

Electronic Supporting Information

Reaction of Antiaromatic Porphyrinoid with Active Methylene Compounds

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Crystallographic data

Crystal data for **3c** was collected at room temperature on Bruker APEX-II CCD using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction and analysis were carried out with the *SAINT* program.¹ The structure was solved by using the *SHELXT* program² and refined by the full-matrix least-squares method on all F^2 data using the *SHELXL* program.³ The data was corrected for absorption effects (multi-scans method) using *SADABS* program.⁴ All hydrogen atoms, including those located in the difference density map, were placed in calculated positions and refined as the riding model. The *SQUEEZE/PLATON* procedure⁵ was applied for disordered lattice solvent molecules. See Table S1 for detailed data.

Table S1 Crystal data for **3c**

3c	
Chemical formula	$C_{44}H_{40}N_4NiO_2$
M_r	715.51
Crystal system, space group	Monoclinic, P2 ₁ /c
Temperature (K)	296
a, b, c (Å)	19.861 (8), 13.383 (5), 18.290 (7)
β (°)	117.36 (1)
V (Å³)	4318 (3)
Z	4
Radiation type	Mo K α
μ (mm⁻¹)	0.49
Crystal size (mm)	0.28 × 0.24 × 0.12
Diffractometer	Bruker APEX-II CCD
T_{min}, T_{max}	0.591, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28670, 7501, 4559
R_{int}	0.041
(sin θ/λ)_{max} (Å⁻¹)	0.595
Refinement	
R[$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.054, 0.163, 1.05
No. of reflections	7501
No. of parameters	469
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å⁻³)	0.45, -0.25

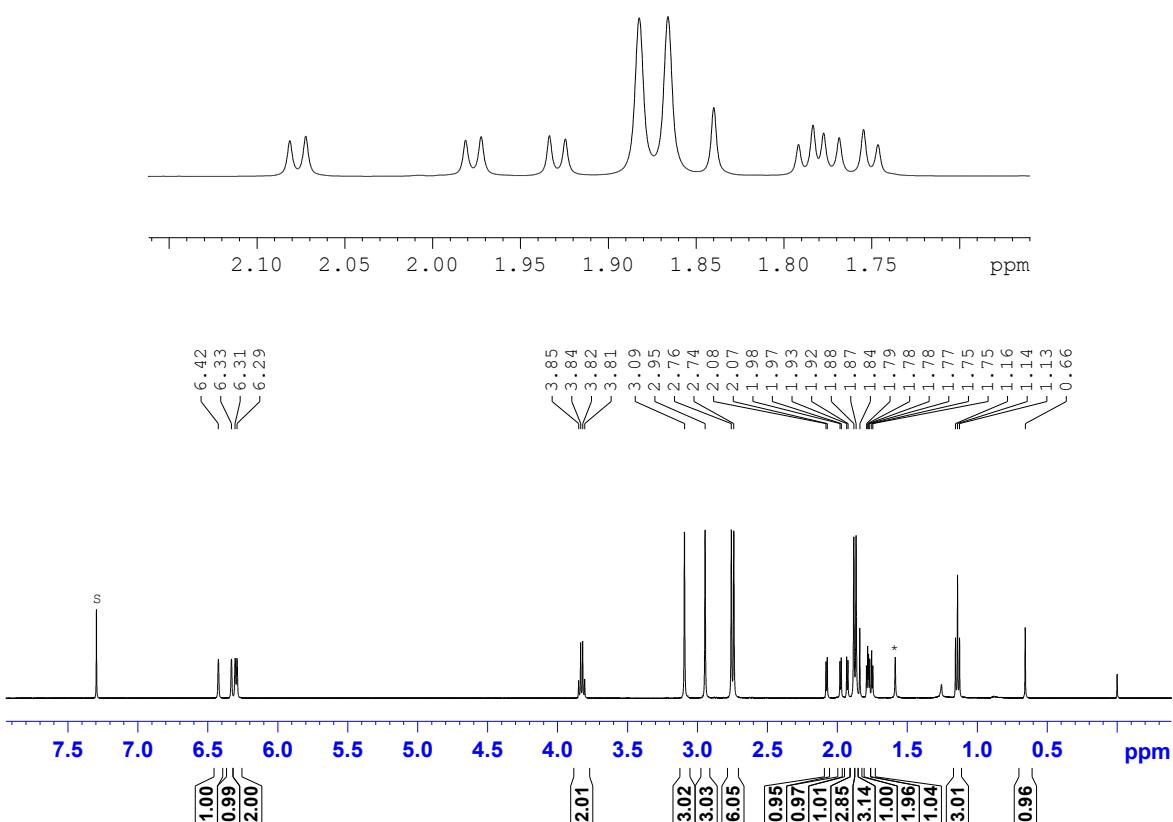
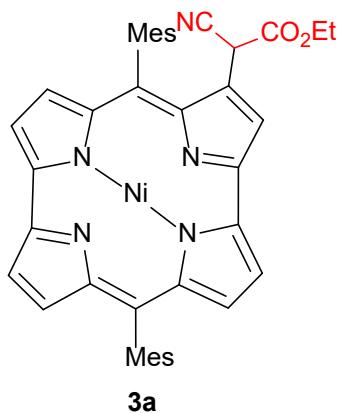


Fig. S1 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3a**.

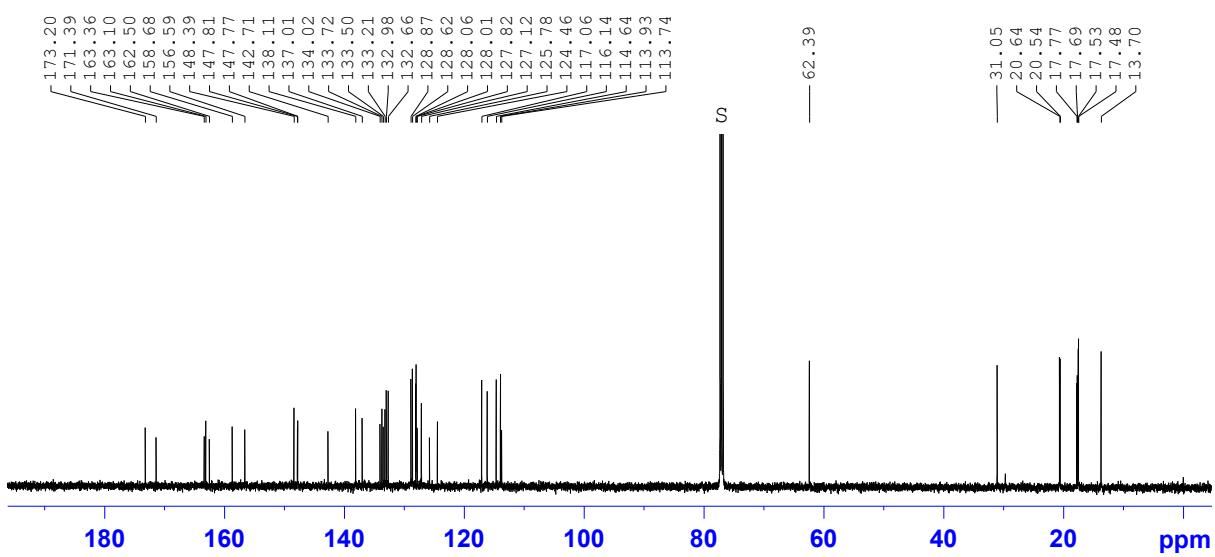
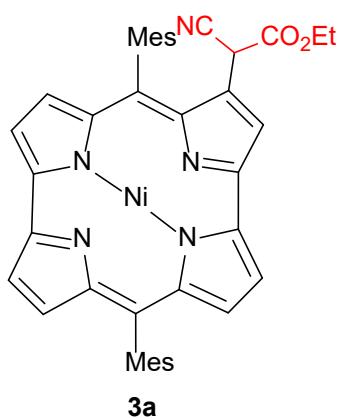


Fig. S2 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3a**.

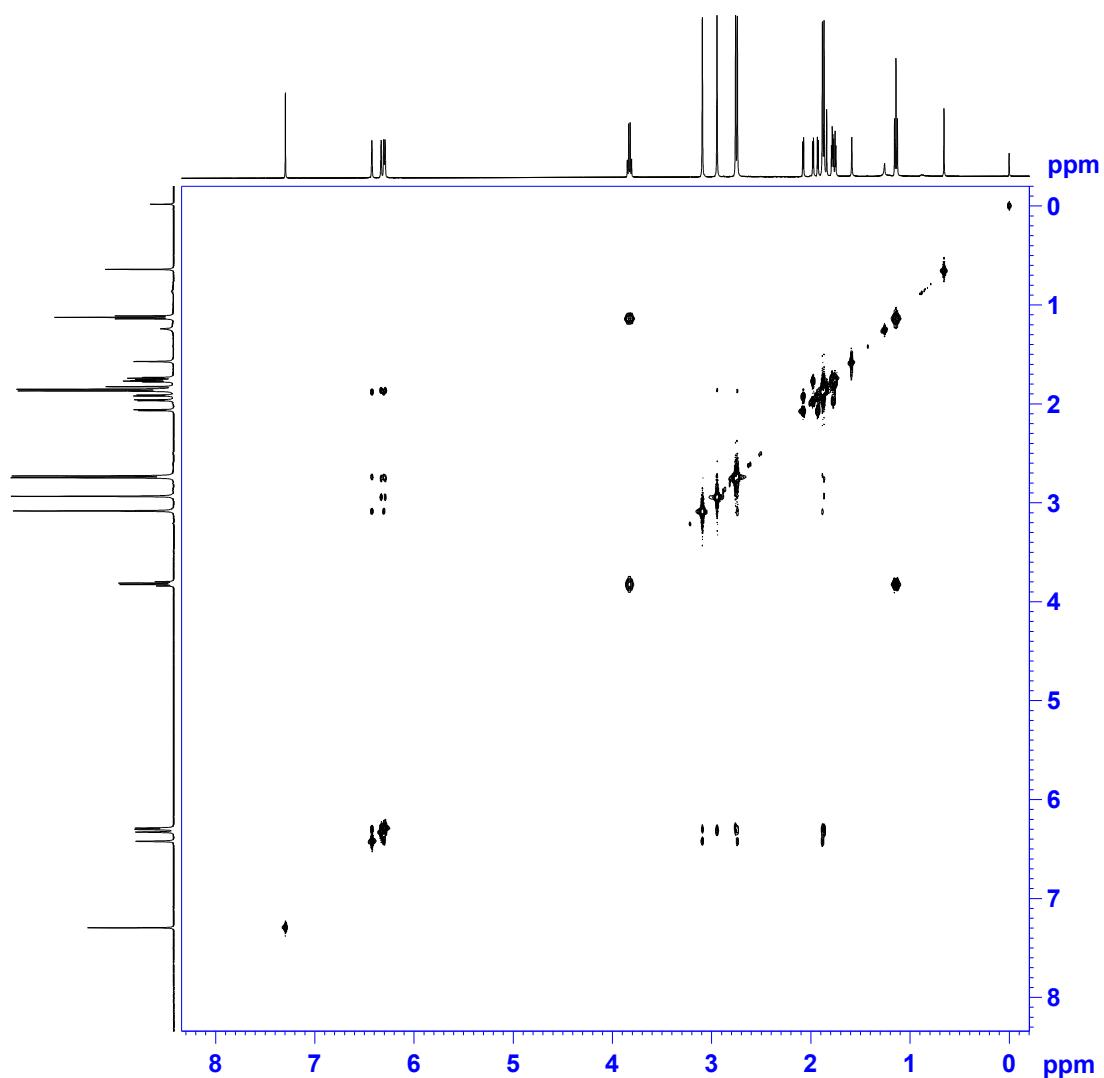
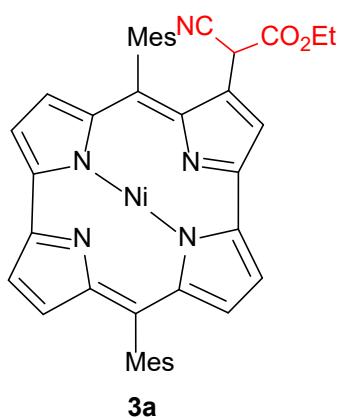


Fig. S3 ^1H , ^1H COSY spectrum (CDCl_3 500 MHz, 298 K) of **3a**.

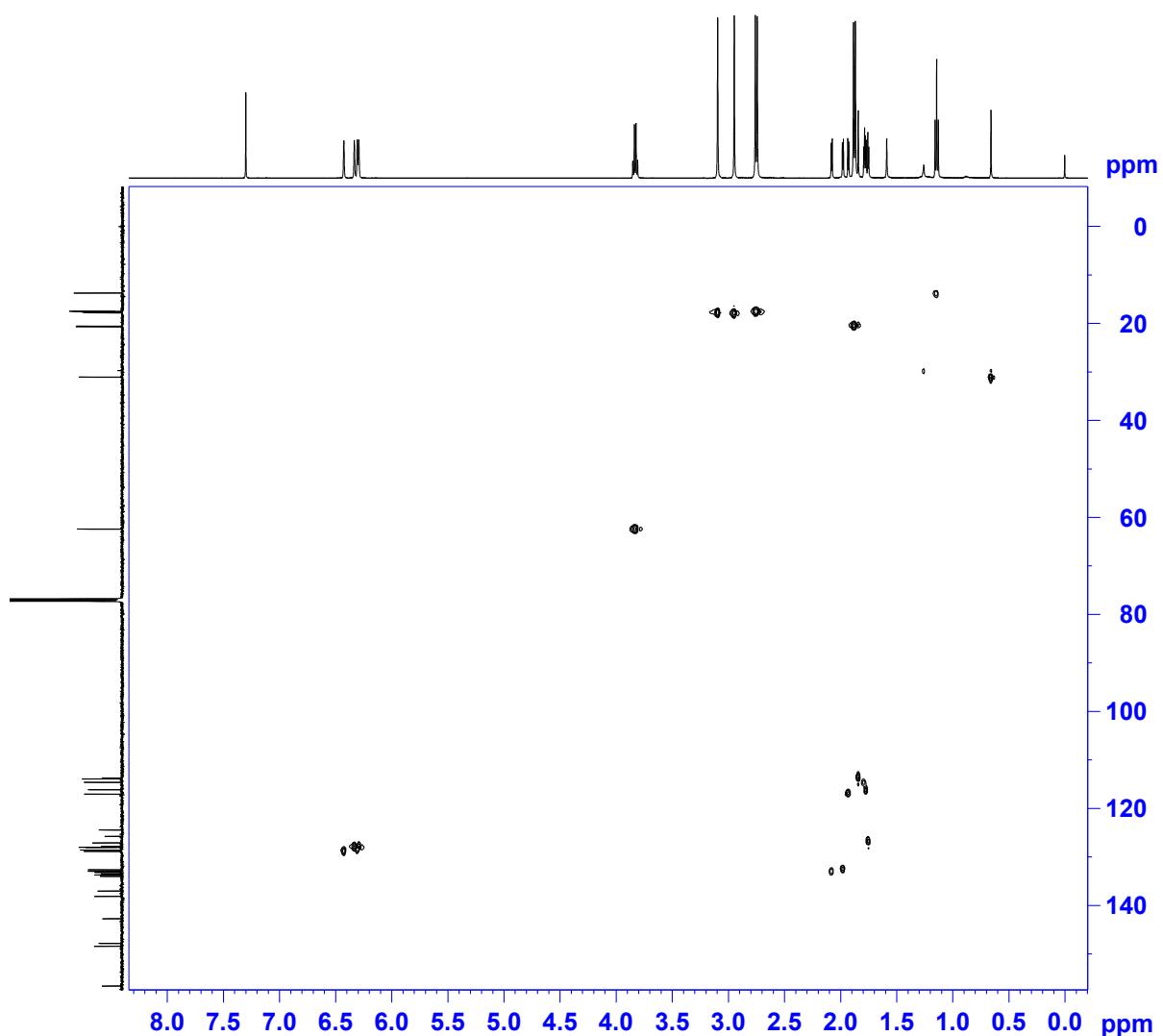
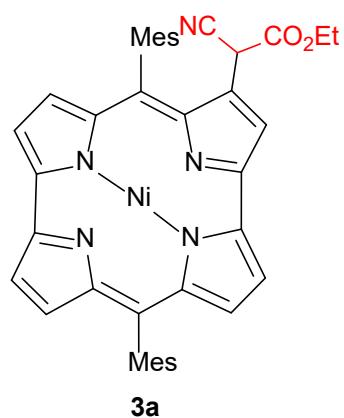


Fig. S4 ^1H , ^{13}C HSQC spectrum (CDCl_3 500/125 MHz, 298 K) of **3a**.

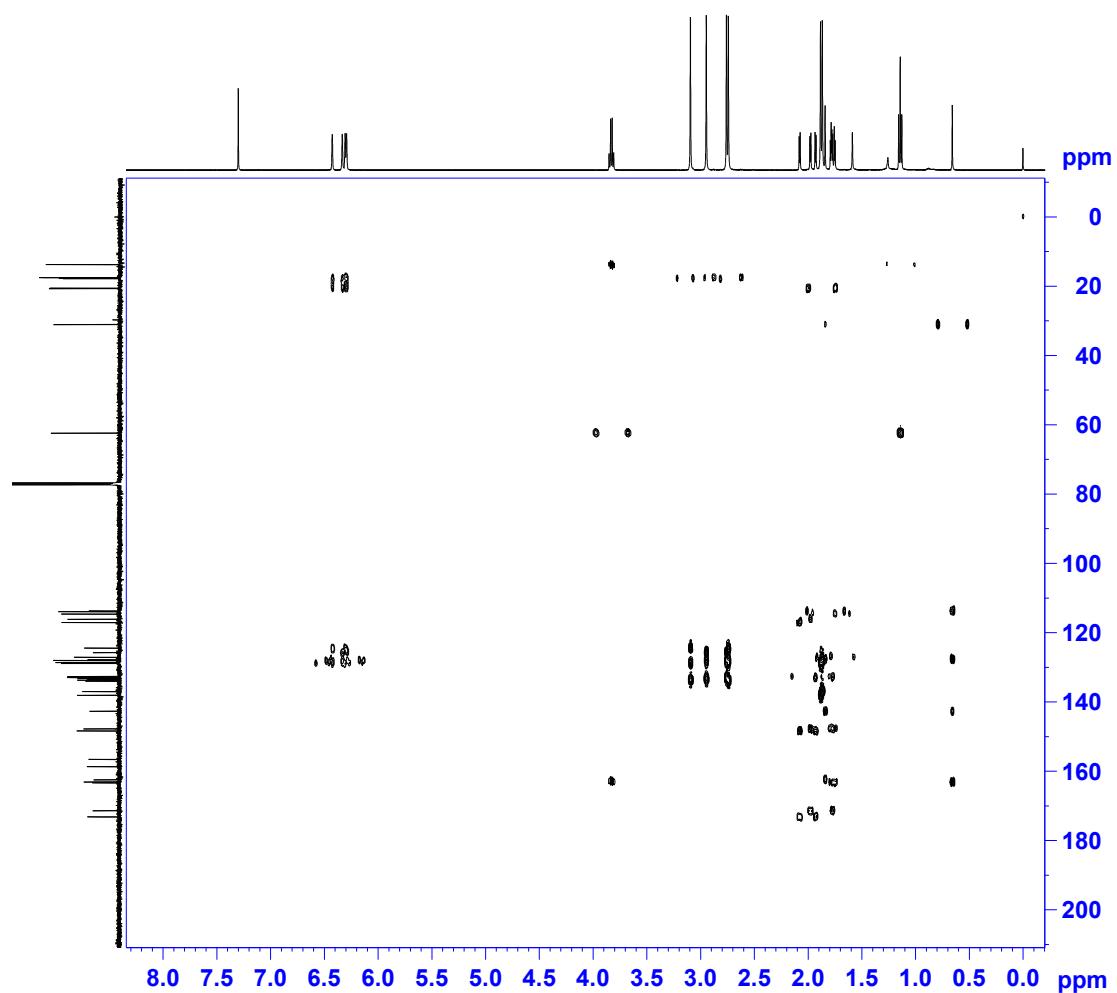
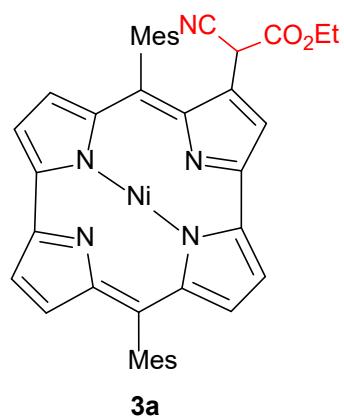


Fig. S5 ^1H , ^{13}C HMBC spectrum (CDCl_3 500/125 MHz, 298 K) of **3a**.

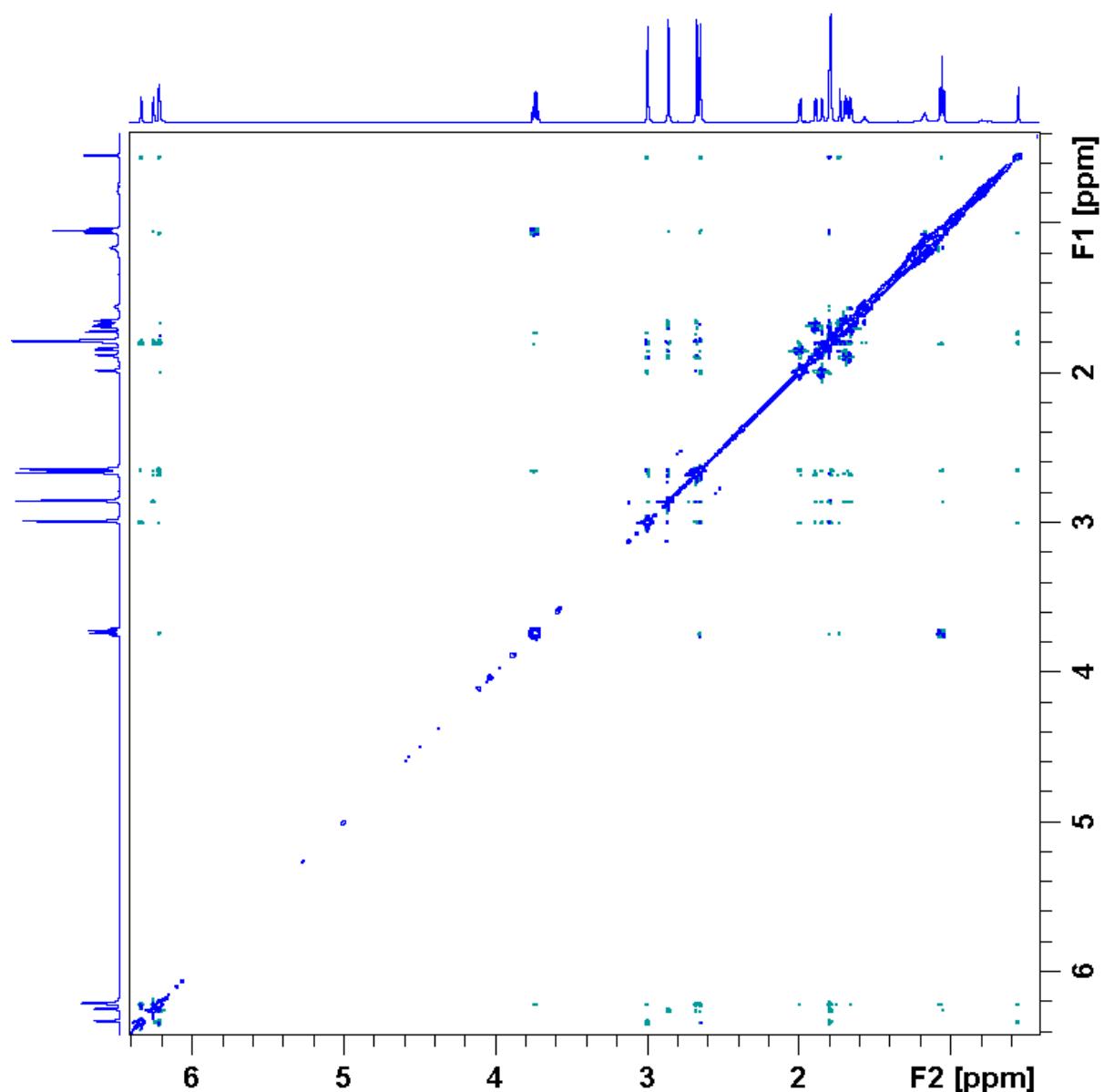
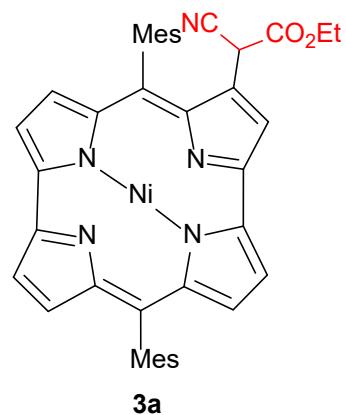
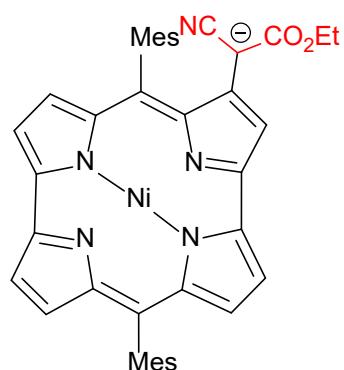


Fig. S6 ^1H , ^1H NOESY spectrum (CDCl_3 500MHz, 298 K) of **3a**.

HRMS of **3a**



Chemical Formula: C₄₁H₃₄N₅NiO₂⁻
Exact Mass: 686.2071

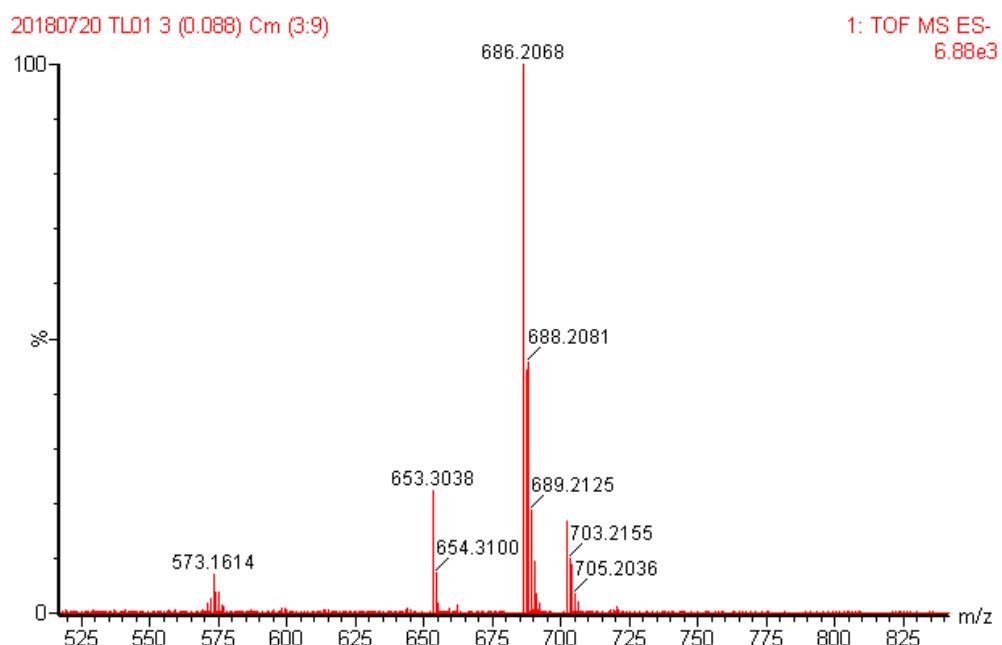


Fig. S7 HRMS ESI(⁻) spectrum of **3a**.

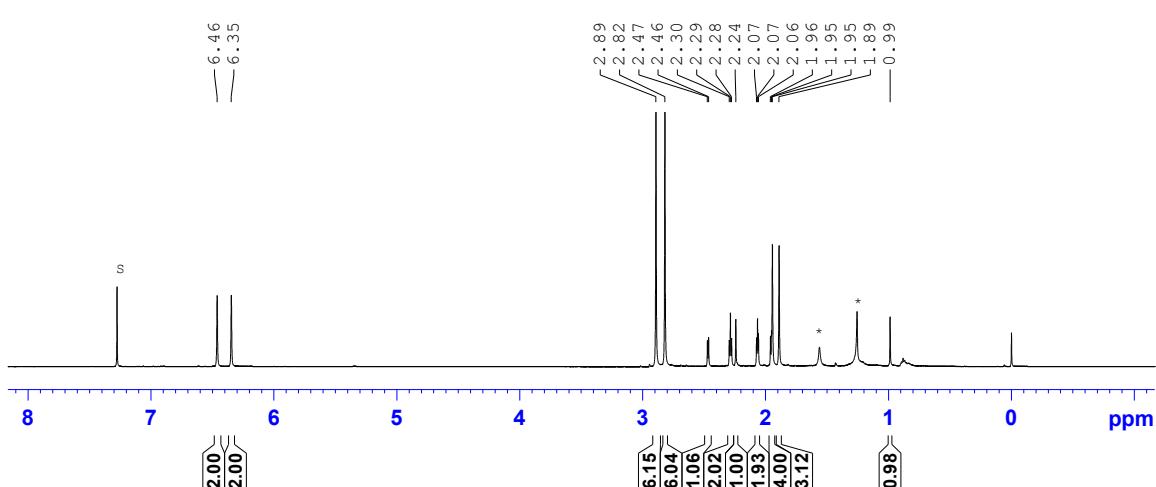
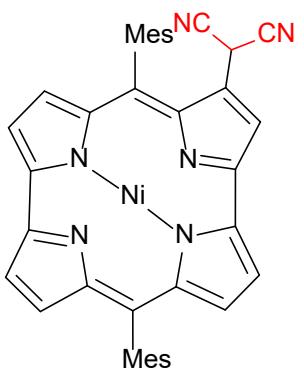


Fig. S8 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3b**.

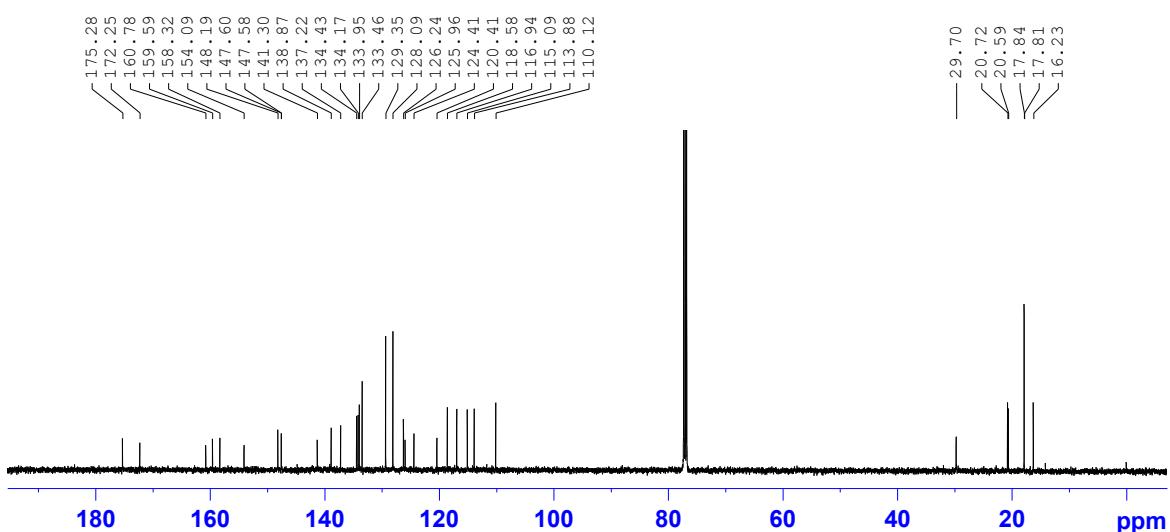


Fig. S9 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3b**.

Chemical Formula: C₃₉H₂₉N₆Ni⁻
Exact Mass: 639.1813

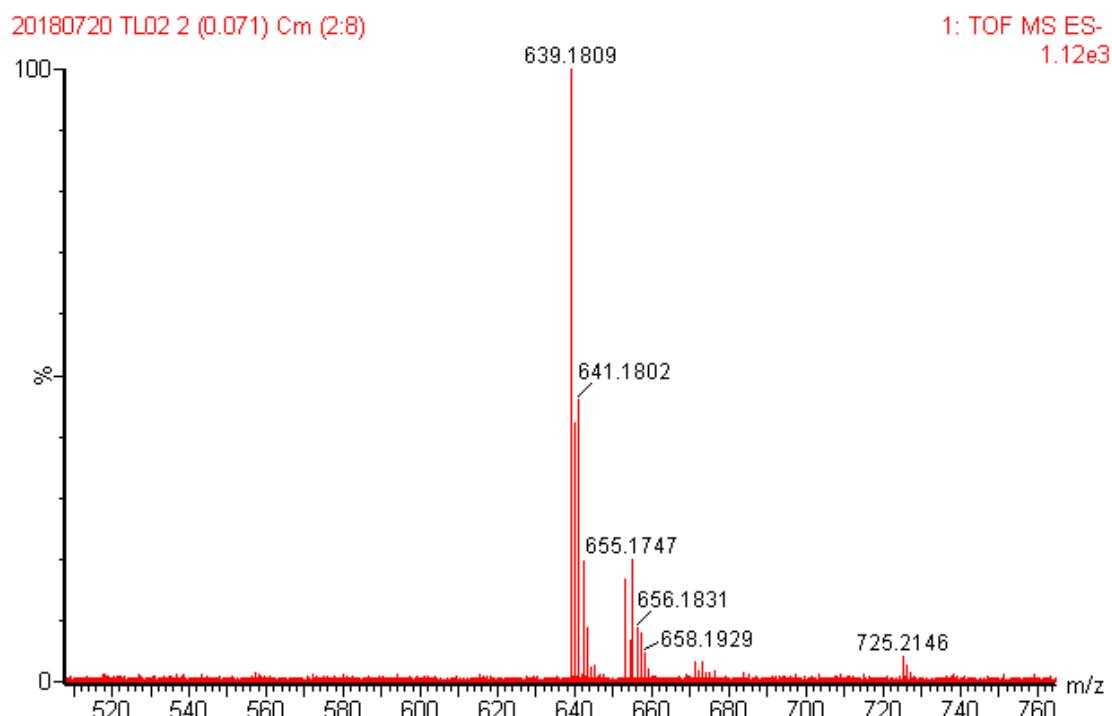
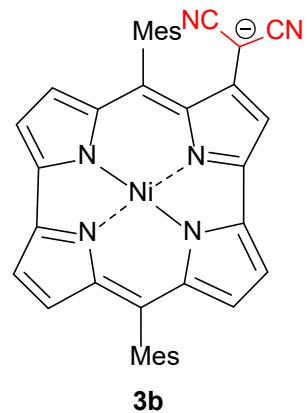


Fig. S10 HRMS ESI(⁻) spectrum of **3b**.

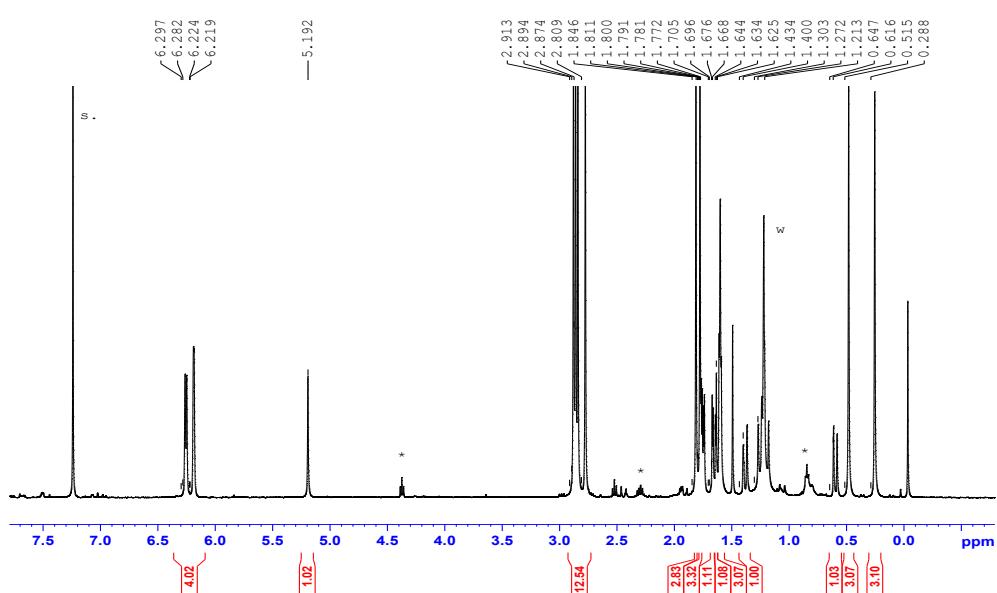
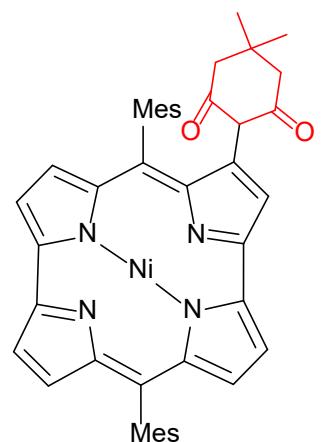


Fig. S11 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3c**.

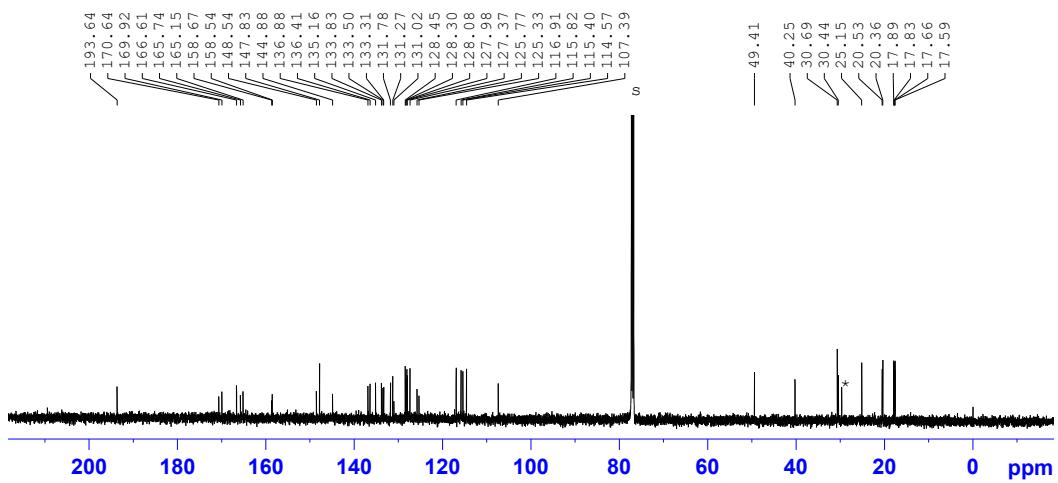


Fig. S12 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3c**.

Chemical Formula: C₄₄H₃₉N₄NiO₂⁻
Exact Mass: 713.2432

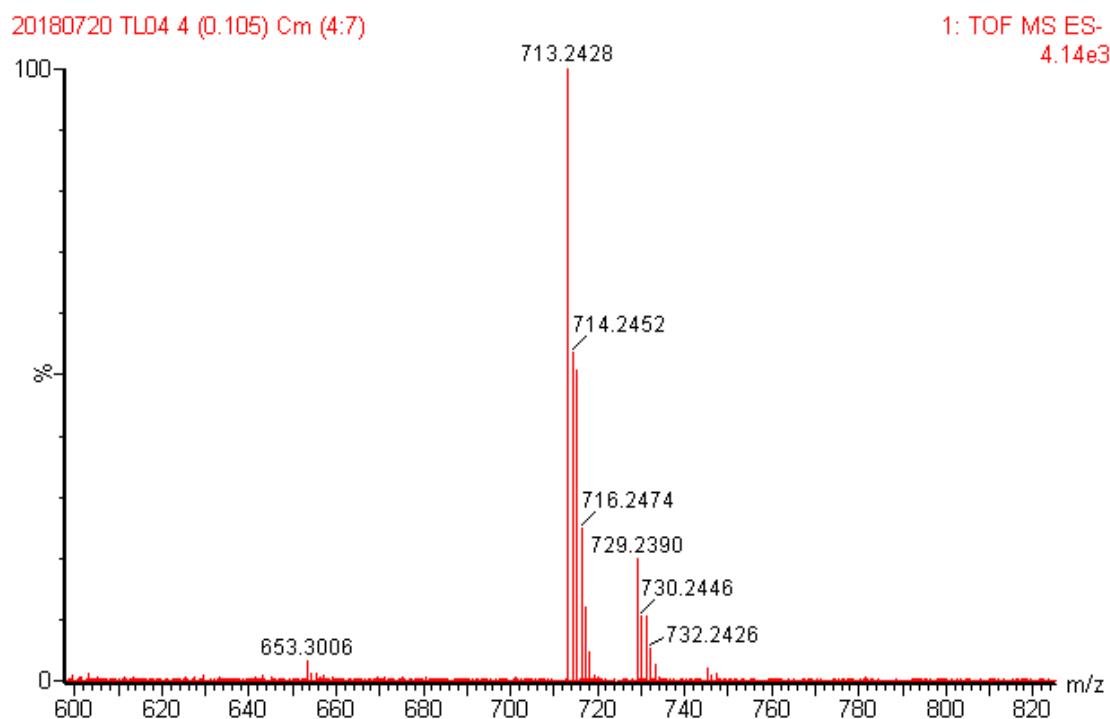
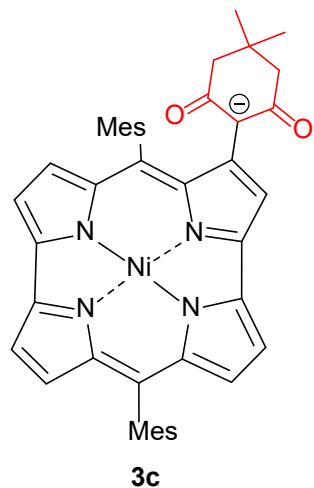


Fig. S13 HRMS ESI(⁻) spectrum of **3c**.

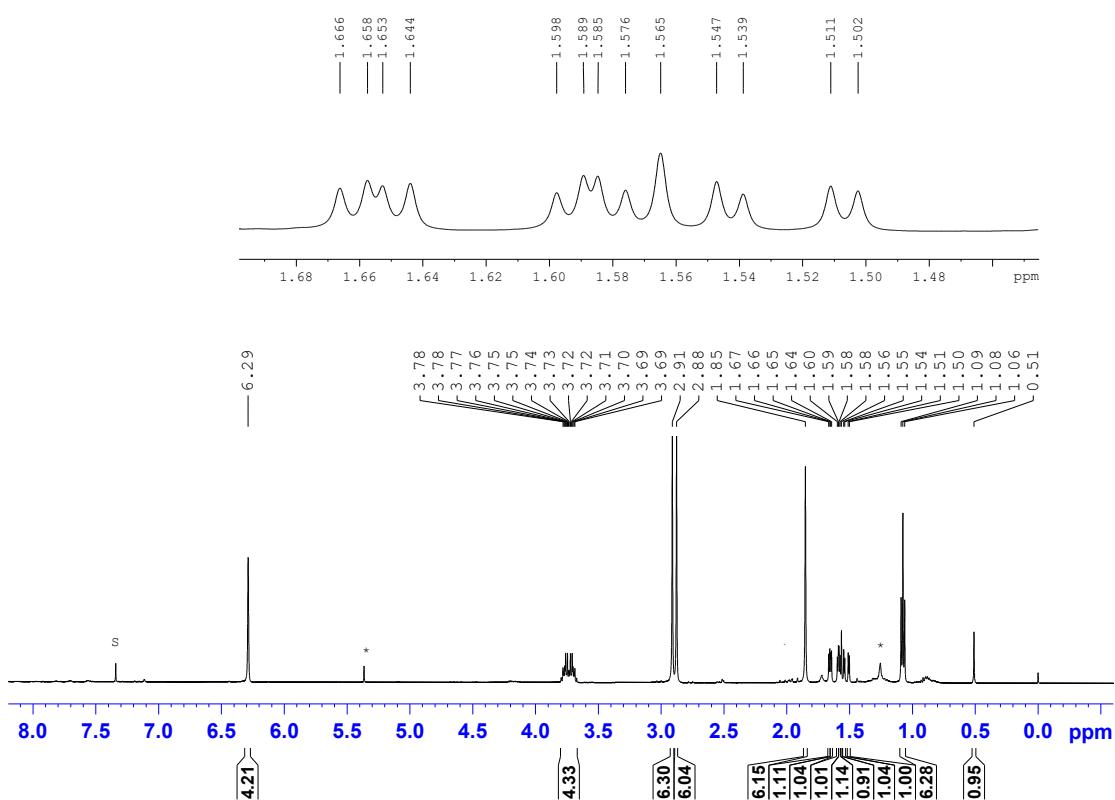
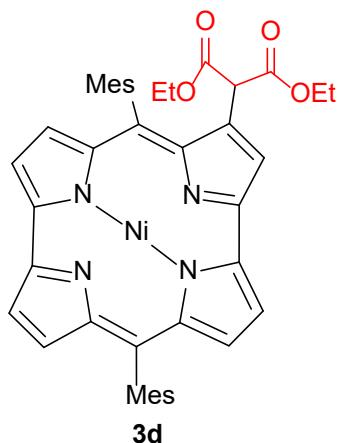


Fig. S14 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3d**.

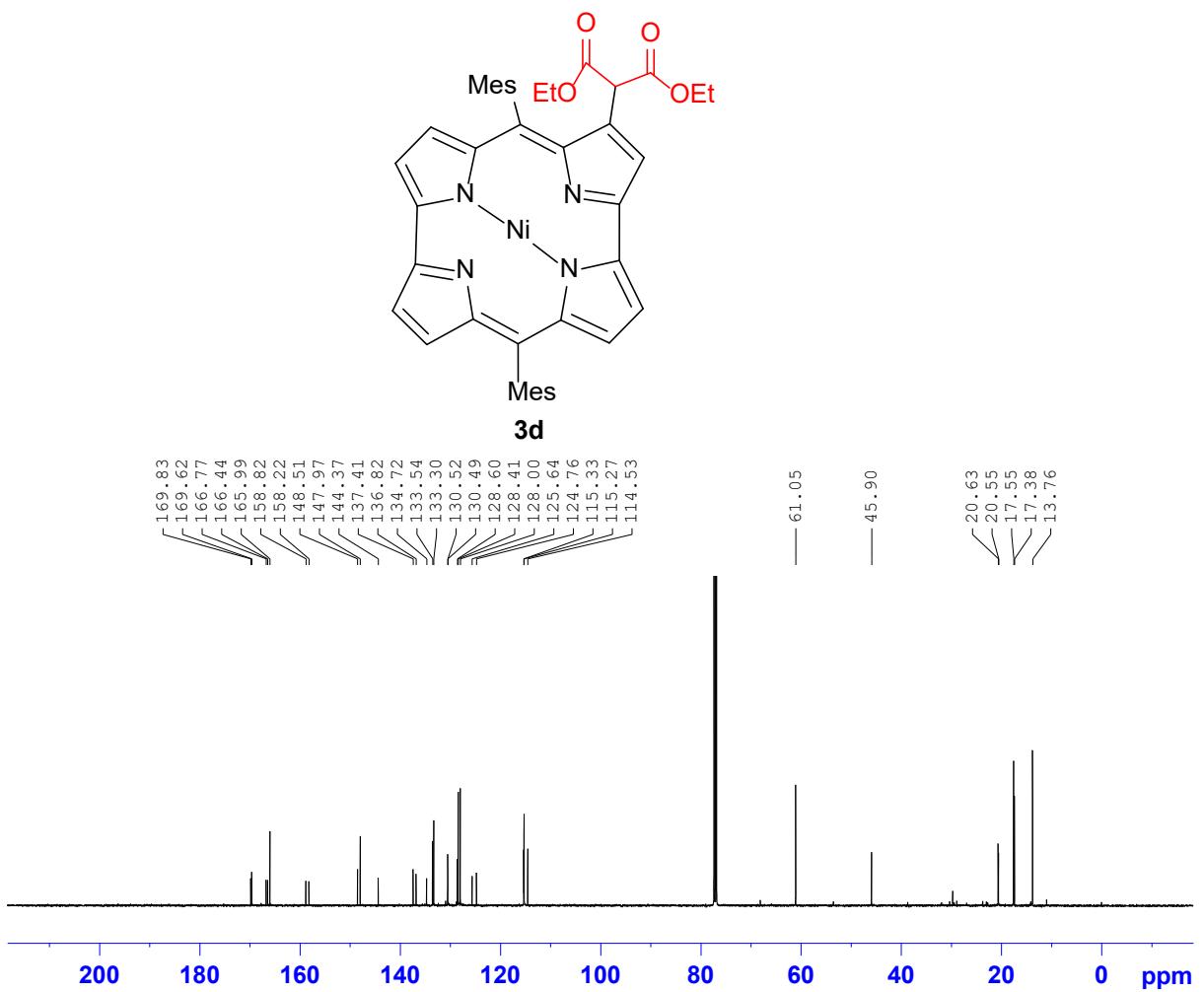


Fig. S15 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3d**.

Chemical Formula: C₄₃H₄₀N₄NiO₄
Exact Mass: 734.2403

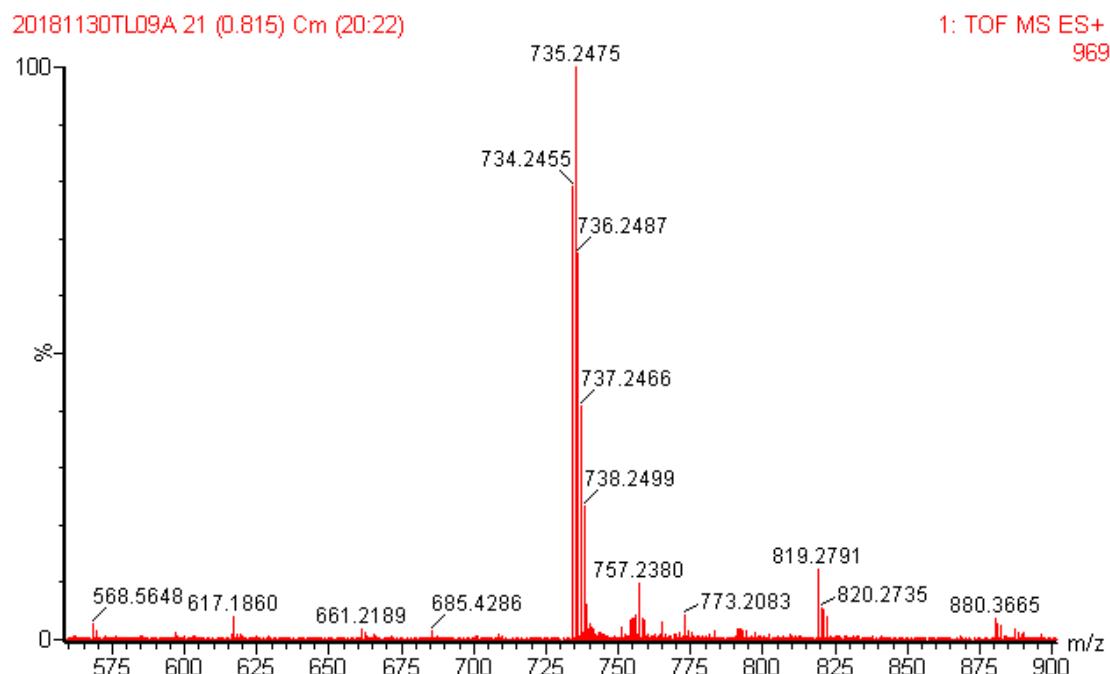
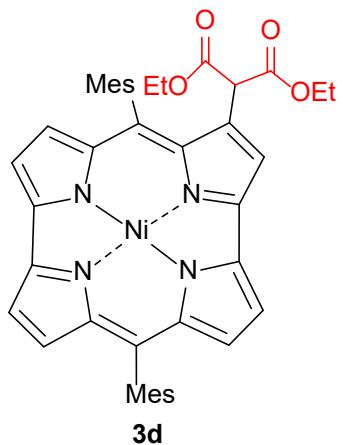
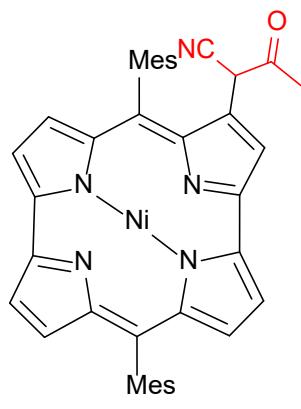


Fig. S16 HRMS ESI(+) spectrum of **3d**.



3e

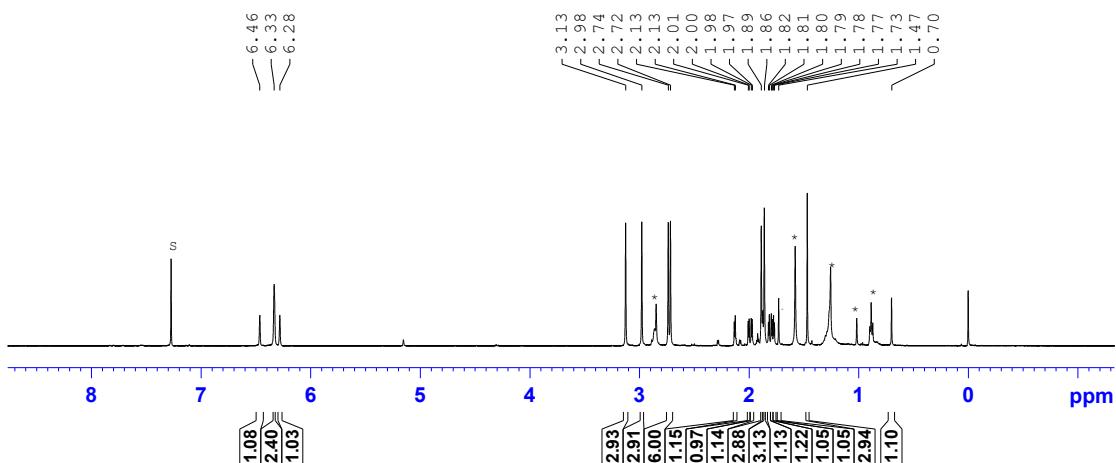


Fig. S17 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3e**.

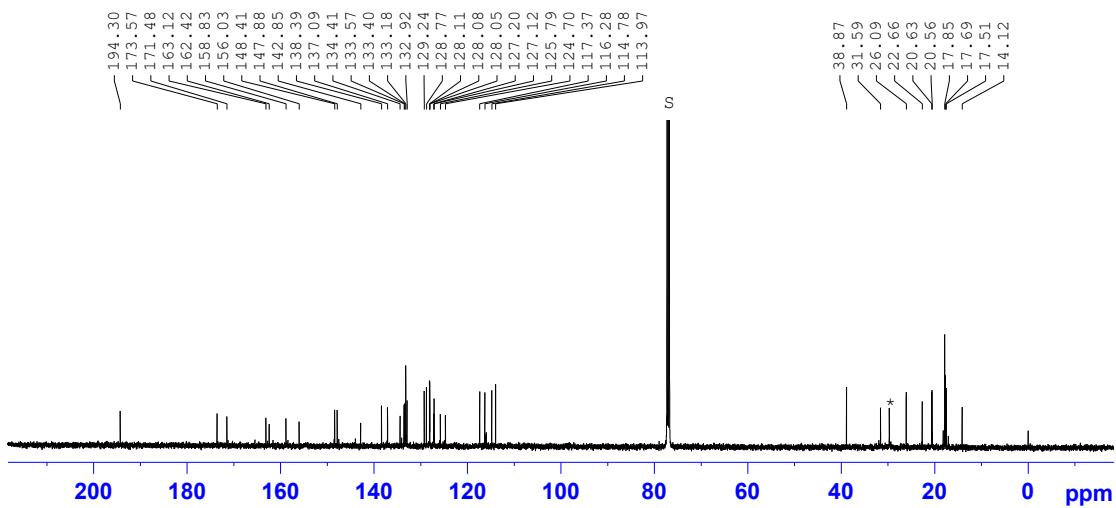


Fig. S18 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3e**.

Chemical Formula: C₄₀H₃₂N₅NiO⁻
Exact Mass: 656.1966

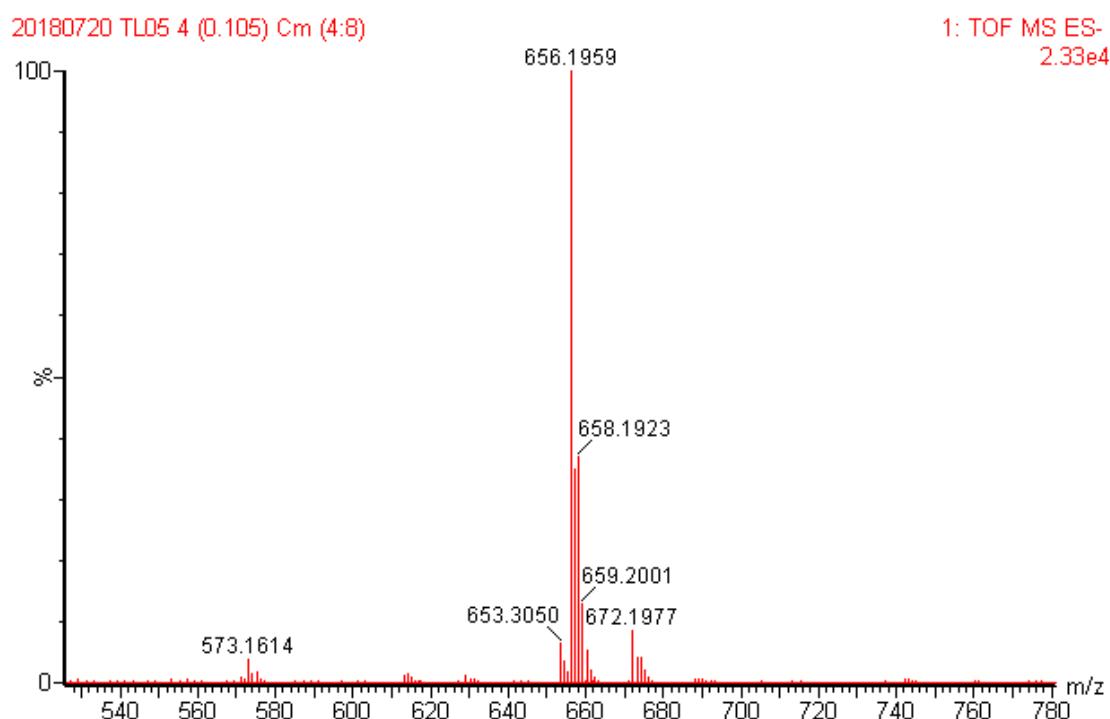
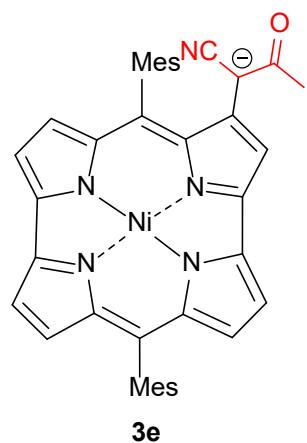
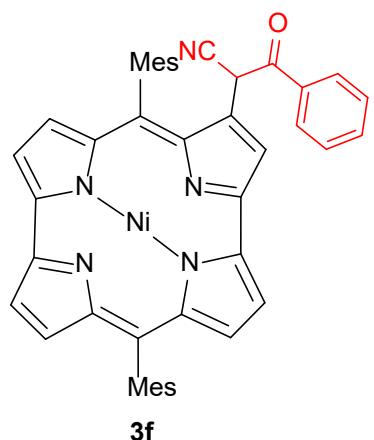


Fig. S19 HRMS ESI(⁻) spectrum of **3e**.



¹H NMR of **3f**

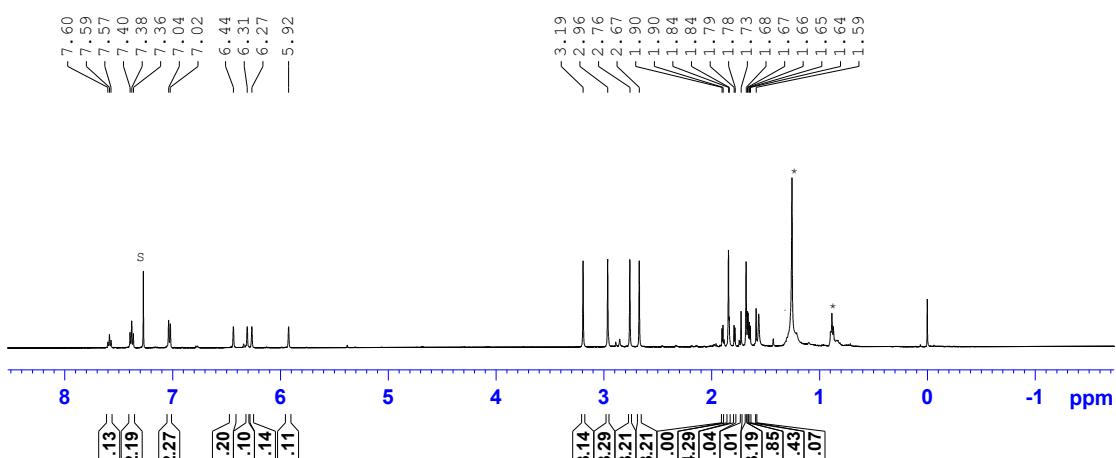
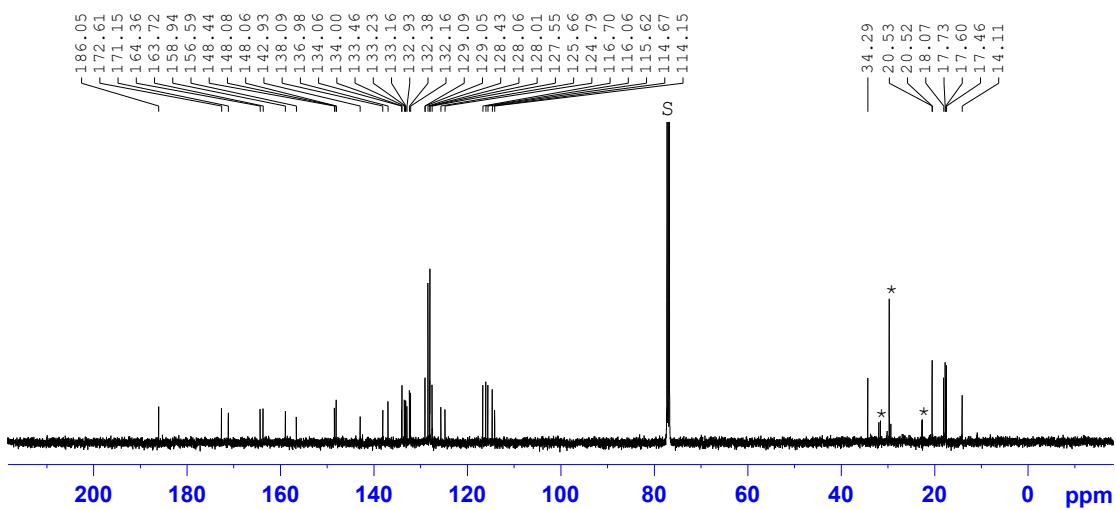
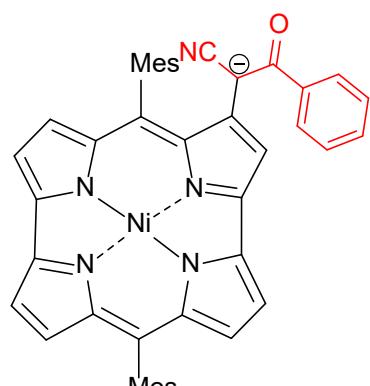


Fig. S20 ¹H NMR spectrum (CDCl₃ 500 MHz, 298 K) of **3f**.



Chemical Formula: C₄₅H₃₄N₅NiO⁻

Exact Mass: 718.2122



3f

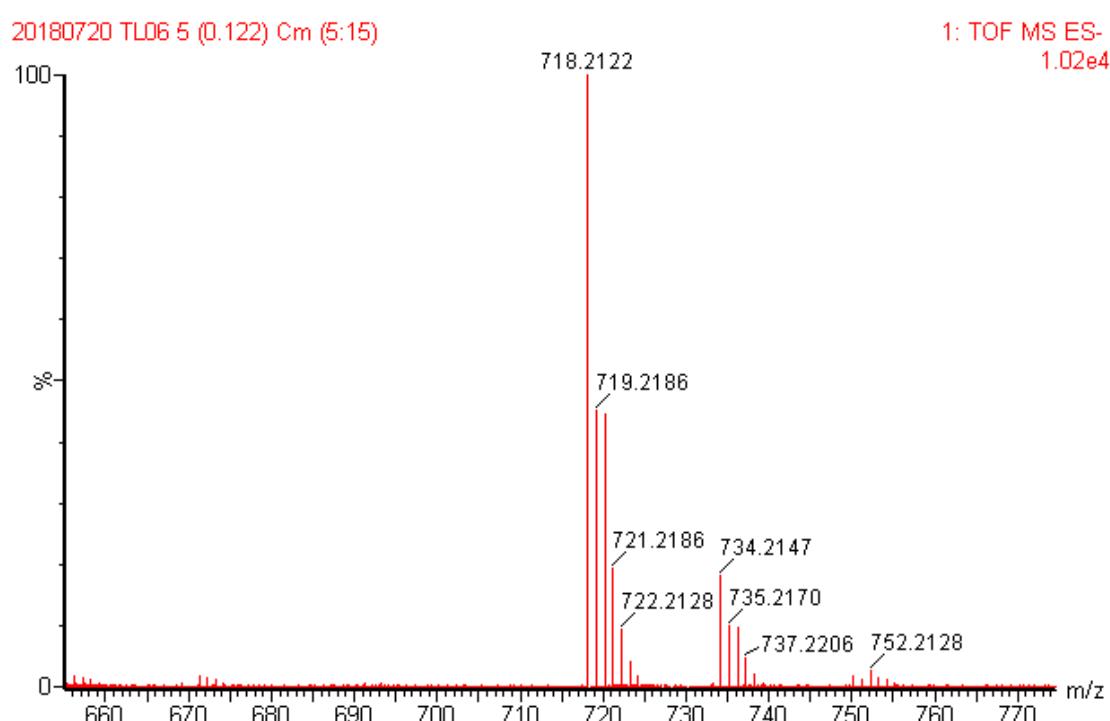


Fig. S22 HRMS ESI(⁻) spectrum of **3f**.

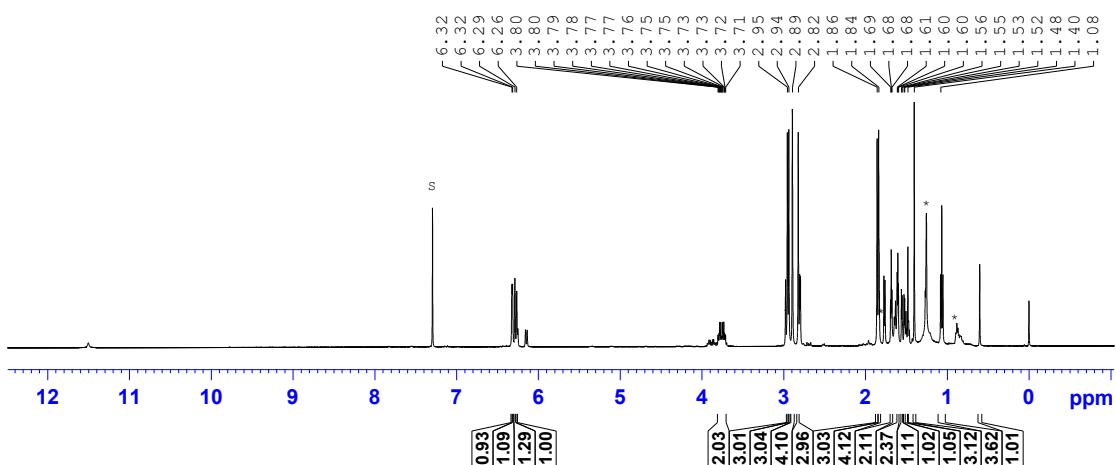
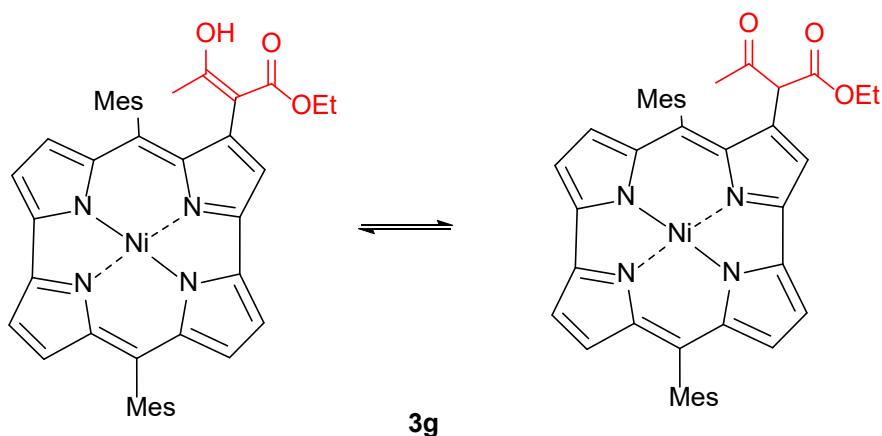


Fig. S23 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3g**.

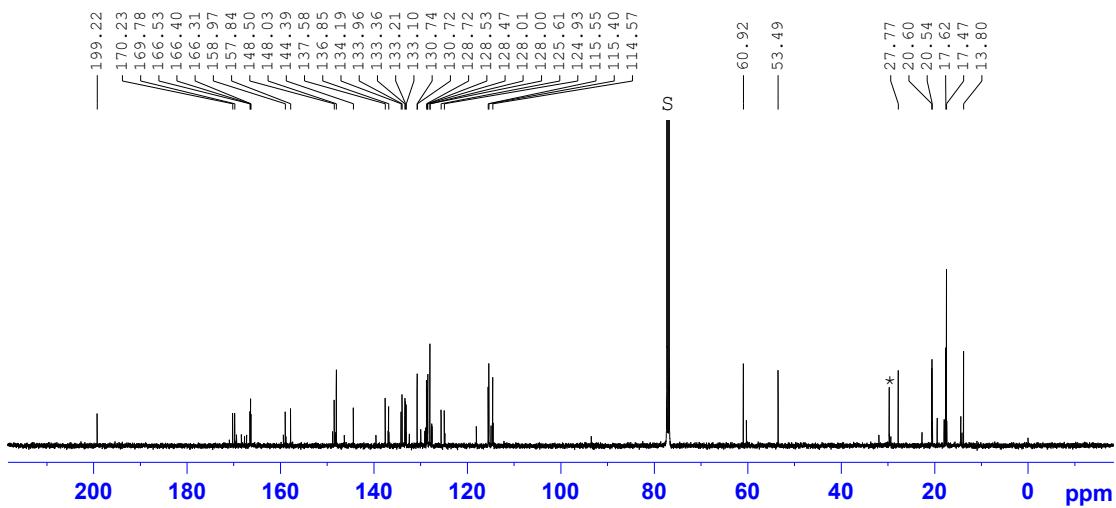


Fig. S24 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3g**.

Chemical Formula: C₄₂H₃₉N₄NiO₃⁺
Exact Mass: 705.2370

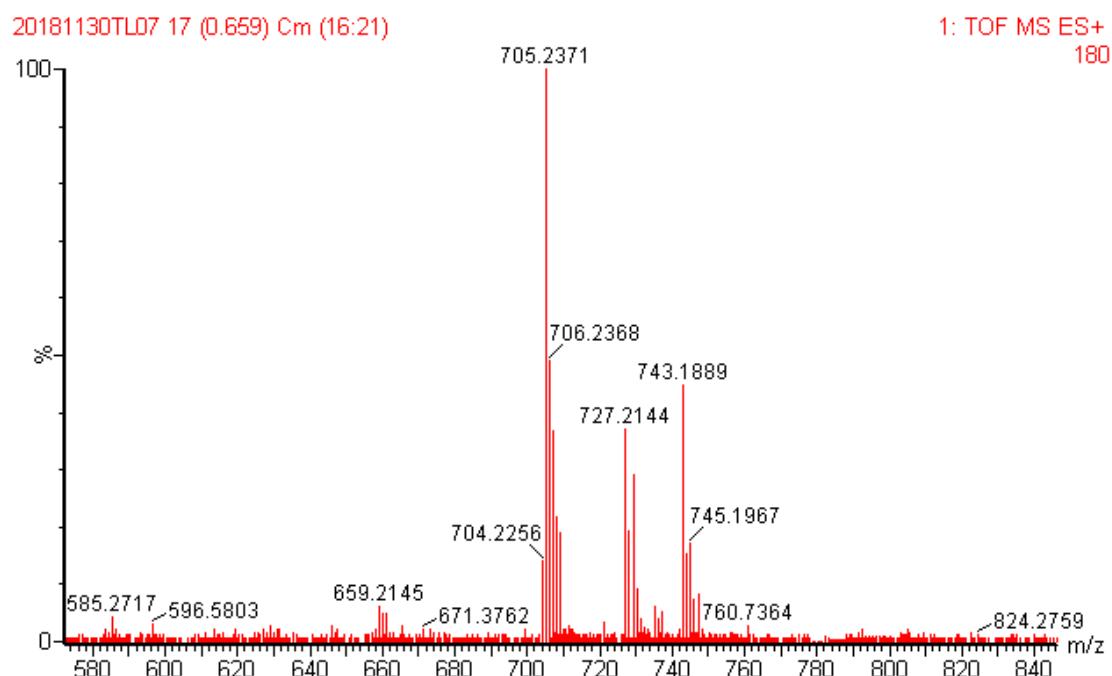
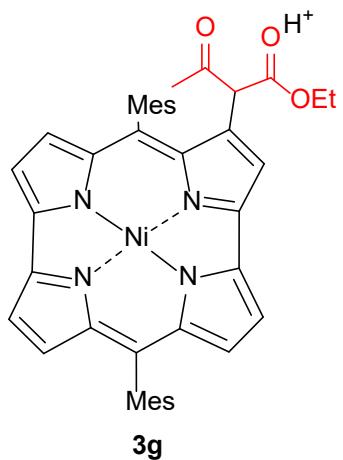
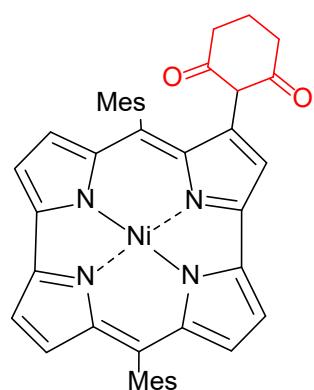


Fig. S25 HRMS ESI(+) spectrum of **3g**.



3h

¹H NMR of **3h**

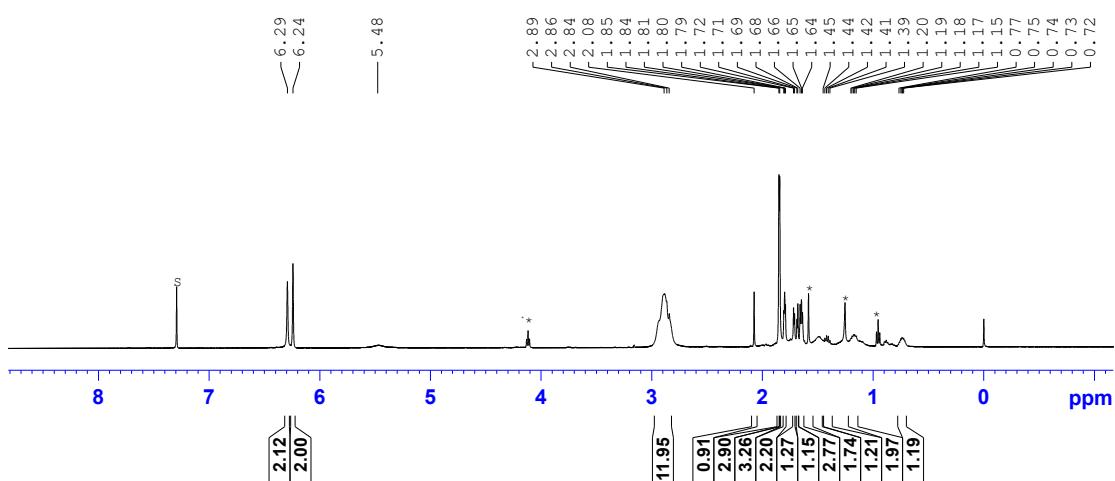


Fig. S26 ¹H NMR spectrum (CDCl₃ 500 MHz, 298 K) of **3h**.

¹³C NMR of **3h**

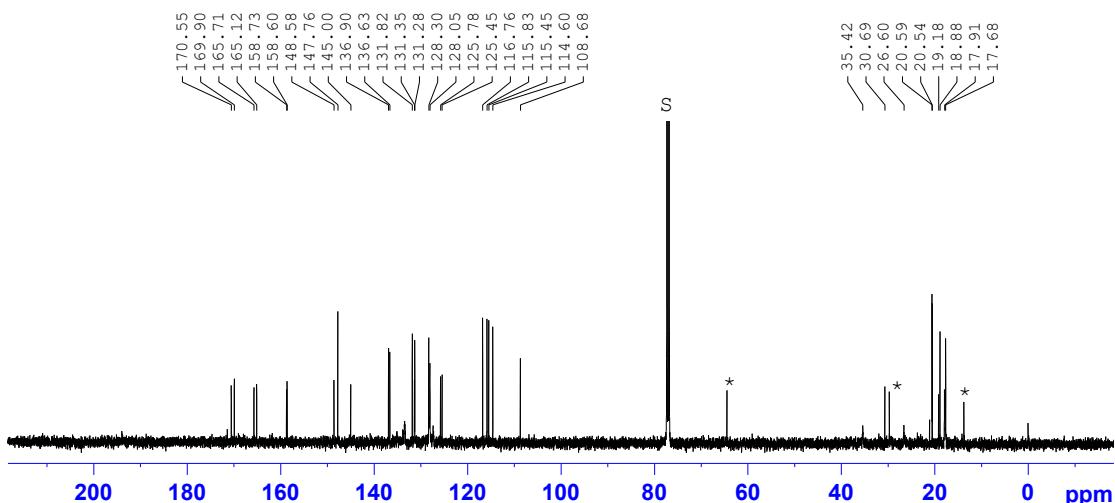
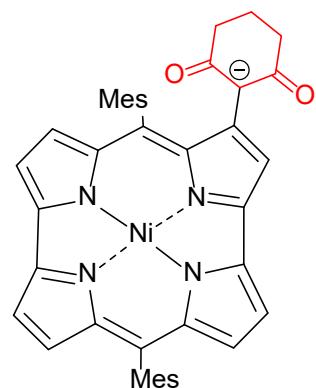


Fig. S27 ¹³C NMR spectrum (CDCl₃, 125 MHz, 298 K) of **3h**.

Chemical Formula: C₄₂H₃₅N₄NiO₂⁻
Exact Mass: 685.2119



3h

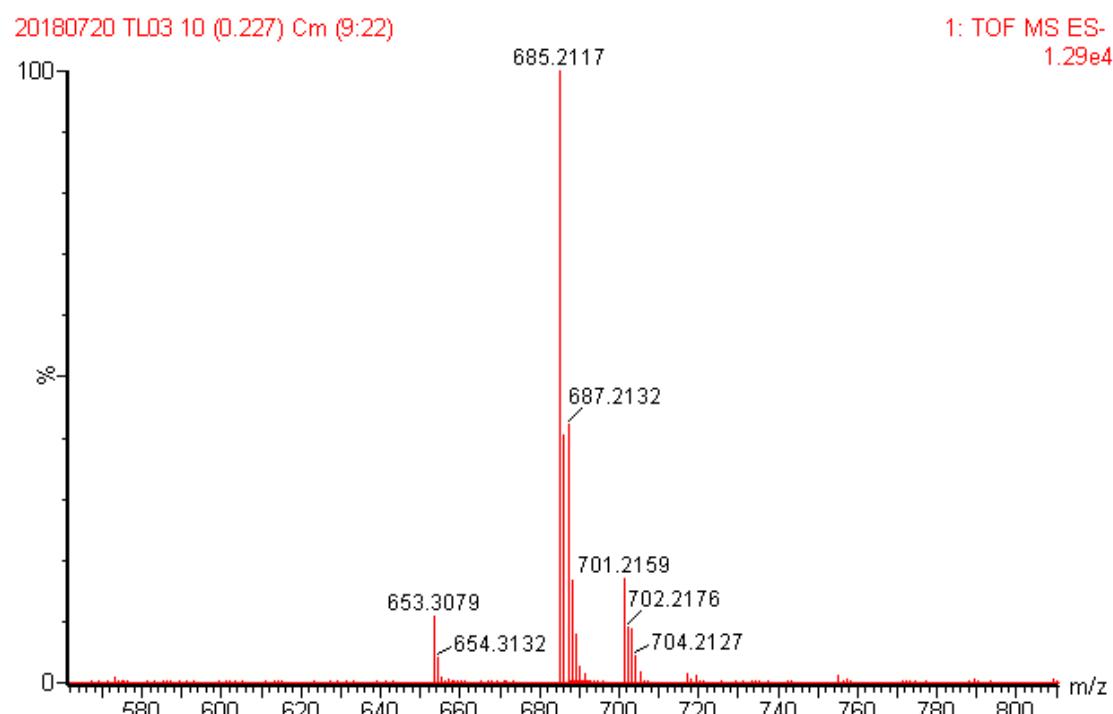
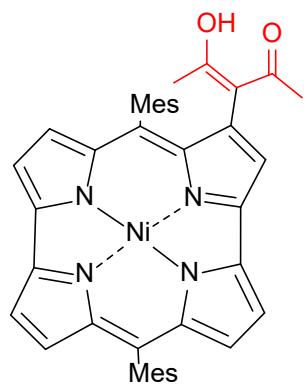


Fig. S28 HRMS ESI(-) spectrum of **3h**.



3i

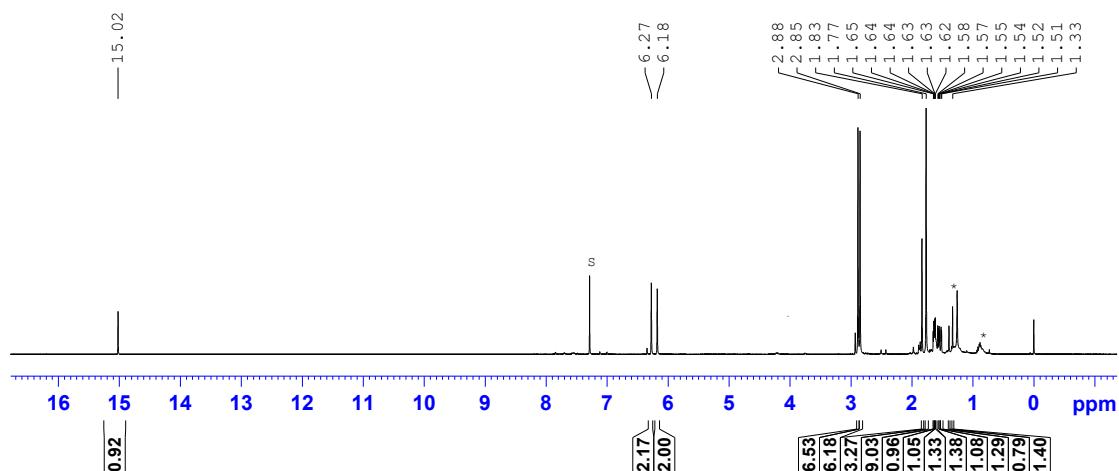


Fig. S29 ^1H NMR spectrum (CDCl_3 500 MHz, 298 K) of **3i**.

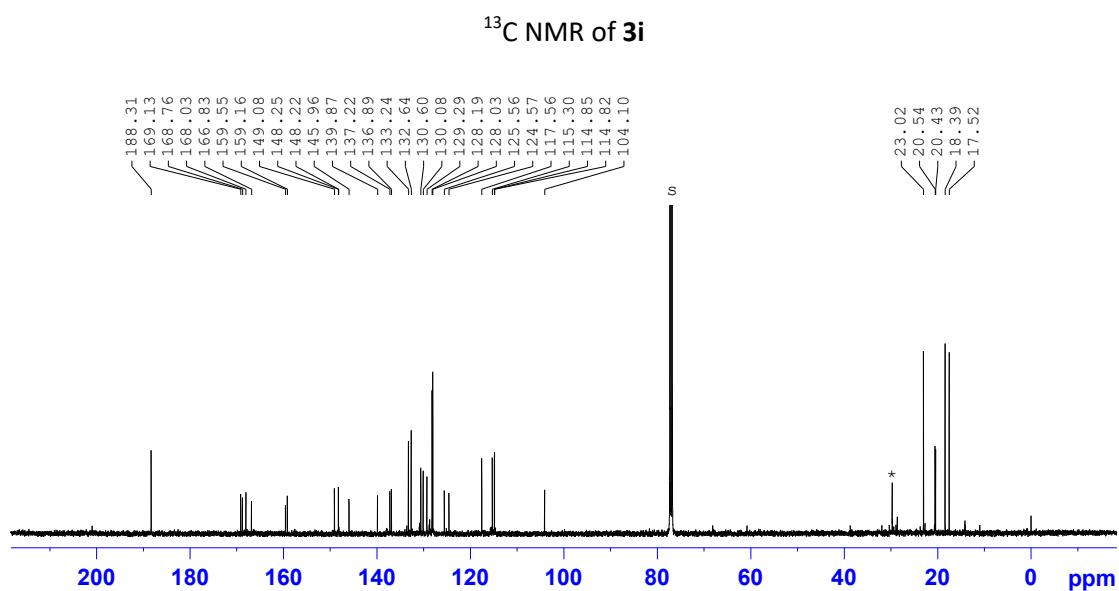
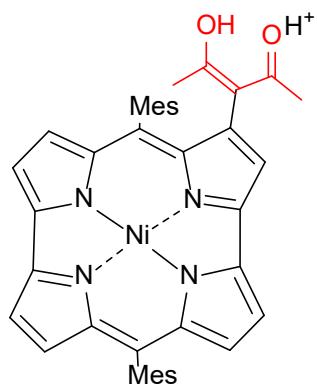


Fig. S30 ^{13}C NMR spectrum (CDCl_3 , 125 MHz, 298 K) of **3i**.

Chemical Formula: C₄₁H₃₇N₄NiO₂⁺
Exact Mass: 675.2265



3i

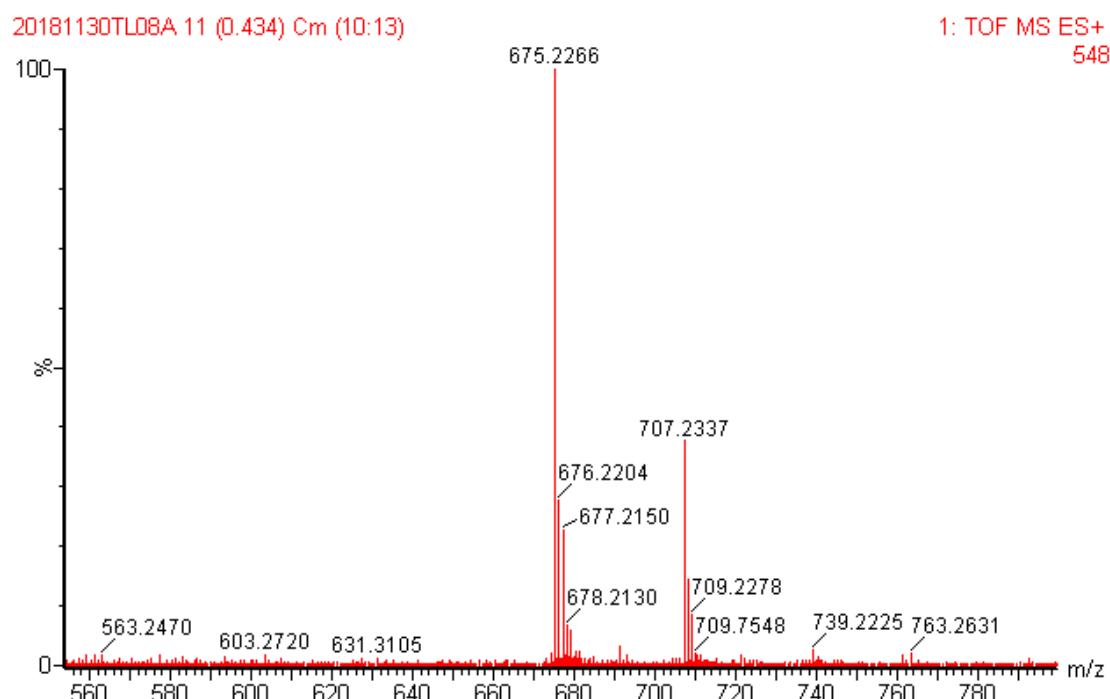


Fig. S31 HRMS ESI(+) spectrum of **3i**.

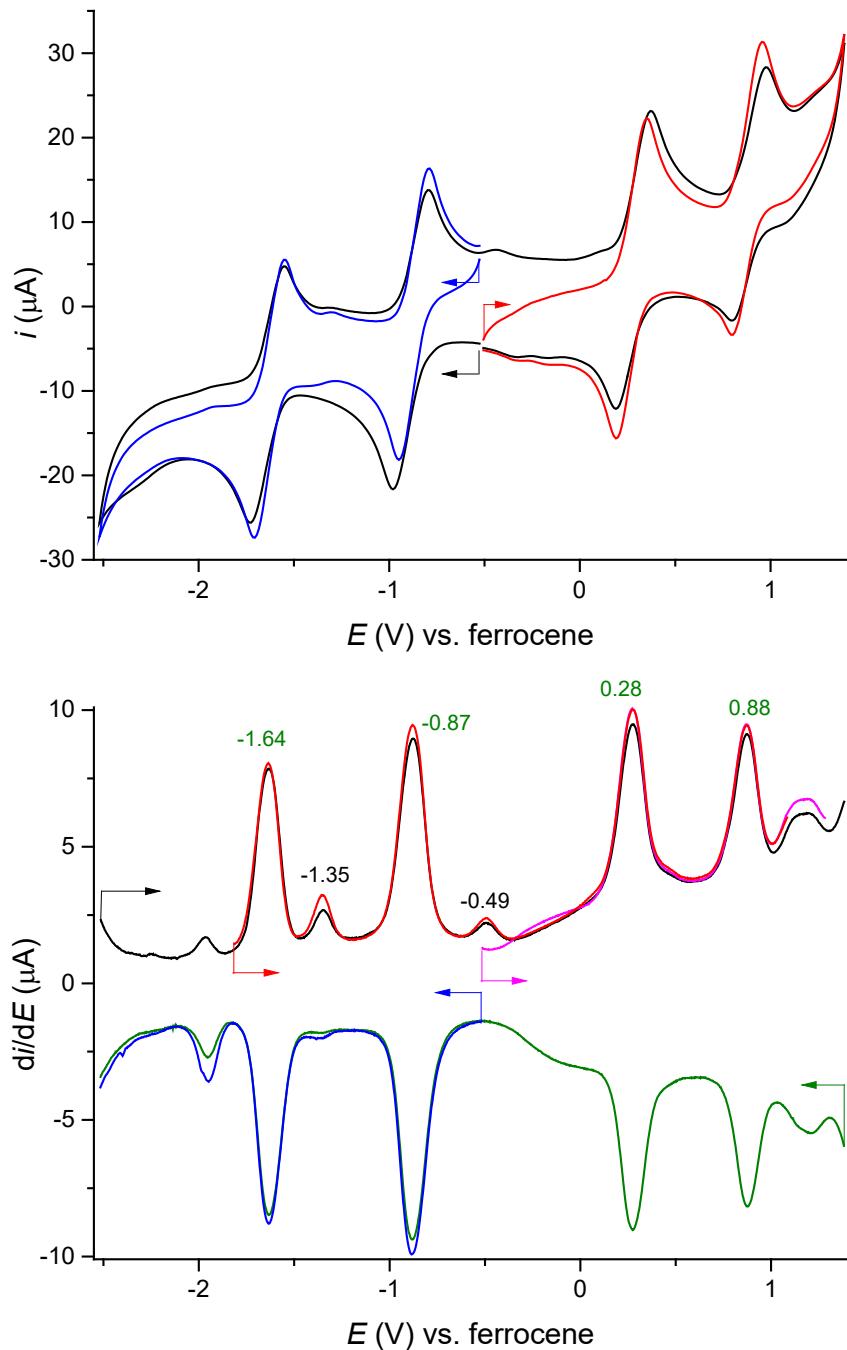


Fig. S32 Cyclic (top) and differential pulse (bottom) voltammetry for **3a** recorded within various potential limits, with various starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, $[\text{Bu}_4\text{N}]\text{PF}_6$; working electrode, glassy carbon; reference electrode, AgCl/Ag ; auxiliary electrode, platinum rod. The number associated with peaks are halfwave potentials (in volts) referenced with ferrocene/ferrocenium couple.

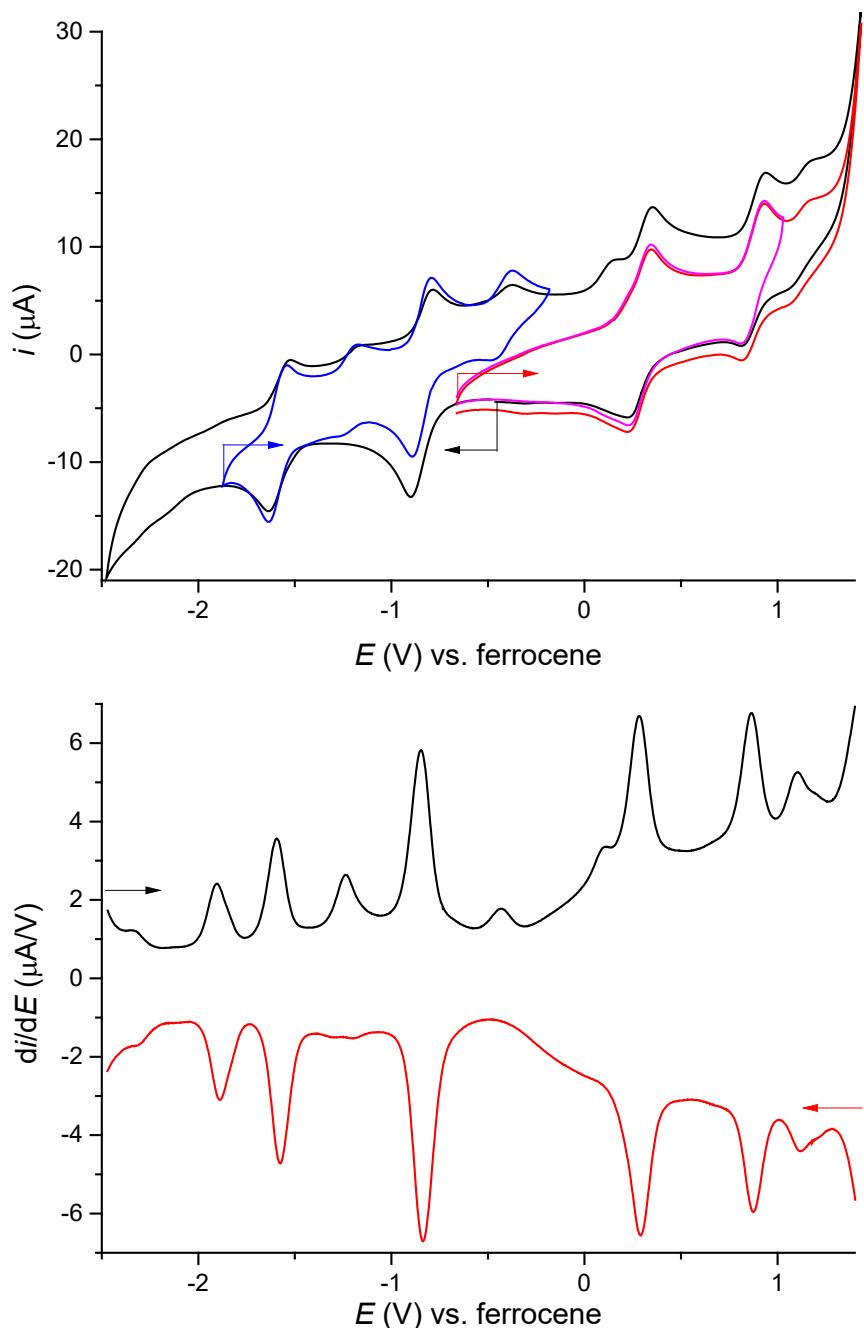


Fig. S33 Cyclic (top) and differential pulse (bottom) voltammetry for **3e** recorded within various potential limits, with various starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, $[\text{Bu}_4\text{N}]\text{PF}_6$; working electrode, glassy carbon; reference electrode, AgCl/Ag ; auxiliary electrode, platinum rod.

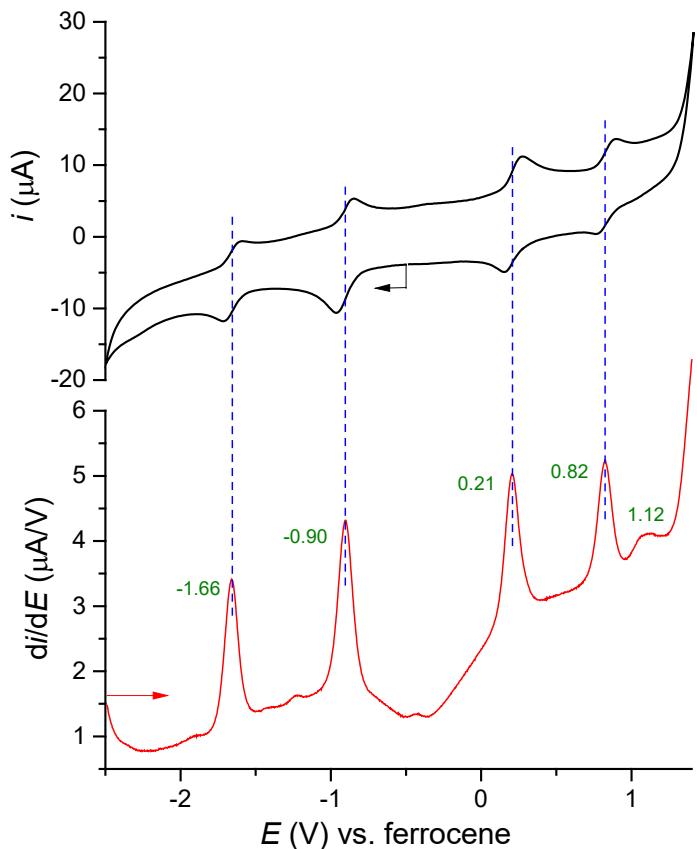


Fig. S34 Cyclic (black trace) and differential pulse (red trace) voltammetry for **3g** with starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, $[\text{Bu}_4\text{N}]\text{PF}_6$; working electrode, glassy carbon; reference electrode, AgCl/Ag ; auxiliary electrode, platinum rod. The number associated with peaks are halfwave potentials (in volts) referenced with ferrocene/ferrocenium couple.

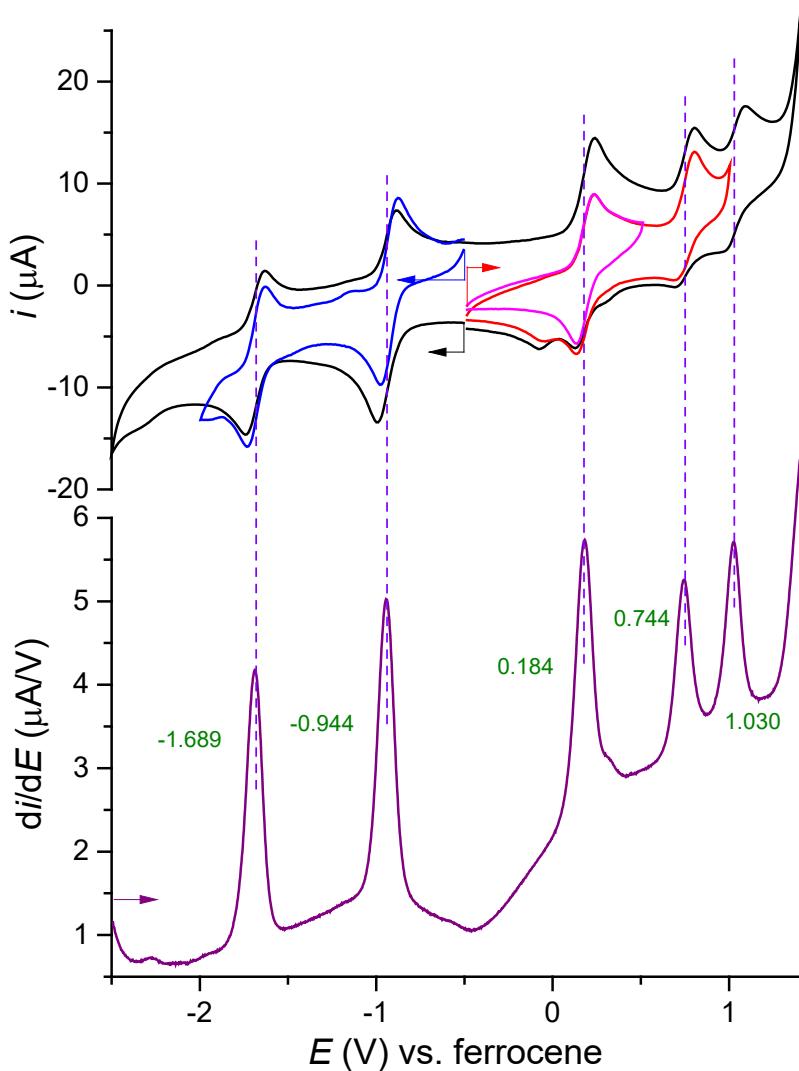


Fig. S35 Cyclic (top) and differential pulse (bottom) voltammetry for **3i** recorded within various potential limits, with various starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, $[\text{Bu}_4\text{N}]\text{PF}_6$; working electrode, glassy carbon; reference electrode, AgCl/Ag ; auxiliary electrode, platinum rod. The number associated with peaks are halfwave potentials (in volts) referenced with ferrocene/ferrocenium couple.

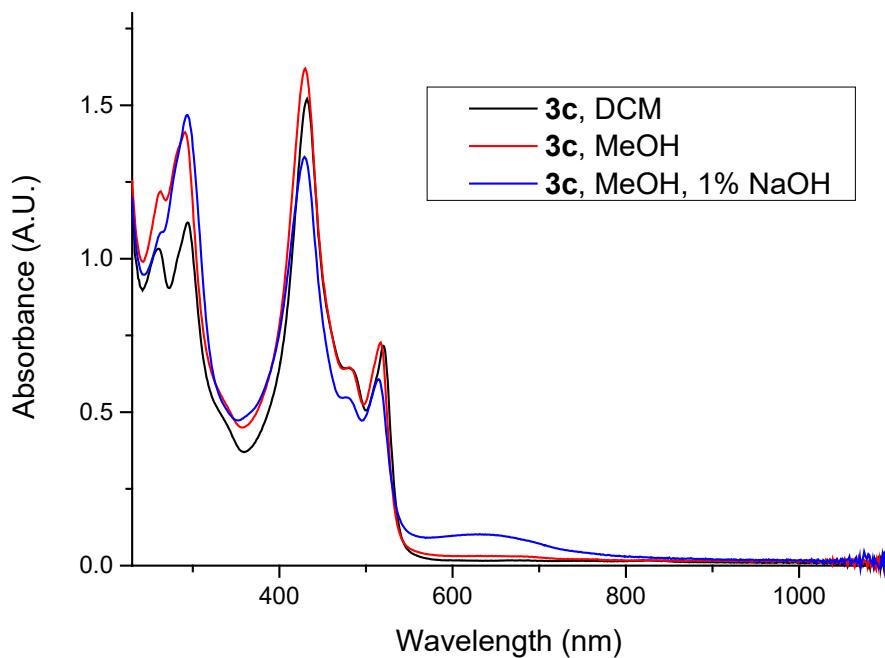


Fig. S36 Optical spectra of **3c** in DCM (black), methanol (red), and in methanol containing 1% of NaOH (blue).

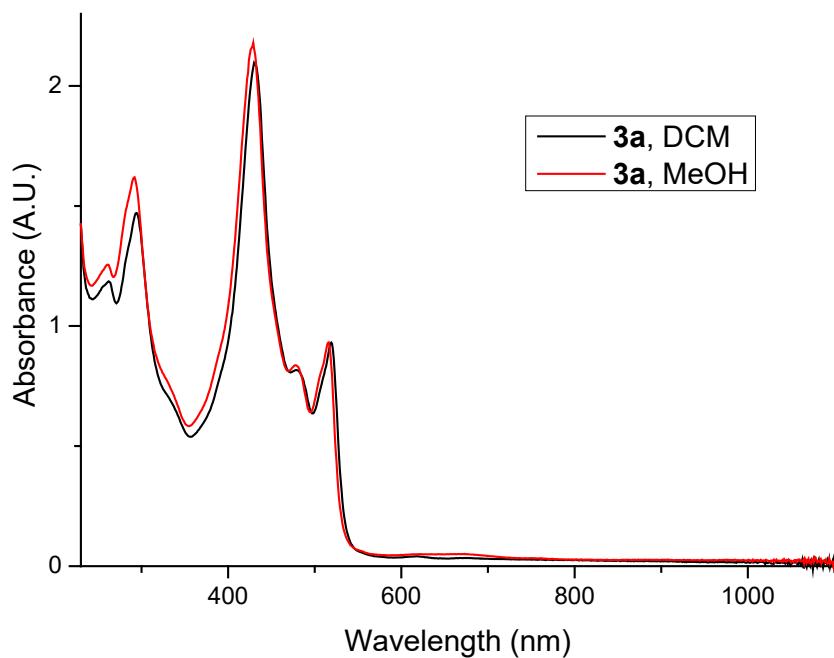


Fig. S37 Optical spectra of **3a** in DCM (black) and in methanol (red).

References

- [1] Bruker (2016). *SAINT V8.38A*. Bruker AXS Inc., Madison, Wisconsin, USA.
- [2] G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3.
- [3] G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3.
- [4] Bruker (2016). *SADABS-2016/2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- [5] A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9.