Structure and Reactivities of Rhenium and Technetium bis-arene Sandwich Complexes $[M(\eta^6\text{-arene})_2]^+$

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Supplementary Information

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1. General Information

Caution: ^{99}Tc is a weak β^--emitters. All experiments have to be performed in laboratories approved for working with low-level radioactive materials.

1.1 Materials

All Re and ^{99}Tc reactions were carried out under nitrogen atmosphere on standard nitrogen/vacuum lines unless otherwise stated. For the Re reactions, the glassware was dried by the use of a heat gun or in an oven at 120 °C at least overnight. Commercially available reagents were purchased reagent-grade and used without further purification. THF was dried over Na/Benzophenone. All chemicals were purchased from Sigma Aldrich (Switzerland), except hydrochloric acid (32%, Honeywell, Germany), hexamethylbenzene (abcr), trifluoroacetic acid (99%, Alfa Aesar, Germany), and $(NH_4)[^{99}TcO_4]$ (Oak Ridge). The chemicals were used without farther purification. Deuterated NMR solvents were obtained from Armar Chemicals (Switzerland). $Ka[ReO_4]$ was synthesized according to literature.[1,2] The $SiMe_3$ protected aniline ($PhN(SiMe_3)_2$) was prepared, following literature procedure.[3]

1.2 Characterization

^{1}H, ^{13}C, ^{13}C HSQC, ^{29}Si, ^{31}P and ^{99}Tc NMR spectra were recorded on a BrukerDRX 400 MHz or BrukerDRX 500 MHz spectrometer. Chemical shifts of ^{1}H and ^{13}C were referenced with the residual solvent resonances relative to TMS, while ^{99}Tc was referenced relative to the signal of $[^{99}TcO_4]^-$ ($\delta = 0$). Due to a scalar coupling to the ^{99}Tc nucleus (nuclear spin = 9/2), signals of directly bond carbon atoms are very broad, poorly resolved and rarely observed. Therefore, chemical shifts of ^{13}C signals of carbon atoms directly bond to the ^{99}Tc nucleus are not given in the analytical data of the synthetic procedures. Electronspray-ionisation mass spectrometry (ESI-MS) was performed on a Bruker esquireTM/LC spectrometer or on a Bruker esquire^{TM}/HCT^{TM} spectrometer. High-resolution mass spectrometry (HR-ESI-MS) was performed on a Bruker maXis QTof high-resolution mass spectrometer (Bruker GmbH, Bremen, Germany).

Preparative HPLC was performed on a Varian ProStar 320 system, using a Dr. Maisch Reprosil C18 100-7 (40 x 250 mm) column. The solvents (HPLC grade) were 0.1% trifluoroacetic acid (solvent A) and acetonitrile (solvent B). The HPLC gradients used are as follow (G1): 0-2 minutes: 75% A (25% B); 2.1-45 minutes: linear gradient from 75% A (25% B) to 65% A (35% B); 45-51 minutes: 100% B. The flow rate was 40 mL/min. Detection was performed at 273 nm; (G2): 0-2 minutes: 55% A (45% B); 2.1-45 minutes: linear gradient from 55% A (45% B) to 0% A (100% B); 45-50 minutes: 100% B. The flow rate was 40 mL/min. Detection was performed at 300 nm; (G3): 0-2 minutes: 40% A (60% B); 2.1-45 minutes: linear gradient from 40% A (60% B) to 0% A (100% B); 45-50 minutes: 100% B. The flow rate was 40 mL/min. Detection was performed at 300 nm. Analytical HPLC was performed on a VWR

HITACHI Chromaster system, using a Macherey-Nagel Nucleosil C18 100-5 column. HPLC solvents were 0.1% trifluoroacetic acid (solvent A) and methanol (solvent B). Applied HPLC gradient: 0-3 minutes: 100% A; 3.1-9 minutes: 75% A, 25% B; 9.1-20 minutes: linear gradient from 66% A (34% B) to 0% A (100% B); 20-28 minutes: 100% B; 28.1-30: 100% A. The flow rate was 0.5 mL/min. Detection was performed at 250 nm. HPLC analyses of the ^{99}Tc were performed on a Merck Hitachi LaChrom L 7100 pump coupled to a Merck Hitachi LaChrom L7200 tunable UV detector and a radiodetector. UV/Vis detection was performed at 250 nm. The detection of the radioactive ^{99}Tc complexes were performed with a Berthold LB513 radiodetector equipped with YG cell. Separations were achieved on a Macherey-Nagel C18 reversed-phase column (Nucleosil 10 lm, 250 4 mm) using a gradient of MeOH/ 0.1% CF_3COOH as eluent, and a flow rate of 0.5 mL/min. Gradient: t = 0 – 3 min: 0% MeOH; 3 – 3.1 min: 0 – 25% MeOH; 3.1 – 9 min: 25% MeOH; 9 – 9.1 min: 25 – 34% MeOH; 9.1 – 18 min: 34 - 100% MeOH; 18 – 25 min: 100% MeOH, 25 – 25.1 min: 100 - 0% MeOH; 25.1 – 30 min: 0% MeOH. For technetium content measurements, pure compounds were dissolved in the appropriate solvents. The measurements were carried out with a scintillation cocktail (Packard Ultimate Gold XR) and a liquid scintillation counter (*Hidex 300 SL*).

Elemental Analysis (EA) measurements were performed on a LecoCHNS-932 elemental analyzer. UPLC-ESI-MS was performed on a Waters Acquity UPLC System coupled to a Bruker HCT^{TM}, using an Acquity UPLC BEH C18 1.7 µm (2.1 x 50 mm) column. UPLC solvents were formic acid (0.1% in millipore water) (solvent A) and acetonitrile HPLC grade (solvent B). Applied UPLC gradient: 0-0.5 minutes: 95% A, 5% B; 0.51-4.0 minutes: linear gradient from 95% A (5% B) to 0% A (100% B); 4-5 minutes: 100% B. The flow rate was 0.6 ml/min. Detection was performed at 250 nm and 480 nm (DAD). IR-Spectra were recorded on a Perkin-Elmer FT-IR Spectrum Two spectrometer, using KBr pallets (^{99}Tc complexes) or by ATR technique (Re complexes).

2. Synthetic procedures

^{99}Tc-complexes

2.1 [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_3)](PF_6)$_2$ ([**1-H**](PF_6)$_2$) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-NH_3)](PF_6)$_2$ ([**2-H**](PF_6)$_2$)

K[^{99}TcO_4] (10 mg, 0.05 mmol), hexamethylbenzene (407.7 mg, 2.51 mmol), $AlCl_3$ (206 mg, 1.55 mmol), PhN($SiMe_3$)$_2$ (240.7 mg, 1.01 mmol) and Zn-powder (9.5 mg, 0.15 mmol) were added in a 50 mL two-necked flask. The reaction mixture was suspended in cyclohexane (6 mL) and stirred at 80 °C for 4 h. H_2O (7 mL) was added to quench the reaction. The red solution was filtered and phases were separated. HPLC of the aqueous phase showed a mixture of product (61.6%), [^{99}TcO_4]$^-$ (27.6%) and [^{99}Tc(Me_6Ph)$_2$]$^+$ (10.8%). For workup, conc. HCl (0.1 mL) was added to the aq. solution and it was stirred at room temperature until ^{29}Si-NMR showed full deprotection of the amine (ca. 23 h). The byproduct [^{99}Tc(η^6-hmbz)$_2$]$^+$ was extracted from the acidic aqueous phase with DCM. NH_4PF_6 (106 mg, 0.65 mmol) was added to the aqueous phase and the formed colorless precipitate was filtered off and dried *in vacuo* to afford [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_3)](PF_6)$_2$ ([**1-H**](PF_6)$_2$) as colorless powder (4.7 mg, 0.007 mmol, 15%).

It has to be mentioned, the powder contains [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-NH_3)](PF_6)$_2$ ([**2-H**](PF_6)$_2$) as second minor specie. Due to extremely similar physical properties all attempts to separate the two species failed. Analytical data are given for the product mixture. Crystal of [**1-H**](PF_6)$_2$ suitable for X-ray diffraction analysis were obtained by vapor diffusion of Et_2O into a solution of [**1**](PF_6) in acetone.

^{99}Tc NMR (90 Hz, MeCN-d_3): δ = -1415 ($\Delta\nu_{1/2}$ = 40 Hz), -1461 ppm ($\Delta\nu_{1/2}$ = 30).

^{1}H NMR (500 MHz, acetone-d_6): δ = 5.29 (*t*, *J* = 5.94 Hz, 2 H, NCCHC*H*), 5.09 (*t*, *J* = 5.23 Hz, 1 H, NCCHCHC*H*), 5.05 (*d*, *J* = 5.94 Hz, 2 H, NCC*H*), 2.29 ppm (*s*, 18 H, CH_3).

^{13}C NMR (125 Hz, acetone-d_6): δ = 17.03 ppm (6 CH_3).

IR (KBr): ν = 3495*m*, 3399*s*, 3241*w*, 2923*w*, 1633*m*, 1541*s*, 1458*m*, 1391*m*, 1288*m*, 1147*w*, 1072*m*, 1026*w*, 992*w*, 836*s*, 652*w*, 559*s*, 447*w*, 430*w*, 407*m* cm^{-1}.

^{99}Tc analysis calc. for $C_{18}H_{26}F_{12}NP_2Tc$ (%): 15.33; found: 14.95.

2.2 [^{99}Tc(η^6-hmbz)$_2$](PF$_6$) ([**3a**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-hmbz)](PF$_6$) ([**3b**](PF$_6$))

In a 50 mL, two-necked flask, K[^{99}TcO$_4$] (10 mg, 0.05 mmol), hexamethylbenzene (160 mg, 0.98 mmol) and AlCl$_3$ (206.3 mg, 1.55 mmol) were dissolved in cyclohexane (6 mL). The solution was stirred at 80 C for 4 h when H$_2$O (6 mL) was added to quench the reaction. The solution was filtered and phases were separated. NH$_4$PF$_6$ (106.2 mg, 0.65 mmol) was added to the aq. phase and the colorless precipitate was filtered off and dried *in vacuo* to afford a colorless powder [^{99}Tc(η^6-hmbz)$_2$](PF$_6$) ([**3a**](PF$_6$)) (20.9 mg, 0.04 mmol, 71%).

It has to be mentioned, the powder contains [^{99}Tc(η^6-pmbz)(η^6-hmbz)](PF$_6$) ([**3b**](PF$_6$)) as by product (ratio 1: 0.7). Due to extremely similar physical properties all attempts to separate the two species failed. Analytical data are given for the product mixture. Crystal of [**3a**](PF$_6$) suitable for X-ray diffraction analysis were obtained by vapor diffusion of Et$_2$O into a solution of [**3a**](PF$_6$) in acetone.

^{99}Tc NMR (90 Hz, CD$_2$Cl$_2$): δ = -1308 ($\Delta\nu_{1/2}$ = 103 Hz), -1346 ppm ($\Delta\nu_{1/2}$ = 83 Hz).

^{1}H NMR (500 MHz, acetone-d$_6$): δ = 5.237 (s, 1H, [^{99}Tc(η^6-hmbz)(η^6-pmbz*H*)]), 2.152 (s, 18 H, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)]), 2.083 (s, 6 H, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)]), 2.075 (s, 36 H, [^{99}Tc(η^6-*hm*bz)$_2$]), 2.069 (s, 3 H, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)]), 2.028 ppm (s, 6 H, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)]).

^{13}C NMR (125 MHz, acetone-d$_6$): δ = 18.37 (2 C, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)], 16.34 (6 C, [^{99}Tc(η^6-*hm*bz)(η^6-pmbzH)]), 16.16 (12 C, [^{99}Tc(η^6-*hm*bz)$_2$]), 15.34 (1 C, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)]), 14.74 ppm (2 C, [^{99}Tc(η^6-hmbz)(η^6-*pm*bzH)]).

IR (KBr): ν = 3416*w* 2920*m*, 1448*m*, 1392*s*, 1294*w*, 1070*m*, 1013*m*, 877*m*, 840*s*, 557*s*, 444*w*, 425*m* cm^{-1}.

^{99}Tc analysis calc. for C$_{24}$H$_{36}$F$_6$PTc (%): 17.40; found: 17.0.

2.3 [^{99}Tc(η^6-hmbz)(η^6-C$_6$H$_5$-Br)](PF$_6$) ([**4**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-C$_6$H$_5$-Br)](PF$_6$) ([**5**](PF$_6$))

In contrast to the published synthesis of [^{99}Tc(η^6-hmbz)(η^6-C$_6$H$_5$-Br)](PF$_6$) ([**4**](PF$_6$)),[4] this improved procedure allows the separation of simultaneously formed [^{99}Tc(η^6-hmbz)(η^6-C$_6$H$_5$-Br)](PF$_6$) ([**4**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-C$_6$H$_5$-Br)](PF$_6$) ([**5**](PF$_6$)). In a 50 mL two-necked flask, K[^{99}TcO$_4$] (13.2 mg, 0.07 mmol), hexamethylbenzene (80 mg, 0.5 mmol) and AlCl$_3$ (200 mg, 1.50 mmol) were suspended in bromobenzene (4 mL). The solution was stirred at 80°C for 4 h when H$_2$O (5 mL) was added to quench the reaction. The solution was filtered and phases were separated. NH$_4$PF$_6$ (100 mg, 0.61 mmol) was added to the aq. phases and the pale yellow precipitate was filtered off. Following this procedure,

30.4 mg (0.05 mmol, 77%) of a mixture of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)](PF_6) ([**4**](PF_6)) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)](PF_6) ([**5**](PF_6)) was isolated.

IR (KBr): ν = 3430*w*, 3083*w*, 2923*w*, 1430*w*, 1391*m*, 1054*w*, 1019*w*, 833*s*, 670*w*, 558*s*, 451*w*, 426*m* cm^{-1}.

^{99}Tc analysis calc. for $C_{18}H_{23}BrF_6PTc$ (%): 17.56; found: 16.54.

For anion metathesis the solid was dissolved in 20 ml THF and Ph_3PCl_2 (100 mg, 0.3 mmol) dissolved in 1 ml THF was added. The pale yellow precipitate was filtered off and dissolved in 0.5 ml H_2O. The solution was loaded on a C18 syringe column. Separation of the two products [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)]$^+$ and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)]$^+$ was achieved by passing through the column ca. 20 ml H_2O and collecting 1 ml fractions. Finally, the column was washed with 2ml MeOH. All fractions were checked by radio HPLC. Fractions which contained the products were checked by ^{99}Tc-NMR. Only fractions, which were pure and showed the same ^{99}Tc signal in the ^{99}Tc-NMR were combined. [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)]$^+$ eluted slightly faster from the column as [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)]$^+$. Evaporating the solvent under high vacuum leads to the isolation of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)]Cl and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)]Cl as pale yellow powders.

[^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)](PF_6) ([**4**](PF_6))

^{99}Tc NMR (90 MHz,D_2O): δ = -1563 ppm ($\Delta\nu_{1/2}$ = 54 Hz).

^{1}H NMR (400 MHz, D_2O): δ = 5.585 (*d*, *J* = 5.44 Hz, 2 H, [^{99}Tc(η^6-C_6H_5Br)(η^6-hmbz)]), 5.241 (*m*, 3 H, [^{99}Tc(η^6-C_6H_5Br)(η^6-hmbz)]), 2.318 ppm (*s*, 18 H, [^{99}Tc (η^6-*hm*bz)]).

^{13}C NMR (125 MHz, D_2O): δ = 15.9 ppm (6 C, [^{99}Tc(η^6-*hm*bz)(η^6-C_6H_5Br)]).

[^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)](PF_6) ([**5**](PF_6))

^{99}Tc NMR (112.5 MHz, D_2O): δ = -1603 ppm ($\Delta\nu_{1/2}$ = 41 Hz).

^{1}H NMR (500 MHz, D_2O): δ = 5.90 (s, 1 H, [^{99}Tc(η^6-pmbz*H*)(η^6-C_6H_5-Br)]), 5.69 (d, *J* = 5.71 Hz, 2 H, [^{99}Tc(η^6-pmbzH)(η^6-C_6H_5-Br)]), 5.35 (t, *J* = 5.44 Hz 2 H, [^{99}Tc(η^6-pmbzH)(η^6-C_6H_5-Br)]), 5.30 (t, 5.37 Hz, 1 H, [^{99}Tc(η^6-pmbzH)(η^6-C_6H_5-Br)]), 2.31 (s, 3 H, [^{99}Tc(η^6-*pm*bzH)(η^6-C_6H_5-Br)]), 2.25 (s, 6 H, [^{99}Tc(η^6-*pm*bzH)(η^6-C_6H_5-Br)], 2.21 ppm (s, 6 H, [^{99}Tc(η^6-*pm*bzH)(η^6-C_6H_5-Br)]).

^{13}C NMR (125 MHz, D_2O): δ = 19.25 (br, 2 C, [^{99}Tc(η^6-*pm*bzH)(η^6-C_6H_5-Br)], 16.36 (br, 1 C, [^{99}Tc(η^6-*pm*bzH)(η^6-C_6H_5-Br)]), 15.75 ppm (br, 2 C, [^{99}Tc(η^6-*pm*bzH)(η^6-C_6H_5-Br)]).

2.4 [^{99}Tc(η^6-hmbz)(η^6-C_6H_6)](PF_6) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_6)](PF_6)

K[^{99}TcO4] (10 mg, 0.05 mmol), hexamethylbenzene (406.3 mg, 2.5 mmol) and AlCl3 (204 mg, 1.5 mmol) were dissolved in benzene (5 mL) in a 50 mL two-necked flask. The solution was stirred at 80°C for 4 h when H_2O (4 mL) was added to quench the reaction. The reaction mixture was filtered, washed with H_2O (2 mL) and phases were separated. NH_4PF_6 (104 mg, 0.64 mmol) was added to the aq. phase and the formed colorless precipitate was filtered off and dried *in vacuo* to afford [^{99}Tc(Me_6Ph)(C_6H_6)](PF_6) as colorless powder (18.7 mg, 0.04 mmol, 79%).

It has to mentioned, the product contains a second minor specie, most likely [^{99}Tc(Me_5HPh)(C_6H_6)](PF_6). Due to extremely similar physical properties all attempts to separate the two species failed. Analytical data are given for the product mixture.

^{99}Tc NMR (112.5 MHz, acetone-d_6): δ = -1546 ($\Delta\nu_{1/2}$ = 49 Hz), -1594 ($\Delta\nu_{1/2}$ = 53 Hz) ppm.

^{1}H NMR (500 MHz, acetone-d_6): δ = 5. 996 (s, 1H, [^{99}Tc(η^6-C_6H_6)(η^6-pmbz*H*)]), 5.483 (s, 6 H, [^{99}Tc(η^6-C_6*H*$_6$)(η^6-pmbzH)]), 5.392 (s, 6 H, [^{99}Tc(η^6-C_6*H*$_6$)(η^6-hmbz)]), 2.418 (s, 18 H, [^{99}Tc(η^6-C_6H_6)(η^6-*hm*bz)]) + (s, 3 H, [^{99}Tc(η^6-C_6H_6)(η^6-*pm*bzH)]), 2.360 (s, 6 H, [^{99}Tc(η^6-C_6H_6)(η^6-*pm*bzH)]), 2.314 ppm (s, 6 H, [^{99}Tc(η^6-C_6H_6)(η^6-*pm*bzH)]).

^{13}C NMR (125 MHz, acetone-d_6): δ = 19.78 (2 C, [^{99}Tc(η^6-C_6H_6)(η^6-*pm*bzH)]), 17.63 (6 C, [^{99}Tc(η^6-C_6H_6)(η^6-*hm*bz)]), 16.95 (1 C, [^{99}Tc(η^6-C_6H_6)(η^6-*hm*bz)]), 16.32 ppm (2 C, [^{99}Tc(η^6-C_6H_6)(η^6-*pm*bzH)]).

IR (KBr): ν = 3435*w*, 3082*w*, 2924*w*, 1855*w*, 1640*w*, 1453*m*, 1386*m*, 1293*w*, 1074*m*, 1026*w*, 974*w*, 838*s*, 558*s*, 451*w, 415m* cm^{-1}.

^{99}Tc analysis calc. for $C_{18}H_{24}F_6PTc$ (%): 20.42; found: 19.54.

Re-complexes

2.5 [Re(η^6-C_6H_6)(η^6-napht)](OTF) ([**6**](OTf))

$KReO_4$ (500 mg, 1.73 mmol), zinc dust (339 mg, 5.18 mmol) and anhydrous $AlCl_3$ (2.3 g, 17.3 mmol) were suspended in a mixture of naphthalene (3.33 g, 25.95 mmol) and benzene (3.45 mL, 38.93 mmol). The reaction mixture was stirred for 18 h at 90°C. Afterwards, the mixture was cooled to room temperature, washed under vigorously stirring with hot heptane (3 x 50 mL) and Et_2O (2 x 50 mL). The mixture was filtrated and the solid residue was suspended in 50 ml of H_2O and filtered again. All aqueous solutions were reduced in volume to less than 8 ml. The crude product was purified by

preparative HPLC (Reprosil 100 C18, 250 mm x 40 mm, 0.1% TFA/CH_3CN, gradient G1). The solvent was evaporated and the solid dissolved in water. After the addition of lithium triflate (404 mg, 2.6 mmol), [**6**](OTf) precipitated as analytically pure, orange crystalline powder, which was filtered and dried. Single crystals, suitable for X-ray diffraction analysis were obtained by vapour diffusion of Et_2O into a solution of [**6**](OTf) in acetone. Yield: 206.1 mg (0.381 mmol, 22%).

^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.72 (m, 2H, C*H*$_{arom}$), 7.51 (m, 2H, C*H*$_{arom}$), 7.32 (m, 2H, C*H*$_{arom}$), 6.38 (m, 2H, C*H*$_{arom}$) 5.83 (s, 6H, C*H*$_{arom}$).
^{13}C NMR (100 MHz, acetone-d_6) δ [ppm]: 131.90 (2C, *C*H$_{arom}$), 131.43 (2C, *C*H$_{arom}$), 93.28 (2C, *C*-CH$_{arom}$), 80.03 (2C, *C*H$_{arom}$), 77.15 (6C, *C*H$_{arom}$), 75.1 (2C, *C*H$_{arom}$).
ESI-MS: m/z = 393.1 $[M]^+$.
IR ν: 3052*w*, 1454*w*,1413*w*, 1242*s*, 1221*m*, 1143*s*, 1027*s*, 1008*m*, 906*w*, 858*m*, 830*m*, 753*w* cm^{-1}.
HR-ESI-MS $C_{16}H_{14}Re$ $[M]^+$: calculated, 339.0648; found, 339.0646.

2.6 [Re(η^6-napht)$_2$](OTf) ([**7**](OTf))

$KReO_4$ (725 mg, 2.5 mmol), zinc dust (490 mg, 7.5 mmol) and anhydrous $AlCl_3$ (3.34 g, 10 mmol) were suspended in naphthalene (5.0 g, 39 mmol). The reaction mixture was stirred for 18 h at 100°C. The mixture was filtrated and the solid residue was suspended in 50 ml of H_2O and filtered again. Lithium triflate (489 mg, 3 mmol) was added to the filtrate. The product was extracted with dichloromethane (6 x 50 mL). The organic phase was evaporated which afforded [**7**](OTf) as analytically pure, deep red crystalline powder. Single crystals, suitable for X-ray diffraction analysis were obtained by vapour diffusion of Et_2O into a solution of [**7**](OTf) in acetone. Yield: 474.7 mg (0.381 mmol, 32%).

^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.38 (m, 4H, C*H*$_{arom}$), 6.86 (m, 4H, C*H*$_{arom}$), 6.78 (m, 4H, C*H*$_{arom}$), 6.33 (m, 4H, C*H*$_{arom}$).
^{13}C NMR (100 MHz, acetone-d_6) δ [ppm]: 129.7 (*C*H$_{arom}$), 129.5 (*C*H$_{arom}$), 90.3 (*C*-CH$_{arom}$), 78.0 (*C*H$_{arom}$), 73.3 (*C*H$_{arom}$).
ESI-MS: m/z =443.0 $[M]^+$.
IR ν: 3059*w*, 1469*w*, 1407*w*, 1371*w*, 1257*s*, 1224*m*, 1139*s*, 1028*s*, 1006*m*, 996*w*, 858*m*, 852*s*, 743*w* cm^{-1}.
Anal. calcd. for $C_{21}H_{16}F_3O_3ReS$: C 42.63, H 2.73; found: C 42.43, H 2.65.
HR-ESI-MS $C_{20}H_{16}Re$ $[M]^+$: calculated, 443.0804; found, 443.0806.

[Re(η^6-C_6H_6)(tep)$_3$](OTf) ([**8**](OTf))

[**6**](OTf) (30 mg, 0.055 mmol) was dissolved in 2 mL acetone. After the addition of triethyl phosphite (188 µL, 1.1 mmol) to the yellow solution, the reaction mixture was stirred for 6 h at 80°C in a microwave reactor. The solvent was evaporated *in vacuo* and the residue washed with Et_2O (4 x 2.5 mL) and water (2 x 2 mL). The product was recrystallized from acetonitrile, yielding colourless single crystals of [**8**](OTf), suitable for X-ray diffraction analysis. Yield: 38 mg (0.041 mmol, 75%) of [**8**](OTf).

^{1}H NMR (500 MHz, MeCN-d_3) δ [ppm]: 5.22 (s, 6H, CH_{arom}), 3.92 (m, 18H, CH_2), 1.23 (t, 27H, CH_3).
^{13}C NMR (125 MHz, MeCN-d_3) δ [ppm]: 84.6 (C_{arom}), 62.3 (CH_2), 16.3 (CH_3).
^{31}P NMR (202 MHz, MeCN-d_3) δ [ppm]: 111.03 (P(OEt)$_3$).
ESI-MS: m/z =763.2 $[M]^+$.
IR ν: 2983*w*, 2932*w*, 2852*w*, 1436*w*, 1386*w*, 1267*s*, 1224*w*, 1144*m*, 1024*s*, 929*s*, 819*w*, 775*m*, 714*m* cm^{-1}.
HR-ESI-MS $C_{24}H_{51}O_9P_3Re$ $[M]^+$: calculated, 763.2298; found, 763.2300.

2.7 [Re(η^6-C_6H_6)(CN-^{t}Bu)$_3$](OTf) ([**9**](OTf))

[**6**](OTf) (30 mg, 0.055 mmol) was dissolved in 2 mL acetone. After the addition of *tert*-butyl isocyanide (62 µL, 0.55 mmol) to the yellow solution, the reaction mixture was stirred for 9 h at 80°C in a microwave reactor. The solvent was evaporated *in vacuo* and the residue washed with hexane (4 x 2.5 mL) and water (2 x 2 mL). The product was recrystallized from acetonitrile, yielding colourless single crystals of [**9**](OTf), suitable for X-ray diffraction analysis. Yield: 24 mg (0.036 mmol, 65%) of [**9**](OTf).

^{1}H NMR (500 MHz, MeCN-d_3) δ [ppm]: 5.24 (s, 6H, CH_{arom}) 1.48 (s, 27H, CH_3).
^{13}C NMR (125 MHz, MeCN-d_3) δ [ppm]: 139.74 (N*C*), 85.35 (C_{arom}), 58.58 (C(CH_3)$_3$), 31.30 (CH_3).
ESI-MS: m/z =514.2 $[M]^+$.
IR ν: 2978*w*, 2147*s* (NC), 2107*s* (NC), 2059*s* (NC), 1370*w*, 1263*s*, 1199*m*, 1147*s*, 1029*s*, 901*s*, 809*w* cm^{-1}.
HR-ESI-MS $C_{21}H_{33}N_3Re$ $[M]^+$: calculated, 514.2227; found, 514.2225.

2.8 [Re(η^6-C_6H_6)(HB(pyz)$_3$)] (**10**)

[**6**](OTf) (30 mg, 0.055 mmol) was dissolved in 2 mL acetone. After the addition of Potassium tri(1*H*-pyrazol-1-yl)hydroborate (69 mg, 0.275 mmol) to the yellow solution, the reaction mixture was stirred for 6 h at 80°C in a microwave reactor. The solvent was evaporated *in vacuo* and the residue washed with water (4 x 2.5 mL) and extracted with Et_2O (2 x 2 mL). Yellow single crystals of **10**, suitable for X-ray diffraction analysis were obtained by slow evaporation of a Et_2O solution of the ligand/**10** mixture.

2.9 [Re(η^6-napht)(tep)$_3$](PF_6) ([**11**](PF_6))

[**7**](OTf) (40 mg, 0.068 mmol) was dissolved in 4 mL acetone. After the addition of triethyl phosphite (118 µL, 0.68 mmol) to the red solution, the reaction mixture was stirred for 9 h at 100°C in a microwave reactor. The solvent was evaporated *in vacuo* and the residue washed with hexane (2 x 2 mL) and Et_2O (2 x 2.5 mL). The residue was purified by *preparative HPLC* (Reprosil 100 C18, 250x40 mm, 0.1% TFA/CH_3CN, Gradient: G2). Analytically pure yellow [**11**](PF_6) precipitated from the solution upon addition of NH_4PF_6. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of a acetonitrile solution of [**11**](OTf). Yield: 39 mg (0.041 mmol, 60%) for [**11**](PF_6).

^{1}H NMR (500 MHz, MeCN-d_3) δ [ppm]: 7.53 (m, 2H, C*H*$_{arom}$), 7.45 (m, 2H, C*H*$_{arom}$), 6.08 (s, 2H, C*H*$_{arom}$), 5.33 (t, 2H, C*H*$_{arom}$), 3.78 (t, 18H, C*H*$_2$), 1.15 (t, 27H, C*H*$_3$).
^{13}C NMR (125 MHz, MeCN-d_3) δ [ppm]: 130.83 (*C*H$_{arom}$), 130.21 (*C*H$_{arom}$), 102.7 (*C*$_{arom}$), 84.95 (*C*H$_{arom}$), 80.98 (*C*H$_{arom}$), 62.35 (*C*H$_2$), 16.39 (*C*H$_3$).
^{31}P NMR (202 MHz, MeCN-d_3) δ [ppm]: 108.96 (s, *P*(OEt$_3$)$_3$), -144.62 (sept, *P*F$_6$).
ESI-MS: m/z =813.2 $[M]^+$.
IR ν: 2982*w*, 2914*w*, 1442*w*, 1386*w*, 1158*w*, 1089*w*, 1020*s*, 939*s*, 833*s*, 772*m*, 710*w* cm^{-1}.
HR-ESI-MS $C_{28}H_{53}O_9P_3Re$ $[M]^+$: calculated, 813.2454; found, 813.2440.

2.10 [Re(η^6-napht)(triphos)](PF_6) ([**12**](PF_6))

[**7**](OTF) (50 mg, 0.084 mmol) was dissolved in 4 mL acetone. After the addition of 1,1,1-tris(diphenylphosphinomethyl)ethane (262 mg, 0.42 mmol) to the red solution, the reaction mixture was stirred for 9 h at 100°C in a microwave reactor. The solvent was evaporated *in vacuo* and the residue washed with hexane (2 x 2 ml) and Et_2O (2 x 2.5 mL). The residue was purified by *preparative HPLC* (Reprosil 100 C18, 250x40 mm, 0.1% TFA/CH_3CN, Gradient: G2). Analytically pure orange-red

[**12**](PF_6) precipitated from the solution upon addition of NH_4PF_6. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution of [**12**](PF_6). Yield: 52 mg (0.047 mmol, 56%) for [**12**](PF_6).

^{1}H NMR (500 MHz, MeCN-d_3) δ [ppm]: 7.49 (m, 2H, C*H*$_{arom}$), 7.36 (m, 2H, C*H*$_{arom}$), 7.23 (t, 6H, C*H*$_{arom}$), 7.03 (t, 12H, C*H*$_{arom}$), 6.63 (s, 12H, C*H*$_{arom}$), 6.19 (t, 2H, C*H*$_{arom}$), 5.35 (m, 2H, C*H*$_{arom}$), 2.36 (d, 6H, C*H*$_2$), 1.36 (t, 3H, C*H*$_3$).
^{13}C NMR (125 MHz, MeCN-d_3) δ [ppm]: 141.8 (*C*$_{arom}$), 133.01 (*C*H$_{arom}$), 132.8 (*C*H$_{arom}$), 130.24 (*C*H$_{arom}$), 129.78 (*C*H$_{arom}$), 128.87 (*C*H$_{arom}$), 103.21 (*C*$_{arom}$), 83.11 (*C*H$_{arom}$), 76.22 (*C*H$_{arom}$), 40.75 (*C*-CH_3), 39.24 (*C*H_3), 37.86 (*C*H_2).
^{31}P NMR (202 MHz, MeCN-d_3) δ [ppm]: 3.13 (s, *P*$(Ph)_2$),-144.62 (sept, *P*F_6).
ESI-MS: m/z =939.2 $[M]^+$.
IR ν: 3059*w*, 2918*w*, 2851*w*, 1611*w*, 1574*w*, 1482*w*, 1433*m*, 1250*w*, 1088*m*, 1001*w*, 828*s*, 733*w* cm^{-1}.
HR-ESI-MS $C_{51}H_{47}P_3Re$ $[M]^+$: calculated, 939.2443; found, 913.2449.

2.11 [Re(CN-^{t}Bu)$_6$](PF_6) ([**13**](PF_6))

[**7**](OTF) (40 mg, 0.068 mmol) was dissolved in 2 mL acetone. After the addition of *tert*-butyl isocyanide (77 µL, 0.68 mmol) to the red solution, the reaction mixture was stirred for 4 h at 100°C in a microwave reactor. The solvent was evaporated *in vacuo* and the residue washed with hexane (2 x 2 ml) and Et_2O (2 x 2.5 mL). The residue was purified by *preparative HPLC* (Reprosil 100 C18, 250x40 mm, 0.1% TFA/CH_3CN, Gradient: G3). Analytically pure colorless [**13**](PF_6) precipitated from the solution upon addition of NH_4PF_6. Single crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile solution of [**13**](OTf) Yield: 46 mg (0.056 mmol, 82%) for [**13**](PF_6).

^{1}H NMR (500 MHz, MeCN-d_3) δ [ppm]: 1.44 (s, 54 H, C*H*$_3$).
^{13}C NMR (125 MHz, MeCN-d_3) δ [ppm]: 144.3 (N*C*), 57.65 (*C*(CH_3)), 31.53 (*C*H_3).
^{31}P NMR (202 MHz, MeCN-d_3) δ [ppm]: -144.62 (sept, *P*F_6).
ESI-MS: m/z =685.39 $[M]^+$.
IR ν: 2976*w*, 2937*w*, 2039*s* (NC), 1460*w*, 1369*w*, 1232*m*, 1198*m*, 834*s*, 727*w* cm^{-1}.
HR-ESI-MS $C_{30}H_{54}N_6Re$ $[M]^+$: calculated, 685.3973; found, 685.3970.

3. NMR Spectra (^{1}H, ^{2}H, ^{13}C, HSQC, ^{1}H NOE, HMBC)

3.1 [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**1-H**]$(PF_6)_2$) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**2-H**]$(PF_6)_2$)

3.1.1 ^{99}Tc NMR

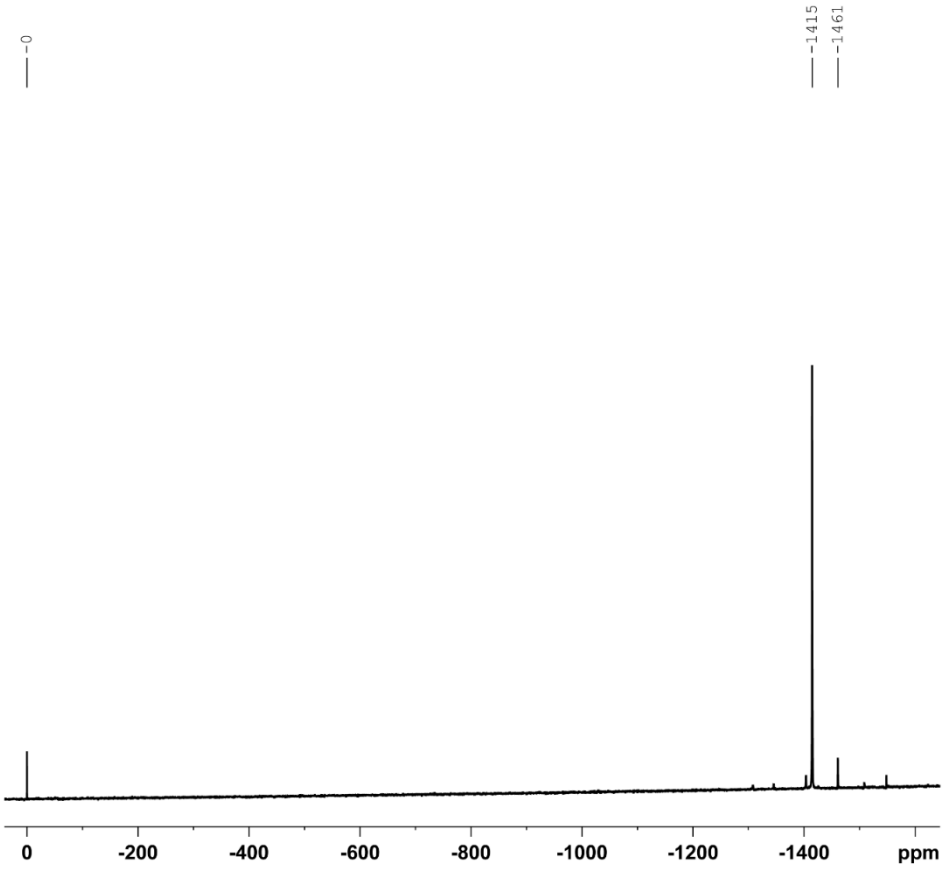

Figure 3.1.1: ^{99}Tc NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**1-H**]$(PF_6)_2$) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**2-H**]$(PF_6)_2$)

3.1.2 ^{1}H NMR

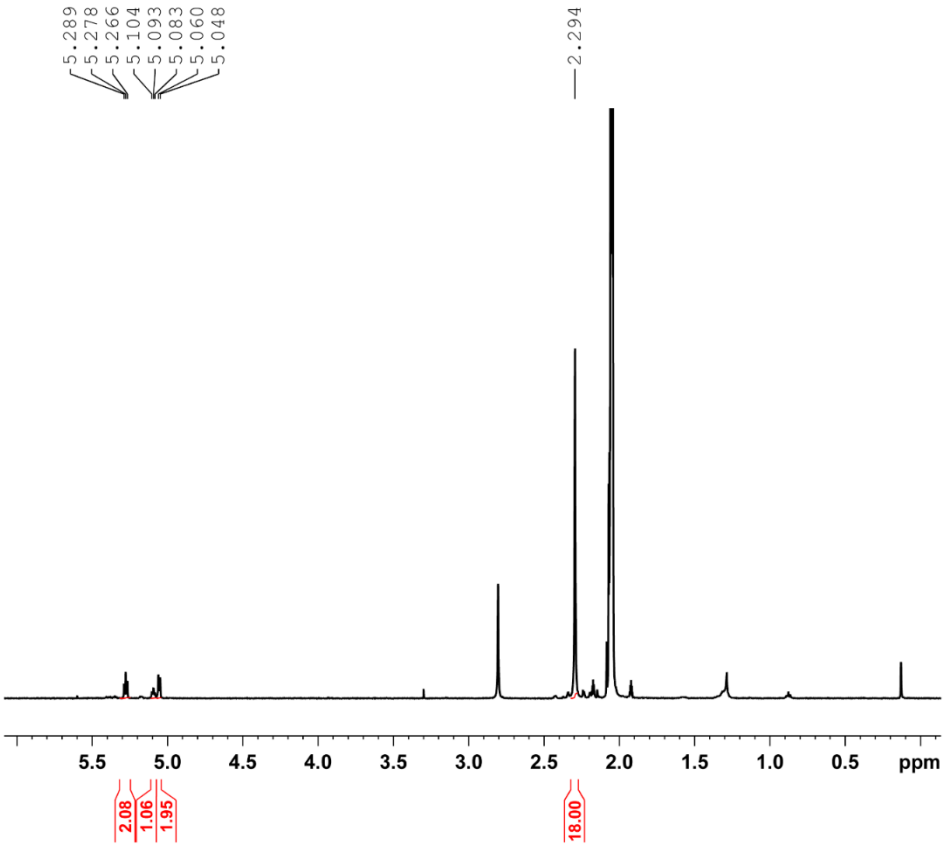

Figure 3.1.2: ^{1}H NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**1-H**]$(PF_6)_2$) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**2-H**]$(PF_6)_2$)

3.1.3 ^{13}C HSQC

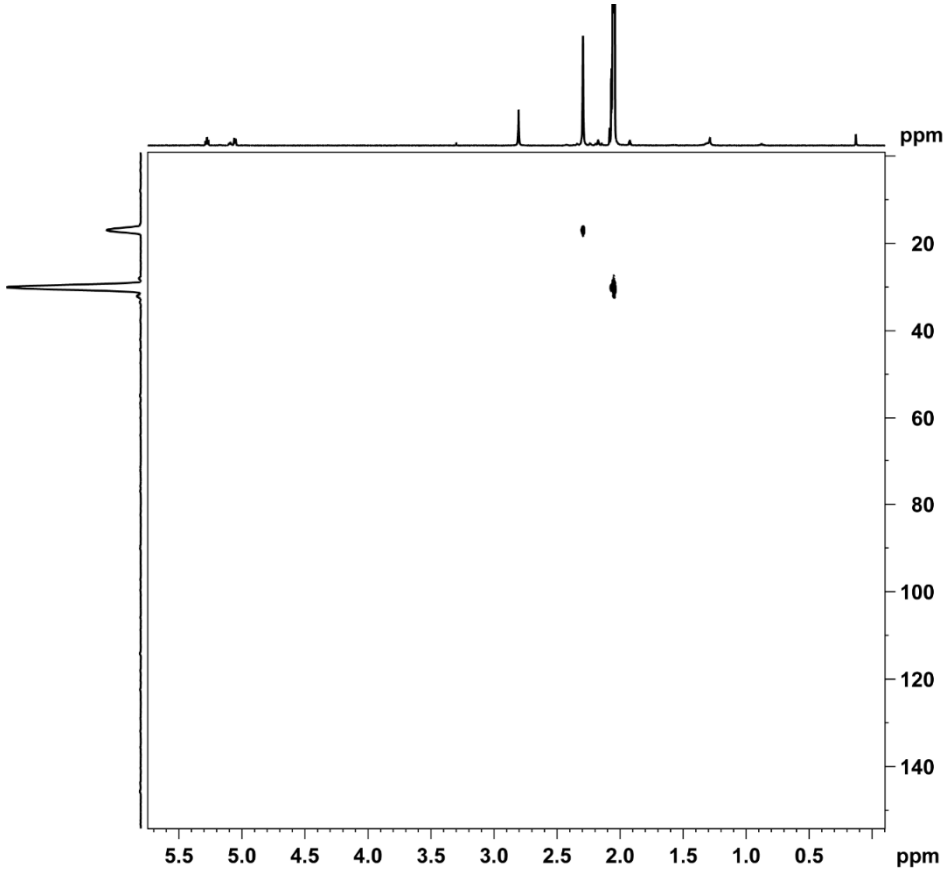

Figure 3.1.3: ^{13}C HSQC of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**1-H**]$(PF_6)_2$) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-NH_3)]$(PF_6)_2$ ([**2-H**]$(PF_6)_2$)

3.2 [^{99}Tc(η^6-hmbz)$_2$](PF$_6$) ([**3a**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-hmbz)](PF$_6$) ([**3b**](PF$_6$))

3.2.1 ^{99}Tc NMR

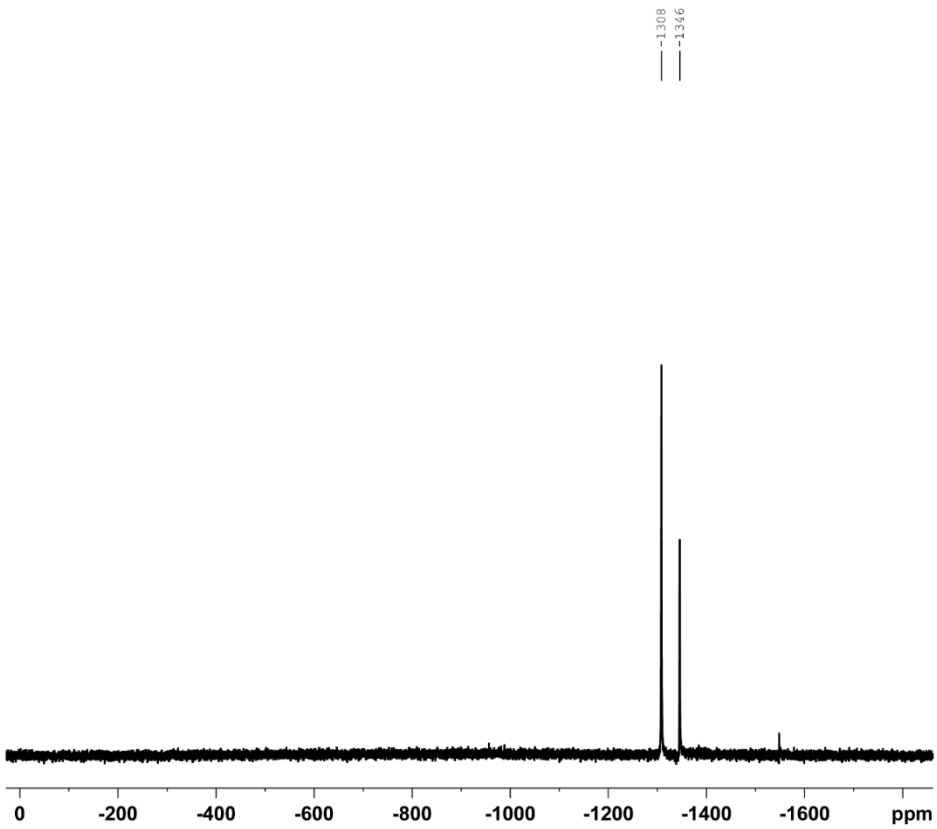

Figure 3.2.1: ^{99}Tc NMR of [^{99}Tc(η^6-hmbz)$_2$](PF$_6$) ([**3a**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-hmbz)](PF$_6$) ([**3b**](PF$_6$))

3.2.2 ^{1}H NMR

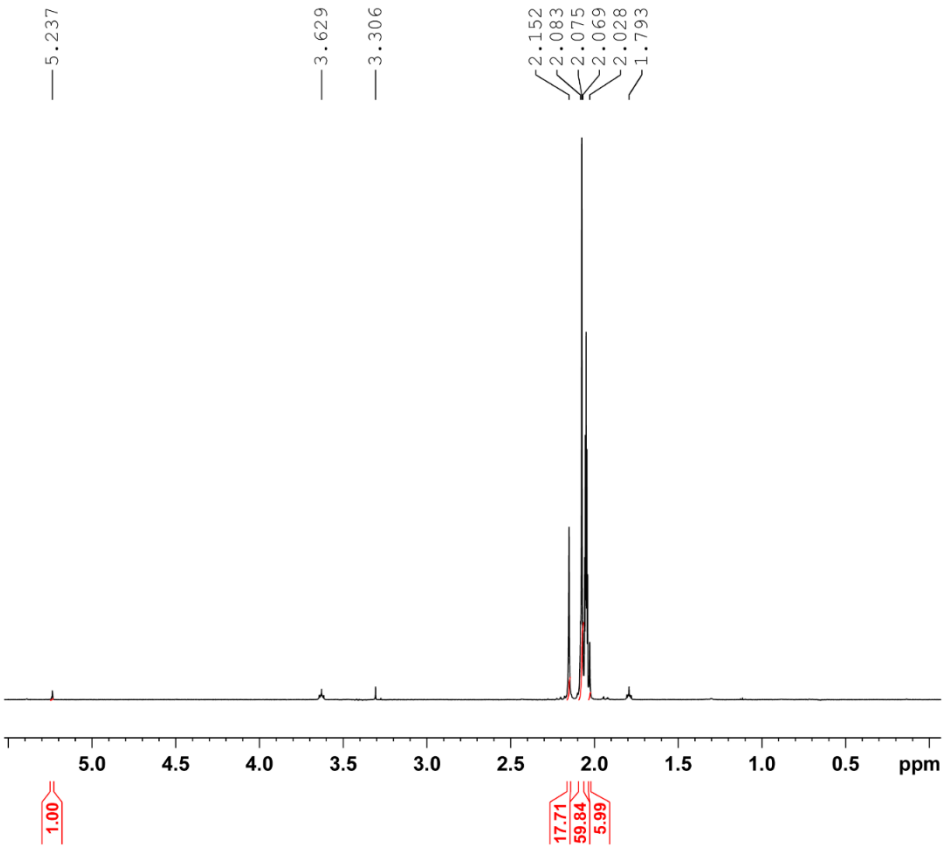

Figure 3.2.2: ^{1}H NMR of [^{99}Tc(η^6-hmbz)$_2$](PF$_6$) ([**3a**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-hmbz)](PF$_6$) ([**3b**](PF$_6$))

3.2.3 ^{13}C HSQC

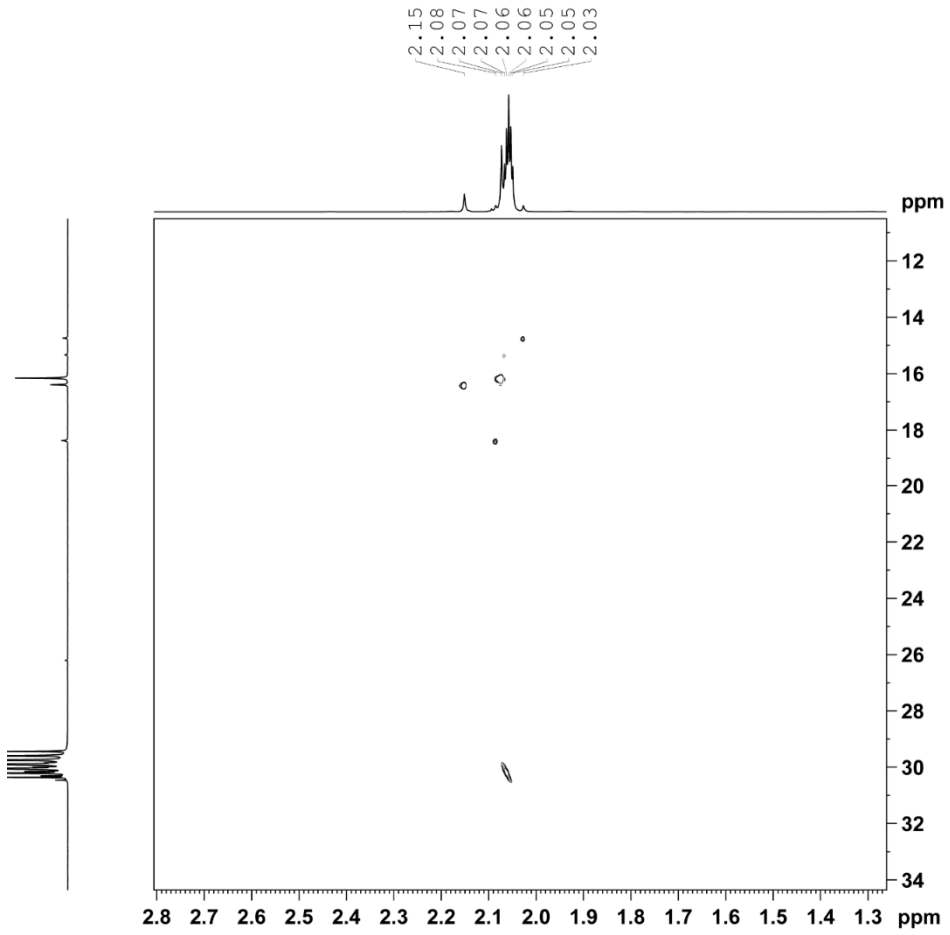

Figure 3.2.3: ^{13}C HSQC of [^{99}Tc(η^6-hmbz)$_2$](PF$_6$) ([**3a**](PF$_6$)) and [^{99}Tc(η^6-pmbz)(η^6-hmbz)](PF$_6$) ([**3b**](PF$_6$))

3.3 [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)](PF_6) ([**4**](PF_6))

3.3.1 ^{99}Tc NMR

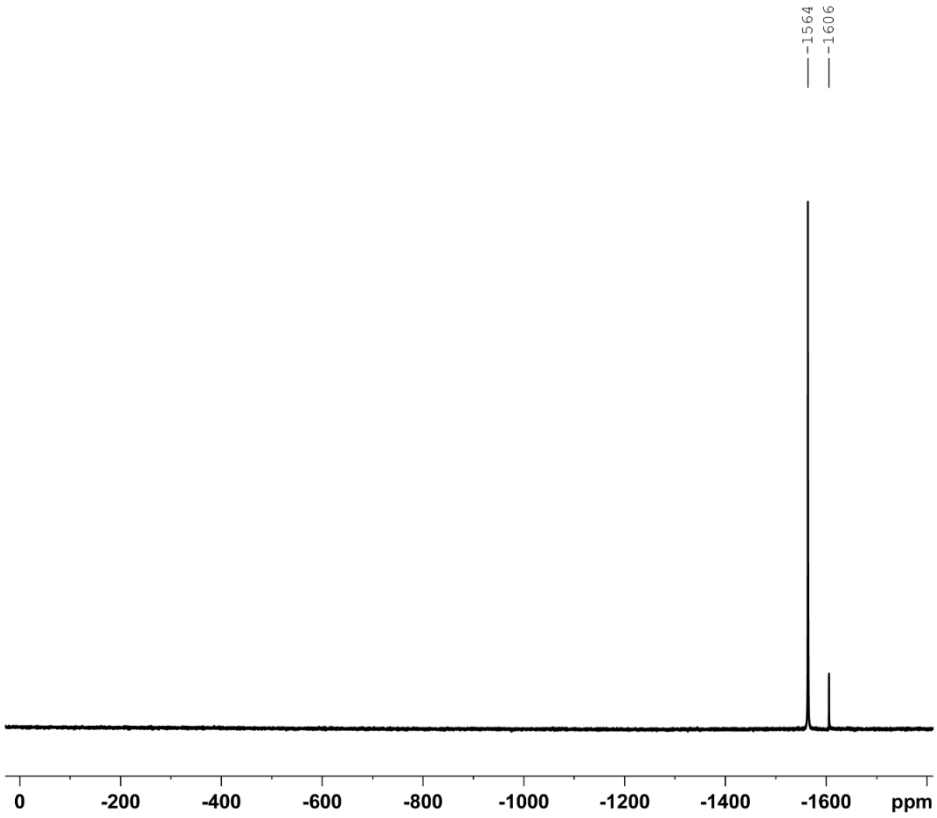

Figure 3.3.1: ^{99}Tc NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)](PF_6) ([**4**](PF_6))

3.3.2 ^{1}H NMR

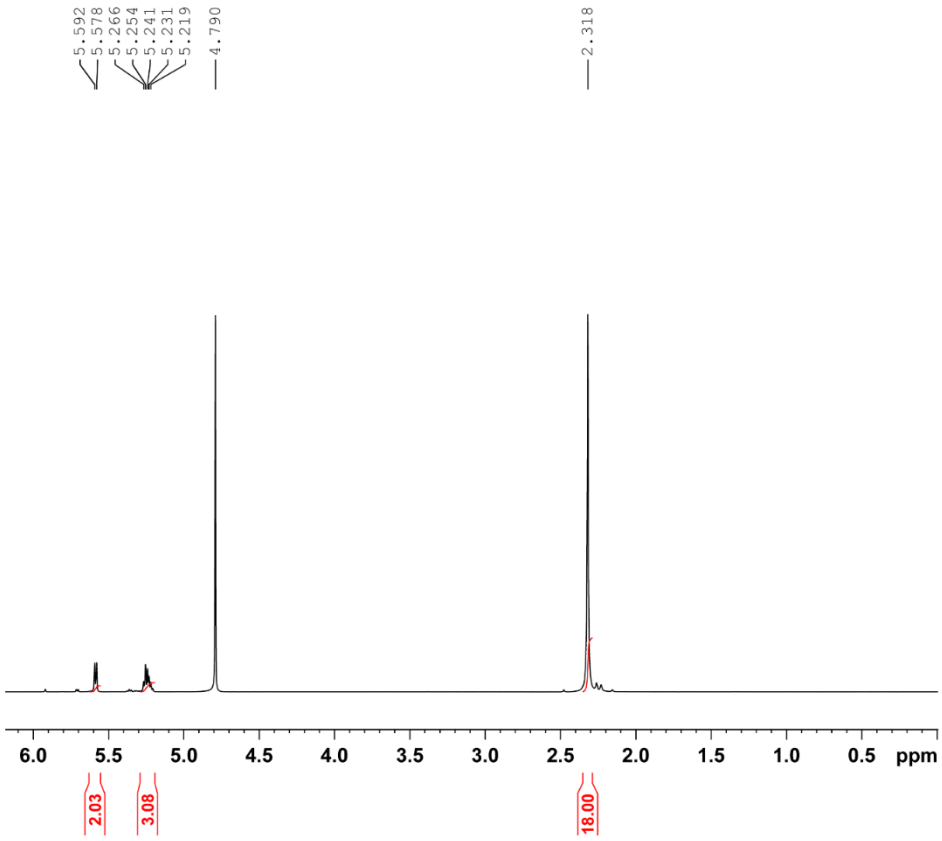

Figure 3.3.2: ^{1}H NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)](PF_6) ([**4**](PF_6))

3.3.3 ^{13}C HSQC

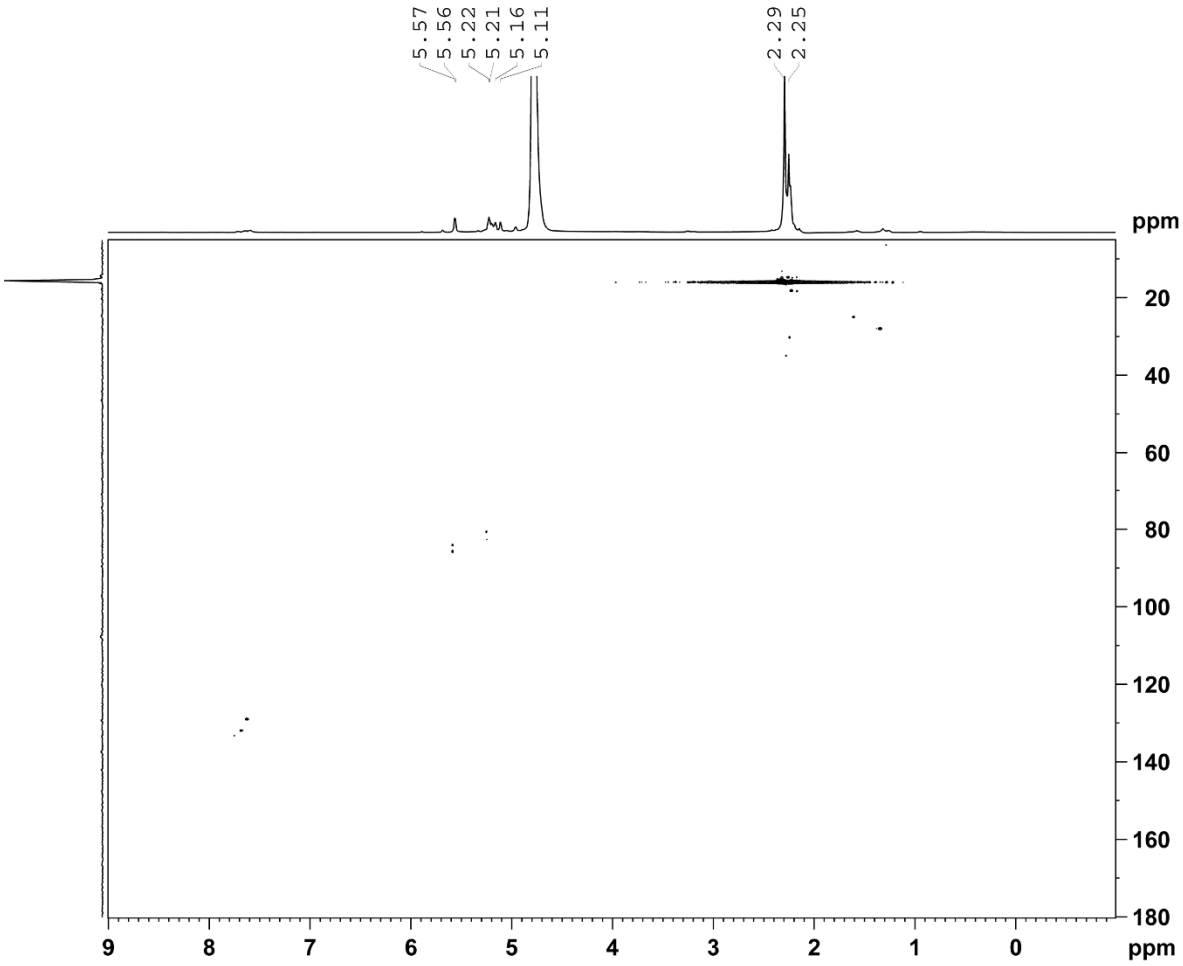

Figure 3.3.3: ^{13}C HSQC of [^{99}Tc(η^6-hmbz)(η^6-C_6H_5-Br)](PF_6) ([**4**](PF_6))

3.4 [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)](PF_6) ([**5**](PF_6))

3.4.1 ^{99}Tc NMR

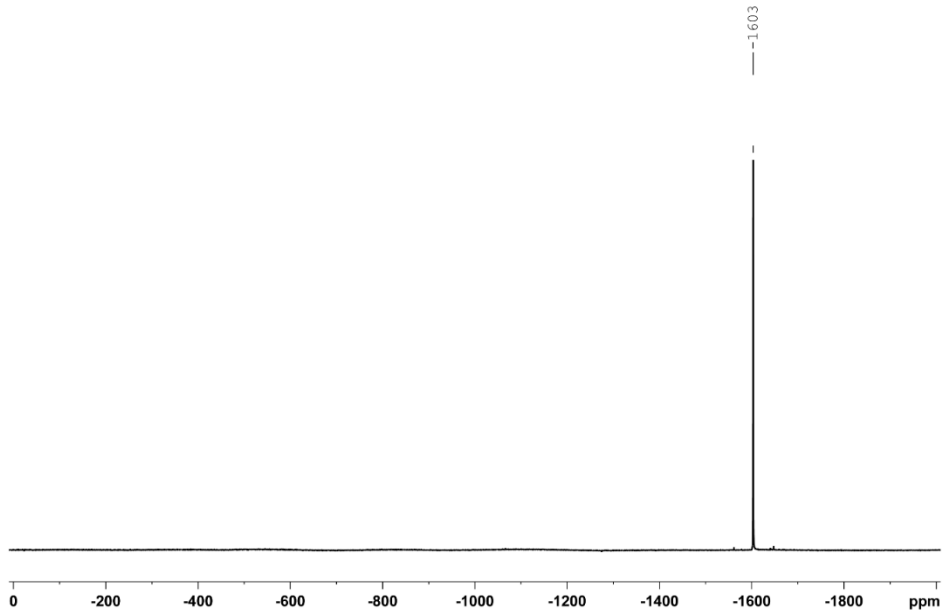

Figure 3.4.1: ^{99}Tc NMR of [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)](PF_6) ([**5**](PF_6))

3.4.2 ^{1}H NMR

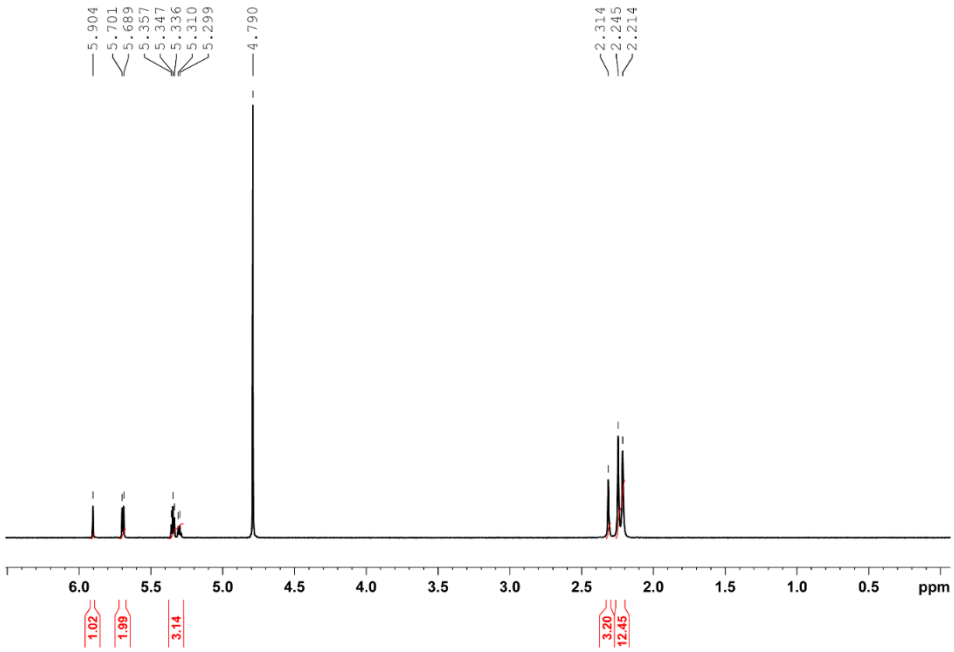

Figure 3.4.2: ^{1}H NMR of [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)](PF_6) ([**5**](PF_6))

3.4.3 ^{13}C HSQC

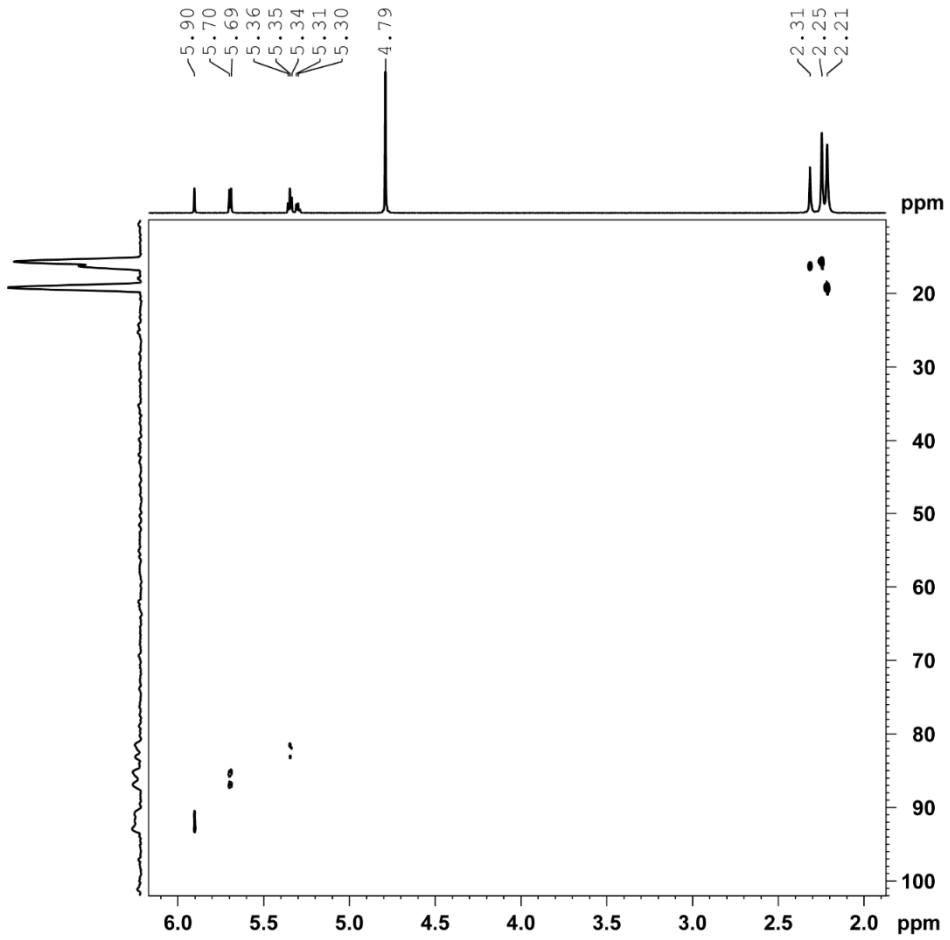

Figure 3.4.3: ^{13}C HSQC of [^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)](PF_6) ([**5**](PF_6))

3.5 [^{99}Tc(η^6-hmbz)((η^6-C_6H_6)](PF$_6$) and [^{99}Tc(η^6-pmbz)((η^6-C_6H_6)](PF$_6$)

3.5.1 ^{99}Tc NMR

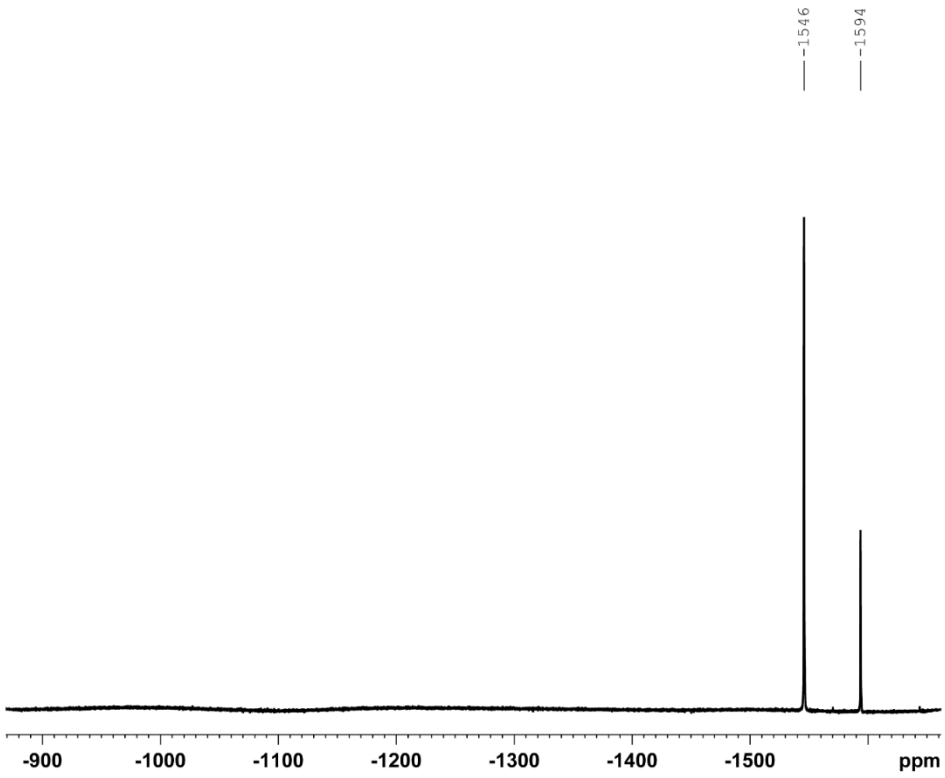

Figure 3.5.1: ^{99}Tc NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_6)](PF$_6$) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_6)](PF$_6$)

3.5.2 ^{1}H NMR

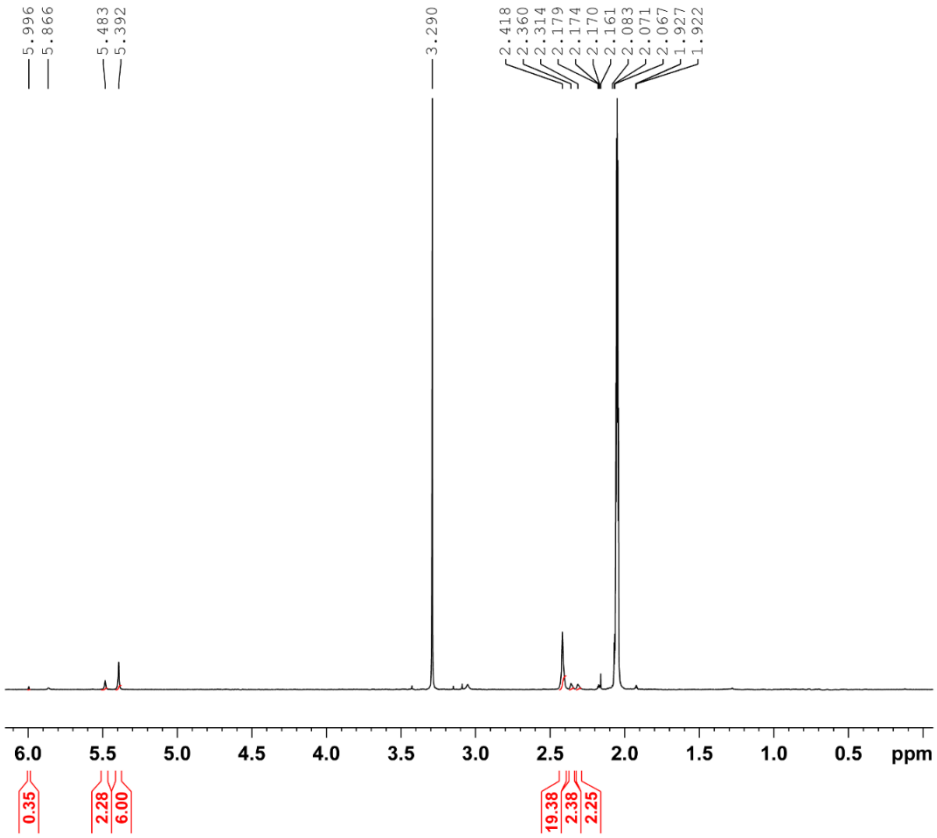

Figure 3.5.2: ^{1}H NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_6)](PF_6) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_6)](PF_6)

3.5.3 ^{13}C HSQC

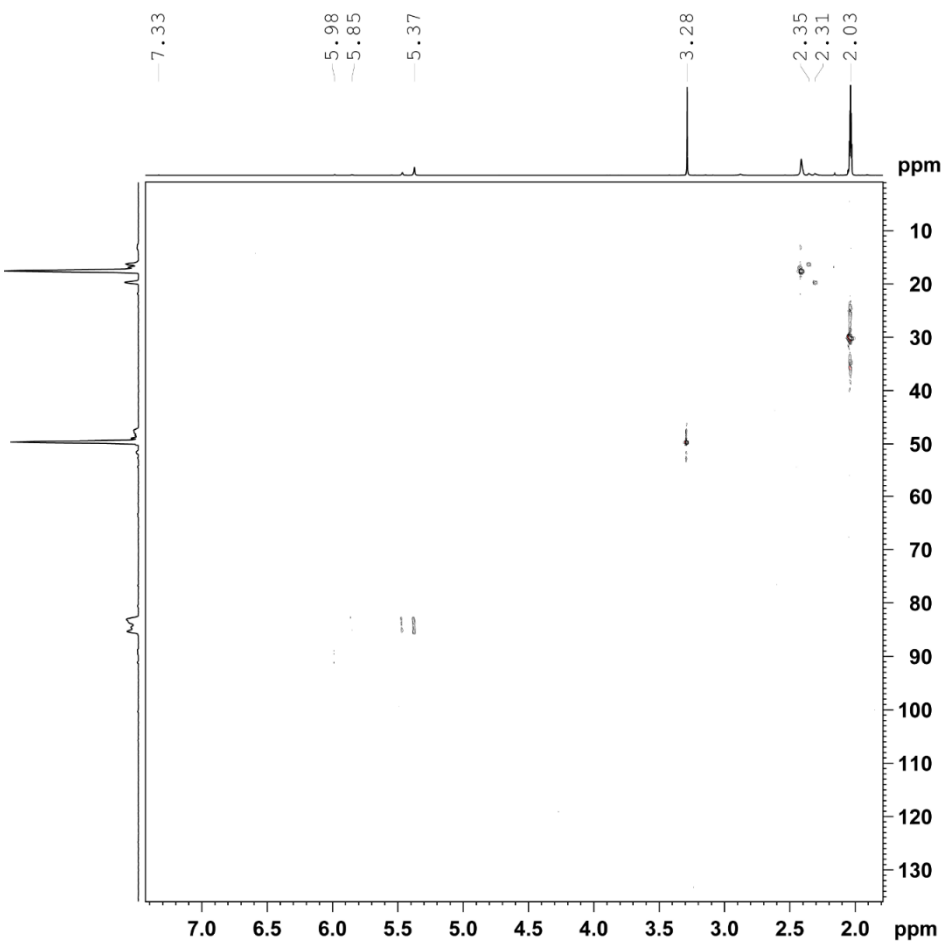

Figure 3.5.3: ^{1}H NMR of [^{99}Tc(η^6-hmbz)(η^6-C_6H_6)](PF_6) and [^{99}Tc(η^6-pmbz)(η^6-C_6H_6)](PF_6)

3.6 [Re(η^6-C_6H_6)(η^6-napht)](OTF) ([**6**](OTf))

3.6.1 ^{1}H NMR

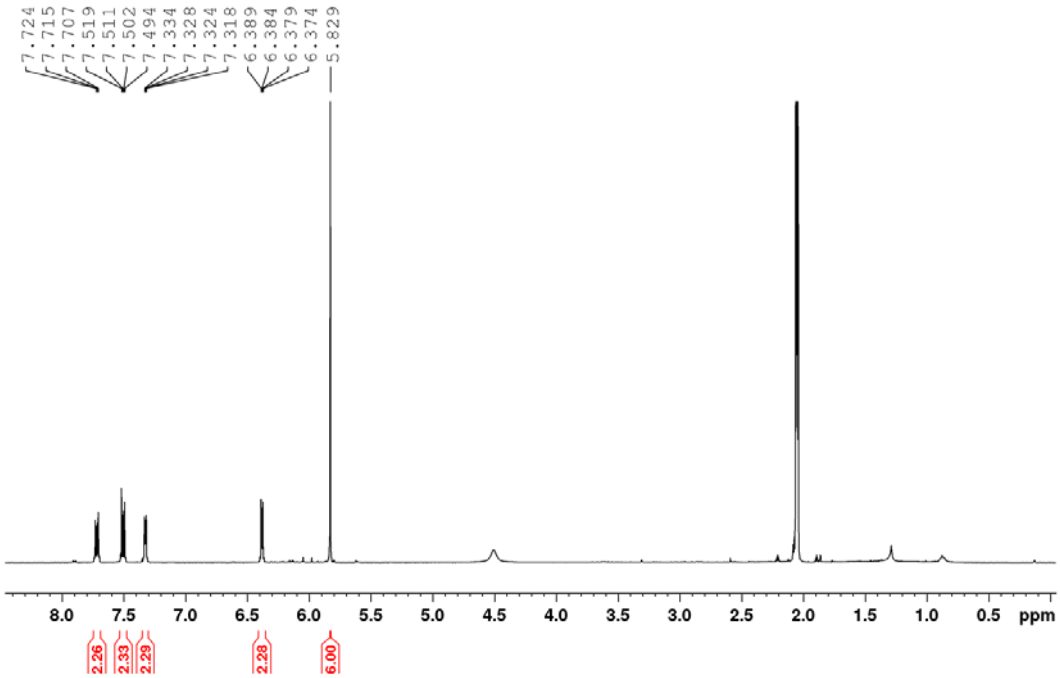

Figure 3.6.1: ^{1}H NMR of [Re(η^6-C_6H_6)(η^6-napht)](OTF) ([**6**](OTf))

3.6.2 ^{13}C NMR

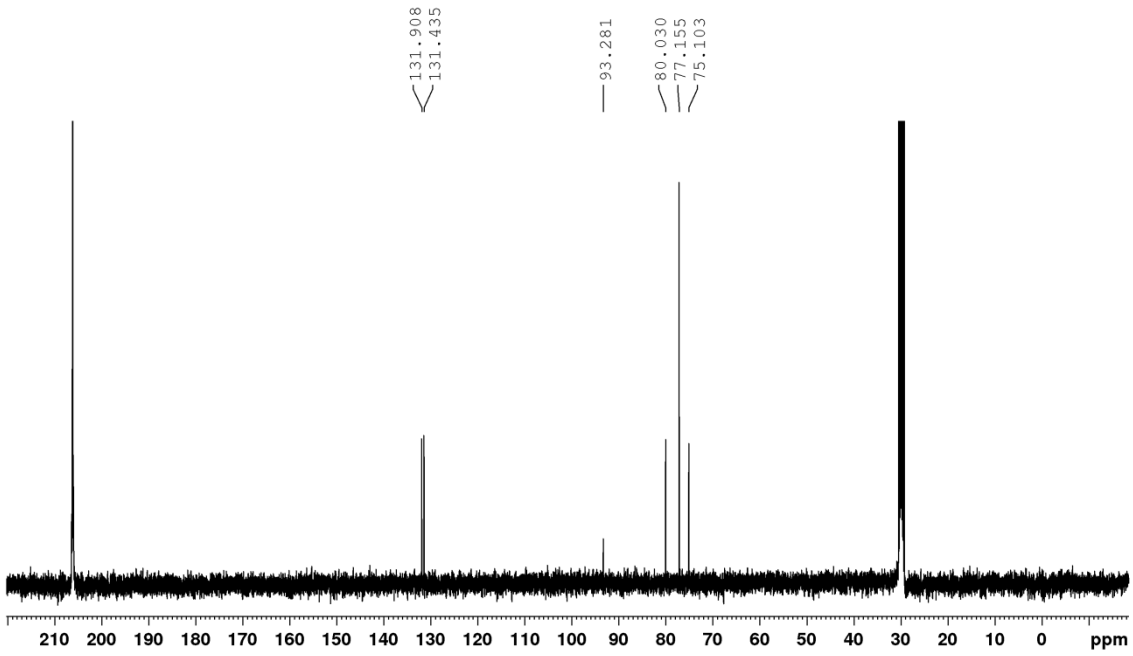

Figure 3.6.2: ^{13}C NMR of [Re(η^6-C_6H_6)(η^6-napht)](OTF) ([**6**](OTf))

3.7 [Re(η^6-napht)$_2$](OTf) ([**7**](OTf))

3.7.1 ^{1}H NMR

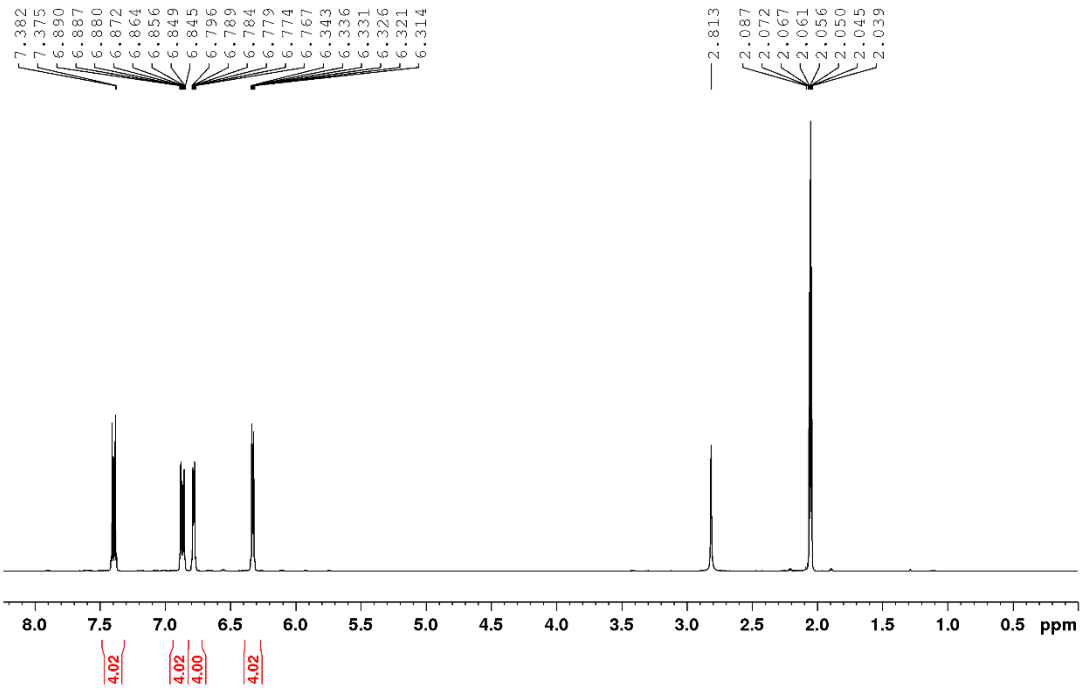

Figure 3.7.1: ^{1}H NMR of [Re(η^6-napht)$_2$](OTf) ([**7**](OTf))

3.7.2 ^{13}C NMR

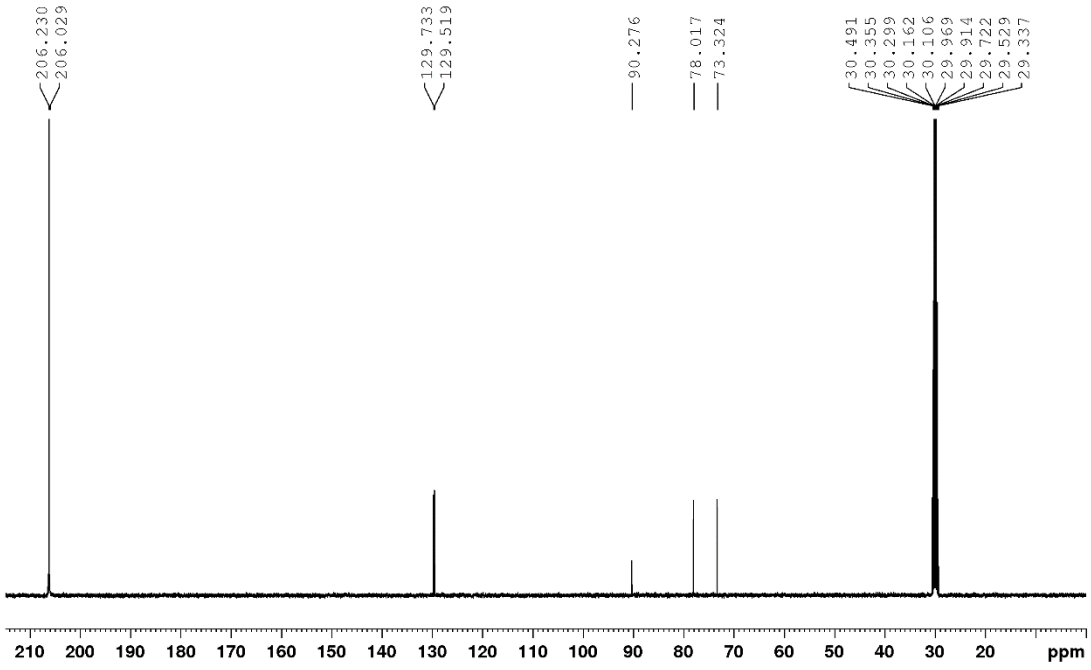

Figure 3.7.2: ^{13}C NMR of [Re(η^6-napht)$_2$](OTf) ([**7**](OTf))

3.8 $[Re(\eta^6\text{-}C_6H_6)(tep)_3](OTf)$ ([**8**](OTf))

3.8.1 ^1H NMR

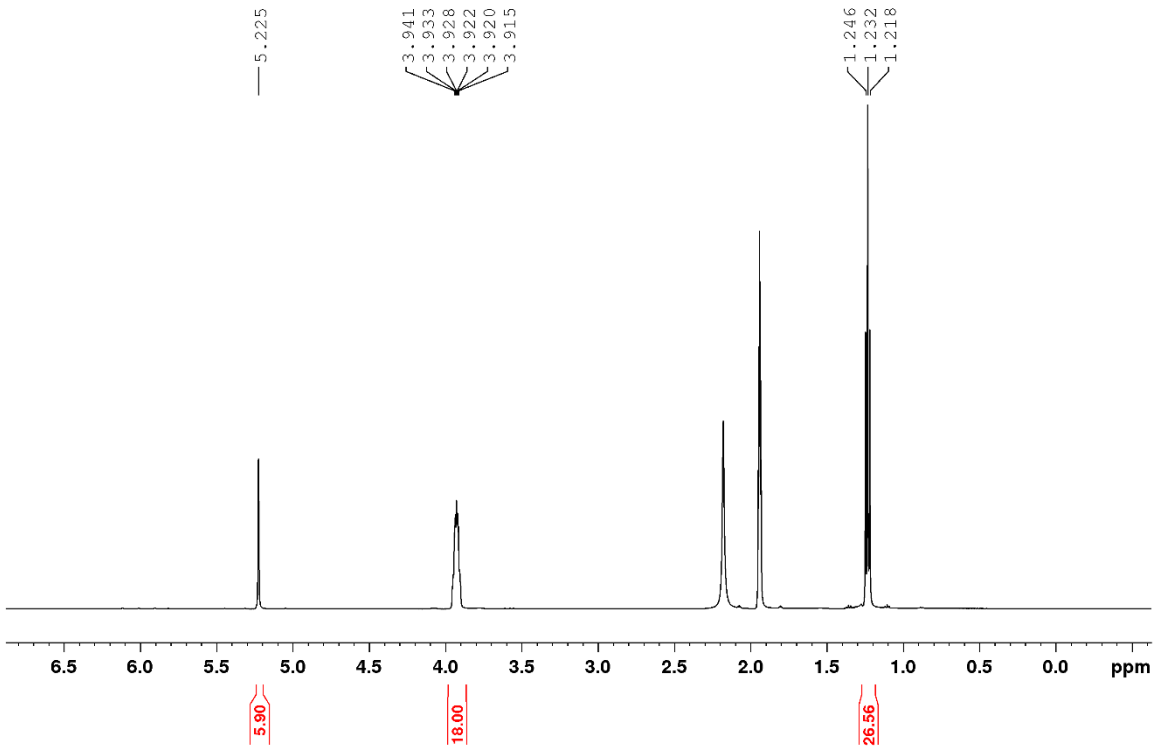

Figure 3.8.1: ^1H NMR of $[Re(\eta^6\text{-}C_6H_6)(tep)_3](OTf)$ ([**8**](OTf))

3.8.2 ^{13}C NMR

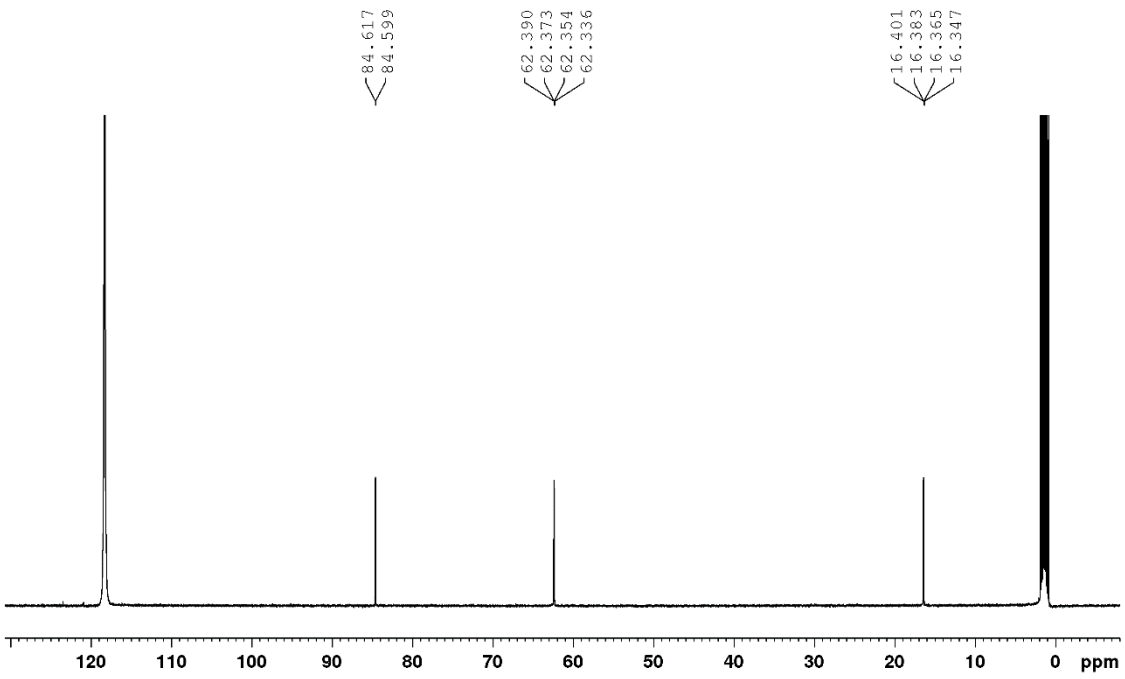

Figure 3.8.2: ^{13}C NMR of [Re(η^6-C_6H_6)(tep)$_3$](OTf) ([**8**](OTf))

3.9 $[Re(\eta^6\text{-}C_6H_6)(CN\text{-}^tBu)_3](OTf)$ ([**9**](OTf))

3.9.1 ^1H NMR

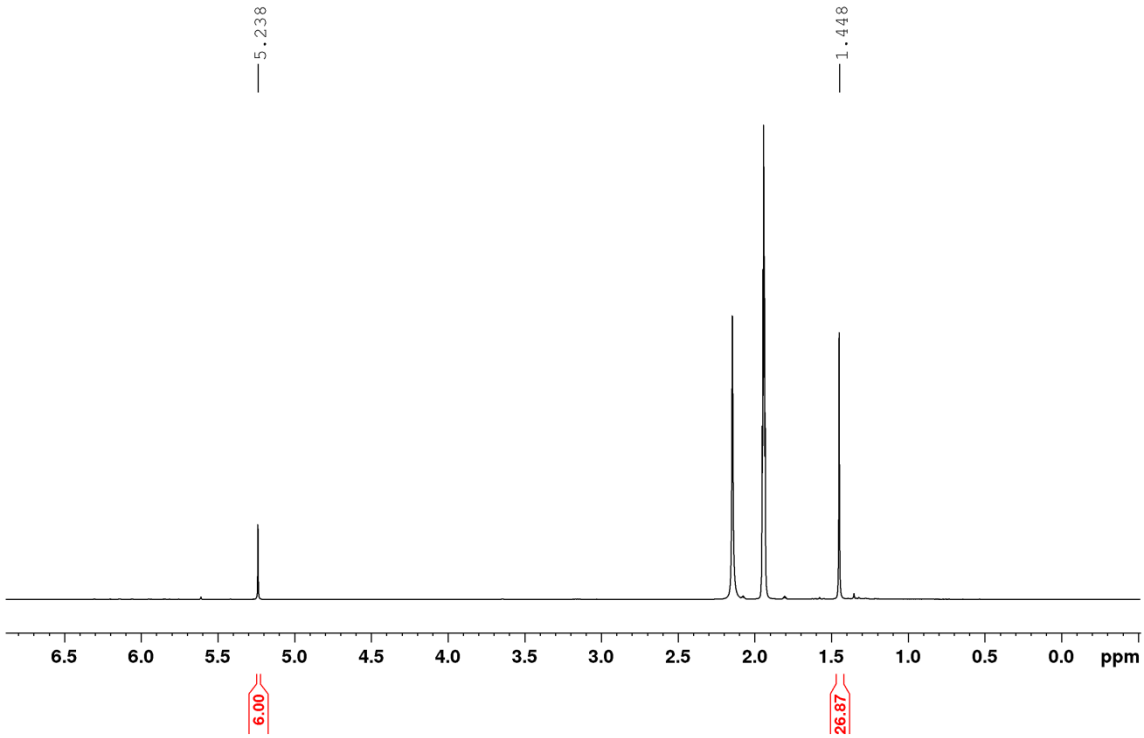

Figure 3.9.1: ^1H NMR of $[Re(\eta^6\text{-}C_6H_6)(CN\text{-}^tBu)_3](OTf)$ ([**9**](OTf))

3.9.2 ^{13}C NMR

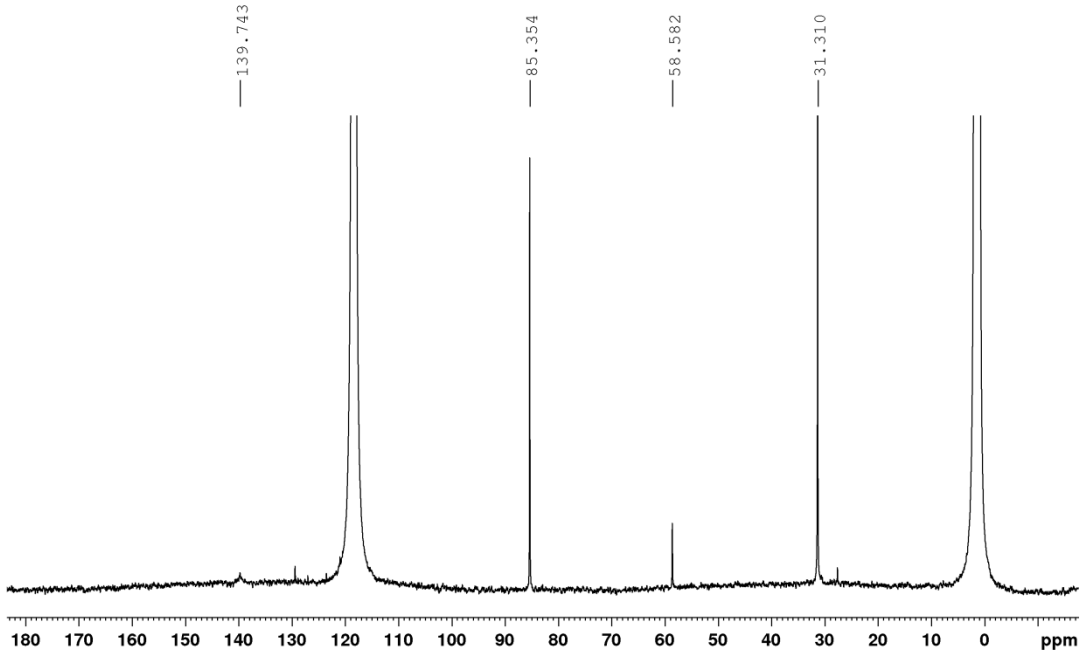

Figure 3.9.2: ^{13}C NMR of [Re(η^6-C_6H_6)(CN-^{t}Bu)$_3$](OTf) ([**9**](OTf))

3.10 [Re(η^6-napht)(tep)$_3$](PF$_6$) ([**11**](PF$_6$))

3.10.1 ^{1}H NMR

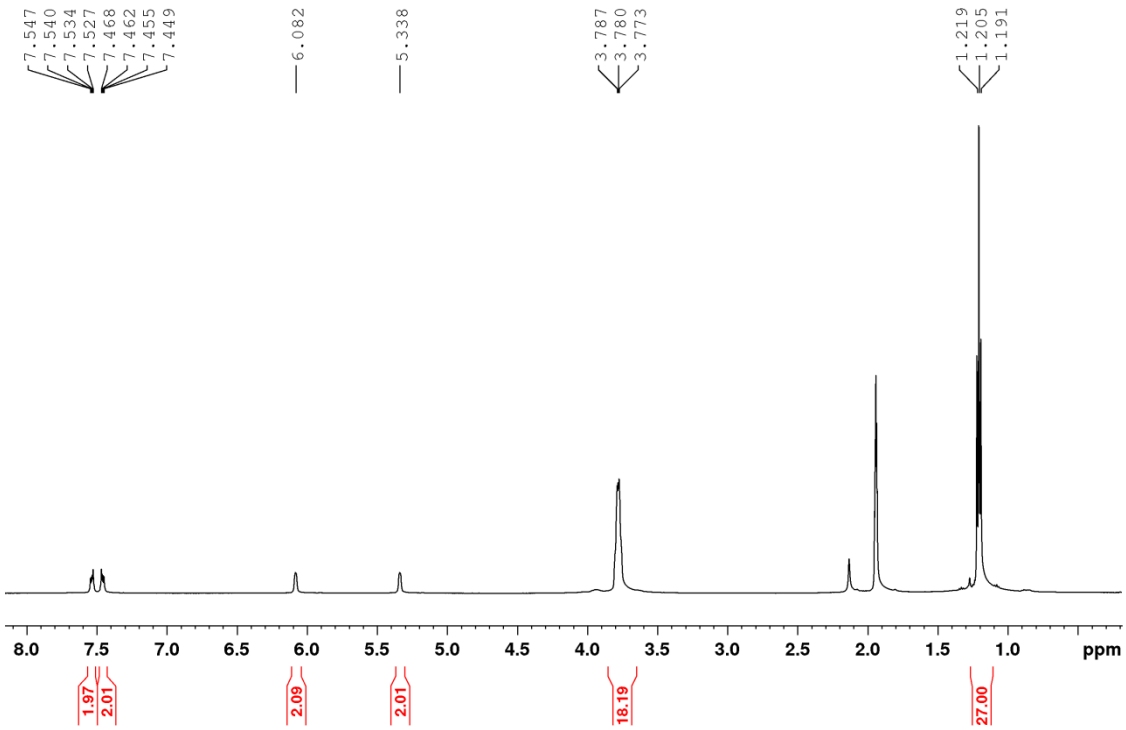

Figure 3.10.1: ^{1}H NMR of [Re(η^6-napht)(tep)$_3$](PF$_6$) ([**11**](PF$_6$))

3.10.2 ^{13}C NMR

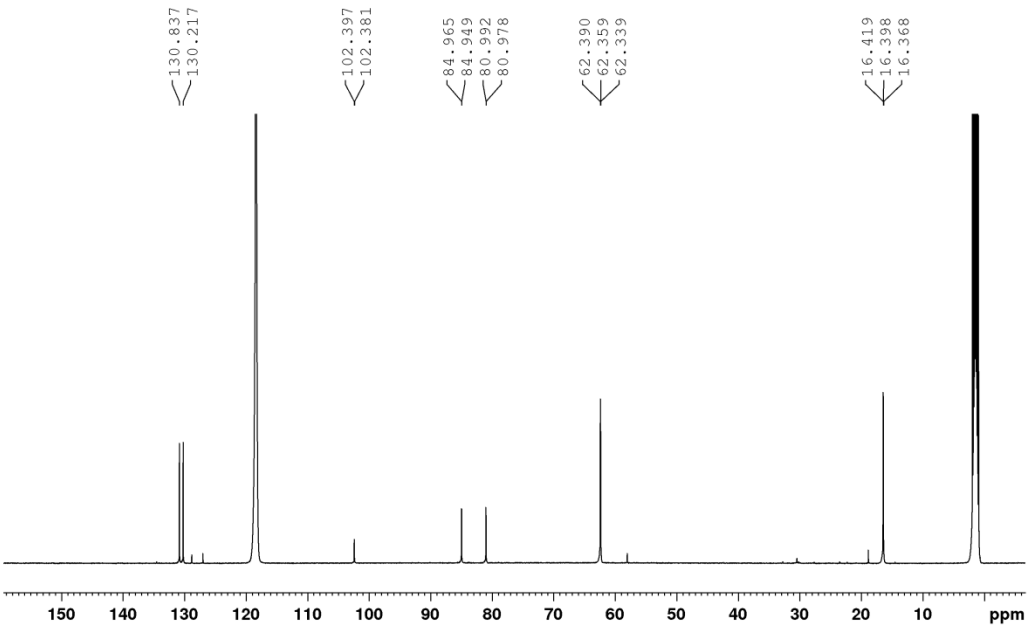

Figure 3.10.2: ^{13}C NMR of [Re(η^6-napht)(tep)$_3$](PF$_6$) ([**11**](PF$_6$))

3.11 [Re(η^6-napht)(triphos)](PF$_6$) ([**12**](PF$_6$))

3.11.1 ^{1}H NMR

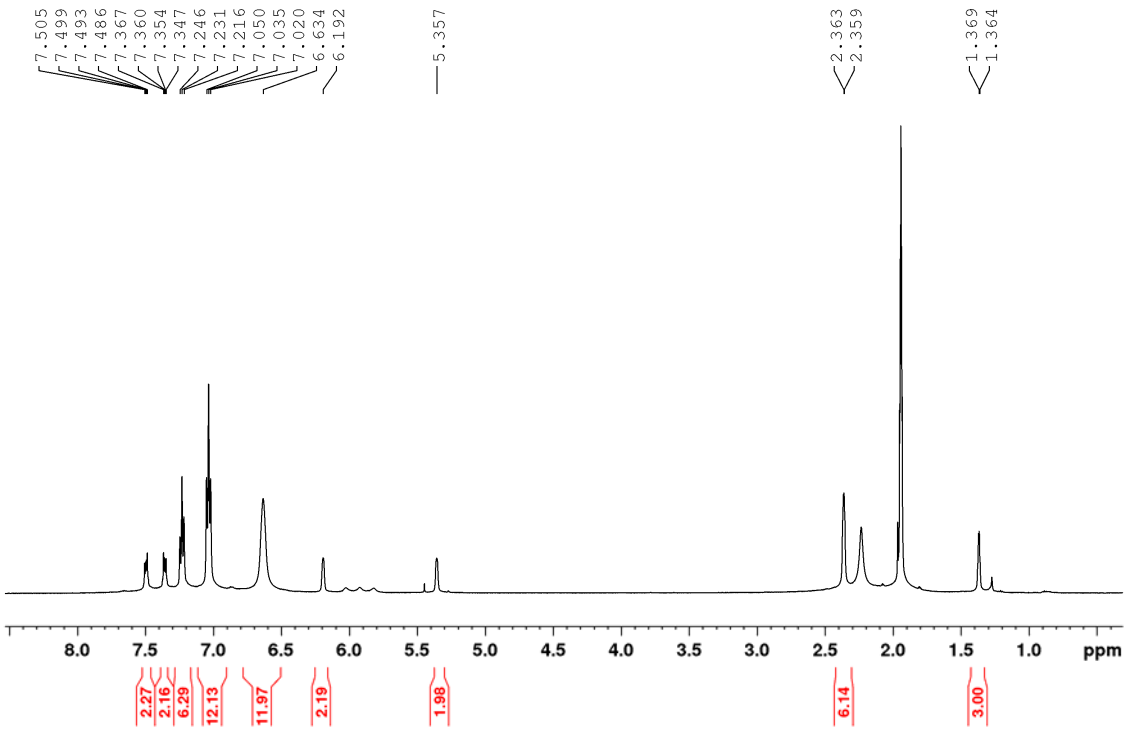

Figure 3.11.1: ^{1}H NMR of [Re(η^6-napht)(triphos)](PF$_6$) ([**12**](PF$_6$))

3.11.2 ^{13}C NMR

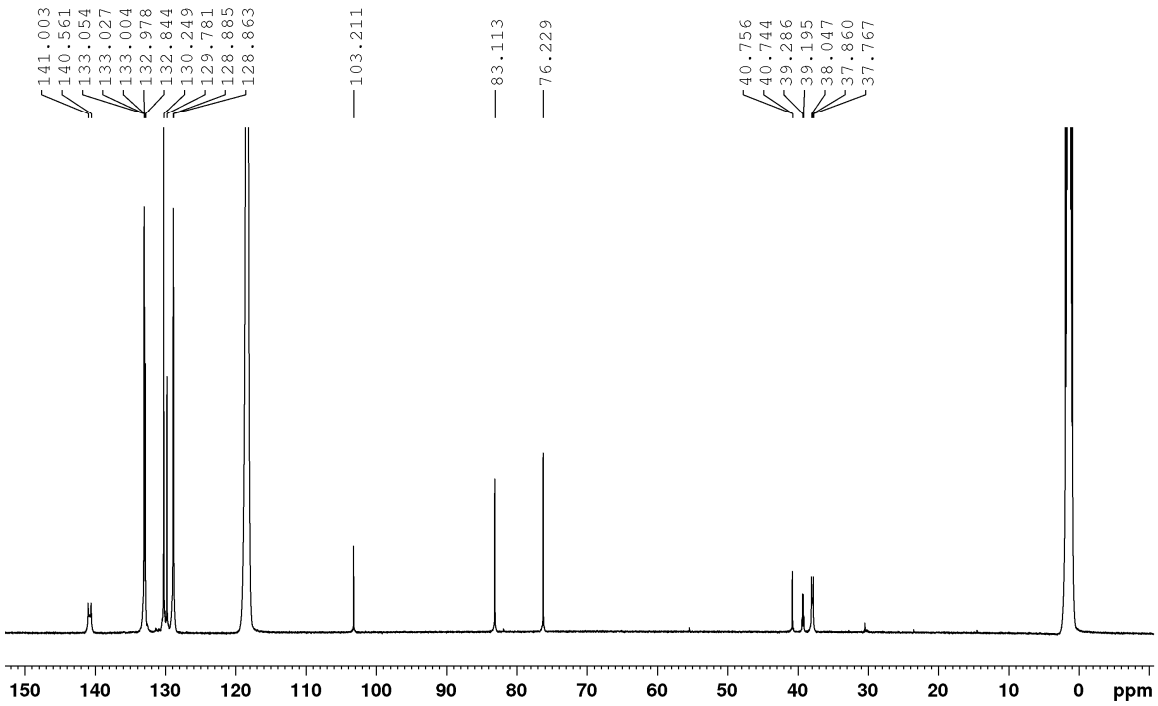

Figure 3.11.2: ^{13}C NMR of [Re(η^6-napht)(triphos)](PF_6) ([**12**](PF_6))

3.12 $[Re(CN\text{-}^tBu)_6](PF_6)$ ([**13**](PF_6))

3.12.1 ^1H NMR

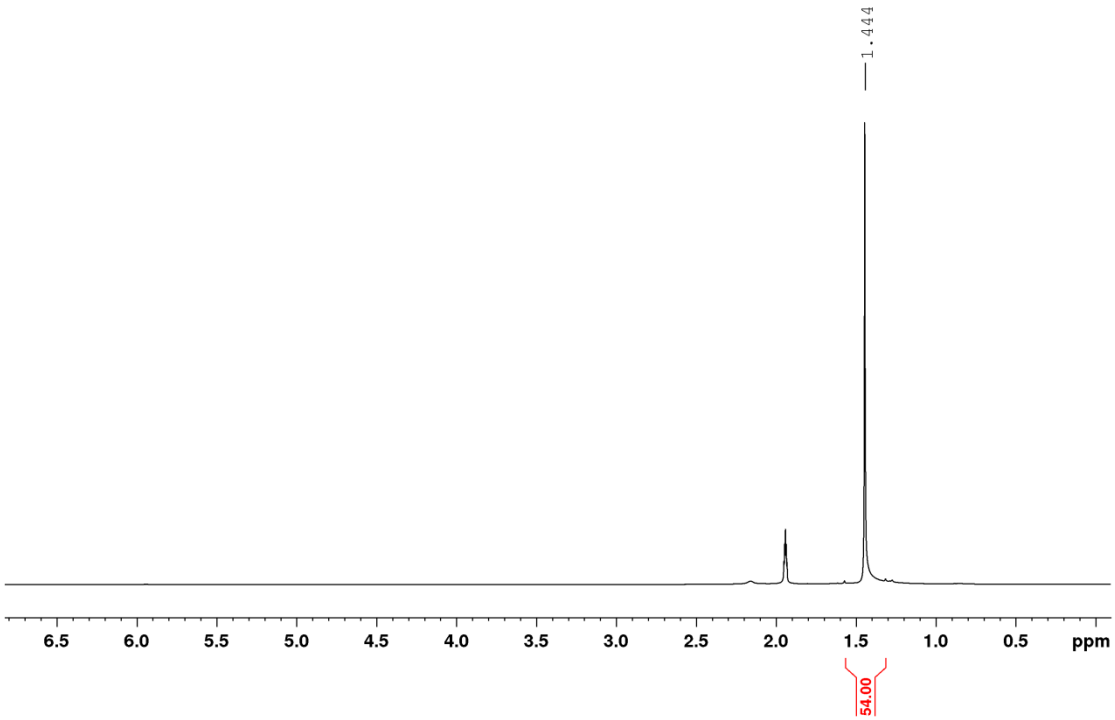

Figure 3.12.1: ^1H NMR of $[Re(\eta^6\text{-}C_6H_6)(tep)_3](OTf)$ ([**8**](OTf))

3.12.2 ^{13}C NMR

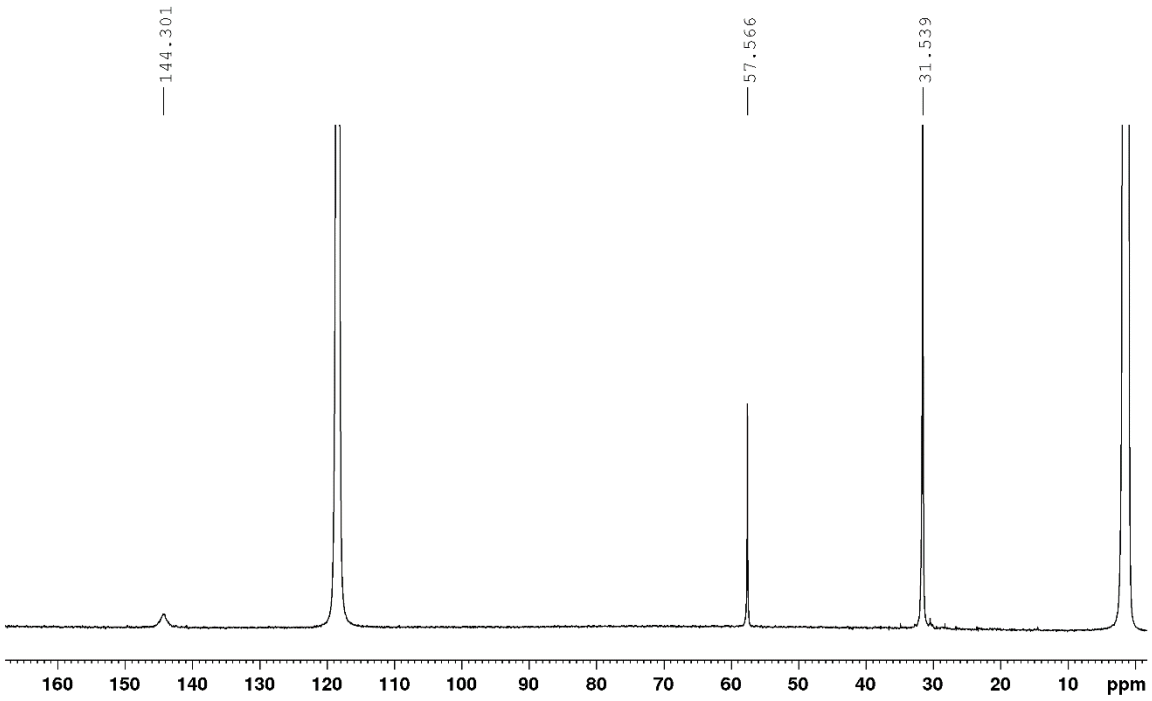

Figure 3.12.2: ^{13}C NMR of [Re(η^6-C_6H_6)(tep)$_3$](OTf) ([**8**](OTf))

4. Crystal Data

Crystallographic data were collected at 183(2) K. Compound [**1**](PF_6), [**5**]Cl, [**8**](OTf), [**12**](PF_6) were measured on an Rigaku OD XtaLAB Synergy Dualflex diffractometer with a Pilatus 200 K detector, compound [**3a**](PF_6), [**6**](OTf), [**9**](OTf), [**10**], [**11**](OTF) and [**13**](OTf) were measured on an Oxford Diffraction CCD Xcalibur system with a Ruby detector with either Mo K_α radiation (λ = 0.7107 Å) or Cu K_α radiation (λ = 1.54184 Å) that were graphite-monochromated. Suitable crystals were covered with oil (Infineum V8512, formerly known as Paratone N), placed on a nylon loop that is mounted in a CrystalCap Magnetic™ (Hampton Research) and immediately transferred to the diffractometer. The program suite CrysAlis^{Pro} was used for data collection, multi-scan absorption correction and data reduction.[5] The structure was solved with direct methods using SIR97[6] and was refined by full-matrix least-squares methods on F^2 with SHELXL-2014.[7] For some structures the GUI ShelXle was used.[8]

The structure of [**1**](PF_6) was refined as a 2-component perfect twin, with a twin ratio of about 70 : 30. The final SHELXL refinements were done on a HKLF5 file containing all component data including overlapped reflections. In the crystal structure of [**9**](OTf), in addition to the $(OTf)^-$ anion, ReO_4^- was found as counter ion (ration 90 : 10). In [**8**](OTf), one single high residual electron density was observed next to the rhenium atom. Maybe this was caused by the needed use of the copper radiation of this 5d-element containing structure.

Supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (CCDC nr. 1554159 - 1554161 and 155438 - 155443).

Name	**[^{99}Tc(η^6-hmbz)(η^6-C_6H_5-NH_2)](PF_6) [1](PF_6)**	**[^{99}Tc(η^6-hmbz)$_2$](PF_6) [3a](PF_6)**	**[^{99}Tc(η^6-pmbz)(η^6-C_6H_5-Br)]Cl [5]Cl**	**[Re(η^6-C_6H_6)(η^6-napht)](OTF) ([6](OTf))**
Empirical formula	$C_{18}H_{25}F_6NPTc$	$C_{24}H_{36}F_6PTc$	$C_{17}H_{21}BrTcCl$	$C_{18}H_{14}F_6LiO_6ReS_2$
Diffractometer	XtaLAB Synergy	Xcalibur Ruby	XtaLAB Synergy	Xcalibur Ruby
Wavelength (Å)	0.7107	0.7107	0.7107	0.71073
mol. weight (g/mol)	499.36	568.51	438.70	697.55
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	Cc	Pnnm	P-1	P1
a (Å)	8.1171(4)	8.1154(6)	7.0418(4)	9.0801(3)
b (Å)	15.7539(7)	10.4942(6)	9.2033(5)	10.7870(3)
c (Å)	15.0788(7)	13.6880(8)	12.4028(7)	11.5849(3)
α (°)	90	90	87.599(5)	104.912(2)
β (°)	91.370(4)	90	86.191(5)	98.624(2)
γ (°)	90	90	85.980(4)	91.639(2)
Volume (Å^3)	1927.67(16)	1165.73(13)	799.48(8)	1081.41(5)
Z	4	2	2	2
Dens.(calc.) (g/cm^3)	1.717	1.617	1.822	2.142
Abs. coeff. (mm^{-1})	0.89	0.74	3.55	5.897
F(000)	1008	584	436	668
Crystal size (mm^3)	0.21 × 0.07 × 0.04	0.12 × 0.10 × 0.08	0.23 × 0.19 × 0.01	0.360 x 0.210 x 0.070
Crystal description	yellow needle	yellow prism	yellow plate	yellow plate
θ range (°)	2.5–31.0	2.9–31.1	2.8–29.9	2.274-35.022
Index ranges	-10<=h<=10, -19<=k<=19,	-11<=h<=11, -14<=k<=14,	-9<=h<=9, -12<=k<=12,	-14<=h<=14, -17<=k<=17,
	-18<=l<=18	-19<=l<=19	-16<=l<=16	-18<=l<=18
Refl. collected	21006	7912	8837	34421
Indep. reflections	21006	1853	3914	17403 [R(int) = 0.0427]
Reflections obs.	20410	1390	3075	15889
Criterion for obs.	>2sigma(I)	>2sigma(I)	>2sigma(I)	I > 2(I)
Completeness to θ	99% to 25.24°	100% to 30.49°	99% to 28.28°	99.5 % to 33.07°
Absorption corr.	analytical	analytical	analytical	Semi-empirical from equivalents
Max. and min. transm.	0.871, 0.969	0.942 and 0.914	0.495 and 0.986	1.00000 and 0.41615
Data / restraints / param.	21006 / 2 / 250	1853 / 0 / 81	3914 / 0 / 186	17403 / 3 / 613
Goodness-of-fit on F^2	1.06	1.10	1.04	1.021
Fin. R ind. [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1344	R1 = 0.0355, wR2 = 0.0769	R1 = 0.0428, wR2 = 0.0992	R1 = 0.0372, wR2 = 0.0759
R indices (all data)	R1 = 0.0508, wR2 = 0.1356	R1 = 0.0545, wR2 = 0.0846	R1 = 0.0601, wR2 = 0.1043	R1 = 0.0424, wR2 = 0.0806
Fin. diff. ρ_{max} (e^-/Å^{-3})	0.51 and -0.56	0.43 and -0.47	1.50 and -0.85	1.219 and -1.488
CCDC Nr.	1554160	1554161	1554159	1554400

Name	**[Re(η⁶-C₆H₆)(tep)₃](OTF) ([8](OTf))**	**[Re(η⁶-C₆H₆)(CN-ᵗBu)₃](OTF) ([9](OTf))**	**[Re(η⁶-C₆H₆)(HB(pyz)₃)] (10)**	**[Re(η⁶-napht)(tep)₃](OTF) ([11](OTF))**
Empirical formula	$C_{25}H_{50}F_3O_{12}P_3ReS$	$C_{21.90}H_{33}F_{2.70}N_3O_{3.10}Re_{1.10}S_{0.90}$	$C_{15}H_{16}BN_6Re$	$C_{29}H_{53}F_3O_{12}P_3ReS$
Diffractometer	XtaLAB Synergy	Xcalibur Ruby	Xcalibur Ruby	Xcalibur Ruby
Wavelength (Å)	1.54184	0.71073	0.71073	0.71073
mol. weight (g/mol)	910.82	672.89	477.35	961.88
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	I2/a	P-1	P21/m	P-1
a (Å)	16.22709(11)	9.7977(5)	8.2517(4)	10.4629(3)
b (Å)	15.78790(12)	10.9136(7)	10.2422(6)	12.2103(3)
c (Å)	30.1873(3)	13.8305(6)	8.9263(5)	15.7908(4)
α (°)	90	104.511(5)	90	97.165(2)
β (°)	101.4536(8)	109.525(4)	92.507(5)	102.359(2)
γ (°)	90	93.636(5)	90	94.246(2)
Volume (Å^3)	7579.73(10)	1331.70(12)	753.69(7)	1944.62(8)
Z	8	2	2	2
Dens.(calc.) (g/cm^3)	1.596	1.678	2.103	1.643
Abs. coeff. (mm^{-1})	8.574	5.130	8.069	3.371
F(000)	3672	663	456	972
Crystal size (mm^3)	0.120 x 0.110 x 0.040	0.300 x 0.180 x 0.130	0.120 x 0.050 x 0.040	0.570 x 0.260 x 0.170
Crystal description	colorless block	colorless block	yellow prism	yellow block
θ range (°)	3.173-78.974	2.153-36.318	2.284-32.874	2.483-33.380
Index ranges	-20<=h<=20, -19<=k<=20,	-16<=h<=16, -18<=k<=18,	-11<=h<=12, -15<=k<=15,	-13<=h<=14, -17<=k<=17,
	-30<=l<=38	-23<=l<=23	-13<=l<=13	-23<=l<=23
Refl. collected	41327	55166	9097	42674
Indep. reflections	8073 [R(int) = 0.0472]	12802 [R(int) = 0.0457]	2736 [R(int) = 0.0692]	13377 [R(int) = 0.0423]
Reflections obs.	7249	11886	2473	11837
Criterion for obs.	I > 2(I)	I > 2(I)	I > 2(I)	I > 2(I)
Completeness to θ	100.0 % to 67.684°	99.1 % to 36.23°	100.0 % to 26.32°	99.7 % to 30.44°
Absorption corr.	Gaussian	Semi-empirical from equivalents	Analytical	Semi-empirical from equivalents
Max. and min. transm.	1.000 and 0.458	1.00000 and 0.57410	0.831 and 0.538	1.00000 and 0.38979
Data / restraints / param.	8073 / 87 / 484	12802 / 0 / 316	2736 / 0 / 120	13377 / 0 / 451
Goodness-of-fit on F^2	1.051	1.058	1.051	1.058
Fin. R ind. [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1724	R1 = 0.0257, wR2 = 0.0662	R1 = 0.0344, wR2 = 0.0691	R1 = 0.0315, wR2 = 0.0715
R indices (all data)	R1 = 0.0598, wR2 = 0.1765	R1 = 0.0287, wR2 = 0.0683	R1 = 0.0398, wR2 = 0.0722	R1 = 0.0401, wR2 = 0.0769
Fin. diff. ρ_{max} (e$^-$/Å^{-3})	4.771 and -2.578	1.550 and -1.758	2.324 and -2.491	1.617 and -1.161
CCDC Nr.	1554399	1554398	1554397	1554401

Name	**[Re(η^6-napht)(triphos)](PF$_6$) ([12](PF$_6$))**	**[Re(CN-^{t}Bu)$_6$](OTF) ([13](OTf))**
Empirical formula	$C_{52}H_{49}Cl_2F_6P_4Re$	$C_{33}H_{54}F_9Li_2N_6O_{11}ReS_3$
Diffractometer	XtaLAB Synergy	Xcalibur Ruby
Wavelength (Å)	1.54184	0.71073
mol. weight (g/mol)	1168.89	1178.08
Crystal system	Orthorhombic	Triclinic
Space group	P212121	P-1
a (Å)	11.00550(4)	10.191(2)
b (Å)	18.56730(7)	17.740(3)
c (Å)	24.45640(9)	17.909(4)
α (°)	90	117.46(2)
β (°)	90	102.485(19)
γ (°)	90	93.314(16)
Volume (Å^3)	4997.48(3)	2758.0(11)
Z	4	2
Dens.(calc.) (g/cm^3)	1.554	1.419
Abs. coeff. (mm^{-1})	7.435	2.397
F(000)	2336	1184
Crystal size (mm^3)	0.190 x 0.060 x 0.040	0.540 x 0.250 x 0.190
Crystal description	red prism	colorless prism
θ range (°)	2.988-79.687	2.251-30.508
Index ranges	-13<=h<=13, -23<=k<=23,	-14<=h<=11, -25<=k<=25,
	-30<=l<=30	-23<=l<=25
Refl. collected	57867	40102
Indep. reflections	10772 [R(int) = 0.0330]	16824 [R(int) = 0.0387]
Reflections obs.	10651	13188
Criterion for obs.	I > 2(I)	I > 2(I)
Completeness to θ	100.0 % to 67.684°	99.7 % to 30.44°
Absorption corr.	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transm.	1.00000 and 0.73035	1.00000 and 0.56980
Data / restraints / param.	10772 / 0 / 587	16824 / 0 / 604
Goodness-of-fit on F^2	1.067	1.046
Fin. R ind. [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0828	R1 = 0.0419, wR2 = 0.1002
R indices (all data)	R1 = 0.0325, wR2 = 0.0830	R1 = 0.0586, wR2 = 0.1114
Fin. diff. ρ_{max} (e$^-$/Å^{-3})	1.154 and -0.807	1.332 and -1.682
CCDC Nr.	1554402	1554403

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