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

![Structure of compound 2b]

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

![1H NMR spectrum of 2b in MeCN-d$_3$ at 400.13 MHz]

**Figure S2.** $^1$H NMR of 2b in MeCN-$d_3$ at 400.13 MHz.
Figure S3. $^{13}$C{$^{1}$H} NMR of 2b in MeCN-$d_3$ at 125.83 MHz.
2. NMR spectra of 3a

Figure S4. Structure of compound 3a.

Figure S5. $^1$H NMR of 3a in MeCN-$d_3$ at 400.13 MHz.
Figure S6. $^{13}$C$^{[1]H}$ NMR of 3a in MeCN-$d_3$ at 125.83 MHz.
3. NMR spectra of 3b

Figure S7. Structure of compound 3b.

Figure S8. $^1$H NMR of 3b in MeCN-$d_3$ at 400.13 MHz.
Figure S9. $^{13}$C-$^1$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. $^1$H NMR of 4a in MeCN-$d_3$ at 400.13 MHz.
Figure S12. $^{13}$C{¹H} NMR of 4a in MeCN-$d_3$ at 125.83 MHz.
5. NMR spectra of 4b

Figure S13. Structure of compound 4b.

Figure S14. $^1$H NMR of 4b in MeCN-$d_3$ at 400.13 MHz.
Figure S15. $^{13}$C{$^1$}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. $^1$H NMR of 5a in MeCN-$d_3$ at 400.13 MHz.
Figure S18. $^{13}$C{¹H} NMR of 5a in MeCN-$d_3$ at 125.83 MHz.
7. NMR spectra of 5b

Figure S19. Structure of compound 5b.

Figure S20. $^1$H NMR of 5b in MeCN-$d_3$ at 400.13 MHz.
Figure S21. $^{13}$C{H} NMR of 5b in MeCN-$d_3$ at 125.83 MHz.
8. Identification of disubstituted intermediate 2c

Figure S22. $^1$H NMR after 40 min of the time-dependent monitoring of the reaction of 1 with 5 equiv. CN'Bu. 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).