



Supporting Information

for

Radical reactivity of antiaromatic Ni(II) norcorroles with azo radical initiators

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Experimental procedures, compound characterization data including NMR and MS spectra, additional crystal data and details from DFT calculations

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1. Instrumentation and materials

¹H NMR (500 MHz) and ¹³C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to CHCl₃ (δ = 7.26 ppm) for ¹H NMR and CDCl₃ (δ = 77.16 ppm) for ¹³C NMR.

UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V 670 spectrometer.

High-resolution and electron spray ionization time-of-flight (ESI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive ionization mode.

X-ray data were obtained using a Bruker D8 QUEST X-ray diffractometer with an $1\mu\text{S}$ microfocus X-ray source and a PHOTON II detector.

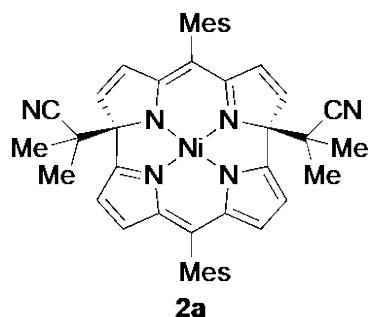
Cyclic voltammograms were obtained under the following conditions: solvent: CH₂Cl₂, electrolyte: 0.1 M Bu₄NPF₆, working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgNO₃, scan rate: 50 mV s⁻¹.

Dry toluene was purchased from KANTO CHEMICAL CO., INC. as a dehydrated grade. AIBN and V-40 were purchased from Wako Pure Chemical Industries, Ltd. Ni(II) mesitylnorcorrole **1** was prepared according to the literature.¹

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Experimental procedures and compound data

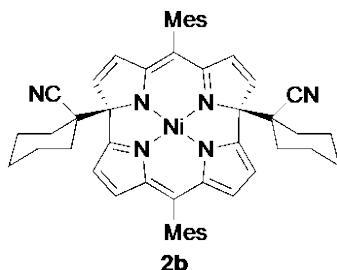
Synthesis of dialkylated macrocycle **2a**



To a Schlenk flask was added compound **1** (23.0 mg, 40 µmol), AIBN (13.2 mg, 80 µmol) and dry toluene (4 mL) under N₂ atmosphere. The reaction mixture was stirred at reflux for 1 h. After removing the solvent in vacuo, the mixture was purified by PTLC (eluent: CH₂Cl₂/hexane = 1:2) and compound **2a** (26.2 mg, 37 µmol, 92%) was obtained as a maroon solid.

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 7.19 (d, *J* = 5.4 Hz, 2H), 6.93 (s, 1H), 6.92 (s, 1H), 6.91 (s, 1H), 6.87 (s, 1H), 6.49 (d, *J* = 4.2 Hz, 2H), 6.46 (d, *J* = 4.2 Hz, 2H), 6.09 (d, *J* = 5.4 Hz, 2H), 2.34 (s, 3H), 2.31 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H), 2.14 (s, 3H), 1.86 (s, 3H), 1.60 (s, 6H), 1.42 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 174.3, 153.4, 145.8, 145.6, 140.7, 139.0, 137.9, 136.9, 136.4, 136.3, 133.5, 133.3, 132.7, 131.9, 128.3, 128.2, 128.0, 127.9, 127.7, 123.7, 115.2, 98.0, 92.4, 40.1, 24.4, 23.0, 21.3, 21.2, 21.2, 21.2, 20.3, 20.0, ppm; HRMS (ESI): [M+Na]⁺ Calcd for (C₄₄H₄₂N₆Ni)Na⁺: 735.2717; Found: 735.2721

Synthesis of dialkylated macrocycle **2b**



To a Schlenk flask was added compound **1** (23.0 mg, 40 µmol), V–40 (19.5 mg, 80 µmol) and dry toluene (4 mL) under N₂ atmosphere. The reaction mixture was stirred at reflux for 1 h. After removing the solvent in vacuo, the mixture was purified by PTLC (eluent: CH₂Cl₂/hexane = 1:1) and compound **2b** (27.4 mg, 35 µmol, 87%) was obtained as a maroon solid.

¹H NMR (500 MHz, CDCl₃, 298 K): δ = 7.18 (d, *J* = 5.4 Hz, 2H), 6.93–6.90 (m, 3H), 6.86 (s, 1H), 6.49 (d, *J* = 4.3 Hz, 2H), 6.44 (d, *J* = 4.3 Hz, 2H), 6.06 (d, *J* = 5.4 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 2.24–2.15 (m, 13H), 1.94–1.86 (m, 2H), 1.85–1.78 (m, 2H), 1.82 (s, 3H), 1.78–1.69 (m, 4H), 1.69–1.58 (m, 4H), 1.32–1.22 (m, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 174.7, 153.6, 145.8, 145.3, 140.7, 139.1, 137.8, 136.8, 136.5, 136.4, 133.7, 133.4, 132.6, 132.0, 128.2, 128.2, 128.0, 127.9, 127.7, 122.1, 115.3, 98.2, 92.9, 47.4, 32.4, 30.6, 25.0, 23.7, 23.4, 21.5, 21.3, 21.2, 21.1, 20.5, 19.9 ppm; HRMS (ESI): [M+Na]⁺ Calcd for (C₅₀H₅₀N₆Ni)Na⁺: 815.3343; Found: 815.3348

3. NMR spectra

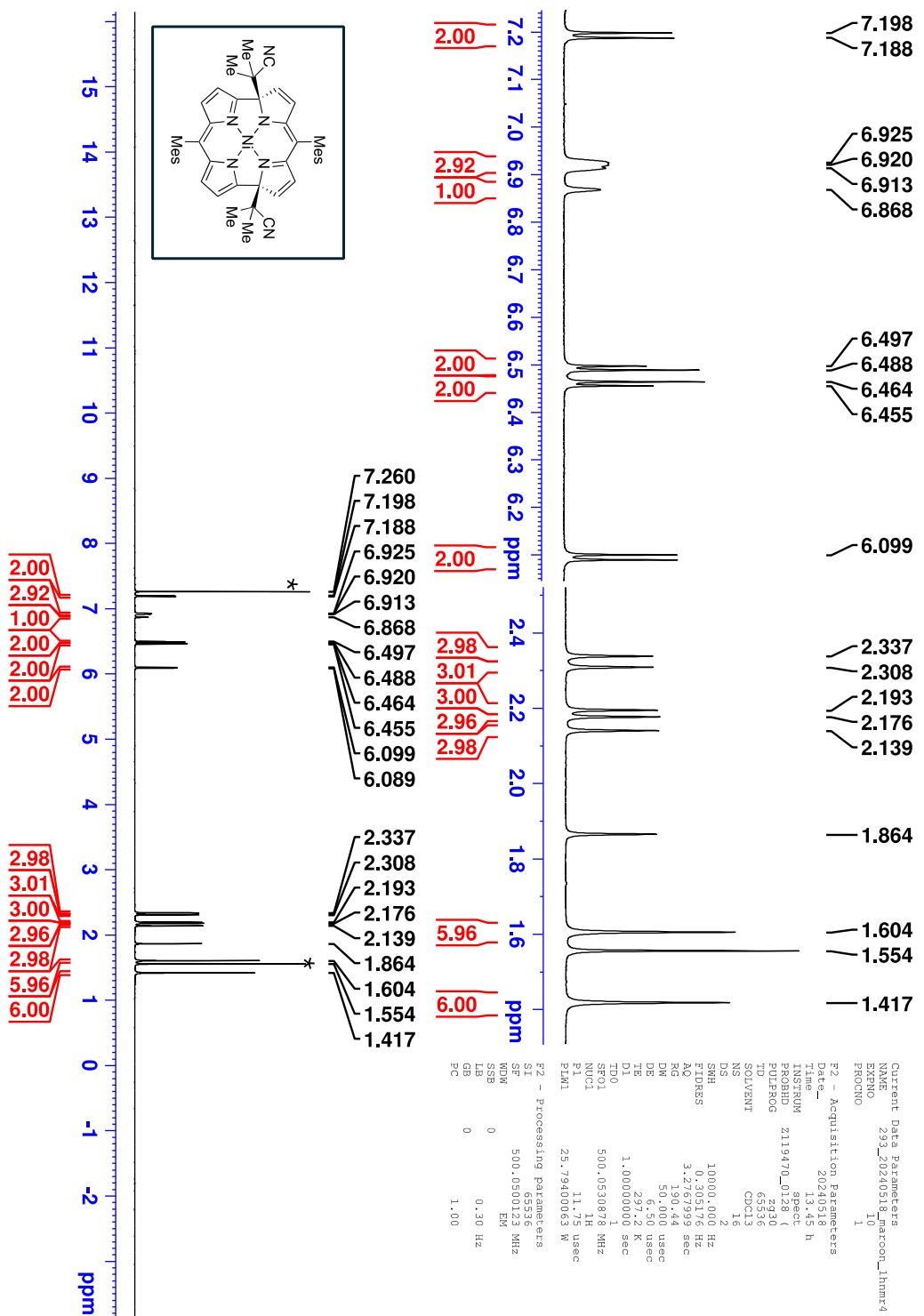


Figure S1. ^1H NMR spectrum of **2a** in CDCl_3 at 25°C .

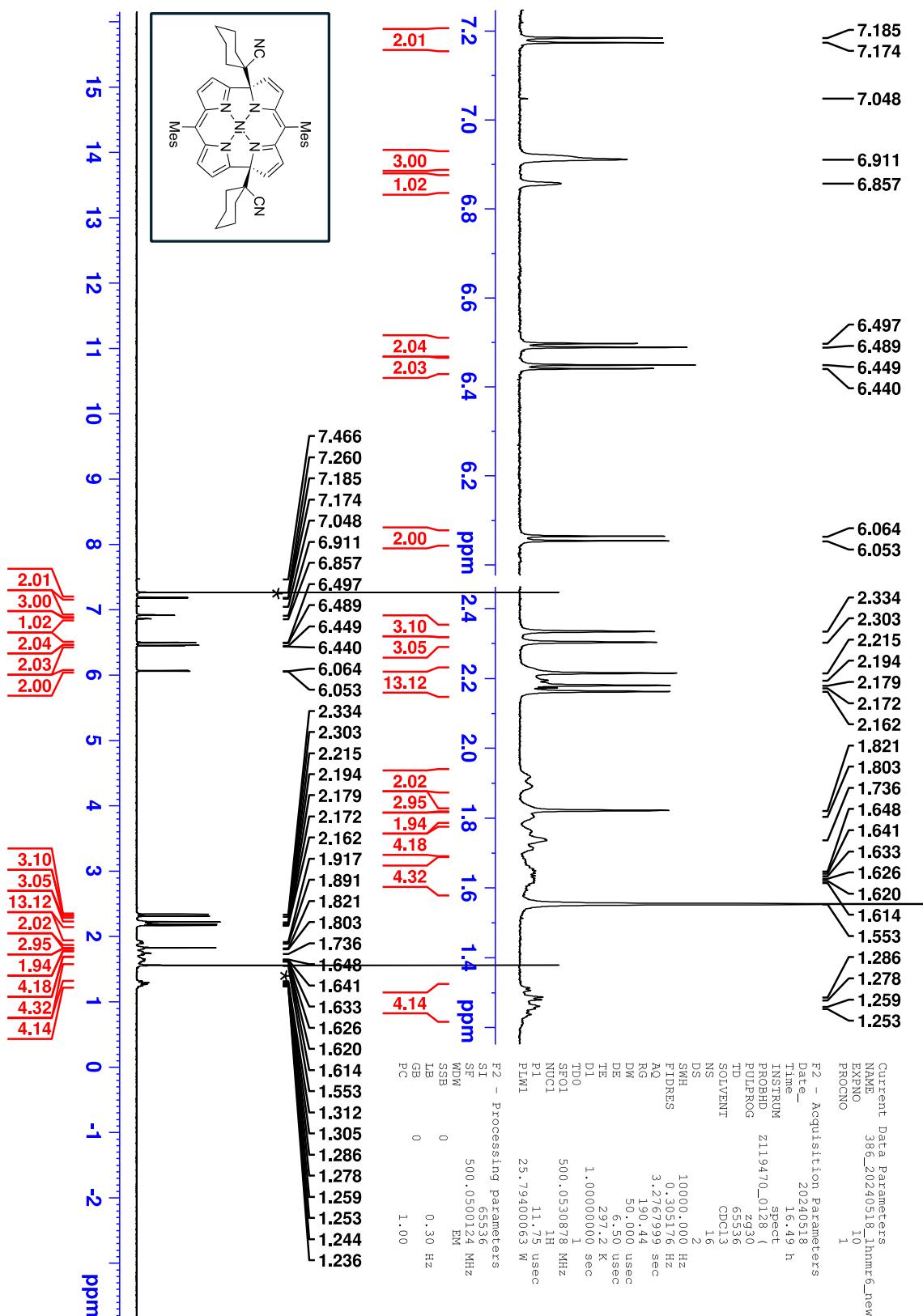


Figure S3. ¹H NMR spectrum of **2b** in CDCl₃ at 25 °C.

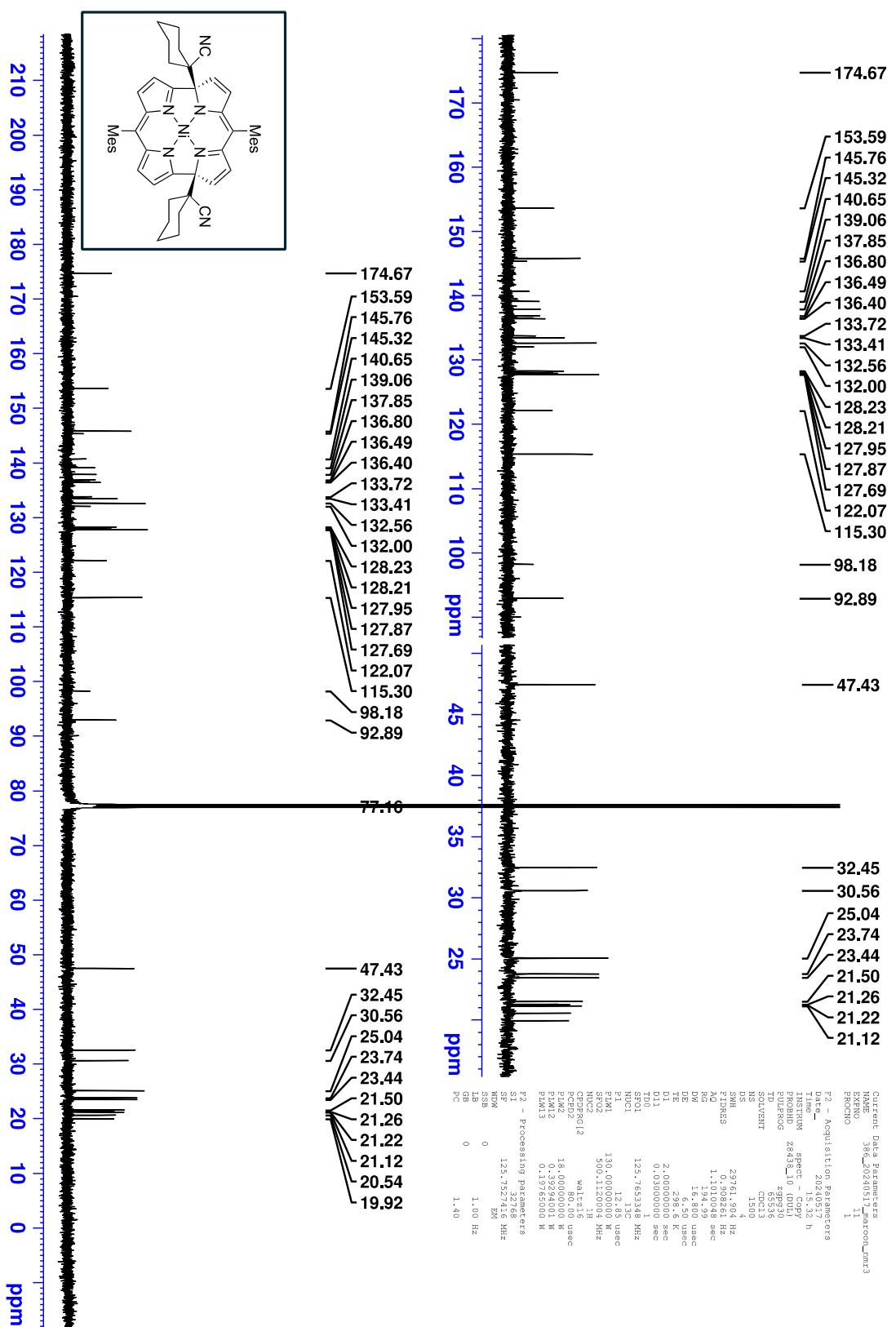
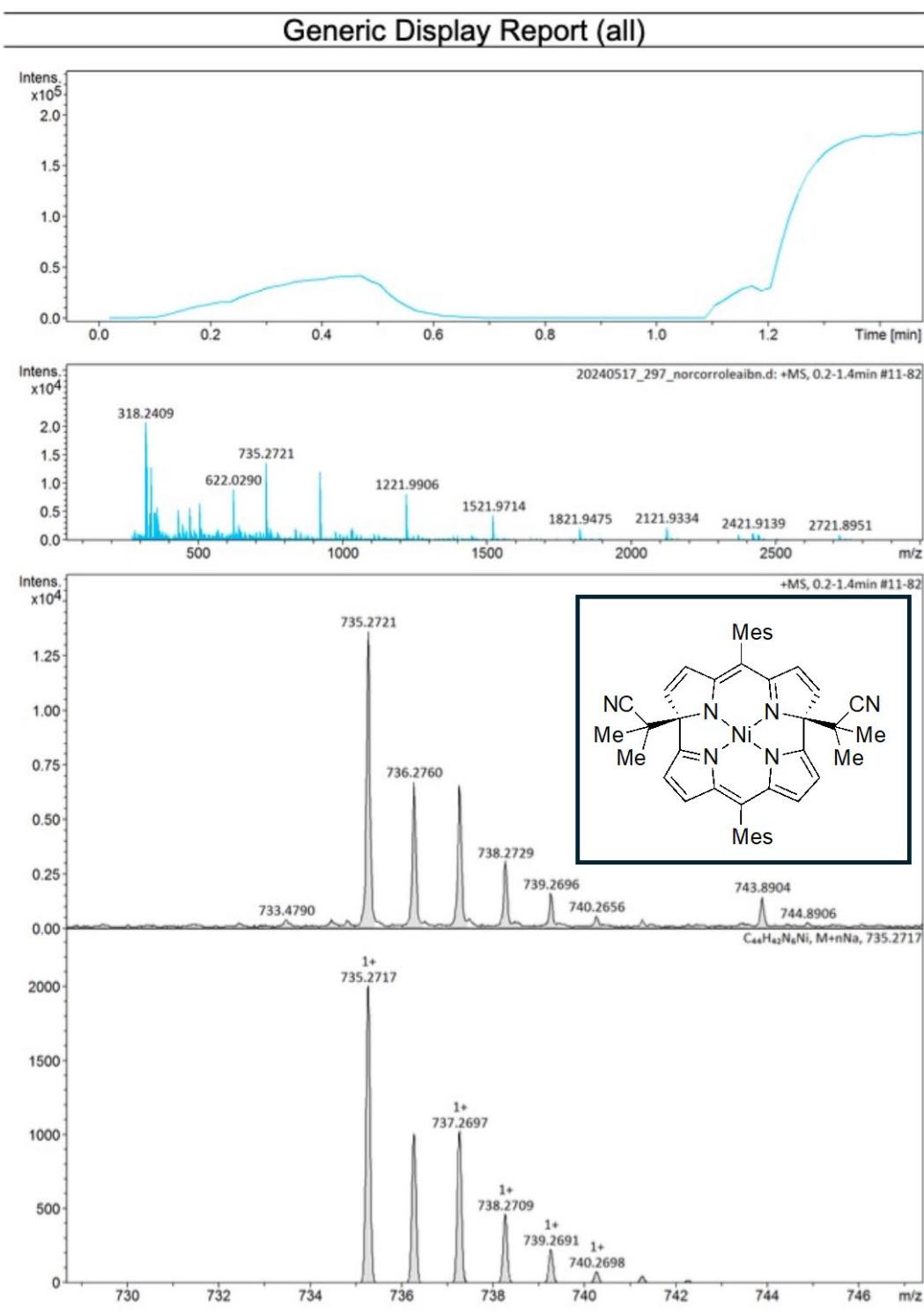


Figure S4. ¹³C NMR spectrum of **2b** in CDCl₃ at 25 °C.

4. Mass spectra



Bruker Compass DataAnalysis 4.2 printed: 5/17/2024 11:55:12 AM by: BDAL@DE Page 1 of 1

Figure S5. ESI-TOF mass spectrum of **2a**.

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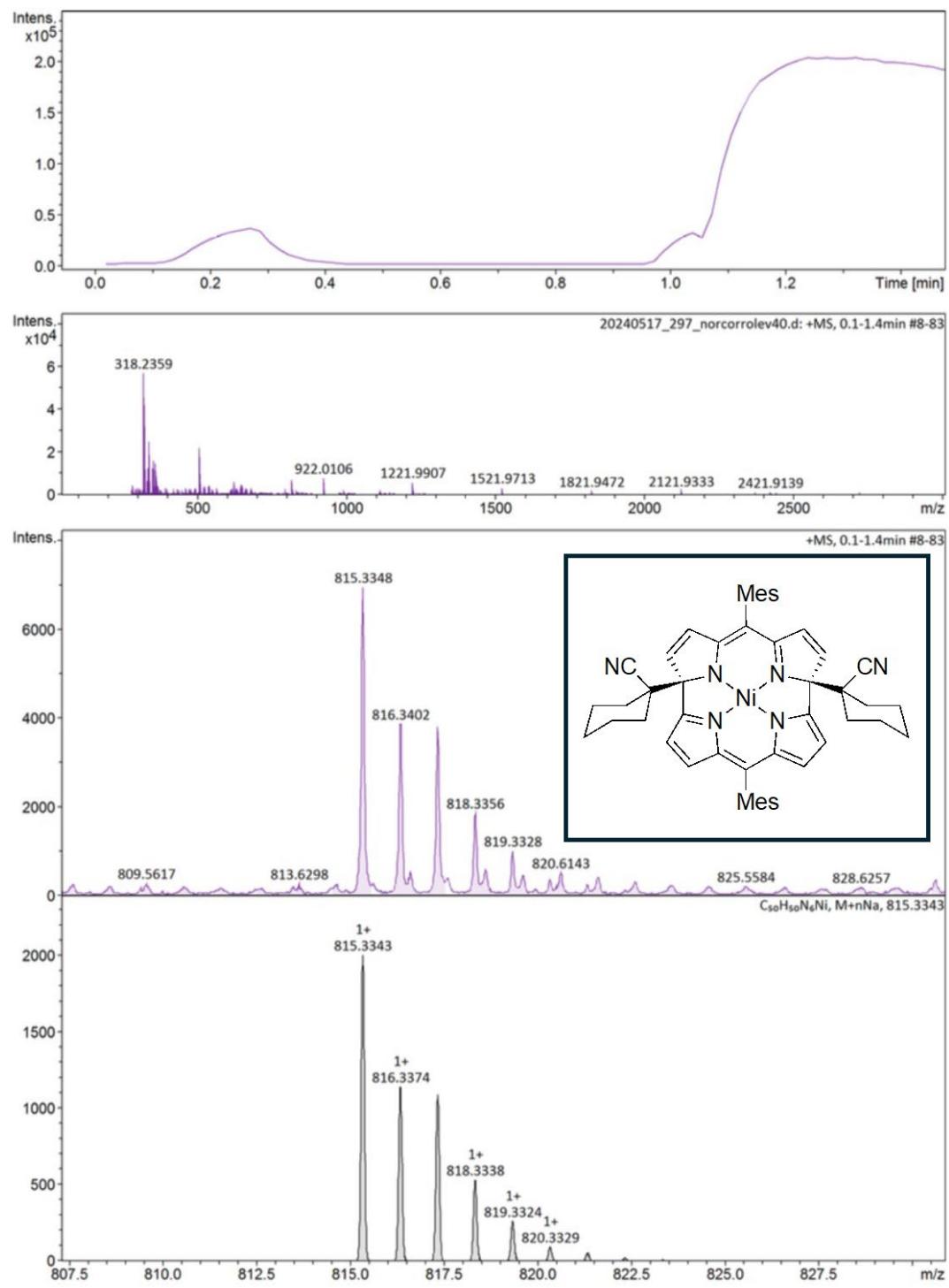


Figure S6. ESI-TOF mass spectrum of **2b**.

5. Crystal data

Crystallographic data for **2a:** Single crystals were obtained by vapour diffusion of acetonitrile into a chloroform solution of **2a**. $C_{44}H_{42}N_6Ni$, $M_w = 713.54$, monoclinic, space group $P2_1/c$, $a = 23.594(5)$, $b = 15.092(5)$, $c = 10.888(5)$ Å, $\alpha = \gamma = 90.000(5)^\circ$, $\beta = 101.917(4)^\circ$, $V = 3793(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.249$ g/cm³, $T = 93$ K, $R_1 = 0.0433$ ($I > 2.0 \sigma(I)$), $wR_2 = 0.0945$ (all data), GOF = 1.037, CCDC No. = 2356750.

Table S1. Crystallographic data of **2a**

compound	2a
Formula	$C_{44}H_{42}N_6Ni$
Formula weight	713.54
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Crystal color	green
Crystal description	block
a [Å]	23.594(5)
b [Å]	15.092(5)
c [Å]	10.888(5)
α [°]	90.000(5)
β [°]	101.917(4)
γ [°]	90.000(5)
V [Å ³]	3793.(2)
Z	4
d_{calcd} [g cm ⁻³]	1.249
R_1 ($I > 2\sigma(I)$)	0.0433
wR_2 (all data)	0.0945
Goodness-of-fit	1.037
Temperature [K]	93(2)
Solvent	CHCl ₃ /MeCN
CCDC No.	2356750

Excited State	5:	Singlet-A	2.5380 eV	488.51 nm	f=0.0001	$\langle S^{**2} \rangle = 0.000$
	171 ->185		0.16419			
	171 ->188		-0.25654			
	172 ->185		0.14928			
	172 ->188		-0.23511			
	173 ->185		0.22274			
	173 ->188		-0.33981			
	178 ->185		0.23145			
	178 ->188		-0.26364			
	182 ->184		0.10040			
	183 ->185		-0.11918			
Excited State	6:	Singlet-A	2.7064 eV	458.11 nm	f=0.0360	$\langle S^{**2} \rangle = 0.000$
	173 ->185		-0.12028			
	173 ->188		0.15877			
	181 ->184		0.13044			
	182 ->184		0.51325			
	183 ->185		-0.29729			
	183 ->188		-0.21415			

7. References

1. Ito, T.; Hayashi, Y.; Shimizu, S.; Shin, J.-Y.; Kobayashi, N.; Shinokubo, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 8542–8545.