

## Supporting Information

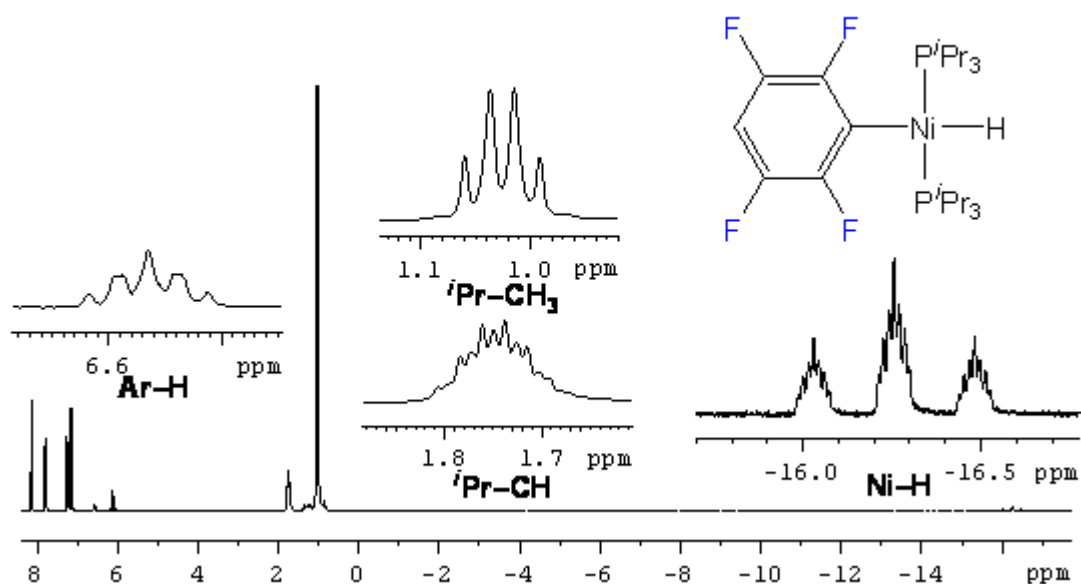
### Carbon–Hydrogen Bond Oxidative Addition of Partially Fluorinated Aromatics to a $\text{Ni}(\text{P}^i\text{Pr}_3)_2$ Synthon: The Remarkable Influence of Steric Bulk on the Thermodynamics and Kinetics of C–H Bond Activation

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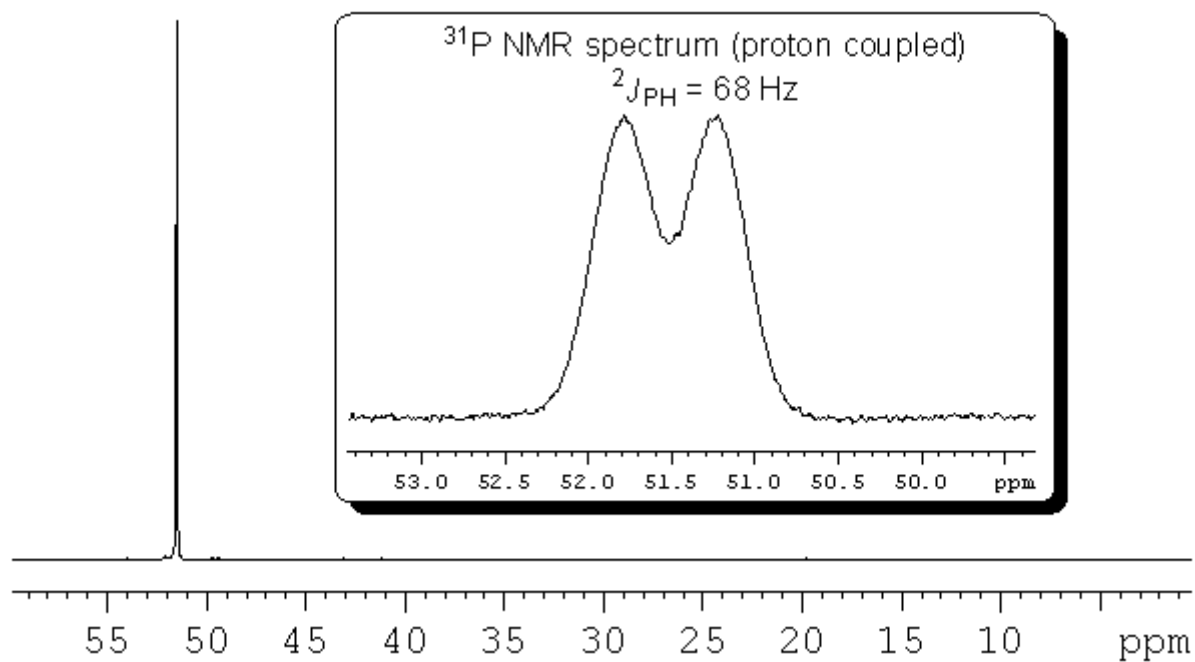
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Canada N9B 3P4.*

#### Contents:

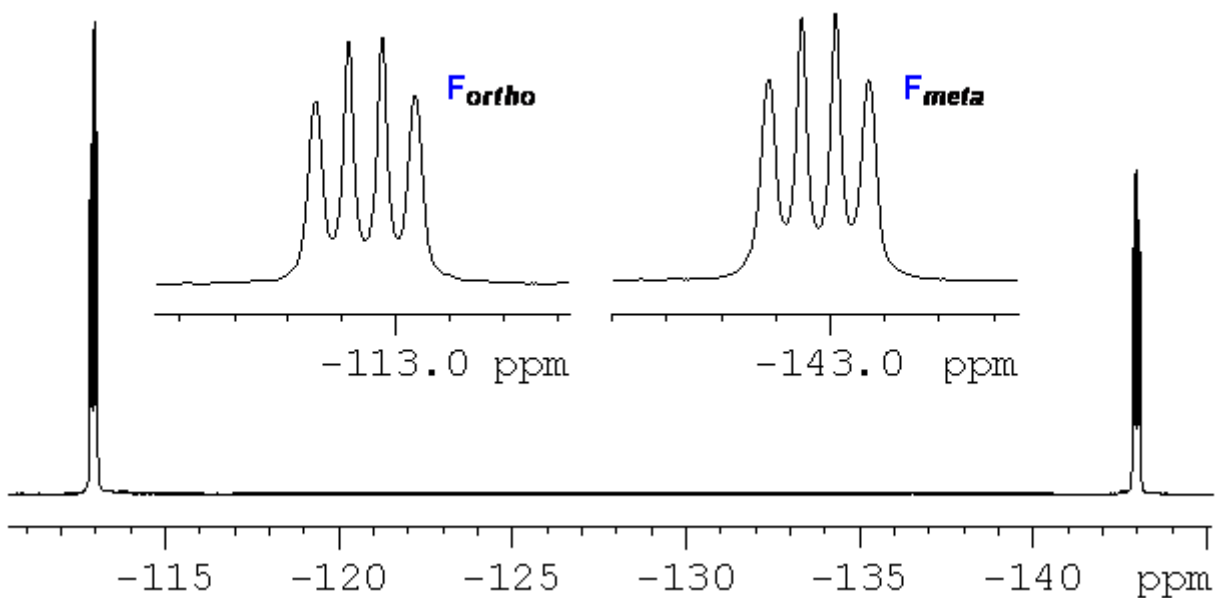
Select NMR spectroscopic characterization for compounds 3–7 and 10–17.



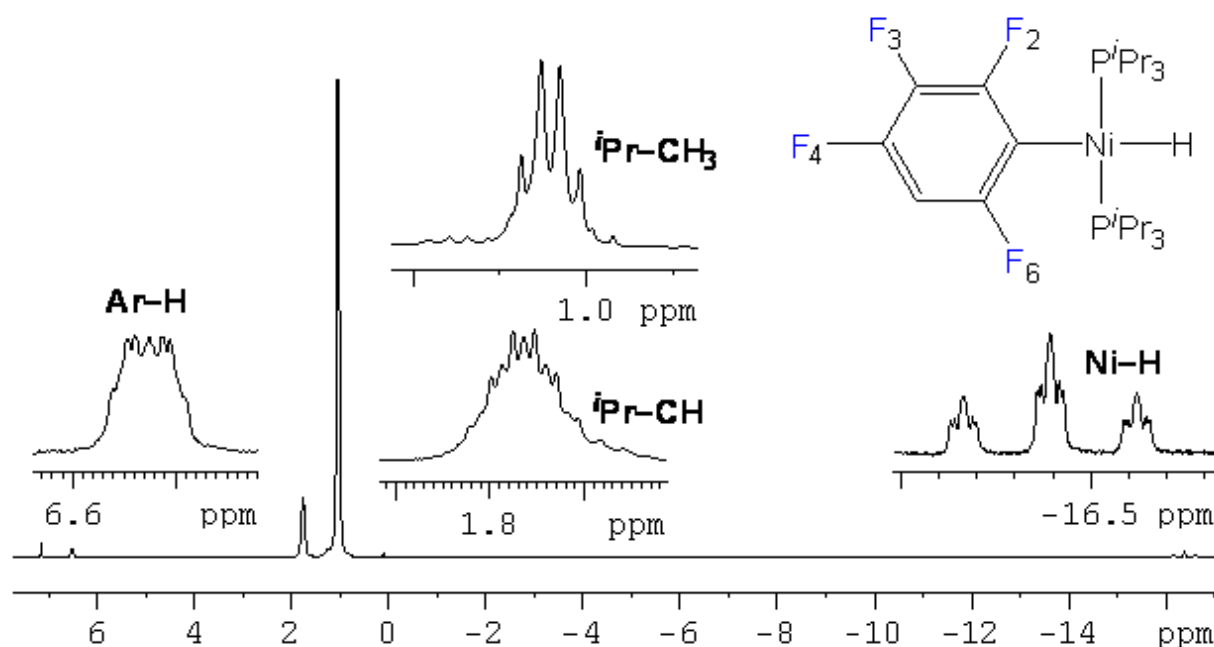
**Figure 1.**  $^1\text{H}$  NMR spectrum of the crude reaction mixture containing  $(\text{P}^i\text{Pr}_3)_2\text{NiH}(2,3,5,6\text{-C}_6\text{F}_4\text{H})$ , **3**, prepared on an NMR scale from **1** and 1,2,4,5-tetrafluorobenzene in  $\text{C}_6\text{D}_6$  at 298 K. Expansions for the resonances associated with **3** are shown. Resonances between  $\delta$  7.0–8.5 are associated with  $\text{C}_6\text{D}_5\text{H}$  and the byproduct anthracene.



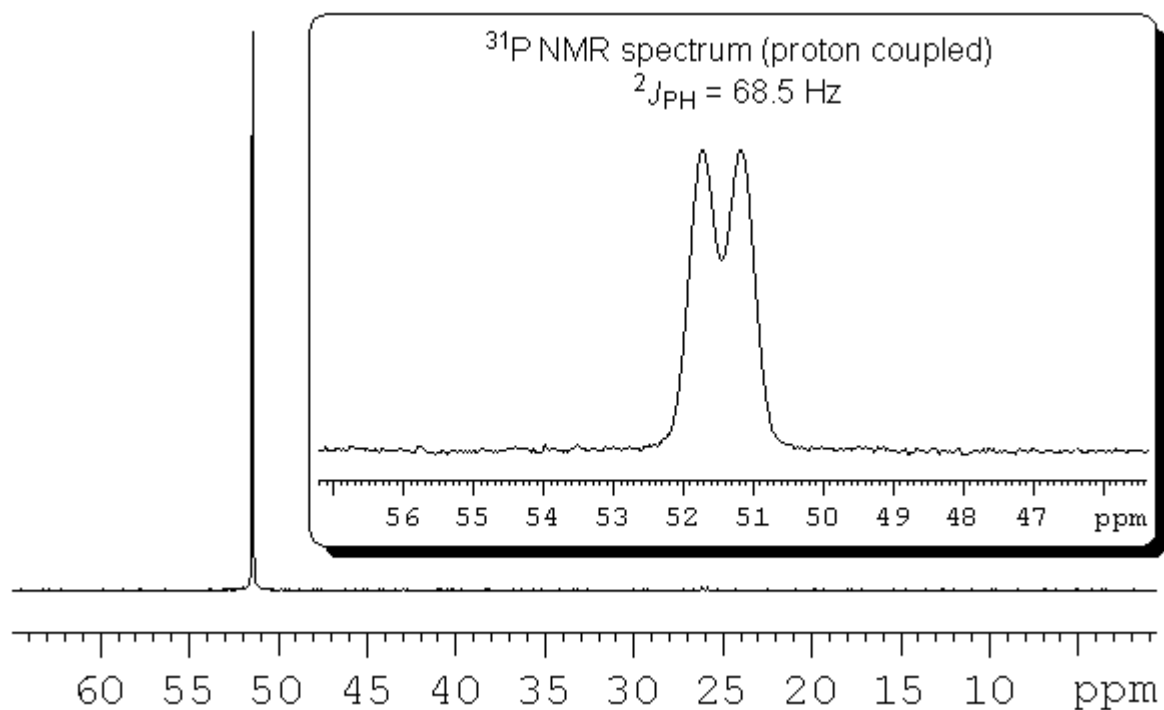
**Figure 2.** The  $^{31}\text{P}\{^1\text{H}\}$  and  $^{31}\text{P}$  (inset) NMR spectra of **3** in  $\text{C}_6\text{D}_6$  at 298 K.



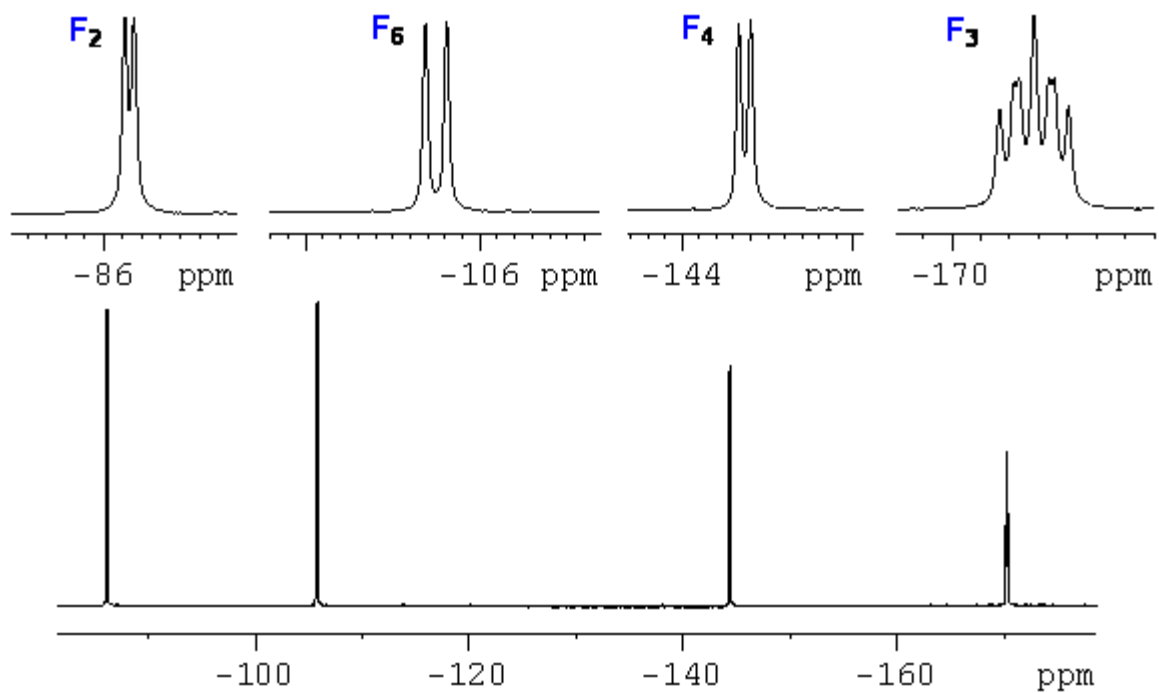
**Figure 3.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  at 298 K. Expansions for the resonances associated with **3** are shown.



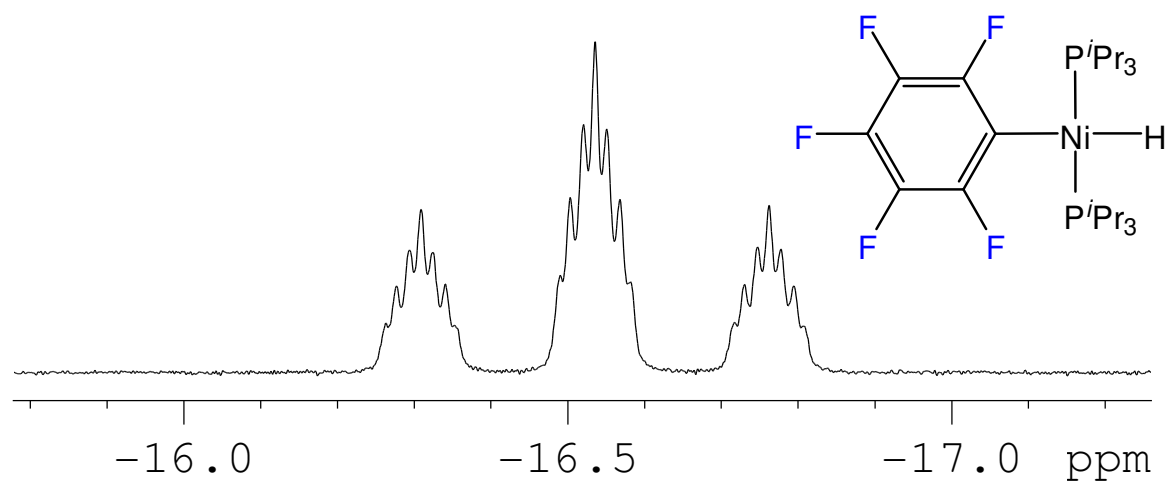
**Figure 4.**  $^1\text{H}$  NMR spectrum of **4** in  $\text{C}_6\text{D}_6$  at 298 K, along with expansions of resonances.



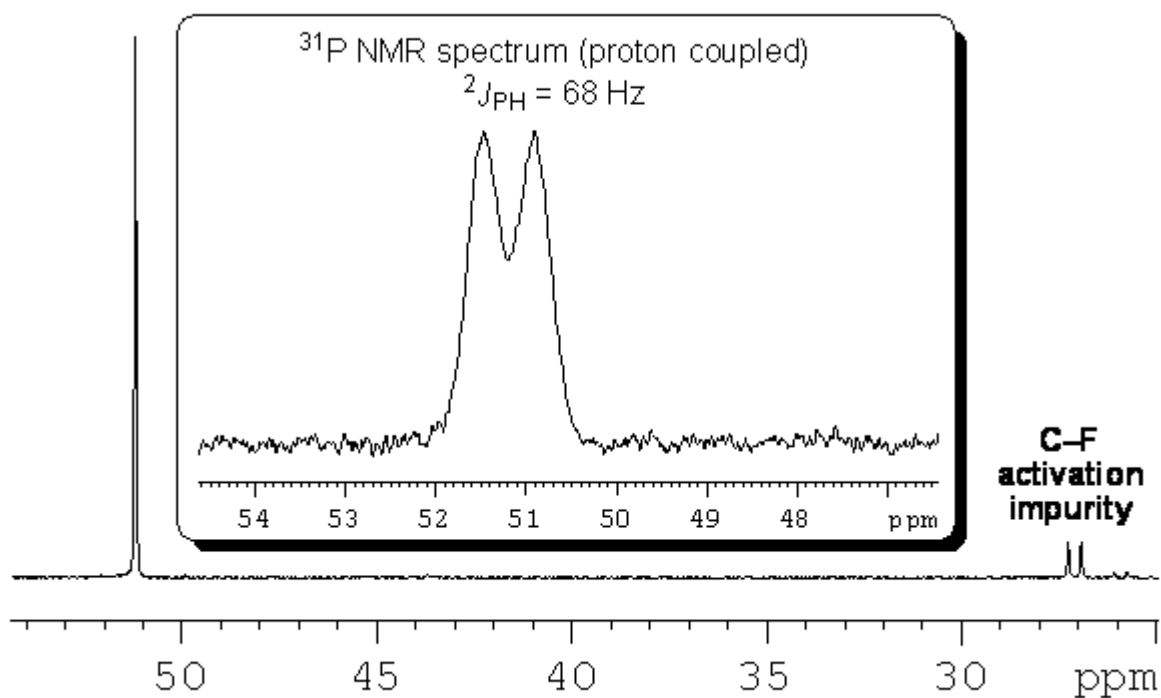
**Figure 4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR and  $^{31}\text{P}$  (inset) spectra of **4** in  $\text{C}_6\text{D}_6$  at 298 K.



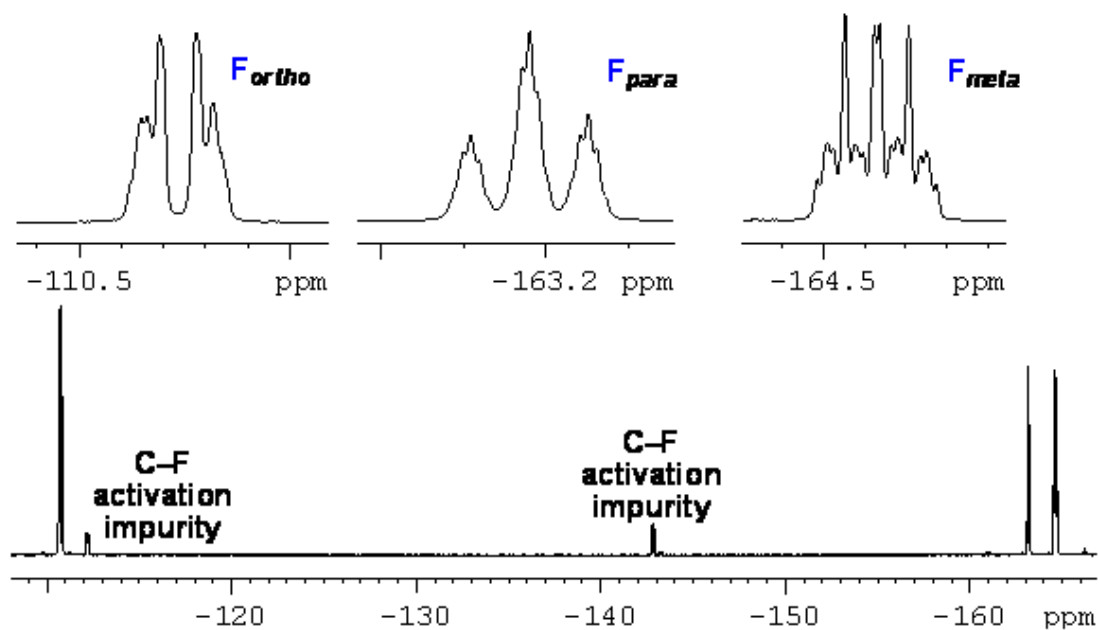
**Figure 5.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of **4** in  $\text{C}_6\text{D}_6$  at 298 K. Expansions for the resonances associated with **4** are shown.



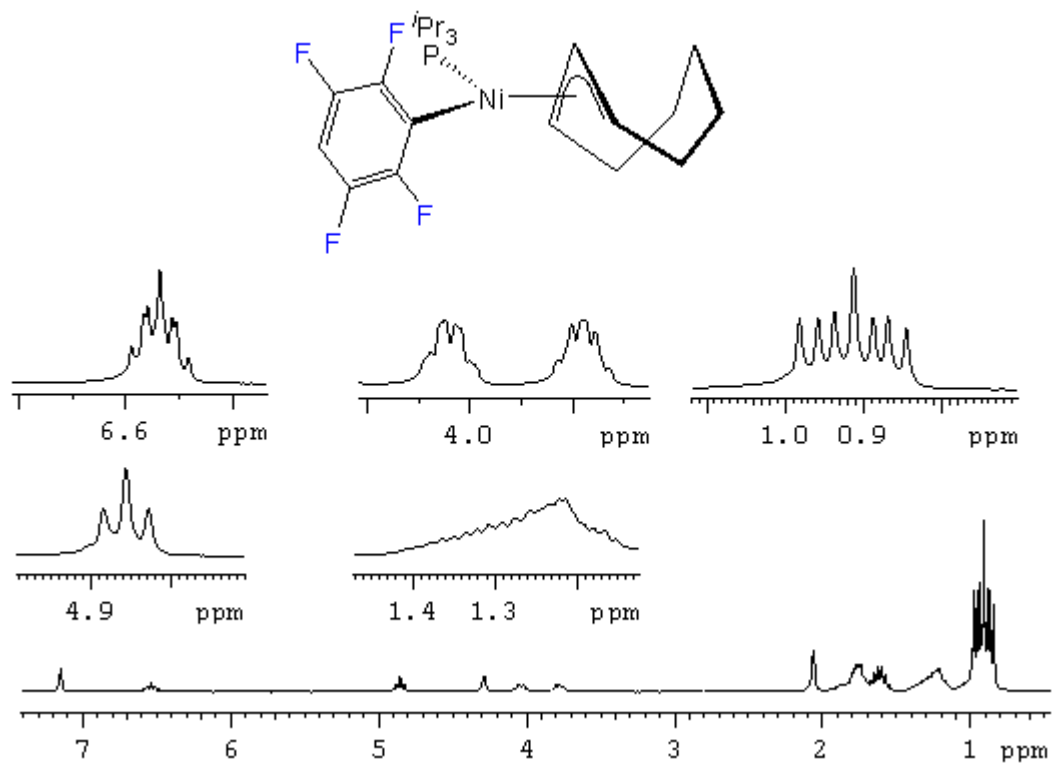
**Figure 6.**  $^1\text{H}$  NMR spectrum of the hydridic region of **5** in  $\text{C}_6\text{D}_6$  at 298 K.



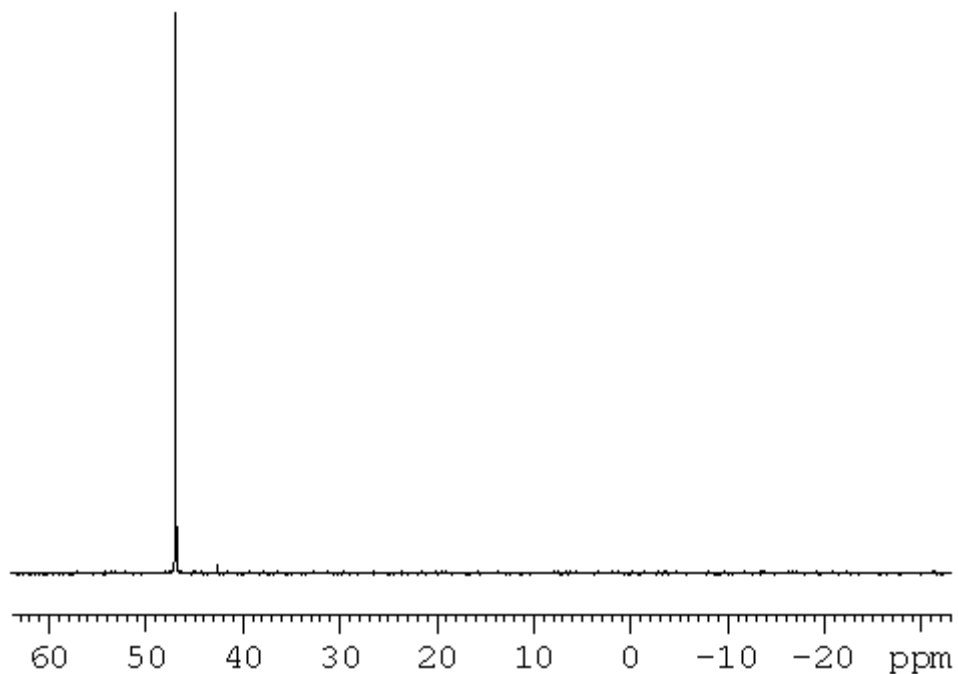
**Figure 7.**  $^{31}\text{P}\{^1\text{H}\}$  NMR and  $^{31}\text{P}$  (inset) spectra of **5** in  $\text{C}_6\text{D}_6$  at 298 K.



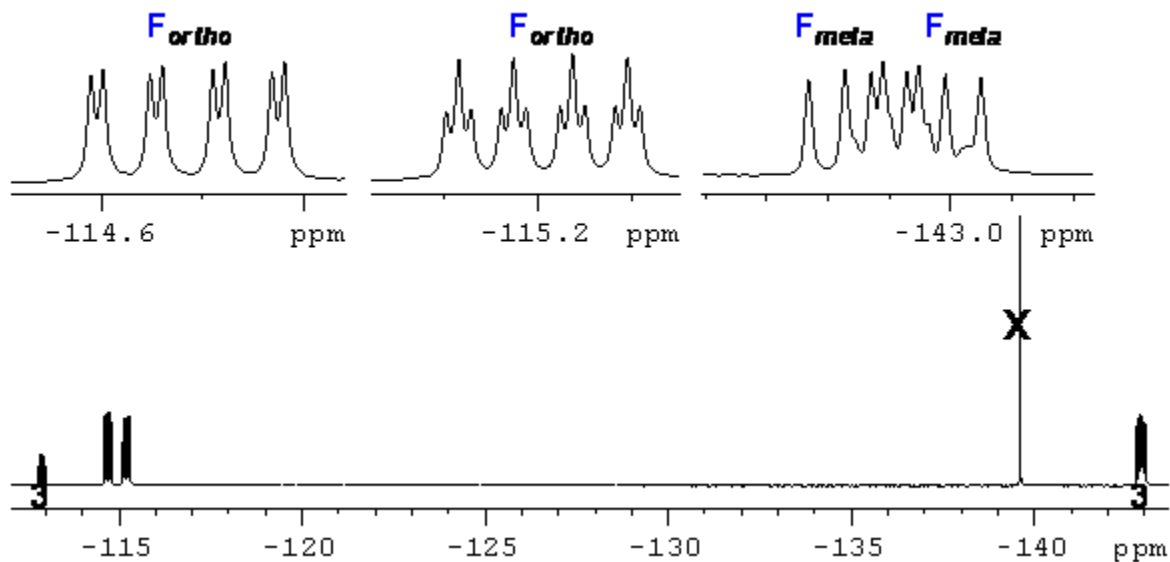
**Figure 8.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of **5** in  $\text{C}_6\text{D}_6$  at 298 K. Expansions for the resonances associated with **5** are shown.



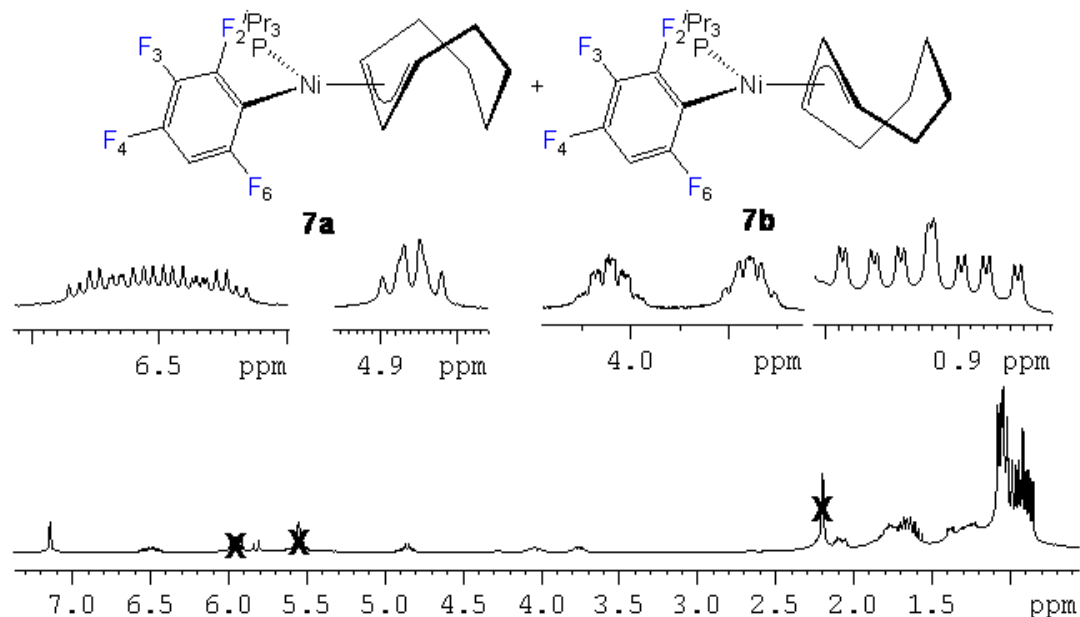
**Figure 9.**  $^1\text{H}$  NMR spectrum of **6** in  $\text{C}_6\text{D}_6$  at 298 K. Expansions for the resonances associated with **6** are shown.



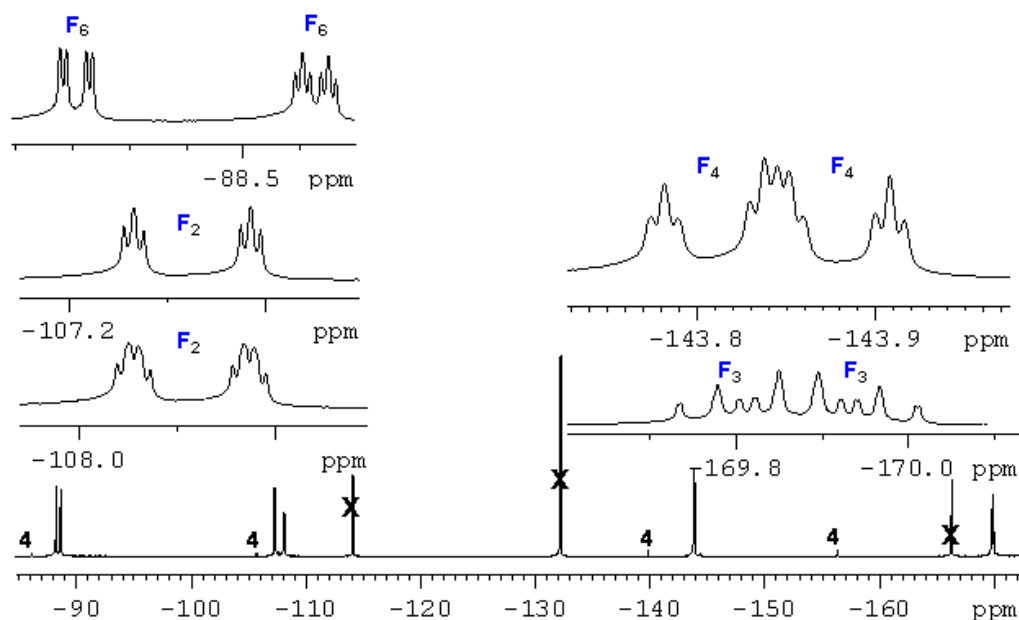
**Figure 10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{C}_6\text{D}_6$  at 298 K.



**Figure 11.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the reaction of  $\text{Ni}(\text{COD})_2$ ,  $i\text{Pr}_3\text{P}$ , and 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$  mixture in  $\text{C}_6\text{D}_6$  at 298 K, partway through the reaction to form **6**, where X indicates the resonance associated with 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ , and the resonances associated with hydride complex **3** also labeled. Expansions of the resonances associated with **6** are provided.

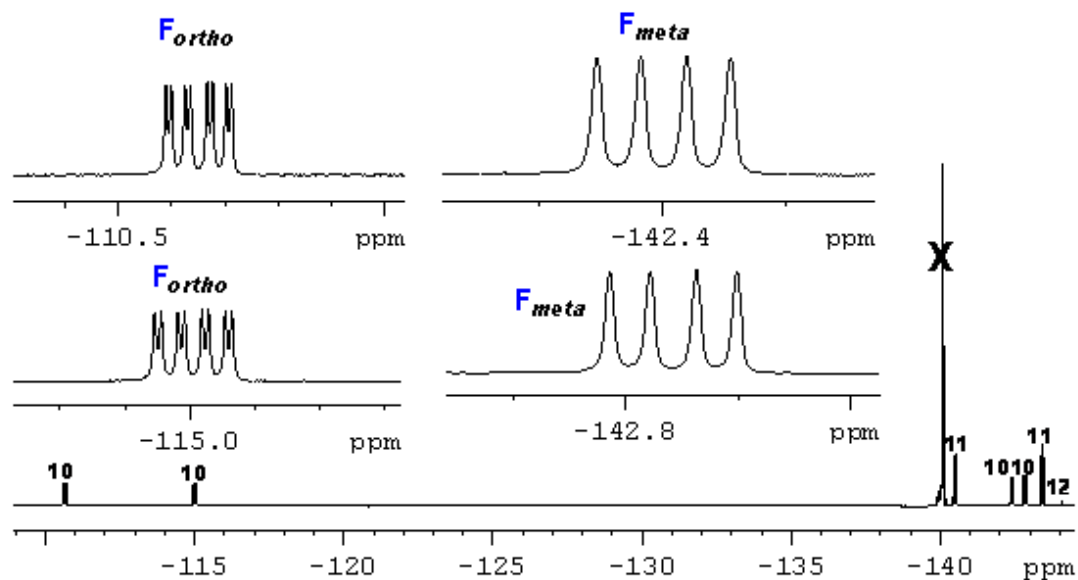


**Figure 12.**  $^1\text{H}$  NMR spectrum of the crude mixture in the synthesis of **7** in  $\text{C}_6\text{D}_6$  at 298 K, where X indicates the resonances associated with 1,5-cyclooctadiene and 1,2,3,5- $\text{C}_6\text{F}_4\text{H}_2$ . Expansions for the resonances associated with **7** are shown.

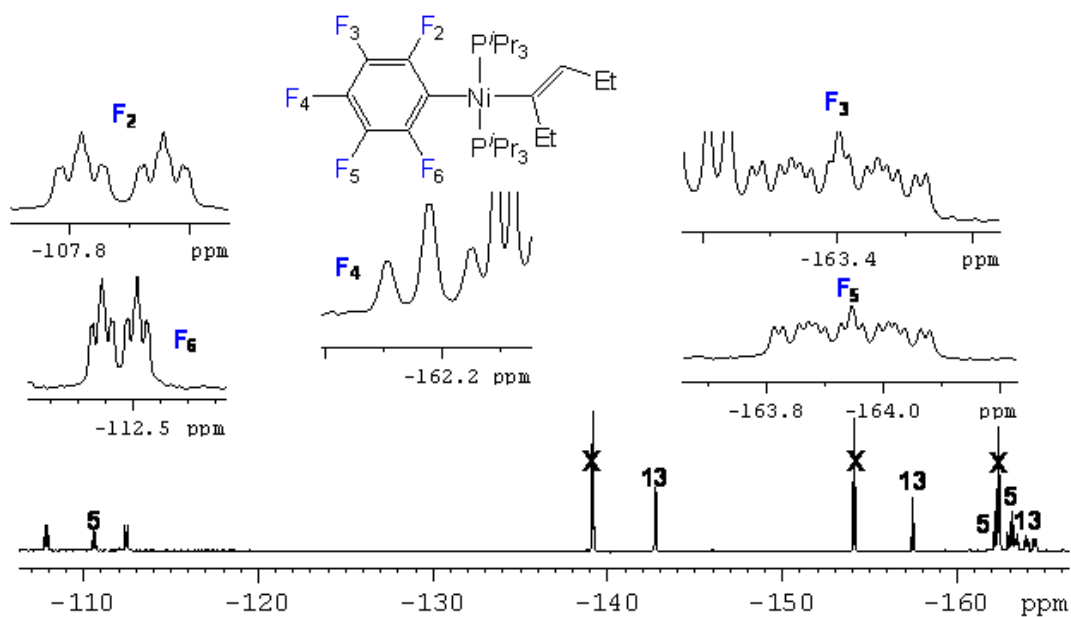


**Figure 13.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the crude mixture in the synthesis of **7** in  $\text{C}_6\text{D}_6$  at 298 K, where X indicates the resonances associated with 1,2,3,5- $\text{C}_6\text{F}_4\text{H}_2$ , and a small amount of **4** is also labeled. Expansions of the resonances associated with **7** are provided.

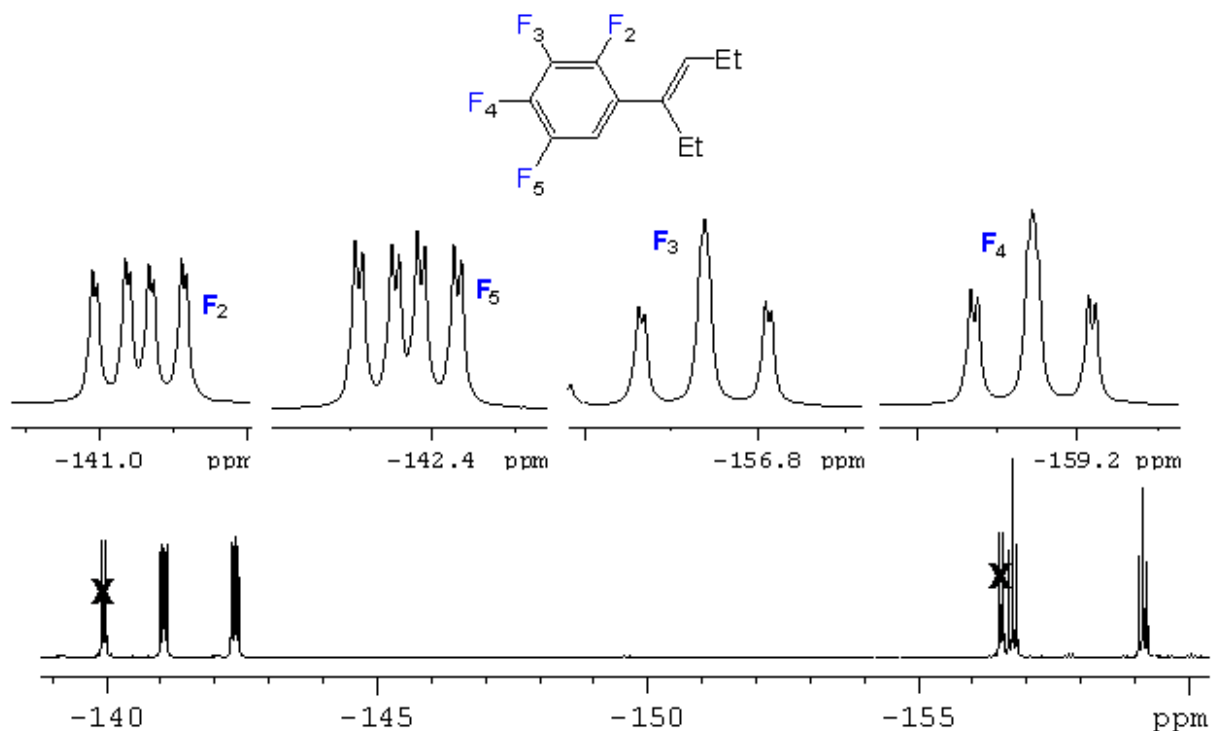




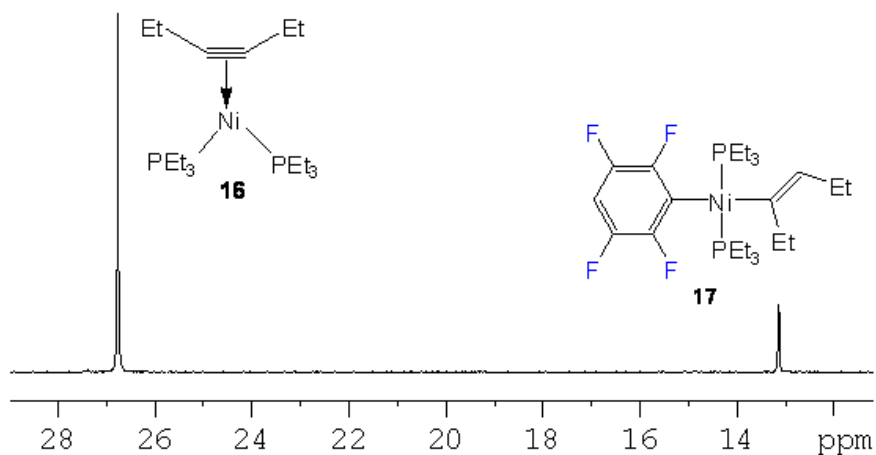
**Figure 14.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the intermediate crude (after 1 h heating at 50 °C) NMR mixture from the catalytic reaction of 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$  with 3-hexyne using 10 mol % **9** in  $\text{C}_6\text{D}_6$  at 298 K (470.4 MHz). The X indicates the resonance associated with 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ . Expansions for the resonances associated with **10** are shown.



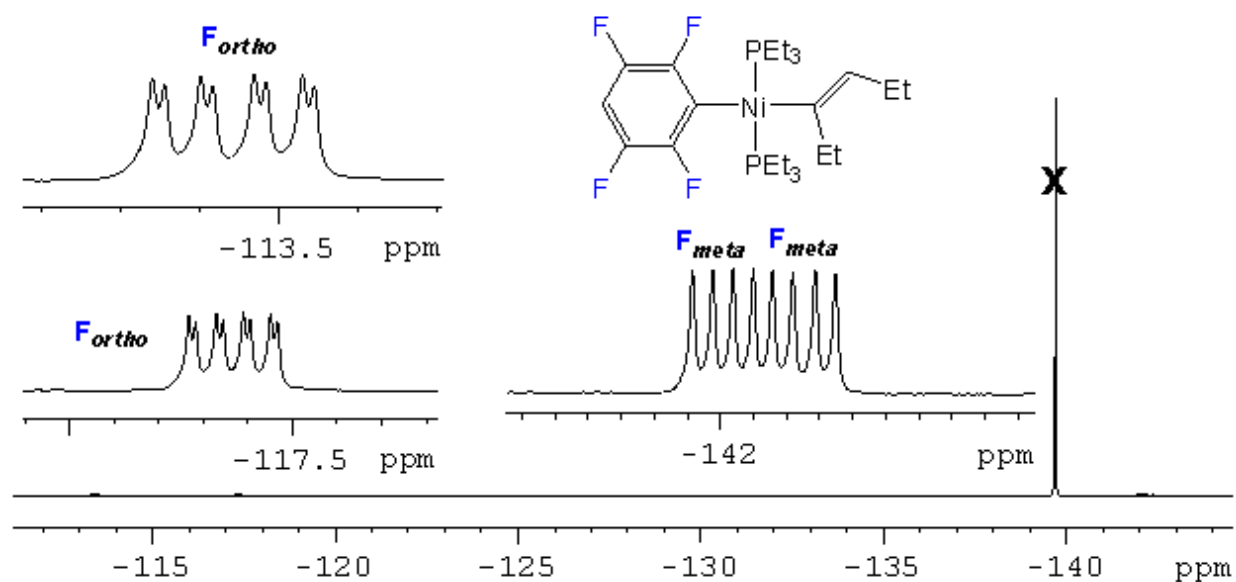
**Figure 15.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the stoichiometric reaction of **2** with  $\text{C}_6\text{F}_5\text{H}$  followed by 3-hexyne after 4 h of heating at 50 °C. The X indicates the resonance associated with  $\text{C}_6\text{F}_5\text{H}$ , and the resonances associated with **14** are shown as expansions.



**Figure 16.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the intermediate crude NMR mixture from the catalytic 80 °C reaction of 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> with 3-hexyne using 10 mol % **9** in C<sub>6</sub>D<sub>6</sub> at 298 K. The X indicates the resonance associated with 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, and the resonances associated with **15** are shown as expansions.



**Figure 17.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the intermediate crude NMR mixture from the catalytic 80 °C reaction of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> with 3-hexyne using 10 mol % **16** in C<sub>6</sub>D<sub>6</sub> at 298 K.



**Figure 18.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the intermediate crude NMR mixture from the catalytic 80 °C reaction of 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$  with 3-hexyne using 10 mol % **16** in  $\text{C}_6\text{D}_6$  at 298 K. The X indicates the resonance associated with 1,2,4,5- $\text{C}_6\text{F}_4\text{H}_2$ , and the resonances associated with **17** are shown as expansions.