Electronic Supporting Information

Zero valent iron complexes as base partners in Frustrated Lewis Pair chemistry

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Experimental

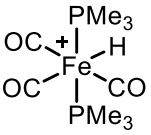
General information

All manipulations were carried out under nitrogen using a glove box and/or Schlenk techniques. All reactions were performed in glassware that was oven-dried for at least 12 h. Benzene was distilled over sodium and benzophenone under a nitrogen atmosphere and stored over 4 Å molecular sieves prior to use. Diethyl ether and *n*-hexane were dried over activated alumina using an LC Technology Solution Inc. SP-1 Solvent Purification System and deoxygenated prior to use. PhCl, 1,2-$C_6H_4F_2$ (1,2-DFB), C_6D_6 and CD_2Cl_2 used was stirred over CaH_2 at room temperature under a nitrogen atmosphere overnight prior to distillation under reduced pressure and stored over 4 Å molecular sieves. $[Fe(CO)_3(PMe_3)_2]$ (**1**) [1], $B(C_6F_5)_3$[2] (BCF) and $[^nBu_4N][HB(C_6F_5)_3]$[3] were prepared according to reported methods. The cation $[FeH(CO)_3(PMe_3)_2]^+$ ($[\mathbf{1}\text{-H}]^+$)[4] and the anions $[BH(C_6F_5)_3]^-$[3], $[BD(C_6F_5)_3]^-$[3], $[BCl(C_6F_5)_3]^-$[5], $[(\mu\text{-OH})\{B(C_6F_5)_3\}_2]^-$[6] and $[B(SPh)(C_6F_5)_3]^-$[7] have be reported in literature and are in good agreement with the observed analytical data. All other reagents were purchased from commercial sources and used as received.

NMR spectroscopy data were obtained using Bruker AV-300, AV-400 and AV-500 spectrometers. GC-MS studies were performed on Shimadzu QP-2010-SE GC-MS system. HRMS (ESI-TOF) spectra were obtained using an Agilent Technologies 6230 TOF LC/MS. IR spectroscopy data were obtained using Bruker ALPHA FTIR spectrometers. ^1H and ^{13}C chemical shifts are given in ppm relative to TMS, using the solvent signals as references and converting the chemical shifts to the TMS scale. ^{31}P and ^{19}F chemical shifts are given in ppm relative to H_3PO_4 and $CFCl_3$ respectively (external standard). NMR yields were obtained using triphenylmethane as an internal standard. X-Ray diffraction analysis was performed by the XRAY department at NUS. The X-ray intensity data were measured on a Bruker D8 Venture dual source diffractometer. The crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-2014 using Olex3. The crystals suitable for X-ray analysis were grown by slow diffusion of different solvent mixtures of the metal complexes or

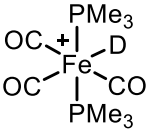
by slow solvent evaporation/cooling of saturated solutions of the corresponding compounds. Where accurate elemental analysis could not be obtained, a compounds purity was ascertained by ^{1}H and ^{31}P NMR spectroscopies.

Activation of H_2, D_2, H_2O and PhSH by 1 and BCF



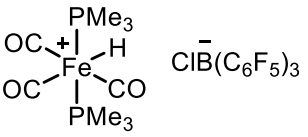
Compound **[1-H][BH(C$_6$F$_5$)$_3$]**: Chlorobenzene (0.5 mL) was added to a mixture of **1** (11.4 mg, 0.039 mmol) and BCF (20 mg, 0.039 mmol, 1 equiv.) in a Young NMR tube and the resultant solution was subjected to three freeze-pump-thaw cycles and then charged with 1 atm of hydrogen at 77 K. Upon slow warming of the solution the colour changed to light yellow. The solution was mixed for 24 hours with a modified rotatory evaporator, NMR analysis confirmed the formation of **[1-H][BH(C$_6$F$_5$)$_3$]** in 63% yield.

^{1}H NMR (500 MHz, PhCl) δ_H 4.00 – 3.07 (m, 1H, B-*H*), 1.77 (d, J = 7.6 Hz, 18H; P*Me*$_3$), -9.59 (t, J = 36.3 Hz, 1H, Fe-*H*); **^{11}B NMR** (160 MHz, PhCl) δ_B -24.96 (d, *J* = 93.0 Hz); **^{31}P NMR** (202 MHz, CD_2Cl_2): δ_P 16.17.



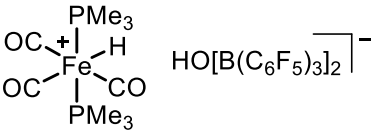
Compound **[1-D][BD(C$_6$F$_5$)$_3$]**: Chlorobenzene (0.5 mL) was added to a mixture of **1** (11.4 mg, 0.039 mmol) and BCF (20 mg, 0.039 mmol, 1 equiv.) in a Young NMR tube and the resultant solution was subjected to three freeze-pump-thaw cycles and then charged with 1 atm of deuterium at 77 K. After slow warming of the solution to room temperature the resulting solution was heated to 60 °C for 3 h, the colour changed to light yellow. NMR analysis confirmed the formation of **[1-D][BD(C$_6$F$_5$)$_3$]** in 65% yield.

^{2}H NMR (77 MHz, PhCl) δ_D 3.91 (br, 1 H), -10.40 (t, *J* = 5.6 Hz, 1 H); **^{11}B NMR** (160 MHz, PhCl) δ_B -24.96 (br. s); **^{31}P NMR** (202 MHz, PhCl): δ_P 16.05.



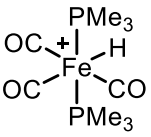
Compound **[1-H][BCl(C$_6$F$_5$)$_3$]**: Chlorobenzene (0.5 mL) was added to a mixture of **1** (11.4 mg, 0.039 mmol) and BCF (20 mg, 0.039 mmol, 1 equiv.) in a Young NMR tube, then HCl·OEt$_2$ (17.1 µL, 2M in Et$_2$O, 1 equiv.) was added and the solution was mixed for 10 min with a modified rotatory evaporator. After evaporation of volatiles NMR analysis in CD_2Cl_2 confirmed quantitative formation of **[1-H][BCl(C$_6$F$_5$)$_3$]**.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.70 (d, *J* = 8.4 Hz, 18 H), -9.63 (br s, 1 H); **^{11}B NMR** (160 MHz, $CDCl_3$) δ_B -7.41; **^{13}C NMR** (126 MHz, CD_2Cl_2): δ_C 205.53, 148.06 (d, *J* = 239.9 Hz), 140.51 – 137.70 (m), 136.70 (d, *J* = 249.8 Hz), 123.43 – 122.44 (m), 20.98 (dt, *J* = 32.7, 15.2 Hz); **^{19}F NMR** (471 MHz, CD_2Cl_2) δ -129.93 – -136.81 (m), -162.47 (t, *J* = 19.8 Hz), -167.20 (t, *J* = 20.3 Hz); **^{31}P NMR** (202 MHz, $CDCl_3$): δ_P 17.24; **HRMS** (ESI-TOF) *m/z*: $[M]^+$ *calcd.* for $C_9H_{19}FeO_3P_2$: 293.0153; *found*: 293.0135; **IR** (solution in CD_2Cl_2): ν_{CO} 2087, 2020 cm^{-1}.

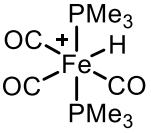


Compound **[1-H][(µ-OH){B(C$_6$F$_5$)$_3$}$_2$]:** Chlorobenzene (0.5 mL) was added to a mixture of **1** (11.4 mg, 0.039 mmol) and BCF (40 mg, 0.078 mmol, 2 equiv.) in a Young NMR tube, then H_2O was added and the solution was mixed for 10 min with a modified rotatory evaporator. Recrystallization from C_6D_6 gave **[1-H][(µ-OH){B(C$_6$F$_5$)$_3$}$_2$]** quantitatively.

^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 6.65 (s, 1 H), 1.84 – 1.59 (m, 18 H), -9.61 (t, *J* = 36.4 Hz, 1 H); **^{11}B NMR** (160 MHz, CD_2Cl_2) δ_B -3.64; **^{13}C NMR** (126 MHz, CD_2Cl_2): δ_C 206.20 (t, *J* = 24.2 Hz), 204.77 – 202.66 (m), 148.24 (d, *J* = 241.2 Hz), 140.04 (d, *J* = 248.2 Hz), 137.23 (d, *J* = 247.1 Hz), 120.03 – 119.17 (m), 20.89 (dt, *J* = 33.5, 15.4 Hz); **^{19}F NMR** (471 MHz, CD_2Cl_2) δ -136.1, -160.1, -165.5; **^{31}P NMR** (202 MHz, CD_2Cl_2): δ_P 15.28; **HRMS** (ESI-TOF) *m/z*: $[M]^-$-B(C_6F_5)$_3$ *calcd.* for $C_{18}HBF_{15}O$: 528.9890; *found*: 528.9891; **IR** (solution in CD_2Cl_2): ν_{CO} 2087, 2020 cm^{-1}.



Compound **[1-H][B(SPh)(C_6F_5)$_3$]:** Chlorobenzene (0.5 mL) was added to a mixture of **1** (11.4 mg, 0.039 mmol) and BCF (40 mg, 0.078 mmol, 2 equiv.) in a Young NMR tube, then PhSH (4.3 mg, 0.039 mmol, 1.0 eq) was added and the resulting solution was mixed for 10 min with a modified rotatory evaporator. NMR analysis confirmed formation of **[1-H][B(SPh)(C_6F_5)$_3$]** quantitatively. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ_H 7.15 – 7.07 (m, 2 H), 7.00 – 6.87 (m, 3 H), 1.74 (d, *J* = 9.5 Hz, 18 H), -9.58 (t, *J* = 36.3 Hz, 1 H; **^{11}B NMR** (160 MHz, CD_2Cl_2): δ_B 21.24; **^{13}C NMR** (126 MHz, CD_2Cl_2): δ_C 206.3 (t, *J* = 23.6 Hz), 203.9 – 203.4 (m), 148.8 (d, *J* = 244.8 Hz), 143.8 – 140.7 (m), 140.3, 139.5 – 136.1 (m), 132.6, 128.1, 124.4, 120.3 – 117.9 (m), 21.3 – 20.4 (m); **^{19}F NMR** (471 MHz, CD_2Cl_2) δ_F -130.04, -154.43, -164.49; **^{31}P NMR** (202 MHz, CD_2Cl_2): δ_P 16.00; **IR** (solution in CD_2Cl_2): ν_{CO} 2087, 2020 cm^{-1}.



Compound **[1-H][BAr$^F{}_4$]:** 1,2-Difluorobenzene (0.5 mL) was added to a mixture of **1** (10 mg, 0.034 mmol) and H·OEt$_2$ BAr$^F{}_4$ (32.1 mg, 0.034 mmol, 1 equiv.) in a Young NMR tube and the solution was mixed for 10 min with a modified rotatory evaporator. After evaporation of the solvent and redissolving in difluorobenzene NMR analysis confirmed quantitative formation of **[1-H][BAr$^F{}_4$]**.

^{1}H NMR (500 MHz, PhF_2) δ 8.32 (s, 12H), 7.69 (s, 7H), 1.71 (d, *J* = 7.9 Hz, 18H), -9.58 (t, *J* = 36.3 Hz, 1H); **^{11}B NMR** (160 MHz, PhF_2) δ -6.39; **^{13}C NMR** (126 MHz, C_6D_6) δ 205.39 (t, *J* = 23.9 Hz), 202.71 (t, *J* = 14.0 Hz), 162.28 (q, *J* = 50.0 Hz), 134.84, 129.45 (q, *J* = 31.1 Hz), 124.65 (q, *J* = 272.2 Hz), 117.34, 20.24 – 17.15 (m); **^{19}F NMR** (471 MHz, PhF_2) δ -62.99. **^{31}P NMR** (202 MHz, PhF_2) δ 13.28; **HRMS** (ESI-TOF) *m/z*: [M]$^+$ *calcd.* for $C_9H_{19}FeO_3P_2$: 293.0148; *found*: 293.0135; **IR** (solution in PhF_2): ν_{CO} 2087, 2043, 2020 cm^{-1}.

General Procedure for catalytic experiments

In a representative experiment (see Figure 7, substrate **2a**); diphenylethylene (54.1 mg, 0.3 mmol, 1 eq), **1** (4.4 mg, 0.015 mmol, 0.05 eq) and BCF (7.7 mg, 0.015 mmol, 0.05 equiv.) were weighed into a J. Young's NMR tube and chlorobenzene (0.5 ml, 0.6 M) was added. The resultant solution was subjected to three freeze-pump-thaw cycles and then charged with 1 atm of hydrogen or deuterium gas at 77 K. Upon slow warming of the solution, the colour changed to light yellow. After heating for 24 h at 130 °C triphenylmethane (73.3 mg, 1 eq) was added as internal standard and the reaction yield was determined by ^{1}H-NMR or GCMS analysis.

Control reaction of [1-H][BAr$^{F}_{4}$] and [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$]

Chlorobenzene (0.5 ml) was added to a mixture of **[1-H][BAr$^{F}_{4}$]** (15.3 mg, 0.013 mmol, 1 eq) and **[^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$]** (10 mg, 0.013 mmol, 1 eq) in a J. Young's NMR tube. The resulting solution was subjected to NMR analysis after 3 and 24 h. The solution was heated at 100 °C for 24 h and subject to NMR analysis again. No formation of **1** and/or BCF was detected.

Control reaction of PMe$_3$ and B(C$_6$F$_5$)$_3$ with H$_2$

PMe$_3$ (1.98 µL, 0.019 mmol, 0.05 eq) and BCF (10 mg, 0.019 mmol, 1.0 equiv.) were weighed into a Young NMR tube and chloroform (0.5 ml) was added. The resultant solution was subjected to three freeze-pump-thaw cycles and then charged with 1 atm of hydrogen gas at 77 K and analysed by ^{1}H and ^{31}P NMR.

Control reaction of diphenylethylene, PMe$_3$ and B(C$_6$F$_5$)$_3$ with H$_2$

Diphenylethylene (53 µL, 0.34 mmol, 1 eq), PMe$_3$ (1.77 µL, 0.019 mmol, 0.05 eq) and BCF (8.8 mg, 0.019 mmol, 0.05 equiv.) were weighed into a Young NMR tube and chlorobenzene (0.5 ml, 0.6 M) was added. The resultant solution was subjected to three freeze-pump-thaw cycles and then charged with 1 atm of hydrogen gas at 77 K. After heating for 24 h at 130 °C the solution was analysed by ^{1}H-NMR.

Control reaction of [1], Ph_3CBArF_{24} with H_2

[1] (10 mg, 0.034 mmol, 1.0 eq) and Ph_3CBArF_{24} (14.1 mg, 0.034 mmol, 1.0 equiv.) were weighed into a Young NMR tube and chlorobenzene (0.5 ml, 0.6 M) was added. The resultant solution was subjected to three freeze-pump-thaw cycles and then charged with 1 atm of hydrogen gas at 77 K. The corresponding solution was analysed by ^{1}H and ^{31}P NMR.

Control reaction of [1-H][$BArF_{24}$], [*n*Bu_4N][$HB(C_6F_5)_3$] with diphenylethylene

[1-H][$BArF_{24}$] (20 mg, 0.017 mmol, 1.0 eq) and **[*n*Bu_4N][$HB(C_6F_5)_3$]** (13.1 mg, 0.017 mmol, 1.0 equiv.) and diphenylethylene (3.1 mg, 0.017 mmol, 1.0 equiv.) were weighed into a J. Young's NMR tube and chlorobenzene (0.5 ml, 0.034 M) was added. The resultant solution was heated for 48 h at 80 °C. After addition of Ph_3CH (4.4 mg, 0.017 mmol, 1.0 equiv.) in C_6D_6 (0.2 ml) the corresponding solution was analysed by ^{1}H NMR spectroscopy showing conversion to **3a** in 35%.

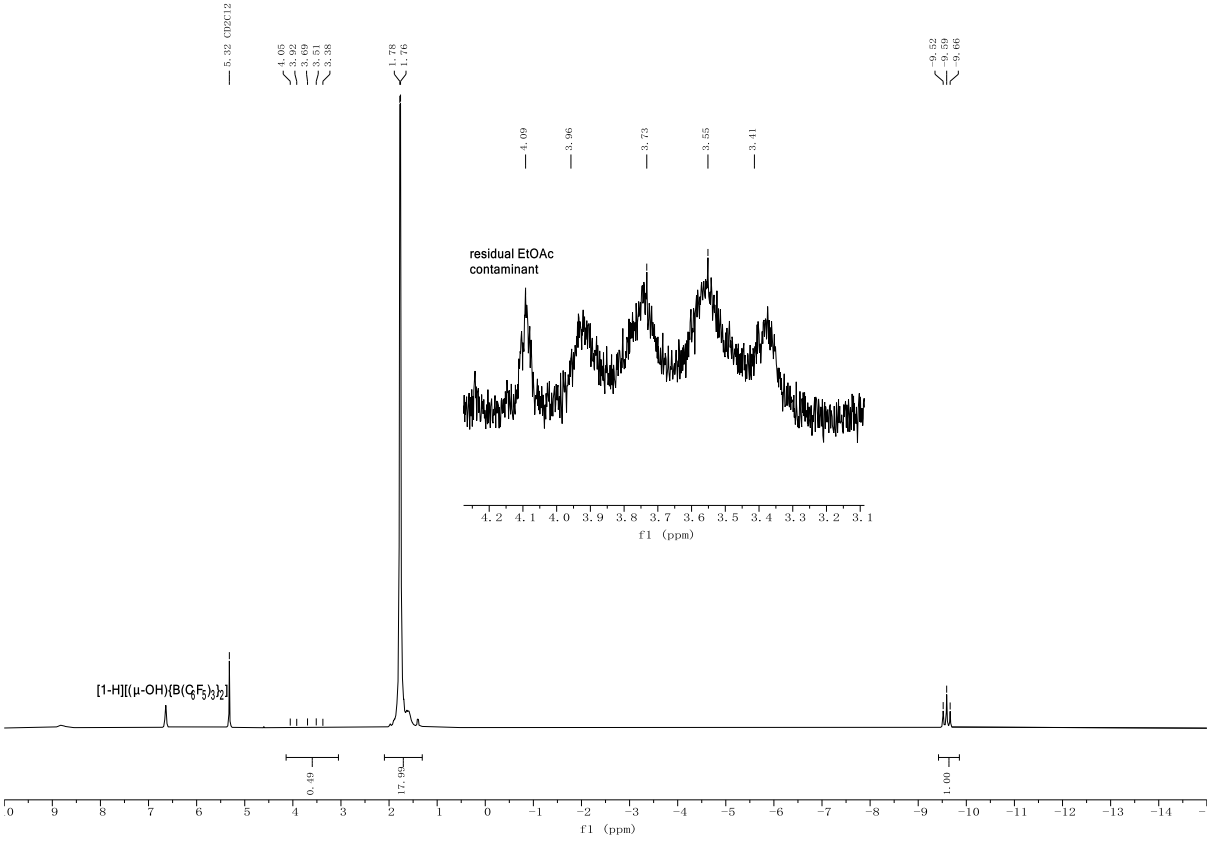
X-Ray Crystallography Data Tables

Data	[1-H][BCl(C_6F_5)$_3$]	[1-H][(μ-OH){B(C_6F_5)$_3$}$_2$]	[1-H][B(SPh)(C_6F_5)$_3$]
Formula	$C_{27}H_{19}BClF_{15}FeO_3P_2$	$C_{51}H_{25.50}B_2F_{30.50}FeO_4P_2$	$C_{33}H_{24}BF_{15}FeO_3P_2S$
Formula weight	840.47	1421.12	914.18
Colour	colourless	colourless	colourless
Crystal size / mm^3	0.316 x 0.211 x 0.11	0.559 x 0.48 x 0.379	0.154 x 0.134 x 0.132
Temperature / K	100	100	100
Crystal system	triclinic	triclinic	monoclinic
Space group	P -1	P -1	P21/c
a / Å	8.6538(3)	12.4374(9)	12.5412(4)
b / Å	11.4042(4)	14.0427(9)	13.0207(4)
c / Å	16.5963(6)	15.3107(10)	21.9702(7)
α / °	91.4570(10)	84.826(2)	90
β / °	97.0820(10)	83.992(3)	90.1400(10)
γ / °	102.6010(10)	80.351(3)	90
V / Å^3	1583.92(10)	2614.6(3)	3587.6(2)
Z	2	2	4
ρ_{calcd} / g cm^{-3}	1.762	1.805	1.693
Radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ / mm^{-1}	0.781	0.507	0.682
2θ max / °	75.688	69.326	57.346
No. of unique reflns	16888	22249	9224
No. of variables	461	834	515
GoF (S)	1.059	1.032	1.083
R factor (I > 2σ)	0.0592 (10196 reflections)	0.0439 (15738 reflections)	0.0370 (7160 reflections)

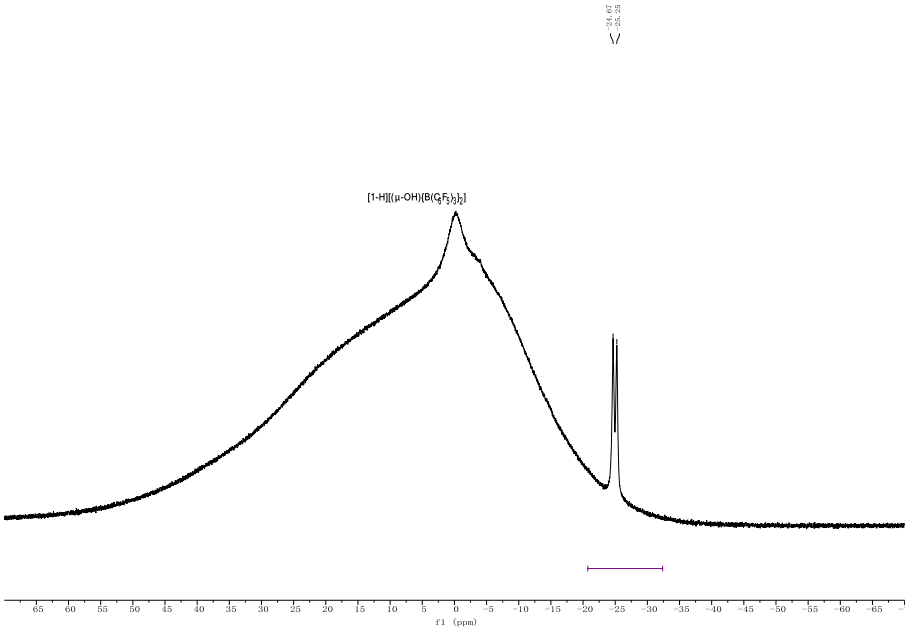
Table S1 Crystal Data, Data Collection and Refinement Parameters for the structures of **[1-H][BCl(C_6F_5)$_3$]**, **[1-H][(μ-OH){B(C_6F_5)$_3$}$_2$]** and **[1-H][B(SPh)(C_6F_5)$_3$]**.

^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{31}P NMR spectra of compounds [1-H][BH(C_6F_5)$_3$], [1-D][BD(C_6F_5)$_3$], [1-H][BCl(C_6F_5)$_3$], [1-H][(μ-OH){B(C_6F_5)$_3$}$_2$] and [1-H][B(SPh)(C_6F_5)$_3$]

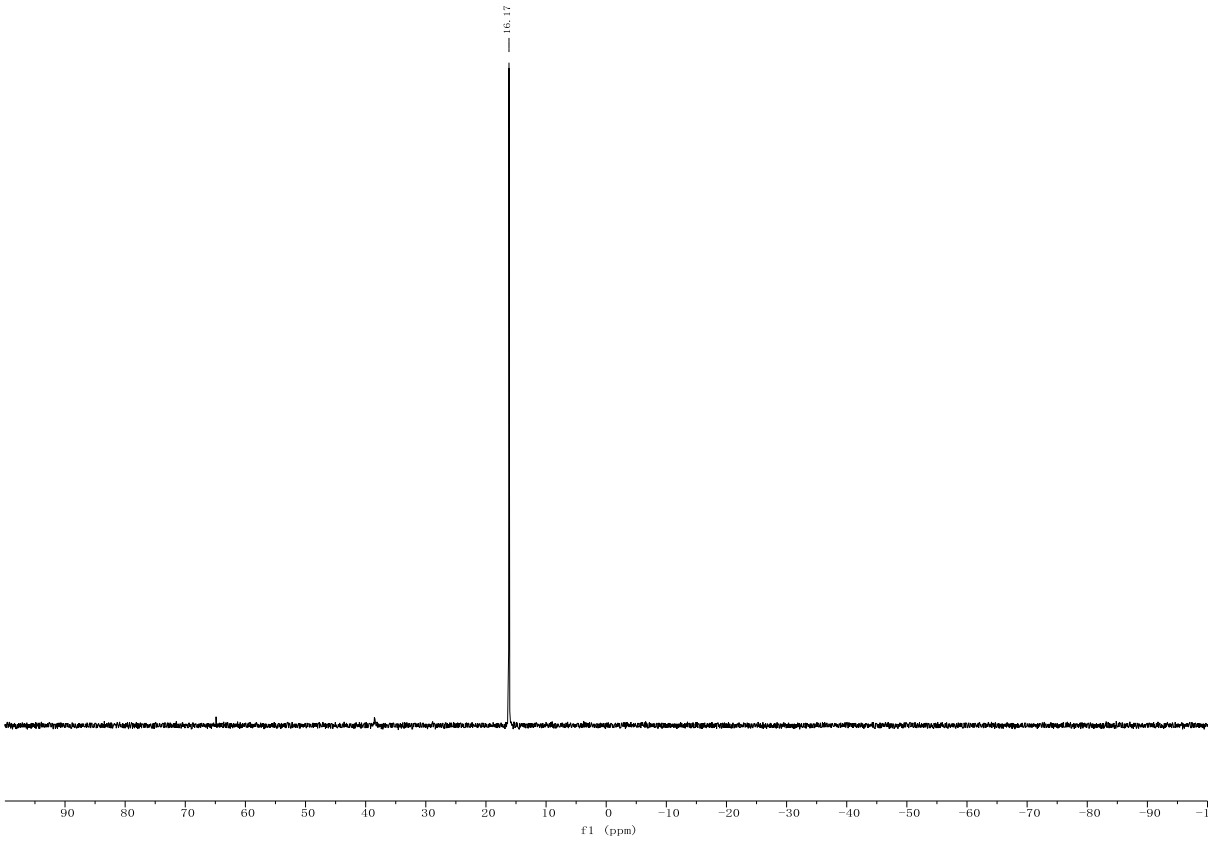
Compound [1-H][BH(C_6F_5)$_3$]: ^{1}H-NMR (500 MHz, CD_2Cl_2)



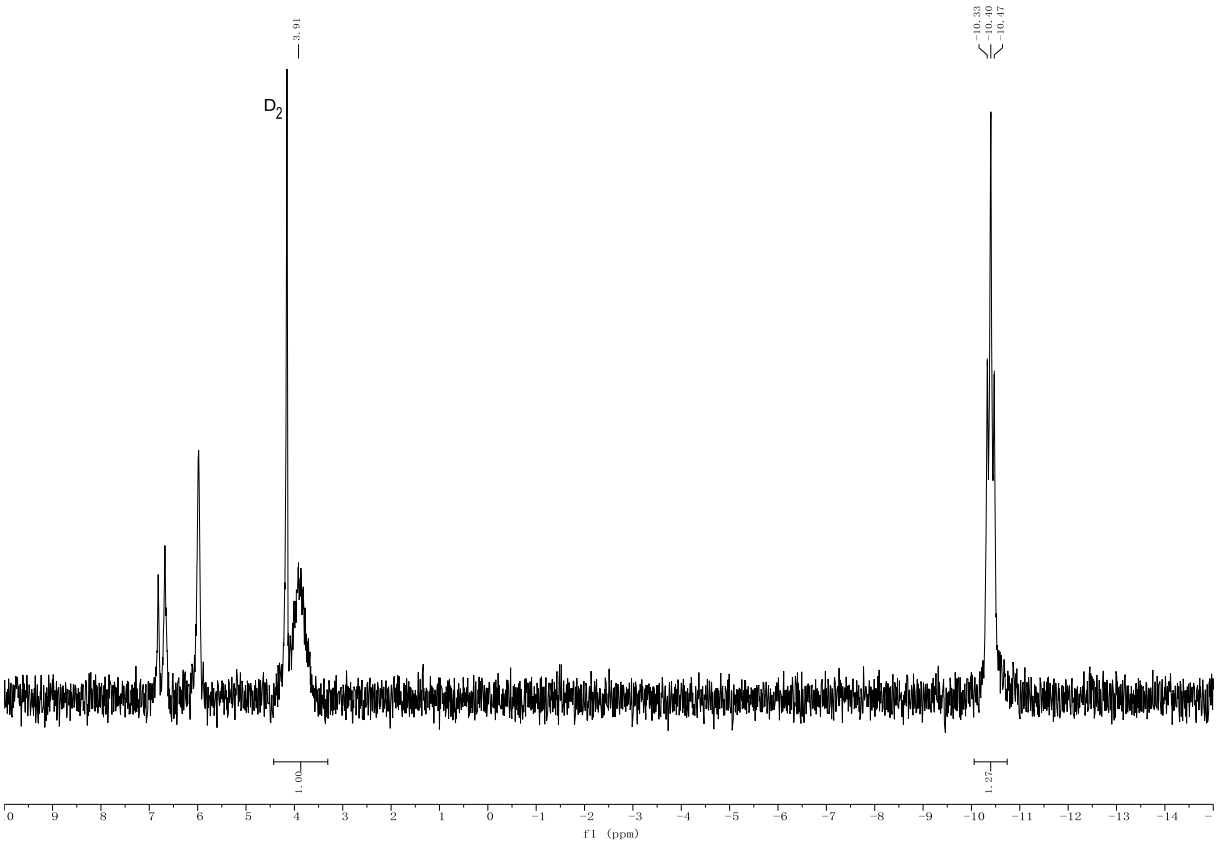
Compound [1-H][BH(C_6F_5)$_3$]: ^{11}B-NMR (160 MHz, PhCl):



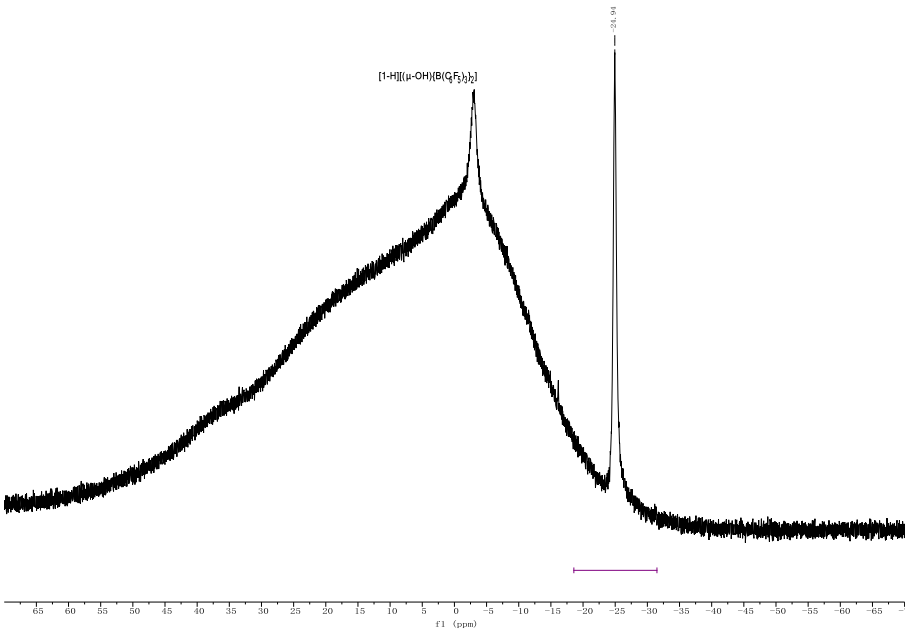
Compound [1-H][BH(C_6F_5)$_3$]: ^{31}P-NMR (202 MHz, CD_2Cl_2)



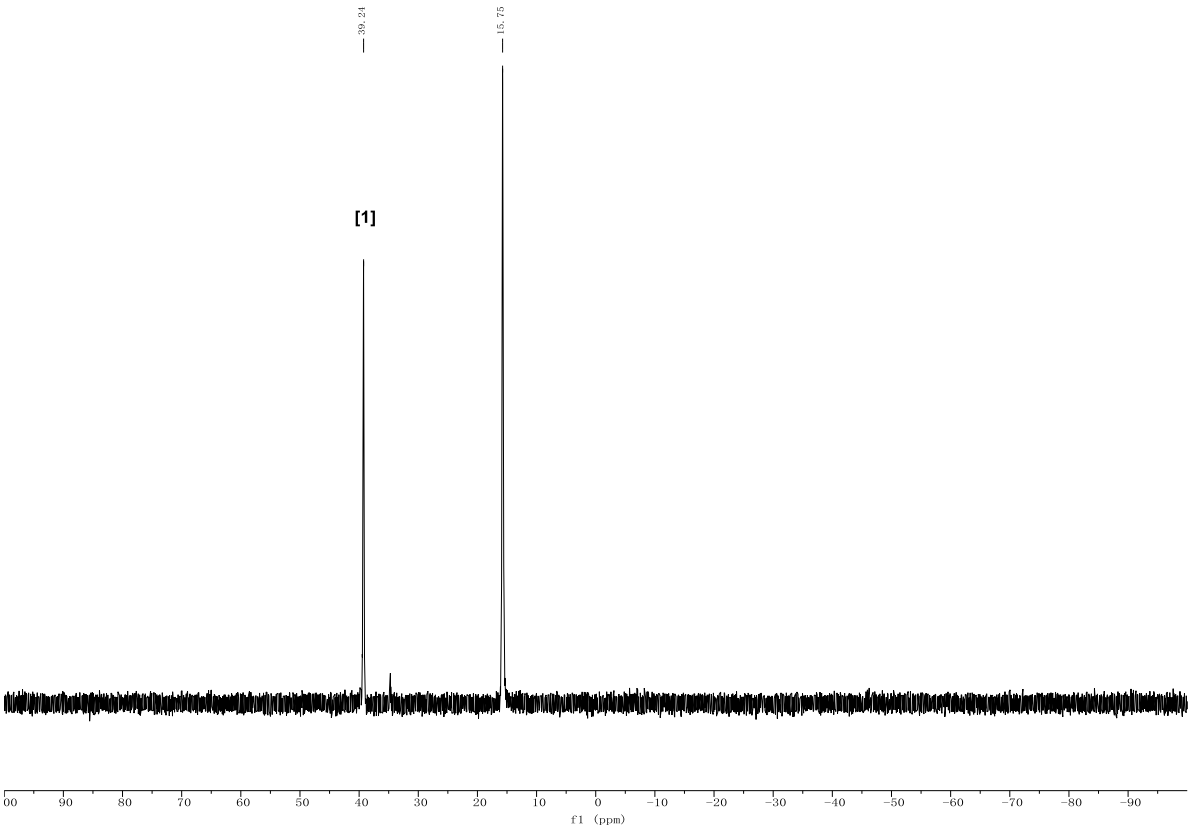
Compound [1-D][BD(C$_6$F$_5$)$_3$]: ^{2}H-NMR (77 MHz, PhCl):



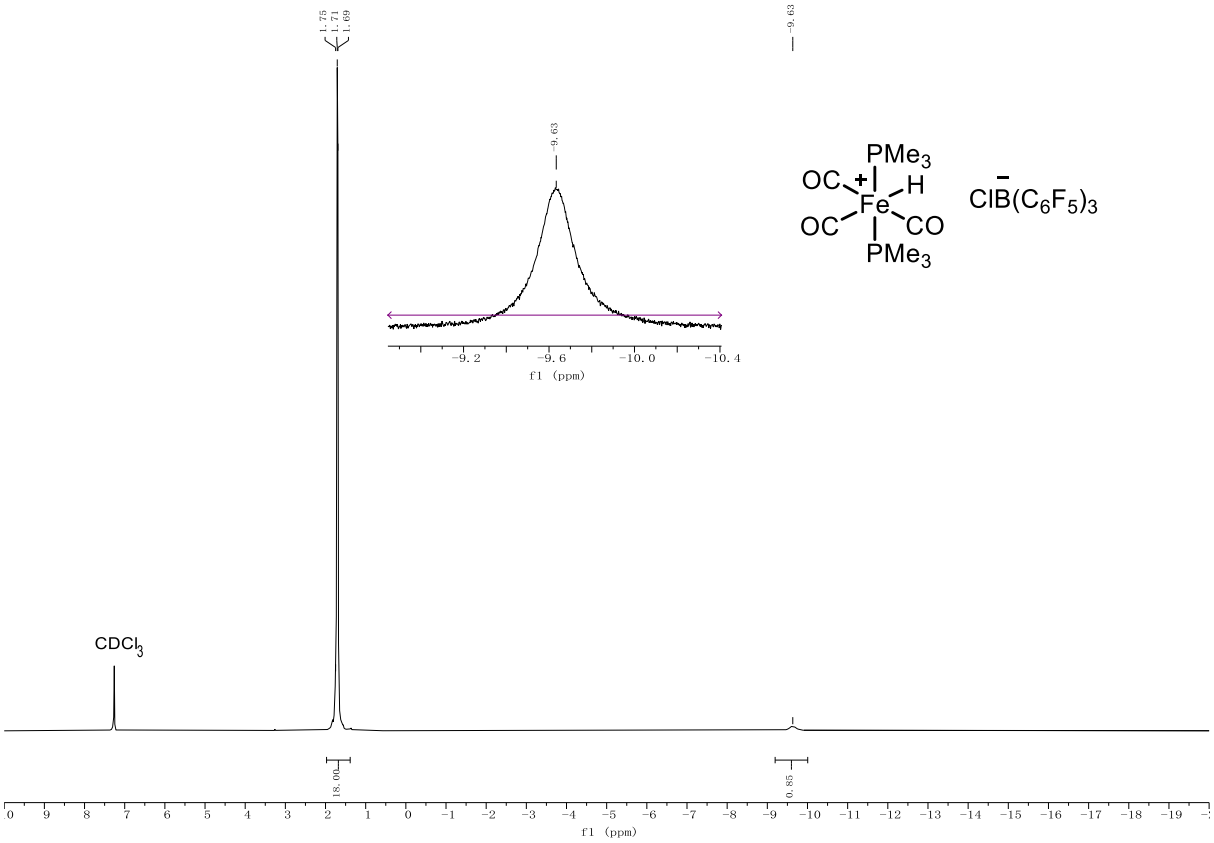
Compound [1-D][BD(C$_6$F$_5$)$_3$]: ^{11}B-NMR (160 MHz, PhCl):



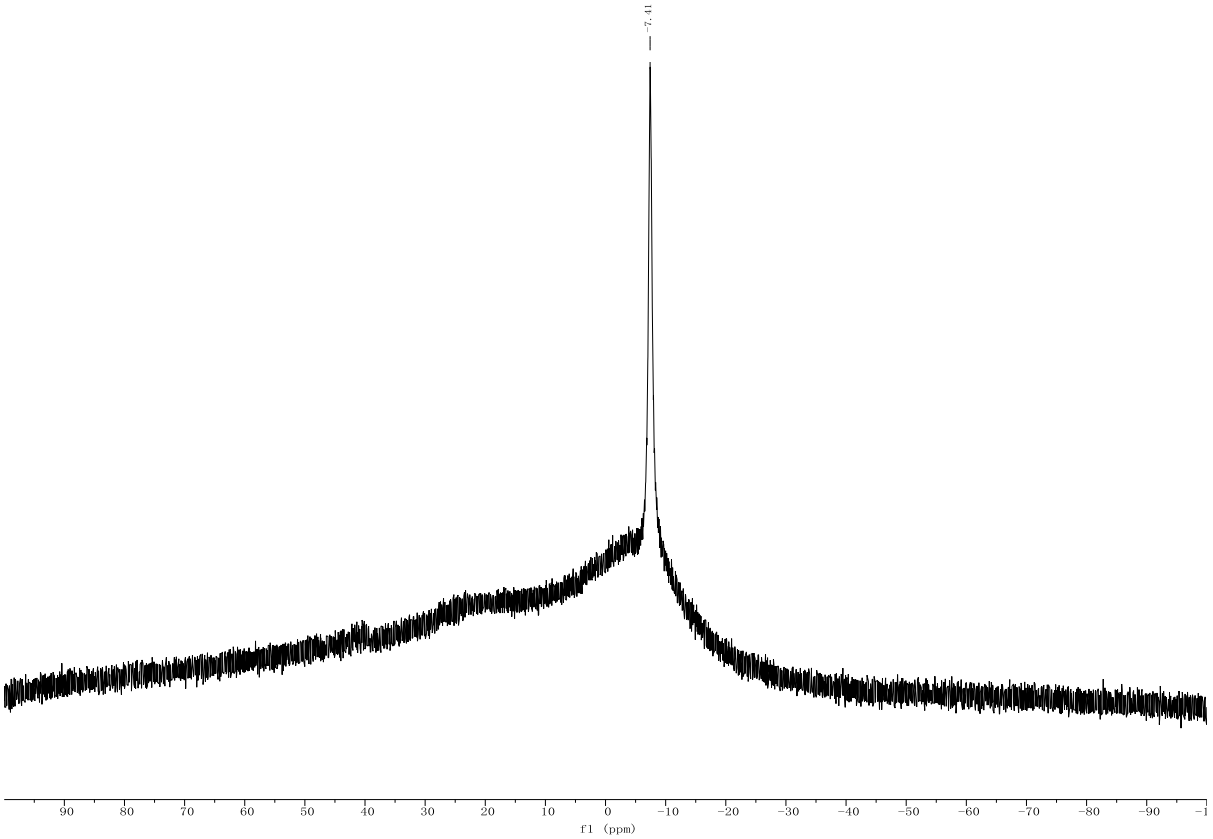
Compound [1-D][BD(C_6F_5)$_3$]: ^{31}P-NMR (202 MHz, PhCl)



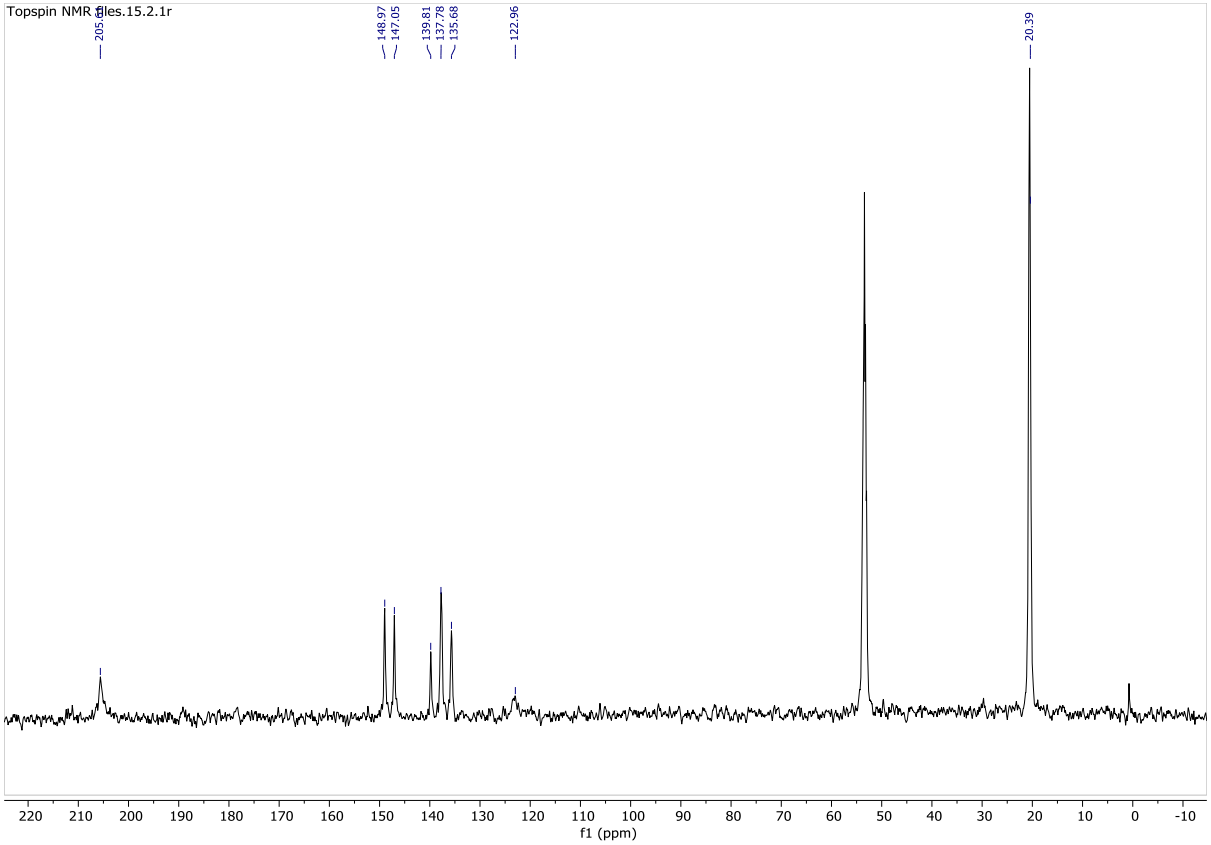
Compound [1-H][BCl(C_6F_5)$_3$]: ^{1}H-NMR (500 MHz, $CDCl_3$)



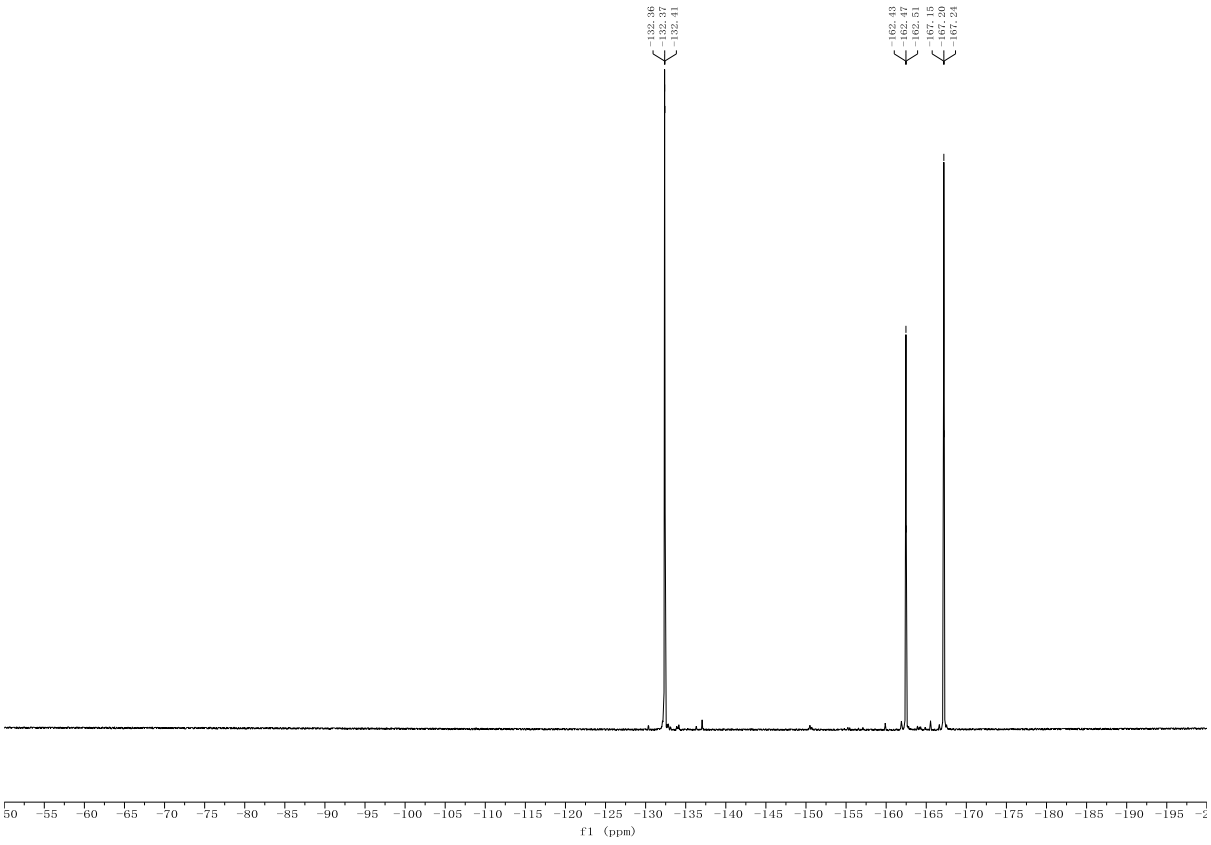
Compound [1-H][BCl(C_6F_5)$_3$]: ^{11}B-NMR (160 MHz, CD_2Cl_2)



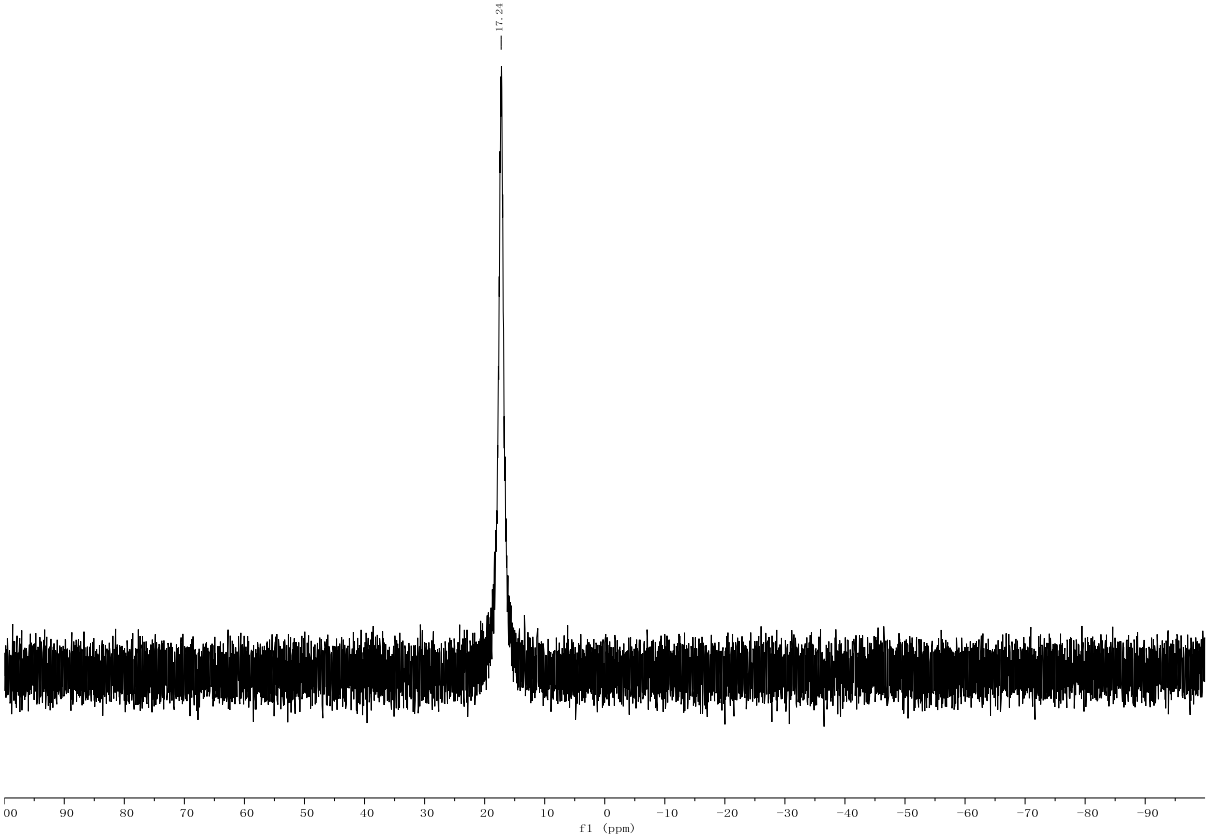
Compound [1-H][BCl(C_6F_5)$_3$]: ^{13}C-NMR (126 MHz, CD_2Cl_2)



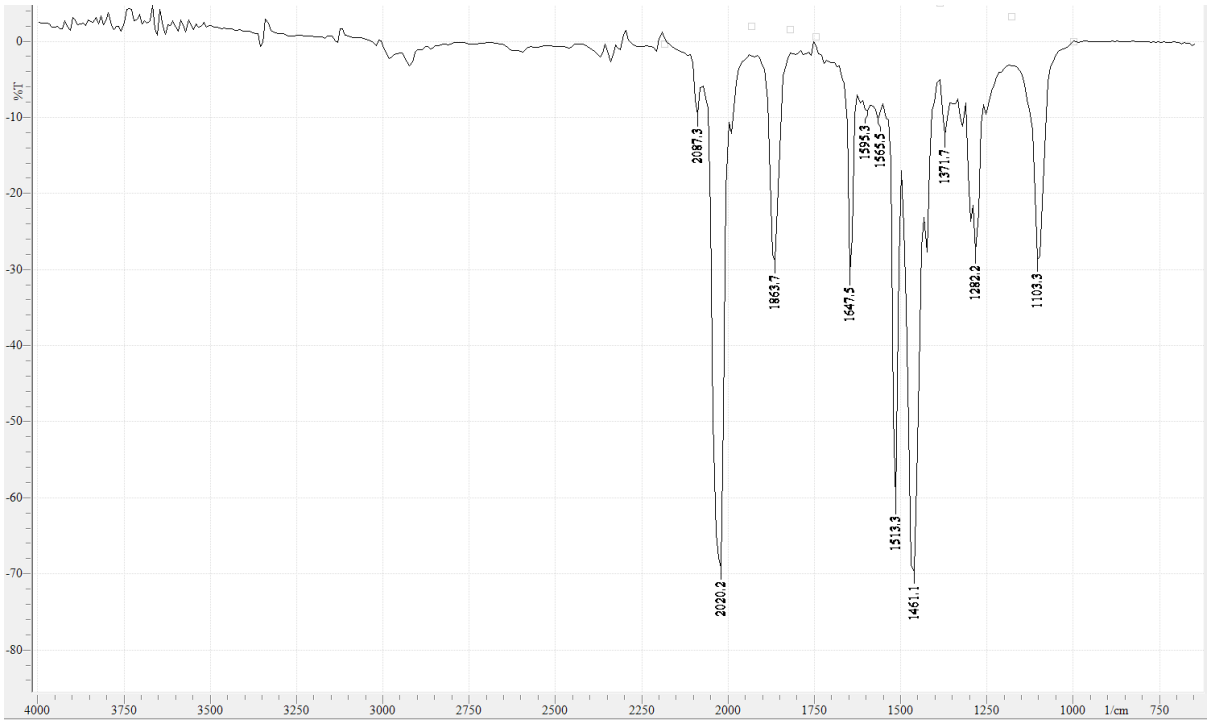
Compound [1-H][BCl(C_6F_5)$_3$]: ^{19}F-NMR (470 MHz, CD_2Cl_2)



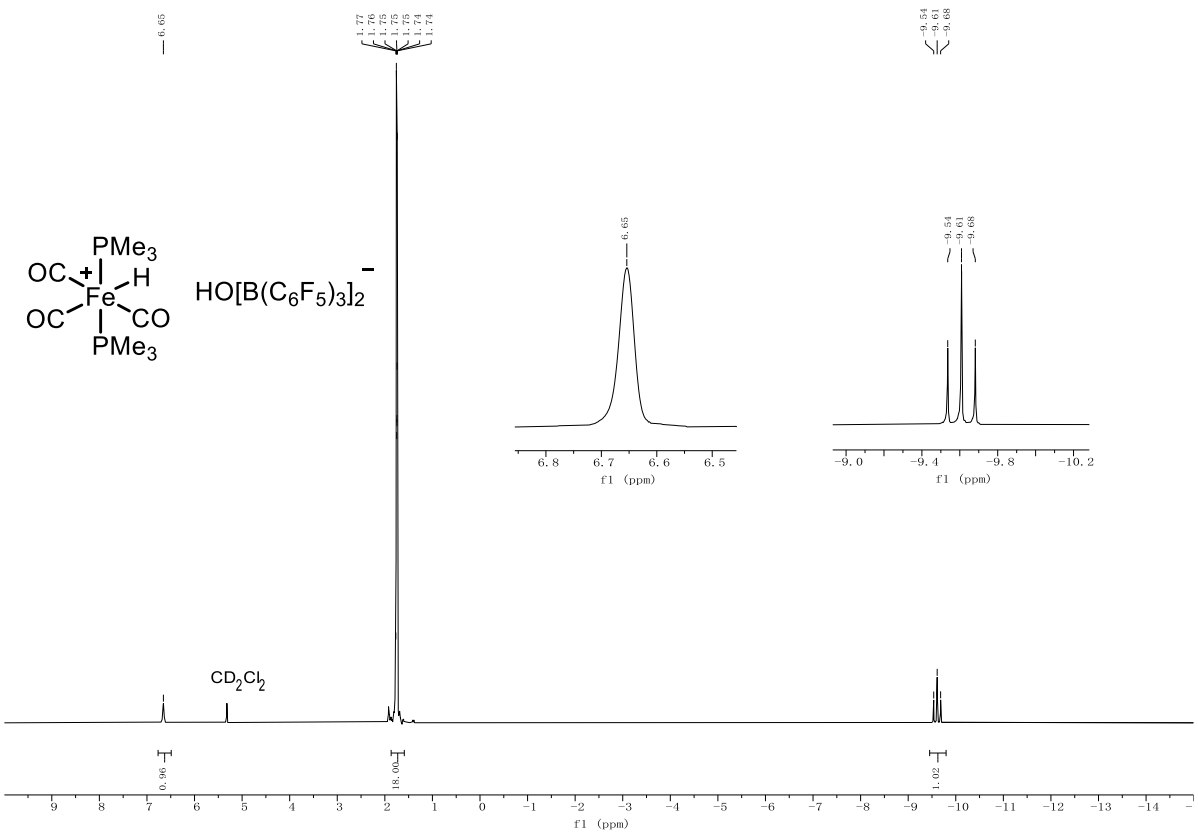
Compound [1-H][BCl(C_6F_5)$_3$]: ^{31}P-NMR (202 MHz, $CDCl_3$)



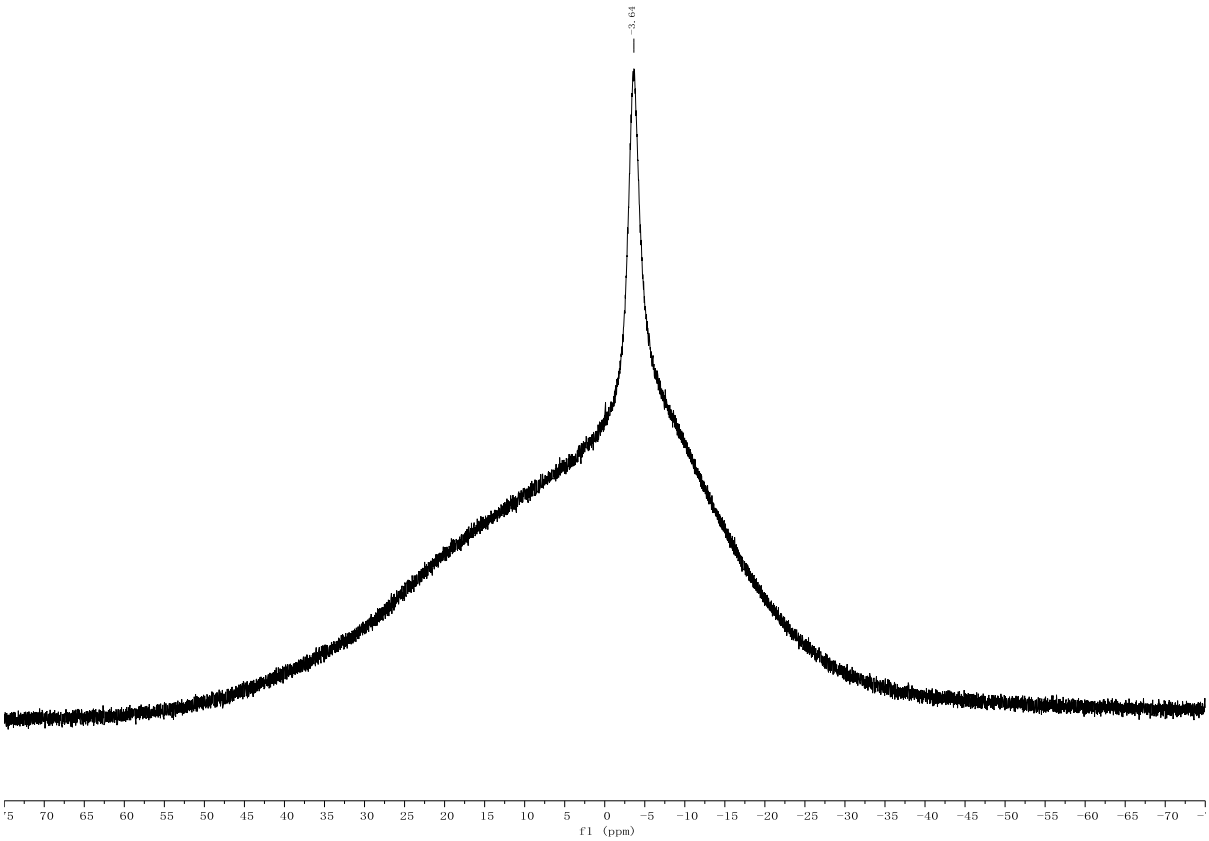
Compound [1-H][BCl(C_6F_5)$_3$]: IR in CD_2Cl_2



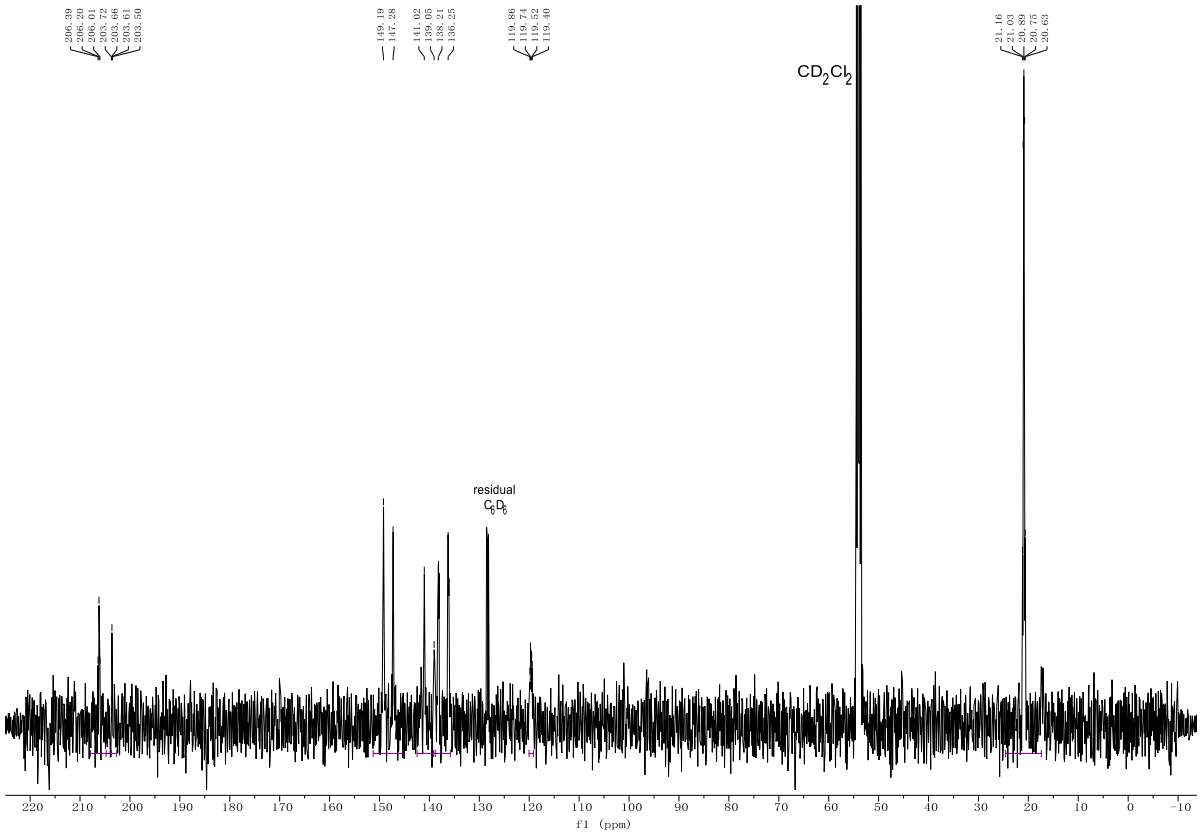
Compound [1-H][(μ-OH){B(C$_6$F$_5$)$_3$}$_2$]: ^{1}H-NMR (500 MHz, CD_2Cl_2)



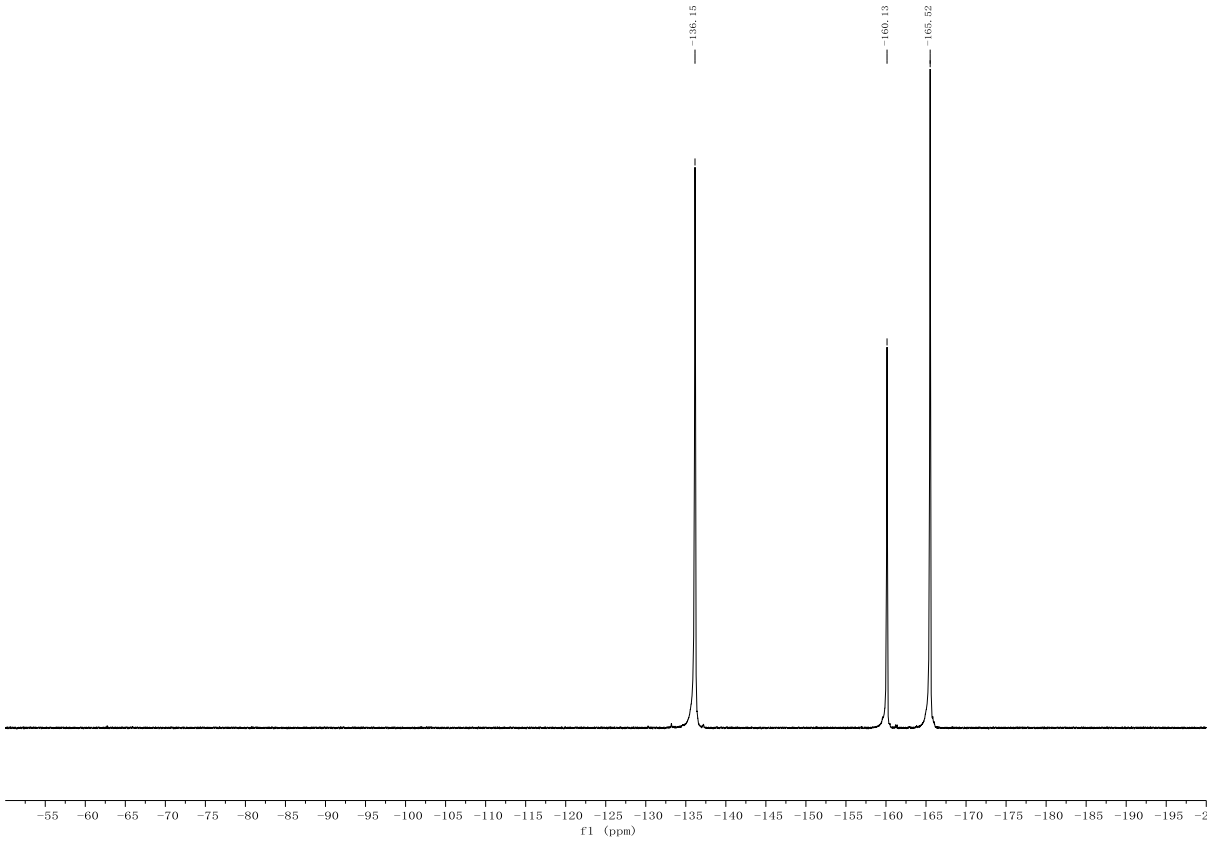
Compound [1-H][(μ-OH){B(C$_6$F$_5$)$_3$}$_2$]: ^{11}B-NMR (160 MHz, CD_2Cl_2)



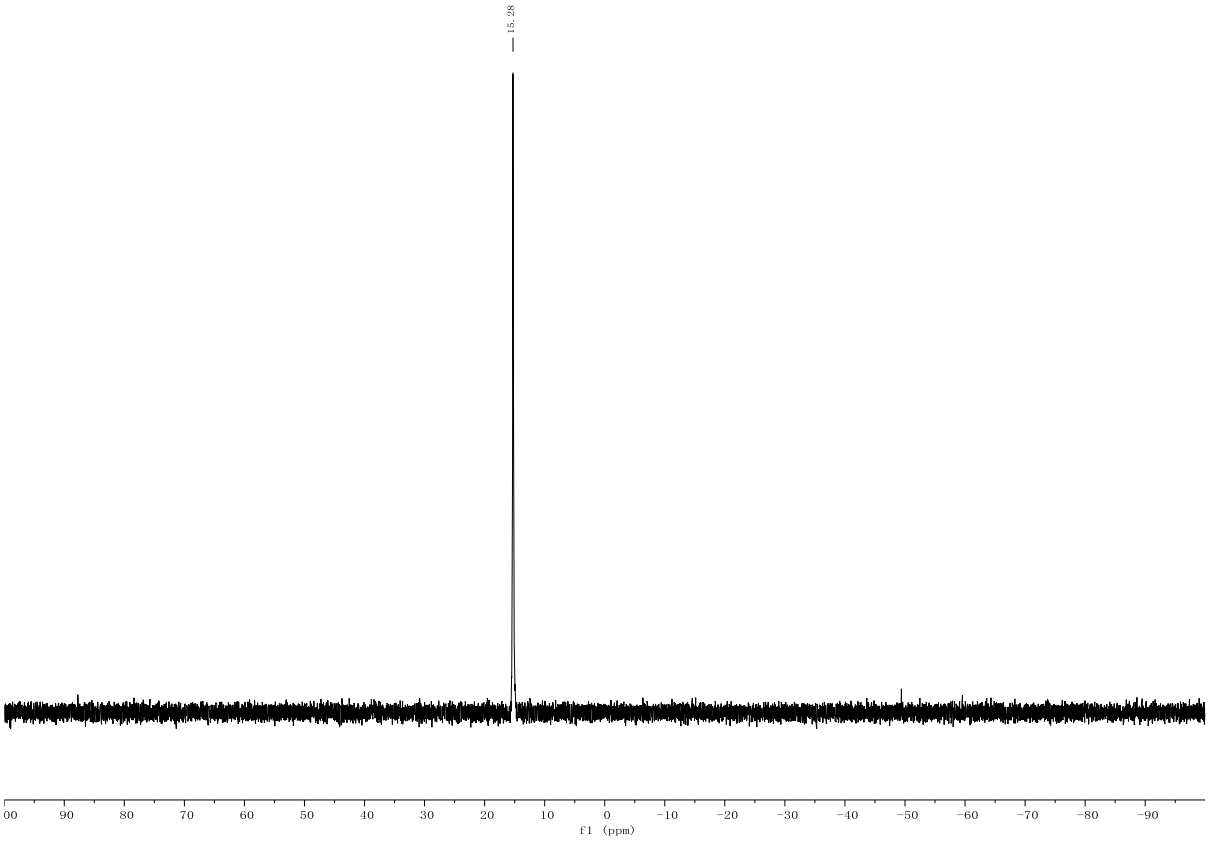
Compound [1-H][(μ-OH){B(C_6F_5)$_3$}$_2$]: ^{13}C-NMR (126 MHz, CD_2Cl_2)



Compound [1-H][(μ-OH){B(C_6F_5)$_3$}$_2$]: ^{19}F-NMR (470 MHz, CD_2Cl_2)

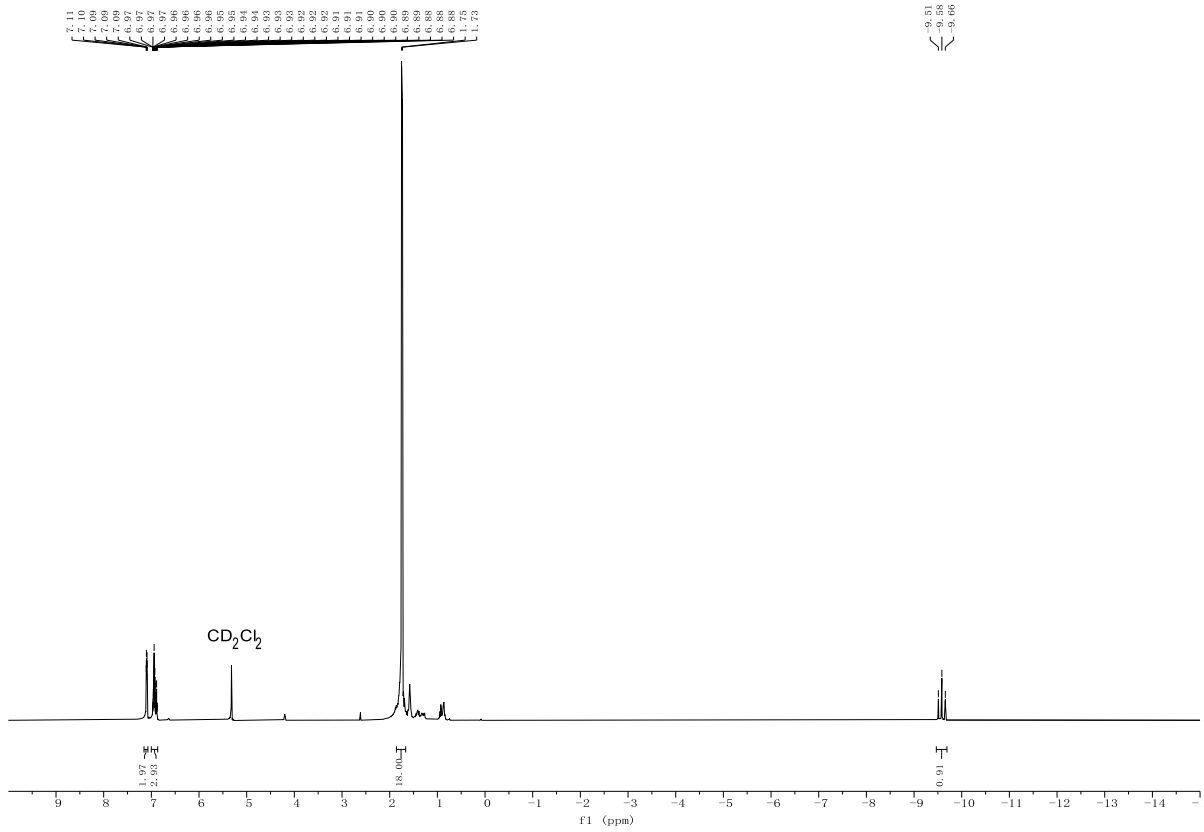


Compound [1-H][(μ-OH){B(C$_6$F$_5$)$_3$}$_2$]: ^{31}P-NMR (202 MHz, CD_2Cl_2)

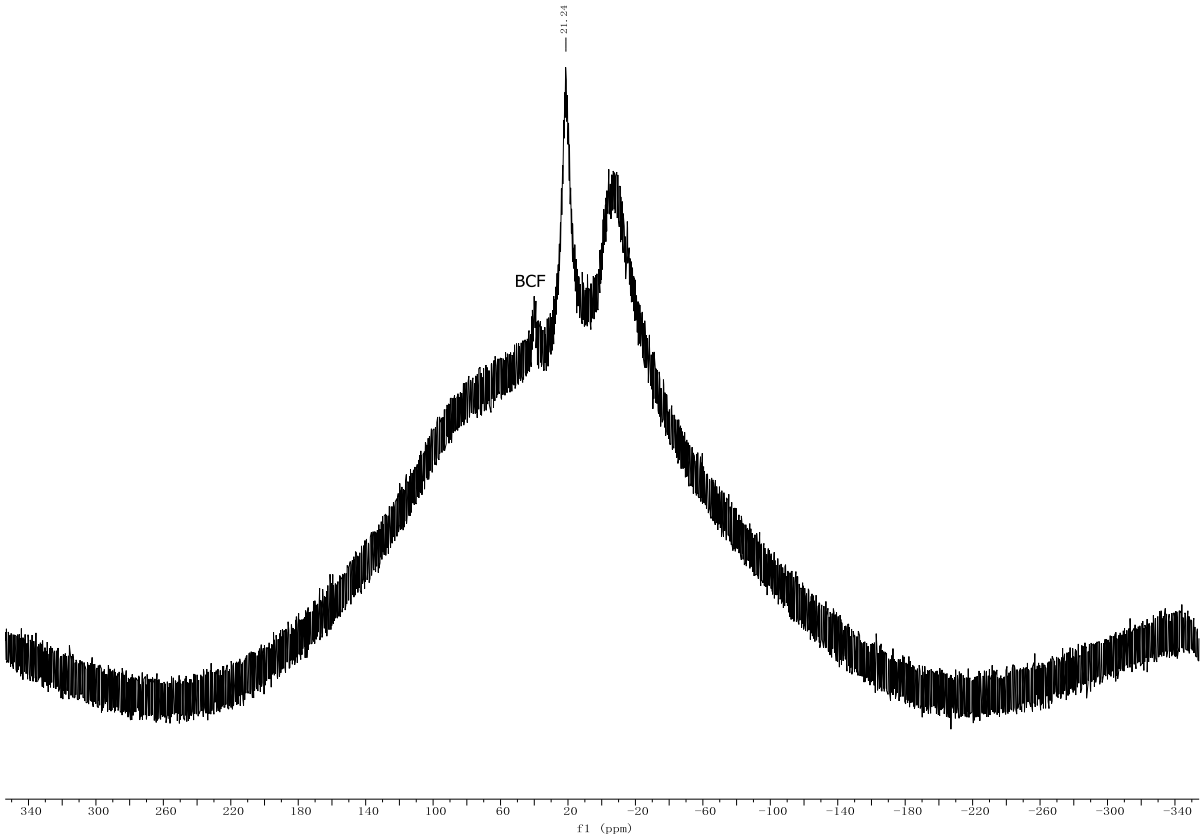


Compound [1-H][(μ-OH){B(C$_6$F$_5$)$_3$}$_2$]: IR in CD_2Cl_2

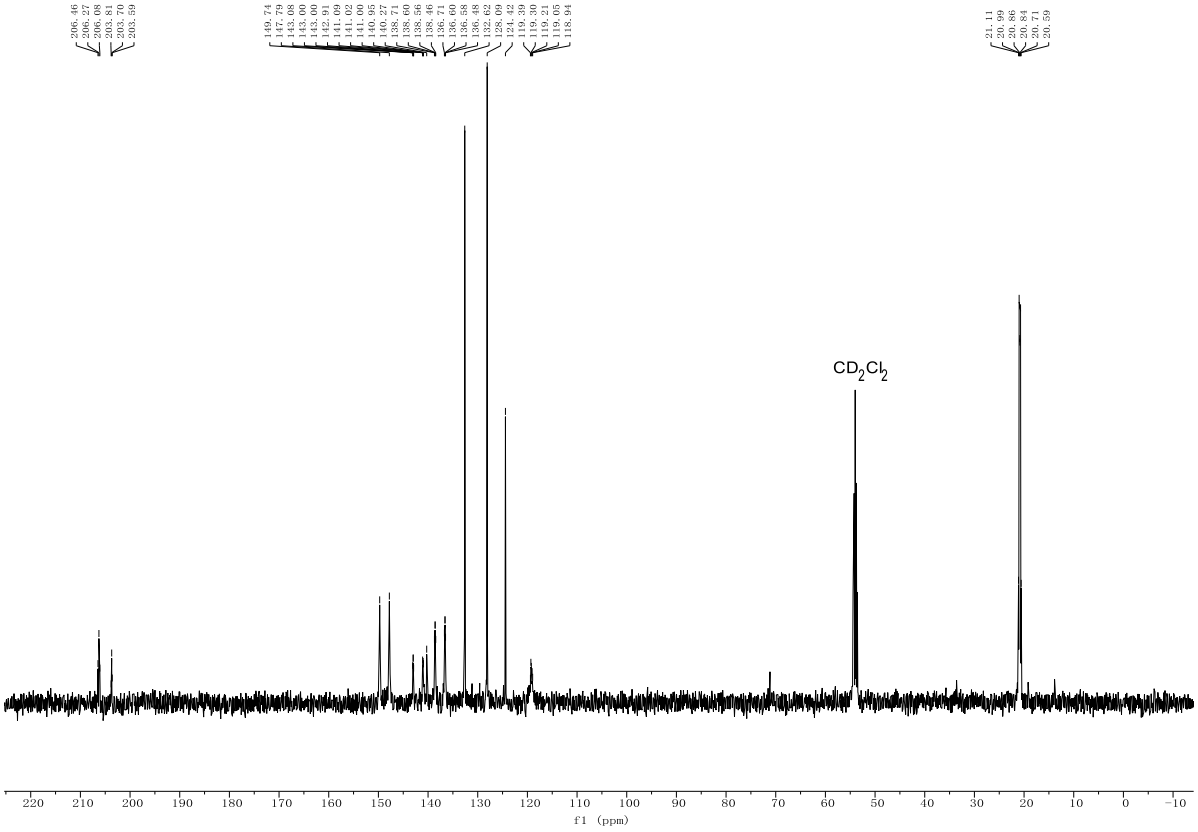
Compound [1-H][B(SPh)(C_6F_5)$_3$]: ^{1}H-NMR (500 MHz, CD_2Cl_2)



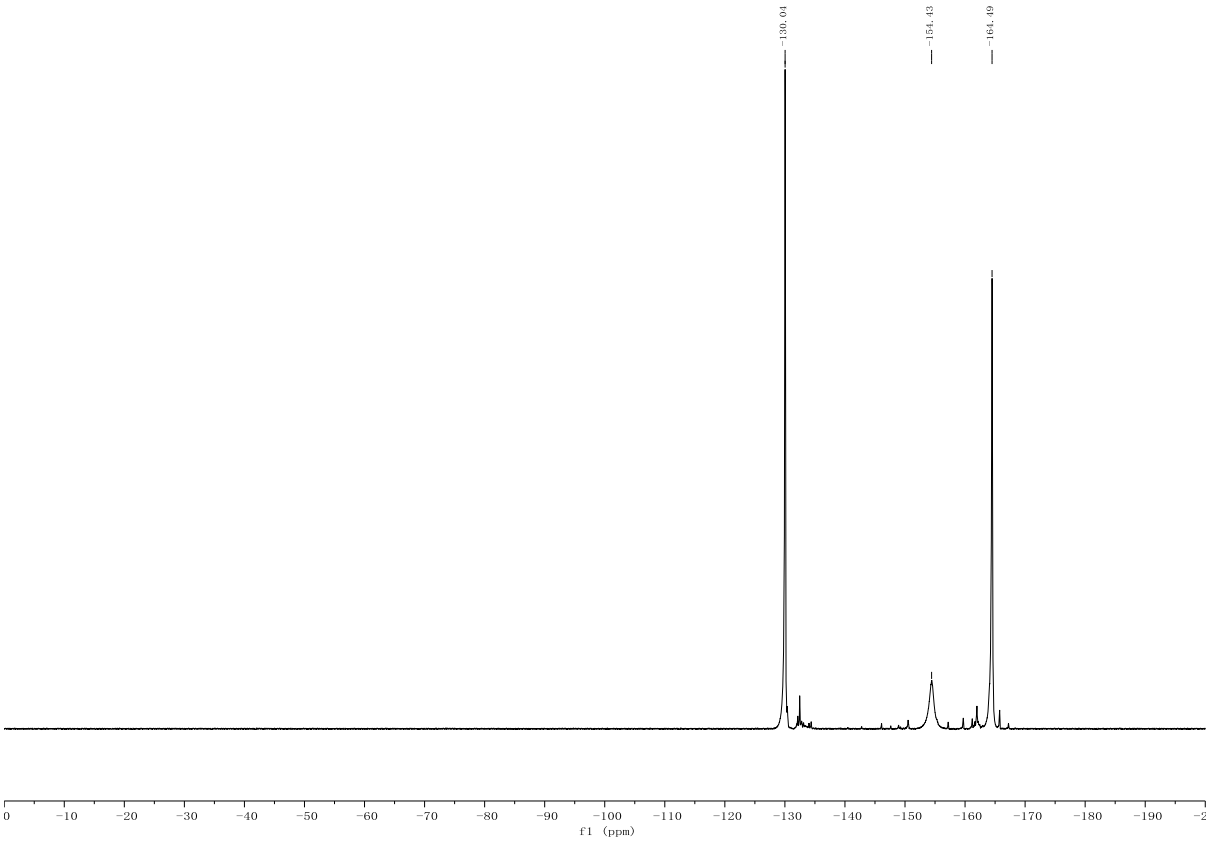
Compound [1-H][B(SPh)(C_6F_5)$_3$]: ^{11}B-NMR (160 MHz, CD_2Cl_2)



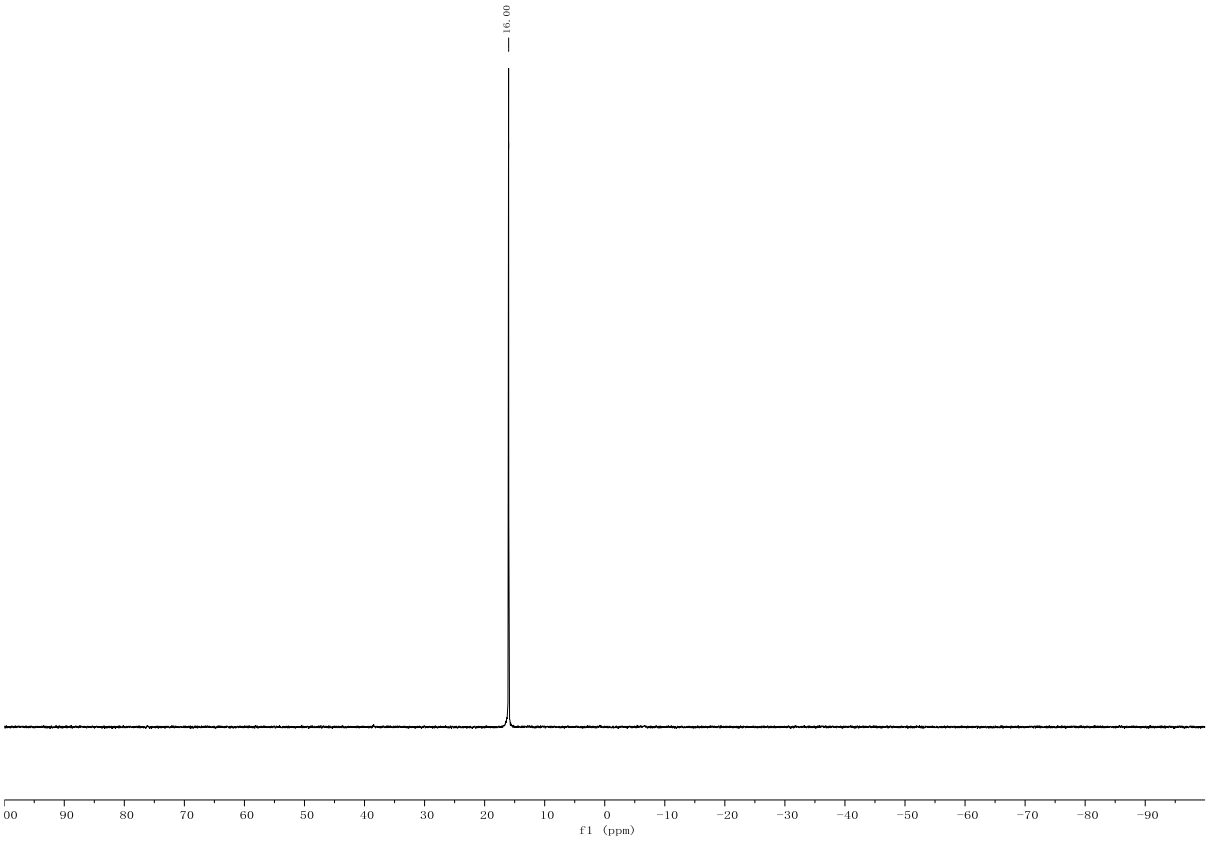
Compound [1-H][B(SPh)(C_6F_5)$_3$]: ^{13}C-NMR (160 MHz, CD_2Cl_2)



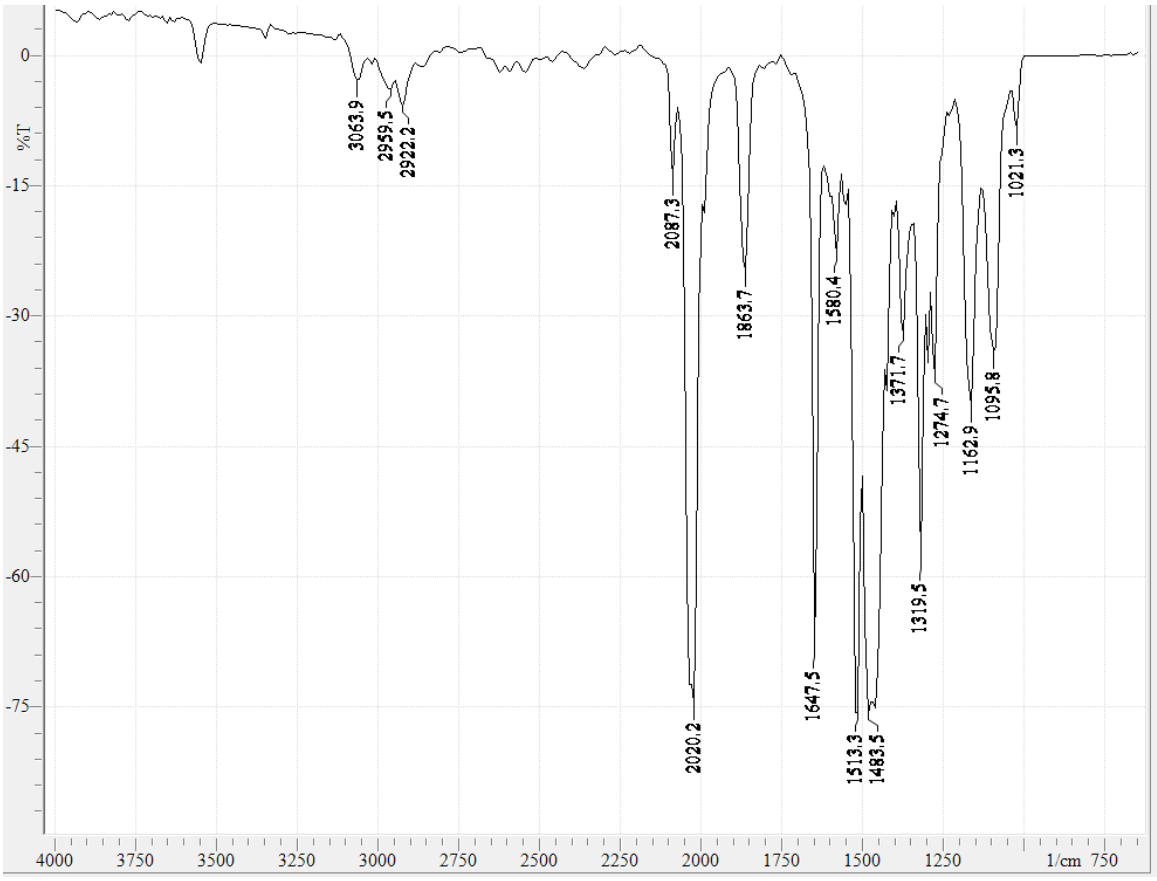
Compound [1-H][B(SPh)(C_6F_5)$_3$]: ^{19}F-NMR (471 MHz, CD_2Cl_2)



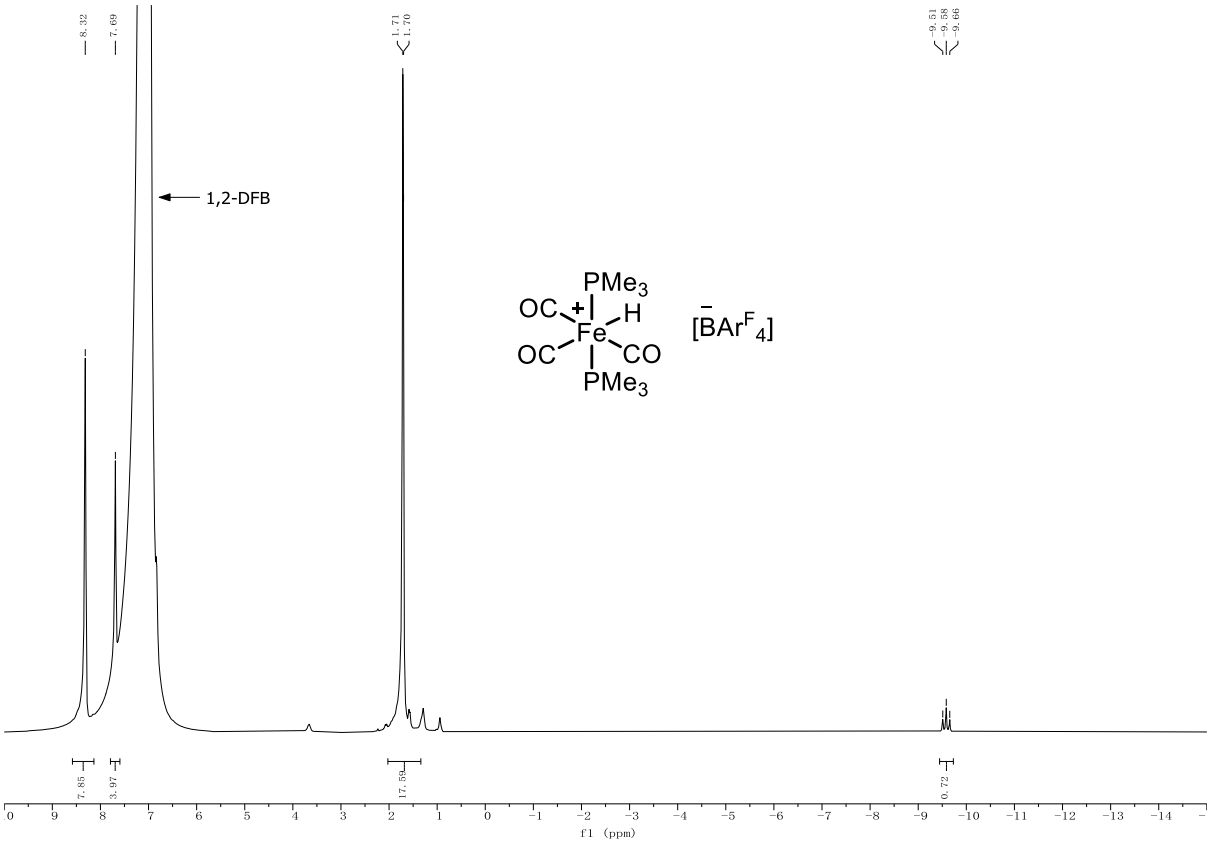
Compound [1-H][B(SPh)(C_6F_5)$_3$]: ^{31}P-NMR (202 MHz, CD_2Cl_2)



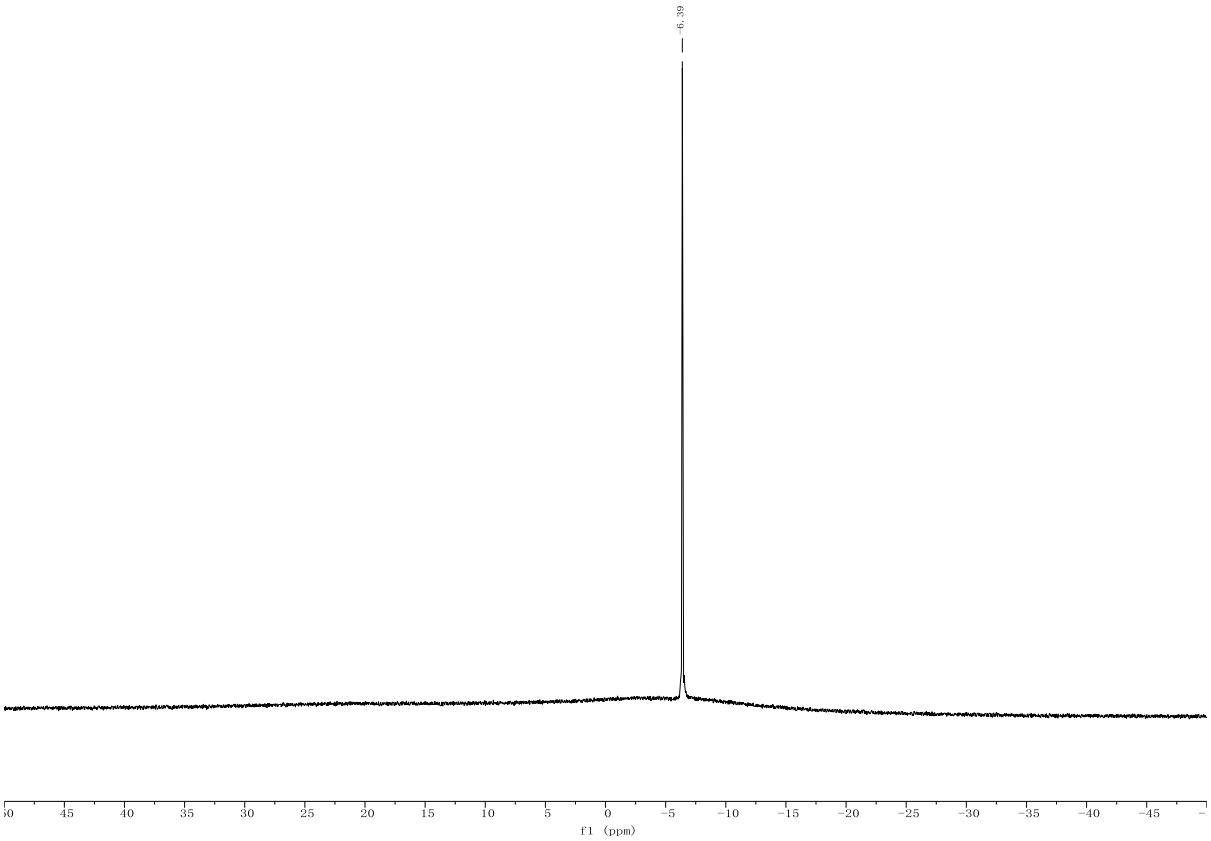
Compound [1-H][B(SPh)(C_6F_5)$_3$]: IR in CD_2Cl_2



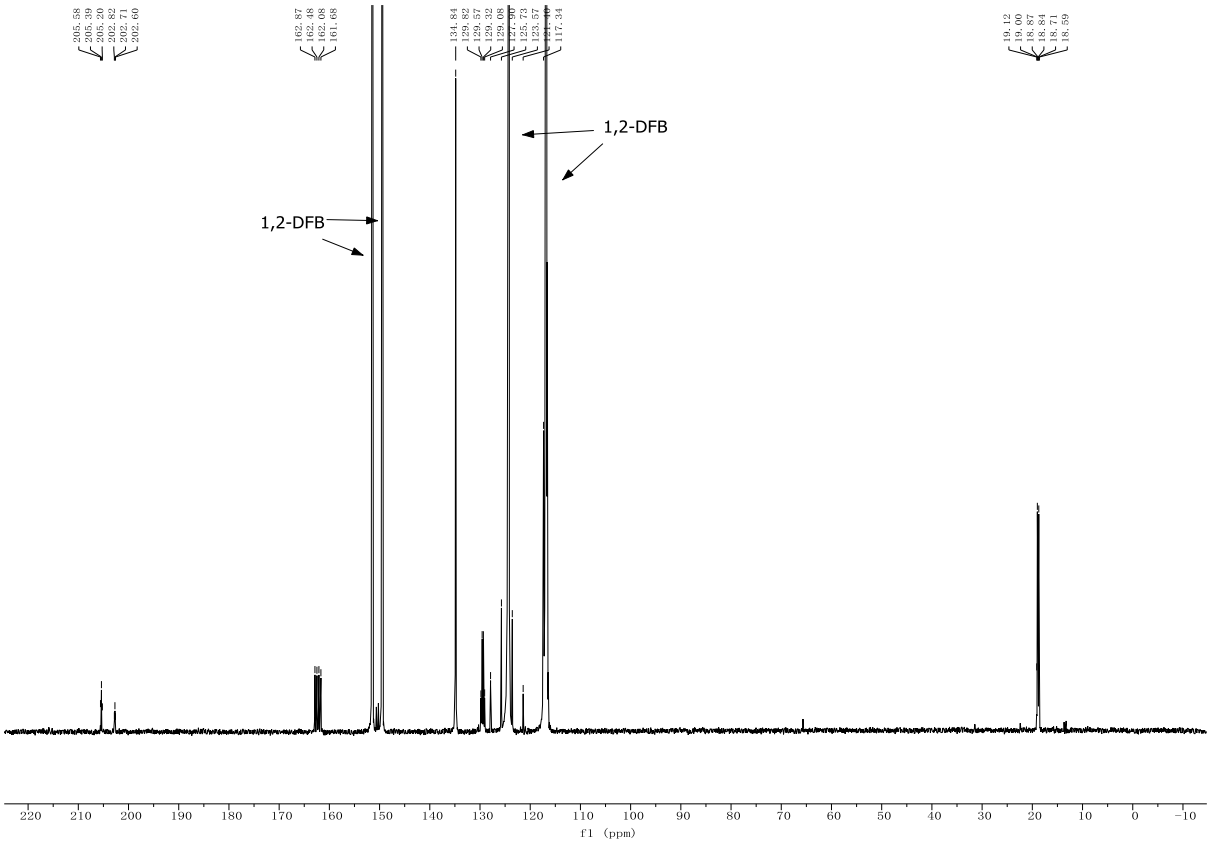
Compound [1-H][BAr$^F_4$]: ^{1}H-NMR (500 MHz, 1,2-DFB)



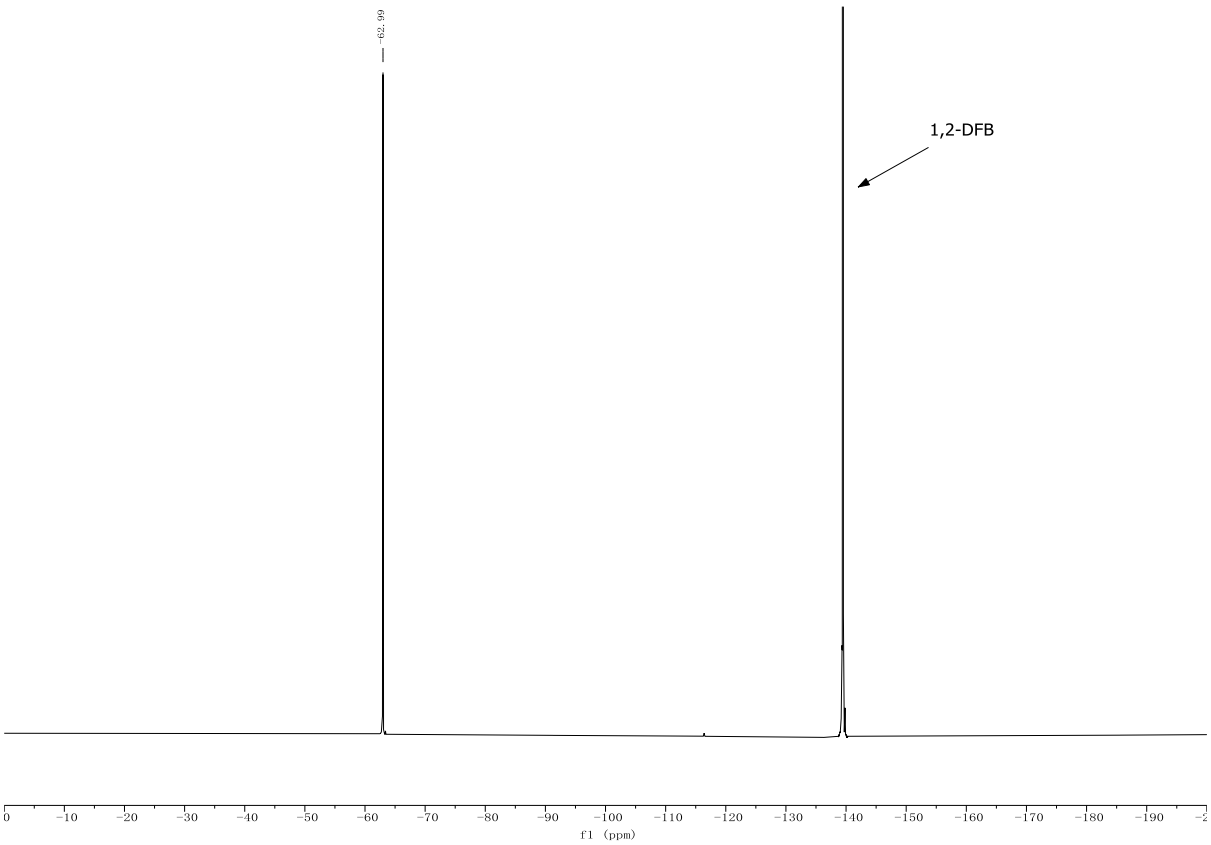
Compound [1-H][BAr$^F_4$]: ^{11}B-NMR (160 MHz, 1,2-DFB)



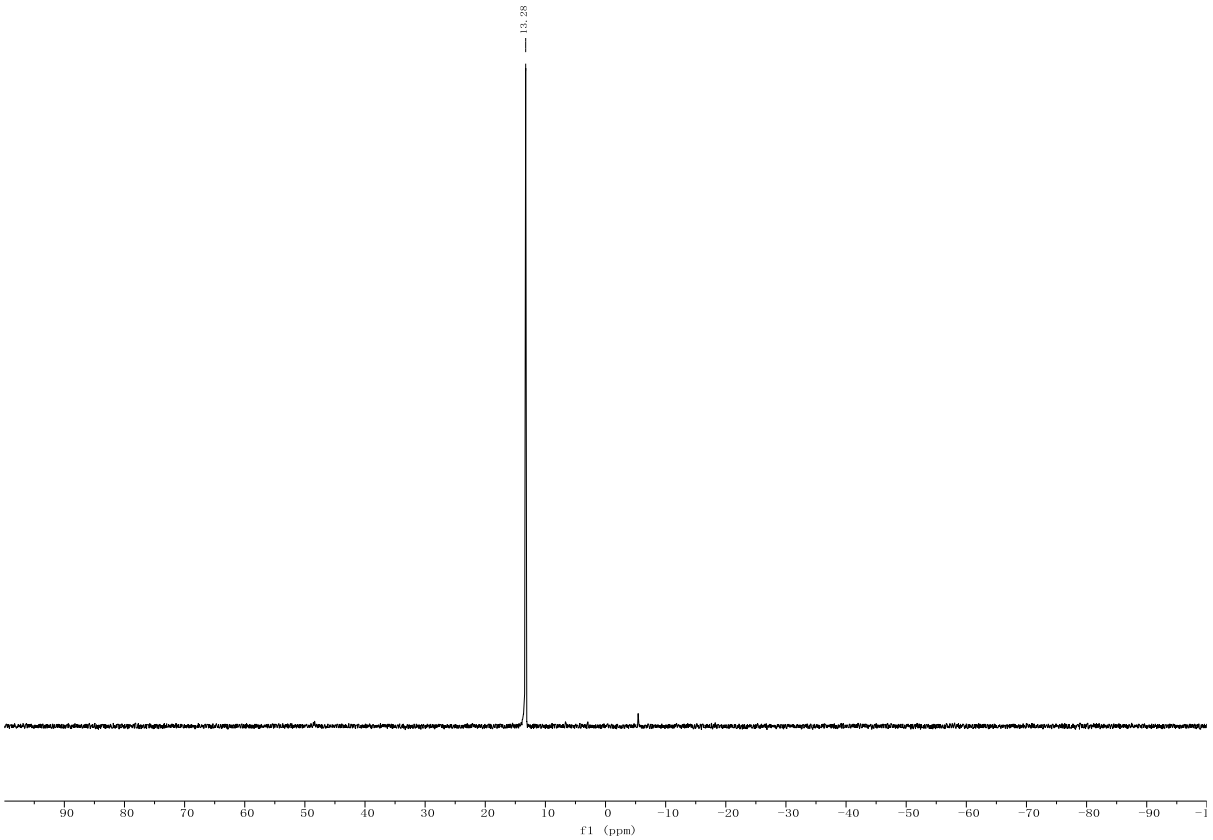
Compound [1-H][BAr$^F_4$]: ^{13}C-NMR (160 MHz, 1,2-DFB)



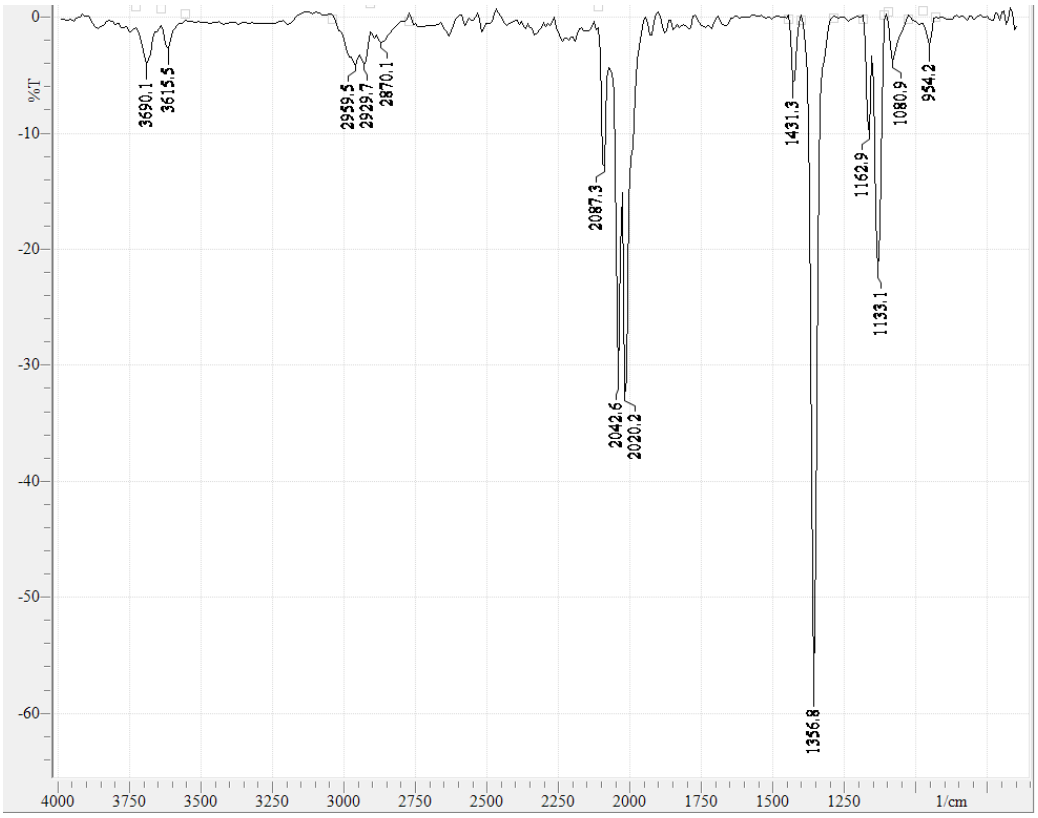
Compound [1-H][BAr$^F_4$]: ^{19}F-NMR (471 MHz, 1,2-DFB)



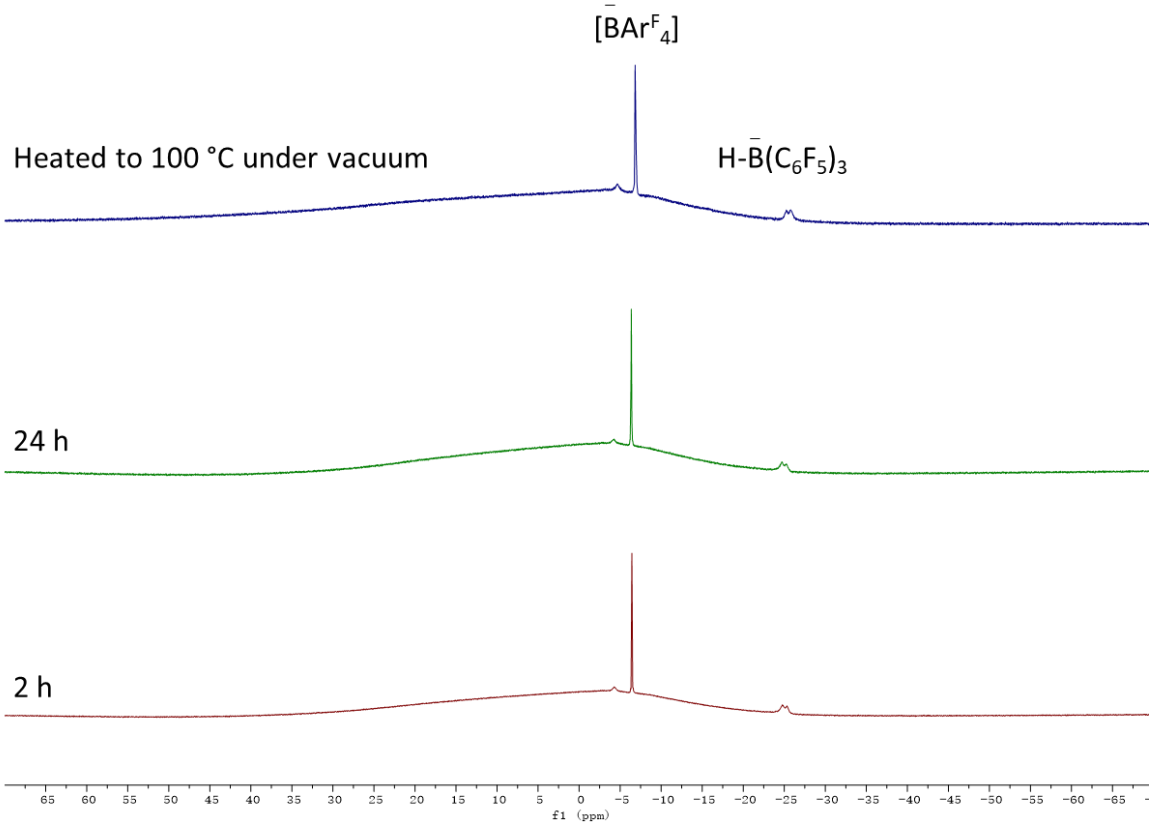
Compound [1-H][BAr$^F_4$]: ^{31}P-NMR (202 MHz, 1,2-DFB)



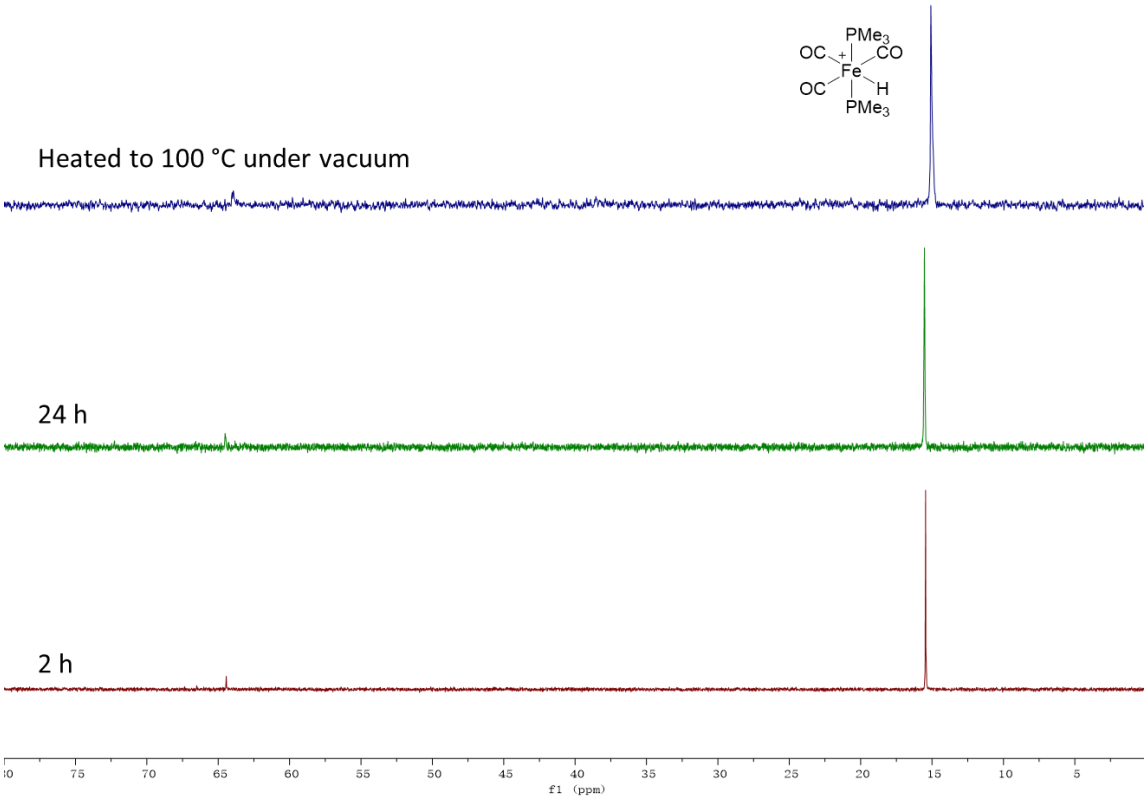
Compound [1-H][BAr$^F_4$]: IR in 1,2-DFB



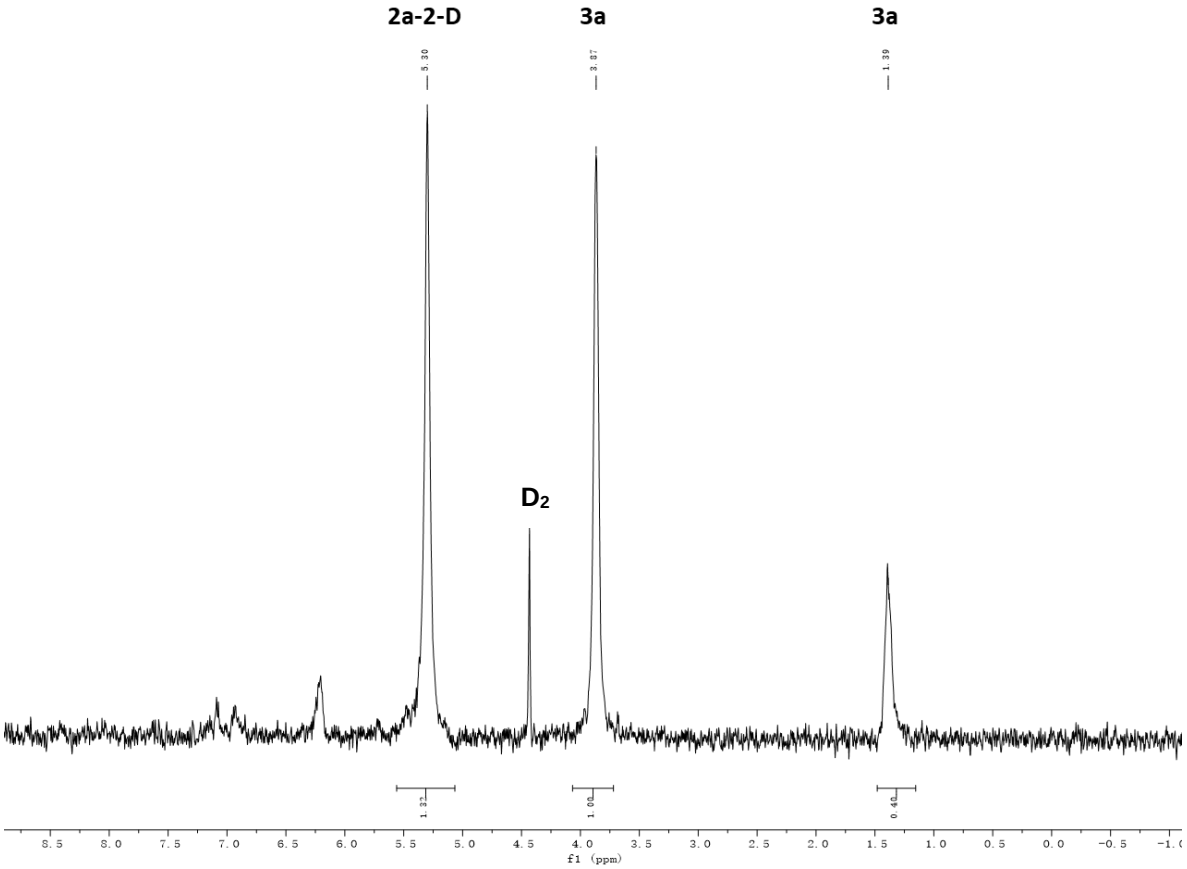
Control reaction **[1-H][BAr$^F_4$]** and **[^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$]:** ^{11}B-NMR (160 MHz, PhCl)



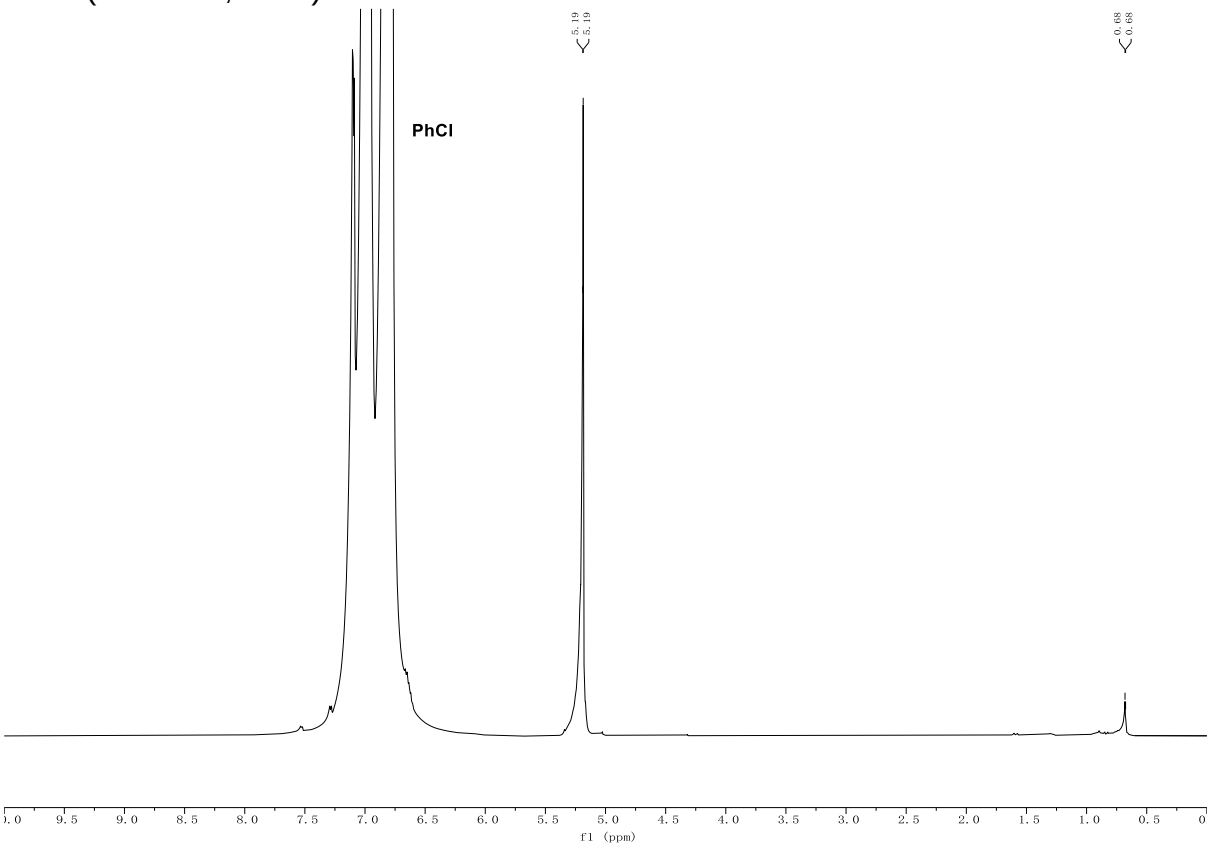
Control reaction **[1-H][BAr$^F_4$]** and **[^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$]:** ^{31}P-NMR (202 MHz, PhCl)



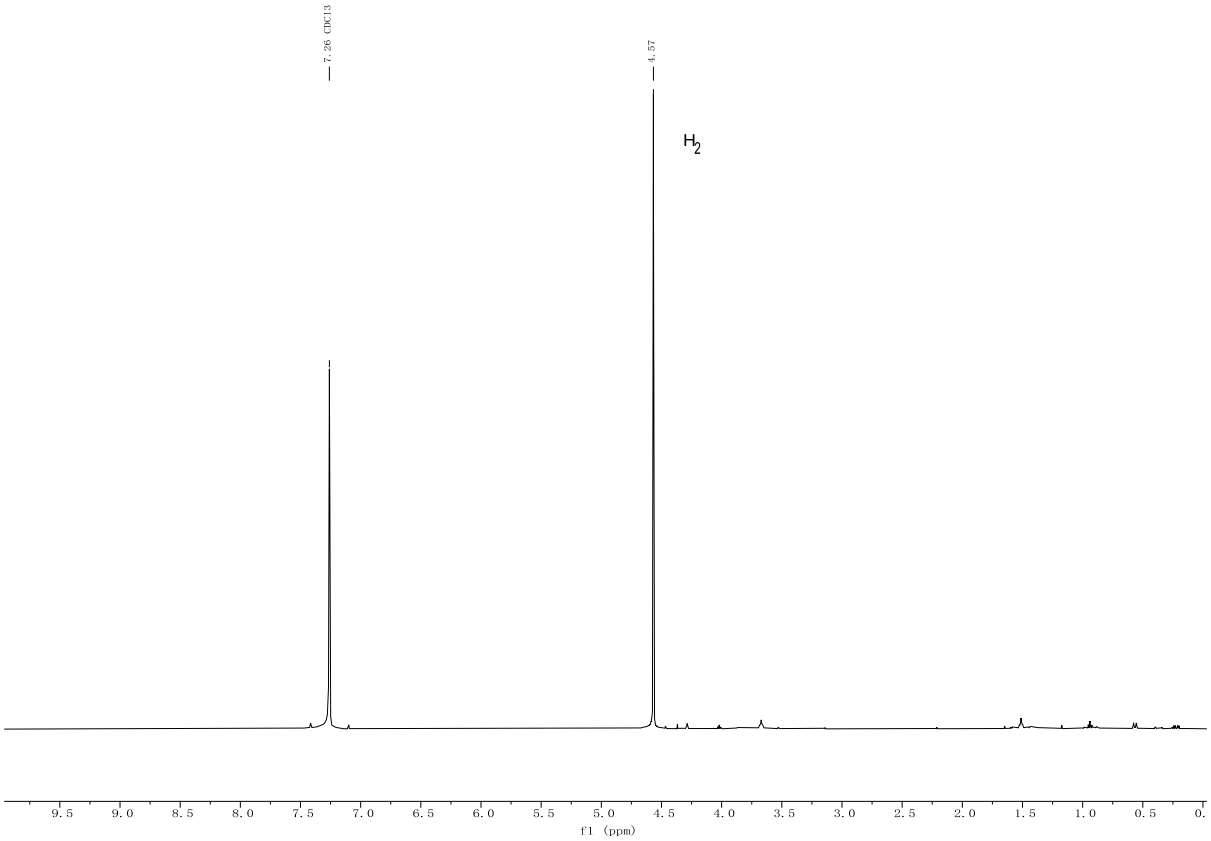
Deuteration of **diphenylethylene**: ^{2}H-NMR (77 MHz, PhCl):



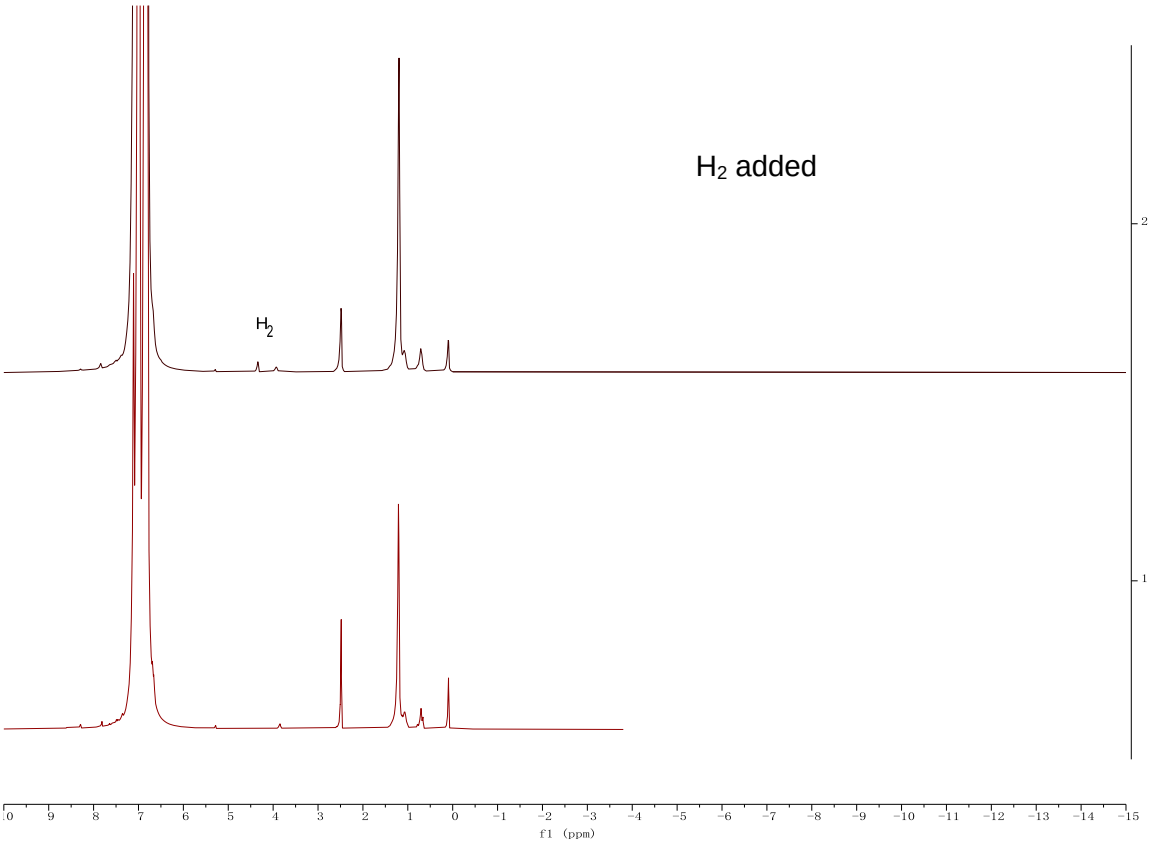
Control reaction **diphenylethylene**, **PMe_3** (5 mol%), **$B(C_6F_5)_3$** (5 mol%) and **H_2**: ^{1}H-NMR (500 MHz, PhCl)



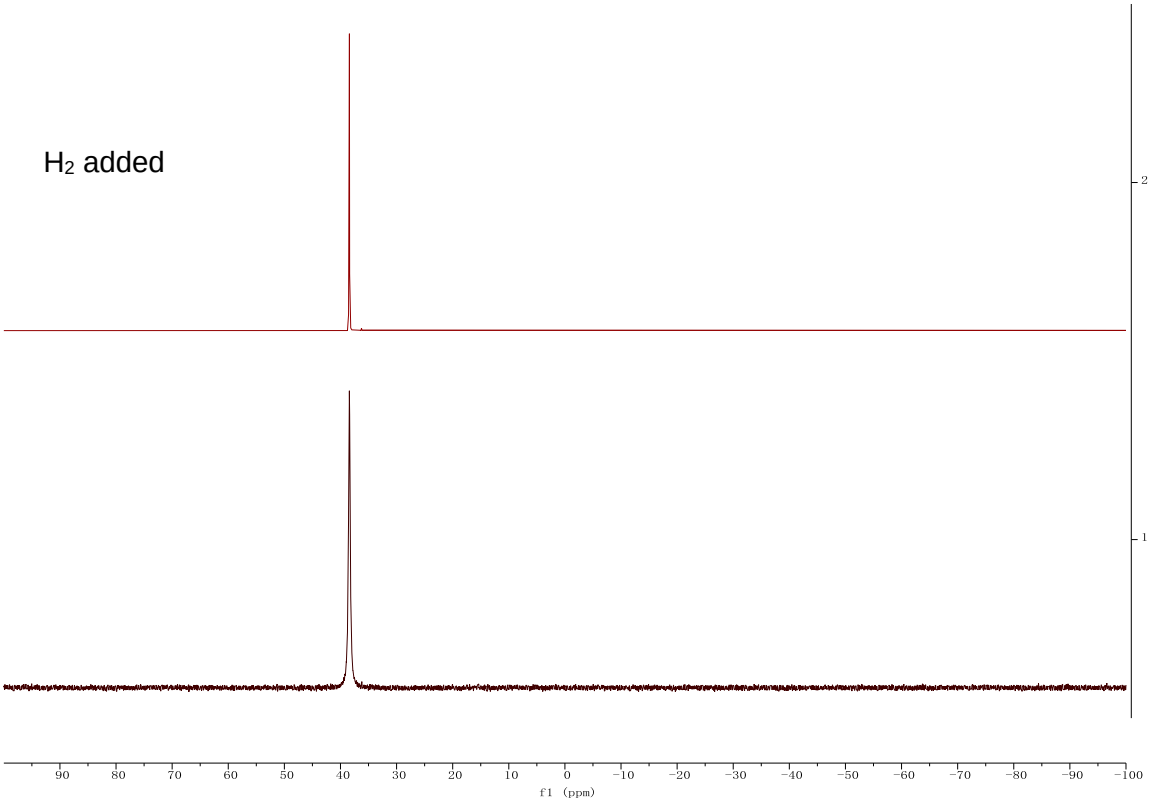
Control reaction **PMe_3** (1 equiv.), **$B(C_6F_5)_3$** (1 equiv.) and **H_2** (adduct crushed out) ^{1}H-NMR (500 MHz, $CDCl_3$)



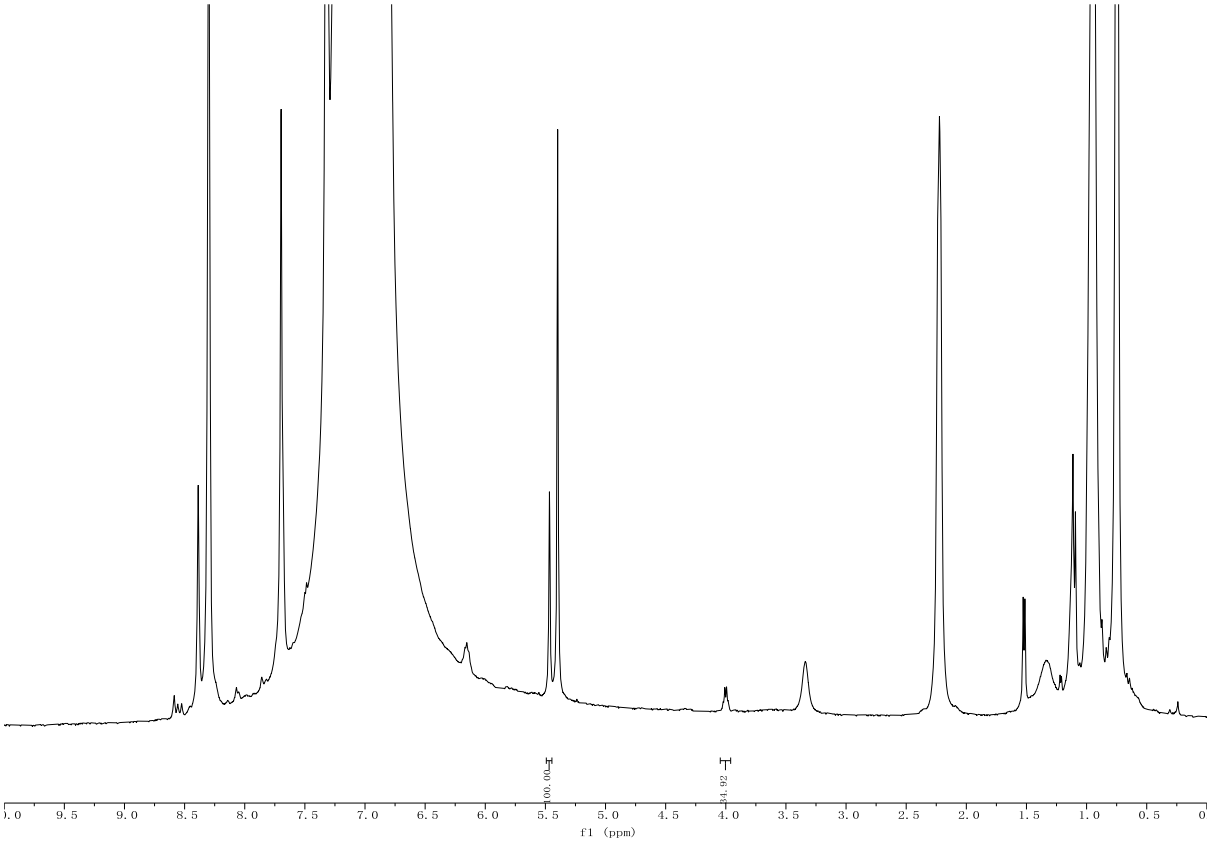
Control **[1]**, **Ph_3CBArF_{24}** and **H_2**: 1H-NMR (500 MHz, PhCl)



Control **[1]**, **Ph_3CBArF_{24}** and **H_2**: ^{31}P-NMR (500 MHz, PhCl)



Control reaction of [1-H][$BArF_{24}$], [*n*Bu_4N][$HB(C_6F_5)_3$] with diphenylethylene



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