**Electronic Supplementary Material (ESI) for**

# Structurally well-defined conjugated *meso*-aminoporphyrin oligomers analogous to polyanilines

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# 1. Experimental Section

## Generals

5-Amino-10,20-bis[3,5-bis(3-methylbutoxy)phenyl]porphyrin (**1**) was synthesized as a previously reported procedure.[1] All other chemicals were of reagent grades and used without any further purification. $CDCl_3$, $C_2D_2Cl_4$, $CD_2Cl_2$, $CD_3CN$, and $CD_3OD$ were acquired from Acros Organics. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 $F_{254}$ plates. Flash column chromatography was performed using silica gel 60N (spherical, neutral, 40–50 μm). HPLC-GPC was performed by Japan Analytical Industry JAI LC-9204 equipment with JAI-GEL-2.5H columns. All NMR spectral data were recorded on a Bruker AV-500 (500 MHz) spectrometer. These data were collected at ambient temperature (25 °C) unless otherwise noted. Spectra were referenced internally to tetramethylsilane as a standard. ESI-MS data were measured on a Bruker micrOTOF II spectrometer or a Thermo Fisher Scientific Q-Exactive spectrometer. MALDI-MS data were measured on a SHIMADZU AXIMA-PERFORMANCE spectrometer. IR spectral data were recorded on a PerkinElmer Spectrum Two spectrometer equipped with an ATR unit. UV/Vis/NIR spectral data were recorded on a HITACHI U-3500 spectrometer or a Shimadzu UV-3600 spectrometer. Melting points were determined on a Yanaco MP-S3 melting point apparatus. Cyclic voltammetry (CV) measurements were carried out using ALS 650C electrochemical analyser in argon-saturated $CH_2Cl_2$ or butyronitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte at ambient temperature (298 K). A conventional three-electrode cell was used with a glassy carbon working electrode, a platinum wire counter electrode, and an $Ag/Ag^+$ reference electrode. Ferrocene was used as the internal standard in all electrochemical experiments and reported potentials were corrected for $Fc/Fc^+$ couple.

## General procedure for the oxidative oligomerization of 1

A solution of **1** in toluene/AcOH was stirred at 60 °C or 100 °C in an $O_2$ atmosphere. The reaction progress was monitored using TLC. After **1** completely disappeared, the reaction mixture was diluted with toluene. And then, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/toluene = 1:5, then 1:10). The first, and second fractions contained **2(0)**, and **2(1)**, respectively. The latter fraction eluted by $CHCl_3$ contained the higher oligomers, which were further purified by HPLC-GPC (JAI-GEL-2.5H, $CHCl_3$).

**Physical properties of 2(0)**

$^1$H NMR (500 MHz, $CDCl_3$, 323 K) $\delta$ = 13.37 (s, 2H, Qui-NH), 9.86 (s, 1H, Por-$H_{meso}$), 9.11 (d-like, 2×2H, Por-$H_\beta$), 8.97 (d, *J*=4.6 Hz, 2H, Por-$H_\beta$), 8.84 (d, *J*=4.7 Hz, 2H, Por-$H_\beta$), 7.33 (s, 4H), 7.27 (d, *J*=4.5 Hz, 2H, Qui-$H_\beta$), 6.85 (t, *J*=2.3 Hz, 2H), 6.67 (d, *J*=4.5 Hz, 2H, Qui-$H_\beta$), 6.50 (brs, 6H), 4.15 (t, *J*=6.7 Hz, 8H, $OCH_2$), 3.99 (t, *J*=5.4 Hz, 8H, $OCH_2$), 1.86 (m, *J*=6.7 Hz, 4H, CH), 1.75 (q, J=6.7 Hz, 8H, $CH_2$), 1.70 (brs), 1.55 (brs, 8H), 0.97 (d, *J*=6.6 Hz, 24H, $CH_3$), 0.85 (brs, 24H, $CH_3$), −2.08 ppm (s, 2H, Por-NH), several signals for quinoid moiety were not observed because of significant broadening (please see the main text for details); IR (ATR): $\tilde{\nu}$ = 3343, 2954, 2928, 2869, 1585, 1575, 1569, 1564, 1558, 1464, 1429, 1383, 1344, 1237, 1197, 1154, 1048, 991, 922, 811, 795, 731, 693, 563, 466 cm$^{-1}$; UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 426 (5.34), 502 (4.69), 560 (4.43) 661 (3.98), 803 nm (4.04); HRMS(ESI): *m/z* calcd for $C_{104}H_{122}N_9O_9$: 821.4733 ([M+2H]$^{2+}$), found 821.4735; elemental analysis calcd (%) for $C_{104}H_{121}N_9O_9$: C, 76.11; H, 7.43; N, 7.68; found: C, 76.18; H, 7.45; N, 7.71.

**Physical properties of 2(1)**

$^1$H NMR (500 MHz, $CDCl_3$, 323 K) $\delta$ = 13.33 (s, 2H, Qui-NH), 13.26 (s, 2H, Qui-NH), 9.85 (s, 1H, Por-$H_{meso}$), 9.24 (d, *J*=4.7 Hz, 2H, Por-$H_\beta$), 9.12 (d, *J*=4.6 Hz, 2H, Por-$H_\beta$), 9.06 (d, *J*=4.7 Hz, 2H, Por-$H_\beta$), 8.99 (d, *J*=4.7 Hz, 2H, Por-$H_\beta$), 8.96 (d, *J*=4.8 Hz, 2H, Por-$H_\beta$), 8.89 (d, *J*=4.7 Hz, 2H, Por-$H_\beta$), 8.74 (d, *J*=4.8 Hz, 2H, Por-$H_\beta$), 8.71 (d, *J*=4.8 Hz, 2H, Por-$H_\beta$), 7.37 (brs, 4H), 7.33–7.27 (m, 6H), 6.88 (t, *J*=2.3 Hz, 2H), 6.83 (t, *J*=2.3 Hz, 2H), 6.70 (d, *J*=4.5 Hz, 2H, Qui-$H_\beta$), 6.51 – 6.27 (m, 12H), 4.18 (t, *J*=6.7 Hz, 8H, $OCH_2$), 4.14 (t, *J*=6.6 Hz, 8H, $OCH_2$), 3.88 (brs, 8H, $OCH_2$), 3.73 (brs, 8H, $OCH_2$), 1.95 – 1.81 (m, 8H), 1.82 – 1.69 (m, 19H), 1.58 (brs), 1.45 (brs), 0.98 (d, *J*=6.6 Hz, 24H, $CH_3$), 0.95 (d, *J*=6.6 Hz, 24H, $CH_3$), 0.86 (brs, 24H, $CH_3$), 0.75 (d, *J*=6.6 Hz, 24H, $CH_3$), −1.15 (s, 2H, Por$_{inner}$NH), −2.01 ppm (s, 2H, Por$_{end}$-NH), several signals for quinoid moiety were not observed because of significant broadening (please see the main text for details); IR (ATR): $\tilde{\nu}$ = 3334, 2954, 2927, 2869, 1586, 1558, 1464, 1432, 1383, 1345, 1237, 1157, 1112, 1059, 991, 918, 795, 731, 694, 635, 516 cm$^{-1}$; UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 426 (5.49), 508 (5.07), 564 (sh, 4.76) 593 (sh, 4.68), 705 (4.32), 913 nm (4.55); MS(ESI): *m/z* 3280.0 ([M+H]$^+$), 1640.5 ([M+2H]$^{2+}$); elemental analysis calcd (%) for $C_{208}H_{241}N_{19}O_{17}$: C, 76.18; H, 7.41; N, 8.12; found: C, 75.91; H, 7.41; N, 8.01.

**Physical properties of 2(2)**

$^1$H NMR (500 MHz, $CDCl_3$, 323 K) $\delta$ = 13.33 (s, 2H, Qui-NH), 13.31 (s, 2H, Qui-NH), 13.26 (s, 2H, Qui-NH), 9.85 (s, 1H, Por-H$_{meso}$), 9.25 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 9.13 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 9.11 – 9.03 (m, 3×2H, Por-H$_\beta$), 8.99 (d, $J$=4.6 Hz, 2H, Por-H$_\beta$), 8.96 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 8.90 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 8.77 (d, $J$=4.8 Hz, 2×2H, Por-H$_\beta$), 8.75 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 8.72 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 1.01 – 0.93 (m, 72H, $CH_3$), 0.91 – 0.82 (brs, 24H, $CH_3$), 0.77 (m, 48H, $CH_3$), −1.13 (s, 2H, Por$_{inner}$NH), −1.15 (s, 2H, Por$_{inner}$NH), −2.00 ppm (s, 2H, Por$_{end}$-NH), several signals for quinoid moiety were not observed because of significant broadening (please see the main text for details); UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 427 (5.62), 509 (5.28), 591 (4.93) 702 (4.55), 942.5 nm (4.82); MS(ESI): *m/z* 2458.9 ([M+2H]$^{2+}$), 1639.6 ([M+3H]$^{3+}$), 1223.0 ([M+4H]$^{4+}$).

**Physical properties of 2(3)**

$^1$H NMR (500 MHz, $CDCl_3$, 323 K) $\delta$ = 13.33 (s, 2H, Qui-NH), 13.31 (s, 4H, Qui-NH), 13.26 (s, 2H, Qui-NH), 9.85 (s, 1H, Por-H$_{meso}$), 9.25 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 9.12 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 9.11 – 9.04 (m, 5×2H, Por-H$_\beta$), 8.99 (d, $J$=4.6 Hz, 2H, Por-H$_\beta$), 8.96 (d, $J$=4.8 Hz, 2H, Por-H$_\beta$), 8.90 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 8.77 (d, $J$=4.7 Hz, 4×2H, Por-H$_\beta$), 8.75 (d, $J$=4.6 Hz, 2H, Por-H$_\beta$), 8.72 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), −1.14 (m, 6H, Por$_{inner}$NH), −2.00 ppm (s, 2H, Por$_{end}$-NH), several signals for quinoid moiety were not observed because of significant broadening (please see the main text for details); UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 427.5 (5.71), 510 (5.39), 592 (5.06) 703 (4.68), 952 nm (4.96); MS(ESI): *m/z* 3277.9 ([M+2H]$^{2+}$), 2185.6 ([M+3H]$^{3+}$), 1639.5 ([M+4H]$^{4+}$), 1311.8 ([M+5H]$^{5+}$).

**Preparation of Ni-2(0)**

A mixture of **2(0)** (32.76 mg, 0.020 mmol) and $Ni(acac)_2$ (51.32 mg, 0.20 mmol) in toluene (5 mL) was refluxed for 17 h. The reaction mixture was directly poured on top of a silica gel column packed with toluene, and then eluted with toluene. The solvent was removed under reduced pressure to give **2(0)** as a dark brown powder (34.89 mg, 0.020 mmol, quant). An analytically pure product was obtained by the recrystallization from hot toluene–hexane. $^1$H NMR (500 MHz, $CDCl_3$, 0°C) $\delta$ = 9.61 (s, 1H, Por-H$_{meso}$), 9.31 (d, $J$=4.9 Hz, 2H, Por-H$_\beta$), 9.00 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 8.92 (d, $J$=4.9 Hz, 2H, Por-H$_\beta$), 8.86 (d, $J$=4.7 Hz, 2H, Por-H$_\beta$), 7.72 – 7.64 (m, 3H, ArH and Qui-H$_\beta$), 7.04 (d, $J$=4.6 Hz, 1H, Qui-H$_\beta$), 6.99 (d,

*J*=4.4 Hz, 1H, Qui-H$_\beta$), 6.87 (d, *J*=4.4 Hz, 1H, Qui-H$_\beta$), 6.80 (t, *J*=2.2 Hz, 2H, ArH), 6.66 (d, *J*=2.1 Hz, 2H, ArH), 6.62 (t, *J*=2.2 Hz, 1H, ArH), 6.60 (d, *J*=4.4 Hz, 1H, Qui-H$_\beta$), 6.58 (brs, 2H, ArH) 6.41 (d, *J*=4.4 Hz, 1H, Qui-H$_\beta$), 6.25 (t, *J*=2.3 Hz, 1H, ArH), 6.13 (brs, 2H, ArH), 5.49 (d, *J*=4.9 Hz, 1H, Qui-H$_\beta$), 4.21 (t, *J*=7.2 Hz, 4H, $OCH_2$), 4.03 (t, *J*=6.8 Hz, 4H, $OCH_2$), 3.95 (t, *J*=6.8 Hz, 4H, $OCH_2$), 3.72 – 3.64 (m, 5H, Qui-H$_\beta$ and $OCH_2$), 1.96 – 1.71 (m, 14H), 1.68 – 1.54 (m), 1.44 (q, *J*=6.8 Hz, 4H), 1.02 (d, *J*=6.6 Hz, 12H), 1.00 (d, *J*=6.7 Hz, 12H), 0.89 (d, *J*=6.6 Hz, 12H), 0.77 ppm (d, *J*=6.6 Hz, 12H); IR (ATR): $\tilde{\nu}$ = 2953, 2927, 2869, 1587, 1539, 1464, 1432, 1383, 1343, 1322, 1276, 1224, 1157, 1054, 1021, 835, 791, 725, 757, 696, 653, 560, 446, 418 $cm^{-1}$; UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 420 (5.08), 475 (4.77), 539 (4.49) 564 (sh, 4.60), 585 (4.66), 784 (sh, 4.14) 886 nm (4.27); HRMS(ESI): *m/z* calcd for $C_{104}H_{118}N_9O_9Ni_2$: 1754.7728 ($[M+H]^+$); found 1754.7728, calcd for $C_{104}H_{117}N_9O_9Ni_2Na$: 1776.7538 ($[M+Na]^+$); found 1776.7555; elemental analysis calcd (%) for $C_{104}H_{117}N_9O_9Ni_2$: C, 71.20; H, 6.72; N, 7.19; found: C, 71.14; H, 6.68; N, 7.09.

**Preparation of 5,15-dioxo-10,20-bis(3,5-bis(3-methylbutoxy)phenyl)porphodimethene 3**

This compound was synthesized by the modified procedure reported by us.[2] A mixture of 5,15-bis(3,5-bis(3-methylbutoxy)phenyl)porphyrin (80.7 mg, 0.10 mmol) and $PhI(OAc)_2$ (112.7 mg, 0.35 mmol) in acetic acid (10 mL) was stirred at 100 °C for 0.5 h. The resultant solution was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane : toluene = 1:3) to give **3** as a brown solid (72.3 mg, 0.0086 mmol 86%). An analytically pure sample was obtained by recrystallization from EtOAc/MeOH as dark brown crystals (57.1 mg 0.068 mmol, 68%). $^1$H NMR (500 MHz, $CDCl_3$, 50 °C) $\delta$ = 13.96 (s, 2H, Qui-NH), 7.16 (d, *J* = 4.5 Hz, 4H, Qui-H$_\beta$), 6.62 (brs, 4H, Qui-H$_\beta$), 6.58 (d, *J* = 2.2 Hz, 2H), 6.56 (d, *J* = 2.2 Hz, 4H), 4.00 (t, *J* = 6.7 Hz, 8H), 1.83 (m, *J* = 6.7 Hz, 4H), 1.69 (q, *J* = 6.7 Hz, 8H), 0.97 (d, *J* = 6.6 Hz, 24H); UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 402 (sh, 4.62), 414 (4.65), 475 (4.26), 504 nm (4.36); HRMS(ESI): *m/z* calcd for $C_{52}H_{61}N_4O_6$: 837.4586 ($[M+H]^+$); found 837.4567; elemental analysis calcd (%) for $C_{52}H_{60}N_4O_6$: C, 74.61; H, 7.22; N, 6.69; found: C, 74.59; H, 7.24; N, 6.71.

**Preparation of 4b**

A mixture of **2(0)** (65.62 mg, 0.040 mmol), sodium ascorbate (79.24 mg, 0.40 mmol), $K_2CO_3$ (82.94 mg,

0.60 mmol) and 1-iodobutane (88 μL, 0.80 mmol, 20 equiv) in DMF (1 mL) was stirred at 60 °C under $N_2$ for 2.5 h. The reaction mixture was diluted with $CHCl_3$, washed with water (5 × 4 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/EtOAc 15:1) to give **4b** as a purple solid (53.58 mg, 0.031 mmol 79%). An analytically pure sample was obtained by recrystallization from toluene/MeOH as purple crystals (49.10 mg 0.029 mmol, 73%). M.p. 248–250 ºC; $^1$H NMR (500 MHz, $CDCl_3$, 0°C) $\delta$ = 10.71 (s, 1H, NH), 9.75 (s, 1H, Por-H$_{meso}$), 9.35 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$) 9.19 (d, $J$ = 4.5 Hz, Por-H$_\beta$), 9.12 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 9.06 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 8.91 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 8.86 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 8.52 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 8.47 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 7.23 (m, 8H, Ar-H), 6.74 (m, 4H, Ar-H), 4.99 (t, $J$ = 6.6 Hz, 2H, $OCH_2$), 4.03 (m, 16H, $OCH_2$), 2.36 (m, 2H, $CH_2$), 1.95 (m, 2H, CH), 1.78 (m, 8H, CH), 1.66 (m, 16H, $CH_2$), 1.21 (t, $J$ = 7.4 Hz, 3H, $CH_3$), 0.89 (d, $J$ = 6.5 Hz, 48H, $CH_3$), −1.68 (s, 2H, Por-NH), −1.82 (s, 2H, Por-NH); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ = 158.38 (Cq), 158.36 (Cq), 143.32 (Cq), 143.28 (Cq), 137.3 (Cq), 130.5, 127.3, 119.9 (Cq), 119.6 (Cq), 114.20 (CH), 114.17 (CH), 102.3 (CH), 100.8 (CH), 84.2 ($CH_2$), 66.6 ($CH_2$), 38.0 ($CH_2$), 33.2 ($CH_2$), 25.0 (CH), 22.6 ($CH_3$), 19.8 ($CH_2$), 14.2 ($CH_3$) (Several signals were overlapped. Moreover, signals corresponding to the pyrrole α and $\beta$ carbons were not observed due to severe exchange broadening through NH tautomerism); IR (ATR): ν˜ = 3312, 2955, 2929, 2869, 1587, 1464, 1432, 1384, 1339, 1294, 1274, 1245, 1156, 1061, 996, 983, 833, 797, 732, 696, 638, 464 cm$^{-1}$; UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 418 (5.36), 471 (sh, 4.95), 586 (4.33) 606 (4.30), 702 nm (4.45); HRMS(ESI): *m/z* calcd for $C_{108}H_{132}N_9O_9$: 1700.0175 ([M+H]$^+$); found 1700.0168; elemental analysis calcd (%) for $C_{108}H_{131}N_9O_9$: C, 76.34; H, 7.77; N, 7.42; found: C, 76.19; H, 7.69; N, 7.47.

**Reduction of 2(1)**

A mixture of **2(1)** (16.45 mg, 0.0050 mmol), sodium ascorbate (9.93 mg, 0.050 mmol) in DMF (1 mL) was stirred at 40 °C under $N_2$ for 1 h. The reaction mixture was diluted with $CHCl_3$, washed with water (3 × 4 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The NMR spectrum of the resultant product indicated the almost quantitative formation of partially oxidized tetramer **6**, which would be formed by the aerobic oxidation of **5a**. As described in the main text, **6** was gradually oxidized to **2(1)** in the solution.

**Physical properties of 6**

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ = 13.17 (s, 2H, Qui-NH), 10.60 (s, 1H, NH), 10.35 (s, 1H, NH), 9.78 (s, 1H, Por-H$_{meso}$), 9.26 (d, $J$ = 4.8 Hz, 2H, Por-H$_\beta$), 9.15 – 9.07 (m, 4H, Por-H$_\beta$), 9.06 – 8.99 (brs, 4H, Por-H$_\beta$), 8.96 – 8.89 (m, 4H, Por-H$_\beta$), 8.66 (d, $J$ = 4.8 Hz, 2H, Por-H$_\beta$), 8.57 (d, $J$ = 4.8 Hz, 2H, Por-H$_\beta$), 8.49 – 8.32 (m, 6H, Por-H$_\beta$), −0.71 (s, 2H, Por-NH), −0.83 (s, 2H, Por-NH), −1.68 ppm (s, 2H, Por-NH), several signals for quinoid moiety were not observed because of significant broadening (please see the main text for details.

**Acetylation reaction of the reduced products of 2(1)**

A mixture of **2(1)** (16.40 mg, 0.0050 mmol), sodium ascorbate (9.89 mg, 0.050 mmol) in DMF (1 mL) was stirred at 40 °C under $N_2$ for 1 h. The reaction mixture was diluted with $CHCl_3$, washed with water (3 × 4 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant product containing **5a** and **6** was added $CHCl_3$ (1 mL), *N*,*N*-dimethylaminopyridine (2.50 mg, 0.020 mmol, 4 equiv), and acetic anhydride (25 μL, 0.26 mmol, 52 equiv). The resultant solution was stirred at room temperature for 1 h. The reaction mixture was diluted with $CHCl_3$, washed with water (3 × 4 mL) and aq. $NaHCO_3$ (1 × 4 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/$CH_2Cl_2$ 1:5). The desired product **5b** was obtained as a purple solid from the third fractions (5.05 mg, 0.0015 mmol, 30%). The second fractions contained the mixture of **7a** and **7b**, which would be formed by the aerobic oxidation of **5b** during the workup process (8.85 mg, 0.0027 mmol 53%).

**Physical properties of 5b**

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ = 10.57 (s, 1H, NH), 10.48 (s, 1H, NH), 10.35 (s, 1H, NH), 9.76 (s, 1H, Por-H$_{meso}$), 9.24 (d, $J$ = 4.9 Hz, 2H, Por-H$_\beta$), 9.15 (brs, 2H, Por-H$_\beta$), 9.13 – 9.07 (m, 6H, Por-H$_\beta$), 9.05 (brs, 4H, Por-H$_\beta$), 9.00 (d, $J$ = 4.8 Hz, 2H, Por-H$_\beta$), 8.93 (d, $J$ = 4.7 Hz, 2H, Por-H$_\beta$), 8.84 (d, $J$ = 4.9 Hz, 2H, Por-H$_\beta$), 8.55 (d, $J$ = 4.8 Hz, 2H, Por-H$_\beta$), 8.49 (d, $J$ = 4.8 Hz, 2H, Por-H$_\beta$), 8.47 – 8.37 (m, 8H, Por-H$_\beta$), 7.27 (d, $J$ = 2.3 Hz, 4H, Ar-H), 7.23 (d, $J$ = 2.2 Hz, 4H, Ar-H), 7.13 (d-like, 8H, Ar-H), 6.79 – 6.74 (m, 4H, Ar-H), 6.64 – 6.59 (m, 4H, Ar-H), 4.10 – 4.02 (m, 16H, $OCH_2$), 3.97 – 3.90 (m, 16H, $OCH_2$), 2.95 (s, 3H, $CH_3CO$-), 1.85 – 1.76 (m, 8H), 1.74 – 1.64 (m, 24H), 1.60 – 1.54 (m, 16H), 0.91 (d, $J$ = 6.6 Hz, 48H,

$CH_3$), 0.83 – 0.78 (m, 48H, $CH_3$), −0.79 (s, 4H, Por-NH), −1.50 (s, 2H, Por-NH), −1.63 ppm (s, 2H, Por-NH); UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 421 (5.48), 484 (sh, 5.17), 588 (4.49) 633 (sh, 4.50), 758.5 nm (4.75).

**Physical properties of the mixture of 7a and 7b**

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$ = 13.35 (s, 4H, 2×Qui-NH), 10.61 (s, 1H, NH), 10.52 (s, 1H, NH), 9.89 (s, 1H, Por-H$_{meso}$), 9.78 (s, 1H, Por-H$_{meso}$), 9.27 (d, $J$ = 4.7 Hz, Por-H$_\beta$), 9.21 (d, $J$ = 4.7 Hz, Por-H$_\beta$), 9.15 (d, $J$ = 4.7 Hz, Por-H$_\beta$), 9.13 – 9.04 (m, Por-H$_\beta$), 9.01 (d, $J$ = 4.7Hz, Por-H$_\beta$), 8.97 – 8.89 (m, Por-H$_\beta$), 8.89 – 8.82 (m, Por-H$_\beta$), 8.79 – 8.72 (m, Por-H$_\beta$) 2.97 (s, 3H, $CH_3$CO-), 2.96 (s, 3H, $CH_3$CO-), −1.03 (s, 2H, Por-NH), −1.07 (s, 2H, Por-NH), −1.54 (s, 2H, Por-NH), −1.67 (s, 2H, Por-NH), −1.96 (s, 2H, Por-NH), −2.08 (s, 2H, Por-NH), several signals for quinoid moiety were not observed because of significant broadening (please see the main text for details); UV/Vis/NIR (toluene): $\lambda_{max}$ (log$\varepsilon$) = 425 (5.58), 496 (sh, 5.06), 564 (4.69) 604 (sh, 4.58), 718 (4.53), 842 nm (4.45); HRMS(ESI): *m/z* calcd for $C_{210}H_{247}N_{19}O_{18}$: 1662.4526 ($[M+2H]^{2+}$); found 1662.4515.

## 2. Crystallographic data

Single crystals of **Ni-2(0)** suitable for X-ray diffraction study were obtained by slow diffusion of MeOH vapour into a solution of **Ni-2(0)** in butyronitrile. Single-crystal X-ray diffraction data were collected on Rigaku VariMax with Saturn 724+ diffractometer using multilayer mirror monochromated Mo-Kα radiation ($\lambda$ = 0.71075 Å) by the ω scan mode. The crystal was cooled by a stream of cold $N_2$ gas. Collection, indexing, peak integration, cell refinement, and scaling of the diffraction data were performed using the CrystalClear-SM Expert 2.0 r4 software (Rigaku, 2009). The data were corrected for Lorentz and polarization effects, and empirical absorption correction was applied. The structures were solved by the SHELXS[3] program and refined by full-matrix least-squares calculations on $F^2$ (SHELXL2018)[4]. All nonhydrogen atoms were modelled anisotropically. All hydrogen atoms were placed in idealized positions and refined using a riding model [$U_{iso}$(H) = 1.2$U_{eq}$(C)]. The crystallographic data are summarized in Tables S1 and S2. CCDC 2092977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

**Table S1** Crystallographic data for Ni-**2(0)**·(MeOH).

| | | |
|---|---|---|
| Identification code | Ni-2(0) | |
| Empirical formula | C105 H121 N9 Ni2 O10 | |
| Formula weight | 1786.52 | |
| Temperature | 93(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 21.230(13) Å | α= 90°. |
| | b = 28.360(16) Å | β= 105.110(7)°. |
| | c = 16.320(10) Å | γ = 90°. |
| Volume | 9486(10) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.251 $Mg/m^3$ | |
| Absorption coefficient | 0.461 $mm^{-1}$ | |
| F(000) | 3800 | |
| Crystal size | 0.110 x 0.090 x 0.080 $mm^3$ | |
| Theta range for data collection | 3.002 to 25.346°. | |
| Index ranges | -25<=h<=25, -32<=k<=34, -19<=l<=14 | |
| Reflections collected | 51756 | |
| Independent reflections | 17188 [R(int) = 0.1421] | |
| Completeness to theta = 25.242° | 99.6 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 17188 / 173 / 1258 | |
| Goodness-of-fit on $F^2$ | 1.064 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1137, wR2 = 0.2902 | |
| R indices (all data) | R1 = 0.1819, wR2 = 0.3520 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.050 and -0.739 $e.Å^{-3}$ | |

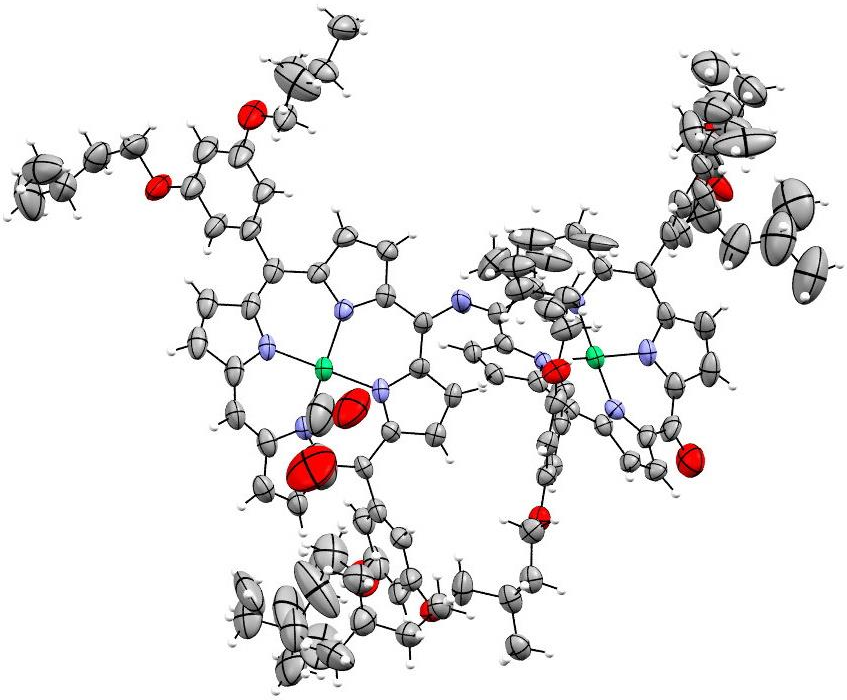

**Fig. S1** ORTEP view (40% probability level) of the asymmetric unit of Ni-**2(0)**·(MeOH) (C = grey, H = white, N = blue, O = red, and Ni = green).

## 3. Additional spectroscopic data

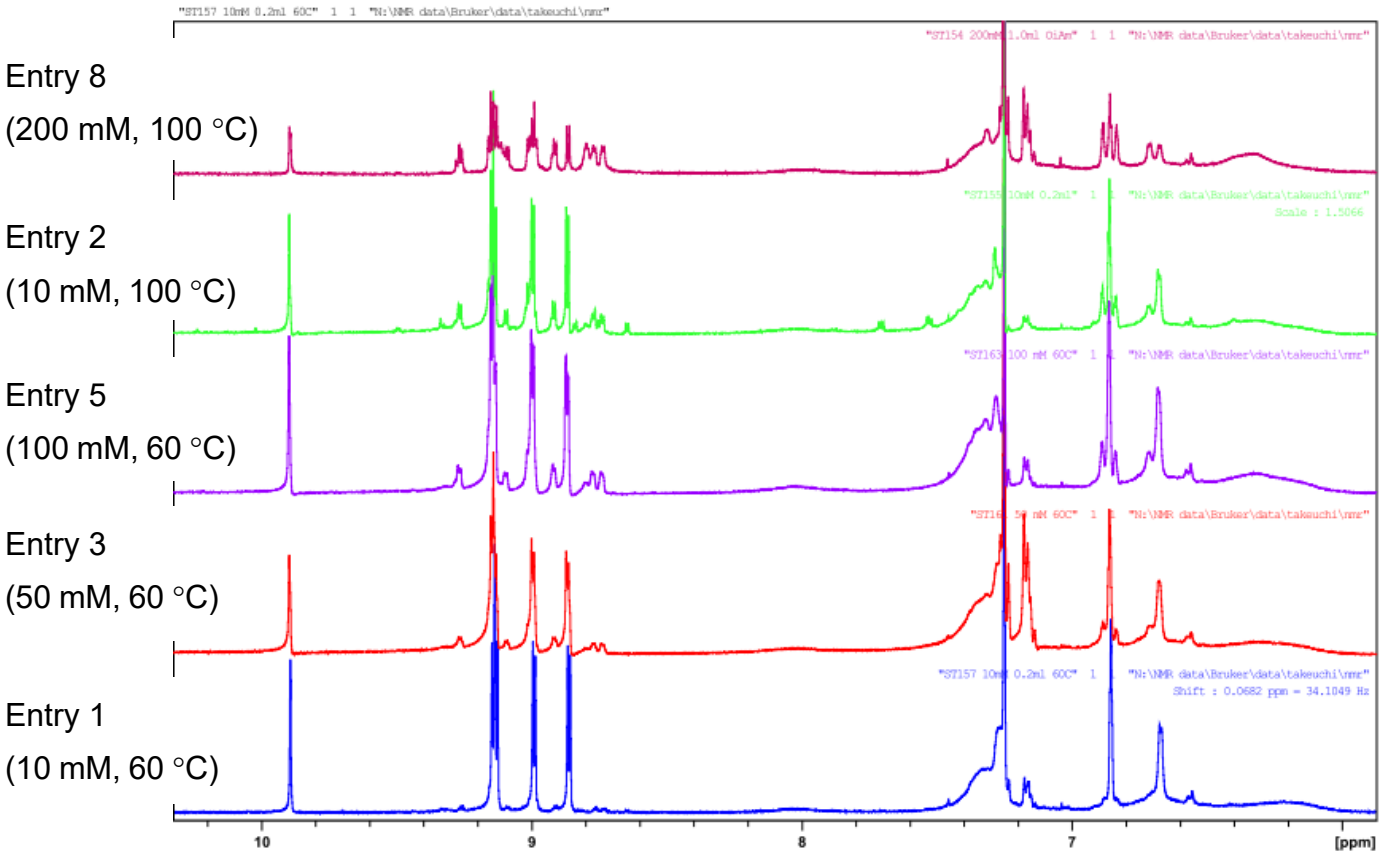


**Fig. S2** $^{1}$H NMR spectra (500 MHz, $CDCl_3$, r.t.) of the crude mixture of **2(n)**.

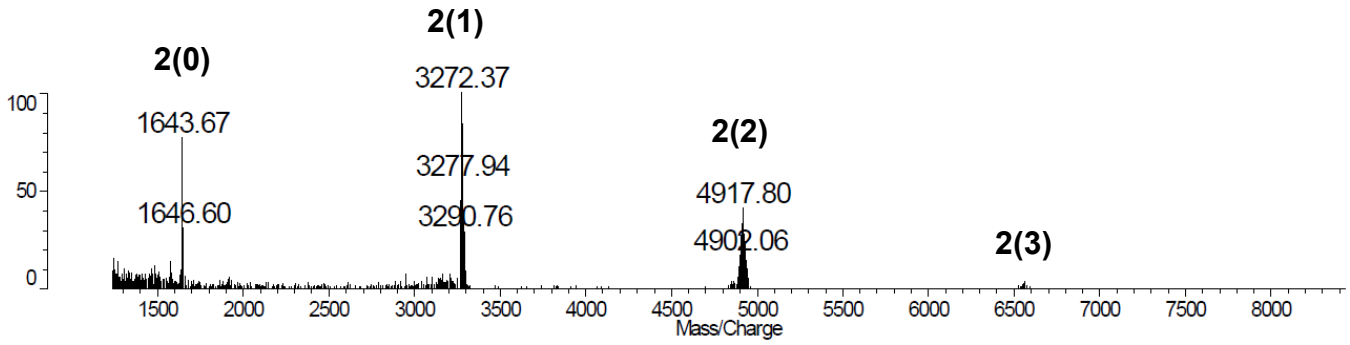


**Fig. S3** MALDI-TOF MS spectrum (matrix: dithranol) of the crude product for the oligomerization of **1** (entry 8 in Table 1).

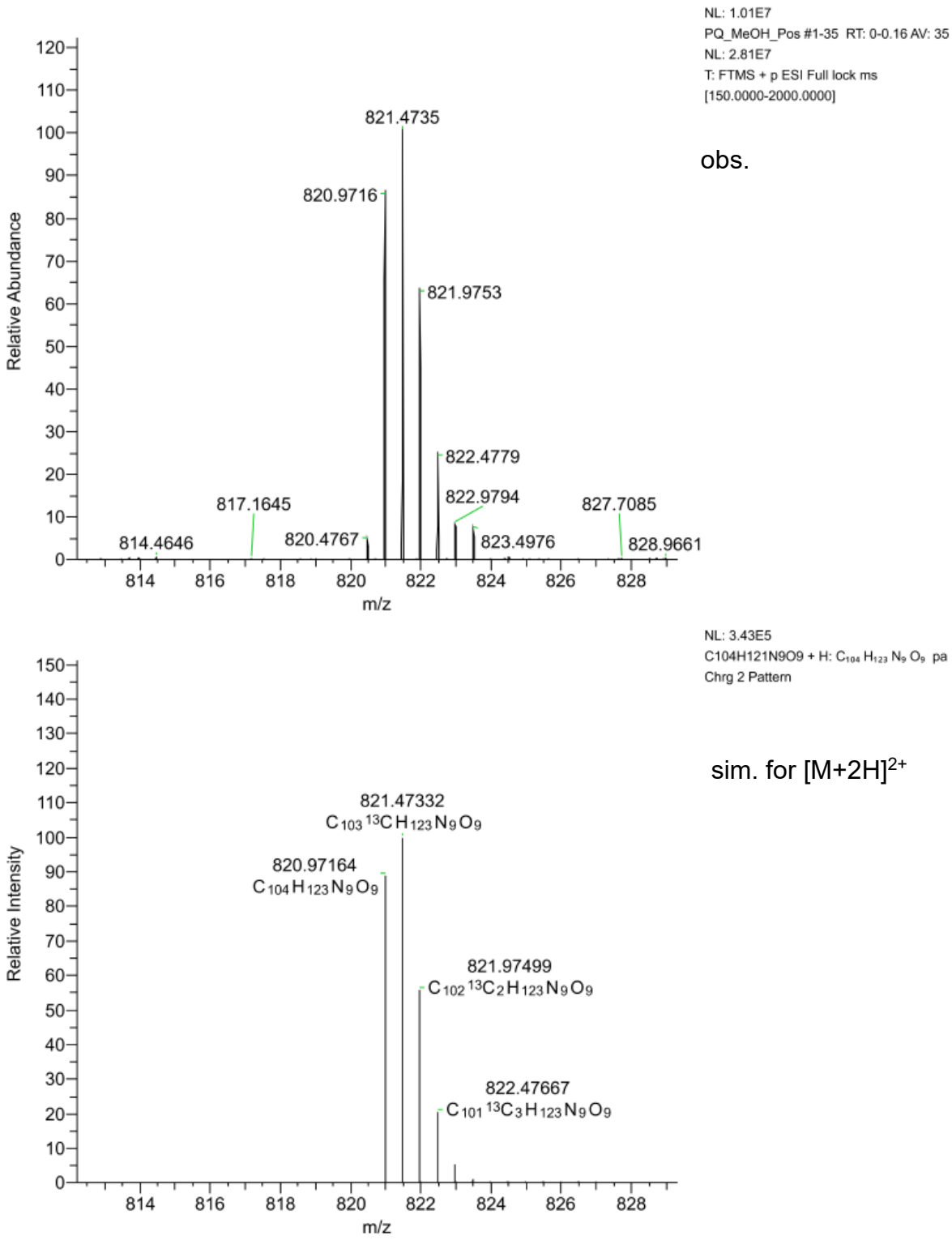


**Fig. S4** HR-ESI MS spectrum of **2(0)**.

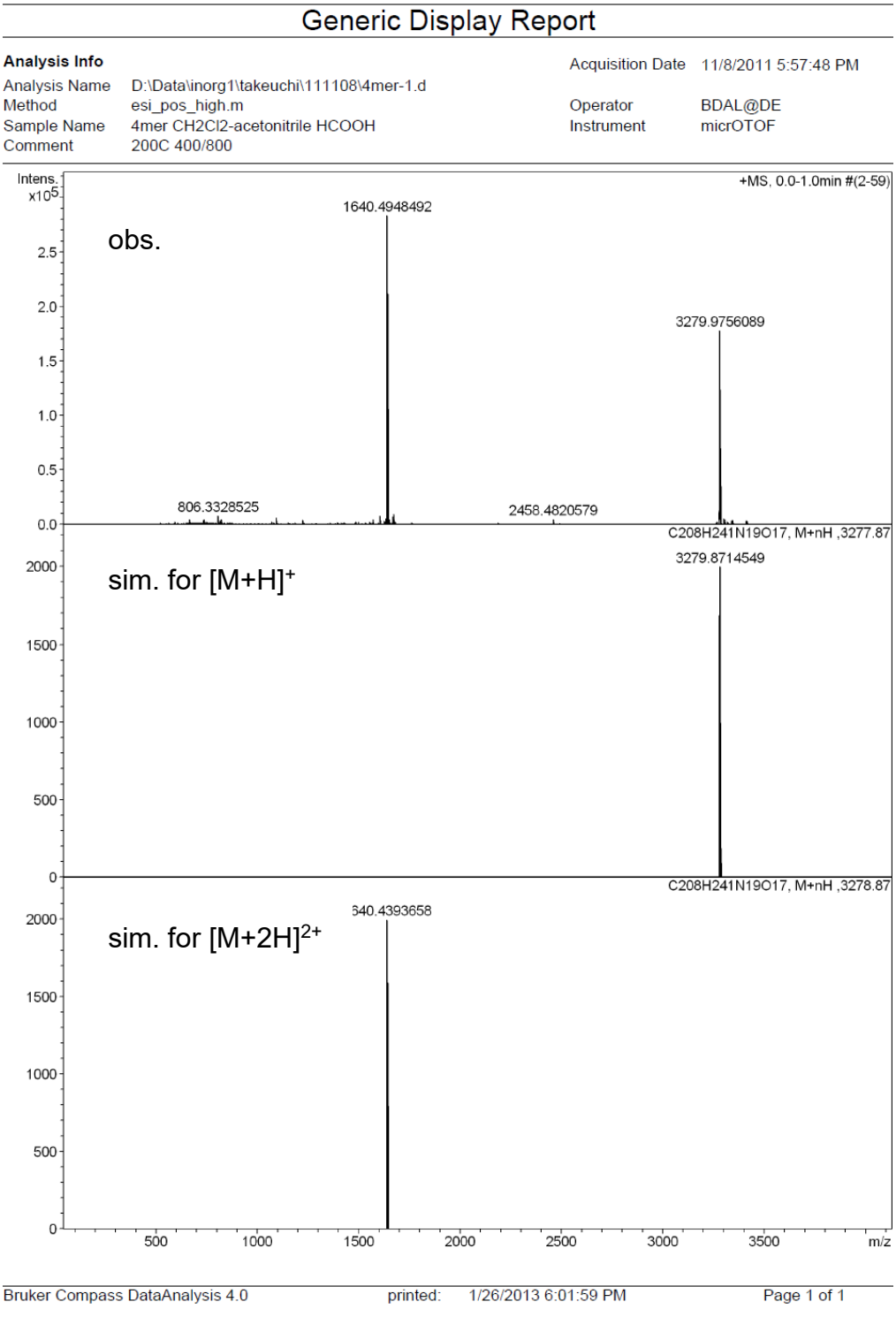


**Fig. S5** ESI MS spectrum of **2(1)**.

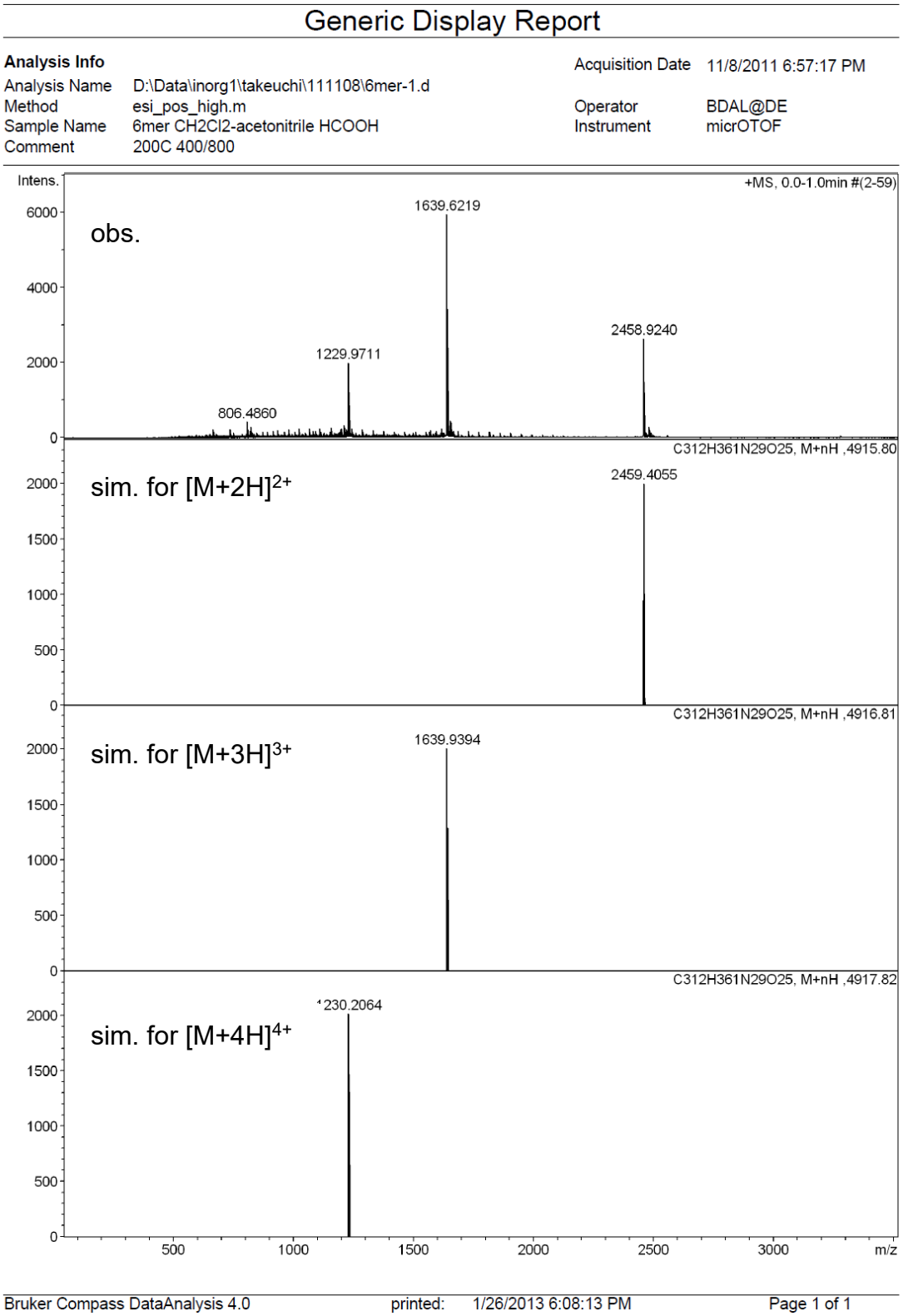


**Fig. S6** ESI MS spectrum of **2(2)**.

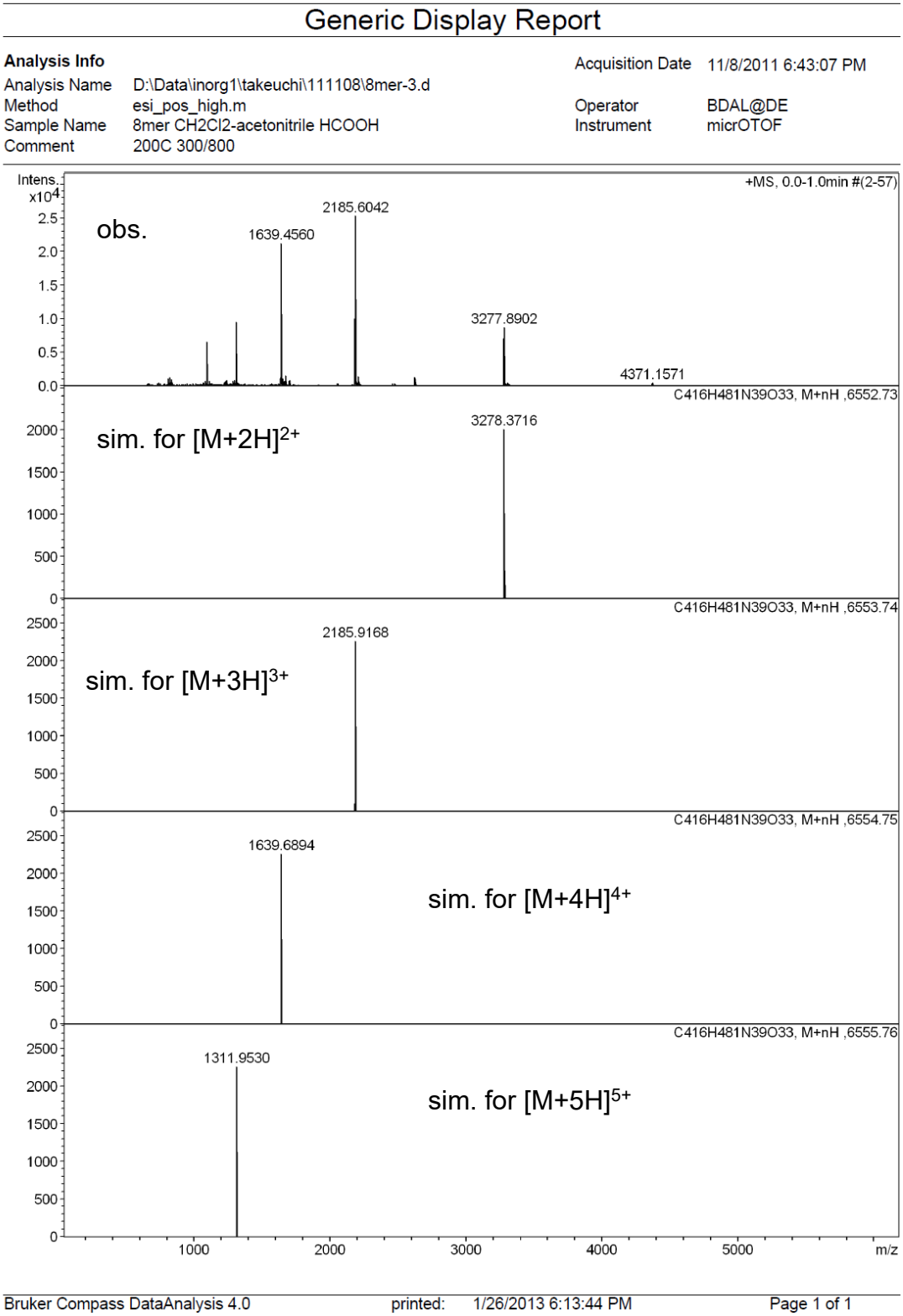


**Fig. S7** ESI MS spectrum of **2(3)**.

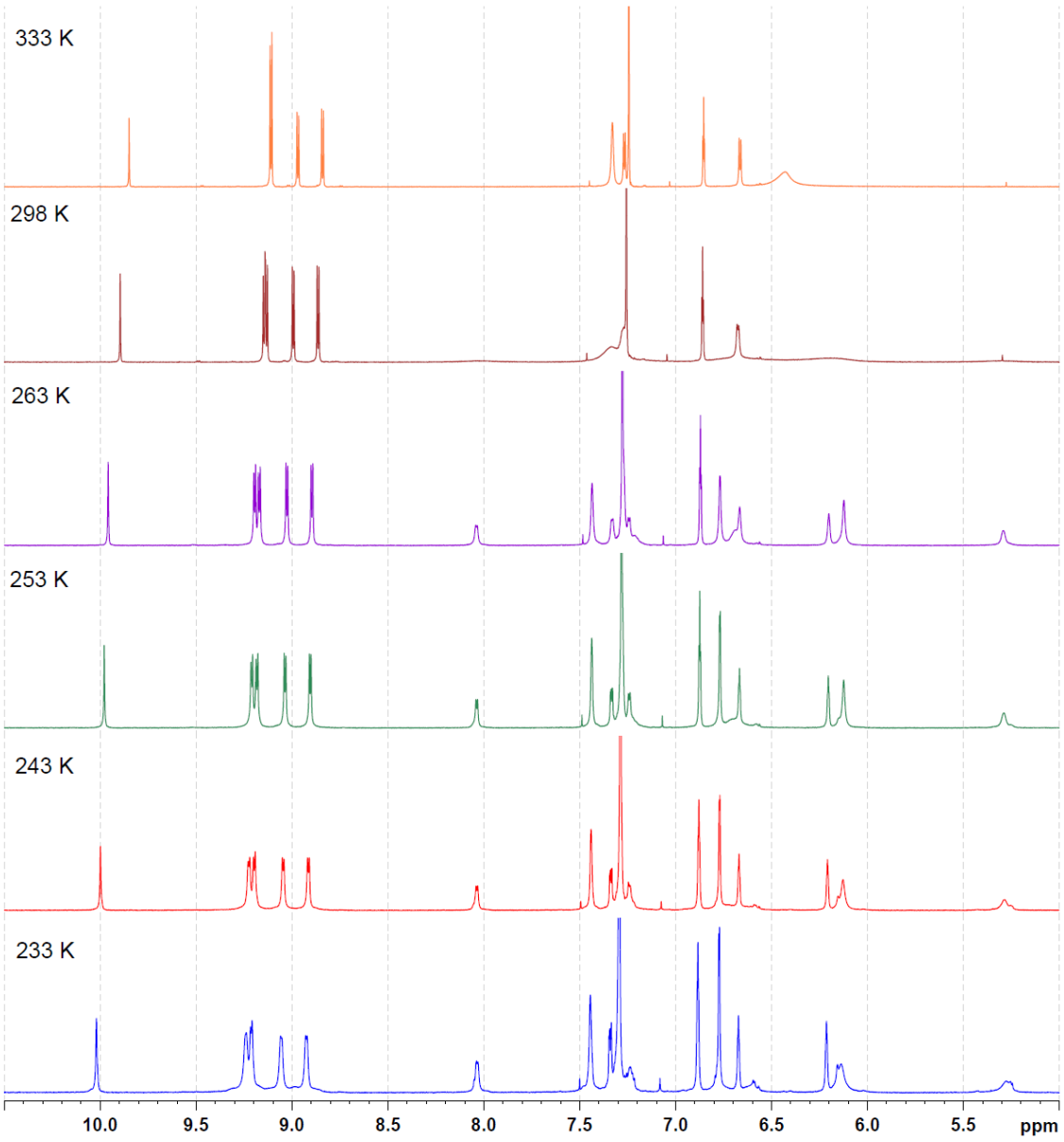


**Fig. S8** $^{1}$H VT NMR spectra (500 MHz, $CDCl_3$) of **2(0)**.

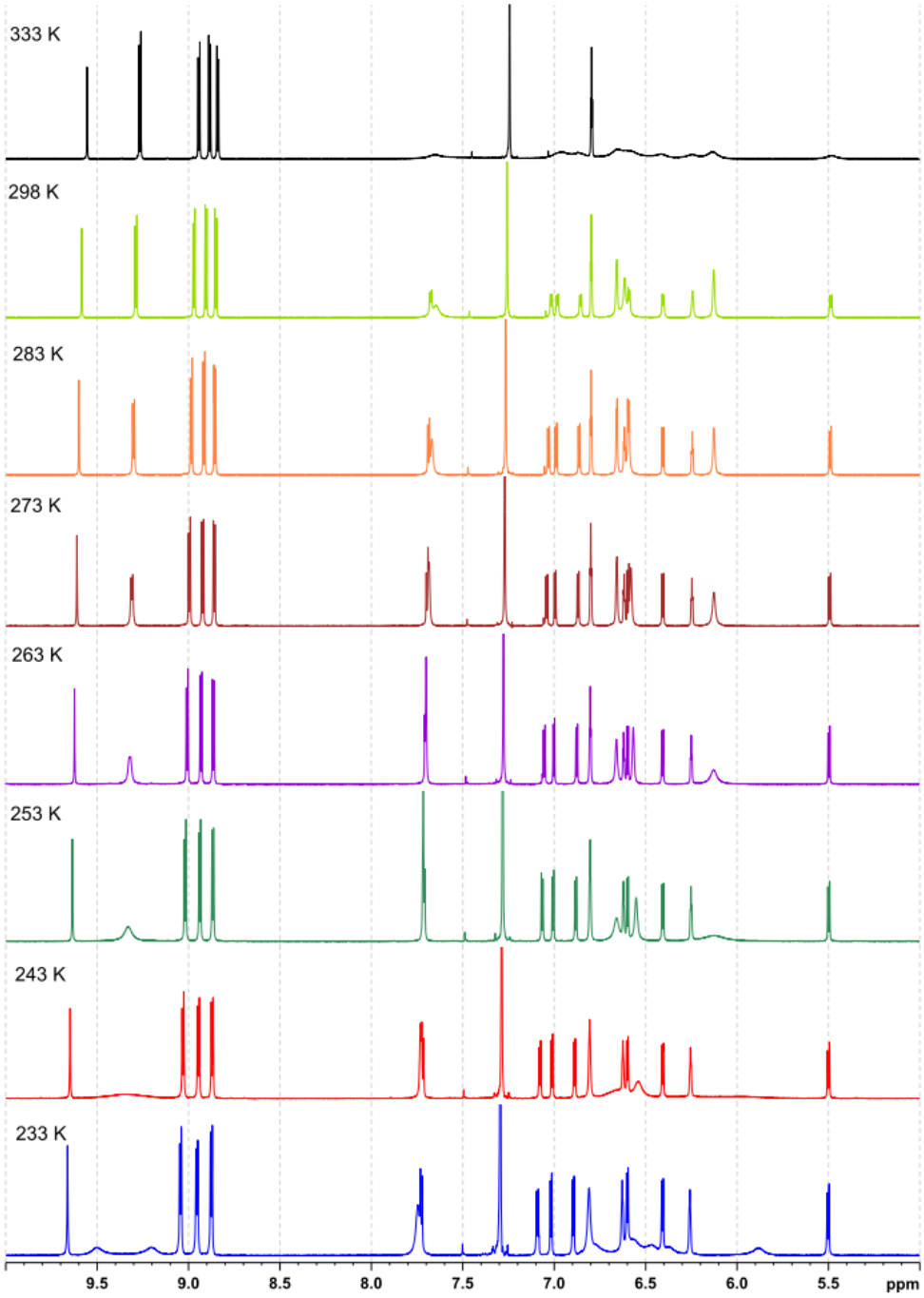


**Fig. S9** $^{1}$H VT NMR spectra (500 MHz, $CDCl_3$) of **Ni-2(0)**.

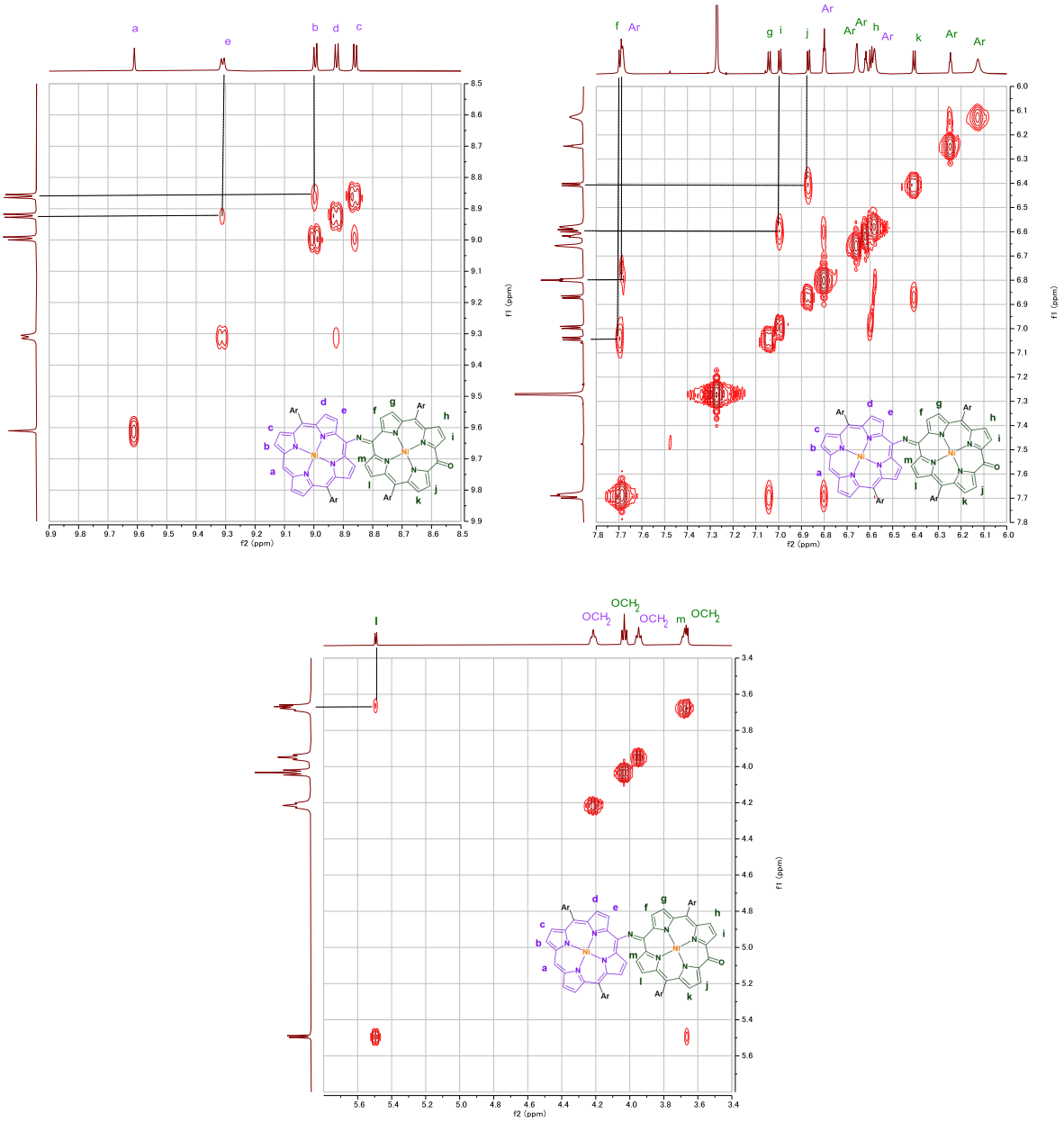


**Fig. S10** $^{1}$H COSY NMR spectra (500 MHz, $CDCl_3$, 273 K) of **Ni-2(0)**.

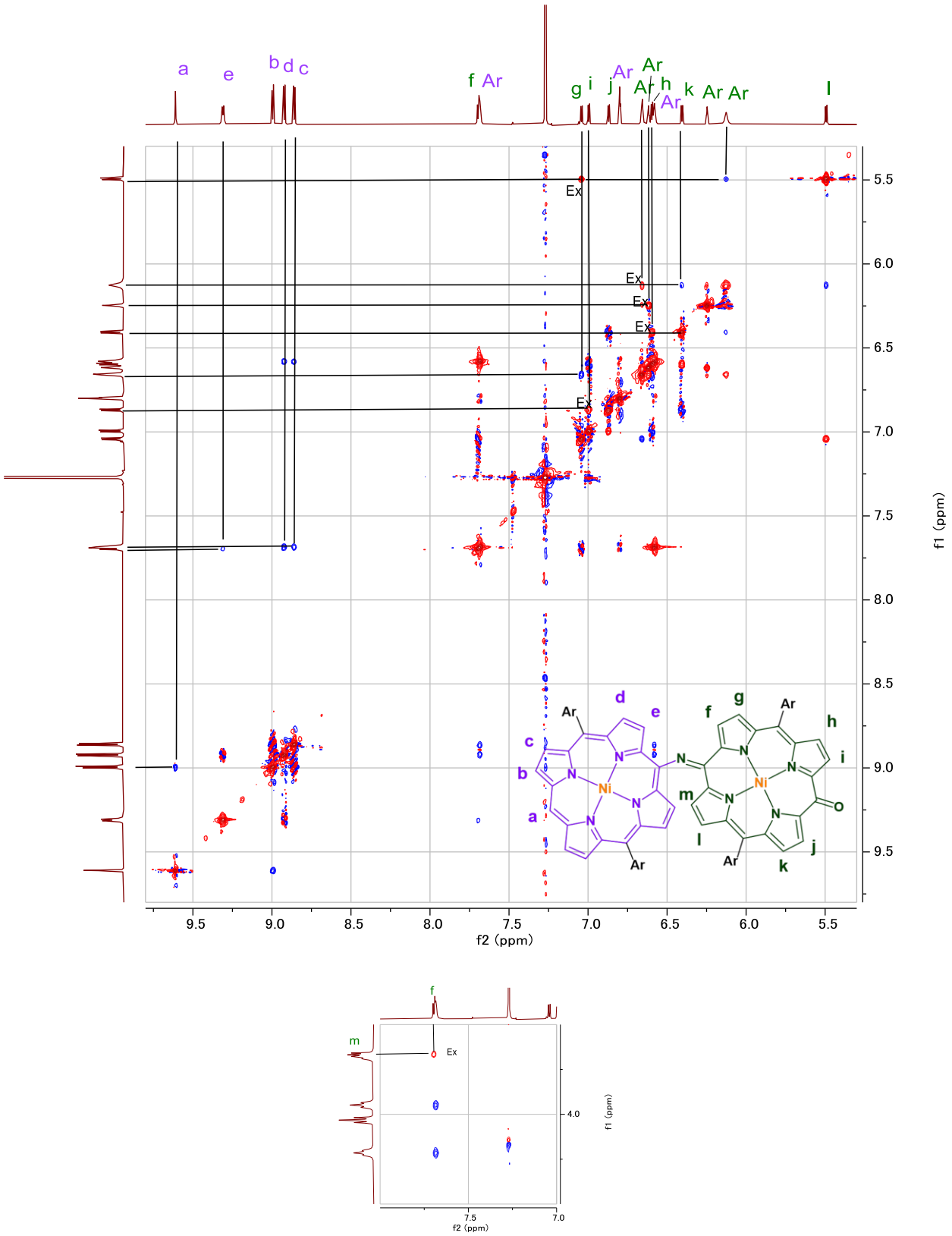


**Fig. S11** $^{1}$H ROESY NMR spectra (500 MHz, $CDCl_3$, 273 K) of **Ni-2(0)**.

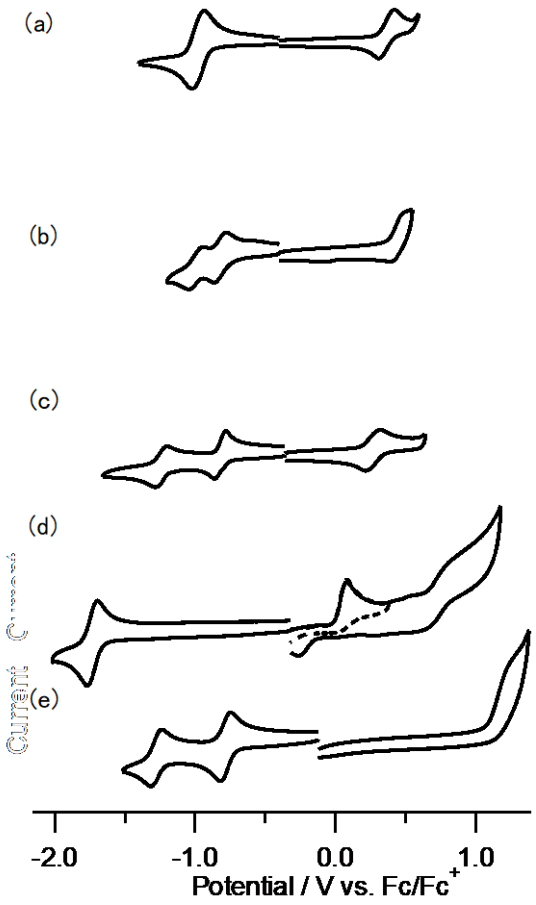


**Fig. S12** Cyclic voltammograms of (a) **2(0)**, (b) **Ni-2(0)**, (c) **2(1)**, (d) **1**, and (e) **3**. Solvent: $CH_2Cl_2$ containing 0.1 M $^{n}Bu_4NPF_6$ (for **2(0)**, **Ni-2(0)**, and **2(1)**), or butyronitrile containing 0.1 M $^{n}Bu_4NPF_6$ (for **1** and **3**).

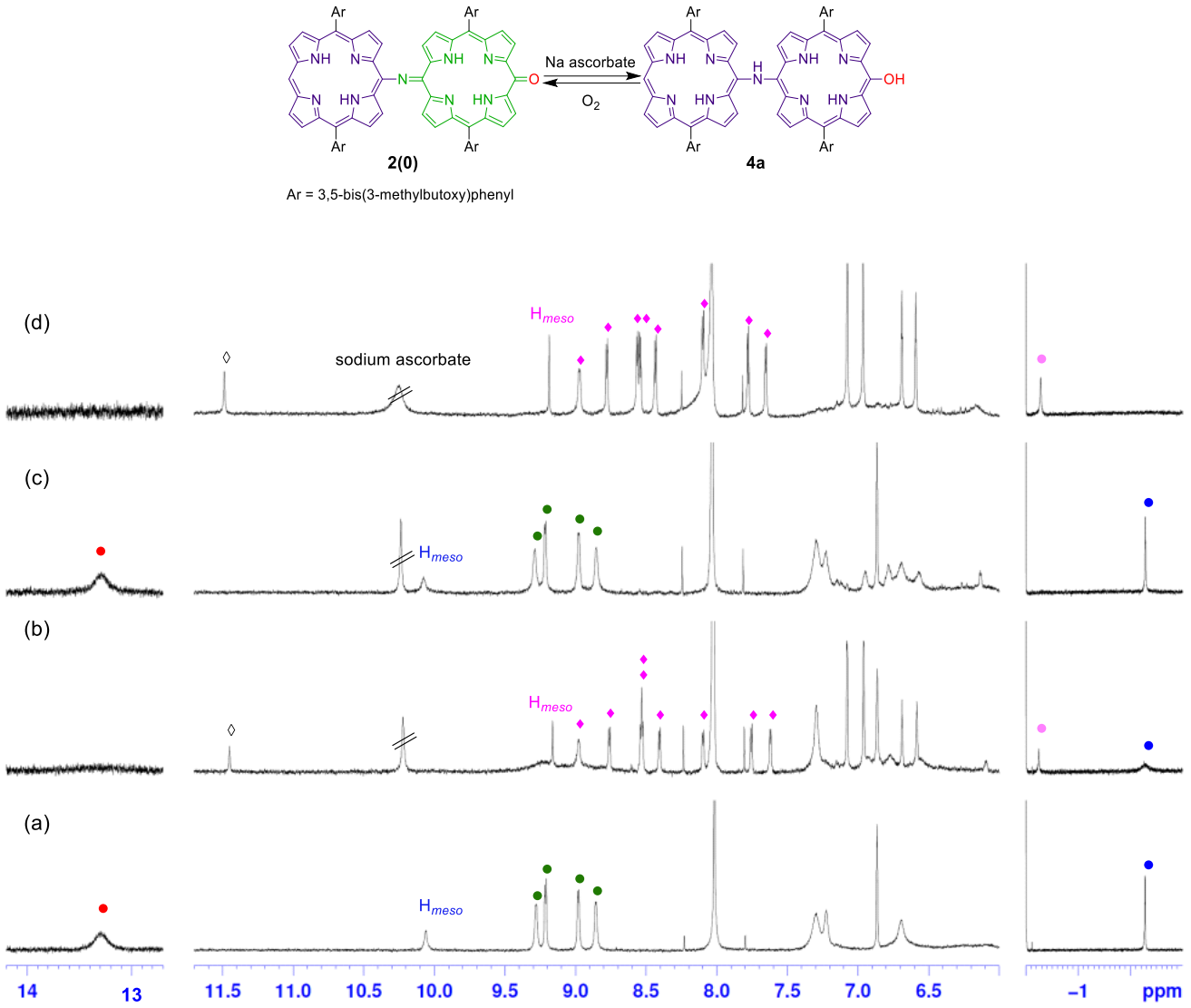


**Fig. S13** $^{1}$H NMR spectra (500 MHz, $CDCl_3$–DMSO-$d_6$) showing reversible redox interconversion between **2(0)** and **4a**. (a) Before the addition of sodium ascorbate, (b) after the addition of sodium ascorbate, (c) after 4 h under air, and (d) second addition of sodium ascorbate.

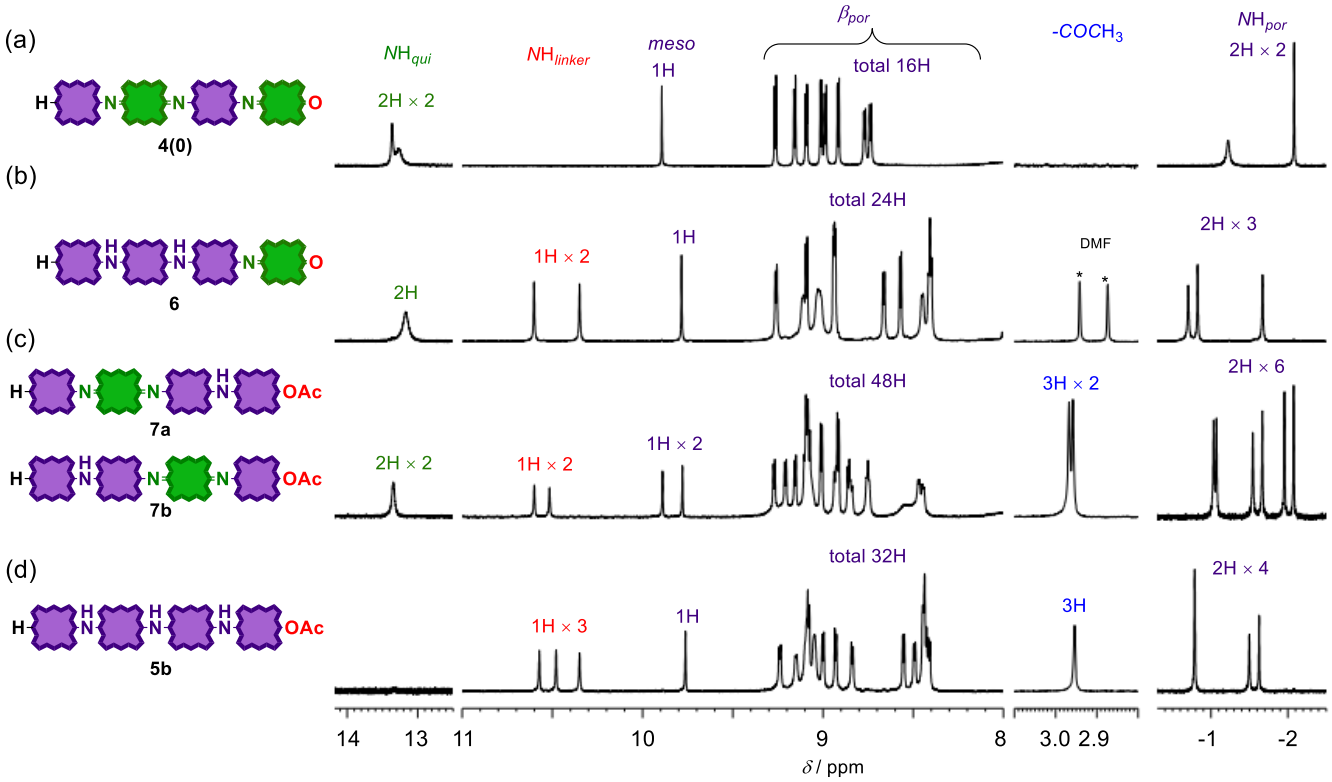


**Fig. S14** $^{1}$H NMR spectra (500 MHz, $CDCl_3$, 300 K) of (a) **4(0)**, (b) **6**, (c) an equilibrium mixture of **7a** and **7b**, and (d) **5b**.

## 4. 1D $^{1}$H EXSY measurements for partially reduced tetramers 7

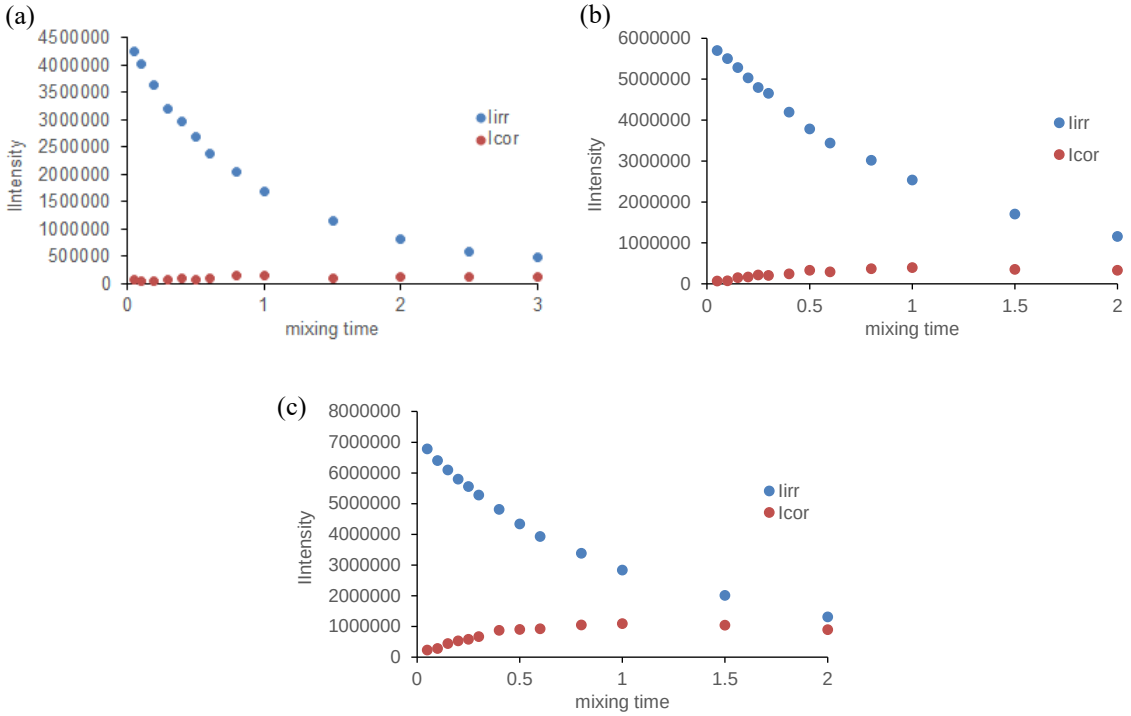


**Fig. S15** Plots of the intensity of irradiated and correlated peaks against the mixing time at (a) 278, (b) 298, and (c) 318 K.

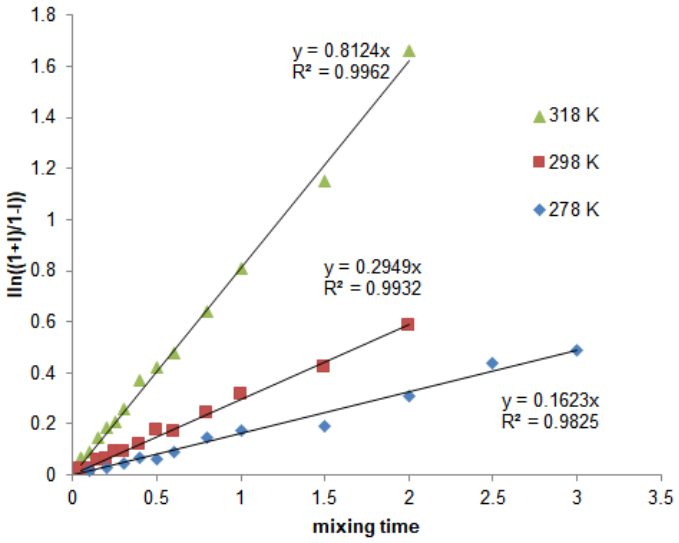


**Fig. S16** Plots of the EXSY results to determine exchange rate constants.

**Table S2** Exchange rate constants determined by EXSY measurements.

| $T$ (K) | $2k$ ($s^{-1}$) |
|---|---|
| 278 | 0.1624±0.0004 |
| 298 | 0.2949±0.0005 |
| 318 | 0.8124±0.0010 |

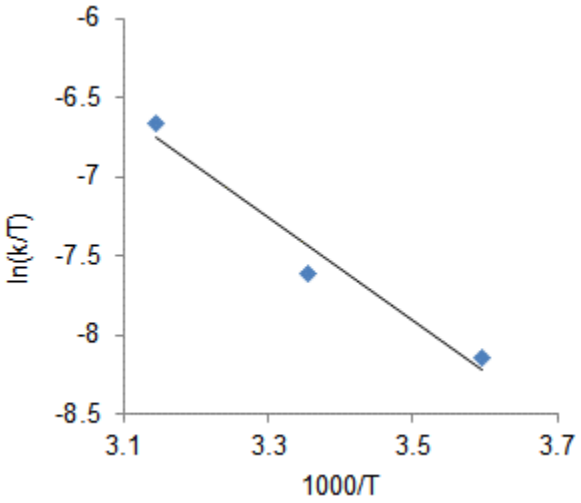


**Fig. S17** Eyring plot.

## 4. DFT calculations

All calculations were carried out using the Gaussian 16 program package (Revision C.01).[5] Geometries of **2′(0)** and **2′(1)** were optimized by the DFT method at the B3LYP-D3/6-31G(d,p) level while that of the cation radical of **1′** (**1**$^{\bullet+}$) was optimized at the UB3LYP-D3/6-31+G(d,p) level. To confirm that the optimized geometries were not in the saddle in stable points, frequency calculations were performed. TDDFT calculations of **2′(0)** and **2′(1)** were performed at the same level using the geometry-optimized models.

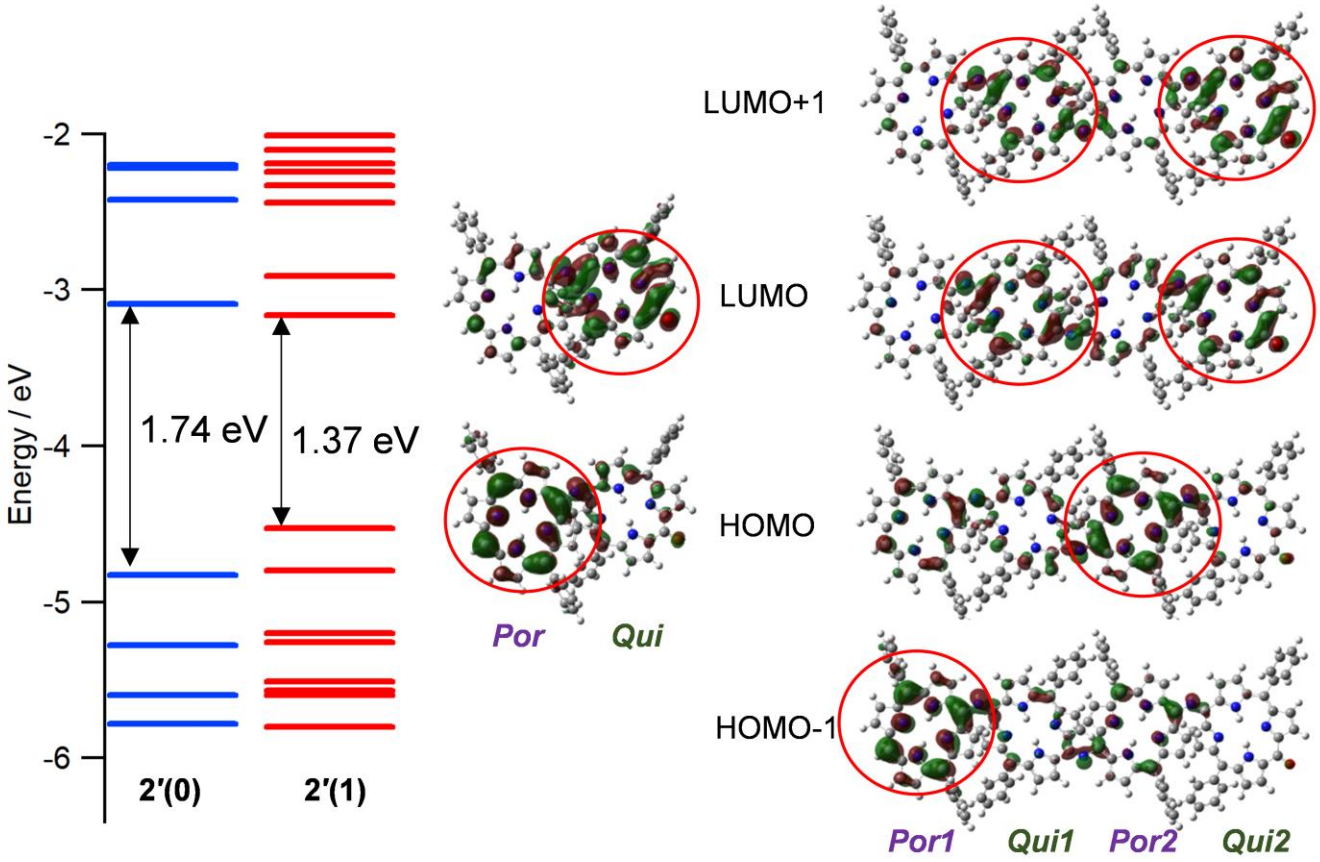


**Fig. S18** Frontier orbitals and energy diagrams of **2′(0)** and **2′(1)** (B3LYP-D3/6-31G(d,p)).

**Table S3.** Summary of the TDDFT calculation of **2′(0)**.

| No. | Energy ($cm^{-1}$) | Wavelength (nm) | Osc. Strength | Major contribution |
|---|---|---|---|---|
| 1 | 12109.61 | 825.7905 | 0.4233 | HOMO->LUMO (97%) |
| 2 | 14209.07 | 703.7759 | 0.0085 | H-1->LUMO (83%) |
| 3 | 15860.89 | 630.4815 | 0.0139 | H-2->LUMO (71%), HOMO->L+1 (23%) |
| 4 | 16826.34 | 594.3064 | 0.0766 | H-2->LUMO (19%), H-1->LUMO (10%), HOMO->L+1 (55%) |
| 5 | 17753.88 | 563.2573 | 0.0197 | H-3->LUMO (11%), HOMO->L+2 (71%) |
| 6 | 18188.61 | 549.7947 | 0.0417 | H-1->L+2 (14%), HOMO->L+3 (64%) |
| 7 | 19453.29 | 514.052 | 0.0875 | H-3->LUMO (65%), H-2->L+1 (11%), H-1->L+3 (12%) |
| 8 | 21039.78 | 475.2902 | 0.4085 | H-1->L+1 (68%), H-1->L+2 (11%) |
| 9 | 21612.43 | 462.6966 | 0.0005 | H-5->LUMO (12%), H-4->LUMO (83%) |
| 10 | 22083.46 | 452.8276 | 0.0077 | H-9->LUMO (77%) |
| 11 | 22573.04 | 443.0064 | 0.3026 | H-2->L+1 (48%), H-1->L+3 (26%) |
| 12 | 22898.89 | 436.7025 | 0.1415 | H-6->LUMO (10%), H-3->L+1 (20%), H-2->L+2 (12%), H-1->L+2 (29%) |
| 13 | 23064.23 | 433.5718 | 0.0161 | H-6->LUMO (75%) |
| 14 | 23627.21 | 423.2409 | 0.0305 | H-7->LUMO (55%), H-5->LUMO (18%) |
| 15 | 23754.64 | 420.9704 | 0.0124 | H-7->LUMO (35%), H-5->LUMO (37%) |
| 16 | 23794.97 | 420.2569 | 0.0338 | H-3->L+1 (46%), H-2->L+2 (26%) |
| 17 | 24299.87 | 411.5248 | 0.1021 | H-5->LUMO (10%), H-2->L+3 (51%), HOMO->L+4 (15%) |
| 18 | 25101.59 | 398.3812 | 0.0866 | H-8->LUMO (40%), H-3->L+2 (23%), H-2->L+3 (10%) |
| 19 | 25190.31 | 396.9781 | 0.0307 | H-3->L+2 (15%), H-3->L+3 (33%), HOMO->L+4 (38%) |
| 20 | 25365.33 | 394.2389 | 0.1439 | H-8->LUMO (24%), H-3->L+3 (19%), H-2->L+2 (20%), HOMO->L+4 (11%) |
| 21 | 26063 | 383.6857 | 0.3373 | H-5->L+1 (10%), H-4->L+1 (14%), H-3->L+2 (20%), H-3->L+3 (14%) |
| 22 | 26582.42 | 376.1885 | 0.1608 | H-4->L+1 (54%) |
| 23 | 26724.37 | 374.1902 | 0.2218 | H-13->LUMO (11%), H-12->LUMO (18%), H-10->LUMO (13%), H-3->L+3 (12%) |
| 24 | 26897.78 | 371.7778 | 0.1153 | H-12->LUMO (11%), H-11->LUMO (39%), H-10->LUMO (23%) |
| 25 | 26970.37 | 370.7772 | 0.0944 | H-11->LUMO (27%), H-10->LUMO (46%) |
| 26 | 27214.76 | 367.4477 | 0.1348 | H-15->LUMO (26%) |
| 27 | 27370.42 | 365.3579 | 0.0435 | H-12->LUMO (21%), H-5->L+1 (14%) |
| 28 | 27819.68 | 359.4578 | 0.2418 | H-15->LUMO (12%), H-14->LUMO (30%) |
| 29 | 28183.43 | 354.8184 | 0.0657 | H-15->LUMO (13%), H-14->LUMO (15%), H-5->L+1 (21%), H-4->L+3 (11%) |
| 30 | 28386.68 | 352.2779 | 0.0105 | H-13->LUMO (30%), H-12->LUMO (16%), H-4->L+3 (10%) |

| | | | | |
|---|---|---|---|---|
| 31 | 28419.75 | 351.868 | 0.0451 | H-17->LUMO (67%), H-16->LUMO (17%) |
| 32 | 28494.76 | 350.9417 | 0.004 | H-15->LUMO (12%), H-14->LUMO (21%), H-13->LUMO (18%) |
| 33 | 28604.45 | 349.5959 | 0.1157 | H-5->L+1 (15%), H-5->L+3 (11%), H-4->L+3 (31%) |
| 34 | 28776.25 | 347.5088 | 0.0128 | H-16->LUMO (39%), H-13->LUMO (10%), H-4->L+2 (21%) |
| 35 | 28932.72 | 345.6294 | 0.003 | H-6->L+1 (66%), H-6->L+3 (10%) |
| 36 | 29071.45 | 343.9801 | 0.1552 | H-4->L+2 (25%) |
| 37 | 29139.2 | 343.1803 | 0.0117 | H-21->LUMO (10%), H-18->LUMO (58%) |
| 38 | 29235.98 | 342.0442 | 0.0068 | H-19->LUMO (68%) |
| 39 | 29373.91 | 340.4382 | 0.1799 | H-7->L+1 (32%), H-1->L+4 (27%) |
| 40 | 29433.59 | 339.7479 | 0.2136 | H-21->LUMO (17%), H-7->L+1 (24%), H-1->L+4 (27%) |

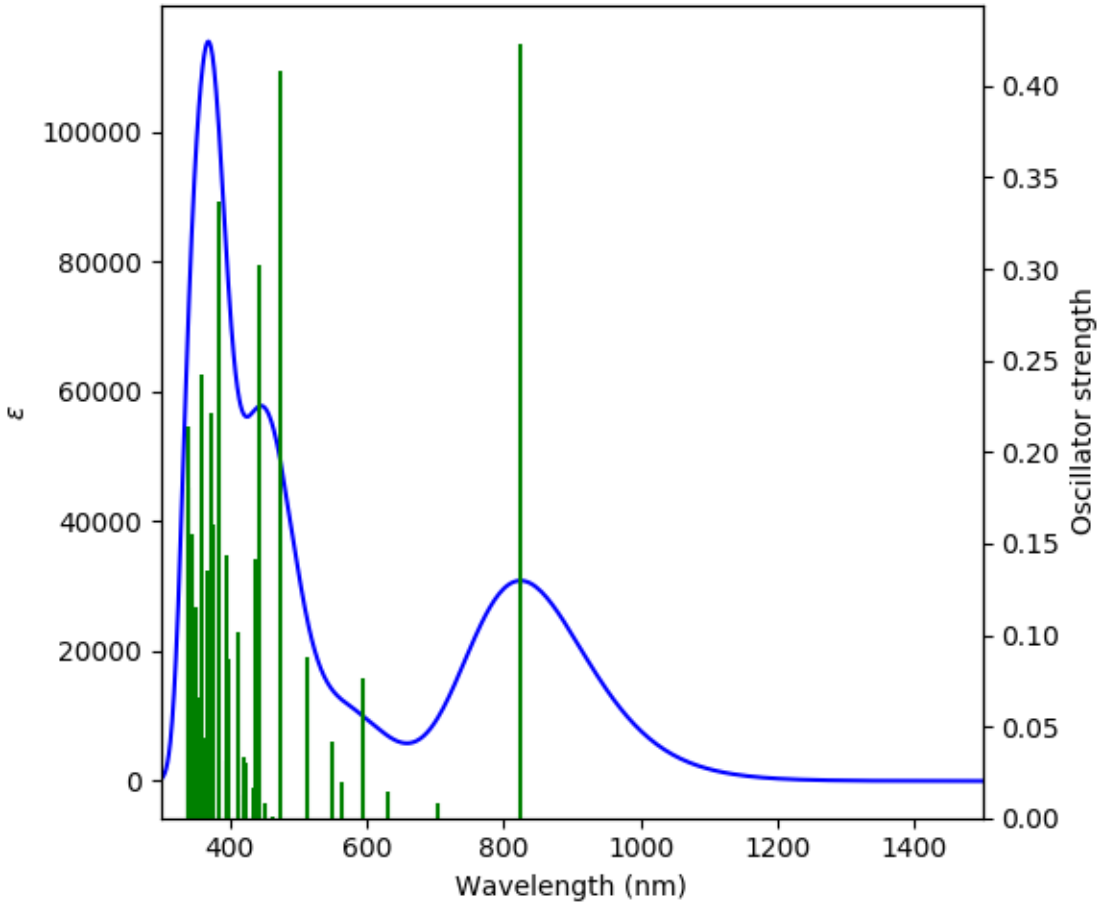


**Fig. S19** Calculated (TDDFT) UV/vis/NIR absorption spectrum of **2′(0)**.

**Table S4.** Summary of the TDDFT calculation of **2′(1)**.

| No. | Energy ($cm^{-1}$) | Wavelength (nm) | Osc. Strength | Major contribution |
|---|---|---|---|---|
| 1 | 9349.579 | 1069.567 | 1.8069 | HOMO->LUMO (98%) |
| 2 | 11230.46 | 890.4352 | 0.0002 | H-1->LUMO (31%), HOMO->L+1 (64%) |
| 3 | 11714.4 | 853.6505 | 0.0103 | H-1->LUMO (62%), HOMO->L+1 (32%) |
| 4 | 13211.36 | 756.9243 | 0.0072 | H-3->LUMO (13%), H-2->LUMO (53%), HOMO->L+2 (23%) |
| 5 | 13499.3 | 740.7791 | 0.0845 | H-1->L+1 (87%) |
| 6 | 14013.08 | 713.6192 | 0.0254 | H-3->LUMO (48%), H-2->LUMO (14%), H-2->L+1 (13%) |
| 7 | 14471.2 | 691.0277 | 0.0068 | H-2->LUMO (12%), HOMO->L+2 (60%) |
| 8 | 15085.79 | 662.8753 | 0.0131 | H-4->LUMO (36%), H-3->L+1 (21%), H-2->L+1 (11%), HOMO->L+3 (12%) |
| 9 | 15481.01 | 645.9529 | 0.048 | H-3->LUMO (13%), HOMO->L+3 (51%), HOMO->L+5 (10%) |
| 10 | 16014.94 | 624.4168 | 0.0125 | H-6->LUMO (35%), H-4->L+1 (12%), HOMO->L+6 (11%) |
| 11 | 16110.92 | 620.6968 | 0.0071 | H-6->LUMO (11%), H-4->LUMO (20%), H-2->L+1 (28%) |
| 12 | 16267.4 | 614.7265 | 0.0074 | HOMO->L+4 (73%) |
| 13 | 16516.62 | 605.4507 | 0.0615 | H-4->LUMO (14%), H-3->LUMO (10%), H-3->L+1 (12%), HOMO->L+5 (27%) |
| 14 | 16798.11 | 595.3051 | 0.0803 | H-1->L+2 (65%) |
| 15 | 16953.77 | 589.8392 | 0.0143 | H-3->L+1 (22%), H-2->L+1 (16%), HOMO->L+5 (18%), HOMO->L+6 (10%) |
| 16 | 17365.12 | 575.8671 | 0.047 | H-5->LUMO (53%) |
| 17 | 17473.2 | 572.3052 | 0.0021 | H-6->LUMO (10%), H-3->L+1 (13%), HOMO->L+6 (50%) |
| 18 | 17739.36 | 563.7183 | 0.0624 | H-5->LUMO (16%), HOMO->L+7 (37%) |
| 19 | 18059.56 | 553.7233 | 0.0038 | H-1->L+2 (10%), H-1->L+3 (62%) |
| 20 | 18417.67 | 542.9568 | 0.0067 | H-1->L+4 (46%), H-1->L+5 (13%), HOMO->L+7 (22%) |
| 21 | 18757.23 | 533.1278 | 0.0099 | H-1->L+4 (10%), H-1->L+5 (30%), H-1->L+6 (20%) |
| 22 | 18804.82 | 531.7787 | 0.078 | H-6->LUMO (13%), H-4->L+1 (61%) |
| 23 | 19227.45 | 520.0897 | 0.0017 | H-7->LUMO (26%), H-6->L+1 (37%), H-5->L+1 (17%) |
| 24 | 19257.29 | 519.2838 | 0.2929 | H-7->LUMO (44%), H-6->L+1 (10%), H-5->L+1 (11%) |
| 25 | 19507.33 | 512.6279 | 0.0324 | H-6->L+1 (29%), H-5->L+1 (45%) |
| 26 | 19731.55 | 506.8026 | 0.0015 | H-1->L+5 (17%), H-1->L+6 (40%), H-1->L+7 (12%) |
| 27 | 19951.74 | 501.2095 | 0.2632 | H-2->L+2 (17%), H-1->L+7 (42%) |
| 28 | 20105.79 | 497.3692 | 0.9714 | H-2->L+2 (59%) |
| 29 | 20701.83 | 483.049 | 0.0754 | H-8->LUMO (10%), H-7->L+1 (45%) |
| 30 | 20817.17 | 480.3727 | 0.0123 | H-3->L+2 (55%) |

| | | | | |
|---|---|---|---|---|
| 31 | 21250.29 | 470.5818 | 0.0092 | H-8->LUMO (14%), H-3->L+3 (12%), H-2->L+3 (38%) |
| 32 | 21440.64 | 466.4041 | 0.0006 | H-8->LUMO (46%), H-7->L+1 (23%) |
| 33 | 21526.13 | 464.5517 | 0.0068 | H-9->LUMO (60%), H-9->L+1 (14%) |
| 34 | 21928.6 | 456.0254 | 0.0162 | H-11->LUMO (61%) |
| 35 | 21945.54 | 455.6735 | 0.0351 | H-3->L+3 (41%), H-2->L+3 (16%), H-2->L+6 (11%) |
| 36 | 22019.74 | 454.1379 | 0.0222 | H-17->LUMO (39%), H-17->L+1 (26%) |
| 37 | 22127.82 | 451.9198 | 0.1146 | H-5->L+2 (22%), H-4->L+2 (18%), H-2->L+4 (30%) |
| 38 | 22160.89 | 451.2454 | 0.304 | H-5->L+2 (10%), H-4->L+2 (18%), H-3->L+4 (11%), H-2->L+4 (23%) |
| 39 | 22340.75 | 447.6125 | 0.1063 | H-5->L+2 (16%), H-3->L+5 (10%), H-2->L+5 (27%) |
| 40 | 22452.86 | 445.3775 | 0.0044 | H-12->LUMO (15%), HOMO->L+8 (38%) |

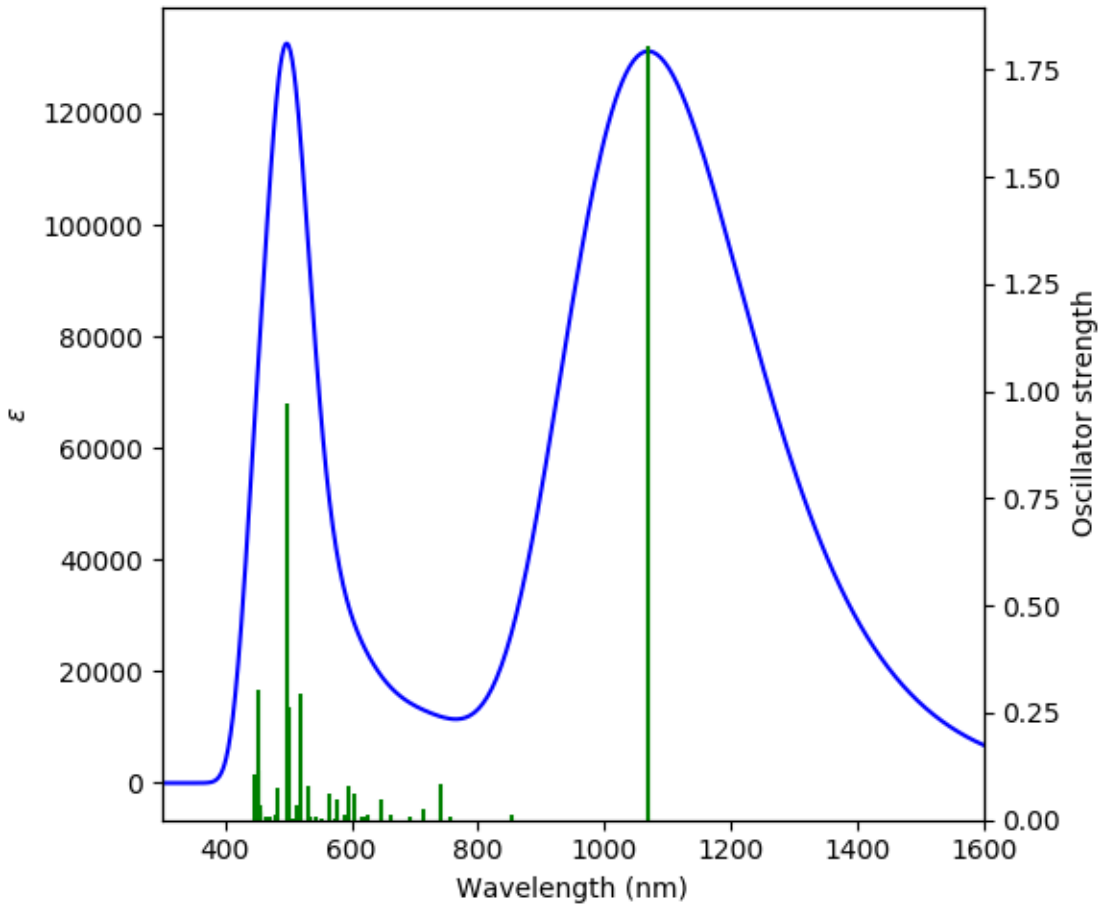


**Fig. S20** Calculated (TDDFT) UV/vis/NIR absorption spectrum of **2′(1)**.

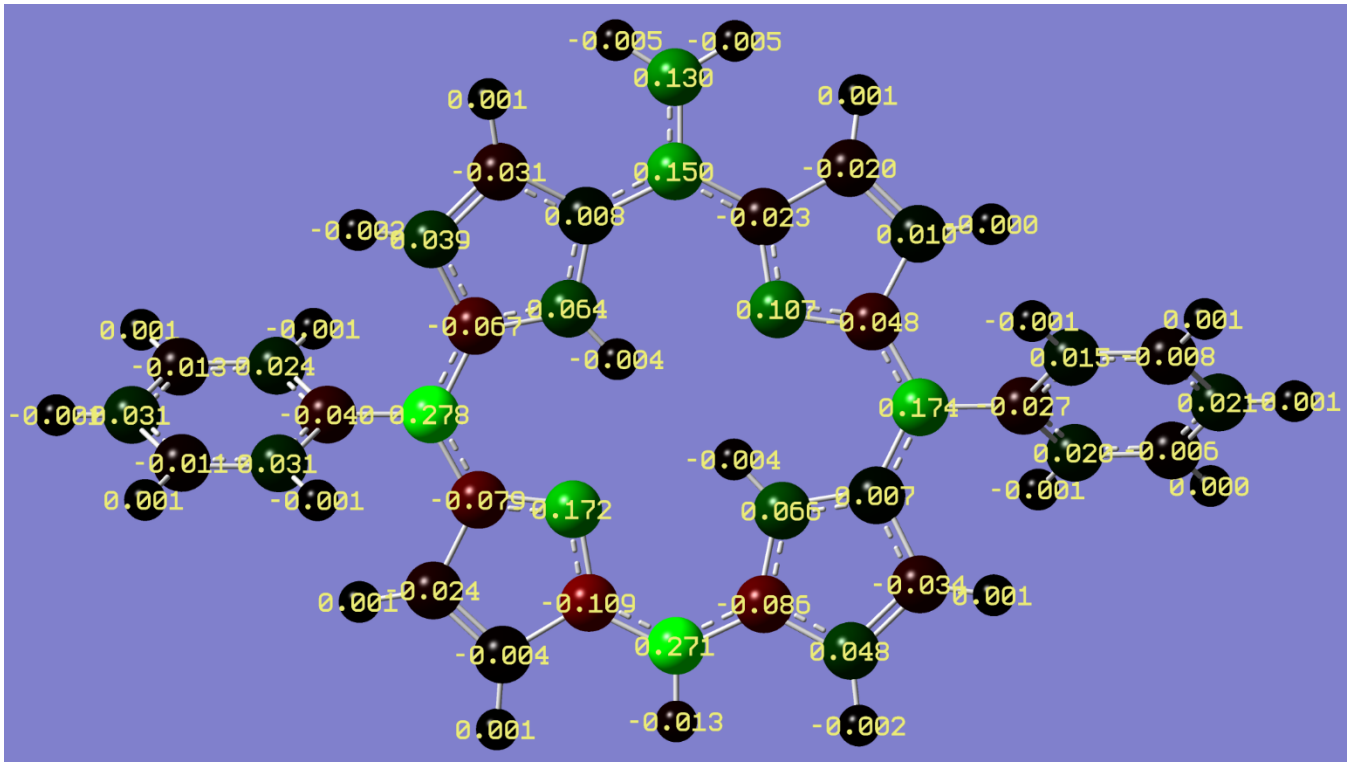


**Fig. S21** Spin distribution of the oxidized radical cation of **1′** (**1′**$^{\bullet+}$).

**Table S5** Cartesian coordinates for the optimized structure of **2′(0)**.

Stoichiometry: $C_{64}H_{41}N_9O$, full point group: C1, charge: 0, multiplicity: 1.

Total energy: −3031.6670144 a.u., No. of imaginary freq: 0.

| Center No. | Atomic No. | Atomic type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | 6.325698 | -3.78207 | -0.79745 |
| 2 | 6 | 0 | 5.084039 | -4.20873 | -1.19425 |
| 3 | 6 | 0 | 4.199637 | -3.07893 | -1.16888 |
| 4 | 7 | 0 | 4.94569 | -2.00474 | -0.74895 |
| 5 | 6 | 0 | 6.246864 | -2.3789 | -0.52306 |
| 6 | 6 | 0 | 8.063599 | 1.898608 | 0.488601 |
| 7 | 6 | 0 | 8.461262 | 0.608057 | 0.373243 |
| 8 | 6 | 0 | 7.263916 | -0.1632 | 0.064046 |
| 9 | 7 | 0 | 6.163402 | 0.639034 | 0.000569 |
| 10 | 6 | 0 | 6.617111 | 1.900066 | 0.267082 |
| 11 | 6 | 0 | 7.295411 | -1.5438 | -0.14905 |
| 12 | 6 | 0 | 2.251167 | 3.711691 | -0.03042 |
| 13 | 6 | 0 | 3.517557 | 4.159039 | 0.250671 |
| 14 | 6 | 0 | 4.422867 | 3.062069 | 0.085529 |
| 15 | 7 | 0 | 3.664559 | 1.982021 | -0.30961 |
| 16 | 6 | 0 | 2.340423 | 2.331469 | -0.386 |
| 17 | 6 | 0 | 5.810221 | 3.054523 | 0.324271 |
| 18 | 6 | 0 | 0.666255 | -1.83617 | -1.9905 |
| 19 | 6 | 0 | 0.228562 | -0.57049 | -1.78064 |
| 20 | 6 | 0 | 1.346139 | 0.151673 | -1.18721 |
| 21 | 7 | 0 | 2.454025 | -0.62995 | -1.11015 |
| 22 | 6 | 0 | 2.058596 | -1.86623 | -1.56236 |
| 23 | 6 | 0 | 2.850008 | -3.03274 | -1.55363 |
| 24 | 6 | 0 | 1.248994 | 1.492627 | -0.71209 |
| 25 | 1 | 0 | 7.230846 | -4.36758 | -0.71437 |
| 26 | 1 | 0 | 4.792743 | -5.20297 | -1.49647 |
| 27 | 1 | 0 | 8.670348 | 2.768492 | 0.69132 |
| 28 | 1 | 0 | 9.460132 | 0.201802 | 0.468254 |
| 29 | 1 | 0 | 8.259618 | -2.03022 | -0.03665 |
| 30 | 1 | 0 | 1.327537 | 4.267961 | -0.00766 |
| 31 | 1 | 0 | 3.810719 | 5.151417 | 0.556182 |
| 32 | 1 | 0 | 0.109261 | -2.66551 | -2.39902 |
| 33 | 1 | 0 | -0.74915 | -0.171 | -1.9998 |
| 34 | 6 | 0 | -1.04592 | 1.60337 | -0.08798 |
| 35 | 6 | 0 | -1.06659 | 0.347062 | 0.693223 |
| 36 | 6 | 0 | -2.25169 | 2.415816 | -0.2238 |
| 37 | 6 | 0 | 0.034317 | -0.09467 | 1.53107 |
| 38 | 7 | 0 | -2.07454 | -0.5174 | 0.672909 |
| 39 | 6 | 0 | -2.30528 | 3.803637 | -0.44779 |
| 40 | 7 | 0 | -3.52811 | 1.9552 | -0.12493 |
| 41 | 6 | 0 | -0.31987 | -1.32639 | 1.985401 |
| 42 | 1 | 0 | 0.944023 | 0.452489 | 1.72793 |
| 43 | 6 | 0 | -1.62936 | -1.61128 | 1.428433 |
| 44 | 6 | 0 | -3.64469 | 4.170255 | -0.4589 |
| 45 | 1 | 0 | -1.43777 | 4.434664 | -0.55894 |
| 46 | 6 | 0 | -4.41937 | 2.997925 | -0.28405 |
| 47 | 1 | 0 | 0.238636 | -1.97414 | 2.64434 |

| | | | | | |
|---|---|---|---|---|---|
| 48 | 6 | 0 | -2.31618 | -2.80977 | 1.55682 |
| 49 | 7 | 0 | -4.54028 | -2.05744 | 0.73157 |
| 50 | 7 | 0 | -5.98771 | 0.415394 | -0.01739 |
| 51 | 1 | 0 | -4.04765 | 5.164277 | -0.57427 |
| 52 | 6 | 0 | -5.83593 | 2.871587 | -0.29805 |
| 53 | 6 | 0 | -3.65843 | -3.03845 | 1.119967 |
| 54 | 6 | 0 | -5.7366 | -2.61733 | 0.393009 |
| 55 | 6 | 0 | -6.55242 | 1.681861 | -0.19896 |
| 56 | 6 | 0 | -7.01606 | -0.43025 | -0.10303 |
| 57 | 6 | 0 | -4.34063 | -4.27241 | 1.007743 |
| 58 | 6 | 0 | -5.62917 | -4.00637 | 0.554412 |
| 59 | 6 | 0 | -6.95539 | -1.90711 | -0.01106 |
| 60 | 6 | 0 | -7.9884 | 1.56518 | -0.38722 |
| 61 | 6 | 0 | -8.27673 | 0.236137 | -0.33386 |
| 62 | 1 | 0 | -3.9081 | -5.23599 | 1.228811 |
| 63 | 1 | 0 | -6.43268 | -4.69912 | 0.357419 |
| 64 | 1 | 0 | -8.66635 | 2.386126 | -0.56719 |
| 65 | 1 | 0 | -9.22512 | -0.26698 | -0.44656 |
| 66 | 7 | 0 | 0.022456 | 2.130784 | -0.61008 |
| 67 | 8 | 0 | -7.97039 | -2.56468 | -0.25608 |
| 68 | 6 | 0 | 6.439136 | 4.358943 | 0.686132 |
| 69 | 6 | 0 | 6.422722 | 5.4356 | -0.21479 |
| 70 | 6 | 0 | 7.053901 | 4.538039 | 1.93554 |
| 71 | 6 | 0 | 7.007278 | 6.655985 | 0.122768 |
| 72 | 1 | 0 | 5.953951 | 5.303708 | -1.18511 |
| 73 | 6 | 0 | 7.639137 | 5.758118 | 2.272708 |
| 74 | 1 | 0 | 7.063174 | 3.712942 | 2.640827 |
| 75 | 6 | 0 | 7.617725 | 6.820995 | 1.367536 |
| 76 | 1 | 0 | 6.99067 | 7.475963 | -0.5893 |
| 77 | 1 | 0 | 8.106649 | 5.880003 | 3.245471 |
| 78 | 1 | 0 | 8.073207 | 7.771142 | 1.630457 |
| 79 | 6 | 0 | 2.216709 | -4.32956 | -1.94038 |
| 80 | 6 | 0 | 1.765995 | -4.56494 | -3.24749 |
| 81 | 6 | 0 | 2.051559 | -5.33911 | -0.98008 |
| 82 | 6 | 0 | 1.152836 | -5.7732 | -3.57958 |
| 83 | 1 | 0 | 1.897811 | -3.79248 | -3.99869 |
| 84 | 6 | 0 | 1.435949 | -6.54614 | -1.30998 |
| 85 | 1 | 0 | 2.407684 | -5.16027 | 0.029692 |
| 86 | 6 | 0 | 0.982511 | -6.7655 | -2.61185 |
| 87 | 1 | 0 | 0.808997 | -5.94008 | -4.59615 |
| 88 | 1 | 0 | 1.301552 | -7.3088 | -0.54849 |
| 89 | 1 | 0 | 0.499951 | -7.70307 | -2.87101 |
| 90 | 6 | 0 | -1.61912 | -3.97419 | 2.170319 |
| 91 | 6 | 0 | -0.4088 | -4.44522 | 1.634553 |
| 92 | 6 | 0 | -2.17044 | -4.62751 | 3.285229 |
| 93 | 6 | 0 | 0.232084 | -5.54279 | 2.208028 |
| 94 | 1 | 0 | 0.013337 | -3.95921 | 0.760629 |
| 95 | 6 | 0 | -1.51878 | -5.71506 | 3.863 |
| 96 | 1 | 0 | -3.10673 | -4.26785 | 3.699457 |
| 97 | 6 | 0 | -0.31602 | -6.17688 | 3.324133 |
| 98 | 1 | 0 | 1.159802 | -5.90704 | 1.779334 |
| 99 | 1 | 0 | -1.94972 | -6.20116 | 4.733132 |
| 100 | 1 | 0 | 0.189354 | -7.02839 | 3.770148 |
| 101 | 6 | 0 | -6.60682 | 4.139814 | -0.46705 |
| 102 | 6 | 0 | -6.49838 | 4.89701 | -1.64329 |
| 103 | 6 | 0 | -7.45997 | 4.585871 | 0.553194 |

| | | | | | |
|---|---|---|---|---|---|
| 104 | 6 | 0 | -7.23014 | 6.074139 | -1.79535 |
| 105 | 1 | 0 | -5.84699 | 4.550307 | -2.43914 |
| 106 | 6 | 0 | -8.18435 | 5.767891 | 0.402319 |
| 107 | 1 | 0 | -7.54668 | 4.000528 | 1.462925 |
| 108 | 6 | 0 | -8.07227 | 6.51416 | -0.77217 |
| 109 | 1 | 0 | -7.14497 | 6.645098 | -2.71511 |
| 110 | 1 | 0 | -8.83627 | 6.104823 | 1.202705 |
| 111 | 1 | 0 | -8.63948 | 7.432532 | -0.89056 |
| 112 | 1 | 0 | 4.569086 | -1.06944 | -0.6394 |
| 113 | 1 | 0 | 4.050366 | 1.055732 | -0.45922 |
| 114 | 1 | 0 | -3.80313 | 0.986232 | -0.00331 |
| 115 | 1 | 0 | -4.32049 | -1.07075 | 0.668058 |

**Table S6** Cartesian coordinates for the optimized structure of **2′(1)**.

Stoichiometry: $C_{128}H_{81}N_{19}O$, full point group: C1, charge: 0, multiplicity: 1.

Total energy: −6042.2590294 a.u., No. of imaginary freq: 0.

| Center No. | Atomic No. | Atomic type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | 14.80774 | -3.85298 | -0.56257 |
| 2 | 6 | 0 | 13.59591 | -4.24922 | -1.06819 |
| 3 | 6 | 0 | 12.73402 | -3.10232 | -1.10022 |
| 4 | 7 | 0 | 13.46227 | -2.04925 | -0.60152 |
| 5 | 6 | 0 | 14.73253 | -2.45226 | -0.27355 |
| 6 | 6 | 0 | 16.5299 | 1.772429 | 0.97002 |
| 7 | 6 | 0 | 16.91487 | 0.477817 | 0.858331 |
| 8 | 6 | 0 | 15.73442 | -0.26573 | 0.435949 |
| 9 | 7 | 0 | 14.6562 | 0.557098 | 0.300252 |
| 10 | 6 | 0 | 15.10624 | 1.804528 | 0.63223 |
| 11 | 6 | 0 | 15.76088 | -1.64302 | 0.200154 |
| 12 | 6 | 0 | 10.80339 | 3.691562 | 0.038011 |
| 13 | 6 | 0 | 12.04944 | 4.111773 | 0.432029 |
| 14 | 6 | 0 | 12.95115 | 3.007313 | 0.304236 |
| 15 | 7 | 0 | 12.21416 | 1.951726 | -0.1842 |
| 16 | 6 | 0 | 10.90404 | 2.322922 | -0.35377 |
| 17 | 6 | 0 | 14.3154 | 2.97043 | 0.653934 |
| 18 | 6 | 0 | 9.312569 | -1.77361 | -2.207 |
| 19 | 6 | 0 | 8.879589 | -0.50421 | -2.00665 |
| 20 | 6 | 0 | 9.953019 | 0.183215 | -1.30256 |
| 21 | 7 | 0 | 11.03584 | -0.62068 | -1.14664 |
| 22 | 6 | 0 | 10.65971 | -1.83964 | -1.65833 |
| 23 | 6 | 0 | 11.42495 | -3.02229 | -1.59963 |
| 24 | 6 | 0 | 9.832679 | 1.511539 | -0.79533 |
| 25 | 1 | 0 | 15.69155 | -4.45759 | -0.41301 |
| 26 | 1 | 0 | 13.31211 | -5.23327 | -1.40871 |
| 27 | 1 | 0 | 17.13208 | 2.626809 | 1.240953 |
| 28 | 1 | 0 | 17.896 | 0.051923 | 1.025331 |
| 29 | 1 | 0 | 16.70412 | -2.14872 | 0.383048 |
| 30 | 1 | 0 | 9.887179 | 4.259843 | 0.00607 |
| 31 | 1 | 0 | 12.32938 | 5.089704 | 0.791748 |
| 32 | 1 | 0 | 8.780778 | -2.58352 | -2.68284 |
| 33 | 1 | 0 | 7.932177 | -0.07998 | -2.30073 |
| 34 | 6 | 0 | 7.491369 | 1.628807 | -0.37032 |
| 35 | 6 | 0 | 7.393004 | 0.378996 | 0.408728 |
| 36 | 6 | 0 | 6.308356 | 2.427175 | -0.67519 |
| 37 | 6 | 0 | 8.451229 | -0.10401 | 1.275482 |
| 38 | 7 | 0 | 6.348539 | -0.44941 | 0.364966 |
| 39 | 6 | 0 | 6.281561 | 3.795579 | -0.99755 |
| 40 | 7 | 0 | 5.036443 | 1.948134 | -0.76231 |
| 41 | 6 | 0 | 8.043396 | -1.32522 | 1.711147 |
| 42 | 1 | 0 | 9.37214 | 0.408882 | 1.506564 |
| 43 | 6 | 0 | 6.73315 | -1.55304 | 1.133166 |
| 44 | 6 | 0 | 4.963807 | 4.128763 | -1.28108 |
| 45 | 1 | 0 | 7.150746 | 4.433939 | -1.00788 |
| 46 | 6 | 0 | 4.180929 | 2.954589 | -1.16676 |
| 47 | 1 | 0 | 8.560245 | -1.99425 | 2.382563 |

| | | | | | |
|---|---|---|---|---|---|
| 48 | 6 | 0 | 5.983556 | -2.70892 | 1.322791 |
| 49 | 7 | 0 | 3.761892 | -1.886 | 0.548801 |
| 50 | 7 | 0 | 2.457215 | 0.503481 | -0.59542 |
| 51 | 1 | 0 | 4.57932 | 5.101092 | -1.54668 |
| 52 | 6 | 0 | 2.812156 | 2.780201 | -1.5113 |
| 53 | 6 | 0 | 4.609949 | -2.8812 | 0.991965 |
| 54 | 6 | 0 | 2.486871 | -2.36161 | 0.474949 |
| 55 | 6 | 0 | 2.076372 | 1.6079 | -1.36188 |
| 56 | 6 | 0 | 1.422884 | -0.33672 | -0.6691 |
| 57 | 6 | 0 | 3.820569 | -4.0458 | 1.149122 |
| 58 | 6 | 0 | 2.505468 | -3.71684 | 0.848356 |
| 59 | 6 | 0 | 1.310506 | -1.57331 | 0.126778 |
| 60 | 6 | 0 | 0.785271 | 1.368661 | -1.9749 |
| 61 | 6 | 0 | 0.382621 | 0.13759 | -1.55976 |
| 62 | 1 | 0 | 4.199147 | -5.00936 | 1.45241 |
| 63 | 1 | 0 | 1.63304 | -4.35022 | 0.878026 |
| 64 | 1 | 0 | 0.277629 | 2.036944 | -2.65416 |
| 65 | 1 | 0 | -0.52532 | -0.38552 | -1.8182 |
| 66 | 7 | 0 | 8.608893 | 2.156675 | -0.78408 |
| 67 | 6 | 0 | 14.93088 | 4.254435 | 1.101243 |
| 68 | 6 | 0 | 14.99776 | 5.356547 | 0.233906 |
| 69 | 6 | 0 | 15.44915 | 4.389505 | 2.399096 |
| 70 | 6 | 0 | 15.56959 | 6.558171 | 0.651081 |
| 71 | 1 | 0 | 14.60373 | 5.259131 | -0.77302 |
| 72 | 6 | 0 | 16.02189 | 5.590748 | 2.815952 |
| 73 | 1 | 0 | 15.39308 | 3.544869 | 3.078587 |
| 74 | 6 | 0 | 16.08399 | 6.679007 | 1.943435 |
| 75 | 1 | 0 | 15.61834 | 7.398124 | -0.03583 |
| 76 | 1 | 0 | 16.41409 | 5.67817 | 3.82505 |
| 77 | 1 | 0 | 16.52961 | 7.614557 | 2.268384 |
| 78 | 6 | 0 | 10.80236 | -4.29962 | -2.0617 |
| 79 | 6 | 0 | 10.47966 | -4.51137 | -3.40992 |
| 80 | 6 | 0 | 10.52009 | -5.31459 | -1.1347 |
| 81 | 6 | 0 | 9.878272 | -5.70254 | -3.81726 |
| 82 | 1 | 0 | 10.70221 | -3.73396 | -4.13417 |
| 83 | 6 | 0 | 9.917907 | -6.50533 | -1.54088 |
| 84 | 1 | 0 | 10.774 | -5.15308 | -0.09158 |
| 85 | 6 | 0 | 9.593006 | -6.70158 | -2.88436 |
| 86 | 1 | 0 | 9.634822 | -5.85118 | -4.86522 |
| 87 | 1 | 0 | 9.695614 | -7.2757 | -0.80805 |
| 88 | 1 | 0 | 9.121788 | -7.62674 | -3.2024 |
| 89 | 6 | 0 | 6.661892 | -3.88053 | 1.951305 |
| 90 | 6 | 0 | 7.781493 | -4.46119 | 1.333085 |
| 91 | 6 | 0 | 6.197118 | -4.41887 | 3.161935 |
| 92 | 6 | 0 | 8.410323 | -5.56294 | 1.911968 |
| 93 | 1 | 0 | 8.148375 | -4.05131 | 0.397168 |
| 94 | 6 | 0 | 6.838648 | -5.51038 | 3.744903 |
| 95 | 1 | 0 | 5.33715 | -3.96736 | 3.645966 |
| 96 | 6 | 0 | 7.944538 | -6.08841 | 3.118379 |
| 97 | 1 | 0 | 9.264128 | -6.01352 | 1.417138 |
| 98 | 1 | 0 | 6.475828 | -5.9076 | 4.68822 |
| 99 | 1 | 0 | 8.440815 | -6.9431 | 3.568561 |
| 100 | 6 | 0 | 2.117131 | 3.961673 | -2.09895 |
| 101 | 6 | 0 | 2.587811 | 4.573278 | -3.2721 |
| 102 | 6 | 0 | 0.969598 | 4.479099 | -1.47475 |
| 103 | 6 | 0 | 1.925454 | 5.674892 | -3.81114 |

| | | | | | |
|---|---|---|---|---|---|
| 104 | 1 | 0 | 3.467467 | 4.169888 | -3.7631 |
| 105 | 6 | 0 | 0.320145 | 5.591314 | -2.00816 |
| 106 | 1 | 0 | 0.597579 | 4.010681 | -0.56879 |
| 107 | 6 | 0 | 0.792855 | 6.190105 | -3.17721 |
| 108 | 1 | 0 | 2.292826 | 6.129032 | -4.7266 |
| 109 | 1 | 0 | -0.55334 | 5.990952 | -1.5044 |
| 110 | 1 | 0 | 0.281058 | 7.052895 | -3.59334 |
| 111 | 1 | 0 | 13.09489 | -1.10867 | -0.50698 |
| 112 | 1 | 0 | 12.59891 | 1.024193 | -0.32899 |
| 113 | 1 | 0 | 4.766501 | 0.986868 | -0.58736 |
| 114 | 1 | 0 | 4.036466 | -0.93104 | 0.348038 |
| 115 | 6 | 0 | -1.04334 | -1.45559 | 0.493626 |
| 116 | 6 | 0 | -2.09483 | -2.27018 | 0.010915 |
| 117 | 6 | 0 | -1.2024 | -0.12835 | 0.990748 |
| 118 | 6 | 0 | -1.97881 | -3.63034 | -0.39838 |
| 119 | 7 | 0 | -3.39444 | -1.88946 | -0.21187 |
| 120 | 6 | 0 | -0.15013 | 0.604533 | 1.678626 |
| 121 | 7 | 0 | -2.32029 | 0.630336 | 0.843421 |
| 122 | 6 | 0 | -3.20698 | -4.03705 | -0.8606 |
| 123 | 1 | 0 | -1.06594 | -4.20165 | -0.33627 |
| 124 | 6 | 0 | -4.10813 | -2.93099 | -0.75844 |
| 125 | 1 | 0 | -3.76896 | -0.96464 | -0.03441 |
| 126 | 6 | 0 | -0.63121 | 1.856568 | 1.876404 |
| 127 | 1 | 0 | 0.818733 | 0.22315 | 1.960529 |
| 128 | 6 | 0 | -1.99057 | 1.86281 | 1.351945 |
| 129 | 1 | 0 | -3.47403 | -5.00615 | -1.2529 |
| 130 | 6 | 0 | -5.4445 | -2.88698 | -1.20033 |
| 131 | 1 | 0 | -0.12609 | 2.689042 | 2.342051 |
| 132 | 6 | 0 | -2.8166 | 3.002859 | 1.345309 |
| 133 | 6 | 0 | -6.27332 | -1.7533 | -1.18595 |
| 134 | 6 | 0 | -6.01557 | -4.17463 | -1.70324 |
| 135 | 6 | 0 | -4.15564 | 3.041288 | 0.920606 |
| 136 | 6 | 0 | -2.23818 | 4.299232 | 1.816396 |
| 137 | 6 | 0 | -7.63219 | -1.74158 | -1.71423 |
| 138 | 7 | 0 | -5.95332 | -0.53025 | -0.64336 |
| 139 | 6 | 0 | -6.34868 | -4.35231 | -3.05351 |
| 140 | 6 | 0 | -6.23971 | -5.23211 | -0.80916 |
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| 142 | 7 | 0 | -4.87995 | 1.990601 | 0.401867 |
| 143 | 6 | 0 | -2.03542 | 5.345432 | 0.903408 |
| 144 | 6 | 0 | -1.88603 | 4.499655 | 3.158784 |
| 145 | 6 | 0 | -8.12266 | -0.50018 | -1.48169 |
| 146 | 1 | 0 | -8.13007 | -2.56433 | -2.20422 |
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| 180 | 1 | 0 | -7.75979 | 0.392875 | 2.103629 |
| 181 | 6 | 0 | -10.257 | -1.68406 | 1.454751 |
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| 184 | 6 | 0 | -12.9397 | 2.981328 | -0.27921 |
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| 192 | 6 | 0 | -15.0553 | 1.644017 | -0.4396 |
| 193 | 6 | 0 | -15.1164 | 4.111494 | -0.60198 |
| 194 | 7 | 0 | -13.0851 | -2.12211 | 0.478698 |
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| 221 | 1 | 0 | -10.7736 | -6.47553 | 4.436787 |
| 222 | 1 | 0 | -17.6735 | -0.31185 | -1.0068 |
| 223 | 6 | 0 | -16.5792 | 6.48475 | -0.92885 |
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| 227 | 1 | 0 | -17.1454 | 7.402634 | -1.0557 |
| 228 | 7 | 0 | 0.182545 | -2.09168 | 0.524365 |
| 229 | 8 | 0 | -16.4127 | -2.60556 | -0.82212 |

**Table S7** Cartesian coordinates for the optimized structure of **1′**$^{\bullet+}$.

Stoichiometry: $C_{32}H_{23}N_5$, full point group: C1, charge: 1, multiplicity: 1.

Total energy: −1506.94400346 a.u., No. of imaginary freq: 0.

| Center No. | Atomic No. | Atomic type | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | -3.476628 | 2.341656 | 0.347143 |
| 2 | 6 | 0 | -2.482155 | 3.300187 | 0.374394 |
| 3 | 6 | 0 | -1.248321 | 2.65309 | 0.106603 |
| 4 | 7 | 0 | -1.51755 | 1.319669 | -0.066595 |
| 5 | 6 | 0 | -2.866139 | 1.089172 | 0.064945 |
| 6 | 6 | 0 | -2.533792 | -3.638941 | -0.263749 |
| 7 | 6 | 0 | -3.515934 | -2.703354 | -0.280999 |
| 8 | 6 | 0 | -2.849684 | -1.41094 | -0.117383 |
| 9 | 7 | 0 | -1.492528 | -1.563028 | -0.042162 |
| 10 | 6 | 0 | -1.280898 | -2.91097 | -0.110797 |
| 11 | 6 | 0 | -3.51937 | -0.172819 | -0.029203 |
| 12 | 6 | 0 | 3.47648 | -2.708029 | 0.249718 |
| 13 | 6 | 0 | 2.474195 | -3.651419 | 0.221758 |
| 14 | 6 | 0 | 1.231477 | -2.962805 | 0.077855 |
| 15 | 7 | 0 | 1.513833 | -1.623215 | 0.020833 |
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| 17 | 6 | 0 | -0.038529 | -3.544868 | -0.017639 |
| 18 | 6 | 0 | 2.546966 | 3.287203 | -0.407708 |
| 19 | 6 | 0 | 3.51515 | 2.329528 | -0.372485 |
| 20 | 6 | 0 | 2.841797 | 1.077011 | -0.089857 |
| 21 | 7 | 0 | 1.482097 | 1.271259 | 0.028795 |
| 22 | 6 | 0 | 1.298029 | 2.603292 | -0.138481 |
| 23 | 6 | 0 | 0.03627 | 3.273056 | -0.012799 |
| 24 | 6 | 0 | 3.511354 | -0.162484 | 0.01774 |
| 25 | 1 | 0 | -4.52867 | 2.489021 | 0.534837 |
| 26 | 1 | 0 | -2.626021 | 4.347329 | 0.59946 |
| 27 | 1 | 0 | -2.628765 | -4.712957 | -0.355589 |
| 28 | 1 | 0 | -4.577766 | -2.855506 | -0.402951 |
| 29 | 1 | 0 | 4.535413 | -2.879177 | 0.365542 |
| 30 | 1 | 0 | 2.575762 | -4.724862 | 0.29997 |
| 31 | 1 | 0 | 2.696156 | 4.332857 | -0.641913 |
| 32 | 1 | 0 | 4.571596 | 2.454506 | -0.556483 |
| 33 | 1 | 0 | 0.828019 | -0.878317 | -0.031984 |
| 34 | 1 | 0 | -0.830601 | 0.584138 | -0.195174 |
| 35 | 7 | 0 | 0.051737 | 4.625778 | -0.002047 |
| 36 | 1 | 0 | -0.795701 | 5.168668 | -0.041484 |
| 37 | 1 | 0 | 0.918676 | 5.136216 | 0.047801 |
| 38 | 6 | 0 | -5.004907 | -0.156542 | -0.007242 |
| 39 | 6 | 0 | -5.711614 | -0.848378 | 0.993065 |
| 40 | 6 | 0 | -5.725072 | 0.554514 | -0.984676 |
| 41 | 6 | 0 | -7.106177 | -0.823616 | 1.016902 |
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| 43 | 6 | 0 | -7.119983 | 0.560229 | -0.969087 |
| 44 | 1 | 0 | -5.187608 | 1.080242 | -1.768081 |
| 45 | 6 | 0 | -7.813494 | -0.124436 | 0.033789 |
| 46 | 1 | 0 | -7.63974 | -1.34894 | 1.802905 |
| 47 | 1 | 0 | -7.664506 | 1.096483 | -1.740084 |

| | | | | | |
|---|---|---|---|---|---|
| 48 | 1 | 0 | -8.898887 | -0.113353 | 0.049041 |
| 49 | 6 | 0 | 4.998624 | -0.161469 | 0.028566 |
| 50 | 6 | 0 | 5.69603 | 0.531059 | 1.03446 |
| 51 | 6 | 0 | 5.726238 | -0.846461 | -0.960851 |
| 52 | 6 | 0 | 7.090996 | 0.527075 | 1.055819 |
| 53 | 1 | 0 | 5.139582 | 1.053816 | 1.806261 |
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| 57 | 1 | 0 | 7.618192 | 1.051528 | 1.846698 |
| 58 | 1 | 0 | 7.672264 | -1.349151 | -1.726359 |
| 59 | 1 | 0 | 8.891974 | -0.145932 | 0.07699 |
| 60 | 1 | 0 | -0.048722 | -4.630866 | -0.019696 |

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1 K. Yamashita, K. Kataoka, S. Takeuchi and K. Sugiura, *J. Org. Chem.*, 2016, **81**, 11176–11184.

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5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Rev. C.01, Gaussian, Inc., Wallingford CT*, 2016.

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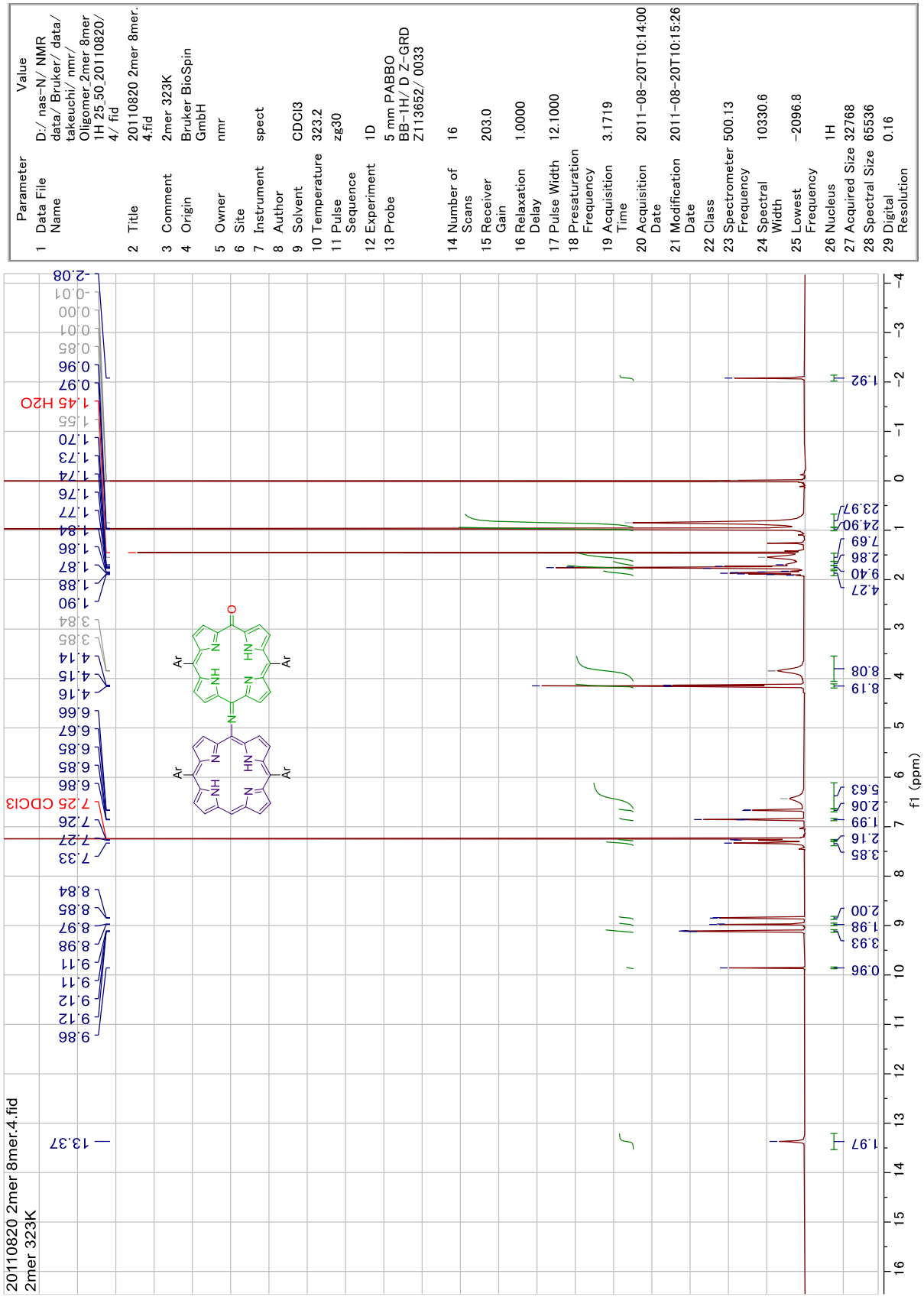
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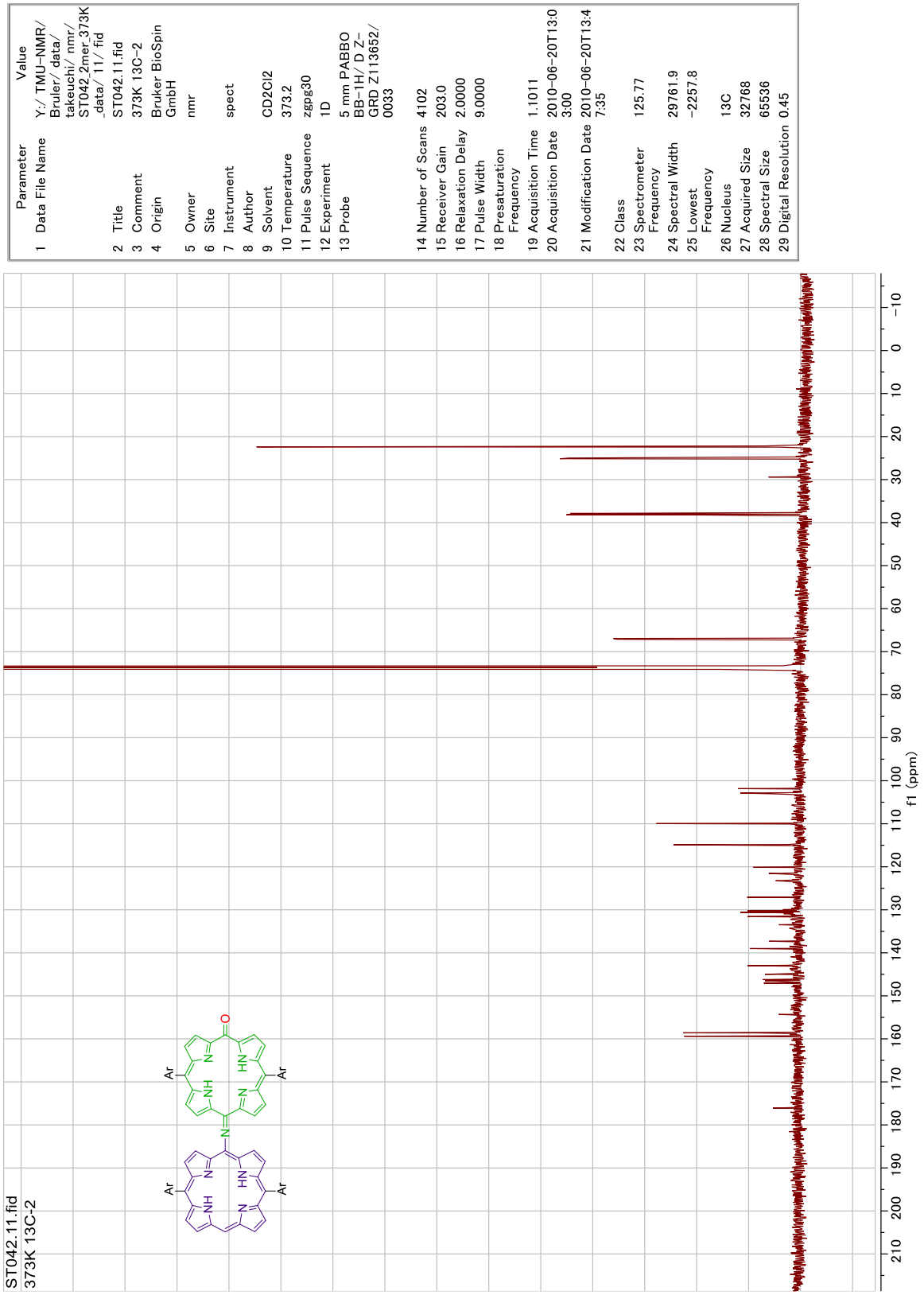

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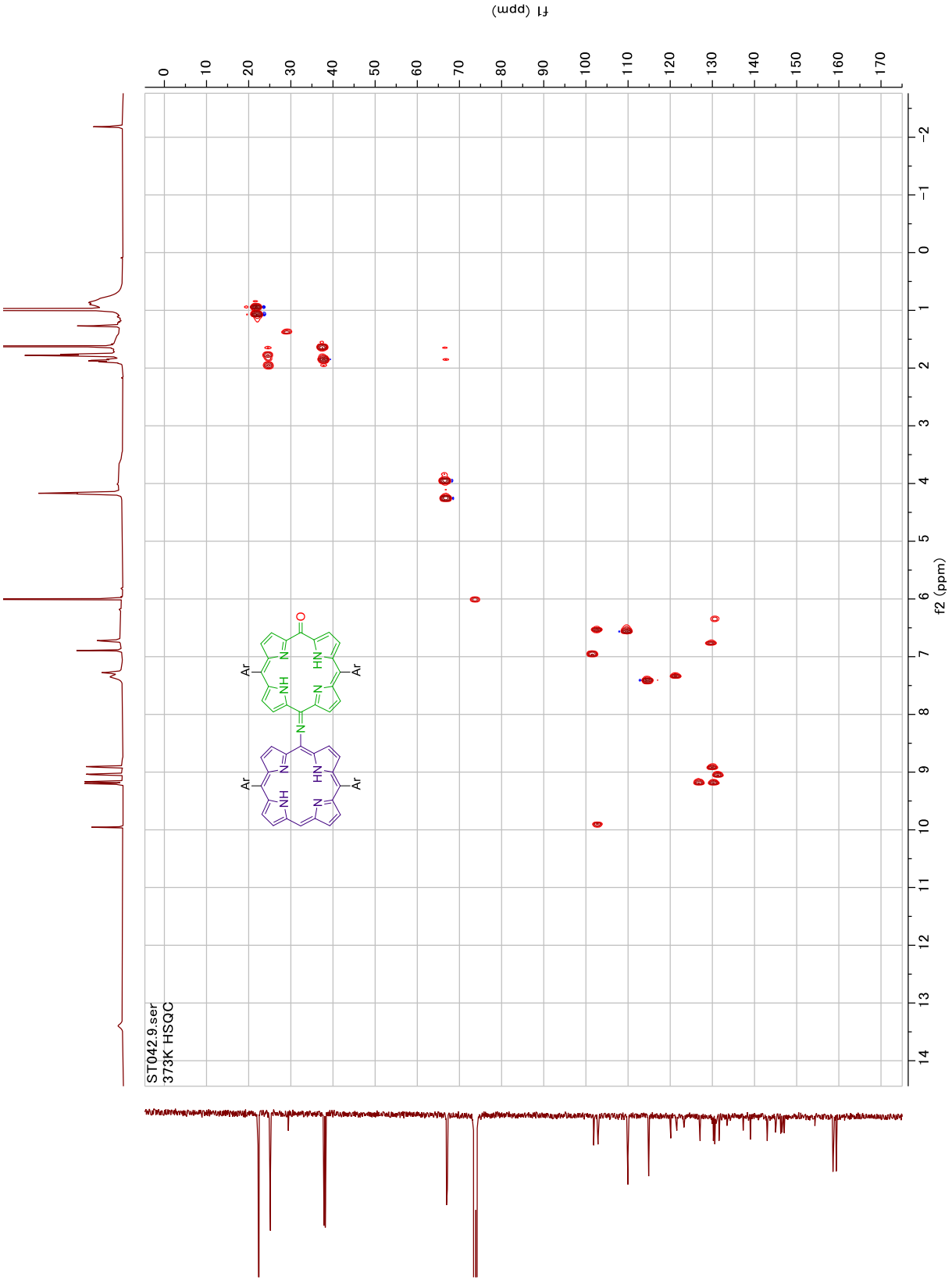

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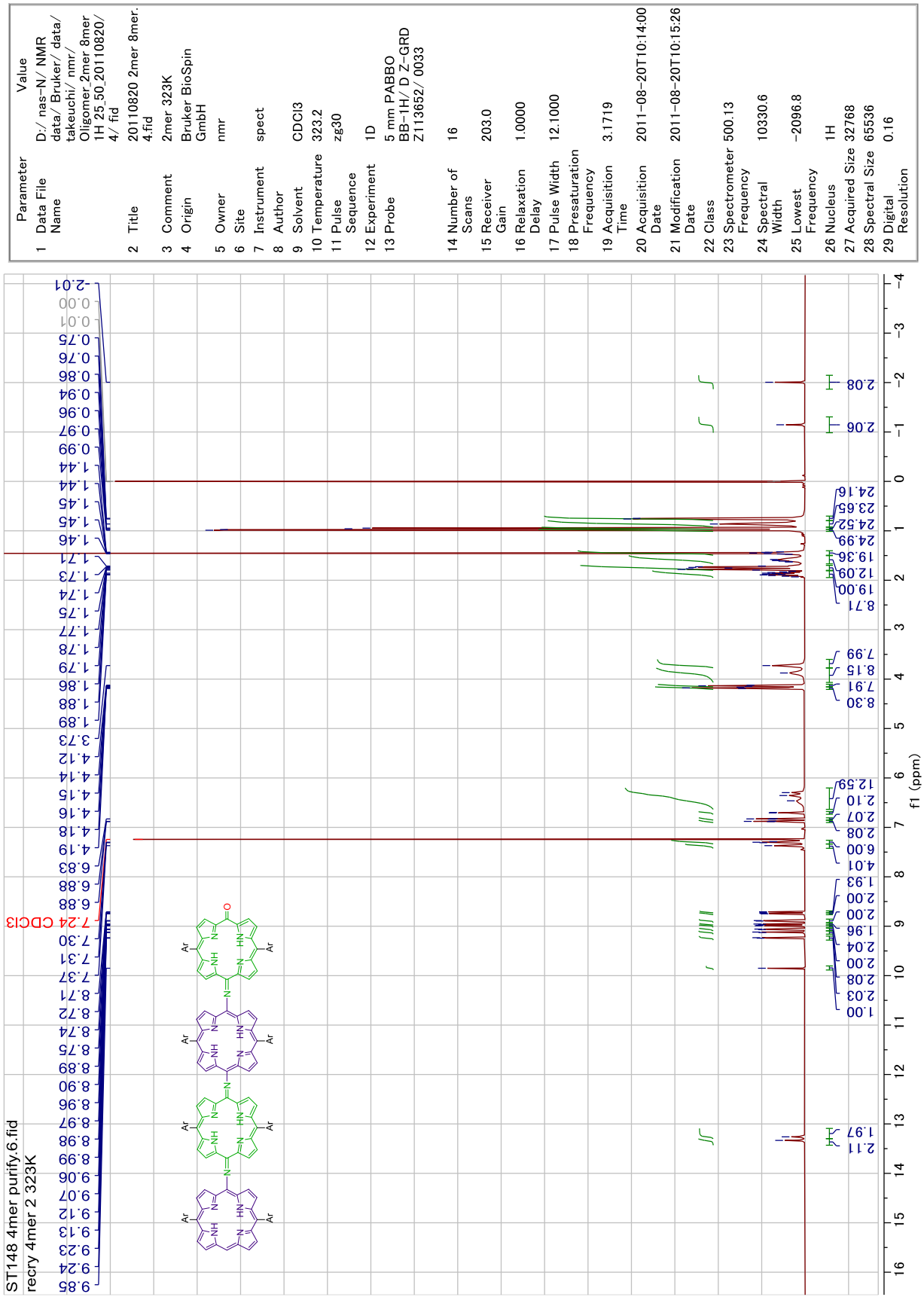
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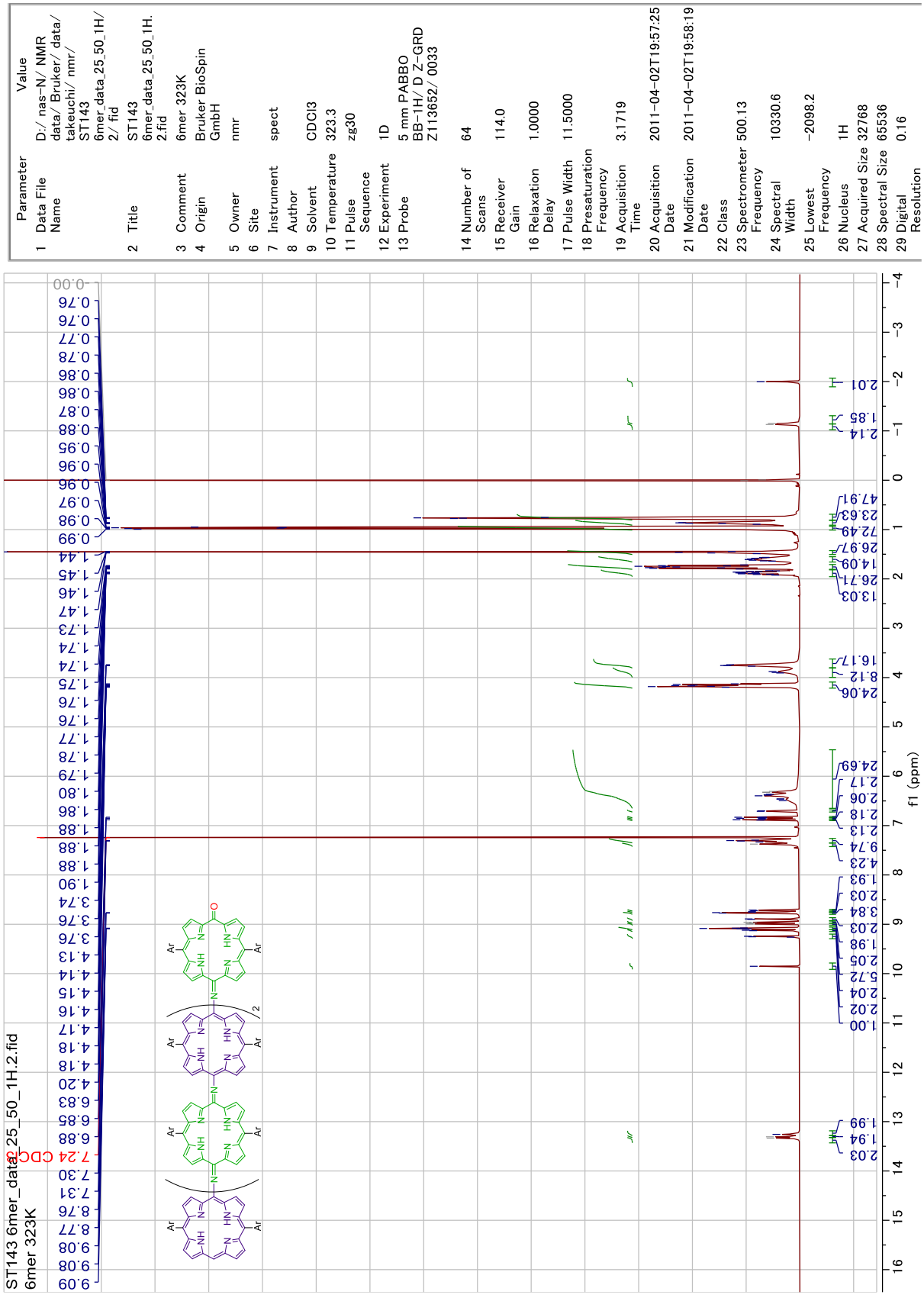
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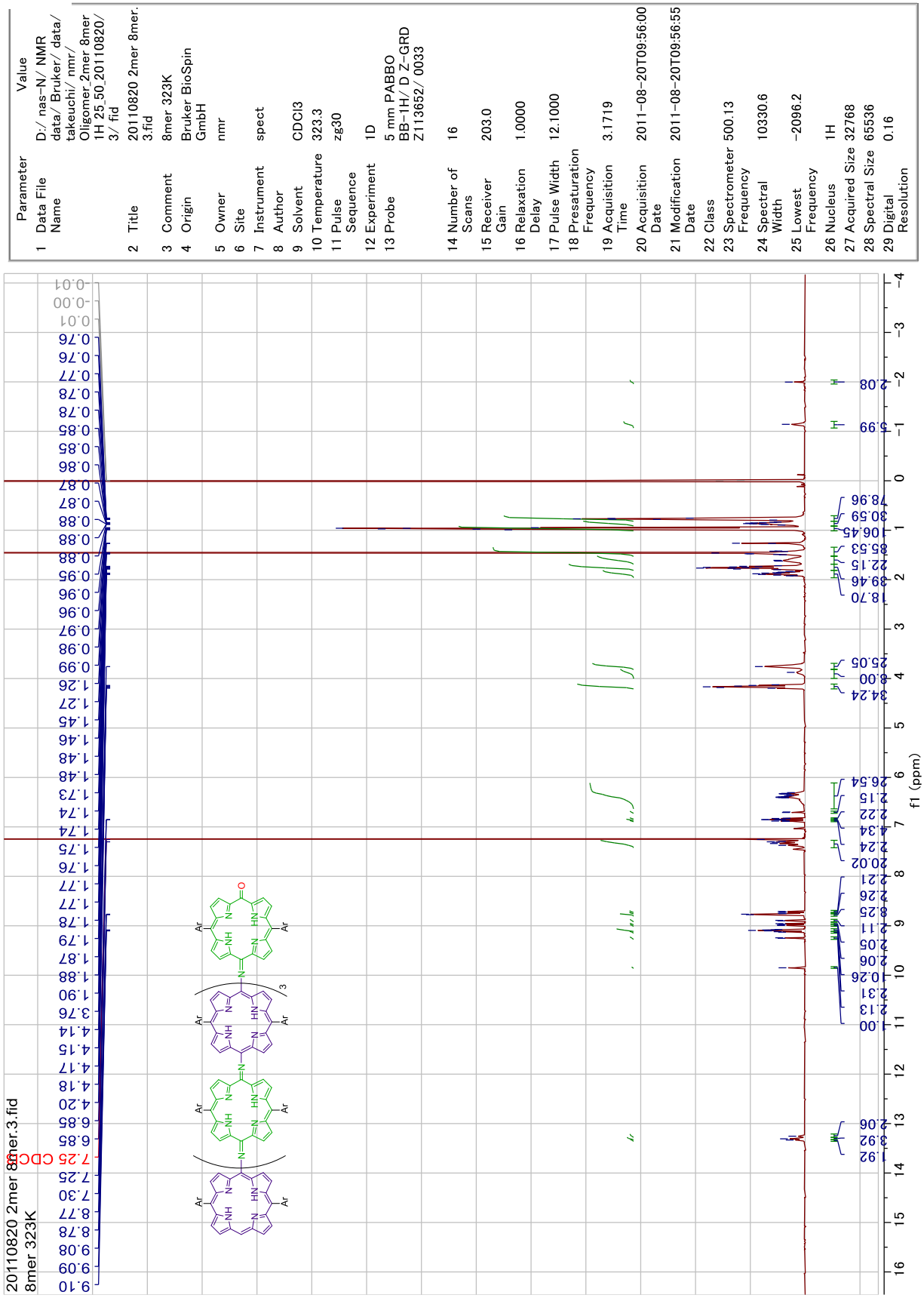
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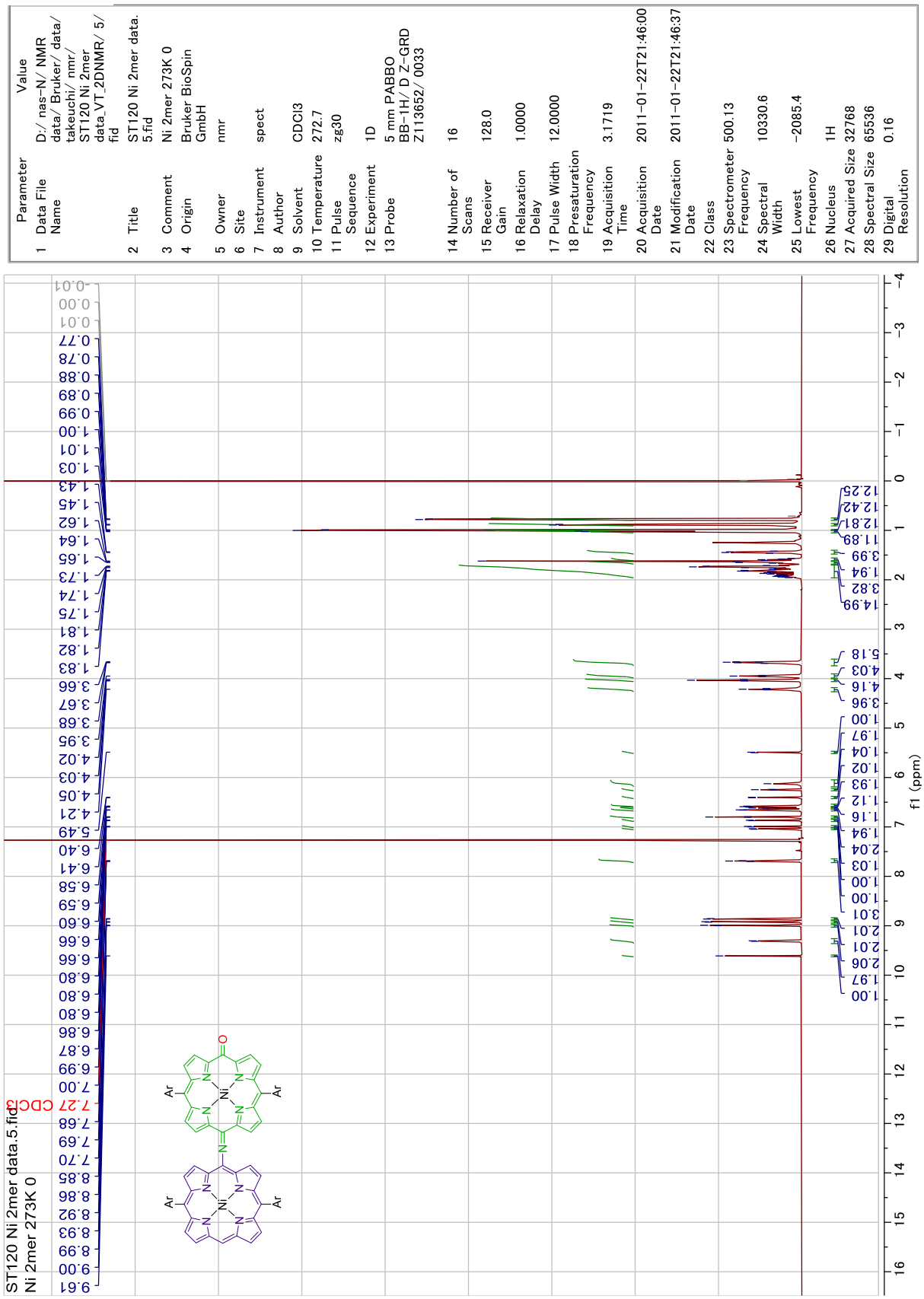
**Ni-2(0)**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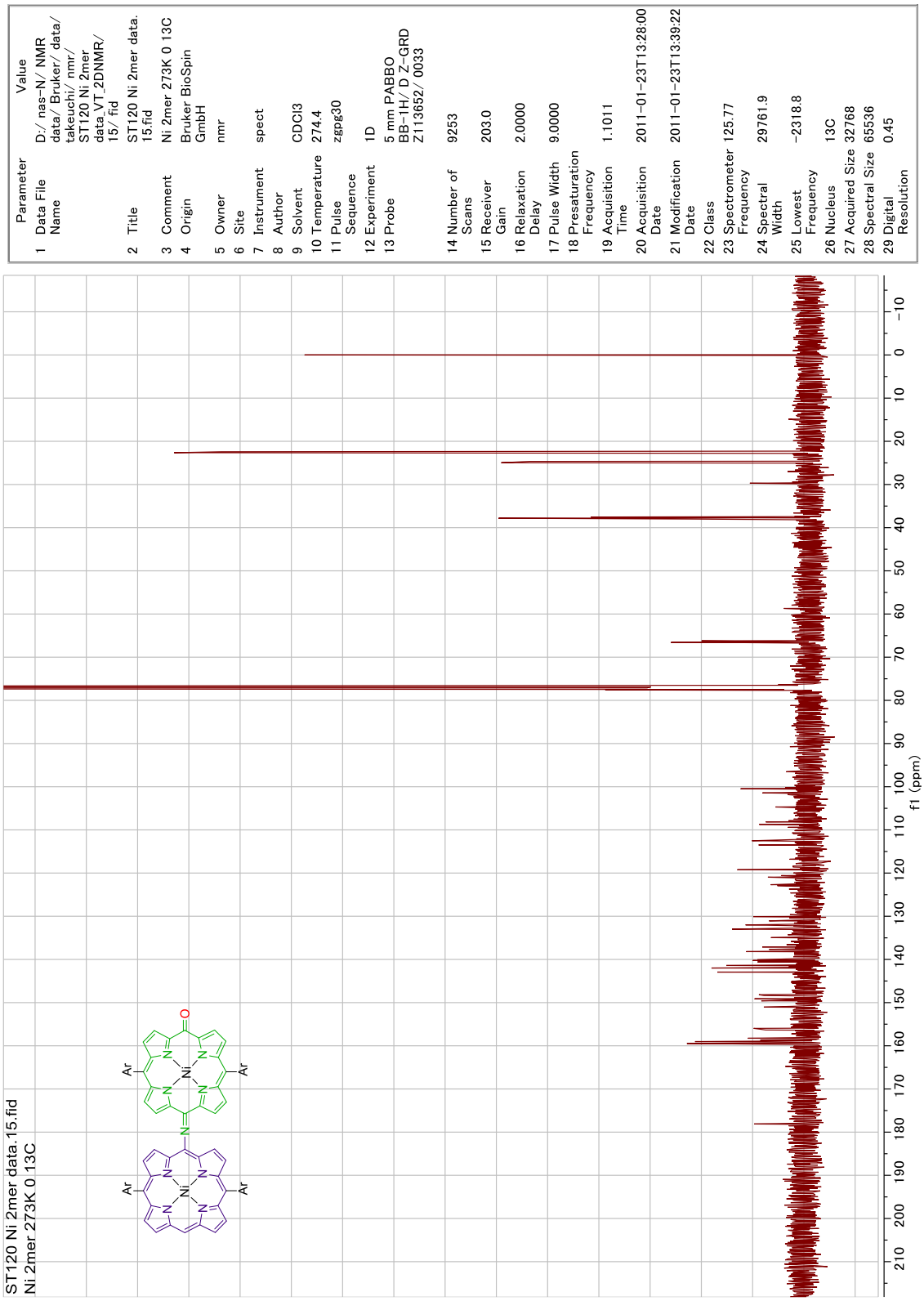
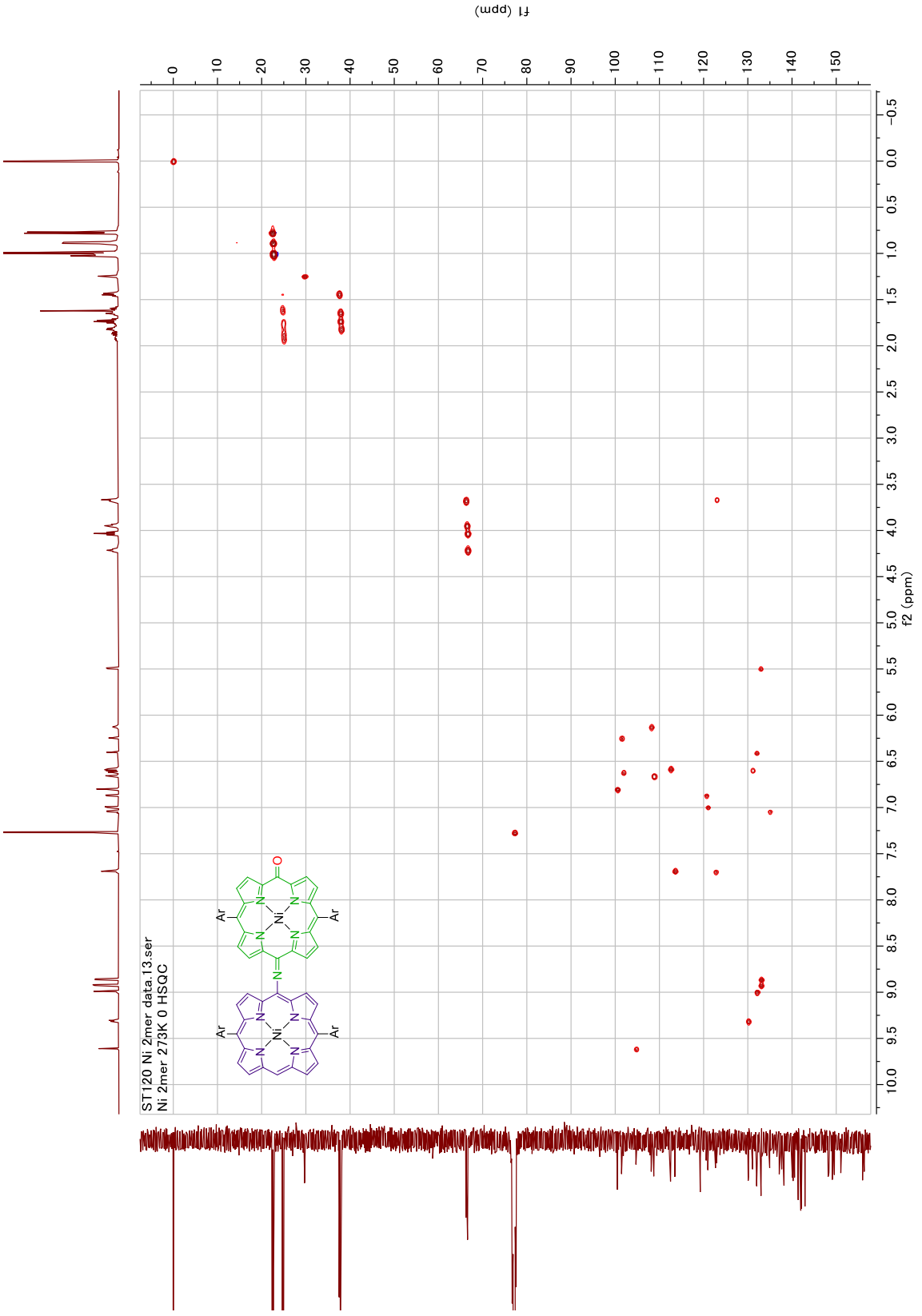
f1 (ppm)

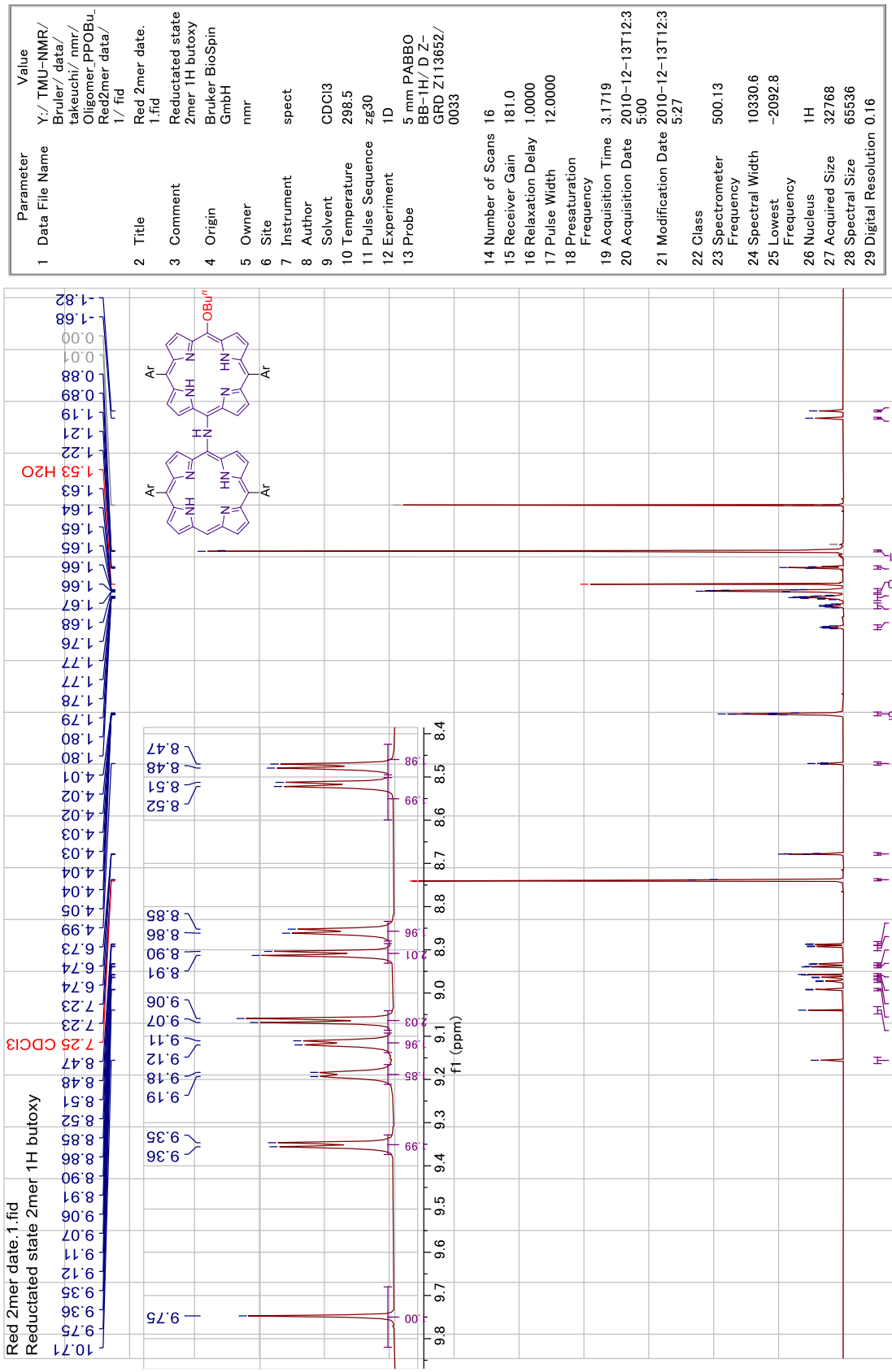
$^{13}C$ NMR (125 MHz, $CDCl_3$, 273 K)



HSQC NMR ($CDCl_3$, 273 K)



**4b**




| Parameter | Value |
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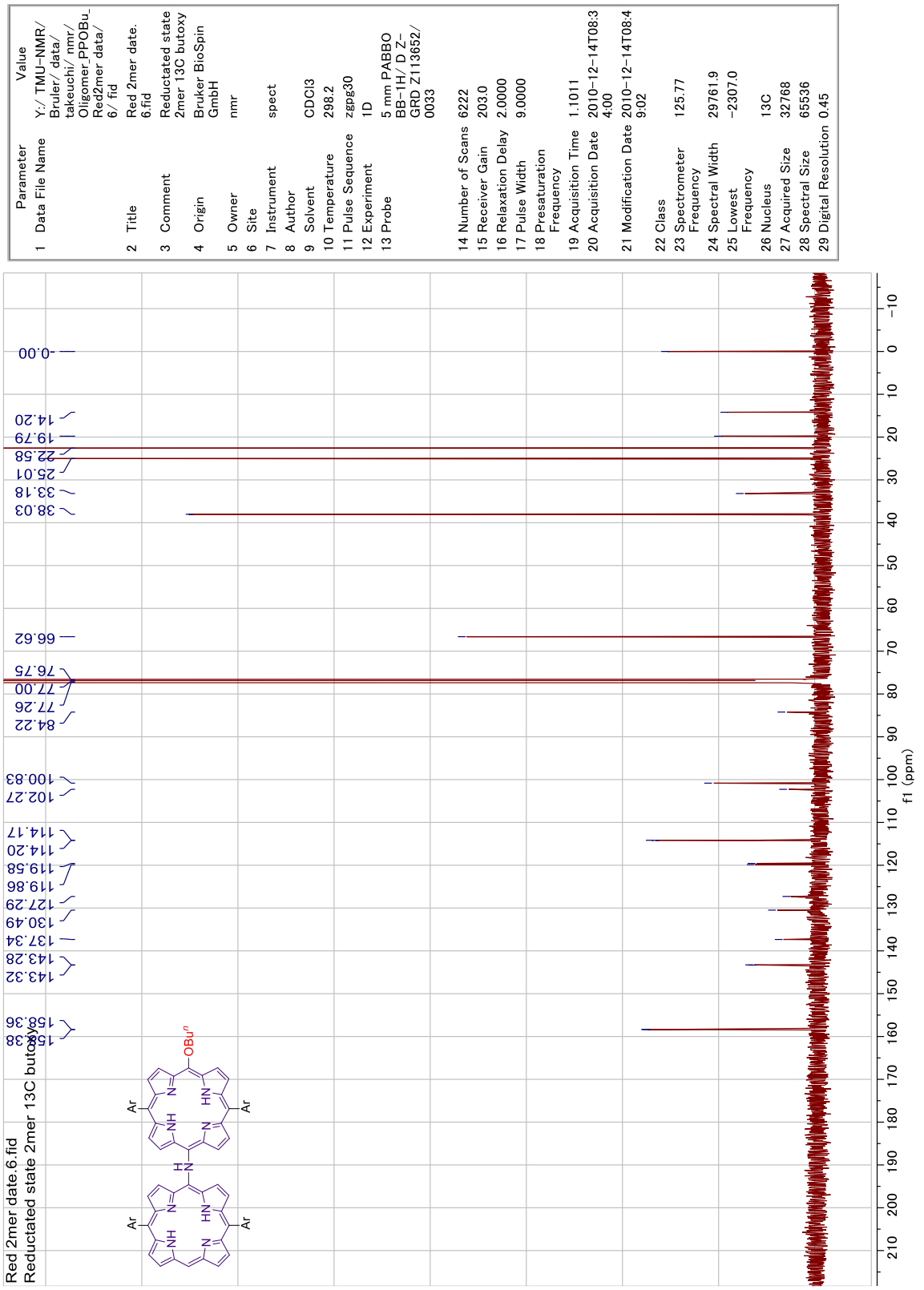
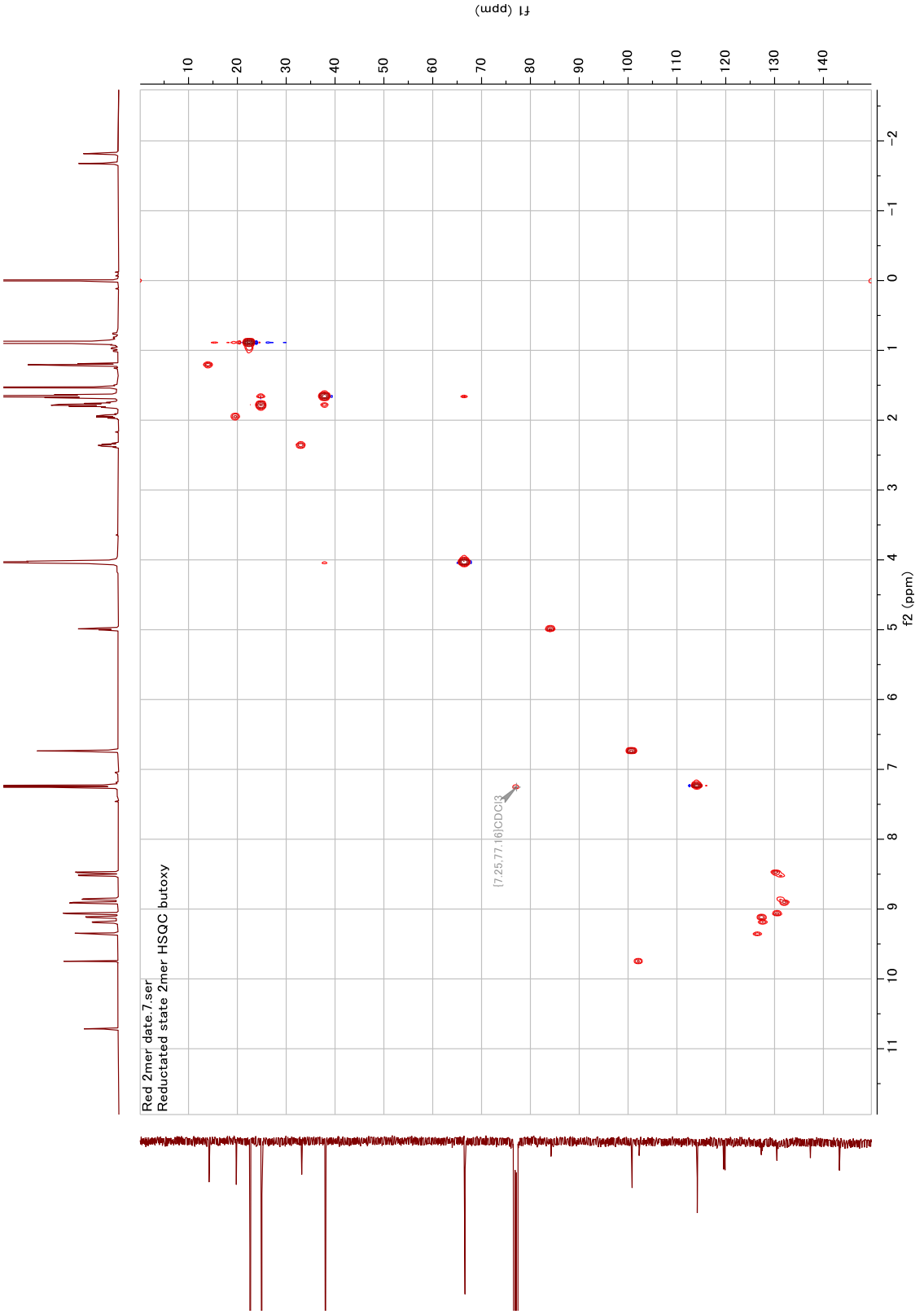
| 2 Title | Red 2mer date. 1.fid |
| 3 Comment | Reductated state 2mer 1H butoxy |
| 4 Origin | Bruker BioSpin GmbH |
| 5 Owner | nmr |
| 6 Site | |
| 7 Instrument | spect |
| 8 Author | |
| 9 Solvent | CDCl3 |
| 10 Temperature | 298.5 |
| 11 Pulse Sequence | zg30 |
| 12 Experiment | 1D |
| 13 Probe | 5 mm PABBO BB-1H/ D Z-GRD Z113652/ 0033 |
| 14 Number of Scans | 16 |
| 15 Receiver Gain | 181.0 |
| 16 Relaxation Delay | 1.0000 |
| 17 Pulse Width | 12.0000 |
| 18 Presaturation Frequency | |
| 19 Acquisition Time | 3.1719 |
| 20 Acquisition Date | 2010-12-13T12:3 5:00 |
| 21 Modification Date | 2010-12-13T12:3 5:27 |
| 22 Class | |
| 23 Spectrometer Frequency | 500.13 |
| 24 Spectral Width | 10330.6 |
| 25 Lowest Frequency | -2092.8 |
| 26 Nucleus | 1H |
| 27 Acquired Size | 32768 |
| 28 Spectral Size | 65536 |
| 29 Digital Resolution | 0.16 |

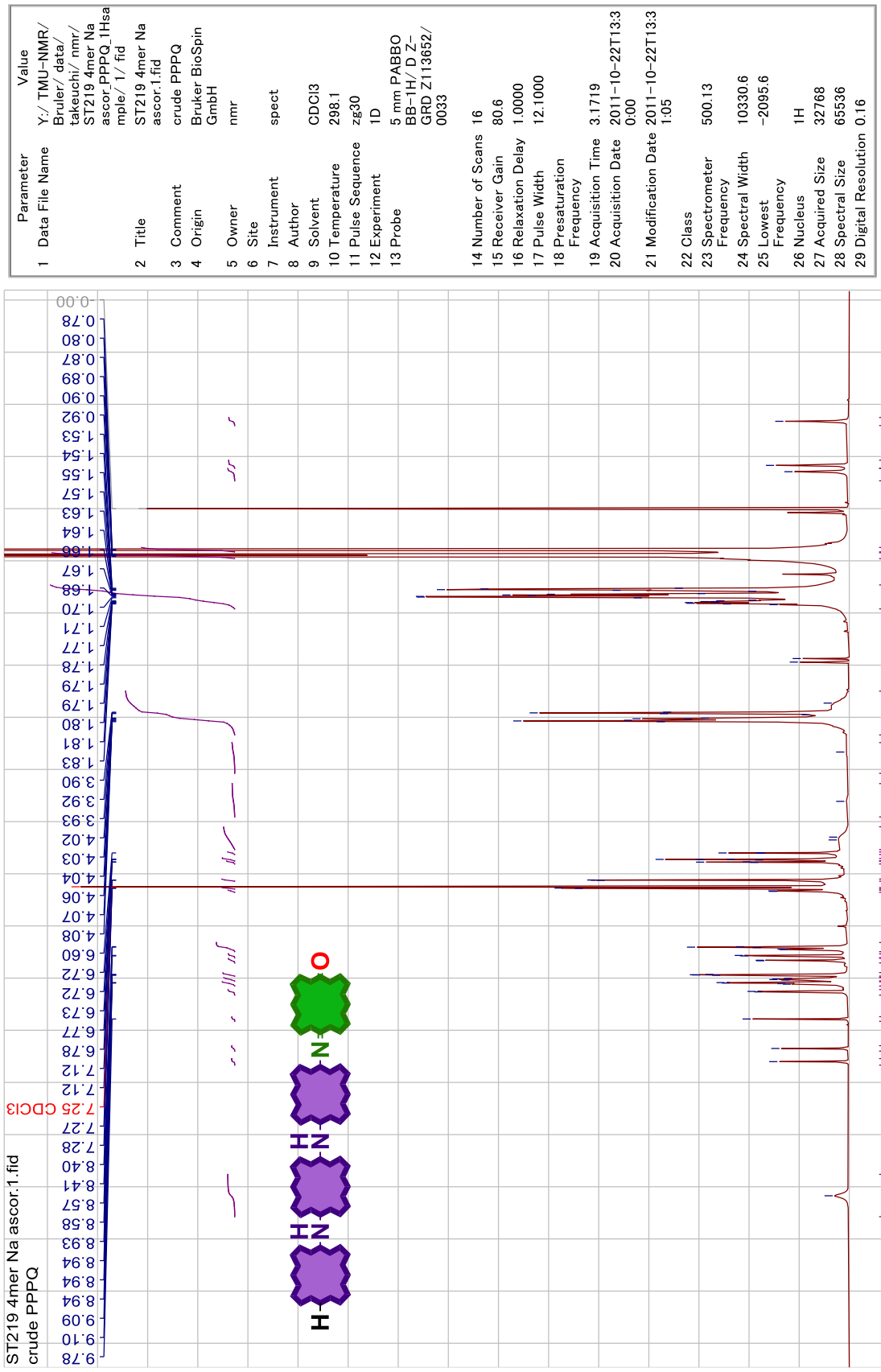
$^{13}C$ NMR (125 MHz, $CDCl_3$)



HSQC NMR ($CDCl_3$)



**6**


Parameter
Value
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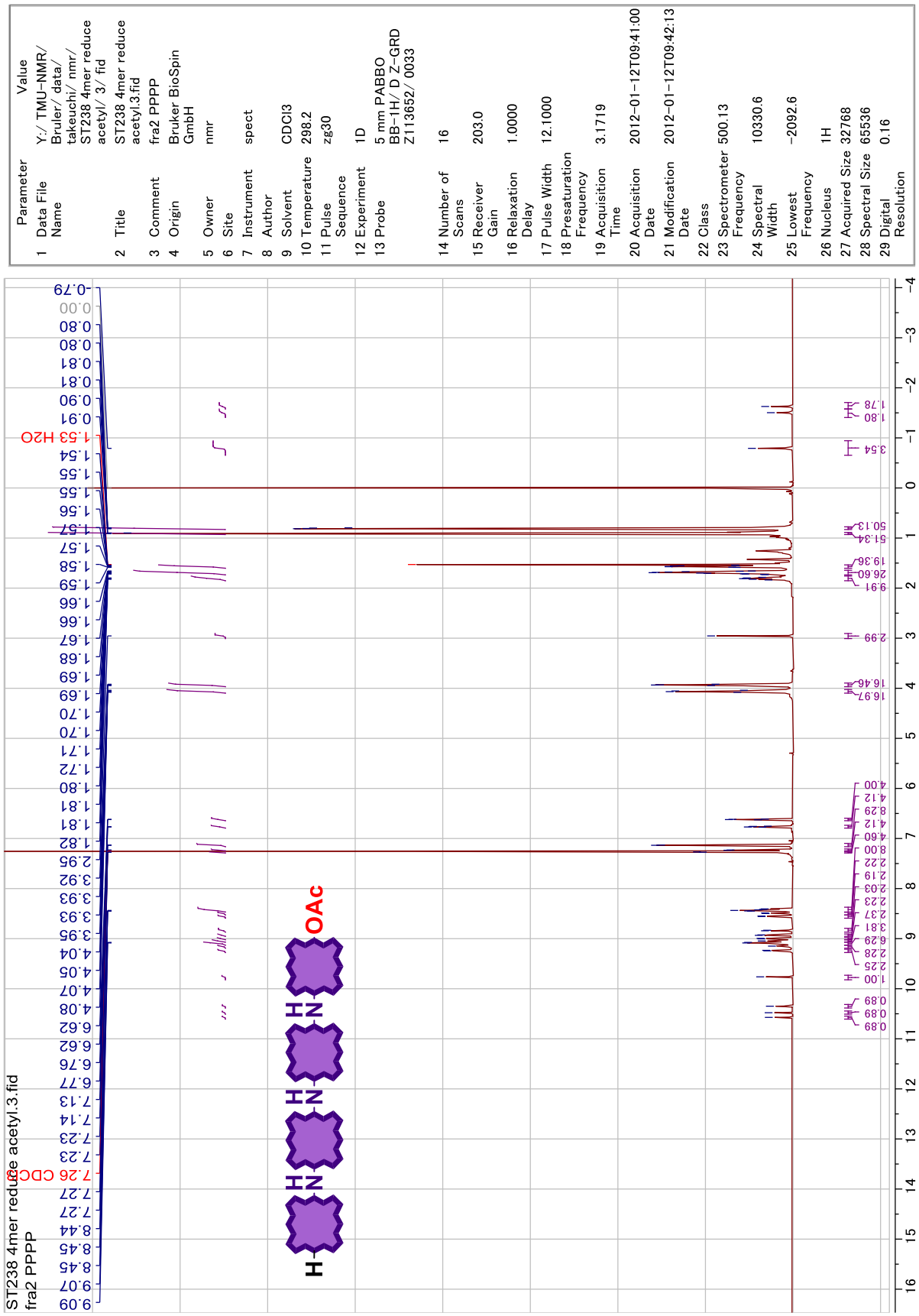
2 Title
ST219 4mer Na ascor.1.fid
3 Comment
crude PPPQ
4 Origin
Bruker BioSpin GmbH
5 Owner
nmr
6 Site
7 Instrument
spect
8 Author
9 Solvent
CDCl3
10 Temperature
298.1
11 Pulse Sequence
zg30
12 Experiment
1D
13 Probe
5 mm PABBO BB-1H/ D Z-GRD Z113652/ 0033
14 Number of Scans
16
15 Receiver Gain
80.6
16 Relaxation Delay
1.0000
17 Pulse Width
12.1000
18 Presaturation Frequency
19 Acquisition Time
3.1719
20 Acquisition Date
2011-10-22T13:3 0:00
21 Modification Date
2011-10-22T13:3 1:05
22 Class
23 Spectrometer Frequency
500.13
24 Spectral Width
10330.6
25 Lowest Frequency
-2095.6
26 Nucleus
1H
27 Acquired Size
32768
28 Spectral Size
65536
29 Digital Resolution
0.16
ST219 4mer Na ascor.1.fid
crude PPPQ
7.25 CDCl3
f1 (ppm)

**5b**




| Parameter | | Value |
|---|---|---|
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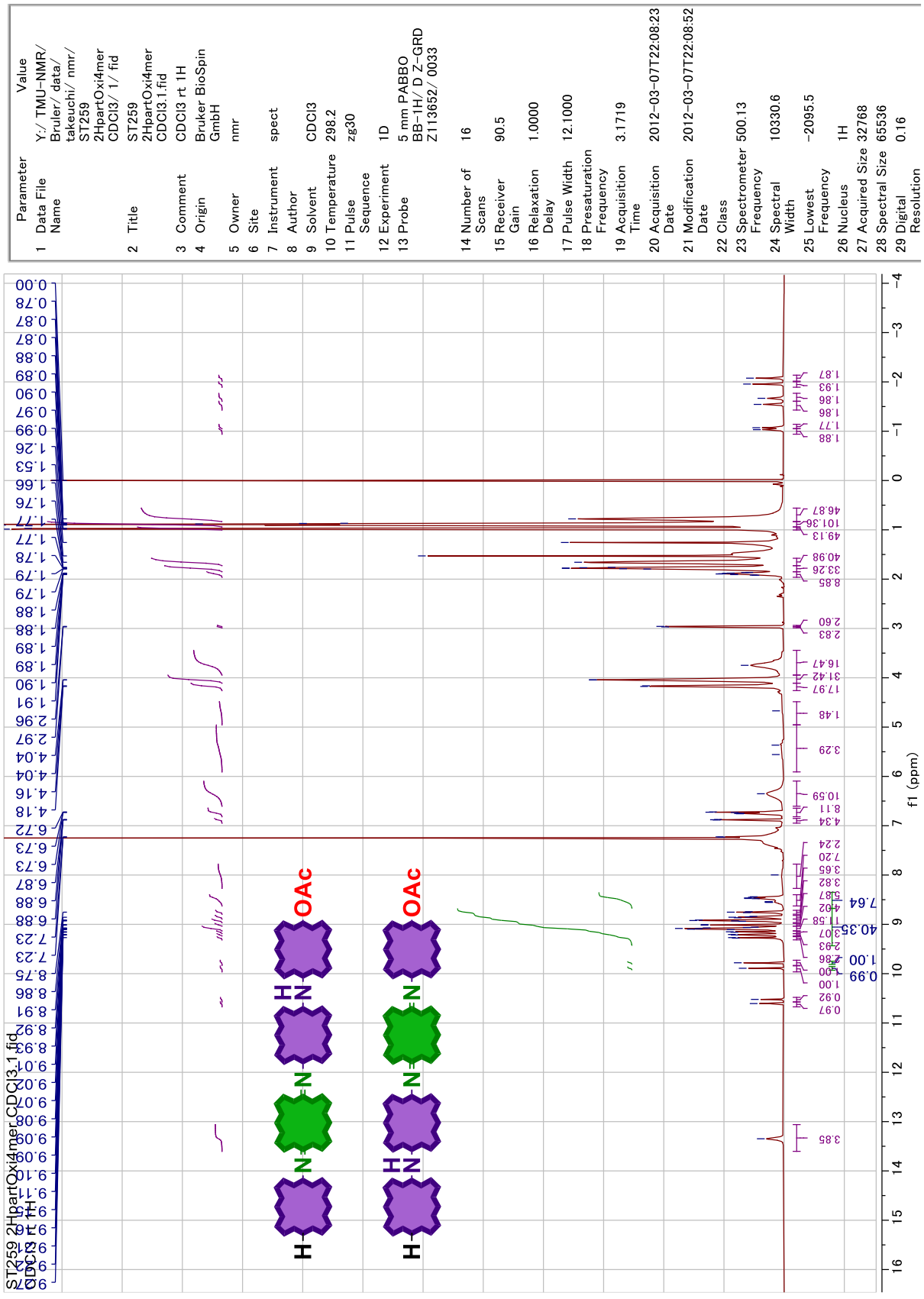
| 2 | Title | ST238 4mer reduce acetyl.3.fid |
| 3 | Comment | fra2 PPPP |
| 4 | Origin | Bruker BioSpin GmbH |
| 5 | Owner | nmr |
| 6 | Site | |
| 7 | Instrument | spect |
| 8 | Author | |
| 9 | Solvent | CDCl3 |
| 10 | Temperature | 298.2 |
| 11 | Pulse Sequence | zg30 |
| 12 | Experiment | 1D |
| 13 | Probe | 5 mm PABBO BB-1H/ D Z-GRD Z113652/ 0033 |
| 14 | Number of Scans | 16 |
| 15 | Receiver Gain | 203.0 |
| 16 | Relaxation Delay | 1.0000 |
| 17 | Pulse Width | 12.1000 |
| 18 | Presaturation Frequency | |
| 19 | Acquisition Time | 3.1719 |
| 20 | Acquisition Date | 2012-01-12T09:41:00 |
| 21 | Modification Date | 2012-01-12T09:42:13 |
| 22 | Class | |
| 23 | Spectrometer Frequency | 500.13 |
| 24 | Spectral Width | 10330.6 |
| 25 | Lowest Frequency | -2092.6 |
| 26 | Nucleus | 1H |
| 27 | Acquired Size | 32768 |
| 28 | Spectral Size | 65536 |
| 29 | Digital Resolution | 0.16 |

**7a + 7b**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2 Title ST259 2HpartOxi4mer CDCl3.1.fid
3 Comment CDCl3 rt 1H
4 Origin Bruker BioSpin GmbH
5 Owner nmr
6 Site
7 Instrument spect
8 Author
9 Solvent CDCl3
10 Temperature 298.2
11 Pulse Sequence zg30
12 Experiment 1D
13 Probe 5 mm PABBO BB-1H/ D Z-GRD Z113652/ 0033
14 Number of Scans 16
15 Receiver Gain 90.5
16 Relaxation Delay 1.0000
17 Pulse Width 12.1000
18 Presaturation Frequency
19 Acquisition Time 3.1719
20 Acquisition Date 2012-03-07T22:08:23
21 Modification Date 2012-03-07T22:08:52
22 Class
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24 Spectral Width 10330.6
25 Lowest Frequency -2095.5
26 Nucleus 1H
27 Acquired Size 32768
28 Spectral Size 65536
29 Digital Resolution 0.16
OAc
OAc
f1 (ppm)