Supporting Information

Title

Rhodium(II) catalyzed synthesis of macrocycles incorporating oxindole *via* O-H/N-H insertion reactions

Author(s)

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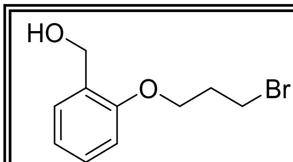
General Remarks: Melting points were determined on a capillary melting point apparatus and are uncorrected. IR spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance at 400 MHz using $CDCl_3$ in ppm (δ) related to tetramethylsilane (δ = 0.00) as an internal standard and are reported as follows; chemical shift (ppm), multiplicity (br = broad, s = singlet, d = doublet, m = multiplet), coupling constant (Hz) and integration. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz in $CDCl_3$. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.7 ppm for $CDCl_3$. Carbon types were determined from ^{13}C NMR and DEPT experiments. High resolution mass spectra (HRMS) were obtained on a Bruker APEX 47e FT-ICR mass spectrometer (ESIMS) or Waters QTof-micromass spectrometer. Optical rotations were taken on a Jasco P-2000 polarimeter. All solvents were purified by distillation following standard procedure. Thin layer chromatography was performed on silica or alumina plates and components visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh). All the reactions were conducted in oven-dried glassware under a positive pressure of argon with magnetic stirring. Reagents were added *via* syringe through septa.

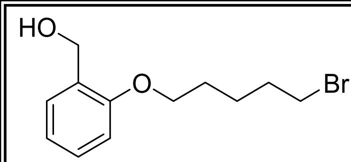
General procedure for the synthesis of compound 2: To the stirred solution of bromo aldehyde **1** (4.0 mmol) in MeOH (40 mL) was added $NaBH_4$ (8.0 mmol) slowly at 0 ˚C. The reaction mixture was stirred at 0 ˚C for 4 hrs and the solvent evaporated. To the residue water was added and extracted with DCM (3 X 50 mL). The entire organic layers were combined, dried over Na_2SO_4, evaporated the solvent. The residue was subjected to silica gel (100-200 mesh) column purification (70:30 hexane/EtOAc) to furnish the corresponding alcohol **2**.

Synthesis of compound 2a. Colourless liquid (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.22-2.28 (m, 2H), 2.96 (br s, H), 3.50 (t, 2H, J = 6.4 Hz), 4.06 (t, 2H, J = 6.0 Hz), 4.59 (s, 2H), 6.80 (d, 1H, J = 8.0 Hz), 6.87 (td, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.16-7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.02 (CH$_2$), 32.50 (CH$_2$), 65.52 (CH$_2$), 67.31 (CH$_2$), 111.34 (=CH), 120.82 (=CH), 127.24 (*quat-C*), 128.58 (=CH), 129.10 (=CH), 156.19 (*quat-C*); Anal. Calcd for $C_{10}H_{13}BrO_2$ (245.11): C, 49.00; H, 5.35. Found: C, 48.92; H, 5.40.



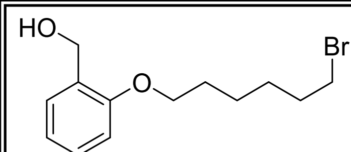
2a

Synthesis of compound 2b. Colourless liquid (86%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.54-1.60 (m, 2H), 1.74-1.79 (m, 2H), 1.83-1.90 (m, 2H), 3.37 (t, 2H, *J* = 6.8 Hz), 3.95 (t, 2H, *J* = 6.4 Hz), 4.62 (s, 2H), 6.78 (d, 1H, *J* = 8.0 Hz), 6.86 (td, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.16-7.196 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 28.67 (CH_2), 29.32 (CH_2), 32.67 (CH_2), 34.55 (CH_2), 64.88 (CH_2), 66.45 (CH_2), 111.23 (=*C*H), 118.43 (=*C*H), 119.30 (=*C*H), 126.87 (=*C*H), 129.82 (*quat-C*), 156.73 (*quat-C*); Anal. Calcd for $C_{12}H_{17}BrO_2$ (273.17): C, 52.76; H, 6.27. Found: C, 52.89; H, 6.35.



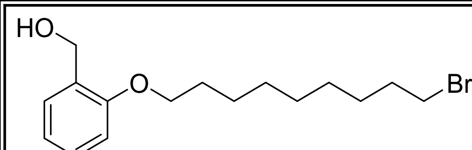
2b

Synthesis of compound 2c. Colourless liquid (80%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.39-1.56 (m, 4H), 1.82-1.93 (m, 4H), 3.18 (br s, 1H), 3.43 (t, 2H, *J* = 6.8 Hz), 4.03 (t, 2H, *J* = 6.4 Hz), 4.70 (s, 2H), 6.87 (d, 1H, *J* = 8.0 Hz), 6.94 (td, 1H, J_1 = 7.2 Hz, J_2 = 0.8 Hz), 7.24-7.30 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 25.39 (CH_2), 27.95 (CH_2), 29.16 (CH_2), 32.71 (CH_2), 33.76 (CH_2), 67.45 (CH_2), 67.79 (CH_2), 111.09 (=*C*H), 120.37 (=*C*H), 128.35 (=*C*H), 128.72 (=*C*H), 135.92 (*quat-C*), 158.67 (*quat-C*); Anal. Calcd for $C_{13}H_{19}BrO_2$ (287.19): C, 54.37; H, 6.67. Found: C, 54.51; H, 6.75.



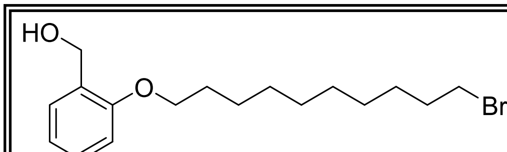
2c

Synthesis of compound 2d. Colourless liquid (86%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.21-1.34 (m, 8H), 1.57-1.63 (m, 2H), 1.76-1.81 (m, 4H), 2.92 (br s, 1H), 3.44 (t, 2H, *J* = 6.8 Hz), 4.05 (t, 2H, *J* = 6.8 Hz), 4.67 (s, 2H), 6.85 (d, 1H, *J* = 7.6 Hz), 6.91-6.97 (m, 1H), 7.05-7.12 (m, 2H); [13]C NMR (100 MHz, $CDCl_3$) δ 26.23 (CH_2), 27.34 (CH_2), 28.72 (CH_2), 29.12 (CH_2), 29.31 (CH_2), 29.38 (CH_2), 32.81 (CH_2), 34.27 (CH_2), 62.12 (CH_2), 68.04 (CH_2), 111.12 (=*C*H), 120.34 (=*C*H), 126.98 (=*C*H), 128.34 (=*C*H), 129.12 (*quat-C*), 156.65 (*quat-C*); Anal. Calcd for $C_{16}H_{25}BrO_2$ (329.27): C, 58.36; H, 7.65. Found: C, 58.47; H, 7.57.



2d

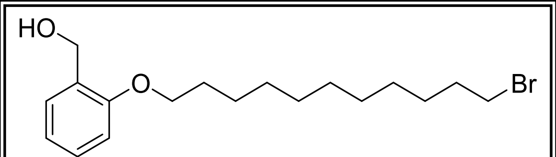
Synthesis of compound 2e. Colourless liquid (83%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.33-1.48 (m, 12H), 1.80-1.88 (m, 4H), 2.75 (br s, 1H), 3.41 (t, 2H, *J* = 6.8 Hz), 4.01 (t, 2H, *J* = 6.4 Hz), 4.69 (s, 2H), 6.87 (d,



2e

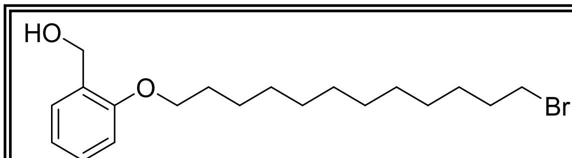
1H, J = 8.0 Hz), 6.94 (td, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.24-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.17 (CH$_2$), 28.18 (CH$_2$), 28.77 (CH$_2$), 29.30 (CH$_2$), 29.35 (CH$_2$), 29.40 (CH$_2$), 29.47 (CH$_2$), 32.85 (CH$_2$), 34.07 (CH$_2$), 62.02 (CH$_2$), 67.93 (CH$_2$), 111.02 (=*C*H), 120.48 (=*C*H), 128.48 (=*C*H), 128.75 (=*C*H), 129.26 (*quat-C*), 156.84 (*quat-C*); Anal. Calcd for $C_{17}H_{27}BrO_2$ (343.30): C, 59.48; H, 7.93. Found: C, 59.56; H, 7.86.

Synthesis of compound 2f. Colourless liquid (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.28-1.36 (m, 10H), 1.46-1.53 (m, 4H), 1.65-1.84 (m, 4H), 2.72 (br s, 1H), 3.45 (t, 2H, J = 6.8 Hz), 4.05 (t, 2H, J = 6.4 Hz), 4.73 (s, 2H), 6.85 (d, 1H, J = 8.0 Hz), 6.91 (t, 1H, J = 7.8 Hz) 7.21-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.34 (CH$_2$), 26.78 (CH$_2$), 28.12 (CH$_2$), 28.57 (CH$_2$), 28.75 (CH$_2$), 29.17 (CH$_2$), 29.63 (CH$_2$), 29.87 (CH$_2$), 32.12 (CH$_2$), 34.89 (CH$_2$), 62.32 (CH$_2$), 67.87 (CH$_2$), 111.12 (=*C*H), 119.56 (=*C*H), 126.89 (=*C*H), 128.01 (=*C*H), 129.65 (*quat-C*), 156.74 (*quat-C*); Anal. Calcd for $C_{18}H_{29}BrO_2$ (357.33): C, 60.50; H, 8.18. Found: C, 60.65; H, 8.26.



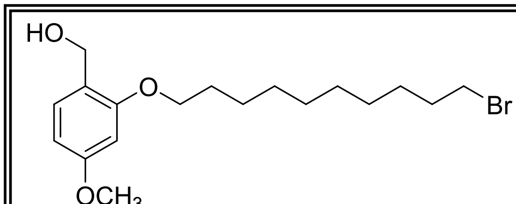
2f

Synthesis of compound 2g. Colourless liquid (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.31-1.48 (m, 16H), 1.78-1.90 (m, 4H), 3.41 (t, 2H, J = 7.2 Hz), 3.72 (br s, 1H), 4.01 (t, 2H, J = 6.4 Hz), 4.70 (s, 2H), 6.87 (d, 1H, J = 8.4 Hz), 6.93 (t, 1H, J = 7.2 Hz) 7.23-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.08 (CH$_2$), 26.17 (CH$_2$), 28.19 (CH$_2$), 28.77 (CH$_2$), 29.31 (CH$_2$), 29.37 (CH$_2$), 29.43 (CH$_2$), 29.53 (CH$_2$), 32.86 (CH$_2$), 34.00 (CH$_2$), 62.20 (CH$_2$), 68.00 (CH$_2$), 111.09 (=*C*H), 120.50 (=*C*H), 128.59 (=*C*H), 128.81 (=*C*H), 129.25 (*quat-C*), 156.94 (*quat-C*); Anal. Calcd for $C_{19}H_{31}BrO_2$ (371.35): C, 61.45; H, 8.41. Found: C, 61.59; H, 8.32.



2g

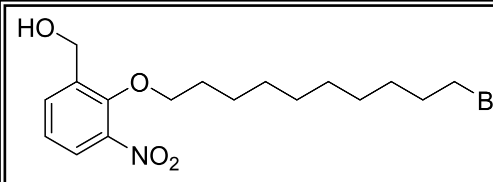
Synthesis of compound 2h. Colourless liquid (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.18-1.36 (m, 8H), 1.36-1.45 (m, 4H), 1.77-1.86 (m, 4H), 2.508 (br s, 1H), 3.39 (t, 2H, J = 6.8 Hz), 3.77 (s, 3H), 3.95 (t, 2H, J = 6.4 Hz), 4.60 (s, 2H), 6.41-6.43 (m, 2H), 7.15 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.16 (CH$_2$), 28.23 (CH$_2$), 28.54 (CH$_2$),



2h

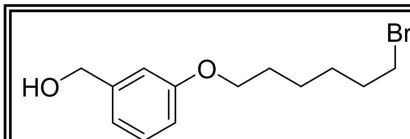
28.62 (CH_2), 28.82 (CH_2), 29.44 (CH_2), 29.51 (CH_2), 32.89 (CH_2), 34.01 (CH_2), 55.37 (CH_3), 68.11 (CH_2), 68.39 (CH_2), 99.38 (=CH), 99.02 (*quat-C*), 104.77 (=*C*H), 130.33 (=*C*H), 132.16 (*quat-C*), 157.90 (*quat-C*); Anal. Calcd for $C_{18}H_{29}BrO_3$ (373.33): C, 57.91; H, 7.83. Found: C, 57.79; H, 7.92.

Synthesis of compound 2i. Colourless liquid (82%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.31-1.49 (m, 12H), 1.82-1.89 (m, 4H), 2.57 (br s, 1H), 3.41 (t, 2H, *J* = 6.8 Hz), 4.10 (t, 2H, *J* = 6.4 Hz), 4.74 (s, 2H), 6.89 (d, 1H, *J* = 8.8 Hz), 8.15 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.8 Hz), 8.25 (d, 1H, *J* = 2.8 Hz); [13]C NMR (100 MHz, $CDCl_3$) δ 25.97 (CH_2), 28.12 (CH_2), 28.70 (CH_2), 28.95 (CH_2), 28.21 (CH_2), 29.30 (CH_2), 29.36 (CH_2), 32.79 (CH_2), 34.00 (CH_2), 60.57 (CH_2), 69.08 (CH_2), 104.43 (=*C*H), 123.61 (=*C*H), 125.00 (=*C*H), 130.45 (*quat-C*), 141.28 (*quat-C*), 161.36 (*quat-C*); Anal. Calcd for $C_{17}H_{26}BrNO_4$ (388.30): C, 52.58; H, 6.75; N, 3.61. Found: C, 52.72; H, 6.61; N, 3.58.



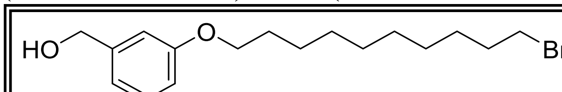
2i

Synthesis of compound 2j. Colourless liquid (80%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.41-1.45 (m, 4H), 1.70-1.73 (m, 2H), 1.79-1.83 (m, 2H), 3.34 (t, 2H, *J* = 6.4 Hz), 3.88 (t, 2H, *J* = 6.4 Hz), 4.57 (s, 2H), 6.73 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 6.833 (d, 2H, *J* = 1.6 Hz), 7.15-7.28 (m, 1H); [13]C NMR (100 MHz, $CDCl_3$) δ 26.54 (CH_2), 27.93 (CH_2), 29.45 (CH_2), 30.63 (CH_2), 32.65 (CH_2), 66.34 (CH_2), 67.23 (CH_2), 111.78 (=*C*H), 113.56 (=*C*H), 117.89 (=*C*H), 128.34 (=*C*H), 137.41 (*quat-C*), 159.53 (*quat-C*); Anal. Calcd for $C_{13}H_{19}BrO_2$ (287.19): C, 54.37; H, 6.67. Found: C, 54.15; H, 6.60.



2j

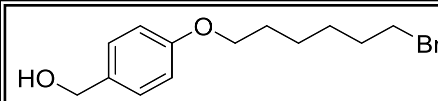
Synthesis of compound 2k. Colourless liquid (83%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.33-1.47 (m, 12H), 1.77-1.89 (m, 4H), 1.96 (br s, 1H), 3.42 (t, 2H, *J* = 6.8 Hz), 3.97 (t, 2H, *J* = 6.4 Hz), 4.67 (s, 2H), 6.82-6.85 (m, 1H), 6.92-6.94 (m, 2H), 7.25-7.29 (m, 1H); [13]C NMR (100 MHz, $CDCl_3$) δ 26.03 (CH_2), 28.16 (CH_2), 28.73 (CH_2), 29.27 (CH_2), 29.32 (CH_2), 29.35 (CH_2), 29.43 (CH_2), 32.82 (CH_2), 34.04 (CH_2), 65.30 (CH_2), 67.94 (CH_2), 112.90 (=*C*H), 113.82 (=*C*H), 118.92 (=*C*H), 129.56 (=*C*H), 142.46 (*quat-C*),



2k

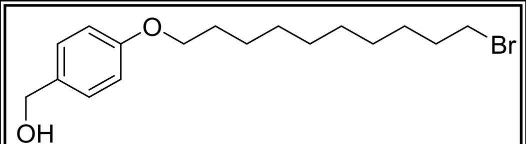
159.42 (*quat-C*); Anal. Calcd for $C_{17}H_{27}BrO_2$ (343.30): C, 59.48; H, 7.93. Found: C, 59.61; H, 7.86.

Synthesis of compound 2l. Colourless liquid (87%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.42-1.47 (m, 2H), 1.71-1.74 (m, 2H), 1.81-1.84 (m, 2H), 3.35 (t, 2H, J = 6.4 Hz), 3.89 (t, 2H, J = 6.4 Hz), 4.54 (s, 2H), 6.81 (dd, 2H, J_1 = 6.4 Hz, J_2 = 2.0 Hz), 7.19 (dd, 2H, J_1 = 6.8 Hz, J_2 = 2.4 Hz); [13]C NMR (100 MHz, $CDCl_3$) δ 25.31 (CH_2), 27.93 (CH_2), 29.10 (CH_2), 32.69 (CH_2), 33.74 (CH_2), 67.78 (CH_2), 71.49 (CH_2), 114.42 (=*C*H), 129.40 (=*C*H), 130.42 (*quat-C*), 158.67 (*quat-C*); Anal. Calcd for $C_{13}H_{19}BrO_2$ (287.19): C, 54.37; H, 6.67. Found: C, 54.51; H, 6.59.



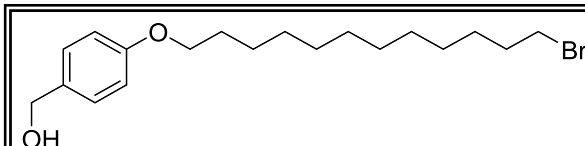
2l

Synthesis of compound 2m. Colourless liquid (83%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.19-1.38 (m, 12H), 1.68-1.80 (m, 4H), 3.33 (t, 2H, J = 6.8 Hz), 3.88 (t, 2H, J = 6.4 Hz), 4.54 (s, 2H), 6.81 (d, 2H, J = 8.8 Hz), 7.21 (d, 2H, J = 8.0 Hz), 7.25-7.29 (m, 1H); [13]C NMR (100 MHz, $CDCl_3$) δ 26.01 (CH_2), 28.16 (CH_2), 28.73 (CH_2), 29.25 (CH_2), 29.31 (CH_2), 29.34 (CH_2), 29.42 (CH_2), 32.83 (CH_2), 33.98 (CH_2), 65.13 (CH_2), 68.07 (CH_2), 114.62 (=*C*H), 128.63 (=*C*H), 132.95 (*quat-C*), 158.84 (*quat-C*); Anal. Calcd for $C_{17}H_{27}BrO_2$ (343.30): C, 59.48; H, 7.93. Found: C, 59.61; H, 7.86.



2m

Synthesis of compound 2n. Colourless liquid (79%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.43-1.27 (m, 12H), 1.32-1.38 (m, 4H), 1.68-1.82 (m, 4H), 3.33 (t, 2H, J = 6.8 Hz), 3.88 (t, 2H, J = 6.8 Hz), 4.54 (s, 2H), 6.81 (d, 2H, J = 8.8 Hz), 7.20 (d, 2H, J = 8.4 Hz); [13]C NMR (100 MHz, $CDCl_3$) δ 26.04 (CH_2), 28.18 (CH_2), 28.76 (CH_2), 29.27 (CH_2), 29.37 (CH_2), 29.42 (CH_2), 29.51 (CH_2), 32.85 (CH_2), 34.01 (CH_2), 65.13 (CH_2), 68.10 (CH_2), 114.62 (=*C*H), 128.63 (=*C*H), 132.93 (*quat-C*), 158.85 (*quat-C*); Anal. Calcd for $C_{12}H_{17}BrO_2$ (273.17): C, 52.76; H, 6.27. Found: C, 52.89; H, 6.35.



2n

General procedure for compounds 4

To an oven-dried flask, a solution containing 3-diazooxindole **3** (200 mg, 1.25 mmol) and potassium carbonate (434 mg, 3.14 mmol) in dry DMF was taken under argon atmosphere. To this reaction mixture, a solution of appropriate bromobenzyl alcohol **2** (1.35 mmol) in dry DMF was slowly added over a period of 30 min and then a catalytic amount of tetrabutylammonium iodide. The progress of the reaction was monitored using TLC. The mixture was extracted with dichloromethane (3×25 mL) and the combined organic layers were washed with water (3×25 mL), brine (2×25 mL) and dried (anhydrous Na_2SO_4). The solvent was removed under reduced pressure and the resulting residue purified using column chromatography (SiO_2, hexane/ethyl acetate 80:20) to afford the respective diazoamides **4**.

Synthesis of diazoamide 4a. Red viscous liquid (357 mg, 88%); IR (neat): ν_{max} 3454, 2933, 2876, 2093, 1674, 1610, 1468, 1399, 1241, 1178, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 2.16-2.22 (m, 2H), 3.99 (t, 2H, *J* = 6 Hz), 4.04 (t, 2H, *J* = 6.4 Hz), 4.71 (s, 2H), 6.78 (d, 1H, *J* = 8.4 Hz), 6.92 (t, 1H, *J* = 7.2 Hz), 6.96 (d, 1H, *J* = 8 Hz), 7.04-7.08 (m, 1H), 7.13-7.23 (m, 3H), 7.31 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.81 (CH_2), 37.31 (CH_2), 60.89 (*quat-C*), 61.41 (CH_2), 64.19 (CH_2), 108.86 (=*C*H), 111.01 (=*C*H), 116.85 (*quat-C*), 118.40 (=*C*H), 120.84 (=*C*H), 122.58 (=*C*H), 125.58 (=*C*H), 128.88 (=*C*H), 129.31 (=*C*H), 129.58 (*quat-C*), 133.55 (*quat-C*), 156.35 (*quat-C*), 166.81 (*quat-C*); HRMS (ESI) Calcd for $C_{18}H_{17}N_3O_3$ $[M+Na]^+$ 346.1168; found, 346.1159.

Synthesis of diazoamide 4b. Red viscous liquid (384 mg, 87%); IR (neat): ν_{max} 3432, 2927, 2831, 2056, 1646, 1612, 1467, 1321, 1245, 1137, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.23-1.65 (m, 4H), 1.74-1.81 (m, 2H), 3.76 (t, 2H, *J* = 8.0 Hz), 3.96 (t, 2H, *J* = 7.2 Hz), 4.54 (s, 2H), 6.74 (d, 1H, *J* = 7.6 Hz), 6.82-6.91 (m, 2H), 7.11 (t, 1H, *J* = 8.0 Hz), 7.16 (t, 2H, *J* = 7.6 Hz), 7.25-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.76 (CH_2), 26.12 (CH_2), 28.93 (CH_2), 40.33 (CH_2), 63.16 (CH_2), 66.64 (CH_2), 108.12 (=*C*H), 109.56 (=*C*H), 116.17 (*quat-C*), 118.47 (=*C*H), 120.34 (=*C*H), 121.26 (=*C*H), 125.41 (=*C*H), 127.96 (=*C*H), 128.34 (=*C*H), 129.07 (*quat-C*), 133.23 (*quat-C*), 156.38 (*quat-C*), 166.19 (*quat-C*); Anal. Calcd for $C_{20}H_{21}N_3O_3$ (351.40): C, 68.36; H, 6.02; N, 11.96. Found: C, 68.50; H, 6.10; N, 12.02.

Synthesis of diazoamide 4c. Red viscous liquid (409 mg, 89%); IR (neat): ν_{max} 3443, 2934, 2859, 2091, 1672, 1609, 1491, 1398, 1238, 1197, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.38-1.56 (m, 4H), 1.70-1.84 (m, 4H), 3.83 (t, 2H, *J* = 7.6 Hz), 3.99 (t, 2H, *J* = 6.4 Hz), 4.67 (s, 2H), 6.84 (d, 1H, *J* = 8 Hz), 6.90-6.94 (m, 2H), 7.07 (t, 1H, *J* = 7.2 Hz), 7.12 (t, 2H, *J* = 7.6 Hz), 7.20-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.90 (CH_2), 26.53 (CH_2), 27.97 (CH_2), 29.14 (CH_2), 40.52 (CH_2), 62.07 (CH_2), 67.75 (CH_2), 108.92 (=CH), 111.04 (=CH), 116.89 (*quat-C*), 118.37 (=CH), 120.54 (=CH), 121.96 (=CH), 125.43 (=CH), 128.70 (=CH), 128.84 (=CH), 129.22 (*quat-C*), 133.81 (*quat-C*), 156.83 (*quat-C*), 166.82 (*quat-C*); Anal. Calcd for $C_{21}H_{23}N_3O_3$ (365.43): C, 69.02; H, 6.34; N, 11.50. Found: C, 69.18; H, 6.37; N, 11.46.

Synthesis of diazoamide 4d. Red viscous liquid (430 mg, 84%); IR (neat): ν_{max} 3441, 2919, 2832, 2076, 1689, 1637, 1467, 1212, 1167, 1034, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.22-1.42 (m, 12H), 1.76-1.83 (m, 2H), 2.31 (s, 1H), 3.84 (t, 2H, *J* = 7.6 Hz), 4.02 (t, 2H, *J* = 6.4 Hz), 4.62 (s, 2H), 6.63 (d, 1H, *J* = 7.6 Hz), 6.96 (t, 2H, *J* = 8.0 Hz), 7.09 (t, 1H, *J* = 7.6 Hz), 7.13-7.19 (m, 2H), 7.21-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.34 (CH_2), 27.17 (CH_2), 28.46 (CH_2), 28.85 (CH_2), 29.13 (CH_2), 29.43 (CH_2), 29.95 (CH_2), 40.56 (CH_2), 60.76 (*quat-C*), 63.15 (CH_2), 66.84 (CH_2), 108.13 (=CH), 110.43 (=CH), 116.74 (*quat-C*), 118.39 (=CH), 120.41 (=CH), 121.76 (=CH), 124.29 (=CH), 127.87 (=CH), 128.64 (=CH), 129.24 (*quat-C*), 133.94 (*quat-C*), 158.76 (*quat-C*), 167.85 (*quat-C*); Anal. Calcd for $C_{24}H_{29}N_3O_3$ (407.51): C, 70.74; H, 7.17; N, 10.31. Found: C, 70.81; H, 7.21; N, 10.39.

Synthesis of diazoamide 4e. Red viscous liquid (455 mg, 86%); IR (neat): ν_{max} 3445, 2927, 2854, 2089, 1672, 1607, 1455, 1238, 1103, 906, 724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29-1.32 (m, 10H), 1.40-1.45 (m, 2H), 1.67-1.70 (m, 2H), 1.74-1.80 (m, 2H), 2.69 (s, 1H), 3.79 (t, 2H, *J* = 7.2 Hz), 3.97 (t, 2H, *J* = 6.4 Hz), 4.68 (s, 2H), 6.83 (d, 1H, *J* = 8 Hz), 6.90 (t, 2H, *J* = 8 Hz), 7.05 (t, 1H, *J* = 8 Hz), 7.15-7.18 (m, 2H), 7.20-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.12 (CH_2), 26.87 (CH_2), 28.06 (CH_2), 29.25 (CH_2), 29.27 (CH_2), 29.29 (CH_2), 29.38 (CH_2), 29.44 (CH_2), 40.77 (CH_2), 60.70 (*quat-C*), 62.02 (CH_2), 67.95 (CH_2), 108.93 (=CH), 111.02 (=CH), 116.88 (*quat-C*), 118.35 (=CH), 120.47 (=CH), 121.88 (=CH), 125.39 (=CH), 128.47 (=CH), 128.72 (=CH), 129.34 (*quat-C*), 133.92 (*quat-C*), 159.86 (*quat-C*), 166.76 (*quat-C*); Anal. Calcd for $C_{25}H_{31}N_3O_3$ (421.53): C, 71.23; H, 7.41; N, 11.39. Found: C, 71.31; H, 7.36; N, 11.44.

Synthesis of diazoamide 4f. Red viscous liquid (440 mg, 82%); IR (neat): ν_{max} 3427, 2940, 2855, 2093, 1672, 1610, 1458, 1243, 1198, 903, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29-1.40 (m, 10H), 1.49-1.67 (m, 4H), 1.72-1.84 (m, 2H), 2.67 (s, 1H), 3.65 (t, 2H, *J* = 7.2 Hz), 3.93 (t, 2H, *J* = 6.8 Hz), 4.87 (s, 2H), 6.73 (d, 1H, *J* = 7.2 Hz), 6.99 (d, 2H, *J* = 7.6 Hz), 7.03-7.17 (m, 3H), 7.31-7.34 (m, 1H), 7.39 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.32 (CH_2), 26.45 (CH_2), 27.47 (CH_2), 28.16 (CH_2), 28.76 (CH_2), 29.45 (CH_2), 29.63 (CH_2), 29.98 (CH_2), 30.12 (CH_2), 40.18 (CH_2), 60.69 (*quat-C*), 63.74 (CH_2), 66.34 (CH_2), 108.12 (=CH), 109.89 (=CH), 114.45 (*quat-C*), 116.56 (=CH), 119.97 (=CH), 121.26 (=CH), 124.17 (=CH), 126.39 (=CH), 128.92 (=CH), 129.04 (*quat-C*), 134.18 (*quat-C*), 157.34 (*quat-C*), 167.55 (*quat-C*); Anal. Calcd for $C_{26}H_{33}N_3O_3$ (435.56): C, 71.70; H, 7.64; N, 9.65. Found: C, 71.82; H, 7.60; N, 9.58.

Synthesis of diazoamide 4g. Red viscous liquid (486 mg, 86%); IR (neat): ν_{max} 3447, 2926, 2854, 2090, 1674, 1608, 1467, 1399, 1239, 1194, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.31-1.32 (m, 14H), 1.41-1.49 (m, 2H), 1.65-1.72 (m, 2H), 1.76-1.83 (m, 2H), 2.54 (br, s, 1H), 3.80 (t, 2H, J = 7.8 Hz), 4.00 (t, 2H, J = 6.4 Hz), 4.68 (s, 2H), 6.86 (d, 1H, J = 8 Hz), 6.91 (t, 2H, J = 8 Hz), 7.06 (td, 1H, J_1 = 7.2 Hz, J_2 = 0.8 Hz), 7.18 (t, 2H, J = 7.2 Hz), 7.22-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.17 (CH_2), 26.89 (CH_2), 28.08 (CH_2), 29.29 (CH_2), 29.35 (CH_2), 29.47 (CH_2), 29.52 (CH_2), 40.79 (CH_2), 62.27 (CH_2), 67.98 (CH_2), 108.92 (=CH), 111.05 (=CH), 116.89 (*quat-C*), 118.33 (=CH), 120.48 (=CH), 121.85 (=CH), 125.37 (=CH), 128.58 (=CH), 128.81 (=CH), 129.26 (*quat-C*), 133.95 (*quat-C*), 156.95 (*quat-C*), 166.74 (*quat-C*); Anal. Calcd for $C_{27}H_{35}N_3O_3$ (449.59): C, 72.13; H, 7.85; N, 9.35. Found: C, 72.02; H, 7.91; N, 9.26.

Synthesis of diazoamide 4h. Red viscous liquid (505 mg, 89%); IR (neat): ν_{max} 3410, 2925, 2853, 2086, 1677, 1608, 1467, 1399, 1260, 1160, 1038, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.20-1.44 (m, 10H), 1.68-1.82 (m, 6H), 3.75-3.89 (m, 5H), 3.97 (t, 2H, J = 6.8 Hz), 4.61 (s, 2H), 6.33-6.46 (m, 2H), 6.89-6.96 (m, 2H), 7.02-7.09 (m, 1H), 7.13-7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.10 (CH_2), 26.86 (CH_2), 28.06 (CH_2), 29.17 (CH_2), 29.26 (CH_2), 29.37 (CH_2), 29.42 (CH_2), 40.78 (CH_2), 55.40 (OCH_3), 61.85 (CH_2), 68.02 (CH_2), 99.31 (=CH), 108.82 (=CH), 108.92 (=CH), 116.89 (*quat-C*), 118.33 (=CH), 121.86 (=CH), 121.95 (*quat-C*), 125.38 (=CH), 129.52 (=CH), 133.94 (*quat-C*), 157.07 (*quat-C*), 160.58 (*quat-C*), 166.76 (*quat-C*); Anal. Calcd for $C_{26}H_{33}N_3O_4$ (451.56): C, 69.16; H, 7.37; N, 9.31. Found: C, 69.03; H, 7.44; N, 9.39.

Synthesis of diazoamide 4i. Red viscous liquid (504 mg, 86%); IR (neat): ν_{max} 3420, 2931, 2857, 2093, 1671, 1610, 1490, 1339, 1266, 1091, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.25-1.33 (m, 10H), 1.42-1.47 (m, 2H), 1.66-1.71 (m, 2H), 1.79-1.86 (m, 2H), 2.95 (br, s, 1H), 3.80 (t, 2H, J = 7.2 Hz), 4.08 (t, 2H, J = 6.4 Hz), 4.74 (s, 2H), 6.87 (d, 1H, J = 8.8 Hz), 6.93 (d, 1H, J = 7.6 Hz), 7.07 (t, 1H, J = 7.6 Hz), 7.18 (t, 2H, J = 8 Hz), 8.12 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.8 Hz), 8.28 (d, 1H, J = 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.88 (CH_2), 26.82 (CH_2), 28.01 (CH_2), 28.86 (CH_2), 29.06 (CH_2), 29.13 (CH_2), 29.22 (CH_2), 29.27 (CH_2), 40.77 (CH_2), 60.12 (CH_2), 60.78 (*quat-C*), 68.99 (CH_2), 108.96 (=CH), 110.26 (=CH), 116.85 (*quat-C*), 118.35 (=CH), 121.96 (=*C*H), 123.32 (=*C*H), 124.77 (=*C*H), 125.41 (=*C*H), 130.79 (*quat-C*), 133.81 (*quat-C*), 141.22 (*quat-C*), 161.21 (*quat-C*), 161.89 (*quat-C*); Anal. Calcd for $C_{25}H_{30}N_4O_5$ (466.53): C, 64.36; H, 6.48; N, 12.01. Found: C, 64.49; H, 6.53; N, 12.09.

Synthesis of diazoamide 4j. Red viscous liquid (390 mg, 85%); IR (neat): ν_{max} 3415, 2931, 2861, 2091, 1667, 1605, 1462, 1352, 1259, 1197, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.38-1.52 (m, 4H), 1.69-1.79 (m, 4H), 2.37 (br, s, 1H), 3.81 (t, 2H, *J* = 7.2 Hz), 3.93 (t, 2H, *J* = 6.4 Hz), 4.63 (s, 2H), 6.77 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 6.90 (t, 2H, *J* = 7.2 Hz), 6.94 (s, 1H), 7.07 (t, 1H, *J* = 7.2 Hz), 7.16-7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.78 (CH_2), 26.59 (CH_2), 28.00 (CH_2), 29.08 (CH_2), 40.64 (CH_2), 60.77 (*quat-C*), 65.14 (CH_2), 67.70 (CH_2), 108.93 (=*C*H), 112.87 (=*C*H), 113.72 (=*C*H), 116.88 (*quat-C*), 118.37 (=*C*H), 118.96 (=*C*H), 121.95 (=*C*H), 125.42 (=*C*H), 129.50 (=*C*H), 133.82 (*quat-C*), 142.71 (*quat-C*), 159.28 (*quat-C*), 166.83 (*quat-C*); Anal. Calcd for $C_{21}H_{23}N_3O_3$ (365.43): C, 64.02; H, 6.34; N, 11.50. Found: C, 64.21; H, 6.41; N, 11.59.

Synthesis of diazoamide 4k. Red viscous liquid (434 mg, 82%); IR (neat): ν_{max} 3440, 2924, 2854, 2091, 1670, 1605, 1466, 1397, 1260, 1158, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.24-1.44 (m, 12H), 1.65-1.79 (m, 4H), 2.06 (br, s, 1H), 3.80 (t, 2H, *J* = 7.6 Hz), 3.94 (t, 2H, *J* = 6.4 Hz), 4.65 (s, 2H), 6.79-6.82 (m, 1H,), 6.92 (t, 3H, *J* = 8 Hz), 7.07 (t, 1H, *J* = 7.6 Hz), 7.18 (t, 2H, *J* = 7.6 Hz), 7.24 (t, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.00 (CH_2), 26.87 (CH_2), 28.06 (CH_2), 29.25 (CH_2), 29.28 (CH_2), 29.38 (CH_2), 29.43 (CH_2), 40.79 (CH_2), 65.25 (CH_2), 67.94 (CH_2), 108.93 (=*C*H), 112.91 (=*C*H), 113.77 (=*C*H), 116.90 (*quat-C*), 118.32 (=*C*H), 118.91 (=*C*H), 121.88 (=*C*H), 125.38 (=*C*H), 129.53 (*quat-C*), 133.93 (*quat-C*), 142.60 (*quat-C*), 159.42 (*quat-C*), 166.78 (*quat-C*); Anal. Calcd for $C_{25}H_{31}N_3O_3$ (421.53): C, 71.23; H, 7.41; N, 9.97. Found: C, 71.36; H, 7.45; N, 10.06.

Synthesis of diazoamide 4l. Red viscous liquid (376 mg, 82%); IR (neat): ν_{max} 3426, 2940, 2866, 2093, 1672, 1610, 1468, 1352, 1243, 1198, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.44-1.54 (m, 4H), 1.69-1.79 (m, 4H), 2.12 (br, s, 1H), 3.81 (t, 2H, *J* = 7.2 Hz), 3.91 (t, 2H, *J* = 6.4 Hz), 4.58 (s, 2H), 6.83 (d, 2H, *J* = 8.4 Hz), 6.92 (d, 1H, *J* = 8 Hz), 7.07 (t, 1H, *J* = 7.2 Hz), 7.17 (t, 2H, *J* = 7.6 Hz), 7.24 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.79 (CH_2), 26.62 (CH_2), 28.01 (CH_2), 29.11 (CH_2), 40.63 (CH_2), 60.73 (*quat-C*), 64.95 (CH_2), 67.79 (CH_2), 108.90 (=*C*H), 114.51 (=*C*H), 116.88 (*quat-C*), 118.37 (=*C*H), 121.94 (=*C*H), 125.41 (=*C*H), 128.60

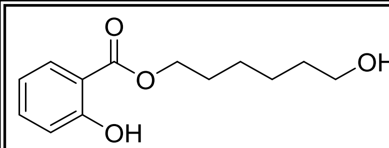
(=*C*H), 133.14 (*quat-C*), 133.84 (*quat-C*), 158.62 (*quat-C*), 166.80 (*quat-C*); Anal. Calcd for $C_{21}H_{23}N_3O_3$ (365.43): C, 69.02; H, 6.34; N, 11.50. Found: C, 69.18; H, 6.40; N, 11.57.

Synthesis of diazoamide 4m. Red viscous liquid (424 mg, 80%); IR (neat): ν_{max} 3419, 2931, 2858, 2094, 1673, 1611, 1511, 1468, 1399, 1245, 1173, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29-1.46 (m, 12H), 1.65-1.78 (m, 4H), 1.91 (br, s, 1H), 3.79 (t, 2H, *J* = 7.2 Hz), 3.93 (t, 2H, *J* = 6.4 Hz), 4.59 (s, 2H), 6.84-6.88 (m, 2H), 6.92 (d, 1H, *J* = 8 Hz), 7.06 (t, 1H, *J* = 8 Hz), 7.18 (t, 2H, *J* = 7.6 Hz), 7.26 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.00 (CH_2), 26.87 (CH_2), 28.06 (CH_2), 29.26 (CH_2), 29.31 (CH_2), 29.40 (CH_2), 29.45 (CH_2), 40.78 (CH_2), 65.03 (CH_2), 68.04 (CH_2), 108.92 (=*C*H), 114.55 (=*C*H), 116.89 (*quat-C*), 118.33 (=*C*H), 121.87 (=*C*H), 125.38 (=*C*H), 128.61 (=*C*H), 133.02 (*quat-C*), 133.92 (*quat-C*), 158.75 (*quat-C*), 166.76 (*quat-C*); Anal. Calcd for $C_{25}H_{31}N_3O_3$ (421.53): C, 71.23; H, 7.41; N, 9.97. Found: C, 71.32; H, 7.35; N, 10.06.

Synthesis of diazoamide 4n. Red viscous liquid (457 mg, 81%); IR (neat): ν_{max} 3196, 2925, 2854, 2089, 1674, 1610, 1465, 1394, 1199, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29-1.42 (m, 14H), 1.61-1.69 (m, 4H), 2.78 (s, 1H), 3.79 (t, 2H, *J* = 7.2 Hz), 3.95 (t, 2H, *J* = 6.8 Hz), 4.74 (s, 2H), 6.76 (d, 1H, *J* = 8 Hz), 6.98 (t, 2H, *J* = 7.6 Hz), 7.02-7.12 (m, 1H), 7.14 (t, 2H, *J* = 7.6 Hz), 7.25-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.21 (CH_2), 26.72 (CH_2), 28.12 (CH_2), 28.46 (CH_2), 29.15 (CH_2), 29.27 (CH_2), 29.31 (CH_2), 29.78 (CH_2), 40.32 (CH_2), 62.14 (CH_2), 66.78 (CH_2), 107.54 (=*C*H), 110.12 (=*C*H), 114.72 (*quat-C*), 116.12 (=*C*H), 120.98 (=*C*H), 121.85 (=*C*H), 124.12 (=*C*H), 128.21 (=*C*H), 129.16 (*quat-C*), 133.35 (*quat-C*), 157.15 (*quat-C*), 167.12 (*quat-C*); Anal. Calcd for $C_{27}H_{35}N_3O_3$ (449.59): C, 71.23; H, 7.85; N, 9.35. Found: C, 71.35; H, 7.78; N, 9.41.

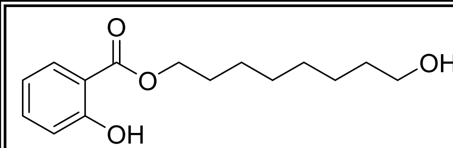
General procedure for the synthesis of compound 8: To an oven-dried flask salicylic acid **6** (2.25 mmol) in dry DCM (50 mL) was charged under inert atmosphere. To the above solution, dialcohol **7** (2.95 mmol) was added and the reaction mixture cooled to 0 °C. To this cooled reaction mixture, DCC (3.1 mmol) and a catalytic amount of DMAP were added. The reaction mixture was stirred at 0 °C for 6 hrs. Initially, the reaction mixture was homogeneous. The white solid separates out from the reaction mixture after 2 hours duration. Progress of the reaction was monitored using TLC. Filtered the reaction mixture and the filtrate was concentrated in *vacuo*. To the residue, 20 mL of EtOAc:MeOH (10:1) was added and kept at 0 °C for overnight. Filtered the solid obtained and the filtrate was concentrated. The final residue was subjected to 100-200 mesh silica column chromatography (hexane/EtOAc) to furnish the corresponding hydroxyl compound **8** in good yield.

Synthesis of compound 8a. Colourless liquid (69%); %); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.37-1.41 (m, 4H), 1.47-1.54 (m, 2H), 1.66-1.73 (m, 2H), 2.18 (br s, 1H), 3.55 (t, 2H, *J* = 6.8 Hz), 4.25 (t, 2H, *J* = 6.8 Hz), 6.79 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 6.88 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.8 Hz), 7.33-7.37 (m, 1H), 7.74 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 10.77 (s, H); [13]C NMR (100 MHz, $CDCl_3$) δ 25.41 (CH_2), 25.77 (CH_2), 28.51 (CH_2), 32.50 (CH_2), 62.53 (CH_2), 65.36 (CH_2), 112.59 (*quat-C*), 117.51 (=*C*H), 119.14 (=*C*H), 129.85 (=*C*H), 135.60 (=*C*H), 161.57 (*quat-C*), 170.22 (*quat-C*); Anal. Calcd for $C_{13}H_{18}O_4$ (238.28): C, 65.53; H, 7.61. Found: C, 65.42; H, 7.54.



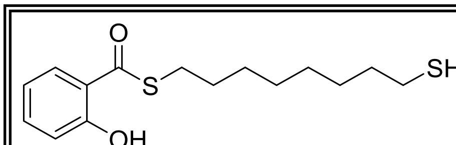
8
a

Synthesis of compound 8b. Colourless liquid (72%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.36-1.46 (m, 8H), 1.54-1.59 (m, 2H), 1.75-1.81 (m, 2H), 3.63 (td, 1H, J_1 = 6.4 Hz, J_2 = 1.6 Hz), 4.34 (td, 1H, J_1 = 6.4 Hz, J_2 = 1.2 Hz), 6.86-6.90 (m, 1H), 6.97 (d, 1H, *J* = 8.4 Hz), 7.43-7.47 (m, 1H), 7.83-7.85 (m, 1H), 10.85 (s, H); [13]C NMR (100 MHz, $CDCl_3$) δ 25.66 (CH_2), 25.89 (CH_2), 28.55 (CH_2), 29.17 (CH_2), 29.27 (CH_2), 32.71 (CH_2), 62.99 (CH_2), 65.45 (CH_2), 112.67 (*quat-C*), 117.57 (=*C*H), 119.09 (=*C*H), 129.86 (=*C*H), 135.58 (=*C*H), 161.67 (*quat-C*), 170.24 (*quat-C*); Anal. Calcd for $C_{15}H_{22}O_4$ (266.33): C, 67.64; H, 8.33. Found: C, 67.79; H, 8.42.



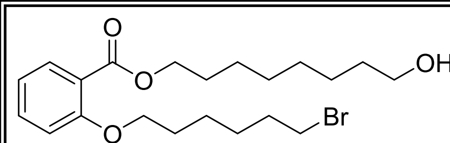
8b

Synthesis of compound 8c. Colourless liquid (61%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.24-1.33 (m, 8H), 1.66-1.72 (m, 2H), 2.01-2.21 (m, 2H), 3.02-3.09 (m, 2H), 4.01 (t, 2H, *J* = 6.4 Hz), 6.64 (d, 1H, *J* = 7.6 Hz), 6.69-7.02 (m, 2H), 7.12 (dd, 1H, J_1 = 7.4 Hz, J_2 = 0.8 Hz), 9.67 (s, H); [13]C NMR (100 MHz, $CDCl_3$) δ 25.78 (CH_2), 26.12 (CH_2), 28.12 (CH_2), 32.32 (CH_2), 62.12 (CH_2), 67.34 (CH_2), 111.34 (*quat-C*), 119.23 (=*C*H), 120.15 (=*C*H), 128.23 (=*C*H), 132.45 (=*C*H), 166.45 (*quat-C*), 172.23 (*quat-C*); Anal. Calcd for $C_{15}H_{22}O_2S_2$ (298.11): C, 60.39; H, 7.43. Found: C, 60.48; H, 7.38.



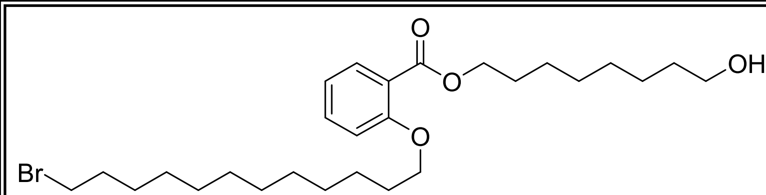
8c

General procedure for the synthesis of compound 10: To an oven-dried flask, a solution containing compound **8** (1.25 mmol) and potassium carbonate (3.14 mmol) in dry DMF was taken under argon atmosphere. To this reaction mixture, a solution of appropriate dibromoalkane **9** (1.35 mmol) in dry DMF was slowly added over a period of 30 min and then a catalytic amount of tetrabutylammonium iodide. The progress of the reaction was monitored using TLC. The mixture was extracted with dichloromethane (3×25 mL) and the combined organic layer washed with water (3×25 mL), brine (2×25 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue purified using column chromatography (SiO_2, hexane/ethyl acetate 75:25) to afford the respective bromoalcohol **10**



10a

Synthesis of compound 10a. Colourless liquid (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.35-1.38 (m, 6H), 1.40-1.56 (m, 8H), 1.71-1.78 (m, 2H), 1.81-1.91 (m, 4H), 3.42 (t, 2H, *J* = 6.4 Hz), 3.63 (t, 2H, *J* = 6.8 Hz), 4.03 (t, 2H, *J* = 6.8 Hz), 4.29 (t, 2H, *J* = 6.8 Hz), 6.93-6.98 (m, 2H), 7.41-7.45 (m, 1H), 7.76 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.22 (CH$_2$), 25.65 (CH$_2$), 26.05 (CH$_2$), 27.88 (CH$_2$), 28.78 (CH$_2$), 29.04 (CH$_2$), 29.27 (CH$_2$), 29.33 (CH$_2$), 32.69 (CH$_2$), 32.73 (CH$_2$), 33.73 (CH$_2$), 63.01 (CH$_2$), 64.91 (CH$_2$), 68.64 (CH$_2$), 113.16 (=*C*H), 120.07 (=*C*H), 120.92 (*quat-C*), 131.51 (=*C*H), 133.15 (=*C*H), 158.67 (*quat-C*), 166.62 (*quat-C*); Anal. Calcd for $C_{21}H_{33}BrO_4$ (429.39): C, 58.74; H, 7.75. Found: C, 58.86; H, 7.68.

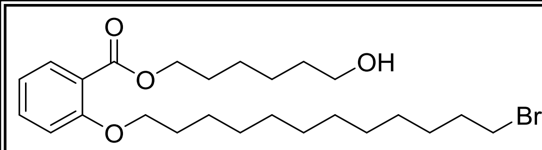


10b

Synthesis of compound 10b. Colourless liquid (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.19-1.30 (m, 18H), 1.33-1.42 (m, 6H), 1.47-1.51 (m, 2H), 1.64-1.81 (m, 6H), 3.33 (t, 2H, *J* = 7.2 Hz), 3.56 (t, 2H, *J* = 6.8 Hz), 3.94 (t, 2H, *J* = 6.4 Hz), 4.21 (t, 2H, *J* = 6.8 Hz), 6.86-6.89 (m, 2H), 7.33-7.37 (m, 1H), 7.69 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.65 (CH$_2$), 25.69 (CH$_2$), 25.98 (CH$_2$), 26.07 (CH$_2$), 28.17 (CH$_2$), 28.76 (CH$_2$), 29.23 (CH$_2$), 29.30 (CH$_2$), 29.34 (CH$_2$), 29.38 (CH$_2$), 29.43 (CH$_2$), 29.52 (CH$_2$), 29.55 (CH$_2$), 32.73 (CH$_2$), 32.84 (CH$_2$), 34.00 (CH$_2$), 63.00 (CH$_2$), 64.91 (CH$_2$), 68.92 (CH$_2$), 113.15 (=*C*H), 119.95 (=*C*H), 120.91 (*quat-C*), 131.50 (=*C*H), 133.12 (=*C*H), 158.56

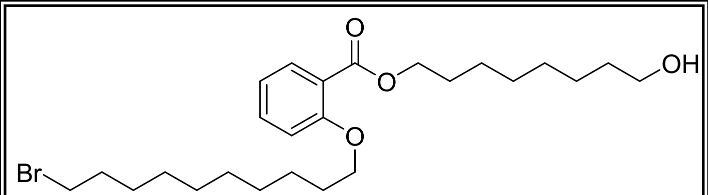
(*quat-C*), 166.75 (*quat-C*); Anal. Calcd for $C_{27}H_{45}BrO_4$ (513.55): C, 63.15; H, 8.83. Found: C, 63.27; H, 8.89.

Synthesis of compound 10c. Colourless liquid (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27-1.29 (m, 8H), 1.38-1.58 (m, 12H), 1.76-1.86 (m, 8H), 3.38-3.42 (m, 4H), 3.65 (t, 2H, *J* = 6.4 Hz), 4.02 (t, 2H, *J* = 6.4 Hz), 4.29 (t, 2H, *J* = 6.8 Hz), 6.93-6.98 (m, 2H), 7.42 (t, 1H, *J* = 8.0 Hz), 7.75 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.53 (*C*H_2), 25.79 (*C*H_2), 25.87 (*C*H_2), 25.96 (*C*H_2), 28.17 (*C*H_2), 28.76 (*C*H_2), 29.23 (*C*H_2), 29.37 (*C*H_2), 29.43 (*C*H_2), 29.51 (*C*H_2), 29.54 (*C*H_2), 29.56 (*C*H_2), 32.65 (*C*H_2), 32.84 (*C*H_2), 34.00 (*C*H_2), 62.87 (*C*H_2), 64.77 (*C*H_2), 68.92 (*C*H_2), 113.16 (=*C*H), 119.11 (=*C*H), 120.83 (*quat-C*), 131.51 (=*C*H), 133.15 (=*C*H), 158.59 (*quat-C*), 166.69 (*quat-C*); Anal. Calcd for $C_{25}H_{41}BrO_4$ (485.49): C, 61.85; H, 8.51. Found: C, 61.76; H, 8.44.



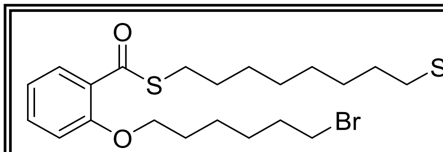
10c

Synthesis of compound 10d. Colourless liquid (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.85-1.37 (m, 16H), 1.47-1.51 (m, 4H), 1.69-1.81 (m, 8H), 3.33 (t, 2H, *J* = 6.8 Hz), 3.57 (t, 2H, *J* = 6.4 Hz), 4.27 (t, 2H, *J* = 6.8 Hz), 6.79-6.83 (m, 1H), 6.90 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.35-7.39 (m, 1H), 7.76 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.23 (*C*H_2), 26.76 (*C*H_2), 26.98 (*C*H_2), 27.34 (*C*H_2), 28.12 (*C*H_2), 29.12 (*C*H_2), 29.30 (*C*H_2), 29.46 (*C*H_2), 29.55 (*C*H_2), 29.57 (*C*H_2), 29.63 (*C*H_2), 29.77 (*C*H_2), 32.69 (*C*H_2), 32.90 (*C*H_2), 33.67 (*C*H_2), 62.92 (*C*H_2), 63.73 (*C*H_2), 67.90 (*C*H_2), 111.12 (=*C*H), 117.13 (=*C*H), 119.20 (*quat-C*), 130.34 (=*C*H), 132.23 (=*C*H), 156.40 (*quat-C*), 164.40 (*quat-C*); Anal. Calcd for $C_{25}H_{41}BrO_4$ (485.49): C, 61.85; H, 8.51. Found: C, 61.93; H, 8.43.



10d

Synthesis of compound 10e. Colourless liquid (59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.41-1.59 (m, 10H), 1.70-1.91 (m, 4H), 2.56 (t, 2H, *J* = 7.2 Hz), 2.72-2.79 (m, 4H), 3.02 (t, 2H, *J* = 7.2 Hz), 3.39-3.45 (m, 4H),

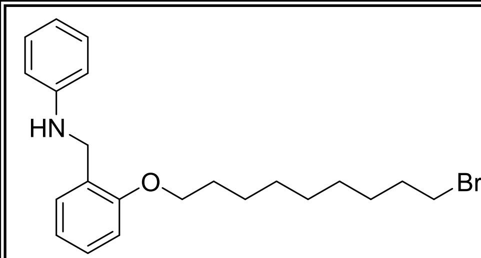


10

e

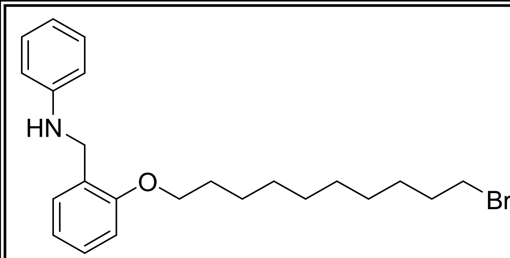
4.08 (t, 2H, J = 6.0 Hz), 6.93-7.00 (m, 2H), 7.41-7.45 (m, 1H), 7.76 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.34 (CH_2), 25.67 (CH_2), 26.23 (CH_2), 28.56 (CH_2), 28.71 (CH_2), 29.23 (CH_2), 29.28 (CH_2), 29.33 (CH_2), 29.52 (CH_2), 29.67 (CH_2), 32.81 (CH_2), 32.93 (CH_2), 34.03 (CH_2), 64.72 (CH_2), 69.92 (CH_2), 112.34 (=*C*H), 118.34 (=*C*H), 121.34 (*quat-C*), 132.50 (=*C*H), 132.78 (=*C*H), 159.34 (*quat-C*), 172.75 (*quat-C*); Anal. Calcd for $C_{21}H_{33}BrO_2S_2$ (461.52): C, 54.65; H, 7.21. Found: C, 54.53; H, 7.16.

General procedure for the synthesis of compounds 14: The bromobenzaldehyde **1** (4 mmol) and aniline (1 mmol) in ethanol was allowed to reflux (100 mL) for 4 hrs. The solvent was evaporated and the residue **13** subjected to reduction using portion-wise addition of $NaBH_4$ (8.0 mmol) in MeOH (40 mL) at 0 ˚C. The reaction mixture was stirred at 0 ˚C for 4 hrs and the solvent evaporated. To the residue, water was added and extracted with DCM (3 x 50 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated and the residue subjected to silica gel (100-200 mesh) column purification (60:40 hexane/EtOAc) to furnish the corresponding amine **14**.



14a

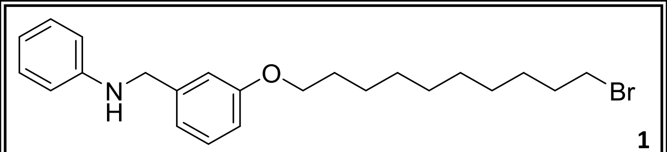
Synthesis of compound 14a. Colourless liquid (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23-1.40 (m, 10H), 1.68-1.79 (m, 4H), 3.30 (t, 2H, J = 6.8 Hz), 3.90 (t, 2H, J = 6.4 Hz), 4.26 (s, 2H), 6.58-6.65 (m, 3H), 6.75-6.83 (m, 2H), 7.05-7.10 (m, 3H), 7.22 (d, 1H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.84 (CH_2), 25.91 (CH_2), 26.53 (CH_2), 26.86 (CH_2), 29.80 (CH_2), 29.95 (CH_2), 32.72 (CH_2), 33.80 (CH_2), 57.23 (CH_2), 68.07 (CH_2), 111.37 (=*C*H), 119.56 (=*C*H), 120.62 (=*C*H), 120.88 (=*C*H), 123.13 (=*C*H), 129.45 (=*C*H), 129.84 (=*C*H), 129.97 (*quat-C*), 131.70 (*quat-C*), 157.48 (*quat-C*); Anal. Calcd for $C_{22}H_{30}BrNO$ (403.38): C, 65.34; H, 7.48; N, 3.46. Found: C, 65.26; H, 7.39; N, 3.42.



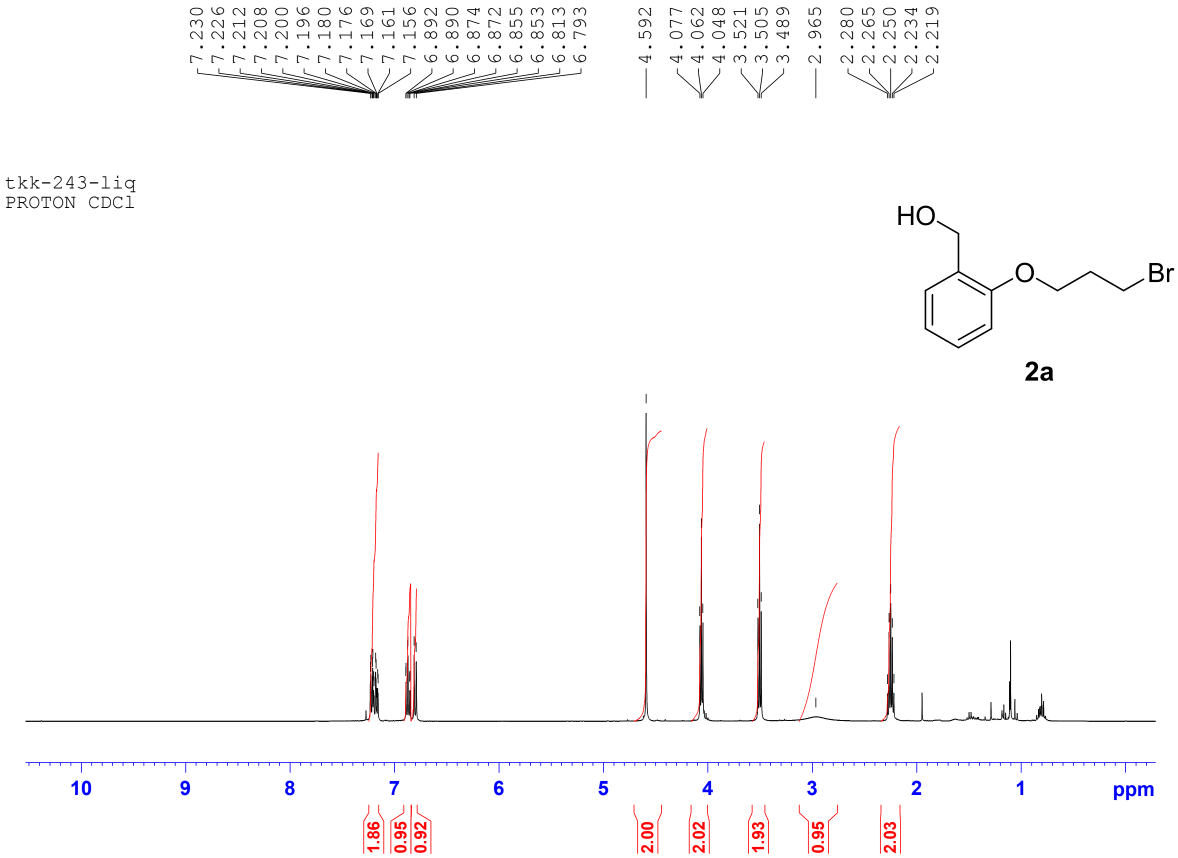
14b

Synthesis of compound 14b. Colourless liquid (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.28-1.41 (m, 12H), 1.68-1.79 (m, 4H), 3.28-3.33 (m, 2H), 3.92 (t, 2H, J = 6.4 Hz), 4.25 (s, 2H), 6.55-6.59 (m, 3H), 6.77-6.82 (m, 2H), 7.05-7.15 (m, 3H), 7.21 (d, 1H, *J* = 7.6 Hz); [13]C NMR (100 MHz, $CDCl_3$) δ 25.34 (*C*H_2), 26.08 (*C*H_2), 26.64 (*C*H_2), 26.92 (*C*H_2), 28.15 (*C*H_2), 29.12 (*C*H_2), 29.45 (*C*H_2), 32.23 (*C*H_2), 34.12 (*C*H_2), 56.34 (*C*H_2), 67.23 (*C*H_2), 111.12 (=*C*H), 118.23 (=*C*H), 119.98 (=*C*H), 120.23 (=*C*H), 122.87 (=*C*H), 127.34 (=*C*H), 129.12 (=*C*H), 129.34 (*quat-C*), 132.12 (*quat-C*), 155.97 (*quat-C*); Anal. Calcd for $C_{23}H_{32}BrNO$ (418.41): C, 66.02; H, 7.71; N, 3.35. Found: C, 66.13; H, 7.78; N, 3.39.

Synthesis of compound 14c. Colourless liquid (71%); [1]H NMR (400 MHz, $CDCl_3$) δ = 1.22-1.37 (m, 8H), 1.38-1.47 (m, 4H), 1.72-1.81 (m, 4H), 3.29 (t, 2H, *J* = 6.8 Hz), 3.89 (t, 2H, *J* = 6.8 Hz), 4.31 (s, 2H), 6.34-6.45 (m, 2H), 6.51-6.69 (m, 1H), 6.71-6.79 (m, 2H), 7.03-7.18 (m, 3H), 7.22 (d, 1H, *J* = 8.0 Hz); [13]C NMR (100 MHz, $CDCl_3$) δ 26.06 (*C*H_2), 26.16 (*C*H_2), 26.78 (*C*H_2), 27.34 (*C*H_2), 28.09 (*C*H_2), 28.87 (*C*H_2), 29.23 (*C*H_2), 32.89 (*C*H_2), 34.76 (*C*H_2), 42.78 (*C*H_2), 68.67 (*C*H_2), 110.54 (=*C*H), 115.56 (=*C*H), 120.98 (=*C*H), 121.78 (=*C*H), 122.23 (=*C*H), 126.89 (=*C*H), 128.45 (*quat-C*), 129.34 (=*C*H), 132.45 (*quat-C*), 157.12 (*quat-C*); Anal. Calcd for $C_{23}H_{32}BrNO$ (418.17): C, 66.02; H, 7.71; N, 3.35. Found: C, 66.13; H, 7.79; N, 3.29.



4c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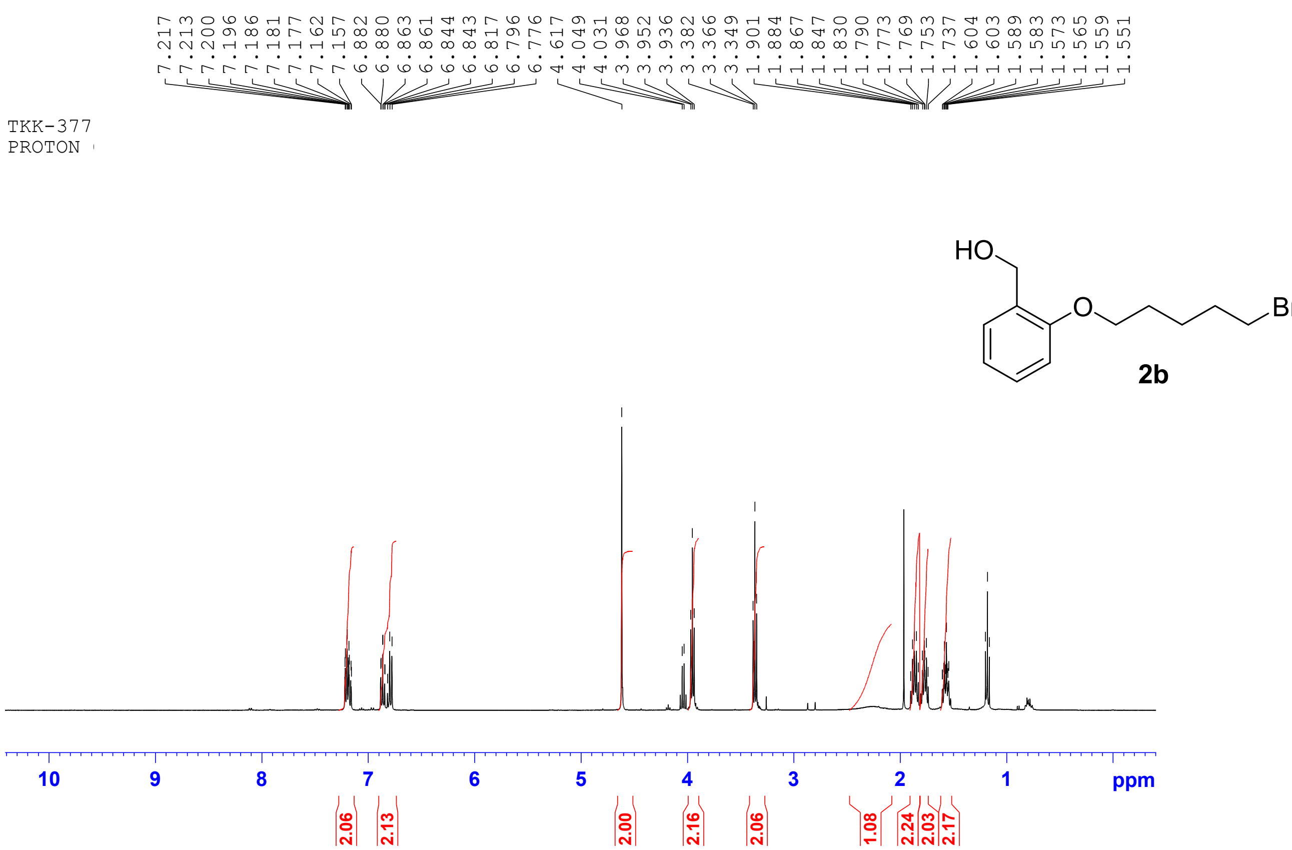
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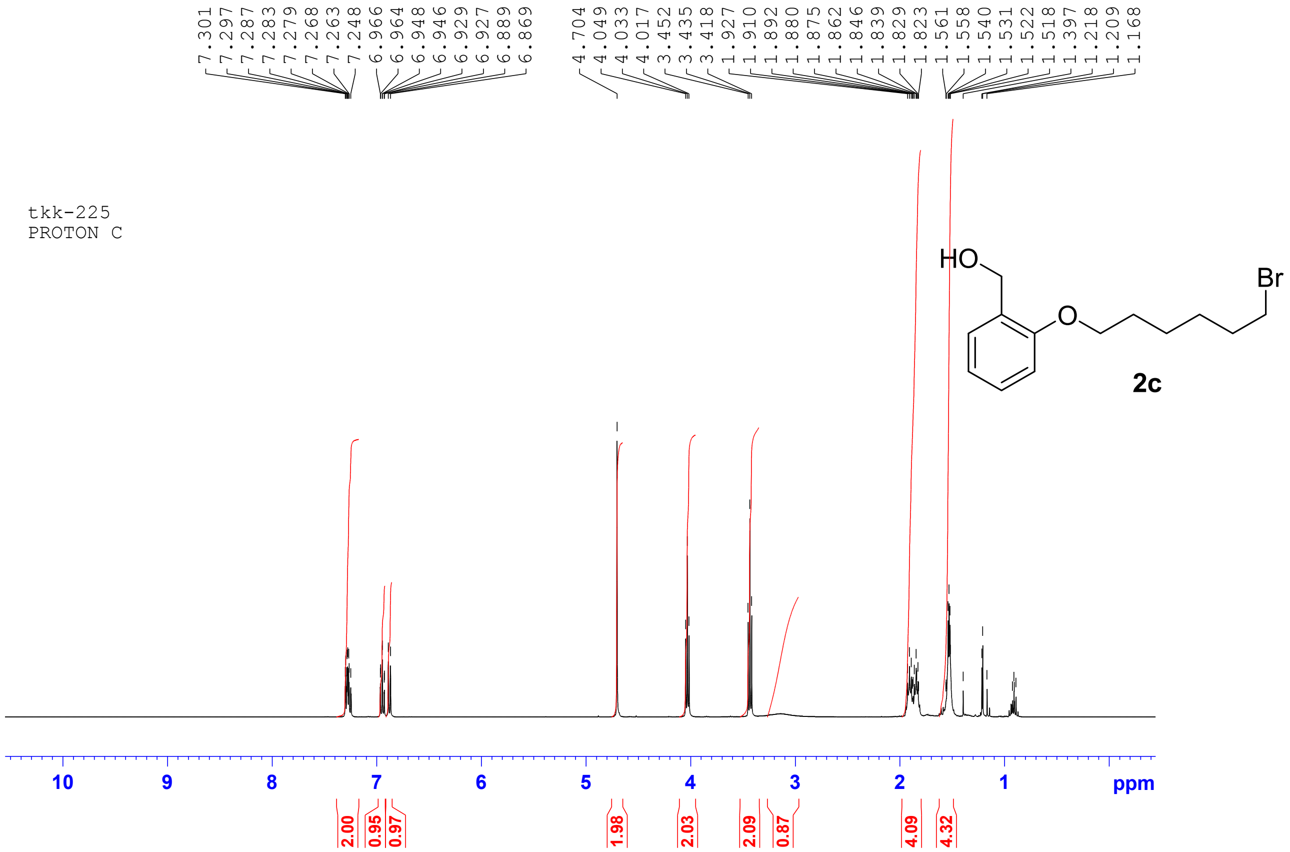
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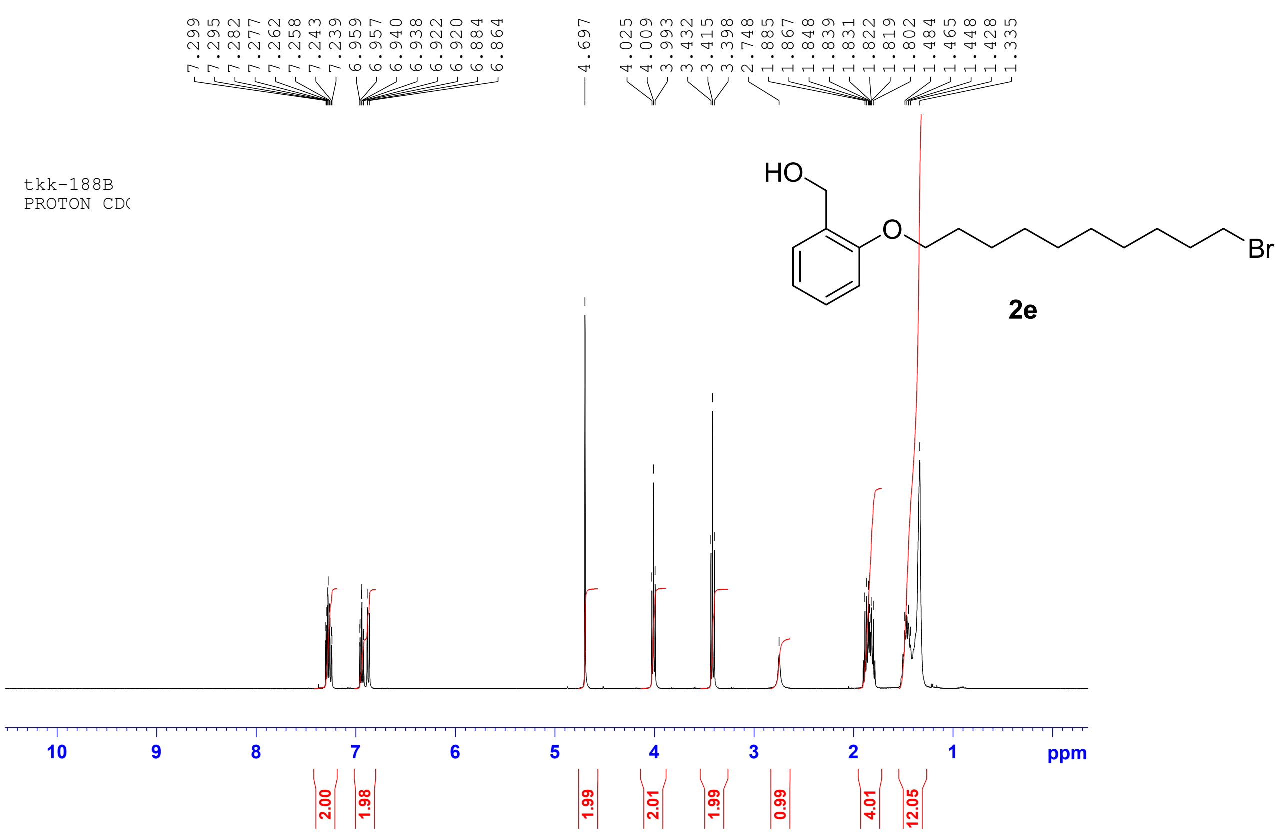
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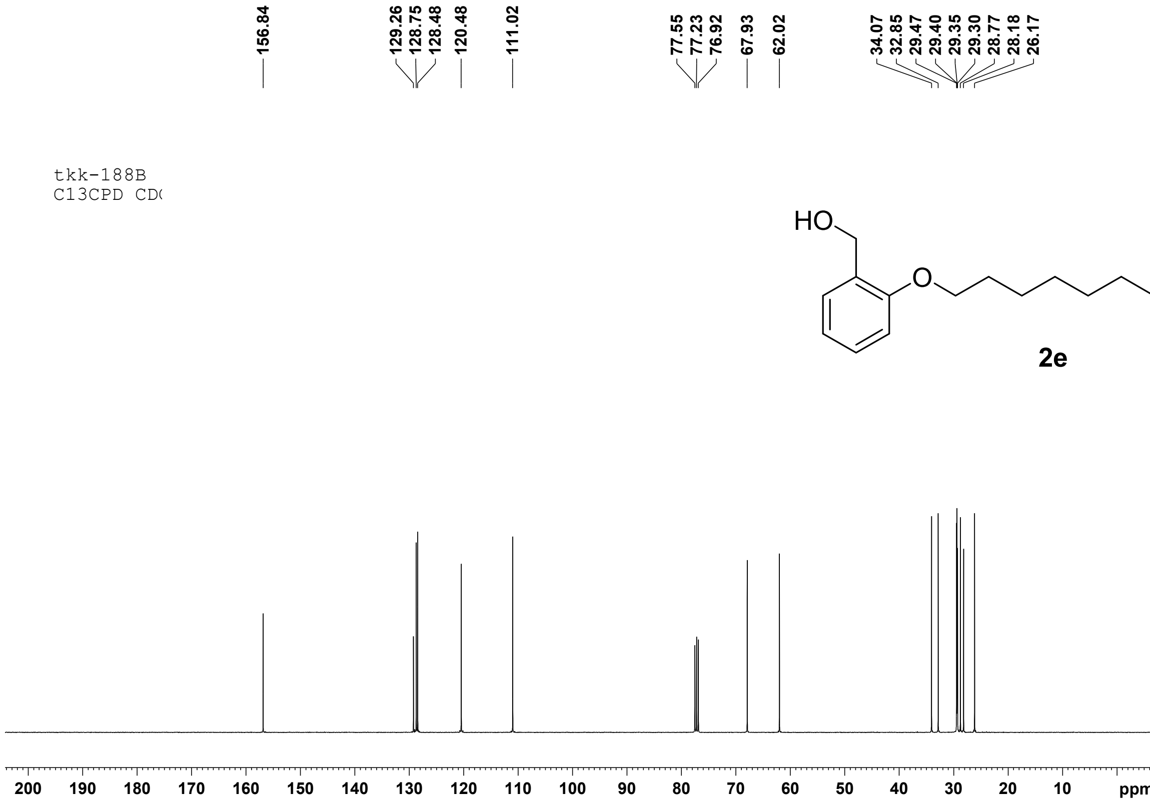
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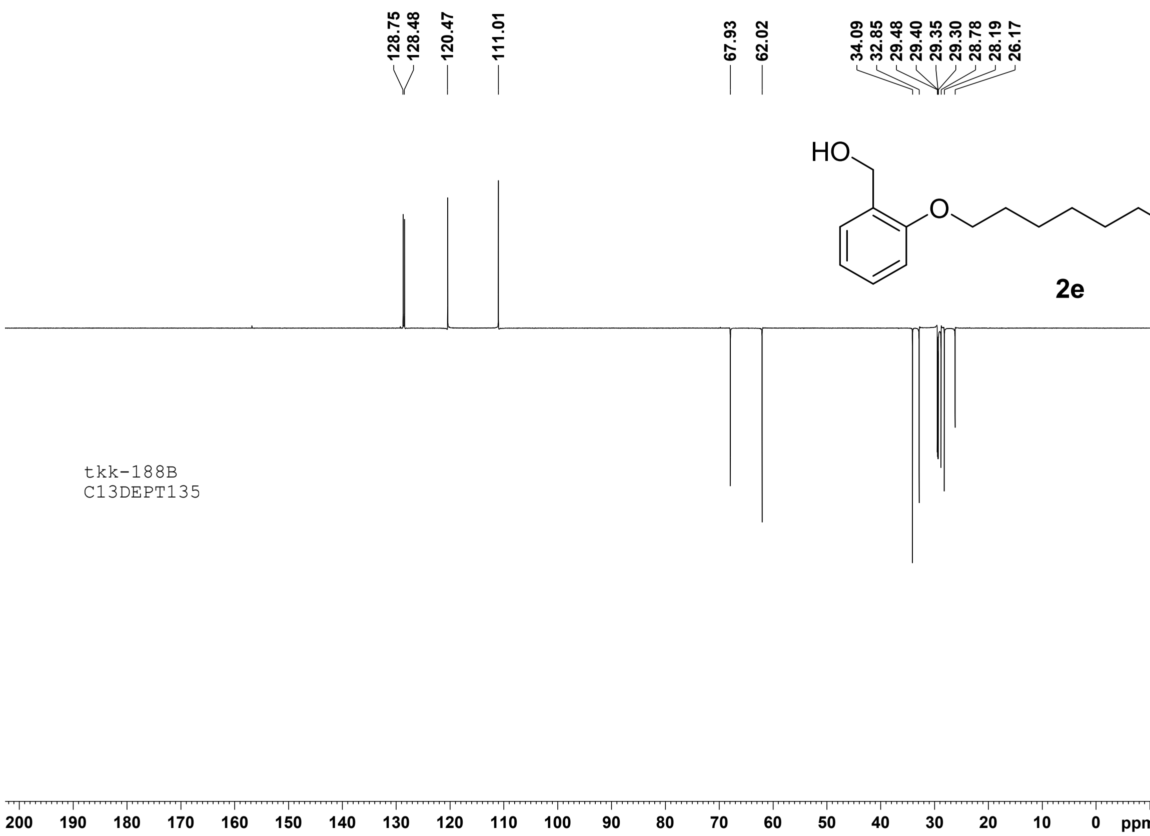
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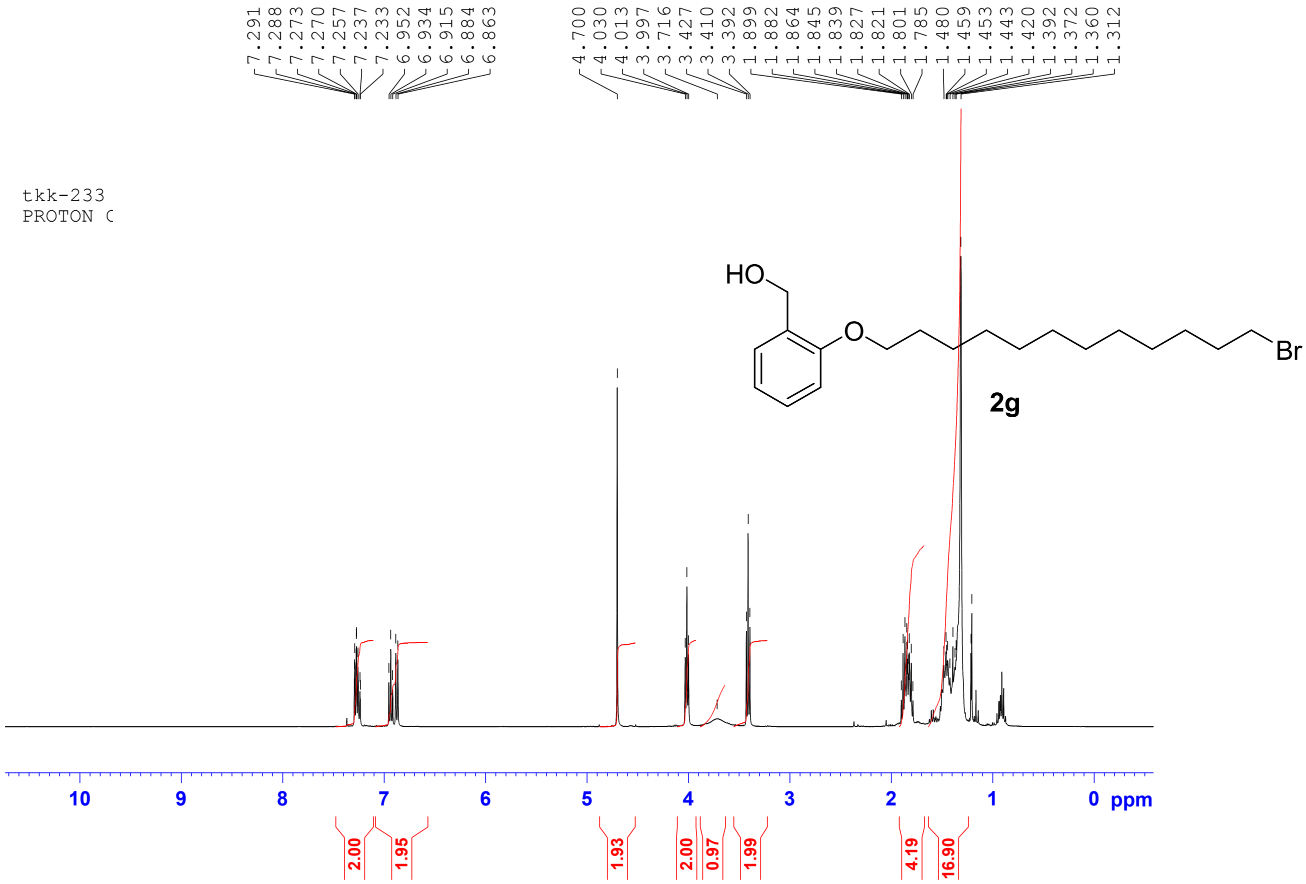
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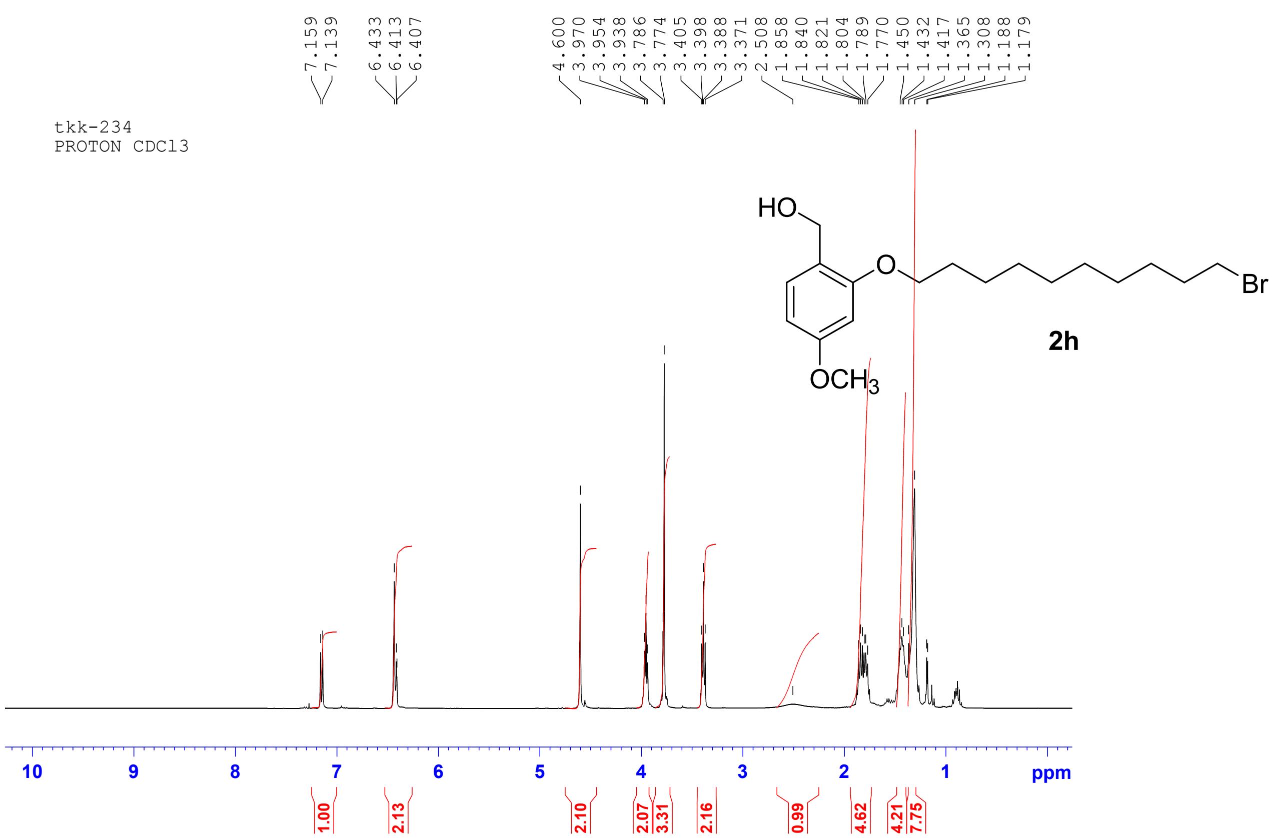
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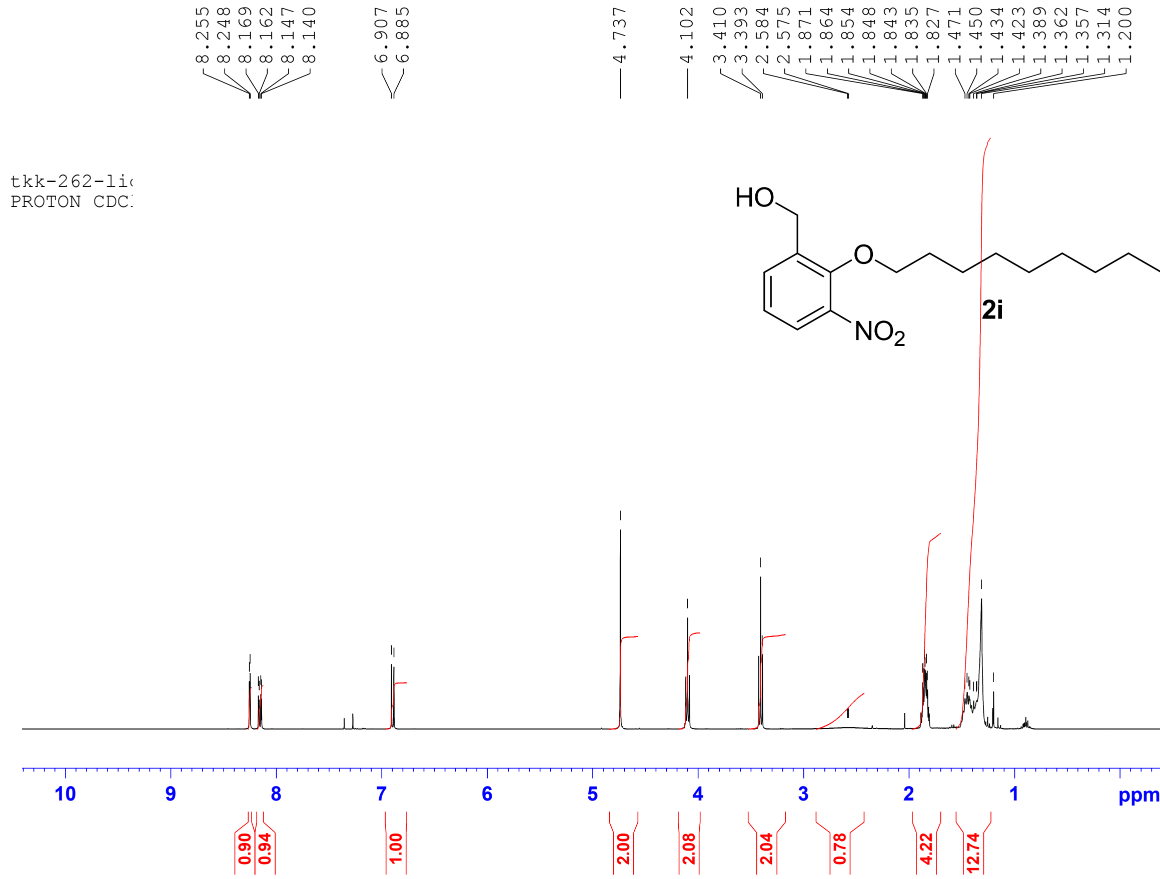
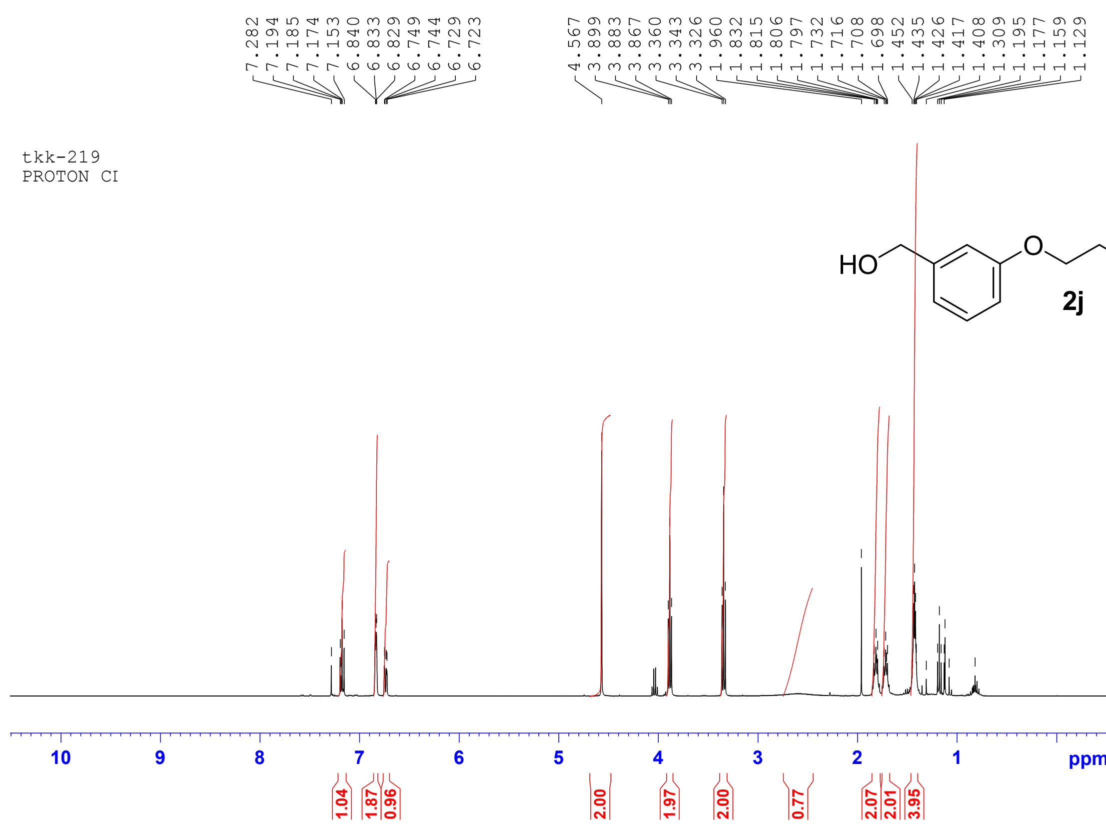
1.179
tkk-234
PROTON CDCl3
HO
O
Br
OCH3
2h
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.13
2.10
2.07
3.31
2.16
0.99
4.62
4.21
7.75


8.255
8.248
8.169
8.162
8.147
8.140
6.907
6.885
4.737
4.102
3.410
3.393
2.584
2.575
1.871
1.864
1.854
1.848
1.843
1.835
1.827
1.471
1.450
1.434
1.423
1.389
1.362
1.357
1.314
1.200
tkk-262-li
PROTON CDC
HO
O
NO2
Br
2i
10
9
8
7
6
5
4
3
2
1
ppm
0.90
0.94
1.00
2.00
2.08
2.04
0.78
4.22
12.74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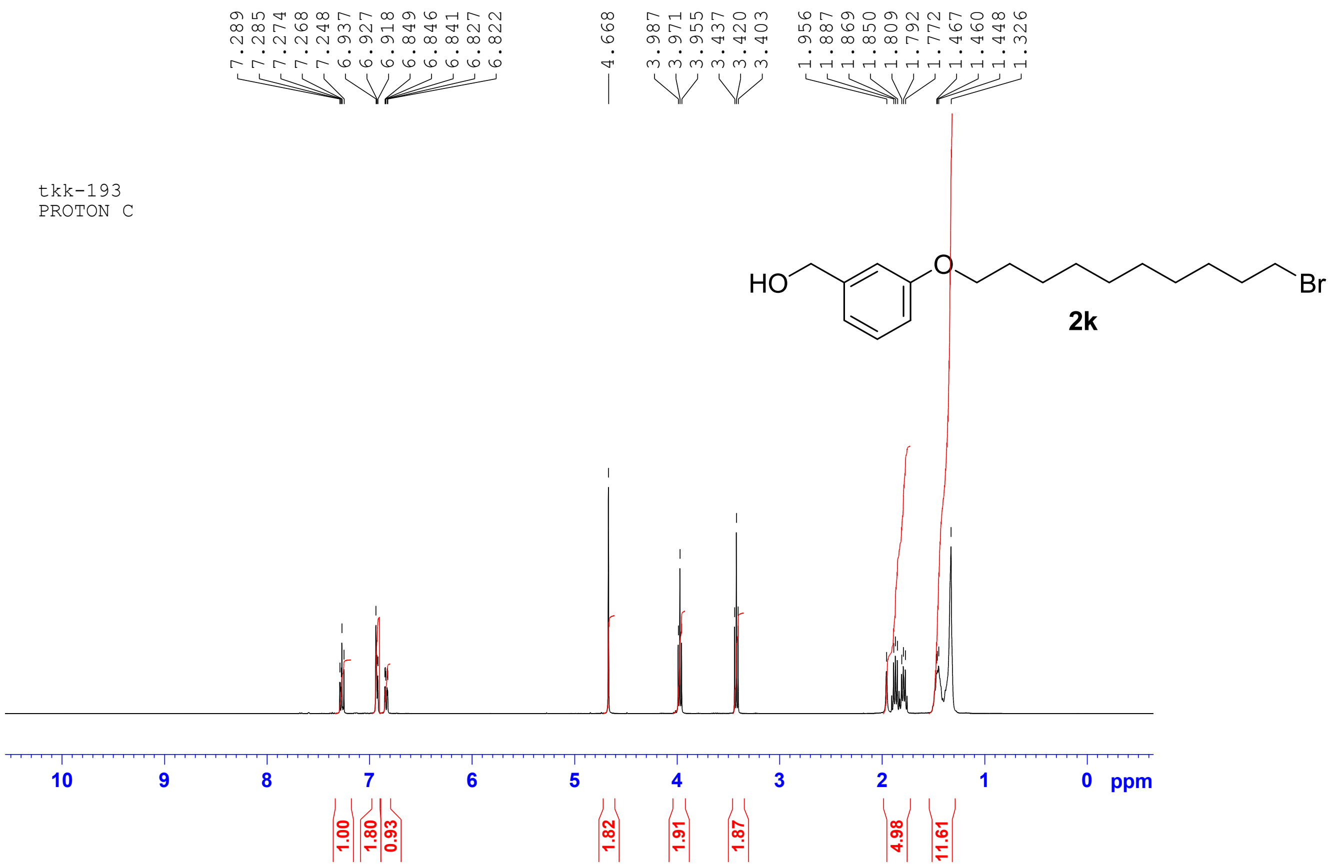
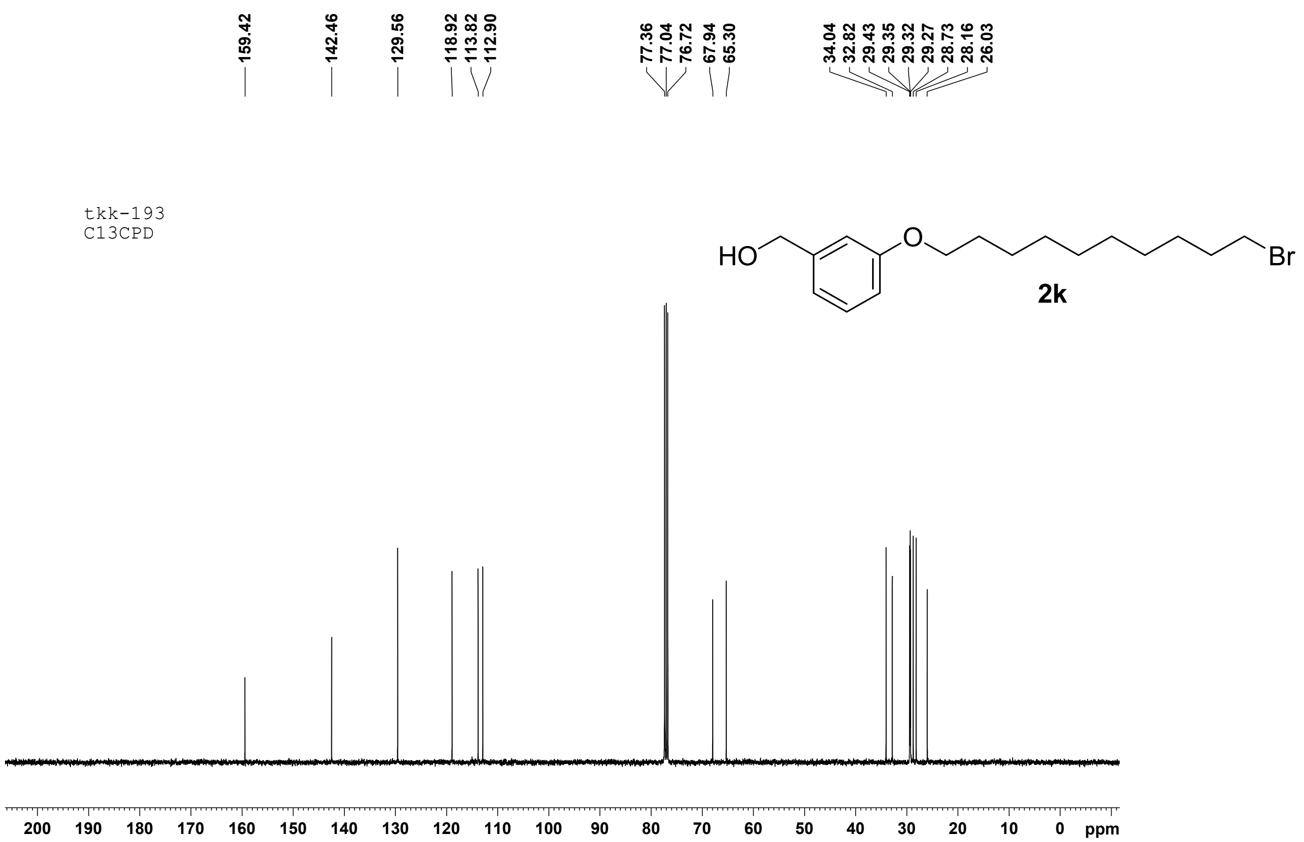
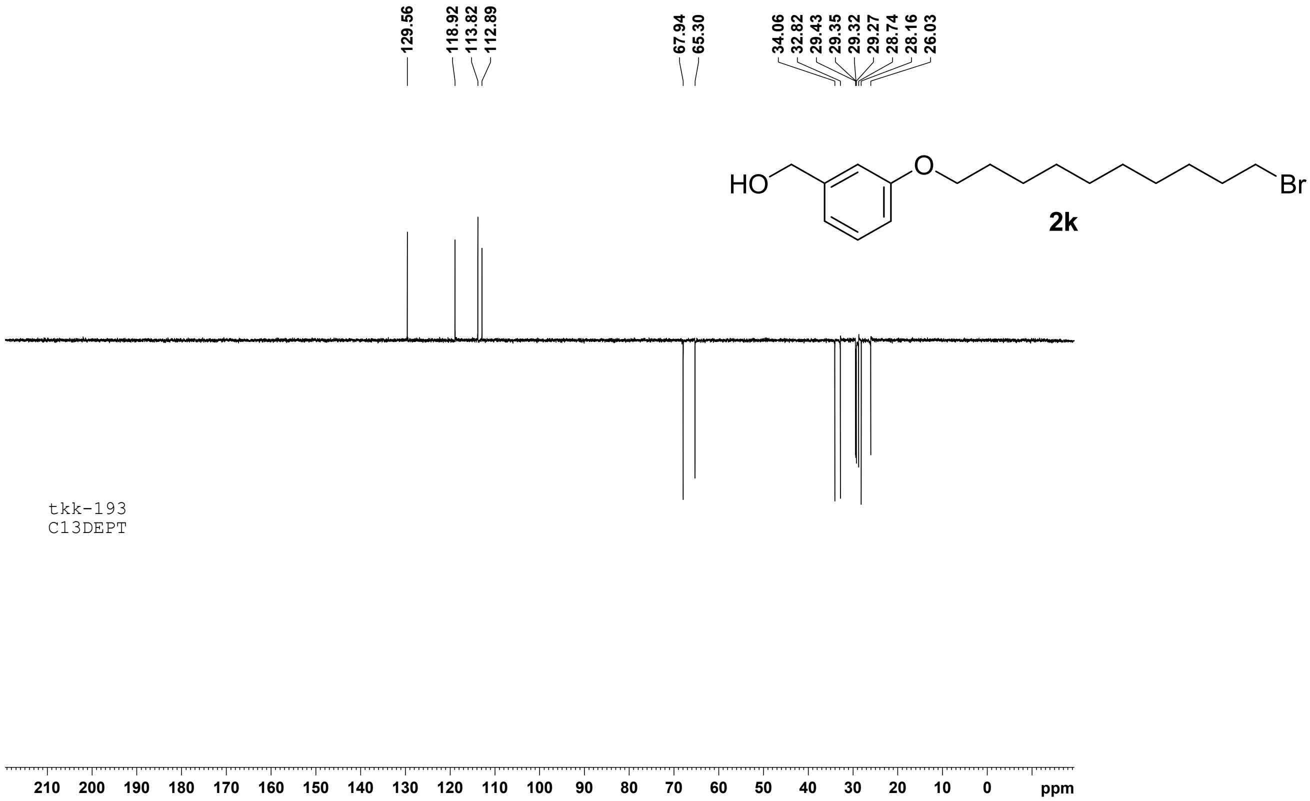
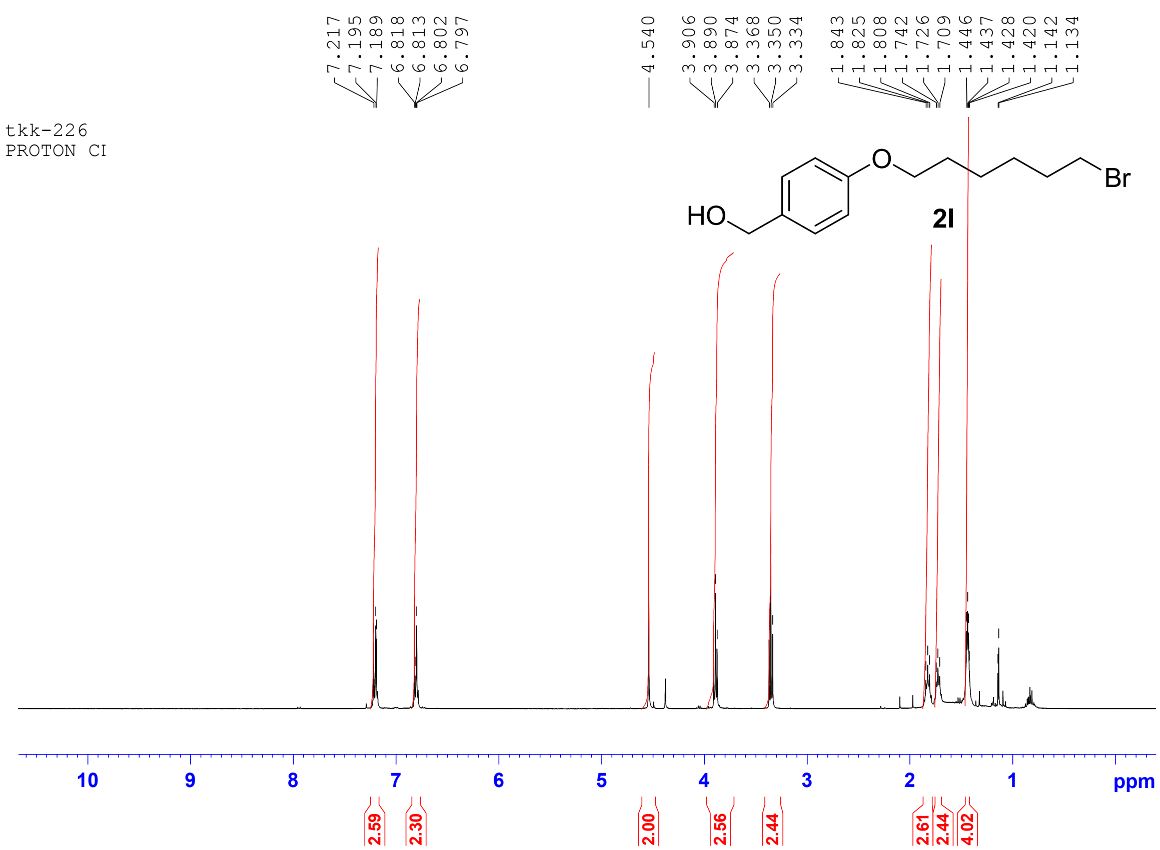
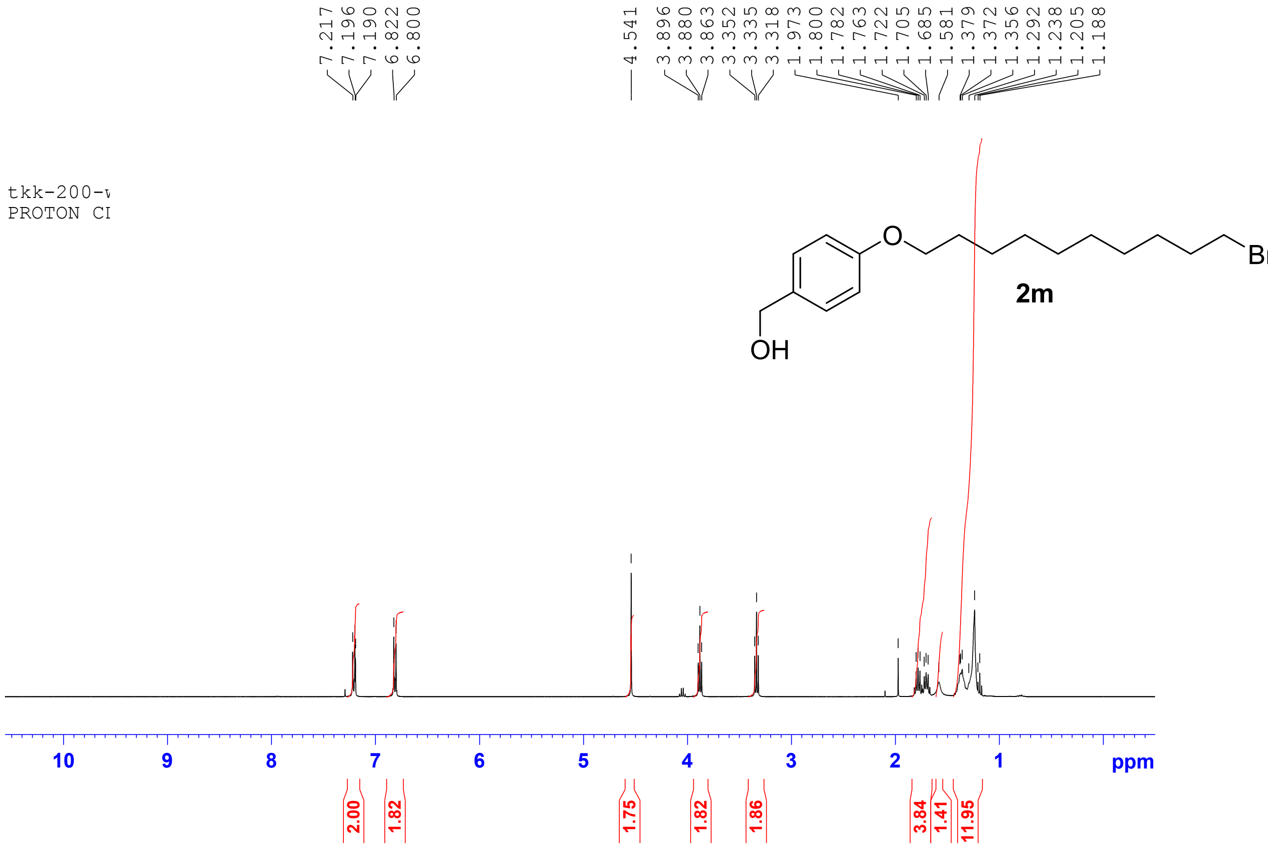
7.194
7.185
7.174
7.153
6.840
6.833
6.829
6.749
6.744
6.729
6.723
4.567
3.899
3.883
3.867
3.360
3.343
3.326
1.960
1.832
1.815
1.806
1.797
1.732
1.716
1.708
1.698
1.452
1.435
1.426
1.417
1.408
1.309
1.195
1.177
1.159
1.129
tkk-219
PROTON CI
HO
O
Br
2j
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.87
0.96
2.00
1.97
2.00
0.77
2.07
2.01
3.95

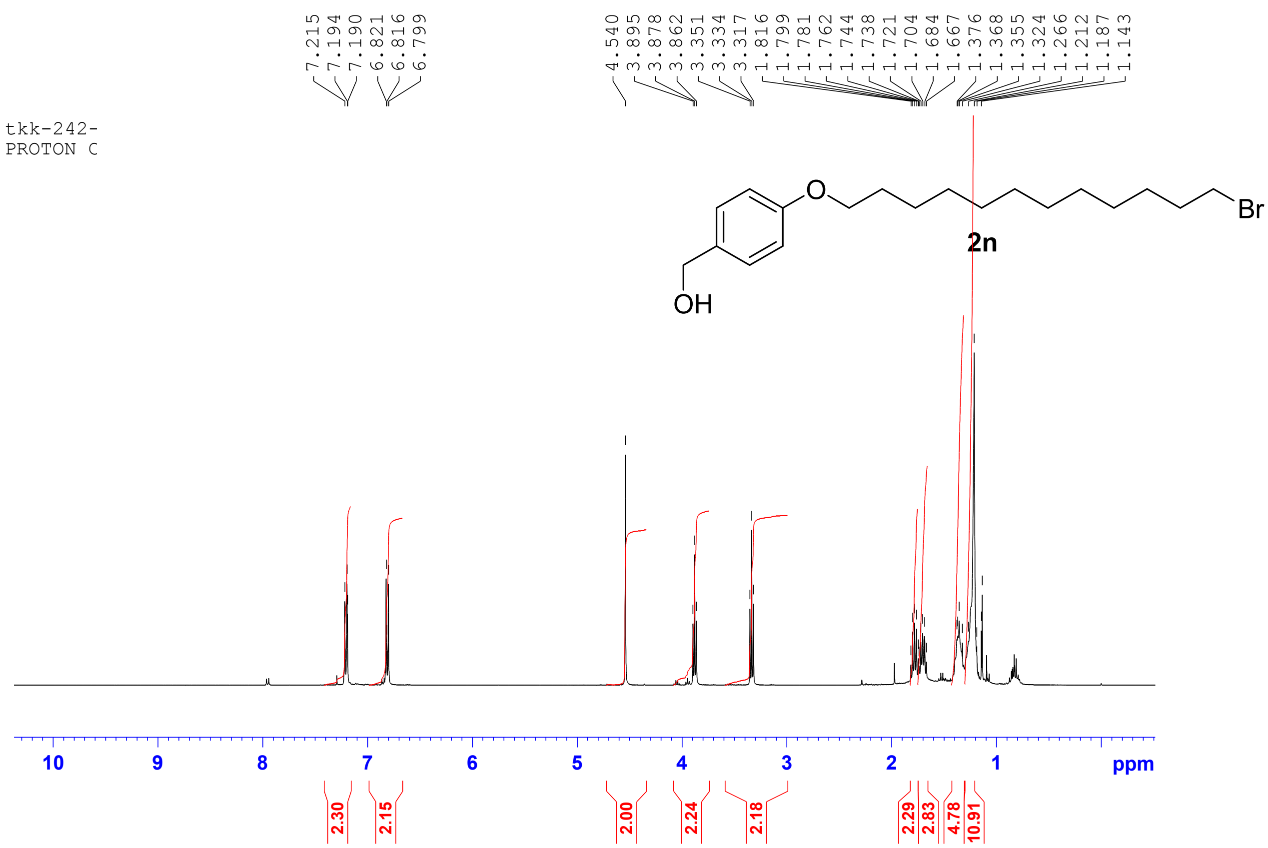

7.289
7.285
7.274
7.268
7.248
6.937
6.927
6.918
6.849
6.846
6.841
6.827
6.822
4.668
3.987
3.971
3.955
3.437
3.420
3.403
1.956
1.887
1.869
1.850
1.809
1.792
1.772
1.467
1.460
1.448
1.326
tkk-193
PROTON C
HO
O
Br
2k
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.80
0.93
1.82
1.91
1.87
4.98
11.61

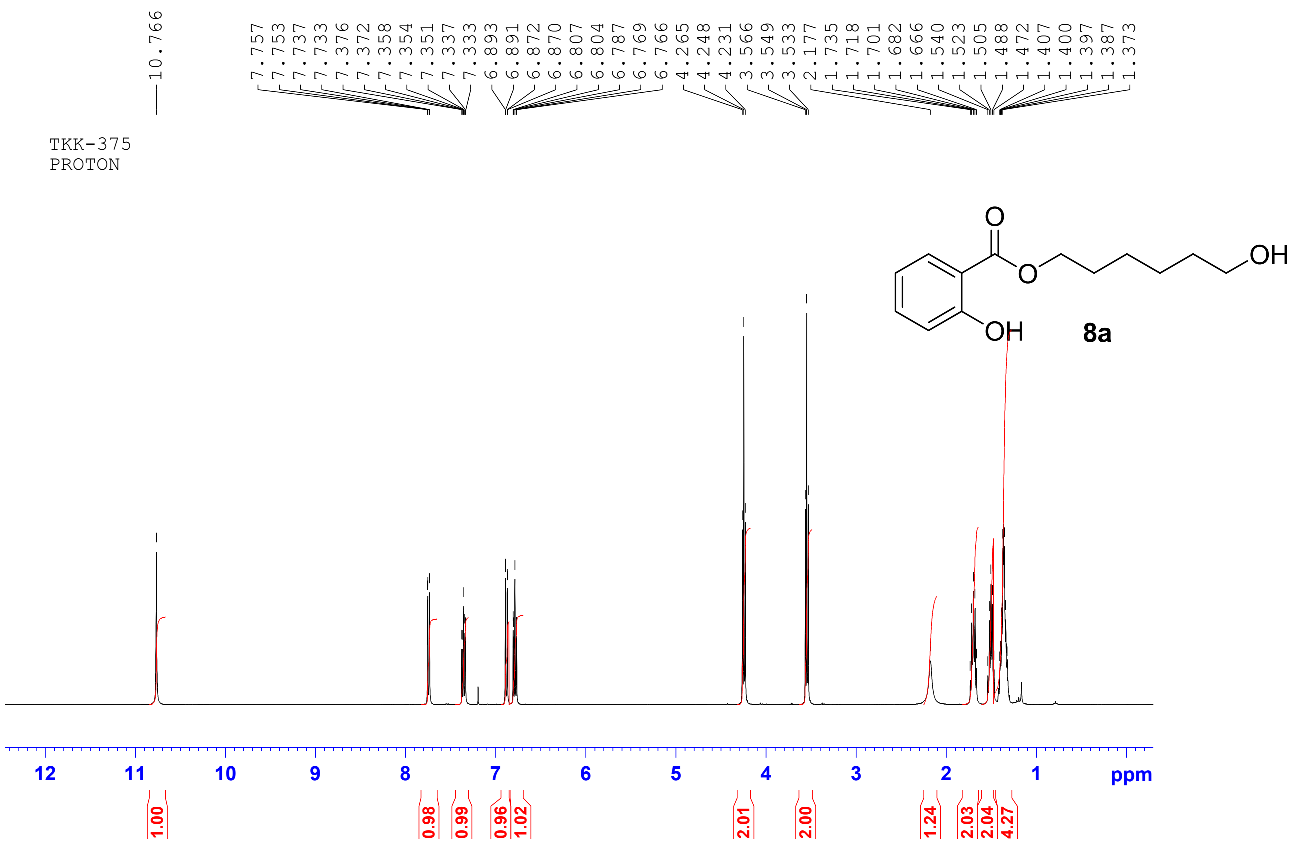

159.42
142.46
129.56
118.92
113.82
112.90
77.36
77.04
76.72
67.94
65.30
34.04
32.82
29.43
29.35
29.32
29.27
28.73
28.16
26.03
tkk-193
C13CPD
HO
O
Br
2k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

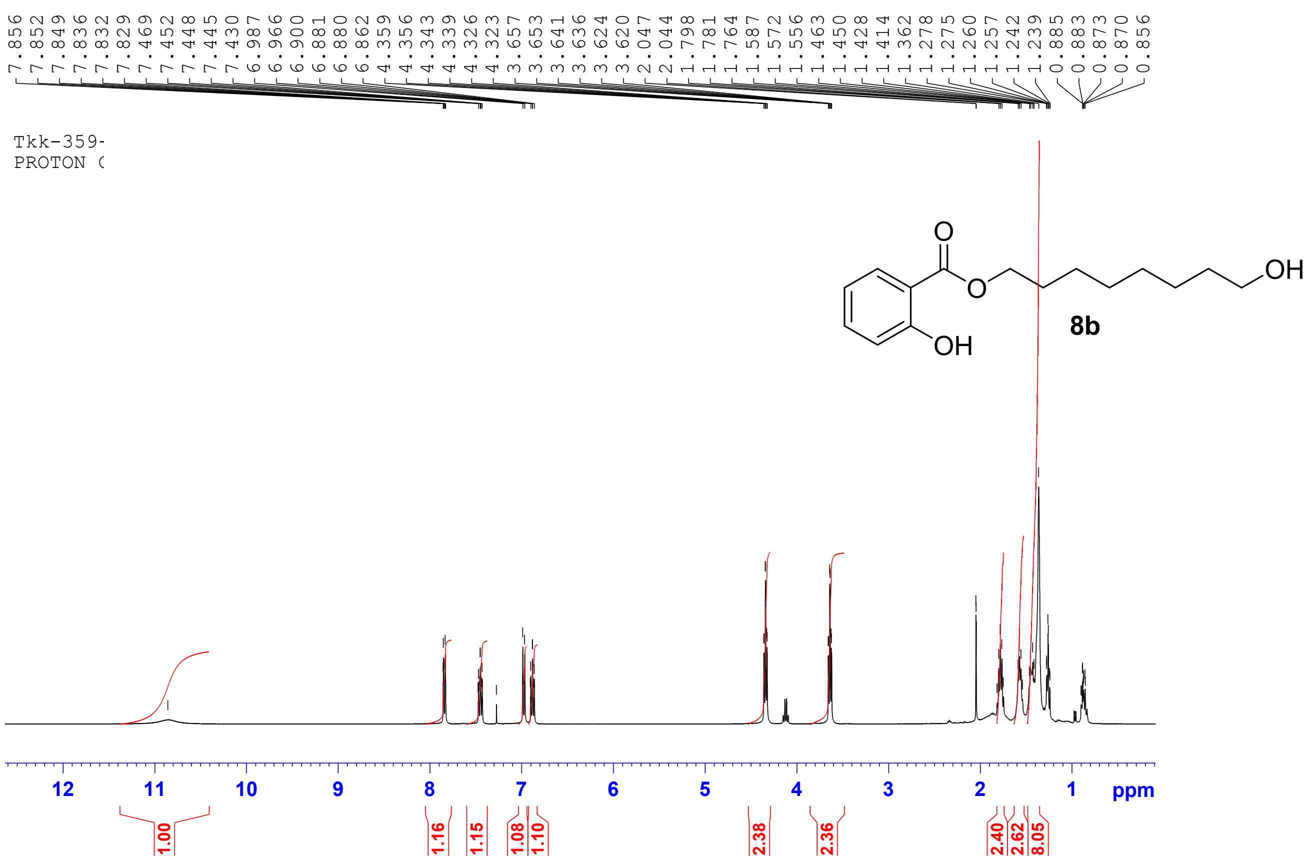

129.56
118.92
113.82
112.89
67.94
65.30
34.06
32.82
29.43
29.35
29.32
29.27
28.74
28.16
26.03
HO
O
Br
2k
tkk-193
C13DEPT
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

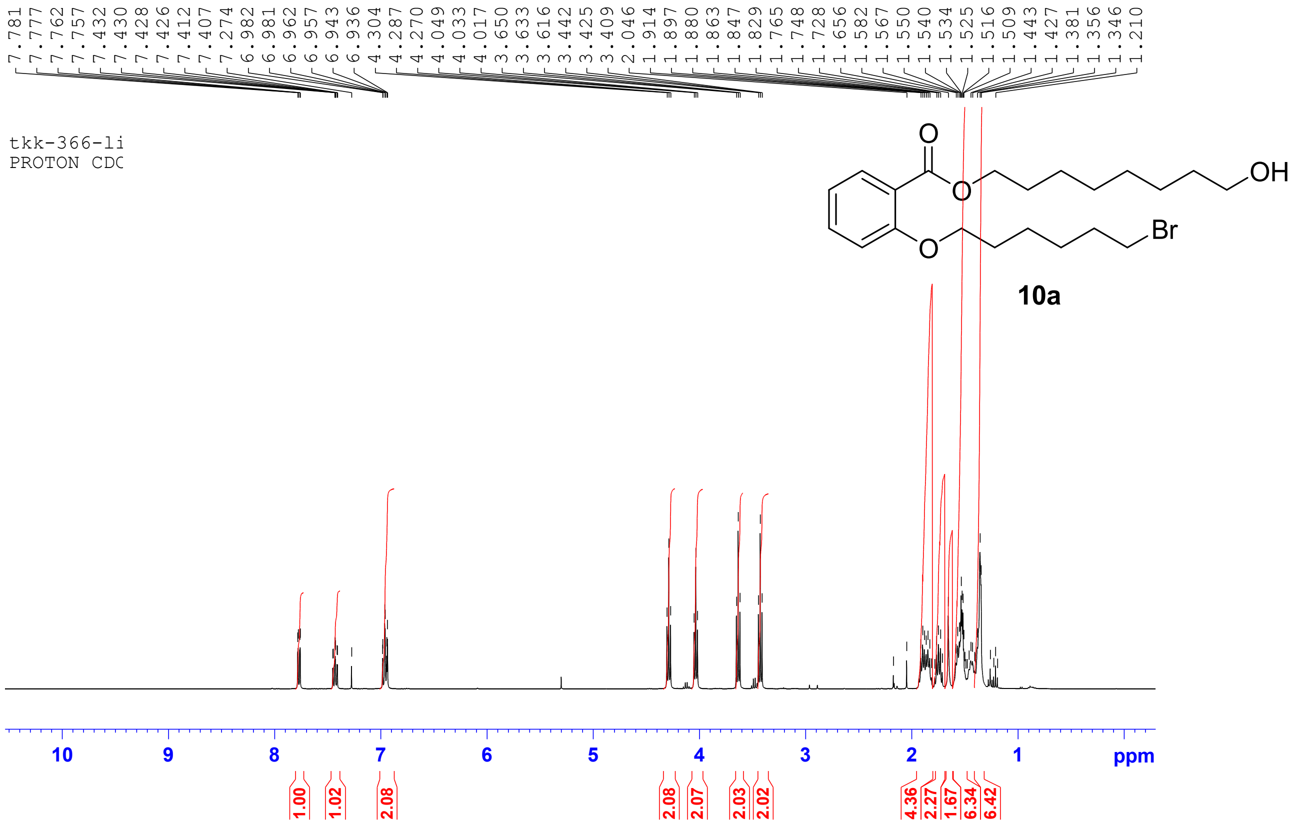

7.217
7.195
7.189
6.818
6.813
6.802
6.797
4.540
3.906
3.890
3.874
3.368
3.350
3.334
1.843
1.825
1.808
1.742
1.726
1.709
1.446
1.437
1.428
1.420
1.142
1.134
tkk-226
PROTON CI
HO
O
Br
2l
10 9 8 7 6 5 4 3 2 1 ppm
2.59
2.30
2.00
2.56
2.44
2.61
2.44
4.02


7.217
7.196
7.190
6.822
6.800
4.541
3.896
3.880
3.863
3.352
3.335
3.318
1.973
1.800
1.782
1.763
1.722
1.705
1.685
1.581
1.379
1.372
1.356
1.292
1.238
1.205
1.188
tkk-200-
PROTON C
O
Br
OH
2m
10 9 8 7 6 5 4 3 2 1 ppm
2.00
1.82
1.75
1.82
1.86
3.84
1.41
11.95


7.215
7.194
7.190
6.821
6.816
6.799
4.540
3.895
3.878
3.862
3.351
3.334
3.317
1.816
1.799
1.781
1.762
1.744
1.738
1.721
1.704
1.684
1.667
1.376
1.368
1.355
1.324
1.266
1.212
1.187
1.143
tkk-242-
PROTON C
O
Br
OH
2n
10 9 8 7 6 5 4 3 2 1 ppm
2.30
2.15
2.00
2.24
2.18
2.29
2.83
4.78
10.91

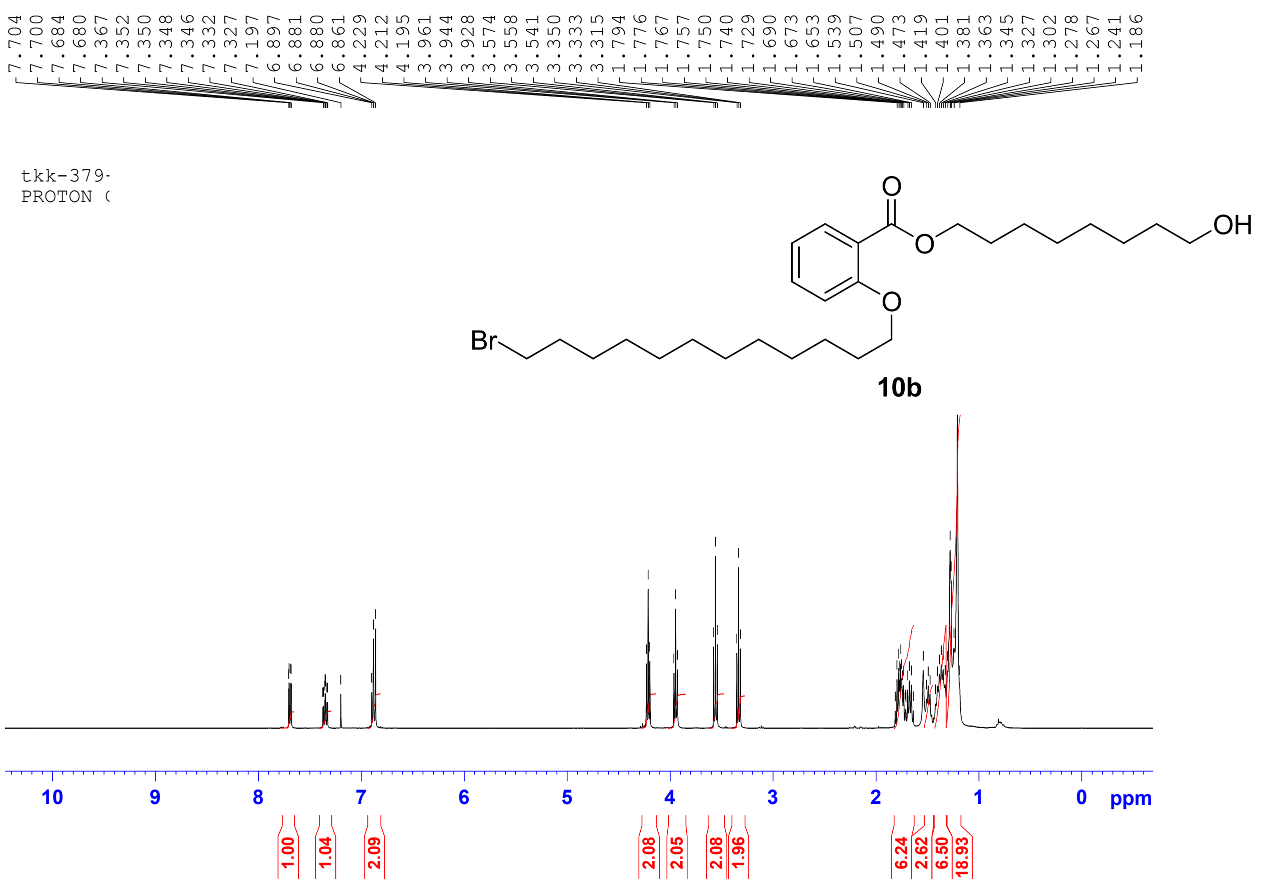

10.766
7.757 7.753 7.737 7.733 7.376 7.372 7.358 7.354 7.351 7.337 7.333 6.893 6.891 6.872 6.870 6.807 6.804 6.787 6.769 6.766 4.265 4.248 4.231 3.566 3.549 3.533 2.177 1.735 1.718 1.701 1.682 1.666 1.540 1.523 1.505 1.488 1.472 1.407 1.400 1.397 1.387 1.373
TKK-375
PROTON
O
O
OH
OH
8a
12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 0.98 0.99 0.96 1.02 2.01 2.00 1.24 2.03 2.04 4.27


7.856 7.852 7.849 7.836 7.832 7.829 7.469 7.452 7.448 7.445 7.430 6.987 6.966 6.900 6.881 6.880 6.862 4.359 4.356 4.343 4.339 4.326 4.323 3.657 3.653 3.641 3.636 3.624 3.620 2.047 2.044 1.798 1.781 1.764 1.587 1.572 1.556 1.463 1.450 1.428 1.414 1.362 1.278 1.275 1.260 1.257 1.242 1.239 0.885 0.883 0.873 0.870 0.856
Tkk-359-
PROTON (
O
O
OH
OH
8b
12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.16 1.15 1.08 1.10 2.38 2.36 2.40 2.62 8.05



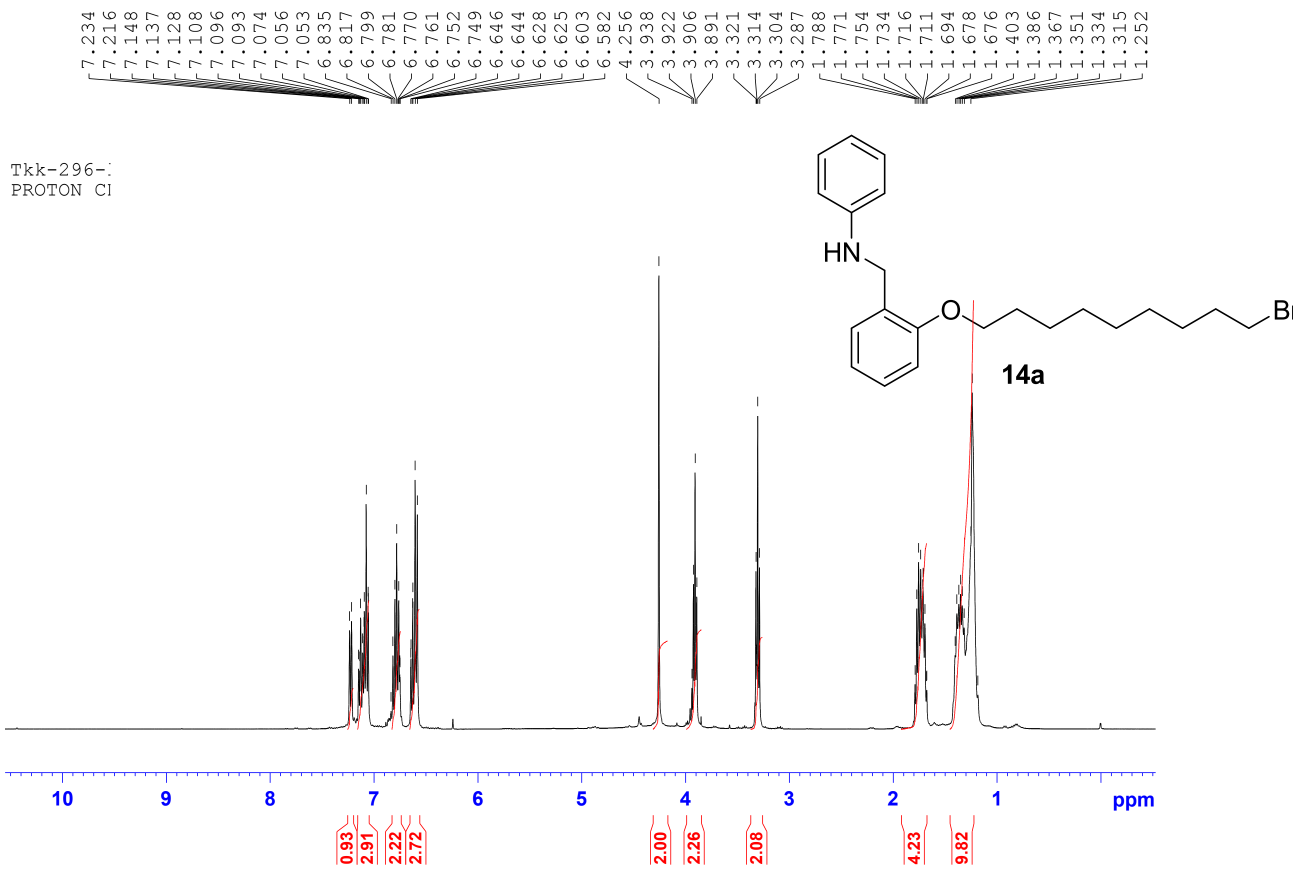
7.781 7.777 7.762 7.757 7.432 7.430 7.428 7.426 7.412 7.407 7.274 6.982 6.981 6.962 6.957 6.943 6.936 4.304 4.287 4.270 4.049 4.033 4.017 3.650 3.633 3.616 3.442 3.425 3.409 2.046 1.914 1.897 1.880 1.863 1.847 1.829 1.765 1.748 1.728 1.656 1.582 1.567 1.550 1.540 1.534 1.525 1.516 1.509 1.443 1.427 1.381 1.356 1.346 1.210
tkk-366-li
PROTON CDC
O
O
OH
O
Br
10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.02 2.08 2.08 2.07 2.03 2.02 4.36 2.27 1.67 6.34 6.42

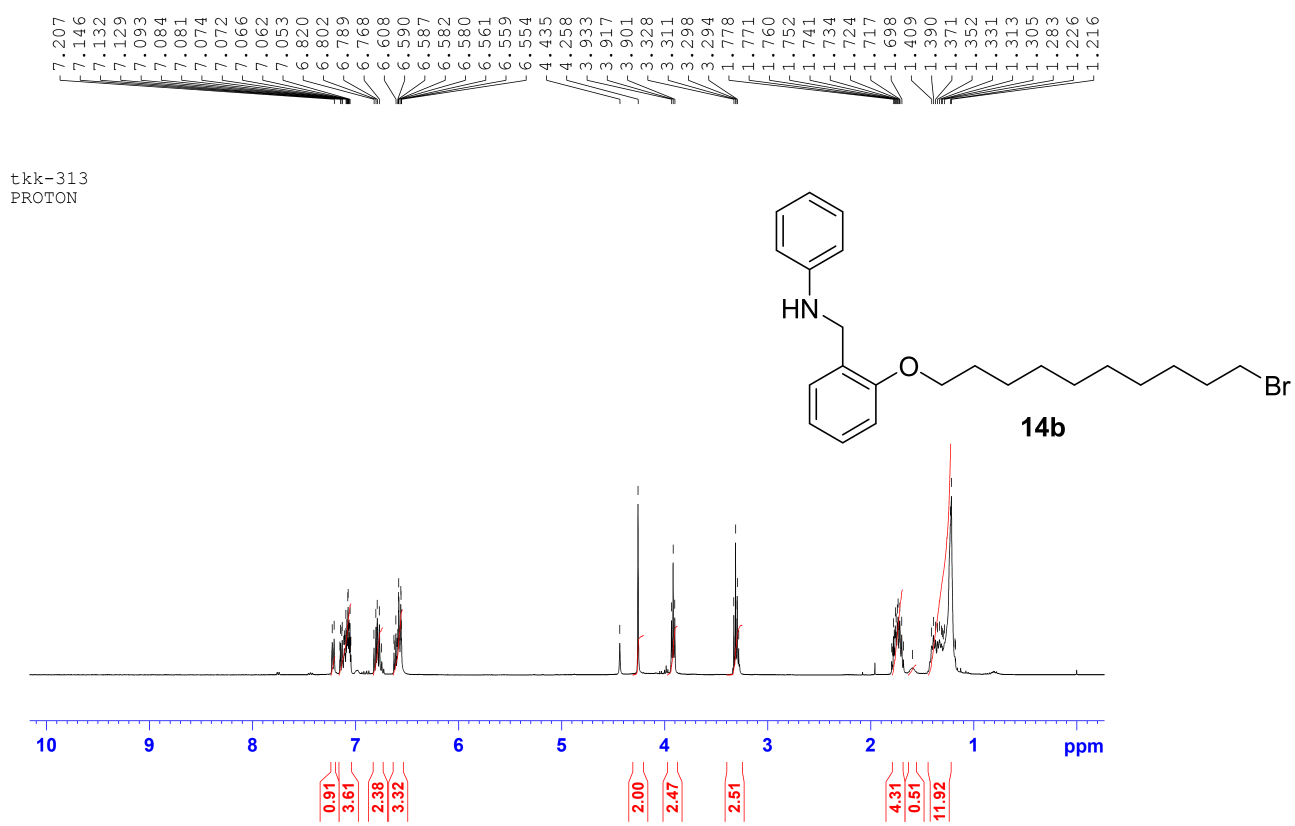
10a

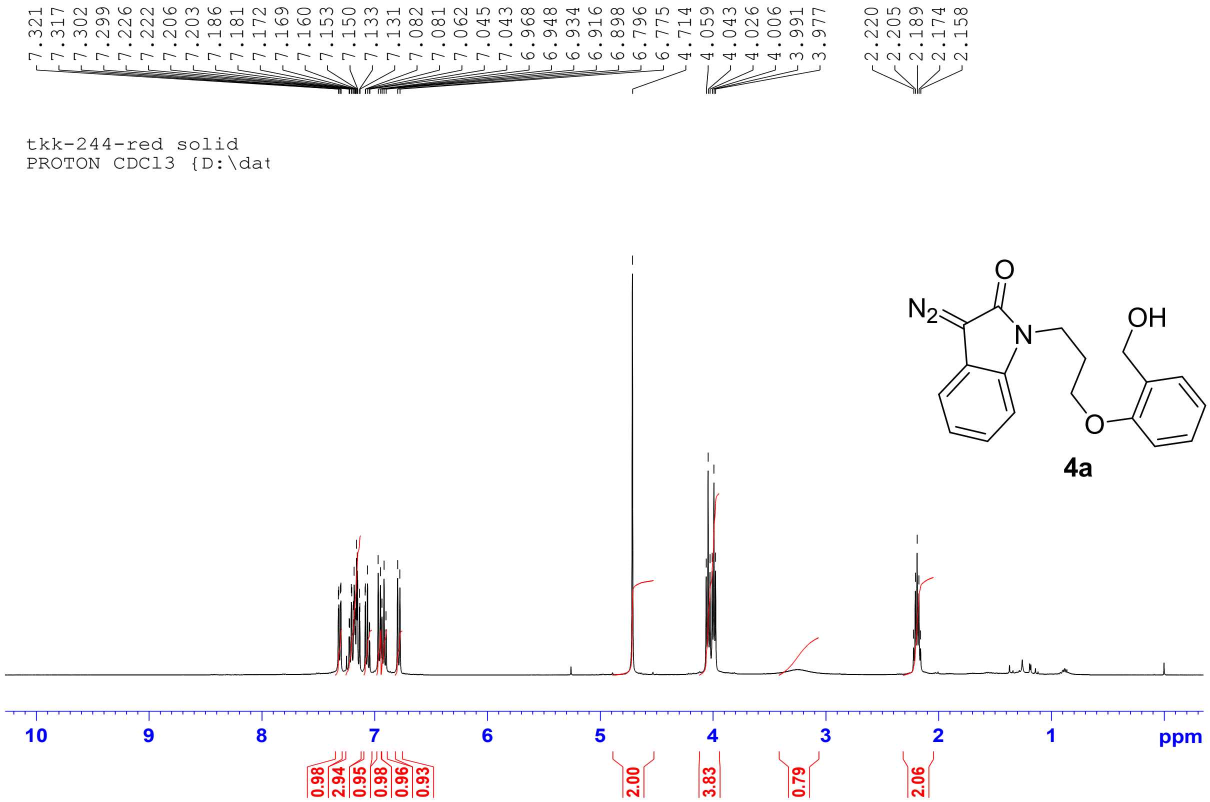


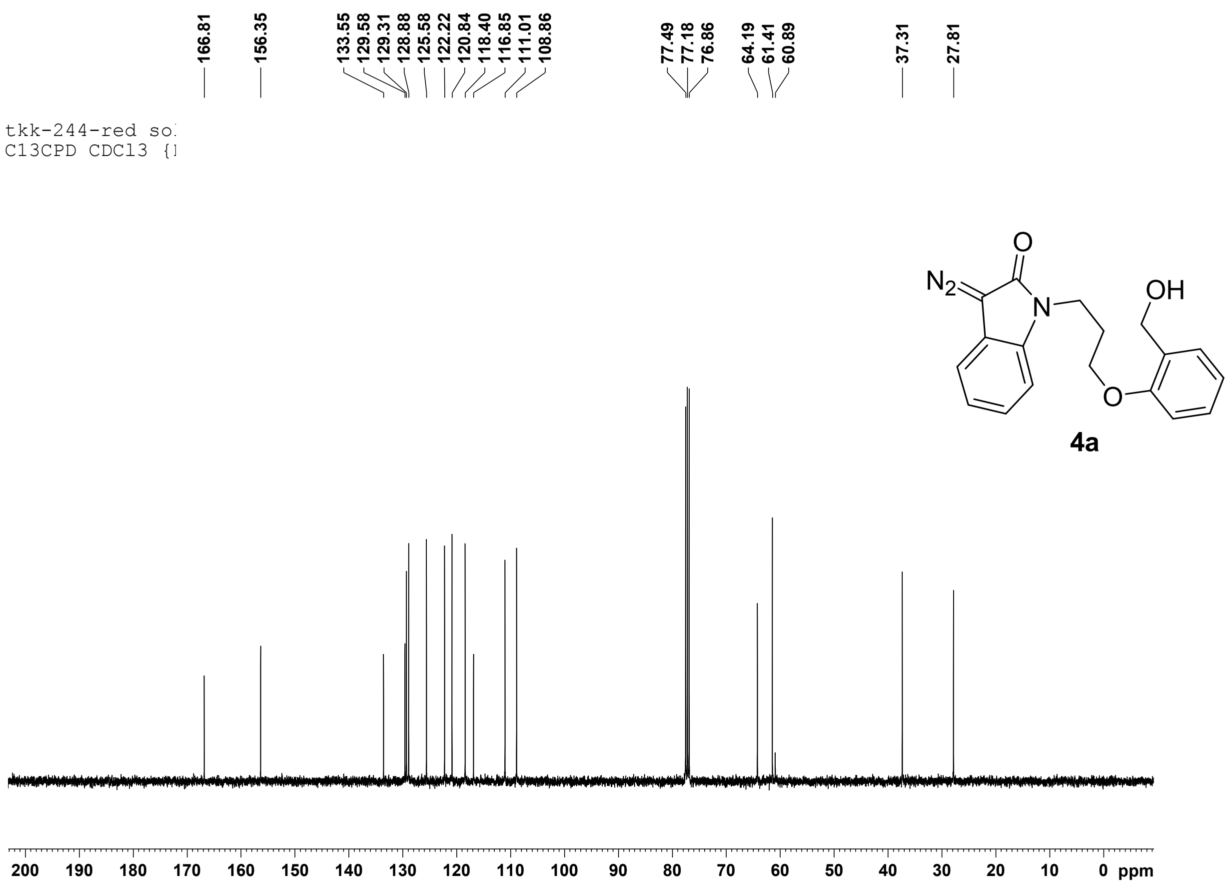
7.704 7.700 7.684 7.680 7.367 7.352 7.350 7.348 7.346 7.332 7.327 7.197 6.897 6.881 6.880 6.861 4.229 4.212 4.195 3.961 3.944 3.928 3.574 3.558 3.541 3.350 3.333 3.315 1.794 1.776 1.767 1.757 1.750 1.740 1.729 1.690 1.673 1.653 1.539 1.507 1.490 1.473 1.419 1.401 1.381 1.363 1.345 1.327 1.302 1.278 1.267 1.241 1.186
tkk-379-
PROTON (
O
O
OH
O
Br
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.04 2.09 2.08 2.05 2.08 1.96 6.24 2.62 6.50 18.93

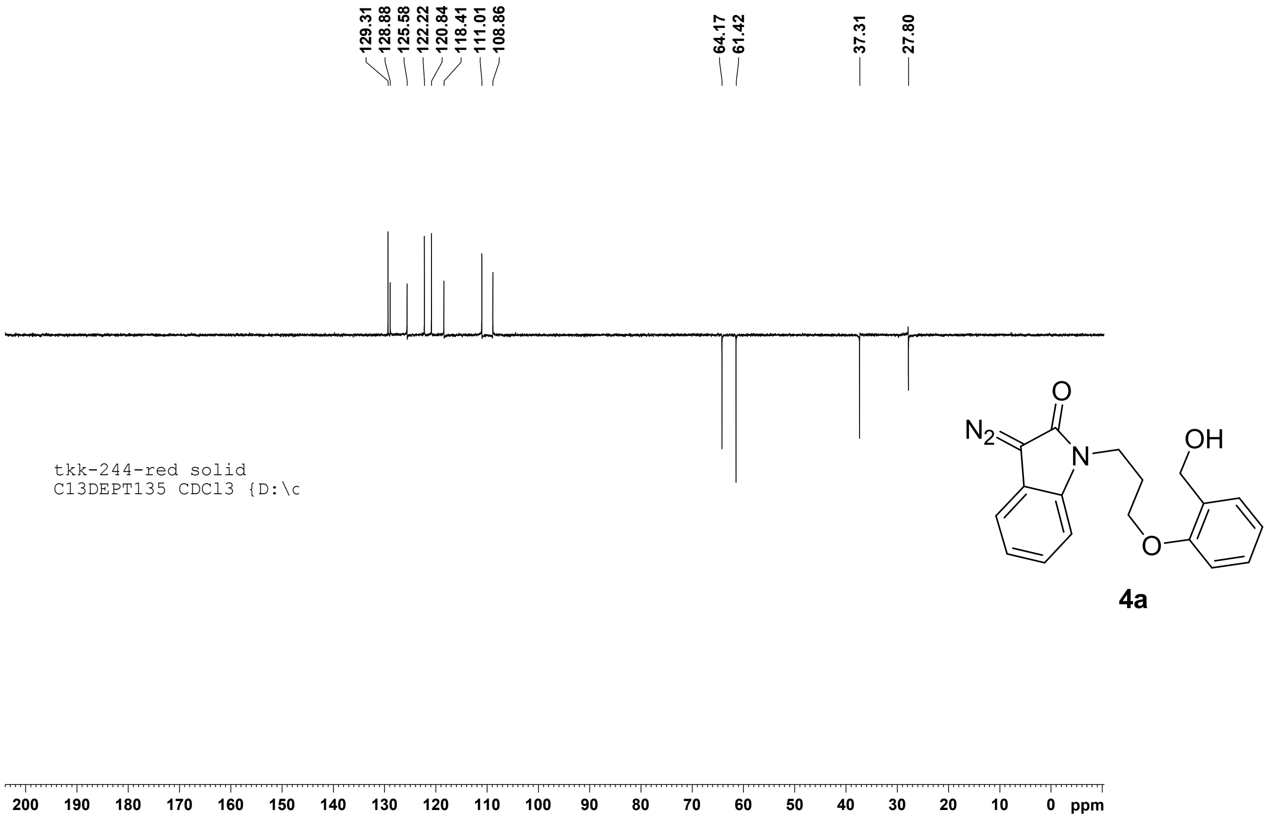
10b


7.234 7.216 7.148 7.137 7.128 7.108 7.096 7.093 7.074 7.056 7.053 6.835 6.817 6.799 6.781 6.770 6.761 6.752 6.749 6.646 6.644 6.628 6.625 6.603 6.582 4.256 3.938 3.922 3.906 3.891 3.321 3.314 3.304 3.287 1.788 1.771 1.754 1.734 1.716 1.711 1.694 1.678 1.676 1.403 1.386 1.367 1.351 1.334 1.315 1.252
Tkk-296-1
PROTON CD
HN
O
Br
14a
10 9 8 7 6 5 4 3 2 1 ppm
0.93 2.91 2.22 2.72 2.00 2.26 2.08 4.23 9.82

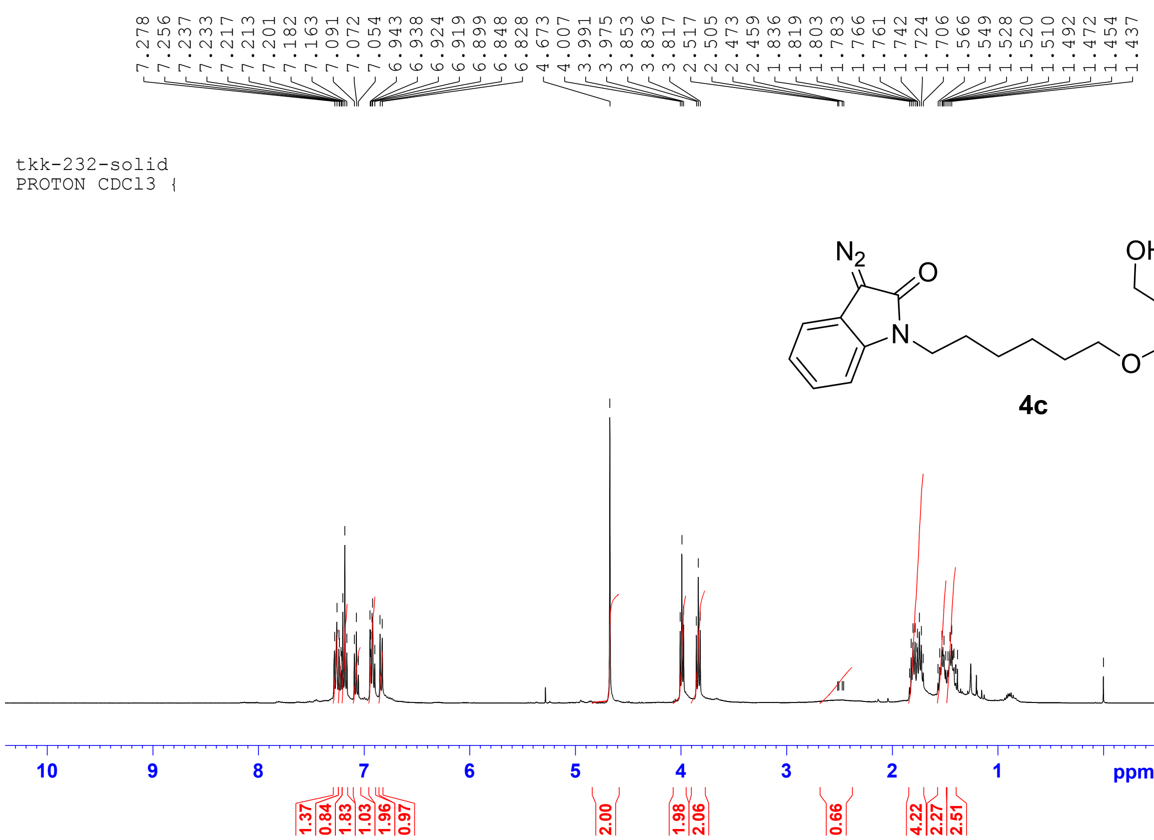

7.207 7.146 7.132 7.129 7.093 7.084 7.081 7.074 7.072 7.066 7.062 7.053 6.820 6.802 6.789 6.768 6.608 6.590 6.587 6.582 6.580 6.561 6.559 6.554 4.435 4.258 3.933 3.917 3.901 3.328 3.311 3.298 3.294 1.778 1.771 1.760 1.752 1.741 1.734 1.724 1.717 1.698 1.409 1.390 1.371 1.352 1.331 1.313 1.305 1.283 1.226 1.216
tkk-313
PROTON
HN
O
Br
14b
10 9 8 7 6 5 4 3 2 1 ppm
0.91 3.61 2.38 3.32 2.00 2.47 2.51 4.31 0.51 11.92


7.321 7.317 7.302 7.299 7.226 7.222 7.206 7.203 7.186 7.181 7.172 7.169 7.160 7.153 7.150 7.133 7.131 7.082 7.081 7.062 7.045 7.043 6.968 6.948 6.934 6.916 6.898 6.796 6.775 4.714 4.059 4.043 4.026 4.006 3.991 3.977 2.220 2.205 2.189 2.174 2.158
tkk-244-red solid
PROTON CDCl3 {D:\dat
N_2
O
N
OH
O
4a
0.98 2.94 0.95 0.98 0.96 0.93 2.00 3.83 0.79 2.06
ppm

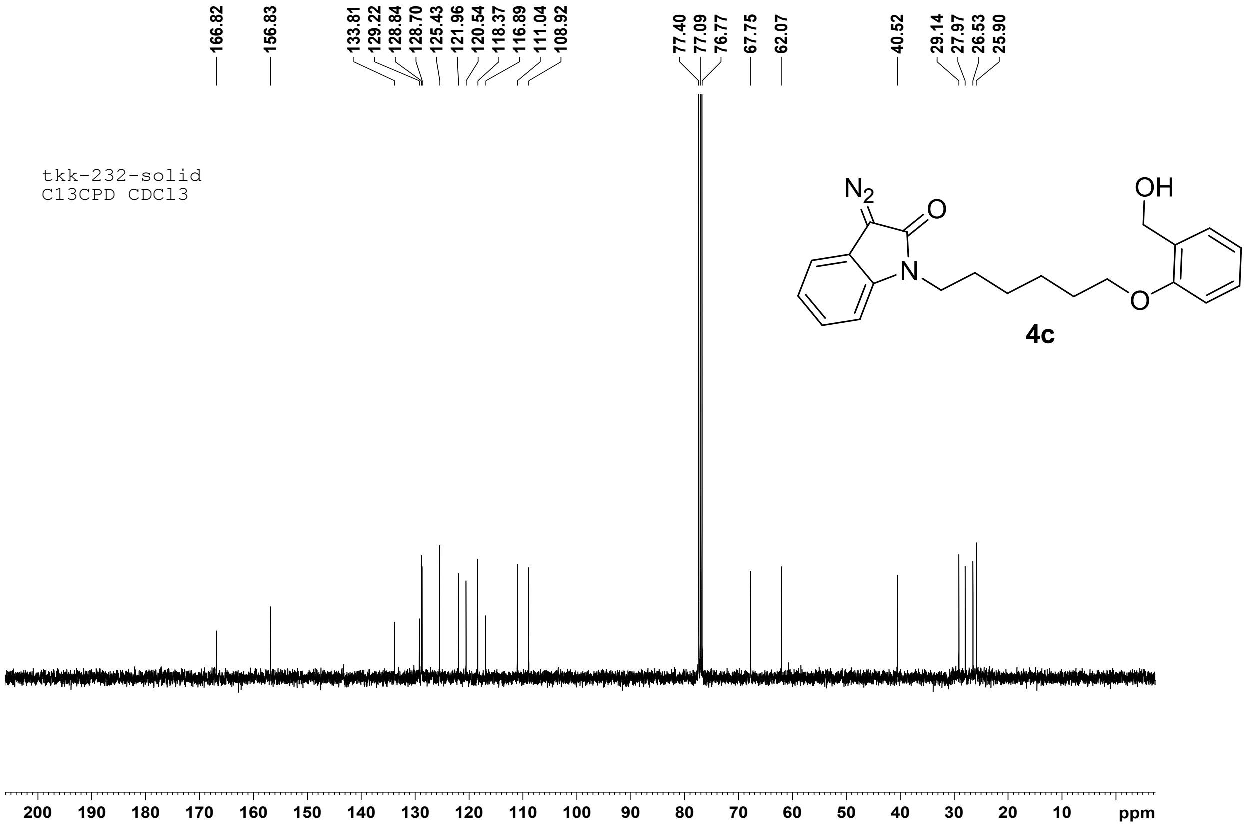

166.81 156.35 133.55 129.58 129.31 128.88 125.58 122.22 120.84 118.40 116.85 111.01 108.86 77.49 77.18 76.86 64.19 61.41 60.89 37.31 27.81
tkk-244-red so
C13CPD CDCl3 {
N_2
O
N
OH
O
4a
ppm

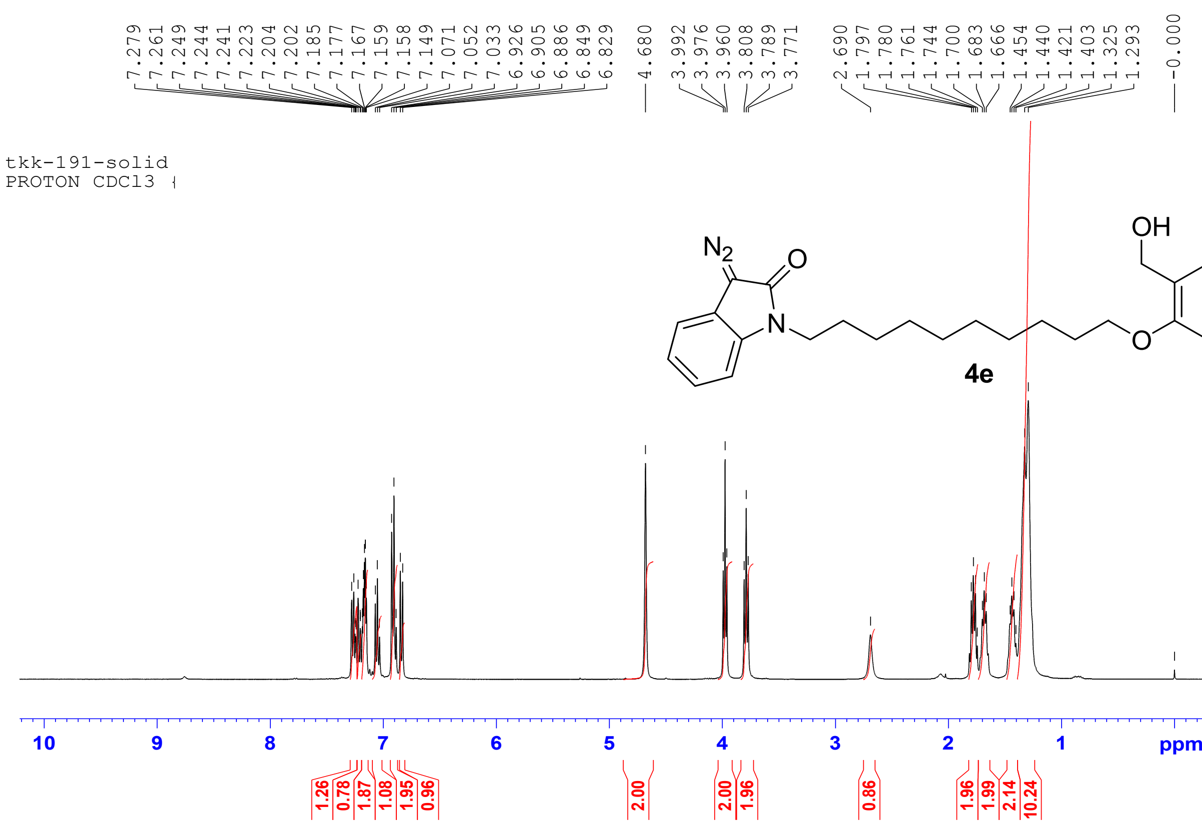

129.31
128.88
125.58
122.22
120.84
118.41
111.01
108.86
64.17
61.42
37.31
27.80
tkk-244-red solid
C13DEPT135 CDCl3 {D:\c
N2
O
N
OH
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

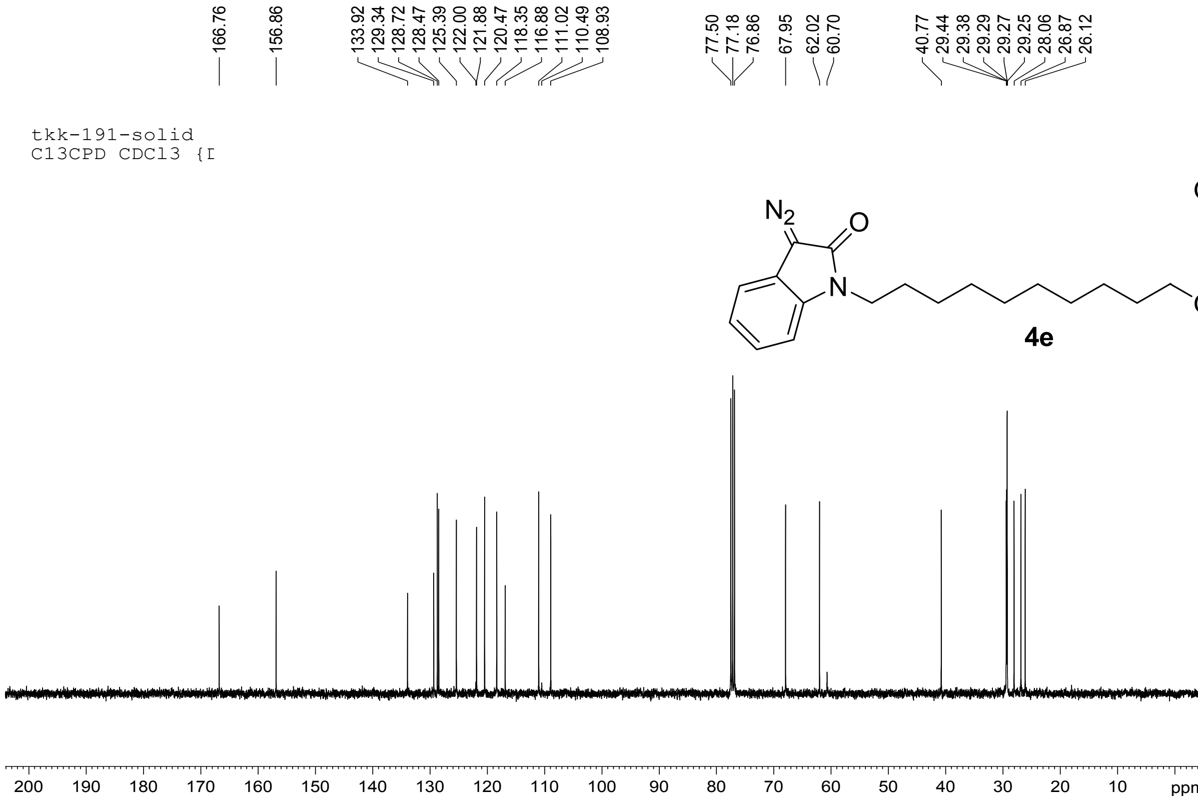
4a

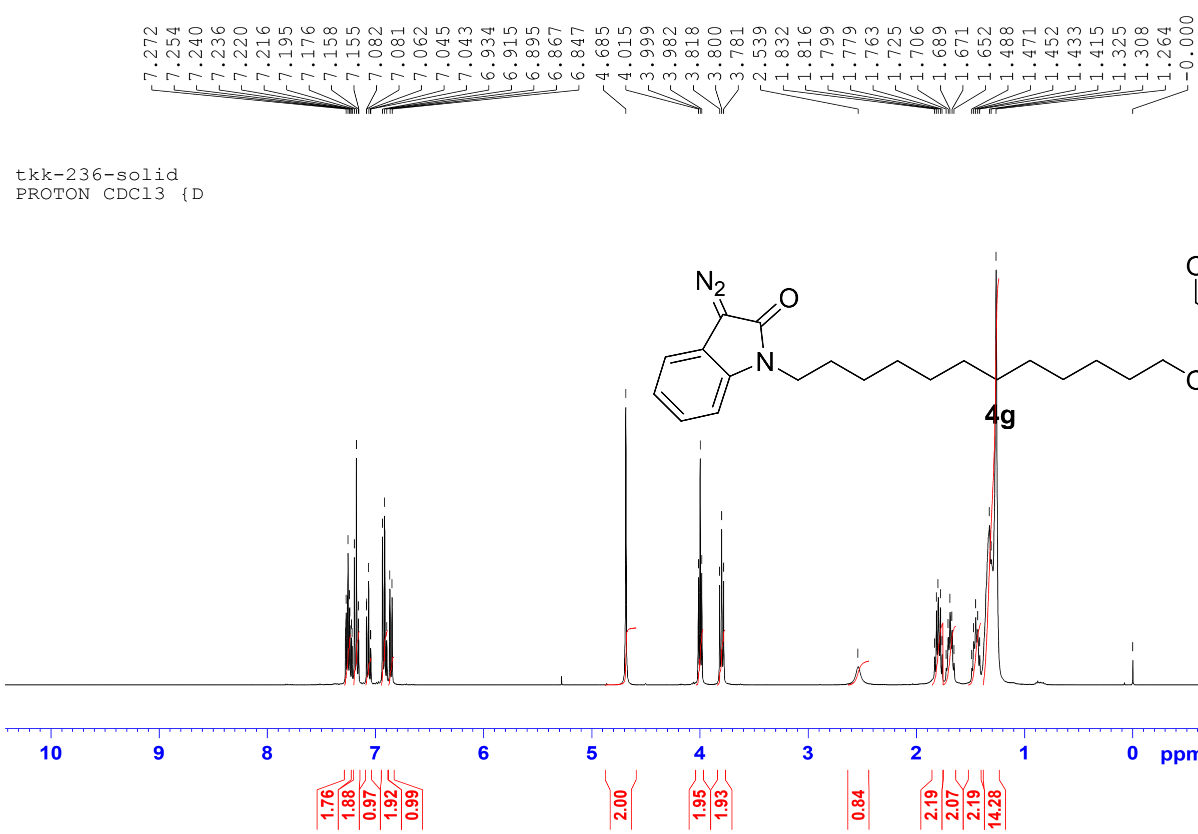

7.278
7.256
7.237
7.233
7.217
7.213
7.201
7.182
7.163
7.091
7.072
7.054
6.943
6.938
6.924
6.919
6.899
6.848
6.828
4.673
4.007
3.991
3.975
3.853
3.836
3.817
2.517
2.505
2.473
2.459
1.836
1.819
1.803
1.783
1.766
1.761
1.742
1.724
1.706
1.566
1.549
1.528
1.520
1.510
1.492
1.472
1.454
1.437
tkk-232-solid
PROTON CDCl3 {
N2
O
N
OH
O
10 9 8 7 6 5 4 3 2 1 ppm
1.37
0.84
1.83
1.03
1.96
0.97
2.00
1.98
2.06
0.66
4.22
2.27
2.51

4c

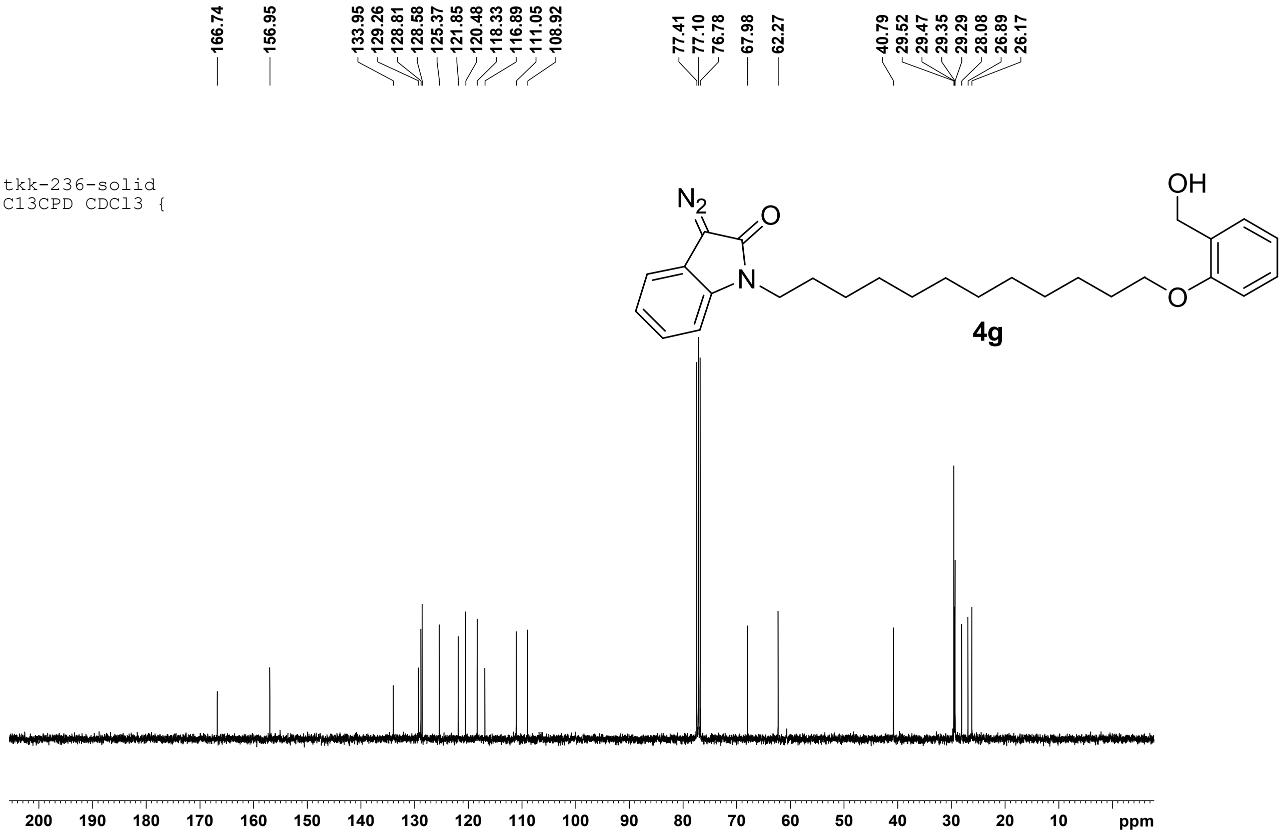

166.82
156.83
133.81
129.22
128.84
128.70
125.43
121.96
120.54
118.37
116.89
111.04
108.92
77.40
77.09
76.77
67.75
62.07
40.52
29.14
27.97
26.53
25.90
tkk-232-solid
C13CPD CDCl3
N2
O
N
OH
O
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.279
7.261
7.249
7.244
7.241
7.223
7.204
7.202
7.185
7.177
7.167
7.159
7.158
7.149
7.071
7.052
7.033
6.926
6.905
6.886
6.849
6.829
4.680
3.992
3.976
3.960
3.808
3.789
3.771
2.690
1.797
1.780
1.761
1.744
1.700
1.683
1.666
1.454
1.440
1.421
1.403
1.325
1.293
-0.000
tkk-191-solid
PROTON CDCl3
N2
O
N
OH
O
4e
10 9 8 7 6 5 4 3 2 1 ppm
1.26
0.78
1.87
1.08
1.95
0.96
2.00
2.00
1.96
0.86
1.96
1.99
2.14
10.24

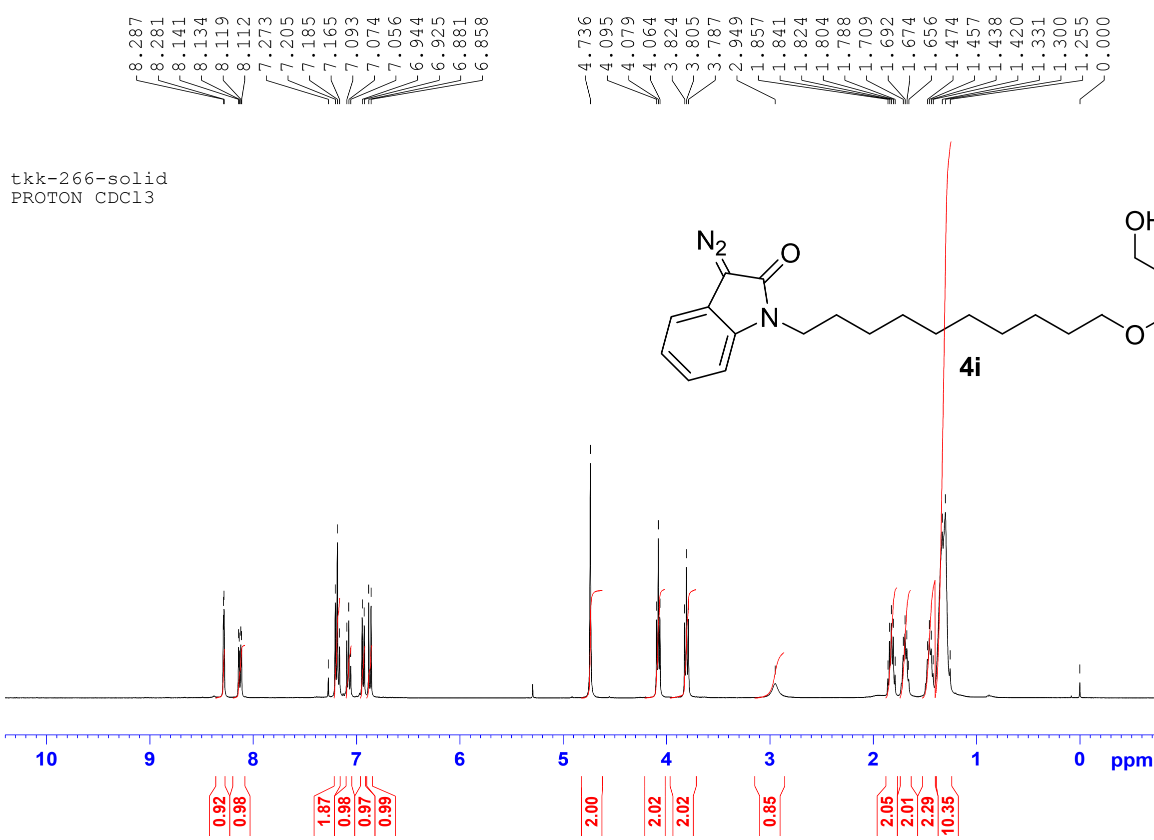

166.76
156.86
133.92
129.34
128.72
128.47
125.39
122.00
121.88
120.47
118.35
116.88
111.02
110.49
108.93
77.50
77.18
76.86
67.95
62.02
60.70
40.77
29.44
29.38
29.29
29.27
29.25
28.06
26.87
26.12
tkk-191-solid
C13CPD CDCl3 {D
N_2
O
N
OH
O
4e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

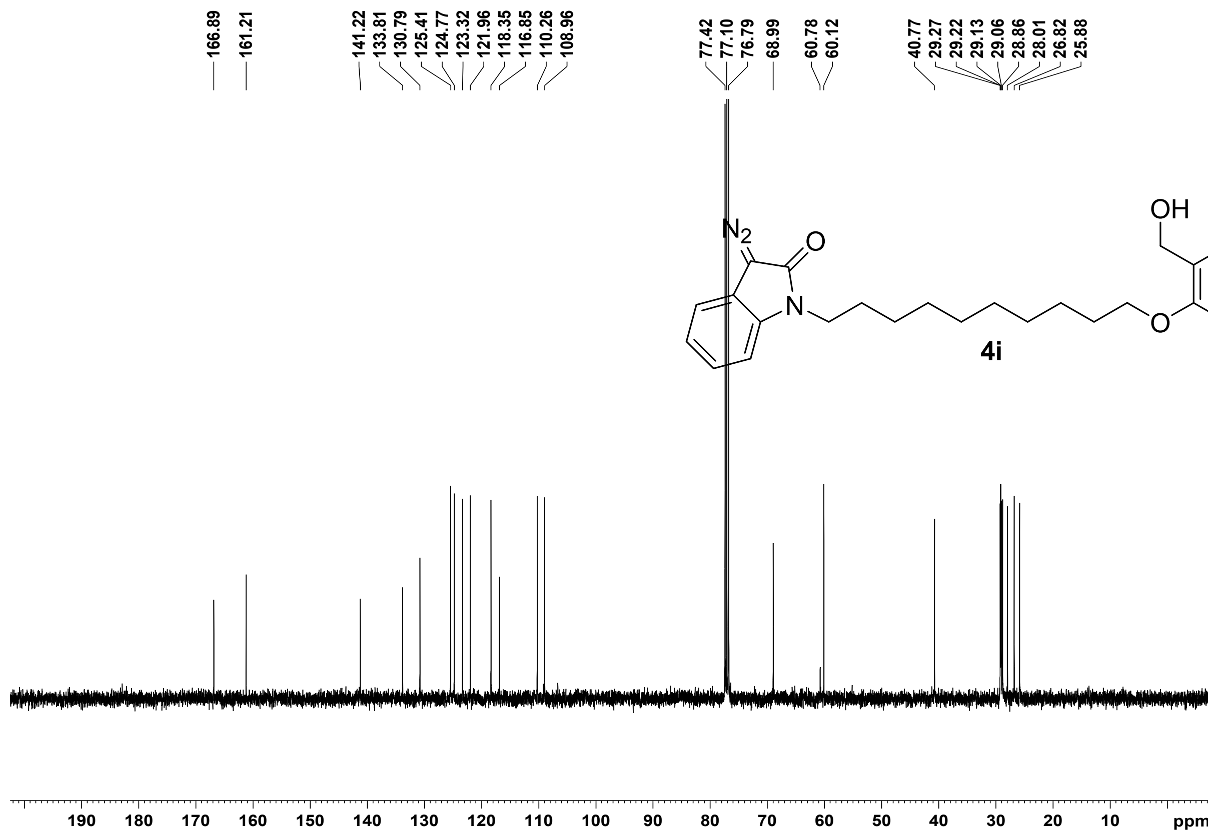

7.272
7.254
7.240
7.236
7.220
7.216
7.195
7.176
7.158
7.155
7.082
7.081
7.062
7.045
7.043
6.934
6.915
6.895
6.867
6.847
4.685
4.015
3.999
3.982
3.818
3.800
3.781
2.539
1.832
1.816
1.799
1.779
1.763
1.725
1.706
1.689
1.671
1.652
1.488
1.471
1.452
1.433
1.415
1.325
1.308
1.264
-0.000
tkk-236-solid
PROTON CDCl3 {D
N_2
O
N
OH
O
4g
10 9 8 7 6 5 4 3 2 1 0 ppm
1.76
1.88
0.97
1.92
0.99
2.00
1.95
1.93
0.84
2.19
2.07
2.19
14.28

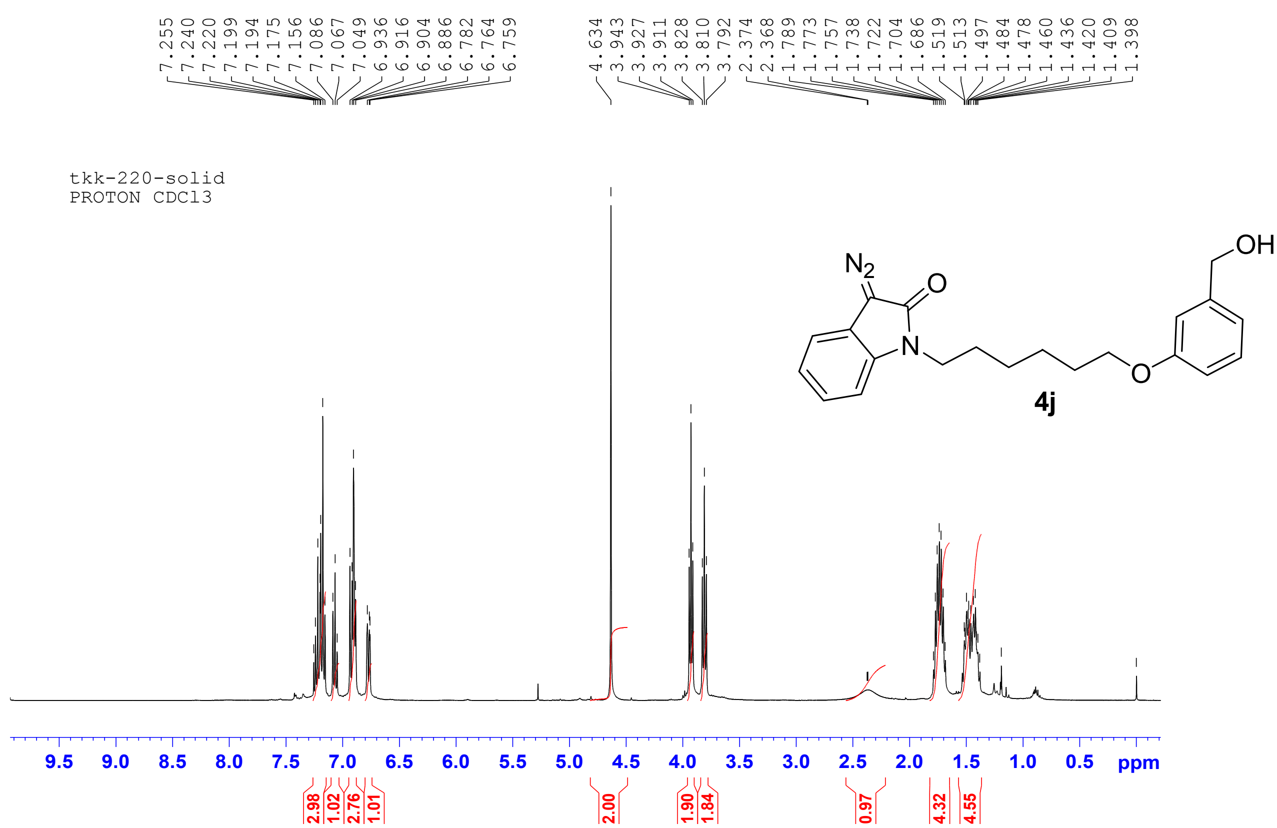
tkk-236-solid
C13CPD CDCl3 {

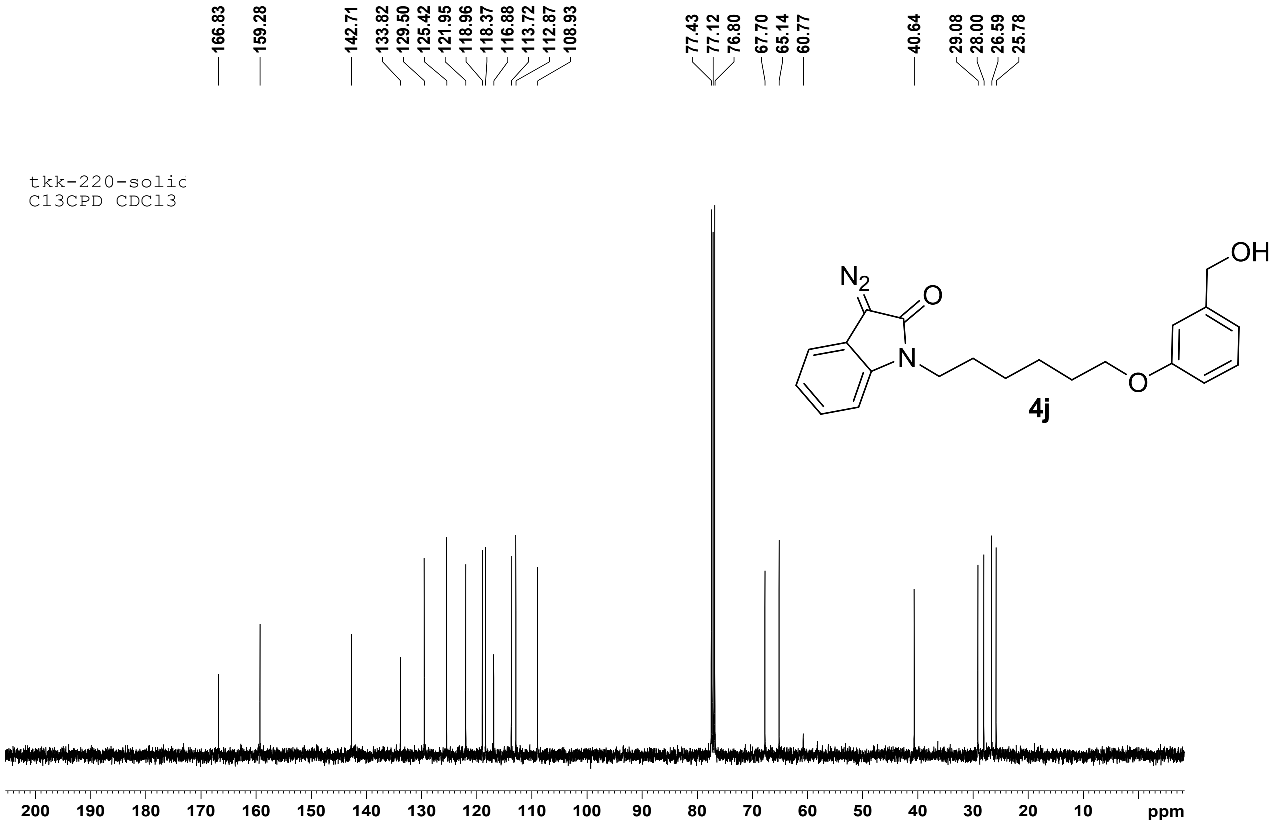


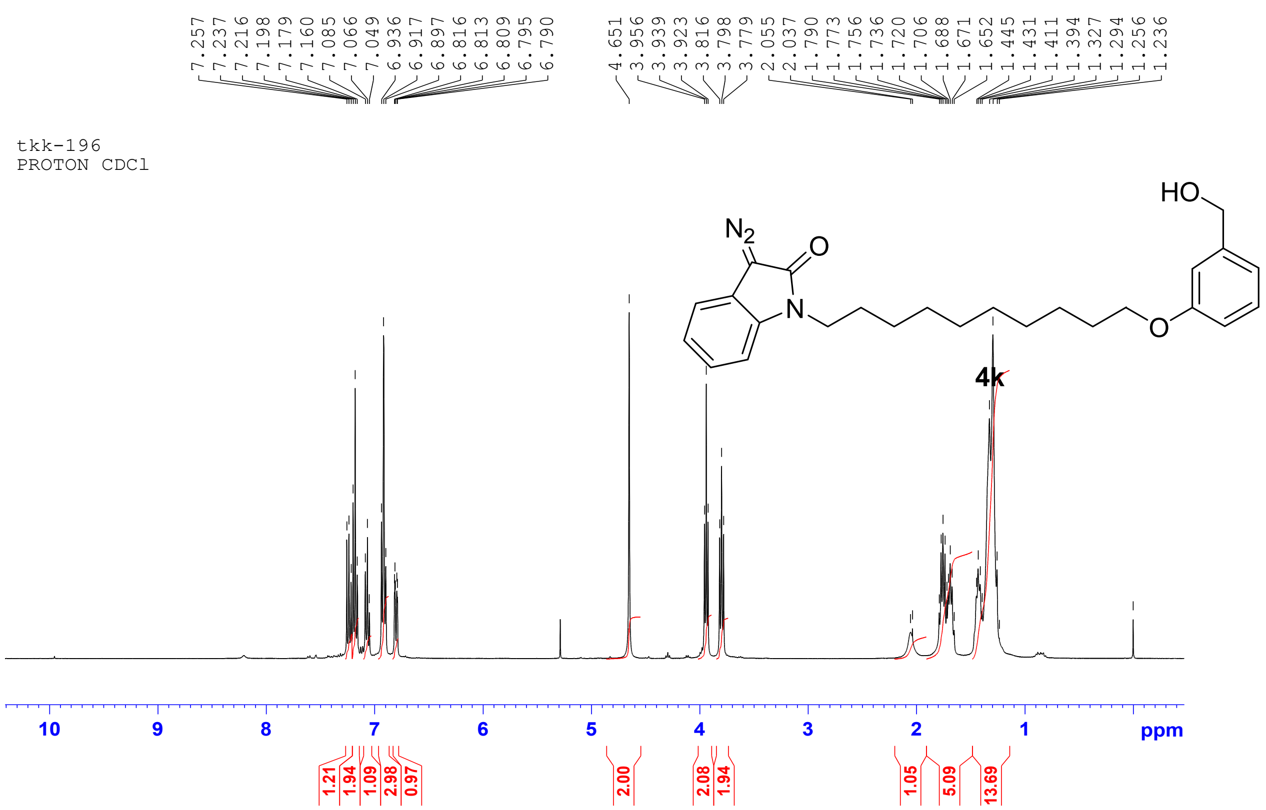
tkk-266-solid
PROTON CDCl3

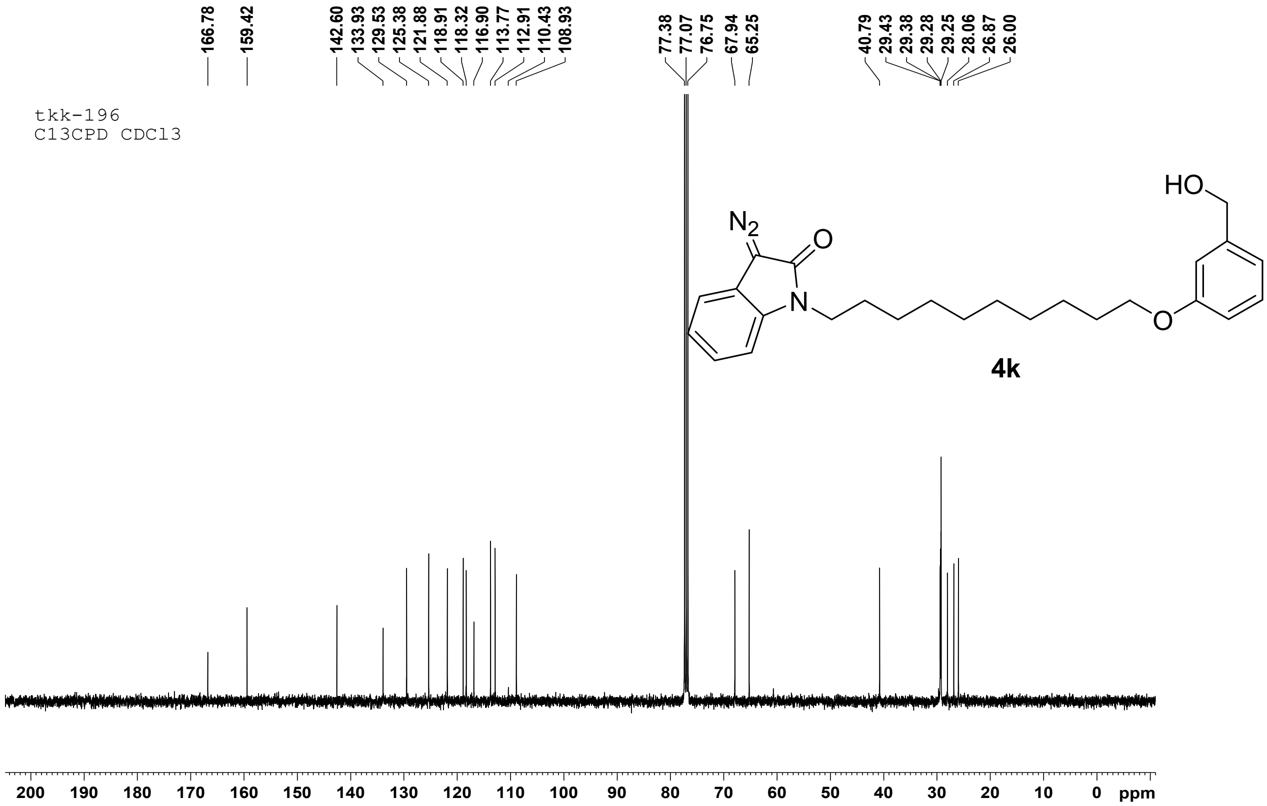



166.89
161.21
141.22
133.81
130.79
125.41
124.77
123.32
121.96
118.35
116.85
110.26
108.96
77.42
77.10
76.79
68.99
60.78
60.12
40.77
29.27
29.22
29.13
29.06
28.86
28.01
26.82
25.88
4i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

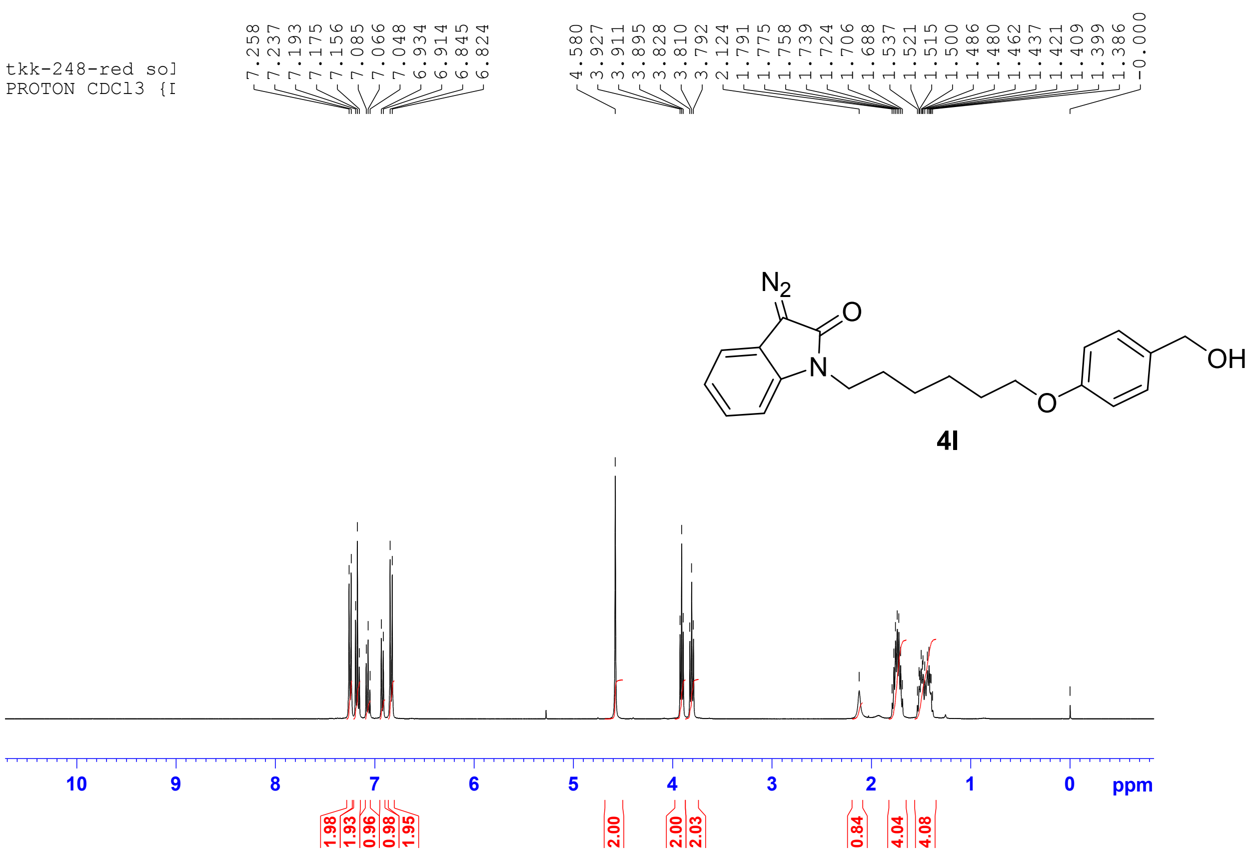

7.255
7.240
7.220
7.199
7.194
7.175
7.156
7.086
7.067
7.049
6.936
6.916
6.904
6.886
6.782
6.764
6.759
4.634
3.943
3.927
3.911
3.828
3.810
3.792
2.374
2.368
1.789
1.773
1.757
1.738
1.722
1.704
1.686
1.519
1.513
1.497
1.484
1.478
1.460
1.436
1.420
1.409
1.398
tkk-220-solid
PROTON CDCl3
4j
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.98
1.02
2.76
1.01
2.00
1.90
1.84
0.97
4.32
4.55


166.83
159.28
142.71
133.82
129.50
125.42
121.95
118.96
118.37
116.88
113.72
112.87
108.93
77.43
77.12
76.80
67.70
65.14
60.77
40.64
29.08
28.00
26.59
25.78
tkk-220-solic
C13CPD CDCl3
N_2
O
N
O
OH
4j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

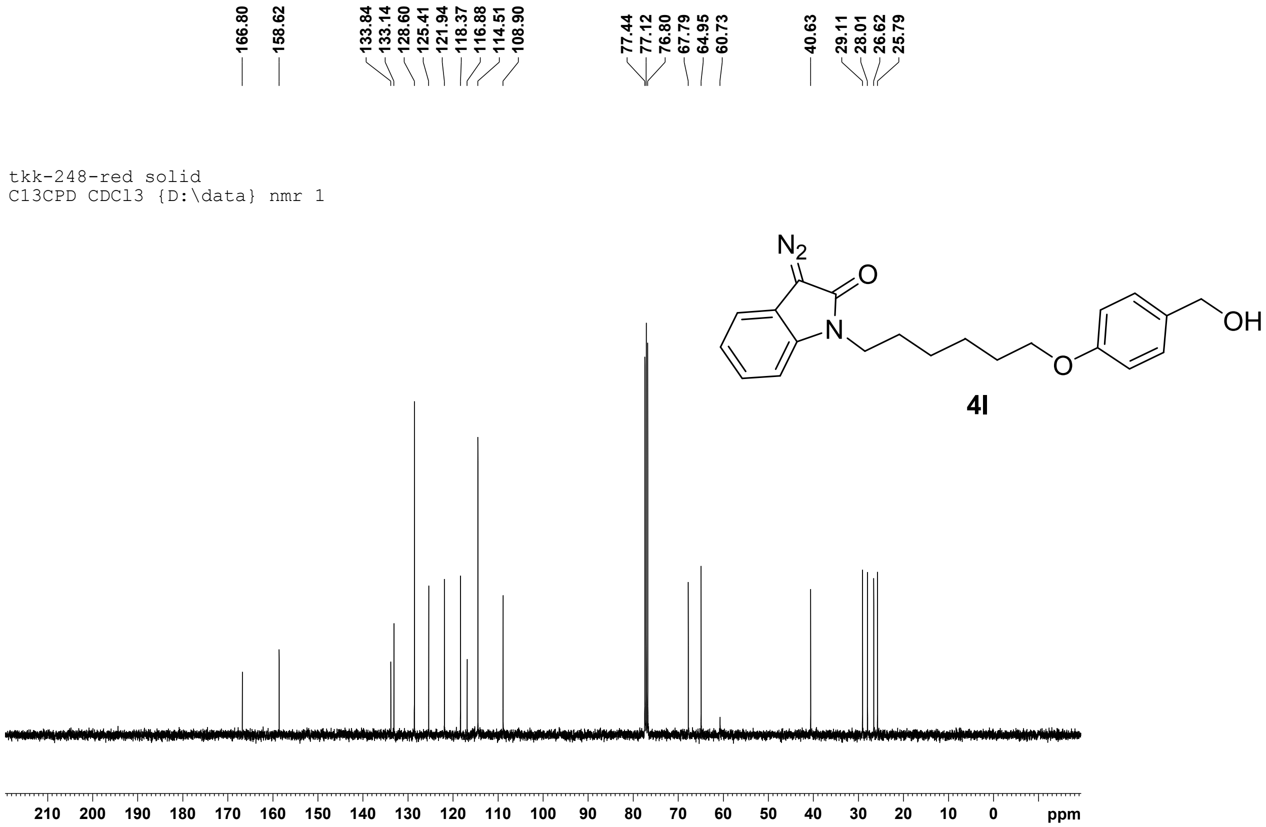

7.257
7.237
7.216
7.198
7.179
7.160
7.085
7.066
7.049
6.936
6.917
6.897
6.816
6.813
6.809
6.795
6.790
4.651
3.956
3.939
3.923
3.816
3.798
3.779
2.055
2.037
1.790
1.773
1.756
1.736
1.720
1.706
1.688
1.671
1.652
1.445
1.431
1.411
1.394
1.327
1.294
1.256
1.236
tkk-196
PROTON CDCl
HO
N_2
O
N
O
4k
10 9 8 7 6 5 4 3 2 1 ppm
1.21
1.94
1.09
2.98
0.97
2.00
2.08
1.94
1.05
5.09
13.69

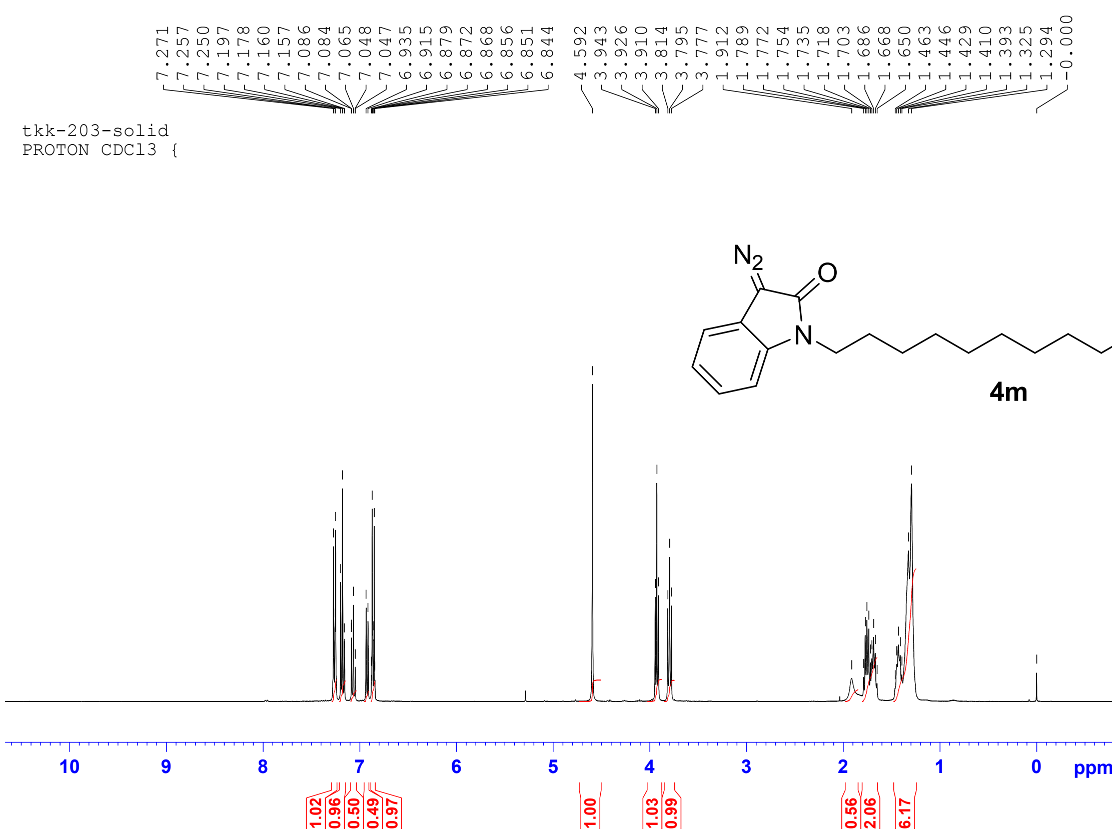

166.78
159.42
142.60
133.93
129.53
125.38
121.88
118.91
118.32
116.90
113.77
112.91
110.43
108.93
77.38
77.07
76.75
67.94
65.25
40.79
29.43
29.38
29.28
29.25
28.06
26.87
26.00
tkk-196
C13CPD CDCl3
HO
N2
O
N
O
ppm

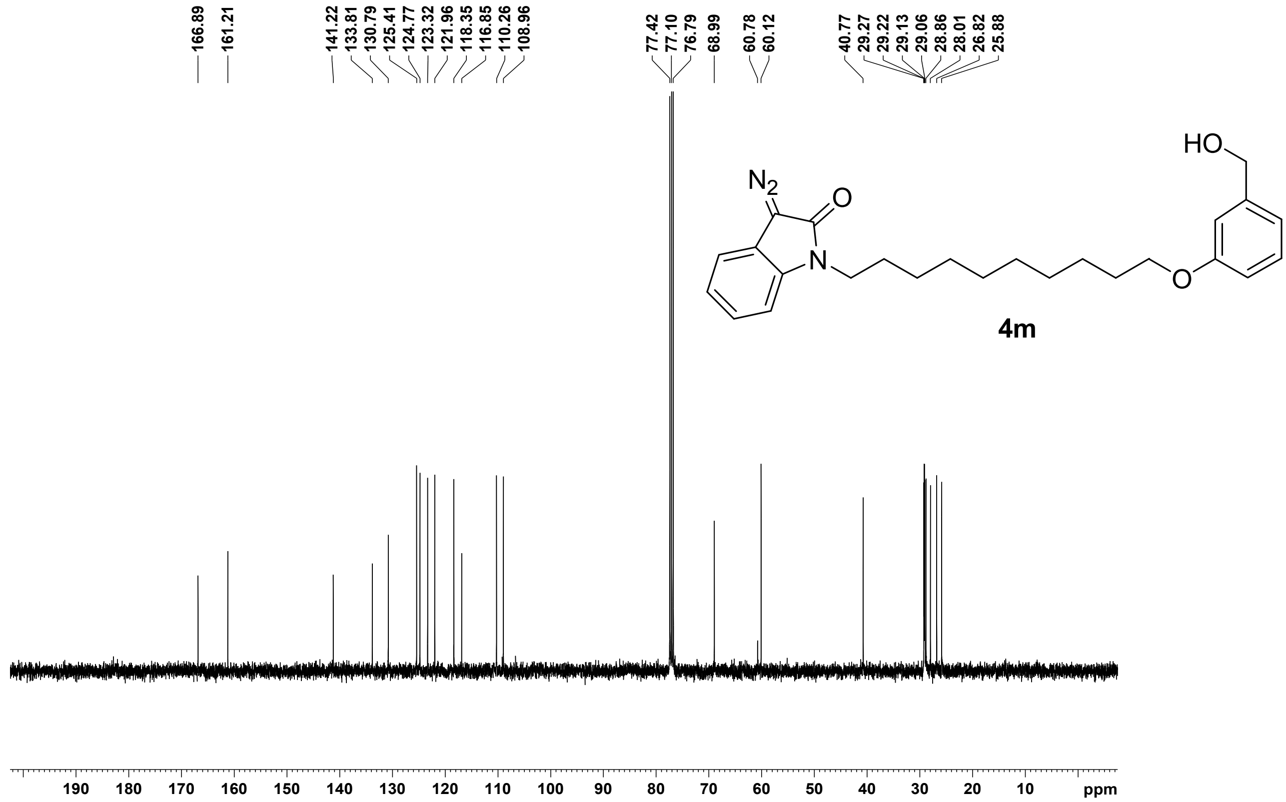
4k

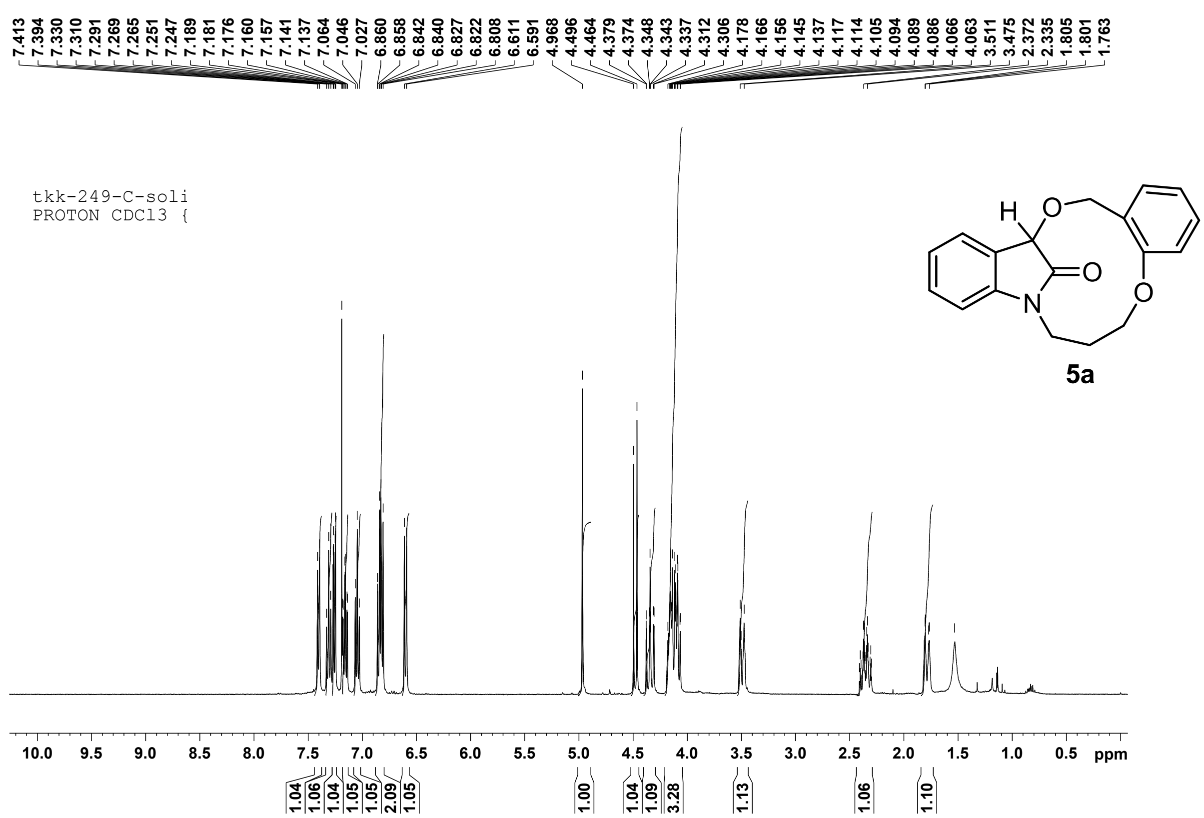

tkk-248-red sol
PROTON CDCl3 {I
7.258
7.237
7.193
7.175
7.156
7.085
7.066
7.048
6.934
6.914
6.845
6.824
4.580
3.927
3.911
3.895
3.828
3.810
3.792
2.124
1.791
1.775
1.758
1.739
1.724
1.706
1.688
1.537
1.521
1.515
1.500
1.486
1.480
1.462
1.437
1.421
1.409
1.399
1.386
-0.000
N2
O
N
O
OH
ppm
1.98
1.93
0.96
0.98
1.95
2.00
2.00
2.03
0.84
4.04
4.08

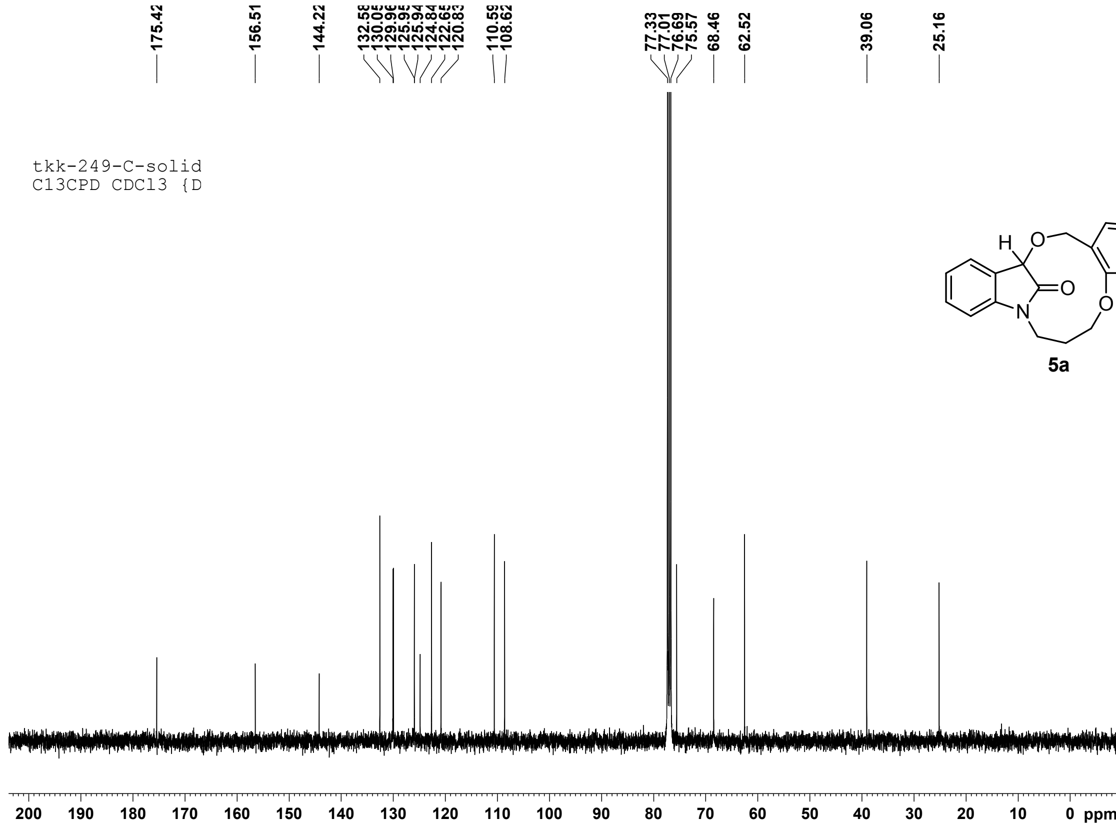
4l


166.80
158.62
133.84
133.14
128.60
125.41
121.94
118.37
116.88
114.51
108.90
77.44
77.12
76.80
67.79
64.95
60.73
40.63
29.11
28.01
26.62
25.79
tkk-248-red solid
C13CPD CDCl3 {D:\data} nmr 1
N2
O
N
O
OH
4l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

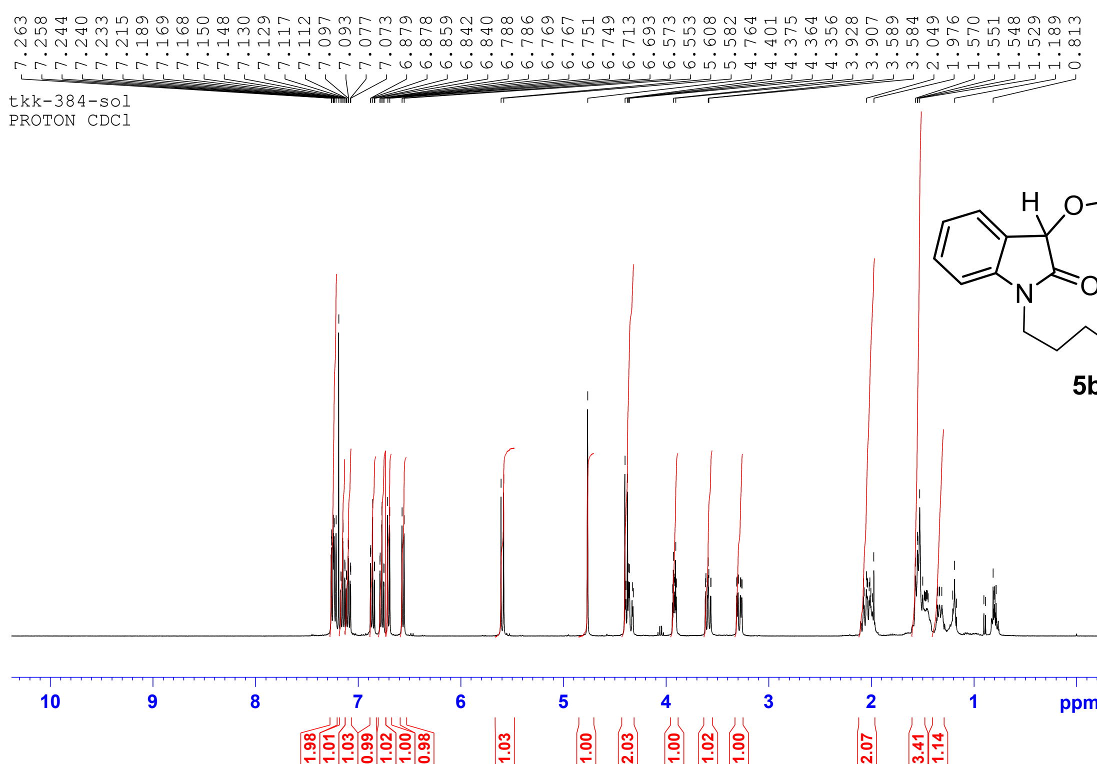

7.271
7.257
7.250
7.197
7.178
7.160
7.157
7.086
7.084
7.065
7.048
7.047
6.935
6.915
6.879
6.872
6.868
6.856
6.851
6.844
4.592
3.943
3.926
3.910
3.814
3.795
3.777
1.912
1.789
1.772
1.754
1.735
1.718
1.703
1.686
1.668
1.650
1.463
1.446
1.429
1.410
1.393
1.325
1.294
-0.000
tkk-203-solid
PROTON CDCl3 {
HO
N2
O
N
O
4m
10 9 8 7 6 5 4 3 2 1 0 ppm
1.02
0.96
0.50
0.49
0.97
1.00
1.03
0.99
0.56
2.06
6.17


4m

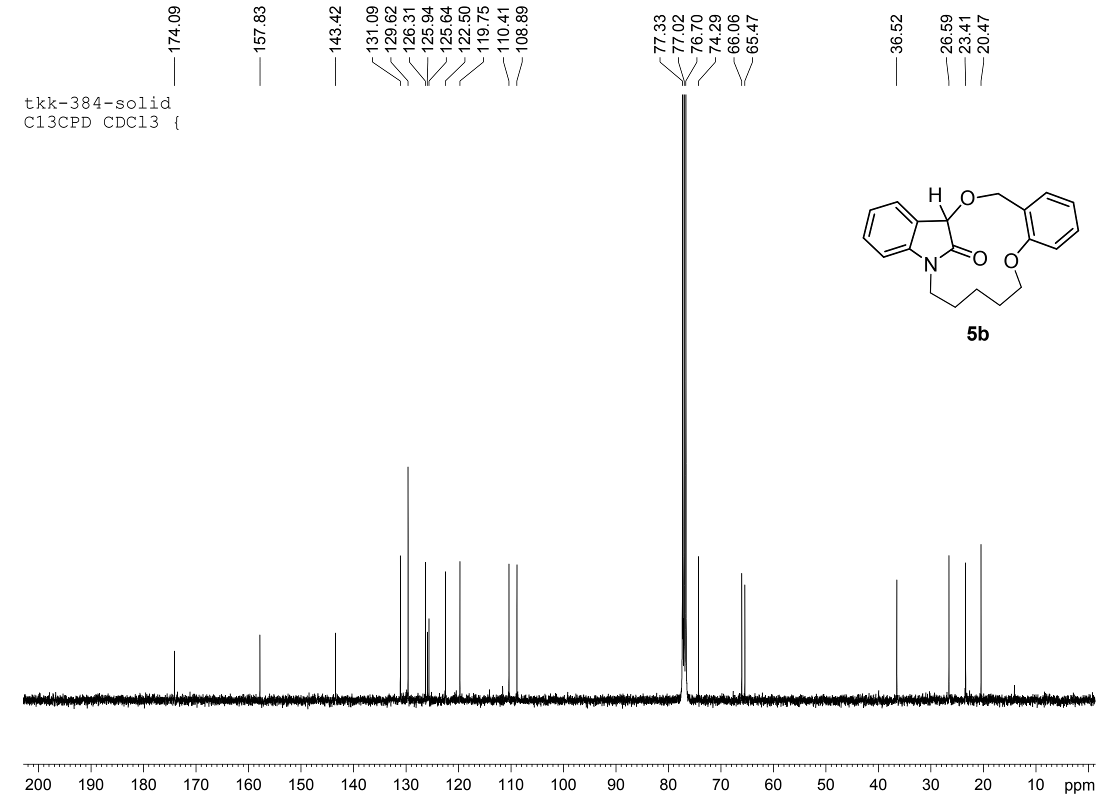

tkk-249-C-soli
PROTON CDCl3 {
5a

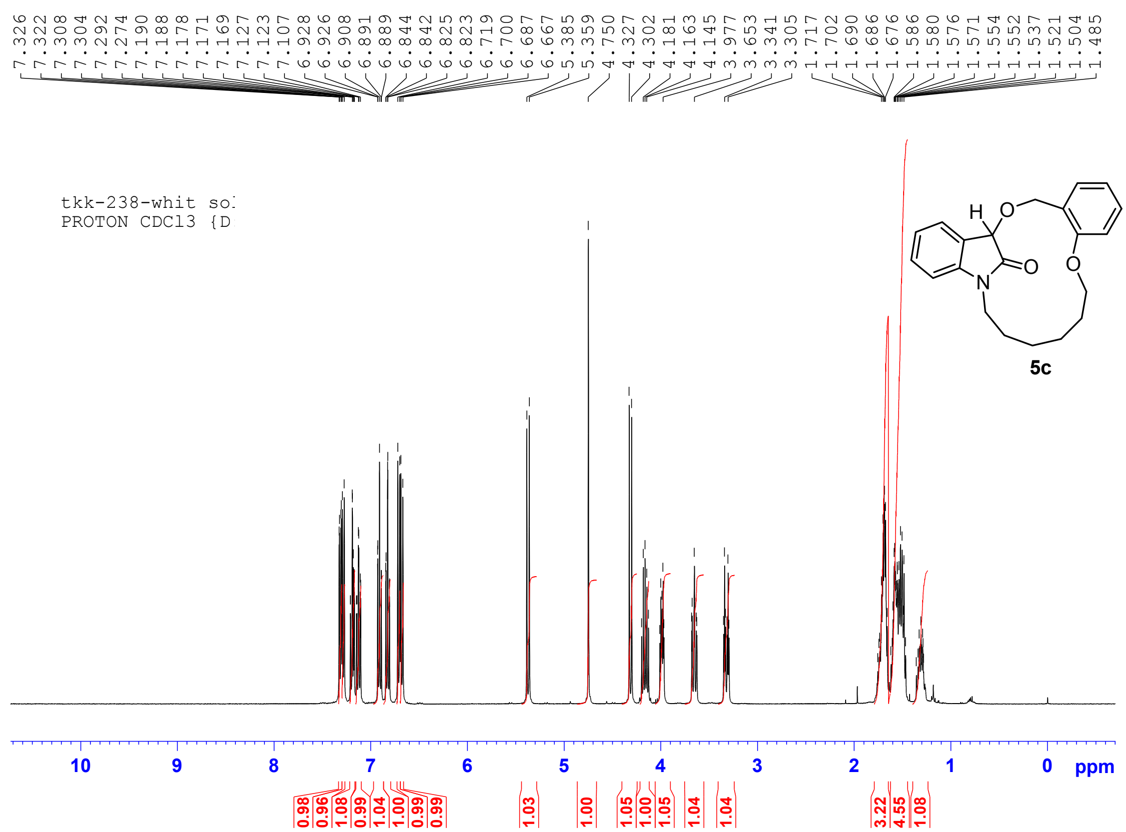


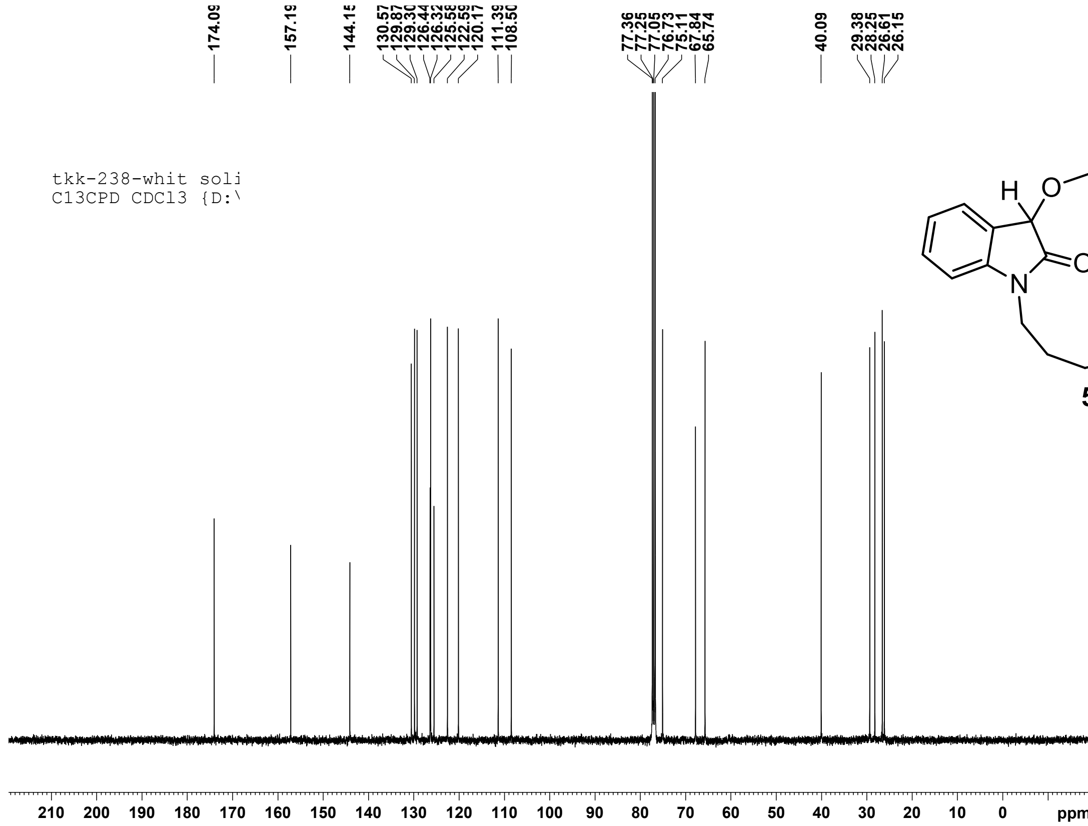
175.42
156.51
144.22
132.58
130.05
129.96
125.95
125.94
124.84
122.65
120.83
110.59
108.62
77.33
77.01
76.69
75.57
68.46
62.52
39.06
25.16
tkk-249-C-solid
C13CPD CDCl3 {D
H
O
N
5a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



7.263
7.258
7.244
7.240
7.233
7.215
7.189
7.169
7.168
7.150
7.148
7.130
7.129
7.117
7.112
7.097
7.093
7.077
7.073
6.879
6.878
6.859
6.842
6.840
6.788
6.786
6.769
6.767
6.751
6.749
6.713
6.693
6.573
6.553
5.608
5.582
4.764
4.401
4.375
4.364
4.356
3.928
3.907
3.589
3.584
2.049
1.976
1.570
1.551
1.548
1.529
1.189
0.813
tkk-384-sol
PROTON CDCl
H
O
N
5b
10 9 8 7 6 5 4 3 2 1 ppm
1.98 1.01 1.03 0.99 1.02 1.00 0.98 1.03 1.00 2.03 1.00 1.02 1.00 2.07 3.41 1.14

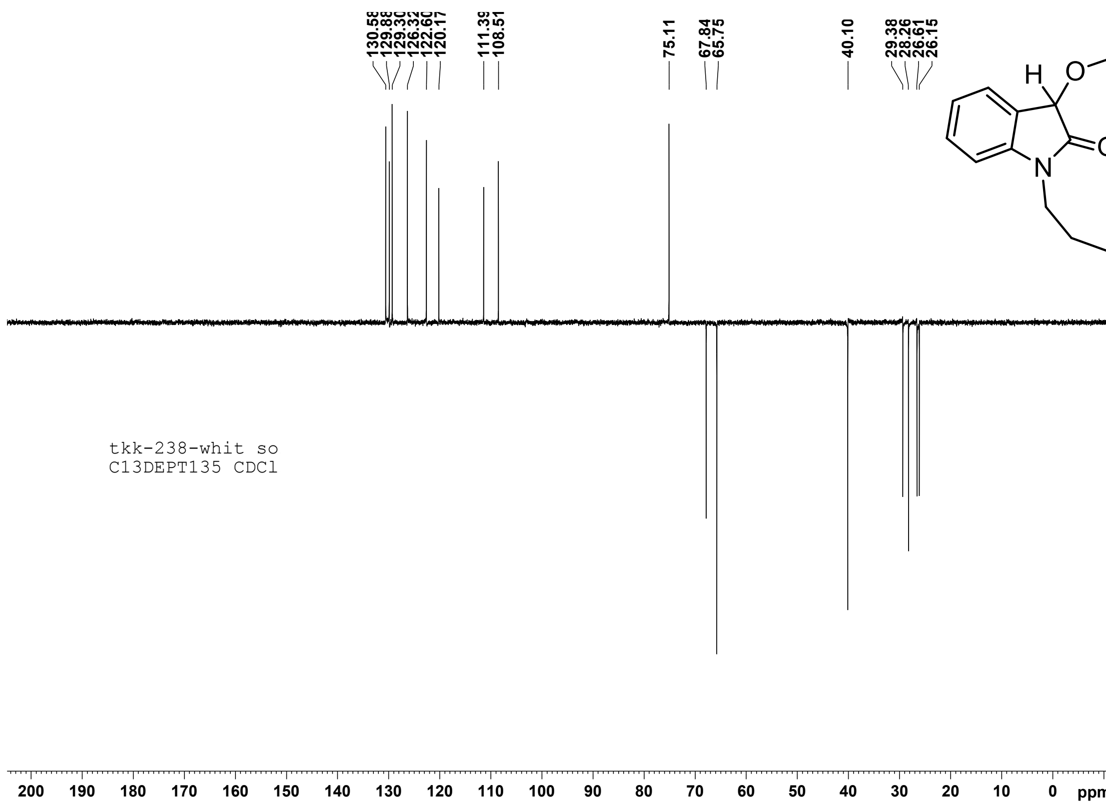

174.09
157.83
143.42
131.09
129.62
126.31
125.94
125.64
122.50
119.75
110.41
108.89
77.33
77.02
76.70
74.29
66.06
65.47
36.52
26.59
23.41
20.47
tkk-384-solid
C13CPD CDCl3 {
5b
ppm


7.326
7.322
7.308
7.304
7.292
7.274
7.190
7.188
7.178
7.171
7.169
7.127
7.123
7.107
6.928
6.926
6.908
6.891
6.889
6.844
6.842
6.825
6.823
6.719
6.700
6.687
6.667
5.385
5.359
4.750
4.327
4.302
4.181
4.163
4.145
3.977
3.653
3.341
3.305
1.717
1.702
1.690
1.686
1.676
1.586
1.580
1.576
1.571
1.554
1.552
1.537
1.521
1.504
1.485
tkk-238-whit so
PROTON CDCl3 {D
5c
ppm
0.98
0.96
1.08
0.99
1.04
1.00
0.99
0.99
1.03
1.00
1.05
1.00
1.05
1.04
1.04
3.22
4.55
1.08



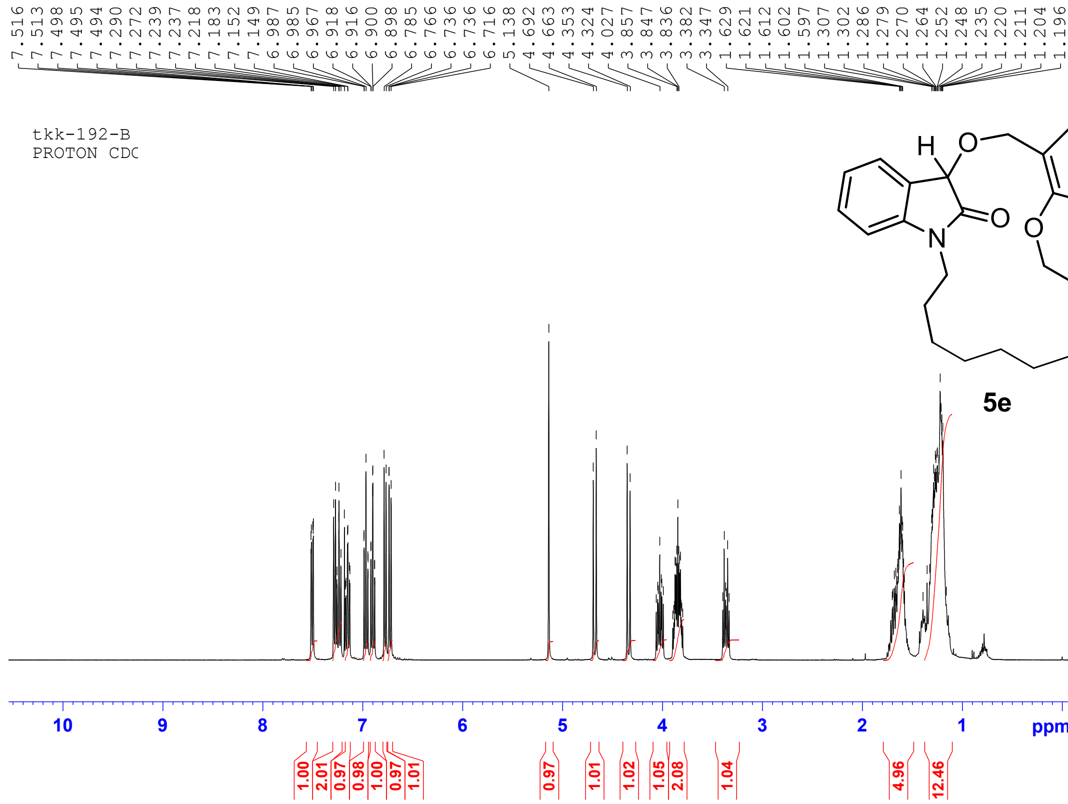
174.09
157.19
144.15
130.57
129.87
129.30
126.44
126.32
122.58
122.59
120.17
111.39
108.50
77.36
77.25
77.05
76.73
75.11
67.84
65.74
40.09
29.38
28.25
26.61
26.15
tkk-238-whit soli
C13CPD CDCl3 {D:\
H
O
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

5c

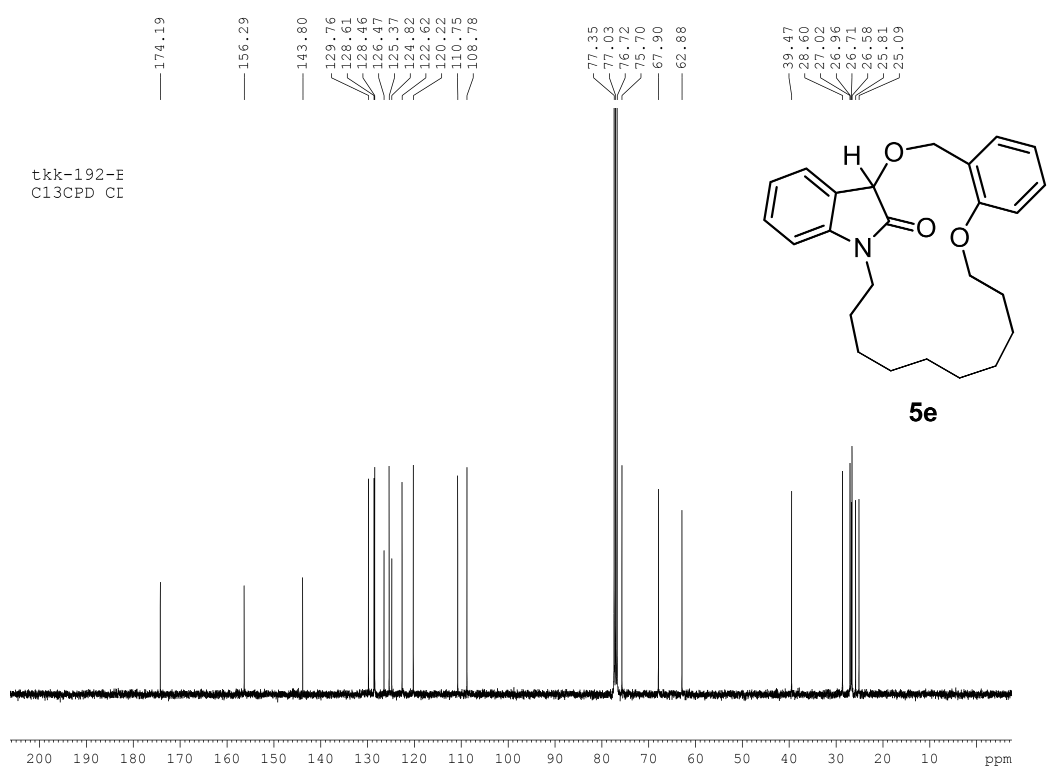


130.58
129.88
129.30
126.32
122.60
120.17
111.39
108.51
75.11
67.84
65.75
40.10
29.38
28.26
26.61
26.15
tkk-238-whit so
C13DEPT135 CDCl
H
O
O
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

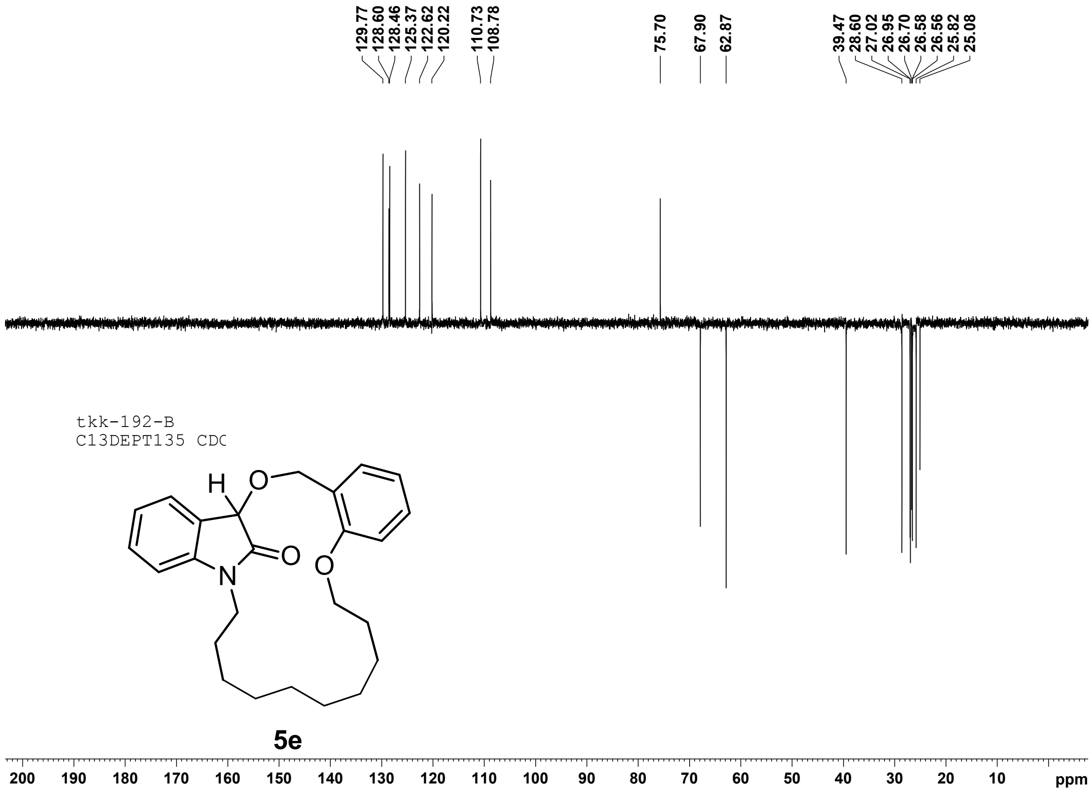
5c

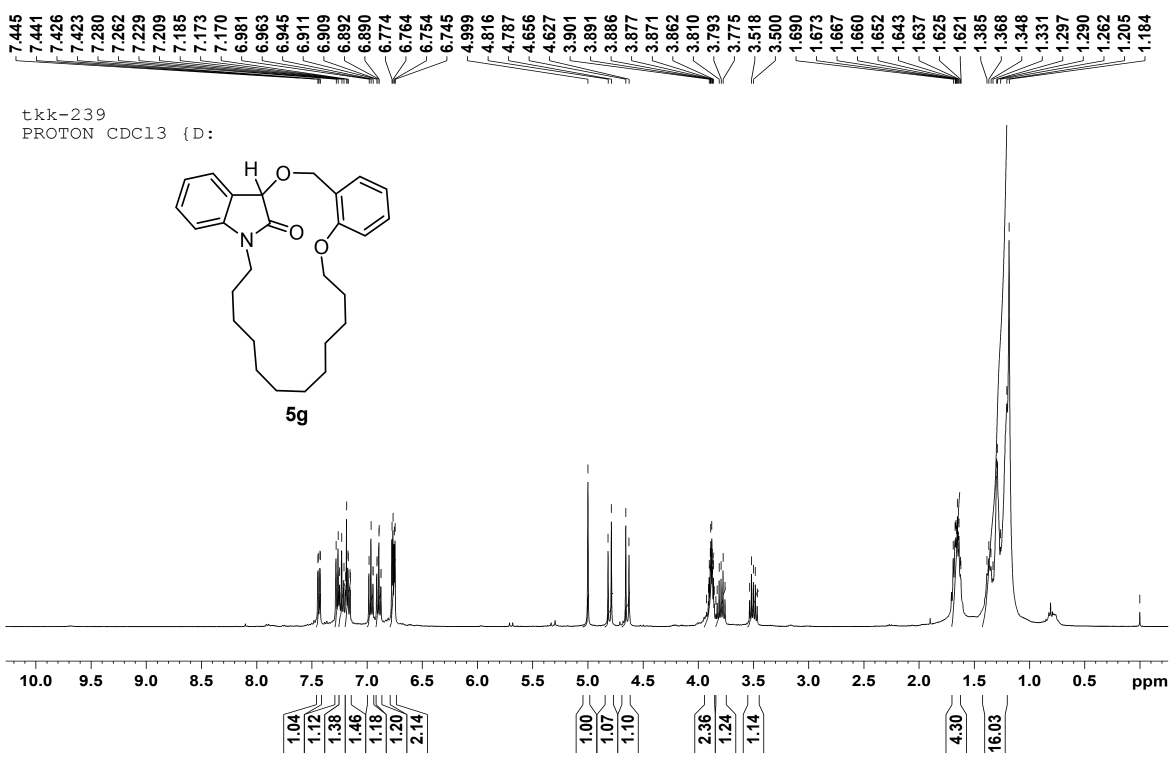


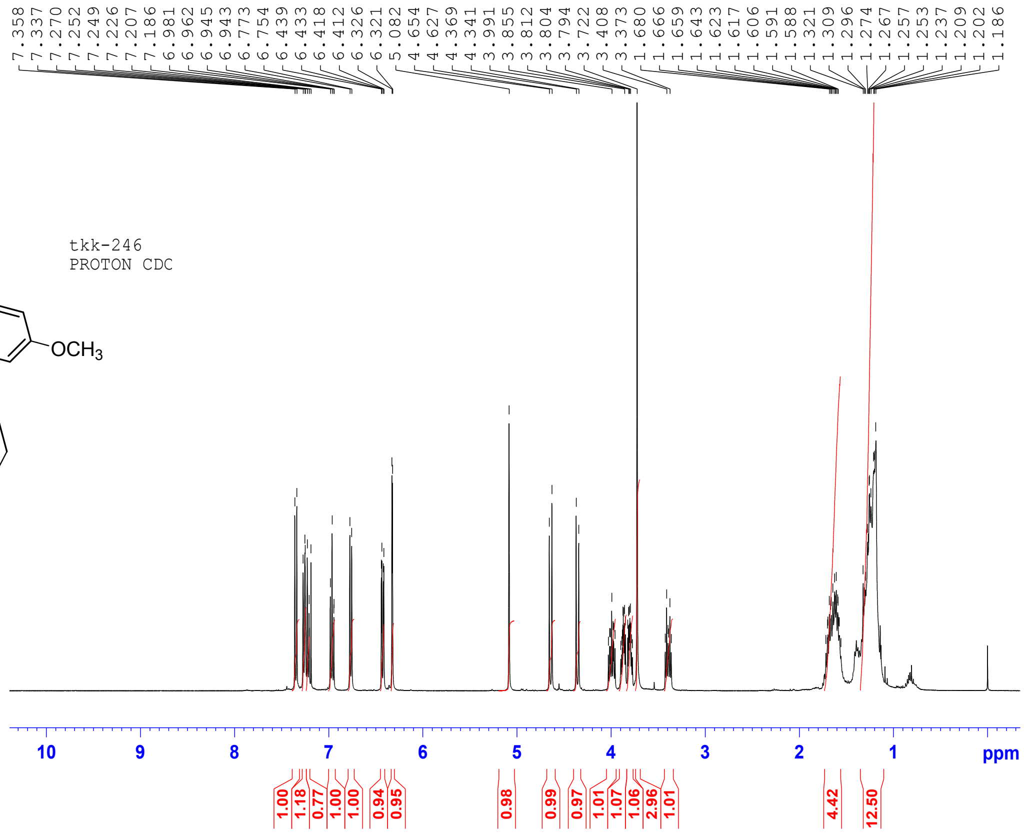
7.516
7.513
7.498
7.495
7.494
7.290
7.272
7.239
7.237
7.218
7.183
7.152
7.149
6.987
6.985
6.967
6.918
6.916
6.900
6.898
6.785
6.766
6.736
6.736
6.716
5.138
4.692
4.663
4.353
4.324
4.027
3.857
3.847
3.836
3.382
3.347
1.629
1.621
1.612
1.602
1.597
1.307
1.302
1.286
1.279
1.270
1.264
1.252
1.248
1.235
1.220
1.211
1.204
1.196
tkk-192-B
PROTON CDC
5e
ppm
1.00
2.01
0.97
0.98
1.00
0.97
1.01
0.97
1.01
1.02
1.05
2.08
1.04
4.96
12.46

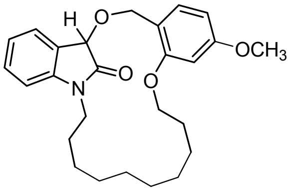


174.19
156.29
143.80
129.76
128.61
128.46
126.47
125.37
124.82
122.62
120.22
110.75
108.78
77.35
77.03
76.72
75.70
67.90
62.88
39.47
28.60
27.02
26.96
26.71
26.58
25.81
25.09
tkk-192-E
C13CPD CI
5e
ppm

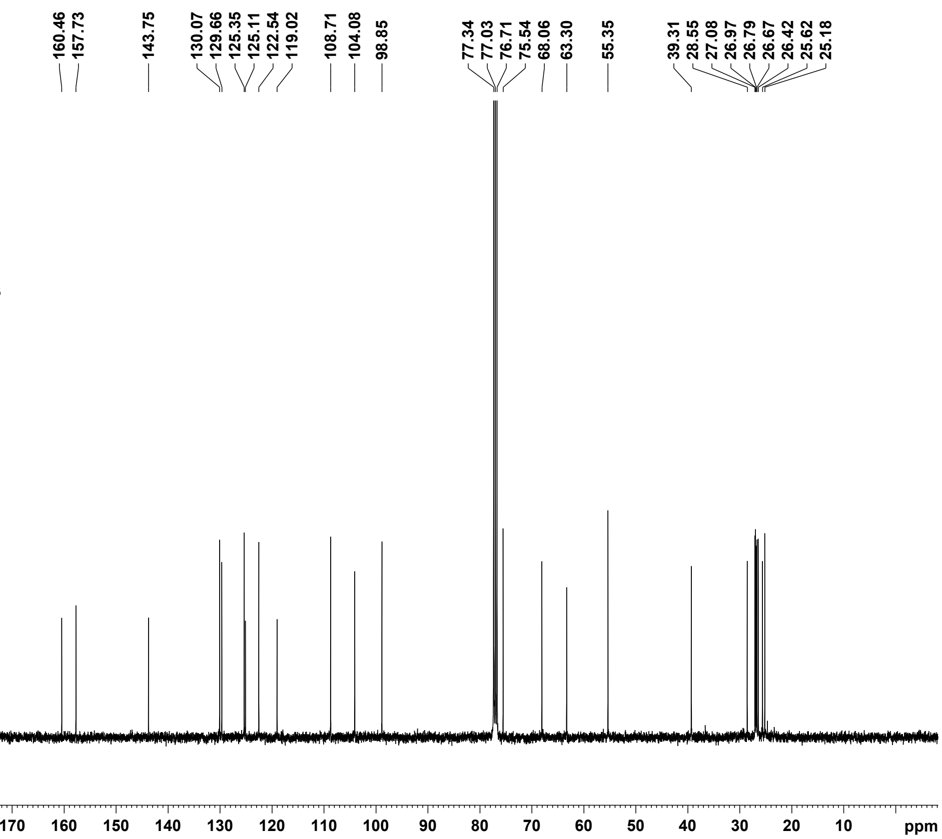

129.77
128.60
128.46
125.37
122.62
120.22
110.73
108.78
75.70
67.90
62.87
39.47
28.60
27.02
26.95
26.70
26.58
26.56
25.82
25.08
tkk-192-B
C13DEPT135 CDC
H
O
O
N
O
5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

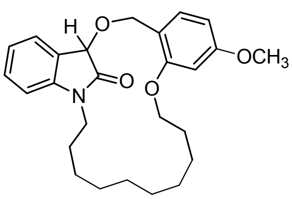

7.445
7.441
7.426
7.423
7.280
7.262
7.229
7.209
7.185
7.173
7.170
6.981
6.963
6.945
6.911
6.909
6.892
6.890
6.774
6.764
6.754
6.745
4.999
4.816
4.787
4.656
4.627
3.901
3.891
3.886
3.877
3.871
3.862
3.810
3.793
3.775
3.518
3.500
1.690
1.673
1.667
1.660
1.652
1.643
1.637
1.625
1.621
1.385
1.368
1.348
1.331
1.297
1.290
1.262
1.205
1.184
tkk-239
PROTON CDCl3 {D:
H
O
O
N
O
5g
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.04
1.12
1.38
1.46
1.18
1.20
2.14
1.00
1.07
1.10
2.36
1.24
1.14
4.30
16.03


7.358 7.337 7.270 7.252 7.249 7.226 7.207 7.186 6.981 6.962 6.945 6.943 6.773 6.754 6.439 6.433 6.418 6.412 6.326 6.321 5.082 4.654 4.627 4.369 4.341 3.991 3.855 3.812 3.804 3.794 3.722 3.408 3.373 1.680 1.666 1.659 1.643 1.623 1.617 1.606 1.591 1.588 1.321 1.309 1.296 1.274 1.267 1.257 1.253 1.237 1.209 1.202 1.186
tkk-246
PROTON CDC
10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.18 0.77 1.00 1.00 0.94 0.95 0.98 0.99 0.97 1.01 1.07 1.06 2.96 1.01 4.42 12.50

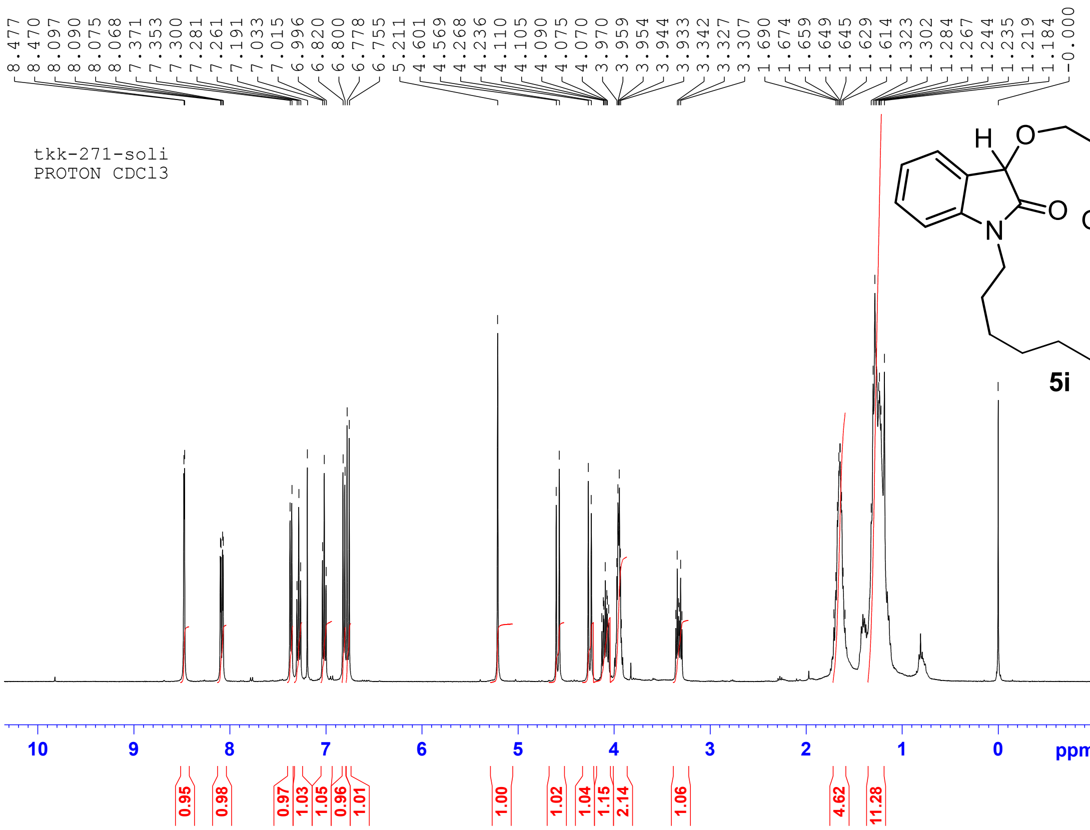

H
O
OCH3
O
N
O

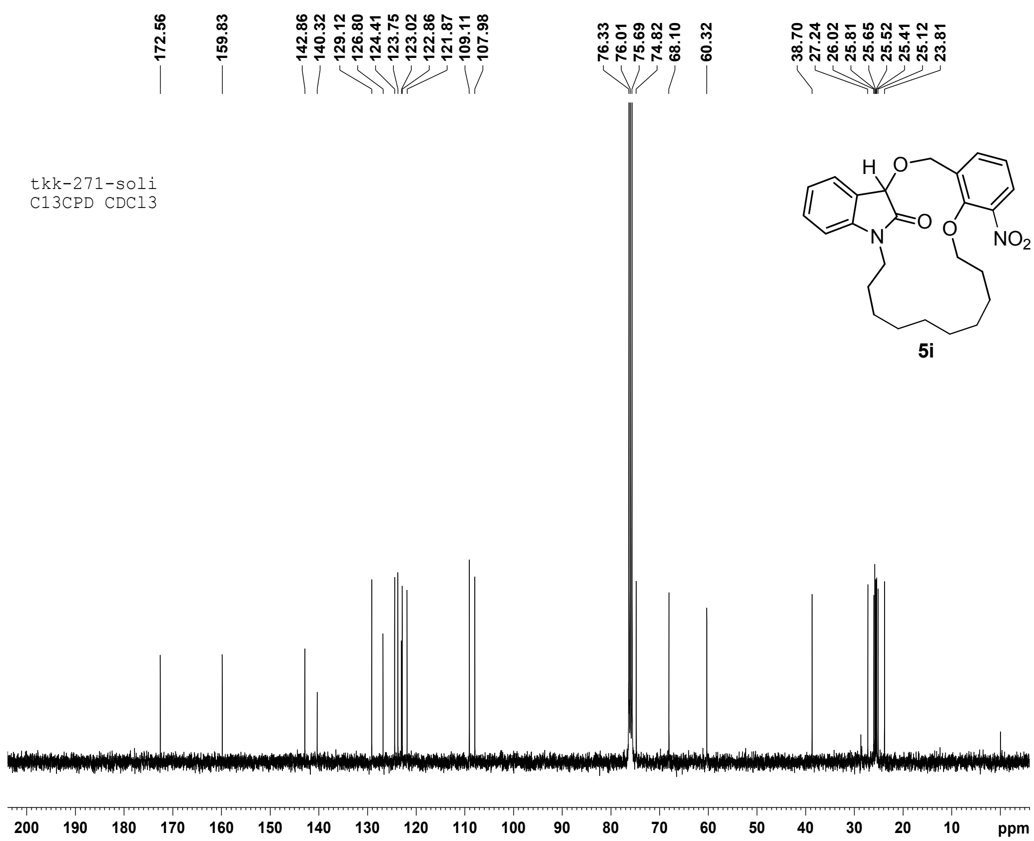
5h

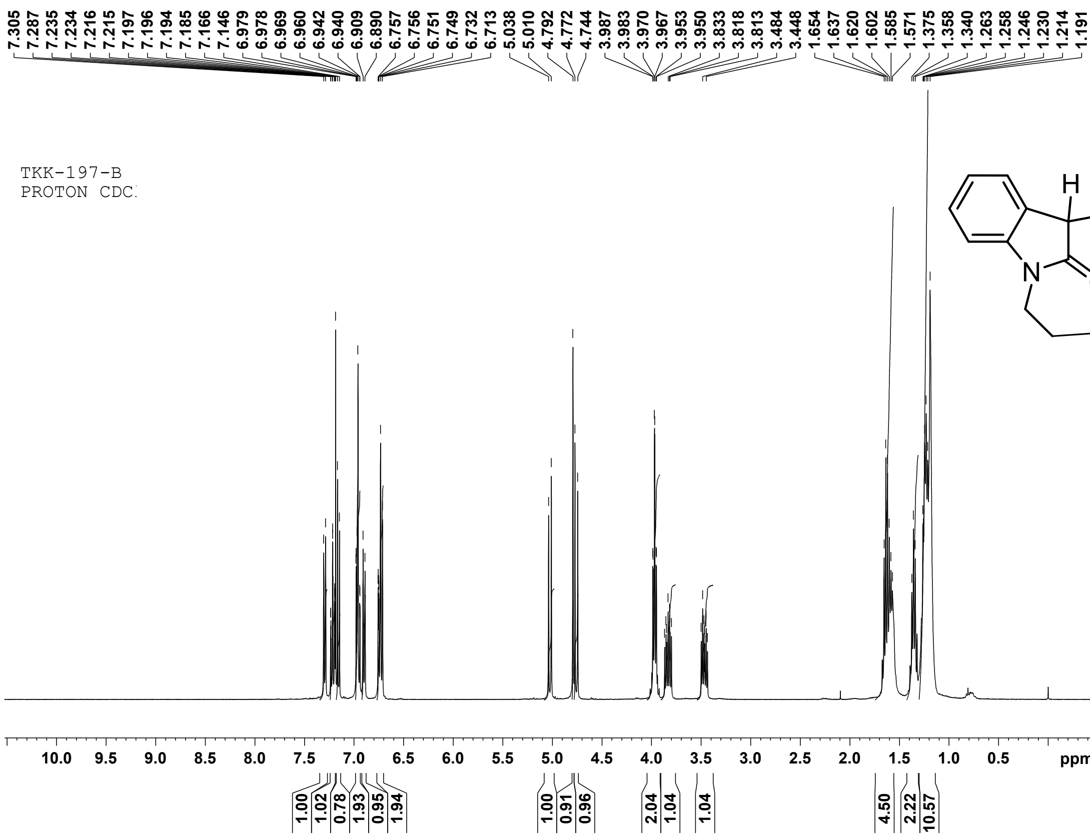

174.39 160.46 157.73 143.75 130.07 129.66 125.35 125.11 122.54 119.02 108.71 104.08 98.85 77.34 77.03 76.71 75.54 68.06 63.30 55.35 39.31 28.55 27.08 26.97 26.79 26.67 26.42 25.62 25.18
tkk-246
C13CPD CD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

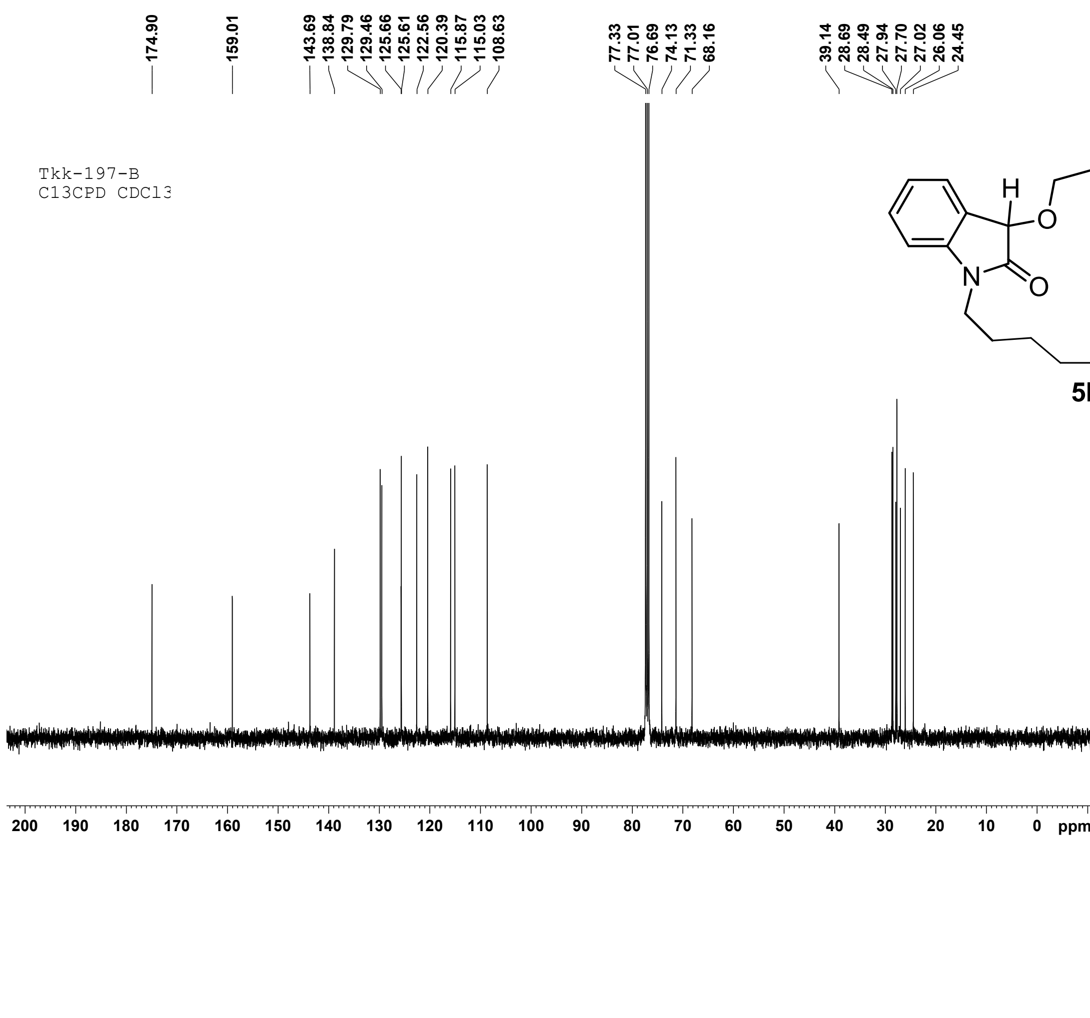

H
O
OCH3
O
N
O

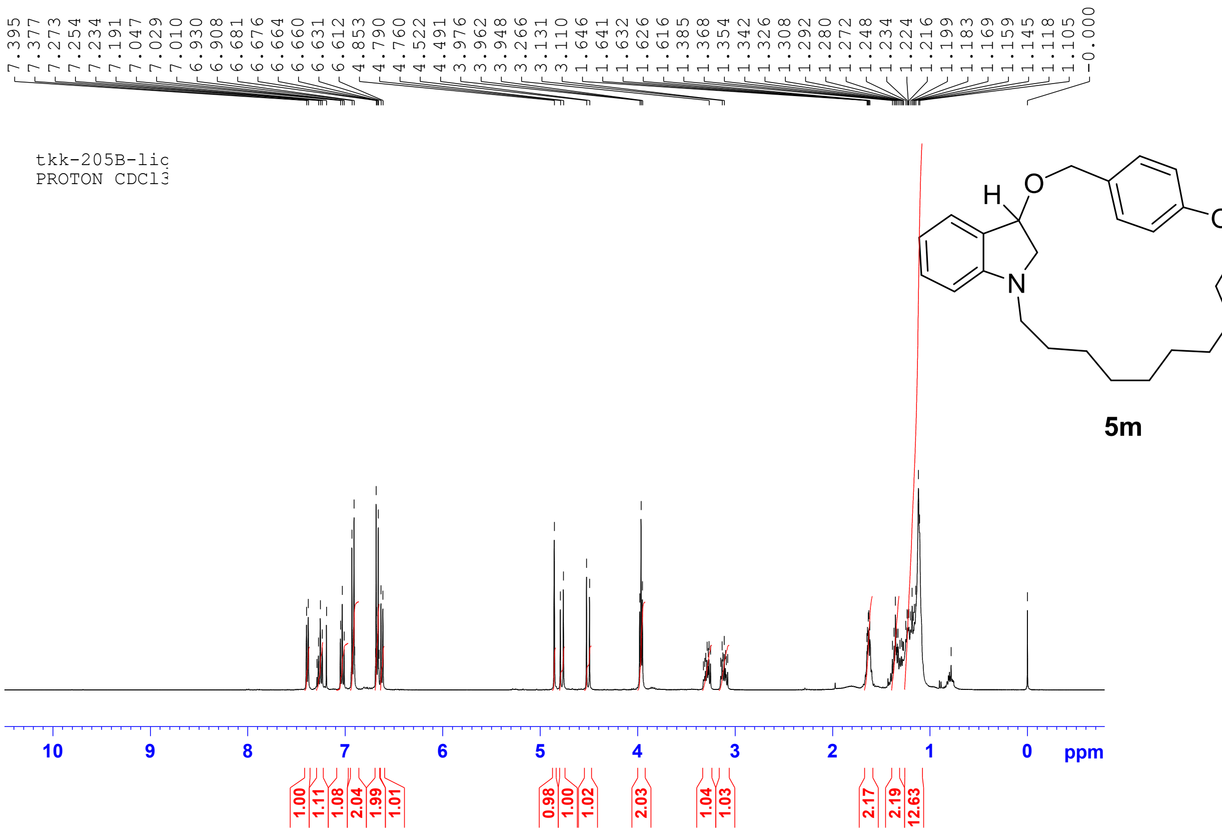
5h

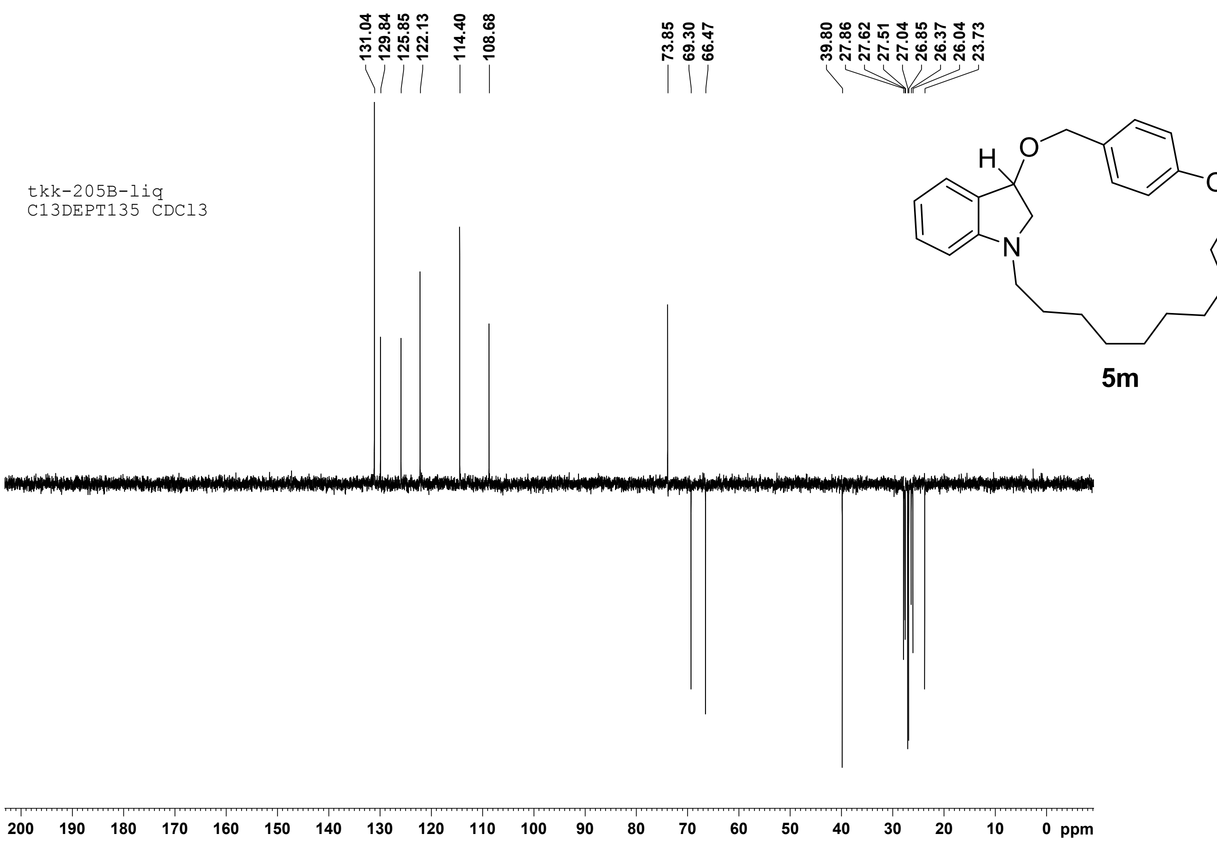

8.477 8.470 8.097 8.090 8.075 8.068 7.371 7.353 7.300 7.281 7.261 7.191 7.033 7.015 6.996 6.820 6.800 6.778 6.755 5.211 4.601 4.569 4.268 4.236 4.110 4.105 4.090 4.075 4.070 3.970 3.959 3.954 3.944 3.933 3.342 3.327 3.307 1.690 1.674 1.659 1.649 1.645 1.629 1.614 1.323 1.302 1.284 1.267 1.244 1.235 1.219 1.184 -0.000
tkk-271-soli
PROTON CDCl3
H
O
N
O
O
NO2
5i
10 9 8 7 6 5 4 3 2 1 0 ppm
0.95 0.98 0.97 1.03 1.05 0.96 1.01 1.00 1.02 1.04 1.15 2.14 1.06 4.62 11.28

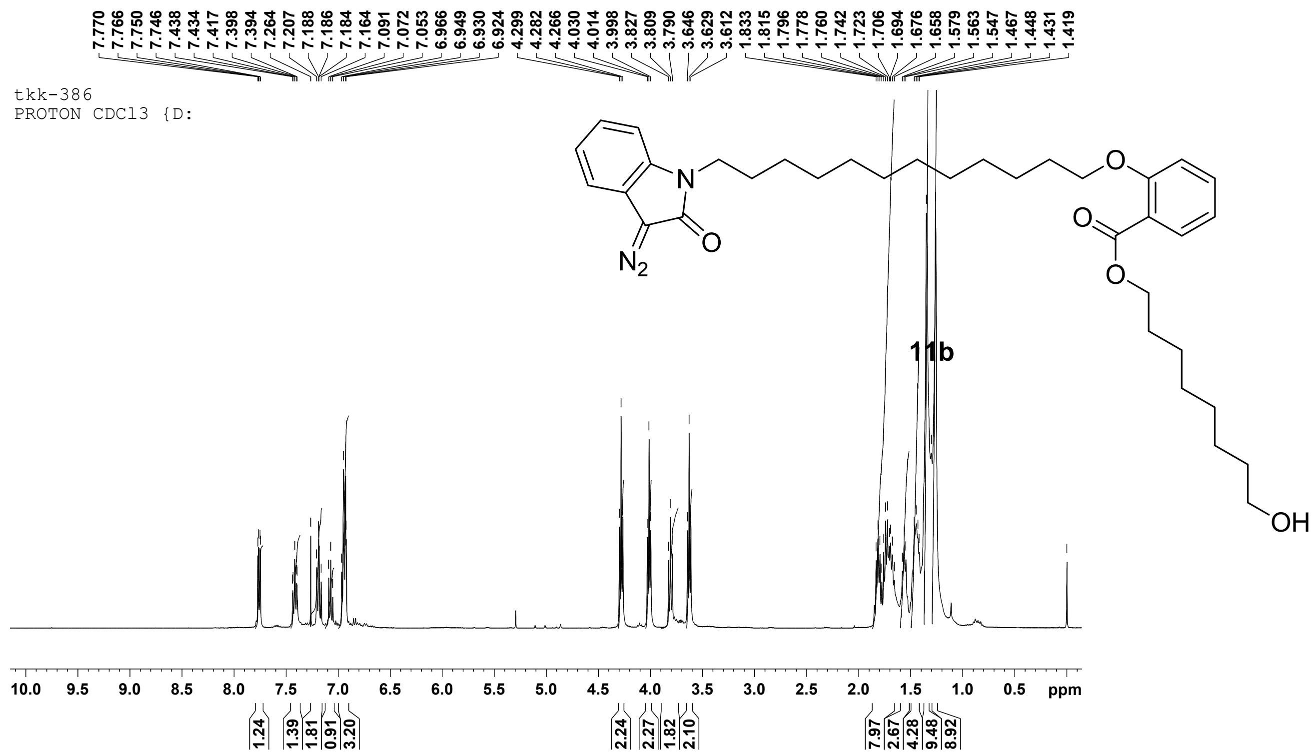

172.56 159.83 142.86 140.32 129.12 126.80 124.41 123.75 123.02 122.86 121.87 109.11 107.98 76.33 76.01 75.69 74.82 68.10 60.32 38.70 27.24 26.02 25.81 25.65 25.52 25.41 25.12 23.81
tkk-271-soli
C13CPD CDCl3
H
O
N
O
O
NO2
5i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

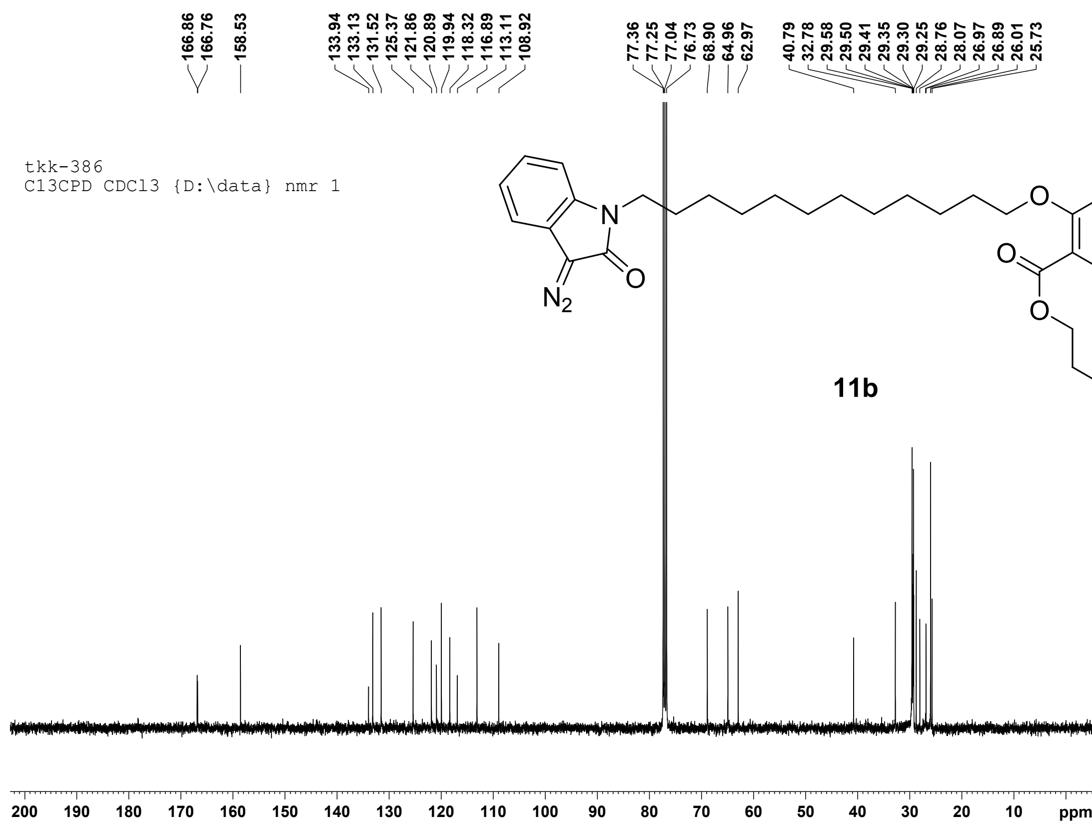

7.305 7.287 7.235 7.234 7.216 7.215 7.197 7.196 7.194 7.185 7.166 7.146 6.979 6.978 6.969 6.960 6.942 6.940 6.909 6.890 6.757 6.756 6.751 6.749 6.732 6.713 5.038 5.010 4.792 4.772 4.744 3.987 3.983 3.970 3.967 3.953 3.950 3.833 3.818 3.813 3.484 3.448 1.654 1.637 1.620 1.602 1.585 1.571 1.375 1.358 1.340 1.263 1.258 1.246 1.230 1.214 1.191
TKK-197-B
PROTON CDC
5k
ppm
1.00 1.02 0.78 1.93 0.95 1.94 1.00 0.91 0.96 2.04 1.04 1.04 4.50 2.22 10.57

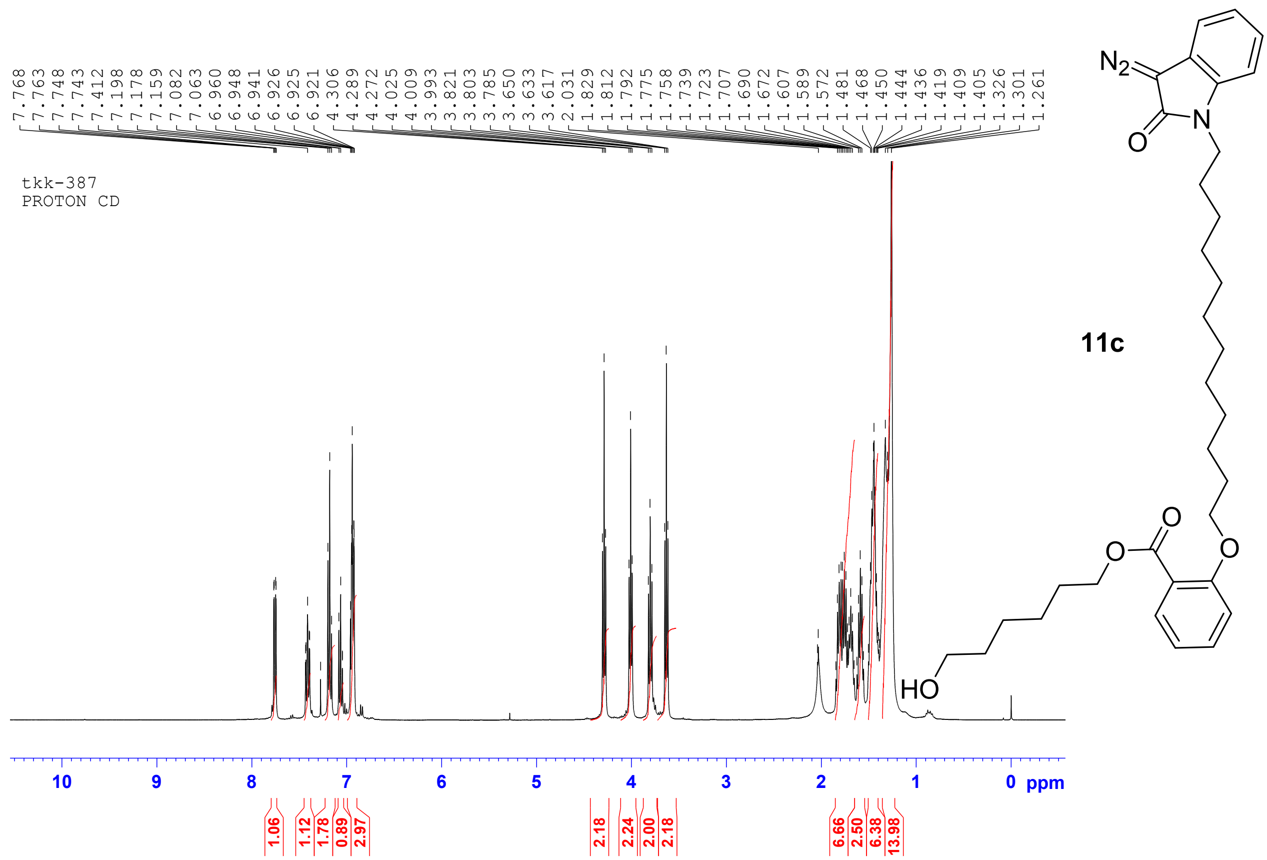

174.90 159.01 143.69 138.84 129.79 129.46 125.66 125.61 122.56 120.39 115.87 115.03 108.63 77.33 77.01 76.69 74.13 71.33 68.16 39.14 28.69 28.49 27.94 27.70 27.02 26.06 24.45
Tkk-197-B
C13CPD CDCl3
5k
ppm

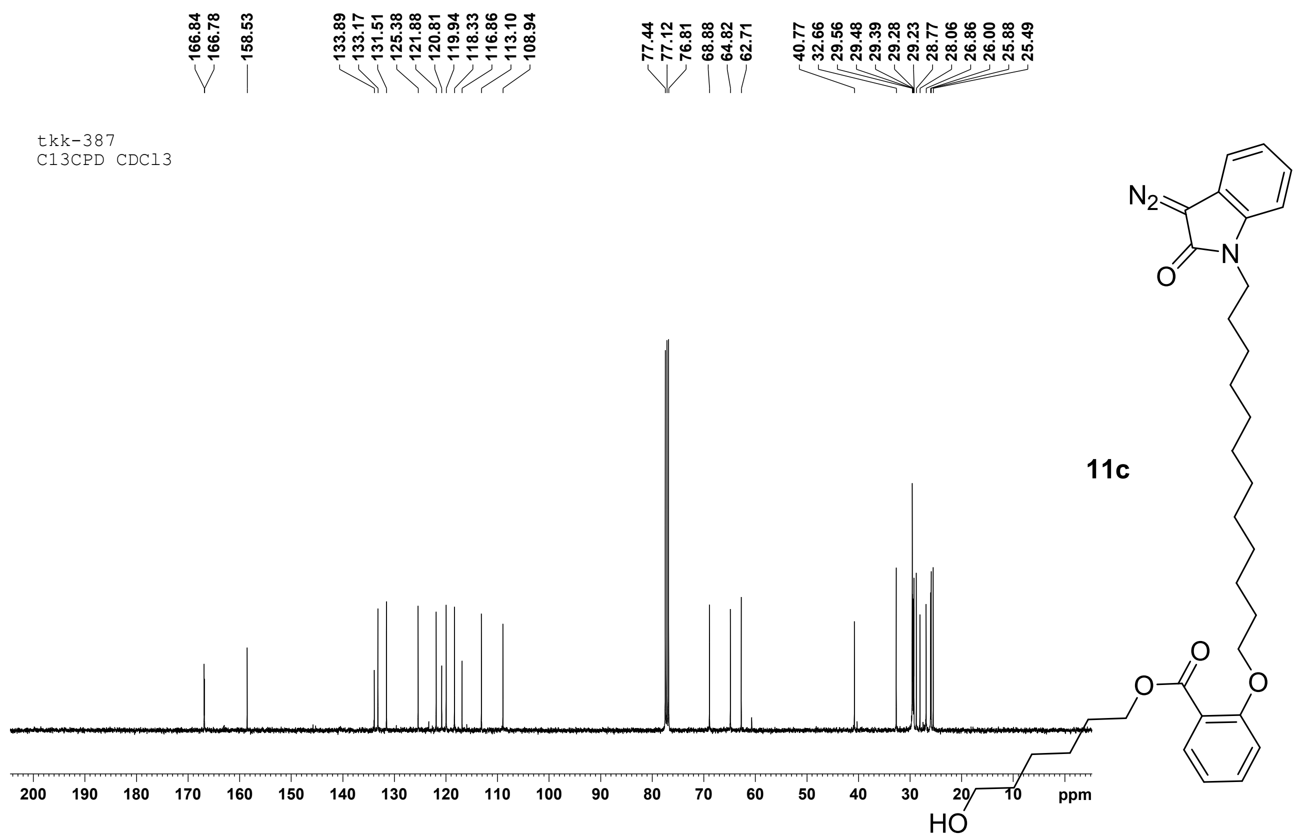

7.395 7.377 7.273 7.254 7.234 7.191 7.047 7.029 7.010 6.930 6.908 6.681 6.676 6.664 6.660 6.631 6.612 4.853 4.790 4.760 4.522 4.491 3.976 3.962 3.948 3.266 3.131 3.110 1.646 1.641 1.632 1.626 1.616 1.385 1.368 1.354 1.342 1.326 1.308 1.292 1.280 1.272 1.248 1.234 1.224 1.216 1.199 1.183 1.169 1.159 1.145 1.118 1.105 -0.000
tkk-205B-lic
PROTON CDCl3
H
O
O
N
5m
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.11 1.08 2.04 1.99 1.01 0.98 1.00 1.02 2.03 1.04 1.03 2.17 2.19 12.63

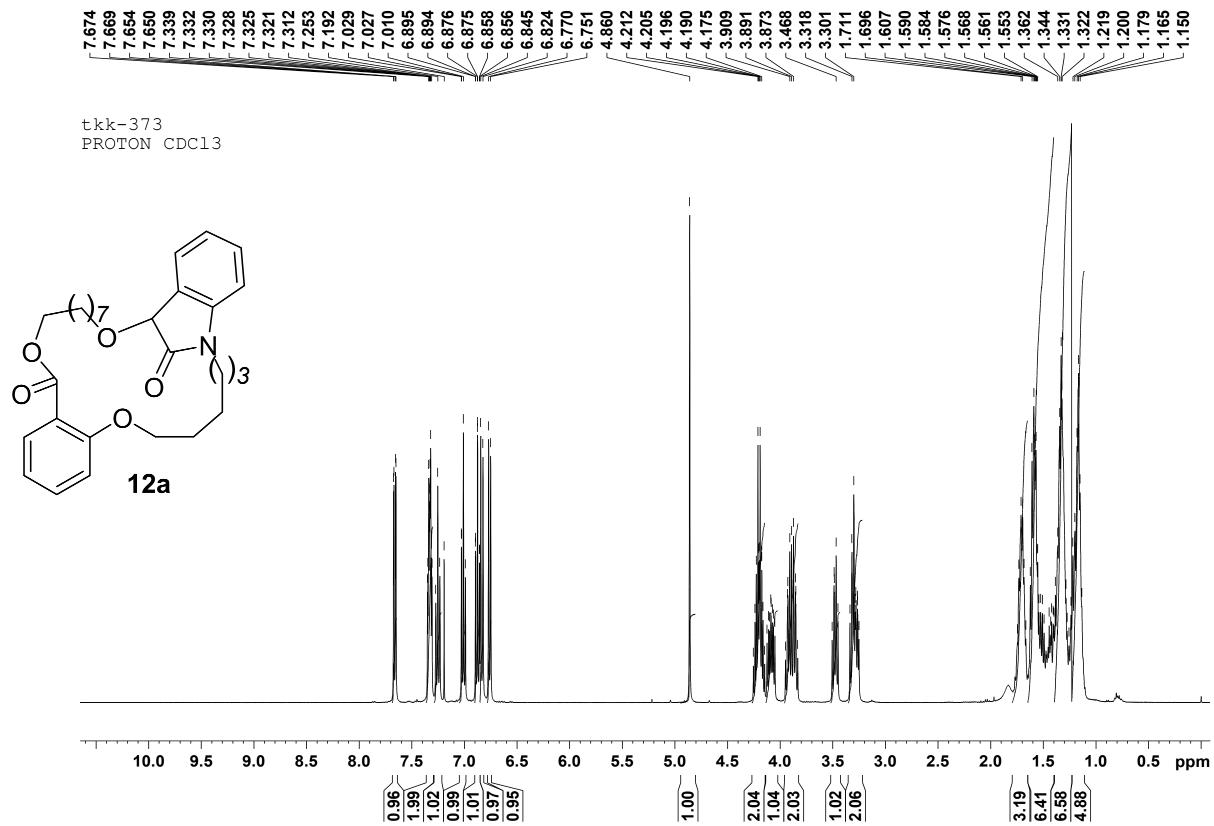

131.04 129.84 125.85 122.13 114.40 108.68 73.85 69.30 66.47 39.80 27.86 27.62 27.51 27.04 26.85 26.37 26.04 23.73
tkk-205B-liq
C13DEPT135 CDCl3
H
O
O
N
5m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

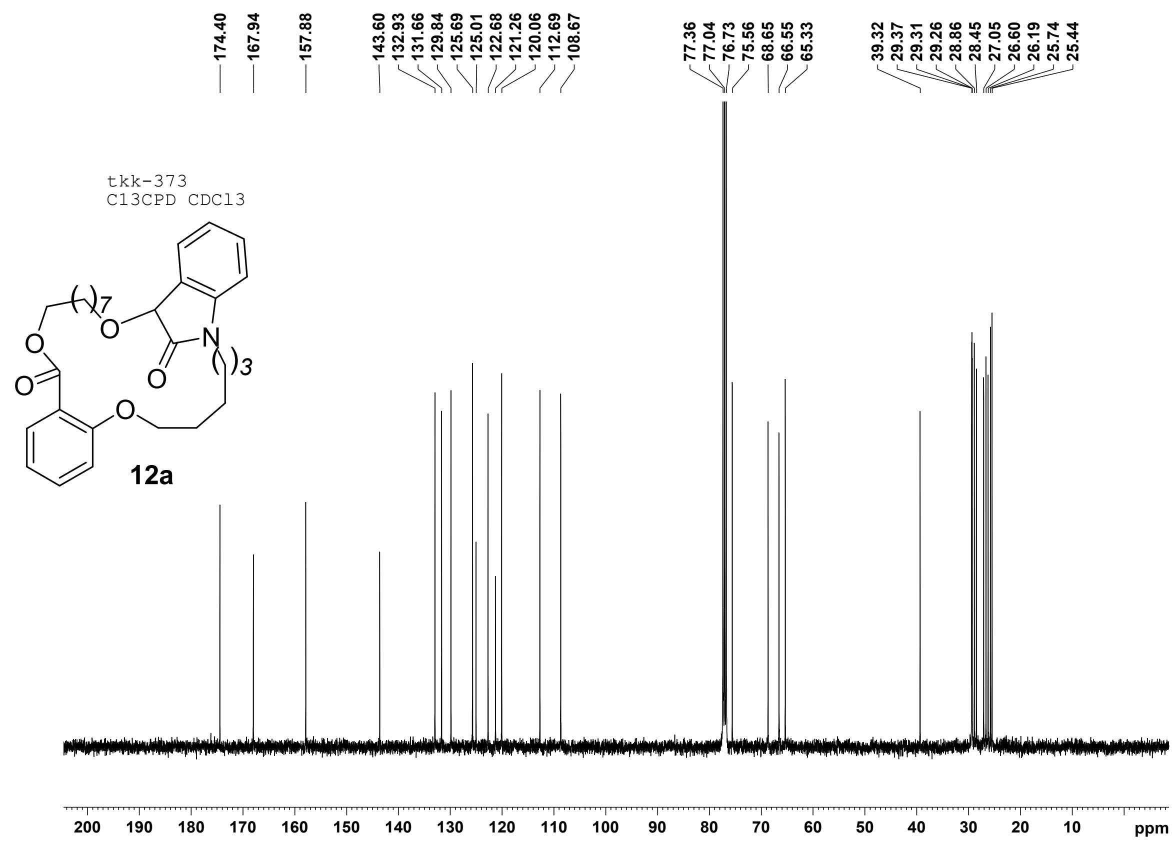

tkk-386
PROTON CDCl3 {D:
11b
OH
ppm

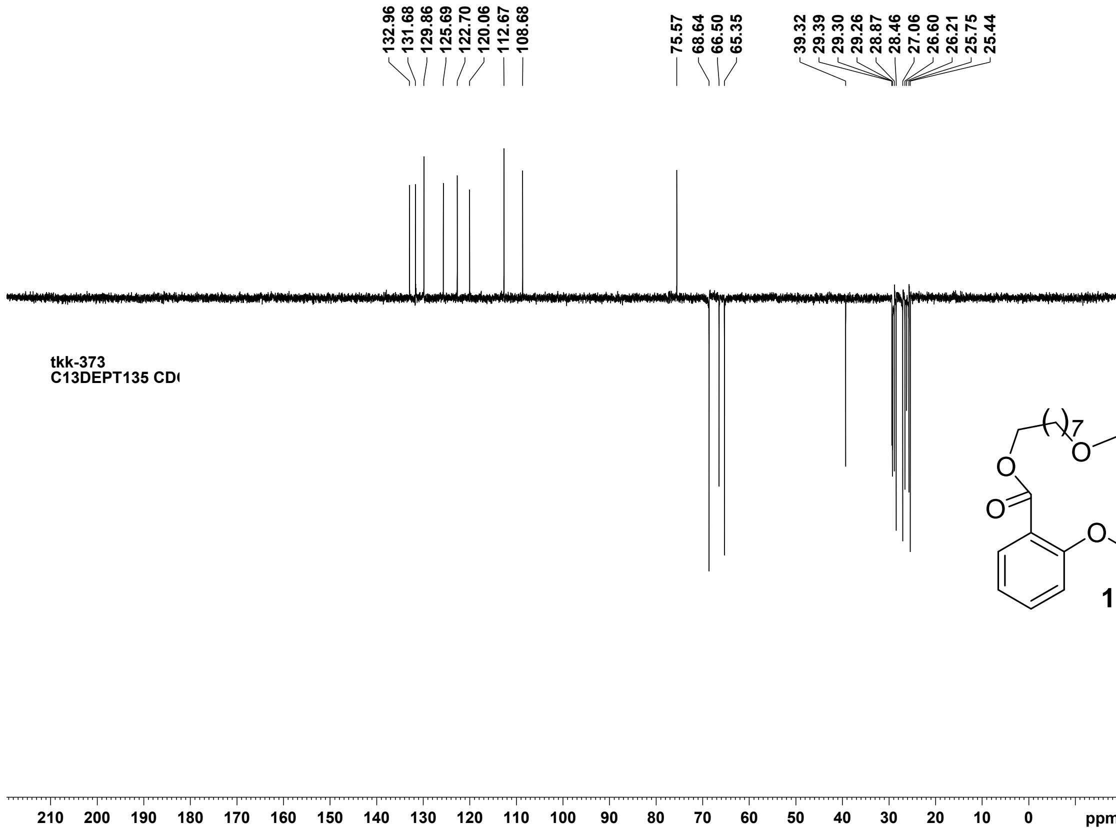

tkk-386
C13CPD CDCl3 {D:\data} nmr 1
11b
OH
ppm

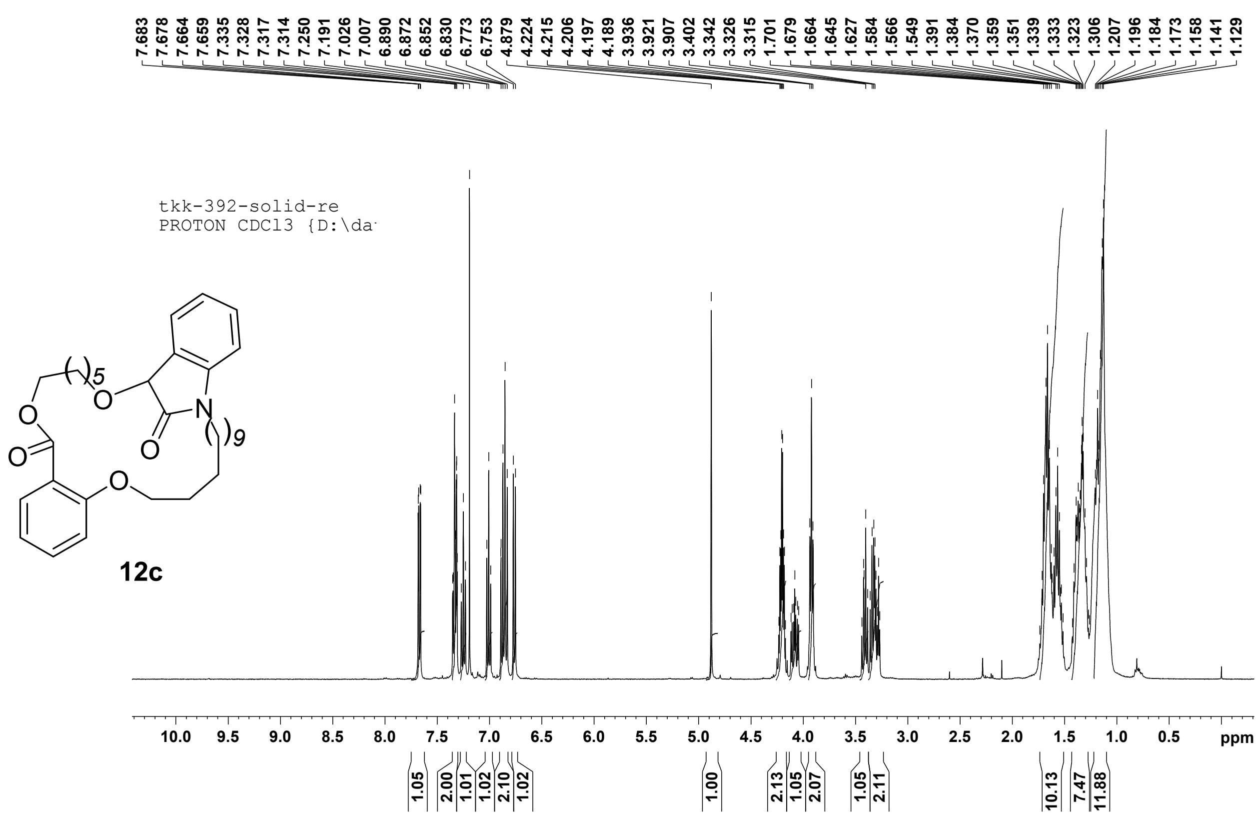

7.768
7.763
7.748
7.743
7.412
7.198
7.178
7.159
7.082
7.063
6.960
6.948
6.941
6.926
6.925
6.921
4.306
4.289
4.272
4.025
4.009
3.993
3.821
3.803
3.785
3.650
3.633
3.617
2.031
1.829
1.812
1.792
1.775
1.758
1.739
1.723
1.707
1.690
1.672
1.607
1.589
1.572
1.481
1.468
1.450
1.444
1.436
1.419
1.409
1.405
1.326
1.301
1.261
tkk-387
PROTON CD
N_2
O
N
11c
O
O
O
HO
10
9
8
7
6
5
4
3
2
1
0 ppm
1.06
1.12
1.78
0.89
2.97
2.18
2.24
2.00
2.18
6.66
2.50
6.38
13.98

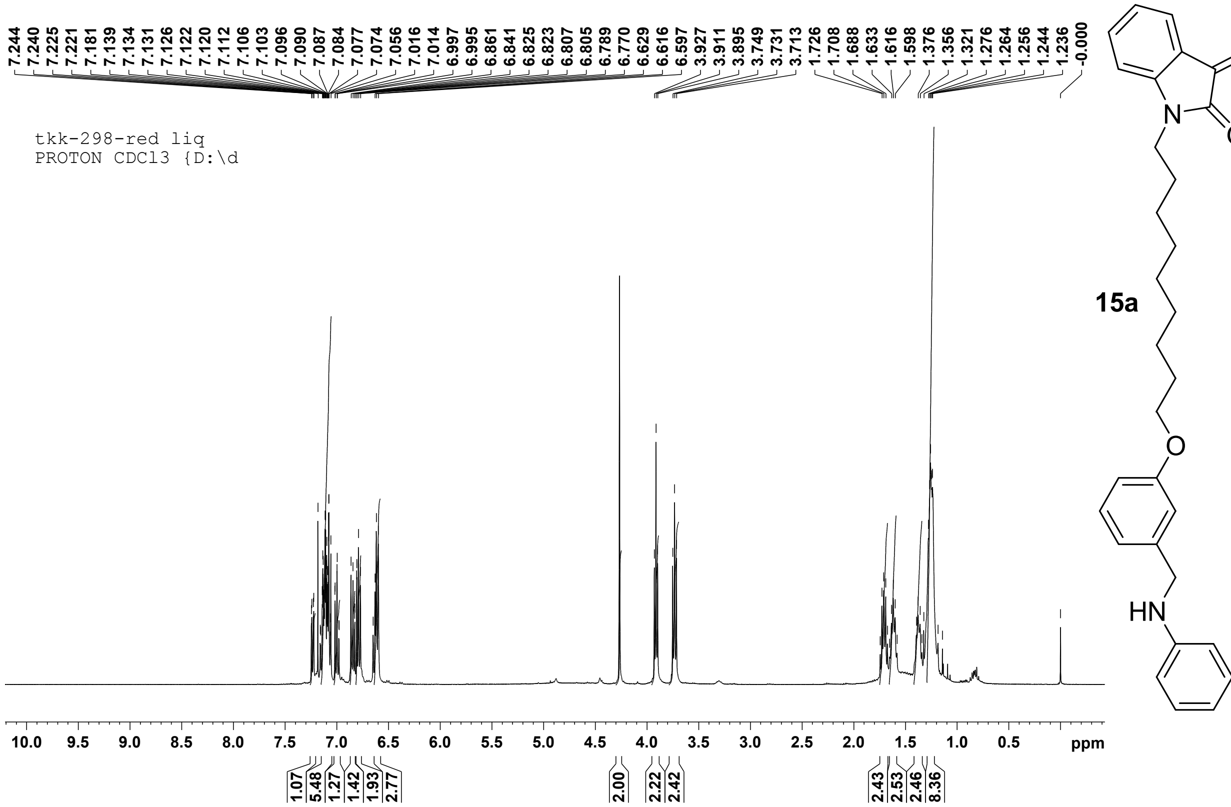

166.84
166.78
158.53
133.89
133.17
131.51
125.38
121.88
120.81
119.94
118.33
116.86
113.10
108.94
77.44
77.12
76.81
68.88
64.82
62.71
40.77
32.66
29.56
29.48
29.39
29.28
29.23
28.77
28.06
26.86
26.00
25.88
25.49
tkk-387
C13CPD CDCl3
N_2
O
N
11c
O
O
O
HO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

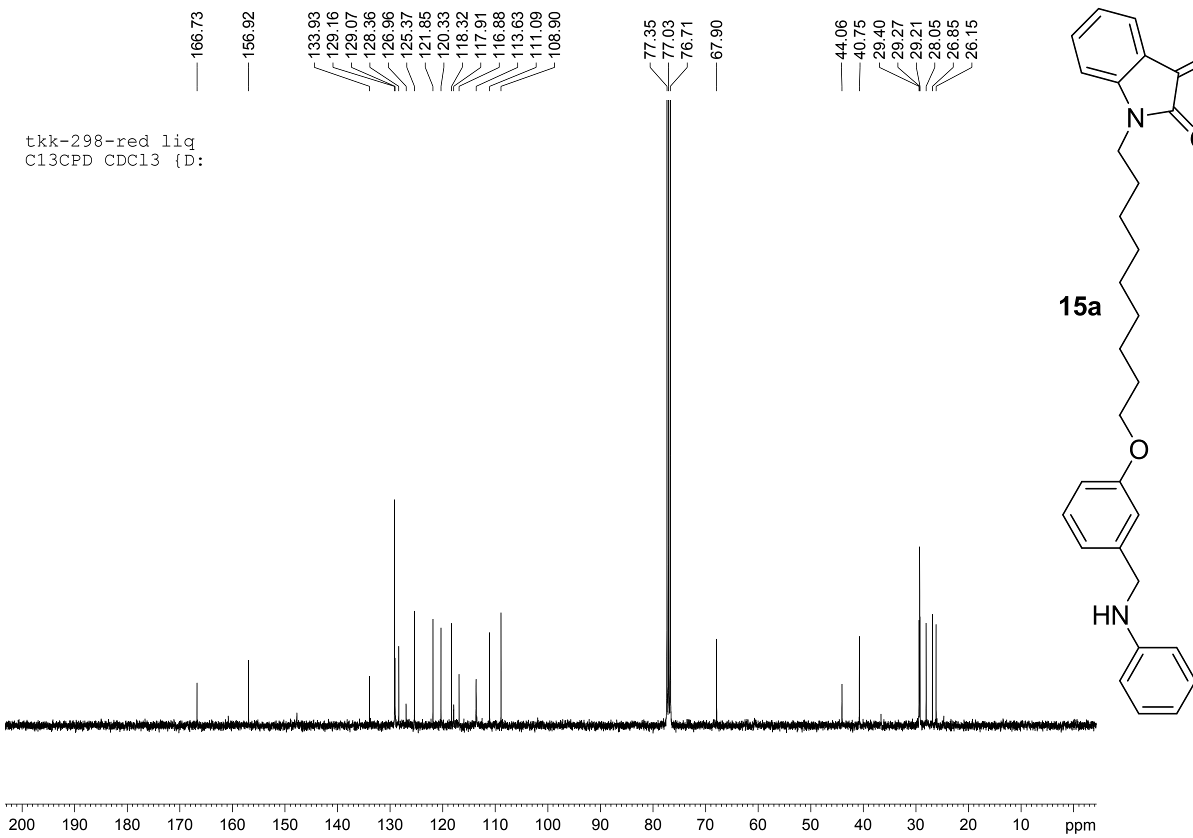

tkk-373
PROTON CDCl3
12a
ppm

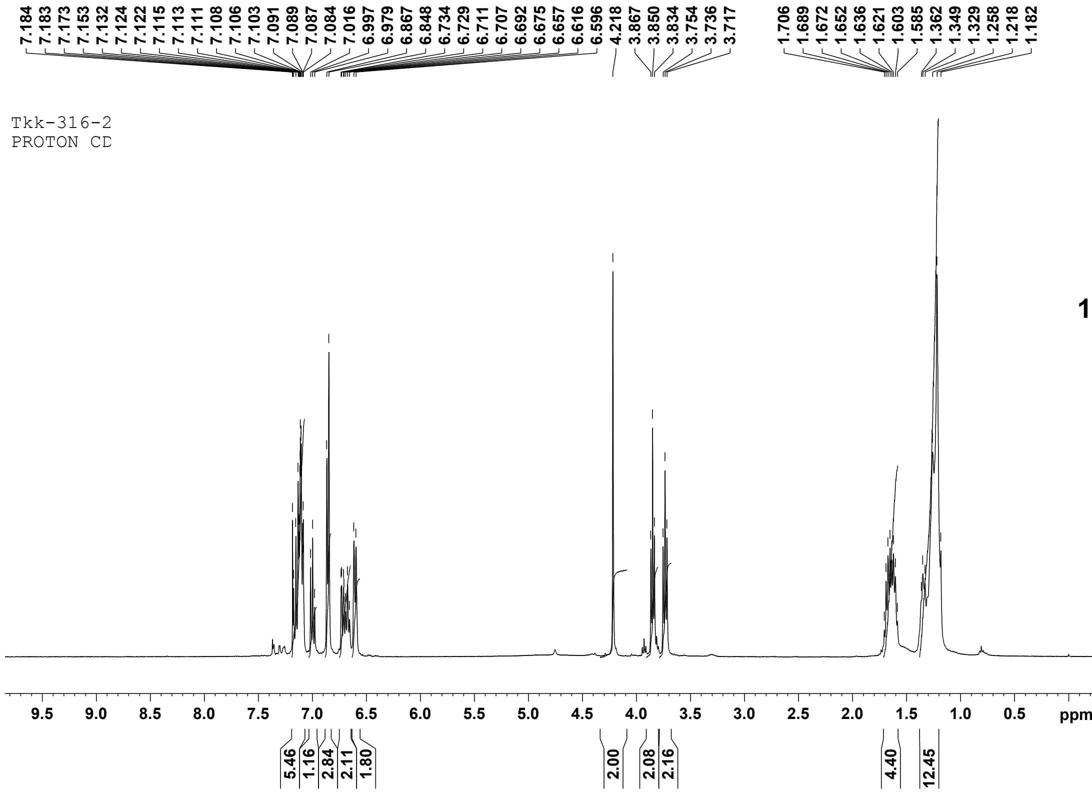

tkk-373
C13CPD CDCl3
12a
ppm

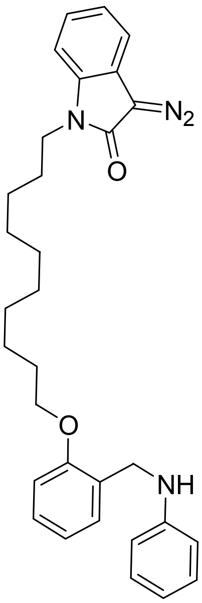

132.96
131.68
129.86
125.69
122.70
120.06
112.67
108.68
75.57
68.64
66.50
65.35
39.32
29.39
29.30
29.26
28.87
28.46
27.06
26.60
26.21
25.75
25.44
tkk-373
C13DEPT135 CD
12a
ppm


tkk-392-solid-re
PROTON CDCl3 {D:\da
12c
ppm

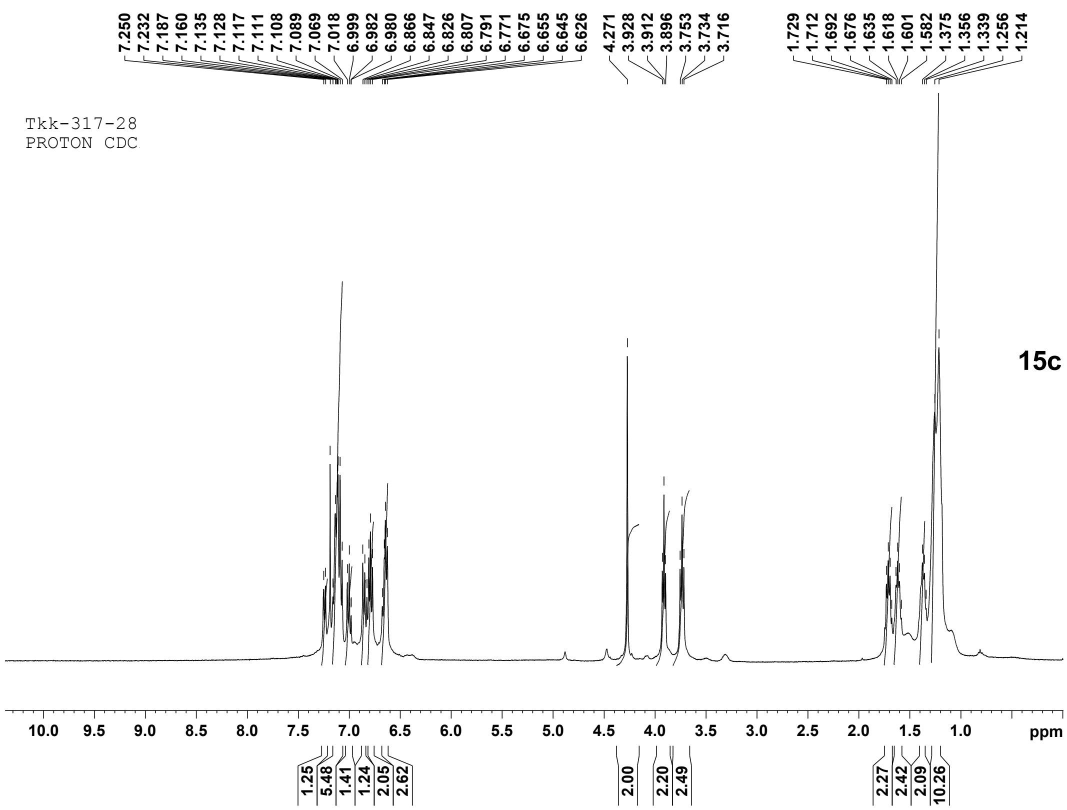

7.244 7.240 7.225 7.221 7.181 7.139 7.134 7.131 7.126 7.122 7.120 7.112 7.106 7.103 7.096 7.090 7.087 7.084 7.077 7.074 7.056 7.016 7.014 6.997 6.995 6.861 6.841 6.825 6.823 6.807 6.805 6.789 6.770 6.629 6.616 6.597 3.927 3.911 3.895 3.749 3.731 3.713 1.726 1.708 1.688 1.633 1.616 1.598 1.376 1.356 1.321 1.276 1.264 1.256 1.244 1.236 -0.000
tkk-298-red liq
PROTON CDCl3 {D:\d
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.07 5.48 1.27 1.42 1.93 2.77 2.00 2.22 2.42 2.43 2.53 2.46 8.36
N2
N
O
O
HN
15a

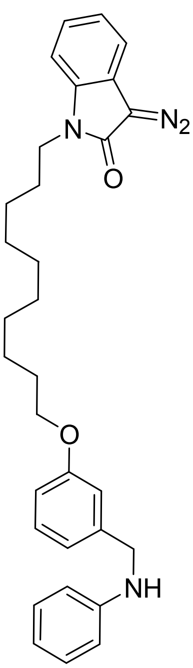

166.73 156.92 133.93 129.16 129.07 128.36 126.96 125.37 121.85 120.33 118.32 117.91 116.88 113.63 111.09 108.90 77.35 77.03 76.71 67.90 44.06 40.75 29.40 29.27 29.21 28.05 26.85 26.15
tkk-298-red liq
C13CPD CDCl3 {D:
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
N2
N
O
O
HN
15a


7.184
7.183
7.173
7.153
7.132
7.124
7.122
7.115
7.113
7.111
7.108
7.106
7.103
7.091
7.089
7.087
7.084
7.016
6.997
6.979
6.867
6.848
6.734
6.729
6.711
6.707
6.692
6.675
6.657
6.616
6.596
4.218
3.867
3.850
3.834
3.754
3.736
3.717
1.706
1.689
1.672
1.652
1.636
1.621
1.603
1.585
1.362
1.349
1.329
1.258
1.218
1.182
Tkk-316-2
PROTON CD
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.46
1.16
2.84
2.11
1.80
2.00
2.08
2.16
4.40
12.45

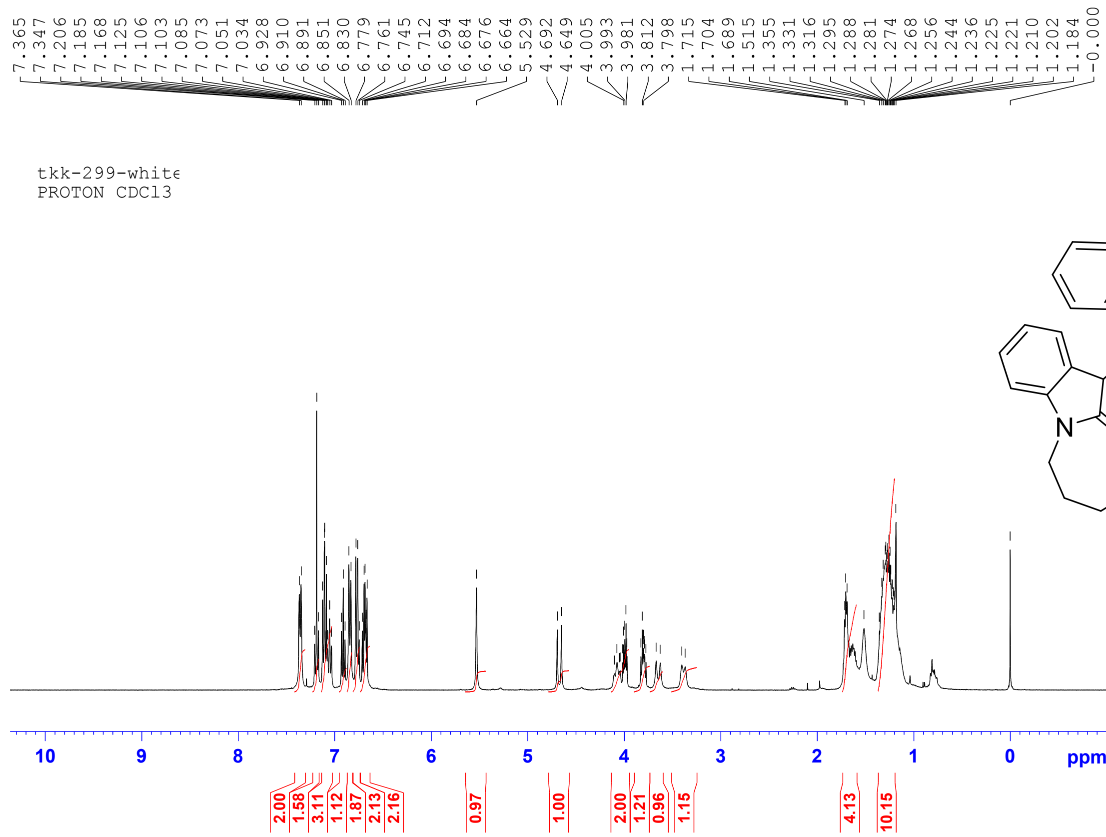

N
N2
O
O
NH

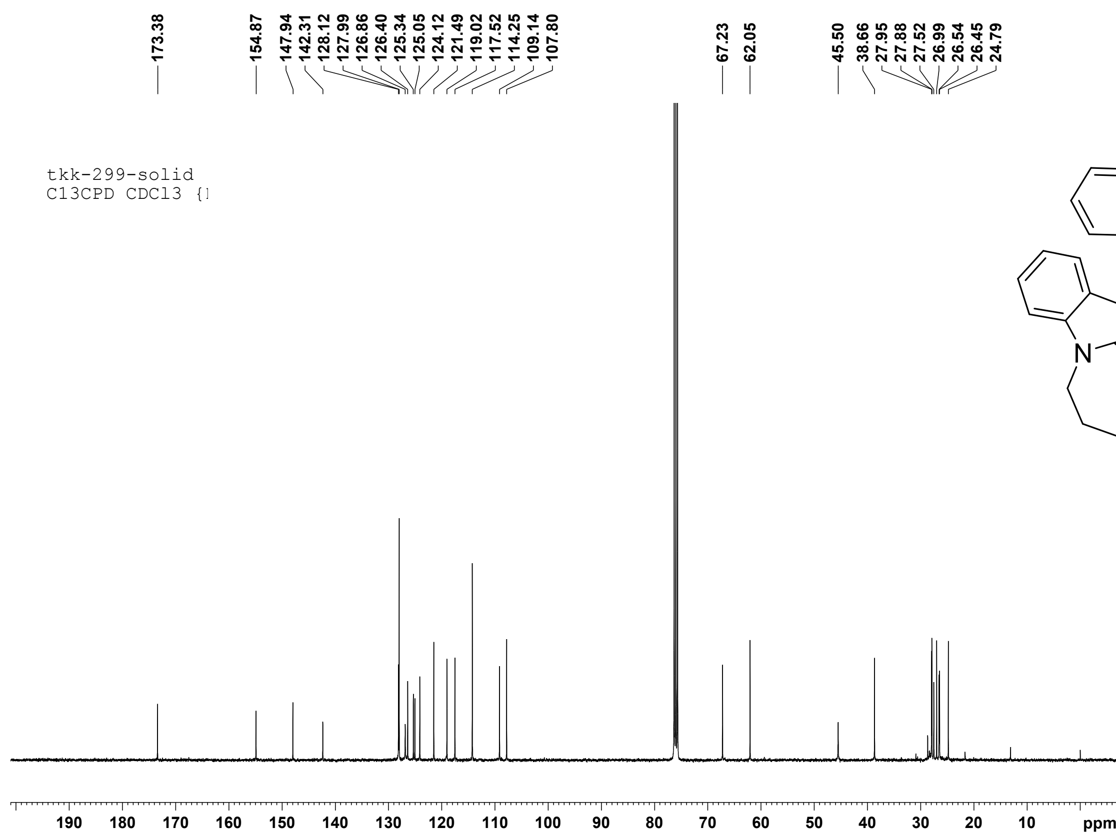
15b

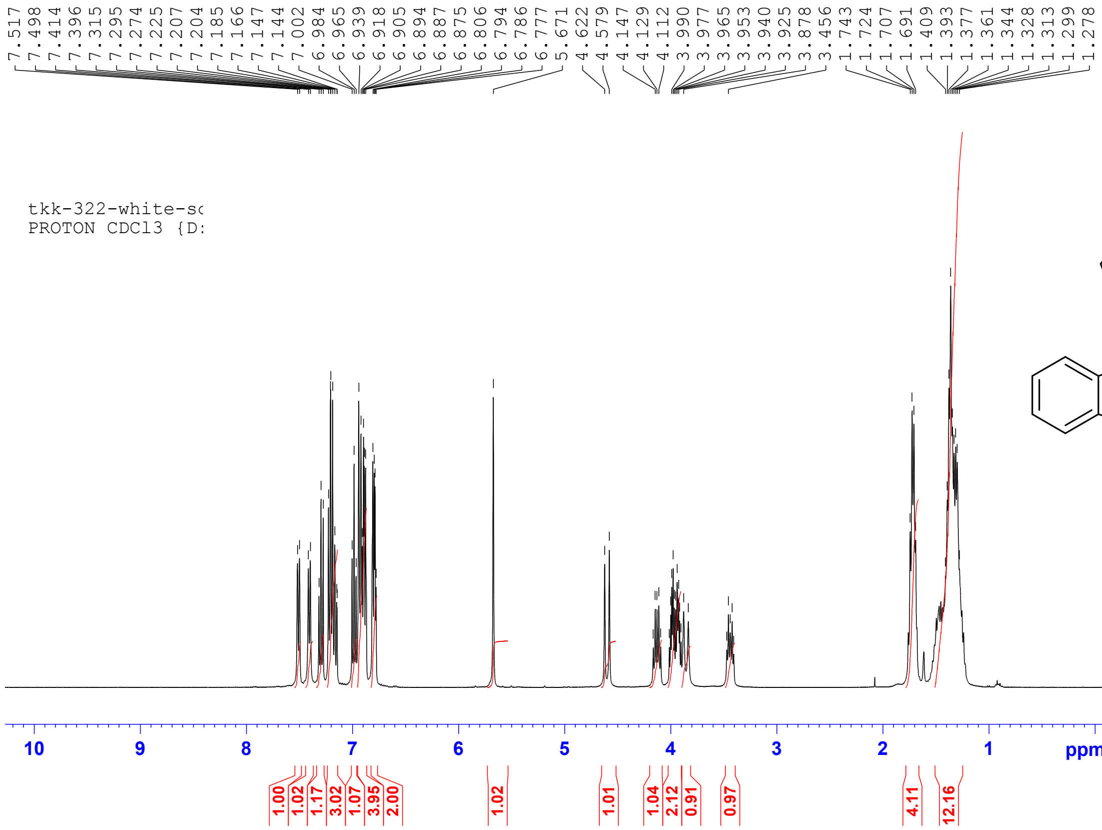

7.250
7.232
7.187
7.160
7.135
7.128
7.117
7.111
7.108
7.089
7.069
7.018
6.999
6.982
6.980
6.866
6.847
6.826
6.807
6.791
6.771
6.675
6.655
6.645
6.626
4.271
3.928
3.912
3.896
3.753
3.734
3.716
1.729
1.712
1.692
1.676
1.635
1.618
1.601
1.582
1.375
1.356
1.339
1.256
1.214
Tkk-317-28
PROTON CDC
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.25
5.48
1.41
1.24
2.05
2.62
2.00
2.20
2.49
2.27
2.42
2.09
10.26

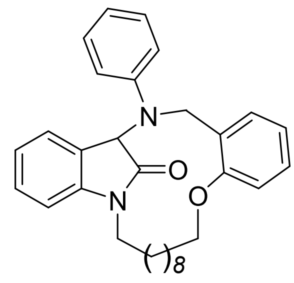

N
N2
O
O
NH

15c

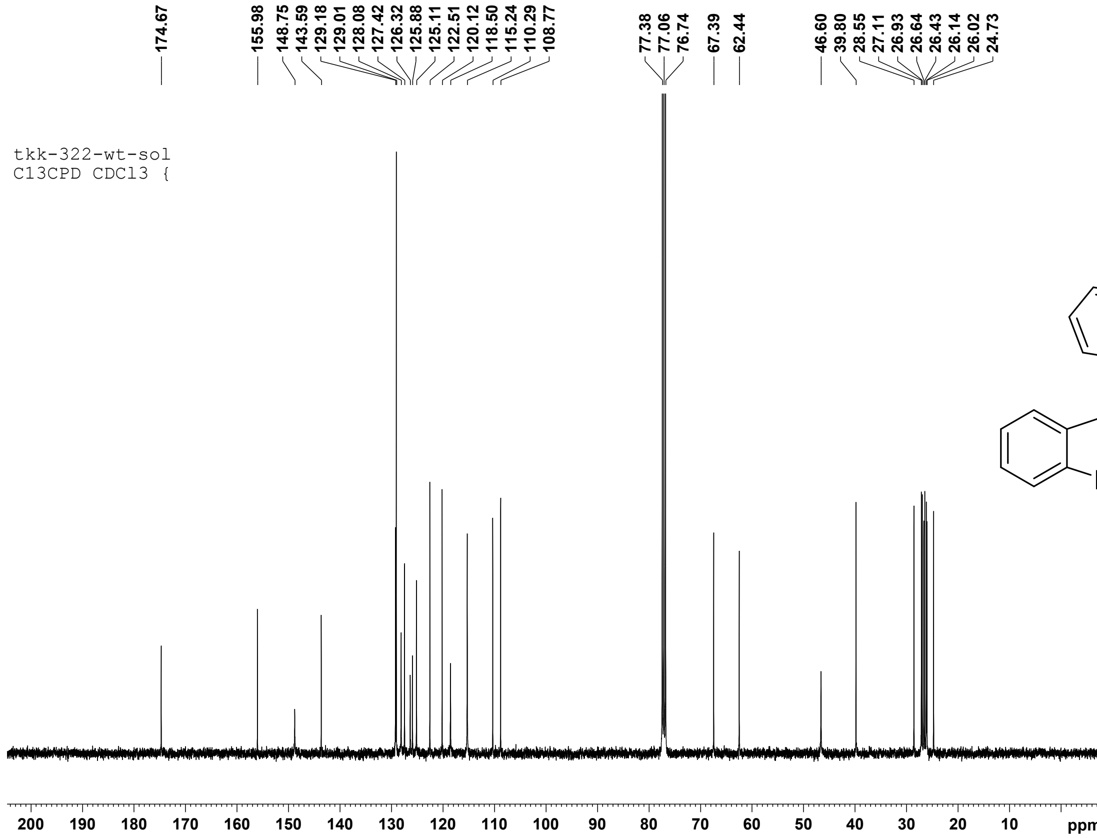

7.365 7.347 7.206 7.185 7.168 7.125 7.106 7.103 7.085 7.073 7.051 7.034 6.928 6.910 6.891 6.851 6.830 6.779 6.761 6.745 6.712 6.694 6.684 6.676 6.664 5.529 4.692 4.649 4.005 3.993 3.981 3.812 3.798 1.715 1.704 1.689 1.515 1.355 1.331 1.316 1.295 1.288 1.281 1.274 1.268 1.256 1.244 1.236 1.225 1.221 1.210 1.202 1.184 -0.000
tkk-299-white
PROTON CDCl3
N
O
N
O
16a
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00 1.58 3.11 1.12 1.87 2.13 2.16 0.97 1.00 2.00 1.21 0.96 1.15 4.13 10.15

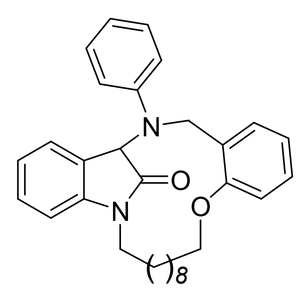

173.38 154.87 147.94 142.31 128.12 127.99 126.86 126.40 125.34 125.05 124.12 121.49 119.02 117.52 114.25 109.14 107.80 67.23 62.05 45.50 38.66 27.95 27.88 27.52 26.99 26.54 26.45 24.79
tkk-299-solid
C13CPD CDCl3
N
O
N
O
16a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.517 7.498 7.414 7.396 7.315 7.295 7.274 7.225 7.207 7.204 7.185 7.166 7.147 7.144 7.002 6.984 6.965 6.939 6.918 6.905 6.894 6.887 6.875 6.806 6.794 6.786 6.777 5.671 4.622 4.579 4.147 4.129 4.112 3.990 3.977 3.965 3.953 3.940 3.925 3.878 3.456 1.743 1.724 1.707 1.691 1.409 1.393 1.377 1.361 1.344 1.328 1.313 1.299 1.278
tkk-322-white-sc
PROTON CDCl3 {D:
10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.02 1.17 3.02 1.07 3.95 2.00 1.02 1.01 1.04 2.12 0.91 0.97 4.11 12.16

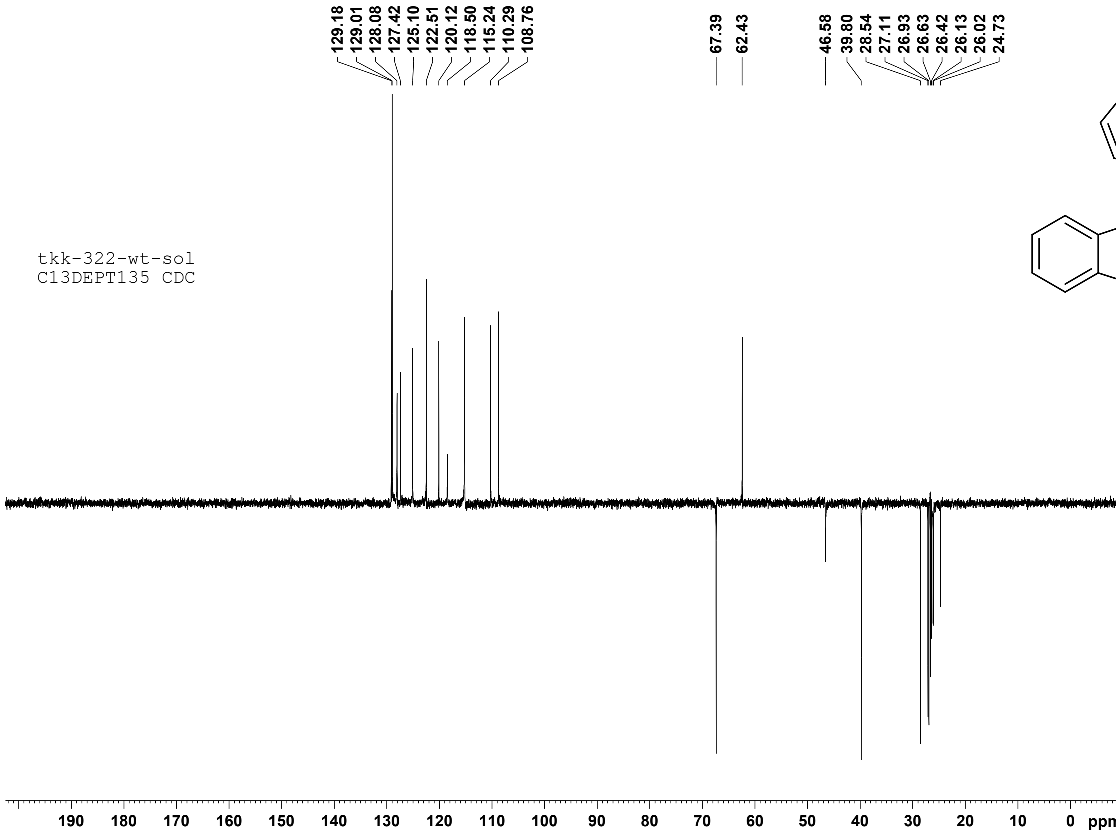

N
O
N
O
8

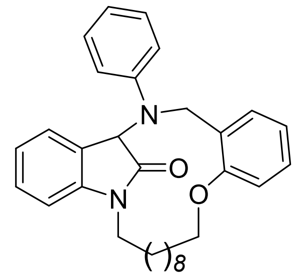
16b


174.67 155.98 148.75 143.59 129.18 129.01 128.08 127.42 126.32 125.88 125.11 122.51 120.12 118.50 115.24 110.29 108.77 77.38 77.06 76.74 67.39 62.44 46.60 39.80 28.55 27.11 26.93 26.64 26.43 26.14 26.02 24.73
tkk-322-wt-sol
C13CPD CDCl3 {
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

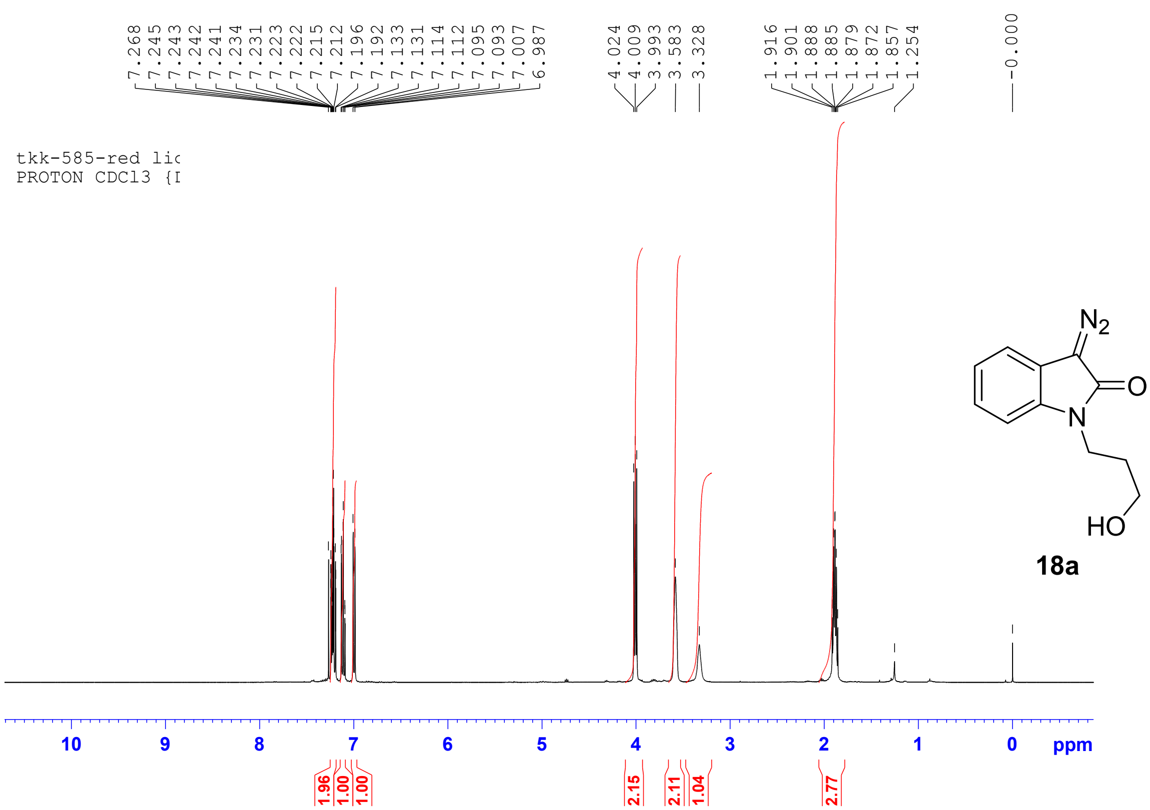

N
O
N
O
8

16b

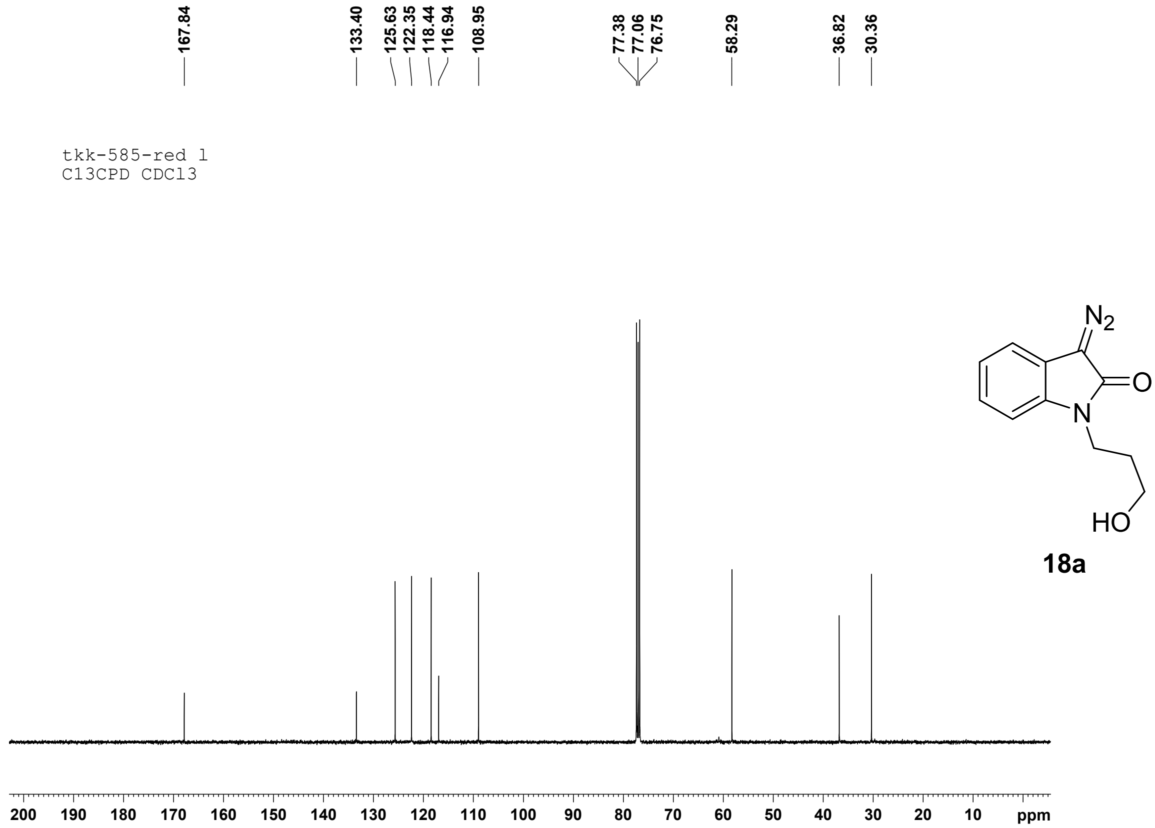

129.18
129.01
128.08
127.42
125.10
122.51
120.12
118.50
115.24
110.29
108.76
67.39
62.43
46.58
39.80
28.54
27.11
26.93
26.63
26.42
26.13
26.02
24.73
tkk-322-wt-sol
C13DEPT135 CDC
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

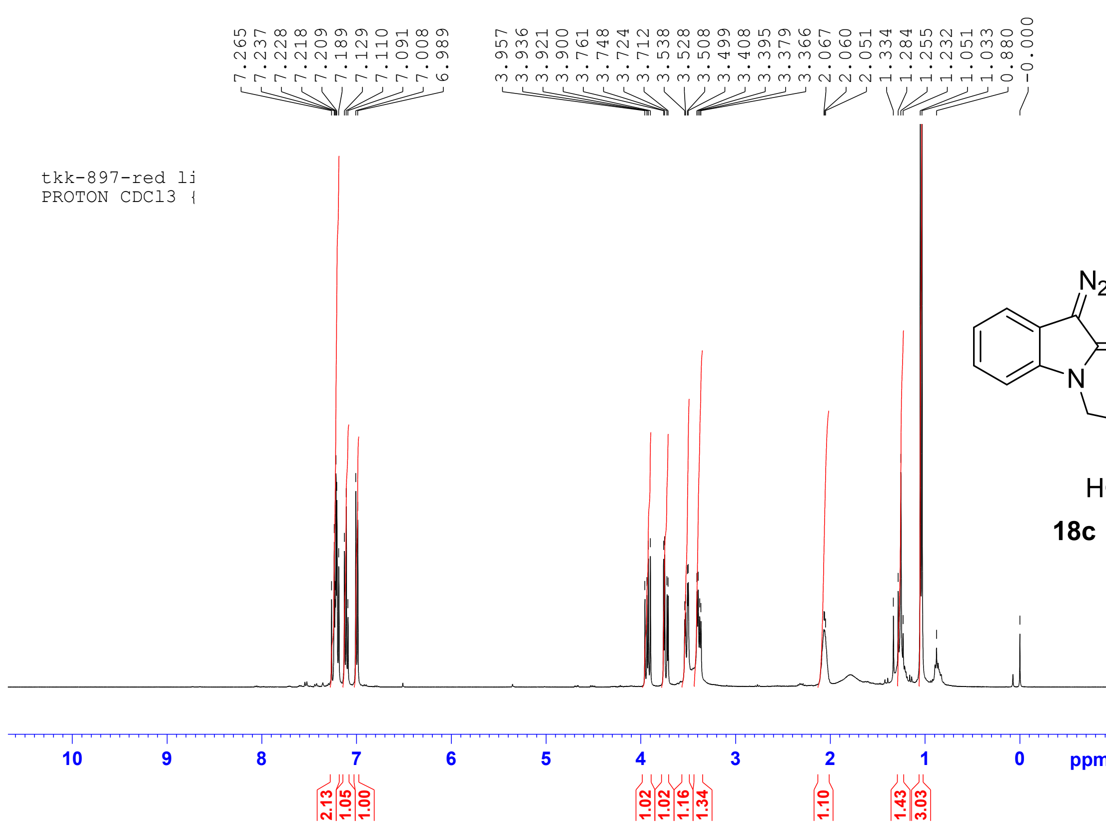

N
O
N
O
8

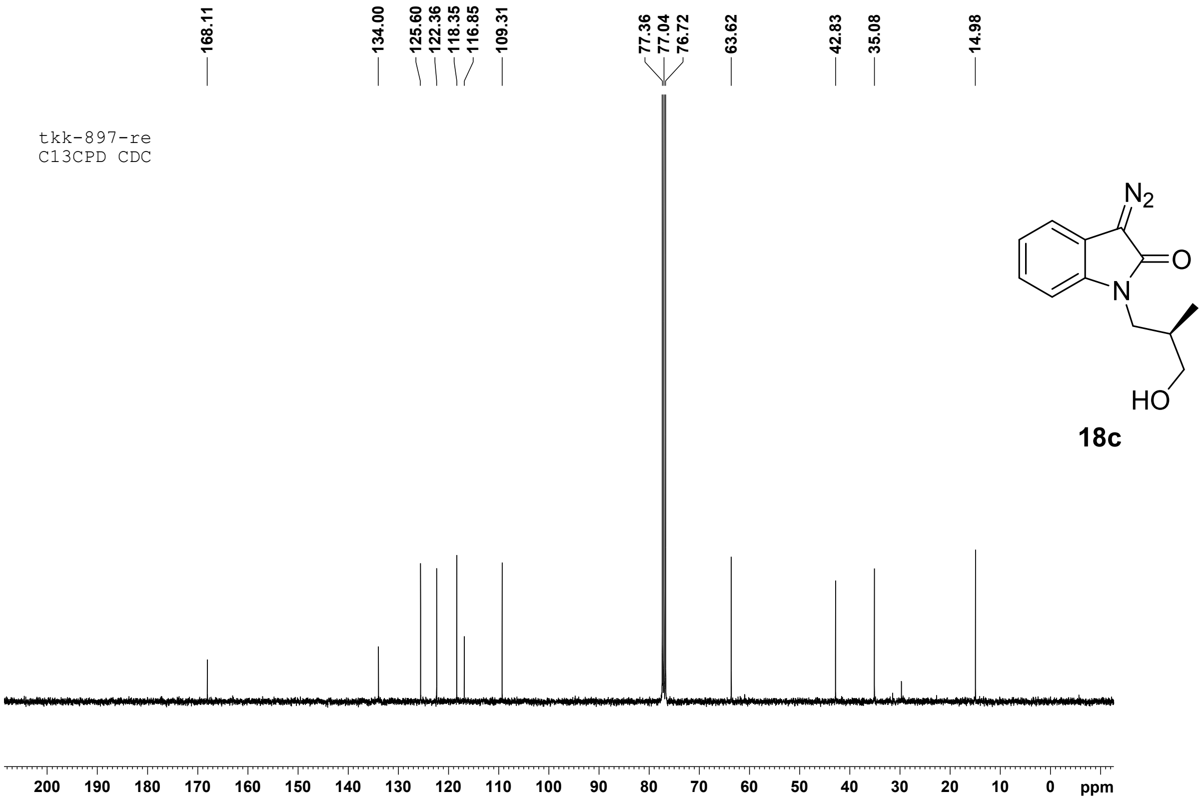
16b


7.268
7.245
7.243
7.242
7.241
7.234
7.231
7.223
7.222
7.215
7.212
7.196
7.192
7.133
7.131
7.114
7.112
7.095
7.093
7.007
6.987
4.024
4.009
3.993
3.583
3.328
1.916
1.901
1.888
1.885
1.879
1.872
1.857
1.254
0.000
tkk-585-red lic
PROTON CDCl3 {I
N2
O
N
HO
10 9 8 7 6 5 4 3 2 1 0 ppm
1.96
1.00
1.00
2.15
2.11
1.04
2.77

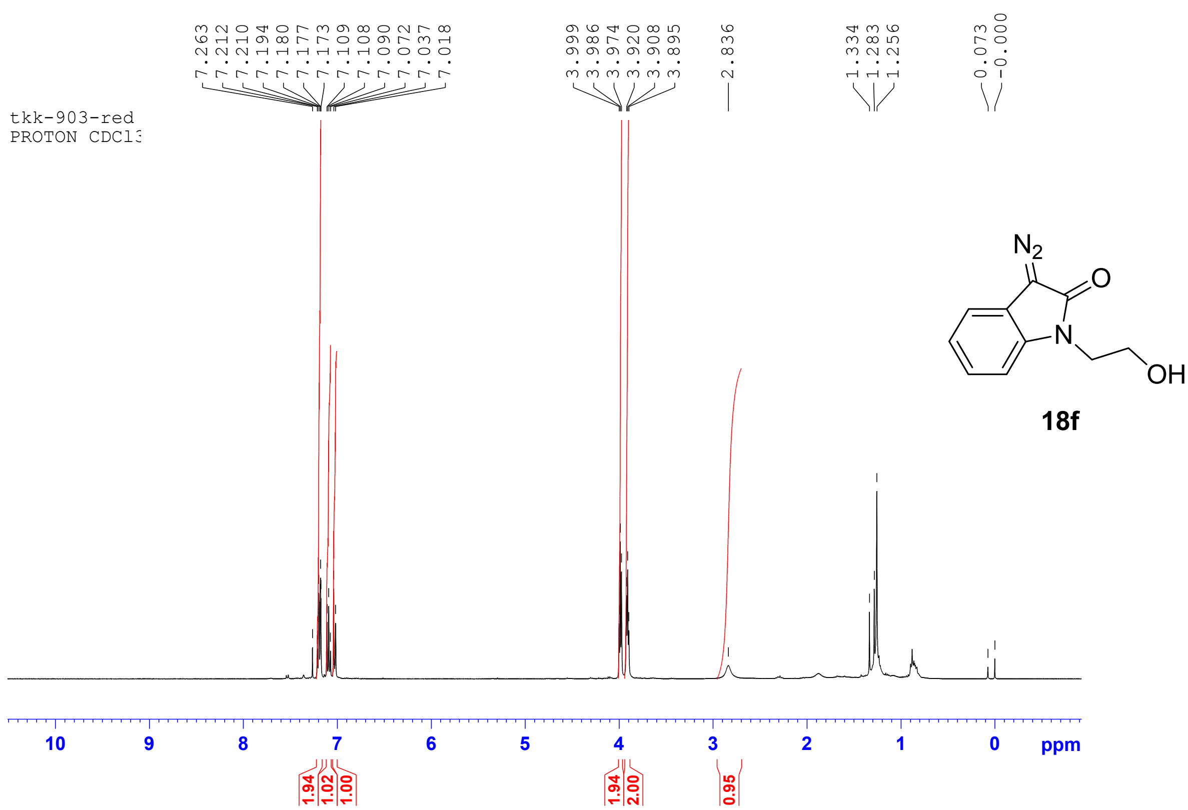
18a


167.84
133.40
125.63
122.35
118.44
116.94
108.95
77.38
77.06
76.75
58.29
36.82
30.36
tkk-585-red 1
C13CPD CDCl3
N2
O
N
HO
18a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

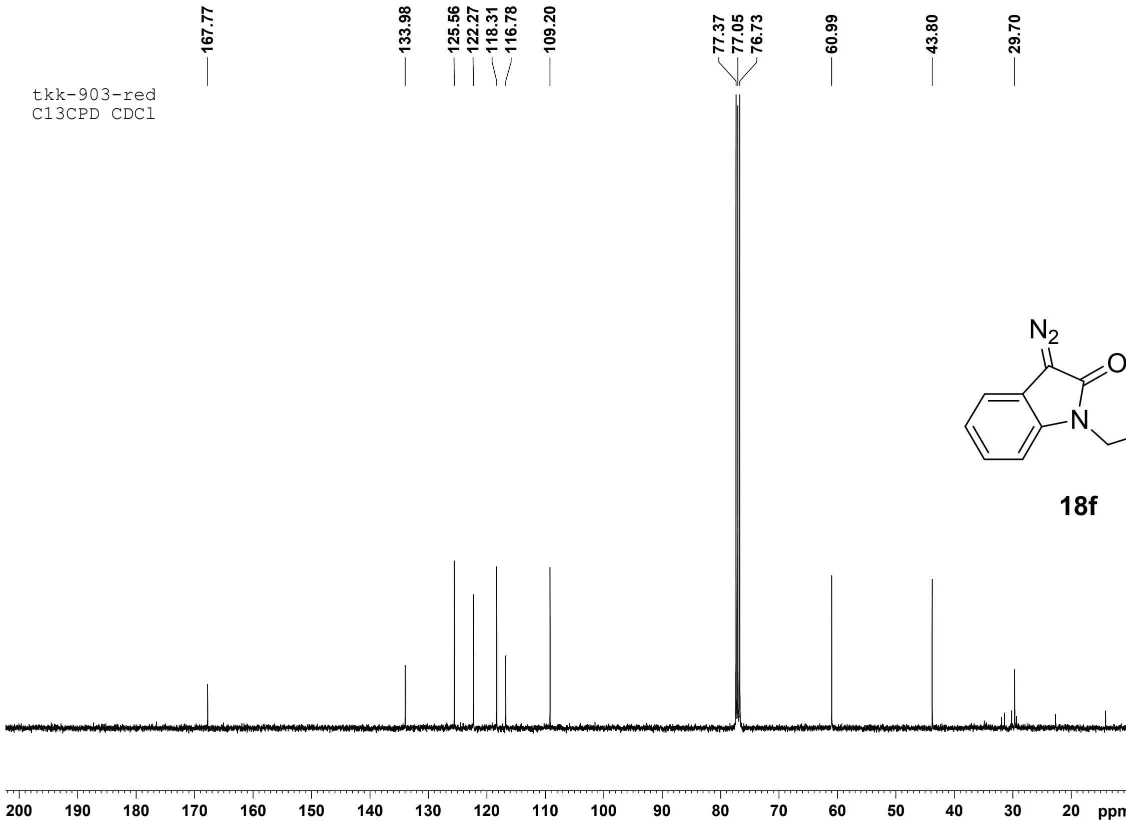

7.265
7.237
7.228
7.218
7.209
7.189
7.129
7.110
7.091
7.008
6.989
3.957
3.936
3.921
3.900
3.761
3.748
3.724
3.712
3.538
3.528
3.508
3.499
3.408
3.395
3.379
3.366
2.067
2.060
2.051
1.334
1.284
1.255
1.232
1.051
1.033
0.880
-0.000
tkk-897-red li
PROTON CDCl3
N2
O
N
HO
18c
10 9 8 7 6 5 4 3 2 1 0 ppm
2.13
1.05
1.00
1.02
1.02
1.16
1.34
1.10
1.43
3.03


168.11
134.00
125.60
122.36
118.35
116.85
109.31
77.36
77.04
76.72
63.62
42.83
35.08
14.98
tkk-897-re
C13CPD CDC
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
N2
O
N
HO

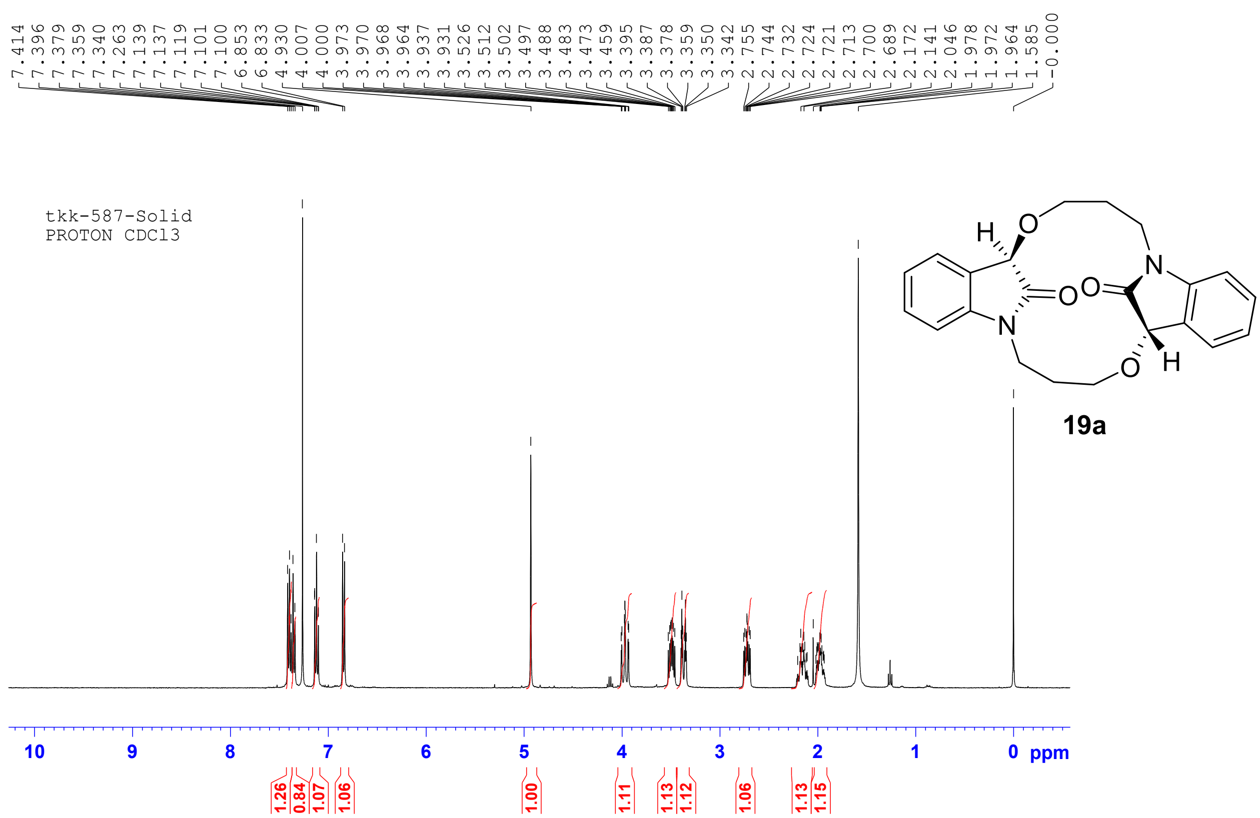
18c


7.263
7.212
7.210
7.194
7.180
7.177
7.173
7.109
7.108
7.090
7.072
7.037
7.018
3.999
3.986
3.974
3.920
3.908
3.895
2.836
1.334
1.283
1.256
0.073
-0.000
tkk-903-red
PROTON CDCl3
10 9 8 7 6 5 4 3 2 1 0 ppm
1.94
1.02
1.00
1.94
2.00
0.95
N2
O
N
OH

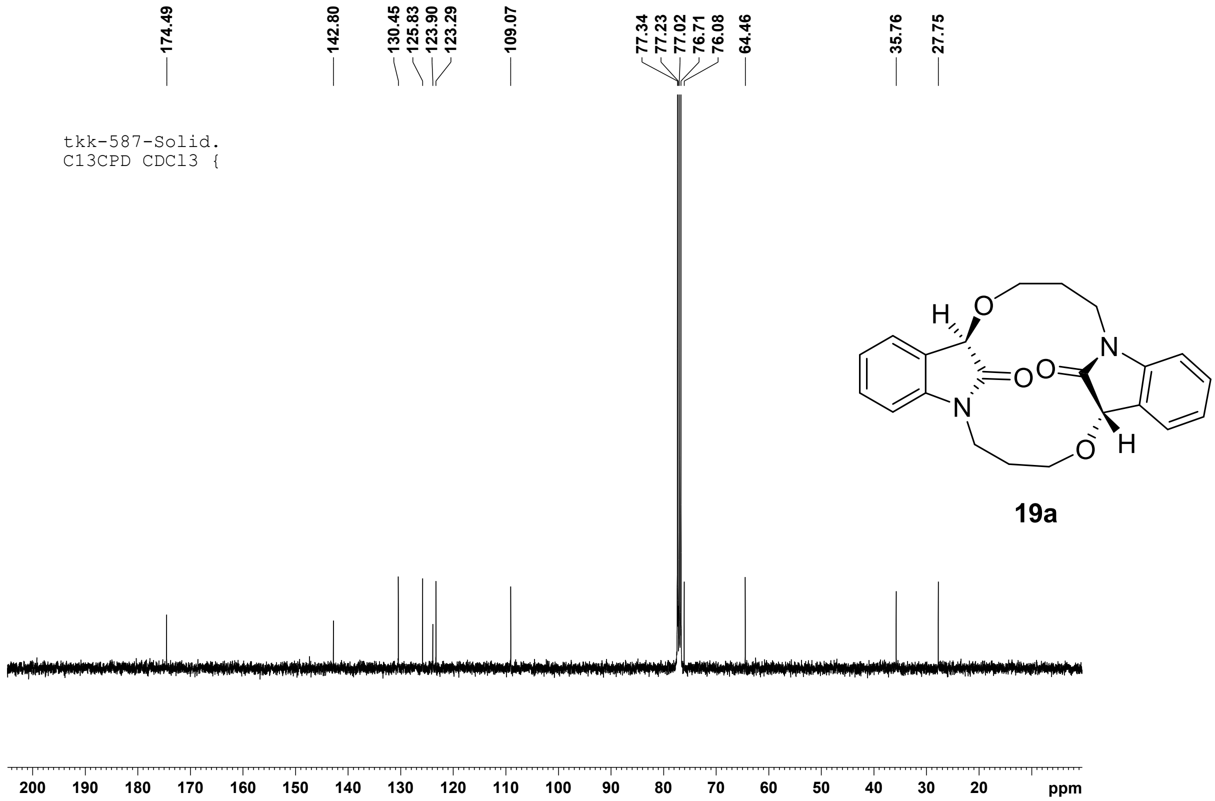
18f

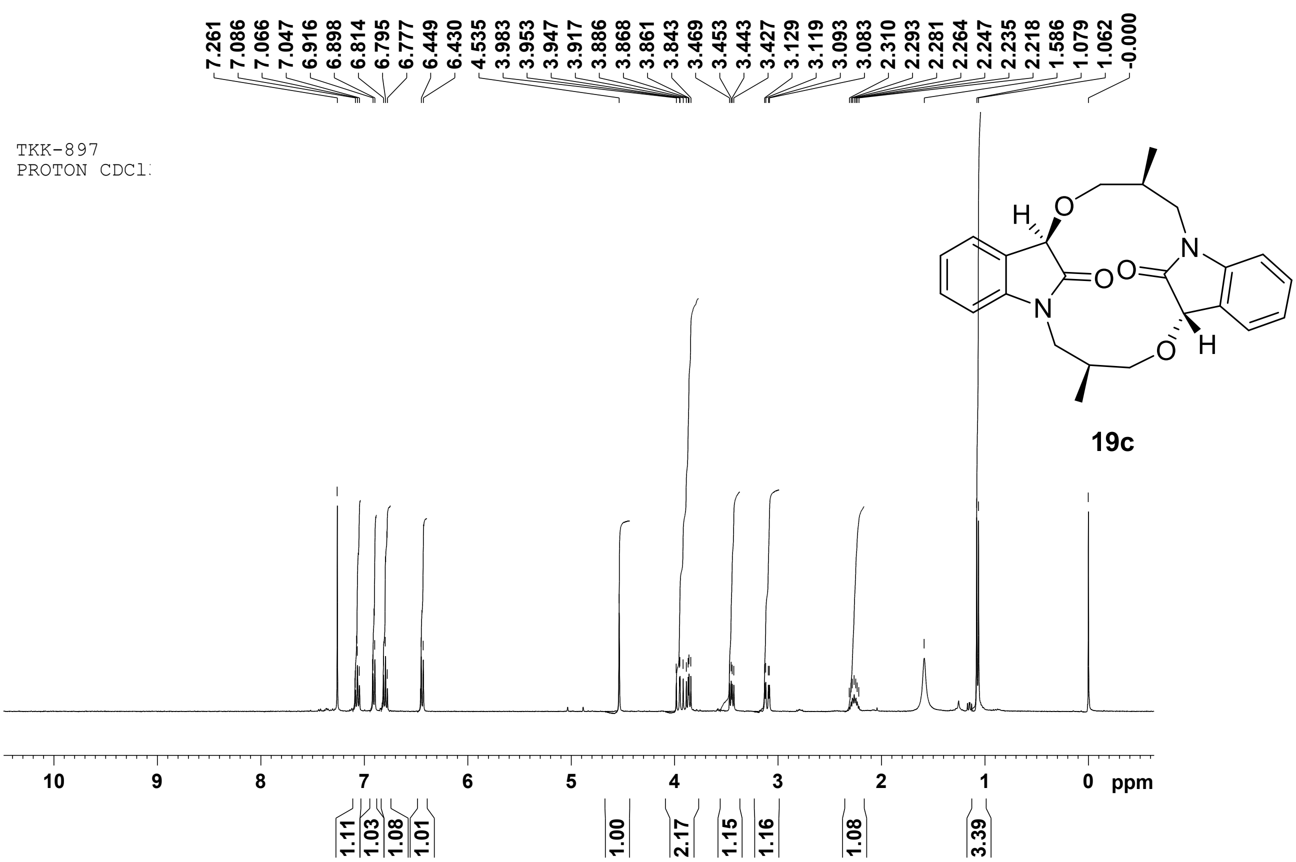


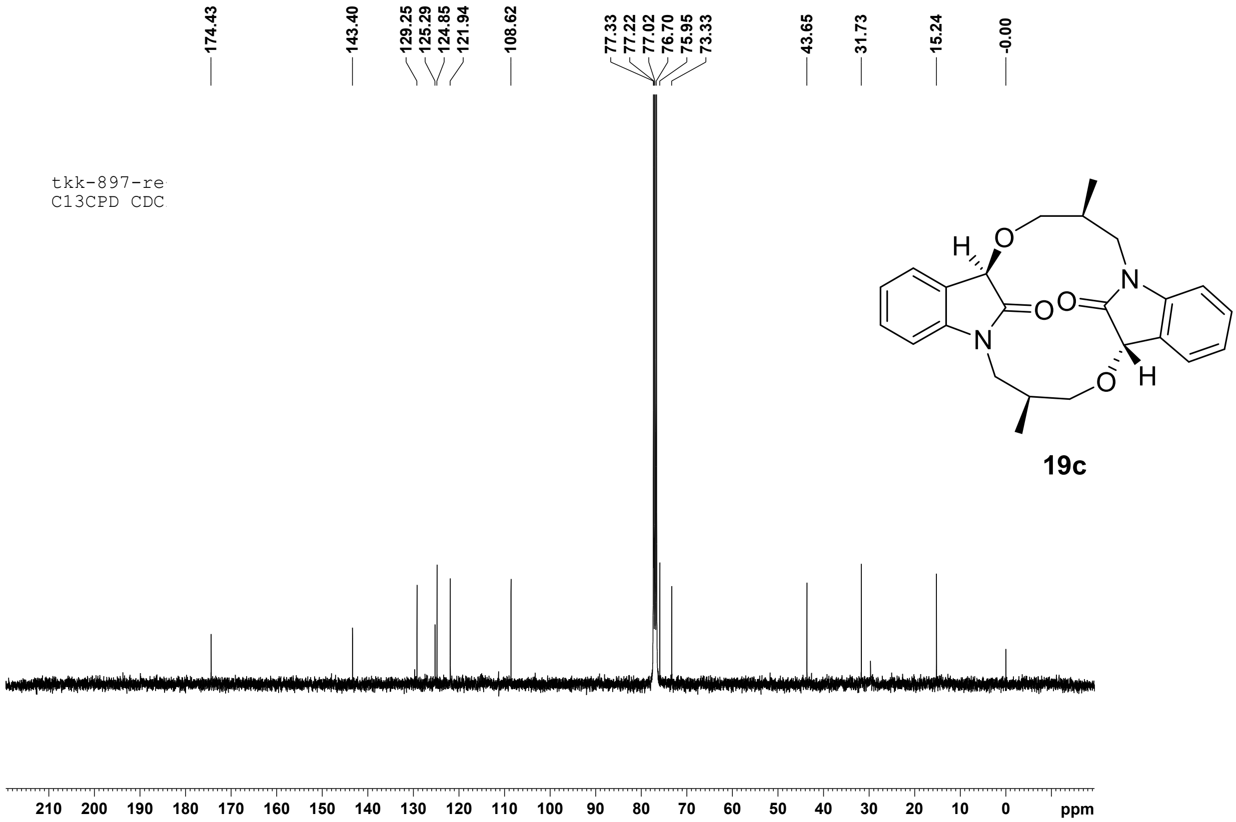
167.77
133.98
125.56
122.27
118.31
116.78
109.20
77.37
77.05
76.73
60.99
43.80
29.70
tkk-903-red
C13CPD CDCl
N2
O
N
OH
18f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



7.414
7.396
7.379
7.359
7.340
7.263
7.139
7.137
7.119
7.101
7.100
6.853
6.833
4.930
4.007
4.000
3.973
3.970
3.968
3.964
3.937
3.931
3.526
3.512
3.502
3.497
3.488
3.483
3.473
3.459
3.395
3.387
3.378
3.359
3.350
3.342
2.755
2.744
2.732
2.724
2.721
2.713
2.700
2.689
2.172
2.141
2.046
1.978
1.972
1.964
1.585
-0.000
tkk-587-Solid
PROTON CDCl3
H
O
N
O
O
N
O
H
19a
10 9 8 7 6 5 4 3 2 1 0 ppm
1.26
0.84
1.07
1.06
1.00
1.11
1.13
1.12
1.06
1.13
1.15


174.49
142.80
130.45
125.83
123.90
123.29
109.07
77.34
77.23
77.02
76.71
76.08
64.46
35.76
27.75
tkk-587-Solid.
C13CPD CDCl3 {
19a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.261
7.086
7.066
7.047
6.916
6.898
6.814
6.795
6.777
6.449
6.430
4.535
3.983
3.953
3.947
3.917
3.886
3.868
3.861
3.843
3.469
3.453
3.443
3.427
3.129
3.119
3.093
3.083
2.310
2.293
2.281
2.264
2.247
2.235
2.218
1.586
1.079
1.062
-0.000
TKK-897
PROTON CDCl
19c
10 9 8 7 6 5 4 3 2 1 0 ppm
1.11
1.03
1.08
1.01
1.00
2.17
1.15
1.16
1.08
3.39


174.43
143.40
129.25
125.29
124.85
121.94
108.62
77.33
77.22
77.02
76.70
75.95
73.33
43.65
31.73
15.24
-0.00
tkk-897-re
C13CPD CDC
H
O
N
O
O
N
O
H
19c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Packing diagram of macrocycle **12a** viewed down *ac*-axis, the molecules are arranged in the L-shape manner. The molecular arrangements are depicted in Figures 1 and 2. The molecules are arranged in three dimensional network with the presence of a C–H···π interaction and five intermolecular hydrogen bondings. The intermolecular H-bonding interactions are: C(11)–H(11b)···O(2); H11b···O2 = 2.641 Å, C11···O2 = 3.578 Å and < C(11)–H(11b)···O(2) = 162.31 Å;

C(22)–H(22b)···O(5); H22b···O5 = 2.710 Å, C22···O5 = 3.527 Å and < C(22)–H(22b)···O(5) = 158.67 Å;

C(25)–H(25b)···O(1); H25b···O1 = 2.583 Å, C25···O1 = 3.491(4) Å and < C(25)–H(25b)···O(1) = 130.01 Å;

C(32)–H(32b)···O(4); H32b···O4 = 2.599 Å, C32···O4 = 3.501 Å and < C(32)–H(32b)···O(4) = 154.66 Å;

C(34)–H(34a)···O(31); H34a···O31 = 2.708 Å, C34···O31 = 3.445 Å and < C(34)–H(34a)···O(31) = 133.15 Å;

The C–H···π interaction; C(7)–H(7a)···Cg(16); H7a···Cg(16) =3.066 Å, C7···Cg(16) = 3.905 Å, <C(7)–H(7a)···Cg(16) = 145.52 Å.

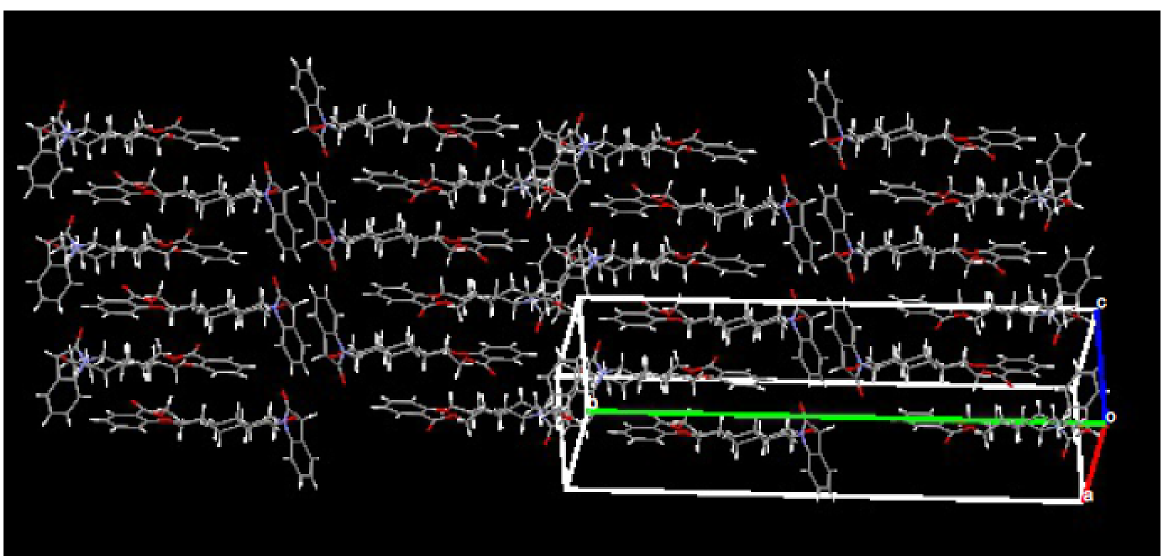


Figure 1. View through *ac*-axis of molecular packing arrangement of **12a**

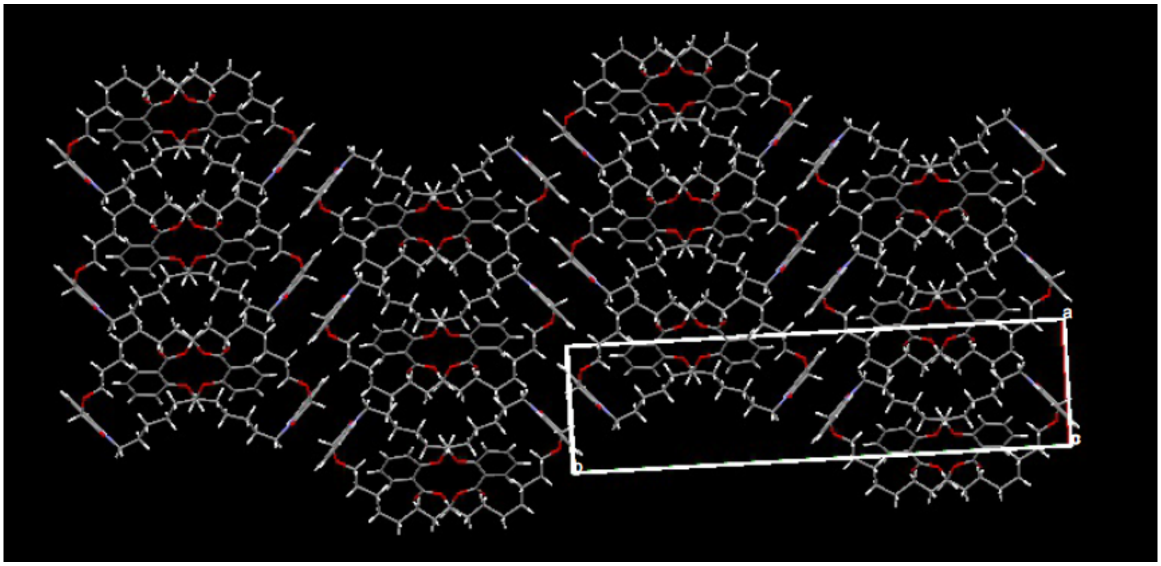


Figure 2. Viewed through *c*-axis of molecular packing arrangement of **12a**

Packing diagrams of macrocycle **19a** are depicted in Figures 3 and 4. The solid-state structure is having two layers based on the vertical and horizontal arrangement of molecule **19a**. The reasons for the solid-state arrangement are due to the presence of a C–H···π interaction and three intermolecular hydrogen bondings;

C–H···π interaction: C(18)–H(18)···Cg(16): H18···Cg(16) = 2.674 Å, C18···Cg(16) = 3.523 Å, <C(18)–H(18)···Cg(16) = 145.07 Å;

C–H···O interactions are: C(4)–H(4)···O(1); H4···O1 = 2.711 Å, C4···O1 = 3.581 Å and < C(11)–H(11b)···O(2) = 155.96 Å;

C(8)–H(8)···O(1); H8···O1 = 2.421 Å, C8···O1 = 3.237(4) Å and < C(11)–H(11b)···O(2) = 140.41 Å;

C(10)–H(10b)···O(3); H10b···O3 = 2.511 Å, C10···O3 = 3.261 Å and < C(10)–H(10b)···O(3) = 134.10 Å.

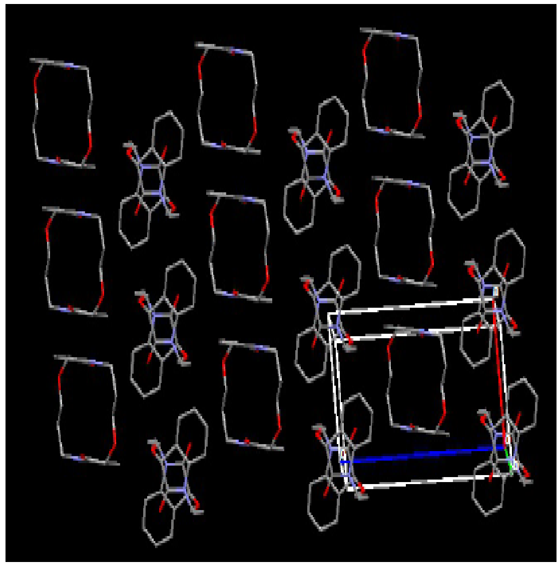
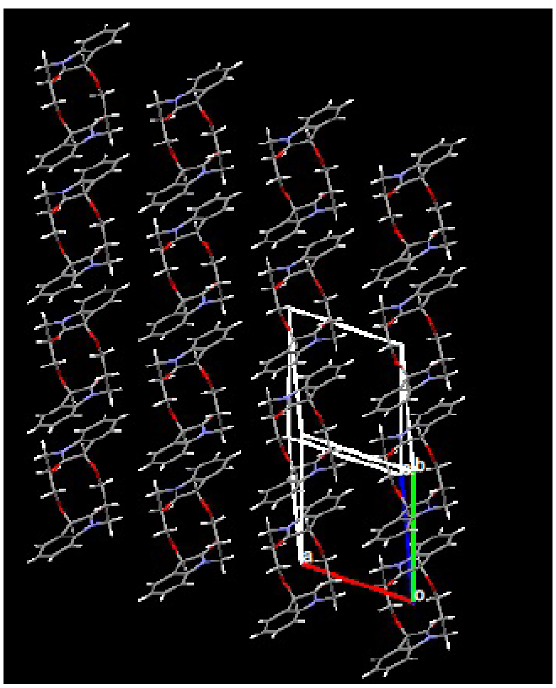


Figure 3. Molecules arrangement *via b*-axis; for better clarity hydrogen atoms are removed for **19a.**



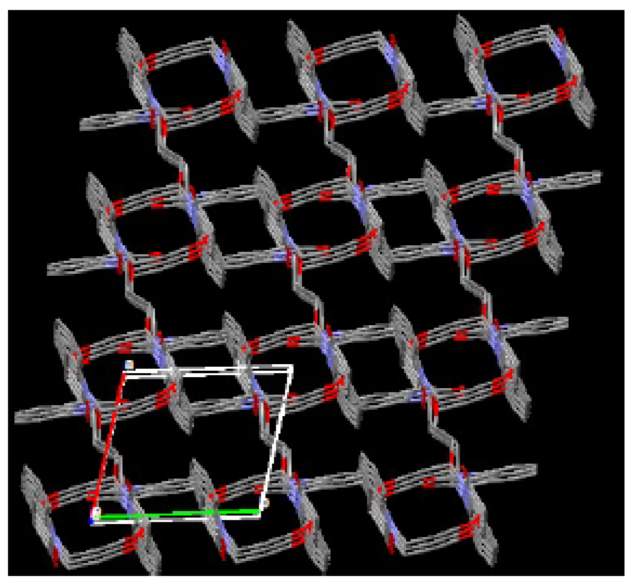


Figure 4. Zigzag packing arrangement of macrocycle of **19a** when viewed through *c*-axis**.**

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