# Supporting Information

# [2.2]Paracyclophane Bisphosphines for the Activation of Hydrogen by FLPs: Application in Domino Hydrosilylation/Hydrogenation of Enones

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## General Information

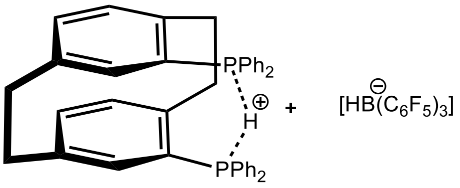
All preparations were done under an atmosphere of dry, $O_2$-free Ar employing both Schlenk line techniques and an MBraun inert atmosphere glove box. Solvents (pentane, hexanes, toluene and $CH_2Cl_2$) were purified employing a Grubbs' type column system manufactured by MBraun and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were dried at 140 °C under vacuum for 24 h prior to use. Deuterated solvents were distilled from sodium/benzophenone ($C_7D_8$) or $CaH_2$ ($CD_2Cl_2$). Hydrogen 5.0 were purchased from AirLiquid and passed over a column of DrieRite and activated molecular sieves. $^1H$, $^{13}C$, $^{11}B$, $^{19}F$ and $^{31}P$-NMR spectra were recorded on a *Bruker* AC 300 (300 MHz), *Bruker* AM 400 (400 MHz) or a *Bruker* DRX 500 (500 MHz) spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, $\delta$) downfield from tetramethylsilane (TMS) and are referenced to $d_8$-toluene (7.11 ppm) or $CHCl_3$ (7.26 ppm) as internal standards. $^{31}P$, $^{11}B$ and $^{19}F$ NMR spectra are referenced to 85% $H_3PO_4$, $BF_3(OEt_2)$ and $CFCl_3$ respectively. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The description of signals include: s = singlet, br. s = broad singlet, d =

doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc. The spectra were analyzed according to first order. Arene protons of the [2.2]Paracyclophane moiety are labeled as $H_{PC}$. $B(C_6F_5)_3$ was purchased from ABCR and sublimed, stirred over $Me_2SiClH$, dried in vacuum and sublimed again prior to use. PhanePhos (**1**) and $Ph_2MeSiH$ (**5**) was purchased from ABCR and used as received. GemPhos (**2a**) and CyGemPhos (**2b**) were prepared according to the literature procedure.[1] All other common organic substrates were purchased and used as received.

### 4,13-bis-(diphenylphosphino)-[2.2]paracyclophane (2a) + $B(C_6F_5)_3$ (3)

0.020 mmol (12 mg, 1.0 equiv.) 4,13-bis-(diphenylphosphino)-[2.2]paracyclophane (**2a**) and 0.020 mmol (10 mg, 1.0 equiv.) $B(C_6F_5)_3$ (**3**) were dissolved in *d*$_8$-toluene (0.5 ml). $^1H$ NMR (400 MHz, *d*$_8$-toluene, 298 K): $\delta$ = 7.79–7.65 (m, 4H, $H_{Ar}$), 7.49–7.33 (m, 4H, $H_{Ar}$), 7.20–7.07 (m, 6H, $H_{Ar}$), 7.06–6.95 (m, 6H, $H_{Ar}$), 6.40–6.30 (m, 4H, $H_{PC}$), 6.27–6.20 (m, 2H, $H_{PC}$), 3.90–3.60 (m, 2H, $CH_2$), 2.71–2.48 (m, 4H, $CH_2$), 2.42–2.25 (m, 2H, $CH_2$) ppm; $^{31}P$ {$^1H$} NMR (162 Mhz, *d*$_8$-toluene, 298 K): $\delta$ = -8.10 ppm; $^{19}F$ NMR (377 Mhz, *d*$_8$-toluene, 298 K): $\delta$ = -129.0 (br s, *o*-$C_6F_5$), -142.1 (br s, *p*-$C_6F_5$), -160.4 (br s, *m*-$C_6F_5$) ppm; $^{11}B$ {$^1H$} NMR (128 Mhz, *d*$_8$-toluene, 298 K): $\delta$ = 58.4 ppm.

### $[H\text{-}4,13\text{-bis-(diphenylphosphino)-[2.2]paracyclophane}]^+[HB(C_6F_5)_3]^-$

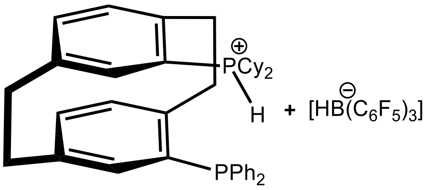


A solution of 0.060 mmol (35 mg, 1.0 equiv.) 4,13-bis-(diphenylphosphino)-[2.2]paracyclophane (**2a**) and 0.060 mmol (31 mg, 1.0 equiv.) $B(C_6F_5)_3$ (**3**) in toluene (2 ml) was transferred in a glovebox in a sealable flask with Teflon tap and magnetic stirbar. The solution was freeze-pump thawed for 2 cycles, charged with $H_2$ at 77 K and stirred for 24 h. To the colorless reaction mixture pentane (5 ml) was added, resulting in the formation of a white precipitate. After decantation of the solvents, rinsing with pentane (5 ml) and drying in vacuum, the salt was collected as white solid (49 mg, 75%). $^1$H NMR (400 MHz, $d_8$-toluene, 298 K): $\delta$ = 9.84 (t, $J_{PH}$ = 251 Hz, 1H, P*H*), 7.45–7.33 (m, 4H, $H_{Ar}$), 7.30–7.20 (m, 4H, $H_{Ar}$), 7.19–7.09 (m, 6H, $H_{Ar}$), 7.08–6.96 (m, 6H, $H_{Ar}$), 6.44–6.36 (m, 2H, $H_{PC}$), 6.35–6.29 (m, 2H, $H_{PC}$), 6.20–6.11 (m, 2H, $H_{PC}$), 4.81–4.19 (br m, 1H, B*H*), 3.06 (dd, *J* = 14.1 Hz, 4.4 Hz, 2H, $CH_2$), 2.63 (dd, *J* = 13.5 Hz, 3.8 Hz, 2H, $CH_2$), 2.58 (dd, *J* = 13.2 Hz, 4.1 Hz, 2H, $CH_2$), 2.27 (dd, *J* = 12.9 Hz, 3.5 Hz, 2H, $CH_2$) ppm; $^{13}$C-NMR (75 MHz, $d_8$-toluene, 298 K): δ = 149.1 (dm, $J_{CF}$ = 235 Hz, 6 x C, *o*-$C_6F_5$), 143.8 (m, 2 x *C*(CH2) $_{\text{quart. PC}}$), 141.3 (m, 2 x *C*(CH2) $_{\text{quart. PC}}$), 137.1 (dm, $J_{CF}$ = 259 Hz, 6 x C, *m*-$C_6F_5$), 136.9 (m, 2 x *C*H $_{PC}$), 136.2 (m, 2 x *C*H $_{PC}$), 135.3 (m, 2 x *C*H $_{PC}$), 135.0 (t, *J* = 8.2 Hz, 4 x *C*H $_{Ph}$), 135.5 (dm, $J_{CF}$ = 252 Hz, 3 x C, *p*-$C_6F_5$), 133.0 (m, 2 x *C*H $_{Ph}$), 132.9 (t, *J* = 8.2 Hz, 4 x *C*H $_{Ph}$), 132.7 (m, 2 x *C*H $_{Ph}$), 130.0 (t, J = 6.0 Hz, 4 x *C*H $_{Ph}$), 129.8 (t, *J* = 5.0 Hz, 4 x *C*H $_{Ph}$), 34.8–34.7 (m, 4 x *C*$H_2$) ppm [C(*i*-PC) and C(*i*-Ph) were not observed]; $^{31}$P {$^1$H} NMR (162 Mhz, $d_8$-toluene, 298 K): $\delta$ = -2.01 ppm; ]; $^{31}$P NMR (202 Mhz, $d_8$-toluene, 298 K): $\delta$ = -2.01 (d, $J_{PH}$ = 253 Hz) ppm; ]; $^{31}$P {$^1$H} NMR (162 Mhz, $d_8$-toluene, 213 K ): $\delta$ = -0.42 (d, $J_{PP}$ = 86 Hz), -4.80 (d, $J_{PP}$ = 86 Hz) ppm; $^{31}$P NMR (162 Mhz, $d_8$-toluene, 213 K): $\delta$ = -0.42 (dd, $J_{PH}$ = 515 Hz, $J_{PP}$ = 86 Hz), -4.80 (d, $J_{PP}$ = 86 Hz) ppm; $^{19}$F NMR (377 Mhz, $d_8$-toluene, 298 K): $\delta$ = -132.2 (m, *o*-$C_6F_5$), -163.8 (m, *p*-$C_6F_5$), -166.5 (m, *m*-$C_6F_5$) ppm; $^{11}$B {$^1$H} NMR (128 Mhz, $d_8$-toluene, 298 K): $\delta$ = -24.5 ppm; $^{11}$B NMR (128 Mhz, $d_8$-toluene, 298 K): $\delta$ = -24.5 (d, $J_{BH}$ = 92 Hz) ppm.

### 4-diphenylphosphino-13-dicyclohexylphosphino-[2.2]paracyclophane (2b) + $B(C_6F_5)_3$ (3)

0.020 mmol (12 mg, 1.0 equiv.) 4-diphenylphosphino-13-dicyclohexylphosphino-[2.2]paracyclophane (**2b**) and 0.020 mmol (10 mg, 1.0 equiv.) $B(C_6F_5)_3$ (**3**) were dissolved in $d_8$-toluene (0.5 ml). $^1$H NMR (400 MHz, $d_8$-toluene, 298 K): $\delta$ = 7.65–7.58 (m, 2H, $H_{Ar}$), 7.57–7.50 (m, 2H, $H_{Ar}$), 7.07–6.95 (m, 6H, $H_{Ar}$), 6.61–6.55 (m, 1H, $H_{PC}$), 6.47–6.38 (m, 3H, $H_{PC}$), 6.37–6.32 (m, 1H, $H_{PC}$), 6.27–6.21 (m, 1H, $H_{PC}$), 4.36–4.23 (m, 1H, $CH_2$), 3.36 (ddd, *J* = 13.4 Hz, 9.2 Hz, 3.5 Hz, 1H, $CH_2$), 2.88–2.66 (m, 3H, $CH_2$), 2.62–2.43 (m, 3H, $CH_2$), 2.32–2.16 (m, 1H, Cy), 2.08–1.79 (m, 5H, Cy), 1.76–1.14 (m, 12H, Cy), 1.08–0.69 (m, 3H, Cy), 0.49–0.31 (m, 1H, Cy) ppm; $^{31}$P {$^{1}$H} NMR (162 Mhz, $d_8$-toluene, 298 K): $\delta$ = -6.06 (m$_c$) ppm; $^{19}$F NMR (377 Mhz, $d_8$-toluene, 298 K): $\delta$ = -128.9 (br s, *o*-$C_6F_5$), -142.3 (br s, *p*-$C_6F_5$), -160.3 (br s, *m*-$C_6F_5$) ppm; $^{11}$B {$^{1}$H} NMR (128 Mhz, $d_8$-toluene, 298 K): $\delta$ = 56.1 ppm.

### [H-4-diphenylphosphino-13-dicyclohexylphosphino [2.2]paracyclophane]$^+$[HB($C_6F_5$)$_3$]$^-$



A solution of 0.085 mmol (50 mg, 1.0 equiv.) 4-diphenylphosphino-13-dicyclohexylphosphino-[2.2]paracyclophane (**2b**) and 0.085 mmol (43 mg, 1.0 equiv.) $B(C_6F_5)_3$ (**3**) in toluene (3 ml) was transferred in a glovebox to a sealable flask equipped with teflon tap and magnetic stirbar. The solution was freeze-pump thawed for 2 cycles, charged with $H_2$ at 77 K and stirred for 24 h. To the colorless reaction mixture pentane (7 ml) was added, resulting in the formation of a white precipitate. After decantation of the the solvents, rinsing with pentane (7 ml) and drying in vacuum, the salt was collected as white solid (80 mg, 85%). $^{1}$H NMR (400 MHz, $d_8$-toluene, 298 K): $\delta$ = 7.14 (d, $J_{HP}$ = 472 Hz, 1H), 7.48–7.41 (m, 2H, $H_{Ar}$), 7.41–7.35 (m, 2H, $H_{Ar}$), 7.09–6.95 (m, 6H, $H_{Ar}$), 6.60–6.42 (m, 2H, $H_{PC}$), 6.40–6.32 (m, 2H, $H_{PC}$), 6.32–6.26 (m, 1H, $H_{PC}$), 6.08–6.00 (dd, J = 9.6 Hz, 1.8Hz, 1H, $H_{PC}$), 4.84–3.98 (br m, 1H, B*H*), 3.16–2.98 (m, 1H, $CH_2$), 2.94–2.72 (m, 3H, $CH_2$), 2.67–2.58 (m, 1H, $CH_2$), 2.57–2.42 (m, 3H, $CH_2$), 2.40–2.28 (m, 1H, Cy), 1.98–0.64 (m, 20H, Cy), 0.37–0.21 (m, 1H, Cy) ppm; $^{13}$C-NMR (100 MHz, $d_8$-toluene, 298 K): δ = 149.2 (dm, $J_{CF}$ = 236 Hz, 6 x C, *o*-$C_6F_5$), 144.5 (d, *J* = 5.9 Hz, C$_{\text{quart. PC}}$), 142.1 (d, *J* = 11.7 Hz, C$_{\text{quart. PC}}$), 141.3 (dd, *J* = 11.7 Hz, C$_{\text{quart. PC}}$), 139.7–139.5 (m, 3 x C$_{\text{quart. PC}}$ ), 137.2 (dm, $J_{CF}$ = 250 Hz, 6 x C, *m*-$C_6F_5$), 137.0 (d, *J* = 8.1 Hz, C$_{\text{quart Ph}}$), 136.7 (d, *J* = 5.9 Hz, C$_{\text{quart Ph}}$), 136.0 (dm, $J_{CF}$ = 251 Hz, 3 x C, *p*-$C_6F_5$), 135.0 (d, *J* = 2.2 Hz, CH), 134.9 (d, *J* = 6.6 Hz, CH), 134.8 (CH), 134.6 (CH), 133.2 (CH), 133.0 (CH), 132.6 (d,

$J$ = 8.8 Hz, CH), 132.5 (CH), 130.4 (CH), 130.1 (CH), 129.3 (CH), 129.4 (CH), 129.4 (CH), 128.3 (CH), 36.4 (d, $J$ = 4.4 Hz, $CH_2$), 34.8 ($CH_2$), 34.6 ($CH_2$), 32.9 (CH), 32.1 (dd, $J$ = 43.3 Hz, 3.6 Hz, $CH_2$), 30.1 (CH), 29.3 (dd, $J$ = 44.7 Hz, 4.4 Hz, $CH_2$), 28.5 (d, $J$ = 3.7 Hz, $CH_2$), 27.6 (d, $J$ = 3.7 Hz, $CH_2$), 26.6 (d, $J$ = 13.2 Hz, $CH_2$), 26.2 (d, $J$ =5.1 Hz, $CH_2$), 26.1 (d, $J$ = 5.9 Hz, $CH_2$), 25.8 (d, $J$ = 2.9 Hz, $CH_2$), 25.6 (d, $J$ = 14.7 Hz, $CH_2$), 25.2 ($CH_2$), 25.0 ($CH_2$) ppm [2 x $CH_{Ar}$ not observed due to solvent signals]; $^{31}P\ \{^1H\}$ NMR (162 Mhz, $d_8$-toluene, 298 K ): $\delta$ = 14.3 (d, $J_{PP}$ = 47 Hz), -2.79 (d, $J_{PP}$ = 47 Hz) ppm; $^{31}P$ NMR (162 Mhz, $d_8$-toluene, 298 K): $\delta$ = 14.3 (dd, $J_{PH}$ = 473 Hz, $J_{PP}$ = 47 Hz), -2.79 (d, $J_{PP}$ = 47 Hz) ppm; $^{19}F$ NMR (377 Mhz, $d_8$-toluene, 298 K): $\delta$ = -133.2 (m, $o$-$C_6F_5$), -164.6 (m, $p$-$C_6F_5$), -167.4 (m, $m$-$C_6F_5$) ppm; $^{11}B\ \{^1H\}$ NMR (128 Mhz, $d_8$-toluene, 298 K): $\delta$ = -24.7 ppm; $^{11}B$ NMR (128 Mhz, $d_8$-toluene, 298 K): $\delta$ = -24.7 (d, $J_{BH}$ = 83 Hz) ppm.

### 4,12-bis-(diphenylphosphino)-[2.2]paracyclophane (1) + $B(C_6F_5)_3$ (3)

0.020 mmol (12 mg, 1.0 equiv.) 4,12-bis-(diphenylphosphino)-[2.2]paracyclophane (**1**) and 0.020 mmol (10 mg, 1.0 equiv.) $B(C_6F_5)_3$ (**3**) were dissolved in $d_8$-toluene (0.5 ml). $^1H$ NMR (400 MHz, $d_8$-toluene, 298 K): $\delta$ = 7.73–7.67 (m, 4H, $H_{Ar}$), 7.53–7.44 (m, 4H, $H_{Ar}$), 7.25–7.17 (m, 4H, $H_{Ar}$), 7.16–7.09 (m, 2H, $H_{Ar}$), 7.09–6.94 (m, 6H, $H_{Ar}$), 6.94–6.89 (m, 2H, $H_{PC}$), 6.41–6.35 (m, 4H, $H_{PC}$), 3.17–3.05 (m, 4H, $CH_2$), 2.80–2.70 (m, 2H, $CH_2$), 2.49–2.38 (m, 2H, $CH_2$) ppm; $^{31}P\ \{^1H\}$ NMR (162 Mhz, $d_8$-toluene, 298 K): $\delta$ = -0.53 ppm; $^{19}F$ NMR (377 Mhz, $d_8$-toluene, 298 K): $\delta$ = -128.7 (br s, $o$-$C_6F_5$), -142.5 (br s, $p$-$C_6F_5$), -160.3 (br s, $m$-$C_6F_5$) ppm; $^{11}B\ \{^1H\}$ NMR (128 Mhz, $d_8$-toluene, 298 K): $\delta$ = 57.5 ppm.

-> Spectra of the intermediate Phosphonium Borate/P-B adduct after reaction with hydrogen *vide infra*.

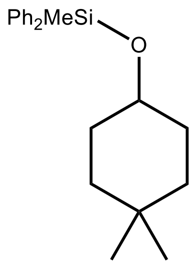
### Hydrogenation of Trimethyl(1-phenylvinyloxy)silane (6)

In a glove box, a solution of the bisphosphine **1/2ab** (10 mol%), $B(C_6F_5)_3$ **3** (10 mol%) and Trimethyl(1-phenylvinyloxy)silane (**6**) (20 mg) in $d_8$-toluene (0.5 ml) was transferred to a sealable NMR tube equipped with a Teflon tap. The solution was freeze-pump thawed for 2 cycles, charged with $H_2$ at 77 K and stand for the corresponding time. The NMR data agrees with the literature.[2]

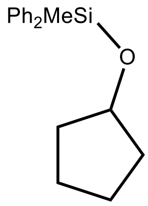
**General procedure for the reduction of enones**

In a glovebox, $B(C_6F_5)_3$ (**3**) (10-20 mol%), $Ph_2MeSiH$ (**5**) (1.0 eq.) and the enone **8** (25 mg, 1.0 eq.) were dissolved in toluene (2 ml) followed by immediate addition of PhanePhos **1** (10-20 mol%) (in case of **9e** GemPhos **2a**). The solution was transferred to a sealable flask equipped with a Teflon tap and magnetic stirbar. The solution was freeze-pump thawed for 2 cycles, charged with $H_2$ at 77 K and stirred for 24-48 h at 50°C. The reaction mixture was directly subjected to column chromatography (cyclohexane/EtOAc 99:1) yielding the corresponding silylether **9a-e** as colorless oil.

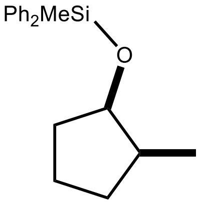
*4,4-Dimethylcyclohexyloxy(methyl)diphenylsilane (**9b**)*: 24 h, 48 mg, yield 74%, $R_f$ = 0.15. $^1$H NMR (300 Mhz, $CDCl_3$): δ = 7.66–7.58 (m, 4H, $H_{Ar}$), 7.43–7.32 (m, 6H, $H_{Ar}$), 3.73 (sept, *J* = 4.7 Hz, 1H, C*H*), 1.73–1.50 (m, 4H, $CH_2$), 1.48–1.36 (m, 2H, $CH_2$), 1.19–1.05 (m, 2H, $CH_2$), 0.93 (s, 3H, $CH_3$), 0.87 (s, 3H, $CH_3$), 0.67 (s, 3H, $CH_3$) ppm. $^{13}$C-NMR (75 MHz, $CDCl_3$): δ = 137.2 (2xC$_{\text{quart Ph}}$), 134.5 (4xCH$_{\text{Ph}}$), 129.8 (2xCH$_{\text{Ph}}$), 127.9 (4xCH$_{\text{Ph}}$), 71.9 (CH), 36.9, 31.6, 30.8, 29.7, 26.2, -2.1 ppm.



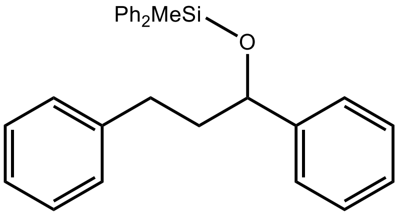
*Cyclopentyloxy(methyl)diphenylsilane (**9a**):* 24 h, 50 mg, yield 58% (10% silane impurity), $R_f$ = 0.20. $^1$H NMR (300 Mhz, $CDCl_3$): δ = 7.63–7.56 (m, 4H, $H_{Ar}$), 7.42–7.32 (m, 6H, $H_{Ar}$), 4.40–4.30 (m, 1H, C*H*), 1.86–1.46 (m, 8H, $CH_2$), 0.64 (s, 3H, $CH_3$) ppm. $^{13}$C-NMR (75 MHz, CDCl3): δ = 137.1 (2xC$_{\text{quart Ph}}$), 134.5 (4xCH$_{\text{Ph}}$), 129.7 (2xCH$_{\text{Ph}}$), 127.9 (4xCH$_{\text{Ph}}$), 75.3 (CH), 35.7, 23.3, -2.2 ppm. The NMR data agrees with the literature.[3]



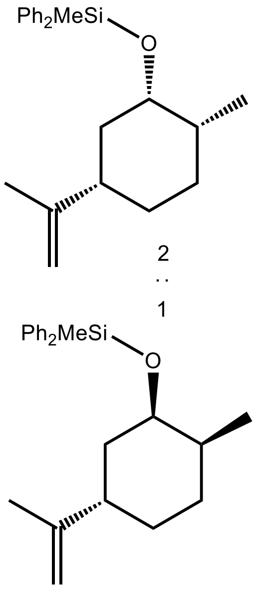
*cis-2-Methylcyclopentyloxy(methyl)diphenysilane (**9d**):* 24 h, 69 mg, yield 90%, $R_f$ = 0.10. $^1$H NMR (300 Mhz, $CDCl_3$): δ = 7.66–7.56 (m, 4H, $H_{Ar}$), 7.45–7.32 (m, 6H, $H_{Ar}$), 4.16 (q, *J* = 4.6 Hz, 1H, C*H*), 1.88–1.61 (m, 5H), 1.59–1.38 (m, 2H), 1.00 (d, *J* = 7.0 Hz, 3H, $CH_3$), 0.66 (s, 3H, $CH_3$) ppm. $^{13}$C-NMR (75 MHz, CDCl3): δ = 137.3 (2xC $_{quart\ Ph}$), 134.5 (4xCH $_{Ph}$), 129.7 (2xCH $_{Ph}$), 127.8 (4xCH $_{Ph}$), 40.0, 34.8, 31.0, 21.9, 14.6, -2.3 ppm [*C*H(O) was not observed]. The NMR data agrees with the literature.[3]



*1,3-Diphenylpropoxy(methyl)diphenylsilane (**9c**):* 48 h, 38 mg, yield 78%, $R_f$ = 0.1. $^1$H NMR (300 Mhz, $CDCl_3$): δ = 7.51–6.92 (m, 20H, $H_{Ar}$), 4.68 (dd, J = 6.7 Hz, 5.6 Hz, 1H, C*H*), 2.68–2.39 (m, 2H, $CH_2$), 2.15–1.83 (m, 2H, $CH_2$), 0.36 (s, 3H, $CH_3$) ppm. $^{13}$C-NMR (75 MHz, CDCl3): δ = 144.6, 142.2, 134.7, 134.5, 129.9, 128.8, 128.5, 128.4, 128.3, 127.9, 127.9, 127.3, 126.4, 125.8, 75.3, 42.0, 31.8, -2.3 ppm.



*(1S,2R,5S)-2-methyl-5-(prop-1-en-2-yl)cyclohexyloxy(methyl)diphenylsilane and (1R,2S,5S)-2-methyl-5-(prop-1-en-2-yl)cyclohexyloxy(methyl)diphenylsilane (**9e**):* 48 h, 100 °C, 29 mg, yield 50 %, $R_f$ = 0.6; d:r = 2:1;



Diastereomer 1: $^1$H NMR (300 Mhz, $CDCl_3$): δ = 7.66–7.55 (m, 4H, $H_{Ar}$), 7.44–7.32 (m, 6H, $H_{Ar}$), 5.09 (s, 1H), 4.89 (s, 1H), 3.94 ($m_c$, 1H), 2.75–2.62 (m, 1H), 1.83–1.68 (m, 2H), 1.57 (s, 3H, $CH_3$), 1.33–1.11 (m, 5H), 0.91 (d, J = 6.6 Hz, 3H, $CH_3$), 0.66 (s, 3H, $CH_3$) ppm.

Diastereomer 2: $^1$H NMR (300 Mhz, $CDCl_3$): δ = 7.68–7.54 (m, 4H, $H_{Ar}$), 7.45–7.30 (m, 6H, $H_{Ar}$), 4.62 (br s, 2H), 3.95 (br s, 1H), 2.49–2.36 (m, 1H), 1.80–1.66 (m, 2H), 1.62 (s, 3H, $CH_3$), 1.31–1.13 (m, 5H), 0.89 (d, J = 6.4 Hz, 3H, $CH_3$), 0.65 (s, 3H, $CH_3$) ppm. Assignment of diastereomers based on spectra for unprotected alcohols.[4]

## Quantum chemical calculations

The structures were optimised at DFT (density functional theory) level employing the gradient corrected Becke-Perdew functional BP86[5] in connection with a double-ζ def2-SVP basis set.[6] Recently Grimme[7] showed that dispersion interactions play a crucial role in structure stabilisation of the FLPs. Therefore, we decided to augment the DFT approach with the D3 empirical corrections.[8] To speed up the calculations we took advantage of the Resolution of Identity (RI) approximation.[9] Obtained geometries were confirmed to be energy minima on the potential energy surfaces by frequency calculations and possessed no imaginary frequencies. As multiple energy minima were obtained we recalculated the energies of each with the more sophisticated def2-TZVP basis set.[6] However, this did not alternate the energetic order of different isomers obtained with the smaller basis set. All calculations were performed with Turbomole 6.3 program. (TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com)

For atomic coordinates *vide infra*.

## X-ray Crystallographic Studies of [2aH]$^+$[BF$_4$]$^-$ and [2bH]$^+$[BF$_4$]$^-$

A suitable crystal of each of the compound was covered in mineral oil (Aldrich) and mounted onto a glass fiber. Data were collected on diffractometer equipped with a STOE imagine plate detector system plate detector system IPDS2T using Mo$_{K\alpha}$ radiation with graphite monochromatization ($\lambda$ = 0.71073) at 200 K. Structure solution was performed by direct methods; full-matrix-least squares refinement against $F^2$ using SHELXL-97 software[10] and OLEX2.[11]

Crystal structure determination of **[2aH]$^+$[BF$_4$]$^-$**

**Crystal Data.** $C_{40}H_{35}BF_4P_2$, $M$ =664.49, monoclinic, $a$ = 9.6069(19) Å, $b$ = 17.796(4) Å, $c$ = 10.210(2) Å, $\beta$ = 107.14(3)°, $V$ = 1668.0(7) Å$^3$, $T$ = 200, space group P2$_1$ (no. 4), $Z$ = 2, μ(MoKα) = 0.182, 15812 reflections measured, 8685 unique ($R_{int}$ = 0.0379) which were used in all calculations. The final $wR_2$ was 0.099 (all data) and $R_1$ was 0.0411 (I>=2u(I)).

Crystal structure determination of **$[2bH]^+[BF_4]^-$**

**Crystal Data.** $C_{40}H_{47}BF_4P_2$, *M* =676.53, monoclinic, *a* = 9.4616(19) Å, *b* = 18.149(4) Å, *c* = 10.749(2) Å, *β* = 109.34(3)°, *V* = 1741.7(6) Å$^3$, *T* = 200.15, space group P2$_1$ (no. 4), *Z* = 2, μ(MoKα) = 0.175, 14298 reflections measured, 7282 unique ($R_{int}$ = 0.1477) which were used in all calculations. The final $wR_2$ was 0.2270 (all data) and $R_1$ was 0.0836 (>2sigma(I)).

CCDC 867393 (**$[2aH]^+[BF_4]^-$**), 867456 (**$[2aH]^+[BF_4]^-$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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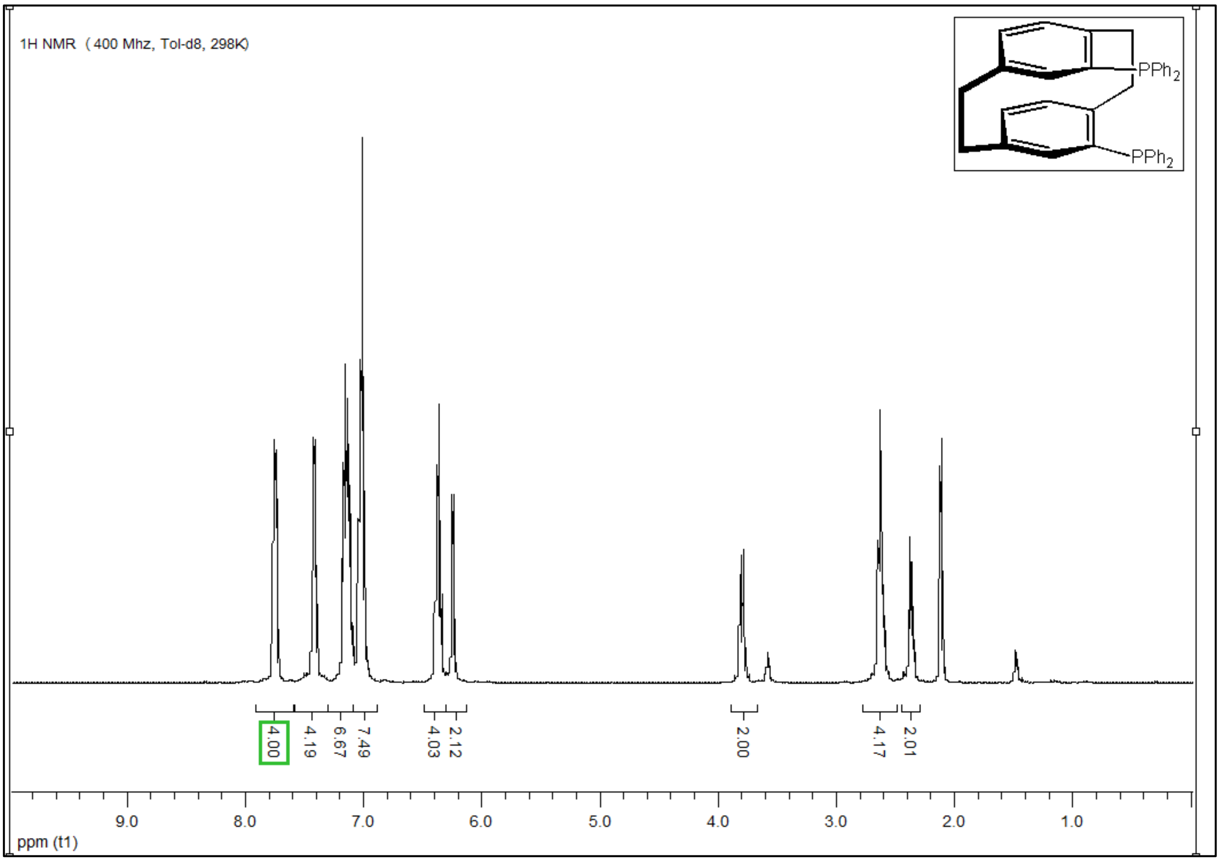
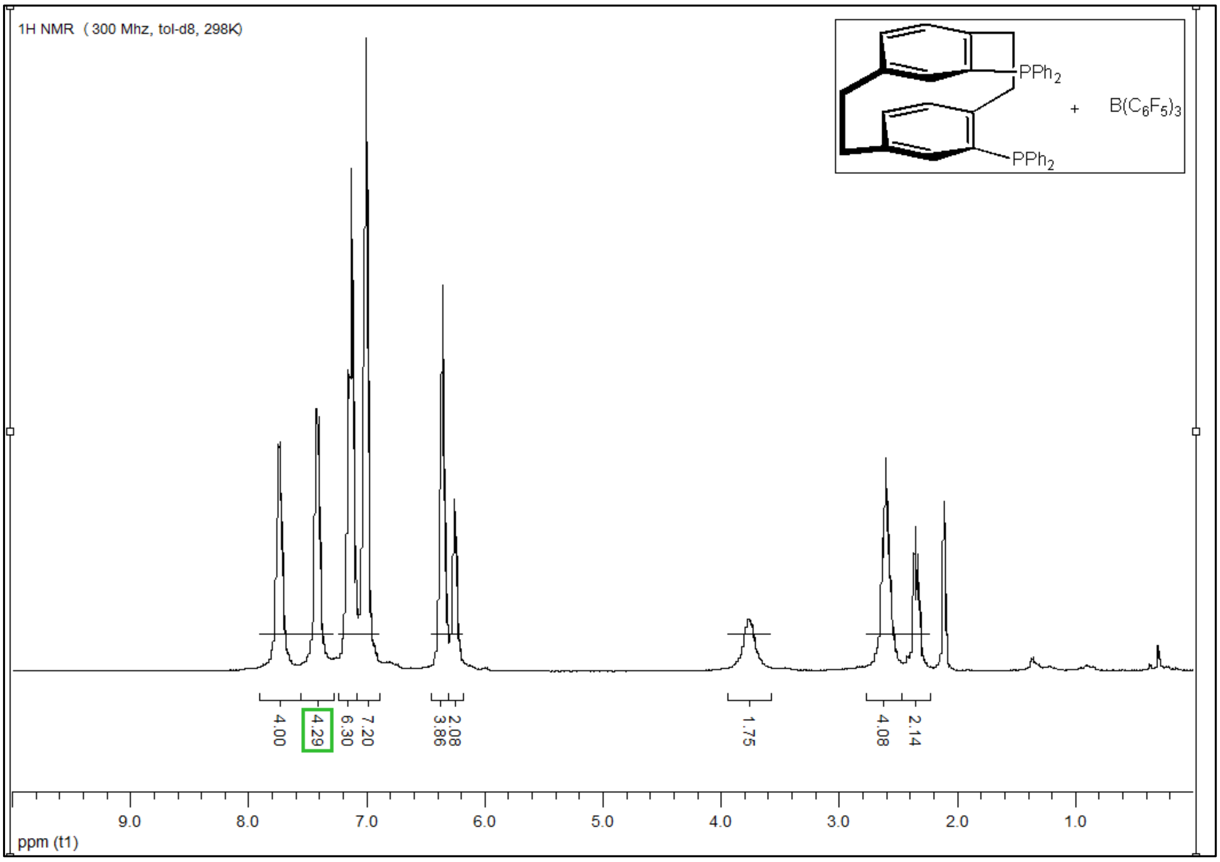
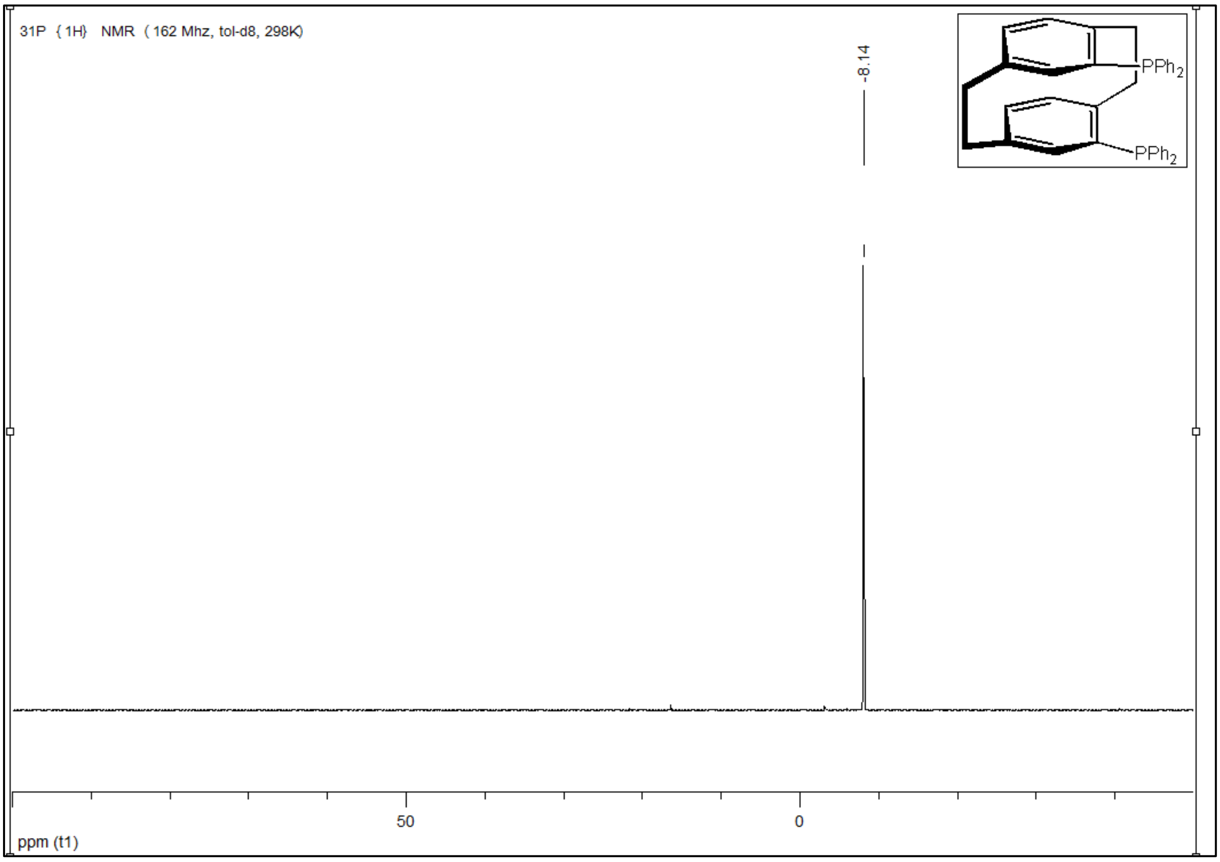
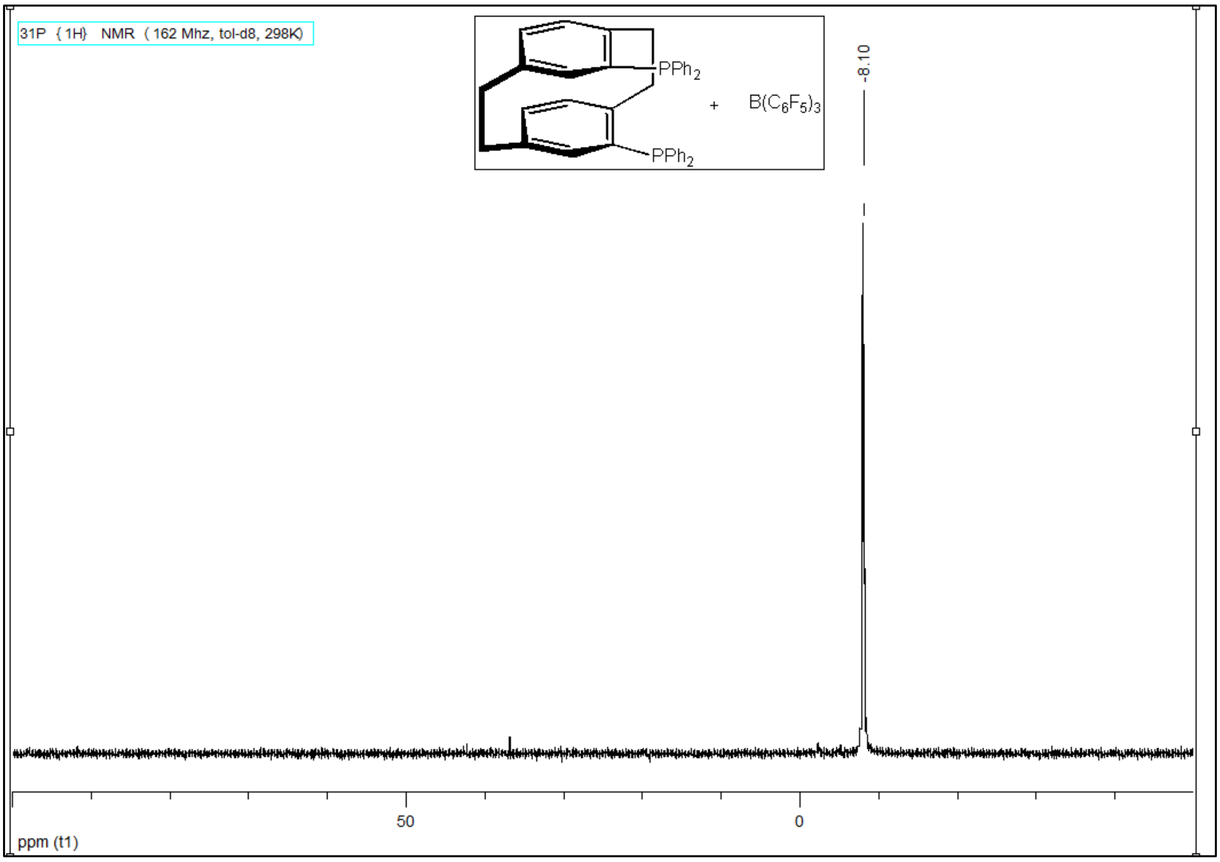

1H NMR ( 400 Mhz, Tol-d8, 298K)
PPh$_2$
PPh$_2$
4.00
4.19
6.67
7.49
4.03
2.12
2.00
4.17
2.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


1H NMR ( 300 Mhz, tol-d8, 298K)
PPh$_2$
PPh$_2$
+ B(C$_6$F$_5$)$_3$
4.00
4.29
6.30
7.20
3.86
2.08
1.75
4.08
2.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


31P {1H} NMR (162 Mhz, tol-d8, 298K)
-8.14
PPh$_2$
PPh$_2$
50
0
ppm (t1)


31P {1H} NMR (162 Mhz, tol-d8, 298K)
PPh$_2$
PPh$_2$
+
B(C$_6$F$_5$)$_3$
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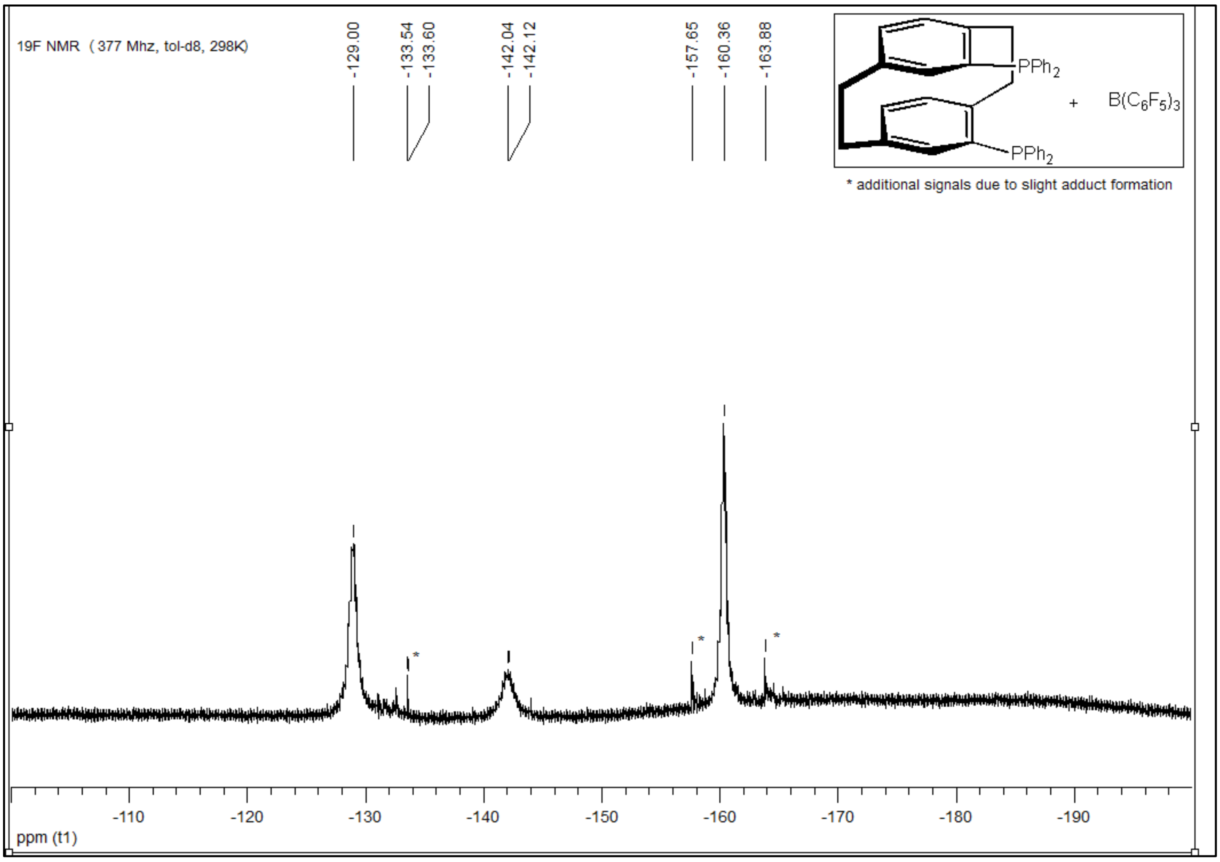
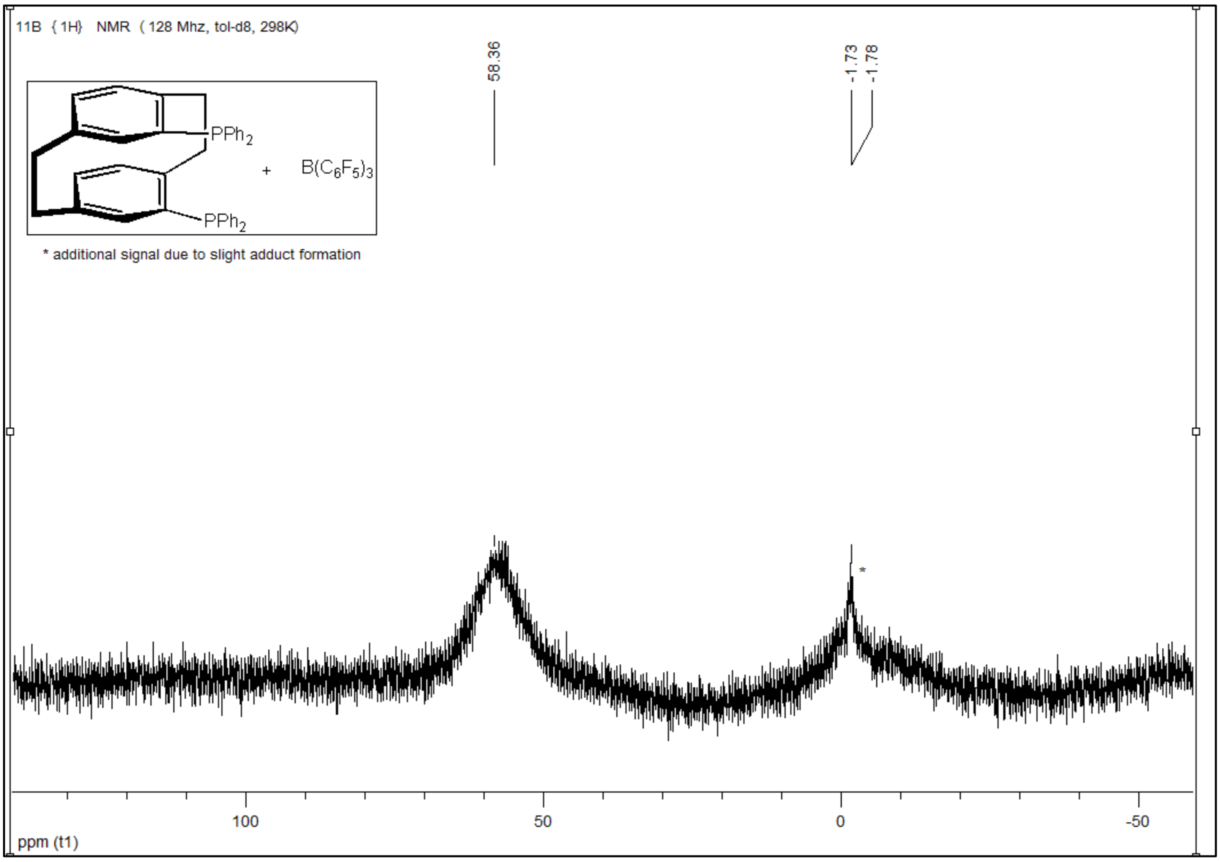
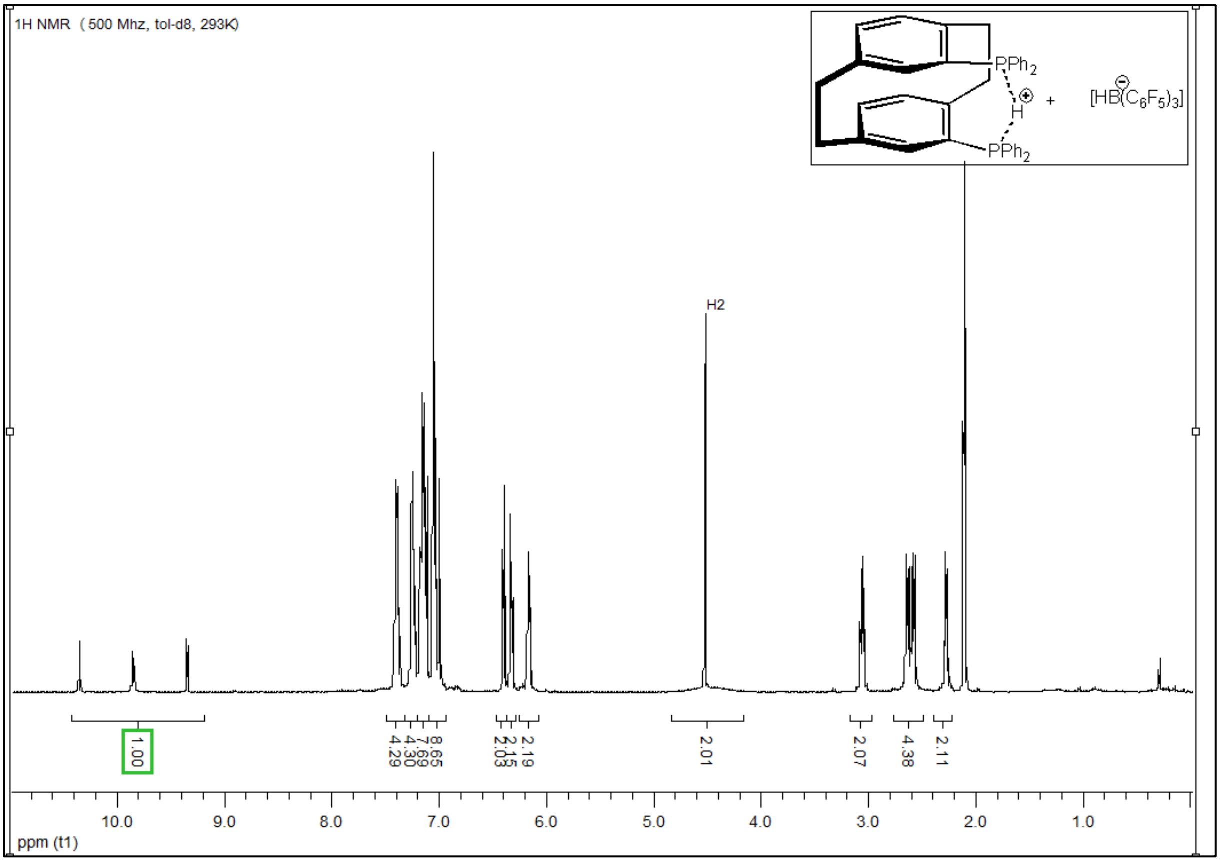
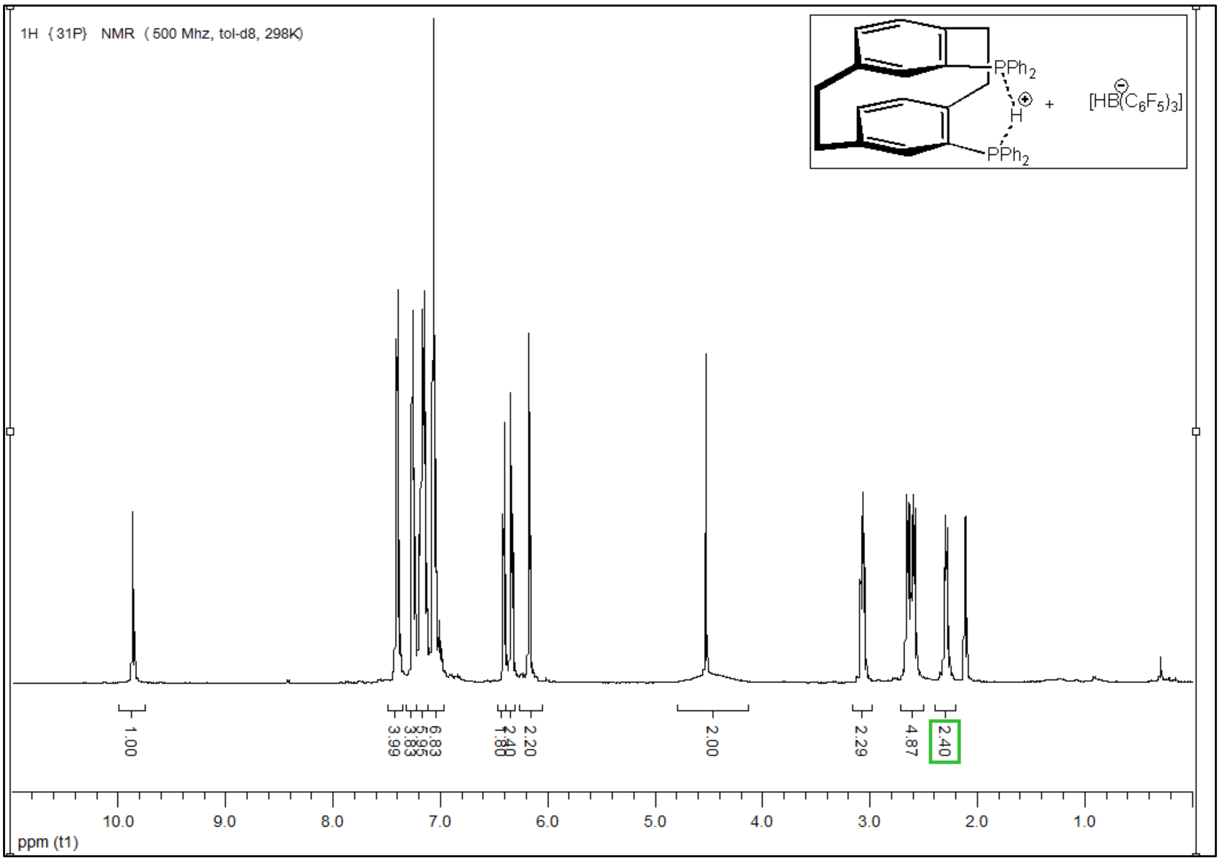
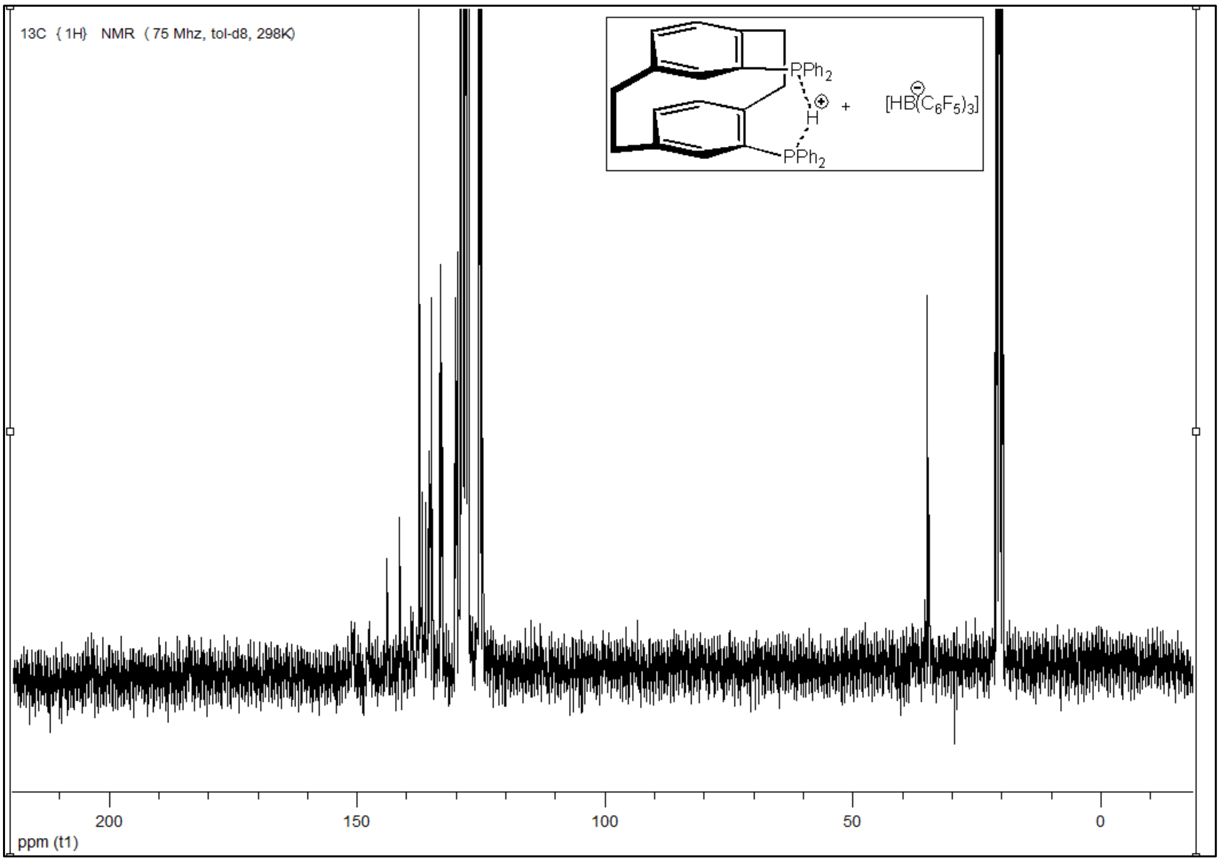
50
0
ppm (t1)

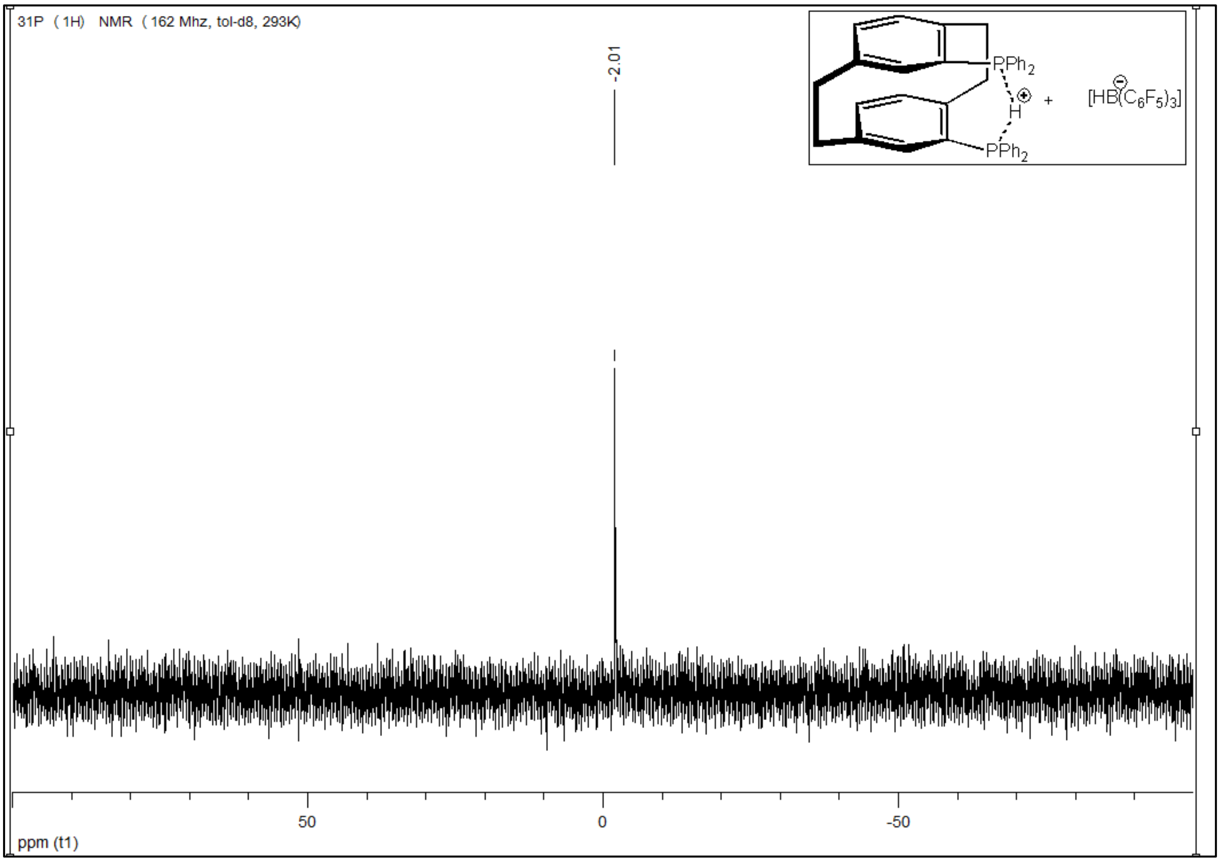

19F NMR (377 Mhz, tol-d8, 298K)
-129.00
-133.54
-133.60
-142.04
-142.12
-157.65
-160.36
-163.88
PPh$_2$
+
B(C$_6$F$_5$)$_3$
PPh$_2$
* additional signals due to slight adduct formation
*
*
*
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm (t1)

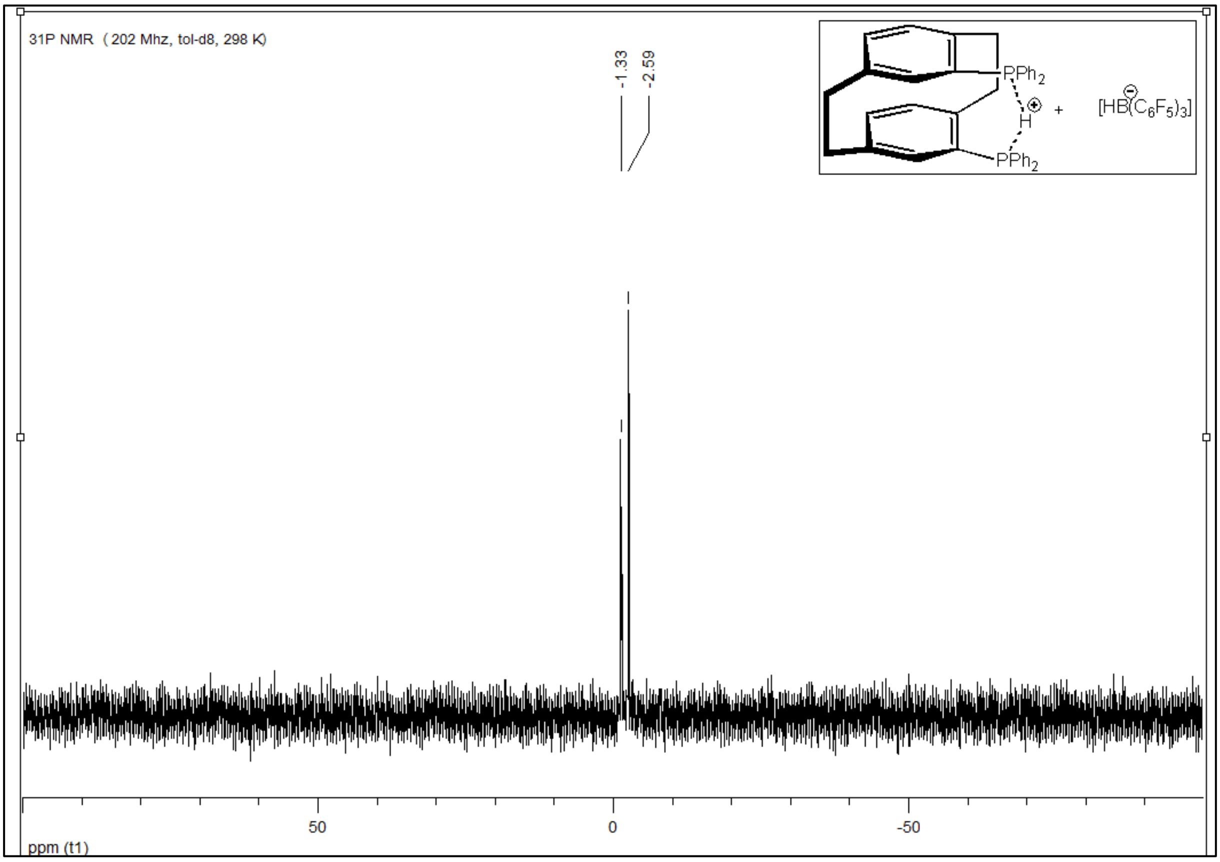

11B {1H} NMR (128 Mhz, tol-d8, 298K)
PPh$_2$
+
B(C$_6$F$_5$)$_3$
PPh$_2$
* additional signal due to slight adduct formation
58.36
-1.73
-1.78
*
100
50
0
-50
ppm (t1)

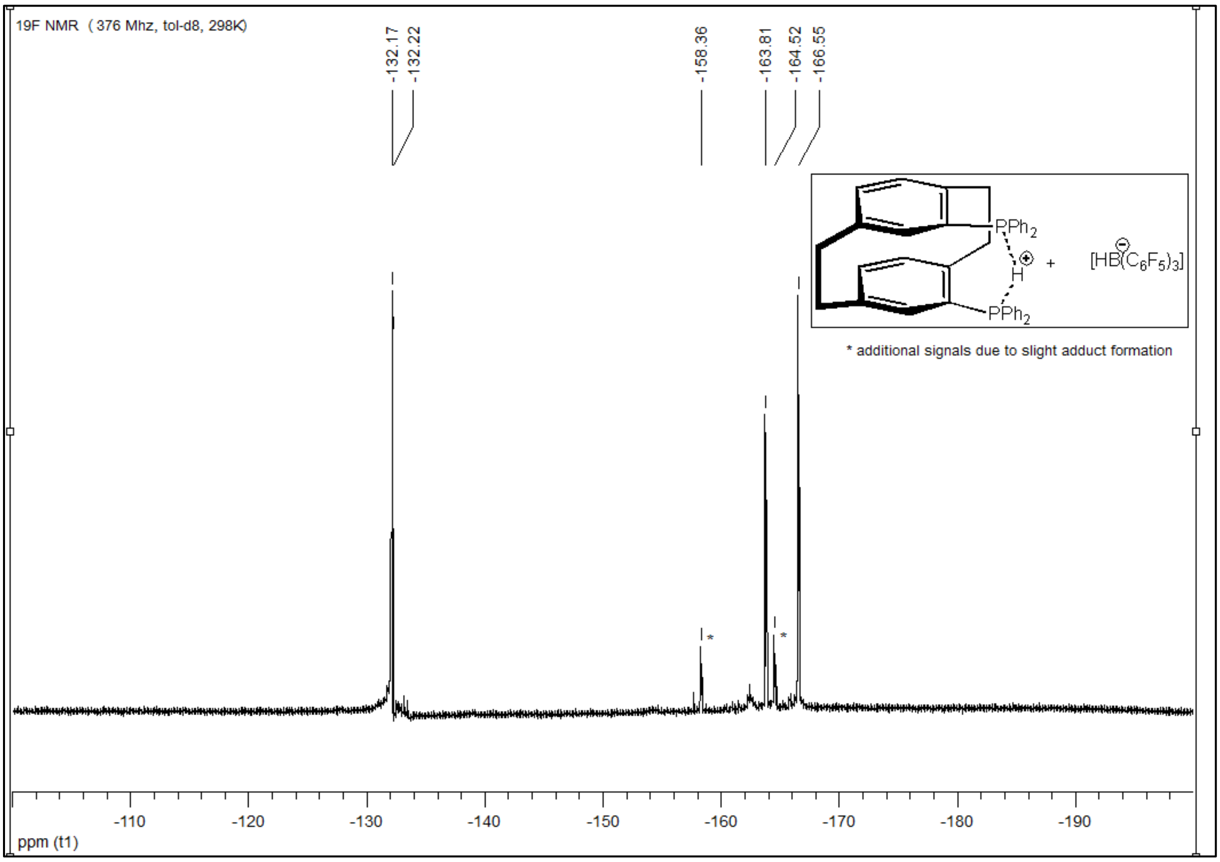

1H NMR (500 Mhz, tol-d8, 293K)
PPh$_2$
H
PPh$_2$
+
[HB(C$_6$F$_5$)$_3$]
H2
1.00
4.29
4.30
7.69
8.65
2.05
2.15
2.19
2.01
2.07
4.38
2.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

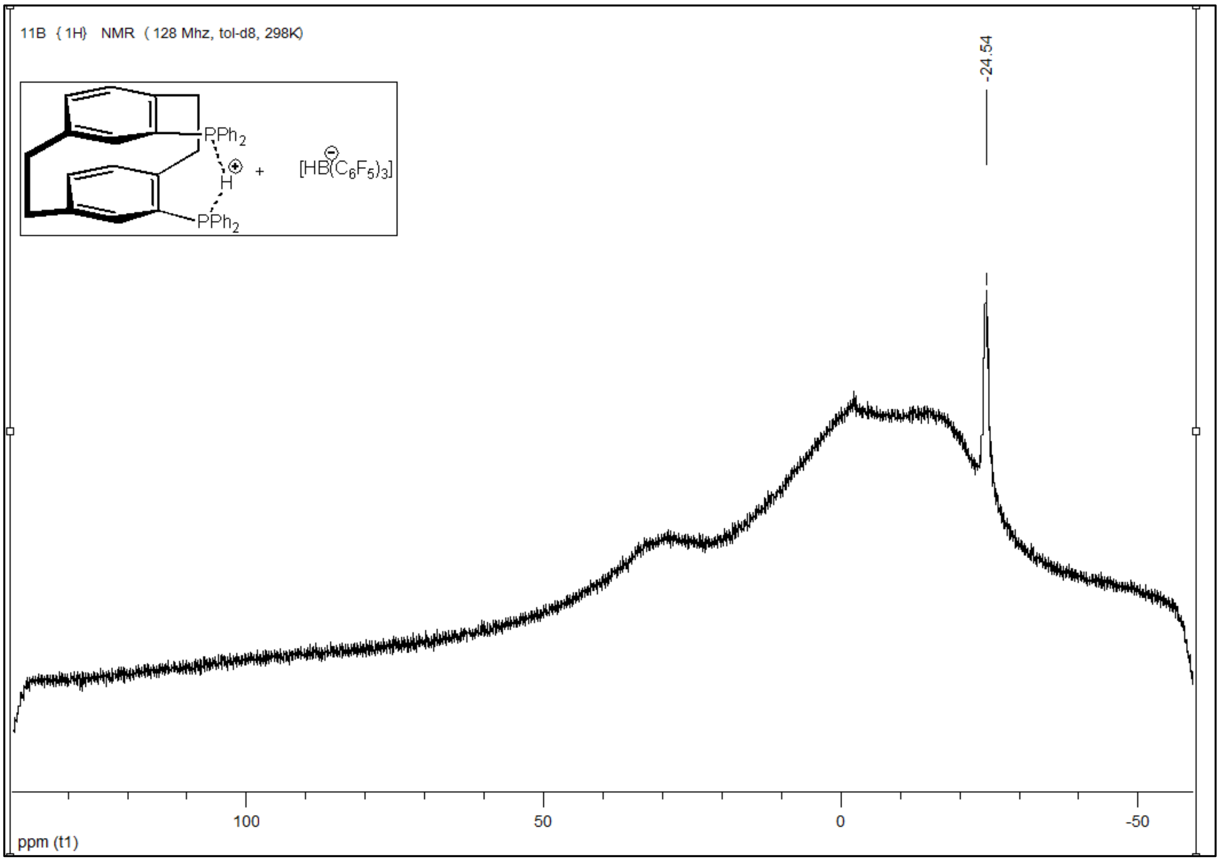

1H {31P} NMR (500 Mhz, tol-d8, 298K)
PPh$_2$
H
PPh$_2$
+
[HB(C$_6$F$_5$)$_3$]
1.00
3.99
3.83
5.95
6.83
1.80
2.40
2.20
2.00
2.29
4.87
2.40
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

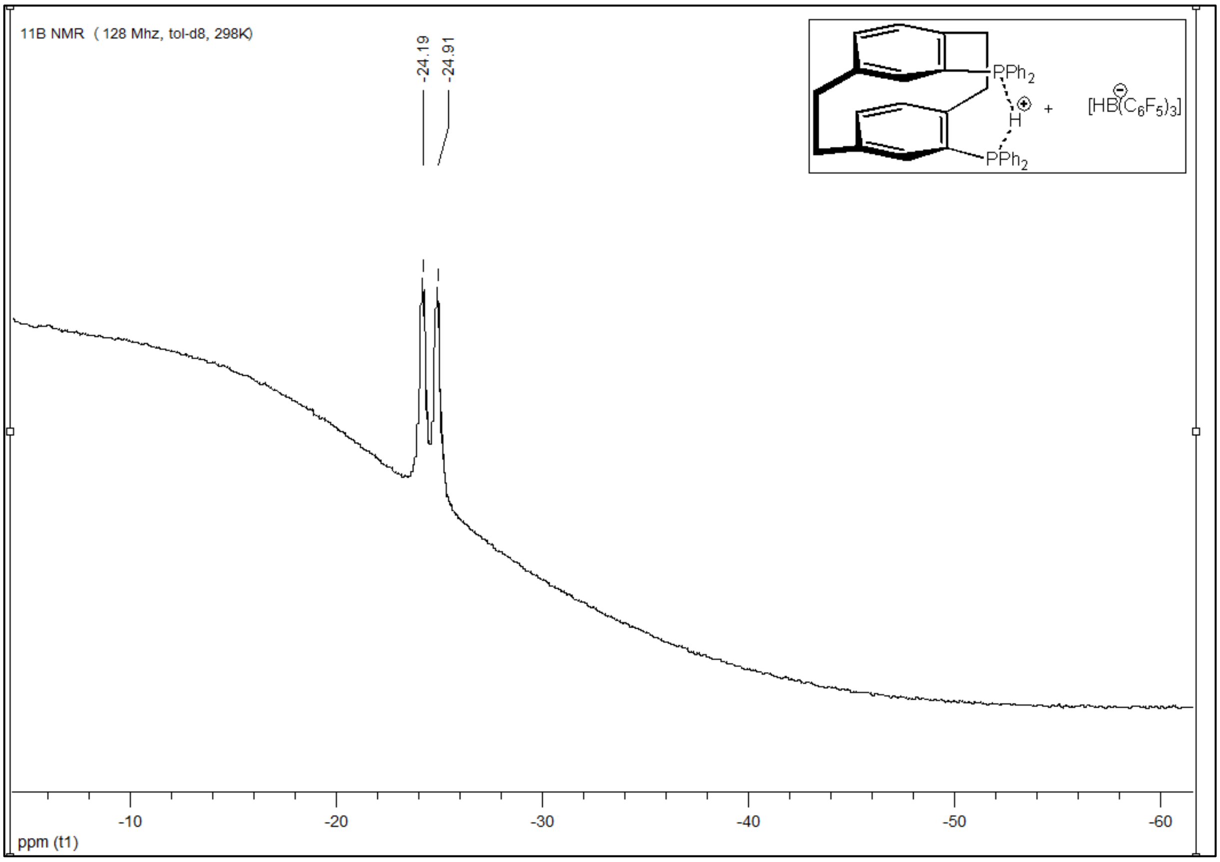

13C {1H} NMR (75 Mhz, tol-d8, 298K)
PPh2
H
+
[HB(C6F5)3]
PPh2
200
150
100
50
0
ppm (t1)

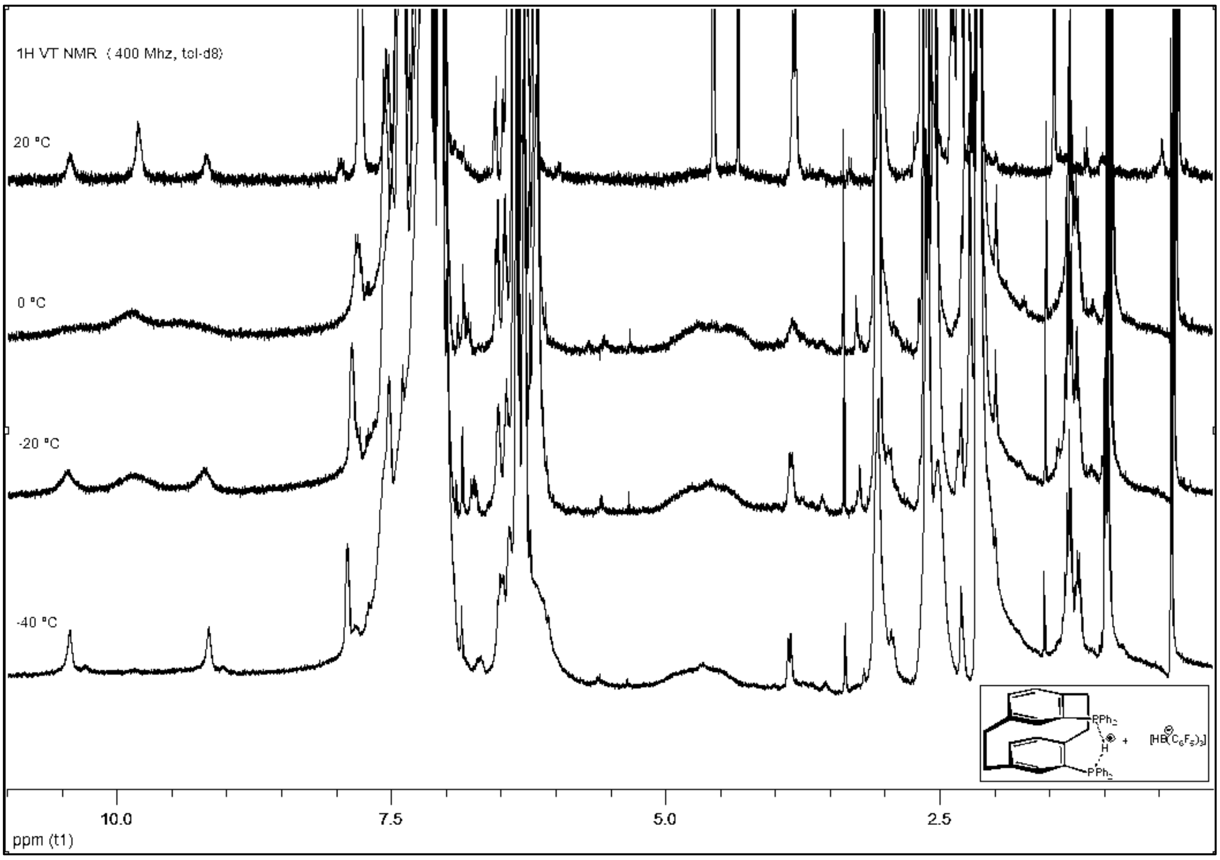

31P (1H) NMR (162 Mhz, tol-d8, 293K)
-2.01
PPh2
H
+
[HB(C6F5)3]
PPh2
50
0
-50
ppm (t1)

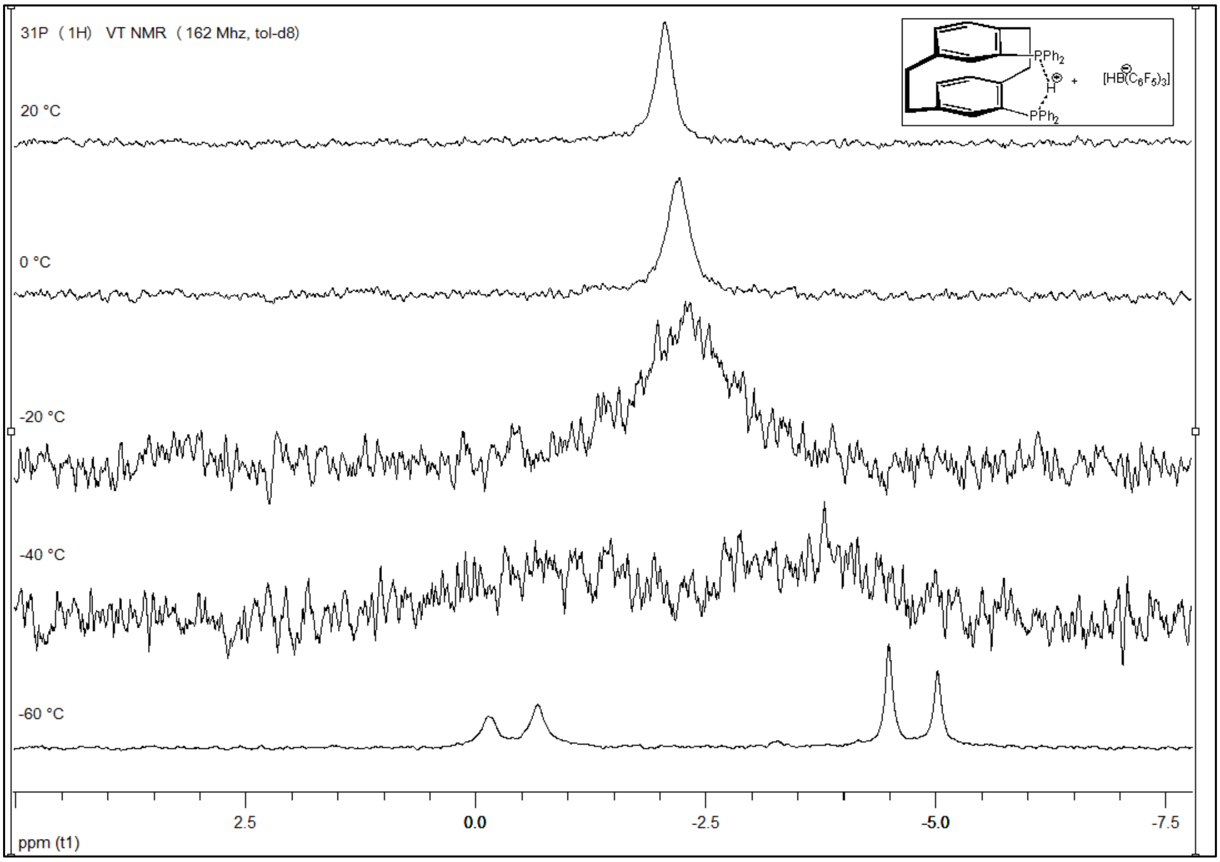

31P NMR (202 Mhz, tol-d8, 298 K)
-1.33
-2.59
PPh2
H
+
[HB(C6F5)3]
PPh2
50
0
-50
ppm (t1)

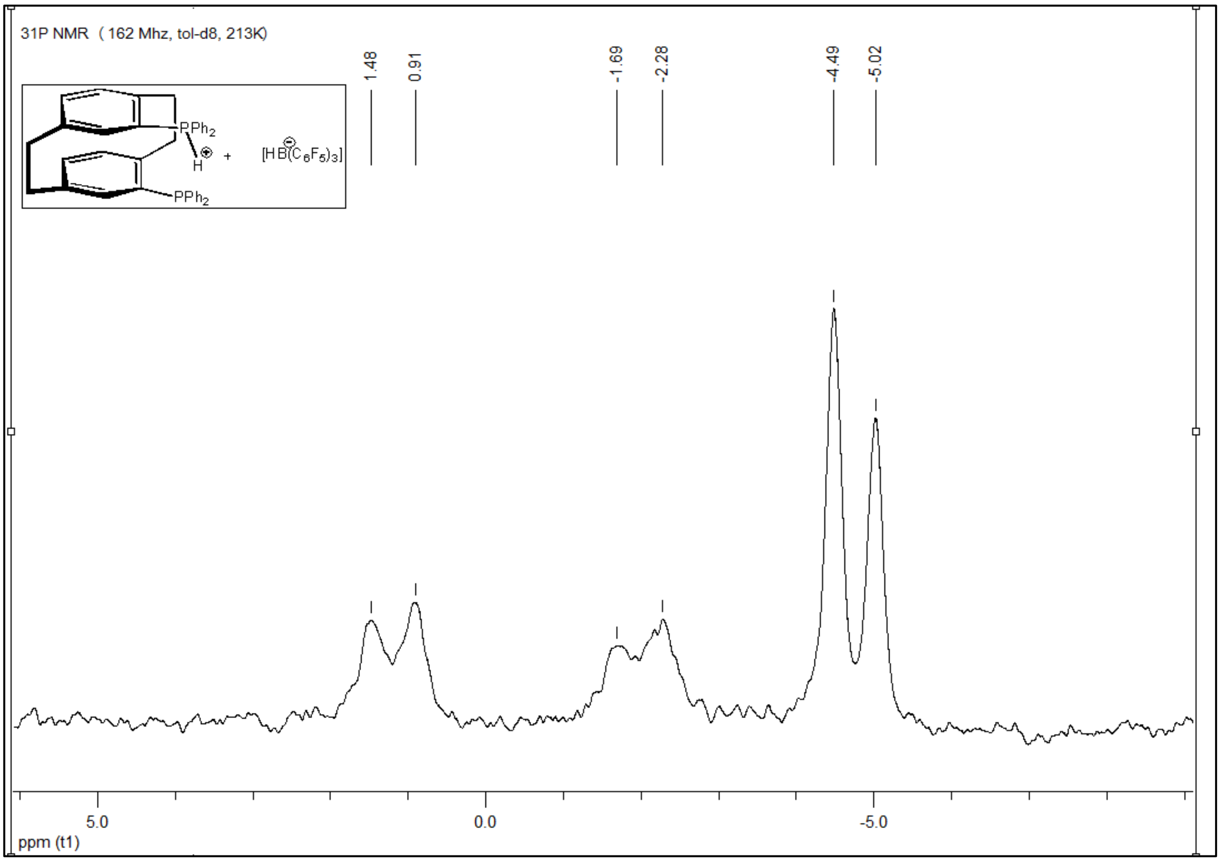

19F NMR (376 Mhz, tol-d8, 298K)
-132.17
-132.22
-158.36
-163.81
-164.52
-166.55
PPh2
H
+
[HB(C6F5)3]
PPh2
* additional signals due to slight adduct formation
*
*
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm (t1)


11B {1H} NMR (128 Mhz, tol-d8, 298K)
-24.54
PPh2
H
PPh2
+
[HB(C6F5)3]
100
50
0
-50
ppm (t1)


11B NMR (128 Mhz, tol-d8, 298K)
-24.19
-24.91
PPh2
H
PPh2
+
[HB(C6F5)3]
-10
-20
-30
-40
-50
-60
ppm (t1)


1H VT NMR (400 Mhz, tol-d8)
20 °C
0 °C
-20 °C
-40 °C
PPh2
H
+
[HB(C6F5)3]
PPh2
10.0
7.5
5.0
2.5
ppm (t1)


31P (1H) VT NMR (162 Mhz, tol-d8)
20 °C
0 °C
-20 °C
-40 °C
-60 °C
PPh2
H
+
[HB(C6F5)3]
PPh2
2.5
0.0
-2.5
-5.0
-7.5
ppm (t1)


31P NMR ( 162 Mhz, tol-d8, 213K)
PPh2
H
+
[HB(C6F5)3]
PPh2
1.48
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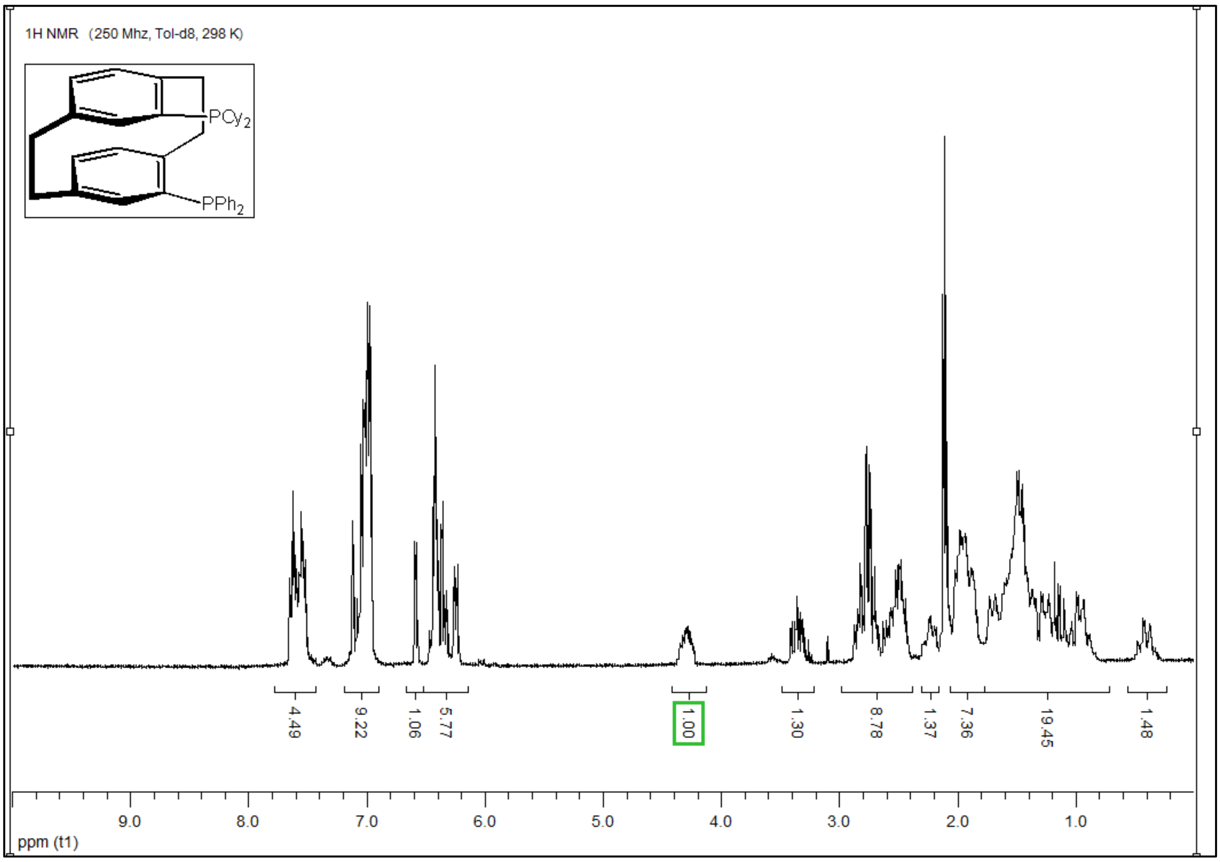
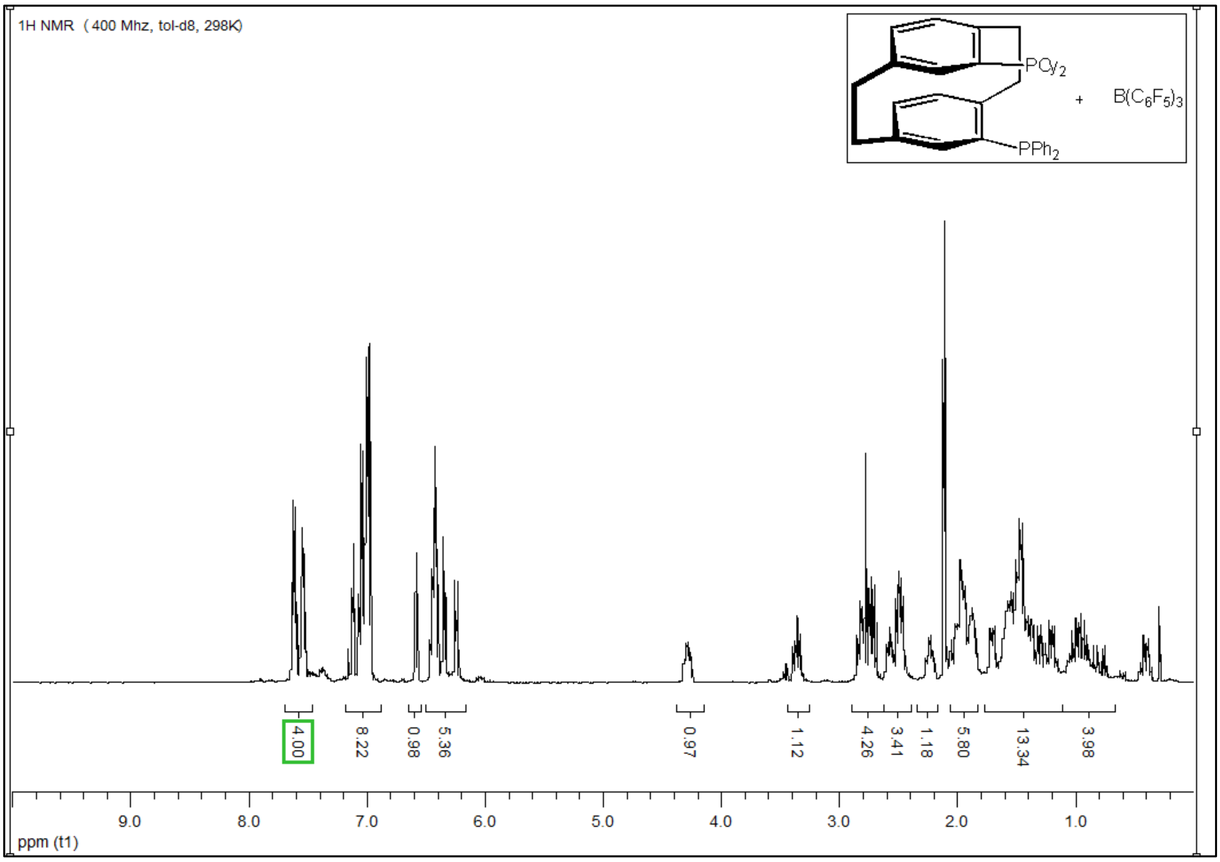
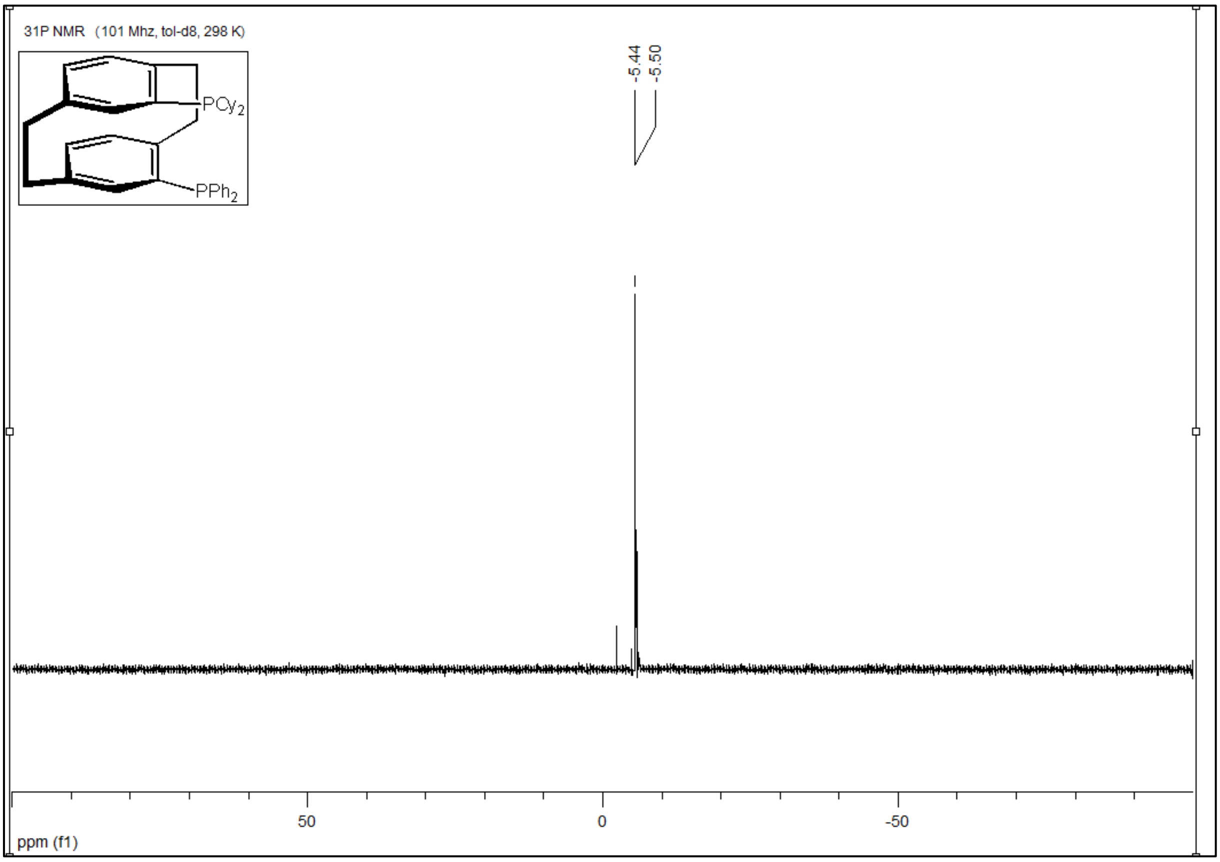
-1.69
-2.28
-4.49
-5.02
5.0
0.0
-5.0
ppm (t1)


1H NMR (250 Mhz, Tol-d8, 298 K)
PCy2
PPh2
4.49
9.22
1.06
5.77
1.00
1.30
8.78
1.37
7.36
19.45
1.48
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


1H NMR (400 Mhz, tol-d8, 298K)
PCy2
+
B(C6F5)3
PPh2
4.00
8.22
0.98
5.36
0.97
1.12
4.26
3.41
1.18
5.80
13.34
3.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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PPh2
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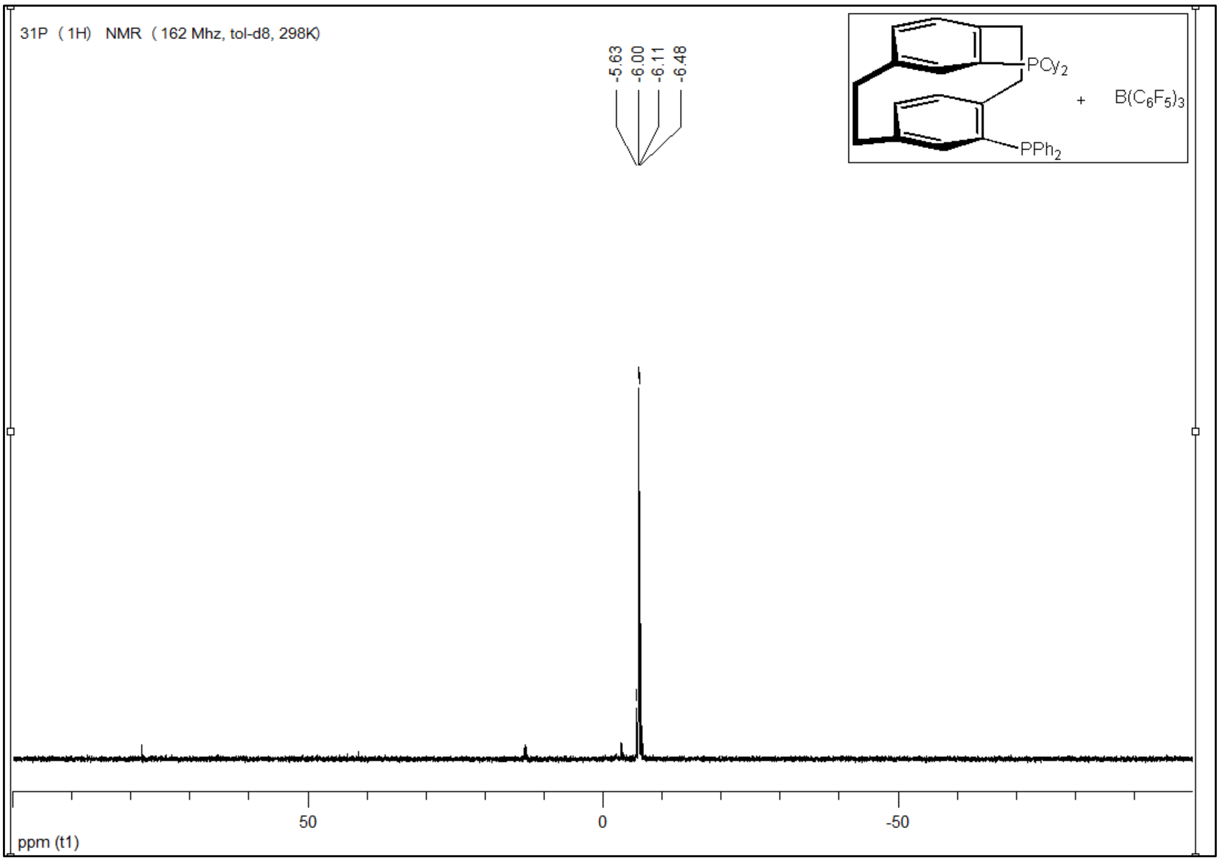
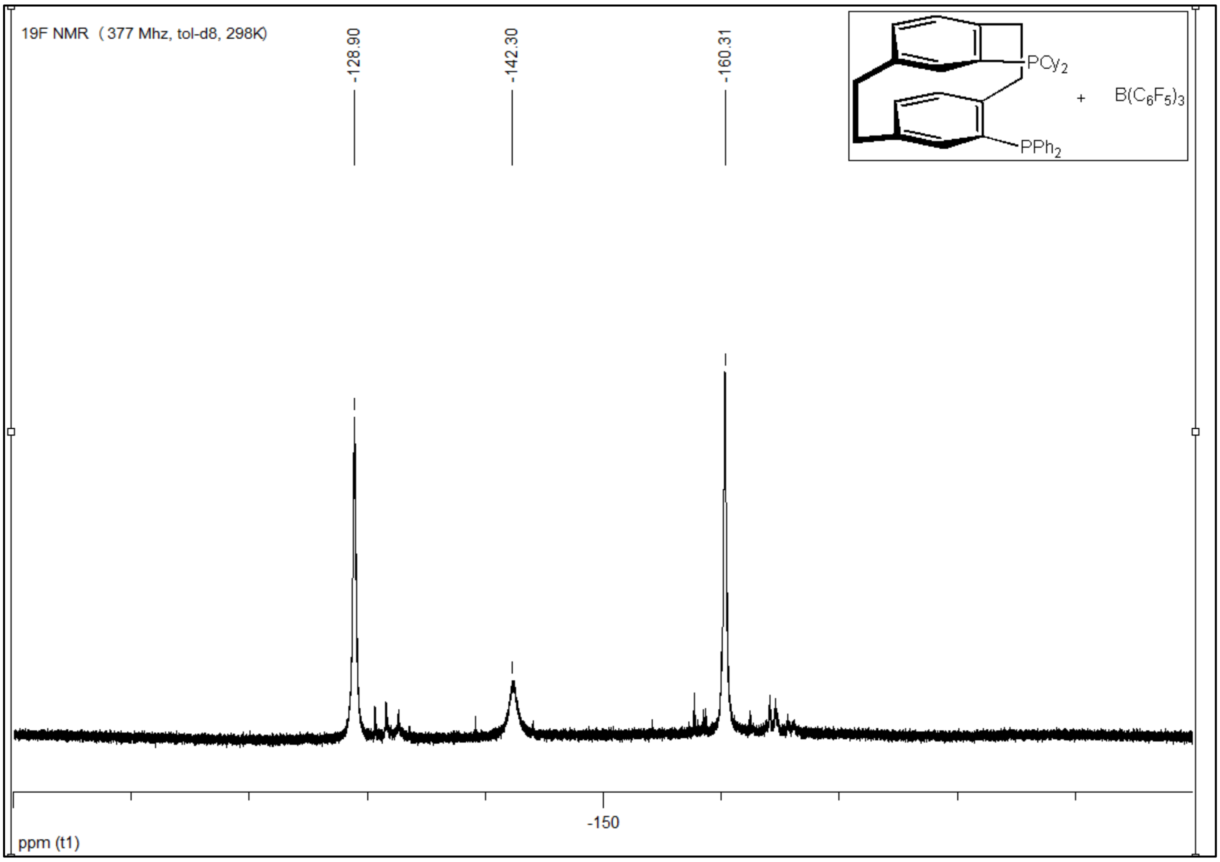
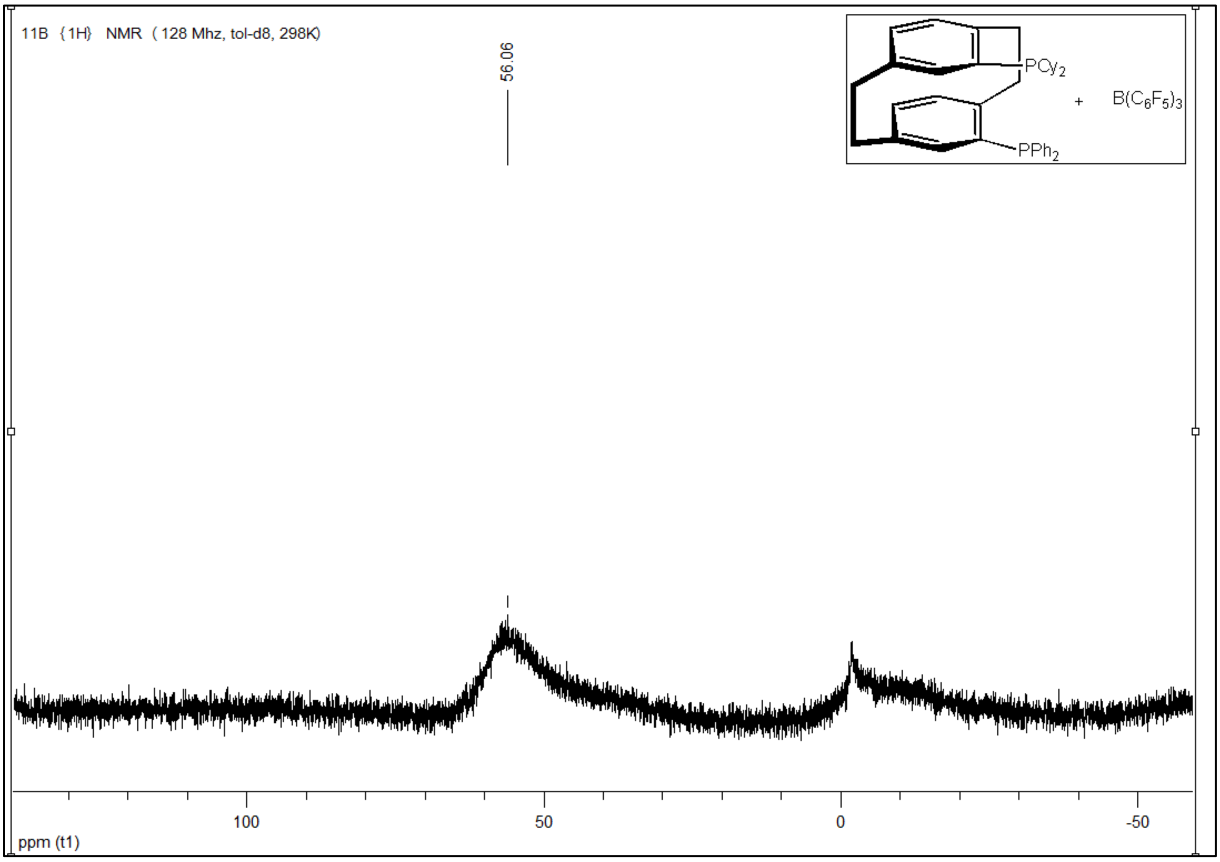
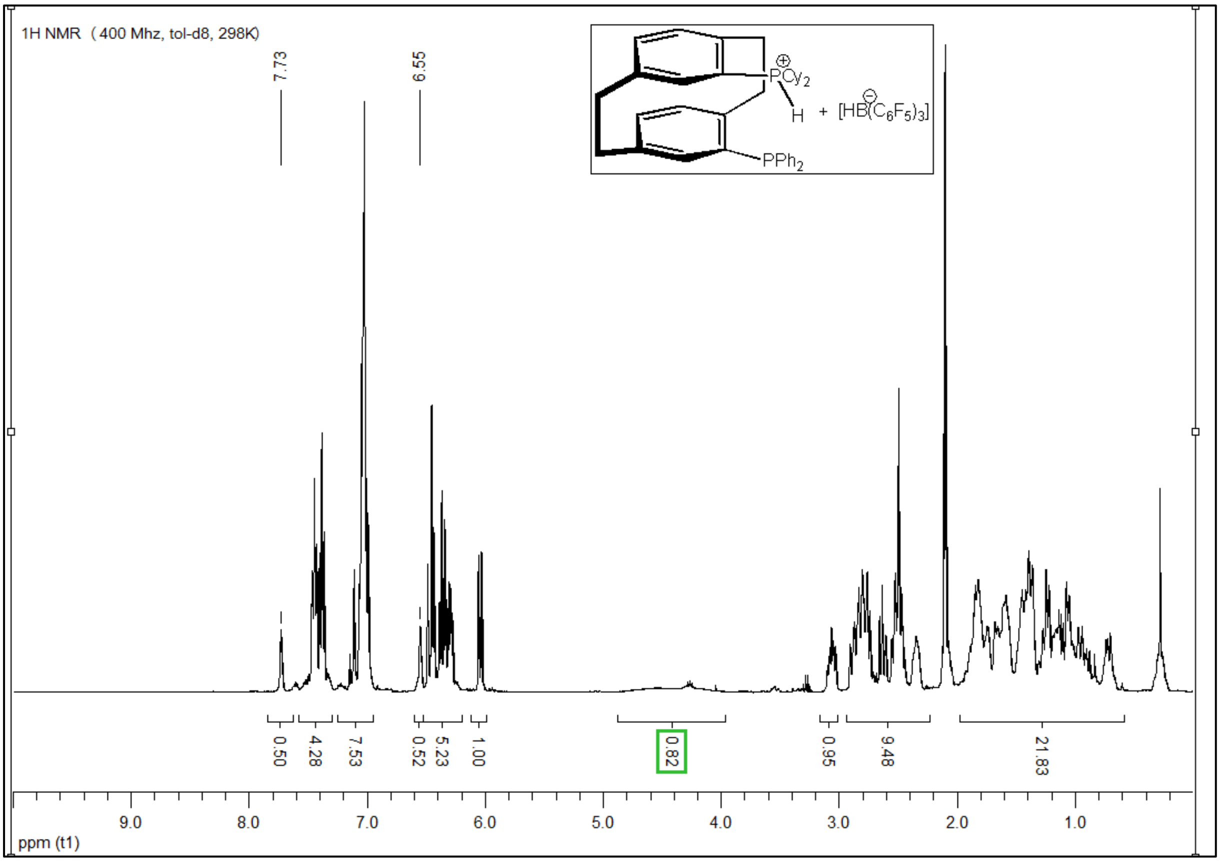
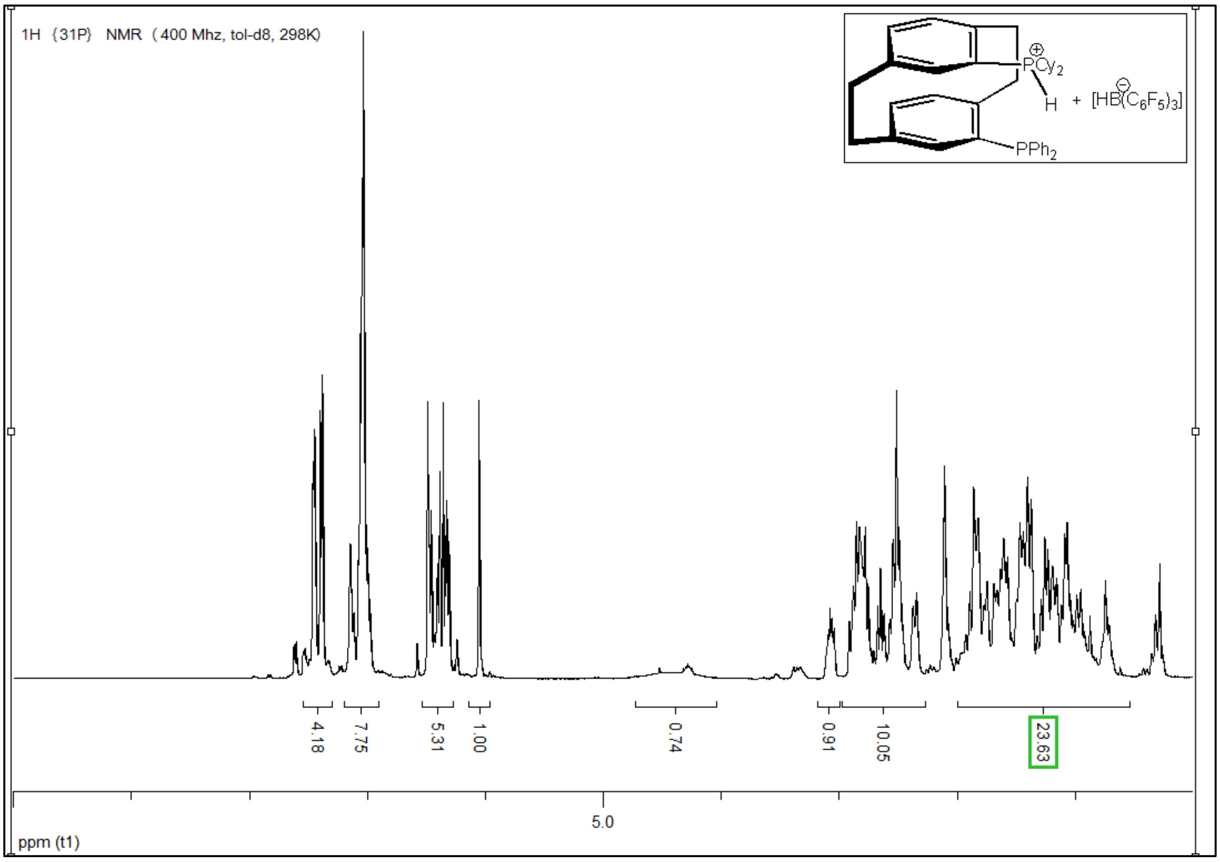
-5.50
50
0
-50
ppm (f1)


31P (1H) NMR (162 Mhz, tol-d8, 298K)
-5.63
-6.00
-6.11
-6.48
PCy2
+
B(C6F5)3
PPh2
50
0
-50
ppm (t1)


19F NMR（377 Mhz, tol-d8, 298K)
-128.90
-142.30
-160.31
PCy2
+
B(C6F5)3
PPh2
-150
ppm (t1)


11B {1H} NMR（128 Mhz, tol-d8, 298K)
56.06
PCy2
+
B(C6F5)3
PPh2
100
50
0
-50
ppm (t1)


1H NMR (400 Mhz, tol-d8, 298K)
7.73
6.55
PCy2
H
+ [HB(C6F5)3]
PPh2
0.50
4.28
7.53
0.52
5.23
1.00
0.82
0.95
9.48
21.83
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


1H {31P} NMR (400 Mhz, tol-d8, 298K)
PCy2
H
+ [HB(C6F5)3]
PPh2
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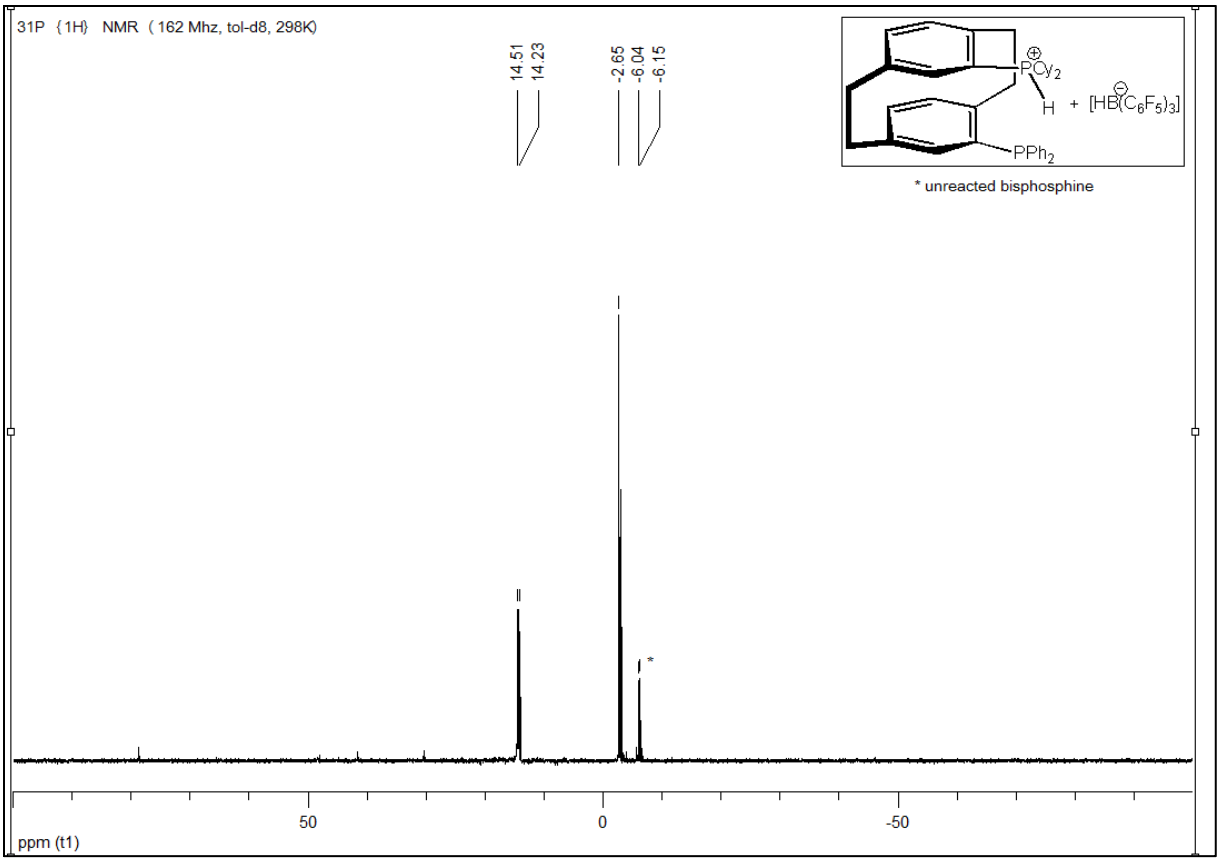
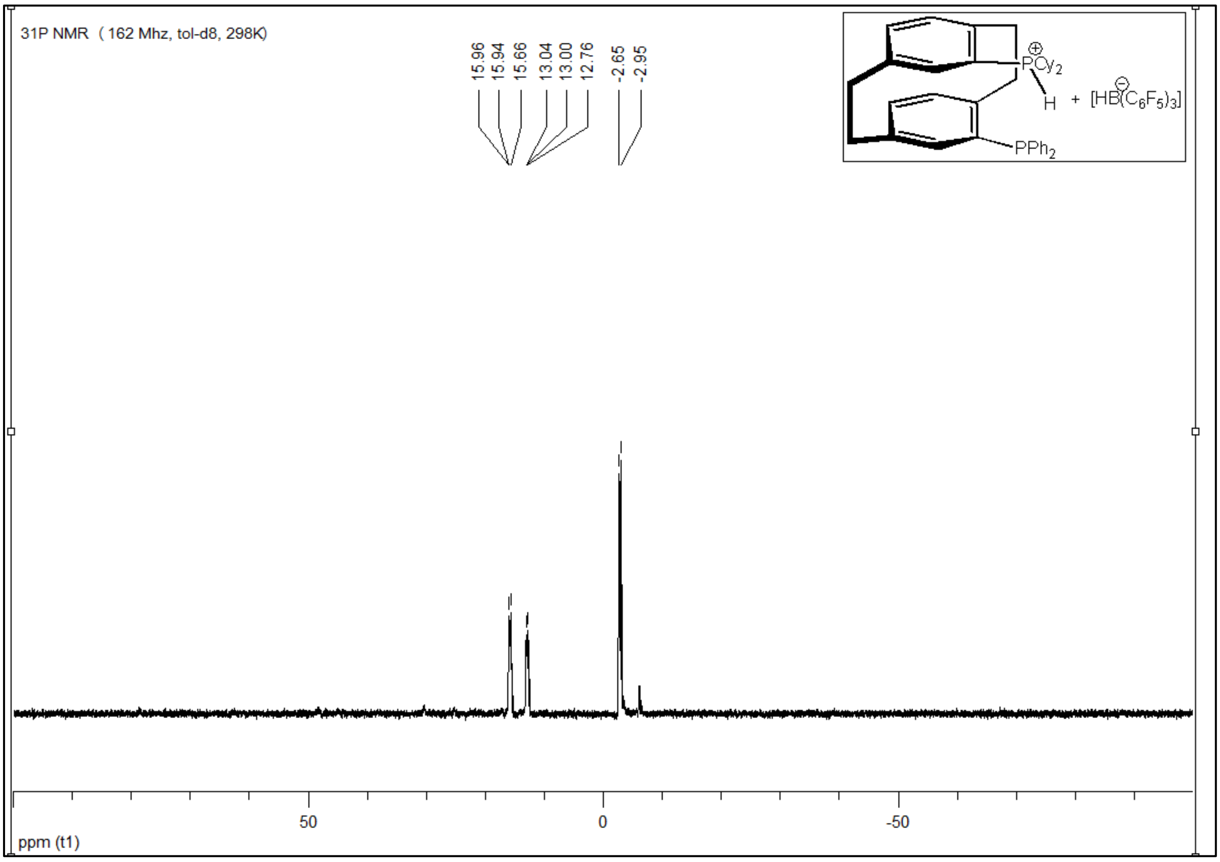
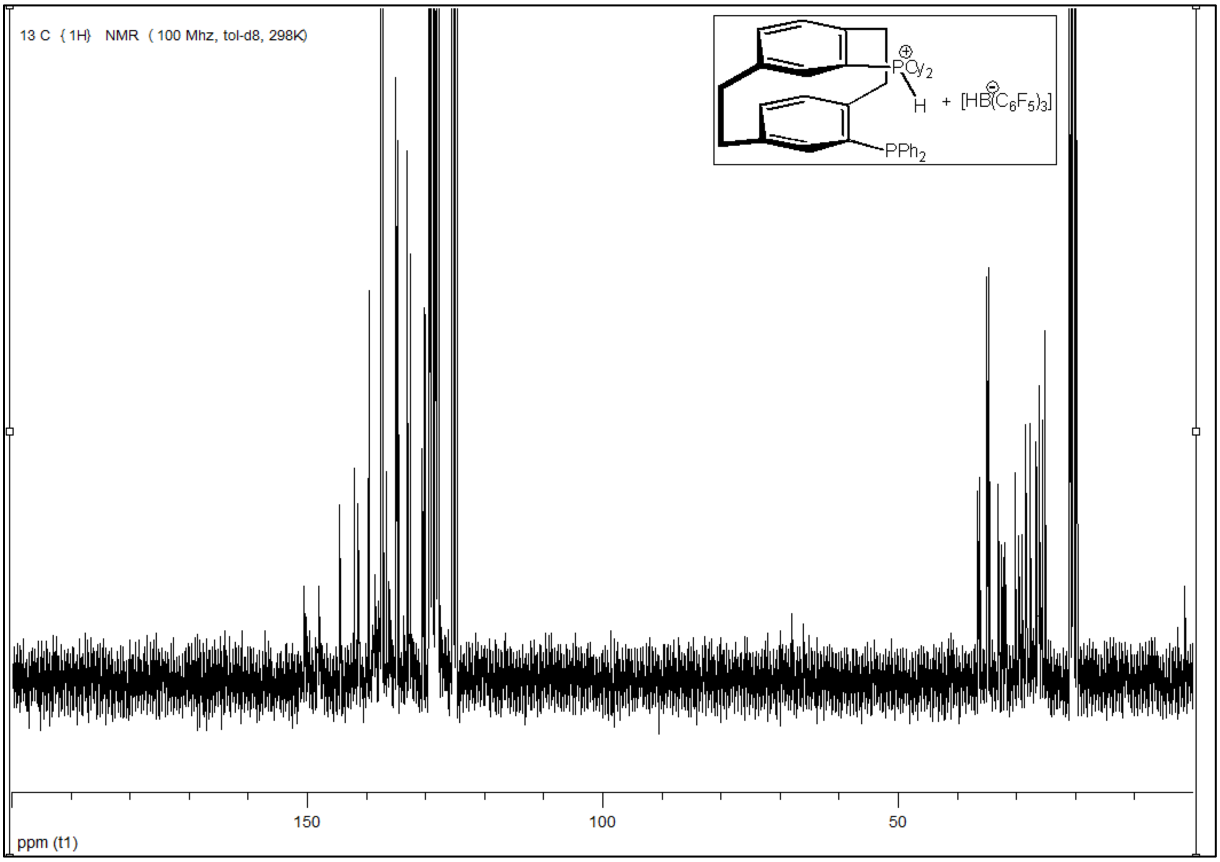
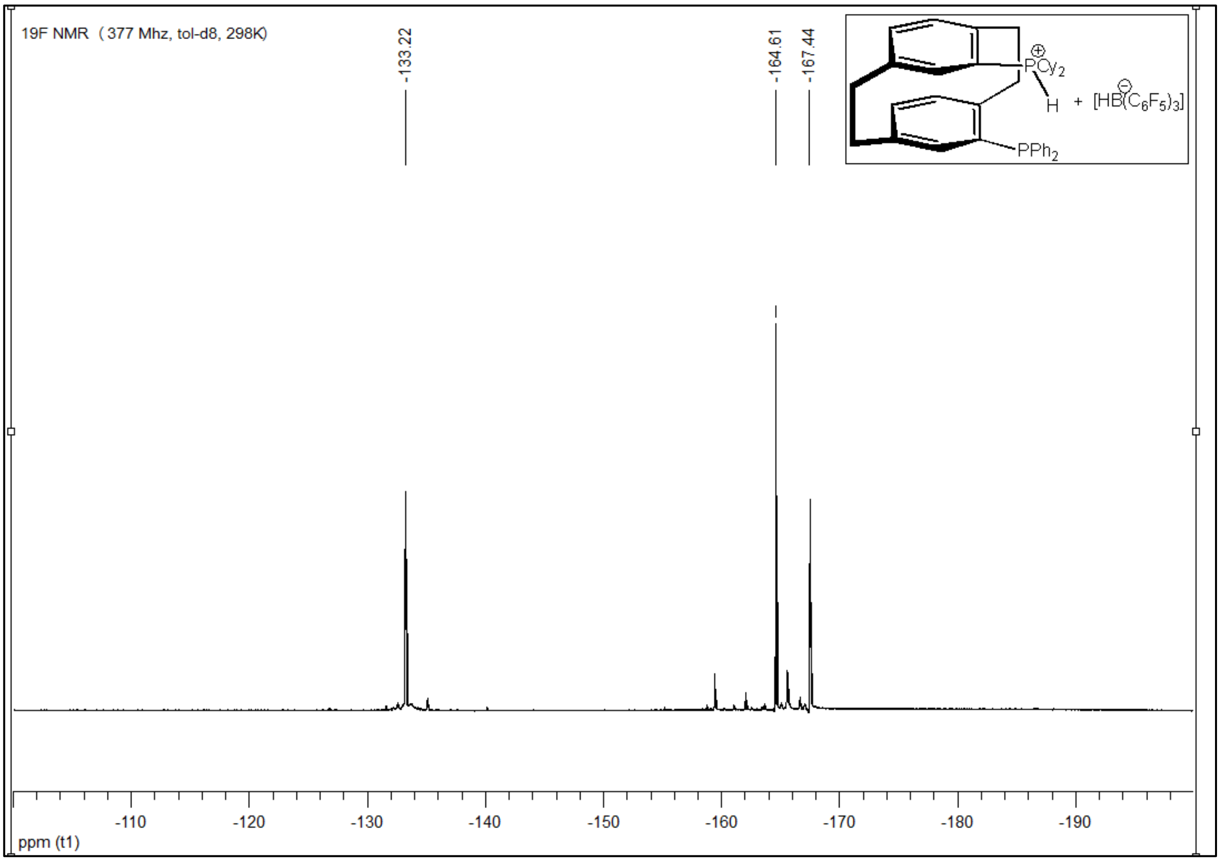
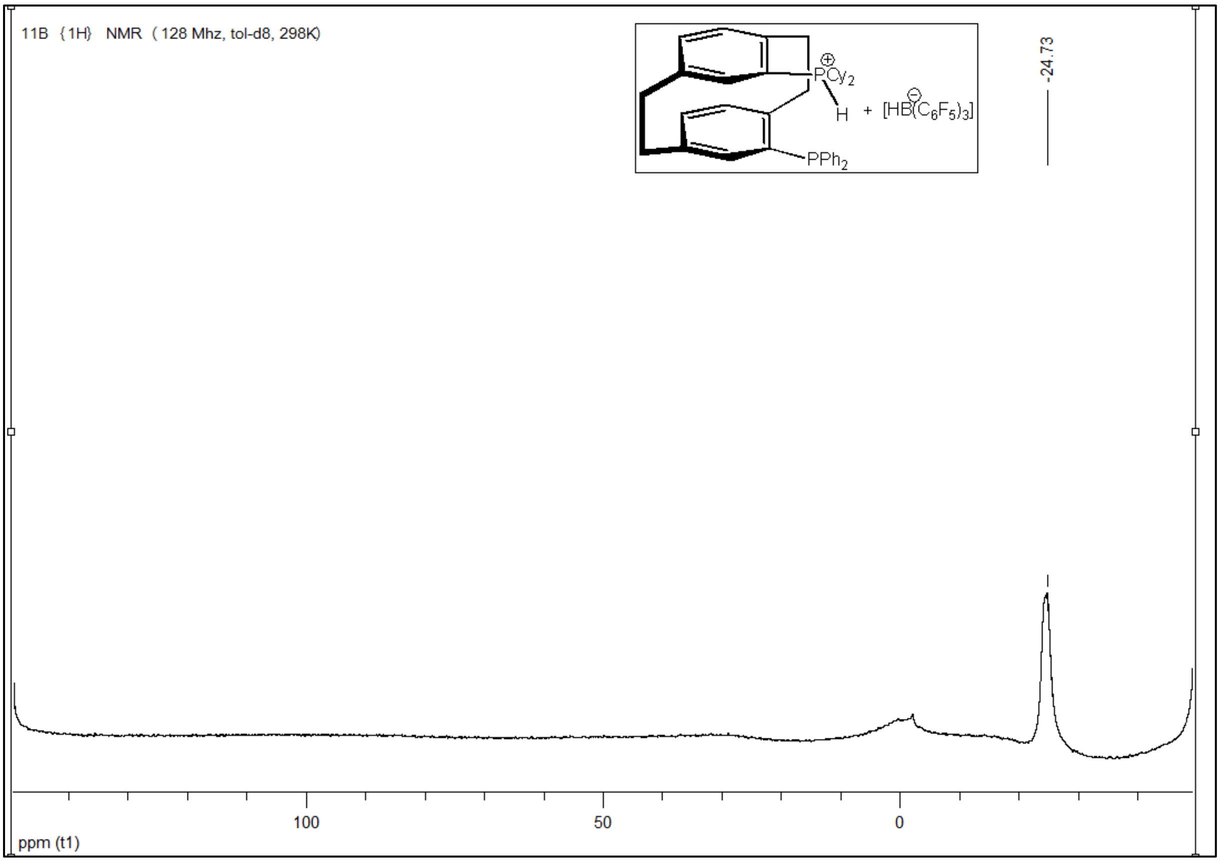
7.75
5.31
1.00
0.74
0.91
10.05
23.63
5.0
ppm (t1)

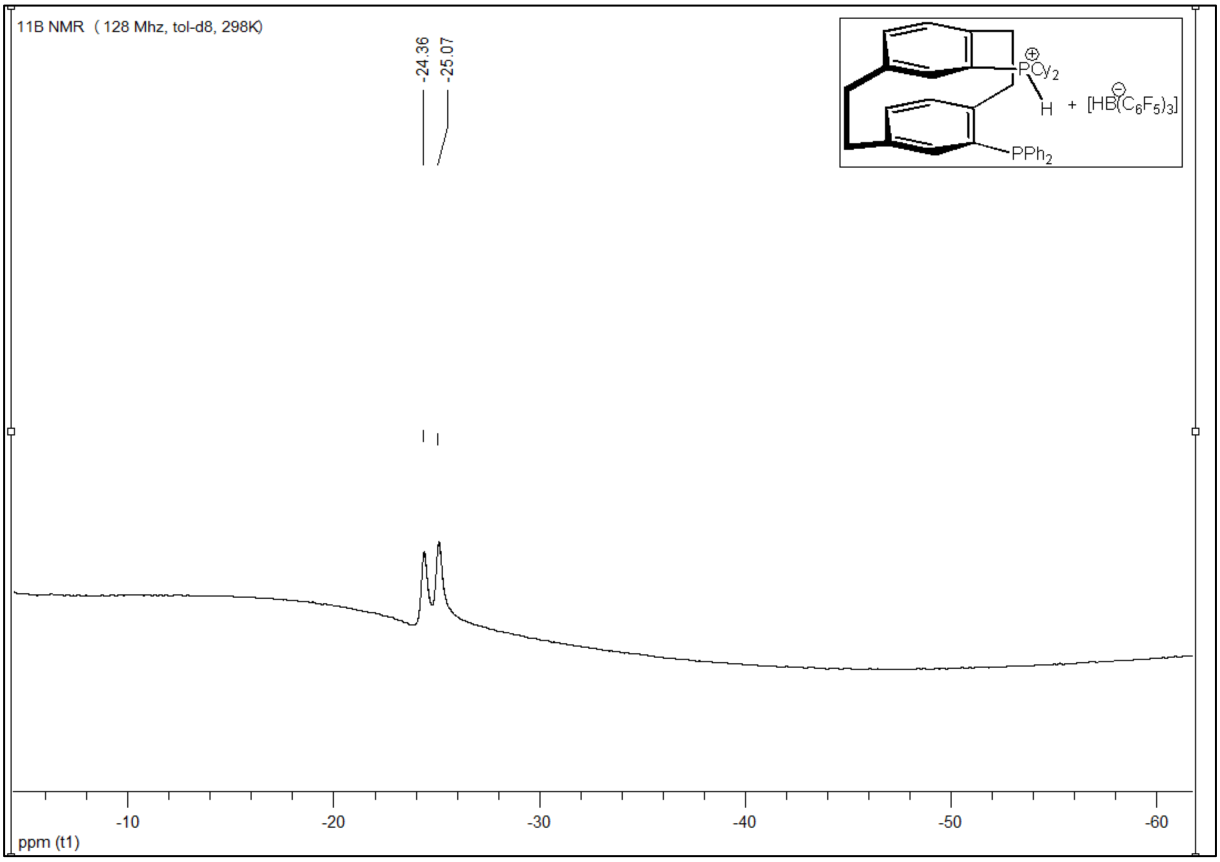

31P {1H} NMR ( 162 Mhz, tol-d8, 298K)
14.51
14.23
-2.65
-6.04
-6.15
*
PCy2
H
+ [HB(C6F5)3]
PPh2
* unreacted bisphosphine
50
0
-50
ppm (t1)

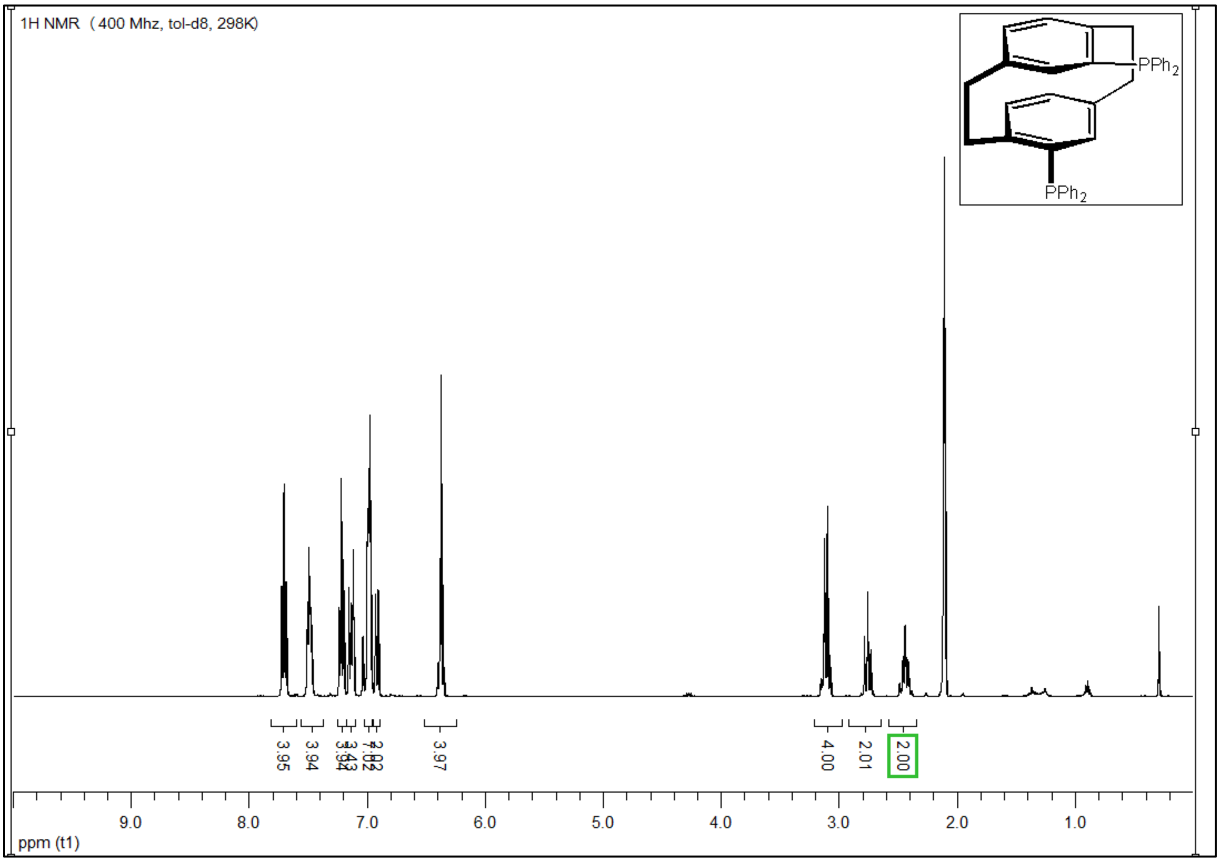

31P NMR ( 162 Mhz, tol-d8, 298K)
15.96
15.94
15.66
13.04
13.00
12.76
-2.65
-2.95
PCy2
H
+ [HB(C6F5)3]
PPh2
50
0
-50
ppm (t1)

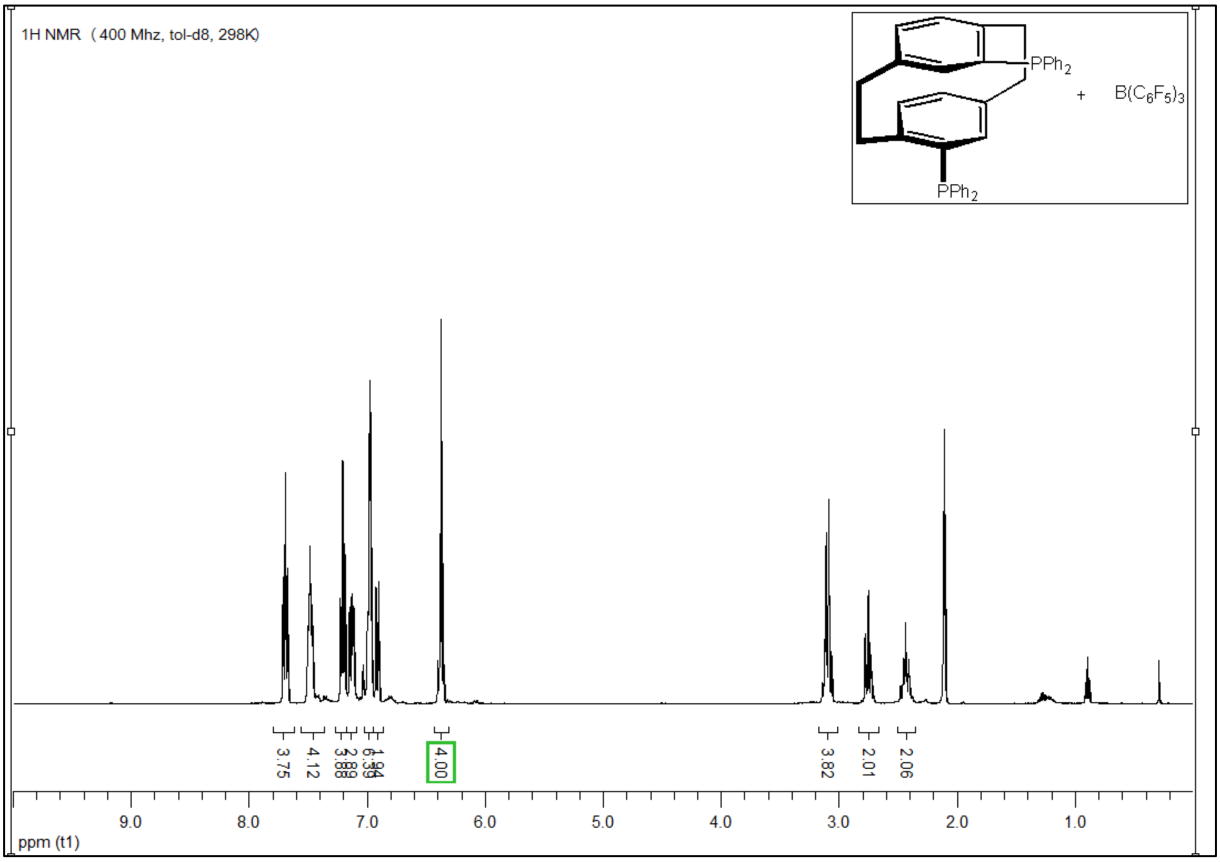

13 C {1H} NMR (100 Mhz, tol-d8, 298K)
PCy2
H
+ [HB(C6F5)3]
PPh2
150
100
50
ppm (t1)

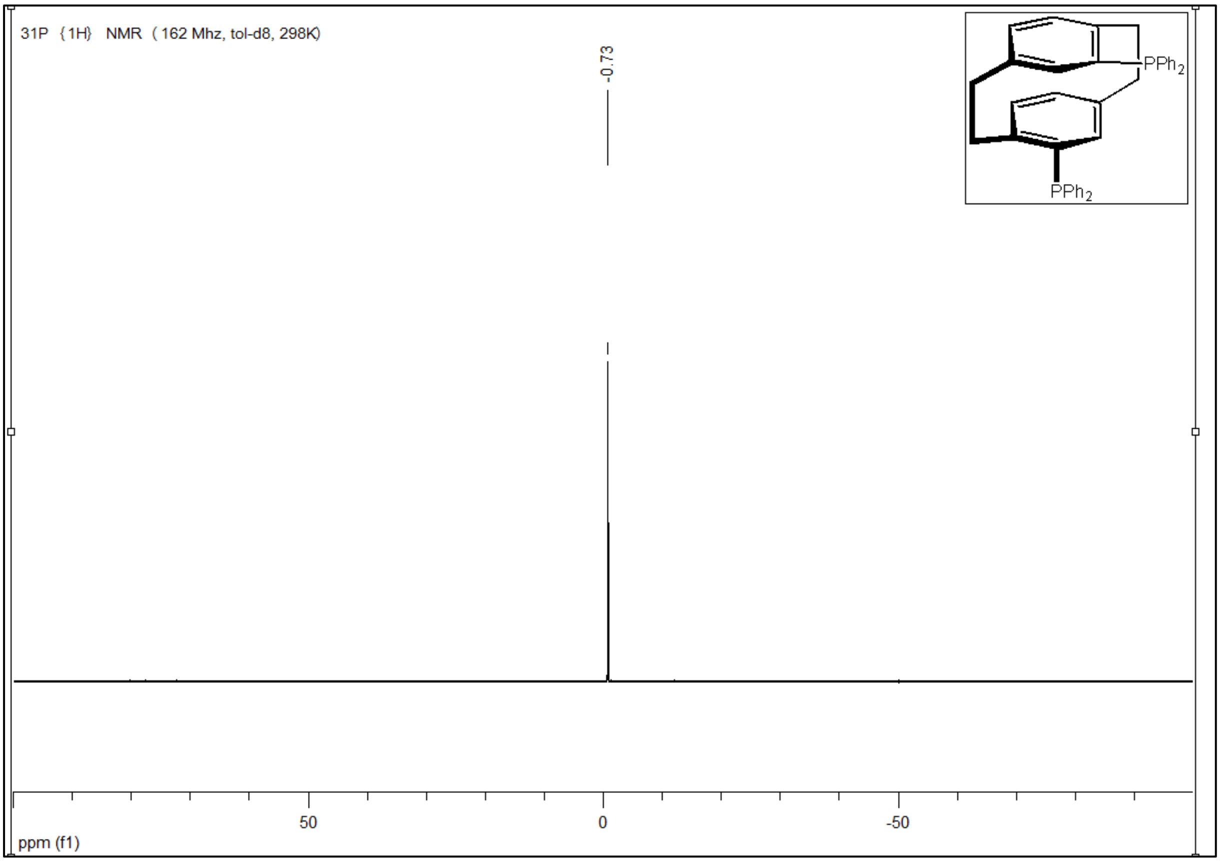

19F NMR (377 Mhz, tol-d8, 298K)
-133.22
-164.61
-167.44
PCy2
H
+ [HB(C6F5)3]
PPh2
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm (t1)

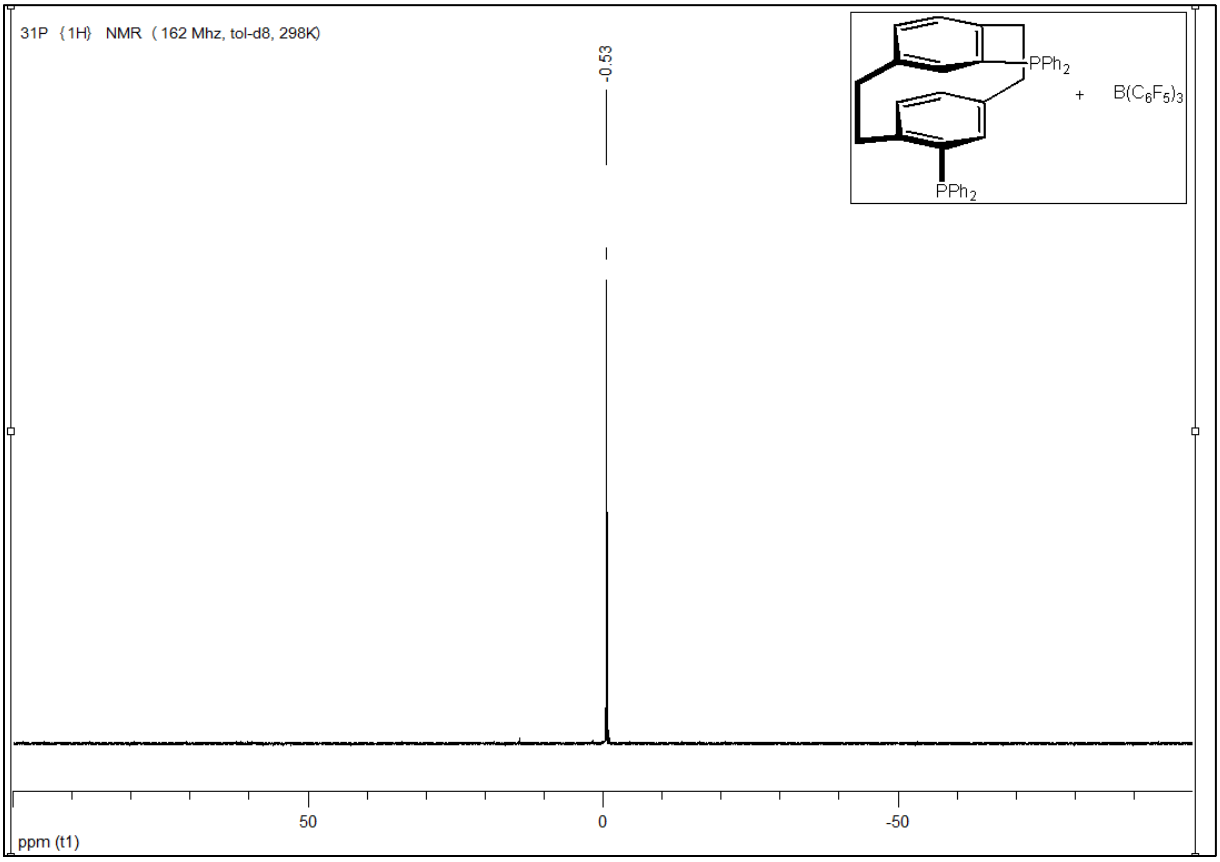

11B {1H} NMR (128 Mhz, tol-d8, 298K)
PCy2
H
+ [HB(C6F5)3]
PPh2
-24.73
100
50
0
ppm (t1)

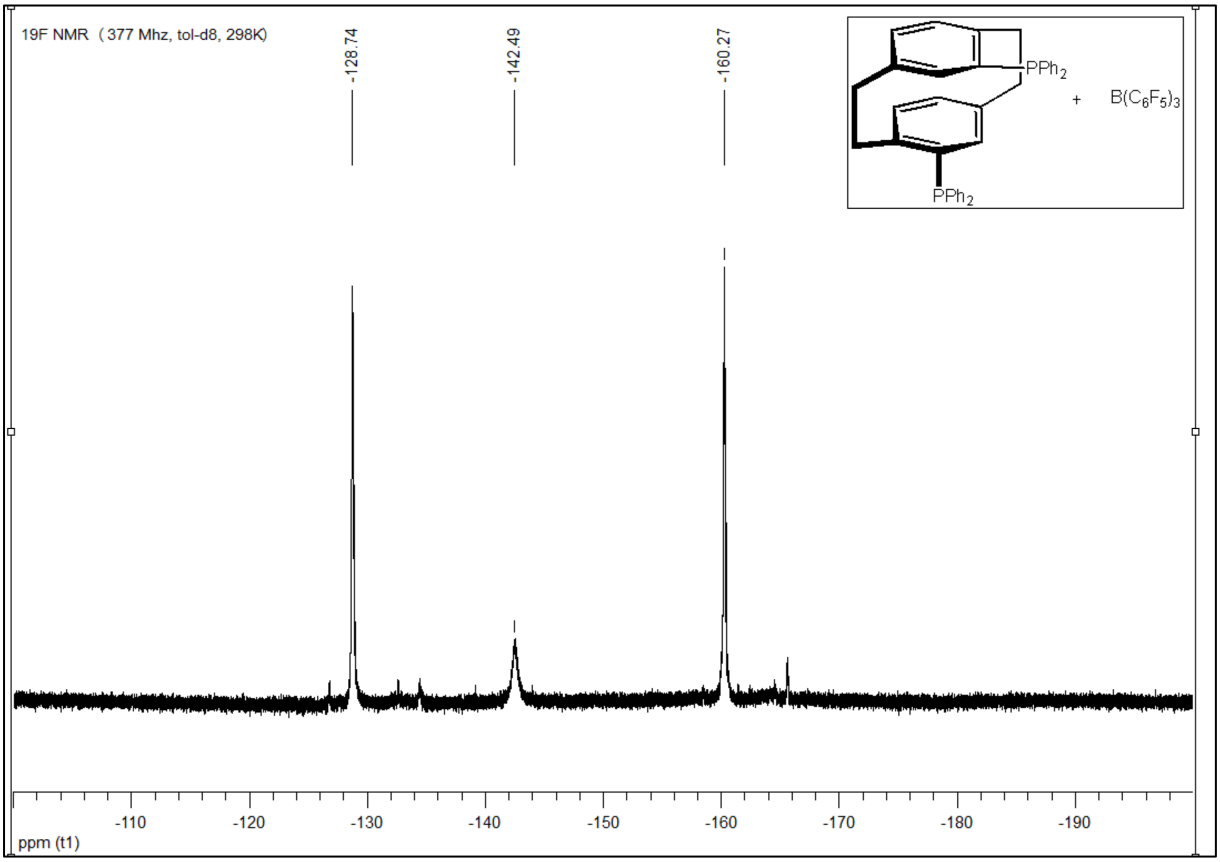

11B NMR (128 Mhz, tol-d8, 298K)
-24.36
-25.07
PCy2
H
+ [HB(C6F5)3]
PPh2
-10
-20
-30
-40
-50
-60
ppm (t1)

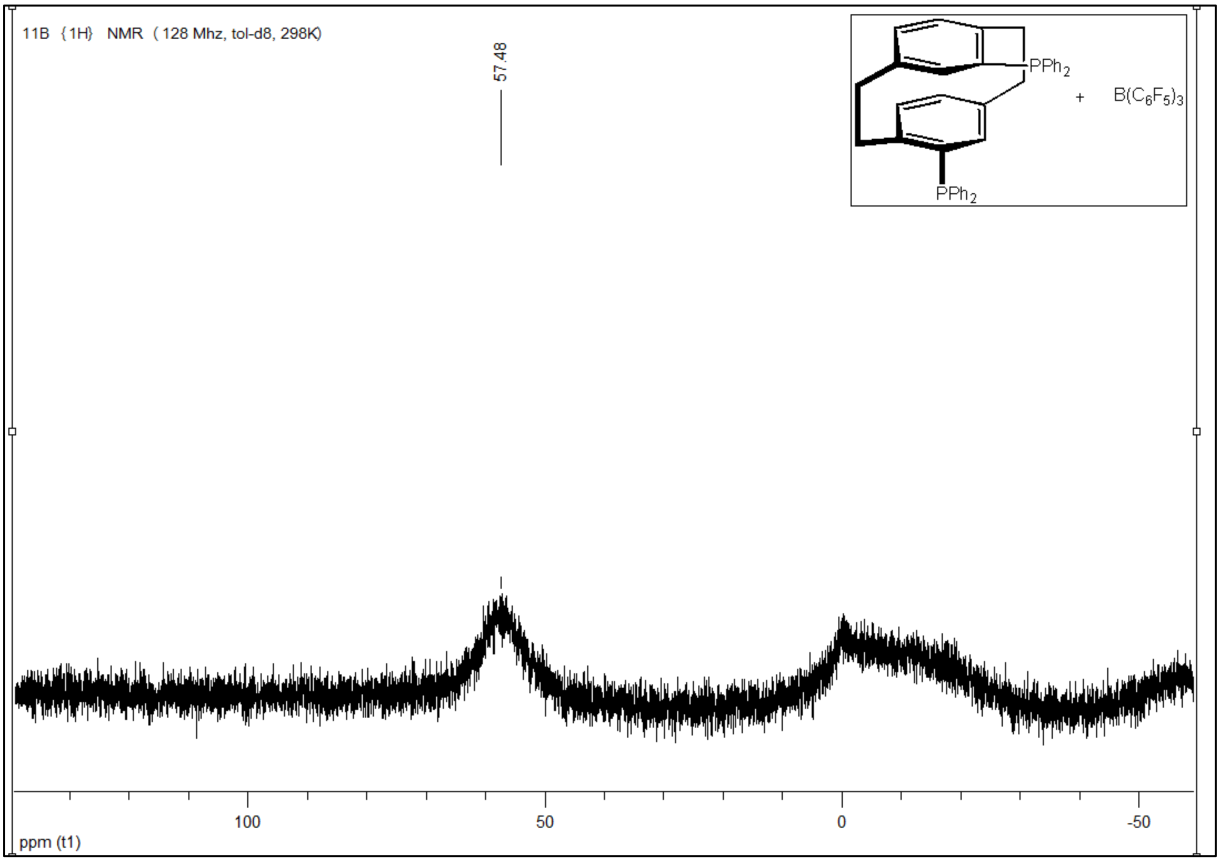

1H NMR（400 Mhz, tol-d8, 298K)
PPh2
PPh2
3.95
3.94
3.94
3.43
7.82
2.02
3.97
4.00
2.01
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

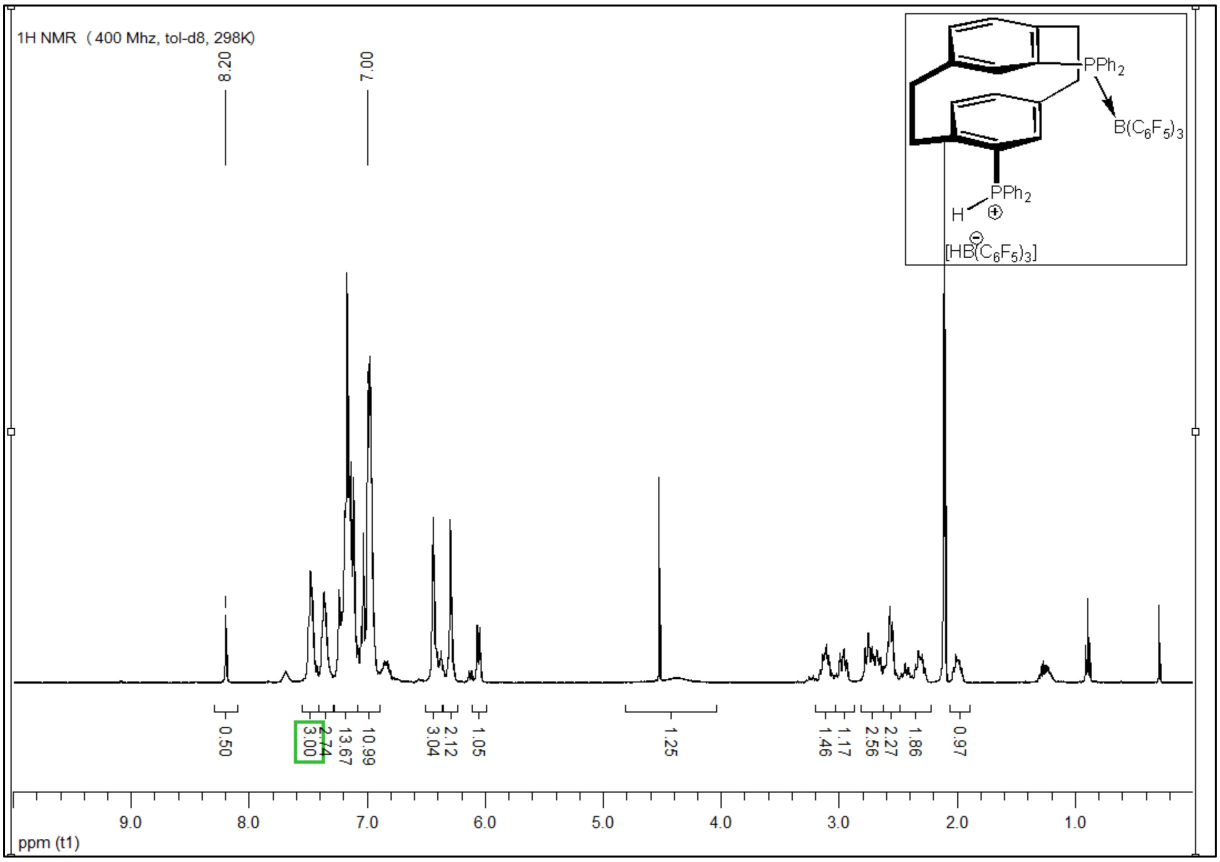

1H NMR（400 Mhz, tol-d8, 298K)
PPh2
+
B(C6F5)3
PPh2
3.75
4.12
3.88
2.89
6.39
1.94
4.00
3.82
2.01
2.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

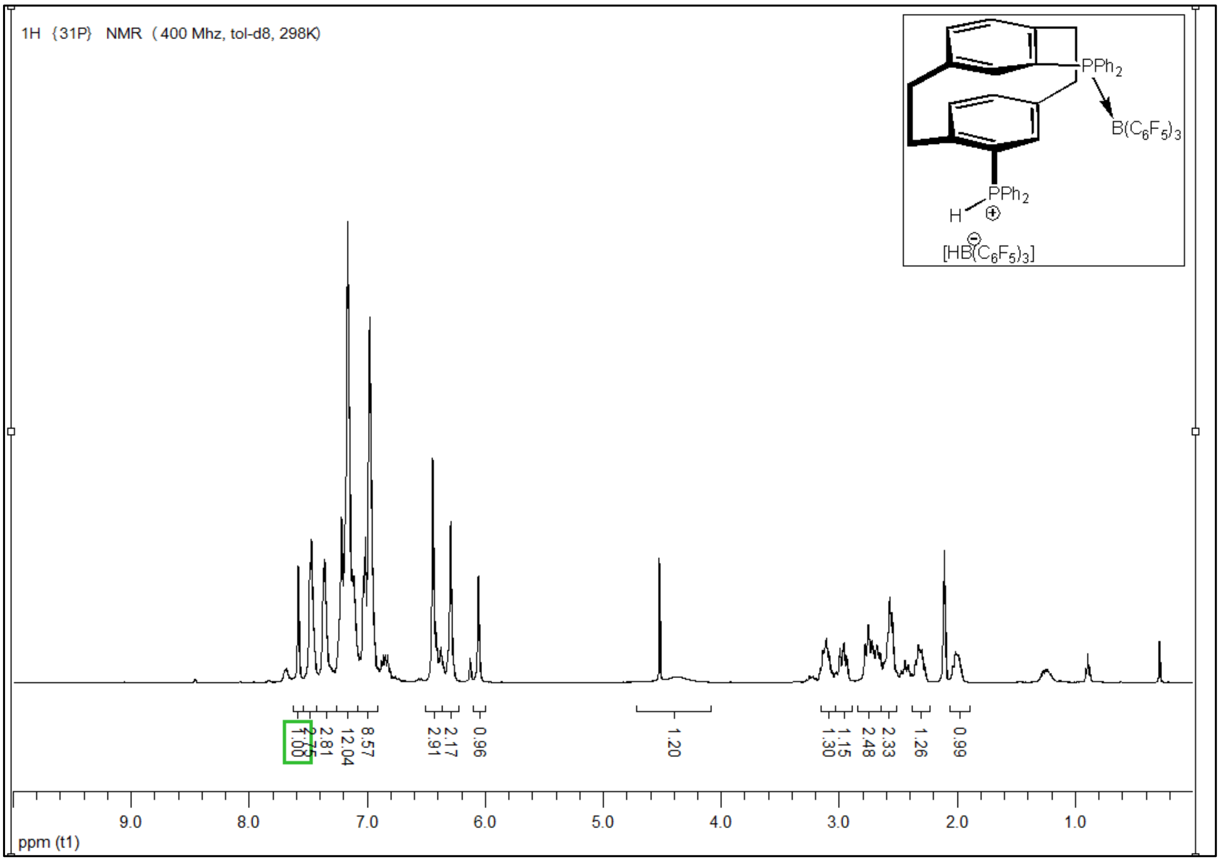

31P {1H} NMR (162 Mhz, tol-d8, 298K)
-0.73
PPh$_2$
PPh$_2$
50
0
-50
ppm (f1)

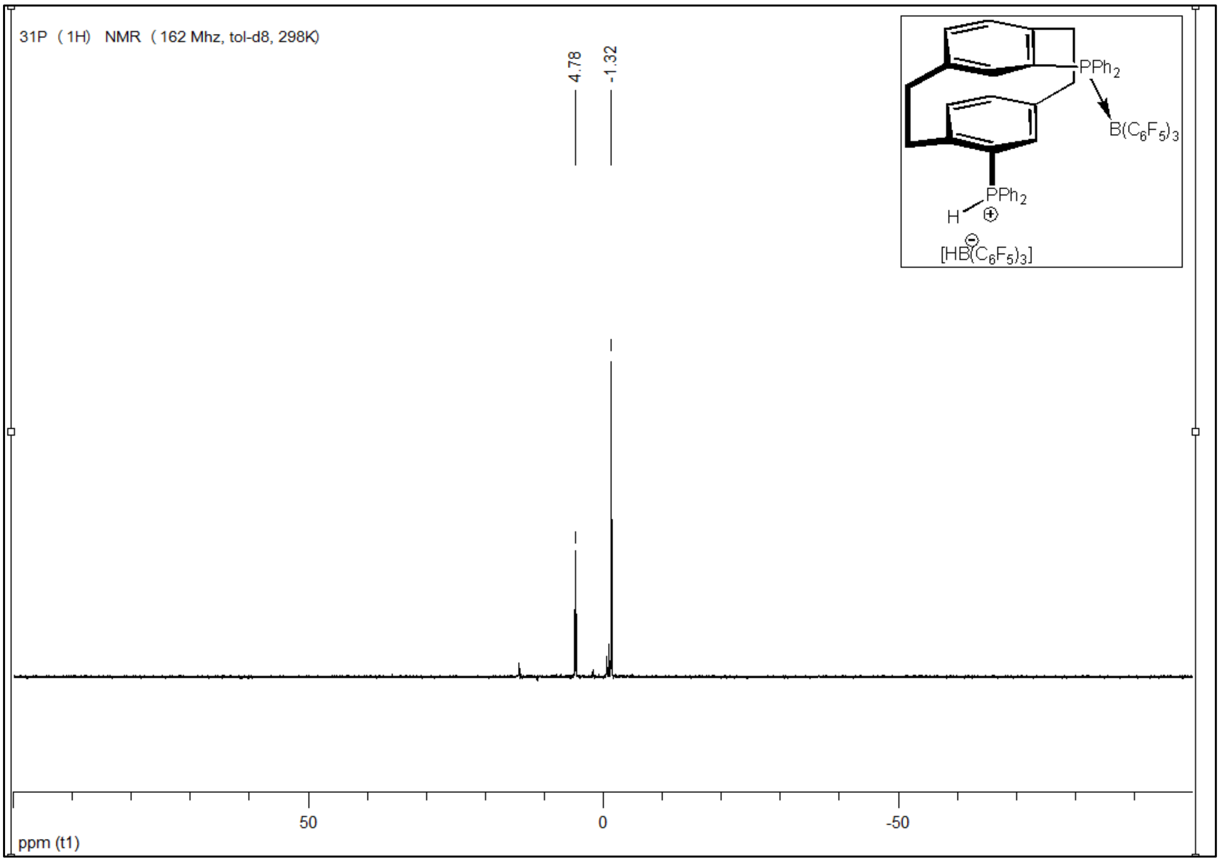

31P {1H} NMR (162 Mhz, tol-d8, 298K)
-0.53
PPh$_2$
+
B(C$_6$F$_5$)$_3$
PPh$_2$
50
0
-50
ppm (t1)

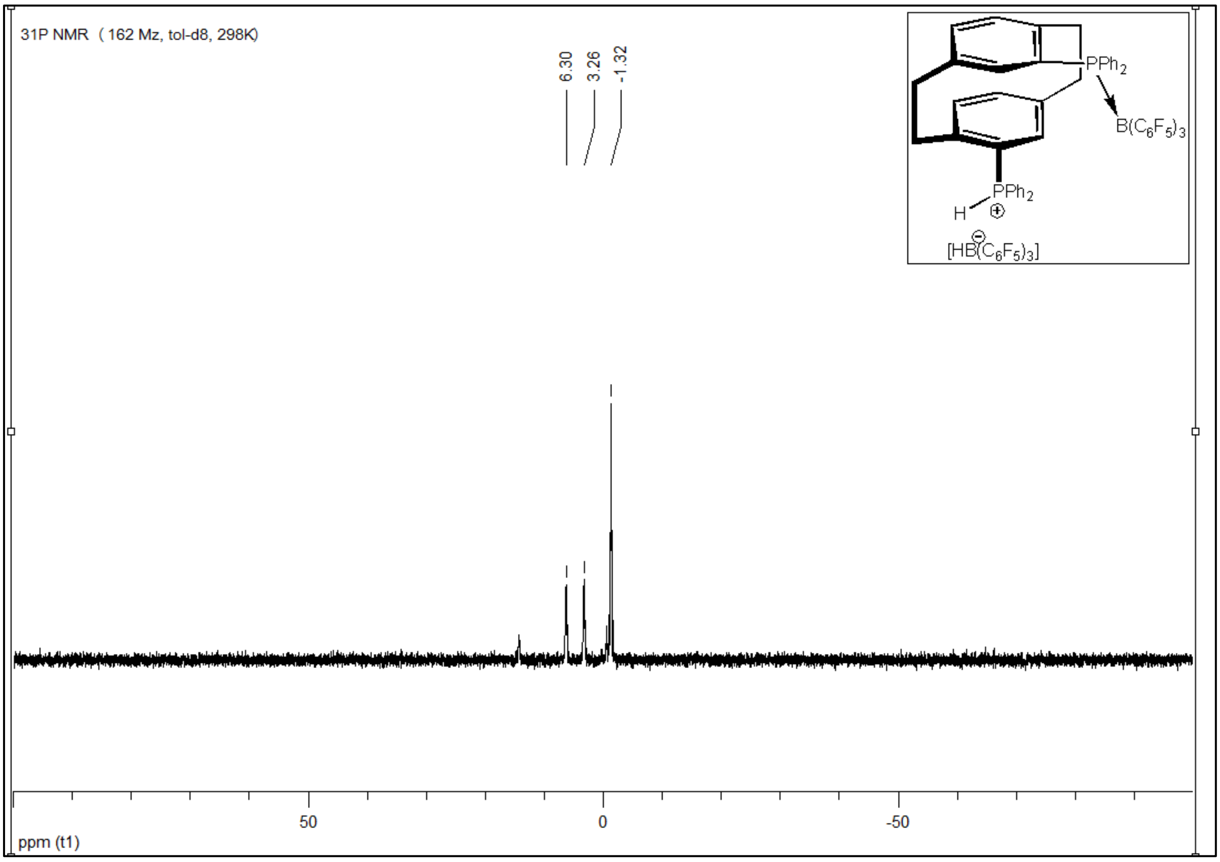

19F NMR (377 Mhz, tol-d8, 298K)
-128.74
-142.49
-160.27
PPh2
+
B(C6F5)3
PPh2
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm (t1)

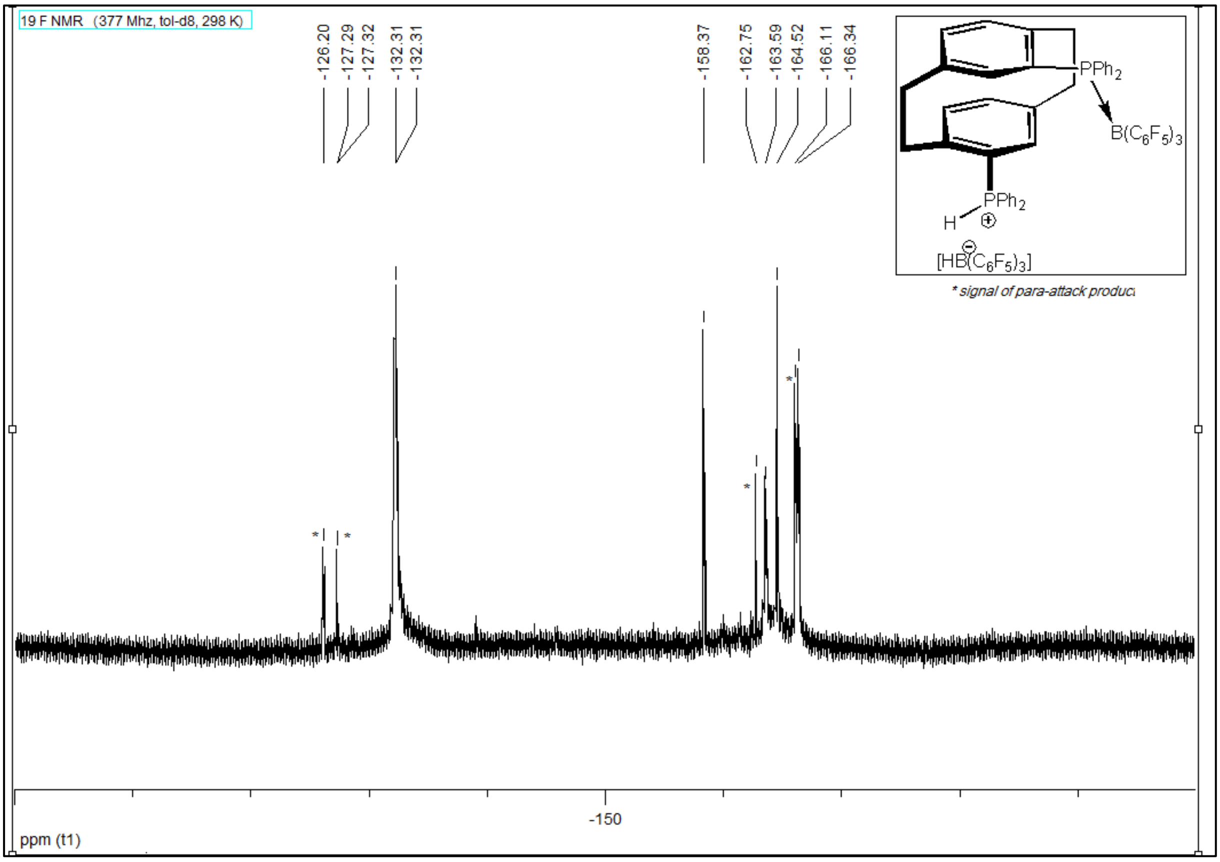

11B {1H} NMR (128 Mhz, tol-d8, 298K)
57.48
PPh2
+
B(C6F5)3
PPh2
100
50
0
-50
ppm (t1)

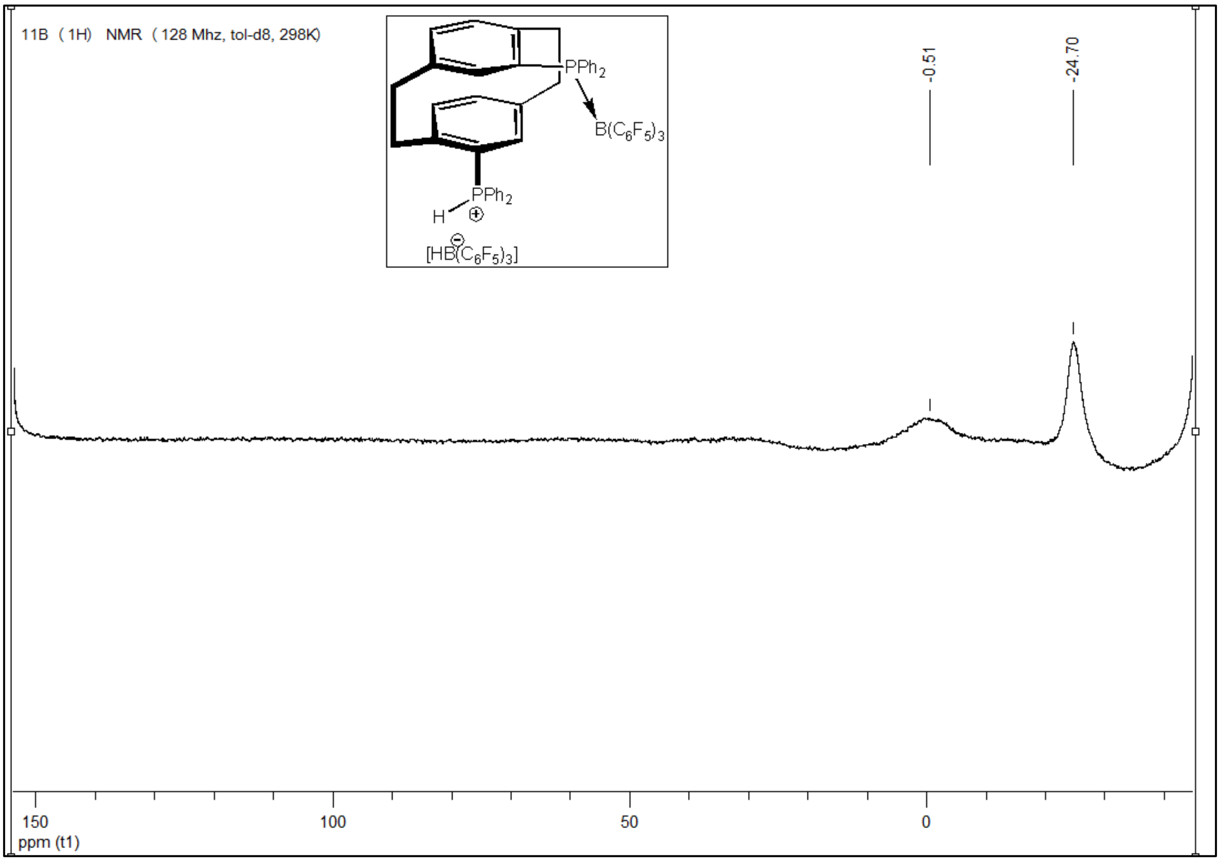

1H NMR (400 Mhz, tol-d8, 298K)
8.20
7.00
PPh$_2$
B(C$_6$F$_5$)$_3$
PPh$_2$
H
⊕
⊖
[HB(C$_6$F$_5$)$_3$]
0.50
3.00
2.74
13.67
10.99
3.04
2.12
1.05
1.25
1.46
1.17
2.56
2.27
1.86
0.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

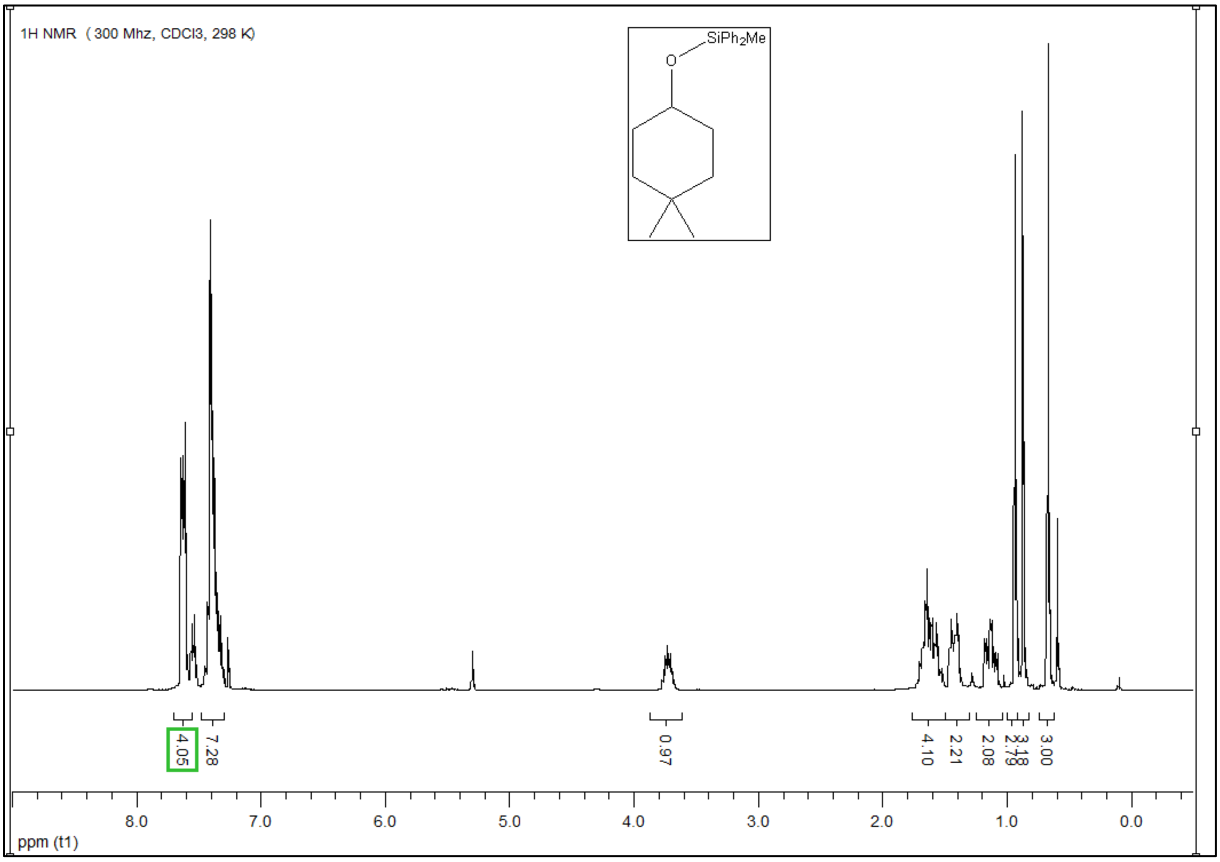

1H {31P} NMR (400 Mhz, tol-d8, 298K)
PPh$_2$
B(C$_6$F$_5$)$_3$
PPh$_2$
H
⊕
⊖
[HB(C$_6$F$_5$)$_3$]
1.00
2.75
2.81
12.04
8.57
2.91
2.17
0.96
1.20
1.30
1.15
2.48
2.33
1.26
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

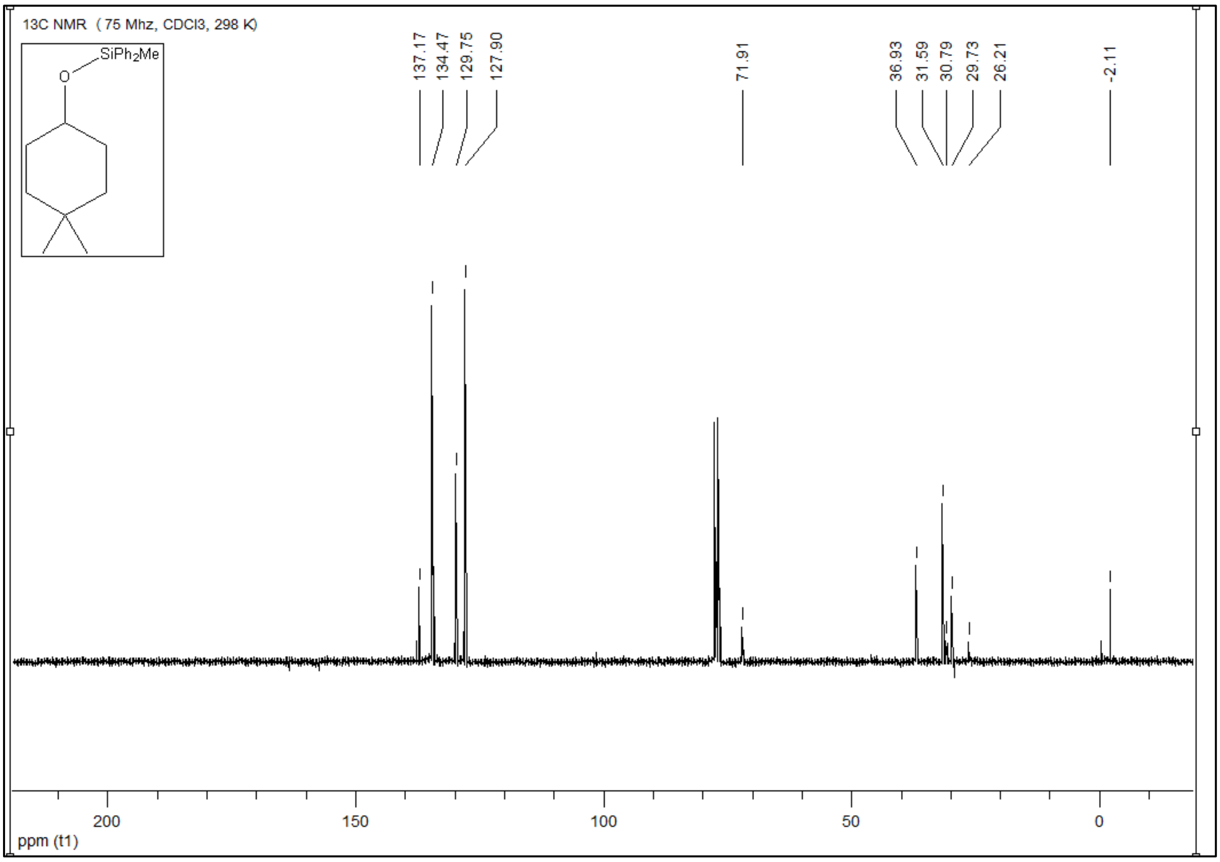

31P (1H) NMR (162 Mhz, tol-d8, 298K)
4.78
-1.32
PPh$_2$
B(C$_6$F$_5$)$_3$
PPh$_2$
H
⊕
⊖
[HB(C$_6$F$_5$)$_3$]
50
0
-50
ppm (t1)

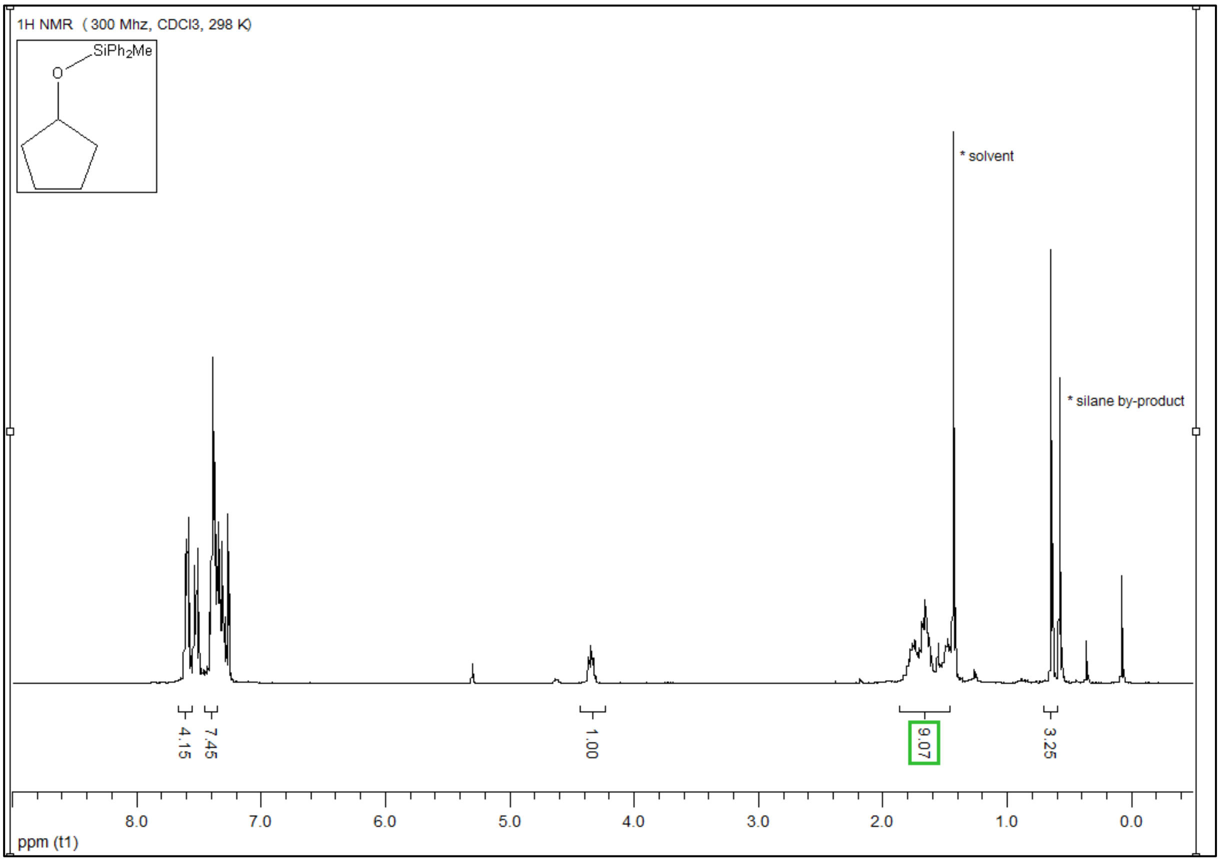

31P NMR (162 Mz, tol-d8, 298K)
6.30
3.26
-1.32
PPh$_2$
B(C$_6$F$_5$)$_3$
PPh$_2$
H
⊕
⊖
[HB(C$_6$F$_5$)$_3$]
50
0
-50
ppm (t1)

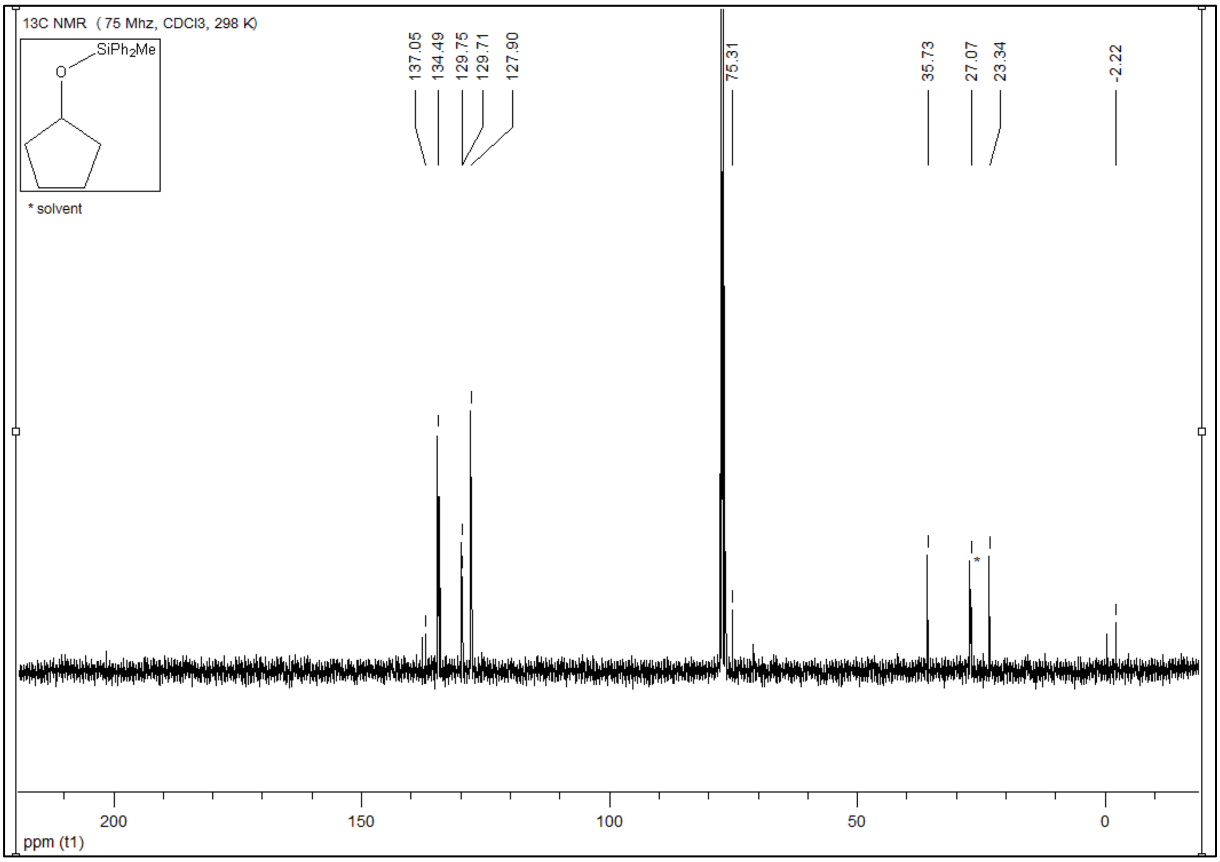

19 F NMR (377 Mhz, tol-d8, 298 K)
-126.20
-127.29
-127.32
-132.31
-132.31
-158.37
-162.75
-163.59
-164.52
-166.11
-166.34
PPh2
B(C6F5)3
PPh2
H
⊕
⊖
[HB(C6F5)3]
* signal of para-attack produc
*
*
*
*
-150
ppm (t1)

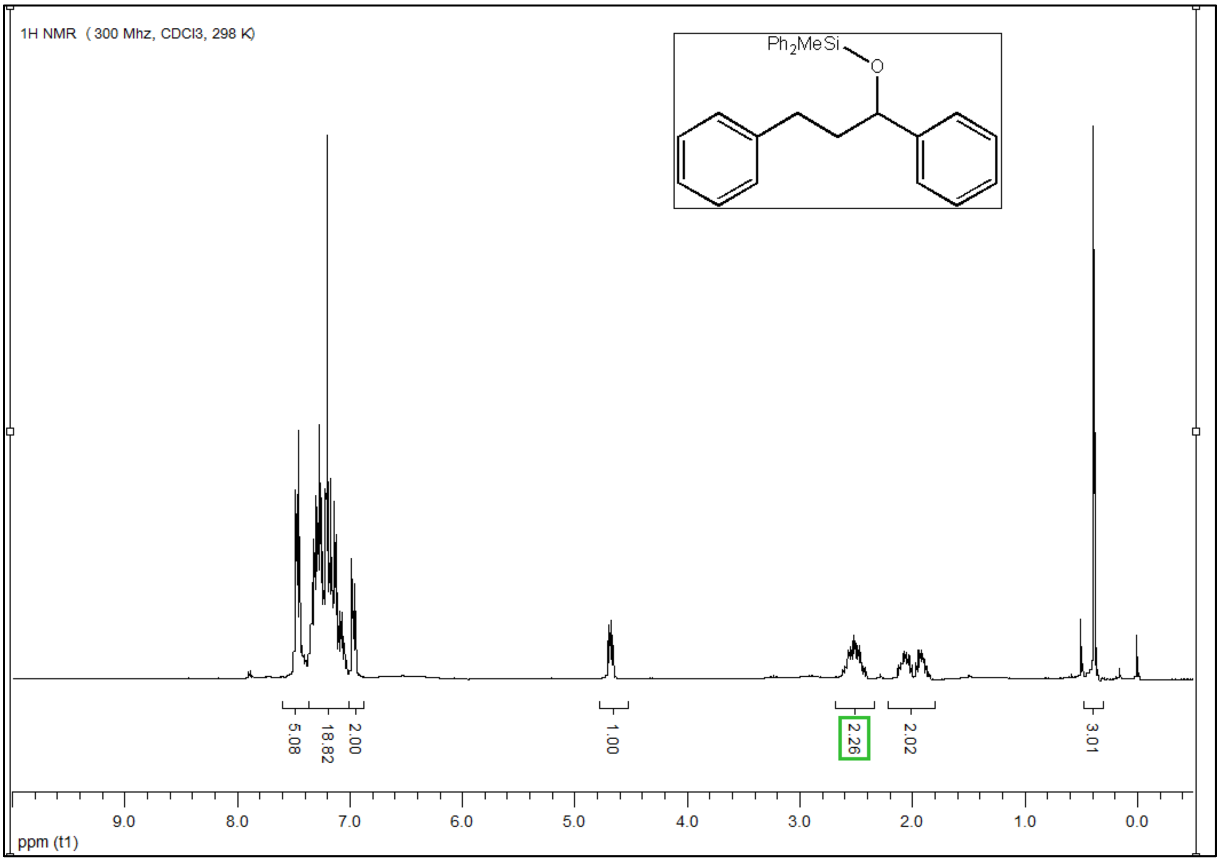

11B (1H) NMR (128 Mhz, tol-d8, 298K)
PPh2
B(C6F5)3
PPh2
H
⊕
⊖
[HB(C6F5)3]
-0.51
-24.70
150
100
50
0
ppm (t1)

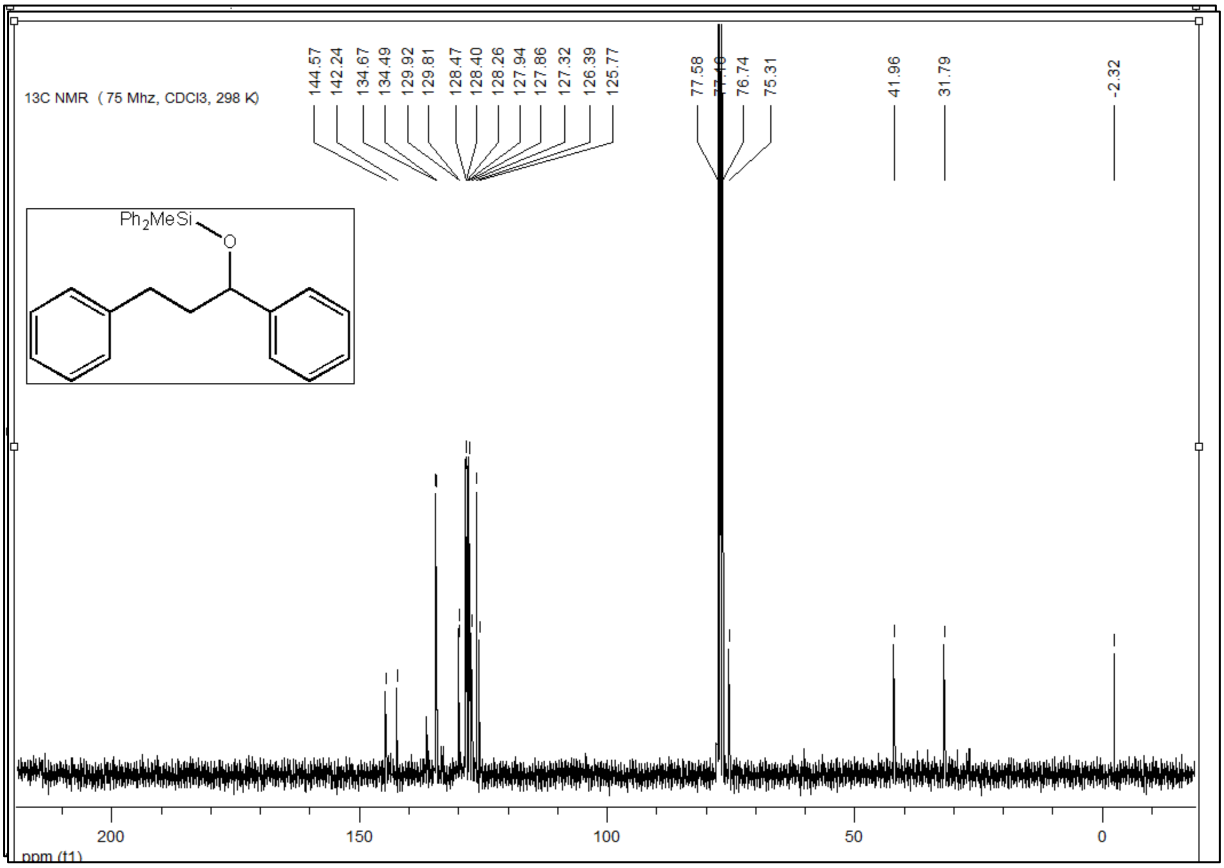

1H NMR ( 300 Mhz, CDCl3, 298 K)
SiPh2Me
O
4.05
7.28
0.97
4.10
2.21
2.08
2.79
3.18
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

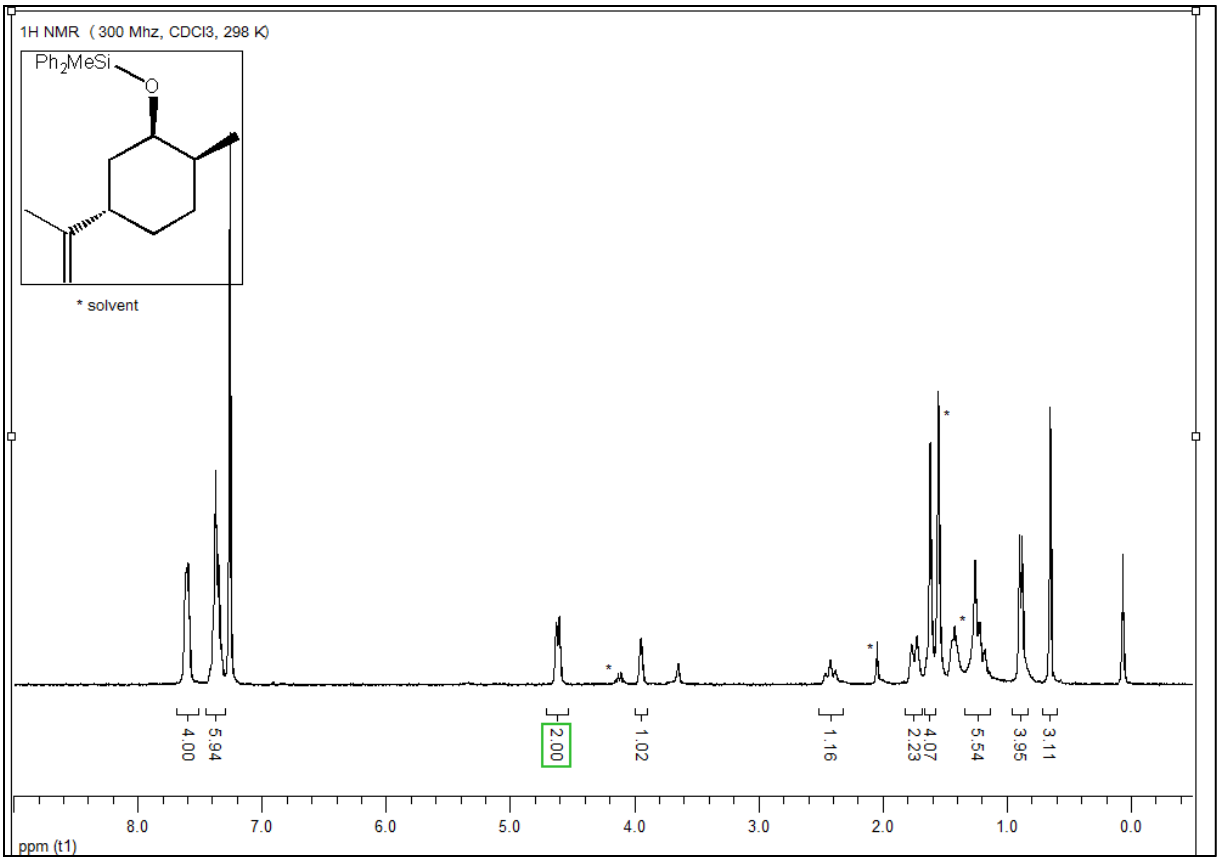

13C NMR ( 75 Mhz, CDCl3, 298 K)
SiPh2Me
O
137.17
134.47
129.75
127.90
71.91
36.93
31.59
30.79
29.73
26.21
-2.11
200
150
100
50
0
ppm (t1)

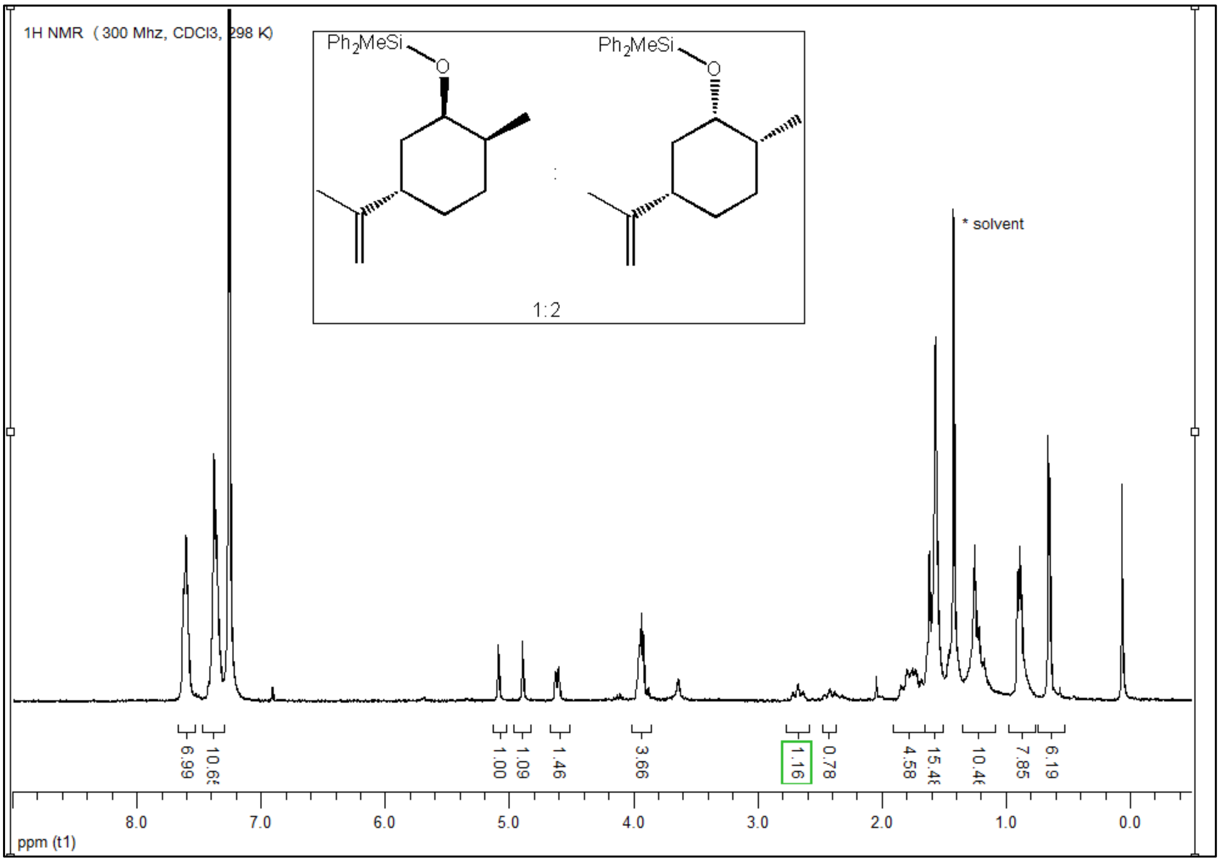

1H NMR ( 300 Mhz, CDCl3, 298 K)
SiPh2Me
O
* solvent
* silane by-product
4.15
7.45
1.00
9.07
3.25
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


13C NMR ( 75 Mhz, CDCl3, 298 K)
SiPh2Me
O
* solvent
137.05
134.49
129.75
129.71
127.90
75.31
35.73
27.07
23.34
-2.22
*
200
150
100
50
0
ppm (t1)


1H NMR (300 Mhz, CDCl3, 298 K)
$Ph_2MeSi$
O
5.08
18.82
2.00
1.00
2.26
2.02
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


13C NMR (75 Mhz, CDCl3, 298 K)
144.57
142.24
134.67
134.49
129.92
129.81
128.47
128.40
128.26
127.94
127.86
127.32
126.39
125.77
77.58
77.16
76.74
75.31
41.96
31.79
-2.32
$Ph_2MeSi$
O
200
150
100
50
0
ppm (t1)


1H NMR (300 Mhz, CDCl3, 298 K)
$Ph_2MeSi$
O
* solvent
*
*
*
*
4.00
5.94
2.00
1.02
1.16
2.23
4.07
5.54
3.95
3.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


1H NMR (300 Mhz, CDCl3, 298 K)
$Ph_2MeSi$
O
$Ph_2MeSi$
O
:
1:2
* solvent
6.99
10.6
1.00
1.09
1.46
3.66
1.16
0.78
4.58
15.4
10.4
7.85
6.19
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

Calculated atom coordinates for [**1**•H•**3**]$^{+}$[H•**3**]$^{-}$

| | | | | |
|---|---|---|---|---|
| C | C | -0.524304 | 11.7091 | 3.27057 |
| C | C | 0.694915 | 11.8489 | 2.57371 |
| C | C | 0.696371 | 11.8749 | 1.15761 |
| C | C | -0.507187 | 11.712 | 0.457153 |
| C | C | -1.71587 | 11.5401 | 1.1522 |
| C | C | -1.72125 | 11.554 | 2.55543 |
| C | C | 2.08613 | 12.2697 | 5.2284 |
| C | C | 2.77547 | 13.3619 | 5.80669 |
| C | C | 2.73751 | 13.5524 | 7.19516 |
| C | C | 2.00446 | 12.6717 | 8.00802 |
| C | C | 1.30305 | 11.6 | 7.43123 |
| C | C | 1.34309 | 11.3892 | 6.0445 |
| C | C | 3.01496 | 9.8374 | 1.92162 |
| C | C | 3.4363 | 10.7402 | 2.90915 |
| C | C | 4.79151 | 10.717 | 3.35346 |
| C | C | 5.69677 | 10.0232 | 2.52842 |
| C | C | 5.26683 | 9.14275 | 1.52238 |
| C | C | 3.89409 | 8.90962 | 1.32914 |
| C | C | 5.21212 | 11.0895 | 4.75968 |

| | | | | |
|---|---|---|---|---|
| C | C | 4.68283 | 10.0291 | 5.83449 |
| C | C | 4.21427 | 8.7278 | 5.21219 |
| C | C | 2.84942 | 8.38817 | 5.10183 |
| C | C | 2.36733 | 7.44289 | 4.16625 |
| C | C | 3.29798 | 6.89429 | 3.21847 |
| C | C | 4.65932 | 7.00185 | 3.5659 |
| C | C | 5.12024 | 7.87671 | 4.55581 |
| C | C | 3.00774 | 6.48945 | 1.7833 |
| C | C | 3.35245 | 7.63897 | 0.71428 |
| P | P | 0.662695 | 6.76611 | 4.45159 |
| C | C | -0.255216 | 8.01134 | 5.48171 |
| C | C | -1.28566 | 8.79437 | 4.91371 |
| C | C | -2.07849 | 9.62346 | 5.72276 |
| C | C | -1.87353 | 9.67366 | 7.11042 |
| C | C | -0.846982 | 8.90609 | 7.68217 |
| C | C | -0.0367377 | 8.09016 | 6.87771 |
| C | C | -0.277832 | 6.8473 | 2.8734 |
| C | C | -1.38492 | 6.01474 | 2.60514 |
| C | C | -2.10643 | 6.1779 | 1.41015 |
| C | C | -1.75346 | 7.17985 | 0.490856 |
| C | C | -0.678198 | 8.03991 | 0.775047 |

| | | | | |
|---|---|---|---|---|
| C | C | 0.0493531 | 7.87075 | 1.96015 |
| H | H | 4.08085 | 7.23371 | -0.0155318 |
| H | H | 2.42289 | 7.85798 | 0.150251 |
| H | H | 1.95758 | 6.20136 | 1.63687 |
| H | H | 3.61032 | 5.5945 | 1.53343 |
| H | H | 2.13888 | 8.90359 | 5.75965 |
| H | H | 6.20246 | 7.99298 | 4.71693 |
| H | H | 5.39792 | 6.4869 | 2.93189 |
| H | H | 5.50503 | 9.83609 | 6.55305 |
| H | H | 3.85496 | 10.486 | 6.4095 |
| H | H | 4.86726 | 12.0966 | 5.06253 |
| H | H | 6.31856 | 11.1224 | 4.79548 |
| H | H | 6.00826 | 8.528 | 0.988589 |
| H | H | 6.76831 | 10.0599 | 2.7806 |
| H | H | -1.69673 | 5.2513 | 3.32598 |
| H | H | -2.95897 | 5.51382 | 1.20344 |
| H | H | -2.32549 | 7.29882 | -0.441659 |
| H | H | -0.408701 | 8.85266 | 0.0845524 |
| H | H | 0.876651 | 8.5478 | 2.20218 |
| H | H | -1.48593 | 8.75844 | 3.83492 |
| H | H | -2.87914 | 10.2209 | 5.2616 |

| | | | | |
|---|---|---|---|---|
| H | H | -2.51499 | 10.3046 | 7.7435 |
| H | H | -0.681225 | 8.9211 | 8.77008 |
| H | H | 0.744813 | 7.48736 | 7.34935 |
| H | H | 3.34836 | 14.0637 | 5.18271 |
| H | H | 3.28158 | 14.4002 | 7.63699 |
| H | H | 1.97546 | 12.8228 | 9.09778 |
| H | H | 0.724305 | 10.9099 | 8.05881 |
| H | H | 0.799953 | 10.5365 | 5.61399 |
| H | H | 1.63132 | 12.0484 | 0.607371 |
| H | H | -0.500936 | 11.7628 | -0.641177 |
| H | H | -2.65912 | 11.4301 | 0.598133 |
| H | H | -2.6693 | 11.4612 | 3.10471 |
| H | H | -0.556454 | 11.7472 | 4.36671 |
| P | P | 2.28551 | 12.0594 | 3.43632 |
| H | H | 1.9585 | 9.81606 | 1.62956 |
| F | F | 5.23256 | 2.53097 | 4.49106 |
| C | C | 4.5577 | 3.50547 | 5.11426 |
| C | C | 3.15065 | 3.541 | 5.06298 |
| C | C | 5.25377 | 4.48209 | 5.84105 |
| F | F | 2.57937 | 2.51761 | 4.40141 |
| C | C | 2.37623 | 4.55496 | 5.66376 |

| | | | | |
|---|---|---|---|---|
| C | C | 4.52685 | 5.47165 | 6.52004 |
| F | F | 6.58985 | 4.47037 | 5.8926 |
| B | B | 0.767157 | 4.72863 | 5.47688 |
| C | C | 3.13113 | 5.47203 | 6.42169 |
| F | F | 5.16892 | 6.40448 | 7.2374 |
| C | C | 0.0497611 | 3.71134 | 4.42777 |
| C | C | -0.096839 | 4.96217 | 6.83181 |
| F | F | 2.50108 | 6.44937 | 7.1191 |
| C | C | -1.0493 | 2.88044 | 4.72742 |
| C | C | 0.474779 | 3.64366 | 3.09087 |
| C | C | -1.41002 | 5.46341 | 6.77122 |
| C | C | 0.371401 | 4.70046 | 8.13371 |
| C | C | -1.72578 | 2.12242 | 3.75062 |
| F | F | -1.52645 | 2.76267 | 5.98008 |
| C | C | -0.152226 | 2.90476 | 2.08202 |
| F | F | 1.5479 | 4.37498 | 2.7196 |
| C | C | -2.18571 | 5.79089 | 7.88845 |
| F | F | -1.97487 | 5.70067 | 5.56169 |
| C | C | -0.362531 | 5.02159 | 9.29115 |
| F | F | 1.56934 | 4.124 | 8.33952 |
| C | C | -1.2791 | 2.13673 | 2.41895 |

| | | | | |
|---|---|---|---|---|
| F | F | -2.77835 | 1.36794 | 4.0878 |
| F | F | 0.295756 | 2.93616 | 0.820644 |
| C | C | -1.64878 | 5.57282 | 9.16744 |
| F | F | -3.40369 | 6.32903 | 7.75098 |
| F | F | 0.143808 | 4.78432 | 10.5077 |
| F | F | -1.9149 | 1.42415 | 1.4847 |
| F | F | -2.35541 | 5.8897 | 10.257 |
| H | H | 2.95483 | 13.2993 | 3.01556 |
| F | F | -0.718913 | 14.6867 | -0.928738 |
| C | C | -0.175414 | 14.8733 | 0.285217 |
| C | C | 1.21043 | 15.064 | 0.434469 |
| C | C | -0.996554 | 14.8119 | 1.42179 |
| F | F | 1.93196 | 15.0822 | -0.703432 |
| C | C | 1.83377 | 15.1957 | 1.68571 |
| C | C | -0.423363 | 14.9522 | 2.69386 |
| F | F | -2.30908 | 14.5659 | 1.29278 |
| B | B | 3.44236 | 15.324 | 1.95775 |
| C | C | 0.96267 | 15.1528 | 2.78861 |
| F | F | -1.18849 | 14.8413 | 3.79266 |
| C | C | 4.38768 | 14.9936 | 0.671807 |
| C | C | 3.78038 | 16.6916 | 2.76415 |

| | | | | |
|---|---|---|---|---|
| F | F | 1.46785 | 15.2581 | 4.0436 |
| C | C | 5.16231 | 15.9204 | -0.0462084 |
| C | C | 4.47062 | 13.6765 | 0.198806 |
| C | C | 4.52686 | 16.6972 | 3.94919 |
| C | C | 3.29516 | 17.9396 | 2.34332 |
| C | C | 5.96157 | 15.5658 | -1.15101 |
| F | F | 5.17402 | 17.2238 | 0.291069 |
| C | C | 5.24338 | 13.2645 | -0.894466 |
| F | F | 3.74053 | 12.6935 | 0.809114 |
| C | C | 4.80656 | 17.864 | 4.68146 |
| F | F | 5.01448 | 15.5335 | 4.46012 |
| C | C | 3.54959 | 19.136 | 3.0339 |
| F | F | 2.56389 | 18.0228 | 1.21338 |
| C | C | 6.00119 | 14.2291 | -1.57992 |
| F | F | 6.67819 | 16.493 | -1.80253 |
| F | F | 5.26471 | 11.9792 | -1.28703 |
| C | C | 4.31343 | 19.0937 | 4.21421 |
| F | F | 5.52957 | 17.8194 | 5.81343 |
| F | F | 3.07962 | 20.3099 | 2.5873 |
| F | F | 6.75352 | 13.8764 | -2.63094 |
| F | F | 4.57195 | 20.2217 | 4.89053 |

| | | | | |
|---|---|---|---|---|
| H | H | 3.72333 | 14.4064 | 2.77005 |

Calculated atom coordinates for [**2a**•H•**3**]$^+$[H•**3**]$^-$

| | | | | |
|---|---|---|---|---|
| C | C | -1.56734 | -4.03468 | 2.42344 |
| C | C | -0.610897 | -3.19698 | 3.04345 |
| C | C | 0.698664 | -3.14993 | 2.52543 |
| C | C | 1.04225 | -3.91588 | 1.39861 |
| C | C | 0.0853471 | -4.73574 | 0.779757 |
| C | C | -1.22383 | -4.78867 | 1.29176 |
| C | C | -2.18716 | -0.881661 | 3.71337 |
| C | C | -2.30421 | -0.753961 | 2.31422 |
| C | C | -3.14089 | 0.222435 | 1.74971 |
| C | C | -3.85873 | 1.10362 | 2.57294 |
| C | C | -3.73708 | 0.999688 | 3.96955 |
| C | C | -2.91914 | 0.0097607 | 4.53433 |
| C | C | 0.395369 | -1.28673 | 4.97213 |

| | | | | |
|---|---|---|---|---|
| C | C | 0.584828 | 0.0537363 | 4.57801 |
| C | C | 1.72338 | 0.782199 | 4.97641 |
| C | C | 2.80567 | 0.0404735 | 5.48987 |
| C | C | 2.63415 | -1.29376 | 5.87766 |
| C | C | 1.37567 | -1.92204 | 5.79341 |
| C | C | 1.68457 | 2.28871 | 5.13004 |
| C | C | 0.849619 | 2.73 | 6.41855 |
| C | C | 0.716592 | 1.61406 | 7.43356 |
| C | C | -0.450998 | 0.834801 | 7.50558 |
| C | C | -0.427982 | -0.475412 | 8.04473 |
| C | C | 0.807097 | -1.06048 | 8.4353 |
| C | C | 1.8684 | -0.156557 | 8.65093 |
| C | C | 1.82746 | 1.15897 | 8.1749 |
| C | C | 1.12151 | -2.53891 | 8.29555 |
| C | C | 1.04878 | -3.0301 | 6.78301 |
| P | P | -1.96644 | -1.42482 | 7.95608 |
| C | C | -3.43509 | -0.422793 | 8.30391 |
| C | C | -3.36761 | 0.835882 | 8.92723 |
| C | C | -4.556 | 1.52678 | 9.21069 |
| C | C | -5.79934 | 0.951611 | 8.90662 |
| C | C | -5.86206 | -0.308773 | 8.28264 |

| | | | | |
|---|---|---|---|---|
| C | C | -4.68355 | -0.998362 | 7.97052 |
| C | C | -2.0327 | -2.98552 | 8.86798 |
| C | C | -2.10076 | -4.193 | 8.13503 |
| C | C | -2.16089 | -5.41004 | 8.82997 |
| C | C | -2.1667 | -5.41915 | 10.237 |
| C | C | -2.12563 | -4.21162 | 10.9557 |
| C | C | -2.06001 | -2.98846 | 10.2748 |
| H | H | 1.73855 | -3.89278 | 6.67535 |
| H | H | 0.0339278 | -3.42512 | 6.57331 |
| H | H | 0.465551 | -3.18334 | 8.9114 |
| H | H | 2.14695 | -2.70101 | 8.68142 |
| H | H | -1.36853 | 1.21915 | 7.03372 |
| H | H | 2.72721 | 1.78872 | 8.2472 |
| H | H | 2.80855 | -0.543912 | 9.07214 |
| H | H | 1.33645 | 3.61357 | 6.87643 |
| H | H | -0.161036 | 3.0498 | 6.09428 |
| H | H | 1.23471 | 2.77606 | 4.2431 |
| H | H | 2.72027 | 2.67577 | 5.21803 |
| H | H | -0.228405 | 0.577364 | 4.05839 |
| H | H | 3.44933 | -1.80111 | 6.41779 |
| H | H | 3.75671 | 0.547131 | 5.71532 |

| | | | | |
|---|---|---|---|---|
| H | H | -2.10461 | -4.18274 | 7.03302 |
| H | H | -2.20537 | -6.35564 | 8.26872 |
| H | H | -2.2132 | -6.37695 | 10.7772 |
| H | H | -2.14207 | -4.20913 | 12.0552 |
| H | H | -2.03401 | -2.03864 | 10.8217 |
| H | H | -2.40743 | 1.26406 | 9.23443 |
| H | H | -4.49672 | 2.50265 | 9.71442 |
| H | H | -6.72702 | 1.47987 | 9.171 |
| H | H | -6.83701 | -0.760798 | 8.04635 |
| H | H | -4.73407 | -1.98663 | 7.4867 |
| H | H | -1.74448 | -1.42713 | 1.65316 |
| H | H | -3.208 | 0.300698 | 0.654469 |
| H | H | -4.49968 | 1.87992 | 2.12892 |
| H | H | -4.28999 | 1.68594 | 4.62859 |
| H | H | -2.86255 | -0.0544741 | 5.63018 |
| H | H | 1.45159 | -2.50157 | 2.9927 |
| H | H | 2.06391 | -3.85189 | 0.994981 |
| H | H | 0.351175 | -5.32234 | -0.112644 |
| H | H | -1.98132 | -5.42031 | 0.804129 |
| H | H | -2.59527 | -4.07893 | 2.81851 |
| P | P | -1.15291 | -2.20387 | 4.5049 |

| | | | | |
|---|---|---|---|---|
| H | H | -2.09491 | -1.89357 | 6.59743 |
| F | F | -2.65236 | 2.87328 | -2.38542 |
| C | C | -2.02001 | 2.6682 | -1.22704 |
| C | C | -0.891512 | 1.83602 | -1.15719 |
| C | C | -2.48448 | 3.29079 | -0.0529027 |
| F | F | -0.481386 | 1.27492 | -2.30633 |
| C | C | -0.185574 | 1.59334 | 0.0427873 |
| C | C | -1.80314 | 3.0983 | 1.16036 |
| F | F | -3.57516 | 4.05502 | -0.0854969 |
| B | B | 1.04683 | 0.612825 | 0.0990481 |
| C | C | -0.68383 | 2.25896 | 1.18272 |
| F | F | -2.25666 | 3.66897 | 2.27989 |
| C | C | 1.01802 | -0.710703 | -0.752269 |
| C | C | 2.25468 | 0.927057 | 1.05755 |
| F | F | -0.105161 | 2.07709 | 2.38361 |
| C | C | 2.19005 | -1.29415 | -1.28666 |
| C | C | -0.174557 | -1.43424 | -0.980024 |
| C | C | 3.02209 | -0.0847117 | 1.68296 |
| C | C | 2.60383 | 2.25147 | 1.41967 |
| C | C | 2.19914 | -2.53442 | -1.94153 |
| F | F | 3.36821 | -0.661192 | -1.17565 |

| | | | | |
|---|---|---|---|---|
| C | C | -0.208797 | -2.68349 | -1.61216 |
| F | F | -1.3588 | -0.967525 | -0.543711 |
| C | C | 4.02475 | 0.175887 | 2.62412 |
| F | F | 2.78728 | -1.38307 | 1.4294 |
| C | C | 3.59887 | 2.55558 | 2.3593 |
| F | F | 1.97735 | 3.29829 | 0.859644 |
| C | C | 0.989103 | -3.23602 | -2.09352 |
| F | F | 3.33514 | -3.05356 | -2.41463 |
| F | F | -1.3545 | -3.35794 | -1.73729 |
| C | C | 4.30283 | 1.50663 | 2.97389 |
| F | F | 4.67543 | -0.822025 | 3.22573 |
| F | F | 3.85577 | 3.82007 | 2.70463 |
| F | F | 0.981612 | -4.4407 | -2.66475 |
| F | F | 5.20352 | 1.77314 | 3.92011 |
| F | F | 3.71234 | 1.73436 | 12.3738 |
| C | C | 2.5074 | 1.94932 | 11.821 |
| C | C | 1.39346 | 1.16993 | 12.1928 |
| C | C | 2.35246 | 2.96404 | 10.8668 |
| F | F | 1.63127 | 0.249117 | 13.15 |
| C | C | 0.114402 | 1.31665 | 11.6254 |
| C | C | 1.08332 | 3.1878 | 10.313 |

| | | | | |
|---|---|---|---|---|
| F | F | 3.40585 | 3.69535 | 10.4654 |
| B | B | -1.15633 | 0.308912 | 11.8591 |
| C | C | 0.0166274 | 2.36741 | 10.6995 |
| F | F | 0.922181 | 4.13759 | 9.3706 |
| C | C | -0.823959 | -0.987205 | 12.7999 |
| C | C | -2.56234 | 1.0426 | 12.2521 |
| F | F | -1.16881 | 2.63171 | 10.0877 |
| C | C | -1.40433 | -1.26703 | 14.0473 |
| C | C | 0.0716493 | -1.96594 | 12.3393 |
| C | C | -3.77936 | 0.383024 | 12.0187 |
| C | C | -2.68927 | 2.33255 | 12.7934 |
| C | C | -1.13152 | -2.4391 | 14.7822 |
| F | F | -2.26481 | -0.400471 | 14.6204 |
| C | C | 0.38414 | -3.145 | 13.0272 |
| F | F | 0.687498 | -1.79232 | 11.1425 |
| C | C | -5.0411 | 0.948964 | 12.2525 |
| F | F | -3.78332 | -0.871826 | 11.5032 |
| C | C | -3.92996 | 2.95317 | 13.0376 |
| F | F | -1.59364 | 3.05195 | 13.1132 |
| C | C | -0.228512 | -3.38453 | 14.2689 |
| F | F | -1.71431 | -2.65447 | 15.972 |

| | | | | |
|---|---|---|---|---|
| F | F | 1.23946 | -4.04509 | 12.5106 |
| C | C | -5.11751 | 2.25586 | 12.7586 |
| F | F | -6.16792 | 0.281349 | 11.9425 |
| F | F | -3.99391 | 4.19398 | 13.547 |
| F | F | 0.0504248 | -4.50284 | 14.9563 |
| F | F | -6.31159 | 2.83338 | 12.9651 |
| H | H | -1.34905 | -0.167888 | 10.7189 |