Electronic Supplementary Information

1,10-Penanthroline ring-opening mediated by cis-{Re(CO)$_2$} complexes

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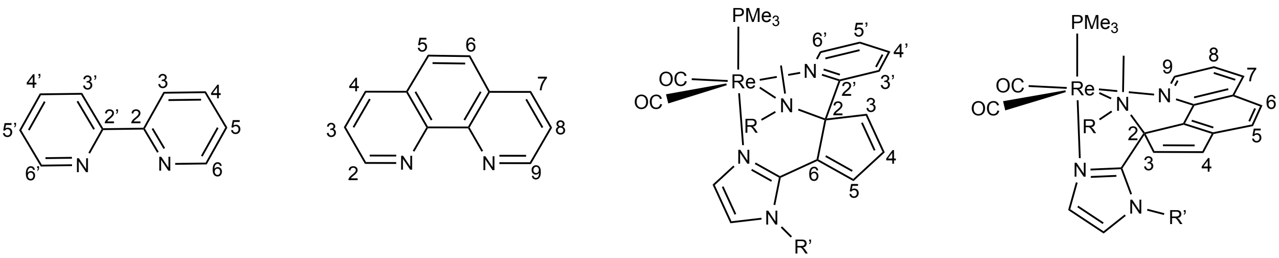
Experimental Section

General: All manipulations were carried out under an argon atmosphere using Schlenk techniques. Solvents were distilled from Na (hexane), Na/benzophenone (THF and Et_2O) and CaH_2 (MeCN and CH_2Cl_2). Compounds *fac*-[Re(CO)$_3$(N-N)(OTf)] (N-N= bipy, phen) were prepared as previously reported.[1] Deuterated dichloromethane, was stored under nitrogen in a Young tube and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400, Bruker Advance 300 or DPX-300 spectrometer. NMR spectra are referred to the internal residual solvent peak for ^{1}H and ^{13}C{^{1}H} NMR. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm. CaF_2 cells.
NMR Labelling Schemes:



Synthesis of *fac*-[Re(bipy)(CO)$_3$(PMe$_3$)]OTf.[2] PMe$_3$ (38 μL, 0.43 mmol) was added to a solution of *fac*-[Re(bipy)(CO)$_3$(OTf)] (210 mg, 0.36 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred at room temperature overnight. Then, the solution was evaporated under reduced pressure 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 (1 × 20 mL) and dried under vacuum. Yield: 220 mg (93 %). IR (CH_2Cl_2, cm^{-1}): 2038, 1952, 1923 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): δ 8.98 [d (J= 5.4 Hz), 2H, $H_{6,6'}$], 8.75 [d (J= 8.2 Hz), 2H, $H_{3,3'}$], 8.32 [m, 2H, $H_{4,4'}$], 7.72 [m, 2H, $H_{5,5'}$], 1.13 [d (J_{HP}= 9.0 Hz), 9H, P(CH_3)$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 195.0 [d (J_{CP}= 7.5 Hz), 2*C*O], 188.4 [d (J_{CP}= 59.9 Hz), *C*O], 156.0 [$C_{2,2'}$], 153.6 [$C_{6,6'}$], 141.4 [$C_{4,4'}$], 129.0 [$C_{5,5'}$], 126.1 [$C_{3,3'}$], 13.9 [d (J_{CP}= 31.9 Hz), P(*C*H$_3$)$_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2): -27.8.

Synthesis of *fac*-[Re(CO)$_3$(phen)(PMe$_3$)]OTf.[3] Complex *fac*-[Re(CO)$_3$(phen)(PMe$_3$)]OTf was prepared as described above for the synthesis of the bipy analog starting from *fac*-[Re(bipy)(CO)$_3$(OTf)] (200 mg, 0.33 mmol) and PMe$_3$ (35 μL, 0.40 mmol). Compound *fac*-[Re(CO)$_3$(phen)(PMe$_3$)]OTf was obtained as a yellow solid. Yield: 210 mg (95 %). IR (CH_2Cl_2, cm^{-1}): 2038, 1953, 1926 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): δ 9.39 [d (J= 4.6 Hz), 2H, $H_{2,9}$], 8.87 [d (J= 8.3 Hz), 2H, $H_{4,7}$], 8.27 [s, 2H, $H_{5,6}$], 8.10 [m, 2H, $H_{3,8}$], 1.00 [d (J_{HP}= 8.4 Hz), 9H, P(CH_3)$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 195.1 [d (J_{CP}= 6.7 Hz), 2*C*O], 188.4 [d (J_{CP}= 60.7 Hz), *C*O], 154.4 [$C_{2,9}$], 146.9, 132.0 [quaternary], 140.4 [$C_{4,7}$], 129.1 [$C_{5,6}$], 127.6 [$C_{3,8}$], 13.8 [d (J_{CP}= 32.0 Hz), P(*C*H$_3$)$_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2): -28.5.

Synthesis of *cis,trans*-[Re(bipy)(CO)$_2$(NCMe)(PMe$_3$)]OTf (1). Me$_3$NO·2H$_2$O (98 mg, 0.88 mmol) was added to a solution of *fac*-[Re(bipy)(CO)$_3$(PMe$_3$)]OTf (380 mg, 0.58 mmol) in MeCN (25 mL), and the mixture was refluxed for 5 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane-acetone (1:1 v/v) as eluent. The resulting orange solution was evaporated to a volume of 5 mL and addition of hexane (20 mL) caused the precipitation of compound **1** as an orange solid, which was washed with diethyl ether (20 mL), and dried under vacuum. Yield: 336 mg (87 %). IR (CH$_2$Cl$_2$, cm^{-1}): 1937, 1863 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): δ 8.98 [d (J= 5.4 Hz), 2H, H$_{6,6'}$], 8.63 [d (J= 8.0 Hz), 2H, H$_{3,3'}$], 8.23 [m, 2H, H$_{4,4'}$], 7.60 [m, 2H, H$_{5,5'}$], 2.16 [s, 3H, NCC*H$_3$*], 1.13 [d (J_{HP}= 9.2 Hz), 9H, P(C*H*$_3$)$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 201.7 [d (J_{CP}= 7.2 Hz), *C*O], 156.4 [C$_{2,2'}$], 152.7 [C$_{6,6'}$], 140.4 [C$_{4,4'}$], 128.3 [C$_{5,5'}$], 125.1 [C$_{3,3'}$], 123.0 [d (J_{CP}= 9.7 Hz), N*C*CH$_3$], 17.1 [d (J_{CP}= 35.6 Hz), P(*C*H$_3$)$_3$], 4.2 [NC*C*H$_3$]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): -21.1. Anal. Calcd. for C$_{18}$H$_{20}$F$_3$N$_3$O$_5$PReS: C 32.53, H 3.03, N 6.32. Found: C 32.49, H 3.10, N 6.20.

Synthesis of *cis,trans*-[Re(CO)$_2$(NCMe)(phen)(PMe$_3$)]OTf (2). Compound **2** was prepared as described above for compound **1**, starting from *fac*-[Re(CO)$_3$(phen)(PMe$_3$)]OTf (340 mg, 0.50 mmol) and Me$_3$NO·2H$_2$O (85 mg, 0.76 mmol). Compound **2** was obtained as an orange microcrystalline solid. Yield: 256 mg (74 %). IR (CH$_2$Cl$_2$, cm^{-1}): 1933, 1866 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.38 [d (J= 5.2 Hz), 2H, H$_{2,9}$], 8.77 [d (J= 8.0 Hz), 2H, H$_{4,7}$], 8.23 [s, 2H, H$_{5,6}$], 8.01 [dd (J= 8.0, 5.2 Hz), 2H, H$_{3,8}$], 2.06 [s, 3H, NCC*H$_3$*], 1.03 [d (J_{HP}= 9.1 Hz), 9H, P(C*H$_3$*)$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 201.6 [d (J_{CP}= 6.7 Hz), *C*O], 153.2 [C$_{2,9}$], 147.0, 131.4 [quaternary], 139.5 [C$_{4,7}$], 128.5 [C$_{5,6}$], 126.8 [C$_{3,8}$], 123.1 [d (J_{CP}= 11.2 Hz), N*C*CH$_3$), 17.0 [d (J_{CP}= 35.9 Hz), P(*C*H$_3$)$_3$], 4.1 [NC*C*H$_3$]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): -21.5. Anal. Calcd. for C$_{18}$H$_{20}$F$_3$N$_3$O$_5$PReS: C 34.88, H 2.93, N 6.10. Found: C 34.96, H 2.88, N 5.91.

Synthesis of *cis,trans*-[Re(bipy)(CO)$_2$(N-MeIm)(PMe$_3$)]OTf (1a). N-MeIm (38 μL, 0.47 mmol) was added to a solution of *cis,trans*-[Re(bipy)(CO)$_2$(NCMe)(PMe$_3$)]OTf (**1**) (240 mg, 0.36 mmol) in THF (30 mL), and the mixture was refluxed for 3 h. The solvent was evaporated under reduced pressure to a volume of 5 mL, addition of hexane (20 mL) caused the precipitation of compound **1a** as an orange solid, which was washed with hexane (2 x 20 mL), diethyl ether (2 x 20 mL), and dried under vacuum. Yield: 235 mg (92 %). IR (CH$_2$Cl$_2$, cm^{-1}): 1922, 1817 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.05 [d (J= 5.1 Hz), 2H, H$_{6,6'}$], 8.57 [d (J= 8.1 Hz), 2H, H$_{3,3'}$], 8.20 [m, 2H, H$_{4,4'}$], 7.61 [m, 2H, H$_{5,5'}$], 7.23 [s, 1H, NC*H*N N-MeIm], 6.72, 6.45 [s, 1H each, C*H* N-MeIm], 3.55 [s, 3H, C*H$_3$* N-MeIm], 1.19 [d (J_{HP}= 9.0 Hz), 9H, P(C*H$_3$*)$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 204.4 [*C*O], 156.0 [C$_{2,2'}$], 152.2 [C$_{6,6'}$], 140.1 [C$_{4,4'}$], 139.9 (N*C*HN N-MeIm), 130.2 (*C*H N-MeIm), 128.2 [C$_{5,5'}$], 125.1 [C$_{3,3'}$], 122.2 (*C*H N-MeIm), 34.7 (*C*H$_3$ N-MeIm), 17.8 [d (J_{CP}= 34.5 Hz), P(*C*H$_3$)$_3$]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): -21.2. Anal. Calcd. for C$_{20}$H$_{23}$F$_3$N$_4$O$_5$PReS: C 34.04, H 3.29, N 7.94. Found: C 34.23, H 3.18, N 7.98.

Synthesis of *cis,trans*-[Re(bipy)(CO)$_2$(N-MesIm)(PMe$_3$)]OTf (1b). N-MesIm (67 mg, 0.36 mmol) was added to a solution of *cis,trans*-[Re(bipy)(CO)$_2$(NCMe)(PMe$_3$)]OTf (**1**) (200 mg, 0.30 mmol) in THF (30 mL), and the mixture was refluxed for 3 h. The solvent was evaporated under reduced pressure to a volume of 5 mL, addition of hexane (20 mL) caused the precipitation of compound **1b** as an orange solid, which was washed with hexane (2 x 20 mL), diethyl ether (2 x 20 mL), and dried under vacuum. Yield: 210 mg (86 %). IR (CH$_2$Cl$_2$, cm^{-1}): 1923, 1849 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.08 [d (J= 4.7 Hz), 2H, H$_{6,6'}$], 8.62 [d (J= 8.3 Hz), 2H, H$_{3,3'}$], 8.23 [m, 2H, H$_{4,4'}$], 7.61 [m, 2H, H$_{5,5'}$], 7.24 [s, 1H, NC*H*N N-MesIm], 6.92 [s, 2H, Mes], 6.72, 6.58 [s, 1H each, C*H* N-MesIm], 2.28 [s, 3H, C*H$_3$* Mes], 1.69[s, 6H, C*H$_3$* Mes], 1.24 [d (J_{HP}= 8.9 Hz), 9H, P(C*H$_3$*)$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 204.4 [d (J_{CP}= 7.5 Hz), *C*O], 156.1 [C$_{2,2'}$], 152.2 [C$_{6,6'}$], 140.5, 135.1, 130.2 [quaternary Mes], 140.4 [C$_{4,4'}$], 139.8 [N*C*HN N-MesIm], 130.2 (*C*H N-MesIm), 129.6 (2×*C*H Mes), 128.4 [C$_{5,5'}$], 125.3 [C$_{3,3'}$], 122.6 [*C*H N-MesIm], 21.1[*C*H$_3$ Mes], 17.9 [d (J_{CP}= 34.7 Hz), P(*C*H$_3$)$_3$], 17.2 [2×*C*H$_3$ Mes]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): -21.2. Anal. Calcd. for C$_{28}$H$_{31}$F$_3$N$_4$O$_5$PReS: C 41.53, H 3.86, N 6.92. Found: C 41.25, H 3.60, N 6.82.

Synthesis of *cis,trans*-[Re(CO)$_2$(N-MeIm)(phen)(PMe$_3$)]OTf (2a). Compound **2a** was prepared as decribed above for **1a**, starting from *cis,trans*-[Re(CO)$_2$(NCMe)(phen)(PMe$_3$)]OTf (**2**) (262 mg, 0.38 mmol) and N-MeIm (40 μL, 0.49 mmol). Compound **2a** was obtained as an orange solid. Yield: 245 mg (88 %). IR (CH$_2$Cl$_2$, cm^{-1}): 1925, 1850 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.47 [d (J= 5.1 Hz), 2H, H$_{2,9}$], 8.72 [d (J= 8.2 Hz), 2H, H$_{4,7}$], 8.17 [s, 2H, H$_{5,6}$], 8.01 [dd (J= 8.2, 5.1 Hz), 2H, H$_{3,8}$], 7.27 [s, 1H, NC*H*N N-MeIm], 6.60, 6.28 [s, 1H each, C*H* N-MeIm], 3.46 [s, 3H, C*H$_3$* N-MeIm], 1.04 [d (J_{HP}= 8.9 Hz), 9H, P(C*H$_3$*)$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 204.4 [*C*O], 153.0 [C$_{2,9}$], 147.1, 131.5 [quaternary], 140.3 [N*C*HN N-MeIm], 139.4 [C$_{4,7}$], 129.9 [*C*H N-MeIm], 128.8 [C$_{5,6}$], 127.0 [C$_{3,8}$], 122.3 [*C*H N-MeIm], 34.8 [*C*H$_3$ N-MeIm], 17.9 [d (J_{CP}= 34.5 Hz), P(*C*H$_3$)$_3$]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): -21.6. Anal. Calcd. for C$_{22}$H$_{23}$F$_3$N$_4$O$_5$PReS: C 36.21, H 3.18, N 7.68. Found: C 36.16, H 2.97, N 7.32.

Synthesis of *cis,trans*-[Re(CO)$_2$(N-MesIm)(phen)(PMe$_3$)]OTf (2b). Compound **2b** was prepared as decribed above for **1b**, starting from *cis,trans*-[Re(CO)$_2$(NCMe)(phen)(PMe$_3$)]OTf (**2**) (230 mg, 0.33 mmol) and N-MesIm (81 mg, 0.43 mmol). Compound **2b** was obtained as an orange solid. Yield: 225 mg (82 %). IR (CH$_2$Cl$_2$, cm^{-1}): 1926, 1851 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.49 [d (J= 5.0 Hz), 2H, H$_{2,9}$], 8.76 [d (J= 8.2 Hz), 2H, H$_{4,7}$], 8.20 [s, 2H, H$_{5,6}$], 8.01 [dd (J= 8.2, 5.0 Hz), 2H, H$_{3,8}$], 7.09 [s, 1H, NC*H*N N-MesIm], 6.85 [s, 2H, Mes], 6.57, 6.47 [s, 1H each, C*H* N-MesIm], 2.24 [s, 3H, C*H$_3$* Mes], 1.49 [s, 6H, C*H$_3$* Mes], 1.14 [d (J_{HP}= 9.0 Hz), 9H, P(C*H$_3$*)$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 204.2 [d ($^2J_{CP}$= 6.8 Hz), *C*O], 152.7 [C$_{2,9}$], 146.8, 140.4, 134.9, 131.8, 131.4 [quaternary], 139.5 [N*C*HN N-MesIm], 139.4 [C$_{4,7}$], 130.1 (*C*H N-MesIm), 129.5 (2×*C*H Mes), 128.7 [C$_{5,6}$], 127.0 [C$_{3,8}$], 122.4 [*C*H N-MesIm], 21.2 [*C*H$_3$ Mes], 17.8 [d (J_{CP}= 34.8 Hz), P(*C*H$_3$)$_3$], 17.1 (2×*C*H$_3$ Mes]. ^{31}P{^{1}H} NMR

(CD_2Cl_2): -21.7. Anal. Calcd. for $C_{30}H_{31}F_3N_4O_5PReS$: C 43.21, H 3.75, N 6.72. Found: C 43.13, H 3.33, N 6.34.

Reaction of *cis,trans*-[Re(bipy)(CO)$_2$(N-MeIm)(PMe$_3$)]OTf (1a) with KN(SiMe$_3$)$_2$ and MeOTf (2 eq.). Synthesis of 3a. KN(SiMe$_3$)$_2$ (0.22 mL of a 0.5 M solution in toluene, 0.11 mmol) was added to a solution of *cis,trans*-[Re(bipy)(CO)$_2$(N-MeIm)(PMe$_3$)]OTf (**1a**) (65 mg, 0.09 mmol) in THF (20 mL) previously cooled to -78 ºC. The mixture was allowed to reach room temperature, and after 15-20 min the solvent was evaporated to dryness under reduced pressure. A solution of MeOTf (21 μL, 0.189mmol) in CH_2Cl_2 (20 mL) was added to the solid residue, and after 30 min., the mixture was filtered via canula and evaporated to dryness. The resulting brown solid was washed with diethylether (3 × 15 mL) and dried in vacuo. Slow diffusion of hexane (15 mL) into a concentrated solution of **3a** in CH_2Cl_2 (5 mL) at -20 ºC afforded crystals, one of which was used for a solid state structure determination. Yield: 46 mg (68 %). IR (CH_2Cl_2, cm^{-1}): 1929, 1850 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.72 [d (J= 5.4 Hz), 1H, $H_{6'}$], 7.88 [m, 1H, $H_{4'}$], 7.55 [s, 1H, C*H* N-MeIm], 7.41 [m, 2H, $H_{3'}$, $H_{5'}$], 7.26 [m, 1H, H_4], 7.04 [s, 1H, C*H* N-MeIm], 6.98, 6.91 [m, 1H each, H_3, H_5], 3.82 [s, 3H, CH_3 N-MeIm], 3.20 [d (J_{HP}= 3.5 Hz), 3H, CH_3 NMe$_2$], 2.63 [s, 3H, CH_3 NMe$_2$],1.61 [d (J_{HP}= 8.1 Hz), 9H, P(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 204.6 [d ($^2J_{CP}$= 6.9 Hz), *C*O], 202.2 [d ($^2J_{CP}$= 5.4 Hz), *C*O], 158.8 [$C_{2'}$], 153.5 [$C_{6'}$], 141.1 [C_4], 140.7 [$C_{4'}$], 135.8, 126.0 [C_6, N*C*N N-MeIm], 135.5 [*C*H N-MeIm], 133.9, 131.1[C_3, C_5], 126.5, 124.0 [$C_{3'}$, $C_{5'}$], 126.1 [*C*H N-MeIm], 88.6 [C_2], 56.5 [d (J_{CP}= 7.5 Hz), *C*H$_3$ NMe$_2$], 47.6 [*C*H$_3$ NMe$_2$], 37.8 [*C*H$_3$ N-MeIm], 20.5 [d (J_{CP}= 33.5 Hz), P(*C*H$_3$)$_3$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -28.5. Anal. Calcd. for $C_{22}H_{24}F_3N_4O_5PReS$: C 36.01, H 3.71, N 7.64. Found: C 35.92, H 3.40, N 7.69.

Reaction of *cis,trans*-[Re(bipy)(CO)$_2$(N-MesIm)(PMe$_3$)]OTf (1b) with KN(SiMe$_3$)$_2$ and MeOTf (2 eq.). Synthesis of 3b and 4b. Following the procedure described for the synthesis of compound **3a,** starting from *cis,trans*-[Re(bipy)(CO)$_2$(N-MesIm)(PMe$_3$)]OTf (**1b**) (60 mg, 0.074 mmol), KN(SiMe$_3$)$_2$ (0.18 mL of a 0.5 M solution in toluene, 0.089 mmol), and MeOTf (16 μL, 0.148 mmol), a mixture of compounds **3b** and **4b** was obtained. Slow diffusion of hexane (20 mL) into a concentrated solution of the mixture of **3b** and **4b** in CH_2Cl_2 (5 mL) afforded orange (**3b**) and yellow crystals (**4b**), which could be only partially separated. One of the yellow crystals was employed for the X-ray structure determination of compound **4b**. IR (CH_2Cl_2, cm^{-1}): 1927, 1849 (ν_{CO}). **Compound 3b**: ^1H NMR (CD_2Cl_2): δ 8.76 [d (J= 5.5 Hz), 1H, $H_{6'}$], 7.86 [m, 1H, $H_{4'}$], 7.77 [s, 1H, C*H* N-MesIm], 7.42 [m, 1H, $H_{5'}$], 7.34 [m, 1H, $H_{3'}$], 7.08 [s, 1H , Mes], 6.95 [m, 4H, C*H* N-MesIm, Mes, H_3, H_4], 5.48 [m, 1H, H_5], 3.22 [d (J_{HP}= 3.4 Hz), 3H, CH_3 NMe$_2$], 2.64 [s, 3H, CH_3 NMe$_2$], 2.35, 2.00 [s, 3H each, CH_3 Mes], 1.64 [d (J_{HP}= 8.4 Hz), 9H, P(CH_3)$_3$], 1.24 [s, 3H, CH_3 Mes]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 204.6 [d (J_{CP}= 5.5 Hz), *C*O], 202.1 [d (J_{CP}= 4.7 Hz), *C*O], 158.9 [$C_{2'}$], 153.5 [$C_{6'}$], 141.4, 139.9, 135.8, 134.8, 134.3, 132.9, [quaternary], 141.0 [C_3], 140.7 [$C_{4'}$], 136.9 [*C*H N-MesIm], 130.7 [C_5], 130.1, 129.6 [*C*H Mes], 126.5 [$C_{5'}$], 124.3 [$C_{3'}$], 123.3 [*C*H N-MesIm], 88.5 [C_2], 56.6 [d (J_{CP}= 7.2 Hz), *C*H$_3$ NMe$_2$], 47.7 [CH$_3$

NMe_2], 21.3 [CH_3 N-MesIm], 20.5 [d (J_{CP}= 33.9 Hz), P(CH_3)$_3$], 17.9, 16.6 [CH_3 N-MesIm]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -28.4. **<u>Compound 4b</u>**: ^1H NMR (CD_2Cl_2): δ 8.73 [d (J= 5.4 Hz), 1H, $H_{6'}$], 7.73 [m, 1H, $H_{4'}$], 7.69 [s, 1H, C*H* N-MesIm], 7.28 [m, 1H, $H_{5'}$], 7.22 [d (J= 5.4 Hz), 1H, H_3], 7.19 [d (J= 8.3 Hz), 1H, $H_{3'}$], 7.08, 6.95 [s, 1H each, Mes], 6.90 [s, 1H, C*H* N-MesIm], 6.73 [s, 1H, H_4], 6.09 (s_{br}, 1H, N*H*], 5.48 [m, 1H, H_5], 2.56 [d (J= 5.9 Hz), 3H, N(H)(C*H*$_3$)], 2.64 [s, 3H, C*H*$_3$ NMe_2], 2.35, 2.00 [s, 3H each, C*H*$_3$ Mes], 1.64 [d (J_{HP}= 8.4 Hz), 9H, P(C*H*$_3$)$_3$], 1.28 [s, 3H, C*H*$_3$ Mes]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 205.1 [d (J_{CP}= 7.8 Hz), *C*O], 202.8 [d (J_{CP}= 6.3 Hz), *C*O], 159.9 [$C_{2'}$], 153.1 [$C_{6'}$], 141.1, 135.3, 134.9, 134.1, 133.2, 119.0 [quaternary], 140.3 [C_3], 139.7 [$C_{4'}$], 138.1 [C_4], 137.1 [*C*H N-MesIm], 131.1 [C_5], 130.4, 130.3 [*C*H Mes], 125.5 [$C_{5'}$], 123.6 [*C*H N-MesIm], 122.3 [$C_{3'}$], 83.4 [C_2], 36.2 [N(H)(*C*H$_3$)], 21.3 [CH_3 N-MesIm], 18.7 [d (J_{CP}= 34.4 Hz), P(*C*H$_3$)$_3$], 17.8, 16.5 [*C*H$_3$ N-MesIm]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -20.8.

Reaction of *cis,trans*-[Re(CO)$_2$(N-MeIm)(phen)(PMe$_3$)]OTf (2a) with KN(SiMe$_3$)$_2$ and MeOTf (2 eq.). Synthesis of 5a and 6a. KN(SiMe$_3$)$_2$ (0.15 mL of a 0.5 M solution in toluene, 0.075 mmol) was added to a solution of *cis,trans*-[Re(CO)$_2$(N-MeIm)(phen)(PMe$_3$)]OTf (**2a**) (45 mg, 0.062 mmol) in THF (25 mL) previously cooled to -78 ºC. The mixture was allowed to reach room temperature, and after 20 min the solvent was evaporated to dryness under reduced pressure. A solution of MeOTf (17 μL, 0.15 mmol) in CH_2Cl_2 (15 mL) was added to the residue and stirred for 30 min. The resulting slurry was then filtered via canula, concentrated under vacuum to a volume of 5 mL, and the addition of hexane (20 mL) caused the precipitation of a brown solid, which was washed with hexane (2 x 20 mL) and dried under vacuum. Slow diffusion of hexane (10 mL) into a concentrated solution in CH_2Cl_2 (5 mL) at room temperature, afforded orange crystals of **5a**, one of which was used for a solid-state structure determination by X-ray diffraction. Crystallization of the mother liquor by slow diffusion of hexane (15 mL) into a concentrated solution in CH_2Cl_2 (5 mL) at -20 ºC, afforded orange crystals of **6a**. **<u>Compound 5a</u>**: Yield: 17 mg (36 %). IR (CH_2Cl_2, cm^{-1}): 1930, 1848 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.42 [dd (J= 5.3, 1.5 Hz), 1H, H_9], 8.49 [dd (J= 8.3, 1.5 Hz), 1H, H_7], 8.13, 7.82 [d (J= 8.3 Hz), 1H each, H_5 and H_6], 7.69 [d (J= 5.8 Hz), 1H, H_3/H_4], 7.45 [dd (J= 8.3, 5.3 Hz), 1H, H_8], 7.34 [s, 1H, C*H* N-MeIm], 7.19 [d (J= 5.8 Hz), 1H, H_3/H_4], 6.84 [d (J= 1.2 Hz), 1H, C*H* N-MeIm], 3.53 [s, 3H, C*H*$_3$ N-MeIm], 3.29 [s, 3H, C*H*$_3$ NMe_2], 2.56 [d (J_{HP}= 1.9 Hz), 3H, C*H*$_3$ NMe_2], 1.51 [d ($^2J_{HP}$= 8.2 Hz), 9H, P(C*H*$_3$)$_3$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 159.0 [C_9], 144.5, 141.2, 130.1, 115.8, 115.4 [quaternay], 142.0 [C_3/C_4], 141.3 [C_7], 134.2 [C_5/C_6], 132.6 [C_3/C_4],131.3, 126.0 [*C*H N-MeIm], 124.2 [C_5/C_6], 122.2 [C_8], 81.2 [C_2], 55.4 [*C*H$_3$ NMe_2], 45.7 [d ($^3J_{CP}$= 2.9 Hz), *C*H$_3$ NMe_2], 36.8 [*C*H$_3$ N-MeIm], 19.6 [d (J_{CP}= 33.4 Hz), P(*C*H$_3$)$_3$]. Unfortunately, the signals corresponding to the CO ligands are not observed, probably due to their low intensity, and to the low solubility of compound **5a** in CD_2Cl_2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -23.4. Anal. Calcd. for $C_{24}H_{27}F_3N_4O_5PReS$: C 38.04, H 3.59, N 7.39. Found: C 39.18, H 3.67, N 7.18. **<u>Compound 6a</u>**: Yield: 14 mg (31 %). IR (CH_2Cl_2, cm^{-1}): 1917, 1835 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.68 [d (J= 5.2 Hz), 1H, H_9], 8.35 [dd (J= 8.3, 1.7 Hz), 1H, H_7], 8.04 [d (J= 8.2 Hz), 1H, H_5/H_6], 7.71 [d (J=

8.2 Hz), 1H, H_5/H_6], 7.59 [d (*J*= 5.7 Hz), 1H, H_3/H_4], 7.40 [d (*J*= 5.7 Hz), 1H, H_3/H_4], 7.33 [dd (*J*= 8.3, 5.2 Hz), 1H, H_8], 7.07, 6.72 [d (*J*= 1.6 Hz), 1H each, C*H* N-MeIm], 6.11 [s_{br}, 1H, N*H*], 3.51 [s, 3H, CH_3 N-MeIm], 2.51 [d (*J*= 5.9 Hz), 3H, N(H)(CH_3)], 1.65 [d (J_{HP}= 9.2 Hz), 9H, P(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 205.9 [d (J_{CP} = 8.1 Hz), *C*O], 202.7 [d (J_{CP} = 7.2 Hz), *C*O], 161.1 [C_9], 149.3, 145.2, 142.1, 133.8, 129.6 [quaternay], 139.3, 139.2, 138.6 [C_7, C_3 and C_4], 133.4 [C_5/C_6], 129.2, 125.0 [*C*H N-MeIm], 123.2 [C_5/C_6], 122.1 [C_8], 75.0 [C_2], 36.4 [*C*H_3 N-MeIm], 35.2 [N(H)(*C*H_3)], 18.6 [d (J_{CP}= 34.7 Hz), P(*C*H_3)$_3$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -18.5. Anal. Calcd. for $C_{23}H_{25}F_3N_4O_5PReS{\cdot}0.25$hex: C 38.45, H 3.75, N 7.32. Found: C 38.81, H 3.34, N 7.14.

Reaction of *cis,trans*-[Re(CO)$_2$(N-MeIm)(phen)(PMe$_3$)]OTf (2a) with KN(SiMe$_3$)$_2$ and MeI (2 eq.). Synthesis of 5a/I. KN(SiMe$_3$)$_2$ (0.13 mL of a 0.5 M solution in toluene, 0.065 mmol) was added to a solution of *cis,trans*-[Re(CO)$_2$(N-MeIm)(phen)(PMe$_3$)]OTf (**2a**) (40 mg, 0.055 mmol) in THF (25 mL) previously cooled to -78 ºC. The mixture was allowed to reach room temperature, and after 20 min the solvent was evaporated to dryness under reduced pressure. A solution of freshly passes through alumina MeI (7 μL, 0.11 mmol) in CH_2Cl_2 (15 mL) was added to the residue and stirred overnight. The resulting slurry was then filtered via canula, concentrated under vacuum to a volume of 5 mL, and the addition of hexane (20 mL) caused the precipitation of a brown solid, which was washed with hexane (2 x 20 mL) and dried under vacuum. Compound 5a/I was obtained as a brown solid. Yield: 18 mg (45 %). IR (CH_2Cl_2, cm^{-1}): 1927, 1846 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.42 [d (*J*= 4.9 Hz), 1H, H_9], 8.54 [dd (*J*= 8.1 Hz), 1H, H_7], 8.16, 7.85 [d (*J*= 8.4 Hz), 1H each, H_5 and H_6], 7.74 [d (*J*= 5.7 Hz), 1H, H_3/H_4], 7.48 [m, 1H, H_8], 7.35 [d (*J*= 5.7 Hz), 1H, H_3/H_4], 7.32, 6.89 [s, 1H each, C*H* N-MeIm], 3.58 [s, 3H, CH_3 N-MeIm], 3.31 [s, 3H, CH_3 NMe$_2$], 2.55 [d (J_{HP}= 1.7 Hz), 3H, CH_3 NMe$_2$], 1.51 [d (J_{HP}= 5.2 Hz), 9H, P(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 158.9 [C_9], 146.3, 144.5, 141.1, 135.2, 130.1 [quaternay], 142.0 [C_3/C_4], 141.3 [C_7], 134.1 [C_5/C_6], 133.1 [C_3/C_4],131.2, 126.1 [*C*H N-MeIm], 124.2 [C_8], [C_5/C_6], 122.2, 81.1 [C_2], 55.7 [*C*H_3 NMe$_2$], 45.7 [d (J_{CP}= 2.6 Hz), *C*H_3 NMe$_2$], 37.1 [*C*H_3 N-MeIm], 19.6 [d (J_{CP}= 33.5 Hz), P(*C*H_3)$_3$]. Unfortunately, the signals corresponding to the CO ligands are not observed, probably due to their low intensity, and to the low solubility of compound **5a/I** in CD_2Cl_2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -22.8.

Reaction of *cis,trans*-[Re(CO)$_2$(N-MesIm)(phen)(PMe$_3$)]OTf (2b) with KN(SiMe$_3$)$_2$ and MeOTf (2 eq.). Synthesis of 5b. KN(SiMe$_3$)$_2$ (0.13 mL of a 0.5 M solution in toluene, 0.065 mmol) was added to a solution of *cis,trans*-[Re(CO)$_2$(N-MeIm)(phen)(PMe$_3$)]OTf (**2a**) (45 mg, 0.054 mmol) in THF (25 mL) previously cooled to -78 ºC. The mixture was allowed to reach room temperature, and after 30 min the solvent was evaporated to dryness under reduced pressure. A solution of MeOTf (12 μL, 0.11 mmol) in CH_2Cl_2 (15 mL) was added to the residue and stirred for 30 min. The resulting slurry was then filtered via canula, concentrated under vacuum to a volume of 5 mL, and the addition of hexane (20 mL) caused the precipitation of a brown solid, which was washed with diethyl ether (2 x

20 mL) and dried under vacuum. Slow diffusion of hexane (10 mL) into a concentrated solution in CH_2Cl_2 (5 mL) at room temperature, afforded light red crystals of **5b**, one of which was used for a solid-state structure determination by X-ray diffraction. Yield: 25 mg (57 %). IR (CH_2Cl_2, cm^{-1}): 1930, 1849 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): δ 9.47 [d (J= 5.2 Hz), 1H, H_9], 8.54 [d (J= 8.1 Hz), 1H, H_7], 8.14, 7.65 [d (J= 8.3 Hz), 1H each, H_5 and H_6], 7.57 [s, 1H, C*H* N-MesIm], 7.50 [dd (J= 8.1, 5.2 Hz), 1H, H_8], 7.04 [s, 1H, Mes], 6.85 [s, 1H, C*H* N-MesIm], 6.78 [m, 2H, H_3/H_4 and Mes], 6.23 [d (J= 5.7 Hz), 1H, H_3/H_4], 3.30 [s, 3H, CH_3 NMe_2], 2.51 [s_{br}, 3H, CH_3 NMe_2], 2.35, 2.13 (s, 3H each, CH_3 Mes), 1.54 (d (J_{HP}= 8.4 Hz), 9H, $P(CH_3)_3$), 0.64 (s, 3H, CH_3 Mes). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 207.3 [d (J_{CP} = 6.4 Hz), *C*O], 159.2 [C_9], 145.1, 141.4, 140.9, 135.9, 134.3, 131.9, 130.4, 129.9, 126.2 [quaternay], 141.6 [C_7], 139.8 [Mes], 134.5 [C_5/C_6], 132.7 [*C*H N-MesIm], 130.1, 129.7, 129.5 [Mes, C_3, C_4], 124.8 [*C*H N-MesIm], 123.7 [C_5/C_6], 122.3 [C_8], 80.7 [C_2], 55.1 [CH_3 NMe_2], 45.7 [d (J_{CP}= 2.9 Hz), CH_3 NMe_2], 21.3 [CH_3 Mes], 19.5 [d (J_{CP}= 33.6 Hz), $P(CH_3)_3$], 18.2, 16.1 [CH_3 Mes]. Unfortunately, the signals corresponding to one of the CO ligands is not observed, probably due to its low intensity, and to the low solubility of compound **5b** in CD_2Cl_2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -23.3. Anal. Calcd. for $C_{32}H_{35}F_3N_4O_5PReS$: C 44.59, H 4.09, N 6.50. Found: C 44.46, H 3.92, N 6.25.

Reaction of *cis,trans*-[Re(CO)$_2$(N-MesIm)(phen)(PMe$_3$)]OTf (2b) with KN(SiMe$_3$)$_2$ and MeI (2 eq.). Synthesis of 5b/I. Following the procedure described for the synthesis of compound **5a/I,** starting from *cis,trans*-[Re(CO)$_2$(N-MesIm)(phen)(PMe$_3$)]OTf (**1b**) (40 mg, 0.048 mmol), $KN(SiMe_3)_2$ (0.12 mL of a 0.5 M solution in toluene, 0.060 mmol), and MeI (6 μL, 0.096 mmol), allowed the isolation of compound **5b/I** as a brown solid. Yield: 21 mg (52 %). IR (CH_2Cl_2, cm^{-1}): 1930, 1849 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): δ 9.48 [d (J= 5.2 Hz), 1H, H_9], 8.59 [d (J= 8.3 Hz), 1H, H_7], 8.18, 7.66 [d (J= 8.3 Hz), 1H each, H_5 and H_6], 7.56 [s, 1H, C*H* N-MesIm], 7.53 [m, 1H, H_8], 7.04 [s, 1H, Mes], 6.86 [s, 1H, C*H* N-MesIm], 6.81 [d (J= 5.8 Hz), 1H, H_3/H_4], 6.76 [s, 1H, Mes], 6.26 [d (J= 5.8 Hz), 1H, H_3/H_4], 3.32 [s, 3H, CH_3 NMe_2], 2.53 [d (J_{HP}= 2.0 Hz), 3H, CH_3 NMe_2], 2.35, 2.13 (s, 3H each, CH_3 Mes), 1.55 (d (J_{HP}= 8.2 Hz), 9H, $P(CH_3)_3$), 0.65 (s, 3H, CH_3 Mes). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 202.2, 201.5 [*C*O], 159.3 [C_9], 147.5, 145.1, 141.4, 140.9, 137.7, 137.1, 135.9, 135.7, 120.5 [quaternay], 141.7 [C_7], 139.8 [C_3/C_4], 134.5 [C_5/C_6], 134.5 [C_5/C_6], 132.6 [*C*H N-MesIm], 30.1 [C_3/C_4], 129.9, 129.5 [Mes], 124.8 [*C*H N-MesIm], 123.7 [C_5/C_6], 122.4 [C_8], 80.8 [C_2], 55.2 [CH_3 NMe_2], 45.8 [d (J_{CP}= 2.8 Hz), CH_3 NMe_2], 21.2 [CH_3 Mes], 19.5 [d (J_{CP}= 33.9 Hz), $P(CH_3)_3$], 18.0, 16.1 [CH_3 Mes]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -23.4.

X-ray structures of 3a, 4b, 5a, 5b and 6a.

General Description: For compounds **3a** and **4b**: data collection was performed on a Bruker APPEX II diffractometer using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine-focus sealed tube source at 100 K. Computing data and reduction were made with the APPEX II software.[4] In all cases empirical absorption corrections were applied using SADABS.[5] For compounds **5a**, **5b** and **6a**: Crystal data were collected on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-Kα radiation (λ= 1.5418 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and variable exposure time per image (4-16 s). Data collection strategy was calculated with the program CrysAlis^{Pro} CCD.[6] Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.[6] An empirical absorption correction was applied using the SCALE3 ABSPACK.[6] Using the program suite WINGX,[7] the structures were solved by Patterson interpretation and phase expansion using SHELXL and refined with full-matrix least squares on F2 using SHELXL.[8] In general, all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding mode. Molecular graphics were made with ORTEP 3.[9]

Computational Details

The geometry and energy of the two possible ring-opening product complexes for bipy and phen were optimized in CH_2Cl_2 solution from the outset with the Conductor-like Polarizable Continuum Model[10] (CPCM) and the Universal Force Field[11] (UFF) radii in conjunction with the hybrid density functional B3LYP[12] and the 6-31+G(d) basis set for nonmetal atoms[13] together with the valence double-ζ basis set LANL2DZ plus the effective core potential of Hay and Wadt for the Re atom,[14] and by using a modified Schlegel algorithm.[15] Electrostatic, cavitation, dispersion, and repulsion terms[16] were considered in the CPCM computations, wherein a relative permittivity of 8.93 was assumed to simulate CH_2Cl_2 as the solvent experimentally used. The nature of the stationary points was confirmed by analytical computations of harmonic vibrational frequencies. Gibbs free energies in CH_2Cl_2 solution (ΔG) were also calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations at a pressure of 1 atm and a temperature of 298.15 K.[17] The calculation of thermodynamic magnitudes in solution starting with molecular partition functions developed for computing gas-phase thermodynamics properties is a standard procedure that has proven to be a correct and useful approach.[18] For interpretation purposes a natural bond order (NBO) analysis[19] in conjunction with a topological analysis of the electron density based on the Atoms-in-Molecules (AIM) theory of Bader[20] were performed. Besides, using the Gauge-independent atomic orbital (GIAO) method[21] at the above-mentioned theory level, nucleus-independent chemical shifts (NICS)[22] were also calculated at the ring critical point (RCP) located at the center of relevant rings, NICS(0), as well as 1.0 Å above these RCP, NICS(1), as aromaticity indexes. The latter, NICS(1), were recommended as a better measure of the π electron delocalization as compared to the former, NICS(0).[23] Thus, in the present work, we only discuss NICS(1) values.

The computational protocol used in this work is equal or similar to those employed in related investigations on related carbonyl Re(I) complexes.[24] All the quantum chemical calculations were performed with the Gaussian 09 (G09) suite of programs.[25]

Table S1. Wiberg bond index in the natural atomic orbital basis obtained for the bond distances between Re and the two carbonyl carbons, the pyridine nitrogen (N_{py}), the dimethylated nitrogen (N_{Me}), the imidazole nitrogen directly linked to Re (N_{im}) and the phosphorous atom (P) in the two-possible ring-opening products for the bipy case at the CPCM-B3LYP/6-31+G(d)-LANL2DZ level of theory.

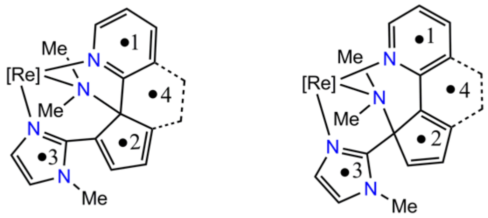
Species	Re-CO	Re-CO	Re-N_{py}	Re-N_{Me}	Re-N_{im}	Re-P
I_bipy_NC$_{py}$	1.4811	1.4338	0.4686	0.3824	0.5019	0.8201
I_bipy_NC$_{im}$	1.4828	1.4638	0.4340	0.3761	0.5147	0.8144

Table S2. CPCM-B3LYP/6-31+G(d)-LANL2DZ absolute and relative energies in CH_2Cl_2 solution without and with including thermal corrections (E and G, in hartree, and ∆E and ∆G, in kcal/mol, respectively) of the two possible ring-opening products for bipy and phen.

Species	**E**	**G**	**∆E**	**∆G**
I_bipy_NC$_{py}$	-1606.373371	-1605.974930	0.0	0.0
I_bipy_NC$_{im}$	-1606.364898	-1605.967041	5.3	5.0
I_phen_NC$_{py}$	-1682.609352	-1682.197761	0.0	0.0
I_phen_NC$_{im}$	-1682.569475	-1682.158755	-25.0	-24.5

Table S3. Electron density (ρ*(r)*, e/Å^3) and its Laplacian of the electron density (∇^{2}ρ*(r)*, e/Å^5) at some relevant ring critical points (1-3/4) located in the two possible ring-opening products for bipy and phen.

[Re]=*cis*-{Re(CO)$_2$(PMe$_3$)}$^+$

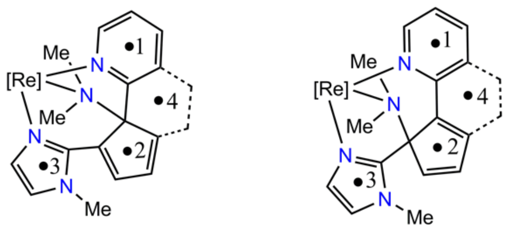


I_bipy_NC$_{py}$/I_phen_NC$_{py}$ **I_bipy_NC$_{im}$/I_phen_NC$_{im}$**

	Ring 1		Ring 2		Ring 3		Ring 4	
Species	ρ*(r)*	∇^{2}ρ*(r)*	ρ*(r)*	∇^{2}ρ*(r)*	ρ*(r)*	∇^{2}ρ*(r)*	ρ*(r)*	∇^{2}ρ*(r)*
I_bipy_NC$_{py}$	0.0220	0.1720	0.0466	0.3119	0.0519	0.4158		
I_bipy_NC$_{im}$	0.0219	0.1692	0.0436	0.3140	0.0527	0.4209		
I_phen_NC$_{py}$	0.0219	0.1708	0.0428	0.3077	0.0519	0.4162	0.0182	0.1281
I_phen_NC$_{im}$	0.0213	0.1615	0.0428	0.3085	0.0527	0.4207	0.0199	0.1517

Table S4. B3LYP/6-311+G(d,p)-LANL2DZ nucleus-independent chemical shifts (NICS) (in ppm) calculated at the ring critical points located at the center of the rings 1-3/4, NICS(0), and at points 1.0 Å above them, NICS(1), for the two possible ring-opening products for bipy and phen.

[Re]=*cis*-{Re(CO)$_2$(PMe$_3$)}$^+$



I_bipy_NC$_{py}$/I_phen_NC$_{py}$ **I_bipy_NC$_{im}$/I_phen_NC$_{im}$**

	Ring 1		Ring 2		Ring 3		Ring 4	
Species	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)
I_bipy_NC$_{py}$	-6.8	-9.4	-1.1	-3.3	-11.4	-9.1		
I_bipy_NC$_{im}$	-6.0	-8.7	-0.8	-3.7	-11.8	-9.2		
I_phen_NC$_{py}$	-5.6	-9.1	1.0	-2.0	-11.1	-8.7	2.7	-0.2

I_phen_NC$_{im}$	-7.0	-9.8	0.8	-2.1	-11.6	-9.1	-8.6	-10.4

Table S5. CPCM-B3LYP/6-31+G(d)-LANL2DZ cartesian coordinates, in Å,of the optimized structures of the two possible ring-opening products for bipy and phen in CH_2Cl_2 solution.

I_bipy_NC$_{py}$

N	-3.354720	-1.914551	0.625209
C	-2.434383	-1.012252	0.155370
N	-1.190933	-1.482762	0.379874
C	-1.333447	-2.709353	0.986479
C	-2.664957	-2.982937	1.144563
C	-2.719264	0.215453	-0.540806
C	-1.617882	1.265845	-0.828865
C	-2.384572	2.307866	-1.632334
C	-3.673394	1.940558	-1.749082
C	-3.886942	0.660405	-1.078514
C	-1.115855	1.829856	0.508300
N	-0.093360	1.165584	1.095502
C	0.341520	1.576496	2.306754
C	-0.216811	2.654746	2.979556
C	-1.269035	3.344521	2.376969
C	-1.720923	2.925398	1.127326
Re	0.773462	-0.557032	0.004152
C	1.513892	-1.469800	1.476992
O	1.935929	-2.037419	2.417433
N	-0.437997	0.664693	-1.581921
C	-0.901944	-0.215375	-2.693925
C	-4.810597	-1.804216	0.629631
P	2.948037	0.531611	-0.270111
C	3.105357	2.343545	0.067720
C	1.361497	-1.952976	-1.140524
O	1.711871	-2.806323	-1.868866
C	0.358135	1.764583	-2.198110
C	3.798375	0.361232	-1.902817
C	4.256250	-0.131914	0.850997
H	1.157371	1.007157	2.733770
H	0.170625	2.939598	3.950268
H	-1.729531	4.194049	2.868821
H	-2.536131	3.439019	0.632887
H	-1.938577	3.223873	-1.993165
H	-4.455273	2.497394	-2.251113
H	-4.842997	0.158285	-1.052537
H	0.601129	2.514552	-1.445902
H	-0.196718	2.237656	-3.014360
H	1.273947	1.340325	-2.603189
H	-1.610914	0.317347	-3.337334
H	-1.363606	-1.115458	-2.294357
H	-0.028296	-0.500436	-3.280428
H	-0.481032	-3.303498	1.271716
H	-3.177790	-3.826145	1.579684
H	-5.214366	-1.945633	-0.375076
H	-5.112242	-0.829442	1.015917
H	-5.202858	-2.582675	1.282154
H	3.255356	0.880566	-2.695815
H	3.857560	-0.699018	-2.163379
H	4.809926	0.774858	-1.842879
H	3.976326	0.037656	1.893869
H	5.211463	0.362967	0.650607
H	4.368838	-1.208164	0.695621
H	2.687874	2.577107	1.050765
H	2.574577	2.932117	-0.683100
H	4.161663	2.628265	0.053541

I_bipy_NC$_{im}$

Re	-0.796843	-0.493802	-0.295481
P	-2.777444	0.297121	0.892083
N	1.091521	-1.066304	-1.150007
N	0.704463	-0.640291	1.511388
N	0.053743	1.645885	-0.499661
N	3.283474	-1.318808	-1.094419
C	1.485077	-1.619197	-2.346320
H	0.774503	-1.859660	-3.120942
O	-1.829704	-3.364201	-0.018178
C	-1.737424	-0.409468	-1.925350
C	1.265892	2.117205	-0.084326
C	4.690959	-1.281589	-0.689495
H	4.861281	-1.937347	0.165125
H	4.982254	-0.263217	-0.432862
H	5.286215	-1.626833	-1.533685
C	2.185360	-0.902745	-0.408221
C	2.151593	1.294195	0.744973
C	0.360635	0.214806	2.679758
H	0.165962	1.235827	2.358005
H	1.170545	0.208404	3.417599
H	-0.536955	-0.195182	3.141449
C	2.844830	-1.775797	-2.322481
H	3.534748	-2.170240	-3.051315
C	-1.434010	-2.261275	-0.123207
C	-0.387745	3.785120	-1.552524
H	-1.077639	4.391609	-2.126648
C	2.063073	-0.234220	0.943224
C	1.682586	3.422410	-0.419727
C	0.756554	-2.055019	1.990120
H	1.102116	-2.706353	1.187315
H	-0.248712	-2.355716	2.282139
H	1.418396	-2.149492	2.856059
C	-4.285579	0.444073	-0.160328
H	-4.110398	1.164260	-0.964878
H	-5.140866	0.772469	0.438050
H	-4.510509	-0.525155	-0.613028
C	3.867541	0.637309	2.160071
H	4.737913	0.749837	2.794008
C	3.225290	-0.512519	1.885503
H	3.481105	-1.499928	2.243603
C	-3.402321	-0.780910	2.254472
H	-2.682454	-0.822899	3.075834
H	-3.550768	-1.794462	1.872753
H	-4.352184	-0.396246	2.638837
C	3.223339	1.740795	1.452031
C	-0.735066	2.488033	-1.213227
H	-1.689598	2.086592	-1.525871
C	0.861176	4.263827	-1.150677
H	1.188410	5.265239	-1.407296
C	-2.742882	1.955657	1.708603
H	-1.998935	1.975979	2.508644
H	-3.725367	2.175952	2.137493
H	-2.490548	2.731884	0.981954
O	-2.289630	-0.377412	-2.964037
H	2.662386	3.762343	-0.110554
H	3.562953	2.766035	1.517419

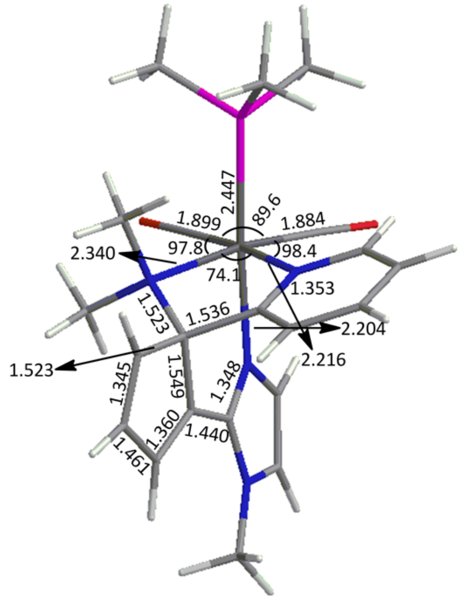
I_phen_NC$_{py}$

Re	0.870154	-0.661522	-0.034305
P	2.862112	0.736388	-0.379870
N	-0.881632	-1.873108	0.388076
N	-0.622840	0.566649	-1.436410
N	-0.098467	0.836664	1.320290
N	-2.959207	-2.583252	0.703027
C	-0.839695	-3.161496	0.868296
H	0.093746	-3.671510	1.040561
O	1.904626	-2.559119	-2.213641
C	1.856796	-1.606954	1.260438
C	-1.056098	1.584309	0.734170
C	-4.414201	-2.640942	0.820632

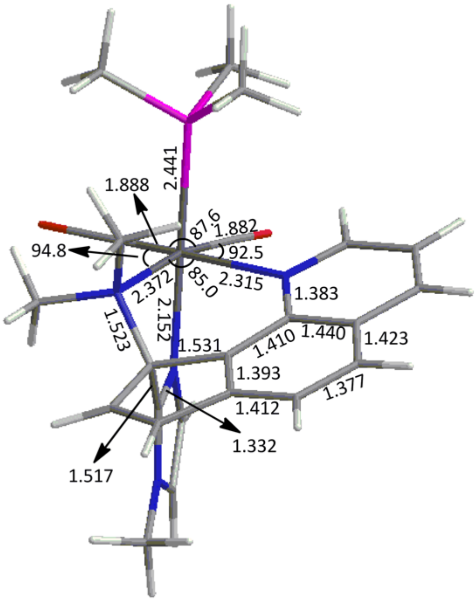
H	-4.875094	-2.867860	-0.143935
H	-4.792574	-1.688855	1.194395
H	-4.666737	-3.428759	1.529735
C	-2.179403	-1.535115	0.280427
C	-1.762334	0.967418	-0.470107
C	-0.025661	1.795695	-2.030440
H	0.252461	2.503679	-1.251897
H	-0.735279	2.275860	-2.712062
H	0.859879	1.504402	-2.590206
C	-2.117548	-3.606053	1.071606
H	-2.498134	-4.539421	1.455268
C	1.526768	-1.829303	-1.374035
C	0.190750	2.526896	2.995022
H	0.667317	2.841885	3.915432
C	-2.654355	-0.290532	-0.260221
C	-1.273767	2.926629	1.110780
C	-1.084253	-0.267342	-2.584550
H	-1.383911	-1.257288	-2.249103
H	-0.241133	-0.370875	-3.268828
H	-1.914689	0.217293	-3.110225
C	4.346603	0.129590	0.535101
H	4.160213	0.142210	1.612100
H	5.209269	0.764671	0.311171
H	4.569075	-0.898670	0.238147
C	-3.937271	1.301892	-1.341241
H	-4.837457	1.758057	-1.735716
C	-3.858764	-0.059961	-0.854783
H	-4.660169	-0.775975	-0.967154
C	3.556045	0.820782	-2.092673
H	2.885084	1.347477	-2.774337
H	3.705009	-0.193944	-2.471616
H	4.517682	1.343711	-2.075795
C	-2.677525	3.385842	-0.848249
H	-3.260348	4.058362	-1.470405
C	-2.784021	1.959210	-1.052144
C	-2.019984	3.835952	0.245575
H	-2.026394	4.887184	0.514002
C	0.480411	1.276681	2.456848
H	1.216046	0.619288	2.903556
C	-0.643170	3.380548	2.281378
H	-0.800935	4.403804	2.606530
C	2.864129	2.516535	0.124286
H	2.132175	3.089917	-0.448016
H	3.857526	2.941955	-0.049761
H	2.621316	2.607804	1.186305
O	2.436266	-2.207935	2.088789

I_phen_NC$_{im}$

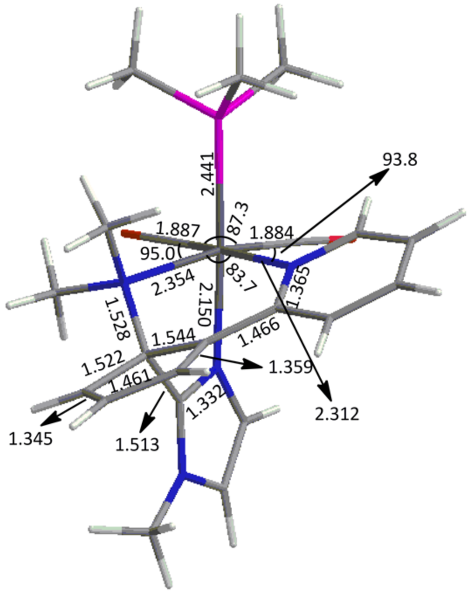
C	1.526927	3.798589	-1.451214
C	0.267676	3.510878	-1.926349
C	-0.342888	2.303830	-1.543773
N	0.223296	1.381985	-0.761454
C	1.508435	1.627275	-0.313845
C	2.182432	2.863354	-0.618210
Re	-1.073621	-0.463048	-0.237376
C	-2.113194	-1.981563	0.183403
O	-2.768910	-2.926790	0.430076
C	2.208433	0.700582	0.485577
C	1.830328	-0.726388	0.892444
C	2.992854	-1.109046	1.804994
C	3.905110	-0.123013	1.845511
C	3.460910	1.002516	1.014376
N	0.456710	-0.769969	1.548270
C	0.231599	-2.108385	2.170051
C	1.727790	-1.572831	-0.362466
N	0.581620	-1.578728	-1.041945
C	0.773127	-2.346315	-2.166408
C	2.065409	-2.797322	-2.165645
N	2.666593	-2.302858	-1.023708
C	4.077000	-2.523404	-0.690579
P	-2.730571	0.940022	0.878923
C	-2.228676	2.618472	1.467254
C	-2.048766	-0.336785	-1.842062
O	-2.628717	-0.282070	-2.864823
C	-4.211975	1.344228	-0.142289
C	-3.527709	0.242797	2.391825
C	0.367399	0.250525	2.627084
H	-0.018883	-2.518633	-2.877420
H	4.168893	-3.042641	0.263579
H	4.608932	-1.572684	-0.642120
H	4.508268	-3.138642	-1.479010
H	0.404035	1.252293	2.202728
H	1.180797	0.127955	3.351430
H	-0.583082	0.113395	3.141285
H	2.608608	-3.422016	-2.856467
H	-0.271847	4.193918	-2.570896
H	0.359033	-2.891158	1.422496
H	-0.788606	-2.143141	2.549528
H	0.923564	-2.275389	3.001646
H	-3.909051	1.894463	-1.037124
H	-4.916642	1.953048	0.432259
H	-4.703003	0.420006	-0.458201
H	4.839985	-0.139808	2.392939
H	3.062755	-2.066700	2.303493
H	-2.801217	0.129590	3.200314
H	-3.943127	-0.741879	2.161976
H	-4.329515	0.904868	2.733414
H	-1.346762	2.085181	-1.885432
H	2.024604	4.729716	-1.703368
H	-1.488483	2.540594	2.267726
H	-3.106622	3.148555	1.849271
H	-1.793164	3.196029	0.648076
C	4.111552	2.223344	0.732725
C	3.475564	3.128808	-0.087163
H	5.090757	2.435656	1.147008
H	3.947396	4.072708	-0.341376



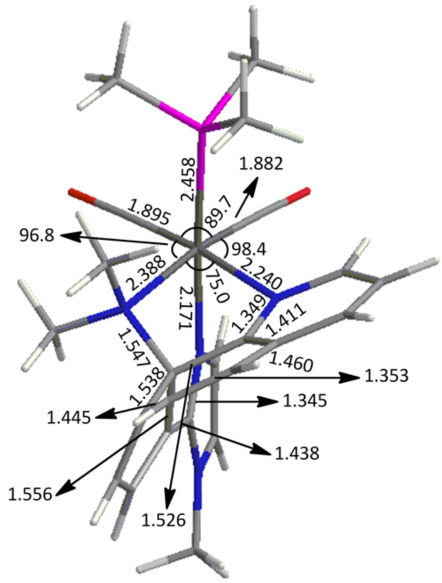
I_bipy_NC$_{py}$



I_phen_NC$_{im}$

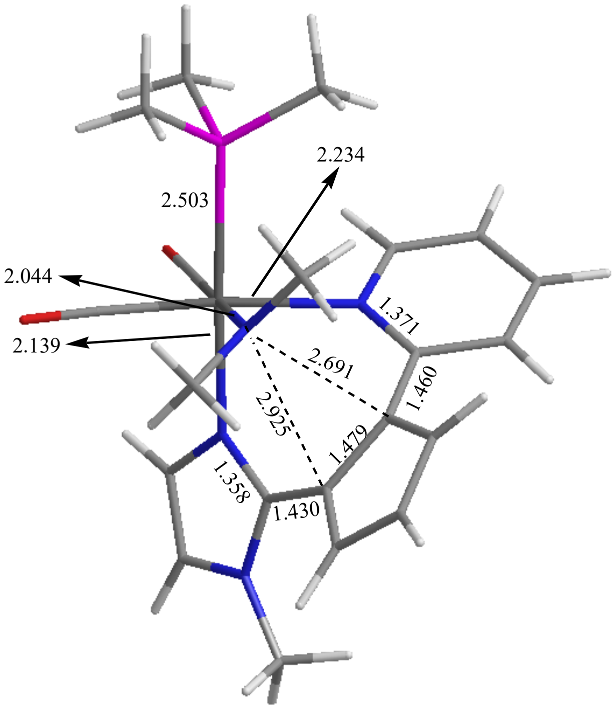


I_bipy_NC$_{im}$



I_phen_NC$_{py}$

Figure S1. CPCM-B3LYP/6-31+G(d)-LANL2DZ optimized geometry of the two possible ring-opening products for bipy and phen. Some relevant distances and bond angles are given in Å and degrees, respectively.



E = -1606.324311 hartree
ΔE = 25.5 kcal/mol

G = -1605.929130 hartree
ΔG = 23.7 kcal/mol

TS_IIIa'_IIIa

Re	-0.636643	-0.589068	-0.033940	C	1.501874	-2.423915	-1.435010
C	-1.472427	-1.320314	-1.656590	C	2.845807	-2.624578	-1.549686
O	-1.971791	-1.781012	-2.597559	N	3.463729	-1.587716	-0.884511
C	-0.969264	-2.310114	0.747167	C	4.910797	-1.397069	-0.820835
O	-1.131599	-3.369205	1.204809	H	5.317707	-1.824847	0.098287
P	-2.925756	0.265762	0.510532	H	5.138987	-0.331732	-0.853162
C	-3.255633	2.080993	0.608943	H	5.359734	-1.896356	-1.679154
C	-3.611659	-0.368417	2.099190	H	3.413049	-3.393327	-2.049953
C	-4.218105	-0.267446	-0.690702	H	0.692515	-3.021596	-1.821180
H	-2.791021	2.516006	1.494954	C	2.493985	-0.765900	-0.378604
H	-2.867371	2.588343	-0.277735	C	2.726482	0.374126	0.453393
H	-4.336148	2.243994	0.667226	C	3.751411	0.508058	1.392426
H	-3.010736	-0.031444	2.947035	C	3.622397	1.778873	2.007979
H	-4.637731	-0.010402	2.226279	C	2.561706	2.475577	1.404656
H	-3.608568	-1.460958	2.082572	C	1.951477	1.634196	0.456518
H	-5.193935	0.106102	-0.367891	C	0.993451	2.115028	-0.535130
H	-3.998315	0.125685	-1.687022	C	1.167821	3.424724	-1.037942
H	-4.251444	-1.357862	-0.746934	N	-0.052209	1.348709	-0.980535
N	0.101958	0.146916	1.724389	C	-0.845018	1.853271	-1.960603
C	0.816987	-0.672974	2.697390	C	-0.699869	3.118432	-2.500434
C	-0.328569	1.387701	2.366111	C	0.324672	3.935060	-2.010074
H	-1.144520	1.158230	3.065905	H	-1.640076	1.204846	-2.306614
H	-0.676152	2.108772	1.629499	H	-1.377473	3.451552	-3.277082
H	0.490935	1.827726	2.942460	H	0.474644	4.936390	-2.397949
H	0.162571	-0.893419	3.552241	H	4.476193	-0.250043	1.655643
H	1.161536	-1.602507	2.246955	H	4.243331	2.150866	2.813902
H	1.683796	-0.112146	3.077153	H	2.239499	3.479448	1.647344
N	1.276127	-1.269986	-0.706557	H	2.003503	4.006721	-0.671756

Figure S2. CPCM-B3LYP/6-31+G(d)-LANL2DZ optimized structure including only some relevant bond distances (in Å), absolute and relative electronic energy (E and ΔE, respectively), absolute and relative Gibbs free energy (G and ΔG, respectively), and cartesian coordinates (in Å) of the transition state **TS_IIIa'_IIIa** connecting isomers **IIIa'** and **IIIa**. Relative electronic and Gibbs free energies refer to **IIIa'**.

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3. The method used herein is a variation of the previously reported in: R. Arévalo, M. I. Menéndez, R. López, I. Merino, L. Riera, J. Pérez, *Chem. Eur. J.*, **2016**, *22*, 17972.

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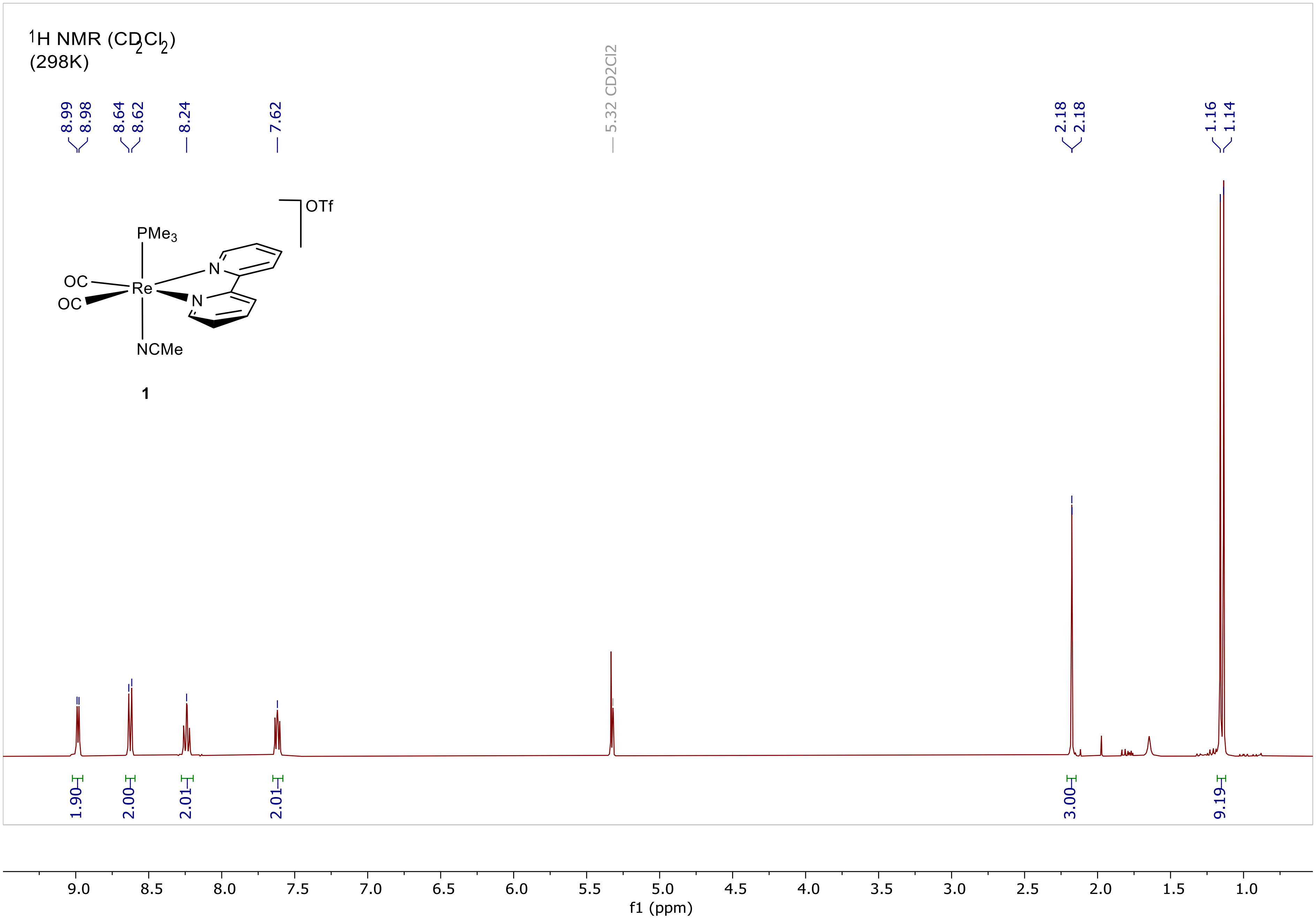
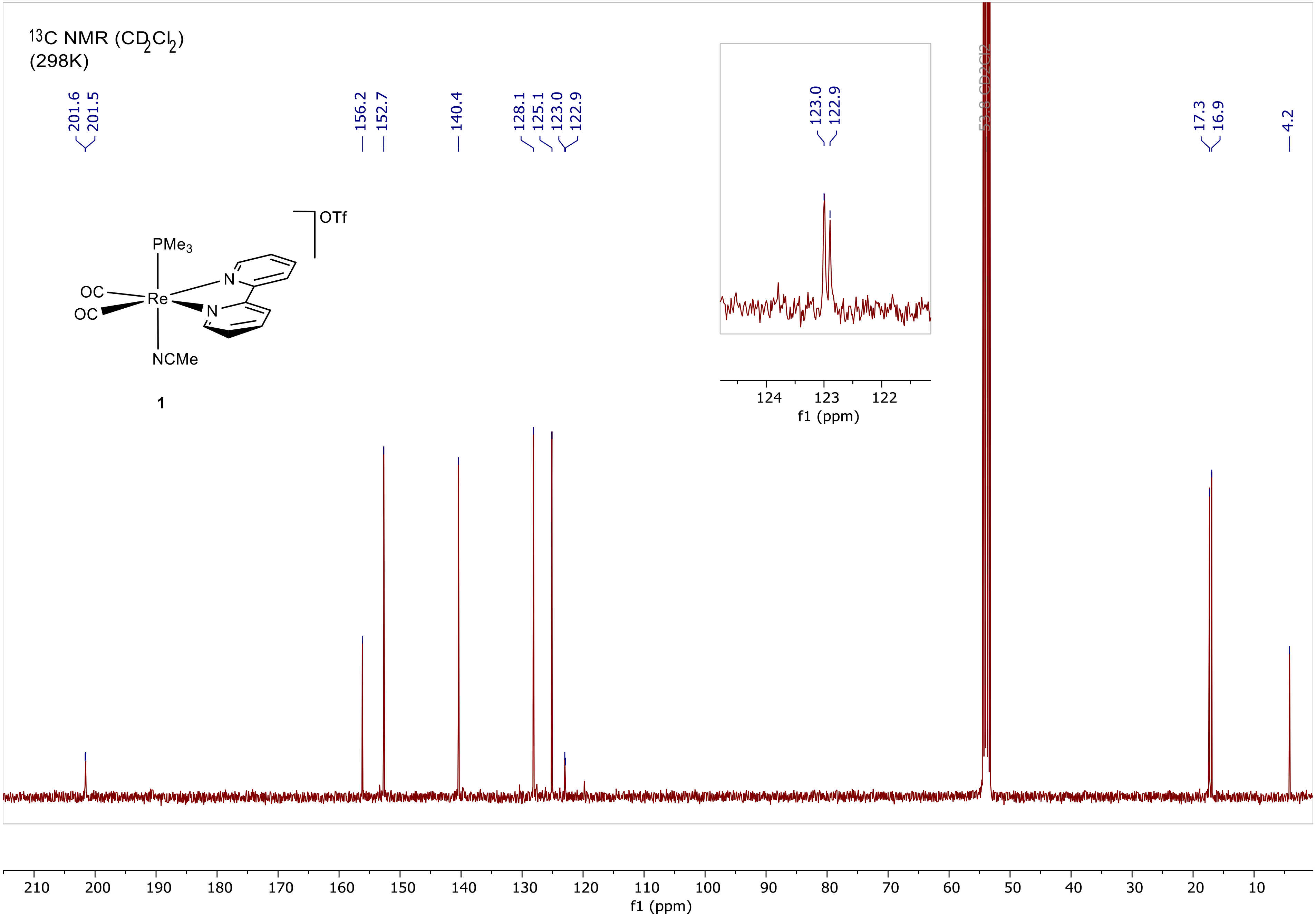
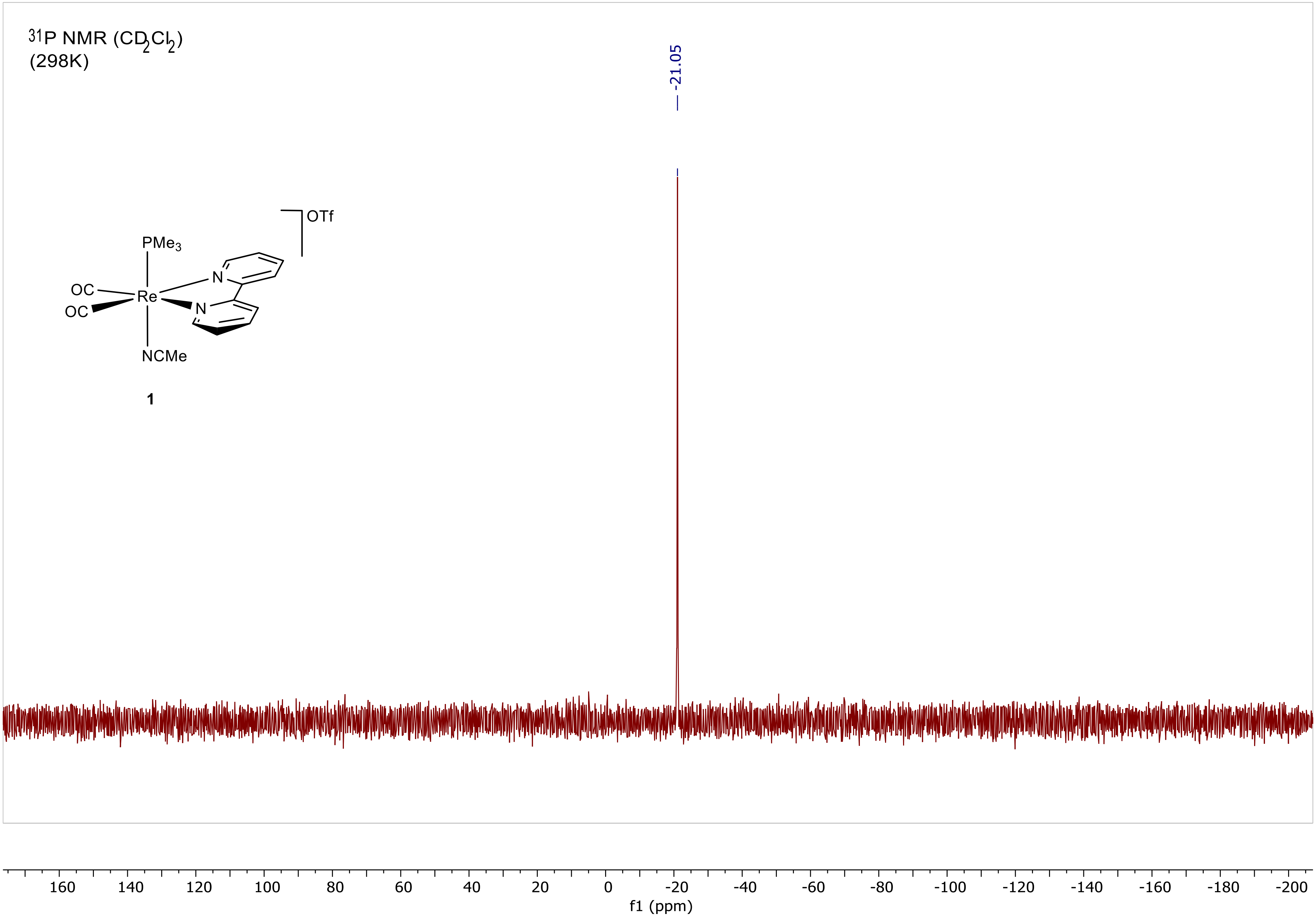
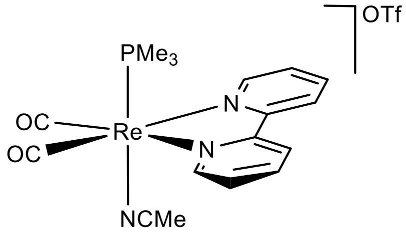


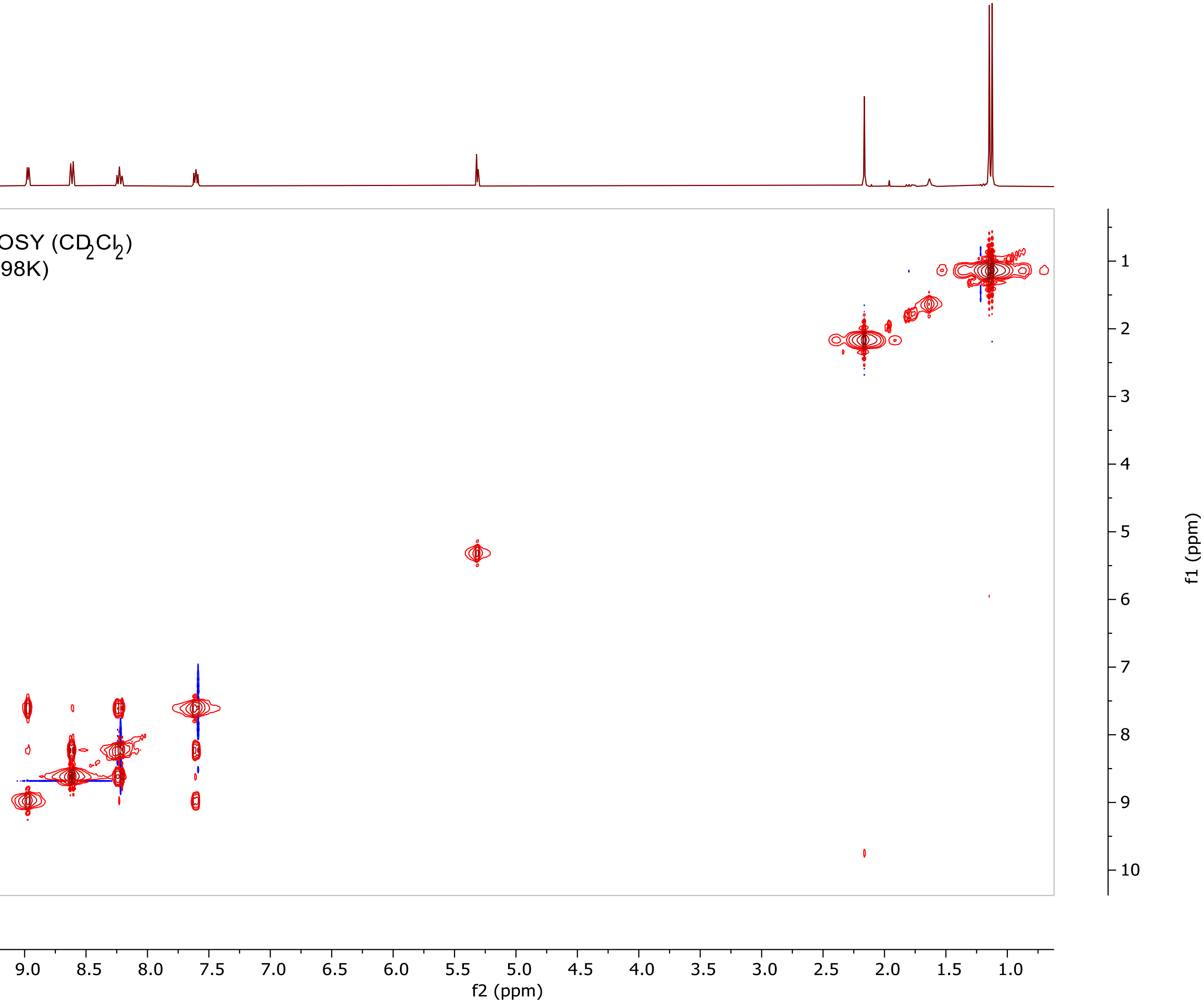
^{1}H NMR (CD_2Cl_2)
(298K)
8.99
8.98
8.64
8.62
8.24
7.62
5.32 CD2Cl2
2.18
2.18
1.16
1.14
OTf
PMe3
OC
Re
N
OC
N
NCMe
1
1.90
2.00
2.01
2.01
3.00
9.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

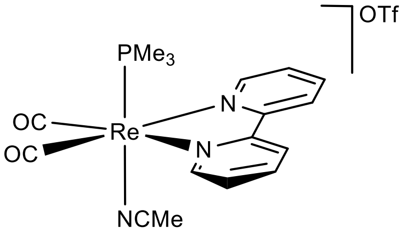

13C NMR (CD2Cl2)
(298K)
201.6
201.5
156.2
152.7
140.4
128.1
125.1
123.0
122.9
123.0
122.9
53.8 CD2Cl2
17.3
16.9
4.2
OTf
PMe3
OC
OC
Re
N
N
NCMe
1
124
123
122
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


31P NMR (CD2Cl2)
(298K)
-21.05
OTf
PMe3
OC
Re
N
OC
N
NCMe
1
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

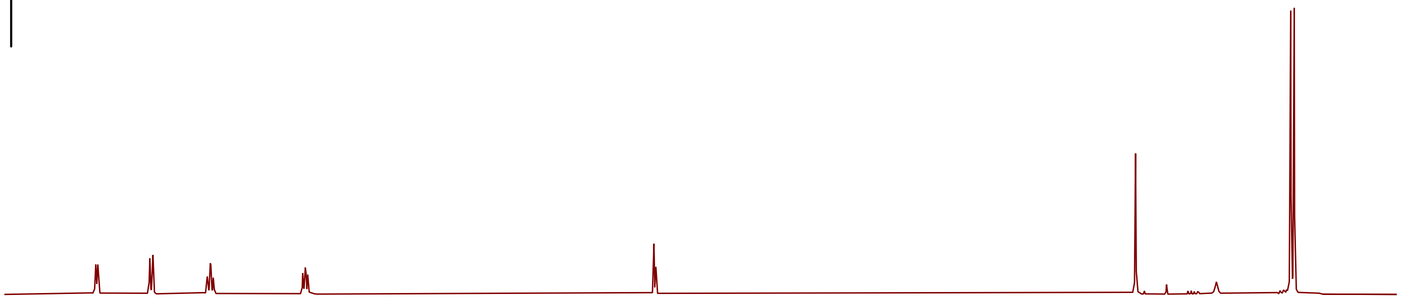

OTf
PMe3
OC
OC
Re
N
N
NCMe

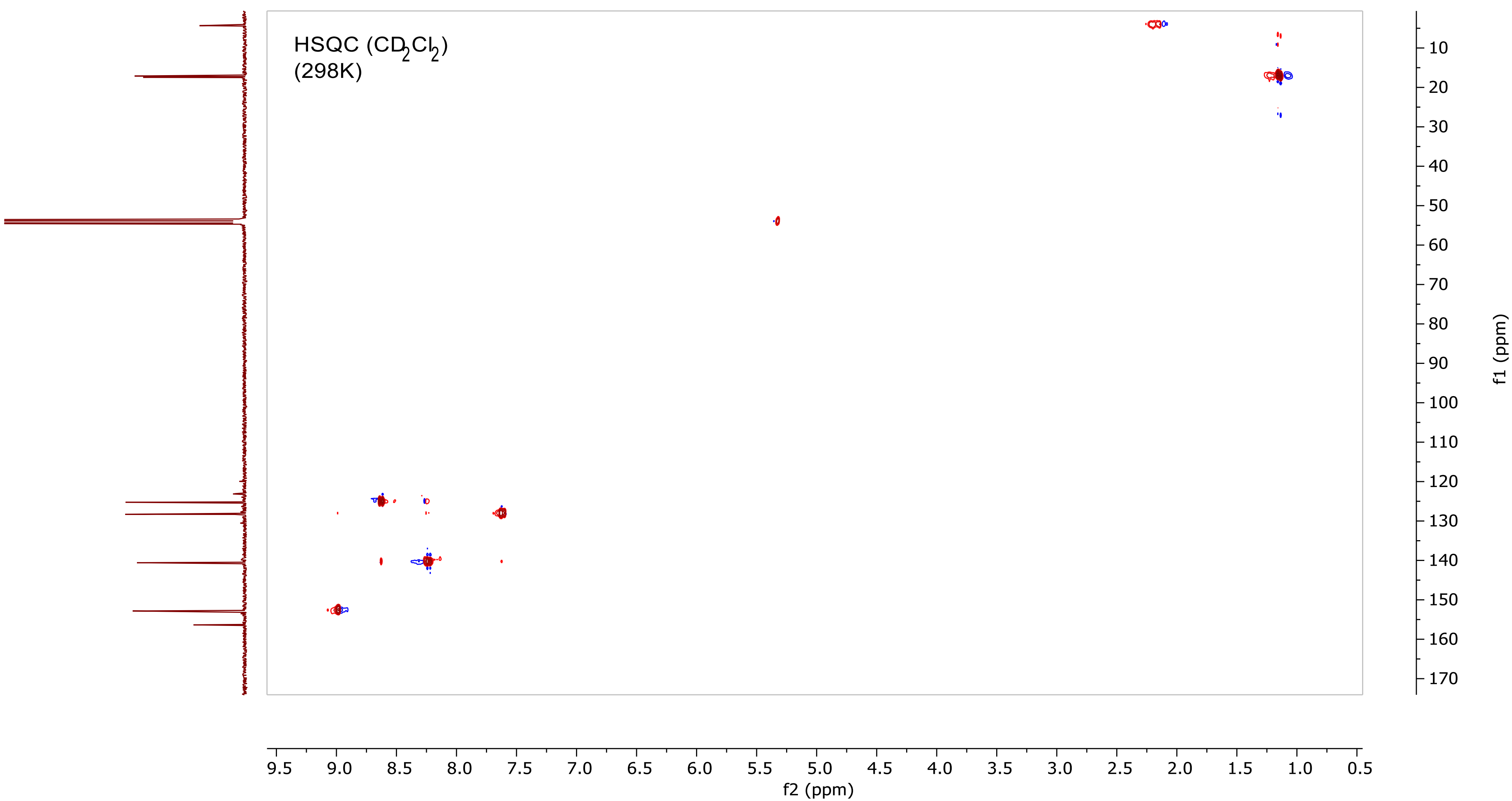
1

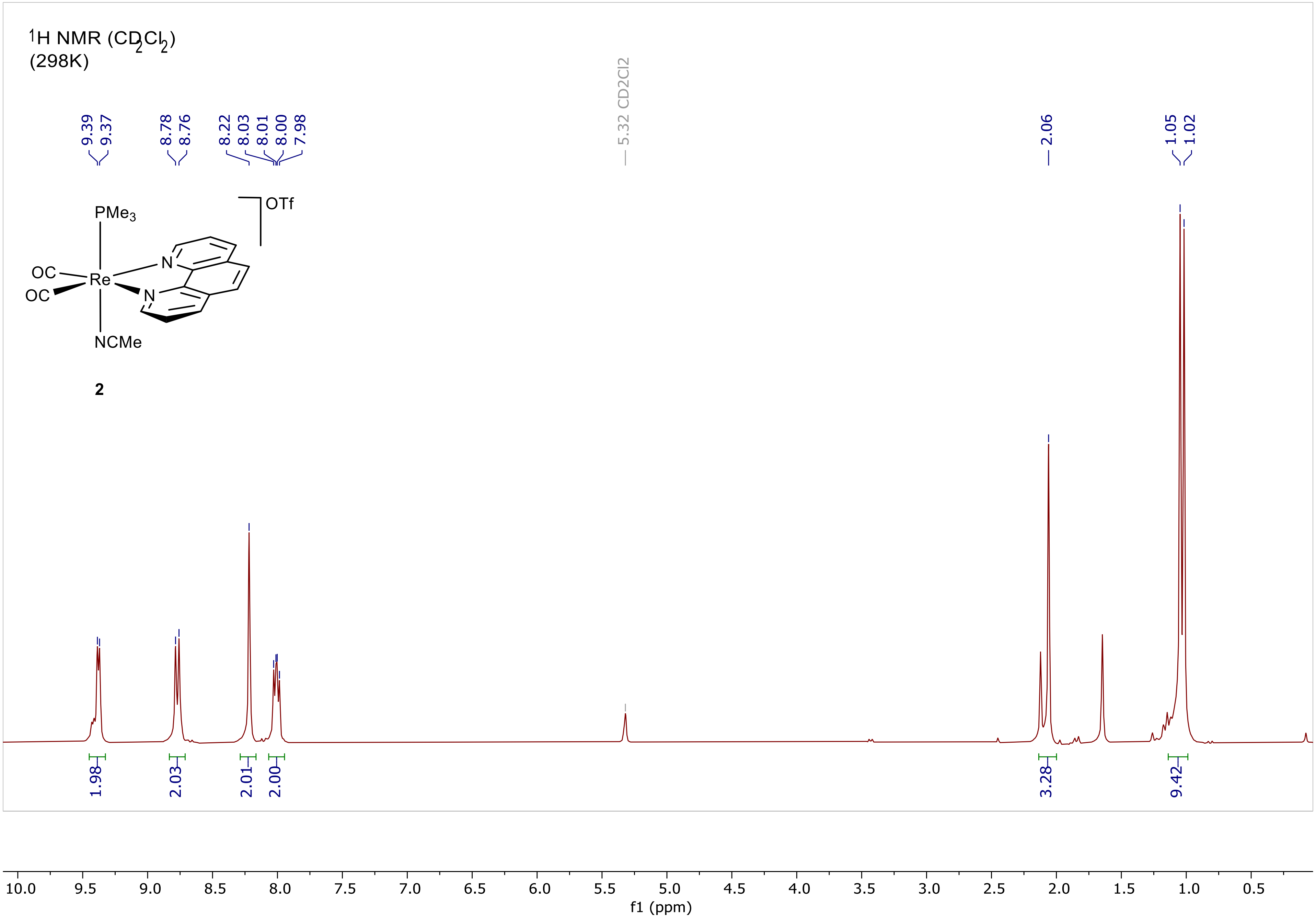

COSY (CD2Cl2)
(298K)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
9
10
f1 (ppm)


OTf
PMe3
OC
Re
N
OC
N
NCMe

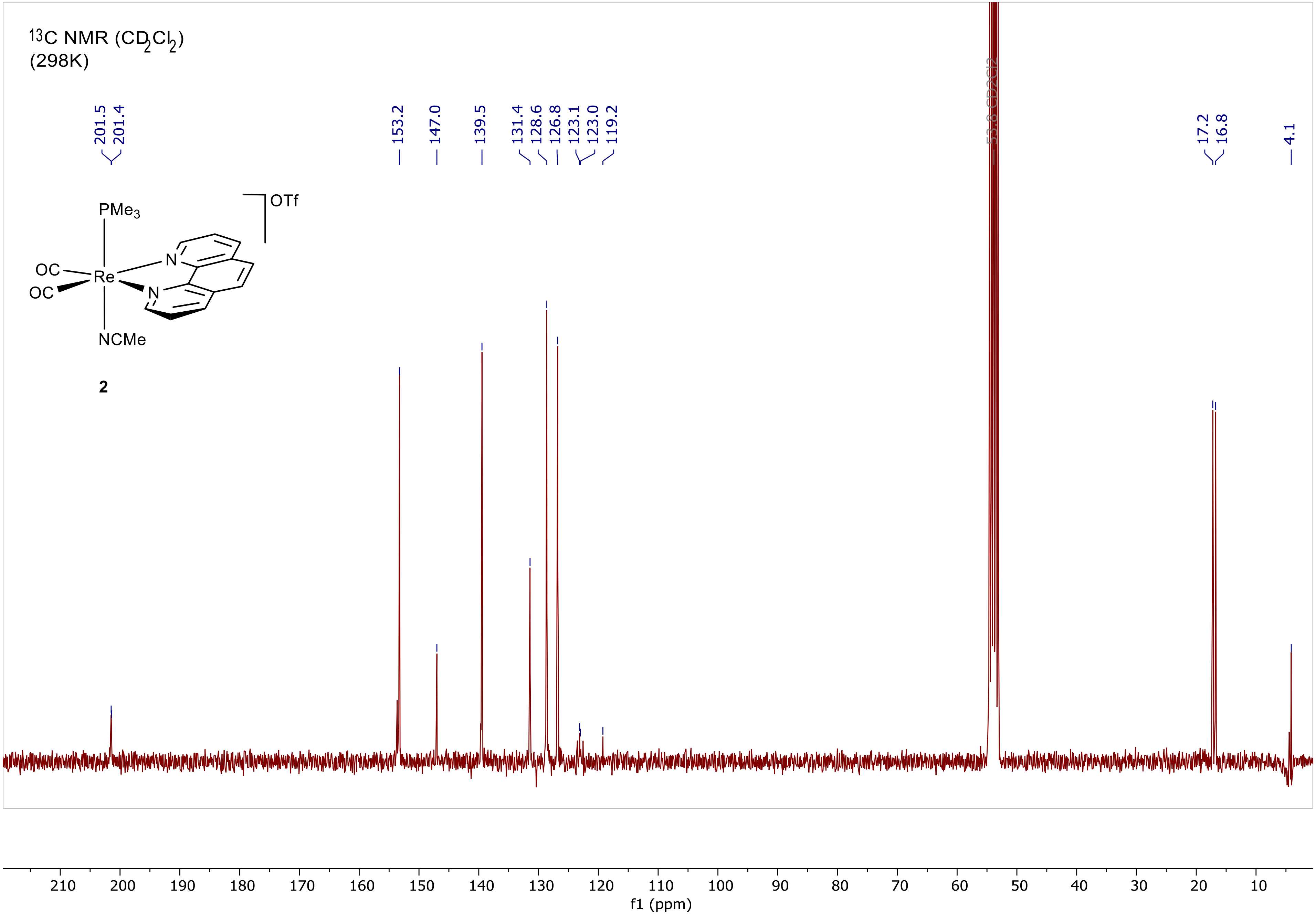
1



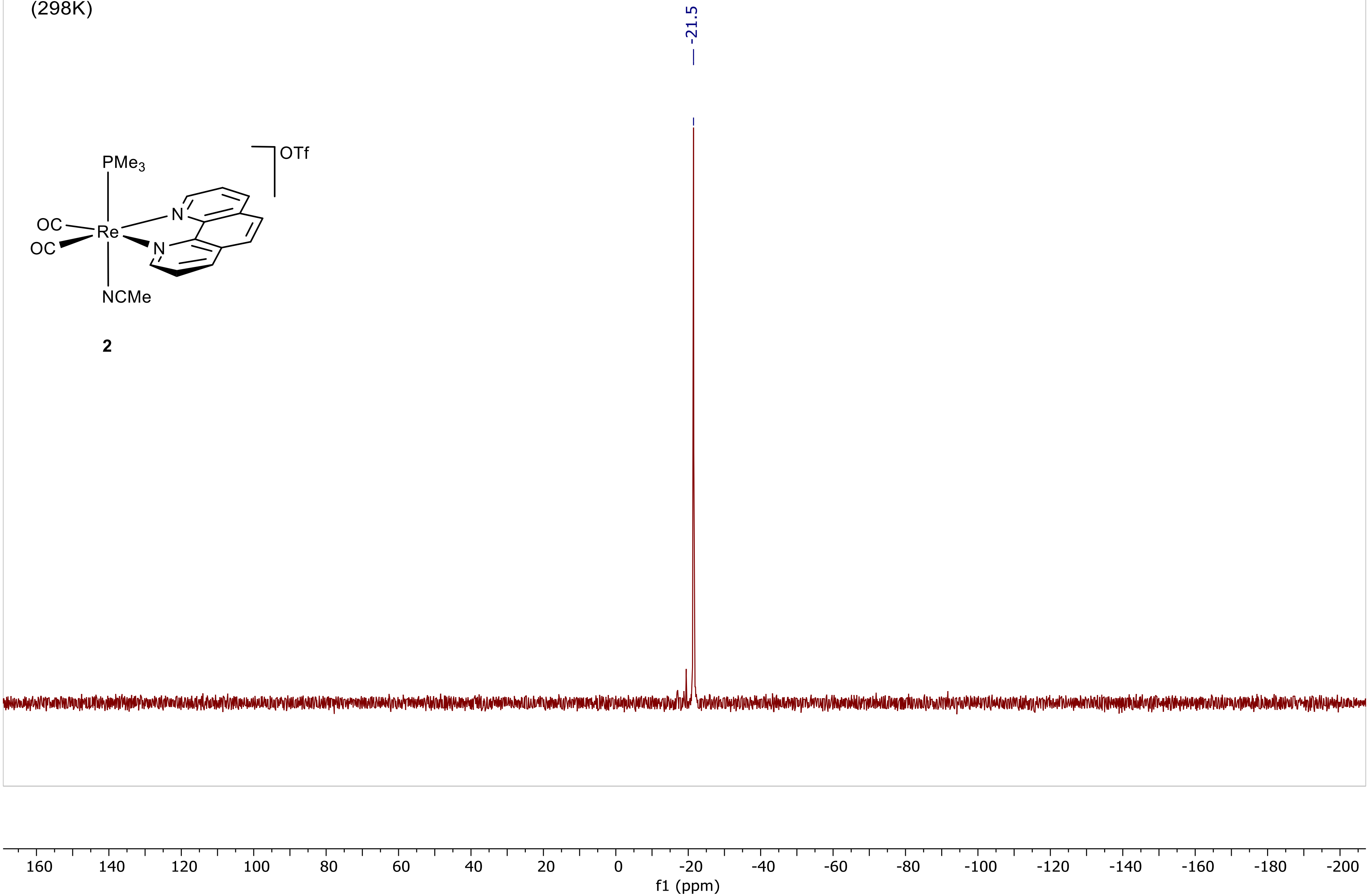

HSQC (CD2Cl2)
(298K)
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

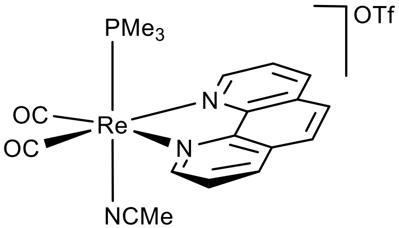


^{1}H NMR (CD_2Cl_2)
(298K)
9.39
9.37
8.78
8.76
8.22
8.03
8.01
8.00
7.98
5.32 CD2Cl2
2.06
1.05
1.02
PMe3
OTf
OC
Re
N
N
OC
NCMe
2
1.98
2.03
2.01
2.00
3.28
9.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

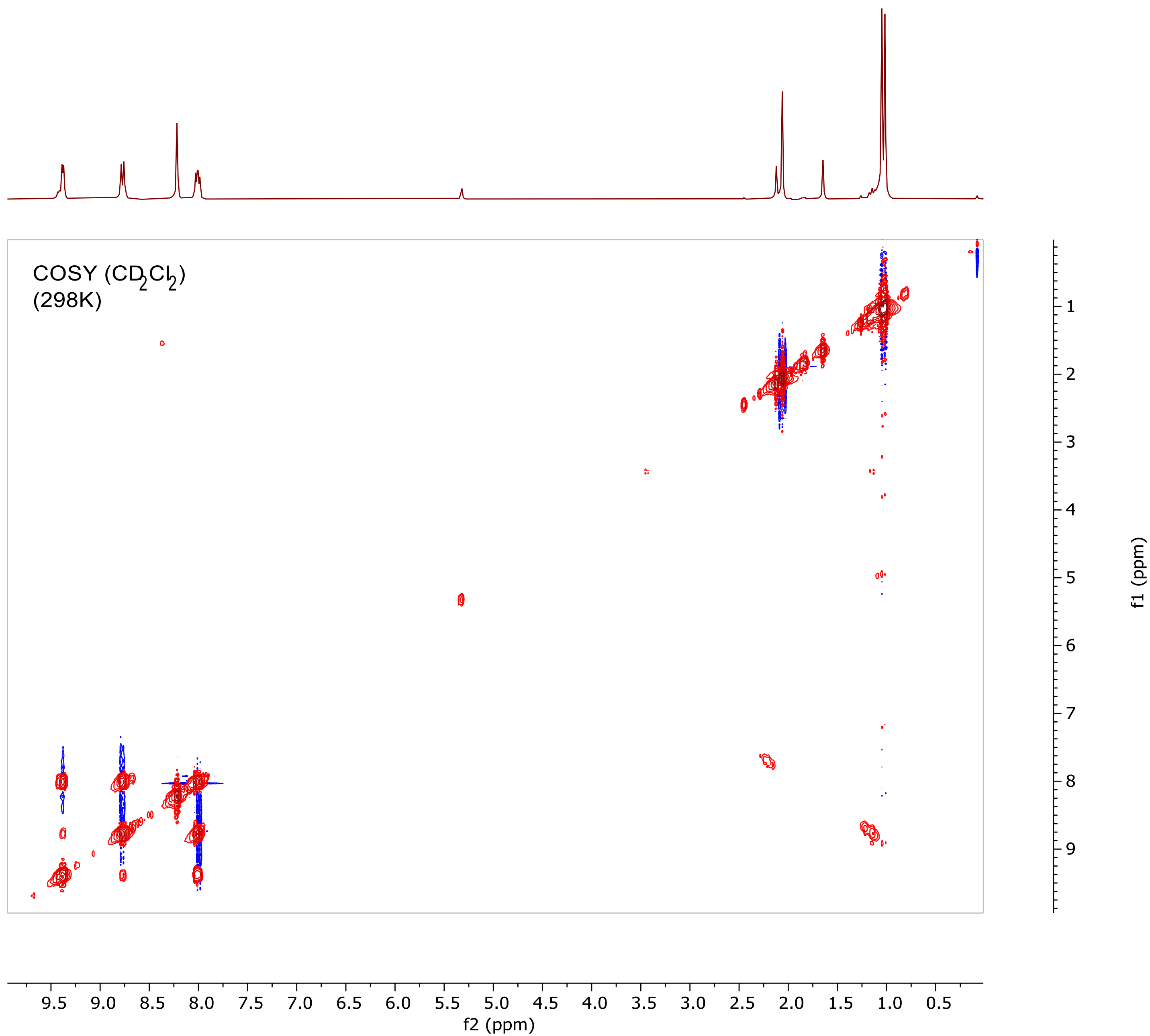

13C NMR (CD2Cl2)
(298K)
201.5
201.4
153.2
147.0
139.5
131.4
128.6
126.8
123.1
123.0
119.2
53.8 CD2Cl2
17.2
16.8
4.1
PMe3
OTf
OC
OC
Re
N
N
NCMe
2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

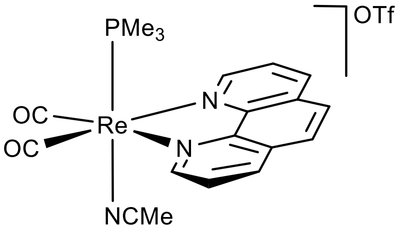
31P NMR (CD_2Cl_2)
(298K)




PMe3
OTf
OC
OC
Re
N
N
NCMe

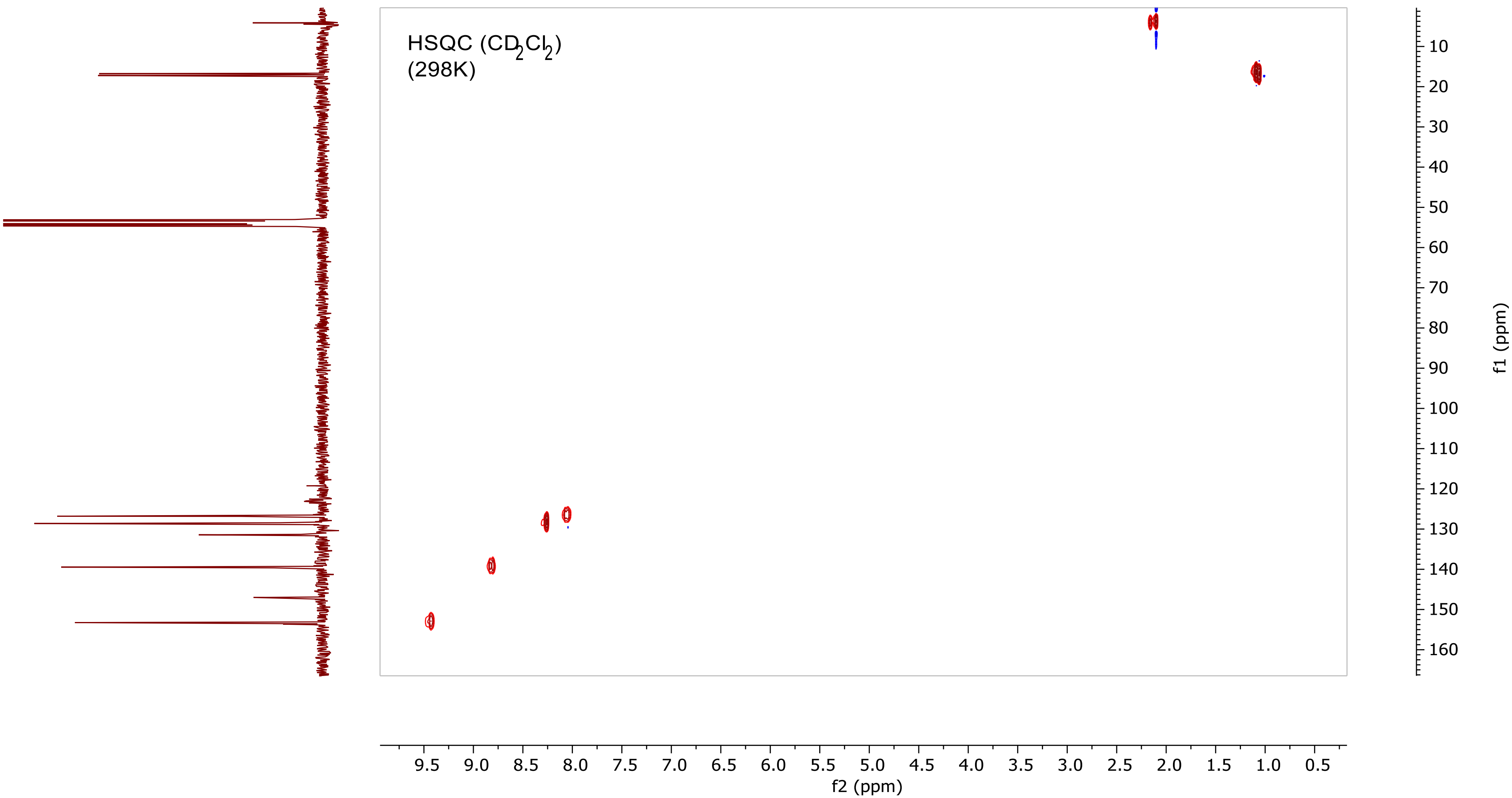
2


COSY (CD2Cl2)
(298K)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
1 2 3 4 5 6 7 8 9
f1 (ppm)

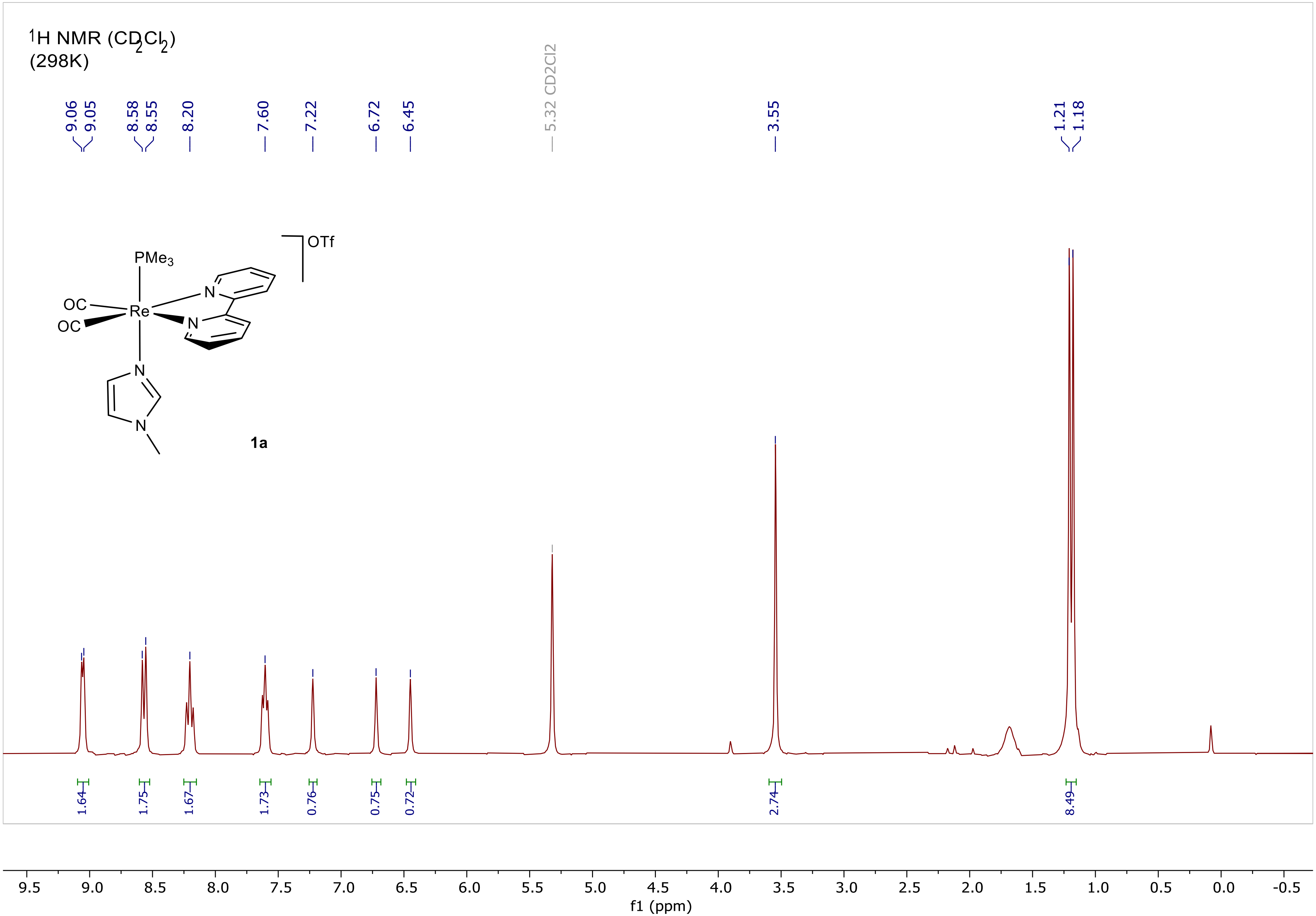


PMe3
OTf
OC
Re
N
OC
N
NCMe

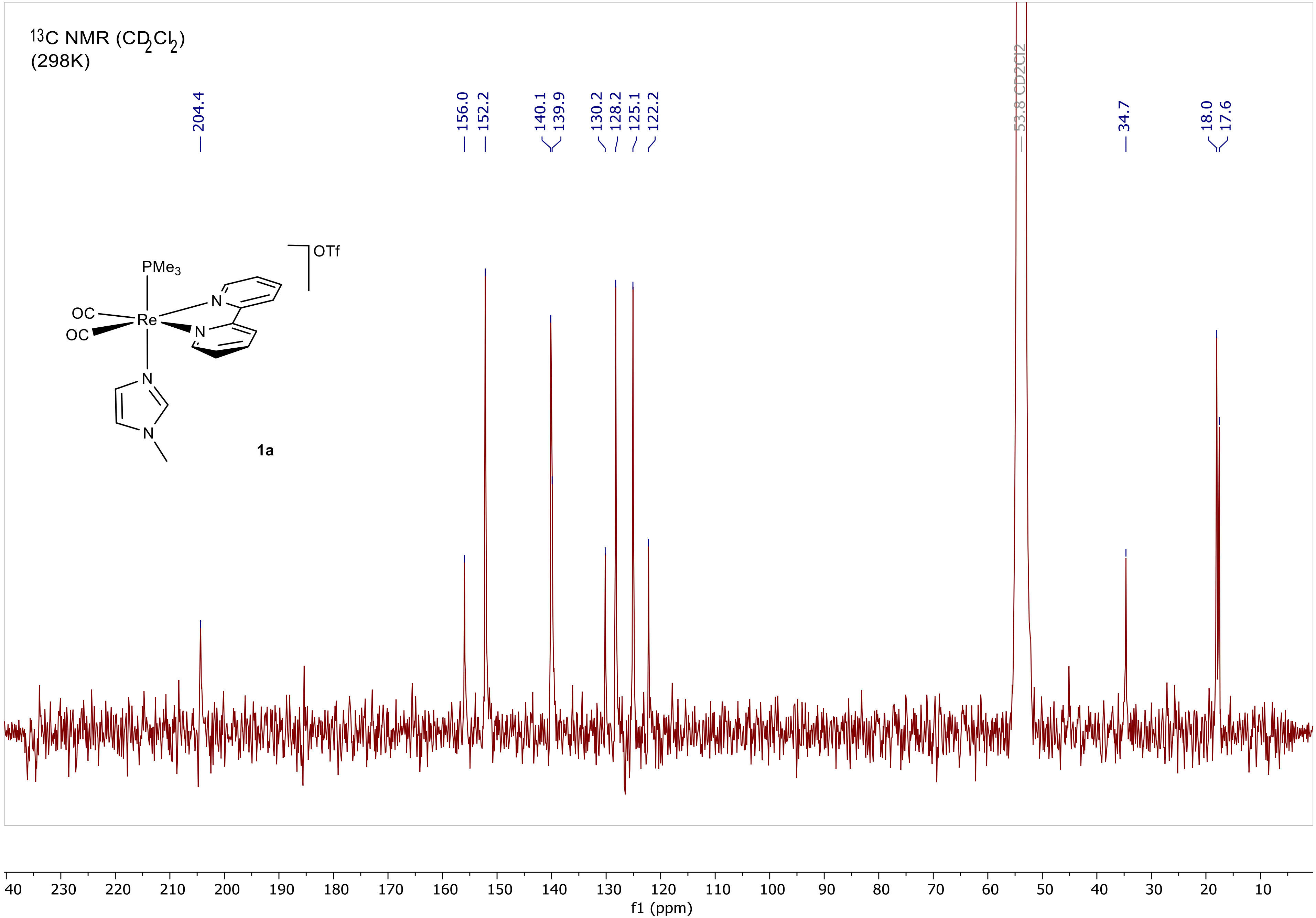
2



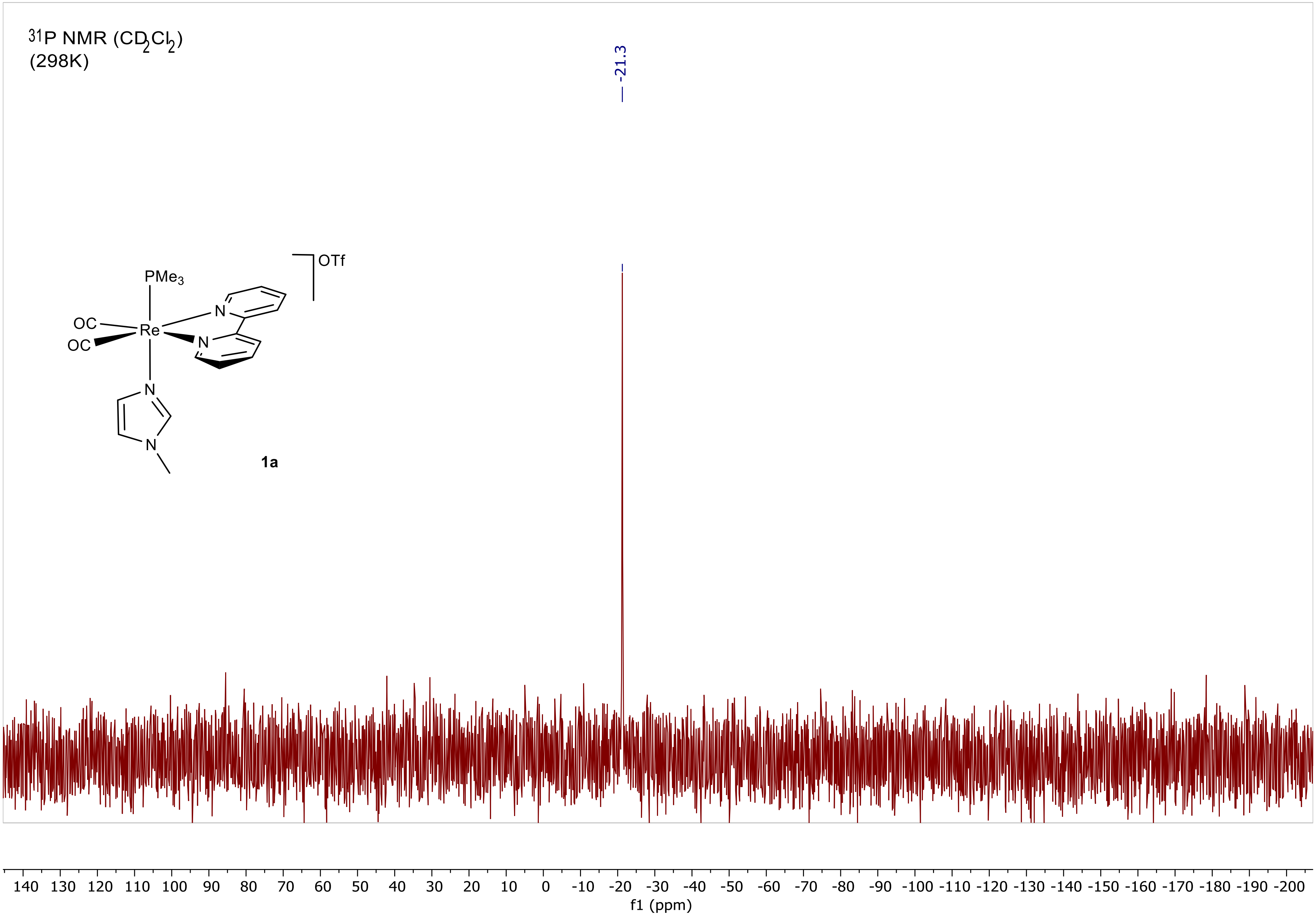
HSQC (CD2Cl2)
(298K)
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)



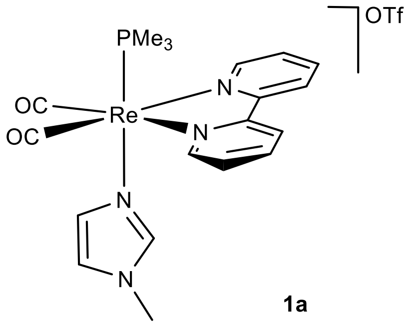
1H NMR (CD2Cl2)
(298K)
9.06
9.05
8.58
8.55
8.20
7.60
7.22
6.72
6.45
5.32 CD2Cl2
3.55
1.21
1.18
PMe3
OTf
OC
OC
Re
N
N
N
N
1a
1.64
1.75
1.67
1.73
0.76
0.75
0.72
2.74
8.49
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



13C NMR (CD2Cl2)
(298K)
204.4
156.0
152.2
140.1
139.9
130.2
128.2
125.1
122.2
53.8 CD2Cl2
34.7
18.0
17.6
PMe3
OTf
OC
OC
Re
N
N
N
N
1a
f1 (ppm)

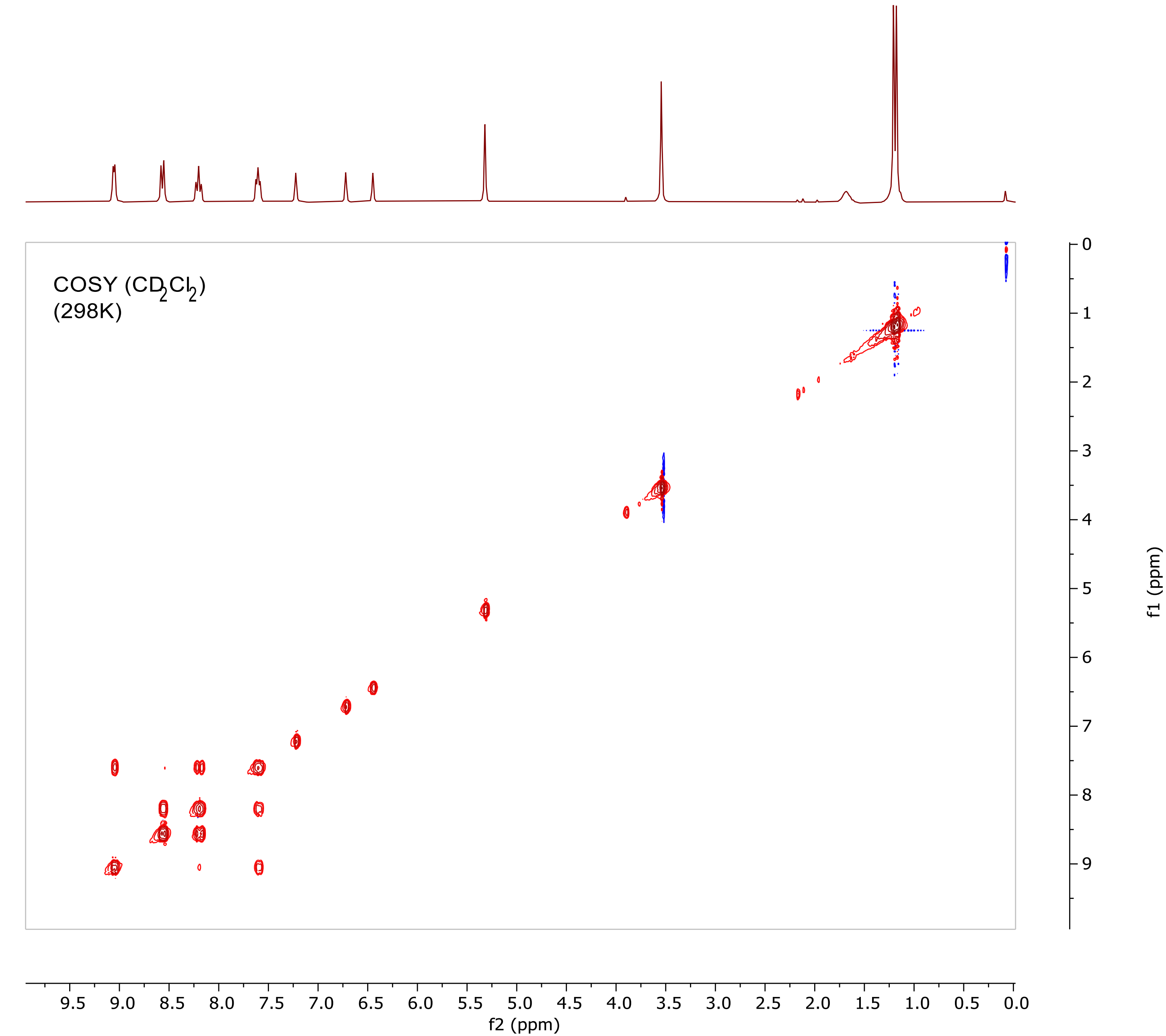


31P NMR (CD2Cl2)
(298K)
-21.3
PMe3
OTf
OC
OC
Re
N
N
N
N
1a
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

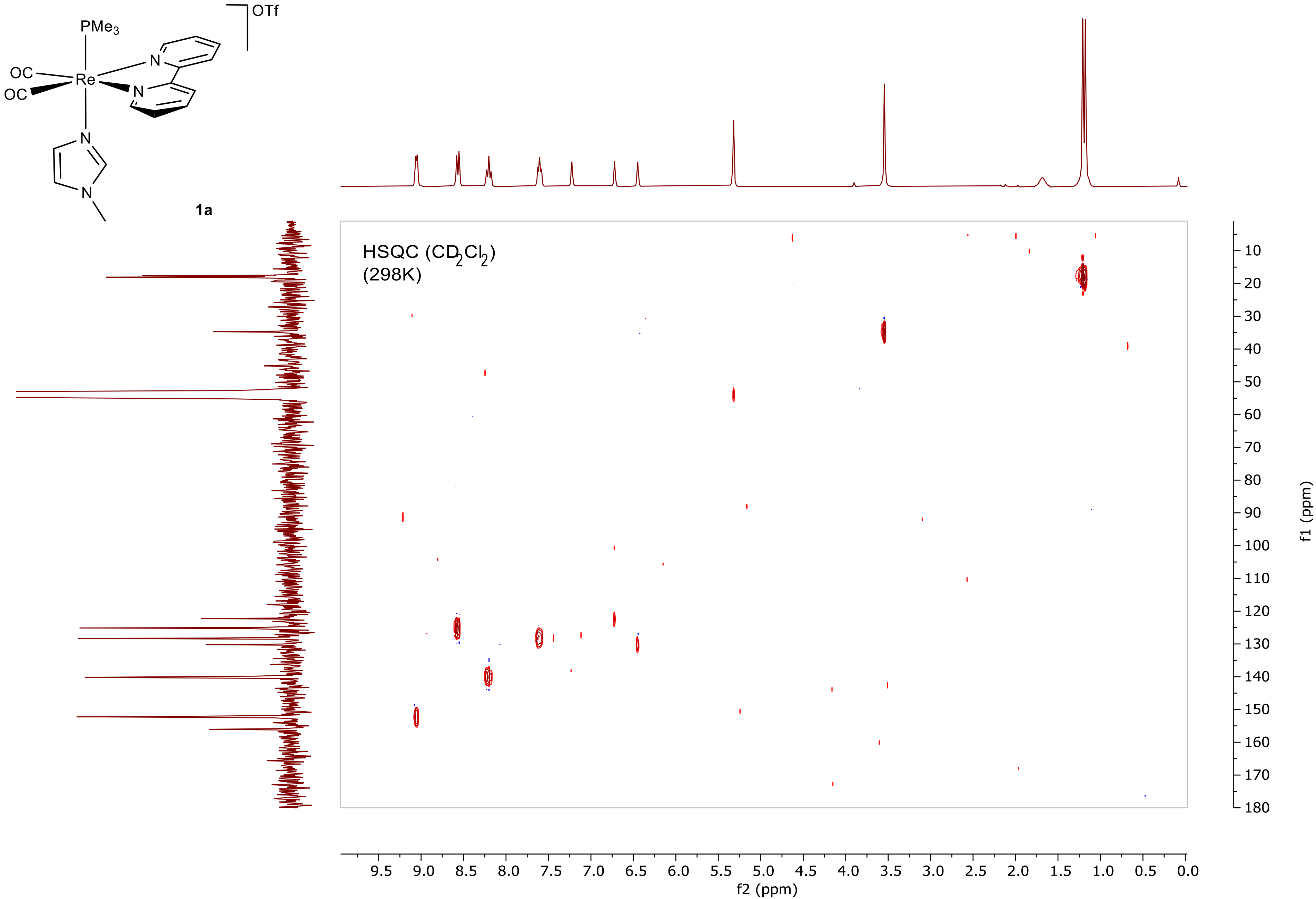


OTf
PMe3
OC
OC
Re
N
N
N
N

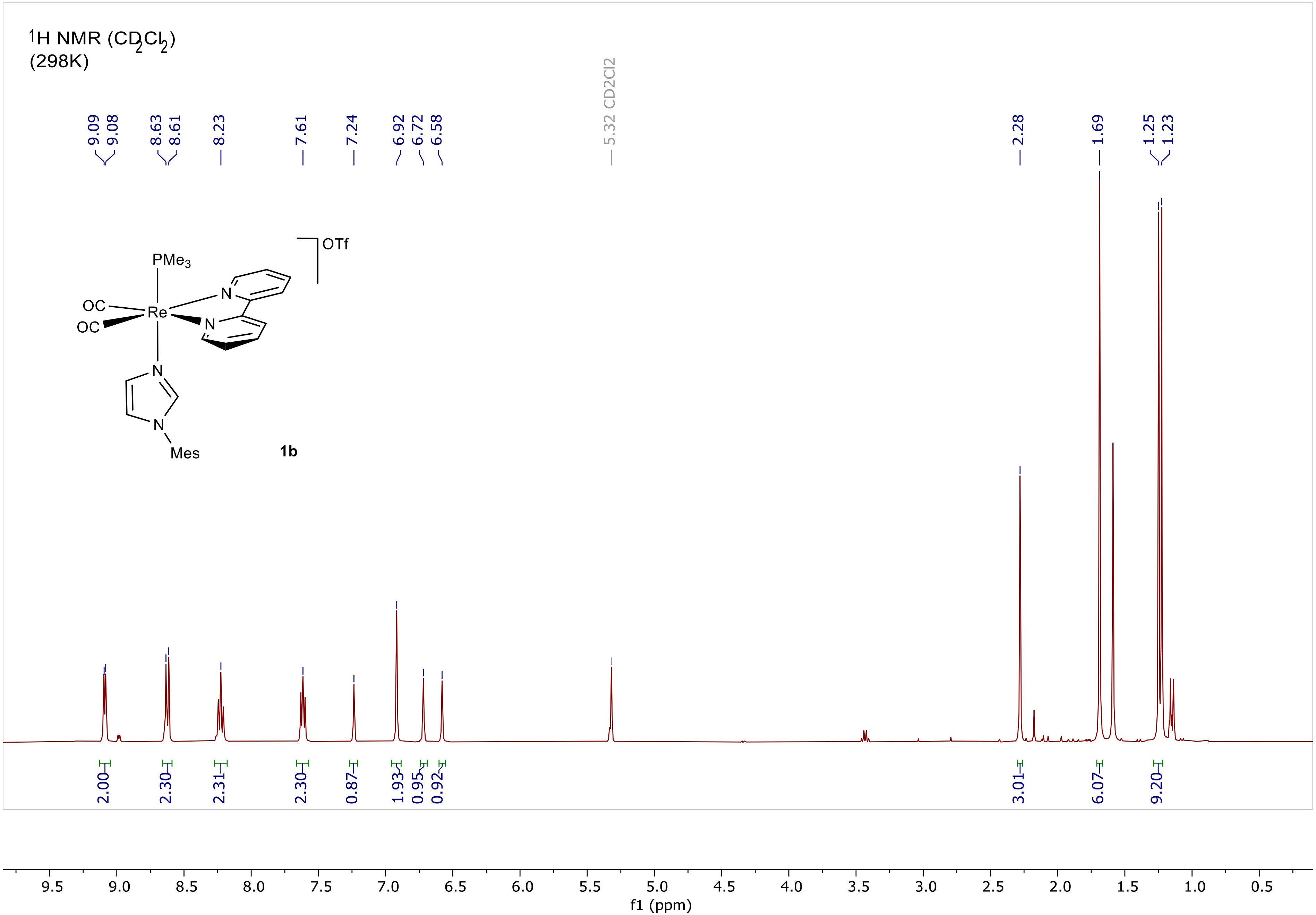
1a



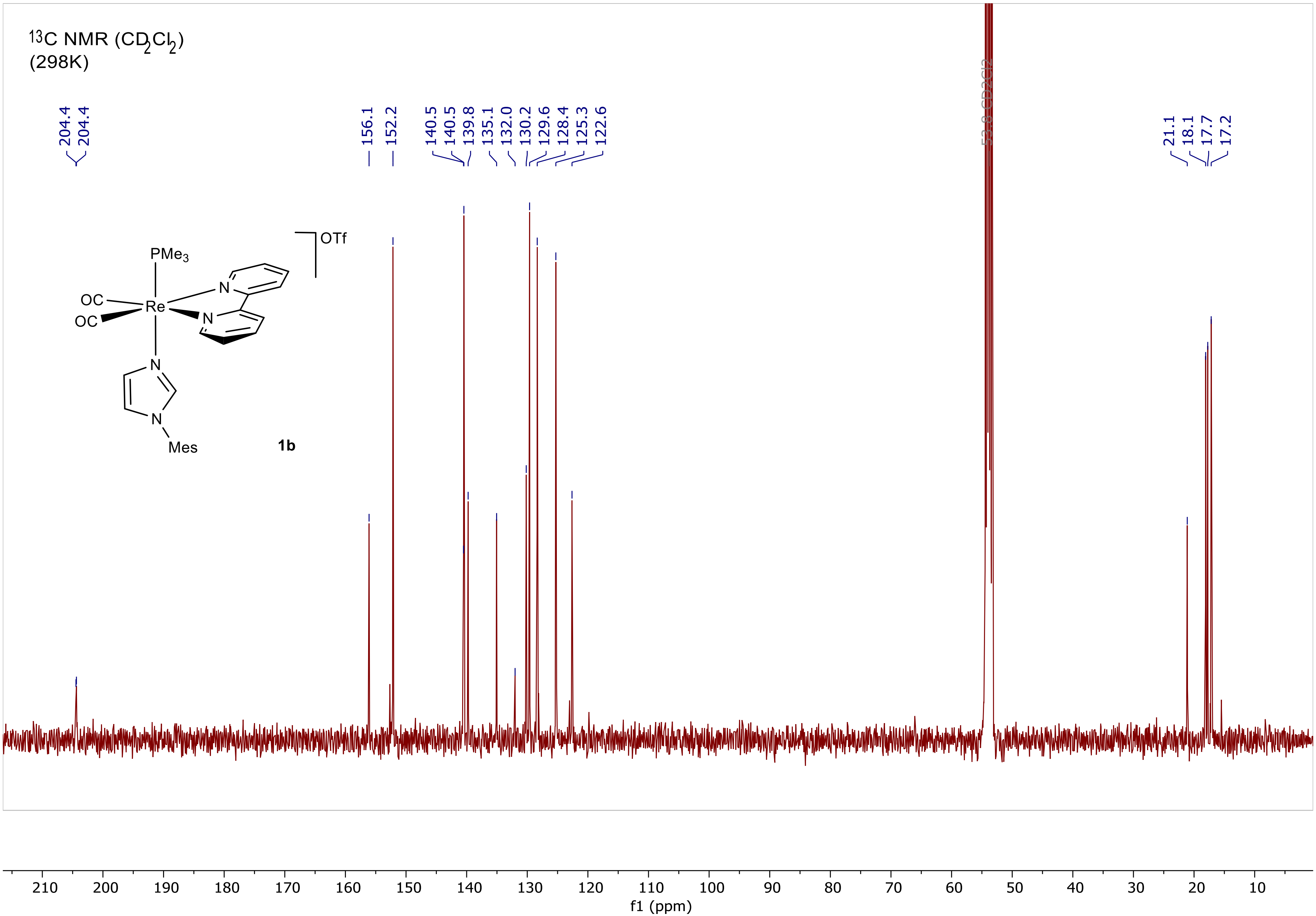
COSY (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8 9



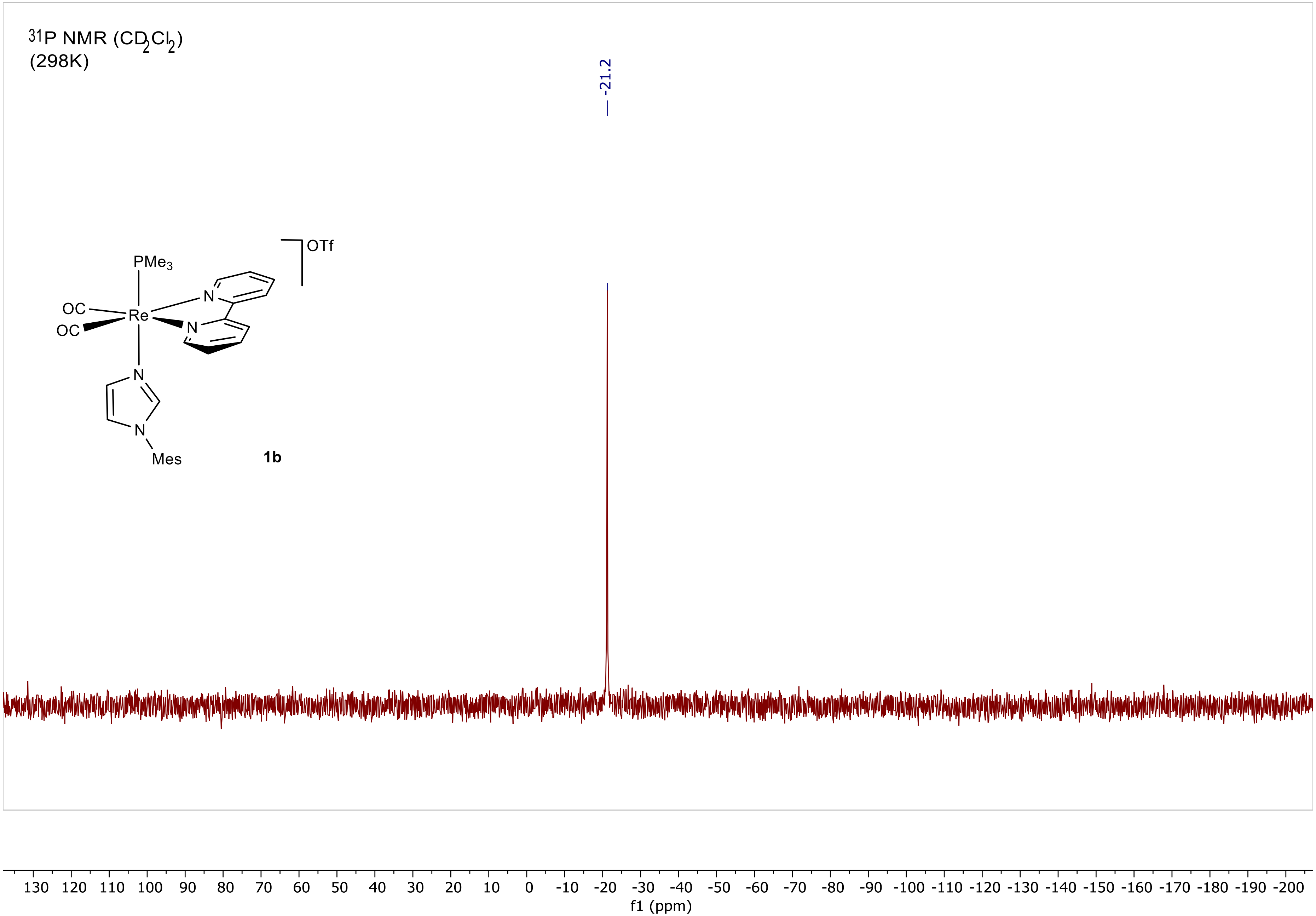
PMe3
OTf
OC
OC
Re
N
N
N
N
1a
HSQC (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180



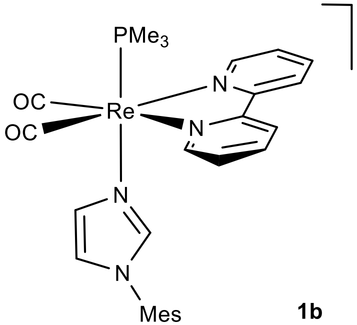
1H NMR (CD2Cl2)
(298K)
9.09
9.08
8.63
8.61
8.23
7.61
7.24
6.92
6.72
6.58
5.32 CD2Cl2
2.28
1.69
1.25
1.23
PMe3
OTf
OC
OC
Re
N
N
N
N
Mes
1b
2.00
2.30
2.31
2.30
0.87
1.93
0.95
0.92
3.01
6.07
9.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



13C NMR (CD2Cl2)
(298K)
204.4
204.4
156.1
152.2
140.5
140.5
139.8
135.1
132.0
130.2
129.6
128.4
125.3
122.6
21.1
18.1
17.7
17.2
OTf
PMe3
OC
OC
Re
N
N
N
N
Mes
1b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

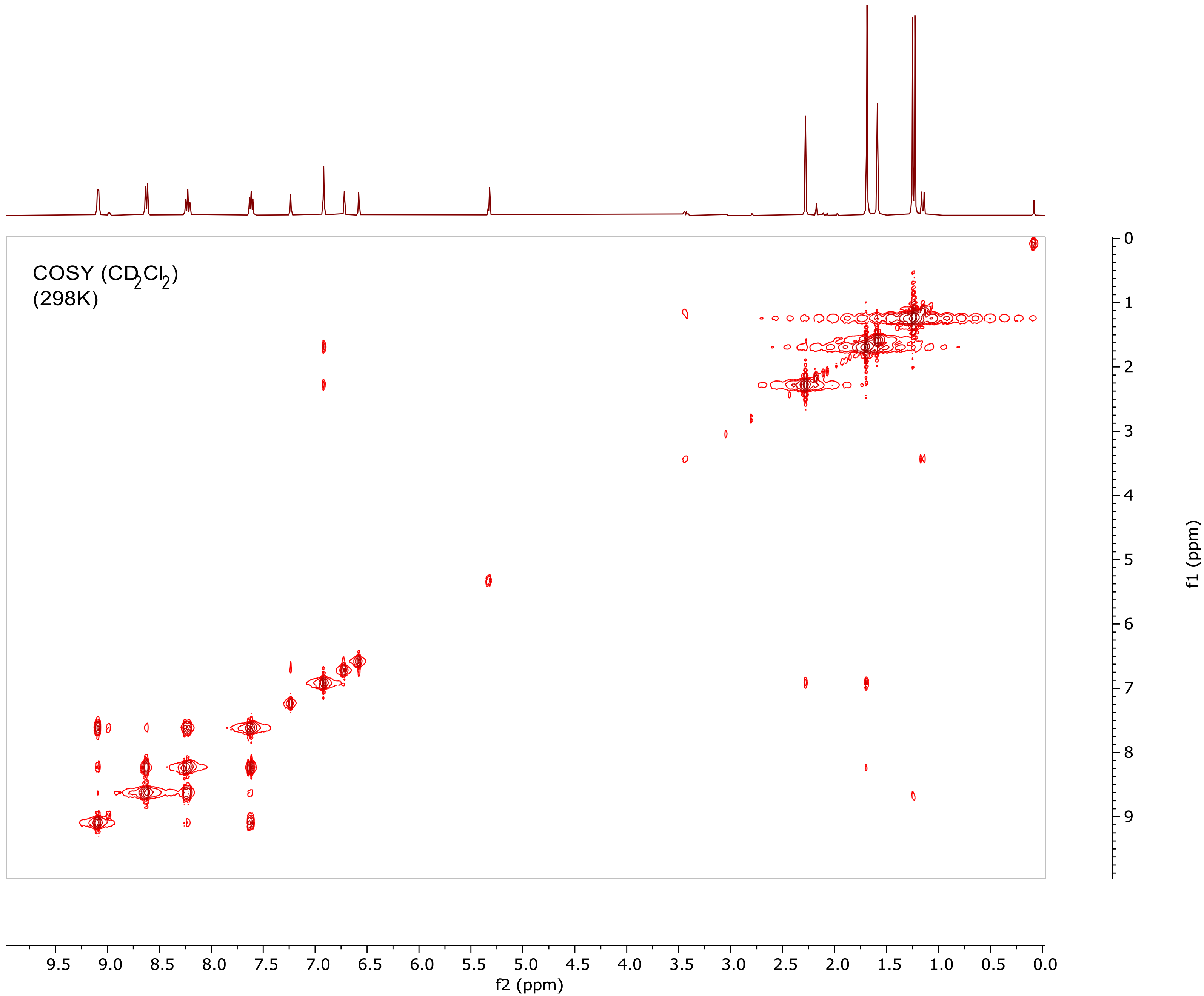


31P NMR (CD2Cl2)
(298K)
-21.2
PMe3
OTf
OC
OC
Re
N
N
N
N
Mes
1b
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

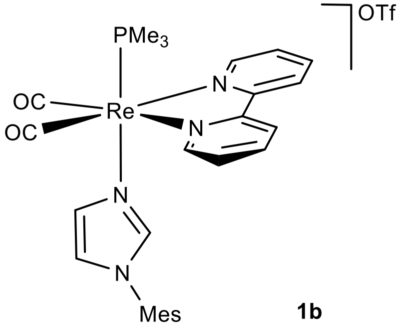


OTf
PMe3
OC
OC
Re
N
N
N
N
Mes

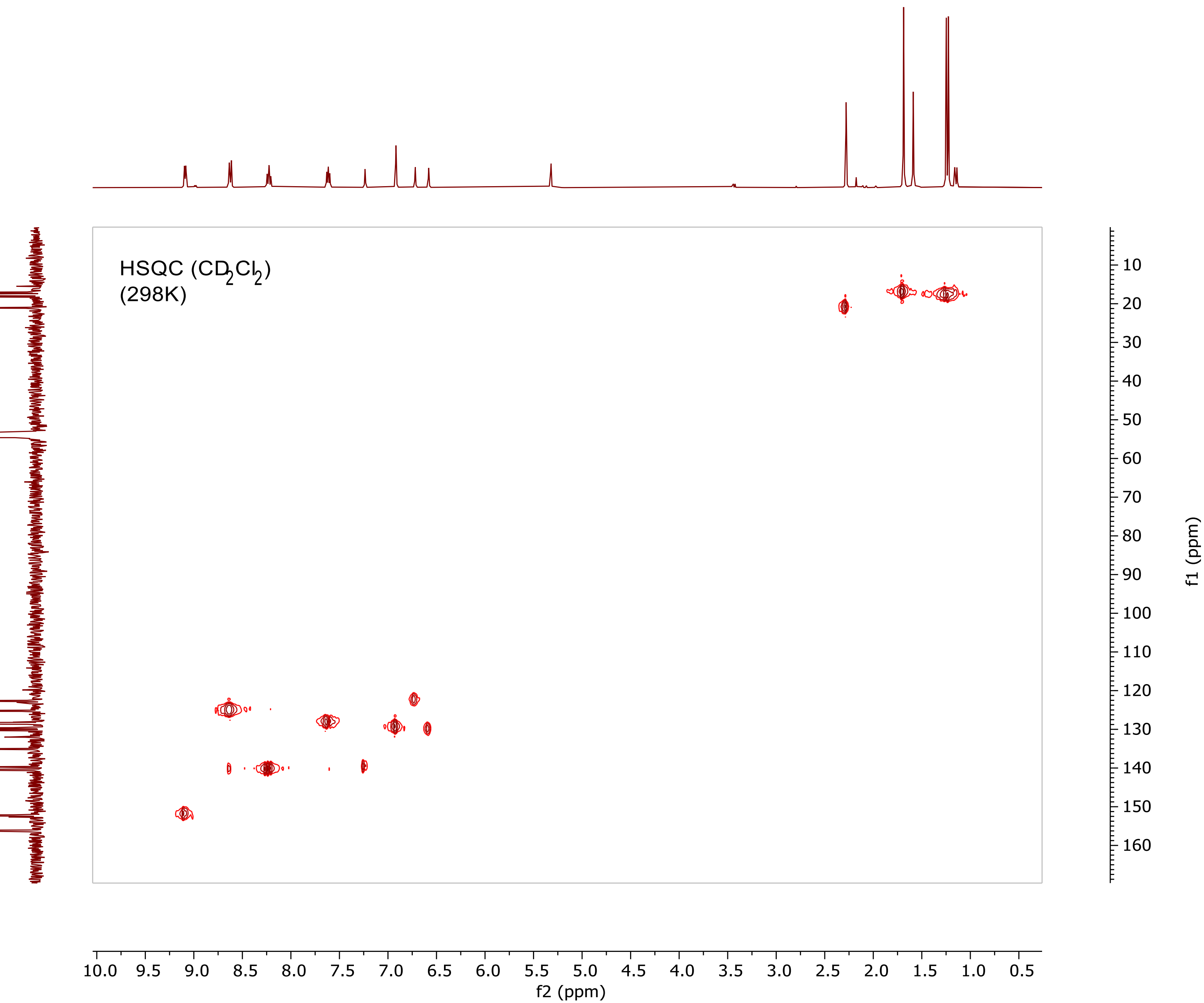
1b

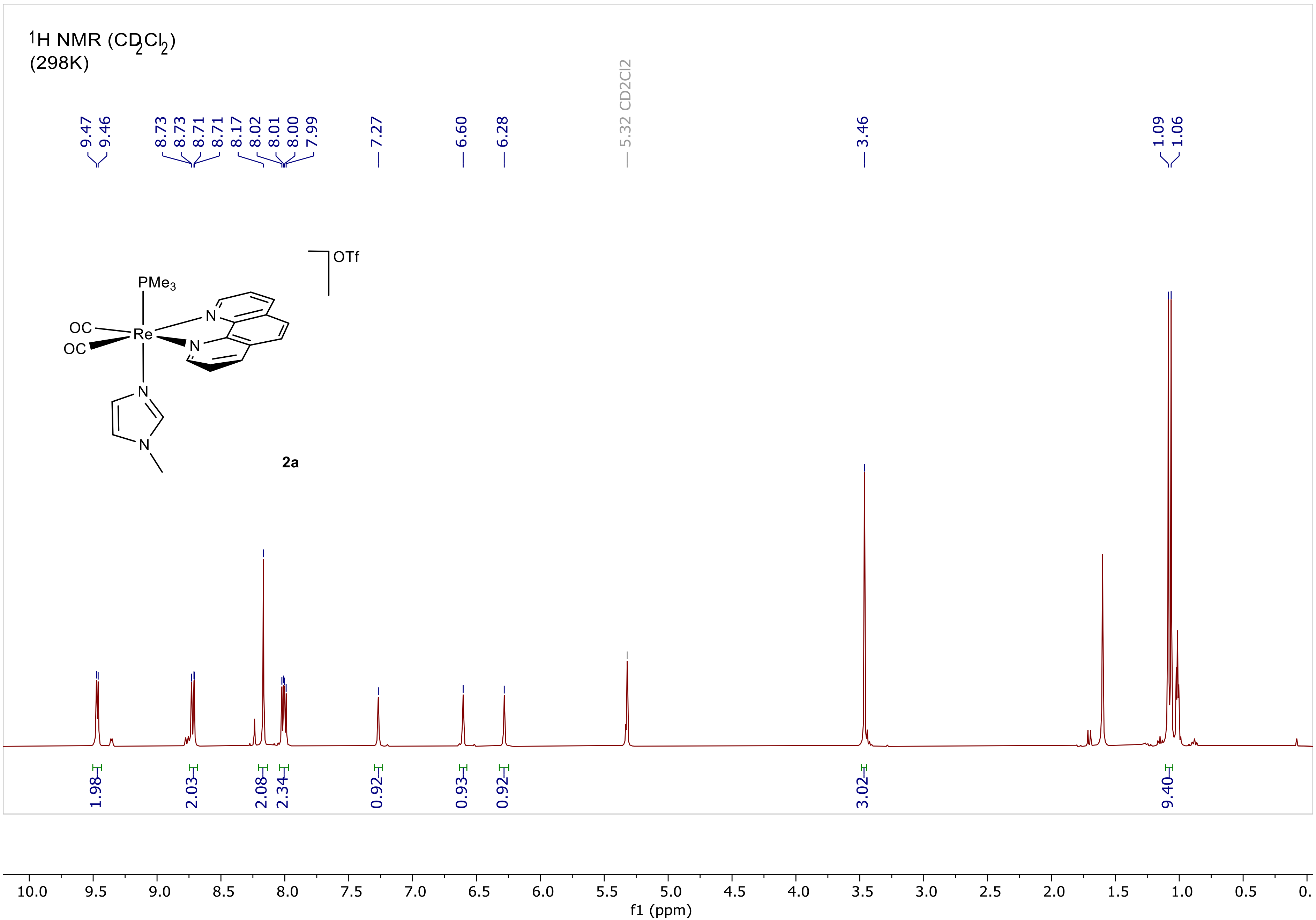


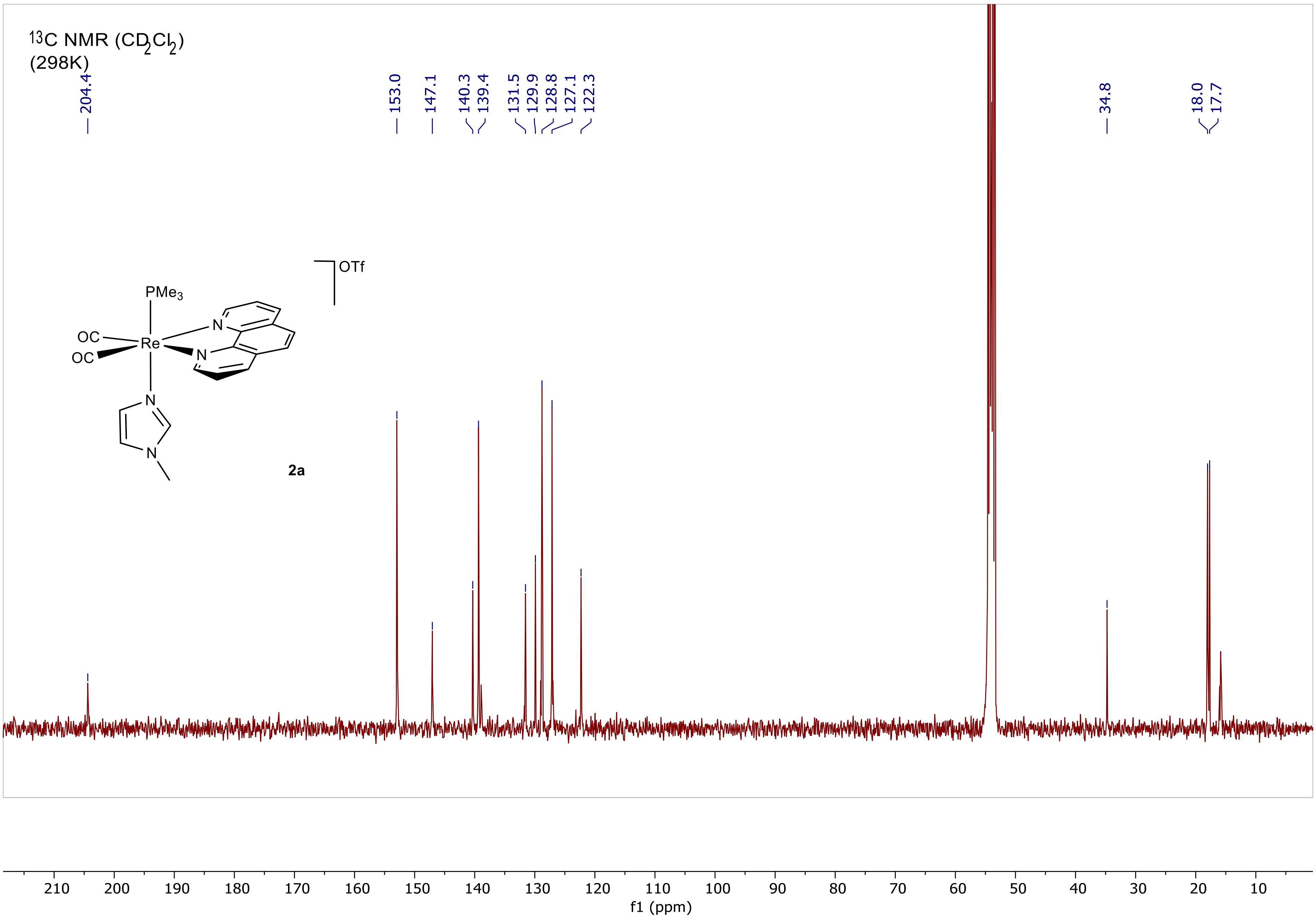
COSY (CD2Cl2)
(298K)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)



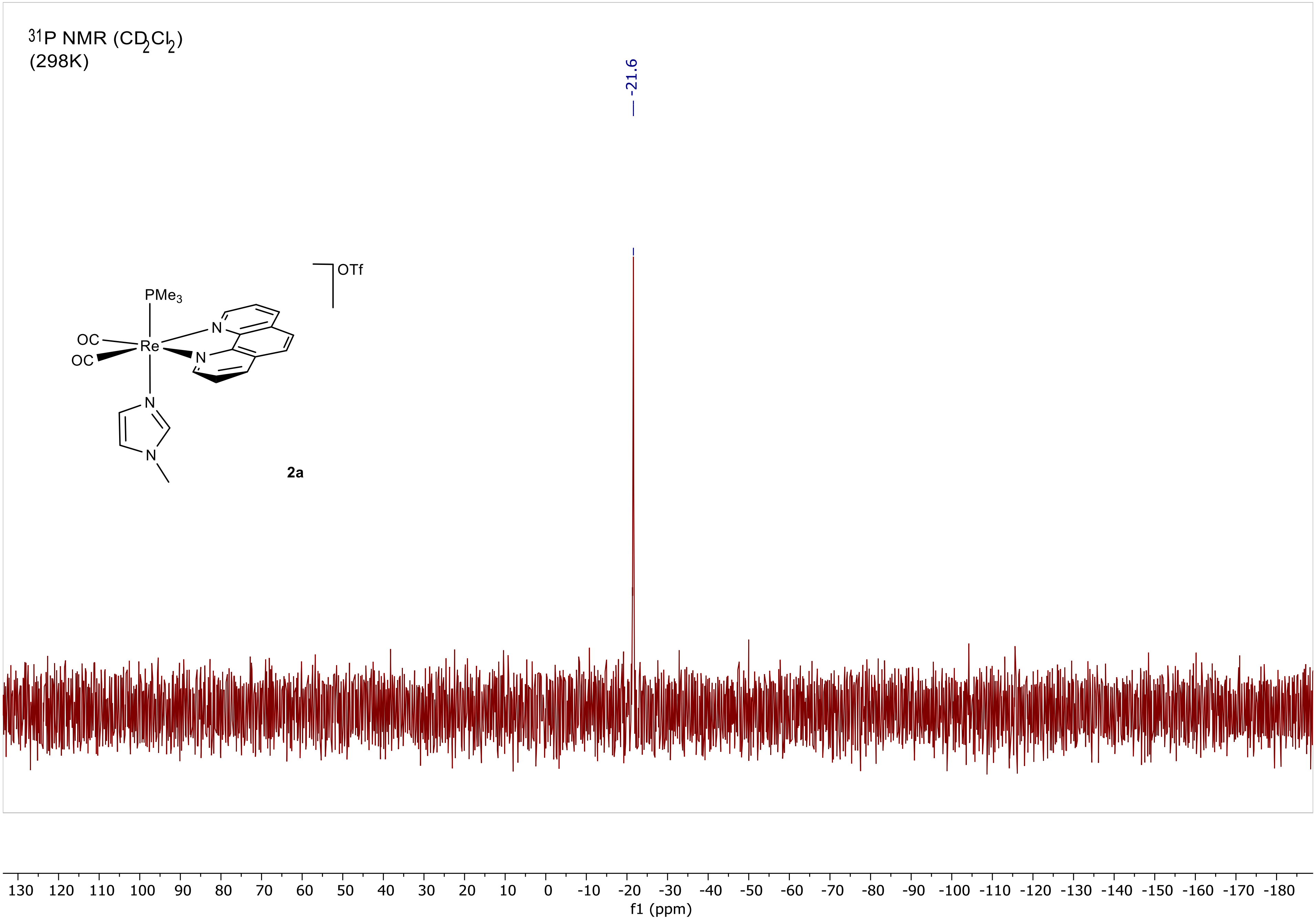
1b

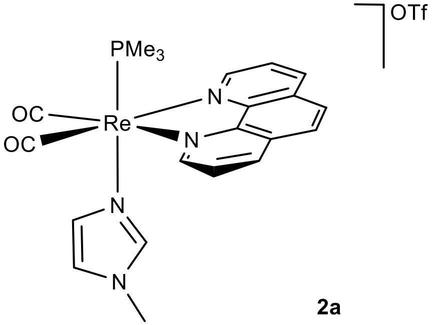



1H NMR (CD2Cl2)
(298K)
9.47
9.46
8.73
8.73
8.71
8.71
8.17
8.02
8.01
8.00
7.99
7.27
6.60
6.28
5.32 CD2Cl2
3.46
1.09
1.06
OTf
PMe3
OC
OC
Re
N
N
N
N
2a
1.98
2.03
2.08
2.34
0.92
0.93
0.92
3.02
9.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

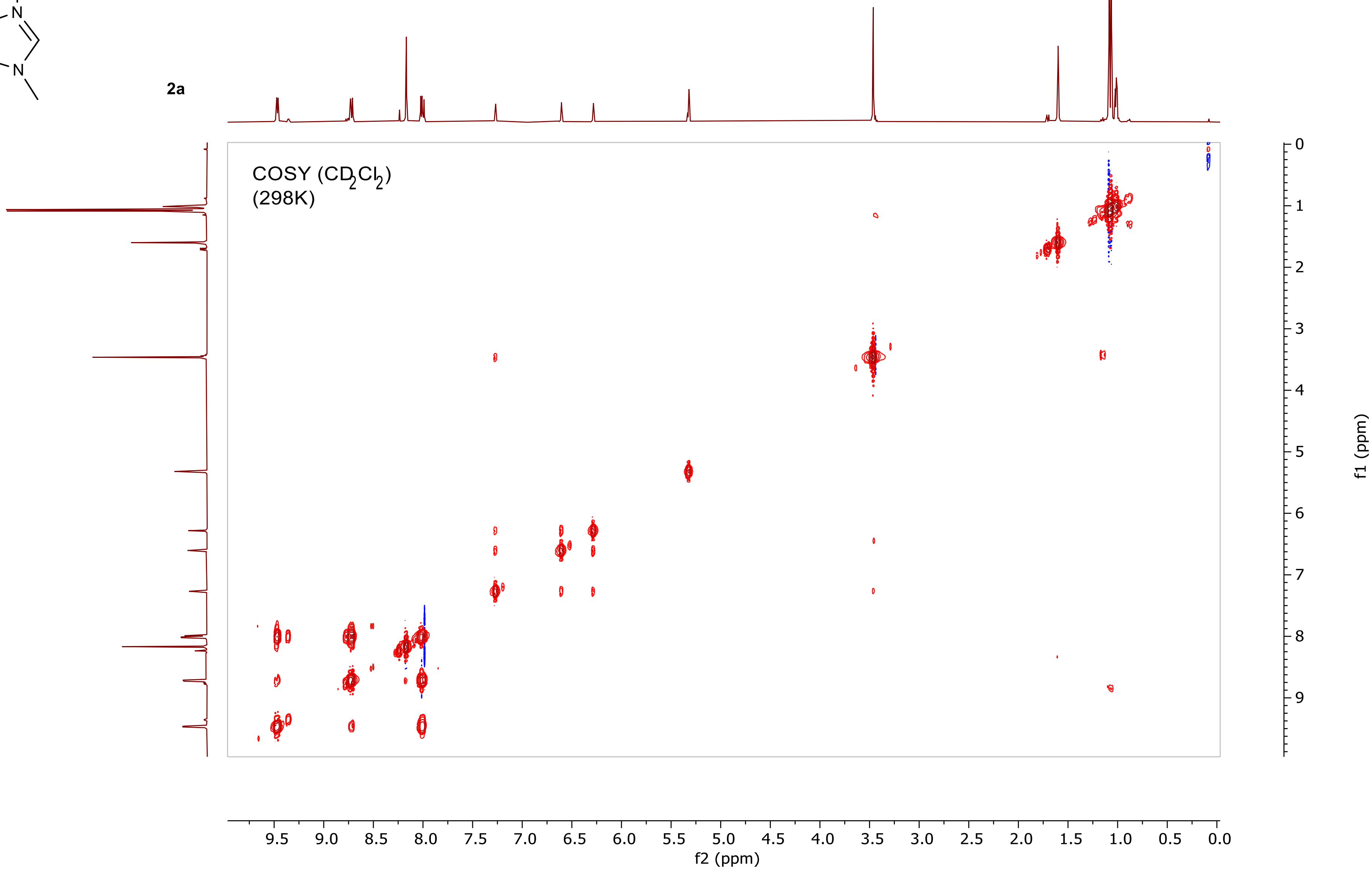


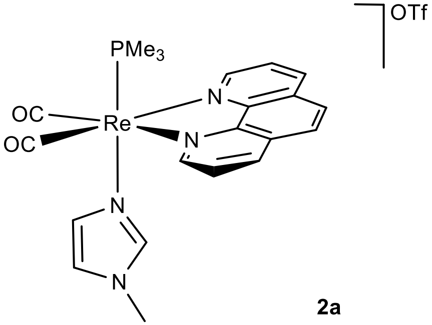
^{13}C NMR (CD_2Cl_2)
(298K)
204.4
153.0
147.1
140.3
139.4
131.5
129.9
128.8
127.1
122.3
34.8
18.0
17.7
PMe3
OC
OC
Re
N
N
N
N
OTf
2a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


^{31}P NMR (CD_2Cl_2)
(298K)
-21.6
PMe3
OC
OC
Re
N
N
N
N
OTf
2a
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

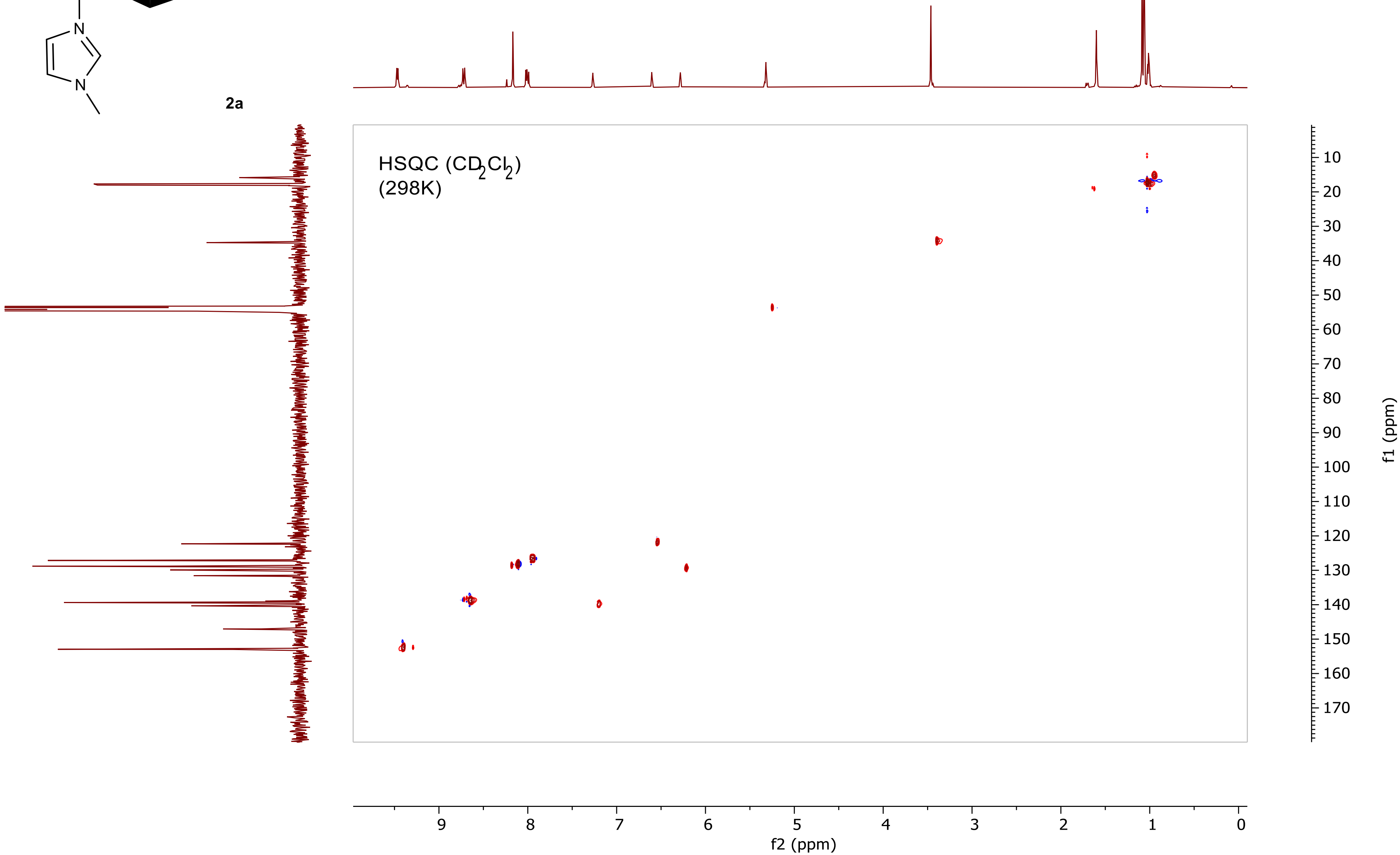

OTf
PMe3
OC
OC
Re
N
N
N
N

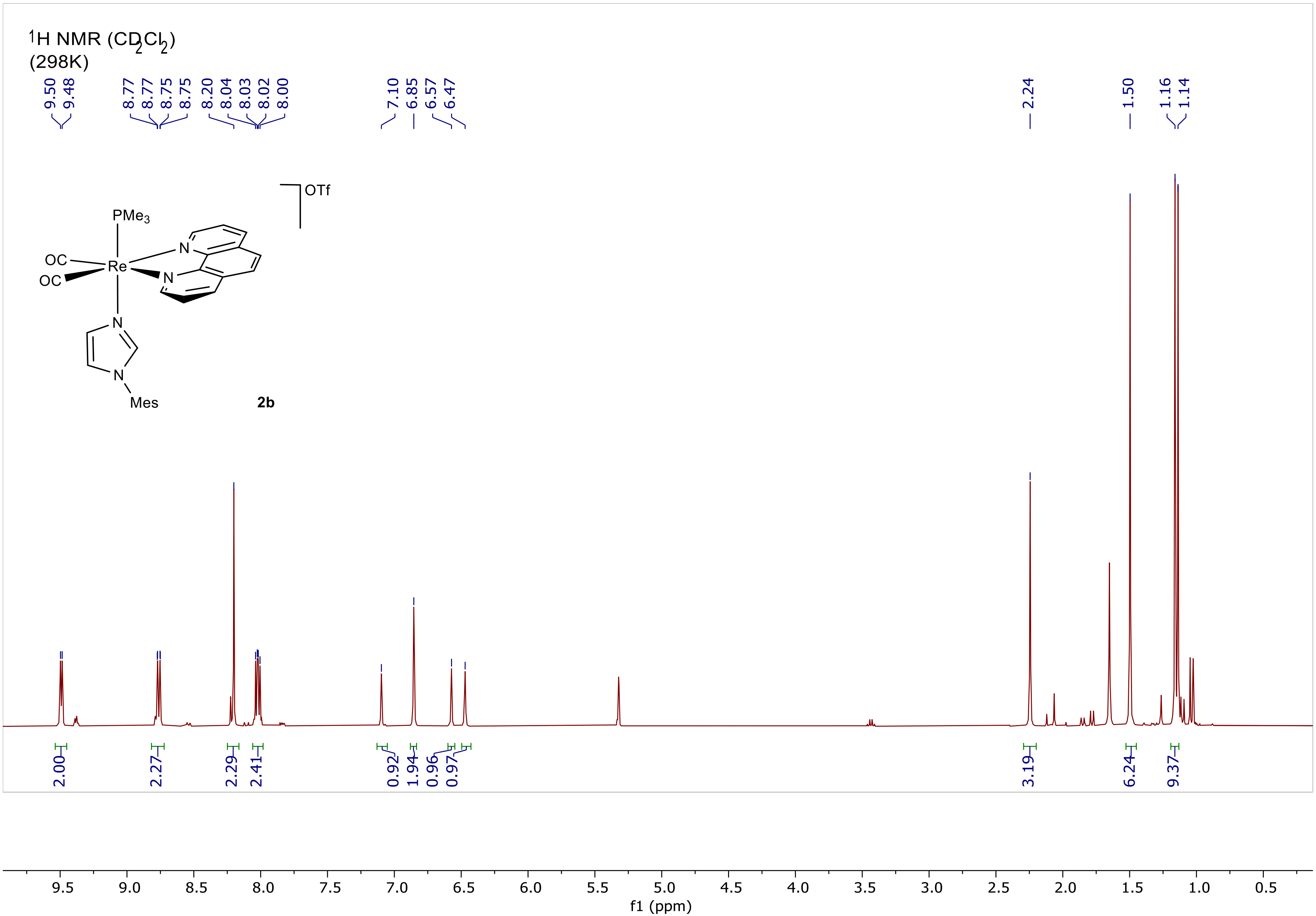
2a


COSY (CD2Cl2)
(298K)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)

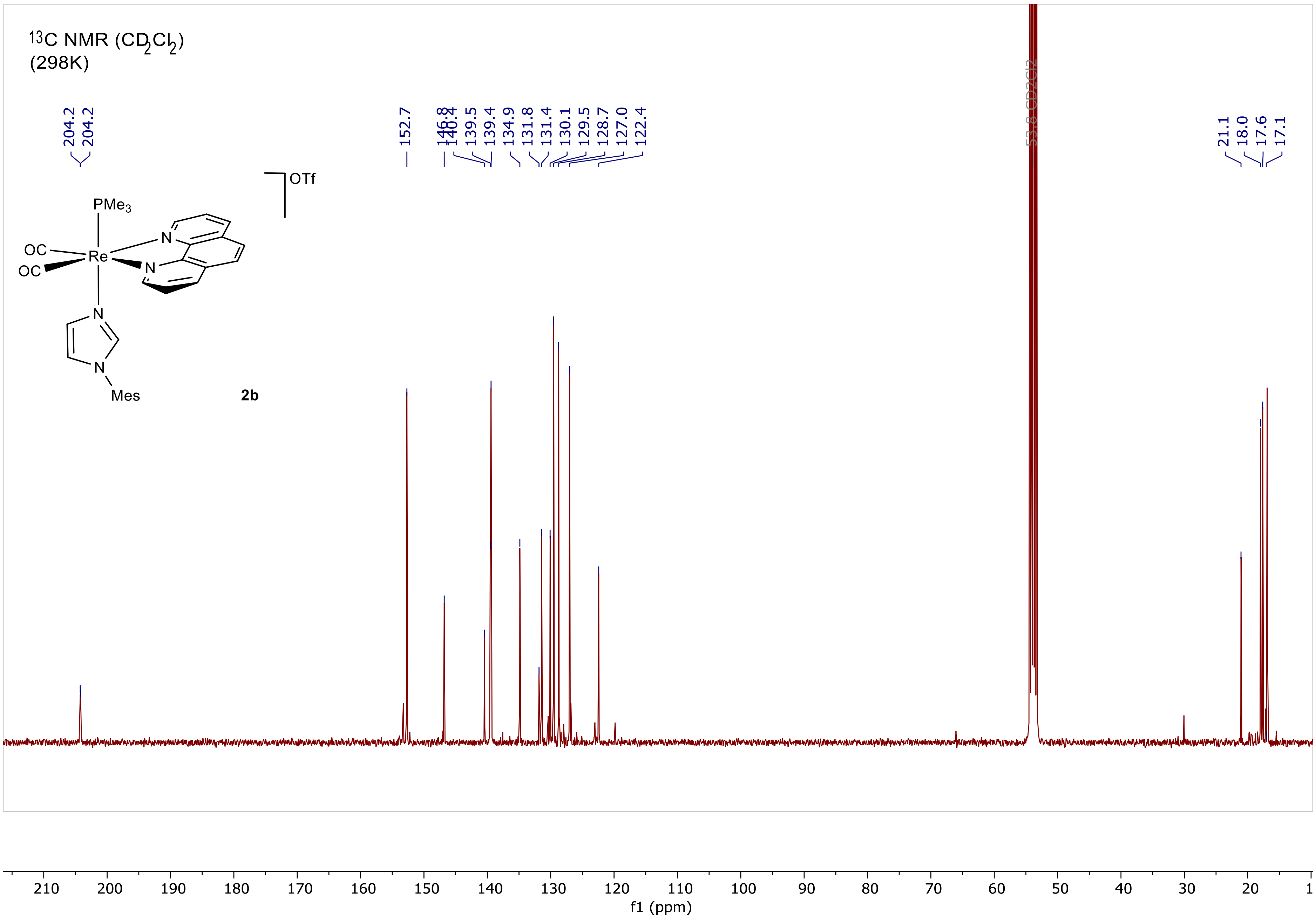


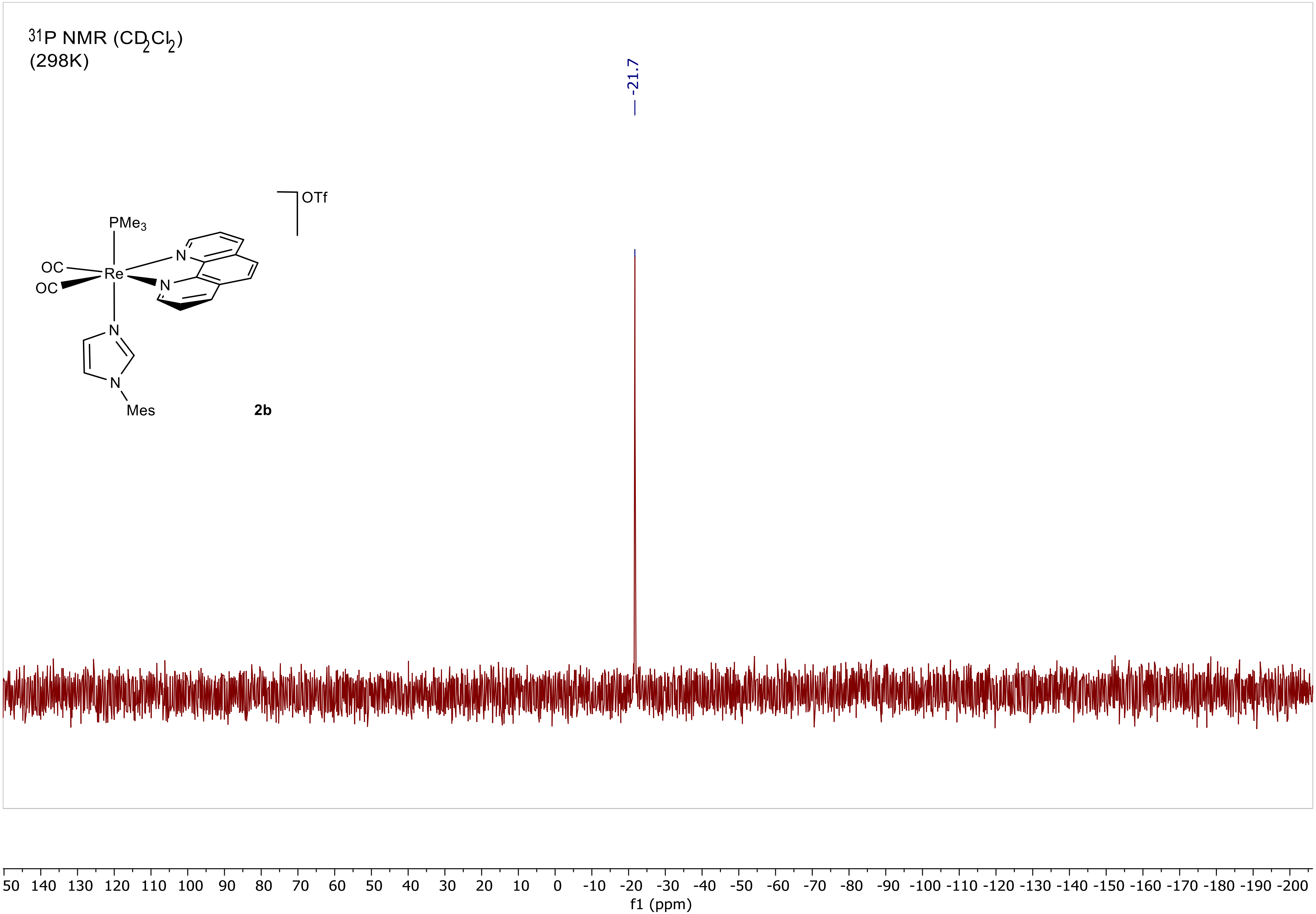
2a



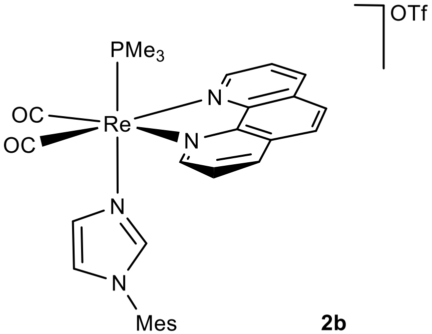


1H NMR (CD2Cl2)
(298K)
9.50
9.48
8.77
8.77
8.75
8.75
8.20
8.04
8.03
8.02
8.00
7.10
6.85
6.57
6.47
2.24
1.50
1.16
1.14
OTf
PMe3
OC
OC
Re
N
N
N
N
Mes
2b
2.00
2.27
2.29
2.41
0.92
1.94
0.96
0.97
3.19
6.24
9.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

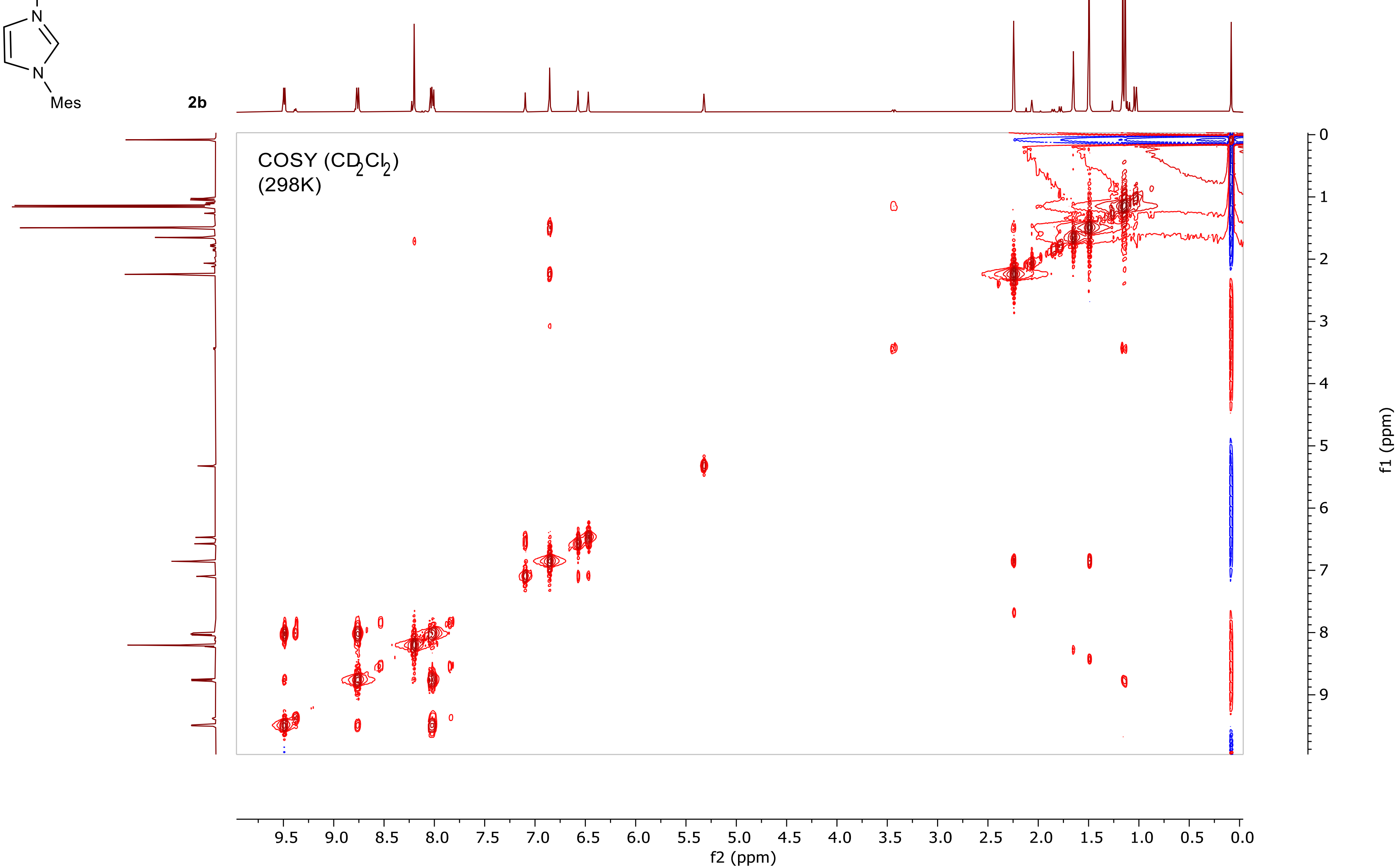

^{13}C NMR (CD_2Cl_2)
(298K)
204.2
204.2
152.7
146.8
140.4
139.5
139.4
134.9
131.8
131.4
130.1
129.5
128.7
127.0
122.4
53.8 CD2Cl2
21.1
18.0
17.6
17.1
OTf
PMe3
OC
OC
Re
N
N
N
N
Mes
2b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

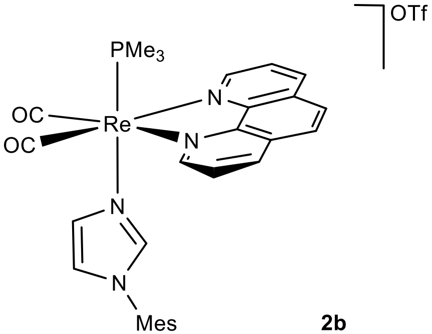


^{31}P NMR (CD_2Cl_2)
(298K)
-21.7
PMe3
OC
OC
Re
N
N
N
N
Mes
OTf
2b
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

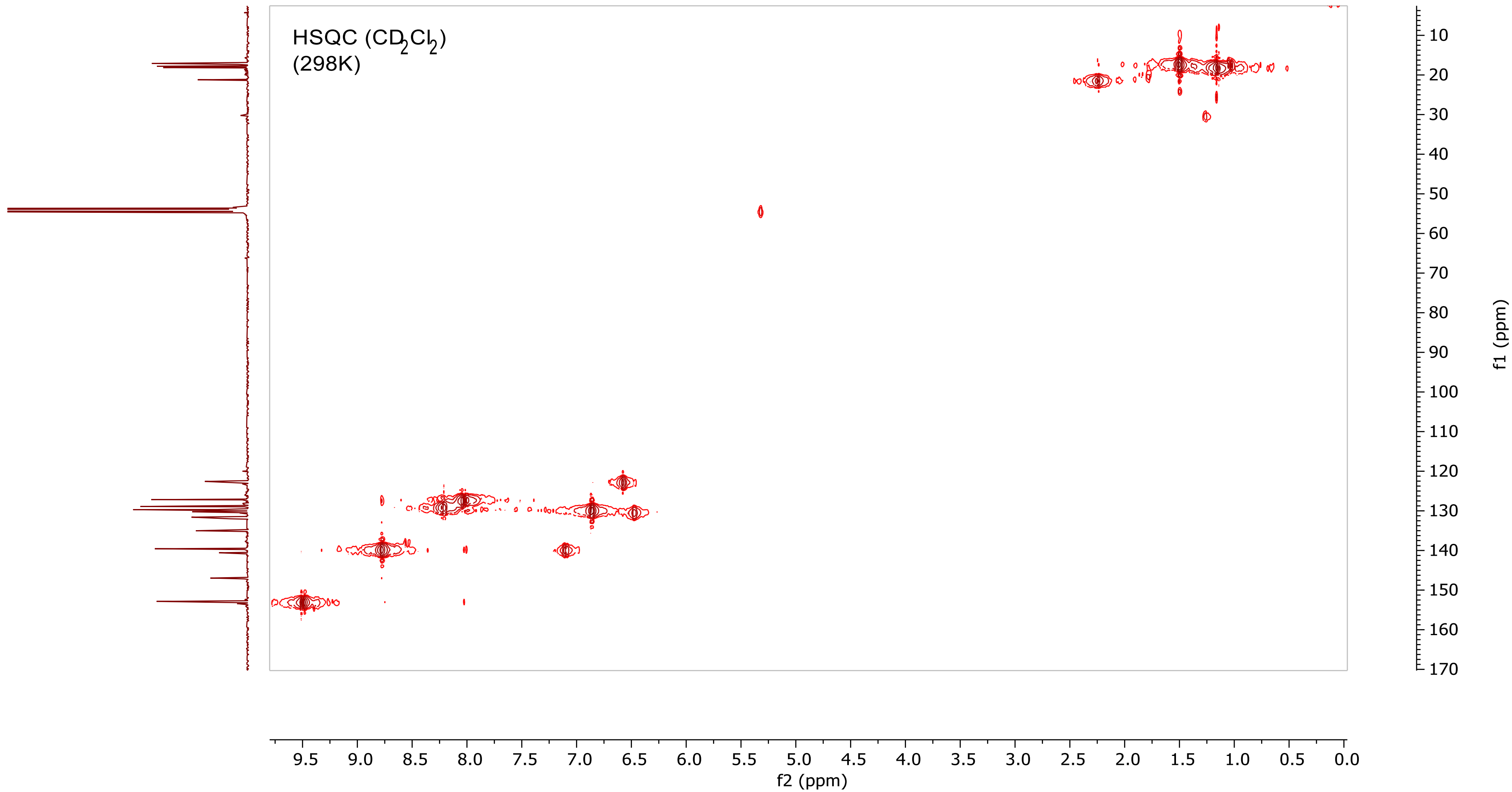

OTf
PMe3
OC
OC
Re
N
N
N
N
Mes

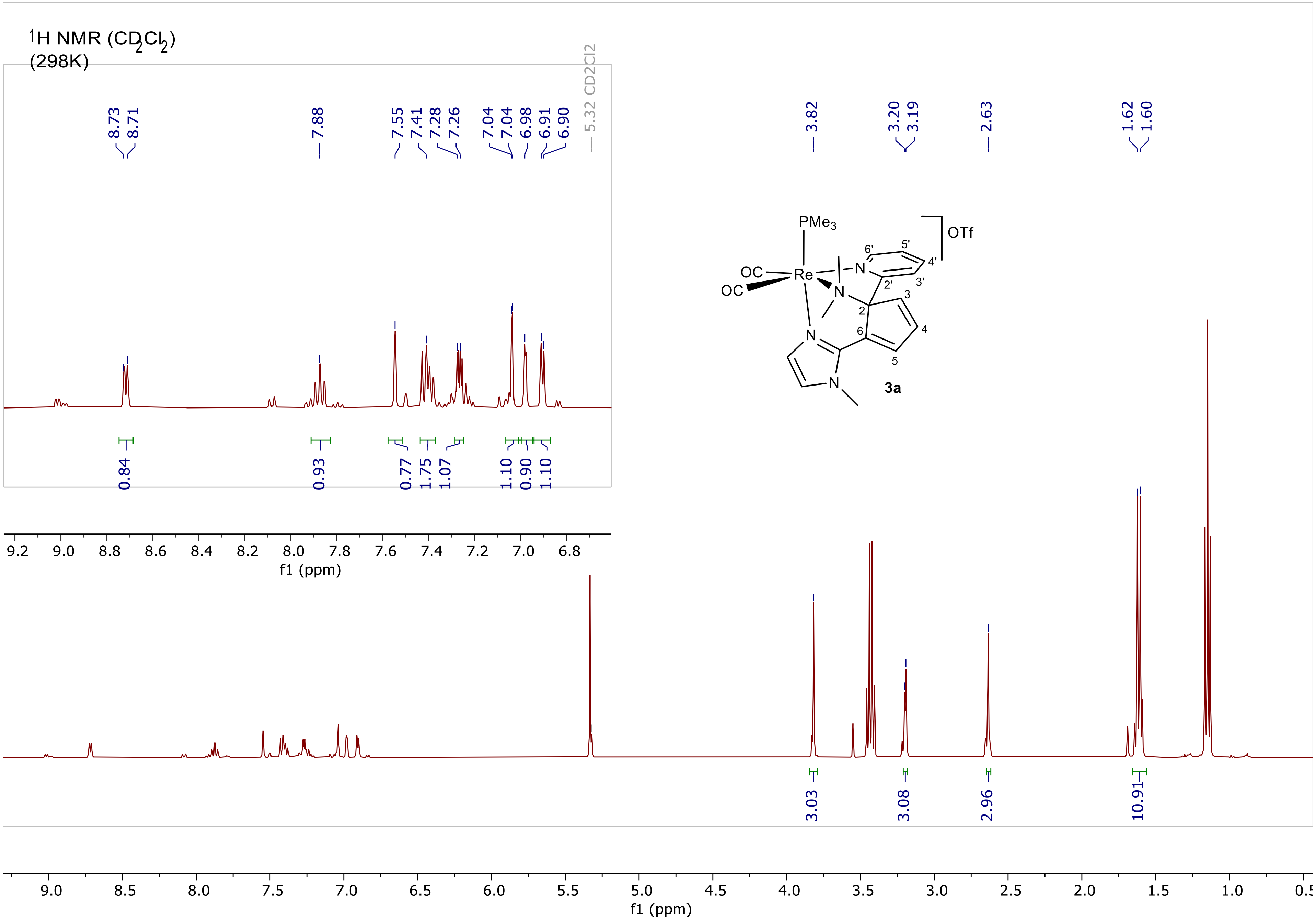
2b


COSY (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8 9

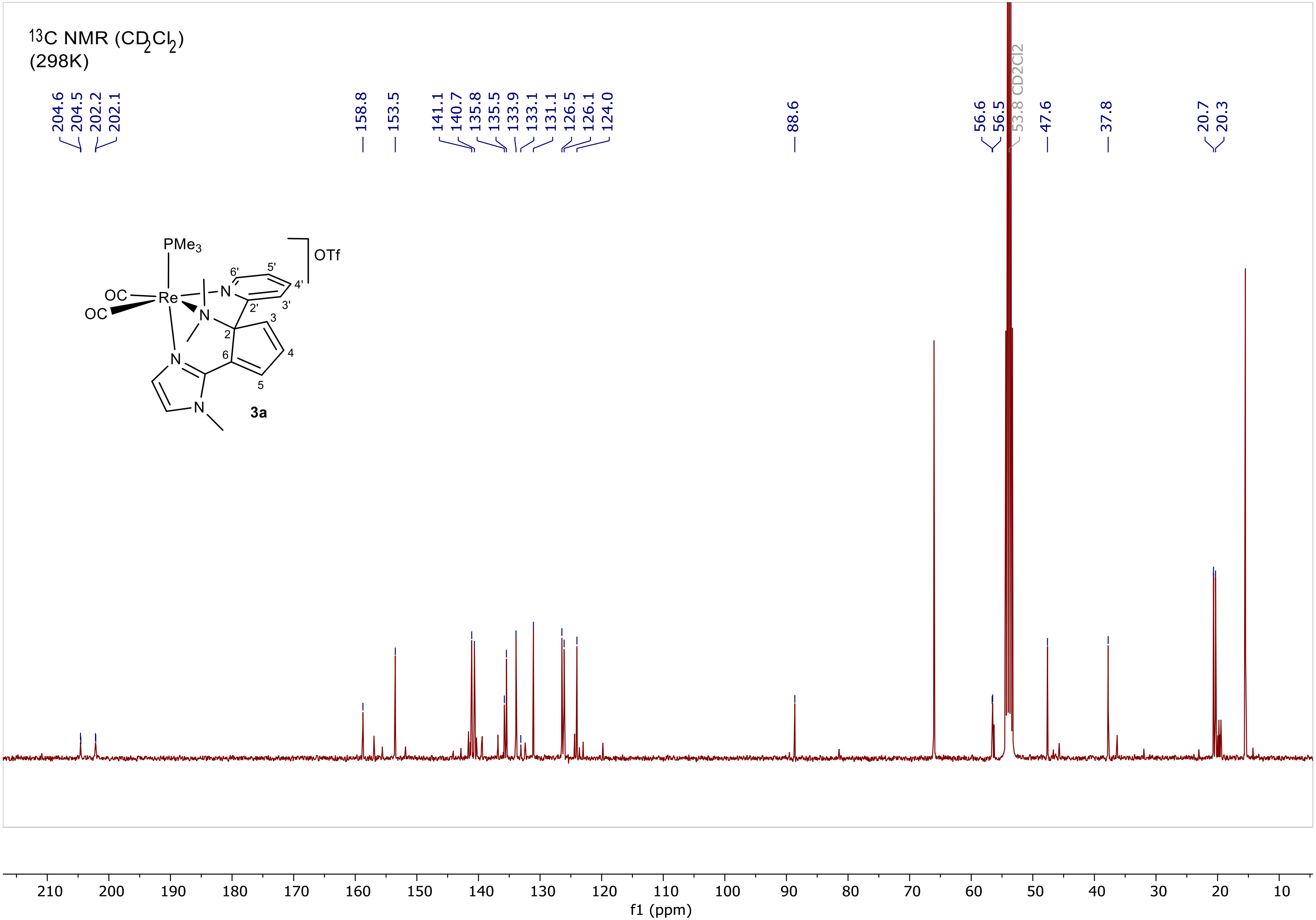


2b

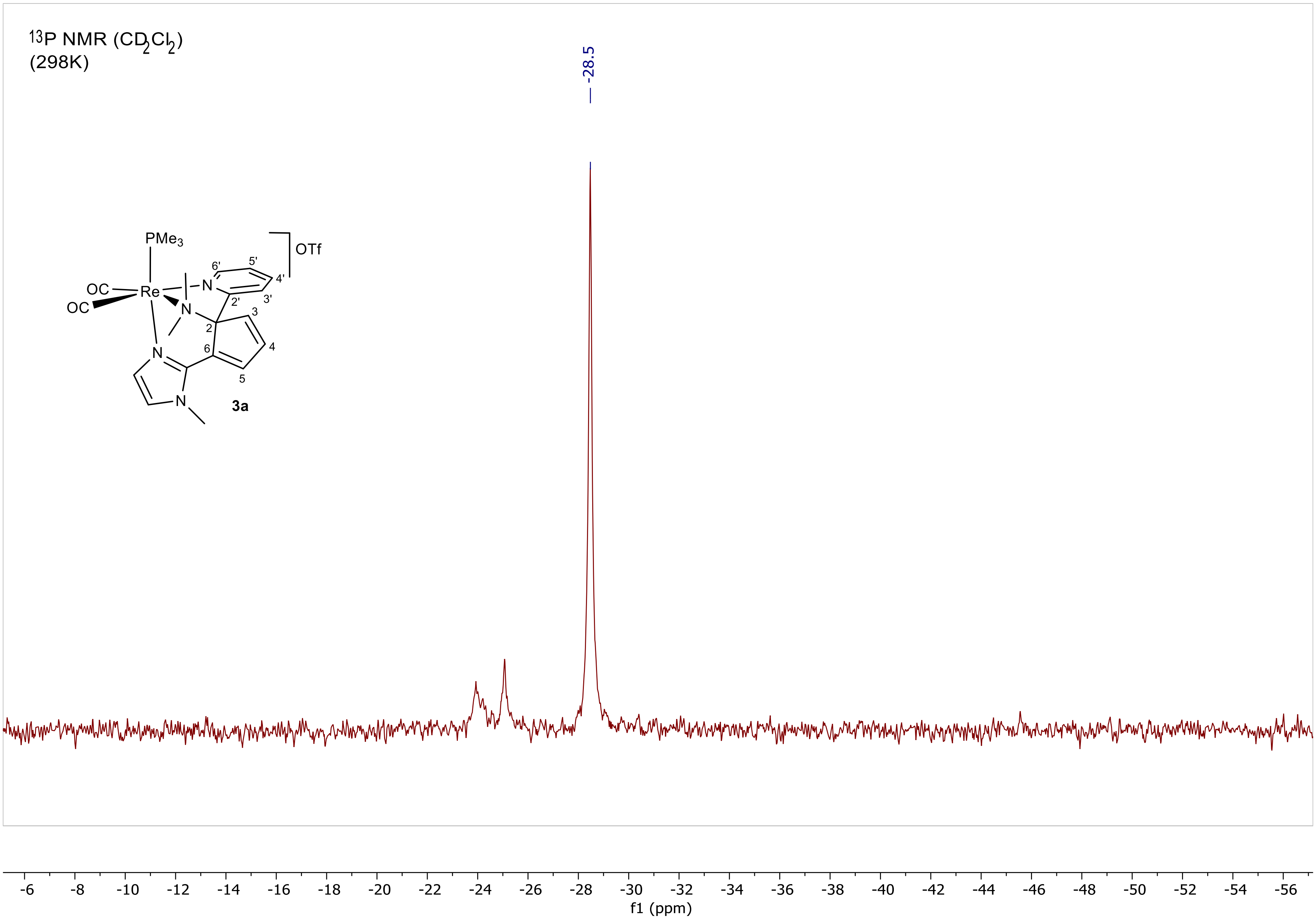


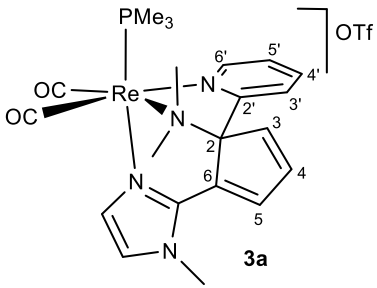


1H NMR (CD2Cl2)
(298K)
8.73
8.71
7.88
7.55
7.41
7.28
7.26
7.04
7.04
6.98
6.91
6.90
5.32 CD2Cl2
3.82
3.20
3.19
2.63
1.62
1.60
PMe3
OTf
OC
OC
Re
N
N
N
N
6'
5'
4'
3'
2'
2
3
4
5
6
3a
0.84
0.93
0.77
1.75
1.07
1.10
0.90
1.10
3.03
3.08
2.96
10.91
f1 (ppm)
f1 (ppm)

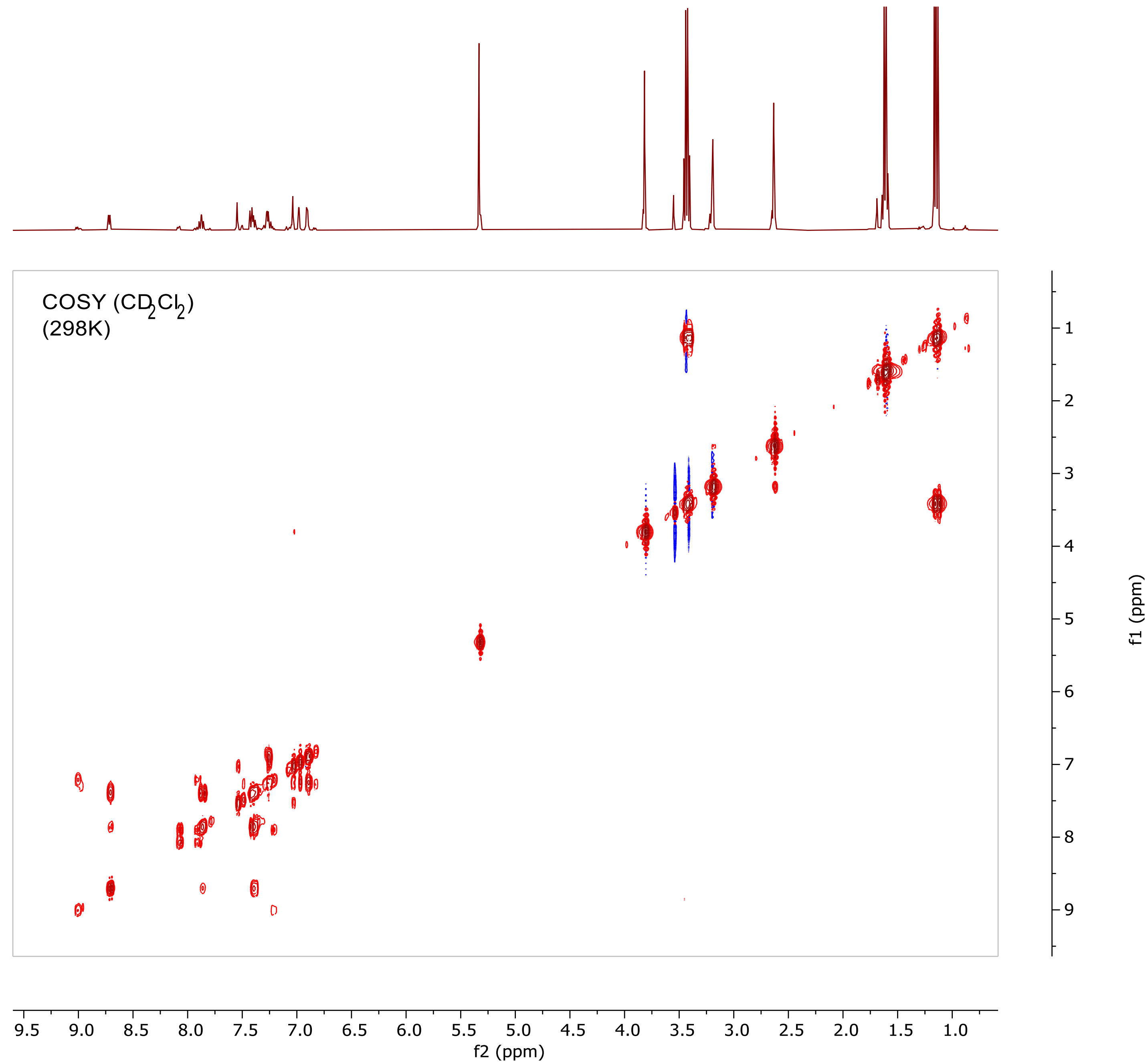


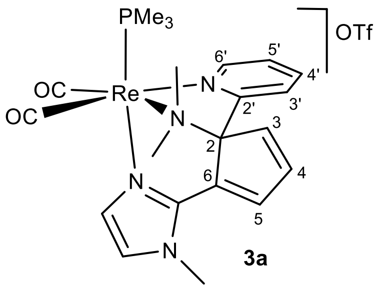
^{13}C NMR (CD$_2$Cl$_2$)
(298K)
204.6
204.5
202.2
202.1
158.8
153.5
141.1
140.7
135.8
135.5
133.9
133.1
131.1
126.5
126.1
124.0
88.6
56.6
56.5
53.8 CD2Cl2
47.6
37.8
20.7
20.3
PMe$_3$
OC
OC
Re
N
N
N
N
OTf
6'
5'
4'
3'
2'
2
3
4
5
6
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

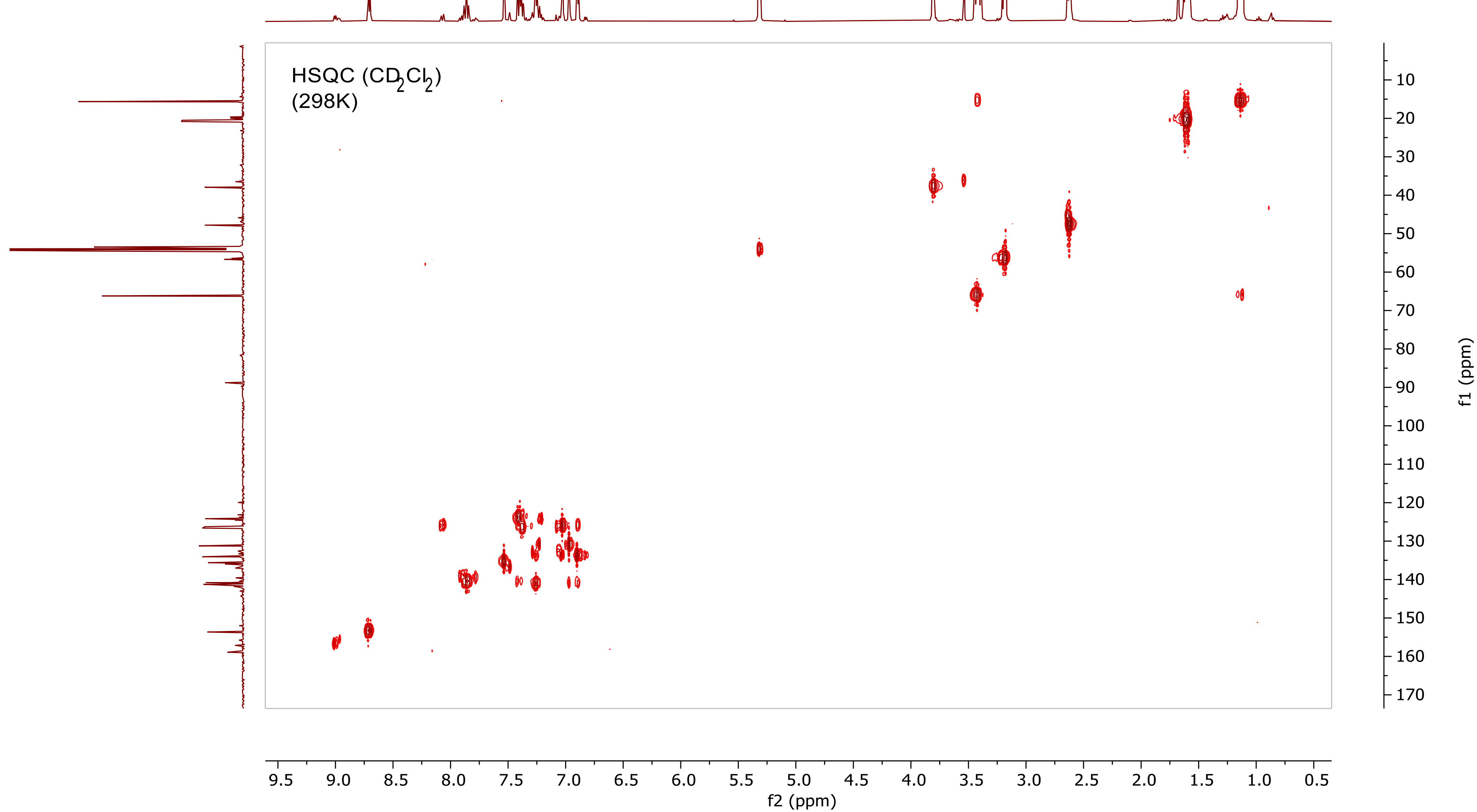

13P NMR (CD2Cl2)
(298K)
-28.5
PMe3
OTf
OC
OC
Re
N
N
N
N
6'
5'
4'
3'
2'
2
3
4
5
6
3a
-6
-8
-10
-12
-14
-16
-18
-20
-22
-24
-26
-28
-30
-32
-34
-36
-38
-40
-42
-44
-46
-48
-50
-52
-54
-56
f1 (ppm)

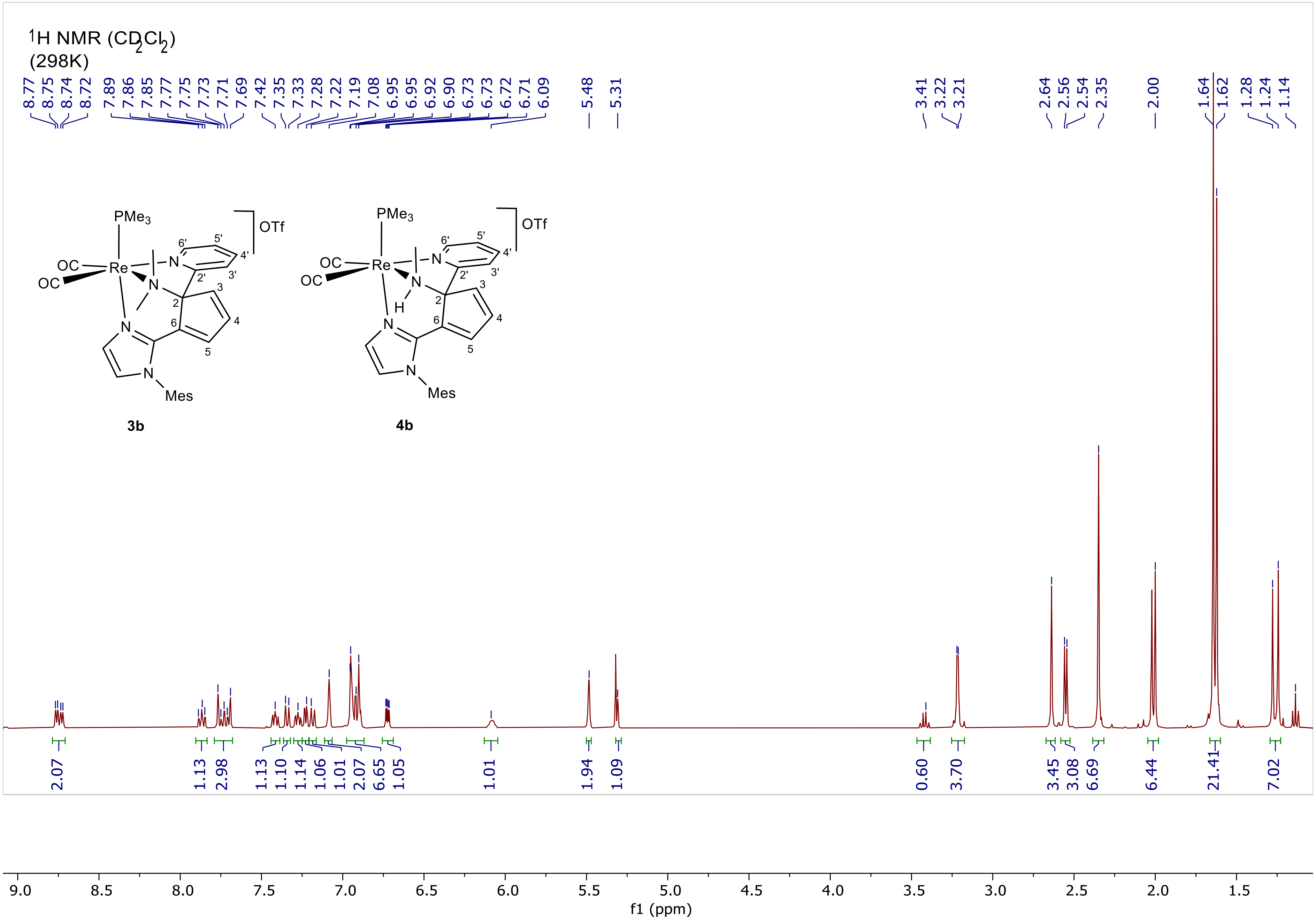

PMe3
OTf
OC
OC
Re
N
N
N
N
6'
5'
4'
3'
2'
2
3
4
5
6

3a

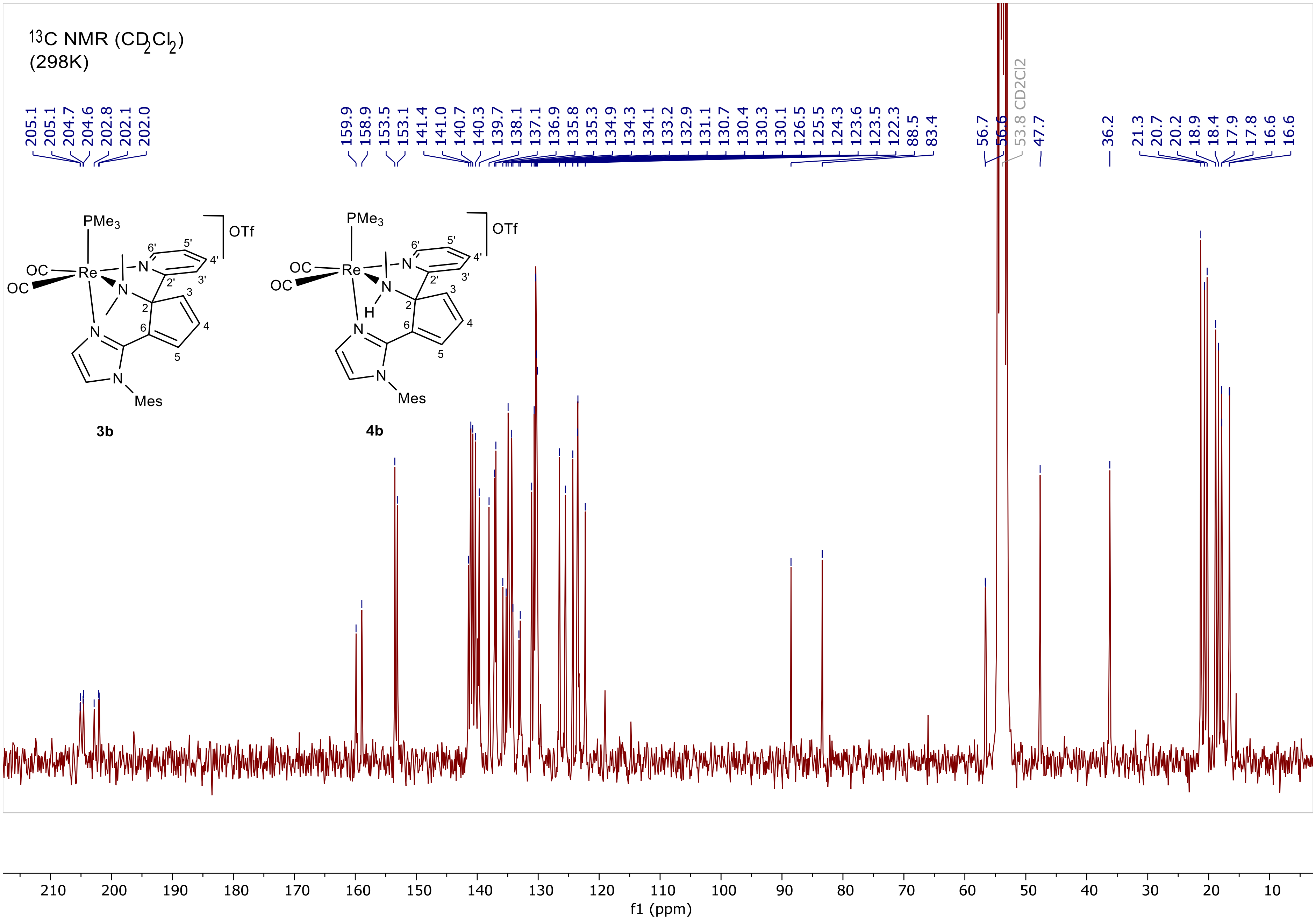

COSY (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)

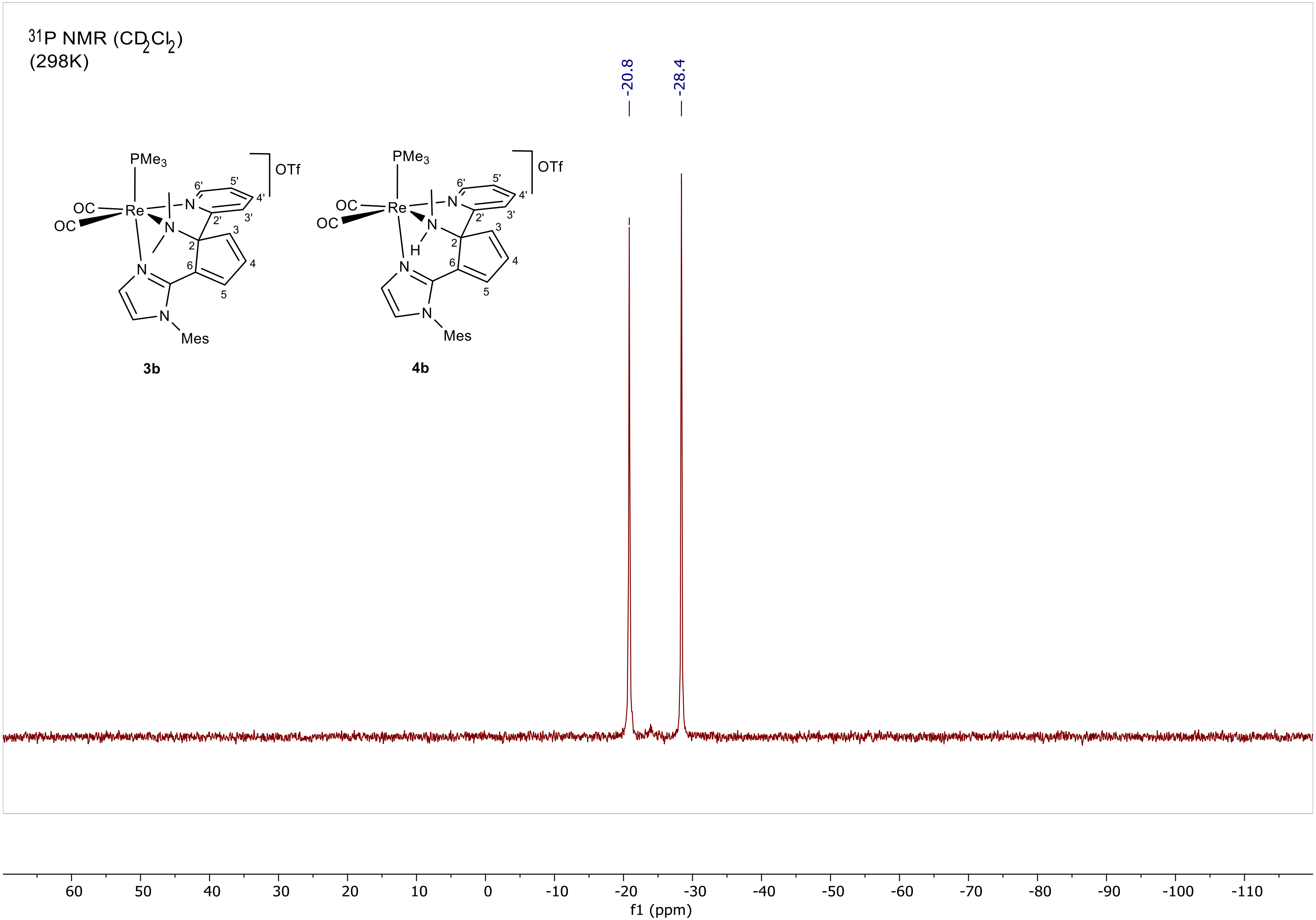

PMe3
OTf
OC
OC
Re
N
6'
5'
4'
3'
2'
3
2
4
6
5
3a


HSQC (CD2Cl2)
(298K)
f1 (ppm)
f2 (ppm)

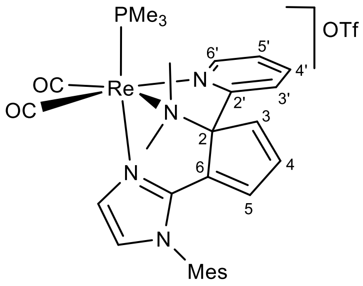


1H NMR (CD2Cl2)
(298K)
8.77 8.75 8.74 8.72 7.89 7.86 7.85 7.77 7.75 7.73 7.71 7.69 7.42 7.35 7.33 7.28 7.22 7.19 7.08 6.95 6.95 6.92 6.90 6.73 6.73 6.72 6.71 6.09
5.48
5.31
3.41 3.22 3.21
2.64 2.56 2.54 2.35
2.00
1.64 1.62
1.28 1.24 1.14
PMe3
OTf
OC
Re
N
Mes
H
3b
4b
2.07 1.13 2.98 1.13 1.10 1.14 1.06 1.01 2.07 6.65 1.05 1.01 1.94 1.09 0.60 3.70 3.45 3.08 6.69 6.44 21.41 7.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

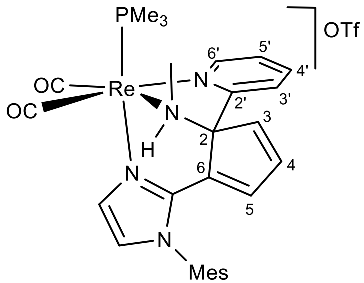

13C NMR (CD2Cl2)
(298K)
205.1 205.1 204.7 204.6 202.8 202.1 202.0
159.9 158.9 153.5 153.1 141.4 141.0 140.7 140.3 139.7 138.1 137.1 136.9 135.8 135.3 134.9 134.3 134.1 133.2 132.9 131.1 130.7 130.4 130.3 130.1 126.5 125.5 124.3 123.6 123.5 122.3 88.5 83.4
56.7 56.6 53.8 CD2Cl2 47.7 36.2 21.3 20.7 20.2 18.9 18.4 17.9 17.8 16.6 16.6
PMe3
OTf
OC
Re
N
Mes
H
3b
4b
f1 (ppm)



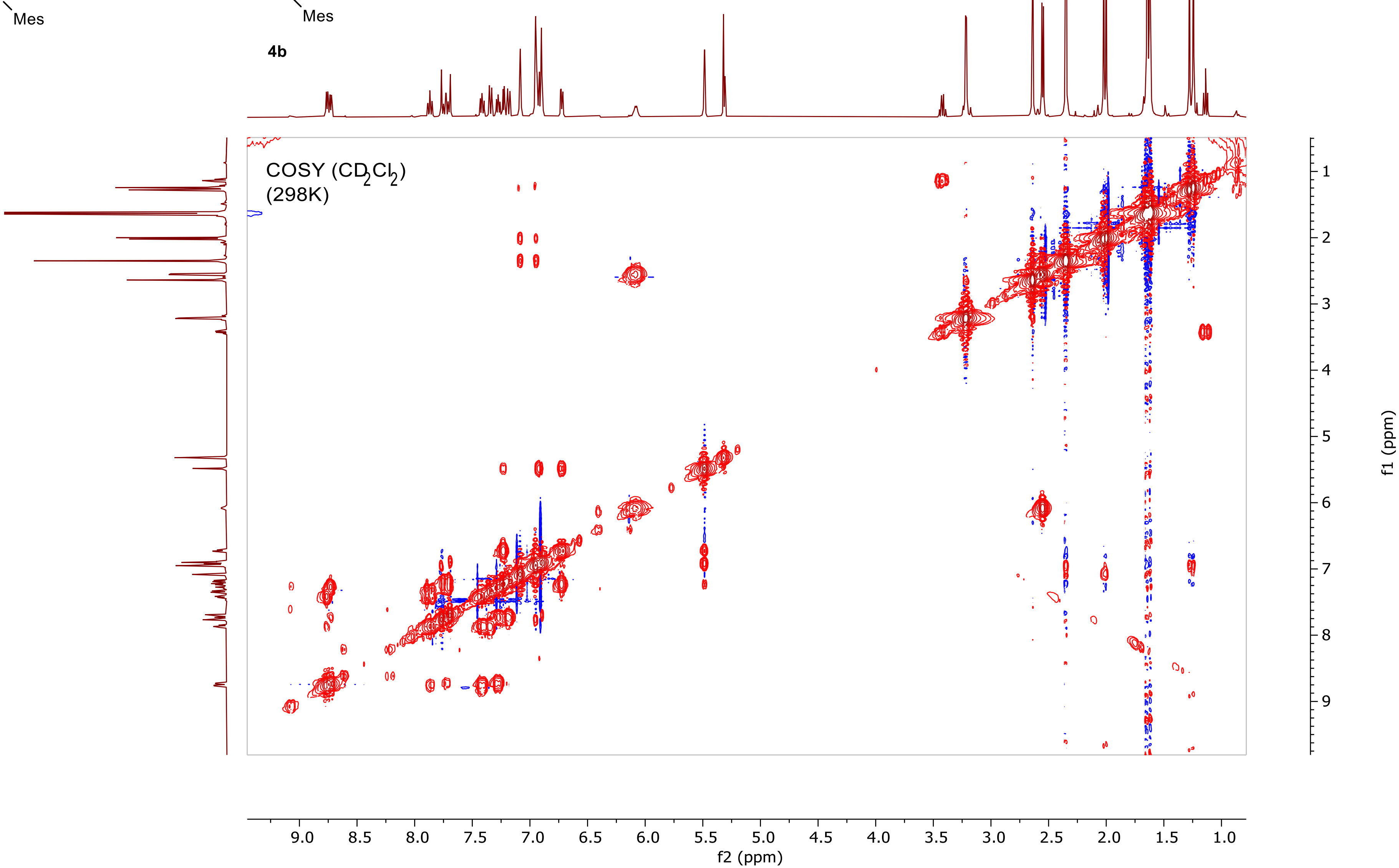
31P NMR (CD2Cl2)
(298K)
-20.8
-28.4
PMe3
OTf
OC
Re
N
Mes
3b
4b
f1 (ppm)
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110

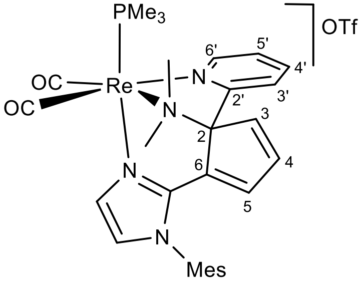


3b

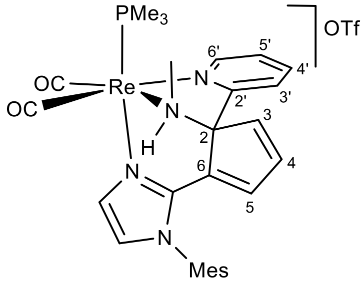


4b

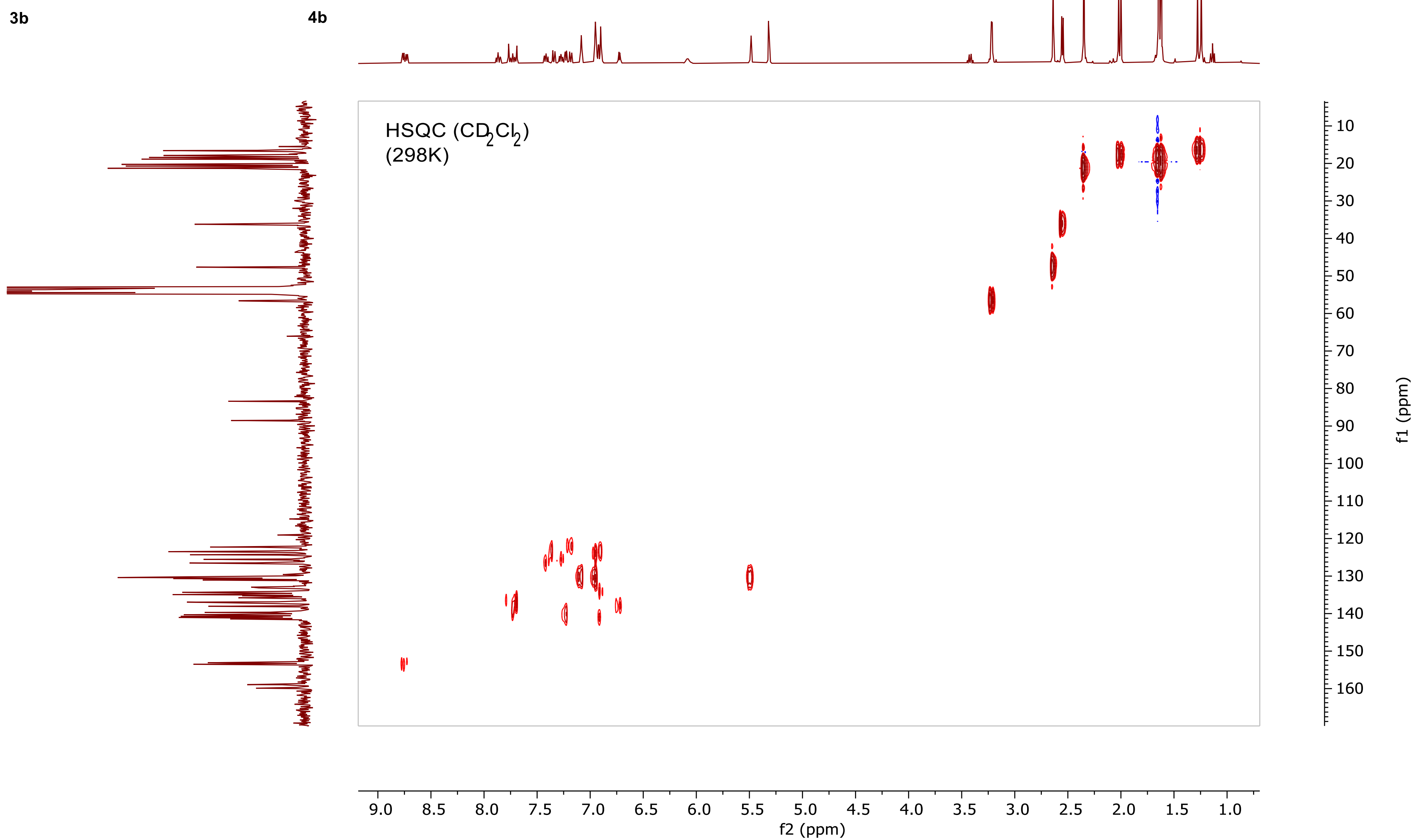


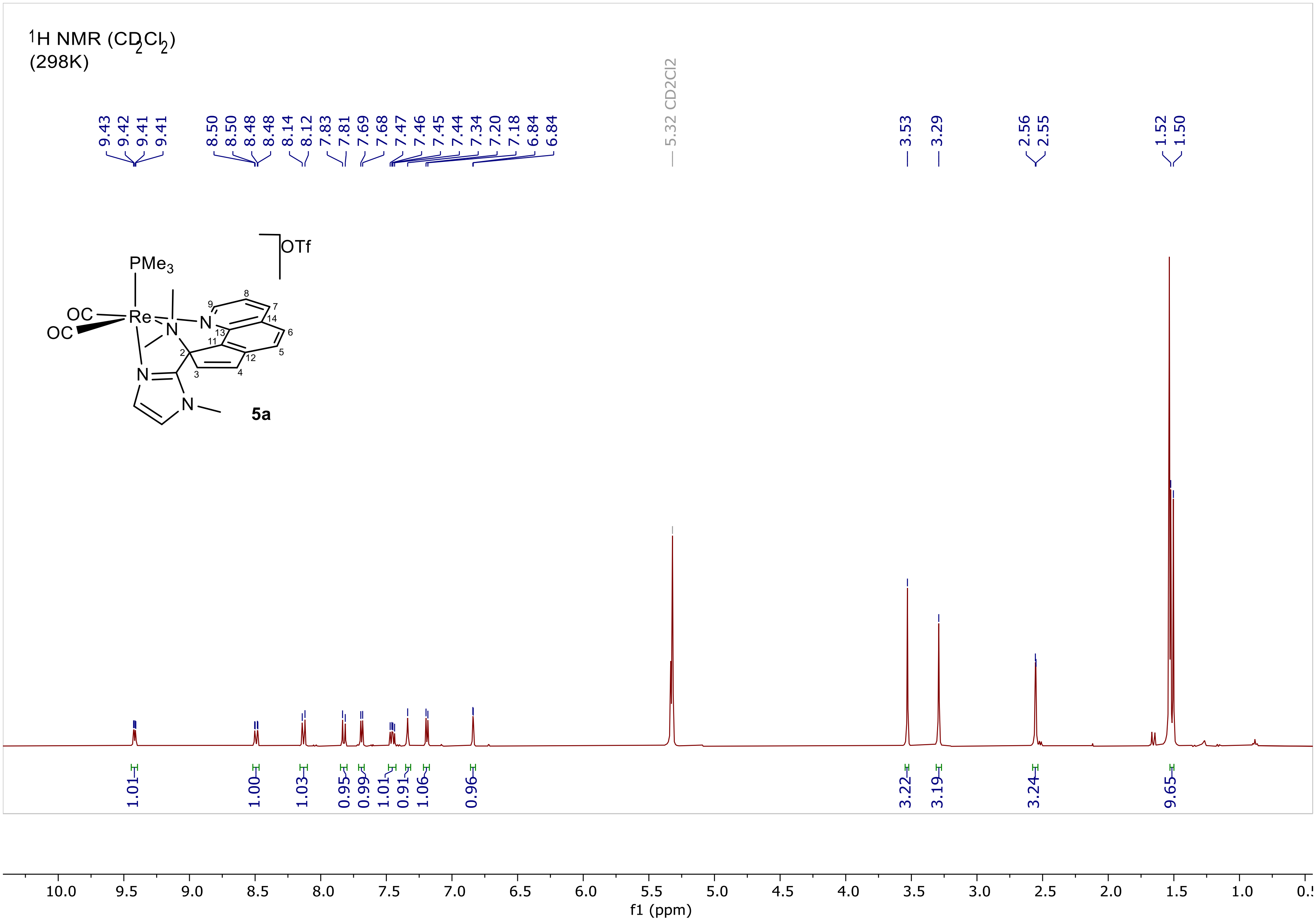

PMe3
OTf
OC
OC
Re
N
6'
5'
4'
3'
2'
2
3
4
5
6
Mes

3b

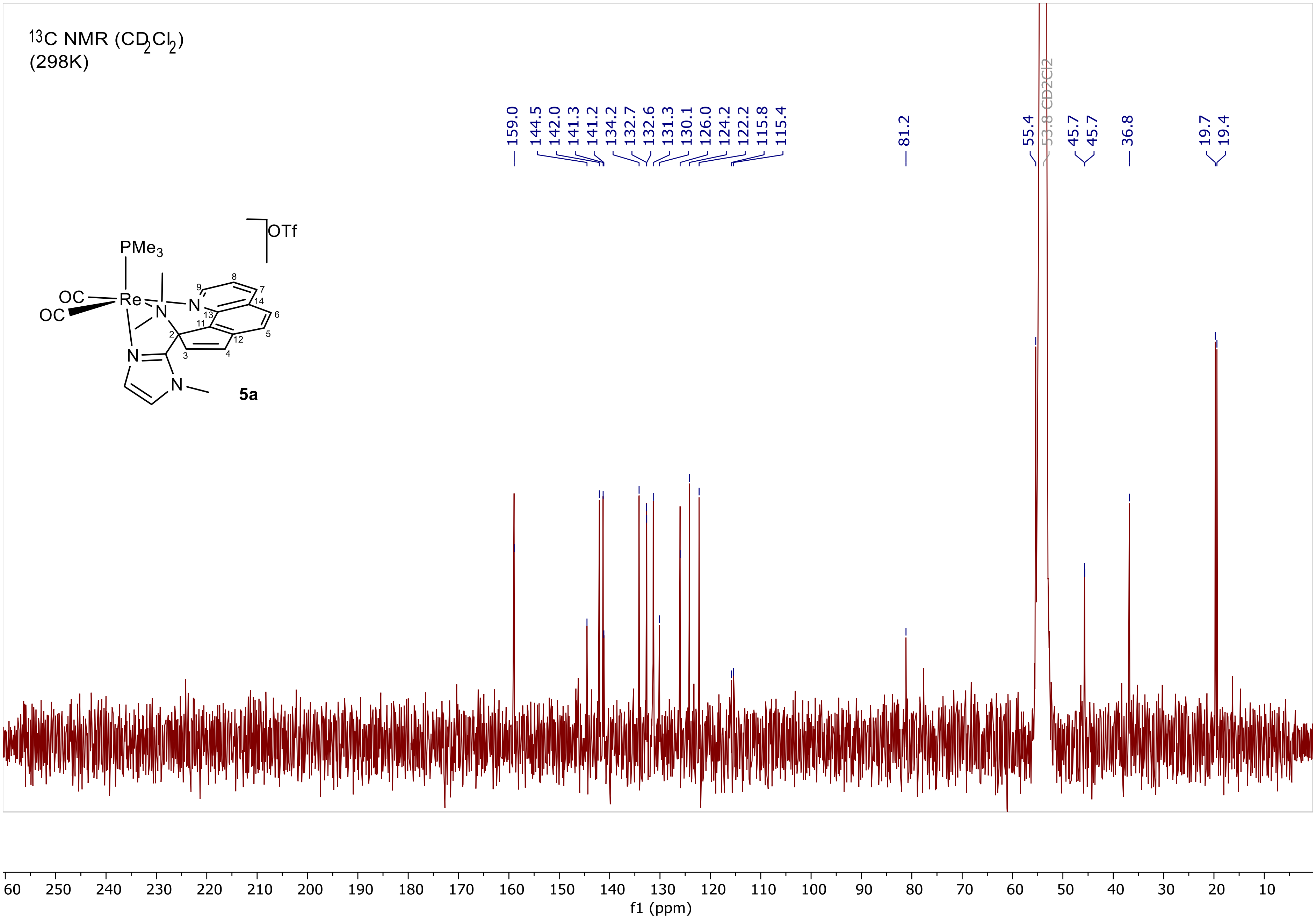

PMe3
OTf
OC
OC
Re
N
H
6'
5'
4'
3'
2'
2
3
4
5
6
Mes

4b

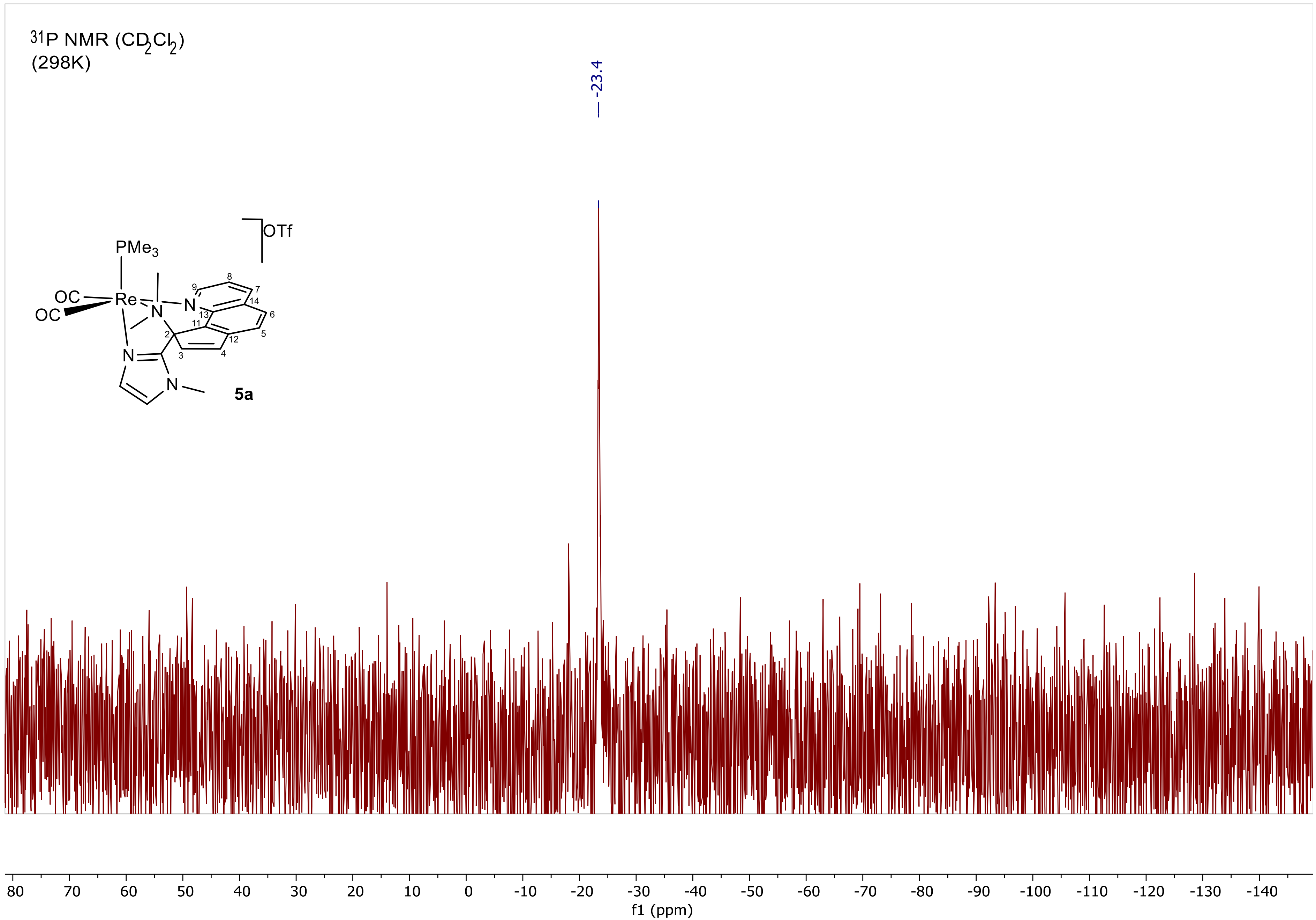

HSQC (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)

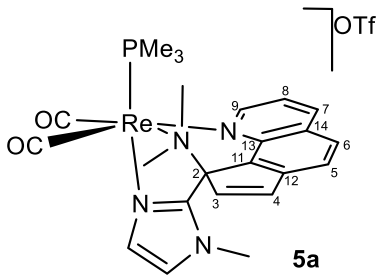


^{1}H NMR (CD_2Cl_2)
(298K)
9.43 9.42 9.41 9.41 8.50 8.50 8.48 8.48 8.14 8.12 7.83 7.81 7.69 7.68 7.47 7.46 7.45 7.44 7.34 7.20 7.18 6.84 6.84
5.32 CD2Cl2
3.53 3.29 2.56 2.55 1.52 1.50
OTf
PMe3
OC
OC
Re
N
5a
1.01 1.00 1.03 0.95 0.99 1.01 0.91 1.06 0.96 3.22 3.19 3.24 9.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

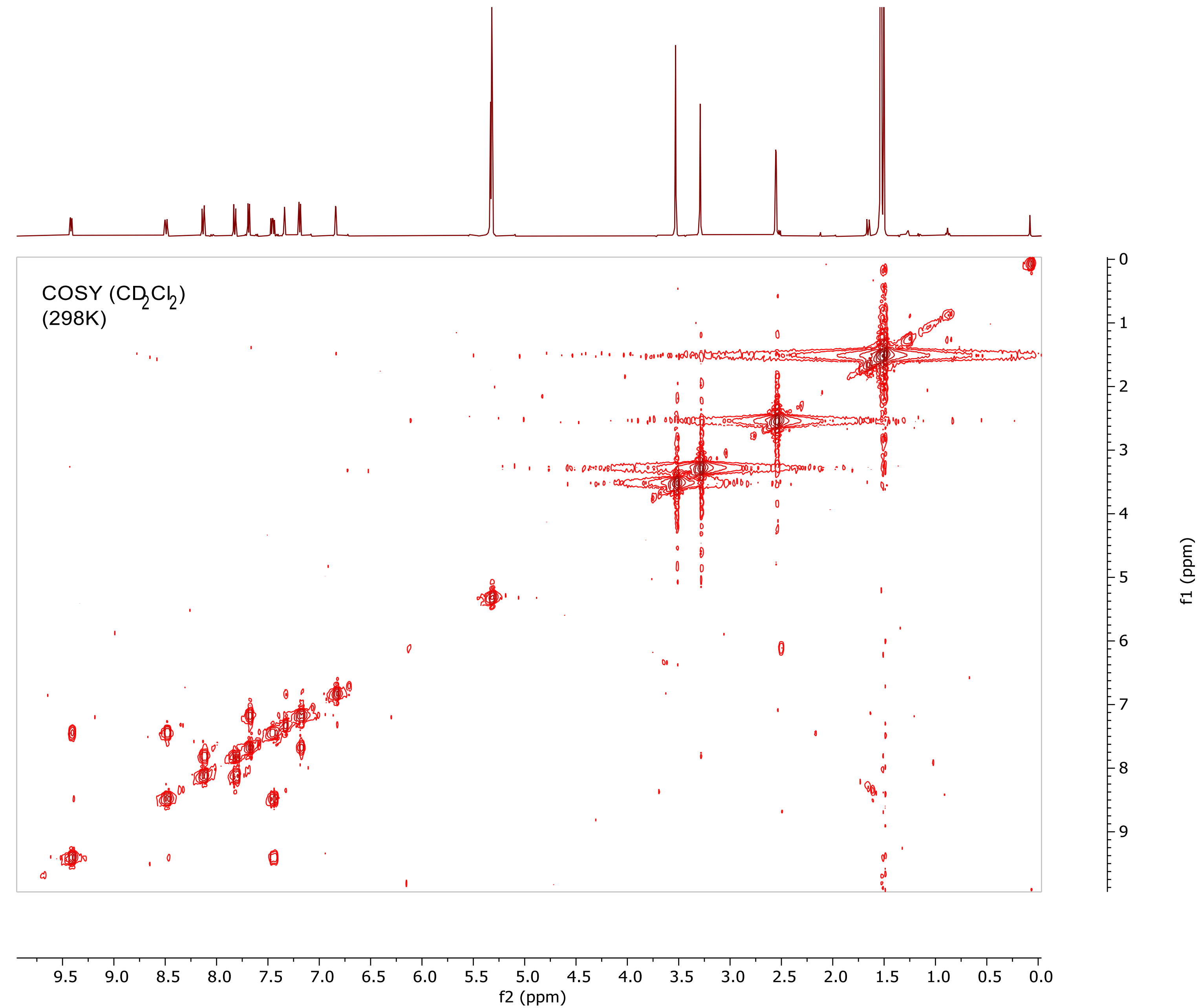


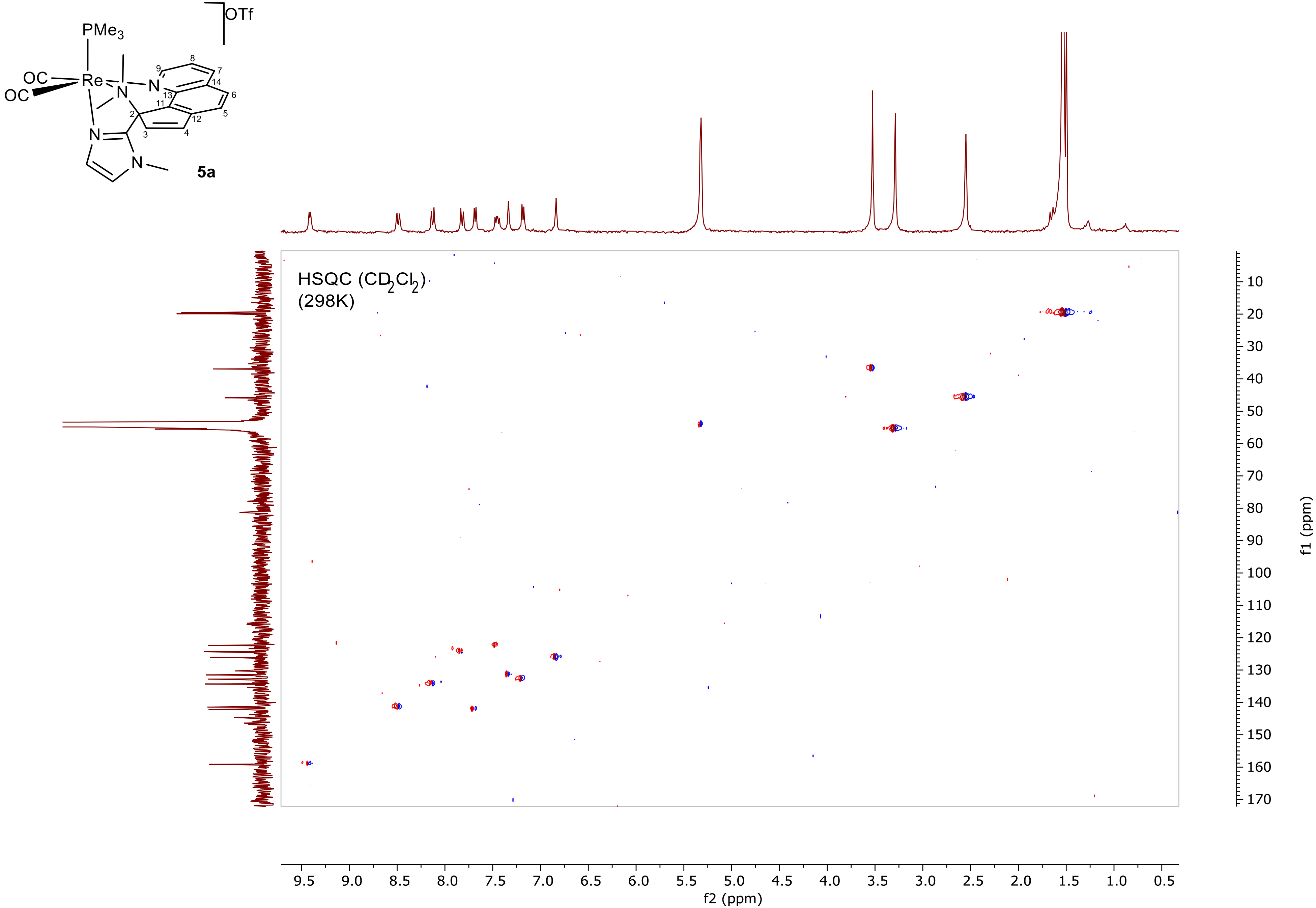
^{13}C NMR (CD_2Cl_2)
(298K)
159.0
144.5
142.0
141.3
141.2
134.2
132.7
132.6
131.3
130.1
126.0
124.2
122.2
115.8
115.4
81.2
55.4
53.8 CD2Cl2
45.7
45.7
36.8
19.7
19.4
OTf
PMe3
OC
OC
Re
N
N
N
N
5a
f1 (ppm)

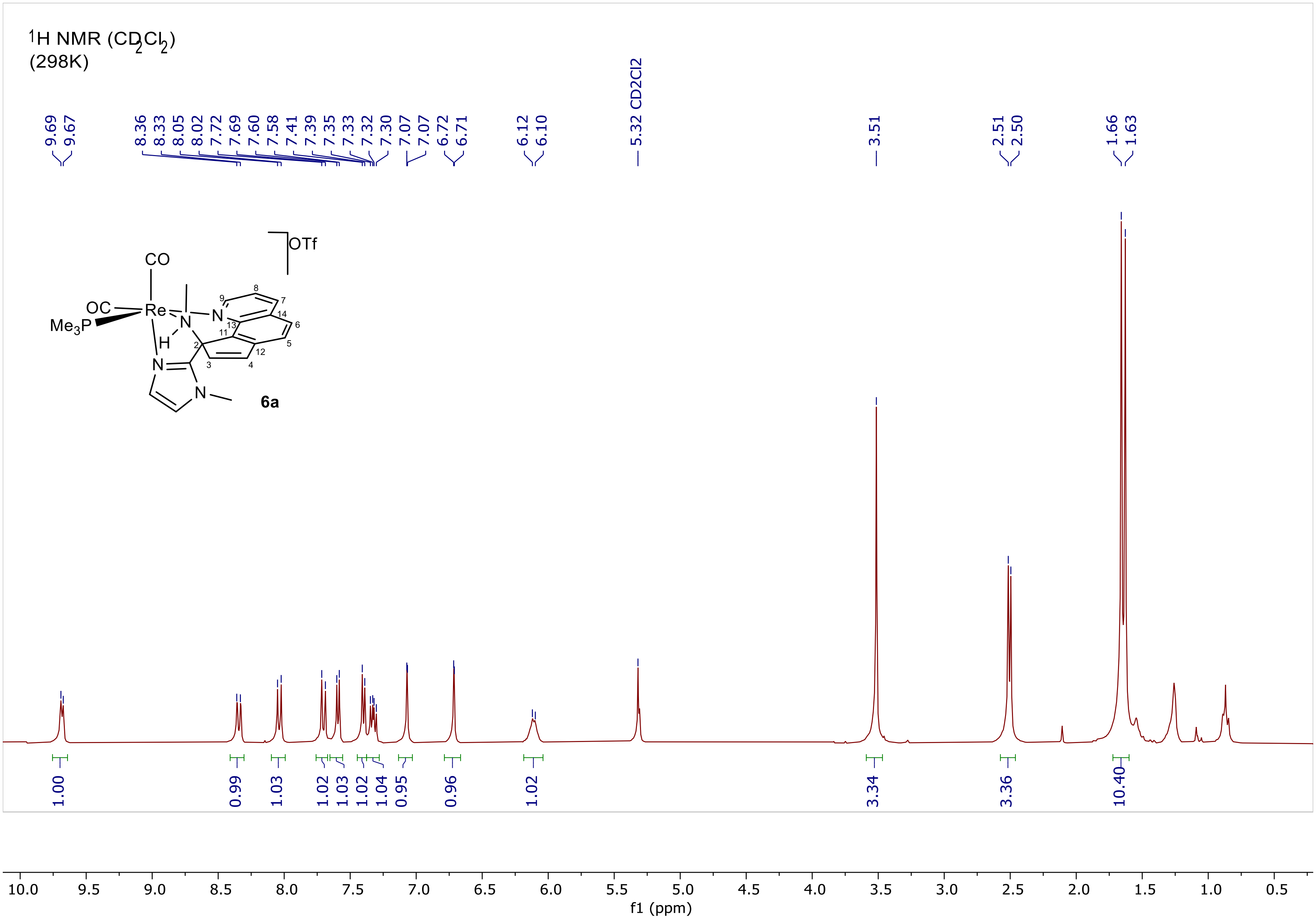

31P NMR (CD2Cl2)
(298K)
-23.4
PMe3
OC
OC
Re
N
N
N
N
OTf
5a
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


PMe3
OTf
OC
OC
Re
N
N
N
N
9
8
7
14
6
13
11
2
12
5
3
4

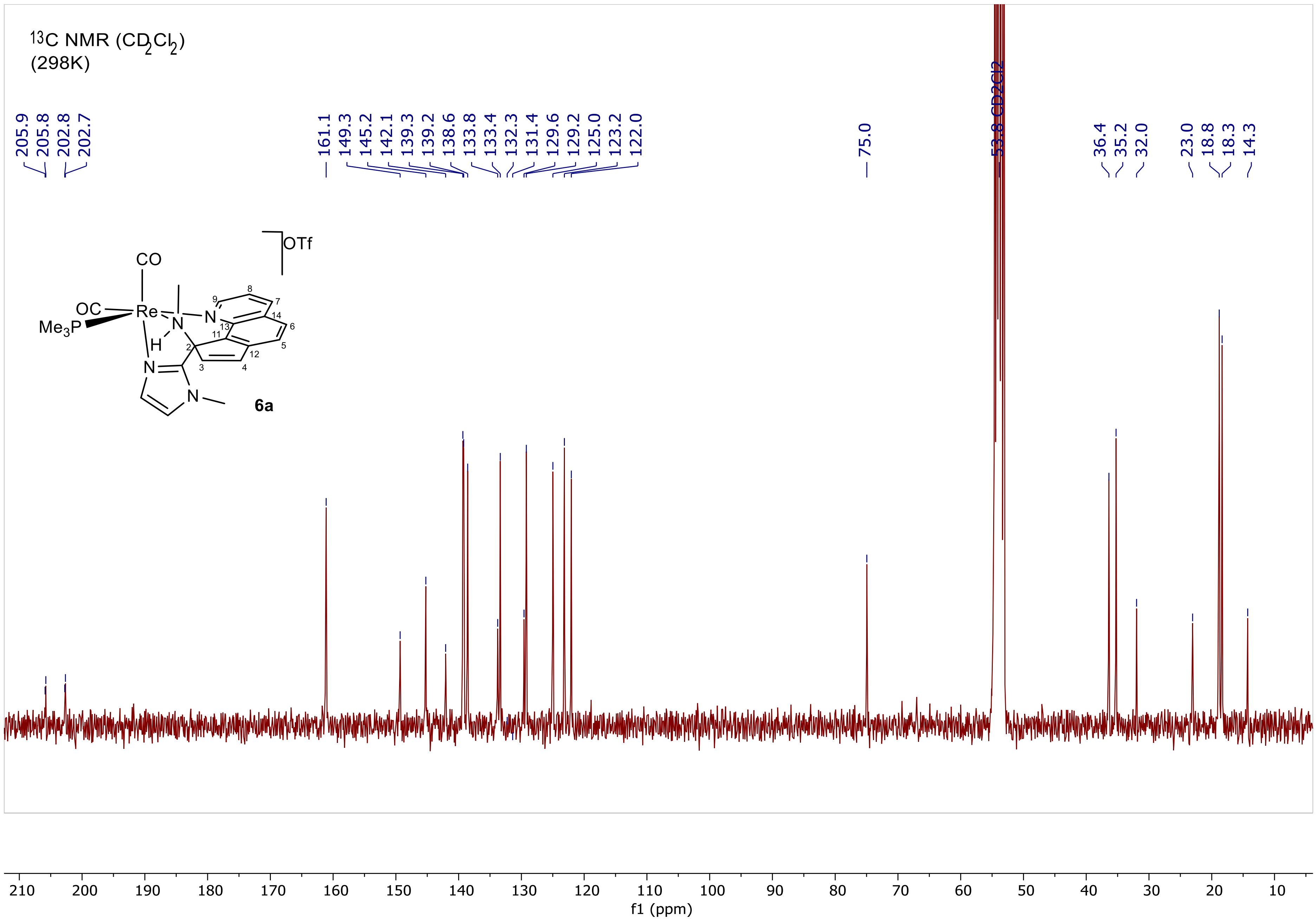
5a


COSY (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)

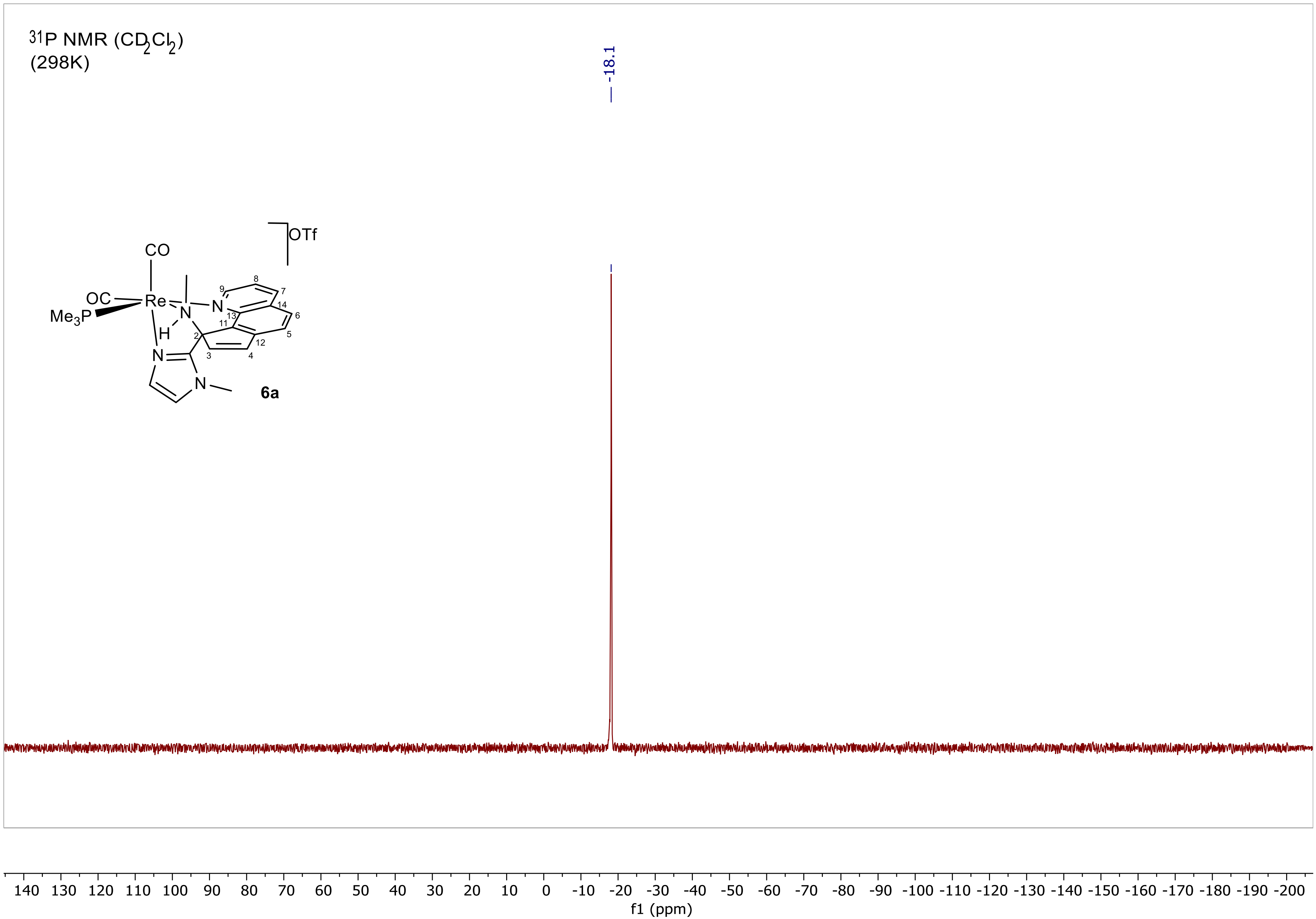

PMe3
OTf
OC
OC
Re
N
N
N
N
2
3
4
5
6
7
8
9
11
12
13
14
5a
HSQC (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)



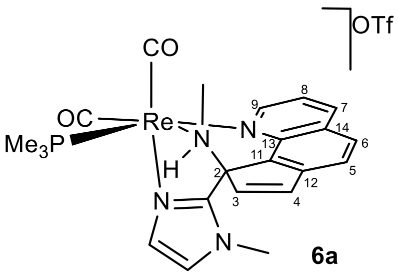
1H NMR (CD2Cl2)
(298K)
9.69
9.67
8.36
8.33
8.05
8.02
7.72
7.69
7.60
7.58
7.41
7.39
7.35
7.33
7.32
7.30
7.07
7.07
6.72
6.71
6.12
6.10
5.32 CD2Cl2
3.51
2.51
2.50
1.66
1.63
OTf
CO
OC
Re
Me3P
N
H
N
N
N
6a
1.00
0.99
1.03
1.02
1.03
1.02
1.04
0.95
0.96
1.02
3.34
3.36
10.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



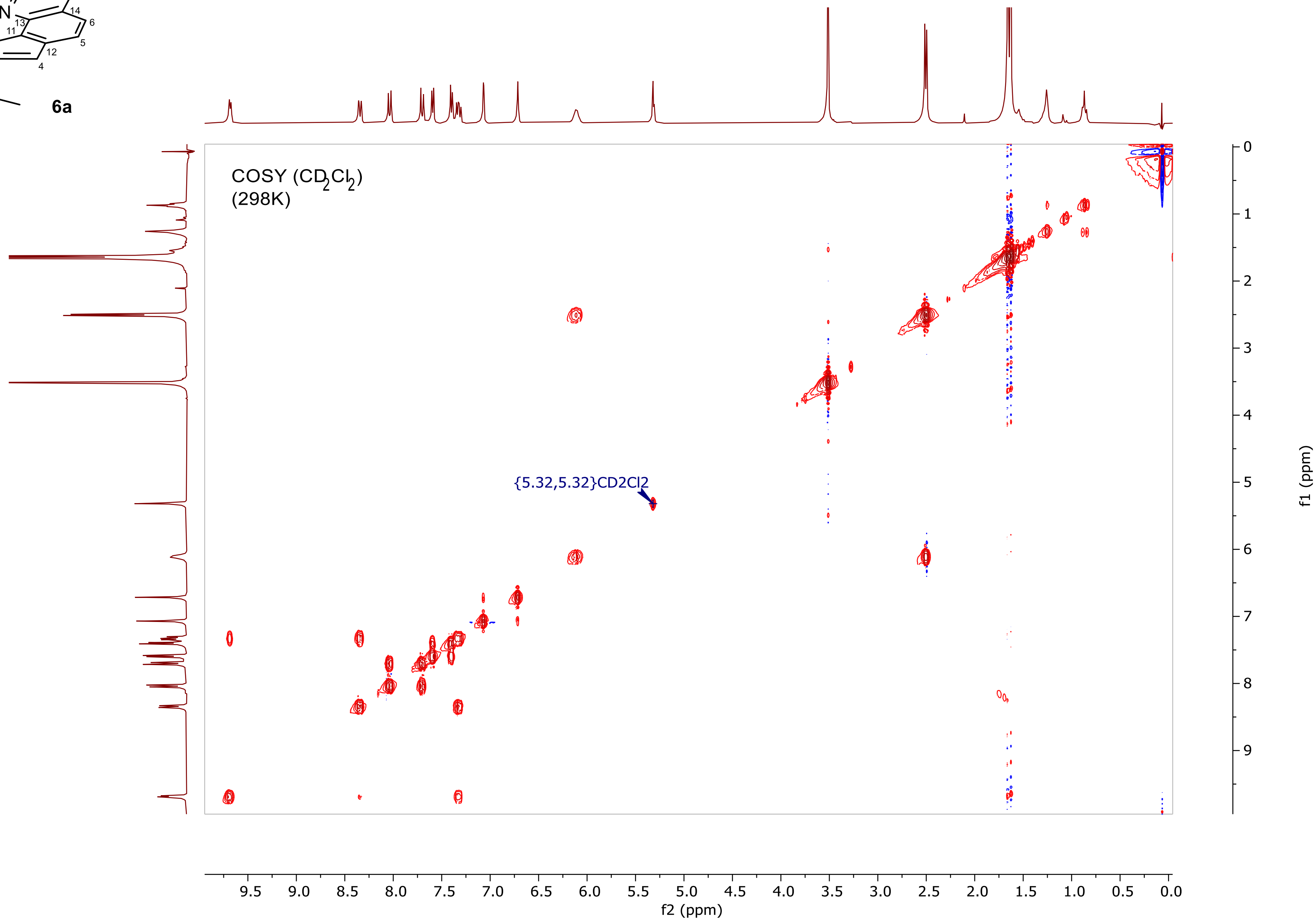
^{13}C NMR (CD_2Cl_2)
(298K)
205.9
205.8
202.8
202.7
161.1
149.3
145.2
142.1
139.3
139.2
138.6
133.8
133.4
132.3
131.4
129.6
129.2
125.0
123.2
122.0
75.0
53.8 CD2Cl2
36.4
35.2
32.0
23.0
18.8
18.3
14.3
OTf
CO
OC
Re
Me$_3$P
N
H
6a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

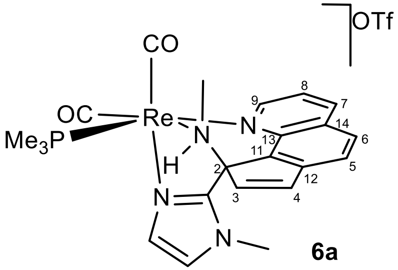


31P NMR (CD2Cl2)
(298K)
-18.1
OTf
CO
OC
Re
Me3P
N
H
6a
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

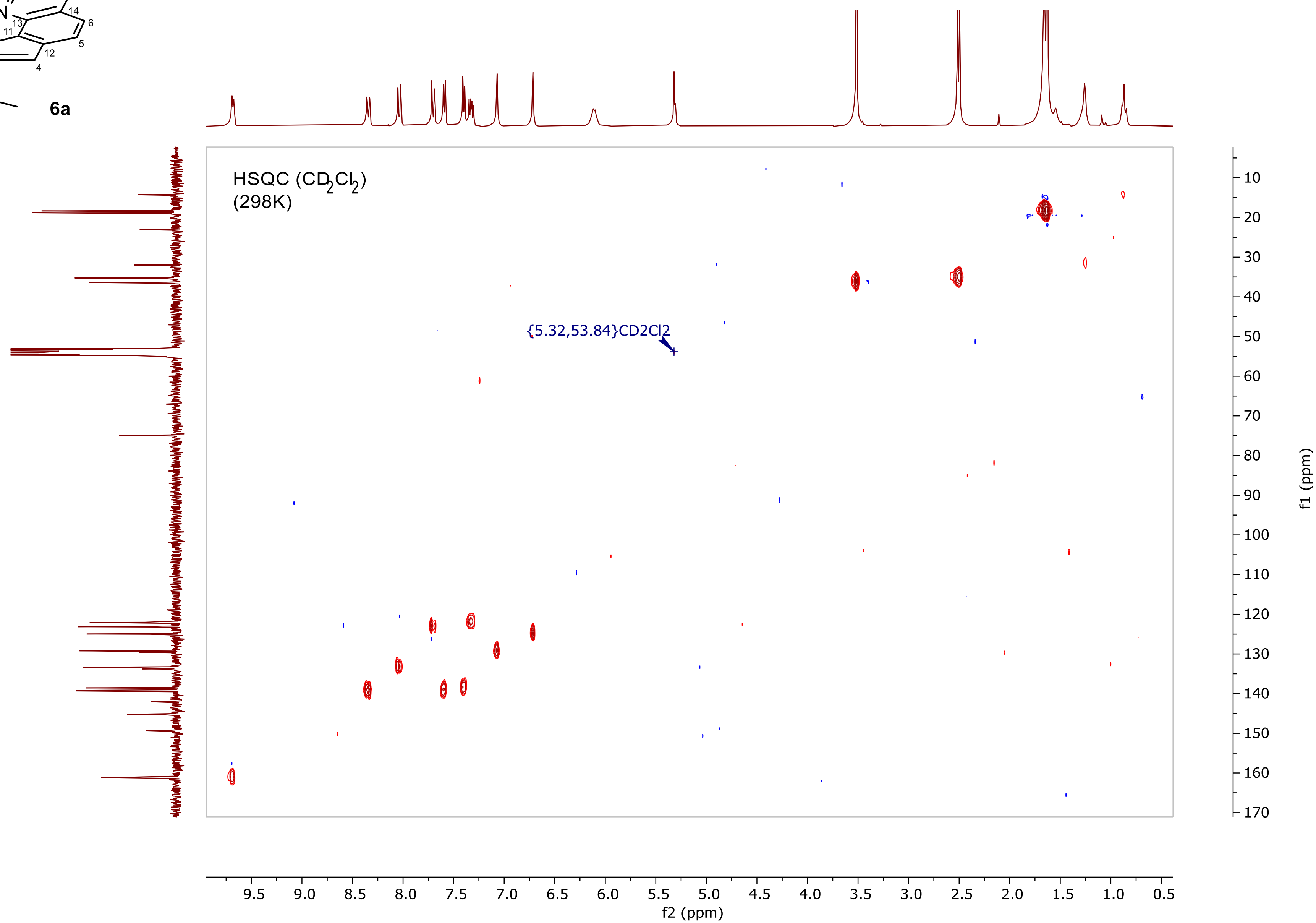

CO
OC
Me3P
Re
N
H
N
N
N
OTf
2
3
4
5
6
7
8
9
11
12
13
14

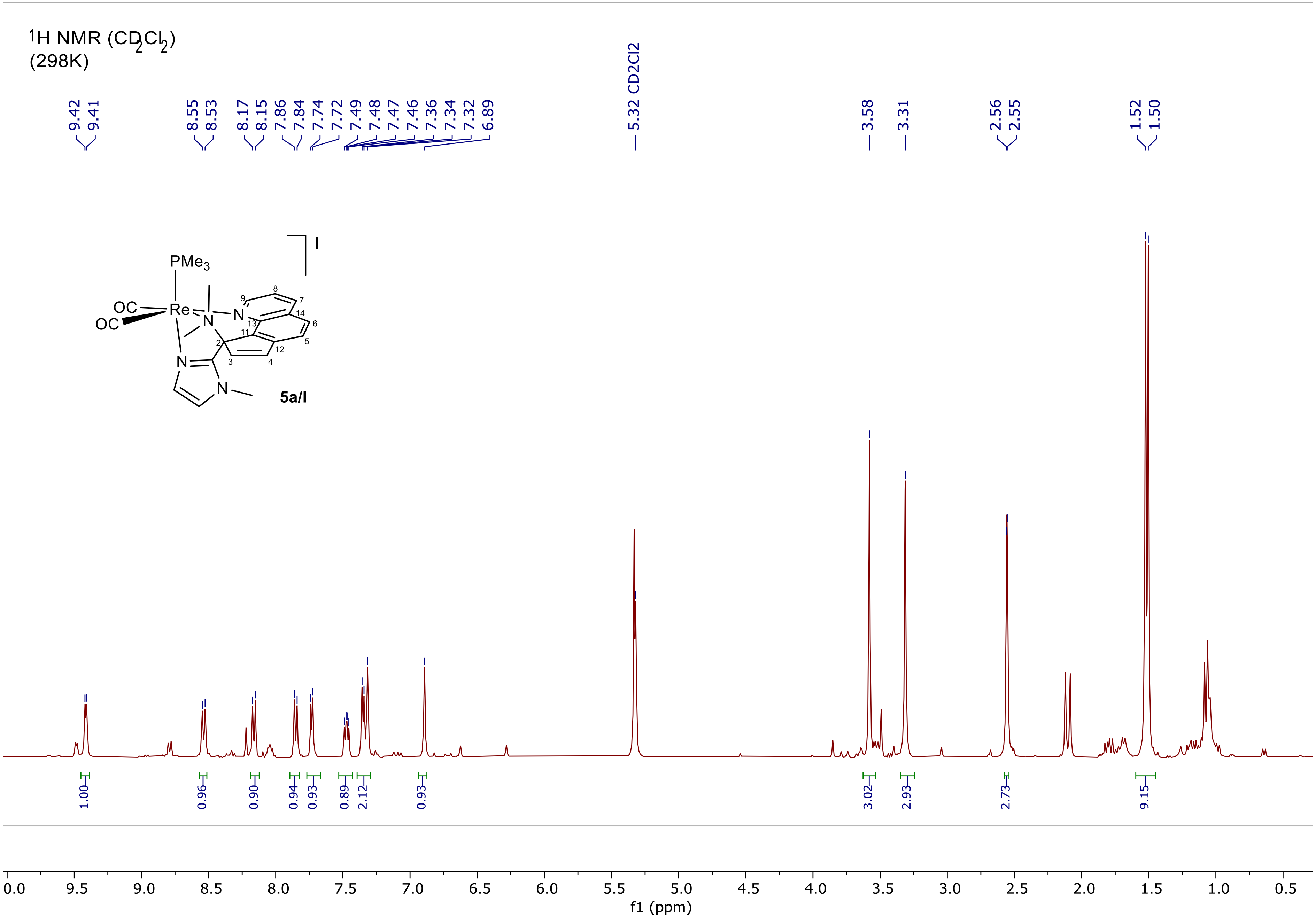
6a


COSY (CD2Cl2)
(298K)
{5.32,5.32}CD2Cl2
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8 9

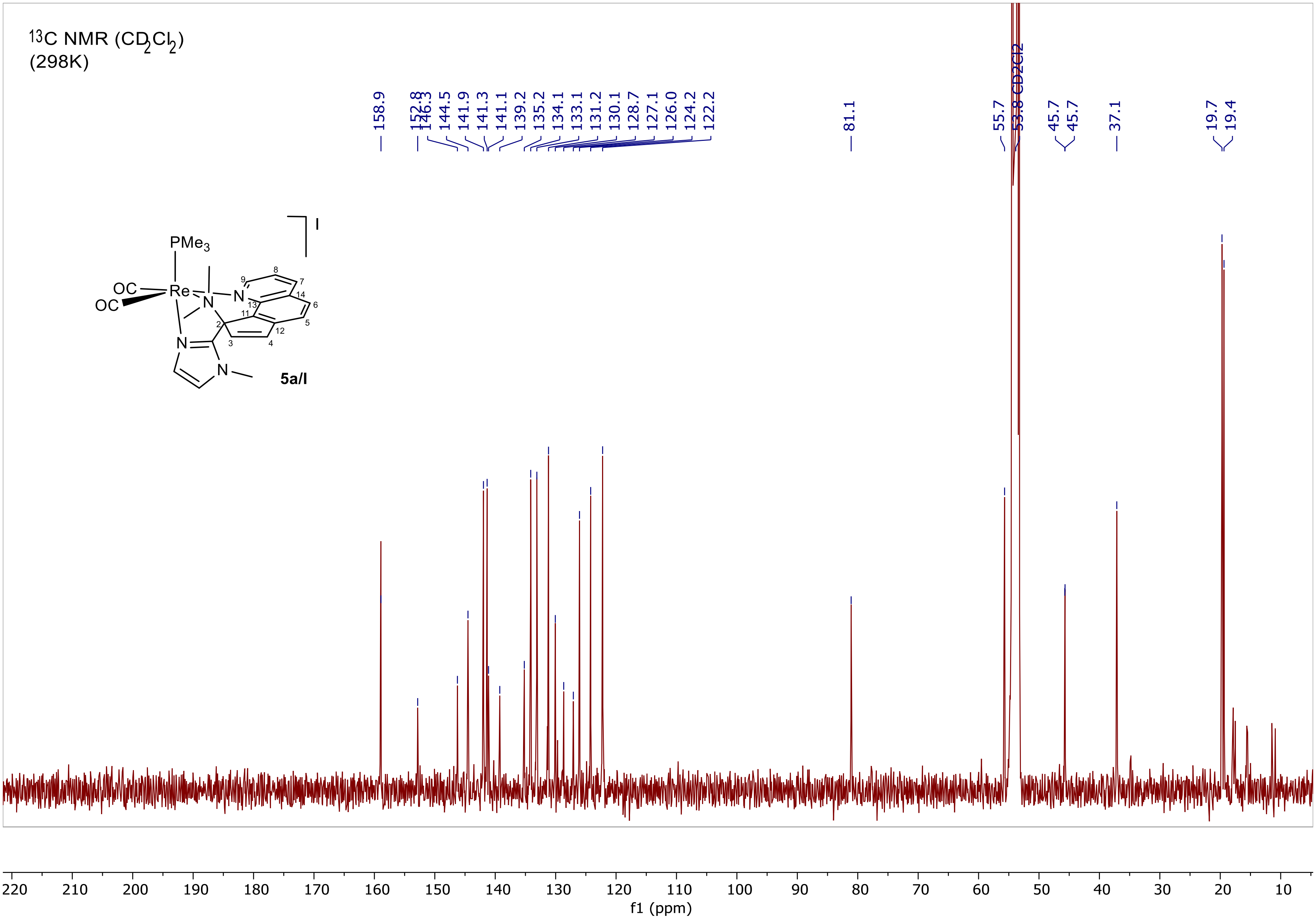

CO
OC
Me3P
Re
N
N
H
N
N
OTf
2
3
4
5
6
7
8
9
11
12
13
14

6a

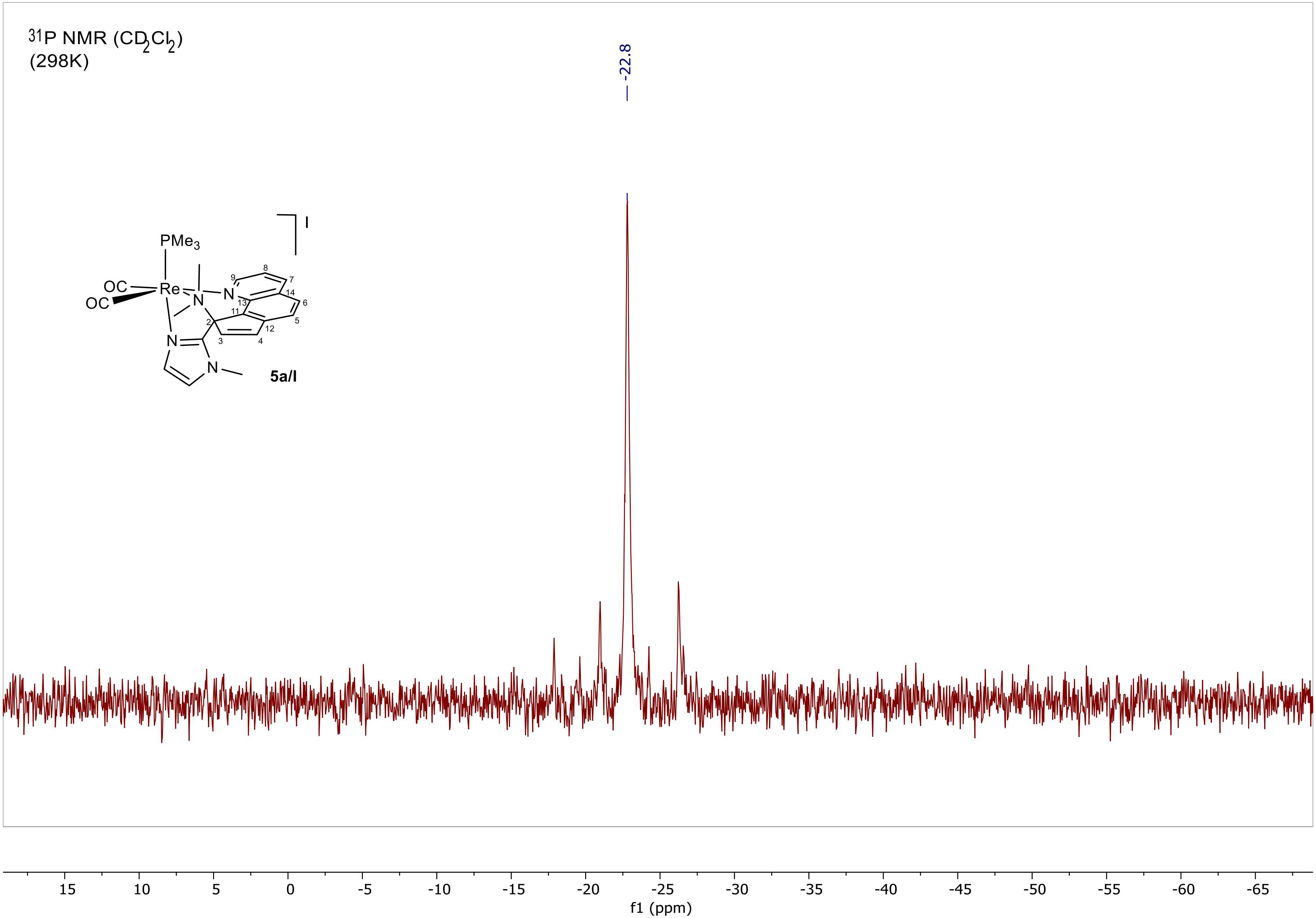

HSQC (CD2Cl2)
(298K)
{5.32,53.84}CD2Cl2
f2 (ppm)
f1 (ppm)

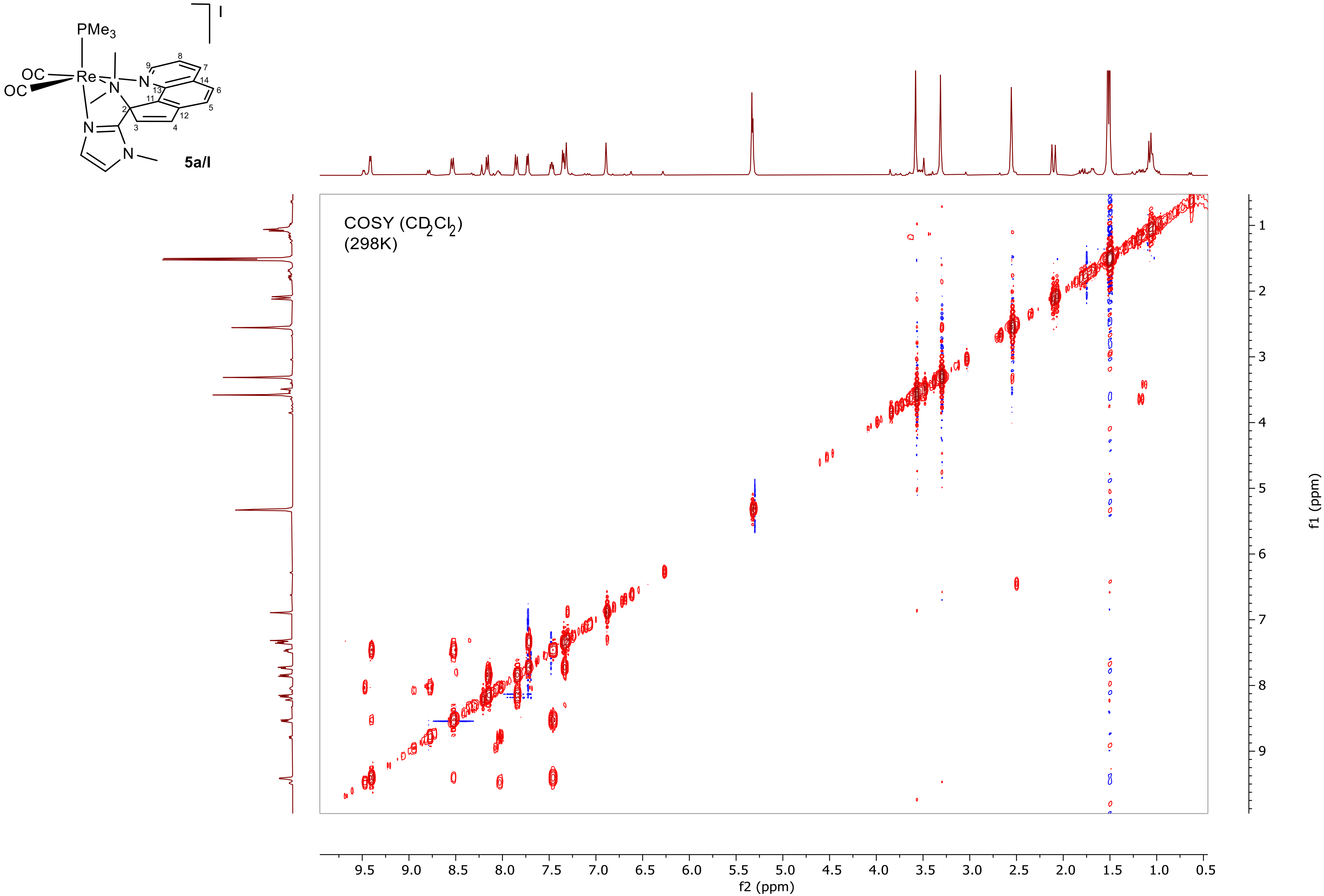


^1H NMR (CD_2Cl_2)
(298K)
9.42
9.41
8.55
8.53
8.17
8.15
7.86
7.84
7.74
7.72
7.49
7.48
7.47
7.46
7.36
7.34
7.32
6.89
5.32 CD2Cl2
3.58
3.31
2.56
2.55
1.52
1.50
PMe3
OC
OC
Re
N
N
N
N
I
5a/I
1.00
0.96
0.90
0.94
0.93
0.89
2.12
0.93
3.02
2.93
2.73
9.15
f1 (ppm)

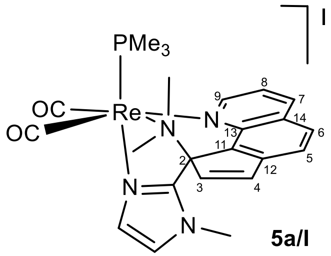


13C NMR (CD2Cl2)
(298K)
158.9
152.8
146.3
144.5
141.9
141.3
141.1
139.2
135.2
134.1
133.1
131.2
130.1
128.7
127.1
126.0
124.2
122.2
81.1
55.7
53.8 CD2Cl2
45.7
45.7
37.1
19.7
19.4
PMe3
OC
OC
Re
N
N
N
N
I
9
8
7
14
6
13
11
2
12
5
3
4
5a/I
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

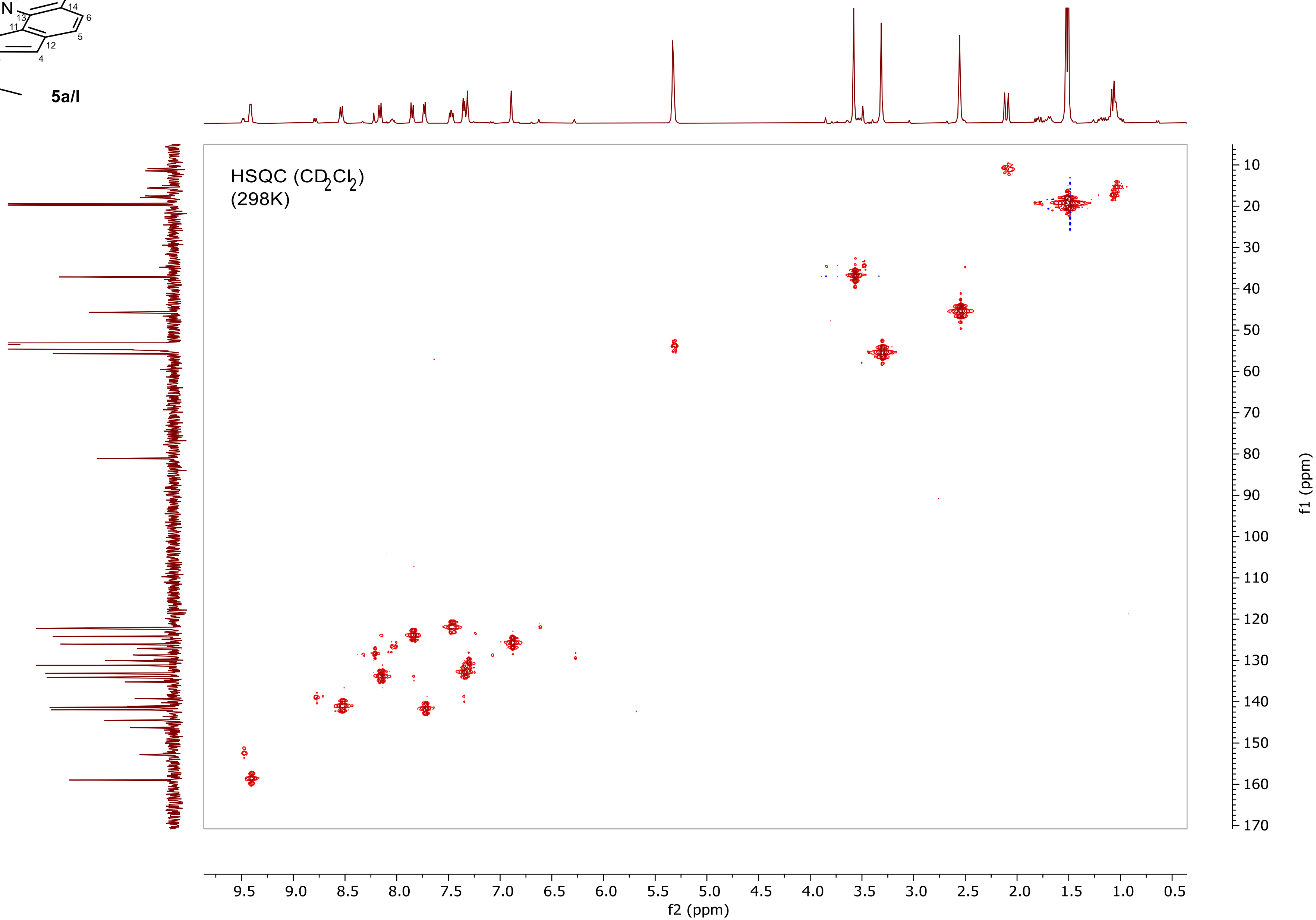

^{31}P NMR (CD_2Cl_2)
(298K)
-22.8
PMe3
OC
OC
Re
N
N
N
N
I
5a/I
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

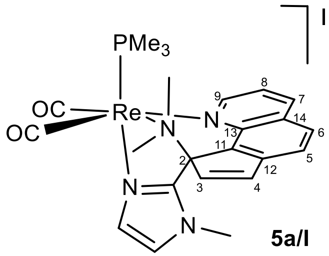


PMe3
OC
OC
Re
N
N
N
N
I
5a/I
COSY (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)



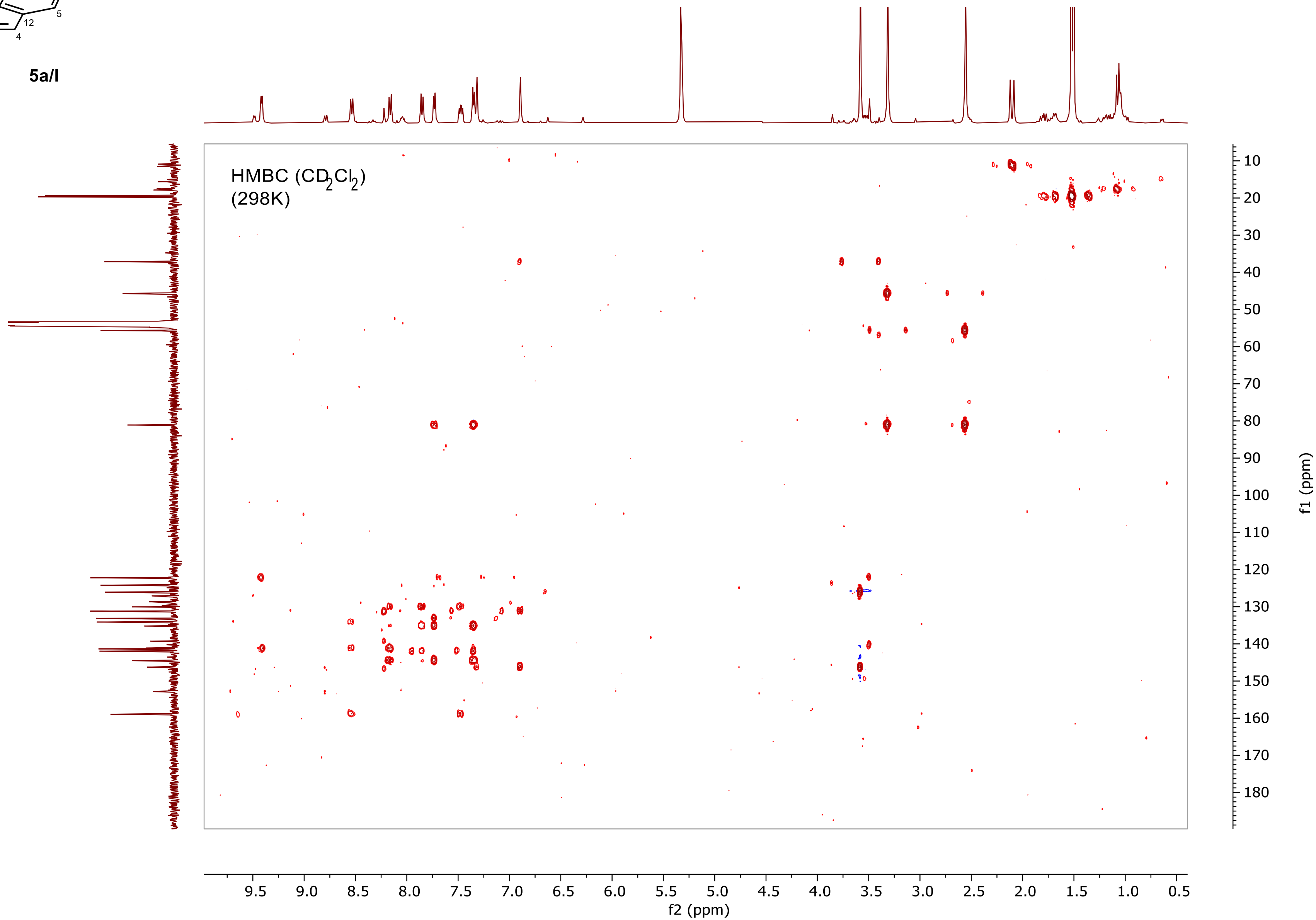
5a/I



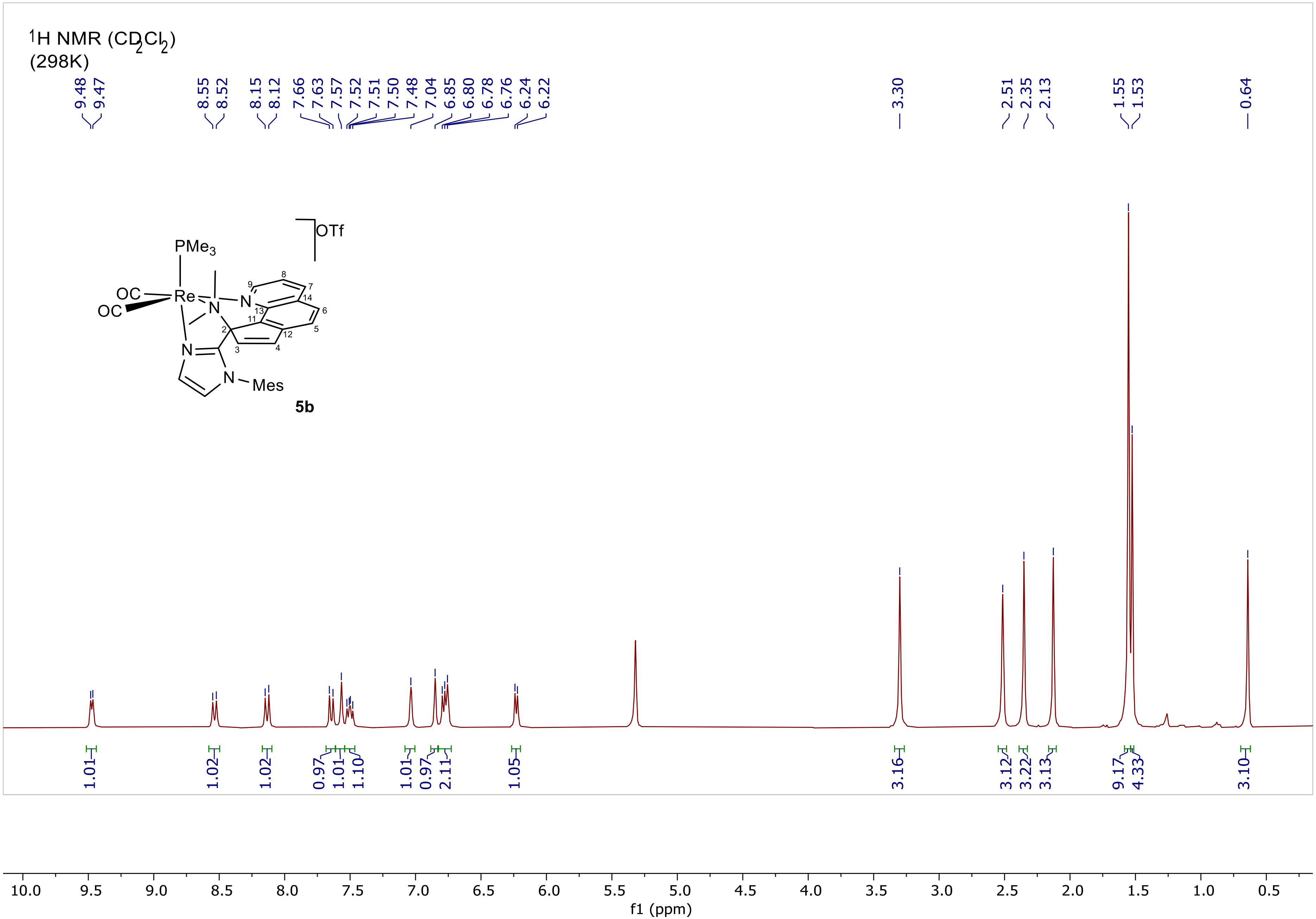


I
PMe3
OC
OC
Re
N
N
N
N
9
8
7
14
6
13
11
2
12
5
3
4

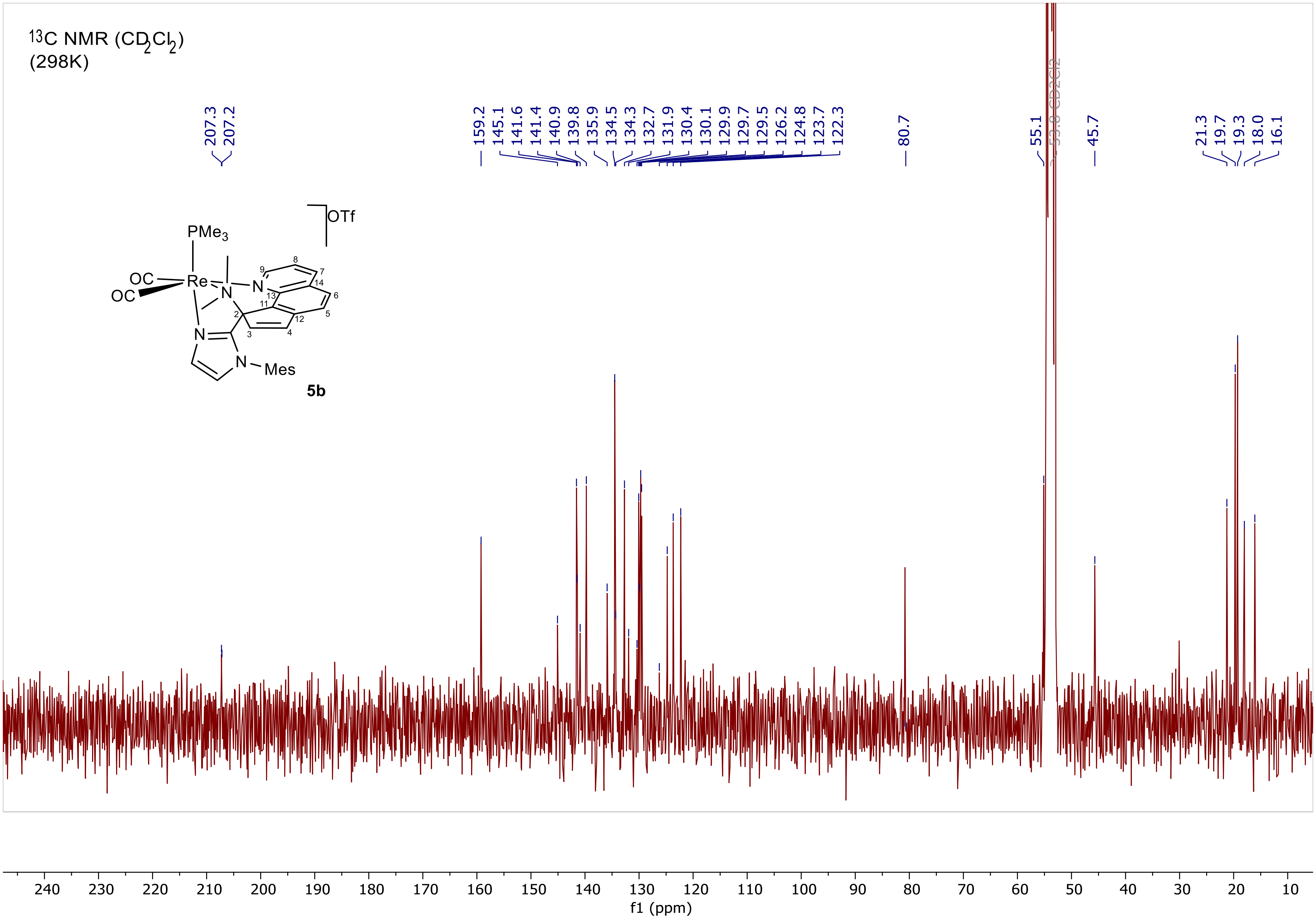
5a/I

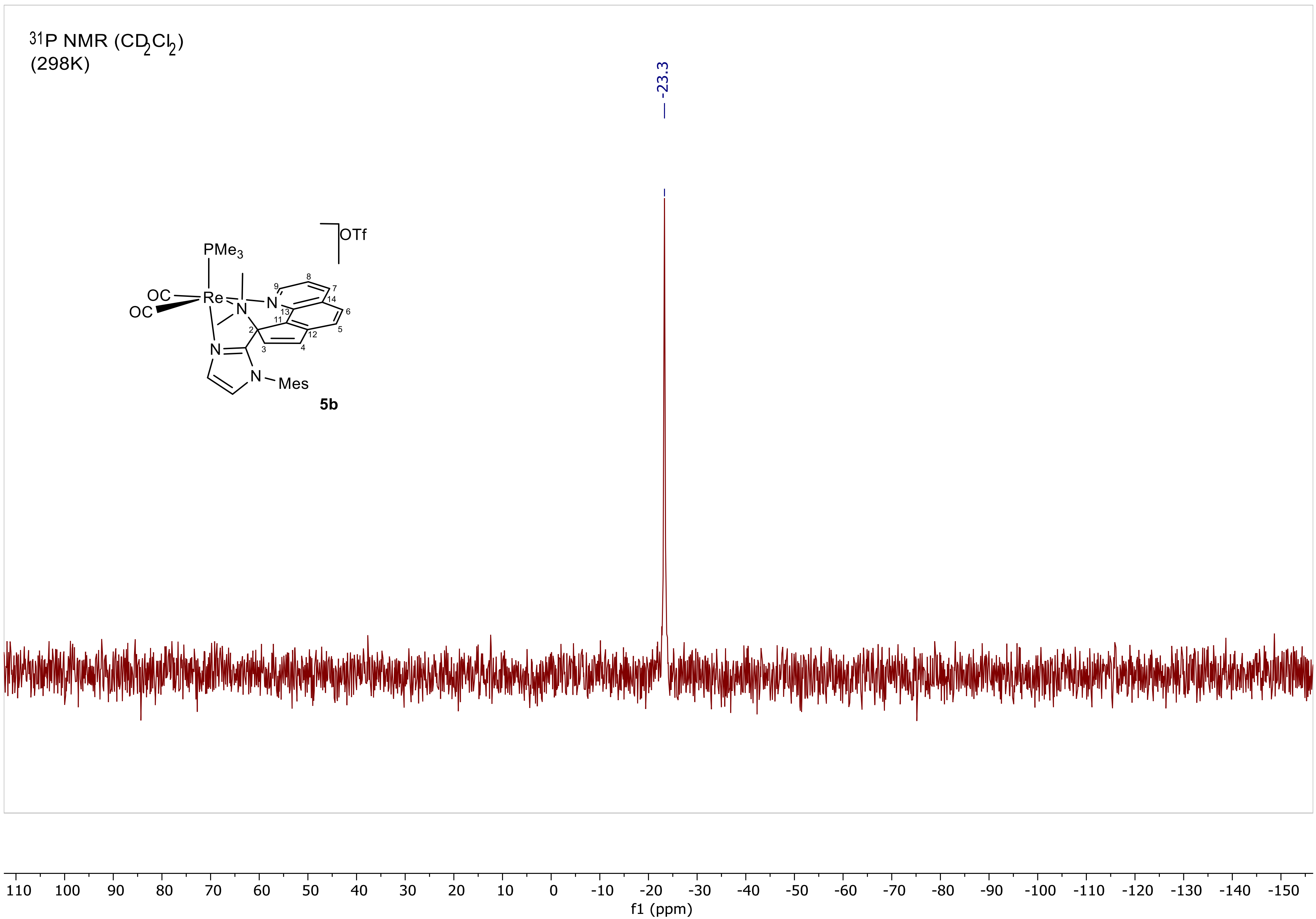


HMBC (CD_2Cl_2)
(298K)
f2 (ppm)
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

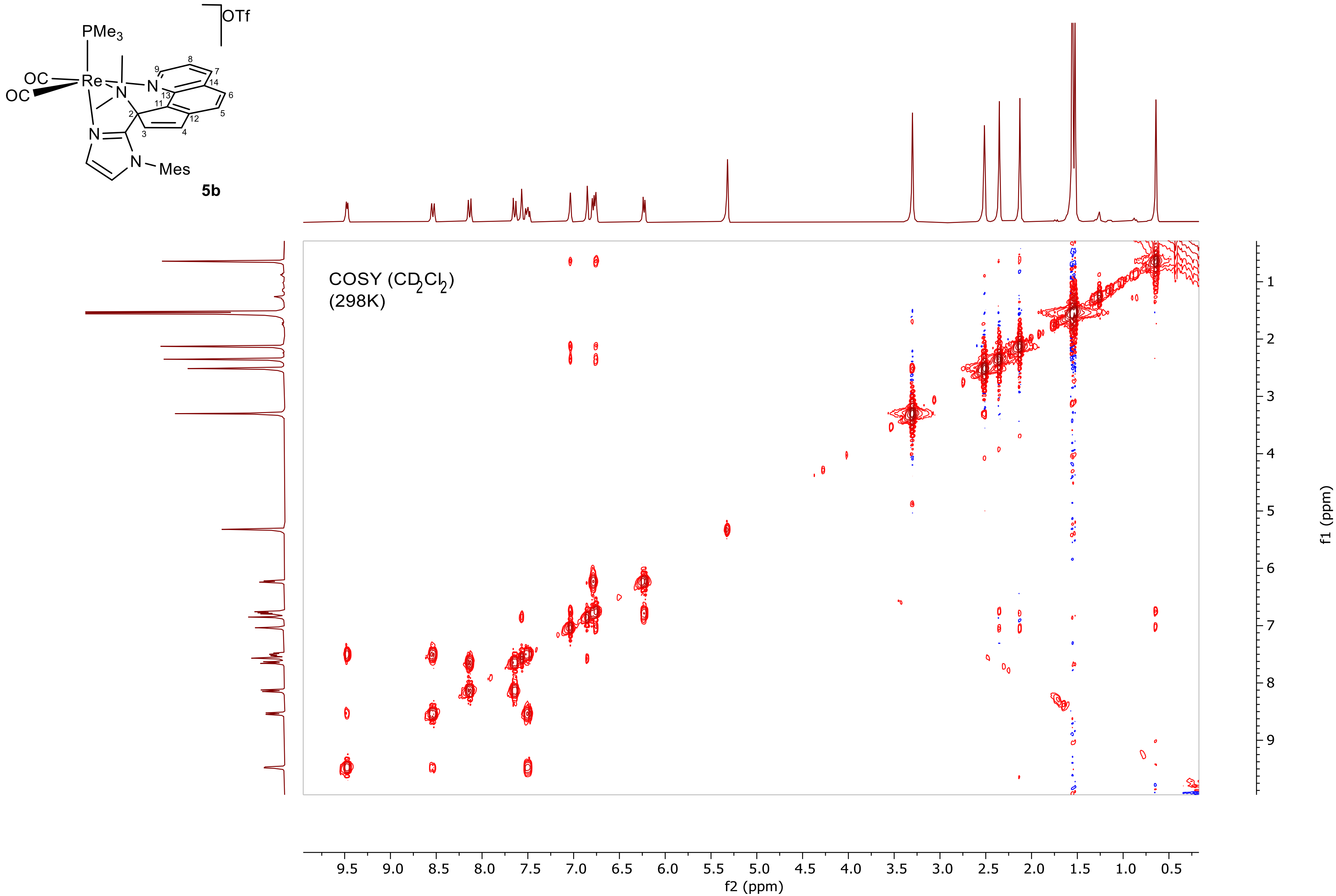


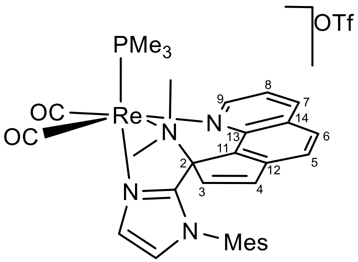
1H NMR (CD2Cl2)
(298K)
9.48
9.47
8.55
8.52
8.15
8.12
7.66
7.63
7.57
7.52
7.51
7.50
7.48
7.04
6.85
6.80
6.78
6.76
6.24
6.22
3.30
2.51
2.35
2.13
1.55
1.53
0.64
PMe3
OTf
OC
OC
Re
N
N
N
N
Mes
5b
1.01
1.02
1.02
0.97
1.01
1.10
1.01
0.97
2.11
1.05
3.16
3.12
3.22
3.13
9.17
4.33
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


13C NMR (CD2Cl2)
(298K)
207.3
207.2
159.2
145.1
141.6
141.4
140.9
139.8
135.9
134.5
134.3
132.7
131.9
130.4
130.1
129.9
129.7
129.5
126.2
124.8
123.7
122.3
80.7
55.1
45.7
21.3
19.7
19.3
18.0
16.1
OTf
PMe3
OC
OC
Re
N
N
N
N
Mes
5b
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

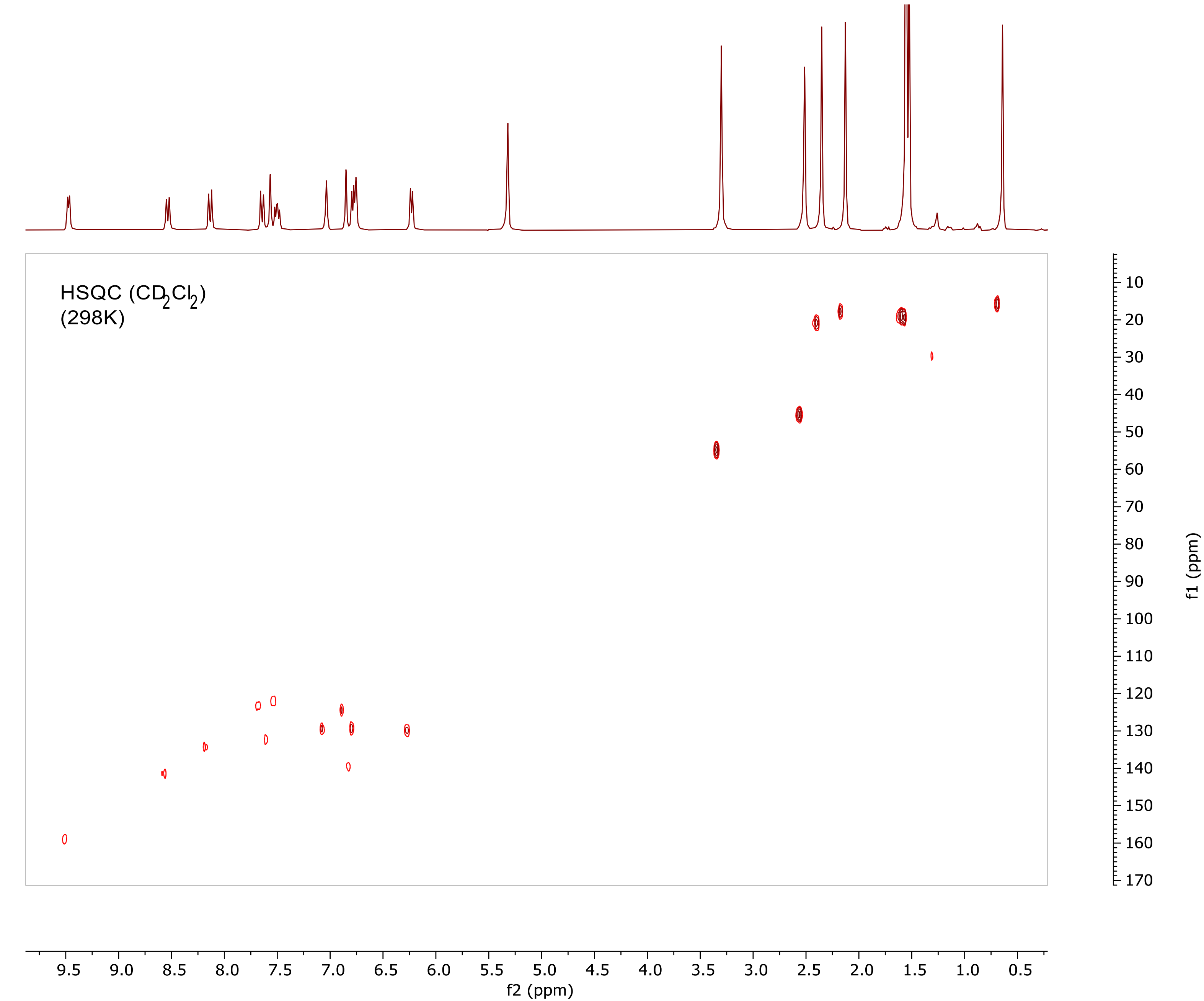


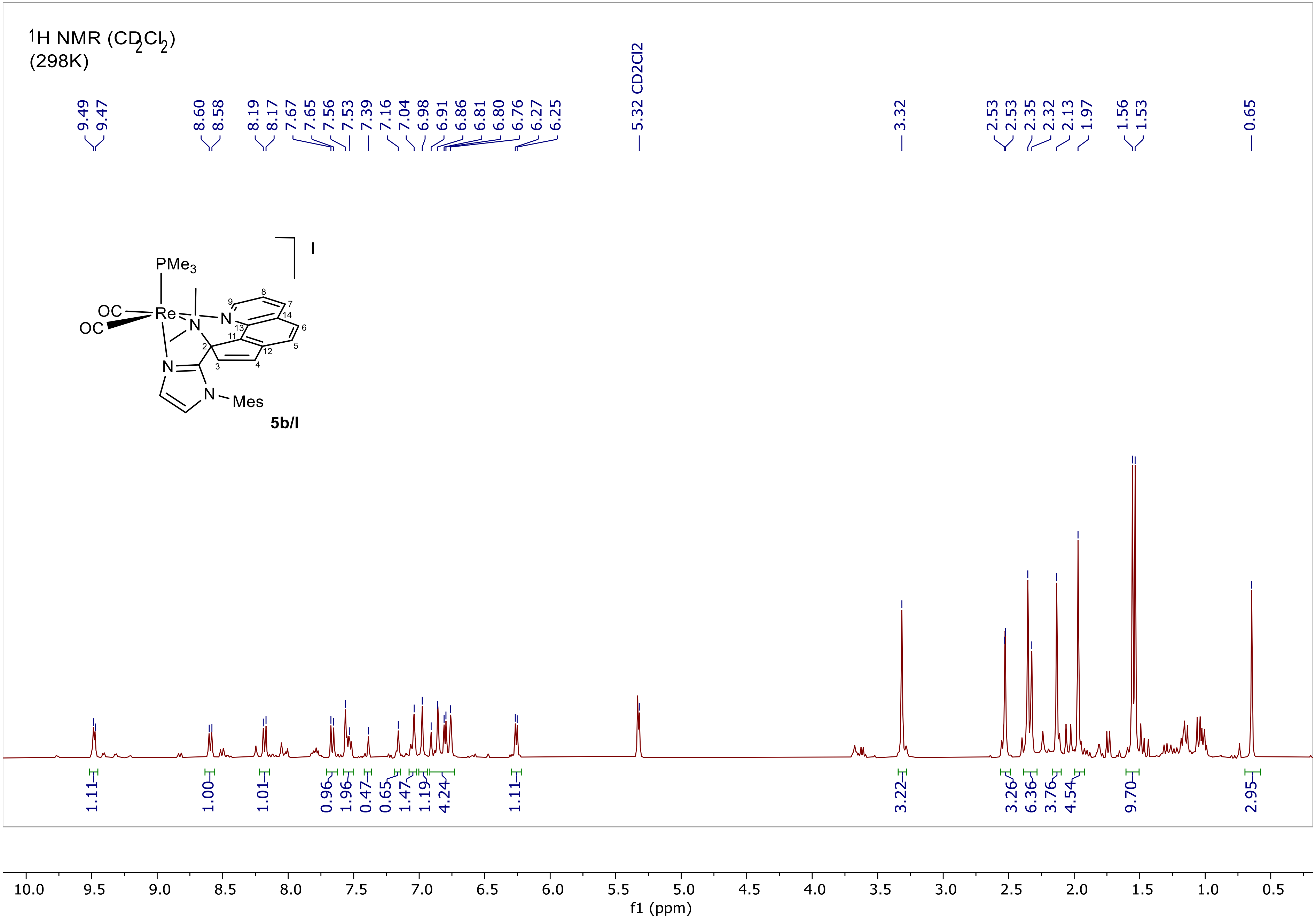
^{31}P NMR (CD_2Cl_2)
(298K)
-23.3
PMe$_3$
OTf
OC
OC
Re
N
N
N
N
Mes
2
3
4
5
6
7
8
9
11
12
13
14
5b
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


PMe3
OTf
OC
OC
Re
N
N
N
N
Mes
5b
COSY (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)

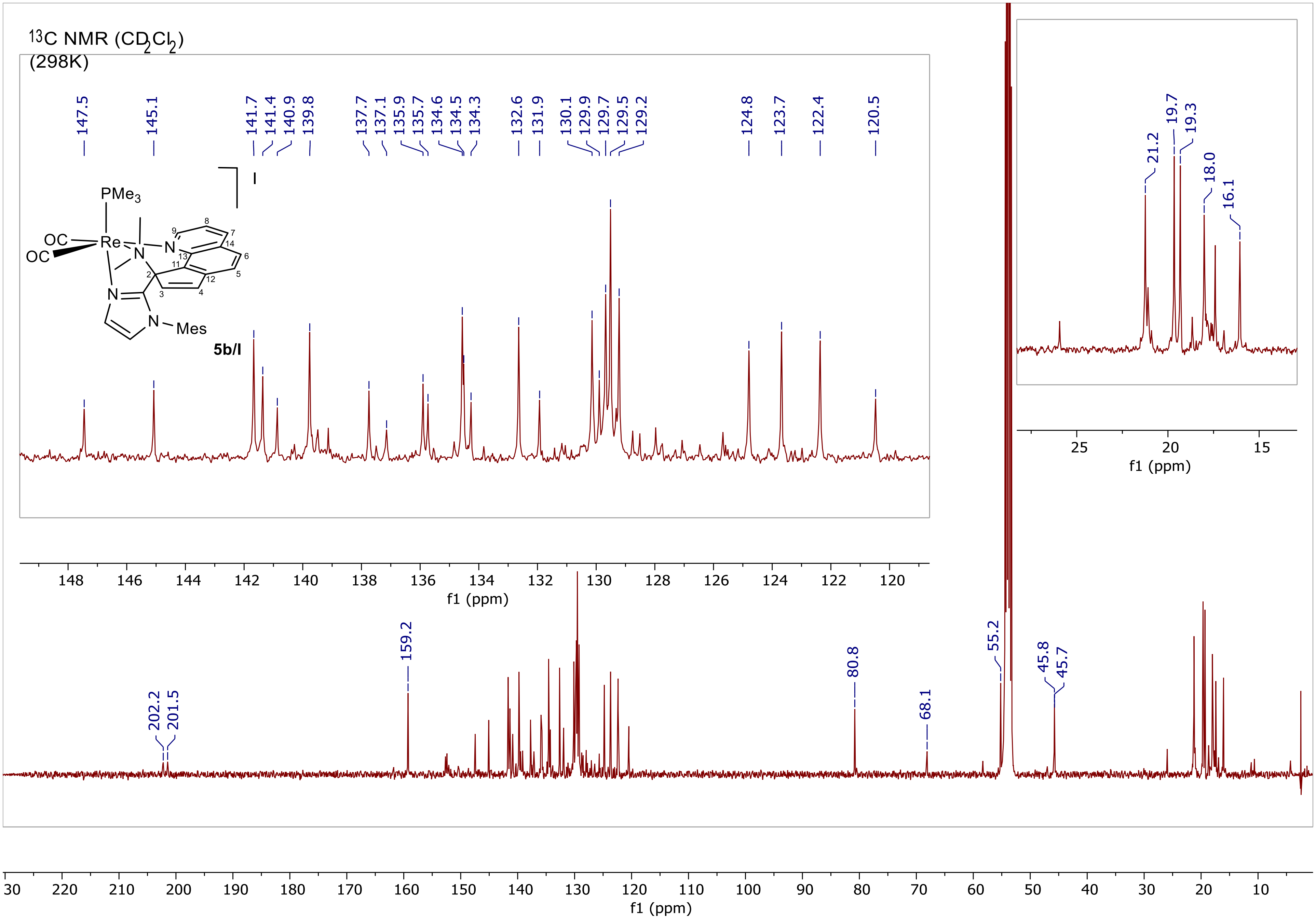

PMe3
OTf
OC
OC
Re
N
N
N
N
Mes
9
8
7
14
6
5
12
4
3
2
11
13

5b

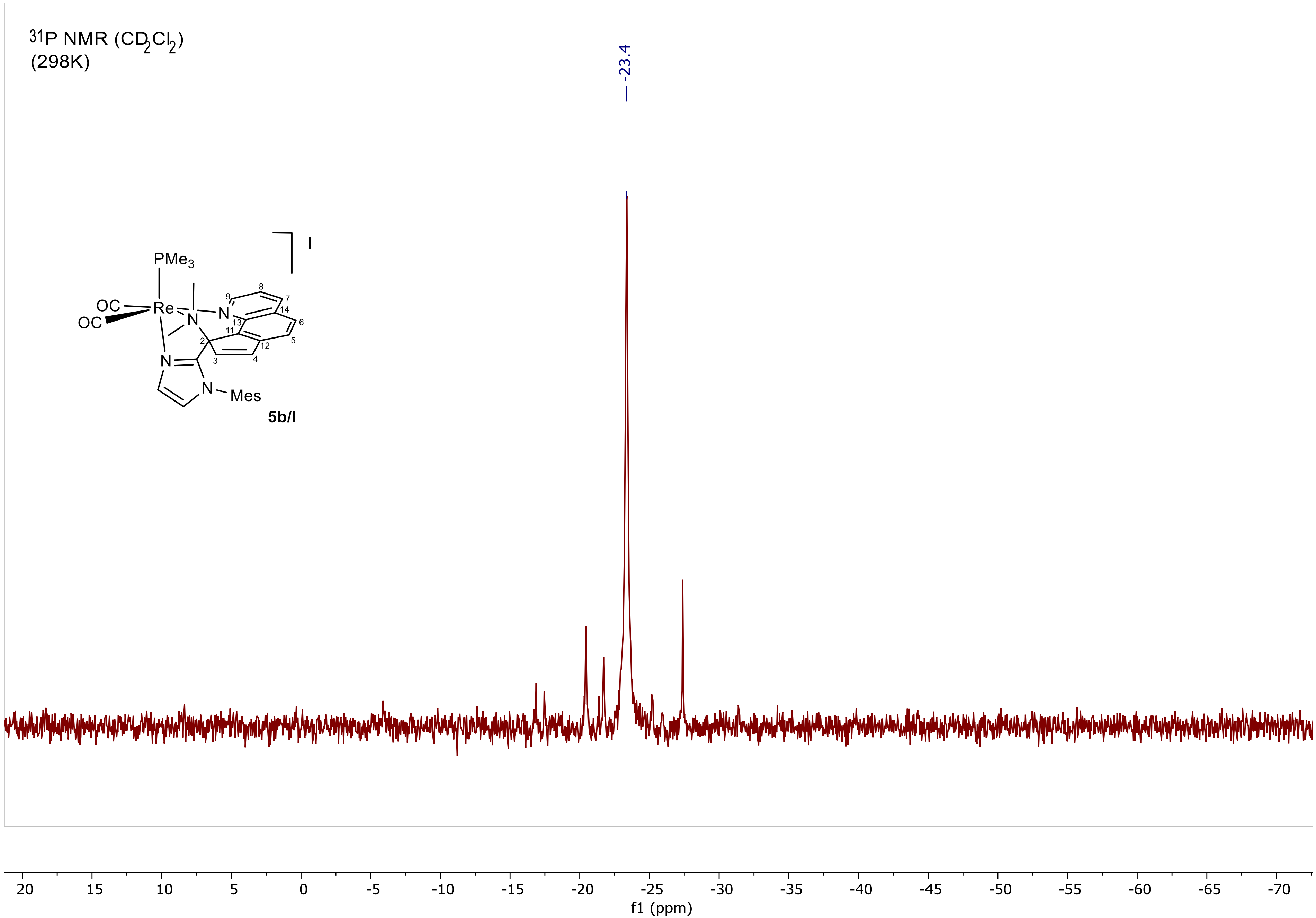

HSQC (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170



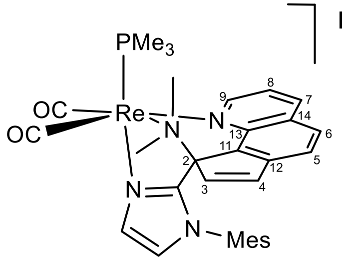
^{1}H NMR (CD_2Cl_2)
(298K)
9.49
9.47
8.60
8.58
8.19
8.17
7.67
7.65
7.56
7.53
7.39
7.16
7.04
6.98
6.91
6.86
6.81
6.80
6.76
6.27
6.25
5.32 CD2Cl2
3.32
2.53
2.53
2.35
2.32
2.13
1.97
1.56
1.53
0.65
PMe3
OC
OC
Re
N
N
N
N
Mes
I
5b/I
1.11
1.00
1.01
0.96
1.96
0.47
0.65
1.47
1.19
4.24
1.11
3.22
3.26
6.36
3.76
4.54
9.70
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



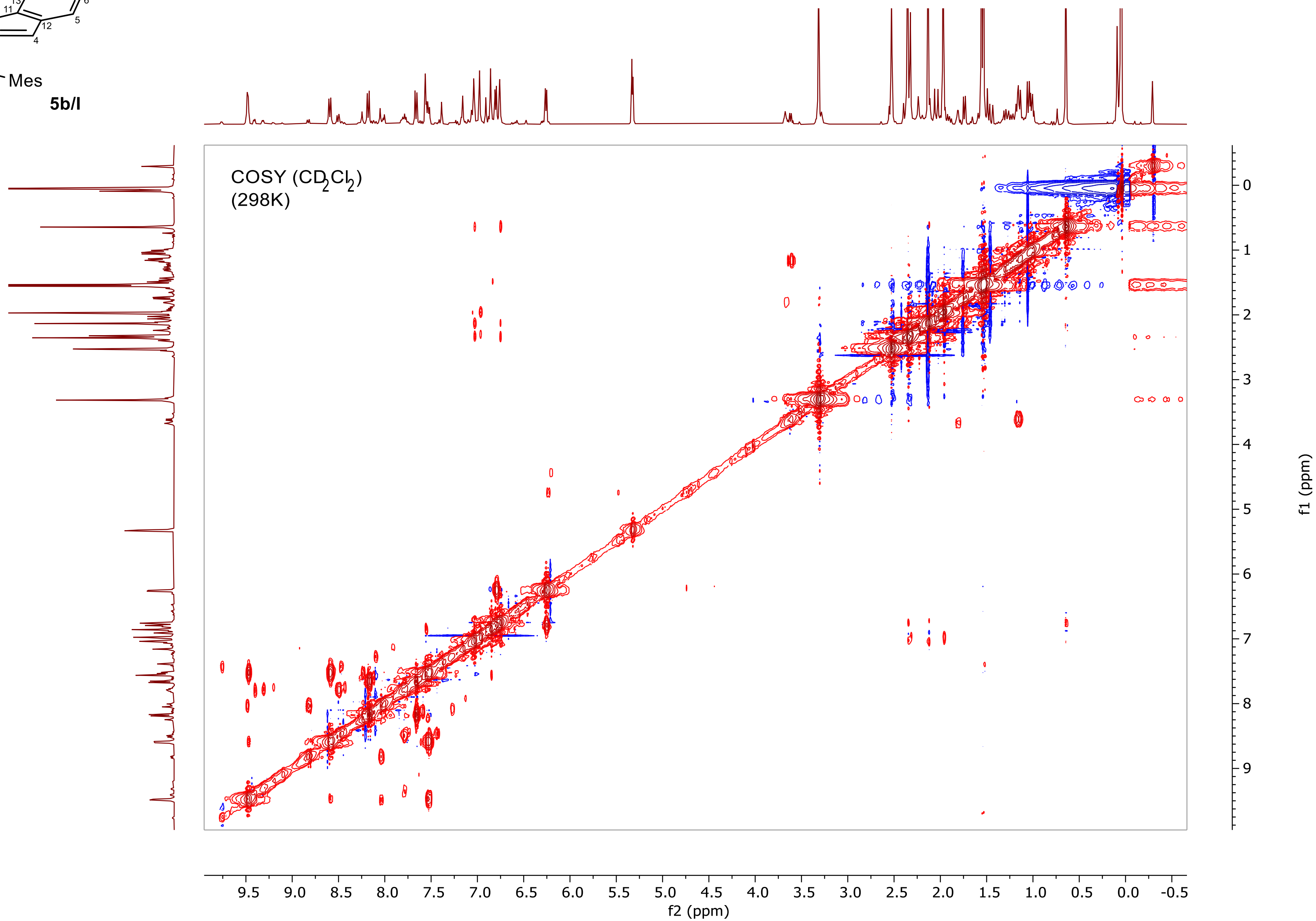
13C NMR (CD2Cl2)
(298K)
147.5
145.1
141.7
141.4
140.9
139.8
137.7
137.1
135.9
135.7
134.6
134.5
134.3
132.6
131.9
130.1
129.9
129.7
129.5
129.2
124.8
123.7
122.4
120.5
PMe3
OC
OC
Re
N
N
N
N
Mes
I
5b/I
f1 (ppm)
21.2
19.7
19.3
18.0
16.1
f1 (ppm)
202.2
201.5
159.2
80.8
68.1
55.2
45.8
45.7
f1 (ppm)

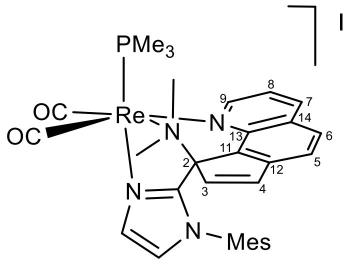


31P NMR (CD2Cl2)
(298K)
-23.4
PMe3
OC
OC
Re
N
N
N
N
Mes
5b/I
I
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
f1 (ppm)

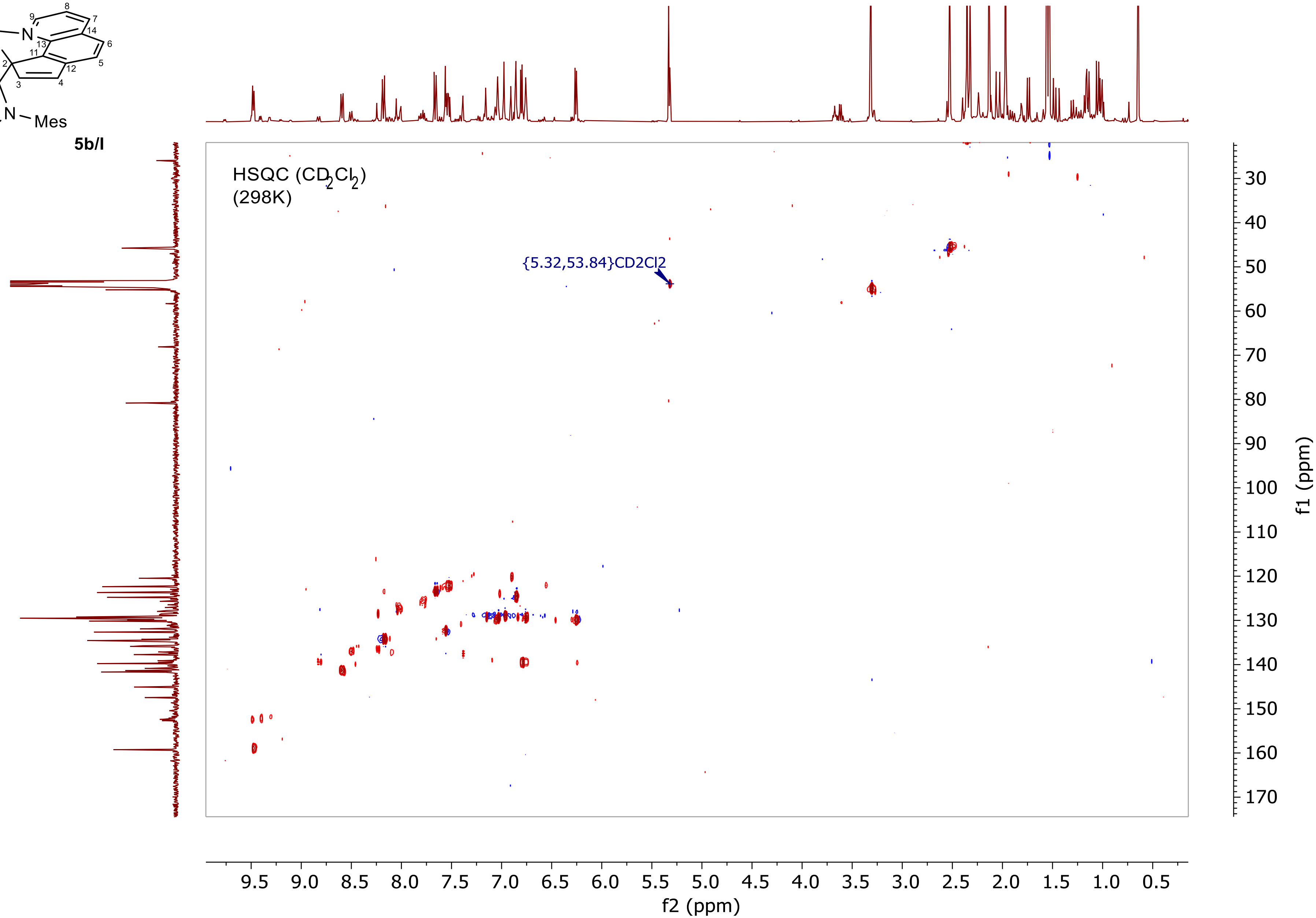


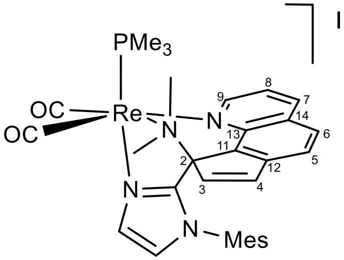
5b/I



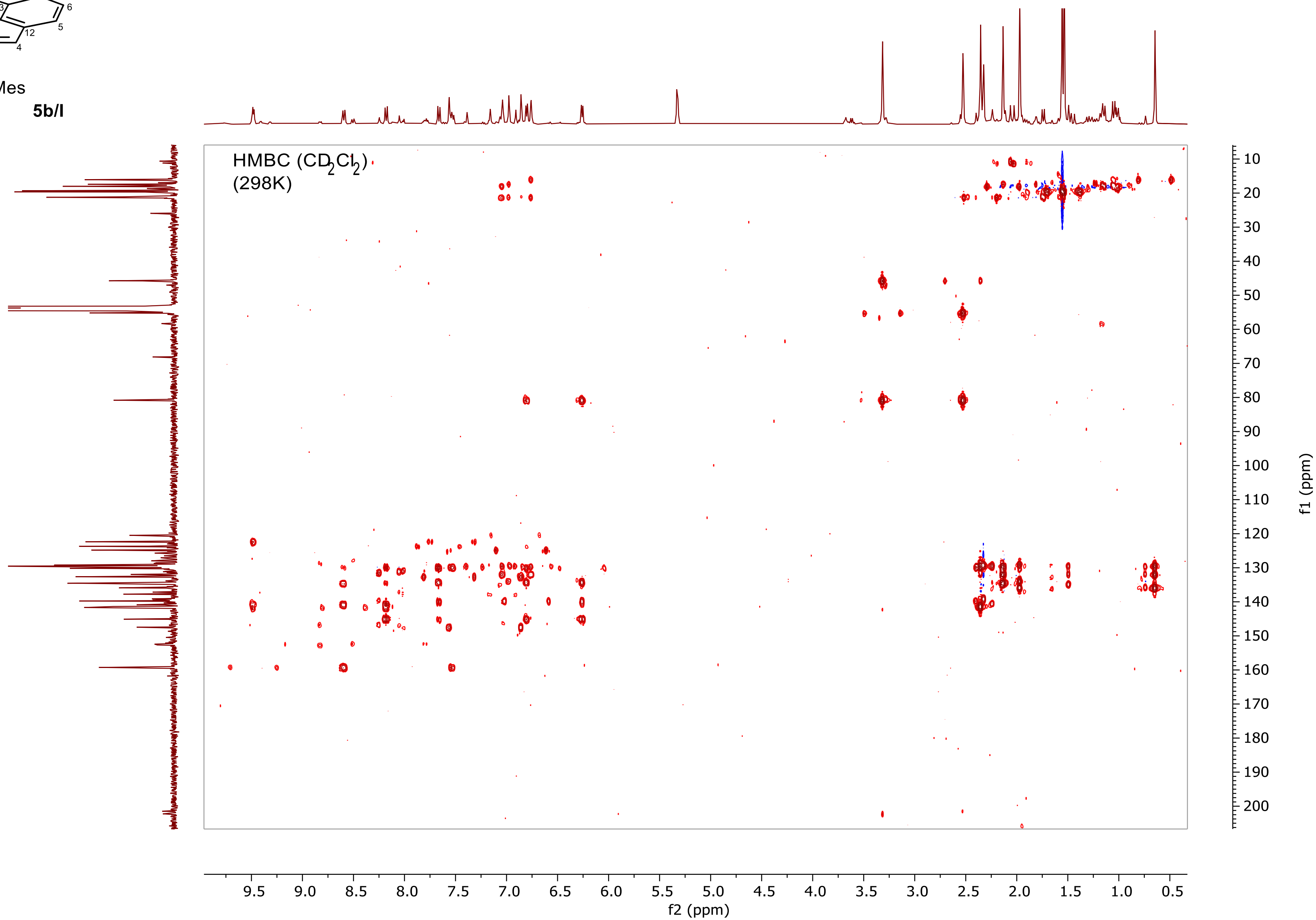

PMe3
OC
OC
Re
N
N
N
N
Mes
I

5b/I


HSQC (CD2Cl2)
(298K)
{5.32,53.84}CD2Cl2
f2 (ppm)
f1 (ppm)


PMe3
OC
OC
Re
N
N
N
N
Mes
I
2
3
4
5
6
7
8
9
11
12
13
14

5b/I


HMBC (CD2Cl2)
(298K)
f2 (ppm)
f1 (ppm)