

## Supplementary Data for:

### Activation of CO<sub>2</sub> by Phosphinoamide Hafnium Complexes

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**General Considerations** All preparations were performed under an atmosphere of dry, O<sub>2</sub>-free N<sub>2</sub> employing both Schlenk line techniques and inert atmosphere glove boxes. Solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, hexane and pentane) were purified employing a Grubbs' type column system manufactured by Innovative Technology. C<sub>6</sub>H<sub>5</sub>Br was dried over CaH<sub>2</sub> and distilled. Solvents were stored in the glove box over 4 Å molecular sieves. <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR were internally referenced to deuterated CD<sub>2</sub>Cl<sub>2</sub> (δ = 5.32 ppm (<sup>1</sup>H), 53.84 ppm (<sup>13</sup>C)) and C<sub>6</sub>D<sub>5</sub>Br (δ = 6.94 ppm (<sup>1</sup>H), 122.167 ppm (<sup>13</sup>C)) relative to Me<sub>4</sub>Si. NMR samples were prepared in the glove box, capped and sealed with parafilm. <sup>11</sup>B, <sup>19</sup>F and <sup>31</sup>P resonances were referenced externally to (BF<sub>3</sub>·Et<sub>2</sub>O), CFC<sub>3</sub> and 85% H<sub>3</sub>PO<sub>4</sub>, respectively. <sup>1</sup>H-<sup>13</sup>C HSQC experiments were carried out using conventional pulse sequences to aid in the assignment of peaks in the <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. Coupling constants (*J*) are reported as absolute values. All glassware was dried overnight at 120°C and evacuated for 1 hour prior to use. Combustion analyses were performed in-house employing a Perkin Elmer 2400 Series II CHNS Analyzer. CD<sub>2</sub>Cl<sub>2</sub> d<sub>8</sub>-THF and C<sub>6</sub>D<sub>5</sub>Br were purchased from the Cambridge Isotope Laboratories and were dried over CaH<sub>2</sub>, distilled, degassed and stored under N<sub>2</sub> in a glove box. Hf(CH<sub>2</sub>Ph)<sub>4</sub> was obtained from Strem Chemicals Inc. 2,2'-Thiobisethylamine was obtained from TCI America. ClPPh<sub>2</sub>, n-BuLi, <sup>13</sup>CO<sub>2</sub>, and CO<sub>2</sub> were obtained from Aldrich Chemical Co.

#### Synthesis of S(CH<sub>2</sub>CH<sub>2</sub>NHPPH<sub>2</sub>)<sub>2</sub> (1)

Neat 2,2'-thiobisethylamine (2 mL, 0.017 mol) was combined with 300 mL of THF and cooled to 0°C. A hexane solution of n-BuLi (21.6 mL, 0.035 mol) was added dropwise over 20 minutes giving a slightly cloudy pale yellow solution. The mixture was maintained at 0°C and neat chlorodiphenylphosphine (6.34 mL, 0.035 mol) was added dropwise over 5 minutes giving a clear pale yellow solution. The mixture was stirred for 12 h at which point the solvents were removed *in vacuo*. The remaining oily solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through celite to a clear pale yellow solution. The volatiles were removed and the product was obtained as a pale yellow oil in 89 % yield (7.5 g, 0.015 mol). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ ppm) 7.41 (m, 8H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, *Ar*-H PPh<sub>2</sub>), 7.22 (m, 12H, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, *Ar*-H PPh<sub>2</sub>), 3.06 (m, 4H, <sup>3</sup>J<sub>HH</sub> 6.7 Hz, <sup>3</sup>J<sub>HP</sub> 9.4 Hz, CH<sub>2</sub>), 2.47 (t, 4, <sup>3</sup>J<sub>HP</sub> 6.7 Hz, CH<sub>2</sub>), 2.39 (m, 2H, <sup>3</sup>J<sub>HH</sub> 6.3 Hz, <sup>2</sup>J<sub>HP</sub> 5.9 Hz, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ ppm) 142.12 (d, <sup>1</sup>J<sub>CP</sub> 12 Hz, *Cipso* PPh<sub>2</sub>), 131.57 (d, J<sub>CP</sub> 20 Hz, *m*-C PPh<sub>2</sub>), 128.70 (d, J<sub>CP</sub> 25 Hz, *o*-C PPh<sub>2</sub>), 128.63 (s, *p*-C PPh<sub>2</sub>), 46.03 (d, <sup>2</sup>J<sub>CP</sub> 16 Hz, CH<sub>2</sub>), 35.13 (d, <sup>3</sup>J<sub>CP</sub> 7 Hz, CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ ppm) 40.83 (s).

### Synthesis of $\kappa^5$ -*P,N,S,N,P*-S(CH<sub>2</sub>CH<sub>2</sub>NPPh<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub> (3)

A solution of **1** in THF (90 mg, 0.184 mmol; 2 mL) was added to a stirring yellow suspension of Hf(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and THF (100 mg, 0.184 mmol; 2 mL) in a scintillation vial immediately giving a clear yellow solution. The reaction mixture was stirred for 12 hours at which point it was dried to an orange solid. Pentane (2 mL) was added to the crude product and it was placed in the freezer over night. The pale yellow clear supernatant was decanted off of the orange solid, and the solid was dried. The solution was placed back in the freezer and a second crop of crystals was obtained. The yellow product was obtained in 78 % yield (134 mg, 0.142 mmol). <sup>1</sup>H (C<sub>6</sub>D<sub>5</sub>Br, δ ppm) 7.35 (m, 8H, *o*-H PPh<sub>2</sub>), 7.22 (m, 12H, <sup>3</sup>J<sub>HH</sub> 7.1 Hz, *p*-/*m*-H PPh<sub>2</sub>), 7.05 (m, 8H, <sup>3</sup>J<sub>HH</sub> 7.1 Hz, *o*-/*m*-H C<sub>6</sub>H<sub>5</sub>), 6.76 (m, 2H, <sup>3</sup>J<sub>HH</sub> 7.1 Hz, *p*-H C<sub>6</sub>H<sub>5</sub>), 3.40 (d of t, 4H, <sup>3</sup>J<sub>HH</sub> 6.4 Hz, <sup>3</sup>J<sub>HP</sub> 6.4 Hz, CH<sub>2</sub>), 2.62 (t, 4H, <sup>3</sup>J<sub>HP</sub> 5.3 Hz, CH<sub>2</sub>Ph), 1.85 (t, 4H, <sup>3</sup>J<sub>HH</sub> 6 Hz, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>5</sub>Br, δ ppm) 147.56 (t, <sup>2</sup>J<sub>CP</sub> 3 Hz, Ar-C<sub>1</sub> C<sub>6</sub>H<sub>5</sub>), 136.86 (d, <sup>1</sup>J<sub>CP</sub> 9 Hz, *Cipso* PPh<sub>2</sub>) 132.75 (d, <sup>2</sup>J<sub>CP</sub> 18 Hz, *o*-C PPh<sub>2</sub>), 128.91 (s, *p*-C PPh<sub>2</sub>), 128.17 (m, *m*-C PPh<sub>2</sub>) 127.74 (s, Ar-C<sub>3</sub> C<sub>6</sub>H<sub>5</sub>), 127.67 (s, Ar-C<sub>2</sub> C<sub>6</sub>H<sub>5</sub>), 120.76 (s, Ar-C<sub>4</sub> C<sub>6</sub>H<sub>5</sub>), 73.22 (t, <sup>2</sup>J<sub>CP</sub> 7 Hz, CH<sub>2</sub>-Ph), 50.78 (s, CH<sub>2</sub>), 37.63 (d, CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>5</sub>Br, δ ppm) 4.00 (s). Elemental Analysis for C<sub>42</sub>H<sub>42</sub>N<sub>2</sub>P<sub>2</sub>HfS: Calculated C, 59.52; H, 5.00; N, 3.31; Actual C, 59.01; H, 5.16; N, 3.33.

### Synthesis of $\kappa^5$ -*P,N,S,N,P*-S(CH<sub>2</sub>CH<sub>2</sub>NPiPr<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub> (4)

A solution of **2** in THF (65 mg, 0.184 mmol; 2 mL) was added to a stirring yellow suspension of Hf(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and THF (100 mg, 0.184 mmol; 2 mL) in a scintillation vial immediately giving a clear yellow solution. The reaction mixture was stirred for 12 hours at which point it was dried to an orange solid. Pentane (2 mL) was added to the crude product and it was placed in the freezer over night. The pale yellow clear supernatant was decanted off of the orange solid, and the solid was dried. The solution was placed back in the freezer and a second crop of crystals was obtained. The orange product was obtained in 72 % yield (94 mg, 0.132 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Br, δ ppm) 7.19 (d, 8H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, *o*-/*m*-Ar-H), 6.75 (bt, 2H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, *p*-Ar-H), 3.25 (d of t, 4H, <sup>3</sup>J<sub>HH</sub> 6.3 Hz, <sup>3</sup>J<sub>HP</sub> 6.3 Hz, CH<sub>2</sub>), 2.42 (t, 4H, <sup>3</sup>J<sub>HP</sub> 5.4 Hz, CH<sub>2</sub>Ph), 2.21 (t, 4H, <sup>3</sup>J<sub>HH</sub> 6.3 Hz, CH<sub>2</sub>), 1.91 (sept of d, 4H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.97 (d of d, 12H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, <sup>3</sup>J<sub>HP</sub> 16.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (d of d, 12H, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, <sup>3</sup>J<sub>HP</sub> 13.4 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Br, δ ppm) 151.30 (t, <sup>2</sup>J<sub>CP</sub> 3 Hz, Ar-C<sub>1</sub> C<sub>6</sub>H<sub>5</sub>), 127.27 (s, Ar-C<sub>3</sub> C<sub>6</sub>H<sub>5</sub>), 127.19 (s, Ar-C<sub>2</sub> C<sub>6</sub>H<sub>5</sub>), 119.76 (s, Ar-C<sub>4</sub> C<sub>6</sub>H<sub>5</sub>), 73.81 (t, <sup>2</sup>J<sub>CP</sub> 7 Hz, CH<sub>2</sub>-Ph), 50.12 (d, J<sub>CP</sub> 4 Hz, CH<sub>2</sub>), 36.82 (d, J<sub>CP</sub> 4 Hz, CH<sub>2</sub>), 24.36 (d, <sup>1</sup>J<sub>CP</sub> 12 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 19.60 (d, <sup>2</sup>J<sub>CP</sub> 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 19.31 (d, <sup>2</sup>J<sub>CP</sub> 15 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Br, δ ppm) 11.77 (s). Elemental Analysis for C<sub>30</sub>H<sub>50</sub>N<sub>2</sub>P<sub>2</sub>HfS: Calculated C, 50.65; H, 7.09; N, 3.94; Actual C, 50.39; H, 7.25; N, 3.92.

### Synthesis of [ $\kappa^3$ -*N,S,N*-S(CH<sub>2</sub>CH<sub>2</sub>NPPh<sub>2</sub>)<sub>2</sub>Hf(CO<sub>2</sub>)(CH<sub>2</sub>Ph)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5)

A solution of **3** in C<sub>6</sub>H<sub>5</sub>Br (15 mg, 0.018 mmol; 0.5 mL) was added to a yellow solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>H<sub>5</sub>Br (16mg, 0.018 mmol; 0.5 mL) giving a pale yellow solution. The mixture was transferred to a J-Young NMR tube a degassed using three freeze-pump-thaw cycles. The mixture was then charged with CO<sub>2</sub> and allowed to stand. It is important to note that the CO<sub>2</sub> must be allowed to slowly diffuse into solution and not be shaken in. After 12 h white plates are formed in the tube. After transferring the mixture to a 2 dram vial, the solvent was decanted and the product was washed three times with C<sub>6</sub>H<sub>5</sub>Br. The product was washed

once more with pentane and the crystals dried *in vacuo*. The product was obtained as white plates in 62 % yield (15 mg, 0.006 mmol).  $^1\text{H}$  NMR ( $d_8$ -THF,  $\delta$  ppm) 7.85 (t, 1H,  $^3J_{\text{HH}}$  7.5 Hz, Ar-*H* PPh<sub>2</sub>), 7.76 (m, 2H,  $^3J_{\text{HH}}$  7.5 Hz, Ar-*H* PPh<sub>2</sub>), 7.67 (m, 4H, Ar-*H* PPh<sub>2</sub>), 7.59 (bm, 2H, Ar-*H* PPh<sub>2</sub>), 7.49 (m, 6H, Ar-*H* PPh<sub>2</sub>), 7.17 (t, 1H,  $^3J_{\text{HH}}$  7.5 Hz, Ar-*H* PPh<sub>2</sub>), 7.04 (t, 2H,  $^3J_{\text{HH}}$  8.0 Hz, *m*-H C<sub>6</sub>H<sub>5</sub>), 6.95 (t, 2H,  $^3J_{\text{HH}}$  7.5 Hz, Ar-*H* PPh<sub>2</sub>), 6.86 (d, 2H,  $^3J_{\text{HH}}$  8.0 Hz, *o*-H C<sub>6</sub>H<sub>5</sub>), 6.79 (t, 1H,  $^3J_{\text{HH}}$  8.0 Hz, *p*-H C<sub>6</sub>H<sub>5</sub>), 6.56 (t, 2H,  $^3J_{\text{HH}}$  7.5 Hz, Ar-*H* PPh<sub>2</sub>), 4.06 (m, 3H,  $J_{\text{HP}}$  15.0 Hz, CH<sub>2</sub>), 3.59 (m, 2H, CH<sub>2</sub>), 3.17 (bd, 1H,  $J_{\text{HP}}$  15.0 Hz, CH<sub>2</sub>), 2.79 (m, 1H, CH<sub>2</sub>), 2.64 (m, 1H, CH<sub>2</sub>), 2.27 (bs, 2H, CH<sub>2</sub>Ph).  $^{11}\text{B}$  NMR ( $d_8$ -THF,  $\delta$  ppm) -16.56 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -THF,  $\delta$  ppm) 168.06 (d,  $^1J_{\text{CP}}$  139 Hz, P-CO<sub>2</sub>), 149.19 (dm,  $^1J_{\text{CF}}$  243 Hz, *o*-C<sub>6</sub>F<sub>5</sub>), 148.56 (s, C<sub>1</sub> Ar-C C<sub>6</sub>H<sub>5</sub>), 139.13 (dm,  $^1J_{\text{CF}}$  243 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 137.11 (dm,  $^1J_{\text{CF}}$  246 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 135.86 (b, Ar-C PPh<sub>2</sub>), 134.42 (d,  $J_{\text{CP}}$  11 Hz, Ar-C PPh<sub>2</sub>), 133.81 (d,  $J_{\text{CP}}$  11 Hz, Ar-C PPh<sub>2</sub>), 133.04 (d,  $J_{\text{CP}}$  19 Hz, Ar-C PPh<sub>2</sub>), 132.80 (d,  $J_{\text{CP}}$  16 Hz, Ar-C PPh<sub>2</sub>), 130.87 (d,  $J_{\text{CP}}$  12 Hz, Ar-C PPh<sub>2</sub>), 129.96 (d,  $J_{\text{CP}}$  9 Hz, Ar-C PPh<sub>2</sub>), 129.38 (d,  $J_{\text{CP}}$  7 Hz, Ar-C PPh<sub>2</sub>), 129.01 (s, Ar-C<sub>3</sub> C<sub>6</sub>H<sub>5</sub>), 127.57 (s, Ar-C<sub>2</sub> C<sub>6</sub>H<sub>5</sub>), 122.79 (s, Ar-C<sub>4</sub> C<sub>6</sub>H<sub>5</sub>), 74.17 (d,  $J_{\text{CP}}$  15 Hz, CH<sub>2</sub>-Ph), 52.18 (d,  $J_{\text{CP}}$  5 Hz, CH<sub>2</sub>), 48.72 (d,  $J_{\text{CP}}$  3 Hz, CH<sub>2</sub>), 40.17 (d,  $J_{\text{CP}}$  5 Hz, CH<sub>2</sub>), 38.73 (d,  $J_{\text{CP}}$  12 Hz, CH<sub>2</sub>).  $^{19}\text{F}$  NMR ( $d_8$ -THF,  $\delta$  ppm) -132.70 (bd, *o*-F), -164.96 (t,  $^3J_{\text{FF}}$  21 Hz, *p*-F), -168.45 (bt,  $^3J_{\text{FF}}$  16 Hz, *m*-F).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF,  $\delta$  ppm) 36.31 (s, Ph<sub>2</sub>P-CO<sub>2</sub>), 2.53 (s, PPh<sub>2</sub>). Elemental Analysis for C<sub>96</sub>H<sub>86</sub>N<sub>4</sub>P<sub>4</sub>Hf<sub>2</sub>S<sub>2</sub>O<sub>4</sub>B<sub>2</sub>F<sub>40</sub>·3C<sub>6</sub>H<sub>5</sub>Br: Calculated C, 48.01; H, 2.53; N, 1.56; Actual C, 47.52; H, 2.48; N, 1.86.

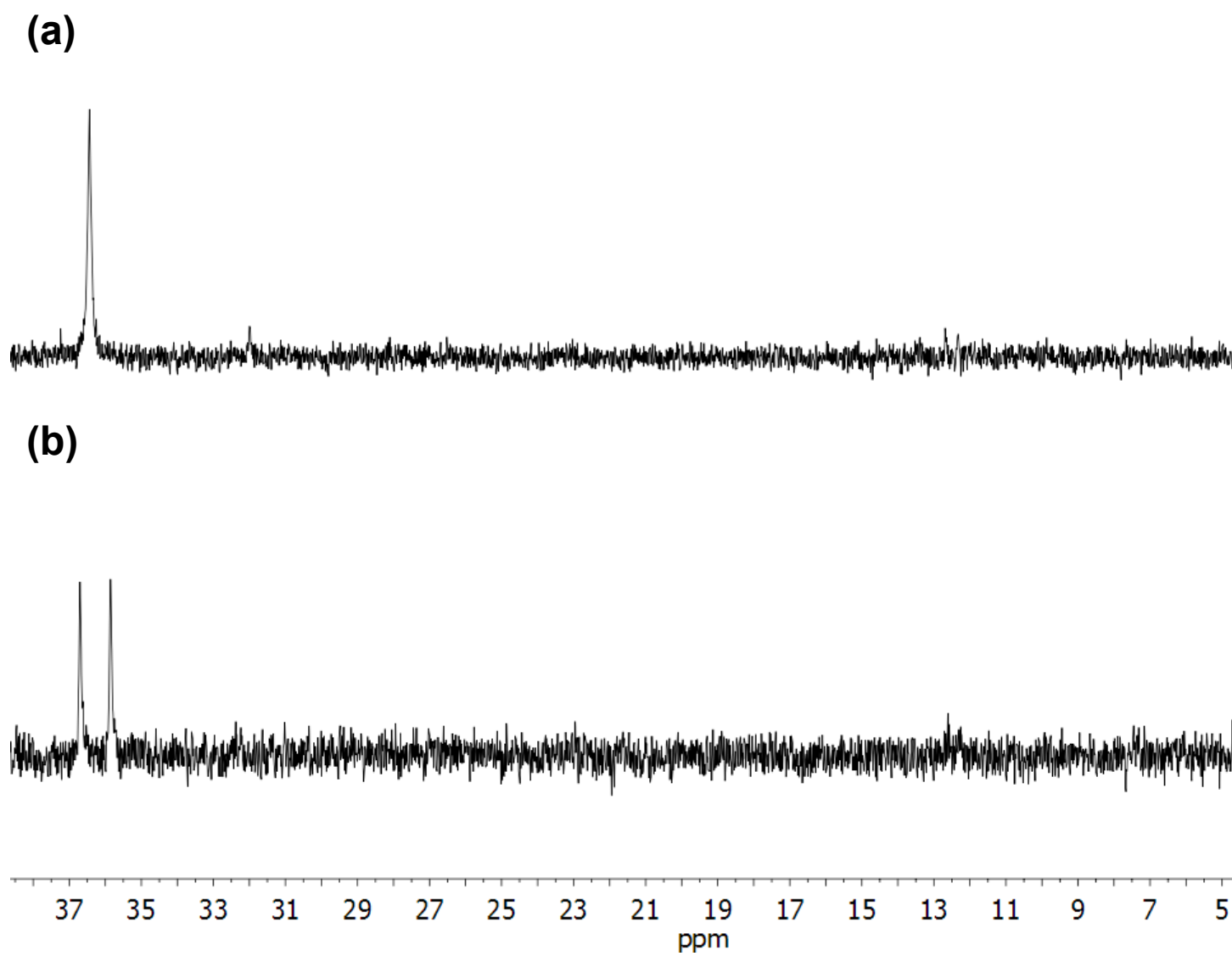
### Synthesis of [ $\kappa^3$ -*N,S,N*-S(CH<sub>2</sub>CH<sub>2</sub>NPPh<sub>2</sub>)<sub>2</sub>Hf(CO<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (6)

A sample of **5** was dissolved in  $d_8$ -THF and transferred to a J-Young NMR tube. The solution was degassed using three freeze-pump-thaw cycles and charged with 1 atm. of CO<sub>2</sub>. Quantitative conversion to **6** is observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.  $^1\text{H}$  NMR ( $d_8$ -THF,  $\delta$  ppm) 7.77 (m, 4H,  $^3J_{\text{HH}}$  7.4 Hz, Ar-*H* PPh<sub>2</sub>), 7.62 (m, 12H,  $^3J_{\text{HH}}$  7.4 Hz, Ar-*H* PPh<sub>2</sub>), 7.40 (m, 4H,  $^3J_{\text{HH}}$  7.4 Hz, Ar-*H* PPh<sub>2</sub>), 7.14 (m, 4H,  $^3J_{\text{HH}}$  6.7 Hz, *o*-/*m*-H-C<sub>6</sub>H<sub>5</sub>), 6.89 (m, 1H,  $^3J_{\text{HH}}$  6.7 Hz, *p*-H-C<sub>6</sub>H<sub>5</sub>), 3.88 (m, 4H, CH<sub>2</sub>), 2.95 (m, 4H, CH<sub>2</sub>), 2.62 (s, 2H, CH<sub>2</sub>Ph).  $^{11}\text{B}$  NMR ( $d_8$ -THF,  $\delta$  ppm) -16.56 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -THF,  $\delta$  ppm) 166.48 (d,  $^1J_{\text{CP}}$  133 Hz, P-CO<sub>2</sub>), 149.15 (s, Ar-C<sub>1</sub> C<sub>6</sub>H<sub>5</sub>), 148.98 (dm,  $^1J_{\text{CF}}$  244 Hz, *o*-C<sub>6</sub>F<sub>5</sub>), 138.95 (dm,  $^1J_{\text{CF}}$  247 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.95 (dm,  $^1J_{\text{CF}}$  254 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 135.24 (d of d,  $J_{\text{CP}}$  14 Hz, 3 Hz Ar-C PPh<sub>2</sub>), 133.82 (d,  $J_{\text{CP}}$  11 Hz, Ar-C PPh<sub>2</sub>), 133.21 (d,  $J_{\text{CP}}$  11 Hz, Ar-C PPh<sub>2</sub>), 130.59 (d of d,  $J_{\text{CP}}$  13 Hz, 4 Hz, Ar-C PPh<sub>2</sub>), 128.80 (s, Ar-C<sub>3</sub> C<sub>6</sub>H<sub>5</sub>), 127.97 (s, Ar-C<sub>2</sub> C<sub>6</sub>H<sub>5</sub>), 123.88 (s, Ar-C<sub>4</sub> C<sub>6</sub>H<sub>5</sub>), 78.03 (s, CH<sub>2</sub>-Ph), 48.10 (s, CH<sub>2</sub>), 36.98 (d,  $J_{\text{CP}}$  10 Hz, CH<sub>2</sub>).  $^{19}\text{F}$  NMR ( $d_8$ -THF,  $\delta$  ppm) -132.71 (bd, *o*-F), -164.92 (t,  $^3J_{\text{FF}}$  21 Hz, *p*-F), -168.43 (bt,  $^3J_{\text{FF}}$  18 Hz, *m*-F).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF,  $\delta$  ppm) 31.90 (s, Ph<sub>2</sub>P-CO<sub>2</sub>).

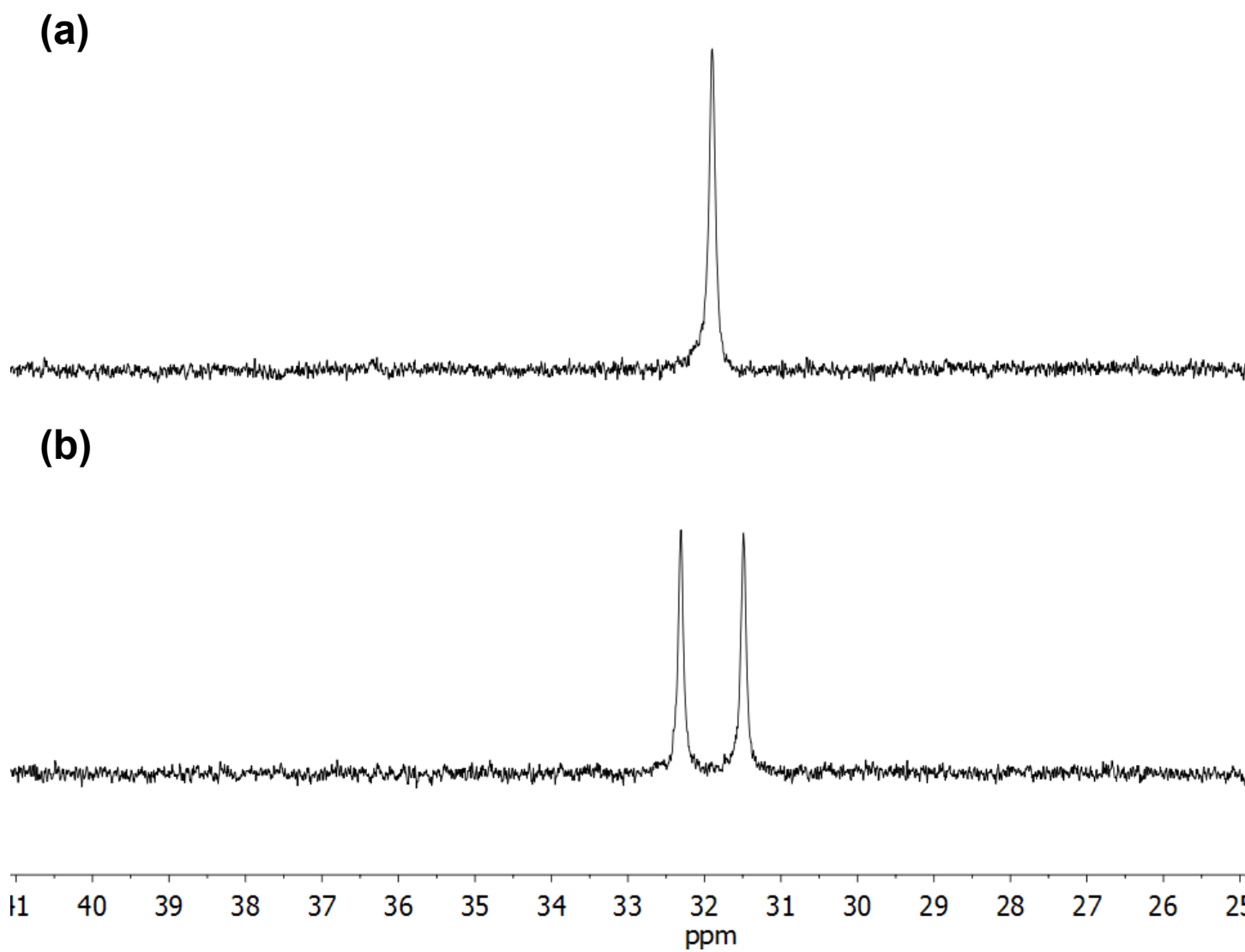
### Synthesis of [ $\kappa^3$ -*N,S,N*-S(CH<sub>2</sub>CH<sub>2</sub>N*i*Pr<sub>2</sub>)<sub>2</sub>Hf(CO<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (7)

A deep yellow solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>H<sub>5</sub>Br (97 mg, 0.106 mmol; 2 mL) was added to a stirring yellow solution of **4** in C<sub>6</sub>H<sub>5</sub>Br (75 mg, 0.106 mmol; 2 mL) immediately giving a clear pale-yellow solution. The mixture was transferred to a bomb, degassed using three freeze-pump-thaw cycles and charged with 1 atm. of CO<sub>2</sub>. The reaction mixture was stirred for 12 hours at which point it was layered with pentane. The colorless supernatant was decanted off of the colourless solid, and the solid was dried. The off-white product was obtained in 77 % yield (112 mg, 0.081 mmol).  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>5</sub>Br,  $\delta$  ppm) 7.13 (t, 2H,  $^3J_{\text{HH}}$  7.5 Hz, *m*-Ar-H), 6.95 (d,

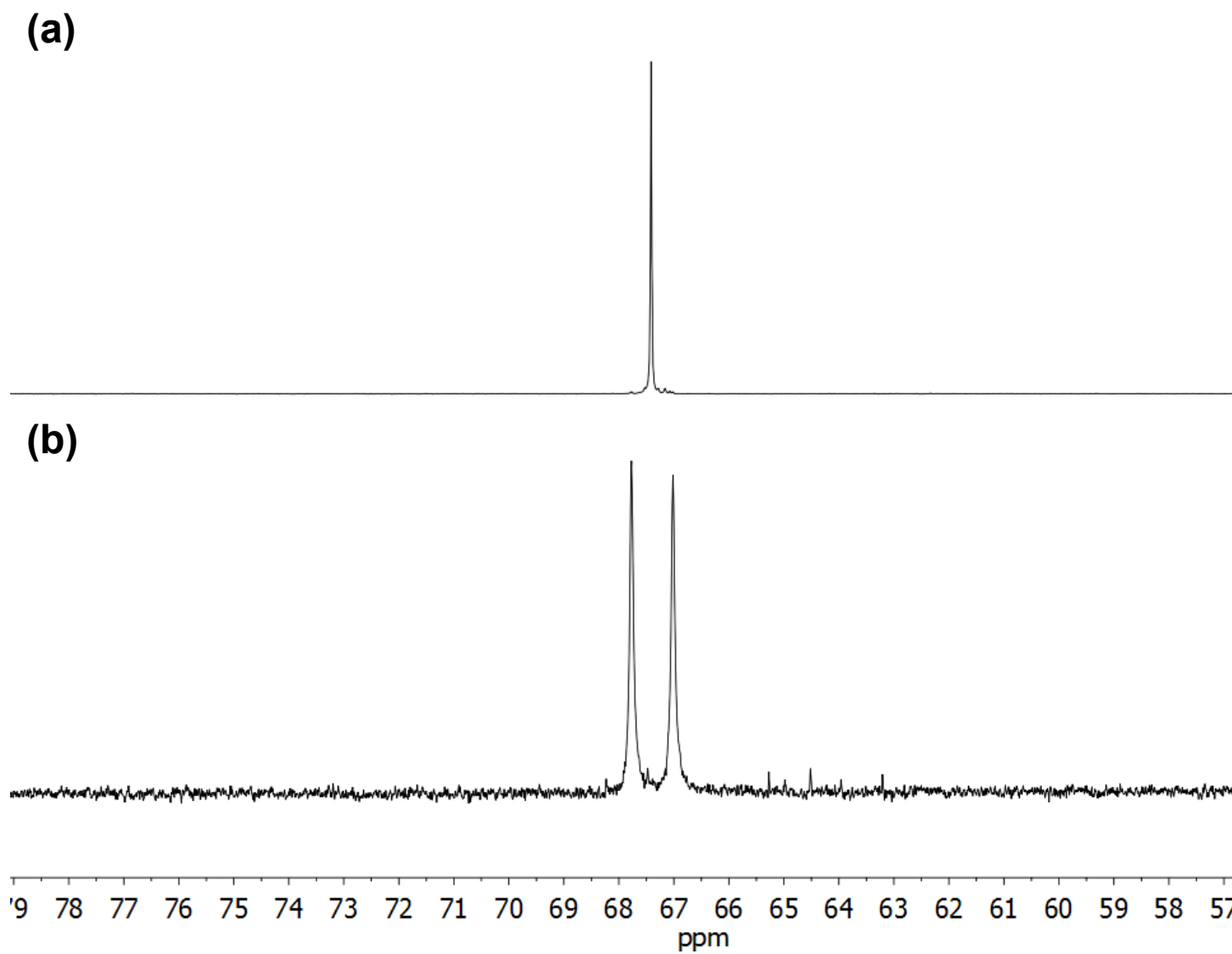
2H,  $^3J_{\text{HH}}$  7.5 Hz, *o*-Ar-H), 6.82 (t, 1H,  $^3J_{\text{HH}}$  7.5 Hz, *p*-Ar-H), 3.35 (m, 2H,  $^3J_{\text{HH}}$  6.3 Hz,  $J_{\text{HP}}$  3.0 Hz, 13.7 Hz, CH<sub>2</sub>), 3.16 (m, 2H,  $^3J_{\text{HH}}$  6.3 Hz,  $J_{\text{HP}}$  3.9 Hz, 14.4 Hz, CH<sub>2</sub>), 2.76 (m, 2H,  $^3J_{\text{HP}}$  6.3 Hz,  $J_{\text{HP}}$  14.2 Hz, CH<sub>2</sub>), 2.59 (m, 2H,  $^3J_{\text{HH}}$  6.0 Hz,  $J_{\text{HP}}$  11.3 Hz, CH<sub>2</sub>), 2.32 (s, 2H, CH<sub>2</sub>Ph), 2.08 (d of sept, 4H,  $^3J_{\text{HH}}$  7.1 Hz,  $J_{\text{HP}}$  10.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.93 (m, 9H,  $^3J_{\text{HH}}$  7.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (m, 6H,  $^3J_{\text{HH}}$  7.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.83 (m, 6H,  $^3J_{\text{HH}}$  7.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.78 (m, 3H,  $^3J_{\text{HH}}$  7.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>).  $^{11}\text{B}$  NMR (C<sub>6</sub>D<sub>5</sub>Br,  $\delta$  ppm) -16.18 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>5</sub>Br,  $\delta$  ppm) 166.43 (d,  $^1J_{\text{CP}}$  123 Hz, P-CO<sub>2</sub>), 148.39 (dm,  $^1J_{\text{CF}}$  241 Hz, *o*-C<sub>6</sub>F<sub>5</sub>), 142.41 (s, Ar-C<sub>1</sub> C<sub>6</sub>H<sub>5</sub>), 138.24 (dm,  $^1J_{\text{CF}}$  246 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.39 (dm,  $^1J_{\text{CF}}$  250 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 128.29 (s, Ar-C<sub>3</sub> C<sub>6</sub>H<sub>5</sub>), 127.62 (s, Ar-C<sub>2</sub> C<sub>6</sub>H<sub>5</sub>), 123.18 (s, Ar-C<sub>4</sub> C<sub>6</sub>H<sub>5</sub>), 79.42 (s, CH<sub>2</sub>-Ph), 47.55 (d,  $J_{\text{CP}}$  3 Hz, CH<sub>2</sub>), 38.16 (d,  $J_{\text{CP}}$  8 Hz, CH<sub>2</sub>), 23.95 (d,  $^1J_{\text{CP}}$  41 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 22.98 (d,  $^1J_{\text{CP}}$  40 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 15.06 (d,  $^2J_{\text{CP}}$  3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 15.01 (d,  $^2J_{\text{CP}}$  2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 14.82 (d,  $^2J_{\text{CP}}$  1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 14.70 (d,  $^2J_{\text{CP}}$  4 Hz, CH(CH<sub>3</sub>)<sub>2</sub>).  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>5</sub>Br,  $\delta$  ppm) -131.74 (bd, *o*-F), -161.52 (t,  $^3J_{\text{FF}}$  21 Hz, *p*-F), -165.59 (bt,  $^3J_{\text{FF}}$  18 Hz, *m*-F).  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>5</sub>Br,  $\delta$  ppm) 67.40 (s). IR: 1644 cm<sup>-1</sup>. Elemental Analysis for C<sub>49</sub>H<sub>43</sub>N<sub>2</sub>P<sub>2</sub>HfSO<sub>4</sub>F<sub>20</sub>B: Calculated C, 42.40; H, 3.13; N, 2.02; Actual C, 41.91; H, 3.25; N, 1.94.



**Figure 1:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $d_8$ -THF) of **5** with (a)  $^{12}\text{CO}_2$  and (b)  $^{13}\text{CO}_2$



**Figure 2:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $d_8$ -THF) of **6** with (a)  $^{12}\text{CO}_2$  and (b)  $^{13}\text{CO}_2$



**Figure 3:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra ( $\text{C}_6\text{D}_5\text{Br}$ ) of **7** with (a)  $^{12}\text{CO}_2$  and (b)  $^{13}\text{CO}_2$