Supporting Information for:

Bis-Boranes in the Frustrated Lewis Pair Activation of Carbon Dioxide

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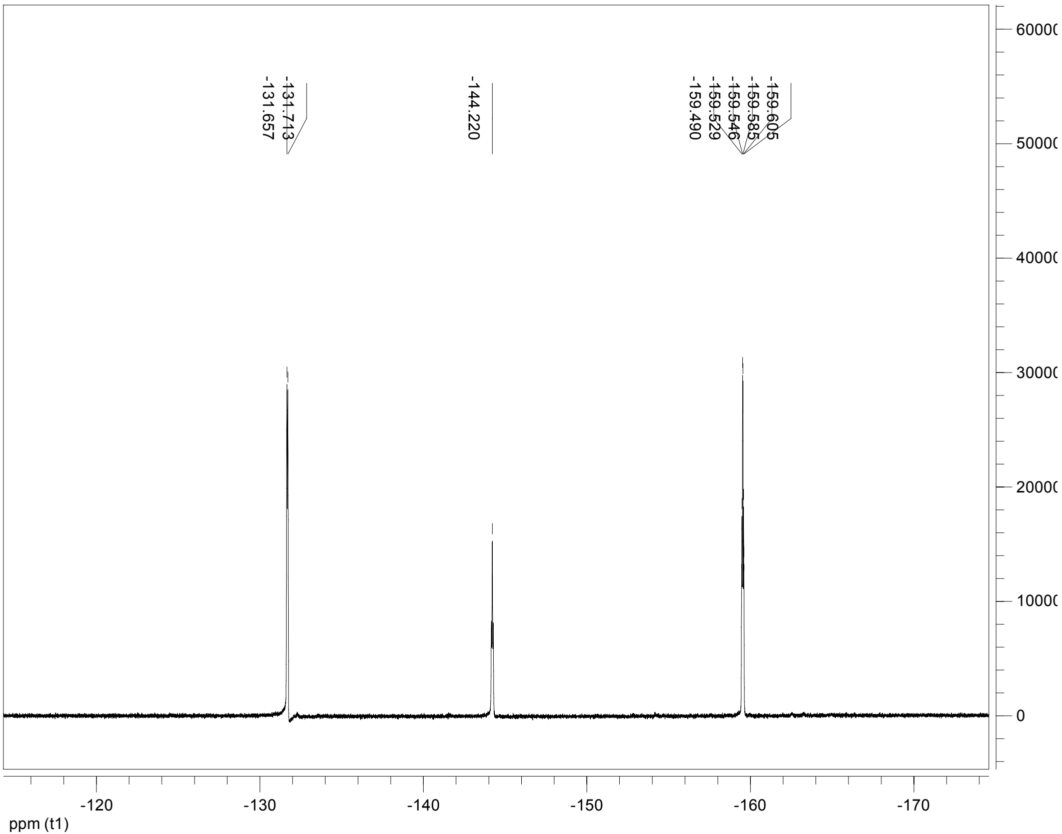
General considerations:

All preparations and manipulations were performed on a double manifold N_2/vacuum line with Schlenk-type glassware or in a N_2-filled M-Braun glove box. Solvents (Aldrich) were dried using an Innovative Technologies solvent system. NMR spectra were obtained on a Bruker or Varian System 400 MHz spectrometer and spectra were referenced to residual solvent (^1H, ^{13}C) or externally (^{11}B; BF_3OEt_2, ^{19}F; $CFCl_3$, ^{31}P; 85% H_3PO_4). NMR solvents were purchased from Cambridge Isotopes, dried over Na/benzophenone or CaH_2, distilled prior to use, and stored over 4Å molecular sieves in the glovebox. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Combustion analysis was performed in house on a Perkin-Elmer CHN Analyzer. $ClB(C_6F_5)_2$[1], $Me_2CC(BCl_2)_2$[2] and $Zn(C_6F_5)_2.C_6H_8$[3] were prepared as previously described.

$O(B(C_6F_5)_2)_2$ (1):

In a Schlenk tube, $ClB(C_6F_5)_2$ (1.774 g, 4.66 mmol) was dissolved in dichloromthane (20 mL), and cool at -78 °C. Distilled H_2O (40.0 µL, 2.22 mmol) was added in two portions, and the reaction stirred at -78 °C for 1 h. Particular attention was paid to venting of the reaction vessel. The reaction was then warmed up to room temperature, and volatiles pumped off to dryness. The residue solid was thoroughly washed with pentane (30 mL) to yield a white microcrystalline product. More product was recrystallized from the pentane washings. Yield: 0.779 g, 50 %. Single crystals suitable for X-ray diffraction were grown by recrystallization from pentane at -35°C. ^{11}B NMR (128 MHz, C_6D_5Br, 298 K): no resonance was observed. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br, 298 K): δ 148.78 (dm, $^1J_{CF}$ = 249 Hz, *ortho*-C_6F_5), 143.70 (dm, $^1J_{CF}$ = 262 Hz, *para*-C_6F_5), 136.84 (dm, $^1J_{CF}$ = 254 Hz, *meta*-C_6F_5), 107.43 (br, *ipso*-C_6F_5). ^{19}F (376 MHz, C_6D_5Br, 298 K): δ -131.68 (d, $^3J_{FF}$ = 21.4 Hz, 8H, *ortho*-C_6F_5), -144.20 (tt, $^3J_{FF}$ = 21.0 Hz, $^4J_{FF}$ = 4.8 Hz, 4H, *para*-C_6F_5), -159.53 (m, 8H, *meta*-C_6F_5). Anal. Calcd. for $C_{24}B_2F_{20}O$: C, 40.84; H, 0; N, 0. Found: C, 40.48; H, 0.18; N, 0.43 %.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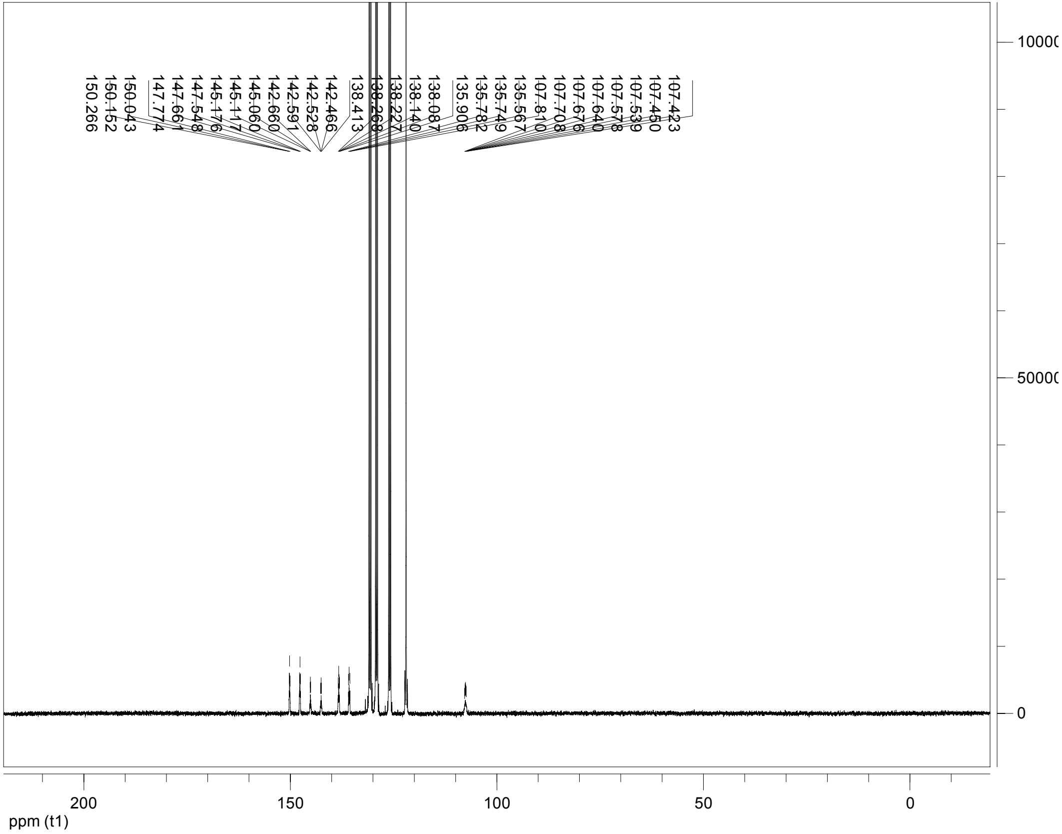
ppm (t1)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135.749
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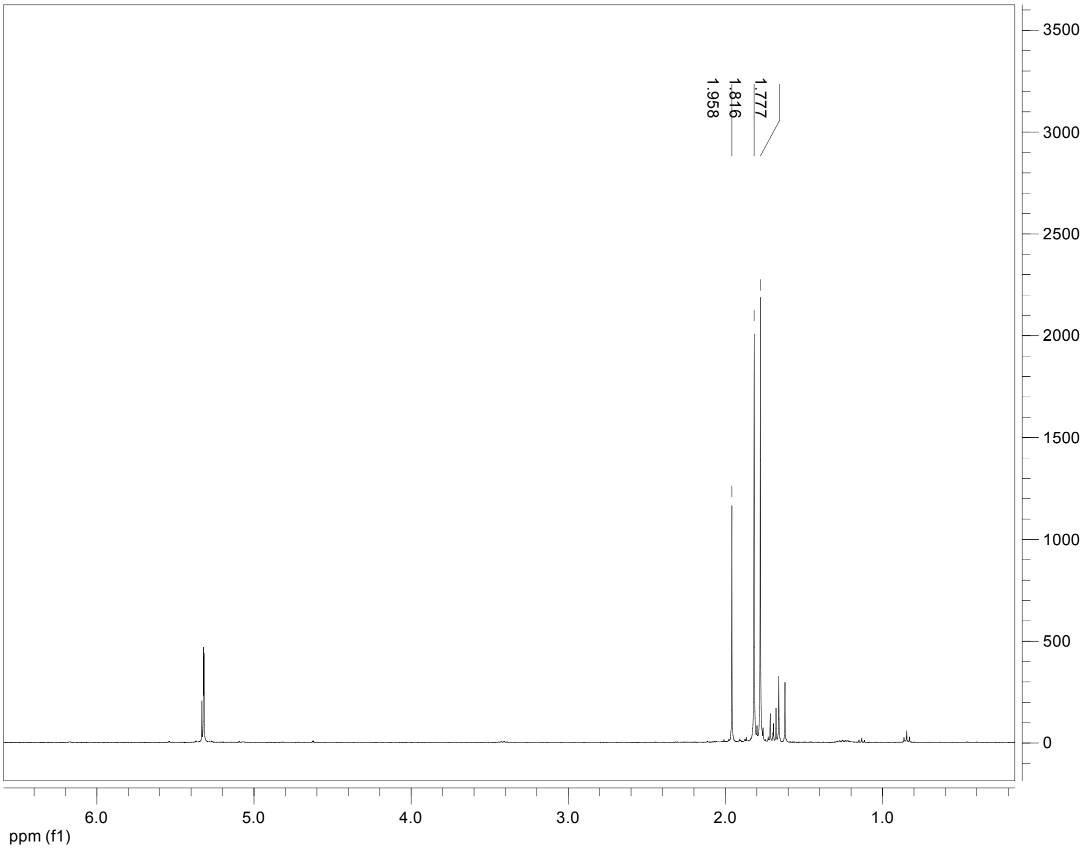
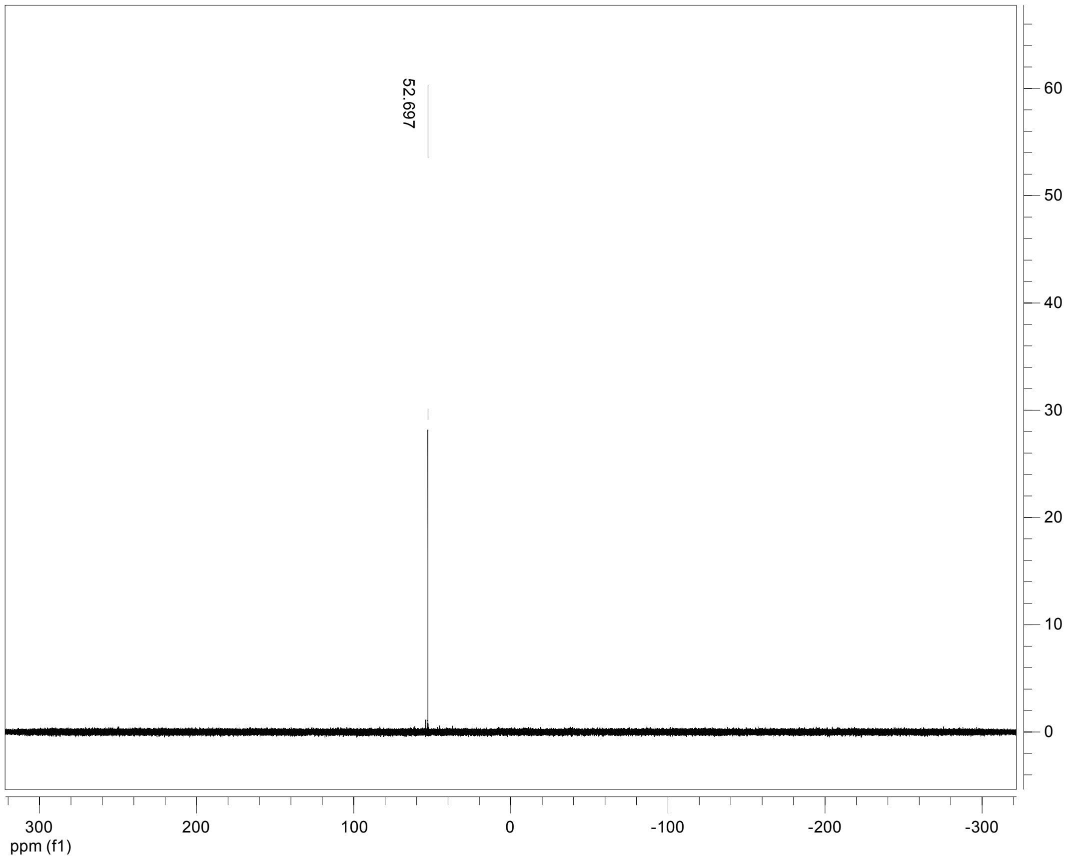
107.708
107.676
107.640
107.578
107.539
107.450
107.423
10000
50000
0
200
150
100
50
0
ppm (t1)

$Me_2CC(BCl_2)_2(CO_2)P$*t*Bu_3 (4):

$Me_2CC(BCl_2)_2$ was prepared according to a modified literature procedure. It was not possible to completely separate Me_3SnCl byproduct from $Me_2CC(BCl_2)_2$ (27 % contamination), but the sample was used as it is since Me_3SnCl does not affect the reaction in reasonable lengths of time. In a well-dried Schlenk flask, $Me_2CC(BCl_2)_2$ (200 mg, 0.69 mmol of the diborane, 27 % Me_3SnCl) and P*t*Bu_3 (186 mg, 0.92 mmol) were dissolved in cold bromobenzene (5 mL). 1 atm of CO_2 was introduced to the reaction while keeping the flask in an ice bath. A precipitate immediately started to come out. The reaction was quickly filtered while kept cold. The white solid was further washed with cold bromobenzene and cold pentane. Yield: 219 mg, 68 %. Single crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 solution of the product with pentane at -35°C. ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K): δ 1.96 (s, 6H, CH_3), 1.79 (d, $^3J_{HP}$ = 15.7 Hz, 27H, *t*Bu_3). ^{11}B {^{1}H} NMR (128 MHz, CD_2Cl_2, 253 K): δ 10.30 (br). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 253 K): δ 169.72 (d, $^1J_{CP}$ = 85.7 Hz, P*C*O), 152.95 (s, =CMe_2), 43.59 (d, $^1J_{CP}$ = 15.6 Hz, quarternary-*t*Bu), 30.44 (s, *t*Bu), 26.45 (s, CH_3). The olefinic carbon bound to boron atoms was not observed. ^{31}P {^{1}H} (162 MHz, CD_2Cl_2, 253 K): δ 52.70 (s). IR (KBr): 1608 cm^{-1} (C-O asym. stretch). Anal. Calcd. for $C_{17}H_{33}B_2Cl_4O_2P$: C, 44.02; H, 7.17. Found: C, 43.92; H, 7.27 %.

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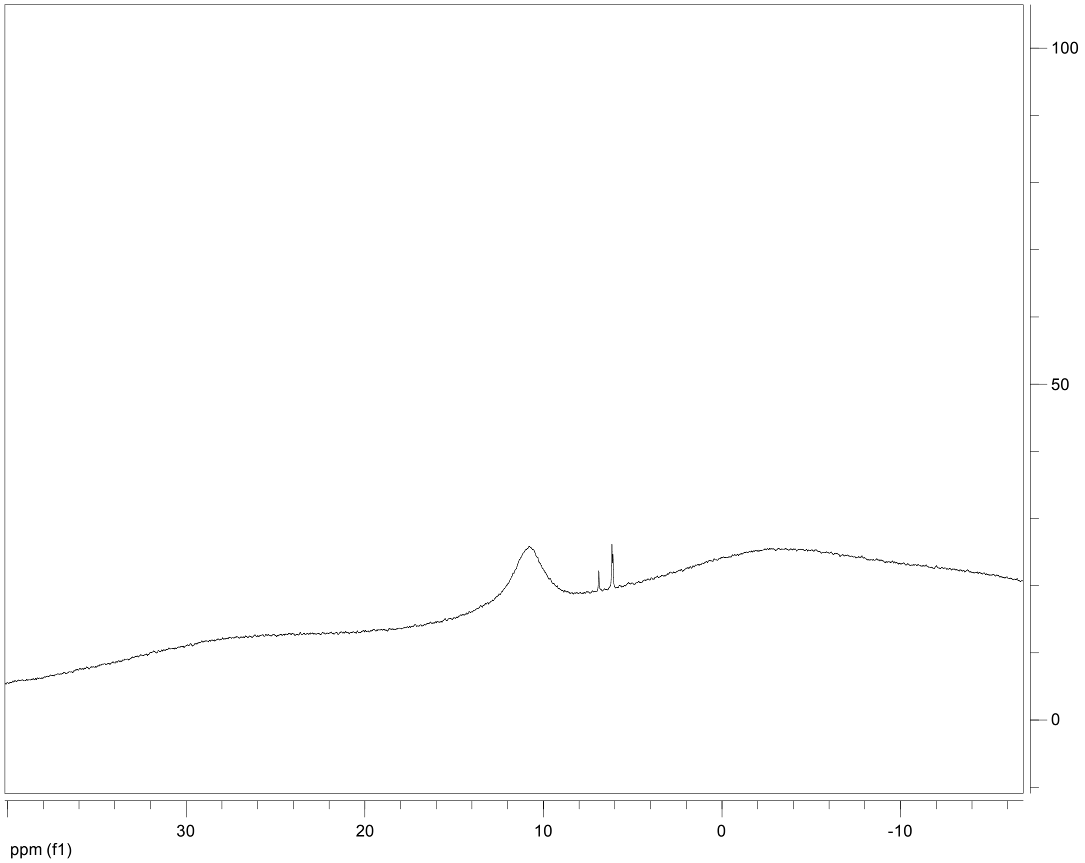
ppm (f1)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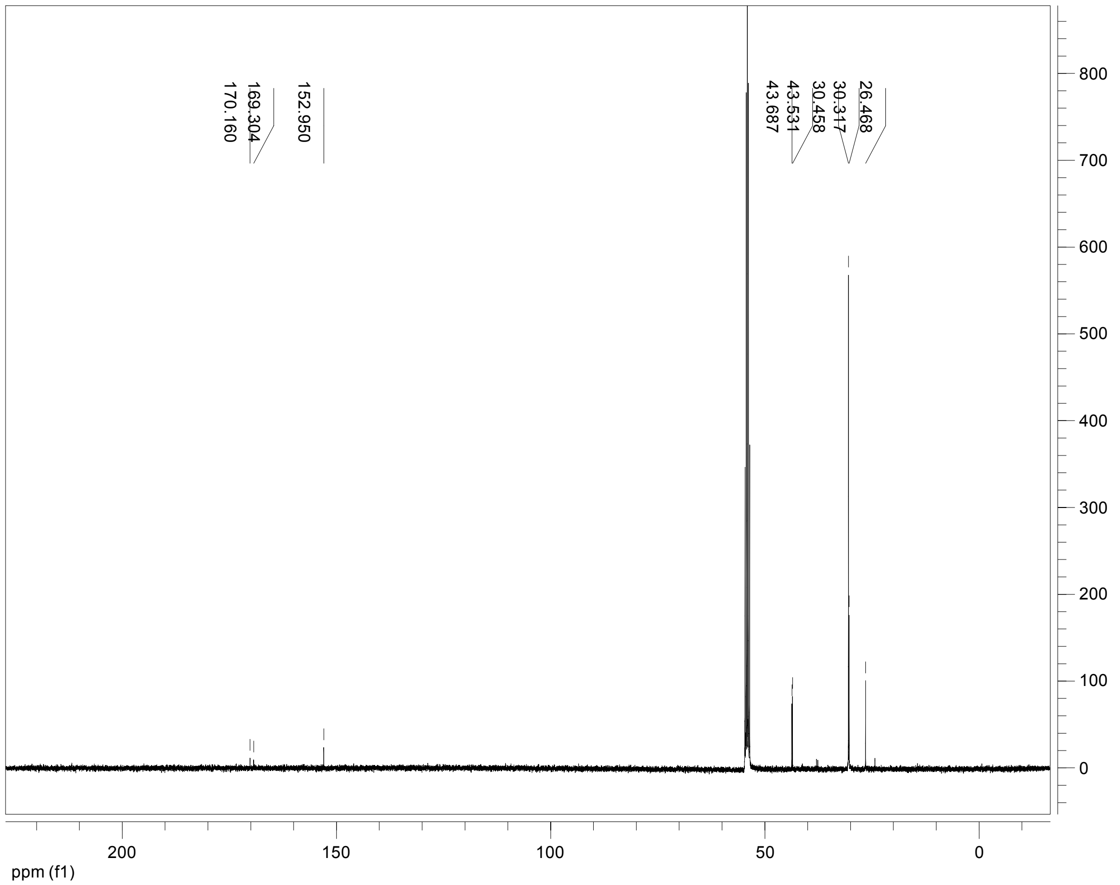
ppm (f1)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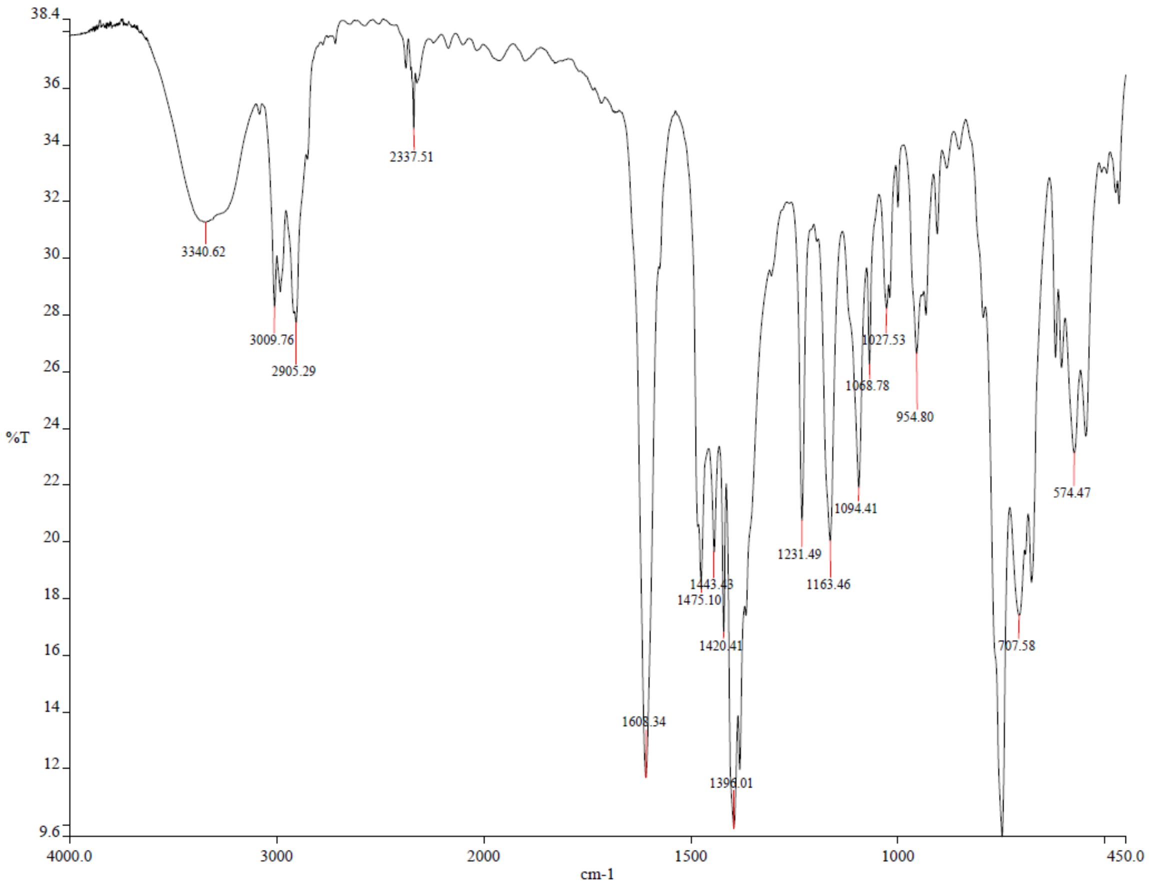
ppm (f1)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16
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9.6
%T
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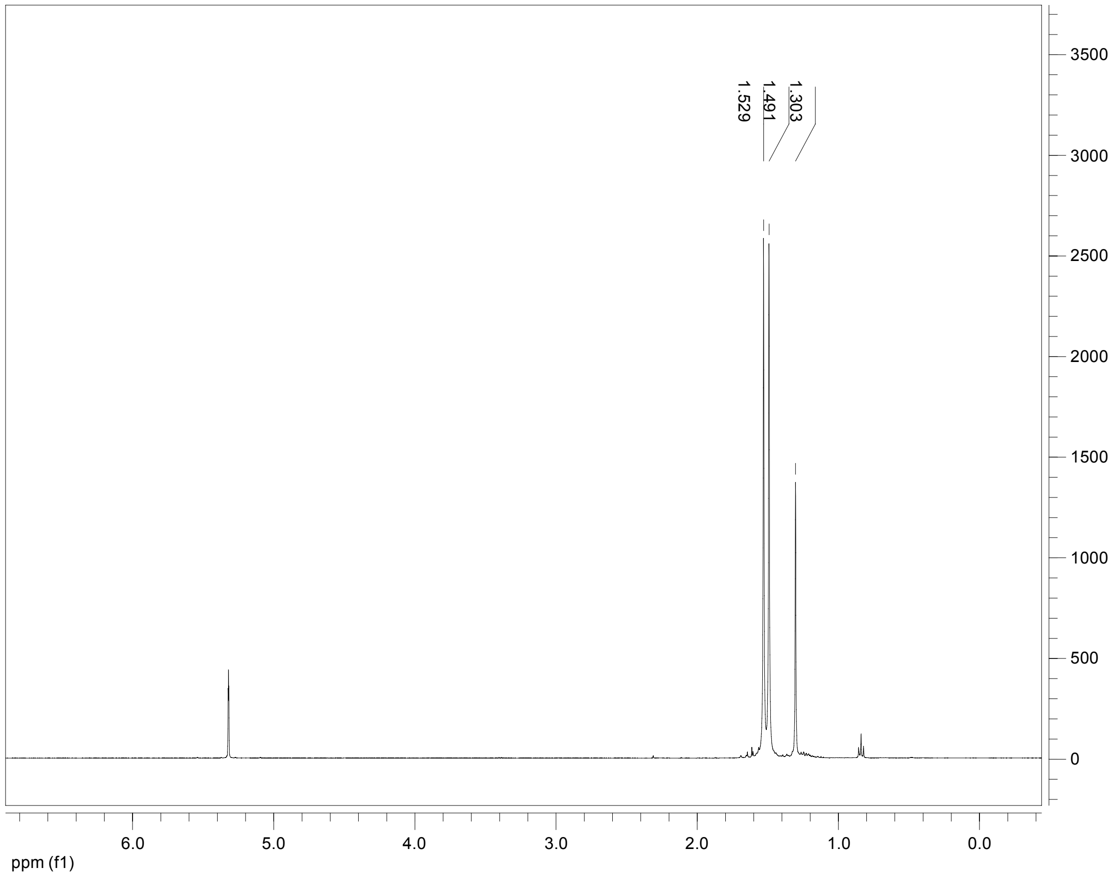
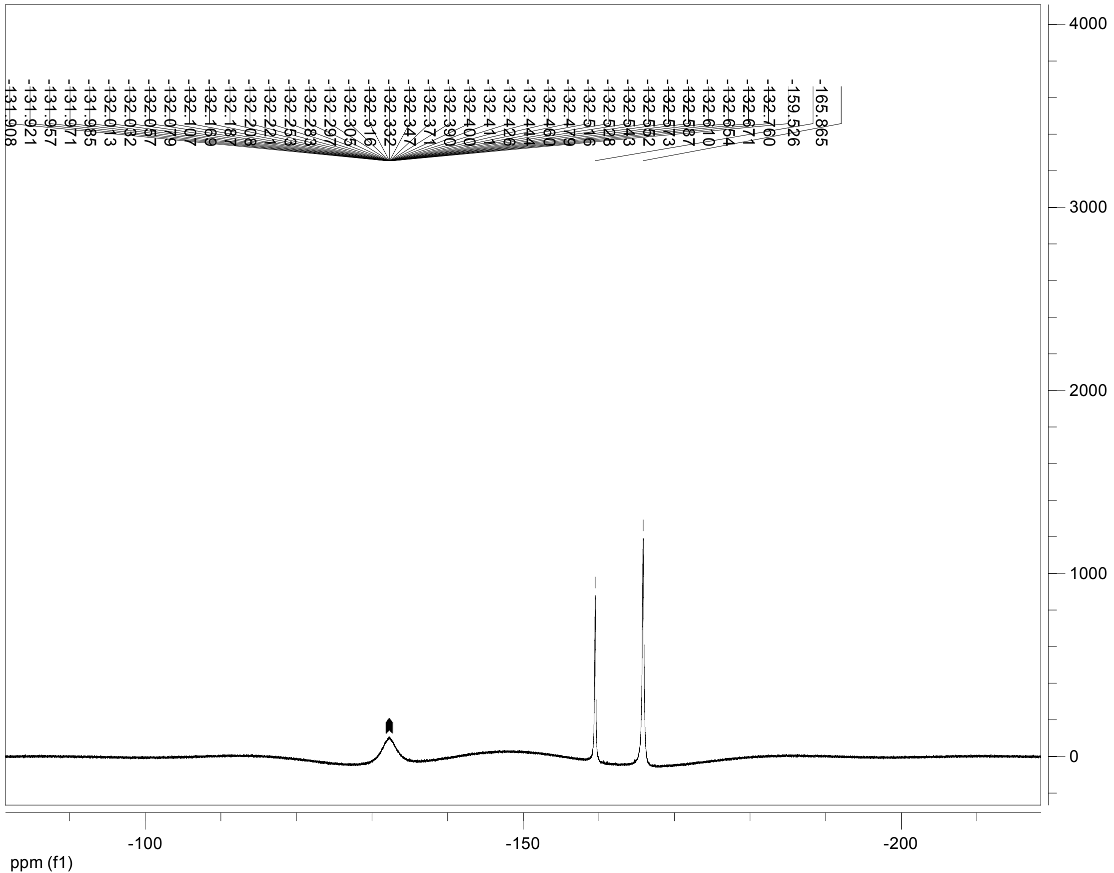
2905.29
2337.51
1608.34
1475.10
1443.43
1420.41
1396.01
1231.49
1163.46
1094.41
1068.78
1027.53
954.80
707.58
574.47
4000.0
3000
2000
1500
1000
450.0
cm-1

$Me_2CC(B(C_6F_5)_2)_2(CO_2)P\textit{t}Bu_3$ (6):

To $Me_2CC(BCl_2)_2$ (113 mg, 0.27 mmol of the diborane, 50 % Me_2SnCl_2) stirring in toluene (1 mL) was added $Zn(C_6F_5)_2{\cdot}C_6H_8$ (266 mg, 0.54 mmol) dissolved in toluene (2 mL), and the mixture was stirred at RT overnight. A white precipitate formed in a yellow solution. The entire reaction mixture was then transferred to a well-dried Schlenk bomb, and was heated at 60 °C for 2 days. The reaction mixture was passed though a plug of Celite in order to eliminate $ZnCl_2$ byproduct. Volatiles were pumped down from the filtrate, and the resulting yellow oil was redissolved in toluene-d_8 (1.0 mL) along with P*t*Bu$_3$ (20 mg, 0.10 mmol). After 30 min the mixture separated into a yellow solution on the top layer and an orange oil at the bottom layer. The top layer was transferred to a NMR tube equipped with a J-Young tap, and the sample was charged with 1 atm of CO_2. Leaving the sample at RT under a CO_2 atmosphere over 1 day resulted in the precipitation of a colourless crystalline product. The product was quickly filtered on a frit, and washed with cold toluene and pentane, and lightly dried *in vacuo*. Yield: 34 mg, 35 %. Single crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 solution of the product with pentane at -35°C. ^1H NMR (400 MHz, CD_2Cl_2, 243 K): δ 1.51 (d, $^3J_{HP}$ = 16.0 Hz, 27H, *t*Bu$_3$), 1.30 (s, 6H, CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, 243 K): δ no signal was observed. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 243 K): δ 170.85 (d, $^1J_{CP}$ = 91.9 Hz, P*C*O), 148.00 (dm, $^1J_{CF}$ = 236 Hz, *ortho*-C_6F_5), 140.50 (s, =*C*Me$_2$), 139.20 (dm, $^1J_{CF}$ = 263 Hz, *para*-C_6F_5), 136.53 (dm, $^1J_{CF}$ = 238 Hz, *meta*-C_6F_5), 136.27 (br s, =*C*(B(C_6F_5)$_2$)$_2$), 119.59 (br s, quarternary-C_6F_5), 42.36 (d, $^1J_{CP}$ = 17.2 Hz, quarternary-*t*Bu), 30.02 (s, *t*Bu), 24.75 (s, CH_3). ^{19}F NMR (376 MHz, CD_2Cl_2, 243 K): δ -132.28 (br s, 8F, *ortho*-C_6F_5), -159.53 (br s, 4F, *para*-C_6F_5), -165.88 (br s, 8F, *meta*-C_6F_5). ^{31}P $\{^1H\}$ (162 MHz, CD_2Cl_2, 243 K): δ 54.96 (s). IR (KBr): 1617 cm^{-1} (C-O asym. stretch). Anal. Calcd. for $C_{41}H_{33}B_2F_{20}O_2P$: C, 49.73; H, 3.36. Found: C, 49.34; H, 3.21 %.

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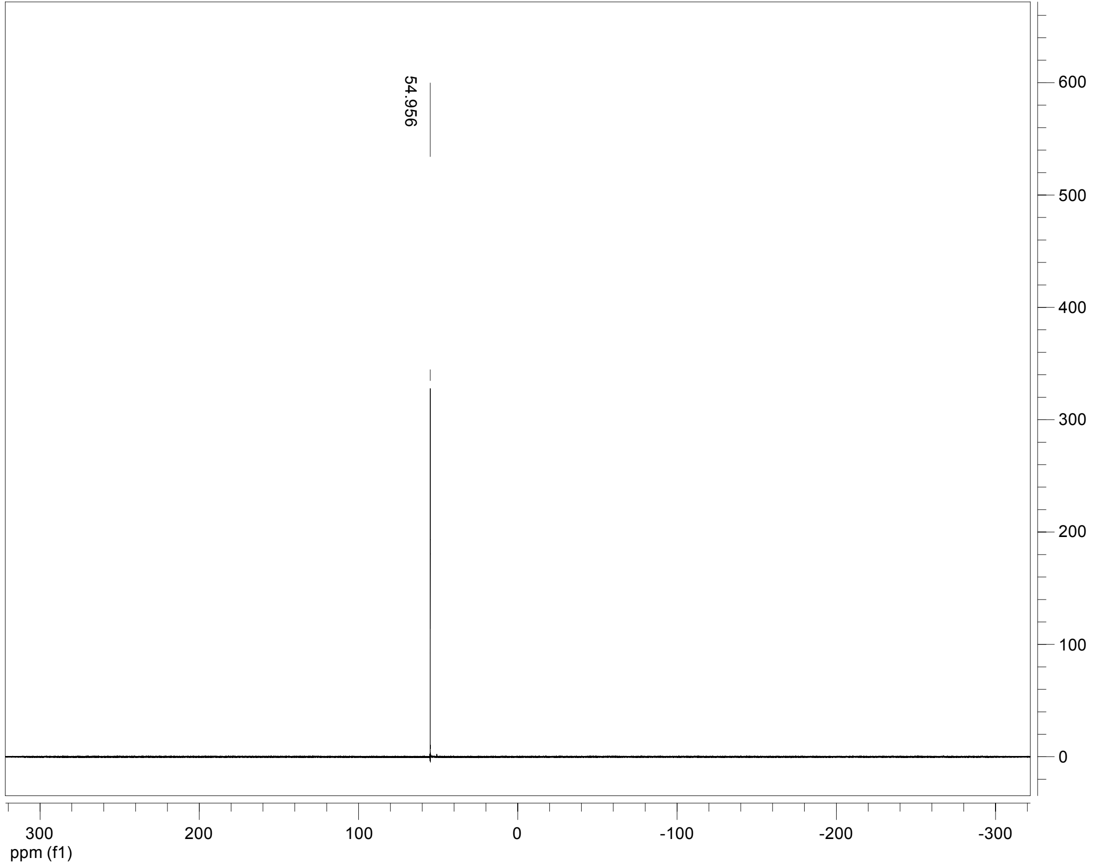
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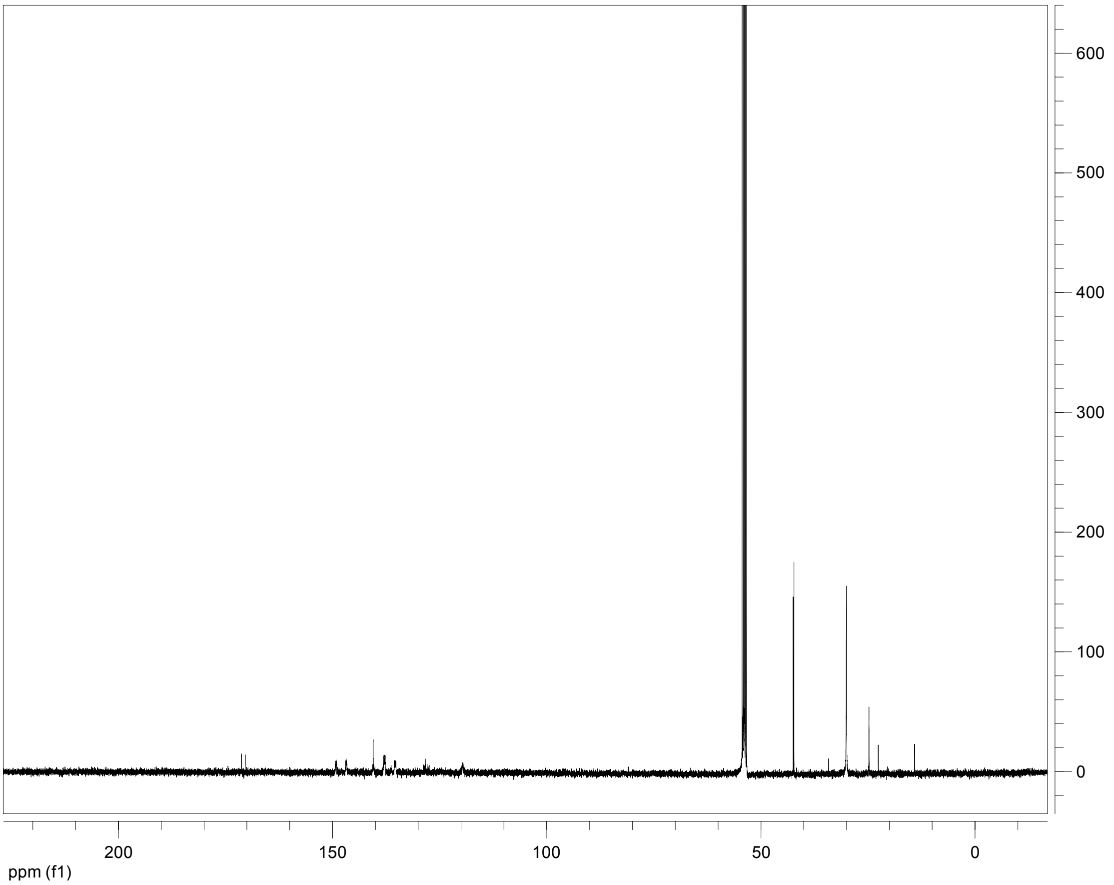
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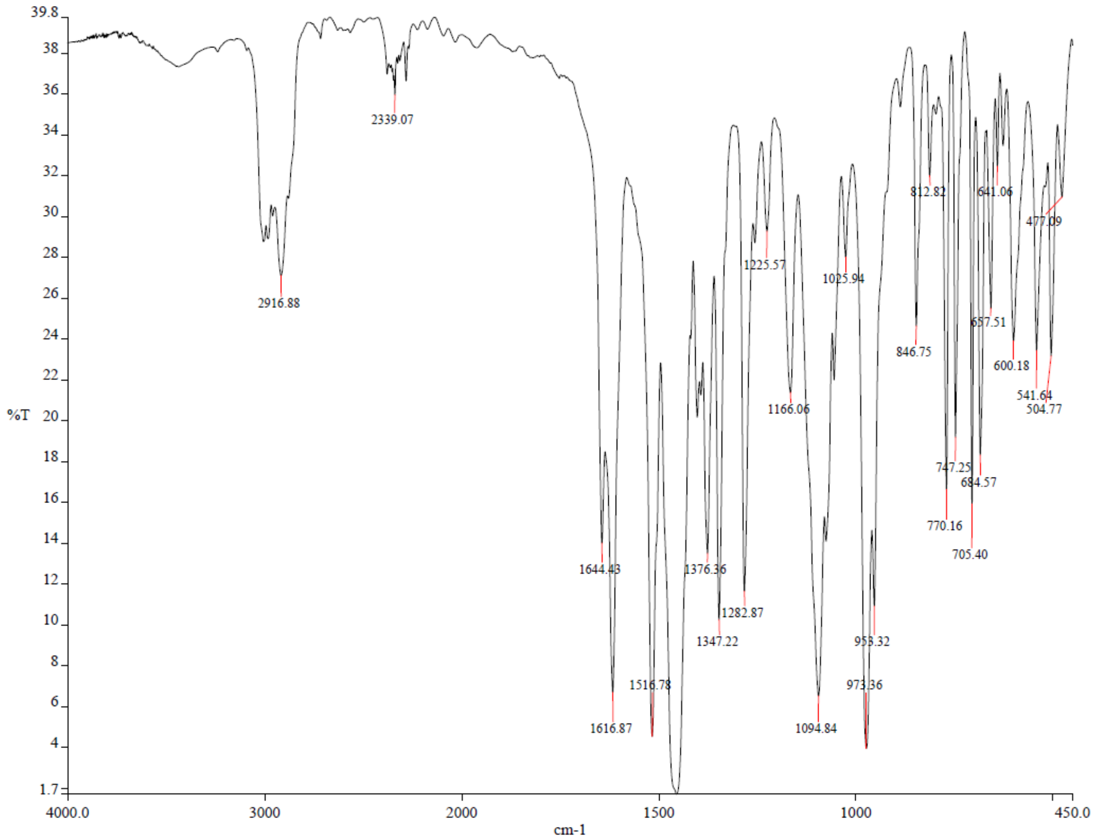
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%T
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1.7
4000.0
3000
2000
1500
1000
450.0
cm-1
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2339.07
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1616.87
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1376.36
1347.22
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973.36
953.32
846.75
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770.16
747.25
705.40
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657.51
641.06
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477.09

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(2) Siebert, W.; Hildenbrand, M.; Hornbach, P.; Karger, G.; Pritzkow, H. *Z. Naturforsch.* **1989**, *44b*, 1179.

(3) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772.