

Supporting Information for:

## Unexpected Formal Insertion of CO<sub>2</sub> into the C–Si Bonds of a Zinc Compound

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## Experimental details

### *General Considerations*

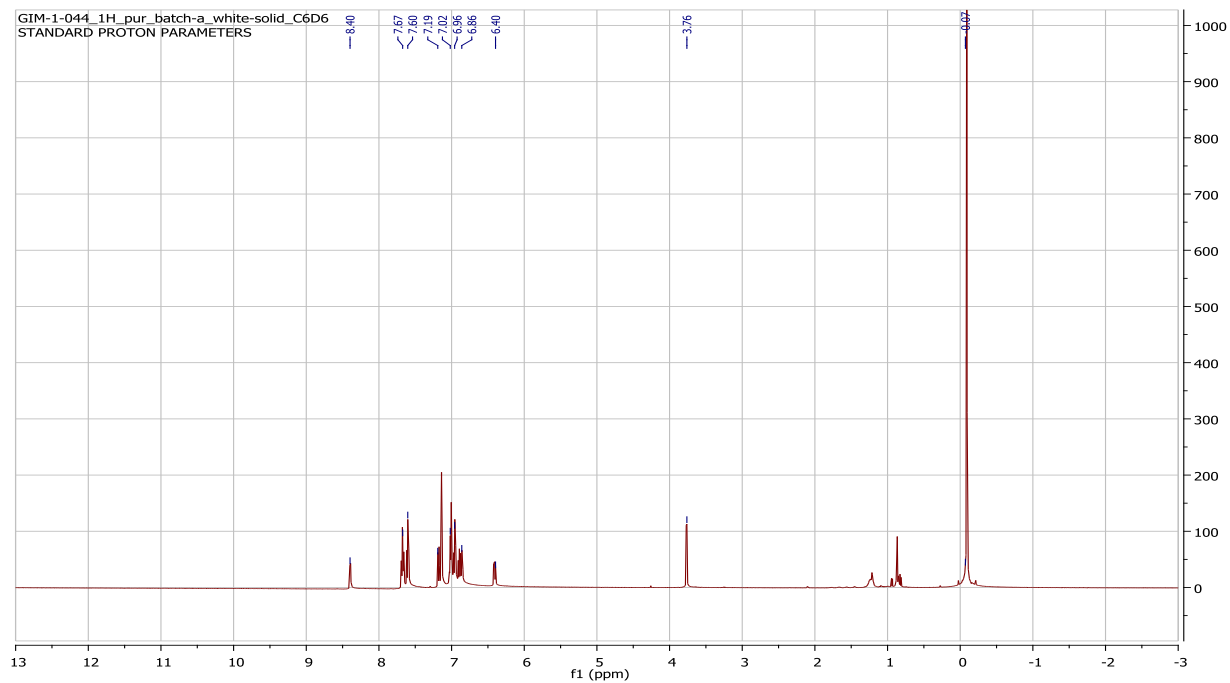
Manipulations were performed under an inert atmosphere of N<sub>2</sub> using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents unless otherwise specified. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C (125 MHz) NMR spectra were referenced to residual solvent resonances. <sup>31</sup>P (200 MHz) and <sup>29</sup>Si (99 MHz) NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> and tetramethylsilane standards, respectively. All spectra were collected in benzene-*d*<sub>6</sub>, which was degassed and dried over NaK alloy. Infrared spectra were recorded on a Bruker Alpha-P FTIR. Elemental analyses were obtained using an Elementar VarioMicro analyzer.

### Preparation of PPh<sub>2</sub>CH(SiMe<sub>3</sub>)py (**1a**)

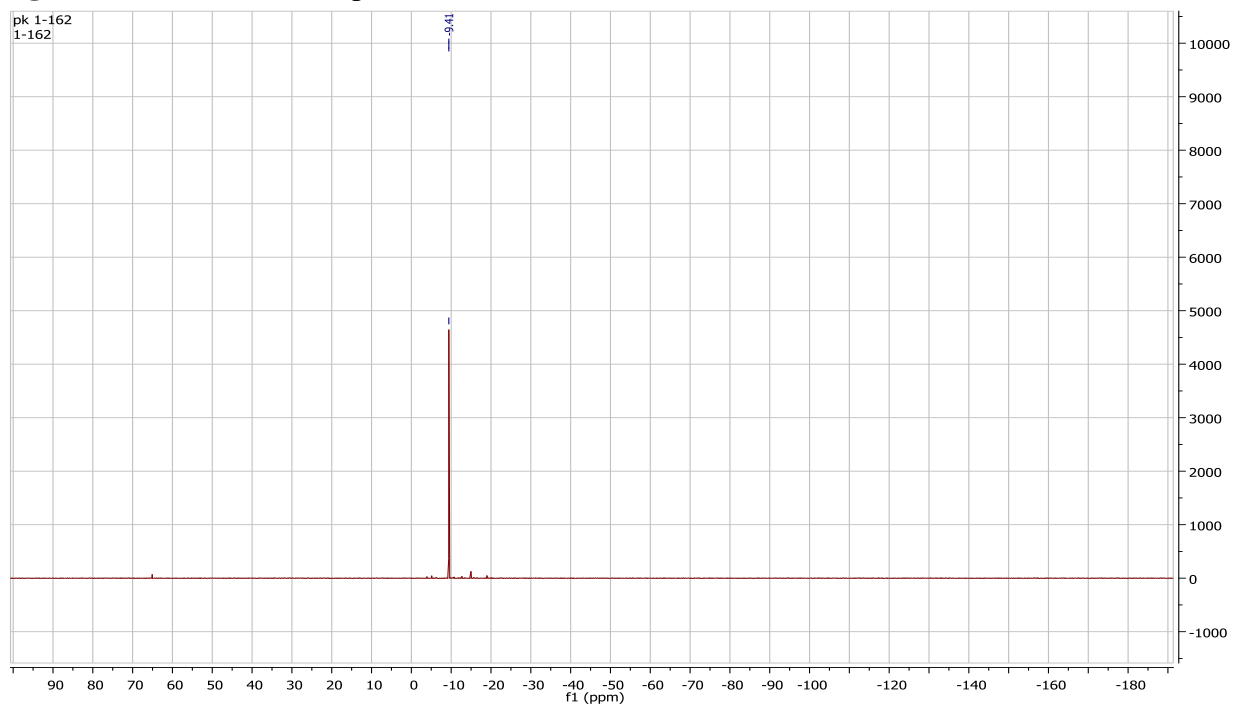
To a 50 mL round-bottom Schlenk flask equipped with a magnetic stir bar and sealed with a septum, *n*-butyllithium (6.6 mL of a 1.6 M solution in hexanes, 11 mmol, 2.1 equiv.) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 1.5 mL, 10 mmol, 2.0 equiv.) were added by syringe, resulting in a clear, slightly yellow solution. After stirring for 20 min, 2-picoline (0.49 mL, 5.0 mmol, 1.0 equiv) was added dropwise over 10 min. The resulting deep red solution was stirred for an additional 20 min and then cooled to 0 °C. Chlorotrimethylsilane (0.63 mL, 5.0 mmol, 1.0 equiv.) was then added dropwise over 30 min, and the resulting orange slurry was stirred for an additional 0.5 h, when 1 mL of Et<sub>2</sub>O was added. Last, chlorodiphenylphosphine (0.95 mL, 5.1 mmol, 1.0 equiv.) was added dropwise over 30 min. The reaction mixture was allowed to warm to ambient temperature and stirred for an additional 14 h. Volatile components were removed under reduced pressure, resulting in a chalky yellow solid that was extracted with 15 mL of hexanes. Solids were removed by filtration, and the filtrate was evaporated to 1.2 g of yellow solid. The crude ligand was redissolved in methylene chloride, filtered through a 1 cm pad of silica gel. The solution was then evaporated to a solid, which was crystallized at -28 °C from a 1:1 mixture of Et<sub>2</sub>O:hexanes. After decanting the supernatant liquid, rinsing with cold hexanes, and drying under reduced pressure, the first crop was obtained as an off-white solid (566 mg). A second crop (120 mg) was crystallized from the supernatant liquid by concentration and further cooling (0.686 g, 1.96 mmol, 39%). <sup>1</sup>H δ: 8.40 (*app.* d, *J* = 4.6 Hz, 1 H), 7.70–7.66 (m, 2 H), 7.62 - 7.59 (m, 3 H), 7.20–7.18 (m, 3 H), 7.02 (d, *J* = 7.9 Hz, 1 H), 7.98–7.94 (m, 3 H), 6.88 - 6.83 (1 H), 3.76 (d, *J* = 4.6 Hz, 1 H), -0.07 (s, 9 H); <sup>13</sup>C {<sup>1</sup>H} δ: 162.2 (d, *J*<sub>CP</sub> = 6.5 Hz), 149.4, 135.5 (d, *J*<sub>CP</sub> = 19.4 Hz), 135.09 (d, *J*<sub>CP</sub> = 12.5 Hz), 134.9, 133.1 (d, *J*<sub>CP</sub> = 22.8 Hz), 132.9 (d, *J*<sub>CP</sub> = 19.3 Hz), 129.4, 128.5 (d, *J*<sub>CP</sub> = 8.4 Hz), 128.5 (d, *J*<sub>CP</sub> = 7.3 Hz), 122.6 (d, *J*<sub>CP</sub> = 11.2 Hz), 119.5 (d, *J*<sub>CP</sub> = 2.3 Hz), 39.4

(d,  $J_{CP} = 29.2$  Hz),  $-1.2$  (d,  $J_{CP} = 3.7$  Hz);  $^{31}\text{P}\{^1\text{H}\}$   $\delta$ :  $-9.4$ . ATR FTIR: 3050, 3000, 2956, 2894, 2872, 1584, 1562, 1462, 1426, 1248, 1215, 1052, 845, 817, 739, 694, 511, 470, 431, 403  $\text{cm}^{-1}$ .

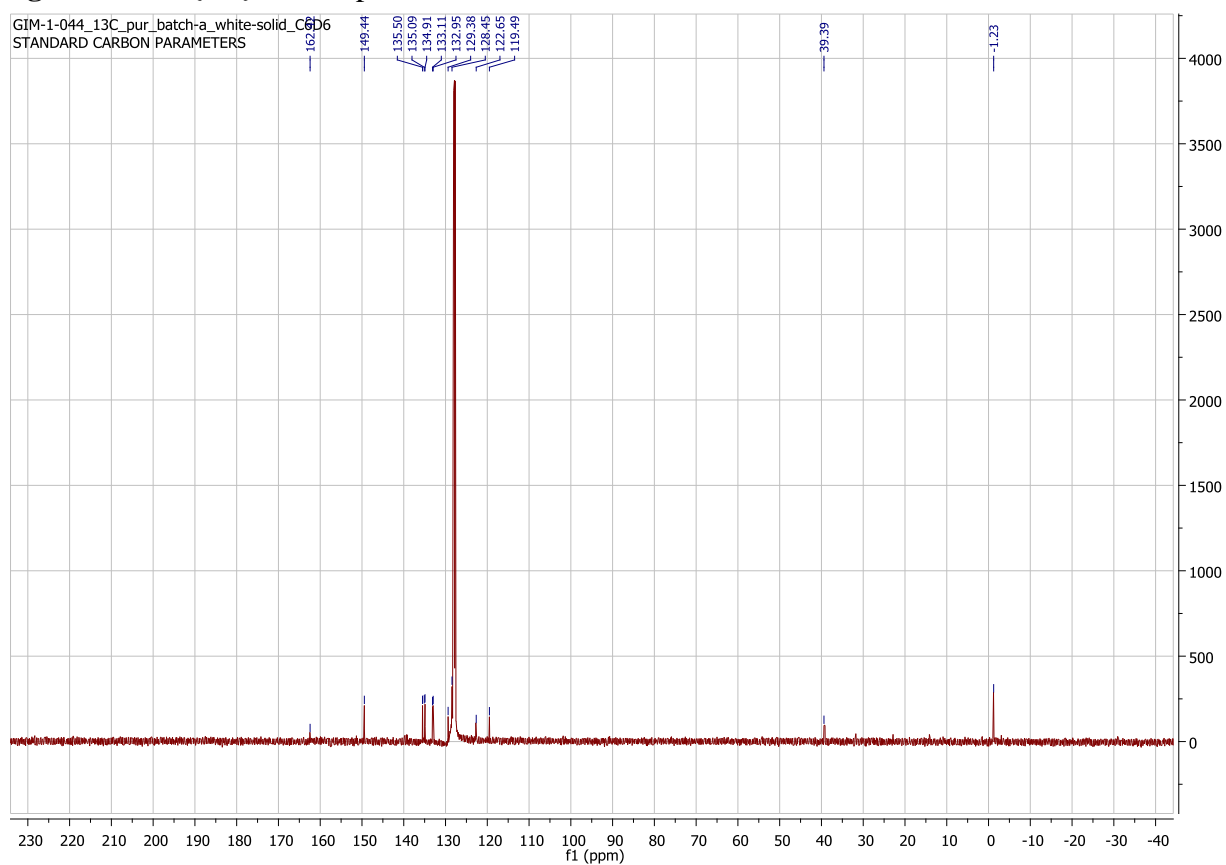
**Figure S1.**  $^1\text{H}$  NMR spectrum of **1a**



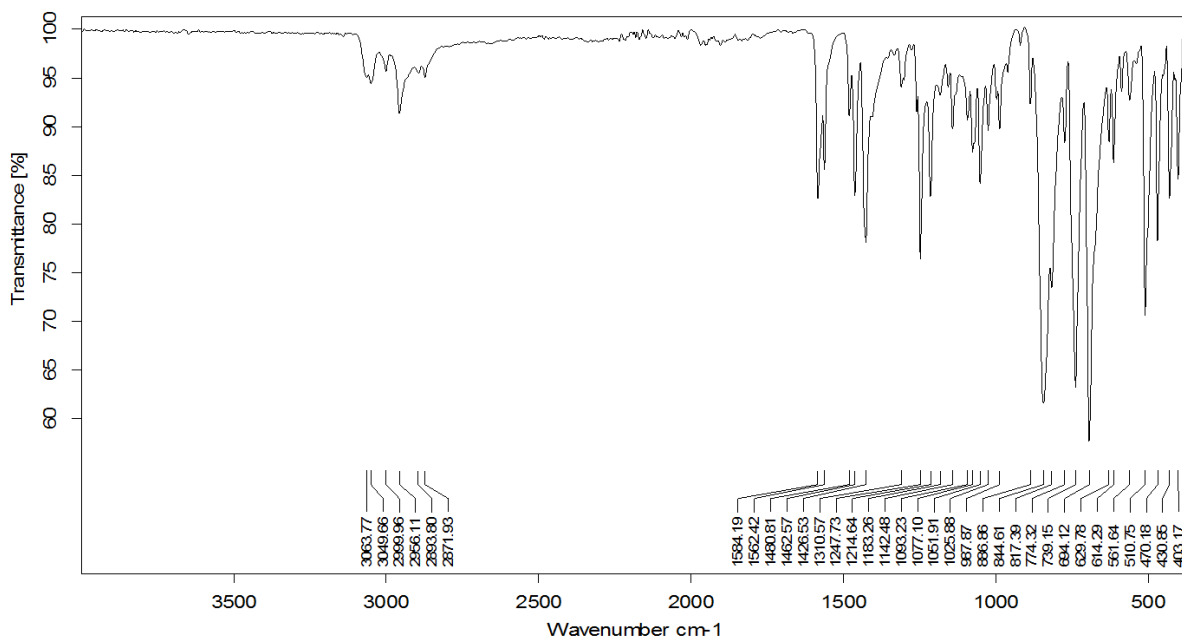
**Figure S2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1a**



**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1a**



**Figure S4.** FTIR spectrum of **1a** (neat, ATR)



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### Preparation of $P^iPr_2CH(SiMe_3)py$ (**1b**)

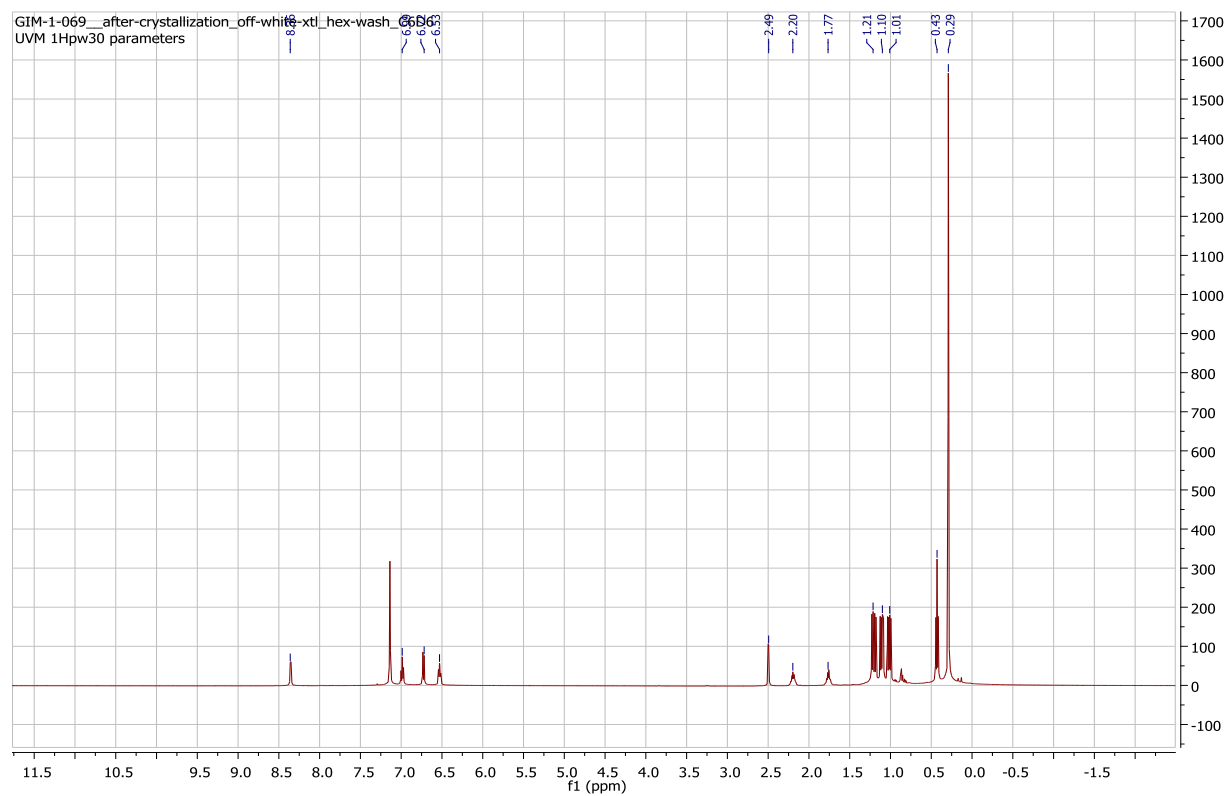
To a 50 mL round-bottom Schlenk flask equipped with a magnetic stir bar and sealed with a septum, butyllithium (6.6 mL of a 1.6 M solution in hexanes, 11 mmol, 2.1 equiv) and  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA, 1.5 mL, 10 mmol, 2.0 equiv) were added by syringe, resulting in a clear, slightly yellow solution. After stirring for 20 min, 2-picoline (0.49 mL, 5.0 mmol, 1.0 equiv) was added dropwise over 10 min. The resulting deep red solution was stirred for an additional 20 min and then cooled to 0 °C. Chlorotrimethylsilane (0.63 mL, 5.0 mmol, 1.0 equiv) was added dropwise over 30 min, and the resulting orange slurry was stirred for an additional 0.5 h, when 1 mL of Et<sub>2</sub>O was added. Finally, chlorodiisopropylphosphine (0.82 mL, 5.1 mmol, 1.0 equiv) was added dropwise over 30 min. The reaction mixture was allowed to warm to ambient temperature and stir an additional 5 h. Volatile components were removed under reduced pressure, resulting in a pale yellow solid that was extracted with 15 mL of hexanes. Solids were removed by filtration, and the filtrate was evaporated to 1.28 g of yellow powder. The crude ligand was redissolved in methylene chloride, then filtered through a 1 cm pad of silica gel. The solution was then evaporated to a solid, which was recrystallized at -28 °C from a minimum amount of pentane (~2 mL). A colorless crystalline solid was obtained (0.947 g, 3.36 mmol, 66%).

<sup>1</sup>H δ: 8.36 (ddd,  $J = 4.8, 1.9, 0.9$  Hz, 1 H), 7.99 (dt,  $J = 1.9, 7.6$  Hz, 1 H), 6.72 (*app* d,  $J = 7.8$  Hz, 1 H), 6.53 (ddd,  $J = 7.4, 4.9, 1.1$  Hz, 1 H), 2.49 (d,  $J = 3.0$  Hz), 2.20 (d sept,  $J = 7.3, 3.1$  Hz, 1 H), 1.77 (d sept,  $J = 6.9, 4.3$  Hz, 1 H), 1.21 (dd,  $J = 17.7, 7.6$  Hz, 3 H), 1.10 (dd,  $J = 13.5, 7.0$  Hz, 3 H), 1.01 (dd,  $J = 13.4, 6.9$  Hz, 3 H), 0.43 (*app.* t,  $J = 7.2$  Hz, 3 H), 0.29 (d,  $J = 0.8$  Hz, 9 H);

<sup>13</sup>C{<sup>1</sup>H} δ: 149.6, 135.4, 124.2, 119.8, 33.9 (d,  $J_{CP} = 43.7$  Hz), 23.9 (d,  $J_{CP} = 28.7$  Hz), 22.2 (d,  $J_{CP} = 7.5$  Hz), 21.1 Hz (9.3 Hz), 18.6 (*app.* t,  $J_{CP} = 17.0$  Hz), -0.17 (d,  $J_{CP} = 5.9$  Hz); <sup>31</sup>P{<sup>1</sup>H} δ:

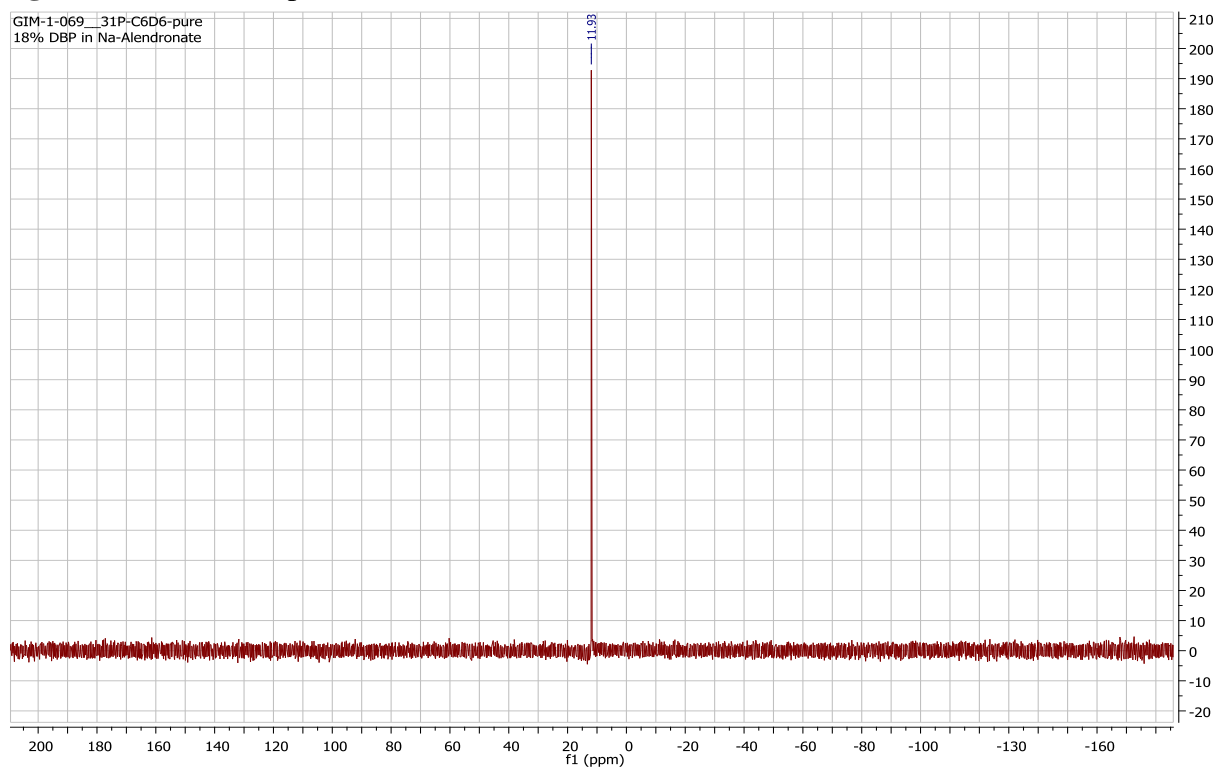
11.9 (s);  $^{29}\text{Si}\{^1\text{H}\}$   $\delta$ : 3.85. Bruker ATR FTIR: 3074, 2992, 2948, 2923, 2896, 2864, 1583, 1465, 1427, 1239, 1058, 832, 745, 506, 408  $\text{cm}^{-1}$ .

**Figure S5.**  $^1\text{H}$  NMR spectrum of **1b**

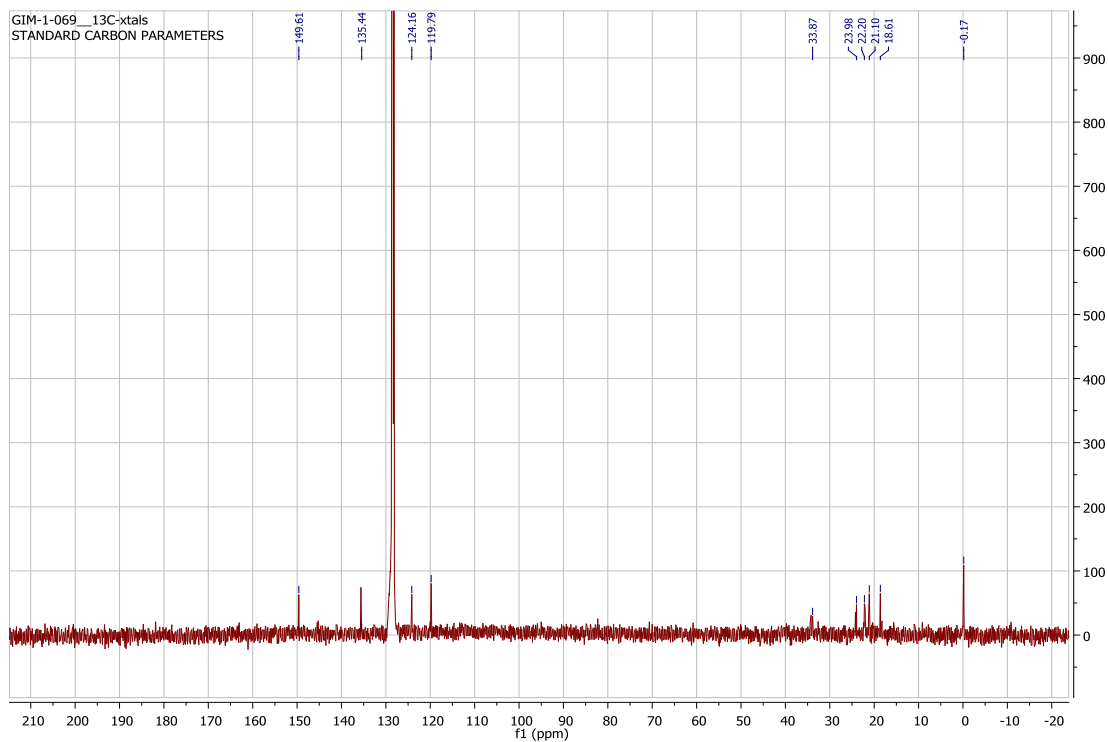




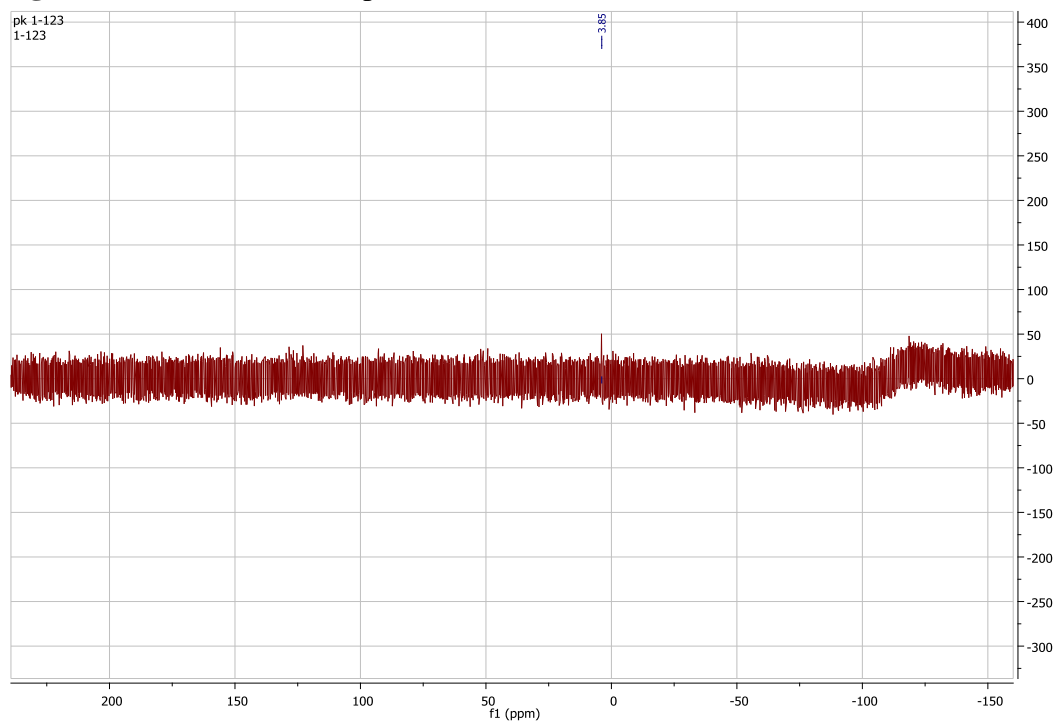
**Figure S6.**  $^{31}\text{P}$  NMR spectrum of **1b**



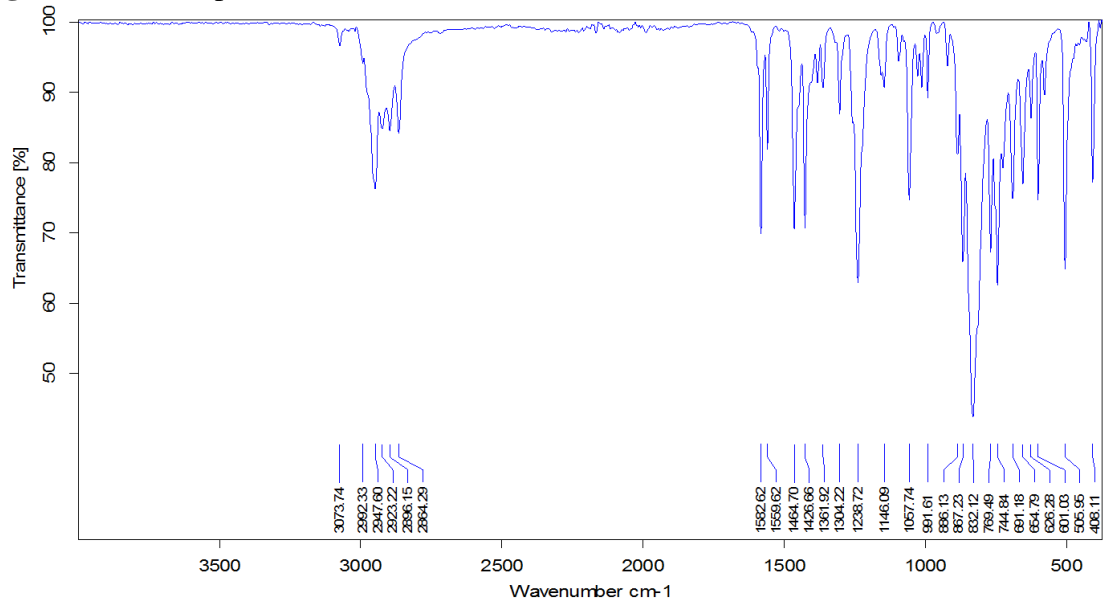
**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1b**



**Figure S8.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **1b**



**Figure S9.** FTIR spectrum of **1b** (neat, ATR)

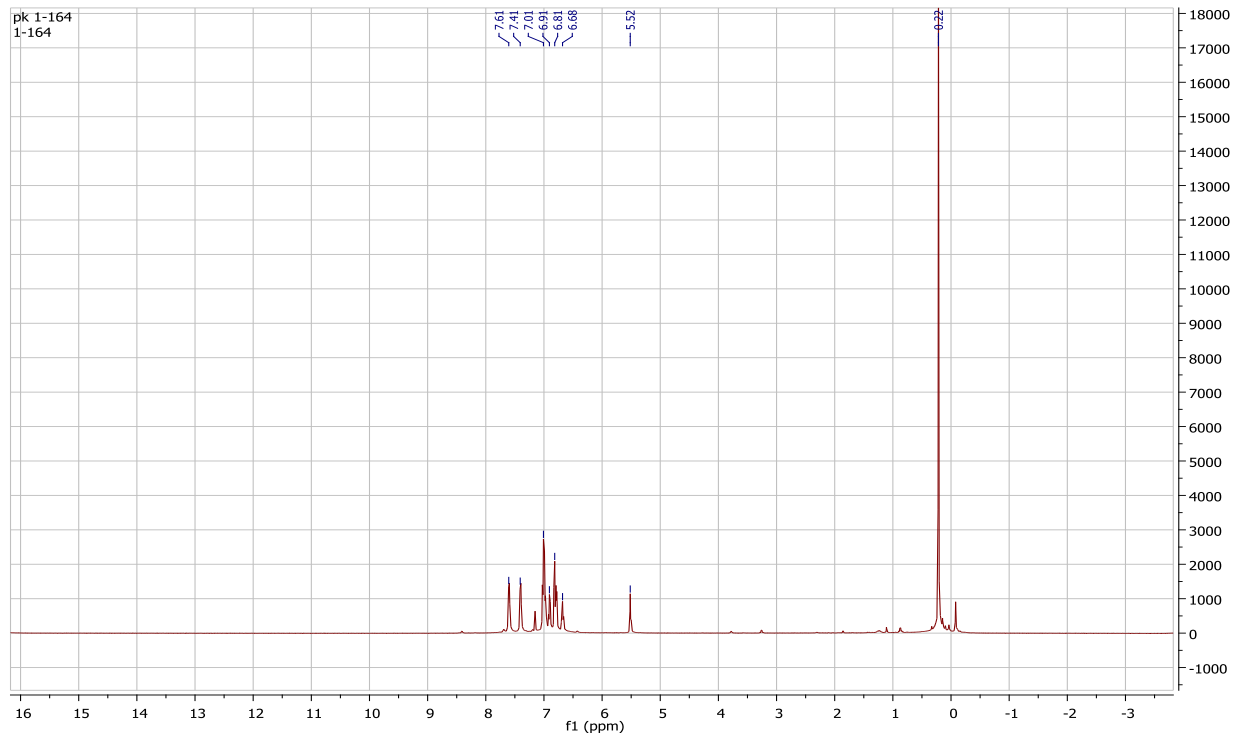


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### Preparation of $[\kappa^2\text{-PPh}_2\text{C}(\text{SiMe}_3)\text{py}]_2\text{Zn}$ (**2a**)

In a vial equipped with a magnetic stir bar, ligand **1a** (131 mg, 0.375 mmol, 2.1 equiv) was dissolved in Et<sub>2</sub>O (3.75 mL). BuLi (0.24 mL of a 1.6 M solution in hexanes, 0.40 mmol, 2.2 equiv) was added dropwise to the colorless solution, resulting in a clear, intensely orange solution that was stirred for 20 min. Solvent was removed under reduced pressure to afford a sticky red solid. The solid was dissolved in 1:1 ratio of pentane:hexanes and placed in -28 °C freezer for 18 h, which precipitated the orange, lithiated solid. The lithiated solid (128 mg, 0.375, 2.1 equiv) was dissolved in Et<sub>2</sub>O (3.75 mL). Solid, anhydrous zinc(II) chloride (25 mg, 0.18 mmol, 1.0 equiv) was then added in one portion. The reaction immediately became cloudy and lightened to a bright yellow. After stirring for 18 h, the slurry was. The solution was then evaporated to a yellow residue and dissolved in methylene chloride and hexanes, then put in a -28 °C freezer to yield a first crop (40.2 mg) of bright yellow solid. A second crop was obtained by drying the supernatant liquid and then crystallizing the residue in methylene chloride and hexanes (62.7 mg), for a combined yield of the title compound (103 mg, 0.134 mmol, 74%) as a yellow solid. <sup>1</sup>H δ: 7.63–7.59 (m, 2 H), 7.43–7.39 (m, 2 H), 7.04–6.98 (m, 4 H), 6.91 (t, *J* = 7.2 Hz, 1 H), 6.84–6.79 (m, 3 H), 6.70–6.67 (m, 1 H), 5.52 (t, *J* = 6.2 Hz, 1 H), 0.22 (s, 9 H); <sup>13</sup>C{<sup>1</sup>H} δ: 170.4 (s), 146.4 (s), 135.1 (d), 134.8 (d), 132.3 (d), 131.4 (d), 128.5–127.9 (m Ph), 107.2 (s), 2.05 (s SiMe<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} δ: -19.9. Bruker ATR FTIR: 3050, 3019, 2950, 2891, 1603, 1521, 1461, 1416, 1131, 1244, 1164, 1093, 1002, 961, 909, 829, 740, 693, 489, 466 cm<sup>-1</sup>. Anal calcd for C<sub>42</sub>H<sub>48</sub>N<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>Zn C, 66.00; H, 6.33; N, 3.66. Found C, 65.61; H, 6.17; N 3.56.

**Figure S10.**  $^1\text{H}$  NMR spectrum of **2a**



**Figure S11.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2a**

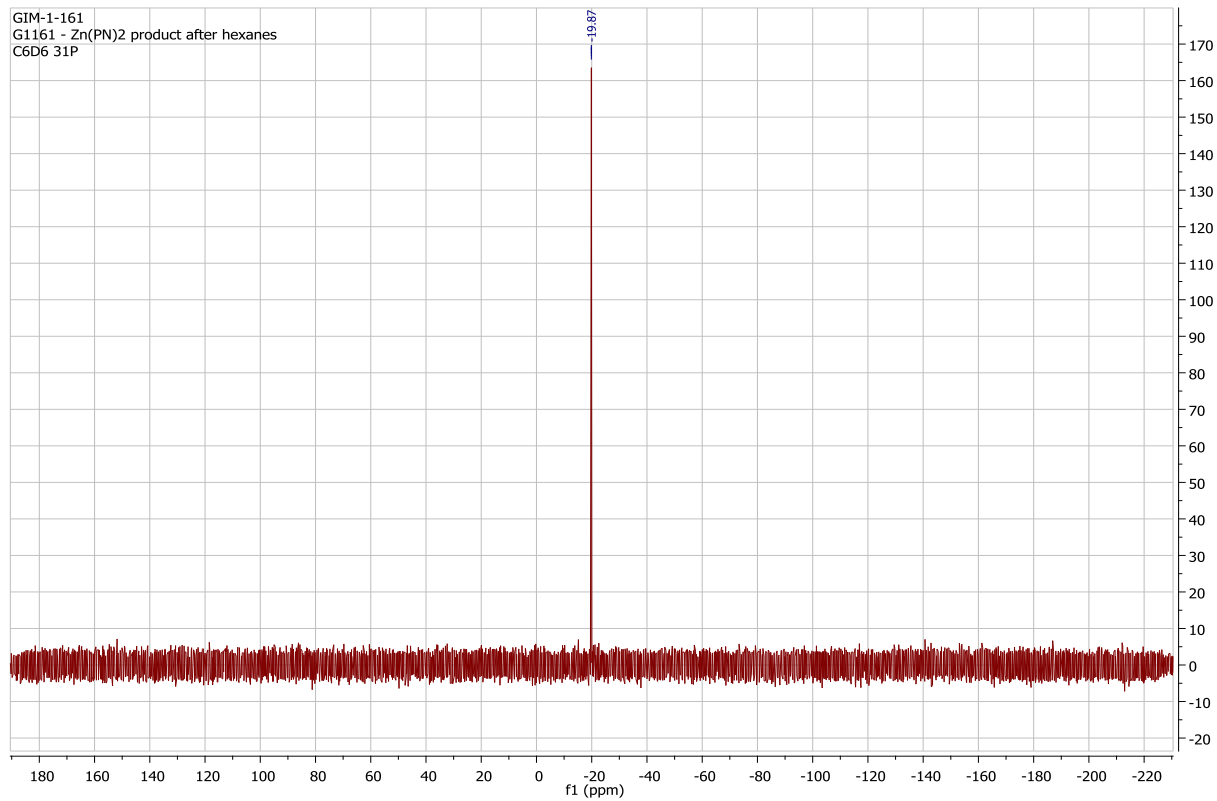


Figure S12.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2a**

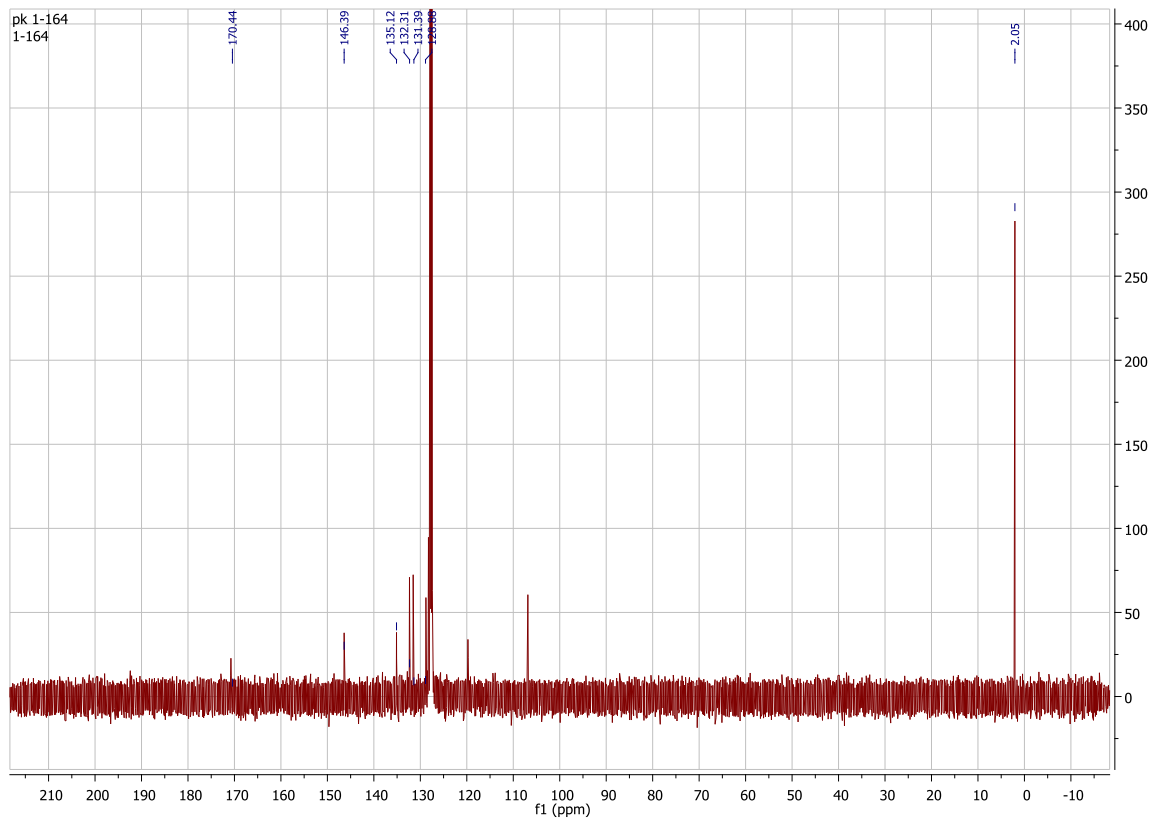
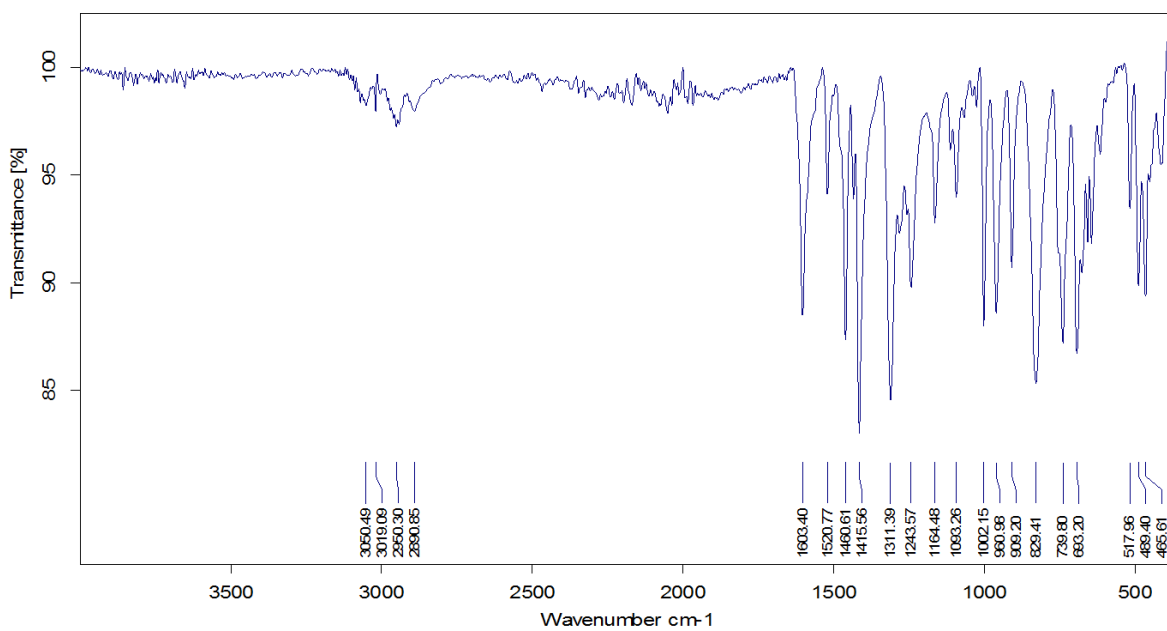


Figure S13. FTIR spectrum of **2a** (neat, ATR)

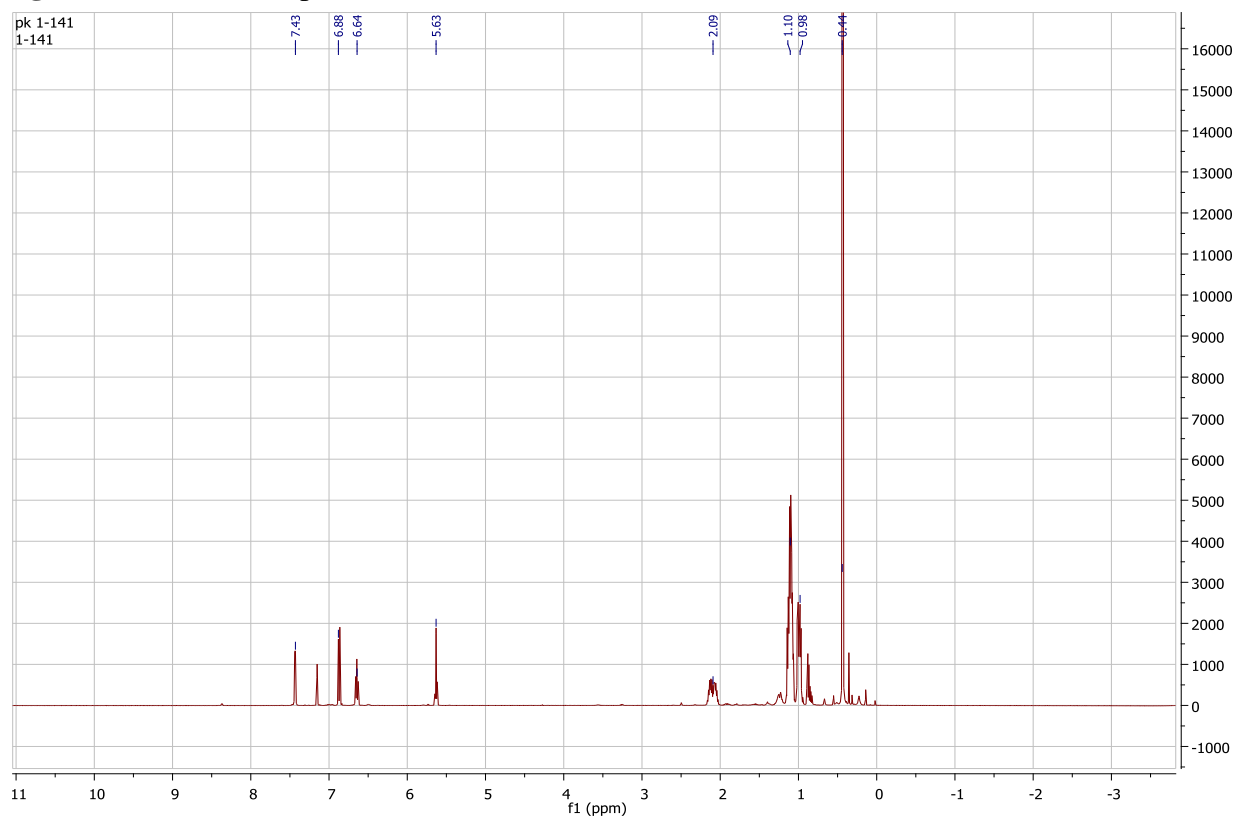


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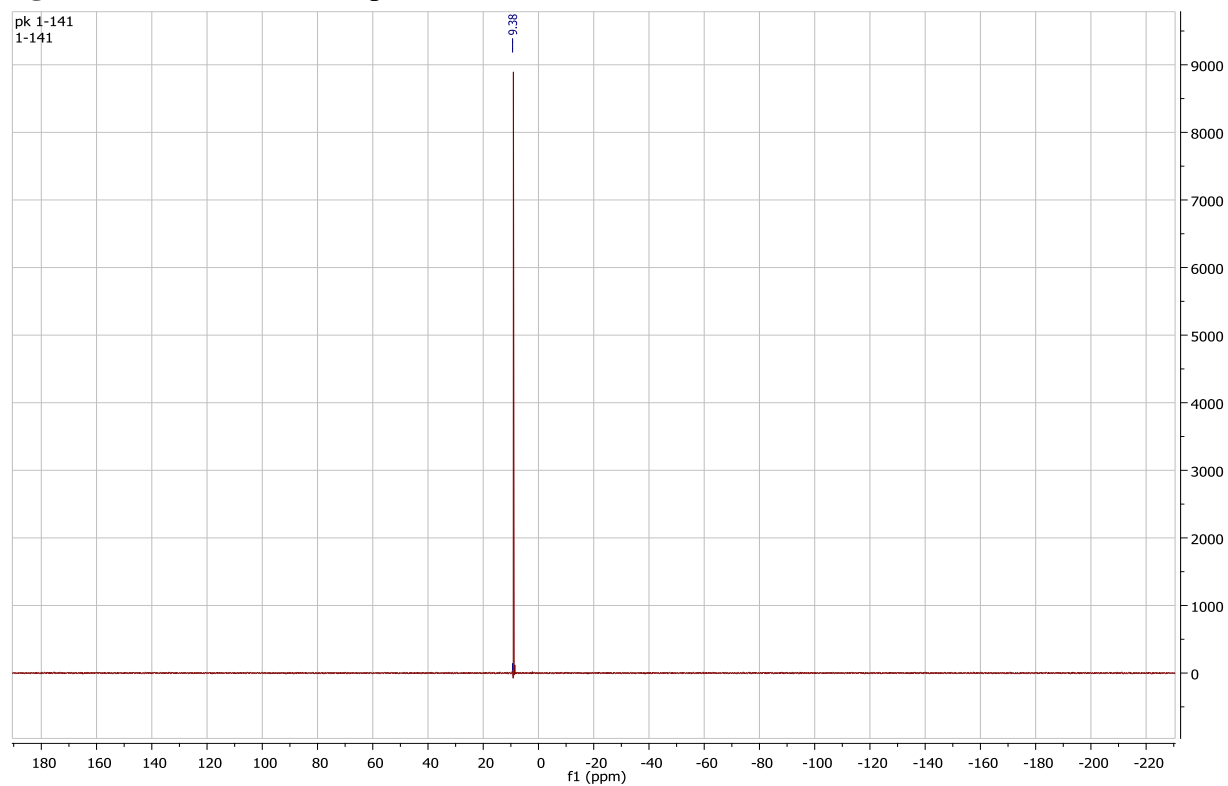
### Preparation of [ $\kappa^2$ -P<sup>*i*</sup>Pr<sub>2</sub>C(SiMe<sub>3</sub>)py]<sub>2</sub>Zn (**2b**)

In a vial equipped with a magnetic stir bar, ligand **1b** (105 mg, 0.373 mmol, 2.0 equiv) was dissolved in Et<sub>2</sub>O (5.0 mL). BuLi (0.24 mL of a 1.6 M solution in hexanes, 0.37 mmol, 2.0 equiv) was added dropwise to the colorless solution, resulting in an intensely orange solution that was stirred for 20 min. Solvent was removed under reduced pressure to give a sticky red-orange solid. The solid was dissolved in 1:1 ratio of pentane:hexanes and placed in -28 °C freezer for 18 h, which precipitated an orange solid. The solid (102 mg, 0.375, 2.1 equiv) was dissolved in Et<sub>2</sub>O (3.75 mL). Solid, anhydrous zinc(II) chloride (30 mg, 0.22 mmol, 1.2 equiv) was then added in one portion. The reaction immediately became cloudy and lightened to yellow. After stirring for 18 h, the slurry was filtered through a medium fritted glass filter, and evaporated to a yellow residue. The solid was redissolved in a minimum amount of methylene chloride, filtered, and then diluted with 10 mL hexanes and evaporated under reduced pressure to yield the title compound as a bright yellow solid (103 mg, 0.164 mmol, 88%). <sup>1</sup>H δ: 7.43 (d, *J* = 5.6 Hz, 1 H), 6.88 (d, *J* = 9.0 Hz, 1 H), 6.64 (d, *J* = 7.7 Hz, 1 H), 5.63 (d, *J* = 6.1 Hz, 1 H), 2.16–2.05 (m, 2 H), 1.15–1.08 (m, 9 H), 1.02–0.97 (m, 3 H), 0.44 (d, *J* = 1.4 Hz, 9 H); <sup>13</sup>C{<sup>1</sup>H} δ: 171.4 (*app. t*, *J*<sub>CP</sub> = 6.2 Hz), 146.8 (*app. t*, *J*<sub>CP</sub> = 3.2 Hz), 134.6 (s), 119.9 (*app. t*, *J*<sub>CP</sub> = 6.1 Hz), 105.9 (s), 51.9 (m), 27.4 (*app. t*, *J*<sub>CP</sub> = 13.0 Hz), 24.5 (*app. t*, *J*<sub>CP</sub> = 15.2 Hz), 22.9 (*app. t*, *J*<sub>CP</sub> = 5.4 Hz), 20.5 (s), 20.4 (*app. t*, *J*<sub>CP</sub> = 2.7 Hz), 19.9 (s), 2.9 (s); <sup>31</sup>P{<sup>1</sup>H} δ: 9.4; <sup>29</sup>Si{<sup>1</sup>H} δ: -9.4. Bruker ATR FTIR: 2954, 2893, 2867, 1603, 1461, 1412, 1308, 1237, 996, 954, 904, 824, 754, 671, 642 cm<sup>-1</sup>. Anal Calcd for C<sub>30</sub>H<sub>54</sub>N<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>Zn C, 57.53; H, 8.69; N, 4.47. Found C, 57.17; H, 8.63; N, 4.22.

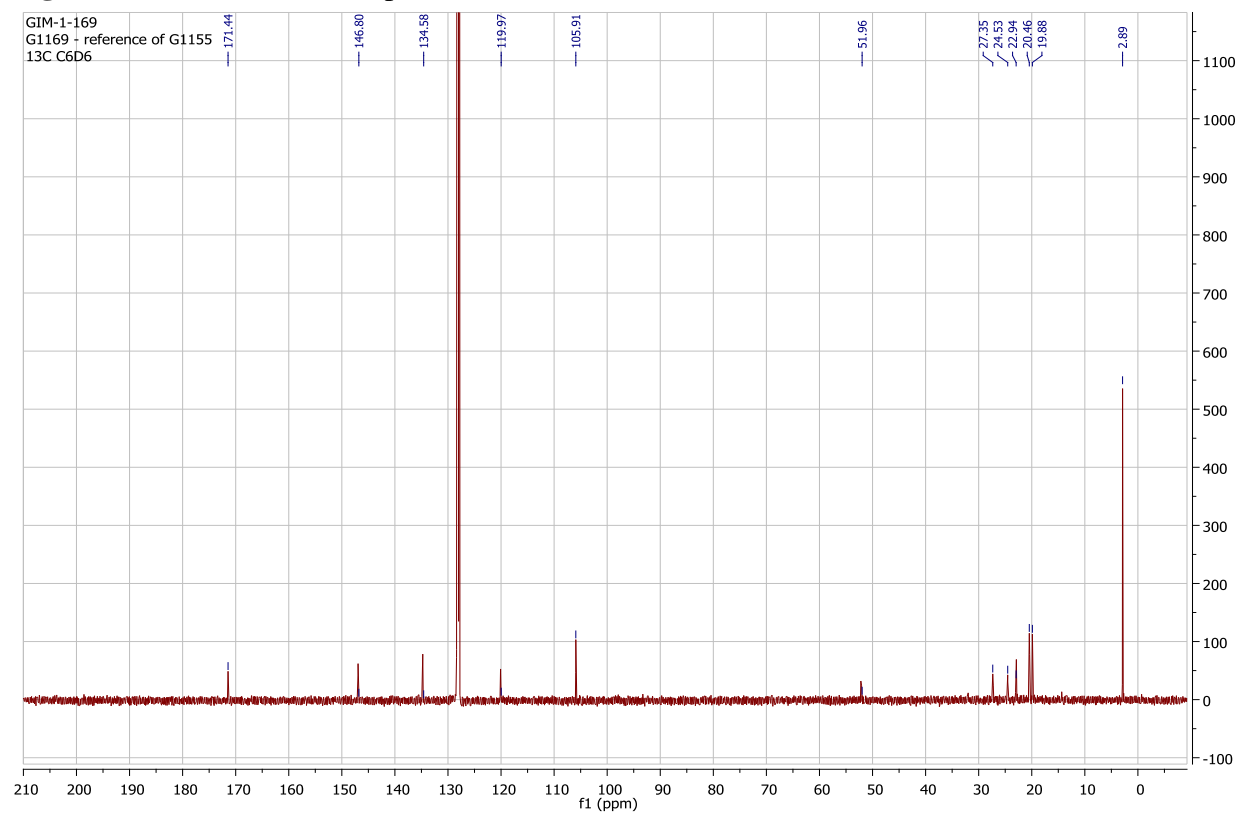
**Figure S14.**  $^1\text{H}$  NMR spectrum of **2b**



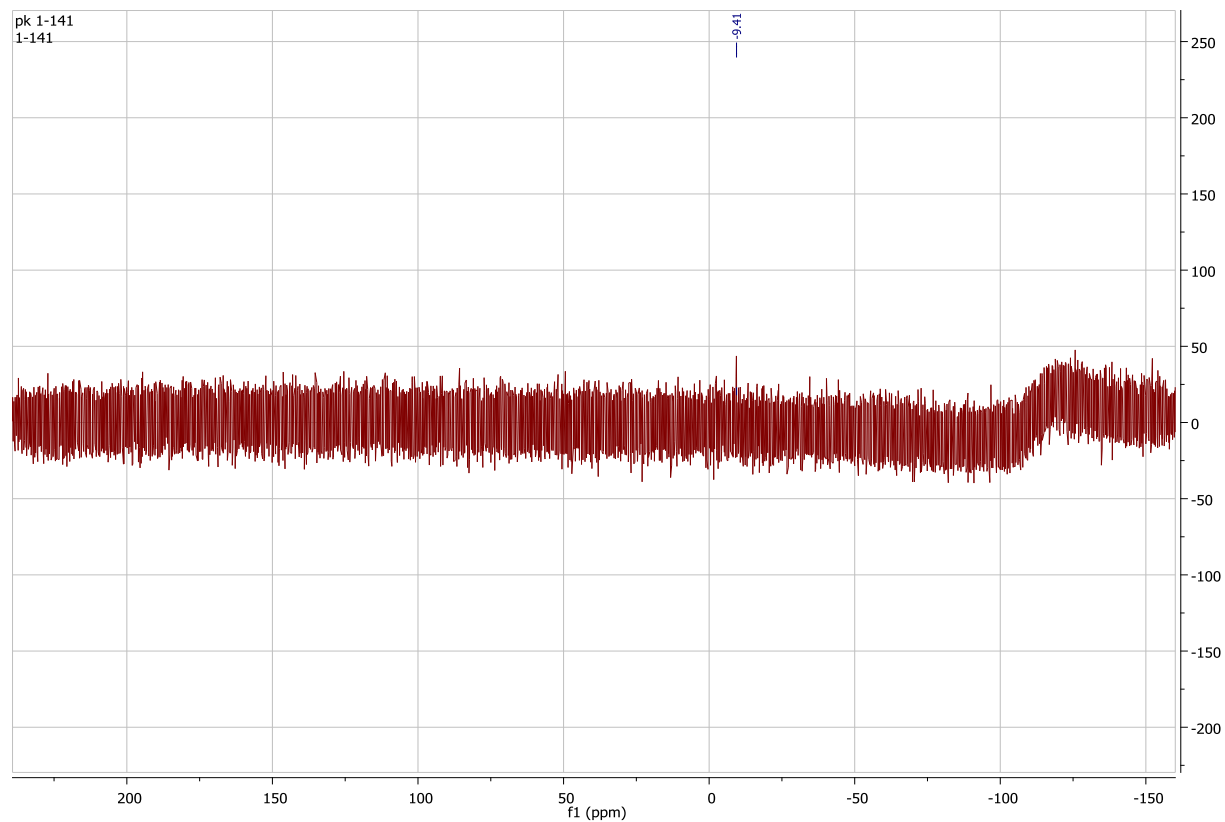
**Figure S15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2b**



**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2b**

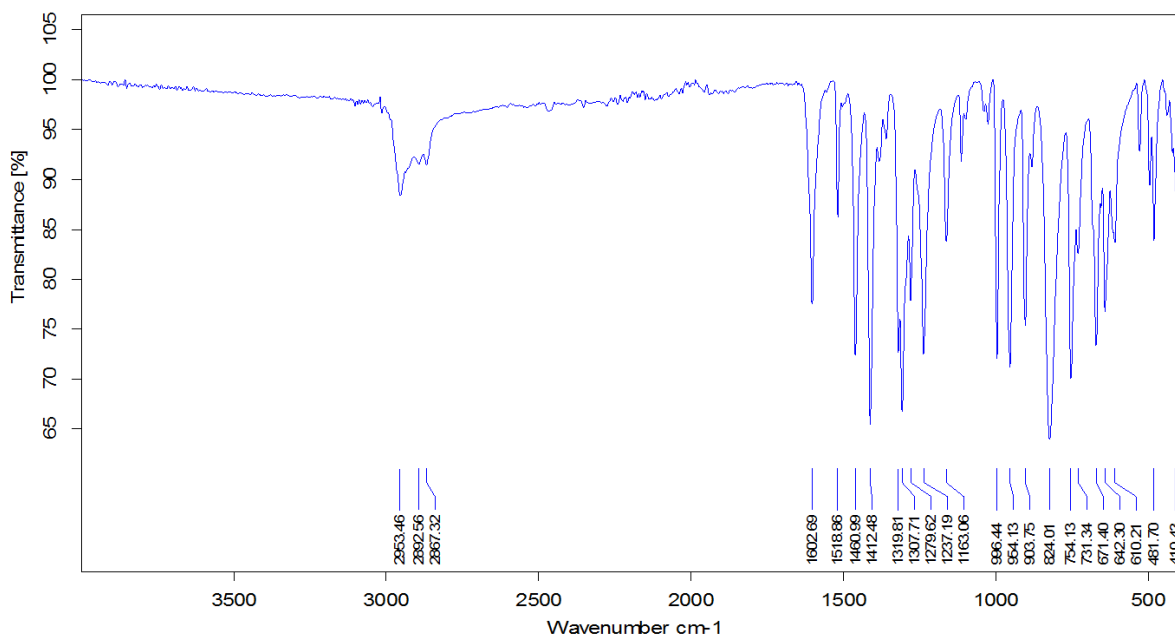


**Figure S17.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **2b**





**Figure S18.** FTIR spectrum of **2b** (neat, ATR)



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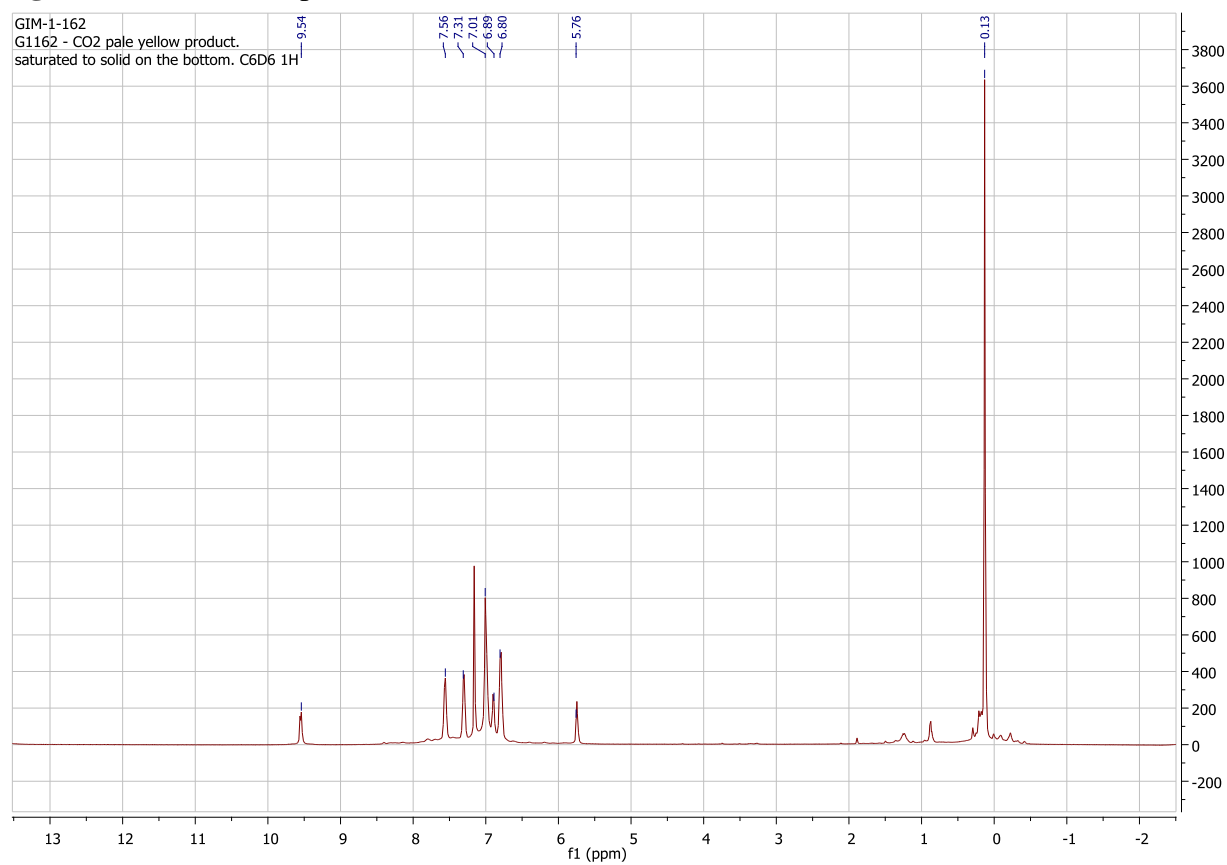
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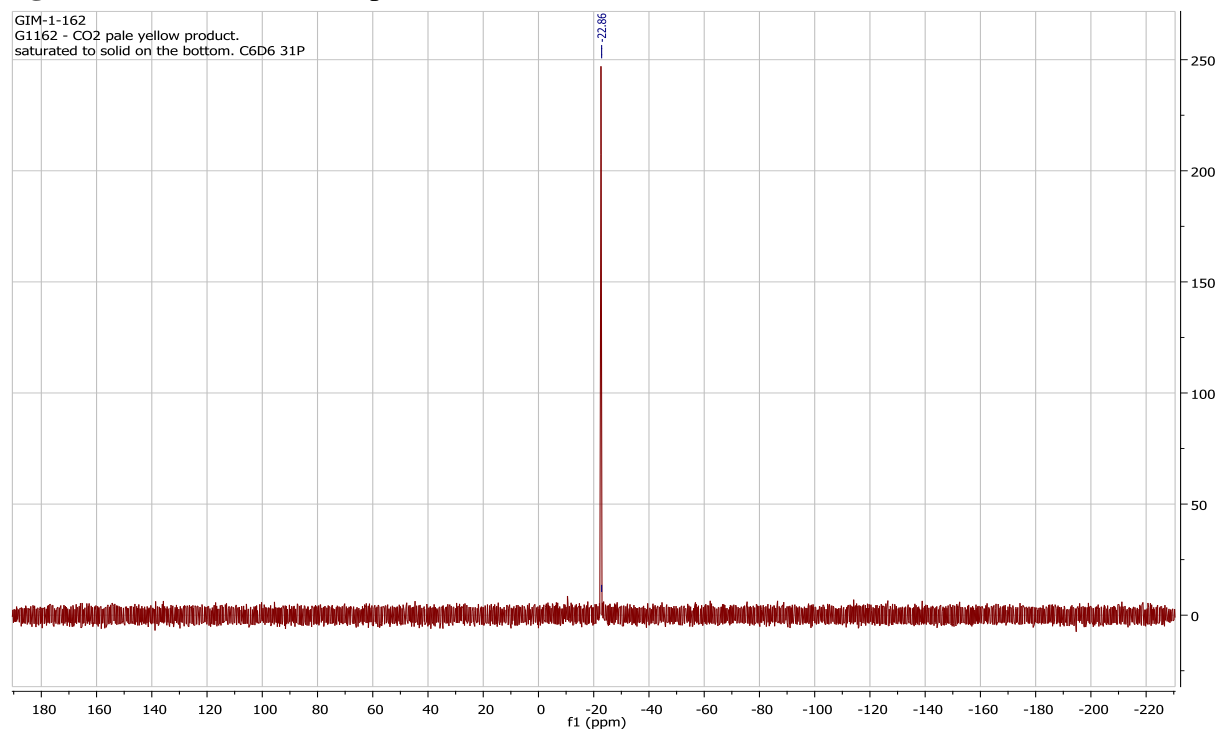
Preparation of  $[\kappa^2\text{-P}^i\text{Ph}_2\text{CC}(\text{O})\text{OSiMe}_3\text{py}]_2\text{Zn}$  (**3a**)

To a 50 ml reaction tube equipped with a magnetic stir bar and a threaded teflon seal, a solution of **2a** (40 mg, 0.052 mmol) in benzene (5 mL) was degassed by freezing by a freeze-pump-thaw sequence. Carbon dioxide gas (1 atm) was added to the frozen orange solution via a vacuum manifold, and the reaction was allowed to warm to ambient temperature with vigorous stirring. The reaction mixture lightened in color within minutes. The benzene was evaporated under reduced pressure after two hours, and the resulting pale yellow solid was suspended in pentane, filtered, and evaporated again to remove all solvent to give a yellow powder (29.2 mg, 0.034 mmol, 65%).  $^1\text{H}$   $\delta$ : 9.54 (d,  $J = 8.9$  Hz, 1 H), 7.58–7.54 (m, 2 H), 7.31 (*app* q,  $J = 6.7$  Hz, 2 H), 7.02–6.97 (m, 4 H), 6.89 (t,  $J = 7.4$  Hz, 1 H), 6.82–6.77 (m, 3 H), 5.76 (t,  $J = 6.2$  Hz, 1 H), 0.13 (s, 9 H);  $^{13}\text{C}\{^1\text{H}\}$   $\delta$ : 168.2, 166.8, 145.5, 137.9, 133.2, 132.1, 129.8, 0.5;  $^{31}\text{P}\{^1\text{H}\}$   $\delta$ : –22.9 (s). Bruker ATR FTIR: 3054, 3014, 2955, 2896, 1613, 1596, 1464, 1425, 1328, 1247, 1223, 1111, 1045, 1011, 956, 841, 780, 738, 691, 512, 478  $\text{cm}^{-1}$ . Anal Calcd for  $\text{C}_{44}\text{H}_{48}\text{N}_2\text{O}_4\text{P}_2\text{Si}_2\text{Zn}$  C, 62.00; H, 5.68; N, 3.29. Found C, 62.39; H, 5.55; N 3.25.

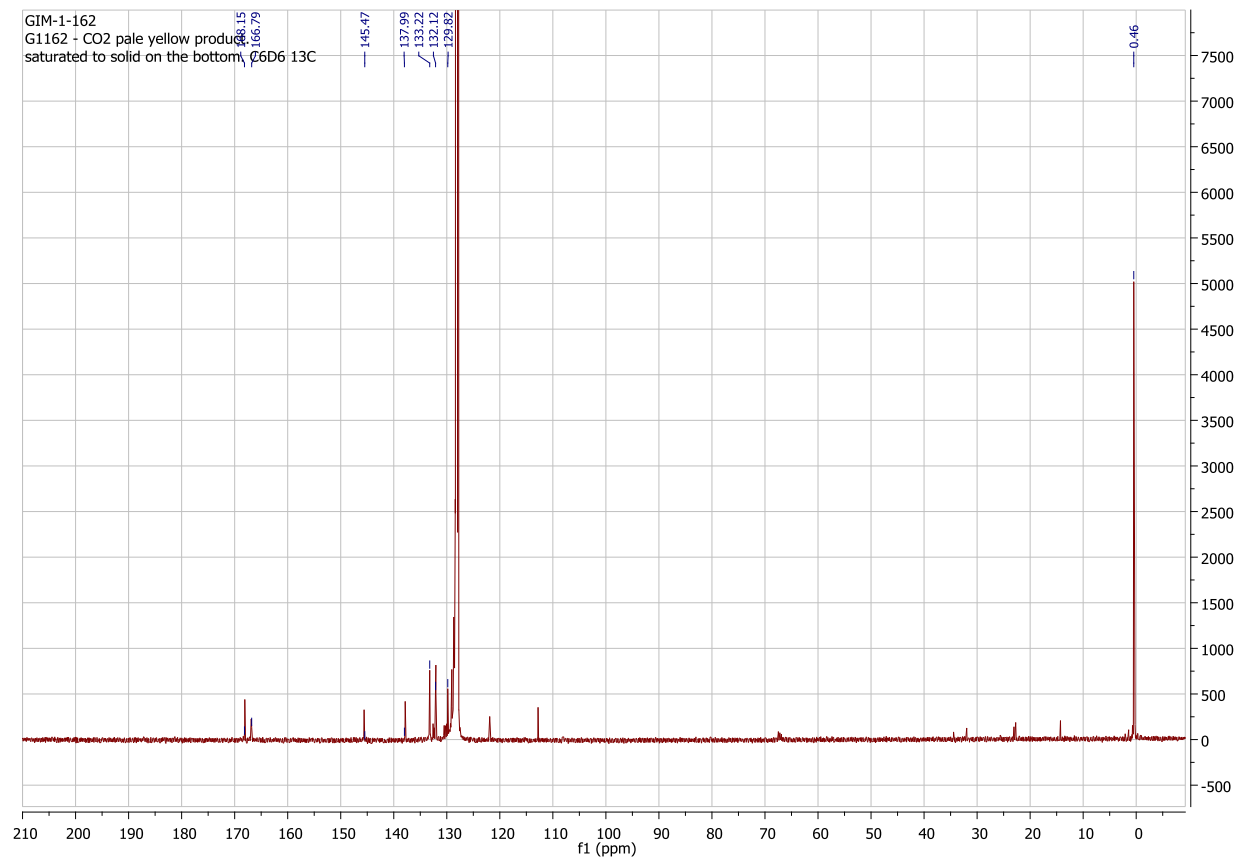
**Figure S19.**  $^1\text{H}$  NMR spectrum of **3a**



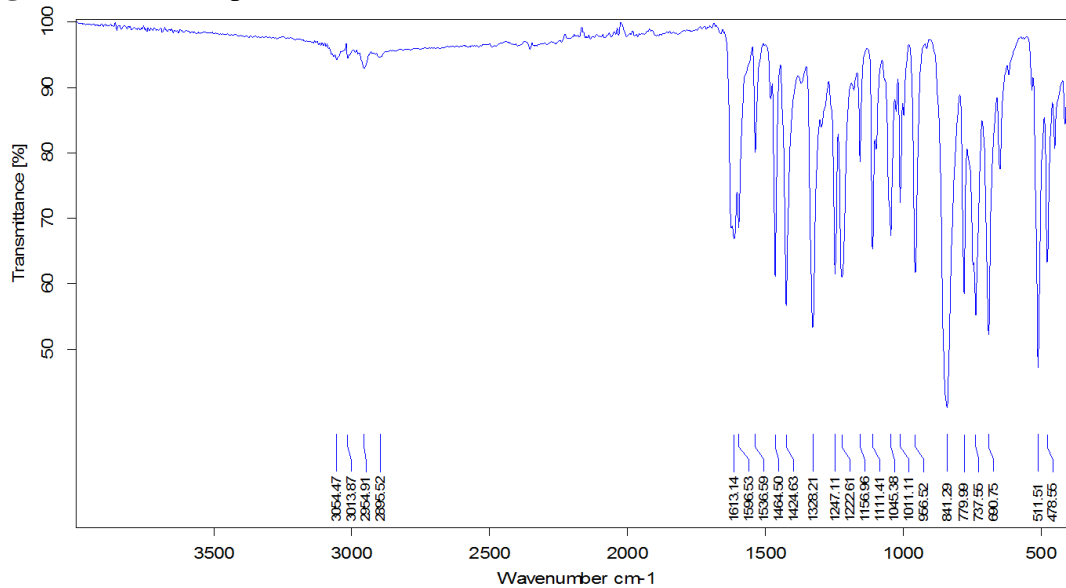
**Figure S20.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3a**



**Figure S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3a**



**Figure S22.** FTIR spectrum of **3a** (neat, ATR)

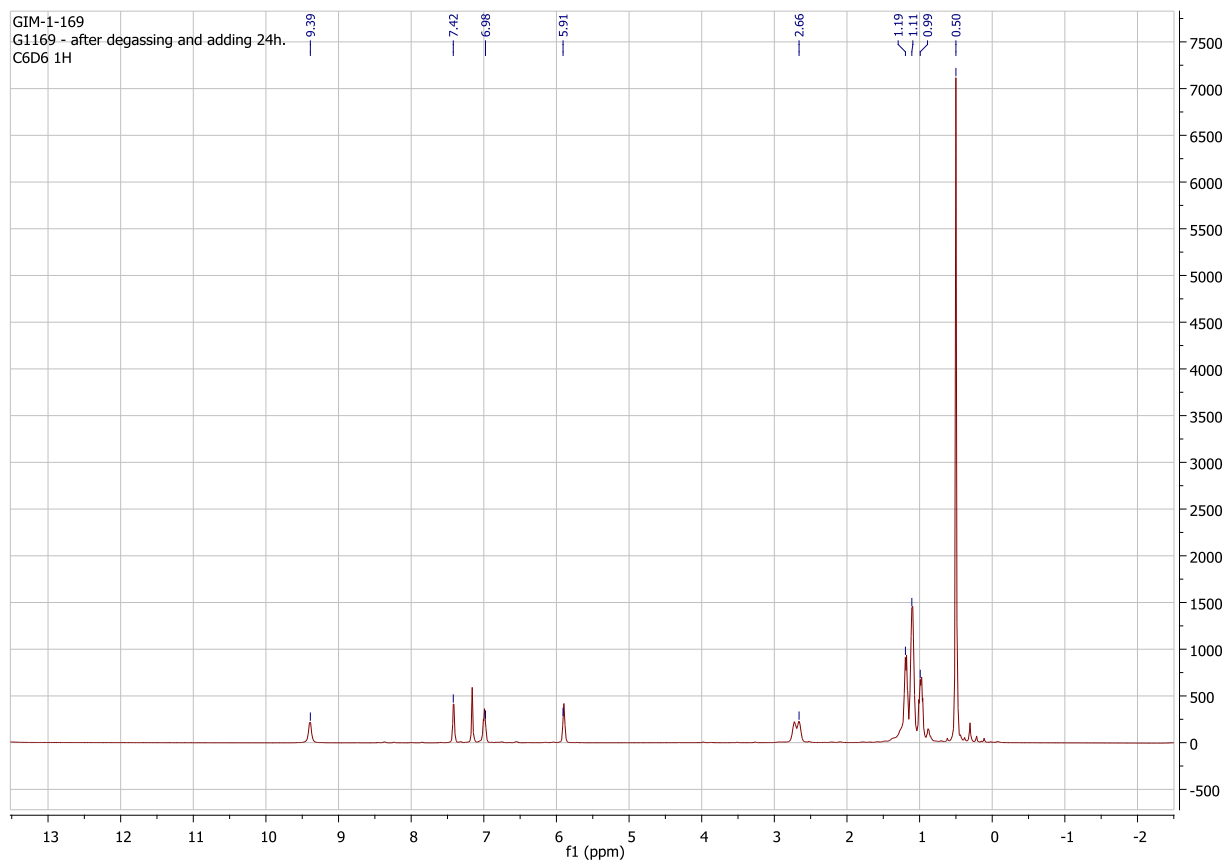


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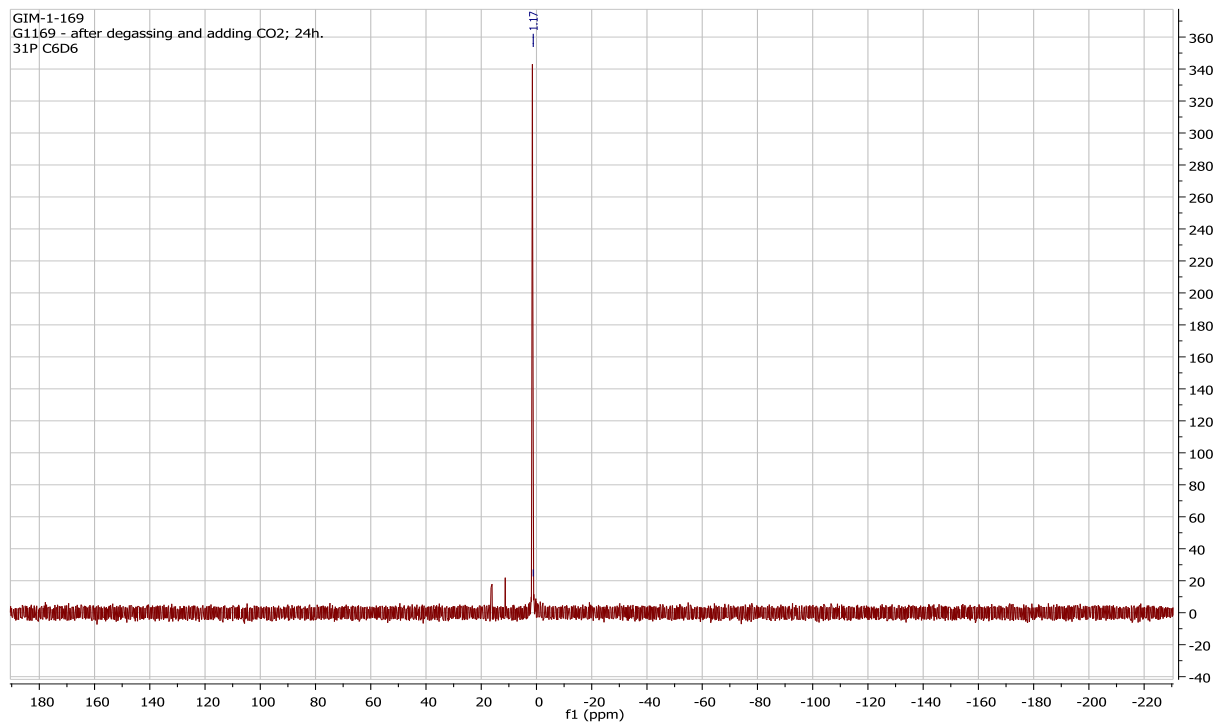
Preparation of [ $\kappa^2$ -P<sup>i</sup>Pr<sub>2</sub>CC(O)OSiMe<sub>3</sub>)py]<sub>2</sub>Zn (**3b**)

To a 50 ml reaction tube equipped with a magnetic stir bar and a threaded teflon seal, a solution of **2b** (40 mg, 0.064 mmol) in benzene (5 mL) was degassed by freezing by a freeze-pump-thaw sequence. Carbon dioxide gas was added to the frozen orange solution, and the reaction was allowed to warm to ambient temperature with vigorous stirring. The benzene was evaporated under reduced pressure after two hours, and the resulting pale yellow solid was suspended in pentane, filtered, and evaporated to remove all solvent to afford a yellow powder (25.3 mg, 0.035 mmol, 55%). <sup>1</sup>H δ: 9.39 (*br s*, 1 H), 7.42 (*d*, 1 H), 6.98 (*t*, 1 H), 5.91 (*t*, Hz), 2.70–2.64 (*m*, 2 H), 1.21–1.17 (*m*, 3 H), 1.11–1.09 (*m*, 6 H), 1.01–0.96 (*m*, 3 H), 0.50 (*s*, 9 H); <sup>13</sup>C{<sup>1</sup>H} δ: 168.6, 167.7 (*app t*, *J*<sub>CP</sub> = 8.5 Hz), 145.5, 137.1, 121.8, 112.0, 66.6 (*br m*), 25.5 (*app t*, *J*<sub>CP</sub> = 14.6 Hz), 24.3 (*app t*, *J*<sub>CP</sub> = 16.0 Hz), 22.0 (*app t*, *J*<sub>CP</sub> = 5.4 Hz), 20.3 (*br s*), 19.9, 19.6, 0.94; <sup>31</sup>P{<sup>1</sup>H} δ: 1.17 (*br. s*); <sup>29</sup>Si{<sup>1</sup>H} δ: 14.7; Bruker ATR FTIR: 2952, 2868, 1612, 1594, 1464, 1422, 1329, 1244, 1214, 1109, 1037, 1006, 947, 844, 780, 515 cm<sup>-1</sup>. Anal Calcd for C<sub>32</sub>H<sub>56</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Si<sub>2</sub>Zn C, 53.66; H, 7.88; N, 3.91. Found C, 53.43; H, 7.55; N, 3.85.

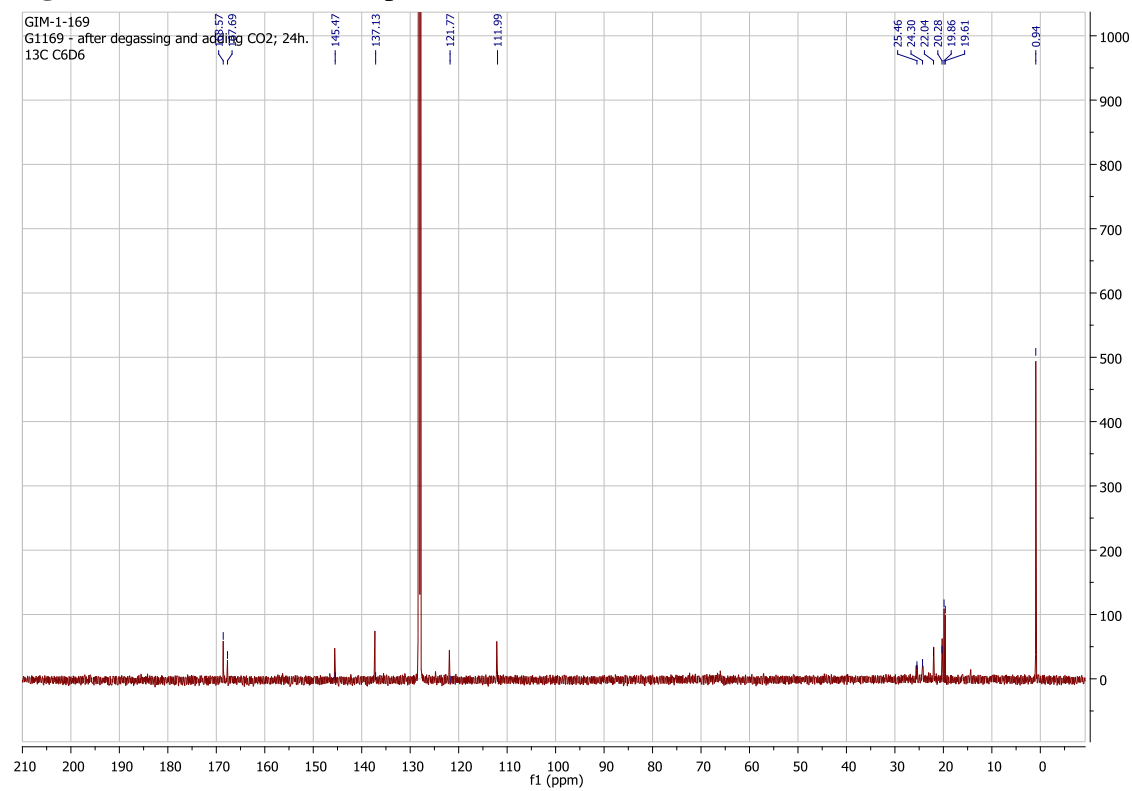
**Figure S23.**  $^1\text{H}$  NMR spectrum of **3b**



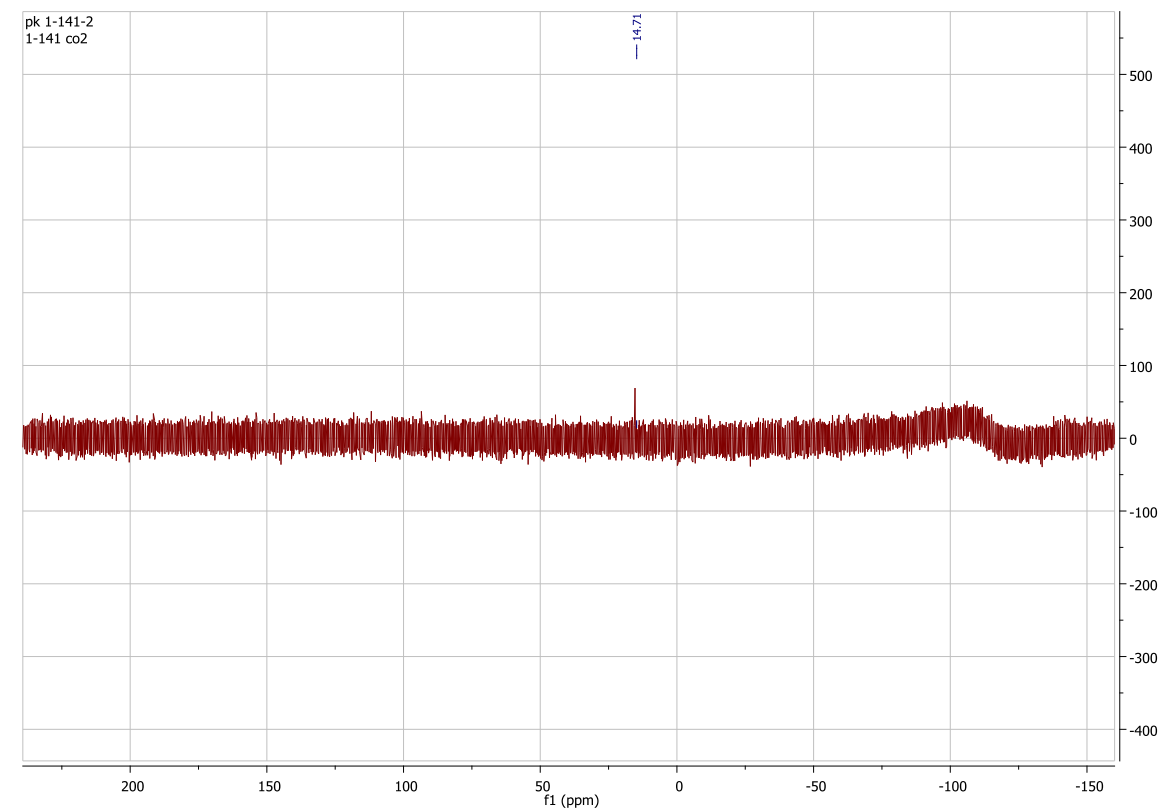
**Figure S24.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3b**



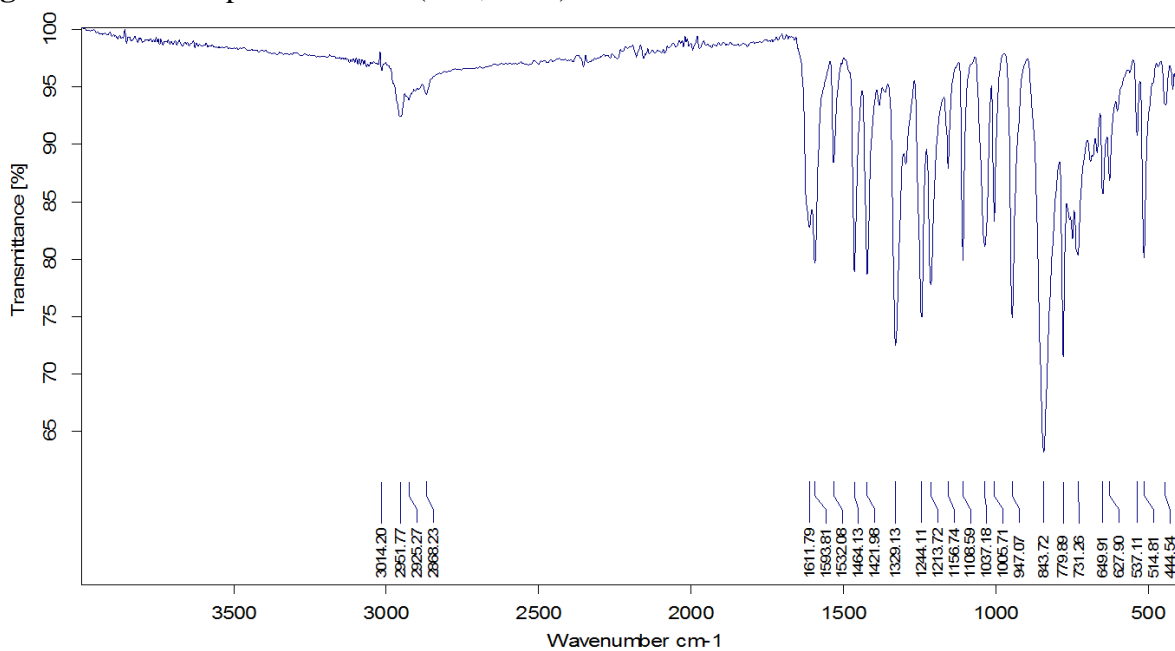
**Figure S25.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3b**



**Figure S26.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **3b**



**Figure S27.** FTIR spectrum of **3b** (neat, ATR)



C:\Program Files\OPUS_65\MEAS\GIM1169a.0	GIM1169a	ATR platinum Diamond 1 Ref	11/12/2012
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### X-ray crystallographic data

X-Ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer

(MoK $\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) at 125 K. Suitable crystals of each complex were mounted in a nylon

loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and

standard difference map techniques and were refined by full-matrix least squares procedures on

$F^2$  with SHELXTL (version 6.14).<sup>1</sup> All non-hydrogen atoms were refined anisotropically.

Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model.

**Table S1.** Crystal data and structure refinement parameters for **2a** and **3b**.

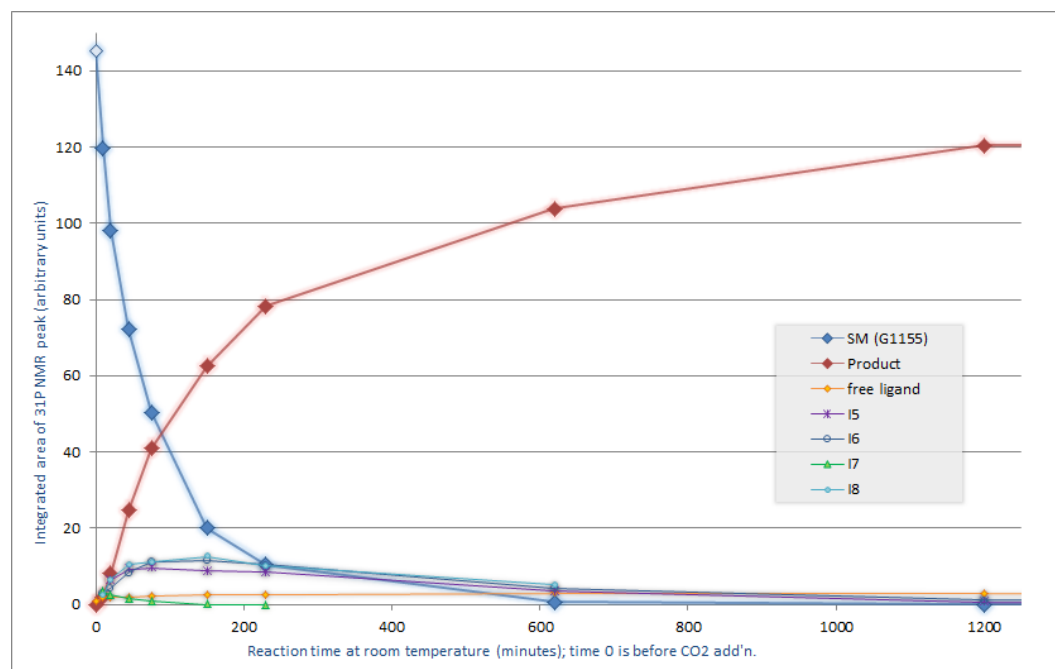
	<b>2a</b>	<b>3b</b>
formula	C <sub>42</sub> H <sub>46</sub> N <sub>2</sub> P <sub>2</sub> Si <sub>2</sub> Zn	C <sub>32</sub> H <sub>54</sub> N <sub>2</sub> O <sub>4</sub> PSi <sub>2</sub> Zr
M	762.30	714.26
crystal system	monoclinic	triclinic
color	yellow	yellow
<i>a</i> /Å	9.3979(17)	9.3607(7)
<i>b</i> /Å	16.240(3)	4.5830(11)
<i>c</i> /Å	13.490(2)	15.9704(13)
$\alpha$ /°	90	63.8570(10)
$\beta$ /°	100.870(2)	81.9860(10)
$\gamma$ /°	90	78.5180(10)
unit cell vol./Å <sup>3</sup>	2021.9(6)	1914.6(3)
space group	P2 <sub>1</sub>	P-1
Z	2	2
$\theta$ range/°	1.54 to 23.34	1.42 to 27.48
$\mu$ /mm <sup>-1</sup>	0.777	0.822
<i>N</i>	17240	22768
<i>N</i> <sub>ind</sub>	5853	8684
<i>R</i> <sub>int</sub>	0.0381	0.0162
Completeness/%	99.9	98.7
<i>R</i> <sub>1</sub> <sup>d</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0291	0.0245
<i>wR</i> <sub>2</sub> <sup>e</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0565	0.0636
Flack( <i>x</i> )	-0.003(9)	
$\Delta\rho_{\max}$ ; $\Delta\rho_{\min}$ /e Å <sup>3</sup>	0.286; -0.272	0.359; -0.228
GoF on <i>R</i> <sub>1</sub>	0.957	1.026

<sup>d</sup> $R_1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$ . <sup>e</sup> $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$ .

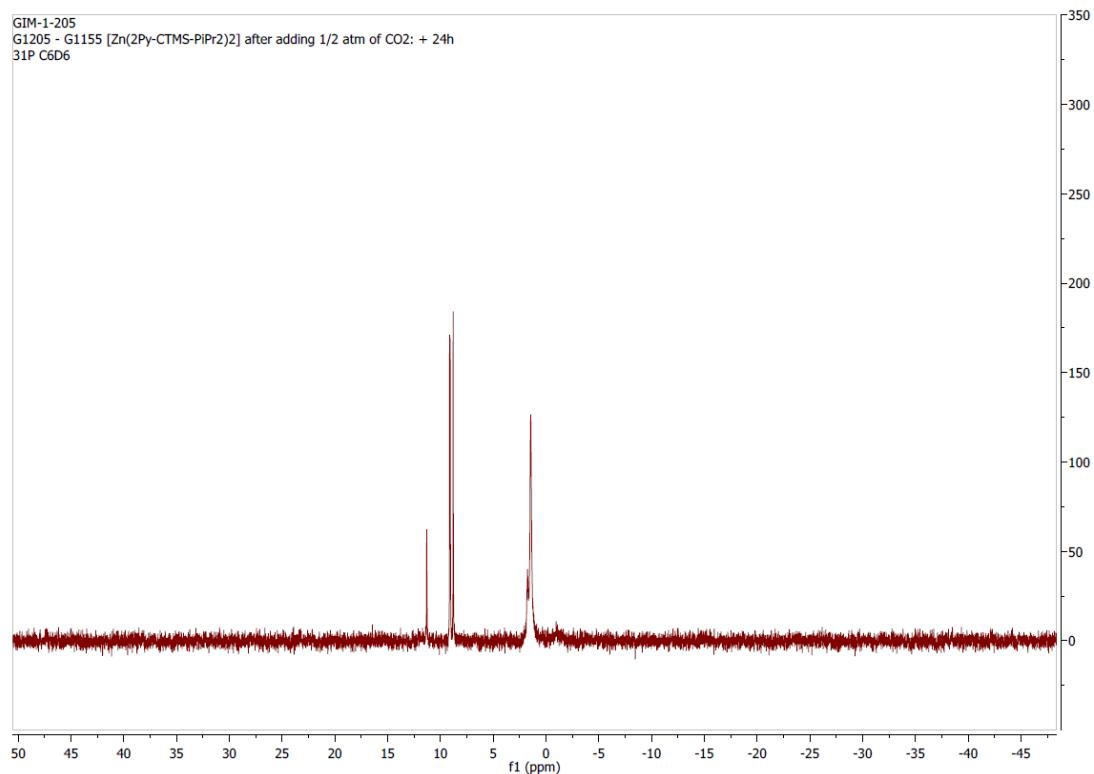
## Kinetic data

A PTFE-valved NMR tube was charged with stock, benzene- $d_6$  solutions of **2b**. The solution was degassed by a freeze-pump-thaw cycle, and bone dry  $\text{CO}_2$  was introduced via a vacuum manifold at a measured pressure. Using the volume of  $\text{CO}_2$ , calculated from the difference in volume of an NMR tube of known total volume, an approximate value for the concentration of  $\text{CO}_2$  can be calculated based on the solubility of  $\text{CO}_2$  in benzene. The NMR tube was sealed,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were collected at 295 K. The reaction was monitored for at least four half-lives of **2b** consumption. Relative integration of  $^{31}\text{P}$  NMR resonances was for most runs because experiments with an internal standard (capillary of  $\text{PPh}_3$ ) demonstrated no significant change in total concentration over time.

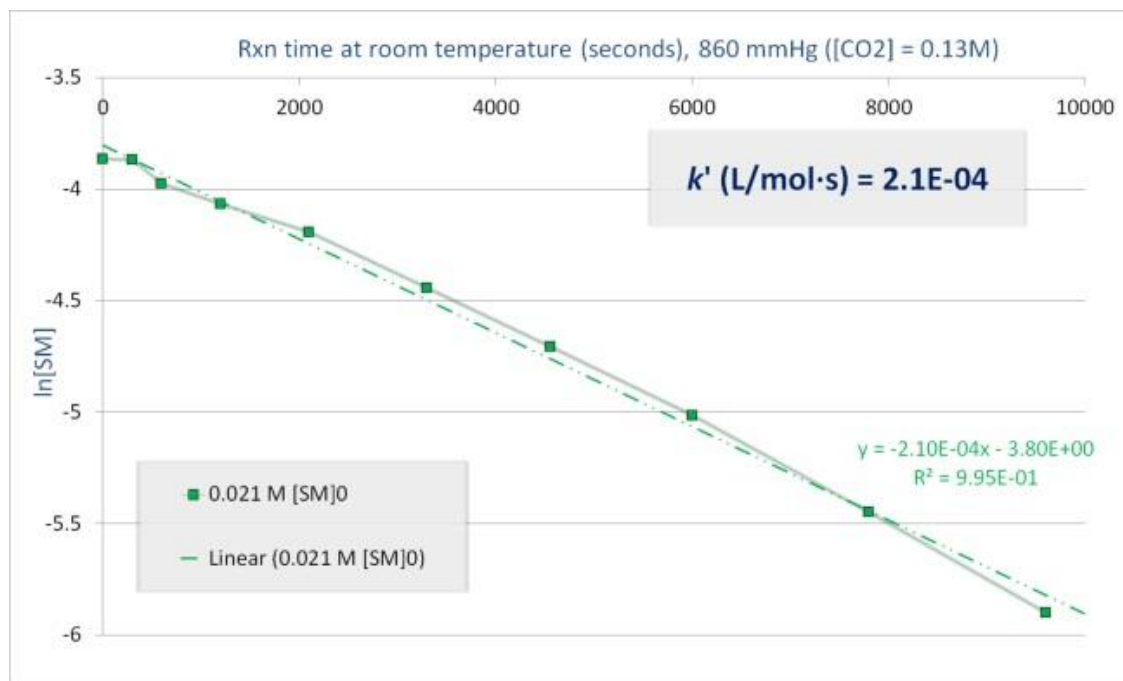
**Figure S28.** Distribution of species plot for the reaction of **2b** under 1.1 atm  $\text{CO}_2$  pressure to illustrate the relative concentration of intermediate species.



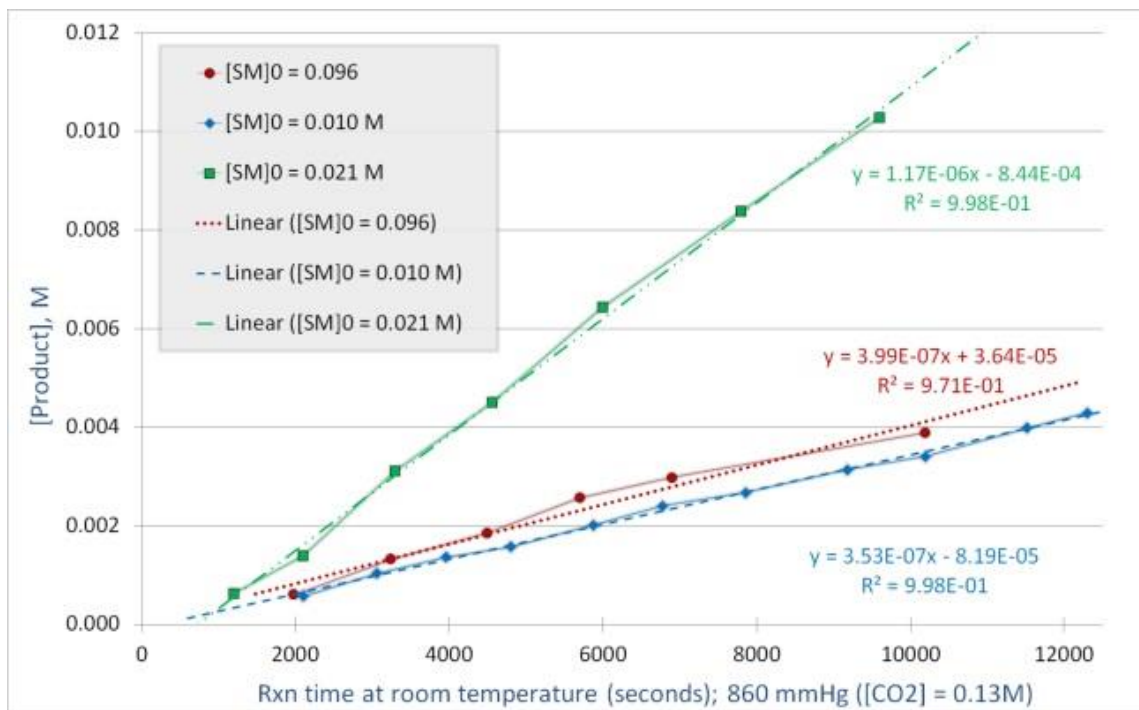
**Figure 29.** Example  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum during a kinetic run.



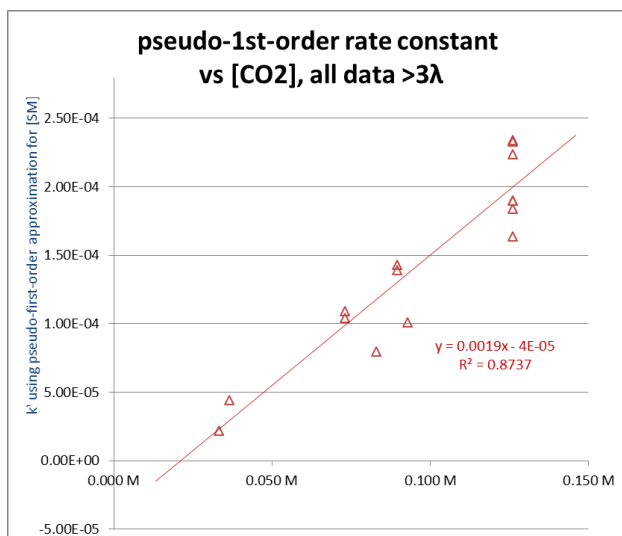
**Figure S30.** First-order consumption of starting material **2b** at 1.1 atm  $\text{CO}_2$  pressure.



**Figure S31.** Initial product (**3a**) formation shows a linear dependence up to ~50% conversion at 0.010, 0.021 M **2b**. At higher concentrations of starting material (0.096 M), the linear formation of **3b** ends earlier in the reaction.



**Figure S32.** Plot of pseudo first-order rate constant against calculated  $\text{CO}_2$  concentration for kinetic runs.



## References

1. Sheldrick, G. M., *Acta Cryst.* **2008**, *A64*, 112-122.