Supporting Information

Reaction of a polydentate Cysteine-based ligand and its nickel(II) complex with electrophilic and nucleophilic methyl-transfer reagents - From S-methylation to acetyl coenzyme A synthase reactivity

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1. Mass spectra

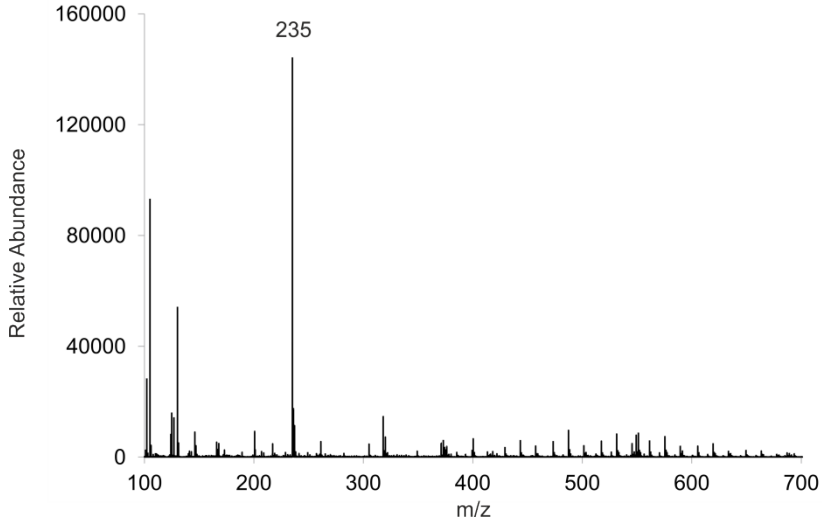

Figure S1. High-resolution ESI-MS of Me_2L.

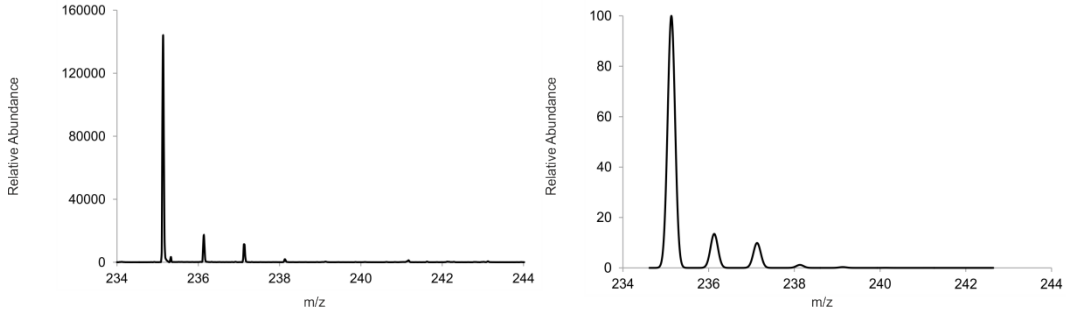

Figure S2. Measured (left) and calculated (right) isotopic pattern for the peak at m/z = 235.1295 in the high-resolution ESI-MS of Me_2L.

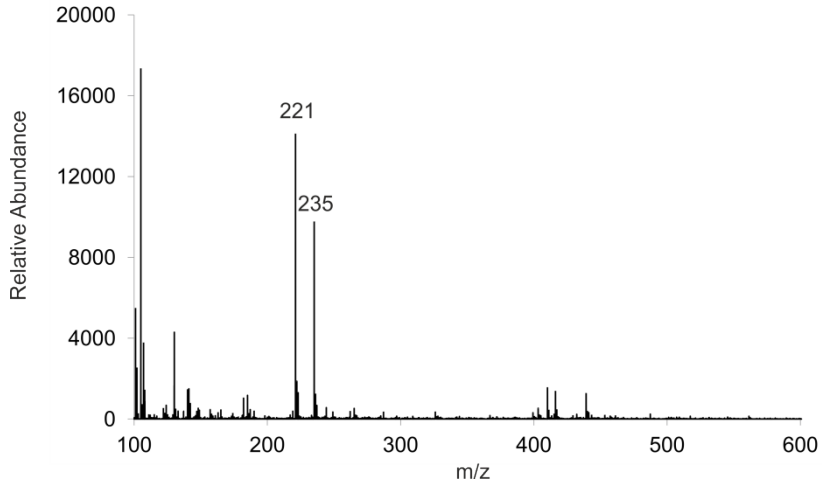

Figure S3. High-resolution ESI-MS of MeLH: *m/z* = 221 for $[MeLH]H^+$ and *m/z* = 235 for $[Me_2L]H^+$.

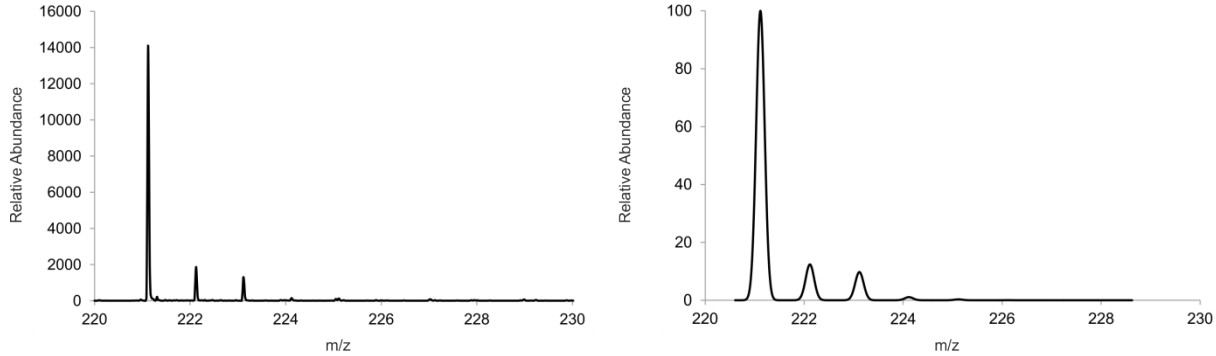

Figure S4. Measured (left) and calculated (right) isotopic pattern for the peak at m/z = 221.1206 in the high-resolution ESI-MS of MeLH.

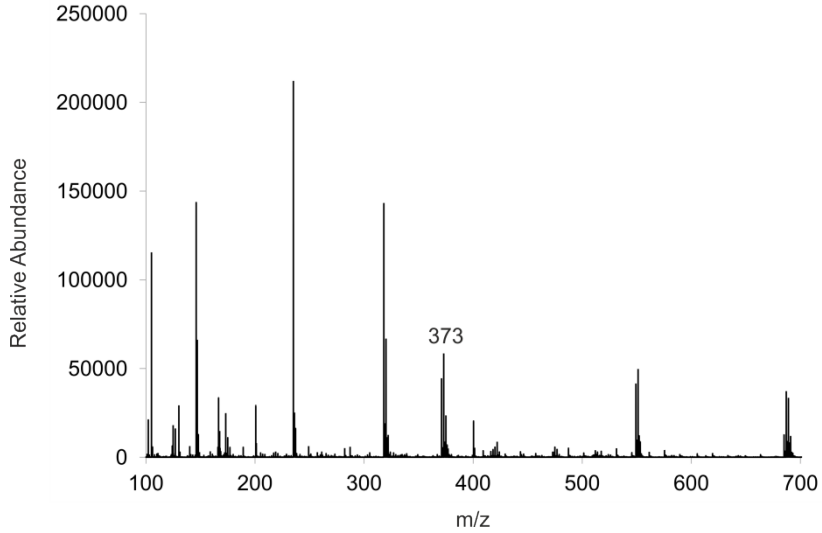

Figure S5. High-resolution ESI-MS of Me_2LNiBr_2 (**2**): *m/z* = 373 for $[Me_2LNiBr]^+$.

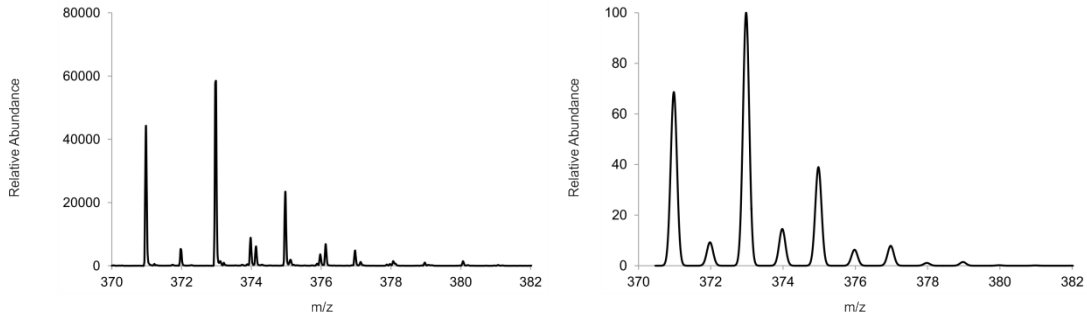

Figure S6. Measured (left) and calculated (right) isotopic pattern for the peak at m/z = 372.9720 in the high-resolution ESI-MS of Me_2LNiBr_2 (**2**).

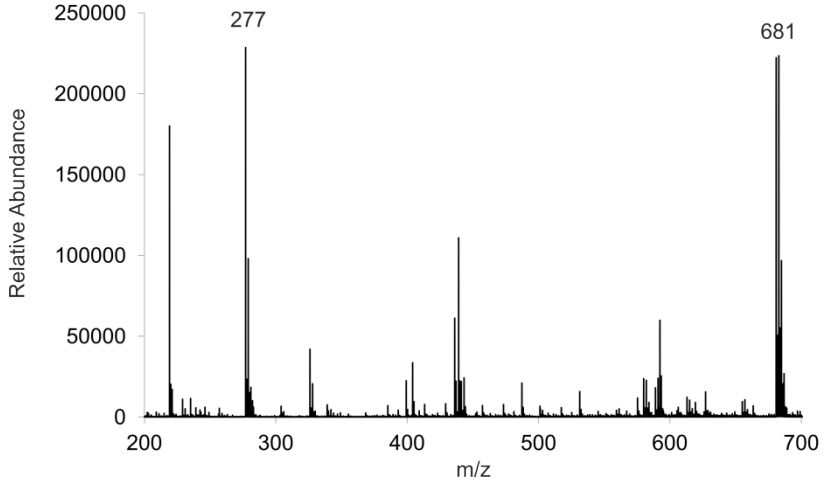

Figure S7. High-resolution ESI-MS of $[(MeNi)_3I]I_2$ (**3**).

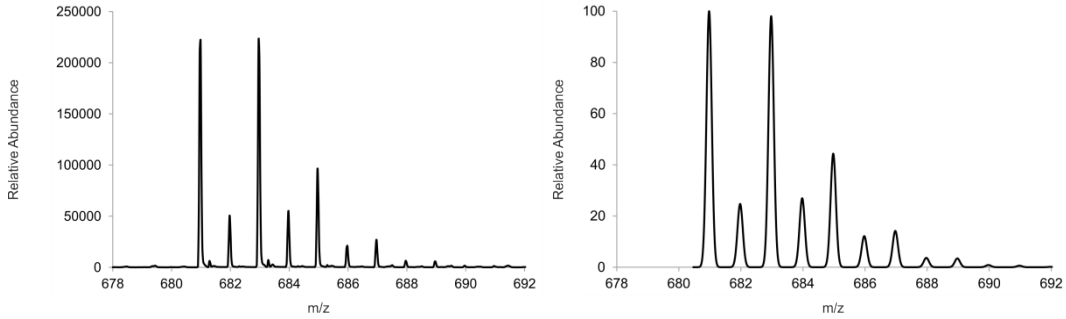

Figure S8. Measured (left) and calculated (right) isotopic pattern for the peak at m/z = 680.9673 in the high-resolution ESI-MS of $[(MeNi)_3I]I_2$ (**3**).

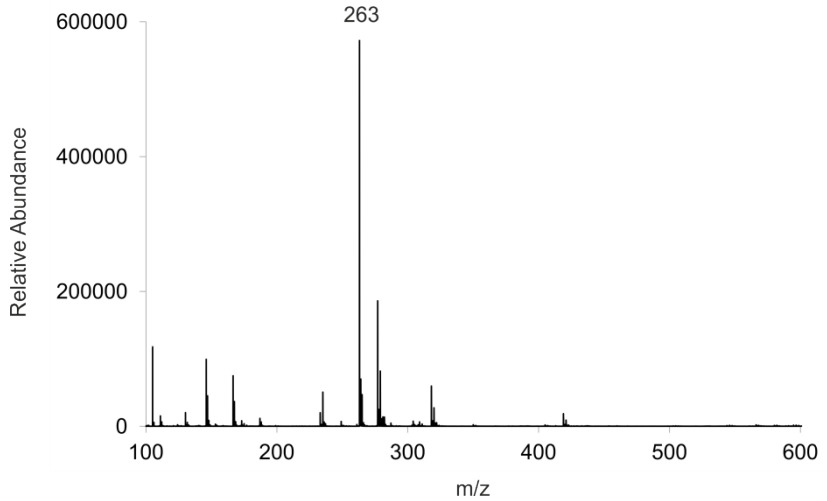

Figure S9. High-resolution ESI-MS of MeL(CO)Me (**4**).

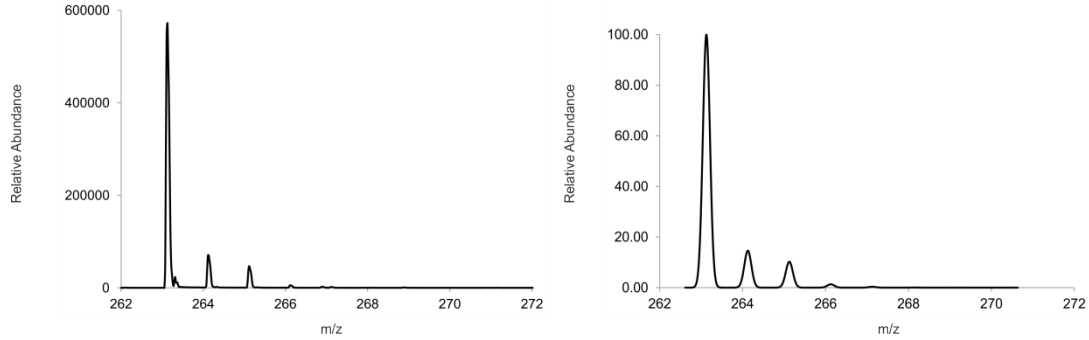

Figure S10. Measured (left) and calculated (right) isotopic pattern for the peak at m/z = 263.1291 in the high-resolution ESI-MS of MeL(CO)Me (**4**).

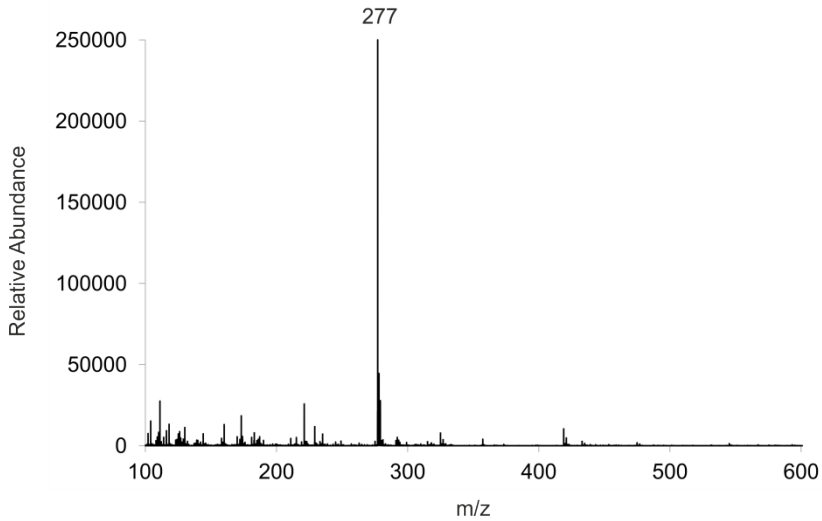

Figure S11. High-resolution ESI-MS of MeL(CO)Et (**5**).

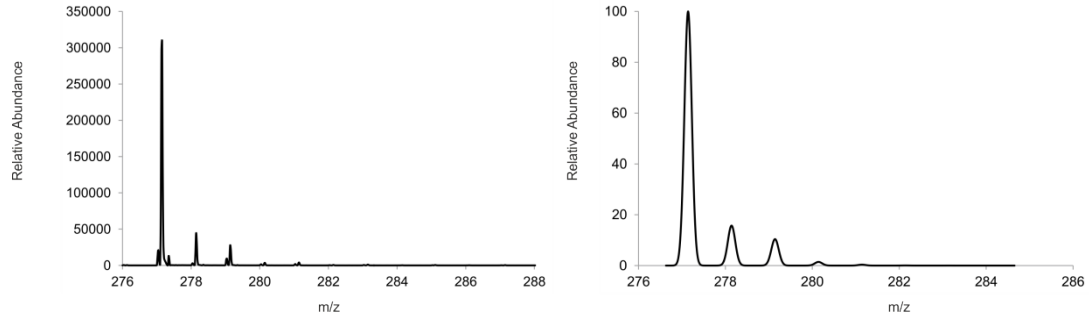

Figure S12. Measured (left) and calculated (right) isotopic pattern for the peak at m/z = 277.1439 in the high-resolution ESI-MS of MeL(CO)Et (**5**).

2. Liquid ATR-FTIR spectra

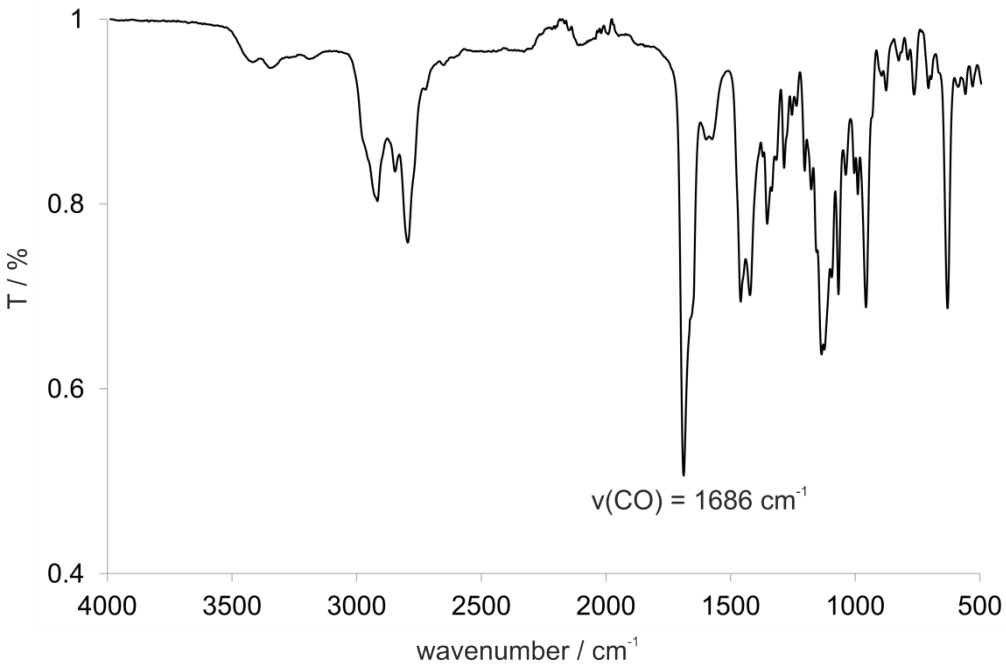

Figure S13. Liquid ATR-FTIR spectrum of MeL(CO)Me (**4**).

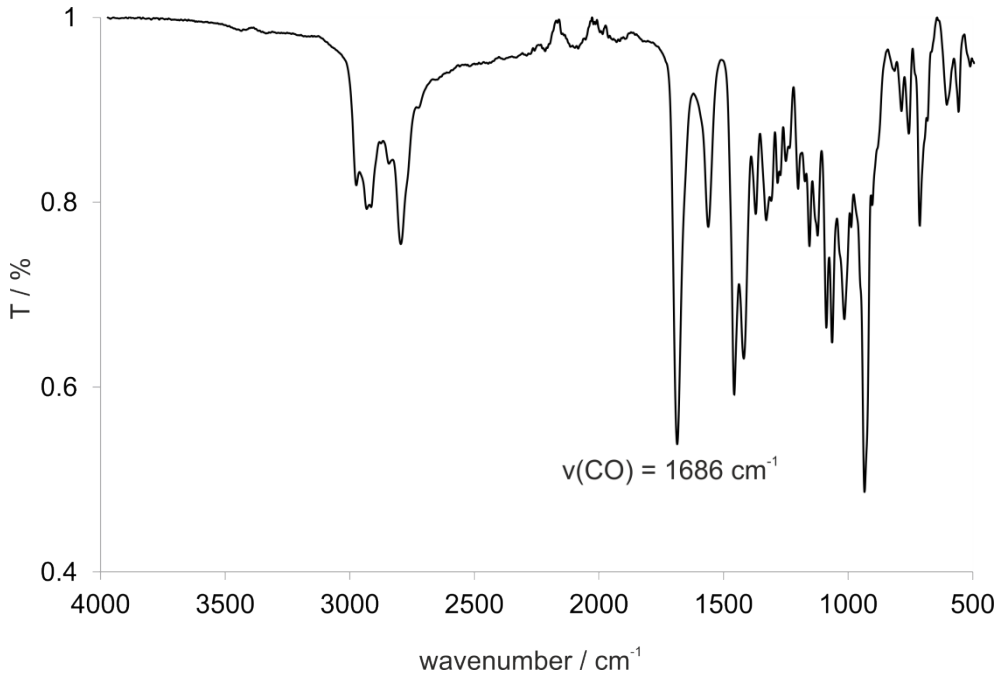

Figure S14. Liquid ATR-FTIR spectrum of MeL(CO)Et (**5**).

3. NMR spectra

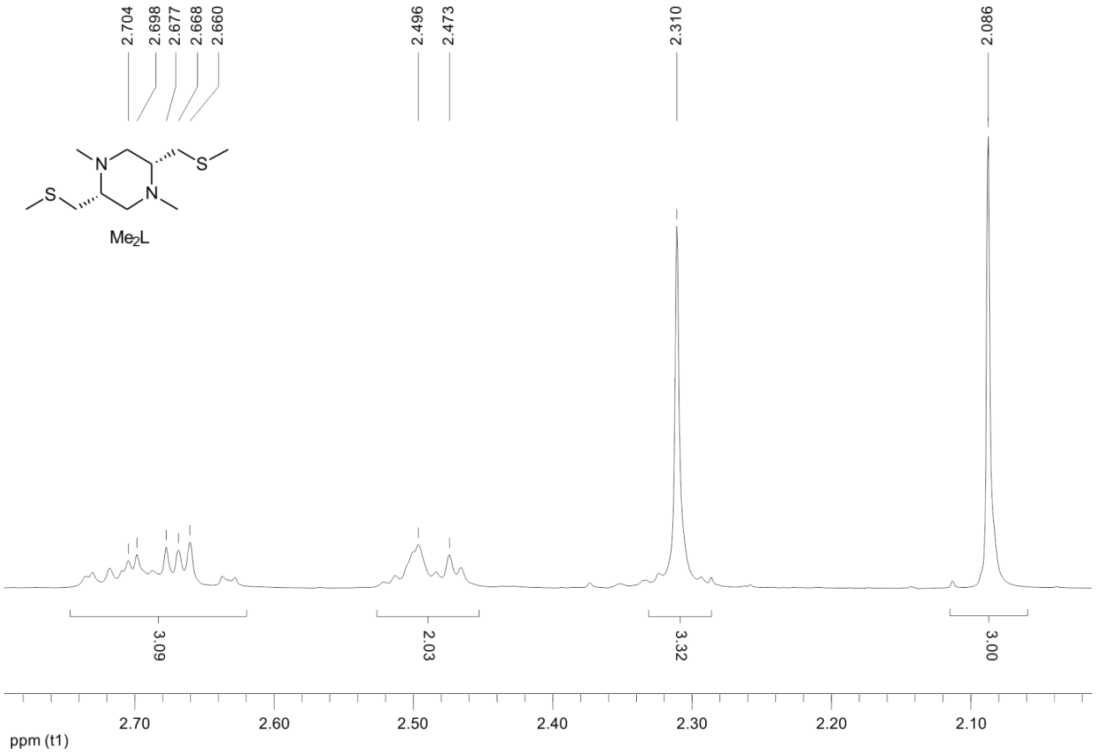

Figure S15: ^{1}H NMR (400 MHz, 297 K) spectrum of Me_2L in $CDCl_3$.

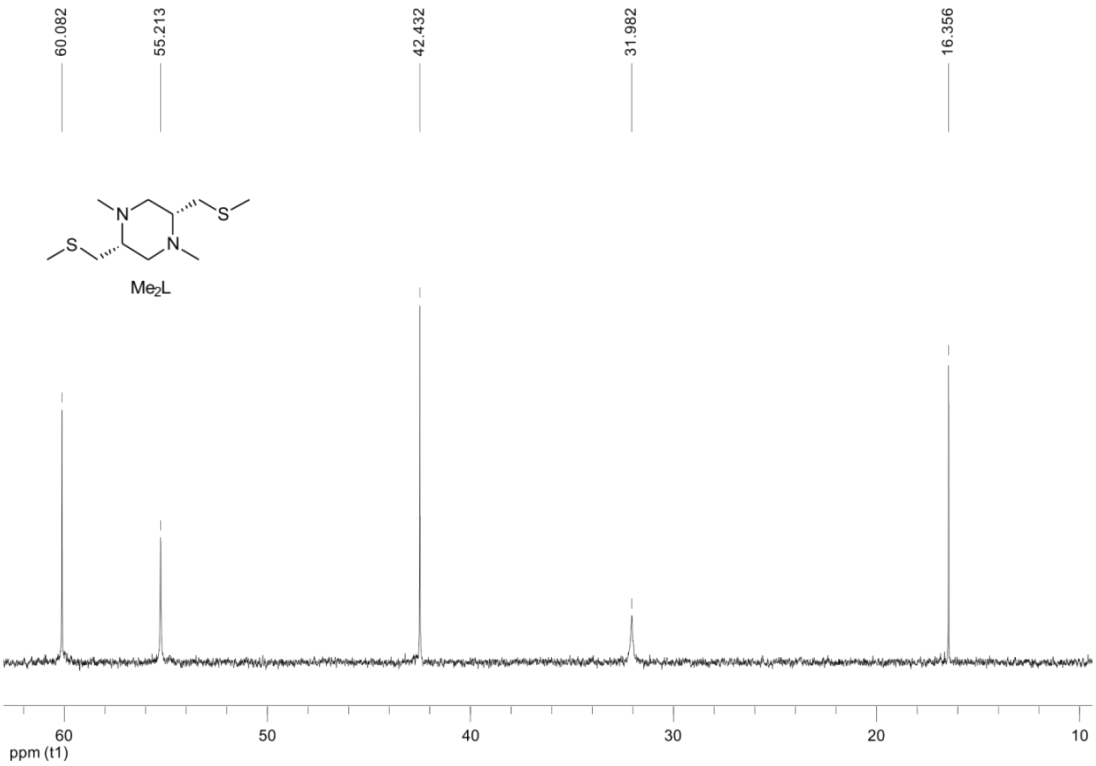

Figure S16. ^{13}C NMR (100 MHz, 297 K) spectrum of Me_2L in $CDCl_3$.

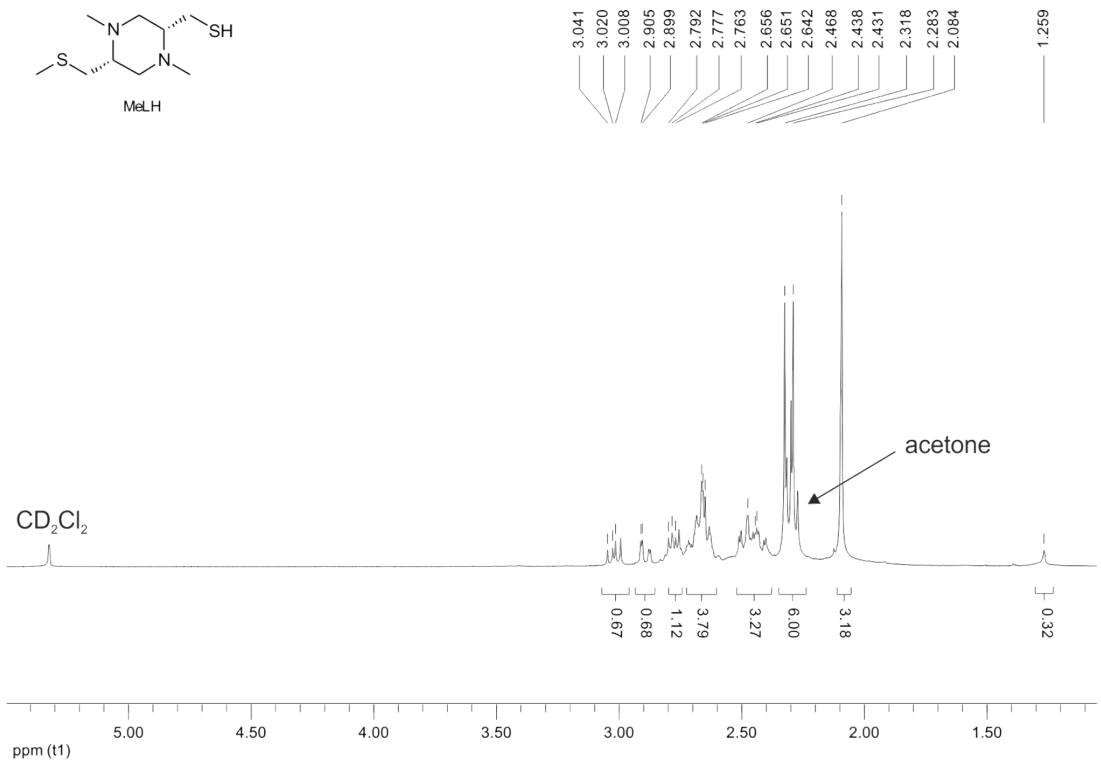

Figure S17. ^{1}H NMR (400 MHz, 297 K) spectrum of MeLH in CD_2Cl_2.

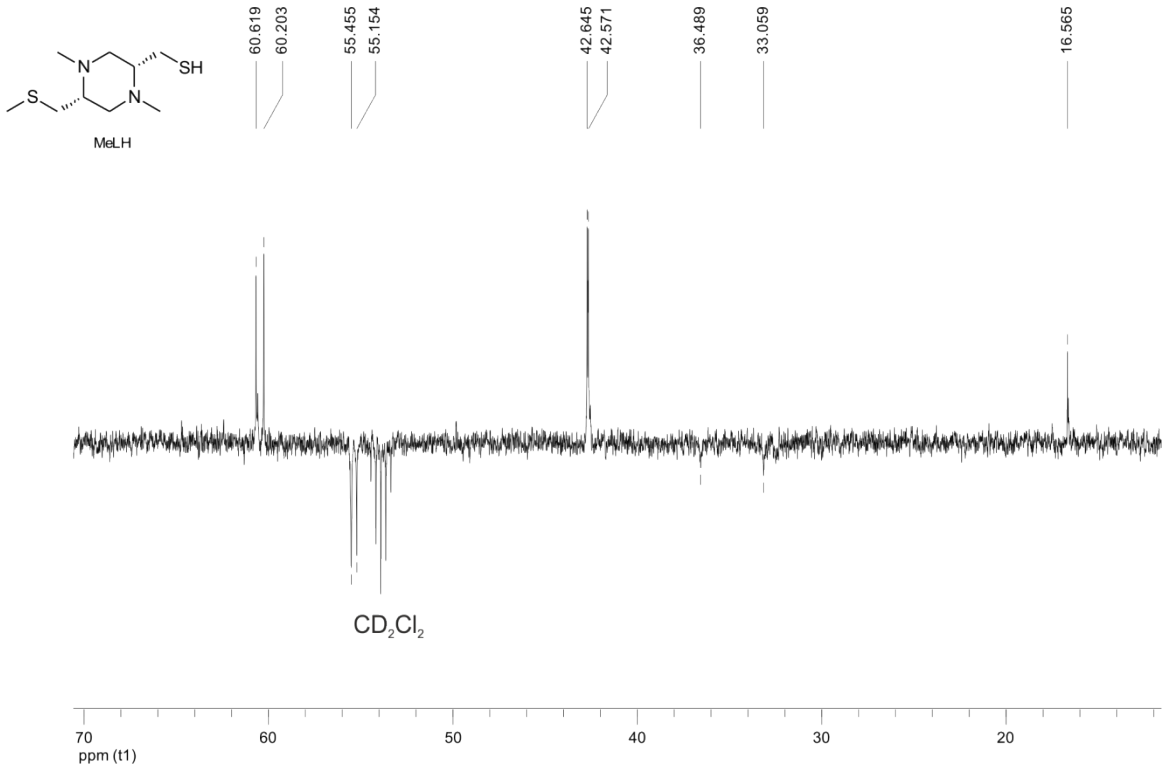

Figure S18. APT NMR (100 MHz, 297 K) spectrum of MeLH in CD_2Cl_2.

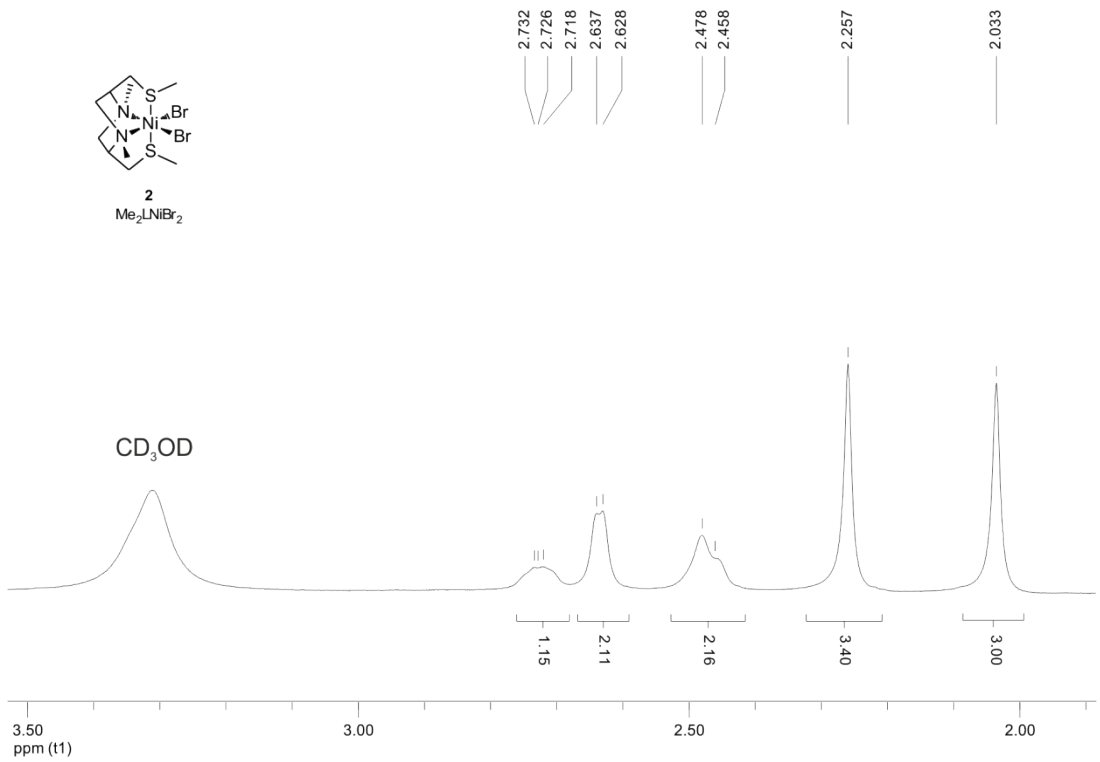

Figure S19. ^{1}H NMR (400 MHz, 297 K) spectrum of Me_2LNiBr_2 (**2**) in CD_3OH.

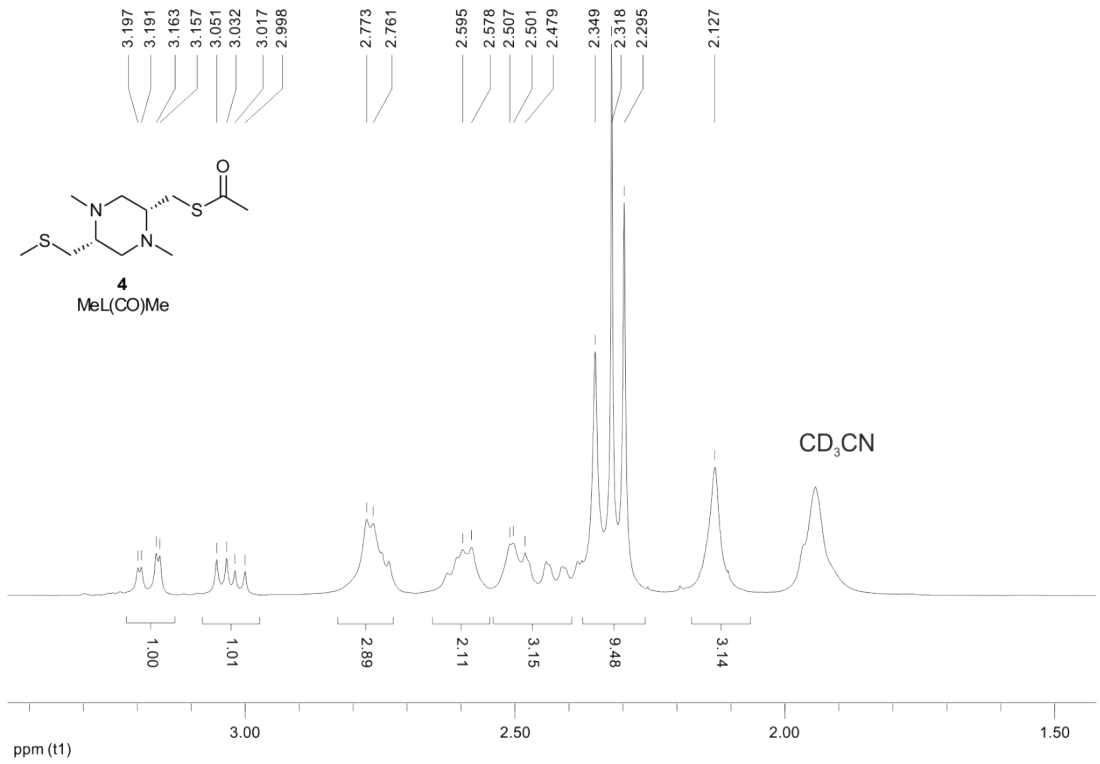

Figure S20. ^{1}H NMR (400 MHz, 297 K) spectrum of MeL(CO)Me (**4**) in CD_3CN.

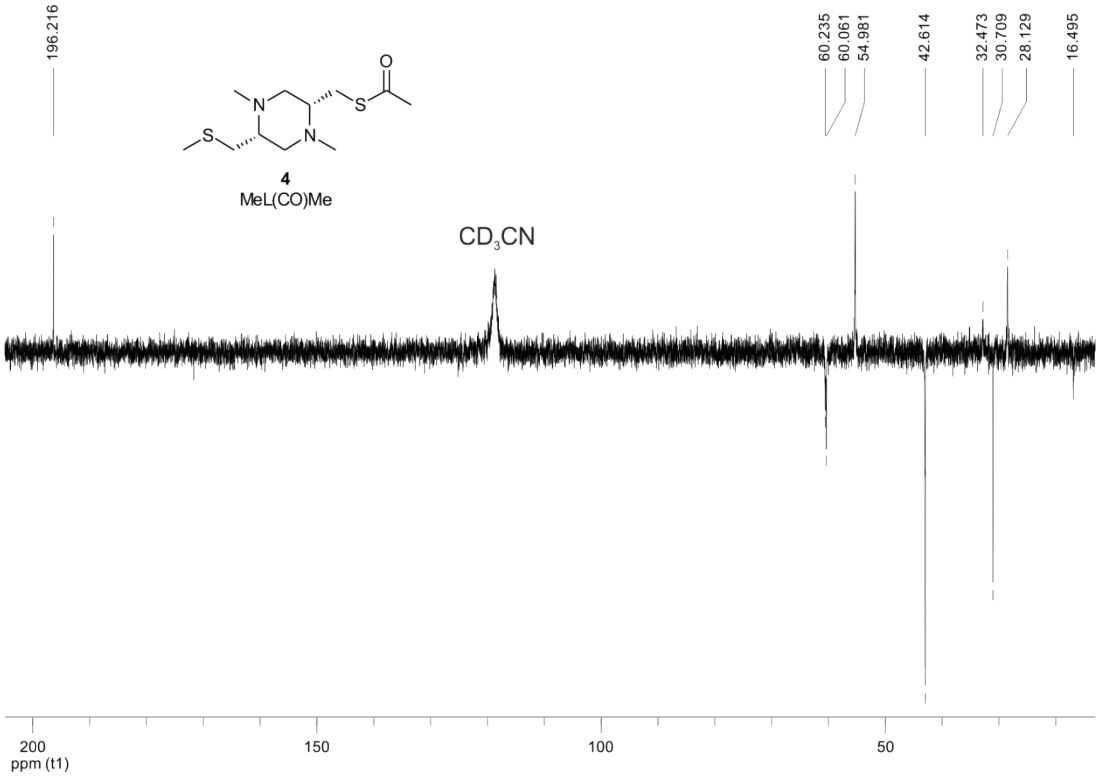

Figure S21. APT NMR (100 MHz, 297 K) spectrum of MeL(CO)Me (**4**) in CD_3CN.

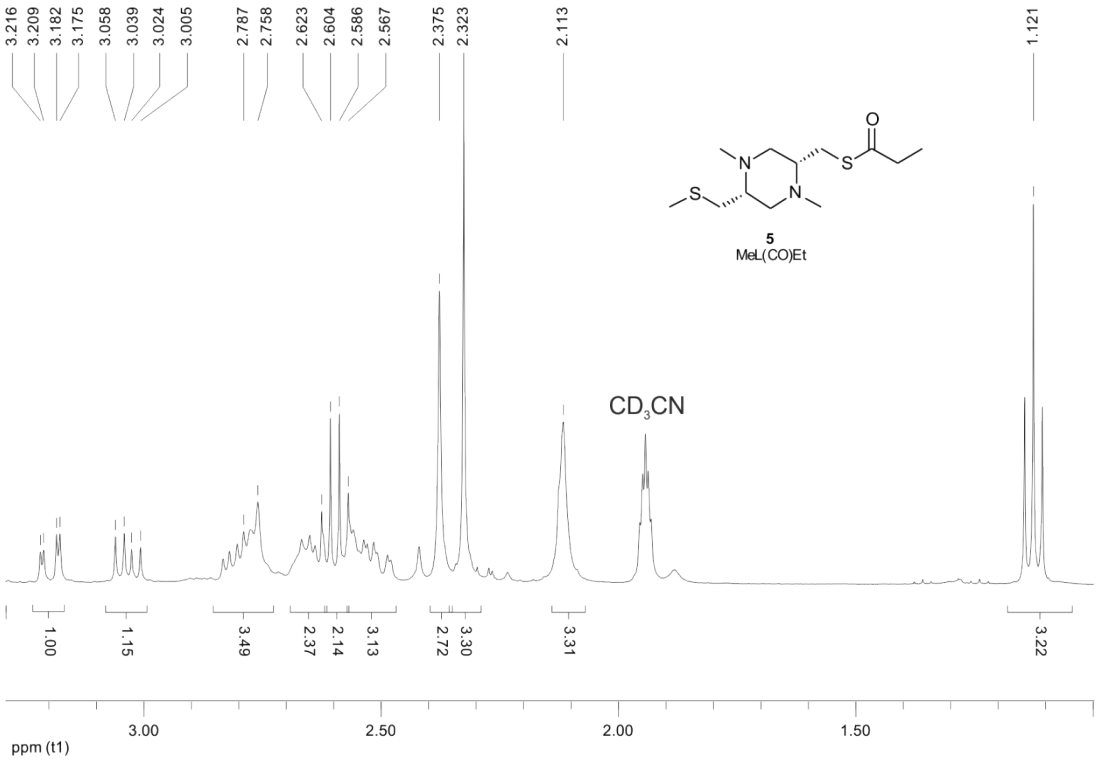

Figure S22. ^1H NMR (400 MHz, 297 K) spectrum of MeL(CO)Et (**5**) in CD_3CN.

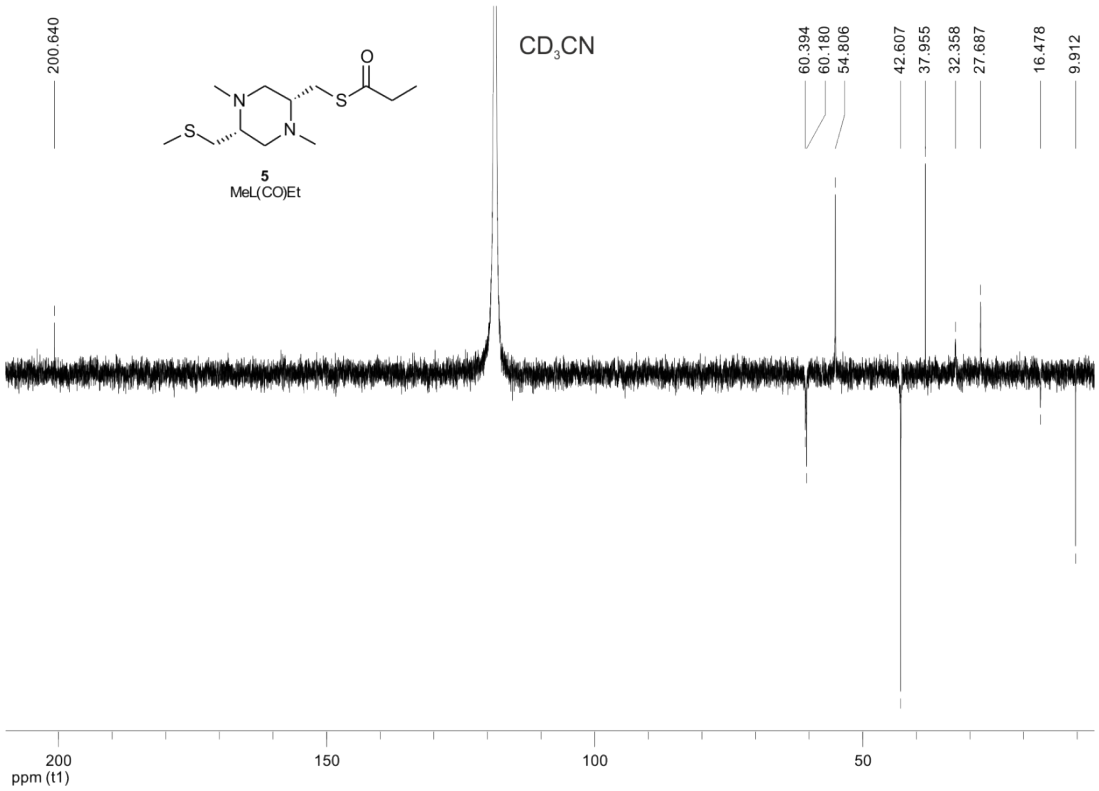

Figure S23. APT NMR (100 MHz, 297 K) spectrum of MeL(CO)Et (**5**) in CD_3CN.

4. UV-vis spectrum

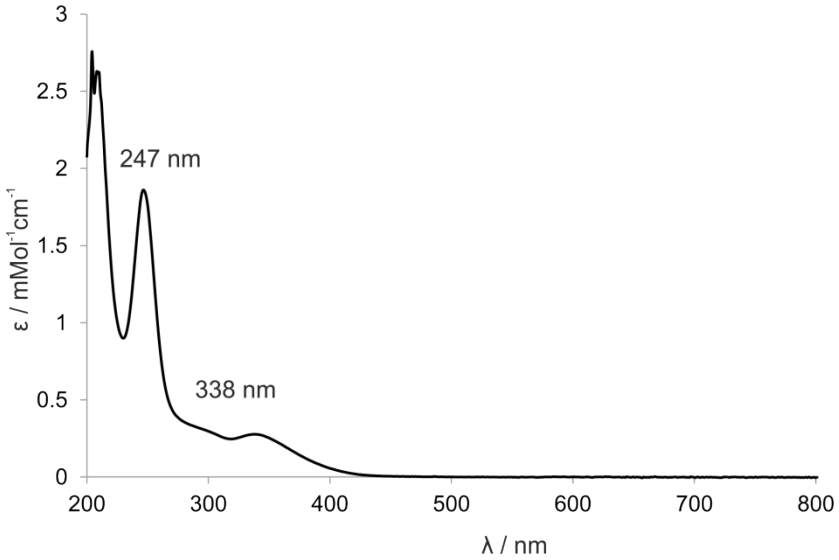

Figure S24: UV-vis spectrum of $[(MeLNi)_3I]I_2$ (**3**) in MeCN, 0.025 mM.