Supporting Information

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

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1. Instrumentation and materials

^{1}H NMR (500 MHz) and ^{13}C 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 $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C 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 IμS microfocus X-ray source and a PHOTON II detector.

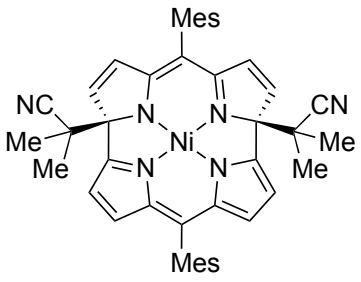
Cyclic voltammograms were obtained under the following conditions: solvent: CH_2Cl_2, electrolyte: 0.1 M Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt, reference electrode: $Ag/AgNO_3$, scan rate: 50 mV s^{-1}.

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

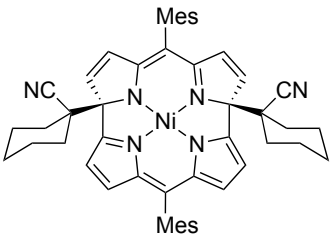


2a

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 N_2 atmosphere. The reaction mixture was stirred at 130 °C for 1 h while refluxing. After removing the solvent *in vacuo*, the mixture was purified by PTLC (eluent: CH_2Cl_2/hexane = 1/2) and compound **2a** (26.2 mg, 37 μmol, 92%) was obtained as a maroon solid.

^{1}H NMR (500 MHz, $CDCl_3$, 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; ^{13}C NMR (126 MHz, $CDCl_3$, 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 $(C_{44}H_{42}N_6Ni)Na^+$: 735.2717; Found: 735.2721

Synthesis of dialkylated macrocycle 2b



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 N_2 atmosphere. The reaction mixture was stirred at 130 °C for 1 h while refluxing. After removing the solvent *in vacuo*, the mixture was purified by PTLC (eluent: CH_2Cl_2/hexane = 1/1) and compound **2b** (27.4 mg, 35 μmol, 87%) was obtained as a maroon solid.

^{1}H NMR (500 MHz, $CDCl_3$, 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; ^{13}C NMR (126 MHz, $CDCl_3$, 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 $(C_{50}H_{50}N_6Ni)Na^+$: 815.3343; Found: 815.3348

3. NMR spectra

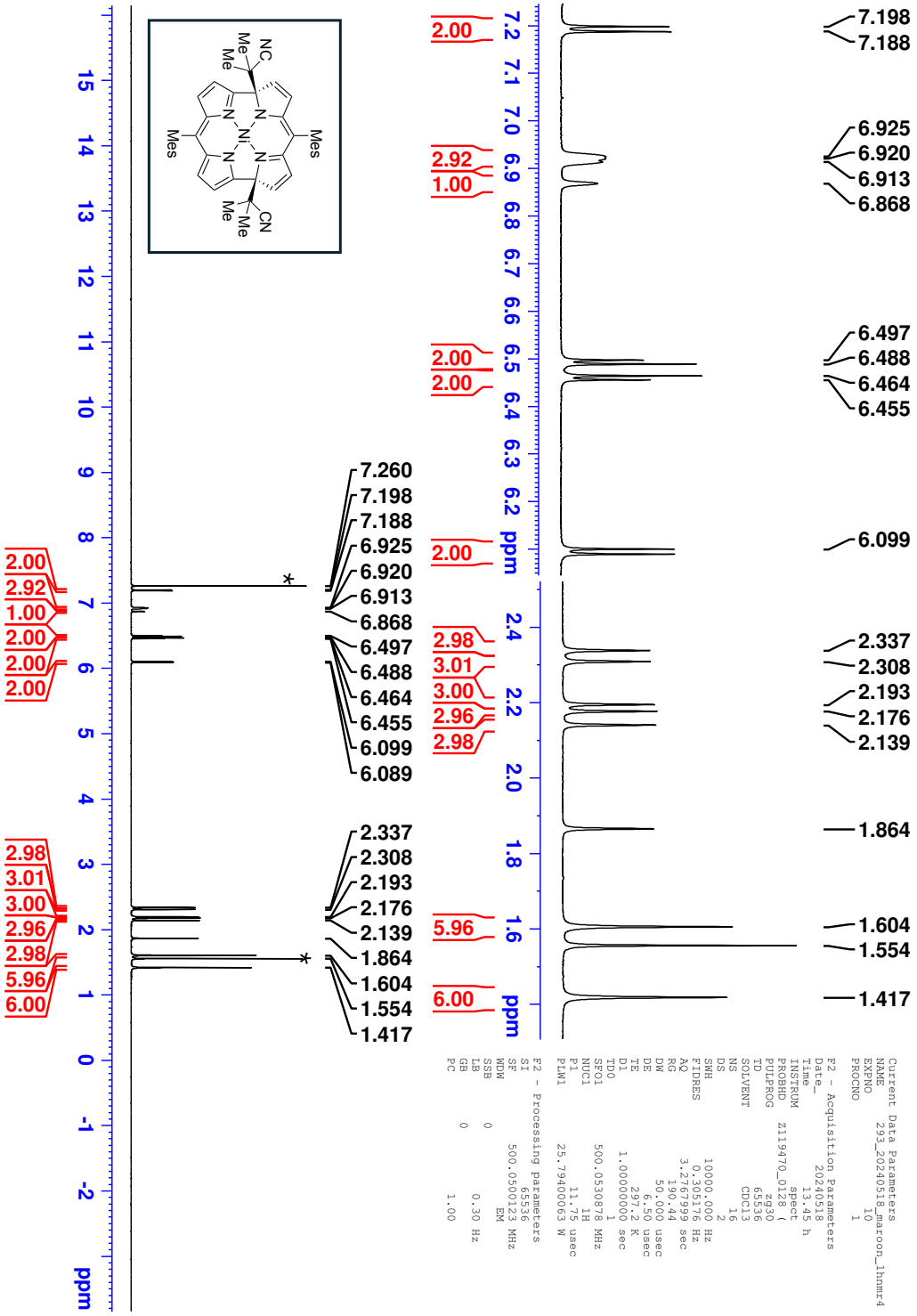


Figure S1. ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

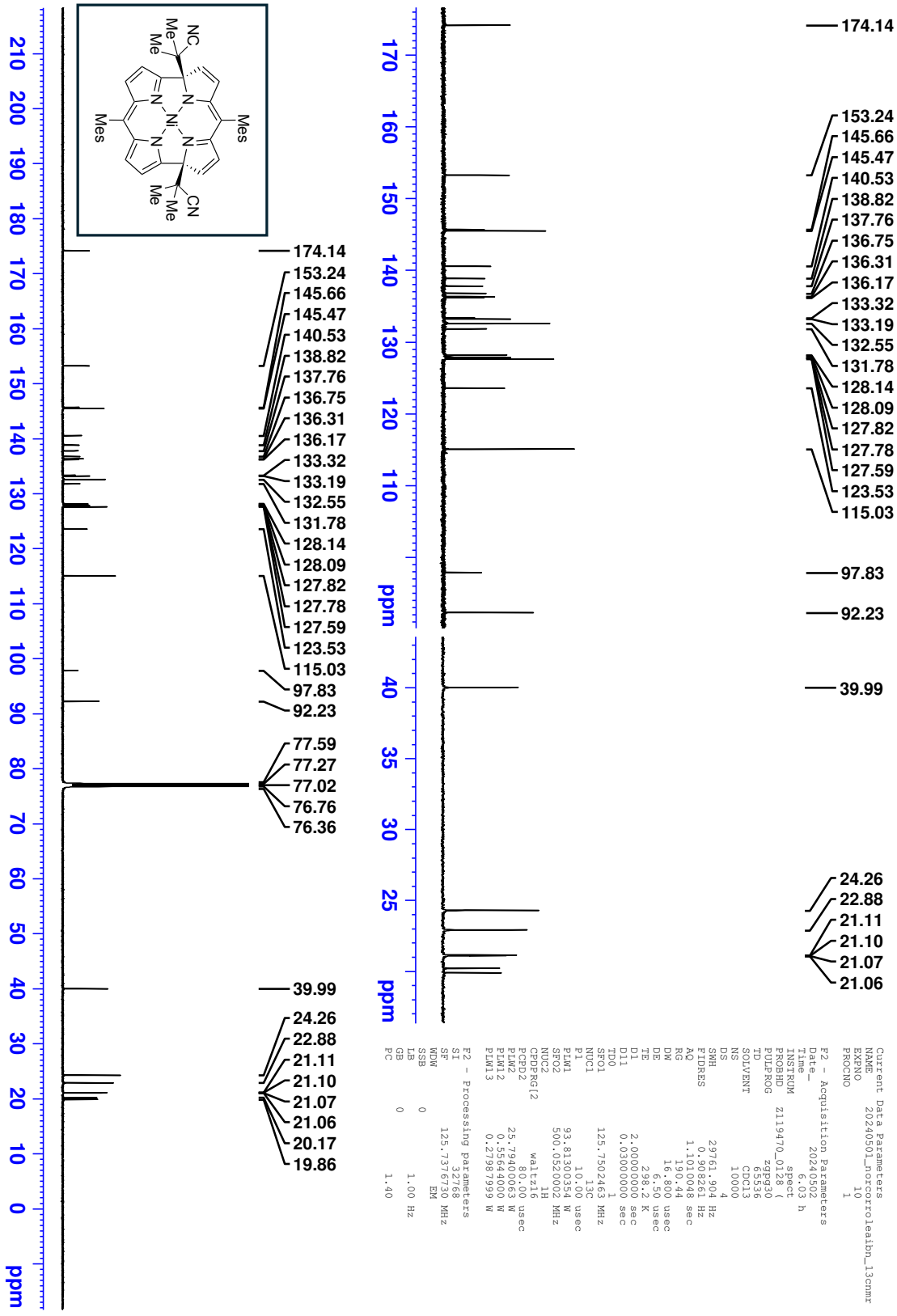


Figure S2. ^{13}C NMR spectrum of **2a** in $CDCl_3$ at 25 °C.

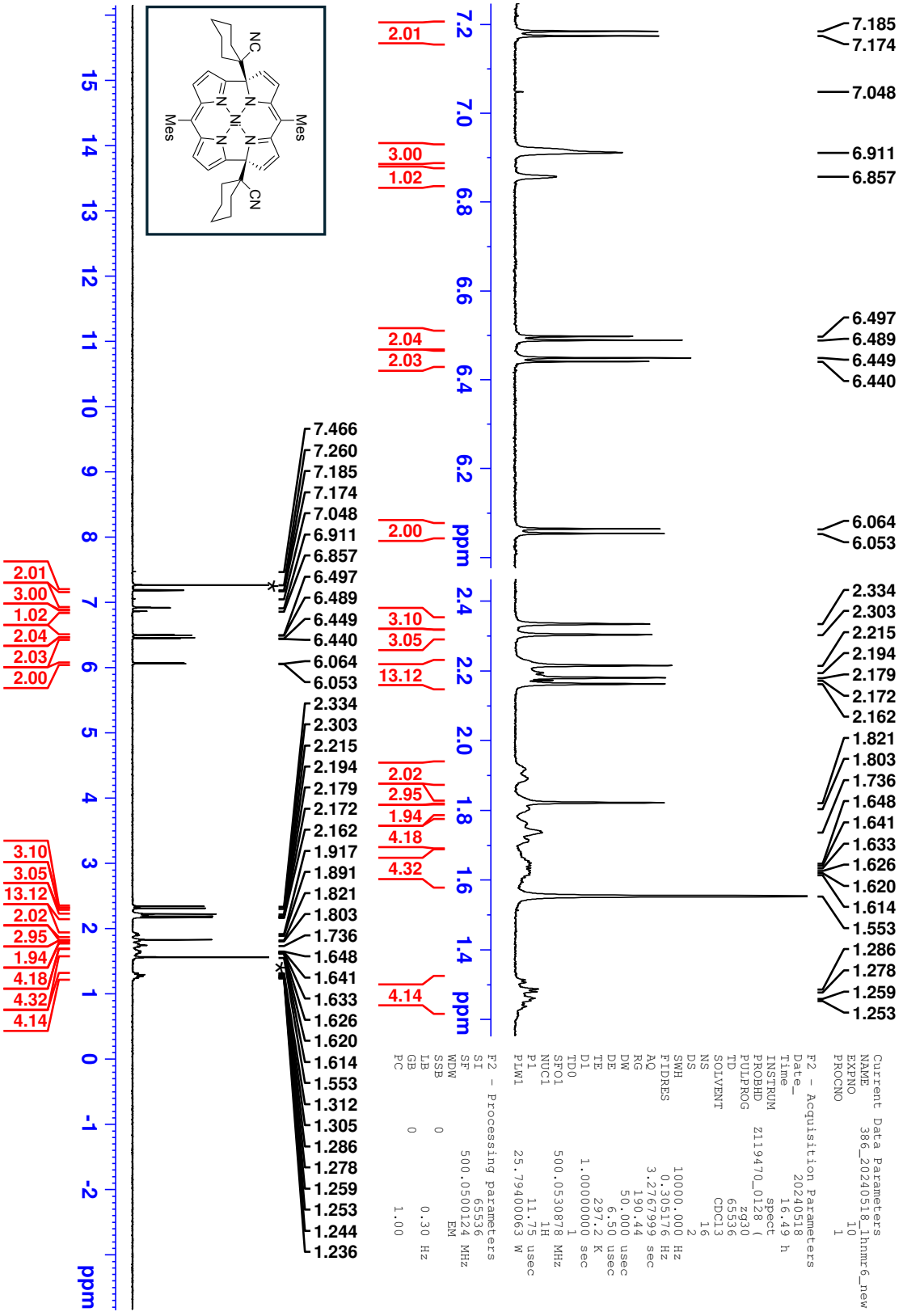


Figure S3. ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

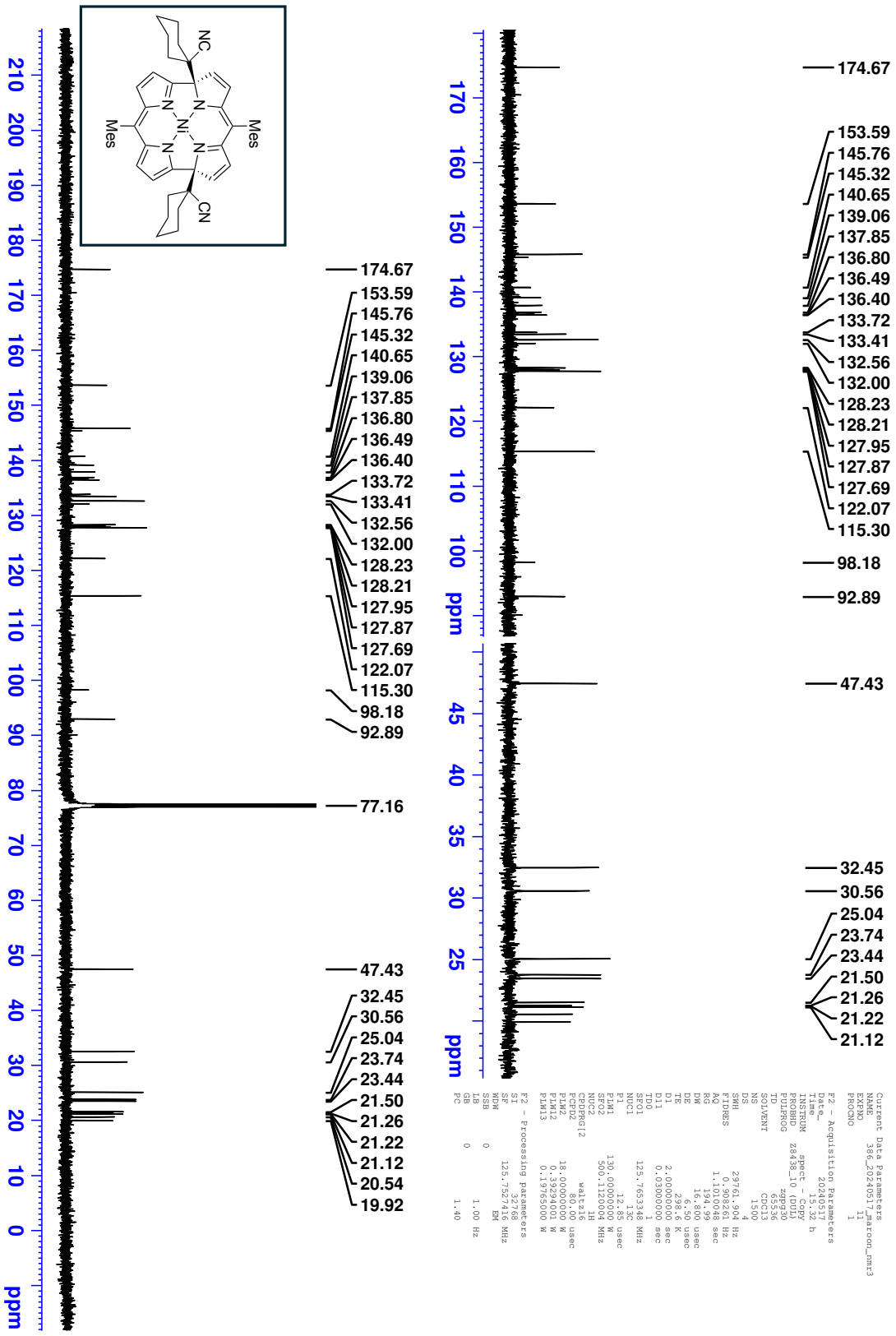


Figure S4. ^{13}C NMR spectrum of **2b** in $CDCl_3$ at 25 °C.

4. Mass spectra

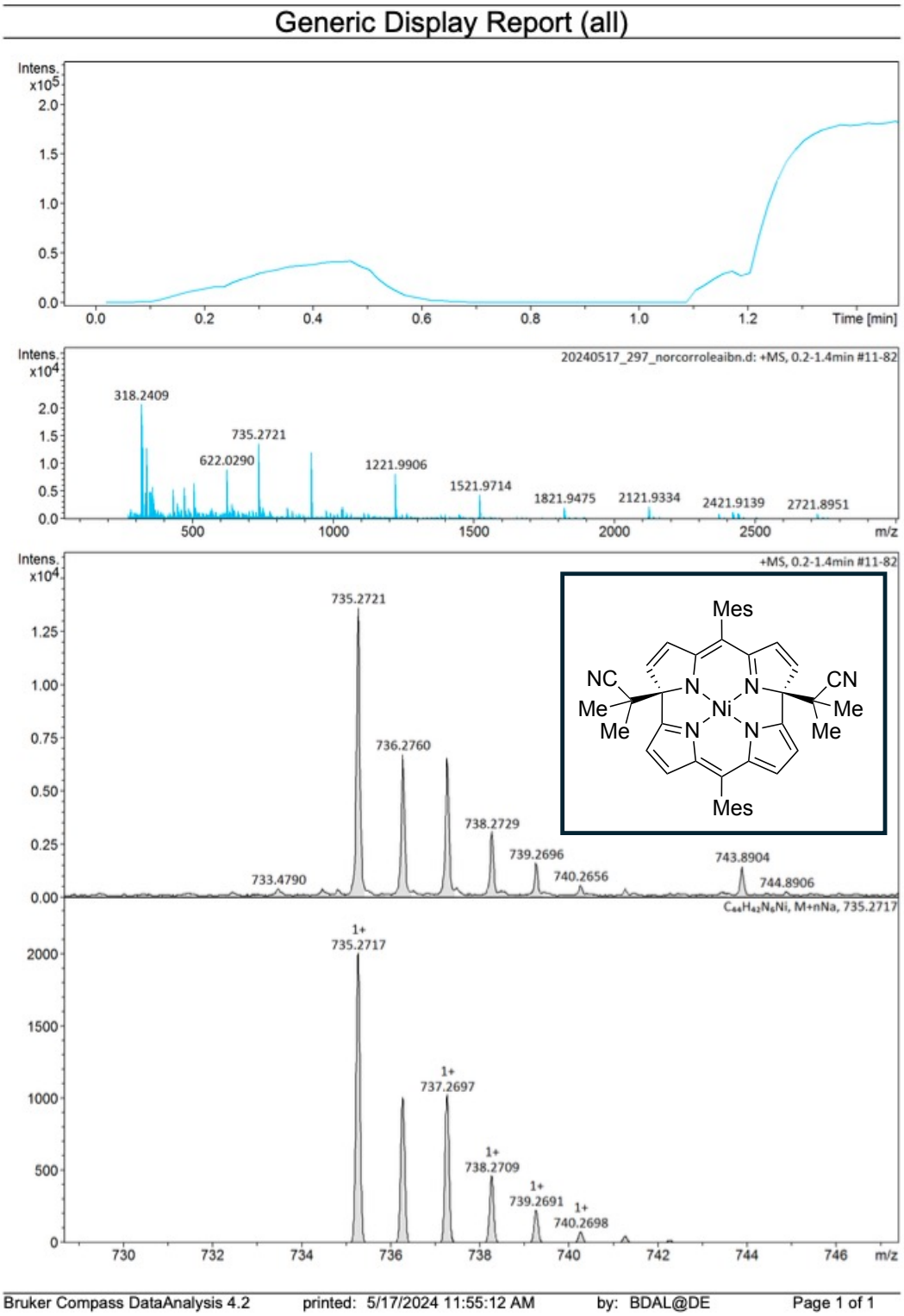


Figure S5. ESI-TOF mass spectrum of **2a**.

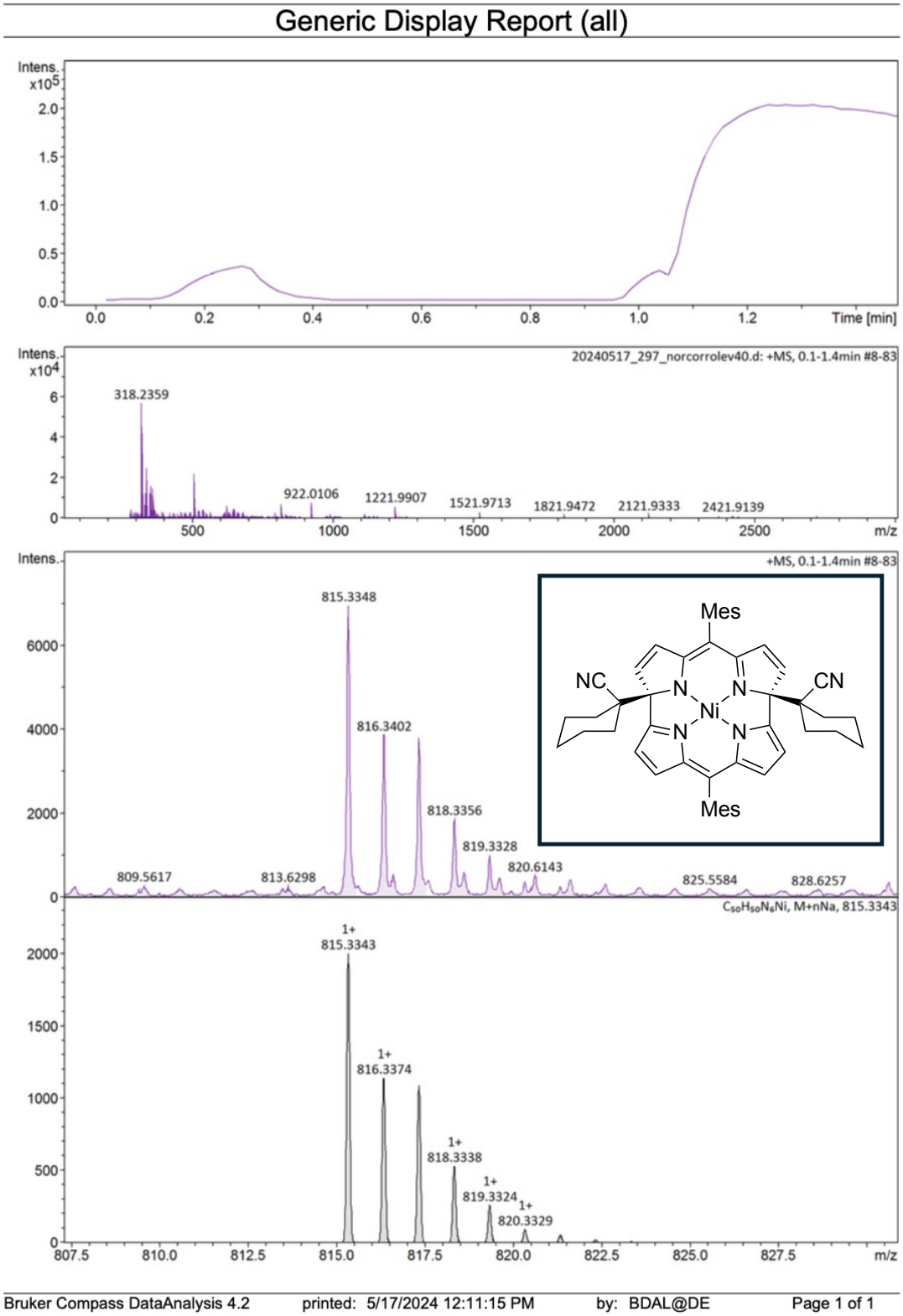


Figure S6. ESI-TOF mass spectrum of **2b**.

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)°, β = 101.917(4)°, V = 3793(2) Å^3, Z = 4, D_{calc} = 1.249 g/cm^3, 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

6. DFT Calculations

Cartesian coordinate of the optimized structures

Isobutyronitrile radical

C	-1.32841100	3.08648100	0.26478700
C	0.15290600	2.95254200	0.46721800
H	-1.72947300	3.99366900	0.72299500
H	-1.56999700	3.10297900	-0.80803400
H	-1.85469400	2.21993900	0.69106400
C	0.86450200	1.75908900	-0.10069700
H	1.93605500	1.77480700	0.11219100
H	0.44256000	0.82932800	0.30806900
H	0.72743000	1.71247200	-1.19093400
C	0.85769700	3.92266800	1.17260600
N	1.45376700	4.74315100	1.76919200

Norcorrole (**1**)

C	0.74868700	2.56943500	0.49147600
C	1.86096300	3.41251400	0.18722600
C	2.99609000	2.59730200	0.17826000
C	2.57314500	1.25511100	0.46876400
N	1.22006700	1.32519300	0.68673700
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H	-4.01024800	2.90702800	-0.02783300
C	2.57201500	-1.25790800	0.46962700
C	2.99375500	-2.60091900	0.18117700
C	1.85779700	-3.41496100	0.19039800

C	0.74618300	-2.57036800	0.49294500
N	1.21870700	-1.32637000	0.68673700
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H	1.82420400	-4.47760000	-0.00971100
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C	-2.99622400	-2.59800300	0.18242100
H	-1.82858400	-4.47582600	-0.00892900
C	-2.57305500	-1.25539800	0.47067100
H	-4.01343600	-2.90418200	-0.02357700
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C	-3.23716800	0.00141400	0.37901200
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C	5.62815600	0.00773200	1.12824700
C	6.50708300	-0.00415700	-1.52825000
C	6.99239700	0.01085700	0.82296200
C	7.45202000	0.00193200	-0.49762500
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H	7.71332800	0.02179100	1.63811000
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C	-5.62769000	0.01361500	1.13050100
C	-5.13344200	-0.00312700	-1.26742100
C	-6.99204900	0.01806600	0.82576200
C	-6.50769600	0.00184300	-1.52564000
C	-7.45221200	0.00922400	-0.49463800
H	-7.71264100	0.02999100	1.64119600
H	-6.84781600	0.00132000	-2.55937600
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H	-4.53459100	-0.85287300	2.78462500
H	-4.53541500	0.90660700	2.77137000

H	-5.99814400	0.02975900	3.26238400
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H	-3.48470200	-0.89087100	-2.35108600
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H	-9.30127200	-1.05314300	-0.86156000
H	-9.51265200	0.48508900	-0.01981200
H	-9.15508600	0.46263700	-1.75647500
C	4.13300300	-0.01210300	-2.40321600
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H	3.47931000	0.86693000	-2.35668400
H	4.63619300	-0.01343100	-3.37480200
C	5.15532800	0.01917800	2.56387300
H	4.53739300	0.90133000	2.76979200
H	4.53489200	-0.85815200	2.78257900
H	5.99948000	0.02295400	3.25998500
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H	9.29980000	-1.06225400	-0.86572200
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Intermediate **I**

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H	1.76272600	4.23975100	-0.06018200
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C	-1.71647800	3.26963900	-0.31633700
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C	-2.93508400	-2.70038000	-0.09679100
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C	6.93106100	0.13238700	-0.22566300
C	6.03549200	-0.25052700	1.96819500
C	7.14584600	-0.03585900	1.14586100
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C	-7.23673700	-0.02609800	1.07278400
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H	-4.72778300	0.81824500	-2.52457300
H	-4.75037900	-0.94116200	-2.53504300
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H	-9.04955600	-1.05088800	1.66130200
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H	3.05704200	-1.47838400	2.17132400
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N	0.07129300	5.72141200	-2.33472600

2a

C	0.69601100	2.73481100	-0.78956600
C	1.67288600	3.40389400	0.15449700
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C	2.33329900	1.23008700	-0.13964100
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C	-3.12630800	0.00033700	0.31765000
Ni	-0.00981800	0.00149100	-0.83308300
C	4.14626400	-0.00483200	1.08859900
C	5.44323900	0.00952600	0.53716800
C	3.98000600	-0.01434000	2.48989100
C	6.55095200	0.01199700	1.39110600
C	5.11159600	-0.01172300	3.31225800
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H	4.98041300	-0.01575800	4.39279300
C	-4.51244700	-0.00027200	0.87505500
C	-4.70341600	-0.00531400	2.27018800
C	-5.61291700	0.00976800	-0.00262800
C	-6.01031800	-0.00151900	2.76715900
C	-6.90216800	0.01317500	0.53789100
C	-7.12197500	0.00456400	1.91884500
H	-6.16285800	-0.00199800	3.84462000
H	-7.75549800	0.02408600	-0.13729800
C	-3.51900400	-0.00998800	3.20964100
H	-2.88724200	-0.89084100	3.04435400
H	-2.88422600	0.86974000	3.04988700
H	-3.84270000	-0.01276200	4.25474200
C	-5.40106800	0.02101800	-1.49925800
H	-4.82992500	0.90368200	-1.81125100
H	-4.82977000	-0.85690800	-1.82408400
H	-6.35488800	0.02479500	-2.03522300
C	-8.52471100	-0.02640300	2.47981000
H	-8.87351500	-1.05935000	2.61231500
H	-8.57660000	0.46218400	3.45883600
H	-9.23524800	0.47335000	1.81252200
C	5.63217500	0.02707600	-0.96281500

H	5.16467400	-0.84630800	-1.43346600
H	5.16182800	0.90939100	-1.41373500
H	6.69353500	0.03205400	-1.23060900
C	2.59409600	-0.02193700	3.09544700
H	2.01428900	0.85367200	2.77926300
H	2.02278900	-0.90222300	2.77676900
H	2.63932600	-0.02354300	4.18904800
C	7.61493900	-0.03403000	3.68774700
H	7.91903100	-1.06700900	3.90436600
H	8.47412700	0.46757600	3.22916600
H	7.41071700	0.45197800	4.64806100
C	0.69147000	3.44929500	-2.22089900
C	2.10961100	3.47494200	-2.83179800
H	2.81830500	4.00656400	-2.19262700
H	2.45640300	2.44618000	-2.96102000
H	2.08698300	3.96695500	-3.80881800
C	-0.27809800	2.73156700	-3.18569200
H	0.02334100	1.68398200	-3.27647400
H	-1.30791300	2.76552600	-2.82326800
H	-0.23822500	3.20204200	-4.17293200
C	0.23207800	4.83398100	-2.00892900
N	-0.12103600	5.92205900	-1.80843100
C	0.68753600	-3.43983600	-2.23813600
C	2.10561100	-3.46407500	-2.84924500
C	-0.28115700	-2.71597500	-3.19921900
H	2.81368500	-3.99988800	-2.21290200
H	2.08230000	-3.95096400	-3.82881300
H	2.45366600	-2.43508300	-2.97312200
H	-1.31096900	-2.75020300	-2.83680600
H	0.02181800	-1.66840400	-3.28492400
H	-0.24211500	-3.18165000	-4.18876600
C	0.22650200	-4.82504600	-2.03327300
N	-0.12784000	-5.91373300	-1.83831300

Selected absorption wavelengths, energies, and oscillator strengths (f) of 2a calculated at the M06/6-31G(d)+SDD//B3LYP-D3/6-31G(d)+SDD level of theory.

Excited State 1: Singlet-A 1.8500 eV 670.17 nm f=0.0026 <S**2>=0.000

169 ->185	0.11936
169 ->188	-0.19458
173 ->188	0.13363
178 ->185	0.15996
178 ->188	-0.22009
183 ->185	0.46660
183 ->188	-0.34879

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -2199.89793617

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1748 eV 570.09 nm f=0.0042 <S**2>=0.000

170 ->185	-0.12632
170 ->188	0.21684
174 ->188	0.13791
181 ->185	-0.38318
181 ->188	0.45789
183 ->184	-0.17508

Excited State 3: Singlet-A 2.1957 eV 564.67 nm f=0.0000 <S**2>=0.000

175 ->185	-0.40637
175 ->188	0.52789
178 ->185	-0.12213
178 ->188	0.16151
175 <-188	-0.10937

Excited State 4: Singlet-A 2.2784 eV 544.17 nm f=0.0054 <S**2>=0.000

181 ->188	0.12892
183 ->184	0.68084

Excited State	5:	Singlet-A	2.5380 eV	488.51 nm	f=0.0001	<S**2>=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	<S**2>=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.