Electronic Supporting Information

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Benzannulated Re(I)-NHC complexes: Synthesis, photophysical properties and antimicrobial activity

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Contents

1. Crystallographic data

Table 1: Crystallographic data for compounds **2b**, **3a**, **3c** and **4a**.

Compound	**2b**	**3a**	**3c**	**4a**
Empirical formula	$C_{31}H_{27}N_2P$	$C_{11}H_6N_2O_4ReBr$	$C_{21}H_{18}N_2O_4ReBr$	$C_{21}H_{18}N_4O_4ReBr$
Formula weight	458.51	496.29	628.48	656.50
Temperature [K]	173(2)	173(2)	173(2) K	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P-1	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a [Å]	9.426(8)	7.4456(2)	15.8757(5)	10.1361(4)
b [Å]	9.712(8)	14.2674(4)	19.1959(5)	12.5694(4)
c [Å]	13.810(11)	24.4414(7)	7.0599(2)	17.6326(6)
α [°]	86.810(18)	90	90	90
β [°]	79.90(2)	90	91.732(2)	92.792(4)
γ [°]	84.897(15)	90	90	90
Volume [$Å^3$]	1238.7(17)	2596.39(13)	2150.51(11)	2243.81(14)
Z	2	8	4	4
Density (calculated) [Mg/m^3]	1.229	2.539	1.941	1.943
F(000)	484	1824	1200	1256
θ range [°]	2.923 to 27.495	2.860 to 27.497	3.076 to 27.496	2.824 to 29.997
Reflections collected / unique	12951/ 5648	26383 / 5924	21527 / 4925	37715 / 6390
Data / restraints / parameters	5648/ 0 / 307	5924 / 0 / 343	4925 / 0 / 263	6390 / 0 / 282
Goodness-of-fit on F^2	1.030	1.148	1.161	0.973
R_1/ wR_2 [I>2σ (I)]	0.0683 / 0.1757	0.0246 / 0.0557	0.0209 / 0.0501	0.0239 / 0.0416
R_1/ wR_2 (all data)	0.0800 / 0.1932	0.0263 / 0.0565	0.0233 / 0.0514	0.0369 / 0.0445
CCDC Number	1504039	1504036	1504037	1504038

Table 2: Crystallographic data for compounds **4b**, **4c**, **5a** and **5c**.

Compound	**4b**	**4c**	**5a**	**5c**
Empirical formula	$C_{28}H_{22}N_4O_3ReBrCl_2$	$C_{30}H_{26}N_4O_3ReBr$	$C_{24}H_{22}N_4O_5ReBr$	$C_{33}H_{30}N_4O_4ReBr$
Formula weight	799.50	756.66	712.56	812.72
Temperature [K]	173(2)	173(2)	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	28.4252(15)	11.1298(5)	11.113(13)	18.0169(4)
b [Å]	8.7539(5)	20.0627(9)	13.659(15)	28.4257(6)
c [Å]	23.4708(14)	14.1870(6)	17.18(2)	12.1002(3)
α [°]	90	90	90	90
β [°]	93.646(5)	101.435(4)	91.820(17)	99.558(2)
γ [°]	90	90	90	90
Volume [$Å^3$]	5828.5(6)	3105.0(2)	2607(5)	6111.0(2)
Z	8	4	4	8
Density (calculated) [Mg/m^3]	1.822	1.619	1.816	1.767
F(000)	3088	1472	1376	3184
θ range [°]	2.872 to 27.499	2.945 to 27.496	2.363 to 27.498	2.864 to 27.499
Reflections collected / unique	27340 / 6666	30694 / 7097	26529 / 5939	61683/ 14006
Data / restraints / parameters	6666 / 0 / 380	7097 / 0 / 355	5939 / 0 / 320	14006 / 0 / 788
Goodness-of-fit on F^2	1.133	0.997	1.060	1.092
R_1/ wR_2 [$I>2\sigma(I)$]	0.0369 / 0.0669	0.0289 / 0.0589	0.0348 / 0.0834	0.0303 / 0.0650
R_1/ wR_2 (all data)	0.0492 / 0.0732	0.0420 / 0.0635	0.0388 / 0.0861	0.0418 / 0.0695
CCDC Number	1504040	1504043	1504041	1564565

Table 3: Crystallographic data for compound **6a**.

Compound	**6a**
Empirical formula	$C_{28}H_{30}N_4O_3ReBr$
Formula weight	736.67
Temperature [K]	173(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	10.943(2)
b [Å]	21.014(4)
c [Å]	14.500(3)
α [°]	90
β [°]	107.75(3)
γ [°]	90
Volume [$Å^3$]	3175.7(12)
Z	4
Density (calculated) [Mg/m^3]	1.541
F(000)	1440
θ range [°]	3.154 to 27.500
Reflections collected / unique	51233 / 7250
Data / restraints / parameters	7250 / 0 / 334
Goodness-of-fit on F^2	1.144
R_1/ wR_2 [I>2σ (I)]	0.0323 / 0.0726
R_1/ wR_2 (all data)	0.0436 / 0.0818
CCDC Number	1504042

2. ORTEP plots of compounds 2b, 5a, 5c and 6a.

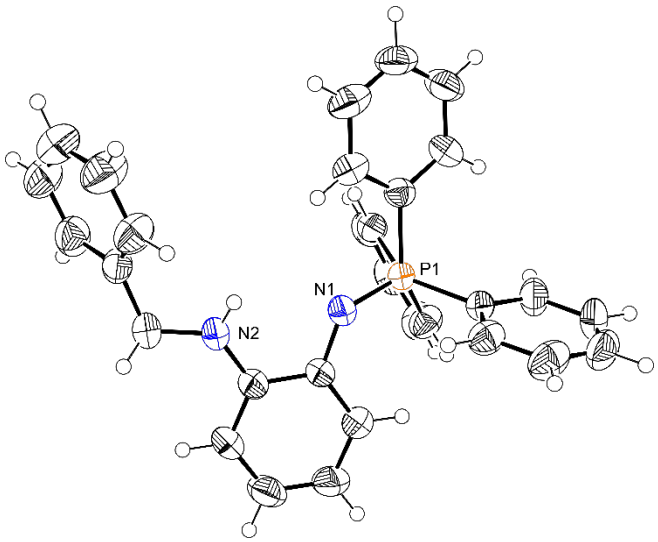


Figure 1: ORTEP plot of compound **2b**. Ellipsoids are drawn at 50% probability.

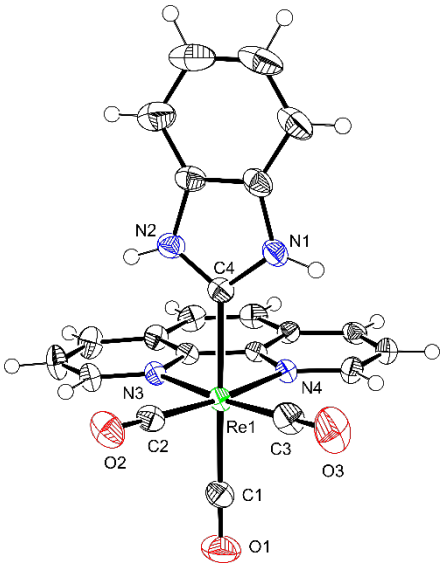


Figure 2: ORTEP plot of compound **5a**. Ellipsoids are drawn at 50% probability. The bromide counterion and two molecules of cocrystallized methanol were omitted for clarity.

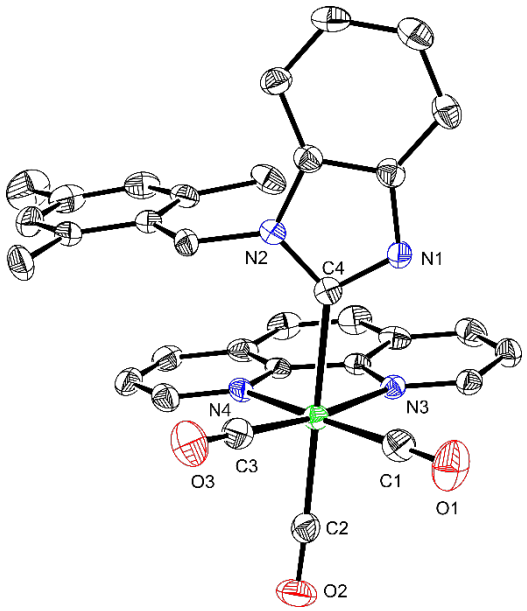


Figure 3: ORTEP plot of compound **5c**. Ellipsoids are drawn at 50% probability. A second molecule of **5c** as well as the bromide counterions and two molecules of methanol were omitted for clarity.

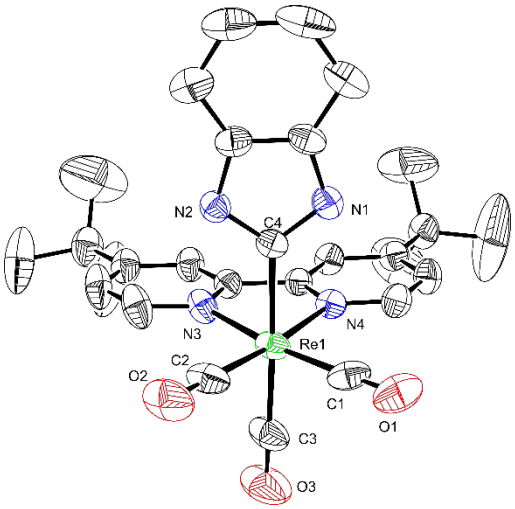


Figure 4: ORTEP plot of compound **6a**. Ellipsoids are drawn at 50% probability. The bromide counterion and hydrogen atoms were omitted for clarity.

3. Selected bond lengths and angles of the complexes

Table 4: Selected bond lengths and angles for complexes **3a** and **3c**.

3a		**3c**	
Re(1)-C(1)	1.938(9)	Re(1)-C(1)	1.995(3)
Re(1)-C(2)	2.004(9)	Re(1)-C(2)	1.911(3)
Re(1)-C(3)	1.987(8)	Re(1)-C(3)	1.975(3)
Re(1)-C(4)	2.005(9)	Re(1)-C(4)	2.022(3)
Re(1)-C(5)	2.166(6)	Re(1)-C(5)	2.181(3)
Re(1)-Br(1)	2.6436(8)	Re(1)-Br(1)	2.6394(3)
C(1)-O(1)	1.109(10)	C(1)-O(1)	1.130(4)
C(2)-O(2)	1.140(10)	C(2)-O(2)	1.144(4)
C(3)-O(3)	1.136(9)	C(3)-O(3)	1.137(4)
C(4)-O(4)	1.131(10)	C(4)-O(4)	1.117(4)
C(5)-N(1)	1.344(9)	C(5)-N(1)	1.350(4)
C(5)-N(2)	1.353(9)	C(5)-N(2)	1.361(4)
C(1)-Re(1)-C(3)	91.5(3)	C(2)-Re(1)-C(3)	92.09(14)
C(1)-Re(1)-C(4)	91.8(3)	C(2)-Re(1)-C(1)	89.59(14)
C(3)-Re(1)-C(4)	90.8(3)	C(3)-Re(1)-C(1)	91.02(13)
C(1)-Re(1)-C(2)	93.3(4)	C(2)-Re(1)-C(4)	92.58(14)
C(3)-Re(1)-C(2)	92.1(3)	C(3)-Re(1)-C(4)	87.84(13)
C(4)-Re(1)-C(2)	174.1(3)	C(1)-Re(1)-C(4)	177.59(13)
C(1)-Re(1)-C(5)	91.2(3)	C(2)-Re(1)-C(5)	97.74(13)
C(3)-Re(1)-C(5)	177.2(3)	C(3)-Re(1)-C(5)	169.73(12)
C(4)-Re(1)-C(5)	90.0(3)	C(1)-Re(1)-C(5)	92.00(12)
C(2)-Re(1)-C(5)	86.8(3)	C(4)-Re(1)-C(5)	88.76(12)
C(1)-Re(1)-Br(1)	177.1(2)	C(2)-Re(1)-Br(1)	175.84(11)
C(3)-Re(1)-Br(1)	90.9(2)	C(3)-Re(1)-Br(1)	86.01(10)
C(4)-Re(1)-Br(1)	89.9(2)	C(1)-Re(1)-Br(1)	86.75(9)
C(2)-Re(1)-Br(1)	84.9(3)	C(4)-Re(1)-Br(1)	91.05(9)
C(5)-Re(1)-Br(1)	86.41(19)	C(5)-Re(1)-Br(1)	84.36(7)

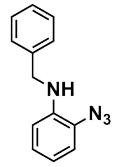
Table 5: Selected bond lengths and angles for complexes **4a**, **4b** and **4c**.

4a		**4b**		**4c**	
Re(1)-C(1)	1.913(3)	Re(1)-C(1)	1.915(5)	Re(1)-C(1)	1.913(4)
Re(1)-C(2)	1.970(3)	Re(1)-C(2)	1.969(5)	Re(1)-C(2)	1.924(4)
Re(1)-C(3)	1.929(3)	Re(1)-C(3)	1.922(5)	Re(1)-C(3)	1.958(4)
Re(1)-C(4)	2.163(3)	Re(1)-C(4)	2.189(4)	Re(1)-C(4)	2.186(4)
Re(1)-N(3)	2.185(2)	Re(1)-N(3)	2.184(3)	Re(1)-N(3)	2.184(3)
Re(1)-N(4)	2.185(2)	Re(1)-N(4)	2.192(3)	Re(1)-N(4)	2.183(3)
C(1)-O(1)	1.157(3)	C(1)-O(1)	1.145(5)	C(1)-O(1)	1.158(4)
C(2)-O(2)	1.137(3)	C(2)-O(2)	1.133(5)	C(2)-O(2)	1.152(5)
C(3)-O(3)	1.149(3)	C(3)-O(3)	1.140(5)	C(3)-O(3)	1.140(5)
C(4)-N(1)	1.357(3)	C(4)-N(1)	1.361(5)	C(4)-N(1)	1.347(4)
C(4)-N(2)	1.347(3)	C(4)-N(2)	1.350(5)	C(4)-N(2)	1.376(4)
C(3)-Re(1)-C(1)	88.50(12)	C(1)-Re(1)-C(3)	88.2(2)	C(1)-Re(1)-C(2)	86.02(16)
C(3)-Re(1)-C(2)	91.29(11)	C(1)-Re(1)-C(2)	87.59(18)	C(1)-Re(1)-C(3)	90.53(16)
C(1)-Re(1)-C(2)	90.83(11)	C(3)-Re(1)-C(2)	89.00(18)	C(2)-Re(1)-C(3)	87.11(17)
C(3)-Re(1)-C(4)	90.80(11)	C(1)-Re(1)-N(3)	97.71(17)	C(1)-Re(1)-N(4)	174.15(14)
C(1)-Re(1)-C(4)	91.18(10)	C(3)-Re(1)-N(3)	172.99(16)	C(2)-Re(1)-N(4)	99.26(14)
C(2)-Re(1)-C(4)	177.14(10)	C(2)-Re(1)-N(3)	95.06(15)	C(3)-Re(1)-N(4)	92.26(14)
C(3)-Re(1)-N(4)	99.19(10)	C(1)-Re(1)-C(4)	95.30(16)	C(1)-Re(1)-N(3)	100.52(14)
C(1)-Re(1)-N(4)	172.10(9)	C(3)-Re(1)-C(4)	85.82(17)	C(2)-Re(1)-N(3)	173.24(13)
C(2)-Re(1)-N(4)	90.76(9)	C(2)-Re(1)-C(4)	173.97(17)	C(3)-Re(1)-N(3)	91.07(15)
C(4)-Re(1)-N(4)	86.98(8)	N(3)-Re(1)-C(4)	89.80(13)	N(4)-Re(1)-N(3)	74.29(11)
C(3)-Re(1)-N(3)	173.46(10)	C(1)-Re(1)-N(4)	171.80(16)	C(1)-Re(1)-C(4)	90.70(15)
C(1)-Re(1)-N(3)	97.43(10)	C(3)-Re(1)-N(4)	99.95(17)	C(2)-Re(1)-C(4)	90.12(15)
C(2)-Re(1)-N(3)	91.37(9)	C(2)-Re(1)-N(4)	91.33(16)	C(3)-Re(1)-C(4)	176.88(15)
C(4)-Re(1)-N(3)	86.34(8)	N(3)-Re(1)-N(4)	74.28(13)	N(4)-Re(1)-C(4)	86.77(12)
N(4)-Re(1)-N(3)	74.79(8)	C(4)-Re(1)-N(4)	86.55(13)	N(3)-Re(1)-C(4)	91.52(13)

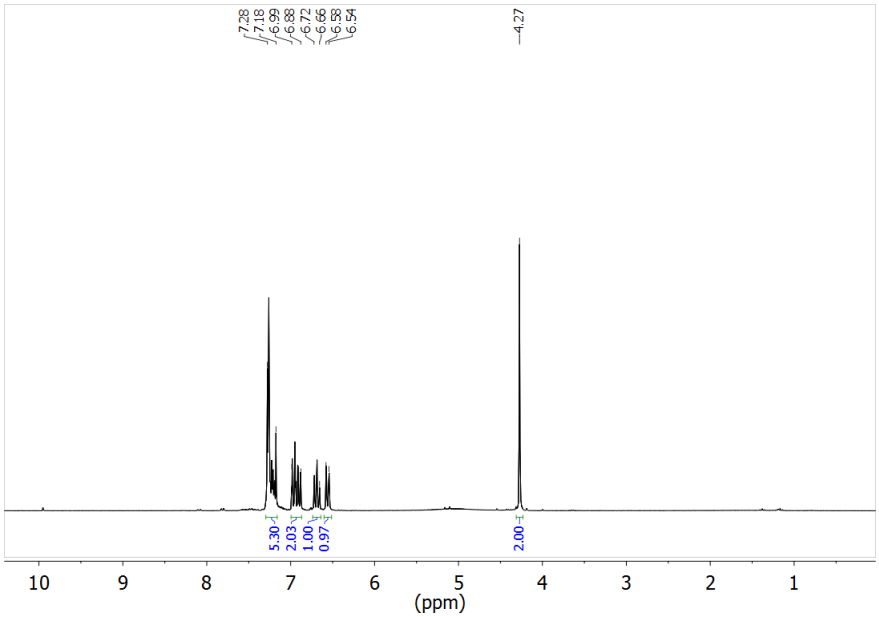
Table 6: Selected bond lengths and angles for complexes **5a**, **5c** and **6a**.

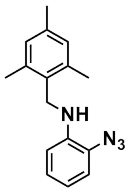
5a		**5c**		**6a**	
Re(1)-C(1)	1.976(5)	Re(1)-C(1)	1.920(4)	Re(1)-C(1)	1.921(5)
Re(1)-C(2)	1.924(4)	Re(1)-C(2)	1.951(4)	Re(1)-C(2)	1.917(4)
Re(1)-C(3)	1.902(5)	Re(1)-C(3)	1.912(4)	Re(1)-C(3)	1.953(5)
Re(1)-C(4)	2.177(4)	Re(1)-C(4)	2.182(3)	Re(1)-C(4)	2.167(4)
Re(1)-N(3)	2.172(4)	Re(1)-N(3)	2.180(3)	Re(1)-N(3)	2.174(4)
Re(1)-N(4)	2.185(4)	Re(1)-N(4)	2.189(3)	Re(1)-N(4)	2.173(3)
C(1)-O(1)	1.139(5)	C(1)-O(1)	1.143(5)	C(1)-O(1)	1.143(6)
C(2)-O(2)	1.157(5)	C(2)-O(2)	1.152(4)	C(2)-O(2)	1.145(5)
C(3)-O(3)	1.157(6)	C(3)-O(3)	1.155(4)	C(3)-O(3)	1.143(6)
C(4)-N(1)	1.358(5)	C(4)-N(1)	1.354(4)	C(4)-N(1)	1.348(5)
C(4)-N(2)	1.332(5)	C(4)-N(2)	1.359(4)	C(4)-N(2)	1.352(5)
C(3)-Re(1)-C(2)	87.2(2)	C(3)-Re(1)-C(1)	87.41(16)	C(2)-Re(1)-C(1)	88.8(2)
C(3)-Re(1)-C(1)	90.8(2)	C(3)-Re(1)-C(2)	88.70(16)	C(2)-Re(1)-C(3)	88.78(19)
C(2)-Re(1)-C(1)	90.64(19)	C(1)-Re(1)-C(2)	89.41(16)	C(1)-Re(1)-C(3)	90.3(2)
C(3)-Re(1)-N(3)	173.69(16)	C(3)-Re(1)-N(3)	173.28(13)	C(2)-Re(1)-C(4)	89.47(16)
C(2)-Re(1)-N(3)	98.78(15)	C(1)-Re(1)-N(3)	96.56(13)	C(1)-Re(1)-C(4)	91.28(17)
C(1)-Re(1)-N(3)	91.05(15)	C(2)-Re(1)-N(3)	96.74(13)	C(3)-Re(1)-C(4)	177.62(18)
C(3)-Re(1)-C(4)	92.27(19)	C(3)-Re(1)-C(4)	91.54(15)	C(2)-Re(1)-N(4)	173.66(18)
C(2)-Re(1)-C(4)	92.71(17)	C(1)-Re(1)-C(4)	90.68(15)	C(1)-Re(1)-N(4)	97.11(17)
C(1)-Re(1)-C(4)	175.55(16)	C(2)-Re(1)-C(4)	179.74(14)	C(3)-Re(1)-N(4)	93.35(16)
N(3)-Re(1)-C(4)	85.54(13)	N(3)-Re(1)-C(4)	83.01(12)	C(4)-Re(1)-N(4)	88.23(13)
C(3)-Re(1)-N(4)	98.20(17)	C(3)-Re(1)-N(4)	100.78(14)	C(2)-Re(1)-N(3)	99.55(18)
C(2)-Re(1)-N(4)	173.65(15)	C(1)-Re(1)-N(4)	171.54(13)	C(1)-Re(1)-N(3)	171.46(16)
C(1)-Re(1)-N(4)	92.58(17)	C(2)-Re(1)-N(4)	88.64(13)	C(3)-Re(1)-N(3)	91.5(2)
N(3)-Re(1)-N(4)	75.70(13)	N(3)-Re(1)-N(4)	75.50(11)	C(4)-Re(1)-N(3)	87.24(14)
C(4)-Re(1)-N(4)	83.81(15)	C(4)-Re(1)-N(4)	91.24(12)	N(4)-Re(1)-N(3)	74.44(12)

4. ^{1}H NMR spectra of the presented compounds

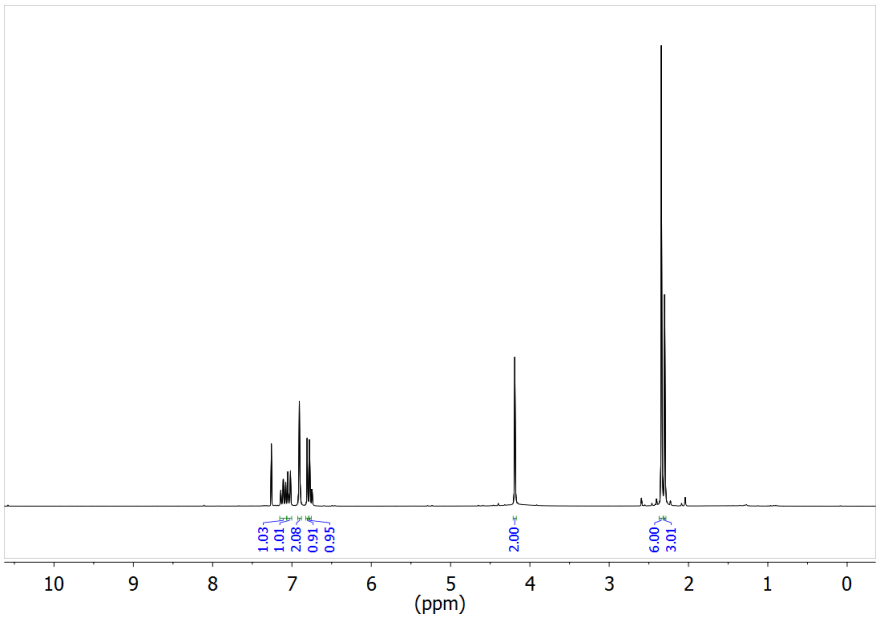


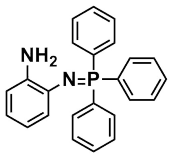
^{1}H NMR (250 MHz, $CDCl_3$)



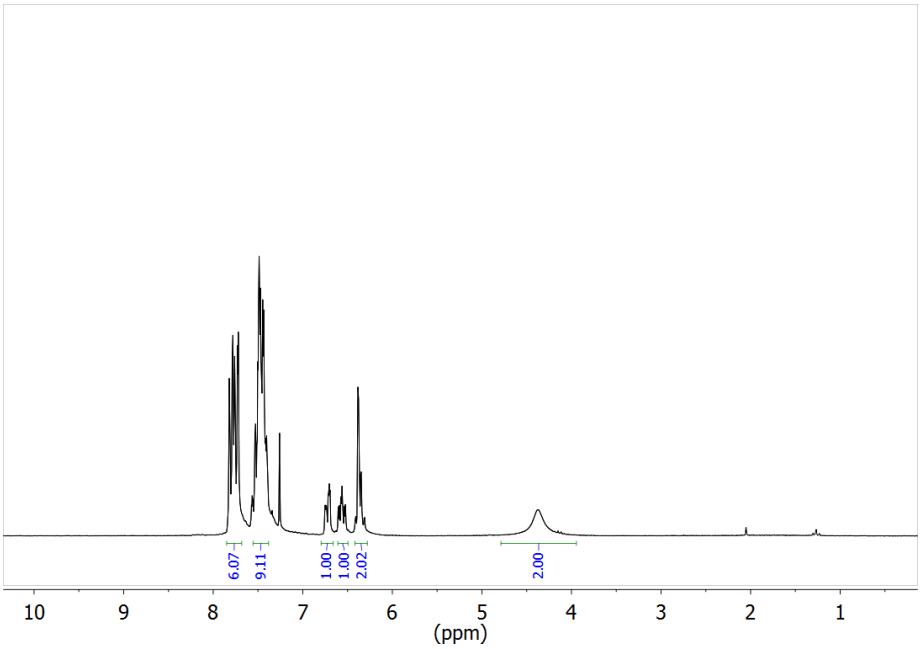


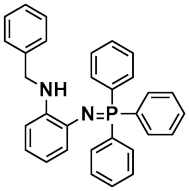
^{1}H NMR (250 MHz, $CDCl_3$)



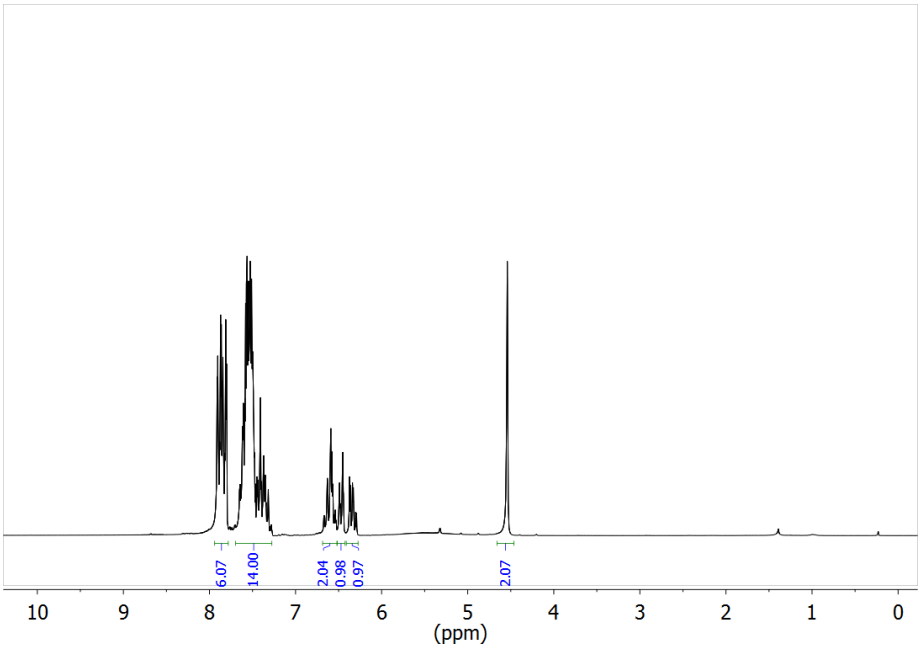


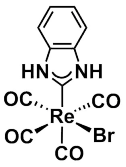
^{1}H NMR (250 MHz, $CDCl_3$)



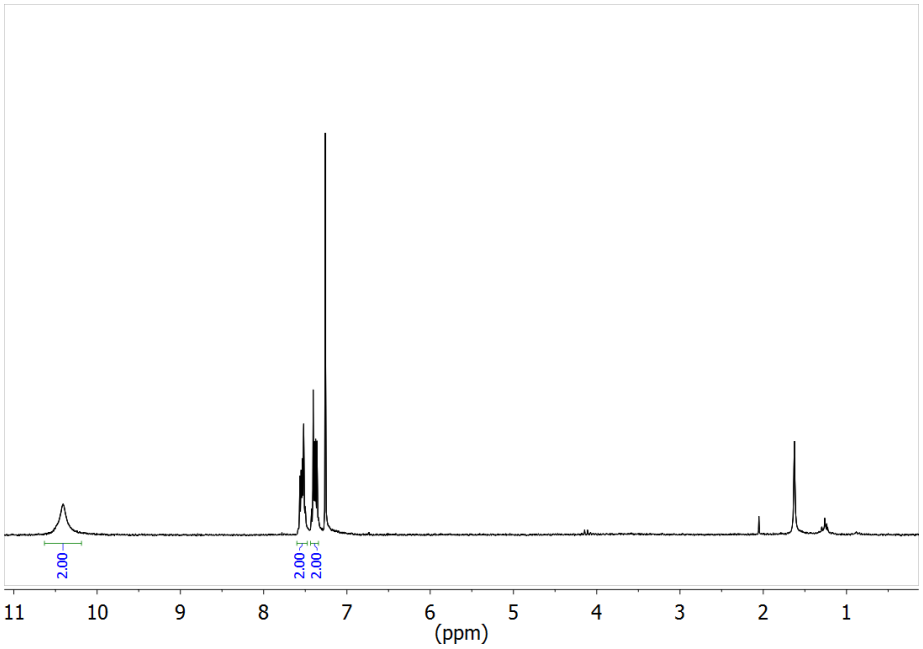


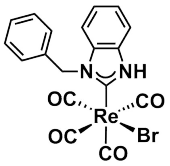
^{1}H NMR (250 MHz, CD_2Cl_2)



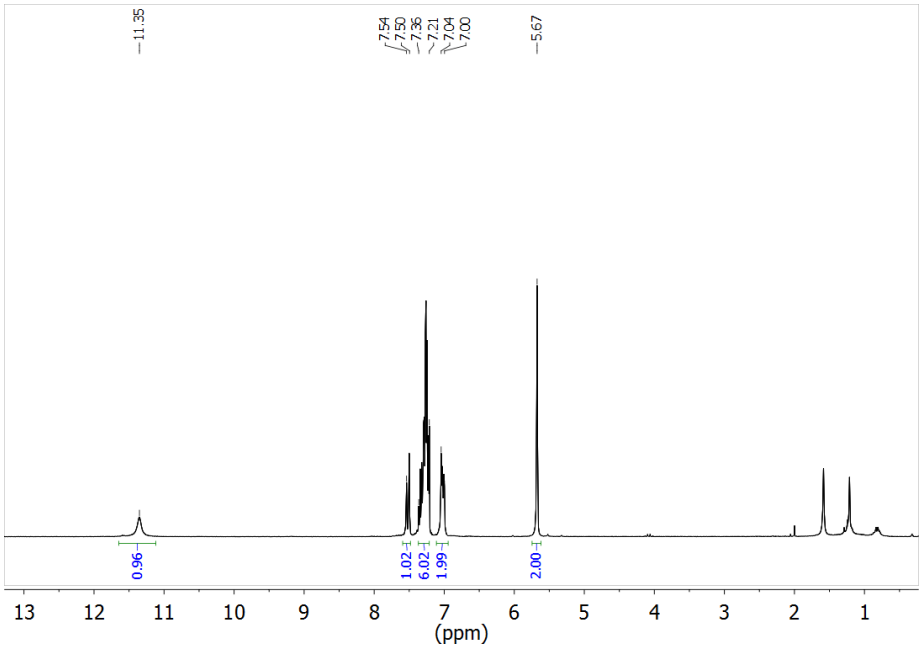


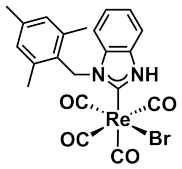
^{1}H NMR (200 MHz, $CDCl_3$)



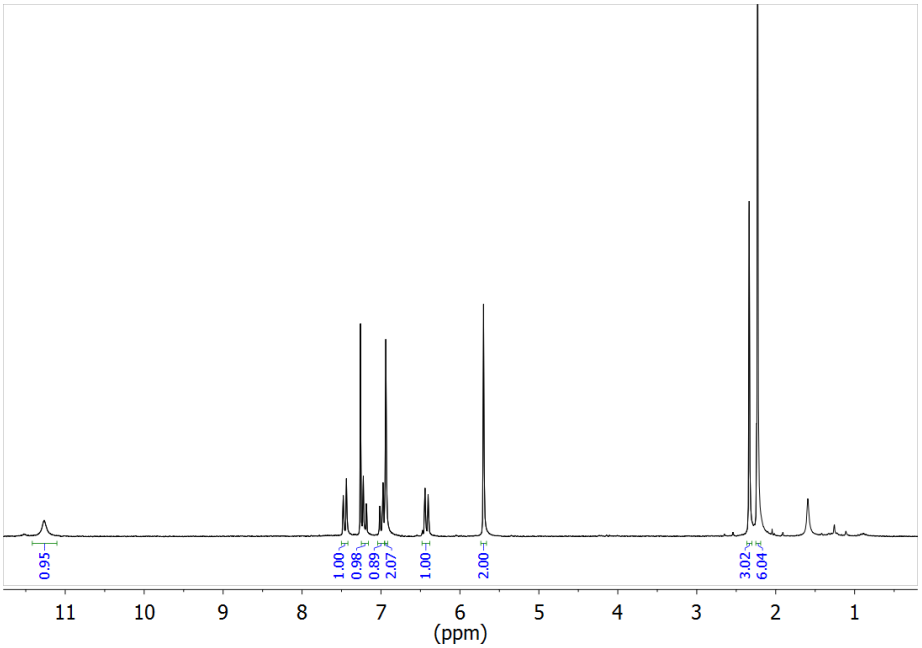


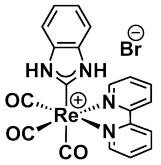
^{1}H NMR (200 MHz, $CDCl_3$)



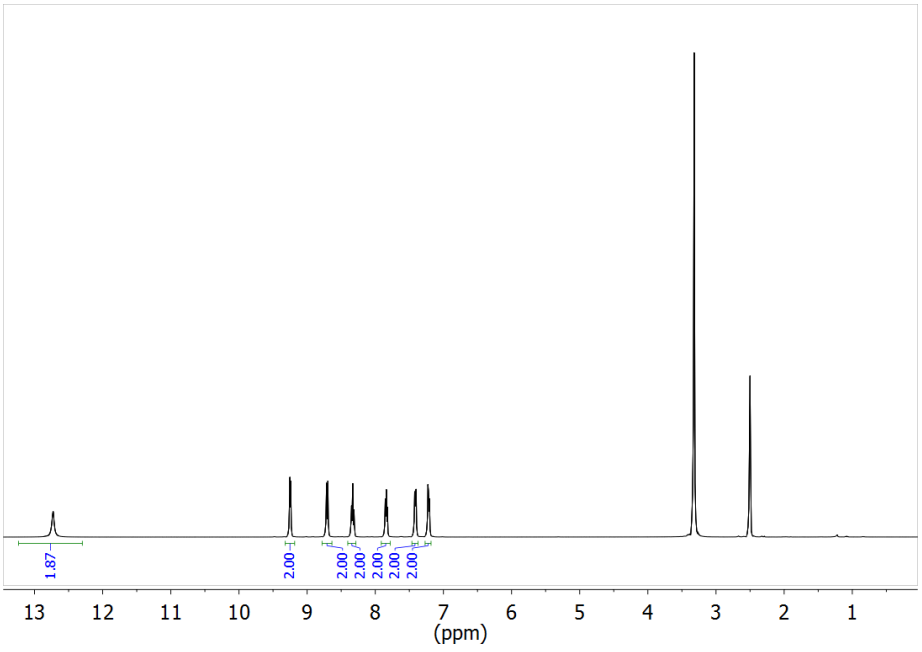


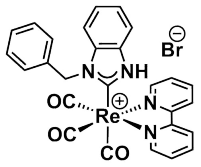
^{1}H NMR (250 MHz, $CDCl_3$)



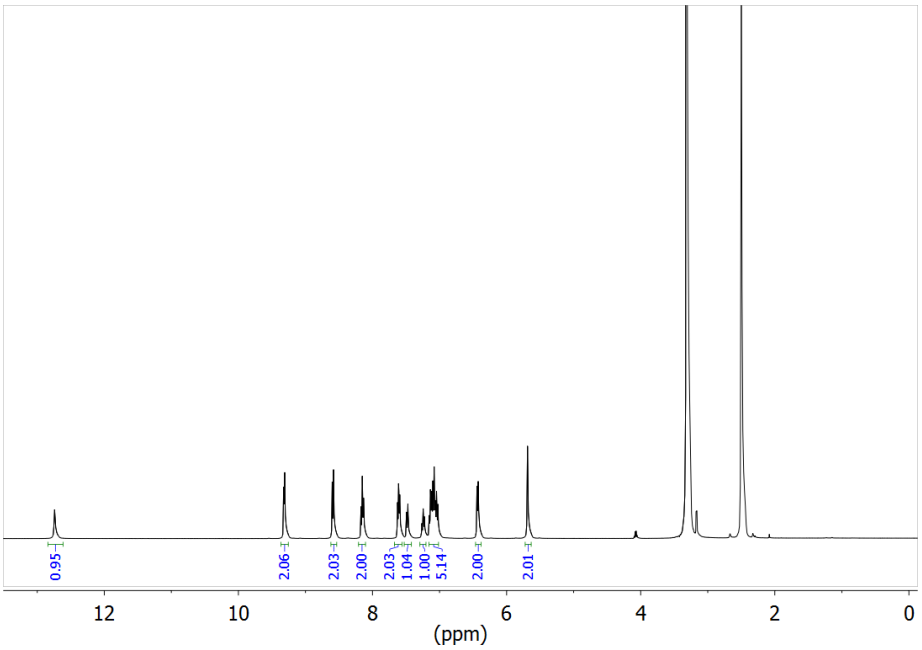


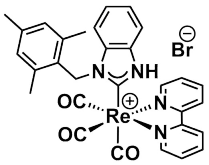
^{1}H NMR (400 MHz, DMSO[d_6])



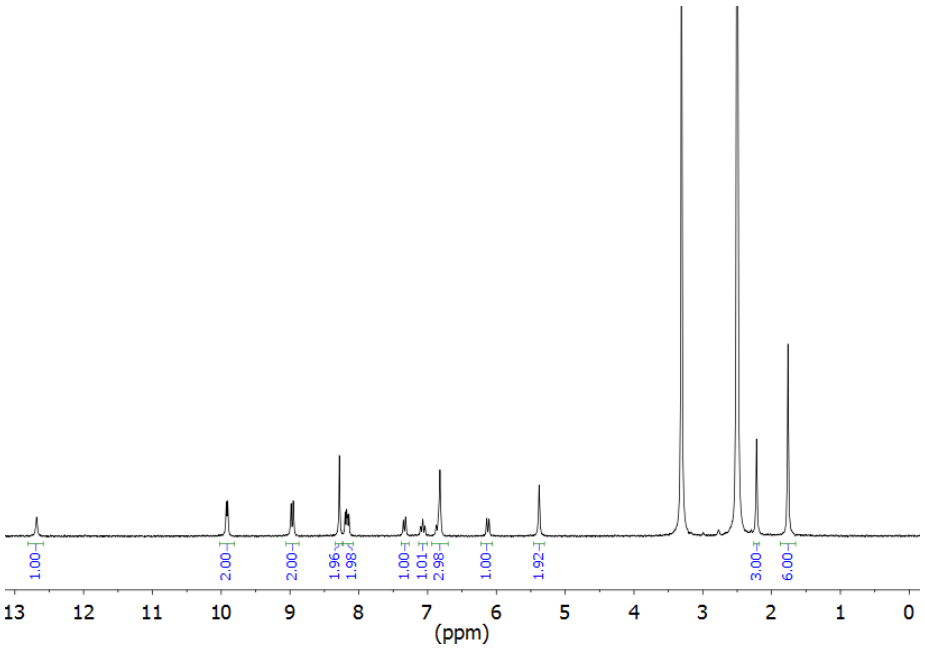


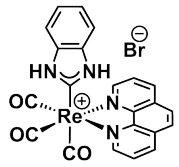
^{1}H NMR (400 MHz, DMSO[d_6])



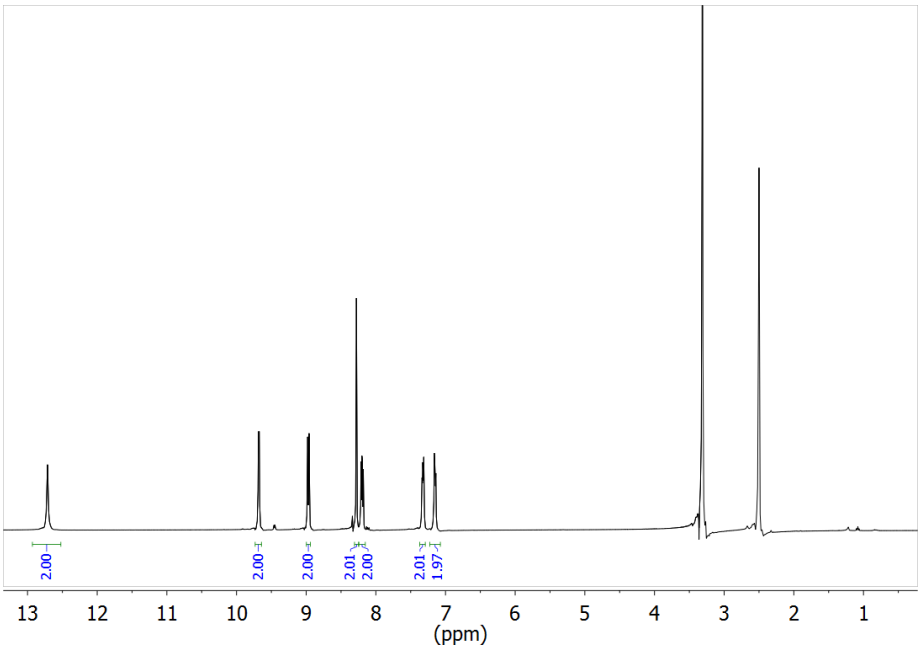


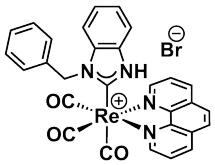
^{1}H NMR (400 MHz, DMSO[d_6])



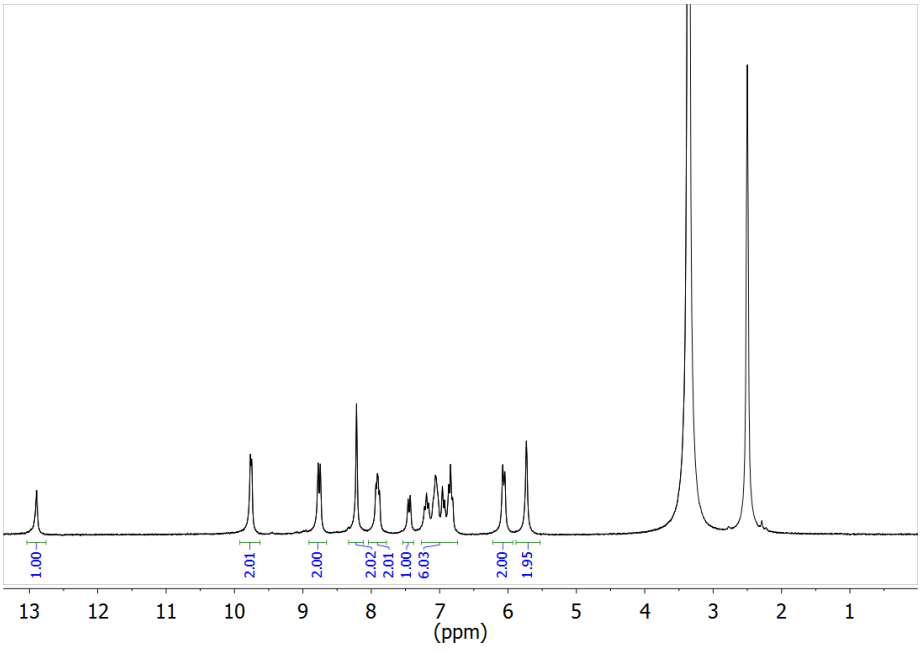


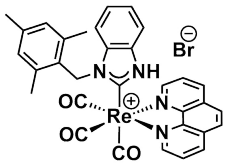
^{1}H NMR (400 MHz, DMSO[d_6])



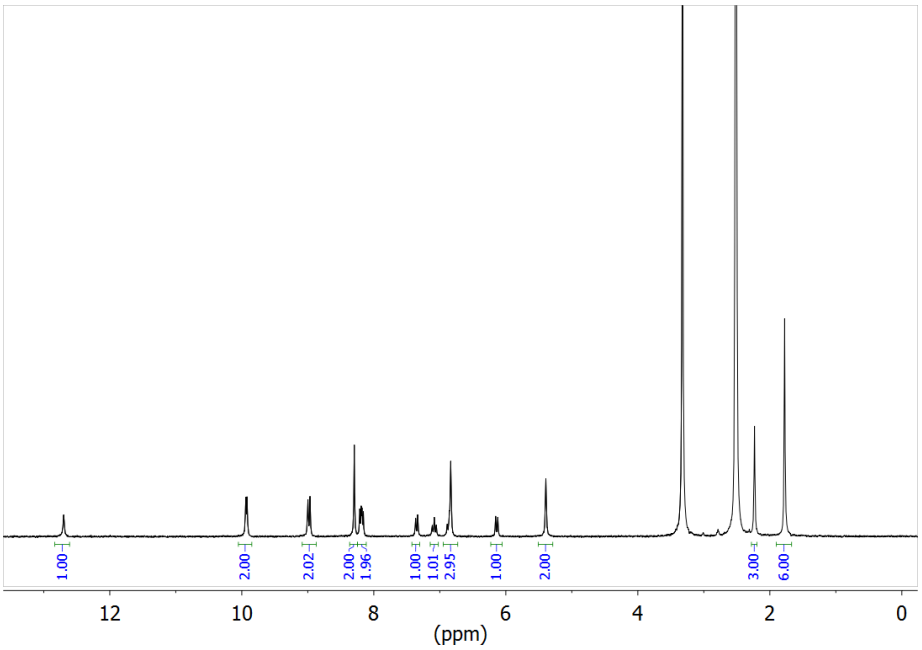


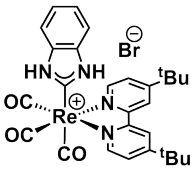
^{1}H NMR (250 MHz, DMSO[d_6])



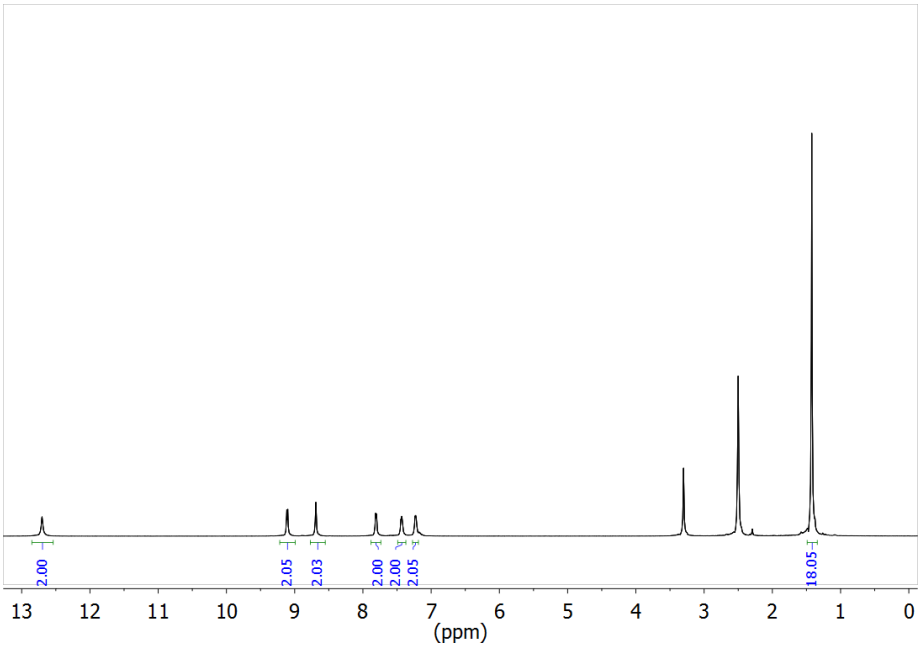


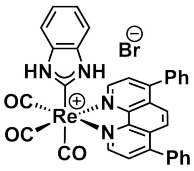
^{1}H NMR (250 MHz, DMSO[d_6])



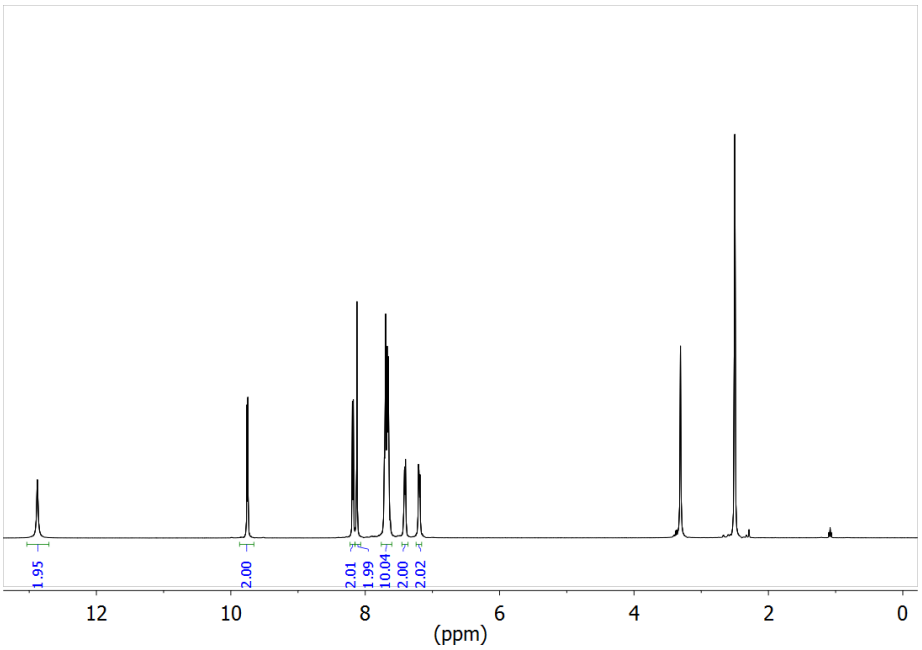


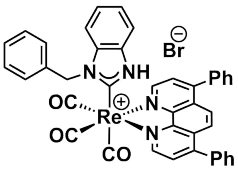
^{1}H NMR (400 MHz, DMSO[d_6])



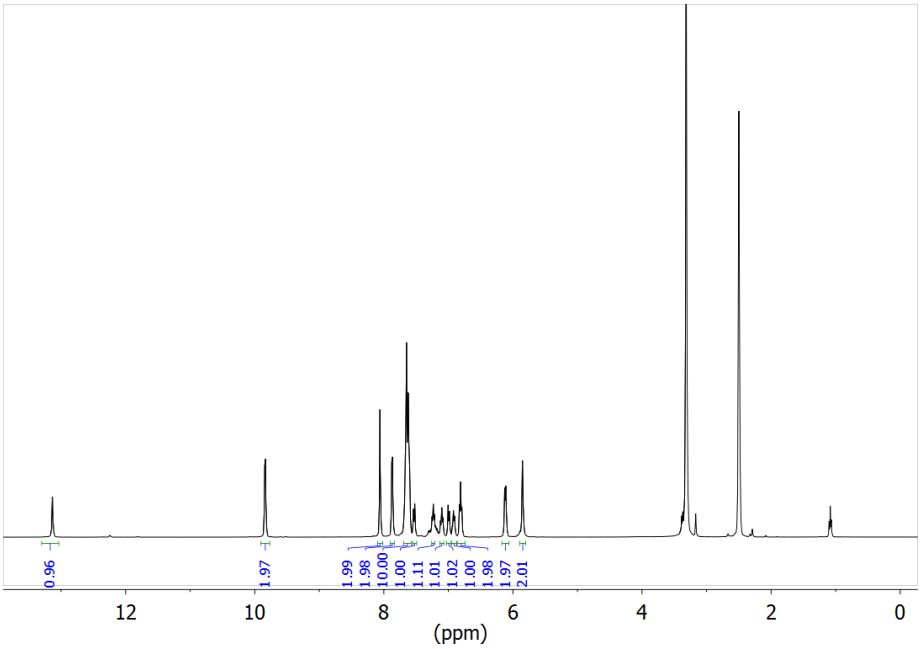


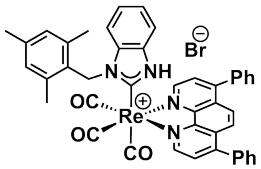
^{1}H NMR (400 MHz, DMSO[d_6])





^{1}H NMR (400 MHz, DMSO[d_6])





^{1}H NMR (250 MHz, DMSO[d_6])