Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Sulfonium cations as versatile strongly π-acidic ligands

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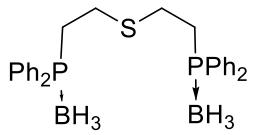
1. Synthetic procedures and characterization

1.1. General information

All air sensitive reactions were carried out under an atmosphere of purified nitrogen in a glovebox equipped with an inert gas purifier. Tetrahydrofuran (THF), acetonitrile (MeCN), diethyl ether (E_2O), dichloromethane (DCM), toluene, and MeOH were purified by passing through a column of activated alumina under inert atmosphere. Divinyl sulfide,[1] diphenylphosphine,[2] bis(2-bromophenyl)sulfide,[3] bis(2-fluorophenyl)iodonium trifluoromethanesulfonate,[4] bis(diphenyl)phosphanylethylene sulfoxide (PS(O)P)[5] were prepared according to the literature procedures. $Pt(COD)Me_2$ and $[Rh(COE)_2Cl]_2$ were purchased from STREM Chemicals and used without further purification. Anhydrous hexane, N,N-dimethylformamide (DMF), dichloroethane (DCE) and dimethyl sulfoxide (DMSO) packed under inert gas over molecular sieves were used as purchased. All chromatographic purifications were performed on CombiFlash EZ-Prep and SiO_2 columns. In particular, this allowed fast purification of phosphine-containing ligands under air without noticeable oxidation. The microwave reaction was carried out in a Monowave 200 (Anton Paar, Austria) reactor. NMR spectra were recorded on Bruker Avance 400 or Bruker Avance 500 spectrometers at 296K. Residual solvent peaks were used as internal standards for ^1H and ^{13}C respectively ($CDCl_3$: δ 7.26/77.0 ppm; CD_2Cl_2: δ 5.31/53.8 ppm, CD_3OD: δ 3.31/47.7 ppm, CD_3NO_2: δ 4.33/62.8 ppm, and $C_2D_2Cl_4$: δ 5.94/74.4 ppm). ^{31}P NMR and ^{31}F NMR signals were referenced to internal standards (capillary) of 85% H_3PO_4 (δ 0.00 ppm) and neat C_6F_6 (δ -164.9 ppm). ^{103}Rh and ^{195}Pt signals were referenced using Ξ values of 0.03186447 and 0.21496784, respectively, using the IUPAC recommendations.[6] NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, v = virtual), coupling constant(s), and integration. High resolution mass spectra (HRMS) were recorded on HR Q-TOF-MS mass instrument, using an electrospray ionization (ESI+) technique (MeCN/H_2O 80%, flow: 0.2 ml/min). All reactions involved in the preparation of sulfonium complexes were performed in degassed dry solvents under the atmosphere of purified nitrogen inside a glovebox, unless specified otherwise.

1.2. Synthetic procedures for the preparation of sulfonium ligands

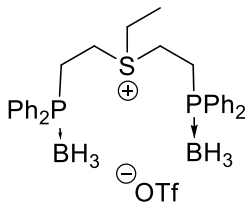
*Bis-diphenyl-phosphanylethylene sulfide bis-borane complex (**2a**)*



First bis-diphenyl-phosphanylethylene sulfide (**1a**) was prepared by a radical-catalyzed addition of diphenylphosphine to divinyl sulfide by an adapted literature procedure, as follows.1 Diphenylphosphine (35 mmol, 6.1 mL), divinyl sulfide (14 mmol, 1.3 mL) and AIBN (0.18 mmol, 30 mg) were added to a Schlenk tube under nitrogen atmosphere. The tube was sealed, and the reaction mixture was heated at 120°C for 1.5h, then exposed to vacuum at that temperature for another 1.5 h. The obtained crude **1a** was cooled down to room temperature and treated with 1.0 M BH_3 solution in THF (35 mmol, 35 ml) which resulted in precipitation of a white solid. This was collected by filtration, washed three times with ether and dried, affording **2a** in a quantitative yield.

^1H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.68 (m, 20H, P*Ph*$_2$) ppm, 2.62-2.67 (m, 4H, P*CH*$_2$), 2.39-2.45 (m, 4H, *CH*$_2$S), 0.61-1.35 (br, 6H, 2B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 132.3 (d, $^3J_{CP}$ = 9.1Hz, meta-C, Ph), 131.7 (d, $^4J_{CP}$ = 2.3 Hz, para-C, Ph), 129.3 (d, $^2J_{CP}$ = 10.1 Hz, ortho-C, Ph), 128.7 ($^1J_{CP}$ = 32.4 Hz, ipso-C, Ph), 26.4 (d, $^1J_{CP}$ = 32.4 Hz, *C*H$_2$P), 25.0 (d, $^2J_{CP}$ = 2.1 Hz, *C*H$_2$S) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.5 ppm. HRMS: calcd. for $C_{28}H_{33}B_2P_2S^+(M+H)^+$: 485.1959; found 485.1969.

*Bis-diphenyl-phosphanylethylene (ethyl) sulfonium trifluoromethanesulfonate bis-borane complex (**3a**[OTf])*

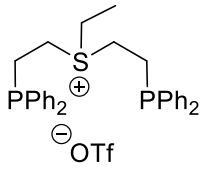


Ethyl triflate (156 µl, 1.2 mmol) and **2a** (389 mg, 0.8 mmol) were dissolved in 6 mL DCM and heated to 50 °C in a sealed Schlenk tube under nitrogen atmosphere for 2 days. All volatiles were removed under reduced pressure, forming **3a**[OTf] as a white foam. The product was purified by a silica gel column chromatography (MeOH/DCM, 3:97) resulting in 240 mg of the product (52% yield).

^1H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.81 (m, 20H, P*Ph*$_2$), 3.35-3.43 (m, S*CH*$_2$, 4H and S*CH*$_2$CH$_3$, 2H), 2.83-2.89 (m, 2H, P*CH*$_2$), 2.64-2.72 (m, 2H, P*CH*$_2$), 1.33 (t, SCH$_2$*CH*$_3$, 3H, $^3J_{HH}$ = 7.4Hz), 0.53-1.22 (br q, 6H, 2*BH*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 132.2-132.4 (*meta*-C and *para*-C, Ph), 129.4 (dd, $^2J_{CP}$ = 5.1 Hz, *ortho*-C, Ph), 126.4

(dd, $^{1}J_{CP}$ = 51.6 Hz, *ipso*-C, Ph), 34.0-34.2 (S*C*H$_2$CH$_3$ and S*C*H$_2$), 20.8 (d, $^{1}J_{CP}$ = 34.5 Hz, P*C*H$_2$), 8.3 (SCH$_2$*C*H$_3$) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 16.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -78.2 ppm. HRMS: calcd. for $C_{30}H_{39}B_2P_2S^+$ $(M)^+$: 515.2428; found 515.2431.

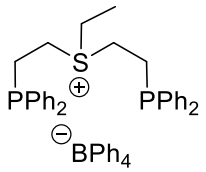
*Bis-diphenyl-phosphanylethylene(ethyl)sulfonium trifluoromethanesulfonate (**4a**[OTf])*



3a[OTf] (240 mg, 0.36 mmol) was dissolved in 5 mL of MeOH and heated to 80°C in a sealed Schlenk tube under nitrogen atmosphere for 4h. The solvent was removed, and the residue was washed with ether, forming **4a**[OTf] as a white foam. Quantitative yield.

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.37-7.40 (m, 20H, P*Ph*$_2$), 3.28-3.40 (m, S*CH*$_2$CH$_3$, 2H and S*CH*$_2$, 4H), 2.39-2.43 (m, *CH*$_2$P, 4H), 1.28 (t, SCH$_2$*CH*$_3$, 3H, $^{3}J_{HH}$ = 7.6 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 135.9 (d, $^{3}J_{CP}$ = 12.5Hz, *ipso*-C, Ph), 133.3 (d, $^{4}J_{CP}$ = 19.5 Hz, *meta*-C, Ph), 130.4 (d, $^{2}J_{CP}$ = 2.7 Hz, *para*-C, Ph), 129.6 (d, $^{1}J_{CP}$ = 7.0 Hz, *ortho*-C, Ph), 37.2 (d, $^{2}J_{CP}$ = 24.1 Hz, *C*H$_2$S), 34.9 (S*C*H$_2$CH$_3$), 23.3 (d, $^{1}J_{PC}$ = 19.0 Hz, P*C*H$_2$), 9.4 (SCH$_2$*C*H$_3$) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) δ = -18.2 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2) δ = -78.2 ppm. HRMS: calcd. for $C_{30}H_{33}P_2S^+$ $(M)^+$: 487.1773; found 487.1793.

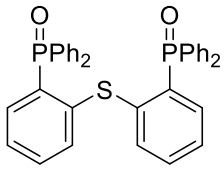
*Bis-diphenyl-phosphanylethylene(ethyl)sulfonium tetraphenylborate (**4a**[BPh$_4$])*



3a[OTf] (240 mg, 0.36 mmol) was dissolved in 5 mL of MeOH and heated to 80°C in a sealed Schlenk tube under nitrogen atmosphere for 4h. After the solution cooled down to room temperature, sodium tetraphenylborate (200 mg, 0.58 mmol) was added, forming a white precipitate immediately. The precipitate was collected by filtration through a cotton plug and consecutively washed with MeOH and ether, resulting in 280 mg (0.35 mmol, 96.4%) of **4a**[BPh$_4$]. XRD quality single crystals were grown by slow evaporation of a DCM solution of **4a**[BPh$_4$] at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39-6.79 (m, 20H (B*Ph*$_4$) + 20H (P*Ph*$_2$)), 2.11-2.16 (m, 4H, *CH*$_2$S), 1.82-1.85 (m, 4H, *CH*$_2$P), 1.44-1.49 (q, S*CH*$_2$CH$_3$, 2H, $^{3}J_{HH}$ = 7.4 Hz), 0.63 (t, SCH$_2$*CH*$_3$, 3H, $^{3}J_{HH}$ = 7.4 Hz) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.9-163.8 (*ipso*-C, B*Ph*$_4$), 136.3 (B*Ph*$_4$), 135.0 (*ipso*-C, PPh$_2$), 132.8 (d, $^{4}J_{CP}$ = 18.2 Hz, *meta*-C, P*Ph*), 130.3 (d, $^{2}J_{CP}$ = 2.5 Hz, *para*-C, *Ph*), 129.4 (d, $^{1}J_{CP}$ = 6.8 Hz, *ortho*-C, Ph), 126.1 (B*Ph*$_4$), 122.2 (B*Ph*$_4$), 36.3 (d, $^{2}J_{PC}$ = 22.9 Hz, *C*H$_2$S), 33.5 (S*C*H$_2$CH$_3$), 23.0 (d, $^{1}J_{PC}$ = 18.3 Hz, *C*H$_2$P), 9.1 (SCH$_2$*C*H$_3$) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ = -18.1 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = -6.5 ppm. HRMS: calcd. for $C_{30}H_{33}P_2S^+$ $(M)^+$: 487.1773; found 487.1776.

*1,1'-(Thiodi-2,1-phenylene)bis[1,1-diphenylphosphine oxide] (**2b**)*

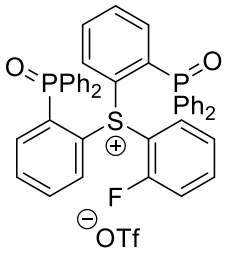


First 1,1'-(Thiodi-2,1-phenylene)bis[1,1-diphenylphosphine] (**1b**) was prepared from bis(2-bromophenyl) sulfide by adapted literature procedures,[7] as follows. In a dry 3-neck Schlenk flask under inert gas 2.5 g (7.26 mmol) of bis(2-bromophenyl) sulfide[3] was added, vacuum was applied, and the flask was purged with inert gas again. 45 ml of dry THF and 7.61 ml (50.7 mmol 7 eq.) of anhydrous TMEDA was added, and the solution was cooled to -78°C. Subsequently, 9.54 ml of n-BuLi (1.6M, 15.26 mmol, 2.1 eq.) were added dropwise which resulting in the solution turning light yellow. After stirring for additional 40 minutes 2.74 ml of ClPPh$_2$ (15.26 mmol, 2.1 eq.) were added dropwise, and the solution was allowed to stir for 30 minutes at -78°C and afterwards for additional 2 hours at RT. Completion of the reaction was established by ^{31}P-NMR. The reaction solution was then diluted with 150 ml of degassed DCM and washed with 100 ml of degassed H_2O in a 500ml separatory funnel. The organic layer was collected, dried over Na_2SO_4, filtered, and all volatiles were removed in vacuo resulting in a yellow-brown crude **1b**. This was then purified by flash-chromatography on silica-gel eluting with $CHCl_3$/Hexane (15:85%) mixture affording 2.12 g of pure **1b** as white foam (53% yield). ^{1}H NMR (400MHz, $CDCl_3$) 7.25-7.18 (m, 12H), 7.17-7.12 (m, 8H), 7.11-7.06 (m, 2H), 7.04-6.99 (m, 4H), 6.78-6.74 (m, 2H). ^{31}P NMR (400MHz, $CDCl_3$) -12.45ppm.

In a round bottom flask, **1b** (3.0 g, 5.41 mmol) was dissolved in 85 ml of MeCN. Benzoyl peroxide (3.28 g, 2.5 eq.) was added gradually to the solution and the reaction was stirred for 30 min. The reaction completion was established by ^{31}P NMR. The solvent was removed in vacuo resulting in a yellow-brown oil. The crude product was then purified by automatic flash chromatography on silica-gel eluting with MeOH/DCM (12:88%) mixture to afford the product as white foam (3.18 g, quantitative yield).

^{1}H NMR (500 MHz, $CDCl_3$): 7.70-7.64 (m, 2H), 7.63-7.57 (m, 8H), 7.47-7.40 (m, 4H), 7.39-7.31 (m, 8H), 7.25-7.18 (m, 2H), 6.83-6.79 (m, 2H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): 28.9 (s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 140.93 (d, *J* = 6.7 Hz), 134.39 (d, *J* = 9.6 Hz), 133.83 (d, *J* = 8.0 Hz), 132.66 (s), 132.03 (d, *J* = 9.5 Hz), 131.6 (s), 131.3 (s), 129.8 (s), 128.2 (d, *J* = 12 Hz), 126.8 (d, *J* = 11.0 Hz) ppm. HRMS: calcd. for $C_{36}H_{29}O_2P_2S^+$ $(M+H)^+$: 587.1363; found 587.1510.

*Bis(2-(diphenylphosphoryl)phenyl)(2-fluorophenyl)sulfonium trifluoromethanesulfonate (**3b**[OTf])*

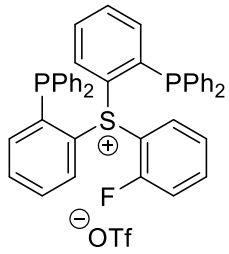


Compound **3b**[OTf] was prepared by an adapted literature procedure.[8] An oven-dried 10 ml microwave tube was loaded under an inert atmosphere with **2b** (800 mg, 1.364 mmol), bis-(2-fluorophenyl)iodonium triflate (1.59 g, 2 eq.), copper(II) benzoate (33.4 mg, 0.08 eq.) and 8 ml of degassed chlorobenzene. The tube was sealed and placed inside a Monowave 200 reactor, where it was heated with stirring to 125 °C for 2.5h. The solvent was then removed in vacuo and the residue was extracted into MeCN. The obtained MeCN solution was washed with hexane, the hexane phase was discarded, while the MeCN phase was evaporated, affording the crude product as a brown-yellow oil. This was then purified by an automatic flash chromatography on silica-gel eluting with an Acetone/$CHCl_3$ (35-55:65-45%) to afford the pure product as a beige-colored foam (0.86 g, 76% yield). Crystals suitable for XRD were grown by layer diffusion of hexane into a concentrated DCM solution.

Due to dynamic equilibrium that resulting a significant peak broadening at r.t., multinuclear NMR measurements of **3b**[OTf] were all performed at 98.5±1.00 °C.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 98.5°C): 7.84-7.76 (m, 4H), 7.68-7.60 (m, 8H), 7.59-7.50 (m, 7H), 7.50-7.39 (m, 8H), 7.34-7.29 (m, 2H), 7.29-7.20 (m, 2H), 6.98 (bt, 1H, *J* = 7.0 Hz) ppm. ^{31}P NMR (202.4 MHz, $C_2D_2Cl_4$, 98.5°C): 28.6 (s) ppm. ^{13}C NMR (125.8 MHz, $C_2D_2Cl_4$): 160.4 (d, *Ar*F, *J* = 257.5 Hz), 136.8 (d, *J* = 8.2 Hz), 136.1 (d, *J* = 10 Hz), 134.8 (s), 133.8 (d, *J* = 10.5 Hz), 133.5 (d, *J* = 2.7 Hz), 133.4 (d, *J* = 2.7 Hz), 133.2-133.1 (m), 132.7 (d, *J* = 10.5 Hz), 132.4 (d, *J* = 10.0 Hz), 132.3 (d, *J* = 8.0 Hz), 132.1 (d, *J* = 10.3 Hz), 131.1 (s), 130.2 (s), 129.4 (d, *J* = 4.4 Hz), 129.3 (d, *J* = 4.4 Hz), 126.9 (d, *J* = 3.3 Hz), 121.5 (q, *OTf*, *J* = 322.5 Hz), 118.2 (d, *J* = 19.5 Hz), 116.7 (d, *J* = 15.0 Hz) ppm. ^{19}F NMR (470.6 MHz, $C_2D_2Cl_4$, 98.5°C): -76.9 (s, *OTf*, 3F), -104.4 (q, *ArF*, 1F, *J* = 6.7 Hz) ppm. HRMS: calcd. For $C_{42}H_{32}FO_2P_2S_2^+$ $(M)^+$: 681.1571; found 681.1551.

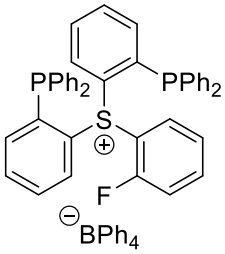
*Bis(2-(diphenylphosphaneyl)phenyl)(2-fluorophenyl)sulfonium trifluoromethanesulfonate (**4b**[OTf])*



Compound **4b**[OTf] was prepared by an adapted literature procedure.[9] Compound **3b**[OTf] (1.675 g, 2.016 mmol) was charged into an oven dried Schlenk tube and suspended in 60 ml of 1:2 DCE/Toluene mixture under nitrogen atmosphere. Then 54 µL (0.3 eq.) of triflic acid were added and the reaction mixture was stirred for 10 minutes. Next, 4.00 ml (16 eq.) of $PhSiH_3$ were added, the tube was sealed and placed in a pre-heated oil bath at 85 °C. During the reaction, the suspension turned into a clear pale-yellow solution. The reaction progress was monitored by ^{31}P NMR which showed a complete conversion after 40 h. The solvents were evaporated, affording the crude product as a yellow oil. This was then purified by automatic flash chromatography on silica-gel eluting with Acetone/$CHCl_3$ (35-55:65-45%) affording the product as a white foam (0.86 g, 88% yield). Crystals suitable for XRD were grown by layer diffusion of hexane into a concentrated DCM solution.

^{1}H NMR (500 MHz, $CDCl_3$) 7.68 (dt, 2H, *J* = 7.7, 1.4 Hz), 7.59 (dt, 2H, *J* = 7.5, 1.0 Hz), 7.58-7.53 (m, 1H), 7.48 (dd, 2H, *J* = 8.3, 2.7 Hz), 7.37-7.32 (m, 3H), 7.32-7.28 (m, 6H), 7.28-7.21 (m, 8H), 7.15-7.07 (m, 8H) ppm. ^{31}P NMR (202MHz, $CDCl_3$): -13.0 (s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 160.4 (d, ArF, J = 257.0 Hz), 141.9 (d, J = 17.5 Hz), 137.8 (d, J = 8.5 Hz), 137.3 (s), 135.0 (s), 134.1 (d, *J* = 14 Hz), 133.9 (d, *J* = 14 Hz), 133.0 (s), 132.9 (s), 132.8 (d, *J* = 5.5 Hz), 132.4 (d, *J* = 5.5 Hz) 132.1 (t, *J* = 3.2 Hz), 130.4 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 3.3 Hz), 129.3 (d, *J* = 3.3 Hz), 127.6 (d, *J* = 3.2 Hz), 121.4 (q, OTf, *J* = 321.0 Hz), 118.3 (d, *J* = 19.5 Hz), 111.1 (dt, *J* = 7.6 Hz) ppm.^{19}F NMR (376 MHz, $CDCl_3$): -76.5 (s, OTf), -105.3 (br s, ArF) ppm. HRMS: calcd. For $C_{42}H_{32}FP_2S^+$ $(M)^+$: 649.1678; found 649.1684.

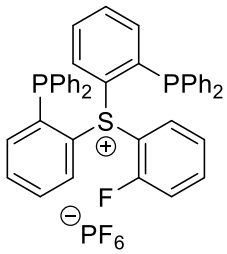
*Bis(2-(diphenylphosphaneyl)phenyl)(2-fluorophenyl)sulfonium tetraphenylborate (**4b**[BPh_4])*



Compound **4b**[OTf] (150 mg, 0.19 mmol) was dissolved in 2.0 ml of MeOH. Separately, sodium tetraphenylborate (64.3 mg, 1.0 eq.) was dissolved in additional 2.0 ml of MeOH and added to the solution of **4b**[OTf]. Immediately a white precipitate formed, and this suspension was then stirred for additional 15-20 minutes. The precipitate was then filtered out, and washed several times with MeOH, affording 160 mg of the product, as a white powder (88% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) 7.61 (t, 2H, *J* = 7.5 Hz), 7.58-7.53 (m, 1H), 7.42-7.36 (m, 6H), 7.35-7.32 (m, 5H), 7.31-7.25 (m, 14H), 7.20 (t, 1H, *J* = 9.0 Hz), 7.18-7.09 (m, 8H), 7.03 (t, 1H, *J* = 7.7 Hz), 6.98 (t, 10H, *J* = 7.3 Hz), 6.84 (tt, BPh_4, 4H, *J* = 7.2, 1.3 Hz), 6.72 (t, 1H, *J* = 7.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) -13.1 (s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 164.2 (q, BPh_4, J_{CB} = 49.7), 159.7 (d, ArF, *J* = 257.0 Hz), 141.3 (d, *J* = 18.0 Hz), 137.3 (d, *J* = 8.5 Hz), 136.8 (s), 136.3 (d, BPh_4, *J* = 1.3 Hz), 134.6 (s), 133.7 (d, *J* = 14.8 Hz), 133.5 (d, *J* = 14.8 Hz), 132.9 (s), 132.3-132.2 (m), 132.0 (d, *J* = 6.5 Hz), 131.4 (t, *J* = 3 Hz), 130.1 (d, *J* = 1.5 Hz), 129.1 (q, *J* = 3.7 Hz), 128.8 (d, *J* = 5.6 Hz), 127.5 (d, *J* = 3.0 Hz), 125.4 (q, BPh_4, *J* = 2.7 Hz), 121.6 (s, BPh_4), 117.7 (d, *J* = 19.3 Hz), 110.6 (m, *J* = 7.2 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) -104.3 (q, ArF, *J* = 6.7 Hz) ppm. ^{19}F{H} NMR (376 MHz, $CDCl_3$) -104.3 (s, ArF) ppm.

*Bis(2-(diphenylphosphaneyl)phenyl)(2-fluorophenyl)sulfonium hexafluorophosphate (**4b**[PF_6])*

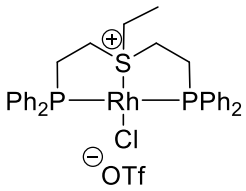


Compound **4b**[BPh_4] (40 mg, 41.3 μmol) was dissolved in 2.3 ml of MeCN. In another vial, $TlPF_6$ (14.4 mg, 1.0 eq.) was dissolved in additional 2.3 ml of MeCN and added to the vial containing the solution of **4b**[BPh_4]. Immediately the solution turned into a white emulsion that was stirred for 6 hours. The $TlBPh_4$ that formed was collected by filtration, washed with MeCN several times, and discarded. The combined filtrate was evaporated in vacuo, affording 31.4 mg of the product as colorless solid (96% yield).

^{1}H NMR (500 MHz, CD_2Cl_2) 7.66 (td, 3H, *J* = 7.5, 1.1 Hz), 7.53 (td, 2H, *J* = 7.8, 1.4 Hz), 7.40-7.35 (m, 4H), 7.35-7.30 (m, 5H), 7.30-7.24 (m, 5H), 7.24-7.18 (m, 2H), 7.18-7.10 (m, 10H), 6.89 (t, 1H, *J* = 7.5 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) -13.11 ppm (s), -143.9 (sept, PF_6, *J* = 710.0 Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2) 160.5 (d, ArF, *J* = 257.0 Hz), 142.0 (d, *J* = 18.0 Hz), 137.8 (d, *J* = 8.5 Hz), 137.4 (s), 135.0 (s), 134.2 (d, *J* = 13.5 Hz), 133.9 (d, *J* = 13.5 Hz), 132.9 (s), 132.8 (d, *J* = 5.0 Hz), 132.4 (d, *J* = 5.5 Hz), 131.9 (t, *J* = 6.0 Hz), 131.1 (d, *J* = 13.5 Hz), 130.4 (d, *J* = 3.0 Hz), 129.4 (q, *J* = 3.5 Hz), 127.6 (d, *J* = 3.0 Hz), 118.4 (d, *J* = 19.3 Hz), 111.2 (dt, *J* = 7.3 Hz) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2) -71.7 (d, PF_6, *J* = 710.0 Hz), -104.7 (q, ArF, *J* = 7.0 Hz) ppm. ^{19}F{H} NMR (376 MHz, CD_2Cl_2) -71.7 (d, PF_6, *J* = 710.0 Hz), -104.7 (s, ArF) ppm.

1.3 Synthetic procedures for the preparation of Rh(I) and Pt(II) sulfonium complexes

*Bis-diphenyl-phosphanylethylene(ethyl)sulfonium rhodium(I) chloride trifluoromethanesulfonate (**5a**[OTf])*

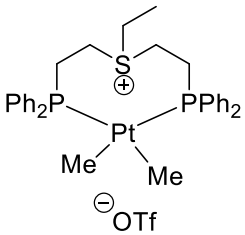


The solution of $[RhCl(COE)_2]_2$ (36 mg, 0.05 mmol) in 2 ml of dry DCM was added dropwise to the solution of sulfonium ligand **4a**[OTf] (64 mg, 0.1 mmol) in 2 ml of DCM. Upon addition, the solution first became dark red then quickly turned yellow. The solution was then stirred for 15 min, then concentrated to less than a half of its initial volume and the product was precipitated by addition of diethyl ether. The solid was then filtered off, washed with ether, and dried under vacuum, affording 70 mg of **5a**[OTf] as a yellow solid (90% yield). XRD quality single crystals were obtained by a slow diffusion of hexane into a difluorbenzene solution of **5a**[BPh_4] at room temperature. Under inert atmosphere, the Complex **5a**[OTf] is stable as solid and as solution in non-chlorinated solvents (more than a week). Under air, as solid the complex **5a**[OTf] is stable for more than a day, but in solution, it decomposes within a few hours.

^{1}H NMR (400 MHz, CD_2Cl_2) 7.37-7.68 (m, 20H, PPh_2), 4.73-4.88 (m, 2H, CH_2S), 3.65 (qd, SCH_2CH$_3$, 2H, $^3J_{RhH}$ = 1.3 Hz; $^3J_{HH}$ = 7.6 Hz), 3.20-3.35 (m, CH_2S, 2H and CH_2P, 2H), 2.50-2.61 (m, 2H, CH_2P), 1.34 (t, 3H, $^3J_{HH}$ = 7.4 Hz, SCH$_2$CH_3) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) 133.6 (*ortho*-C, Ph), 133.3 (*ortho*-C, Ph), 132.0 (*para*-C, Ph), 131.5 (*para*-C, Ph), 131.0-132.1 (m, *ipso*-C, Ph), 129.6 (*meta*-C, Ph), 129.3 (*meta*-C, Ph), 51.3 (*C*H$_2$S), 46.9 (S*C*H$_2$CH$_3$), 30.1 (t, *C*H$_2$P, $^2J_{CP}$ = 13.1 Hz), 11.9

(SCH_2CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) 46.6 (d, $^1J_{RhP}$ = 127.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) -78.2 ppm. ^{103}Rh NMR (16 MHz, CD_2Cl_2) -8577.2 (t, $^1J_{RhP}$ = 129.0 Hz) ppm. HRMS: calcd. for $C_{30}H_{33}ClP_2RhS^+$: 625.0516; found 625.0519.

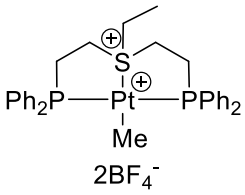
*Bis-diphenyl-phosphanylethylene(ethyl)sulfonium platinum(II) dimethyl trifluoromethanesulfonate (**6a**[OTf])*



The solution of $Pt(COD)Me_2$ (34 mg, 0.1 mmol) in 2 ml of dry DCM was added dropwise to the solution of sulfonium ligand **4a**[OTf] (64 mg, 0.1 mmol) in 2 ml of DCM. The solution was stirred for 15 min, then concentrated to less than a half of the original volume and the product was precipitated by addition of diethyl ether. The solid was then filtered off, washed with ether and dried under vacuum, affording 73 mg of **6a**[OTf], as a white solid (89% yield). XRD quality single crystals were obtained by a slow diffusion of ether into a DCM solution of **6a**[BPh_4] at room temperature. Even under air, the Complex **7a**[OTf] is stable for days (more than a week) as solid and as solution.

^1H NMR (400 MHz, CD_2Cl_2) 7.34-7.68 (m, 20H, P*Ph*$_2$), 4.20-4.29 (m, 2H, C*H*$_2$P), 3.12-3.17 (q, $^3J_{HH}$ = 7.5 Hz, SC*H*$_2$CH$_3$, 2H and SC*H*$_2$, 2H), 2.98-3.06 (m, 2H, SC*H*$_2$), 2.87-2.92 (m, 2H, C*H*$_2$P), 1.09 (t, 3H, $^3J_{HH}$ = 7.4 Hz, SCH$_2$C*H*$_3$), 0.42 (AB q with Pt satellites, 6H, Pt-C*H*$_3$, $^2J_{PtH}$ = 69.1 Hz) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) 134.4 (*ortho*-C, Ph), 132.6 (*ortho*-C, Ph), 132.2 (*ipso*-C, Ph), 131.5 (*para*-C, Ph), 131.1 (*para*-C, Ph)), 129.4 (*meta*-C, Ph), 39.6 (S*C*H$_2$CH$_3$), 39.0 (S*C*H$_2$), 26.6 (d, P*C*H$_2$), 9.7 (SCH$_2$*C*H$_3$), 7.5 (dd, 6H, Pt-*C*H$_3$, $^2J_{Ctrans P}$ = 104.0 Hz, $^2J_{Ccis P}$ = 87.9 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) 11.3 (s with Pt satellites, $^1J_{PtP}$ = 1813.0 Hz) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2) δ = -78.9 ppm. ^{195}Pt NMR (108 MHz, CD_2Cl_2) δ = -4558.2 (t, $^1J_{PtP}$ = 1813.0 Hz) ppm. HRMS: calcd. for $C_{32}H_{39}P_2PtS^+$: 712.1890; found 712.1895.

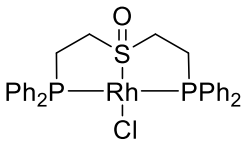
*Bis-diphenyl-phosphanylethylene(ethyl)sulfonium methylplatinum(II) bis-tetrafluoroborate (**7a**[BF_4]$_2$)*



The solution of $Pt(COD)Me_2$ (66.67 mg, 0.2 mmol) in 2 mL of dry DCM was added dropwise to the solution of sulfonium ligand **4a**[BPh_4] (161.36 mg, 0.2 mmol) in 3 mL of DCM. The solution was stirred for 30 min, then treated with 3 eq. of HBF_4*Et_2O (35μL) added dropwise, which resulted in vigorous gas evolution. The reaction mixture was stirred for another 30 min, during which a white precipitate formed slowly. The solution was concentrated to less than a half of its original volume and diethyl ether was added. The precipitate was then filtered off, washed with ether and dried under vacuum, affording 51 mg of **7a**[BF_4]$_2$, as a white solid (67%). XRD quality single crystals were obtained by a slow diffusion of ether into a DCM of **7a**[BF_4]$_2$ at room temperature. Even under air, the Complex **7a**[OTf] is stable for days (more than a week) as solid and as solution in non-coordinating solvents.

^1H NMR (400 MHz, CD_2Cl_2) 7.44-7.70 (m, 20H), 4.44-4.54 (m, 4H), 3.90-3.95 (m, 2H), 3.72-3.82 (m, 2H), 3.21-3.30 (m, 2H), 1.20 (3H, Pt-CH$_3$, $^2J_{PtH}$ = 39.9 Hz), 1.06 (t, 3H, $^3J_{HH}$ = 7.4 Hz, SCH$_2$C*H*$_3$) ppm. ^1H NMR (500 MHz, CD_3NO_2) 7.58-7.95 (m, 20H, PPh$_2$), 4.70-4.76 (m, 2H, SC*H*$_2$), 4.28-4.30 (m, 2H, SC*H*$_2$), 4.08-4.16 (q, 2H, SC*H*$_2$CH$_3$ and m, 2H, PC*H*$_2$), 3.37-3.44 (m, 2H, PC*H*$_2$), 1.45 (t, 3H, $^3J_{HH}$ = 7.3 Hz, SCH$_2$C*H*$_3$), 1.41 (t with Pt satellites, 3H, Pt-C*H*$_3$, $^2J_{PtH}$ = 39.9 Hz, $^3J_{PH}$ = 7.5 Hz) ppm. ^{13}C NMR (126 MHz, CD_3NO_2) 135.5 (*ortho*-C, Ph), 135.1 (*para*-C, Ph), 134.2 (*para*-C, Ph), 134.0 (*ortho*-C, Ph), 131.5 (*meta*-C, Ph), 130.9 (*meta*-C, Ph), 126.6-127.5 (*ipso*-C, Ph), 47.1 (vt, $^2J_{P\text{-}C}$ = 2.7 Hz, S*C*H$_2$), 43.3 (S*C*H$_2$CH$_3$), 35.7 (vt, $^1J_{P\text{-}C}$ = 18.1 Hz, *C*PH$_2$), 11.0 (SCH$_2$*C*H$_3$), 2.3 (t, Pt-*C*H$_3$, $^2J_{PC}$ = 9.8 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) 42.4 (s with Pt satellites, $^1J_{PtP}$ = 2736.0 Hz) ppm. ^{195}Pt NMR (108 MHz, CD_3NO_2) -4813.8 (t, $^1J_{PtP}$ = 2736.0 Hz) ppm. HRMS: calcd. for $C_{31}H_{36}BF_4P_2PtS^+$: 784.1684; found 784.1691.

*Bis-diphenyl-phosphanylethylene sulfoxide chlororhodium(I) (**8**)*

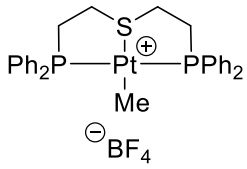


[RhCl(COE)$_2$] (7 mg, 0.01 mmol), dissolved in 1 mL of DCM was added at once to a solution of PS(O)P[5] (10 mg, 0.02 mmol) in an additional 1 mL of dry DCM. The mixture was stirred at room temperature for 30 mins, after which all volatiles were evaporated under vacuum. The residue was dissolved in a minimum amount of DCM and ether was added to precipitate out the complex **8**. The precipitate was collected by filteration and dried under vacuum, affording complex **8** (12 mg, 0.019 mmol, 95%). Crystals suitable for single crystal X-ray diffraction were grown by vapor diffusion of ether into a DCM solution of complex **8** at r.t.

^1H NMR ($CDCl_3$, 500 MHz) 7.95-7.96 (8H, m, P*Ph*$_2$), 7.35-7.42 (12H, m, P*Ph*$_2$), 3.68-3.78 (2H, m, PCH$_2$C*H*$_2$S(O)), 2.82-2.90 (6H, m, PC*H*$_2$C*H*$_2$S(O)). ^{13}C NMR ($CDCl_3$, 126 MHz) 134.0 (t, *o*-P*Ph*, $^2J_{PC}$ = 7.1 Hz), 133.2 (t, *o-Ph*, $^2J_{PC}$ = 7.1 Hz), 133.4 (m,

ipso-P*Ph*), 130.6 (s, *p*-P*Ph*), 130.5 (s, *p*-P*Ph*), 128.9 (t, *m*-P*Ph*, $^{3}J_{P\text{-}C}$ = 4.6 Hz), 128.8 (t, *m*-P*Ph*, $^{3}J_{PC}$ = 4.6 Hz), 60.7 (dt, PCH$_2$*CH*$_2$S(O), $^{2}J_{PC}$ = 8.3 Hz, $^{2}J_{RhC}$ = 5.5 Hz), 27.0 (td, P*CH*$_2$CH$_2$S(O), $^{1}J_{PC}$ = 13.0 Hz, $^{2}J_{RhC}$ = 2.6 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz) 40.5 (d, $^{1}J_{RhP}$ = 147.5). HRMS (ESI +ve mode): m/z calcd for [M−Cl]$^+$ $C_{28}H_{28}OP_2RhS^+$ 577.0386, found 577.0383, m/z calcd for [M−Cl+MeCN]$^+$ $C_{30}H_{31}NOP_2RhS^+$ 618.0651, found 618.0652.

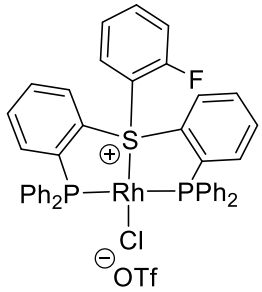
*Bis-diphenyl-phosphanylethylene sulfide methylplatinum(II) bis-tetrafluoroborate (**9**[BF$_4$]$_2$)*



Pt(COD)MeCl (17.5 mg, 0.05 mmol), dissolved in 1 mL of dry DCM was added dropwise to a solution of **1a** (22.9 mg, 0.05 mmol) dissolved in 1.5 mL of DCM. The solution was stirred for 10 min, then treated with 1.5 equiv. of AgBF$_4$ (14.6 mg) and stirred for additional 30 min, while protected from light by aluminum paper. After 30 min, the precipitate was filtered off and washed with ether, the filtrate was dried under reduced vacuum, affording **9**[BF$_4$] as a white solid (29 mg, 0.0384 mmol, 76.8 %). XRD quality single crystals were obtained by a slow evaporation of a DCM solution of **9**[BF$_4$] at room temperature. Even under air, the Complex **7a**[OTf] is stable for days (more than a week) as solid and as solution.

^{1}H NMR (400 MHz, CDCl$_3$) 7.45-7.69 (m, 20H, PPh$_2$), 3.86-4.04 (m, 2H, SC*H*$_2$), 3.56-3.66 (m, 2H, PC*H*$_2$), 3.05-3.13 (m, 2H, SC*H*$_2$), 2.59-2.66 (m, 2H, PC*H*$_2$), 0.79-0.89 (triplet with Pt satellite, 3H, C*H*$_3$-Pt, $^{2}J_{PtH}$ = 74.2 Hz, $^{3}J_{PH}$ = 6.4Hz). ^{13}C NMR (101 MHz, CDCl$_3$) 133.3 (*ortho*-C, Ph), 132.6 (*ortho*-C, Ph), 132.2 (*para*-C, Ph), 131.8 (*para*-C, Ph), 129.3-129.5 (*meta*-C, Ph), 128.0-128.9 (*ipso*-C, Ph), 36.9 (t, P*C*H$_2$) ppm, 35.3 (t, S*C*H$_2$), -9.7 (t, $^{2}J_{PC}$ = 5.6 Hz, $^{1}J_{PtC}$ = 605.7 Hz, *C*H$_3$-Pt) ppm. ^{31}P NMR (162 MHz, CD$_2$Cl$_2$) δ = 37.8 (s with Pt satellites, $^{1}J_{PtP}$ = 2923.0 Hz) ppm. HRMS: calcd. for $C_{29}H_{31}P_2PtS^+$: 668.1264; found 668.1270.

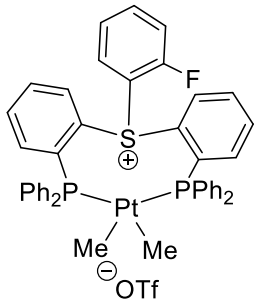
*Bis(2-(diphenylphosphaneyl)phenyl)(2-fluorophenyl)sulfonium chlororhodium(I) trifluoromethanesulfonate (**5b**[OTf])*



Ligand **4b**[OTf] (100 mg, 0.125 mmol) was dissolved in 2.0 ml DCM in a vial. In another vial, [RhCl(COE)$_2$]$_2$ (44.9 mg, 0.5 eq.) was dissolved in additional 2.0 ml of DCM as well and added to the solution of **4b**[OTf]. The solution that immediately turned dark red orange was left stirring overnight. The solvent was then removed in vacuo and the residue was washed several times with hexane to afford the product, as a brown-yellowish powder. (0.12 g, 97% yield). As all attempts to grow single crystals of **5b**[OTf] suitable for XRD analysis failed, instead we prepared compound **5b**[PF$_6$] from ligand **4b**[PF$_6$] following the same procedure. This time XRD quality crystals were obtained by a layer diffusion of toluene into a concentrated DCM solution of **5b**[PF$_6$]. Under inert atmosphere, the Complex **5b**[OTf] is stable as solid and as solution in non-chlorinated solvents (more than a week). Under air, as solid the complex **5a**[OTf] is stable for more than a day, but in solution, it decomposes within a few hours.

^{1}H NMR (500 MHz, CDCl$_3$) 8.88 (d, 2H, *J* = 8.3 Hz), 8.15 (t, 2H, *J* = 7.7 Hz), 7.88 (t, 2H, *J* = 7.5 Hz), 7.80-7.76 (m, 2H), 7.66 (q, 4H, *J* = 6.0 Hz), 7.52 (q, 4H, *J* = 6.5 Hz), 7.50-7.42 (m, 5H), 7.42-7.36 (m, 8H), 6.91 (t, 1H, *J* = 7.9 Hz), 6.85 (t, 1H, *J* = 9.5 Hz), 6.69 (t, 1H, *J* = 7.6 Hz) ppm. ^{31}P NMR (162 MHz, CDCl$_3$) 48.7 (dd, *J* = 126.0, 6.0 Hz) ppm. ^{13}C NMR (125MHz, CDCl$_3$) 157.4 (d, ArF, *J* = 257.0 Hz), 138.9 (vt, *J* = 15.6 Hz), 138.5 (vtd, *J* = 19.3, 1.7 Hz), 136.2 (d, *J* = 8.5 Hz), 135.8 (s), 135.4 (s), 135.0 (s), 133.8 (t, *J* = 6.7 Hz), 133.6 (t, *J* = 7.6 Hz), 131.5 (d, *J* = 9.5 Hz), 130.2 (t, *J* = 5.0 Hz), 129.2 (s), 129.1 (t, *J* = 5.3 Hz), 128.8 (t, *J* = 5.5 Hz), 128.2 (vt, *J* = 21.9 Hz), 125.6 (d, *J* = 3.2 Hz), 120.8 (q, OTf, *J* = 320.0 Hz), 120.0 (d, *J* = 11.7 Hz), 118.1 (d, *J* = 20.1 Hz) ppm. ^{19}F NMR (376 MHz, CDCl$_3$) -76.5 (s, OTf), -104.1 (m, ArF) ppm. ^{19}F{H} NMR (376 MHz, CDCl$_3$) -76.5 (s, OTf), -104.1 (t, ArF, *J* = 6.0 Hz) ppm. HRMS: calcd. For $C_{42}H_{32}ClFP_2RhS^+$: 787.0422; found 787.0345.

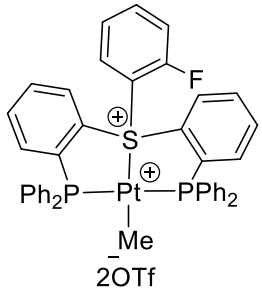
*Bis(2-(diphenylphosphaneyl)phenyl)(2-fluorophenyl)sulfonium dimethylplatinum(II) trifluoromethanesulfonate (**6b**[OTf])*



Ligand **4b**[OTf] (50 mg, 62.6 μmol) was placed in a glass pressure tube and dissolved in 1.6 ml of THF. In a separate vial, Pt(COD)Me_2 (20.9 mg, 1 eq.) was dissolved in additional 1.6 ml of THF and added to the pressure tube containing the solution of **4b**[OTf]. The tube was sealed off, placed in an oil bath at 65°C and left stirring overnight gradually forming a white precipitate. After allowing to cool to r.t., the pressure tube was opened, the precipitate was filtered and washed several times with hexane affording 34 mg the product, as a white powder (53% yield). Even under air, the Complex **7a**[OTf] is stable for days (more than a week) as solid and as solution, however, decomposes under prolonged vacuum. Thus, clean NMR without residual solvent could not be obtained for complex **7b**[OTf].

^{1}H NMR (500 MHz, CD_2Cl_2) 7.76 (dddd, 1H, *J* = 8.0, 5.5, 1.5, 0.6 Hz), 7.59 (t, 2H, *J* = 7.7 Hz), 7.48 (br t, 4H, *J* = 8.2 Hz), 7.43-7.34 (m, 7H), 7.34-7.26 (m, 9H), 7.22 (td, 4H, *J* = 7.5, 1.9 Hz), 7.14 (br t, 2H, *J* = 7.0 Hz), 7.04 (td, 1H, *J* = 7.6, 1.5 Hz), 6.91 (br s, 2H), 0.65 (AB q with Pt satellites, Pt*Me*$_2$, 6H, *J* = 71.2 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) 16.6 (br s with Pt satellites, *J* = 1781.0 Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2) 160.7 (d, ArF, *J* = 255.0 Hz), 137.6 (d, *J* = 8.5 Hz), 137.5-136.1 (m), 135.6 (d, *J* = 8.0 Hz), 134.2 (d, *J* = 12.0 Hz), 133.8 (s), 133.6 (d, *J* = 3.6 Hz), 132.6 (s), 131.5 (s), 131.1 (s, *J* = 13.2), 130.6 (s), 128.9 (d, *J* = 10 Hz), 128.6 (d, *J* = 10 Hz), 127.1 (d, *J* = 2.5 Hz), 121.4 (q, OTf, *J* = 321.5 Hz), 118.0 (d, *J* = 19 Hz), 105.4 (d, *J* = 15.2 Hz), 9.6 (dd, Pt*Me*$_2$) ppm. ^{19}F{H} NMR (376 MHz, CD_2Cl_2) -77.2 (s, OTf), -102.3 (s, ArF) ppm. ^{195}Pt NMR (108 MHz, CD_2Cl_2) -4390.2 (t, *J* = 1781.0 Hz) ppm. HRMS: calcd. For $C_{44}H_{38}FP_2PtS^+$: 874.1796; found 874.1885.

*Bis(2-(diphenylphosphaneyl)phenyl)(2-fluorophenyl)sulfonium methylplatinum(II) bis-trifluoromethanesulfonate (**7b**[OTf]$_2$)*



6b[OTf]) (15 mg, 14.6 μmol) was dissolved in 1.0 ml DCM in a vial forming a light-yellow transparent solution. To this solution 1.3 μL (1 eq.) of triflic acid were added dropwise. The solution that turned colorless was left closed to stir for 40 minutes. The solvent was removed in vacuo to afford the product as a light-yellow powder. (14.8 mg, quantitative yield). As all attempts to grow single crystals of **6b**[OTf]$_2$ suitable for XRD analysis failed, instead we prepared compound **6b**[NTf_2]$_2$ by treating complex **6b**[OTf] with an excess of bistriflimide. XRD quality crystals were then obtained by a layer diffusion of toluene into its concentrated DCM solution. Even under air, the Complex **7a**[OTf] is stable for days (more than a week) as solid and as solution in non-coordinating solvents.

^{1}H NMR (500 MHz, CD_2Cl_2) 9.11 (d, 2H, *J* = 8.5 Hz), 8.29 (t, 2H, *J* = 8.0 Hz), 8.13 (td, 2H, *J* = 7.6, 0.7 Hz), 7.91 (qd, 2H *J* = 4.79, 1.33 Hz), 7.72-7.67 (m, 2H), 7.64-7.56 (m, 11H), 7.56-7.51 (m, 4H), 7.47-7.40 (m, 4H), 7.15 (dt, 1H, *J* = 7.9, 1.2 Hz), 7.05-6.99 (m, 2H,), 1.56 (t with Pt satellites, Pt*Me*, 3H, *J* = 41.2, 7.0 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2) 44.34 (d with Pt satellites, *J* = 2768.0, 3.3 Hz) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2) 158.2 (d, ArF, *J* = 259.5 Hz), 139.8 (d, *J* = 9.1 Hz), 138.8 (vt, *J* = 3.5 Hz), 138.1 (s), 137.9 (vt, *J* = 10 Hz), 134.5 (vt, *J* = 7.8 Hz), 134.4 (vt, *J* = 3.3 Hz), 134.3 (s), 134.1 (vt, *J* = 6.7 Hz), 134.1 (s), 130.7 (vt, *J* = 6 Hz), 127.9 (d, *J* = 3 Hz), 123.7 (vt, *J* = 30 Hz), 122.2 (vt, *J* = 32.2 Hz), 121.2 (q, OTf, *J* = 320.5 Hz), 119.0 (d, *J* = 19.0 Hz), 112.8 (d, *J* = 12.8 Hz), 4.74 (t with Pt satellites, Pt*Me*, *J* = 318.0, 4.5 Hz) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2) -77.26 (s, OTf, 6F), -102.45 (bs, ArF, 1F) ppm. ^{19}F{H} NMR (470 MHz, CD_2Cl_2) -77.26 (s, OTf, 6F), -102.45 (t, ArF, 1F, *J* = 3.3 Hz) ppm. ^{195}Pt NMR (108 MHz, CD_2Cl_2) -4811.0 (t, $^1J_{PtP}$ = 2768.0 Hz) ppm. HRMS: calcd. For $C_{43}H_{35}FP_2PtS^+$: 859.1561; found 859.1521.

1.4 ^{1}H NMR spectra comparison

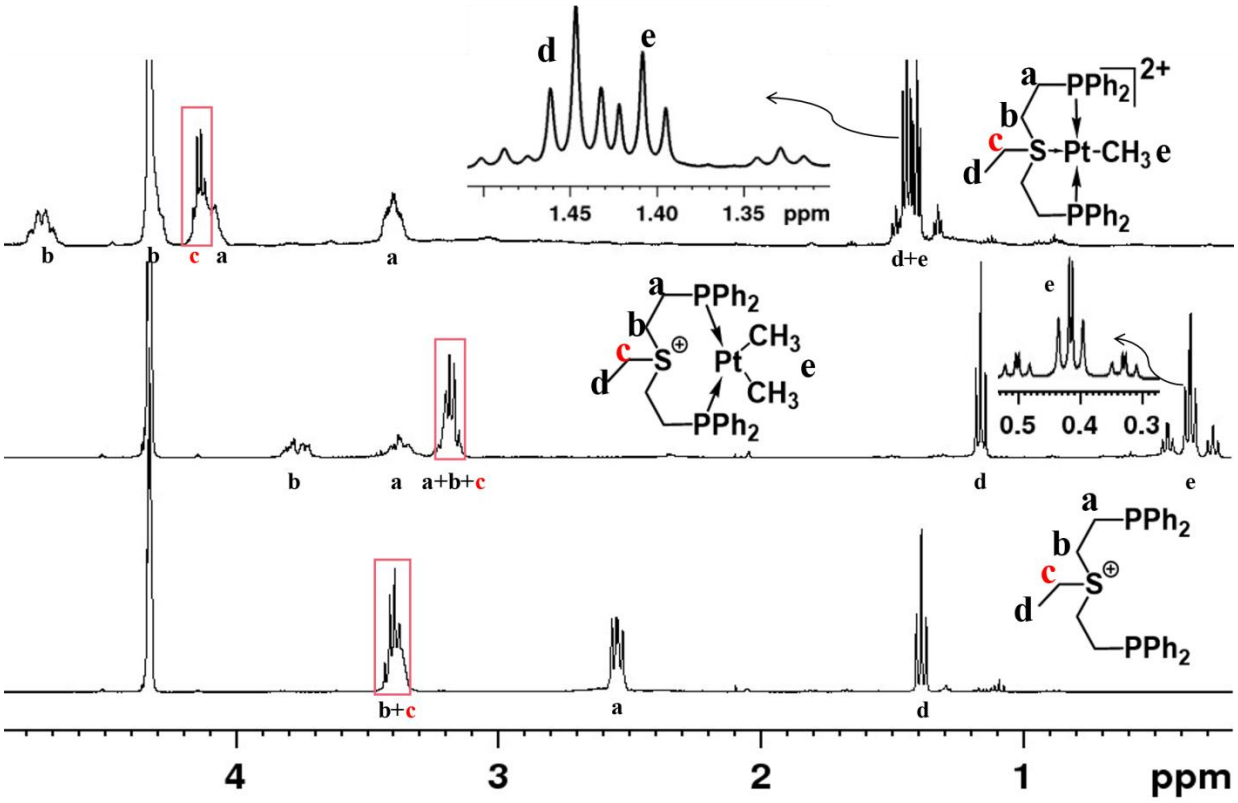


Figure S1: Part of ^{1}H NMR (400 MHz) of **4a**[OTf], **6a**[OTf] and **7a**$[BF_4]_2$ in CD_3NO_2, measured at 298 K.

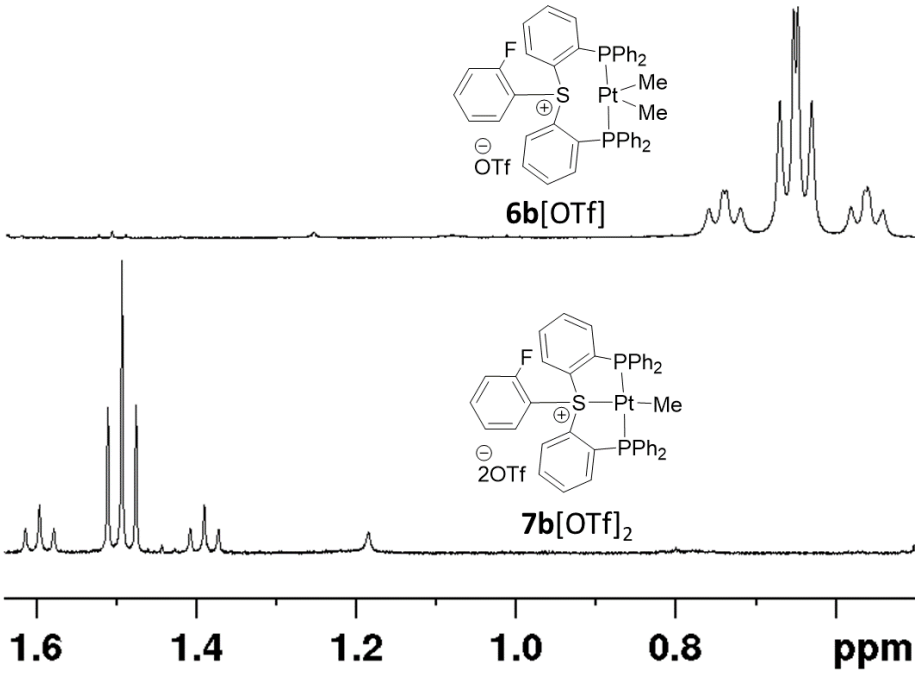


Figure S2: Part of ^{1}H NMR (400 MHz) of **6b**[OTf], and **7b**$[OTf]_2$ in CD_2Cl_2, measured at 298 K.

1.5. Selected 2D NMR spectra of the complexes.

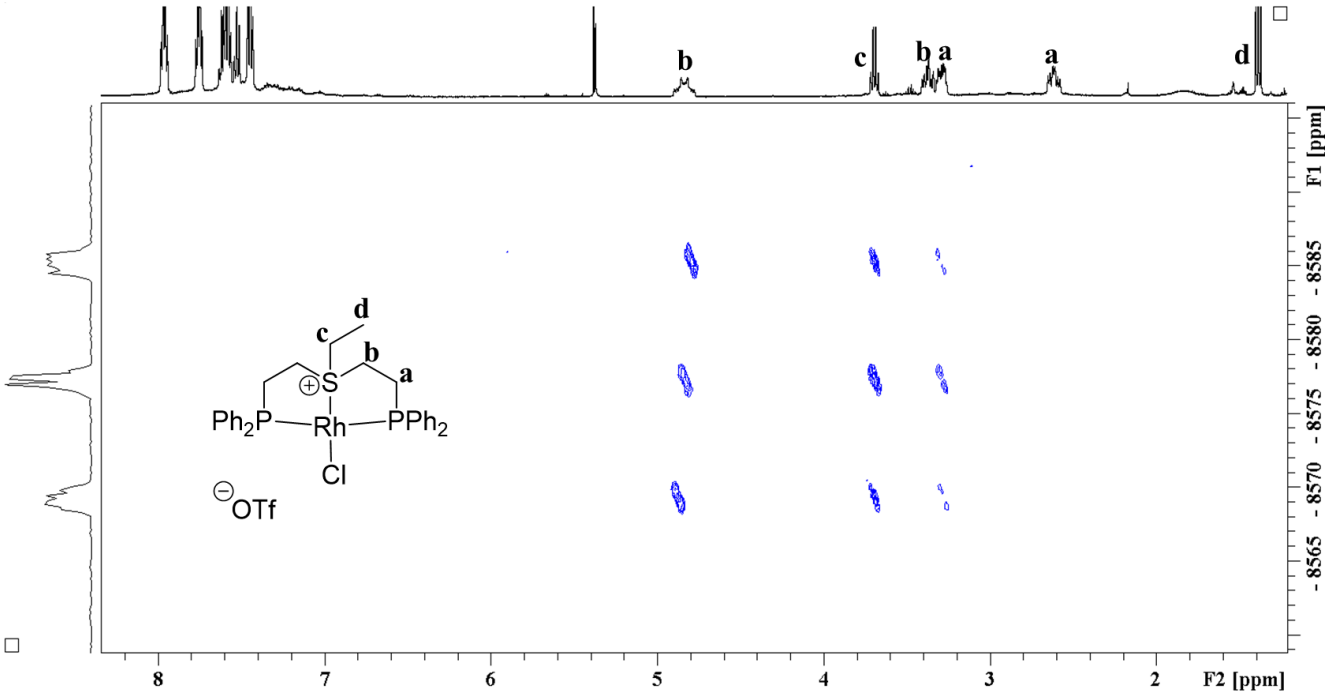


Figure S3: ^{103}Rh-^{1}H HMBC NMR (500 MHz) of **5a**[OTf] in CD_2Cl_2, measured at 298 K.

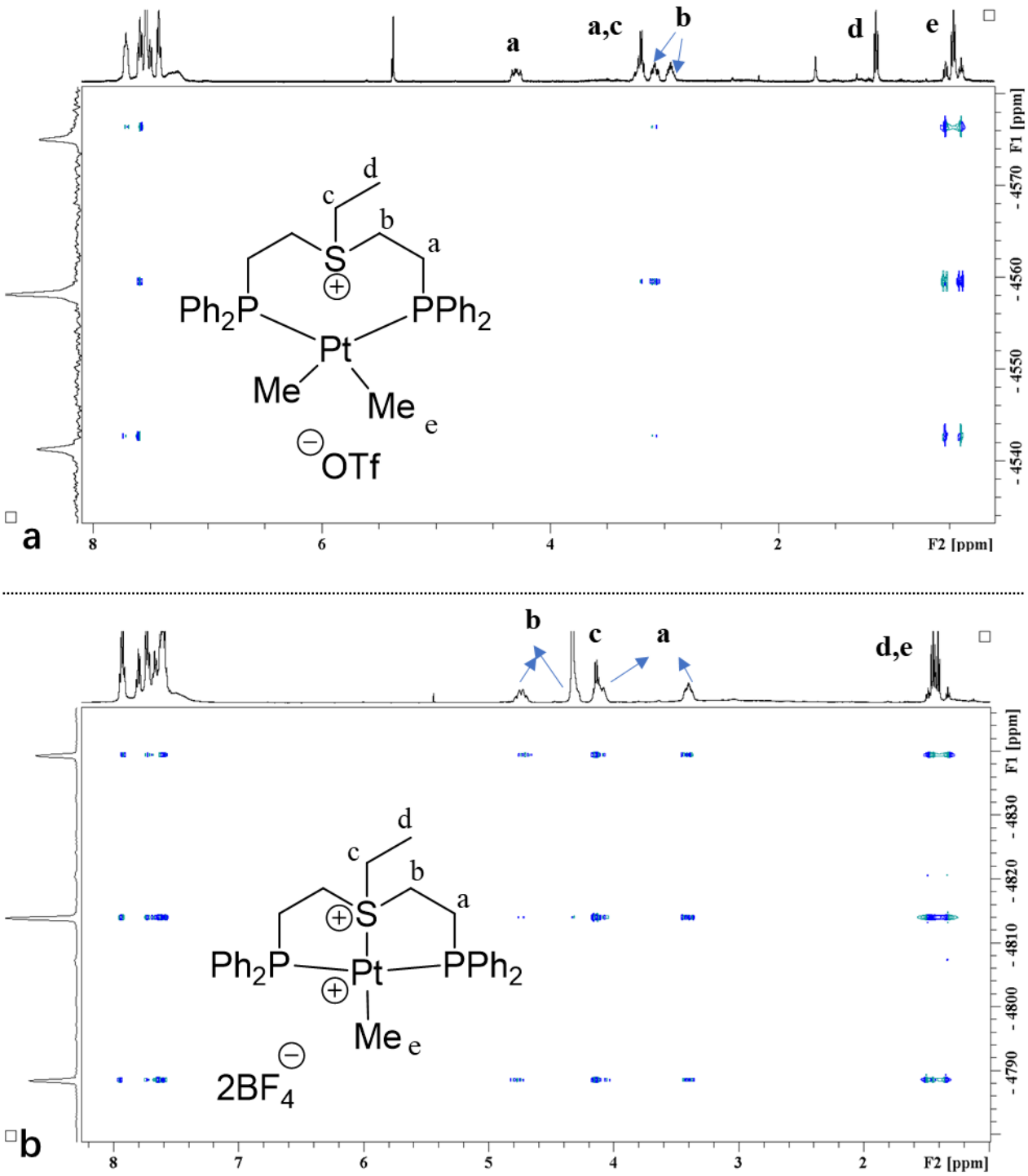


Figure S4: ^{195}Pt-^{1}H HMBC NMR (500 MHz) of **6a**[OTf] in CD_2Cl_2 (**a**) and **7a**$[BF_4]_2$ in CD_3NO_2, (**b**) measured at 298 K.

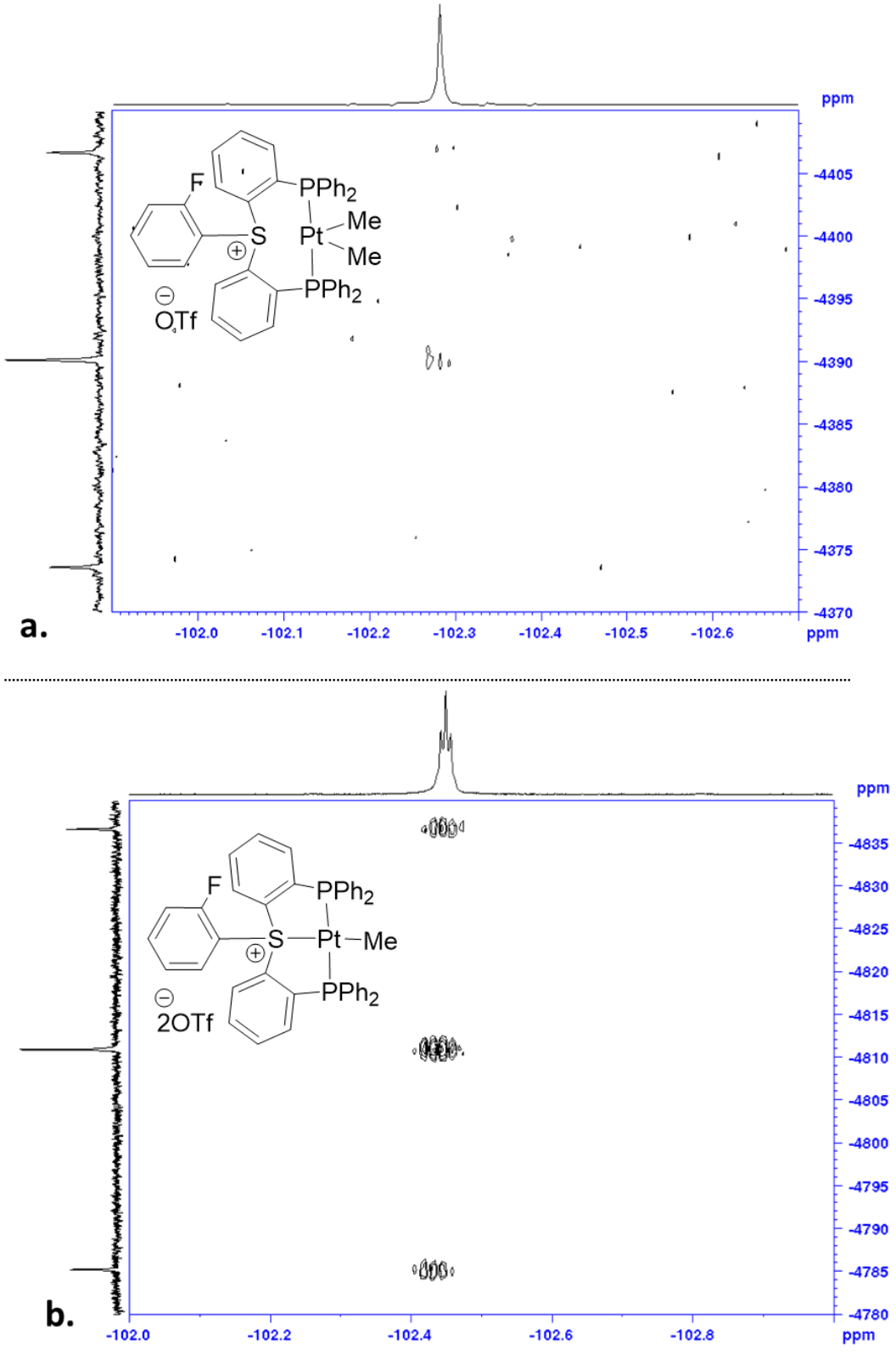


Figure S5: Comparison of ^{195}Pt-^{19}F HMBC NMR (500 MHz) of **6b**[OTf] and **7b**[OTf]$_2$ in CD_2Cl_2, measured at 298 K.

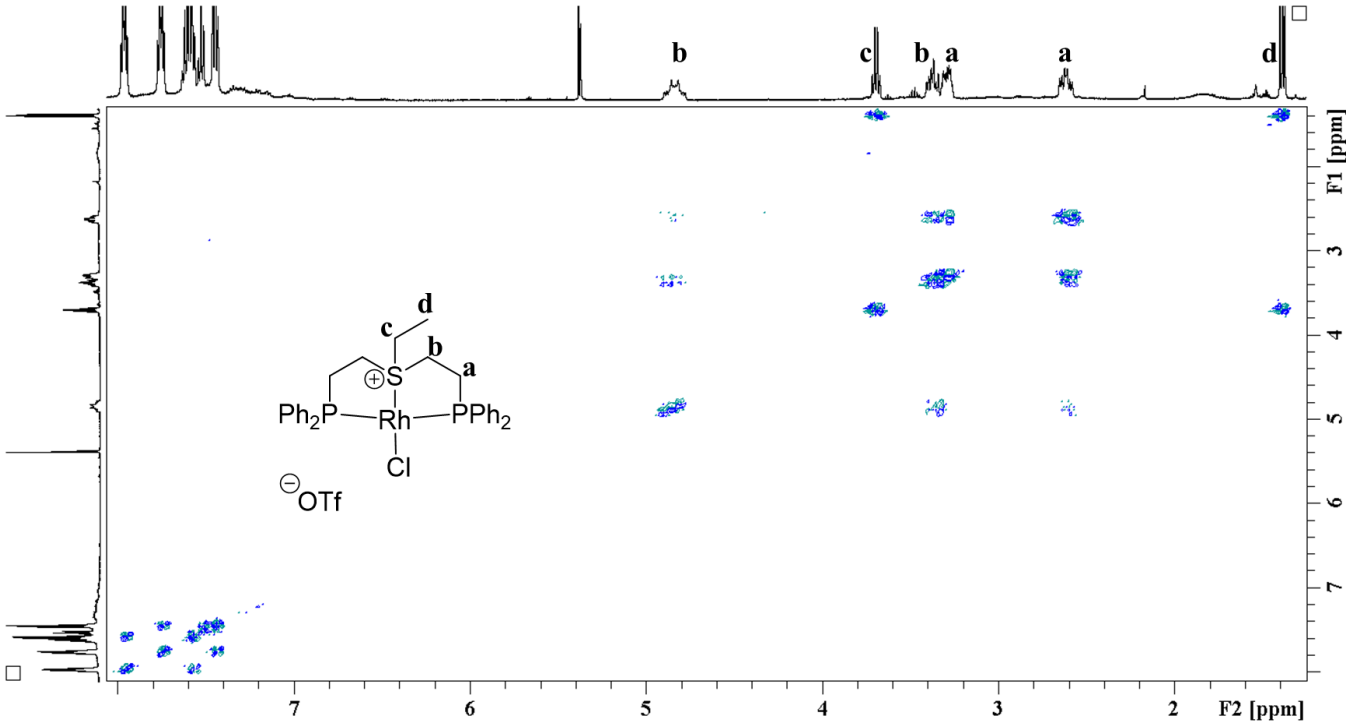


Figure S6: COSY NMR (400 MHz) of **5a**[OTf] in CD_2Cl_2, measured at 298 K.

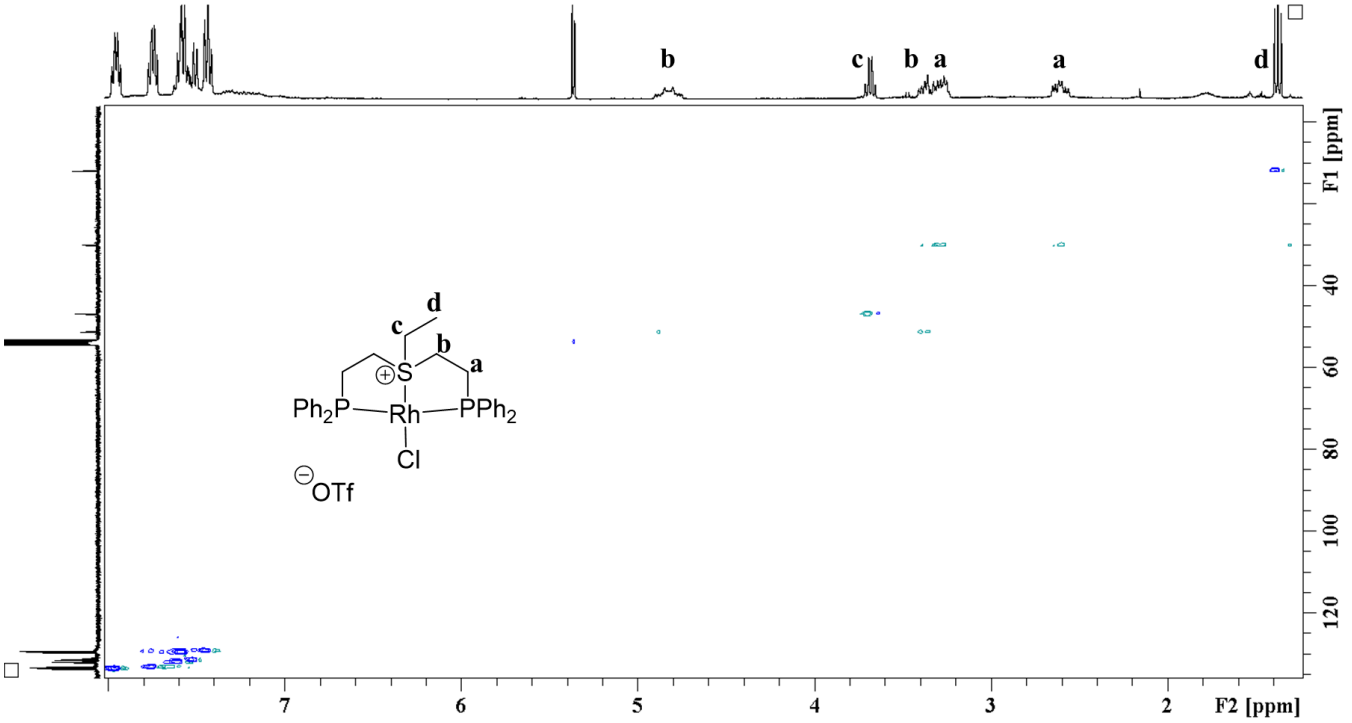


Figure S7: HSQC NMR (400 MHz) of **5a**[OTf] in CD_2Cl_2, measured at 298 K.

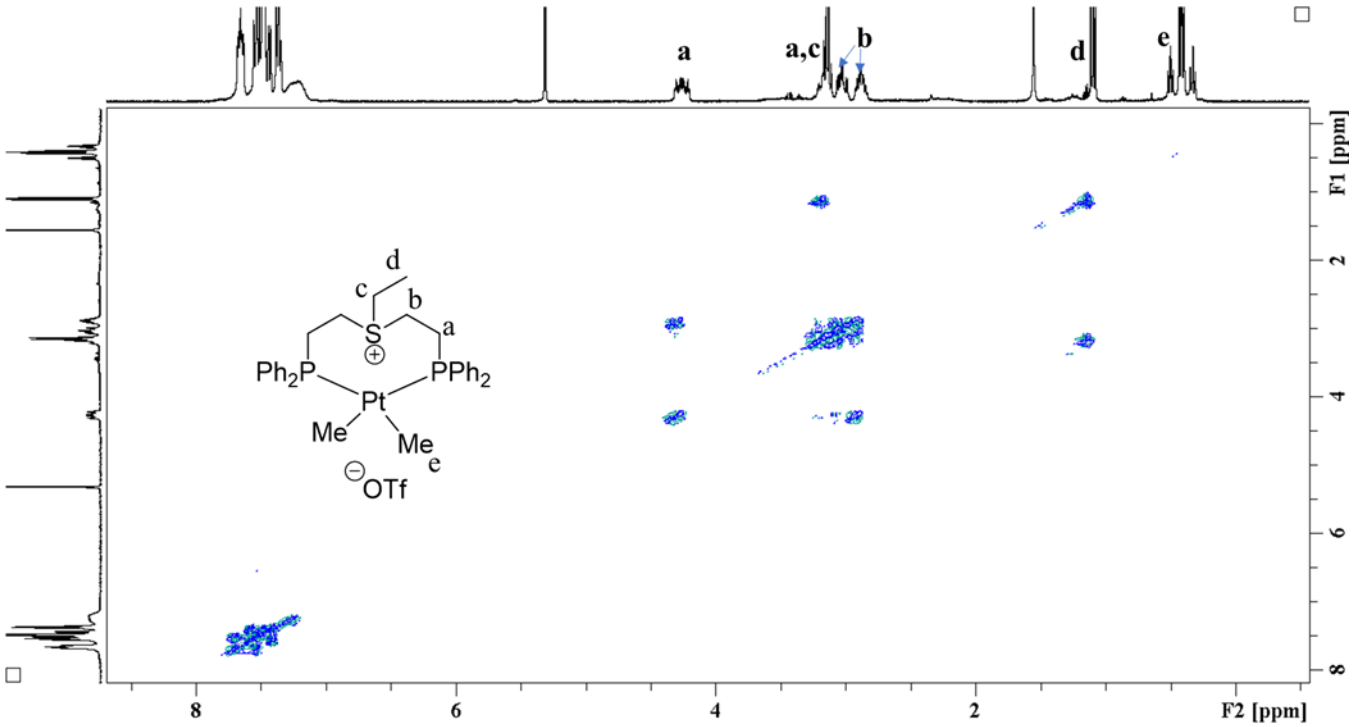


Figure S8: COSY NMR (400 MHz) of **6a**[OTf] in CD_2Cl_2, measured at 298 K.

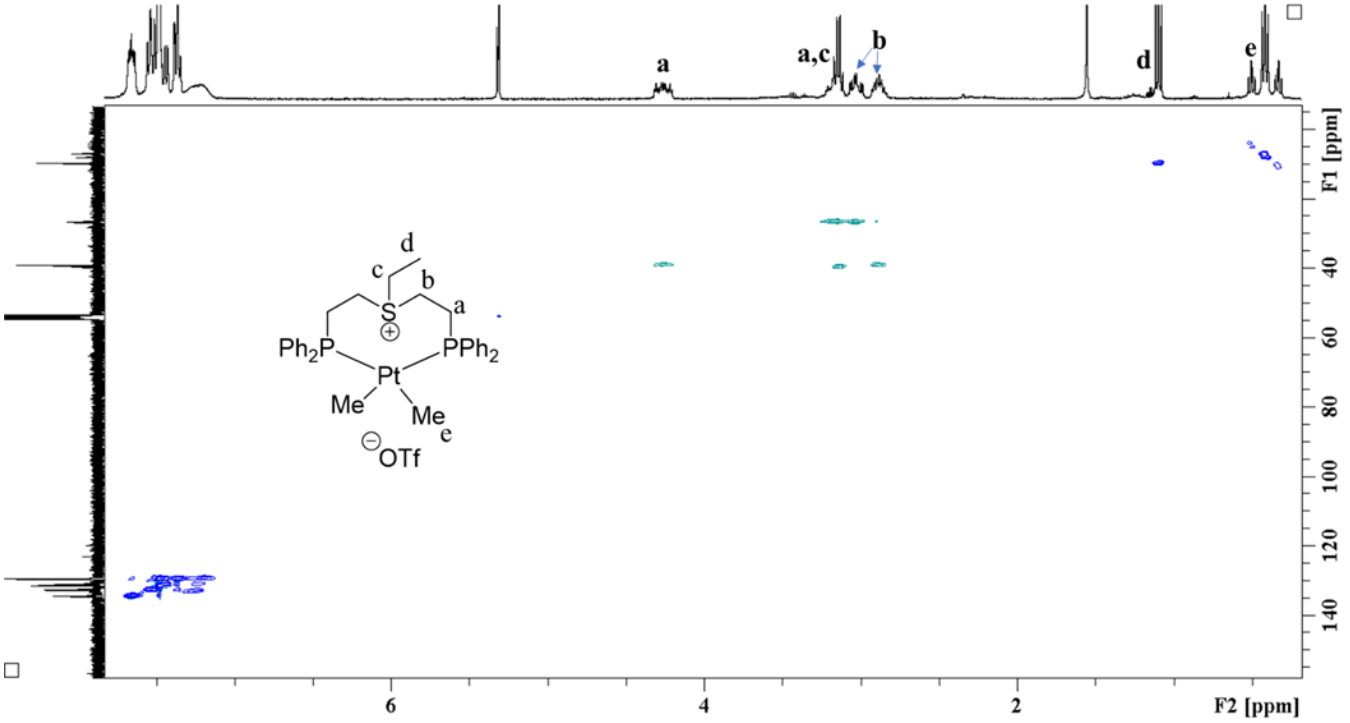


Figure S9: HSQC NMR (400 MHz) of **6a**[OTf] in CD_2Cl_2, measured at 298 K.

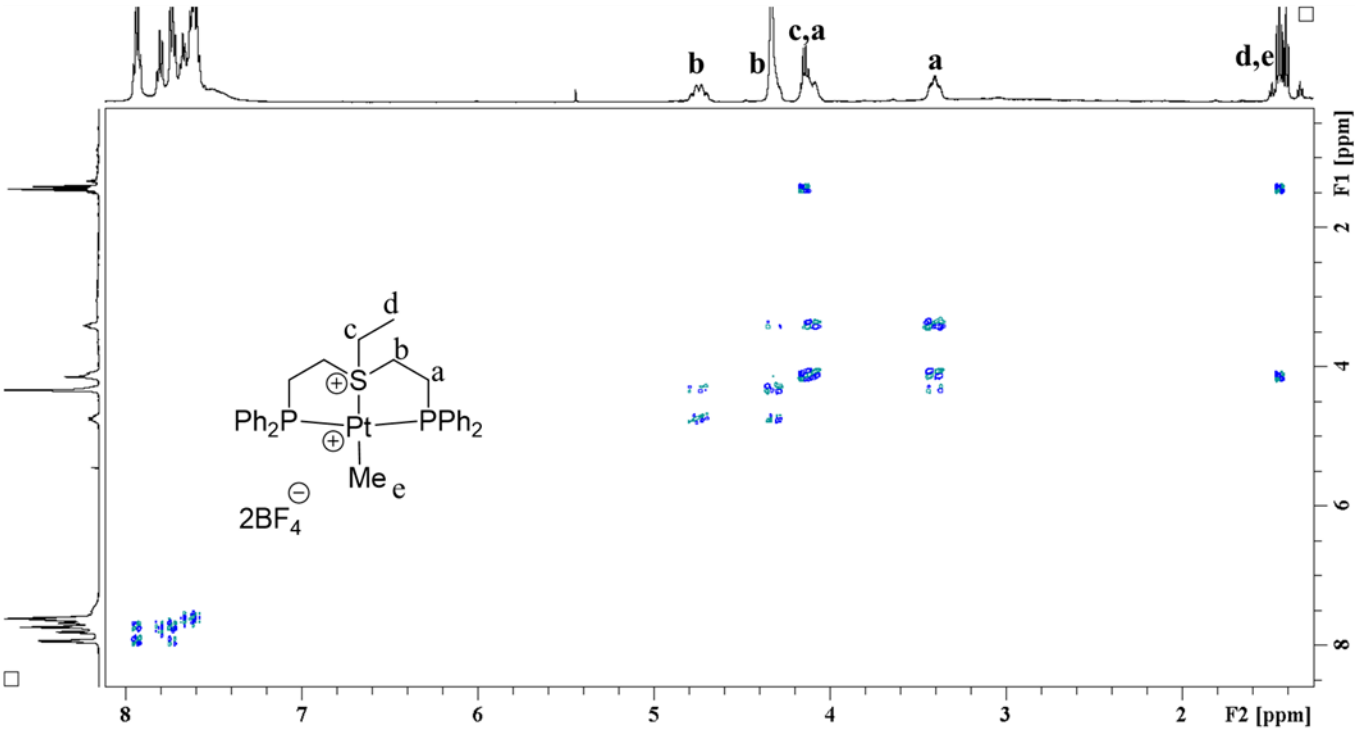


Figure S10: COSY NMR (400 MHz) of **7a**$[BF_4]_2$ in CD_3NO_2, measured at 298 K.

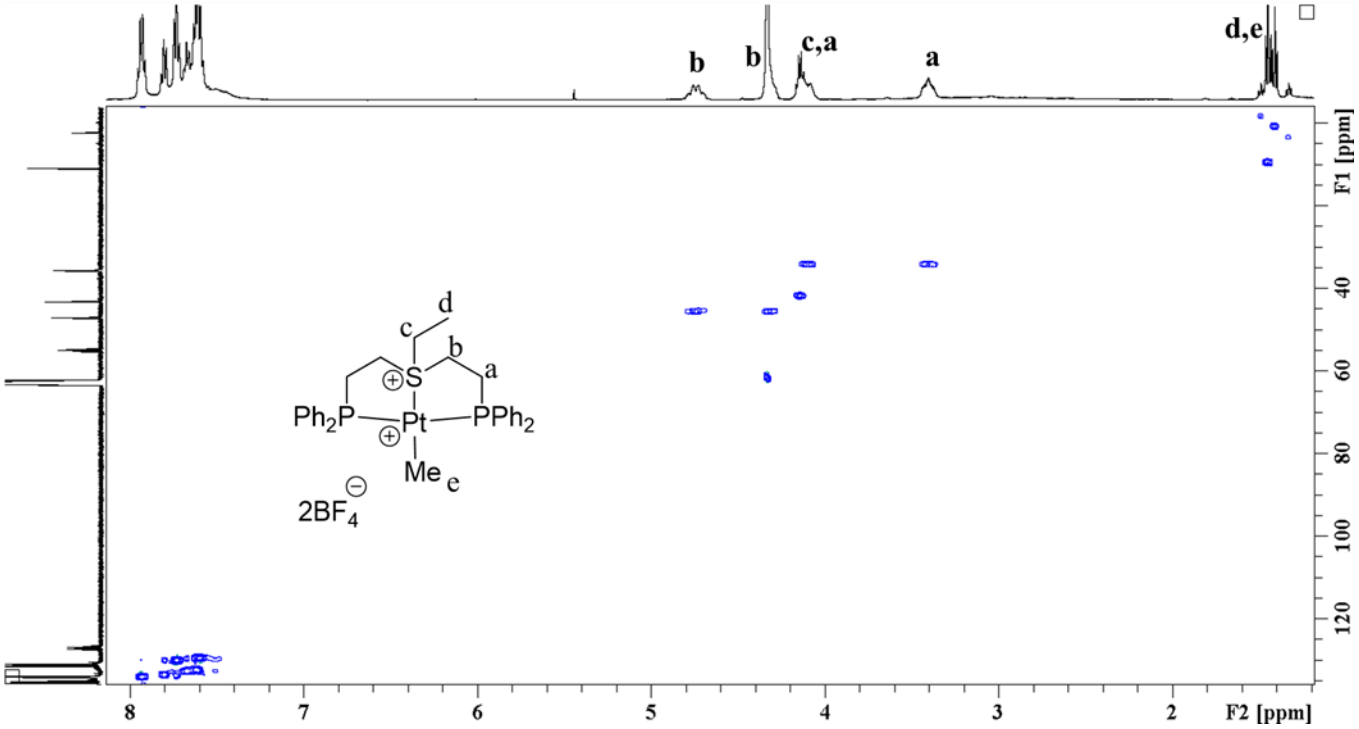


Figure S11: HSQC NMR (400 MHz) of **7a**$[BF_4]_2$ in CD_3NO_2, measured at 298 K.

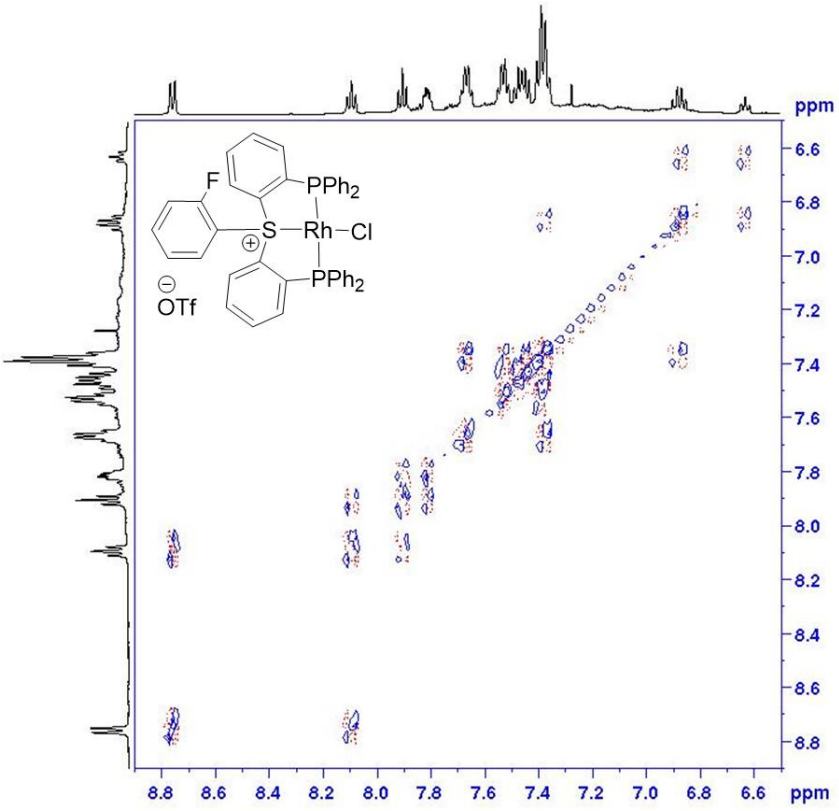


Figure S12: COSY NMR (400 MHz) of **5b**[OTf] in $CDCl_3$, measured at 298 K.

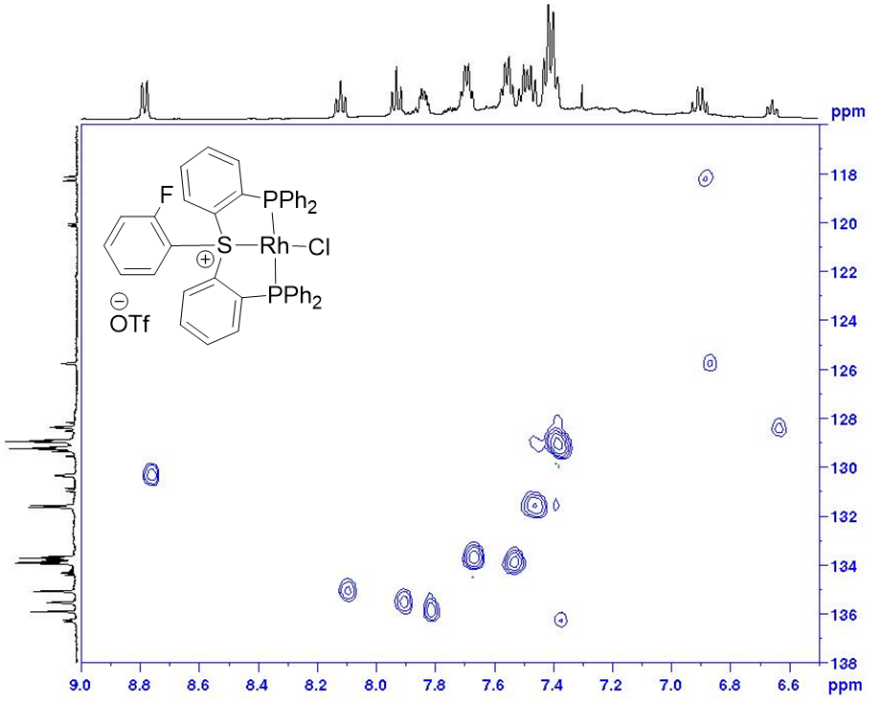


Figure S13: HSQC NMR (500 MHz) of **5b**[OTf] in $CDCl_3$, measured at 298 K.

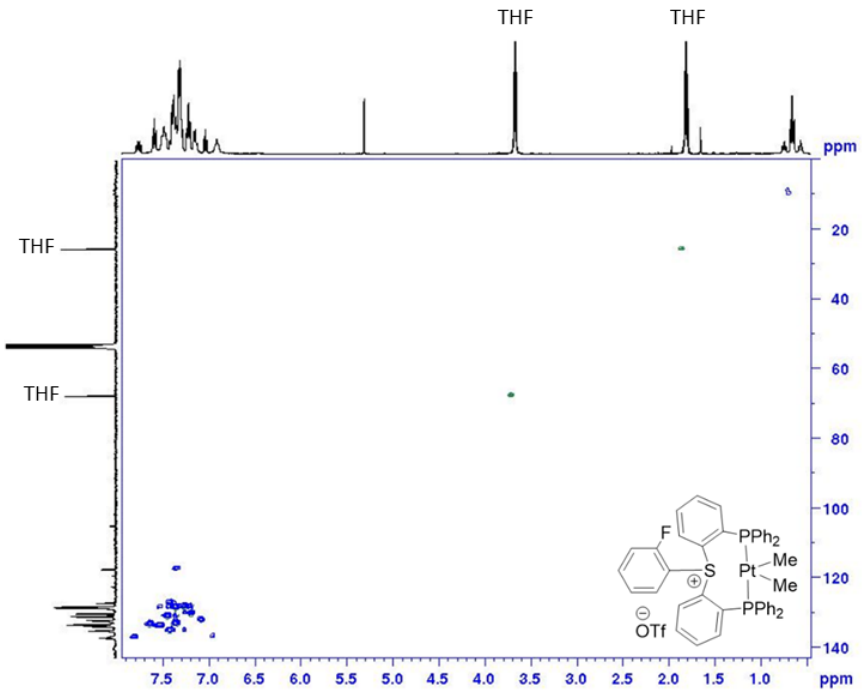


Figure S14: HSQC NMR (400 MHz) of **6b**[OTf] in CD_2Cl_2, measured at 298 K.

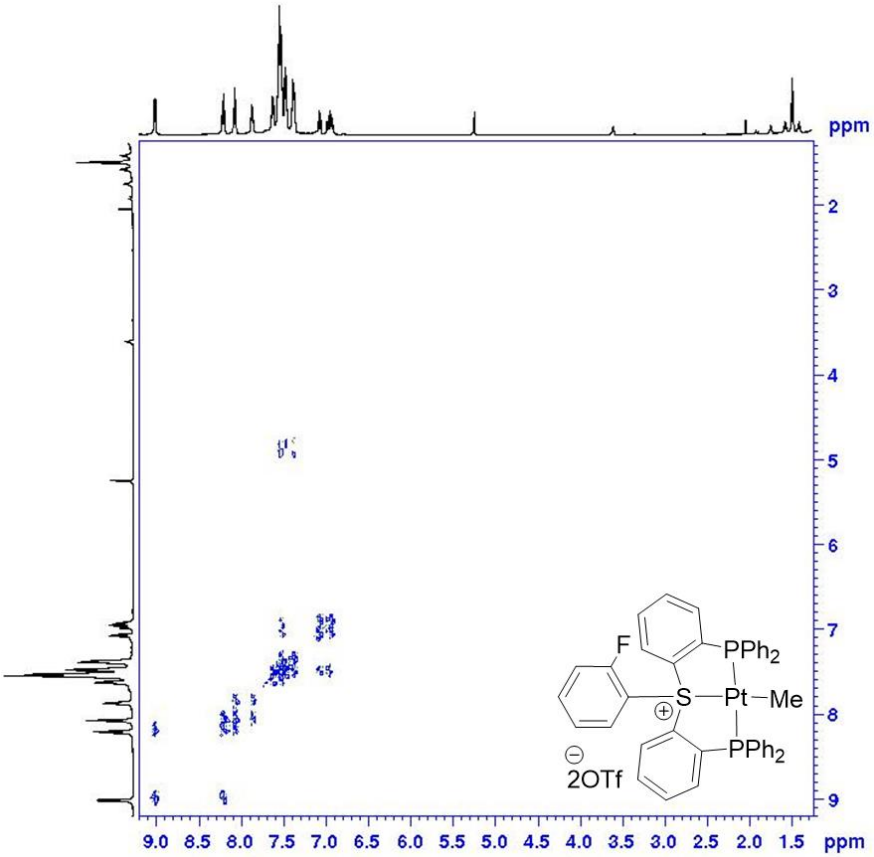


Figure S15: COSY NMR (500 MHz) of **7b**$[OTf]_2$ in CD_2Cl_2, measured at 298 K.

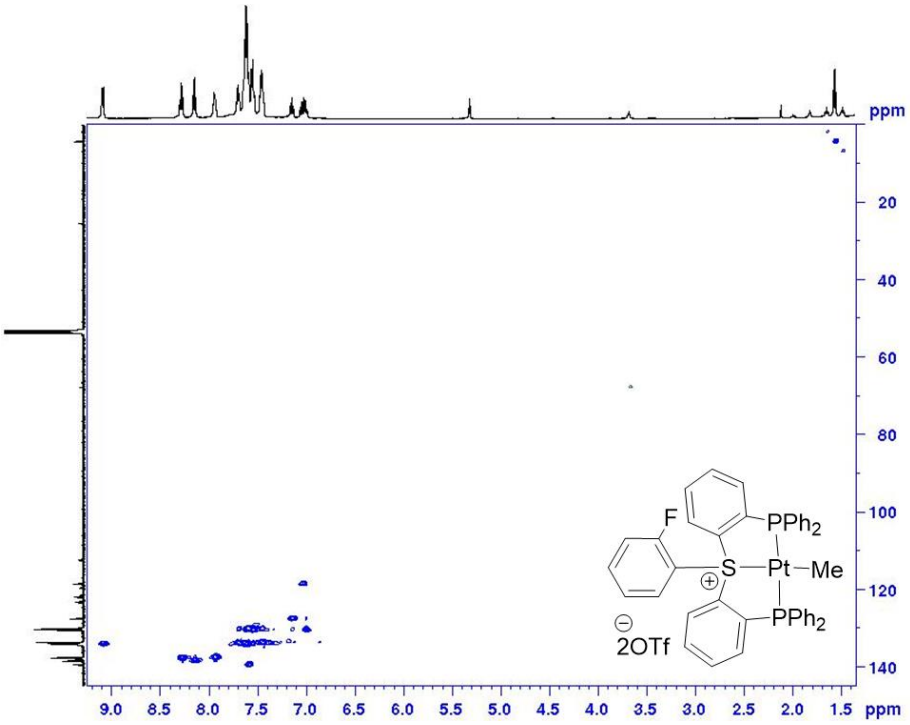


Figure S16: HSQC NMR (500 MHz) of **7b**$[OTf]_2$ in CD_2Cl_2, measured at 298 K.

2. Crystallography

2.1. General crystallographic and refinement details:

Suitable single crystals of **4a**[BPh_4], **4b**[OTf], **5a**[BPh_4], **5b**[PF_6], **6a**[BPh_4], **7a**[BF_4]$_2$, **7b**[NTf_2]$_2$, **8** and **9**[BF_4] were grown from the solvents mentioned in their respective synthetic procedures. Single-crystal X-ray diffraction data collections were performed using Rigaku goniometer diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction intensity details were extracted from the diffraction frames using CrysAlisPro XtalLAB Synergy-S system (version 41.112a) program. The structures were then solved by SHELXT-9740 available in Olex2 crystallographic suite, which located most of the non-hydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL-Version 2018/3 to locate the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were fixed in calculated positions. All disorders were handled with SADI, SIMU, EADP, SAME and RIGU constraints and restraints. The crystallographic parameters of each structure are given bellow. All structures are deposited to CCDC and their corresponding deposition numbers are listed below:

4a[BPh_4] = 2119886; **4b**[OTf] = 2119887; **5a**[BPh_4] = 2119888; **5b**[PF_6] = 2119889; **6a**[BPh_4] = 2119890; **7a**[BF_4]$_2$ = 2119891; **7b**[NTf_2]$_2$ = 2119892; **8** = 2119893; and **9**[BF_4] = 2119894.

2.2 XRD structure of complex 8

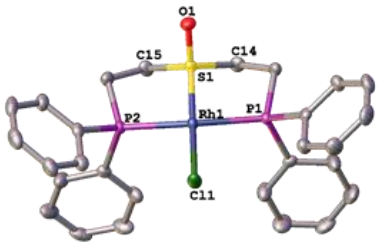


Figure S17: XRD structure of complex **8**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh1–S1 2.135(1), Rh1–Cl1 2.369(1), Rh1–P2 2.314(1), Rh1–P1 2.312(1), S1–O1 1.474(2), S1–C14 1.800(3), S1–C15 1.799(3). Selected bond angles (°): S1–Rh1–Cl1 172.4(1), S1–Rh1–P2 84.4(1), S1–Rh1–P1 84.2(1), P2–Rh1–Cl1 96.8(1), P1–Rh1–Cl1 96.4(1), P1–Rh1–P2 161.2(1), O1–S1–Rh1 118.2(1), O1–S1–C14 107.2(2), O1–S1–C15 106.7(2), C14–S1–Rh1 109.5(1), C15–S1–Rh1 110.1(1), C15–S1–C14 104.3(2).

2.3 Crystallographic parameter tables:

	4a[BPh_4]	**4b**[OTf]	**5a**[BPh_4]	**5b**[PF_6]	**6a**[BPh_4]
Empirical formula	$C_{54.5}H_{53}BClP_2S$	$C_{43}H_{32}F_4O_3P_2S_2$	$C_{54}H_{53}BClP_2RhS$	$C_{45.5}H_{36}ClF_7P_3RhS$	$C_{56}H_{59}BP_2PtS$
Formula weight	848.23	798.74	945.13	979.07	1031.93
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	293(2)	293(2)	150 (2)	150 (2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	Triclinic	monoclinic
Space group	*P-1*	*P21/n*	*P21/n*	*P-1*	*P21/c*
a/Å	8.8424(5)	12.4956(2)	10.9915(4)	9.1404(2)	16.6775(2)
b/Å	11.4067(6)	28.0310(4)	34.1432(10)	12.3384(3)	15.3273(2)
c/Å	24.8662(10)	12.6611(2)	12.5533(4)	19.4965(5)	19.3126(3)
α/degree	81.957(4)	90.00	90	102.063(2)	90.00
β/degree	80.897(4)	119.324(2)	99.760(3)	92.077(2)	102.4960(10)
γ/degree	69.046(5)	90.00	90	103.656(2)	90.00
Volume ($Å^3$)	2303.2(2)	3866.48(12)	4642.9(3)	2080.94(9)	4819.76(12)
Z	2	4	4	2	4
D_{calcd}, g cm^{-3}	1.223	1.372	1.352	1.563	1.422
μ/mm^{-1}	0.234	0.280	0.576	0.705	3.057
F(000)	896.0	1648.0	1960.0	990.0	2096.0
2θ range (degree)	3.332 to 50	4.012 to 49.998	4.066 to 50	4.29 to 50	3.65 to 50
Limiting Indices	*-10 ≤ h ≤ 10* *-13 ≤ k ≤ 13* *-29 ≤ l ≤ 29*	*-14 ≤ h ≤ 14* *-33 ≤ k ≤ 33* *-14 ≤ l ≤ 15*	*-12 ≤ h ≤ 13* *-38 ≤ k ≤ 40* *-14 ≤ l ≤ 14*	*-10 ≤ h ≤ 10* *-14 ≤ k ≤ 14* *-23 ≤ l ≤ 23*	*-19 ≤ h ≤ 19* *-18 ≤ k ≤ 18* *-22 ≤ l ≤ 22*
Total/ unique no. of reflns	20848 / 8109	84590 / 6794	36105/ 8148	31769/ 7313	83399/ 8484
R_{int}	0.0986	0.0628	0.0842	0.0347	0.0328
Data / restr./params.	8109/0/467	6794/186/458	8148/0/518	7313/154/580	8484/1/552
GOF (F^2)	1.062	1.987	1.305	1.025	1.045
R_1, wR_2	0.1202, 0.2962	0.1103, 0.3948	0.1003, 0.2126	0.0308, 0.0739	0.0177, 0.0401
R indices (all data) R_1, wR_2	0.1790, 0.3438	0.1156, 0.4059	0.1215, 0.2204	0.0367, 0.0764	0.0216, 0.0412
Largest different peak and hole (e $Å^{-3}$)	0.73, –0.48	1.07, –1.34	1.01, –1.67	1.12, –0.50	0.65/-0.39

	7a$[BF_4]_2$	**7b**$[NTf_2]_2$	**8**	**7b**$[NTf_2]_2$
Empirical formula	$C_{32}H_{39}B_2F_8NO_2P_2PtS$	$C_{47}H_{35}F_{13}N_2O_8P_2PtS_5$	$C_{28}H_{28}ClOP_2RhS$	$C_{29.25}H_{31.5}BCl_{0.5}F_4P_2PtS$
Formula weight	932.35	1420.10	612.86	776.67
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	293(2)	150 (2)	150 (2)	293(2)
Crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
Space group	*P-1*	*P21/c*	*P212121*	*Pbam*
a/Å	10.7270(2)	23.6369(3)	10.4581(2)	20.9374(6)
b/Å	13.1882(2)	12.7303(2)	14.2792(3)	10.9959(3)
c/Å	15.1430(2)	18.9449(2)	17.4031(4)	14.9555(5)
α/degree	65.687(2)	90	90	90
β/degree	75.1110(10)	98.2970(10)	90	90
γ/degree	75.5460(10)	90	90	90
Volume ($Å^3$)	1861.41(6)	5640.95(13)	2598.86(9)	3443.14(18)
Z	2	4	4	4
D_{calcd}, g cm^{-3}	1.663	1.672	1.566	1.498
μ/mm^{-1}	3.981	2.823	0.984	4.305
F(000)	920.0	2800.0	1248.0	1522.0
2θ range (degree)	3.982 to 50	3.868 to 49.996	4.544 to 49.994	4.992 to 64.214
Limiting Indices	*-12 ≤ h ≤ 12* *-15 ≤ k ≤ 15* *-17 ≤ l ≤ 17*	*-28 ≤ h ≤ 28* *-15 ≤ k ≤ 15* *-22 ≤ l ≤ 21*	*-11 ≤ h ≤ 12* *-16 ≤ k ≤ 16* *-20 ≤ l ≤ 17*	*-24 ≤ h ≤ 30* *-13 ≤ k ≤ 14* *-15 ≤ l ≤ 19*
Total/ unique no. of reflns	25834/ 6546	92765/9935	21884/4575	17185/4698
Rint	0.0281	0.0500	0.0291	0.0391
Data / restr./params.	6546/17/393	9935/9/793	4575/0/307	4698/2/225
GOF (F^2)	1.049	1.033	1.044	1.083
R_1, wR_2	0.0286, 0.0722	0.0346, 0.0897	0.0191, 0.0449	0.0454, 0.1063
R indices (all data) R_1, wR_2	0.0323, 0.0738	0.0385, 0.0923	0.0207, 0.0455	0.0652, 0.1137
Largest different peak and hole (e $Å^{-3}$)	1.51, -0.83	1.17, -0.68	0.35, -0.28	1.52, -0.96

3. Computational details:

3.1. Geometry optimizations:

All molecular models were created using GaussView 6.0[10] and all optimization and frequency calculations were performed using Gaussian 16 program[11] with ωB97XD[12] functional and def2TZVP[13] basis set, def2-ECP was used for Rh and Pt metals. Frequency calculations were performed on the optimized geometries to confirm that they are local minimum in the potential energy surface. The coordinates of the optimized geometries are given in **section 3.9**. Bond Dissociation Energies (BDE) for the simplified monodentate complexes were calculated thermal free energies of the model complexes and the optimized ligand and metal fragments. The BDE values are given in **table S1**.

3.2. General details of ALMO-EDA calculations:

All ALMO-EDA[14] calculations and deformation density plots were calculated using Q-chem 5.4[15] program with ωB97X[16] functional and def2TZVP[13] basis set, def2-ECP was used for Rh and Pt metals. Deformation density plots were visualized using IQmol 2.15.3 program[17]. The results of the ALMO-EDA analysis are given below.

3.3. ALMO-EDA analysis of model pincer complexes 10a-16b:

The results EDA results from ALMO-EDA calculations for the model complexes **10a-16b** are given in the following table.

Table S1: EDA results from ALMO-EDA calculations for the model complexes **10a-16b** (all energies are given in kcal/mol).

Entry	Model complex	BDE	ΔE_{int}	ΔE_{orb}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{disp}
1	**10a**	-38.57	-38.88	-86.04	-73.75	135.11	-14.20
2	**10b**	-36.96	-36.38	-79.21	-80.56	141.81	-18.43
3	**11a**	-36.21	-37.96	-54.94	-85.13	116.01	-13.90
4	**11b**	-38.19	-38.00	-56.18	-87.45	121.81	-16.17
5	**12a**	-39.82	-41.23	-69.41	-95.82	138.71	-14.71
6	**12b**	-44.55	-43.28	-75.80	-105.34	155.19	-17.34
7	**13a**	-70.06	-58.01	-83.95	-150.52	193.26	-16.80
8	**13b**	-57.77	-56.80	-83.83	-144.20	191.32	-20.10
9	**14a**	-56.76	-57.99	-100.38	-125.23	181.39	-13.77
10	**14b**	-53.16	-53.26	-94.00	-116.92	174.61	-16.96
11	**14c**	-51.35	-49.12	-86.58	-124.54	181.48	-19.47
12	**15a**	-30.55	-30.11	-62.61	-64.66	108.55	-11.40
13	**15b**	-57.57	-58.76	-118.80	-80.65	154.40	-13.72
14	**15c**	-53.16	-55.73	-103.95	-115.24	184.08	-20.61
15	**16a**	+48.60	45.47	-58.63	25.85	89.26	-11.01
16	**16b**	+30.66	31.00	-57.45	10.92	92.73	-15.20

3.4. ETS-NOCV analysis results from ALMO-EDA calculations for model complexes 10a-18b.

The ETS-NOCV results from ALMO-EDA calculations for the model complexes **10a**-**18b** are given below (**Table S2-S21**). Each row in the tables corresponds to the relevant NOCV pair, eigenvalue of the deformation density and the orbital interaction energy (ΔE_{orb}) of the corresponding interaction. Deformation densities with the highest orbital interaction energies (ΔE_{orb} > 2.5 kcal/mol) in **Tables S2-S21** are highlighted in bold. The plots of selected deformation densities were visualized (complexes with monodentate ligands in **Table S22**, complexes with pincer ligands in **Table S23**). In model complexes **10a**–**16b**, making two fragments involves breaking only one bond between the metal atom and the donor atom of the ligand. However, in model pincer complexes **17a**-**18b** (shown in **Table S22**), three bonds are broken during such fragmentation. Therefore, all highest energy interactions in the complexes **10a**-**16b** of the monodentate ligands (reported in **Table 1** of the main text) are the interactions between the donor atom and the metal atom. On the other hand, in the model pincer complexes **17a**-**18b**, the interaction energies between the phosphine arms and the metal center are also significant. Hence, deformation density plots of all highest energy interactions of the pincer complexes (shown in **Table S23**) were carefully inspected, in order to discriminate the σ- and π-interaction of the metal with the central donor atom from those with the flanking phosphine arms. Only the energies corresponding to the first category (the highlighted deformation density plots in **Table S23**) are those reported in **Table 2** of the main text.

All energies in the following tables are in kcal/mol.

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Table S2: $[(SMe_3)(PH_3)_2RhCl]^+$, **10a**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 371	**0.483**	**-22.888**
2 -> 370	**0.442**	**-32.2558**
3 -> 369	**0.413**	**-21.0389**
4 -> 368	**0.145**	**-4.54829**
5 -> 367	0.085	-1.11228
6 -> 366	0.071	-1.3517
7 -> 365	0.062	-0.9377
8 -> 364	0.051	-0.60074
9 -> 363	0.046	-0.51722
10 -> 362	0.045	-0.3617
11 -> 361	0.041	-0.44695
12 -> 360	0.034	-0.1825
13 -> 359	0.03	-0.14417
14 -> 358	0.029	-0.26093
15 -> 357	0.022	-0.15586
16 -> 356	0.022	-0.138
17 -> 355	0.02	-0.04464
18 -> 354	0.019	-0.12286
19 -> 353	0.018	-0.05047
20 -> 352	0.015	-0.03079
21 -> 351	0.012	-0.05374
22 -> 350	0.012	-0.02275
23 -> 349	0.011	-0.03451
24 -> 348	0.011	-0.01258
25 -> 347	0.01	-0.03101

Table S3: $[(SPh_3)(PH_3)_2RhCl]^+$, **10b**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 872	**0.47**	**-21.2994**
2 -> 871	**0.441**	**-31.1321**
3 -> 870	**0.389**	**-18.1002**
4 -> 869	**0.138**	**-4.06699**
5 -> 868	0.088	-1.03879
6 -> 867	0.067	-0.97078
7 -> 866	0.057	-0.59784
8 -> 865	0.051	-0.64094

9 -> 864	0.047	-0.54994
10 -> 863	0.043	-0.40006
11 -> 862	0.037	-0.22865
12 -> 861	0.035	-0.18857
13 -> 860	0.031	-0.25474
14 -> 859	0.028	-0.13421
15 -> 858	0.027	-0.15002
16 -> 857	0.025	-0.13596
17 -> 856	0.021	-0.13354
18 -> 855	0.021	-0.08458
19 -> 854	0.019	-0.08117
20 -> 853	0.018	-0.05546
21 -> 852	0.016	-0.05767
22 -> 851	0.015	-0.04757
23 -> 850	0.013	-0.03067
24 -> 849	0.013	-0.05426
25 -> 848	0.011	-0.03511
26 -> 847	0.011	-0.04457
27 -> 846	0.01	-0.02359

Table S4: $[(SMe_2)(PH_3)_2RhCl]$, **11a**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 322	**0.515**	**-35.0343**
2 -> 321	**0.278**	**-8.79744**
3 -> 320	**0.204**	**-6.09343**
4 -> 319	**0.123**	**-3.40781**
5 -> 318	0.058	-0.62537
6 -> 317	0.05	-0.46682
7 -> 316	0.041	-0.31994
8 -> 315	0.034	-0.23309
9 -> 314	0.033	-0.24929
10 -> 313	0.028	-0.12065
11 -> 312	0.027	-0.12907
12 -> 311	0.019	-0.0925
13 -> 310	0.019	-0.07404
14 -> 309	0.017	-0.08474
15 -> 308	0.017	-0.05222
16 -> 307	0.014	-0.03331
17 -> 306	0.012	-0.02938
18 -> 305	0.012	-0.01889
19 -> 304	0.011	-0.0251

Table S5: $[(SPh_2)(PH_3)_2RhCl]$, **11b**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 656	**0.502**	**-34.3907**
2 -> 655	**0.282**	**-9.2015**
3 -> 654	**0.227**	**-6.90653**
4 -> 653	**0.13**	**-3.4416**
5 -> 652	0.061	-0.62894
6 -> 651	0.059	-0.51667
7 -> 650	0.055	-0.40061
8 -> 649	0.04	-0.2735
9 -> 648	0.033	-0.2861
10 -> 647	0.03	-0.13598
11 -> 646	0.03	-0.1801
12 -> 645	0.028	-0.17693
13 -> 644	0.025	-0.11597
14 -> 643	0.024	-0.12672
15 -> 642	0.02	-0.07123
16 -> 641	0.018	-0.07169
17 -> 640	0.016	-0.05282
18 -> 639	0.014	-0.04512
19 -> 638	0.013	-0.03108
20 -> 637	0.012	-0.02827

21 -> 636	0.011	-0.02582
22 -> 635	0.01	-0.04097

Table S6: [(DMSO)(PH_3)$_2$RhCl], **12a**

NOCV pairs	Eigenvalue ($\|\upsilon_n\|$)	$\Delta E_{orb(n)}$
1 -> 353	**0.556**	**-39.8206**
2 -> 352	**0.344**	**-13.005**
3 -> 351	**0.303**	**-11.4101**
4 -> 350	**0.112**	**-3.5472**
5 -> 349	0.054	-0.57684
6 -> 348	0.041	-0.38652
7 -> 347	0.039	-0.39053
8 -> 346	0.035	-0.29374
9 -> 345	0.032	-0.26928
10 -> 344	0.028	-0.14378
11 -> 343	0.025	-0.16414
12 -> 342	0.023	-0.17302
13 -> 341	0.022	-0.10788
14 -> 340	0.02	-0.19195
15 -> 339	0.019	-0.06775
16 -> 338	0.018	-0.06876
17 -> 337	0.015	-0.06492
18 -> 336	0.015	-0.0463
19 -> 335	0.014	-0.03703
20 -> 334	0.011	-0.02352

Table S7: [(Ph_2SO)(PH_3)$_2$RhCl], **12b**

NOCV pairs	Eigenvalue ($\|\upsilon_n\|$)	$\Delta E_{orb(n)}$
1 -> 687	**0.547**	**-40.7343**
2 -> 686	**0.389**	**-15.9253**
3 -> 685	**0.318**	**-12.9919**
4 -> 684	**0.119**	**-3.57595**
5 -> 683	0.062	-0.61553
6 -> 682	0.058	-0.51965
7 -> 681	0.05	-0.43872
8 -> 680	0.041	-0.34486
9 -> 679	0.037	-0.30842
10 -> 678	0.031	-0.24833
11 -> 677	0.03	-0.24041
12 -> 676	0.028	-0.13524
13 -> 675	0.027	-0.32239
14 -> 674	0.024	-0.11978
15 -> 673	0.021	-0.11618
16 -> 672	0.021	-0.12355
17 -> 671	0.018	-0.09854
18 -> 670	0.017	-0.0426
19 -> 669	0.016	-0.06586
20 -> 668	0.015	-0.04783
21 -> 667	0.013	-0.04934
22 -> 666	0.013	-0.03722
23 -> 665	0.012	-0.03991
24 -> 664	0.011	-0.03648

Table S8: [(PMe_3)(PH_3)$_2$RhCl], **13a**

NOCV pairs	Eigenvalue ($\|\upsilon_n\|$)	$\Delta E_{orb(n)}$
1 -> 371	**0.633**	**-56.6936**
2 -> 370	**0.323**	**-11.6232**
3 -> 369	**0.278**	**-10.4428**
4 -> 368	**0.13**	**-3.93**
5 -> 367	0.052	-0.5357
6 -> 366	0.047	-0.44414
7 -> 365	0.036	-0.26834
8 -> 364	0.032	-0.22834
9 -> 363	0.03	-0.08863

10 -> 362	0.028	-0.17419
11 -> 361	0.025	-0.11486
12 -> 360	0.023	-0.0973
13 -> 359	0.021	-0.0959
14 -> 358	0.019	-0.12449
15 -> 357	0.018	-0.08825
16 -> 356	0.016	-0.04632
17 -> 355	0.014	-0.0379
18 -> 354	0.013	-0.03677
19 -> 353	0.013	-0.0312
20 -> 352	0.013	-0.04399
21 -> 351	0.011	-0.04769
22 -> 350	0.011	-0.01363

Table S9: $[(PPh_3)(PH_3)_2RhCl]$, **13b**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 872	**0.62**	**-53.3144**
2 -> 871	**0.348**	**-13.0266**
3 -> 870	**0.294**	**-11.1584**
4 -> 869	**0.13**	**-3.76034**
5 -> 868	0.065	-0.74686
6 -> 867	0.061	-0.57502
7 -> 866	0.049	-0.38122
8 -> 865	0.041	-0.32729
9 -> 864	0.038	-0.17563
10 -> 863	0.032	-0.2579
11 -> 862	0.029	-0.24631
12 -> 861	0.029	-0.17256
13 -> 860	0.027	-0.12845
14 -> 859	0.026	-0.1247
15 -> 858	0.022	-0.09566
16 -> 857	0.02	-0.10673
17 -> 856	0.019	-0.09626
18 -> 855	0.019	-0.0829
19 -> 854	0.017	-0.06175
20 -> 853	0.016	-0.03914
21 -> 852	0.015	-0.05381
22 -> 851	0.013	-0.04728
23 -> 850	0.012	-0.03912
24 -> 849	0.012	-0.03619
25 -> 848	0.011	-0.05906

Table S10: $[(PF_3)(PH_3)_2RhCl]$, **14a**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 317	**0.582**	**-51.8275**
2 -> 316	**0.466**	**-23.5887**
3 -> 315	**0.385**	**-20.0155**
4 -> 314	**0.117**	**-3.8987**
5 -> 313	0.058	-0.57497
6 -> 312	0.048	-0.4679
7 -> 311	0.032	-0.10034
8 -> 310	0.031	-0.57374
9 -> 309	0.026	-0.16001
10 -> 308	0.024	-0.13181
11 -> 307	0.023	-0.16577
12 -> 306	0.02	-0.057
13 -> 305	0.018	-0.07956
14 -> 304	0.017	-0.0576
15 -> 303	0.015	-0.0829
16 -> 302	0.014	-0.05419
17 -> 301	0.013	-0.0474
18 -> 300	0.013	-0.03953
19 -> 299	0.012	-0.04922
20 -> 298	0.011	-0.03379

Table S11: [$(P(CF_3)_3)(PH_3)_2RhCl$], **14b**

NOCV pairs	Eigenvalue (υ_n)	$\Delta E_{orb(n)}$
1 -> 596	**0.557**	**-46.8873**
2 -> 595	**0.465**	**-21.7612**
3 -> 594	**0.398**	**-18.9917**
4 -> 593	**0.13**	**-4.00109**
5 -> 592	0.072	-0.76841
6 -> 591	0.053	-0.56777
7 -> 590	0.037	-0.36535
8 -> 589	0.032	-0.26484
9 -> 588	0.031	-0.22202
10 -> 587	0.031	-0.18706
11 -> 586	0.028	-0.15391
12 -> 585	0.028	-0.17438
13 -> 584	0.025	-0.16387
14 -> 583	0.025	-0.18494
15 -> 582	0.022	-0.18852
16 -> 581	0.02	-0.11386
17 -> 580	0.018	-0.09744
18 -> 579	0.016	-0.08124
19 -> 578	0.015	-0.05035
20 -> 577	0.013	-0.06187
21 -> 576	0.013	-0.0383
22 -> 575	0.012	-0.04176
23 -> 574	0.011	-0.02959
24 -> 573	0.011	-0.03667

Table S12: [$(P(C_6F_5)_3)(PH_3)_2RhCl$], **14c**

NOCV pairs	Eigenvalue (υ_n)	$\Delta E_{orb(n)}$
1 -> 1247	**0.577**	**-47.7922**
2 -> 1246	**0.392**	**-16.6418**
3 -> 1245	**0.365**	**-15.5711**
4 -> 1244	**0.147**	**-3.92066**
5 -> 1243	0.065	-0.65746
6 -> 1242	0.058	-0.63401
7 -> 1241	0.047	-0.45833
8 -> 1240	0.04	-0.35695
9 -> 1239	0.036	-0.27682
10 -> 1238	0.032	-0.20623
11 -> 1237	0.029	-0.17244
12 -> 1236	0.028	-0.17942
13 -> 1235	0.027	-0.18466
14 -> 1234	0.025	-0.21926
15 -> 1233	0.023	-0.16944
16 -> 1232	0.02	-0.10277
17 -> 1231	0.018	-0.0833
18 -> 1230	0.017	-0.07706
19 -> 1229	0.017	-0.07718
20 -> 1228	0.016	-0.06574
21 -> 1227	0.015	-0.06494
22 -> 1226	0.015	-0.0613
23 -> 1225	0.012	-0.04246
24 -> 1224	0.012	-0.05503
25 -> 1223	0.011	-0.04056
26 -> 1222	0.01	-0.04327

Table S13: $[(NHN)(PH_3)_2RhCl]^+$, **15a**

NOCV pairs	Eigenvalue (υ_n)	$\Delta E_{orb(n)}$
1 -> 366	**0.673**	**-21.3717**
2 -> 365	**0.382**	**-25.3039**
3 -> 364	**0.215**	**-7.82381**
4 -> 363	**0.127**	**-3.96461**
5 -> 362	0.071	-0.67709
6 -> 361	0.067	-0.85778

7 -> 360	0.06	-0.92374
8 -> 359	0.05	-0.51031
9 -> 358	0.046	-0.35122
10 -> 357	0.043	-0.37939
11 -> 356	0.036	-0.36331
12 -> 355	0.03	-0.22442
13 -> 354	0.028	-0.18314
14 -> 353	0.023	-0.14244
15 -> 352	0.021	-0.08729
16 -> 351	0.018	-0.08244
17 -> 350	0.014	-0.0804
18 -> 349	0.013	-0.03341
19 -> 348	0.013	-0.03281
20 -> 347	0.012	-0.01574
21 -> 346	0.01	-0.01639
22 -> 345	0.01	-0.01997

Table S14: $[(NHP)(PH_3)_2RhCl]^+$, **15b**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 372	**0.676**	**-34.8235**
2 -> 371	**0.535**	**-42.9273**
3 -> 370	**0.437**	**-27.5978**
4 -> 369	**0.154**	**-5.99222**
5 -> 368	0.1	-1.46431
6 -> 367	0.087	-1.93637
7 -> 366	0.077	-0.72036
8 -> 365	0.069	-1.16698
9 -> 364	0.062	-0.98693
10 -> 363	0.043	-0.46493
11 -> 362	0.043	-0.46949
12 -> 361	0.039	-0.41004
13 -> 360	0.035	-0.22385
14 -> 359	0.03	-0.10188
15 -> 358	0.03	-0.20417
16 -> 357	0.021	-0.03684
17 -> 356	0.02	-0.04188
18 -> 355	0.019	-0.02707
19 -> 354	0.018	-0.02964
20 -> 353	0.017	-0.03833
21 -> 352	0.015	-0.02518
22 -> 351	0.013	-0.02993
23 -> 350	0.013	-0.09566
24 -> 349	0.013	-0.04572
25 -> 348	0.011	-0.03269
26 -> 347	0.011	-0.03744

Table S15: $[(PR_3)(PH_3)_2RhCl]^{3+}$, **15c**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 1277	**0.54**	**-44.4321**
2 -> 1276	**0.497**	**-25.301**
3 -> 1275	**0.431**	**-20.8725**
4 -> 1274	**0.171**	**-5.63568**
5 -> 1273	0.103	-1.41199
6 -> 1272	0.084	-1.60639
7 -> 1271	0.07	-1.0896
8 -> 1270	0.066	-0.75653
9 -> 1269	0.06	-0.84893
10 -> 1268	0.056	-0.84312
11 -> 1267	0.049	-0.6354
12 -> 1266	0.046	-0.4927
13 -> 1265	0.043	-0.40807
14 -> 1264	0.034	-0.18554
15 -> 1263	0.032	-0.18566
16 -> 1262	0.027	-0.14657

17 -> 1261	0.023	-0.09362
18 -> 1260	0.022	-0.07822
19 -> 1259	0.019	-0.05921
20 -> 1258	0.018	-0.06552
21 -> 1257	0.017	-0.08004
22 -> 1256	0.016	-0.07747
23 -> 1255	0.015	-0.04092
24 -> 1254	0.014	-0.03667
25 -> 1253	0.014	-0.02479
26 -> 1252	0.013	-0.03048
27 -> 1251	0.013	-0.0445
28 -> 1250	0.012	-0.04188
29 -> 1249	0.011	-0.02815
30 -> 1248	0.011	-0.02837
31 -> 1247	0.011	-0.03086

Table S16: $[(SMe_3)PtMe]^{2+}$, **16a**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 383	**0.401**	**-33.7422**
2 -> 382	**0.269**	**-8.57897**
3 -> 381	**0.255**	**-8.61754**
4 -> 380	**0.117**	**-2.98668**
5 -> 379	0.058	-0.86551
6 -> 378	0.055	-0.79817
7 -> 377	0.047	-0.50734
8 -> 376	0.045	-0.48626
9 -> 375	0.043	-0.49462
10 -> 374	0.039	-0.38107
11 -> 373	0.038	-0.36336
12 -> 372	0.033	-0.31855
13 -> 371	0.026	-0.28586
14 -> 370	0.024	-0.1745
15 -> 369	0.022	-0.12158
16 -> 368	0.021	-0.0648
17 -> 367	0.019	-0.0965
18 -> 366	0.018	-0.09283
19 -> 365	0.017	-0.07634
20 -> 364	0.015	-0.06713
21 -> 363	0.014	-0.07255
22 -> 362	0.014	-0.05678
23 -> 361	0.013	-0.05333
24 -> 360	0.011	-0.03648

Table S17: $[(SPh_3)PtMe]^{2+}$, **16b**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 884	**0.422**	**-32.8406**
2 -> 883	**0.239**	**-7.10914**
3 -> 882	**0.209**	**-6.42324**
4 -> 881	**0.115**	**-2.63633**
5 -> 880	0.08	-1.2755
6 -> 879	0.076	-1.0993
7 -> 878	0.07	-0.9593
8 -> 877	0.058	-0.69593
9 -> 876	0.051	-0.64102
10 -> 875	0.049	-0.45998
11 -> 874	0.042	-0.61147
12 -> 873	0.039	-0.38542
13 -> 872	0.035	-0.30014
14 -> 871	0.032	-0.24353
15 -> 870	0.028	-0.21758
16 -> 869	0.027	-0.19831
17 -> 868	0.024	-0.18473
18 -> 867	0.023	-0.15245
19 -> 866	0.022	-0.11772

20 -> 865	0.021	-0.12382
21 -> 864	0.02	-0.12914
22 -> 863	0.02	-0.0881
23 -> 862	0.019	-0.09682
24 -> 861	0.019	-0.0941
25 -> 860	0.019	-0.07836
26 -> 859	0.018	-0.08292
27 -> 858	0.017	-0.07783
28 -> 857	0.017	-0.06199
29 -> 856	0.017	-0.05942
30 -> 855	0.016	-0.0701
31 -> 854	0.015	-0.05282
32 -> 853	0.014	-0.05544
33 -> 852	0.014	-0.04637
34 -> 851	0.013	-0.04687
35 -> 850	0.012	-0.04973
36 -> 849	0.012	-0.04498
37 -> 848	0.011	-0.03466
38 -> 847	0.011	-0.04279
39 -> 846	0.011	-0.05184
40 -> 845	0.01	-0.04327

Table S18: $[(Me\text{-}PSP)RhCl]^+$, **17a**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 433	**1.167**	**-102.502**
2 -> 432	**0.588**	**-33.3825**
3 -> 431	**0.465**	**-29.9982**
4 -> 430	**0.332**	**-16.7944**
5 -> 429	**0.265**	**-19.911**
6 -> 428	**0.217**	**-25.7976**
7 -> 427	**0.207**	**-7.80713**
8 -> 426	**0.119**	**-5.5175**
9 -> 425	0.091	-1.24735
10 -> 424	0.071	-0.87367
11 -> 423	0.038	-0.32443
12 -> 422	0.036	-0.38011
13 -> 421	0.035	-0.25358
14 -> 420	0.03	-0.13826
15 -> 419	0.03	-0.28195
16 -> 418	0.027	-0.13421
17 -> 417	0.025	-0.08412
18 -> 416	0.022	-0.03912
19 -> 415	0.018	-0.03264
20 -> 414	0.017	-0.12274
21 -> 413	0.016	-0.06353
22 -> 412	0.015	-0.01788
23 -> 411	0.015	0.001872
24 -> 410	0.013	-0.0059
25 -> 409	0.013	-0.02734
26 -> 408	0.011	-0.01692
27 -> 407	0.011	-0.0151
28 -> 406	0.01	-0.0251

Table S19: $[(aromaticPh\text{-}PSP)RhCl]^+$, **17b**

NOCV pairs	Eigenvalue ($\lvert\upsilon_n\rvert$)	$\Delta E_{orb(n)}$
1 -> 848	**1.156**	**-99.5774**
2 -> 847	**0.542**	**-29.0778**
3 -> 846	**0.468**	**-30.0241**
4 -> 845	**0.338**	**-17.5962**
5 -> 844	**0.262**	**-18.1708**
6 -> 843	**0.221**	**-26.4948**
7 -> 842	**0.205**	**-8.00894**
8 -> 841	**0.118**	**-5.59308**
9 -> 840	0.08	-1.10971

10 -> 839	0.072	-0.88824
11 -> 838	0.039	-0.3558
12 -> 837	0.037	-0.32621
13 -> 836	0.035	-0.31332
14 -> 835	0.031	-0.20827
15 -> 834	0.028	-0.11995
16 -> 833	0.028	-0.18907
17 -> 832	0.025	-0.08532
18 -> 831	0.022	-0.07699
19 -> 830	0.021	-0.02825
20 -> 829	0.02	-0.04608
21 -> 828	0.018	-0.08162
22 -> 827	0.017	-0.04668
23 -> 826	0.017	-0.09103
24 -> 825	0.015	-0.06166
25 -> 824	0.014	-0.0187
26 -> 823	0.013	-0.04584
27 -> 822	0.011	-0.03641

Table S20: [(Me-PSP)PtMe]$^{2+}$, **18a**

NOCV pairs	Eigenvalue ($\|\upsilon_n\|$)	$\Delta E_{orb(n)}$
1 -> 445	**1.072**	**-142.996**
2 -> 444	**0.399**	**-22.17**
3 -> 443	**0.369**	**-47.1645**
4 -> 442	**0.35**	**-17.5457**
5 -> 441	**0.312**	**-17.8781**
6 -> 440	**0.287**	**-15.3321**
7 -> 439	**0.235**	**-21.7597**
8 -> 438	**0.166**	**-10.3801**
9 -> 437	0.089	-2.23205
10 -> 436	0.088	-1.76839
11 -> 435	0.072	-1.43573
12 -> 434	0.063	-0.70258
13 -> 433	0.053	-0.35237
14 -> 432	0.053	-0.54012
15 -> 431	0.042	-0.60214
16 -> 430	0.04	-0.62148
17 -> 429	0.04	-0.41076
18 -> 428	0.038	-0.29592
19 -> 427	0.037	-0.41438
20 -> 426	0.034	-0.34438
21 -> 425	0.033	-0.3089
22 -> 424	0.03	-0.31162
23 -> 423	0.029	-0.25843
24 -> 422	0.028	-0.18734
25 -> 421	0.028	-0.1841
26 -> 420	0.027	-0.18194
27 -> 419	0.024	-0.14599
28 -> 418	0.023	-0.17234
29 -> 417	0.015	-0.04411
30 -> 416	0.015	-0.06374
31 -> 415	0.015	-0.06372
32 -> 414	0.011	0.004104

Table S21: [(aromaticPh-PSP)PtMe]$^{2+}$, **18b**

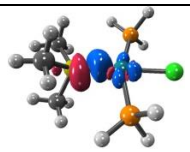
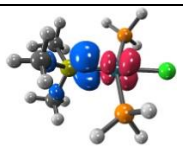
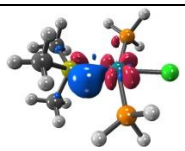
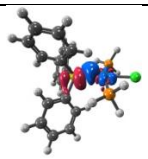
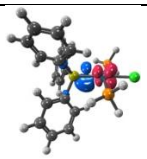
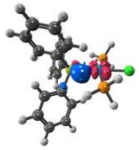
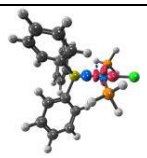
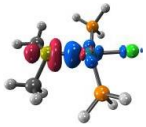
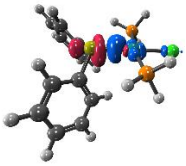
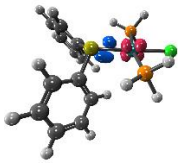
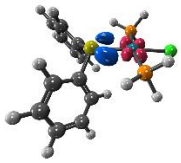
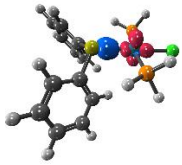
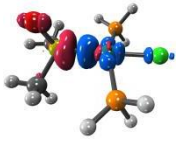
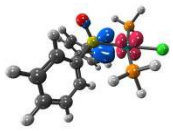
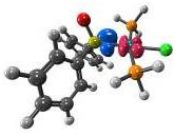
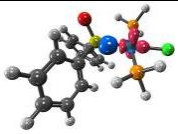
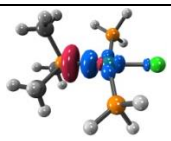
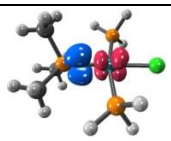
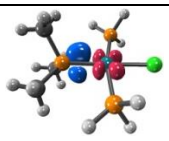
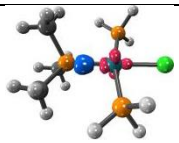
NOCV pairs	Eigenvalue ($\|\upsilon_n\|$)	$\Delta E_{orb(n)}$
1 -> 860	**1.077**	**-141.346**
2 -> 859	**0.387**	**-45.023**
3 -> 858	**0.354**	**-22.7034**
4 -> 857	**0.342**	**-18.8704**
5 -> 856	**0.306**	**-16.9536**
6 -> 855	**0.285**	**-15.5201**
7 -> 854	**0.247**	**-21.9136**
8 -> 853	**0.16**	**-9.86916**

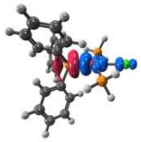
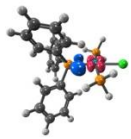
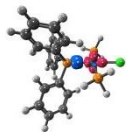
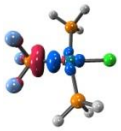
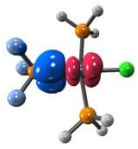
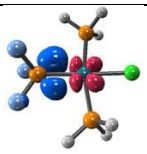
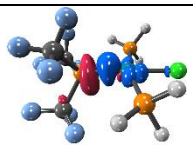
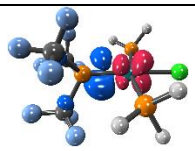
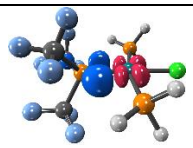
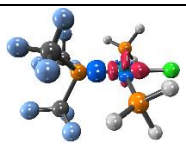
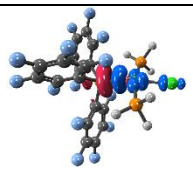
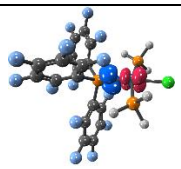
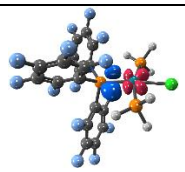
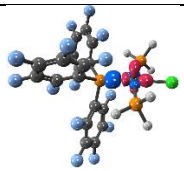
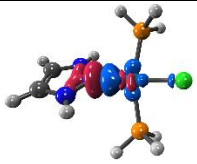
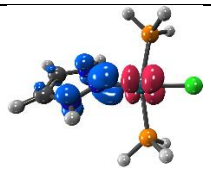
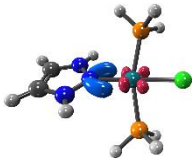
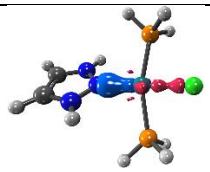
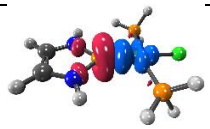
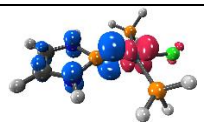
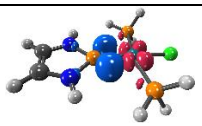
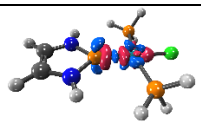
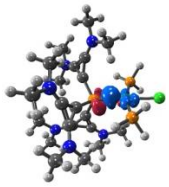
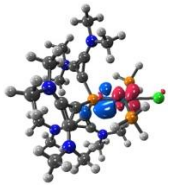
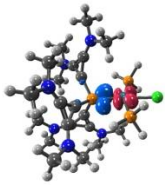
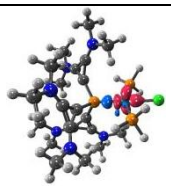
9 -> 852	0.09	-1.90375
10 -> 851	0.087	-1.33541
11 -> 850	0.083	-1.4735
12 -> 849	0.077	-1.37455
13 -> 848	0.075	-1.37494
14 -> 847	0.065	-1.18411
15 -> 846	0.061	-0.8267
16 -> 845	0.057	-0.69043
17 -> 844	0.055	-0.63746
18 -> 843	0.049	-0.75062
19 -> 842	0.047	-0.50297
20 -> 841	0.043	-0.33451
21 -> 840	0.04	-0.51814
22 -> 839	0.037	-0.34997
23 -> 838	0.036	-0.27924
24 -> 837	0.033	-0.33835
25 -> 836	0.032	-0.34255
26 -> 835	0.03	-0.19577
27 -> 834	0.028	-0.19056
28 -> 833	0.027	-0.17563

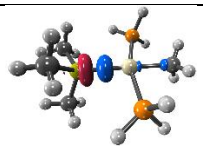
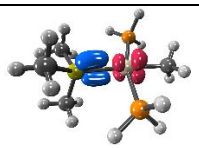
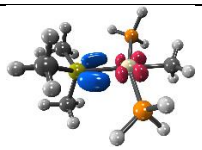
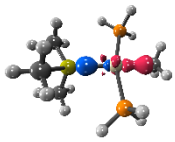
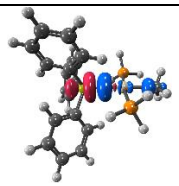
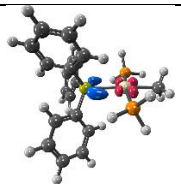
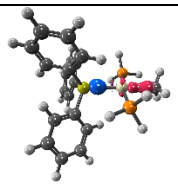
29 -> 832	0.024	-0.1457
30 -> 831	0.024	-0.13435
31 -> 830	0.023	-0.1265
32 -> 829	0.023	-0.12002
33 -> 828	0.02	-0.12631
34 -> 827	0.019	-0.14436
35 -> 826	0.019	-0.09864
36 -> 825	0.018	-0.09103
37 -> 824	0.017	-0.09295
38 -> 823	0.016	-0.05986
39 -> 822	0.016	-0.05402
40 -> 821	0.014	-0.07579
41 -> 820	0.014	-0.05426
42 -> 819	0.013	-0.0511
43 -> 818	0.013	-0.05422
44 -> 817	0.012	-0.05011
45 -> 816	0.012	-0.03372
46 -> 815	0.011	-0.03898
47 -> 814	0.01	-0.02546
48 -> 813	0.01	-0.03871

3.5. Selected deformation density plots of model complexes 10a-16b

Table S22: Selected deformation density plots of model complexes **10a-16b** (all energies are in kcal/mol).

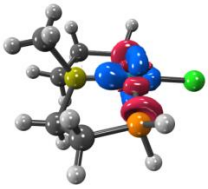
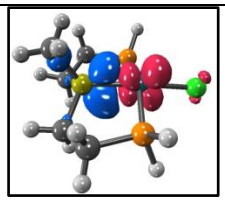
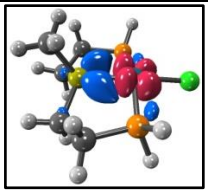
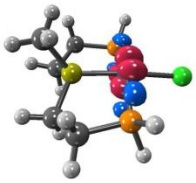
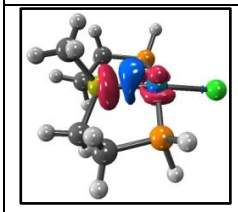
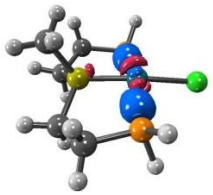
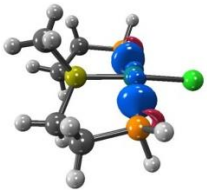
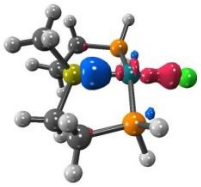
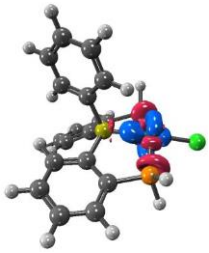
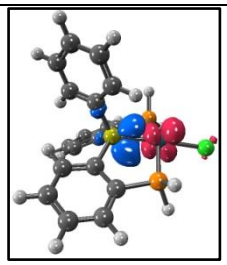
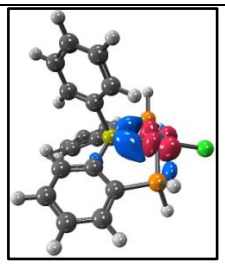
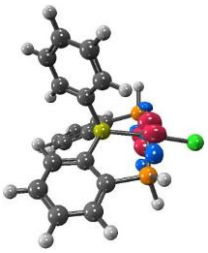
Model complex	L→M σ-donation	M→L π-backdonation		M→L σ-backdonation
10a	 $\|\upsilon_2\|$ = 0.442 ΔE = -32.26	 $\|\upsilon_1\|$ = 0.483 ΔE = -22.89	 $\|\upsilon_3\|$ = 0.413 ΔE = -21.04	 $\|\upsilon_4\|$ = 0.145 ΔE = -4.55
10b	 $\|\upsilon_2\|$ = 0.441 ΔE = -31.13	 $\|\upsilon_1\|$ = 0.470 ΔE = -21.30	 $\|\upsilon_3\|$ = 0.389 ΔE = -18.10	 $\|\upsilon_4\|$ = 0.138 ΔE = -4.07
11a	 $\|\upsilon_1\|$ = 0.515 ΔE = -35.03	 $\|\upsilon_2\|$ = 0.278 ΔE = -8.80	 $\|\upsilon_3\|$ = 0.204 ΔE = -6.09	 $\|\upsilon_4\|$ = 0.123 ΔE = -3.41
11b	 $\|\upsilon_1\|$ = 0.502 ΔE = -34.39	 $\|\upsilon_3\|$ = 0.227 ΔE = -6.90	 $\|\upsilon_2\|$ = 0.282 ΔE = -9.20	 $\|\upsilon_4\|$ = 0.130 ΔE = -3.44
12a	 $\|\upsilon_1\|$ = 0.556 ΔE = -39.82	 $\|\upsilon_2\|$ = 0.344 ΔE = -13.01	 $\|\upsilon_3\|$ = 0.303 ΔE = -11.41	 $\|\upsilon_4\|$ = 0.112 ΔE = -3.55
12b	 $\|\upsilon_1\|$ = 0.547 ΔE = -40.73	 $\|\upsilon_2\|$ = 0.389 ΔE =-15.93	 $\|\upsilon_3\|$ = 0.318 ΔE =-12.99	 $\|\upsilon_4\|$ = 0.119 ΔE =-3.58
13a	 $\|\upsilon_1\|$ = 0.633 ΔE = -56.69	 $\|\upsilon_2\|$ = 0.323 ΔE = -11.62	 $\|\upsilon_3\|$ = 0.278 ΔE = -10.44	 $\|\upsilon_4\|$ = 0.130 ΔE = -3.93

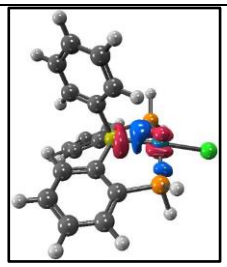
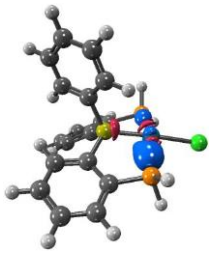
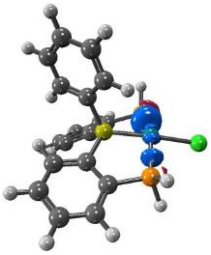
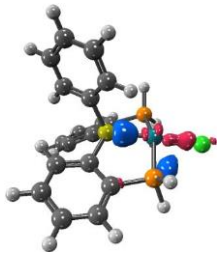
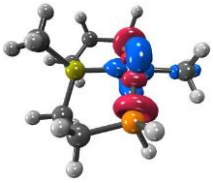
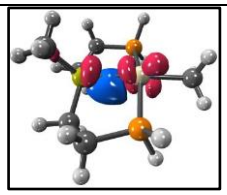
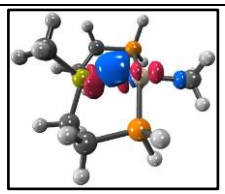
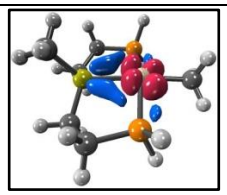
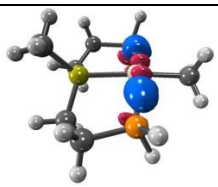
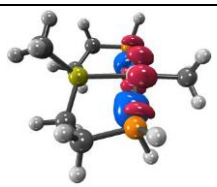
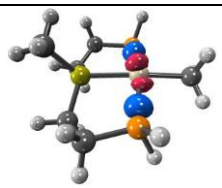
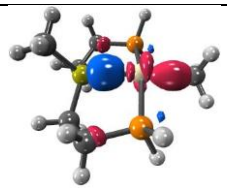
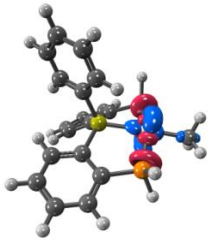
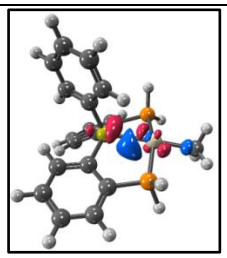
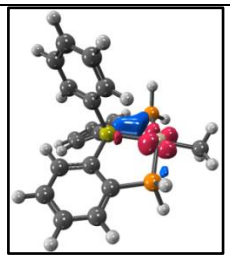
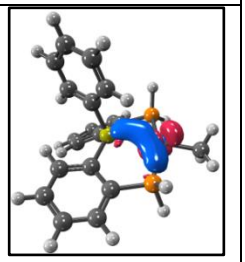
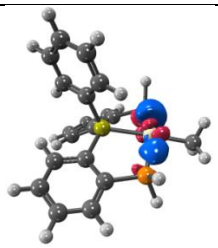
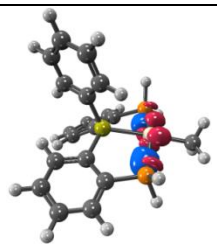
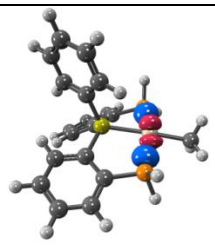
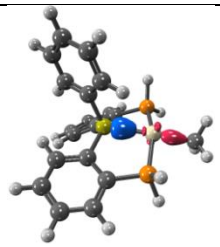
13b	 $\|\upsilon_1\|$ = 0.620 ΔE = -53.31	 $\|\upsilon_2\|$ = 0.348 ΔE = -13.03	 $\|\upsilon_3\|$ = 0.294 ΔE = -11.16	 $\|\upsilon_4\|$ = 0.130 ΔE = -3.76
14a	 $\|\upsilon_1\|$ = 0.582 ΔE = -51.83	 $\|\upsilon_2\|$ = 0.466 ΔE = -23.59	 $\|\upsilon_3\|$ = 385 ΔE = -21.02	 $\|\upsilon_4\|$ = 0.117 ΔE = -3.90
14b	 $\|\upsilon_1\|$ = 0.557 ΔE = -46.89	 $\|\upsilon_2\|$ = 0.465 ΔE = -21.76	 $\|\upsilon_3\|$ = 0.398 ΔE = -18.99	 $\|\upsilon_4\|$ = 0.130 ΔE = -4.00
14c	 $\|\upsilon_1\|$ = 0.577 ΔE = -47.79	 $\|\upsilon_2\|$ = 0.392 ΔE = -16.64	 $\|\upsilon_3\|$ = 0.365 ΔE = -15.57	 $\|\upsilon_4\|$ = 0.147 ΔE = -3.92
15a	 $\|\upsilon_2\|$ = 0.382 ΔE = -25.30	 $\|\upsilon_1\|$ = 0.673 ΔE = -21.37	 $\|\upsilon_3\|$ = 0.215 ΔE = -7.82	 $\|\upsilon_4\|$ = 0.127 ΔE = -3.96
15b	 $\|\upsilon_2\|$ = 0.535 ΔE = -42.93	 $\|\upsilon_1\|$ = 0.676 ΔE = -34.82	 $\|\upsilon_3\|$ = 0.437 ΔE = -27.60	 $\|\upsilon_4\|$ = 0.154 ΔE = -5.99
15c	 $\|\upsilon_1\|$ = 0.540 ΔE = -44.43	 $\|\upsilon_2\|$ = 0.497 ΔE = -25.30	 $\|\upsilon_3\|$ = 0.431 ΔE = -20.87	 $\|\upsilon_4\|$ = 0.171 ΔE = -5.64

16a	 $\|\upsilon_1\|$ = 0.401 ΔE = -33.74	 $\|\upsilon_3\|$ = 0.269 ΔE = -8.58	 $\|\upsilon_2\|$ = 0.255 ΔE = -8.62	 $\|\upsilon_4\|$ = 0.117 ΔE = -2.99
16b	 $\|\upsilon_1\|$ = 0.422 ΔE = -32.84	 $\|\upsilon_3\|$ = 0.239 ΔE = -7.11	 $\|\upsilon_2\|$ = 0.209 ΔE = -6.42	 $\|\upsilon_4\|$ = 0.115 ΔE = -2.64

3.6 Selected deformation density plots of model complexes 17a-18b

Table S23: Selected deformation density plots of model pincer complexes **17a-18b** (all energies are given in kcal/mol).

Model complex				
17a	 $\|\upsilon 1\|$ = 1.167 ΔE = -102.50	 $\|\upsilon_2\|$ = 0.588 ΔE = -33.38	 $\|\upsilon_3\|$ = 0.465 ΔE = -30.00	 $\|\upsilon_4\|$ = 0.332 ΔE = -16.79
	 $\|\upsilon_5\|$ = 0.265 ΔE = -19.91	 $\|\upsilon_6\|$ = 0.217 ΔE = -25.80	 $\|\upsilon_7\|$ = 0.207 ΔE = -7.81	 $\|\upsilon_8\|$ = 0.119 ΔE = -5.52
17b	 $\|\upsilon_1\|$ = 1.156 ΔE = -99.58	 $\|\upsilon_2\|$ = 0.542 ΔE = -29.08	 $\|\upsilon_3\|$ = 0.468 ΔE = -30.02	 $\|\upsilon_4\|$ = 0.338 ΔE = -17.60

	 $\|\upsilon_5\|$ = 0.262 ΔE = -18.17	 $\|\upsilon_6\|$ = 0.221 ΔE = -26.50	 $\|\upsilon_7\|$ = 0.205 ΔE = -8.01	 $\|\upsilon_8\|$ = 0.118 ΔE = -5.59
18a	 $\|\upsilon_1\|$ = 1.072 ΔE = -143.00	 $\|\upsilon_2\|$ = 0.399 ΔE = -22.17	 $\|\upsilon_3\|$ = 0.369 ΔE = -47.16	 $\|\upsilon_4\|$ = 0.350 ΔE = -17.55
	 $\|\upsilon_5\|$ = 0.312 ΔE = -17.88	 $\|\upsilon_6\|$ = 0.287 ΔE = -15.33	 $\|\upsilon_7\|$ = 0.235 ΔE = -21.76	 $\|\upsilon_8\|$ = 0.166 ΔE = -10.38
18b	 $\|\upsilon_1\|$ = 1.077 ΔE = -141.35	 $\|\upsilon_2\|$ = 0.387 ΔE = -45.02	 $\|\upsilon_3\|$ = 0.354 ΔE = -22.70	 $\|\upsilon_4\|$ = 0.342 ΔE = -18.87
	 $\|\upsilon_5\|$ = 0.306 ΔE = -16.95	 $\|\upsilon_6\|$ = 0.285 ΔE = -16.95	 $\|\upsilon_7\|$ = 0.247 ΔE = -15.52	 $\|\upsilon_8\|$ = 0.160 ΔE = -9.87

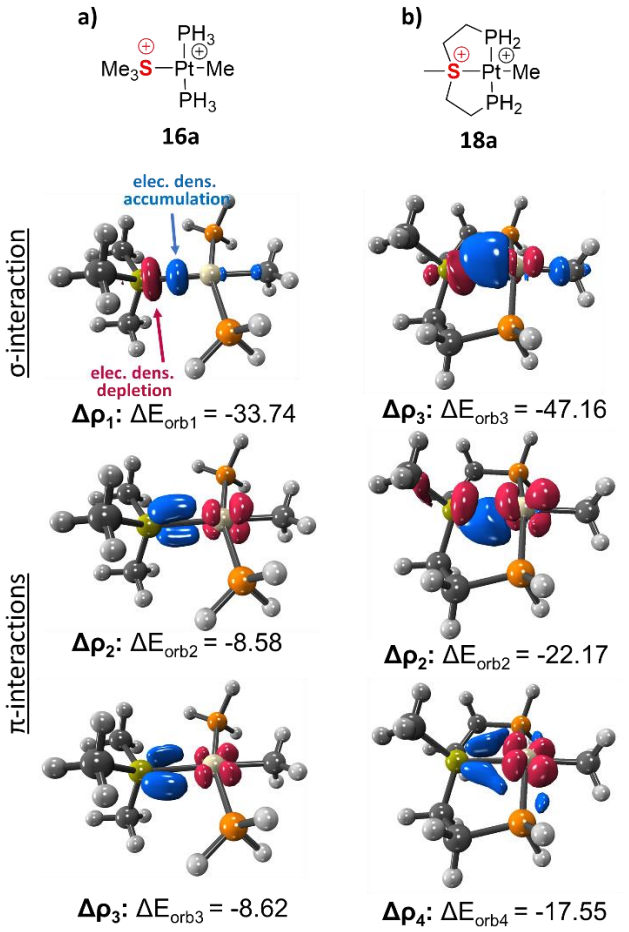


Figure S18: Selected deformation density plots of model complexes **16a** and **18a** (All energies are given in kcal/mol).

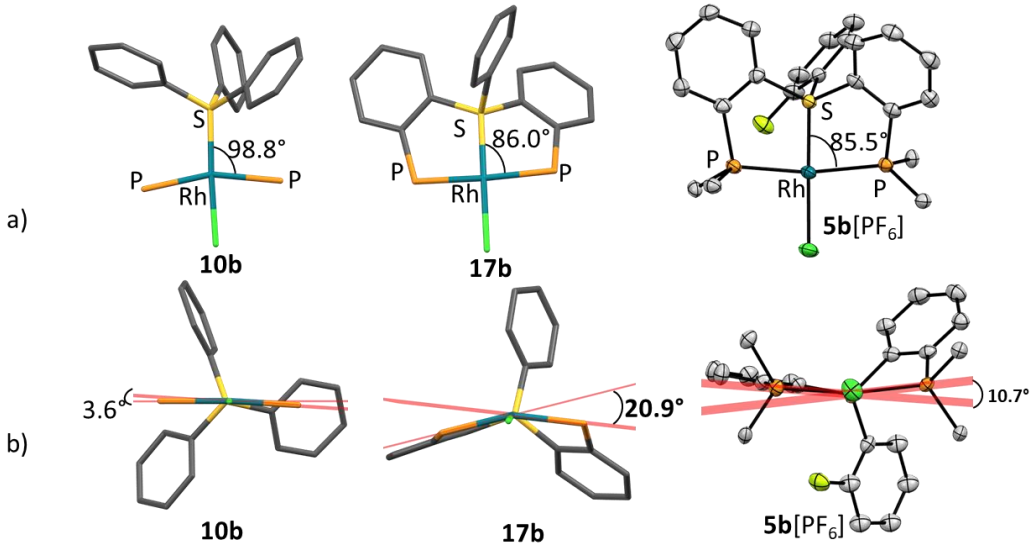


Figure S19: The in-plane (**a**) and out-of-plane (**b**) deformations in model complexes **10b**, **17b** and XRD structure of **5b**[PF_6].

3.7 Coordinates of the optimized model complexes 10a-18b.

$[(SMe_3)(PH_3)_2RhCl]^+$, **10a**

Rh	-0.30350100	-0.00024000	-0.12111400
Cl	-2.66847000	-0.00100300	-0.01323000
P	-0.63394600	-2.23652100	0.17720600
P	-0.63610000	2.23615000	0.17512000
H	-1.27362800	-2.54307700	1.38942300
H	-1.51667800	-2.89442700	-0.69685100
H	-1.51829400	2.89289700	-0.70033200
H	-1.27725200	2.54292000	1.38647500
H	0.35590800	-3.24450000	0.23397600
H	0.35312700	3.24478300	0.23223100
C	2.82423000	-1.37272300	0.28952600
C	2.82166000	1.37366500	0.29705300
H	3.89157200	-1.26010800	0.10140800
H	2.63131000	-1.42634000	1.36025700
H	2.62867100	1.42089400	1.36806300
H	3.88922100	1.26434900	0.10821500
S	1.94303300	0.00172200	-0.47138000
H	2.46988900	2.28567700	-0.17873200
H	2.47450300	-2.28283500	-0.19136500

$[(SPh_3)(PH_3)_2RhCl]^+$, **10b**

Rh	1.20076900	0.75134000	1.64556500
P	1.21305800	-1.14986600	2.95930500
H	2.49371300	-1.58095600	3.33264700
H	0.61000700	-1.03026200	4.21983200
H	0.66370400	-2.38165200	2.54808700
P	1.62733100	2.88152700	0.85632400
H	1.00337400	3.92191200	1.56074000
H	2.96755000	3.27381800	0.97333400
H	1.36931300	3.30035300	-0.46315100
Cl	2.23928500	1.62822600	3.52884700
C	1.01520100	-1.73272500	-0.51231900
C	0.30061200	-2.85428500	-0.89968100
C	2.40210900	-1.75727500	-0.41228100
C	0.99427500	-4.01695900	-1.20206200
H	-0.77758400	-2.84747100	-0.95046200
C	3.08053900	-2.92036400	-0.73059400
H	2.93917200	-0.87718800	-0.07974800
C	2.37720100	-4.05004900	-1.12475000
H	0.44385600	-4.90104700	-1.49460300
H	4.15967400	-2.94491600	-0.65971700
H	2.90930400	-4.96159500	-1.36271500
C	-1.50545300	-0.55658200	0.09054000
C	-2.27056700	-0.89087200	-1.02199000
C	-2.06636100	-0.47817800	1.35472900
C	-3.61121400	-1.18098400	-0.84898300
H	-1.83338000	-0.91223000	-2.01145200
C	-3.41245900	-0.77098300	1.51381300
H	-1.46628100	-0.16119100	2.19755100
C	-4.18021600	-1.12642500	0.41735600
H	-4.21593300	-1.44207200	-1.70708300
H	-3.85979800	-0.70658800	2.49647300
H	-5.23148600	-1.34896900	0.54433800
C	0.22034200	0.73478100	-1.62994600
C	1.03757100	0.38010800	-2.68753000
C	-0.60988500	1.84695800	-1.69166800
C	1.01715000	1.16037700	-3.83648100
H	1.67800000	-0.48870400	-2.63650800
C	-0.62488400	2.60905800	-2.84496300
H	-1.24338000	2.11139800	-0.85388100
C	0.19012700	2.26735700	-3.91695300

H	1.65025300	0.89092700	-4.67115700
H	-1.27405400	3.47223500	-2.90630700
H	0.17672400	2.86736500	-4.81709900
S	0.23901400	-0.16881300	-0.07469000

[$(SMe_2)(PH_3)_2RhCl$], **11a**

Rh	-0.30350100	-0.00024000	-0.12111400
Cl	-2.66847000	-0.00100300	-0.01323000
P	-0.63394600	-2.23652100	0.17720600
P	-0.63610000	2.23615000	0.17512000
H	-1.27362800	-2.54307700	1.38942300
H	-1.51667800	-2.89442700	-0.69685100
H	-1.51829400	2.89289700	-0.70033200
H	-1.27725200	2.54292000	1.38647500
H	0.35590800	-3.24450000	0.23397600
H	0.35312700	3.24478300	0.23223100
C	2.82423000	-1.37272300	0.28952600
C	2.82166000	1.37366500	0.29705300
H	3.89157200	-1.26010800	0.10140800
H	2.63131000	-1.42634000	1.36025700
H	2.62867100	1.42089400	1.36806300
H	3.88922100	1.26434900	0.10821500
S	1.94303300	0.00172200	-0.47138000
H	2.46988900	2.28567700	-0.17873200
H	2.47450300	-2.28283500	-0.19136500

[$(SPh_2)(PH_3)_2RhCl$], **11b**

C	2.29600400	-0.24789400	1.19598200
C	2.04642400	0.07414100	-0.13378200
C	3.60463000	-0.42150900	1.61796200
C	3.09483200	0.20548200	-1.03365200
C	4.65594400	-0.28058600	0.72308000
H	3.81157300	-0.67645900	2.64814300
C	4.40101700	0.02949500	-0.60262100
H	2.88976900	0.43314300	-2.07198400
H	5.67467800	-0.42240300	1.06052100
H	5.21723600	0.12906400	-1.30655800
C	-0.00623500	2.93300000	-1.35825000
C	-0.22762300	4.27355700	-1.07032900
C	0.14198200	2.02243800	-0.32422600
C	-0.29103700	4.69944600	0.24548300
H	-0.34823300	4.98289800	-1.87899700
C	0.06859600	2.44507200	0.99744700
C	-0.14073300	3.78324900	1.27907100
H	-0.46172600	5.74458400	0.46958800
H	0.15998500	1.72330800	1.79924100
H	-0.19546600	4.11229900	2.30889700
S	0.37706500	0.29807300	-0.74976900
H	1.46638000	-0.38328300	1.87849700
H	0.04750600	2.59319400	-2.38463600
H	-2.78271500	1.72429800	0.22200900
H	-3.11709400	0.63191000	2.01371100
H	-0.35972800	-4.02680800	-0.64397600
P	0.23428500	-2.94433700	0.02565700
P	-2.77400300	0.38622100	0.67146000
H	0.63500000	-3.61534700	1.19485100
H	-4.03980600	-0.00333400	0.20390700
Cl	-2.57110400	-2.63202300	1.28860000
Rh	-1.07903600	-1.09596500	0.29235600
H	1.48168900	-2.94694400	-0.63613300

[$(DMSO)(PH_3)_2RhCl$], **12a**

C	-2.47814300	-1.34308000	-0.77461300
C	-2.47784700	1.34367600	-0.77456900

H	-3.55759100	-1.20036300	-0.80226100
H	-2.04974500	-1.36200400	-1.77592500
H	-2.04945000	1.36253900	-1.77588300
H	-3.55732600	1.20119500	-0.80221700
O	-2.44032200	0.00025800	1.46661300
S	-1.75461000	0.00020300	0.17101200
H	-2.24496200	2.26385700	-0.24477500
H	-2.24546000	-2.26332900	-0.24484700
Rh	0.45352800	-0.00005600	0.16242700
Cl	2.81716100	-0.00034400	0.26655100
P	0.82500700	-2.24453200	-0.10692400
P	0.82554600	2.24432300	-0.10695700
H	1.57377900	-2.54047400	-1.25682800
H	1.63448500	-2.87864700	0.84973100
H	1.63517300	2.87825900	0.84969200
H	1.57439900	2.54006600	-1.25686000
H	-0.14581700	-3.26077900	-0.24383700
H	-0.14502200	3.26081200	-0.24389500

[$(Ph_2SO)(PH_3)_2RhCl$], **12b**

C	2.29600400	-0.24789400	1.19598200
C	2.04642400	0.07414100	-0.13378200
C	3.60463000	-0.42150900	1.61796200
C	3.09483200	0.20548200	-1.03365200
C	4.65594400	-0.28058600	0.72308000
H	3.81157300	-0.67645900	2.64814300
C	4.40101700	0.02949500	-0.60262100
H	2.88976900	0.43314300	-2.07198400
H	5.67467800	-0.42240300	1.06052100
H	5.21723600	0.12906400	-1.30655800
C	-0.00623500	2.93300000	-1.35825000
C	-0.22762300	4.27355700	-1.07032900
C	0.14198200	2.02243800	-0.32422600
C	-0.29103700	4.69944600	0.24548300
H	-0.34823300	4.98289800	-1.87899700
C	0.06859600	2.44507200	0.99744700
C	-0.14073300	3.78324900	1.27907100
H	-0.46172600	5.74458400	0.46958800
H	0.15998500	1.72330800	1.79924100
H	-0.19546600	4.11229900	2.30889700
S	0.37706500	0.29807300	-0.74976900
H	1.46638000	-0.38328300	1.87849700
H	0.04750600	2.59319400	-2.38463600
H	-2.78271500	1.72429800	0.22200900
H	-3.11709400	0.63191000	2.01371100
H	-0.35972800	-4.02680800	-0.64397600
P	0.23428500	-2.94433700	0.02565700
P	-2.77400300	0.38622100	0.67146000
H	0.63500000	-3.61534700	1.19485100
H	-4.03980600	-0.00333400	0.20390700
Cl	-2.57110400	-2.63202300	1.28860000
Rh	-1.07903600	-1.09596500	0.29235600
H	1.48168900	-2.94694400	-0.63613300

[$(PMe_3)(PH_3)_2RhCl$], **13a**

Rh	1.18803600	0.96524100	1.81435200
P	0.79173200	-0.74928500	3.24986400
H	1.91371600	-1.27270200	3.91540800
H	0.00278900	-0.44689700	4.37314100
H	0.18027300	-1.98065700	2.91694600
P	1.79004000	2.92069400	0.81816700
H	1.23735500	4.08698800	1.37492300
H	3.14860800	3.26680900	0.91886300
H	1.60834700	3.25357900	-0.54206600

Cl	2.09944200	2.01555800	3.75912400
C	-1.42830800	-0.56440700	0.19227800
H	-2.03669000	0.32449600	0.35835100
H	-1.77579600	-1.08002800	-0.70524000
H	-1.55315500	-1.22337900	1.05173700
C	0.30782000	0.77377200	-1.57514600
H	-0.14308100	0.14042500	-2.34095700
H	-0.26149400	1.70064000	-1.50053800
H	1.32718500	1.02033400	-1.87329800
C	1.11762600	-1.65657800	-0.40655100
H	1.06484200	-2.34599600	0.43631500
H	0.63290300	-2.11380300	-1.27148800
H	2.16927000	-1.47973800	-0.63153900
P	0.32676800	-0.07053800	0.04586200

[$(PPh_3)(PH_3)_2RhCl$], **13b**

Rh	1.24701300	0.79324700	1.70986300
P	1.20433100	-1.12438600	2.93972100
H	2.46160100	-1.62423500	3.32018600
H	0.61051200	-1.05593700	4.21259800
H	0.62842500	-2.33781100	2.50643300
P	1.62357500	2.86239500	0.82780100
H	0.97753800	3.94308000	1.45553700
H	2.94582700	3.32490700	0.93647400
H	1.37896400	3.22820200	-0.51154800
Cl	2.30831100	1.70604000	3.64096400
P	0.25423900	-0.15249300	-0.04374200
C	1.02848800	-1.75311400	-0.50715200
C	0.32480300	-2.88590500	-0.90187100
C	2.42030600	-1.82260300	-0.43010300
C	0.99690300	-4.05659700	-1.22344900
H	-0.75546000	-2.87051200	-0.94633100
C	3.09197800	-2.98652400	-0.76429600
H	2.97402600	-0.95491500	-0.08871400
C	2.37985200	-4.10859700	-1.16211200
H	0.43315300	-4.93223800	-1.51967200
H	4.17228300	-3.02013400	-0.70183700
H	2.90157000	-5.02337500	-1.41341500
C	-1.52732900	-0.54625800	0.13822600
C	-2.31895900	-0.90395400	-0.95398600
C	-2.11784600	-0.47105600	1.39505900
C	-3.65926500	-1.20499200	-0.78583500
H	-1.88665100	-0.93536400	-1.94674600
C	-3.46154200	-0.77249900	1.56560800
H	-1.52330900	-0.14633300	2.24040000
C	-4.23251700	-1.14453300	0.47717300
H	-4.26029100	-1.48076000	-1.64312100
H	-3.90599700	-0.70481700	2.55037700
H	-5.28213500	-1.37591000	0.60791800
C	0.23587600	0.76094100	-1.63417800
C	1.12406500	0.49036400	-2.66772900
C	-0.65002200	1.82925500	-1.77221000
C	1.12592400	1.26986400	-3.81697200
H	1.81795600	-0.33619900	-2.58675300
C	-0.65271700	2.60238800	-2.91970300
H	-1.34709100	2.05644900	-0.97353100
C	0.23877600	2.32484900	-3.94709000
H	1.82289800	1.04451500	-4.61427700
H	-1.35094800	3.42465600	-3.01217200
H	0.23917800	2.92944000	-4.84508400

[$(PF_3)(PH_3)_2RhCl$], **14a**

Rh	1.18950200	0.96239600	1.82339000
P	0.77951000	-0.78129600	3.25325600

H	1.91013100	-1.29448600	3.90694200
H	-0.01745700	-0.46558800	4.36416900
H	0.16947700	-1.99246200	2.87613900
P	1.78404600	2.92028400	0.78935400
H	1.21735600	4.08292800	1.33406000
H	3.14306100	3.25848100	0.87977000
H	1.57337600	3.18101200	-0.57663100
Cl	2.09084700	2.00232300	3.74503500
P	0.36900200	-0.01456000	0.12776800
F	-1.12621700	-0.48003000	0.15689500
F	0.33408100	0.67870800	-1.27581700
F	0.97453800	-1.38109200	-0.34042600

[$(P(CF_3)_3)(PH_3)_2RhCl$], **14b**

P	0.37020000	-0.04170000	0.07270000
C	0.42240000	0.77940000	-1.65070000
C	-1.48640000	-0.49720000	0.10720000
C	1.08660000	-1.74000000	-0.44290000
F	-2.17730000	0.54240000	0.57020000
F	-2.01390000	-0.84680000	-1.06160000
F	-1.65990000	-1.51960000	0.95670000
F	0.32290000	-2.43970000	-1.27700000
F	1.28780000	-2.49520000	0.64130000
F	2.26970000	-1.54370000	-1.02740000
F	-0.41380000	1.82420000	-1.65250000
F	0.09250000	-0.01120000	-2.66490000
F	1.65430000	1.23970000	-1.88580000
Rh	1.18170000	0.93730000	1.80990000
P	0.79920000	-0.77780000	3.29020000
H	1.95710000	-1.31890000	3.86940000
H	0.11190000	-0.37840000	4.44520000
H	0.10740000	-1.96830000	3.01080000
P	1.74240000	2.97370000	0.90150000
H	1.22390000	4.06680000	1.61030000
H	3.11000000	3.28470000	0.94620000
H	1.45860000	3.39770000	-0.40840000
Cl	2.09490000	1.94380000	3.74110000

[$(P(C_6F_5)_3)(PH_3)_2RhCl$], **14c**

P	0.23957700	-0.18038100	-0.02679800
C	1.13824800	-1.70920800	-0.52864000
C	0.72593900	-3.00432500	-0.25131500
C	2.44000600	-1.56931300	-0.99970500
C	1.53882700	-4.10479900	-0.46985700
C	3.27177700	-2.64530900	-1.23188600
C	2.81609600	-3.92678700	-0.96710000
C	-1.54806500	-0.64949800	0.00396200
C	-2.14783800	-1.33207600	-1.05125800
C	-2.39172400	-0.25149000	1.03559900
C	-3.49391900	-1.63294200	-1.08233700
C	-3.74900800	-0.53968400	1.03023900
C	-4.30162600	-1.23381800	-0.02906200
C	0.11708600	0.85096300	-1.56430900
C	0.49289200	0.52548600	-2.86282100
C	-0.44308000	2.11516100	-1.39155700
C	0.36101700	1.41794100	-3.91565300
C	-0.59079400	3.02263400	-2.42318700
C	-0.17900000	2.67188500	-3.69742600
F	-1.94744100	0.43660700	2.07644500
F	-4.51713800	-0.14586700	2.03269700
F	-5.59011000	-1.51125700	-0.04207700
F	-4.01524800	-2.29559700	-2.10178800
F	-1.41548800	-1.73411500	-2.08524600
F	-0.47710300	-3.25150200	0.26776000

F	1.09785600	-5.32292100	-0.19740300
F	3.59830000	-4.96749600	-1.18123600
F	4.49524200	-2.46171500	-1.69915200
F	2.92851400	-0.35687600	-1.25114800
F	0.98558200	-0.66597800	-3.17316900
F	0.73824000	1.06753700	-5.13428500
F	-0.31222800	3.52224900	-4.69646300
F	-1.12422300	4.21283600	-2.20177600
F	-0.87693300	2.49060300	-0.19145300
Rh	1.28669600	0.55590400	1.74889600
P	0.55126700	-1.09626700	3.15445100
H	1.54324700	-1.94218100	3.67591600
H	-0.02329100	-0.64645900	4.35295300
H	-0.40321000	-2.07973100	2.81902600
P	2.36793400	2.33160300	0.80722400
H	2.18462000	3.57122600	1.44072100
H	3.76984900	2.26859400	0.82867000
H	2.19700200	2.74942900	-0.52971600
Cl	2.55760900	1.18313900	3.64870700

$[(NHN)(PH_3)_2RhCl]^+$, **15a**

N	0.79950900	-1.19469500	-0.31209500
C	-0.75251700	-0.49759600	-1.63677100
C	0.08654000	-1.53667900	-1.41839300
H	1.49397200	-1.72824500	0.18937800
H	-1.49641300	-0.32098200	-2.39316900
H	0.23185700	-2.46543000	-1.94089000
N	-0.48380300	0.39387800	-0.64559200
H	-0.87179200	1.31267200	-0.49163300
N	0.46460400	-0.01492000	0.17676400
Rh	1.19684100	0.90324100	1.74328400
P	3.44654000	0.50130500	1.37128000
H	4.21473900	1.65976400	1.19199200
H	4.13675500	-0.10640400	2.42868600
H	3.95507300	-0.26475300	0.29793600
P	-0.78668600	1.64187000	2.68188900
H	-1.04811700	1.12434900	3.95785700
H	-0.85728500	3.01732800	2.94040600
H	-2.06338400	1.45317800	2.10571700
Cl	2.05775200	1.98009700	3.58671500

$[(NHP)(PH_3)_2RhCl]^+$, **15b**

Rh	1.28380800	1.01254200	1.92573000
P	3.49248100	0.34662800	1.73551200
H	4.40095600	1.40778700	1.63633200
H	3.97794800	-0.34200800	2.85413900
H	3.98176600	-0.48556500	0.71000200
P	-0.65092100	2.01939600	2.70133500
H	-0.99014900	1.66549900	4.01312700
H	-0.56969600	3.41446200	2.79342200
H	-1.91059000	1.89191400	2.08453200
Cl	2.15622500	2.09825300	3.78640000
N	1.10833700	-0.94114700	-0.92693400
C	-1.03337900	-0.88395500	-1.57977800
C	0.18293800	-1.37381500	-1.86139200
H	2.07659800	-1.21240000	-0.98218600
H	-1.95587100	-1.03615400	-2.11336800
H	0.47381200	-2.01465500	-2.67599300
N	-0.98780800	-0.09695800	-0.44164100
H	-1.81308400	0.35403100	-0.08148700
P	0.50081700	0.03412300	0.25561000

$[(PR_3)(PH_3)_2RhCl]^{3+}$, **15c**

Rh	0.65163800	0.17458000	1.67670200

P	1.96586200	-1.55376100	2.45920400
H	3.20532800	-1.17575400	2.99472300
H	1.41481800	-2.25499200	3.54009200
H	2.38163300	-2.64771100	1.66836100
P	-0.67255700	2.06574800	1.68047100
H	-1.74144700	2.01529700	2.58646800
H	-0.04409100	3.24848400	2.09376900
H	-1.36012500	2.55645300	0.54759300
Cl	0.88136200	0.82554600	3.90154300
P	0.44770100	-0.32131500	-0.40662900
C	-1.23043800	-0.15439200	-1.07983400
C	-2.21505800	0.41620900	-1.86089800
C	-2.54762100	-0.28269000	-0.68498900
N	-2.57354700	1.14161600	-2.87507800
N	-3.41350200	-0.71777800	0.17479300
C	-2.97715600	-1.34416400	1.42440600
H	-3.37908500	-0.78327800	2.26861200
H	-3.35460500	-2.36578600	1.47306500
H	-1.88956500	-1.33403200	1.48783900
C	-4.85804300	-0.55743300	-0.00421900
H	-5.35299100	-1.47014100	0.32396500
H	-5.22431900	0.27676500	0.59488500
H	-5.09204500	-0.39843000	-1.05275400
C	-3.96790500	1.49855100	-3.14271900
H	-4.03194400	2.57222600	-3.31651300
H	-4.32604000	0.97177700	-4.02755200
H	-4.58842200	1.24954600	-2.28816200
C	-1.58662800	1.64966200	-3.81982600
H	-0.59951500	1.28787800	-3.54422900
H	-1.83420800	1.30896600	-4.82592600
H	-1.59007400	2.74012900	-3.80712700
C	0.88797400	-1.97846500	-1.00117400
C	0.59999600	-3.30975300	-1.21987500
C	1.93015800	-2.86664400	-1.15495000
N	-0.26788800	-4.26709400	-1.33839600
N	3.21012400	-3.08638300	-1.17777000
C	0.11486500	-5.66631900	-1.53132400
C	-1.69886900	-3.99196200	-1.27804900
C	4.14998600	-2.02288900	-0.83502600
C	3.78374000	-4.40727800	-1.44036900
H	-0.40957700	-6.28221200	-0.80132600
H	-0.15698100	-5.99366100	-2.53510800
H	1.18282200	-5.78636200	-1.38099000
H	-1.86121000	-2.92237100	-1.17087200
H	-2.17815000	-4.34116900	-2.19322100
H	-2.13820600	-4.51616300	-0.42861100
H	4.76626200	-2.33901700	0.00768700
H	4.80181400	-1.81374600	-1.68389900
H	3.60441300	-1.12334700	-0.55537800
H	4.67388800	-4.28637400	-2.05591400
H	4.06354900	-4.89459900	-0.50555900
H	3.07353400	-5.02247300	-1.98490100
C	1.43438200	0.64823400	-1.58264300
C	2.01913300	0.86971600	-2.81039700
C	2.34702500	1.68027500	-1.69887200
N	2.16553100	0.53099400	-4.05462000
N	3.02569400	2.64385300	-1.16932600
C	3.08346100	1.21185200	-4.96915800
C	1.40418000	-0.58329900	-4.61142300
C	2.95500800	2.91187400	0.26912400
C	3.91315900	3.51221700	-1.94500600
H	3.69229800	0.46755600	-5.48147000
H	2.52120800	1.78092500	-5.70983800
H	3.73929300	1.87561400	-4.41541300

H	0.71110900	-0.96570400	-3.86441000
H	0.84732800	-0.24645200	-5.48645200
H	2.08365000	-1.37911200	-4.91869500
H	3.96683600	2.94744600	0.67231300
H	2.47544700	3.87635000	0.43904900
H	2.39687000	2.12085900	0.76954500
H	3.74100000	4.54451800	-1.64340800
H	4.95458900	3.25578800	-1.74965100
H	3.69702100	3.42336700	-3.00518800

$[(SMe_3)PtMe]^{2+}$, **16a**

P	1.86964500	-2.45779900	-0.54686800
H	2.94950500	-3.35653200	-0.56020200
H	0.97180000	-3.11489500	0.30453300
H	1.31065000	-2.68349500	-1.81221800
P	1.74959600	2.04517600	0.44148200
H	2.78482800	2.91482700	0.81816200
H	1.16562300	2.74910200	-0.62043800
H	0.82713900	2.23677500	1.47819500
Pt	2.15623200	-0.19932900	-0.03375700
C	0.06835200	-0.24809600	-0.05074200
H	-0.25462600	-0.49051900	0.96300100
H	-0.37084600	0.70342100	-0.34878100
H	-0.32207700	-0.99529700	-0.74119100
S	4.55679700	-0.20891700	0.01858900
C	5.38825200	1.34089100	0.34932500
H	6.46538000	1.18027100	0.33223300
H	5.09068400	2.04724300	-0.42440900
H	5.06561500	1.68579500	1.33057000
C	5.24979500	-1.30324400	1.25456600
H	4.89515800	-2.31011600	1.04218100
H	6.33711400	-1.25602500	1.21122900
H	4.87786500	-0.97421700	2.22403900
C	5.31295500	-0.74655500	-1.51262200
H	4.97701300	-0.06826700	-2.29592700
H	6.39694600	-0.72475200	-1.40851700
H	4.96302300	-1.75650700	-1.71871100

$[(SPh_3)PtMe]^{2+}$, **16b**

Rh	1.20076900	0.75134000	1.64556500
P	1.21305800	-1.14986600	2.95930500
H	2.49371300	-1.58095600	3.33264700
H	0.61000700	-1.03026200	4.21983200
H	0.66370400	-2.38165200	2.54808700
P	1.62733100	2.88152700	0.85632400
H	1.00337400	3.92191200	1.56074000
H	2.96755000	3.27381800	0.97333400
H	1.36931300	3.30035300	-0.46315100
Cl	2.23928500	1.62822600	3.52884700
C	1.01520100	-1.73272500	-0.51231900
C	0.30061200	-2.85428500	-0.89968100
C	2.40210900	-1.75727500	-0.41228100
C	0.99427500	-4.01695900	-1.20206200
H	-0.77758400	-2.84747100	-0.95046200
C	3.08053900	-2.92036400	-0.73059400
H	2.93917200	-0.87718800	-0.07974800
C	2.37720100	-4.05004900	-1.12475000
H	0.44385600	-4.90104700	-1.49460300
H	4.15967400	-2.94491600	-0.65971700
H	2.90930400	-4.96159500	-1.36271500
C	-1.50545300	-0.55658200	0.09054000
C	-2.27056700	-0.89087200	-1.02199000
C	-2.06636100	-0.47817800	1.35472900
C	-3.61121400	-1.18098400	-0.84898300

H	-1.83338000	-0.91223000	-2.01145200
C	-3.41245900	-0.77098300	1.51381300
H	-1.46628100	-0.16119100	2.19755100
C	-4.18021600	-1.12642500	0.41735600
H	-4.21593300	-1.44207200	-1.70708300
H	-3.85979800	-0.70658800	2.49647300
H	-5.23148600	-1.34896900	0.54433800
C	0.22034200	0.73478100	-1.62994600
C	1.03757100	0.38010800	-2.68753000
C	-0.60988500	1.84695800	-1.69166800
C	1.01715000	1.16037700	-3.83648100
H	1.67800000	-0.48870400	-2.63650800
C	-0.62488400	2.60905800	-2.84496300
H	-1.24338000	2.11139800	-0.85388100
C	0.19012700	2.26735700	-3.91695300
H	1.65025300	0.89092700	-4.67115700
H	-1.27405400	3.47223500	-2.90630700
H	0.17672400	2.86736500	-4.81709900
S	0.23901400	-0.16881300	-0.07469000

[(Me-PSP)RhCl]$^{+}$, **17a**

S	1.54610500	0.00209600	0.09054900
P	-0.44564300	2.26532400	-0.13846800
P	-0.43928700	-2.26679300	-0.13855700
C	1.36252100	2.67834800	-0.30766100
H	1.51931000	3.51384900	-0.98906800
H	1.71834400	2.99420400	0.67447700
C	1.37006400	-2.67465900	-0.30773800
H	1.72675200	-2.98956200	0.67439300
H	1.52921800	-3.50969000	-0.98917200
C	2.16043400	-1.46384900	-0.79935300
H	1.95737000	-1.25214800	-1.84964600
H	3.23530600	-1.56219600	-0.64878800
C	2.15629300	1.46979100	-0.79933400
H	3.23088300	1.57116200	-0.64878400
H	1.95381400	1.25757700	-1.84963900
C	2.57485600	0.00352400	1.56828800
H	2.31318900	-0.88211700	2.14395300
H	3.63089100	0.00495900	1.30274900
H	-0.88886200	3.25327000	0.75529300
H	-1.00865800	2.74917000	-1.32937800
H	-0.87967600	-3.25612700	0.75507200
H	-1.00090100	-2.75211400	-1.32953100
H	2.31076700	0.88848200	2.14389500
Rh	-0.56834900	-0.00089000	0.17574000
Cl	-2.86361600	-0.00394000	0.06890500

[(aromaticPh-PSP)RhCl]$^{+}$, **17b**

Rh	-1.65594000	0.26229500	0.48951100
Cl	-3.85669300	0.72963900	0.97280200
S	0.34239800	-0.19534200	-0.11122400
P	-1.31345900	2.33947100	-0.33446900
P	-1.96077500	-2.01007900	0.45344700
H	-1.21601200	3.52459400	0.41769900
H	-2.16466800	2.78817500	-1.35602800
H	-1.75279200	-2.92505800	1.50363000
H	-3.15671400	-2.52472500	-0.06881400
C	1.57784500	-0.59099600	1.12567900
C	1.46894000	0.10886200	2.31928100
C	2.58104100	-1.52471300	0.91444700
C	2.40288400	-0.11975300	3.31480100
C	3.50507500	-1.74561500	1.92331900
H	2.63977200	-2.08995100	-0.00534200
C	3.41947200	-1.04280200	3.11586800

H	2.32773500	0.41640000	4.25116500
H	4.28952300	-2.47594400	1.77687000
H	4.14290400	-1.22406400	3.89974100
C	0.32635800	2.29824300	-1.15059300
C	1.10731500	1.15353300	-1.01506900
C	0.87070800	3.38456000	-1.82694000
C	2.41797000	1.09861600	-1.46541100
C	2.15951000	3.32464100	-2.33070200
H	0.28799500	4.28933100	-1.94704800
C	2.93693200	2.19092100	-2.13764100
H	3.04118700	0.23637900	-1.27118300
H	2.57056900	4.17719500	-2.85481900
H	3.95572600	2.16179000	-2.49988000
C	-0.73214600	-2.55570300	-0.79424300
C	-0.82070200	-3.75601500	-1.48527400
C	0.29226600	-1.67172900	-1.14087900
C	0.06721600	-4.04588200	-2.51095600
H	-1.60588400	-4.46004900	-1.23958400
C	1.17605100	-1.93997400	-2.16997800
C	1.05125500	-3.13603100	-2.86139600
H	-0.02430100	-4.97819500	-3.05202500
H	1.93879700	-1.23174300	-2.45722000
H	1.72537000	-3.35096500	-3.67958000
H	0.65558300	0.80799500	2.47135800

[(Me-PSP)PtMe]$^{2+}$, **18a**

Pt	0.00025100	-0.72801700	0.13200000
C	0.00094700	-2.80950900	-0.00939300
H	0.89296400	-3.18828100	-0.52037600
H	-0.88964300	-3.18854400	-0.52267900
H	-0.00033800	-3.14653500	1.04018400
S	-0.00051500	1.58432600	0.08301000
P	-2.29183600	-0.58661700	-0.15702500
P	2.29216800	-0.58517300	-0.15703900
C	-2.69070800	1.23036700	-0.32720500
H	-3.54863600	1.36660800	-1.00316200
H	-3.00818800	1.59034600	0.66283200
C	2.68990800	1.23206200	-0.32716700
H	3.00711000	1.59222200	0.66289500
H	3.54777400	1.36886200	-1.00309000
C	1.50826300	2.04875400	-0.86296000
H	1.26713400	1.80271400	-1.90779500
H	1.66288800	3.13323200	-0.77004200
C	-1.50957100	2.04780500	-0.86298500
H	-1.66487200	3.13218700	-0.77008000
H	-1.26828100	1.80189500	-1.90781400
C	-0.00091600	2.68463000	1.52135700
H	0.89377100	2.45098600	2.11284500
H	-0.00120400	3.73113600	1.18948800
H	-3.22172100	-1.05543700	0.80466900
H	-2.77456600	-1.19092700	-1.34407900
H	3.22235500	-1.05349200	0.80460600
H	2.77518500	-1.18915600	-1.34414100
H	-0.89557400	2.45046100	2.11268800

[(aromaticPh-PSP)PtMe]$^{2+}$, **18b**

S	0.48364100	-0.22172100	-0.12055200
P	-1.29405300	2.38861200	-0.31272400
P	-1.96078200	-2.03060100	0.45950400
H	-1.18196400	3.48217100	0.56049500
H	-2.15152000	2.90436100	-1.29472800
H	-1.67507600	-2.80191700	1.59800100
H	-3.15289500	-2.61506000	0.01192200
C	1.66141900	-0.61949300	1.14379500

C	1.56411500	0.12013700	2.31700700
C	2.62889800	-1.59650900	0.95469400
C	2.47975400	-0.12334600	3.32481500
C	3.53261500	-1.82650100	1.97904000
H	2.67640500	-2.18159700	0.04651500
C	3.46053200	-1.09166900	3.15423200
H	2.42167400	0.43789800	4.24754100
H	4.29256100	-2.58661200	1.85804900
H	4.17025400	-1.28106500	3.94872400
C	0.33933800	2.30763900	-1.12106500
C	1.14671300	1.16944700	-1.01429700
C	0.85410400	3.40875600	-1.79534800
C	2.44739100	1.14384700	-1.49442400
C	2.13508200	3.37553700	-2.32591800
H	0.25888400	4.30793500	-1.89731000
C	2.93471000	2.25375700	-2.16372200
H	3.08829900	0.28806500	-1.32808000
H	2.51925200	4.24188400	-2.84799100
H	3.94556100	2.24523300	-2.54876200
C	-0.73491300	-2.53613100	-0.79495600
C	-0.86317700	-3.72443600	-1.49979000
C	0.31804200	-1.67642200	-1.14386600
C	0.01464700	-4.03237500	-2.53117300
H	-1.66691300	-4.41026100	-1.26223700
C	1.19020700	-1.96555900	-2.17656200
C	1.02630000	-3.15255800	-2.87712400
H	-0.10752800	-4.95824800	-3.07742700
H	1.97770700	-1.28128800	-2.45718200
H	1.69347100	-3.38383000	-3.69659600
H	0.78834700	0.86446000	2.44885500
C	-3.73545600	0.65214700	0.79097000
H	-3.97682600	1.71240300	0.79078300
H	-4.33809900	0.15551400	0.02982600
H	-3.97963600	0.23749100	1.77028100
Pt	-1.73063300	0.27504800	0.43704400

4. NMR spectra

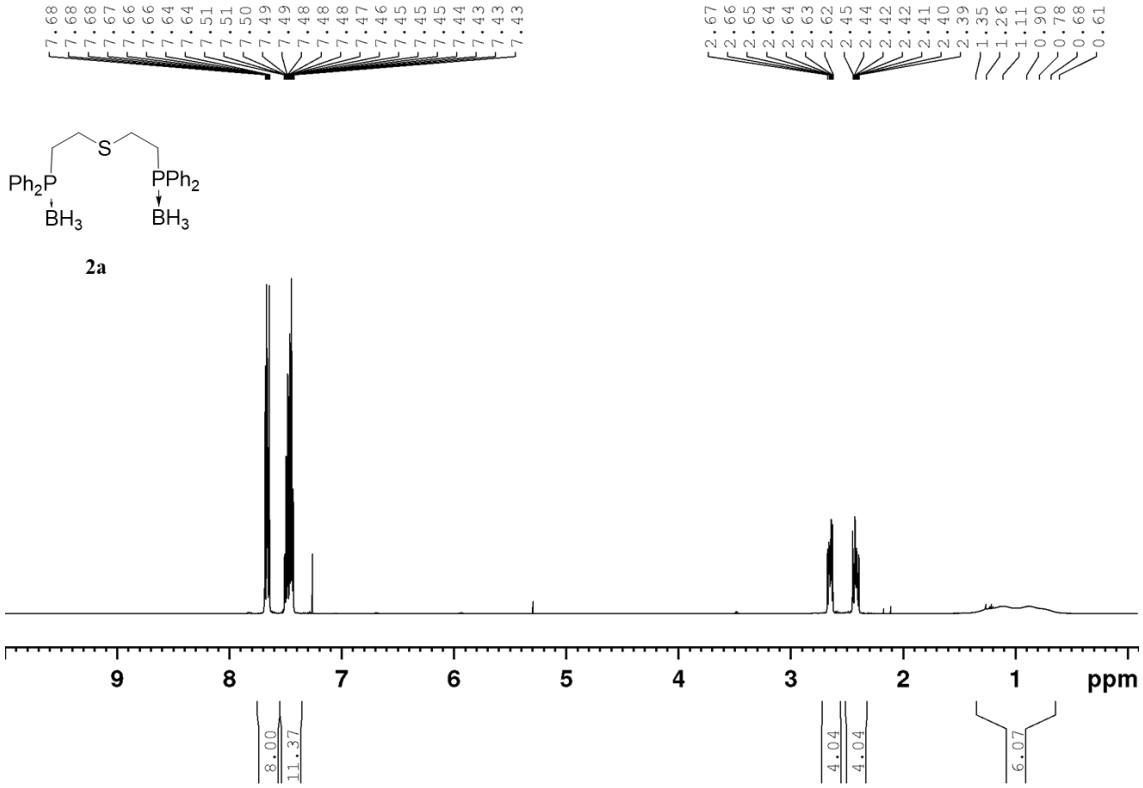


Figure S20: ^{1}H NMR (400 MHz) of **2a** in $CDCl_3$.

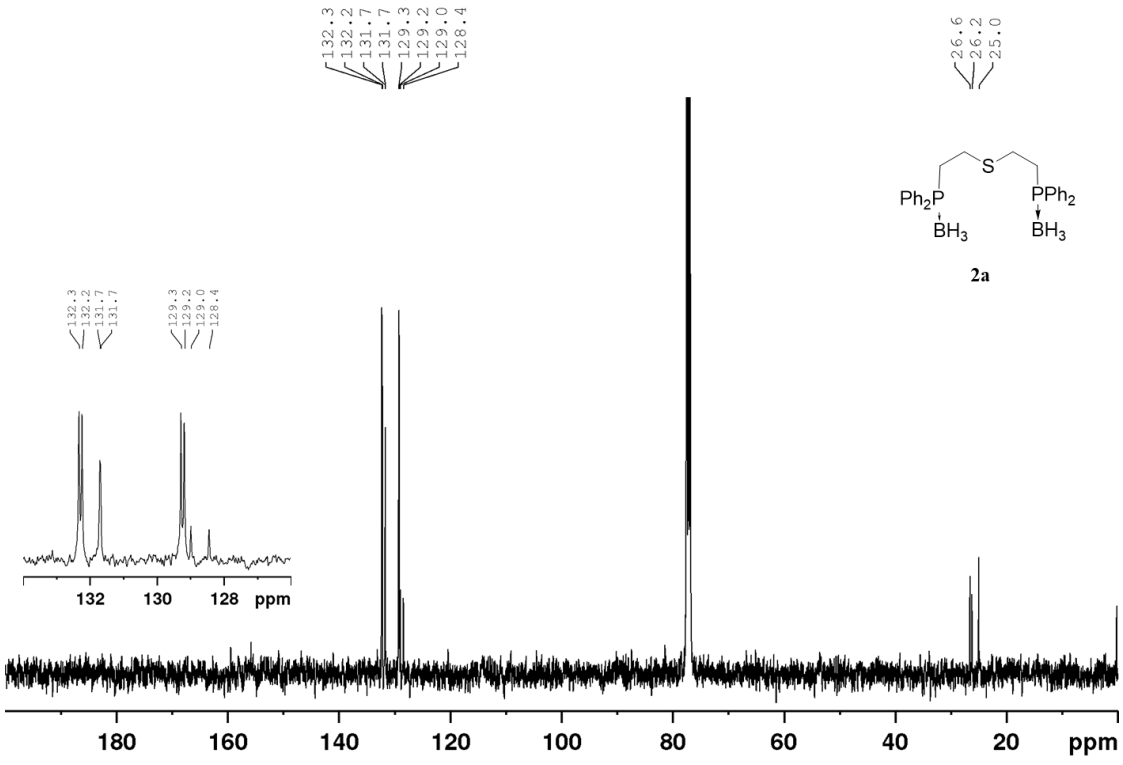


Figure S21: ^{13}C NMR (101 MHz) of **2a** in $CDCl_3$.

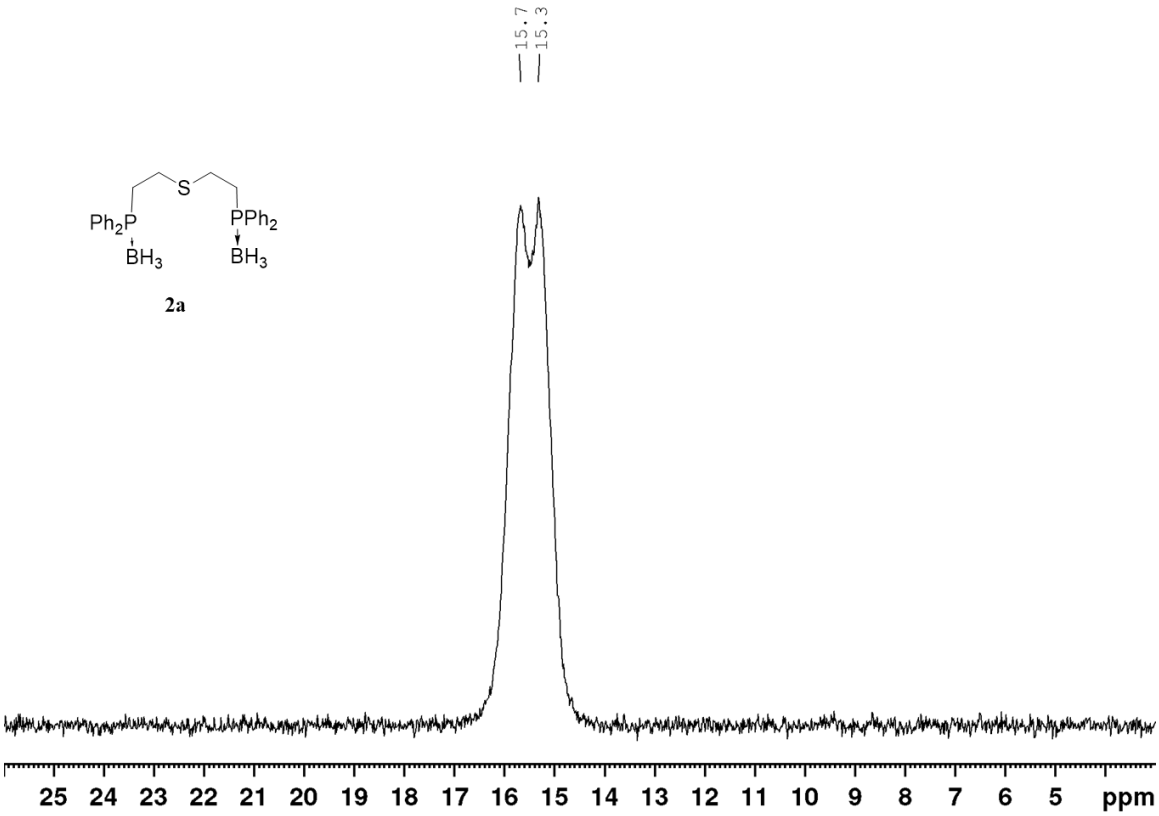


Figure S22: $^{31}P\{H\}$ NMR (162 MHz) of **2a** in $CDCl_3$.

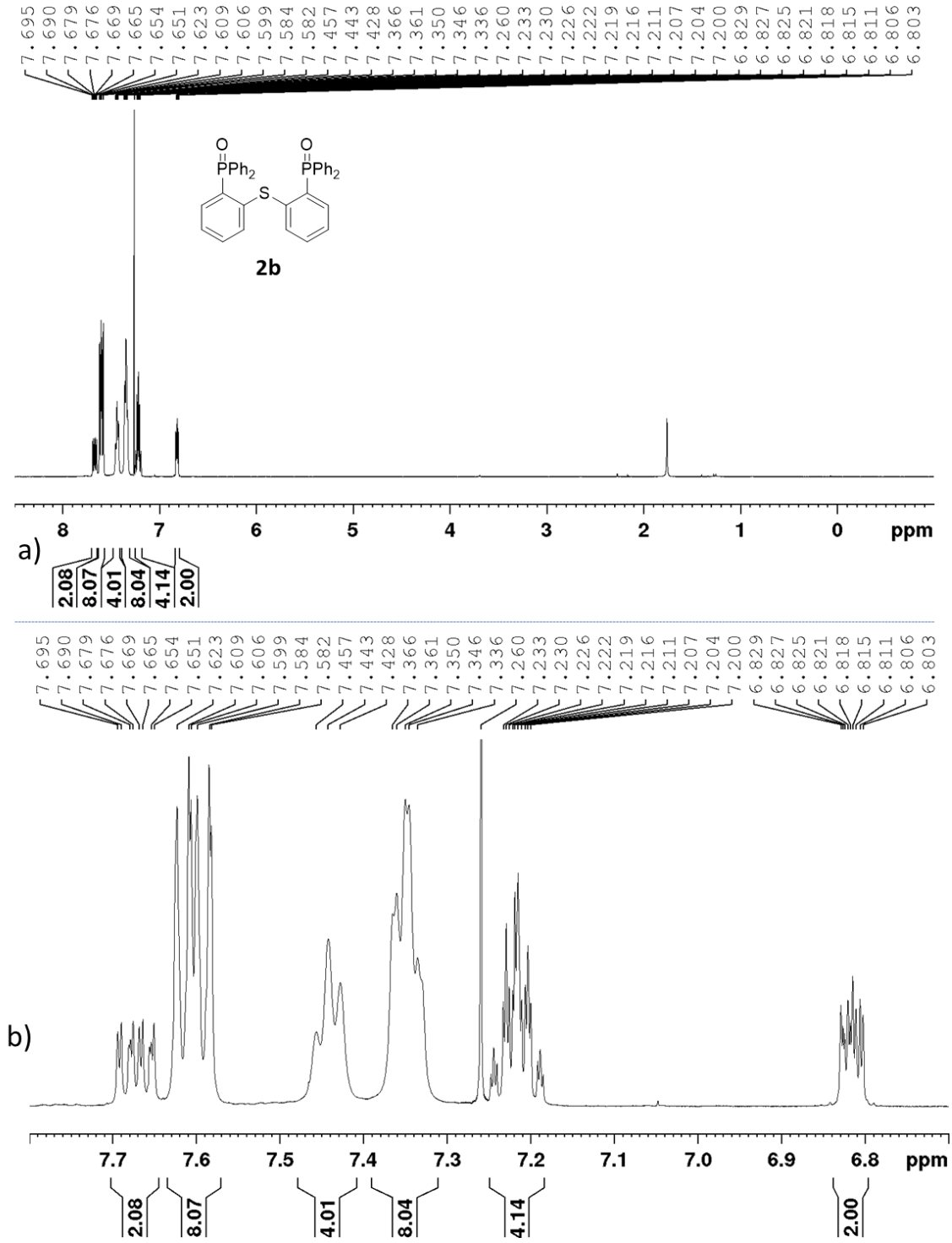


Figure S23: ^{1}H NMR (500 MHz) of **2b** in $CDCl_3$. a) full spectrum, b) aromatic region expanded.

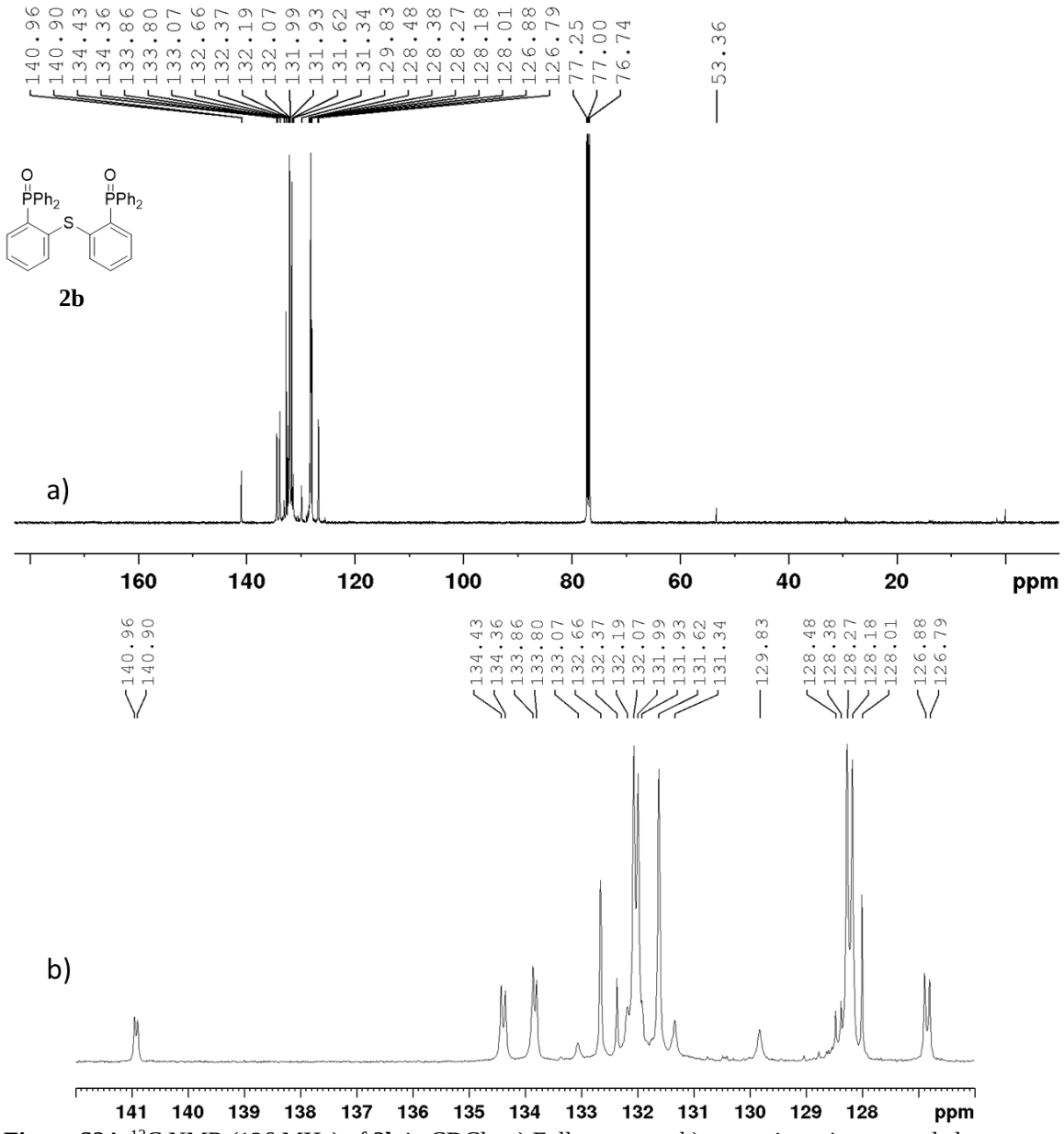


Figure S24: ^{13}C NMR (126 MHz) of **2b** in $CDCl_3$. a) Full spectrum, b) aromatic region expanded.

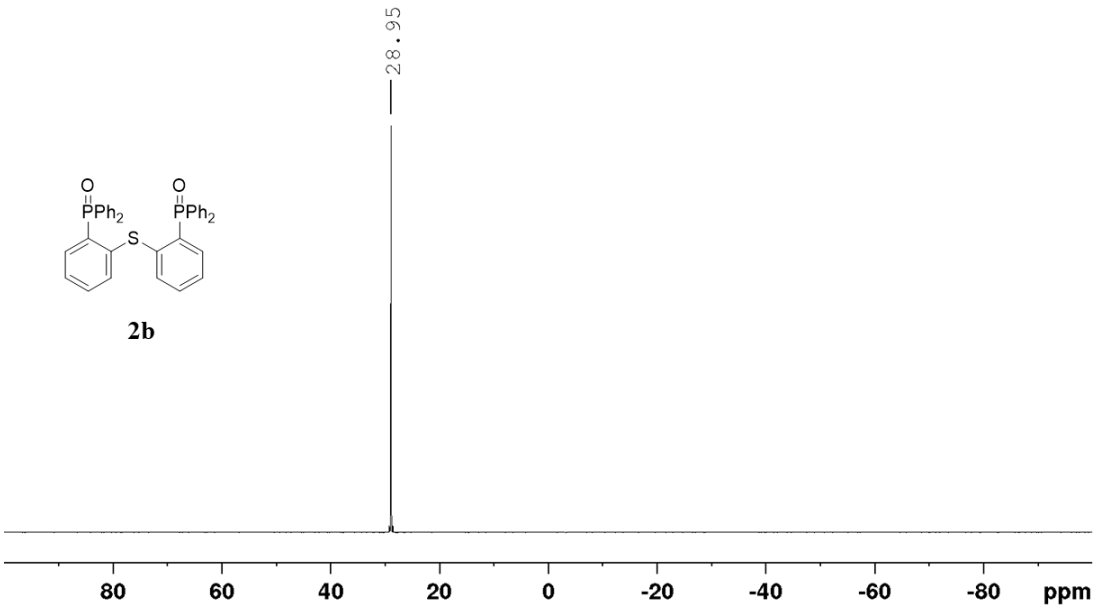


Figure S25: $^{31}P\{H\}$ NMR (162 MHz) of **2b** in $CDCl_3$

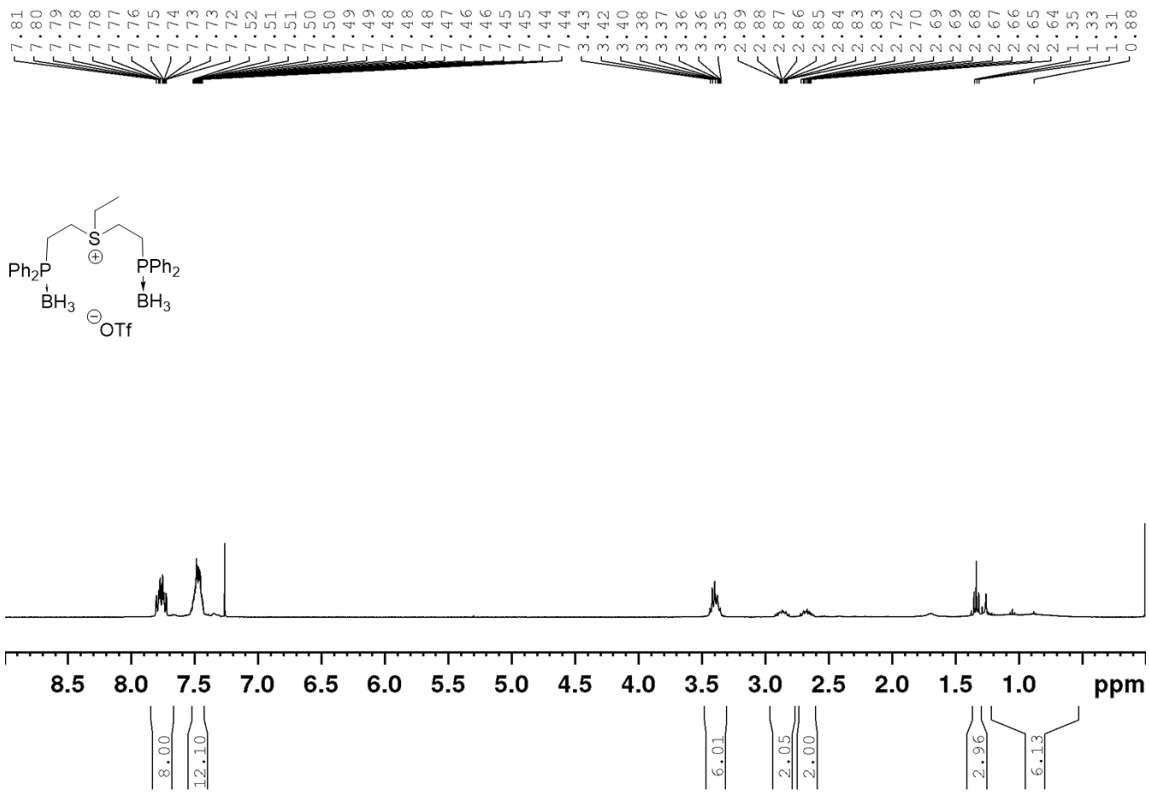


Figure S26: ^{1}H NMR (400 MHz) of **3a**[OTf] in $CDCl_3$, measured at 298 K.

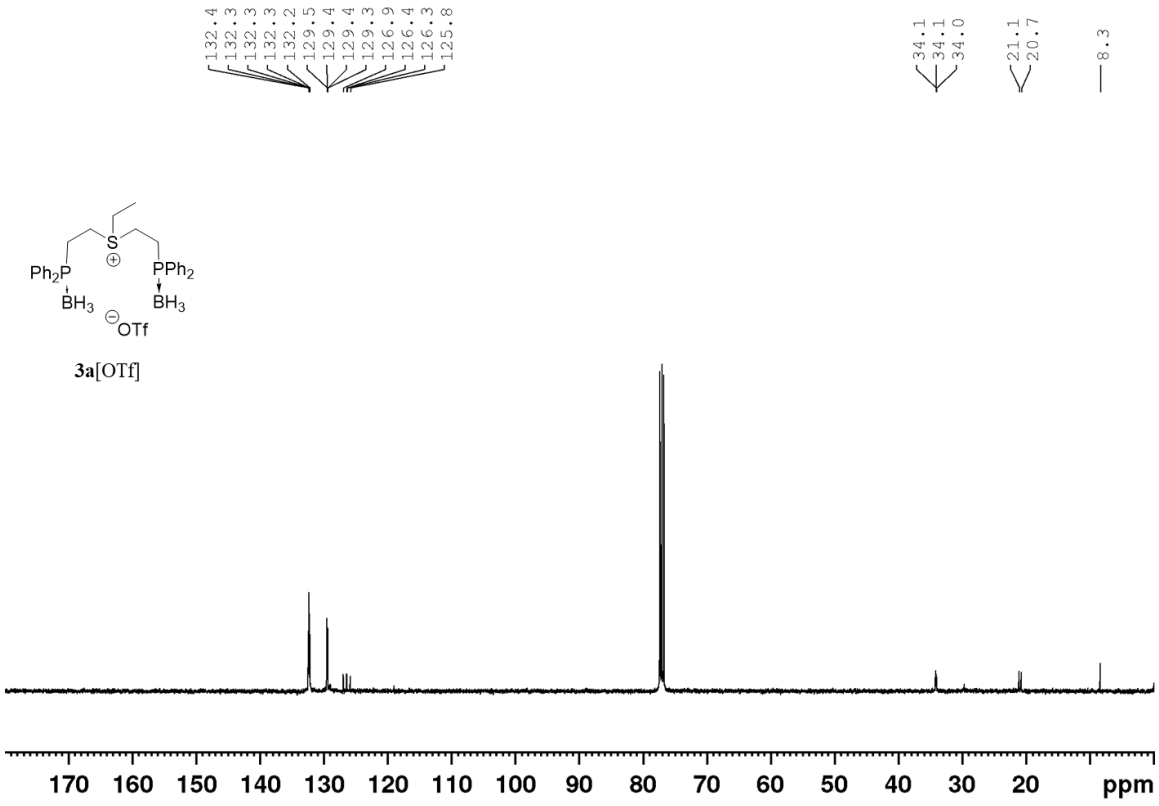


Figure S27: ^{13}C NMR (101 MHz) of **3a**[OTf] in $CDCl_3$.

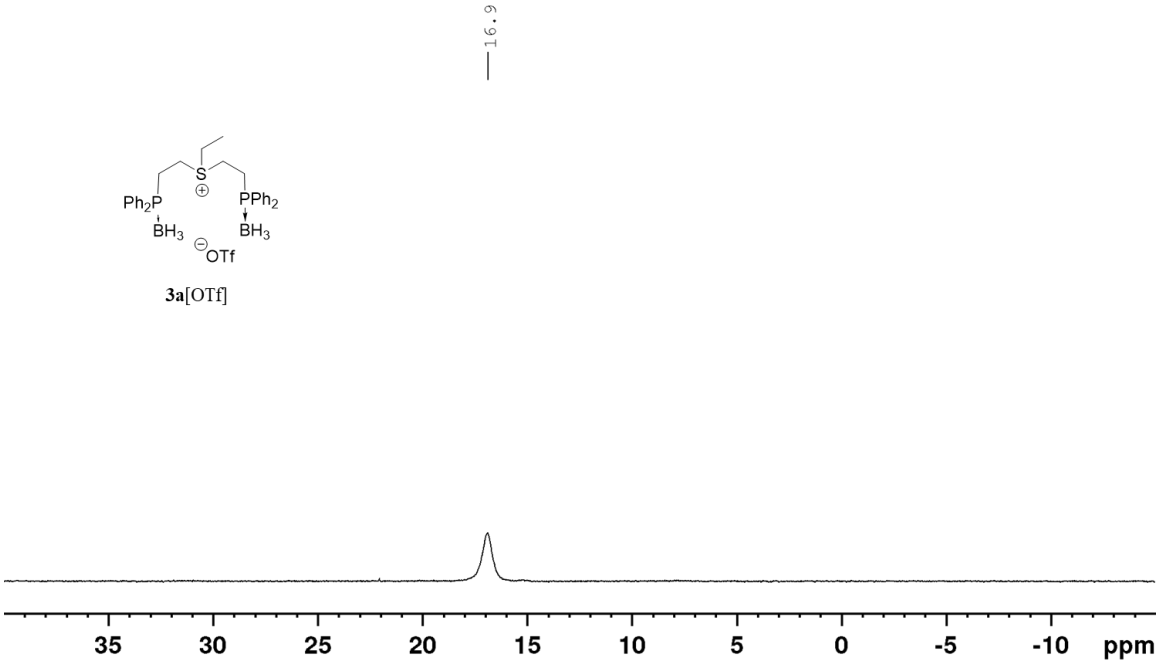


Figure S28: $^{31}P\{H\}$ NMR (162 MHz) of **3a**[OTf] in $CDCl_3$.

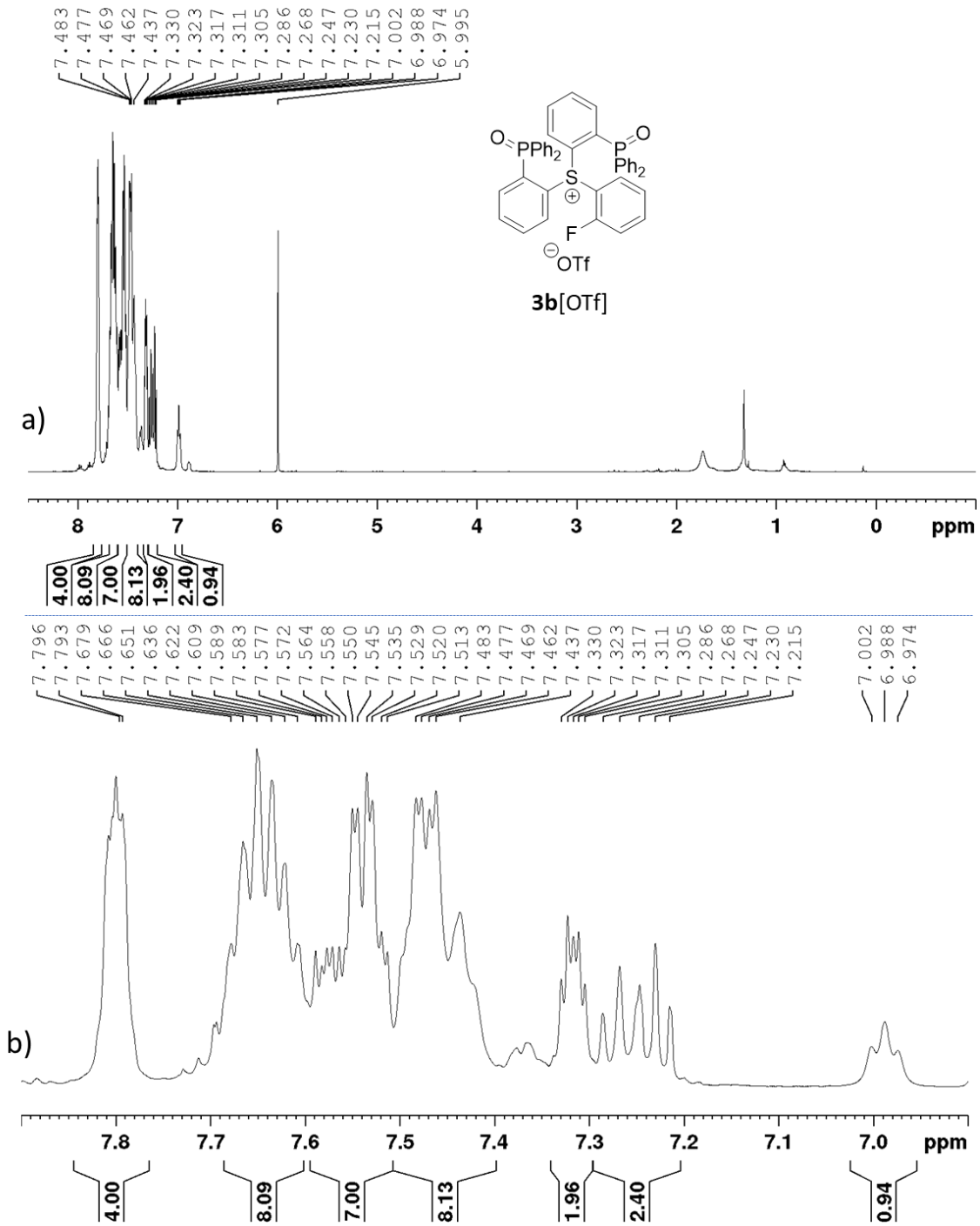


Figure S29: ^{1}H NMR (500 MHz) of **3b**[OTf] in $C_2D_2Cl_4$ at 98.5±1.00 °C. a) Full spectrum, b) aromatic region expanded.

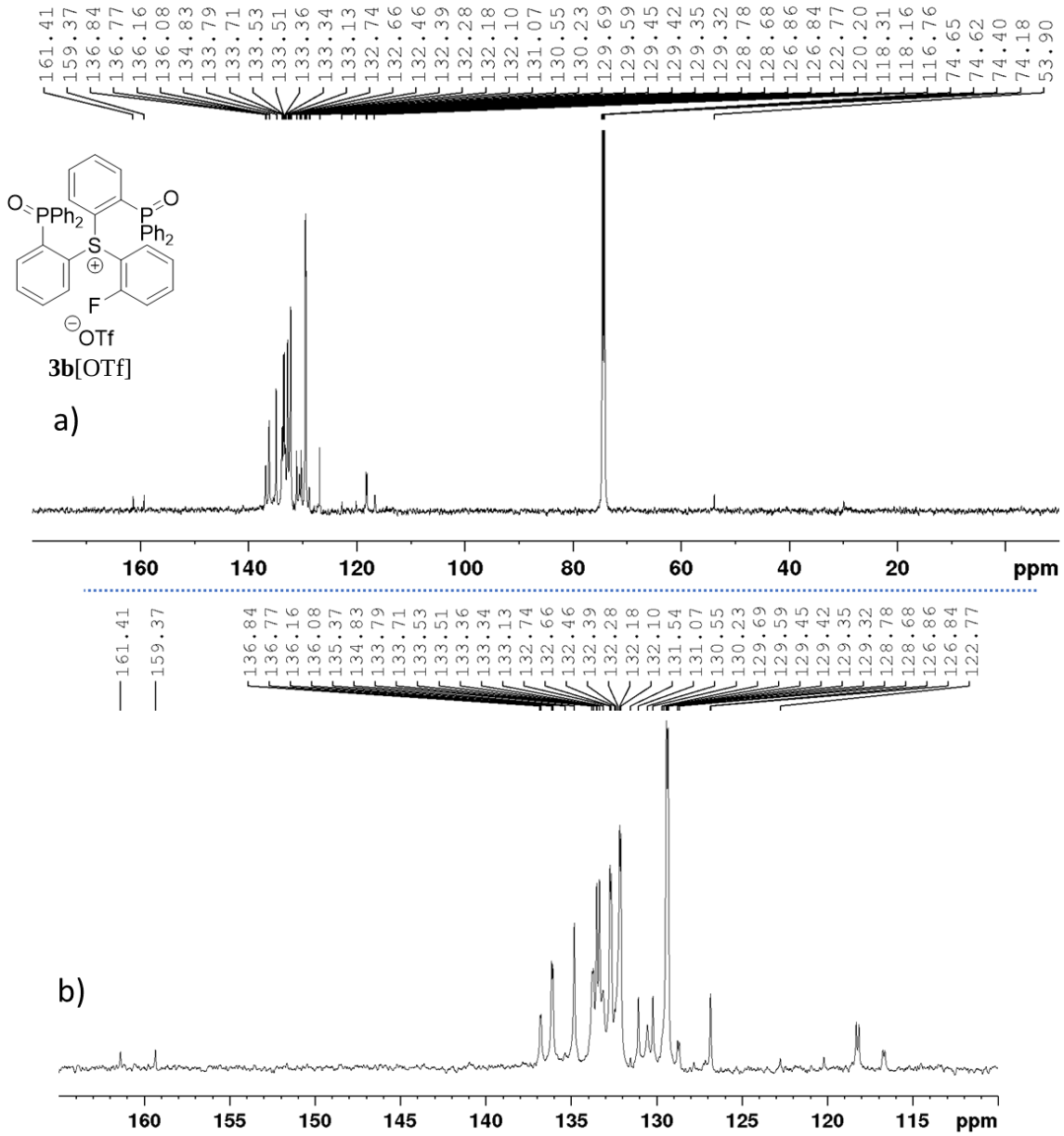
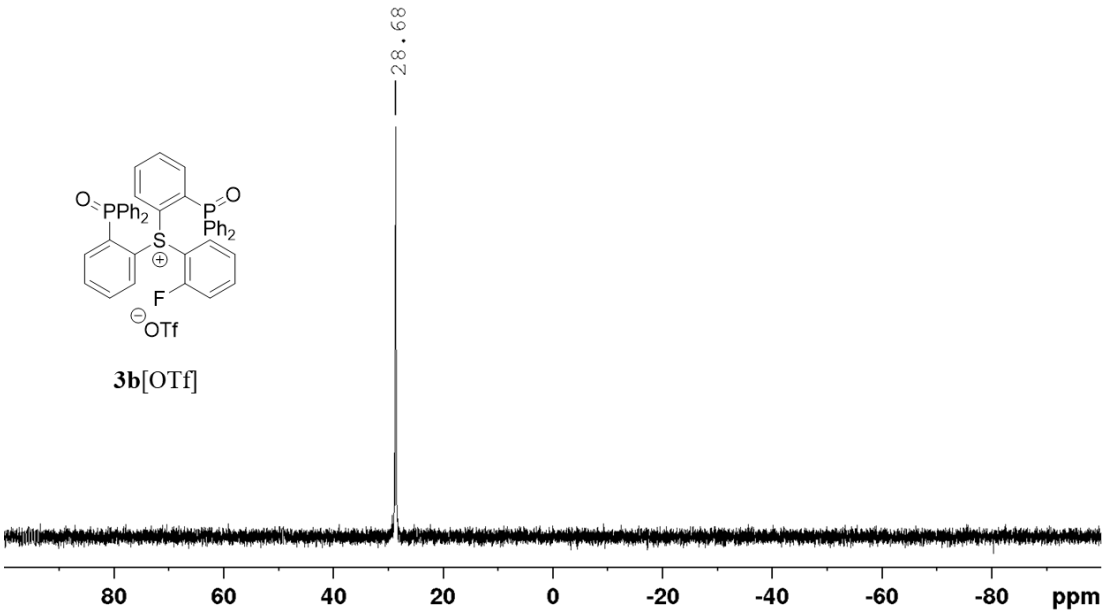
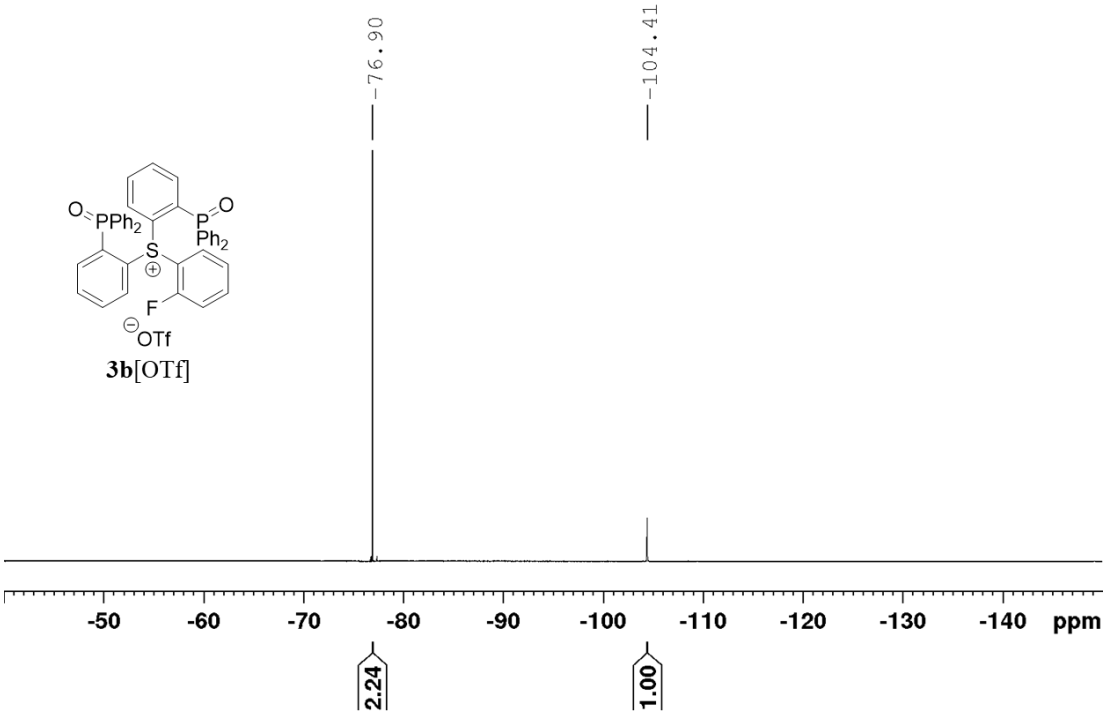


Figure S30: ^{13}C NMR (126 MHz) of **3b**[OTf] in $C_2D_2Cl_4$ at 98.5±1.00 °C. a) full spectrum, b) aromatic region expanded.



3b[OTf]

Figure S31: $^{31}P\{H\}$ NMR (202 MHz) of **3b**[OTf] in $C_2D_2Cl_4$ at 98.5±1.00 °C.



3b[OTf]

Figure S32: $^{19}F\{H\}$ NMR (471 MHz) of **3b**[OTf] in $C_2D_2Cl_4$ at 98.5±1.00 °C.

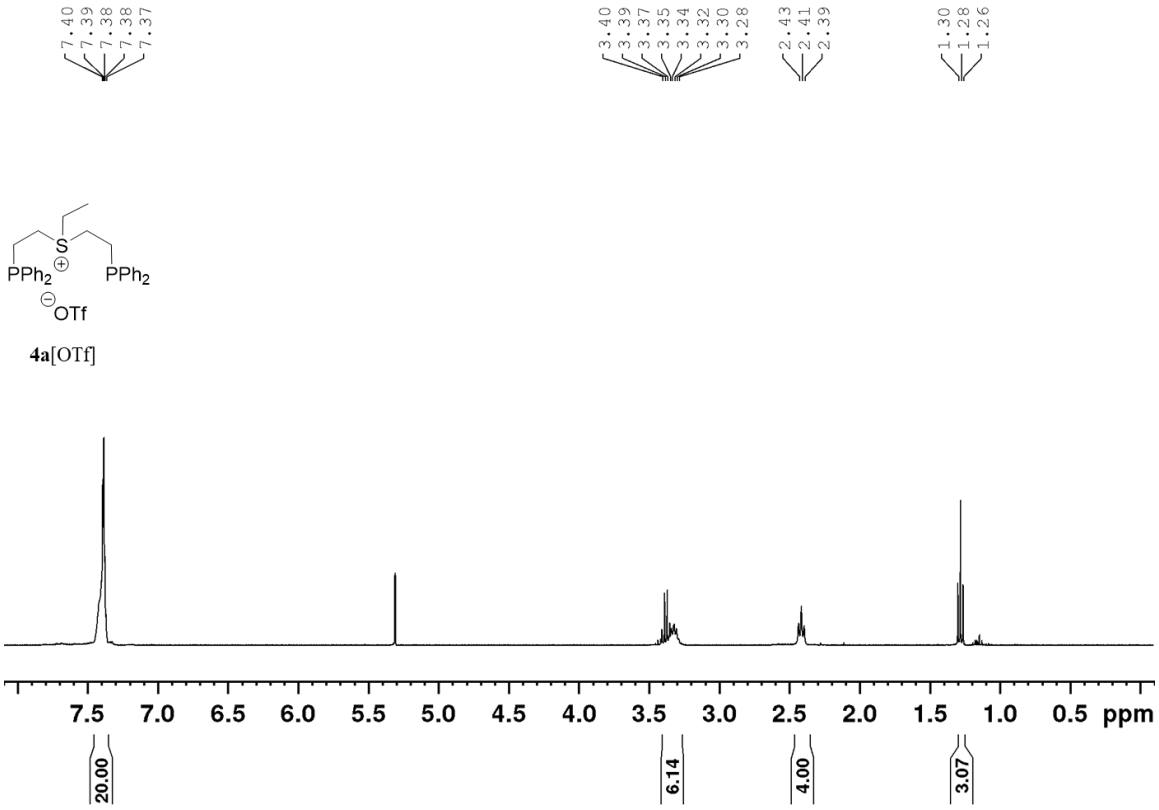


Figure S33: ^{1}H NMR (400 MHz) of **4a**[OTf] in CD_2Cl_2.

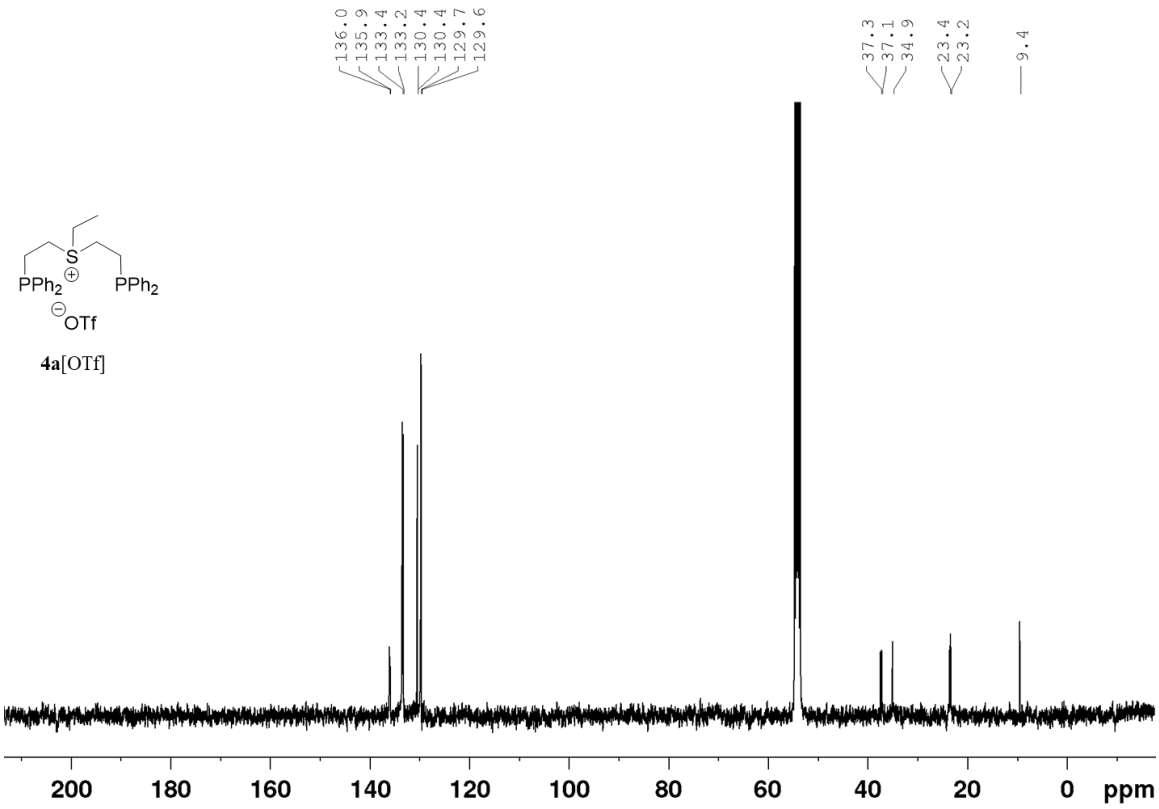


Figure S34: ^{13}C NMR (101 MHz) of **4a**[OTf] in CD_2Cl_2.

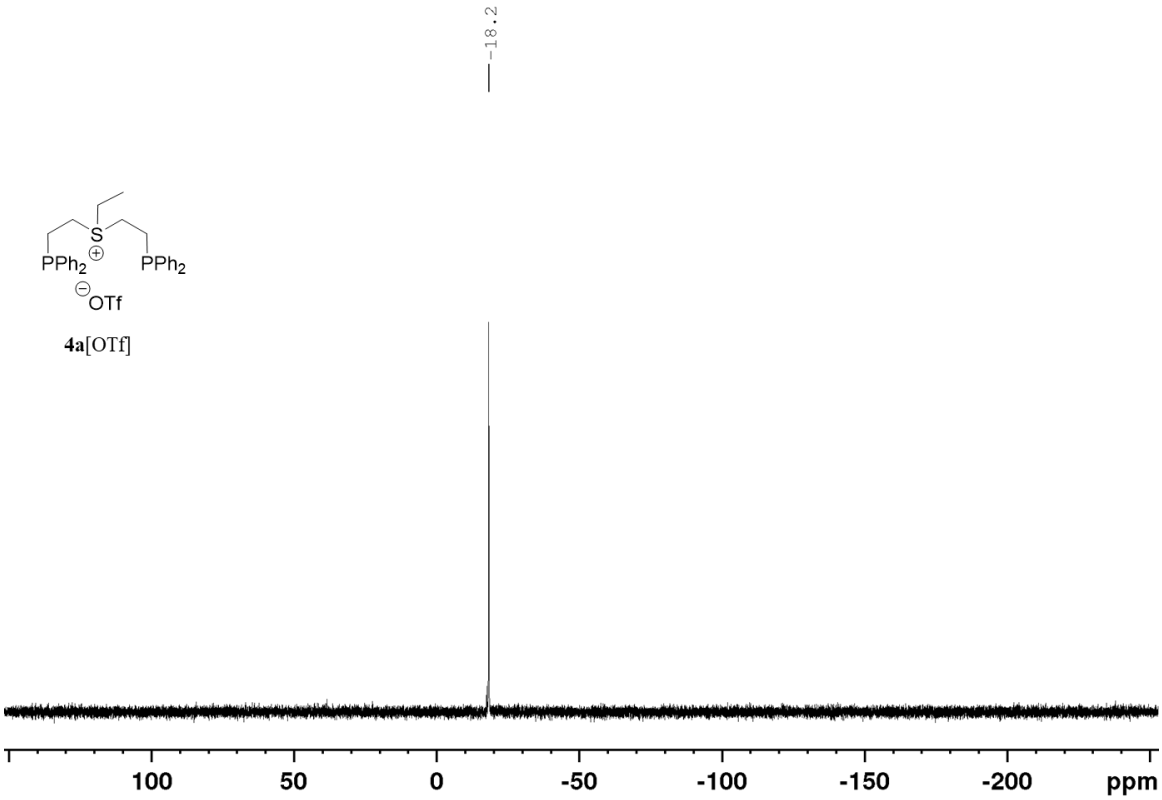


Figure S35: $^{31}P\{H\}$ NMR (162 MHz) of **4a**[OTf] in CD_2Cl_2.

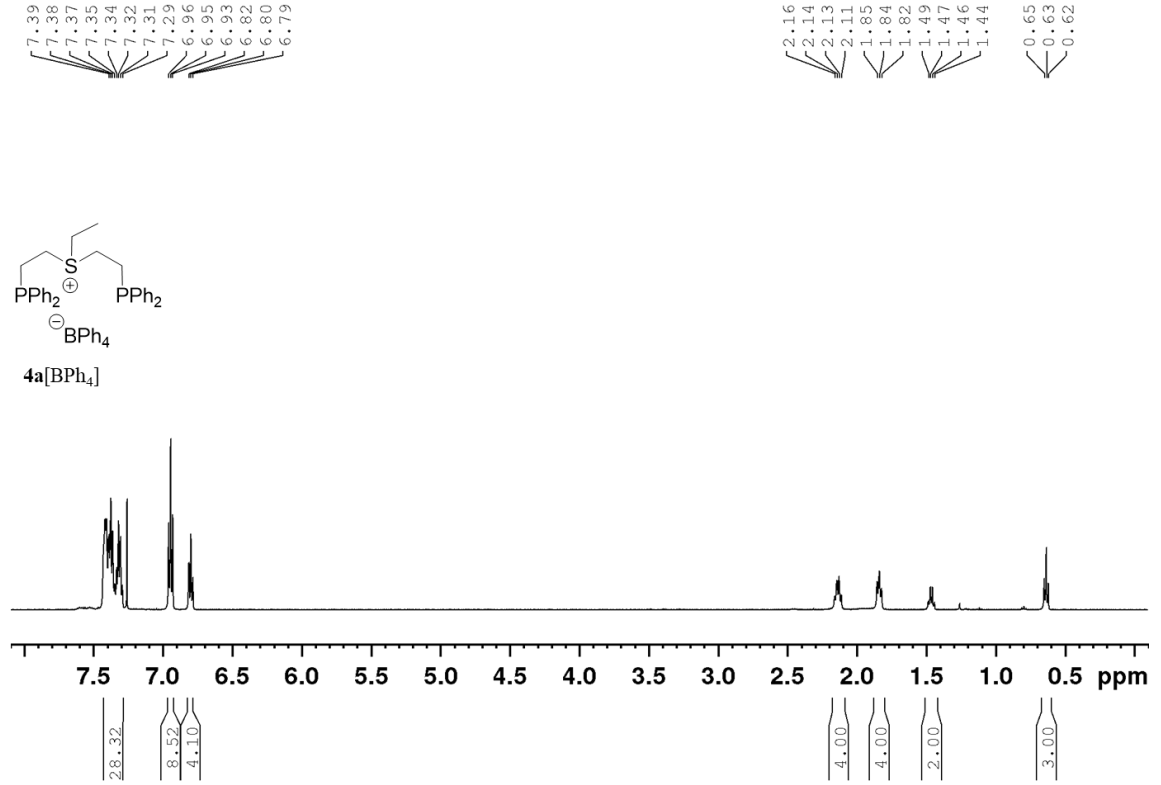


Figure S36: ^{1}H NMR (400 MHz) of **4a**[BPh_4] in $CDCl_3$.

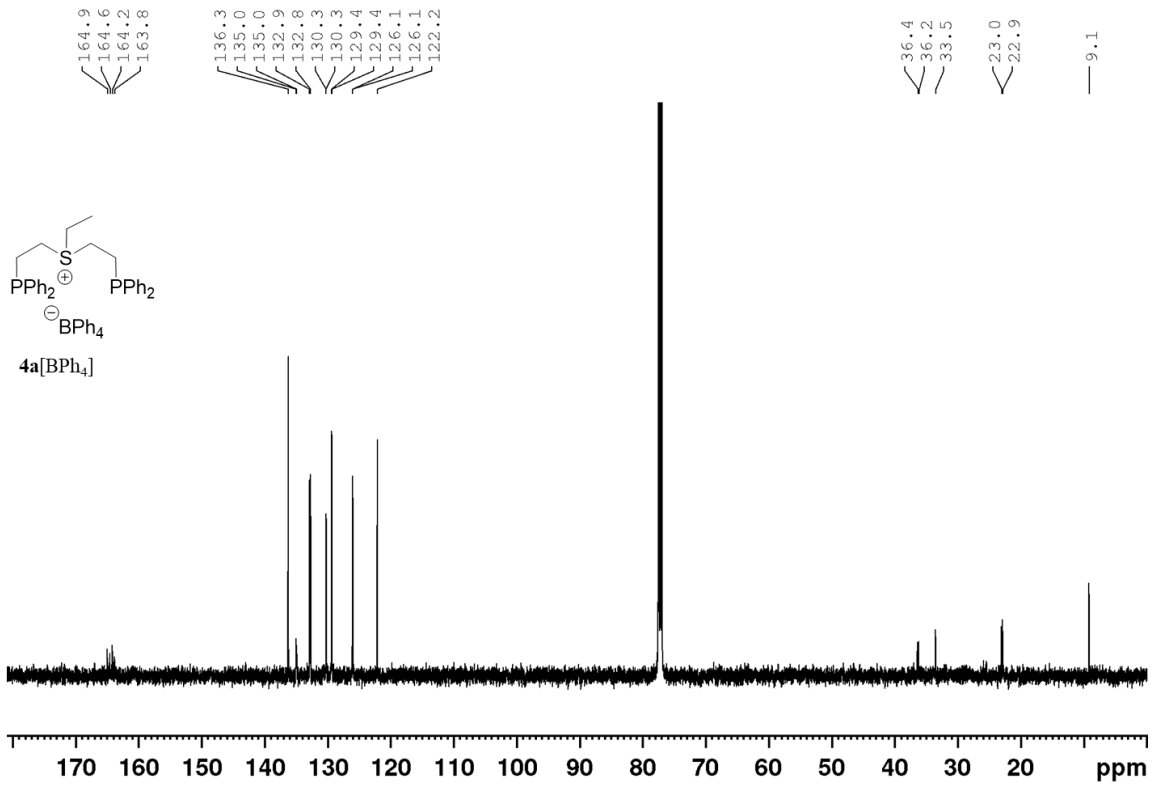


Figure S37: ^{13}C NMR (126 MHz) of **4a**[BPh_4] in $CDCl_3$.

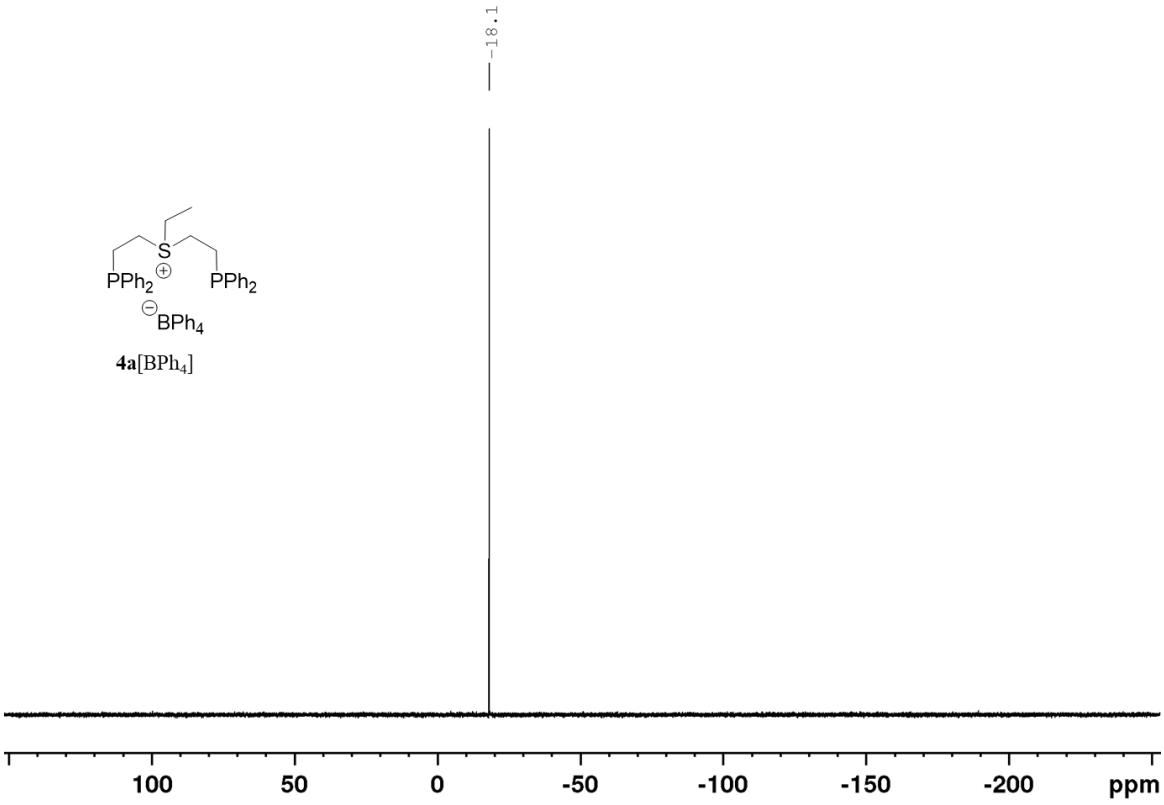


Figure S38: $^{31}P\{H\}$ NMR (162 MHz) of **4a**[BPh_4] in $CDCl_3$.

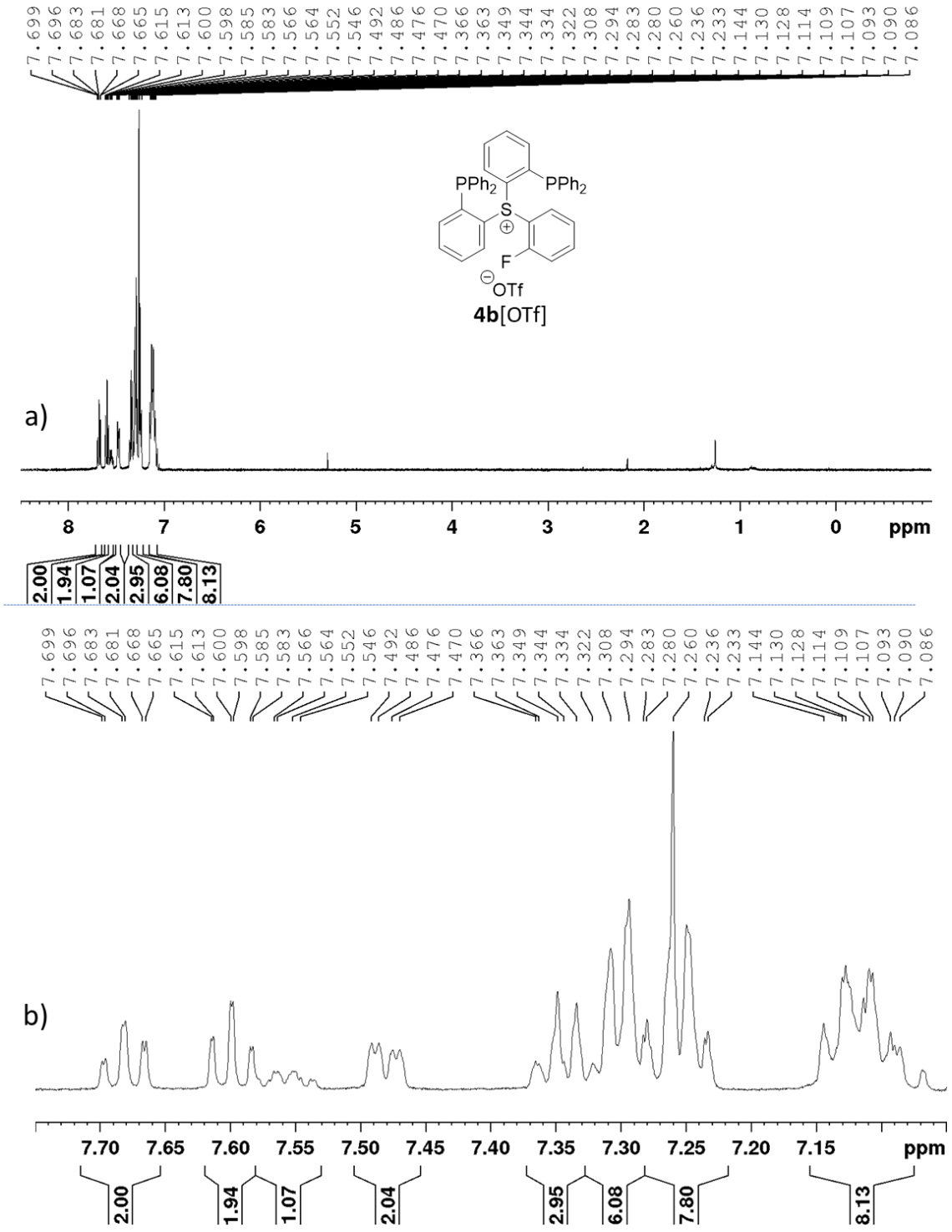


Figure S39: ^{1}H NMR (500 MHz) of **4b**[OTf] in $CDCl_3$. a) full spectrum, b) aromatic region expanded.

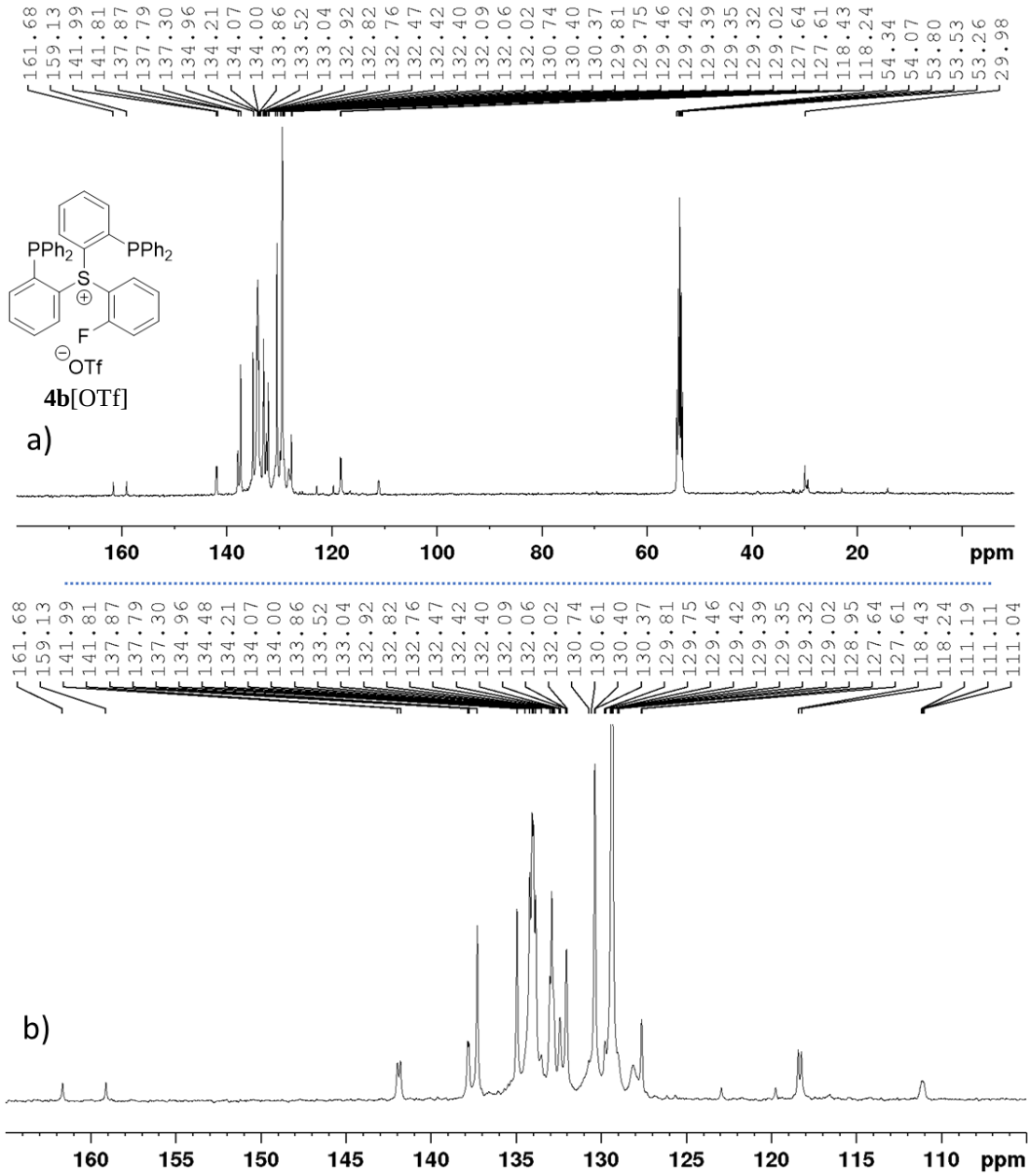
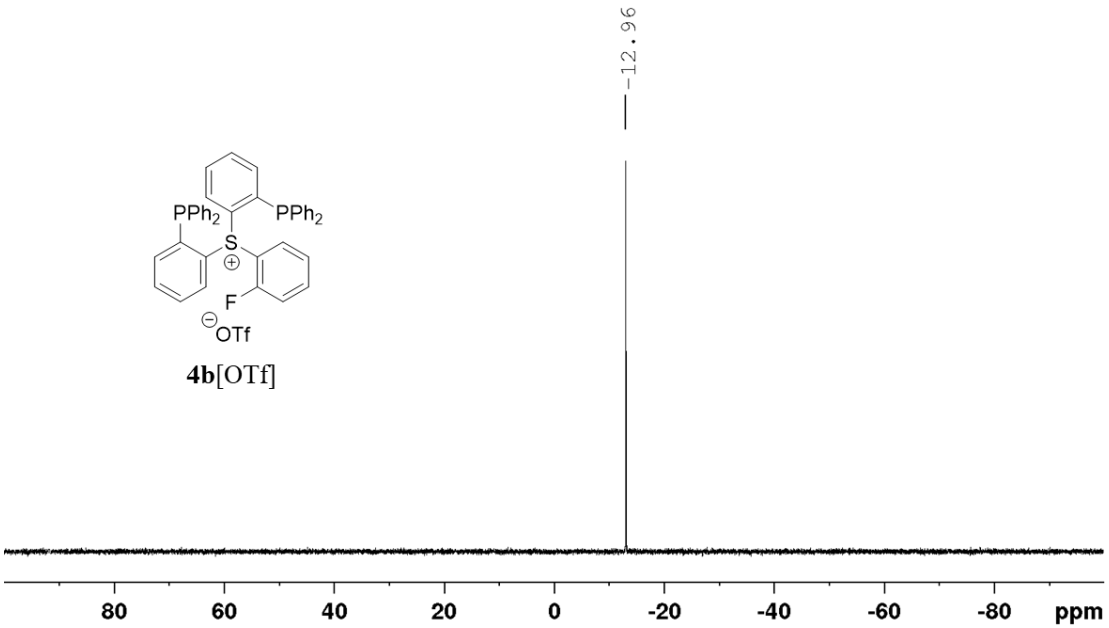
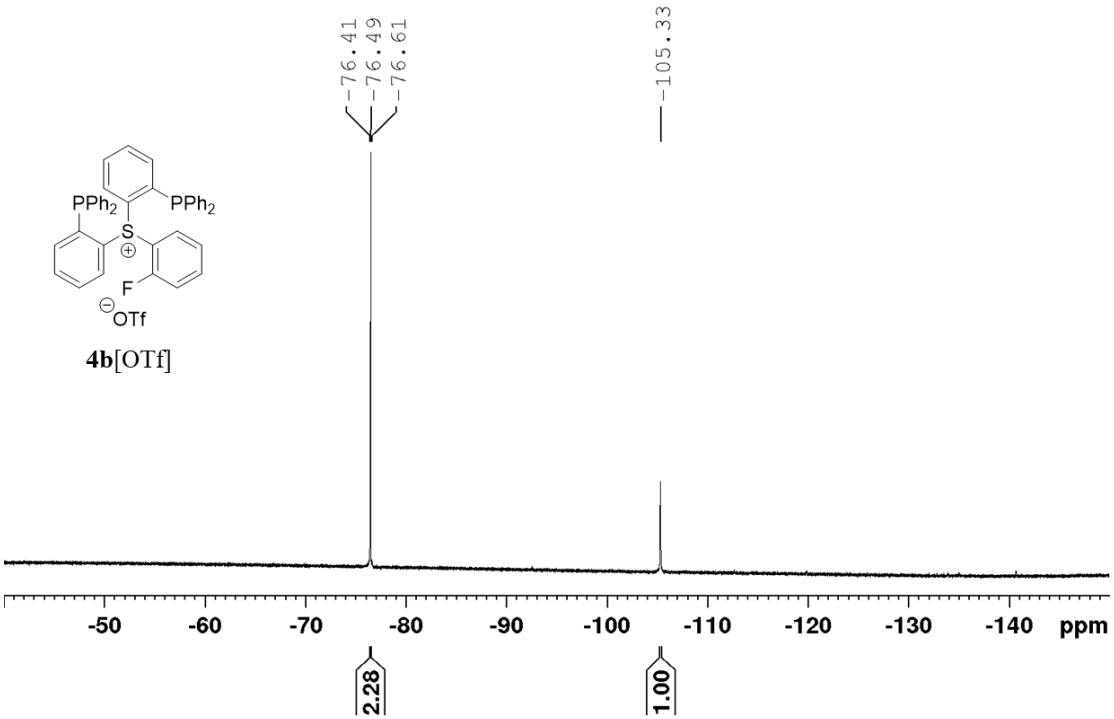


Figure S40: ^{31}C NMR (126 MHz) of **4b**[OTf] in $CDCl_3$. a) full spectrum, b) aromatic region expanded.



4b[OTf]

Figure S41: $^{31}P\{H\}$ NMR (202 MHz) of **4b**[OTf] in $CDCl_3$.



4b[OTf]

Figure S42: $^{19}F\{H\}$ NMR (376 MHz) of **4b**[OTf] in $CDCl_3$.

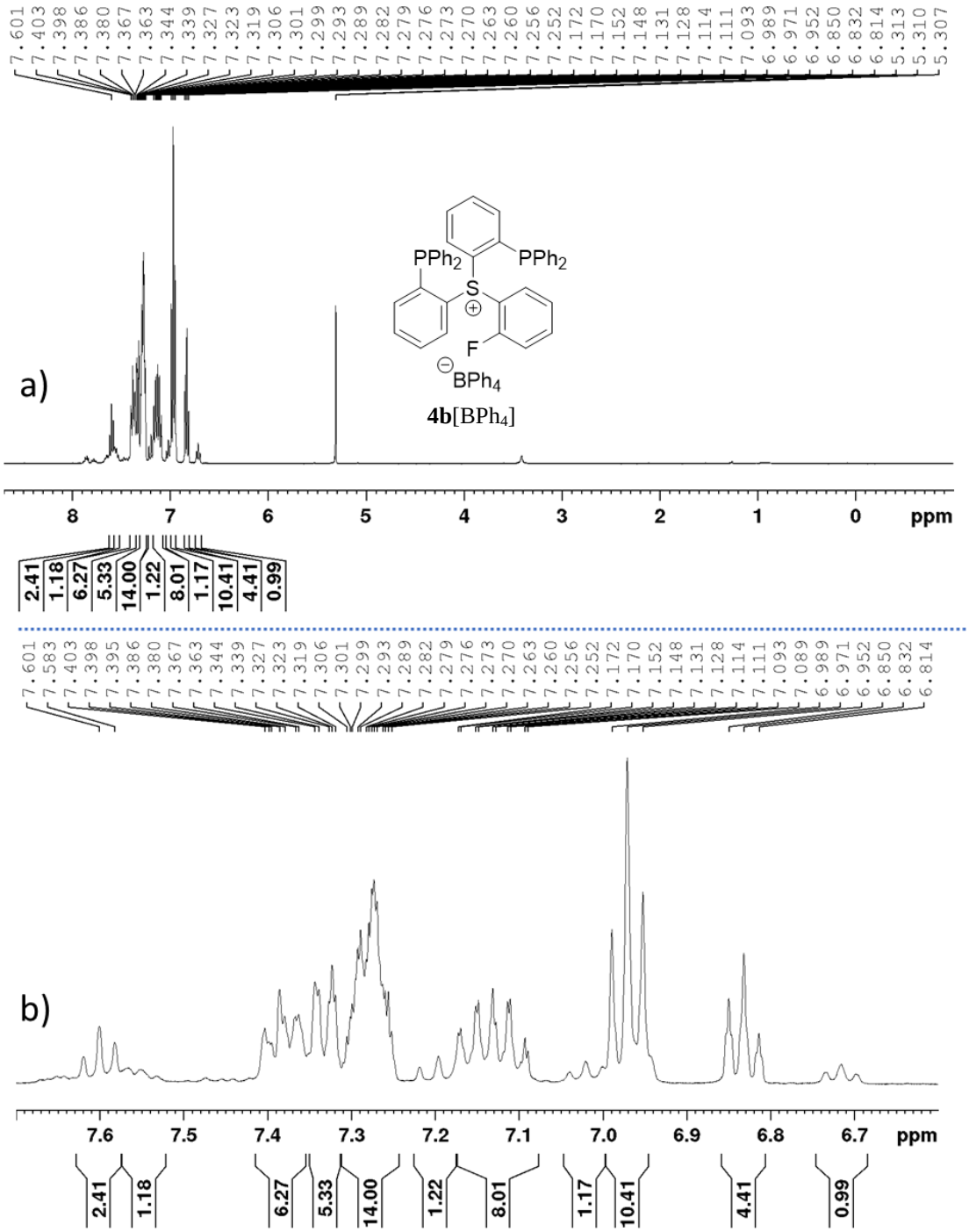


Figure S43: ^{1}H NMR (500 MHz) of **4b**[BPh_4] in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.

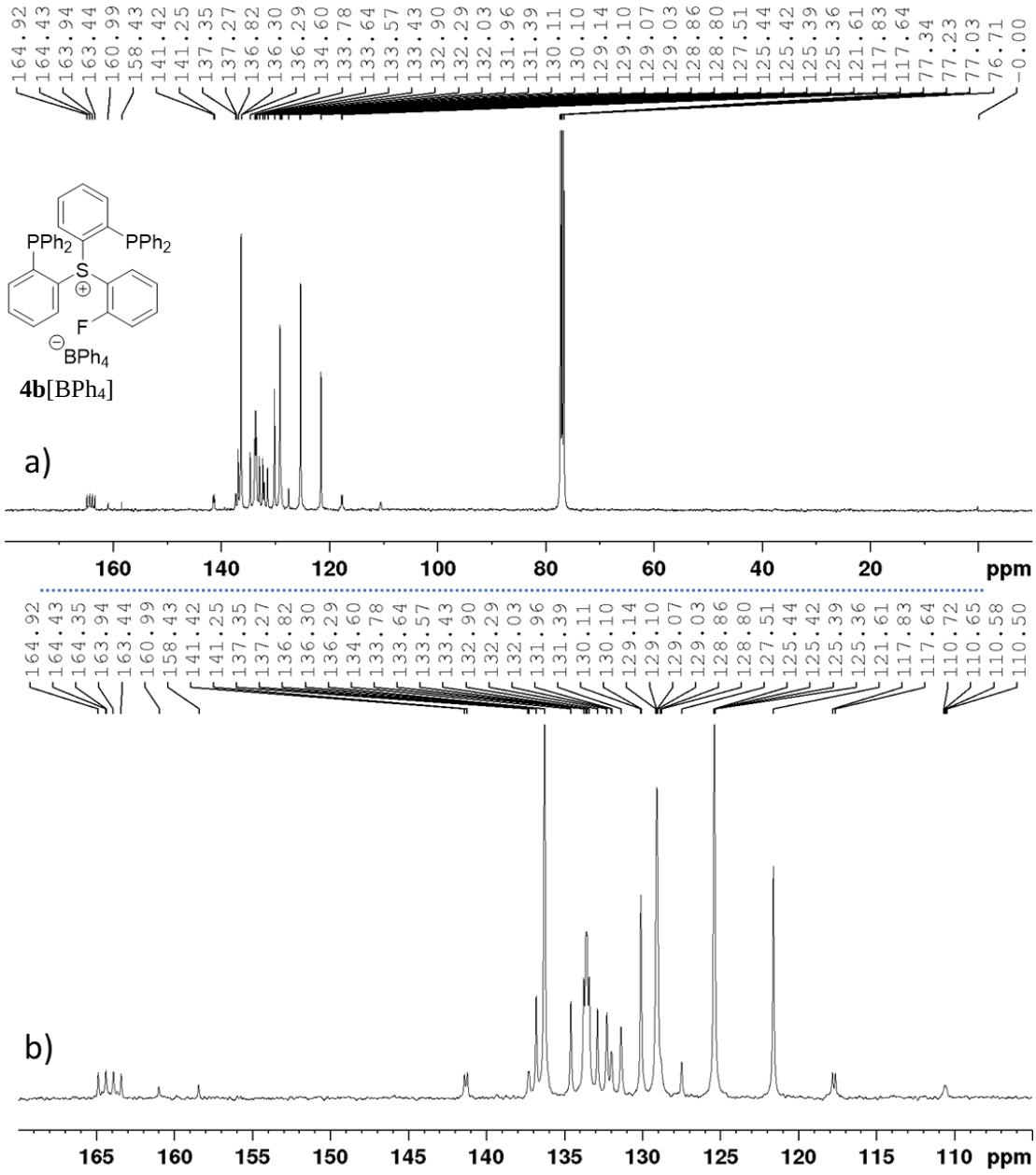
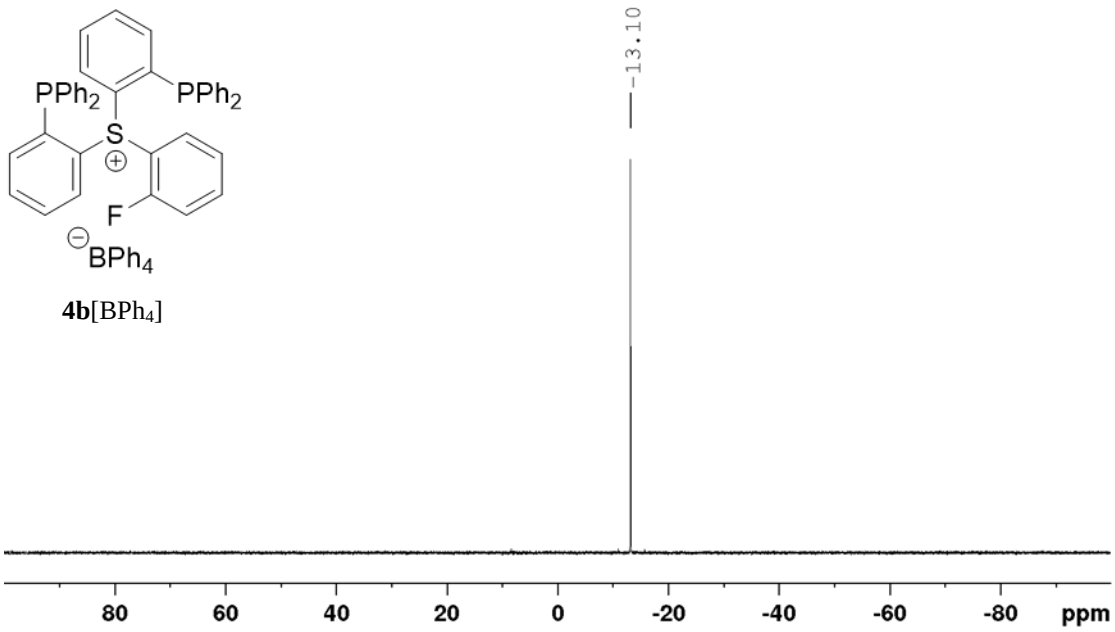
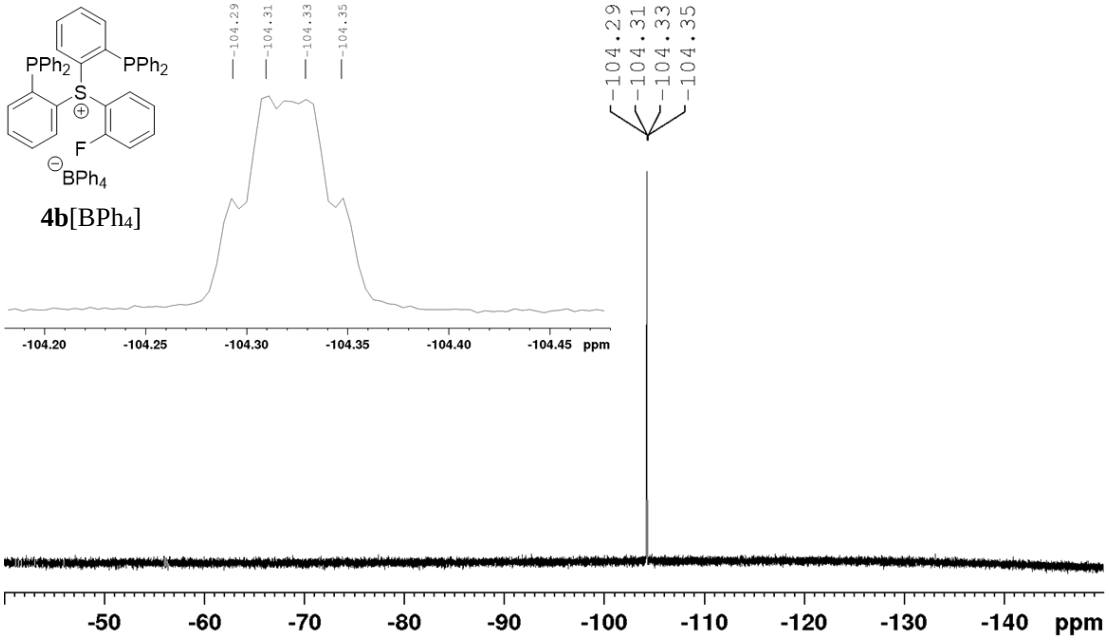


Figure S44: ^{13}C NMR (101 MHz) of **4b**[BPh_4] in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.



4b[BPh_4]

Figure S45: $^{31}P\{H\}$ NMR (162 MHz) of **4b**[BPh_4] in CD_2Cl_2.



4b[BPh_4]

Figure S46: ^{19}F NMR (376 MHz) of **4b**[BPh_4] in CD_2Cl_2.

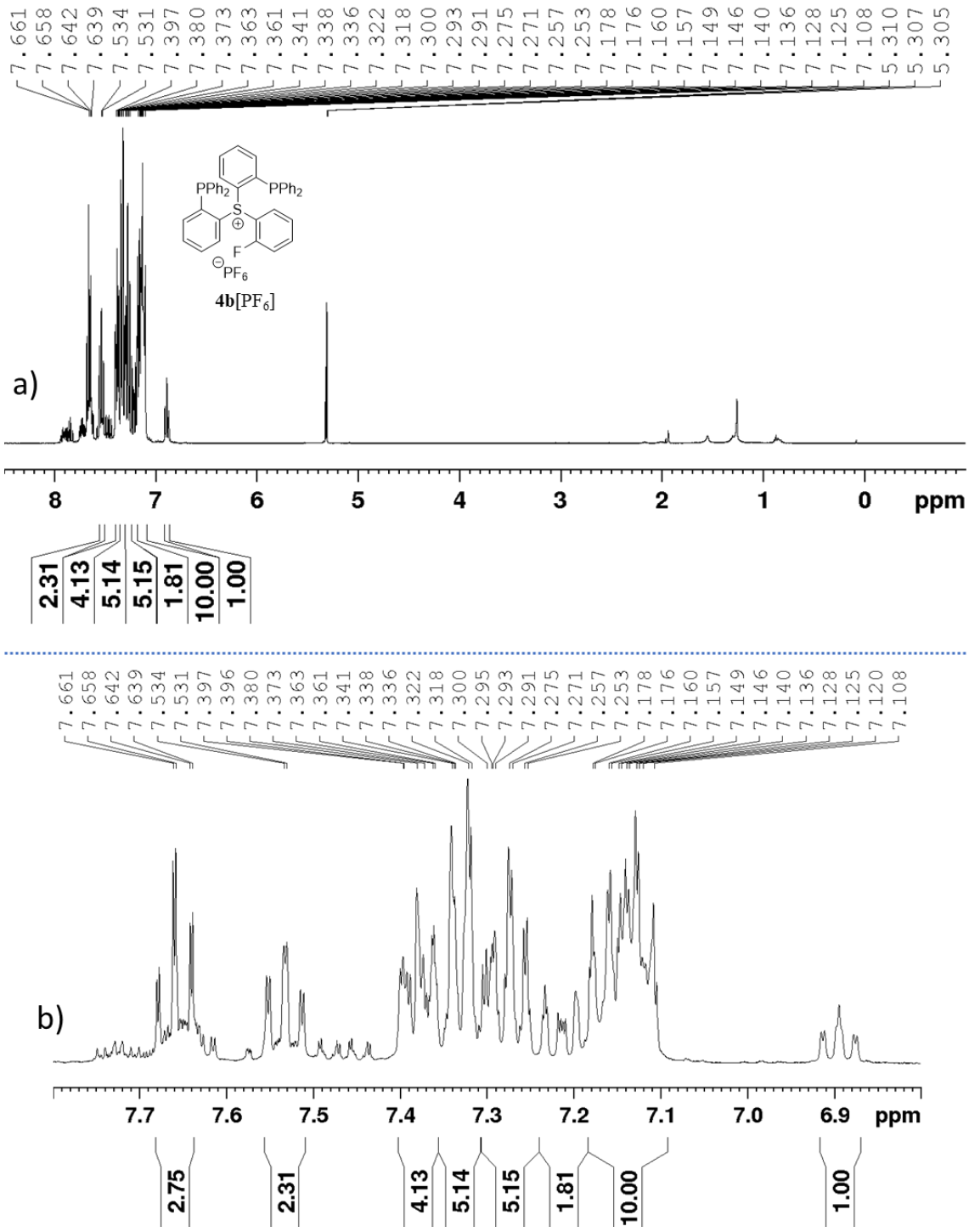


Figure S47: ^{1}H NMR (500 MHz) of **4b**[PF_6] in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.

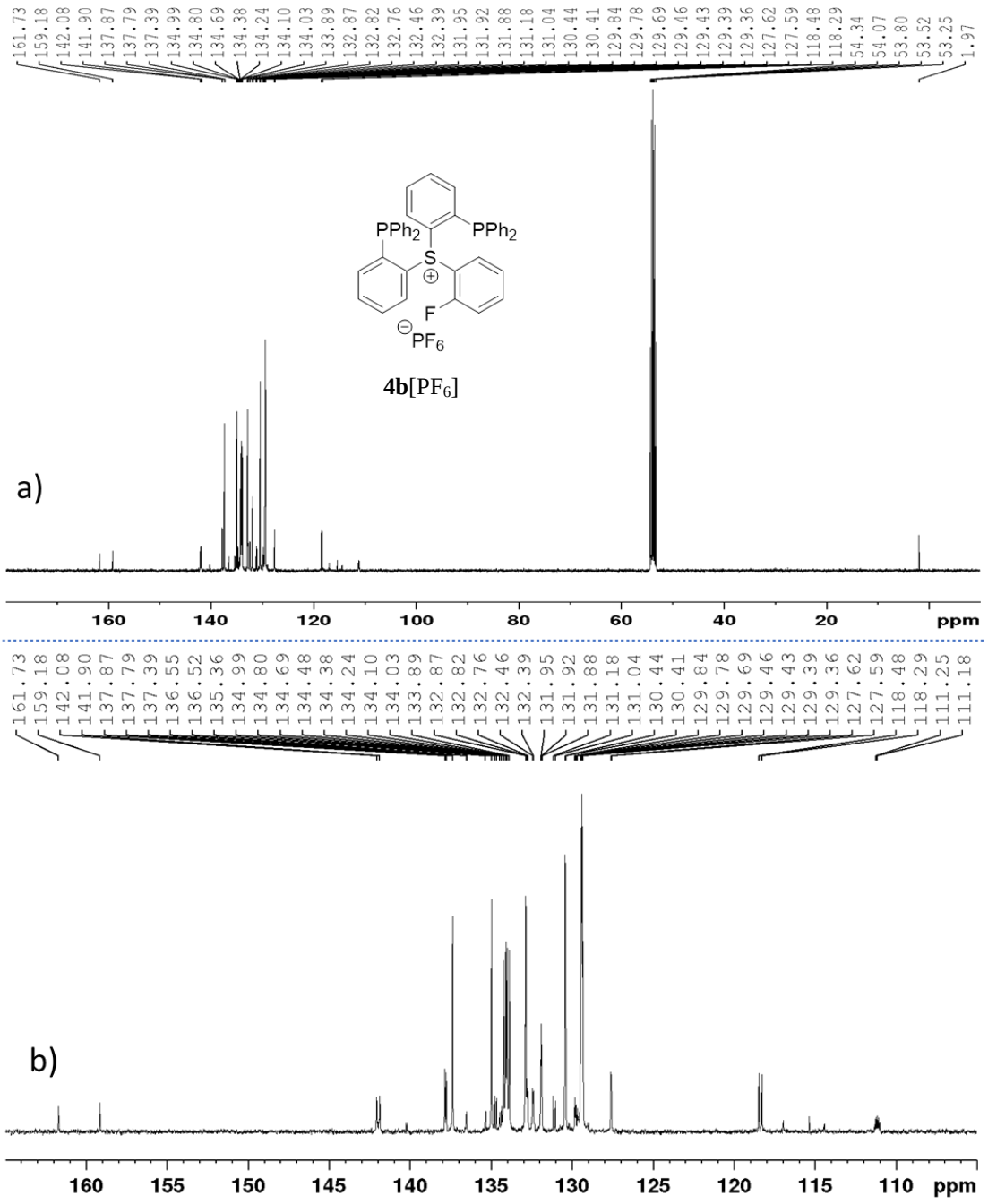
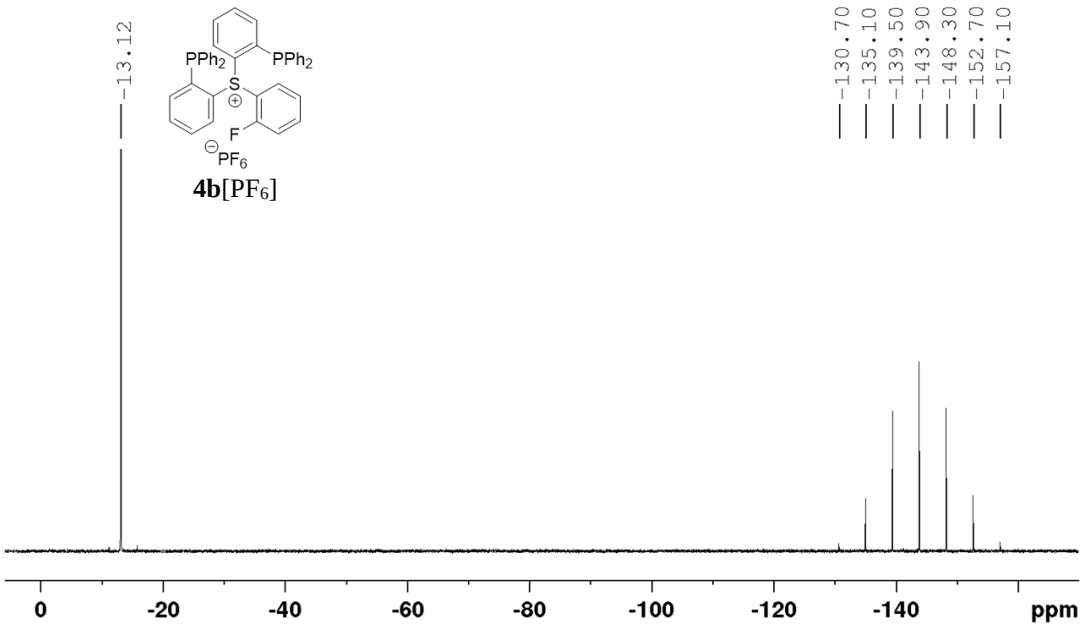
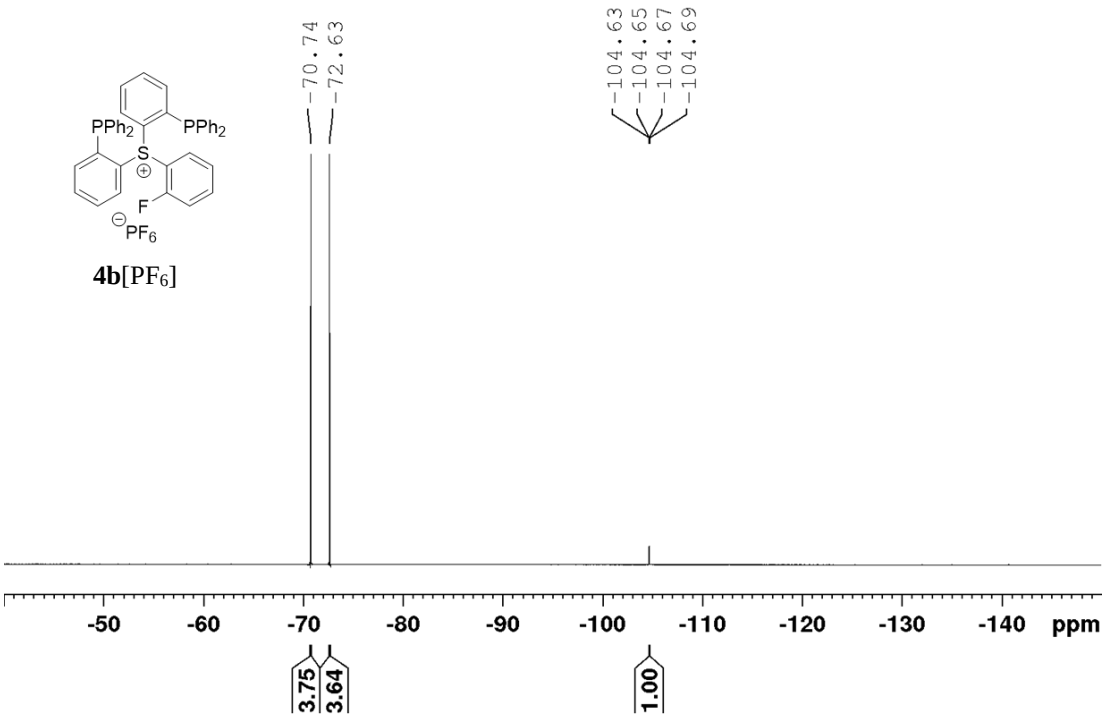


Figure S48: ^{13}C NMR (101 MHz) of **4b**[PF_6] in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.



4b[PF_6]

Figure S49: $^{31}P\{H\}$ NMR (162 MHz) of **4b**[PF_6] in $CDCl_3$.



4b[PF_6]

Figure S50: ^{19}F NMR (376 MHz) of **4b**[PF_6] in $CDCl_3$.

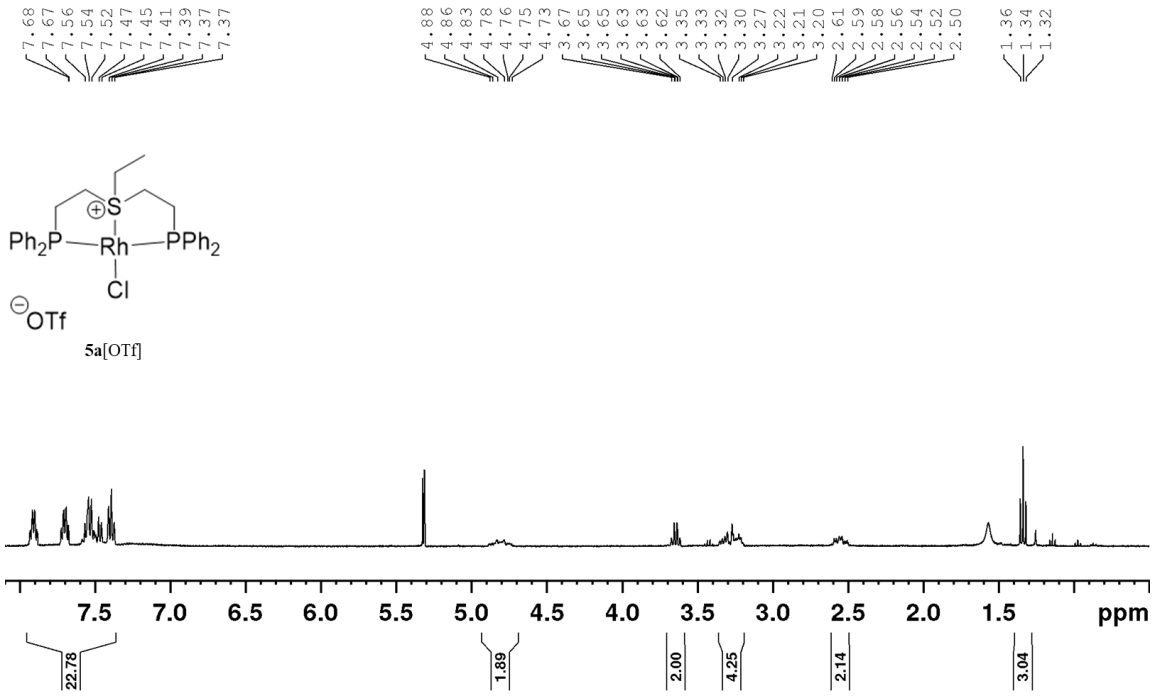


Figure S51: ^{1}H NMR (400 MHz) of **5a**[OTf] in CD_2Cl_2.

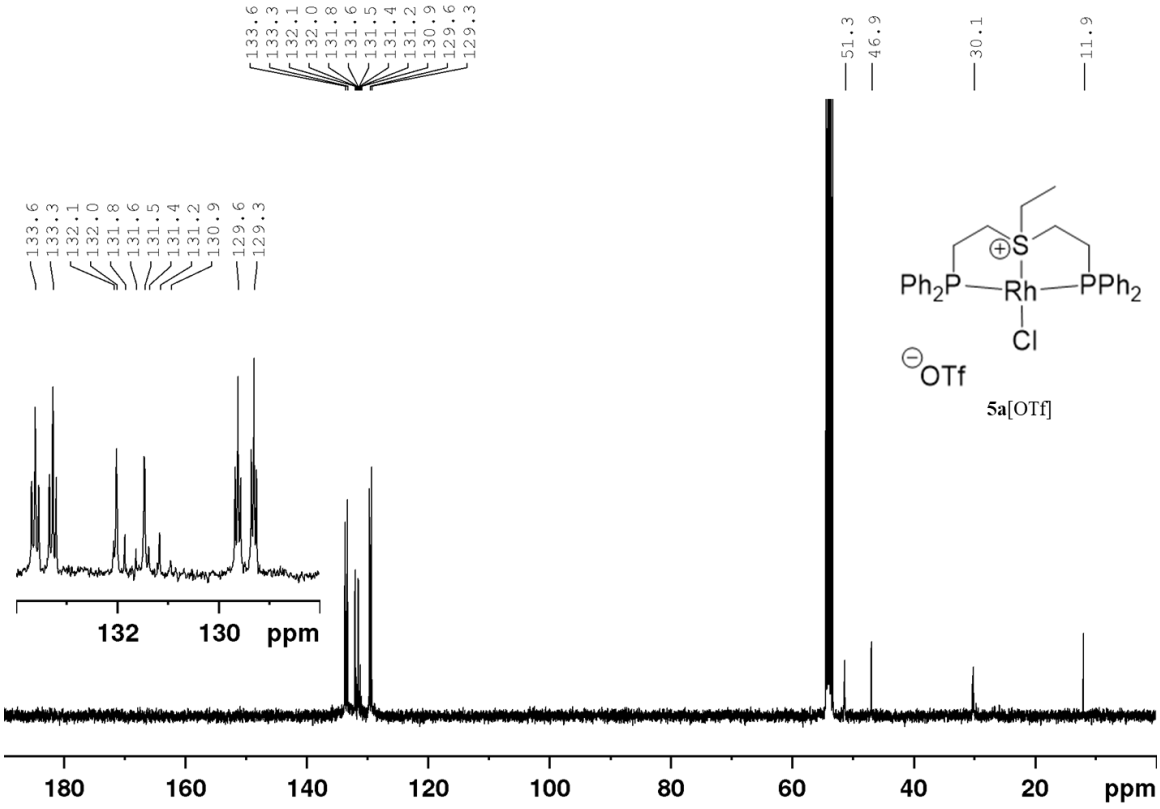


Figure S52: ^{13}C NMR (101 MHz) of **5a**[OTf] in CD_2Cl_2.

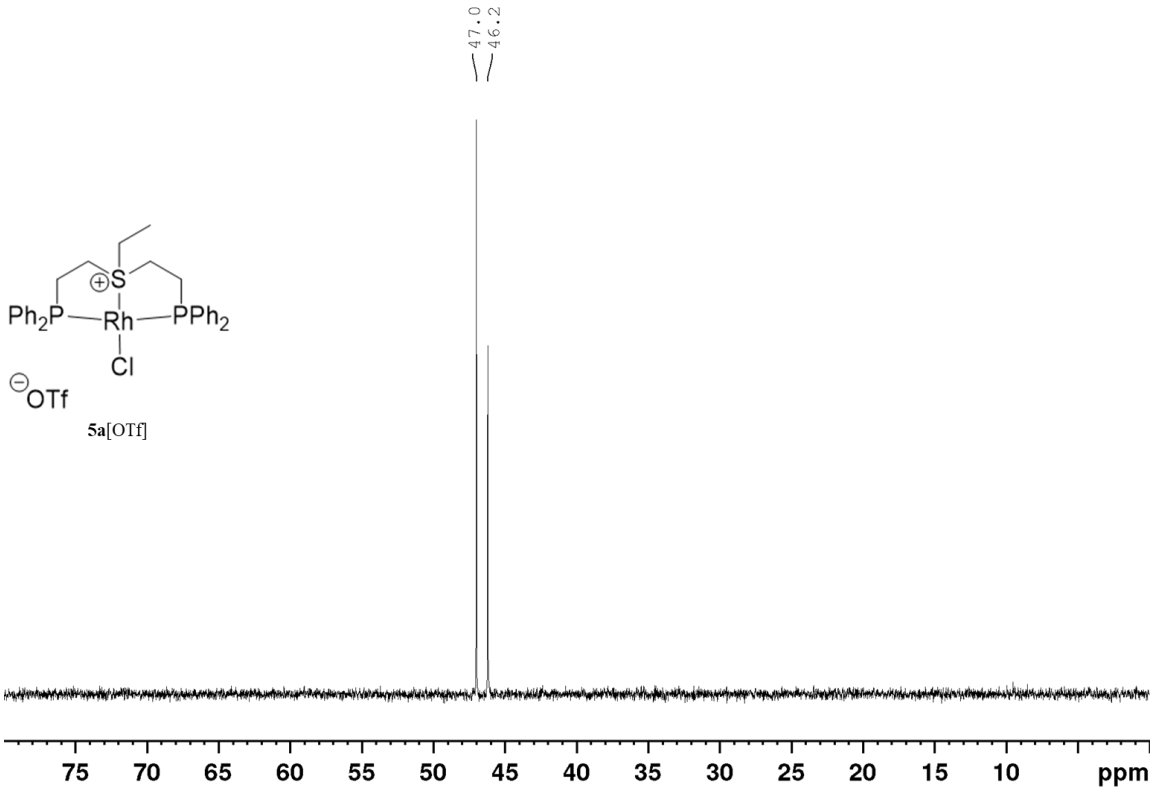


Figure S53: $^{31}P\{H\}$ NMR (162 MHz) of **5a**[OTf] in CD_2Cl_2.

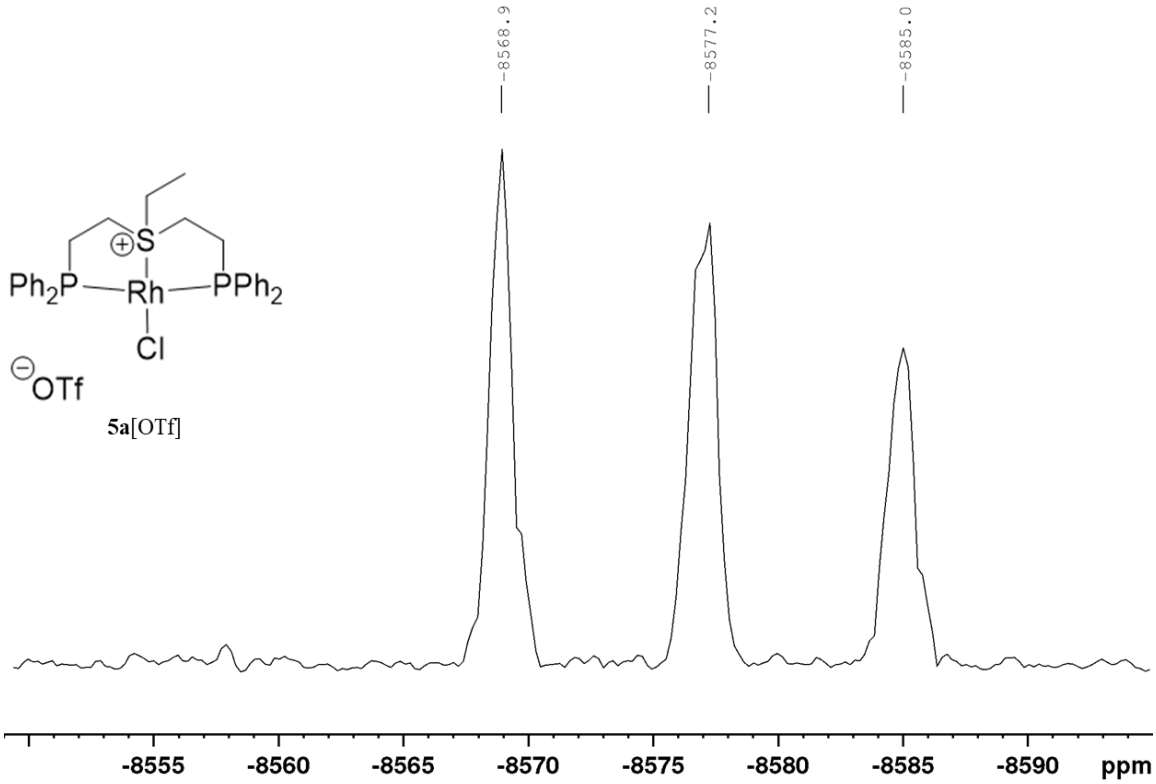


Figure S54: $^{103}Rh\{H\}$ NMR (16 MHz) of **5a**[OTf] in CD_2Cl_2.

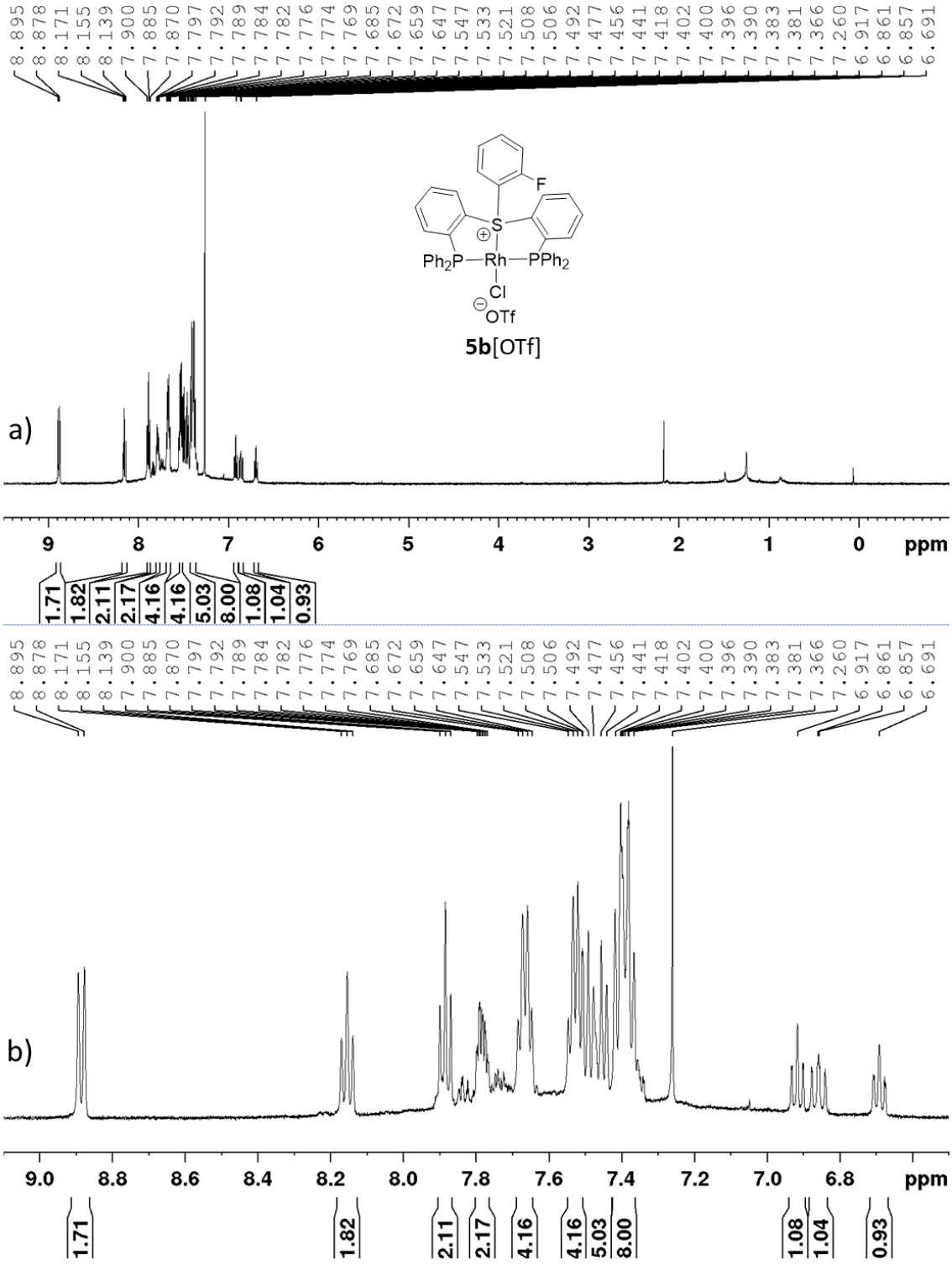


Figure S55: ^{1}H NMR (500 MHz) of **5b**[OTf] in $CDCl_3$. a) full spectrum, b) aromatic region expanded.

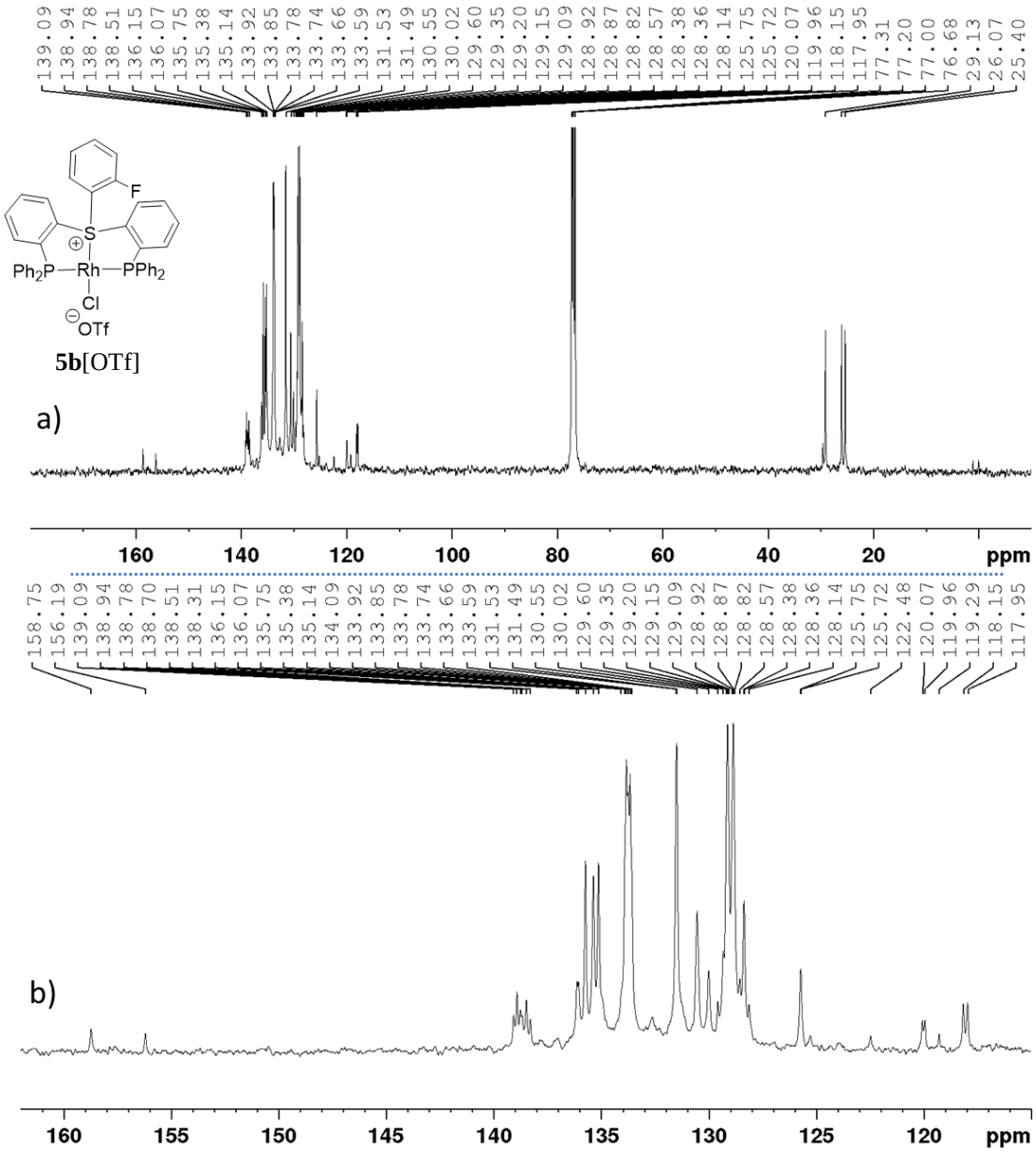
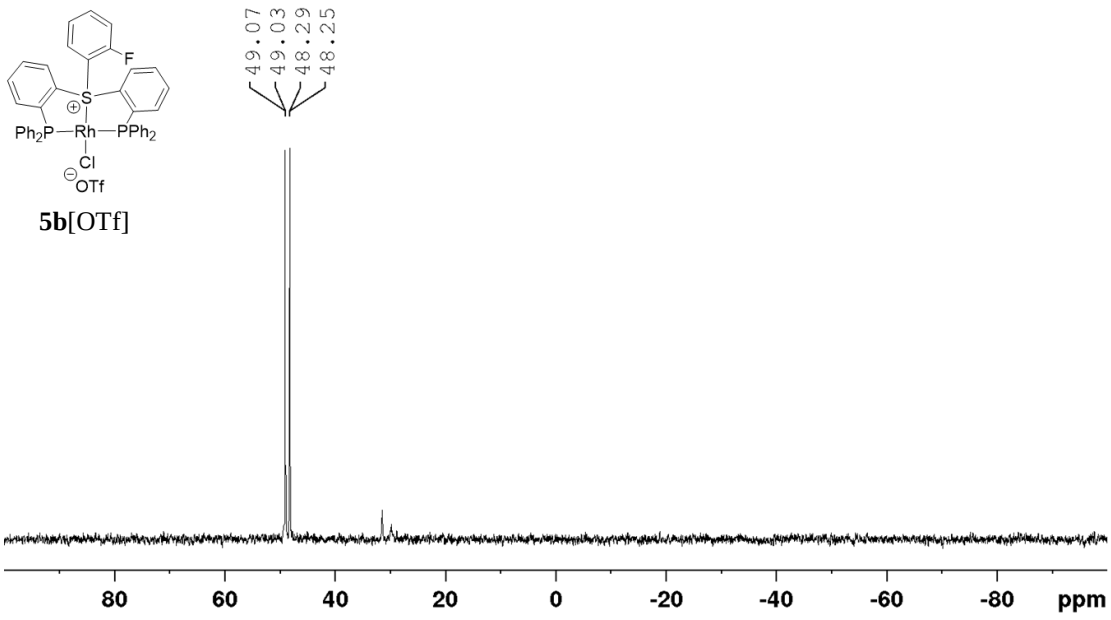
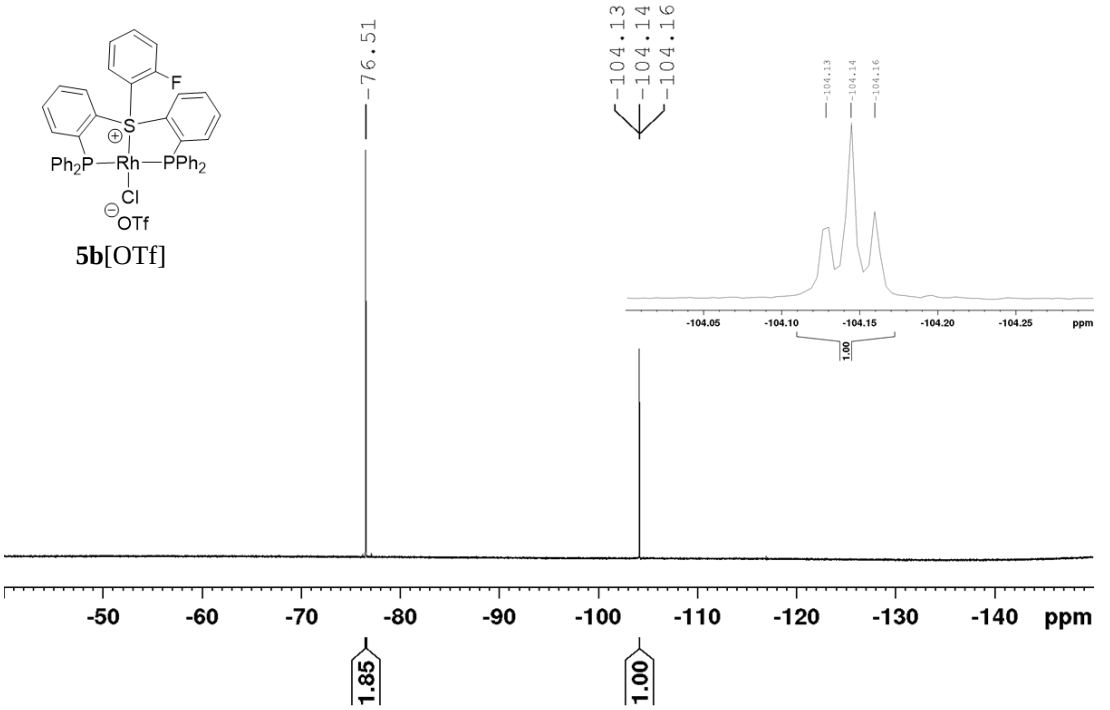


Figure S56: ^{13}C NMR (126 MHz) of **5b**[OTf] in $CDCl_3$. a) full spectrum, b) aromatic region expanded.



5b[OTf]

Figure S57: $^{31}P\{H\}$ NMR (162 MHz) of **5b**[OTf] in $CDCl_3$.



5b[OTf]

Figure S58: $^{19}F\{H\}$ NMR (376 MHz) of **5b**[OTf] in $CDCl_3$.

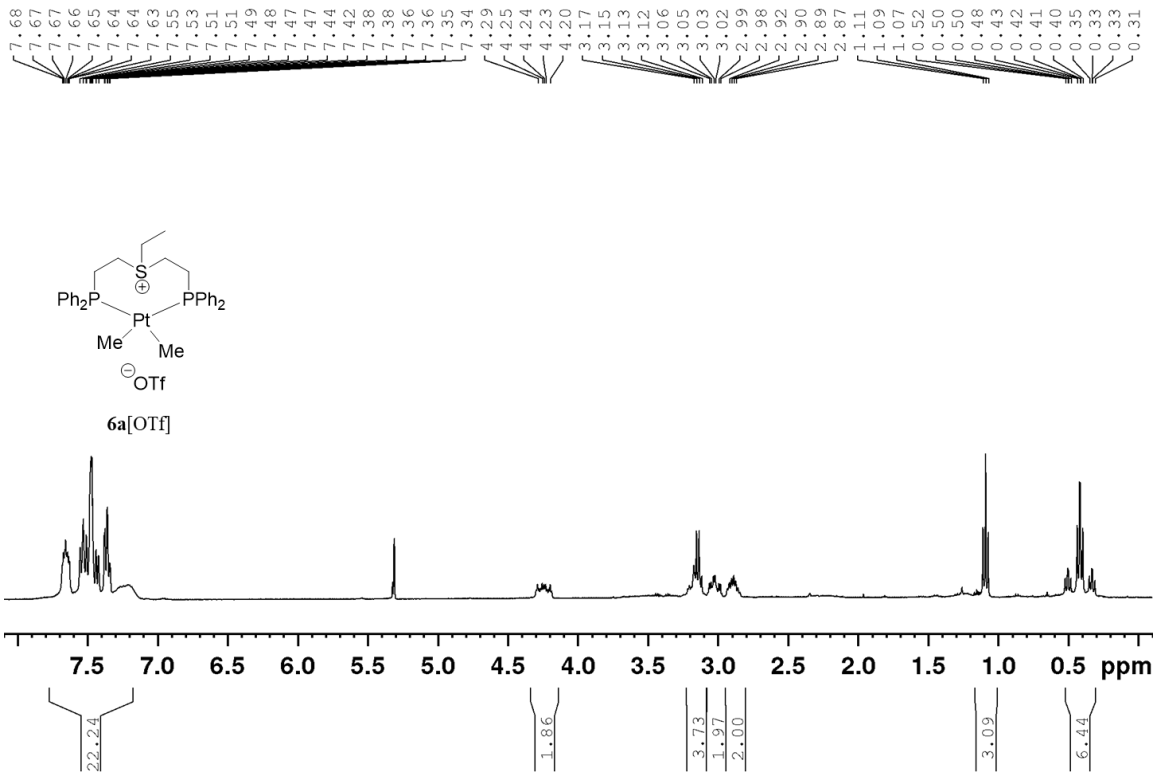


Figure S59: ^{1}H NMR (400 MHz) of **6a**[OTf] in CD_2Cl_2.

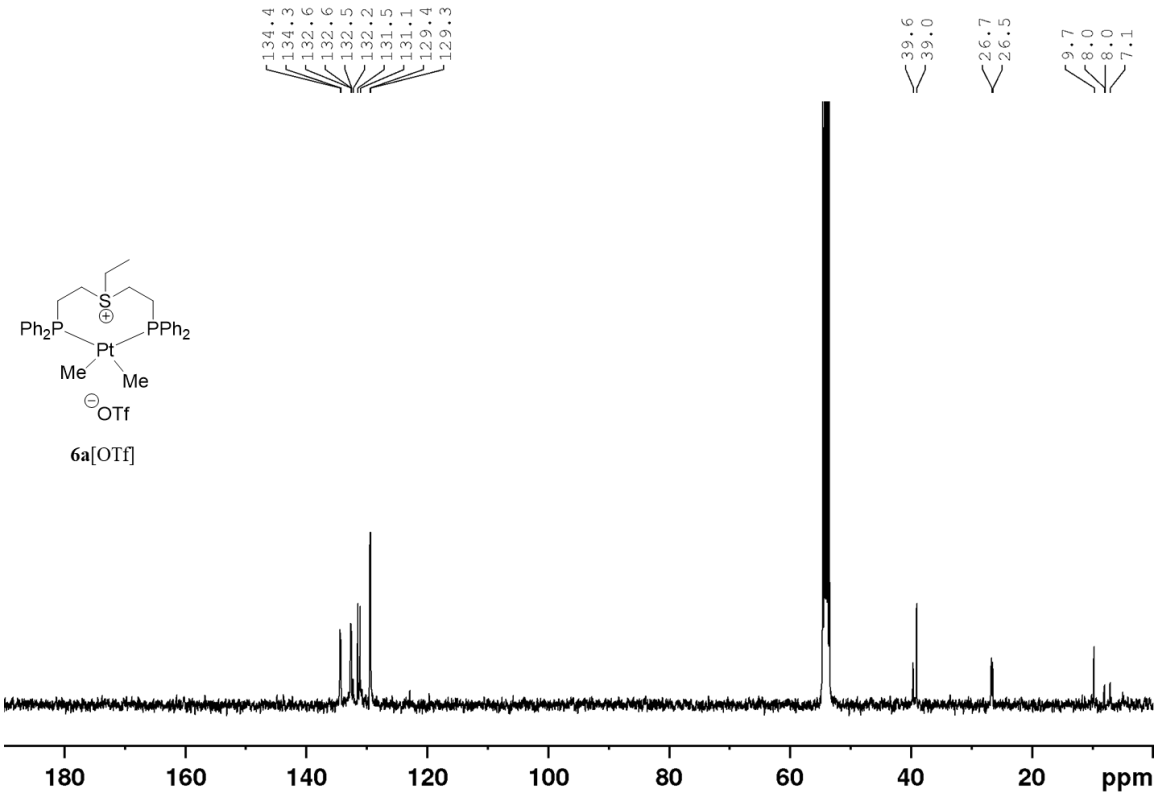


Figure S60: ^{13}C NMR (101 MHz) of **6a**[OTf] in CD_2Cl_2.

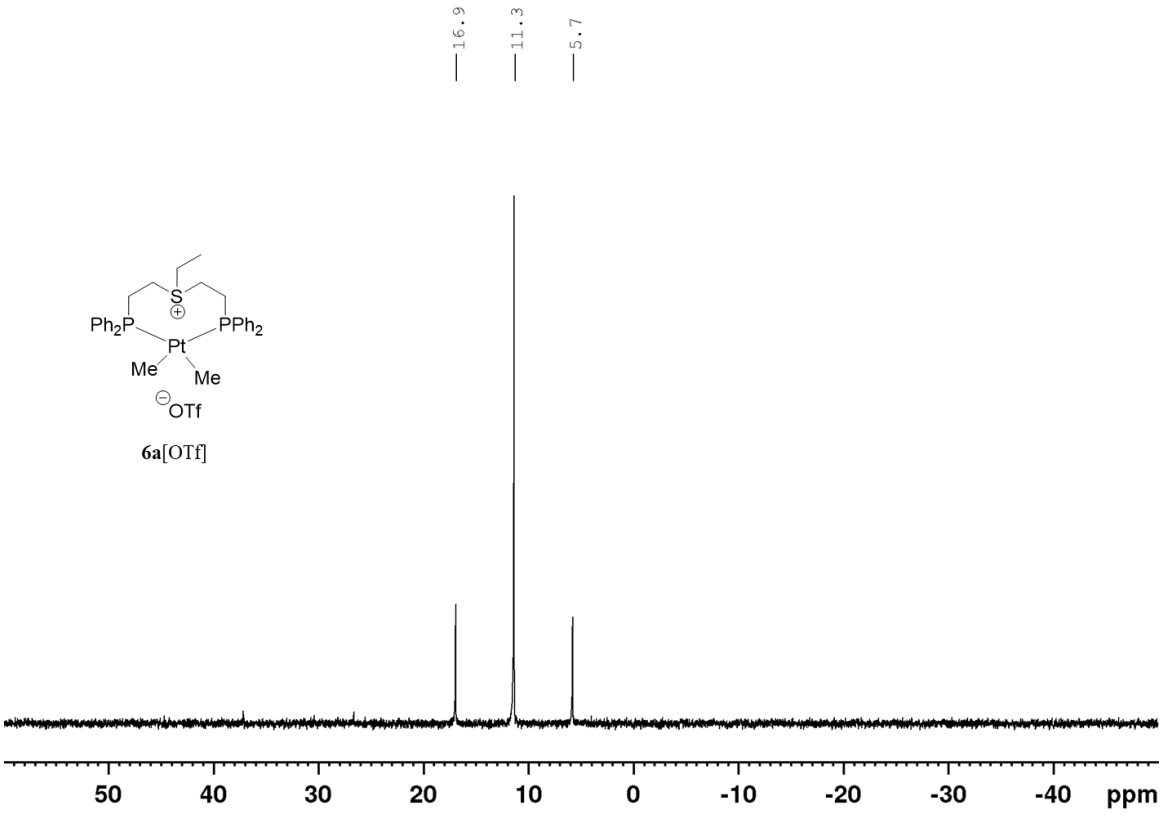


Figure S61: $^{31}P\{H\}$ NMR (162 MHz) of **6a**[OTf] in CD_2Cl_2.

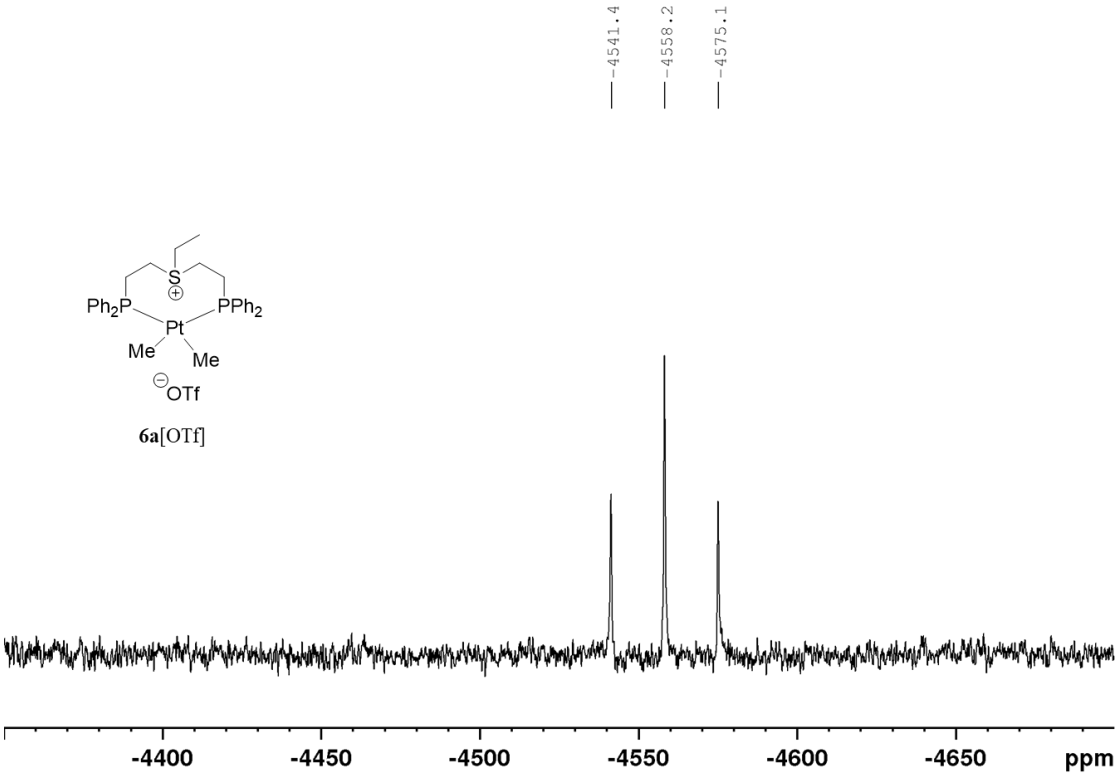


Figure S62: $^{195}Pt\{H\}$ NMR (108 MHz) of **6a**[OTf] in CD_2Cl_2.

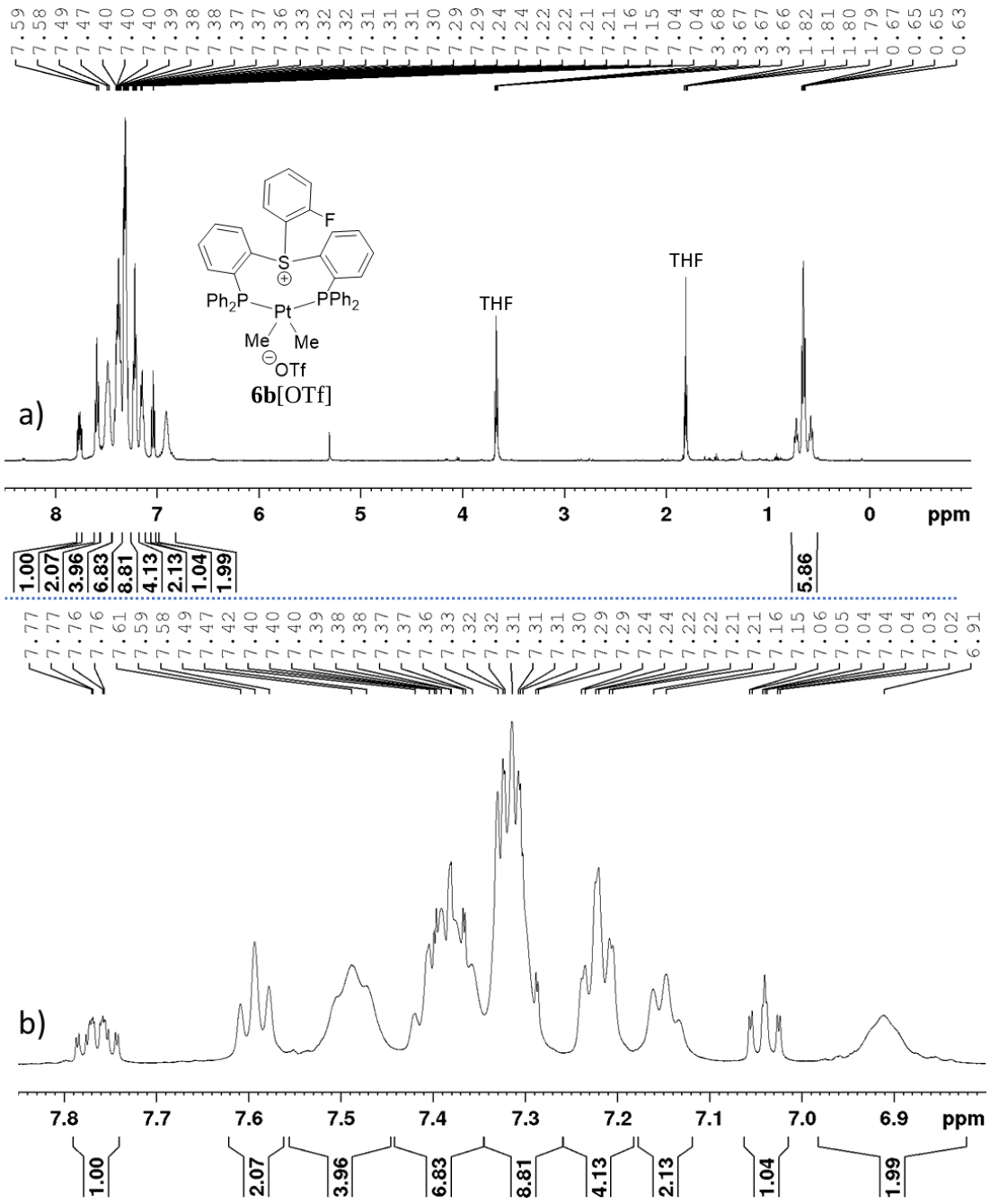


Figure S63: ^{1}H NMR (500 MHz) of **6b**[OTf] in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.

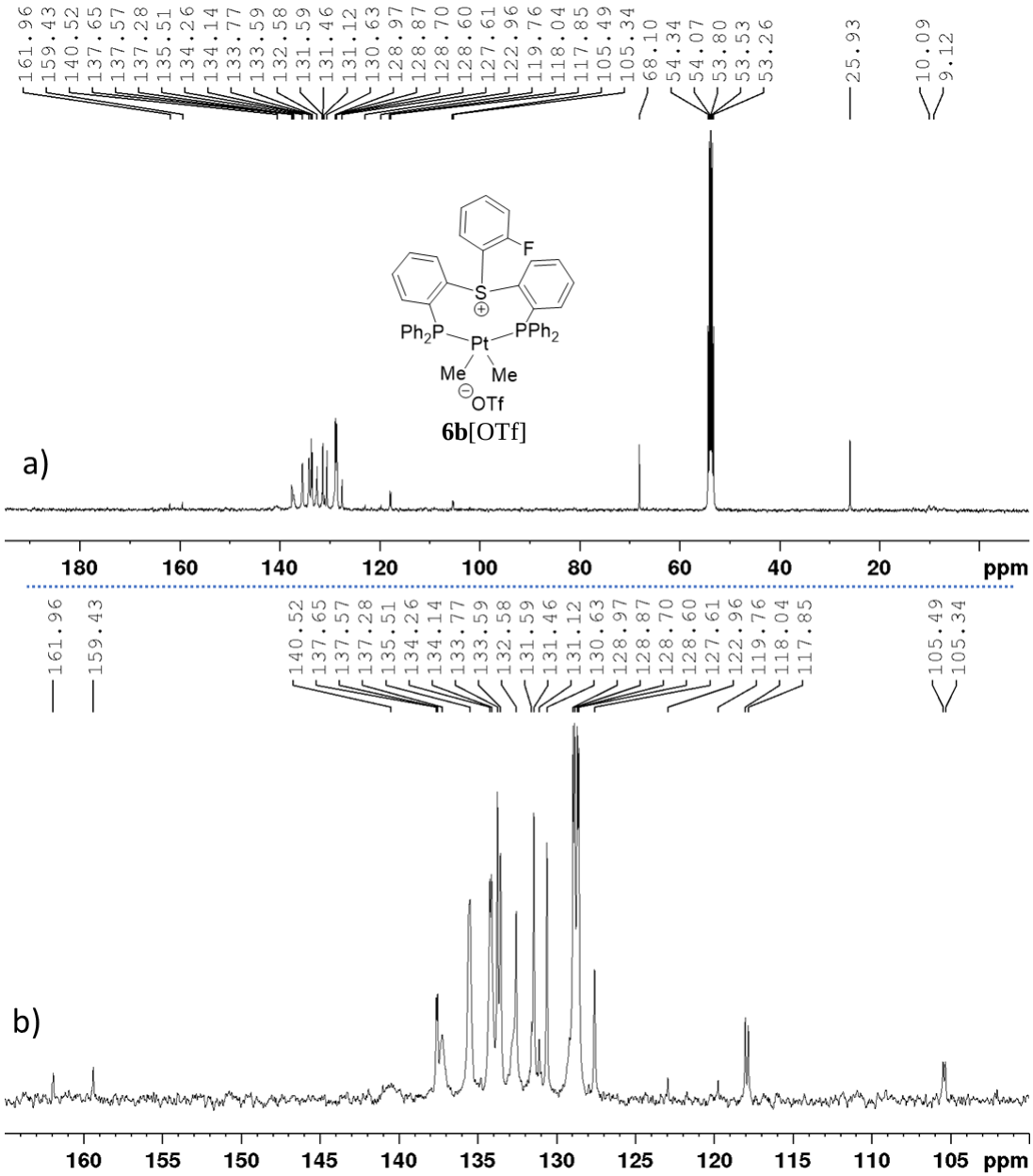


Figure S64: ^{13}C NMR (101 MHz) of **6b**[OTf] in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.

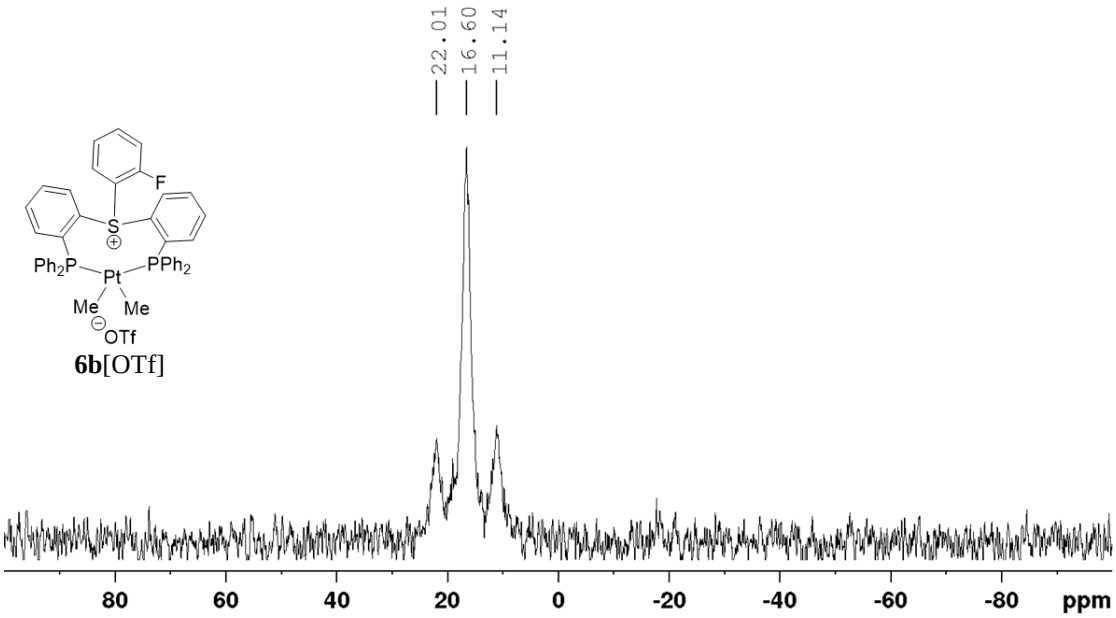


Figure S65: $^{31}P\{H\}$ NMR (162 MHz) of **6b**[OTf] in CD_2Cl_2.

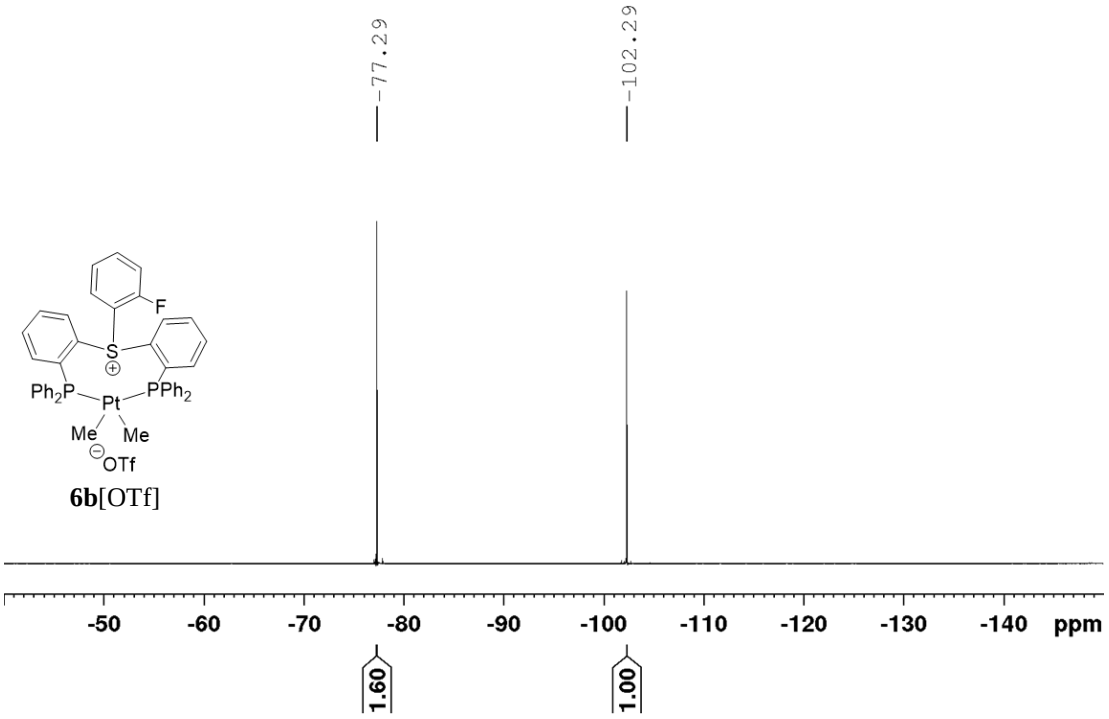


Figure S66: $^{19}F\{H\}$ NMR (376 MHz) of **6b**[OTf] in CD_2Cl_2.

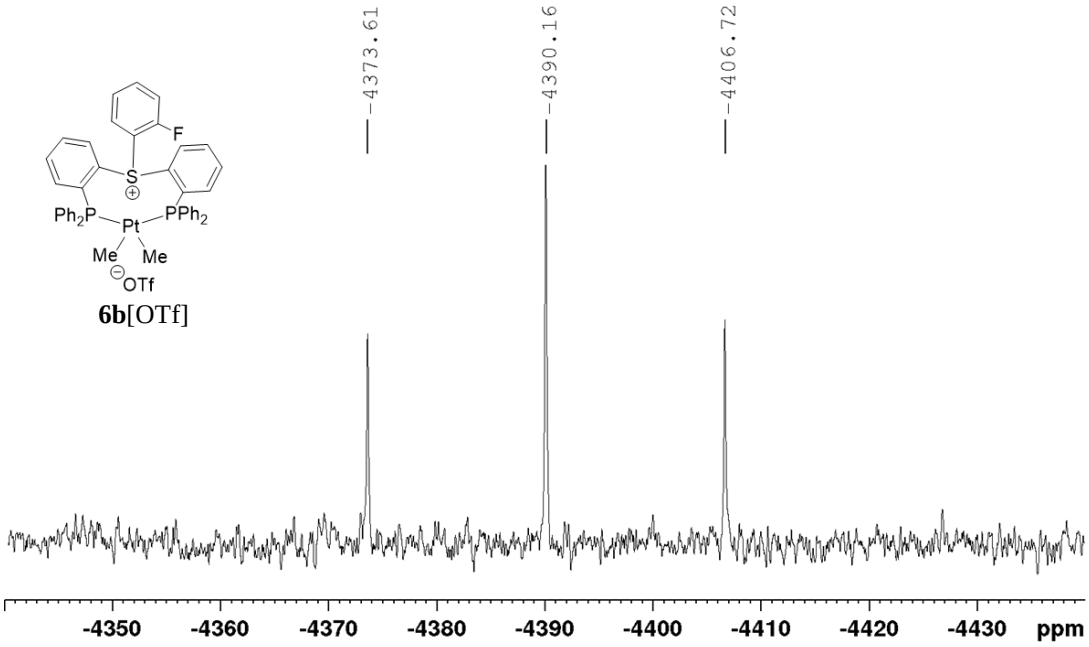


Figure S67: ^{195}Pt{H} NMR (108 MHz) of **6b**[OTf] in CD_2Cl_2.

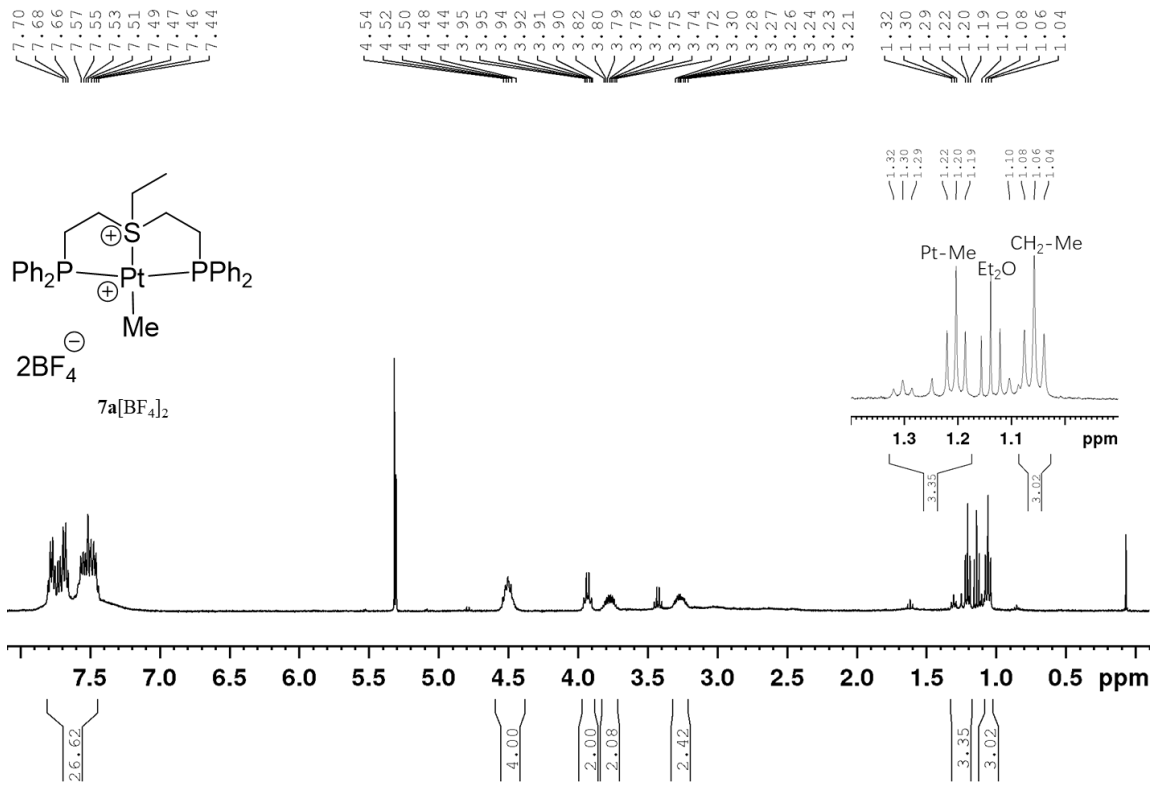


Figure S68: ^{1}H NMR (400 MHz) of **7a**$[BF_4]_2$ in CD_2Cl_2.

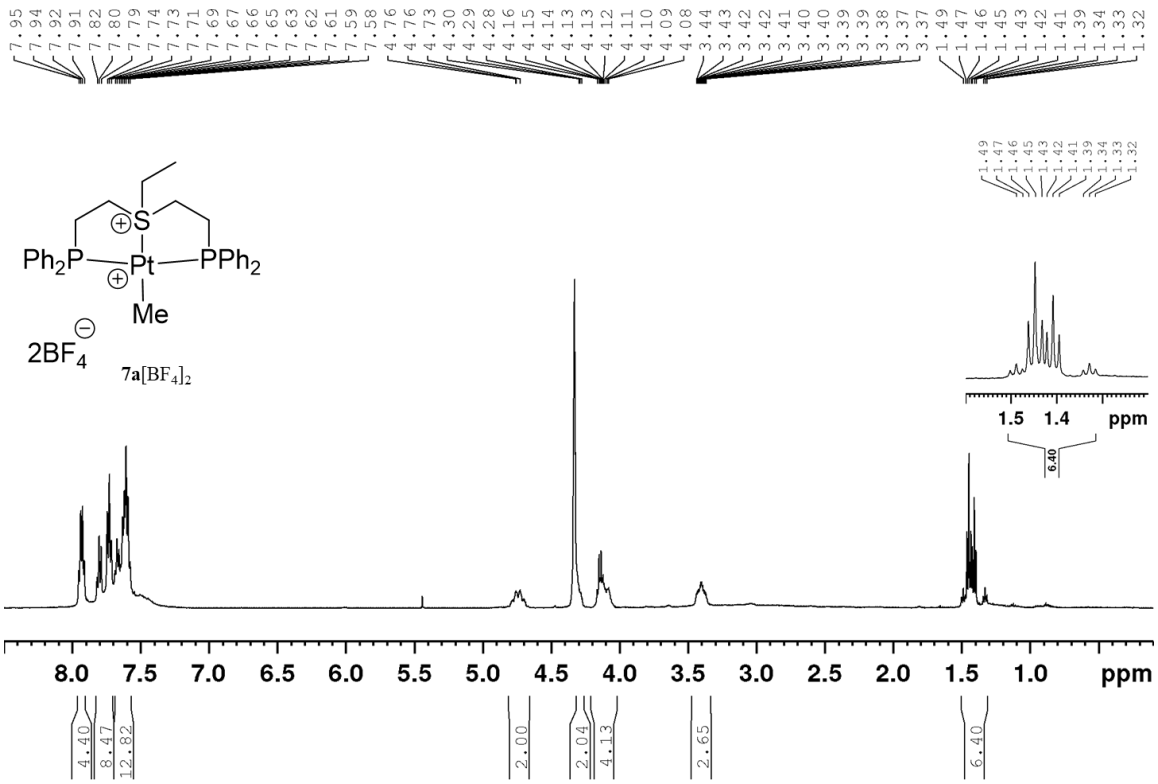


Figure S69: ^{1}H NMR (500 MHz) of **7a**$[BF_4]_2$ in CD_3NO_2.

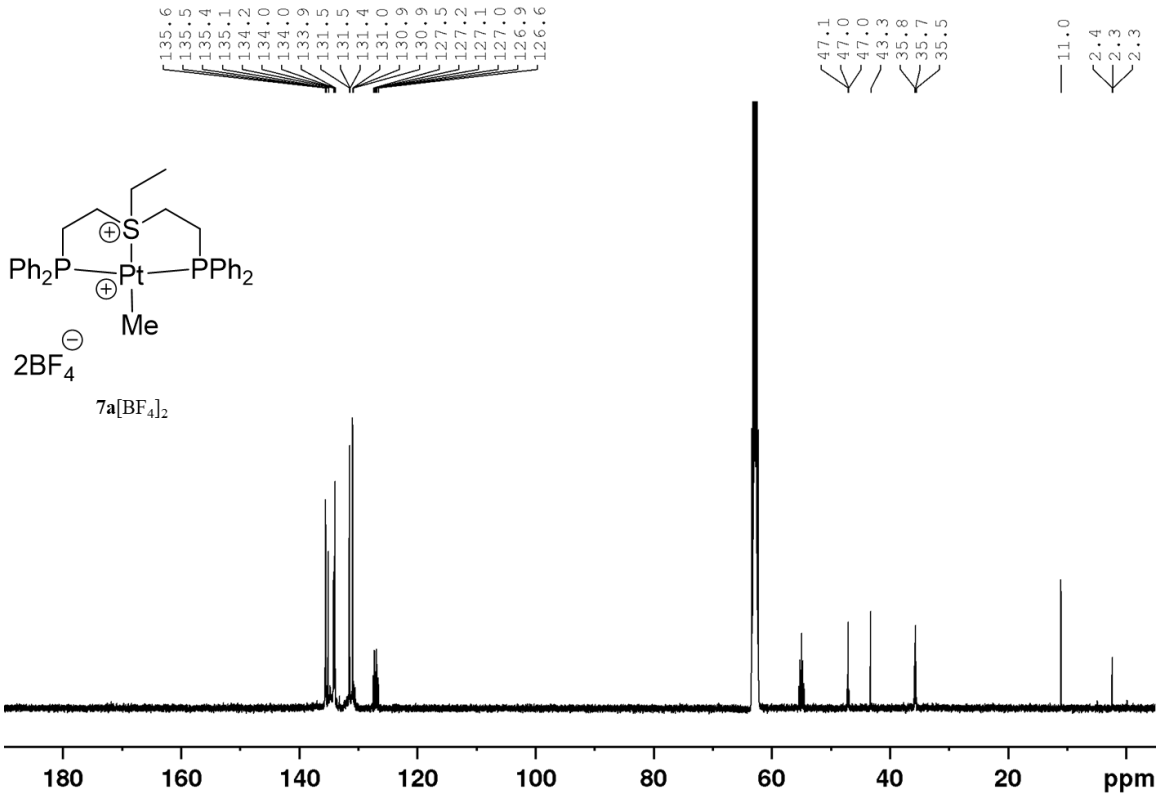
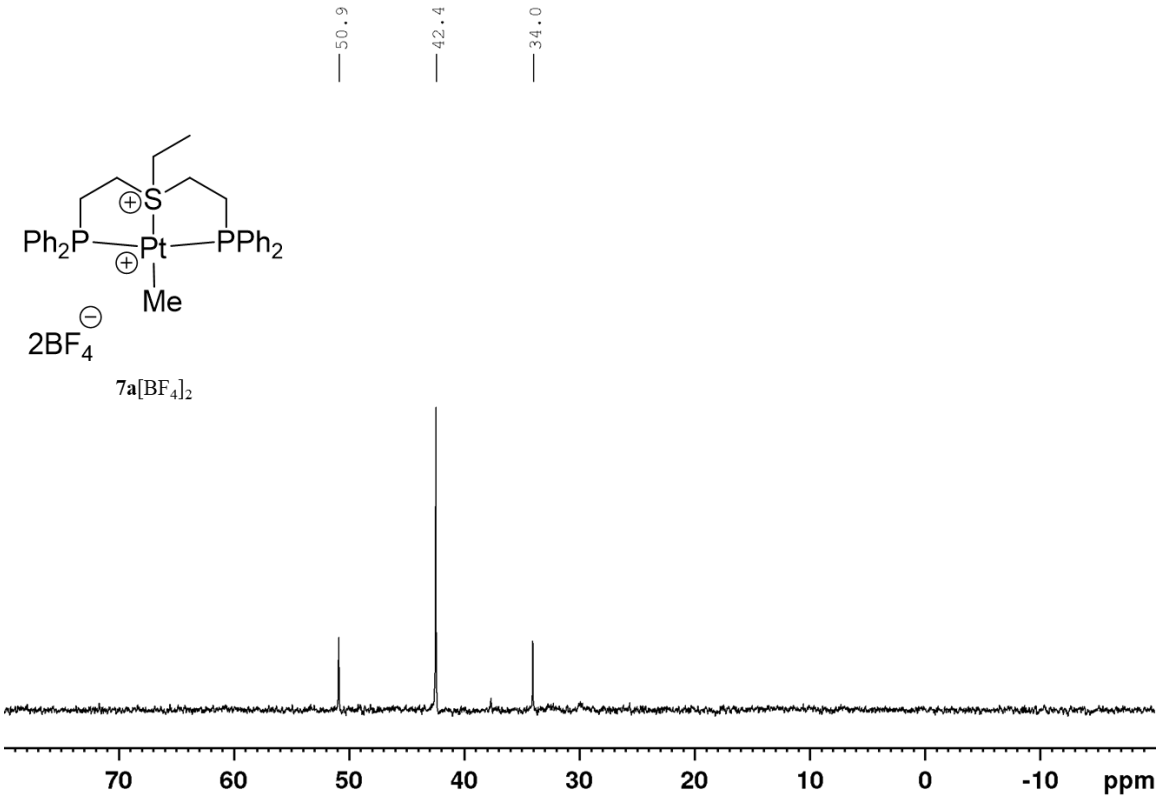
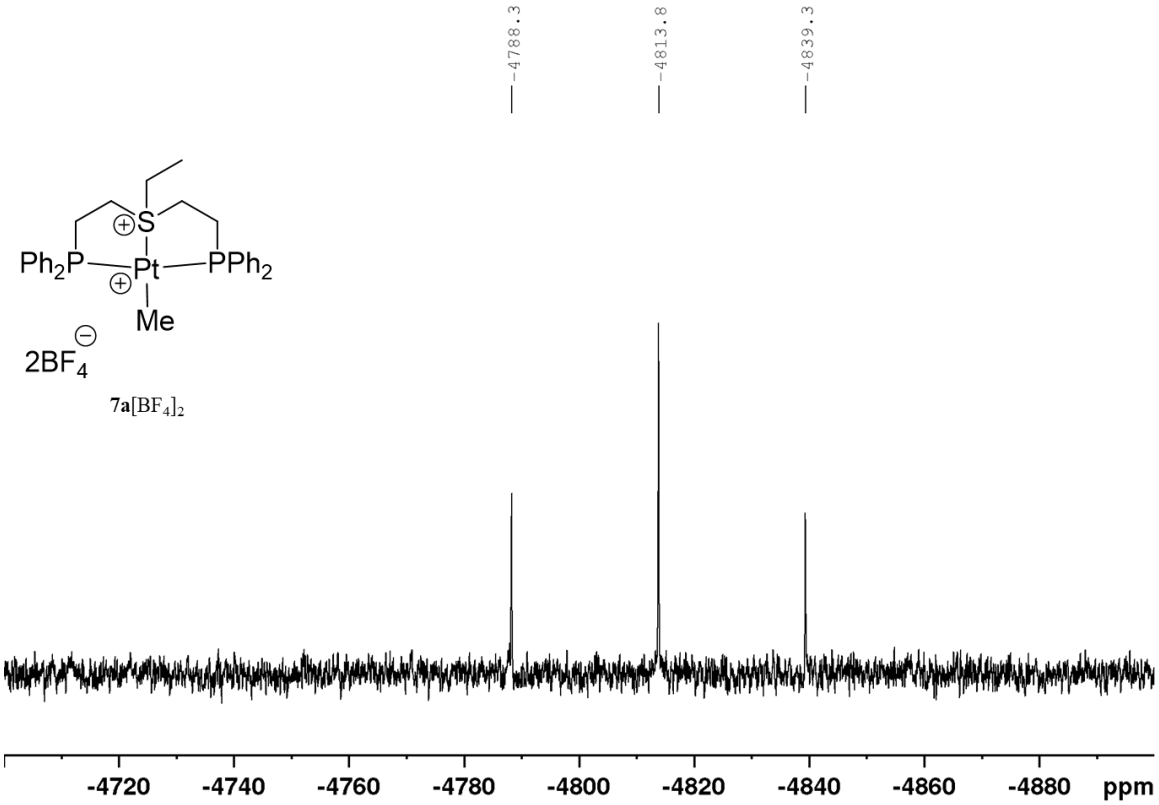


Figure S70: ^{13}C NMR (126 MHz) of **7a**$[BF_4]_2$ in CD_3NO_2.



7a$[BF_4]_2$

Figure S71: $^{31}P\{H\}$ NMR (162 MHz) of **7a**$[BF_4]_2$ in CD_2Cl_2.



7a$[BF_4]_2$

Figure S72: $^{195}Pt\{H\}$ NMR (108 MHz) of **7a**$[BF_4]_2$ in CD_3NO_2.

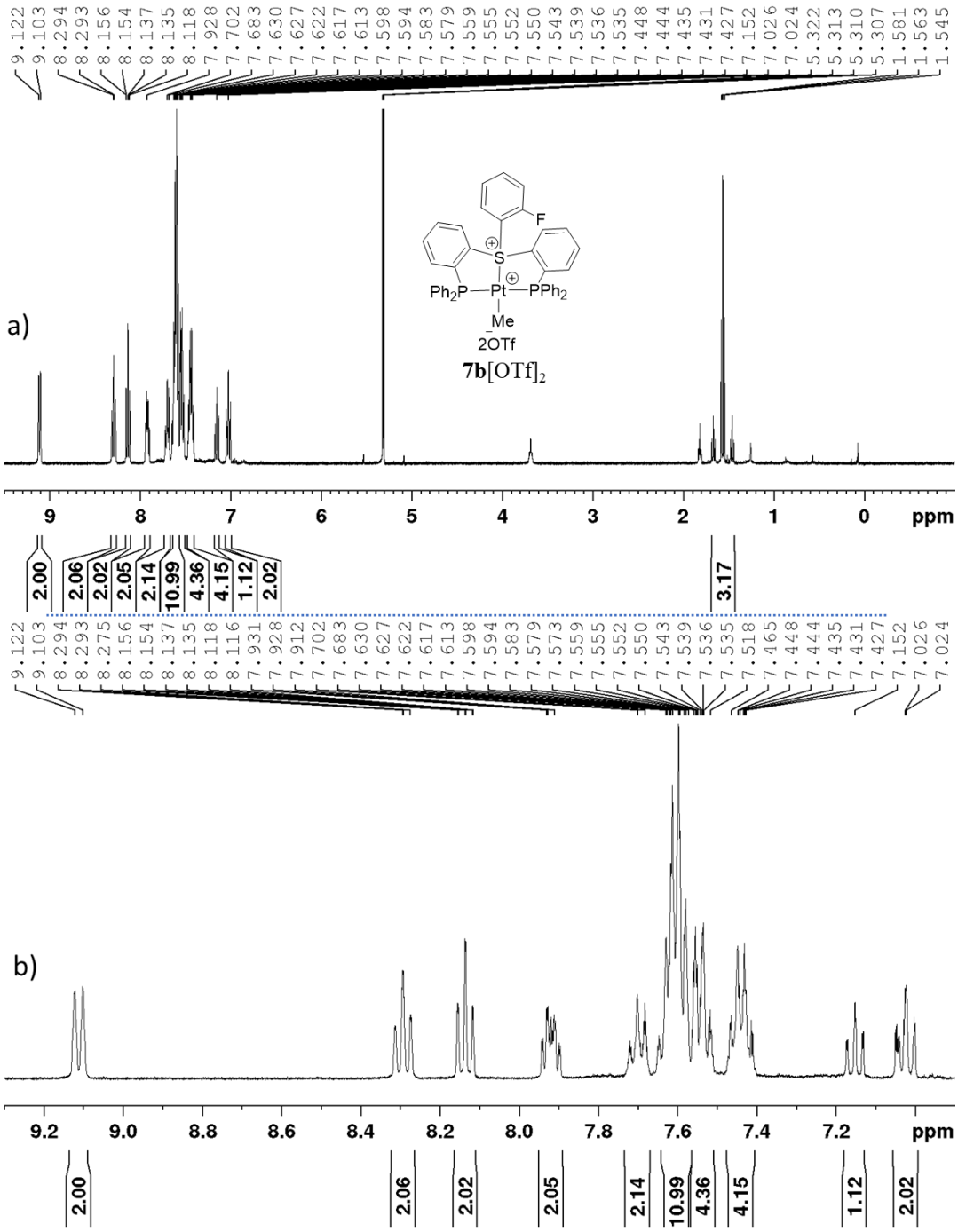


Figure S73: ^{1}H NMR (500 MHz) of **7b**[OTf]$_2$ in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.

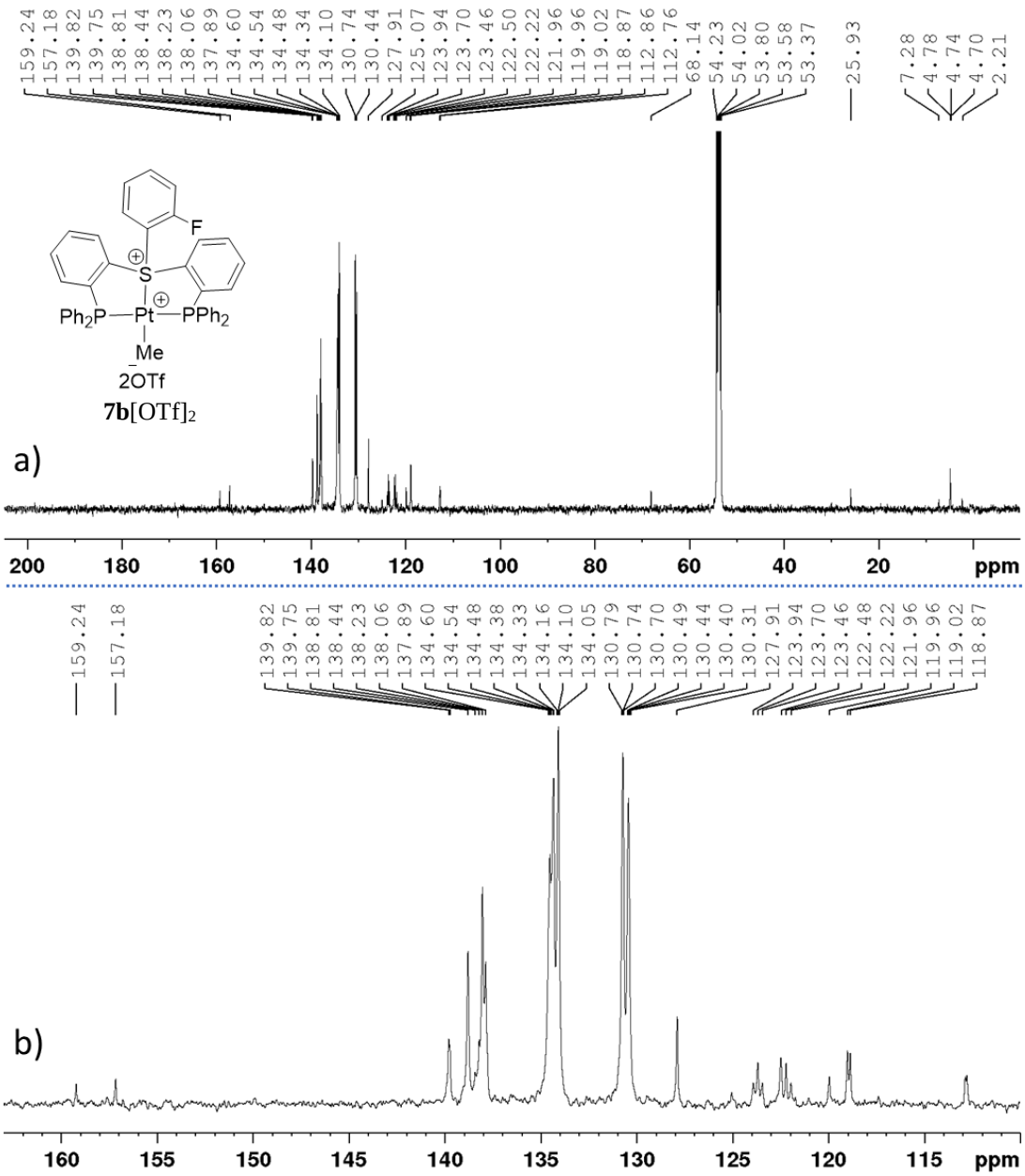
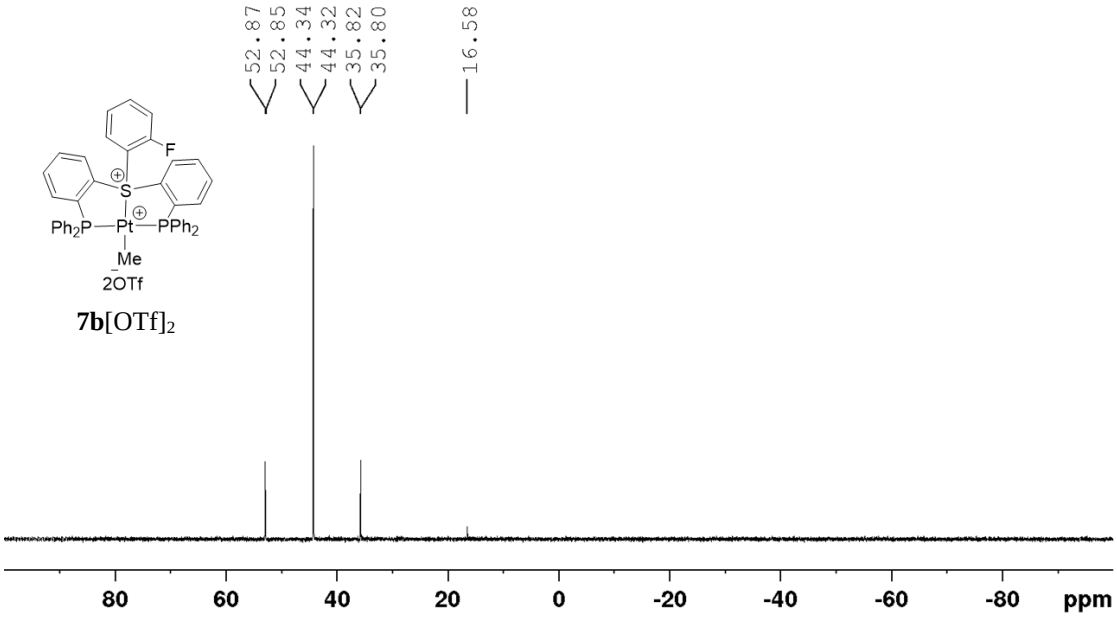
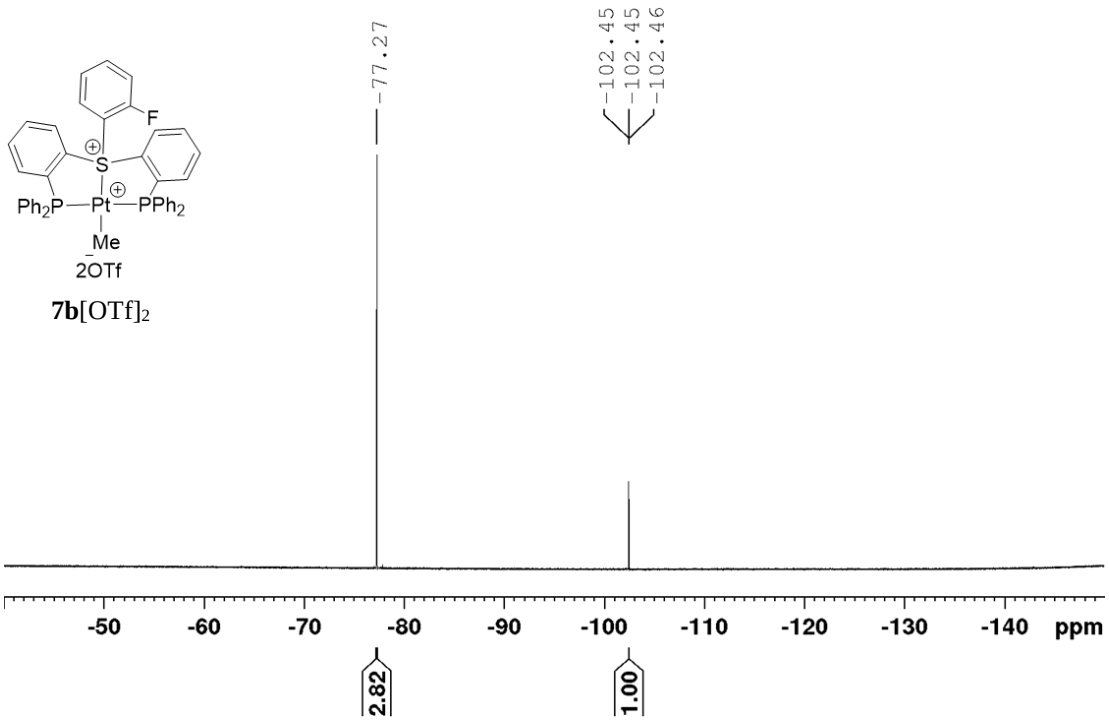


Figure S74: ^{31}C NMR (126 MHz) of **7b**[OTf]$_2$ in CD_2Cl_2. a) full spectrum, b) aromatic region expanded.



7b[OTf]$_2$

Figure S75: $^{31}P\{H\}$ NMR (162 MHz) of **7b**[OTf]$_2$ in CD_2Cl_2.



7b[OTf]$_2$

Figure S76: $^{19}F\{H\}$ NMR (376 MHz) of **7b**[OTf]$_2$ in CD_2Cl_2.

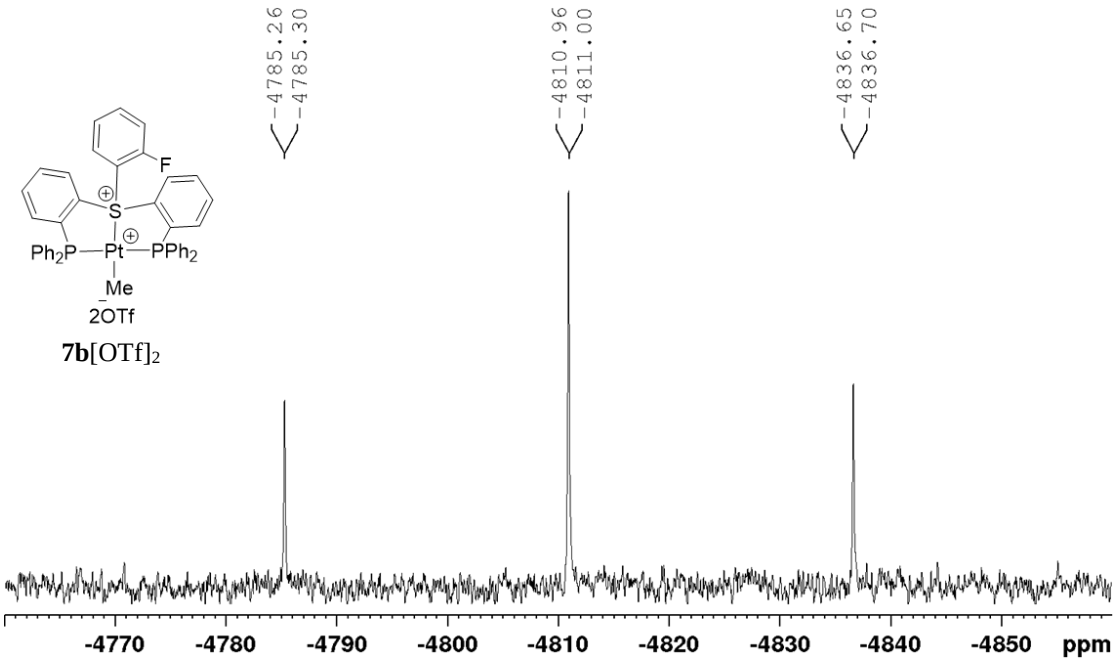


Figure S77: $^{195}Pt\{H\}$ NMR (108 MHz) of **7b**$[OTf]_2$ in CD_2Cl_2.

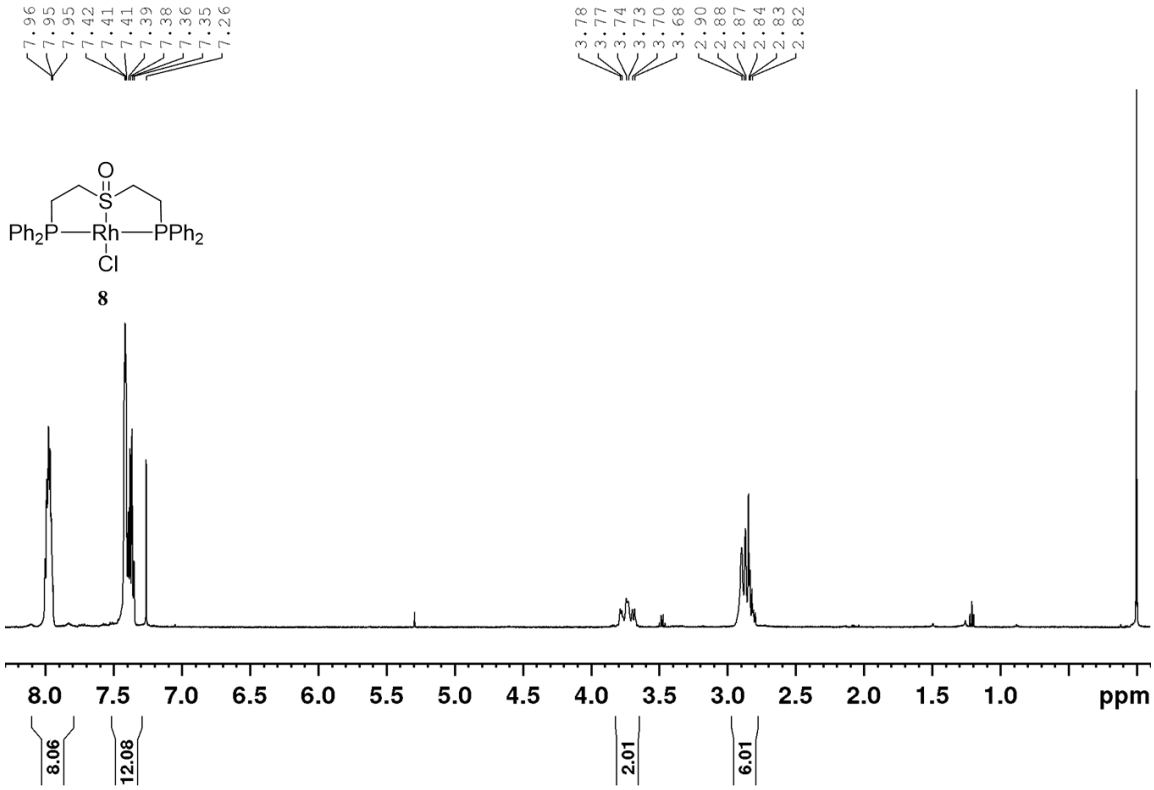


Figure S78: ^{1}H NMR (500 MHz) of **8** in $CDCl_3$.

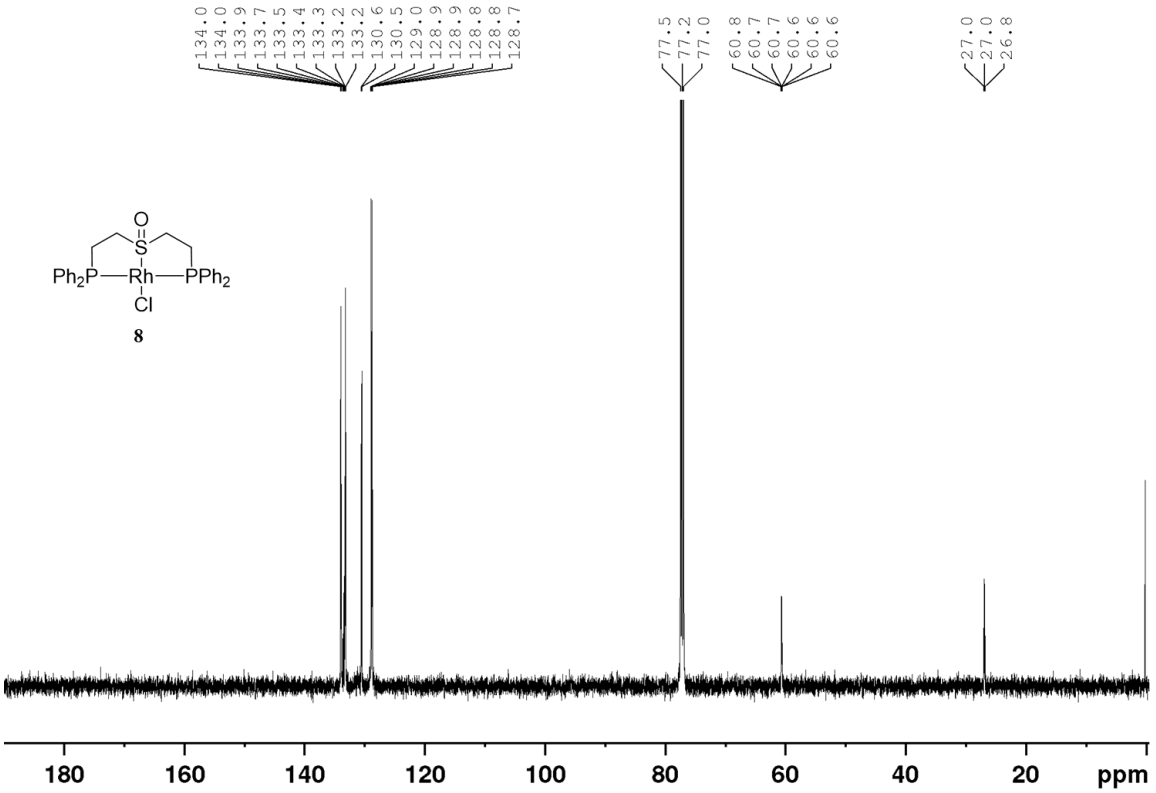


Figure S79: ^{13}C NMR (126 MHz) of **8** in $CDCl_3$.

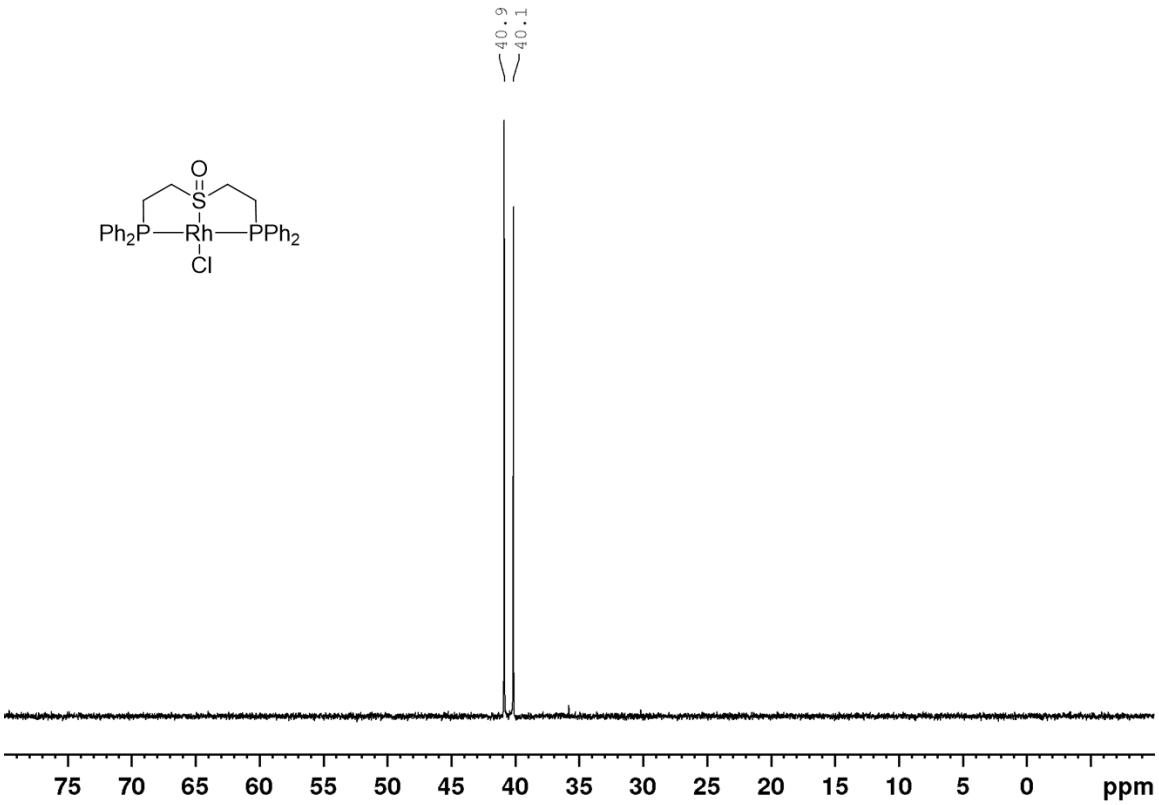


Figure S80: $^{31}P\{H\}$ NMR (202 MHz) of **8** in $CDCl_3$.

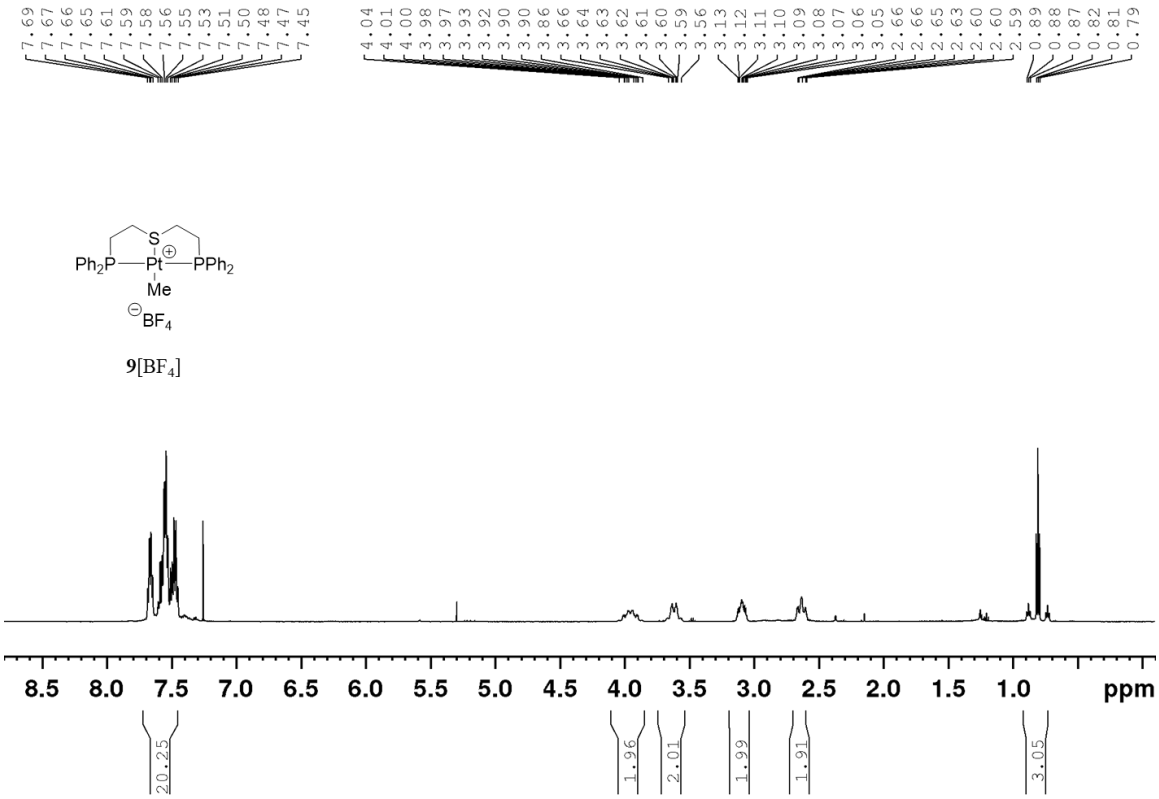


Figure S81: ^{1}H NMR (400 MHz) of **9**[BF_4] in $CDCl_3$.

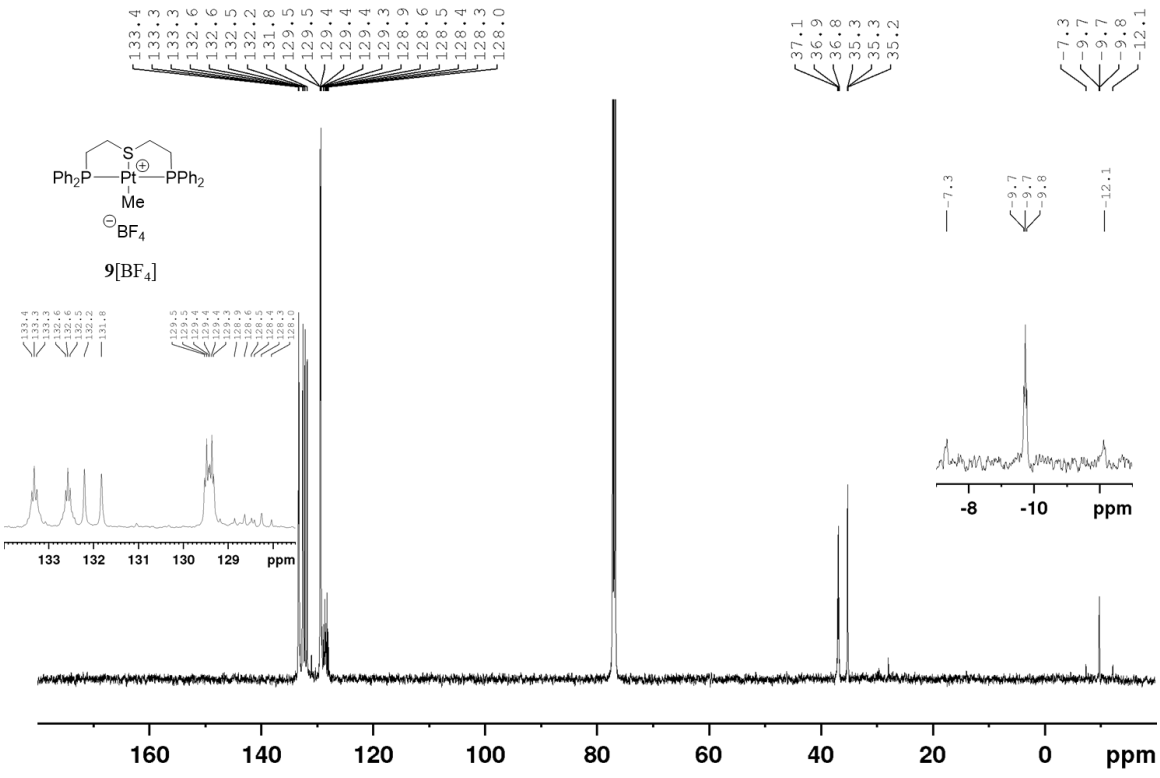


Figure S82: ^{13}C NMR (101 MHz) of **9**[BF_4] in $CDCl_3$.

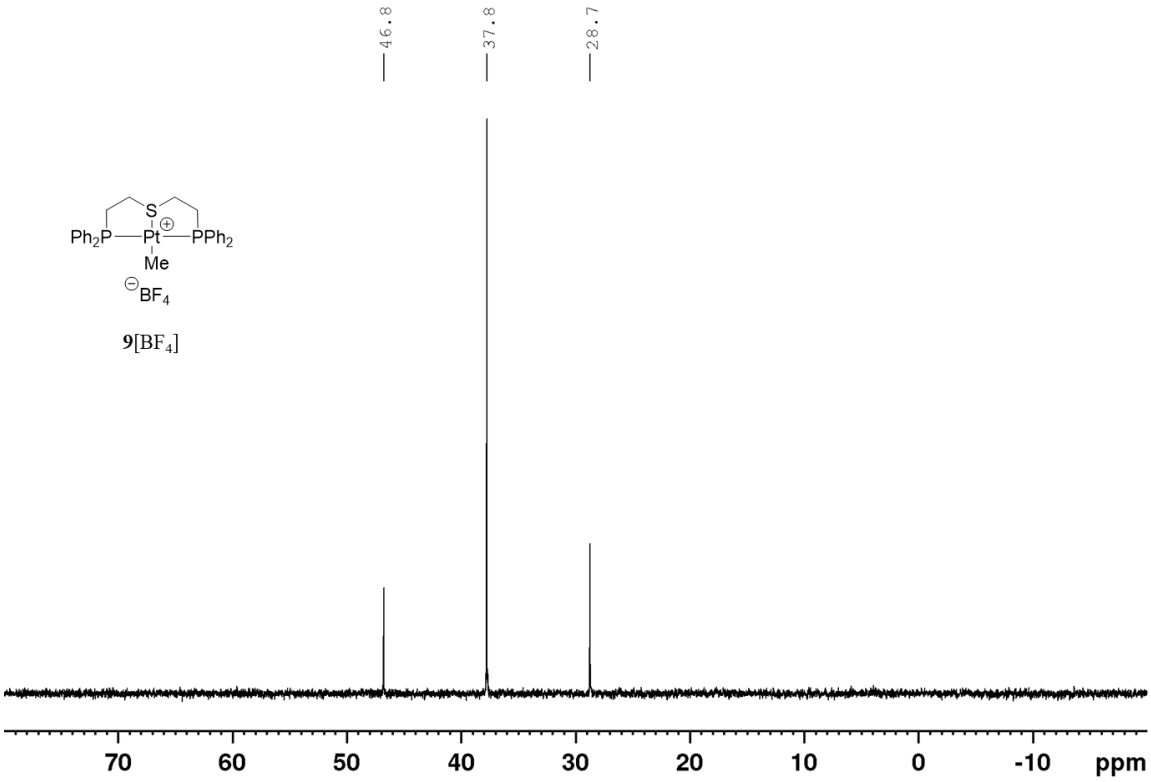


Figure S83: $^{31}P\{H\}$ NMR (162 MHz) of **9**[BF_4] in CD_2Cl_2.

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