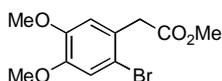


Supporting Information

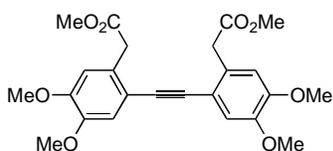
Total Synthesis of Ningalin D

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Methyl 2-Bromo-4,5-dimethoxyphenylacetate. A solution of 2-bromo-4,5-dimethoxyphenylacetonitrile⁸ (25 g, 97.7 mmol) and H₂SO₄ (10.4 mL, 195 mmol) in MeOH (21 mL) was warmed at reflux (65 °C) overnight (no nitrile absorption in IR). The cooled mixture was diluted with H₂O (54 mL) and treated with aqueous 10% NaHCO₃ until the solution was basic. The mixture was extracted with CH₂Cl₂ and the combined organic extracts were washed with saturated aqueous NaCl and dried (MgSO₄). Removal of the solvent in vacuo afford the title compound (25.4 g, 90%) identical in all respects (¹H NMR, ¹³C NMR, mp) with that previously reported.⁹



(3)

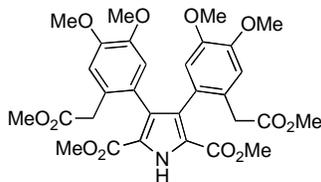
A solution of methyl 2-bromo-4,5-dimethoxyphenylacetate⁹ (5.26 g, 18.2 mmol, 2.2 equiv), bis(tributylstannyl)acetylene (5.00 g, 8.28 mmol) and Pd(PPh₃)₄ (957 mg, 0.828 mmol, 10 mol%) in 50 mL of degassed toluene was warmed at reflux for 6 h before the cooled reaction mixture was filtered through Celite. Removal of the solvent and chromatography (SiO₂, 4 × 15 cm, 50% EtOAc/hexane) afforded **4** (2.60 g, 5.88 mmol, 71%; typically 70–80%) as a colorless solid: mp 146–148 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.02 (s, 2H), 6.80 (s, 2H), 3.89 (s, 12H), 3.85 (s, 4H), 3.68 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.8, 149.3, 147.8,

129.0, 115.5, 114.3, 112.6, 90.4, 55.93, 55.88, 52.0, 39.3; IR (film) ν_{\max} 2953, 1737, 1522, 1358, 1329, 1238, 1008 cm^{-1} ; ESI-TOF HRMS m/z 443.1697 ($\text{C}_{24}\text{H}_{26}\text{O}_8+\text{H}^+$ requires 443.1700).



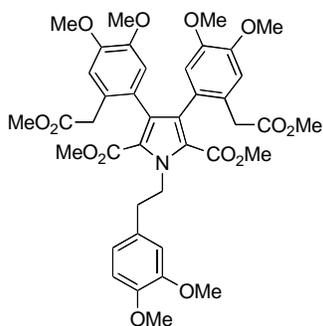
(4)

A solution of dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate¹⁰ (**2**, 888 mg, 4.48 mmol, 1.2 equiv) and acetylene **3** (1.65 g, 3.73 mmol) in toluene (15 mL) was warmed at reflux (110 °C) for 13 h before the reaction mixture was cooled to 25 °C. Additional tetrazine **2** (371 mg, 1.87 mmol, 0.5 equiv) was added and the mixture was warmed at reflux (110 °C) for an additional 23 h. Removal of the solvent and chromatography (SiO_2 , 3×20 cm, 67% EtOAc/hexane) afforded **5** as a yellow solid (1.98 g, 3.23 mmol, 87%) as a mixture of atropisomers (major isomer:minor isomer = 2.5:1): mp 161.2–162.0 °C (EtOAc); ^1H NMR (CDCl_3 , 400 MHz) major isomer: δ 6.73 (s, 2H), 6.42 (s, 2H), 3.83 (s, 6H), 3.77 (s, 6H), 3.65 (s, 6H), 3.56 (s, 6H), 3.27 (d, 2H, $J = 16.0$ Hz), 3.21 (d, 2H, $J = 16.0$ Hz); minor isomer: δ 6.76 (s, 2H), 6.44 (s, 2H), 3.84 (s, 6H), 3.76 (s, 6H), 3.64 (s, 6H), 3.61 (s, 6H), 3.27 (d, 2H, $J = 16.0$ Hz), 3.21 (d, 2H, $J = 16.0$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) major isomer: δ 170.8, 164.7, 154.6, 149.4, 147.7, 138.7, 124.4, 123.9, 112.8, 112.7, 56.0, 55.7, 53.2, 52.0, 38.0; minor isomer: δ 170.8, 164.7, 154.8, 149.3, 147.4, 138.6, 124.2, 123.5, 112.9, 111.8, 55.8, 55.7, 53.4, 52.0, 37.3; IR (film) ν_{\max} 1733 cm^{-1} ; MALDIFTMS (DHB) m/z 613.2028 ($\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_{12}+\text{H}^+$ requires 613.2026).



(5)

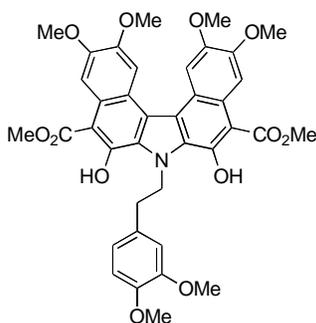
A solution of **4** (2.19 g, 3.58 mmol) in CH₂Cl₂ (15 mL) was treated with activated Zn (3.51 g, 53.7 mmol, 15 equiv) and trifluoroacetic acid (8.2 mL, 107 mmol, 30 equiv) and the mixture was stirred at 25 °C. After 1 h, additional Zn (3.51 g, 53.7 mmol, 15 equiv) was added and the mixture was stirred at 25 °C for an additional 6 h. The reaction mixture was neutralized with the addition of saturated aqueous NaHCO₃, filtered through Celite, and extracted with CH₂Cl₂ (3×). The combined organic layer was dried over Na₂SO₄ and evaporated in vacuo. Chromatography (SiO₂, 2 × 20 cm, 33% EtOAc/CH₂Cl₂) afforded **6** (1.37 g, 2.28 mmol, 64%) as a yellow amorphous solid. The product was obtained as 2:1 mixture of atropisomers: mp 166.3–167.6 °C (EtOAc); ¹H NMR (CDCl₃, 400 MHz) major isomer: δ 9.90 (brs, 1H), 6.79 (s, 2H), 6.37 (s, 2H), 3.84 (s, 6H), 3.74 (s, 6H), 3.58 (s, 6H), 3.57 (s, 6H), 3.35 (d, 2H, *J* = 15.5 Hz), 3.24 (d, 2H, *J* = 15.9 Hz); minor isomer: δ 9.93 (brs, 1H), 6.78 (s, 2H), 6.56 (s, 2H), 3.84 (s, 6H), 3.72 (s, 6H), 3.66 (s, 6H), 3.57 (s, 6H), 3.35 (d, 2H, *J* = 15.5 Hz), 3.24 (d, 2H, *J* = 15.9 Hz); ¹³C NMR (CDCl₃, 150 MHz) major isomer: δ 172.1, 160.42, 148.16, 147.3, 129.9, 125.8, 125.0, 122.3, 113.8, 112.0, 55.80, 55.73, 51.9, 51.72, 38.3; minor isomer: δ 172.0, 160.44, 148.21, 146.9, 129.7, 125.6, 124.7, 122.5, 114.5, 112.4, 55.8, 55.65, 51.9, 51.7, 37.8; IR (film) ν_{max} 3445, 1733, 1715 cm⁻¹; MALDIFTMS (DHB) *m/z* 622.1908 (C₃₀H₃₃NO₁₂+Na⁺ requires 622.1895).



(7)

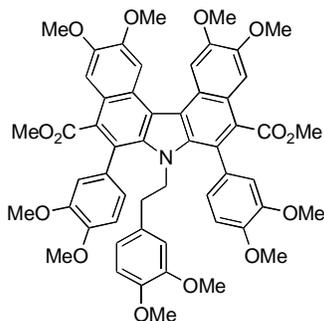
A stirred solution of **5** (1.42 g, 2.37 mmol) in DMF (7 mL) was treated with 4-(2-iodoethyl)-1,2-dimethoxybenzene^{8b} (**6**, 2.08 g, 7.11 mmol, 3 equiv) and Cs₂CO₃ (2.32 g, 7.11 mmol, 3 equiv) at 25 °C. The mixture was stirred at 60 °C for 2 h before being cooled to 25 °C and diluted with EtOAc. The mixture was washed with H₂O and saturated aqueous

NaCl, and aqueous layer was back extracted with EtOAc. The combined organic layer was dried over Na₂SO₄, and the solvent was removed. Chromatography (SiO₂, 3 × 20 cm, 67% EtOAc/hexane) afforded **7** (1.67 g, 2.19 mmol, 92%) as a yellow amorphous solid. The product was obtained as 1.4:1 mixture of atropisomers: ¹H NMR (CDCl₃, 400 MHz) major isomer: δ 6.85 (d, 1H, *J* = 1.4 Hz), 6.80 (s, 2H), 6.72 (s, 2H), 6.35 (s, 2H), 5.12–4.96 (m, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 3.83 (s, 6H), 3.65 (s, 6H), 3.61 (s, 6H), 3.49 (s, 6H), 3.42 (d, 2H, *J* = 15.3 Hz), 3.34 (d, 2H, *J* = 15.3 Hz), 3.10 (t, 2H, *J* = 7.5 Hz); minor isomer: δ 6.85 (d, 1H, *J* = 1.4 Hz), 6.80 (s, 2H), 6.71 (s, 2H), 6.51 (s, 2H), 5.12–4.96 (m, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 3.83 (s, 6H), 3.69 (s, 6H), 3.61 (s, 6H), 3.49 (s, 6H), 3.26 (d, 2H, *J* = 15.7 Hz), 3.19 (d, 2H, *J* = 15.8 Hz), 3.10 (t, 2H, *J* = 7.5 Hz); ¹³C NMR (CDCl₃, 150 MHz) major isomer: δ 172.07, 171.97, 161.4, 147.7, 146.9, 130.9, 129.6, 126.8, 125.3, 124.8, 121.2, 113.3, 112.5, 111.6, 111.2, 60.4, 55.90, 55.89, 55.78, 55.64, 51.77, 51.42, 48.56, 38.3, 37.80; minor isomer: δ 172.07, 171.97, 161.4, 148.9, 146.6, 130.4, 129.5, 126.3, 125.0, 124.4, 121.2, 114.3, 112.4, 111.9, 111.2, 60.4, 55.90, 55.85, 55.74, 55.62, 51.75, 51.45, 48.52, 38.3, 37.83; IR (film) ν_{\max} 1738, 1733 cm⁻¹; MALDIFTMS (DHB) *m/z* 786.2742 (C₄₀H₄₅NO₁₄+Na⁺ requires 786.2732).



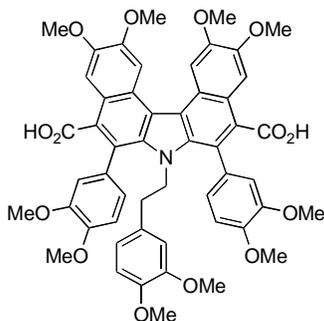
(8)

A solution of **7** (752 mg, 0.985 mmol) in DMF (7 mL) was treated with NaH (60%, 236 mg, 5.91 mmol, 6 equiv, washed with hexane and dried) and the mixture was stirred at 25 °C for 15 h, before being quenched by addition of aqueous 10% HCl. The precipitate was collected by filtration, dissolved in CHCl₃ and dried over Na₂SO₄. Removal of the solvent gave **8** (559 mg, 0.799 mmol, 81%) as a dark yellow solid: mp 241.0–243.5 °C (EtOAc); ¹H NMR



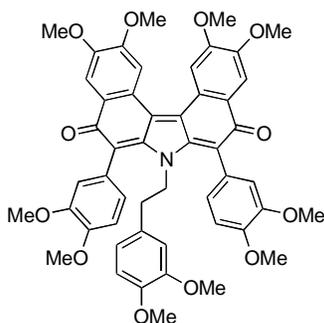
(11)

A solution of **9** (200 mg, 0.208 mmol), 3,4-dimethoxyphenylboronic acid (**10**, 83 mg, 0.458 mmol, 2.2 equiv), Pd(PPh₃)₄ (24 mg, 0.0208 mmol, 10 mol%) and LiCl (19 mg, 0.458 mmol, 2.2 equiv) suspended in degassed DME (1 mL) was treated with 1 M aqueous K₂CO₃ (0.83 mL, 0.832 mmol, 4 equiv), and the mixture was stirred at 80 °C for 15 h. The reaction mixture was diluted with EtOAc and saturated aqueous NaHCO₃, and filtered through Celite. After phase separation and extraction of the aqueous phase with EtOAc (2×), the combined organic layer was dried over Na₂SO₄ and evaporated. The residue and catechol (123 mg, 0.208 mmol) were dissolved in toluene–EtOAc, and the solution was evaporated to dryness. The residue was re-dissolved in toluene and evaporated. This re-dissolution and evaporation was repeated again, and the residue was purified by chromatography (SiO₂, 1 × 25 cm, 67–75% EtOAc/hexane). A second chromatography (SiO₂, 1 × 20 cm, 2.5% MeOH/CH₂Cl₂) afforded pure **11** (172 mg, 0.183 mmol, 88%) as dark yellow amorphous solid: ¹H NMR (CDCl₃, 600 MHz, 50 °C) δ 8.24 (s, 2H), 7.32 (s, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.04 (brs, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 8.1 Hz, 1H), 5.88 (d, *J* = 8.1 Hz, 1H), 5.77 (s, 1H), 4.04 (s, 6H), 3.98 (s, 6H), 3.89 (s, 6H), 3.82 (s, 6H), 3.69 (s, 3H), 3.66 (s, 6H), 3.55 (m, 2H), 3.58 (s, 3H), 2.11 (m, 2H); ¹³C NMR (150 MHz, CDCl₃, 50 °C) δ 170.4, 149.13, 149.06, 148.99, 148.7, 147.7, 137.86, 137.83, 130.5, 130.3, 130.2, 124.1, 123.5, 122.4, 121.7, 120.5, 120.4, 113.7, 112.1, 111.4, 111.3, 106.6, 105.5, 56.3, 56.1, 56.00, 55.97, 55.94, 55.7, 52.0, 46.7, 35.4; IR (film) ν_{max} 1720, 1510, 1258 cm⁻¹; UV (MeOH) λ_{max} 367 (ε 22500), 331 (15900), 288 (49100); MALDIFTMS (DHB) *m/z* 962.3338 (C₅₄H₅₃NO₁₄+Na⁺ requires 962.3358).



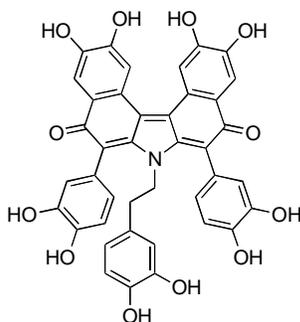
(12)

A solution of **11** (65 mg, 69.1 μ mol), *t*-BuOK (200 mg, 1.78 mmol) and H₂O (9.7 μ L, 0.538 μ mol) in DMSO (0.5 mL) was warmed at 80 °C and stirred for 24 h. The reaction was quenched with the addition of 10% aqueous HCl, and EtOAc was added to dissolve precipitate. After phase separation, the EtOAc layer was washed with H₂O and saturated aqueous NaCl, and dried over Na₂SO₄. Evaporation and chromatography (SiO₂, 1 \times 20 cm, 20% MeOH/CH₂Cl₂) afforded **12** (53 mg, 58.1 μ mol, 84%) as a tan solid: ¹H NMR (CDCl₃, 600 MHz, 50 °C) δ 8.25 (s, 2H), 7.47 (s, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.08 (brs, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 8.2 Hz, 1H), 5.87 (dd, *J* = 1.4, 8.0 Hz, 1H), 5.77 (s, 1H), 4.04 (s, 6H), 3.99 (s, 6H), 3.87 (s, 6H), 3.81 (s, 6H), 3.66 (s, 3H), 3.56 (m, 2H), 3.54 (s, 3H), 2.12 (m, 2H); ¹³C NMR (150 MHz, CD₃OD, 50 °C) δ 173.6, 150.9, 150.6, 150.3, 149.99, 149.95, 149.0, 139.23, 139.21, 132.8, 132.0, 131.5, 124.7, 124.4, 122.8, 122.1, 121.1, 116.0, 113.6, 113.4, 113.1, 108.4, 107.4, 57.1, 56.9, 56.8, 56.7, 56.5, 56.4, 47.5, 36.5; IR (film) ν_{max} 3514, 3288, 2935, 2836, 1725, 1512, 1280 cm⁻¹; UV (MeOH) λ_{max} 373 (ϵ 19800), 328 (15600), 289 (47900); ESI-TOF HRMS *m/z* 912.3223 (C₅₂H₄₉NO₁₄+H⁺ requires 912.3226).



permethyl ningalin D (13).

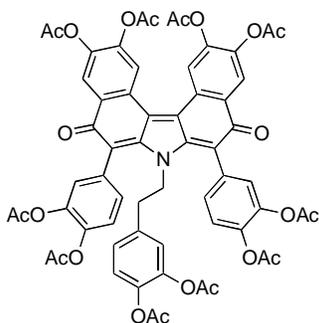
A solution of **12** (15 mg, 16.4 μmol) in CH_2Cl_2 (0.3 mL) was treated with DPPA (17.7 μL , 82.0 μmol , 5.0 equiv) and *i*-Pr₂NEt (14.3 μL , 82.0 μmol , 5.0 equiv). After stirring at 25 °C for 20 h, the mixture was washed with saturated aqueous NaHCO₃ (2 \times) and saturated aqueous NaCl. The organic layer was dried over Na₂SO₄, and solvent was removed. The residue was dissolved in THF (0.3 mL) and H₂O (0.2 mL), and warmed at reflux for 90 h. The mixture was extracted with CH_2Cl_2 (4 \times , dried (Na₂SO₄)) and evaporated. Chromatography (SiO₂, 1 \times 15 cm, 2.5% MeOH/ CH_2Cl_2) gave pure **13** (9.8 mg, 11.5 μmol , 70%) as a dark red amorphous solid: mp 258.0–260.2 °C (CH_2Cl_2); ¹H NMR (CDCl_3 , 400 MHz) δ 7.84 (s, 2H), 7.69 (s, 2H), 7.01–6.97 (m, 4H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.39 (d, *J* = 8.2 Hz, 1H), 6.16 (dd, *J* = 1.9, 8.1 Hz, 1H), 6.04 (d, *J* = 1.9 Hz, 1H), 4.02 (s, 6H), 3.92 (s, 6H), 3.90 (s, 6H), 3.89 (s, 6H), 3.61 (s, 3H), 3.60 (s, 3H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.29 (t, *J* = 7.3 Hz, 2H); ¹³C NMR (CDCl_3 , 100 MHz) δ 183.0, 154.3, 151.1, 151.0, 149.0, 148.6, 148.4, 147.5, 131.1, 129.7, 126.2, 125.4, 124.0, 123.7, 120.8, 117.2, 114.2, 111.7, 110.7, 110.6, 109.7 (split), 108.5 (split), 56.5 (split), 56.2 (split), 56.0 (split), 55.8 (split), 55.5 (split), 55.4 (split), 46.9, 34.0; IR (film) ν_{max} 2917, 1653, 1507, 1464, 1261, 1158, 1026 cm^{-1} ; UV (MeOH) λ_{max} 501 (ϵ 15000); ESI-TOF HRMS *m/z* 854.3190 ($\text{C}_{50}\text{H}_{47}\text{NO}_{12}+\text{H}^+$ requires 854.3171).



ningalin D (1a).

A solution of **13** (14.1 mg, 16.5 μmol) was treated with 1 M BBr₃ in CH_2Cl_2 (0.248 mL, 248 μmol , 15 equiv) at –78 °C and the mixture was allowed to warm to 25 °C over 16 h. The reaction was quenched with the addition of MeOH (0.2 mL), and solvents were removed under a N₂ stream. The residue was dissolved in H₂O (1.0 mL) and extracted with EtOAc (1.0

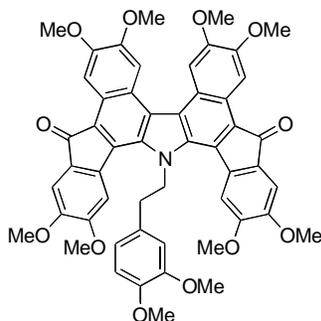
mL, 4×). The combined organic phase was dried (Na₂SO₄) and evaporated. Chromatography (C18 reverse phase, 1 × 10 cm, 40% CH₃CN/5% MeOH/H₂O) afforded pure ningalin D (**1a**) as a dark red amorphous solid (11.3 mg, 15.8 μmol, 96%) identical in all respects with natural **1a**: ¹H NMR (CD₃OD, 400 MHz) δ 7.81 (s, 2H), 7.41 (s, 2H), 6.79–6.78 (overlap of two doublets, 4H), 6.64 (dd, *J* = 1.7, 8.1 Hz, 2H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 2.0 Hz, 1H), 5.91 (dd, *J* = 2.0, 8.0 Hz, 1H), 2.91 (t, *J* = 7.0 Hz, 2H), 2.09 (t, *J* = 6.9 Hz, 2H); ¹³C NMR (CD₃OD, 150 MHz) δ 185.4, 156.5, 150.2, 149.0, 146.6, 146.1, 145.6, 144.6, 132.2, 130.6, 126.5, 126.1, 125.0, 124.2, 121.5, 119.4, 118.9, 117.2, 116.3, 115.7, 115.0, 114.2, 47.8, 35.0; IR (film) ν_{max} 3700–3000, 1759, 1561, 1296 cm⁻¹; UV (MeOH) λ_{max} 507 (ε 26800), 292 (32900); ESI-TOF HRMS *m/z* 714.1596 (C₄₀H₂₇NO₁₂+H⁺ requires 714.1606).



ningalin D decaacetate (**14**).

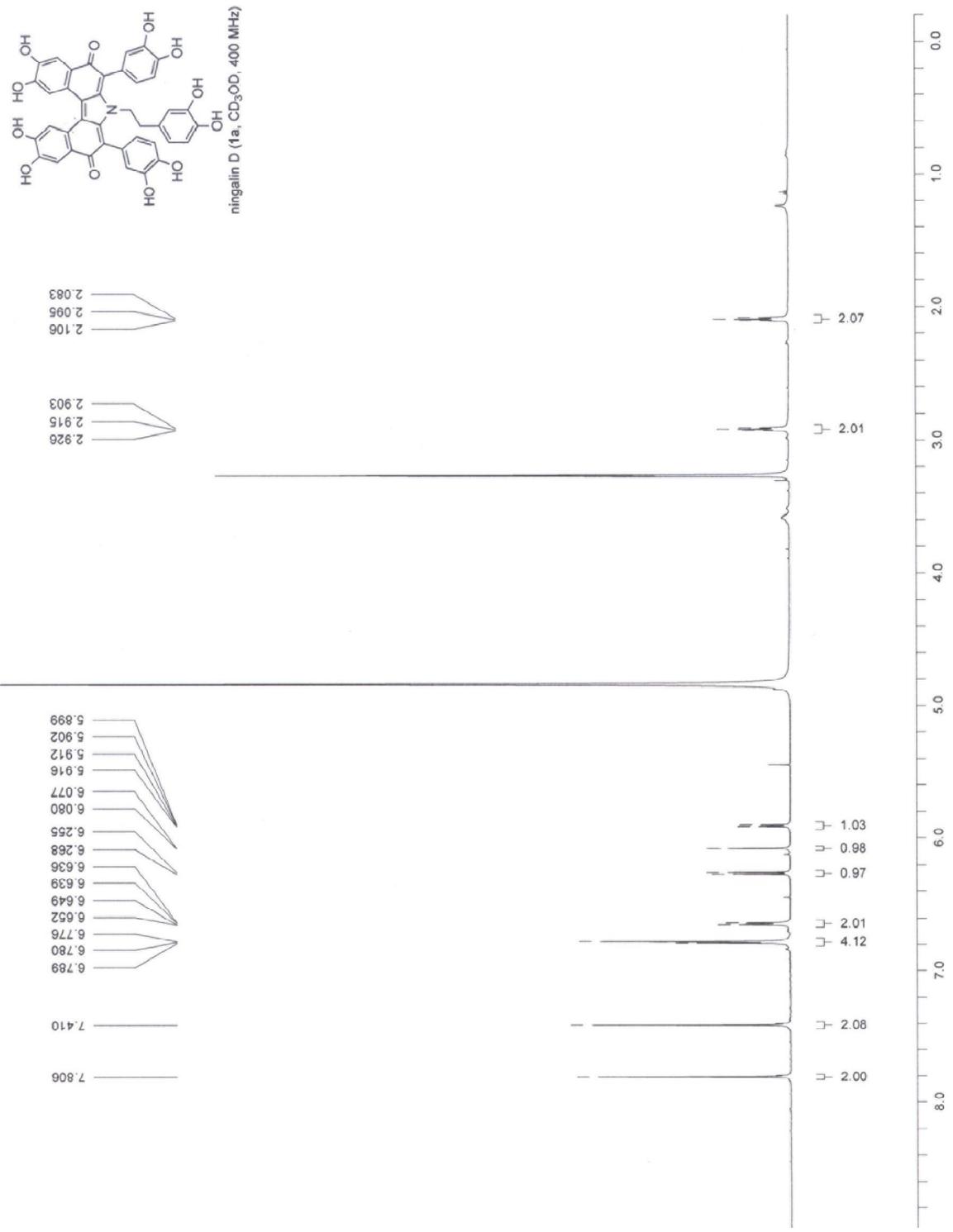
A solution of ningalin D (**1a**, 7.4 mg, 10.4 μmol) in pyridine (0.2 mL) was treated with acetic anhydride (98.3 μL, 1.04 mmol, 100 equiv) at 25 °C. After 3 h, the reaction mixture was diluted with EtOAc. The mixture was washed with aqueous 10% HCl (2×) and saturated aqueous NaHCO₃ (2×), dried (Na₂SO₄) and evaporated. PTLC (5% MeOH/CH₂Cl₂) afforded ningalin D decaacetate (**14**) as a dark green amorphous solid (11.6 mg, 10.2 μmol, 98%) identical in all respects (¹H NMR, HRMS) with the reported title compound: ¹H NMR (CDCl₃, 400 MHz) δ 8.17 (s, 2H), 7.98 (s, 2H), 7.29–7.23 (m, 6H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.48 (dd, *J* = 1.6, 8.3 Hz, 1H), 6.43 (d, *J* = 1.5 Hz, 1H), 3.23 (m, 2H), 2.35 (s, 6H), 2.33 (s, 6H), 2.30 (s, 6H), 2.29 (s, 6H), 2.24 (m, 2H), 2.14 (s, 3H), 2.13 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 181.0, 168.1, 167.88, 167.86, 167.80, 167.77, 167.72, 154.2, 144.6, 144.1, 142.1,

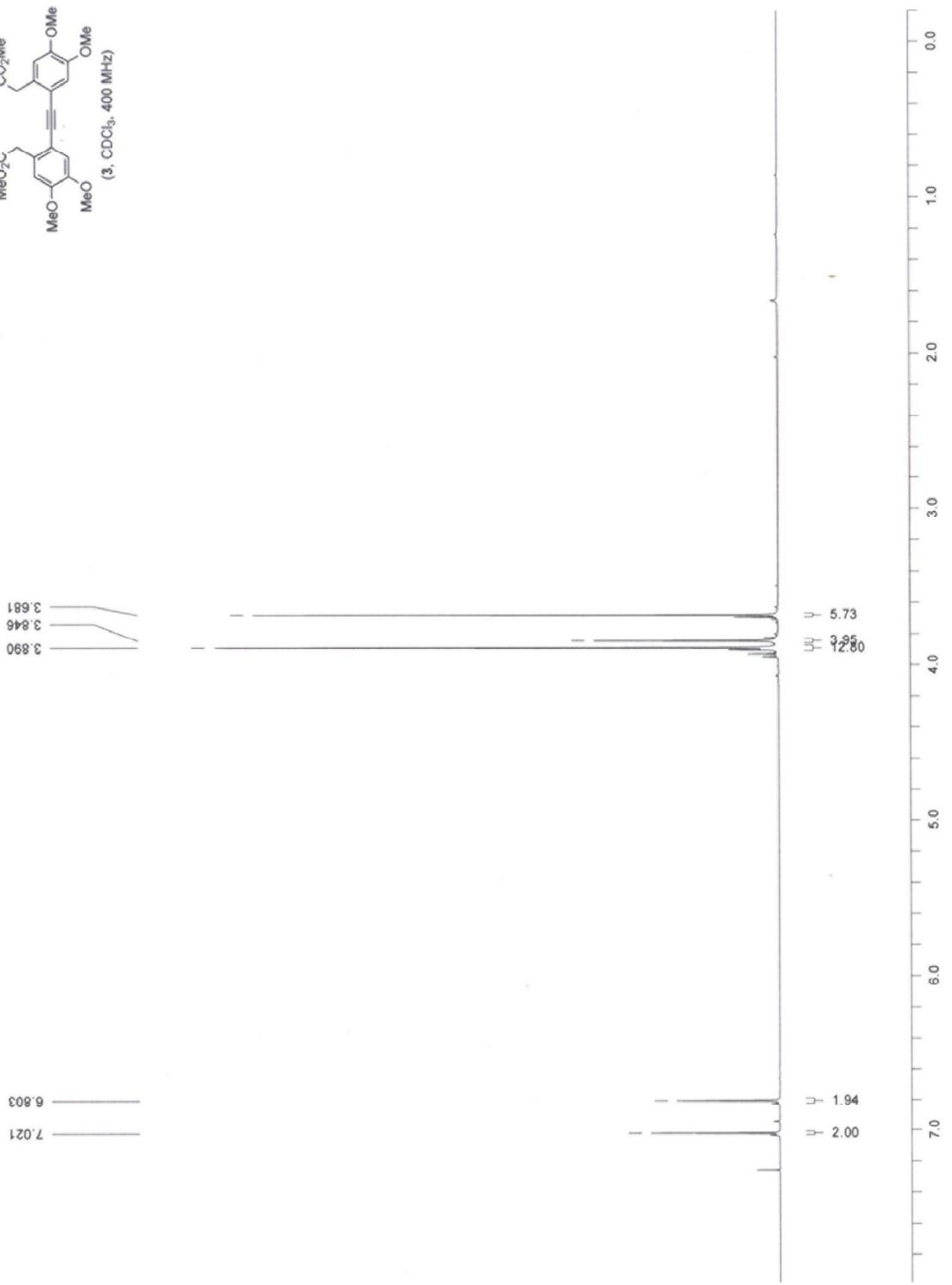
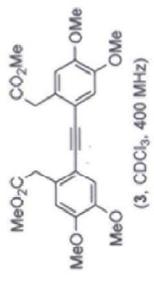
141.7, 141.5, 140.7, 136.1, 131.2, 130.3, 129.9, 129.0, 128.9, 127.6, 127.0, 126.5, 123.6, 123.4, 123.2, 122.0, 116.9, 53.4, 33.7, 20.8, 20.73, 20.68, 20.6, 20.5, 20.4; IR (film) ν_{\max} 2916, 1772, 1203 cm^{-1} ; UV (MeOH) λ_{\max} 574 (ϵ 5600), 468 (23300), 275 (sh); ESI-TOF HRMS m/z 1134.2648 ($\text{C}_{60}\text{H}_{47}\text{NO}_{22}+\text{H}^+$ requires 1134.2662).

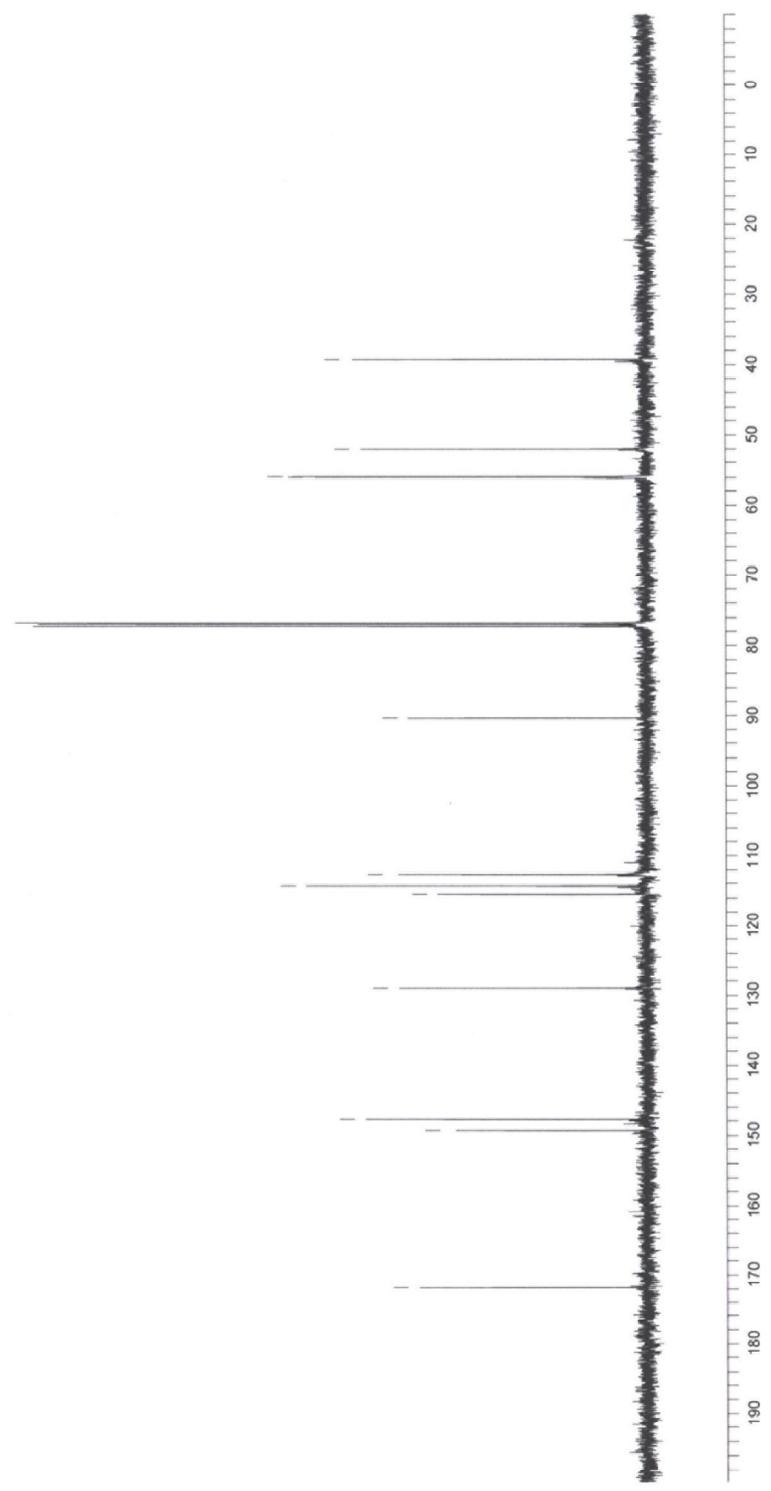
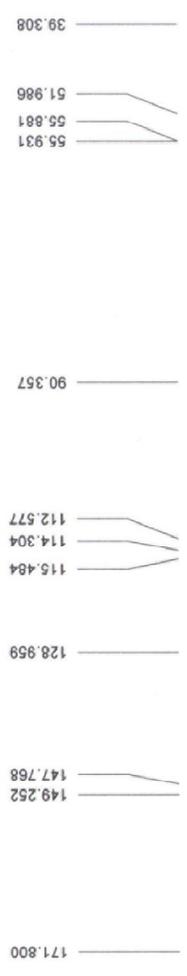
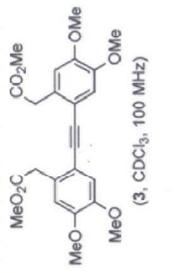


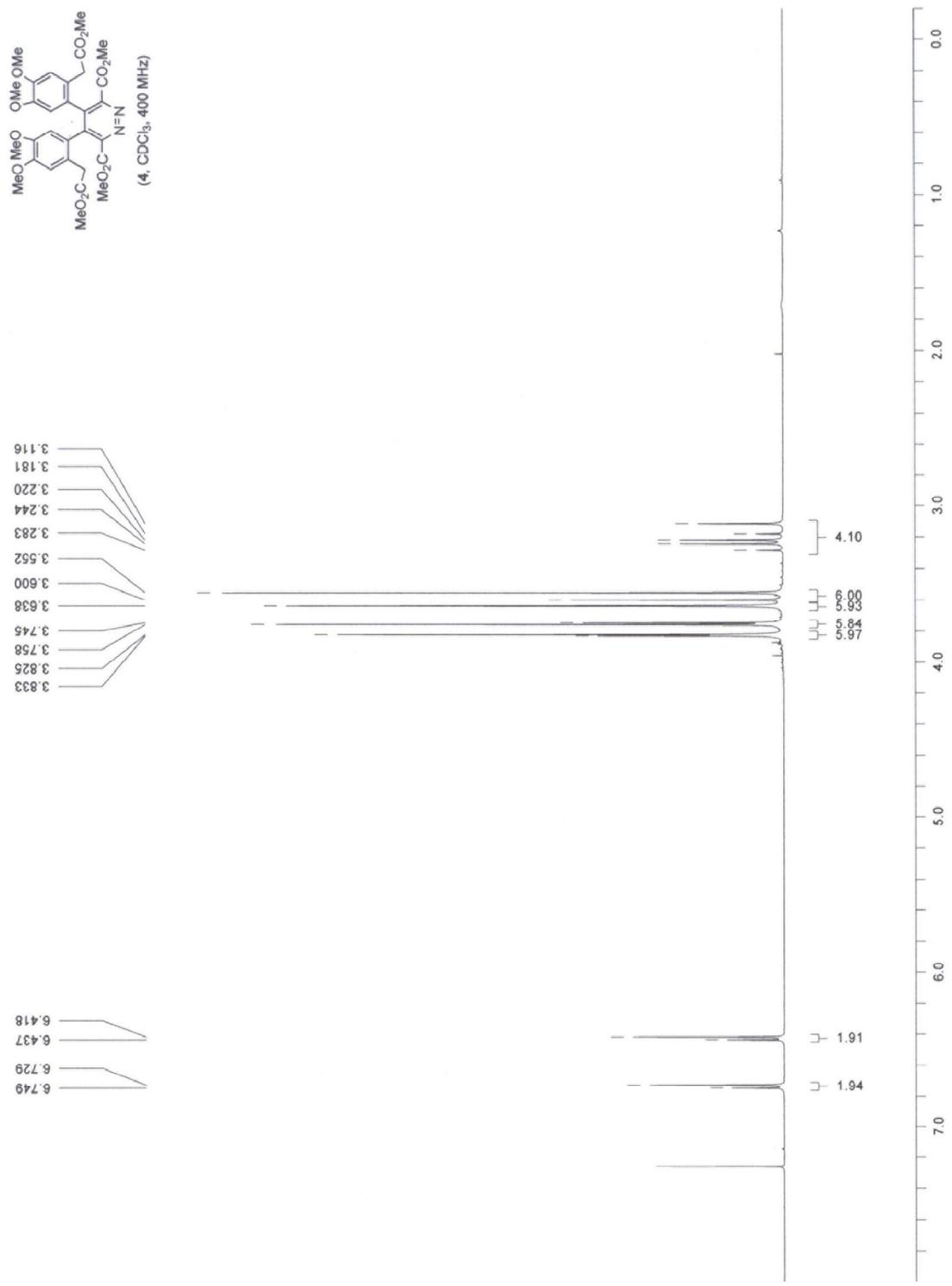
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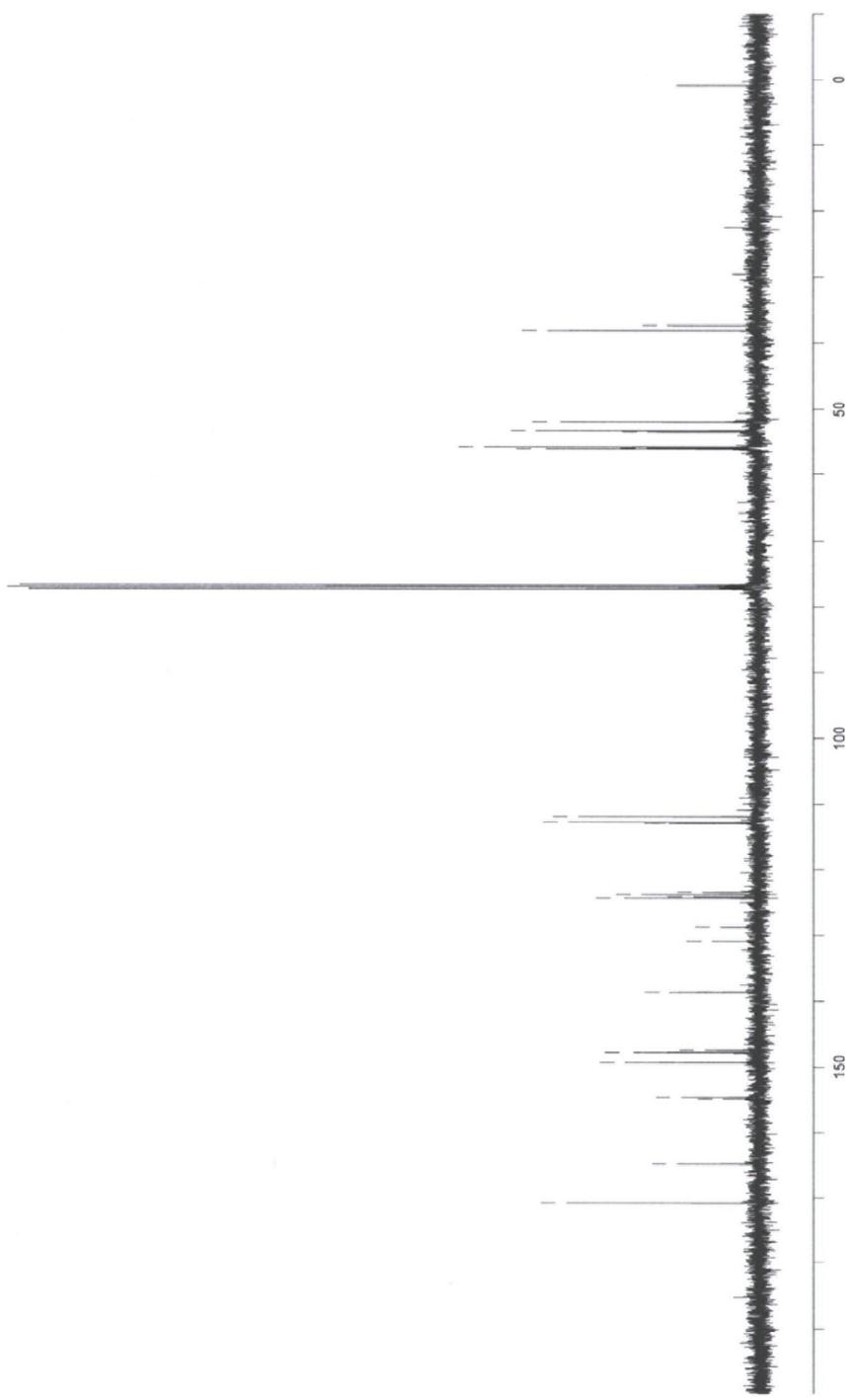
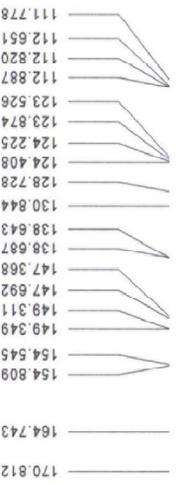
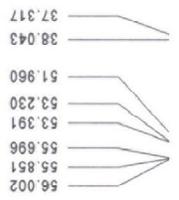
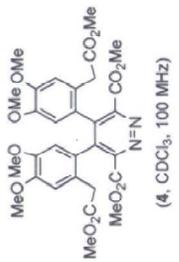
A solution of **12** (15 mg, 16.4 μmol) and Et_3N (6.9 μL , 49.2 μmol , 3 equiv) was treated with SOCl_2 -DMF complex (7.4 μL , 49.2 μmol , 3 equiv) at 25 $^\circ\text{C}$. After 2 h, additional SOCl_2 -DMF complex (7.4 μL , 49.2 μmol , 3 equiv) was added and the mixture was stirred at 25 $^\circ\text{C}$ for 2 h. The mixture was basified by addition of saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 (3 \times). The combined CH_2Cl_2 layer was dried (Na_2SO_4) and evaporated. PTLC (5% MeOH/ CH_2Cl_2) afforded **15** as a black amorphous solid (10 mg, 11.4 μmol , 70%): ^1H NMR (CDCl_3 , 400 MHz) δ 8.57 (s, 2H), 7.75 (s, 2H), 7.32 (s, 2H), 7.24 (s, 2H), 6.00–5.98 (m, 1H), 5.92 (dd, J = 1.9, 8.1 Hz, 1H), 5.71 (d, J = 1.8 Hz, 1H), 4.91 (t, J = 6.7 Hz, 2H), 4.11 (s, 6H), 4.06 (s, 6H), 3.98 (s, 6H), 3.93 (s, 6H), 3.43 (s, 3H), 3.19 (s, 3H), 2.38 (t, J = 6.6 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 194.3, 153.0, 150.8, 149.1, 148.8, 147.8, 147.0, 140.4, 136.7, 131.0, 129.3, 128.4, 128.3, 126.4, 124.9, 124.1, 119.9, 111.2, 110.0 (split), 107.7 (split), 107.2 (split), 105.9 (split), 103.4, 56.3 (split), 56.1 (split), 55.9 (split), 55.6 (split), 55.2 (split), 54.7 (split), 51.8, 33.8; IR (film) ν_{\max} 2916, 1687, 1499, 1299, 1246, 1213, 1051, 1029 cm^{-1} ; UV (CHCl_3) λ_{\max} 572 (ϵ 7600), 452 (10100), 370 (sh), 301 (59700); ESI-TOF HRMS m/z 876.3005 ($\text{C}_{52}\text{H}_{45}\text{NO}_{12}+\text{H}^+$ requires 876.3014).

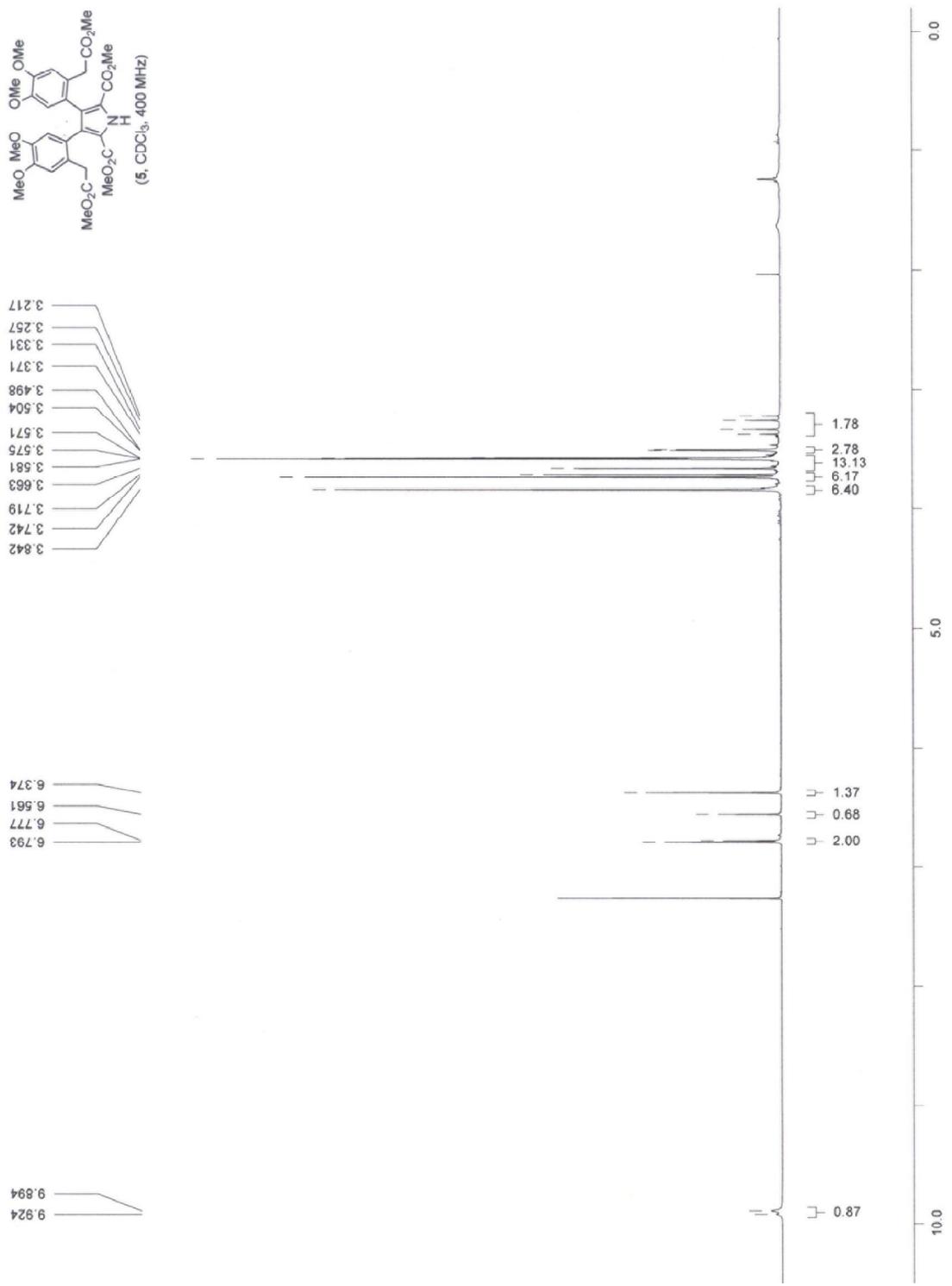


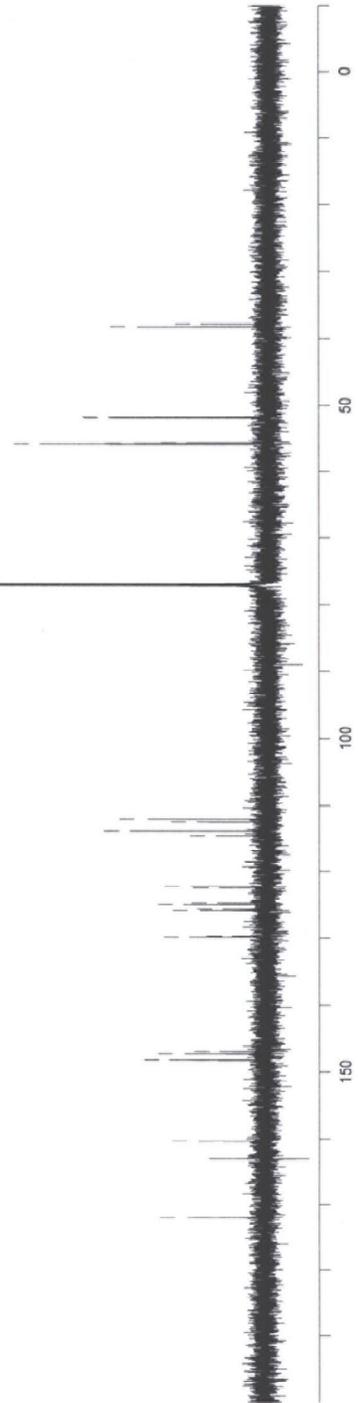
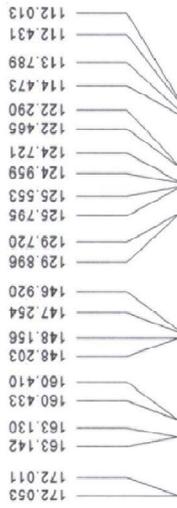
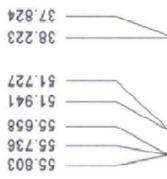
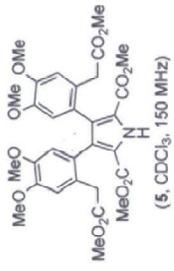


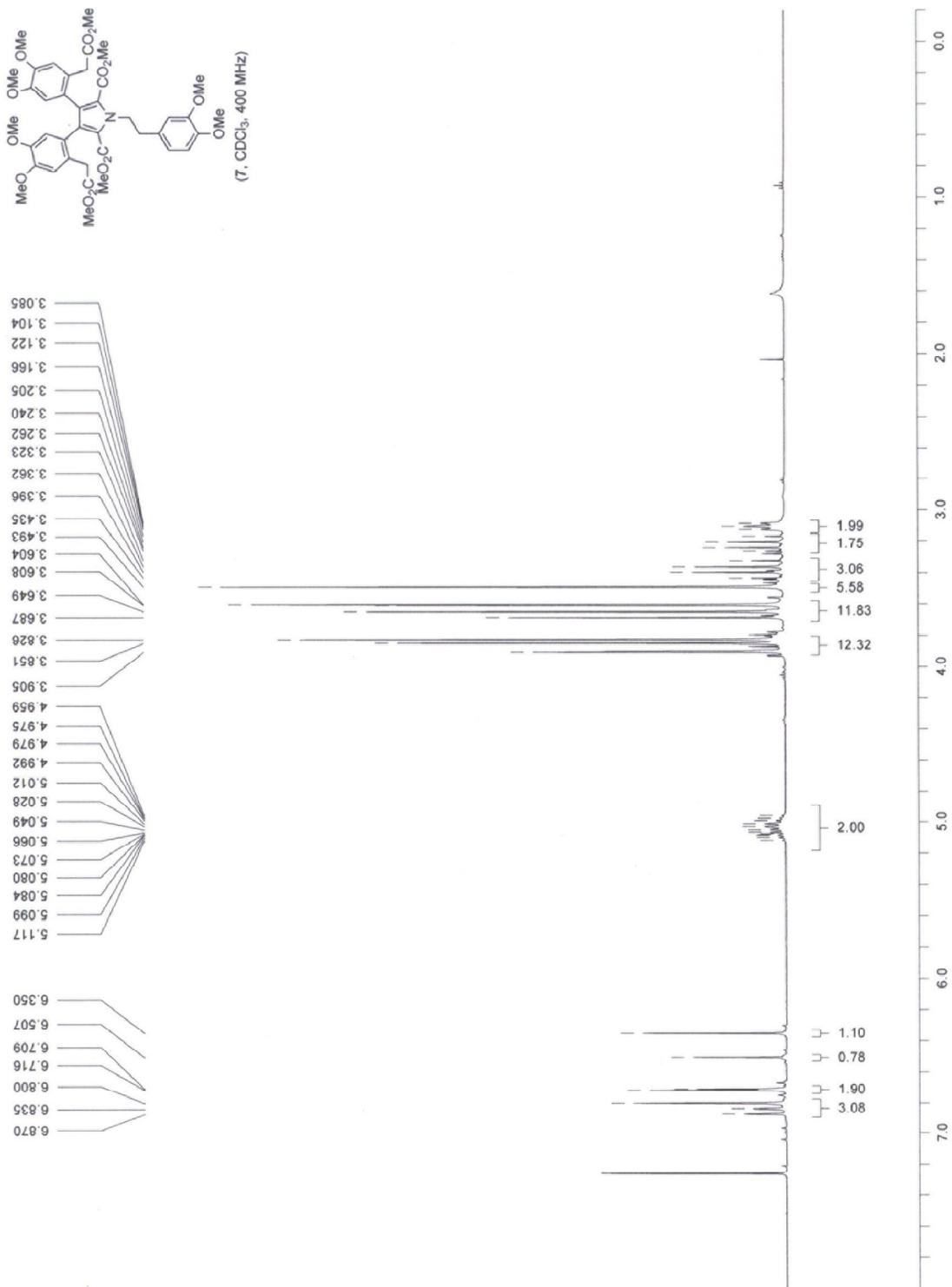


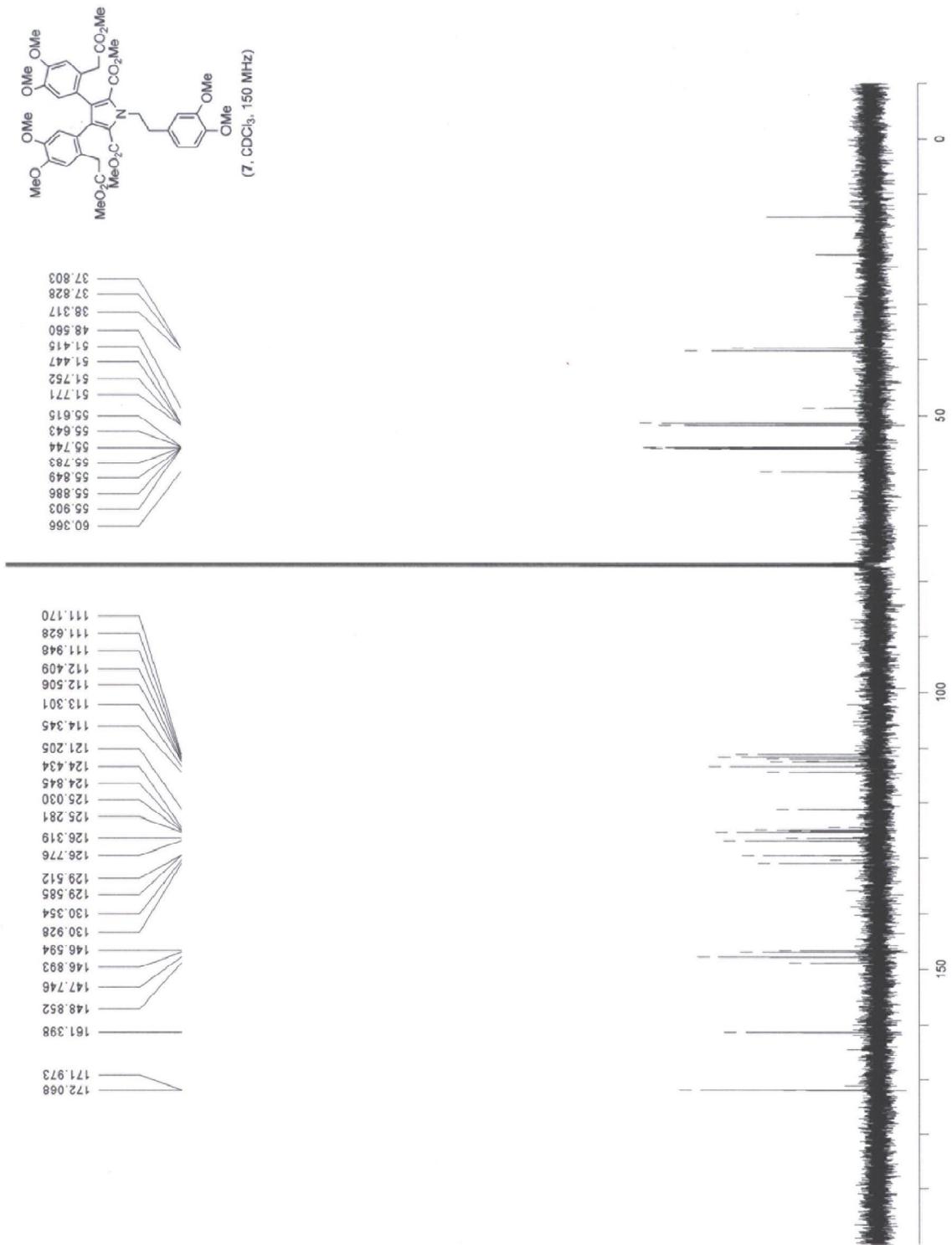


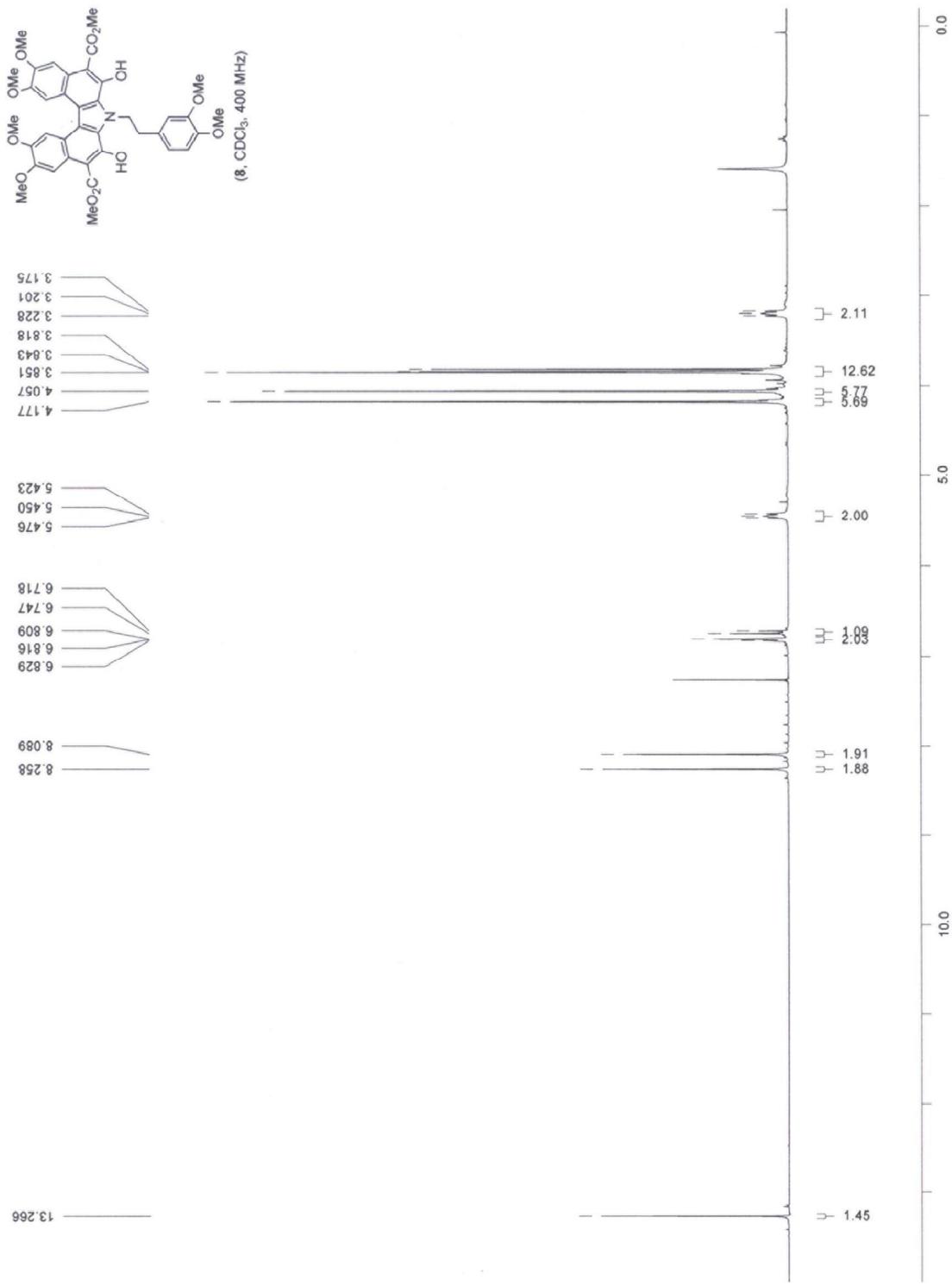


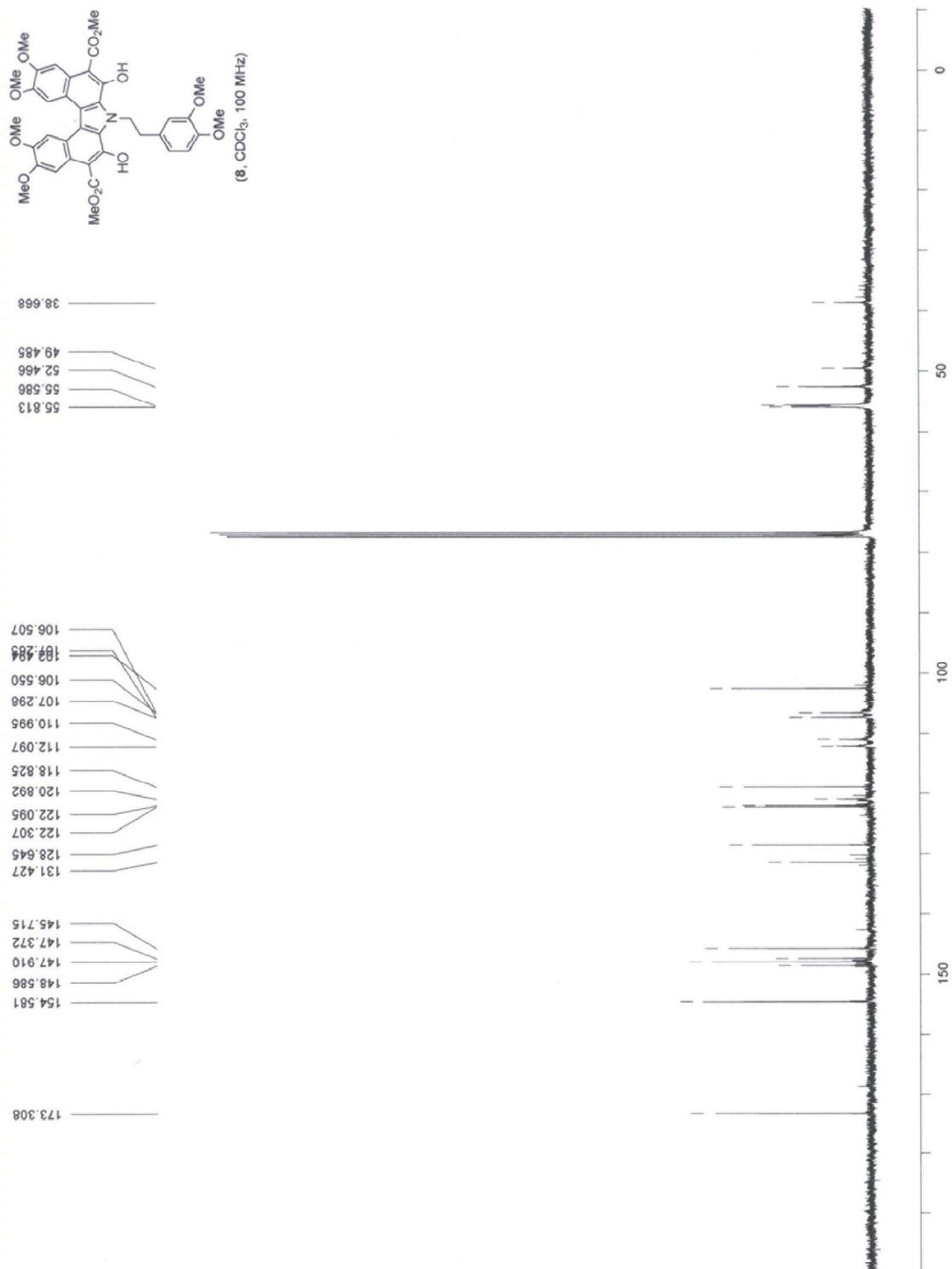


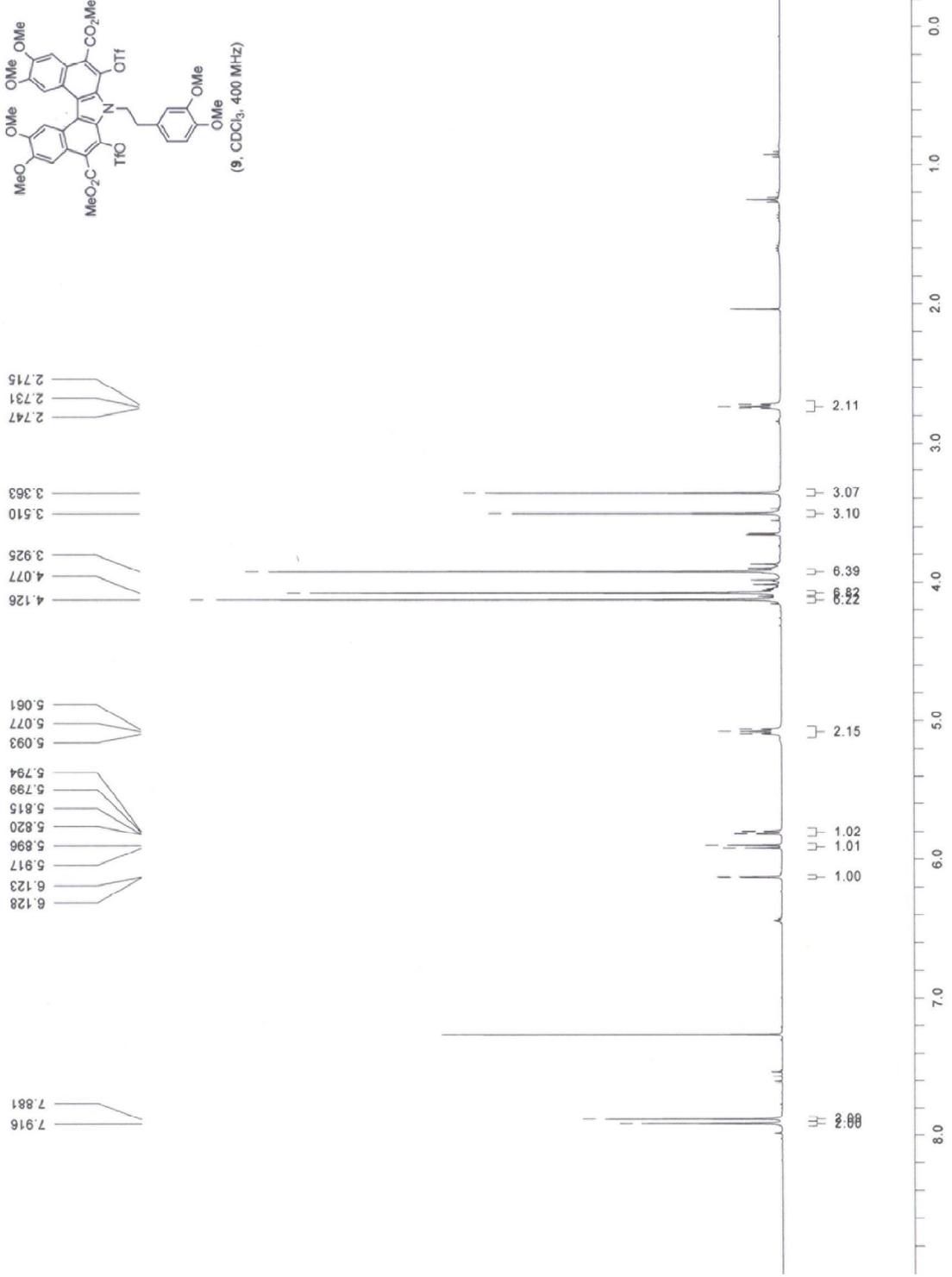


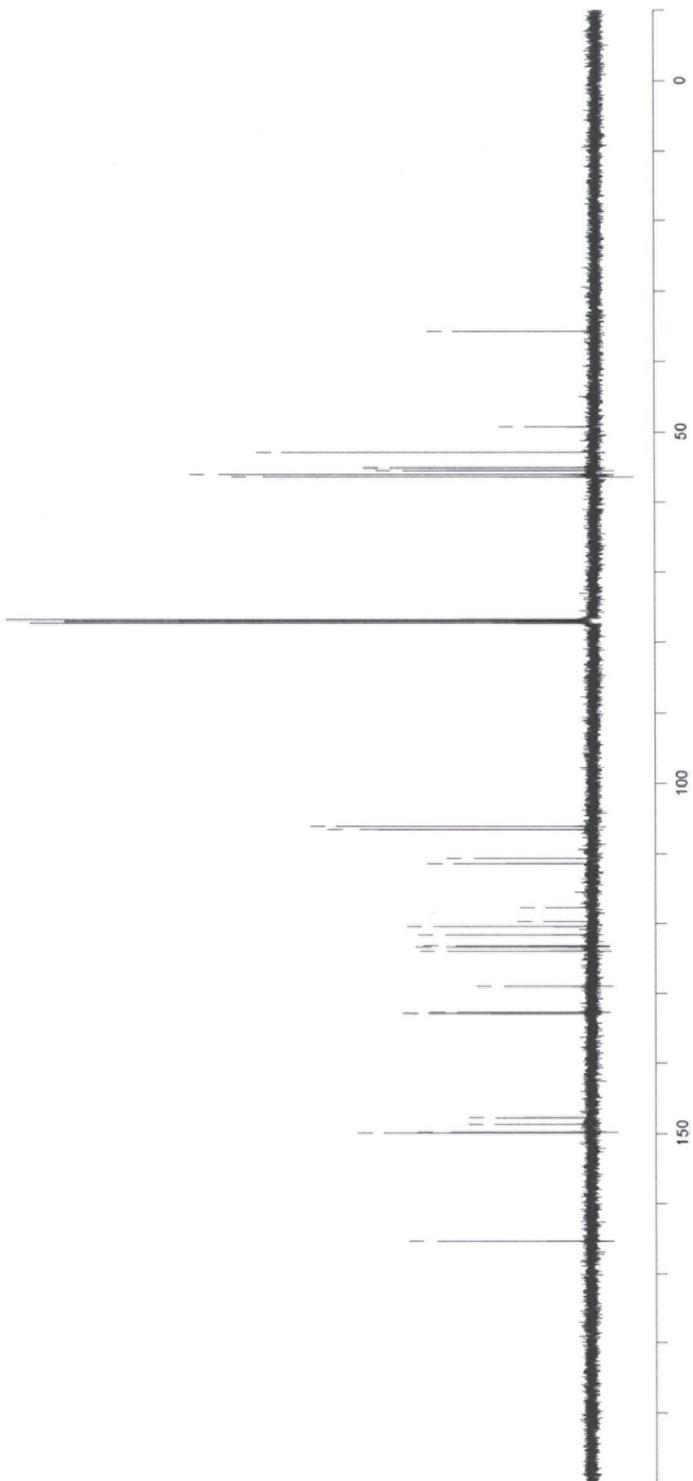
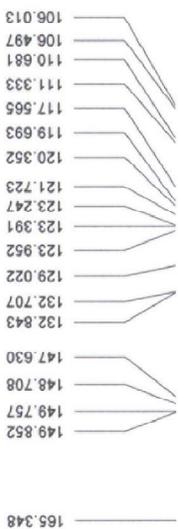
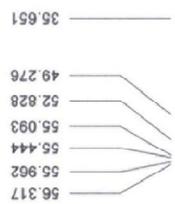
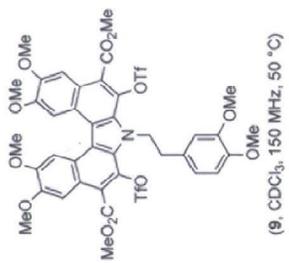


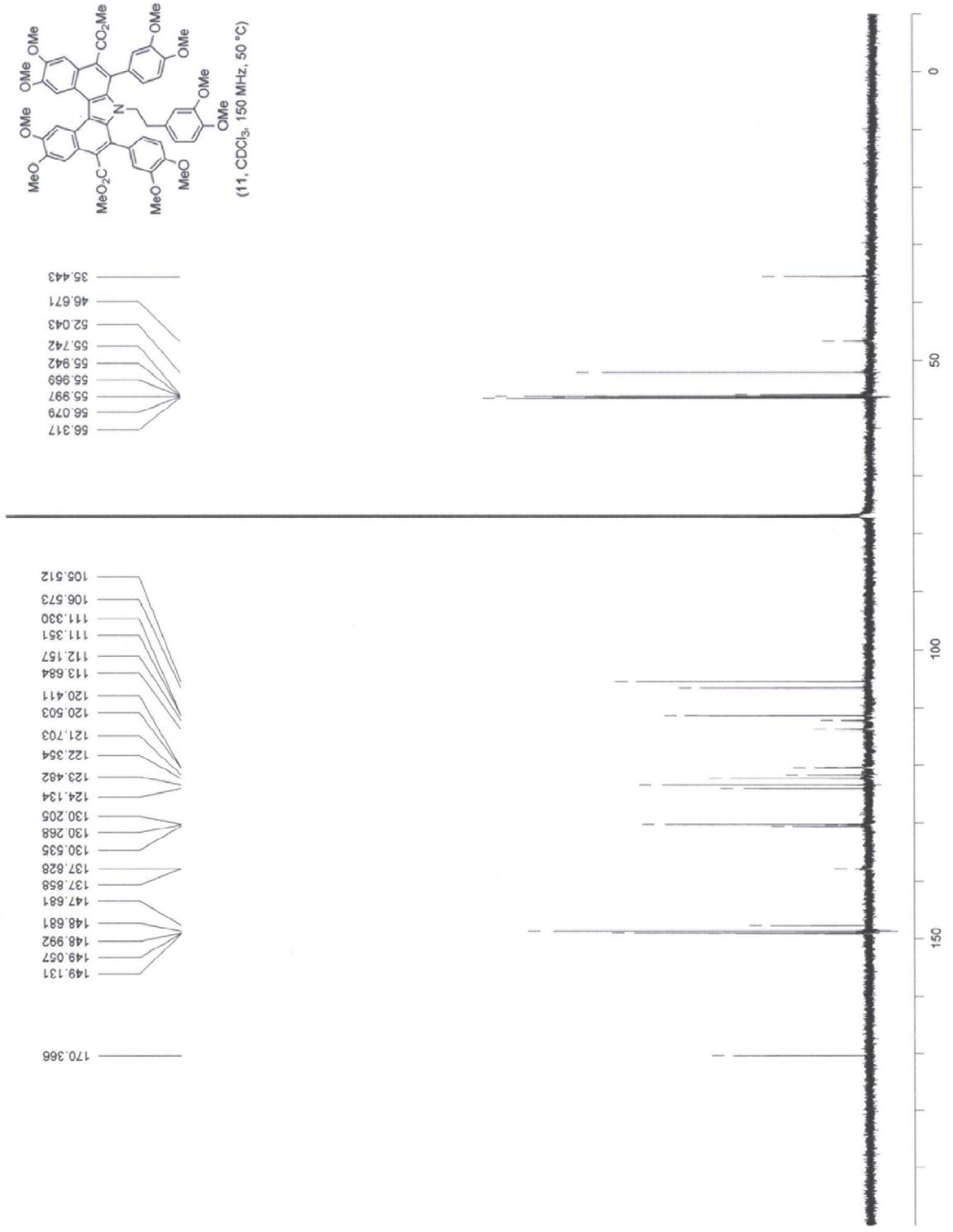


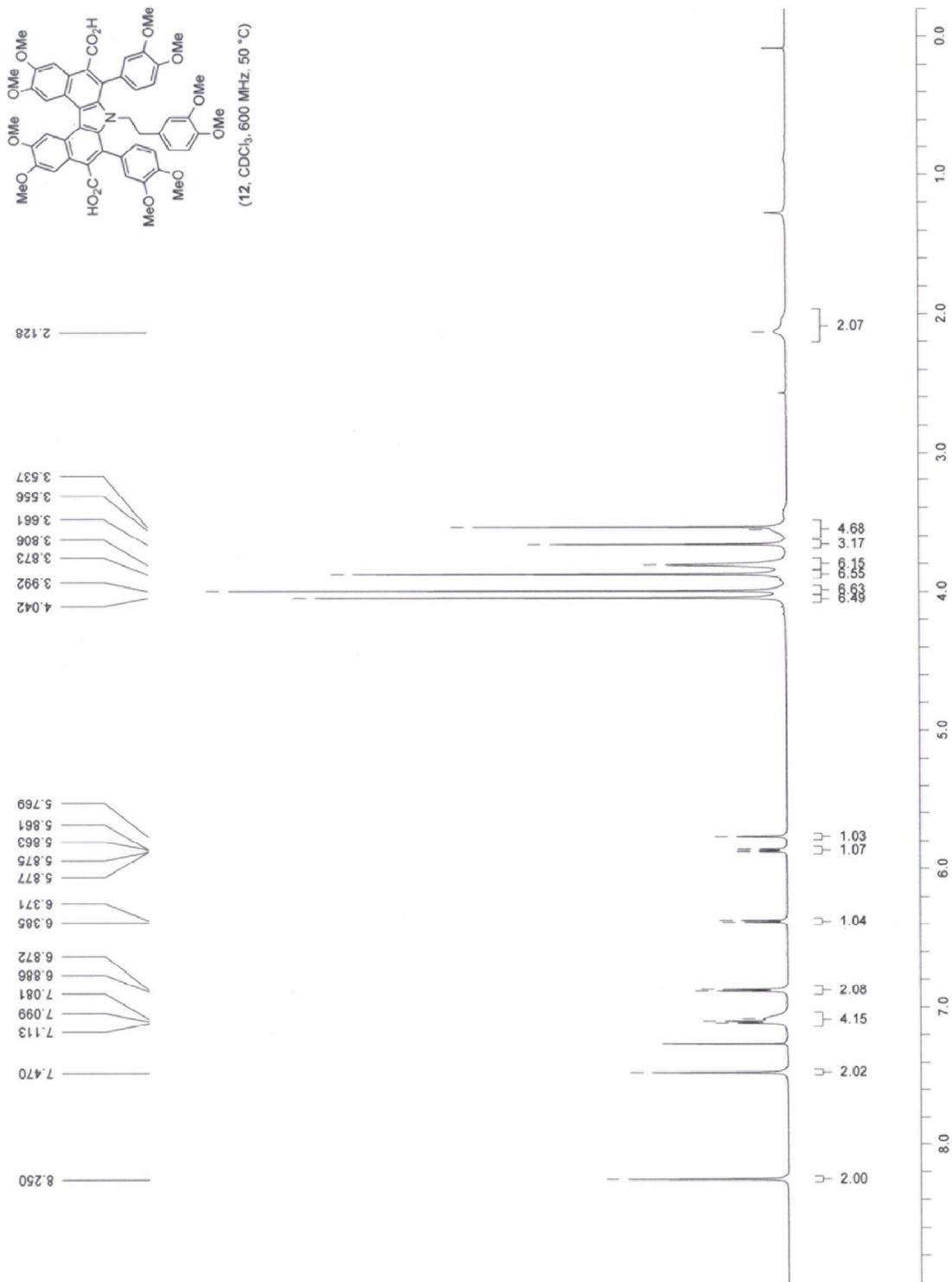


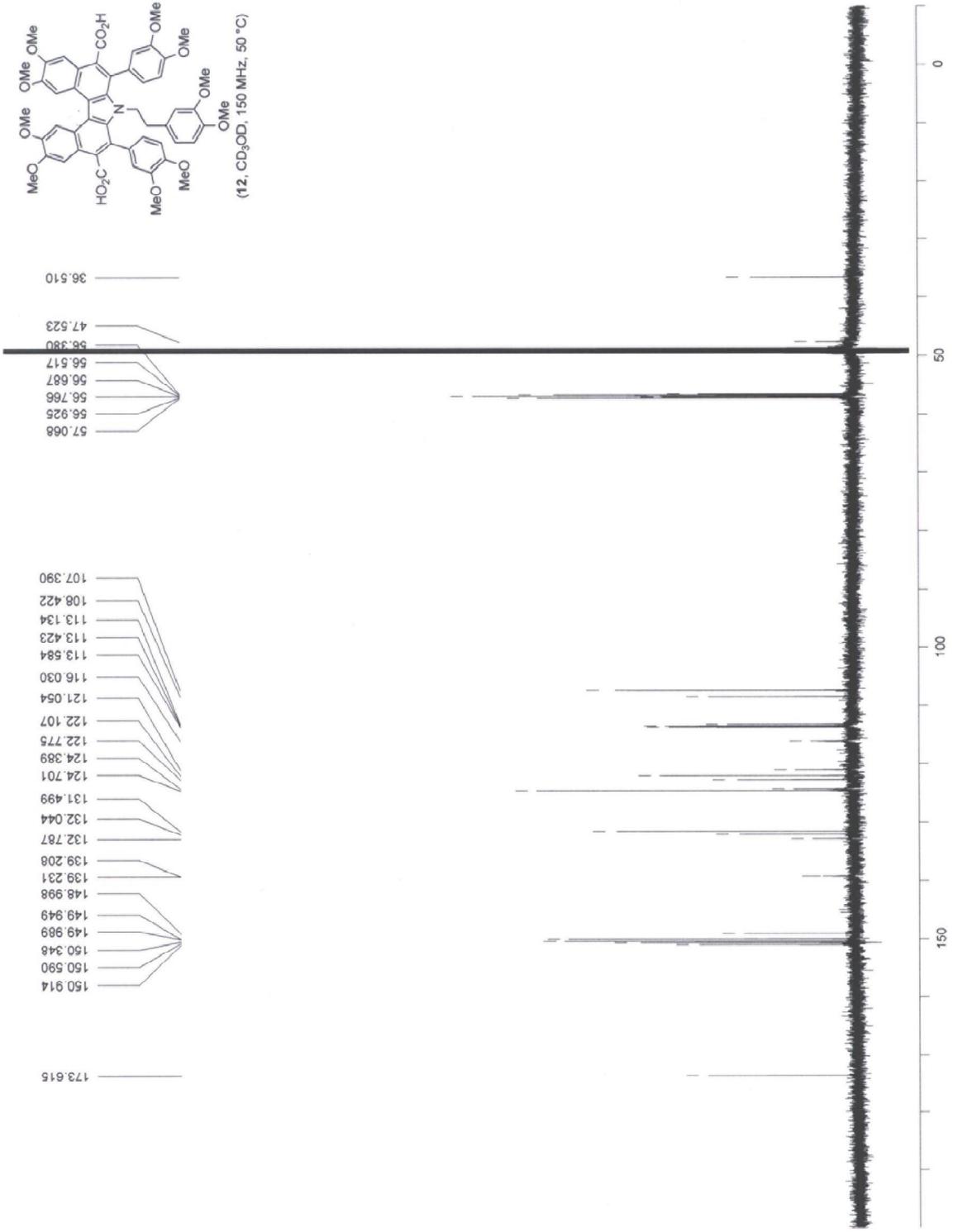


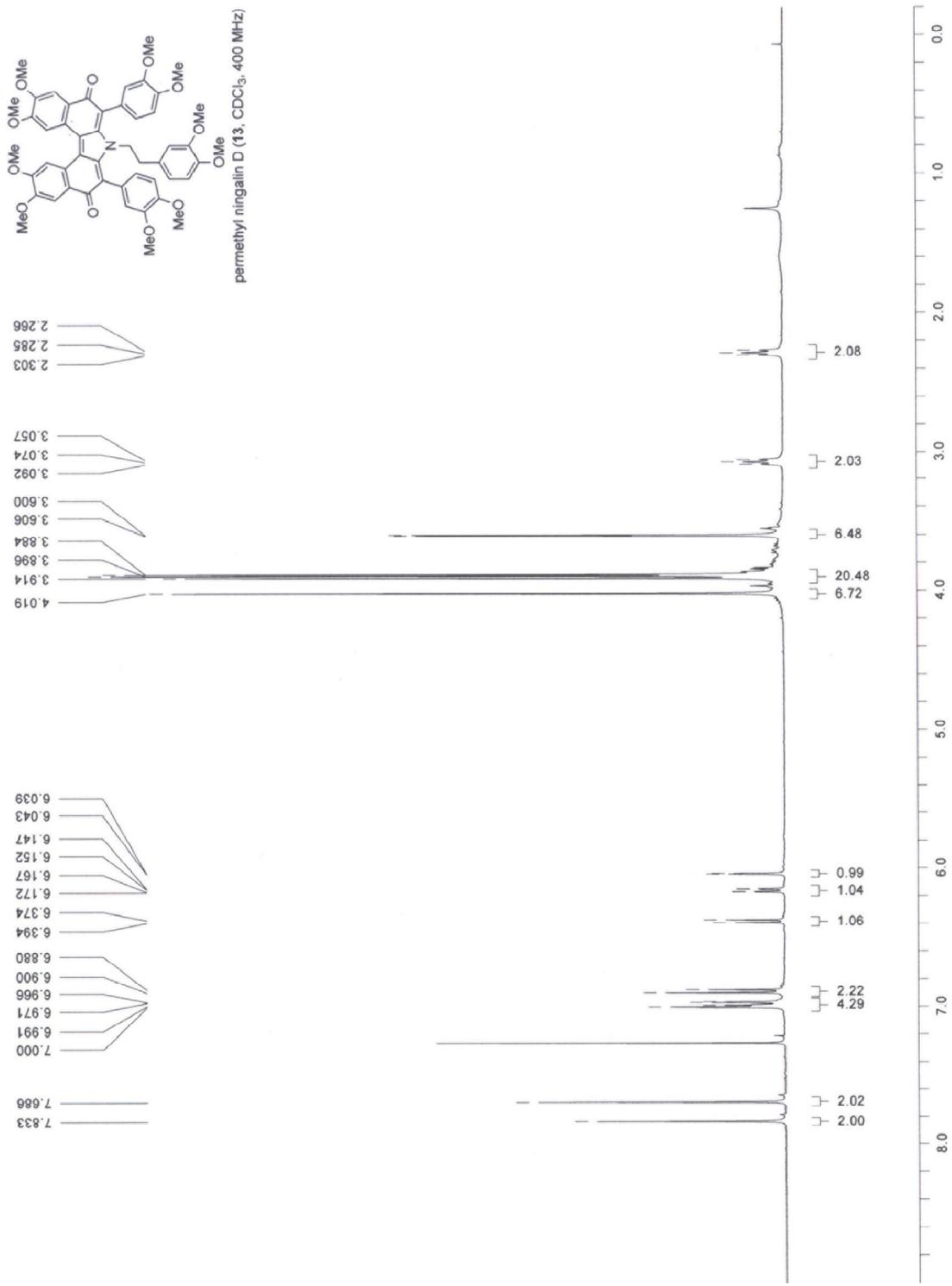


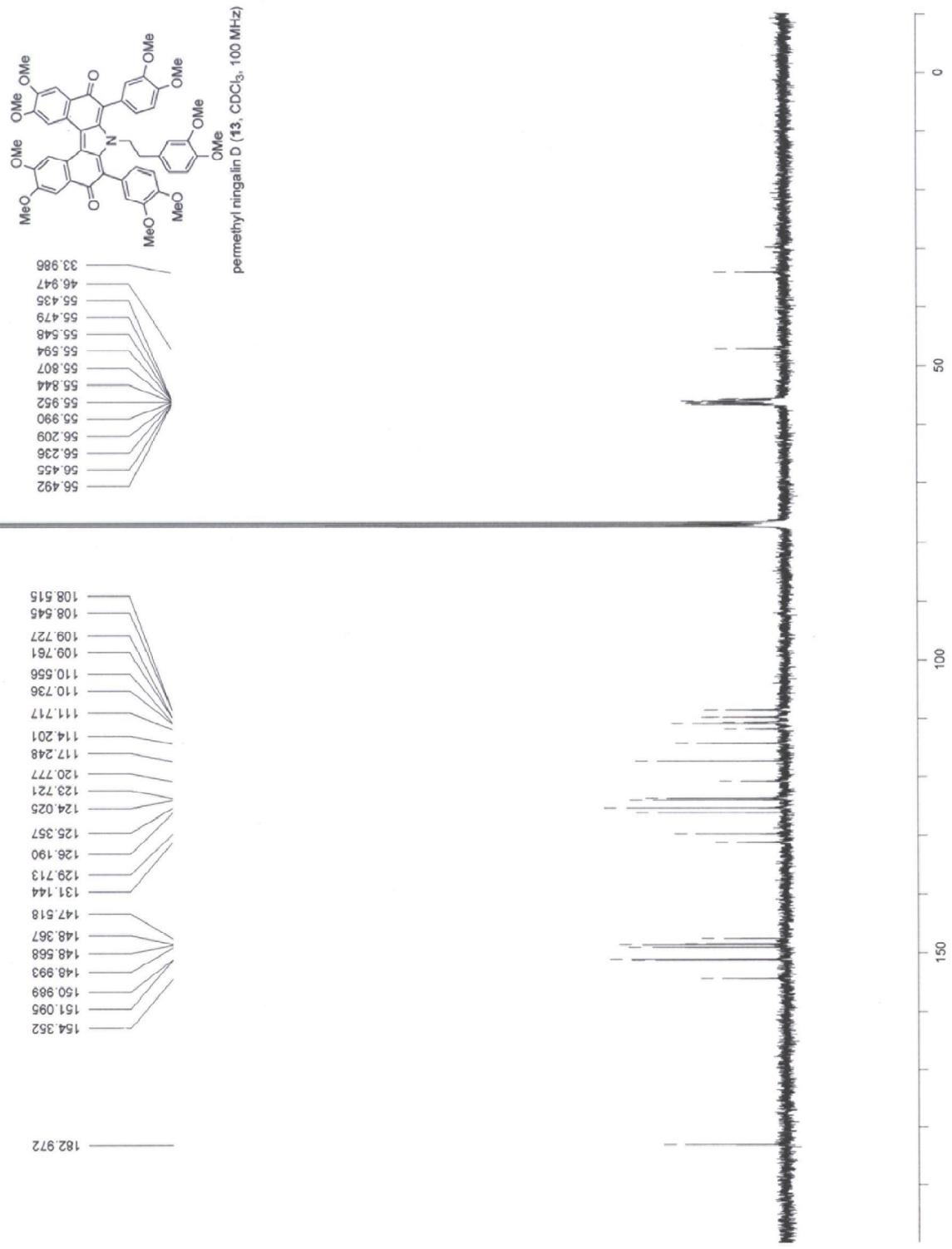


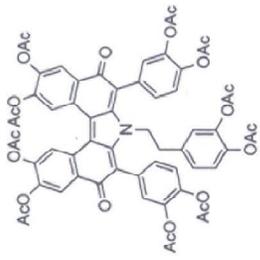




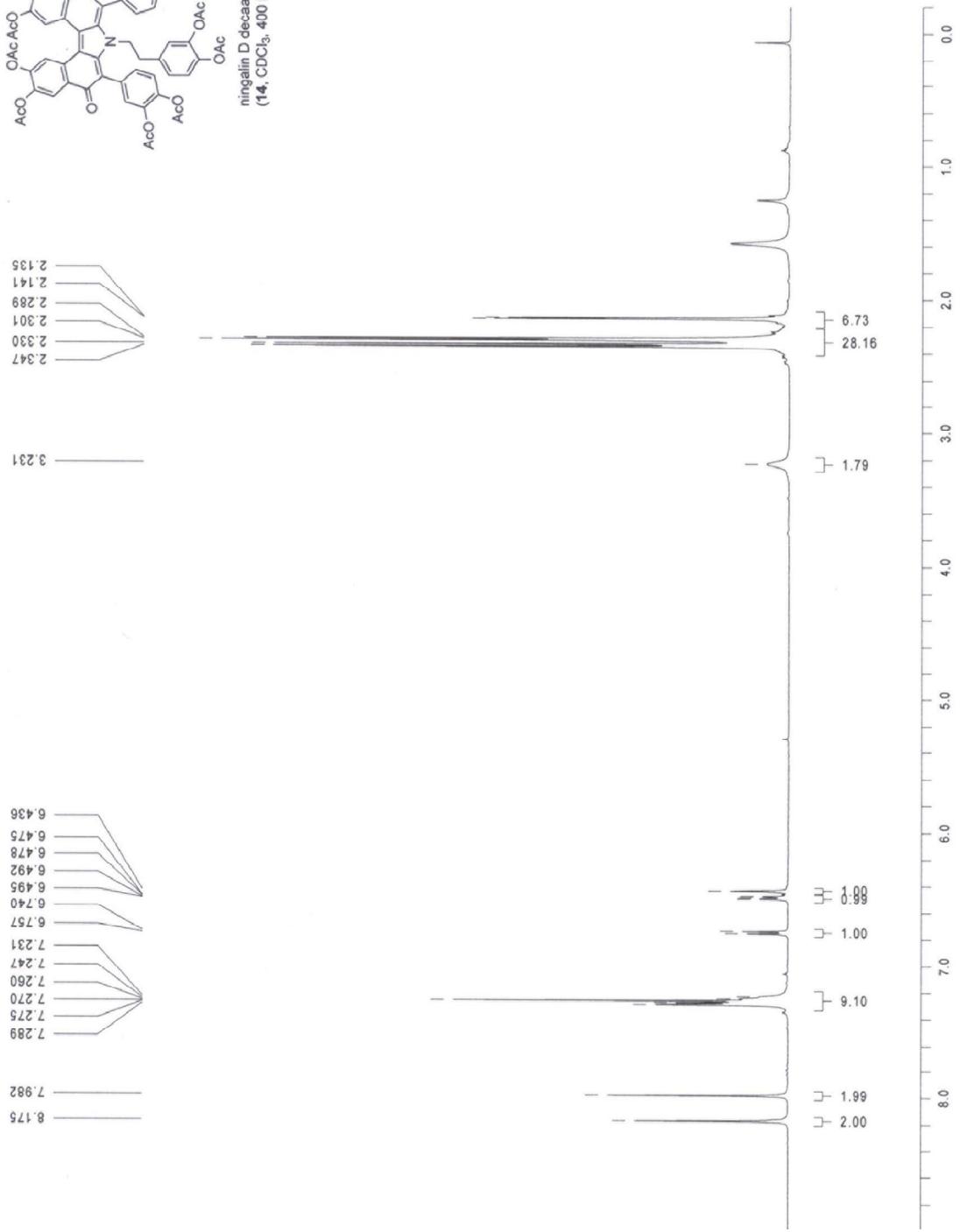


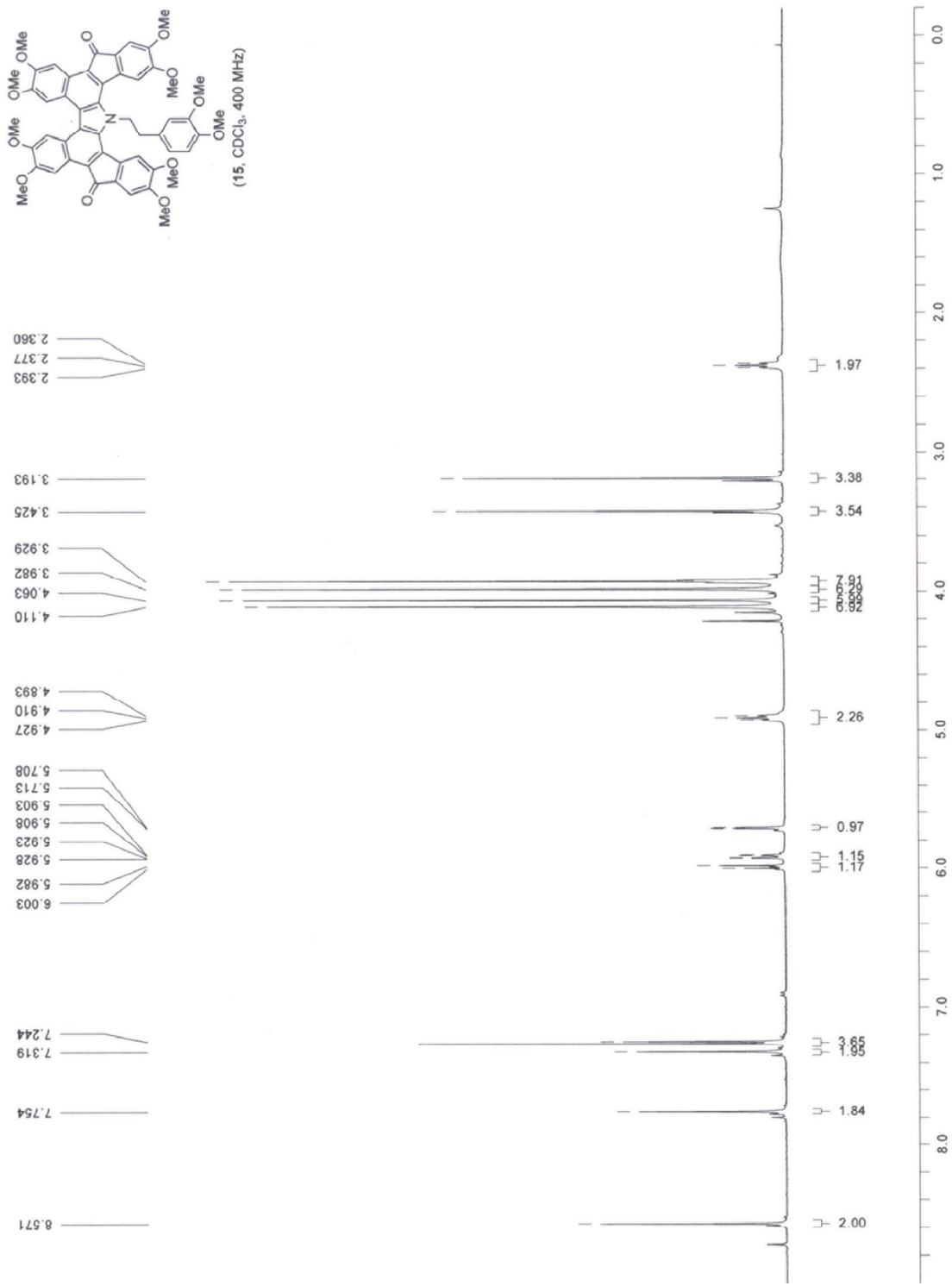


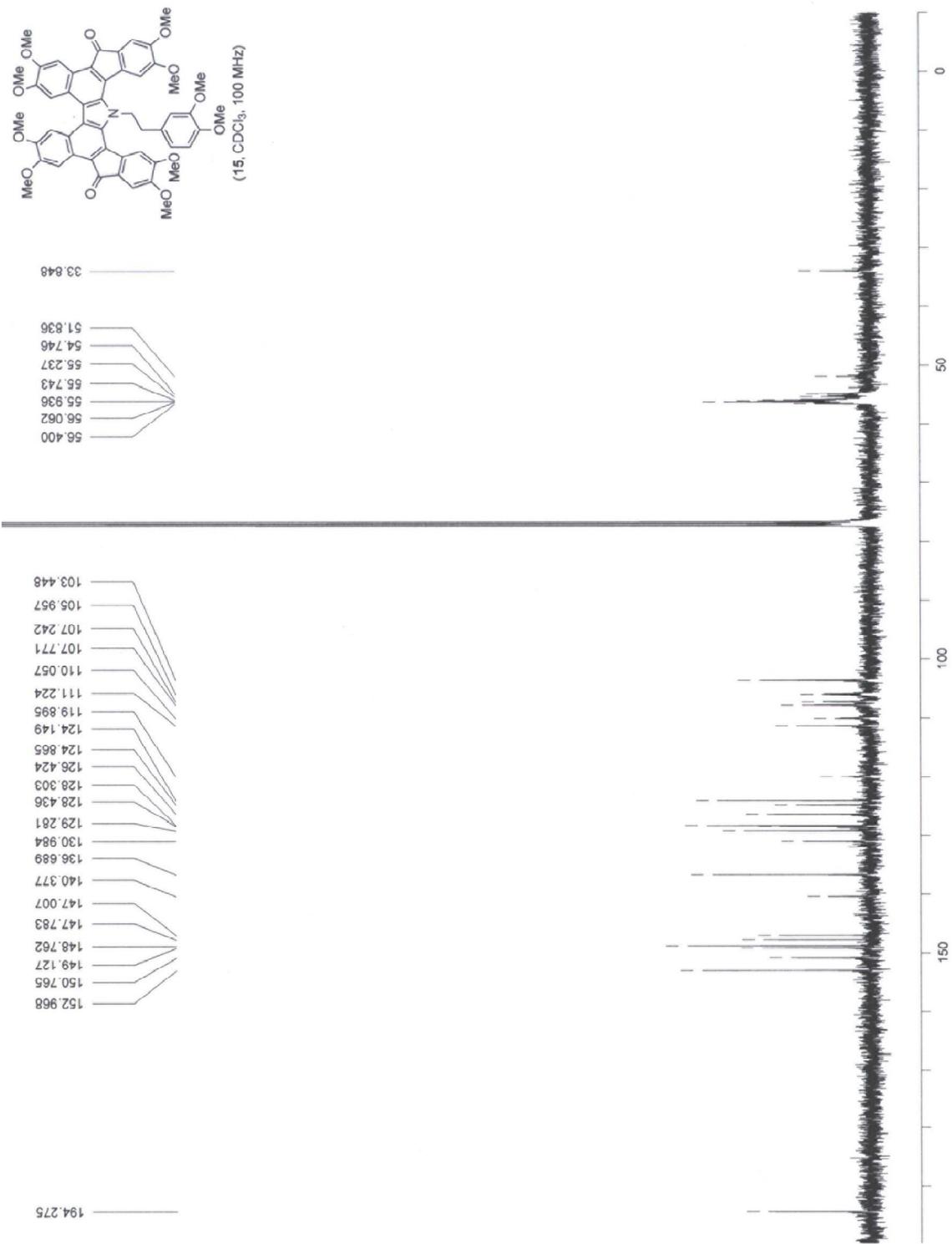


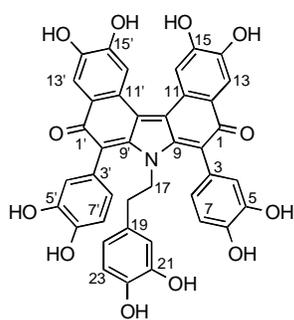


ningelmin D decaacetate
(14, CDCl₃, 400 MHz)









NMR Comparison of Synthetic and Natural **1a**.

C no.	¹³ C: Reported	Observed	¹ H: Reported	Observed
1, 1'	185.4	185.4		
2, 2'	118.9	118.9		
3, 3'	126.1	126.1		
4, 4'	119.4	119.4	6.82 (d)	6.79–6.78 (overlap)
5, 5'	146.1	146.2		
6, 6'	146.5	146.6		
7, 7'	116.2	116.3	6.83 (d)	6.79–6.78 (overlap)
8, 8'	124.2	124.2	6.68 (dd)	6.64 (dd)
9, 9'	156.4	156.5		
10, 10'	126.4	126.5		
11, 11'	125.0	125.0		
12, 12'	132.2	132.2		
13, 13'	115.0	115.0	7.45 (s)	7.41 (s)
14, 14'	148.9	149.0		
15, 15'	150.2	150.2		
16, 16'	114.2	114.2	7.85 (s)	7.81 (s)
17	47.5	47.8	2.95 (t)	2.91 (t)
18	34.5	35.0	2.13 (t)	2.09 (t)
19	130.5	130.6		
20	117.1	117.2	6.12 (d)	6.08 (d)
21	145.5	145.6		
22	144.6	144.7		
23	115.7	115.7	6.30 (d)	6.26 (d)
24	121.4	121.5	5.95 (dd)	5.91 (dd)