Supporting Information

Ruthenium-NHC complex-catalyzed P(III)-directed C-H borylation of Arylphosphines

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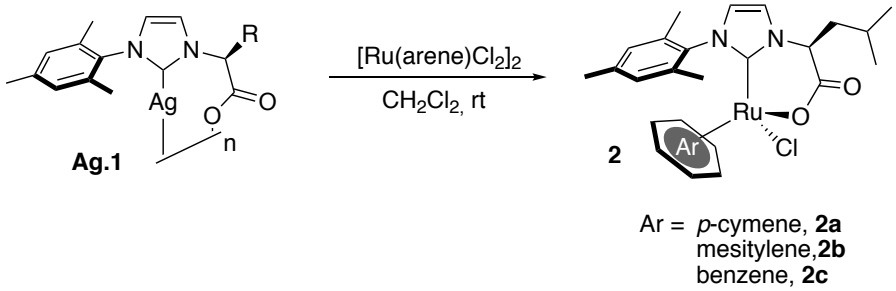
1. General remarks

Unless indicated otherwise, all reactions requiring an inert atmosphere were conducted using standard Schlenk technique. All solvents were distilled and degassed prior to use. [Ru(*p*-cymene)Cl_2]$_2$ (CAS: 12092-47-6) and [Ru(benzene)Cl_2]$_2$ (CAS: 12092-47-6) were purchased from Strem Chemicals. [Ru(mesitylene)Cl_2]$_2$ (CAS: 12092-47-6) was synthesized according to the reported procedure. Pinacolborane (HBpin) was purchased from Fluorochem. All phosphine substrates were obtained from commercial sources and used as received. Other chemicals were used as received unless otherwise noted. Silica gel chromatography was performed with Sigma-Aldrich's silica gel high-purity grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size. Products were visualized using a 254 nm UV lamp on TLC plates unless otherwise noted. Unless indicated otherwise, NMR spectra were acquired on 400 MHz Bruker instruments at Laboratoire de Chimie de Coordination, Toulouse. Chemicals shifts were reported relative to residual solvent peaks ($CDCl_3$ = 7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C; C_6D_6 = 7.16 ppm for ^{1}H and 128.06 ppm for ^{13}C; CD_3CN = 1.94 ppm for ^{1}H and 118.26 and 1.32 ppm for ^{13}C). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, br = broad. NMR yields were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethybenzene as an internal standard unless otherwise noted. Mass spectrometric analyses and elemental analyses were performed at Institut de Chimie de Toulouse. Xray diffraction data were collected on D8 Venture Bruker AXS diffractometer.

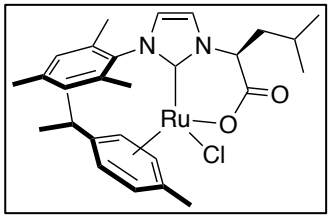
2. Synthesis of ruthenium-NHC complexes 2a-2c.



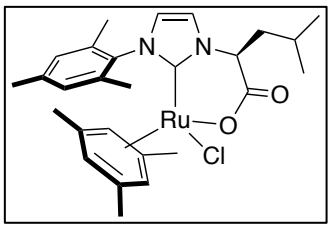
Scheme S1. Synthesis of complexes 2a-2c

*Procedure A for **2a** and **2b***

In a dry round-bottomed flask were placed an equivalence of corresponding silver complex[1] (which is considered as a dimer), [Ru(*p*-cymene)Cl_2]$_2$ or [Ru(mesitylene)Cl_2]$_2$ in CH_2Cl_2 (0.0077 M). The mixture was stirred at room temperature for 24 h under Ar atmosphere excluding from the light. Next, CH_2Cl_2 was removed under reduced pressure. Then, acetone was added, and the mixture was filtered through a celite pad using acetone as eluent. Then the filtrate was re-filtered over a microfilter. Then acetone was evaporated, and pentane was added to induce precipitation. The complex was washed twice with pentane and volatiles were then removed under vacuum.



Complex **2a** was purified by flash column chromatography on silica gel (Acetone:CH_2Cl_2 = 1:1) and obtained as red solid. (94% yield). **For both isomers: ^{1}H NMR (400 MHz, Chloroform-d)** δ 7.14 (s, 3H), 7.12 (s, 3H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.07 (bs, 2H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 5.55 (d, *J* = 6.7 Hz, 1H), 5.50 (bs, 1H), 5.39 (d, *J* = 5.0 Hz, 2H), 5.10 – 5.07 (m, 1H), 5.06 – 5.03 (m, 2H), 4.61 – 4.57 (m, 1H), 3.54 (s, 3H), 3.01 (bs, 1H), 2.77 – 2.71 (m, 1H), 2.69 – 2.61 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.36 – 2.31 (m, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.09 – 2.03 (m, 1H), 1.80 (s, 6H), 1.85 – 1.70 (m, 4H), 1.15 (s, 3H), 1.13 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.1 Hz, 3H). **For both isomers: ^{13}C NMR (101 MHz, Chloroform-d)** δ 173.5, 172.4, 172.2, 170.9, 140.3, 140.3, 138.4, 138.1, 137.6, 137.5, 135.3, 135.2, 129.8, 129.8, 129.1, 129.1, 123.1, 122.8, 121.9, 121.0, 102.5, 101.1, 95.1, 94.8, 94.0, 93.7, 81.0, 78.6, 64.8, 61.1, 46.9, 41.3, 29.7, 29.4, 25.1, 25.0, 23.8, 23.1, 23.0, 22.8, 22.6, 22.5, 21.3, 21.3, 21.1, 20.4, 19.0, 18.9, 18.3, 18.2, 17.9, 17.9 **HRMS (ESI)** calcd for $C_{28}H_{38}ClN_2O_2Ru$-$[M+H]^+$: 571.1660; found: 571.1662. The crystallization in concentrated solution in dichloromethane provides the suitable crystal for X-ray crystallography.

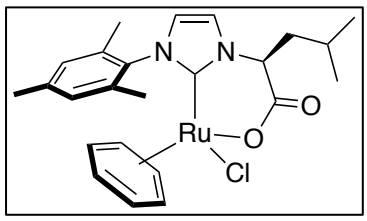


Complex **2b** was purified by flash column chromatography on silica gel (MeOH:CH_2Cl_2 = 5:95) and obtained as red solid (87% yield). **For major isomer: ^{1}H NMR (400 MHz, Chloroform-d)** δ 7.04 (s, 1H), 7.01 (s, 1H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 4.78 (s, 3H), 4.67 (dd, *J* = 9.2, 5.4 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 2.21 (s,

3H), 2.02 – 1.96 (m, 1H), 1.92 (s, 9H), 1.86 – 1.75 (m, 1H), 1.69 – 1.59 (m, 1H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H). **For minor isomer: ^{1}H NMR (400 MHz, Chloroform-d)** δ 7.09 (d, *J* = 2.0 Hz, 1H), 7.04 (bs, 1H), 7.00 (bs,1H), 6.91 (d, *J* = 2.0 Hz, 1H), 4.79 (s, 3H), 4.60 – 4.56 (m, 1H), 2.42 – 2.39 (m, 1H), 2.36 (s, 3H), 2.24 (s, 3H), 2.14 (s, 3H), 2.02 – 1.96 (m, 1H), 1.94 (s, 9H), 1.86 – 1.75 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H). **For major isomer: ^{13}C NMR (101 MHz, Chloroform-d)** δ 175.7, 172.5, 139.5, 139.1, 136.5, 135.4, 130.2, 127.8, 123.9, 122.9, 98.0, 85.6, 64.6, 45.7, 24.7, 23.1, 22.0, 21.0, 20.2, 19.1, 18.4. **For minor isomer: ^{13}C NMR (101 MHz, Chloroform-d)** δ 176.9, 172.7, 139.3, 139.1, 136.4, 134.4, 129.9, 128.0, 123.6, 120.3, 97.8, 85.9, 62.9, 41.7, 25.2, 23.0, 22.6, 21.1, 20.1, 19.3, 18.3. **HRMS (ESI)** calcd for $C_{27}H_{36}ClN_2O_2Ru$-$[M+H]^+$: 556.1431; found: 556.1428. The crystallization in bilayer of dichloromethane and pentane provides the suitable crystal for X-ray crystallography.

*Procedure B for **2c***

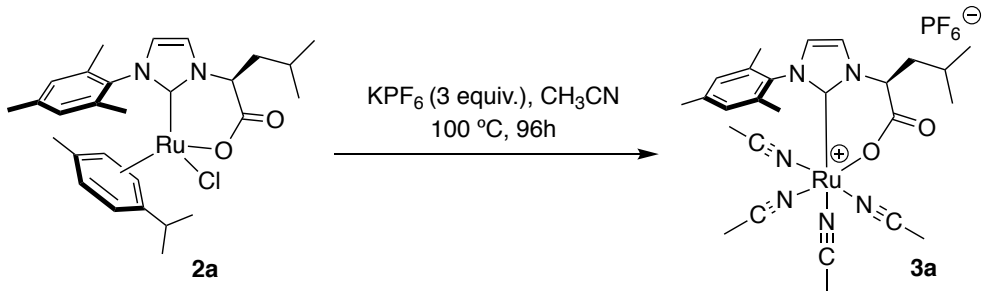
In a dry Schlenk flask were placed an equivalence of corresponding silver complex[1] (which is considered as a dimer) and $[Ru(benzene)Cl_2]_2$ in C_6H_6 (0.0077 M). The mixture was stirred for 24 h under Ar atmosphere excluding from the light. Then, the mixture was filtered via cannula using benzene as eluent. The volatiles were gently removed under reduced pressure affording a red solid. The obtained solid was promptly stored at -15 °C in the glovebox and stable for approximately 2 weeks. The complex tends to decompose in the solution at room temperature.



Complex **2c** was obtained as red solid (75% yield). **For major isomer: ^{1}H NMR (400 MHz, Chloroform-d)** δ 7.11 (bs, 2H), 7.08 (s, 1H), 6.93 (d, *J* = 1.7 Hz, 1H), 5.14 (s, 6H), 5.10 – 5.06 (m, 1H), 2.41 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H), 2.10 – 2.06 (m, 1H), 1.85 – 1.78 (m, 1H), 1.77 – 1.75 (m, 1H), 0.96 (d, *J* = 3.9 Hz, 3H), 0.95 (d, *J* = 5.4 Hz, 3H). **For minor isomer: ^{1}H NMR (400 MHz, Chloroform-d)** δ 7.11 (bs, 1H), 7.07 (s, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 5.10 (s, 6H), 4.61 (dd, *J* = 8.5, 6.1 Hz, 1H), 2.41 (s, 6H), 2.38 – 2.34 (m, 1H), 2.26 (s, 3H), 2.16 (s, 3H), 1.85 – 1.78 (m, 1H), 1.73 – 1.69 (m, 1H), 0.98 (d, *J* = 5.0 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). **For major isomer: ^{13}C NMR (101 MHz, Chloroform-d)** δ 173.1, 171.6, 140.5, 137.9, 137.2, 135.4, 130.0, 129.0, 122.4, 121.4, 86.4, 61.5, 41.9, 25.1, 22.8, 22.8, 21.3, 18.9, 18.1. **For minor isomer: ^{13}C NMR (101 MHz,**

Chloroform-d) δ 172.6, 169.5, 140.5, 138.1, 137.5, 135.4, 129.8, 129.2, 123.1, 123.1, 86.7, 64.7, 47.3, 25.1, 22.9, 22.5, 21.3, 18.8, 18.3. **HRMS (ESI)** calcd for $C_{24}H_{30}ClN_2O_2Ru$-$[M+H]^+$: 515.1034; found: 515.1033. The crystallization in concentrated solution in benzene inside glovebox provides the suitable crystal for X-ray crystallography.

3. Synthesis of ruthenium complex 3a

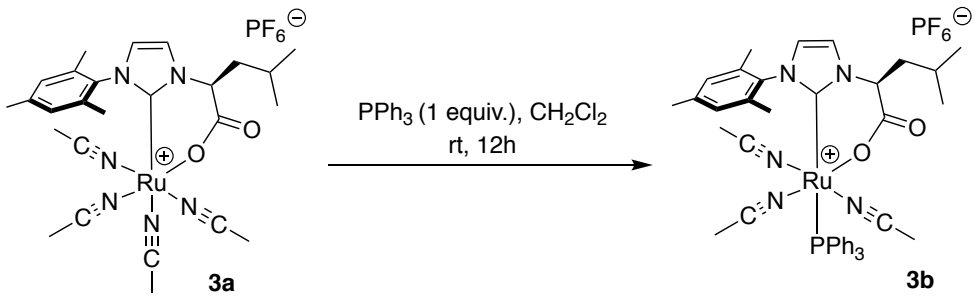


Scheme S2. Synthesis of complex 3a.

CH_3CN was dried, distilled and degassed prior to use. KPF_6 was dried under vacuum at 80 ºC overnight.

In a flamed-dried Schlenk flask were added, **2a** (57.1 mg, 0.1 mmol), dry KPF_6 (55.2 mg, 0.3 mmol). The Schlenk tube was evacuated and back-filled with Ar. Then dry CH_3CN (5 mL) was added. The red mixture was heated at 100 ºC. After 96h, the mixture turned to yellow. After cooled down, the mixture was filtered via cannula using dry CH_3CN as eluent. The volatiles were gently removed under reduced pressure, and the residue was promptly transferred to the glovebox. To the residue was added minimal amount of dry pentane to obtain an off-white solid after trituration and filtration. The solid dissolved in CH_2Cl_2 was further filtered to yield compound **3a** after removal of volatiles (80% yield). **^{1}H NMR (300 MHz, Dichloromethane-d_2)** δ 7.14 (d, *J* = 2.0 Hz, 1H), 7.02 (s, 1H), 6.98 (s, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 4.75 (t, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 2.32 (s, 6H), 2.09 (s, 3H), 1.97 (s, 3H), 1.94 – 1.92 (m, 1H), 1.91 (s, 3H), 1.79 – 1.73 (m, 1H), 1.72 – 1.63 (m, 1H), 0.99 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (101 MHz, Dichloromethane-d_2)** δ 178.2, 174.0, 139.5, 137.4, 137.3, 135.8, 129.4, 129.0, 124.4, 123.8, 123.7, 123.6, 122.9, 120.5, 65.0, 47.3, 25.2, 22.7, 22.7, 21.1, 17.7, 17.6, 4.6, 4.4, 4.3, 3.9. **^{31}P NMR (162 MHz, Dichloromethane-d_2)** δ -144.5 (hept, *J* = 710.7 Hz). **^{19}F NMR (376 MHz, Dichloromethane-d_2)** δ -72.9 (d, *J* = 714.4 Hz). **HRMS (ESI)** calculated for $C_{26}H_{35}N_6O_2Ru$ - $[M]^+$: 565.1865; found: 565.1877. $[\alpha]_D^{20}$ = -13.5 (CH_2Cl_2, 2.45 10^{-2} $mol.L^{-1}$).

4. Synthesis of ruthenium complex 3b

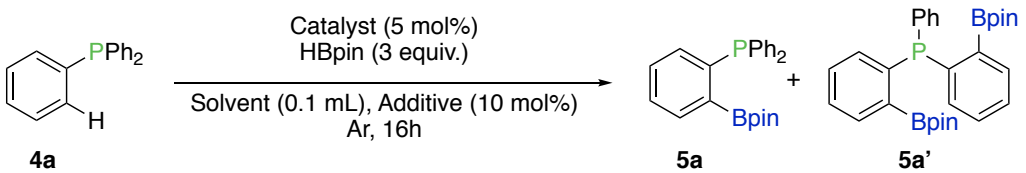


Scheme S3. Synthesis of complex 3b.

In a flamed-dried Schlenk flask were placed an equivalence of **3a** and PPh_3 in CH_2Cl_2 (0.0077 M). The mixture was stirred at room temperature overnight under Ar atmosphere. Next, CH_2Cl_2 was gently removed under vacuum. Then, dry diethyl ether was added to induce precipitation. The complex was washed twice with diethyl ether and volatiles were then removed under vacuum. The complex **3b** was obtained as off-white solid in a quantitative yield.

^{1}H NMR (400 MHz, Dichloromethane-d$_2$) δ 7.60 – 7.56 (m, 6H), 7.47 – 7.40 (m, 9H), 7.23 (d, *J* = 1.8 Hz, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 6.91 (d, *J* = 1.1 Hz, 1H), 4.83 (t, *J* = 7.4 Hz, 1H), 2.25 (s, 3H), 2.10 (s, 3H), 2.08 – 2.07 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.90 – 1.83 (m, 1H), 1.82 – 1.74 (m, 1H), 1.23 (s, 3H), 1.05 (d, *J* = 5.3 Hz, 3H), 1.04 (d, *J* = 5.3 Hz, 3H). **^{13}C NMR (101 MHz, Dichloromethane-d$_2$)** δ 176.5 (d, *J* = 101 Hz), 173.3, 139.4, 137.3, 137.1, 135.5, 134.3 (d, *J* = 10.1 Hz), 132.0 (d, *J* = 30.3 Hz), 130.4 (d, *J* = 10.1 Hz), 129.4, 129.3, 128.9 (d, *J* = 10.1 Hz), 126.3, 125.8, 124.8, 123.9 (d, *J* = 10.1 Hz), 123.8 (d, *J* = 10.1 Hz), 64.8, 46.7, 25.4, 23.0, 22.7, 21.1, 17.8, 17.6, 4.5, 4.1, 4.1. **^{31}P NMR (162 MHz, Dichloromethane-d$_2$)** δ 27.3, -144.5 (hept, *J* = 712.8 Hz). **^{19}F NMR (376 MHz, Dichloromethane-d$_2$)** δ -73.1 (d, *J* = 676.8 Hz). **HRMS (ESI)** calcd for $C_{42}H_{47}N_5O_2RuP$ - $[M]^+$: 786.2511; found: 786.2510.

5. Optimization studies



In a flame-dried Schlenk tube were placed 0.2 mmol of triphenylphosphine (PPh_3, **4a**), ruthenium catalyst (0.01 mmol, 5 mol%), KPF_6 (0.02 mmol, where necessary). The tube was evacuated and back-filled with argon 3 times. Then, HBpin (0.6 mmol) and solvent (0.1 mL,

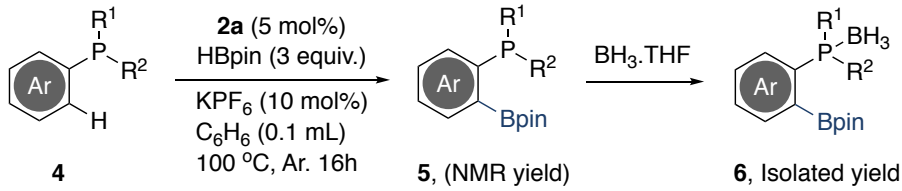
where necessary) were added. The tube was closed with a screw cap. Then the mixture was stirred in a pre-heated oil bath at stated temperature with 300 rpm for 16h. After cooled down, the residue was diluted with $CDCl_3$. The crude residue was analyzed by ^1H and ^{31}P. % conversion was determined from ^{31}P spectrum, and NMR yield was determined versus 1,3,5-trimethylbenzene as an internal standard.

Table S1. Optimization of the reaction conditions

Entry	Catalyst	Solvent	Additive	Temp.(°C)	Conv.	NMR yield (%)	
						5a[a]	**5a'**[b]
1	**3a**	neat	-	110	87	65	8
2	**3b**	neat	-	110	90	72	12
3	**2a**	neat	-	110	92	76	16
4	**2a**	neat	KPF_6	110	94	87	7
5[c]	**2a**	neat	KPF_6	110	86	79	5
6[d]	**2a**	neat	KPF_6	110	4	-	-
7[e]	**2a**	neat	KPF_6	110	88	80	8
8[f]	**2a**	neat	KPF_6	110	89	84	5
9	**2a**	neat	$NaB(C_6F_5)_3$	110	88	77	3
10	**2b**	neat	KPF_6	110	81	55	26
11	**2c**	neat	KPF_6	110	76	66	10
12	**2a**	neat	KPF_6	100	86	73	9
13	**2a**	toluene	KPF_6	100	96	84	4
14	**2a**	1,4-dioxane	KPF_6	100	97	88	3
15	**2a**	C_6H_6	KPF_6	100	98	90	3
16	**2a**	C_6H_6	KPF_6	90	80	78	-
17	**2a**	C_6H_6	KPF_6	80	16	14	-
18[g]	**2a**	C_6D_6	KPF_6	rt	64	30	-
19	**none**	C_6H_6	KPF_6	100	6	-	-

[a] Analytical data for **5a** were consistent with previously reported data.[3] [b] Analytical data for **5a'** were consistent with previously reported data.[2] [c] HBpin (2 equiv.). [d] with 3 equiv. B_2pin_2. [e] KPF_6 (5 mol%). [f] KPF_6 (20 mol%). [g] Irradiated with UV-light (λ_{max} = 365 nm) for 72 h at room temperature.

6. Scope of substrates

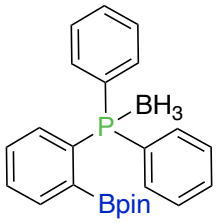


4 **5**, (NMR yield) **6**, Isolated yield

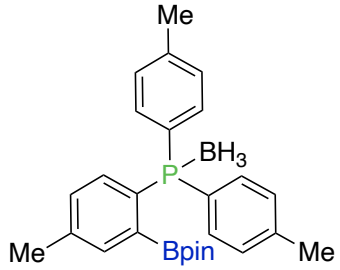
In a flame-dried 15 mL schlenk tube were placed 0.2 mmol of phosphine **4** (if solid), **2a** (0.01 mmol, 5 mol%), KPF_6 (0.02 mmol). The tube was evacuated and back-filled with argon 3 times. Then, HBpin (0.6 mmol), phosphine **4** (0.2 mmol, if liquid), and C_6H_6 (0.1 mL) were added. The tube was closed with a screw cap. Then the mixture was stirred in a pre-heated oil bath at 100 °C with 300 rpm for 16h [Caution is called for with reaction under pressure]. After cooled down, under a strong flush of Ar, dried 1,3,5-trimethylbenzene and ca. 1 mL of dried $CDCl_3$ were added. The crude residue was analyzed by ^1H and ^{31}P. % conversion was determined from ^{31}P spectrum, and NMR yield was determined versus 1,3,5-trimethylbenzene as an internal standard.

Under a strong flush of Ar, to the crude residue was added 1 mL of dried THF. Then 1 mL of BH_3 (1.0 M in THF) was added at once. The mixture was stirred at room temperature under Ar for 2h. After removal of volatiles, the residue was subjected to a flash column chromatography over silica gel.

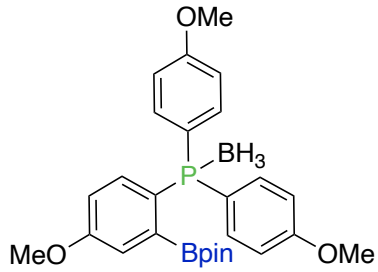
*Characterization of products **5** or **6***



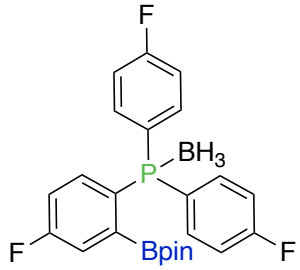
Compound **6a** was obtained as white solid (81% yield). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.96 – 7.87 (m, 1H), 7.74 – 7.60 (m, 4H), 7.51 – 7.44 (m, 3H), 7.43 – 7.33 (m, 5H), 7.32 – 7.21 (m, 1H), 1.02 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 136.8 (d, J = 11.4 Hz), 134.6 (d, J = 10.5 Hz), 134.5 (d, J = 55 Hz) 133.6 (d, J = 9.3 Hz), 130.7 (d, J = 2.5 Hz), 130.7 (d, J = 58 Hz), 130.2 (d, J = 10.0 Hz), 130.0 (d, J = 2.5 Hz), 128.50 (d, J = 10.2 Hz), 84.0, 24.7. **^{31}P NMR (162 MHz, Chloroform-d)** δ 24.8. **^{11}B NMR (128 MHz, Chloroform-d)** δ 31.1, -36.2. Analytical data for this compound were consistent with previously reported data.[3]



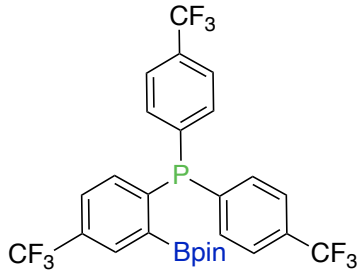
Compound **6b** was obtained as white solid (70% yield). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.70 (s, 1H), 7.60 – 7.48 (m, 4H), 7.24 – 7.13 (m, 6H), 2.38 (s, 6H), 2.37 (s, 3H), 1.04 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 140.7 (d, *J* = 2.3 Hz), 139.9 (d, *J* = 2.6 Hz), 137.3 (d, *J* = 11.6 Hz), 134.6 (d, *J* = 11.0 Hz), 133.4 (d, *J* = 9.7 Hz), 131.5 (d, *J* = 57.5 Hz), 130.6 (d, *J* = 10.4 Hz), 129.0 (d, *J* = 10.6 Hz), 127.6 (d, *J* = 59.7 Hz), 83.8, 24.6, 21.4 (d, *J* = 1.2 Hz), 21.2 (d, *J* = 1.4 Hz). **^{31}P NMR (162 MHz, Chloroform-d)** δ 22.5. **^{11}B NMR (128 MHz, Chloroform-d)** δ 31.0, -36.2. Analytical data for this compound were consistent with previously reported data.[3]



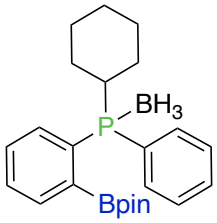
Compound **6c** was obtained as white solid (72% yield). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.61 – 7.52 (m, 4H), 7.42 – 7.38 (m, 1H), 7.21 (dd, *J* = 11.8, 8.6 Hz, 1H), 6.92 (dd, *J* = 8.8, 1.8 Hz, 4H), 6.88 – 6.82 (m, 1H), 3.82 (s, 3H), 3.82 (s, 6H), 1.05 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 161.6 (d, *J* = 2.2 Hz), 160.6 (d, *J* = 2.4 Hz), 136.4 (d, *J* = 12.2 Hz), 135.1 (d, *J* = 10.6 Hz), 125.7 (d, *J* = 61.0 Hz), 122.6 (d, *J* = 13.0 Hz), 122.2 (d, *J* = 63.6 Hz), 114.8 (d, *J* = 11.0 Hz), 114.0 (d, *J* = 11.1 Hz), 84.0, 55.5, 55.3, 24.8. **^{31}P NMR (162 MHz, Chloroform-d)** δ 20.4. **^{11}B NMR (128 MHz, Chloroform-d)** δ 31.0, -36.0. Analytical data for this compound were consistent with previously reported data.[3]



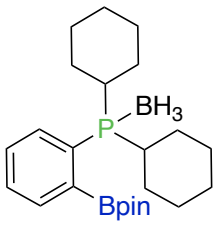
Compound **6d** was obtained as white solid (33% yield). **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.69 – 7.54 (m, 5H), 7.26 – 7.18 (m, 1H), 7.17 – 7.09 (m, 4H), 7.09 – 7.03 (m, 1H), 1.06 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 164.5 (dd, *J* = 253,51, 2.7 Hz), 164.1 (dd, *J* = 254,52, 2.7 Hz), 136.8 (dd, *J* = 12.1, 7.8 Hz), 135.7 (dd, *J* = 10.9, 8.5 Hz), 129.7 (d, *J* = 58.1, 3.5 Hz), 126.0 (dd, *J* = 60.1, 3.5 Hz), 124.3 (dd, *J* = 20.2, 12.7 Hz), 117.1 (dd, *J* = 20.5, 11.3 Hz), 116.0 (dd, *J* = 21.3, 11.3 Hz), 84.5, 24.7. **^{31}P NMR (162 MHz, Chloroform-d)** δ 23.1. **^{11}B NMR (128 MHz, Chloroform-d)** δ 30.1, -35.9. **^{19}F NMR (162 MHz, Chloroform-d)** δ -108.5 (d, *J* = 2.4 Hz), -109.6 (d, *J* = 2.6 Hz). Analytical data for this compound were consistent with previously reported data.[3]



Compound **5e** was obtained as white solid (41 %yield). **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.10 (s, 1H), 7.64 – 7.58 (m, 4H), 7.55 (d, *J* = 8.1, 2.2, 0.7 Hz, 1H), 7.45 – 7.35 (m, 4H), 6.88 (dd, *J* = 8.1, 4.0 Hz, 1H), 1.12 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 147.0 (d, *J* = 21.8 Hz), 142.0 (d, *J* = 15.1 Hz), 134.5 (d, *J* = 20.7 Hz), 132.6 (q, *J* = 5.4, 2.8 Hz), 131.4 (q, *J* = 32.5 Hz), 130.2 (q, *J* = 32.7 Hz), 127.5 (q, *J* = 3.8 Hz), 125.82 – 125.38 (m), 124.1 (q, *J* = 272 Hz), 124.0 (q, *J* = 273 Hz), 84.8, 24.6. **^{31}P NMR (162 MHz, Chloroform-d)** δ -4.7. **^{11}B NMR (128 MHz, Chloroform-d)** δ 31.0. **^{19}F NMR (162 MHz, Chloroform-d)** δ –62.9. Analytical data for this compound were consistent with previously reported data[4]



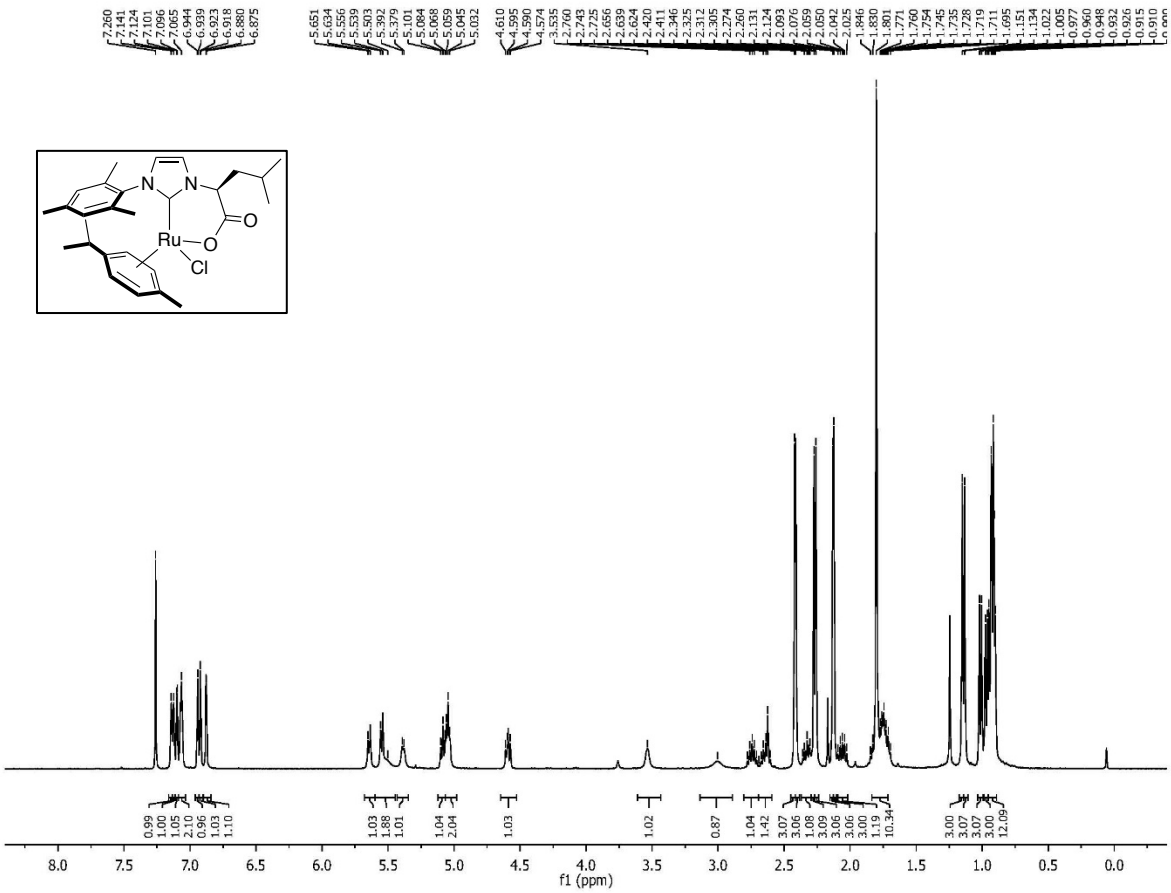
Compound **6f** was obtained as white solid (35% yield). **^{1}H NMR (400 MHz, Chloroform-d)** ^{1}H NMR (400 MHz, Chloroform-d) δ 8.16 (ddd, *J* = 13.2, 7.6, 1.4 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.58 – 7.43 (m, 4H), 7.40 – 7.28 (m, 3H), 3.22 – 3.04 (m, 1H), 2.14 – 2.00 (m, 1H), 1.96 – 1.82 (m, 1H), 1.82 – 1.63 (m, 3H), 1.53 – 1.42 (m, 1H), 1.40 – 1.18 (m, 4H), 1.13 (s, 6H), 1.07 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 136.8 (d, *J* = 9.1 Hz), 136.3 (d, *J* = 16.5 Hz), 133.2 (d, *J* = 51.4 Hz), 132.3 (d, *J* = 8.3 Hz), 131.8, 130.4 (d, *J* = 12.0 Hz), 130.1 (d, *J* = 2.6 Hz), 129.9 (d, *J* = 2.4 Hz), 128.1 (d, *J* = 9.7 Hz), 84.2, 33.4 (d, *J* = 33.7 Hz), 28.9, 27.5, 27.3 (d, *J* = 5.1 Hz), 27.2 (d, *J* = 4.7 Hz), 26.0 (d, *J* = 1.6 Hz), 25.2, 24.5. **^{31}P NMR (162 MHz, Chloroform-d)** δ 28.4 (d, *J* = 78.1 Hz). **^{11}B NMR (128 MHz, Chloroform-d)** δ 31.1, -38.6. Analytical data for this compound were consistent with previously reported data.[3]



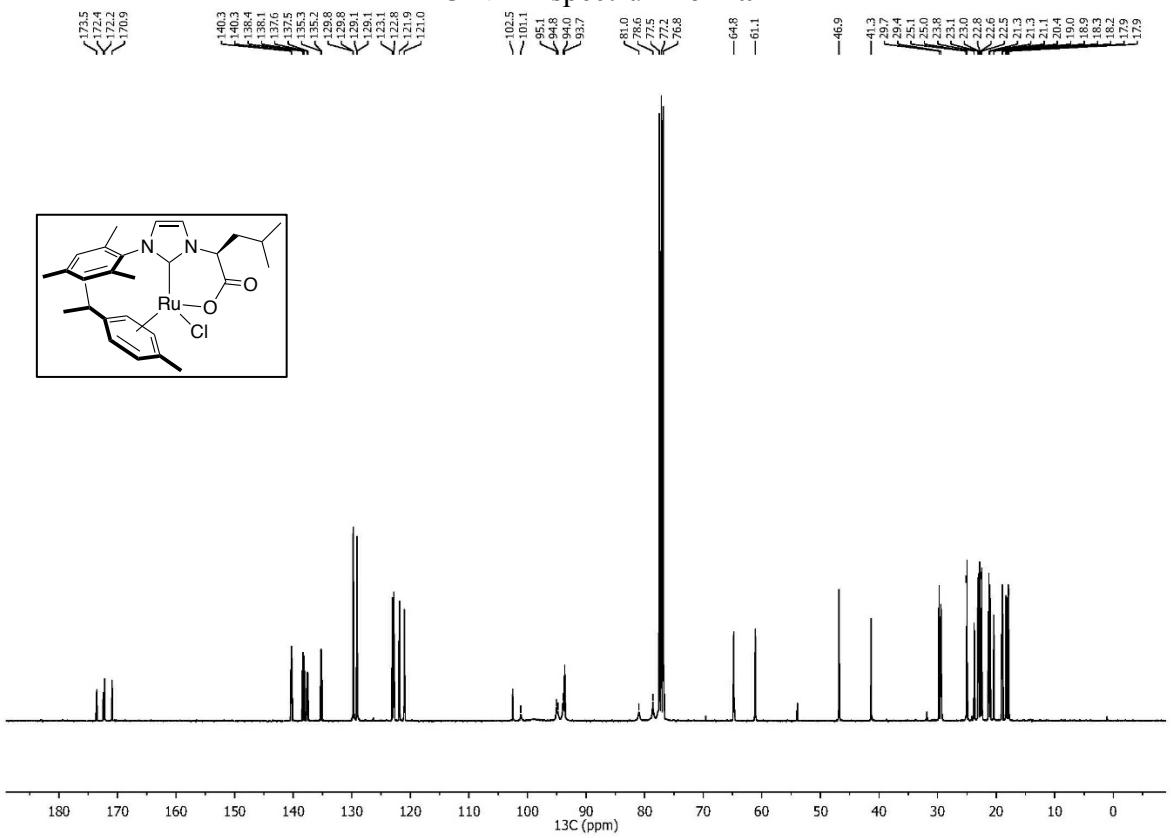
Compound **6i** was obtained as white solid (32% yield). **^{1}H NMR (400 MHz, Chloroform-d)** ^{1}H NMR (400 MHz, Chloroform-d) δ 8.16 – 8.04 (m, 1H), 7.94 – 7.86 (m, 1H), 7.51 – 7.39 (m, 2H), 2.76 – 2.60 (m, 2H), 2.01 – 1.91 (m, 2H), 1.90 – 1.76 (m, 2H), 1.70 – 1.59 (m, 6H), 1.42 (s, 12H), 1.32 – 1.03 (m, 10H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 137.4 (d, *J* = 16.9 Hz), 136.9 (d, *J* = 8.1 Hz), 133.2 (d, *J* = 47.7 Hz), 130.5 (d, *J* = 12.2 Hz), 129.7 (d, *J* = 2.5 Hz), 84.5, 33.9 (d, *J* = 32.9 Hz), 28.7, 27.7, 27.2 (dd, *J* = 13.4, 11.5 Hz), 26.0 (d, *J* = 1.5 Hz), 25.2. **^{31}P NMR (162 MHz, Chloroform-d)** δ 33.9 (d, *J* = 89.1 Hz). **^{11}B NMR (128 MHz, Chloroform-d)** δ 31.4, -43.6. Analytical data for this compound were consistent with previously reported data.[3]

7. NMR Spectra

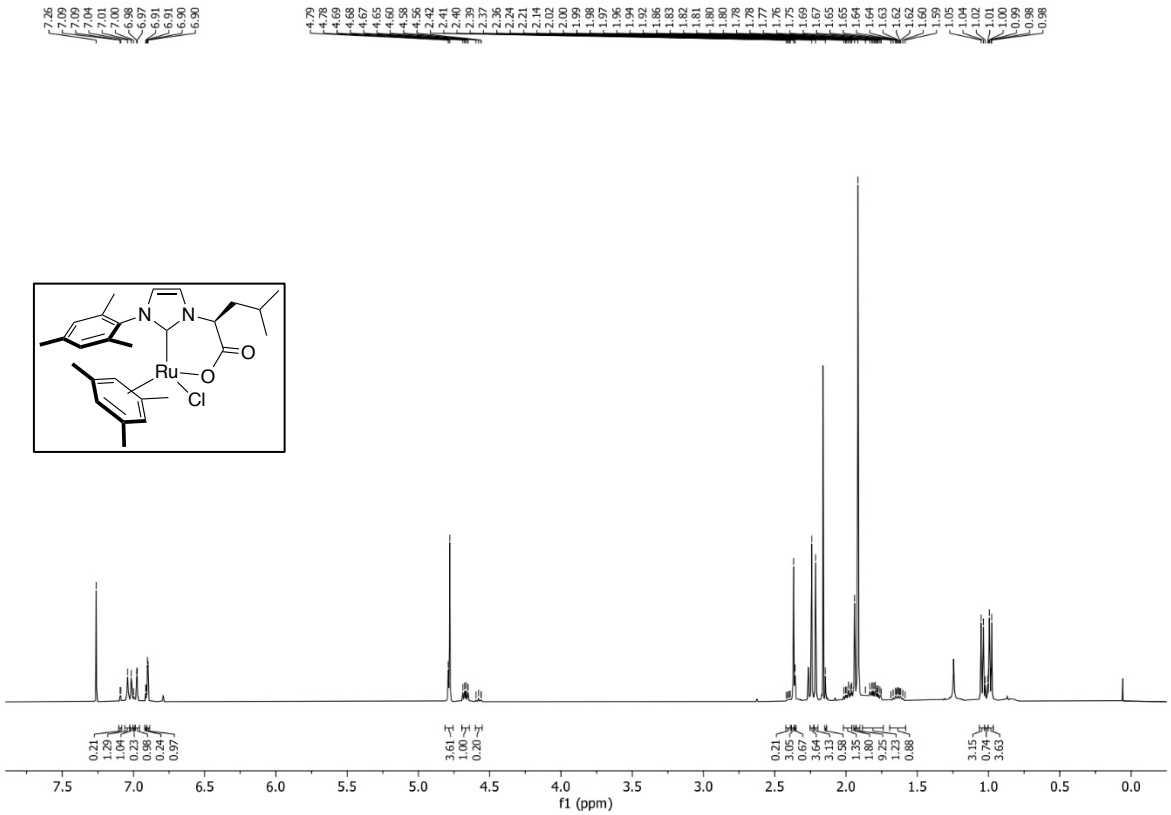
^{1}H NMR spectrum for **2a**



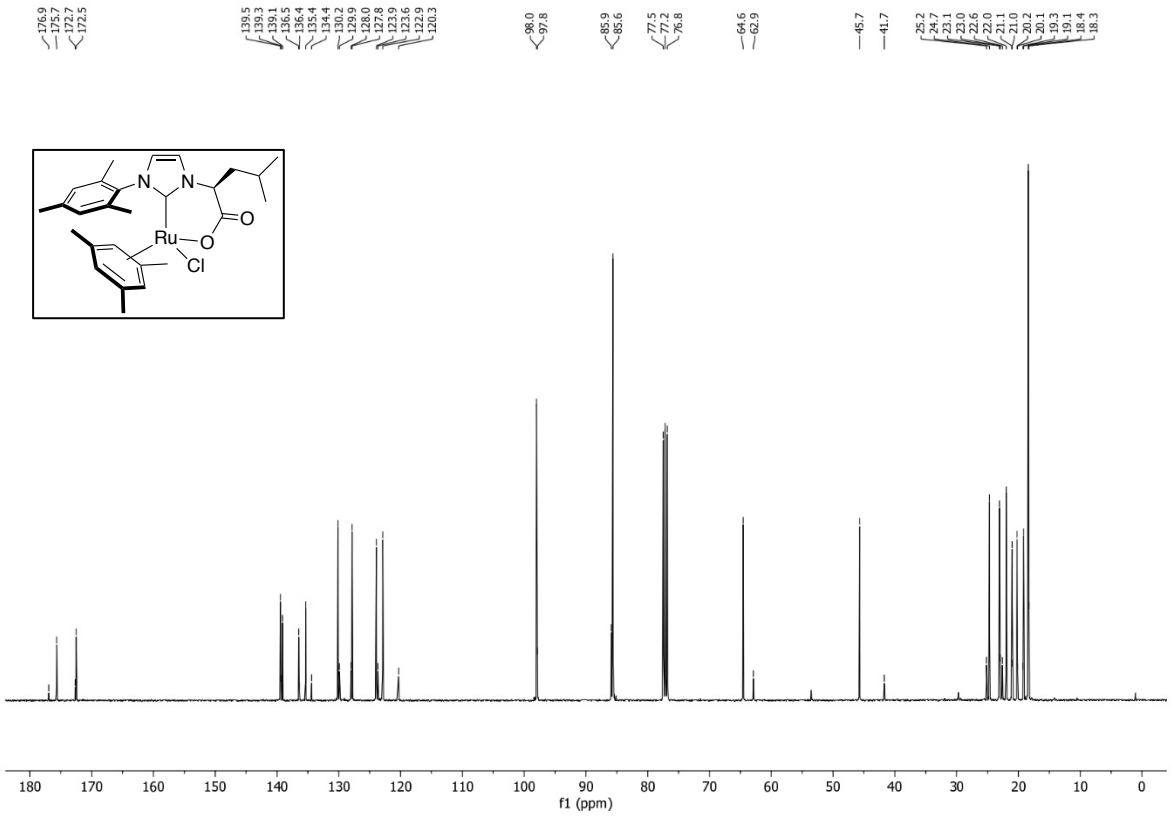
^{13}C NMR spectrum for **2a**



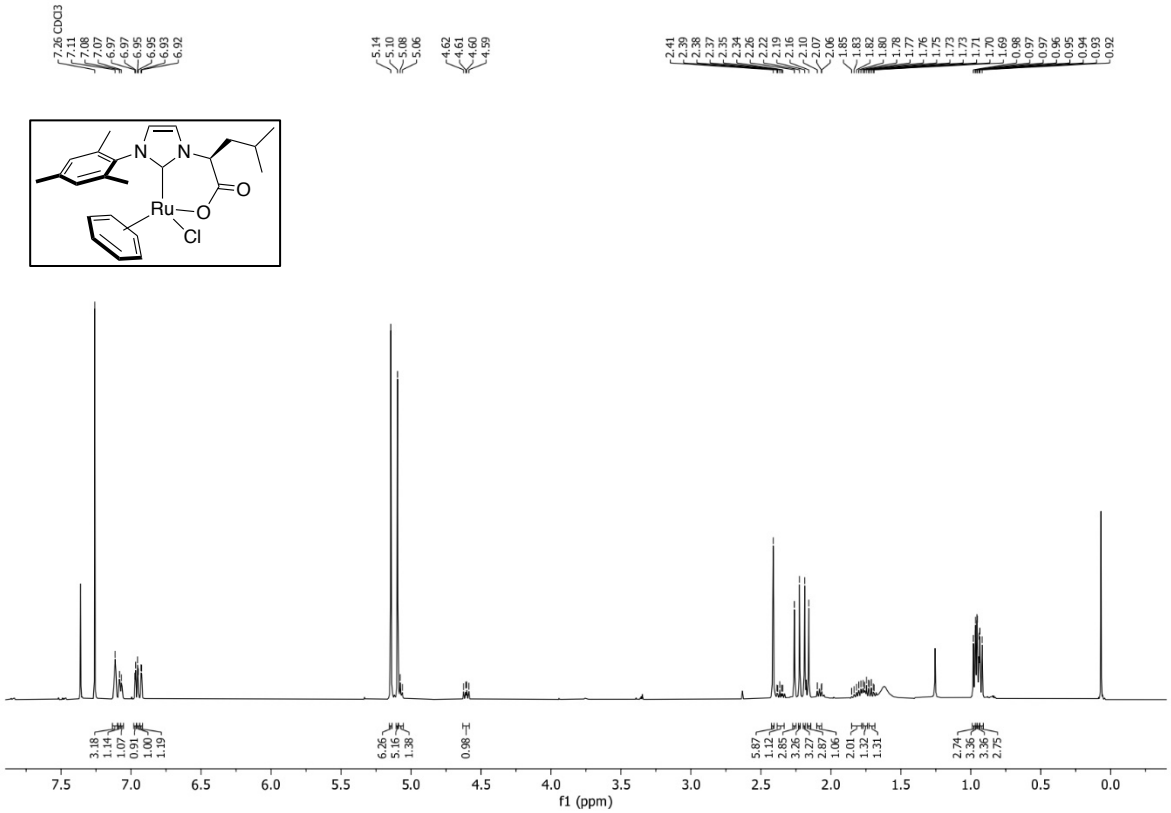
^{1}H NMR spectrum for **2b**



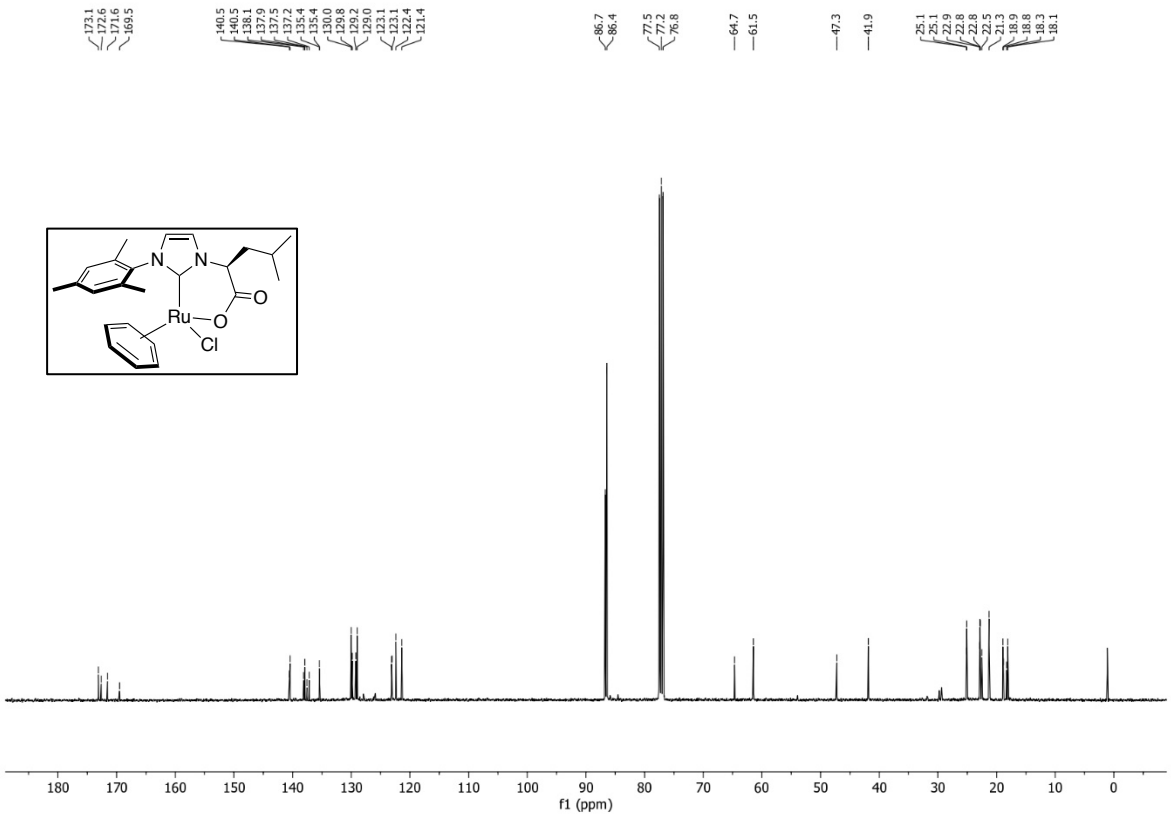
^{13}C NMR spectrum for **2b**



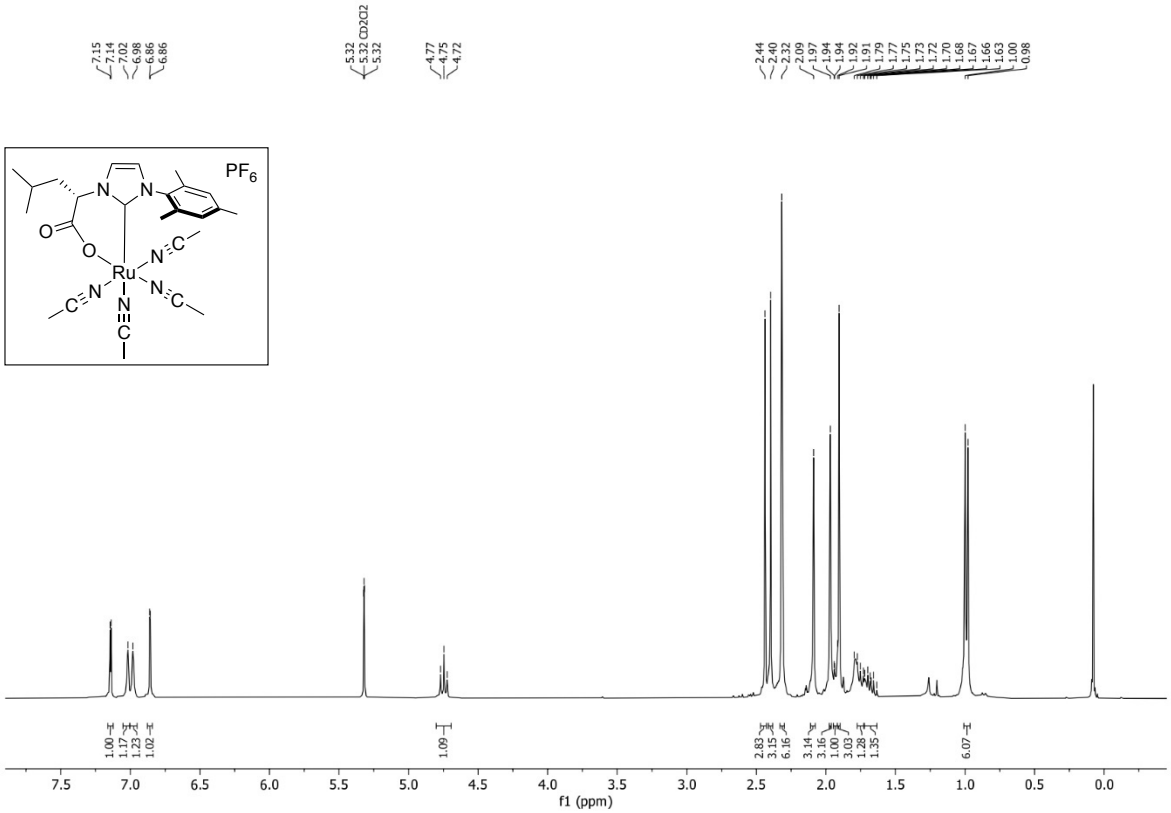
^{1}H NMR spectrum for **2c**



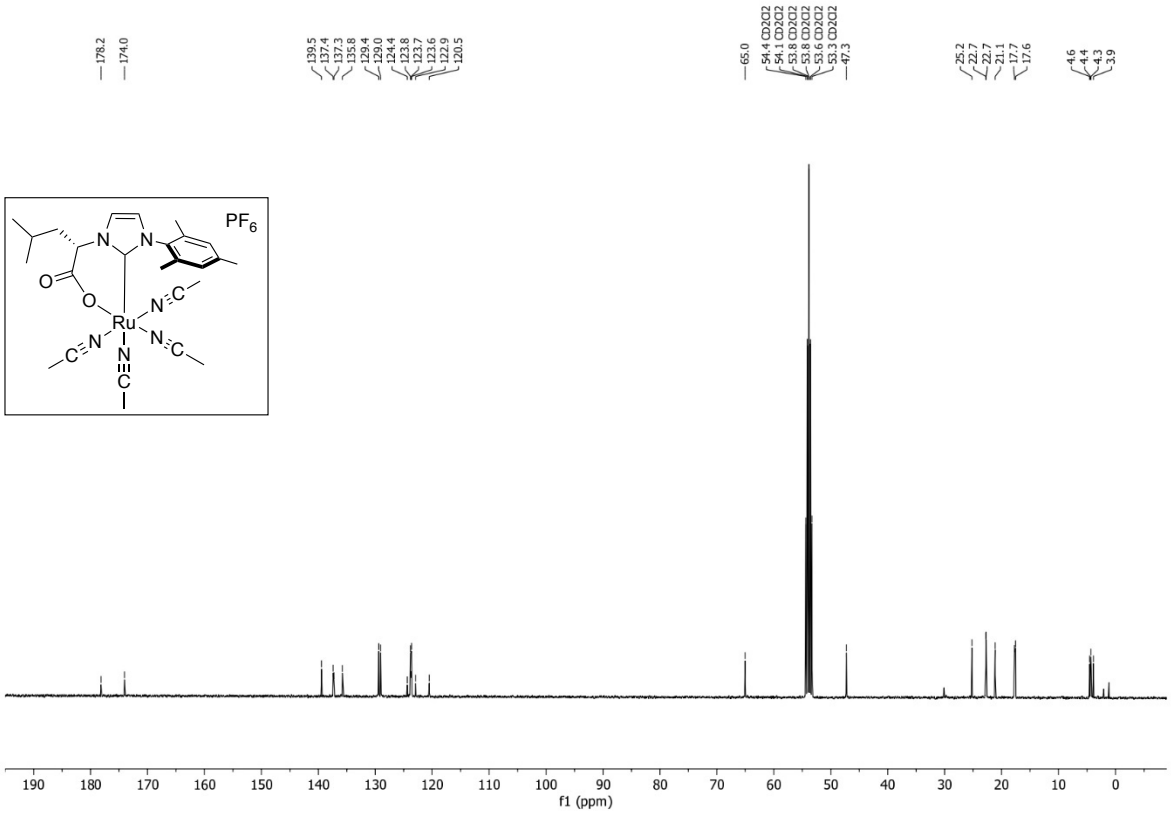
^{13}C NMR spectrum for **2c**



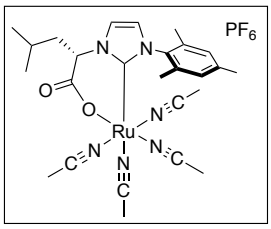
^{1}H NMR spectrum for **3a**



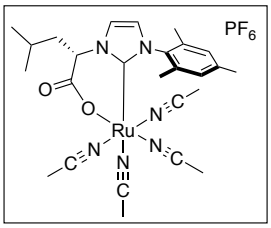
^{13}C NMR spectrum for **3a**



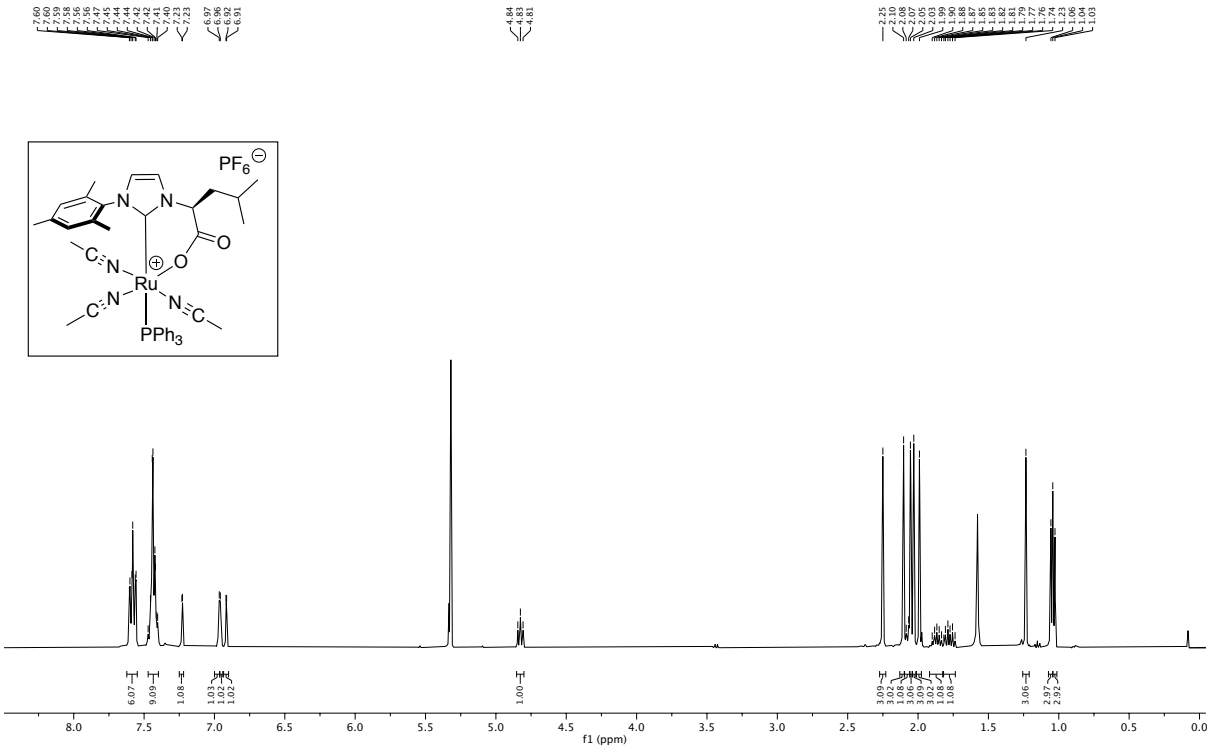
^{31}P NMR spectrum for **3a**



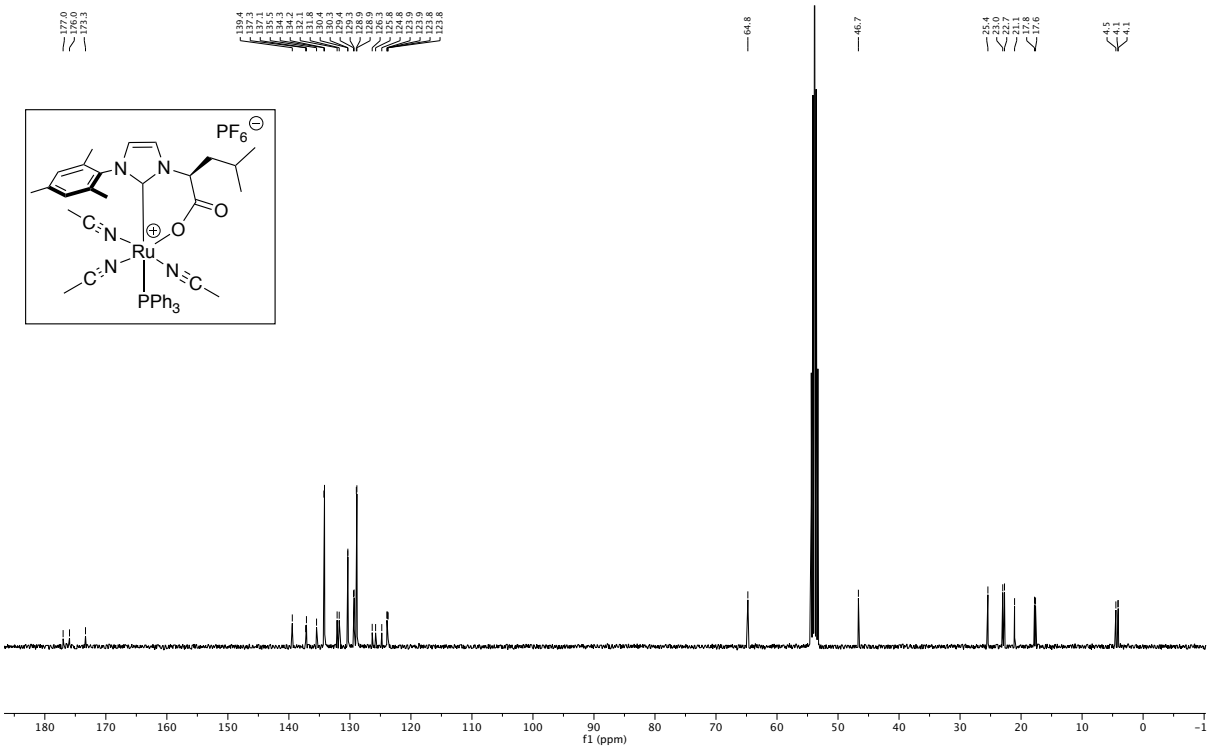
^{19}F NMR spectrum for **3a**



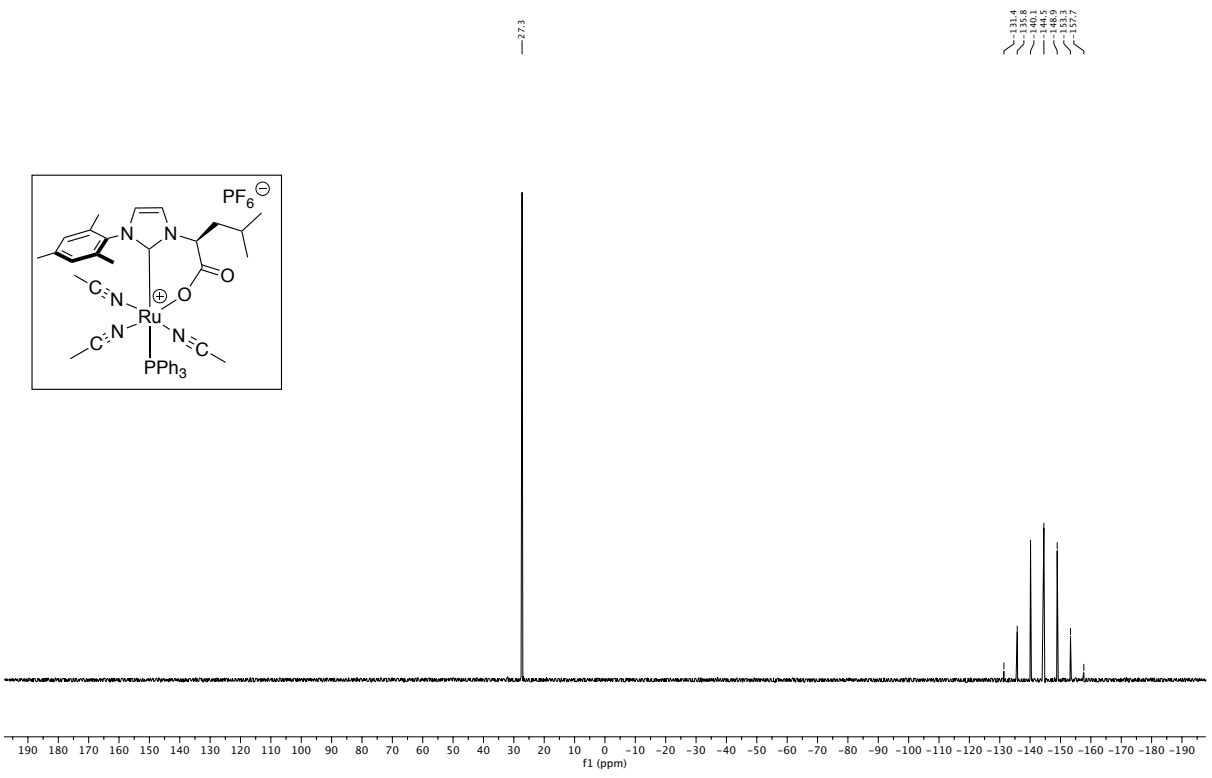
^{1}H NMR spectrum for **3b**



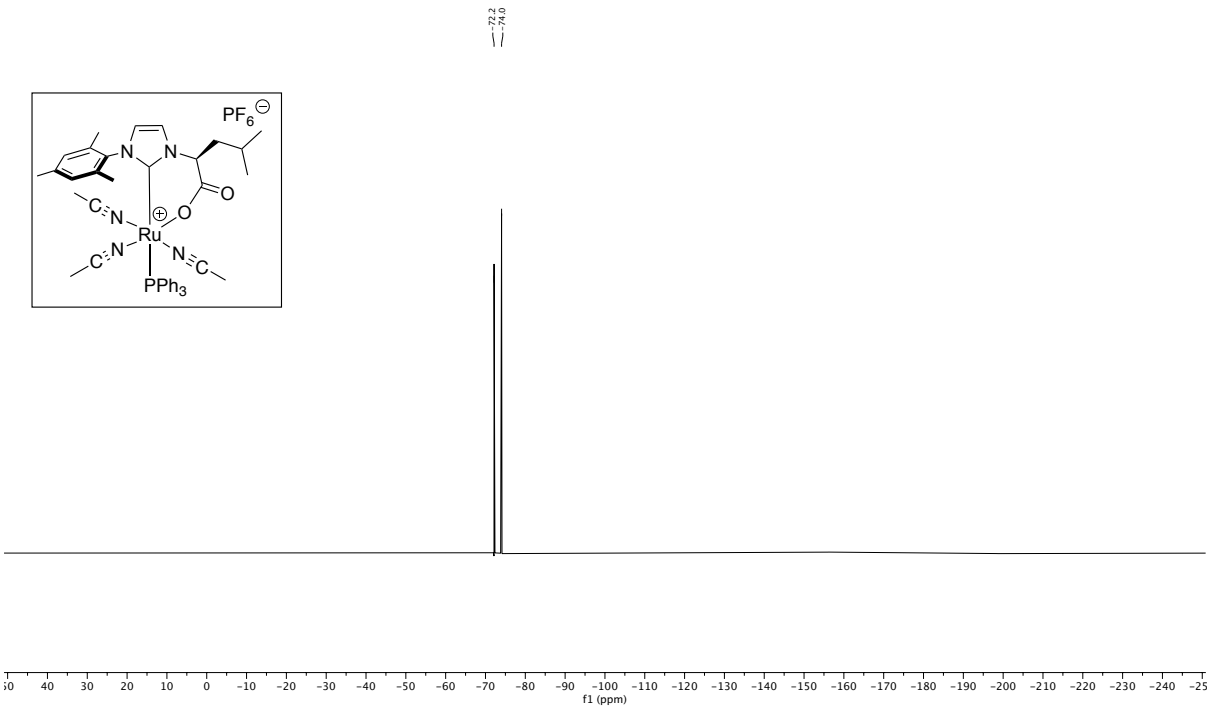
^{13}C NMR spectrum for **3b**



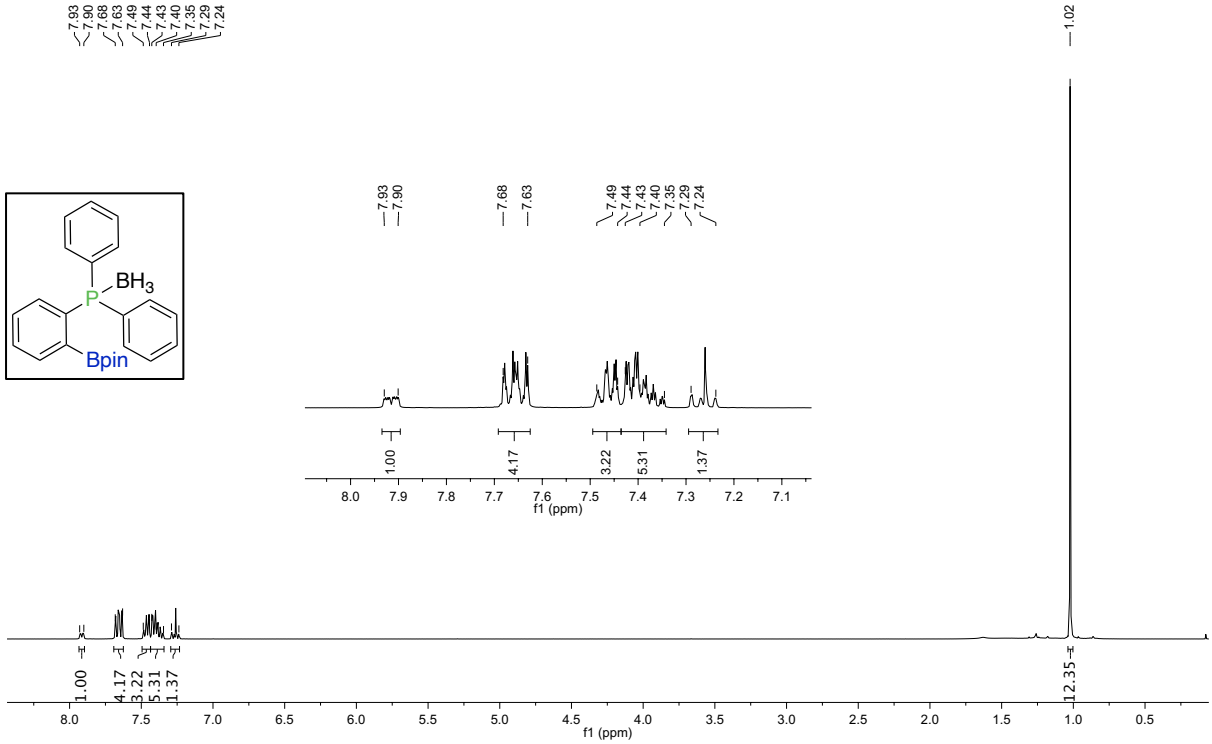
^{31}P NMR spectrum for **3b**



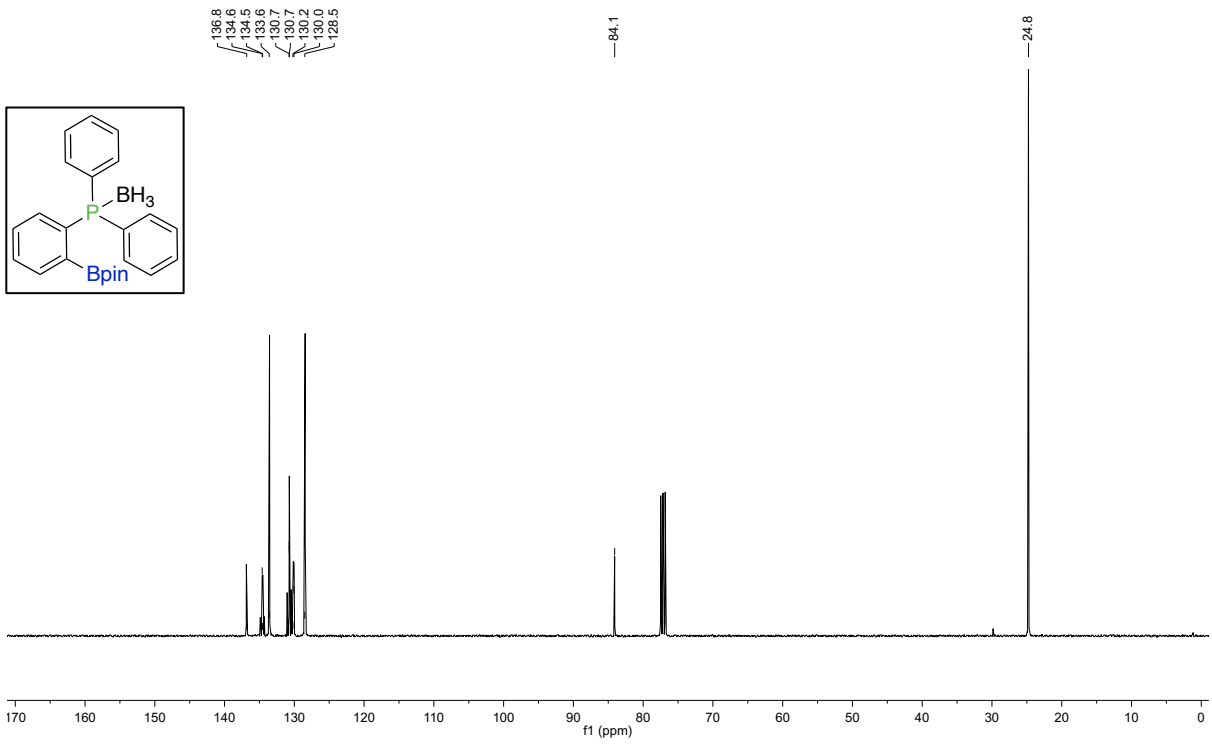
^{19}F NMR spectrum for **3b**



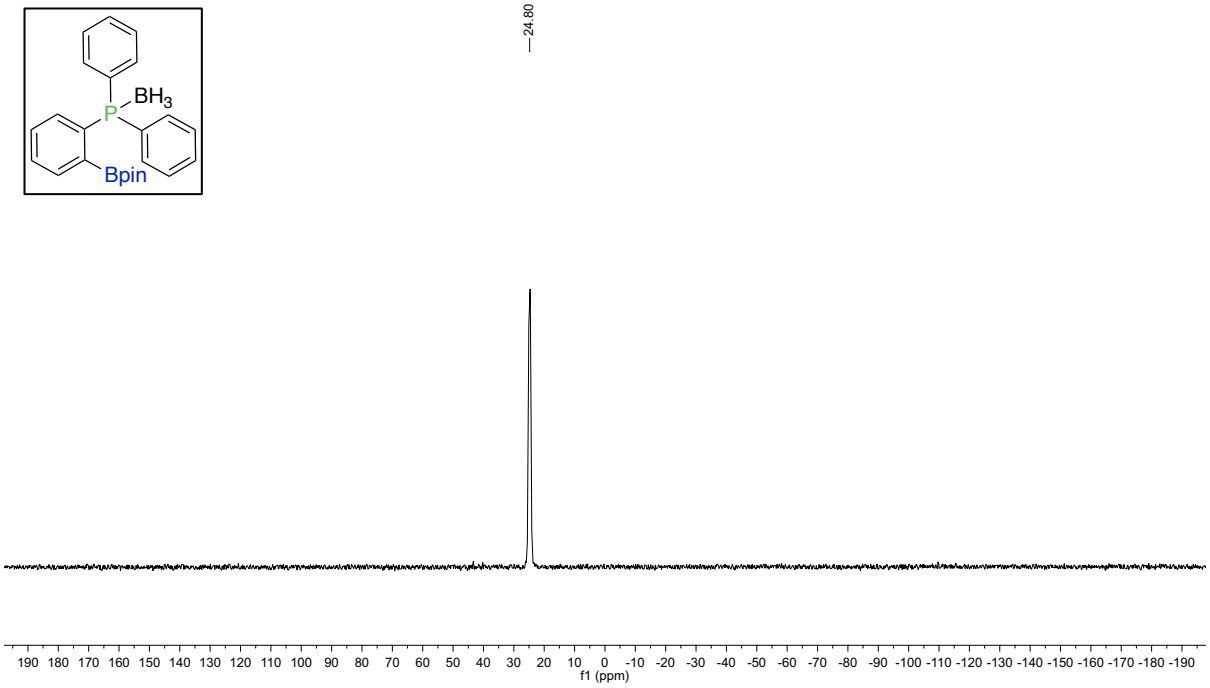
^{1}H NMR spectrum for **6a**



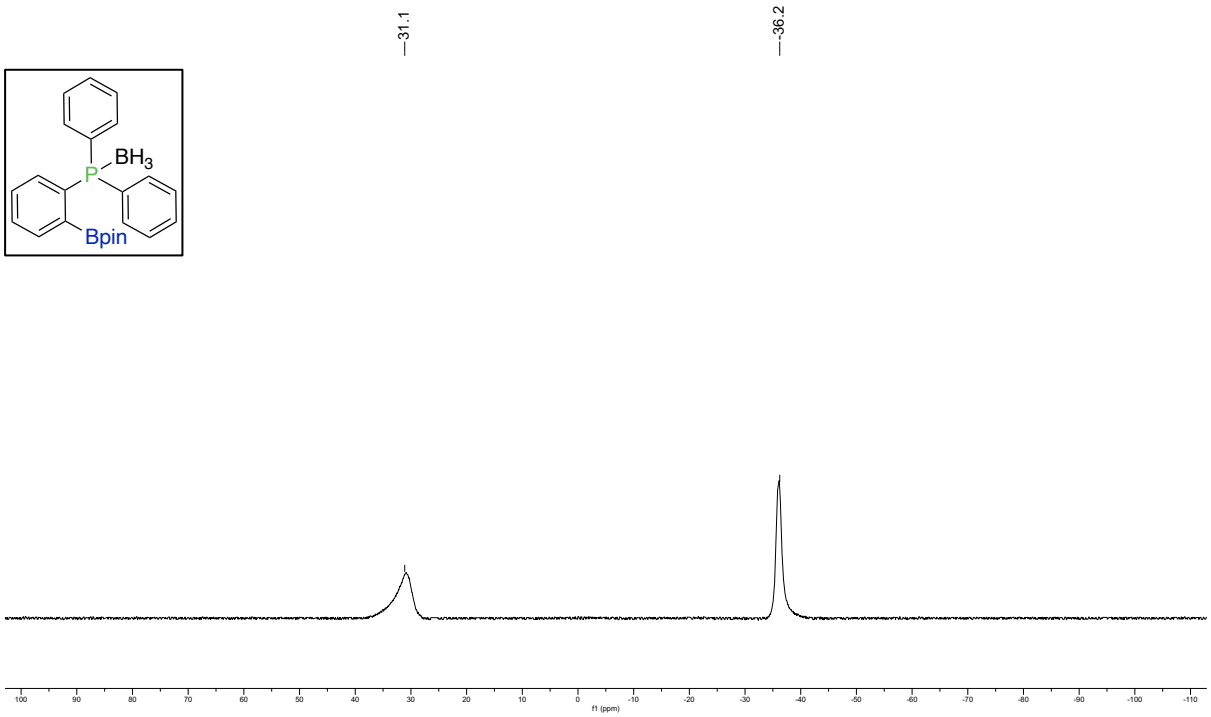
^{13}C NMR spectrum for **6a**



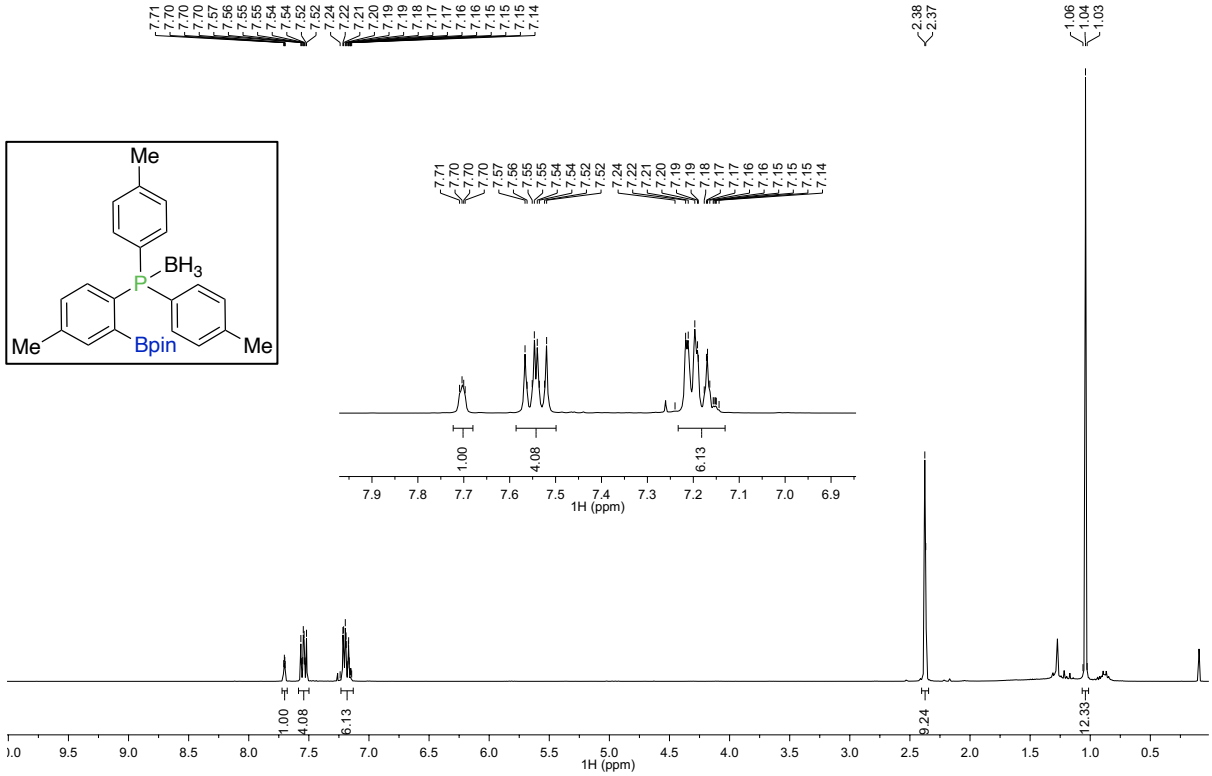
^{31}P NMR spectrum for **6a**



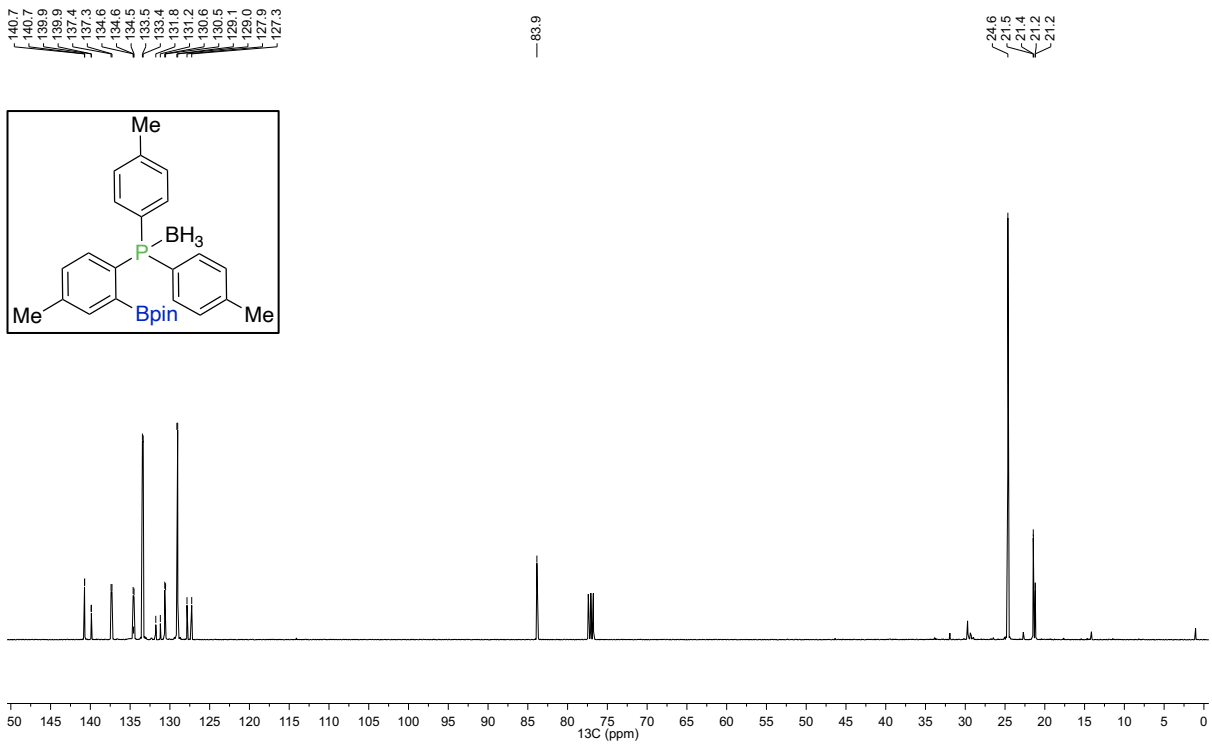
^{13}B NMR spectrum for **6a**



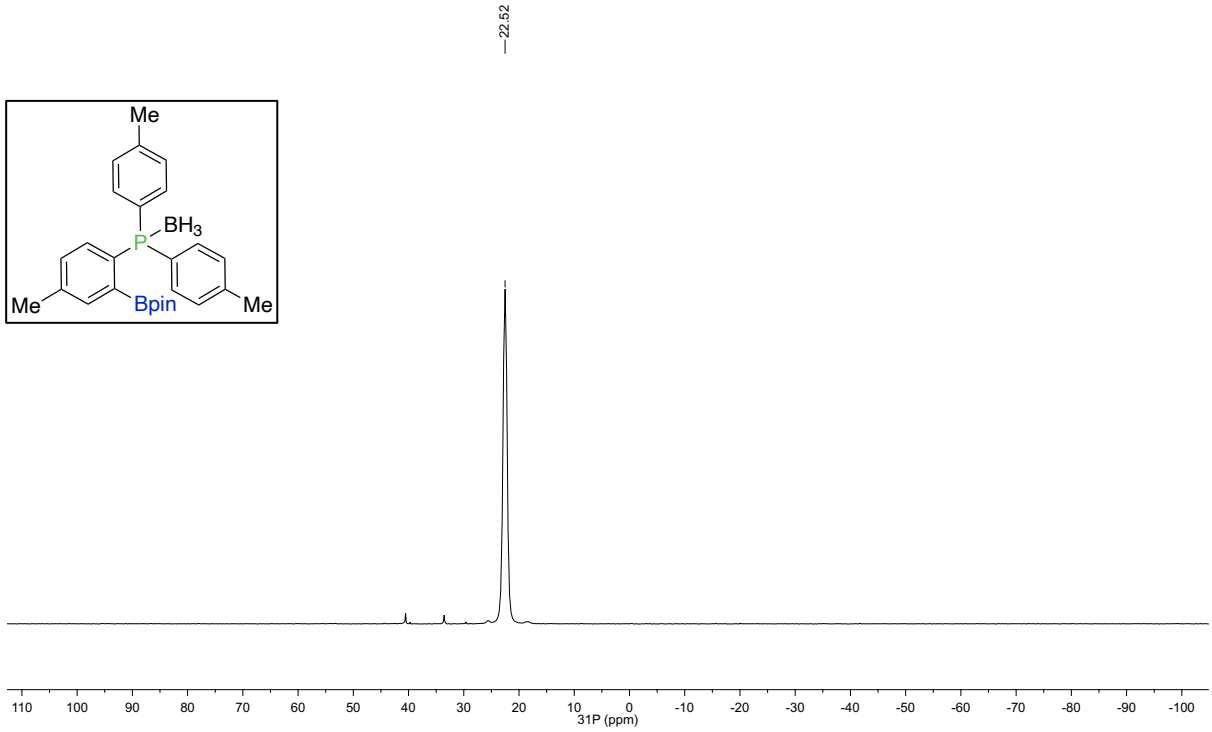
^{1}H NMR spectrum for **6b**



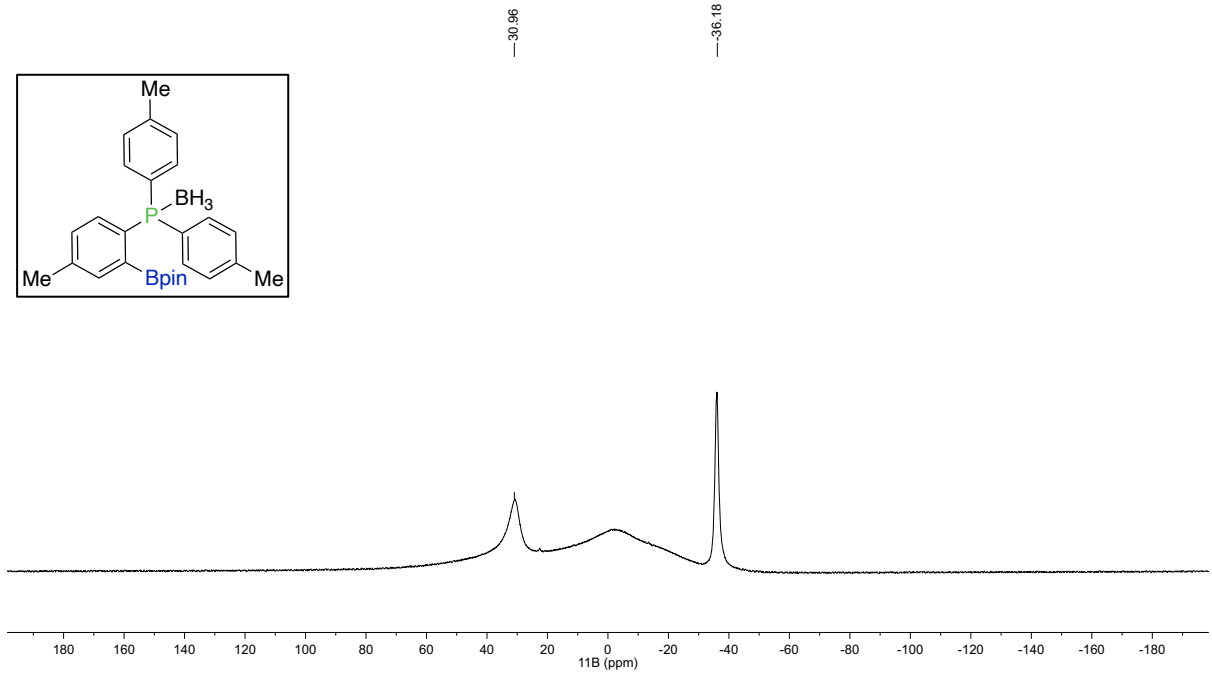
^{13}C NMR spectrum for **6b**



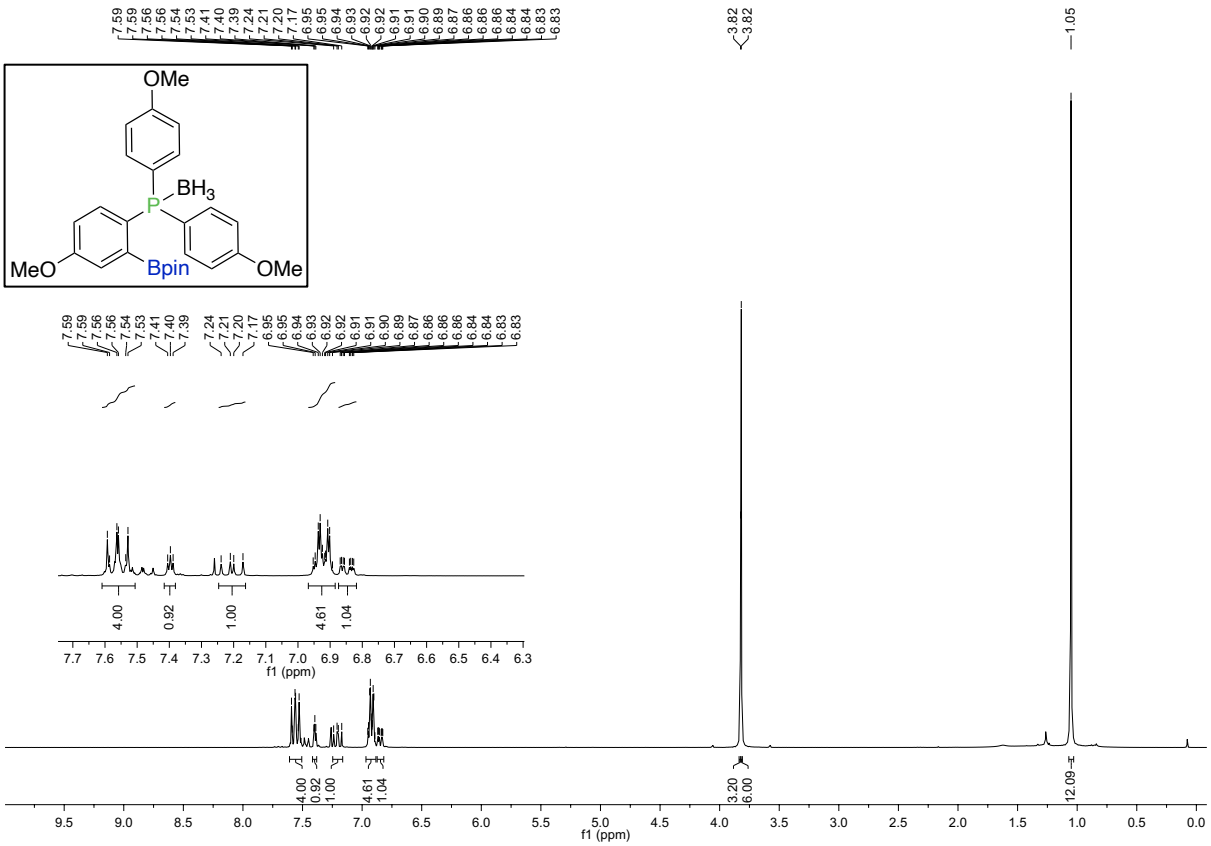
^{31}P NMR spectrum for **6b**



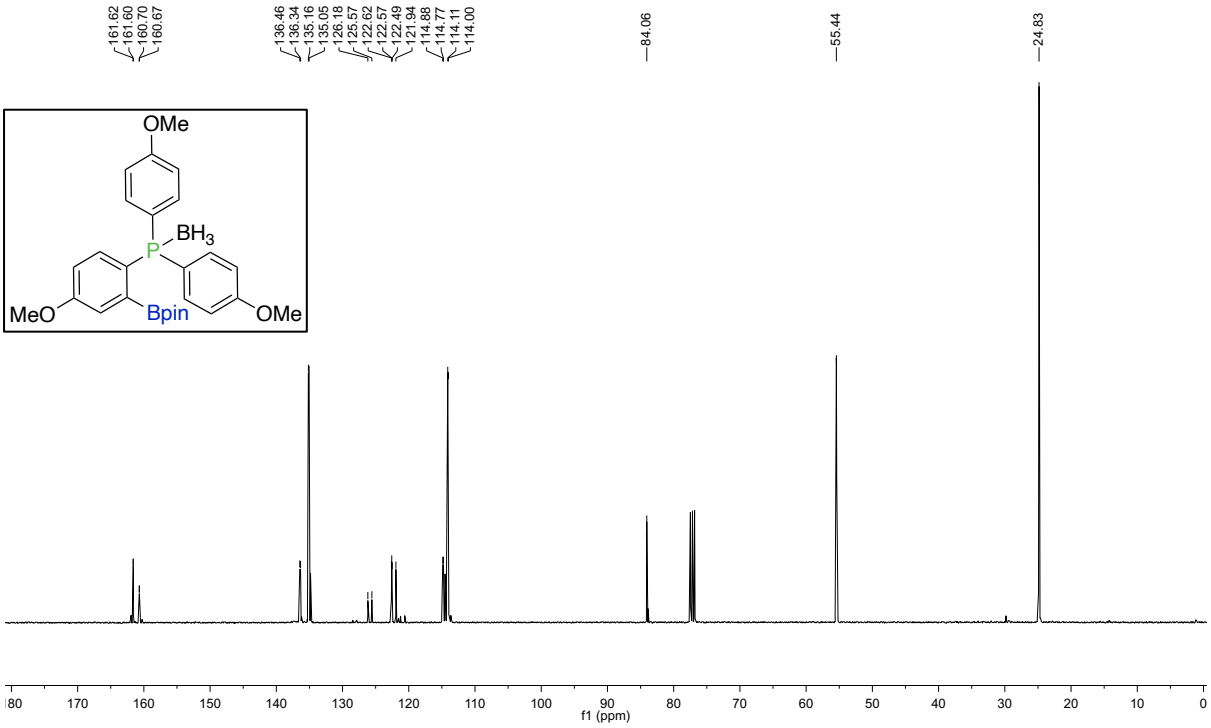
^{13}B NMR spectrum for **6b**



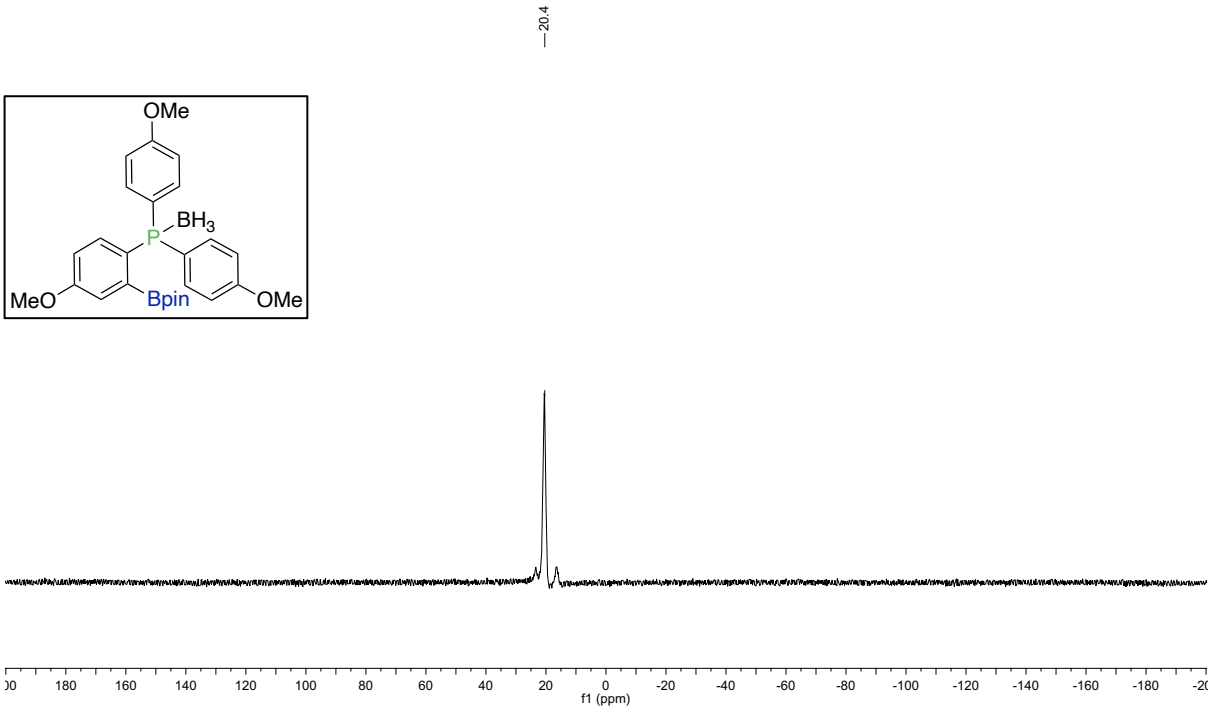
^{1}H NMR spectrum for **6c**



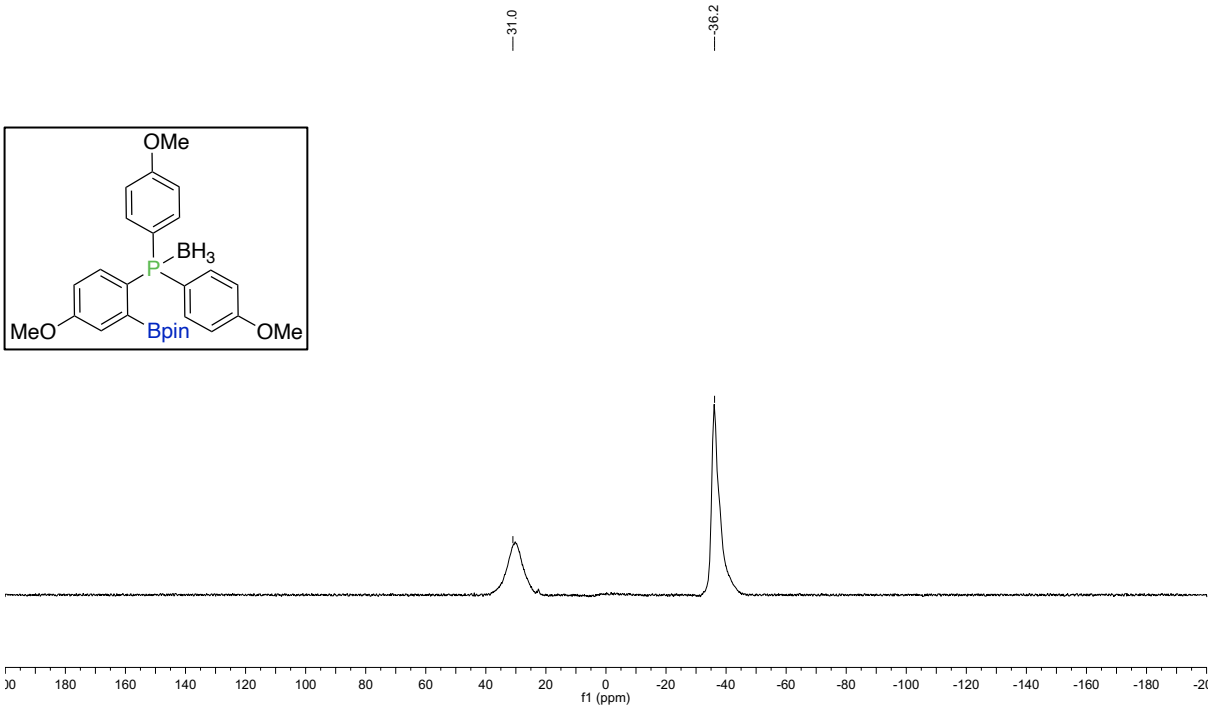
^{13}C NMR spectrum for **6c**



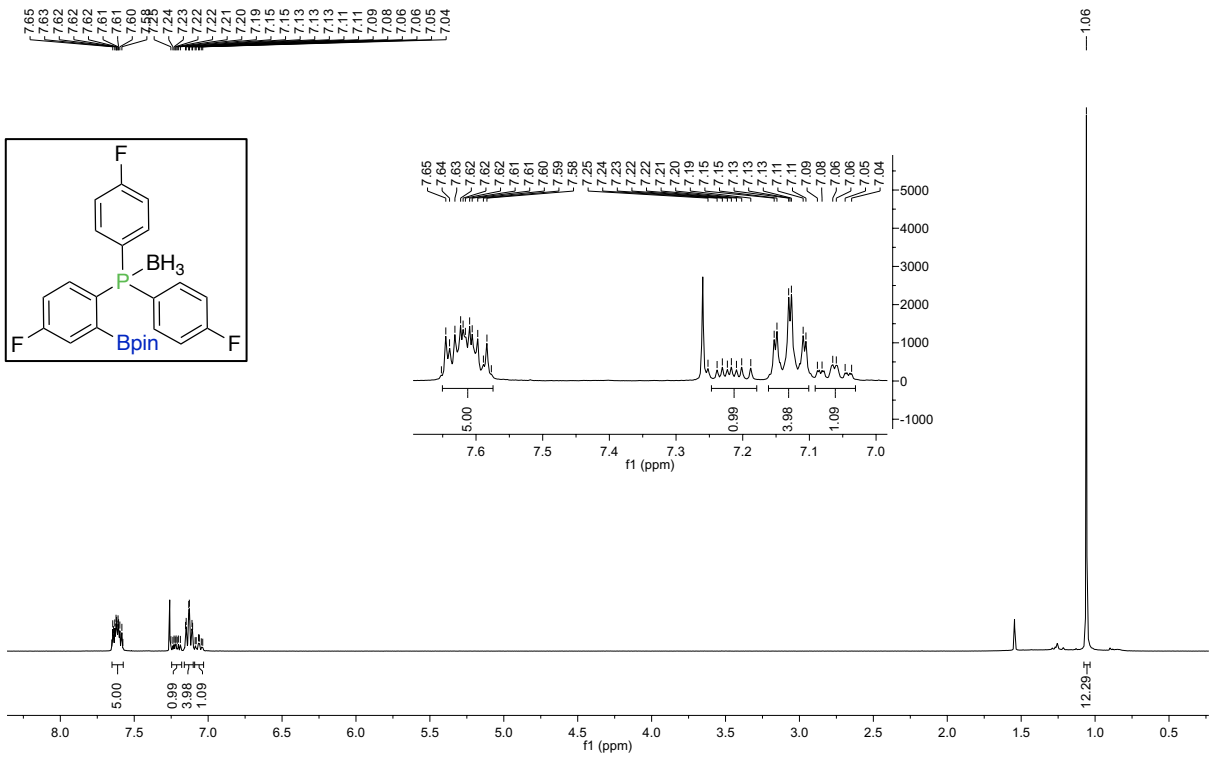
^{31}P NMR spectrum for **6c**



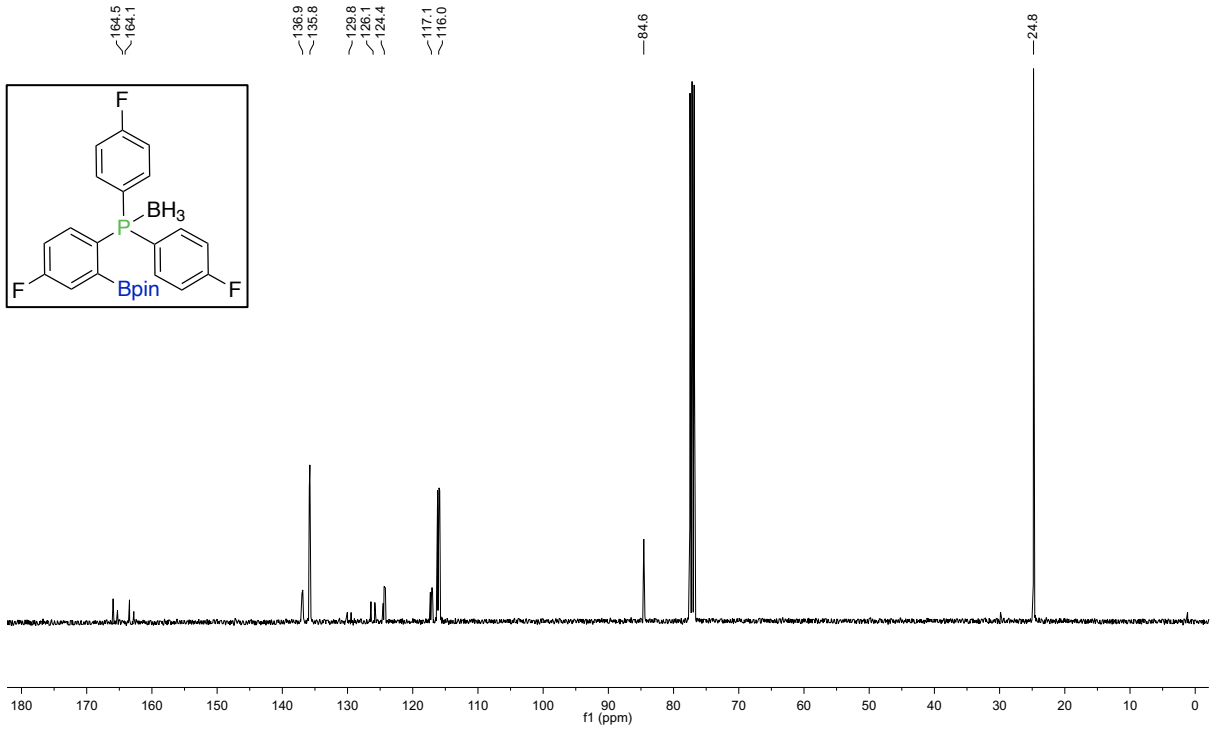
^{13}B NMR spectrum for **6c**



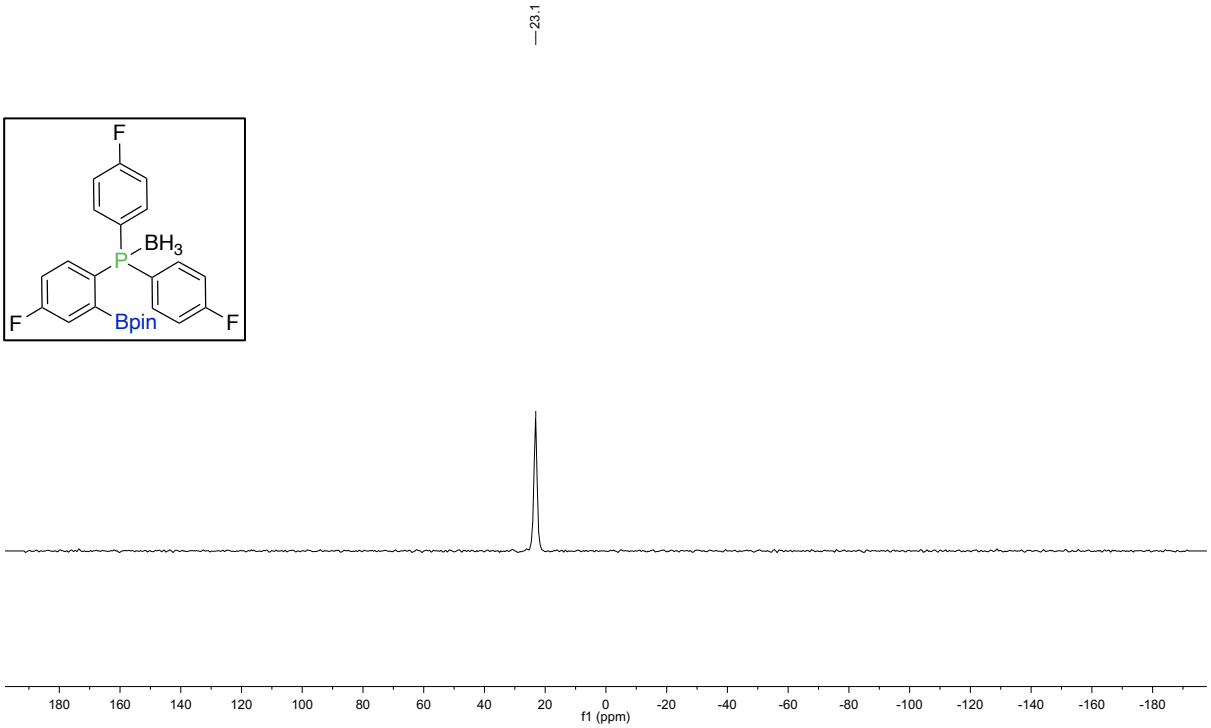
^{1}H NMR spectrum for **6d**



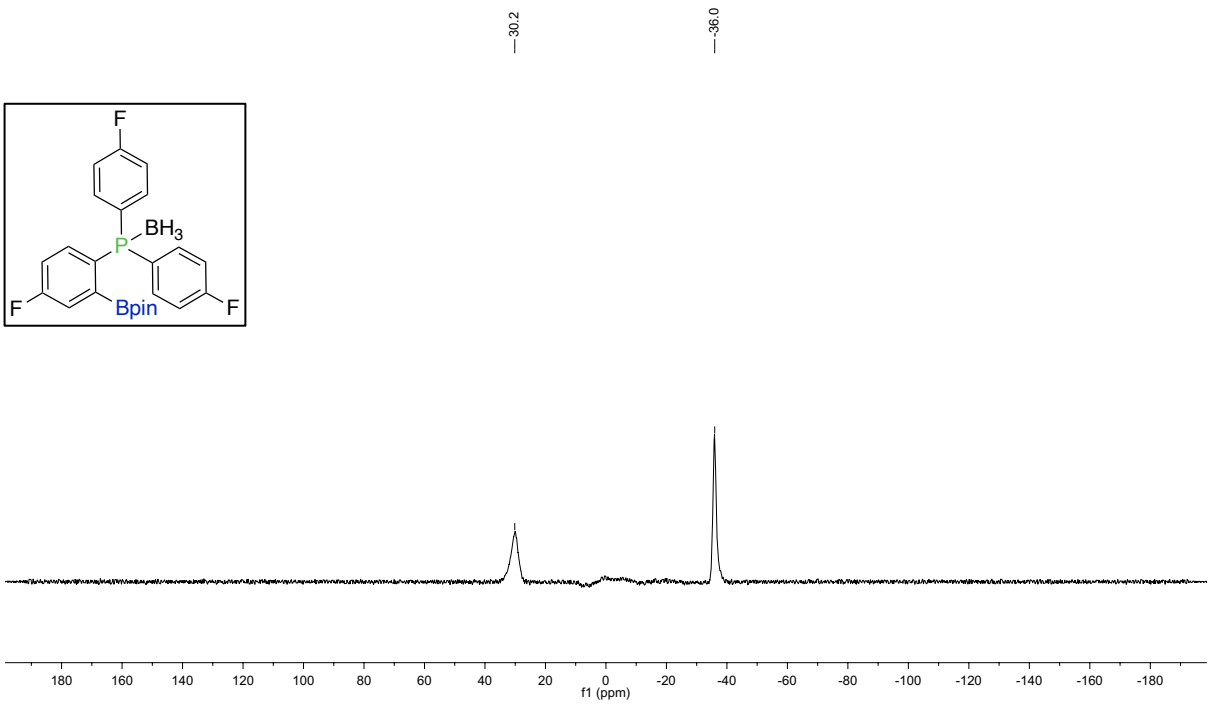
^{13}C NMR spectrum for **6d**



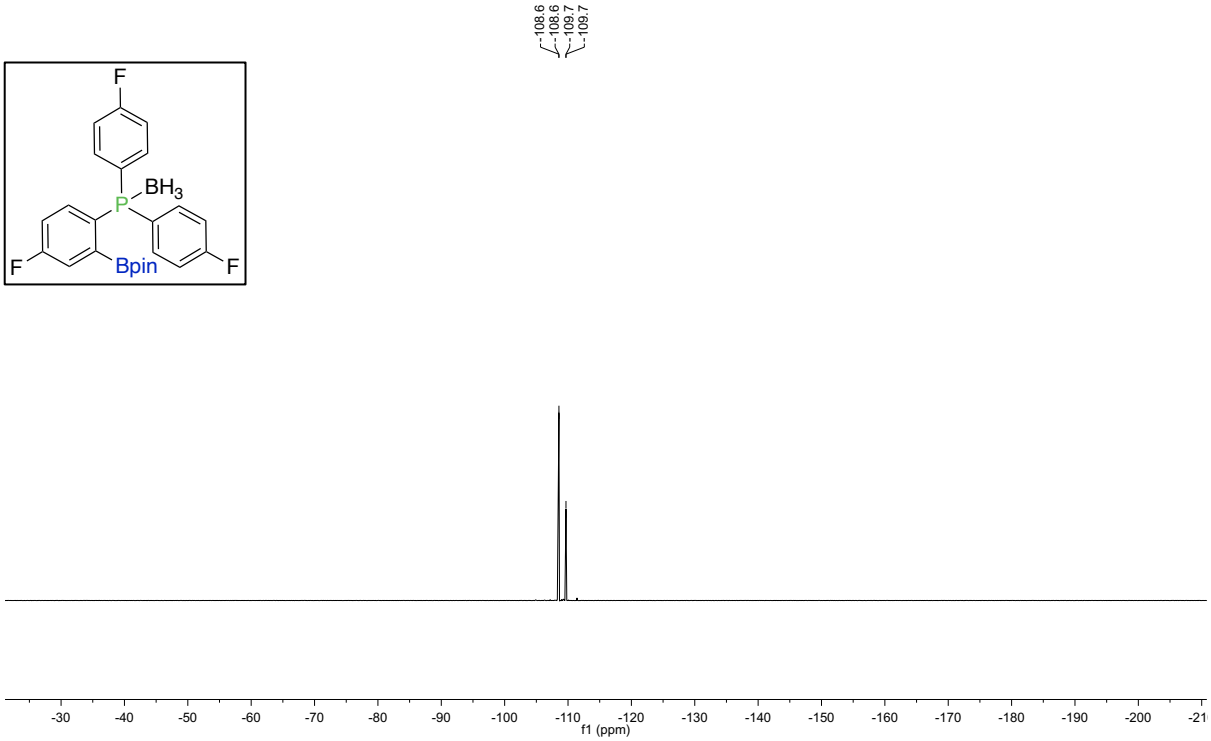
^{31}P NMR spectrum for **6d**



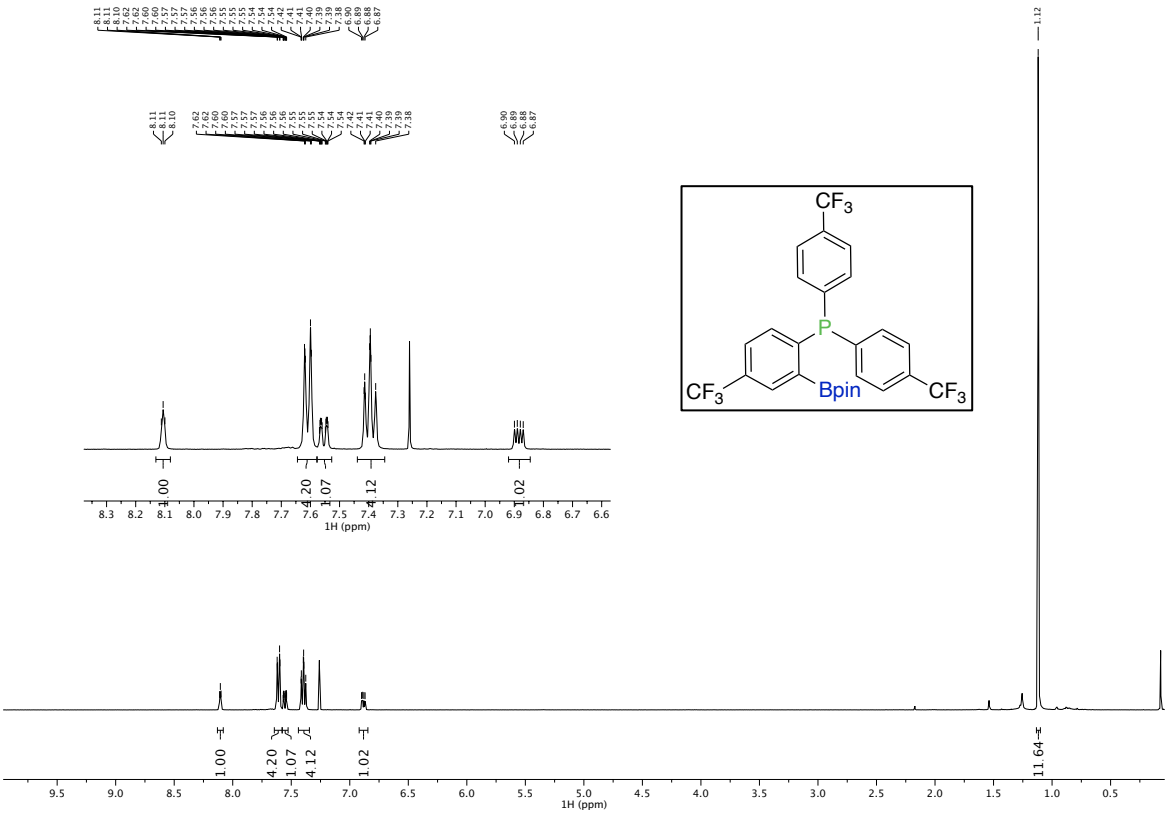
^{13}B NMR spectrum for **6d**



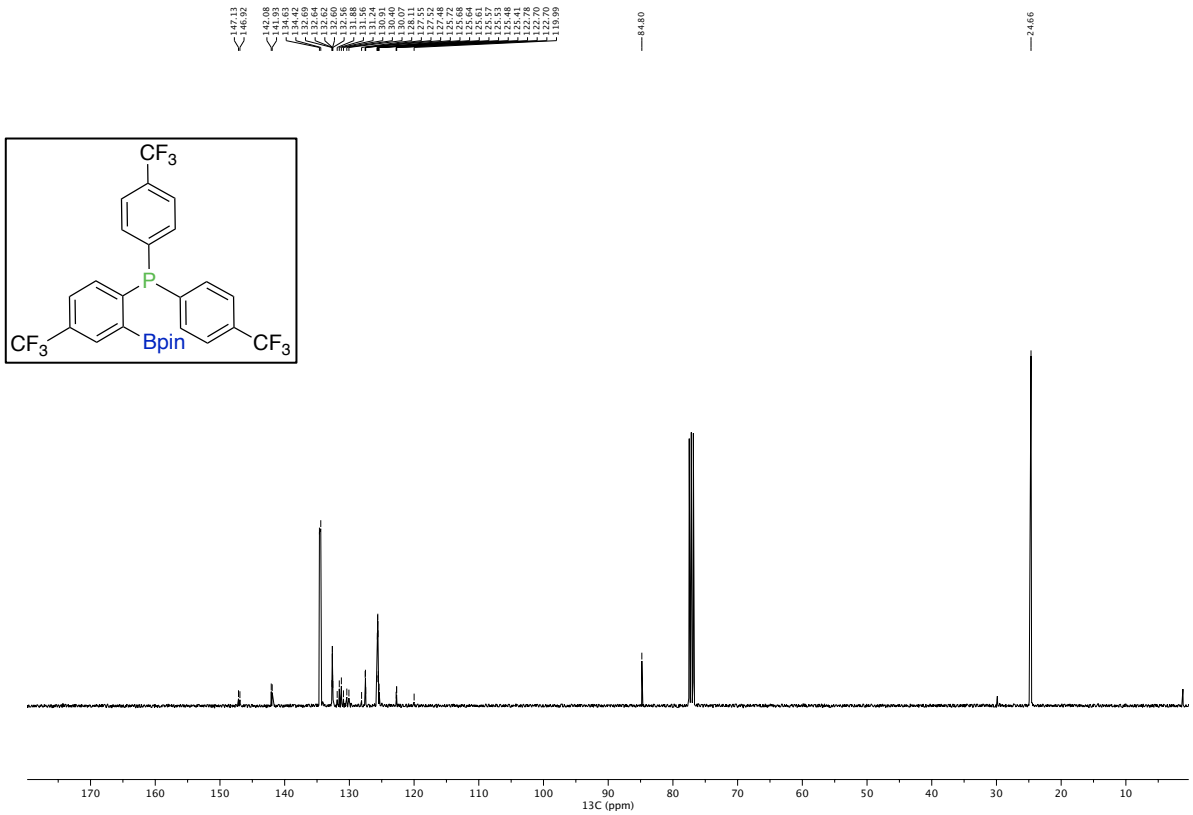
^{19}F NMR spectrum for **6d**



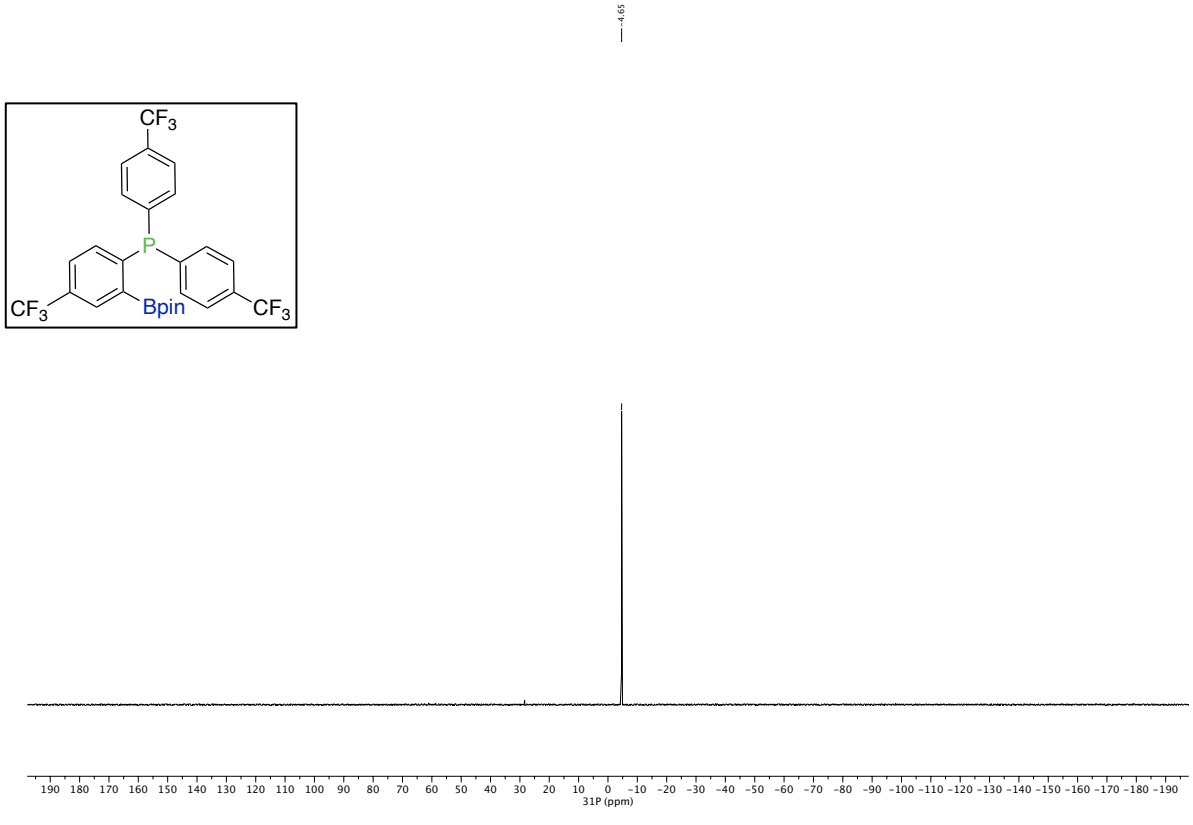
^{1}H NMR spectrum for **5e**



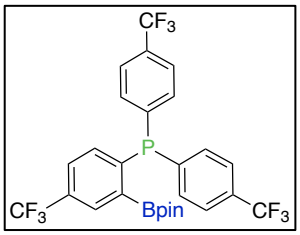
^{13}C NMR spectrum for **5e**

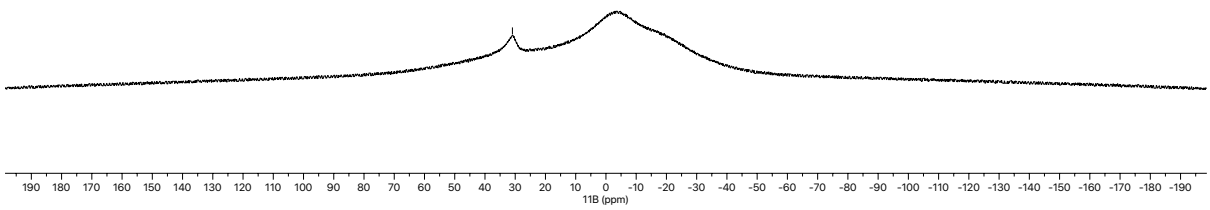


^{31}P NMR spectrum for **5e**

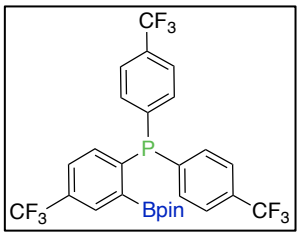


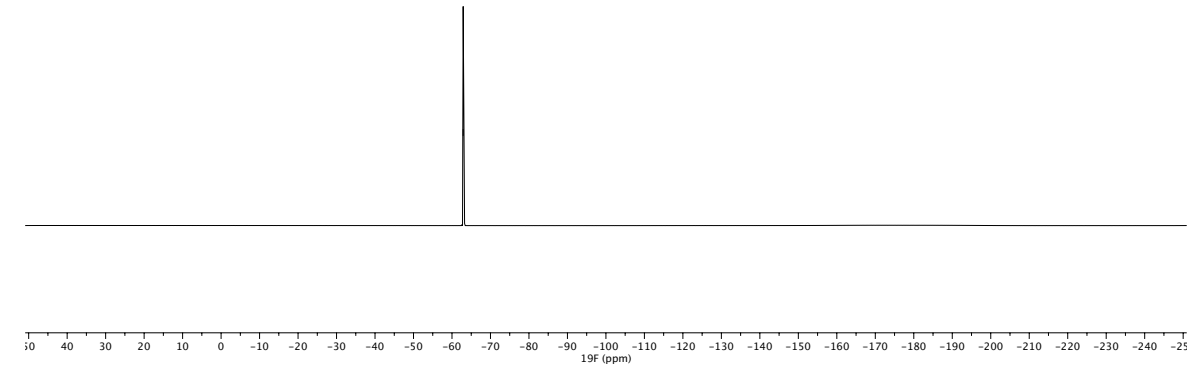
^{13}B NMR spectrum for **5e**



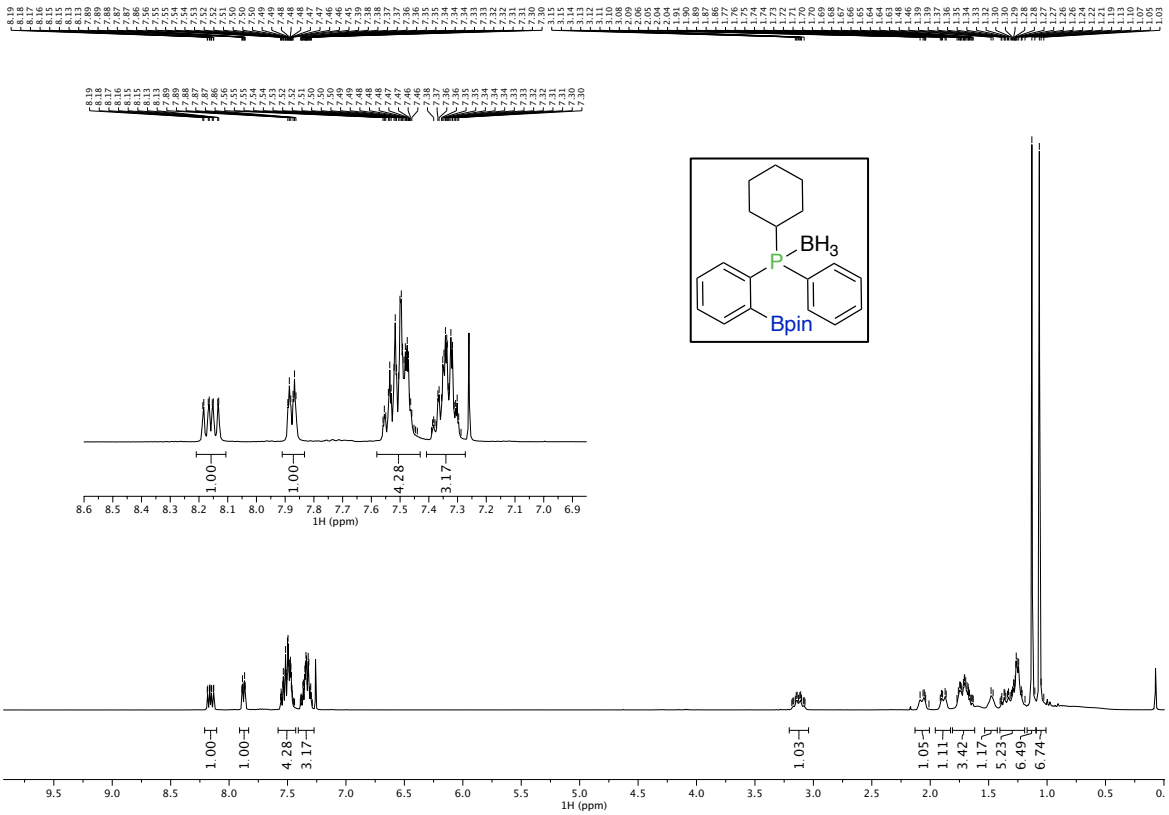


^{19}F NMR spectrum for **5e**

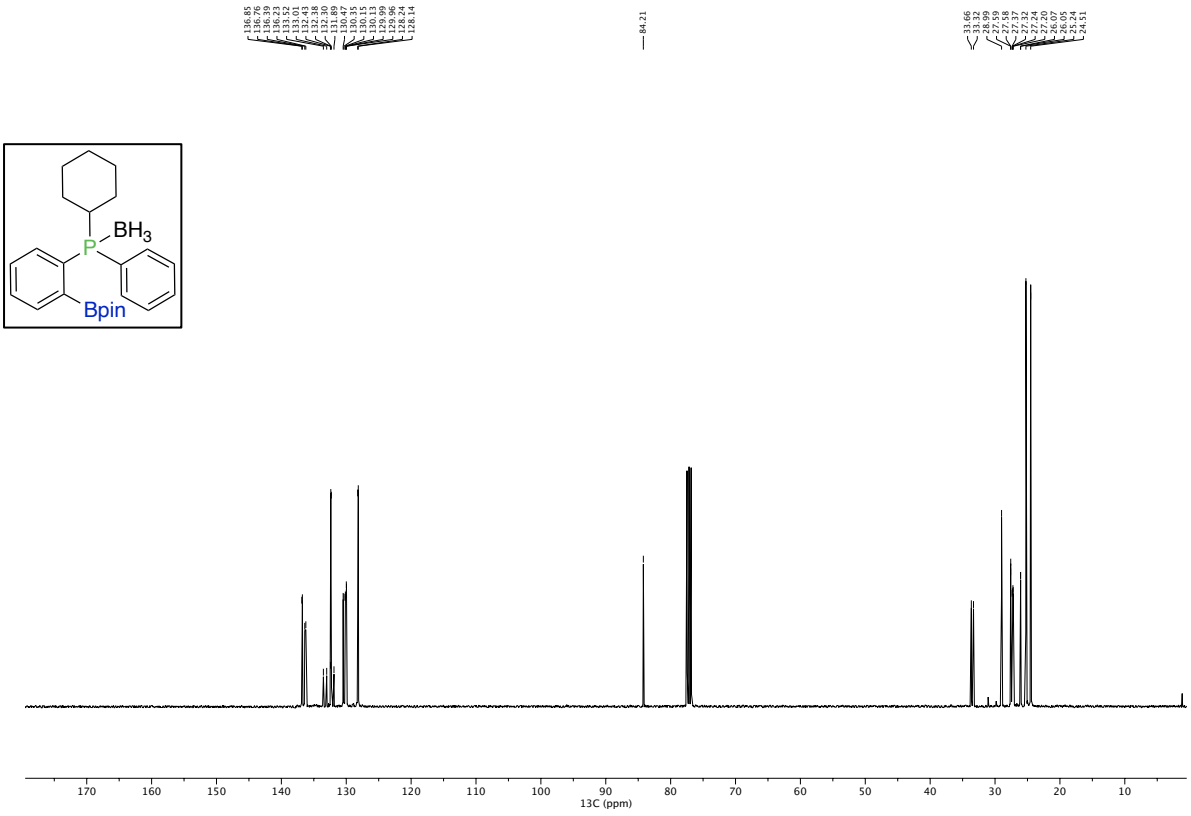




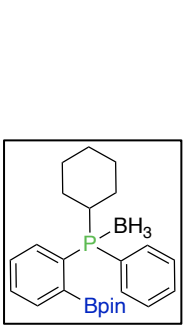
^{1}H NMR spectrum for **6f**



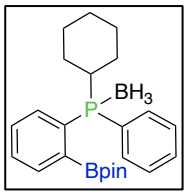
^{13}C NMR spectrum for **6f**



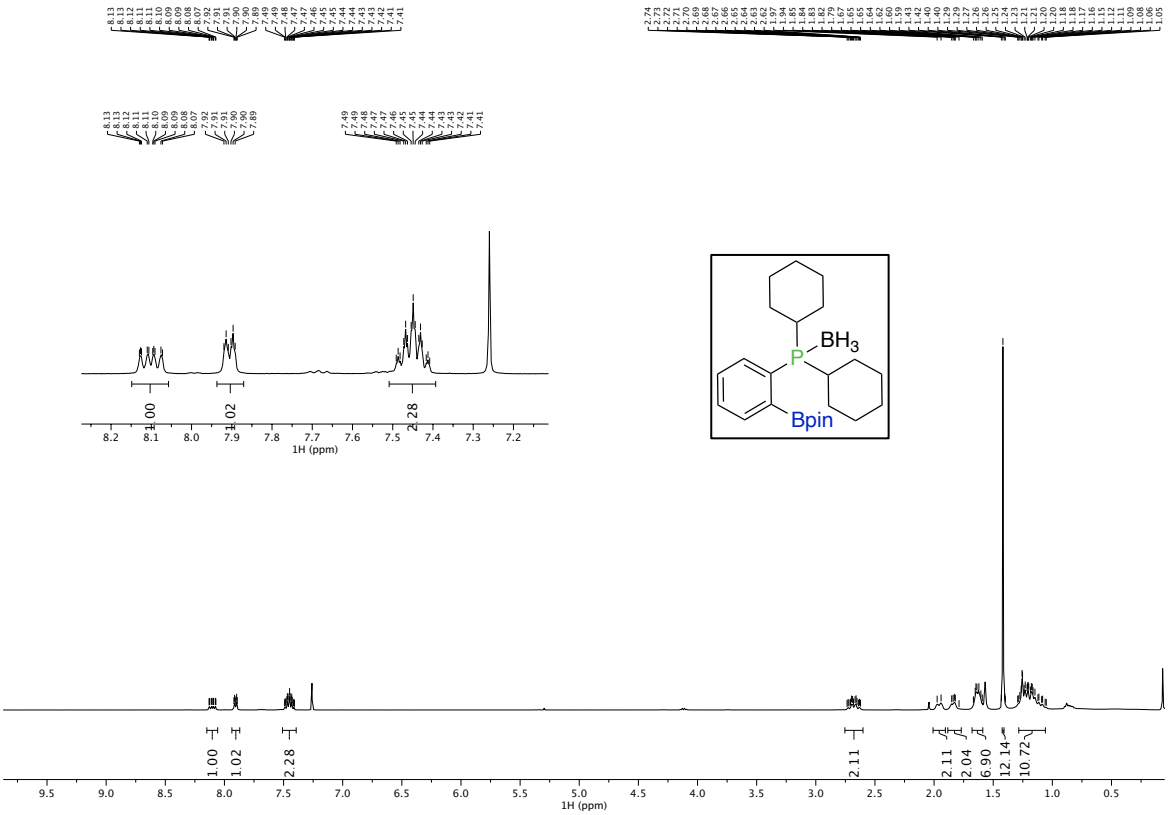
^{31}P NMR spectrum for **6f**



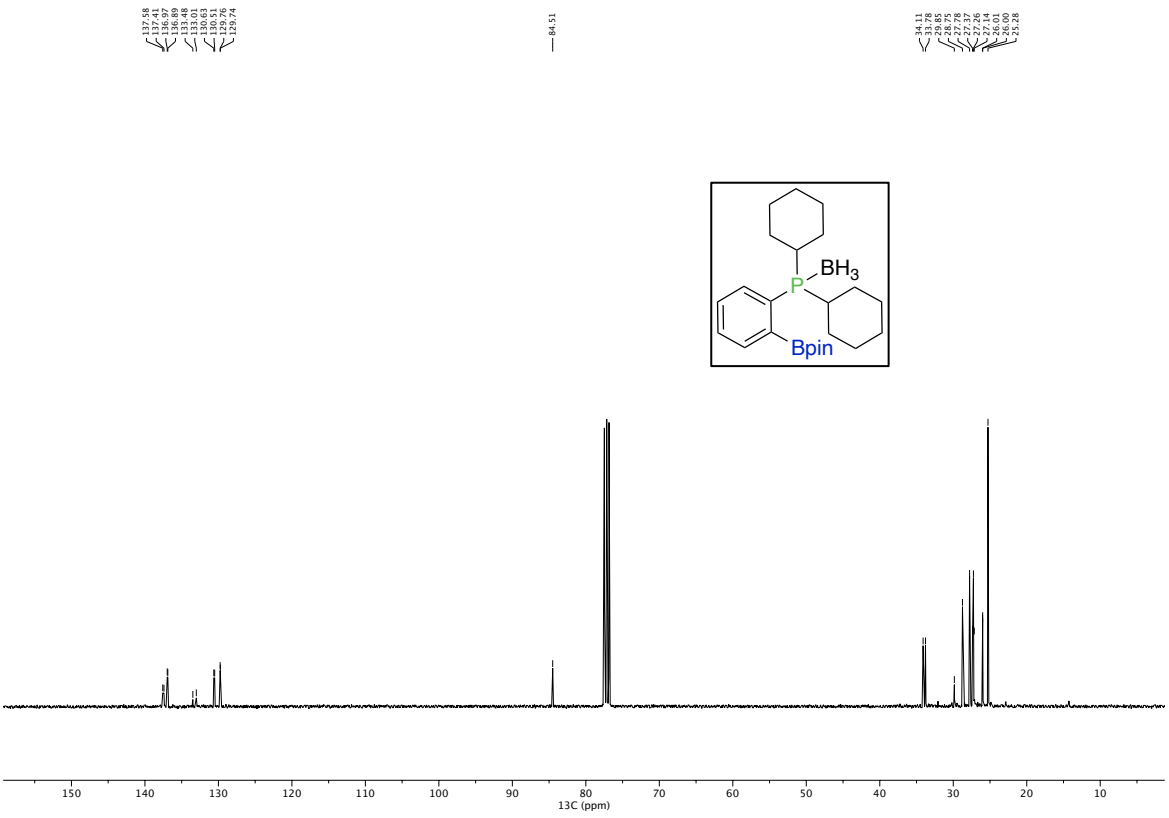
^{13}B NMR spectrum for **6f**



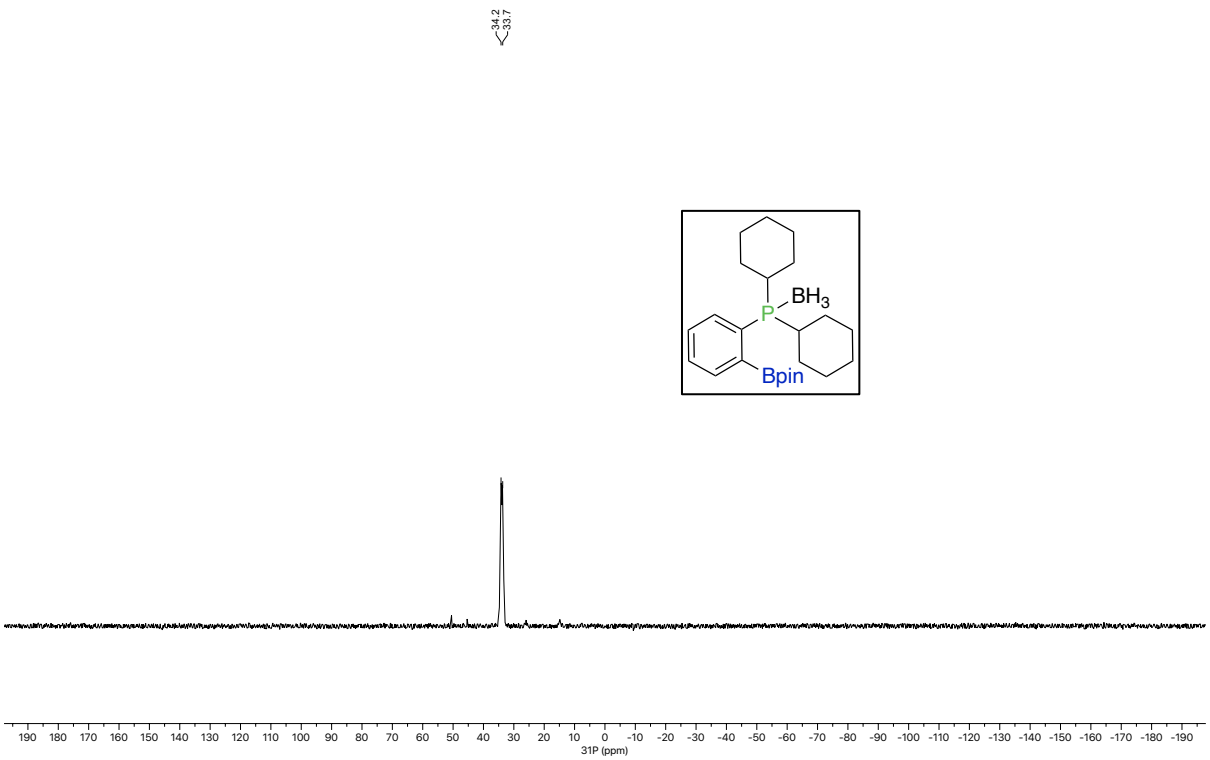
^{1}H NMR spectrum for **6i**



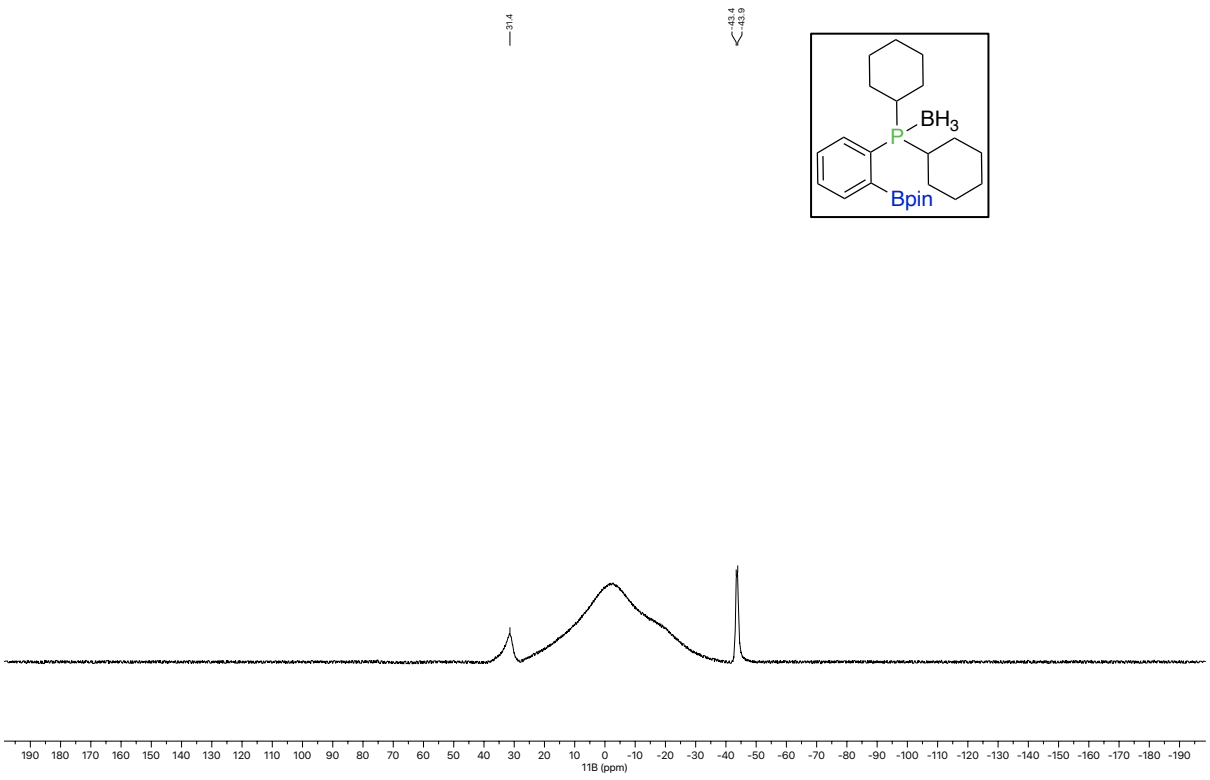
^{13}C NMR spectrum for **6i**



^{31}P NMR spectrum for **6i**

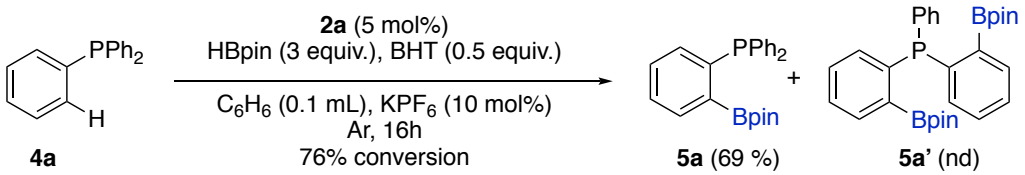


^{13}B NMR spectrum for **6i**



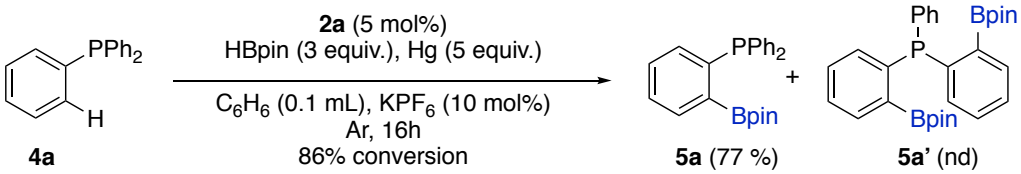
8. Mechanistic studies

8.1 Radical scavenger experiment



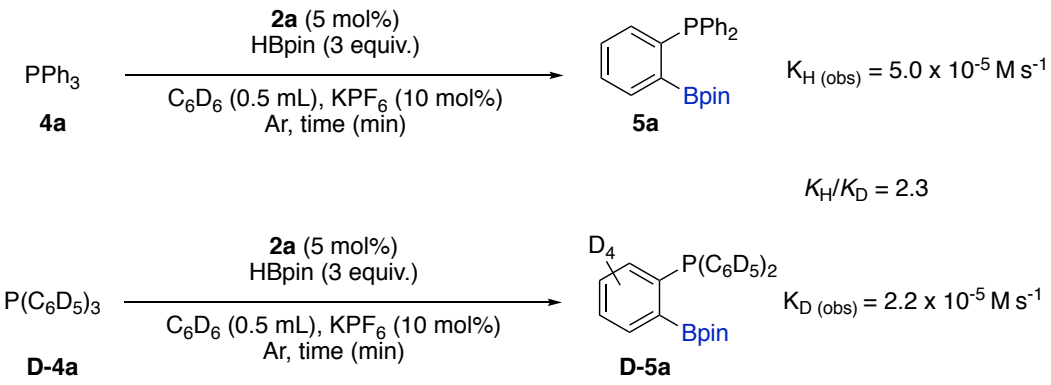
In a flame-dried Schlenk tube were placed 0.2 mmol of PPh_3, ruthenium catalyst **2a** (0.01 mmol, 5 mol%), KPF_6 (0.02 mmol) and butylated hydroxytoluene (0.5 equiv). The tube was evacuated and back-filled with argon 3 times. Then, HBpin (0.6 mmol) and benzene (0.1 mL,) were added. The tube was closed with a screw cap. Then, the mixture was stirred in a pre-heated oil bath at 100 °C with 300 rpm for 16h. After cooled down, the residue was diluted with $CDCl_3$. The crude residue was analyzed by ^1H and ^{31}P NMR spectroscopy. NMR yield was determined versus 1,3,5-trimethylbenzene as an internal standard.

8.2 Mercury test



In a flame-dried Schlenk tube were placed 0.2 mmol of PPh_3, ruthenium catalyst **2a** (0.01 mmol, 5 mol%) and KPF_6 (0.02 mmol). The tube was evacuated and back-filled with argon 3 times. Then, HBpin (0.6 mmol), benzene (0.1 mL,) and Hg (5 equiv.) were added. The tube was closed with a screw cap. Then, the mixture was stirred in a pre-heated oil bath at 100 °C with 300 rpm for 16h. After cooled down, the residue was diluted with $CDCl_3$. The crude residue was analyzed by ^1H and ^{31}P NMR spectroscopy. NMR yield was determined versus 1,3,5-trimethylbenzene as an internal standard.

8.3 Kinetic isotope effect



In a glove box, in a J-Young NMR tube were placed 0.1 mmol of $P(C_6H_5)_3$ or $P(C_6D_5)_3$,[5] ruthenium catalyst **2a** (0.005 mmol, 5 mol%), KPF_6 (0.01 mmol). Then, HBpin (0.6 mmol) and C_6D_6 (0.5 mL,) were added. The tube was closed with a J-Young valve. Outside the glove box, the mixture was stirred in a pre-heated oil bath at 100 °C. The conversion was monitored by ^{31}P NMR spectroscopy.

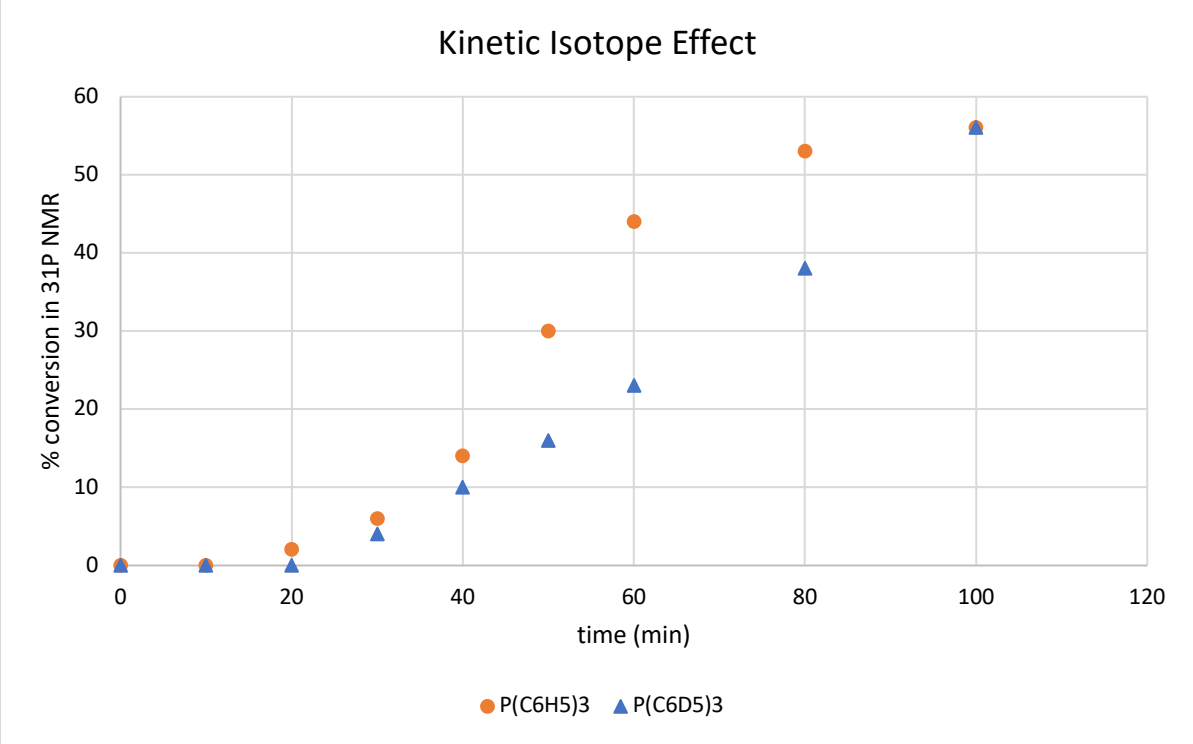


Figure S4. Monitoring of reactions with $P(C_6H_5)_3$ (orange dot) and $P(C_6D_6)_5$ (blue triangle).

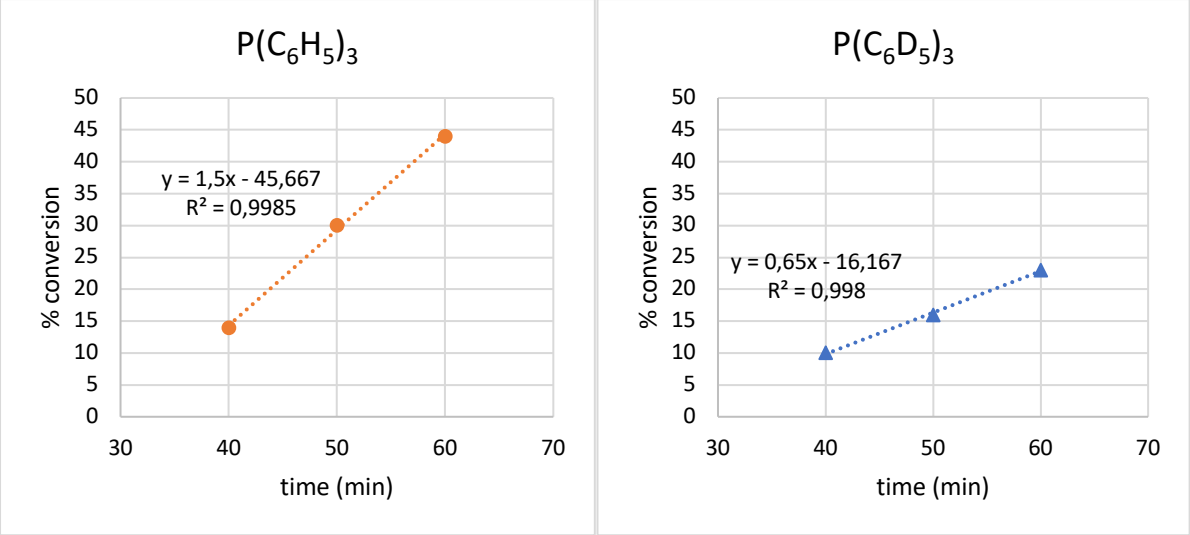


Figure S5. Determination of K_H, K_D and KIE.

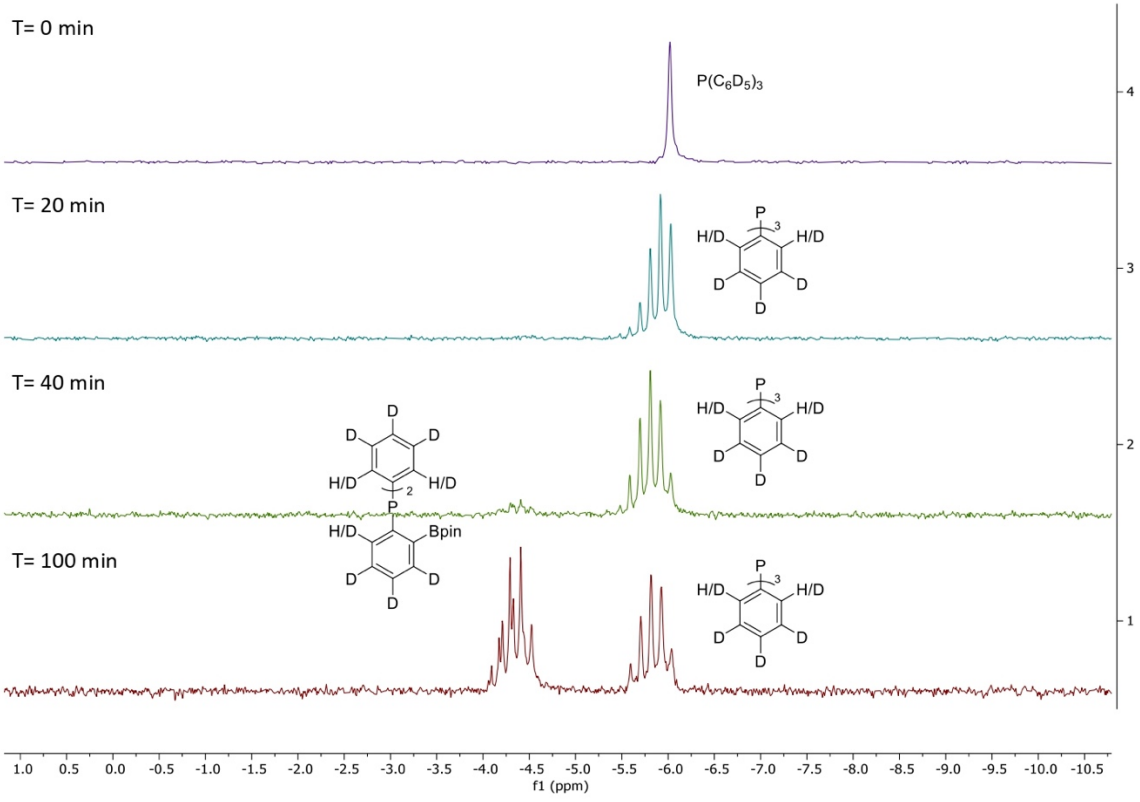


Figure S6. ^{31}P NMR spectroscopy monitoring of the reaction with $P(C_6D_6)_5$.

The monitoring of the reaction with $P(C_6D_6)_3$ shows that D-H exchange occurs before C-B bond formation. This phenomenon could explain why the induction period was longer with $P(C_6D_5)_3$ than with PPh_3, and consequently implies a careful attention in the potential interpretation of the KIE.

9. Crystallographic Data

9.1. Crystal structure of 2a (CCDC No. 1034988)[6]

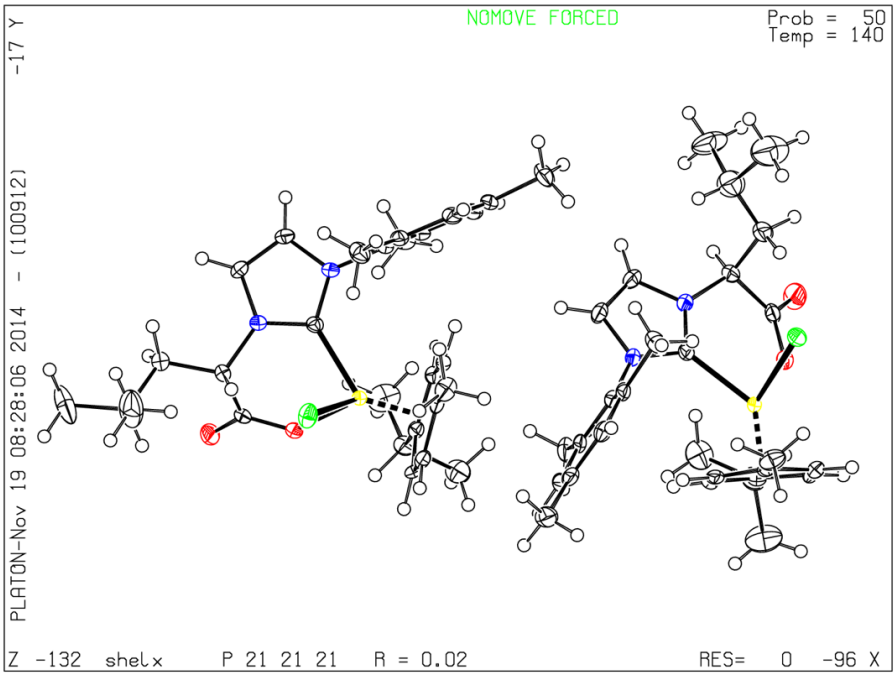


Table S2. Crystal data and structure refinement for 2a.

Identification code	shelx
Empirical formula	C56 H74 Cl2 N4 O4 Ru2
Formula weight	1140.23
Temperature	140(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 13.03730(10) A alpha = 90 deg. b = 19.1815(2) A beta = 90 deg. c = 21.7675(2) A gamma = 90 deg.
Volume	5443.51(9) $Å^3$
Z, Calculated density	4, 1.391 Mg/m^3
Absorption coefficient	0.701 mm^{-1}
F(000)	2368
Crystal size	0.302 x 0.267 x 0.167 mm
Theta range for data collection	3.002 to 26.997 deg.
Limiting indices	-15<=h<=16, -21<=k<=24, -27<=l<=27
Reflections collected / unique	42827 / 11861 [R(int) = 0.0361]
Completeness to theta =	25.242 99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11861 / 0 / 621
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0249, wR2 = 0.0596
R indices (all data)	R1 = 0.0278, wR2 = 0.0611
Absolute structure parameter	-0.034(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.990 and -0.334 $e^-.Å^{-3}$

9.2. Crystal structure of 2b (CCDC No. 2189418)

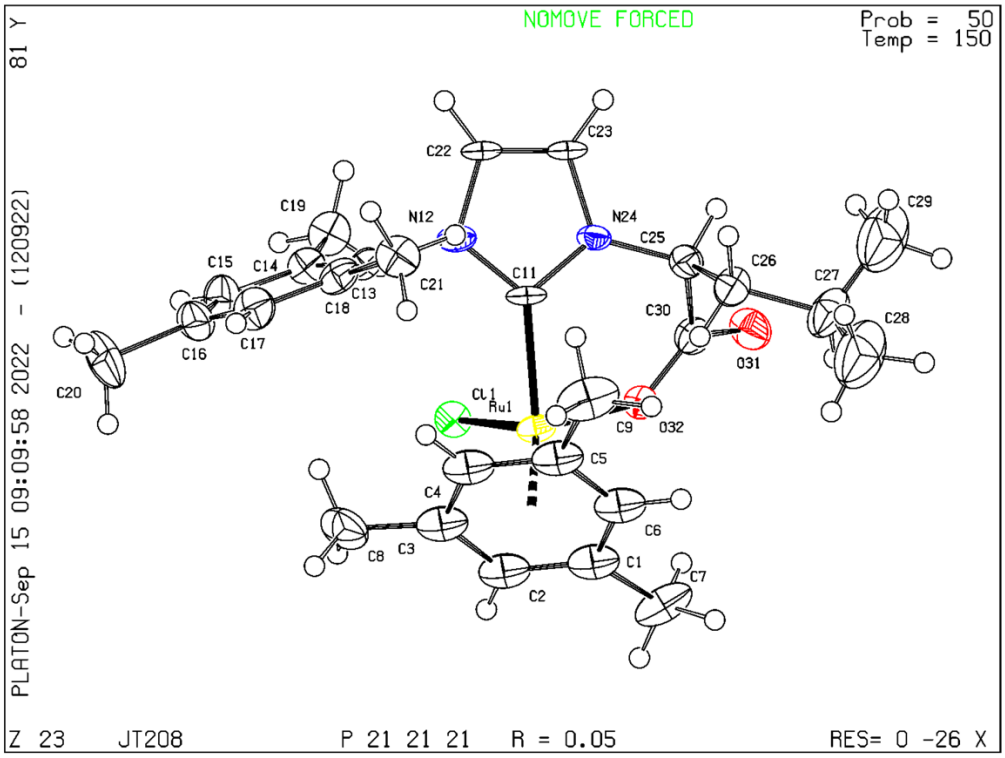


Table S3. Crystal data and structure refinement for 2b.

Empirical formula	$C_{28}H_{37}Cl_3N_2O_2Ru$
Extended formula	$C_{27}H_{35}ClN_2O_2Ru$; CH_2Cl_2
Formula weight	641.04 g/mol
Temperature	150(2) K
Radiation type	Mo-Kalpha
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, P 21 21 21 (I.T.#19)
Unit cell dimensions	a = 8.9971(9) A°, b = 12.0737(12) A°, c = 26.660(3) A°, alpha = 90 °, beta = 90 °, gamma = 90 °
Volume	2896.1(5) A3
Z, Calculated density	4, 1.470 $g.cm^{-3}$
Absorption coefficient	0.846 mm-1
F(000)	1320
Crystal size	0.440 x 0.210 x 0.070 mm
Crystal color	orange
Theta range for data collection	2.925 to 27.484°
(sinTheta/lambda)max (≈-1)	0.649
h_min, h_max	-11, 11
k_min, k_max	-15, 14
l_min, l_max	-34, 34
Reflections collected / unique	59001 / 6645 [R(int) = 0.0439]
Reflections [I>2sigma(I)]	6511
Completeness to theta_max	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.955 , 0.836
Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	6645 / 0 / 247
Goodness-of-fit	1.172
Shelxl weighting scheme parameters	a = 4.9187, b = re P=(
Flack parameter	0.08(7)
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1256
Final R indices [all data]	R1 = 0.0547, wR2 = 0.1262
Largest diff. peak and hole	1.221 and -1.686 e.A-3

9.3. Crystal structure of 2c (CCDC No. 2189419)

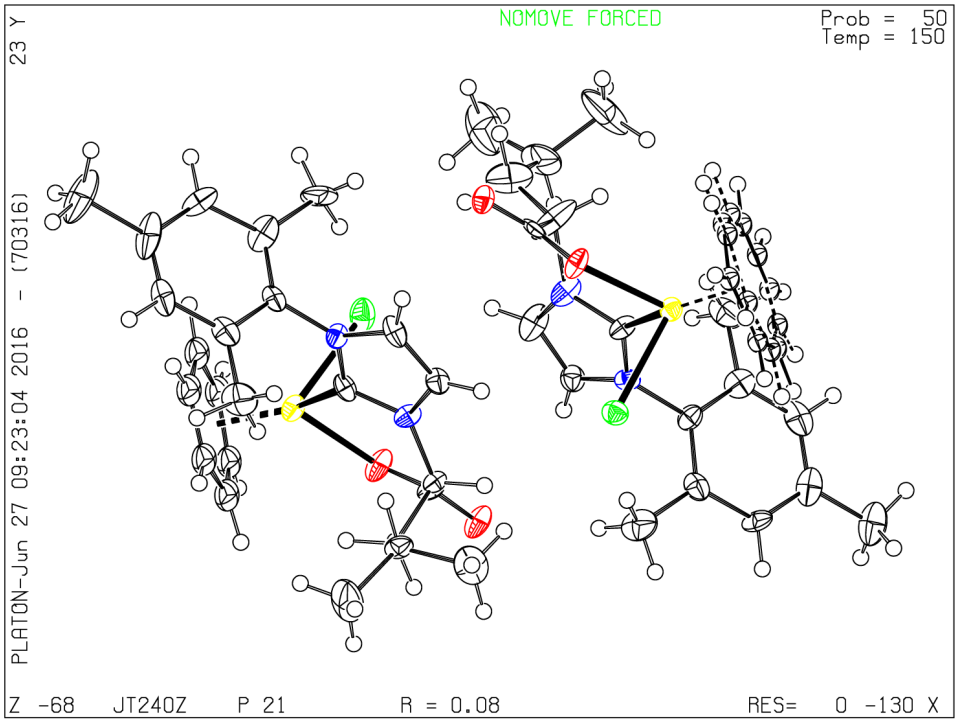


Table S4. Crystal data and structure refinement for 2c.

Empirical formula	C24 H29 Cl N2 O2 Ru
Formula weight	514.01 g/mol
Temperature	150(2) K
Radiation type	Mo-Kalpha
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21 (I.T.#4)
Unit cell dimensions	a = 10.1024(18) A, b = 21.259(4) A, c = 10.8649(19) A, beta = 102.016(5) °
Volume	2282.3(7) A3
Z, Calculated density	4, 1.496 g.cm-3
Absorption coefficient	0.827 mm-1
F(000)	1056
Crystal size	0.140 x 0.070 x 0.030 mm
Theta range for data collection	3.094 to 27.484°
(sinTheta/lambda)max (≈-1)	0.649
h_min, h_max	-13, 12
k_min, k_max	-27, 27
l_min, l_max	-14, 14
Reflections collected / unique	43748 / 10425 [R(int) = 0.1374]
Reflections [I>2sigma(I)]	7677
Completeness to theta_max	0.997
Absorption correction type	multi-scan
Max. and min. transmission	0.975 , 0.836
Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	10425 / 16 / 445
Goodness-of-fit	1.139
Shelxl weighting scheme parameters	a = 0.0233, b = 16.381
Flack parameter	0.04(9)
Final R indices [I>2sigma(I)]	R1 = 0.0787, wR2 = 0.1451
Final R indices [all data]	R1 = 0.1203, wR2 = 0.1575
Largest diff. peak and hole	1.241 and -2.127 e.A-3

The exposure time was 200 seconds per frame with a frame width of 1 degree. The total number of frames was 505.

10. References

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[2] T. Oishi, L. I. Lugo-Fuentes, Y. Jing, J. O. C. Jimenez-Halla, J. Barroso-Flores, M. Nakamoto, Y. Yamamoto, N. Tsunoji, R. Shang, *Chem. Sci*., 2021, **12**, 15603

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[4] K. Fukuda, N. Iwasawa, J. Takaya, *Angew. Chem. Int. Ed.* 2019, **58**, 2850-2853.

[5] E. Carpenter, G. W. Margulieux, M. D. Millard, C. E. Moore, N. Weidemann, A. L. Rheingold, J. S. Figueroa, *Angew. Chem. Int. Ed.* 2012, **51**, 9412-9416

[6] M. Mauduit, *CSD Communication,* **2014**, DOI: 10.5517/cc13qzqj.