C(sp^3)−F Bond Activation of CF_3-Substituted Anilines with Catalytically Generated Silicon Cations: Spectroscopic Evidence for a Hydride-Bridged Ru−S Dimer in the Catalytic Cycle

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Supporting Information

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1 General Information

All reactions were performed in flame-dried glassware using an MBraun glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) or conventional Schlenk techniques under a static pressure of argon or nitrogen. Liquids and solutions were transferred with syringes. Solvents (DMF, THF, toluene, *n*-hexane and CH_2Cl_2) were purified and dried following standard procedures. Technical grade solvents for extraction or chromatography (*n*-pentane, *n*-hexane, cyclohexane, diethyl ether, *tert*-butyl methyl ether) were distilled prior to use. C_6D_6 (purchased from *Eurisotop*) was dried over CaH_2 and stored under nitrogen after distillation. Silanes and *para*-trifluoromethylaniline were obtained from commercial sources and distilled prior to use. 2,6-Bis(2,4,6-trimethylphenyl)phenylthiol[S1], $NaBAr^F{}_4$[S2] and di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)][S3] were prepared according to reported procedures. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si-DEPT, and ^{31}P NMR spectra were recorded in C_6D_6 or $CDCl_3$ on Bruker DRX500, Bruker AV400 and Bruker DRX300 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (C_6HD_5: δ = 7.16 ppm for ^{1}H NMR and C_6D_6: δ = 128.1 ppm for ^{13}C NMR as well as $CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz) and integration. Infrared (IR) spectra were recorded on a Agilent Technologies Cary 630 FTIR spectrophotometer equipped with an ATR unit and are reported as wave numbers (cm^{-1}). Gas liquid chromatography (GLC) was performed on a Shimadzu GC-17A gas chromatograph equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by CS-Chromatographie Service using the following programs: 35-min: N_2 carrier gas, column flow 1.7 mL/min, injection temperature 280 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, final temperature 280 °C for 10 min; 55-min: N_2 carrier gas, column flow 1.1 mL/min, injection temperature 280 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, plateau at 100 °C for 20 min, final temperature 280 °C for 10 min. Melting points (Mp) were determined with a Stuart SMP20 apparatus and are not corrected. Mass spectrometry (MS) was obtained from the Analytical Facility of the Institut für Chemie, Technische Universität Berlin. Elemental analysis were obtained from the Analytical Facility of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster.

2 General Procedures (GPs)

2.1 GP 1: General Procedure for Synthesis of [(R_3P)Ru(SDmp)Cl] (6)

According to the two-step protocol reported by Ohki, Tatsumi, and co-workers[S4], *n*-butyllithium (solution in hexanes, 2.00 equiv) is slowly added to a solution of 2,6-bis(2,4,6-trimethylphenyl)phenylthiol (2.00 equiv) at 0 °C. After stirring for 30 min, the orange solution is added dropwise to a suspension of di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (1.00 equiv) in THF (0.05M) at 0 °C. The cooling bath is removed and the blue suspension is stirred for 3 h. The solvent is completely removed under reduced pressure, followed by the addition of toluene (0.05M). The salts formed during the reaction are filtered off under inert atmosphere. Toluene (0.05M) as well as the phosphine (2.00–3.50 equiv) are added to the filtrate to form a red solution which is maintained at 65 °C for 15 h. The solvent is removed under reduced pressure and the crude product is purified by recrystallization from toluene–*n*-pentane, affording the ruthenium chloride complexes **6** as red powders.

2.2 GP 2: General Procedure for Synthesis of [(R_3P)Ru(SDmp)]BAr^F_4 (1)

According to the procedure by Ohki, Tatsumi, and co-workers[S4], ruthenium chloride complex **6** (1.00 equiv) and $NaBAr^F_4$ [Ar^F = 3,5-bis(trifluoromethyl)phenyl, 1.00 equiv] are suspended in CH_2Cl_2 (0.01M). After stirring at ambient temperature (in case of electron-rich phosphines) or 40 °C (in case of electron-deficient phosphines) for 1.5 h, the suspension is concentrated under reduced pressure. The precipitate is filtered off under inert atmosphere, and the solvent is completely removed from the filtrate by evacuating the flask at 60 °C for 4 h, yielding the ruthenium thiolate complexes **1** as green powders.

2.3 GP 3: General Procedure for *N*,*N*-Dialkylation of Anilines

The aniline dissolved in DMF (0.2M) is added to oil-free sodium hydride (5.5 equiv) and stirred at ambient temperature for 15 min. Bromoethane (2.7 equiv) is slowly added dropwise to the suspension, and the reaction mixture is maintained at ambient temperature for 8 h. The reaction is quenched by careful addition of saturated aqueous NH_4Cl solution (4 mL). After extraction of the organic layer with *tert*-butyl methyl ether (2 × 20 mL), the combined organic phases are washed with water (4 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent is removed under reduced pressure. Purification by bulb-to-bulb condensation afforded *N*,*N*-dialkylated anilines as colorless liquids.

2.4 GP 4: General Procedure for Catalytic C(sp^3)–F Bond Activation

Using the preformed catalyst: In a glovebox, a 2 mL-vial is charged with ruthenium thiolate complex [(R_3P)Ru(SDmp)]BAr^F_4 (**1**, 10 mol %). After the addition of tetracosane as internal standard, the resulting mixture is suspended in toluene (0.4 mL). A color change from green to yellow is observed upon dropwise addition of silane (4.4 equiv). Then, the CF_3-substituted aniline or indole **2** (1.0 equiv) is added, and the reaction mixture is maintained at ambient temperature for 6–72 h. Conversion is monitored by GLC analysis.

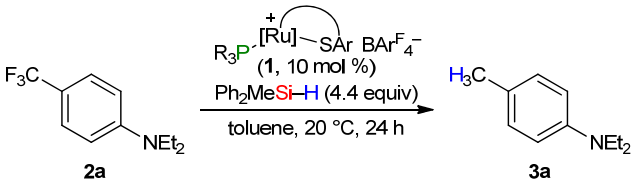
Using the in situ-formed catalyst: In a glovebox, a 2 mL-vial is charged with ruthenium chloride complex [(R_3P)Ru(SDmp)Cl] (**6**, 10 mol %) and $NaBAr^F_4$ (10 mol %). After the addition of tetracosane as internal standard, the resulting mixture is suspended in toluene (0.4 mL). A color change from green to yellow is observed upon dropwise addition of silane (4.4 equiv). Then, the CF_3-substituted aniline or indole **2** (1.0 equiv) is added, and the reaction mixture is maintained at ambient temperature for 6–72 h. Conversion is monitored by GLC analysis.

2.5 GP 5: General Procedure for Catalytic C(sp^3)–F bond Activation with an Additive

In a glovebox, a 2 mL-vial is charged with a mixture of ruthenium thiolate complex [{(*p*-$FC_6H_4)_3P$}Ru(SDmp)]BAr^F_4 (**1e**, 10 mol %) and the additive (5.0 mol %). After the addition of tetracosane as internal standard, the resulting mixture is suspended in *n*-hexane (0.5 mL). A color change from green to yellow is observed upon dropwise addition of Ph_2MeSiH (4.4 equiv). Then, the CF_3-substituted aniline or indole **2** (1.0 equiv) is added, and the reaction mixture is maintained at ambient temperature for 6–72 h. Conversion is monitored by GLC analysis.

3 Optimization of the Procedure for Catalytic Hydrodefluorination

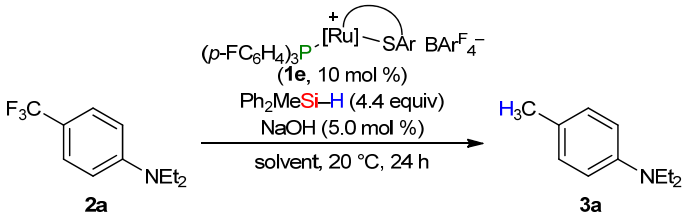
Table S1: Screening of Phosphine Ligands by Using Three Different Procedures[a]



entry	phosphine (complex)	in situ-formed catalyst conv. (%)[b]	preformed catalyst conv. (%)[b]	preformed catalyst with NaOH as additive (5 mol %) conv. (%)[b]
1	Et_3P (**1a**)	67	82	78
2	Me_3P (**1b**)	26	17	46
3	Ph_2MeP (**1c**)	20	0	51
4	Ph_3P (**1d**)	>99	0	23
5	$(p\text{-}FC_6H_4)_3P$ (**1e**)	>99	0	>99

[a]All reactions were performed according to GP 4 and GP 5, respectively. [b]Determined by GLC analysis using tetracosane as internal standard.

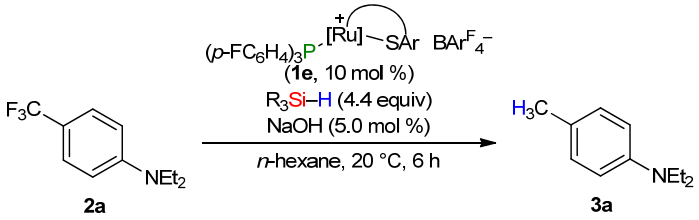
Table S2: Screening of Solvents[a]



entry	solvent	conv. (%)[b]
1	mesityl bromide	54
2	1,2-difluorobenzene	4
3	toluene	>99
4	neat[c]	>99
5	*n*-hexane	>99[d]

[a]All reactions were performed according to GP 5. [b]Determined by GLC analysis using tetracosane as internal standard. [c]Silane used as solvent. [d]Full conversion after 6 h.

Table S3: Screening of Silanes[a]

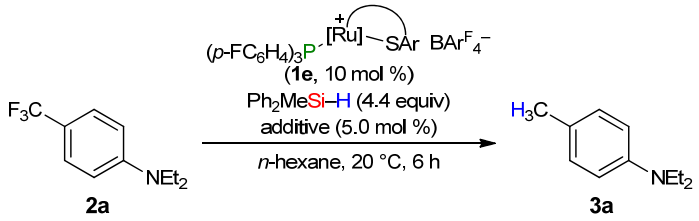


2a **3a**

entry	silane	conv. (%)[b]
1	$ClPh_2Si–H$	0
2	$Et_2MeSi–H$	5
3	$Et_3Si–H$	1
4	$Ph_2MeSi–H$	>99
5	$Me_2PhSi–H$	>99

[a]All reactions were performed according to GP 5. [b]Determined by GLC analysis using tetracosane as internal standard.

Table S4: Screening of Additives[a]

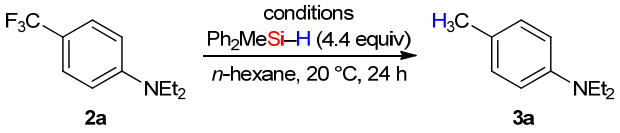


2a **3a**

entry	additive	conv. (%)[b]
1	none	0
2	1,8-bis(dimethylamino)-naphthalene	0
3	Di-*tert*-butylpyridine	12
4	K_2CO_3	6
5	pentamethylpiperidine	25
6	KO*t*-Bu	>99
7	NaOMe	>99
8	NaOH	>99
9	LiOH	78
10	H_2O	0

[a]All reactions were performed according to GP 5. [b]Determined by GLC analysis using tetracosane as internal standard.

Table S5: Control Experiments[a]



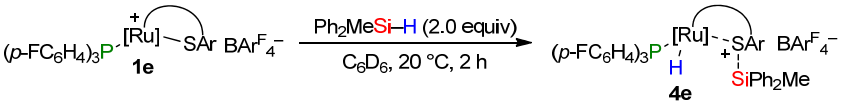
2a **3a**

entry	conditions	conv. (%)[b]
1	$NaBAr^F_4$ (10 mol %)	0
2	[{(*p*-FC_6H_4)$_3$P}Ru(SDmp)Cl] (**6e**, 10 mol %)	0
3	di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (10 mol %)	0

[a]All reactions were performed in 2 mL-vials in a glovebox using tetracosane as internal standard. Aniline **2a** (5.0 mg, 0.023 mmol, 1.0 equiv) was dissolved in *n*-hexane (0.4 mL), followed by the addition of Ph_2MeSiH and additives (column 2). [b]Determined by GLC analysis.

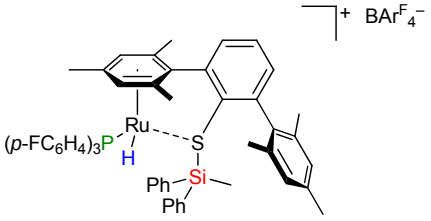
4 Detection of Possible Intermediates in Catalytic Cycle by NMR Spectroscopy

4.1 Formation of Complex 4e



[{(*p*-FC_6H_4)$_3$P}Ru(SDmp)]BAr^F_4 (**1e**, 10 mg, 6.2 µmol, 1.0 equiv) was dissolved in C_6D_6 (0.6 mL) and transferred into an NMR tube. After addition of Ph_2MeSiH (2.4 mg, 12 µmol, 2.0 equiv), the sample was directly subjected to NMR analysis.

^{1}H NMR (500 MHz, C_6D_6): δ = –7.89 (d, *J* = 47.5 Hz, 1H), 0.20 (s, 3H), 0.89 (s, 3H), 1.33 (s, 3H), 1.59 (s, 3H), 1.93 (s, 6H), 2.00 (s, 3H), 3.80 (s, 1H), 5.84 (s, 1H), 6.13 (d, *J* = 7.3 Hz, 2H), 6.61 (s, 1H), 6.66 (t, *J* = 8.0 Hz, 6H), 6.75–6.78 (m, 2H), 6.81–6.89 (m, 9H), 7.67 (s, 4H), 8.39 (s, 8H) ppm. **^{31}P NMR** (202 MHz, C_6D_6): δ = 48.6, 52.3 (assigned to structure **4e** without Ru–S bond) ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –107.4 , –95.7 (assigned to structure **4e** without Ru–S bond), –62.0 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –5.9 ppm.

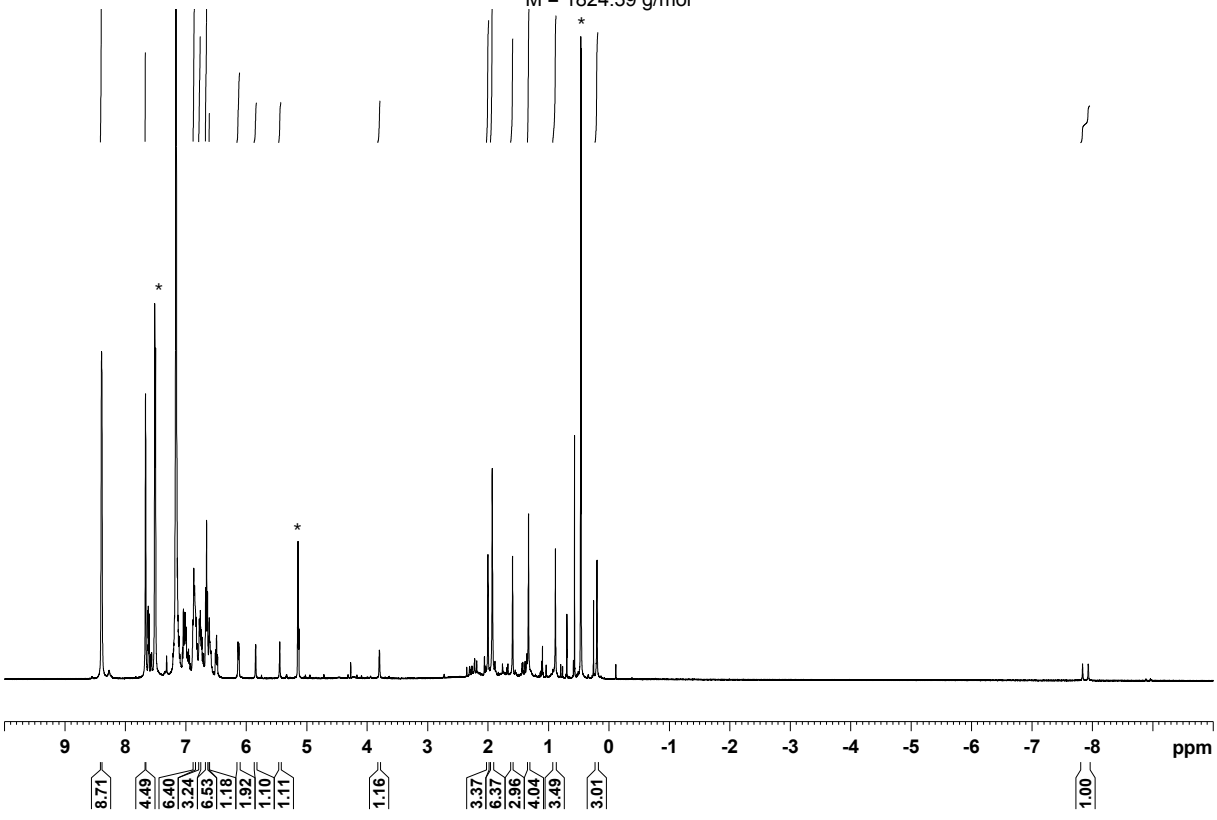


4e

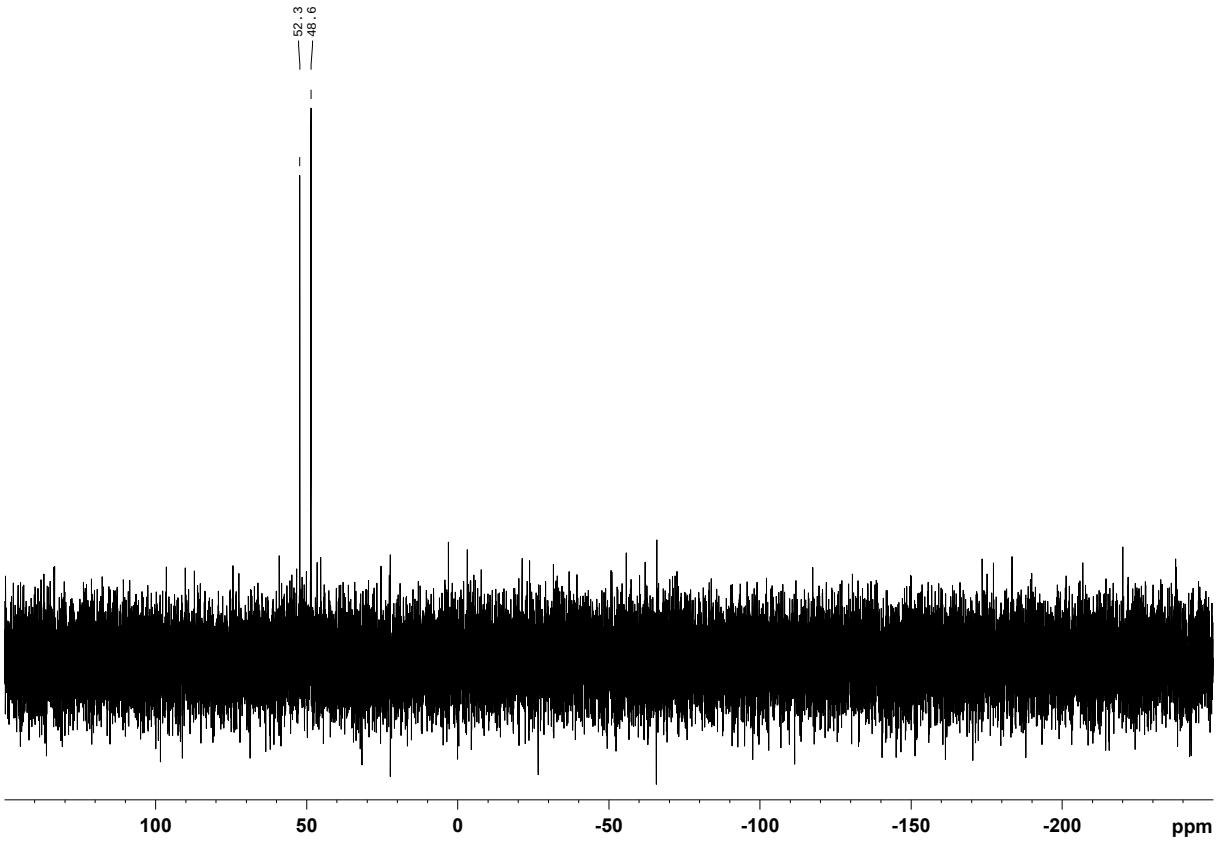
$C_{87}H_{63}BF_{27}PSSiRu$

M = 1824.39 g/mol

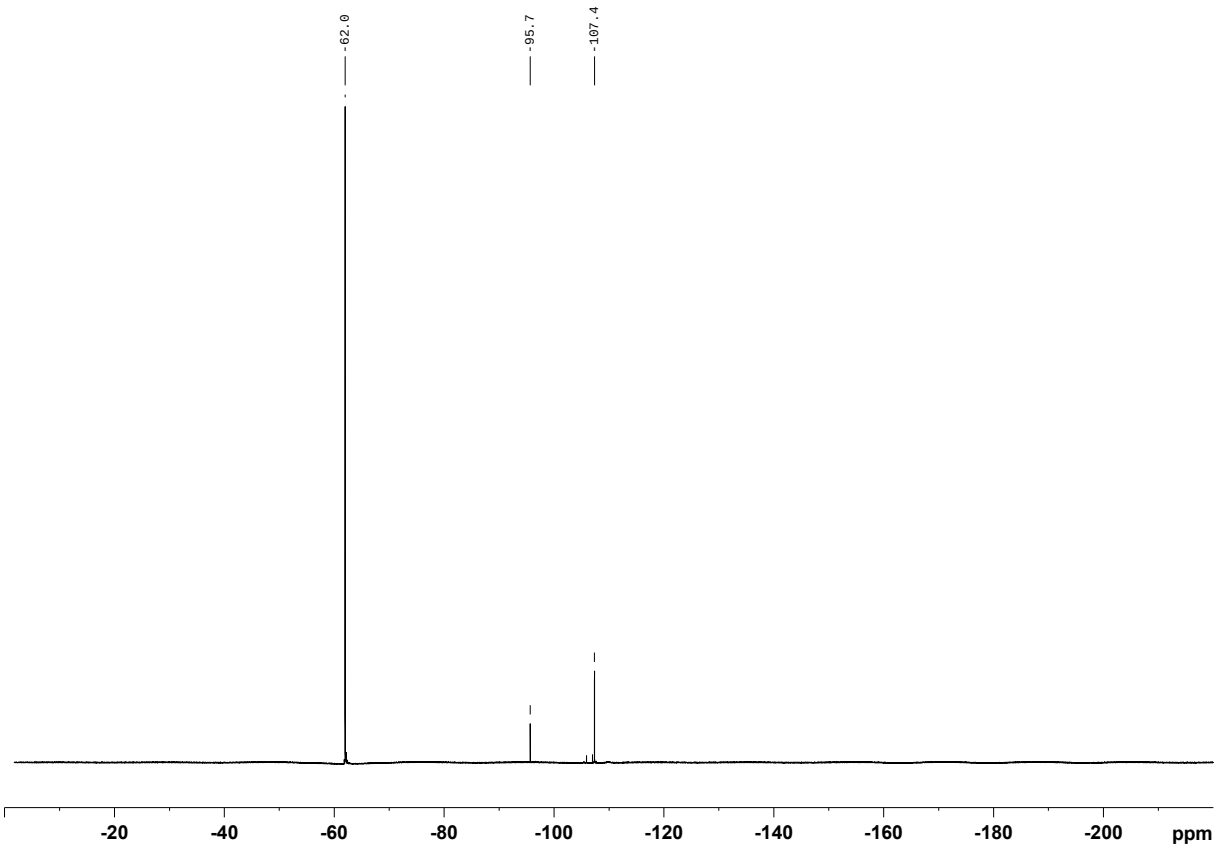
^{1}H NMR (* = Ph_2MeSiH):



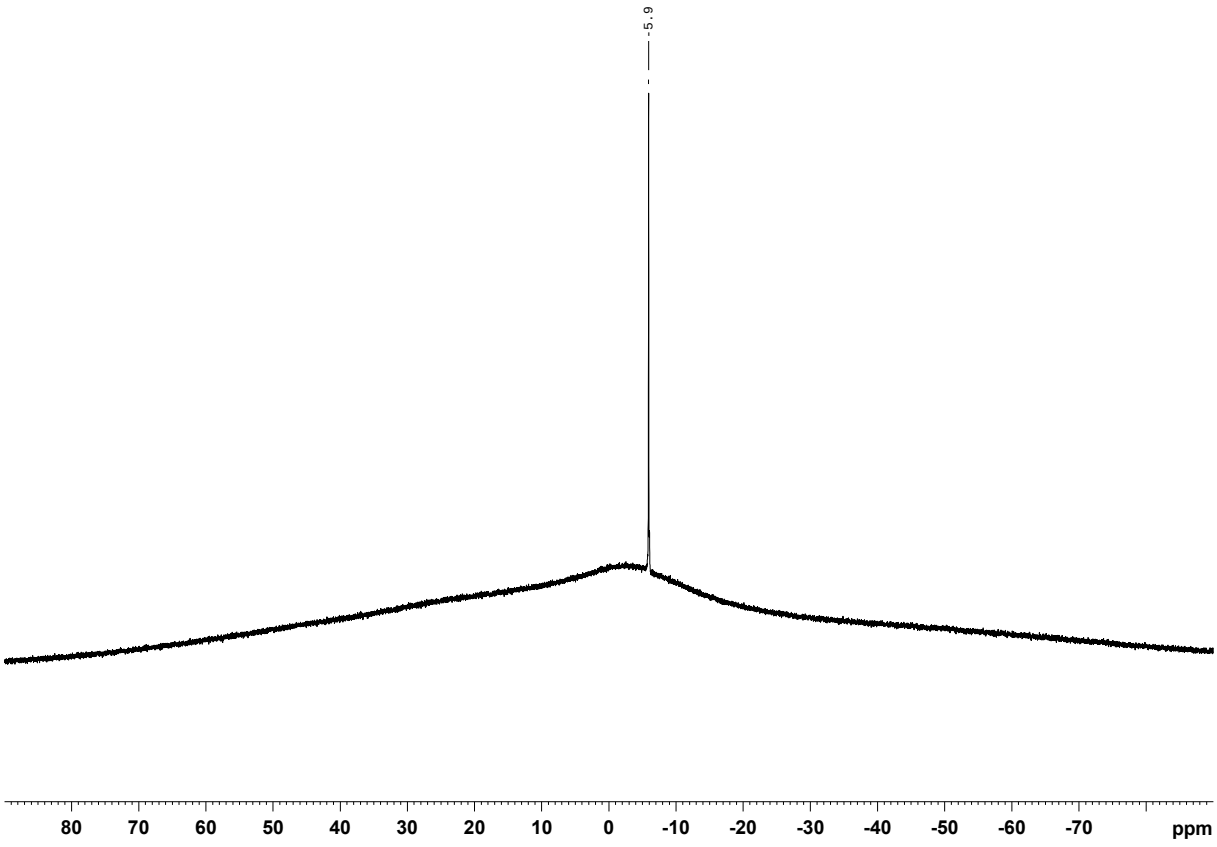
^{31}P NMR:



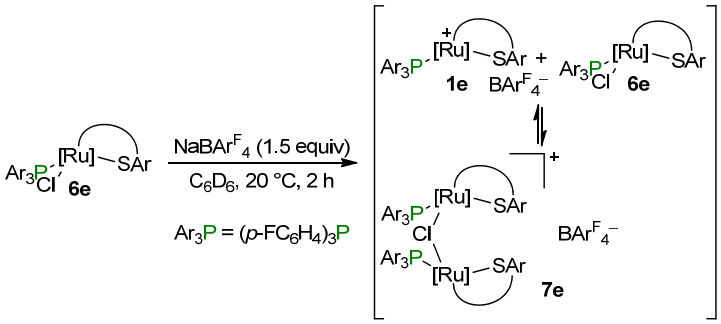
^{19}F NMR:



^{11}B NMR:



4.2 Partial Formation of Complex 7e

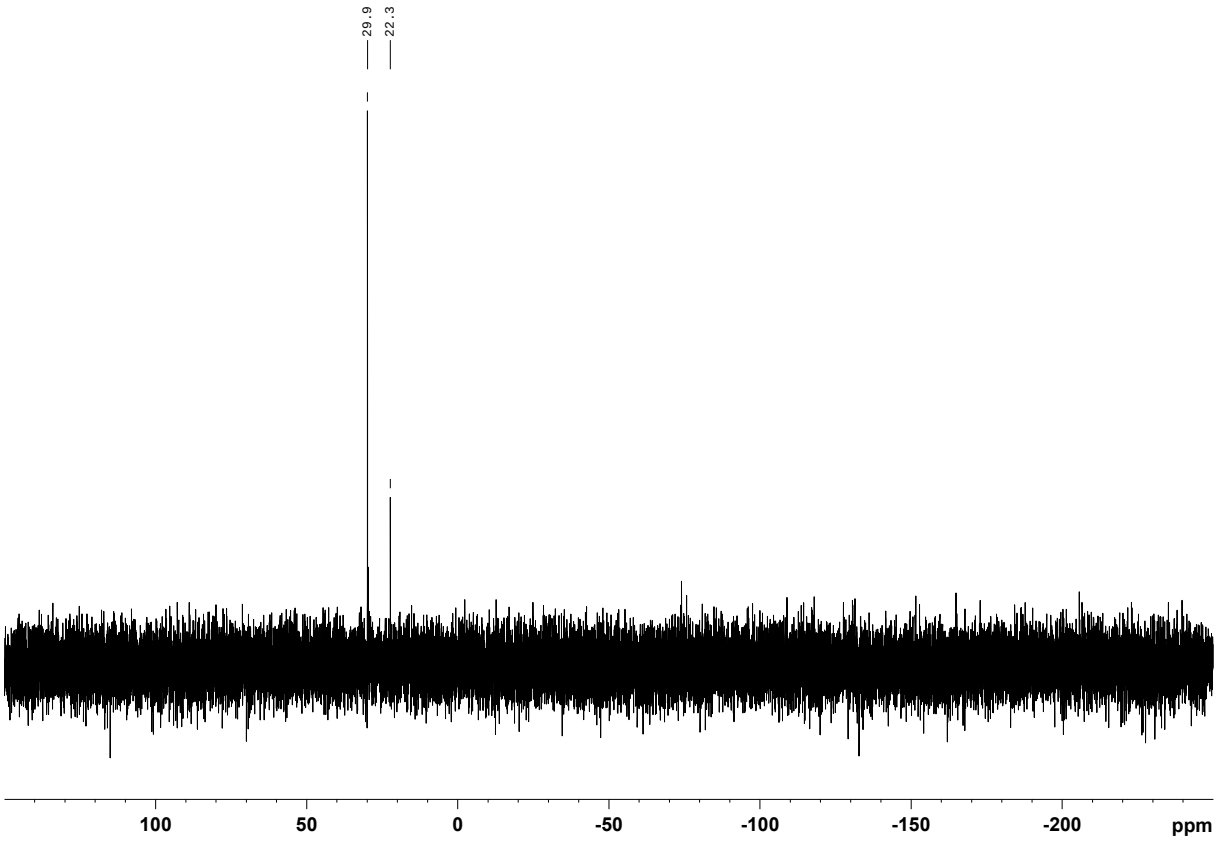


According to GP 2, [{(*p*-FC_6H_4)$_3$P}Ru(SDmp)Cl] (**6e**, 60 mg, 0.075 mmol, 1.00 equiv) and $NaBAr^F_4$ (100 mg, 0.11 mmol, 1.5 equiv) were suspended in CH_2Cl_2 (20 mL). After stirring the dark green reaction mixture at ambient temperature for 14 h, the precipitate was filtered off under inert atmosphere. Removal of the solvent under reduced pressure afforded a green powder (65 mg). NMR analysis was performed in C_6D_6 at 20 °C, indicating an additional resonance signal each in the ^{31}P and ^{19}F NMR spectra.

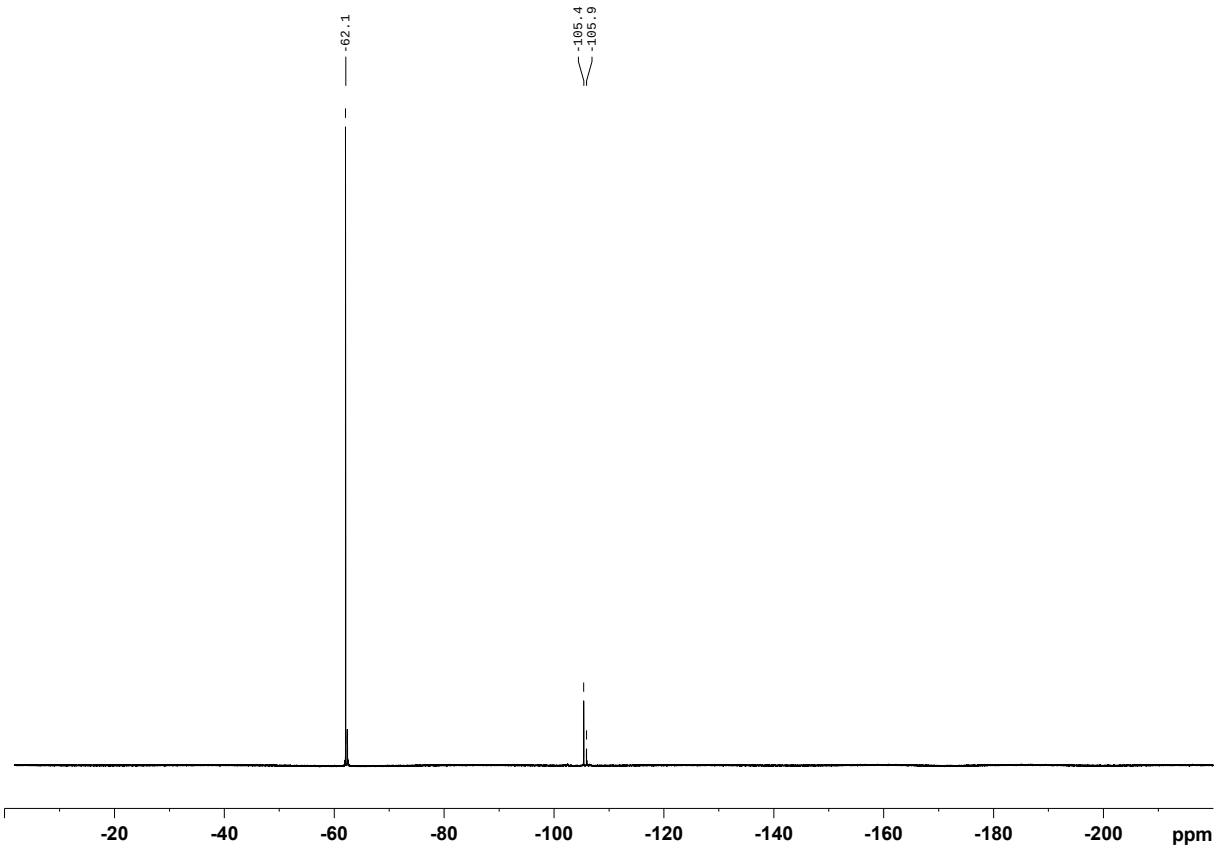
Selected NMR data for **7e**: **^{31}P NMR** (202 MHz, C_6D_6): δ = 22.3 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –105.9, –62.1ppm.

Remaining resonance signals in the ^{31}P and ^{19}F NMRs were assigned to complex **1e**.

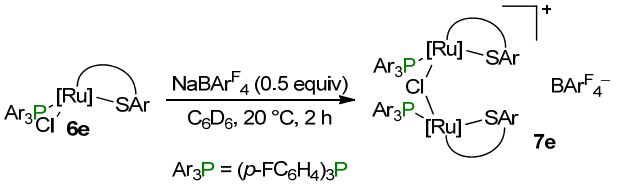
^{31}P NMR:



^{19}F NMR:



4.3 Quantitative Formation of Complex 7e



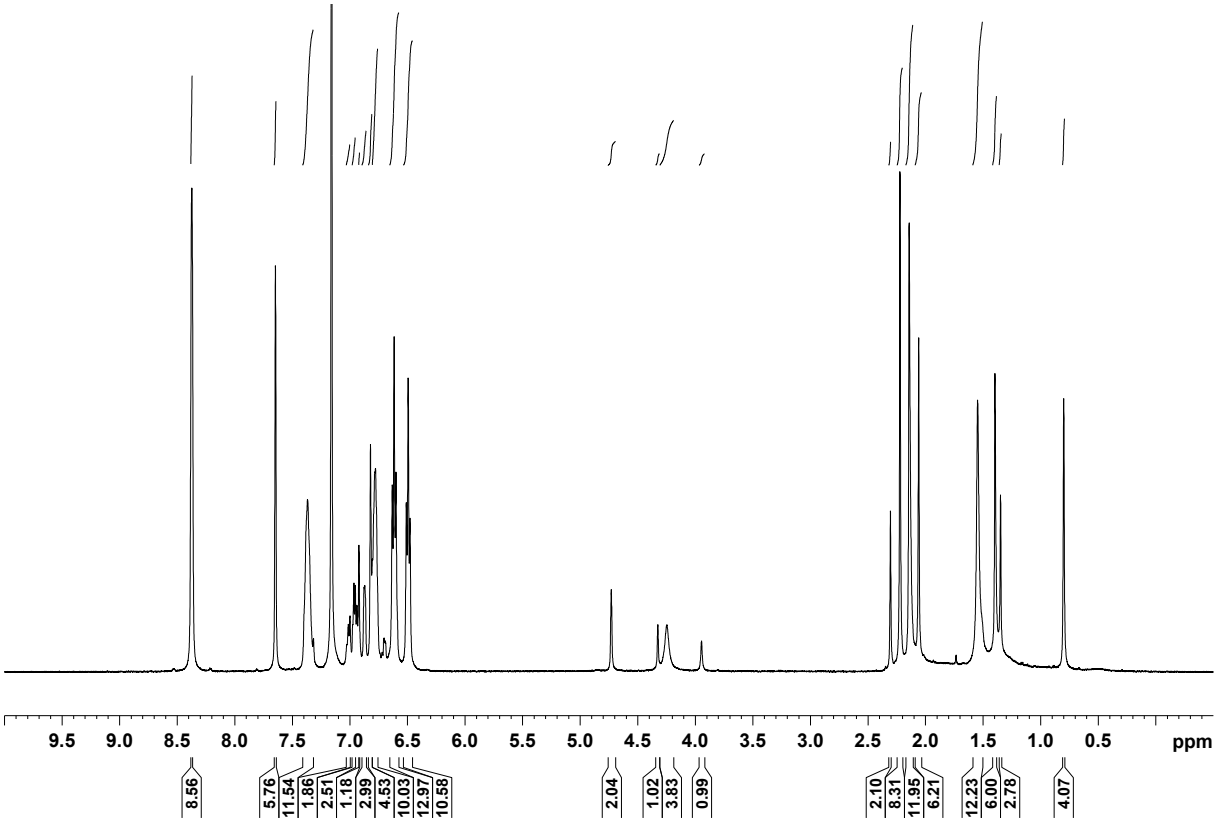
According to GP 2, [{(*p*-FC_6H_4)$_3$P}Ru(SDmp)Cl] (**6e**, 80 mg, 0.10 mmol, 1.0 equiv) and $NaBAr^F_4$ (44 mg, 0.050 mmol, 0.50 equiv) were suspended in CH_2Cl_2 (20 mL). After stirring the dark green reaction at ambient temperature mixture for 14 h, the precipitate was filtered off under inert atmosphere. Removal of the solvent under reduced pressure afforded a brown powder (58 mg). NMR analysis was performed in C_6D_6 at 20 °C, indicating resonance signals for the monomeric complex **6e** and the dimeric chloride-bridged complex **7e**.

This powder is active in hydrodefluorination!

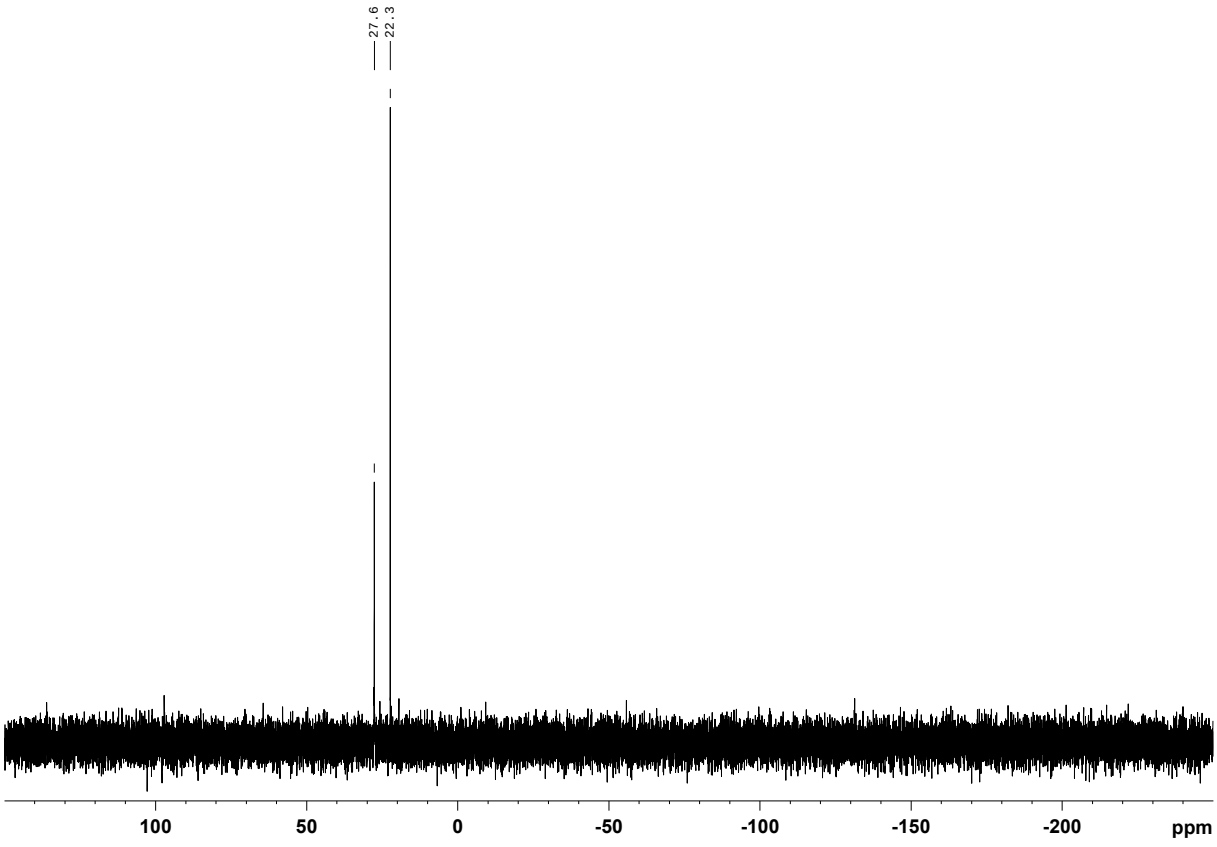
Selected NMR data for **7e**: **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.40 (s, 6H), 1.55 (s, 12H), 2.06 (s, 6H), 2.14 (s, 12H), 4.25 (bs, 4H), 6.62 (t, *J* = 8.6 Hz, 12H) 7.31–7.41 (m, 12H) ppm. **^{31}P NMR** (202 MHz, C_6D_6): δ = 22.3 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –105.9, –62.1ppm. **^{11}B NMR** (160 MHz, C_6D_6): δ = –5.9 ppm.

Remaining resonance signals in the ^{31}P and ^{19}F NMRs were assigned to complex **6e**.

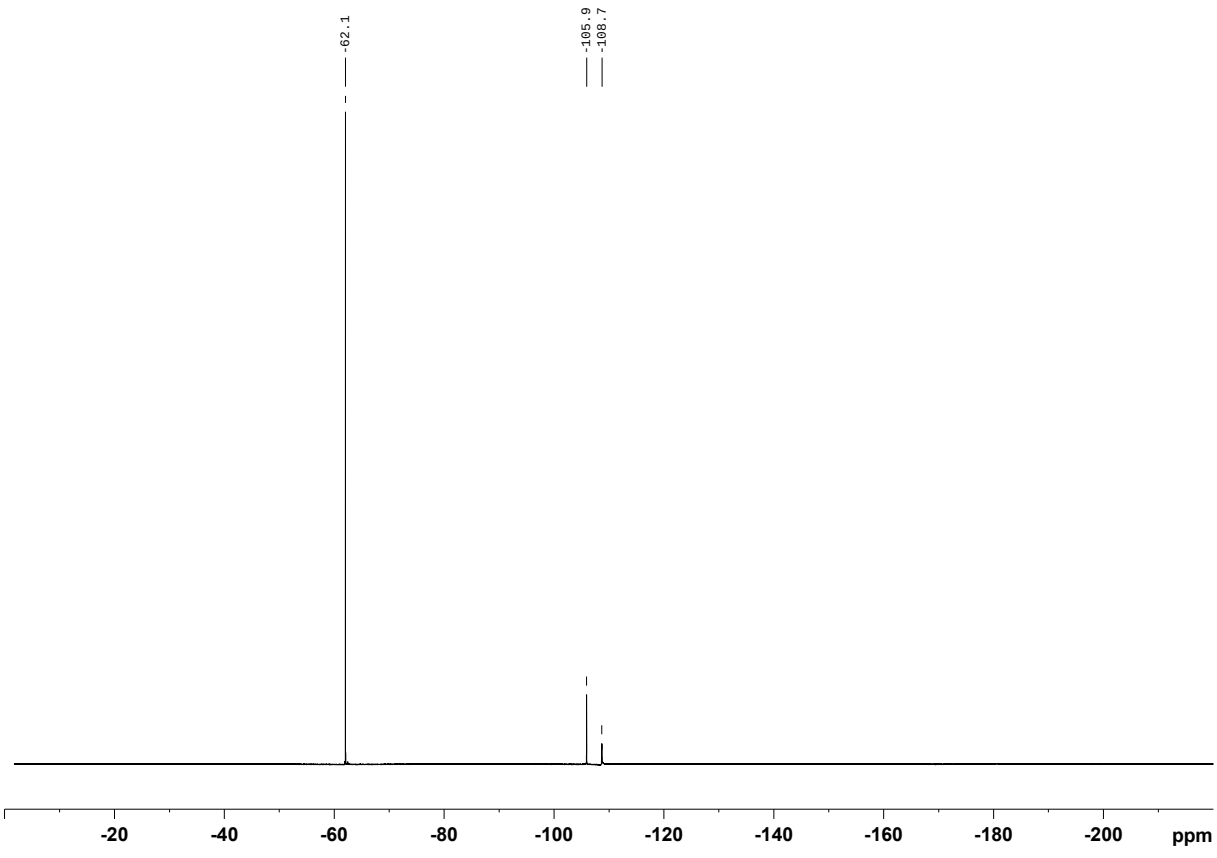
^{1}H NMR:



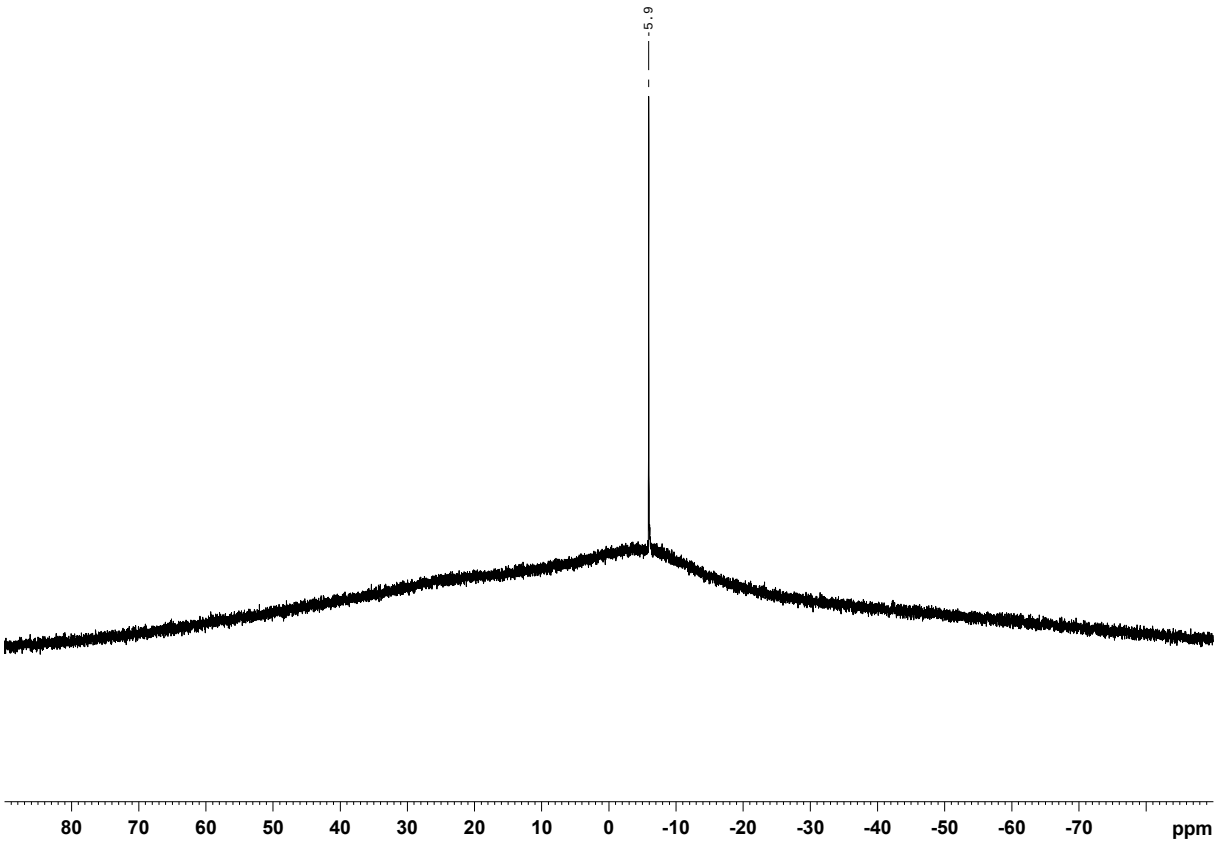
^{31}P NMR:



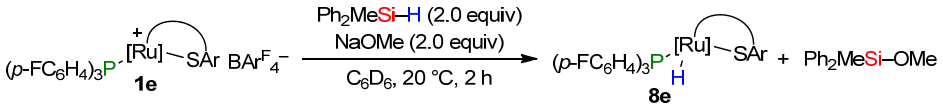
^{19}F NMR:



^{11}B NMR:

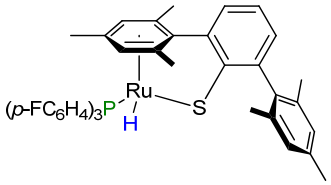


4.4 Formation of Complex 8e

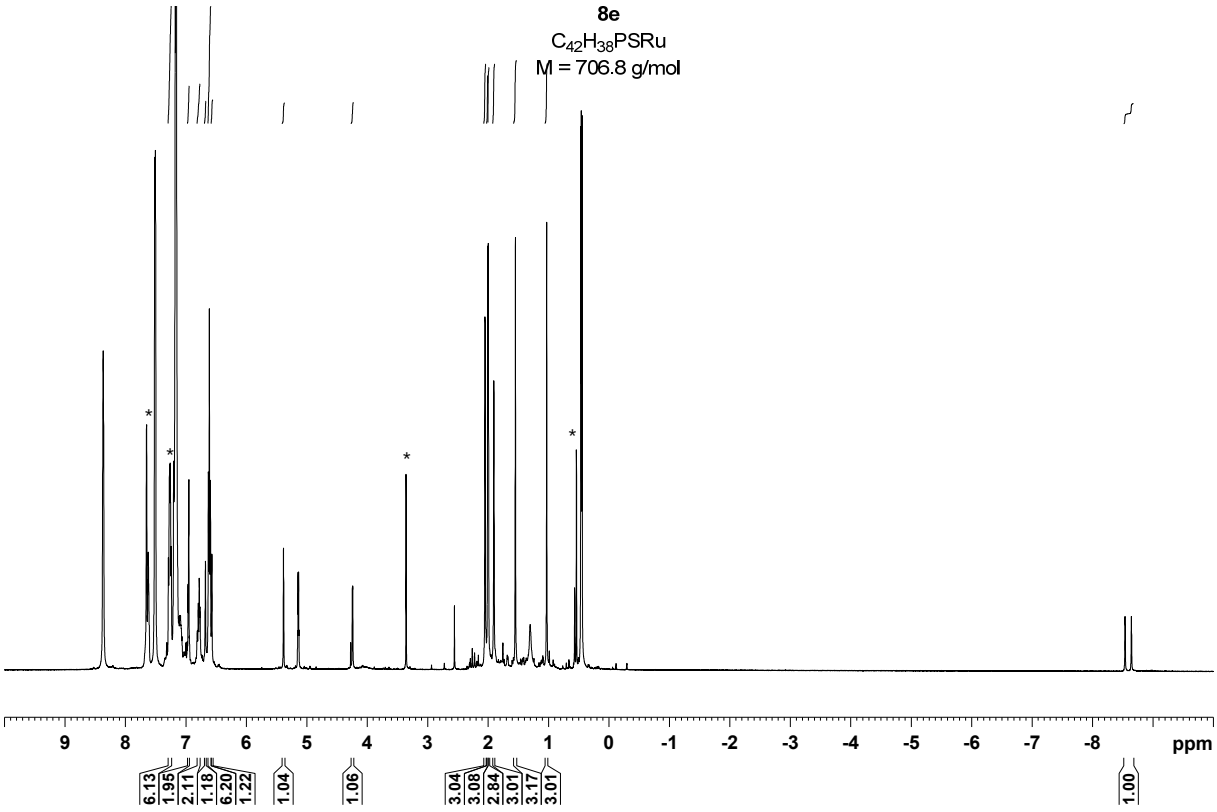


[{(*p*-FC_6H_4)$_3$P}Ru(SDmp)]BAr^F_4 (**1e**, 10 mg, 6.2 µmol, 1.0 equiv) was dissolved in C_6D_6 (0.6 mL) and transferred into a NMR tube. After addition of Ph_2MeSiH (2.4 mg, 12 µmol, 2.0 equiv) and NaOMe (0.6 mg, 12 µmol, 2.0 equiv), the sample was directly subjected to NMR analysis.

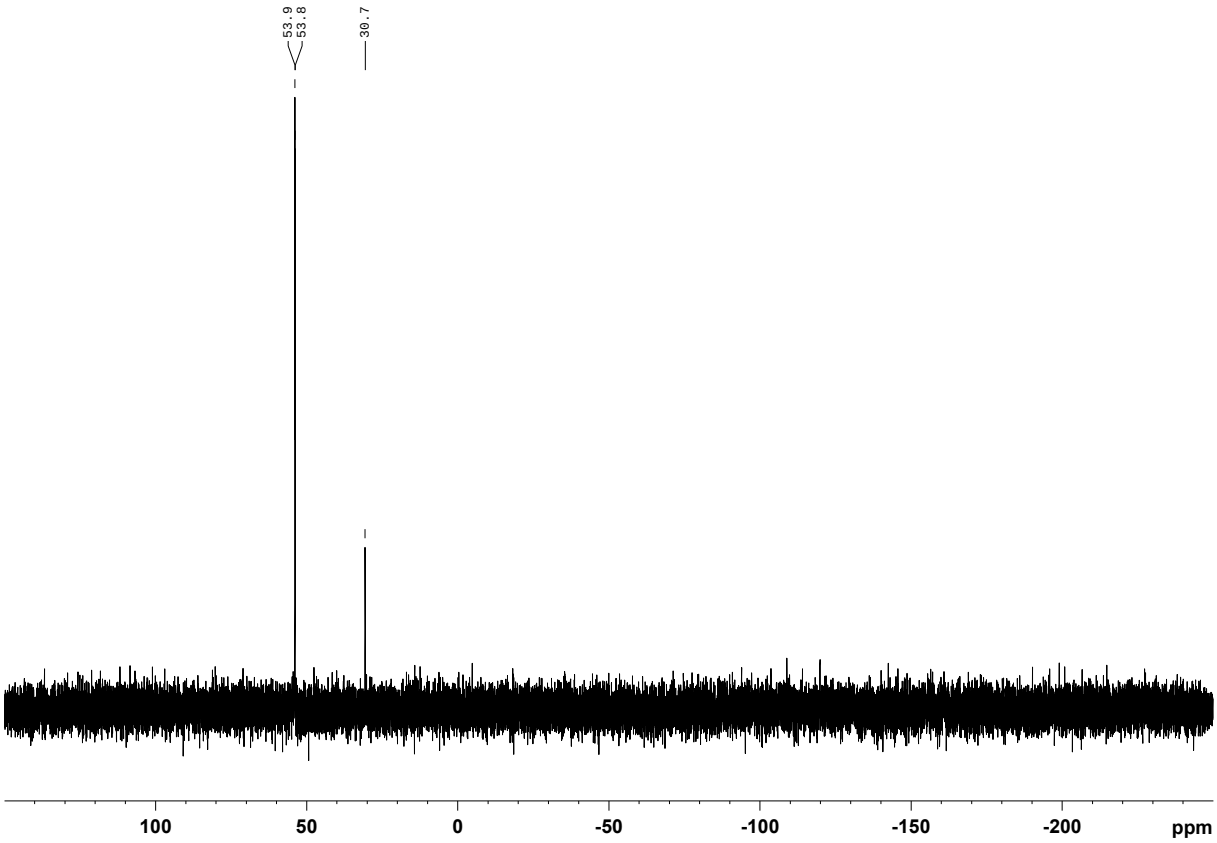
^{1}H NMR (500 MHz, C_6D_6): δ = –8.59 (d, *J* = 53.3 Hz, 1H), 1.04 (s, 3H), 1.55 (s, 3H), 1.91 (s, 3H), 2.00 (s, 3H), 2.05 (s, 6H), 4.24 (s, 1H), 5.39 (s, 1H), 6.57 (s, 1H) 6.61 (d, *J* = 7.9 Hz, 6H), 6.68 (s, 1H), 6.75–6.82 (m, 2H), 6.93–6.98 (m, 2H) 7.27 (q, *J* = 7.9 Hz, 6H) ppm. **^{31}P NMR** (202 MHz, C_6D_6): δ = 53.8/53.9 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –103.0 ppm.



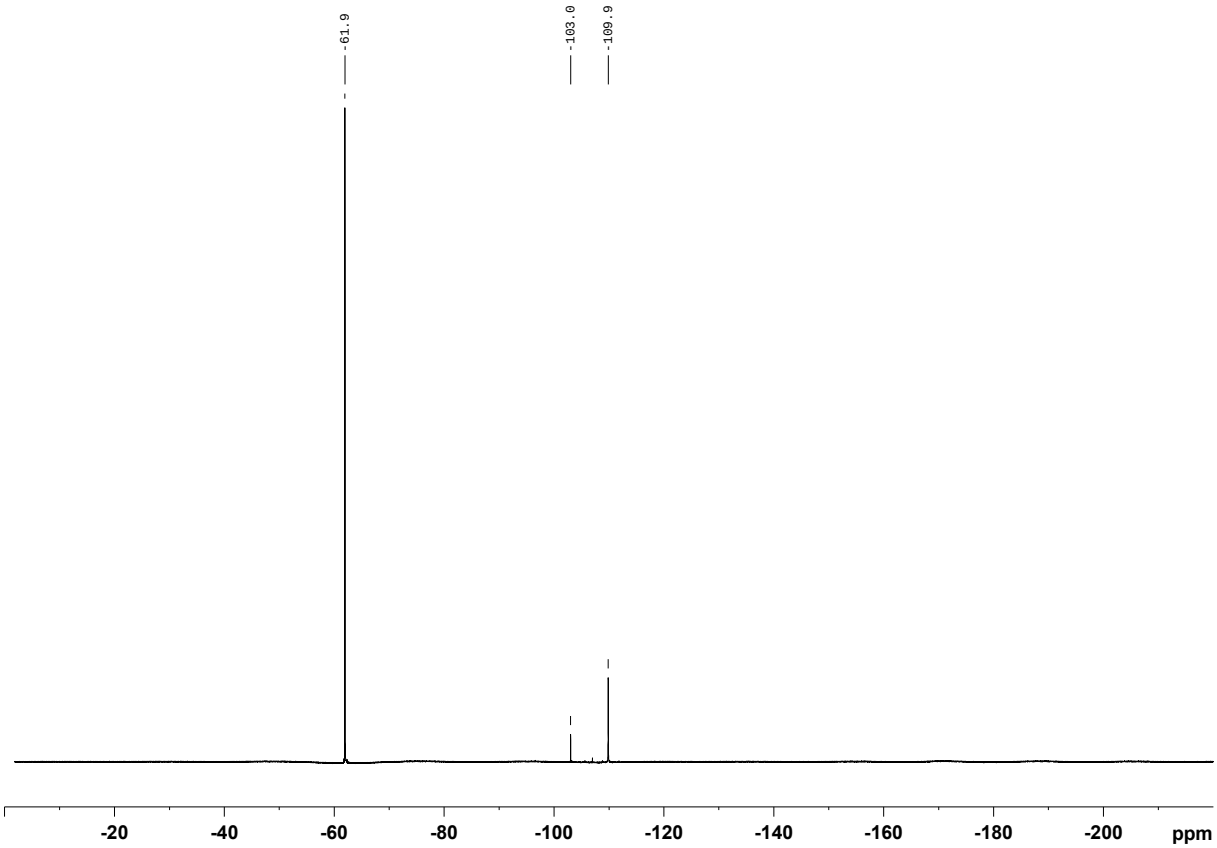
^{1}H NMR (* = $Ph_2MeSiOMe$):



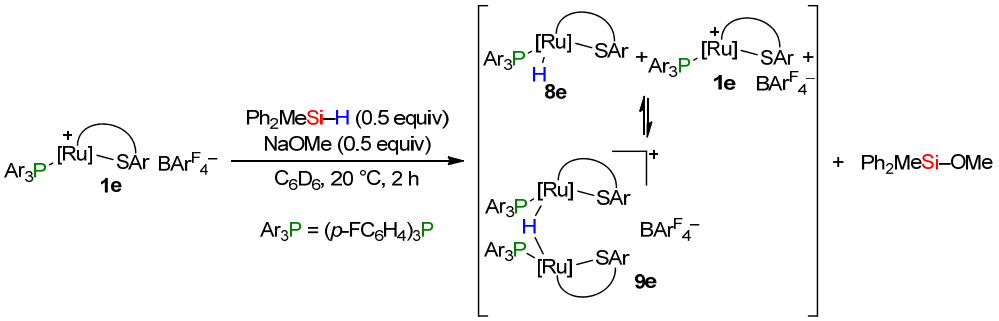
^{31}P NMR:



^{19}F NMR:



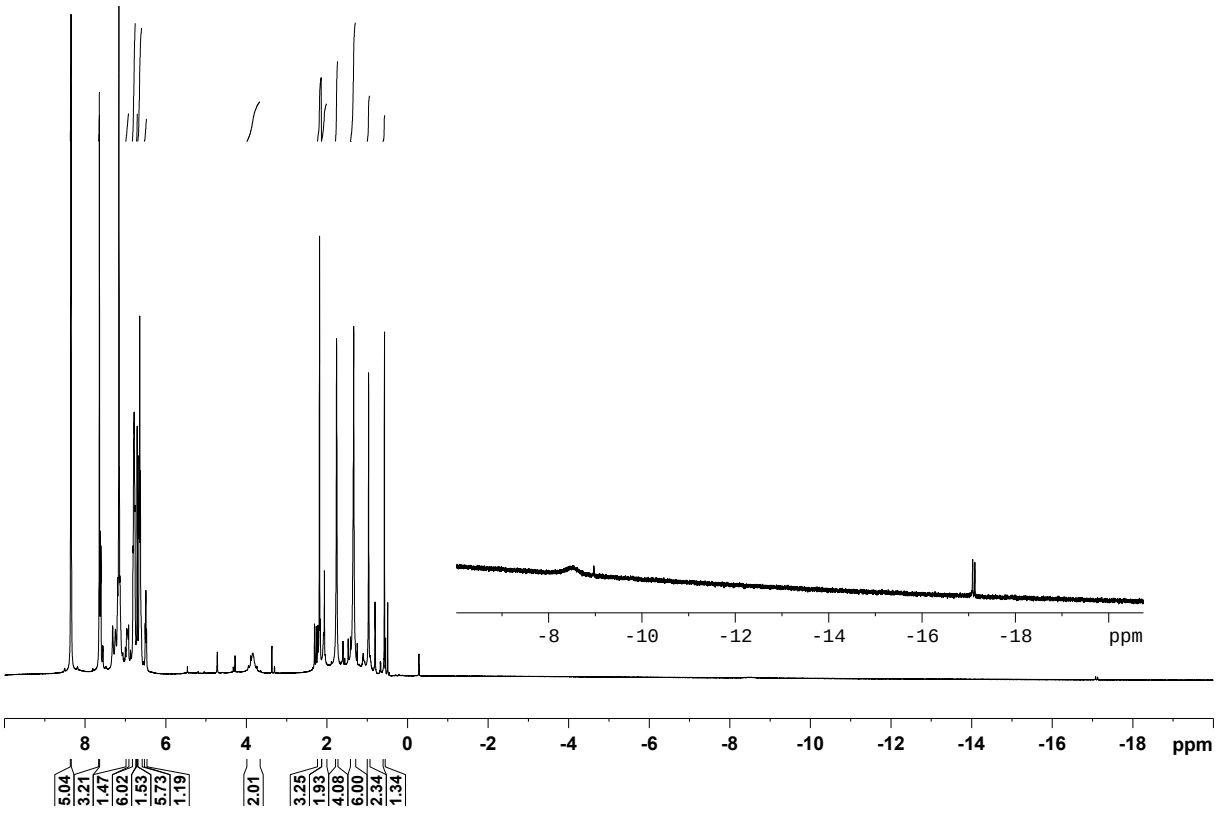
4.5 Formation of Complex 9e



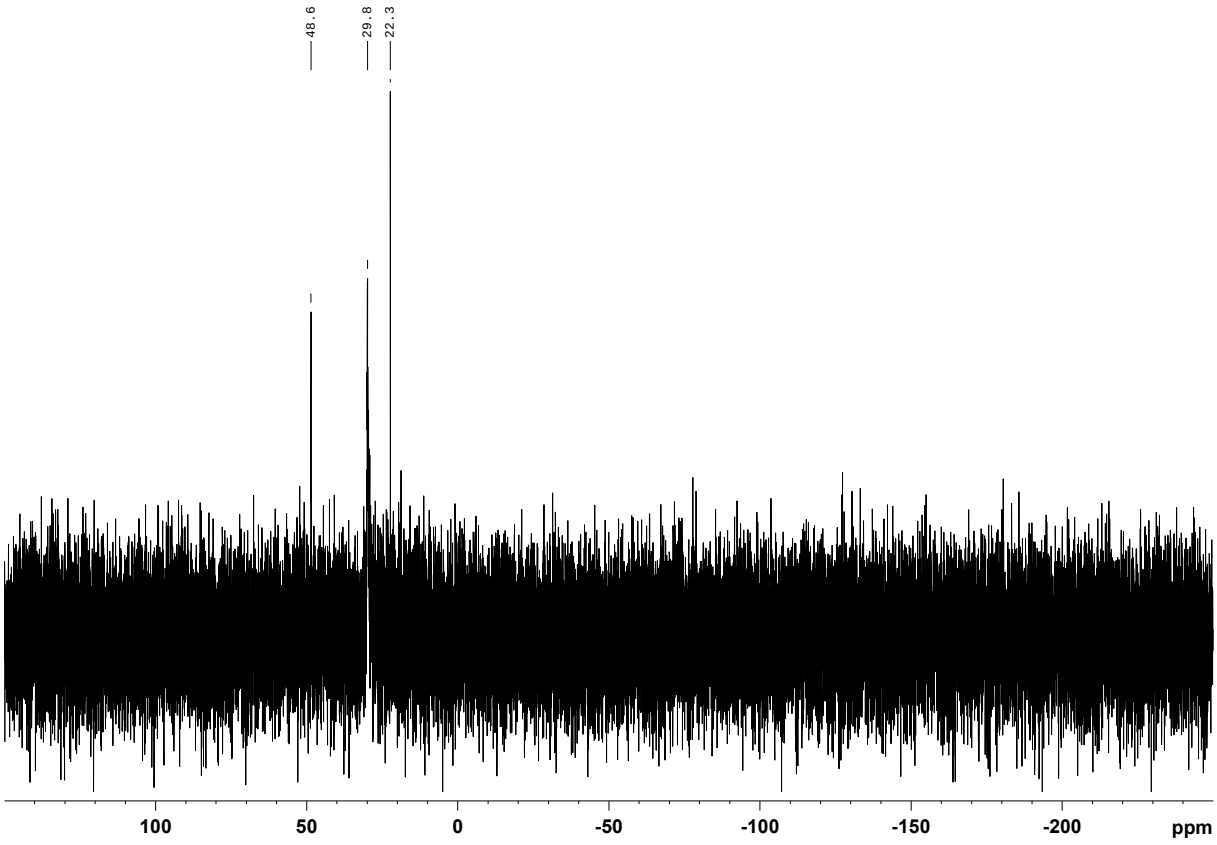
[{(*p*-FC_6H_4)$_3$P}Ru(SDmp)]BAr^F_4 (**1e**, 10 mg, 6.2 µmol, 1.0 equiv) was dissolved in C_6D_6 (0.6 mL) and transferred into a NMR tube. After addition of Ph_2MeSiH (0.6 mg, 3.0 µmol, 0.5 equiv) and NaOMe (0.1 mg, 3.1 µmol, 0.5 equiv), the sample was directly subjected to NMR analysis, indicating resonance signals for ruthenium hydride complex **8e** (–8.59 ppm in ^{1}H NMR) and dimeric hydride-bridged complex **9e** (–17.1 ppm in ^{1}H NMR) along with Ph_2MeSi–OMe.

Selected NMR data for **9e**: **^{1}H NMR** (500 MHz, C_6D_6): δ = –17.1 ppm. **^{31}P NMR** (202 MHz, C_6D_6): δ = 22.3 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –105.9, –62.1ppm. **^{11}B NMR** (160 MHz, C_6D_6): δ = –6.0 ppm.

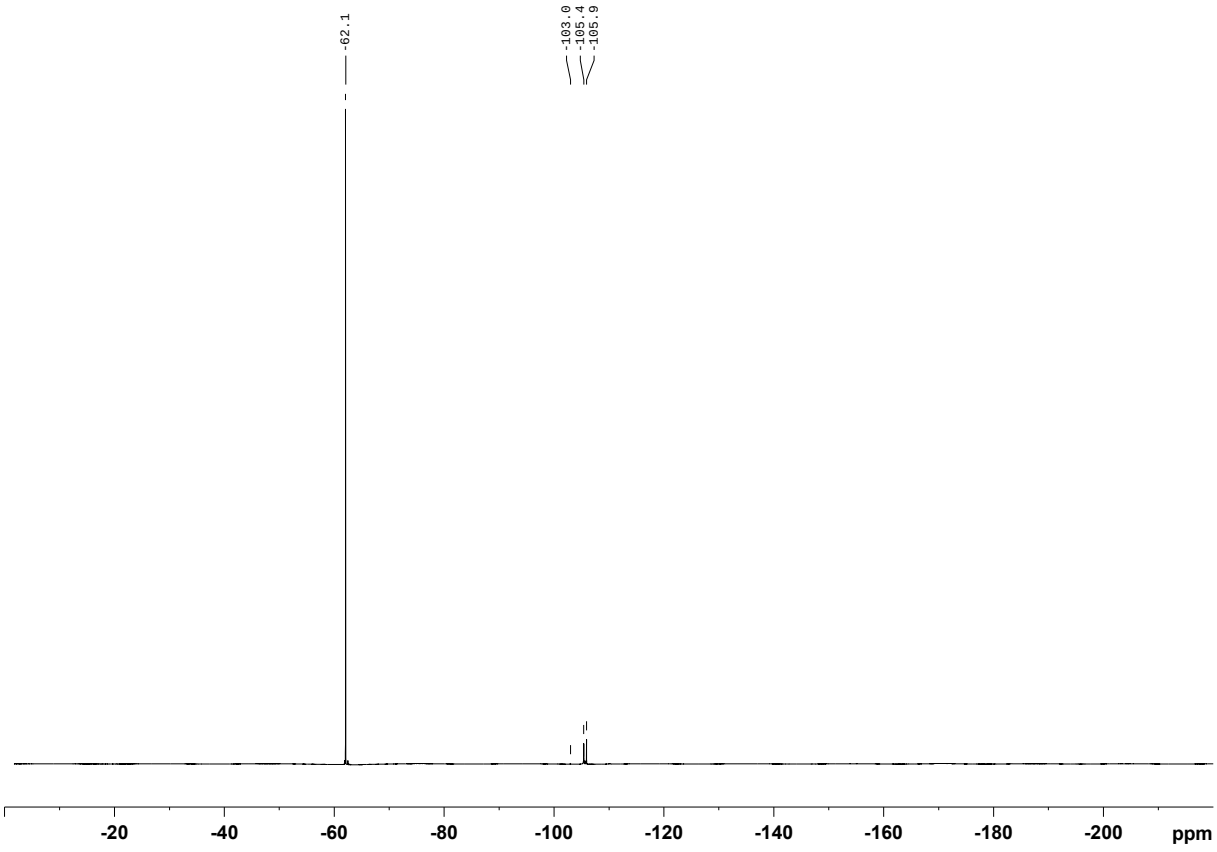
^{1}H NMR:



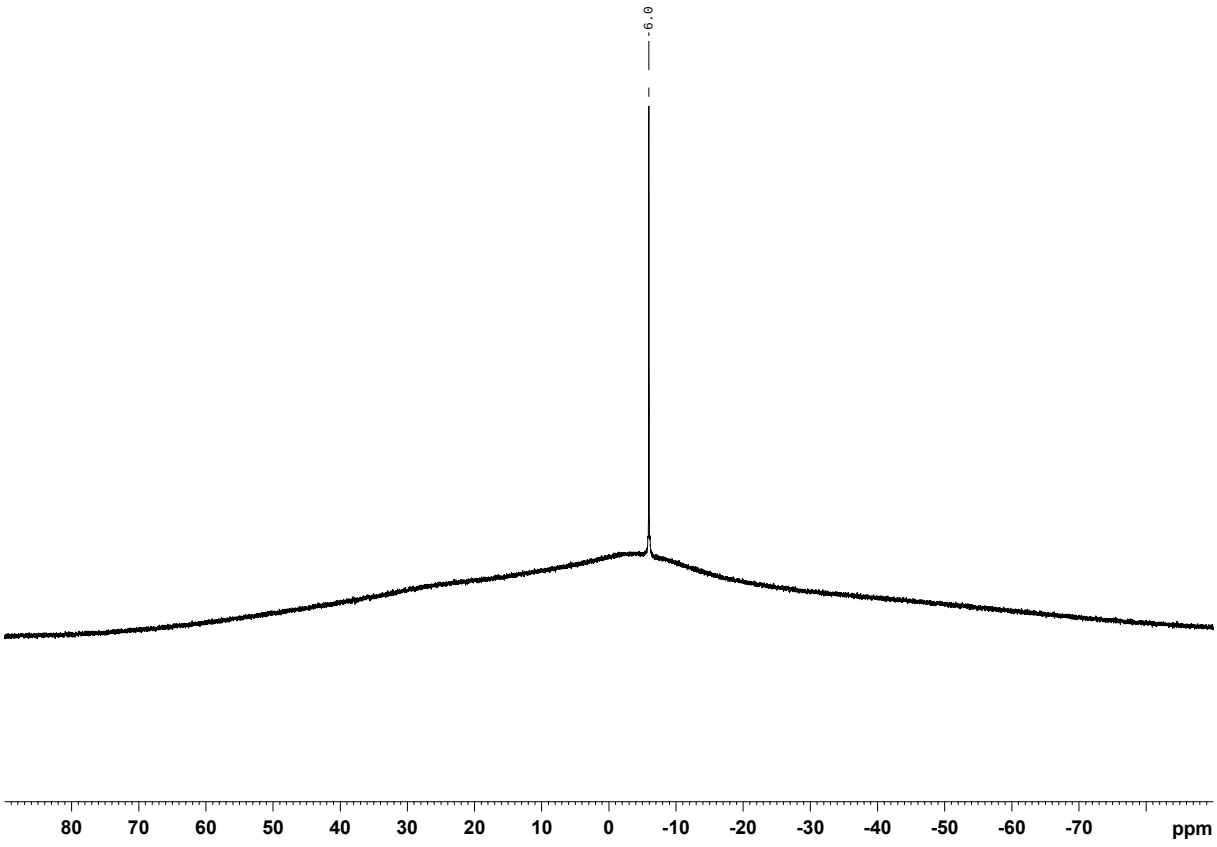
^{31}P NMR:



^{19}F NMR:

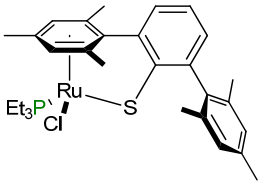


^{11}B NMR:



5 Procedures and Characterization Data

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(triethylphosphine)-ruthenium(II) (6a)



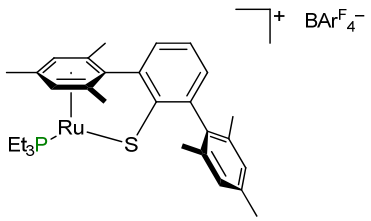
6a
$C_{30}H_{40}PSClRu$
M = 600.20 g/mol

According to GP 1, *n*-butyllithium (1.50M in hexanes, 1.04 mL, 1.57 mmol, 2.00 equiv) was slowly added to a solution of 2,6-bis(2,4,6-trimethylphenyl)phenylthiol (543 mg, 1.57 mmol, 2.00 equiv) at 0 °C. After 30 min, the orange solution was added dropwise to a suspension of di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (480 mg, 0.784 mmol, 1.00 equiv) in THF (15 mL) at 0 °C, and the cooling bath was removed. The blue suspension was stirred for 3 h, and then the solvent was completely removed under reduced pressure and replaced by toluene (15 mL). The salts formed during the reaction were filtered off under inert atmosphere, and toluene (15 mL) and triethylphosphine (10% w/w solution in *n*-hexane, 2.45 g, 2.72 mmol, 3.47 equiv) were added to the filtrate to form a red solution which was maintained at 65 °C for 15 h. The solvent was removed under reduced pressure and the crude product was purified by recrystallization from toluene–*n*-pentane giving ruthenium complex **6a** (431 mg, 46%) as a red powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.75 (dt, *J* = 14.5 Hz, *J* = 7.5 Hz, 9H), 1.47 (m_c, 3H), 1.49 (s, 3H), 1.68 (m_c, 3H), 1.78 (s, 3H), 2.11 (d, *J* = 2.6 Hz, 3H), 2.21 (s, 3H), 2.28 (s, 3H), 2.41 (s, 3H), 4.33 (d, *J* = 4.6 Hz, 1H), 5.16 (s, 1H), 6.82 (dd, *J* = 5.4 Hz, *J* = 3.5 Hz, 1H), 6.94–6.97 (m, 3H), 6.98 (bs, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = 8.0 (d, *J* = 4.1 Hz), 17.2 (d, *J* = 1.8 Hz), 17.9, 18.0, 18.1 (d, *J* = 32.4 Hz), 20.8, 20.9, 21.3, 80.4, 83.9, 93.0, 94.7 (d, *J* = 11.8 Hz), 100.8 (d, *J* = 5.8 Hz), 110.1, 121.5, 126.1, 128.4, 129.0, 129.1, 135.4, 136.3, 136.8, 137.4, 138.4, 142.6, 160.2 (d, *J* = 2.0 Hz) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 21.7 ppm. **HRMS** (ESI) calcd for $C_{30}H_{40}PSRu$ $[M–Cl]^+$: 565.1634, Found: 565.1624.

The analytical and spectroscopic data are in accordance with those reported.[S4]

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]triethylphosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1a)



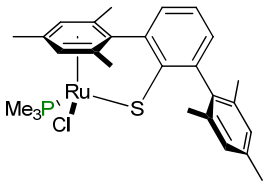
1a
$C_{62}H_{52}BF_{24}PSRu$
M = 1427.96 g/mol

According to GP 2, [(Et$_3$P)Ru(SDmp)Cl] (**6a**, 115 mg, 0.192 mmol, 1.00 equiv) and NaBAr$^F_4$ (170 mg, 0.192 mmol, 1.00 equiv) were suspended in CH_2Cl_2 (15 mL). After stirring the dark green reaction mixture at ambient temperature for 1.5 h, the suspension was concentrated under reduced pressure to a volume of 5 mL. The precipitate was filtered off under inert atmosphere, and the solvent was removed under reduced pressure. Ruthenium thiolate complex **1a** (163 mg, 60%) was obtained as a green powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.28 (dt, *J* = 17.3 Hz, *J* = 7.6 Hz, 9H), 0.99 (dq, *J* = 8.1 Hz, *J* = 7.6 Hz, 6H), 1.19 (s, 6H), 1.47 (s, 3H), 1.94 (s, 6H), 2.09 (s, 3H), 3.76 (s, 2H), 6.80 (s, 2H), 6.94 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 7.06 (dd, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.20 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.67 (s, 4H), 8.37 (s, 8H) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 22.5 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –62.1 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –5.9 ppm. **HRMS** (ESI) calcd for $C_{42}H_{37}PSRu$ [M–BAr$^F_4$]$^+$: 763.1344, Found: 763.1345.

The analytical and spectroscopic data are in accordance with those reported.[S4]

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(trimethylphosphine)-ruthenium(II) (6b)

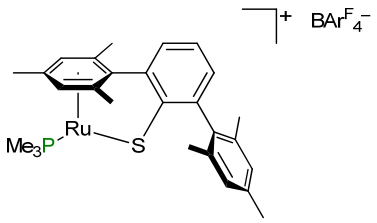


6b
$C_{27}H_{34}PSClRu$
M = 558.12 g/mol

According to GP 1, *n*-butyllithium (1.50M in hexanes, 0.893 mL, 1.33 mmol, 2.00 equiv) was slowly added to a solution of 2,6-bis(2,4,6-trimethylphenyl)phenylthiol (464 mg, 1.33 mmol, 2.00 equiv) at 0 °C. After 30 min, the orange solution was added dropwise to a suspension di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (410 mg, 0.670 mmol, 1.00 equiv) in THF (15 mL) at 0 °C, and the cooling bath was removed. The blue suspension was stirred for 3 h, and then the solvent was completely removed under reduced pressure and replaced by toluene (15 mL). The salts formed during the reaction were filtered off under inert atmosphere, and toluene (15 mL) and trimethylphosphine (1.0M in *n*-hexane, 1.68 mL, 1.68 mmol, 2.50 equiv) were added to the filtrate to form a red solution which was maintained at 65 °C for 15 h. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from toluene–*n*-pentane giving ruthenium complex **6b** (320 mg, 43%) as a red powder.

^{1}H NMR (400 MHz, C_6D_6): δ =1.02 (d, *J* = 10.5 Hz, 9H), 1.37 (s, 3H), 1.76 (s, 3H), 2.10 (d, *J* = 3.6 Hz, 3H), 2.26 (s, 3H), 2.27 (s, 3H), 2.39 (s, 3H), 4.33 (d, *J* = 5.6 Hz, 1H), 5.22 (s, 1H), 6.77 (dd, *J* = 5.7 Hz, *J* = 3.1 Hz, 1H), 6.91–6.96 (m, 2H), 6.97–7.00 (m, 2H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = 15.8 (d, *J* = 32.5 Hz), 17.4 (d, *J* = 2.0 Hz), 17.7, 18.5, 20.7, 20.8, 21.3, 79.9, 84.1, 91.9, 94.0, 101.6 (d, *J* = 7.0 Hz), 109.5, 121.7, 126.1, 128.9 (d, *J* = 2.8 Hz), 135.4, 136.2, 136.9, 137.0, 138.4, 142.7, 159.5 ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 1.1 ppm. **HRMS** (ESI) calcd for $C_{27}H_{34}PSRu$ $[M–Cl]^+$: 523.1157, Found: 523.1178.

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]trimethylphosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1b)

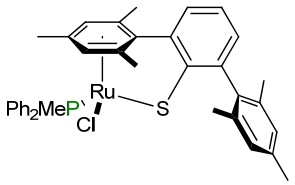


1b
$C_{59}H_{46}BF_{24}PSRu$
M = 1385.88 g/mol

According to GP 2, [(Me$_3$P)Ru(SDmp)Cl] (**6b**, 80.0 mg, 0.143 mmol, 1.00 equiv) and NaBAr$^F_4$ (127 mg, 0.143 mmol, 1.00 equiv) were suspended in toluene (6 mL). After stirring the dark green reaction mixture at 40 °C for 2 h, the precipitate was filtered off under inert atmosphere, and the solvent was removed under reduced pressure. Ruthenium thiolate complex **1b** (72 mg, 37%) was obtained as a green powder.

^{1}H NMR (500 MHz, C_6D_6): δ = 0.69 (bs, 9H), 0.97 (s, 3H), 1.46, (bs, 6H), 2.01 (bs, 6H), 2.15 (s, 3H), 3.82 (bs, 2H), 6.88 (s, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 7.6 Hz, *J* = 7.4 Hz 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.68 (s, 4H), 8.36 (s, 8H) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 20.0 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –62.0 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –6.0 ppm. **HRMS** (ESI) calcd for $C_{27}H_{34}PSRu$ [M–BAr$^F_4$]$^+$: 523.1157, Found: 523.1159.

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(diphenylmethyl-phosphine)-ruthenium(II) (6c)

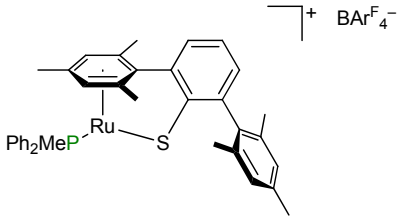


6c
$C_{37}H_{38}PSClRu$
M = 682.26 g/mol

According to GP 1, *n*-butyllithium (1.50M in hexanes, 1.02 mL, 1.02 mmol, 2.00 equiv) was slowly added to a solution of 2,6-bis(2,4,6-trimethylphenyl)phenylthiol (353 mg, 1.02 mmol, 2.00 equiv) at 0 °C. After 30 min, the orange solution was added dropwise to a suspension di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (312 mg, 0.509 mmol, 1.00 equiv) in THF (15 mL) at 0 °C and the cooling bath was removed. The blue suspension was stirred for 3 h , and then the solvent was completely removed under reduced pressure and replaced by toluene (25 mL). The salts formed during the reaction were filtered off under inert atmosphere and diphenylmethylphosphine (204 mg, 1.02 mmol, 2.00 equiv) in toluene (2 mL) was added to the filtrate to form a red solution which was maintained at 65 °C for 15 h. The solvent was removed under reduced pressure and the crude product was purified by recrystallization from toluene–*n*-pentane giving ruthenium complex **6c** (220 mg, 32%) as a red powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.89 (s, 3H), 1.57 (s, 3H), 1.60 (d, *J* = 10.2 Hz, 3H), 2.17 (d, *J* = 4.0 Hz, 3H), 2.28 (s, 3H), 2.38 (s, 3H), 2.43 (s, 3H), 4.05 (d, *J* = 5.4 Hz, 1H), 5.19 (s, 1H), 6.78 (dd, *J* = 7.0 Hz, *J* = 1.8 Hz, 1H), 6.94–7.01 (m, 6H), 7.04 (s, 1H), 7.06–7.10 (m, 3H), 7.39–7.45 (m, 2H), 7.69–7.76 (m, 2H). ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = 14.4 (d, *J* = 34.5 Hz), 16.4, 17.2, 18.4, 20.9, 21.0, 21.4, 80.0, 86.3, 93.7 (d, *J* = 14.1 Hz), 94.6, 98.9 (d, *J* = 4.4 Hz), 113.5 (d, *J* = 3.0 Hz), 122.0, 125.7, 126.1, 129.2, 129.4, 129.6 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 2.6 Hz), 132.5 (d, *J* = 9.2 Hz), 134.5 (d, *J* = 10.5 Hz), 134.9, 135.6, 136.4, 136.5, 137.2, 137.4, 137.6, 138.4, 142.7, 159.5 (d, *J* = 3.6 Hz) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 20.2 ppm. **HRMS** (ESI) calcd for $C_{37}H_{38}PSRu$ $[M–Cl]^+$: 647.1470, Found: 647.1486.

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato](diphenylmethylphosphine)-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1c)

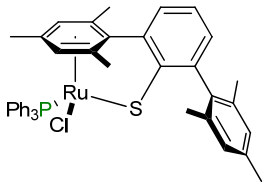


1c
$C_{69}H_{50}BF_{24}PSRu$
M = 1510.02 g/mol

According to GP 2, [(Ph$_2$MeP)Ru(SDmp)Cl] (**6c**, 70.0 mg, 0.102 mmol, 1.00 equiv) and NaBAr$^F_4$ (136 mg, 0.154 mmol, 1.50 equiv) were suspended in CH_2Cl_2 (20 mL). After stirring the dark green reaction mixture at 40 °C for 1 h, the precipitate was filtered off under inert atmosphere, and the solvent was removed under reduced pressure. Ruthenium thiolate complex **1c** (74 mg, 48%) was obtained as a green powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.82 (s, 3H), 0.93 (d, *J* = 7.4 Hz, 3H), 1.26 (s, 6H), 1.90 (s, 6H), 2.08 (s, 3H), 3.72 (s, 2H), 6.76 (s, 2H), 6.81 (t, *J* = 9.7 Hz, 4H), 6.92–6.98 (m, 6H), 6.99–7.04 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 7.9 Hz, *J* = 7.8 Hz, 1H), 7.64 (s, 4H), 8.35 (s, 8H) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 14.2 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –62.1 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –5.9 ppm. **HRMS** (ESI) calcd for $C_{37}H_{38}PSRu$ [M–BAr$^F_4$]$^+$: 647.1470, Found: 647.1464.

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(triphenylphosphine)-ruthenium(II) (6d)



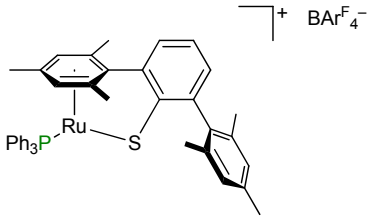
6d
$C_{42}H_{40}PSClRu$
M = 744.33 g/mol

According to GP 1, *n*-butyllithium (1.38M in hexanes, 1.05 mL, 1.46 mmol, 2.00 equiv) was slowly added to a solution of 2,6-bis(2,4,6-trimethylphenyl)phenylthiol (533 mg, 1.46 mmol, 2.00 equiv) at 0 °C. After 30 min, the orange solution was added dropwise to a suspension of di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (448 mg, 0.732 mmol, 1.00 equiv) in THF (15 mL) at 0 °C, and the cooling bath was removed. The blue suspension was stirred for 3 h, and then the solvent was completely removed under reduced pressure and replaced by toluene (25 mL). The salts formed during the reaction were filtered off under inert atmosphere, and triphenylphosphine (383 mg, 1.46 mmol, 2.00 equiv) in toluene (2 mL) was added to the filtrate to form a red solution which was maintained at 65 °C for 15 h. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from toluene–*n*-pentane giving ruthenium complex **6d** (325 mg, 30%) as a red powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 1.21 (s, 3H), 1.51 (s, 3H), 2.16 (d, *J* = 3.4 Hz, 3 H), 2.23 (s, 3H), 2.24 (s, 3H), 2.43 (s, 3H), 3.62 (d, *J* = 4.8 Hz, 1H), 5.13 (s, 1H), 6.78 (s, 1H), 6.85 (dd, *J* = 5.4 Hz, *J* = 3.4 Hz, 1H), 6.87–6.95 (m, 8H), 6.97–7.00 (m, 3H), 7.69–7.87 (m, 7H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = 16.6, 16.9 (d, *J* = 2.2 Hz), 18.3, 20.9, 21.0, 21.3, 83.4, 88.1, 96.4 (d, *J* = 10.7 Hz), 96.7, 97.7 (d, *J* = 3.1 Hz), 112.7 (d, *J* = 3.6 Hz), 121.6, 126.0, 128.7, 129.2, 129.8 (d, *J* = 1.8 Hz), 131.5 (d, *J* = 1.5 Hz), 132.4 (d, *J* = 10.2 Hz), 134.6 (d, *J* = 10.6 Hz), 135.5, 135.8, 135.9, 137.1, 138.0, 142.8, 160.7 (d, *J* = 4.4 Hz) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 28.8 ppm. **HRMS** (ESI) calcd for $C_{42}H_{40}PSRu$ $[M–Cl]^+$: 709.1626, Found: 709.1649.

The analytical and spectroscopic data are in accordance with those reported.[S4]

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]triphenylphosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1d)



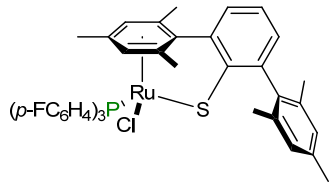
1d
$C_{74}H_{52}BF_{24}PSRu$
M = 1572.09 g/mol

According to GP 2, [(Ph$_3$P)Ru(SDmp)Cl] (**6d**, 90.0 mg, 0.121 mmol, 1.00 equiv) and NaBAr$^F_4$ (161 mg, 0.181 mmol, 1.50 equiv) were suspended in CH_2Cl_2 (20 mL). After stirring the dark green reaction mixture at 40 °C for 1 h, the precipitate was filtered off under inert atmosphere, and the solvent was removed under reduced pressure. Ruthenium thiolate complex **1d** (110 mg, 58%) was obtained as a green powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.88 (s, 3H), 1.31 (s, 6H), 1.79 (s, 6H), 2.12 (s, 3H), 3.81 (s, 2H), 6.68 (s, 2H), 6.91 (dd, *J* = 7.5 Hz, *J* = 6.0, 6H), 6.94–7.03 (m, 10H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H), 7.63 (s, 4H), 8.37 (s, 8H) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 31.4 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –62.1 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –5.9 ppm. **HRMS** (ESI) calcd for $C_{42}H_{40}PSRu$ [M–BAr$^F_4$]$^+$: 709.1626, Found: 709.1623.

The analytical and spectroscopic data are in accordance with those reported.[S4]

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido[tris(4-fluorophenyl)-phosphine]-ruthenium(II) (6e)

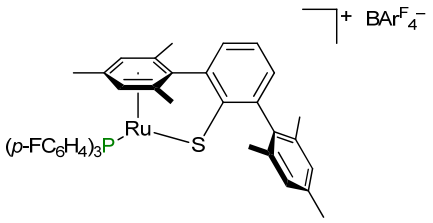


6e
$C_{42}H_{37}F_3PSClRu$
M = 798.30 g/mol

According to GP 1, *n*-butyllithium (1.50M in hexanes, 1.01 mL, 1.52 mmol, 2.00 equiv) was slowly added to a solution of 2,6-bis(2,4,6-trimethylphenyl)phenylthiol (526 mg, 1.52 mmol, 2.00 equiv) at 0 °C. After 30 min, the orange solution was added dropwise to a suspension of di-μ-chloridobis[chlorido(η^6-*p*-cymene)ruthenium(II)] (465 mg, 0.759 mmol, 1.00 equiv) in THF (15 mL) at 0 °C, and the cooling bath was removed. The now blue suspension was stirred for 3 h, and then the solvent was completely removed under reduced pressure and replaced by toluene (15 mL). The salts formed during the reaction were filtered off under inert atmosphere, and toluene (15 mL) and a solution of tris(4-fluorophenyl)phosphine (480 mg, 1.52 mmol, 2.00 equiv) in toluene (15 mL) was added to the filtrate to form a red solution which was maintained at 65 °C for 15 h. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from toluene–*n*-pentane giving ruthenium complex **6e** (993 mg, 82%) as a red powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 1.16 (s, 3H), 1.44 (s, 3H), 2.12 (d, *J* = 3.6 Hz, 3H), 2.16 (s, 3H), 2.26 (s, 3H), 2.39 (s, 3H), 3.39 (d, *J* = 4.7 Hz, 1H), 5.06 (s, 1H), 6.60 (t, *J* = 8.5 Hz, 6H), 6.76 (s, 1H), 6.85 (dd, *J* = 6.5 Hz, *J* = 2.4 Hz, 1H), 6.95–7.02 (m, 3H), 7.54 (m_c, 6H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = 16.8, 17.0 (d, *J* = 2.5 Hz), 18.5, 21.0, 21.3, 83.9, 87.9, 97.2, 97.4, 97.4, 113.3 (d, *J* = 4.1 Hz), 115.4 (dd, *J* = 20.9 Hz, *J* = 10.7 Hz), 122.1, 126.2, 128.8, 129.3, 135.5, 135.7, 136.6, 136.7 (dd, *J* = 10.6, *J* = 8.3 Hz), 137.1, 137.8, 142.9, 160.4 (d, *J* = 5.4 Hz), 136.2 (d, *J* = 2.3 Hz), 165.2 (d, *J* = 2.3 Hz) ppm **^{31}P NMR** (203 MHz, C_6D_6): δ = 27.4 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –109.7 ppm. **HRMS** (ESI) calcd for $C_{42}H_{37}F_3PSRu$ [M–Cl]$^+$: 763.1344, Found: 763.1336.

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]tris(4-fluorophenyl)phosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1e)

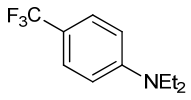


1e
$C_{74}H_{49}BF_{27}PSRu$
M = 1626.06 g/mol

According to GP 2, [{(*p*-FC_6H_4)$_3$P}Ru(SDmp)Cl] (**6e**, 94.4 mg, 0.118 mmol, 1.00 equiv) and $NaBAr^F_4$ (130 mg, 0.147 mmol, 1.24 equiv) were suspended in CH_2Cl_2 (60 mL). After stirring the dark green reaction mixture at 40 °C for 14 h, the precipitate was filtered off under inert atmosphere, and the solvent was removed under reduced pressure. Ruthenium thiolate complex **1e** (134 mg, 70%) was obtained as a green powder.

^{1}H NMR (500 MHz, C_6D_6): δ = 0.90 (s, 3H), 1.29 (s, 6H), 1.76 (s, 6H), 2.17 (s, 3H), 3.77 (s, 2H), 6.48 (dd, *J* = 8.2 Hz, *J* = 8.2 Hz, 1H), 6.63 (t, *J* = 8.5 Hz, 6H), 6.70 (s, 2H), 6.72–6.79 (m, 6H), 6.95 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 4H), 8.35 (s, 8H) ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 29.9 ppm **^{19}F NMR** (471 MHz, C_6D_6): δ = –105.4, –62.1 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –6.0 ppm. **HRMS** (ESI) calcd for $C_{42}H_{37}PSRu$ [M–BAr^F_4]$^+$: 763.1344, Found: 763.1345.

N,*N*-Diethyl-4-trifluoromethylaniline (2a)



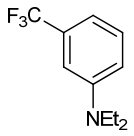
2a
$C_{11}H_{14}F_3N$
M = 217.23 g/mol

According to GP 3, a solution of 4-trifluoromethylaniline (580 mg, 3.60 mmol, 1.00 equiv) in DMF (20 mL) was added to oil-free sodium hydride (480 mg, 20.0 mmol, 5.50 equiv) and stirred at ambient temperature for 15 min. Bromoethane (1.06 g, 9.81 mmol, 2.73 equiv) was slowly added dropwise to the suspension, and the reaction mixture was stirred for further 8 h. After careful addition of saturated aqueous NH_4Cl solution (4 mL) and extraction of the organic layer with *tert*-butyl methyl ether (2 × 20 mL), the combined organic phases were washed with water (4 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by bulb-to-bulb destillation at 120 °C and 0.5 mbar afforded aniline **2a** (570 mg, 73%) as a colorless liquid.

R_f: 0.20 (cyclohexane). **GLC** (35-min): t_R = 12.5 min. **GLC** (55-min): t_R = 19.1 min. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.19 (t, *J* = 7.1 Hz, 6H), 3.39 (q, *J* = 7.1 Hz, 4H), 6.66 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 12.4, 44.4, 110.5, 116.5 (q, *J* = 32.5 Hz), 125.4 (q, *J* = 270.1 Hz), 126.6 (q, *J* = 3.9 Hz), 149.9 ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = –60.2 ppm. **IR** (ATR): $\tilde{\nu}$ = 2976 (w), 2936 (w), 2902 (w), 1616 (s), 1532 (s), 1322 (s), 1269 (s), 1198 (s), 1158 (m), 1099 (m), 1068 (s), 816 (s) cm^{-1}. **HRMS** (ESI) calcd for $C_{11}H_{14}F_3NH$ $[M+H]^+$: 218.1151, Found: 218.1134. **Elemental analysis** calcd for $C_{11}H_{14}F_3N$: C: 60.82; H: 6.50; N: 6.45; Found: C: 61.00; H: 6.49; N: 6.31.

The analytical and spectroscopic data are in accordance with those reported.[S5]

N,*N*-Diethyl-3-trifluoromethylaniline (2b)



2b
$C_{11}H_{14}F_3N$
M = 217.23 g/mol

According to GP 3, a solution of 3-trifluoromethylaniline (276 mg, 1.71 mmol, 1.00 equiv) in DMF (12 mL) was added to oil-free sodium hydride (226 mg, 9.42 mmol, 5.50 equiv) and stirred at ambient temperature for 15 min. Bromoethane (554 mg, 5.13 mmol, 3.00 equiv) was slowly added dropwise to the suspension, and the reaction mixture was maintained at 40 °C for 8 h. After careful addition of saturated aqueous NH_4Cl solution (4 mL) and extraction of the organic layer with *tert*-butyl methyl ether (2 × 20 mL), the combined organic phases were washed with water (4 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by bulb-to-bulb condensation at 120 °C and 0.5 mbar afforded aniline **2b** (312 mg, 85%) as a colorless liquid.

R_f: 0.20 (cyclohexane). **GLC** (35-min): t_R = 11.4 min. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.1 Hz, 6H), 3.38 (q, *J* = 7.1 Hz, 4H), 6.76–6.90 (m, 3H), 7.28 (dd, *J* = 8.1 Hz, *J* = 7.6 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 12.4, 44.4, 107.7 (q, *J* = 4.0 Hz), 111.5 (q, *J* = 4.0 Hz), 114.4, 124.6 (q, *J* = 272.1 Hz), 129.6, 131.7 (q, *J* = 31.4 Hz), 147.8 ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = –62.8 ppm. **IR** (ATR): 2975 (w), 2935 (w), 2876 (w), 1609 (m), 1506 (m), 1456 (m), 1320 (s), 1163 (s), 1117 (m), 1074 (s) cm^{-1}. **HRMS** (ESI) calcd for $C_{11}H_{14}F_3NH$ $[M+H]^+$: 218.1151, Found: 218.1139. **Elemental analysis** calcd for $C_{11}H_{14}F_3N$: C: 60.82; H: 5.50; N: 6.45; Found: C: 61.08; H: 6.41; N: 6.24.

The analytical and spectroscopic data are in accordance with those reported.[S6]

***N*,*N*-Diethyl-2-trifluoromethylaniline (2c)**

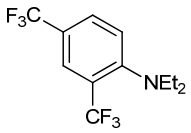
2c
$C_{11}H_{14}F_3N$
M = 217.23 g/mol

According to GP 3, a solution of 2-trifluoromethylaniline (600 mg, 3.72 mmol, 1.00 equiv) in DMF (15 mL) was added to oil-free sodium hydride (446 mg, 11.2 mmol, 3.30 equiv) and stirred for 15 min at ambient temperature. Bromoethane (892 mg, 8.18 mmol, 2.20 equiv) was slowly added dropwise to the suspension, and the reaction mixture was maintained at 40 °C for 8 h. After careful addition of saturated aqueous NH_4Cl solution (4 mL) and extraction of the organic layer with *tert*-butyl methyl ether (2 × 20 mL), the combined organic phases were washed with water (4 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by bulb-to-bulb condensation at 120 °C and 0.5 mbar afforded aniline **2c** (630 mg, 78%) as colorless liquid.

R_f: 0.50 (*n*-pentane:Et_2O:Et_3N = 40:1:1). **GLC** (35-min): t_R = 9.9 min. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.2 Hz, 6H), 2.97 (q, *J* = 7.2 Hz, 4H), 7.21 (dd, *J* = 8.3 Hz, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.50 (ddd, *J* = 8.3 Hz, *J* = 8.1 Hz, *J* = 1.6 Hz, 1H), 7.64 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 12.7, 49.4, 124.0 (q, *J* = 273.6 Hz), 124.5, 125.6, 127.1 (q, *J* = 5.6 Hz), 129.2 (q, *J* = 28.2 Hz), 132.3, 151.7 (q, *J* = 1.2 Hz) ppm. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = –60.1 ppm. **IR** (ATR): $\tilde{\nu}$ = 2977 (w), 2816 (w), 1603 (m), 1585 (m), 1494 (s), 1453 (s), 1312 (s), 1134 (m), 1107 (s), 1055 (s), 1036 (s), 762 (s) cm^{-1}. **HRMS** (ESI) calcd for $C_{11}H_{14}F_3NH$ $[M+H]^+$: 218.1151, Found: 218.1146. **Elemental analysis** calcd for $C_{11}H_{14}F_3N$: C: 60.82; H: 5.50; N: 6.45; Found: C: 60.40; H: 6.08; N: 6.20.

The analytical and spectroscopic data are in accordance with those reported.[S7]

N,*N*-Diethyl-2,4-bis(trifluoromethyl)aniline (2d)

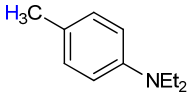


2d
$C_{12}H_{13}F_6N$
M = 285.23 g/mol

According to GP 3, a solution of 2,4-bis(trifluoromethyl)aniline (500 mg, 2.18 mmol, 1.00 equiv) in DMF (12 mL) was added to oil-free sodium hydride (262 mg, 10.9 mmol, 5.00 equiv) and stirred at ambient temperature for 15 min. Bromoethane (593 mg, 5.45 mmol, 2.50 equiv) was slowly added dropwise to the suspension, and the reaction mixture was maintained at 40 °C for 24 h. After careful addition of saturated aqueous NH_4Cl solution (4 mL) and extraction of the organic layer with *tert*-butyl methyl ether (2 × 20 mL), the combined organic phases were washed with water (4 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by bulb-to-bulb condensation at 140 °C and 0.5 mbar afforded aniline **2d** (340 mg, 55%) as a colorless liquid.

R_f: 0.35 (cyclohexane). **GLC** (35-min): t_R = 7.63 min. **^{1}H NMR** (500 MHz, C_6D_6): δ = 1.02 (t, *J* = 7.0 Hz, 6H), 3.04 (q, *J* = 7.0 Hz, 4H), 6.41 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.89 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 12.5, 48.7, 123.4 (q, *J* = 275.3 Hz), 123.7 (q, *J* = 272.0 Hz), 125.0 (q, *J* = 4.1 Hz), 125.7, 126.0 (q, *J* = 33.9 Hz), 128.4 (q, *J* = 29.2 Hz), 129.0 (q, *J* = 3.0 Hz), 154.8 ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –62.1, –60.2 ppm. **IR** (ATR): $\tilde{\nu}$ = 2980 (w), 2824 (w), 1623 (s), 1343 (s), 1276 (s), 1254 (m), 1119 (w), 1083 (s), 1050 (s), 912 (s), 839 (s) cm^{-1}. **HRMS** (EI) calcd for $C_{12}H_{13}F_6N$ $[M]^+$: 285.0946, Found: 284.9940.

_N_,_N_-Diethyl-4-toluidine (3a)



3a
$C_{11}H_{17}N$
M = 163.26 g/mol

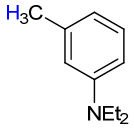
Synthesis via Buchwald–Hartwig amination: To a solution of 4-bromotoluene (0.96 g, 5.6 mmol, 1.0 equiv) and Et_2NH (1.2 mL, 0.82 g, 11 mmol, 2.0 equiv) in THF (60 mL) were successively added lithiumbis(trimethylsilyl)amide (1M in THF, 6.8 mL, 6.8 mmol, 1.2 equiv), $Pd(OAc)_2$ (31 mg, 0.14 mmol, 2.5 mol %) and tris-*tert*-butylphosphine (10% w/w solution in *n*-hexane, 0.57 g, 0.28 mmol, 5.0 mol %). After stirring the reaction mixture at 60 °C for 5 h, Et_2O (200 mL) was added, and the organic layer was washed with water (6 × 80 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Flash column chromatography on silica gel (*n*-pentane:Et_2O:Et_3N = 30:10:1) afforded aniline **3a** (0.35 mg, 38%) as a colorless liquid.

Synthesis via catalytic hydrodefluorination: According to GP 5, a reaction tube was charged in a glovebox with a mixture of [{(*p*-$FC_6H_4)_3P$}Ru(SDmp)]BAr^F_4 (**1e**, 3.6 mg, 2.3 µmol, 10 mol %) and NaOMe (1.2 µmol, 5.0 mol %). After addition of tetracosane (2.0 mg) as internal standard, *n*-hexane (0.5 mL) and diphenylmethylsilane (20 mg, 0.10 mmol, 4.4 equiv) were added dropwise to the suspension. *N*,*N*-Diethyl-3-trifluoromethylaniline (**2a**, 5.0 mg, 23 µmol, 1.0 equiv) was added, and the reaction mixture was maintained at ambient temperature for 6 h (full conversion). Product formation was monitored by GLC and verified by GLC-MS.

R_f: 0.53 (cyclohexane:*tert*-butyl methyl ether = 20:1). **GLC** (35-min): t_R = 12.5 min. **GLC** (55-min): t_R = 18.5 min.**^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 7.1 Hz, 6H), 2.25 (s, 3H), 3.32 (q, *J* = 7.1 Hz, 4H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 12.7, 20.3, 44.7, 112.6, 118.0, 124.9, 129.9 ppm. **IR** (ATR): $\tilde{\nu}$ = 3026 (w), 2969 (w) 2921 (w), 2865 (w), 1655 (m), 1609 (s), 1516 (s), 1312 (s), 1277 (s), 806 (m), 750 (s) cm^{-1}. **HRMS** (ESI) calcd for $C_{11}H_{17}NH$ $[M+H]^+$: 164.1434, Found: 164.1433. **Elemental analysis** calcd for $C_{11}H_{17}N$: C: 80.93; H: 10.50; N: 8.58; Found: C: 80.99; H: 10.18; N: 8.34.

The analytical and spectroscopic data are in accordance with those reported.[S8]

_N_,_N_-Diethyl-3-toluidine (3b)



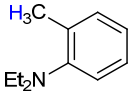
3b
$C_{11}H_{17}N$
M = 163.26 g/mol

S*ynthesis via Buchwald–Hartwig amination*: To a solution of 3-bromotoluene (0.49 g, 2.8 mmol, 1.0 equiv) and Et_2NH (0.59 mL, 0.41 g, 5.7 mmol, 2.0 equiv) in THF (30 mL) were successively added lithiumbis(trimethylsilyl)amide (1M in THF, 3.4 mL, 3.4 mmol, 1.2 equiv), $Pd(OAc)_2$ (30 mg, 0.13 mmol, 4.7 mol %) and tris-*tert*-butylphosphine (10% w/w solution in *n*-hexane, 0.26 g, 0.13 mmol, 4.7 mol %). After stirring the reaction mixture at 60 °C for 12 h, the solvent was removed under reduced pressure, and the residue was extracted with dilute aqueous HCl solution (2M, 3 × 20 mL). The aqueous phase was separated and neutralized by the addition of dilute aqueous NaOH (2M) solution. After extraction with Et_2O (2 × 20 mL), the combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. Flash column chromatography on silica gel (*n*-pentane) afforded toluidine **3b** (0.19 g, 42%) as a colorless liquid.

Synthesis via catalytic hydrodefluorination: According to GP 5, a reaction tube was charged in a glovebox with a mixture of [{(*p*-$FC_6H_4)_3P$}Ru(SDmp)]BAr^F_4 (**1e**, 3.6 mg, 2.3 µmol, 10 mol %) and NaOMe (1.2 µmol, 5.0 mol %). After addition of tetracosane (2.0 mg) as internal standard, *n*-hexane (0.5 mL) and diphenylmethylsilane (20 mg, 0.10 mmol, 4.4 equiv) were added dropwise to the suspension. *N*,*N*-Diethyl-3-trifluoromethylaniline (**2b**, 5.0 mg, 23 µmol, 1.0 equiv) was added, and the reaction mixture was maintained at 100 °C for 72 h (10% conversion). Product formation was monitored by GLC and verified by GLC-MS.

R_f: 0.72 (cyclohexane:*tert*-butyl methyl ether = 5:1). **GLC** (35-min): t_R = 10.3 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.17 (t, *J* = 7.1 Hz, 6H), 2.32 (s, 3H), 3.35 (q, *J* = 7.1 Hz, 4H), 6.49 (d, *J* = 7.4 Hz, 1H), 6.51–6.55 (m, 2H), 7.12 (dd, *J* = 9.1 Hz, *J* = 7.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 12.7, 22.1, 44.4, 109.2, 112.7, 116.4, 129.2, 139.0, 148.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2969 (w), 2928 (w), 1600 (s), 1579 (s), 1497 (s), 1374 (s), 1355 (s), 1273 (s), 1199 (s), 762 (s) 692 (s) cm^{-1}. **HRMS** (ESI) calcd for $C_{11}H_{17}NH$ $[M+H]^+$: 164.1434, Found: 164.1426. **Elemental analysis** calcd for $C_{11}H_{17}N$: C: 80.93; H: 10.50; N: 8.58; Found: C: 80.58; H: 10.51; N: 8.33.

N,*N*-Diethyl-2-toluidine (3c)



3c
$C_{11}H_{17}N$
M = 163.26 g/mol

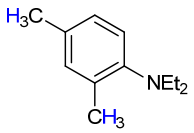
Synthesis via N-alkylation: A solution of 2-toluidine (0.15 g, 1.4 mmol, 1.0 equiv) in DMF (1 mL) was added to oil-free potassium hydride (0.13 g, 3.2 mmol, 2.3 equiv) and stirred for 15 min at ambient temperature. Bromoethane (0.31 g, 2.8 mmol, 2.0 equiv) was slowly added dropwise to the suspension, and the reaction mixture was maintained for 4 d at 50 °C. After careful addition of saturated aqueous NH_4Cl solution (4 mL) and extraction of the organic layer with *n*-pentane (2 × 20 mL), the combined organic phases were washed with water (4 × 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (*n*-pentane:Et_2O:Et_3N = 100:1:1) afforded aniline **3c** (35 mg, 15%) as a colorless liquid.

Synthesis via catalytic hydrodefluorination: According to GP 5, a reaction tube was charged in a glovebox with a mixture of [{(*p*-$FC_6H_4)_3P$}Ru(SDmp)]BAr^F_4 (**1e**, 3.6 mg, 2.3 µmol, 10 mol %) and NaOMe (1.2 µmol, 5.0 mol %). After addition of tetracosane (2.0 mg) as internal standard, *n*-hexane (0.5 mL) and diphenylmethylsilane (20 mg, 0.10 mmol, 4.4 equiv) were added dropwise to the suspension. *N*,*N*-Diethyl-2-trifluoromethylaniline (**2c**, 5.0 mg, 23 µmol, 1.0 equiv) was added, the tube was sealed, and the reaction mixture was maintained at 60 °C for 72 h (full conversion). Product formation was monitored by GLC analysis and verified by GLC-MS analysis.

R_f: 0.27 (*n*-pentane:Et_2O:Et_3N= 40:2:1). **GLC** (35-min): t_R = 8.4 min. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.2 Hz, 6H), 2.32 (s, 3H), 3.01 (q, *J* = 7.2 Hz, 4H), 7.00 (ddd, *J* = 8.1 Hz, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 7.09 (dd, *J* = 8.3 Hz, *J* = 1.3 Hz, 1H), 7.17 (ddd, *J* = 8.3 Hz, 8.1 Hz, 1.6 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 12.7, 18.4, 47.7, 122.3, 123.3, 126.1, 131.0, 135.9, 150.0 ppm. **IR** (ATR): $\tilde{\nu}$ = 2970 (m), 1930 (m), 2814 (w), 1598 (m), 1492 (s), 1377 (m), 1239 (s), 1176 (m), 1108 (s) cm^{-1}. **HRMS** (ESI) calcd for $C_{11}H_{17}NH$ $[M+H]^+$: 164.1434, Found: 164.1408. **Elemental analysis** calcd for $C_{11}H_{17}N$: C: 80.93; H: 10.50; N: 8.58; Found: C: 80.46; H: 10.51; N: 8.31.

The analytical and spectroscopic data are in accordance with those reported.[S9]

_N_,_N_-Diethyl-2,4-dimethylaniline (3d)



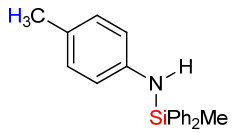
3d
$C_{12}H_{19}N$
M = 177.29 g/mol

Synthesis via N-alkylation: A solution of 2,4-dimethylaniline (0.30 g, 2.5 mmol, 1.0 equiv) in DMF (20 mL) was added to oil-free potassium hydride (0.40 g, 10 mmol, 4.0 equiv) and stirred for 15 min at ambient temperature. Bromoethane (0.81 g, 7.4 mmol, 3.0 equiv) was slowly added dropwise to the suspension, and the reaction mixture was maintained for 7 d at 50 °C. After careful addition of saturated aqueous NH_4Cl solution (4 mL) and extraction of the organic layer with *tert*-butyl methyl ether (2 × 20 mL), the combined organic phases were washed with water (4 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (cyclohexane: *tert*-butyl methyl ether = 50:1) afforded aniline **3d** (121 mg, 28%) as a colorless liquid.

Synthesis via catalytic hydrodefluorination: According to GP 5, a reaction tube was charged in a glovebox with a mixture of [{(*p*-$FC_6H_4)_3P$}Ru(SDmp)]BAr^F_4 (**1e**, 3.6 mg, 2.3 µmol, 10 mol %) and NaOMe (1.2 µmol, 5.0 mol %). After addition of tetracosane (2.0 mg) as internal standard, *n*-hexane (0.5 mL) and diphenylmethylsilane (32 mg, 0.16 mmol, 7.0 equiv) were added dropwise to the suspension. *N*,*N*-Diethyl-2,4-bis(trifluoromethyl)aniline (**2d**, 5.3 mg, 23 µmol, 1.0 equiv) was added, the tube was sealed, and the reaction mixture was maintained at 100 °C for 72 h (97% conversion). Product formation was monitored by GLC and verified by GLC-MS.

R_f: 0.59 (cyclohexane:*tert-butyl methyl ether*:Et_3N = 20:2:1. **GLC** (35-min): t_R = 9.74 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.1 Hz, 6H), 2.29 (s, 3H), 2.31 (s, 3H), 2.97 (q, *J* = 7.1 Hz, 4H), 6.95−7.01 (m, 2H), 7.04 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 12.7, 18.3, 20.9, 48.1, 122.3, 126.7, 131.6, 132.8, 135.5, 147.3 ppm. **IR** (ATR): $\tilde{\nu}$ = 2970 (s), 2923 (m), 2870 (w), 2811 (m), 1499 (s), 1447 (s), 1377 (s) 1297 (m), 1232 (s), 1178 (s), 1113 (s), 873 (s), 817 (s) cm^{-1}. **HRMS** (EI) calcd for $C_{12}H_{19}N$ $[M]^+$: 177.1511, Found: 177.1512.

_N_-(Diphenylmethylsilyl)-4-toluidine (3e)



3e
$C_{20}H_{21}NSi$
M = 303.47 g/mol

Synthesis via silylation: *n*-Butyllithium (1.76M in hexanes, 0.49 mL, 0.87 mmol, 1.1 equiv) was slowly dropped to a solution of 4-toluidine (85 mg, 0.79 mmol, 1.0 equiv) in toluene (2 mL) at ambient temperature. After 15 min, diphenylmethylsilylchloride (185 mg, 0.79 mmol, 1.0 equiv) was added, and the reaction mixture was heated to 110 °C for 10 min. After cooling down, the reaction mixture was filtered over Celite, and the solvent was removed under reduced pressure. Purification of the crude product by flash column chromatography on silica gel (cyclohexane:*tert*-butyl methyl ether:Et_3N = 40:1:2) afforded toluidine **3e** (232 mg, 96%) as a white solid.

Synthesis via catalytic hydrodefluorination: According to GP 5, a reaction tube was charged in a glovebox with a mixture of [{(*p*-$FC_6H_4)_3P$}Ru(SDmp)]BAr^F_4 (**1e**, 3.6 mg, 2.3 µmol, 10 mol %) and NaOMe (1.2 µmol, 5.0 mol %). After addition of tetracosane (2.0 mg) as internal standard, *n*-hexane (0.5 mL) and diphenylmethylsilane (27 mg, 0.14 mmol, 6.0 equiv) were added dropwise to the suspension. 4-Trifluoromethylaniline (3.7 mg, 23 µmol, 1.0 equiv) was added, the tube was sealed, and the reaction mixture was maintained at 70 °C for 72 h (full conversion). Product formation was monitored by GLC and verified by GLC-MS.

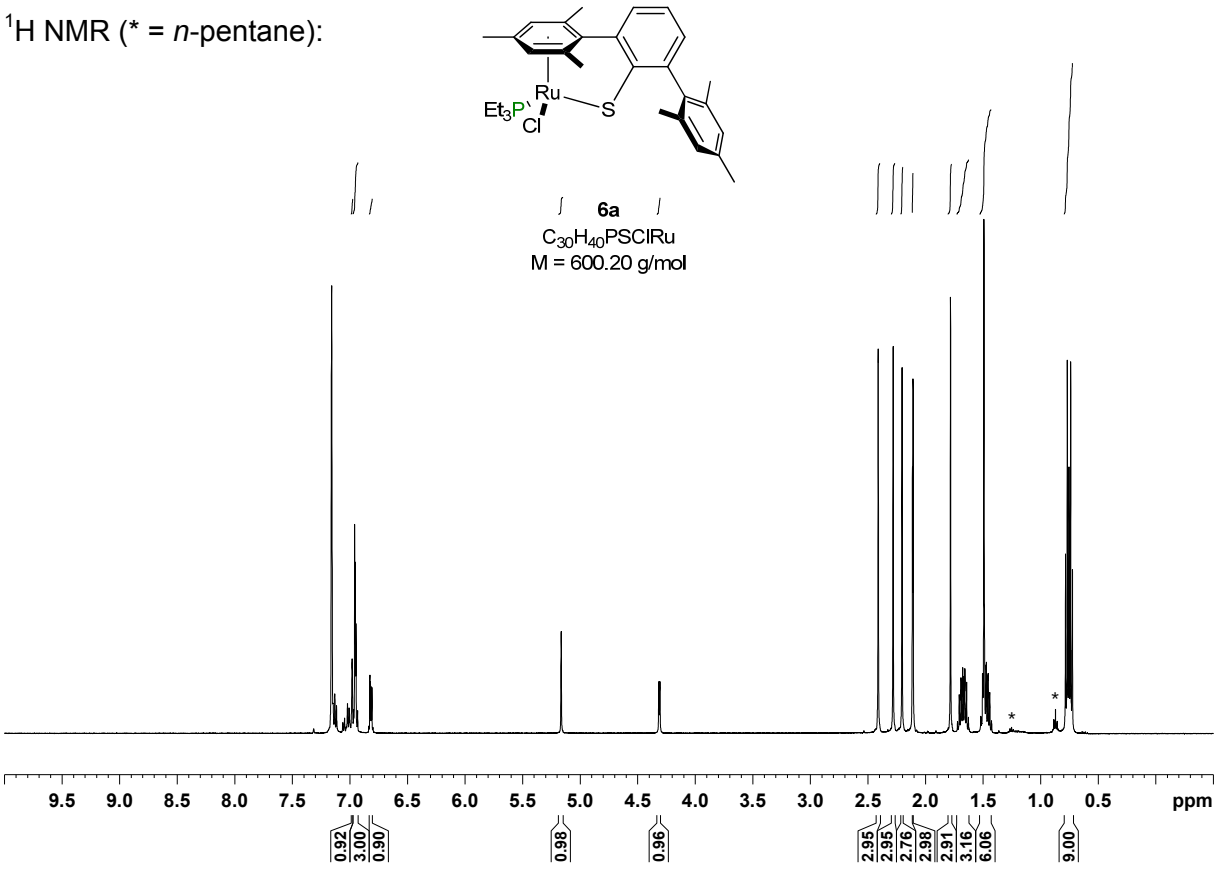
R_f: 0.18 (cyclohexane:*tert*-butyl methyl ether:Et_3N = 20:2:1). **Mp**: 95 °C. **GLC** (35-min): t_R = 22.0 min. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.81 (s, 3H), 2.23 (s, 3H), 3.76 (s, 1H), 6.58 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 2H), 7.38–7.47 (m, 6H), 7.65 (d, *J* = 6.5 Hz, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = –2.9, 20.4, 116.7, 127.2, 128.1, 129.7, 129.9, 134.6, 136.1, 144.1 ppm. **^{29}Si-DEPT NMR** (99 MHz, $CDCl_3$): δ = –12.4 ppm. **IR** (ATR): $\tilde{\nu}$ = 3399 (s), 3009 (w), 1612 (m), 1513 (s), 1427 (s), 1284 (s), 1108 (s), 898 (s), 807 (s) cm^{-1}. **HRMS** (EI) calcd for $C_{20}H_{21}NSi$ $[M]^+$: 303.1438, Found: 303.1441.

6 NMR Spectra of All Compunds

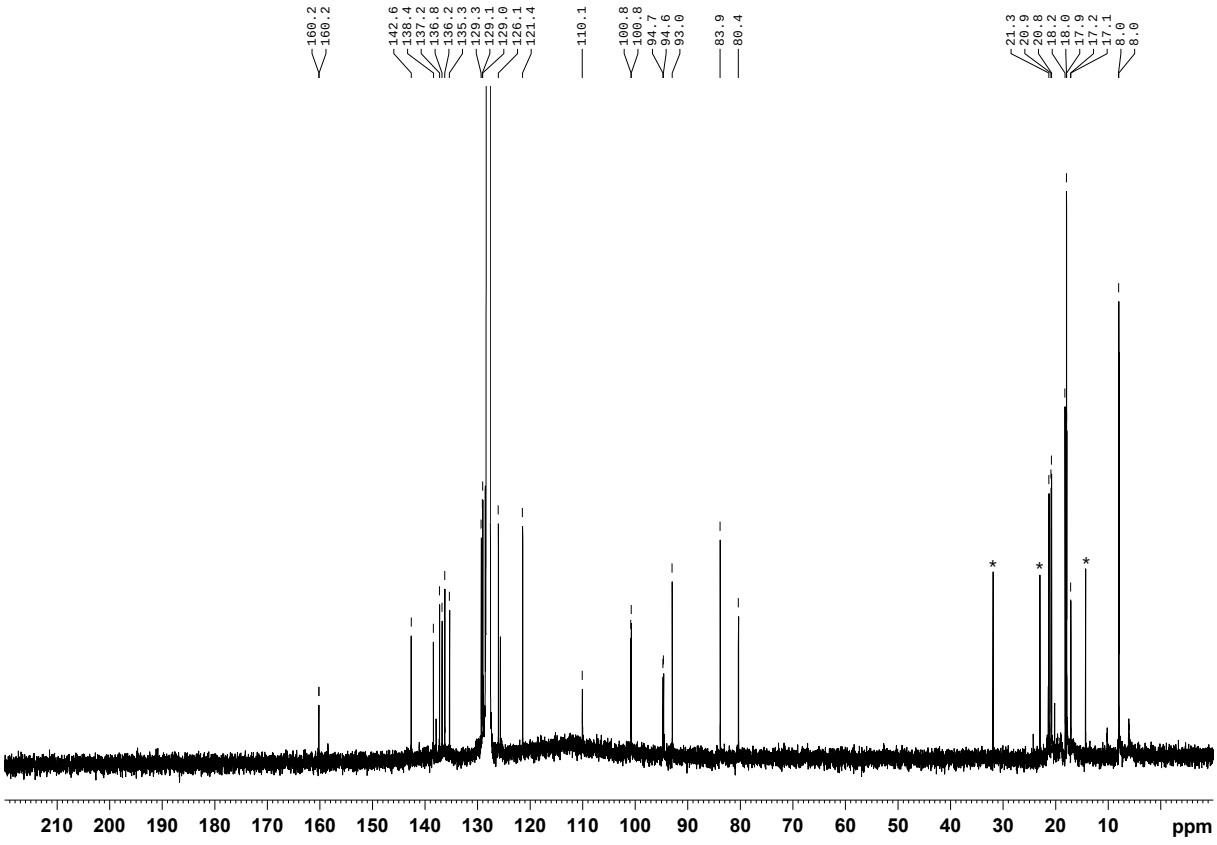
6.1 NMR Spectra of Ruthenium thiolate complexes (1a–e and 6a–e)

[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(triethylphosphine)-ruthenium(II) (6a)

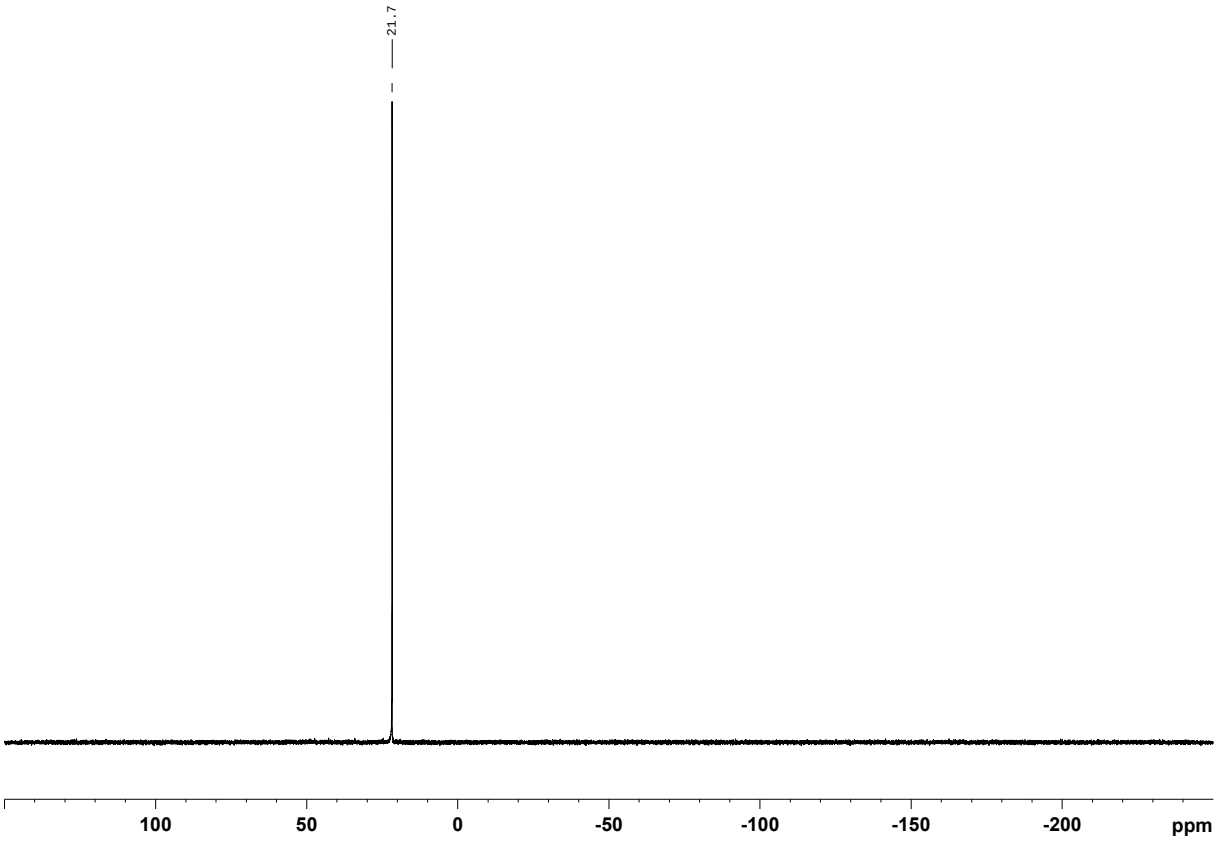
^{1}H NMR (* = *n*-pentane):



^{13}C NMR (* = *n*-pentane):

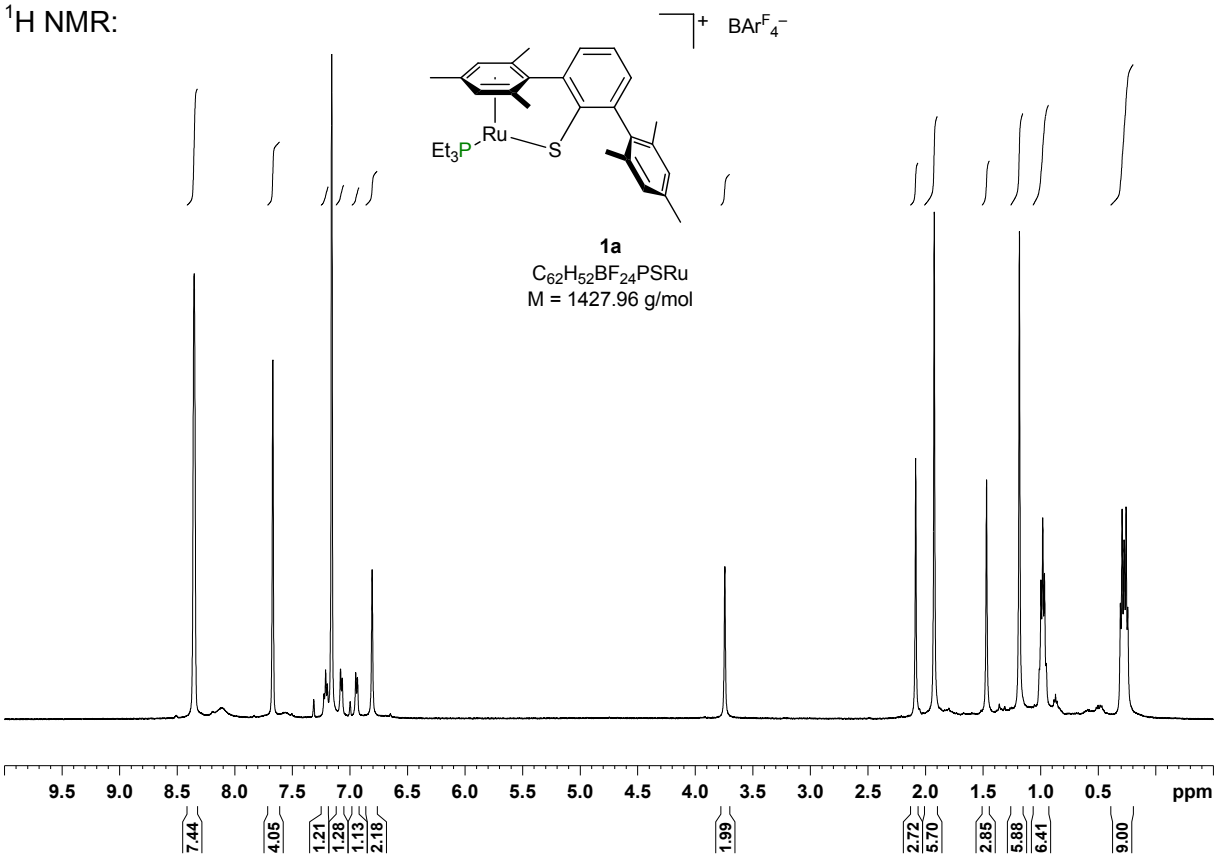


^{31}P NMR:

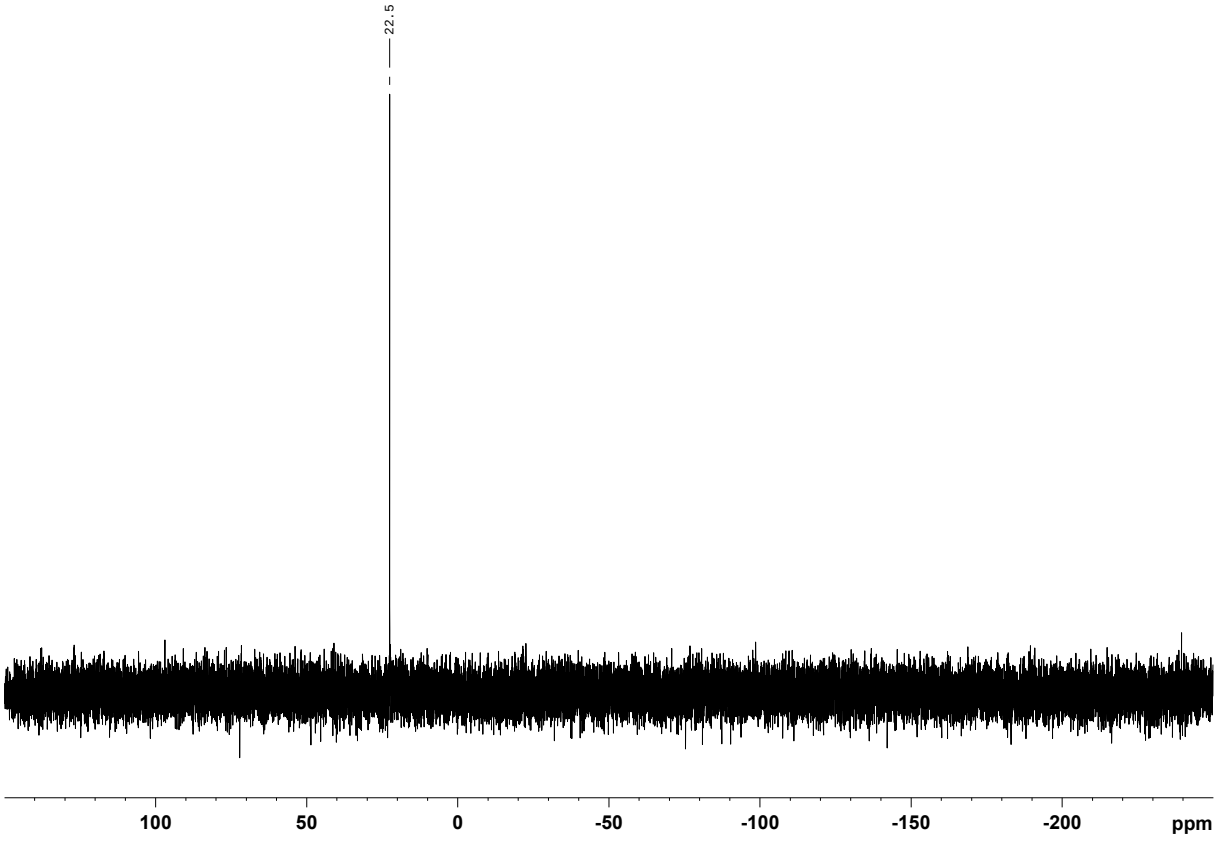


[2,6-η6:η1-Bis(2,4,6-trimethylphenyl)phenylthiolato]triethylphosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1a)

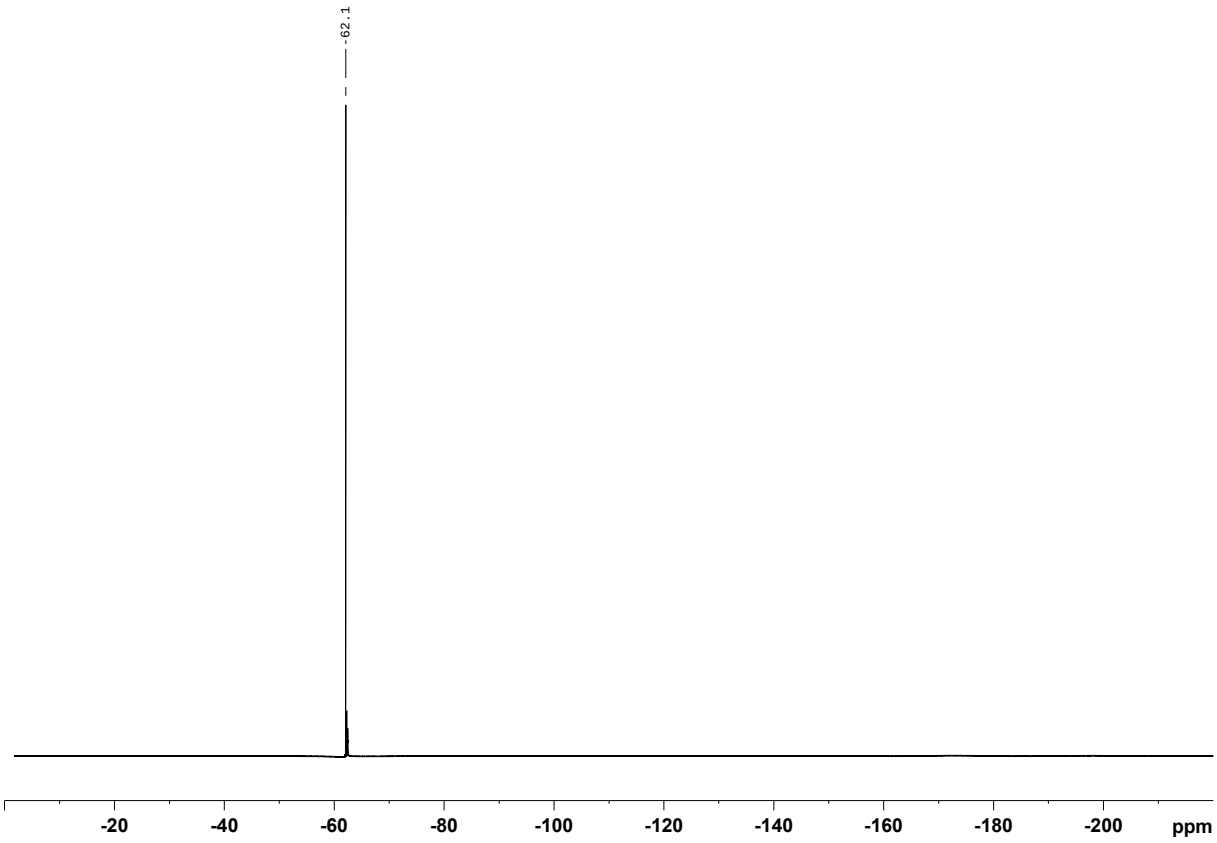
^{1}H NMR:



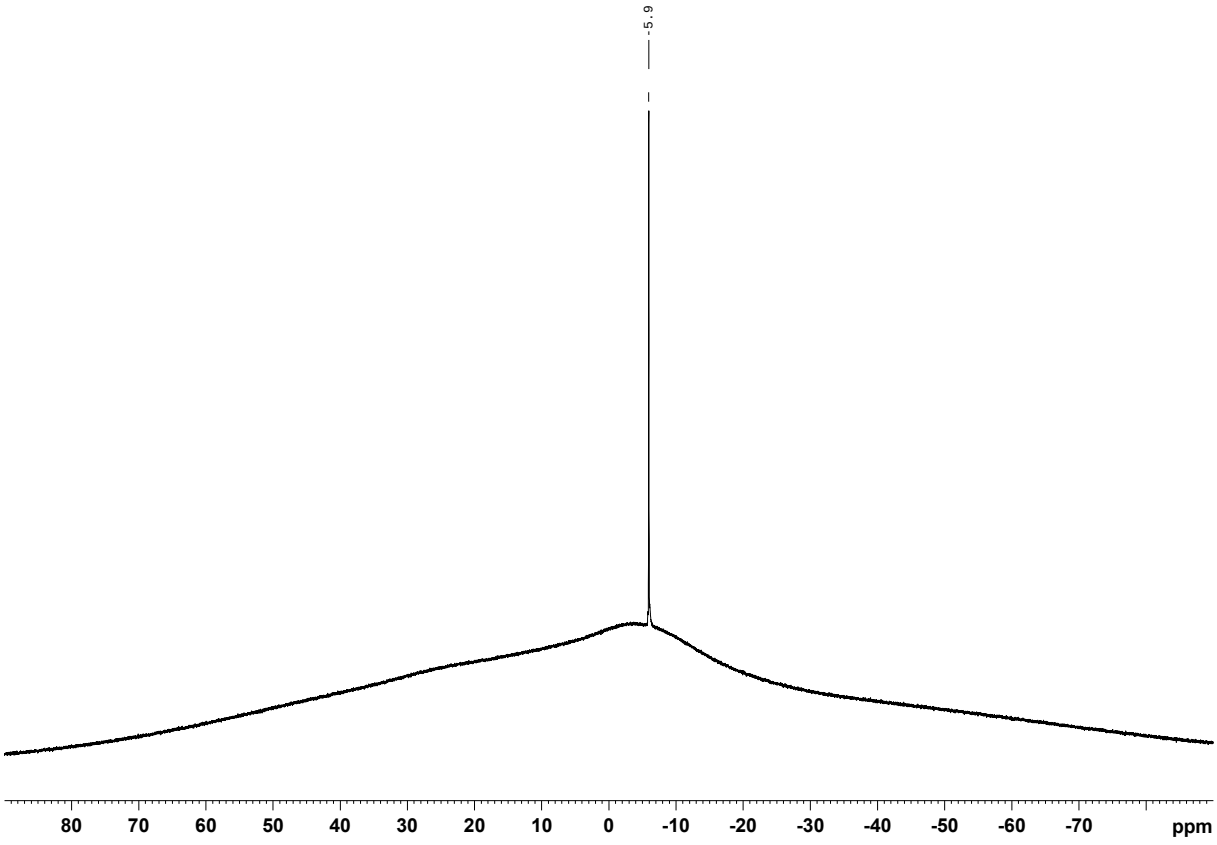
^{31}P NMR:



^{19}F NMR:

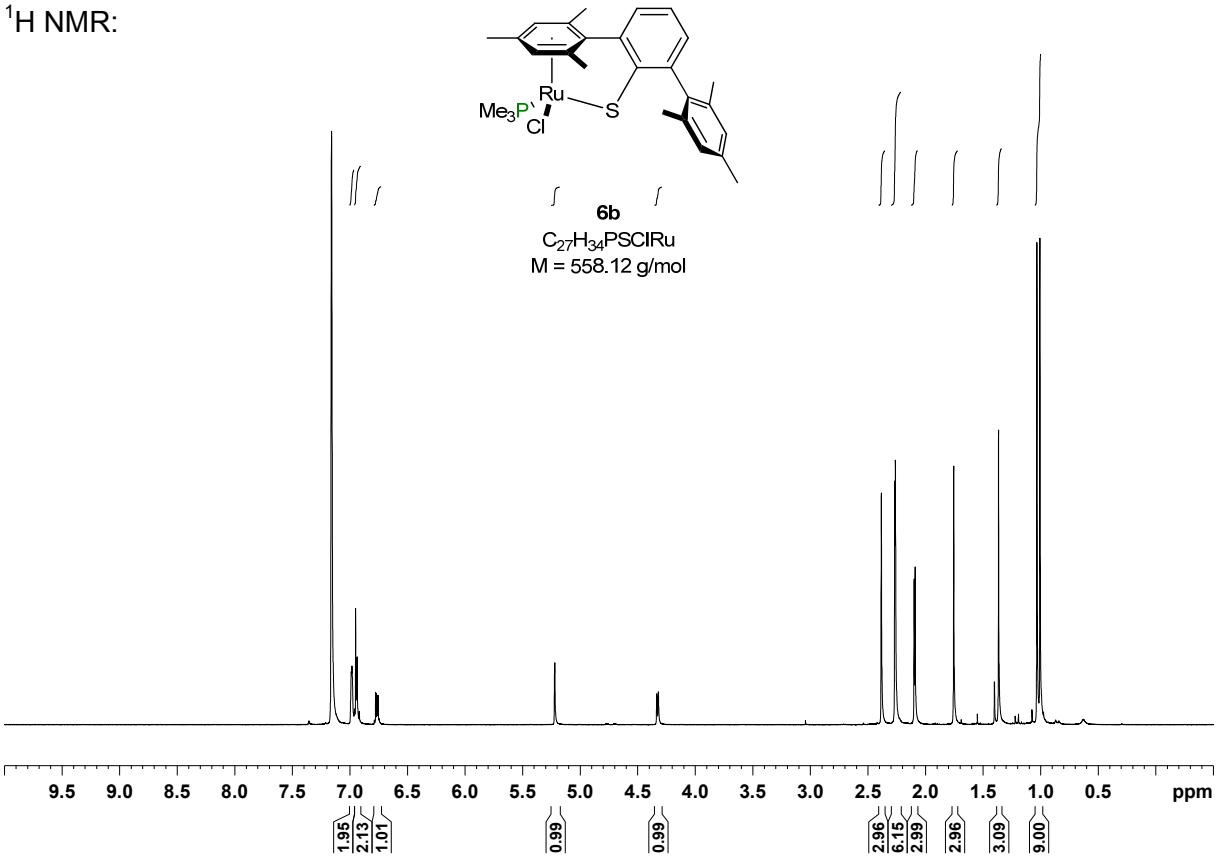


^{11}B NMR:

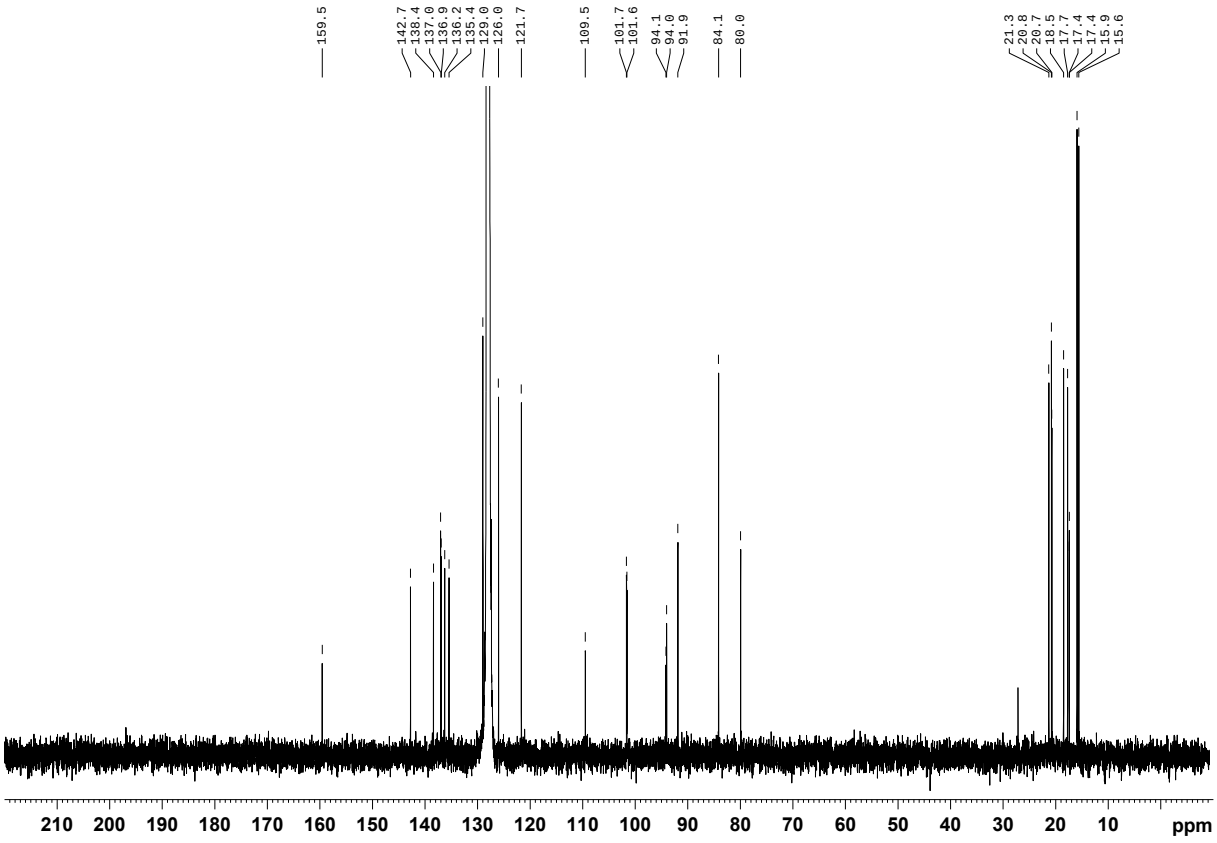


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolat]chlorio(trimethylphosphine)-ruthenium(II) (6b)

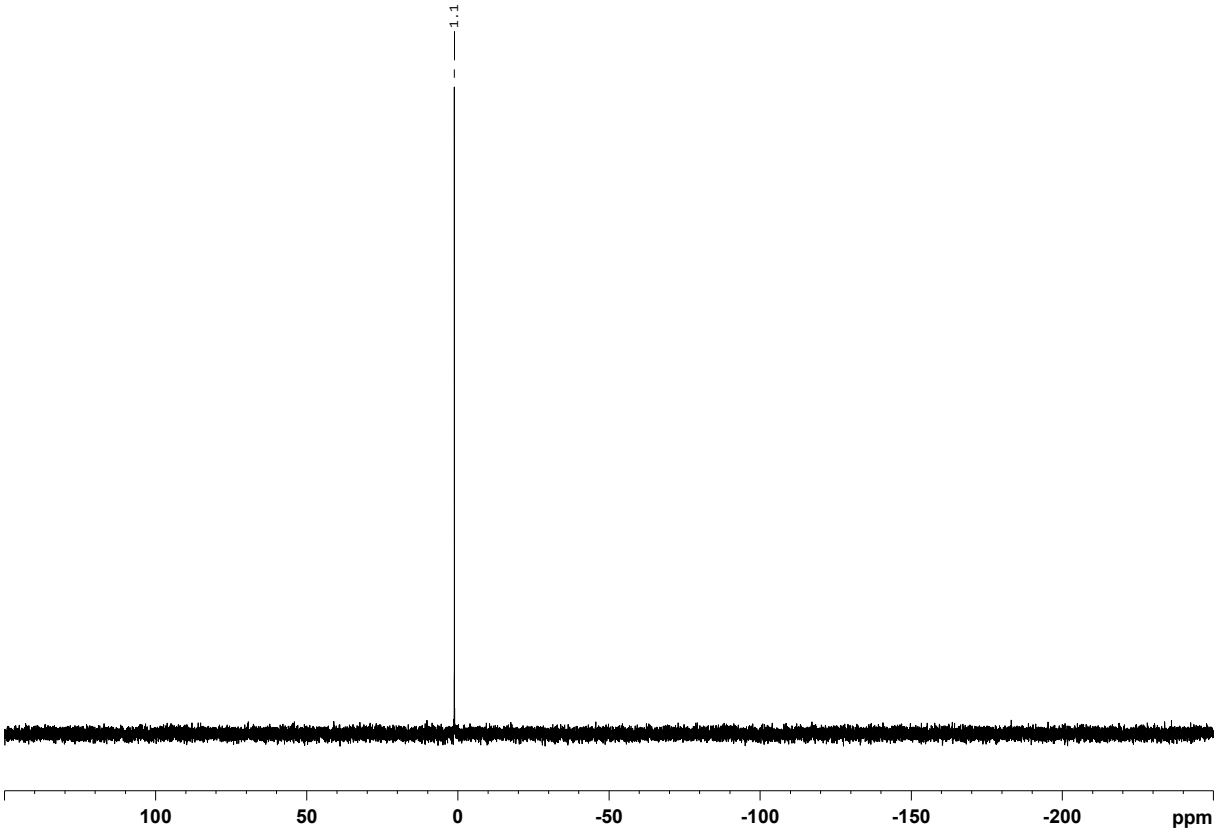
^{1}H NMR:



^{13}C NMR:

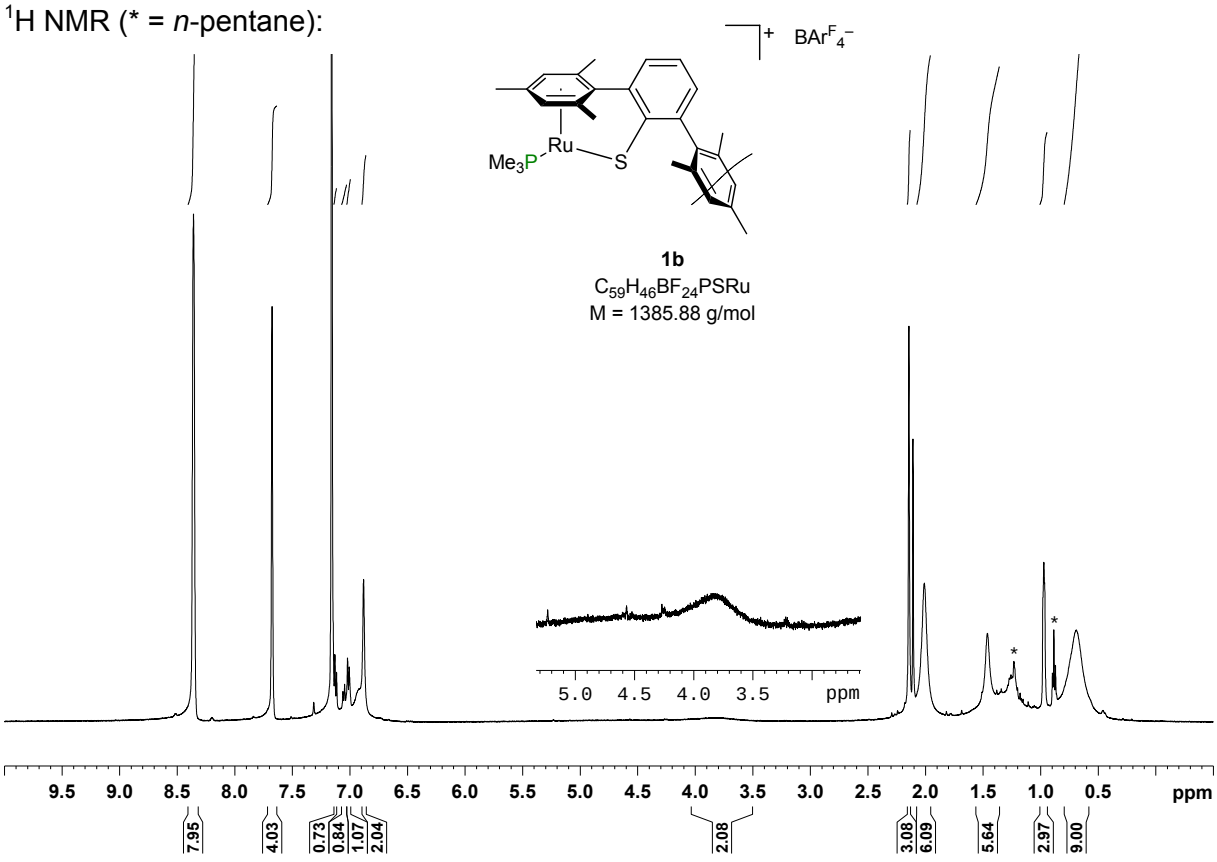


^{31}P NMR:

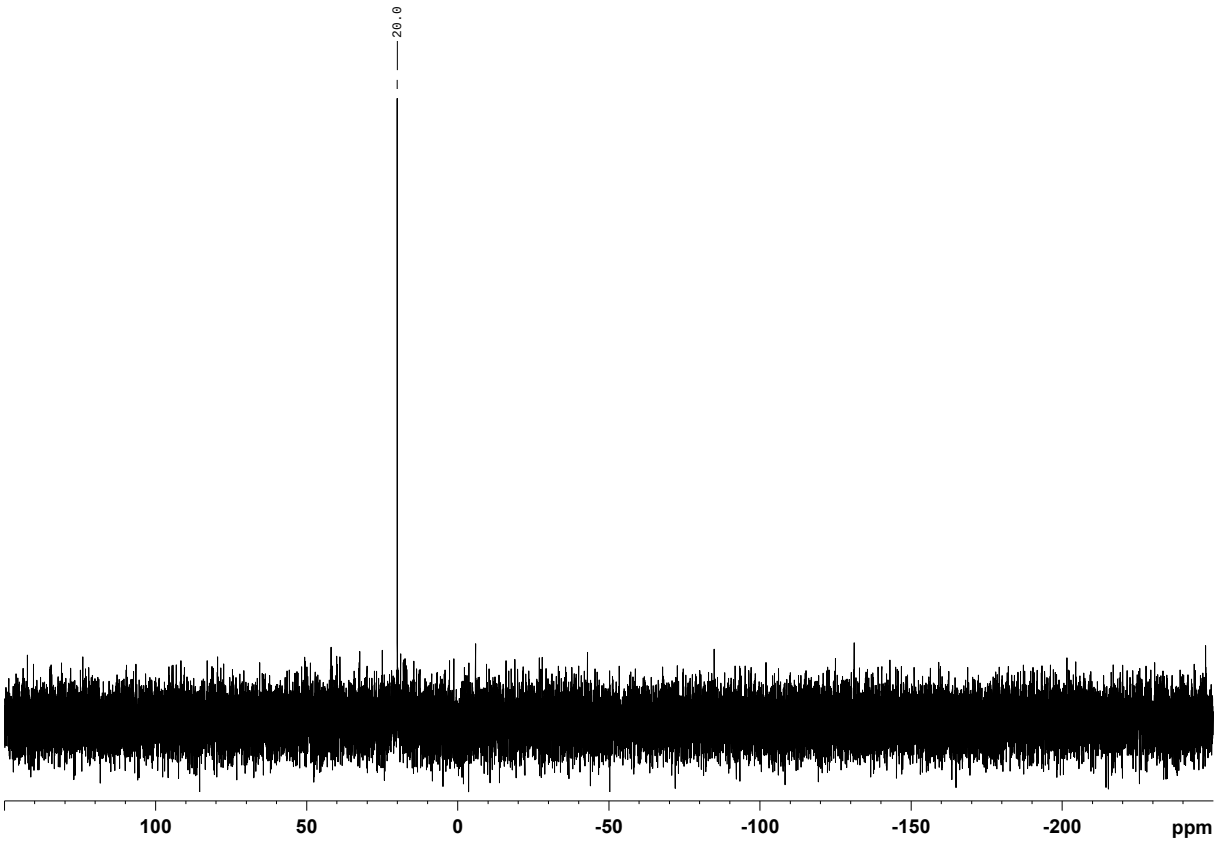


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]trimethylphosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1b)

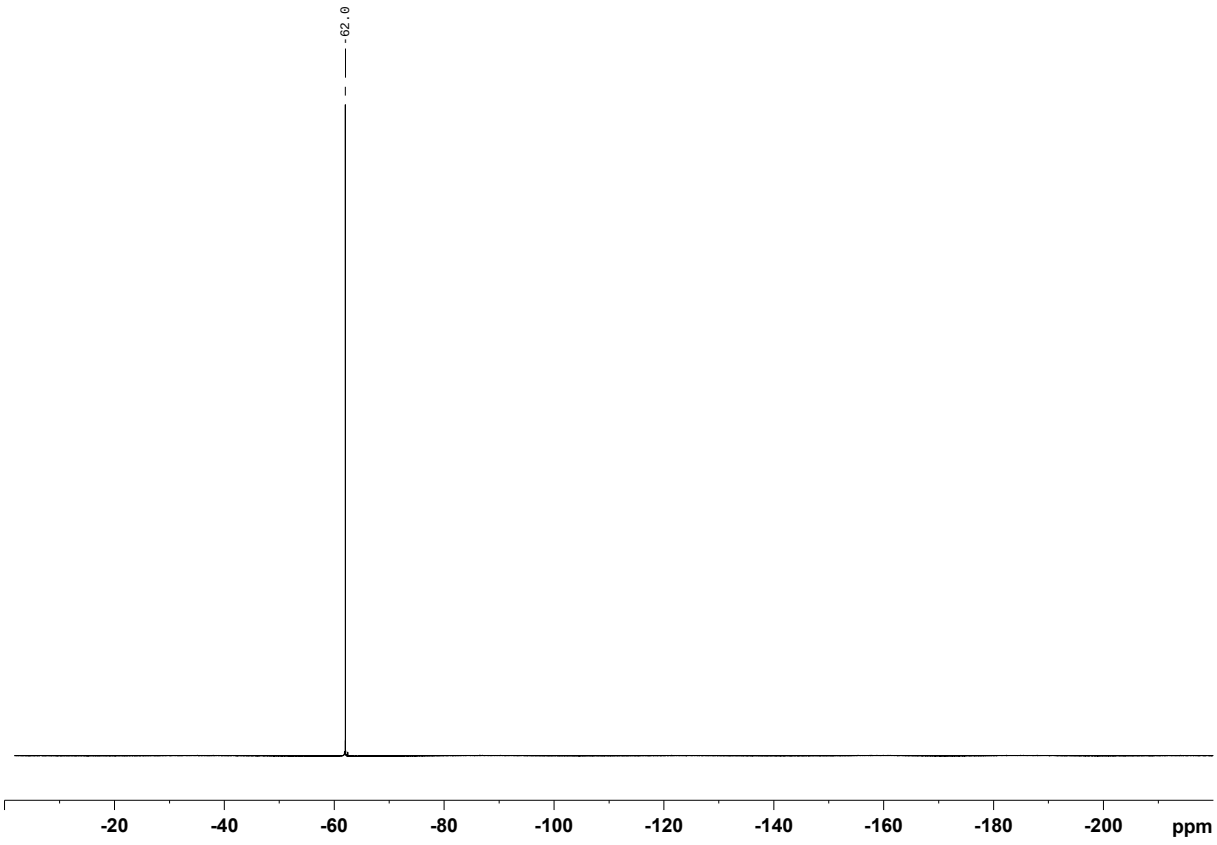
^{1}H NMR (* = *n*-pentane):



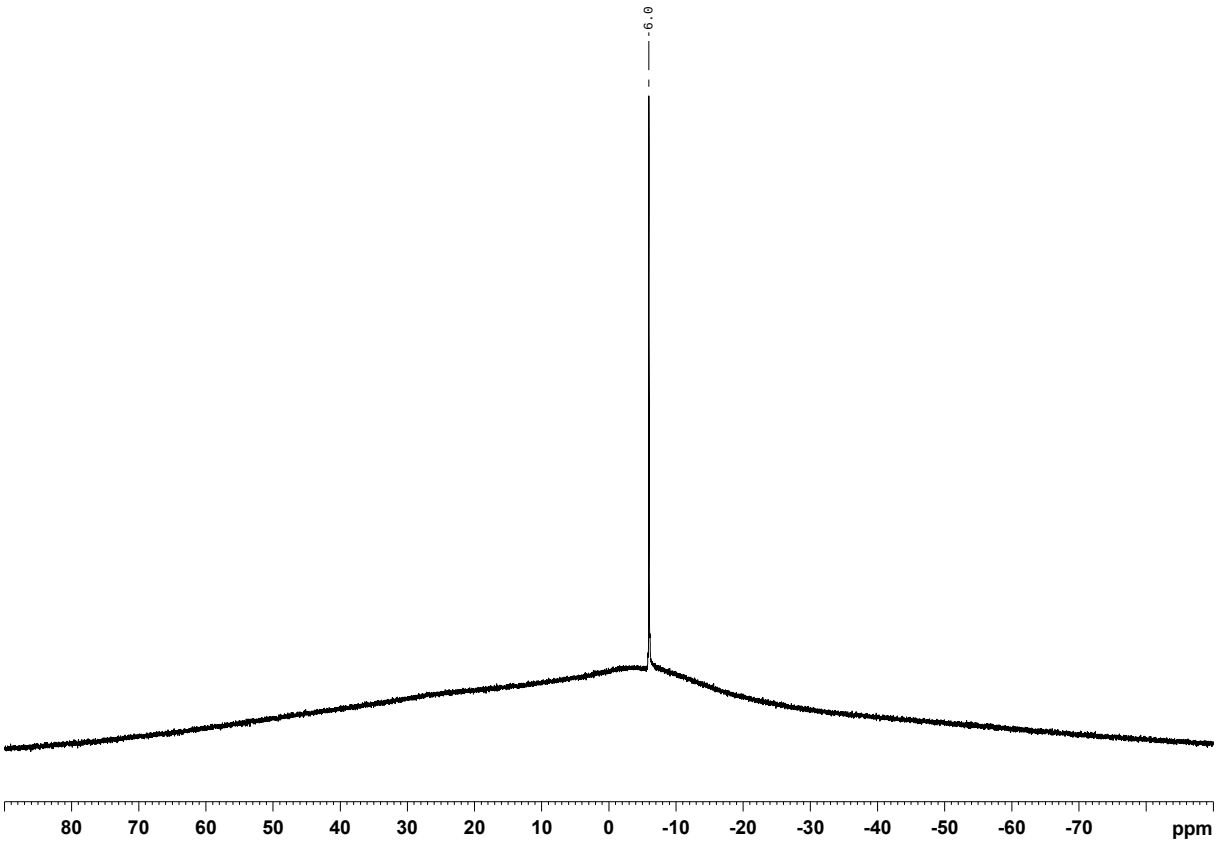
^{31}P NMR:



^{19}F NMR:

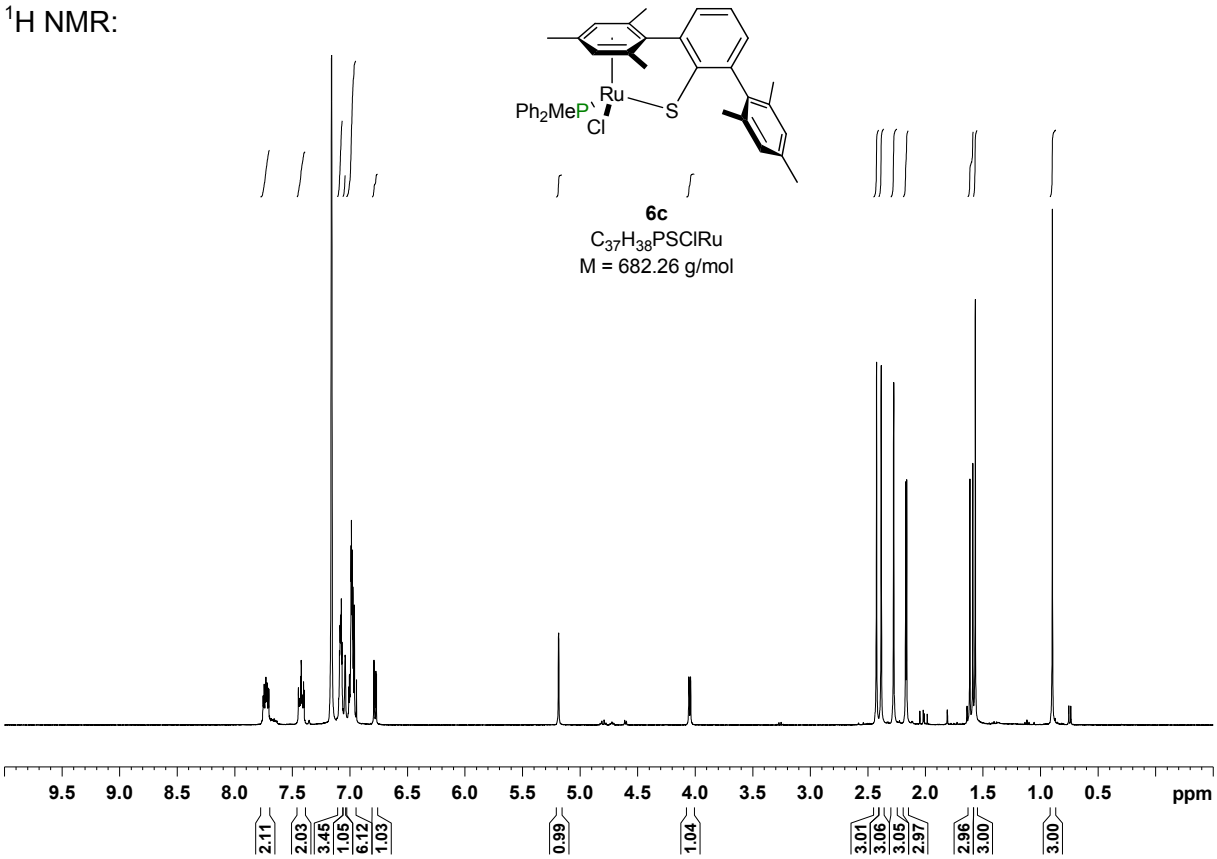


^{11}B NMR:

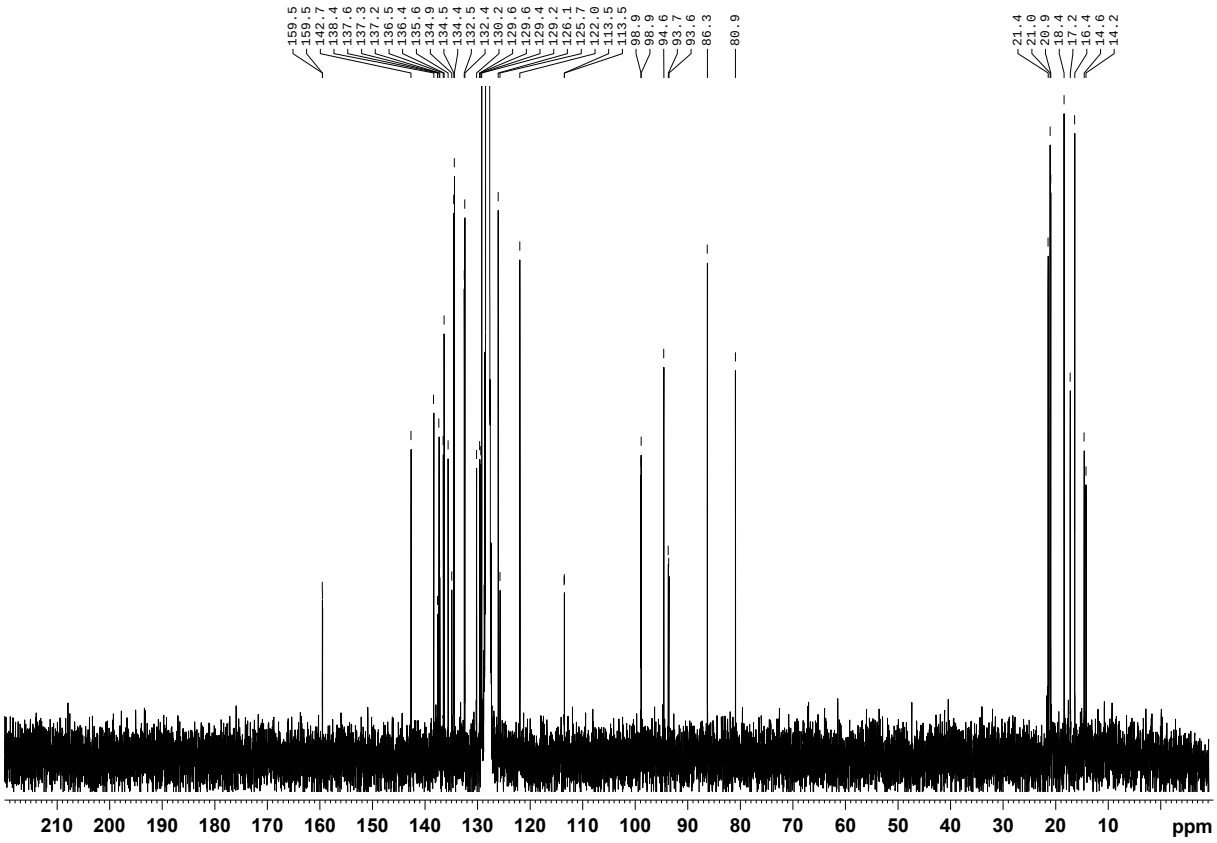


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(diphenylmethyl-phosphine)-ruthenium(II) (6c)

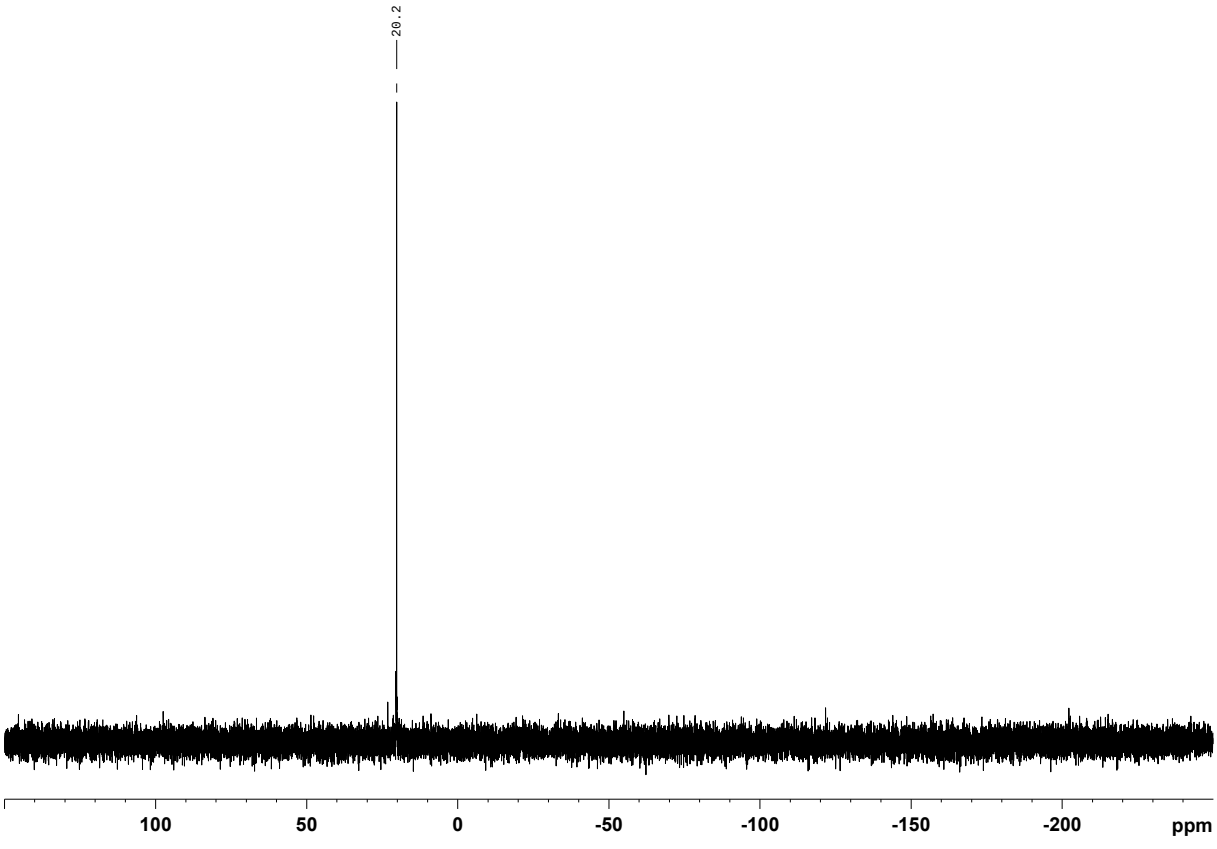
^{1}H NMR:



^{13}C NMR:

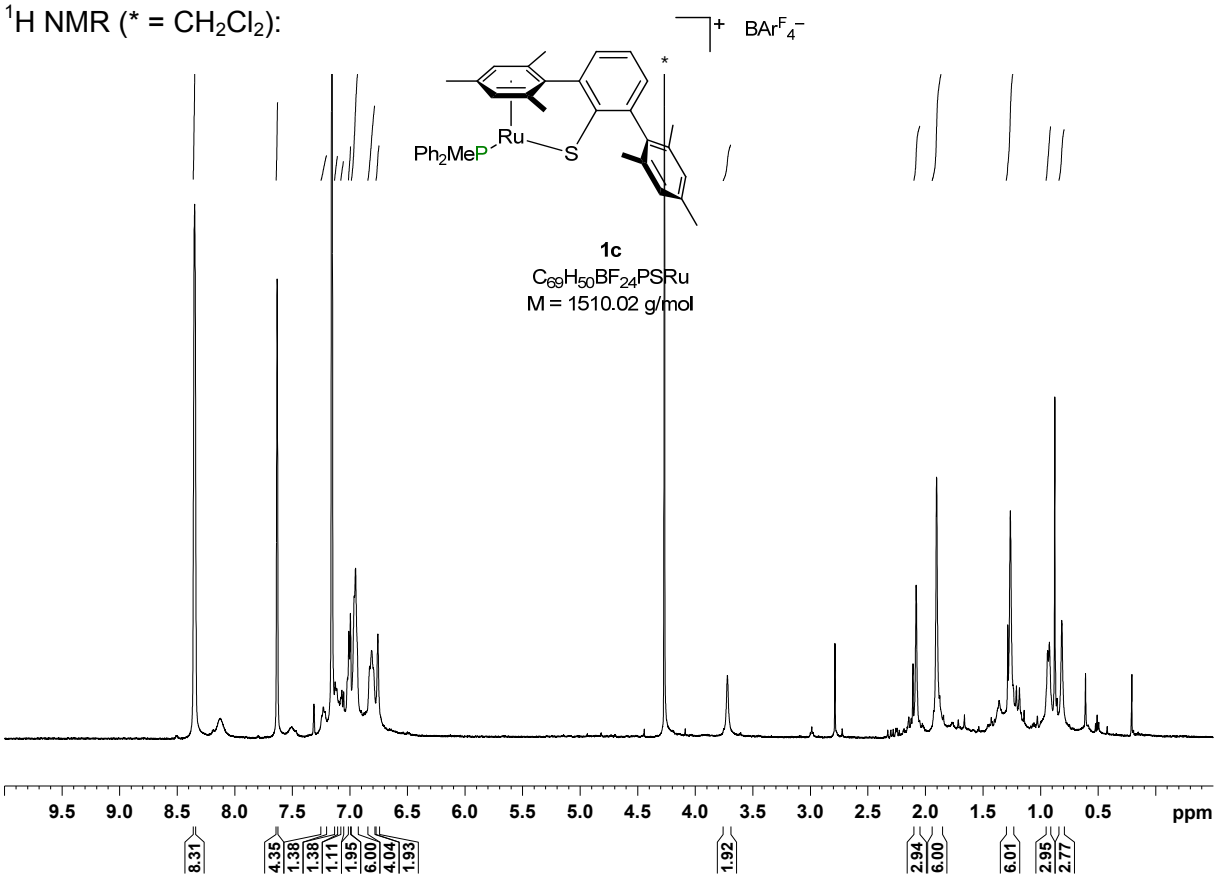


^{31}P NMR:

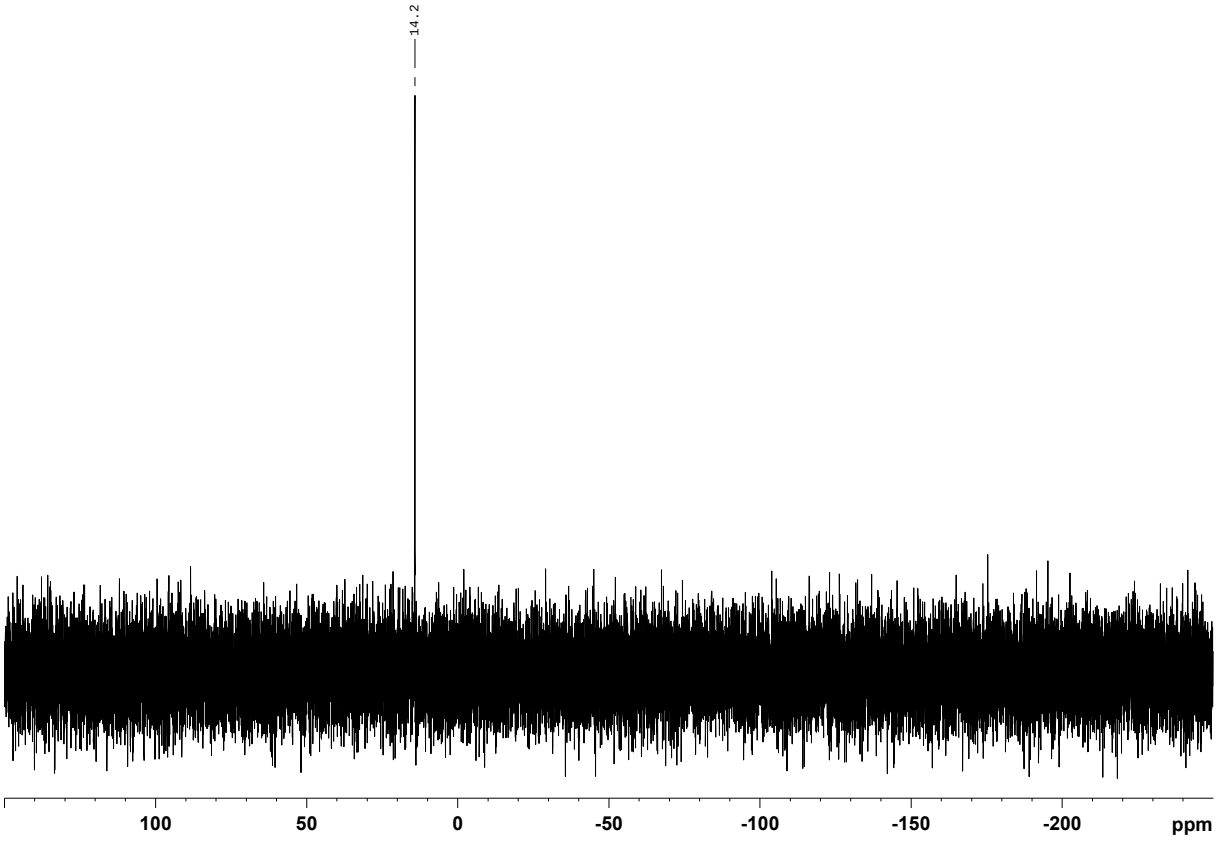


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato](diphenylmethylphosphine)-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1c)

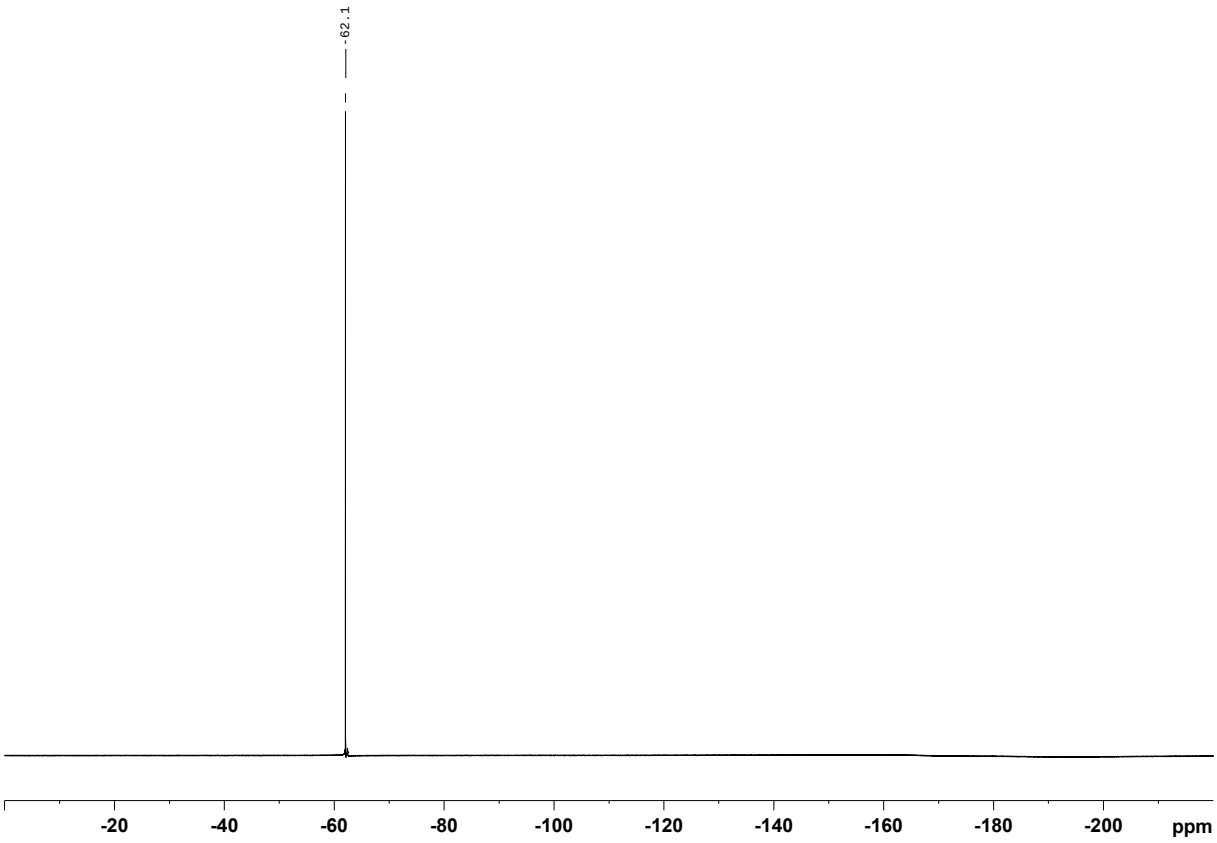
^{1}H NMR (* = CH_2Cl_2):



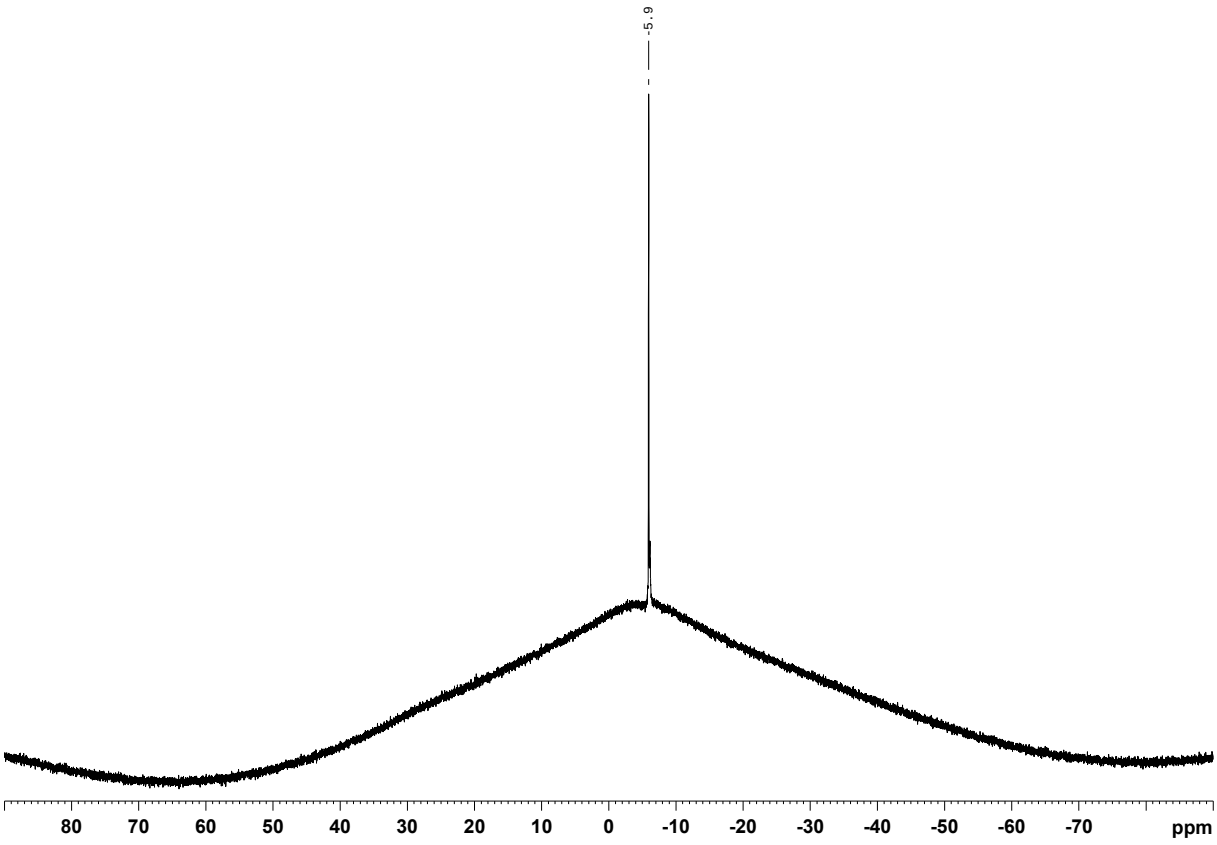
^{31}P NMR:



^{19}F NMR:

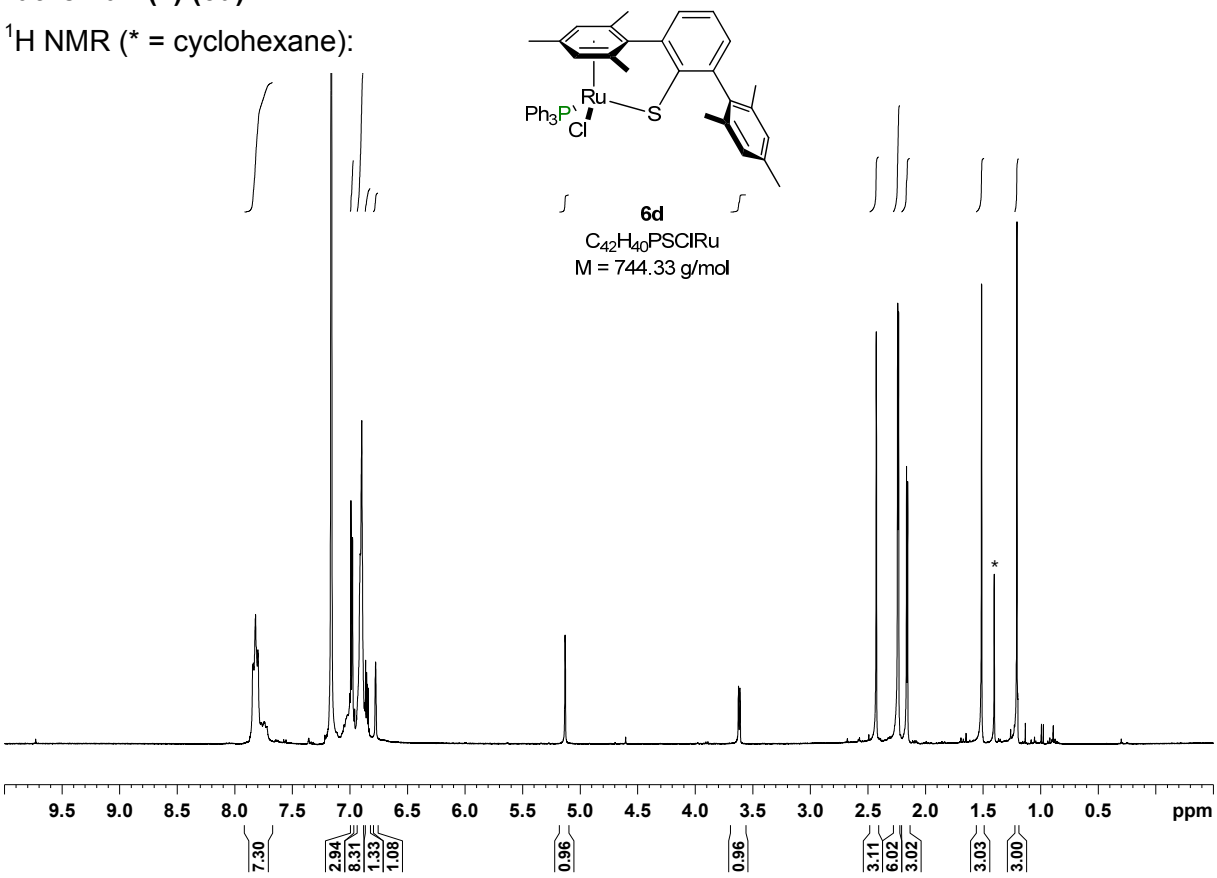


^{11}B NMR:

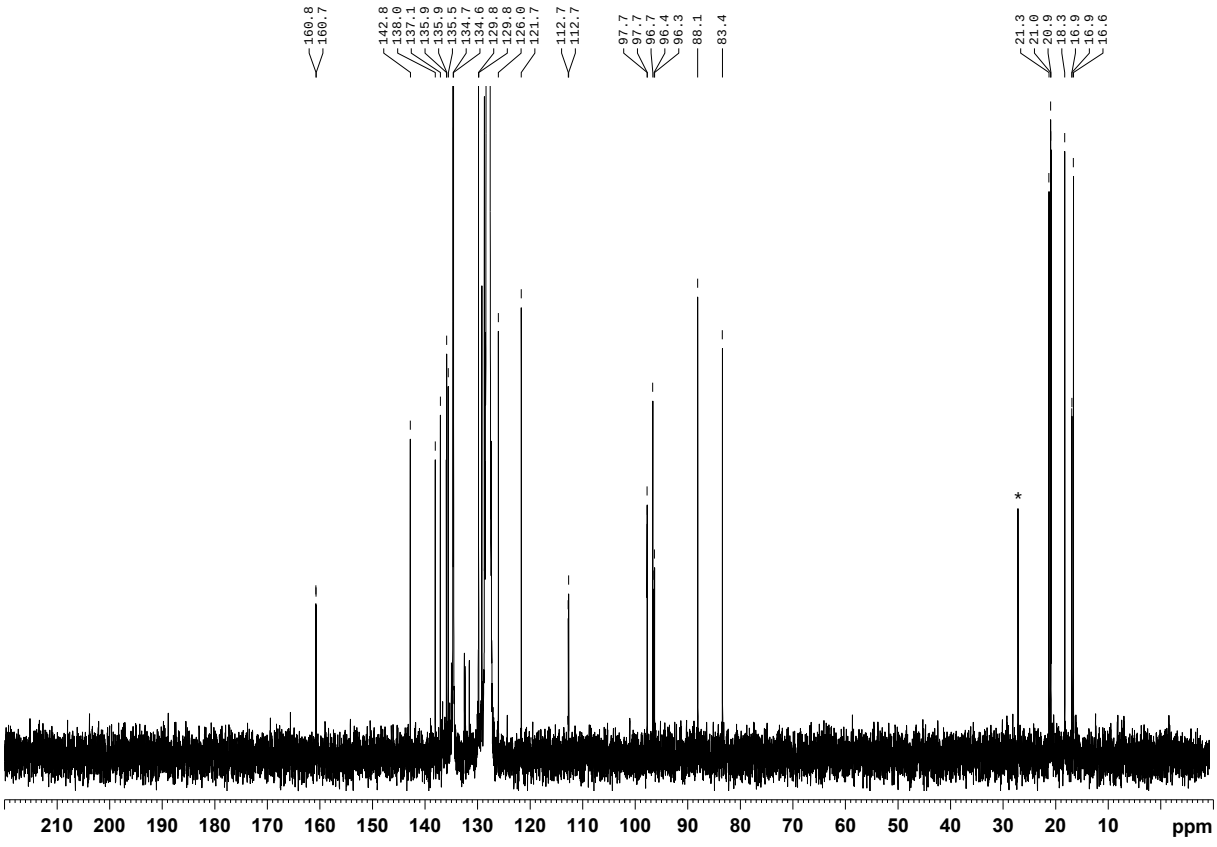


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido(triphenylphosphine)-ruthenium(II) (6d)

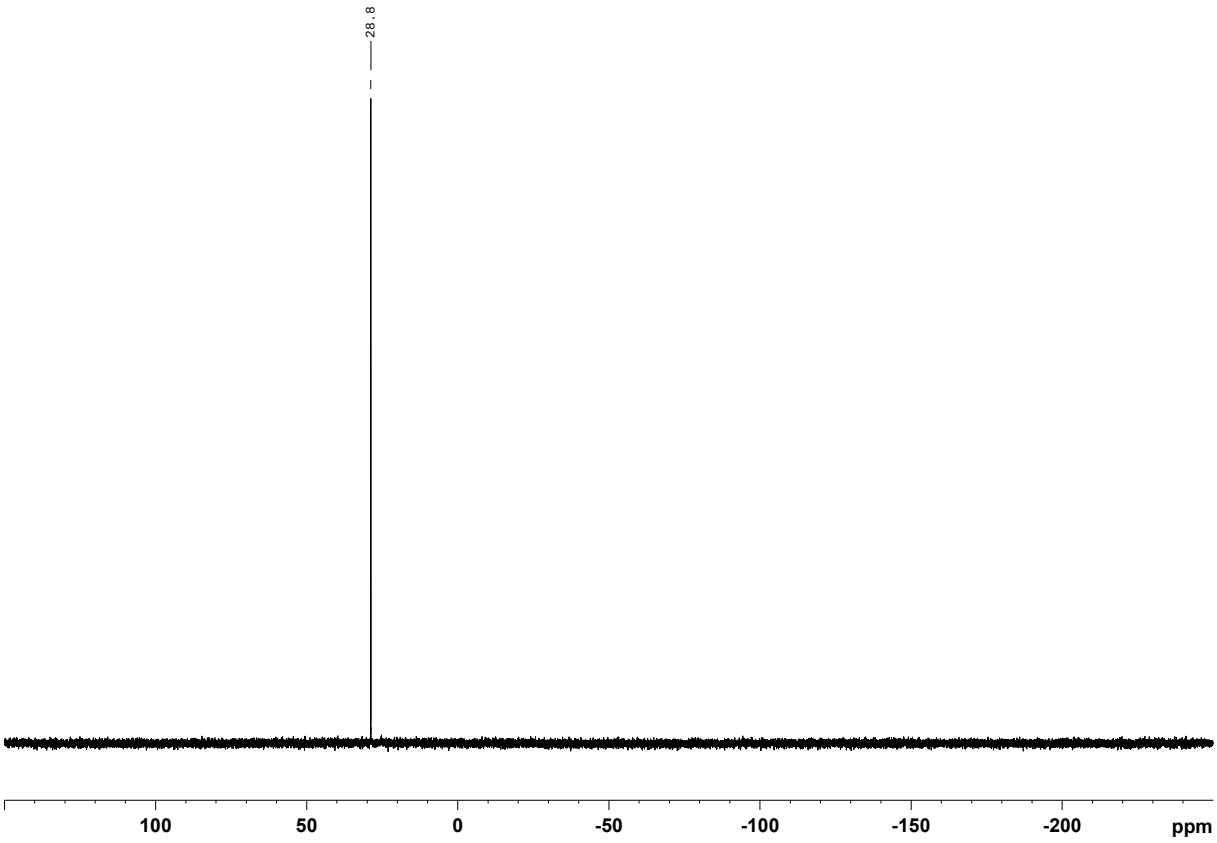
^{1}H NMR (* = cyclohexane):



^{13}C NMR (* = cyclohexane):

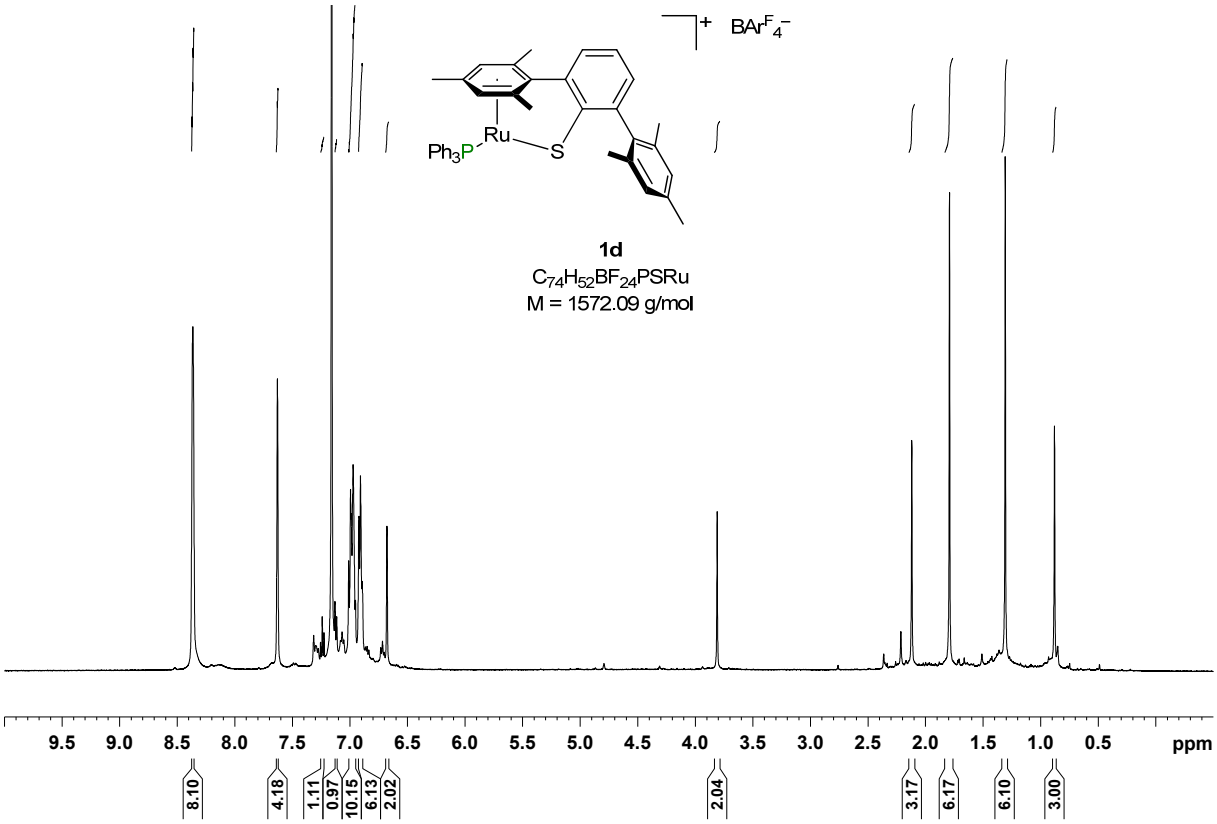


^{31}P NMR:

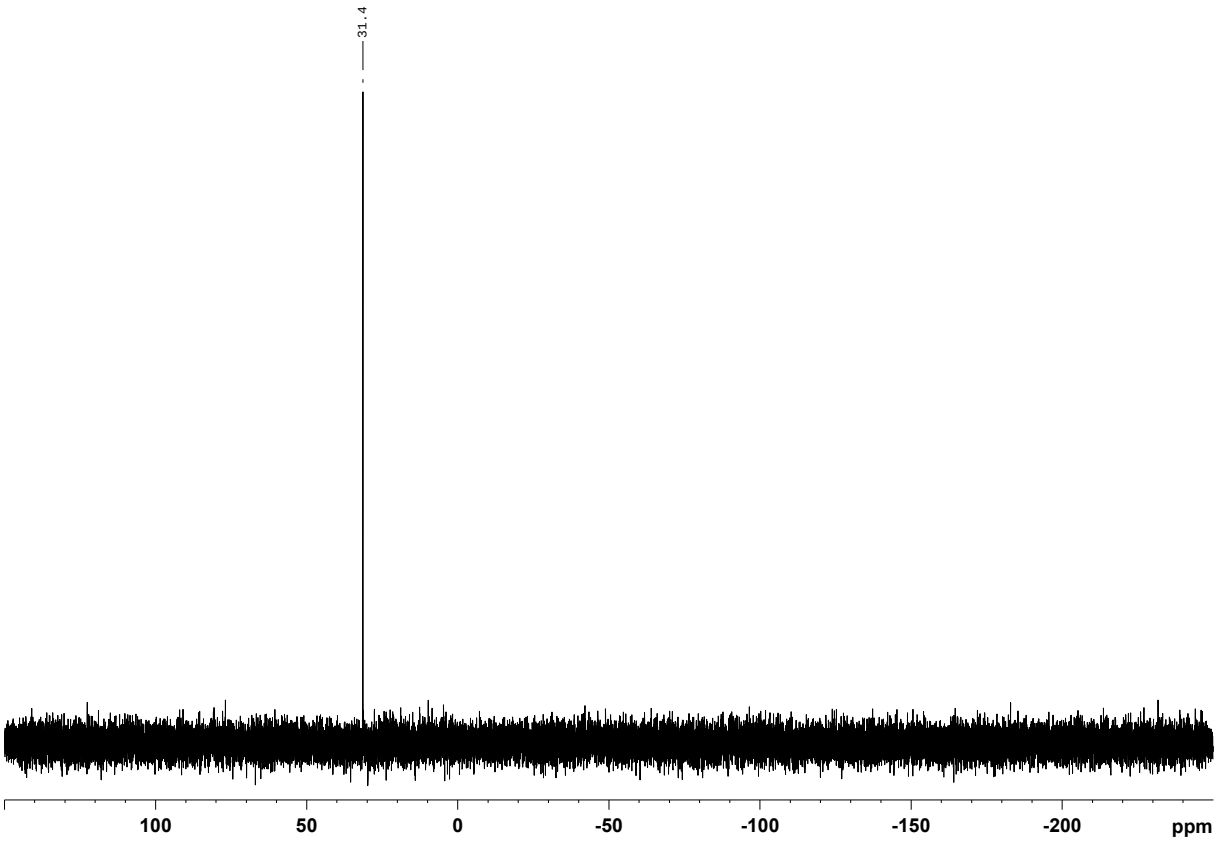


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]triphenylphosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1d)

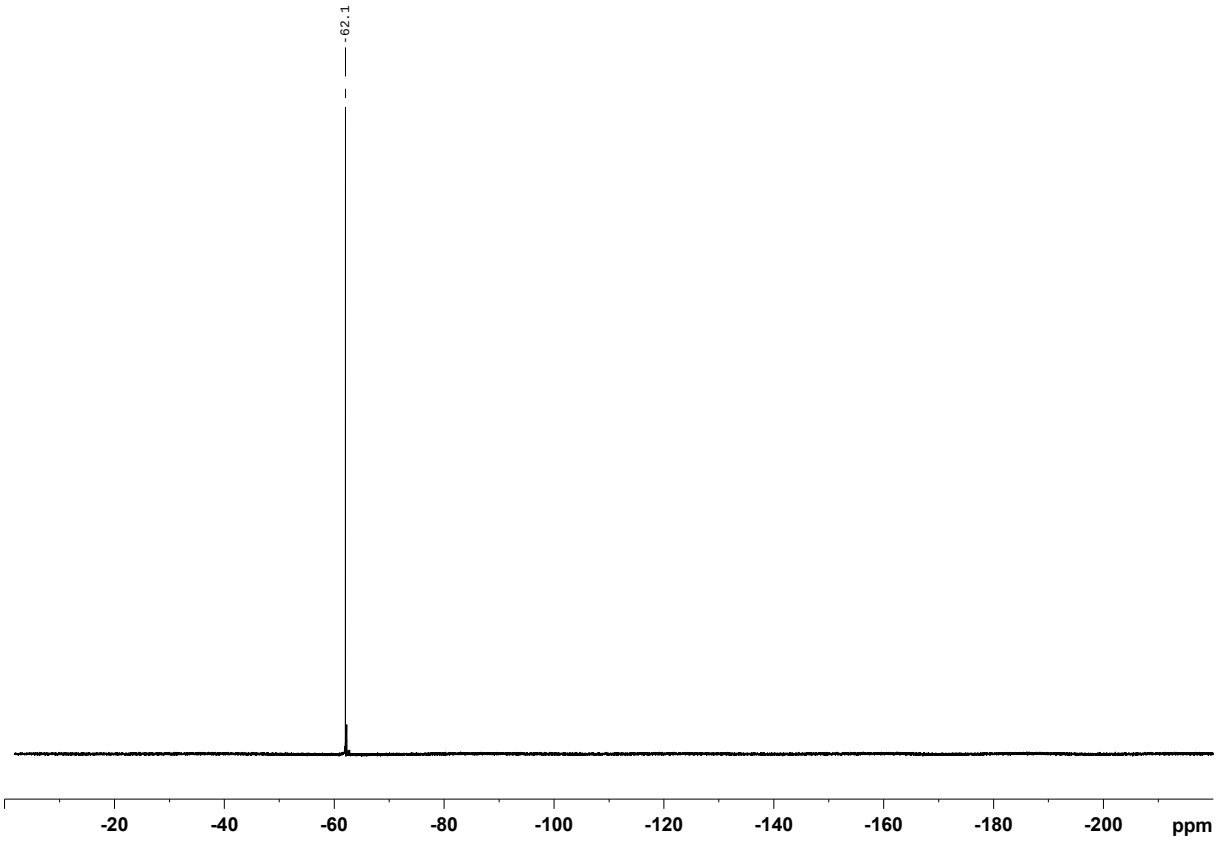
^{1}H NMR:



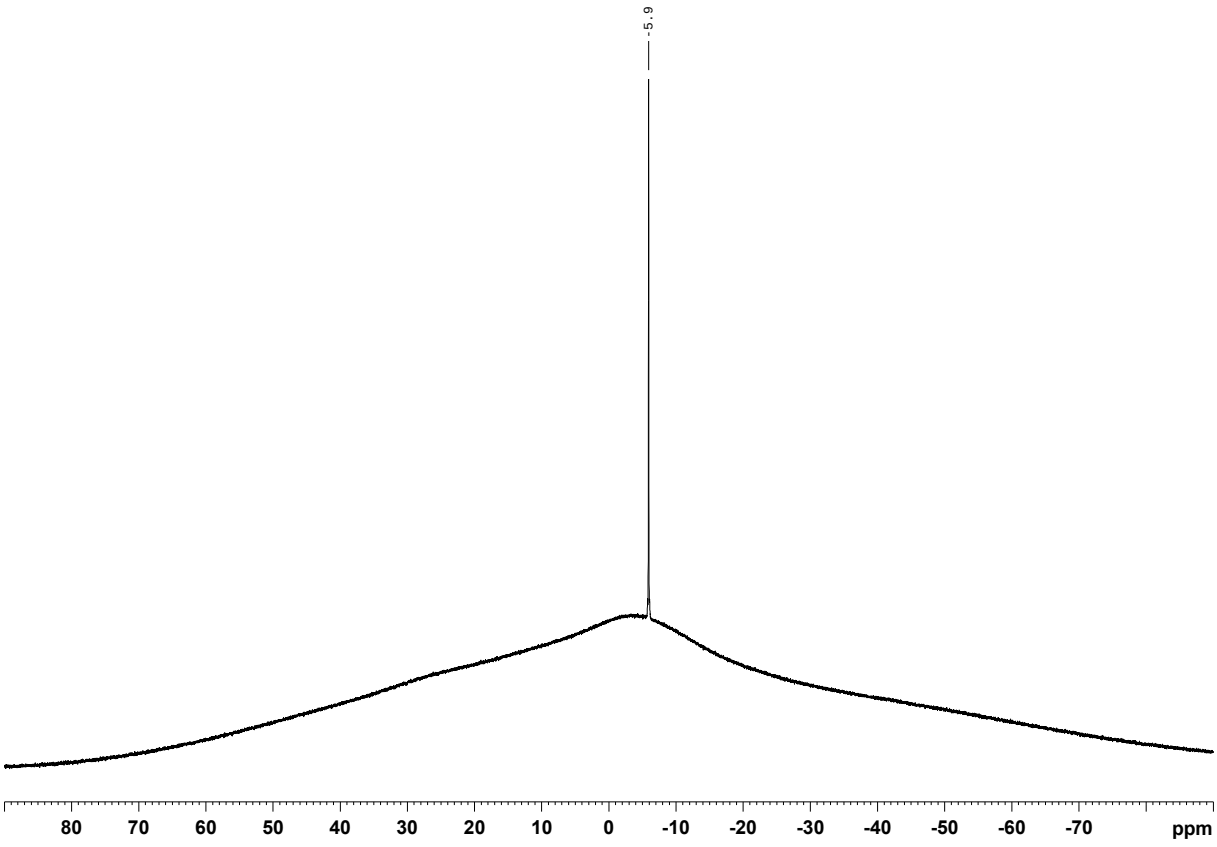
^{31}P NMR:



^{19}F NMR:

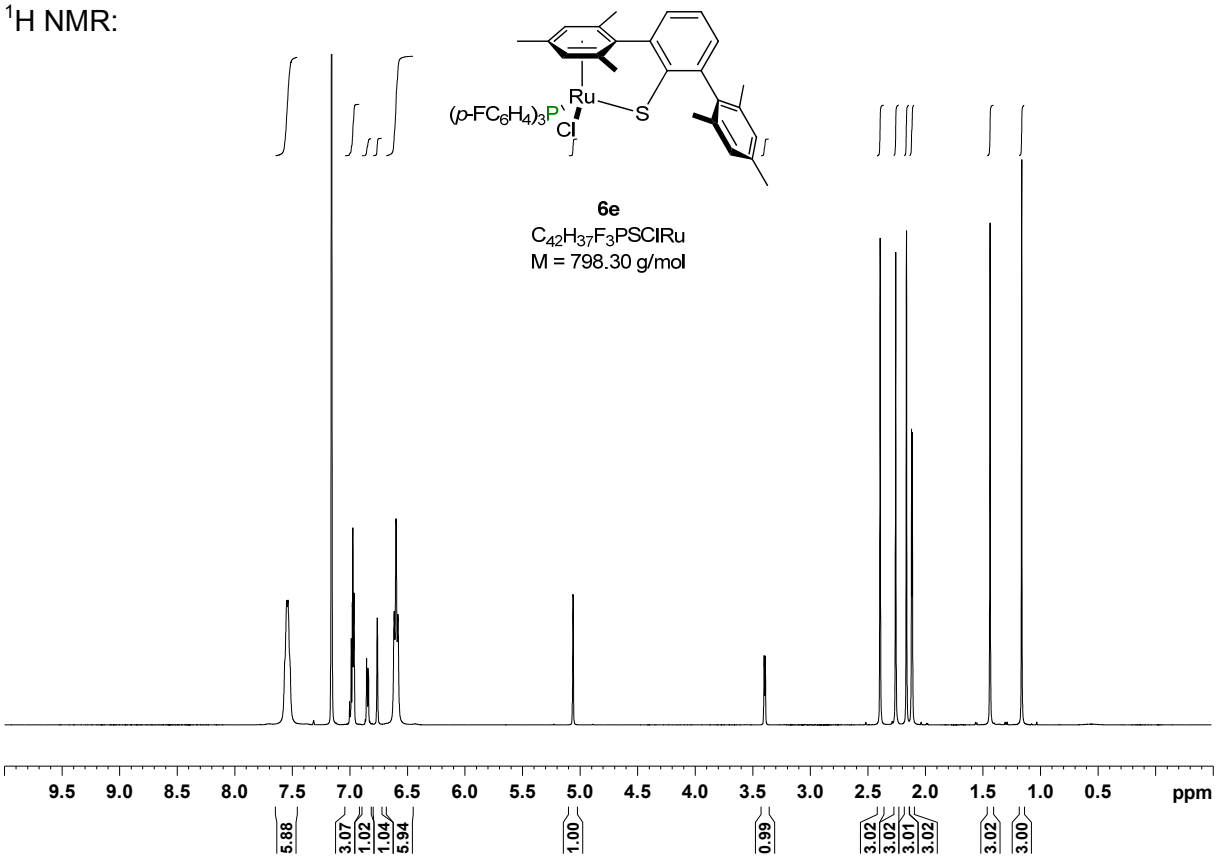


^{11}B NMR:

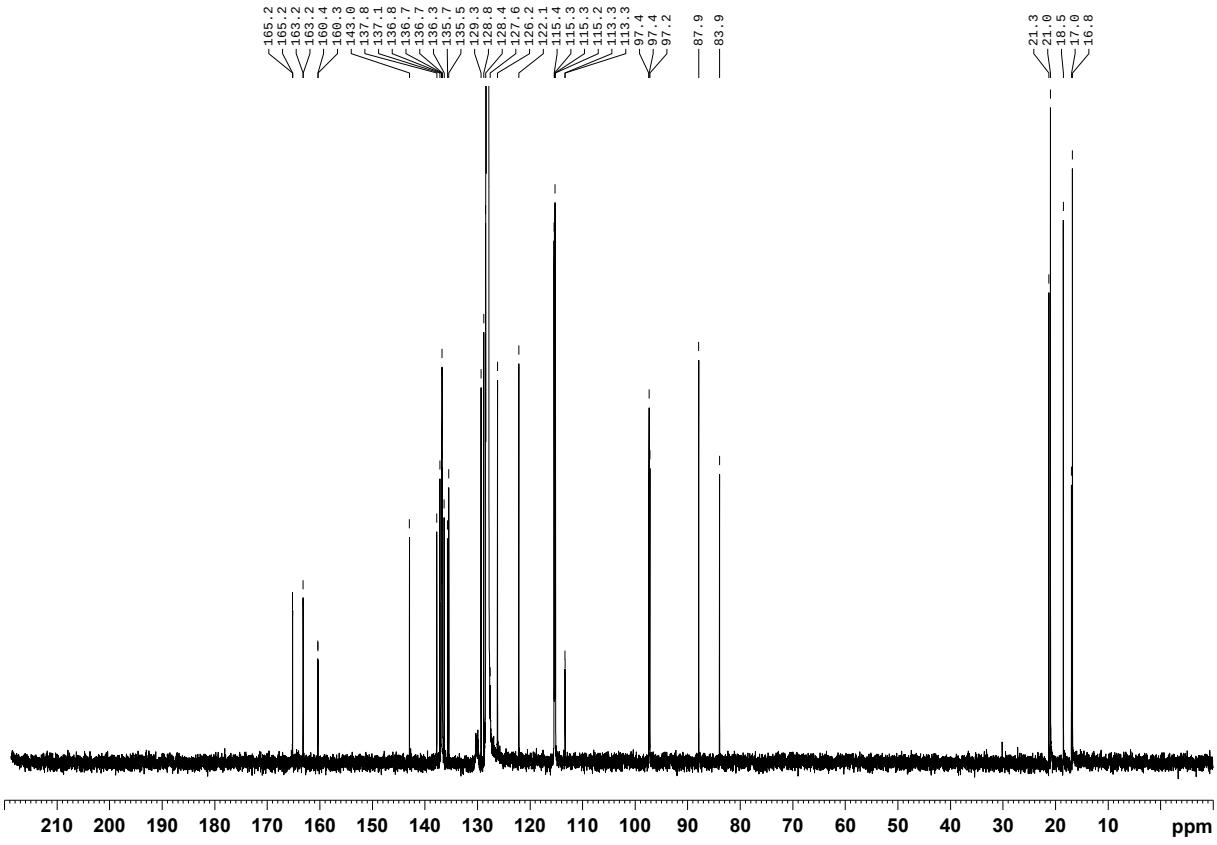


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]chlorido[tris(4-fluorophenyl)phosphine]-ruthenium(II) (6e)

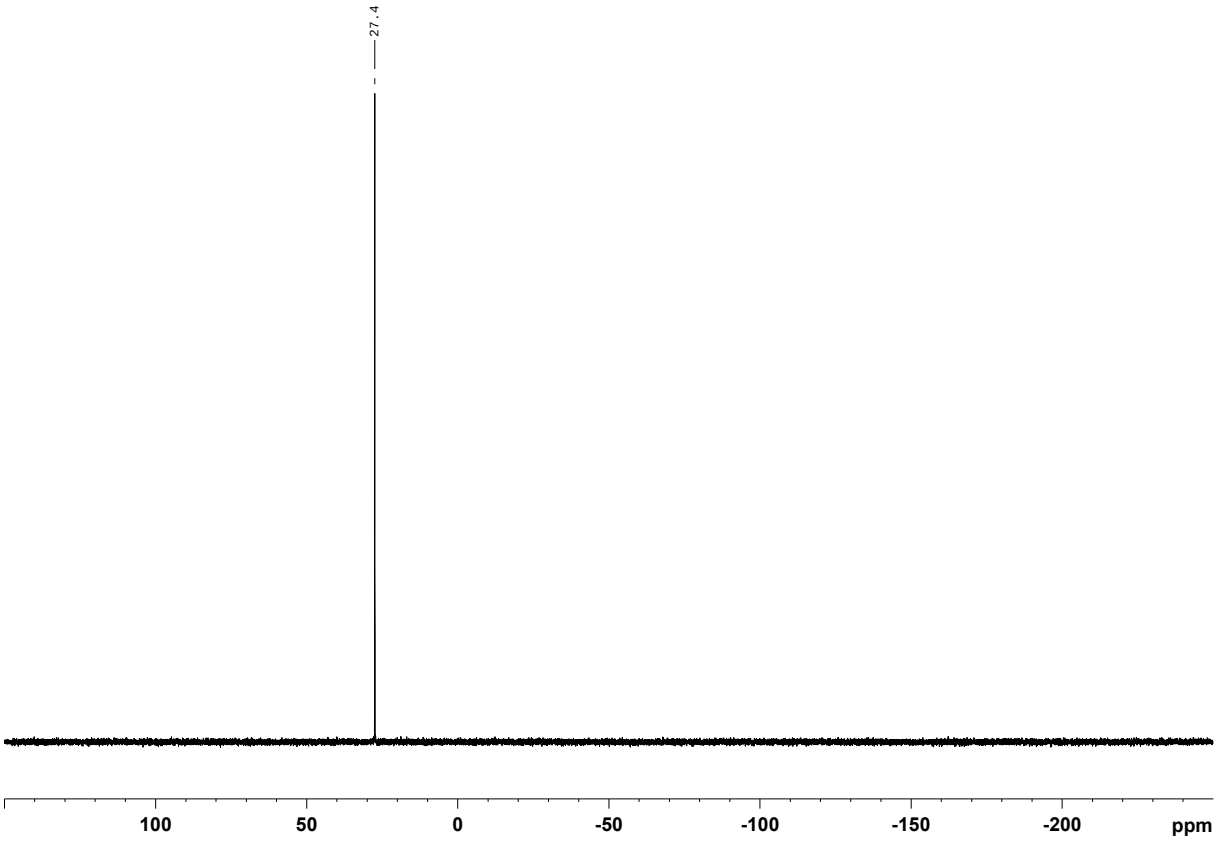
^{1}H NMR:



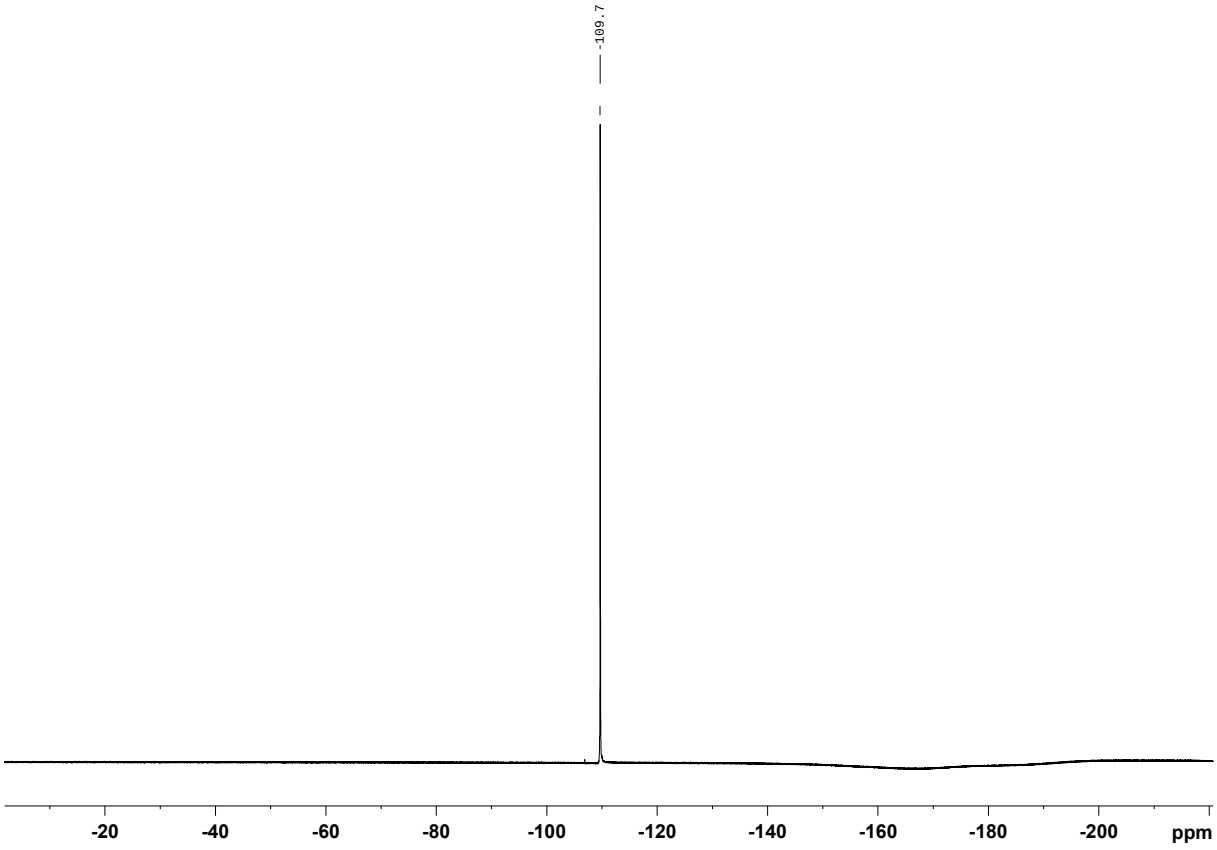
^{13}C NMR:



^{31}P NMR:

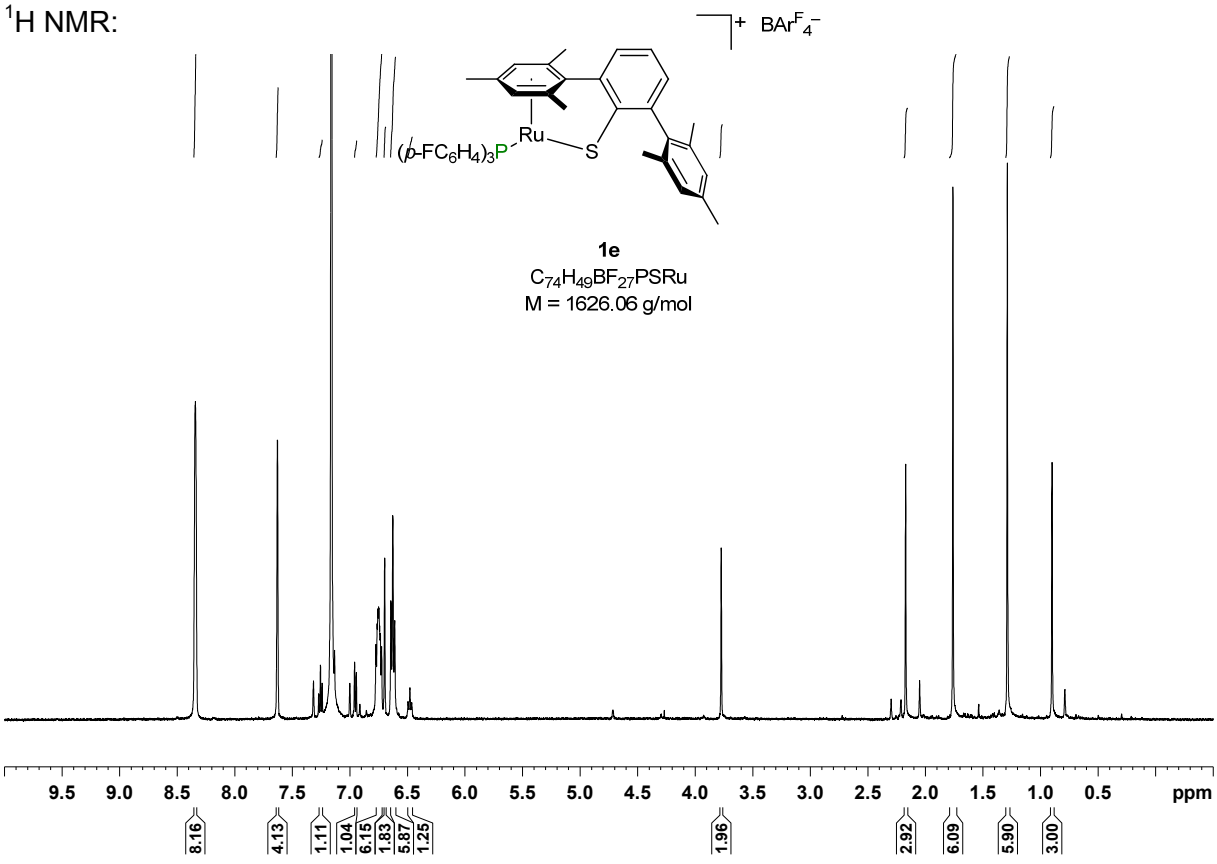


^{19}F NMR:

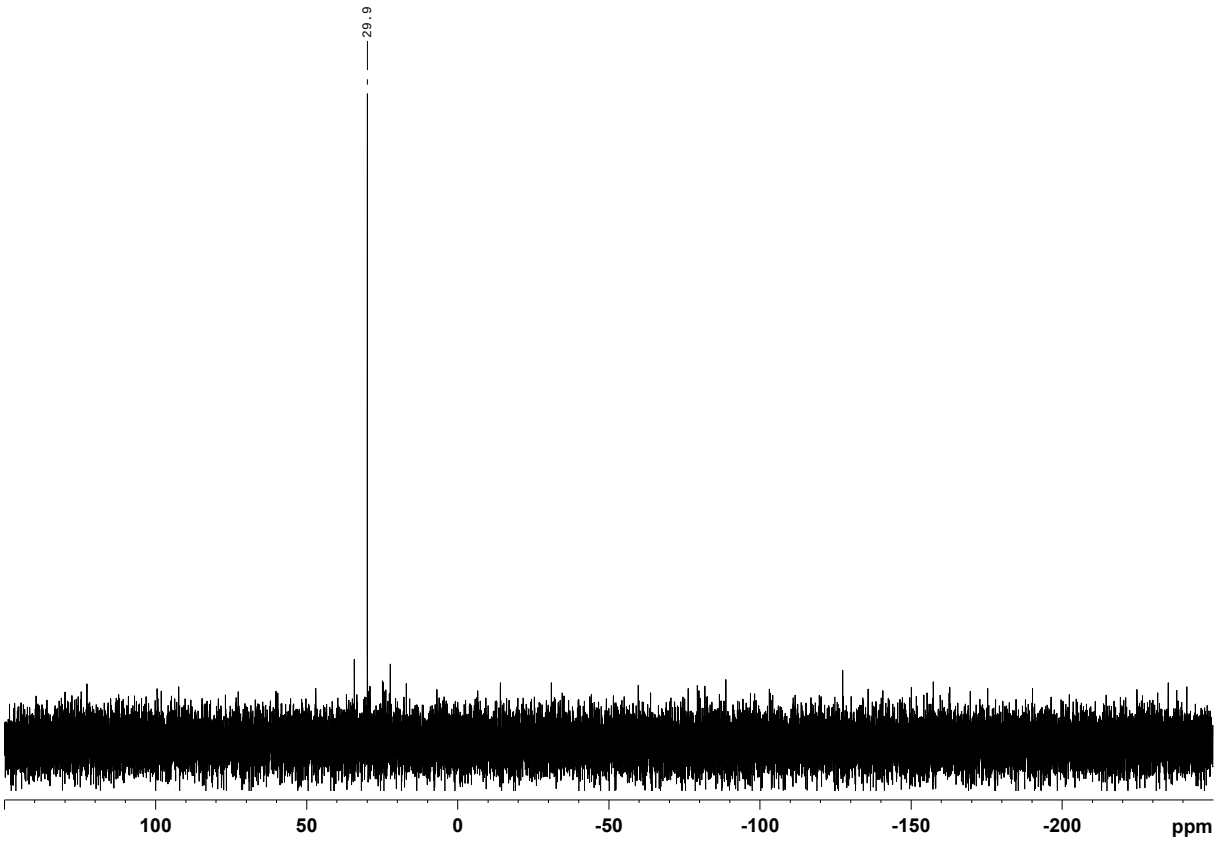


[2,6-η^6:η^1-Bis(2,4,6-trimethylphenyl)phenylthiolato]tris(4-fluorophenyl)phosphine-ruthenium(II)-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1e)

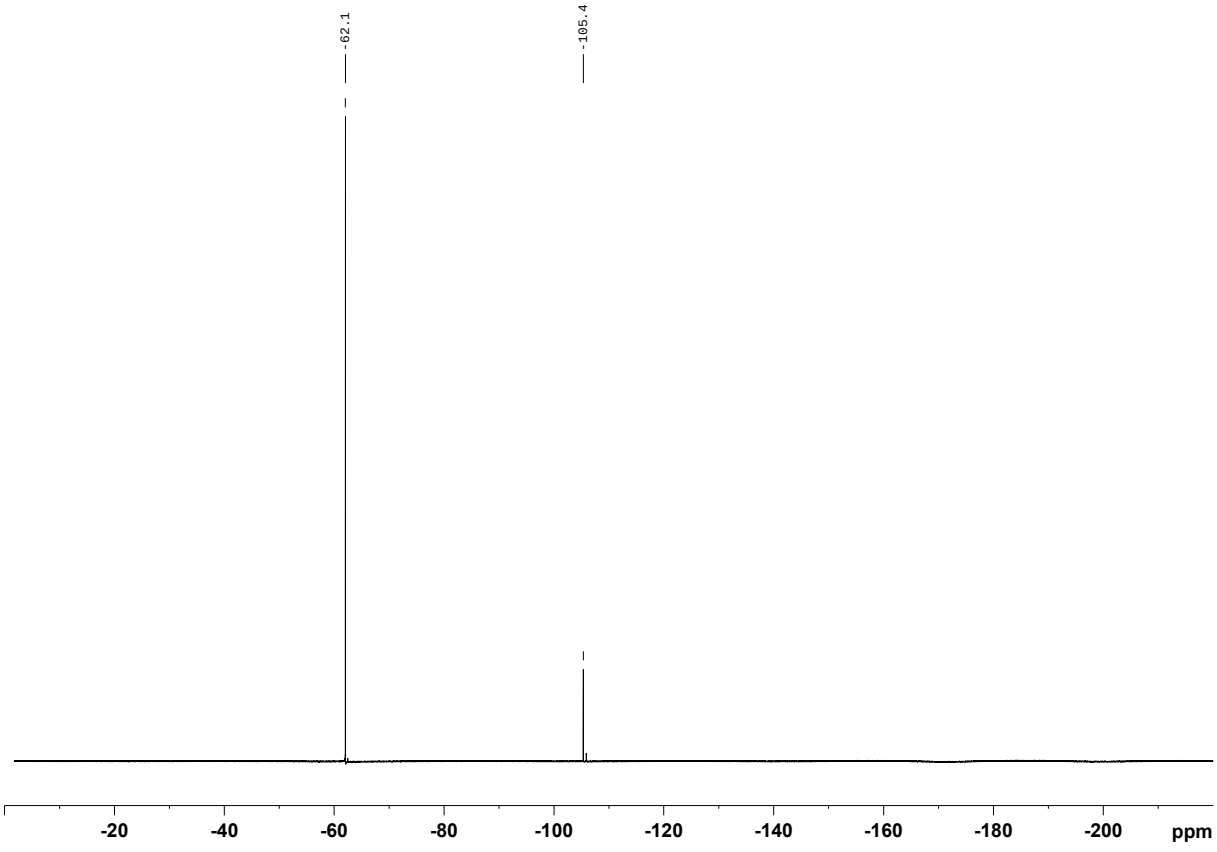
^{1}H NMR:



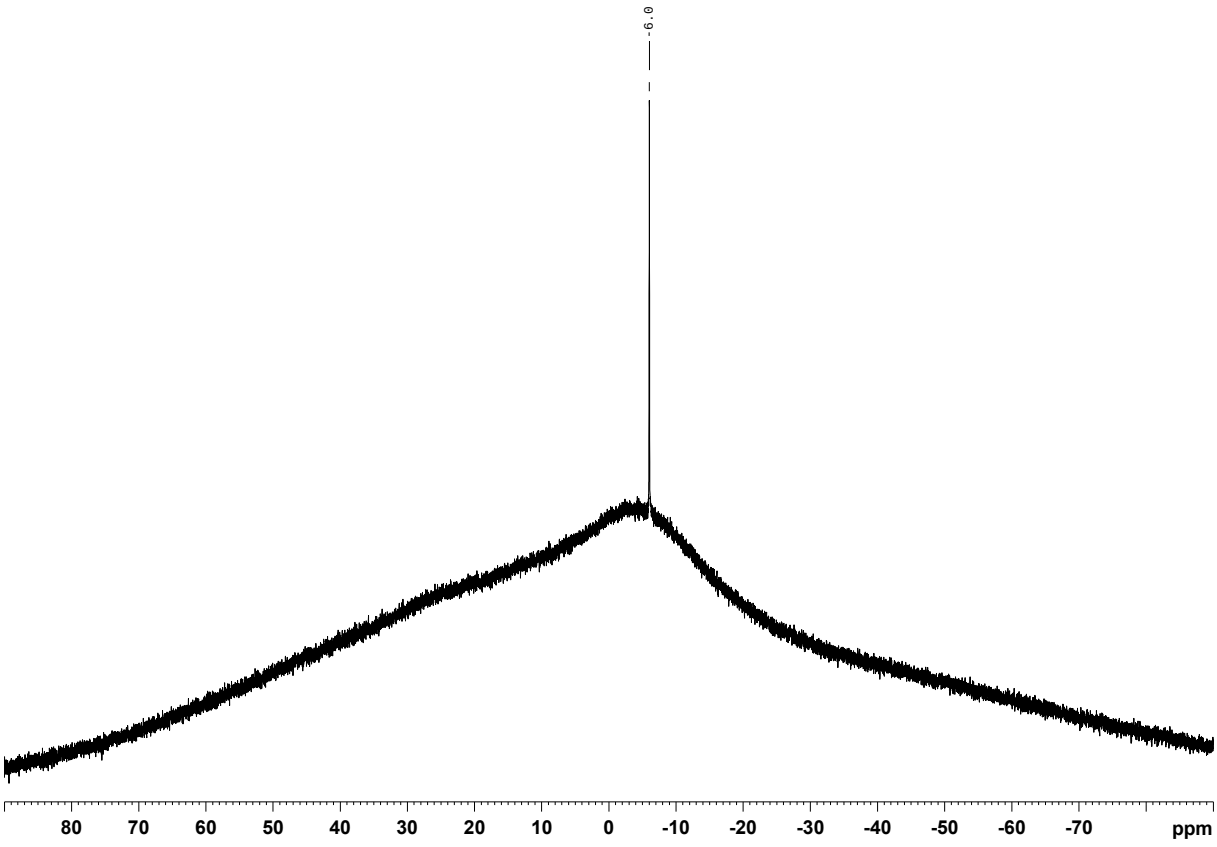
^{31}P NMR:



^{19}F NMR:



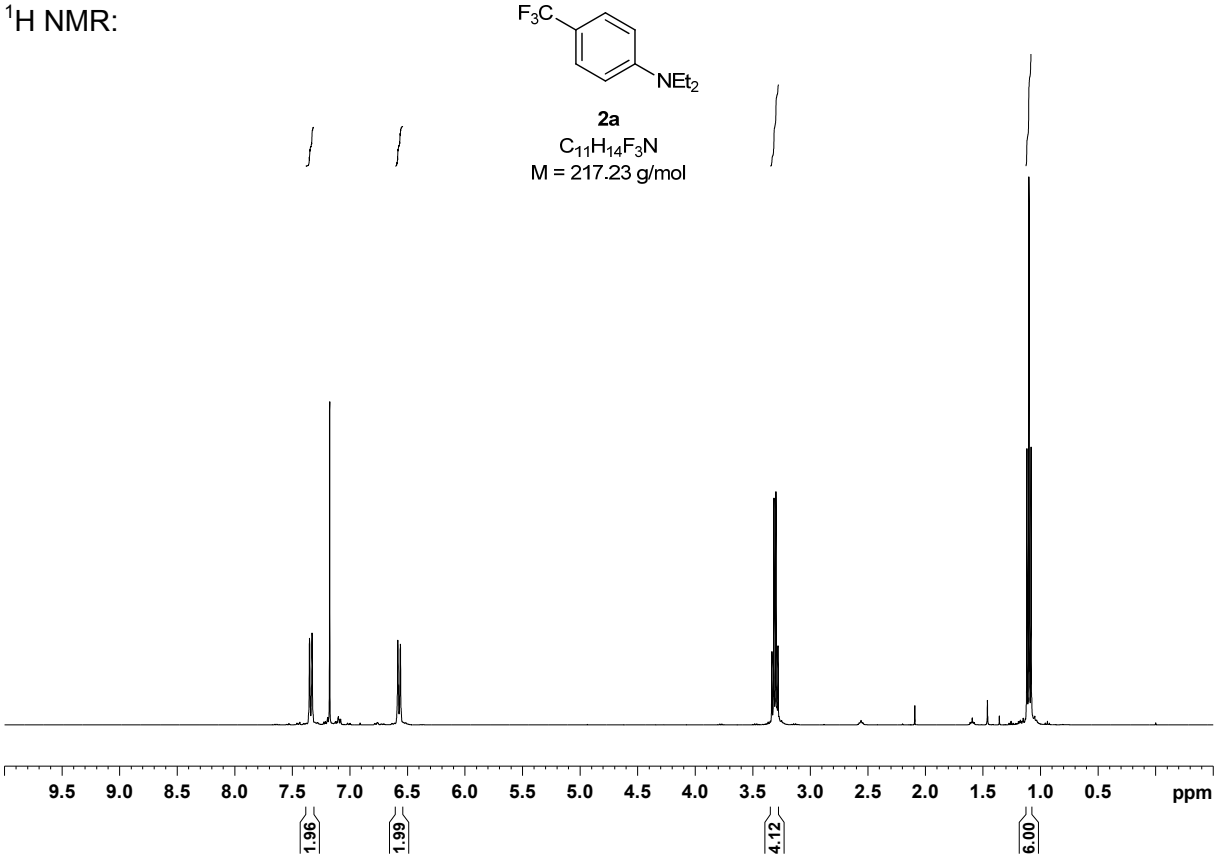
^{11}B NMR:



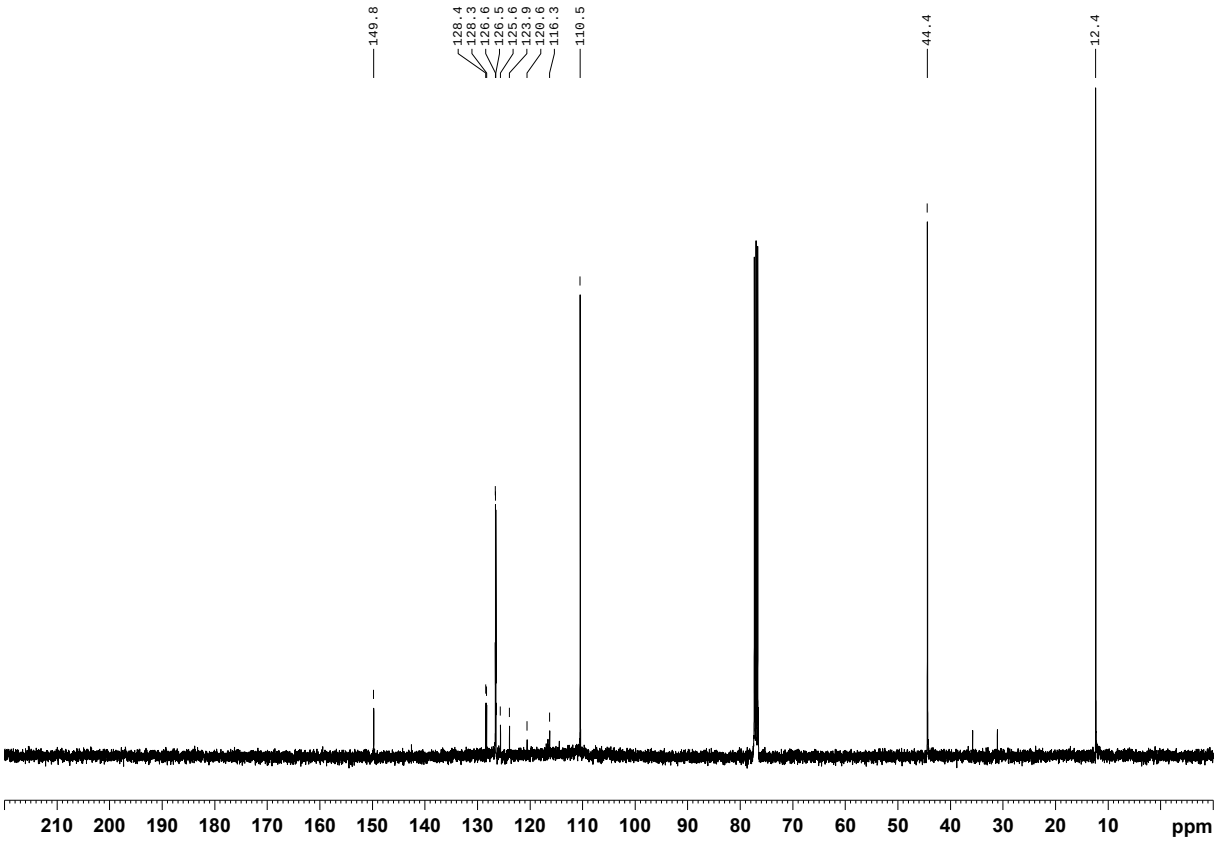
6.2 NMR Spectra of Substrates

N,*N*-Diethyl-4-trifluoromethylaniline (2a)

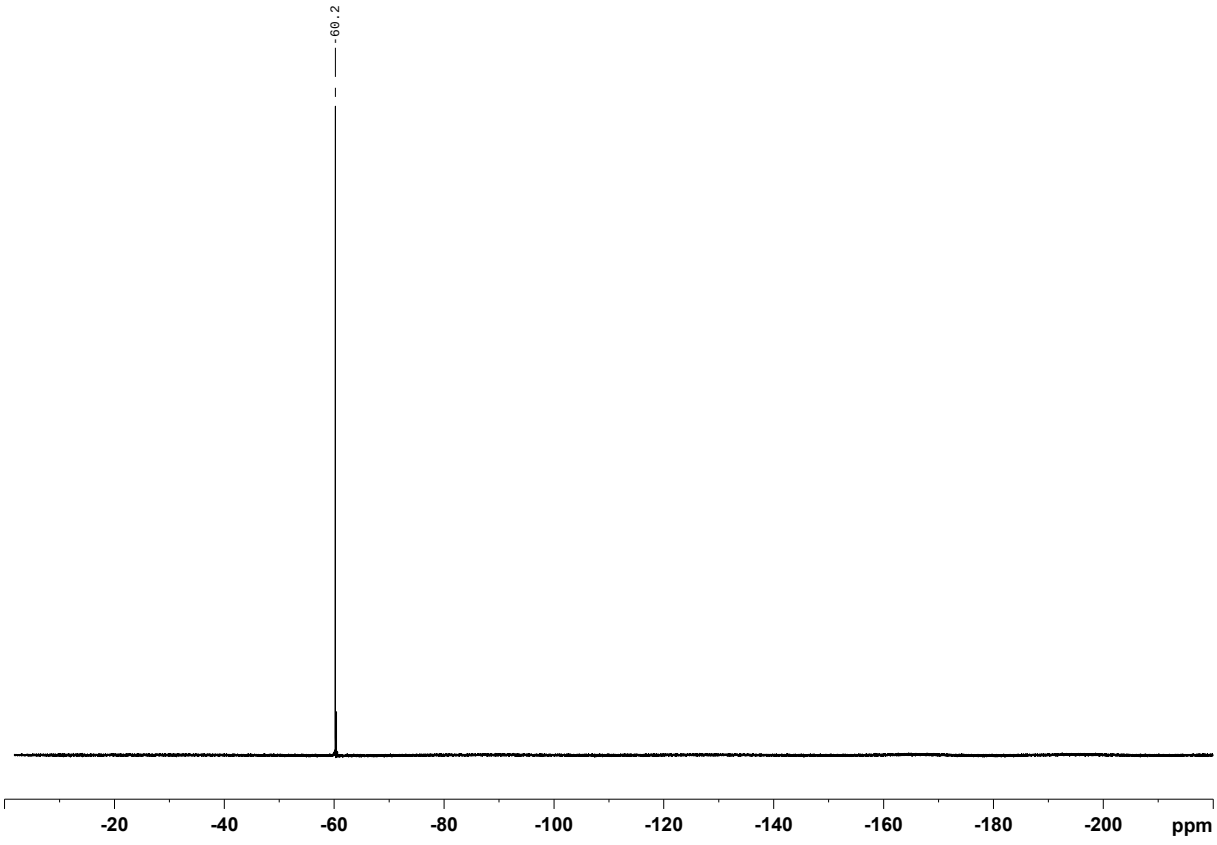
^{1}H NMR:



^{13}C NMR:

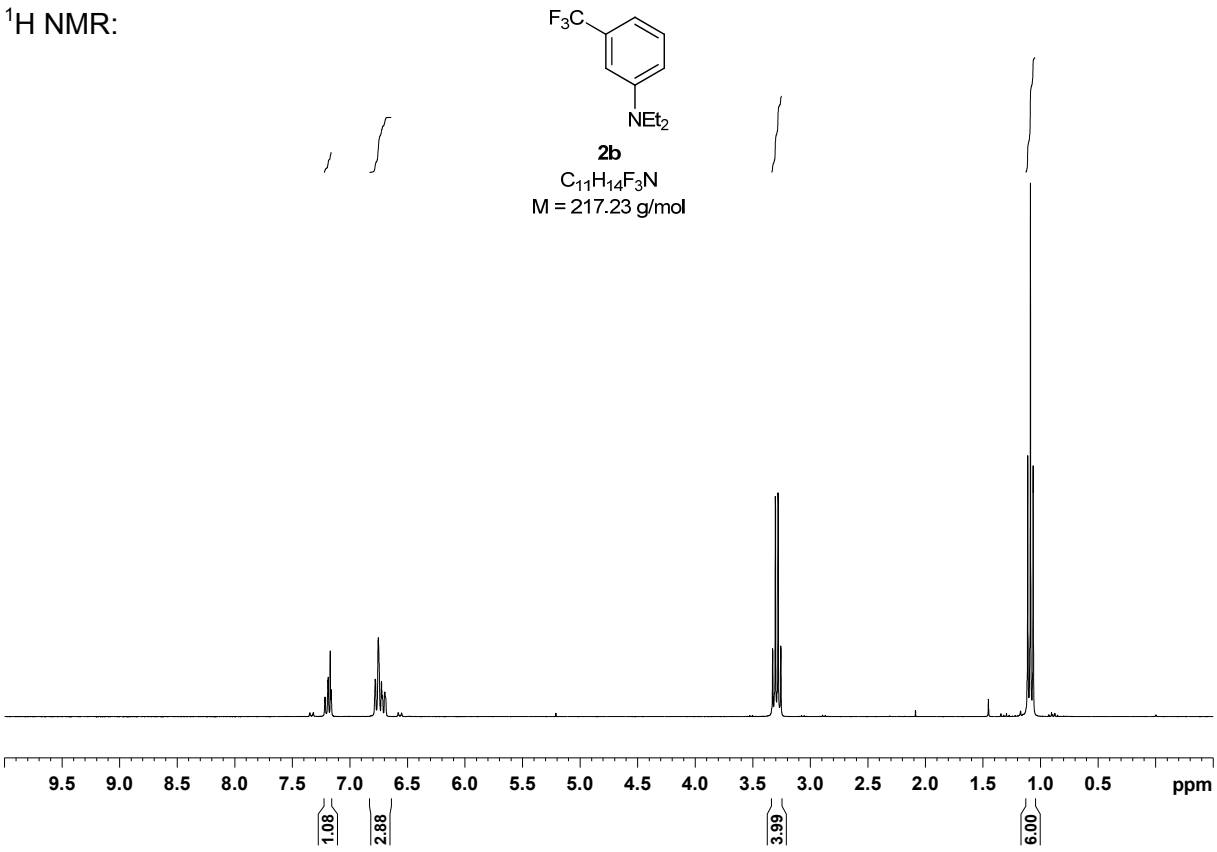


^{19}F NMR:

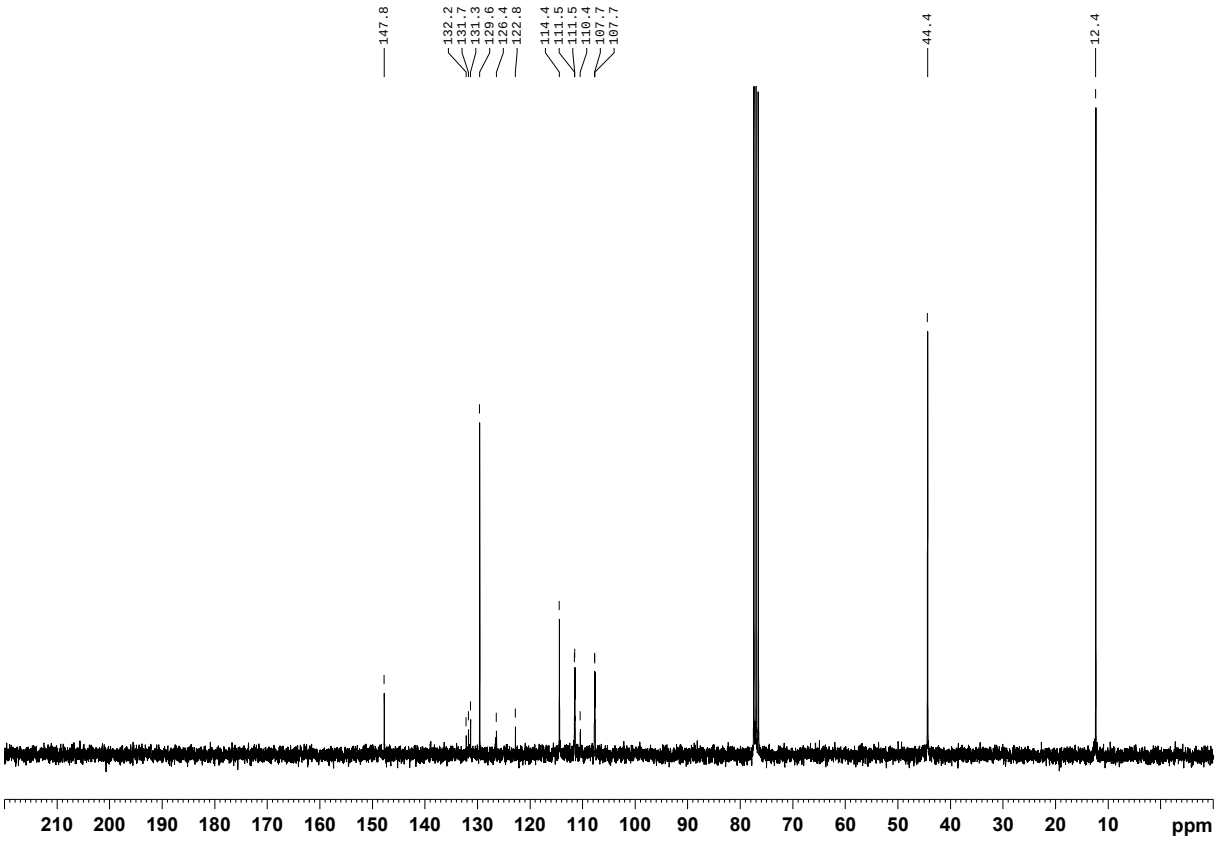


N,*N*-Diethyl-3-trifluoromethylaniline (2b)

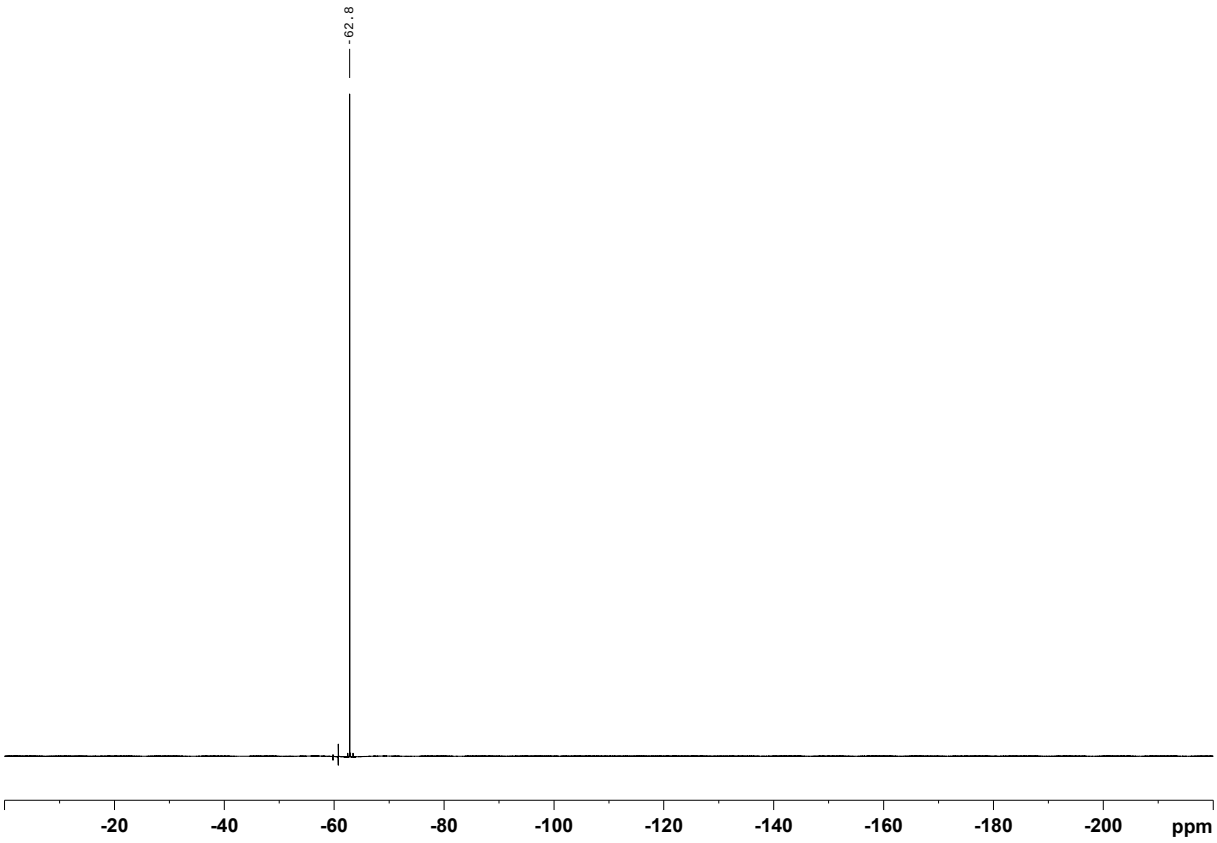
^{1}H NMR:



^{13}C NMR:

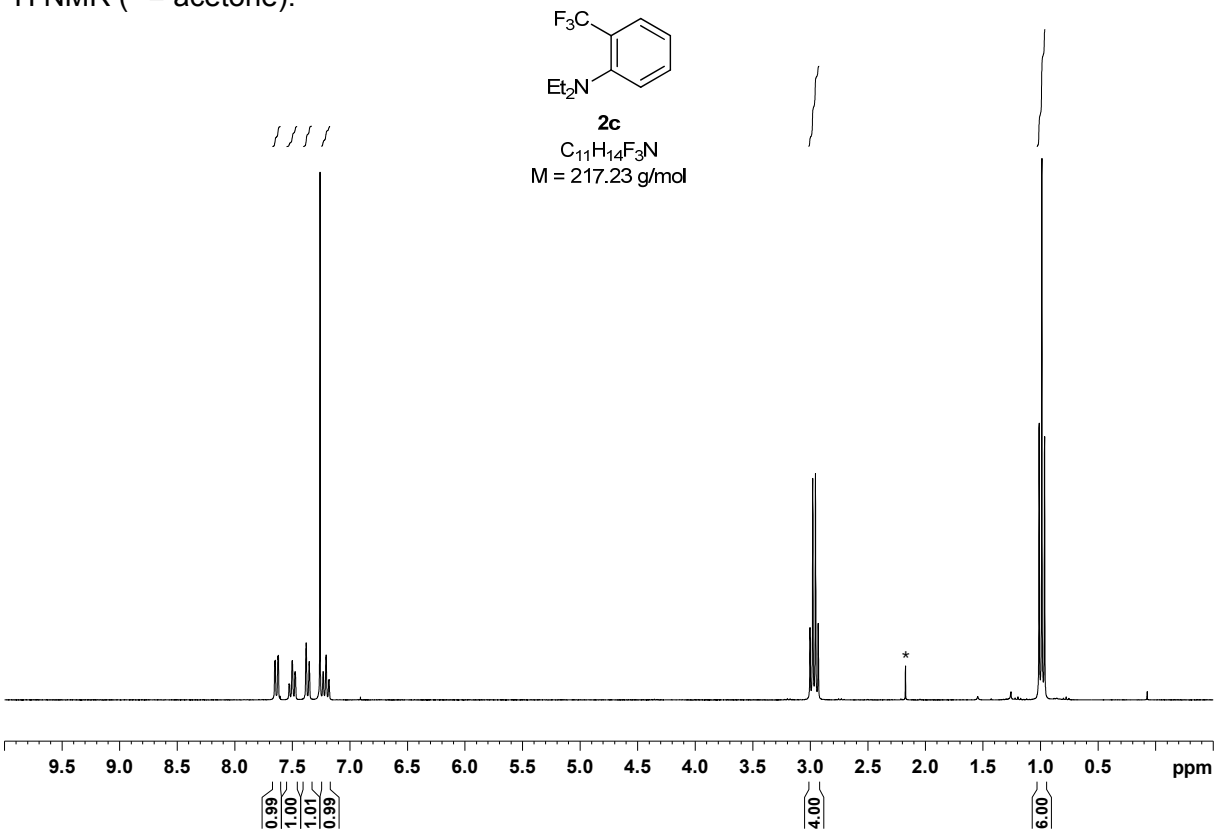


^{19}F NMR:

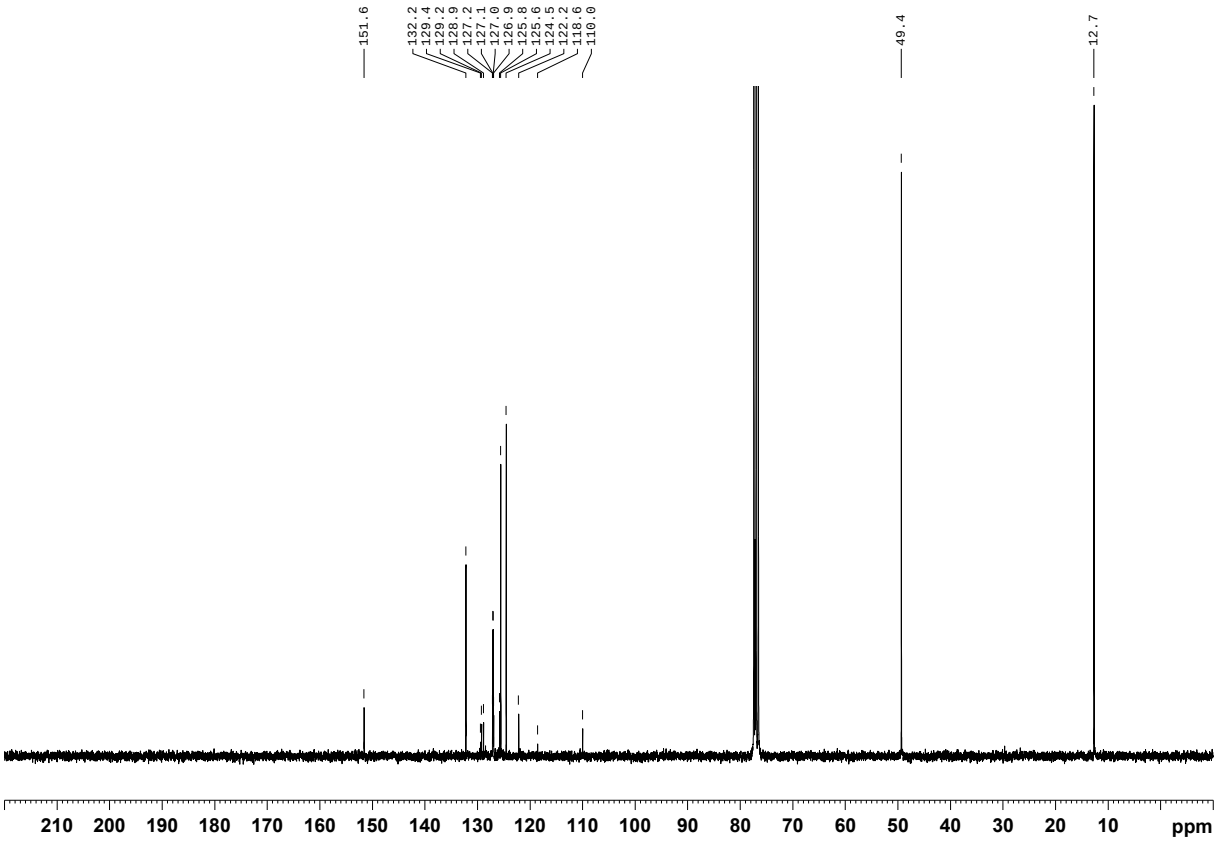


***N*,*N*-Diethyl-2-trifluoromethylaniline (2c)**

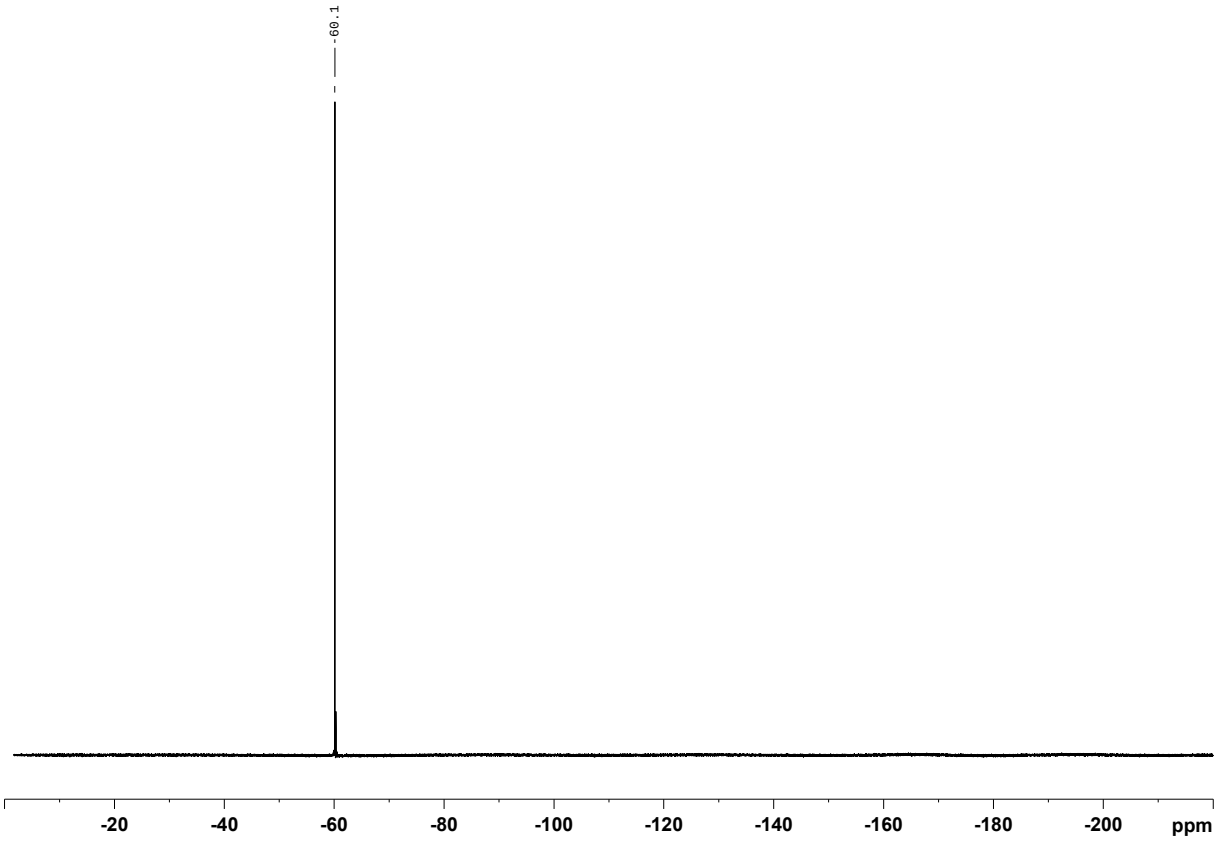
^{1}H NMR (* = acetone):



^{13}C NMR:

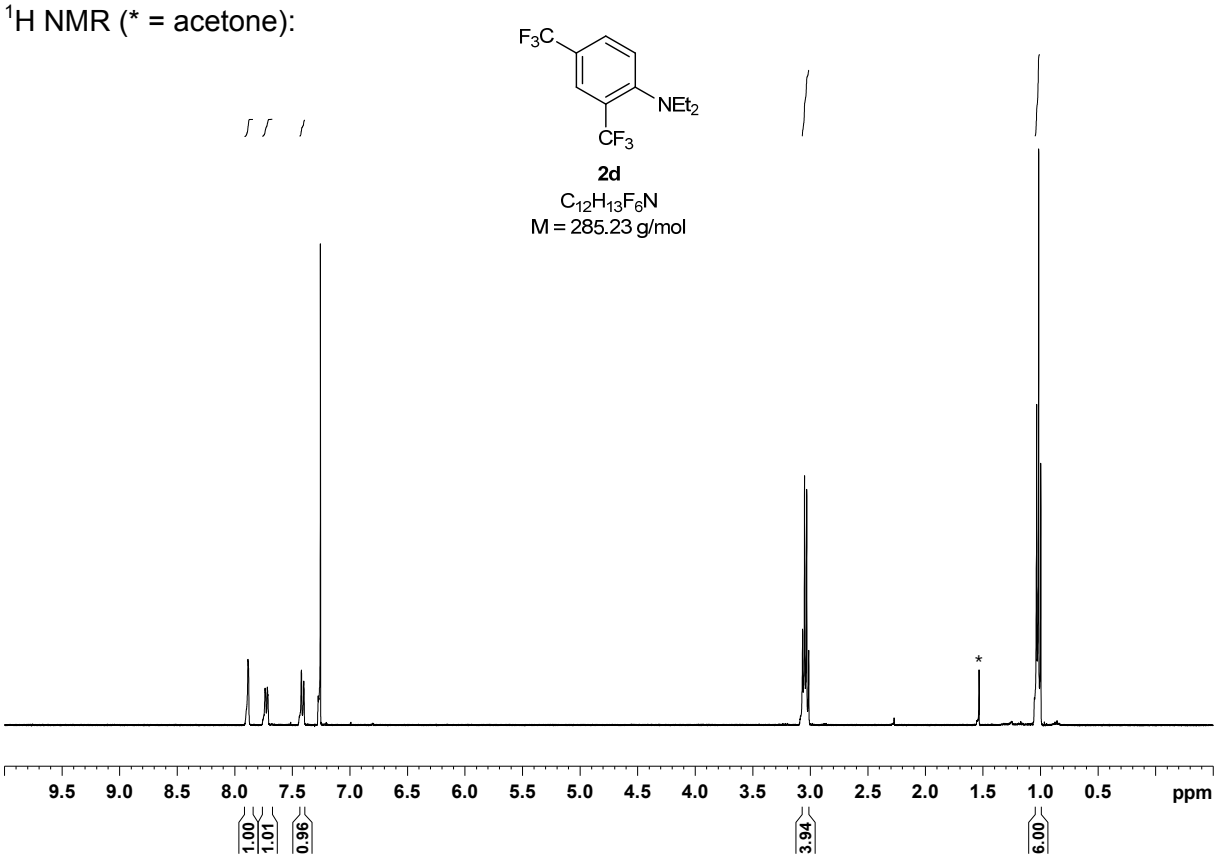


^{19}F NMR:

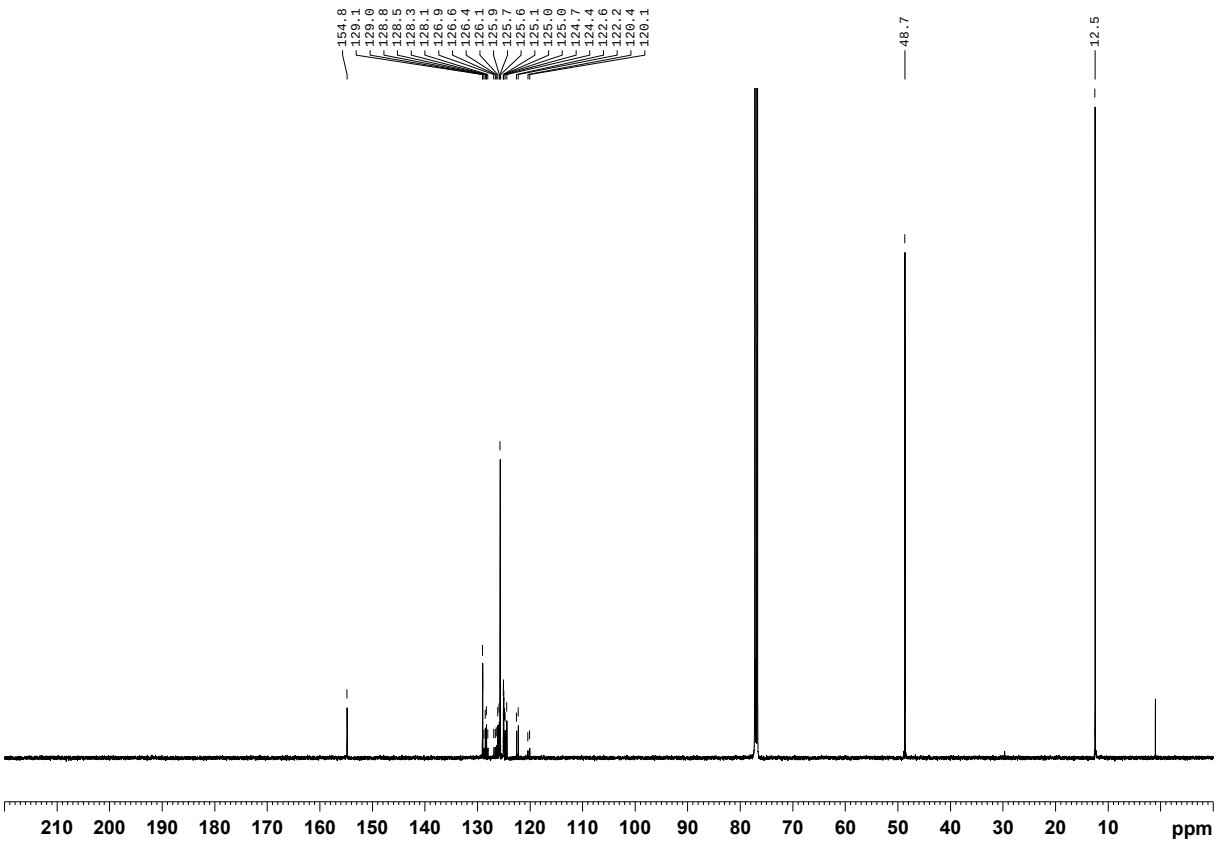


***N*,*N*-Diethyl-2,4-bis(trifluoromethyl)aniline (2d)**

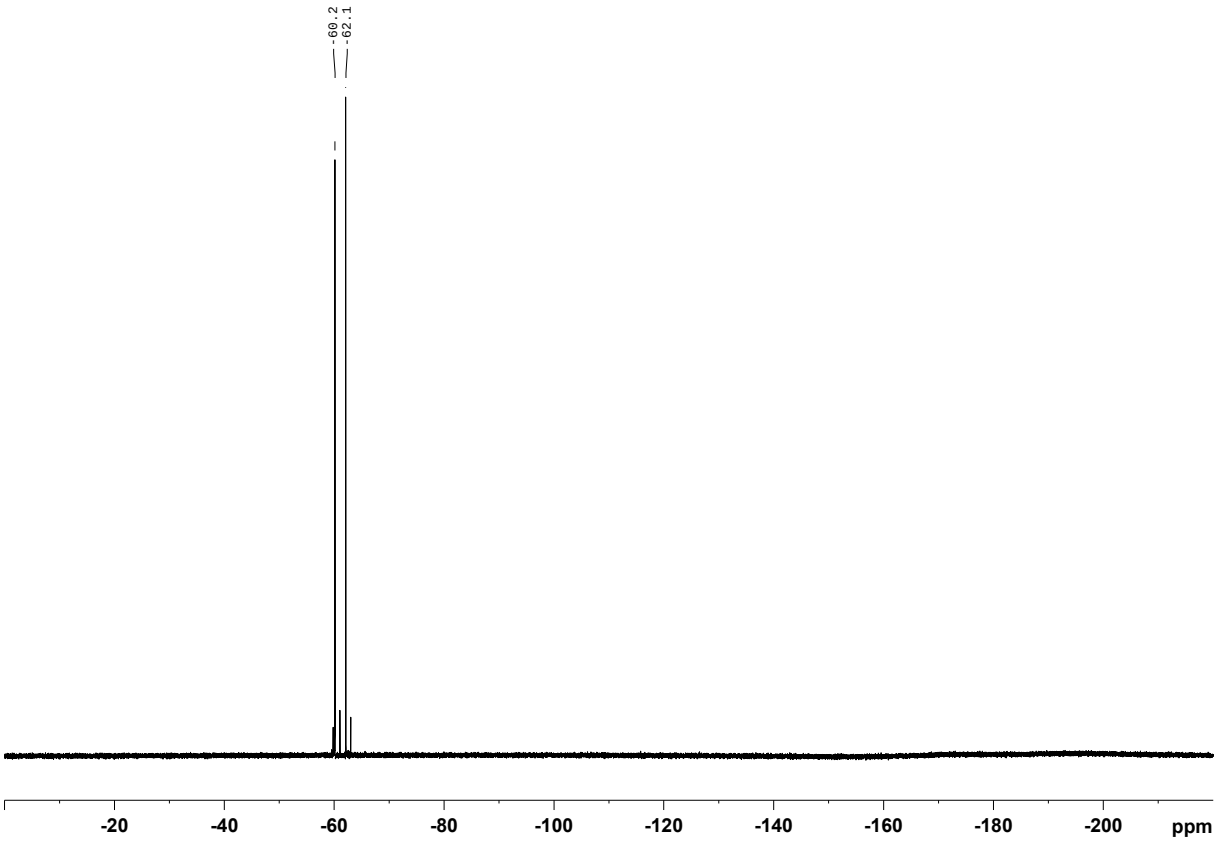
^{1}H NMR (* = acetone):



^{13}C NMR:



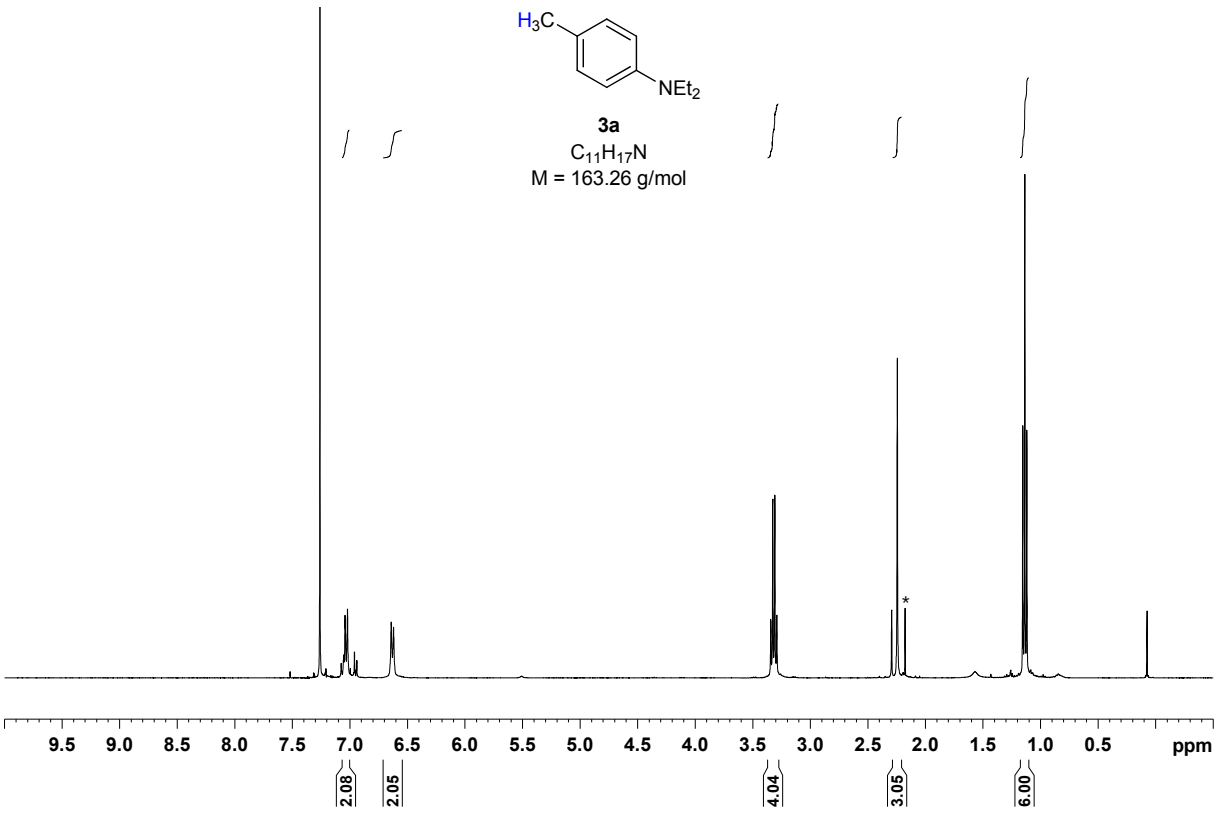
^{19}F NMR:



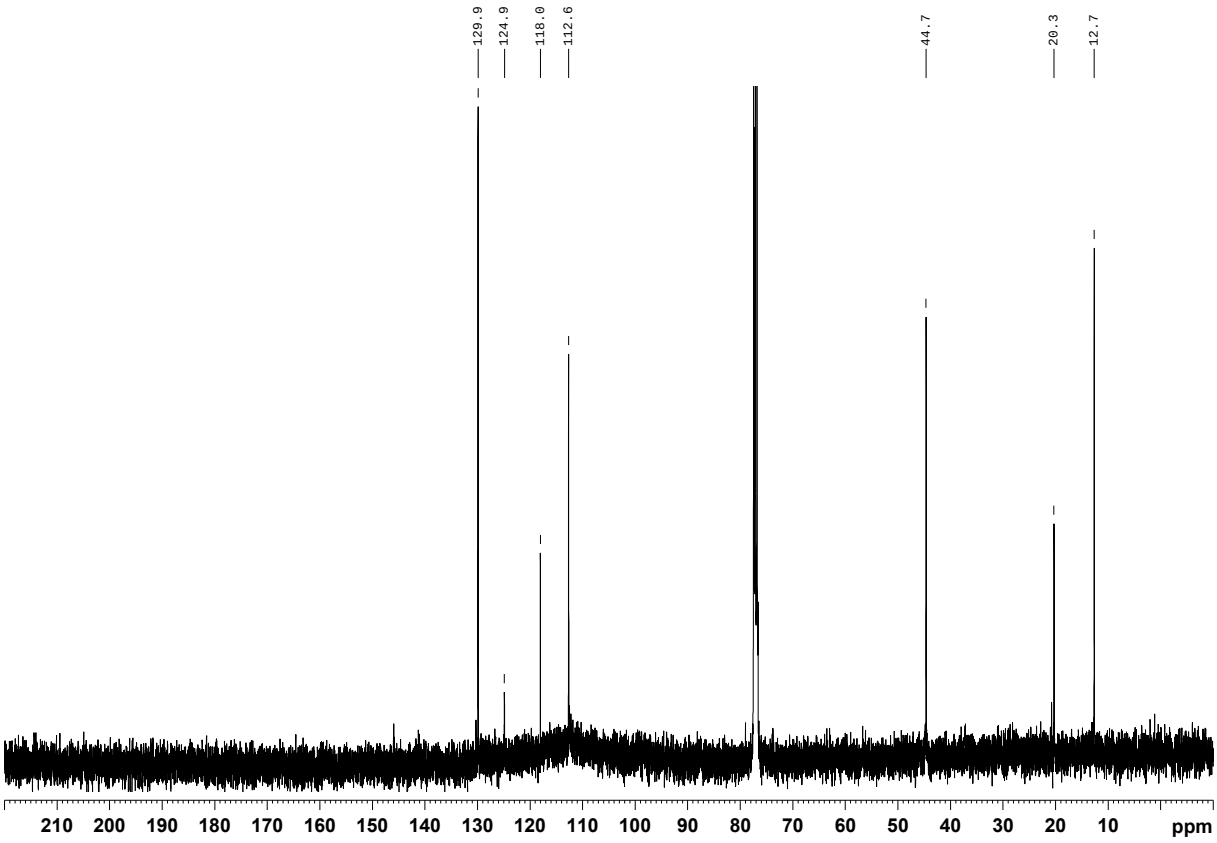
6.3 NMR Spectra of Reference Compounds

N,*N*-Diethyl-4-toluidine (3a)

^{1}H NMR (* = acetone):

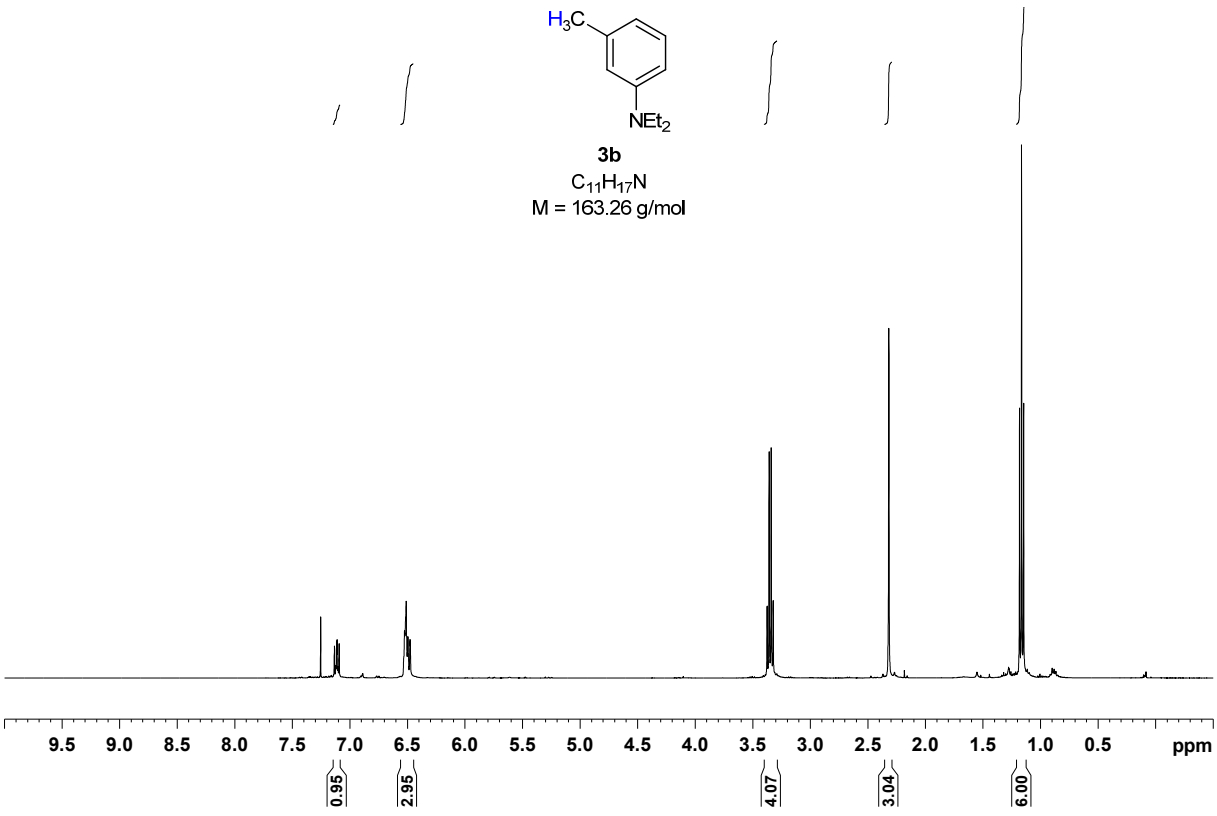


^{13}C NMR:

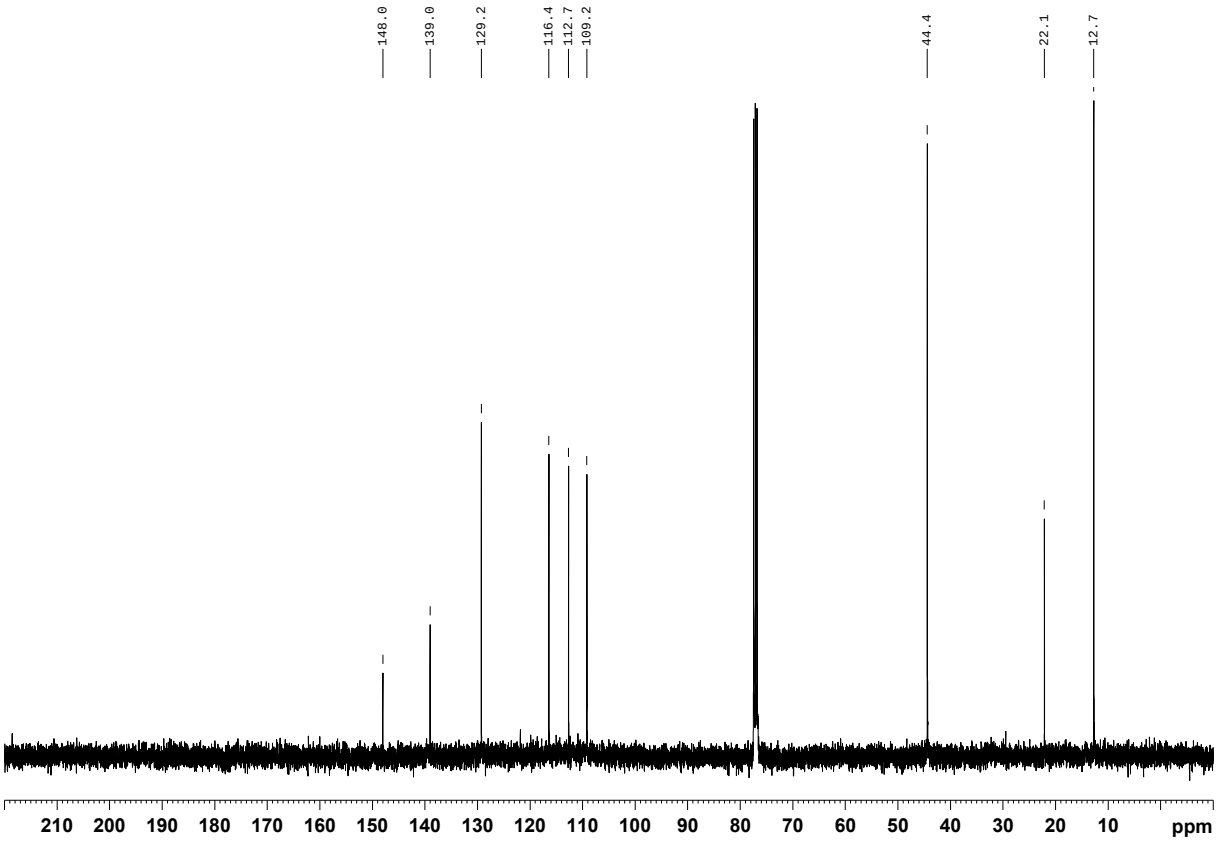


N,*N*-Diethyl-3-toluidine (3b)

^{1}H NMR:

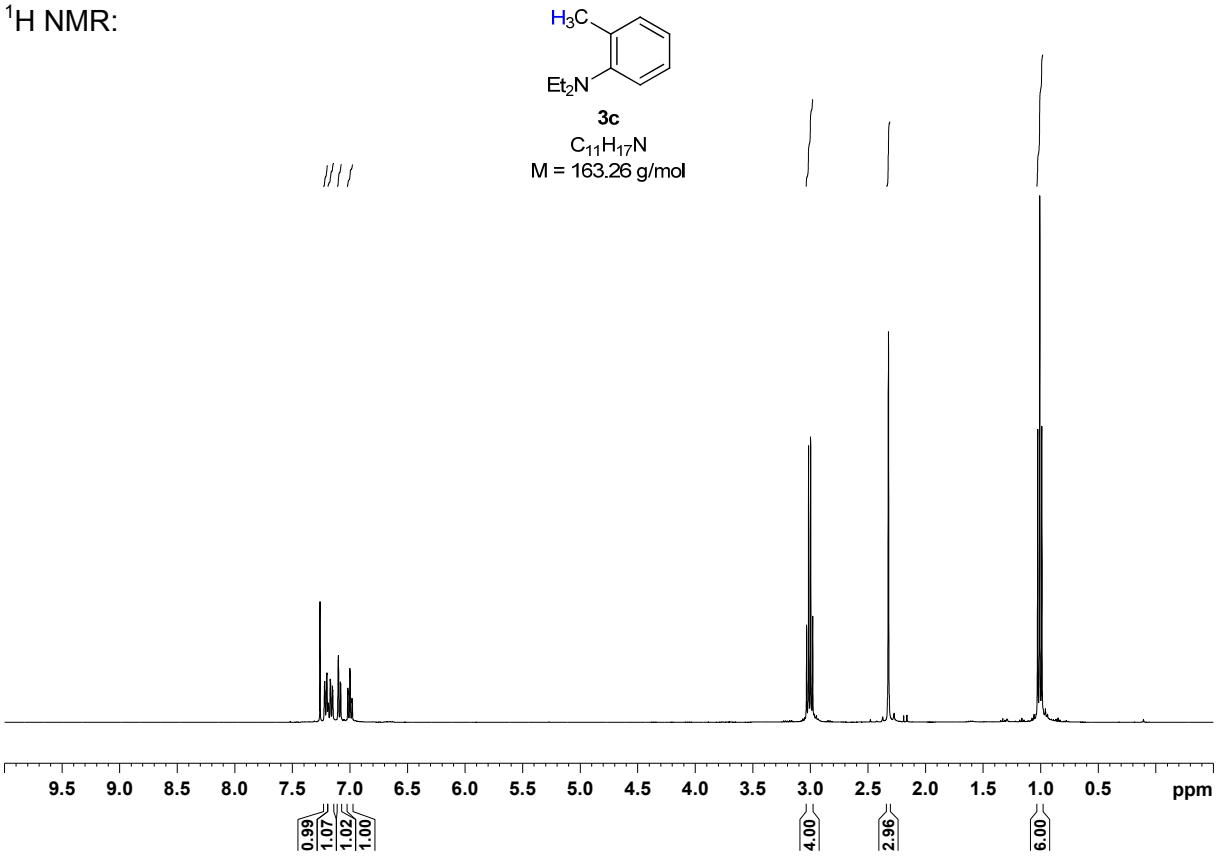


^{13}C NMR:

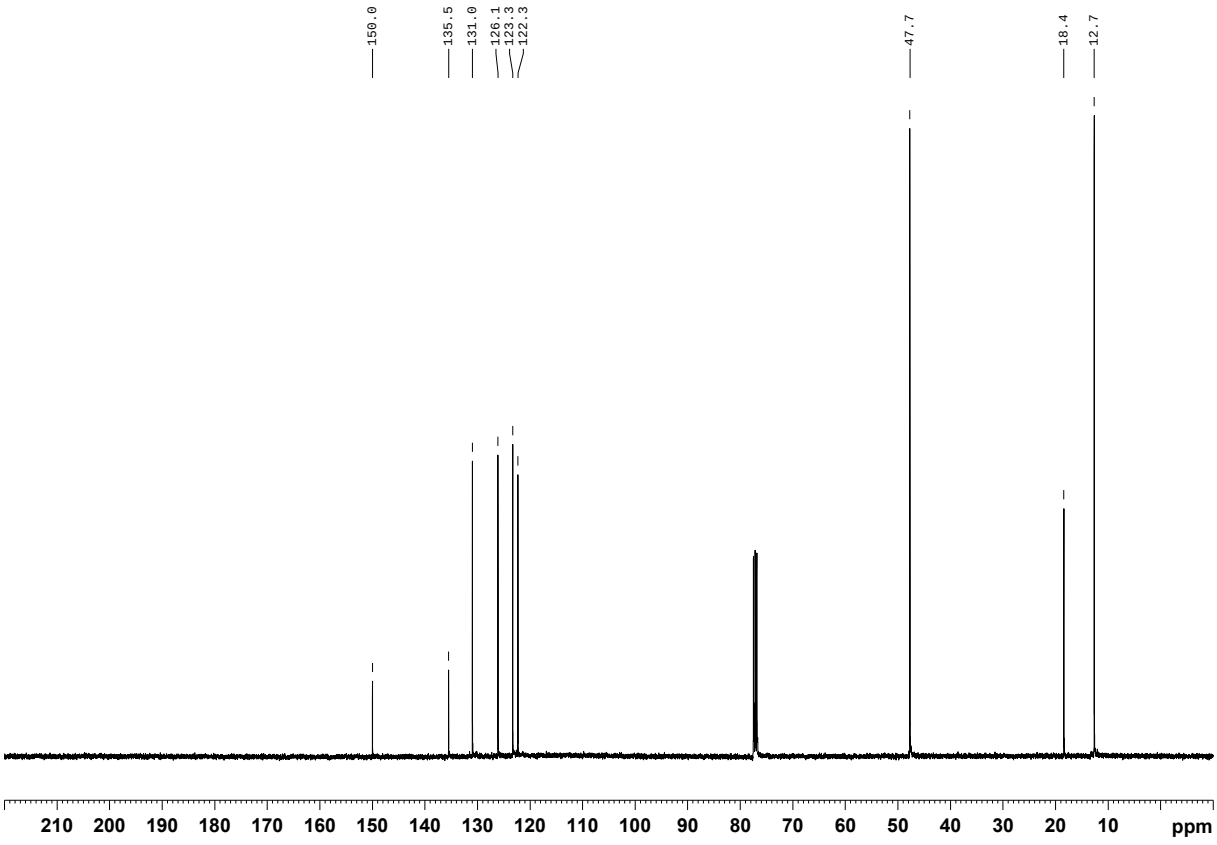


_N_,_N_-Diethyl-2-toluidine (3c)

^{1}H NMR:

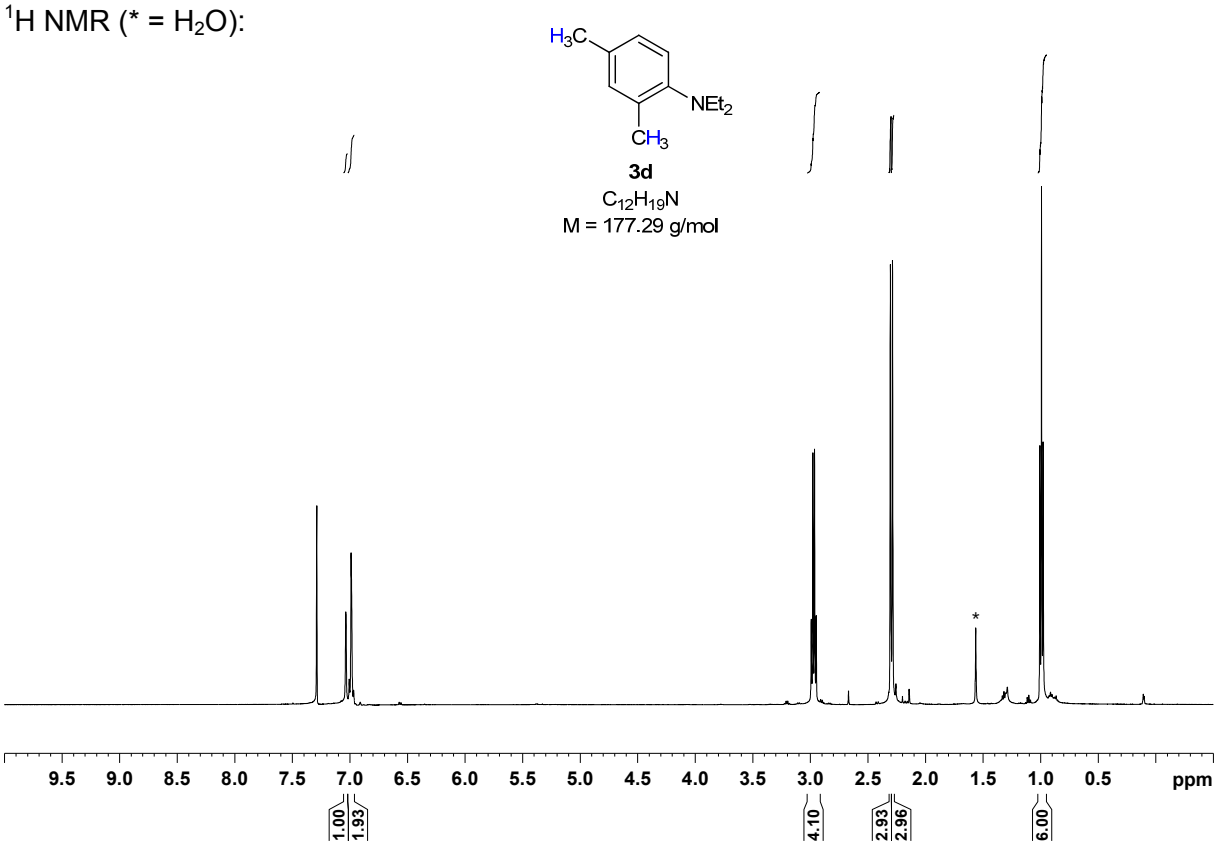


^{13}C NMR:

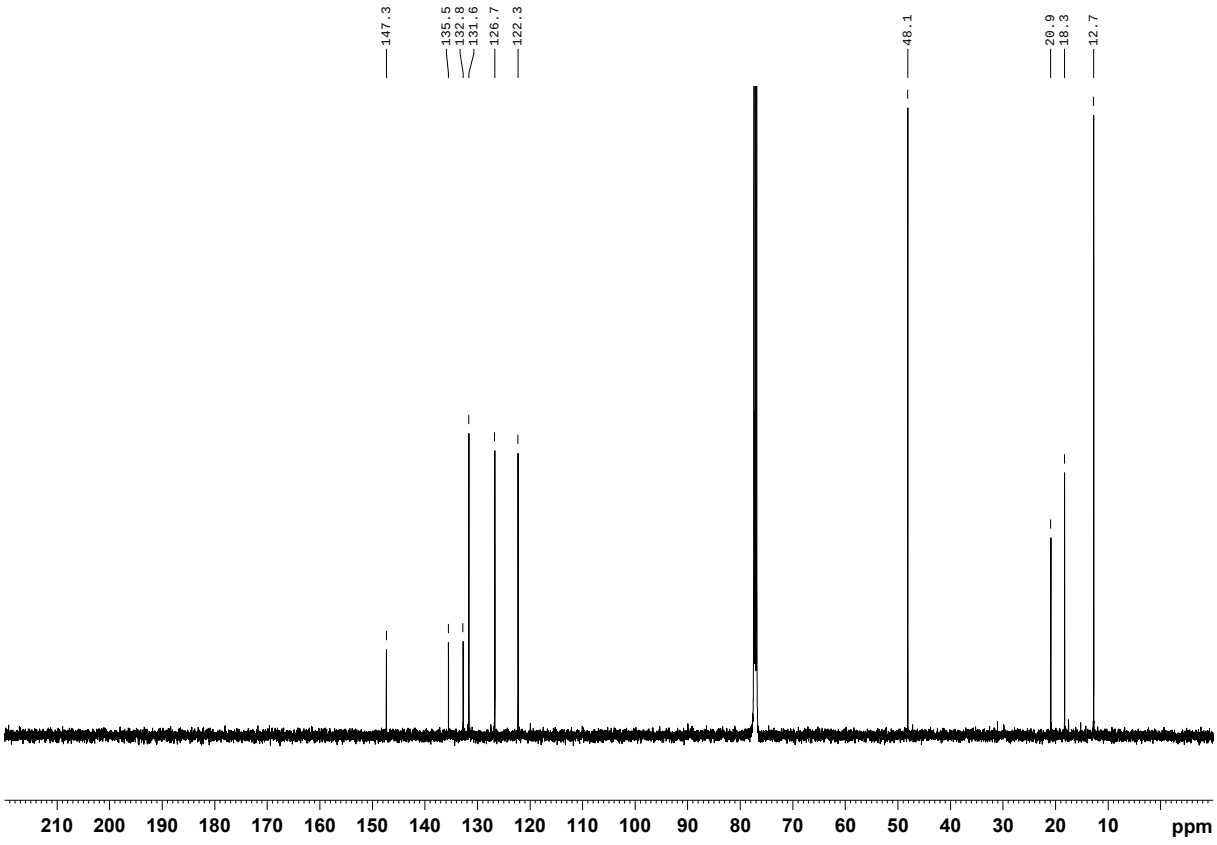


_N_,_N_-Diethyl-2,4-dimethylaniline (3d)

^{1}H NMR (* = H_2O):

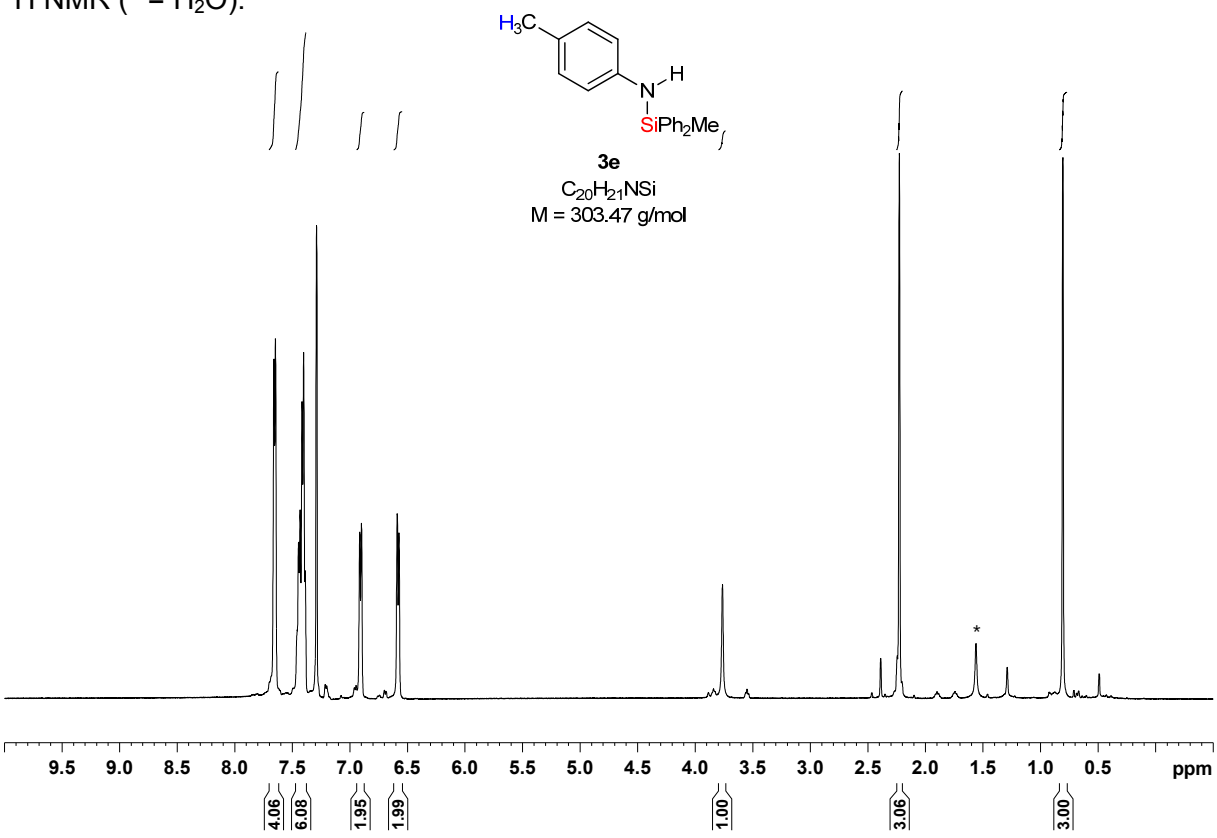


^{13}C NMR:

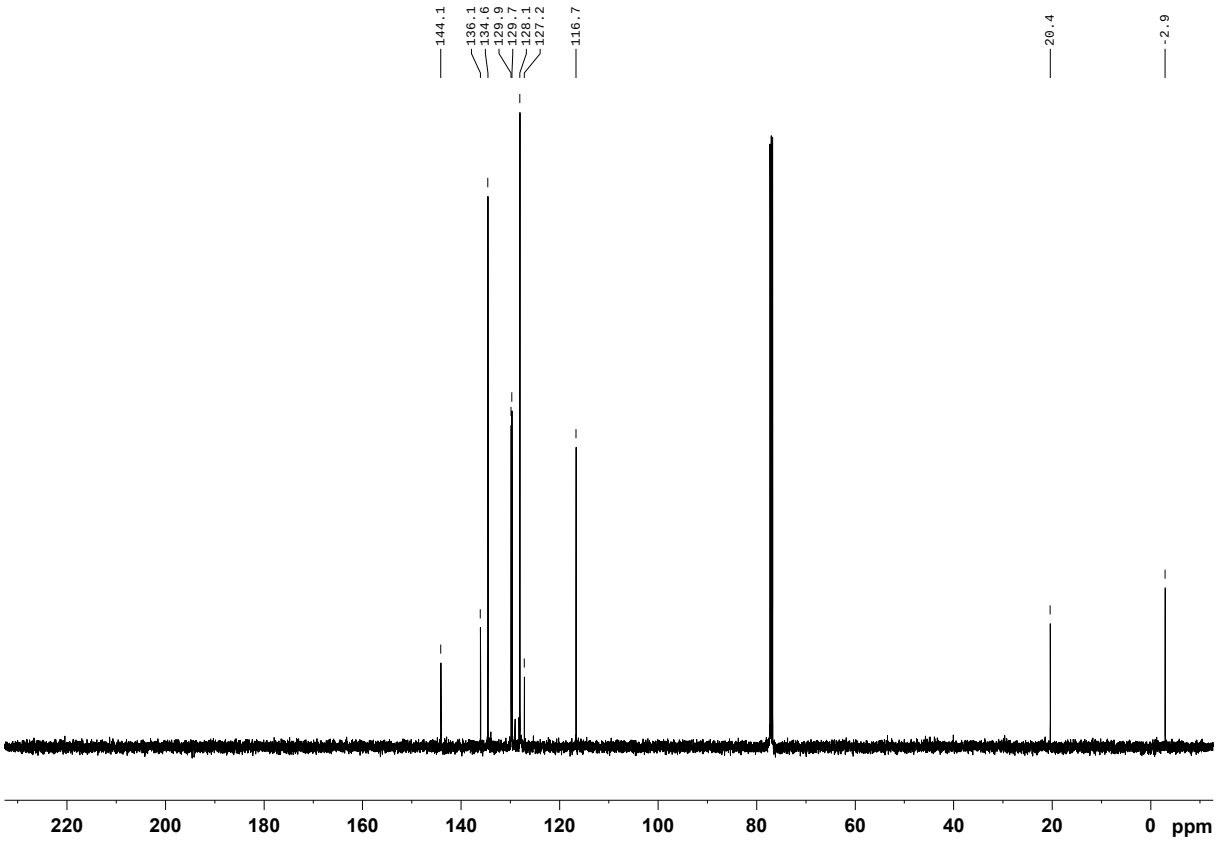


N-(Diphenylmethylsilyl)-4-toluidine (3e)

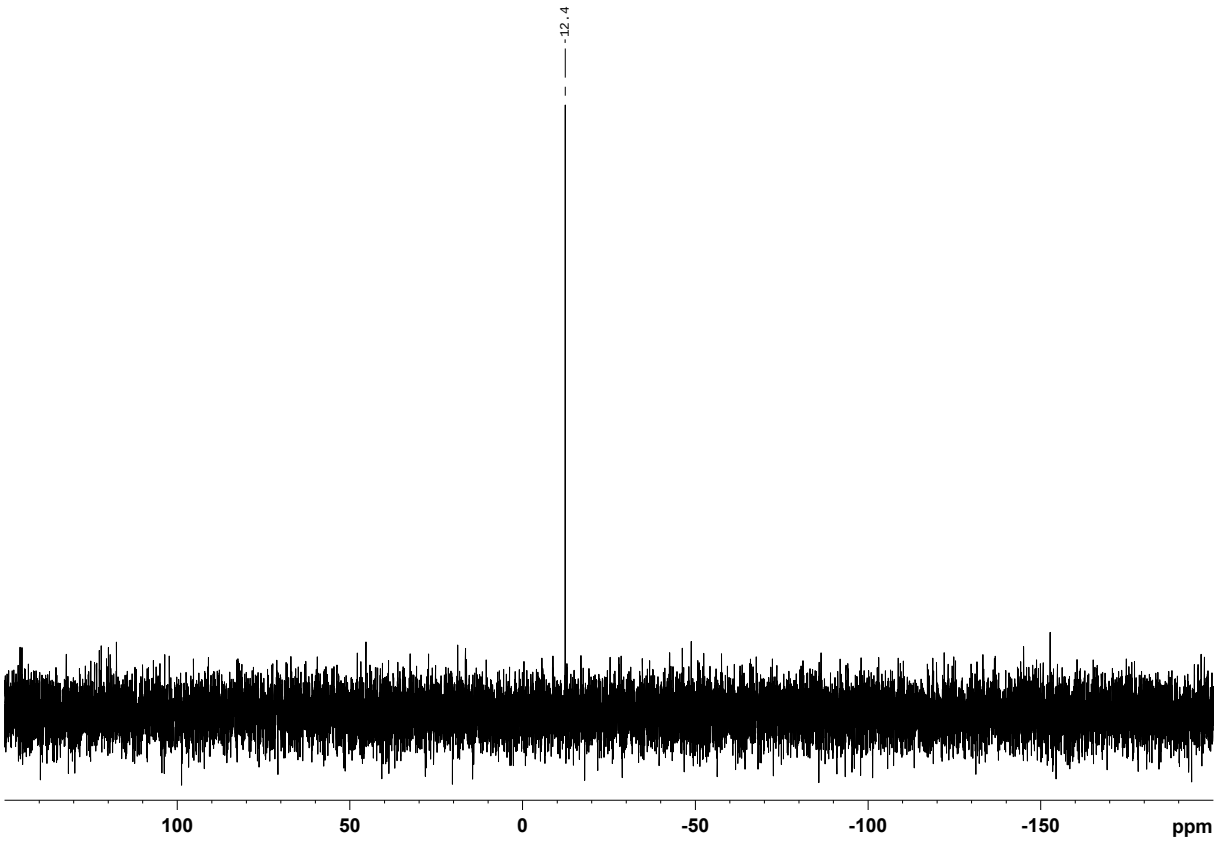
^{1}H NMR (* = H_2O):



^{13}C NMR:



^{29}Si NMR:



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