Supporting Information

Total Syntheses of Pyocyanin, Lavanducyanin, and Marinocyanins A and B

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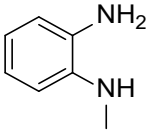
Index

1. General information

All solvents and reagents were used without further purification unless otherwise noted. Analytical TLC was performed using Silica gel 60 F_{254} plates (0.25 mm, normal phase, Merck) and Silica gel 60 RP-18 F_{254}s plates (0.25 mm, reversed phase, Merck). Flash column chromatography was performed using silica gel (particle size 40–63 μm; 230–400 mesh ASTM; SiliaFlash F60, SiliCycle Inc.). Reversed phase flash chromatography was performed using octadecylsilyl (ODS) silica gel (particle size 15–30 μm, FUJIFILM Wako Pure Chemical Co.), unless otherwise noted. Melting point (Mp) data were determined using a Shimadzu MM-2 instrument and were uncorrected. IR spectra were recorded on a Horiba FT-720 spectrometer, using NaCl (neat) or KBr pellets (solid). ^{1}H and proton-decoupled ^{13}C (^{13}C{1H}) NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 and 100 MHz, respectively), using chloroform-*d* ($CDCl_3$) and methanol-d_4 (CD_3OD) as solvent. Chemical shift values are expressed in δ (ppm) relative to tetramethylsilane (TMS, δ 0.00 ppm) or the residual solvent resonance ($CDCl_3$, δ 7.24 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR; CD_3OD, δ 3.30 ppm for ^{1}H NMR and δ 49.0 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (*J*; Hz), and integration. Mass spectra were obtained by a JEOL high-resolution double-focusing mass spectrometer using fast atom bombardment (FAB) or electron ionization (EI), or a Bruker low-resolution ion trap mass spectrometer using electrospray ionization (ESI). Analytical HPLC was performed with a Shimadzu HPLC system (system control: SCL-10A, UV detector: SPD-M10A, pump: LC-M10A) equipped with a TOSOH TSK-gel reversed phase chromatography column (ODS-100Z, 4.6 × 150 mm) column, by eluting with a gradient solvent system of MeOH : H_2O (40:60 to 100:0 over 30 min).

2. Detailed experimental procedures

***N*-methylbenzene-1,2-diamine (12a).**

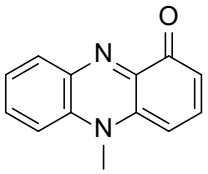


MeI (1.15 mL, 18.5 mmol) was added to a suspension of *o*-phenylendiamine (**6**) (3.01 g, 27.8 mmol) and K_2CO_3 (3.85 g, 27.9 mmol) in DMF (50 mL). The mixture was stirred at rt for 3 h. The reaction was quenched by the addition of water. The mixture was diluted with EtOAc. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by silica gel column chromatography (hexane/EtOAc = 3:1) to give **12a** (1.38 g, 61%) as a brown oil. The structure of **12a** was confirmed by comparison of the ^{1}H NMR spectrum with that of the same compound previously reported.[S1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97–6.93 (m, 1H), 6.80–6.72 (m, 3H), 3.38 (brs, 3H), 2.89 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 138.8, 134.0, 120.6, 118.3, 116.1, 110.8, 30.8; LRMS (ESI/ ion trap) *m*/*z*: 123 ($[M+H]^+$).

General Procedure of Oxidative Condensation between *N*-Methylbenzene-1,2-diamine (12a) and Pyrogallol (13) (Entries 1 and 2 in Table 1).

Oxidant (0.30 mmol) was added to a solution of **12a** (12.2 mg, 0.10 mmol) and **13** (12.6 mg, 0.10 mmol) in 2-propanol (0.8 mL) at 0 °C. The mixture was stirred at 0 °C until no further TLC changes were observed. The reaction was quenched by the addition of 1 M aqueous HCl solution. The mixture was diluted with $CHCl_3$. After the layers were separated, the aqueous layer was neutralized with a 4 M aqueous NaOH solution. The aqueous layer was extracted with $CHCl_3$ twice. The combined organic layer was dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by reversed phase flash chromatography ($MeOH/H_2O$ = 2/1).

Pyocyanin (1) (Entry 3 in Table 1).

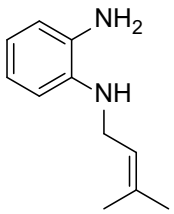


A solution of **12a** (12.2 mg, 0.10 mmol) and **13** (12.6 mg, 0.10 mmol) in 2-propanol (0.8 mL) was stirred under an O_2 atmosphere at rt in the dark for 2 days. The reaction was quenched by the addition of 1 M aqueous HCl solution. The mixture was diluted with $CHCl_3$. After the layers were separated, the aqueous layer was neutralized with a 4 M aqueous NaOH solution. The aqueous layer was extracted with $CHCl_3$ twice. The combined organic layer was dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by reversed phase flash chromatography ($MeOH/H_2O$ = 2/1) to give **1** (9.0 mg, 43%) as a dark blue solid. Mp = 127–128 °C (lit.[S2] 129–131 °C); IR (KBr) ν_{max} = 3087, 3064, 1631, 1602, 1562, 1492 cm^{-1}; H NMR (400 MHz, CD_3OD) δ 8.30 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.8 Hz, 1H), 8.04–7.96 (brm, 1H), 7.88 (t, J = 8.2 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 6.57 (d, J = 8.8 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 4.19 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, CD_3OD) δ 178.0, 146.6, 146.5, 137.8, 137.3, 136.0, 134.1, 133.6, 127.1, 116.4, 115.5, 94.4, 36.0; HRMS (FAB/ double-focusing MS) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2O$ 211.0871; Found 211.0870.

Synthesis of Pyocyanin (1) on 1.0 mmol Scale (Entry 4 in Table 1).

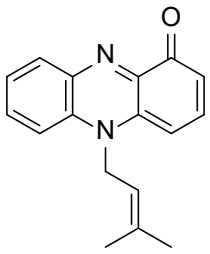
According to the same procedure as entry 3, the reaction was performed using **12a** (122 mg, 1.00 mmol) and **13** (126 mg, 1.00 mmol) in 2-propanol (8.0 mL) under an O_2 atmosphere at rt in the dark for 2 days to afford **1** (73.5 mg, 35%).

***N*-(3-methylbut-2-en-1-yl)benzene-1,2-diamine (12b).**



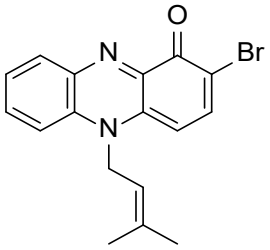
1-Bromo-3-methyl-2-butene (90% purity, 795 μL, 6.16 mmol) was added to a suspension of **6** (1.02 g, 9.43 mmol) and K_2CO_3 (1.33 g, 9.62 mmol) in DMF (25 mL). The mixture was stirred at rt for 25 min. The reaction was quenched by the addition of water. The mixture was diluted with EtOAc. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by silica gel column chromatography (hexane/EtOAc = 3:1) to give **12b** (692 mg, 69%) as a brown oil. IR (neat) ν_{max} = 3396, 3330, 3043, 2970, 2927, 2914, 2856, 1619, 1598, 1508 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (td, *J* = 7.4, 2.1 Hz, 1H), 6.72–6.66 (m, 3H), 5.38 (tt, *J* = 6.7, 1.4 Hz, 1H), 3.69 (d, *J* = 6.7 Hz, 2H), 3.21 (brd, 3H), 1.76 (d, *J* = 1.4 Hz, 3H), 1.72 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.9, 135.5, 134.2, 121.8, 120.6, 118.5, 116.3, 111.8, 42.2, 25.7, 18.0; HRMS (FAB/ double-focusing MS) *m*/*z*: $[M]^+$ Calcd for $C_{11}H_{16}N_2$ 176.1313; Found 176.1312.

5-(3-Methylbut-2-en-1-yl)phenazin-1(5*H*)-one (16).



A solution of **12b** (39.7 mg, 0.189 mmol) and **13** (23.8 mg, 0.189 mmol) in 2-propanol (1.5 mL) was stirred under an O_2 atmosphere at rt in the dark for 2 days. The reaction was quenched by the addition of a 1 M aqueous HCl solution. The mixture was diluted with $CHCl_3$. After the layers were separated, the aqueous layer was neutralized with a 4 M aqueous NaOH solution. The aqueous layer was extracted with $CHCl_3$ twice. The combined organic layer was dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by reversed phase flash chromatography (MeOH/H_2O = 2/1) to give **16** (28.1 mg, 45%) as a dark blue solid. Mp = 127–129 °C; IR (KBr) ν_{max} = 3062, 2910, 1631, 1600, 1493, 1464 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.97 (brd, 1H), 7.92–7.75 (m, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 5.28 (brd, 2H), 5.18 (brd, 1H), 2.02 (s, 3H), 1.79 (d, *J* = 1.1 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, CD_3OD) δ 178.4, 147.3, 146.8, 140.1, 138.2, 137.5, 135.6, 134.0, 133.7, 127.3, 117.5, 116.5, 115.6, 94.5, 48.2*, 25.6, 18.7 (*This carbon signal was not observed in the ^{13}C NMR spectrum, and assigned based on the HMQC spectrum.); HRMS (FAB/ double-focusing MS) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O$ 265.1341; Found 265.1339.

Marinocyanin B (4).

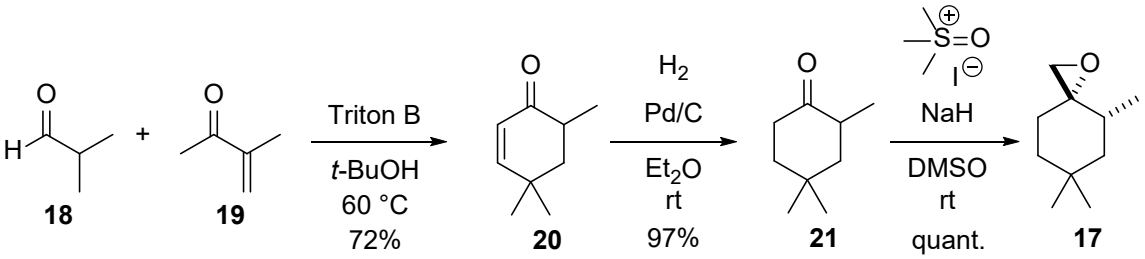


NBS (7.70 mg, 43.1 μmol) was added to a solution of **16** (11.4 mg, 43.1 μmol) in CH_2Cl_2 (4.0 mL). The mixture was stirred at 0 °C for 10 min. The reaction was quenched by the addition of a saturated aqueous $NaHCO_3$ solution. The mixture was diluted with $CHCl_3$. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by reversed phase flash chromatography (MeOH/H_2O = 2/1) to give **4** (11.1 mg, 76%) as a dark blue solid. Mp = 126–127 °C; IR (KBr) ν_{max} = 3043, 2974, 2918, 2850, 1718, 1622, 1562, 1491 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 8.34 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.09–8.04 (m, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.76–7.72 (m, 1H), 6.40 (d, *J* = 8.8 Hz, 1H), 5.38 (d, *J* = 5.5 Hz, 2H), 5.20 (brs, 1H), 2.03 (s, 3H), 1.80 (d, *J* = 0.9 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, CD_3OD) δ 172.1, 147.6, 146.0, 140.4, 139.0, 138.1, 135.3, 134.1, 133.5, 128.0, 117.4, 116.9, 109.0, 94.8, 48.7*, 25.6, 18.7 (*This carbon signal was assigned based on the HMQC spectrum.); HRMS (FAB/ double-focusing MS) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}BrN_2O$ 343.0446; Found 343.0445.

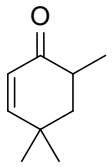
Synthesis of epoxide 17.

The synthesis of epoxide is shown in Scheme S1. Robinson annulation between 2-methylpropanal (**18**) and 3-methyl-3-buten-2-one (**19**) gave cyclohexenone **20** in 72% yield.[S3] Hydrogenation of **20**, followed by a Corey-Chaykovsky reaction of the resultant ketone **21** gave epoxide **17**.[S4] The relative configuration of **17** was determined by NOESY correlations as shown in Figures S1 and S2.

Scheme S1. Synthesis of Epoxide 17

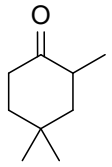


4,4,6-Trimethylcyclohex-2-en-1-one (**20**).



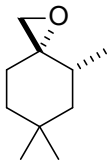
Triton B (a 40% solution in methanol, 1.40 mL, 3.47 mmol) was added dropwise to a solution of **18** (503 mg, 6.98 mmol) and **19** (581 mg, 6.91 mmol) in *tert*-butyl alcohol (5.0 mL). The mixture was stirred at 60 °C for 2.5 h. The reaction was quenched by the addition of a saturated aqueous NH_4Cl solution. The mixture was diluted with Et_2O. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by distillation at 45–60 °C (18 mmHg) to give **20** (688 mg, 72%) as a colorless oil. IR (neat) ν_{max} = 3022, 2962, 2931, 2870, 1685, 1621, 1469, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 10.0, 2.2 Hz, 1H), 5.81 (d, *J* = 10.0 Hz, 1H), 2.54 (dqd, *J* = 13.6, 6.7, 4.8 Hz, 1H), 1.82 (ddd, *J* = 13.6, 4.8, 2.2 Hz, 1H), 1.67 (t, *J* = 13.6 Hz, 1H), 1.21 (s, 3H), 1.14 (s, 3H), 1.12 (d, *J* = 6.7 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.0, 158.7, 126.4, 45.0, 37.6, 33.6, 30.5, 25.4, 14.9; HRMS (EI/ double-focusing MS) *m*/*z*: $[M]^+$ Calcd for $C_9H_{14}O$ 138.1045; Found 138.1045.

2,4,4-Trimethylcyclohexan-1-one (**21**).



A solution of **20** (17.4 g, 0.13 mol) was added to Pd/C (10%, 1.38 g, 1.3 mmol) in Et_2O (0.15 L) was stirred under a H_2 atmosphere at rt for 16 h. The mixture was filtered through Celite and was washed with Et_2O. The resultant mixture was concentrated to give **21** (17.1 g, 97%) as a colorless oil. IR (neat) ν_{max} = 2958, 2929, 2869, 1714, 1469, 1456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.56–2.42 (m, 2H), 2.29–2.21 (m, 1H), 1.78–1.69 (m, 2H), 1.63 (td, *J* = 13.3, 4.6 Hz, 1H), 1.36 (t, *J* = 13.3 Hz, 1H), 1.21 (s, 3H), 1.02–1.00 (m, 3H), 0.98 (d, *J* = 6.5 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 214.0, 48.9, 40.7, 40.0, 38.1, 31.4, 30.8, 24.4, 14.5; HRMS (EI/ double-focusing MS) *m*/*z*: $[M]^+$ Calcd for $C_9H_{16}O$ 140.1201; Found 140.1200.

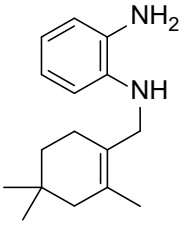
4,6,6-Trimethyl-1-oxaspiro[2.5]octane (**17**).



NaH (a 60% suspension in mineral oil, 610 mg, 15.3 mmol) was added to a solution of trimethylsulfoxonium iodide (3.50 g, 15.7 mmol) in DMSO (30 mL). Then a solution of **21** (2.01 g, 14.3 mmol) in DMSO (10 mL) was

added to the mixture. The resultant mixture was stirred at rt for 1 day. The reaction was quenched by the addition of water. The mixture was diluted with Et_2O. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give **17** (2.27 g, quant.) as a colorless oil. IR (neat) ν_{max} = 3006, 2951, 2910, 2866, 1506, 1448 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.83 (d, *J* = 4.5 Hz 1H), 2.46 (d, *J* = 4.5 Hz, 1H), 2.09–2.00 (m, 2H), 1.54 (td, *J* = 13.7, 4.2 Hz, 1H), 1.37–1.33 (m, 1H), 1.32–1.25 (m, 2H), 1.13 (ddd, *J* = 14.0, 4.2, 2.6 Hz, 1H), 1.00 (s, 3H), 0.95 (s, 3H), 0.68 (d, *J* = 6.7 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 60.2, 50.6, 46.0, 36.5, 32.6, 30.9 (2C), 29.3, 24.3, 14.2; HRMS (EI/ double-focusing MS) *m*/*z*: $[M]^+$ Calcd for $C_{10}H_{18}O$ 154.1358; Found 154.1352.

***N*-((2,4,4-trimethylcyclohex-1-en-1-yl)methyl)benzene-1,2-diamine (12c).**

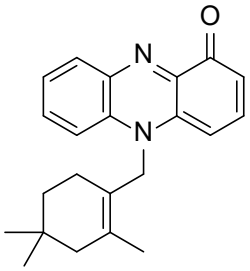


TfOH (57 μL, 0.64 mmol) was added to a solution of **17** (1.00 g, 6.48 mmol) and pyridine (52 μL, 0.65 mmol) in THF (20 mL). The mixture was stirred at 40 °C for 1.5 h. The reaction was quenched by the addition of a saturated aqueous NH_4Cl solution. The mixture was diluted with Et_2O. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a crude alcohol. This compound was used without purification for the next reaction.

PBr_3 (305 μL, 3.24 mmol) was added to a solution of the crude alcohol and pyridine (52 μL, 0.65 mmol) in Et_2O (20 mL). The mixture was stirred at −78 °C for 20 min. The resultant mixture was allowed to warm up to rt. The mixture was stirring for 1.5 h. The reaction was quenched by the addition of water. The mixture was diluted with Et_2O. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a crude **11**. This compound was used without purification for the next reaction.

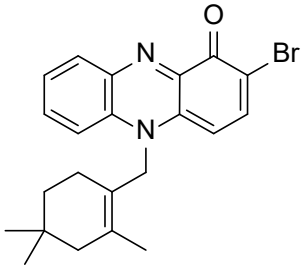
A solution of the crude **11** in DMF (10 mL) was added to a solution of **6** (1.13 g, 10.4 mmol) and K_2CO_3 (1.31 g, 9.78 mmol) in DMF (10 mL). The mixture was stirred at rt for 14 min. The reaction was quenched by the addition of water. The mixture was diluted with EtOAc. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by silica gel column chromatography (toluene/EtOAc = 9:1) to give **12c** (375 mg, 23% over three steps) as a brown oil. IR (neat) ν_{max} = 3396, 3334, 3046, 2948, 2908, 2865, 1733, 1619, 1596, 1506 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (td, *J* = 6.3, 1.7 Hz, 1H), 6.73–6.65 (m, 3H), 3.66 (s, 2H), 3.27 (brs, 3H), 2.16–2.09 (m, 2H), 1.77 (s, 2H), 1.69 (s, 3H), 1.36 (t, *J* = 6.5 Hz, 2H), 0.89 (s, 6H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.4, 134.0, 129.4, 126.1, 120.7, 118.3, 116.3, 111.6, 46.1, 46.2, 35.8, 29.1, 28.2 (2C), 26.4, 19.2; HRMS (FAB/ double-focusing MS) *m*/*z*: $[M]^+$ Calcd for $C_{16}H_{24}N_2$ 244.1939; Found 244.1938.

Lavanducyanin (2).



A solution of **12c** (30.1 mg, 0.123 mmol) and **13** (15.5 mg, 0.123 mmol) in 2-propanol (1.0 mL) was stirred under an O_2 atmosphere at rt in the dark for 1 day. The reaction was quenched by the addition of water. The mixture was diluted with $CHCl_3$. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH =50/1) to give **2** (15.8 mg, 39%) as a dark blue solid. Mp = 140–141 °C (lit.[S5] 161–162 °C); IR (KBr) ν_{max} = 2947, 2915, 2850, 1720, 1635, 1572, 1498 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.75 (t, *J* = 7.1 Hz, 1H), 7.58 (dd, *J* = 9.2, 8.5 Hz, 1H), 7.28 (d, *J* = 5.4 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 6.55 (d, *J* = 9.2 Hz, 1H), 5.86 (d, *J* = 7.6 Hz, 1H), 5.02 (s, 2H), 1.89 (brs, 5H), 1.60–1.52 (brm, 2H), 1.21 (t, *J* = 6.5 Hz, 2H), 0.84 (s, 6H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.8, 147.5, 143.3, 135.8, 135.1, 134.6, 133.9, 133.6, 130.9, 124.4, 121.3, 117.2, 113.3, 91.4, 49.6, 46.2, 34.9, 28.9, 28.0 (2C), 22.8, 19.4; HRMS (FAB/ double-focusing MS) *m*/*z*: $[M+H]^+$ Calcd for $C_{22}H_{25}N_2O$ 333.1967; Found 333.1967.

Marinocyanin A (3).



NBS (10.1 mg, 56.7 μmol) was added to a solution of **2** (17.9 mg, 53.8 μmol) in CH_2Cl_2 (1.0 mL). The mixture was stirred at 0 °C for 7 min. The reaction was quenched by the addition of a saturated aqueous $NaHCO_3$ solution. The mixture was diluted with $CHCl_3$. After the layers were separated, the organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give a residue. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH =50/1) to give **3** (13.6 mg, 61%) as a dark blue solid. Mp = 144–145 °C (lit.[S6] 160 °C); IR (KBr) ν_{max} = 2950, 2920, 2862, 1720, 1626, 1606, 1560, 1489, 1466 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 8.30–8.01 (brm, 4H), 7.72 (s, 1H), 6.35 (s, 1H), 5.48 (s, 2H), 1.98 (s, 3H), 1.89 (s, 2H), 1.43–1.35 (brm, 2H), 1.16 (t, *J* = 6.4 Hz, 2H), 0.80 (s, 6H); ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.57–7.50 (m, 2H), 5.84 (d, *J* = 8.6 Hz, 1H), 5.10 (s, 2H), 1.91 (s, 3H), 1.88 (s, 2H), 1.51–1.42 (brm, 2H), 1.18 (t, *J* = 6.3 Hz, 2H), 0.82 (s, 6H); $^{13}C\{1H\}$ NMR (100 MHz, CD_3OD) δ

172.3, 147.5, 145.8, 138.7, 138.0, 135.8, 134.4, 134.1, 132.8, 128.0, 122.2, 116.9, 109.2, 94.8, 52.2, 47.2, 35.9, 29.8, 28.3 (2C), 23.7, 19.7; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 145.7, 144.3, 136.3, 135.4, 134.4, 134.0, 133.1, 131.5, 125.1, 120.8, 113.8, 110.0, 91.5, 50.2, 46.2, 34.8, 28.9, 27.9 (2C), 22.7, 19.5; HRMS (FAB/ double-focusing MS) *m*/*z*: $[M+H]^+$ Calcd for $C_{22}H_{24}BrN_2O$ 411.1072; Found 411.1069.

3. Determination of the relative configuration of 17

Figure S1. Selected NOESY correlations in **17**.

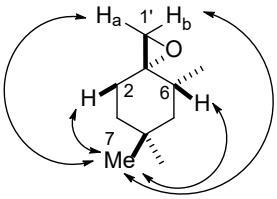
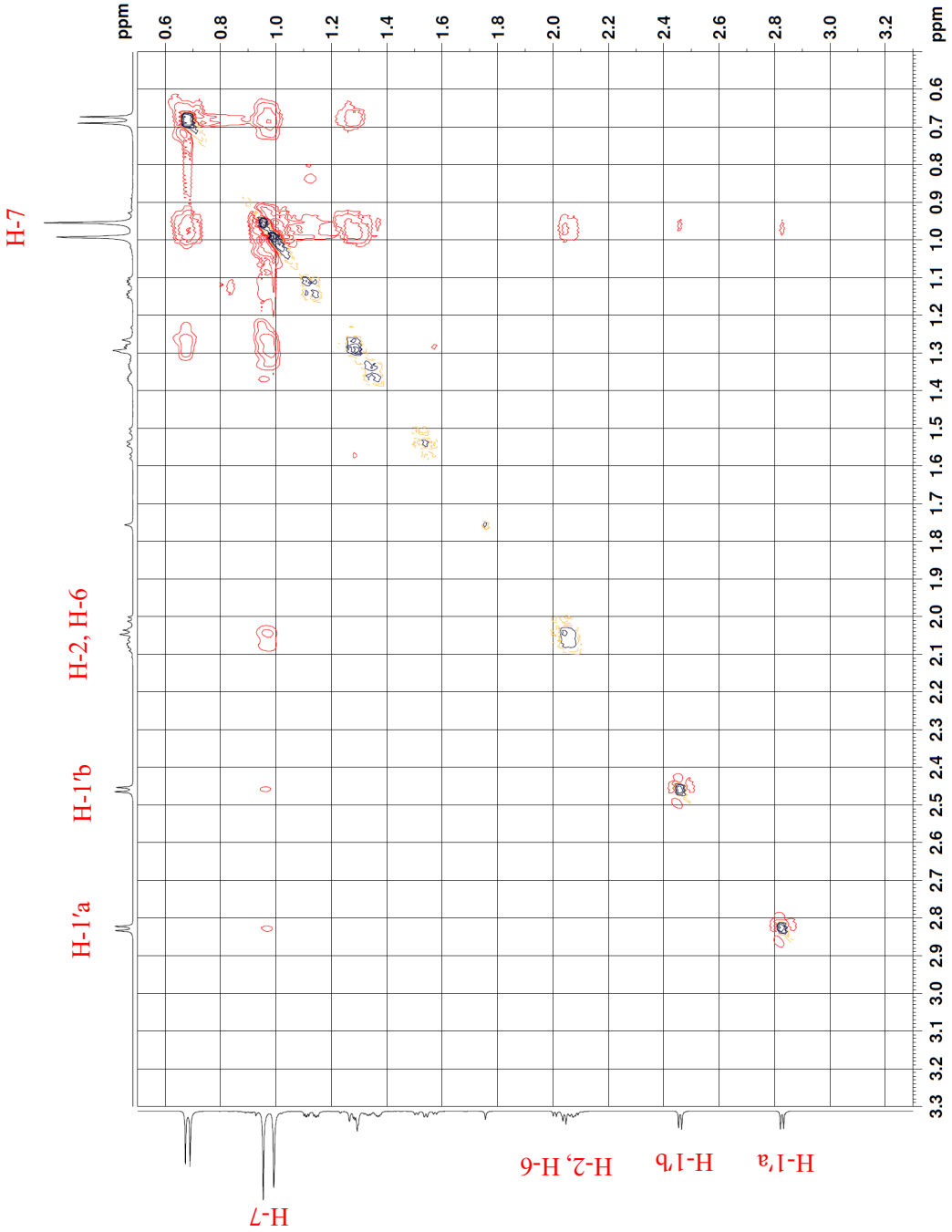


Figure S2. NOESY spectrum of **17**.



4. ^{1}H and ^{13}C NMR spectroscopic data

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12a**.

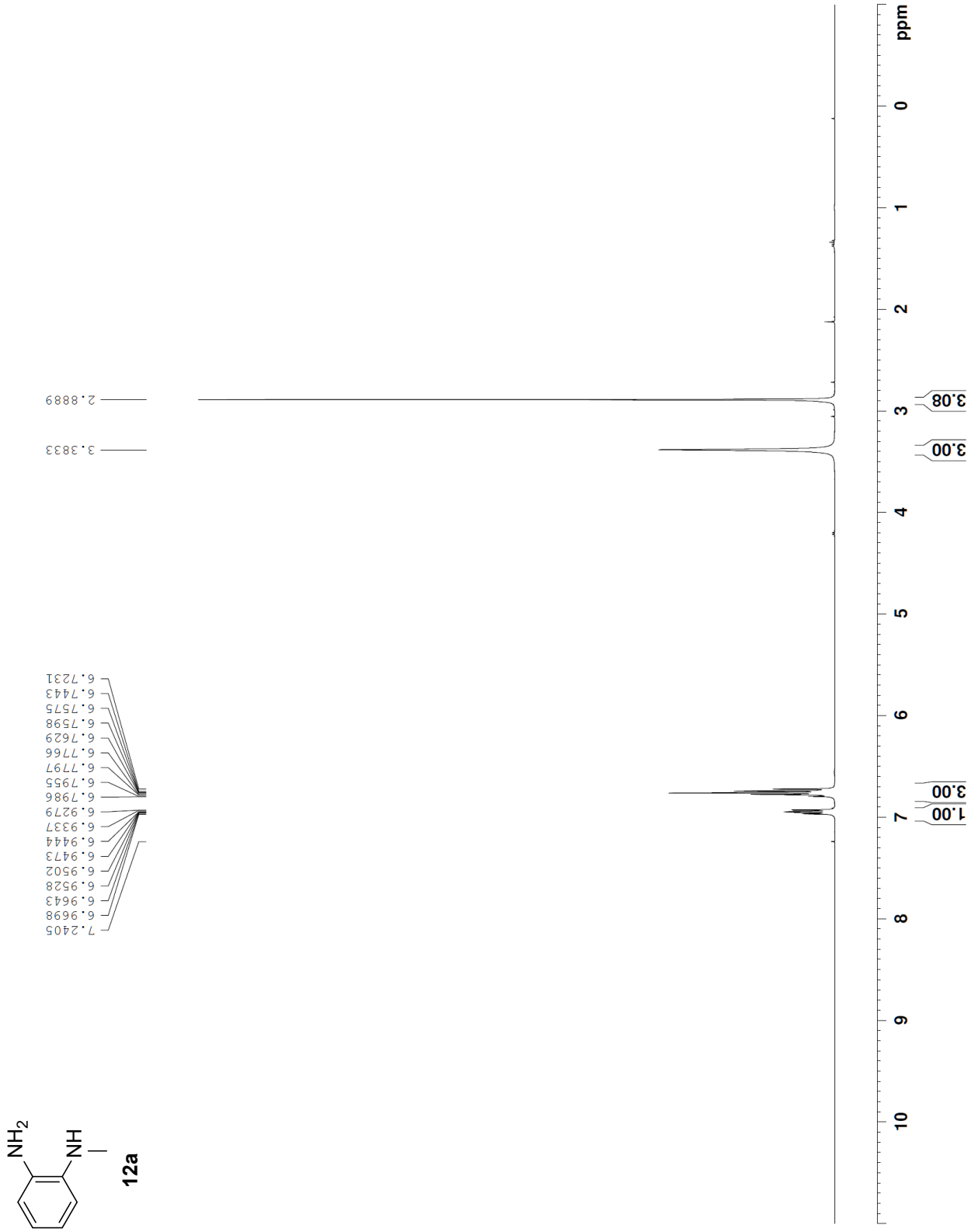


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **12a**.

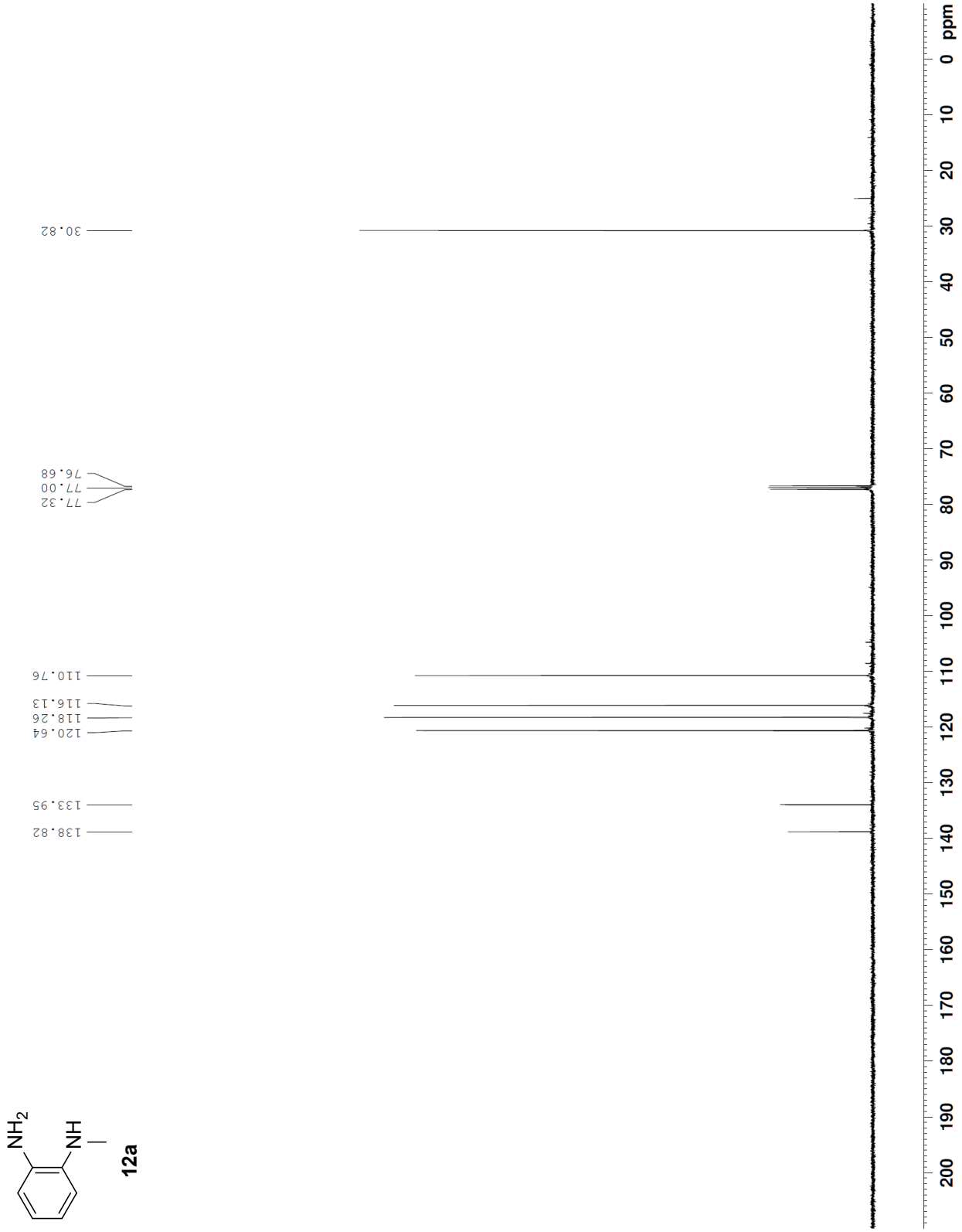


Figure S5. ^{1}H NMR spectrum (400 MHz, CD_3OD) of **1**.

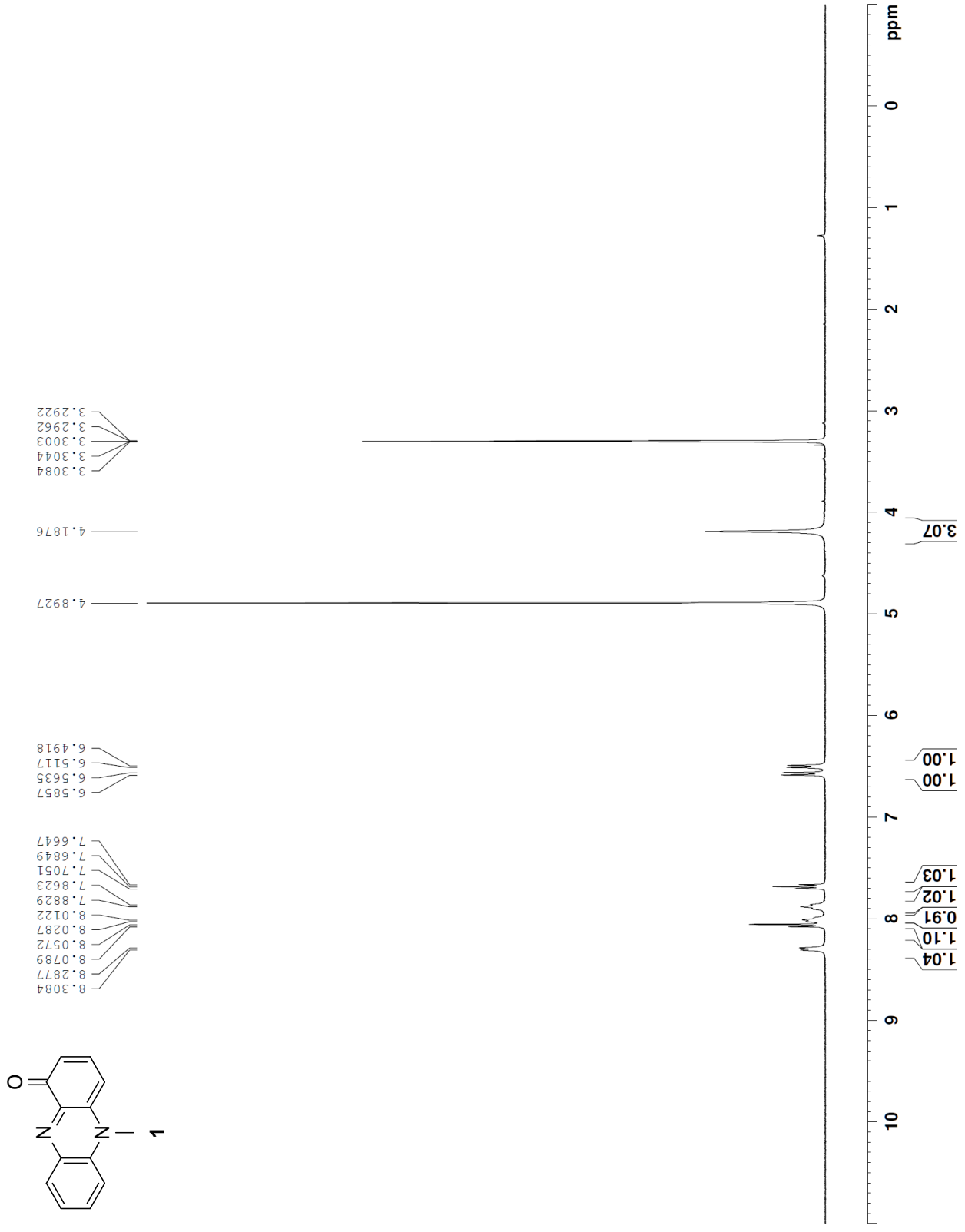


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3OD) of **1**.

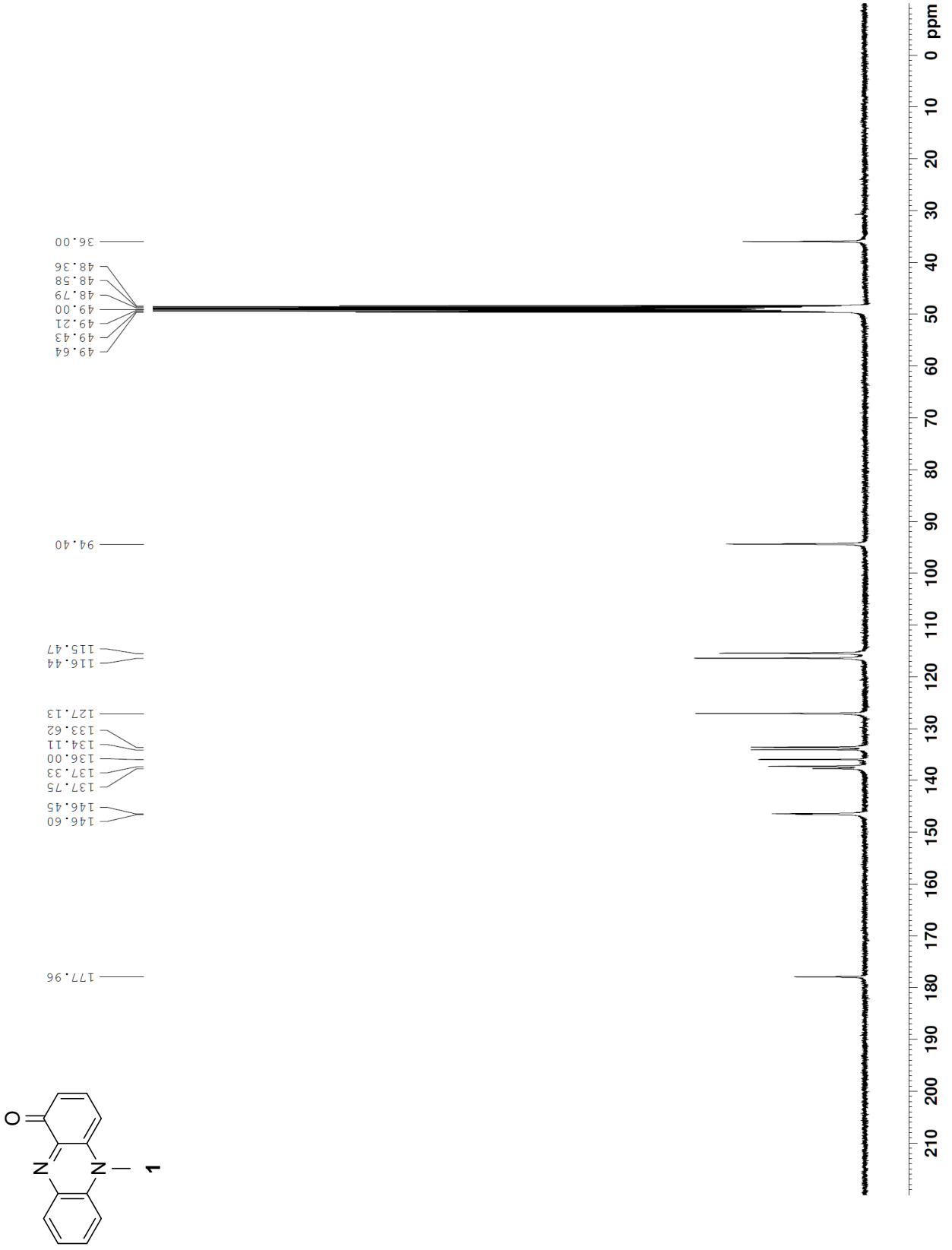


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12b**.

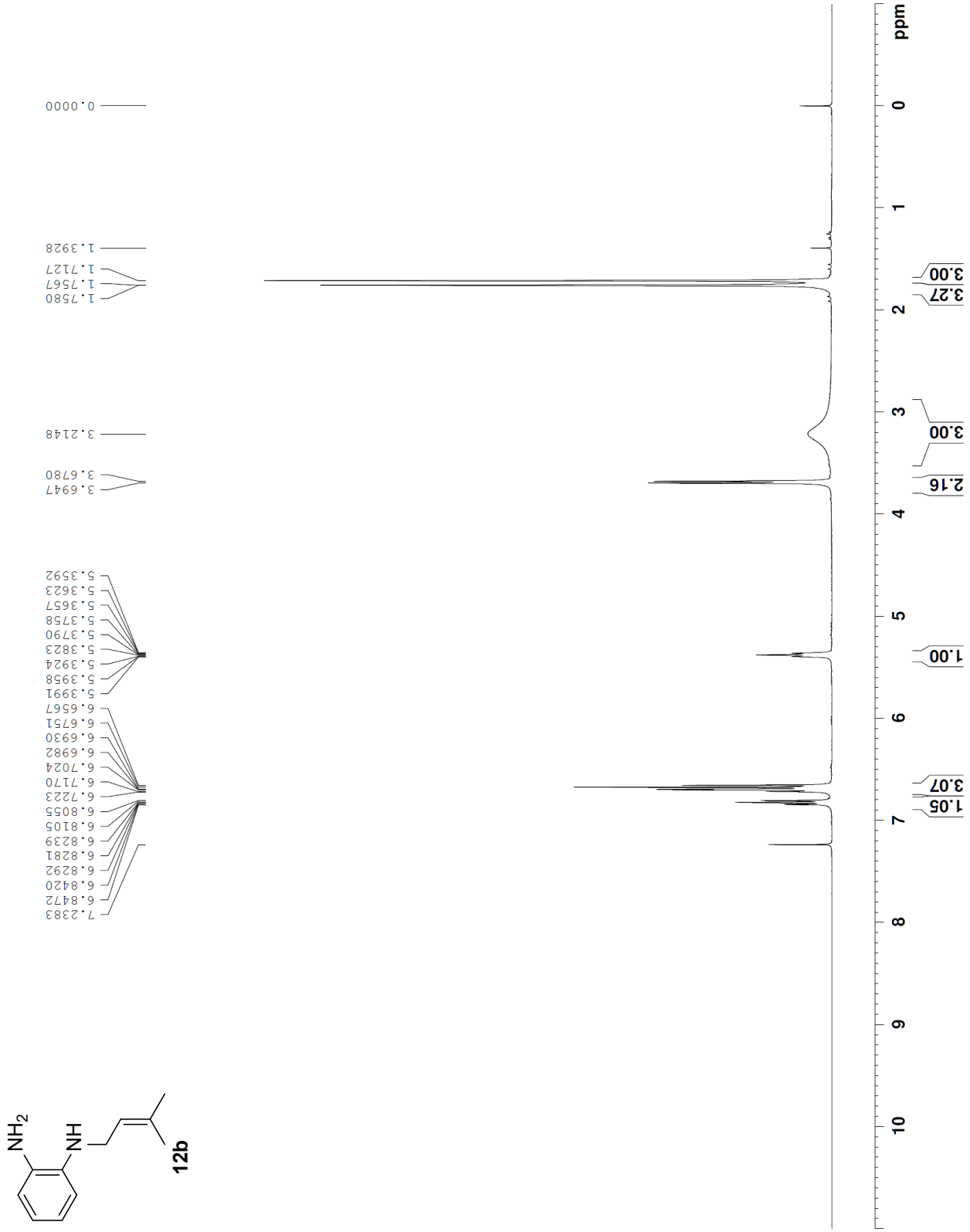


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **12b**.

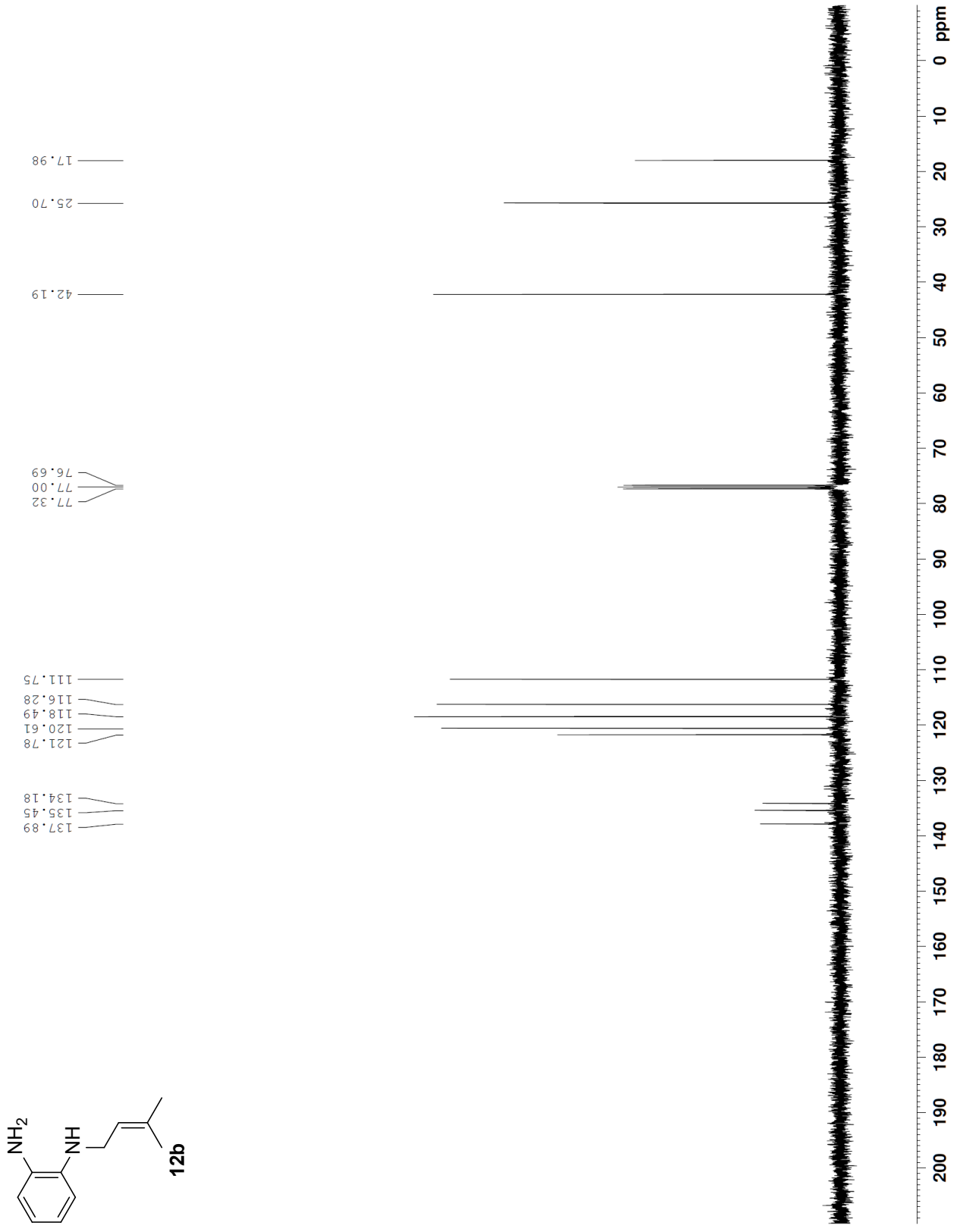


Figure S9. ^{1}H NMR spectrum (400 MHz, CD_3OD) of **16**.

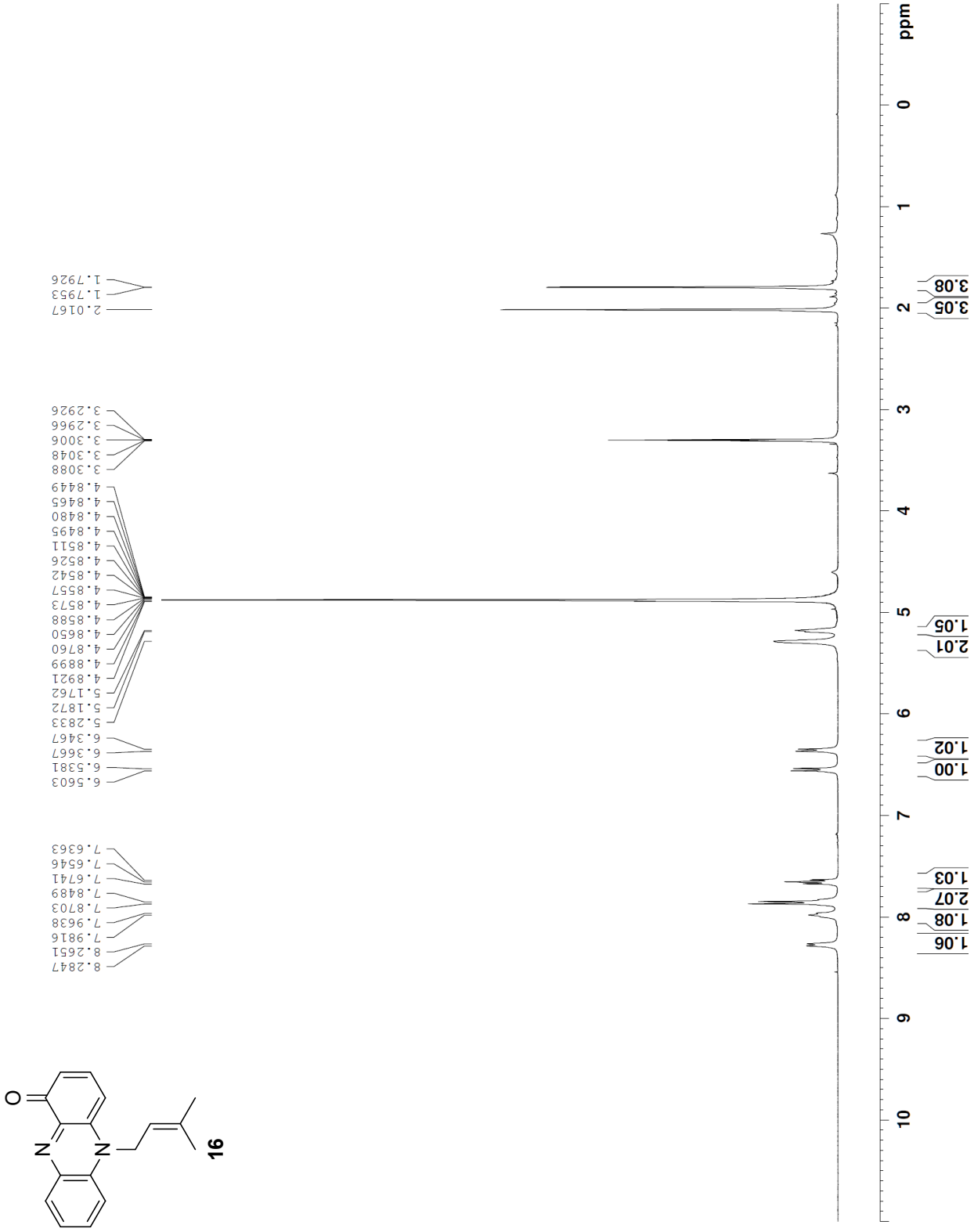


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3OD) of **16**.

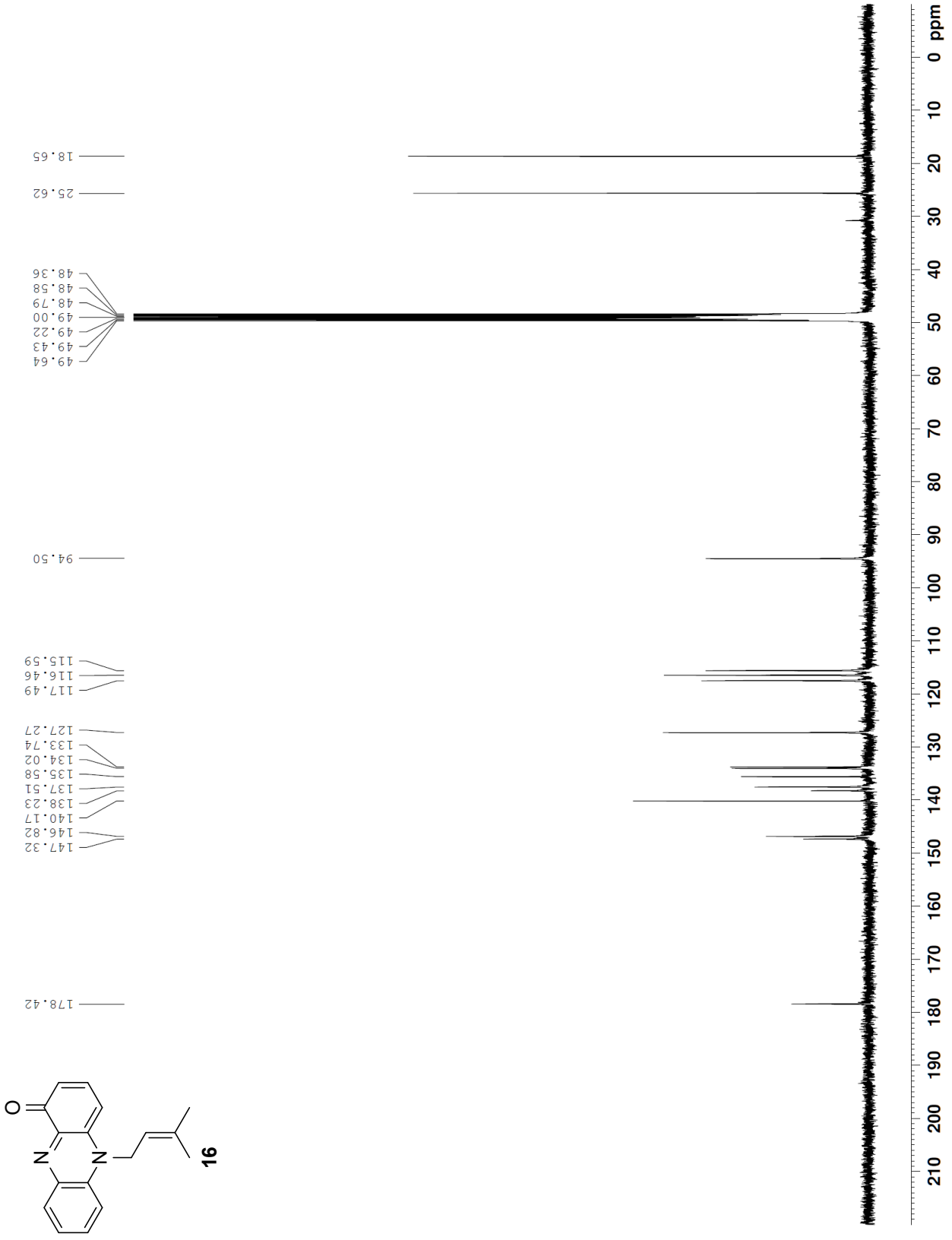


Figure S11. ^{1}H NMR spectrum (400 MHz, CD_3OD) of **4**.

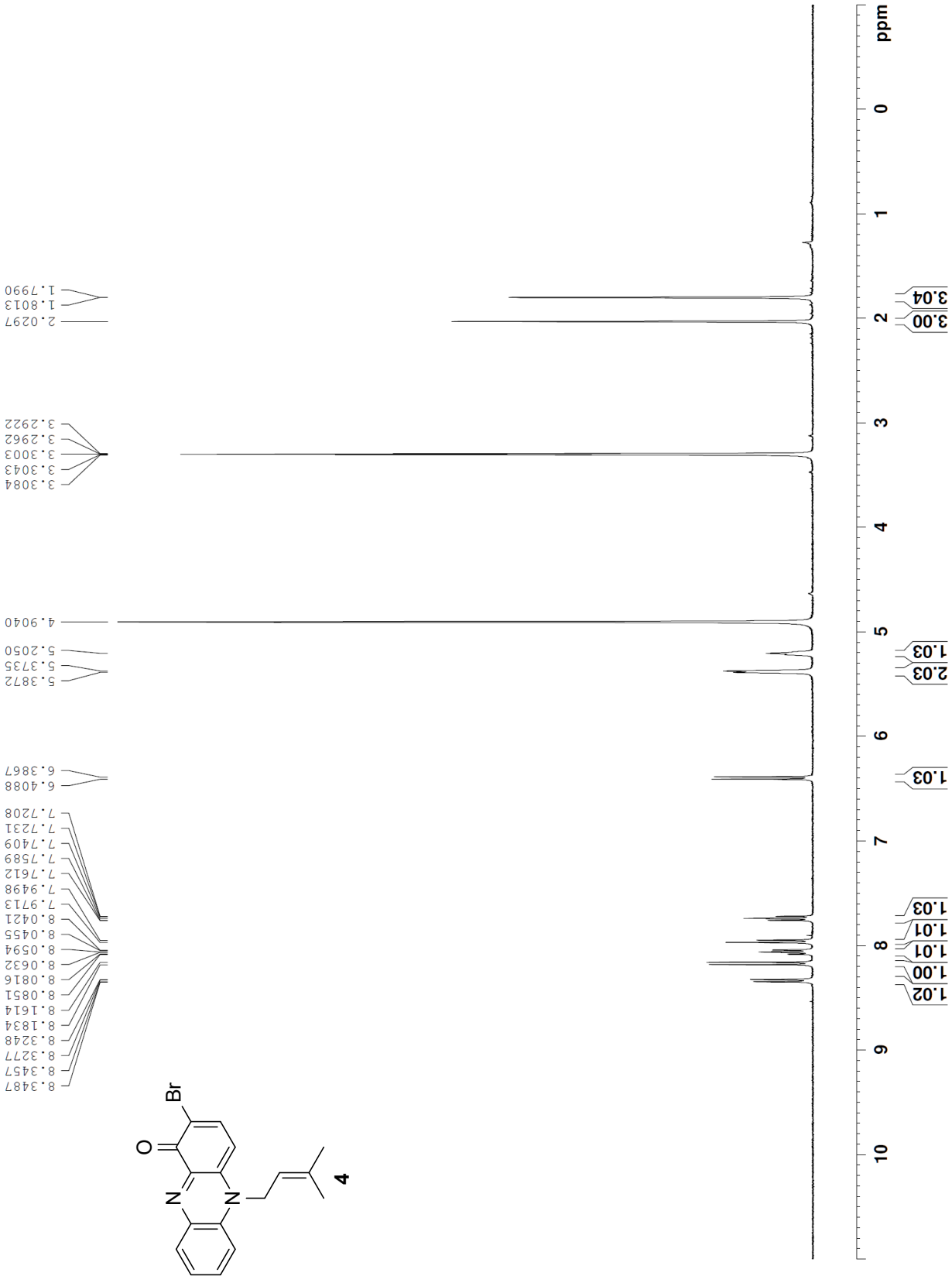


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3OD) of **4**.

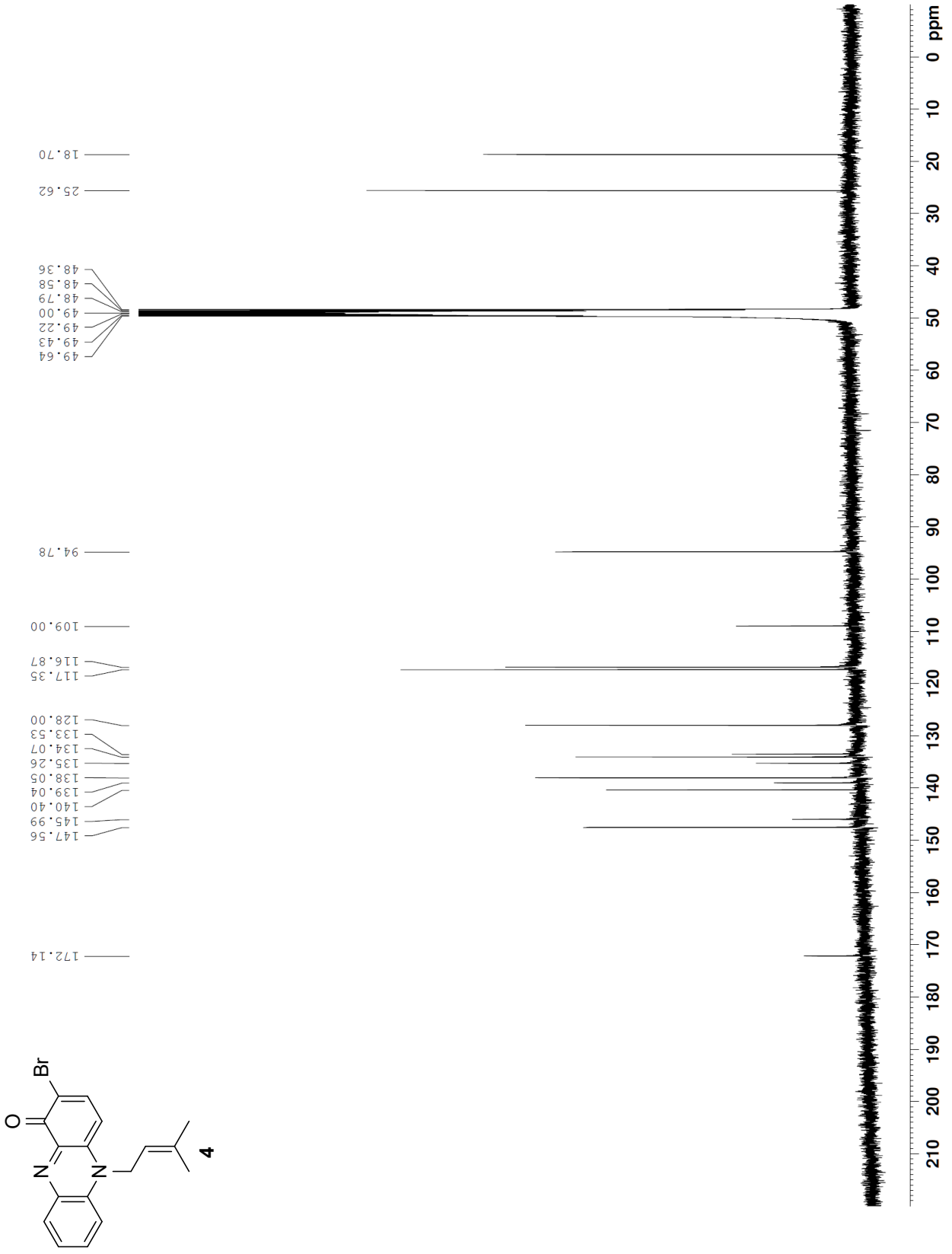


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **20**.

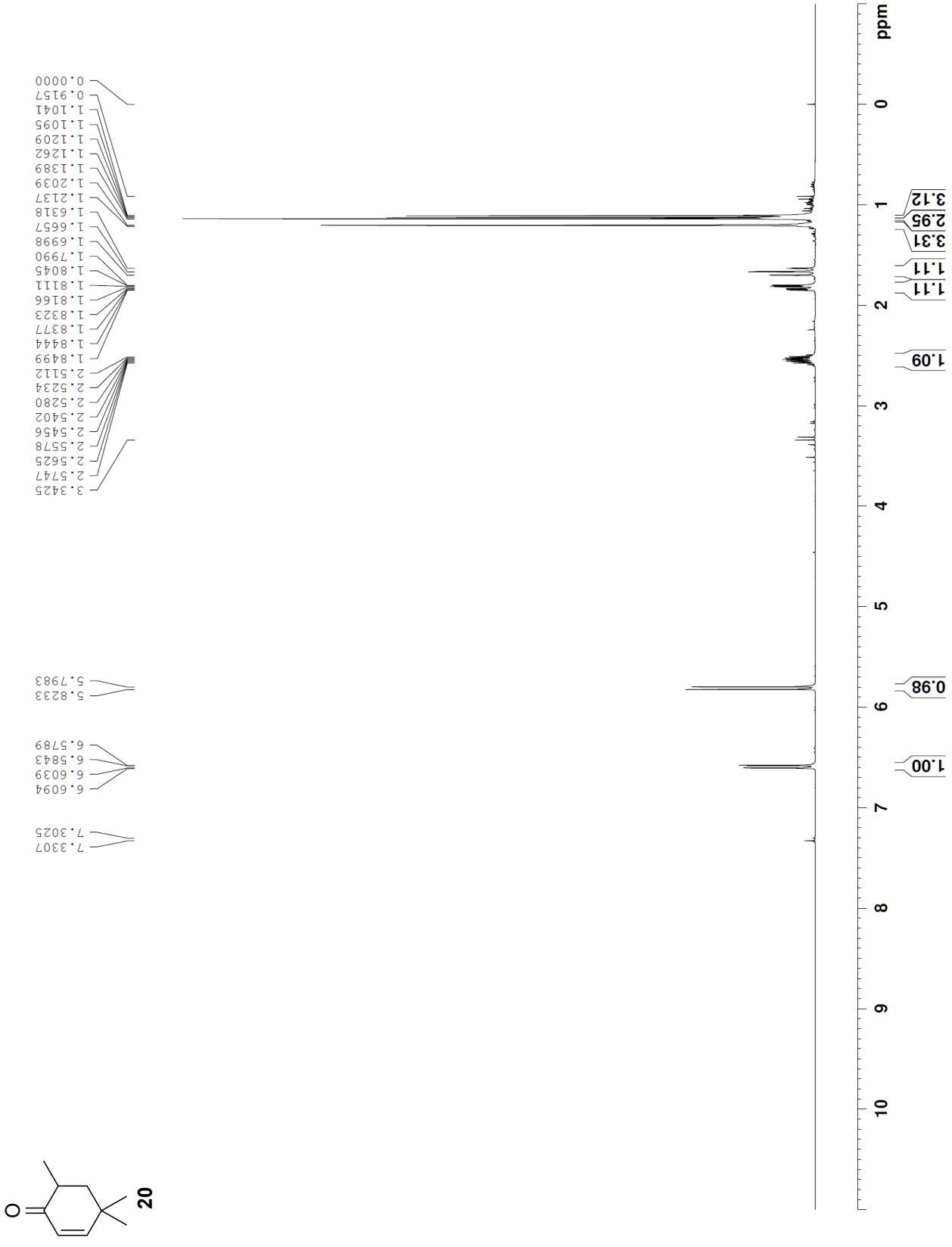


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **20**.

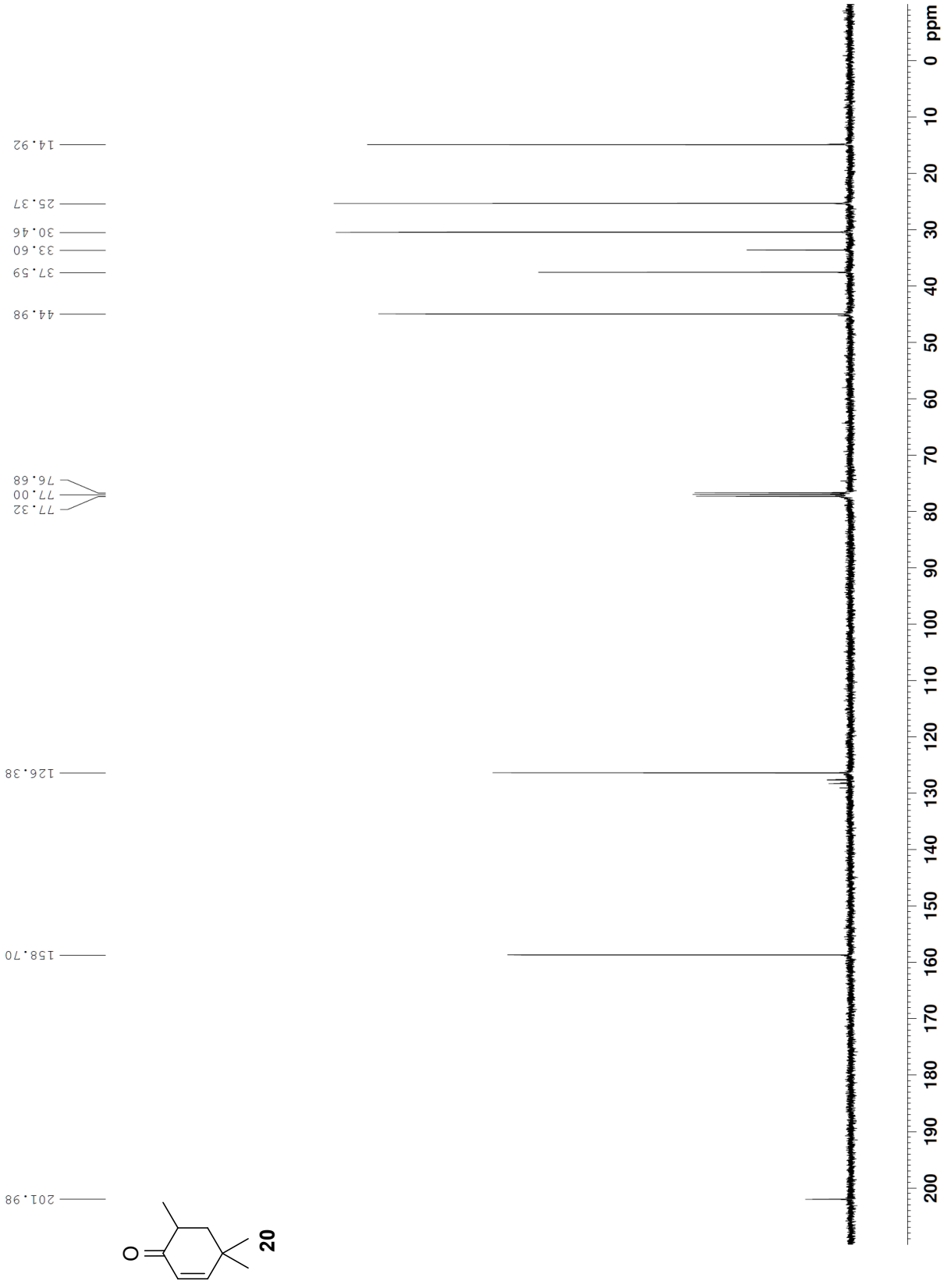


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **21**.

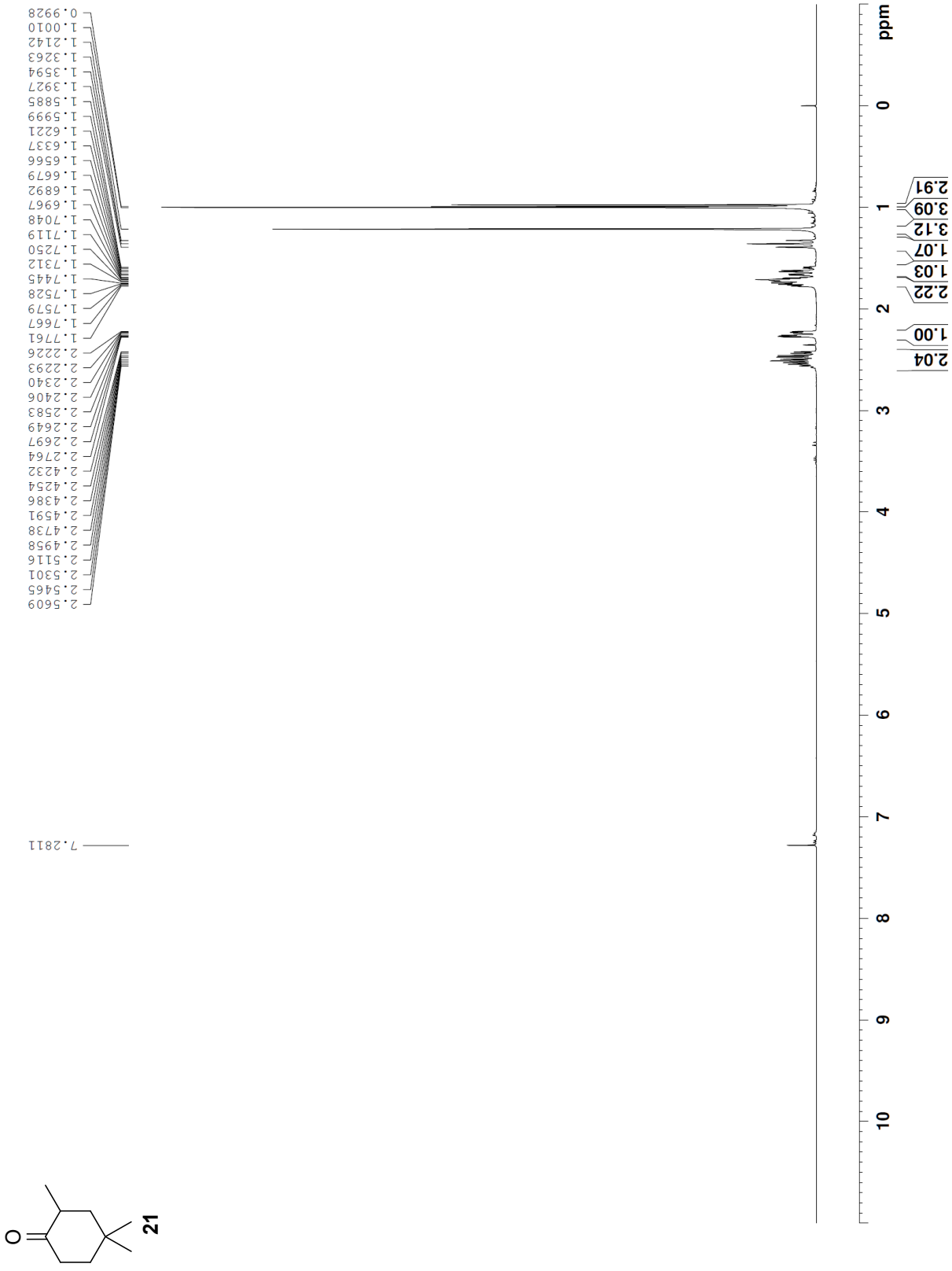
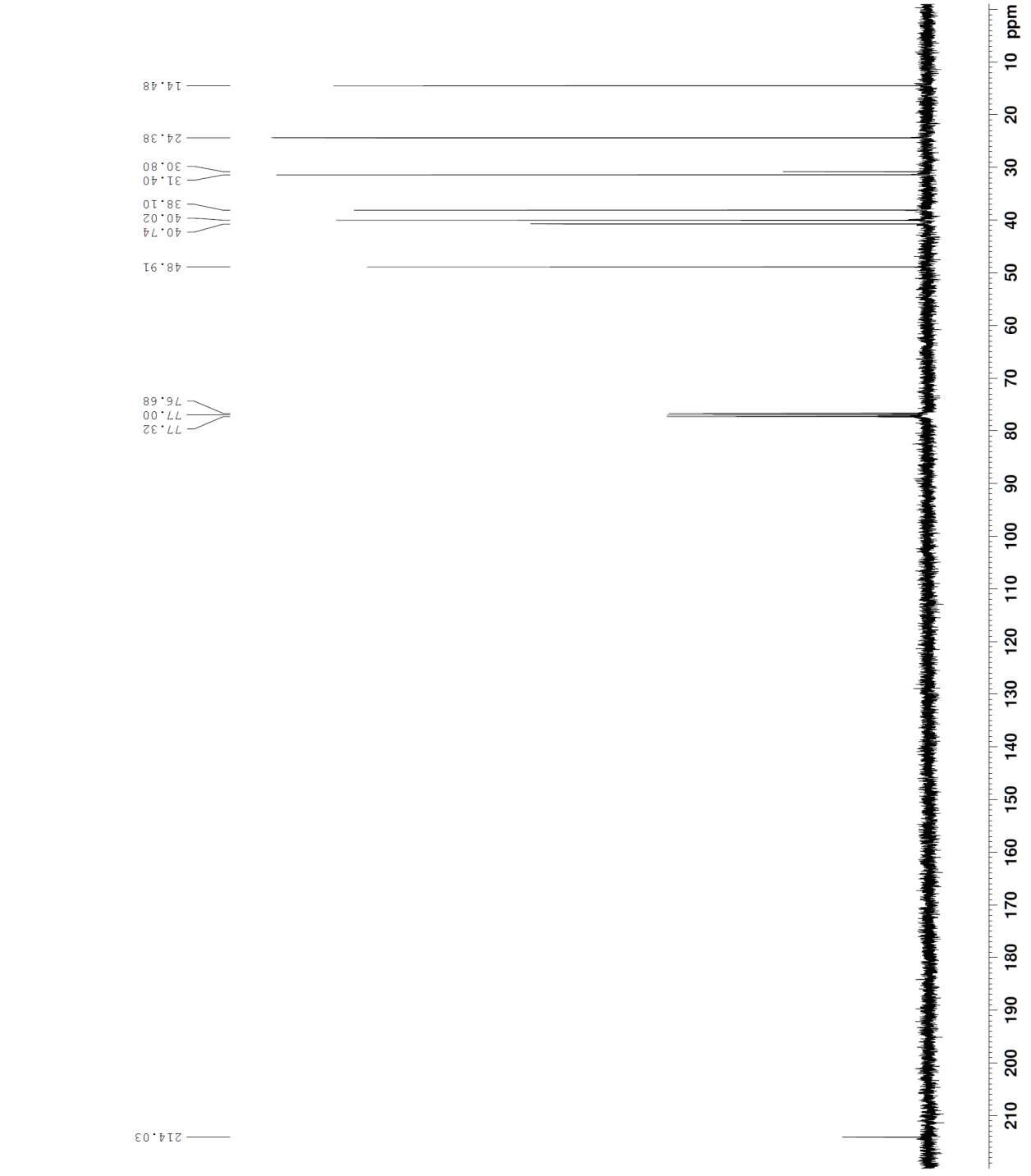


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **21**.



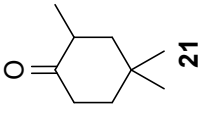


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **17**.

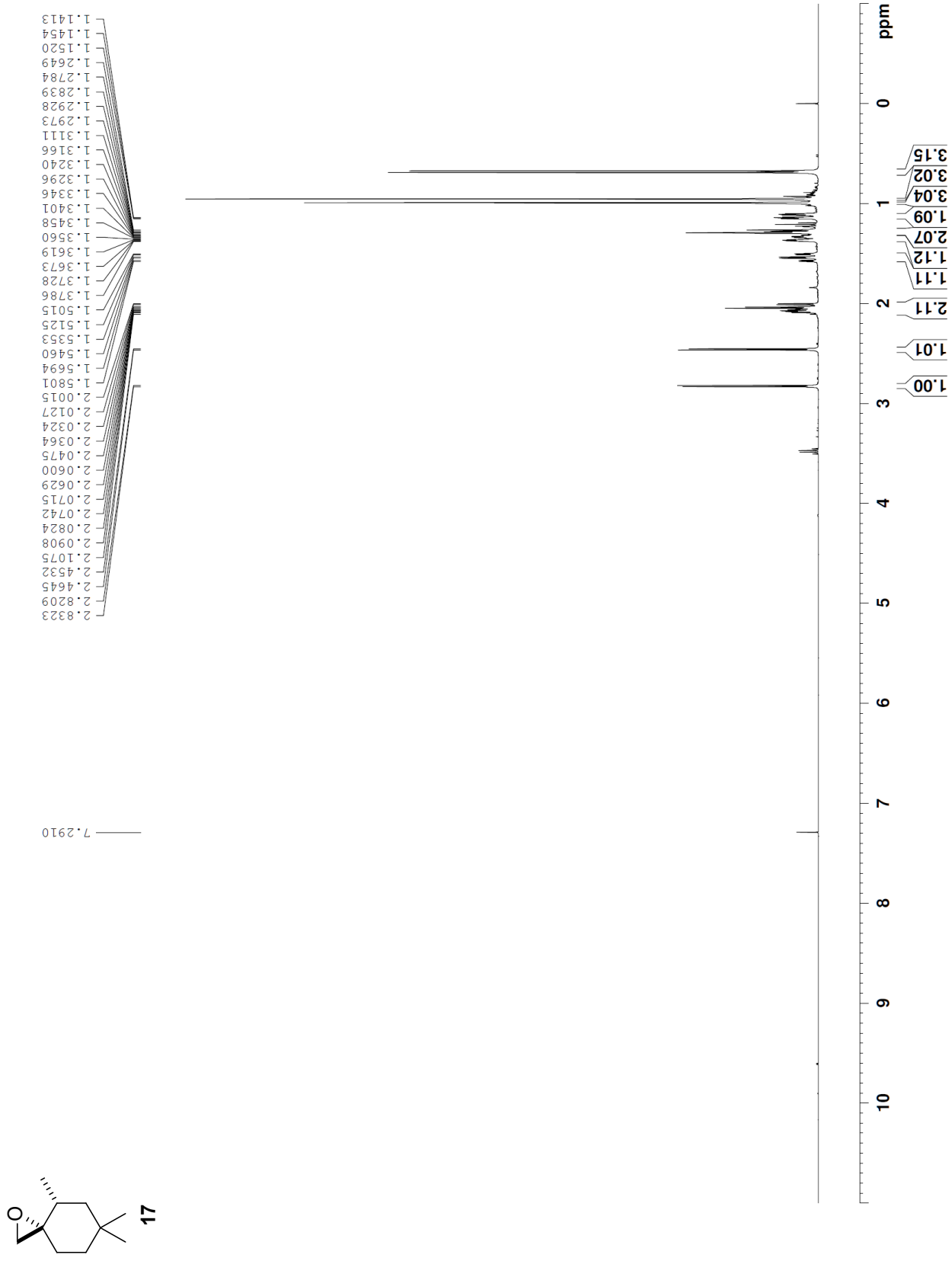


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **17**.

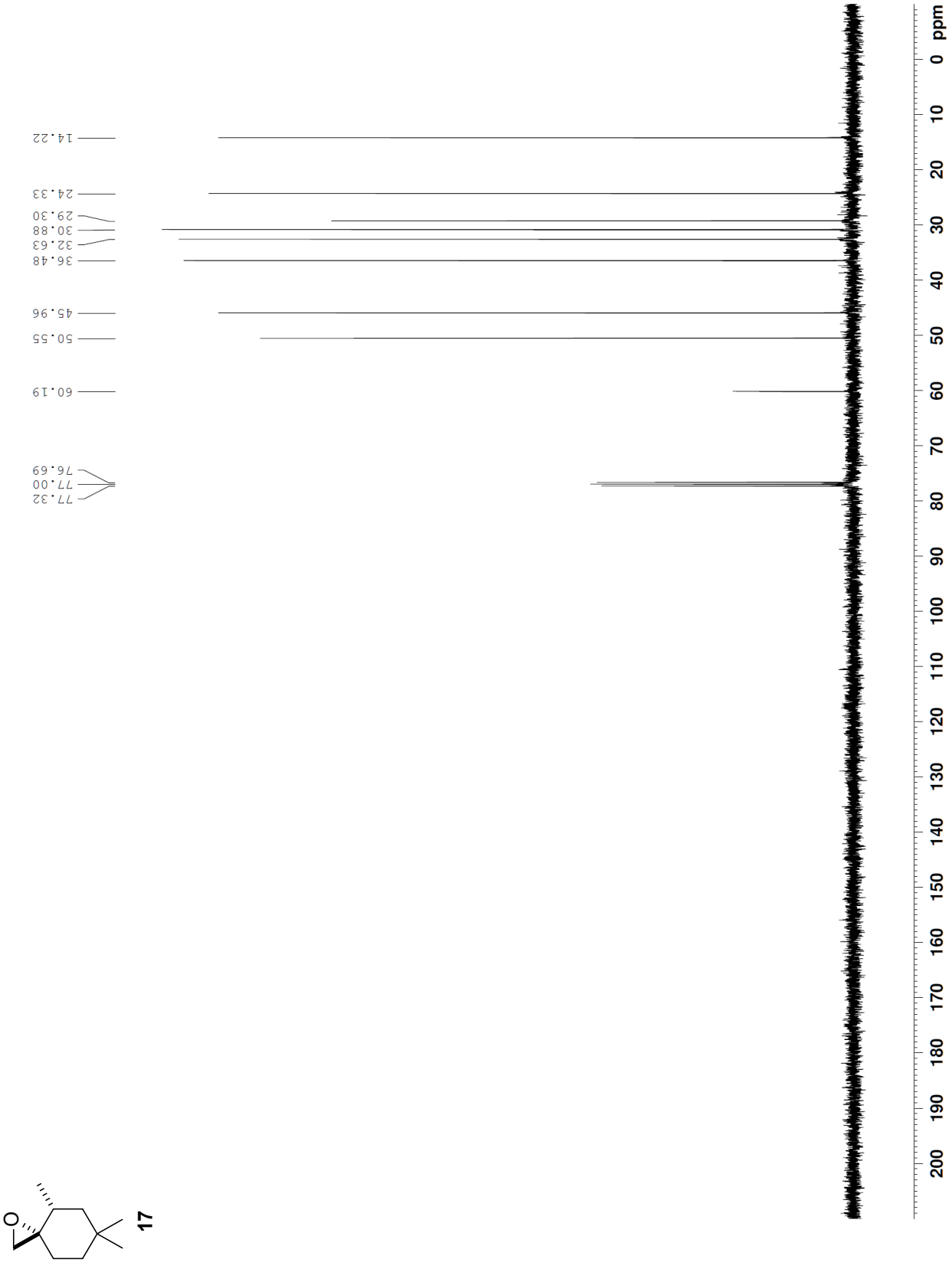


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12c**.

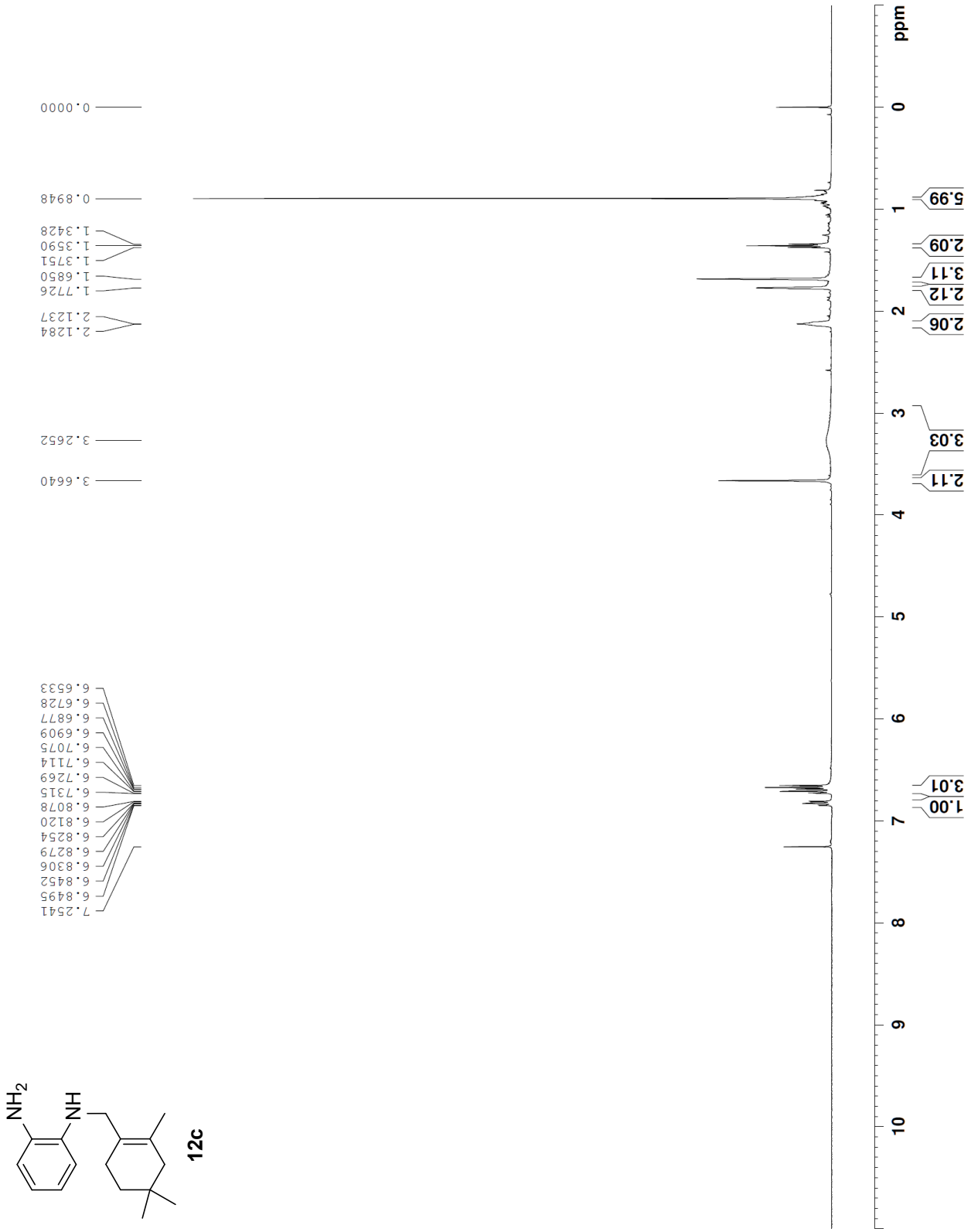


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **12c**.

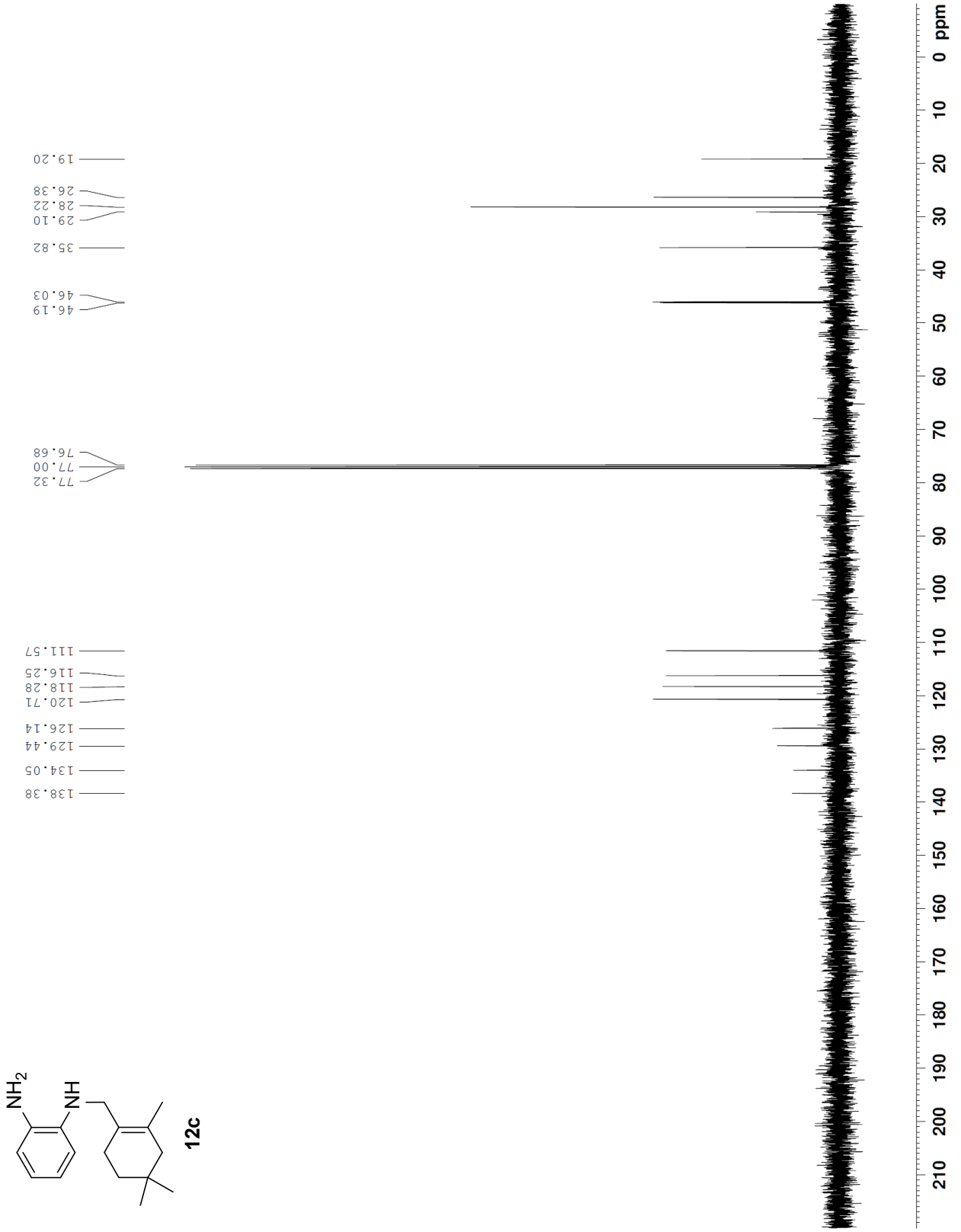


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**.

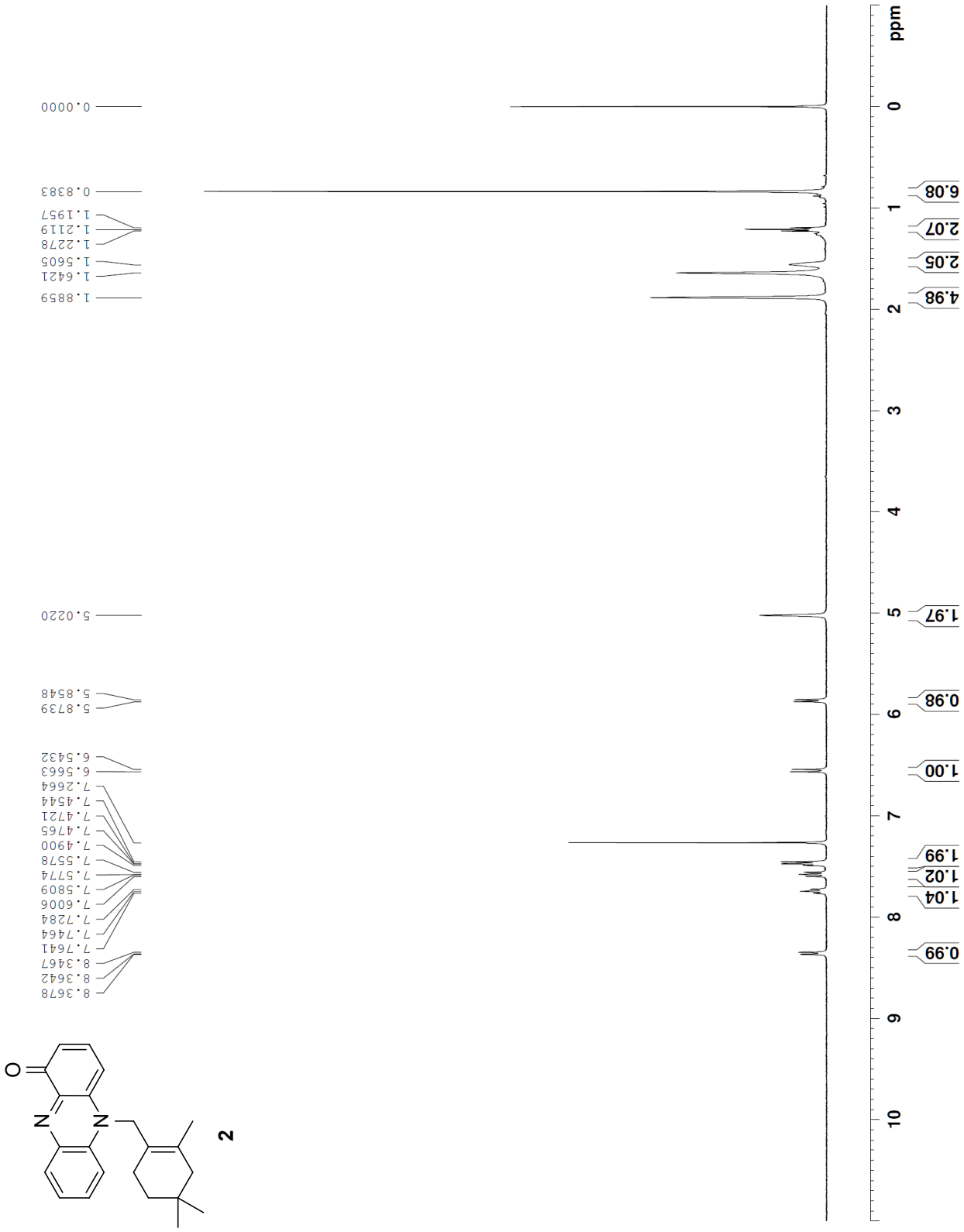


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **2**.

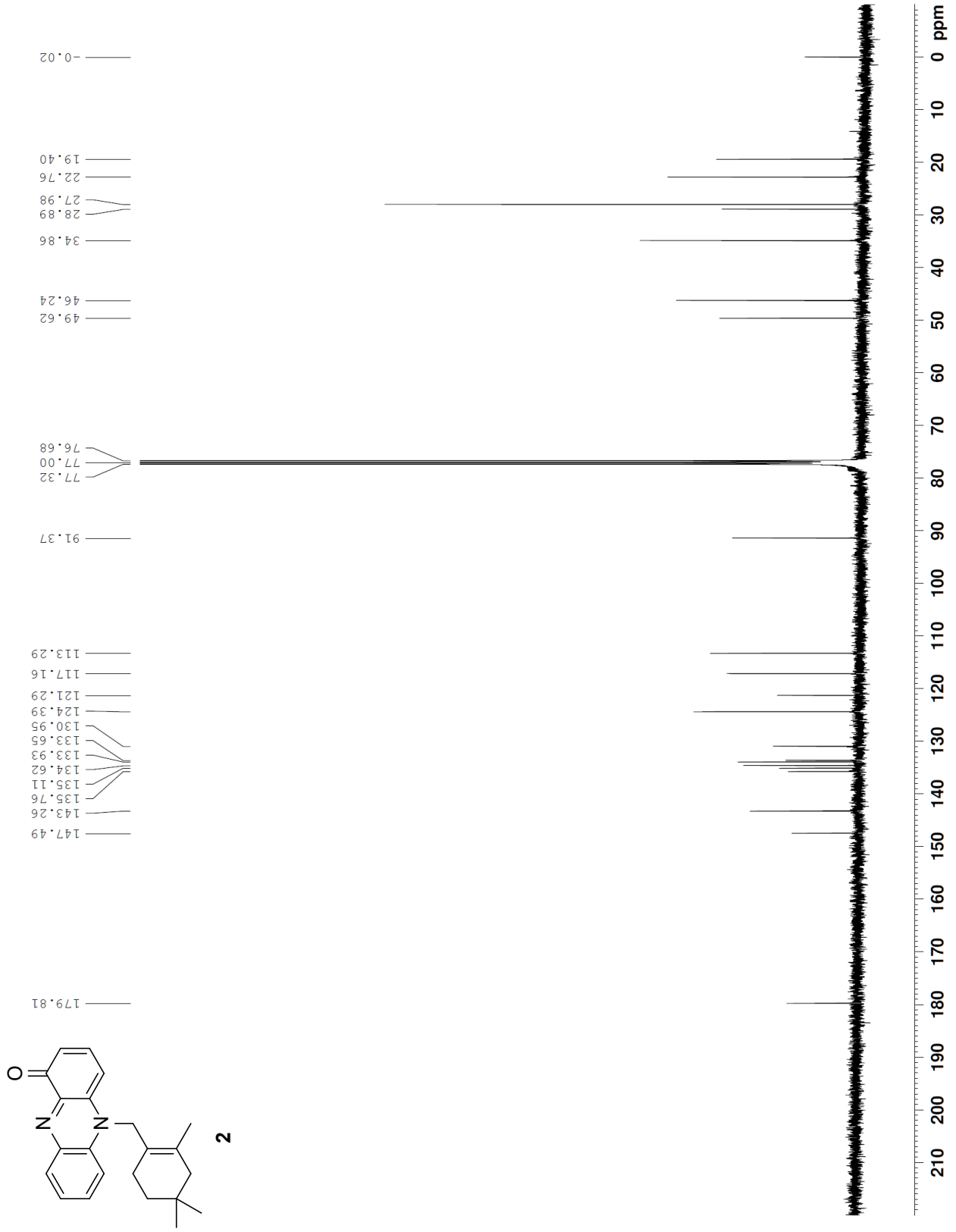


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

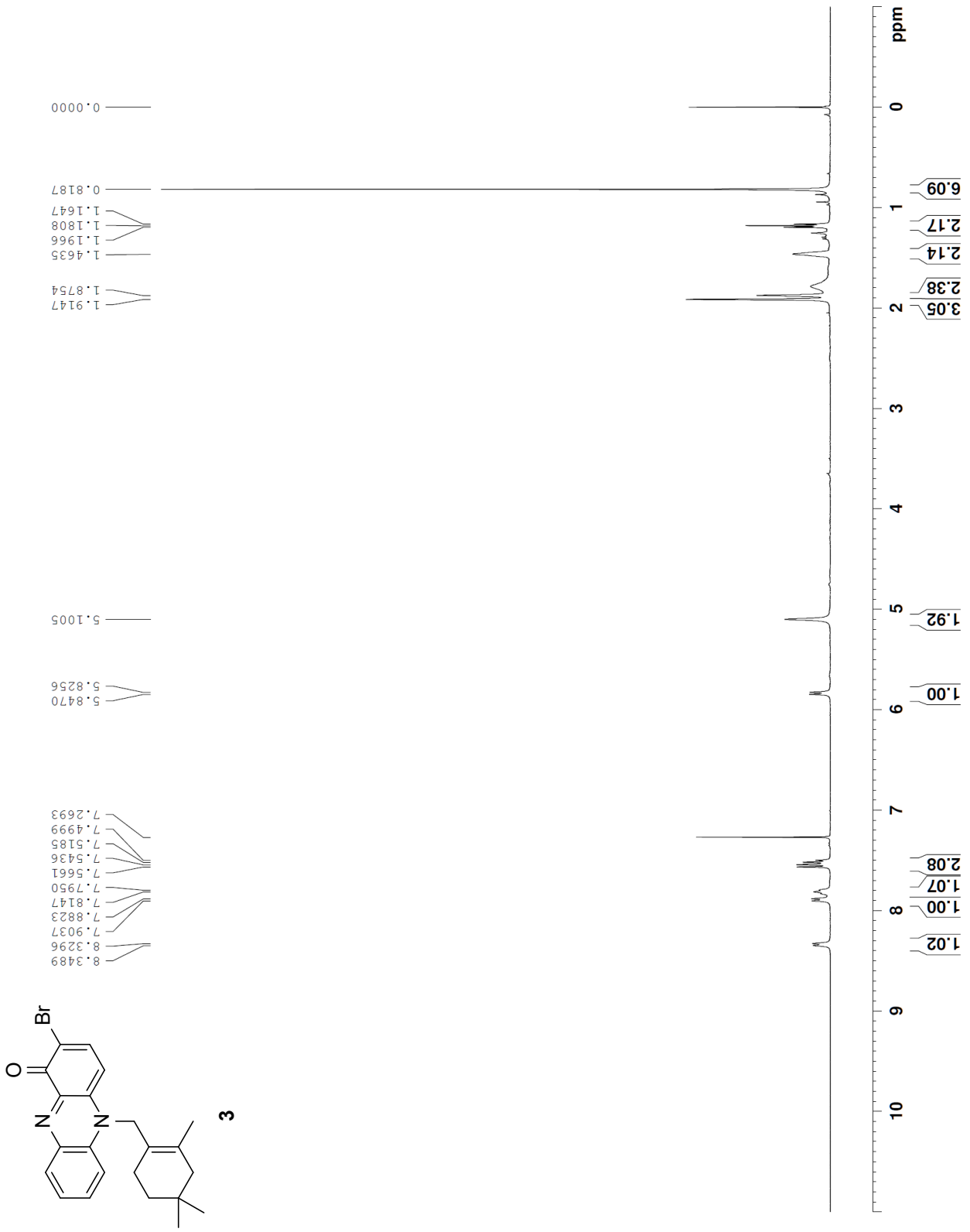


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3**.

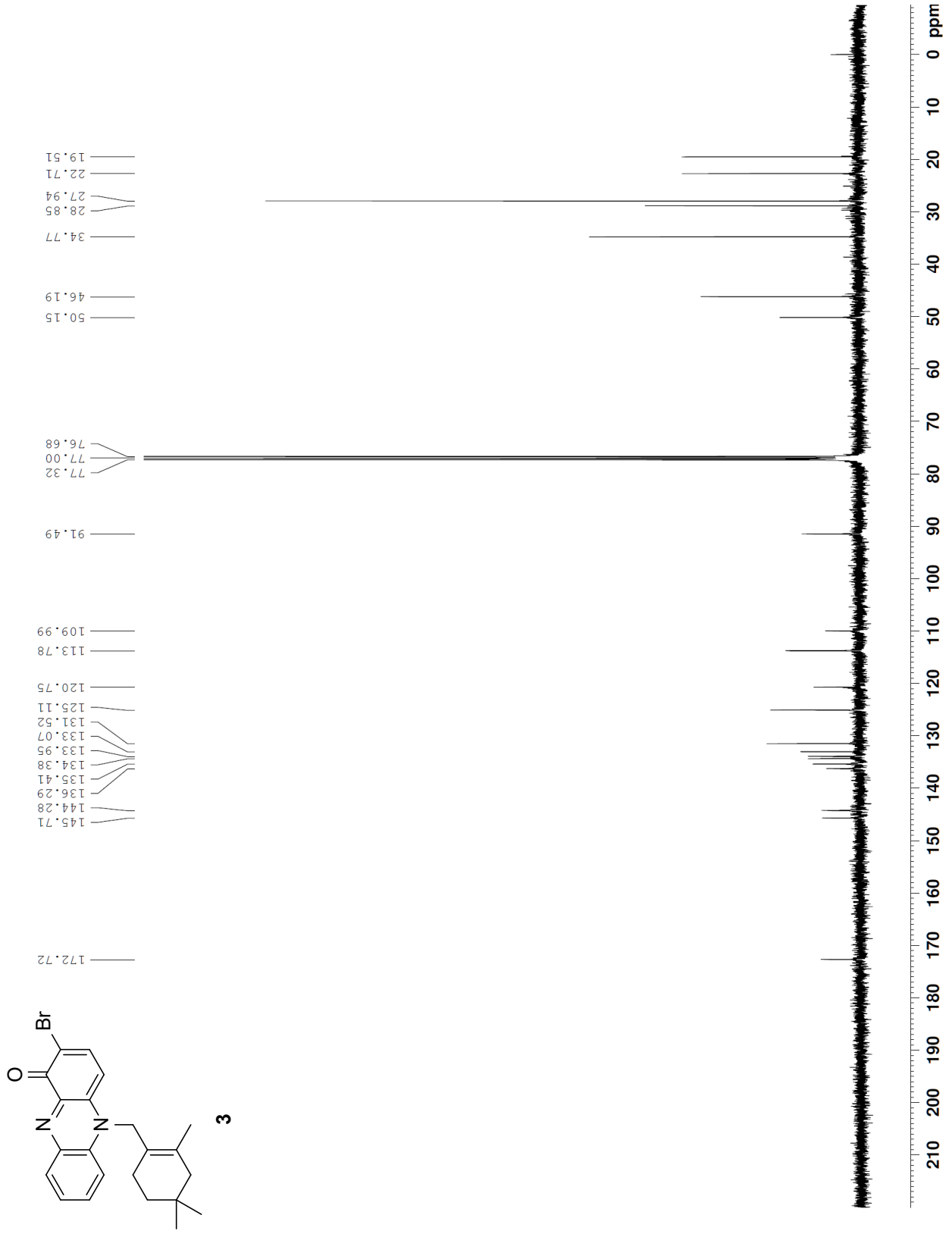
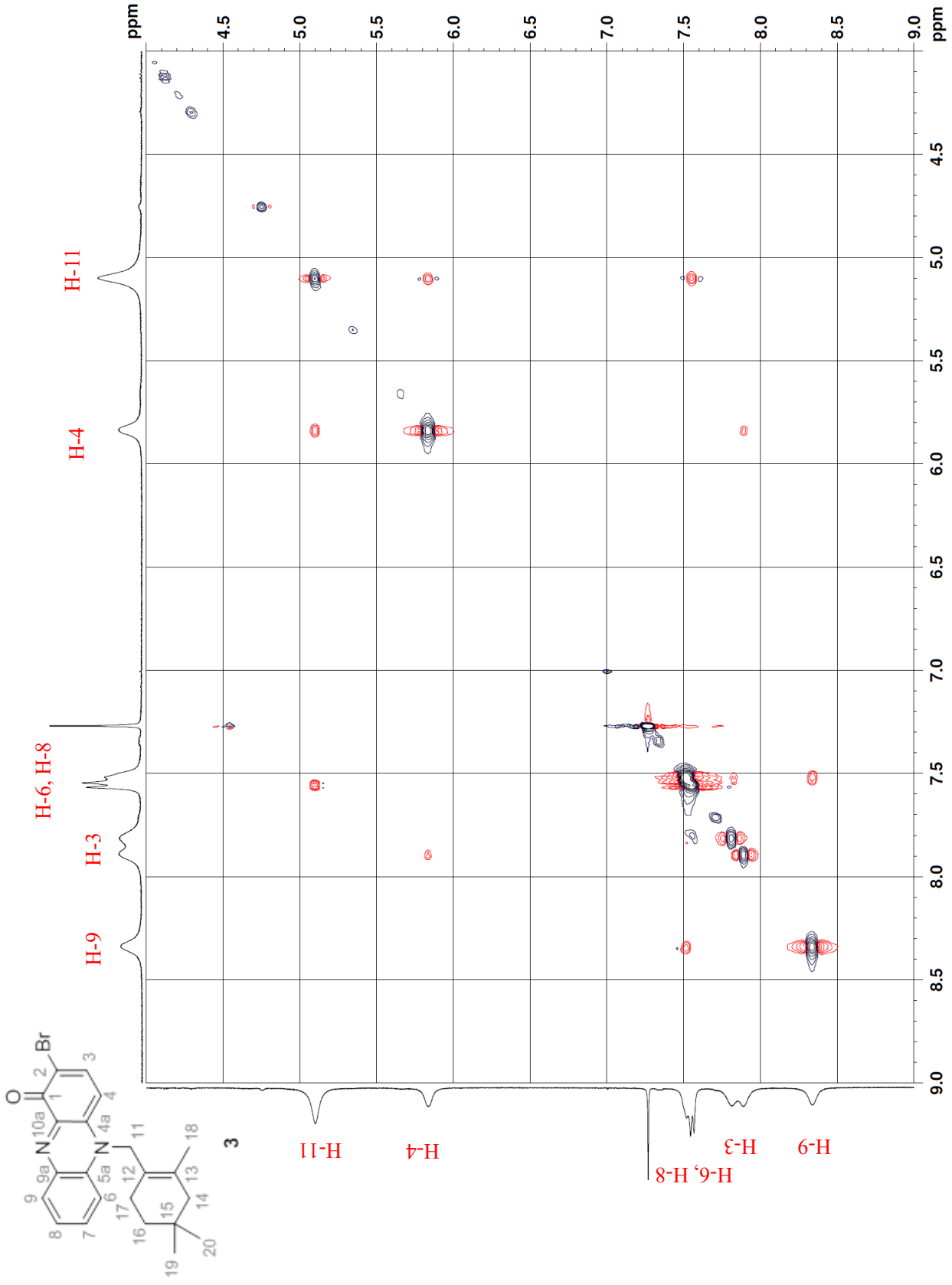


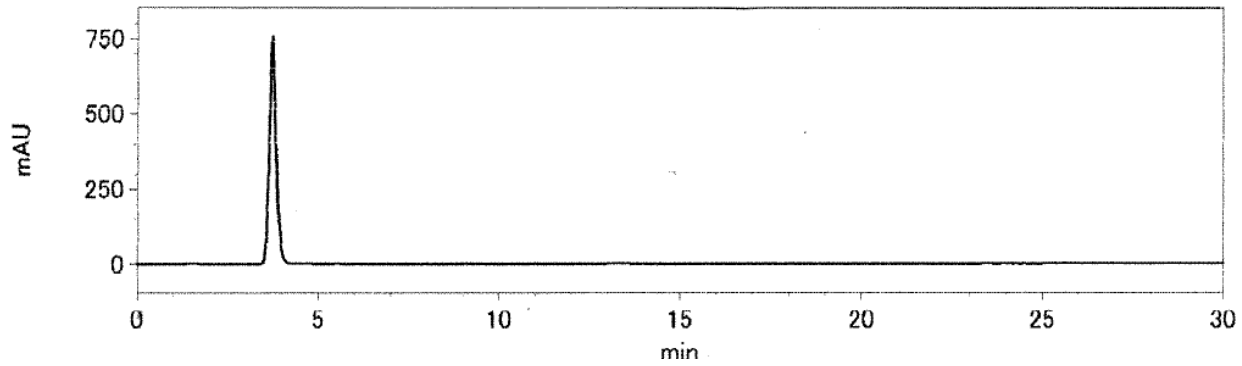
Figure S25. NOESY spectrum of **3**.



5. HPLC analytical data

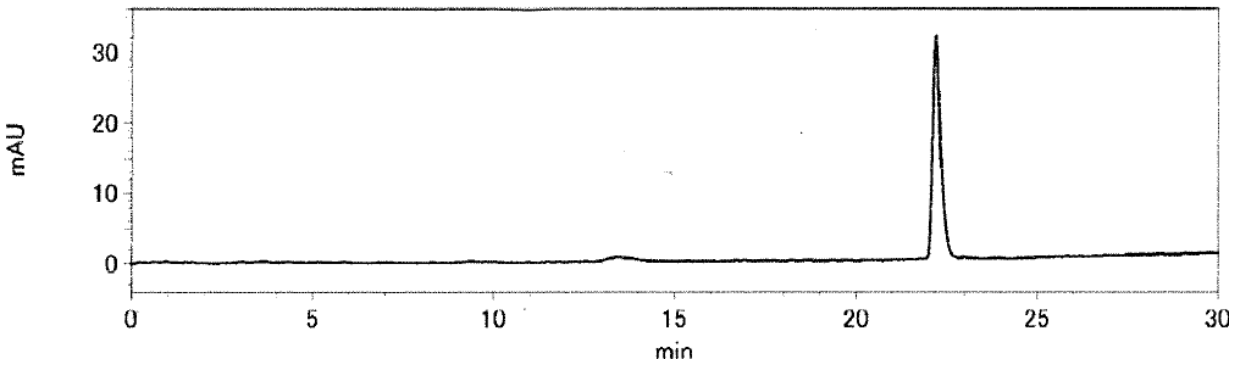
Figure S26. HPLC Chromatograms of **1**–**4**.[a]

(A) Pyocyanin (**1**)



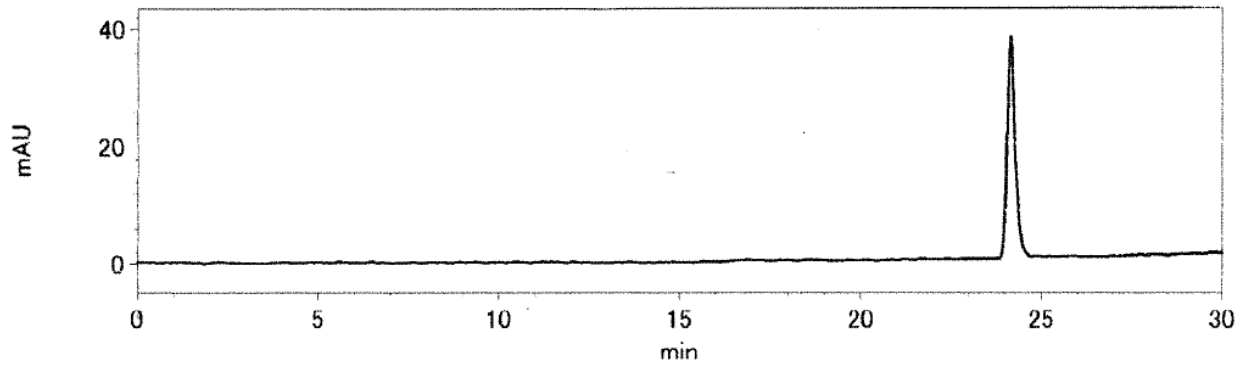
Peak No	Retention time	Area	Area%
1	1.561	4001	0.08
2	3.727	4830434	99.91
3	4.693	179	0.00
Total		4834614	100.00

(B) Lavanducyanin (**2**)



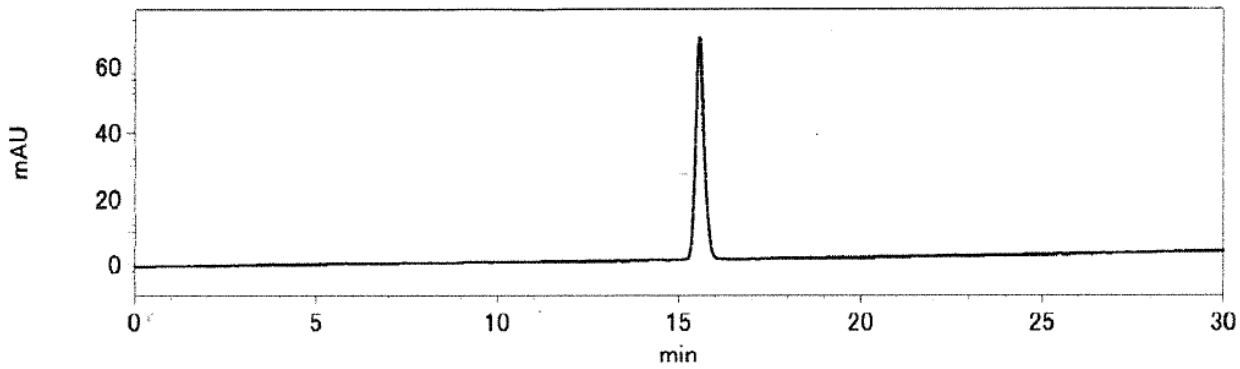
Peak No	Retention time	Area	Area%
1	22.189	187901	100.00
Total		187901	100.00

(C) Marinocyanin A (**3**)



Peak No	Retention time	Area	Area%
1	24.128	181091	100.00
Total		181091	100.00

(D) Marinocyanin B (**4**)



Peak No	Retention time	Area	Area%
1	15.552	361908	100.00
Total		361908	100.00

[a]The purities of compounds **1**–**4** were determined to be >99% by analytical HPLC using a TOSOH TSK-gel reversed phase chromatography column (ODS-100Z, 4.6 × 150 mm) column under the following conditions: mobile phase, a gradient solvent system of MeOH : H_2O (40:60 to 100:0 over 30 min); flow rate, 1 mL/min, temperature, 40 °C; detection at UV 254 nm).

6. References

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