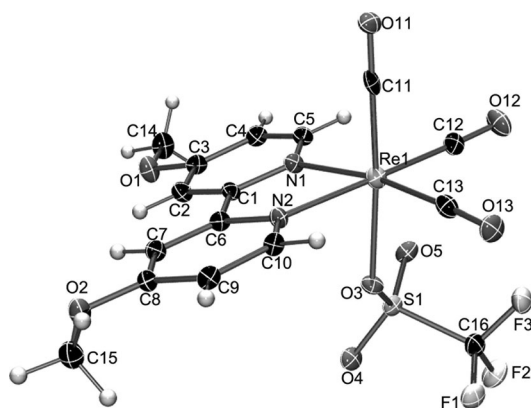


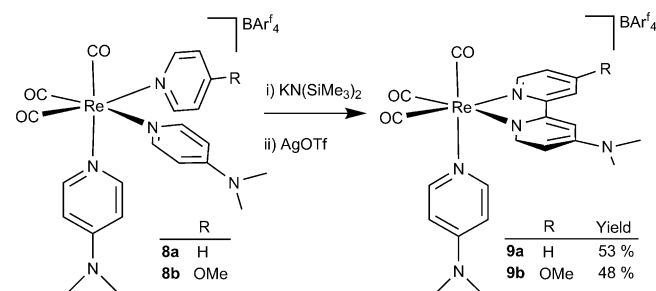
Figure 4. Molecular structure of complex **7b**.

presence of the 4,4'-dimethoxy-2,2'-bipyridine ligand coordinated to a *fac*- $\text{Re}(\text{CO})_3$ fragment. The remaining coordination site (to complete the rhenium pseudo-octahedral geometry) is occupied by a triflate ligand.

For compounds **6a** and **6b**, we found that employment of HOTf as the oxidant afforded better results than AgOTf or other conventional oxidants (such as I_2 , FeCp_2^+ , or 2,2,6,6-tetramethylpiperidine *N*-oxide). In addition, we found that the uncoupled pyridine ligand is substituted by triflate. The formation of complexes **7a** and **7b** that contain 2,2'-bipyridine ligands shows that the deprotonation of an *ortho* C–H group of a pyridyl ligand has been achieved, a reaction that, to our knowledge, has no precedent.^[9] In fact, there are just a few examples of metal-mediated coupling of pyridines, restricted to alkali metals or very reactive early transition metals.^[16a,35]

Finally, going one step further, we synthesized mixed tris(pyridyl) complexes, that is, they simultaneously display two different types of pyridyl ligands coordinated to the rhenium tricarbonyl fragment. Compounds $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{Py-R})]\text{BAR}_4^f$ (**8a**, R=H; **8b**, OMe) were synthesized by addition of pyridine

or 4-methoxypyridine to $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{OTf})]$ in the presence of NaBAR_4^f . The treatment of compounds **8a** and **8b** with $\text{KN}(\text{SiMe}_3)_2$ and AgOTf afforded compounds **9a** and **9b**, respectively, in good yields, as the only reaction products (Scheme 7).



Scheme 7. Reactivity of tris(pyridyl) compounds **8a** and **8b**.

The $^1\text{H NMR}$ spectrum of **9a** in CD_2Cl_2 shows the loss of the molecular mirror plane (present in **8a**) and displayed signals that correspond to an asymmetric complex. This is indicative of a cross-coupling product (the homocoupling reaction would lead to a symmetric derivative). Thus, in the $^1\text{H NMR}$ spectrum three signals are observed at $\delta=8.54, 7.19,$ and 6.73 ppm , which integrate for one hydrogen atom each and correspond to the dmap ligand coupled to the pyridyl ring to form the asymmetric bipy unit. In accordance, three signals at $\delta=9.10, 8.08,$ and 7.60 ppm that correspond to one, two, and one hydrogen atom, respectively, are observed for this pyridyl group. The spectrum also shows the *AA'BB'* system that corresponds to the dmap ligand and the two, now inequivalent, dimethyl-amino groups. The $^{13}\text{C NMR}$ spectrum of **9a** is in agreement with the asymmetry of the molecule, for example, one signal is observed for each bipy carbon atom. Analogously, compound **9b** features an asymmetric 4,4'-disubstituted-2,2'-bipyridine ligand, evidenced by its spectroscopic data in solution. The selectivity of these reactions is remarkable because the employment of very similar heteroaromatic ligands (different types of pyridines) leads only to the cross-coupling products, and the homocoupling products are not observed.

Conclusion

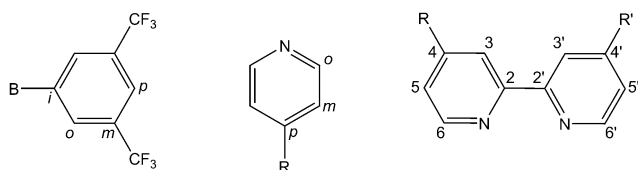
Unprecedented intramolecular oxidative C–H coupling to link either two pyridine or a pyridine and an imidazole ligand allowed the synthesis of 2,2'-heterobiaryl chelate ligands in the coordination sphere of rhenium tricarbonyl complexes. No functionalization of the imidazole or pyridine is needed other than their coordination to the same metal center, which increases the acidity of the C2–H imidazole group and the electrophilic character of the pyridine ligand. Pyridylimidazole complexes are selectively obtained, without any homocoupling (imidazole–imidazole or pyridine–pyridine) products. The extension of this reactivity to tris(pyridyl) complexes led to the synthesis of 2,2'-bipyridine ligands, which implies the deprotonation of an *ortho*-CH group of a pyridine ligand, a reaction without precedent.^[9] The coordination of two different pyridyl

ligands to the same metal center selectively affords the cross-coupling products, asymmetric 4,4'-disubstituted-2,2'-bipyridines, and no homocoupling products are observed.

Experimental Section

General

All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were distilled from Na (toluene and hexanes), Na/benzophenone (THF), and CaH₂ (CH₂Cl₂). Compounds [Re(CO)₃(N-Rlm)₂(OTf)] (R = Me, Mes),^[10e] [Re(CO)₃(dmsO)₃OTf,^[32] N-Meslm,^[36] and NaBAR₄^[37] were prepared as previously reported. Deuterated dichloromethane (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 300, DPX-300 or Avance 400 spectrometer. Samples for NMR spectroscopy were prepared under nitrogen by using Kontes manifolds purchased from Aldrich. ¹H and ¹³C{¹H} NMR spectra were referenced to the internal residual-solvent peak. IR spectra of samples in solution in 0.2 mm CaF₂ cells were measured with a PerkinElmer FT 1720-X spectrometer. Full experimental details for all compounds are given in the Supporting Information, representative compounds are reported below. Labeling scheme for BAR₄^f, pyridine, and 2,2'-bipyridine ligands:



Crystal-structure determination for 3a, 3e, 5b, and 7b

Data collection was performed with an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, by using Cu_{Kα} radiation ($\lambda = 1.5418 \text{ \AA}$). Images were collected at a 65 mm fixed crystal-detector distance, by using the oscillation method, with 1° oscillation and variable exposure time per image (4–16 s). The data-collection strategy was calculated with the program CrysAlis^{Pro} CCD.^[38] Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.^[38] An empirical absorption correction was applied by using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis^{Pro} RED.^[38] In all cases, the structures were solved with SIR92^[39] and finally refined by the full-matrix least-squares method based on F^2 by SHELXL.^[40] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to $\times 1.2$ the U_{eq} of the atoms to which they are attached ($\times 1.5$ for methyl groups). Molecular graphics were constructed with ORTEP.^[41] CCDC-981228 (5b), 981229 (7b), 981230 (3b), and 981231 (3a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 1c

NaBAR₄^f (0.124 g, 0.140 mmol) and pyridine (0.011 mL, 0.140 mmol) were added to a solution of [Re(CO)₃(N-Meslm)₂(OTf)] (0.100 g,

0.126 mmol) in CH₂Cl₂ (20 mL) and the mixture was stirred for 2 h at rt. The solution was filtered from the white solid via cannula and concentrated under reduced pressure to a volume of 5 mL. Hexane (15 mL) was added and caused the precipitation of a white solid, which was washed with hexane (3 \times 15 mL) and dried under vacuum to give **1c** (181 mg, 88%). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 8.49$ (m, 2H; H_o, py), 8.01 (m, 1H; H_p, py), 7.74 (brs, 8H; H_o, BAR₄^f), 7.65 (m, 2H; NCHN N-Meslm), 7.58 (s, 4H; H_p, BAR₄^f), 7.51 (m, 2H; H_m, py), 7.14 (m, 2H; CH N-Meslm), 7.07 (m, 2H; CH N-Meslm), 7.03 (s, 4H; H_m N-Meslm), 2.34 (s, 6H; CH₃ N-Meslm), 1.97 ppm (s, 12H; CH₃ N-Meslm); ¹³C NMR (300 MHz, CD₂Cl₂): $\delta = 194.7$ (2 \times CO), 194.4 (CO), 162.2 (q, $J = 49.8$ Hz; C_i, BAR₄^f), 153.5, 141.6, 141.3, 140.6, 134.7, 131.6, 130.6, 129.9, 127.3, 124.0 (N-Meslm and py), 135.2 (C_o, BAR₄^f), 129.3 (q, $J = 31.5$ Hz; C_m, BAR₄^f), 125.0 (q, $J = 272.3$ Hz; CF₃), 117.9 (C_p, BAR₄^f), 21.0 (2 \times CH₃ N-Meslm), 17.4 ppm (4 \times CH₃ N-Meslm); IR (THF): $\tilde{\nu}_{CO} = 2031, 1918 \text{ cm}^{-1}$; elemental analysis calcd (%) for C₆₄H₄₅BF₂₄N₅O₃Re: C 48.50, H 2.86, N 4.42; found: C 48.72, H 3.07, N 4.50.

Complex 2c

KN(SiMe₃)₂ (0.120 mL, 0.5 M in toluene, 0.060 mmol) was added to a solution of **1c** (0.080 g, 0.050 mmol) in THF (20 mL) previously cooled to -78°C . The color of the solution changed immediately from colorless to bright yellow. The mixture was allowed to reach rt, then AgOTf (0.027 g, 0.105 mmol) was added and the mixture was stirred for 5 min. The solvent was evaporated to dryness under reduced pressure, diethyl ether (25 mL) was added, and the suspension was decanted for 12 h at -20°C . The crude reaction mixture was filtered via cannula and the solvent was evaporated under vacuum. The residue was extracted with CH₂Cl₂ (20 mL), filtered through silica gel, the solvent was evaporated under reduced pressure, and the residue was washed with hexane (3 \times 15 mL). Compound **2c** (55 mg, 69%) was obtained as a yellow oil. ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 9.11$ (m, 1H; *pyim*Mes), 7.75 (m, 1H; *pyim*Mes), 7.83 (s, 1H; CH *pyim*Mes), 7.77 (brs, 8H; H_o, BAR₄^f), 7.59 (brs, 4H; H_p, BAR₄^f), 7.51 (m, 2H; NCHN N-Meslm and *pyim*Mes), 7.30 (s, 1H; CH *pyim*Mes), 7.19 (s, 1H; H_m, *pyim*Mes), 7.11 (s, 1H; H_m, *pyim*Mes), 6.99 (s, 1H; H_m N-Meslm), 6.95 (s, 1H; H_m N-Meslm), 6.88 (s, 1H; CH N-Meslm), 6.73 (s, 1H; *pyim*Mes), 6.60 (s, 1H; CH N-Meslm), 2.40 (s, 3H; CH₃ *pyim*Mes), 2.30 (s, 3H; CH₃ N-Meslm), 2.01 (s, 3H; CH₃ *pyim*Mes), 1.68 (s, 3H; CH₃ *pyim*Mes), 1.85 (s, 3H; CH₃ N-Meslm), 1.63 ppm (s, 3H; CH₃ N-Meslm); ¹³C NMR (300 MHz, CD₂Cl₂): $\delta = 196.3, 195.3, 191.3$ (CO), 162.2 (q, $J = 49.8$ Hz; C_i, BAR₄^f), 154.5, 147.6, 147.0, 142.8, 141.5, 141.2, 140.4, 134.9, 134.8, 134.6, 134.1, 131.9, 131.5, 131.2, 130.9, 130.8, 129.8, 128.9, 127.8, 127.7, 123.2, 121.6 (N-Meslm and *pyim*Mes), 135.2 (C_o, BAR₄^f), 129.3 (q, $J = 31.5$ Hz; C_m, BAR₄^f), 125.0 (q, $J = 272.9$ Hz; CF₃), 117.9 (C_p, BAR₄^f), 21.2, 21.0, 17.4, 17.3 (CH₃ N-Meslm and *pyim*Mes), 17.0 ppm (2 \times CH₃ N-Meslm); IR (THF): $\tilde{\nu}_{CO} = 2031, 1922 \text{ cm}^{-1}$; elemental analysis calcd (%) for C₆₄H₄₃BF₂₄N₅O₃Re: C 48.56, H 2.74, N 4.42; found: C 48.78, H 2.89, N 4.17.

Complex 2a*

N-Methylimidazole (0.015 mL, 0.188 mmol) was added to a solution of [Re(CO)₃(OTf)(*Pyim*-Me)] (0.100 g, 0.173 mmol)^[22] in CH₂Cl₂ (20 mL) and the mixture was stirred overnight. The resultant solution was concentrated to a volume of 5 mL. Hexane (15 mL) was added and the precipitate was washed with hexane (2 \times 15 mL) to give **2a*** (89 mg, 78%) as a yellow solid. ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 9.03$ (m, 1H; *pyim*Me), 8.25 (m, 2H; *pyim*Me), 7.56 (m, 1H; *pyim*Me), 7.44 (s, 1H; CH *pyim*Me), 7.36 (s, 1H; NCHN N-Meslm), 7.18 (s, 1H; CH *pyim*Me), 6.82 (m, 1H; CH N-Meslm), 6.75 (m, 1H;

CH *N*-Melm), 4.27 (s, 3H; CH₃ *pyimMe*), 3.56 ppm (s, 3H; CH₃ *N*-Melm); ¹³C NMR (300 MHz, CD₂Cl₂): δ = 197.1, 196.0, 192.2 (CO), 154.4, 148.4, 147.5, 141.3, 139.8, 130.5, 130.1, 129.1, 127.0, 123.7, 122.7 (*pyimMe* and *N*-Melm), 37.7, 34.9 ppm (CH₃ *pyimMe* and *N*-Melm); IR (CH₂Cl₂): $\tilde{\nu}_{\text{CO}}$ = 2029, 1917 cm⁻¹; elemental analysis calcd (%) for C₁₇H₁₅F₃N₅O₆ReS: C 30.91, H 2.29, N 10.60; found: C 30.80, H 2.15, N 10.69.

Complex 2e

Complex **2e** was prepared as described above for **2a*** from *N*-Meslm (0.035 g, 0.188 mmol) and [Re(CO)₃(OTf)(*Pyim*-Me)] (0.100 g, 0.173 mmol). Complex **2e** (112 mg, 85%) was obtained as a yellow solid. ¹H NMR (300 MHz, CD₂Cl₂): δ = 9.08 (m, 1H; *pyimMe*), 8.35 (m, 2H; *pyimMe*), 7.61 (m, 1H; *pyimMe*), 7.48 (m, 1H; NCHN *N*-Meslm), 7.39 (s, 1H; CH *pyimMe*), 7.32 (s, 1H; CH *pyimMe*), 6.97 (s, 2H; *N*-Meslm), 6.83 (m, 1H; CH *N*-Meslm), 6.64 (m, 1H; CH *N*-Meslm), 4.27 (s, 3H; CH₃ *pyimMe*), 2.36 (s, 3H; CH₃, *N*-Melm), 1.77 (s, 3H, CH₃ *N*-Meslm), 1.74 ppm (s, 3H; CH₃ *N*-Meslm); ¹³C NMR (300 MHz, CD₂Cl₂): δ = 196.9, 195.8, 191.8 (CO), 154.3, 148.4, 147.3, 141.9, 140.8, 140.0, 134.9, 131.7, 130.3, 129.7, 129.5, 129.2, 127.2, 123.8, 123.2 (*pyimMe* and *N*-Meslm), 37.9 (CH₃ *pyimMe*), 21.1 (CH₃ *N*-Meslm), 17.1 ppm (2 × CH₃ *N*-Meslm); IR (CH₂Cl₂): $\tilde{\nu}_{\text{CO}}$ = 2032, 1927, 1917 cm⁻¹; elemental analysis calcd (%) for C₂₅H₂₃F₃N₅O₆ReS: C 39.27, H 3.03, N 9.16; found: C 39.51, H 3.22, N 9.37.

Complex 3a

KN(SiMe₃)₂ (0.260 mL, 0.5 M in toluene, 0.130 mmol) was added to a solution of **2a*** (0.080 g, 0.121 mmol) in THF (20 mL) previously cooled to -78 °C; an immediate color change of the solution from yellow to red was observed. The solvent was evaporated to dryness, the residue extracted with CH₂Cl₂ (20 mL), and HOTf (12 μL, 0.136 mmol) was added. After 15 min stirring at rt, the reaction mixture was filtered via canula and the resultant orange solution was concentrated under reduced pressure to a volume of 5 mL. Addition of hexane (20 mL) caused precipitation. The precipitate was washed with hexane (2 × 15 mL) to give **3a** (46 mg, 58%) as a dark-yellow solid. Slow diffusion of hexane (25 mL) into a concentrated solution of **3a** in CH₂Cl₂ at -20 °C afforded yellow crystals suitable for X-ray structure determination. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.33, 7.09, 7.03, and 6.90 (m, 1H each; CH *pyimMe* and *N*-Melm), 6.67 (m, 3H; *pyimMe*), 5.42 (m, 1H; *pyimMe*), 3.85 and 3.71 ppm (s, 3H each; CH₃ *pyimMe* and *N*-Melm); ¹³C NMR (300 MHz, CD₂Cl₂): δ = 195.4, 194.7, 194.5 (CO), 147.6, 146.9, 130.1, 128.7, 128.3, 126.4, 126.1, 125.6, 124.7, 121.1 (*pyimMe* and *N*-Melm), 56.4 (C_{sp3} *pyimMe*), 35.8, 35.1 ppm (CH₃ *pyimMe* and *N*-Melm); IR (CH₂Cl₂): $\tilde{\nu}_{\text{CO}}$ = 2032, 1925, 1915 cm⁻¹; elemental analysis calcd (%) for C₁₇H₁₅F₃N₅O₆ReS: C 30.91, H 2.29, N 10.60; found: C 31.14, H 2.45, N 10.86.

Complex 3e

Compound **3e** was prepared as described above for **3a**, from KN(SiMe₃)₂ (0.240 mL, 0.5 M in toluene, 0.120 mmol), **2e** (0.080 g, 0.105 mmol), and HOTf (10 μL, 0.113 mmol). Slow diffusion of hexane (25 mL) into a concentrated solution of **3e** in CH₂Cl₂ at -20 °C afforded crystals of **3e** (52 mg, 65%) suitable for X-ray structure determination. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.98 (brs, 1H; NH), 7.38, 7.26, 7.14, and 6.95 (m, 1H each; CH *pyimMe* and *N*-Meslm), 7.09 (s, 1H; *N*-Meslm), 7.01 (s, 1H; *N*-Meslm), 6.54 (m, 1H; *pyimMe*), 6.19 (m, 1H; *pyimMe*), 5.25 (m, 2H; *pyimMe*), 3.86 (s, 3H; CH₃ *pyimMe*), 2.40 (s, 3H; CH₃, *N*-Meslm), 1.98 (s, 3H; CH₃, *N*-Meslm), 1.80 ppm (s, 3H; CH₃, *N*-Meslm); ¹³C NMR (300 MHz,

CD₂Cl₂): δ = 195.7, 195.0, 194.6 (CO), 149.1, 148.2, 141.5, 135.2, 131.1, 130.6, 130.3, 129.9, 129.8, 128.7, 126.8, 125.7, 124.3, 124.0, 121.0 (*pyimMe* and *N*-Meslm), 56.8 (C_{sp3} *pyimMe*), 36.2 (CH₃ *pyimMe*), 21.2 (CH₃ *N*-Meslm), 18.0, 17.1 ppm (CH₃ *N*-Meslm); IR (CH₂Cl₂): $\tilde{\nu}_{\text{CO}}$ = 2032, 1923 cm⁻¹; elemental analysis calcd (%) for C₂₅H₂₃F₃N₅O₆ReS: C 39.27, H 3.03, N 9.16; found: C 39.11, H 3.30, N 9.47.

Compound 4a

A mixture of [ReBr(CO)₃] (0.069 g, 0.170 mmol) and DMAP (0.044 g, 0.357 mmol) were heated at reflux in toluene for 2 h. The solvent was evaporated to dryness, the white residue was dissolved in CH₂Cl₂ (20 mL), AgOTf (0.053 g, 0.206 mmol) was added, and the mixture was stirred in the dark for 2 h. The solution was filtered to separate the white solid (AgBr), the filtrate was evaporated to dryness, and the residue was washed with hexane (2 × 15 mL) and diethylether (2 × 15 mL). [Re(CO)₃(dmap)₂(OTf)] was obtained as a white microcrystalline solid. NaBAR₄^f (0.147 g, 0.166 mmol) and *N*-Melm (0.013 mL, 0.166 mmol) were added to a solution of [Re(CO)₃(dmap)₂(OTf)] (0.100 g, 0.151 mmol) in CH₂Cl₂ (25 mL) and the reaction mixture was stirred for 3 h at rt. The solution was filtered via canula and concentrated under reduced pressure to a volume of 5 mL. Hexane (15 mL) was added and caused a white solid to precipitate. The precipitate was separated, washed with hexane (2 × 15 mL), and dried under vacuum to give **4a** (198 mg, 90%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.87 (d, *J* = 5.9 Hz, 4H; dmap), 7.80 (brs, 8H; H_o BAR₄^f), 7.62 (brs, 4H; H_p BAR₄^f), 7.60 (s, 1H; NCHN *N*-Melm), 6.98 (m, 1H; CH *N*-Melm), 6.90 (m, 1H; CH *N*-Melm), 6.49 (d, *J* = 5.9 Hz, 2H; dmap), 3.69 (s, 3H; CH₃ *N*-Melm), 3.01 ppm (s, 12H; CH₃ dmap); ¹³C NMR (300 MHz, CD₂Cl₂): δ = 195.8 (brs; CO), 162.2 (q, *J* = 50.4 Hz; C_i BAR₄^f), 155.2 (C_p dmap), 152.2 (C_o dmap), 141.2 (NCHN, *N*-Melm), 135.2 (C_o BAR₄^f), 130.5 (CH, *N*-Melm), 129.3 (q, *J* = 31.0 Hz; C_m BAR₄^f), 125.0 (q, *J* = 272.0 Hz; CF₃), 122.9 (CH, *N*-Melm), 117.9 (C_p BAR₄^f), 108.5 (C_m dmap), 39.2 (4 × CH₃ dmap), 34.9 ppm (CH₃ *N*-Melm); IR (THF): $\tilde{\nu}_{\text{CO}}$ = 2024, 1909 cm⁻¹; elemental analysis calcd (%) for C₅₃H₃₈BF₂₄N₆O₃Re: C 43.60, H 2.62, N 5.76; found: C 43.81, H 2.69, N 5.61.

Complex 5a

Compound **5a** was prepared as described above for **2a**, from **4a** (0.088 g, 0.060 mmol), KN(SiMe₃)₂ (0.150 mL, 0.5 M solution in toluene, 0.075 mmol), and AgOTf (0.032 g, 0.124 mmol). Compound **5a** (35 mg, 40%) was obtained as a yellow microcrystalline solid. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.55 (d, *J* = 6.9 Hz, 1H; *dmapimMe*), 7.78 (brs, 8H; H_o BAR₄^f), 7.67 (d, *J* = 6.1 Hz, 2H; dmap), 7.60 (brs, 4H; H_p BAR₄^f), 7.46 (d, *J* = 1.2 Hz, 1H; CH *dmapimMe*), 7.11 (d, *J* = 1.2 Hz, 1H; CH *dmapimMe*), 6.90 (d, *J* = 2.6 Hz, 1H; *dmapimMe*), 6.64 (dd, *J* = 6.9, 2.6 Hz, 1H; *dmapimMe*), 6.29 (d, *J* = 6.1 Hz, 2H; dmap), 4.00 (s, 3H; CH₃ *dmapimMe*), 3.10 and 2.87 ppm (s, 6H each; CH₃ *dmapimMe* and dmap); ¹³C NMR (300 MHz, CD₂Cl₂): δ = 197.6, 196.5, 192.9 (CO), 162.2 (q, *J* = 50.4 Hz; C_i BAR₄^f), 155.4, 154.8, 153.0, 150.7, 149.2, 147.0, 129.7, 128.0, 108.5, 108.1, 104.6 (dmap and *dmapimMe*), 135.2 (C_o BAR₄^f), 129.3 (q, *J* = 31.4 Hz; C_m BAR₄^f), 125.0 (q, *J* = 272.5 Hz; CF₃), 117.9 (C_p BAR₄^f), 39.8, 39.1 (2 × CH₃; *dmapimMe* and dmap), 37.1 ppm (CH₃ *dmapimMe*); IR (THF): $\tilde{\nu}_{\text{CO}}$ = 2024, 1913 cm⁻¹; elemental analysis calcd (%) for C₅₃H₃₆BF₂₄N₆O₃Re: C 43.66, H 2.49, N 5.76; found: C 43.97, H 2.62, N 5.45.

Complex 6a

The synthesis of compound **6a** is an adaptation of those previously reported.^[32,42] A mixture of $[\text{Re}(\text{CO})_3(\text{dmsO})_3]\text{OTf}$ (0.200 g, 0.306 mmol) and pyridine (0.74 mL, 9.18 mmol) was heated at reflux in acetone (40 mL) for 30 h. The solvent was evaporated to dryness and the sticky residue was washed with Et_2O (3×20 mL) and dried under vacuum to afford compound **6a** (149 mg, 73%) as a white solid. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.53$ (m, 6H; H_o py), 8.10 (m, 3H; H_p py), 7.63 ppm (m, 6H; H_m py); ^{13}C NMR (300 MHz, CD_2Cl_2): $\delta = 194.3$ (CO), 153.7 (C_o py), 140.9 (C_p py), 128.0 ppm (C_m py); IR (THF): $\tilde{\nu}_{\text{CO}} = 2033, 1924 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N}_3\text{O}_6\text{ReS}$: C 34.76, H 2.30, N 6.40; found: C 34.55, H 2.24, N 6.12.

Compound 7a

$\text{KN}(\text{SiMe}_3)_2$ (0.340 mL, 0.5 M solution in toluene, 0.170 mmol) was added to a solution of **6a** (0.100 g, 0.152 mmol) in THF (20 mL) at -78°C . The mixture was allowed to stir for 15 min, then the solvent was evaporated to dryness under reduced pressure. A solution of HOTf (15 μL , 0.170 mmol) in toluene (20 mL) was added to the residue and the resultant yellow solution was filtered via canula. The solvent was evaporated under reduced pressure to a volume of 3 mL. Addition of hexane (15 mL) caused the precipitation of **7a** as a yellow solid, determined by comparison of the spectral data with the literature data.^[33]

Compound 8a

A mixture of $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{OTf})]$ (0.105 g, 0.158 mmol), prepared as described above for **4a**, NaBARf_4 (0.151 g, 0.170 mmol), and pyridine (14 μL , 0.173 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 h at rt. The colorless solution was separated from the white solid (NaOTf) via canula and concentrated under reduced pressure to a volume of 4 mL. Addition of hexane (20 mL) caused the precipitation of a white solid, which was washed with hexane (2×15 mL) to give **8a** (399 mg, 74%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.47$ (m, 2H; H_o py), 7.97 (m, 1H; H_p py), 7.83 (d, $J = 7.4$ Hz, 4H; H_o dmap), 7.74 (brs, 8H; H_o BARf_4), 7.57 (brs, 4H; H_p BARf_4), 7.47 (m, 2H; H_m py), 6.50 (d, $J = 7.4$ Hz, 4H; H_m dmap), 3.03 ppm (s, 12H; CH_3 dmap); ^{13}C NMR (300 MHz, CD_2Cl_2): $\delta = 195.4$ (brs; CO), 162.1 (q, $J = 52.8$ Hz; C_i BARf_4), 155.2 (C_p dmap), 153.4 (C_o py), 152.0 (C_o dmap), 140.2 (C_p py), 135.2 (C_o BARf_4), 129.3 (q, $J = 29.9$ Hz; C_m BARf_4), 127.2 (C_m py), 124.9 (q, $J = 272.7$ Hz; CF_3), 117.8 (C_p BARf_4), 108.8 (C_m dmap), 39.4 ppm ($4 \times \text{CH}_3$ dmap); IR (THF): $\tilde{\nu}_{\text{CO}} = 2028, 1916 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{37}\text{BF}_{24}\text{N}_5\text{O}_3\text{Re}$: C 44.52, H 2.56, N 4.81; found: C 44.79, H 2.50, N 5.11.

Compound 9a

$\text{KN}(\text{SiMe}_3)_2$ (0.150 mL, 0.5 M solution in toluene, 0.075 mmol) was added to a solution of **8a** (0.100 g, 0.069 mmol) in THF (20 mL) that was previously cooled to -78°C . The color of the solution changed immediately from colorless to bright yellow. The mixture was allowed to reach room temperature and stirred for 15 min, then AgOTf (38 mg, 0.150 mmol) was added. The solvent was evaporated to dryness, Et_2O (25 mL) was added, and the reaction mixture was allowed to settle down for 12 h at -20°C . The yellow solution was filtered via canula and the solvent evaporated under vacuum. The residue was extracted with CH_2Cl_2 and filtered through silica gel. The filtrate was evaporated to dryness to give a yellow oil, which was washed with hexane (2×15 mL) to give **9a** (54 mg, 53%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 9.10$ (m, 1H; H_6 bipy-

4-NMe₂), 8.54 (d, $J = 6.7$ Hz, 1H; H_6 bipy-4-NMe₂), 8.08 (m, 2H H_3 and H_4 bipy-4-NMe₂), 7.74 (brs, 8H; H_o BARf_4), 7.61 (m, 1H; H_5 bipy-4-NMe₂), 7.55 (m, 6H; H_p BARf_4 and H_o dmap), 7.19 (d, $J = 2.6$ Hz, 1H; H_3 bipy-4-NMe₂), 6.73 (dd, $J = 6.7, 2.6$ Hz, 1H; H_5 bipy-4-NMe₂), 6.25 (d, $J = 6.2$ Hz, 2H; H_m dmap), 3.15 (s, 6H; CH_3 bipy-4-NMe₂), 2.87 ppm (s, 6H; CH_3 bipy-4-NMe₂); ^{13}C NMR (300 MHz, CD_2Cl_2): $\delta = 197.2$ ($2 \times \text{CO}$), 193.0 (CO), 162.1 (q, $J = 52.8$ Hz, C_i BARf_4), 157.3, 155.6, 155.1, 154.9, 153.4, 153.2, 152.1, 152.0, 150.4 (dmap and bipy-4-NMe₂), 135.2 (C_o BARf_4), 129.3 (q, $J = 29.9$ Hz; C_m BARf_4), 128.0, 127.2 (dmap and bipy-4-NMe₂), 124.9 (q, $J = 272.2$ Hz; CF_3), 117.8 (C_p BARf_4), 123.4, 110.1, 108.8, 108.3, 39.9 (dmap and bipy-4-NMe₂), 39.2 ppm (CH_3 dmap and bipy-4-NMe₂); IR (THF): $\tilde{\nu}_{\text{CO}} = 2026, 1916 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{35}\text{BF}_{24}\text{N}_5\text{O}_3\text{Re}$: C 44.58, H 2.42, N 4.81; found: C 44.67, H 2.51, N 4.69.

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- [17] Compound **2a***, analogous to **2a** (with an OTf instead of a BAr^f_4 counteranion), was synthesized from $[ReBr(CO)_3]$ and 1H-pyridylimidazole in good yield; for experimental details, see the Supporting Information.
- [18] Selected crystallographic data for **3a**: $C_{34}H_{30}F_6N_{10}O_{12}Re_2S_2$; $M_r = 1321.20$; monoclinic; $P2_1$; $a = 11.447(5)$ Å; $b = 16.617(5)$ Å; $c = 11.665(5)$ Å; $\alpha = 90^\circ$; $\beta = 105.613(5)^\circ$; $\gamma = 90^\circ$; 123.0(1) K; $V = 2137.0(15)$ Å³; $Z = 2$; 8384 reflections measured; 5665 independent reflns; $R_{int} = 0.0380$; $R_1 = 0.0356$; $wR_2 = 0.0858$ (all data). The results of the structural determination showed the presence of two independent molecules of **3a** in the asymmetric unit, the cation of one molecule is represented in Figure 2a.
- [19] Selected crystallographic data for **3b**: $C_{25}H_{23}F_3N_3O_6ReS$; $M_r = 764.76$; monoclinic; $P2_1/c$; $a = 14.9383(2)$ Å; $b = 8.9059(1)$ Å; $c = 20.7025(2)$ Å; $\alpha = 90^\circ$; $\beta = 100.451(1)^\circ$; $\gamma = 90^\circ$; 100.0(1) K; $V = 2708.55(5)$ Å³; $Z = 4$; 29469 reflections measured, 5433 independent reflns; $R_{int} = 0.0229$; $R_1 = 0.0511$; $wR_2 = 0.0531$ (all data).
- [20] This reaction pattern is reminiscent of that found for the deprotonation of $[Re(CO)_3(N-N)(N-RIm)]OTf$ ($N-N =$ bipy, phenanthroline) complexes, which afforded the C–C coupling and dearomatized products; see ref. [10c].
- [21] Notably, compound **2c** is not easy to prepare by an alternative method because the pyridyl-mesitylimidazole ligand is not known.
- [22] For further experimental details see the Supporting Information.
- [23] Selected crystallographic data for **5b**: $C_{61}H_{44}BF_2N_2O_3Re$; $M_r = 1562.03$; monoclinic; $P2_1/c$; $a = 19.1379(2)$ Å; $b = 18.1429(2)$ Å; $c = 20.2252(2)$ Å; $\alpha = 90^\circ$; $\beta = 114.260(1)^\circ$; $\gamma = 90^\circ$; 149.9 K; $V = 6402.4(1)$ Å³; $Z = 4$; 35956 reflections measured; 12603 independent reflns; $R_{int} = 0.0453$; $R_1 = 0.0535$; $wR_2 = 0.1544$ (all data).
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C–C Coupling of N-Heterocycles at the *fac*-Re(CO)₃ Fragment: Synthesis of Pyridylimidazole and Bipyridine Ligands

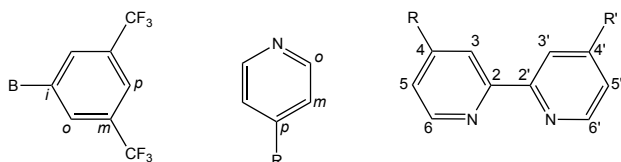
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Experimental Section

All manipulations were performed under an inert atmosphere of dinitrogen by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400 and DPX 300 spectrometers. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm CaF_2 cells. Compounds $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-RIm})_2]$ ($\text{R} = \text{Me}, \text{Mes}$),¹ $[\text{Re}(\text{CO})_3(\text{DMSO})_3]\text{OTf}$,² $N\text{-MesIm}$,³ and NaBAR^f_4 ⁴ were prepared following the reported procedures.

Labelling scheme for BAR^f , pyridyl and 2,2'-bipyridine ligands:



Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{py})]\text{BAR}^f_4$ (1a**).** NaBAR^f_4 (0.134 g, 0.151 mmol) and pyridine (0.012 mL, 0.151 mmol) were added to a solution of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (0.080 g, 0.137 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 2 h. at room temperature. The solution was filtered off the white solid via canula, concentrated under reduced pressure to a volume of 5 mL, and addition of hexane (15 mL) caused the precipitation of a white solid, which was washed with hexane (3×15 mL) and dried in vacuum. Yield: 168 mg (87 %). IR (THF, cm^{-1}): 2028, 1914 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.40 (m, 2H, H_o py), 7.99 (m, 1H, H_p py), 7.73 (s_{br} , 8H, H_o BAR^f_4), 7.60 (s, 2H, NCHN $N\text{-MeIm}$), 7.58 (s_{br} , 4H, H_p BAR^f_4), 7.46 (m, 2H, H_m py), 7.01, 6.71 (s, 2H each, CH $N\text{-MeIm}$), 3.73 (s, 6H, CH_3 $N\text{-MeIm}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 194.8 ($2 \times \text{CO}$), 194.5 (CO), 162.2 (q ($J = 49.6$ Hz), C_i BAR^f_4), 153.5 (C_o py), 141.5 (NCHN , $N\text{-MeIm}$), 140.2 (C_p py), 135.2 (C_o BAR^f_4), 130.4 (CH , $N\text{-MeIm}$), 129.3 (q ($J = 31.4$ Hz), C_m BAR^f_4), 127.1 (C_m py), 125.0 (q ($J = 272.3$ Hz), CF_3 BAR^f_4), 123.4 (CH , $N\text{-MeIm}$), 117.9 (C_p BAR^f_4), 35.0 ($2 \times \text{CH}_3$ $N\text{-MeIm}$). Anal. Calcd. for $\text{C}_{48}\text{H}_{29}\text{BF}_{24}\text{N}_5\text{O}_3\text{Re}$: C 41.87, H 2.12, N 5.09. Found: C 41.49, H 2.31, N 4.85.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{pic})]\text{BAR}^f_4$ (1b**).** Compound **1b** was prepared as described above for **1a** starting from $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (0.100 g, 0.171 mmol), NaBAR^f_4 (0.153 g, 0.173 mmol) and γ -picoline (0.017 mL, 0.171 mmol). Compound **1b** was obtained as a white solid that was washed with hexane (2×20 mL) and dried under reduced pressure. Yield: 190 mg (80 %). IR (THF, cm^{-1}): 2031, 1917 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.23 (d ($J = 5.5$ Hz), 2H, pic), 7.77 (s_{br} , 8H, H_o BAR^f_4), 7.60 (s_{br} , 4H, H_p BAR^f_4), 7.58 (s, 2H, NCHN $N\text{-MeIm}$), 7.25 (d ($J = 5.5$ Hz), 2H, pic), 6.97, 6.73 (m, 2H each, CH $N\text{-MeIm}$), 3.69 (s, 6H, CH_3 $N\text{-MeIm}$), 2.39 (s, 3H, CH_3 pic). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 194.9 ($2 \times \text{CO}$), 194.7 (CO), 162.1 (q ($J = 50.0$ Hz), C_i BAR^f_4), 153.5 (C_o pic), 152.8 (C_p pic), 141.5 (NCHN , $N\text{-MeIm}$), 135.2 (C_o BAR^f_4), 130.4 (CH , $N\text{-MeIm}$), 129.3 (q ($J = 31.3$ Hz), C_m BAR^f_4), 127.9 (C_m pic), 125.0 (q ($J = 272.3$ Hz), CF_3), 123.3 (CH , $N\text{-MeIm}$), 117.9 (C_p BAR^f_4), 35.1 ($2 \times \text{CH}_3$ $N\text{-MeIm}$), 21.3 (CH_3 pic). Anal. Calcd. for $\text{C}_{49}\text{H}_{31}\text{BF}_{24}\text{N}_5\text{O}_3\text{Re}$: C 42.32, H 2.25, N 5.04. Found: C 42.73, H 2.41, N 5.11.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MesIm})_2(\text{py})]\text{BAR}^f_4$ (1c**).** NaBAR^f_4 (0.124 g, 0.140 mmol) and pyridine (0.011 mL, 0.140 mmol) were added to a solution of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MesIm})_2]$ (0.100 g, 0.126 mmol) in

CH₂Cl₂ (20 mL), and the mixture was stirred for 2 h. at room temperature. The solution was filtered off the white solid via canula, concentrated under reduced pressure to a volume of 5 mL, and addition of hexane (15 mL) caused the precipitation of a white solid, which was washed with hexane (3 × 15 mL) and dried in vacuum. Yield: 181 mg (88 %). IR (THF, cm⁻¹): 2031, 1918 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.49 (m, 2H, H_o py), 8.01 (m, 1H, H_p py), 7.74 (s_{br}, 8H, H_o BAr^f₄), 7.65 (m, 2H, NCHN *N*-MesIm), 7.58 (s, 4H, H_p BAr^f₄), 7.51 (m, 2H, H_m py), 7.14, 7.07 (m, 2H each, CH *N*-MesIm), 7.03 (s, 4H, H_m *N*-MesIm), 2.34 (s, 6H, CH₃ *N*-MesIm), 1.97 (s, 12H, CH₃ *N*-MesIm). ¹³C{¹H} NMR (CD₂Cl₂): δ 194.7 (2×CO), 194.4 (CO), 162.2 (q (*J*= 49.8 Hz), C_i BAr^f₄), 153.5, 141.6, 141.3, 140.6, 134.7, 131.6, 130.6, 129.9, 127.3, 124.0 (*N*-MesIm and py), 135.2 (C_o BAr^f₄), 129.3 (q (*J*= 31.5 Hz), C_m BAr^f₄), 125.0 (q (*J*= 272.3 Hz), CF₃), 117.9 (C_p BAr^f₄), 21.0 (2×CH₃ *N*-MesIm), 17.4 (4×CH₃ *N*-MesIm). Anal. Calcd. for C₆₄H₄₅BF₂₄N₅O₃Re: C 48.50 H 2.86, N 4.42. Found: C 48.72, H 3.07, N 4.50.

Synthesis of [Re(CO)₃(*N*-MesIm)₂(pic)]BAr^f₄ (1d**).** Compound **1d** was prepared as described above for **1b** starting from [Re(OTf)(CO)₃(*N*-MesIm)₂] (0.100 g, 0.126 mmol), NaBAr^f₄ (0.124 g, 0.140 mmol) and γ-picoline (0.014 mL, 0.140 mmol). Compound **1d** was obtained as white solid that was washed with hexane (2 × 20 mL) and dried under reduced pressure. Yield: 185 mg (83 %). IR (THF, cm⁻¹): 2030, 1916 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.30 (d (*J*= 5.2 Hz), 2H, pic), 7.75 (s_{br}, 8H, H_o BAr^f₄), 7.63 (m, 2H, NCHN *N*-MesIm), 7.58 (s_{br}, 4H, H_p BAr^f₄), 7.31 (d (*J*= 5.2 Hz), 2H, pic), 7.13, 7.08 (m, 2H each, CH *N*-MesIm), 7.03 (s, 4H, H_m *N*-MesIm), 2.42 (s, 3H, CH₃ pic), 2.33 (s, 6H, CH₃ *N*-MesIm), 1.97 (s, 12H, CH₃ *N*-MesIm). ¹³C{¹H} NMR (CD₂Cl₂): δ 194.8 (2×CO), 194.5 (CO), 162.2 (q (*J*= 49.7 Hz), C_i BAr^f₄), 153.7, 152.8, 141.6, 141.3, 134.8, 131.6, 130.7, 129.9, 128.1, 123.9 (*N*-MesIm and pic), 135.2 (C_o BAr^f₄), 129.3 (q (*J*= 31.7 Hz), C_m BAr^f₄), 125.0 (q (*J*= 272.5 Hz), CF₃), 117.9 (C_p BAr^f₄), 21.3 (CH₃ pic), 21.0 (2×CH₃ *N*-MesIm), 17.4 (4×CH₃ *N*-MesIm). Anal. Calcd. for C₆₅H₄₇BF₂₄N₅O₃Re: C 48.82 H 2.96, N 4.38. Found: C 48.67, H 3.05, N 4.33.

Reaction of 1a with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(*N*-MeIm)(pyimMe)]BAr^f₄ (2a**).** KN(SiMe₃)₂ (0.100 mL of a 0.5 M solution in toluene, 0.050 mmol) was added to a solution of [Re(CO)₃(*N*-MeIm)₂(py)]BAr^f₄ (**1a**) (0.055 g, 0.040 mmol) in THF (20 mL) previously cooled to -78 °C. The color of the solution changed immediately from colorless to bright yellow. The mixture was allowed to reach room temperature, AgOTf (0.021 g, 0.082 mmol) was added and the mixture was stirred for 5 min. The solvent was evaporated to dryness under reduced pressure, diethyl ether (25 mL) was added and the suspension was decanted for 12 h. at -20 °C. The reaction crude was then filtered via canula and the solvent was evaporated in vacuum. The residue was extracted with CH₂Cl₂ (20 mL), filtered through silica gel and the solvent was evaporated under reduced pressure to a volume of 5 mL. Addition of hexane (20 mL) caused the precipitation of a yellow solid that was washed with hexane (3 × 15 mL). Slow diffusion of hexane (15 mL) in a concentrated solution of **2a** in CH₂Cl₂ (5 mL) at -20 °C afforded yellow crystals, one of which was used for an X-ray structure determination. Yield: 26 mg (47 %). IR (THF, cm⁻¹): 2032, 1926, 1920 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.12 (m, 1H, pyimMe), 8.13 (m, 1H, pyimMe), 7.98 (m, 1H, pyimMe), 7.76 (s_{br}, 8H, H_o BAr^f₄), 7.61 (m, 1H, pyimMe), 7.59 (s_{br}, 4H, H_p BAr^f₄), 7.52 (d (*J*= 1.4 Hz), 1H, CH pyimMe), 7.30 (s, 1H, NCHN *N*-MeIm), 7.26 (d (*J*= 1.4 Hz), 1H, CH pyimMe), 6.75, 6.39 (m, 1H each, CH *N*-MeIm), 4.11 (s, 3H, CH₃ pyimMe), 3.56 (s, 3H, CH₃ *N*-MeIm). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.1, 194.9, 190.9 (CO), 162.2 (q (*J*= 49.8 Hz), C_i BAr^f₄), 154.5, 147.7, 146.9, 140.6, 139.5,

130.2, 127.0, 122.3, 122.0 (pyimMe and N-MeIm), 135.2 (C_o BAr₄^f), 129.3 (q (J= 30.5 Hz), C_m BAr₄^f), 125.0 (q (J= 271.7 Hz), CF₃), 117.9 (C_p BAr₄^f), 37.0 (CH₃ pyimMe), 34.4 (CH₃ N-MeIm). Anal. Calcd. for C₄₈H₂₇BF₂₄N₅O₃Re: C 41.94, H 1.98, N 5.09. Found: C 42.20, H 2.09, N 4.78.

Reaction of 1b with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(N-MeIm)(picimMe)]BAr₄^f (2b).

Compound **2b** was prepared as described above for **2a** starting from [Re(CO)₃(N-MeIm)₂(pic)]BAr₄^f (**1b**) (0.100 g, 0.072 mmol), KN(SiMe₃)₂ (0.170 mL of a 0.5 M solution in toluene, 0.085 mmol) and AgOTf (0.038 g, 0.148 mmol). Slow diffusion of hexane (15 mL) into a concentrated solution of **2b** in CH₂Cl₂ (5 mL) at -20 °C afforded orange crystals, one of which was used for an X-ray structure determination. Yield: 55 mg (56 %). IR (THF, cm⁻¹): 2031, 1918 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.94 (d (J= 5.7 Hz), 1H, *picimMe*), 7.76 (s_{br}, 9H, H_o BAr₄^f and 1H *picimMe*), 7.60 (s_{br}, 4H, H_p BAr₄^f), 7.49 (d (J= 1.3 Hz), 1H, *CH picimMe*), 7.41 (d (J= 5.7 Hz), 1H, *picimMe*), 7.29 (s, 1H, NCHN N-MeIm), 7.23 (d (J= 1.3 Hz), 1H, *CH picimMe*), 6.73, 6.28 (m, 1H each, *CH N-MeIm*), 4.11 (s, 3H, CH₃ *picimMe*), 3.55 (s, 3H, CH₃ N-MeIm), 2.56 (s, CH₃ *picimMe*). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.6, 195.5, 191.7 (CO), 162.1 (q (J= 49.9 Hz), C_i BAr₄^f), 154.3, 154.1 (C_o *picimMe*), 148.2 (NCN *picimMe*), 147.0 (C_p *picimMe*), 139.9 (NCHN N-MeIm), 135.2 (C_o BAr₄^f), 130.5, 128.6 (CH *picimMe*), 129.2, 122.6 (CH N-MeIm), 129.1 (q (J= 30.6 Hz), C_m BAr₄^f), 128.2, 123.3 (C_m *picimMe*), 125.0 (q (J= 271.7 Hz), CF₃), 117.9 (C_p BAr₄^f), 37.5 (CH₃ *picimMe*), 34.8 (CH₃ N-MeIm), 22.0 (CH₃ *picimMe*). Anal. Calcd. for C₄₉H₂₉BF₂₄N₅O₃Re: C 42.38, H 2.10, N 5.04. Found: C 42.56, H 2.21, N 5.28.

Reaction of 1c with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(N-MesIm)(pyimMes)] BAr₄^f (2c).

KN(SiMe₃)₂ (0.120 mL of a 0.5 M solution in toluene, 0.060 mmol) was added to a solution of [Re(CO)₃(N-MesIm)₂(py)]BAr₄^f (**1c**) (0.080 g, 0.050 mmol) in THF (20 mL) previously cooled to -78 °C. The color of the solution changed immediately from colorless to bright yellow. The mixture was allowed to reach room temperature, AgOTf (0.027 g, 0.105 mmol) was added and the mixture was stirred for 5 min. The solvent was evaporated to dryness under reduced pressure, diethyl ether (25 mL) was added and the suspension was decanted for 12 h. at -20 °C. The reaction crude was then filtered via cannula and the solvent was evaporated in vacuum. The residue was extracted with CH₂Cl₂ (20 mL), filtered through silica gel, the solvent was evaporated under reduced pressure and the residue was washed with hexane (3 × 15 mL). Compound **2c** was obtained as a yellow oil. Yield: 55 mg (69 %). IR (THF, cm⁻¹): 2031, 1922 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.11 (m, 1H, *pyimMes*), 7.75 (m, 1H, *pyimMes*), 7.83 (s, 1H, *CH pyimMes*), 7.77 (s_{br}, 8H, H_o BAr₄^f), 7.59 (s_{br}, 4H, H_p BAr₄^f), 7.51 (m, 2H, NCHN N-MesIm and *pyimMes*), 7.30 (s, 1H, *CH pyimMes*), 7.19, 7.11 (s, 1H each, H_m *pyimMes*), 6.99, 6.95 (s, 1H each, H_m N-MesIm), 6.88 (s, 1H, *CH N-MesIm*), 6.73 (s, 1H, *pyimMes*), 6.60 (s, 1H, *CH N-MesIm*), 2.40 (s, 3H, CH₃ *pyimMes*), 2.30 (s, 3H, CH₃ N-MesIm), 2.01, 1.68 (s, 3H each, CH₃ *pyimMes*), 1.85, 1.63 (s, 3H each, CH₃ N-MesIm). ¹³C{¹H} NMR (CD₂Cl₂): δ 196.3, 195.3, 191.3 (CO), 162.2 (q (J= 49.8 Hz), C_i BAr₄^f), 154.5, 147.6, 147.0, 142.8, 141.5, 141.2, 140.4, 134.9, 134.8, 134.6, 134.1, 131.9, 131.5, 131.2, 130.9, 130.8, 129.8, 128.9, 127.8, 127.7, 123.2, 121.6 (N-MesIm and *pyimMes*), 135.2 (C_o BAr₄^f), 129.3 (q (J= 31.5 Hz), C_m BAr₄^f), 125.0 (q (J= 272.9 Hz), CF₃), 117.9 (C_p BAr₄^f), 21.2, 21.0, 17.4, 17.3 (CH₃ N-MesIm and *pyimMes*), 17.0 (2×CH₃ N-MesIm). Anal. Calcd. for C₆₄H₄₃BF₂₄N₅O₃Re: C 48.56, H 2.74, N 4.42. Found: C 48.78, H 2.89, N 4.17.

Reaction of 1d with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(N-MesIm)(picimMes)] BAr^f₄ (2d). Compound **2d** was prepared as described above for **2a** starting from [Re(CO)₃(N-MesIm)₂(pic)]BAr^f₄ (**1d**) (0.096 g, 0.060 mmol), KN(SiMe₃)₂ (0.150 mL of a 0.5 M solution in toluene, 0.075 mmol) and AgOTf (0.032 g, 0.124 mmol). Compound **2d** was obtained as a brown oil. Yield: 54 mg (56 %). IR (THF, cm⁻¹): 2030, 1919 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.93 (d (*J*= 5.6 Hz), 1H, *picimMes*), 7.75 (sbr, 9H, H_o BAr^f₄ and *CH picimMes*), 7.58 (sbr, 4H, H_p BAr^f₄), 7.49 (s, 1H, NCHN *N-MesIm*), 7.32 (d (*J*= 5.6 Hz), 1H, *picimMes*), 7.28 (d (*J*= 1.3 Hz), 1H, *CH picimMes*), 7.20, 7.12 (s, 1H each, H_m Mes), 6.99, 6.96 (s, 1H each, H_m Mes), 6.86, 6.60 (m, 1H each, *CH N-MesIm*), 6.46 (s, 1H, *picimMes*), 2.42, 2.01, 1.68 (s, 3H each, CH₃ Mes), 2.30, 1.85, 1.67 (s, 3H each, CH₃ Mes) 2.19 (s, 3H, CH₃ *picimMes*). ¹³C {¹H} NMR (CD₂Cl₂): δ 196.4, 195.4, 191.5 (CO), 162.1 (q (*J*= 49.5 Hz), C_i BAr^f₄), 154.6, 153.7, 147.7, 146.7, 142.8, 141.1, 140.4, 135.0, 134.7, 134.6, 134.2, 131.7, 131.5, 131.1, 131.0, 130.7, 128.9, 128.5, 127.4, 123.2, 122.4 (*N-MesIm* and *picimMes*), 135.2 (C_o BAr^f₄), 129.3 (q (*J*= 31.7 Hz), C_m BAr^f₄), 125.0 (q (*J*= 272.5 Hz), CF₃), 117.9 (C_p BAr^f₄), 21.9, 21.2, 21.0, 17.4, 17.3, 17.2, 16.9 (CH₃ *N-MesIm* and *picimMes*).

Synthesis of [ReBr(CO)₃(pyimH)]. A mixture of [ReBr(CO)₃] (0.200 g, 0.492 mmol) and 1H-pyridylimidazole (0.079 g, 0.544 mmol) was refluxed in toluene (20 mL) for 7 hours. The solvent was then evaporated to dryness, and the yellow solid washed with hexane (2 × 15 mL) and dried in vacuo. Yield: 212 mg (87 %). IR (THF, cm⁻¹): 2019, 1916, 1889 (ν_{CO}). ¹H NMR (Acetone-d₆): δ 9.03 (m, 1H, *pyimH*), 8.26 (m, 2H, *pyimH*), 7.65 (m, 1H, *pyimH*), 7.62, 7.53 (m, 1H each, *CH pyimH*). ¹³C {¹H} NMR (Acetone-d₆): δ 198.0, 197.6, 189.5 (CO), 154.0, 149.1, 147.7, 140.3, 131.1, 126.5, 121.8 (*pyimH*, the last signal corresponds to two carbon atoms). Anal. Calcd. for C₁₁H₇BrN₃O₃Re: C 26.67, H 1.43, N 8.48. Found: C 26.57, H 1.34, N 8.30.

Synthesis of [ReBr(CO)₃(pyimMe)]. To a solution of [ReBr(CO)₃(pyimH)] (0.200 g, 0.404 mmol) in THF (20 mL) at -78 °C, KN(SiMe₃)₂ (0.9 mL of a 0.5 M solution in toluene, 0.450 mmol) was added, the mixture was stirred for 5 min and the solvent was evaporated to dryness. A solution of MeOTf (0.054 mL, 0.477 mmol) in CH₂Cl₂ (20 mL) was transferred via canula over the reaction residue and stirred for 15 min. at room temperature. The slurry was filtered off the white solid via canula and the resulting solution was evaporated under reduced pressure. Compound [ReBr(CO)₃(pyimMe)] was obtained as a yellow solid that was washed with hexane (2 × 15 mL), and diethyl ether (15 mL). Yield: 167 mg (81 %). IR (CH₂Cl₂, cm⁻¹): 2023, 1919, 1895 (ν_{CO}). ¹H NMR (Acetone-d₆): δ 9.03, 8.39, 8.26, 7.66 (m, 1H each, *pyimMe*), 7.55, 7.45 (m, 1H each, *CH pyimMe*), 4.36 (s, 3H, CH₃, *pyimMe*). ¹³C {¹H} NMR (Acetone-d₆): δ 201.5, 201.0, 192.8 (CO), 157.8, 151.3, 151.0, 143.4, 133.2, 131.4, 129.5, 126.3 (*pyimMe*), 40.0 (CH₃, *pyimMe*). Anal. Calcd. for C₁₂H₉BrN₃O₃Re: C 28.30, H 1.78, N 8.25. Found: C 28.19, H 1.71, N 8.30.

Synthesis of [Re(OTf)(CO)₃(pyimMe)]. A mixture of [ReBr(CO)₃(pyimMe)] (0.200 g, 0.393 mmol) and AgOTf (0.111 g, 0.432 mol) in CH₂Cl₂ (30 mL) was stirred in the dark for 2 hours. The reaction mixture was then filtered off the white solid (AgBr) through diatomeous earth, and the resulting yellow solution was concentrated in vacuo to a volume of 10 mL. Addition of hexane (20 mL) caused the precipitation of a yellow solid that was washed with hexane (2 × 15 mL). Yield: 198 mg (87 %). IR (CH₂Cl₂, cm⁻¹): 2035, 1931, 1908 (ν_{CO}). ¹H NMR (Acetone-d₆): δ 9.15 (m, 1H, *pyimMe*), 8.55 (m, 1H, *pyimMe*), 8.44 (m, 1H, *pyimMe*), 7.82 (m, 1H, *pyimMe*), 7.73, 7.58 (s, 1H each, *CH pyimMe*), 4.38 (s, 3H, CH₃ *pyimMe*).

$^{13}\text{C}\{^1\text{H}\}$ NMR (Acetone- d_6): δ 197.4, 196.6, 192.6 (CO), 155.8, 150.0, 148.4, 142.0, 130.9, 129.1, 127.4, 123.7 (pyimMe), 37.4 (CH_3 , pyimMe). Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{F}_3\text{N}_3\text{O}_6\text{ReS}$: C 26.99, H 1.57, N 7.26. Found: C 27.12, H 1.63, N 7.45.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})(\text{pyimMe})]\text{OTf}$ (2a***).** N-MeIm (0.015 mL, 0.188 mmol) was added to a solution of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{pyimMe})]$ (0.100 g, 0.173 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred overnight. The resulting solution was concentrated to a volume of 5 mL and addition of hexane (15 mL) caused the precipitation of a yellow solid, which was washed with hexane (2×15 mL). Yield: 89 mg (78 %). IR (CH_2Cl_2 , cm^{-1}): 2029, 1917 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.03 (m, 1H, pyimMe), 8.25 (m, 2H, pyimMe), 7.56 (m, 1H, pyimMe), 7.44 (s, 1H, CH pyimMe), 7.36 (s, 1H, NCHN N-MeIm), 7.18 (s, 1H, CH pyimMe), 6.82, 6.75 (m, 1H each, CH N-MeIm), 4.27 (s, 3H, CH_3 pyimMe), 3.56 (s, 3H, CH_3 N-MeIm). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 197.1, 196.0, 192.2 (CO), 154.4, 148.4, 147.5, 141.3, 139.8, 130.5, 130.1, 129.1, 127.0, 123.7, 122.7 (pyimMe and N-MeIm), 37.7, 34.9 (CH_3 pyimMe and N-MeIm). Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{N}_5\text{O}_6\text{ReS}$: C 30.91, H 2.29, N 10.60. Found: C 30.80, H 2.15, N 10.69.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MesIm})(\text{pyimMe})]\text{OTf}$ (2e**).** Compound **2e** was prepared as described above for **2a*** starting from N-MesIm (0.035 g, 0.188 mmol) and $[\text{Re}(\text{OTf})(\text{CO})_3(\text{pyimMe})]$ (0.100 g, 0.173 mmol). Compound **2e** was obtained as a yellow solid. Yield: 112 mg (85 %). IR (CH_2Cl_2 , cm^{-1}): 2032, 1927, 1917 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.08 (m, 1H, pyimMe), 8.35 (m, 2H, pyimMe), 7.61 (m, 1H, pyimMe), 7.48 (m, 1H, NCHN N-MesIm), 7.39, 7.32 (s, 1H each, CH pyimMe), 6.97 (s, 2H, N-MesIm), 6.83, 6.64 (m, 1H each, CH N-MesIm), 4.27 (s, 3H, CH_3 pyimMe), 2.36 (s, 3H, CH_3 , N-MesIm), 1.77, 1.74 (s, 3H each, CH_3 , N-MesIm). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 196.9, 195.8, 191.8 (CO), 154.3, 148.4, 147.3, 141.9, 140.8, 140.0, 134.9, 131.7, 130.3, 129.7, 129.5, 129.2, 127.2, 123.8, 123.2 (pyimMe and N-MesIm), 37.9 (CH_3 pyimMe), 21.1 (CH_3 N-MesIm), 17.1 ($2 \times \text{CH}_3$ N-MesIm). Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{F}_3\text{N}_5\text{O}_6\text{ReS}$: C 39.27, H 3.03, N 9.16. Found: C 39.51, H 3.22, N 9.37.

Reaction of $[\text{Re}(\text{CO})_3(\text{N-MesIm})(\text{pyimMe})]\text{OTf}$ (2e**) with $\text{KN}(\text{SiMe}_3)_2$. Synthesis of **IIe**.** $\text{KN}(\text{SiMe}_3)_2$ (0.240 mL of a 0.5 M solution in toluene, 0.120 mmol) was added to a solution of compound $[\text{Re}(\text{CO})_3(\text{N-MesIm})(\text{pyimMe})]\text{OTf}$ (**2e**) (0.080 g, 0.105 mmol) in THF (20 mL), previously cooled to -78 °C. After stirring for 5 min. the solution was evaporated to dryness, and the residue was washed with hexane (2×15 mL). Compound **IIe** was spectroscopically characterized from the crude reaction. IR (THF, cm^{-1}): 2004, 1885 (ν_{CO}). ^1H NMR (THF- d_8): δ 6.9 (m, 6H, CH pyimMe, CH N-MesIm and N-MesIm), 5.77, 5.30, 5.23, 4.18 (m, 1H each, pyimMe), 3.76 (s, 3H, CH_3 pyimMe), 2.32 (s, 3H, CH_3 , N-MesIm), 1.94, 1.93 (s, 3H each, CH_3 , N-MesIm).

Reaction of $[\text{Re}(\text{CO})_3(\text{N-MeIm})(\text{pyimMe})]\text{OTf}$ (2a***) with $\text{KN}(\text{SiMe}_3)_2$ and HOTf. Synthesis of **3a**.** $\text{KN}(\text{SiMe}_3)_2$ (0.260 mL of a 0.5 M solution in toluene, 0.130 mmol) was added to a solution of compound $[\text{Re}(\text{CO})_3(\text{N-MeIm})(\text{pyimMe})]\text{OTf}$ (**2a***) (0.080 g, 0.121 mmol) in THF (20 mL), previously cooled to -78 °C, affording immediately a change in the color of the solution, from yellow to red. The solvent was evaporated to dryness, the residue extracted with CH_2Cl_2 (20 mL) and HOTf (12 μL , 0.136 mmol) was added. After 15 min. stirring at room temperature, the reaction mixture was filtered via canula, and the resulting orange solution was concentrated under reduced pressure to a volume of 5 mL. Addition of hexane (20 mL) caused the precipitation of a dark yellow solid that was washed with hexane (2×15 mL). Slow diffusion of hexane (25 mL) into a concentrated solution of **3a** in CH_2Cl_2 at -20 °C afforded yellow

crystals, one of which was employed for an X-ray structure determination. Yield: 46 mg (58 %). IR (CH₂Cl₂, cm⁻¹): 2032, 1925, 1915 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.33, 7.09, 7.03, 6.90 (m, 1H each, *CH* *pyimMe* and *N-MeIm*), 6.67 (m, 3H, *pyimMe*), 5.42 (m, 1H, *pyimMe*), 3.85, 3.71 (s, 3H each, *CH*₃ *pyimMe* and *N-MeIm*). ¹³C{¹H} NMR (CD₂Cl₂): δ 195.4, 194.7, 194.5 (*CO*), 147.6, 146.9, 130.1, 128.7, 128.3, 126.4, 126.1, 125.6, 124.7, 121.1 (*pyimMe* and *N-MeIm*), 56.4 (C_{sp3} *pyimMe*), 35.8, 35.1 (CH₃ *pyimMe* and *N-MeIm*). Anal. Calcd. for C₁₇H₁₅F₃N₅O₆ReS: C 30.91, H 2.29, N 10.60. Found: C 31.14, H 2.45, N 10.86.

Reaction of [Re(CO)₃(N-MesIm)(pyimMes)]BAR^f₄ (2c) with KN(SiMe₃)₂ and HOTf. Synthesis of 3c.

Compound **3c** was prepared as described for **3a** starting from KN(SiMe₃)₂ (0.111 mL of a 0.5 M solution in toluene, 0.056 mmol), [Re(CO)₃(N-MesIm)(pyimMes)]BAR^f₄ (**2c**) (0.080 g, 0.051 mmol) and HOTf (5 μL, 0.056 mmol). Yield: 55 mg (68 %). IR (CH₂Cl₂, cm⁻¹): 2035, 1928 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.76 (s_{br}, 8H, H_o BAR^f₄), 7.59 (s_{br}, 4H, H_p BAR^f₄), 7.65, 7.32 (m, 1H each, *CH*), 7.01 (m, 6H, *CH* and *N-MesIm*), 5.93, 5.56, 5.27, 5.09 (m, 1H each, *pyimMes*), 2.34, 2.33, 1.97, 1.96 (s, 3H each, *CH*₃), 1.66 (s, 6H, *CH*₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 195.6, 194.5, 194.4 (*CO*), 162.1 (q (*J*= 49.8 Hz), C_i BAR^f₄), 146.3, 146.1, 142.2, 142.1, 134.9, 134.8, 134.7, 134.5, 132.2, 131.0, 130.8, 130.6, 130.4, 130.0, 126.9, 126.6, 126.4, 125.1, 124.8, 121.0 (*N-MesIm* and *pyimMes*), 135.2 (C_o BAR^f₄), 129.3 (q (*J*= 31.5 Hz), C_m BAR^f₄), 125.2 (q (*J*= 273.1 Hz), CF₃), 117.8 (C_p BAR^f₄), 57.4 (C_{sp3}, *pyimMes*), 21.1 (2×CH₃), 17.5, 17.2, 17.1, 17.0 (CH₃). Anal. Calcd. for C₆₄H₄₃BF₂₄N₅O₃Re: C 48.56, H 2.74, N 4.42. Found: C 48.72, H 3.08, N 4.68.

Reaction of [Re(CO)₃(N-MesIm)(pyimMe)]OTf (2e) with KN(SiMe₃)₂ and HOTf. Synthesis of 3e.

Compound **3e** was prepared as described for **3a** starting from KN(SiMe₃)₂ (0.240 mL of a 0.5 M solution in toluene, 0.120 mmol), [Re(CO)₃(N-MesIm)(pyimMe)]OTf (**2e**) (0.080 g, 0.105 mmol) and HOTf (10 μL, 0.113 mmol). Slow diffusion of hexane (25 mL) into a concentrated solution of **3e** in CH₂Cl₂ at -20 °C afforded crystals, one of which was employed for an X-ray structure determination. Yield: 52 mg (65 %). IR (CH₂Cl₂, cm⁻¹): 2032, 1923 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.98 (s_{br}, 1H, *NH*), 7.38, 7.26, 7.14, 6.95 (m, 1H each, *CH* *pyimMe* and *N-MesIm*), 7.09, 7.01 (s, 1H each, *N-MesIm*), 6.54, 6.19 (m, 1H each, *pyimMe*), 5.25 (m, 2H, *pyimMe*), 3.86 (s, 3H, *CH*₃ *pyimMe*), 2.40, 1.98, 1.80 (s, 3H each, *CH*₃, *N-MesIm*). ¹³C{¹H} NMR (CD₂Cl₂): δ 195.7, 195.0, 194.6 (*CO*), 149.1, 148.2, 141.5, 135.2, 131.1, 130.6, 130.3, 129.9, 129.8, 128.7, 126.8, 125.7, 124.3, 124.0, 121.0 (*pyimMe* and *N-MesIm*), 56.8 (C_{sp3} *pyimMe*), 36.2 (CH₃ *pyimMe*), 21.2 (CH₃ *N-MesIm*), 18.0, 17.1 (CH₃ *N-MesIm*). Anal. Calcd. for C₂₅H₂₃F₃N₅O₆ReS: C 39.27, H 3.03, N 9.16. Found: C 39.11, H 3.30, N 9.47.

Synthesis of [Re(CO)₃(dmap)₂(N-MeIm)]BAR^f₄ (4a). A mixture of [ReBr(CO)₅] (0.069 g, 0.170 mmol) and dmap (0.044 g, 0.357 mmol) were refluxed in toluene for 2 h. The solvent was evaporated to dryness, the white residue redissolved in CH₂Cl₂ (20 mL), AgOTf (0.053 g, 0.206 mmol) was added and the mixture was stirred in the dark for 2 h. The solution was then filtered off the white solid (AgBr), the solvent evaporated to dryness and the residue was washed with hexane (2 × 15 mL), and diethylether (2 × 15 mL). Compound [Re(OTf)(CO)₃(dmap)₂] was obtained as a white microcrystalline solid. NaBAR^f₄ (0.147 g, 0.166 mmol) and *N-MeIm* (0.013 mL, 0.166 mmol) were added to a solution of [Re(OTf)(CO)₃(dmap)₂] (0.100 g, 0.151 mmol) in CH₂Cl₂ (25 mL), and the reaction mixture was stirred for 3 h. at room temperature. Then the solution was filtered via canula, concentrated under reduced

pressure to a volume of 5 mL, and addition of hexane (15 mL) caused the precipitation of a white solid, that was washed with hexane (2 × 15 mL) and dried in vacuum. Yield: 198 mg (90 %). IR (THF, cm⁻¹): 2024, 1909 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.87 (d (J= 5.9 Hz), 4H, dmap), 7.80 (s_{br}, 8H, H_o BAr^f₄), 7.62 (s_{br}, 4H, H_p BAr^f₄), 7.60 (s, 1H, NCHN *N*-MeIm), 6.98, 6.90 (m, 1H each, CH *N*-MeIm), 6.49 (d (J= 5.9 Hz), 2H, dmap), 3.69 (s, 3H, CH₃ *N*-MeIm), 3.01 (s, 12H, CH₃ dmap). ¹³C{¹H} NMR (CD₂Cl₂): δ 195.8 (s_{br} CO), 162.2 (q (J= 50.4 Hz), C_i BAr^f₄), 155.2 (C_p dmap), 152.2 (C_o dmap), 141.2 (NCHN, *N*-MeIm), 135.2 (C_o BAr^f₄), 130.5 (CH, *N*-MeIm), 129.3 (q (J= 31.0 Hz), C_m BAr^f₄), 125.0 (q (J= 272.0 Hz), CF₃), 122.9 (CH, *N*-MeIm), 117.9 (C_p BAr^f₄), 108.5 (C_m dmap), 39.2 (4×CH₃ dmap), 34.9 (CH₃ *N*-MeIm). Anal. Calcd. for C₅₃H₃₈BF₂₄N₆O₃Re: C 43.60, H 2.62, N 5.76. Found: C 43.81, H 2.69, N 5.61.

Synthesis of [Re(CO)₃(dmap)₂(*N*-MesIm)]BAr^f₄ (4b**).** NaBAr^f₄ (0.218 g, 0.246 mmol) and *N*-MesIm (0.046 g, 0.246 mmol) were added to a solution of [Re(OTf)(CO)₃(dmap)₂] (0.148 g, 0.224 mmol) in CH₂Cl₂ (25 mL), and the reaction mixture was stirred for 3 h. at room temperature. Then the solution was filtered via canula, concentrated under reduced pressure to a volume of 5 mL, and addition of hexane (15 mL) caused the precipitation of a white solid, that was washed with hexane (2 × 15 mL) and dried in vacuo. Yield: 283 mg (81 %). IR (THF, cm⁻¹): 2025, 1910 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.89 (d (J= 7.2 Hz), 4H, dmap), 7.76 (s_{br}, 8H, H_o BAr^f₄), 7.59 (s_{br}, 4H, H_p BAr^f₄), 7.54 (s, 1H, NCHN *N*-MesIm), 7.22, 7.10 (s, 1H each, CH *N*-MesIm), 7.02 (s, 2H, H_m *N*-MesIm), 6.48 (d (J= 7.2 Hz), 4H, dmap), 3.01 (s, 12H, CH₃ dmap), 2.32 (s, 3H, CH₃ *N*-MesIm), 1.97 (s, 6H, CH₃ *N*-MesIm). ¹³C{¹H} NMR (CD₂Cl₂): δ 195.8 (s_{br} CO), 162.2 (q (J= 50.2 Hz), C_i BAr^f₄), 155.2 (C_p dmap), 152.1 (C_o dmap), 141.3, 141.1, 134.9, 131.9, 131.0, 129.8, 123.4 (*N*-MesIm), 135.2 (C_o BAr^f₄), 129.3 (q (J= 31.3 Hz), C_m BAr^f₄), 125.0 (q (J= 272.7 Hz), CF₃), 117.9 (C_p BAr^f₄), 108.6 (C_m dmap), 39.3 (4×CH₃ dmap), 21.0 (CH₃ *N*-MesIm), 17.4 (2×CH₃ *N*-MesIm). Anal. Calcd. for C₆₁H₄₆BF₂₄N₆O₃Re: C 46.84 H 2.96, N 5.37. Found: C 50.11, H 3.01, N 5.55.

Reaction of 4a with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(dmap)(dmapimMe)]BAr^f₄ (5a**).** Compound **5a** was prepared as described above for **2a** starting from [Re(CO)₃(dmap)₂(*N*-MeIm)]BAr^f₄ (**4a**) (0.088 g, 0.060 mmol), KN(SiMe₃)₂ (0.150 mL of a 0.5 M solution in toluene, 0.075 mmol) and AgOTf (0.032 g, 0.124 mmol). Compound **5a** was obtained as a yellow microcrystalline solid. Yield: 35 mg (40 %). IR (THF, cm⁻¹): 2024, 1913 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.55 (d (J= 6.9 Hz), 1H, dmapimMe), 7.78 (s_{br}, 8H, H_o BAr^f₄), 7.67 (d (J= 6.1 Hz), 2H, dmap), 7.60 (s_{br}, 4H, H_p BAr^f₄), 7.46 (d (J= 1.2 Hz), 1H, CH dmapimMe), 7.11 (d (J= 1.2 Hz), 1H, CH dmapimMe), 6.90 (d (J= 2.6 Hz), 1H, dmapimMe), 6.64 (dd (J= 6.9 Hz, J= 2.6 Hz), 1H, dmapimMe), 6.29 (d (J= 6.1 Hz), 2H, dmap), 4.00 (s, 3H, CH₃ dmapimMe), 3.10, 2.87 (s, 6H each, CH₃ dmapimMe and dmap). ¹³C{¹H} NMR (CD₂Cl₂): δ 197.6, 196.5, 192.9 (CO), 162.2 (q (J= 50.4 Hz), C_i BAr^f₄), 155.4, 154.8, 153.0, 150.7, 149.2, 147.0, 129.7, 128.0, 108.5, 108.1, 104.6 (dmap and dmapimMe), 135.2 (C_o BAr^f₄), 129.3 (q (J= 31.4 Hz), C_m BAr^f₄), 125.0 (q (J= 272.5 Hz), CF₃), 117.9 (C_p BAr^f₄), 39.8, 39.1 (2×CH₃ each, dmapimMe and dmap), 37.1 (CH₃ dmapimMe). Anal. Calcd. for C₅₃H₃₆BF₂₄N₆O₃Re: C 43.66, H 2.49, N 5.76. Found: C 43.97, H 2.62, N 5.45.

Reaction of 4b with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(dmap)(dmapimMes)]BAr^f₄ (5b**).** Compound **5b** was prepared as described above for **2a** starting from [Re(CO)₃(dmap)₂(*N*-MesIm)]BAr^f₄ (**4b**) (0.074 g, 0.047 mmol), KN(SiMe₃)₂ (0.130 mL of a 0.5 M solution in toluene, 0.065 mmol) and AgOTf (0.025 g, 0.097 mmol). Compound **5b** was obtained as a yellow microcrystalline solid.

Slow diffusion of hexane (20 mL) into a concentrated solution of **5b** in THF (5 mL) afforded light yellow crystals, one of which was used for an X-ray structure determination. Yield: 43 mg (55 %). IR (THF, cm^{-1}): 2025, 1913 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.48 (d ($J= 6.8$ Hz), 1H, *dmapimMes*), 7.76 (s_{br}, 8H, H_o BARf_4), 7.68 (d ($J= 1.5$ Hz), 1H, *CH dmapimMes*), 7.64 (d ($J= 5.8$ Hz), 2H, *dmap*), 7.57 (s_{br}, 4H, H_p BARf_4), 7.18 (d ($J= 1.5$ Hz), 1H, *CH dmapimMes*), 7.17 (s, 1H, H_m *dmapimMes*), 7.03 (s, 1H, H_m *dmapimMes*), 6.52 (dd ($J= 6.8$ Hz, $J= 2.7$ Hz), 1H, *dmapimMes*), 6.28 (d ($J= 5.8$ Hz), 2H, *dmap*), 5.76 (d ($J= 2.7$ Hz), 1H, *dmapimMes*), 2.98 (s, 6H, CH_3 *dmapimMes*), 2.92 (s, 6H, CH_3 *dmap*), 2.34 (s, 3H, CH_3 *dmapimMes*), 2.05, 1.40 (s, 3H each, CH_3 *dmapimMes*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 197.5, 196.5, 193.1 (CO), 162.2 (q ($J= 50.0$ Hz), C_i BARf_4), 155.3, 154.8, 152.7, 152.0, 150.6, 148.7, 146.2, 142.4, 134.9, 131.4, 130.9, 130.7, 130.5, 126.2, 108.6, 108.0, 104.0 (*dmapimMes* and *dmap*), 135.2 (C_o BARf_4), 129.3 (q ($J= 31.8$ Hz), C_m BARf_4), 125.0 (q ($J= 272.9$ Hz), CF_3), 117.9 (C_p BARf_4), 108.6 (C_m *dmap*), 39.4 ($2\times\text{CH}_3$ *dmapimMes*), 39.2 ($2\times\text{CH}_3$ *dmap*), 21.0 (CH_3 *N-MesIm*), 17.5, 16.6 (CH_3 *N-MesIm*). Anal. Calcd. for $\text{C}_{61}\text{H}_{44}\text{BF}_{24}\text{N}_6\text{O}_3\text{Re}$: C 46.90, H 2.84, N 5.38. Found: C 46.39, H 2.88, N 5.53.

Synthesis of $[\text{Re}(\text{CO})_3(\text{py})_3]\text{OTf}$ (6a**).** The synthesis of compound **6a** is an adaptation of those previously reported.^{2,5} A mixture of $[\text{Re}(\text{CO})_3(\text{DMSO})_3]\text{OTf}$ (0.200 g, 0.306 mmol) and pyridine (0.74 mL, 9.18 mmol) is refluxed in acetone (40 mL) for 30 h. The solvent was evaporated to dryness and the sticky residue was washed with Et_2O (3×20 mL) to afford compound **6a** as a white solid that was dried under vacuum. Yield: 149 mg (73 %). IR (THF, cm^{-1}): 2033, 1924 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.53 (m, 6H, H_o py), 8.10 (m, 3H, H_p py), 7.63 (m, 6H, H_m py). ^{13}C NMR (CD_2Cl_2): δ 194.3 (CO), 153.7 (C_o py), 140.9 (C_p py), 128.0 (C_m py). Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N}_3\text{O}_6\text{ReS}$: C 34.76, H 2.30, N 6.40. Found: C 34.55, H 2.24, N 6.12.

Synthesis of $[\text{Re}(\text{CO})_3(\text{py-OMe})_3]\text{OTf}$ (6b**).** 4-methoxypyridine (1.00 mL, 10.28 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{DMSO})_3]\text{OTf}$ (200 mg, 0.306 mmol) in acetone (40 mL) and the mixture was refluxed for 30 h. The solvent was evaporated to dryness and the sticky residue was washed with Et_2O (3×20 mL) to afford compound **6b** as a white solid that was dried under vacuum. Yield: 160 mg (70 %). IR (THF, cm^{-1}): 2029, 1917 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.26 (d ($J= 6.5$ Hz), 6H, H_o py-OMe), 7.06 (d ($J= 6.5$ Hz), 6H, H_m py-OMe), 3.97 (s, 9H, CH_3 py-OMe). ^{13}C NMR (CD_2Cl_2): δ 194.9 (CO), 168.5 (C_p py-OMe), 154.6 (C_o py-OMe), 113.8 (C_m py-OMe), 56.9 (CH_3 py-OMe). Anal. Calcd. for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{N}_3\text{O}_9\text{ReS}$: C 35.39, H 2.84, N 5.63. Found: C 35.60, H 2.90, N 5.78.

Reaction of **6a with $\text{KN}(\text{SiMe}_3)_2$ and HOTf. Synthesis of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$ (**7a**).** $\text{KN}(\text{SiMe}_3)_2$ (0.340 mL of a 0.5 M solution in toluene, 0.170 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{py})_3]\text{OTf}$ (**6a**) (0.100 g, 0.152 mmol) in THF (20 mL) at -78 °C. The mixture was allowed to stir for 15 min and the solvent was evaporated to dryness under reduced pressure. A solution of HOTf (15 μL , 0.170 mmol) in toluene (20 mL) was added, and the resulting yellow solution was filtered via canula. The solvent was evaporated under reduced pressure to a volume of 3 mL and addition of hexane (15 mL) caused the precipitation of a yellow solid which spectroscopic data in solution indicated that it was the known complex $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$.⁶

Reaction of **6b with $\text{KN}(\text{SiMe}_3)_2$ and HOTf. Synthesis of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy-4,4'-OMe})]$ (**7b**).** $\text{KN}(\text{SiMe}_3)_2$ (0.300 mL of a 0.5 M solution in toluene, 0.150 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{py-OMe})_3]\text{OTf}$ (**6b**) (0.100 g, 0.134 mmol) in THF (20 mL) previously cooled to -78 °C. The

mixture was allowed to stir for 15 min and the solvent was evaporated to dryness under reduced pressure. A solution of HOTf (14 μ L, 0.158 mmol) in toluene (20 mL) was added, and the resulting yellow solution was filtered via canula. The solvent was evaporated under reduced pressure to a volume of 3 mL and addition of hexane (15 mL) caused the precipitation of a yellow solid that was washed with hexane (2×15 mL). Yield: 50 mg (61 %). IR (CH_2Cl_2 cm^{-1}): 2034, 1929, 1909 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.86 (d ($J=6.0$ Hz), 2H, $\text{H}_{6,6'}$ bipy-4,4'-OMe), 7.63 (d ($J=2.6$ Hz), 2H, $\text{H}_{3,3'}$ bipy-4,4'-OMe), 7.10 (dd ($J=6.0, 2.6$ Hz), 2H, $\text{H}_{5,5'}$ bipy-4,4'-OMe), 4.06 (s, 6H, CH_3 bipy-4,4'-OMe). ^{13}C NMR (CD_2Cl_2): δ 196.6 (2CO), 194.7 (CO), 168.0 ($\text{C}_{4,4'}$ bipy-4,4'-OMe), 157.9 ($\text{C}_{2,2'}$ bipy-4,4'-OMe), 155.6 ($\text{C}_{6,6'}$ bipy-4,4'-OMe), 113.1, 110.8 ($\text{C}_{3,3'}$ and $\text{C}_{5,5'}$ bipy-4,4'-OMe), 56.9 (CH_3 bipy-4,4'-OMe). Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_2\text{O}_8\text{ReS}$: C 30.24, H 1.90, N 4.41. Found: C 30.56, H 2.05, N 4.63.

Synthesis of $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{py})]\text{BARf}_4$ (8a**).** A mixture of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{dmap})_2]$ (0.105 g, 0.158 mmol), prepared as described above for the synthesis of compound **4a**, NaBARf_4 (0.151 g, 0.170 mmol) and pyridine (14 μ L, 0.173 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 h. at room temperature. The colorless solution was filtered off the white solid (NaOTf) via canula and concentrated under reduced pressure to a volume of 4 mL. Addition of hexane (20 mL) caused the precipitation of a white solid which was washed with hexane (2×15 mL). Yield: 399 mg (74 %). IR (THF, cm^{-1}): 2028, 1916 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.47 (m, 2H, H_o py), 7.97 (m, 1H, H_p py), 7.83 (d ($J=7.4$ Hz), 4H, H_o dmap), 7.74 (s_{br} , 8H, H_o BARf_4), 7.57 (s_{br} , 4H, H_p BARf_4), 7.47 (m, 2H, H_m py), 6.50 (d ($J=7.4$ Hz), 4H, H_m dmap), 3.03 (s, 12H, CH_3 dmap). ^{13}C NMR (CD_2Cl_2): δ 195.4 (s_{br} CO), 162.1 (q ($J=52.8$ Hz), C_i BARf_4), 155.2 (C_p dmap), 153.4 (C_o py), 152.0 (C_o dmap), 140.2 (C_p py), 135.2 (C_o BARf_4), 129.3 (q ($J=29.9$ Hz), C_m BARf_4), 127.2 (C_m py), 124.9 (q ($J=272.7$ Hz), CF_3), 117.8 (C_p BARf_4), 108.8 (C_m dmap), 39.4 ($4 \times \text{CH}_3$ dmap). Anal. Calcd. for $\text{C}_{54}\text{H}_{37}\text{BF}_{24}\text{N}_5\text{O}_3\text{Re}$: C 44.52 H 2.56, N 4.81. Found: C 44.79, H 2.50, N 5.11.

Synthesis of $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{py-OMe})]\text{BARf}_4$ (8b**).** Compound **8b** was prepared as described above for **8a**, starting from $[\text{Re}(\text{OTf})(\text{CO})_3(\text{dmap})_2]$ (0.100 g, 0.151 mmol), 4-methoxypyridine (17 mL g, 0.166 mmol) and NaBARf_4 (0.147 g, 0.166 mmol). Compound **8b** was obtained as a white microcrystalline solid. Yield, 183 mg (82 %). IR (THF, cm^{-1}): 2026, 1912 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.25 (d ($J=7.1$ Hz), 2H, H_o py-OMe), 7.86 (d ($J=7.3$ Hz), 4H, H_o dmap), 7.76 (s_{br} , 8H, H_o BARf_4), 7.59 (s_{br} , 4H, H_p BARf_4), 6.95 (d ($J=7.1$ Hz), 2H, H_m py-OMe), 6.52 (d ($J=7.3$ Hz), 4H, H_m dmap), 3.94 (s, 3H, CH_3 py-OMe), 3.07 (s, 12H, CH_3 dmap). ^{13}C NMR (CD_2Cl_2): δ 195.2 (s_{br} CO), 167.8 (C_p py-OMe), 161.7 (q ($J=49.7$ Hz), C_i BARf_4), 162.7 (C_p dmap), 162.0 (C_o py-OMe), 161.4 (C_o dmap), 134.7 (C_o BARf_4), 128.8 (q ($J=31.5$ Hz), C_m BARf_4), 124.5 (q ($J=272.4$ Hz), CF_3), 117.4 (C_p BARf_4), 112.8 (C_m py-OMe), 108.3 (C_m dmap), 56.3 (CH_3 py-OMe), 39.4 ($4 \times \text{CH}_3$ dmap). Anal. Calcd. for $\text{C}_{55}\text{H}_{39}\text{BF}_{24}\text{N}_5\text{O}_4\text{Re}$: C 44.43 H 2.64, N 4.71. Found: C 44.15, H 2.84, N 5.02.

Reaction of **8a with $\text{KN}(\text{SiMe}_3)_2$ and AgOTf . Synthesis of $[\text{Re}(\text{CO})_3(\text{bipy-4-NMe}_2)(\text{dmap})]\text{BARf}_4$ (**9a**).** $\text{KN}(\text{SiMe}_3)_2$ (0.150 mL of a 0.5 M solution in toluene, 0.075 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{dmap})_2(\text{py})]\text{BARf}_4$ (**8a**) (0.100 g, 0.069 mmol) in THF (20 mL) previously cooled to -78 $^\circ\text{C}$. The color of the solution changed immediately from colorless to bright yellow. The mixture was allowed to stir for 15 min and AgOTf (38 mg, 0.150 mmol) was added. The solvent was evaporated to dryness, Et_2O (25 mL) was added and the reaction mixture was allowed to settle down for 12 h at -20 $^\circ\text{C}$. The yellow solution was then filtered via canula and the solvent evaporated in vacuo. The residue was extracted with

CH₂Cl₂ and filtered through silica gel, and evaporated to dryness. Compound **9a** was obtained as a yellow oil that was washed with hexane (2 × 15 mL). Yield: 54 mg (53 %). IR (THF, cm⁻¹): 2026, 1916 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.10 (m, 1H, H₆, bipy-4-NMe₂), 8.54 (d (*J*= 6.7 Hz), 1H, H₆ bipy-4-NMe₂), 8.08 (m, 2H, H₃ and H₄, bipy-4-NMe₂), 7.74 (s_{br}, 8H, H_o BAr^f₄), 7.61 (m, 1H, H₅, bipy-4-NMe₂), 7.55 (m, 6H, H_p BAr^f₄ and H_o dmap), 7.19 (d (*J*= 2.6 Hz), 1H, H₃ bipy-4-NMe₂), 6.73 (dd (*J*= 6.7, 2.6 Hz), 1H, H₅ bipy-4-NMe₂), 6.25 (d (*J*= 6.2 Hz), 2H, H_m dmap), 3.15, 2.87 (s, 6H each, CH₃ bipy-4-NMe₂). ¹³C NMR (CD₂Cl₂): δ 197.2 (2CO), 193.0 (CO), 162.1 (q (*J*= 52.8 Hz), C_i BAr^f₄), 157.3, 155.6, 155.1, 154.9, 153.4, 153.2, 152.1, 152.0, 150.4 (dmap and bipy-4-NMe₂), 135.2 (C_o BAr^f₄), 129.3 (q (*J*= 29.9 Hz), C_m BAr^f₄), 128.0, 127.2 (dmap and bipy-4-NMe₂), 124.9 (q (*J*= 272.2 Hz), CF₃), 117.8 (C_p BAr^f₄), 123.4, 110.1, 108.8, 108.3, 39.9 (dmap and bipy-4-NMe₂), 39.2 (CH₃ dmap and bipy-4-NMe₂). Anal. Calcd. for C₅₄H₃₅BF₂₄N₅O₃Re: C 44.58 H 2.42, N 4.81. Found: C 44.67, H 2.51, N 4.69.

Reaction of 8b with KN(SiMe₃)₂ and AgOTf. Synthesis of [Re(CO)₃(dmap){bipy-4,4'-(NMe₂)(OMe)}]BAr^f₄ (9b**).** Compound **9b** was prepared as described above for **9a** starting from [Re(CO)₃(dmap)₂(py-OMe)]BAr^f₄ (**8b**) (0.100 g, 0.067 mmol), KN(SiMe₃)₂ (0.148 mL of a 0.5 M solution in toluene, 0.0074 mmol) and AgOTf (38 mg, 0.048 mmol). Yield: 48 mg (48 %). IR (THF, cm⁻¹): 2023, 1910 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.88 [d (*J*= 6.5 Hz), 1H, H₆ bipy-4,4'-(NMe₂)(OMe)], 8.52 [d (*J*= 6.8 Hz), 1H, H₆, bipy-4,4'-(NMe₂)(OMe)], 7.75 (s_{br}, 8H, H_o BAr^f₄), 7.57 (m, 6H, H_p BAr^f₄ and H_o dmap), 7.54 (d(*J*= 2.6 Hz), 1H, H₃ bipy-4,4'-(NMe₂)(OMe)], 7.12 [d (*J*= 2.6 Hz), 1H, H₃, bipy-4,4'-(NMe₂)(OMe)], 7.08 [dd (*J*= 6.5, 2.6 Hz), 1H, H₅ bipy-4,4'-(NMe₂)(OMe)], 6.71 [dd (*J*= 6.8, 2.6 Hz), 1H, H₅, bipy-4,4'-(NMe₂)(OMe)], 6.26 (d (*J*= 5.3 Hz), 2H, H_m dmap), 3.99 (s, 3H, CH₃ bipy-4,4'-(NMe₂)(OMe)], 3.14, 2.88 (s, 6H each, CH₃ bipy-4,4'-(NMe₂)(OMe) and dmap). ¹³C NMR (CD₂Cl₂): δ 197.4, 197.3, 193.3, (CO), 162.3 (q (*J*= 49.7 Hz), C_i BAr^f₄), 168.9, 158.7, 155.8, 155.6, 155.1 [bipy-4,4'-(NMe₂)(OMe)], 154.8 (C_p dmap), 152.3 [bipy-4,4'-(NMe₂)(OMe)], 150.6 (C_o dmap), 135.4 (C_o BAr^f₄), 129.5 (q (*J*= 29.1 Hz), C_m BAr^f₄), 125.2 (q (*J*= 272.4 Hz), CF₃), 118.0 (C_p BAr^f₄), 112.9, 111.1, 110.2 [bipy-4,4'-(NMe₂)(OMe)], 108.5 (C_m dmap), 105.8 [bipy-4,4'-(NMe₂)(OMe)], 57.3 [CH₃ bipy-4,4'-(NMe₂)(OMe)], 40.1, 39.4 (2×CH₃ each, bipy-4,4'-(NMe₂)(OMe) and dmap). Anal. Calcd. for C₅₅H₃₇BF₂₄N₅O₄Re: C 44.49, H 2.51, N 4.72. Found: C 44.87, H 2.33, N 4.90.

Crystal Structure Determination.

For Compound 3a, 3e, 5b and 7b. Data collection was performed on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4-16 s). Data collection strategy was calculated with the program CrysAlis^{Pro} CCD.⁷ Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.⁷ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis^{Pro} RED.⁷

Crystal structure was solved by direct methods, using the program SIR-92.⁸ Anisotropic least-squares refinement was carried out with SHELXL-97.⁹ All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups).

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1. M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Angew. Chem. Int. Ed.* **2010**, *49*, 6409.
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5. E. J. Schutte, B. P. Sullivan, *Inorg. Synth.* **2002**, *33*, 227.
6. (a) G. J. Stor, F. Hartl, J. W. van Outerstep, D. J. Stufkens, *Organometallics* **1995**, *14*, 1115. (b) E. Hevia, J. Pérez, L. Riera, V. Riera, I. del Río, S. García-Granga, D. Miguel, D. *Chem.-Eur. J.* **2002**, *8*, 4510
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9. G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

CAPÍTULO 3

Introducción

La Química Organometálica de los complejos halocarbonílicos de molibdeno (II) y wolframio (II) ha sido ampliamente estudiada desde que, en 1956, Piper y Wilkinson publicaron la preparación de los complejos $[\text{MoCpX}(\text{CO})_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).⁷⁶ Dentro de este área tan amplia,⁷⁷ hemos centrado nuestro estudio en los complejos que contienen, además, un ligando π -alilo y, en concreto, en los del tipo $[\text{Mo}(\eta^3\text{-alilo})(\text{CO})_2(\text{L}_2)]$, siendo L_2 un ligando diimina bidentado.

La química de esta familia de compuestos se remonta al año 1968, año en el que Dieck y Friedel publicaron la síntesis de compuestos $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2(\text{N-N})]$ ($\text{N-N} =$ diiminas como la bipy o phen) por sustitución de dos ligandos nitrilo en los compuestos previamente preparados $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2(\text{NCMe})_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$).⁷⁸ A raíz de estos resultados, en los años siguientes se sintetizó una amplia familia de compuestos $[\text{MX}(\eta^3\text{-alilo})(\text{CO})_2(\text{L}_2)]$, ($\text{M} = \text{Mo}, \text{W}$; $\text{X} =$ halógeno o pseudohalógeno; $\text{L}_2 =$ un ligando bidentado neutro N-dador o O-dador; o bien dos ligandos monodentados N-dadores como nitrilos, piridinas, etc.).⁷⁹

Aunque lo más lógico sería considerar los complejos $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2(\text{N-N})]$ heptacoordinados, tradicionalmente se han considerado pseudo-octaédricos,⁸⁰ estableciendo así la aproximación de que el ligando η^3 -alilo ocupa una sola posición de coordinación. Teniendo en cuenta esta premisa podemos considerar que los ligandos η^3 -alilo y X (halógeno) se encuentran en posiciones mutuamente *trans* con respecto al plano ecuatorial, constituido por los dos átomos

⁷⁶ T. S. Piper, G. J. Wilkinson, *Inorg. Nucl. Chem.* **1956**, 3, 104.

⁷⁷ P. K. Baker, *Adv. Organomet. Chem.* **1996**, 40, 45.

⁷⁸ H. Dieck, H. Friedel, *J. Organomet. Chem.* **1968**, 14, 375.

⁷⁹ (a) A. J. Graham, R. H. Fenn, *J. Organomet. Chem.* **1969**, 17, 205. (b) A. J. Graham, R. H. Fenn, *J. Organomet. Chem.* **1970**, 25, 173. (c) A. J. Graham, R. H. Fenn, *J. Organomet. Chem.* **1972**, 37, 137. (d) F. Devans, J. Dewailly, J. Meunier-Piret, *J. Organomet. Chem.* **1974**, 76, 53.

⁸⁰ (a) B. J. Bridson, *J. Organomet. Chem.* **1977**, 125, 225. (b) B. J. Bridson, A. A. Woolf, *J. Chem. Soc., Dalton Trans.* **1978**, 291.

dadores del ligando bidentado y los dos grupos carbonilo, con lo que se puede apreciar claramente que la molécula presenta un plano de simetría.⁸¹

Otro aspecto que cabe señalar con respecto a la geometría de estos compuestos $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2(\text{N-N})]$ es que en ellos el ligando alilo es estático (es decir, no se interconvierte en su modo de coordinación de η^3 a η^1 , y no experimenta rotación en torno al enlace M-alilo) y se encuentra orientado con su cara abierta hacia los ligandos carbonilo. Esto es lo que han demostrado las estructuras cristalinas determinadas hasta la fecha, y además, al mismo tiempo, estudios teóricos empleando la aproximación del método de fragmentos de orbitales moleculares demostraron que, efectivamente, dicha orientación correspondía a una situación de máxima estabilidad.⁸²

En cuanto a la reactividad de los compuestos $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2\text{L}_2]$, cabe destacar su intervención en procesos de alquilación alílica. Especialmente relevantes son los estudios realizados por Trost y colaboradores,⁸³ que en 1982 publicaron el empleo de complejos de molibdeno en reacciones de sustitución alílica tanto a nivel estequiométrico como catalítico.^{83a} Esta alquilación alílica mediada por complejos de molibdeno ha constituido una alternativa útil y muchas veces complementaria a la catalizada por paladio, que ha sido más extensamente estudiada.⁸⁴ Es importante comentar que la regioselectividad de la reacción es mucho más sensible a la naturaleza de los ligandos del complejo metálico en el caso del molibdeno.

El estudio de las reacciones de alquilación alílica catalizada por molibdeno o wolframio ha experimentado un considerable desarrollo,⁸⁵ incluyendo la publicación en 1998 del primer ejemplo de su variante enantioselectiva,^{83f,86} la cual ha dado lugar a estudios posteriores que demuestran la gran regio y enantioselectividad de estos complejos frente a varios sustratos, así como su eficiencia como catalizadores.⁸⁷

⁸¹ Existen algunos ejemplos en los que se ha encontrado que la disposición del ligando quelato es axial en lugar de ecuatorial, lo que se ha atribuido a factores estéricos, al poseer dichos ligando sustituyentes muy voluminosos. Ver, por ejemplo: (a) J. C. Alonso, P. Neves, M. J. P. da Silva, S. Quintal, P. D. Vaz, C. Silva, A. A. Valente, P. Ferreira, M. J. Calhorda, V. Félix, M. G. B. Drew, *Organometallics* **2007**, *26*, 5548. (b) T. Turki, T. Guerfel, F. Bouachir, *Polyhedron* **2009**, *28*, 569.

⁸² M. D. Curtis, O. Eisenstein, *Organometallics*, **1984**, *3*, 887.

⁸³ (a) B. M. Trost, M. Lautens, *J. Am. Chem. Soc.* **1982**, *104*, 5543. (b) B. M. Trost, M-H. Hung, *J. Am. Chem. Soc.* **1983**, *105*, 7757. (c) B. M. Trost, D. J. Murphy, *Organometallics*, **1985**, *4*, 1143. (e) B. M. Trost, M. Lautens, M-H. Hung, *J. Am. Chem. Soc.* **1987**, *109*, 1469. (f) B. M. Trost, I. Hachiya, *J. Am. Chem. Soc.* **1998**, *120*, 1104.

⁸⁴ (a) J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer-Verlag, Berlin **1980**. (b) B. M. Trost, T. R. Verhoeven, *Compr. Org. Chem.* **1982**, *8*, 799.

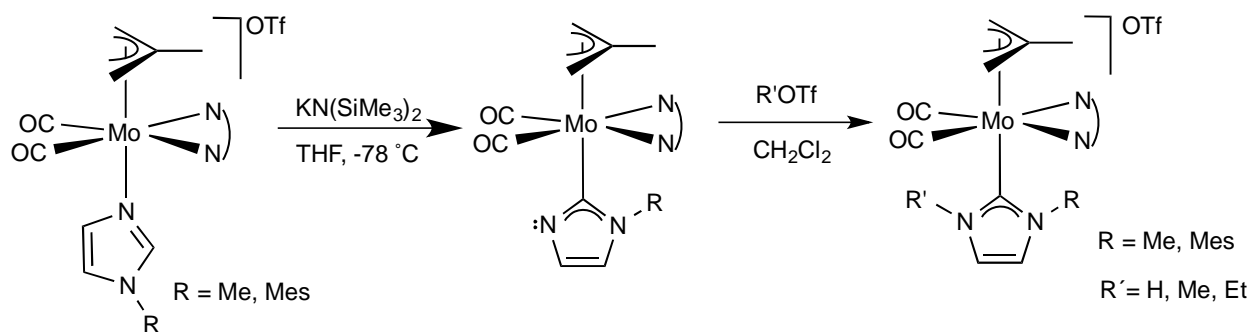
⁸⁵ (a) J. W. Faller, D. Linebarrier, *Organometallics*, **1988**, *7*, 1670. (b) H. Devoràková, D. Dvorák, J. Srogl, P. Kocovsky, *Tetrahedron Lett.* **1995**, *36*, 6351. (c) D. Dvorák, I. Stary, P. Kocovsky, *J. Am. Chem. Soc.* **1995**, *117*, 6130. (d) J. Lehmann, G. C. Lloyd-Jones, *Tetrahedron* **1995**, *51*, 8863. (e) M. P. T. Sjogren, H. Frisell, B. Akermark, P. Norrby, L. Eriksson, A. Vitagliano, *Organometallics*, **1996**, *16*, 942.

⁸⁶ A. V. Malkov, I. R. Bakendale, M. Bella, V. Langer, J. Fawcett, D. R. Russell, D. J. Mansfield, M. Valko, P. Kocovsky, *Organometallics*, **2001**, *20*, 673.

⁸⁷ (a) F. Glorius, A. Pfaltz, *Org. Lett.* **1999**, *1*, 141. (b) B. M. Trost, K. Dogra, *J. Am. Chem. Soc.* **2002**, *124*, 7256. (c) B. M. Trost, Y. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 14548. (d) M. Bandini, A. Eichholzer, P. Kotrusz, A. Umami-Ronchi, *Adv. Synth. Catal.* **2008**, *350*, 531. (e) B. M. Trost, J. R. Miller, C. M. Hoffman, *J. Am. Chem. Soc.* **2011**, *133*, 8165.

En cuanto a la reactividad en el metal, anteriormente a los estudios de nuestro grupo de investigación la reactividad de los complejos $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2(\text{L})_2]$ había sido poco estudiada.^{88,46e,f} Básicamente, los trabajos llevados a cabo se limitaban a la sustitución de los ligandos nitrilo en complejos de tipo $[\text{MoX}(\eta^3\text{-alilo})(\text{CO})_2(\text{NCR})_2]$ por ligandos mono y bidentados, o bien a la preparación de complejos bi o polimetálicos con varios ligandos puente al hacer reaccionar complejos de tipo $[\text{Mo}(\eta^3\text{-alilo})(\text{CO})_2(\text{NMe})_2(\text{L})]\text{BF}_4$ frente a alcóxidos, hidróxidos o fluoruros.⁸⁹

El estudio más reciente de nuestro grupo de investigación empleando complejos derivados del fragmento $\{\text{Mo}(\eta^3\text{-alilo})(\text{CO})_2\}$ se ha centrado en la desprotonación de ligandos N-alquilimidazol coordinados al mismo.⁹⁰ Se ha encontrado que, en la reacción de los compuestos catiónicos de molibdeno $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2(\text{N-RIm})]\text{OTf}$ ($\eta^3\text{-C}_4\text{H}_7 = 2\text{-metilalilo}$) con una base fuerte se produce la desprotonación del grupo CH central del imidazol, de manera análoga a como hemos visto que ocurría para los complejos $[\text{Re}(\text{CO})_3(\text{N-N})(\text{N-RIm})]\text{OTf}$. Sin embargo, en este caso, el ligando imidazol una vez desprotonado, experimenta un cambio en el modo de coordinación de N a C-coordinado, obteniéndose el complejo 2-imidazolilo correspondiente (Esquema 3.1). Este comportamiento contrasta con la formación de los productos de acoplamiento C-C con el ligando bipyridina, también en disposición *cis* al N-RIm, encontrada para los complejos de renio.²³ El posterior tratamiento de estos compuestos neutros 2-imidazolilo con HOTf ó MeOTf da lugar a la protonación o metilación del nitrógeno no sustituido, dando lugar a los correspondientes complejos NHC.



Esquema 3.1 Reactividad de los compuestos $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2(\text{N-RIm})]\text{OTf}$

⁸⁸ (a) J. Pérez, L. Riera, V. Riera, S. García-Granda, E. García-Rodríguez, *J. Am. Chem. Soc.* **2001**, *123*, 7469. (b) J. Pérez, L. Riera, V. Riera, S. García-Granda, E. García-Rodríguez, *Organometallics* **2002**, *21*, 1622. (c) J. Pérez, L. Riera, V. Riera, S. García-Granda, E. García-Rodríguez, D. Miguel, *Chem. Comm.* **2002**, 384. (d) D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, *Inorg. Chem.* **2002**, *41*, 4111. (e) D. Morales, M. E. Navarro Clemente, J. Pérez, L. Riera, V. Riera *Organometallics* **2002**, *21*, 4934. (f) D. C. Gerbino, E. Hevia, D. Morales, M. E. Navarro Clemente, Julio Pérez, L. Riera, V. Riera, D. Miguel *Chem. Commun.* **2003**, 328. (g) D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, M. E. G. Mosquera, S. García-Granda *Chem. Eur. J.* **2003**, *9*, 4132.

⁸⁹ (a) C. Borgmann, C. Limberg, L. Zsolnai, *Chem. Commun.* **1998**, 2729. (b) C. Borgmann, C. Limberg, E. Kaifer, H. Pritzkow, L. Zsolnai, *J. Organomet. Chem.* **1999**, *580*, 214. (c) M. Hunger, C. Limberg, P. Kircher, *Organometallics*, **2000**, *19*, 1044.

⁹⁰ M. Brill, J. Díaz, M. A. Huertos, R. López, J. Pérez, L. Riera, *Chem. Eur. J.* **2011**, *17*, 8584.

Teniendo en cuenta estos resultados experimentales, nos pareció interesante llevar a cabo un estudio teórico que nos ayudara a comprender la diferencia de comportamiento de los compuestos de molibdeno con respecto a los de renio. Dicho estudio se hizo en colaboración con el Dr. Jesús Díaz, de la Universidad de Extremadura, y con el Dr. Ramón López, de la Universidad de Oviedo. Los resultados pusieron de manifiesto que, en el caso de los compuestos de molibdeno, el camino de reacción que conduce a la formación de los complejos 2-imidazolilo, está energéticamente más favorecido que el correspondiente a la formación de los productos de acoplamiento C-C (Figura 3.1). Los resultados teóricos y experimentales están, por tanto, de acuerdo, si bien es cierto que los cálculos DFT ponen de manifiesto una diferencia pequeña entre las energías de activación de uno u otro camino de reacción (de tan sólo 3.5 Kcal/mol).

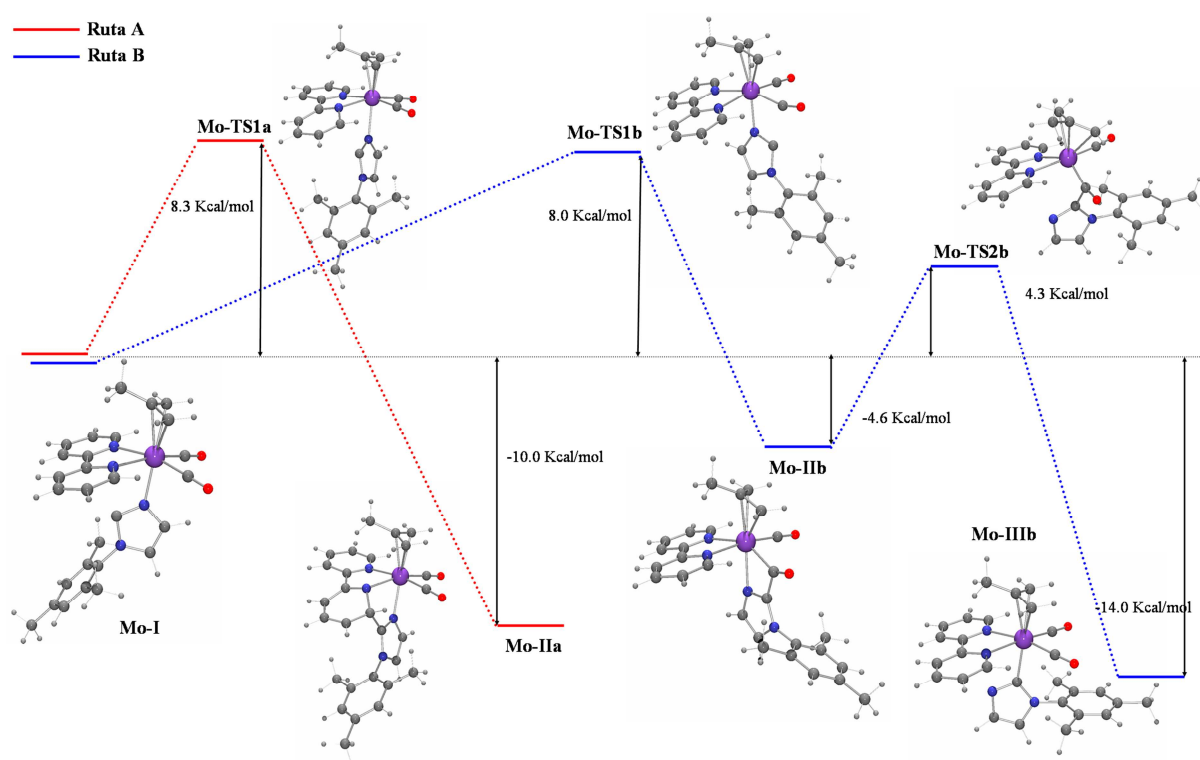


Figura 3.1 Perfiles de reacción para la evolución del producto de desprotonación de $[Mo(\eta^3-C_4H_7)(bipy)(CO)_2(N-MesIm)]OTf$

Nos planteamos entonces el empleo de otros ligandos bidentados diferentes de la bipy, que sean capaces de invertir esta preferencia energética de manera que se obtengan los productos de acoplamiento C-C en lugar de los complejos imidazolilo.⁹¹

⁹¹ A. Cebollada, M. Espinal Viguri, J. Pérez, J. Díaz, R. López, L. Riera, *Inorg. Chem.* **2015**, DOI:10.1021/ic502729z

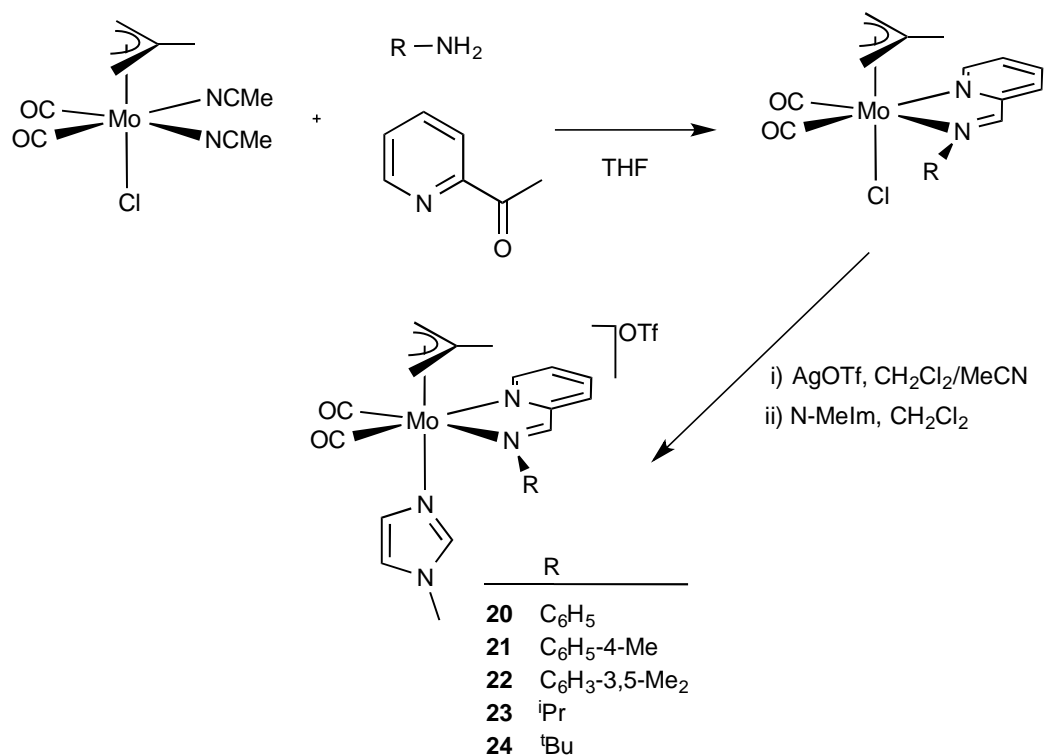
Resultados y discusión

Los resultados teóricos habían puesto de manifiesto que alguna modificación en el entorno de coordinación de los complejos $[\text{MoCl}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{bipy})(\text{N-RIm})]\text{OTf}$ podría dar lugar a un cambio en su reactividad frente a bases fuertes, pudiendo pasar, por ejemplo de obtener complejos imidazol-2-ilo a obtener los productos de acoplamiento C-C. Decidimos entonces utilizar ligandos 2-piridilimino en lugar de la 2,2'-bipiridina.

Para preparar los precursores se añadió a una disolución del complejo $[\text{MoCl}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{NCMe})_2]$ en THF, 2-piridilcarboxaldehído y la amina arílica o alquílica correspondiente, lo que dio lugar a la sustitución de los dos ligandos acetonitrilo por el ligando piridilimina así formado, resultado de la condensación de Schiff entre la amina y el aldehído, (Esquema 3.2). Cabe destacar que en ausencia del complejo metálico la condensación necesitaría para completarse 12 horas a la temperatura de ebullición del tolueno.⁹² Este hecho se ha atribuido previamente a la coordinación $\kappa^2\text{-(N,O)}$ del piridilcarboxaldehído,⁹³ activando así el grupo carbonilo frente al ataque nucleófilo, lo que favorece la reacción. La posterior sustitución del ligando cloruro por N-metilimidazol se llevó a cabo en presencia de AgOTf y unas gotas de acetonitrilo, de manera que una vez formado el complejo intermedio con un ligando nitrilo, éste es fácilmente sustituido por el N-MeIm. (Esquema 3.2).

⁹² R. N. Dominey, B. Hauser, J. Hubbard, J. Dunham, *Inorg. Chem.* **1991**, 30, 4754.

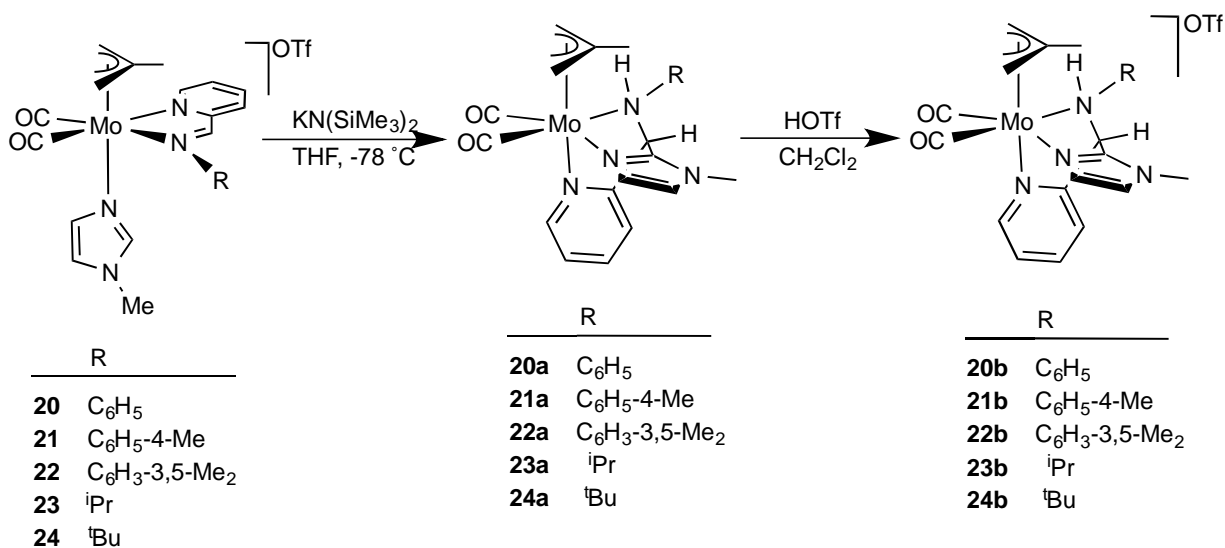
⁹³ (a) R. S. Herrick, K. L. Houde, J. S. McDowell, L. P. Kiczek, G. Bonavia, *J. Organomet. Chem.* **1999**, 589, 29. (b) R. S. Herrick, I. Wrona, N. McMicken, G. Jones, C. J. Ziegler, J. Shaw, *J. Organomet. Chem.* **2004**, 689, 4848. (c) R. García-Rodríguez, D. Miguel, *Dalton Trans.* **2006**, 1218. (d) D. Miguel, L. A. García-Escudero, J. A. Turiel, *J. Organomet. Chem.* **2006**, 691, 3434.



Esquema 3.2 Síntesis de los compuestos 20-24

El espectro de IR en disolución de los nuevos compuestos **20-24** así obtenidos muestra, en la zona correspondiente a los ligandos carbonilo, dos bandas características para un fragmento *cis*-{Mo(CO)₂}. Por otro lado los espectros de RMN (¹H y ¹³C) en disolución confirman la estequiometría propuesta, así como la asimetría de los complejos.

La adición de la base KN(SiMe₃)₂, a baja temperatura, a disoluciones de los compuestos **20-24** dio lugar a los productos **20a-24a** respectivamente, que no pudieron aislarse debido a su baja estabilidad. La caracterización espectroscópica, mediante ¹H RMN, de los complejos **21a** y **22a** puso de manifiesto que se había producido la desprotonación del ligando imidazol, y éste había atacado como nucleófilo al carbono imínico de la 2-piridilimina correspondiente. Decidimos entonces, como en otras ocasiones, hacer reaccionar *in situ* a los derivados neutros **20a-24a** con un electrófilo para intentar obtener productos catiónicos más estables. Se obtuvieron así, por tratamiento con HOTf, los compuestos **20b-24b** como productos únicos y en buen rendimiento (Esquema 3.3).



Esquema 3.3 Síntesis de los compuestos 20b-24b

La caracterización en disolución de los compuestos **20b-24b** mostró la formación de las nuevas especies. Lo primero que llama la atención es la ausencia de la señal correspondiente al hidrógeno imínico, N=CH, y la presencia de un singulete a campo más alto, correspondiente a un carbono con hibridación sp³. Otro aspecto muy significativo de este espectro es que sólo aparecen dos señales que se asignan a los grupos CH del anillo de imidazol, lo que conjuntamente con el hecho anterior, y en concordancia con el espectro de los precursores **21a** y **22a**, nos permite proponer que, efectivamente, se ha producido el acoplamiento C-C entre el imidazol desprotonado y el carbono imínico. Desafortunadamente, para algunos de estos complejos la señal del grupo N-H, originada por la protonación con HOTf, no se observa en el espectro de ¹H RMN, probablemente debido al ensanchamiento cuadrupolar del átomo nitrógeno, o a la acidez de este grupo. No obstante, los espectros de IR en KBr confirman, sin ninguna duda, la presencia del grupo N-H en estos complejos, observándose una banda ancha en el intervalo de 3400-3500 cm⁻¹. Los espectros de ¹³C RMN de los compuestos **20b-24b**, son coherentes con la geometría propuesta, siendo la señal más característica la correspondiente al nuevo carbono sp³ (que originalmente era el carbono imínico).

Es importante destacar que, en los espectros de ¹H RMN de los crudos de reacción de **20b-24b**, se observan dos conjuntos de señales idénticas en distinta proporción, lo que indica que existen dos diastereoisómeros en disolución. Efectivamente, los complejos **20b-24b** poseen tres centros estereogénicos, el metal, el carbono que sufre el ataque nucleófilo y el nitrógeno que se protona. Debido a que la estereoquímica del molibdeno y del carbono vienen fijadas por la geometría de los complejos precursores, es la protonación del nitrógeno mediante la adición de HOTf la que lleva a la formación de dos diastereoisómeros (dos parejas de enantiómeros).

En la Figura 3.2 se muestra una representación gráfica del catión presente en el compuesto **22b** y del catión del precursor, **22**, determinadas ambas mediante difracción de rayos X de monocristal.

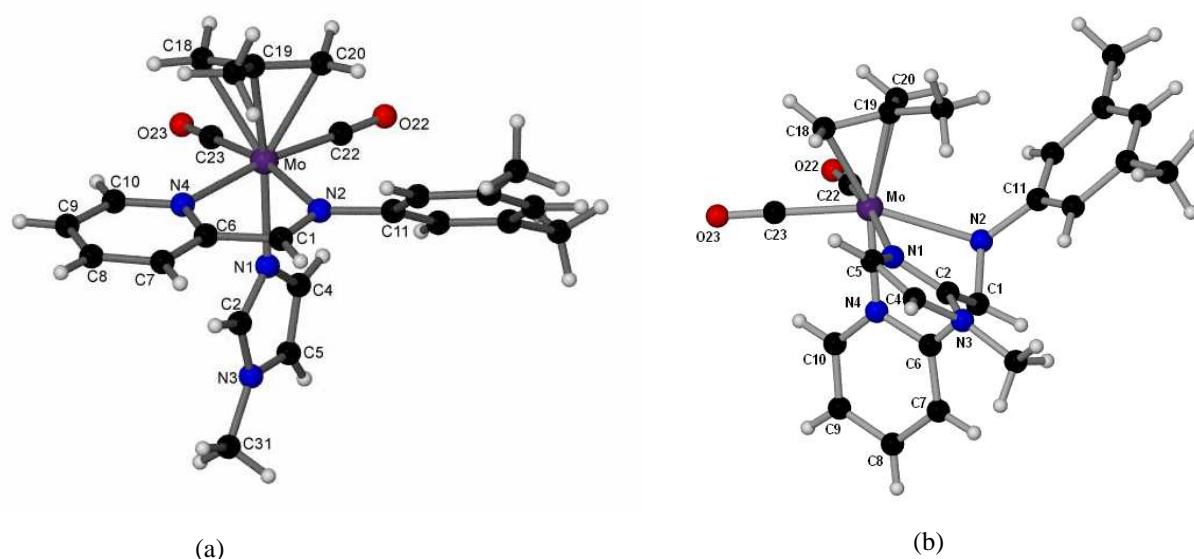


Figura 3.2 Estructura molecular en estado sólido de los cationes presentes en los compuestos (a) **22** y (b) **22b**.

La Figura 3.2.a muestra la estructura en estado sólido del compuesto **22**. En ella se distingue que el compuesto tiene una geometría pseudooctaédrica en torno al átomo de molibdeno y que el plano ecuatorial está formado por el ligando diimina bidentado y los dos ligandos carbonilo. Se observa también cómo las posiciones apicales las ocupan el ligando η^3 -C₄H₇ y el ligando N-MeIm, cada uno en *trans* con respecto al otro.

Como se puede ver en la Figura 3.2.b, la estructura en estado sólido de **22b** coincide con la deducida a partir de sus datos espectroscópicos en disolución. Se puede observar que, efectivamente, se ha producido el acoplamiento entre el carbono central del imidazol (C2) y el átomo de carbono imínico (C1). Se produce así la formación de un ligando tridentado constituido por tres grupos nitrógeno dadores: un grupo piridilo, un grupo amino y un grupo imidazolilo.

Es interesante notar que, en el compuesto **22b** el grupo en *trans* al η^3 -C₄H₇ es el piridilo, mientras que en la estructura del compuesto de partida **22** (Figura 3.2.a) es el N-MeIm el que ocupa esta posición. En las estructuras en estado sólido de los compuestos **23b** y **24b**, con sustituyentes *iso*-propilo y *terc*-butilo respectivamente, es el grupo amino el que ocupa la posición *trans* al ligando η^3 -C₄H₇. Esto indica que la formación del ligando trípode conlleva, además, una rotación de la cara del octaedro en el que se encuentran los tres ligandos N-dadores, probablemente para minimizar la congestión estérica. Para comprobar la existencia o no de un proceso fluxional en disolución, se realizó un experimento de ¹H RMN a temperatura variable del compuesto **23b**. En los espectros se observa que efectivamente hay un proceso dinámico, y aunque no nos hemos centrado en determinar su naturaleza exacta, está en concordancia con que se produzca un “trigonal twist” (rotación de la cara triangular formada por el ligando tridentado

con respecto a la cara formada por el alilo y los dos carbonilos), lo que es bastante habitual para los complejos pseudo-octaédricos con el fragmento $\{\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2\}$.⁹⁴

La reactividad de estos compuestos $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{py-2-CH=N-R})(\text{N-MeIm})]\text{OTf}$ (**20-24**) es, por tanto, diferente de la previamente encontrada para los derivados análogos con 2,2'-bipiridina que, como ya hemos comentado, daba lugar al cambio en el modo de coordinación del ligando N-RIm de N a C-coordinado, formándose los correspondientes complejos 2-imidazolilo (ver Esquema 3.1 de la Introducción de este Capítulo).

Dada esta diferencia, se realizaron cálculos computacionales para comprender la evolución de los productos de desprotonación de los compuestos 2-piridilimidazol **20-24**. Se escogió como compuesto de partida el intermedio denominado como **I**, resultante de la desprotonación del grupo CH central de ligando N-MeIm del compuesto **22**, y se examinaron los posibles caminos de reacción (Figuras 3.3 y 3.4). En primer lugar, debido a los precedentes, se evaluó la posibilidad de que **I** evolucionara para dar lugar a la formación de un complejo con un ligando 2-imidazolilo (**II**) (Figura 3.3). De los dos posibles mecanismos el más favorable es el que transcurre a través del ataque nucleófilo inicial sobre un ligando carbonilo, análogo al encontrado para los derivados con bipy y que presenta una barrera energética de 9.1 kcal/mol.

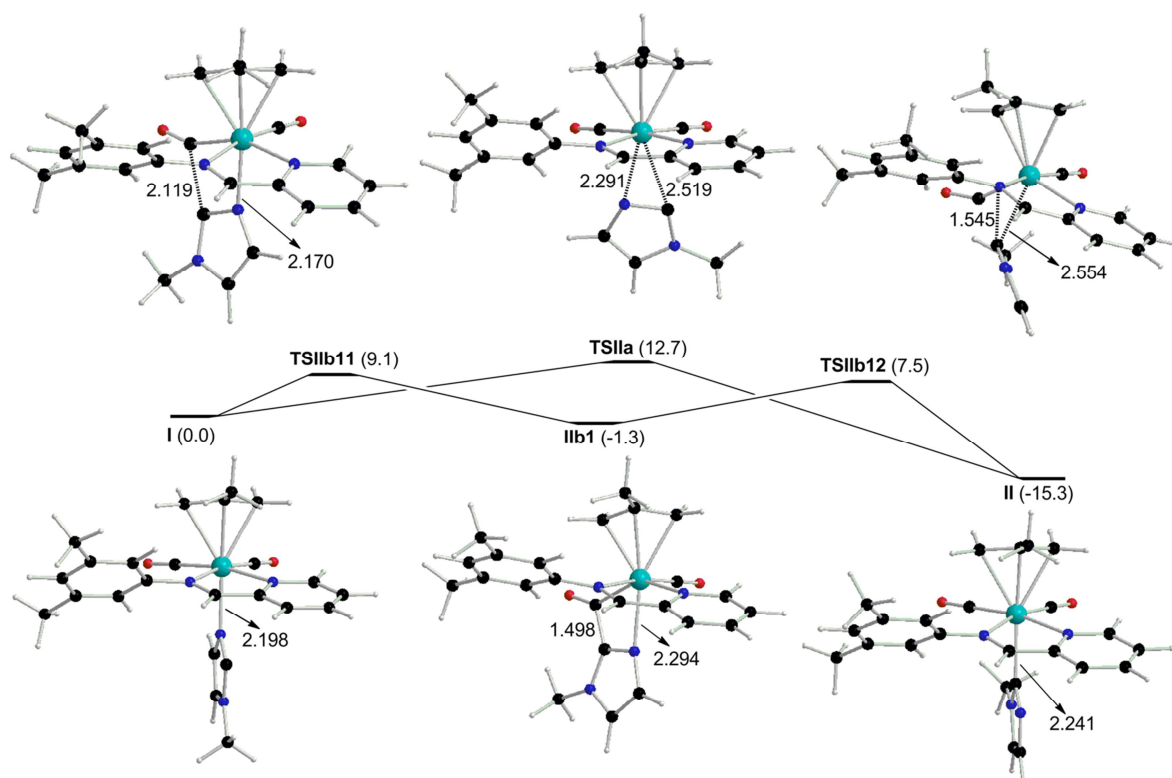


Figura 3.3 Perfiles de reacción para la evolución del producto de desprotonación del compuesto **22** hacia la formación del compuesto 2-imidazolilo. Las energías de Gibbs relativas en disolución de THF se dan entre paréntesis (kcal/mol). Las distancias más relevantes se indican en amstrongs.

⁹⁴ (a) J. W. Faller, D. A. Haitko, R. D. Adams, D. F. Chodosh, *J. Am. Chem. Soc.* **1979**, *101*, 865. (b) R. Davis, L. A. P Kane-Maguire, L. A. P. in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds.; Pergamon: Oxford, U.K., **1982**; Vol. 8, 1156.

A continuación se estudió la evolución del intermedio **I** para dar lugar a productos de acoplamiento C-C con el ligando 2-piridilimina, encontrando que el ataque al carbono imínico es, con diferencia, el camino de reacción más favorecido (Figura 3.4). Ello se debe no sólo a que da lugar a un producto mucho más estable (**Va**, -26 kcal/mol) que los resultantes de las otras vías de evolución, sino que de hecho, no se observa ningún estado de transición para su formación. Esto se puede atribuir a que la reacción es extremadamente favorable, debido a la elevada electrofilia del carbono imínico, conjuntamente con su capacidad para deslocalizar la densidad electrónica hacia el nitrógeno contiguo, y a la gran estabilidad del producto final. Por tanto, aunque la formación de un complejo 2-imidazolilo (**II**) sería cinéticamente posible, la formación del producto de acoplamiento (**Va**) está mucho más favorecida, y es, de hecho, el producto que se obtiene experimentalmente.

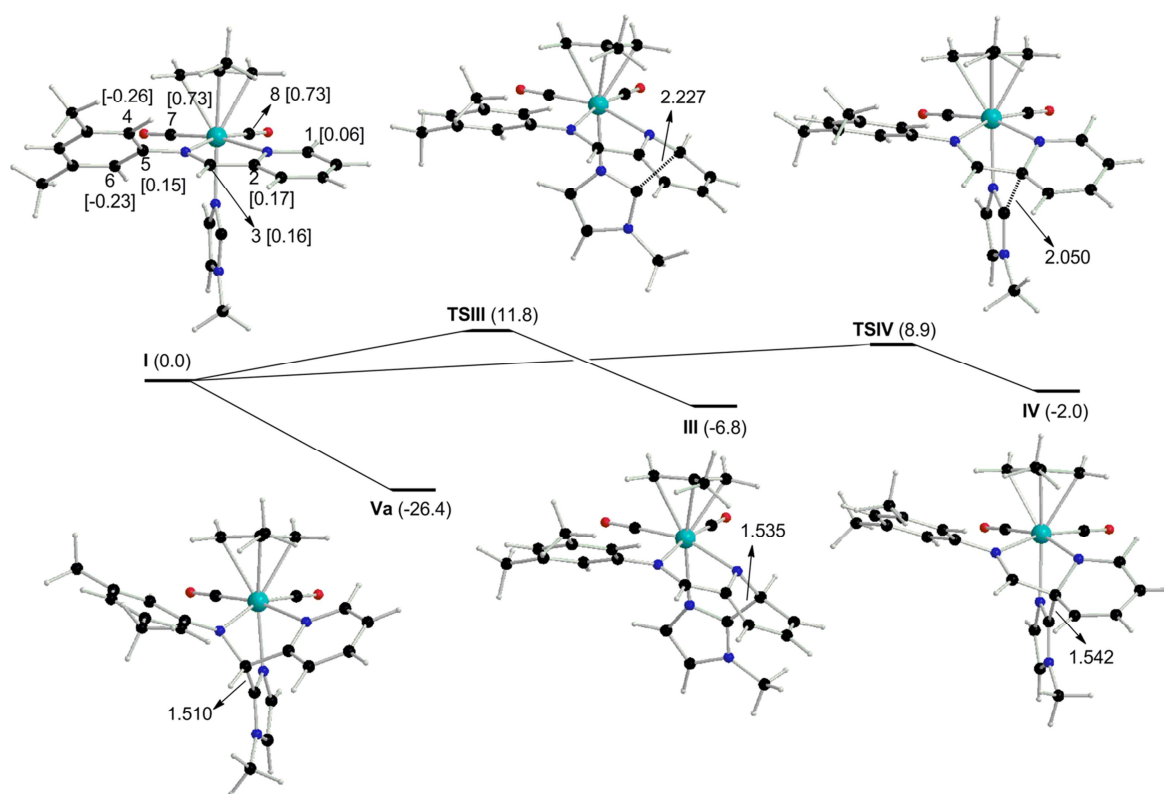


Figura 3.4 Perfiles de reacción para la evolución del producto de desprotonación del compuesto 22 hacia la formación de compuestos de acoplamiento. Las energías de Gibbs relativas en disolución de THF se dan entre paréntesis (kcal/mol). Las distancias más relevantes se indican en amstrongs.

A pesar de su elevada estabilidad la especie **Va** puede evolucionar para dar lugar a los isómeros **Vb** y **Vc** (Figura 3.5). Este proceso podría tener lugar por medio de un mecanismo de trigonal-

twist dissociativo,⁹⁵ en el que el enlace Mo-N(piridilo) se rompe para dar lugar a estados de transición pentacoordinados. Las barreras energéticas asociadas a estos procesos de interconversión de las especies **Va**, **Vb** y **Vc** son coherentes con la existencia de un proceso fluxional entre los mismos.

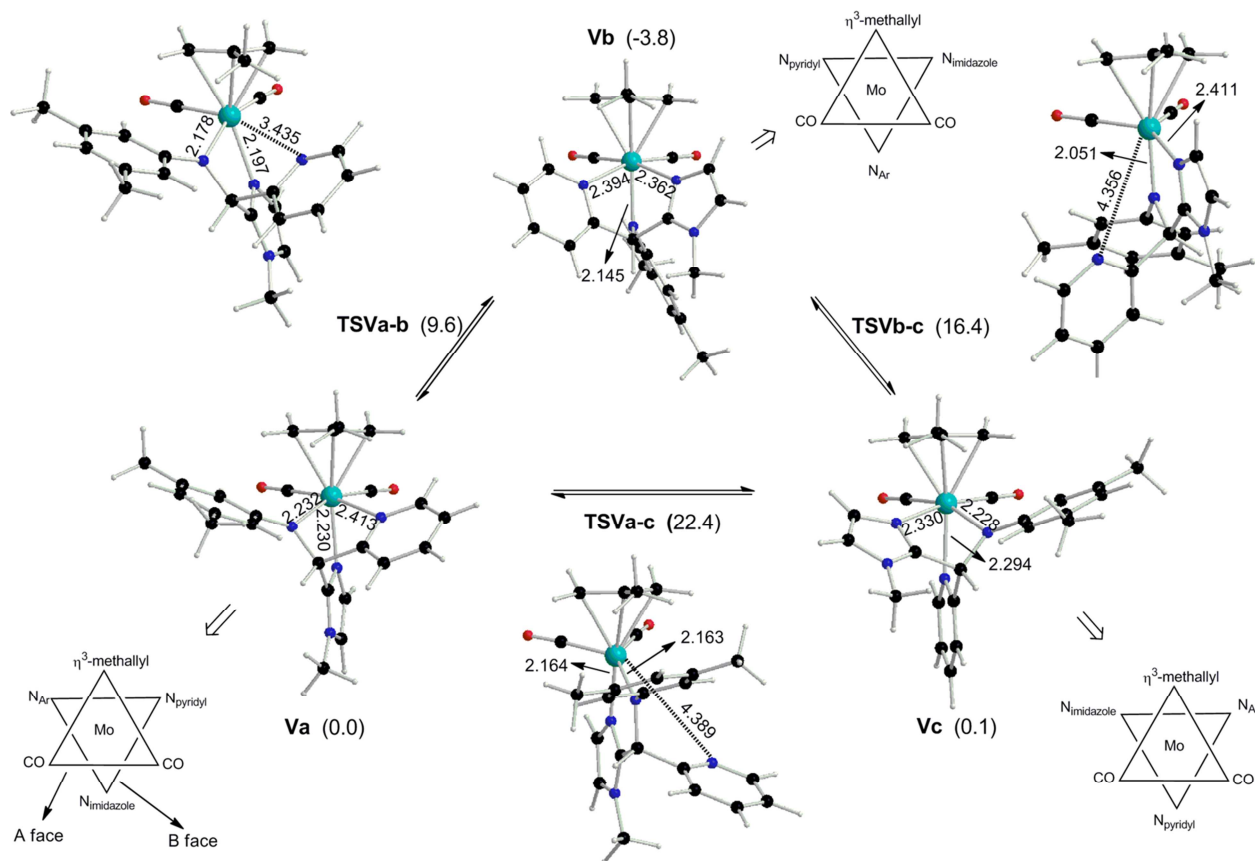


Figura 3.5 Estructuras de los diferentes conformeros posibles de **Va**. Las energías de Gibbs relativas en disolución de THF se dan entre paréntesis (kcal/mol). Las distancias más relevantes se indican en amstrongs.

La protonación de estos conformeros da lugar a dos diastereoisómeros cada uno, denominados **VxH** con $x = a, b, c$. Como se puede apreciar en la Tabla 3.1, el conformero más estable es **VcH**, en el que el grupo piridilo está en *trans* al η^3 -C₄H₇. Este isómero es el que presenta la estructura en estado sólido del compuesto **22b** (así como los compuestos análogos **20b** y **21b**). El estudio análogo para los derivados con un sustituyente *terc*-butilo (denominados **V'xH** en la Tabla 3.1) muestra, por el contrario, que el conformero más estable es **V'bH**, en el que es el grupo amino el que se sitúa en posición *trans* al η^3 -C₄H₇. Aunque en este caso estos resultados también están de acuerdo con la estructura cristalina determinada experimentalmente para el compuesto **24b** (y el compuesto análogo **23b**), la diferencia energética entre **V'bH** y **V'cH** es demasiado pequeña para

⁹⁵ (a) J. Jung, T. A. Albright, D. M. Hoffman, T. R. Lee, *J. Chem. Soc., Dalton Trans.*, **1999**, 24, 4487. (b) J. Leppin, C. Förster, K. Heinze, *Inorg. Chem.* **2014**, 53, 1039.

ser determinante, y factores de empaquetamiento en la cristalización pueden ser también los responsables de la preferencia por este conformero en particular.

	x= a	x= b	x= c
<i>(RR)</i> - VxH	0.0	1.5	0.2
<i>(RS)</i> - VxH	0.7	2.1	-0.2
<i>(RR)</i> - V'xH	0.0	-1.0	5.5
<i>(RS)</i> - V'xH	7.7	-0.7	-0.4

Tabla 3.1 Energías de Gibbs relativas (en kcal/mol) de los diastereoisómeros de **22b** y **24b**

ARTÍCULO

Influence of the N–N Coligand: C–C Coupling Instead of Formation of Imidazol-2-yl Complexes at $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2\}$ Fragments. Theoretical and Experimental Studies

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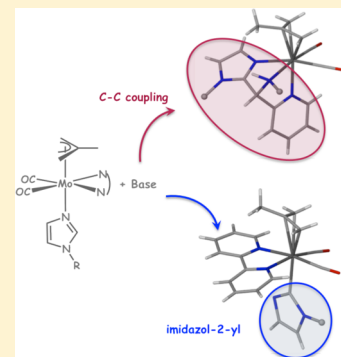
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Supporting Information

ABSTRACT: New *N*-methylimidazole (N-MeIm) complexes of the $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{N}-\text{N})\}$ fragment have been prepared, in which the N,N-bidentate chelate ligand is a 2-pyridylimine. The addition of a strong base to the new compounds deprotonates the central CH group of the imidazole ligand and subsequently forms the C–C coupling product that results from the nucleophilic attack to the imine C atom. This reactivity contrasts with that previously found for the analogous 2,2'-bipyridine compounds $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{bipy})(\text{N}-\text{RIm})]\text{OTf}$ [N-RIm = *N*-methylimidazole (N-MeIm), *N*-mesitylimidazole (N-MesIm, Mes = 2,4,6-trimethylphenyl); OTf = trifluoromethanesulfonate) which afforded imidazol-2-yl complexes upon deprotonation. Density Functional Theory (DFT) computations uncover that the reactivity of the imine C atom along with its ability to delocalize electron density are responsible for the new reactivity pattern found for this kind of molybdenum complexes synthesized herein.



INTRODUCTION

The imidazole moiety is very often encountered in biological systems. The importance of this function is mainly due to its presence in the side chain of the amino acid histidine, and its role as a metal binding site in metalloenzymes.¹ The relatively small size and and the electronic properties (σ -donor and π -acceptor) make imidazole and its derivatives good ligands for a variety of metal fragments.² Whereas the coordination chemistry of imidazoles has been therefore extensively studied, little attention has been paid to the analogy between cationic metal complexes with *N*-alkylimidazole (N-RIm) ligands and *N,N'*-dialkylimidazolium salts instead.³ In fact, the former can be regarded as *N*-metalated analogous of the latter (Figure 1).

The deprotonation of an *N,N'*-dialkylimidazolium salt affords a *N*-heterocyclic carbene (NHC).⁴ Therefore, we focused our attention in the deprotonation of transition metal complexes

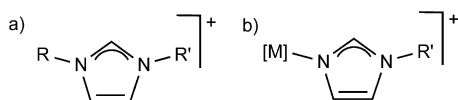
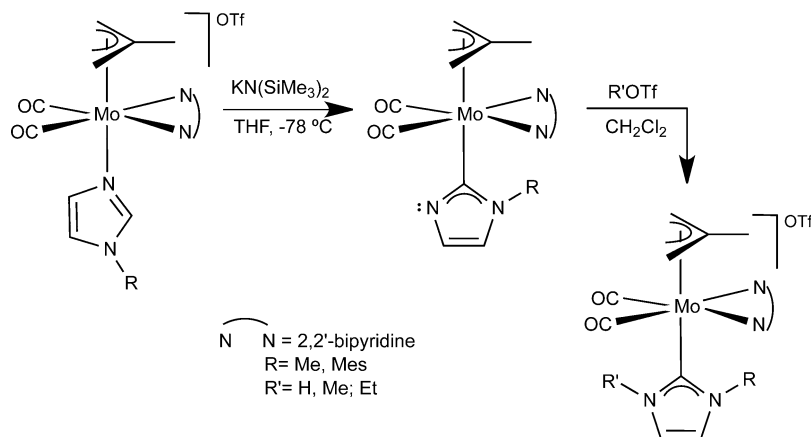


Figure 1. Analogy between imidazolium salts (a) and cationic metal complexes with *N*-alkylimidazole ligands (b).

with *N*-alkylimidazole ligands, trying to generate, in a similar way, a new type of NHC species with a metal fragment as substituent of one of the imidazole nitrogen atoms.⁵ In this research area we have found that the deprotonation of the central C–H group of a coordinated *N*-alkylimidazole affords very reactive species with reaction outcomes strongly depending on the nature of the imidazole substituent and the ancillary ligands.⁶ In particular, for Mo(II) cationic compounds of formula $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2(\text{N}-\text{RIm})]\text{OTf}$ (R = Me, Mes) the addition of a strong base led to imidazol-2-yl complexes resulting from the tautomerization of the heterocycle from N- to C-coordinated once the deprotonation had occurred. The subsequent addition of electrophilic reagents (HOTf, MeOTf, or EtOTf) afforded molybdenum NHC compounds (Scheme 1) by protonation or alkylation of the nonsubstituted nitrogen.⁷

In agreement with the experimental results found for the deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{bipy})(\text{CO})_2(\text{N}-\text{RIm})]\text{OTf}$ compounds, a DFT study showed that the most favorable reaction mechanism was reminiscent of the one found for $[\text{Mn}(\text{bipy})(\text{CO})_3(\text{N}-\text{RIm})]\text{OTf}$ compounds,^{5b,7} involving an

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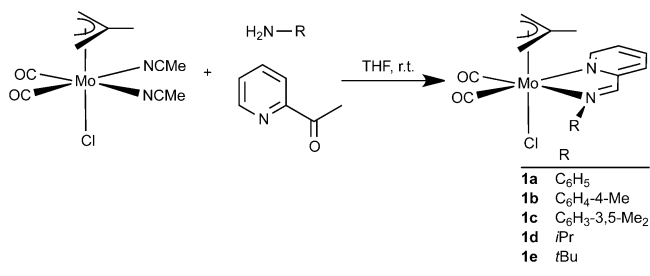
Scheme 1. Synthesis of Imidazol-2-yl and NHC Complexes from *N*-Alkylimidazole Derivatives

62 initial attack of the imidazole deprotonated carbon atom onto a
63 *cis*-CO ligand, to afford in a second step imidazol-2-yl species.
64 Furthermore, these calculations pointed out that the difference
65 in energy between this pathway and the one that would lead to
66 C–C coupling products (analogous to the reactivity pattern
67 found for $[\text{Re}(\text{bipy})(\text{CO})_3(\text{N-RIm})]^+$ complexes) is only 3.5
68 kcal/mol.⁷ This result prompted us to investigate the feasibility
69 of inverting the reactivity pattern in $\{\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2\}$
70 complexes, to obtain C–C coupling products.

71 Herein we report the synthesis and reactivity of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-R})]\text{OTf}$ (R = C₆H₅,
72 C₆H₄-4-Me, C₆H₃-3,5-Me₂, *i*Pr, *t*Bu) compounds, showing
73 that C–C coupling products are obtained upon deprotonation.
74 The DFT computations are in agreement with the experimental
75 findings, and show that the replacement of the α -dimine bipy
76 by the iminopyridines employed in this work results in that the
77 pathway leading to the C–C coupling products becomes
78 preferred.

80 ■ RESULTS AND DISCUSSION

81 The labile complex $[\text{MoCl}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{NCMe})_2]$ reacts
82 with the equimolar amounts of 2-pyridylcarboxaldehyde and
83 aniline in THF to afford complex **1a** as shown in Scheme 2. Its

Scheme 2. One-Pot Synthesis of 2-Pyridylimino Chlorocomplexes **1a–e**

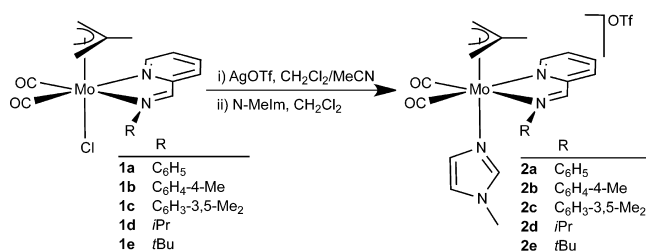
84 spectroscopic data in solution, and the full characterization of
85 some of its reaction products, discussed below, show that **1a**
86 possesses an iminopyridyl ligand coordinated as bidentate
87 chelate to the $\{\text{MoCl}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2\}$ fragment.

88 The metal-free reaction of the aldehyde and aniline takes 12
89 h in refluxing toluene to reach completion.⁸ In contrast, the
90 three-component reaction described above produces **1a** in less
91 than 1 h at room temperature, indicating that the metal exerts a
92 significant templating effect, as previously noted by others.⁹ It

has been proposed that the $\eta^2\text{-(N,O)}$ coordination of the
aldehyde activates the carbonyl group toward the condensation
(enhancing its electrophilic character) making the reaction
more favorable.¹⁰

The employment of 4-methylaniline and 3,5-dimethylaniline
afforded, in the same way, complexes **1b** and **1c**, respectively. In
contrast, *ortho*-substituted anilines (such as 2,4,6-trimethylaniline
or 2,6-diisopropylaniline) precluded the formation of the
desired molybdenum iminopyridine derivatives, probably due
to the steric hindrance. The new compounds **1a–c** were
obtained in good yields, as the only products of the reactions,
and their spectroscopic data in solution were in agreement with
the proposed stoichiometry and geometry showed in Scheme
2,¹¹ and similar to related pyridylimino compounds of the
fragment $\{\text{MoCl}(\eta^3\text{-allyl})(\text{CO})_2\}$.^{9d}

The addition of a few drops of acetonitrile to a 1:1 mixture of
AgOTf and $[\text{MoCl}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{py-2-CH=N-Ar})]$ (Ar = C₆H₅,
C₆H₄-4-Me **1b**, C₆H₃-3,5-Me₂ **1c**) in dichloro-
methane led immediately to the precipitation of a white solid
(AgCl), and the formation of the nitrile compounds $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{NCMe})(\text{py-2-CH=N-Ar})]\text{OTf}$.
From this species the labile MeCN ligand is easily substituted by addition
of the equimolar amount of *N*-methylimidazole (*N*-MeIm)
affording imidazole compounds $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-Ar})]\text{OTf}$ (**2a–c**, see Scheme 3).^{117 53}

Scheme 3. Synthesis of Cationic Imidazole 2-Pyridylimino Complexes **2a–e**

These reactions were followed by IR spectroscopy, showing
first the formation of cationic nitrile species (the IR ν_{CO} bands
showed the typical pattern for *cis*- $\{\text{Mo}^{\text{II}}(\text{CO})_2\}$ fragments, and
the values changed, from 1951, 1876 cm⁻¹ in the case of **1a**, to
1964, 1885 cm⁻¹), and afterward the substitution of the nitrile
by the more σ -donor *N*-MeIm ligand (IR ν_{CO} values
downshifted to 1949, 1869 cm⁻¹ for **2a**).¹²⁴

125 ^1H and ^{13}C NMR spectra in solution of compounds **2a–c**
 126 showed the asymmetry of the new molecules (as the
 127 iminopyridine ligands are nonsymmetric) and the incorpo-
 128 ration of one *N*-MeIm ligand per metallic fragment. The solid
 129 state structure of **2c**, determined by X-ray diffraction (see
 130 Figure 2),¹² shows that the molybdenum atom displays a
 131 pseudo-octahedral coordination geometry.

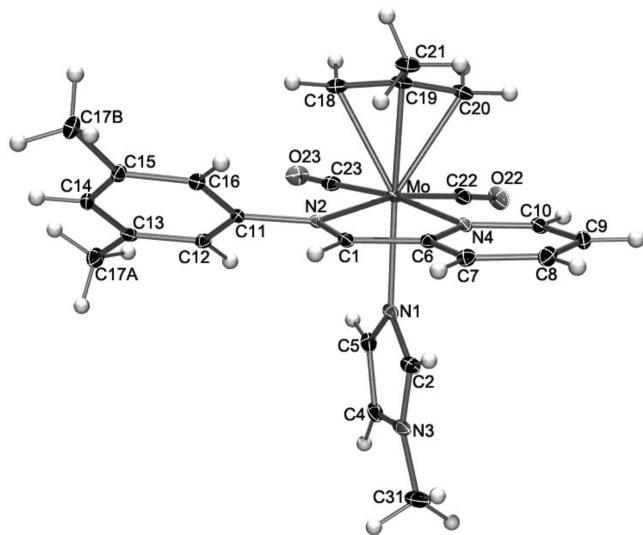
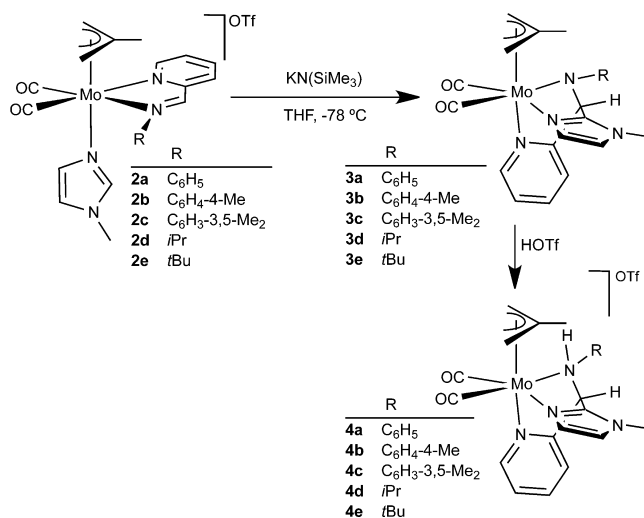


Figure 2. Molecular structure of the cation of compound **2c**.

132 The 2-pyridylimino chelate is coplanar with the two CO
 133 ligands, and the *N*-methylimidazole is *trans* to the η^3 -allyl
 134 ligand. The pyridine and imine moieties of the new bidentate
 135 ligand are virtually coplanar reflecting conjugation, with the
 136 dihedral angle being 4.43° . The Mo–N(imidazole) bond
 137 distance, of $2.220(2)$ Å, is very close to that found for the
 138 only other crystallographically characterized *N*-alkylimidazole
 139 complex of the fragment $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2\}$, of $2.219(8)$ Å.⁷
 140 The reaction of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH}=\text{N-Ph})\text{OTf}]$ (**2a**) with a slight excess of $\text{KN}(\text{SiMe}_3)_2$ in THF at
 142 -78°C afforded, as indicated by the large shift to lower
 143 wavenumbers of the ν_{CO} bands in the IR spectrum (from 1949,
 144 1869 to 1932 , 1835 cm^{-1}), the formation of a neutral species.
 145 The low stability of this deprotonated derivative precluded its
 146 isolation and, upon addition of trifluoromethanesulfonic acid in
 147 CH_2Cl_2 , the stable compound **4a** was obtained as the main
 148 product of the reaction (Scheme 4). The IR ν_{CO} bands of the
 149 new compound **4a**, at 1950 , 1969 cm^{-1} , indicated the
 150 protonation reaction had occurred and a cationic complex
 151 was formed.

152 The molecular structure of the cation of compound **4a**,
 153 determined by X-ray diffraction,¹³ is depicted in Figure 3a
 154 showing that a tridentate *N*-donor ligand is now coordinated to
 155 the $\{\text{Mo}(\eta^3\text{-methylallyl})(\text{CO})_2\}$ fragment in a facial disposition.
 156 This tripodal ligand results from the C–C coupling between
 157 the central C atom of the imidazole (C2) and the imine C atom
 158 of the pyridylimino bidentate ligand (C1). The bond distance
 159 C1–C2, of $1.497(8)$ Å, is typical for a single C–C bond.
 160 Therefore, the C1 atom is sp^3 hybridized, the angles around it
 161 being consistent with an approximately tetrahedral geometry
 162 (C2–C1–N2 $104.0(5)^\circ$, C6–C1–N2 $110.9(5)^\circ$, C2–C1–C6
 163 $107.0(5)^\circ$). The C1–N2 bond distance is in agreement with a
 164 single bond ($1.507(8)$ Å), whereas in the solid state structure of
 165 its precursor **2c** (determined by X-ray diffraction) this bond

Scheme 4. Reactivity of Cationic Imidazole 2-Pyridylimino Complexes **2a–e**



length was typical of a double bond ($1.283(3)$ Å) as expected
 166 for an imine moiety. The originally imino nitrogen atom (N2)
 167 displays in **4a** a tetrahedral geometry, which is consistent with
 168 the protonation of this atom by the HOTf forming an amino
 169 group. The high quality of the results of the structural
 170 determination of compound **4a** allowed the hydrogen atom on
 171 N2 to be refined. Finally, it is interesting to note that in the
 172 solid state structure of the cationic complex of **4a** the pyridyl
 173 moiety is in *trans* disposition to the η^3 -methylallyl ligand, whereas
 174 in the starting compound (**2c**) the imidazole ligand is
 175 occupying this position. This indicates that the C–C coupling
 176 reaction is accompanied by a rotation of the trigonal face
 177 formed by the three nitrogen ligands, probably in order to
 178 minimize the steric hindrance in the resulting product.

The ^1H and ^{13}C NMR data in solution of the new compound
 180 **4a** are in accordance with the structure found in the solid state.
 181 The ^1H NMR spectrum undoubtedly shows the deprotonation
 182 of the imidazole central CH group (as only two signals at 7.17
 183 and 6.90 ppm that correspond to imidazole CH moieties are
 184 observed), and the C–C coupling with the imine N=CH unit
 185 (as evidenced by the disappearance of the signal at 9.08 ppm
 186 assigned to that group in the ^1H NMR spectrum of **2a**).
 187 Moreover, the ^1H NMR spectrum of **4a** includes a singlet at
 188 5.65 ppm that corresponds to the $\text{Csp}^3\text{-H}$ group formed as a
 189 consequence of the C–C coupling reaction. Unfortunately, the
 190 signal of the new NH group is not observed, which can be
 191 attributed to the acidic character of this hydrogen. The ^{13}C
 192 NMR spectrum of **4a** corresponds to an asymmetric complex,
 193 showing for example two low intensity signals at 227.7 and
 194 226.8 ppm for the two carbonyl ligands, and a signal at 64.3
 195 ppm assigned to the new Csp^3 atom.

As we have discussed above, the solid state structure of
 197 compound **4a** showed that the formation of the tridentate
 198 ligand is accompanied by a rotation of the original *N*-donor
 199 ligands. Accordingly, the ^1H NMR spectra of **4a** in CD_2Cl_2 at
 200 variable temperature (from 298 to 213 K) showed the existence
 201 of a dynamic process. The data are in accordance with a
 202 trigonal twist rearrangement (that would involve a rotation of
 203 the triangular face formed by the tripodal ligand relative to the
 204 face formed by the allyl and the two carbonyl groups),¹⁴ a
 205 process that has been frequently found for complexes of the
 206 fragment $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2\}$.^{15,16}

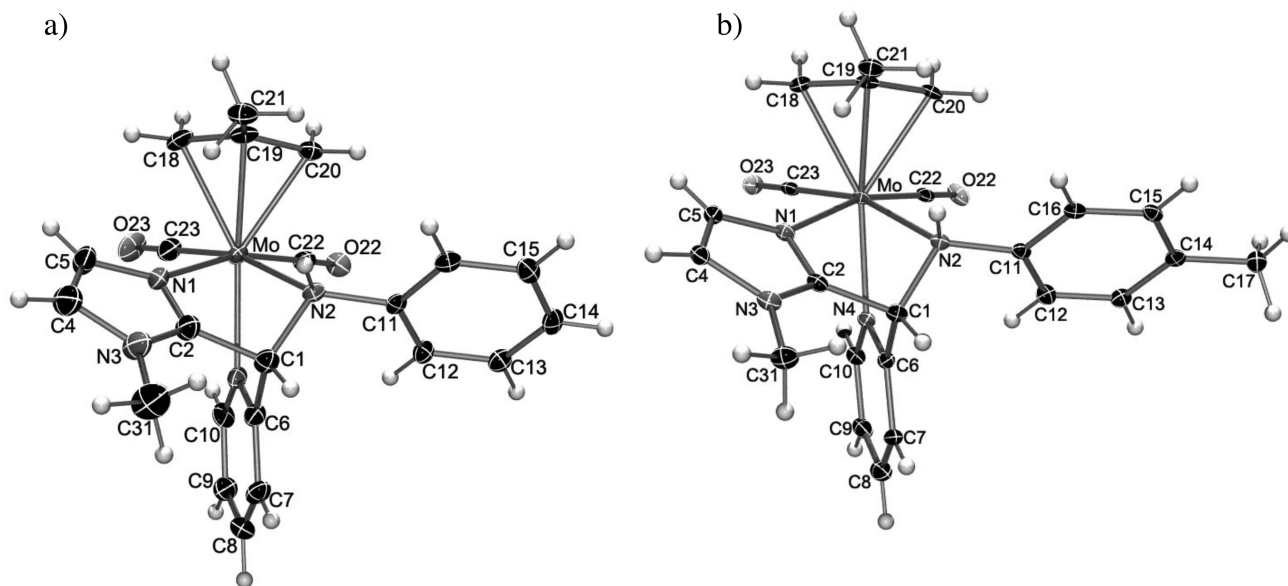


Figure 3. (a) Molecular structure of the cation of compound **4a**; (b) molecular structure of the cation of compound **4b**.

208 The reaction of the related compounds **2b** and **2c** toward the
 209 strong base $\text{KN}(\text{SiMe}_3)_2$ showed the same reactivity pattern
 210 discussed above for **2a**, but for these species the neutral
 211 derivatives, **3b** and **3c**, respectively (Scheme 4), could be
 212 isolated and characterized in solution by means of IR and ^1H
 213 NMR. The IR ν_{CO} bands, at approximately 20 cm^{-1} lower
 214 wavenumbers than those of the imidazole starting compounds,
 215 are typical of neutral complexes displaying a good σ -donor
 216 ligand (such as the deprotonated imidazole). The ^1H NMR
 217 spectra of **3b** and **3c** show characteristic features similar to
 218 those described for the spectrum of compound **4a**: i.e., only
 219 two N-MeIm CH groups are observed (two singlets at 7.02 and
 220 6.19 ppm for **3b**), there is no longer an imine $\text{N}=\text{CH}$ signal
 221 (at 9.03 ppm in the precursor **2b**), and instead there is a signal
 222 (at 5.76 ppm for **3b**) for the new $\text{Csp}^3\text{-H}$ group that originated
 223 as a consequence of the C(imidazolyl)–C(imine) bond
 224 formation. Unfortunately, the stability of complexes **3b** and
 225 **3c** was not enough to obtain the ^{13}C NMR spectra, as they
 226 decomposed after several hours in CD_2Cl_2 solution into a
 227 mixture of unidentified products.

228 The reaction of **3b** or **3c** intermediates with a slight excess of
 229 HOTf led to the formation of the cationic protonated products
 230 **4b** or **4c**, respectively (Scheme 4). The stability of the
 231 protonated products is considerably higher than that of the
 232 neutral species, which can be attributed to the presence of a
 233 highly reactive amido group¹⁷ in **3b** or **3c** that, upon
 234 protonation, is transformed into a more stable amine moiety
 235 in **4b** or **4c**. The spectroscopic data of the new compounds are
 236 analogous to those of **4a**, and the solid state X-ray diffraction
 237 structures were determined for both compounds. In Figure 3b
 238 is depicted the molecular structure of the cation of **4b**,¹⁸
 239 showing the formation of the C–C coupling product. The
 240 central carbon atom of the N-MeIm moiety (C2) is therefore
 241 bonded to the imine carbon (C1), and the resulting tridentate
 242 ligand occupies one face of the octahedral coordination sphere
 243 of the molybdenum atom. The other face is occupied by the
 244 two CO ligands and the η^3 -methylallyl moiety.¹⁴ As discussed for
 245 compound **4a**, the formation of the tridentate ligand implies a
 246 rotation of the N-donor ligands so that the 2-pyridyl group, and
 247 not the 2-imidazolyl, is *trans* to the methylallyl ligand in **4b**.

After numerous attempts, only poor quality crystals were
 248 obtained for compound **4c**. The X-ray structure, although of
 249 low quality,¹⁹ clearly shows that the connectivity of the
 250 molecule is analogous to those described previously for
 251 compounds **4a** and **4b**.
 252

The ^1H NMR spectra of the crude of all the protonated
 253 compounds **4a–c** show the existence of two sets of signals
 254 attributed to the presence of two different diastereomers. The
 255 diastereomer that could be crystallized in each case was found
 256 to be the more abundant (for example in the case of the
 257 formation of **4b** the ratio of diastereomers is of 3.85). The
 258 existence of diastereomers is due to the presence of three
 259 stereocenters: the metal, the carbon atom that is the site of the
 260 nucleophilic attack, and the N atom that is protonated. As the
 261 stereochemistry of the metal and the C atom are prefixed by the
 262 geometry of the starting compounds, it is the final protonation
 263 step that leads to the formation of two diastereomers (each a
 264 pair of enantiomers). A NOESY experiment was carried out for
 265 compound **4a**, showing that the η^3 -allyl ligand is oriented with
 266 its open face toward the carbonyl ligands, i.e. in the same
 267 orientation found in the solid state structures of compounds
 268 **4a–c**, and also found in its precursor **2a**.¹¹ This orientation of
 269 the η^3 -allyl is the one most frequently found for complexes with
 270 the $\{\text{Mo}((\eta^3\text{-allyl})(\text{CO})_2)\}$ fragment.²⁰
 271

Finally, to test the generality of the reactivity pattern
 272 previously described, we extended our study to alkyl- (instead
 273 of aryl-) amines in the Schiff condensation reaction. As a result,
 274 the pyridylimino bidentate ligands would be more electron rich,
 275 and therefore the nucleophilic attack onto the $\text{N}=\text{CH}$ group of
 276 the imidazol-2-yl ligand would be less favorable.
 277

Compounds $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-})\text{R}]\text{OTf}$ (R = *i*Pr, **2d**; *t*Bu, **2e**) were prepared from the
 278 corresponding chloroderivatives (**1d** and **1e**) as described for
 279 compounds **2a–c** (see Scheme 3).¹¹ The addition of the
 281 equimolar amount of $\text{KN}(\text{SiMe}_3)_2$ to a previously cooled THF
 282 solutions of **2d** or **2e** afforded immediately the formation of
 283 neutral species resulting, presumably, from the deprotonation
 284 of the central CH group of the imidazole ligand. The
 285 subsequent addition of the electrophilic reagent HOTf led to
 286 more stable metal complexes,²¹ **4d** and **4e**, respectively, that
 287

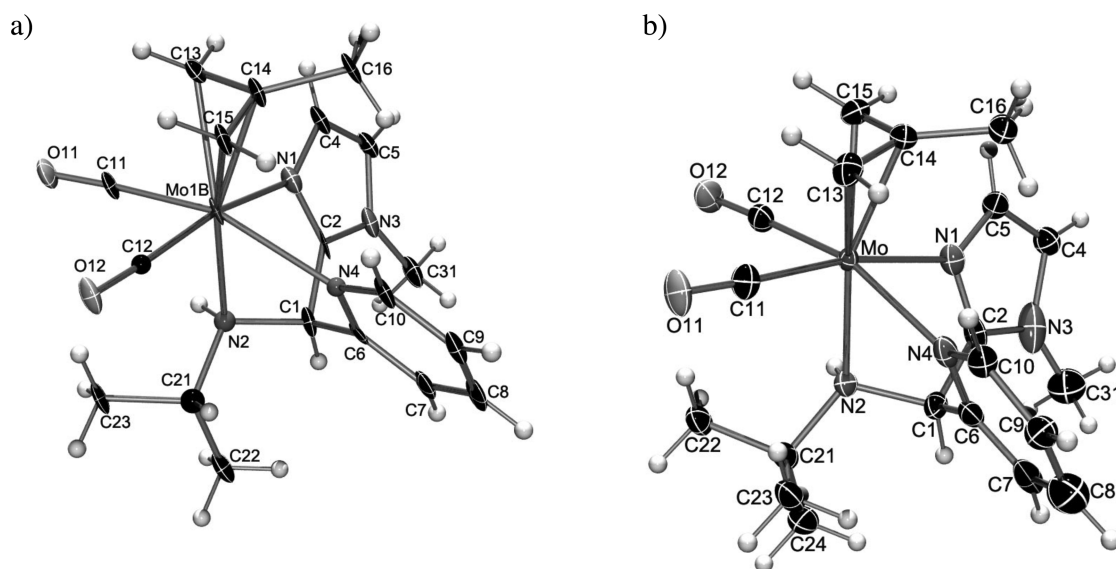


Figure 4. (a) Molecular structure of the cation of compound 4d; (b) molecular structure of the cation of compound 4e.

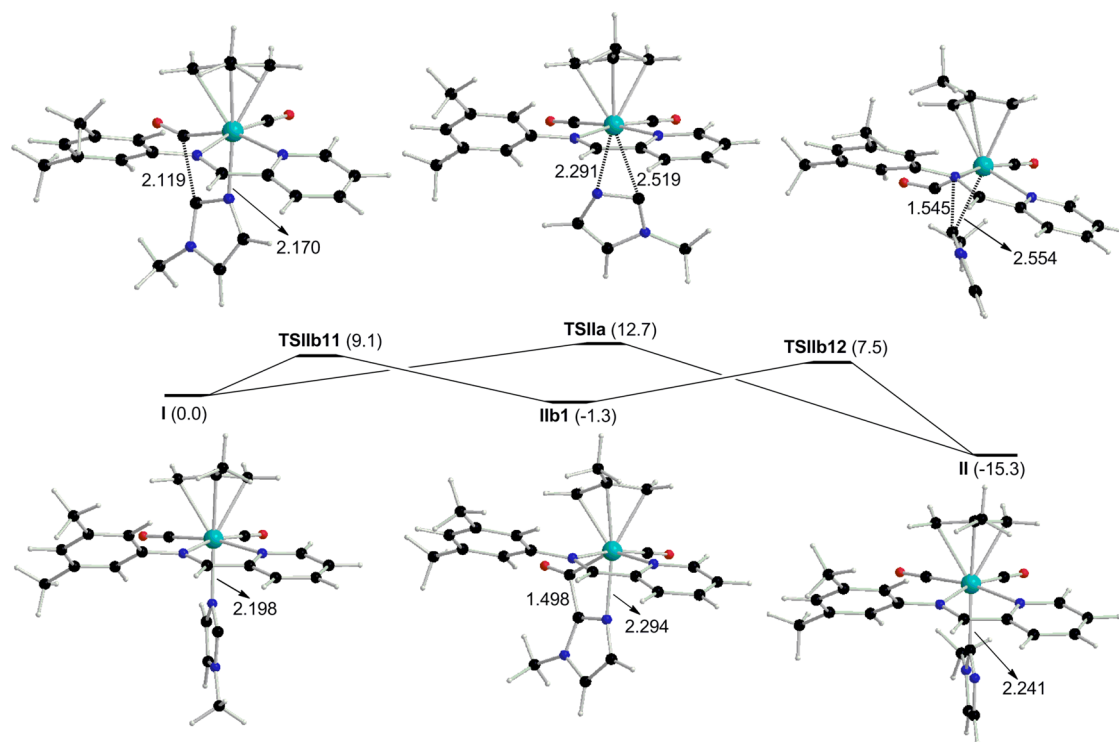


Figure 5. CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) Gibbs energy profiles in THF solution of the mechanisms located for the formation of an imidazol-2-yl product starting from I. Relative Gibbs energies in THF solution, in kcal/mol, are given in parentheses. Most relevant distances are also included in angstroms.

288 were isolated and purified by crystallization. The more
 289 characteristic features of the NMR (^1H and ^{13}C) spectra of
 290 the new compounds are analogous to the pyridyliminoaryl
 291 compounds discussed above, and clearly indicate that (i) the
 292 strong base has deprotonated the central CH group of the *N*-
 293 methylimidazole ligand, and (ii) the generated nucleophile
 294 attacked the imine carbon atom to form a C—C bond,
 295 resulting in the formation of a nitrogen-donor tridentate
 296 ligand.²² The solid state structures were determined by X-ray
 297 diffraction (Figure 4) and are in agreement with the structures
 298 proposed from the spectroscopic data in solution.^{23,24}

A tridentate N-donor ligand, constituted by imidazolyl,
 pyridyl, and amine arms, is bonded in a facial disposition to the
 $\{\text{Mo}(\eta^3\text{-methyllyl})(\text{CO})_2\}$ fragment. The disposition of this
 ligand is different from that found in the aryl derivatives 4a–c,
 since the amine function is *trans* to the allyl group. The fact that
 substituents *iso*-propyl and *tert*-butyl are notably bulkier than
 the phenyl derivatives can explain this different orientation of
 the tripodal ligand.

To confirm that the C—C coupling reaction described in the
 present work proceeds through an intramolecular nucleophilic
 attack, a crossover experiment was conducted employing two

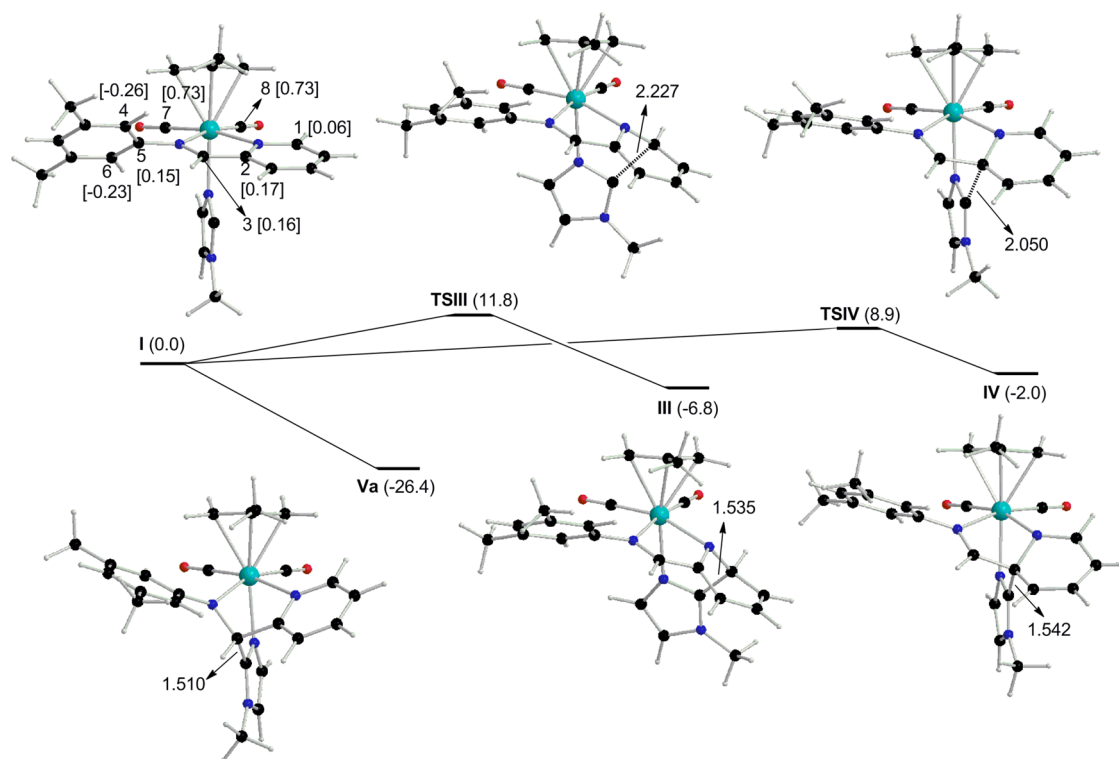


Figure 6. CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) Gibbs energy profiles in THF solution of the mechanisms located for the formation of C–C coupling products starting from I. Relative Gibbs energies in THF solution (in kcal/mol) and NBO charges of the numbered atoms are given in parentheses and in square brackets, respectively. Most relevant distances are also included in angstroms.

310 complexes with different imines (*iso*-propyl vs *para*-tolyl) and
 311 different *N*-alkylimidazole ligands (methyl vs ethyl). The results
 312 showed that the only products obtained were those that
 313 resulted from an intramolecular reaction, with the cross-
 314 coupled products not being observed.¹¹

315 **DFT Computations.** The deprotonation of [Mo(η^3 -C₄H₇)-
 316 (bipy)(CO)₂(N-RIm)]OTf (R = Me, Mes) compounds leads
 317 to the formation of imidazol-2-yl species via the attack of the
 318 imidazole deprotonated carbon atom (C_{imidazole}) on a *cis*-CO
 319 ligand.⁷ In contrast, the deprotonation of [Mo(η^3 -C₄H₇)-
 320 (CO)₂(N-MeIm)(py-2-CH=N-R')]OTf (R' = C₆H₅ (**2a**),
 321 C₆H₄-4-Me (**2b**), C₆H₃-3,5-Me₂ (**2c**), *i*Pr (**2d**), *t*Bu (**2e**))
 322 affords C–C coupling species. Furthermore, these products
 323 differ from the C–C coupling species obtained in the
 324 deprotonation of [Re(CO)₃(bipy)(N-RIm)]⁺ (R = Me, Mes)
 325 complexes.⁷ In the rhenium compounds, the C–C coupling
 326 takes place between C_{imidazole} and an *ortho* carbon atom of the
 327 bipy ligand, while in the present reaction it occurs between
 328 C_{imidazole} and the imine carbon atom (C_{imine}) of the py-2-CH=
 329 N-R' ligand. Aiming at understanding the reasons for the
 330 difference, we investigated the deprotonation of the [Mo(η^3 -
 331 C₄H₇)(CO)₂(N-MeIm)(py-2-CH=N-R')]OTf complexes at
 332 the CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for
 333 Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo)
 334 level of theory (see Computational Methods for details).
 335 Specifically, we first studied in detail the reaction mechanism
 336 for the Mo complex with R' = C₆H₃-3,5-Me₂ (**2c** in Scheme 4).
 337 Next, we analyzed the influence of replacing this aryl group by
 338 *t*Bu (**2e** in Scheme 4) on the nature of the product.

339 As in previous studies,^{6c,d,7} the deprotonated form of **2c** has
 340 been taken as the starting critical structure (I in Figures 5 and
 341 6). The relative orientation of the ligands around the

molybdenum center in I is analogous to that found in **2c**.³⁴²
 Nonetheless, we also found an isomer of I (**Ii** in the Supporting
 Information) that differs from **2c** in having the central C atom
 of the N-MeIm (namely C_{imidazole}) pointing approximately
 toward the bisector of the angle defined by the two Mo–CO
 bonds, instead of toward the chelate ligand, as in I and **2c**. **Ii** is
 only 1.3 kcal/mol in Gibbs energy in THF solution more stable
 than I, and no TS was found for such an isomerization. As a
 consequence, hereafter, unless otherwise stated, Gibbs energies
 in THF solution will be referred to I.³⁵¹

352 First, we evaluated the generation of an imidazol-2-yl species.
 As previously found for related complexes,⁷ this compound can
 be generated through two ways (see Figure 5). I can directly
 transform into the imidazol-2-yl product **II** (–15.3 kcal/mol)
 via the TS **TSIIa** (12.7 kcal/mol) in which C_{imidazole} and the
 initially coordinated nitrogen atom interact simultaneously with
 the molybdenum center. Alternatively, **II** can be achieved
 through the attack of C_{imidazole} onto each of the carbonyl ligands
 via a two-step pathway in both cases. The attack on the
 carbonyl ligand *trans* to the pyridyl group of the chelate ligand
 is found to be more favorable than the other; therefore, we only
 describe here that one for brevity (see the Supporting
 Information for the other carbonyl attack). The first step of
 this mechanism involves an energy jump of 9.1 kcal/mol
 controlled by the TS **TSIIb11** to afford the intermediate **IIb1**
 (–1.3 kcal/mol). In the second step, **IIb1** evolves into **II** via the
 TS **TSIIb12** (7.5 kcal/mol). As in related Mo and Re
 complexes,⁷ the two-step mechanism is the one most favorable.³⁶⁹

370 Next, we analyzed the formation of different C–C coupling
 species between C_{imidazole} and the pyridylimine ligand (see
 Figure 6). The attack of C_{imidazole} on the two *ortho* carbon atoms
 of the pyridine ring and the C_{imine} atom were studied (C1, C2, 373

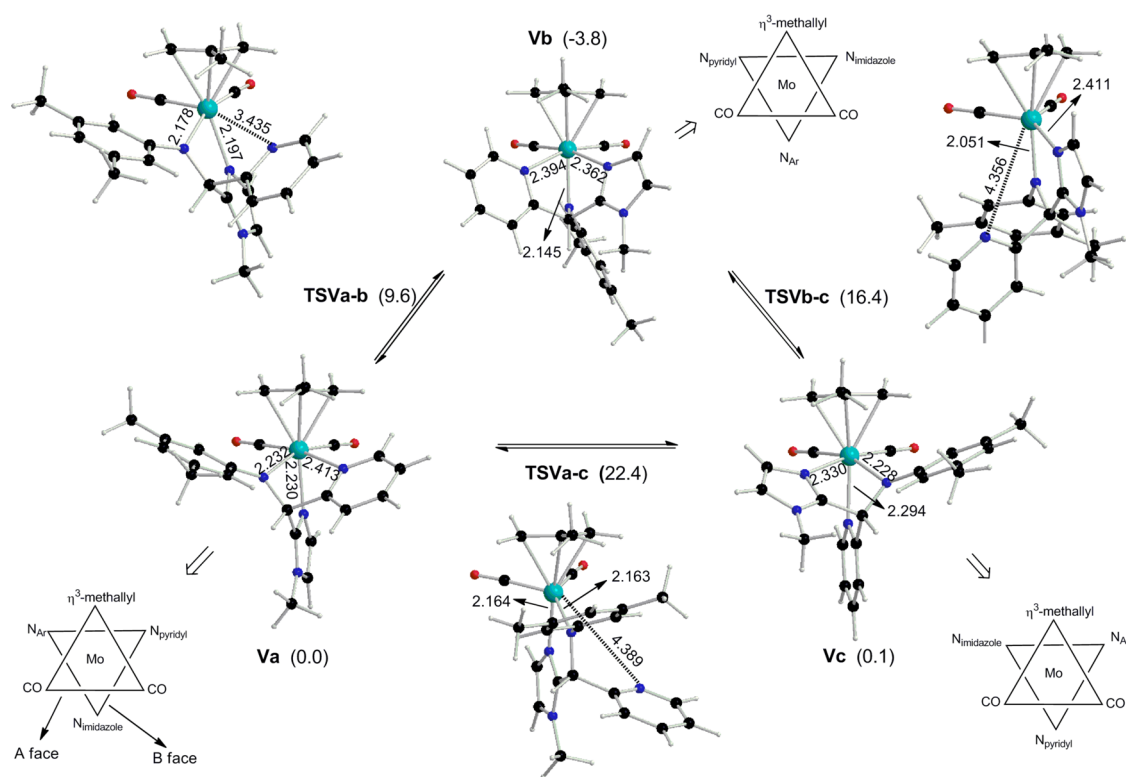


Figure 7. CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) optimized structures of the different $C_{\text{imidazole}}-C_{\text{imine}}$ coupling conformers formed for the $C_6H_3-3,5-Me_2$ derivative and the TS connecting them. CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) Gibbs energies in THF solution referred to Va (in kcal/mol) are given in parentheses. Most relevant distances are also included in angstroms.

374 and C3, respectively in Figure 6). The formation of C–C
 375 coupling products between $C_{\text{imidazole}}$ and the *ipso* carbon atom
 376 and the *ortho* carbon atoms of the aryl ring (C5, C4, and C6,
 377 respectively, in Figure 6) was also considered, but as expected,
 378 they are notably less stable than those mentioned above (see
 379 the Supporting Information). As shown in Figure 6, the
 380 formation of the $C_{\text{imidazole}}-C1$ and $C_{\text{imidazole}}-C2$ coupling
 381 products (III, -6.8 kcal/mol, and IV, -2.0 kcal/mol,
 382 respectively) requires the surmounting of energy barriers of
 383 11.8 (TSIII) and 8.9 (TSIV) kcal/mol, respectively. An NBO
 384 analysis of I reveals that C2 (0.17 *e*) has a larger positive atomic
 385 charge than C1 (0.06 *e*), which makes it more susceptible to a
 386 nucleophilic attack, and, consequently, TSIV is lower in energy
 387 than TSIII. The attack on the C_{imine} atom leads to the
 388 formation of a very stable $C_{\text{imidazole}}-C_{\text{imine}}$ coupling species (Va
 389 in Figure 6, -26.4 kcal/mol). Unlike in the generation of III
 390 and IV, no TS was found for the formation of Va after an
 391 extensive search. This can be ascribed to the high reactivity of
 392 C_{imine} due to its electrophilic character (atomic charge of 0.16 *e*
 393 at I) combined with its ability to delocalize electron density
 394 toward the originally imine nitrogen atom, which in the C–C
 395 coupling product is part of an amido ligand.

396 Taking into account the previous discussion, we conclude
 397 that the generation of an imidazol-2-yl product (II) and of the
 398 $C_{\text{imidazole}}-C1$ (III) and $C_{\text{imidazole}}-C2$ (IV) coupling products is
 399 kinetically accessible as they show energy barriers of 9.1, 11.8,
 400 and 8.9 kcal/mol, respectively. However, the evolution of I to
 401 the $C_{\text{imidazole}}-C_{\text{imine}}$ coupling product (Va) is even much more
 402 favorable due to the nonexistence of a kinetic barrier for such a
 403 molecular rearrangement, along with the fact that Va is a much
 404 more stable product. The transformation of I into Va involves

the formation of a new C–C bond without any bond breaking,
 while the original Mo– $N_{\text{imidazole}}$ bond is replaced by the Mo–
 $C_{\text{imidazole}}$ bond for the process from I to II. This can explain the
 higher stability of Va compared to II. In addition, the
 generation of the $C_{\text{imidazole}}-C_{\text{imine}}$ bond at Va does not require
 dearomatization of the pyridine ring, in contrast with what
 occurs when going from I to III or IV.

Despite the high stability of Va (-26.4 kcal/mol), this
 species can evolve into two isomers that are also very stable, Vb
 (-30.2 kcal/mol) and Vc (-26.3 kcal/mol) (see Figure 7).
 These three isomers present a pseudo-octahedral geometry.
 The two carbonyl ligands and the methylall group occupy one
 triangular face of the pseudo-octahedron (hereafter denoted as
 A), while the other (henceforth referred as B) is determined by
 the tridentate N-donor ligand, consisting of imidazolyl, pyridyl,
 and amido arms (see for instance Va Figure 7). As in 2c and I,
 Va has the imidazole group *trans* to the methylall group, so the
 amido and pyridyl groups are both *trans* to the carbonyl ligands.
 In Vb and Vc the methylall ligand is *trans* to the amido and
 pyridyl group, respectively, and hence, the N-donor groups are
trans to the carbonyls. The interconversion between Va, Vb,
 and Vc could proceed via a trigonal-twist mechanism.¹⁵ Starting
 from Va, a counterclockwise rotation of about 120° of B over A
 would lead to Vb, which in turn become Vc via another similar
 rearrangement. Alternatively, the clockwise rotation of B over A
 would directly transform Va into Vc. However, as shown in
 Figure 7, all the TSs (TSVa-b, TSVb-c, and TSVa-c) for the
 rearrangement of the tridentate ligand (Va → Vb, Vb → Vc,
 and Va → Vc, respectively) are pentacoordinated owing to the
 cleavage of the Mo–pyridyl bond. Accordingly, an NBO
 analysis of Va confirms that the Mo– N_{pyridyl} bond is the

weakest Mo–N interaction between Mo and the tridentate ligand. Specifically, the Mo–N_{pyridyl} bond has a bond order of 0.3857 while values of 0.5169 and 0.5649 were found for the Mo–N_{imidazole} and Mo–N_{imide} bonds, respectively. The breaking of one of the Mo–N bonds seems to be needed in order to favor the interconversion of the conformers containing the tridentate ligand rearrangement when bulky ligands are present in Mo complexes.²⁵ This could change in the absence of bulky ligands as reported in a theoretical study on octahedral vanadium complexes wherein no bond breaking was found at the TS located for trigonal twist.²⁶ Theoretical studies on this trigonal twist in molybdenum octahedral center are scarce,^{25a} although it is common to attribute the dynamics deduced from variable-temperature NMR experiments to such processes.²⁷

Concerning the energetics implied in the transformations **Va** → **Vb** → **Vc**, our results reveal Gibbs energy barriers of 9.6, 20.2, and 22.4 kcal/mol (measured from **Va**, **Vb**, and **Va**, respectively) for the interconversions **Va** → **Vb**, **Vb** → **Vc**, and **Va** → **Vc**, respectively. The highest energy barriers obtained are similar to those reported (~22 kcal/mol) for a dissociative trigonal twist mechanism of other six-coordinate Mo complexes.^{25a} Therefore, we conclude that **Va**, **Vb**, and **Vc** are continuously interconverting, and consequently, the complex should show a fluxional behavior. **Vb** is the most stable conformer in THF solution, but is only 3.8 and 3.9 kcal/mol more stable than **Va** and **Vc**, respectively. The protonation of these three stable conformers leads to the appearance of two diastereomers per deprotonated species, identified as **VxH** with **x** = **a**, **b**, **c**. As seen in Table 1, a diastereomer from **Vc**, (*RS*)-

presents a Gibbs energy barrier still higher (28.5 kcal/mol, **TSV'a-c**). All these energy barriers are higher than those for the arylimino derivative, with differences in the 0.7–6.1 kcal/mol range. This can be mainly ascribed to the steric effect of the *t*Bu group. The results obtained for the *t*Bu-imino complex also suggest a fluxional dynamics between **V'a** and **V'b**, and between **V'b** and **V'c**, but not directly between **V'a** and **V'c**. Besides, the significant stability of **V'b** compared to **V'a** and **V'c** agrees with the finding of a solid state structure of a protonated complex (**4e**) with the *t*Bu-substituted nitrogen atom *trans* to the methallyl ligand (see Figure 4b). Accordingly, the analysis of the relative stability of the diastereomers derived from the protonation of **V'a**, **V'b**, and **V'c** confirms that the protonated conformers of **V'b**, (*RR*)-**V'bH** and (*RS*)-**V'bH**, are the most stable (see Table 1).

CONCLUSIONS

The reaction of the new cationic complexes of [Mo(η^3 -C₄H₇)(CO)₂(*N*-MeIm)(py-2-CH=N-R)]OTf (R= C₆H₅, C₆H₄-4-Me, C₆H₃-3,5-Me₂, *i*Pr, *t*Bu) with the equimolar amount of the strong base KN(SiMe₃)₂ at low temperature leads to the deprotonation of the central CH group of the *N*-alkylimidazole ligand. The neutral species so formed are very reactive and immediately afford the C–C coupling products that result from the nucleophilic attack of the deprotonated imidazole C2 atom onto the imine CH moiety. The resulting *N*-donor tridentate ligand occupies one face of the pseudo-octahedral geometry of the complex, and its disposition depends on the nature of the substituent of the amine N atom. Whereas for aryl derivatives the pyridyl group is *trans* to the methallyl moiety, for the alkyl derivatives it is the amine function that occupies this position, probably in order to minimize steric congestion.

For this family of Mo(II) pyridylimino compounds the formation of the C–C coupling products is preferred over the formation of the imidazol-2-yl species, that had been previously found in the related 2,2'-bipyridine complexes [Mo(η^3 -C₄H₇)(bipy)(CO)₂(*N*-RIm)]OTf (R= Me, Mes). DFT calculations have shown, in agreement with the experimental results, that the formation of the C–C coupling product is undoubtedly the most favorable way of evolution of the deprotonated species, both kinetically (no TS was found for such molecular rearrangement) and thermodynamically (**Va** is 16.9 kcal/mol more stable than the 2-imidazolyl structure **II**). In that respect, the electrophilicity of the imine C atom along with its ability to delocalize electron density toward nitrogen are crucial.

EXPERIMENTAL SECTION

General. All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were distilled from Na (toluene and hexanes), Na/benzophenone (THF), and CaH₂ (CH₂Cl₂). Compound [MoCl(η^3 -C₄H₇)(CO)₂(NCMe)₂]²⁸ was prepared as previously reported. Deuterated dichloromethane (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 300 or DPX-300 spectrometer. NMR spectra are referred to the internal residual solvent peak for ¹H and ¹³C{¹H} NMR. IR solution spectra were obtained in a PerkinElmer FT 1720-X spectrometer using 0.2 mm CaF₂ cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich. Full experimental details of all compounds are given in the Supporting Information, whereas herein only a set of

Table 1. Relative Gibbs Energy, in kcal/mol, of the Different Diastereomers of the Protonated C_{imidazole}–C_{imine} Coupling Products Obtained from the Deprotonation of **2c and **2e** at the CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) Level of Theory^a**

	conformation x = a	conformation x = b	conformation x = c
(<i>RR</i>)- VxH	0.0	1.5	0.2
(<i>RS</i>)- VxH	0.7	2.1	–0.2
(<i>RR</i>)- V'xH	0.0	–1.0	5.5
(<i>RS</i>)- V'xH	7.7	–0.7	–0.4

^aThe most stable diastereomer in conformation **a** is taken as a reference in both cases.

VcH, becomes slightly the most stable species. This isomer is also the one found in the solid state structure of **4c**, in which the pyridine ligand is *trans* to the methallyl group, and of the analogous complexes **4a** and **4b**.

On the basis of the results discussed above, it is also possible to rationalize the product obtained for the deprotonation of the *t*Bu-imine Mo complex (**2e** in Scheme 4). To that end, we focused our attention on the interconversion among the conformers analogous to **Va**, **Vb**, and **Vc** wherein the aryl group is replaced by *t*Bu (denoted as **V'a**, **V'b**, and **V'c**, respectively). As seen in Supporting Information Figure S3, the TSs for the transformations **V'a** → **V'b**, **V'b** → **V'c**, and **V'a** → **V'c** (**TSV'a-b**, **TSV'b-c**, and **TSV'a-c**, respectively) are analogous to those found for the aryl complexes. Concerning the energetics, **V'a** becomes **V'b** via a Gibbs energy barrier of 10.3 kcal/mol (**TSV'a-b**). A value of 21.5 kcal/mol (**TSV'b-c**) was found for the transformation **V'b** → **V'c** because **V'b** is 7.0 kcal/mol more stable than **V'a**. The interconversion **V'a** → **V'c**

544 complexes displaying each type of ligand (alkyl or aryl derivatives) is
545 included as representative examples.

546 **Crystal Structure Determination. General Description.** For
547 Compounds **1c**, **4a**, **4b**, and **4e**. Crystal data were collected on a
548 Bruker APPEX II diffractometer using graphite-monochromated *Mo*
549 *K* α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focus sealed tube source at
550 100 K. Computing data and reduction were made with the APPEX II
551 software.²⁹ In all cases empirical absorption corrections were applied
552 using SADABS.³⁰ For compound **4e**: data collection was performed at
553 150 K on an Oxford Diffraction Xcalibur Nova single crystal
554 diffractometer, using *Cu K* α radiation ($\lambda = 1.5418 \text{ \AA}$). Images were
555 collected at a 65 mm fixed crystal-detector distance, using the
556 oscillation method, with 1° oscillation and variable exposure time per
557 image (4–16 s). Data collection strategy was calculated with the
558 program CrysAlis^{Pro} CCD.³¹ Data reduction and cell refinement was
559 performed with the program CrysAlis^{Pro} RED.³¹ An empirical
560 absorption correction was applied using the SCALE3 ABSPACK.³¹
561 In all cases the structures were solved using SIR92³² and finally refined
562 by full-matrix, least-squares based on F^2 by SHELXL.³³ Molecular
563 graphics were made with ORTEP 3.³⁴

564 **Computational Methods.** Quantum chemical computations were
565 carried out with the Gaussian 09 series of programs.³⁵ Full geometry
566 optimizations of stable species and TS were performed in THF
567 solution from the outset with the Conductor-like Polarizable
568 Continuum Model (CPCM)³⁶ and the Universal Force Field (UFF)
569 radii³⁷ in conjunction with the hybrid density functional B3LYP³⁸ and
570 the 6-31+G(d)³⁹ basis set for nonmetal atoms together with the
571 LANL2DZ⁴⁰ with *f* polarization functions⁴¹ of exponent 1.043 for *Mo*
572 and by using the standard Schlegel's algorithm.⁴² A relative
573 permittivity of 7.58 was assumed in the calculations to simulate
574 THF as the solvent experimentally used for all the cases. To further
575 refine the quality of the above-mentioned energies, we also performed
576 single-point CPCM-B3LYP/6-311++G(d,p)³⁹ (LANL2DZ + *f* for
577 *Mo*) and B3LYP-D3⁴³ dispersion calculations on the CPCM-B3LYP/
578 6-31+G(d) geometries. For the latter computations, we used the
579 Becke–Johnson damping function⁴⁴ to avoid near singularities for
580 small interatomic distances. The nature of the stationary points was
581 verified by analytical computations of harmonic vibrational frequen-
582 cies. Intrinsic reaction coordinate (IRC) calculations with the
583 Gonzalez and Schlegel method⁴⁵ were carried out to check the two
584 minimum energy structures connecting each TS except for the species
585 involved in the trigonal twist mechanism. The complexity of these
586 molecular rearrangements prevented the use of the IRC algorithm; we
587 instead analyzed the transition vector to verify the TS connectivity.
588 Besides this, we also checked how the TS was finally reached from an
589 initial geometry wherein the methallyl ligand is in front of the pyridyl
590 ligand, the imidazole ligand, or the nitrogen atom bearing the *Ar* or
591 *t*Bu group. Thermodynamic magnitudes (ΔH , ΔS , and ΔG) were also
592 calculated within the ideal gas, rigid rotor, and harmonic oscillator
593 approximations at a pressure of 1 atm and a temperature of 195.15
594 K.⁴⁶ For interpretation purposes, a natural bond orbital (NBO)
595 analysis was also performed.⁴⁷

596 **Synthesis of [Mo(η^3 -C₄H₇)(CO)₂(py-2-CH=N-C₆H₄-4-Me)] (1b).**
597 Pyridine-2-carboxaldehyde (29 μL , 0.308 mmol) and *p*-toluidine
598 (0.033 g, 0.308 mmol) were added to a solution of [MoCl(η^3 -
599 C₄H₇)(CO)₂(NCMe)₂] (0.100 g, 0.308 mmol) in THF (20 mL), and
600 the reaction mixture was stirred for 30 min. The solvent was
601 evaporated under reduced pressure to dryness, and the resulting violet
602 powder was washed with hexane (2 \times 20 mL) and dried under
603 vacuum. Compound **1b** was obtained as a violet powder. Yield: 105
604 mg (78%). IR (CH₂Cl₂, cm⁻¹): 1951, 1875 (ν_{CO}). ¹H NMR
605 (CD₂Cl₂): δ 8.79 (m, 1H, py), 8.42 (s, 1H, N=CH), 7.99 (m, 1H,
606 py), 7.87 (m, 1H, py), 7.54 (m, 1H, py), 7.38 (d ($J = 8.2$), 2H, C₆H₄),
607 7.29 (d ($J = 8.2$), 2H, C₆H₄), 2.78 (m, 1H, H_{syn} η^3 -C₄H₇), 2.41 (s, 3H,
608 CH₃ C₆H₄-4-Me), 2.30 (m, 1H, H_{syn} η^3 -C₄H₇), 1.35 (s_{br}, 4H, CH₃ and
609 H_{anti} η^3 -C₄H₇), 1.11 (s, 1H, H_{anti} η^3 -C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂):
610 δ 227.1, 226.8 (CO), 162.5 (N=CH), 153.6, 152.3, 148.7, 139.9,
611 138.8, 130.4, 129.3, 127.5, 122.4 (py-2-CH=N-C₆H₅), 83.8 (C₂ η^3 -
612 C₄H₇), 54.2, 52.7 (C₁ and C₃ η^3 -C₄H₇), 23.2 (CH₃ C₆H₄-4-Me), 19.3

(CH₃ η^3 -C₄H₇). Anal. Calcd for C₁₉H₁₉ClMoN₂O₂: C 52.01, H 4.36, 613
N 6.38. Found: C 51.98, H 4.32, N 6.18. 614

615 **Synthesis of [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-*t*Bu)] (1e).** Com-
616 pound **1e** was prepared as described above for compound **1b**, starting
617 from [MoCl(η^3 -C₄H₇)(CO)₂(NCMe)₂] (100 mg, 0.308 mmol),
618 pyridine-2-carboxaldehyde (29 μL , 0.308 mmol), and tertbutylamine
619 (32 μL , 0.308 mmol). Compound **1e** was obtained as a dark blue solid.
620 Yield: 161 mg (87%). IR (CH₂Cl₂, cm⁻¹): 1949, 1864 (ν_{CO}). ¹H NMR
621 (CD₂Cl₂): δ 8.76 (m, 1H, py), 8.54 (s, 1H, N=CH), 8.01 (m, 1H,
622 py), 7.81 (m, 1H, py), 7.54 (m, 1H, py), 3.13 (m, 1H, H_{syn} η^3 -C₄H₇),
623 2.77 (s_{br}, 1H, H_{syn} η^3 -C₄H₇), 1.59 (s, 9H, *t*Bu), 1.34 (s, 3H, CH₃ η^3 -
624 C₄H₇), 1.31 (s, 1H, H_{anti} η^3 -C₄H₇), 1.27 (s, 1H, H_{anti} η^3 -C₄H₇).
625 ¹³C{¹H} NMR (CD₂Cl₂): δ 228.3, 227.1 (CO), 163.9 (N=CH),
626 154.1, 151.6, 138.6, 128.8, 127.2 (py), 83.4 (C₂ η^3 -C₄H₇), 70.8 (*t*Bu),
627 64.0 (C₁ or C₃ η^3 -C₄H₇), 32.5 (CH₃ *t*Bu), 19.1 (CH₃ η^3 -C₄H₇). The
628 signal of C₁ or C₃ of the methallyl ligand is overlapped with the solvent
629 residual. Anal. Calcd for C₁₆H₂₁ClMoN₂O₂: C 47.48, H 5.23, N 6.92.
630 Found: C 47.49, H 4.99, N 6.83.

631 **Synthesis of [Mo(η^3 -C₄H₇)(CO)₂(N-Melm)(py-2-CH=N-C₆H₄-4-
632 Me)]OTf (2b).** To a solution of [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=
633 N-C₆H₄-4-Me)] (**1b**) (50 mg, 0.114 mmol) in CH₂Cl₂ (20 mL)
634 were added AgOTf (35 mg, 0.136 mmol) and MeCN (3 mL), and the
635 mixture was stirred in the dark for 1 h. The resulting slurry was filtered
636 off the white solid (AgCl), and the solvent was evaporated to dryness.
637 The deep red residue was redissolved in CH₂Cl₂ (20 mL), *N*-Melm
638 (10 μL , 0.125 mmol) was added, and the reaction mixture was allowed
639 to stir for 1 h. The solvent was concentrated under reduced pressure to
640 a volume of 7–10 mL, and addition of hexane (15 mL) caused the
641 precipitation of a dark red solid, which was washed with hexane (2 \times 20
642 mL) and dried under vacuum. Yield: 63 mg (87%). IR (CH₂Cl₂,
643 cm⁻¹): 1951, 1869 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.05 (s, 1H, N=
644 CH), 8.77 (m, 1H, py), 8.41 (m, 1H, py), 8.16 (m, 1H, py), 7.61 (m,
645 1H, py), 7.43 (s, 1H, NCHN), 7.31 (d ($J = 8.4$), 2H, C₆H₄), 7.25 (d (J
646 = 8.4), 2H, C₆H₄), 7.10 (s_{br}, 1H, CH *N*-Melm), 6.97 (s_{br}, 1H, CH *N*-
647 Melm), 3.65 (s, 3H, CH₃ *N*-Melm), 3.05 (m, 1H, H_{syn} η^3 -C₄H₇), 2.59
648 (m, 1H, H_{syn} η^3 -C₄H₇), 2.42 (s, CH₃ C₆H₄-4-Me), 1.59 (s, 1H, H_{anti} η^3 -
649 C₄H₇), 1.34 (s_{br}, 4H, CH₃ and H_{anti} η^3 -C₄H₇). ¹³C{¹H} NMR
650 (CD₂Cl₂): δ 226.0, 225.8 (CO), 166.1 (N=CH), 153.8, 152.4, 147.3,
651 141.1, 140.6, 139.9, 132.0, 130.9, 128.9, 122.9, 122.7 (py-2-CH=N-
652 C₆H₄-4-Me and *N*-Melm), 86.1 (C₂ η^3 -C₄H₇), 58.1, 56.3 (C₁ and C₃
653 η^3 -C₄H₇), 35.2 (CH₃ *N*-Melm), 21.4 (CH₃ C₆H₄-4-Me), 18.9 (CH₃
654 η^3 -C₄H₇). Anal. Calcd for C₂₄H₂₅F₃MoN₄O₅S: C 45.43, H 3.97, N
655 8.83. Found: C 45.91, H 4.06, N 8.96.

656 **Synthesis of [Mo(η^3 -C₄H₇)(CO)₂(N-Melm)(py-2-CH=N-*t*Bu)]OTf**
657 (**2e**). Compound **2e** was prepared following the procedure described
658 for the synthesis of **2b**, starting from [MoCl(η^3 -C₄H₇)(CO)₂(py-2-
659 CH=N-*t*Bu)] (**1e**) (50 mg, 0.124 mmol), AgOTf (35 mg, 0.136
660 mmol), and *N*-Melm (10 μL , 0.125 mmol). Compound **2e** was
661 obtained as a dark red microcrystalline solid. Yield: 64 mg (87%). IR
662 (CH₂Cl₂, cm⁻¹): 1947, 1864 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.97 (s, 1H,
663 N=CH), 8.67 (m, 1H, py), 8.38 (m, 1H, py), 8.22 (m, 1H, py), 7.64
664 (m, 1H, py), 7.22 (s, 1H, NCHN), 6.98 (s_{br}, 1H, CH *N*-Melm), 6.91
665 (s_{br}, 1H, CH *N*-Melm), 3.68 (s, 3H, CH₃ *N*-Melm), 3.42 (m, 1H, H_{syn}
666 η^3 -C₄H₇), 2.94 (m, 1H, H_{syn} η^3 -C₄H₇), 1.62 (s, 1H, H_{anti} η^3 -C₄H₇),
667 1.42 (s, 1H, H_{anti} η^3 -C₄H₇), 1.38 (s, 9H, CH₃ *t*Bu), 1.23 (s, 3H, CH₃
668 η^3 -C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.1, 226.2 (CO), 166.8 (N=
669 CH), 154.5, 151.7, 140.6, 140.3, 131.8, 131.1, 128.6, 122.4 (py-2-
670 CH=N-*t*Bu and *N*-Melm), 86.5 (C₂ η^3 -C₄H₇), 64.9 (*t*Bu), 58.7, 56.2
671 (C₁ and C₃ η^3 -C₄H₇), 34.9 (CH₃ *N*-Melm), 31.9 (CH₃ *t*Bu), 18.6
672 (CH₃ η^3 -C₄H₇). Anal. Calcd for C₂₁H₂₇F₃MoN₄O₅S: C 42.00, H 4.53,
673 N 9.33. Found: C 41.81, H 4.87, N 9.02.

674 **Reaction of [Mo(η^3 -C₄H₇)(CO)₂(N-Melm)(py-2-CH=N-C₆H₄-4-
675 Me)]OTf (2b) with KN(SiMe₃)₂.** **Synthesis of 3b.** KN(SiMe₃)₂ (0.15
676 mg, 0.5 M solution in toluene, 0.076 mmol) was added to a 676
677 solution of compound **2b** (40 mg, 0.063 mmol) in THF (15 mL),
678 previously cooled to -78°C . The color of the solution changed
679 immediately from dark red to orange, and the solvent was evaporated
680 to dryness under reduced pressure. The residue was extracted with
681 CH₂Cl₂ (20 mL) and filtered via canula, and the resulting solution was
682 concentrated to a volume of 5 mL. Addition of hexane (15 mL) caused

683 the precipitation of a dark yellow solid that was washed with hexane (2
684 \times 15 mL). Yield: 19 mg (63%). IR (CH_2Cl_2 , cm^{-1}): 1929, 1833 (ν_{CO}).
685 ^1H NMR (CD_2Cl_2): δ 8.57 (m, 1H, py), 7.77 (m, 1H, py), 7.53 (m,
686 1H, py), 7.17 (m, 1H, py), 6.95 (m, 5H, C_6H_4 and CH N-MeIm), 6.71
687 (s_{br} , 1H, CH N-MeIm), 5.72 (s, 1H, Csp^3H), 3.71 (s, 3H, CH_3 N-
688 MeIm), 3.31 (m, 2H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.20 (s, CH_3 C_6H_4 -4-Me), 1.90
689 (s, 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$), 1.24 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$), 1.08 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-}$
690 C_4H_7). Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{MoN}_4\text{O}_2$: C 57.03, H 4.99, N 11.57.
691 Found: C 57.26, H 4.66, N 12.13.
692 **Reaction of 3b with HOTf. Synthesis of 4b.** HOTf (8 μL , 0.091
693 mmol) was added to a solution of compound 3b (0.040 g, 0.083
694 mmol) in CH_2Cl_2 , and the reaction mixture was stirred for 15 min at
695 room temperature. The solvent was evaporated to a volume of 5 mL,
696 and addition of hexane caused the precipitation of a red solid which
697 was washed with hexane (2 \times 15 mL). Slow diffusion of hexane (15
698 mL) into a concentrated solution of 4b in CH_2Cl_2 (5 mL) afforded red
699 crystals, one of which was employed for an X-ray structure
700 determination. Yield: 36 mg (69%). IR (KBr, cm^{-1}): 3456 (ν_{NH}),
701 1947, 1858 (ν_{CO}). IR (CH_2Cl_2 , cm^{-1}): 1949, 1860 (ν_{CO}). ^1H NMR
702 (CD_2Cl_2): δ 9.66 (m, 1H, py), 8.03 (m, 1H, py), 7.71 (m, 1H, py),
703 7.57 (m, 1H, py), 7.20 (s, 1H, CH N-MeIm), 7.05 (d ($J = 8.2$), 2H,
704 C_6H_4), 6.93 (s, 1H, CH N-MeIm), 6.87 (d ($J = 8.2$), 2H, C_6H_4), 5.64
705 (s, 1H, Csp^3H), 3.81 (s, 3H, CH_3 N-MeIm), 3.53 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-}$
706 C_4H_7), 2.71 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.31 (s, CH_3 C_6H_4 -4-Me), 1.98 (s,
707 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$), 1.52 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$), 1.31 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-}$
708 C_4H_7). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 227.7, 226.9 (CO), 156.7, 146.9,
709 142.1, 141.8, 137.7, 130.6, 130.3, 127.8, 126.2, 124.2, 123.4, 122.7 (py-
710 2- $\text{CH}=\text{N}-\text{C}_6\text{H}_4$ -4-Me and N-MeIm), 85.5 ($\text{C}_2 \eta^3\text{-C}_4\text{H}_7$), 64.5
711 (Csp^3), 58.0 (C_1 or $\text{C}_3 \eta^3\text{-C}_4\text{H}_7$), 34.8 (CH_3 N-MeIm), 20.8, 20.6
712 (CH_3 C_6H_4 -4-Me and $\eta^3\text{-C}_4\text{H}_7$). The signal of C_1 or C_3 of the
713 methallyl ligand is overlapped with the solvent residual peak. Anal.
714 Calcd for $\text{C}_{24}\text{H}_{25}\text{F}_3\text{MoN}_4\text{O}_3\text{S}$: C 45.43, H 3.97, N 8.83. Found: C
715 45.76, H 4.10, N 9.05.
716 **Reaction of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py}-2\text{-CH}=\text{N-tBu})(2\text{e})$**
717 **with $\text{KN}(\text{SiMe}_3)_2$ Followed by Addition of HOTf. Synthesis of 4e.**
718 $\text{KN}(\text{SiMe}_3)_2$ (0.200 mL of a 0.5 M solution in toluene, 0.100 mmol)
719 was added to a solution of compound 2e (50 mg, 0.083 mmol) in
720 THF (20 mL) cooled to -78°C . The reaction mixture was allowed to
721 reach room temperature and stirred for 40 min. The solvent was
722 evaporated to dryness, the residue was extracted with CH_2Cl_2 (20
723 mL), and HOTf (9 μL , 0.101 mmol) was added. After 15 min stirring
724 at room temperature the reaction mixture was filtered via canula, the
725 solvent evaporated under reduced pressure, and the resulting yellow
726 solid was washed with hexane (2 \times 20 mL) and dried under vacuum.
727 Yield: 31 mg (62%). IR (KBr, cm^{-1}): 3451 (ν_{NH}), 1945, 1856 (ν_{CO}).
728 IR (CH_2Cl_2 , cm^{-1}): 1950, 1861 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.07 (m,
729 1H, py), 7.97 (m, 1H, py), 7.81 (m, 1H, py), 7.50 (m, 1H, py), 7.16 (s,
730 1H, CH N-MeIm), 6.90 (s, 1H, CH N-MeIm), 5.71 (s, 1H, Csp^3H),
731 4.56 (s_{br} , 1H, NH), 3.83 (s, 3H, CH_3 N-MeIm), 3.50 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-}$
732 C_4H_7), 3.45 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 1.80 (s, 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$), 1.44
733 (s_{br} , 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$), 1.35 (s_{br} , 10H, tBu and $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$).
734 $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 222.7, 226.9 (CO), 156.0, 152.9, 146.9,
735 141.7, 127.3, 125.5, 124.1, 123.4 (py-2- $\text{CH}=\text{N-tBu}$), 83.1 ($\text{C}_2 \eta^3\text{-}$
736 C_4H_7), 60.0, 56.1 (C_1 and $\text{C}_3 \eta^3\text{-C}_4\text{H}_7$), 57.7 (Csp^3), 35.0 (CH_3 N-
737 MeIm), 29.6 (CH_3 tBu), 19.1 ($\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$). Anal. Calcd for
738 $\text{C}_{21}\text{H}_{27}\text{F}_3\text{MoN}_4\text{O}_3\text{S}$: C 42.00, H 4.53, N 9.33. Found: C 42.11, H 4.69,
739 N 8.97.

740 ■ ASSOCIATED CONTENT

741 ● Supporting Information

742 Full experimental details for all compounds, X-ray crystallo-
743 graphic data for compounds 2c and 4a, 4b, 4d, and 4e in CIF
744 format, discussion about the mechanisms not included in the
745 paper, and full DFT details. This material is available free of
746 charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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- (12) Selected crystallographic data for 2c: $\text{C}_{25}\text{H}_{27}\text{F}_3\text{MoN}_4\text{O}_3\text{RS}$, $M = 806$ 648.51, monoclinic, $P2_1/c$, $a = 10.890(5)$ Å, $b = 17.561(5)$ Å, $c = 14.168(5)$ Å, $\alpha = 90^\circ$, $\beta = 93.464(5)^\circ$, $\gamma = 90^\circ$, 100.0(1) K, $V = 2704(2)$ Å³, $Z = 4$. 5335 reflections measured, 5145 independent ($R_{\text{int}} = 0.0275$). $R1 = 0.0289$, $wR2 = 0.0762$ (all data).

- 811 (13) Selected crystallographic data for **4a**: $C_{23}H_{23}F_3MoN_4O_5S$ ·
812 CH_2Cl_2 , $M = 705.38$, monoclinic, $P2_1/c$, $a = 8.519(5)$ Å, $b = 11.186(5)$
813 Å, $c = 30.020(5)$ Å, $\alpha = 90^\circ$, $\beta = 93.456(5)^\circ$, $\gamma = 90^\circ$, $100.0(1)$ K, $V =$
814 $2856(2)$ Å³, $Z = 4$. 7087 reflections measured, 6136 independent (R_{int}
815 $= 0.0470$). $R1 = 0.0511$, $wR2 = 0.1306$ (all data).
- 816 (14) In these complexes it is customary to describe the structures
817 considering that the η^3 -allyl ligand occupies one coordination site, see
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- 823 (16) It has to be noted that for the starting compound [Mo(η^3 -
824 C_4H_7)(CO)₂(N-RIm)(py-2-CH=N-Ph)]OTf (**2a**) the NMR dynam-
825 ics process is not observed in CD₂Cl₂ at low temperature (198 K). This
826 behavior is similar to that of related allyldicarbonyl molybdenum(II)
827 complexes with diimine chelate ligands, such as 2,2'-bipyridine or 1,10-
828 phenanthroline, see: Davis, R.; Kane-Maguire, L. A. P. *Comprehensive*
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830 Eds.; Pergamon: Oxford, U.K., 1982; Vol. 8, pp 1156–1159.
- 831 (17) Destabilizing interactions between the amido N lone pair and
832 Mo filled d orbitals (a feature imposed by their saturated, 18-electron,
833 nature) are responsible of the high instability of these species. See:
834 Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D.; Mosquera, M. E.
835 G.; García-Granda, S. *Chem.—Eur. J.* **2003**, *9*, 4132–4143 and
836 references therein.
- 837 (18) Selected crystallographic data for **4b**: $C_{24}H_{25}F_3MoN_4O_5S$, $M =$
838 634.48 , monoclinic, $P2_1/n$, $a = 14.315(5)$ Å, $b = 11.167(3)$ Å, $c =$
839 $16.931(6)$ Å, $\alpha = 90^\circ$, $\beta = 108.88(2)^\circ$, $\gamma = 90^\circ$, $100.0(1)$ K, $V =$
840 $2560(1)$ Å³, $Z = 4$. 5532 reflections measured, 5245 independent (R_{int}
841 $= 0.0401$). $R1 = 0.0342$, $wR2 = 0.0808$ (all data).
- 842 (19) The molecular structure of the cation of compound **4c** is
843 displayed in the Supporting Information.
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846 887–895 and references therein.
- 847 (21) For complexes **2d** and **2e** the stability of the neutral derivatives
848 resulting from the deprotonation reaction (**3d** and **3e**, respectively)
849 will be even lower than in the aryl derivatives **3a–c**, as the lone pair on
850 the amide type nitrogen would not have the possibility of
851 delocalization towards an aryl substituent.
- 852 (22) NOESY spectra of *tert*-butyl derivatives **2d** and **4d** showed that,
853 as evidenced for the arylimine complexes, the η^3 -allyl ligand is oriented
854 with the open face towards the carbonyls. See the Supporting
855 Information for further experimental details.
- 856 (23) Selected crystallographic data for **4d**: $C_{16}H_{12}F_3N_2O_8ReS$, $M =$
857 635.54 , monoclinic, $P2_1/c$, $a = 8.7249(1)$ Å, $b = 15.1603(3)$ Å, $c =$
858 $14.7401(3)$ Å, $\alpha = 90^\circ$, $\beta = 91.822(2)^\circ$, $\gamma = 90^\circ$, $100.0(1)$ K, $V =$
859 $1948.74(6)$ Å³, $Z = 4$. 10 569 reflections measured, 3662 independent
860 ($R_{int} = 0.0431$). $R1 = 0.0324$, $wR2 = 0.0889$ (all data).
- 861 (24) Selected crystallographic data for **4e**: $C_{21}H_{27}F_3MoN_4O_5S$ ·
862 CH_2Cl_2 , $M = 685.35$, triclinic, $P1$, $a = 7.953(3)$ Å, $b = 12.934(5)$ Å, $c =$
863 $14.373(5)$ Å, $\alpha = 76.750(3)^\circ$, $\beta = 87.895(3)^\circ$, $\gamma = 76.286(3)^\circ$, $152(4)$
864 K, $V = 1397(1)$ Å³, $Z = 2$. 9654 reflections measured, 5059
865 independent ($R_{int} = 0.0224$). $R1 = 0.0535$, $wR2 = 0.01353$ (all data).
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Supporting Information

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Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were distilled from Na (toluene and hexanes), Na/benzophenone (thf) and CaH₂ (CH₂Cl₂). Compound [MoCl(η^3 -C₄H₇)(CO)₂(NCMe)₂] was prepared as previously reported.¹ Deuterated dichloromethane (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance 300 or DPX-300 spectrometer. NMR spectra are referred to the internal residual solvent peak for ¹H and ¹³C{¹H} NMR. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm. CaF₂ cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich.

Synthesis of [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-C₆H₅)] (1a). Pyridine-2-carboxaldehyde (29 μ L, 0.308 mmol) and aniline (28 μ L, 0.308 mmol) were added to a solution of [MoCl(η^3 -C₄H₇)(CO)₂(NCMe)₂] (100 mg, 0.308 mmol) in THF (20 mL), and the reaction mixture was stirred for 30 min. The solvent was evaporated under reduced pressure to dryness and the resulting violet powder was washed with hexane (2 \times 20 mL) and dried under vacuum. Yield: 118 mg (90 %). IR (CH₂Cl₂, cm⁻¹): 1951, 1876 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.80 (m, 1H, py), 8.45 (s, 1H, N=CH), 8.01 (m, 1H, py), 7.89 (m, 1H, py), 7.56 (m, 1H, py), 7.49 (m, 5H, C₆H₅), 2.81 (m, 1H, H_{syn} η^3 -C₄H₇), 2.31 (m, 1H, H_{syn} η^3 -C₄H₇), 1.37 (s_{br}, 4H, CH₃ and H_{anti} η^3 -C₄H₇), 1.12 (s, 1H, H_{anti} η^3 -C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.0, 226.8 (CO), 163.3 (N=CH), 162.1, 152.4, 138.9, 129.9, 129.5, 129.4, 127.7, 122.5, 122.4, 120.6 (py-2-CH=N-C₆H₅), 84.0 (C₂ η^3 -C₄H₇), 54.3, 52.7 (C₁ and C₃ η^3 -C₄H₇), 19.4 (CH₃ η^3 -C₄H₇). Anal. Calcd. for C₁₈H₁₇ClMoN₂O₂: C 50.90, H 4.03, N 6.60. Found: C 51.08, H 4.31, N 6.62.

Synthesis of [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-C₆H₄-4-Me)] (1b). Compound **1b** was prepared as described above for compound **1a**, starting from [MoCl(η^3 -C₄H₇)(CO)₂(NCMe)₂] (100 mg, 0.308 mmol), pyridine-2-carboxaldehyde (29 μ L, 0.308 mmol) and *p*-toluidine (0.033 g, 0.308 mmol). Compound **1b** was obtained as a violet powder. Yield: 105 mg (78 %). IR (CH₂Cl₂, cm⁻¹): 1951, 1875 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.79 (m, 1H, py), 8.42 (s, 1H, N=CH), 7.99 (m, 1H, py), 7.87 (m, 1H, py), 7.54 (m, 1H, py), 7.38 (d (*J*=8.2), 2H, C₆H₄), 7.29 (d (*J*=8.2), 2H, C₆H₄), 2.78 (m, 1H, H_{syn} η^3 -C₄H₇), 2.41 (s, 3H, CH₃ C₆H₄-4-Me), 2.30 (m, 1H, H_{syn} η^3 -C₄H₇), 1.35 (s_{br}, 4H, CH₃ and H_{anti} η^3 -C₄H₇), 1.11 (s, 1H, H_{anti} η^3 -C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.1, 226.8 (CO), 162.5 (N=CH), 153.6, 152.3, 148.7, 139.9, 138.8, 130.4, 129.3, 127.5, 122.4 (py-2-CH=N-C₆H₅), 83.8 (C₂ η^3 -C₄H₇), 54.2, 52.7 (C₁ and C₃ η^3 -C₄H₇), 23.2 (CH₃ C₆H₄-4-Me), 19.3 (CH₃ η^3 -C₄H₇). Anal. Calcd. for C₁₉H₁₉ClMoN₂O₂: C 52.01, H 4.36, N 6.38. Found: C 51.98, H 4.32, N 6.18.

Synthesis of [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-C₆H₃-3,5-Me₂)] (1c). Compound **1c** was prepared as described above for compound **1a**, starting from [MoCl(η^3 -C₄H₇)(CO)₂(NCMe)₂] (100 mg, 0.308 mmol), pyridine-2-carboxaldehyde (29 μ L, 0.308 mmol) and 3,5-dimethylaniline (38 μ L, 0.308 mmol). Compound **1c** was obtained as a violet solid. Yield: 125 mg (90 %). IR (CH₂Cl₂, cm⁻¹): 1951, 1875 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.77 (m, 1H, py), 8.41 (s, 1H, N=CH), 7.97 (m, 1H, py), 7.86 (m, 1H, py), 7.52 (m, 1H, py), 7.09 (s, 2H, C₆H₃), 7.06 (s,

¹ H. tom Dieck, H. Friedel, *J. Organomet. Chem.* **1968**, *14*, 375-385.

1H, C₆H₅), 2.78 (m, 1H, H_{syn} η³-C₄H₇), 2.38 (s, 6H, CH₃ C₆H₃-3,5-Me₂), 2.32 (m, 1H, H_{syn} η³-C₄H₇), 1.35 (s_{br}, 4H, CH₃ and H_{anti} η³-C₄H₇), 1.11 (s, 1H, H_{anti} η³-C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.2, 227.0 (CO), 162.7 (N=CH), 153.6, 152.3, 151.0, 139.9, 138.8, 131.0, 129.4, 127.5, 120.3 (py-2-CH=N-C₆H₅), 83.8 (C₂ η³-C₄H₇), 54.1, 52.6 (C₁ and C₃ η³-C₄H₇), 21.6 (2×CH₃ C₆H₃-3,5-Me₂), 19.4 (CH₃ η³-C₄H₇). Anal. Calcd. for C₂₀H₂₁ClMoN₂O₂: C 53.05, H 4.67, N 6.19. Found: C 51.25, H 5.02, N 5.76.

Synthesis of [MoCl(η³-C₄H₇)(CO)₂(py-2-CH=N-*i*Pr)] (1d). Compound **1d** was prepared as described above for compound **1a**, starting from [MoCl(η³-C₄H₇)(CO)₂(NCMe)₂] (100 mg, 0.308 mmol), pyridine-2-carboxaldehyde (29 μL, 0.308 mmol) and isopropylamine (26 μL, 0.308 mmol). Compound **1d** was obtained as a violet solid. Yield: 114 mg (95 %). IR (CH₂Cl₂, cm⁻¹): 1951, 1868 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.70 (m, 1H, py), 8.45 (s, 1H, N=CH), 7.97 (m, 1H, py), 7.78 (m, 1H, py), 7.50 (m, 1H, py), 4.42 (m, 1H, CH *i*Pr), 2.95 (m, 1H, H_{syn} η³-C₄H₇), 2.77 (m, 1H, H_{syn} η³-C₄H₇), 1.45 (d (J= 1.5), 6H, CH₃ *i*Pr), 1.35 (s_{br}, 4H, CH₃ and H_{anti} η³-C₄H₇), 1.29 (s, 1H, H_{anti} η³-C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 226.8 (2×CO), 161.4 (N=CH), 153.8, 151.6, 138.5, 128.3, 127.0 (py-2-CH=N-*i*Pr), 83.1 (C₂ η³-C₄H₇), 61.0 (CH *i*Pr), 24.8, 22.6 (CH₃ *i*Pr), 19.3 (CH₃ η³-C₄H₇). The signals of C₁ and C₃ of the methallyl ligand are overlapped with the solvent residual peak. Anal. Calcd. for C₁₅H₁₉ClMoN₂O₂: C 46.11, H 4.90, N 7.17. Found: C 46.42, H 5.13, N 6.95.

Synthesis of [MoCl(η³-C₄H₇)(CO)₂(py-2-CH=N-*t*Bu)] (1e). Compound **1e** was prepared as described above for compound **1a**, starting from [MoCl(η³-C₄H₇)(CO)₂(NCMe)₂] (100 mg, 0.308 mmol), pyridine-2-carboxaldehyde (29 μL, 0.308 mmol) and tertbutylamine (32 μL, 0.308 mmol). Compound **1e** was obtained as a dark blue solid. Yield: 161 mg (87 %). IR (CH₂Cl₂, cm⁻¹): 1949, 1864 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.76 (m, 1H, py), 8.54 (s, 1H, N=CH), 8.01 (m, 1H, py), 7.81 (m, 1H, py), 7.54 (m, 1H, py), 3.13 (m, 1H, H_{syn} η³-C₄H₇), 2.77 (s_{br}, 1H, H_{syn} η³-C₄H₇), 1.59 (s, 9H, *t*Bu), 1.34 (s, 3H, CH₃ η³-C₄H₇), 1.31 (s, 1H, H_{anti} η³-C₄H₇), 1.27 (s, 1H, H_{anti} η³-C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 228.3, 227.1 (CO), 163.9 (N=CH), 154.1, 151.6, 138.6, 128.8, 127.2 (py), 83.4 (C₂ η³-C₄H₇), 70.8 (*t*Bu), 64.0 (C₁ or C₃ η³-C₄H₇), 32.5 (CH₃ *t*Bu), 19.1 (CH₃ η³-C₄H₇). The signal of C₁ or C₃ of the methallyl ligand is overlapped with the solvent residual peak. Anal. Calcd. for C₁₆H₂₁ClMoN₂O₂: C 47.48, H 5.23, N 6.92. Found: C 47.49, H 4.99, N 6.83.

Synthesis of [Mo(η³-C₄H₇)(CO)₂(*N*-MeIm)(py-2-CH=N-C₆H₅)]OTf (2a). To a solution of [MoCl(η³-C₄H₇)(CO)₂(py-2-CH=N-C₆H₅)] (**1a**) (118 mg, 0.278 mmol) in CH₂Cl₂ (20 mL), AgOTf (86 mg, 0.335 mmol) and MeCN (3 mL) were added and the mixture was stirred in the dark for 1 h. The resulting slurry was filtered off the white solid (AgCl) and the solvent was evaporated to dryness. The dark red residue was redissolved in CH₂Cl₂ (20 mL), *N*-MeIm (22 μL, 0.278 mmol) was added and the reaction mixture was allowed to stir for 1h. The solvent was concentrated under reduced pressure to a volume of 7-10 mL and addition of hexane (15 mL) caused the precipitation of a purple solid, which was washed with hexane (2 × 20 mL) and dried under vacuum. Yield: 147 mg (85 %). IR (CH₂Cl₂, cm⁻¹): 1949, 1869 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.08 (s, 1H, N=CH), 8.78 (m, 1H, py), 8.44 (m, 1H, py), 8.17 (m, 1H, py), 7.63 (m, 1H, py), 7.50 (m, 4H, NCHN *N*-MeIm and C₆H₅), 7.33 (m, 2H, C₆H₅), 7.22 (s_{br}, 1H, CH *N*-MeIm), 6.98 (s_{br}, 1H, CH *N*-MeIm), 3.69 (s, 3H, CH₃ *N*-MeIm), 3.05 (m, 1H, H_{syn} η³-C₄H₇), 2.58 (m, 1H, H_{syn} η³-C₄H₇), 1.59 (s, 1H, H_{anti} η³-C₄H₇), 1.35 (s_{br}, 4H, CH₃ and H_{anti} η³-C₄H₇).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 225.7, 225.6 (CO), 167.1 (N=CH), 153.7, 152.5, 149.7, 140.7, 140.0, 132.3, 130.9, 130.5, 130.3, 129.1, 122.9, 122.8 (py-2-CH=N-C₆H₅), 86.2 (C₂ η^3 -C₄H₇), 58.0, 56.3 (C₁ and C₃ η^3 -C₄H₇), 35.2 (CH₃ *N*-MeIm), 19.4 (CH₃ η^3 -C₄H₇). Anal. Calcd. for C₂₃H₂₃F₃MoN₄O₅S: C 44.52, H 3.74, N 9.03. Found: C 44.91, H 3.79, N 8.72.

Synthesis of [Mo(η^3 -C₄H₇)(CO)₂(*N*-MeIm)(py-2-CH=N-C₆H₄-4-Me)]OTf (2b). Compound **2b** was prepared following the procedure described for the synthesis of **2a**, starting from [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-C₆H₄-4-Me)] (**1b**) (50 mg, 0.114 mmol), AgOTf (35 mg, 0.136 mmol) and *N*-MeIm (10 μL , 0.125 mmol). Compound **2b** was obtained as a dark red microcrystalline solid. Yield: 63 mg (87 %). IR(CH_2Cl_2 , cm^{-1}): 1951, 1869 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.05 (s, 1H, N=CH), 8.77 (m, 1H, py), 8.41 (m, 1H, py), 8.16 (m, 1H, py), 7.61 (m, 1H, py), 7.43 (s, 1H, NCHN), 7.31 (d ($J=8.4$), 2H, C₆H₄), 7.25 (d ($J=8.4$), 2H, C₆H₄), 7.10 (s_{br}, 1H, CH *N*-MeIm), 6.97 (s_{br}, 1H, CH *N*-MeIm), 3.65 (s, 3H, CH₃ *N*-MeIm), 3.05 (m, 1H, H_{syn} η^3 -C₄H₇), 2.59 (m, 1H, H_{syn} η^3 -C₄H₇), 2.42 (s, CH₃ C₆H₄-4-Me), 1.59 (s, 1H, H_{anti} η^3 -C₄H₇), 1.34 (s_{br}, 4H, CH₃ and H_{anti} η^3 -C₄H₇). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 226.0, 225.8 (CO), 166.1 (N=CH), 153.8, 152.4, 147.3, 141.1, 140.6, 139.9, 132.0, 130.9, 128.9, 122.9, 122.7 (py-2-CH=N-C₆H₄-4-Me and *N*-MeIm), 86.1 (C₂ η^3 -C₄H₇), 58.1, 56.3 (C₁ and C₃ η^3 -C₄H₇), 35.2 (CH₃ *N*-MeIm), 21.4 (CH₃ C₆H₄-4-Me), 18.9 (CH₃ η^3 -C₄H₇). Anal. Calcd. for C₂₄H₂₅F₃MoN₄O₅S: C 45.43, H 3.97, N 8.83. Found: C 45.91, H 4.06, N 8.96.

Synthesis of [Mo(η^3 -C₄H₇)(CO)₂(*N*-MeIm)(py-2-CH=N-C₆H₃-3,5-Me₂)]OTf (2c). Compound **2c** was prepared as described above for **2a**, starting from [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-C₆H₃-3,5-Me₂)] (**1c**) (125 mg, 0.276 mmol), AgOTf (85 mg, 0.331 mmol) and *N*-MeIm (22 μL , 0.276 mmol). Slow diffusion of hexane (30 mL) into a concentrated solution of compound **2c** in CH_2Cl_2 (10 mL) afforded dark red crystals, one of which was employed for an X-ray structure determination. Yield: 166 mg (93 %). IR (CH_2Cl_2 , cm^{-1}): 1951, 1869 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.03 (s, 1H, N=CH), 8.76 (m, 1H, py), 8.41 (m, 1H, py), 8.16 (m, 1H, py), 7.61 (m, 1H, py), 7.42 (s, 1H, NCHN), 7.12 (s_{br}, 2H, CH *N*-MeIm and C₆H₃), 6.97 (m, 3H, CH *N*-MeIm and C₆H₃), 3.65 (s, 3H, CH₃ *N*-MeIm), 3.04 (m, 1H, H_{syn} η^3 -C₄H₇), 2.59 (m, 1H, H_{syn} η^3 -C₄H₇), 2.38 (s_{br}, 6H, CH₃ C₆H₃-3,5-Me₂), 1.60 (s, 1H, H_{anti} η^3 -C₄H₇), 1.34 (s_{br}, 4H, CH₃ and H_{anti} η^3 -C₄H₇). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 225.9, 225.8 (CO), 165.9 (N=CH), 153.5, 152.2, 149.4, 140.5, 140.3, 131.9, 131.8, 130.7, 128.7, 122.7, 120.5, 120.4 (py-2-CH=N-C₆H₄-4-Me and *N*-MeIm), 85.9 (C₂ η^3 -C₄H₇), 57.9, 56.2 (C₁ and C₃ η^3 -C₄H₇), 35.0 (CH₃ *N*-MeIm), 21.4 (2 \times CH₃ C₆H₃-3,5-Me₂), 18.7 (CH₃ η^3 -C₄H₇). Anal. Calcd. for C₂₅H₂₇F₃MoN₄O₅S: C 46.30, H 4.20, N 8.64. Found: C 46.67, H 3.99, N 8.80.

Synthesis of [Mo(η^3 -C₄H₇)(CO)₂(*N*-MeIm)(py-2-CH=N-*i*Pr)]OTf (2d). Compound **2d** was prepared following the procedure described for the synthesis of **2a**, starting from [MoCl(η^3 -C₄H₇)(CO)₂(py-2-CH=N-*i*Pr)] (**1d**) (50 mg, 0.128 mmol), AgOTf (36 mg, 0.141 mmol) and *N*-MeIm (10 μL , 0.128 mmol). Compound **2d** was obtained as a red microcrystalline solid. Yield: 74 mg (98 %). IR (CH_2Cl_2 , cm^{-1}): 1951, 1868 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.00 (s, 1H, N=CH), 8.67 (m, 1H, py), 8.38 (m, 1H, py), 8.22 (m, 1H, py), 7.62 (m, 1H, py), 7.13 (s_{br}, 2H, *N*-MeIm), 6.99 (s_{br}, 1H, *N*-MeIm), 4.36 (m, 1H, CH *i*Pr), 3.67 (s, 3H, CH₃ *N*-MeIm), 3.23 (m, 1H, H_{syn} η^3 -C₄H₇), 2.97 (m, 1H, H_{syn} η^3 -C₄H₇), 1.58 (s, 1H, H_{anti} η^3 -C₄H₇), 1.53 (s, 1H, H_{anti} η^3 -C₄H₇), 1.48 (d ($J=6.5$), 3H, CH₃ *i*Pr), 1.27 (s, 3H, CH₃ η^3 -C₄H₇), 1.02 (d ($J=6.5$), 3H, CH₃ *i*Pr). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 225.9, 225.7 (CO), 165.6 (N=CH), 154.0, 151.8, 139.8, 131.6, 131.1 (py-2-CH=N-

*t*Bu), 140.3, 128.3, 122.2 (*N*-MeIm), 85.5 ($C_2 \eta^3\text{-C}_4\text{H}_7$), 61.8, 55.45 (C_1 and $C_3 \eta^3\text{-C}_4\text{H}_7$), 57.4 (CH *i*Pr), 34.9 (CH₃ *N*-MeIm), 23.4, 21.8 (CH₃ *i*Pr), 18.7 (CH₃ $\eta^3\text{-C}_4\text{H}_7$). The signal of C_1 or C_3 of the methallyl ligand is overlapped with the solvent residual peak. Anal. Calcd. for C₂₀H₂₅F₃MoN₄O₅S: C 40.96, H 4.30, N 9.55. Found: C 41.33, H 4.15, N 9.51.

Synthesis of [Mo($\eta^3\text{-C}_4\text{H}_7$)(CO)₂(*N*-MeIm)(py-2-CH=N-*t*Bu)]OTf (2e). Compound **2e** was prepared following the procedure described for the synthesis of **2a**, starting from [MoCl($\eta^3\text{-C}_4\text{H}_7$)(CO)₂(py-2-CH=N-*t*Bu)] (**1e**) (50 mg, 0.124 mmol), AgOTf (35 mg, 0.136 mmol) and *N*-MeIm (10 μ L, 0.125 mmol). Compound **2e** was obtained as a dark red microcrystalline solid. Yield: 64 mg (87 %). IR (CH₂Cl₂, cm⁻¹): 1947, 1864 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.97 (s, 1H, N=CH), 8.67 (m, 1H, py), 8.38 (m, 1H, py), 8.22 (m, 1H, py), 7.64 (m, 1H, py), 7.22 (s, 1H, NCHN), 6.98 (s_{br}, 1H, CH *N*-MeIm), 6.91 (s_{br}, 1H, CH *N*-MeIm), 3.68 (s, 3H, CH₃ *N*-MeIm), 3.42 (m, 1H, H_{syn} $\eta^3\text{-C}_4\text{H}_7$), 2.94 (m, 1H, H_{syn} $\eta^3\text{-C}_4\text{H}_7$), 1.62 (s, 1H, H_{anti} $\eta^3\text{-C}_4\text{H}_7$), 1.42 (s, 1H, H_{anti} $\eta^3\text{-C}_4\text{H}_7$), 1.38 (s, 9H, CH₃ *t*Bu), 1.23 (s, 3H, CH₃ $\eta^3\text{-C}_4\text{H}_7$). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.1, 226.2 (CO), 166.8 (N=CH), 154.5, 151.7, 140.6, 140.3, 131.8, 131.1, 128.6, 122.4 (py-2-CH=N-*t*Bu and *N*-MeIm), 86.5 ($C_2 \eta^3\text{-C}_4\text{H}_7$), 64.9 (*t*Bu), 58.7, 56.2 (C_1 and $C_3 \eta^3\text{-C}_4\text{H}_7$), 34.9 (CH₃ *N*-MeIm), 31.9 (CH₃ *t*Bu), 18.6 (CH₃ $\eta^3\text{-C}_4\text{H}_7$). Anal. Calcd. for C₂₁H₂₇F₃MoN₄O₅S: C 42.00, H 4.53, N 9.33. Found: C 41.81, H 4.87, N 9.02.

Reaction of [Mo($\eta^3\text{-C}_4\text{H}_7$)(CO)₂(*N*-MeIm)(py-2-CH=N-C₆H₅)]OTf (2a) with KN(SiMe₃)₂ followed by addition of HOTf. Synthesis of 4a. KN(SiMe₃)₂ (0.19 mL of a 0.5 M solution in toluene, 0.097 mmol) was added to a solution of compound **2a** (50 mg, 0.081 mmol) in THF (20 mL) cooled to -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 40 min. The solvent was evaporated to dryness, the residue extracted with CH₂Cl₂ (20 mL) and HOTf (9 μ L, 0.097 mmol) was added. After 15 min. stirring at room temperature the reaction mixture was filtered via canula, the solvent evaporated under reduced pressure and the resulting red solid was washed with hexane (2 \times 20 mL) and dried under vacuum. Yield: 31 mg (62 %). IR (KBr, cm⁻¹): 3464 (ν_{NH}), 1945, 1855 (ν_{CO}). IR (CH₂Cl₂, cm⁻¹): 1950, 1860 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.65 (m, 1H, py), 8.048(m, 1H, py), 7.66 (m, 1H, py), 7.54 (m, 1H, py), 7.27 (m, 3H, C₆H₅), 7.21 (s_{br}, 1H, CH *N*-MeIm), 6.97 (m, 2H, C₆H₅), 6.94 (s_{br}, 1H, CH *N*-MeIm), 5.70 (s, 1H, Csp³H), 3.81 (s, 3H, CH₃ *N*-MeIm), 3.53 (m, 1H, H_{syn} $\eta^3\text{-C}_4\text{H}_7$), 2.73 (m, 1H, H_{syn} $\eta^3\text{-C}_4\text{H}_7$), 1.98 (s, 3H, CH₃ $\eta^3\text{-C}_4\text{H}_7$), 1.52 (s_{br}, 1H, H_{anti} $\eta^3\text{-C}_4\text{H}_7$), 1.31 (s_{br}, 1H, H_{anti} $\eta^3\text{-C}_4\text{H}_7$). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.6, 226.7 (CO), 156.6, 146.8, 144.5, 142.2, 130.1, 129.9, 127.8, 127.6, 126.2, 123.4, 122.7 (py-2-CH=N-C₆H₅), 84.4 ($C_2 \eta^3\text{-C}_4\text{H}_7$), 64.2 (Csp³), 58.1 (C_1 or $C_3 \eta^3\text{-C}_4\text{H}_7$), 34.8 (CH₃ *N*-MeIm), 20.6 (CH₃ $\eta^3\text{-C}_4\text{H}_7$). The signal of C_1 or C_3 of the methallyl ligand is overlapped with the solvent residual peak. Anal. Calcd. for C₂₃H₂₃F₃MoN₄O₅S: C 44.52, H 3.74, N 9.03. Found: C 44.37, H 4.02, N 8.82.

Reaction of [Mo($\eta^3\text{-C}_4\text{H}_7$)(CO)₂(*N*-MeIm)(py-2-CH=N-C₆H₄-4-Me)]OTf (2b) with KN(SiMe₃)₂. Synthesis of 3b. KN(SiMe₃)₂ (0.15 mL of a 0.5 M solution in toluene, 0.076 mmol) was added to a solution of compound **2b** (40 mg, 0.063 mmol) in THF (15 mL), previously cooled to -78 °C. The color of the solution changed immediately from dark red to orange and the solvent was evaporated to dryness under reduced pressure. The residue was extracted with CH₂Cl₂ (20 mL), filtered via canula and the resulting solution was concentrated to a volume of 5 mL. Addition of hexane (15 mL) caused the precipitation of a dark yellow solid that was washed with hexane (2 \times 15 mL). Yield: 19 mg (63 %). IR (CH₂Cl₂, cm⁻¹): 1929,

1833 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.57 (m, 1H, py), 7.77 (m, 1H, py), 7.53 (m, 1H, py), 7.17 (m, 1H, py), 6.95 (m, 5H, C_6H_4 and CH N -MeIm), 6.71 (s_{br} , 1H, CH N -MeIm), 5.72 (s, 1H, Csp^3H), 3.71 (s, 3H, CH_3 N -MeIm), 3.31 (m, 2H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.20 (s, CH_3 C_6H_4 -4-Me), 1.90 (s, 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$) 1.24 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$), 1.08 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$).

Reaction of 3b with HOTf. Synthesis of 4b. HOTf (8 μL , 0.091 mmol) was added to a solution of compound **3b** (0.040 g, 0.083 mmol) in CH_2Cl_2 , and the reaction mixture was stirred for 15 min at room temperature. The solvent was evaporated to a volume of 5 mL and addition of hexane caused the precipitation of a red solid which was washed with hexane (2×15 mL). Slow diffusion of hexane (15 mL) into a concentrated solution of **4b** in CH_2Cl_2 (5 mL) afforded red crystals, one of which was employed for an X-ray structure determination. Yield: 36 mg (69 %). IR (KBr, cm^{-1}): 3456 (ν_{NH}), 1947, 1858 (ν_{CO}). IR (CH_2Cl_2 , cm^{-1}): 1949, 1860 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.66 (m, 1H, py), 8.03 (m, 1H, py), 7.71 (m, 1H, py), 7.57 (m, 1H, py), 7.20 (s, 1H, CH N -MeIm), 7.05 (d ($J=8.2$), 2H, C_6H_4), 6.93 (s, 1H, CH N -MeIm), 6.87 (d ($J=8.2$), 2H, C_6H_4), 5.64 (s, 1H, Csp^3H), 3.81 (s, 3H, CH_3 N -MeIm), 3.53 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.71 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.31 (s, CH_3 C_6H_4 -4-Me), 1.98 (s, 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$), 1.52 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$), 1.31 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 227.7, 226.9 (CO), 156.7, 146.9, 142.1, 141.8, 137.7, 130.6, 130.3, 127.8, 126.2, 124.2, 123.4, 122.7 (py-2-CH=N- C_6H_4 -4-Me and N -MeIm), 85.5 ($\text{C}_2 \eta^3\text{-C}_4\text{H}_7$), 64.5 (Csp^3), 58.0 (C_1 or $\text{C}_3 \eta^3\text{-C}_4\text{H}_7$), 34.8 (CH_3 N -MeIm), 20.8, 20.6 (CH_3 C_6H_4 -4-Me and $\eta^3\text{-C}_4\text{H}_7$). The signal of C_1 or C_3 of the methallyl ligand is overlapped with the solvent residual peak. Anal. Calcd. for $\text{C}_{24}\text{H}_{25}\text{F}_3\text{MoN}_4\text{O}_5\text{S}$: C 45.43, H 3.97, N 8.83. Found: C 45.76, H 4.10, N 9.05.

Reaction of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(N\text{-MeIm})(\text{py-2-CH=N- C}_6\text{H}_3\text{-3,5-Me}_2)]\text{OTf}$ (2c) with $\text{KN}(\text{SiMe}_3)_2$. Synthesis of 3c. $\text{KN}(\text{SiMe}_3)_2$ (0.15 mL of a 0.5 M solution in toluene, 0.076 mmol) was added to a solution of compound **2b** (40 mg, 0.063 mmol) in THF (15 mL), previously cooled to -78 $^\circ\text{C}$. The color of the solution changed immediately from dark red to orange and the solvent was evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 (20 mL), filtered via canula and the resulting solution was concentrated to a volume of 5 mL. Addition of hexane (15 mL) caused the precipitation of a dark yellow solid that was washed with hexane (2×15 mL). Yield: 19 mg (63 %). IR (CH_2Cl_2 , cm^{-1}): 1929, 1833 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.58 (m, 1H, py), 7.69 (m, 1H, py), 7.53 (m, 1H, py), 7.17 (m, 1H, py), 7.04 (s, 1H, CH N -MeIm), 6.77 (s, 2H, C_6H_3), 6.71 (s, 1H, C_6H_3), 6.19 (s, 1H, CH N -MeIm), 5.76 (s, 1H, Csp^3H), 3.72 (s, 3H, CH_3 N -MeIm), 3.31 (m, 2H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.21 (s, 6H, CH_3 C_6H_4 -3,5-Me $_2$), 1.90 (s, 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$) 1.24 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$), 1.08 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$).

Reaction of 3c with HOTf. Synthesis of 4c. Compound **4c** was prepared as described above for **4b** starting from **3c** (38 mg, 0.077 mmol) and HOTf (8 μL , 0.093 mmol). Slow diffusion of hexane (25 mL) into a concentrated solution of **4c** in THF (10 mL) at 5°C afforded dark orange crystals, one of which was used for an X-ray structure determination. Yield: 45 mg (90 %). IR (KBr, cm^{-1}): 3490 (ν_{NH}), 1945, 1857 (ν_{CO}). IR (CH_2Cl_2 , cm^{-1}): 1946, 1860 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.63 (m, 1H, py), 8.03 (m, 1H, py), 7.67 (m, 1H, py), 7.57 (m, 1H, py), 7.16 (s_{br} , 1H, CH N -MeIm), 6.90 (s_{br} , 1H, CH N -MeIm), 6.86 (m, 1H, CH C_6H_3), 6.53 (s_{br} , 2H, C_6H_3), 5.59 (s_{br} , 1H, $\text{C}_{\text{sp}^3}\text{H}$), 3.78 (s, 3H, CH_3 N -MeIm), 3.49 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.67 (m, 1H, $\text{H}_{\text{syn}} \eta^3\text{-C}_4\text{H}_7$), 2.17 (s_{br} , 6H, CH_3 C_6H_3 -3,5-Me $_2$), 1.94 (s_{br} , 3H, $\text{CH}_3 \eta^3\text{-C}_4\text{H}_7$), 1.78 (s, 1H, $\text{H}_{\text{anti}} \eta^3\text{-C}_4\text{H}_7$).

C₄H₇), 1.48 (s, 1H, H_{anti} η³-C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 227.9, 227.1 (CO), 157.0, 147.2, 144.3, 142.2, 140.3, 140.0, 129.4, 128.0, 126.3, 121.0 (py-2-CH=N-C₆H₃-3,5-Me₂ and N-MeIm), 84.6 (C₂ η³-C₄H₇), 64.7, 58.1 (C₁ and C₃ η³-C₄H₇), 63.3 (C_{sp}³H), 35.0 (CH₃ N-MeIm), 21.5 (2×CH₃ C₆H₃-3,5-Me₂), 20.8 (CH₃ η³-C₄H₇). Anal. Calcd. for C₂₅H₂₇F₃MoN₄O₅S: C 46.30, H 4.20, N 8.64. Found: C 46.12, H 3.95, N 8.40.

Reaction of [Mo(η³-C₄H₇)(CO)₂(N-MeIm)(py-2-CH=N-*i*Pr)OTf (2d) with KN(SiMe₃)₂ followed by addition of HOTf. Synthesis of 4d. KN(SiMe₃)₂ (0.200 mL of a 0.5 M solution in toluene, 0.100 mmol) was added to a solution of compound **2d** (50 mg, 0.085 mmol) in THF (20 mL) cooled to -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 40 min. The solvent was evaporated to dryness, the residue extracted with CH₂Cl₂ (20 mL) and HOTf (9 μL, 0.101 mmol) was added. After 15 min. stirring at room temperature the reaction mixture was filtered via canula, the solvent evaporated under reduced pressure and the resulting yellow solid was washed with hexane (2 × 20 mL) and dried under vacuum. Yield: 31 mg (62 %). IR (KBr, cm⁻¹): 3475 (ν_{NH}), 1947, 1855 (ν_{CO}). IR (CH₂Cl₂, cm⁻¹): 1949, 1860 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.25 (m, 1H, py), 7.99 (m, 1H, py), 7.76 (m, 1H, py), 7.54 (m, 1H, py), 7.13 (s_{br}, 1H, CH N-MeIm), 6.89 (s_{br}, 1H, CH N-MeIm), 5.65 (s, 1H, C_{sp}³H), 4.60 (s_{br}, 1H, NH), 3.83 (s, 3H, CH₃ N-MeIm), 3.47 (m, 1H, H_{syn} η³-C₄H₇), 3.39 (m, 1H, H_{syn} η³-C₄H₇), 3.04 (m, 1H, CH *i*Pr), 1.84 (s, 3H, CH₃ η³-C₄H₇), 1.45 (s_{br}, 1H, H_{anti} η³-C₄H₇), 1.43 (s_{br}, 1H, H_{anti} η³-C₄H₇), 1.39 (m, 6H, CH₃ *i*Pr). ¹³C{¹H} NMR (CD₂Cl₂): δ 228.0, 226.8 (CO), 156.6, 154.0, 146.7, 141.6, 127.1, 125.4, 124.1, 123.2 (py-2-CH=N- *i*Pr), 83.7 (C₂ η³-C₄H₇), 59.6 (C_{sp}³), 58.8, 56.1 (C₁ and C₃ η³-C₄H₇), 34.8 (CH₃ N-MeIm), 22.9, 21.8 (CH₃ *i*Pr), 19.3 (CH₃ η³-C₄H₇). The signal of the isopropyl CH group is overlapped with the solvent residual peak. Anal. Calcd. for C₂₀H₂₅F₃MoN₄O₅S: C 40.96, H 4.30, N 9.55. Found: C 41.17, H 4.46, N 9.92.

Reaction of [Mo(η³-C₄H₇)(CO)₂(N-MeIm)(py-2-CH=N-*t*Bu)OTf(2e) with KN(SiMe₃)₂ followed by addition of HOTf. Synthesis of 4e. KN(SiMe₃)₂ (0.200 mL of a 0.5 M solution in toluene, 0.100 mmol) was added to a solution of compound **2e** (50 mg, 0.083 mmol) in THF (20 mL) cooled to -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 40 min. The solvent was evaporated to dryness, the residue extracted with CH₂Cl₂ (20 mL) and HOTf (9 μL, 0.101 mmol) was added. After 15 min. stirring at room temperature the reaction mixture was filtered via canula, the solvent evaporated under reduced pressure and the resulting yellow solid was washed with hexane (2 × 20 mL) and dried under vacuum. Yield: 31 mg (62 %). IR (KBr, cm⁻¹): 3451 (ν_{NH}), 1945, 1856 (ν_{CO}). IR (CH₂Cl₂, cm⁻¹): 1950, 1861 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.07 (m, 1H, py), 7.97 (m, 1H, py), 7.81 (m, 1H, py), 7.50 (m, 1H, py), 7.16 (s, 1H, CH N-MeIm), 6.90 (s, 1H, CH N-MeIm), 5.71 (s, 1H, C_{sp}³H), 4.56 (s_{br}, 1H, NH), 3.83 (s, 3H, CH₃ N-MeIm), 3.50 (m, 1H, H_{syn} η³-C₄H₇), 3.45 (m, 1H, H_{syn} η³-C₄H₇), 1.80 (s, 3H, CH₃ η³-C₄H₇), 1.44 (s_{br}, 1H, H_{anti} η³-C₄H₇), 1.35 (s_{br}, 10H, *t*Bu and H_{anti} η³-C₄H₇). ¹³C{¹H} NMR (CD₂Cl₂): δ 222.7, 226.9 (CO), 156.0, 152.9, 146.9, 141.7, 127.3, 125.5, 124.1, 123.4 (py-2-CH=N-*t*Bu), 83.1 (C₂ η³-C₄H₇), 60.0, 56.1 (C₁ and C₃ η³-C₄H₇), 57.7 (C_{sp}³), 35.0 (CH₃ N-MeIm), 29.6 (CH₃ *t*Bu), 19.1 (CH₃ η³-C₄H₇). Anal. Calcd. for C₂₁H₂₇F₃MoN₄O₅S: C 42.00, H 4.53, N 9.33. Found: C 42.11, H 4.69, N 8.97.

Synthesis of *N*-ethylimidazole (*N*-EtIm). *N*-EtIm was prepared in a similar way than previously described in the literature.² NaOEt (30 mL of a freshly prepared 1.08 M solution of NaOEt in EtOH, 32.3 mmol) was added to a solution of imidazole (2 g, 29.4 mmol) in dry EtOH (15 mL). 1-bromoethane (2.4 mL, 32.3 mmol) was dropwise added and the mixture was heated at 50 °C for 4 h. The solution was concentrated under reduced pressure to a volume of 10 mL, filtered off the white solid and evaporated to dryness. The oily residue was distilled under reduced pressure to afford the *N*-EtIm as a light yellow oil. ¹H NMR (CDCl₃): δ 7.70, 7.10, 6.96 (s, 1H each, CH), 4.04 (q (*J*= 7.4), 2H, CH₂ Et), 1.48 (t (*J*= 7.4), 3H, CH₃ Et). ¹³C {¹H} NMR (CDCl₃): δ 134.5, 126.6, 116.6 (CH), 40.1 (CH₂ Et), 14.4 (CH₃ Et).

Synthesis of [Mo(η³-C₄H₇)(CO)₂(*N*-EtIm)(py-2-CH=N-*i*Pr)]OTf (2f**).** This compound was prepared following the procedure described for the synthesis of **2d**, starting from [MoCl(η³-C₄H₇)(CO)₂(py-2-CH=N-*i*Pr)] (**1d**) (100 mg, 0.256 mmol), AgOTf (72 mg, 0.282 mmol) and *N*-MeIm (25 μL, 0.282 mmol). [Mo(η³-C₄H₇)(CO)₂(*N*-EtIm)(py-2-CH=N-*i*Pr)]OTf was obtained as a red microcrystalline solid. Yield: 140 mg (91 %). IR (CH₂Cl₂, cm⁻¹): 1951, 1867 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.01 (s, 1H, N=CH), 8.68 (m, 1H, py), 8.39 (m, 1H, py), 8.21 (m, 1H, py), 7.62 (m, 1H, py), 6.99 (s, 1H, *N*-EtIm), 7.04 (s_{br}, 2H, *N*-EtIm), 4.35 (m, 1H, CH *i*Pr), 3.99 (m, 2H, CH₂ *N*-EtIm), 3.22 (m, 1H, H_{syn} η³-C₄H₇), 2.97 (m, 1H, H_{syn} η³-C₄H₇), 1.58 (s, 1H, H_{anti} η³-C₄H₇), 1.52 (s, 1H, H_{anti} η³-C₄H₇), 1.48 (d (*J*= 6.5), 3H, CH₃ *i*Pr), 1.35 (t (*J*= 7.3), 3H, CH₃ *N*-EtIm), 1.26 (s, 3H, CH₃ η³-C₄H₇), 0.99 (d (*J*= 6.5), 3H, CH₃ *i*Pr). ¹³C {¹H} NMR (CD₂Cl₂): δ 225.5, 225.3 (CO), 166.3 (N=CH), 153.4, 151.4, 140.0, 138.6, 130.9, 130.7, 128.0, 120.0 (py-2-CH=N-*i*Bu and *N*-EtIm), 85.1 (C₂ η³-C₄H₇), 57.0 (Csp³), 61.4, 55.0 (C₁ and C₃ η³-C₄H₇), 43.1 (CH₂ *N*-EtIm), 22.9, 21.4 (CH₃ *i*Pr), 18.3, 15.7 (CH₃ η³-C₄H₇ and *N*-EtIm). The signal of the isopropyl CH group is overlapped with the solvent residual peak.

Reaction of [Mo(η³-C₄H₇)(CO)₂(*N*-EtIm)(py-2-CH=N-*i*Pr)]OTf with KN(SiMe₃)₂ followed by addition of HOTf. Synthesis of **4f.** KN(SiMe₃)₂ (0.17 mL of a 0.7 M solution in toluene, 0.121 mmol) was added to a solution of compound [Mo(η³-C₄H₇)(CO)₂(*N*-EtIm)(py-2-CH=N-*i*Pr)]OTf (66 mg, 0.110 mmol) in THF (20 mL) cooled to -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 40 min. The solvent was evaporated to dryness, the residue extracted with CH₂Cl₂ (20 mL) and HOTf (11 μL, 0.121 mmol) was added. After 15 min. stirring at room temperature the reaction mixture was filtered via canula, the solvent evaporated under reduced pressure and the resulting yellow solid was washed with hexane (2 × 20 mL) and dried under vacuum. Yield: 40 mg (61 %). IR (KBr, cm⁻¹): 3482 (ν_{NH}), 1942, 1851 (ν_{CO}). IR (CH₂Cl₂, cm⁻¹): 1949, 1860 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 9.26 (m, 1H, py), 8.02 (m, 1H, py), 7.79 (m, 1H, py), 7.56 (m, 1H, py), 7.16 (s_{br}, 1H, CH *N*-MeIm), 6.96 (s_{br}, 1H, CH *N*-MeIm), 5.68 (s, 1H, Csp³H), 4.54 (s_{br}, 1H, NH), 4.23 (m, 2H, CH₂ *N*-EtIm), 3.47 (m, 1H, H_{syn} η³-C₄H₇), 3.38 (m, 1H, H_{syn} η³-C₄H₇), 3.05 (m, 1H, CH *i*Pr), 1.84 (s, 3H, CH₃ η³-C₄H₇), 1.37 (m, 11H, 2H_{anti} η³-C₄H₇, 2CH₃ *i*Pr, CH₃ *N*-EtIm).

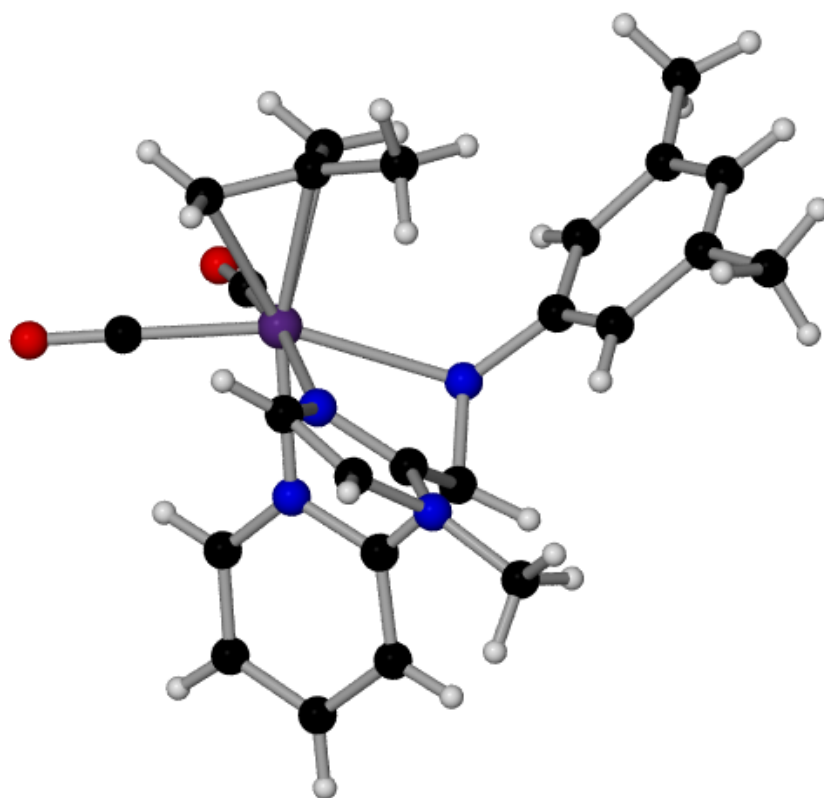
Cross-over experiment.

KN(SiMe₃)₂ (0.19 mL of a 0.7 M solution in toluene, 0.132 mmol) was added to a solution of a mixture of **2b** (38 mg, 0.06 mmol) and **2f** (36 mg, 0.06 mmol) in THF (20 mL) cooled to -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 40 min. The solvent was evaporated to dryness, the residue extracted with CH₂Cl₂ (20 mL) and HOTf (12 μL, 0.132 mmol) was added. After 15 min. stirring at room temperature the reaction mixture was filtered

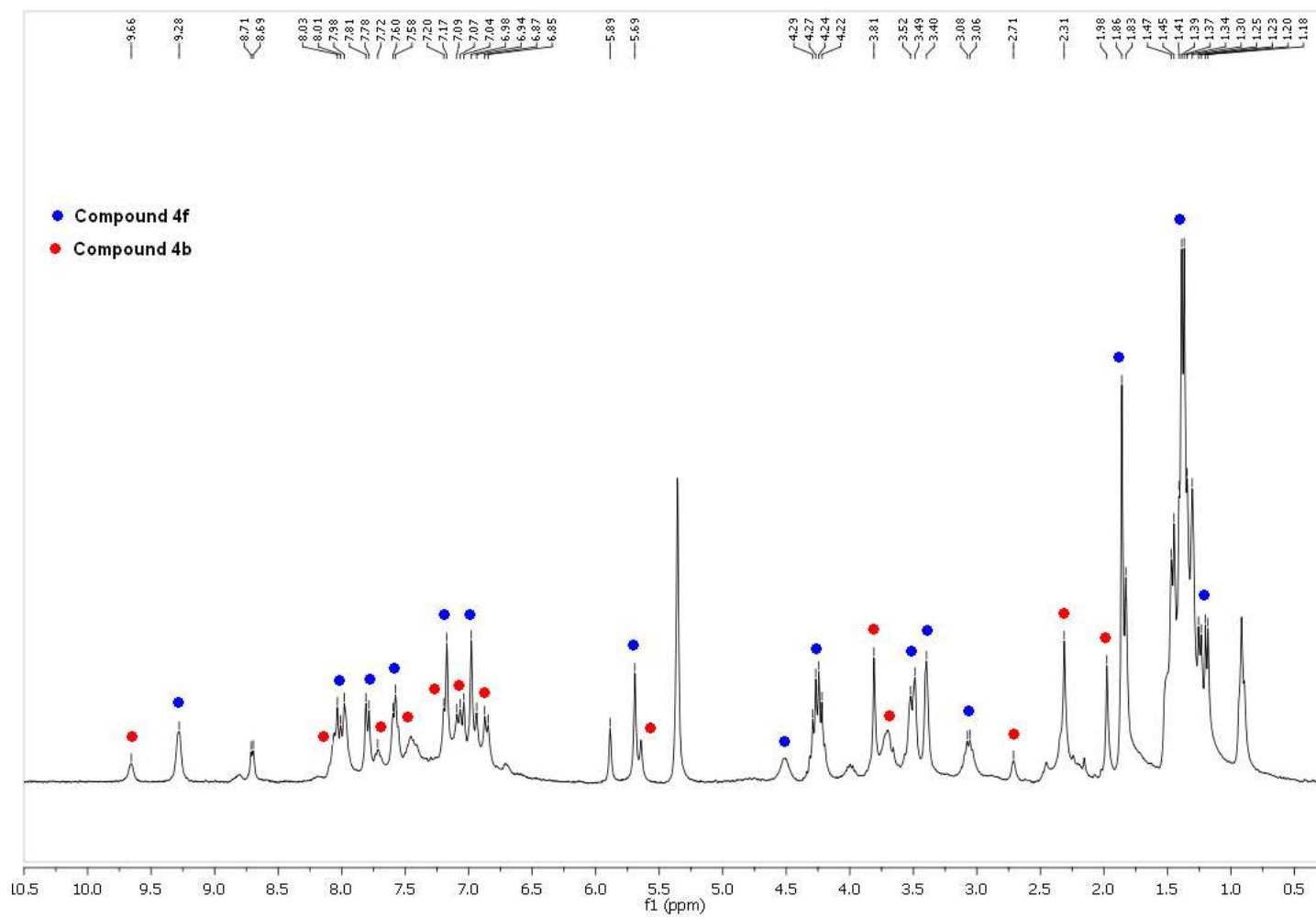
² Dai, Y.; Wang, S.; Wu, J.; Tang, J.; Tang, W. *RSC Advances* **2012**, *2*, 12652.

via canula, the solvent evaporated under reduced pressure and the resulting dark red solid was washed with hexane (2×20 mL) and dried under vacuum. Analysis by ^1H NMR in CD_2Cl_2 showed the formation of compounds **4b** and **4f**, the cross-coupled products not being observed.

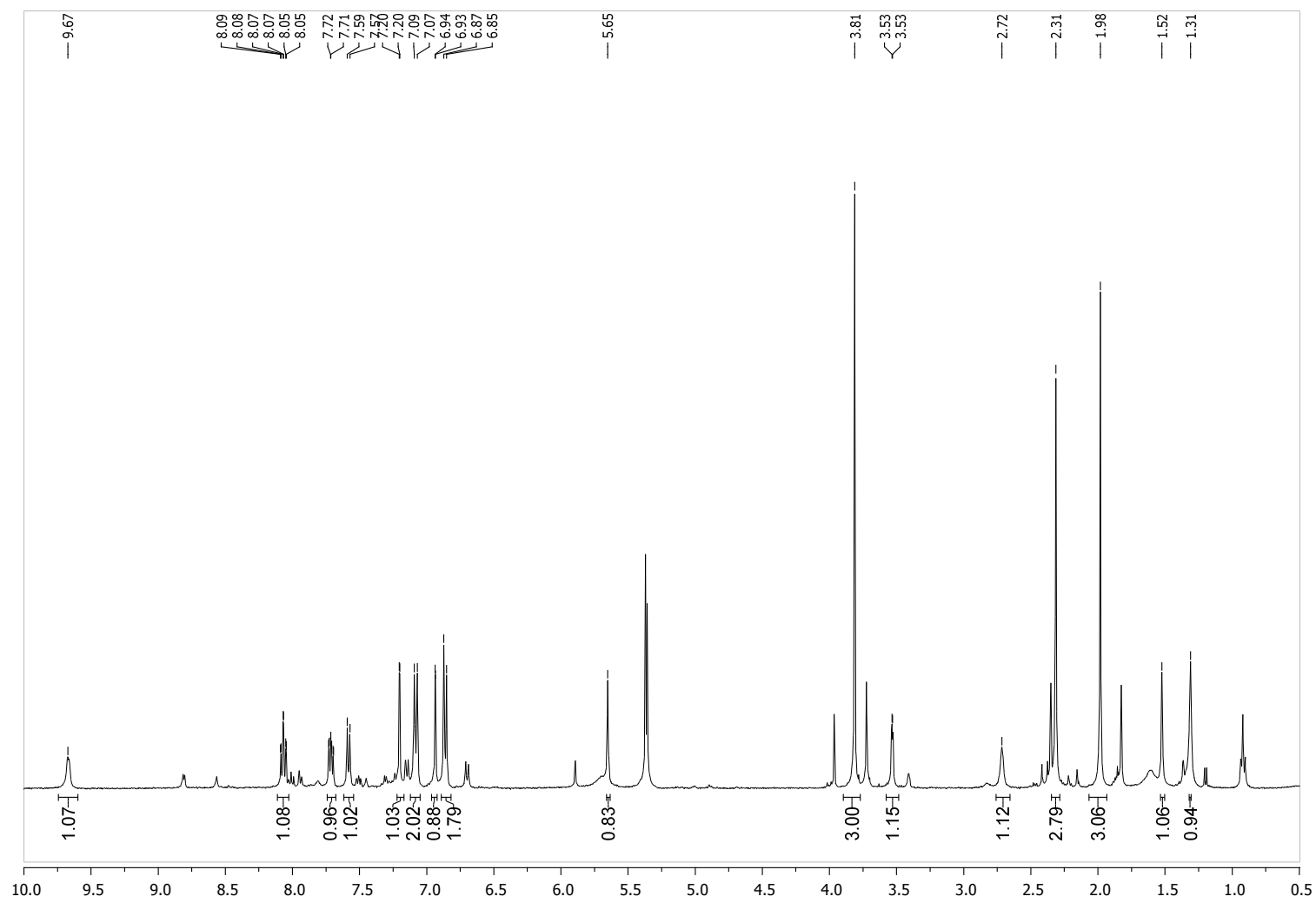
Molecular structure of the cation of compound 4c.



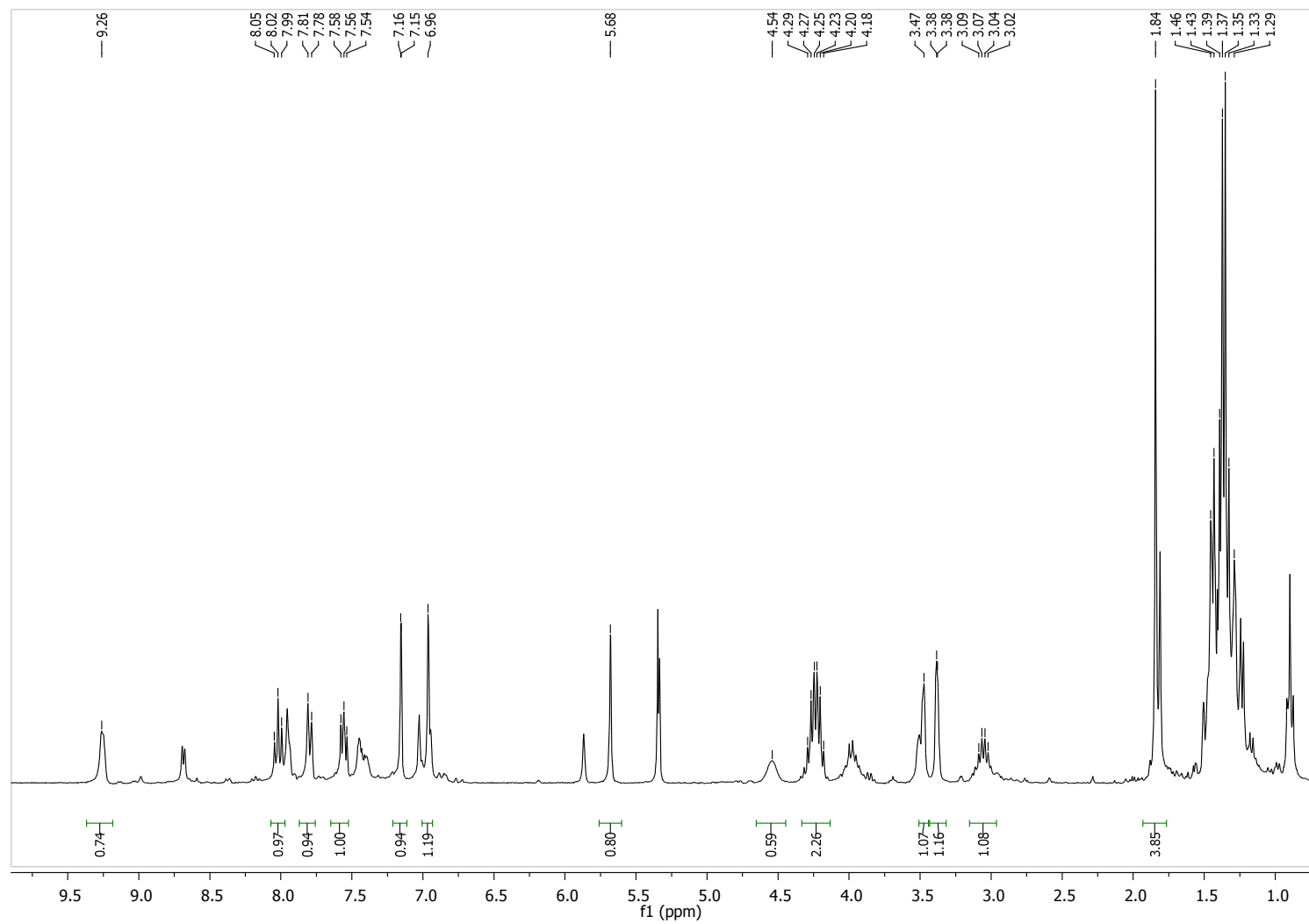
Crossover experiment ^1H NMR spectra



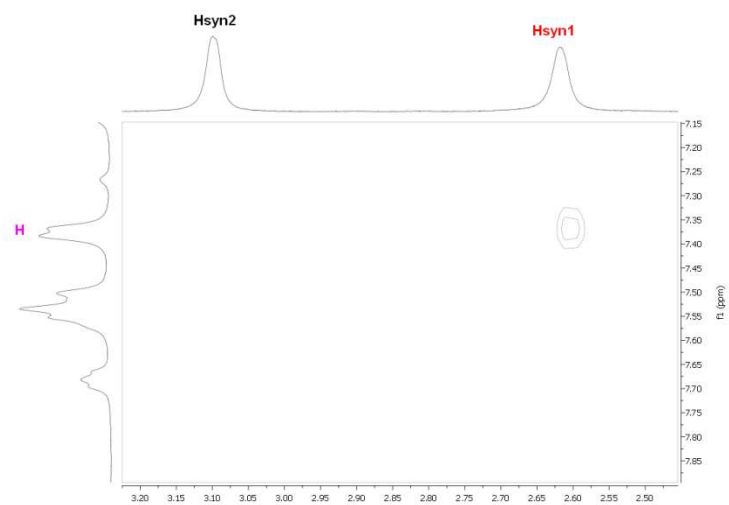
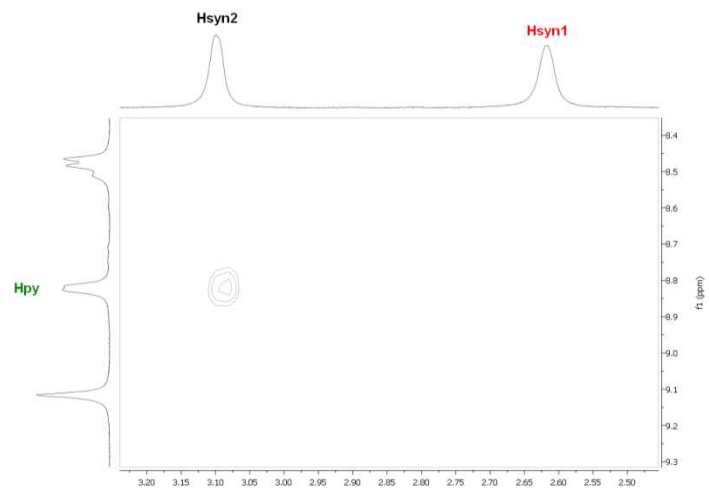
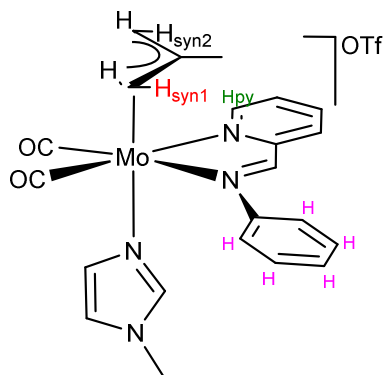
¹H NMR Compound **4b**

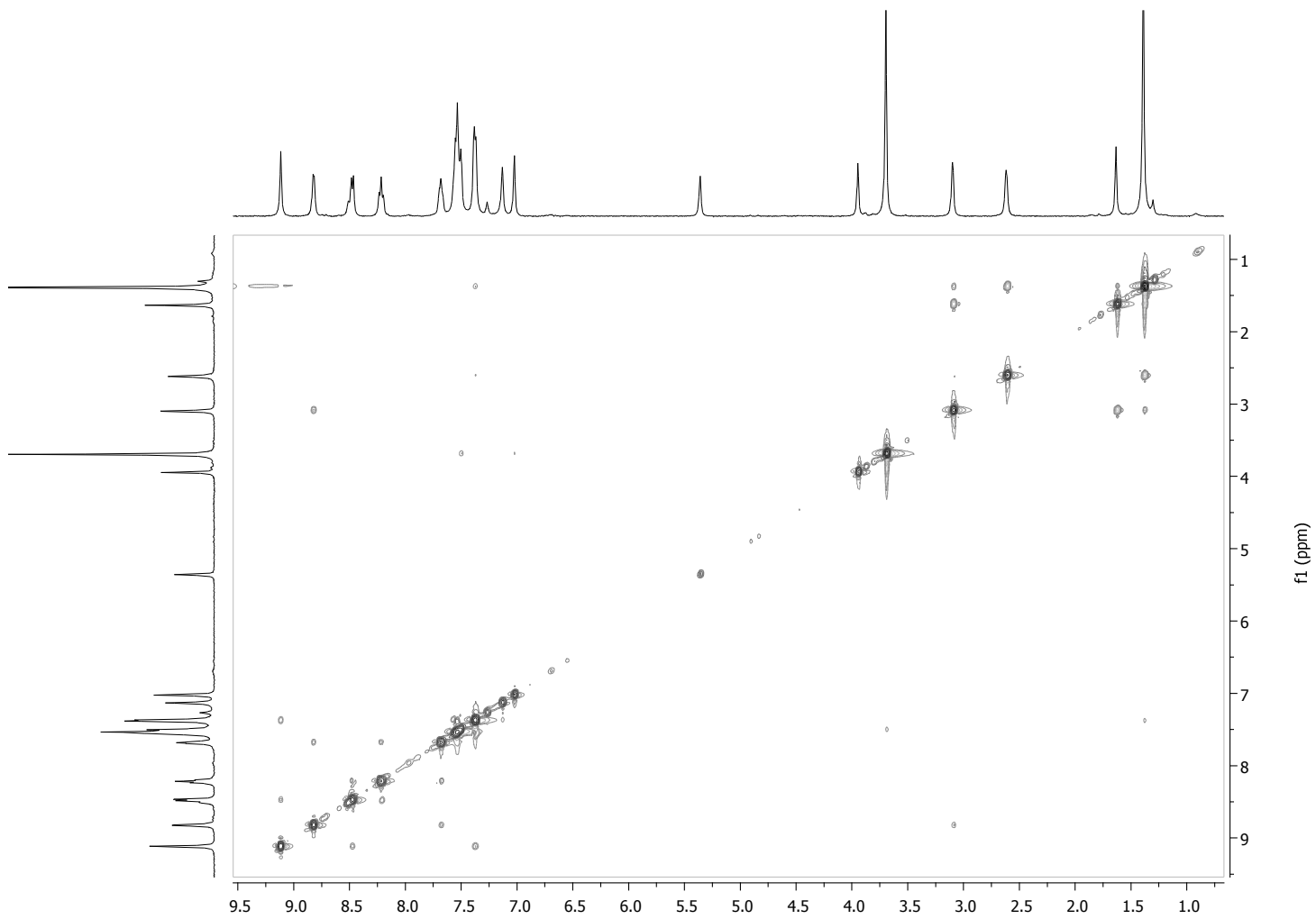


¹H NMR Compound **4f**

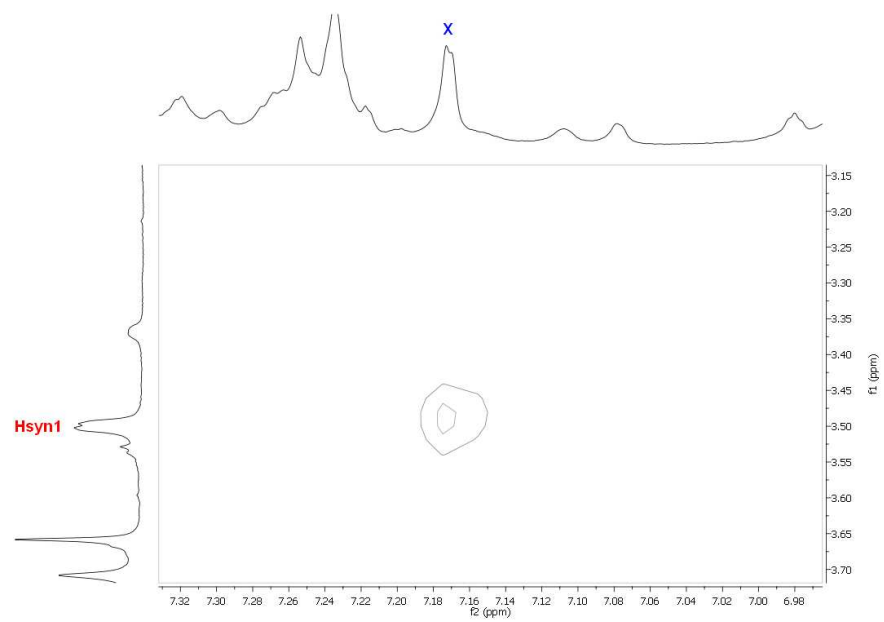
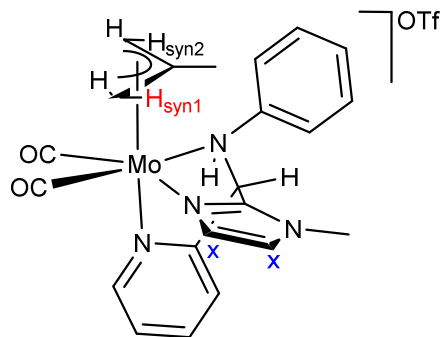


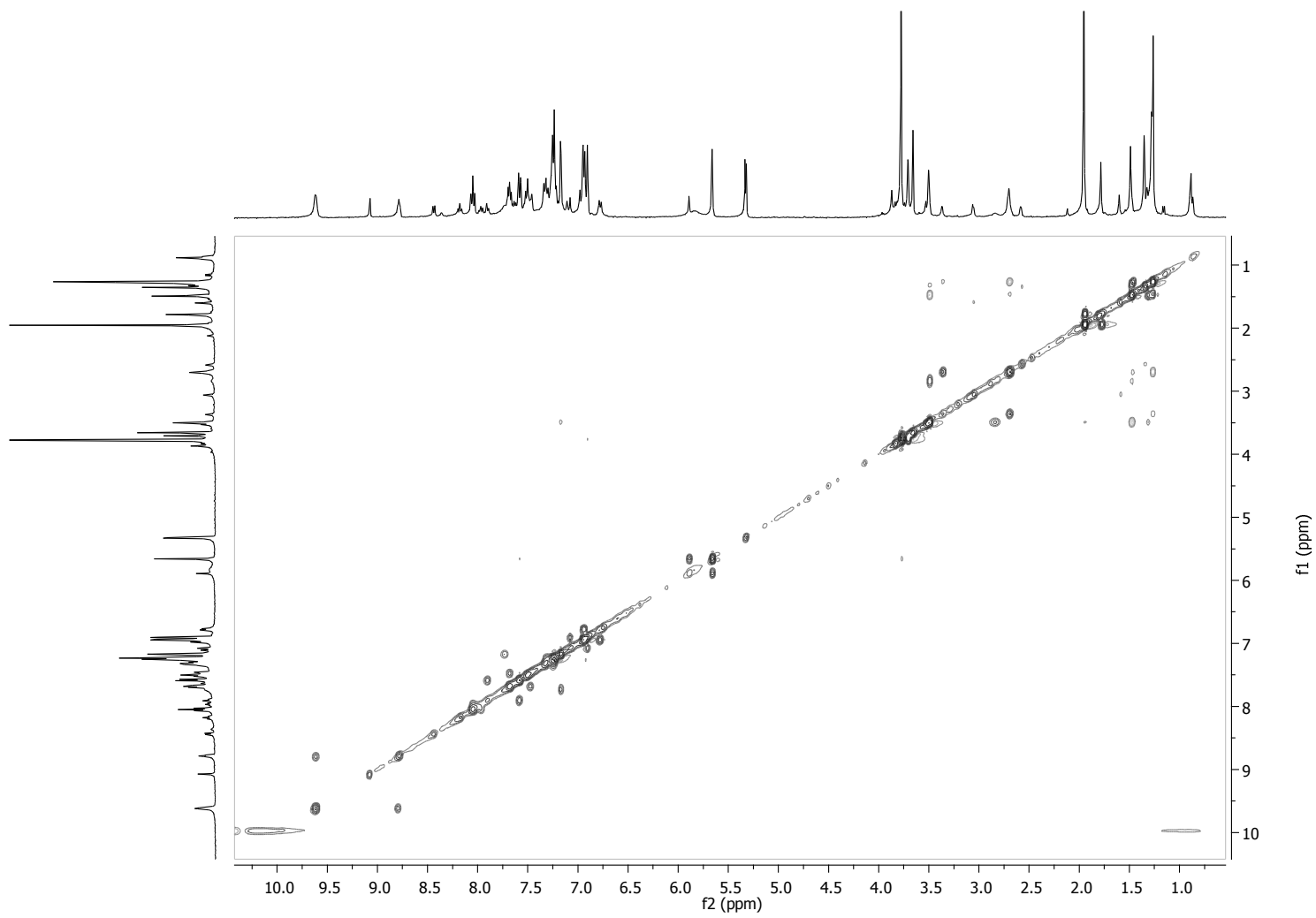
NOESY of compound 2a



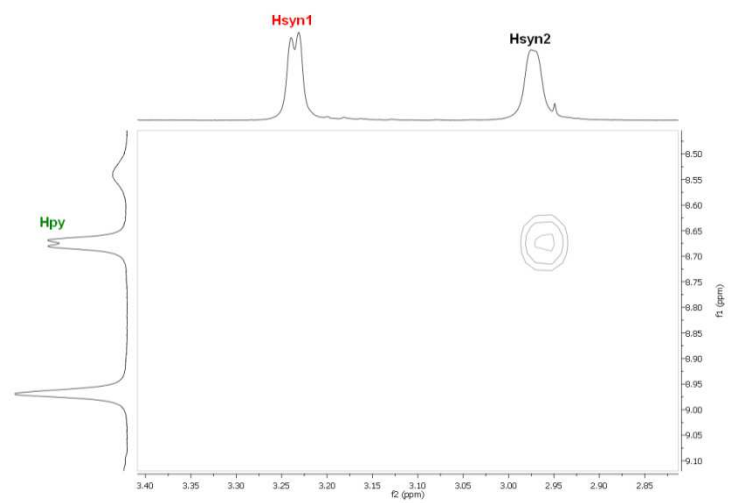
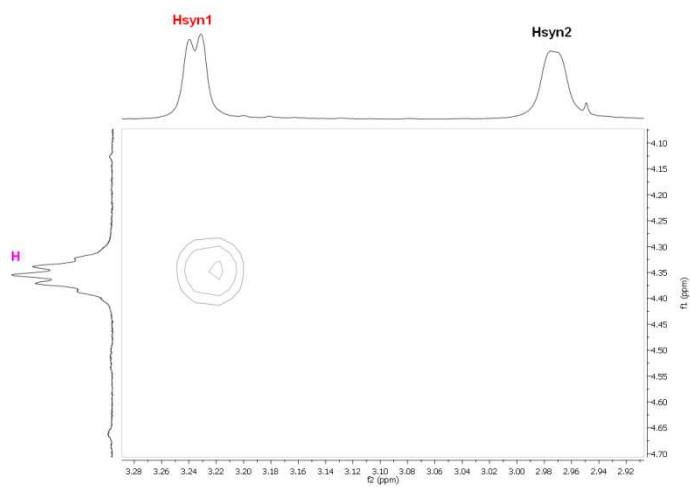
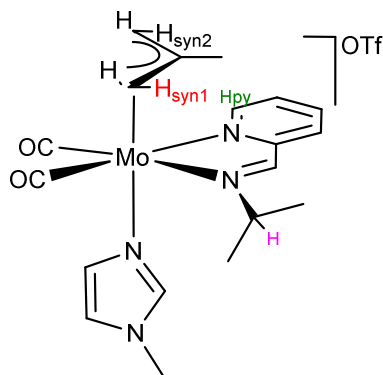


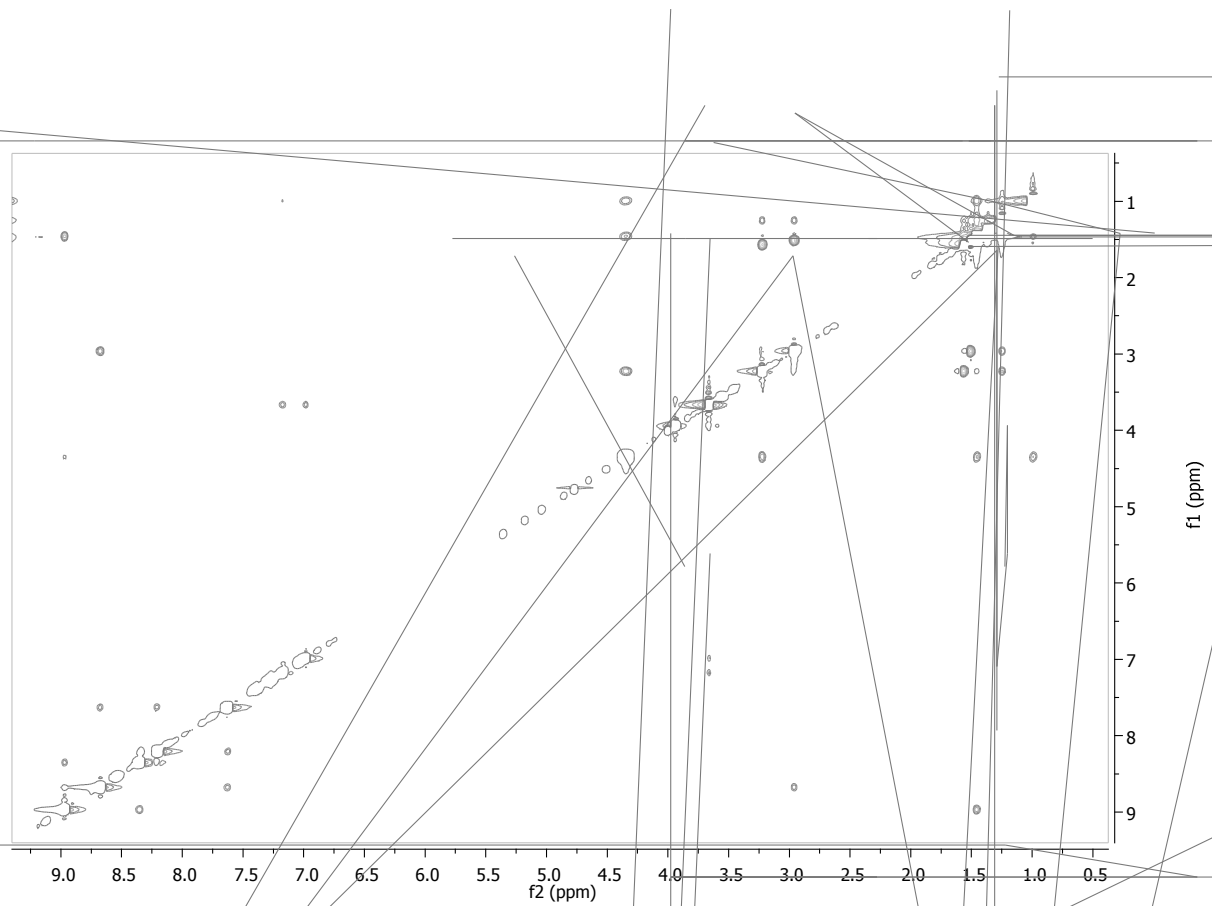
NOESY of compound 4a



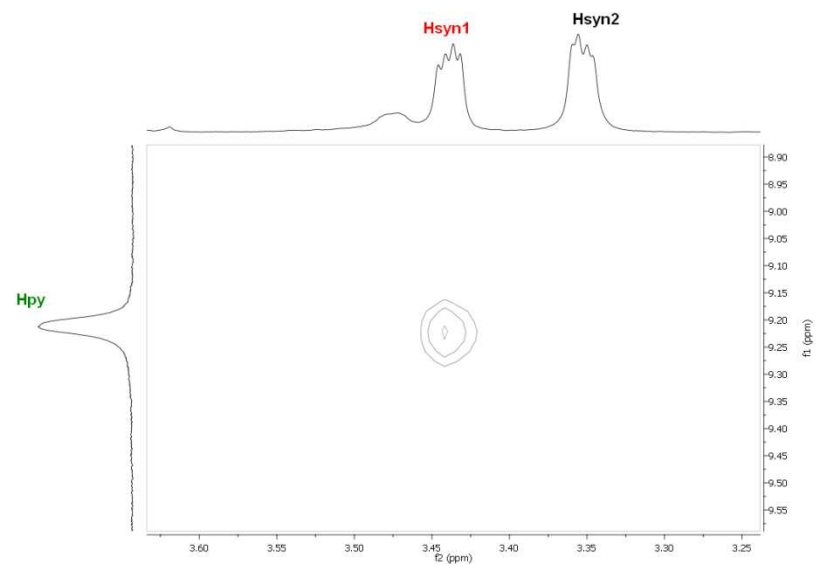
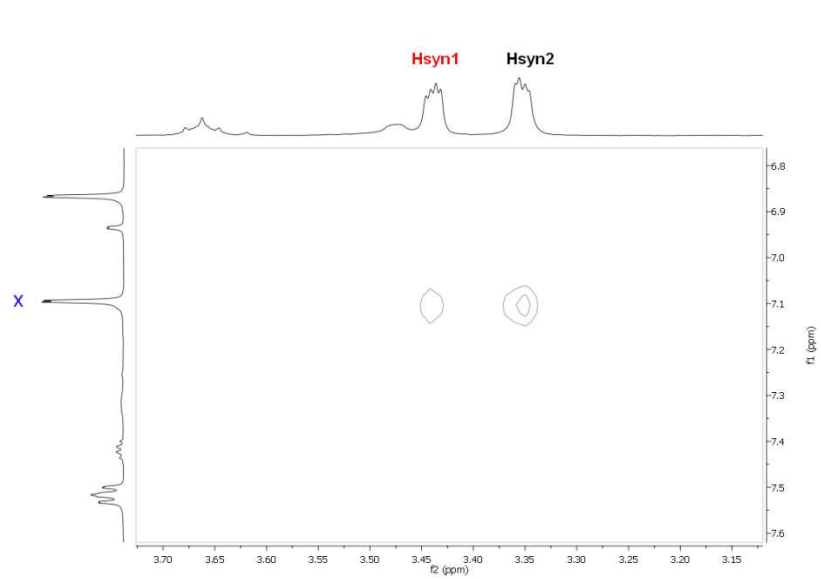
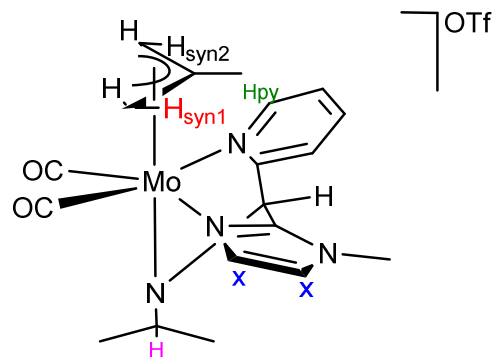


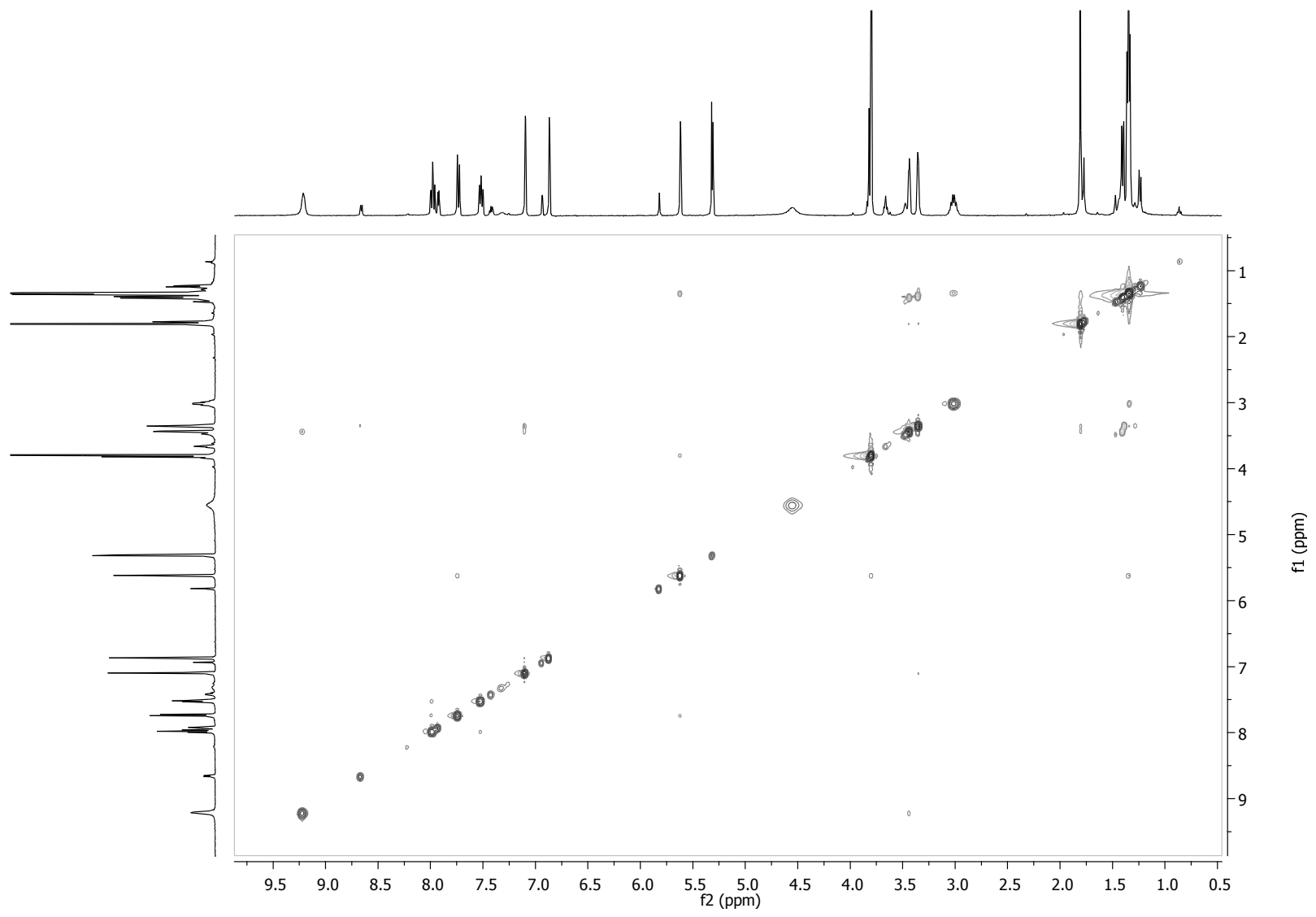
NOESY of compound **2d**





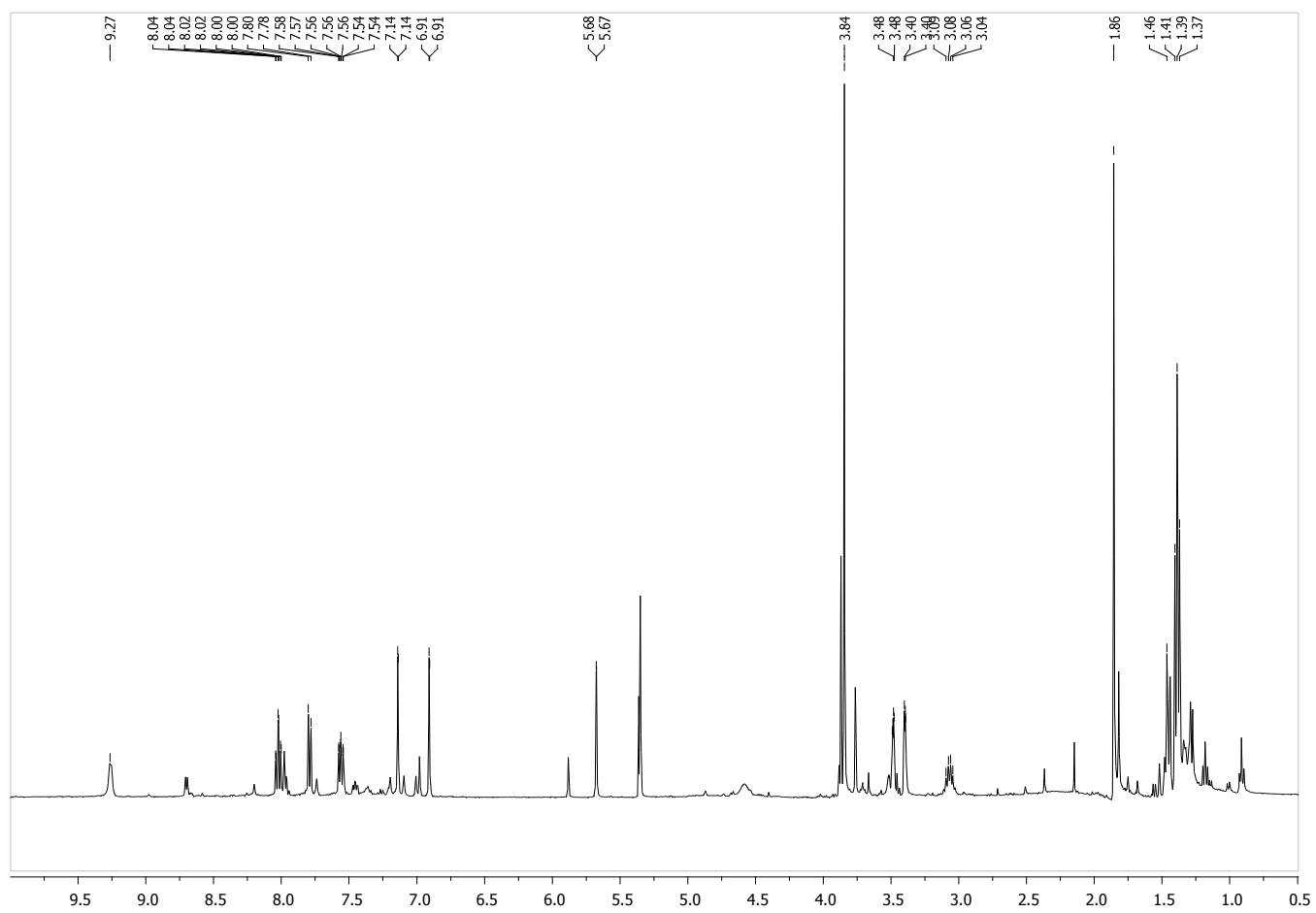
NOESY of compound **4d**



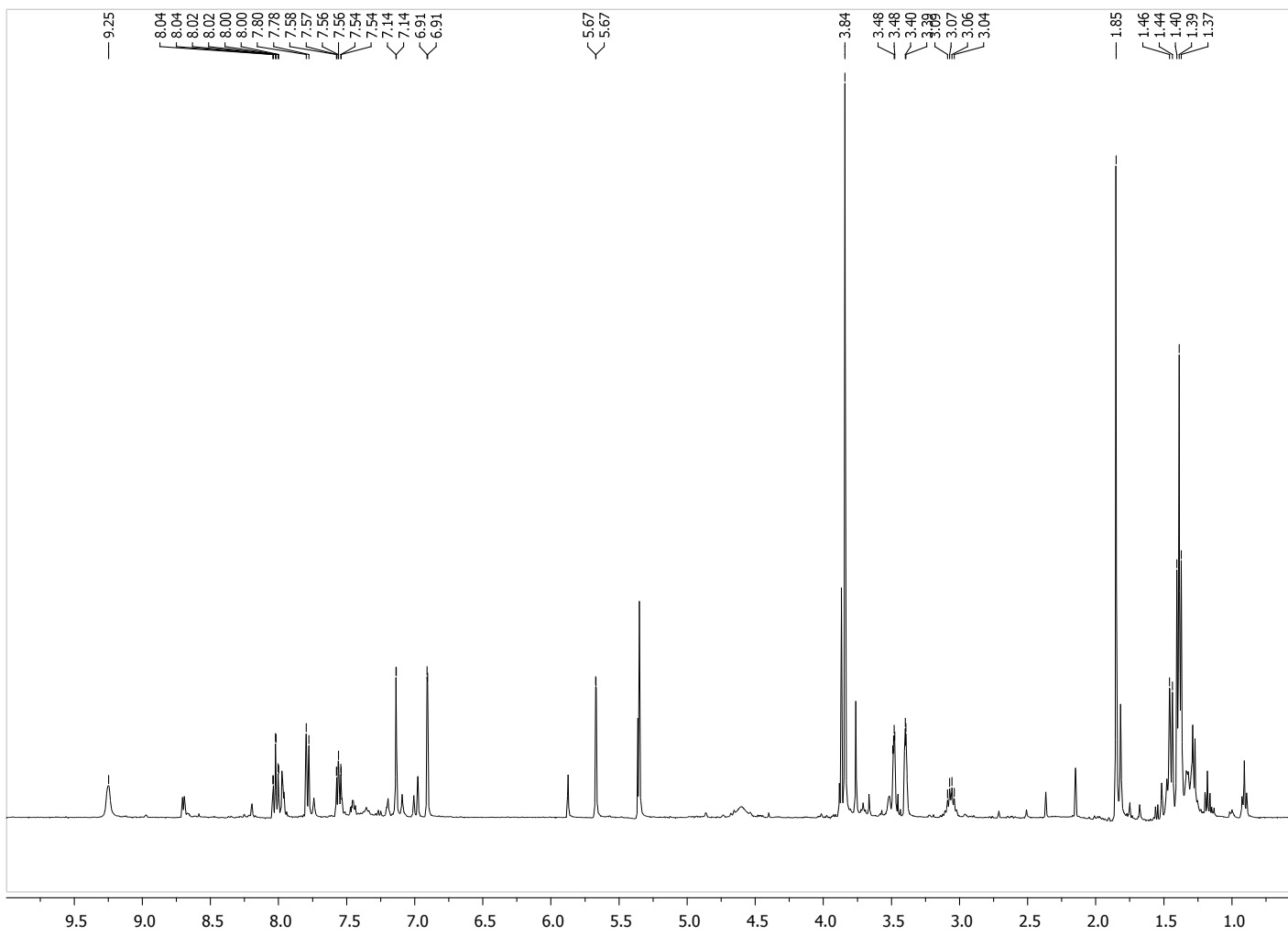


Variable temperature ^1H NMR spectra of compound **4d**

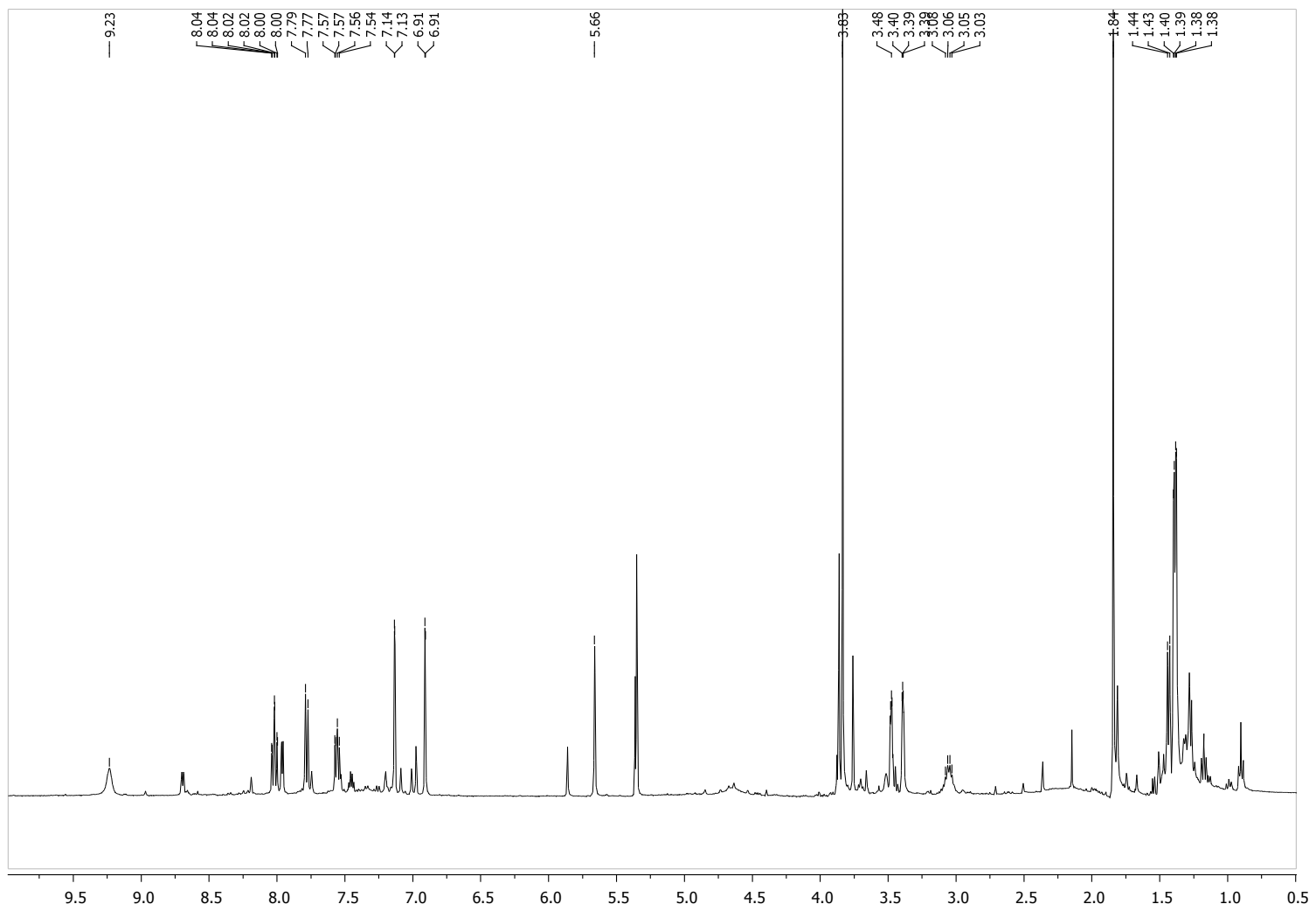
298K



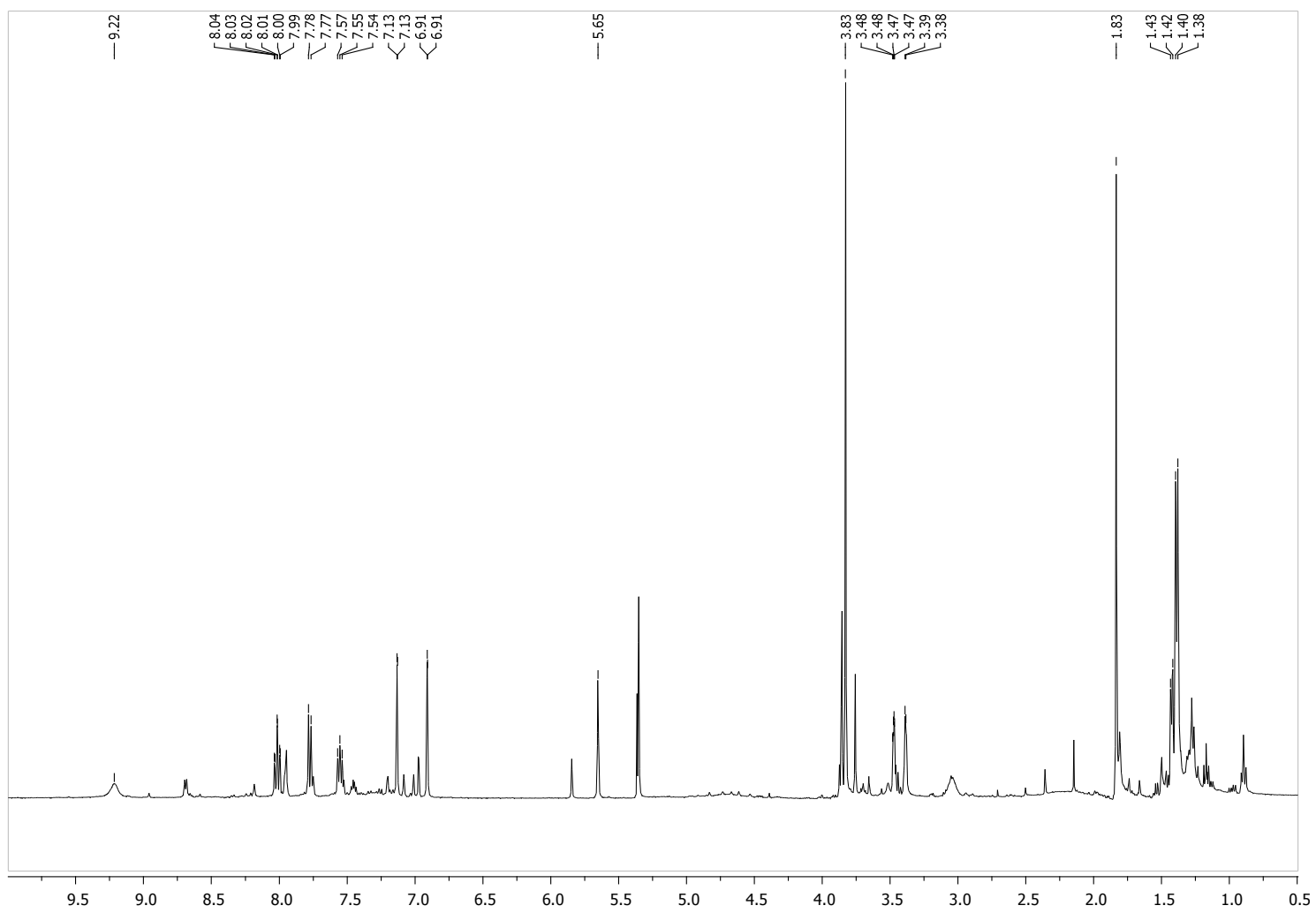
293K



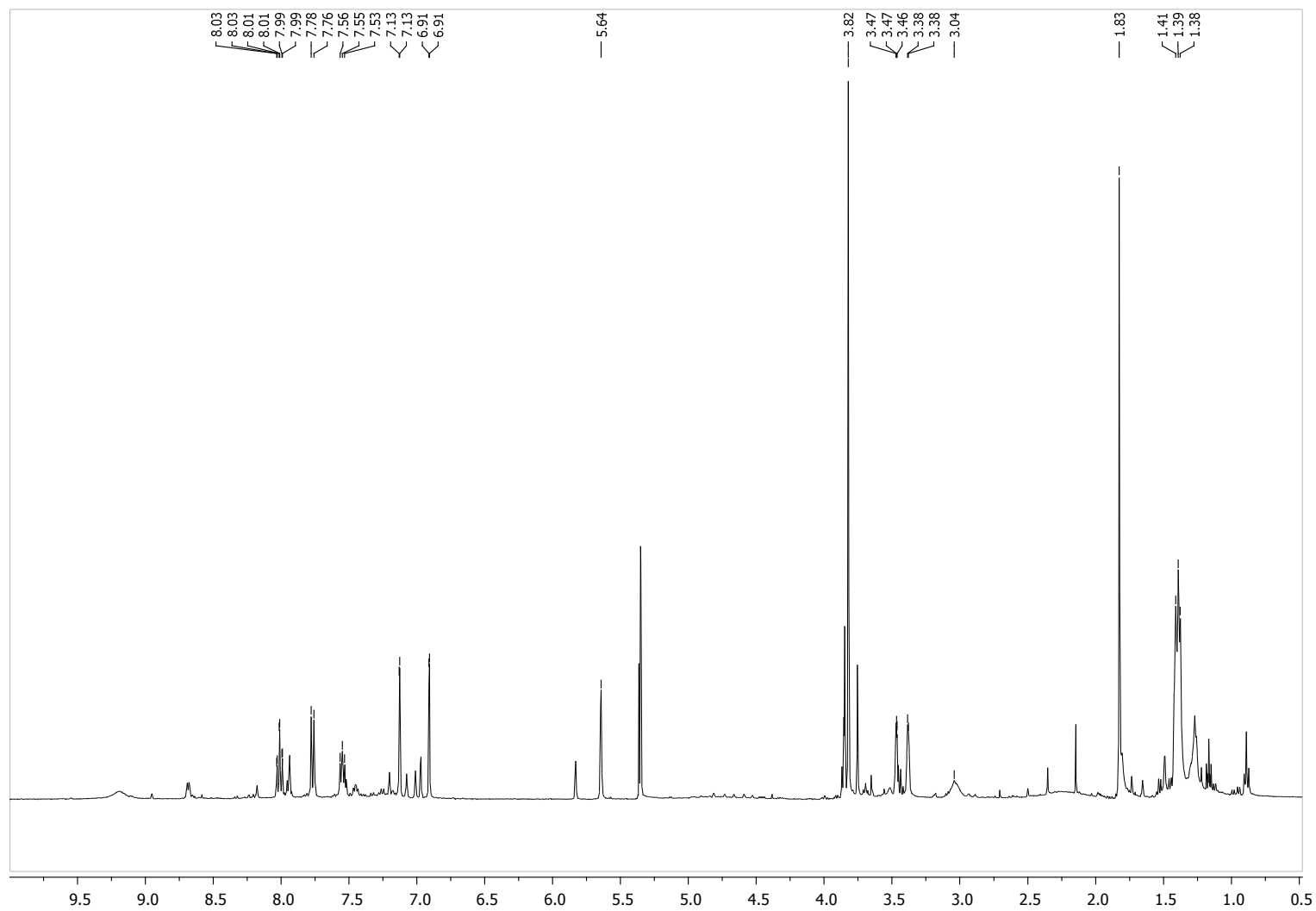
283K



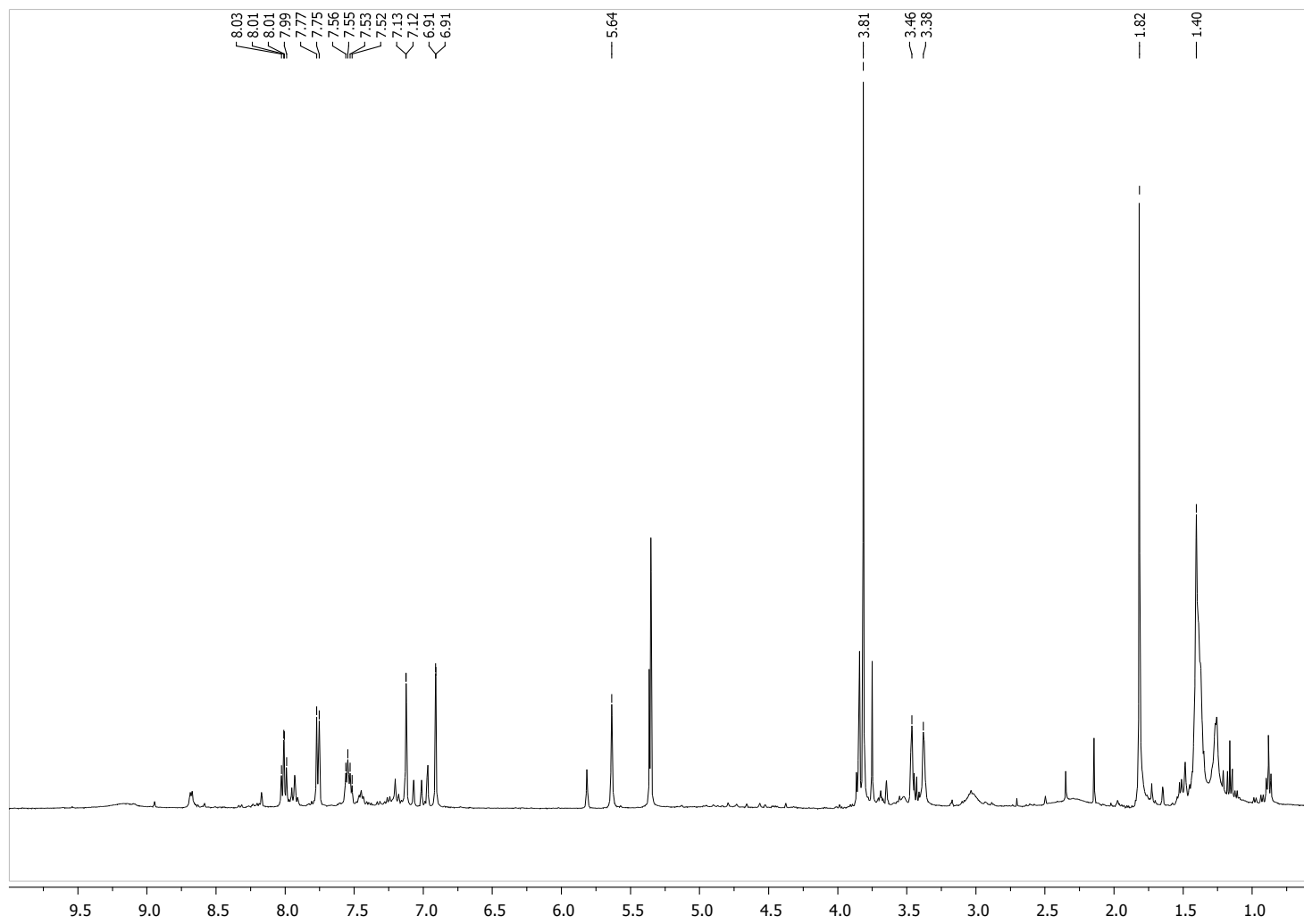
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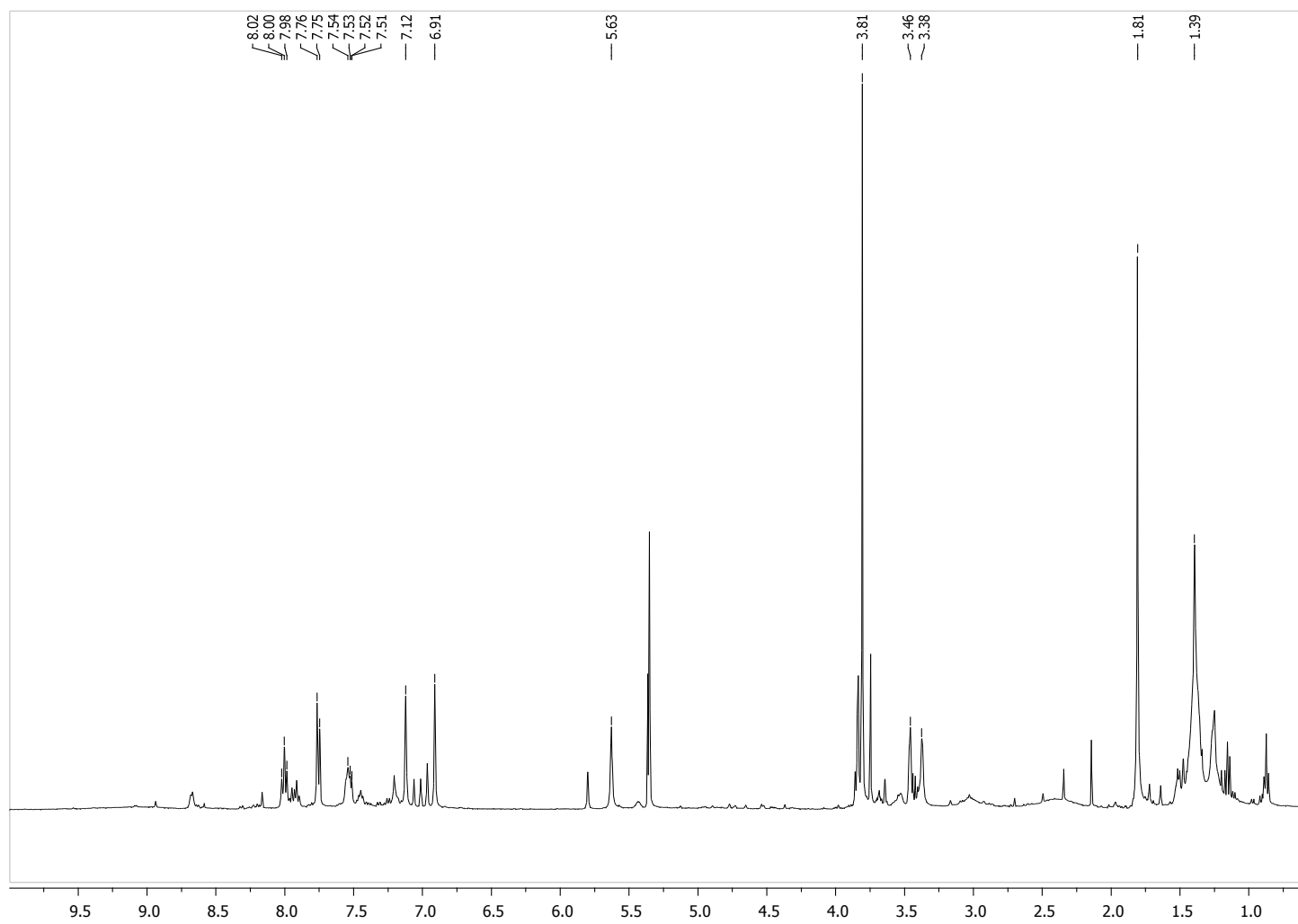
263K



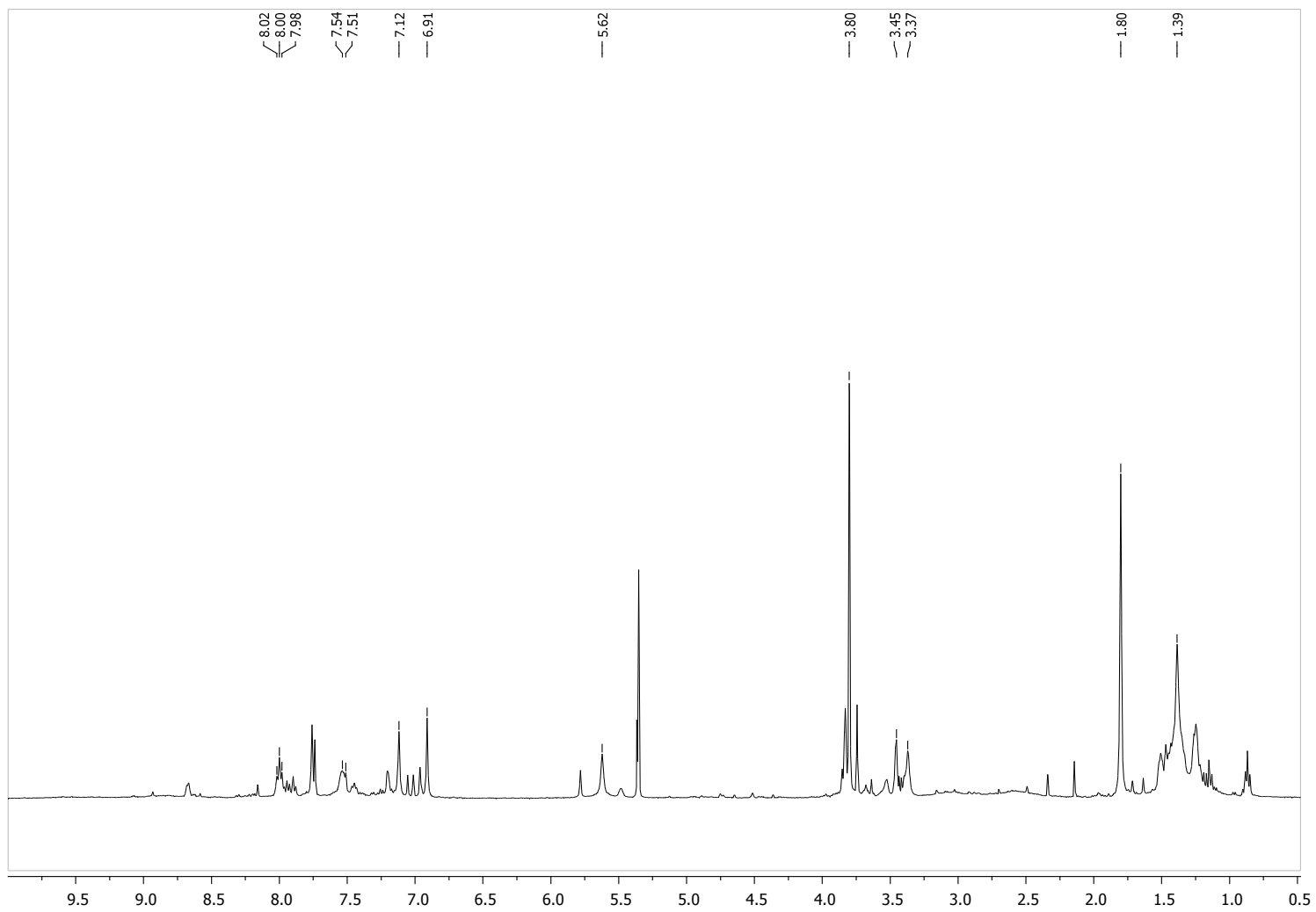
253K



243K



233K



223K

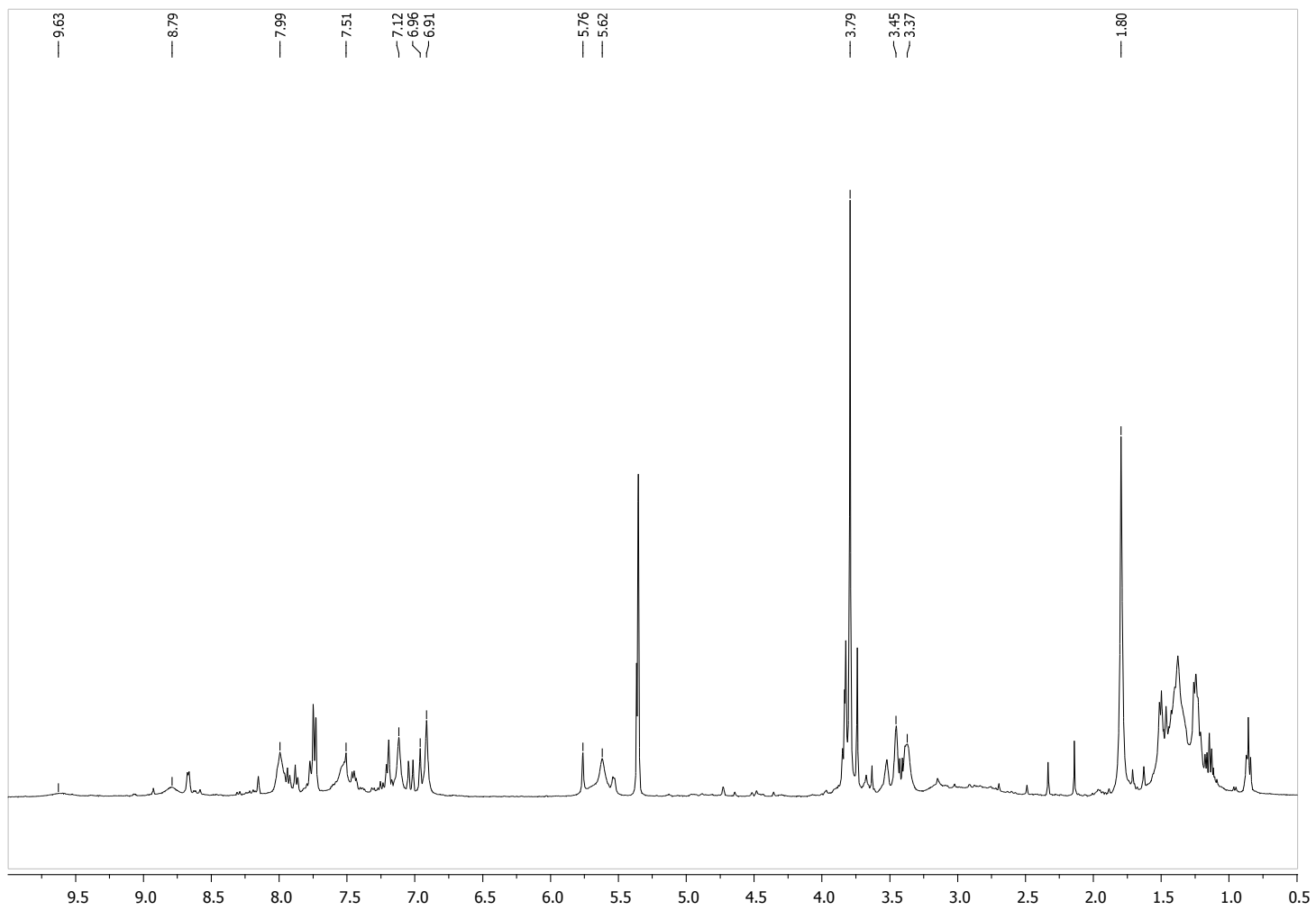


Table S1. CPCM-B3LYP/6-31+G(d) (LANL2DZ + f for Mo) electronic energy (E) and thermodynamic magnitudes (H, S, and G at 1 atm and 195.15 K), CPCM-B3LYP/6-311++G(d,p) (LANL2DZ + f for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + f for Mo) electronic energy (E'), and dispersion energy (E_{disp}) of the critical structures located in THF solution for the deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-R}')^+]$ ($\text{R}' = \text{C}_6\text{H}_3\text{-3,5-Me}_2, t\text{Bu}$). Entropies are given in $\text{calK}^{-1}\text{mol}^{-1}$ while the remaining magnitudes are in hartree.

Species	E	H	S	G	E'	E_{disp}
I	-1367.218537	-1366.747367	153.270	-1366.795033	-1367.546530	-0.154720
Ii	-1367.216386	-1366.744798	153.666	-1366.792587	-1367.544455	-0.154957
TSIa	-1367.198104	-1366.727562	151.119	-1366.774559	-1367.526352	-0.154645
TSIib11	-1367.204100	-1366.734281	148.972	-1366.780610	-1367.531646	-0.155142
Iib1	-1367.227133	-1366.755021	150.026	-1366.801678	-1367.552976	-0.152238
TSIib12	-1367.212280	-1366.740893	150.612	-1366.787732	-1367.537920	-0.152434
TSIib21	-1367.204517	-1366.734099	148.352	-1366.780235	-1367.531993	-0.154796
Iib2	-1367.229473	-1366.757586	151.539	-1366.804713	-1367.555278	-0.151929
II	-1367.241866	-1366.769715	150.732	-1366.816591	-1367.569564	-0.157794
TSII	-1367.198709	-1366.728223	147.933	-1366.774229	-1367.526990	-0.156471
III	-1367.229303	-1366.757397	150.158	-1366.804095	-1367.556936	-0.156814
TSIV	-1367.202677	-1366.732790	149.505	-1366.779285	-1367.531198	-0.155803
IV	-1367.222120	-1366.750263	146.850	-1366.795932	-1367.550172	-0.156920
Va	-1367.262284	-1366.789539	153.328	-1366.837223	-1367.590101	-0.154699
Vb	-1367.271833	-1366.798381	148.302	-1366.844501	-1367.599268	-0.153932
Vc	-1367.263865	-1366.790496	150.046	-1366.837159	-1367.591261	-0.155050
TSVa-b	-1367.250933	-1366.778623	147.384	-1366.824458	-1367.578502	-0.152476
TSVa-c	-1367.232298	-1366.759653	148.974	-1366.805982	-1367.559711	-0.150738
TSVb-c	-1367.243929	-1366.771095	149.961	-1366.817732	-1367.571251	-0.148616
TSVI	-1367.163735	-1366.694254	148.457	-1366.740423	-1367.492590	-0.159023
VI	-1367.249757	-1366.777932	152.296	-1366.825295	-1367.577748	-0.156078
VII	-1367.200779	-1366.728626	145.254	-1366.773799	-1367.528708	-0.162328
TSVIII	-1367.179985	-1366.710236	147.424	-1366.756084	-1367.508474	-0.160300
VIII	-1367.217635	-1366.745666	144.524	-1366.790611	-1367.546276	-0.161301
(RR)-VaH	-1367.732535	-1367.244285	147.335	-1367.290104	-1368.061383	-0.158943
(RS)-VaH	-1367.728929	-1367.241101	151.886	-1367.288336	-1368.058356	-0.158965
(RR)-VbH	-1367.731597	-1367.242799	148.166	-1367.288877	-1368.060314	-0.157922
(RS)-VbH	-1367.731151	-1367.242161	147.357	-1367.287988	-1368.059986	-0.157748
(RR)-VcH	-1367.730319	-1367.242055	151.175	-1367.289069	-1368.059395	-0.159479
(RS)-VcH	-1367.732417	-1367.244000	150.043	-1367.290662	-1368.061288	-0.158727
V'a	-1214.811568	-1214.363073	136.768	-1214.405606	-1215.107955	-0.144656
V'b	-1214.824485	-1214.376332	137.082	-1214.418963	-1215.120868	-0.142483
V'c	-1214.813121	-1214.364521	134.139	-1214.406237	-1215.109634	-0.144404
TSV'a-b	-1214.799106	-1214.351338	135.686	-1214.393535	-1215.095934	-0.139804
TSV'a-c	-1214.770047	-1214.322724	139.775	-1214.366193	-1215.066965	-0.138200
TSV'b-c	-1214.793229	-1214.344963	136.345	-1214.387365	-1215.089719	-0.139714
(RR)-V'aH	-1215.299657	-1214.834944	136.938	-1214.877531	-1215.598091	-0.147931
(RS)-V'aH	-1215.290137	-1214.825238	136.250	-1214.867611	-1215.588914	-0.145271
(RR)-V'bH	-1215.302149	-1214.837564	134.792	-1214.879483	-1215.600354	-0.147812
(RS)-V'bH	-1215.301652	-1214.836931	135.042	-1214.878928	-1215.600062	-0.147696
(RR)-V'cH	-1215.292883	-1214.828510	135.372	-1214.870610	-1215.591319	-0.146111
(RS)-V'cH	-1215.301031	-1214.835811	135.573	-1214.877973	-1215.599560	-0.147999

Table S2. CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative electronic energy (ΔE), enthalpy (ΔH), entropy contribution ($T\Delta S$), and Gibbs free energy (ΔG), CPCM-B3LYP/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative electronic energy ($\Delta E'$), relative dispersion energy (ΔE_{disp}), and CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative Gibbs free energy ($\Delta G'$) of the critical structures located in THF solution for the deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-R}')^+]$ ($\text{R}' = \text{C}_6\text{H}_3\text{-3,5-Me}_2$). All the magnitudes are given in kcal mol^{-1} .

Species	ΔE	ΔH	$T\Delta S$	ΔG	$\Delta E'$	ΔE_{disp}	$\Delta G'^{(a)}$
I	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ii	1.3	1.6	0.1	1.5	1.3	-0.1	1.3
TSIa	12.8	12.4	-0.4	12.8	12.7	0.0	12.7
TSIib11	9.1	8.2	-0.8	9.1	9.3	-0.3	9.1
Iib1	-5.4	-4.8	-0.6	-4.2	-4.0	1.6	-1.3
TSIib12	3.9	4.1	-0.5	4.6	5.4	1.4	7.5
TSIib21	8.8	8.3	-1.0	9.3	9.1	0.0	9.6
Iib2	-6.9	-6.4	-0.3	-6.1	-5.5	1.8	-2.9
II	-14.6	-14.0	-0.5	-13.5	-14.5	-1.9	-15.3
TSII	12.4	12.0	-1.0	13.1	12.3	-1.1	11.8
III	-6.8	-6.3	-0.6	-5.7	-6.5	-1.3	-6.8
TSIV	10.0	9.1	-0.7	9.9	9.6	-0.7	8.9
IV	-2.2	-1.8	-1.3	-0.6	-2.3	-1.4	-2.0
Va	-27.5	-26.5	0.0	-26.5	-27.3	0.0	-26.4
Vb	-33.4	-32.0	-1.0	-31.0	-33.1	0.5	-30.2
Vc	-28.4	-27.1	-0.6	-26.4	-28.1	-0.2	-26.3
TSVa-b	-20.3	-19.6	-1.1	-18.5	-20.1	1.4	-16.8
TSVa-c	-8.6	-7.7	-0.8	-6.9	-8.3	2.5	-4.0
TSVb-c	-15.9	-14.9	-0.6	-14.2	-15.5	3.8	-10.0
TSVI	34.4	33.3	-0.9	34.3	33.8	-2.7	31.0
VI	-19.6	-19.2	-0.2	-19.0	-19.6	-0.9	-19.8
VII	11.1	11.8	-1.6	13.3	11.2	-4.8	8.6
TSVIII	24.2	23.3	-1.1	24.4	23.9	-3.5	20.6
VIII	0.6	1.1	-1.7	2.8	0.2	-4.1	-1.8

^(a) $\Delta G' = \Delta G - \Delta E + \Delta E' + \Delta E_{\text{disp}}$

Table S3. CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative electronic energy (ΔE), enthalpy (ΔH), entropy contribution ($T\Delta S$), and Gibbs free energy (ΔG), CPCM-B3LYP/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative electronic energy ($\Delta E'$), relative dispersion energy (ΔE_{disp}), and CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative Gibbs free energy ($\Delta G'$) of the critical structures located in THF solution for the interconversion of the different $C_{\text{imidazole}}-C_{\text{imino}}$ coupling conformers formed from the deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-}t\text{Bu})]^+$. All the magnitudes are given in kcal mol⁻¹.

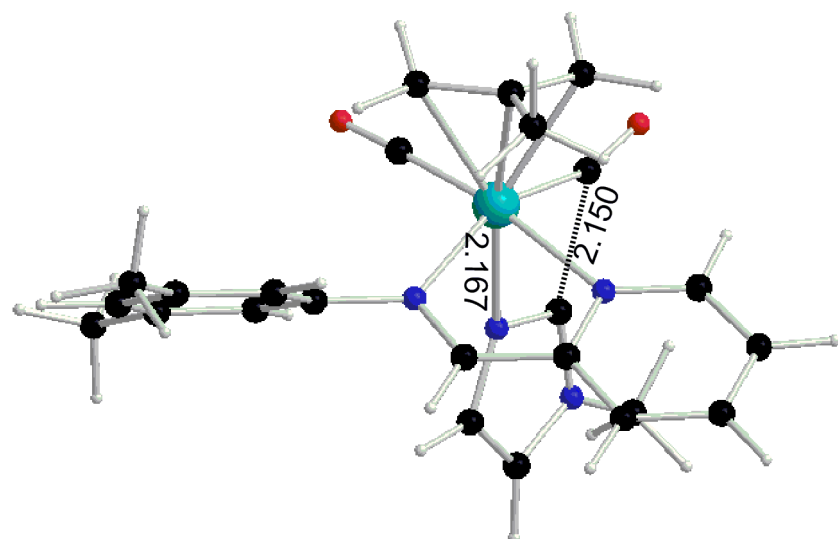
Species	ΔE	ΔH	$T\Delta S$	ΔG	$\Delta E'$	ΔE_{disp}	$\Delta G'^{(a)}$
V'a	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V'b	-8.1	-8.3	0.1	-8.4	-8.1	1.4	-7.0
V'c	-1.0	-0.9	-0.5	-0.4	-1.1	0.2	-0.3
TSV'a-b	7.8	7.4	-0.2	7.6	7.5	3.0	10.3
TSV'a-c	26.1	25.3	0.6	24.7	25.7	4.1	28.5
TSV'b-c	11.5	11.4	-0.1	11.4	11.4	3.1	14.5

^(a) $\Delta G' = \Delta G - \Delta E + \Delta E' + \Delta E_{\text{disp}}$

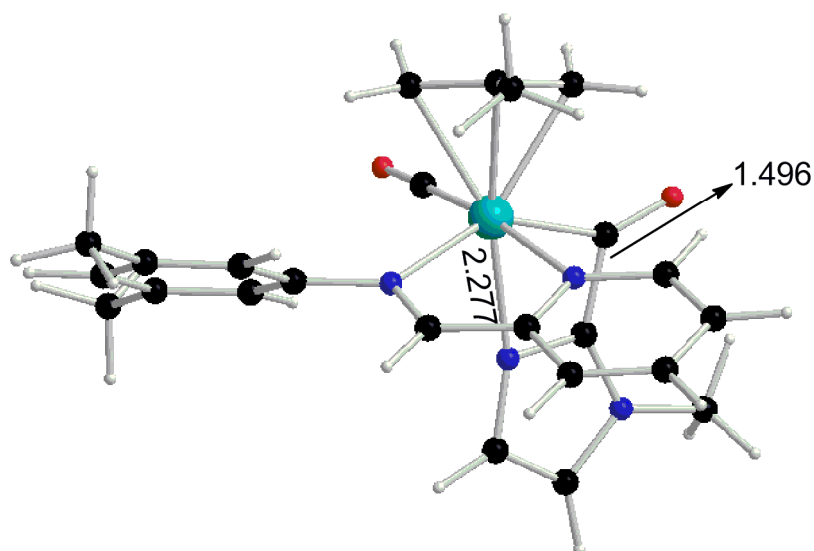
Table S4. CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative electronic energy (ΔE), enthalpy (ΔH), entropy contribution ($T\Delta S$), and Gibbs free energy (ΔG), CPCM-B3LYP/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative electronic energy ($\Delta E'$), relative dispersion energy (ΔE_{disp}), and CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) relative Gibbs free energy ($\Delta G'$) for the different diastereomers of the protonated $C_{\text{imidazole}}-C_{\text{iminic}}$ coupling products obtained from the deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(N\text{-MeIm})(\text{py-2-CH=N-R}')^+]$ ($R' = \text{C}_6\text{H}_3\text{-3,5-Me}_2, t\text{Bu}$). All the magnitudes are given in kcal mol^{-1} .

Species	ΔE	ΔH	$T\Delta S$	ΔG	$\Delta E'$	ΔE_{disp}	$\Delta G'^{(a)}$
<hr/>							
$R' = \text{C}_6\text{H}_3\text{-3,5-Me}_2$							
<i>(RR)</i> - VaH	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>(RS)</i> - VaH	2.3	2.0	0.9	1.1	1.9	0.0	0.7
<i>(RR)</i> - VbH	0.6	0.9	0.2	0.8	0.7	0.6	1.5
<i>(RS)</i> - VbH	0.9	1.3	0.0	1.3	0.9	0.7	2.1
<i>(RR)</i> - VcH	1.4	1.4	0.7	0.6	1.2	-0.3	0.2
<i>(RS)</i> - VcH	0.1	0.2	0.5	-0.4	0.1	0.1	-0.2
<hr/>							
$R' = t\text{Bu}$							
<i>(RR)</i> - V'aH	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>(RS)</i> - V'aH	6.0	6.1	-0.1	6.2	5.8	1.7	7.7
<i>(RR)</i> - V'bH	-1.6	-1.6	-0.4	-1.2	-1.4	0.1	-1.0
<i>(RS)</i> - V'bH	-1.3	-1.2	-0.4	-0.9	-1.2	0.1	-0.7
<i>(RR)</i> - V'cH	4.3	4.0	-0.3	4.3	4.2	1.1	5.5
<i>(RS)</i> - V'cH	-0.9	-0.5	-0.3	-0.3	-0.9	0.0	-0.4

^(a) $\Delta G' = \Delta G - \Delta E + \Delta E' + \Delta E_{\text{disp}}$



TSIIb21 (9.6)



IIb2 (-2.9)

Figure S1. CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) optimized structures of the species involved in the first step of the formation mechanism of an imidazol-2-yl product via the attack on the CO ligand *trans* to aryl-linked nitrogen atom in the deprotonation of $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-C}_6\text{H}_3\text{-3.5-Me}_2)]^+$. CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + *f* for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + *f* for Mo) Gibbs energies in THF solution (in kcal/mol) referred to **I** are given in parentheses. Most relevant distances are also included in angstroms.

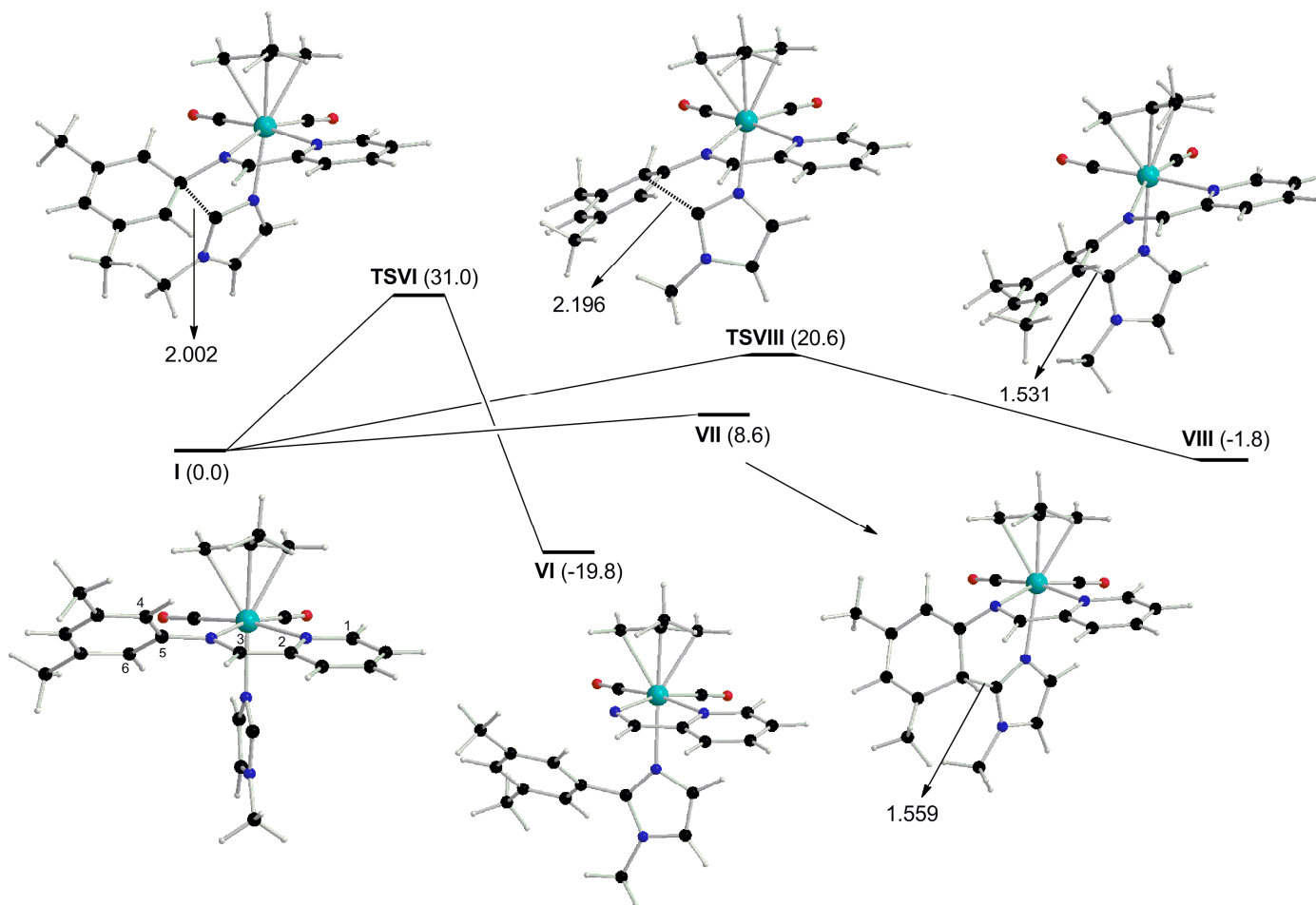


Figure S2. Reaction mechanisms for the formation of C-C coupling products not included in the manuscript that has also been investigated for the deprotonation of the complex $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{N-MeIm})(\text{py-2-CH=N-C}_6\text{H}_3\text{-3.5-Me}_2)]^+$ at the level of theory CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + f for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + f for Mo). Relative Gibbs energies in THF solution, in kcal/mol, are given in parentheses. Most relevant distances are also included in angstroms.

Discussion about the mechanisms not included in the manuscript: Our theoretical investigation about the attack of C_{imidazole} on the CO ligand *trans* to the aryl-linked nitrogen atom to give an imidazol-2-yl product reveals that this mechanism is less favored than that via the attack on the CO ligand *trans* to the pyridyl group of the bidentate ligand. In effect, we found that the first step implies a Gibbs energy barrier in THF solution of 9.6 kcal/mol (**TSIIb21** in Figure S1), 0.5 kcal/mol higher in energy than the rate-determining Gibbs energy barrier obtained for the attack on the other CO ligand. Concerning the formation of C-C coupling products, the attack of C_{imidazole} on the *ipso* carbon atom of the aryl imine substituent (C5 in Figure S2) proceeds through a very unstable TS (**TSVI** in Figure S2), 31.0 kcal/mol higher in energy than **I**, to form a very stable C-C coupling product (**VI** in Figure S2), 19.8 kcal/mol more stable than **I**. This stable species does not present a tridentate ligand as the above-mentioned attack breaks the N-C_{aryl} bond. The formation of the C-C coupling products between C_{imidazole} and the *ortho* carbon atoms (C4, product **VII**, and C6, product **VIII**, in Figure S2) of the aryl group is also penalized. For instance, the attack on the aryl C6 atom (see **I** in Figure S2 for atom numbering) implies the surmounting of a Gibbs energy barrier in solution of 20.6 kcal/mol (**TSVIII**). All the attempts to find a TS for the attack on the aryl C4 atom failed. However, the instability in energy of the corresponding product (**VII** in Figure S2) is 10.4 kcal/mol higher in energy than that obtained for **VIII**, thus suggesting a very energy-demanding process for the transformation **I** → **VII**.

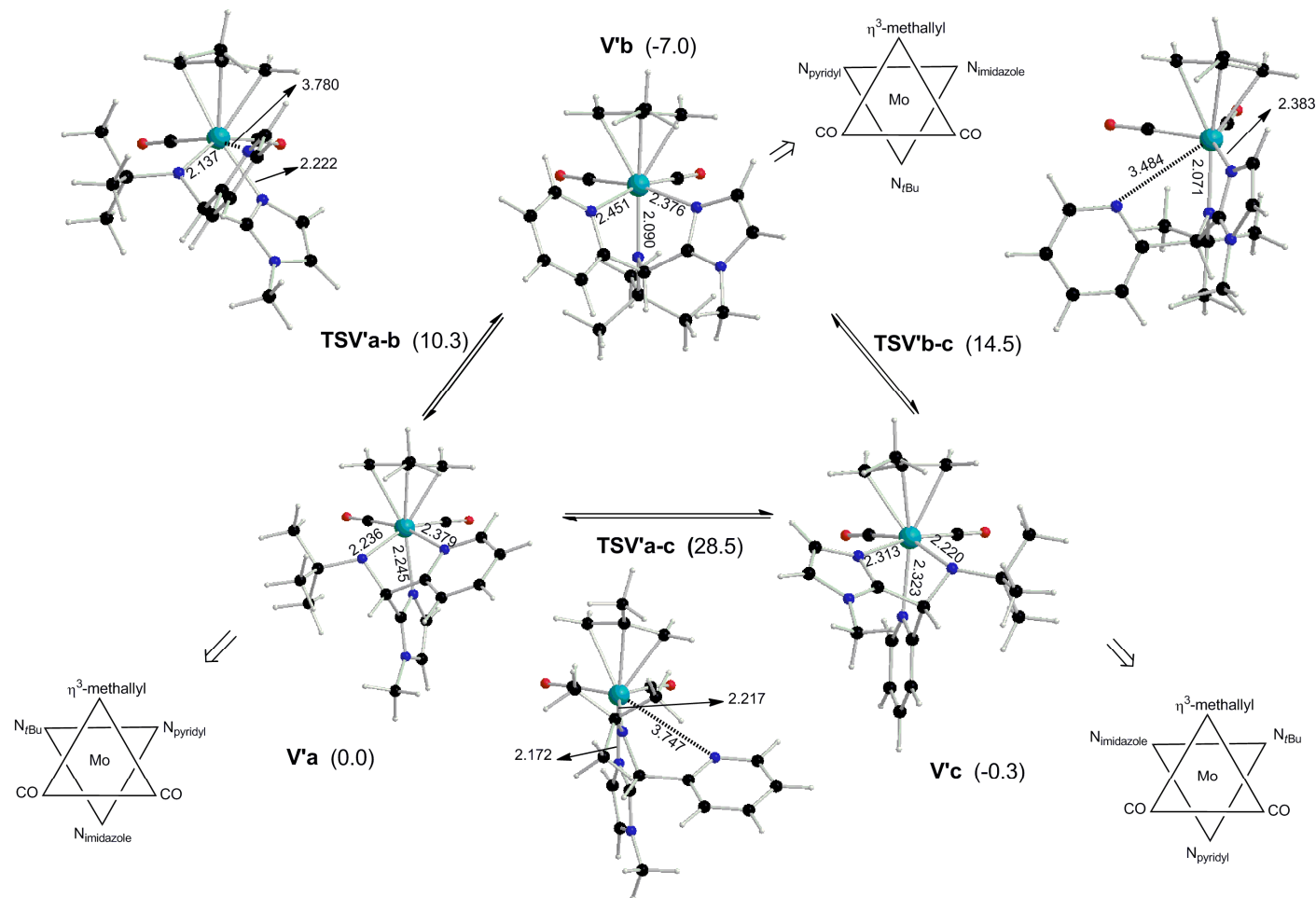


Figure S3. CPCM-B3LYP/6-31+G(d) (LANL2DZ + f for Mo) optimized structures of the different $C_{imidazole}-C_{imine}$ coupling conformers formed in the deprotonation of $[Mo(\eta^3-C_4H_7)(CO)_2(N-MeIm)(py-2-CH=N-tBu)]^+$ and the TS connecting them. CPCM-B3LYP-D3/6-311++G(d,p) (LANL2DZ + f for Mo)//CPCM-B3LYP/6-31+G(d) (LANL2DZ + f for Mo) Gibbs energies in THF solution referred to $V'a$ (in kcal/mol) are given in parentheses. Most relevant distances are also included in angstroms.

CONCLUSIONES

1. Los compuestos $[\text{Re}(\text{CO})_3(\text{bipy-R}^{\wedge})(\text{N-RIm})]\text{OTf}$ ($\text{R}^{\wedge} = \text{}^t\text{Bu, OMe, NMe}_2$, $\text{R} = \text{Me, Mes}$) reaccionan con la base fuerte $\text{KN}(\text{SiMe}_3)_2$ para dar lugar a la desprotonación del grupo CH central del ligando N-alquilimidazol. Los productos neutros que resultan de la desprotonación son muy inestables y reaccionan con electrófilos para dar lugar a la formación de distintas especies dependiendo de los sustituyentes en las posiciones 4,4' de la bipyridina.

2. El empleo de sustituyentes moderadamente dadores (*tert*-butilo, metoxi) no evita el ataque nucleófilo del imidazol desprotonado sobre la bipy, de manera que se obtienen productos de acoplamiento C-C. La densidad electrónica aportada por estos sustituyentes hace más reactivos a los anillos piridínicos frente a la reacción posterior con electrófilos, obteniéndose productos de apertura heterocíclica también en los complejos con N-MesIm cuando reaccionan con MeOTf en exceso. Además, la reacción de las especies desprotonadas que contienen bipy-OMe con HOTf da lugar a la protonación del grupo CH contiguo al que ha experimentado el acoplamiento, formándose un grupo dihidropiridilo. Esta reactividad, difiere de la encontrada para las especies con bipy-^tBu en las que se producía la protonación del nitrógeno del anillo piridínico desaromatizado.

3. Cuando los sustituyentes de la bipy son grupos muy σ -dadores, el producto resultante de la desprotonación evoluciona cambiando su modo de coordinación de N- a C-coordinado, para dar el complejo 2-imidazolilo, evitando así el ataque sobre la bipyridina. Éstos son precursores de complejos con ligandos NHC, que se obtienen por protonación o metilación del nitrógeno no sustituido del ligando 2-imidazolilo.

4. Los complejos $[\text{Re}(\text{CO})_3(\text{N-RIm})_x(\text{py-R}^{\wedge})_{3-x}]^+$ reaccionan con $\text{KN}(\text{SiMe}_3)_2$ y un oxidante para dar lugar, selectivamente, a los productos de acoplamiento cruzado deshidrogenativo entre el imidazol y la piridina, obteniéndose ligandos piridilimidazol. Los compuestos análogos con 3 piridinas monodentadas iguales reaccionan de la misma forma dando lugar a complejos con un ligando 2,2'-bipyridina. En el caso de los compuestos mixtos $[\text{Re}(\text{CO})_3(\text{py-NMe}_2)_2(\text{py-R}^{\wedge})]\text{BAR}_4^f$ ($\text{R}^{\wedge} = \text{H, OMe}$) se obtienen los productos de acoplamiento cruzado selectivamente, con ligandos bipyridina asimétricos, y no se observan productos de homoacoplamiento.

5. La reacción de los compuestos $[\text{Re}(\text{CO})_3(\text{N-RIm})(\text{pimR}^{\wedge})]\text{OTf}$ con $\text{KN}(\text{SiMe}_3)_2$ da lugar a la desprotonación del grupo CH central del N-alquilimidazol, que ataca selectivamente al carbono *orto* del grupo piridilo del ligando 2,2'-piridilimidazol, que resulta, por tanto, desaromatizado. La adición de HOTf conduce a la protonación del nitrógeno piridínico, que se transforma en un nitrógeno de tipo amino.

6. La desprotonación del grupo CH central del imidazol de los compuestos $[\text{Mo}(\eta^3\text{-C}_4\text{H}_7)(\text{CO})_2(\text{py-2-CH=N-R})(\text{N-MeIm})]\text{OTf}$ da lugar al acoplamiento entre el imidazol y el grupo CH imínico formando, de este modo, un ligando tridentado. La posterior adición de HOTf protona el nitrógeno originamente imínico, que pasa de ser de tipo amino. Estudios teóricos confirman que el ataque al carbono imínico es energéticamente más favorable que los ataques a las posiciones *orto* de la piridina, o que la evolución a un ligando 2-imidazolilo.

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