

*Supporting Information for*

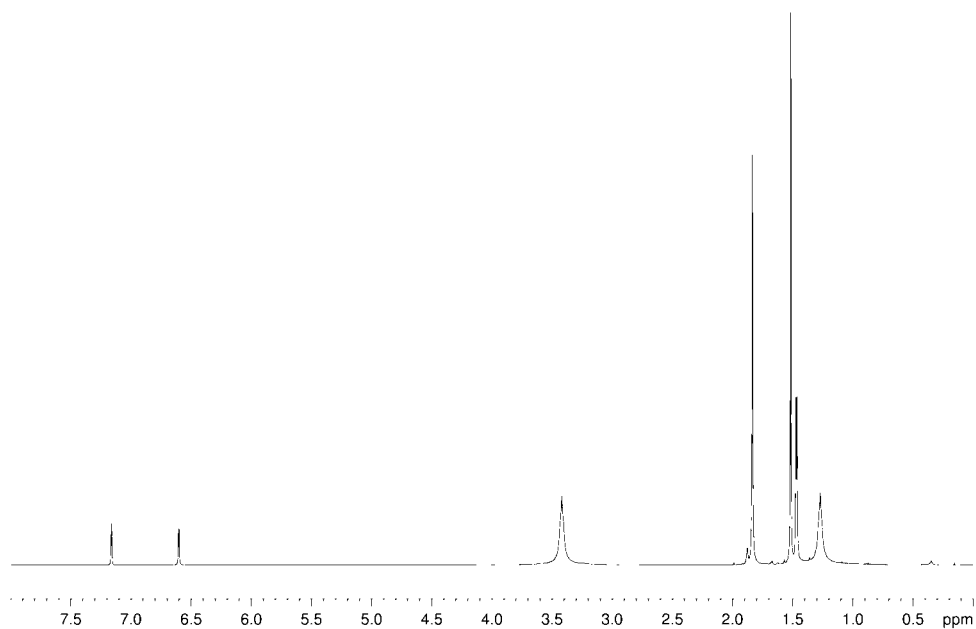
**Phosphine-substituted sterically encumbered  
pyrrolyl ligands – Synthesis and reactivity studies**

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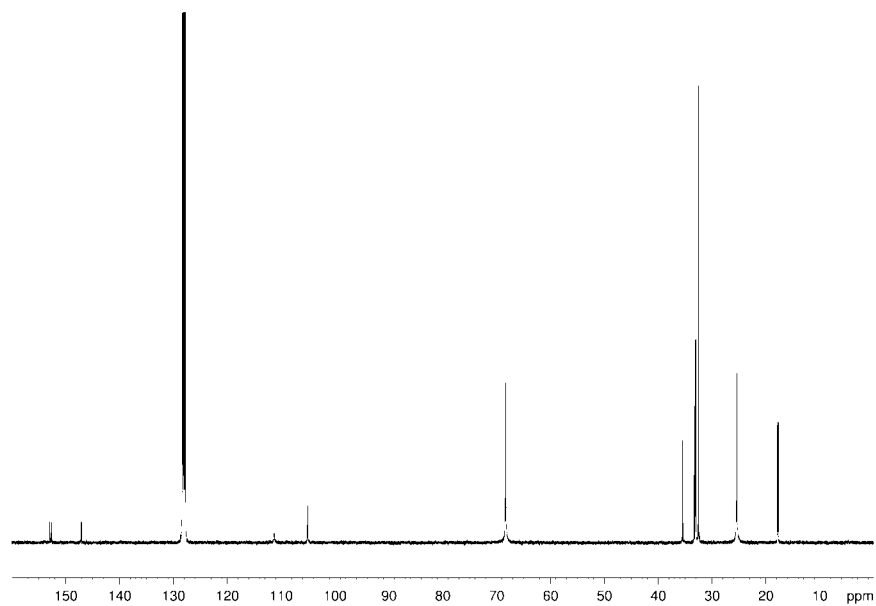
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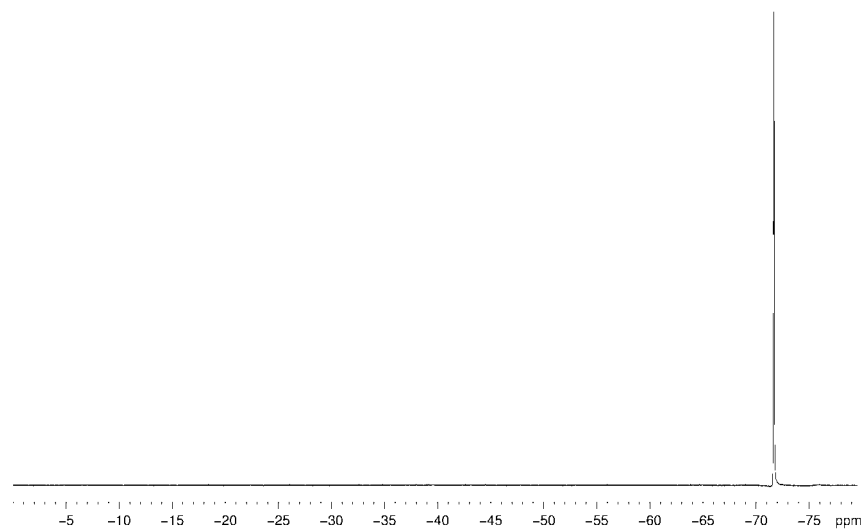
## 1. NMR Spectra of 3-Li(thf)<sub>2</sub>



**Figure S1.** <sup>1</sup>H NMR spectrum of **3-Li(thf)<sub>2</sub>** recorded in C<sub>6</sub>D<sub>6</sub> at 22 °C.

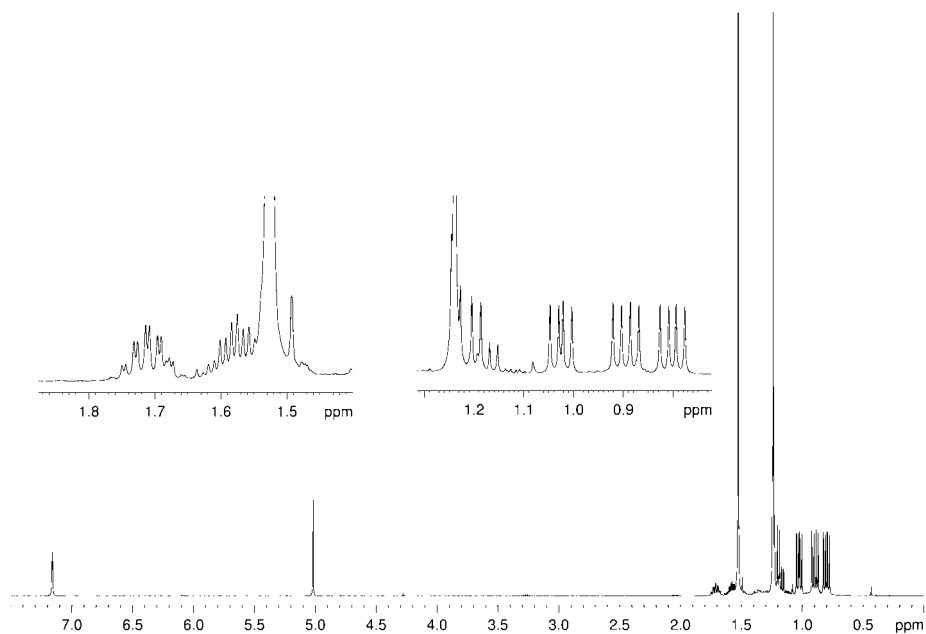


**Figure S2.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3-Li(thf)<sub>2</sub>** recorded in C<sub>6</sub>D<sub>6</sub> at 22 °C.

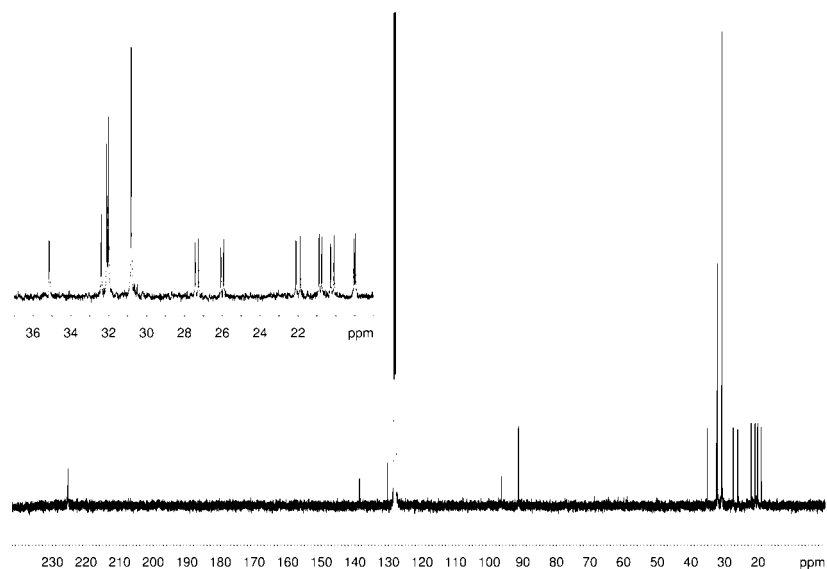


**Figure S3.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3-Li(thf)<sub>2</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.

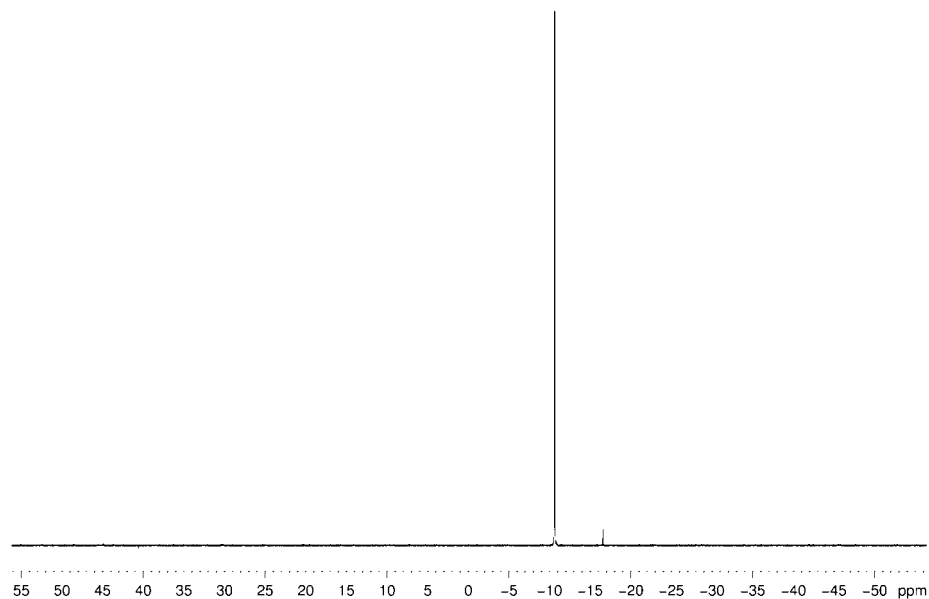
## 2. NMR Spectra of **4-Mn(CO)<sub>3</sub>**



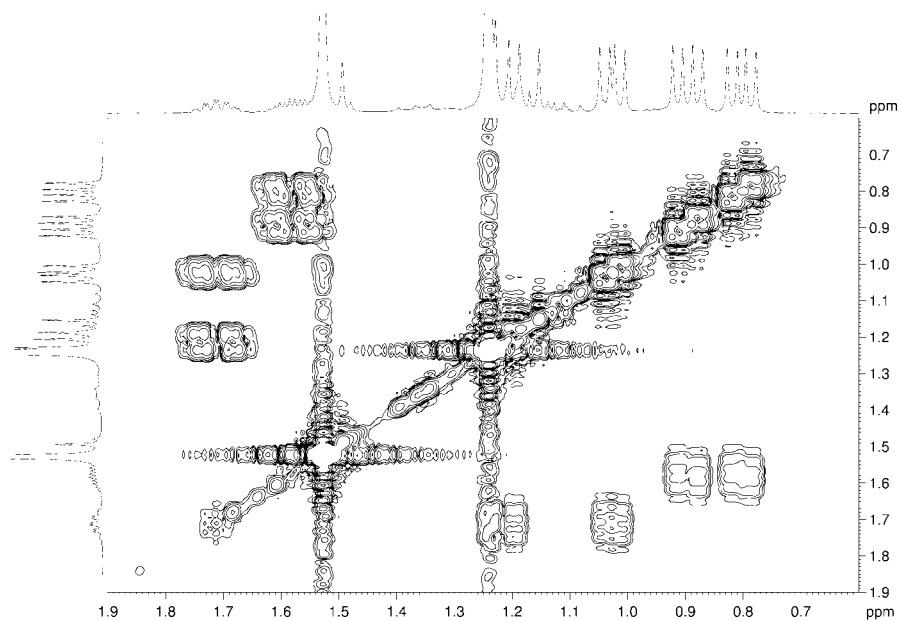
**Figure S4.**  $^1\text{H}$  NMR spectrum of **4-Mn(CO)<sub>3</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.



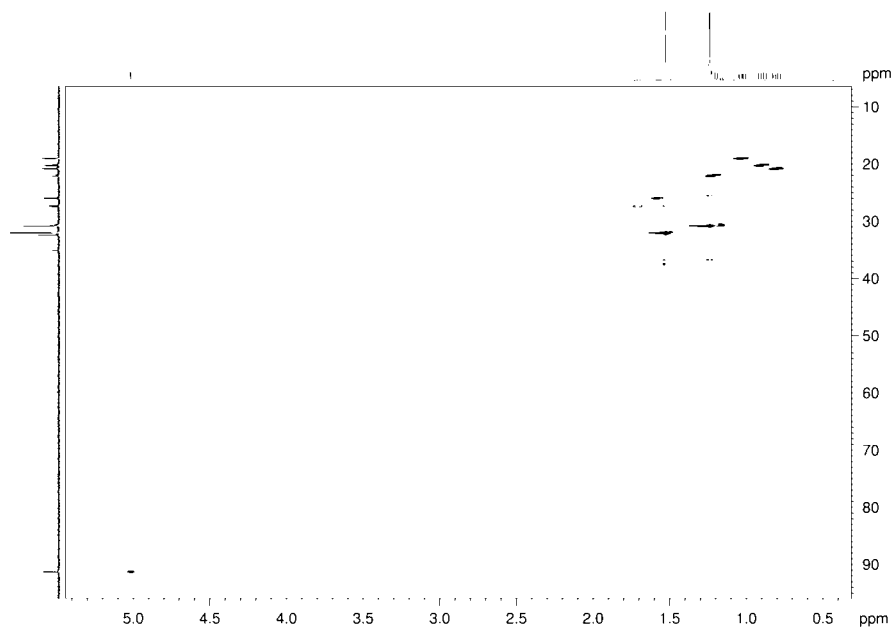
**Figure S5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4-Mn(CO)<sub>3</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.



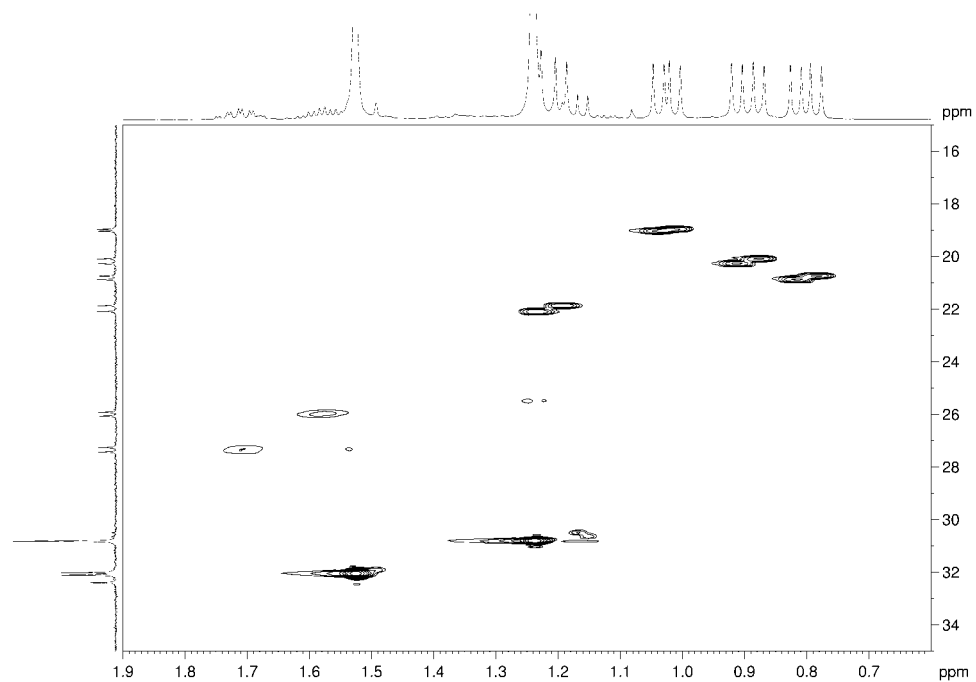
**Figure S6.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4-Mn(CO)<sub>3</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.



**Figure S7.**  $^1\text{H}$ - $^1\text{H}$ -COSY NMR spectrum of **4-Mn(CO)<sub>3</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.



**Figure S8a.**  $^1\text{H}$ - $^{13}\text{C}$ -HMBC NMR spectrum of **4-Mn(CO)<sub>3</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.



**Figure S8b.**  $^1\text{H}$ - $^{13}\text{C}$ -HMBC NMR spectrum of **4-Mn(CO)<sub>3</sub>** recorded in  $\text{C}_6\text{D}_6$  at 22 °C.