

Supporting Information

Isocyanide Substitution Reactions at the Trans Labile Sites of an Iron(II) N-Heterocyclic Carbene Complex

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1. NMR spectra of 2b

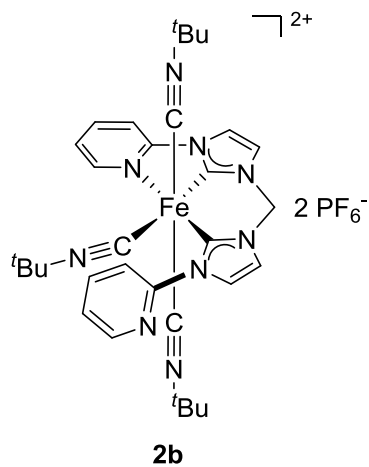


Figure S1. Structure of compound **2b**.

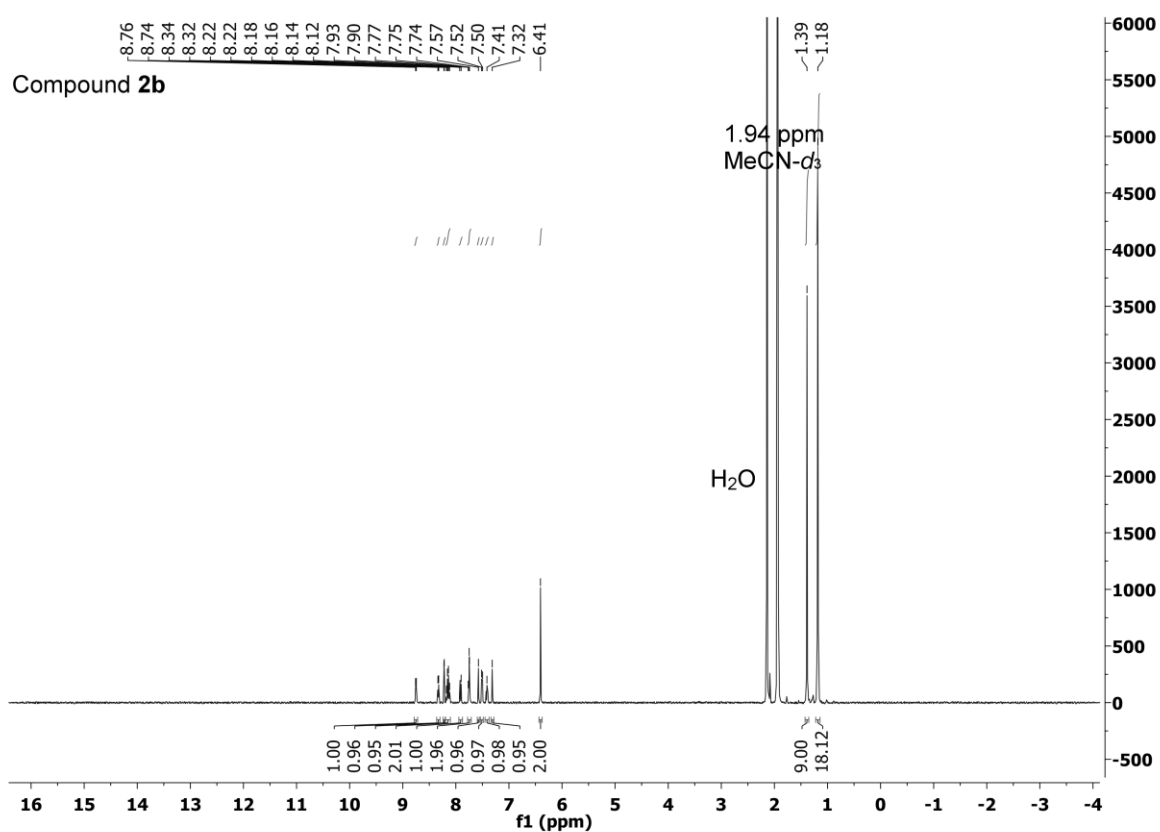


Figure S2. ¹H NMR of **2b** in MeCN-*d*₃ at 400.13 MHz.

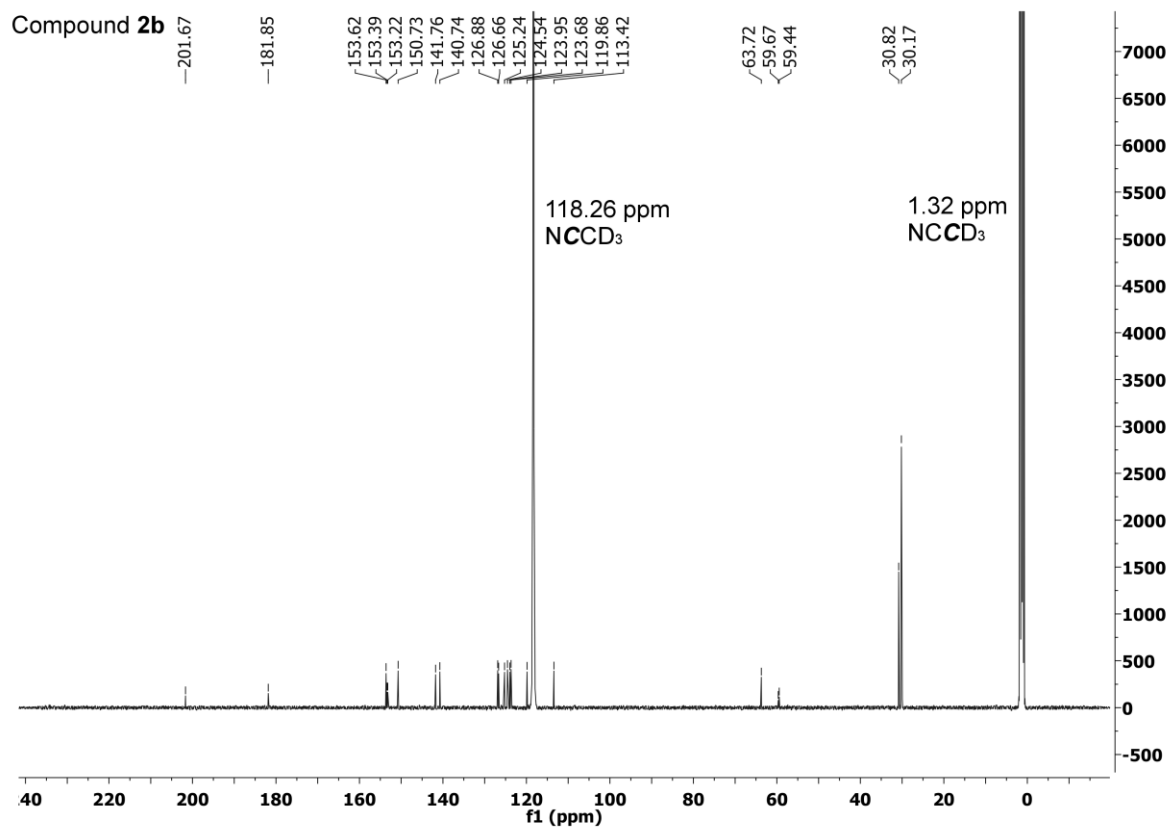


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2b** in $\text{MeCN-}d_3$ at 125.83 MHz.

2. NMR spectra of 3a

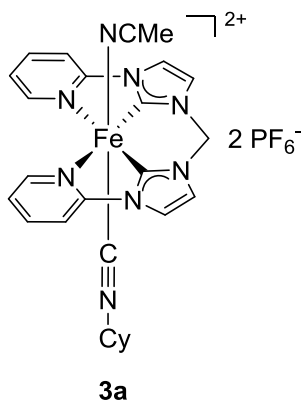


Figure S4. Structure of compound **3a**.

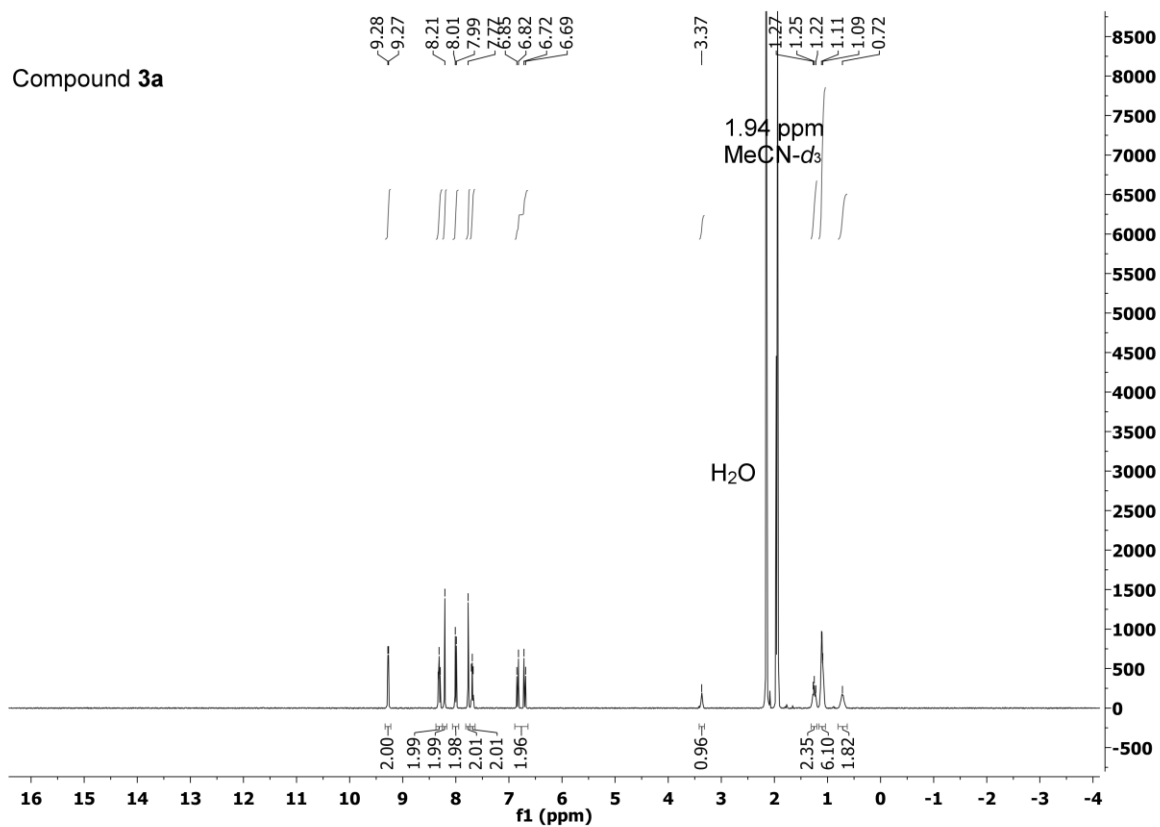


Figure S5. ^1H NMR of **3a** in $\text{MeCN-}d_3$ at 400.13 MHz.

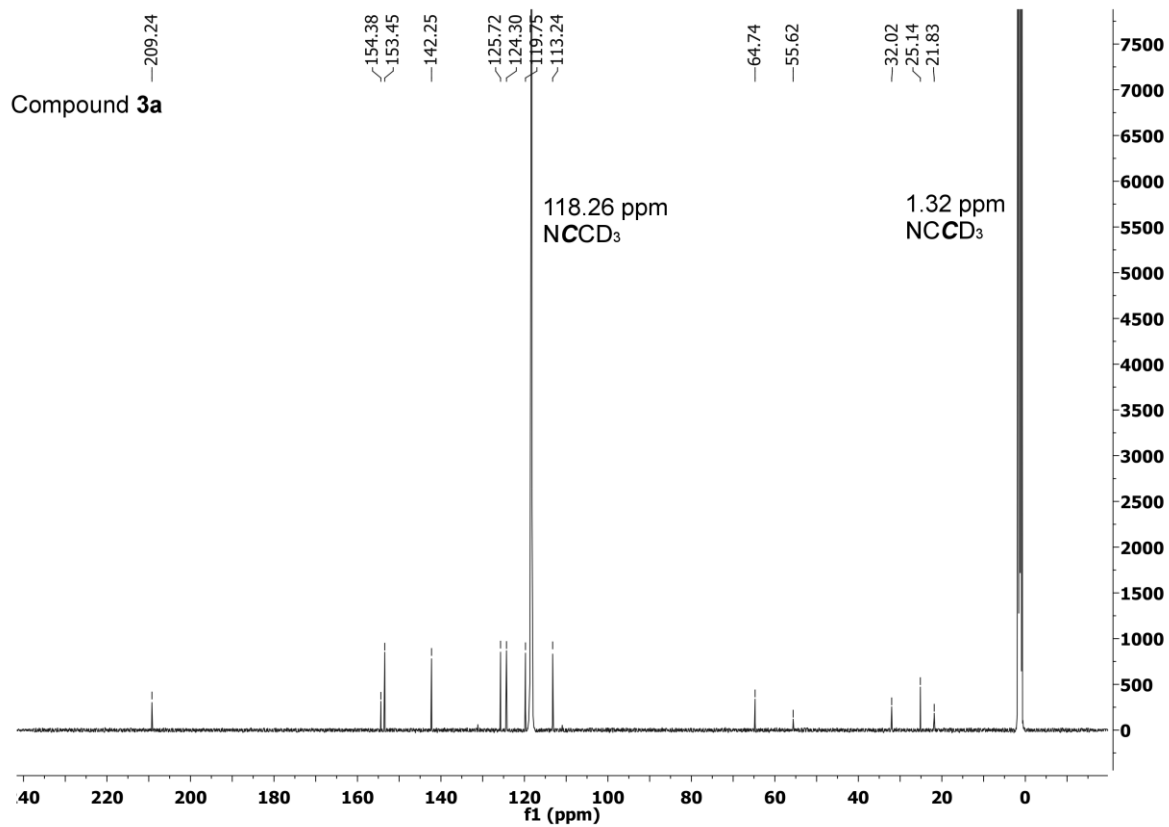


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3a** in $\text{MeCN-}d_3$ at 125.83 MHz.

3. NMR spectra of 3b

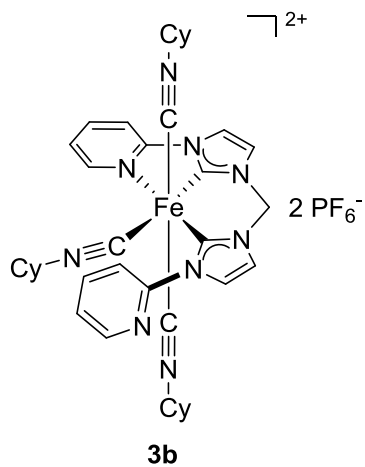


Figure S7. Structure of compound **3b**.

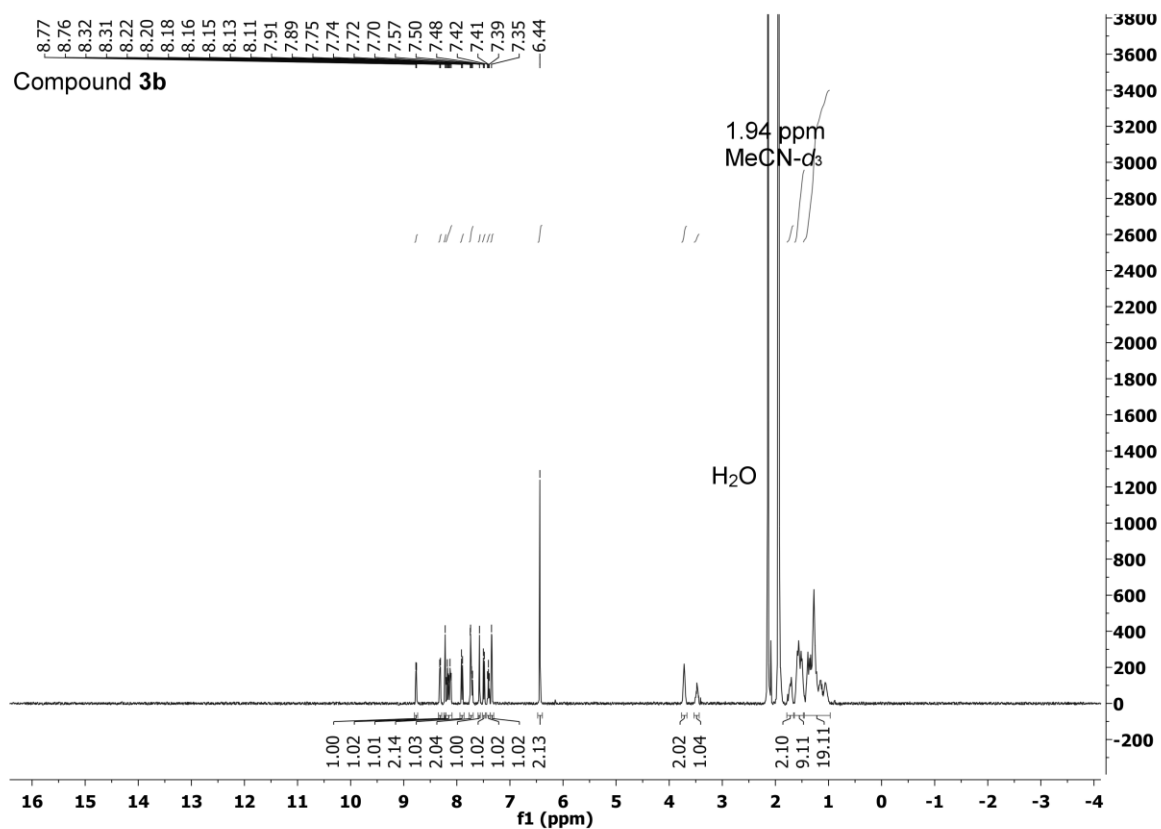


Figure S8. ¹H NMR of **3b** in MeCN-*d*₃ at 400.13 MHz.

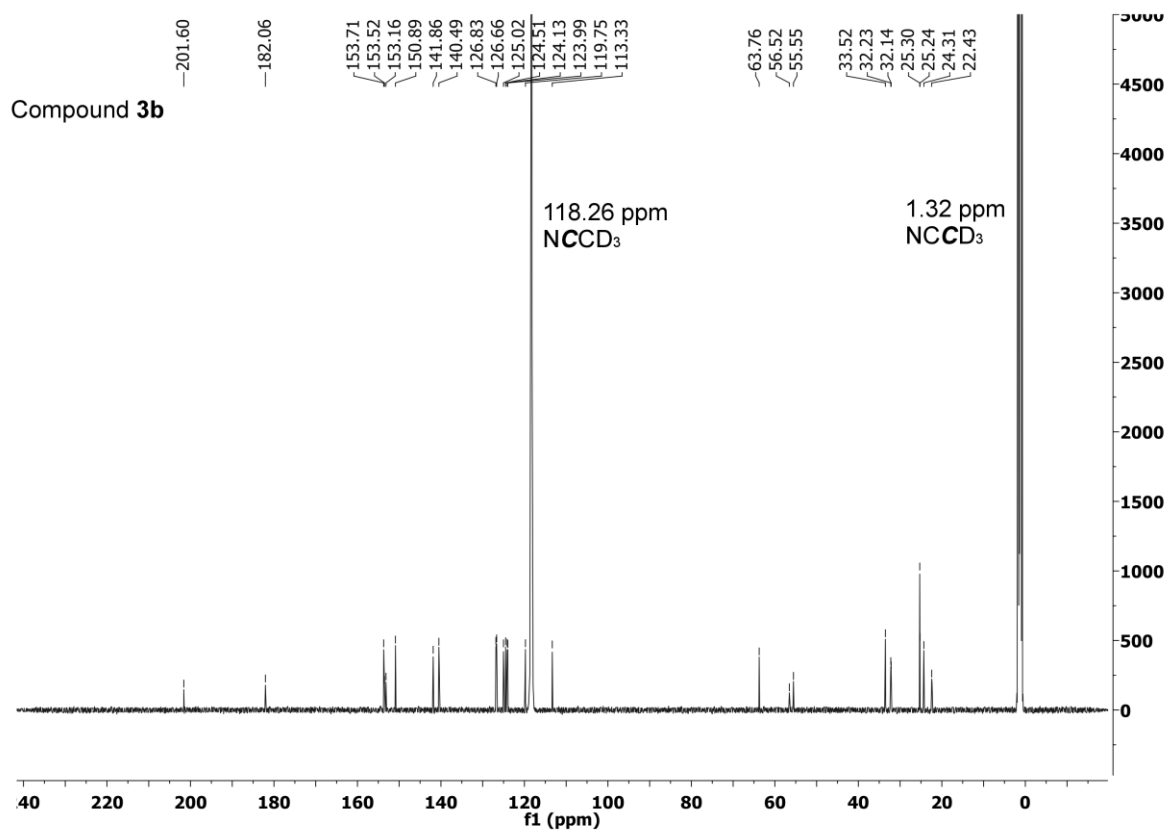


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3b** in MeCN- d_3 at 125.83 MHz.

4. NMR spectra of 4a

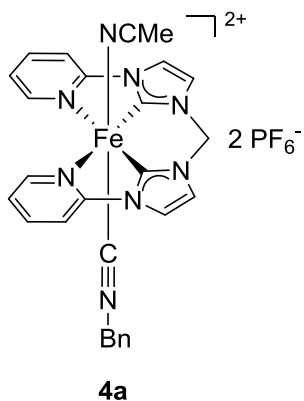


Figure S10. Structure of compound **4a**.

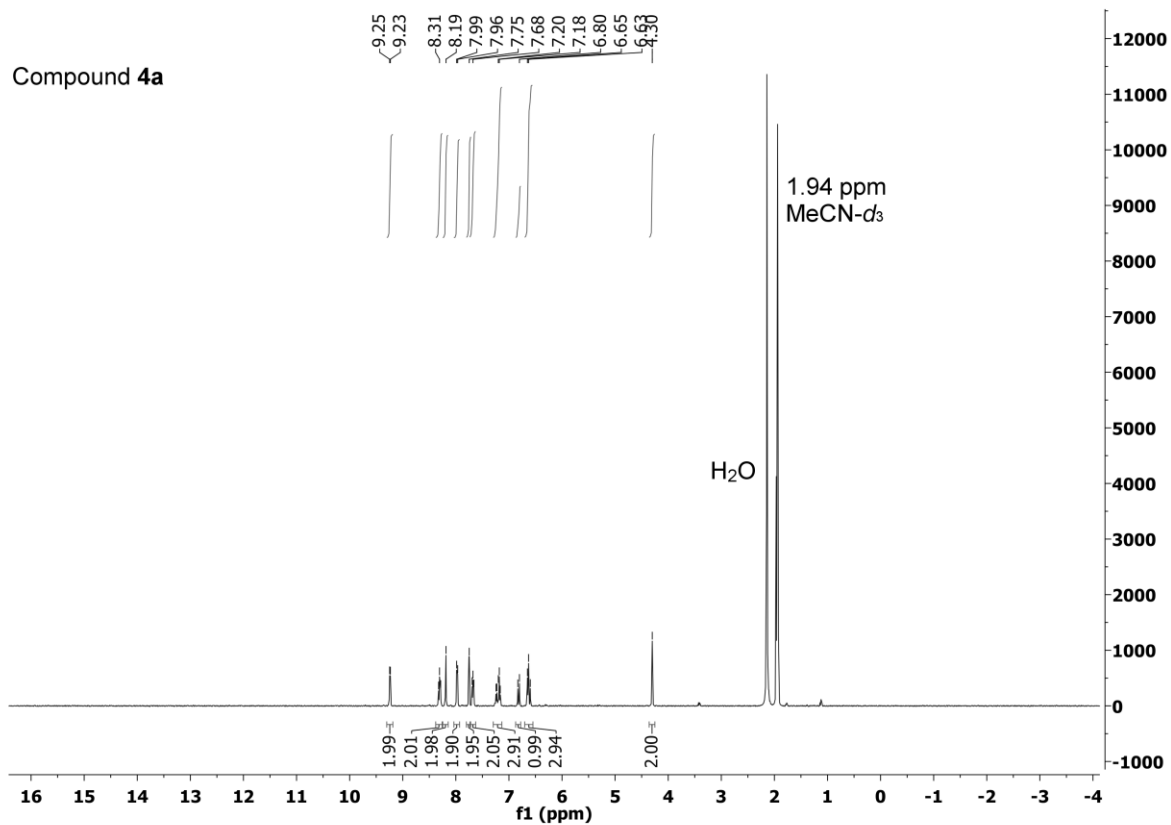


Figure S11. ^1H NMR of **4a** in $\text{MeCN-}d_3$ at 400.13 MHz.

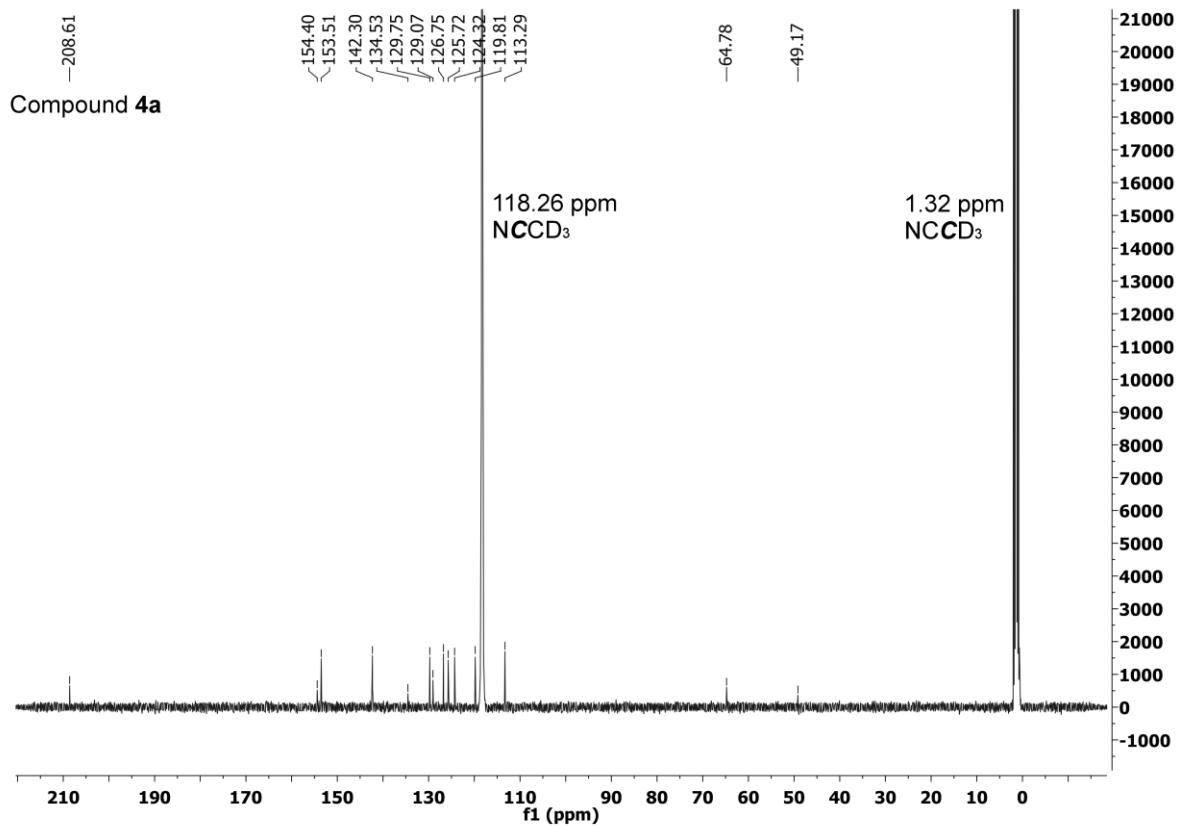


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR of **4a** in MeCN- d_3 at 125.83 MHz.

5. NMR spectra of 4b

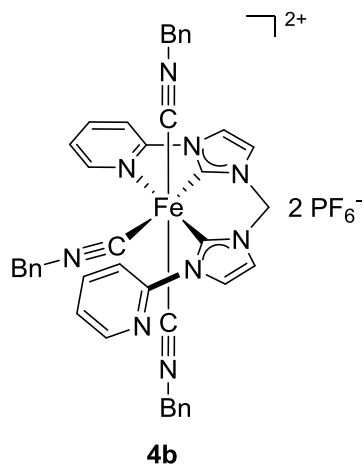


Figure S13. Structure of compound **4b**.

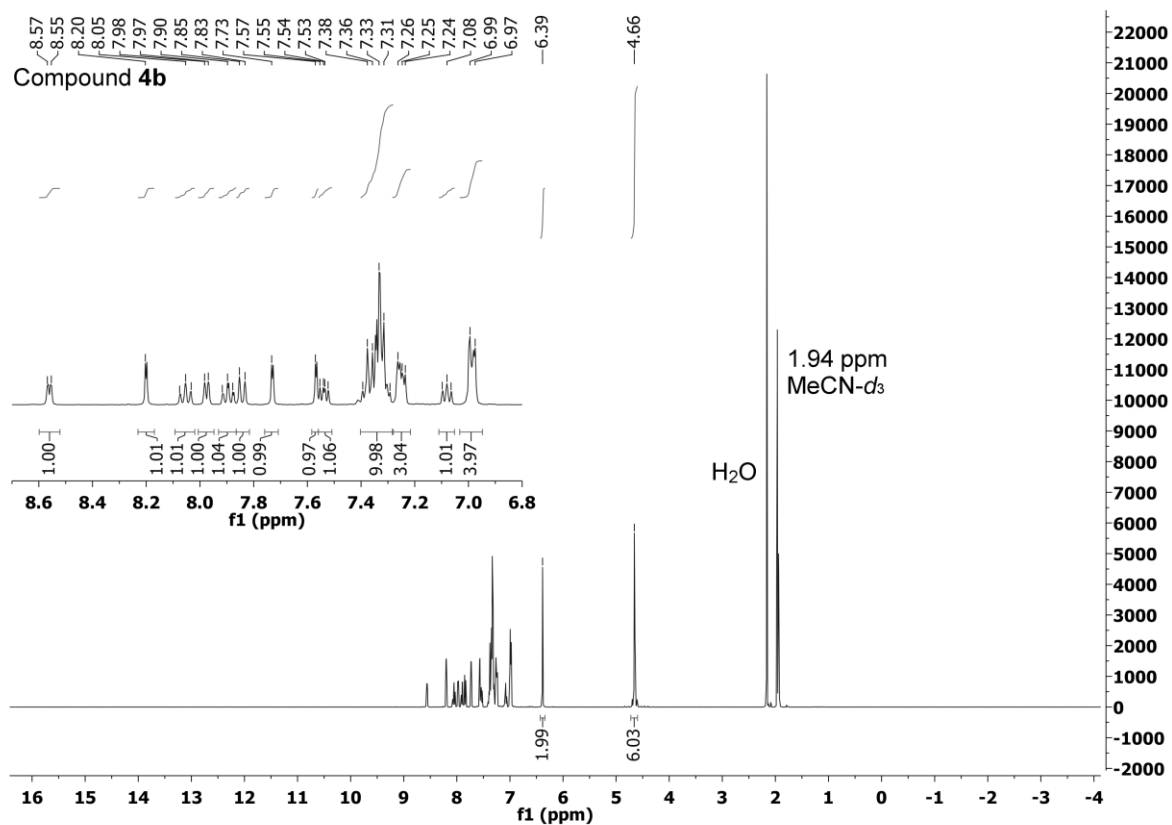


Figure S14. ^1H NMR of **4b** in $\text{MeCN-}d_3$ at 400.13 MHz.

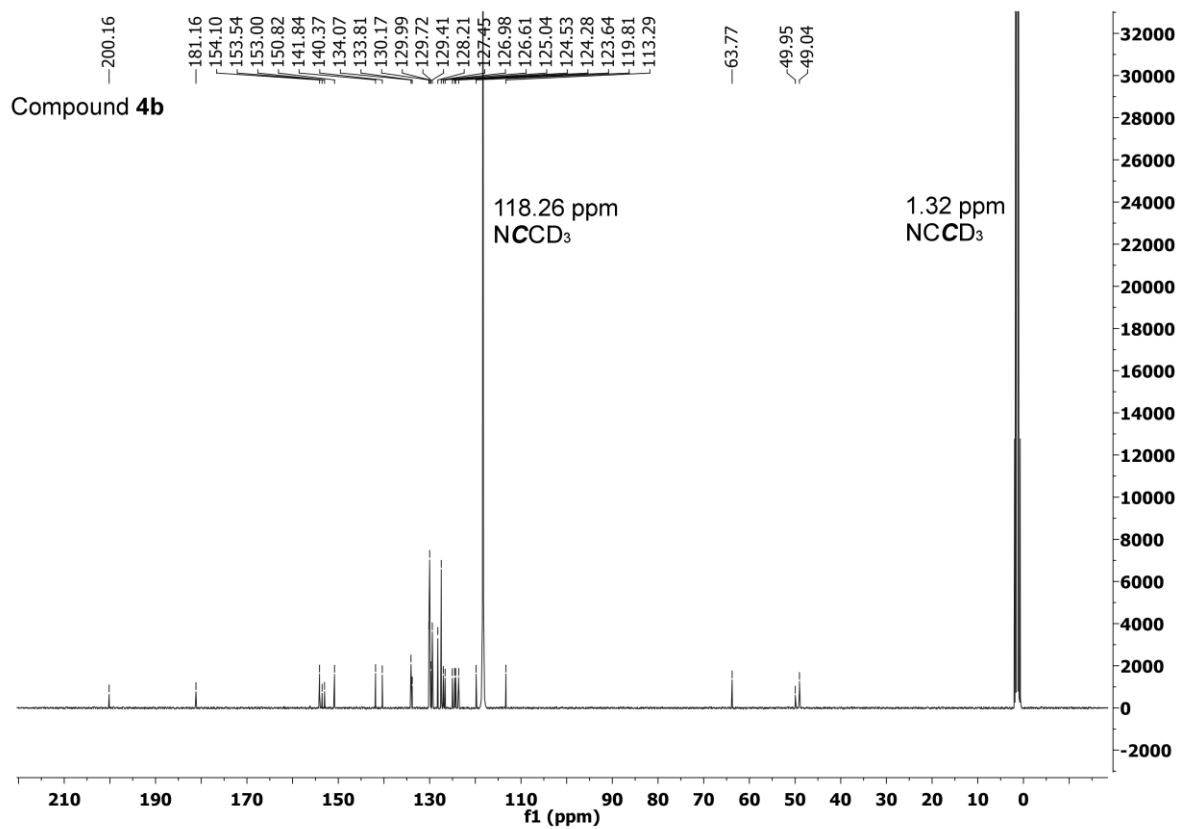


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR of **4b** in MeCN- d_3 at 125.83 MHz.

6. NMR spectra of 5a

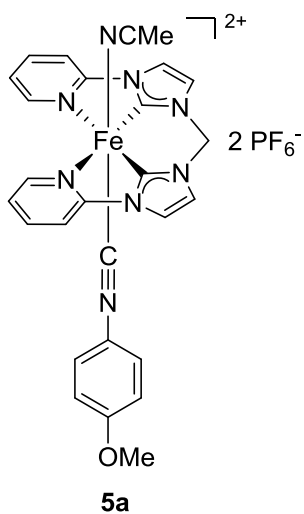


Figure S16. Structure of compound **5a**.

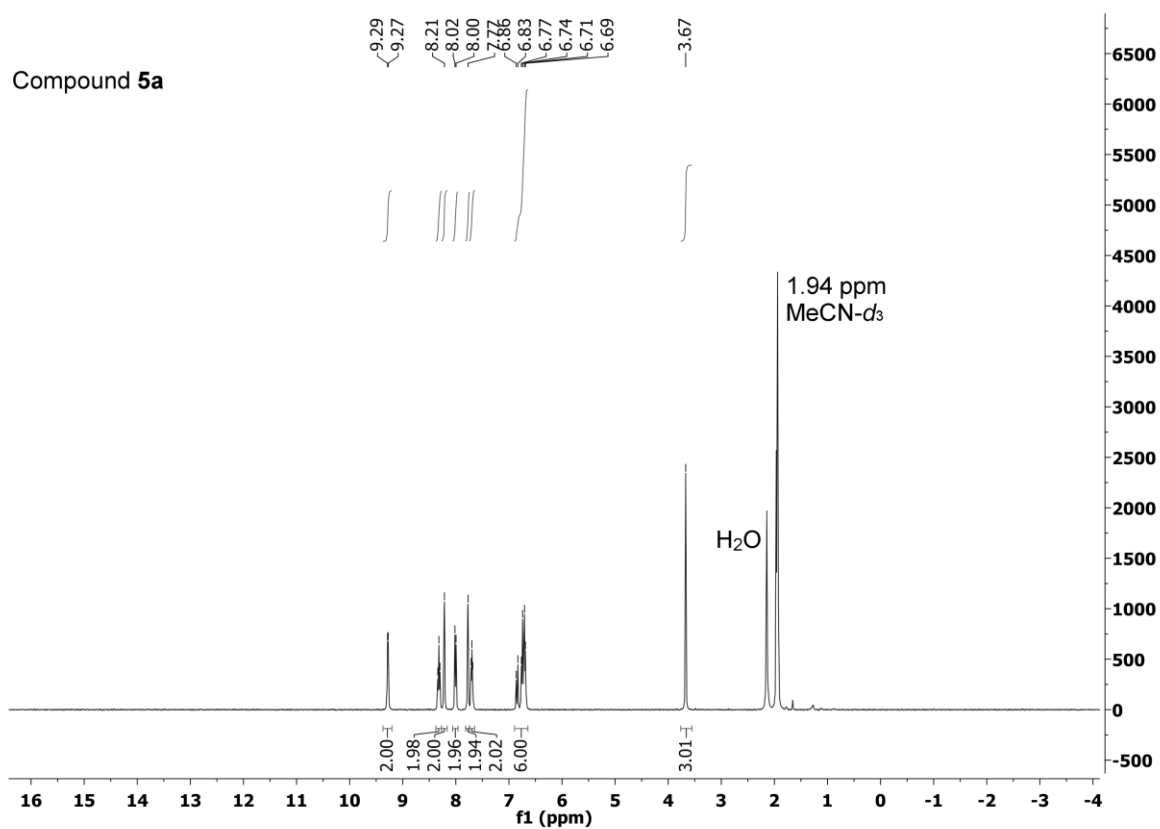


Figure S17. ¹H NMR of **5a** in MeCN-*d*₃ at 400.13 MHz.

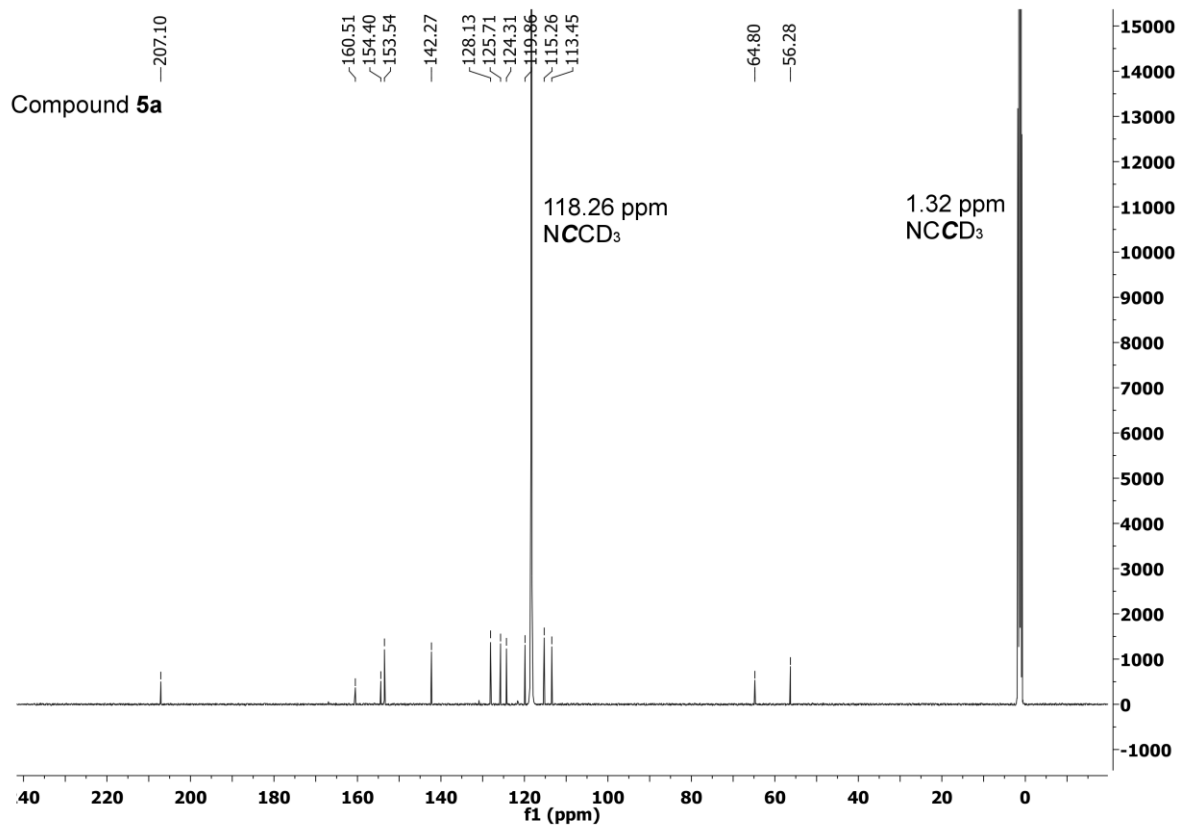


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR of **5a** in $\text{MeCN-}d_3$ at 125.83 MHz.

7. NMR spectra of 5b

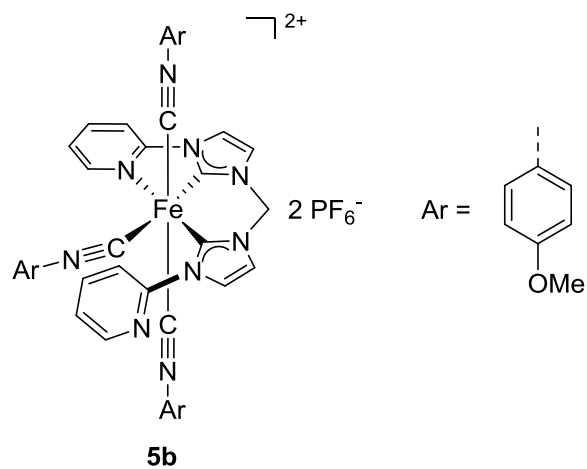


Figure S19. Structure of compound **5b**.

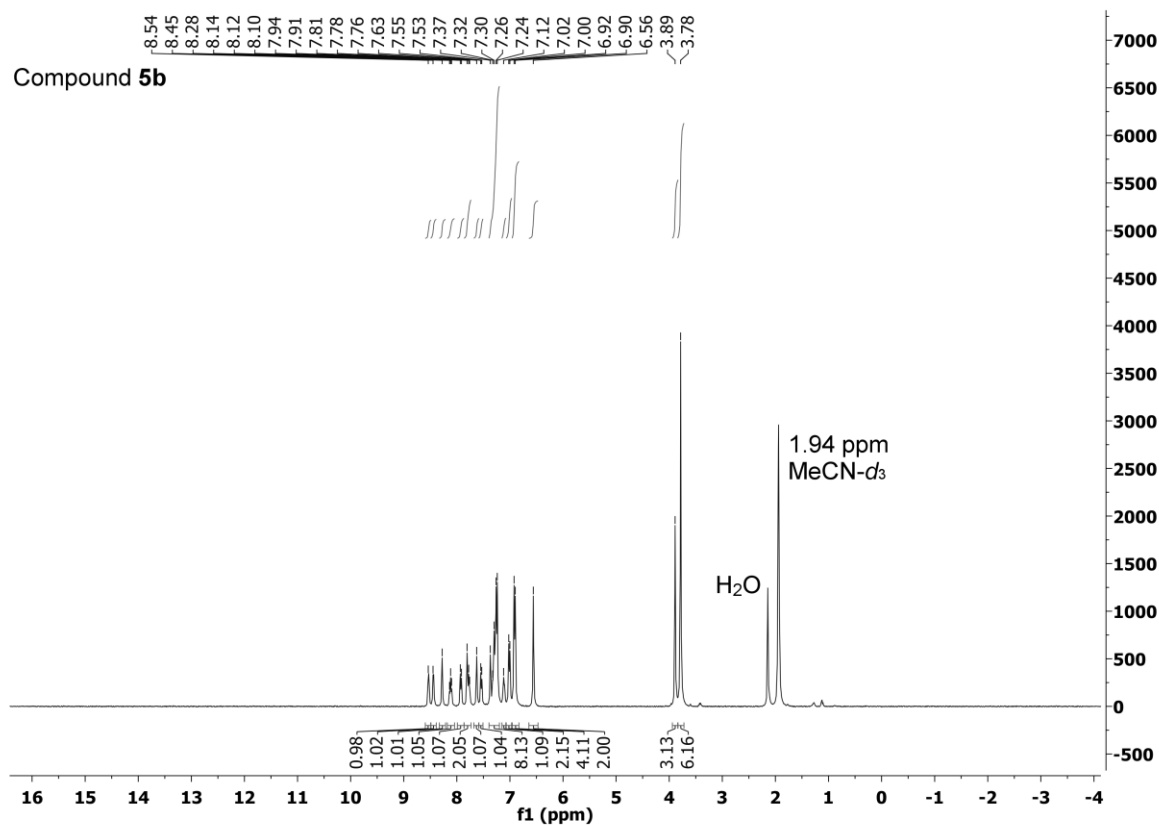


Figure S20. ¹H NMR of **5b** in MeCN-*d*₃ at 400.13 MHz.

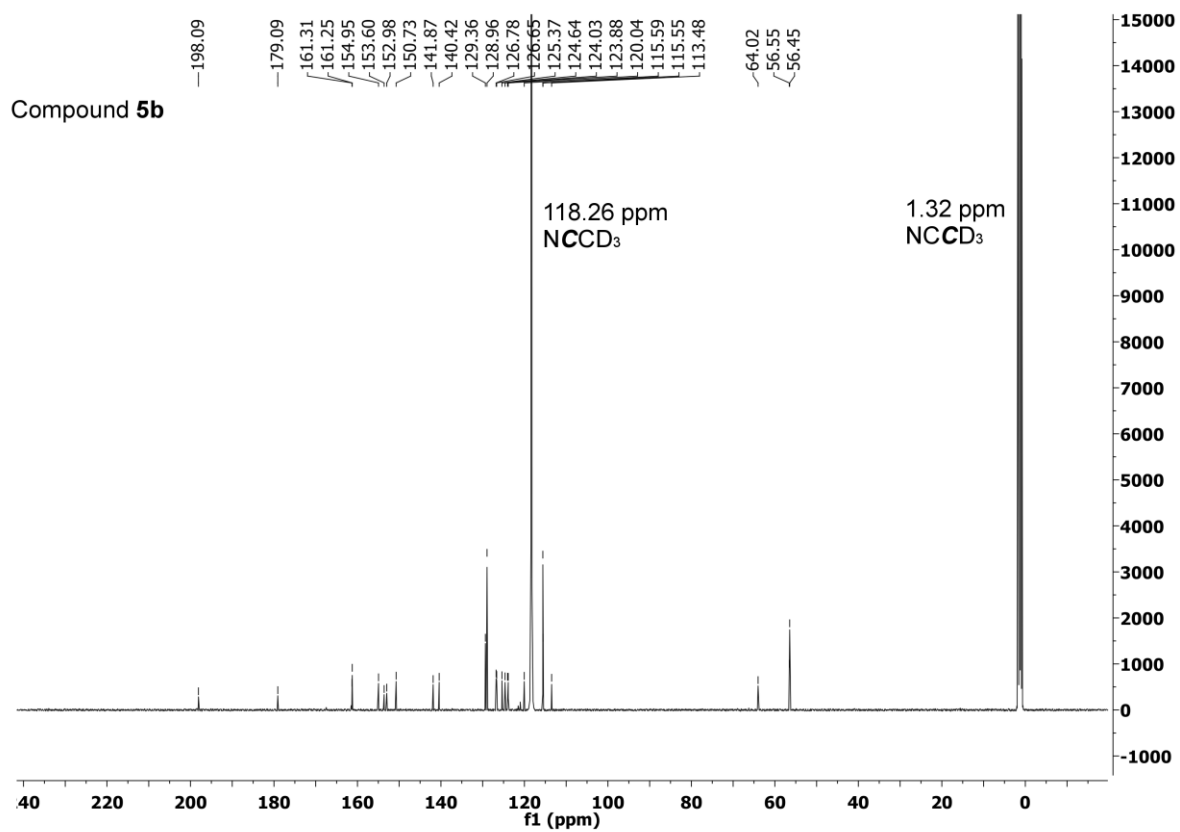


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR of **5b** in MeCN- d_3 at 125.83 MHz.

8. Identification of disubstituted intermediate 2c

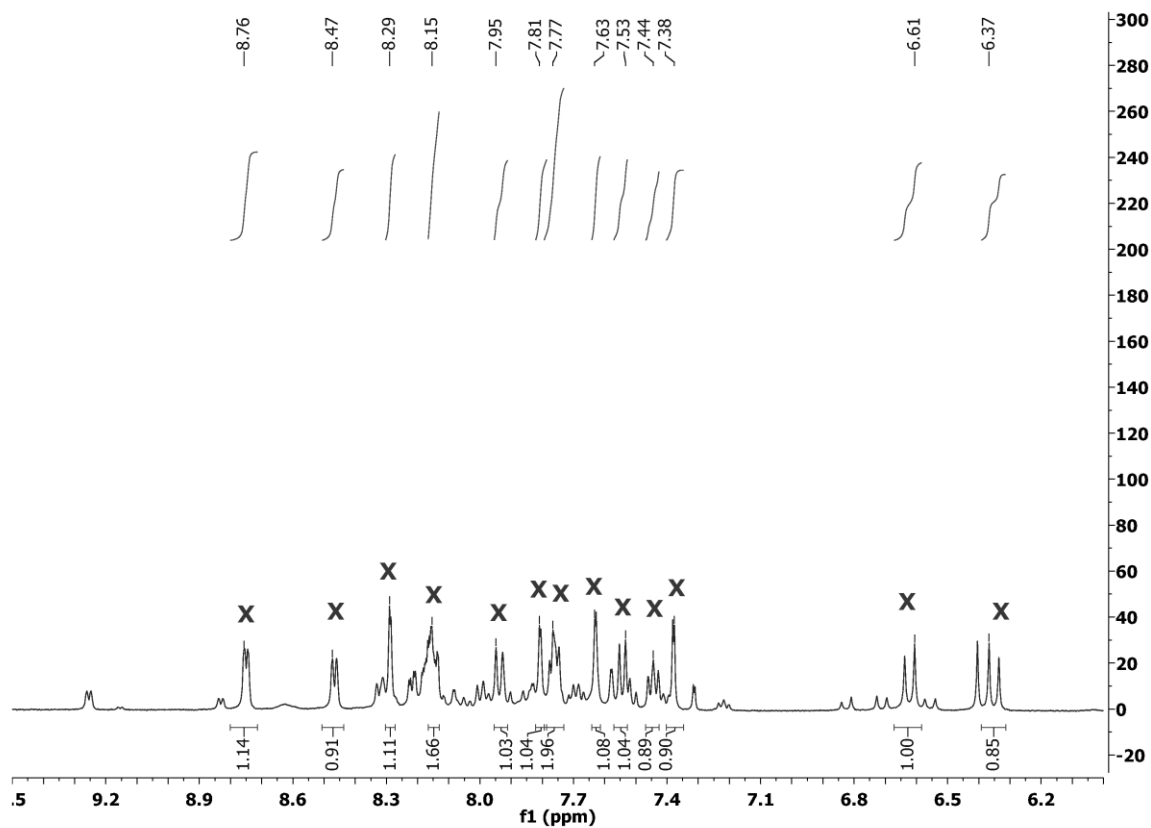


Figure S22. ^1H NMR after 40 min of the time-dependent monitoring of the reaction of **1** with 5 equiv. CN^tBu . At this point the disubstituted intermediate **2c** has reached its peak amount during the reaction. The peaks marked with an X are assigned to **2c**. The two doublet signals at 6.61 ppm and 6.37 ppm are caused by the CH_2 bridge of the NCCN ligand (doublet of doublet due to loss of symmetry).