

# Supplementary Materials: Accessing Low-Valent Titanium CCC-NHC Complexes: Toward Nitrogen Fixation

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Figure S1: Stacked plot of the  $^1\text{H}$  NMR spectra for reoxidation of intermediate **3**. A:  $^1\text{H}$  NMR spectrum of intermediate **3**. B:  $^1\text{H}$  NMR spectrum of intermediate **3** after reoxidation. C:  $^1\text{H}$  NMR spectrum of **2** for reference.

Figure S2: Stacked plot of the  $^1\text{H}$  NMR spectra for reduction of **1** with Mg-metal followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **1**. C:  $^1\text{H}$  NMR spectrum after reduction of **1** to intermediate **3**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3** with  $\text{PhICl}_2$ .

Figure S3:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3** with  $\text{PhICl}_2$ . Figure S4: Stacked plot of the relevant zoomed portions of  $^1\text{H}$  NMR spectra for reduction of **1** with Mg-metal followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **1**. C:  $^1\text{H}$  NMR spectrum after reduction of **1** to intermediate **3**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3** with  $\text{PhICl}_2$ .

Figure S5: Stacked plot of the  $^1\text{H}$  NMR spectra for reduction of **1** with  $\text{KCs}$  followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **1**. C:  $^1\text{H}$  NMR spectrum after reduction of **1** to intermediate **3**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3** with  $\text{PhICl}_2$ .

Figure S6: Stacked plot of the relevant zoomed portions of  $^1\text{H}$  NMR spectra for reduction of **1** with  $\text{KCs}$  followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **1**. C:  $^1\text{H}$  NMR spectrum after reduction of **1** to intermediate **3**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3** with  $\text{PhICl}_2$ .

Figure S7: Stacked plot of the  $^1\text{H}$  NMR spectra for reduction of **2** with  $\text{KCs}$  followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3'** with  $\text{PhICl}_2$ .

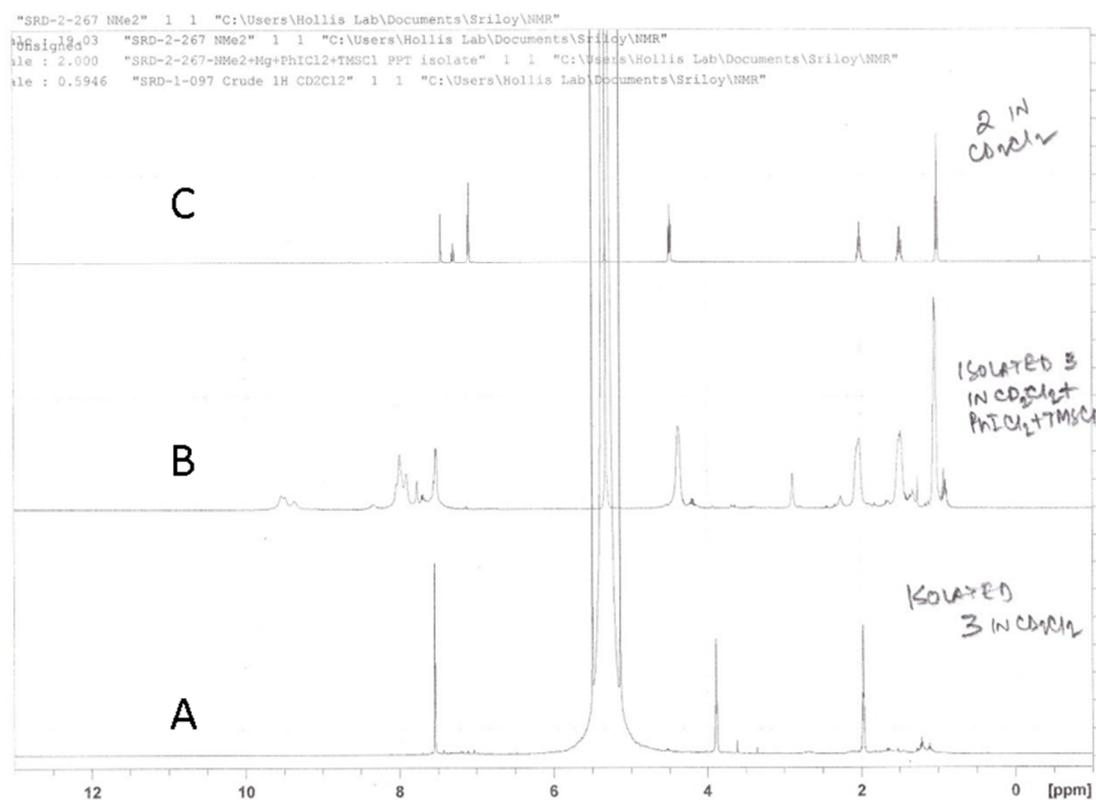
Figure S8: Stacked plot of the relevant zoomed portions of  $^1\text{H}$  NMR spectra for reduction of **2** with  $\text{KCs}$  followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3'** with  $\text{PhICl}_2$ .

Figure S9: Stacked plot of the  $^1\text{H}$  NMR spectra for reduction of **2** with Mg-metal followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3'** with  $\text{PhICl}_2$ . Figure S10: Pictures of NMR tubes from reduction of **2** with 1, 2 and 4 equivalents of  $\text{KCs}$  respectively.

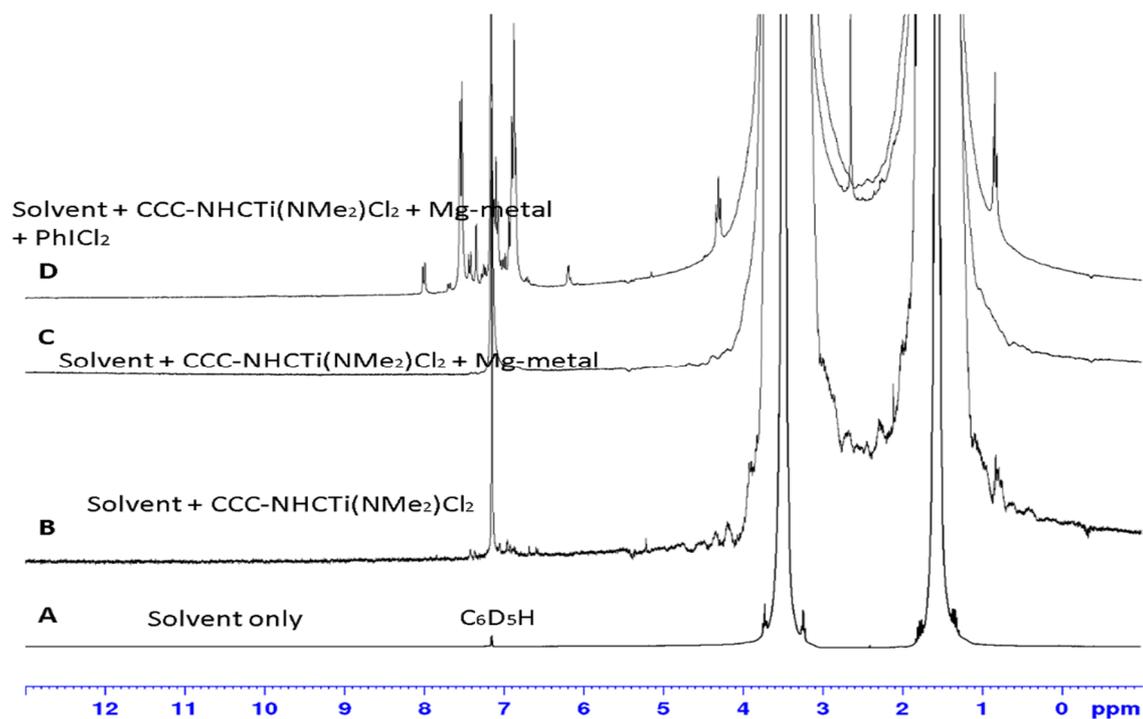
Figure S11: Stacked plot of the  $^1\text{H}$  NMR spectra for reduction of **2** with  $\text{KCs}$  followed by reoxidation with  $\text{PhICl}_2$  in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after reoxidation of intermediate **3'** with  $\text{PhICl}_2$ .

Figure S12: Stacked plot of the  $^1\text{H}$  NMR spectra for reduction of **2** with  $\text{KCs}$  followed by bubbling with CO in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after **3'** was bubbled with CO.

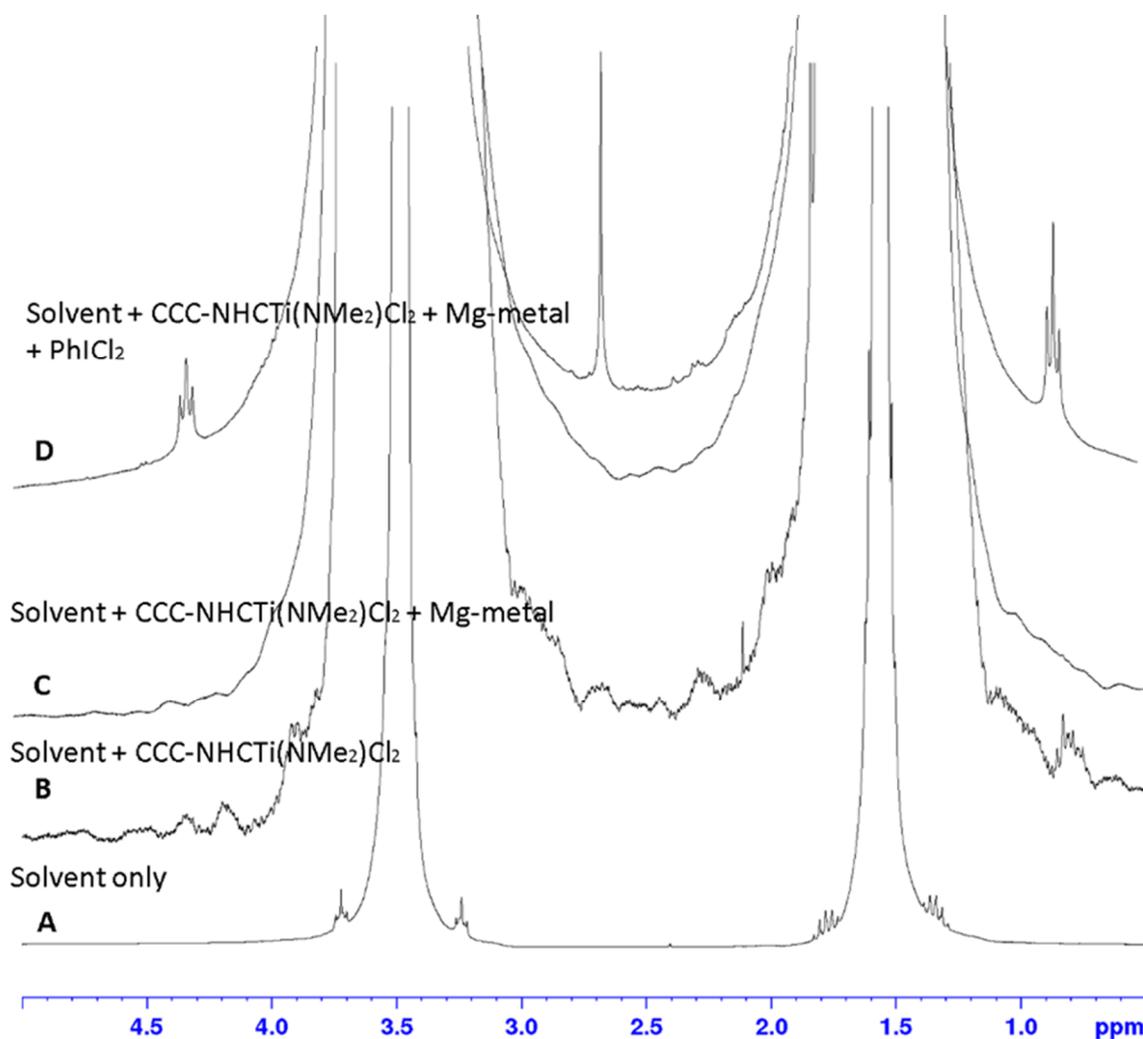
Figure S13: Stacked plot of the relevant zoomed portions of  $^1\text{H}$  NMR spectra for reduction of **2** with  $\text{KCs}$  followed by bubbling with CO in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after **3'** was bubbled with CO.



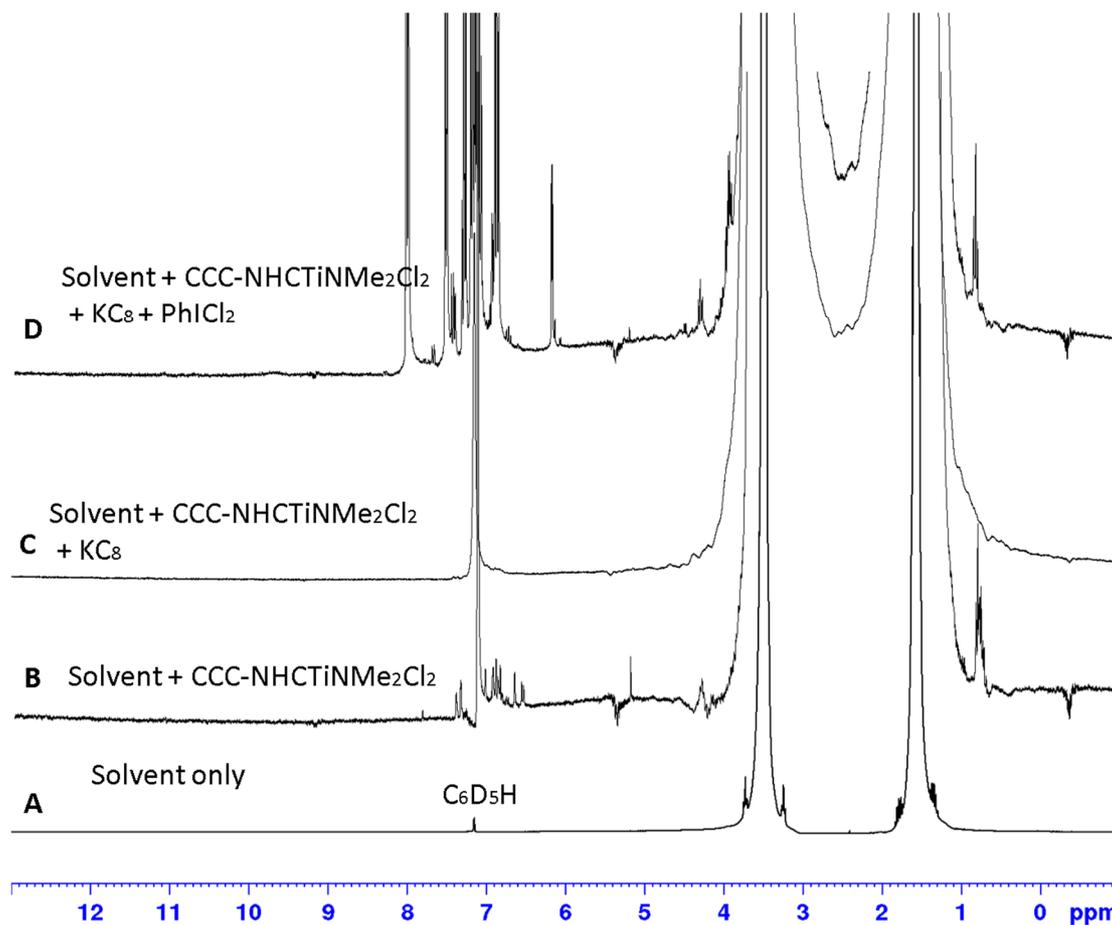
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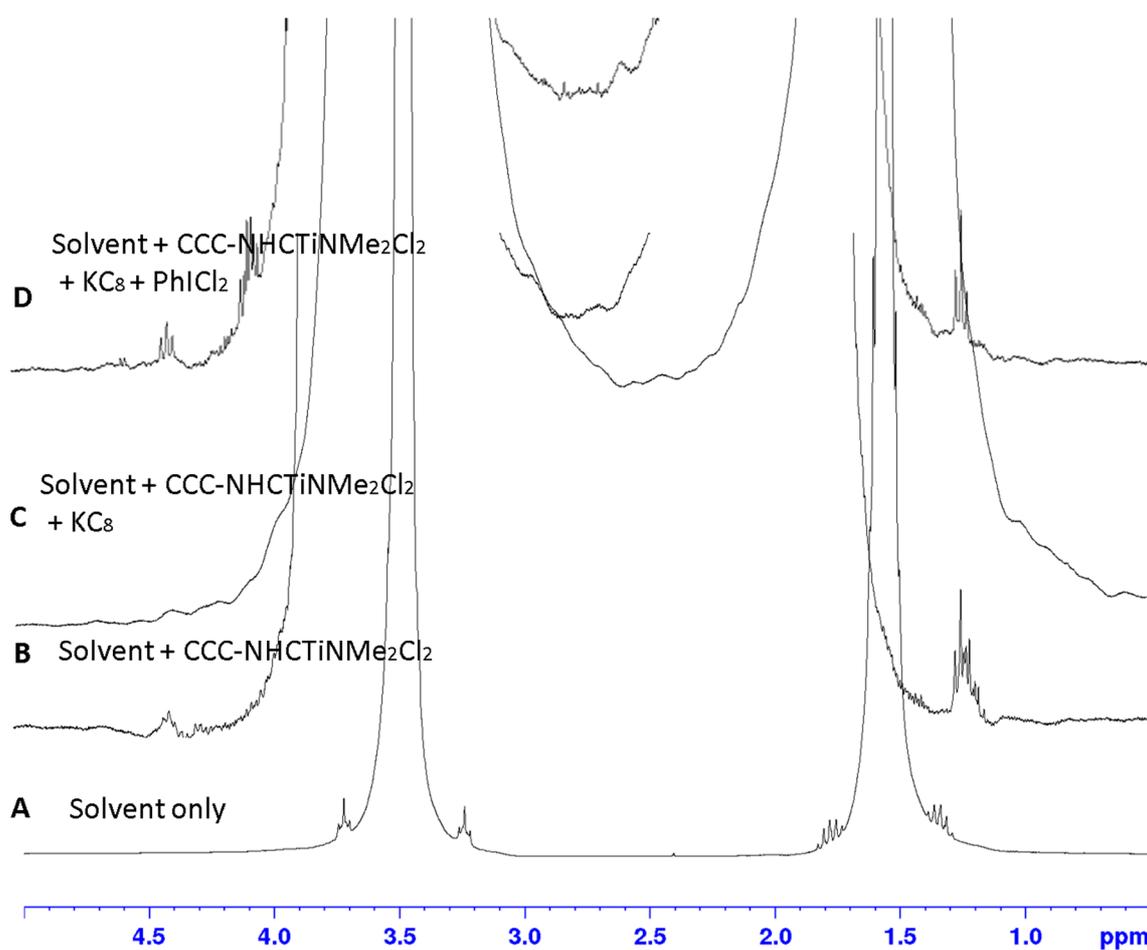




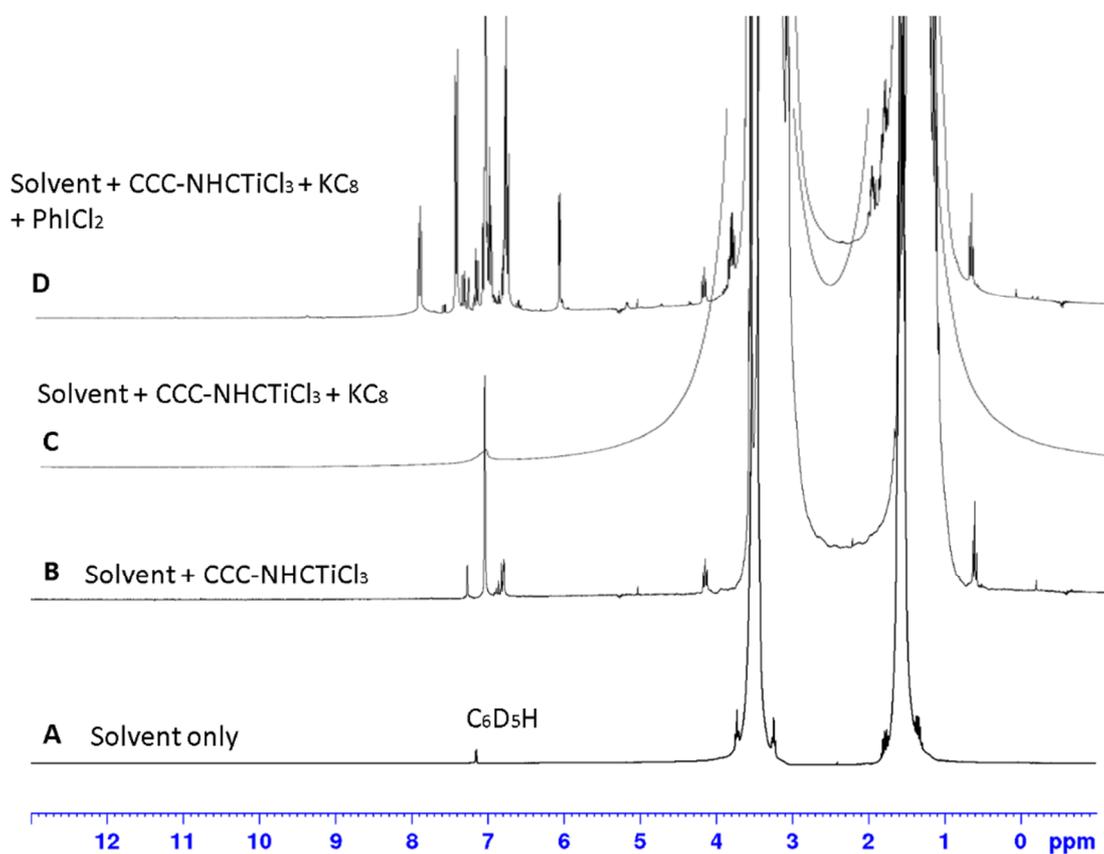
**Figure S4.** Stacked plot of the relevant zoomed portions of <sup>1</sup>H NMR spectra for reduction of **1** with Mg-metal followed by reoxidation with PhICl<sub>2</sub> in no-D THF. A: <sup>1</sup>H NMR spectrum for no-D THF (locked with C<sub>6</sub>D<sub>6</sub>). B: <sup>1</sup>H NMR spectrum for **1**. C: <sup>1</sup>H NMR spectrum after reduction of **1** to intermediate **3**. D: <sup>1</sup>H NMR spectrum after reoxidation of intermediate **3** with PhICl<sub>2</sub>.



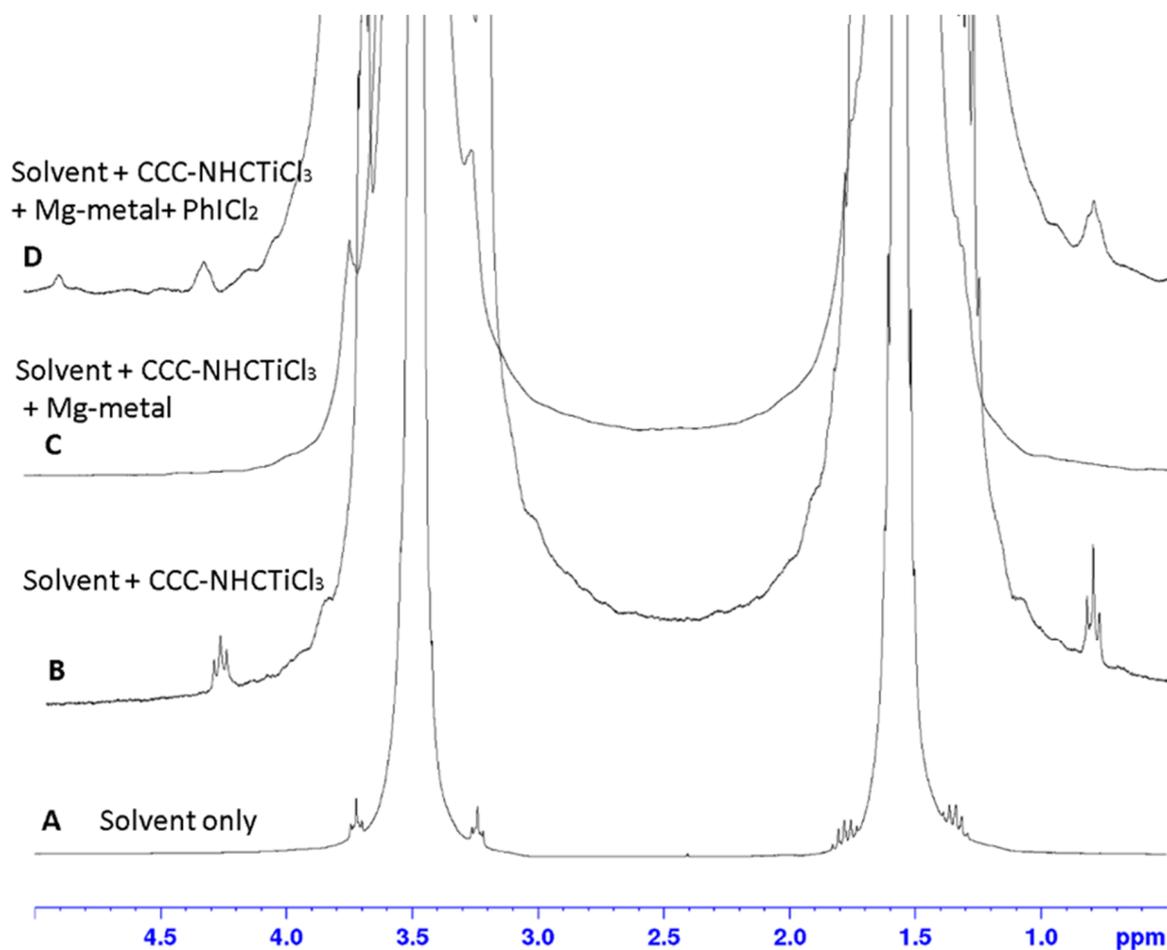
**Figure S5.** Stacked plot of the <sup>1</sup>H NMR spectra for reduction of **1** with KC<sub>8</sub> followed by reoxidation with PhICl<sub>2</sub> in no-D THF. A: <sup>1</sup>H NMR spectrum for no-D THF (locked with C<sub>6</sub>D<sub>6</sub>). B: <sup>1</sup>H NMR spectrum for **1**. C: <sup>1</sup>H NMR spectrum after reduction of **1** to intermediate **3**. D: <sup>1</sup>H NMR spectrum after reoxidation of intermediate **3** with PhICl<sub>2</sub>.



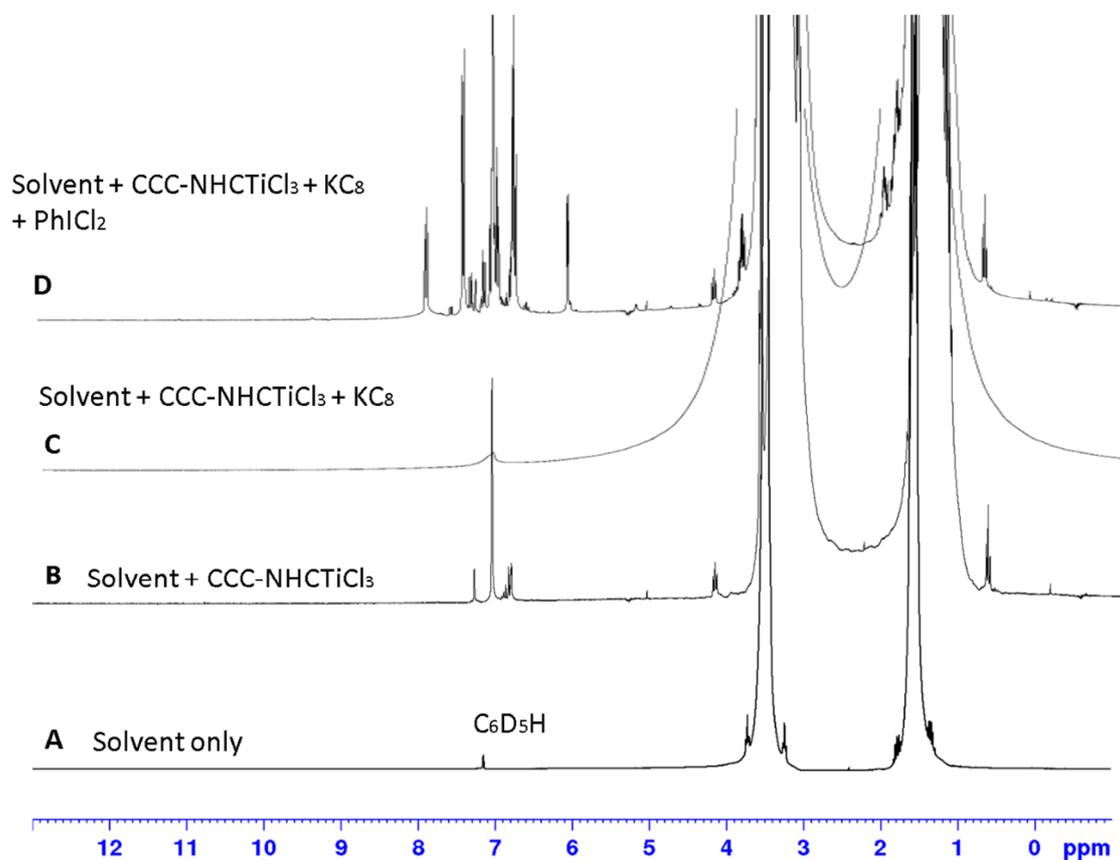
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**Figure S7.** Stacked plot of the <sup>1</sup>H NMR spectra for reduction of **2** with KC<sub>8</sub> followed by reoxidation with PhICl<sub>2</sub> in no-D THF. A: <sup>1</sup>H NMR spectrum for no-D THF (locked with C<sub>6</sub>D<sub>6</sub>). B: <sup>1</sup>H NMR spectrum for **2**. C: <sup>1</sup>H NMR spectrum after reduction of **2** to intermediate **3'**. D: <sup>1</sup>H NMR spectrum after reoxidation of intermediate **3'** with PhICl<sub>2</sub>.



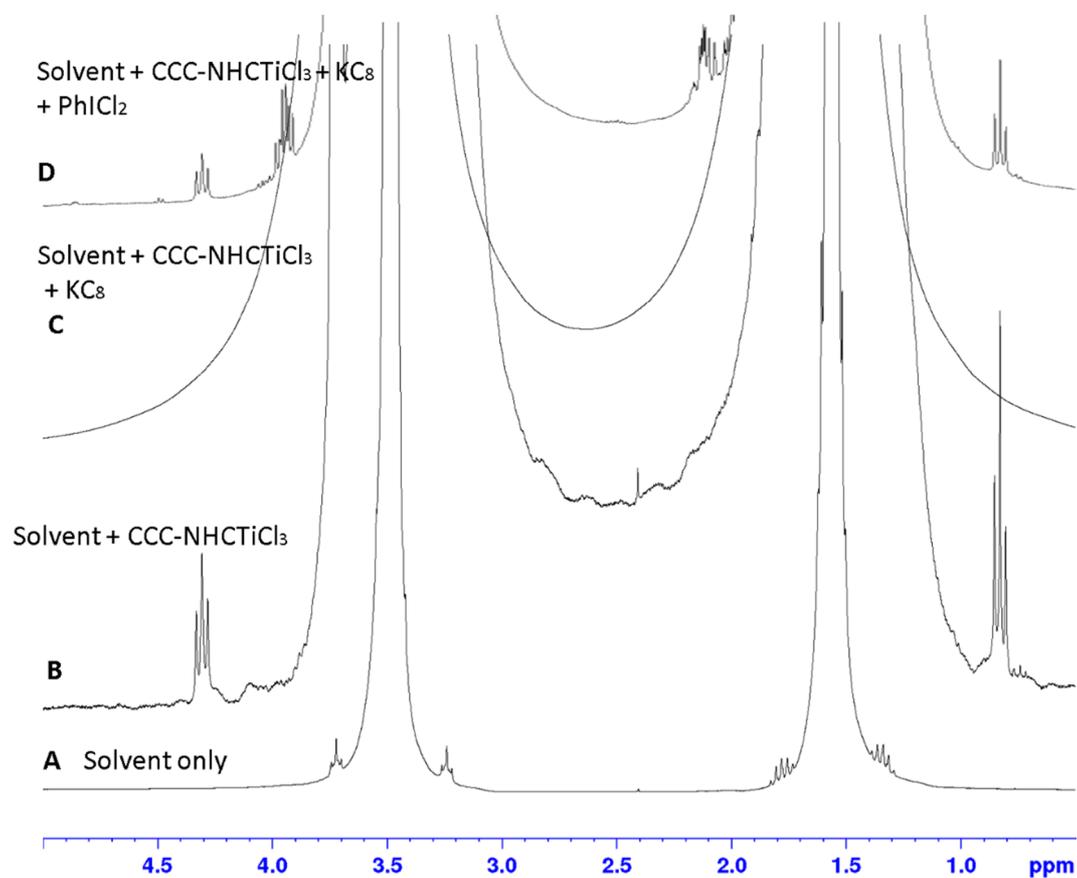
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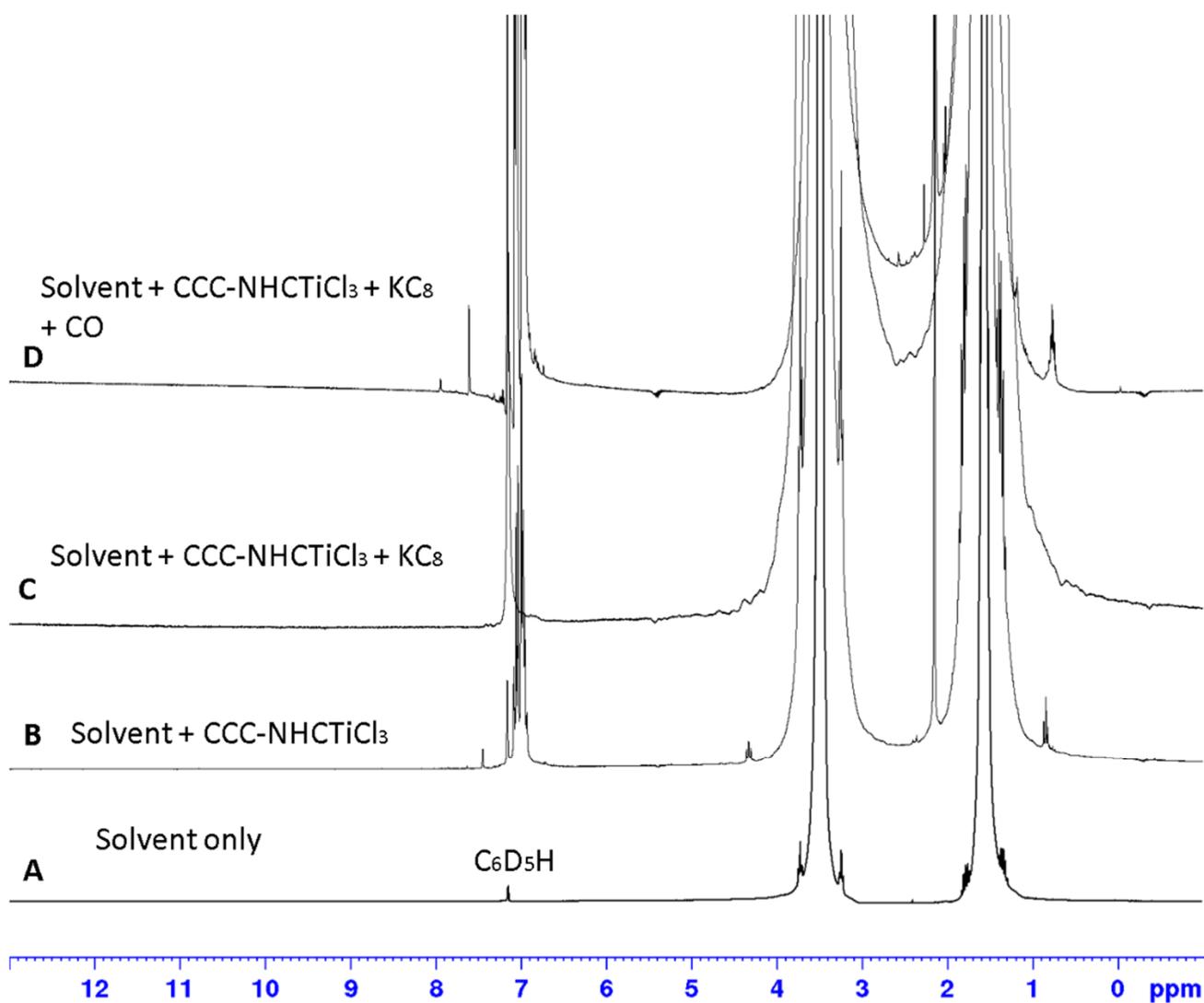
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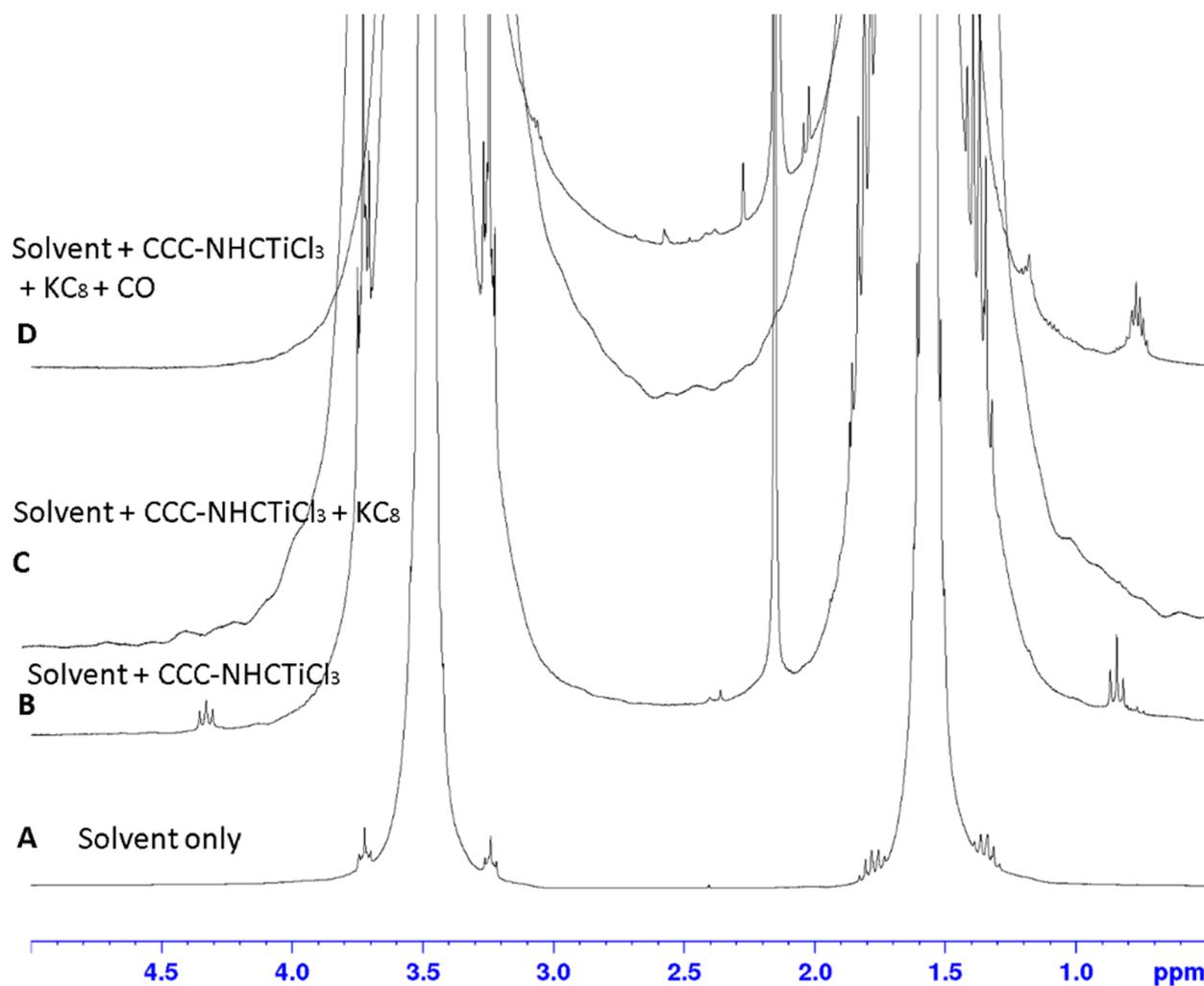
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**Figure S12.** Stacked plot of the <sup>1</sup>H NMR spectra for reduction of **2** with KC<sub>8</sub> followed by bubbling with CO in no-D THF. A: <sup>1</sup>H NMR spectrum for no-D THF (locked with C<sub>6</sub>D<sub>6</sub>). B: <sup>1</sup>H NMR spectrum for **2**. C: <sup>1</sup>H NMR spectrum after reduction of **2** to intermediate **3'**. D: <sup>1</sup>H NMR spectrum after **3'** was bubbled with CO.



**Figure S13.** Stacked plot of the relevant zoomed portions of  $^1\text{H}$  NMR spectra for reduction of **2** with  $\text{KC}_8$  followed by bubbling with CO in no-D THF. A:  $^1\text{H}$  NMR spectrum for no-D THF (locked with  $\text{C}_6\text{D}_6$ ). B:  $^1\text{H}$  NMR spectrum for **2**. C:  $^1\text{H}$  NMR spectrum after reduction of **2** to intermediate **3'**. D:  $^1\text{H}$  NMR spectrum after **3'** was bubbled with CO.