

## Supporting Information

# Methylene-Bridged, Intramolecular Donor-Acceptor Systems Based on Rare-Earth Metals and Phosphinomethanides

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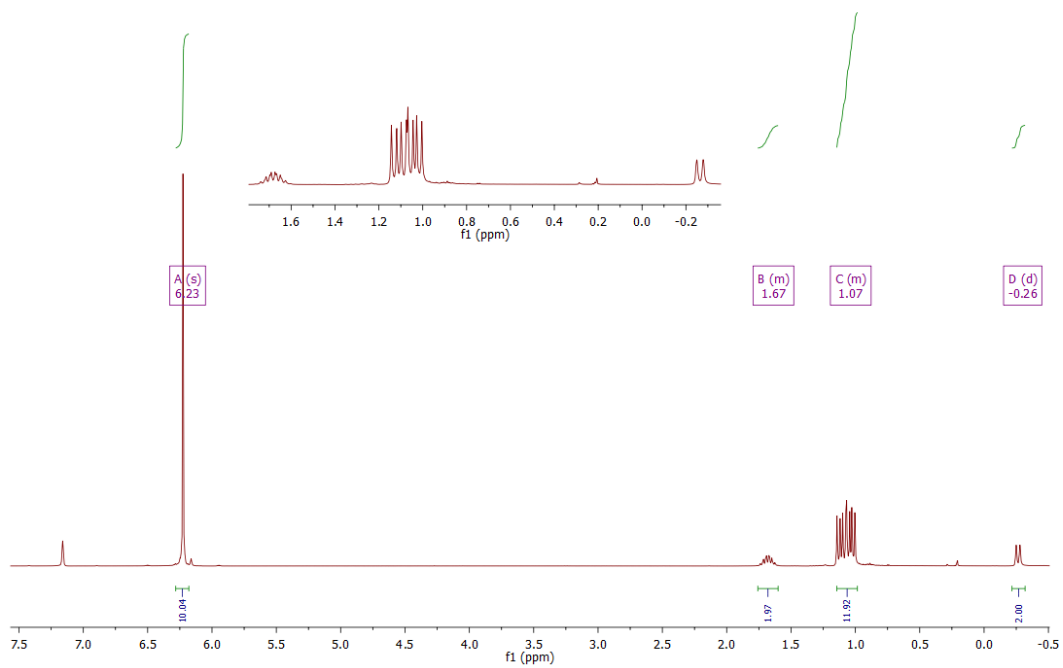
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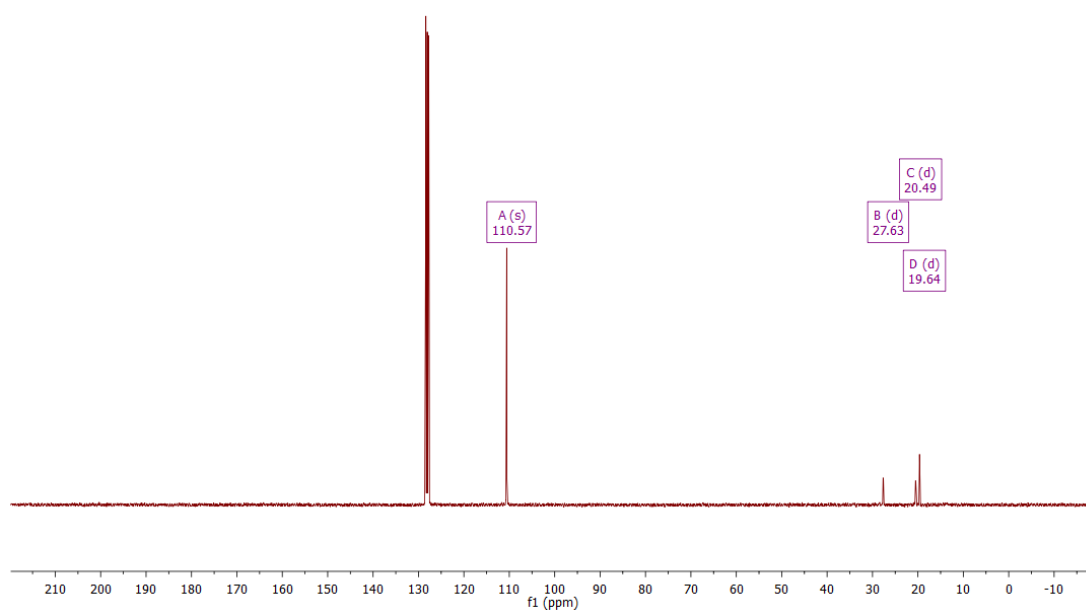
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### NMR spectroscopic Data

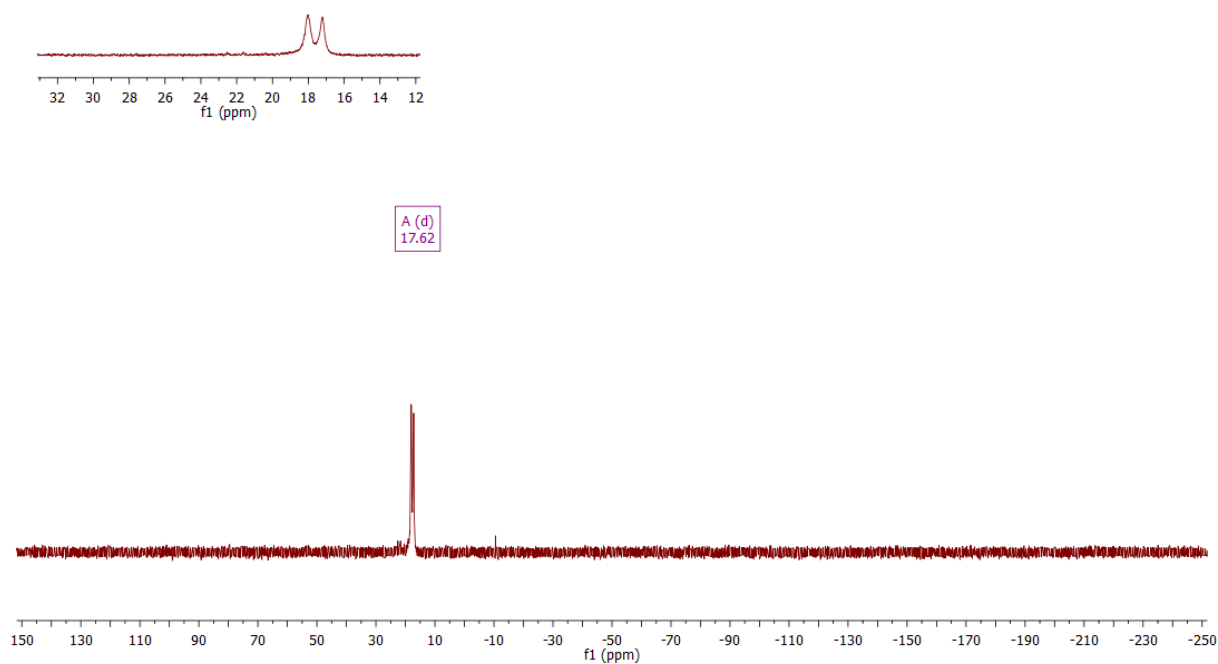
|                    |         |
|--------------------|---------|
| Compound <b>1</b>  | S3 – S4 |
| Compound <b>4</b>  | S4 – S7 |
| Compound <b>10</b> | S7 – S8 |
| Compound <b>14</b> | S8 – S9 |



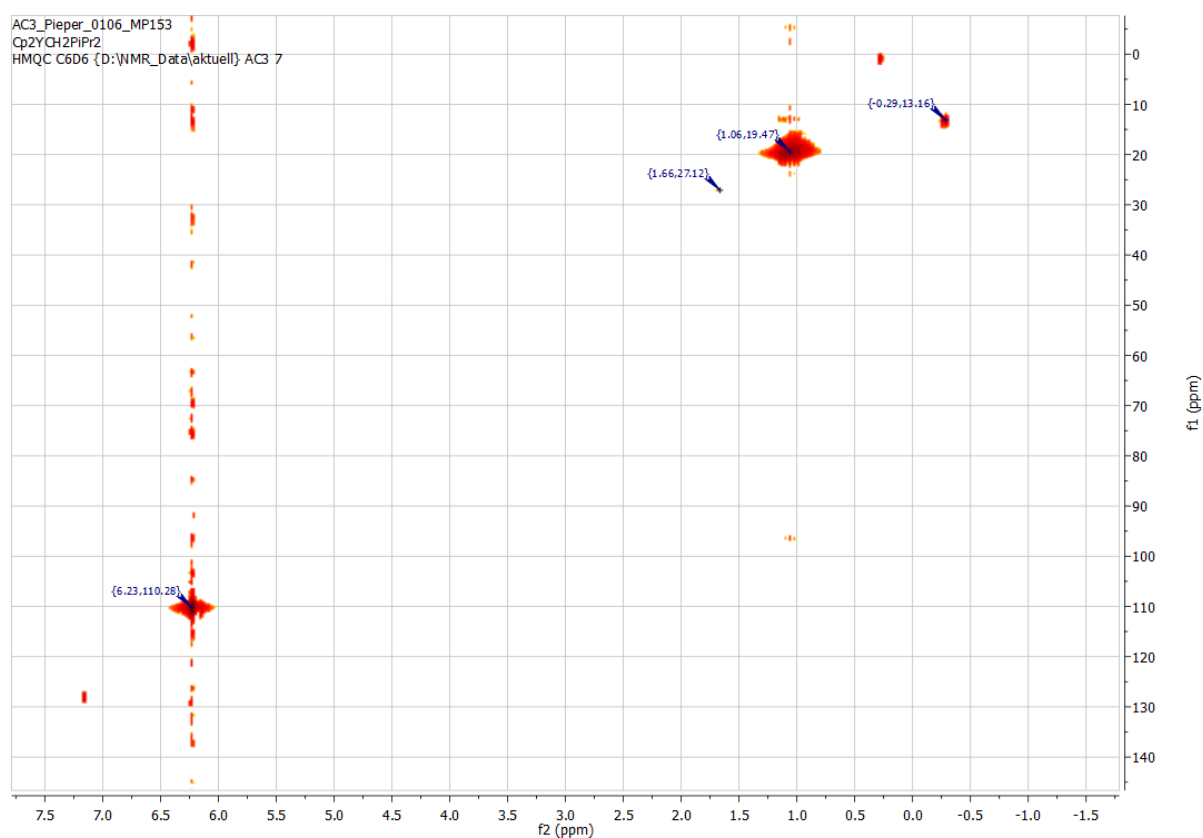
**Figure S1:** <sup>1</sup>H NMR spectrum of a solution of [Cp<sub>2</sub>YCH<sub>2</sub>P(*i*Pr)<sub>2</sub>]**(1)** in C<sub>6</sub>D<sub>6</sub>, measured at 293 K.



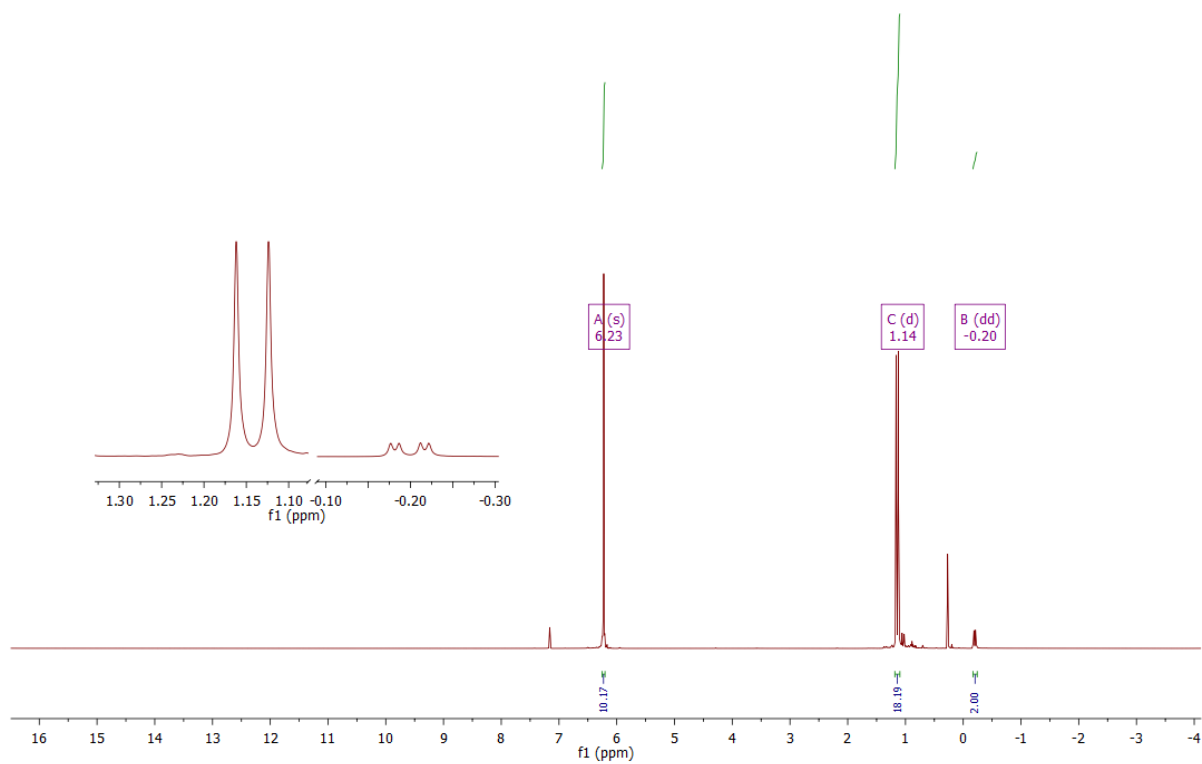
**Figure S2:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of a solution of [Cp<sub>2</sub>YCH<sub>2</sub>P(*i*Pr)<sub>2</sub>]**(1)** in C<sub>6</sub>D<sub>6</sub>, measured at 293 K.



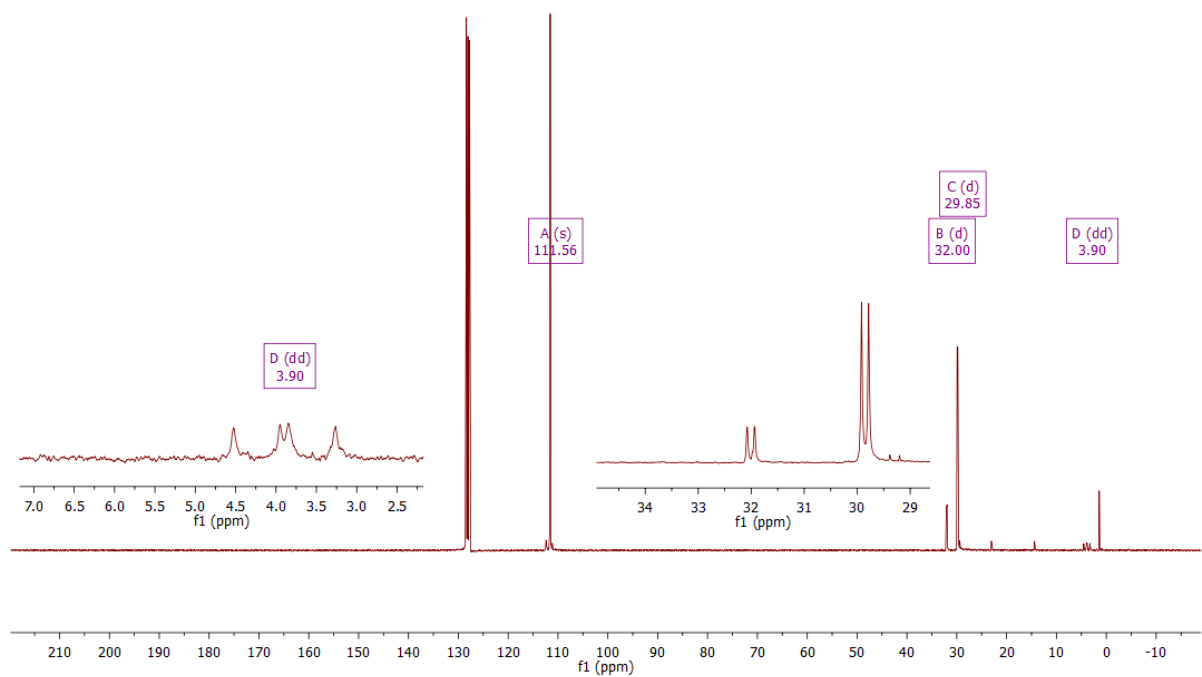
**Figure S3:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a solution of  $[\text{Cp}_2\text{YCH}_2\text{P}(\text{iPr})_2]_2$  (**1**) in  $\text{C}_6\text{D}_6$ , measured at 293 K.



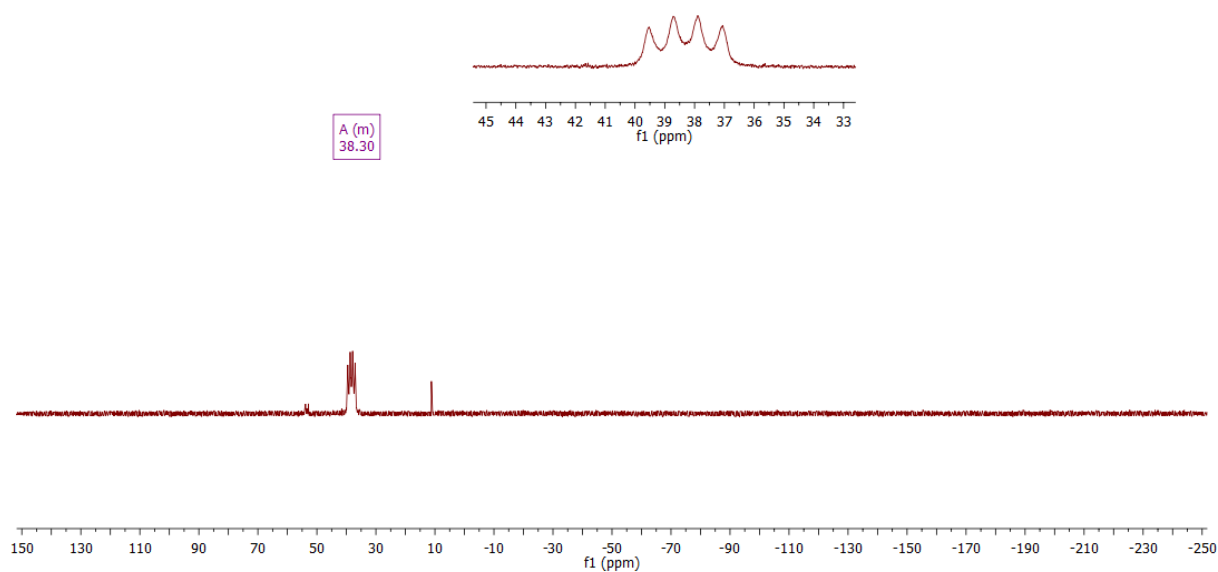
**Figure S4:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR correlation spectrum (HMQC) of a solution of  $[\text{Cp}_2\text{YCH}_2\text{P}(\text{iPr})_2]_2$  (**1**) in  $\text{C}_6\text{D}_6$ , measured at 293 K.



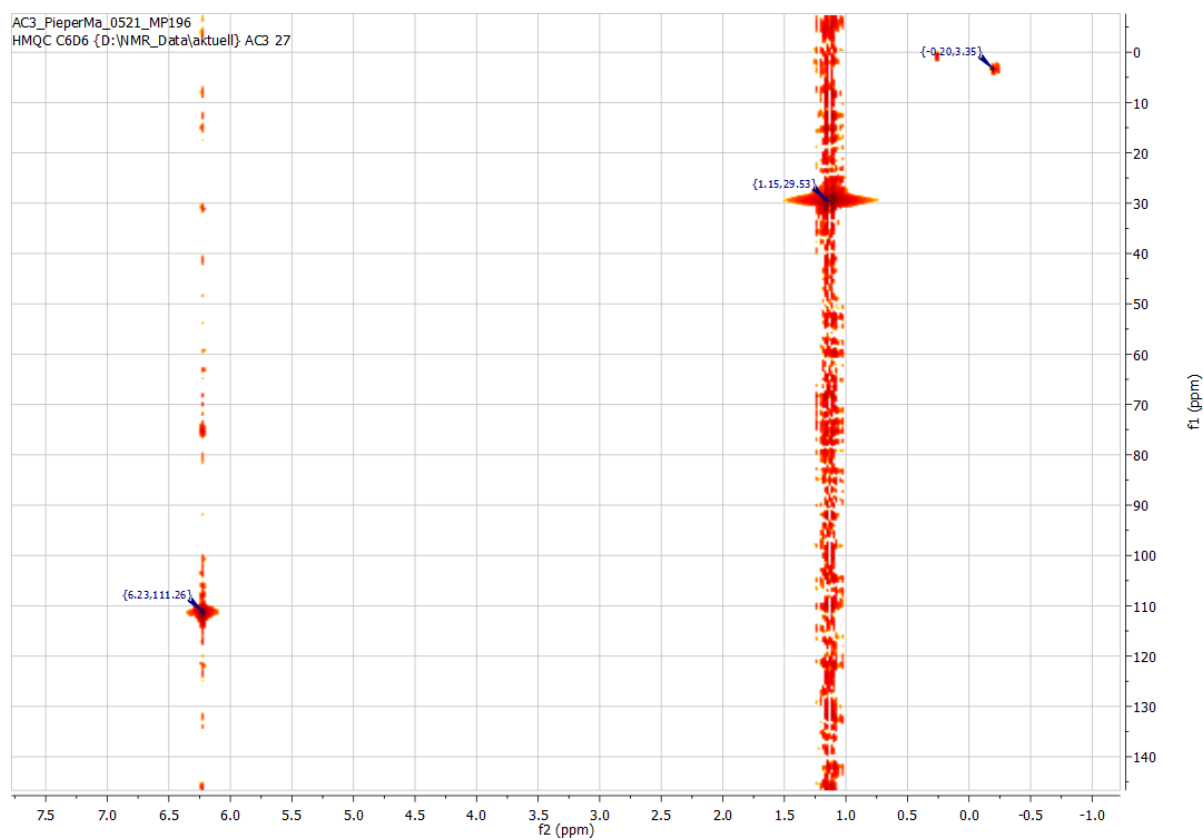
**Figure S5:** <sup>1</sup>H NMR spectrum of a solution of [Cp<sub>2</sub>YCH<sub>2</sub>P(<sup>t</sup>Bu)<sub>2</sub>]<sub>2</sub> · LiCl (**4**) in C<sub>6</sub>D<sub>6</sub>, measured at 293 K.



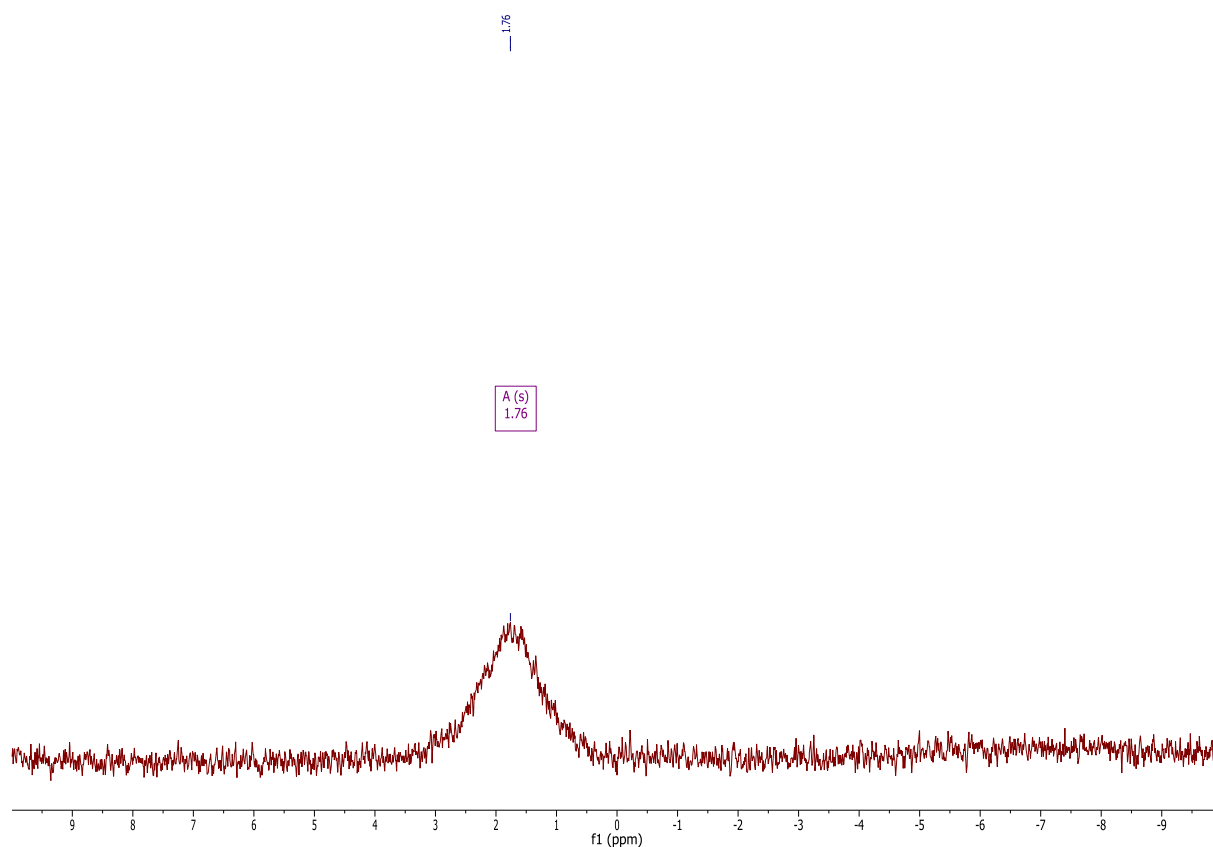
**Figure S6:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of a solution of [Cp<sub>2</sub>YCH<sub>2</sub>P(<sup>t</sup>Bu)<sub>2</sub>]<sub>2</sub> · LiCl (**4**) in C<sub>6</sub>D<sub>6</sub>, measured at 293 K.



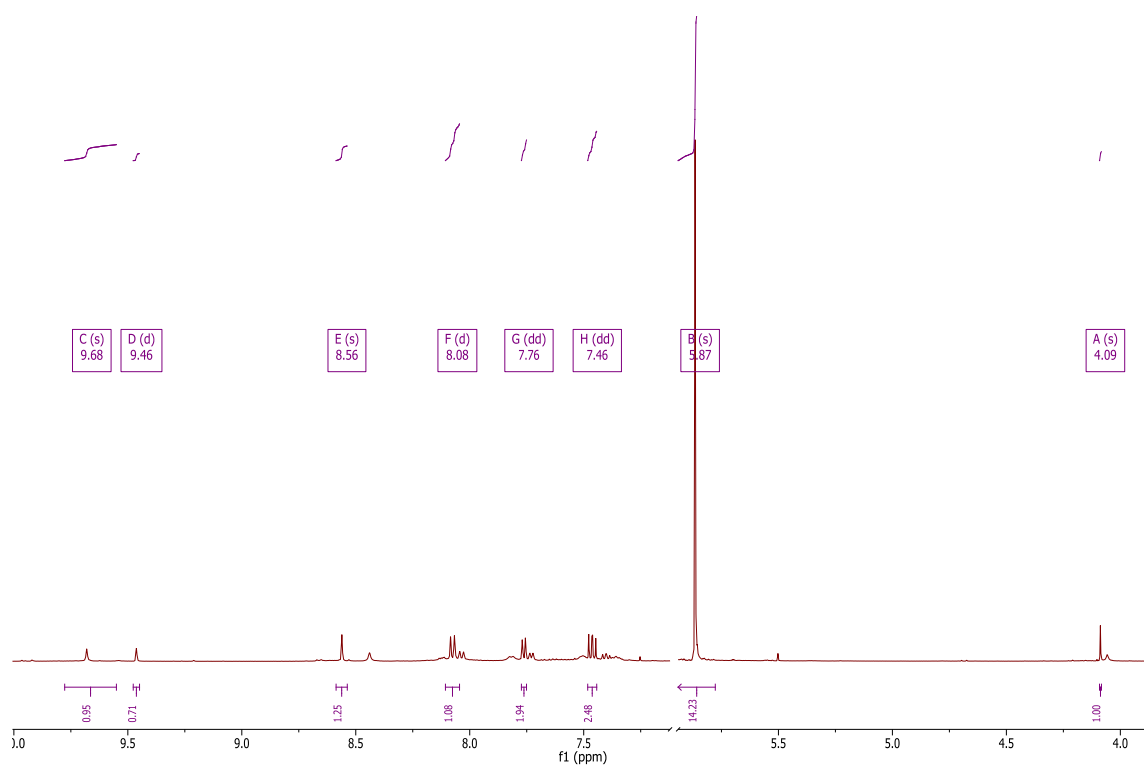
**Figure S7:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a solution of  $[\text{Cp}_2\text{YCH}_2\text{P}(\text{tBu})_2]_2 \cdot \text{LiCl}$  (**4**) in  $\text{C}_6\text{D}_6$ , measured at 293 K.



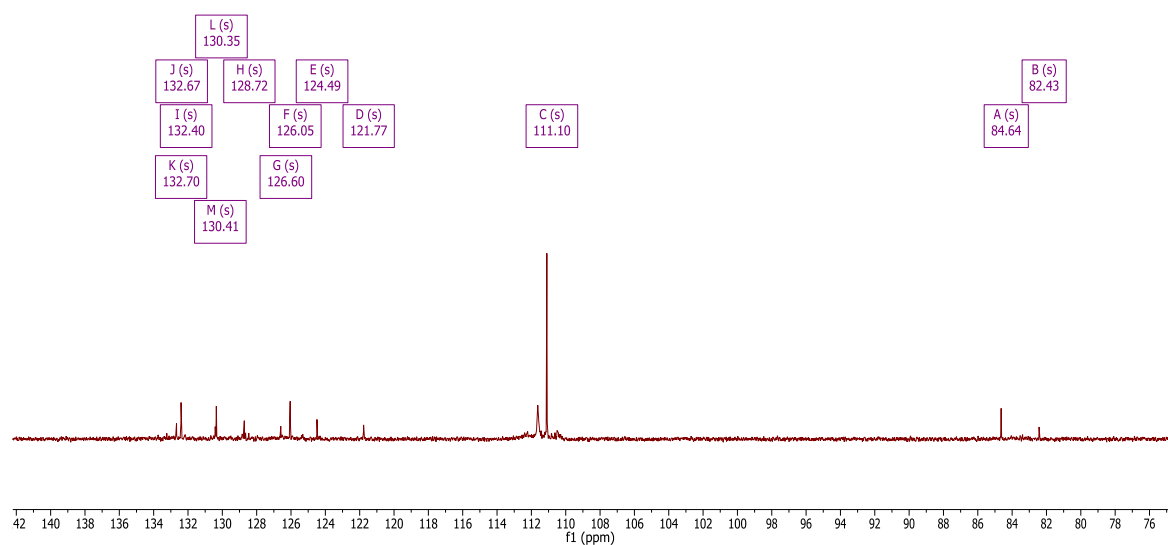
**Figure S8:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR correlation spectrum (HMQC) of a solution of  $[\text{Cp}_2\text{YCH}_2\text{P}(\text{tBu})_2]_2 \cdot \text{LiCl}$  (**4**) in  $\text{C}_6\text{D}_6$ , measured at 293 K.



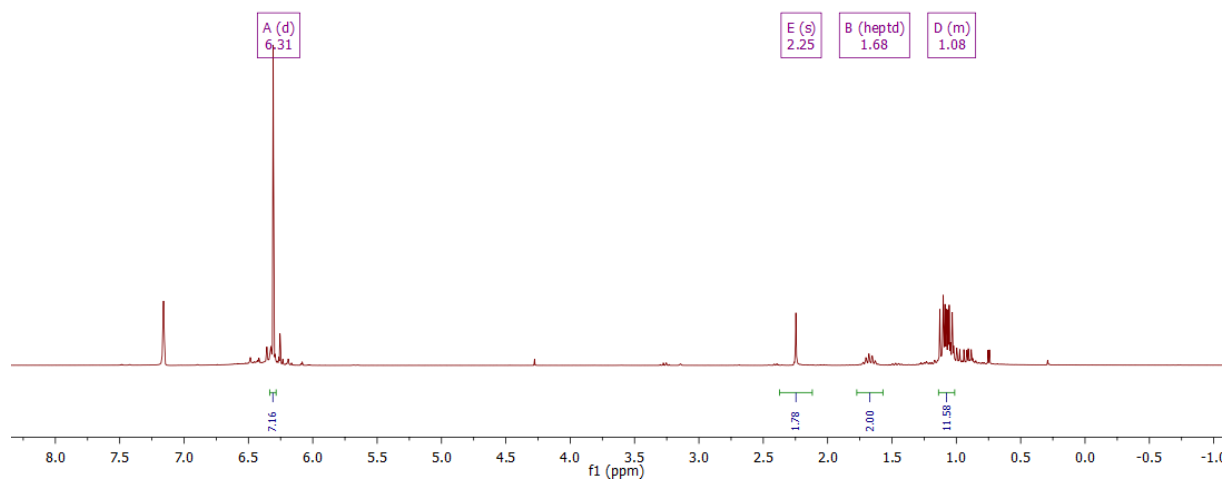
**Figure S9:**  $^7\text{Li}$  NMR spectrum of a solution of  $[\text{Cp}_2\text{YCH}_2\text{P}(\text{tBu})_2]_2 \cdot \text{LiCl}$  (**4**) in  $\text{C}_6\text{D}_6$ , measured at 293 K.



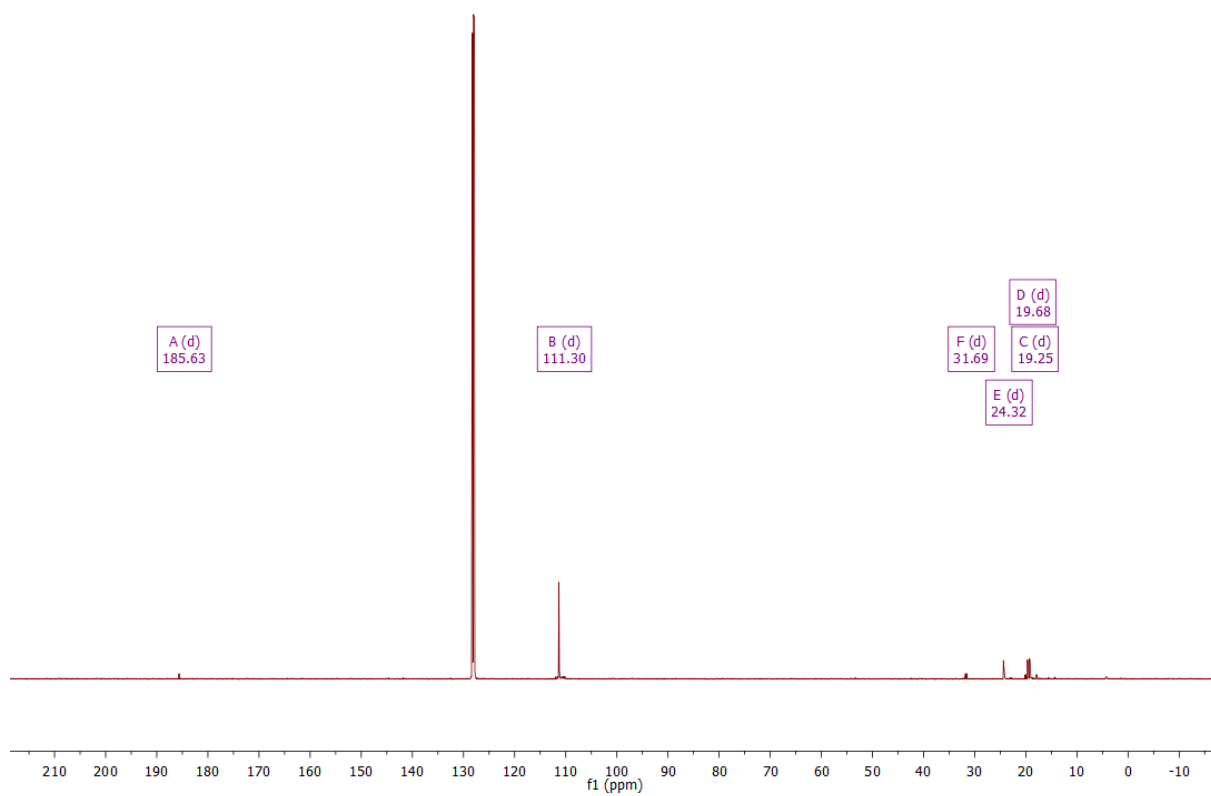
**Figure S10:**  $^1\text{H}$  NMR spectrum of a solution of **10** in  $\text{THF-d}_8$ , measured at 293 K.



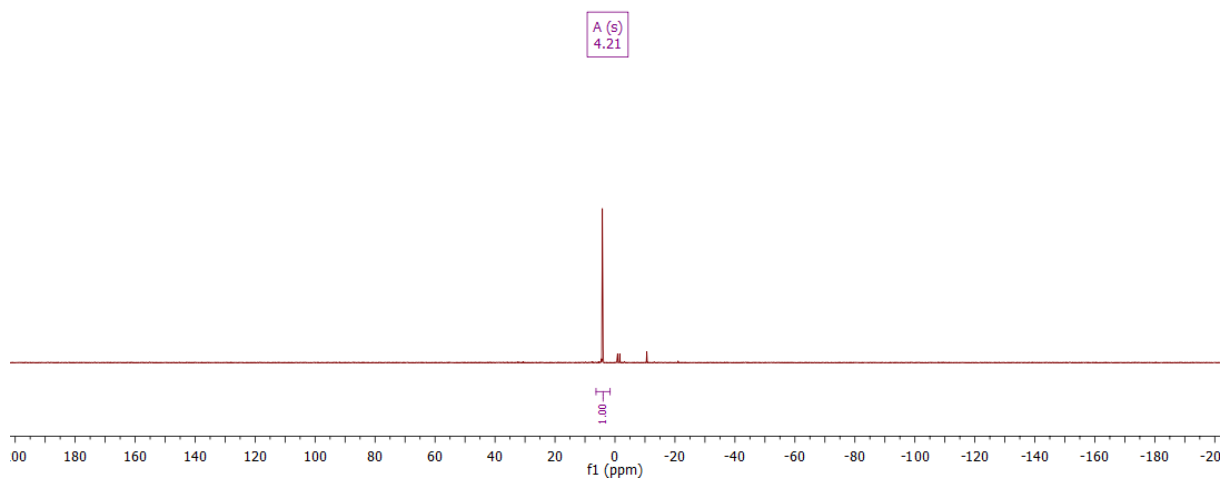
**Figure S11:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a solution of **10** in  $\text{THF-d}_8$ , measured at 293 K.



**Figure S12:**  $^1\text{H}$  NMR spectrum of a solution of **14** in  $\text{C}_6\text{D}_6$ , measured at 293 K.



**Figure S13:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a solution of **14** in  $\text{C}_6\text{D}_6$ , measured at 293 K.



**Figure S14:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of a solution of **14** in  $\text{C}_6\text{D}_6$ , measured at 293 K.