Supporting Information

Persulfonylation of Amines Applied to the Synthesis of Higher Generation Dendrimers

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General Procedure for the Persulfonylation of Amines: A mixture of an amine, triethylamine (sixfold molar excess per amino group), and arylsulfonyl chloride (fourfold molar excess per amino group) was stirred in CH_2Cl_2 (50 mL per 1 g of the amine) at reflux for 12-24 hrs. Then the solvent was removed under reduced pressure and the residue was triturated with methanol. The solid precipitate was filtered and washed with methanol. The raw product was purified by either recrystallization from CH_2Cl_2/CH_3OH or chromatography on silica gel.

Characterization data for the compounds 3-14

General comment: Synthesis and characterization of compounds **1**, **2**, **3f**, **4**, and **5a** were described before. Because compounds **2**, **3f**, **4**, and **5a** were re-synthesized by using the improved procedures described in this paper, copies of their NMR spectra are included.

Compound 3a. Colorless solid; m.p. 143 – 147 °C; ^{1}H NMR (300 MHz, CDCl3): δ = 0.90 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.29 (m, 10 H, CH_2), 1.73 (m, 2H, CH_2), 2.51 (s, 12 H, CH_3), 3.70 (m, 2 H, CH_2), 7.24 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, ArH), 7.38 (d, $^3J_{H,H}$ = 8.1 Hz, 8 H, ArH), 7.82 (d, $^3J_{H,H}$ = 8.4 Hz, 8 H, ArH), 7.95 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, ArH), ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.10, 21.77, 22.62, 26.61, 28.96, 29.16, 30.00, 31.74, 50.02, 128.60, 129.12, 129.86, 132.42, 136.04, 139.45, 140.91, 145.63, ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1078.18 $[M + Na]^+$, $C_{48}H_{53}N_3O_{12}S_6Na$ requires 1078.19; elemental analysis calcd (%) for $C_{48}H_{53}N_3O_{12}S_6$ (1056.34): C 54.58, H 5.06, N 3.98, S 18.21; found C 54.80, H 5.09, N 4.08, S 18.15.

Compound 3b. Colorless solid; m.p. 189 – 193 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.30 (m, 10 H, $(CH_2)_5$), 1.41 (s, 36 H, CH_3), 1.74 (br, 2 H, CH_2), 3.73 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 7.28 (m, 4 H, ArH), 7.60 (m, 8 H, ArH), 7.86 (m, 8 H, ArH), 7.99 (m, 4 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.05, 22.56, 26.56, 28.90, 29.12, 30.00, 31.68, 49.92, 55.75, 114.31, 129.06, 130.26, 130.84, 132.35, 139.59, 140.65, 164.15 ppm; MS (HiRes ESI pos., $CHCl_3/CH_3OH$): *m/z* = 1246.3720 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{60}{}^1H_{77}{}^{14}N_3{}^{16}O_{12}{}^{32}S_6Na$) 1246.3724; elemental analysis calcd (%) for $C_{60}H_{77}N_3O_{12}S_6$ (1124.68): C 58.84, H 6.34, N 3.43, S 15.71; found C 58.66, H 6.38, N 3.58, S 15.88.

Compound 3c. Yellowish solid; m.p. 200 – 203 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.30 (m, 10 H, $(CH_2)_5$), 1.74 (m, 2 H, CH_2), 3.69 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 3.94 (s, 12 H, CH_3), 7.02 (m, 8 H, ArH), 7.25 (m, 4 H, ArH), 7.89 (m, 12 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.06, 22.57, 26.57, 28.93, 29.13, 29.96, 31.01, 31.69, 35.37, 50.01, 126.23, 128.42, 129.08, 132.41, 135.93, 139.50, 140.90, 158.44 ppm; MS (HiRes ESI, $CHCl_3/CH_3OH$): *m/z* = 1142.1642 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{48}{}^1H_{53}{}^{14}N_3{}^{16}O_{16}{}^{32}S_6Na$) 1142.1642; elemental analysis calcd (%) for $C_{48}H_{53}N_3O_{16}S_6$ (1120.35): C 51.46, H 4.77, N 3.75, S 17.17; found C 51.33, H 4.71, N 3.79, S 17.05.

Compound 3d. Recrystallized from THF/methanol; colorless solid; m.p. 209 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.30 (m, 10 H, CH_2), 1.74 (m. 2H, CH_2), 3.74 (m, 2 H, CH_2), 7.26 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, ArH), 7.70 – 7.86 (m, 16 H, ArH), 8.02 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, ArH), ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.11, 22.62, 26.59, 28.98, 29.15, 30.08, 31.73, 50.13, 129.39, 130.05, 130.13,

132.25, 132.71, 137.64, 138.78, 141.43 ppm; MS (HiRes ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1337.7592 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{44}{}^{1}H_{41}{}^{14}N_3{}^{16}O_{12}{}^{32}S_{16}Na$) 1337.7602; elemental analysis calcd (%) for $C_{44}H_{41}Br_4N_3O_{12}S_6$ (1315.82): C 40.16, H 3.14, N 3.19, S 14.62; found C 40.08, H 3.14, N 3.30, S 14.67.

Compound 3e. Colorless solid; m.p. 284 – 286 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.29 (m, 10 H, $(CH_2)_5$), 1.76 (m, 2 H, CH_2), 3.73 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 7.33 (m, 4 H, ArH), 7.54 (m, 8 H, ArH), 7.68 (m, 8 H, ArH), 7.76 (m, 8 H, ArH), 8.0 (m, 12 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 13.98, 22.57, 26.67, 28.56, 29.12, 30.09, 31.73, 50.10, 123.58, 127.60, 128.71, 128.99, 129.24, 129.32, 129.44, 132.42, 137.80, 137.97, 139.40, 141.34, 146.16 ppm; MS (ESI pos., $CHCl_3/CH_3OH$): *m/z* = 1642.88 $[M + Na]^+$, $C_{68}H_{57}N_3O_{12}S_6Br_4Na$ requires 1642.89; elemental analysis calcd (%) for $C_{68}H_{57}N_3O_{12}S_6Br_4$ (1620.22): C 50.41, H 3.55, N 2.59, S 11.87; found C 50.56, H 3.56, N 2.56, S 11.95.

Compound 3g. Yellowish solid; m.p. 215°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.3 (m, 10 H, CH_2), 1.77 (m. 2 H, CH_2), 3.76 (m, 2 H, CH_2), 7.30 (d, $^3J_{H,H}$ = 9.3 Hz, 4 H, ArH), 7.90 (t, $^3J_{H,H}$ = 16.2 Hz, 4 H, ArH), 8.07 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, ArH), 8.29 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, ArH), 8.63 (d, $^3J_{H,H}$ = 7.2 Hz, 4 H, ArH), 8.80 (s, 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.06, 22.58, 26.57, 28.93, 29.11, 30.08, 31.70, 50.73, 123.98, 129.17, 129.78, 130.92, 132.01, 134.01, 138.01, 140.33, 142.01, 148.39 ppm; MS (ESI pos.,$CHCl_3/CH_3OH$): *m/z* = 1202.06 $[M+Na]^+$, $C_{44}H_{41}N_7O_{20}S_6Na$ requires 1202.06; elemental analysis calcd (%) for $C_{44}H_{41}N_7O_{20}S_6$ (1180.22): C 44.78, H 3.50, N 8.31, S 16.15; found C 45.00, H 3.75, N 8.13, S 16.15.

Compound 3h. Colorless solid; m.p. 190ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.29 (m, 10 H, CH_2), 1.74 (m. 2H, CH_2), 3.69 (m, 2 H, CH_2), 7.27 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.61- 7.79 (m, 8 H, ArH), 7.88- 8.08 (m, 22 H, ArH), 8.47 (m, 4 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.11, 22.63, 26.63, 28.96, 29.18, 30.07, 31.74, 49.99, 122.80, 127.94, 128.03, 129.24, 129.66, 129.77, 129.85, 130.78, 131.85, 132.57, 135.50, 135.60, 139.33, 141.01 ppm; MS (ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 1222.18 $[M + Na]^+$, $C_{60}H_{53}N_3O_{12}S_6Na$ requires 1222.19; elemental analysis calcd (%) for $C_{60}H_{53}N_3O_{12}S_6$ (1200.47): C 60.03, H 4.45, N 3.50, S 16.03; found C 59.98, H 4.41, N 3.51, S 16.18.

Compound 3i. Yellowish solid; m.p. 117 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.31 (m, 10 H, $(CH_2)_5$), 1.68 (m, 2 H, CH_2), 3.63 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 7.24 (m, 4 H, ArH), 7.36 (m, 4 H, ArH), 7.59 (m, 8 H, ArH), 7.82 (m, 8 H, ArH), 7.96 (m, 8 H, ArH), 8.15 (m, 8 H, ArH), 8.38 (m, 8 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.05, 22.58, 26.53, 28.87, 29.10, 29.89, 31.66, 49.73, 124.08, 124.11, 127.13, 128.30, 128.59, 128.73, 129.03, 132.91, 133.10, 133.11, 133.83, 136.29, 138.53, 140.99 ppm; MS (HiRes ESI, $CHCl_3$/MeOH): *m/z* = 1222.1849 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{60}{}^{1}H_{53}{}^{14}N_3{}^{16}O_{12}{}^{32}S_6Na$) 1222.1846; elemental analysis calcd (%) for $C_{60}H_{53}N_3O_{12}S_6$ (1200.49): C 60.03, H 4.45, N 3.50, S 16.03; found C 59.96, H 4.46, N 3.37, S 15.92.

Compound 3j. Colorless solid; m.p. 192 – 196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.30 (m, 10 H, $(CH_2)_5$), 1.65 (m, 2 H, CH_2), 2.33 (s, 12 H, CH_3), 2.43 (s, 24 H, CH_3), 3.55 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 6.94 (s, 8 H, ArH), 7.84 (m, 4 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.06, 21.10, 22.58, 22.71, 26.52, 28.85, 29.13, 29.84, 31.67, 49.53, 128.57, 132.00, 132.09, 132.79, 138.71, 140.47, 141.41,

144.72 ppm; MS (HiRes ESI, $CHCl_3$/MeOH): *m/z* = 1190.3098 [*M*+Na]$^+$, calcd monoisotopic peak ($^{12}C_{56}{}^{1}H_{69}{}^{14}N_3{}^{16}O_{12}{}^{32}S_6Na$) 1190.3098; elemental analysis calcd (%) for $C_{56}H_{69}N_3O_{12}S_6$ (1168.57): C 57.56, H 5.95, N 3.60, S 16.49; found C 57.53, H 5.94, N 3.66, S 16.67

Compound 5b. Purified by column chromatography (R_f = 0.75, silica gel, CH_2Cl_2/ethyl acetate 10:1); colorless solid; yield 79%; m.p. 179 – 182 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H, H}$ = 6.3 Hz, 3 H, CH_3), 1.29 (m, 10 H, CH_2), 1.75 (m. 2H, CH_2), 3.76 (m, 2 H, CH_2), 3.93 (s, 24 H, OCH_3), 7.03 (d, $^3J_{H, H}$ = 9 Hz, 16 H, ArH), 7.20 (d, $^3J_{H, H}$ = 8.4 Hz, 4 H, ArH), 7.25 (d, $^3J_{H, H}$ = 8.4 Hz, 8 H, ArH), 7.85 (d, $^3J_{H, H}$ = 8.4 Hz, 8 H, ArH), 7.86 (d, $^3J_{H, H}$ = 9 Hz, 16 H, ArH), 8.01 (d, $^3J_{H, H}$ = 8.4 Hz, 4 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.37, 22.74, 26.70, 29.07, 29.26, 30.36, 31.83, 50.38, 55.99, 114.60, 129.35, 129.71, 130.37, 131.04, 132.53, 132.71, 138.73, 139.44, 140.57, 141.68, 164.43 ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 2442.18 [*M* + Na]$^+$, $C_{100}H_{97}N_7O_{36}S_{14}Na$ requires 2442.20; elemental analysis calcd (%) for $C_{100}H_{97}N_7O_{36}S_{14}$ (2421.78): C 49.59, H 4.04, N 4.05, S 18.54; found C 49.50, H 3.91, N 3.98, S 18.75.

Compound 5c. Recrystallized from methanol/dichloromethane; colorless solid; yield 83%; melting region 175 – 205 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^3J_{H, H}$ = 6.3 Hz, 3 H, CH_3), 1.26 (m, 10 H, CH_2), 1.77 (m. 2H, CH_2), 3.75 (m, 2 H, CH_2), 7.22 (d, $^3J_{H, H}$ = 8.1 Hz, 4 H, ArH), 7.32 (d, $^3J_{H, H}$ = 8.7 Hz, 8 H, ArH), 7.51 (d, $^3J_{H, H}$ = 8.4 Hz, 16 H, ArH), 7.65 (d, $^3J_{H, H}$ = 8.4 Hz, 16 H, ArH), 7.73 (d, $^3J_{H, H}$ = 8.4 Hz, 16 H, ArH), 7.83 (d, $^3J_{H, H}$ = 8.7 Hz, 8 H, ArH), 7.94 (d, $^3J_{H, H}$ = 8.1 Hz, 4 H, ArH), 8.00 (d, $^3J_{H, H}$ = 8.4 Hz, 16 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.52, 23.00, 26.98, 29.34, 29.52, 30.75, 32.08, 50.72, 123.98, 128.03, 129.13, 129.39, 129.64, 129.85, 130.16, 132.79, 132.97, 137.93, 137.98, 138.94, 140.07, 140.39, 141.82, 146.48 ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 3444.20 [*M* + Na]$^+$, $C_{140}H_{105}Br_8N_7O_{28}S_{14}Na$ requires 3444.64; elemental analysis calcd (%) for $C_{140}H_{105}Br_8N_7O_{28}S_{14}$ (3421.50): C 49.14, H 3.09, Br 18.68, N 2.87, S 13.12; found C 48.98, H 3.04, Br 18.90, N 2.88, S 13.30.

Compound 5d. Purified by column chromatography (R_f = 0.5, silica gel, CH_2Cl_2/ethyl acetate 100/1); yellowish solid; 34%; melting region 176 – 195 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, $^3J_{H, H}$ = 6.3 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.78 (m. 2H, CH_2), 3.76 (m, 2 H, CH_2), 7.22 (d, $^3J_{H, H}$ = 8.5 Hz, 4 H, ArH), 7.25 (d, $^3J_{H, H}$ = 8.5 Hz, 8 H, ArH), 7.84-7.90 (m, 16 H, ArH), 7.92 (d, $^3J_{H, H}$ = 8.5 Hz, 4 H, ArH), 8.26 (d, $^3J_{H, H}$ = 8 Hz, 8 H, ArH), 8.57 (m, 8 H, ArH), 8.73 (s, 8 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.49, 22.98, 26.93, 29.35, 29.53, 30.85, 32.10, 50.77, 124.33, 129.68, 130.04, 130.64, 131.50, 132.61, 134.46, 138.64, 139.13, 140.53, 140.96, 141.92, 148.71 ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 2561.89 [*M* + Na]$^+$, $C_{92}H_{73}N_{15}O_{44}S_{14}Na$ requires 2561.99; elemental analysis calcd (%) for $C_{92}H_{73}N_{15}O_{44}S_{14}$ (2541.55): C 43.48, H 2.90, N 8.27, S 17.66; found C 43.60, H 3.05, N 8.00, S 17.44.

Compound 5e. Purified by column chromatography (R_f = 0.31, silica gel, $CHCl_3$); colorless solid; yield 54%; m.p. 185 – 188 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, $^3J_{H, H}$ = 6.3 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.78 (m. 2H, CH_2), 3.76 (m, 2 H, CH_2), 7.18 (d, $^3J_{H, H}$ = 8.7 Hz, 4 H, ArH), 7.28 (m, 4 H, ArH), 7.59 – 7.75 (m, 16 H, ArH), 7.79 (d, $^3J_{H, H}$ = 8.7 Hz, 8 H, ArH), 7.85 – 8.09 (m, 40 H, ArH), 8.46 (m, 8 H, ArH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.08, 22.58, 26.58, 28.94, 29.11, 30.37, 31.66, 50.29, 122.72, 127.99, 128.02, 129.41, 129.69, 129.74, 129.89, 130.78, 131.82, 132.32, 132.70, 135.48, 135.50, 138.54, 139.65, 140.05, 141.43 ppm; MS (MALDI-TOF, DCTB Mix

1:10): *m/z* = 2601.89 $[M + Na]^+$, 2618.84 $[M + K]^+$, $C_{124}H_{97}N_7O_{28}S_{14}Na$ requires 2602.24, $C_{124}H_{97}N_7O_{28}S_{14}K$ requires 2618.21; elemental analysis calcd (%) for $C_{124}H_{97}N_7O_{28}S_{14}$ (2582.04): C 57.68, H 3.79, N 3.80, S 17.39; found C 57.97, H 3.94, N 3.76, S 17.43.

Compound 5f. Purified by column chromatography (R_f = 0.43, silica gel, CH_2Cl_2); colorless solid; 25%; m.p. 185 – 188 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H, H}$ = 6.3 Hz, 3 H, CH_3), 1.28 (m, 10 H, CH_2), 1.74 (m. 2H, CH_2), 2.36 (s, 24 H, $ArCH_3$), 2.48 (s, 48 H, $ArCH_3$), 3.78 (m, 2 H, CH_2), 6.98 (s, 16 H, ArH), 7.06 (d, $^3J_{H, H}$ = 8.4 Hz, 4 H, ArH), 7.35 (d, $^3J_{H, H}$ = 8.4 Hz, 8 H, ArH), 7.76 (d, $^3J_{H, H}$ = 8.4 Hz, 8 H, ArH), 8.10 (d, $^3J_{H, H}$ = 8.4 Hz, 4 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.50, 21.59, 23.01, 23.24, 26.97, 29.39, 29.56, 30.43, 32.10, 50.64, 129.42, 129.74, 132.44, 132.48, 132.60, 133.31, 138.96, 139.88, 139.92, 141.89, 142.23, 145.35 ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 2538.59 $[M + Na]^+$, $C_{116}H_{129}N_7O_{28}S_{14}Na$ requires 2538.49; elemental analysis calcd (%) for $C_{116}H_{129}N_7O_{28}S_{14}$ (2518.21): C 55.33, H 5.16, N 3.89, S 17.83; found C 55.36, H 4.96, N 3.70, S 17.99.

Compound 6. (a) Preparation and characterization of the octaamine precursor are described in Experimental Section of the manuscript. (b) Preparation of hexadecatosylate **6**. A solution of the octaamine precursor (0.8 g, 0.35 mmol), triethylamine (5 mL), and tosyl chloride (5 g, 26 mmol) was stirred at reflux in 40 mL of dichloromethane for 24 hrs. Then the solvent was removed under reduced pressure and the residue was triturated with methanol. The brownish precipitate was filtered, dried in vacuum, and purified by column chromatography (R_f = 0.65, silica gel, CH_2Cl_2/ethyl acetate 50/1). Colorless solid; yield 770 mg (44%); melting region 159 – 180 °C ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79 (t, $^3J_{H, H}$ = 6.4 Hz, 3 H, CH_3), 1.14 (m, 10 H, CH_2), 1.59 (m. 2H, CH_2), 2.39 (s, 48 H, CH_3), 3.66 (m, 2 H, CH_2), 7.21 (d, $^3J_{H, H}$ = 8.5 Hz, 4 H, ArH), 7.25 (d, $^3J_{H, H}$ = 8.5 Hz, 8 H, ArH), 7.30-7.34 (m, 40 H, ArH), 7.58 (m, 8 H, ArH), 7.65 (s, 8 H, ArH), 7.78 (d, $^3J_{H, H}$ = 8 Hz, 32 H, ArH), 7.92 (d, $^3J_{H, H}$ = 8.5 Hz, 8 H, ArH), 8.01 (m, 8 H, ArH), 8.09 (d, $^3J_{H, H}$ = 8.5 Hz, 4 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.49, 22.14, 23.00, 26.89, 29.33, 29.55, 30.40, 32.08, 50.57, 128.97, 130.14, 130.29, 130.35, 130.53, 130.64, 132.21, 132.47, 132.83, 135.99, 136.34, 138.04, 138.99, 139.49, 140.32, 141.11, 142.27, 146.18 ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 4790.00 $[M + Na]^+$, $C_{204}H_{185}N_{15}O_{60}S_{30}Na$ requires 4790.34; elemental analysis calcd (%) for $C_{204}H_{185}N_{15}O_{60}S_{30}$ (4768.67): C 51.38, H 3.91, N 4.41, S 20.17; found C 51.55, H 3.98, N 4.37, S 20.26.

Compound 7a. The octaamine precursor (0.8 g, 0.35 mmol), triethylamine (5 mL), and *m*-nosyl chloride (5 g, 23 mmol) were used in the reaction. The conditions are analogous to the preparation of **6**. Purified by column chromatography (R_f = 0.2, silica gel, CH_2Cl_2/ethyl acetate 50/1); yield 368 mg (20%); yellowish solid; melting region 174 – 186 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, $^3J_{H, H}$ = 6.4 Hz, 3 H, CH_3), 1.21 (m, 10 H, CH_2), 1.68 (m. 2H, CH_2), 3.67 (br. s, 2 H, CH_2), 7.22-7.26 (m, 12 H, ArH), 7.50 (d, $^3J_{H, H}$ = 7.5 Hz, 8 H, ArH), 7.65 (s, 8 H, ArH), 7.73 (m, 8 H, ArH), 7.87-7.90 (m, 24 H, ArH), 7.95 (d, $^3J_{H, H}$ = 8 Hz, 4 H, ArH), 8.03 (d, $^3J_{H, H}$ = 8 Hz, 8 H, ArH), 8.35 (d, $^3J_{H, H}$ = 8 Hz, 8 H, ArH), 8.57 (d, $^3J_{H, H}$ = 8 Hz, 8 H, ArH), 8.73 (s, 8 H, ArH) ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 5287.20 $[M + Na]^+$; elemental analysis calcd (%) for $C_{188}H_{137}N_{31}O_{92}S_{30}$ (5264.20): C 42.89, H 2.62, N 8.25, S 18.27; found C 43.01, H 2.65, N 8.24, S 18.32.

Compound 7b. Obtained from **7a** by the standard reduction procedure. ^{1}H NMR (500 MHz, DMSO[d_6]): δ = 0.87 (t, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 1.11 (br. s, 10 H, CH_2), 1.54 (br. s, 2 H, CH_2), 3.78 (br. s, 2 H, CH_2), 5.78 (s, 32 H, NH_2), 6.85 (d, $^3J_{H,H}$ = 7.5 Hz, 16 H, ArH), 6.91 (d, $^3J_{H,H}$ = 7.5 Hz, 16 H, ArH), 7.08 (s, 16 H, ArH), 7.24 (m, 16 H, ArH), 7.37 (d, $^3J_{H,H}$ = 8 Hz, 8 H, ArH), 7.49 (d, $^3J_{H,H}$ = 8 Hz, 8 H, ArH), 7.53 (d, $^3J_{H,H}$ = 8 Hz, 4 H, ArH), 7.59 (s, 8 H, ArH), 7.80 (m, 8 H, ArH), 7.99 (d, $^3J_{H,H}$ = 7.5 Hz, 8 H, ArH), 8.05 (d, $^3J_{H,H}$ = 7.5 Hz, 8 H, ArH), 8.15 (d, $^3J_{H,H}$ = 8 Hz, 4 H, ArH) ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 4837.35 $[M + Na]^+$.

Compound 8. Prepared from 0.6 g of the octaamine **S9** (see below). Purified by column chromatography on silica gel (R_f = 0.45, CH_2Cl_2/ethylacetate 100/1); colorless solid; yield 0.39 g (34%); melting region 168 – 185 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.78 (t, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.14 (br., 10 H, CH_2), 1.64 (br. s, 2H, CH_2), 2.38 (s, 48 H, $ArCH_3$), 3.64 (br. s, 2 H, CH_2), 7.22-7.27 (m, 14 H, ArH), 7.28 (d, $^3J_{H,H}$ = 8 Hz, 32 H, ArH), 7.32 (d, $^3J_{H,H}$ = 9 Hz, 8 H, ArH), 7.40 (d, $^3J_{H,H}$ = 8 Hz, 2 H, ArH), 7.52 (d, $^3J_{H,H}$ = 8 Hz, 2 H, ArH), 7.56 (m, 8 H, ArH), 7.64 (br. s, 10 H, ArH), 7.77 (d, $^3J_{H,H}$ = 8 Hz, 32 H, ArH), 7.92-8.00 (m, 22 H, ArH), 8.02 (d, $^3J_{H,H}$ = 8 Hz, 2 H, ArH) ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 5242.5 $[M + Na]^+$; $C_{222}H_{197}BrN_{16}O_{64}S_{32}Na$ requires 5242.3; elemental analysis calcd (%) for $C_{222}H_{197}BrN_{16}O_{64}S_{32}$ (5218.99): C 51.09, H 3.80, Br 1.53, N 4.29, S 19.66; found C 51.31, H 4.09, Br 1.50, N 4.13, S 19.38.

Compound 9. Dendron **8** (150 mg, 2.9 10^{-5} mol) and benzene-1,4-bis(boronic acid)propane-1,3-diol diester[1] (3 mg, 1.22 10^{-5} mol) were dissolved in 2 mL of dry THF. A concentrated solution of $NaHCO_3$ in water (0.5 mL) was added to the reaction mixture and the system was degassed. Freshly prepared $Pd[P(p\text{-tolyl})_3]_3$[1] (1 mg) was added and the reaction mixture was allowed to stir at 80°C for 24 hrs under nitrogen atmosphere. Then 20 mL of water were added and the emulsion was taken up with 100 mL of dichloromethane. The organic layer was separated, washed with water and brine, dried over Mg_2SO_4 and evaporated. The brown residue was chromatographed on silica gel column with dichloromethane/ethylacetate (25:1, R_f = 0.60) yielding 88 mg (70%) of **9** as a white crystalline powder. Melting region 162 – 204 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.80 (t, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.17 (br., 20 H, CH_2), 1.68 (br. s, 4 H, CH_2), 2.40 (s, 96 H, $ArCH_3$), 3.69 (br. s, 4 H, CH_2), 7.30-7.33 (m, 28 H, ArH), 7.34 (d, $^3J_{H,H}$ = 8 Hz, 64 H, ArH), 7.38 (d, $^3J_{H,H}$ = 8.2 Hz, 16 H, ArH), 7.61 (m, 16 H, ArH), 7.69 (br. s, 16 H, ArH), 7.71-7.76 (m, 12 H, ArH), 7.80-7.84 (m, 68 H, ArH), 7.97-8.00 (m, 24 H, ArH), 8.04 (d, $^3J_{H,H}$ = 8.2 Hz, 16 H, ArH), 8.07 (d, $^3J_{H,H}$ = 8 Hz, 4 H, ArH), 8.11 (d, $^3J_{H,H}$ = 8 Hz, 4 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.52, 22.17, 23.01, 26.95, 29.39, 29.52, 30.42, 32.11, 50.36, 127.95, 128.04, 128.33, 128.99, 129.26, 129.91, 130.29, 130.38, 130.48, 130.60, 130.70, 132.26, 132.54, 132.70, 132.92, 135.80, 136.01, 136.24, 136.35, 138.08, 138.30, 138.47, 138.64, 139.57, 139.70, 139.86, 140.18, 140.32, 140.91, 141.08, 142.65, 146.21 ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 10379.1 $[M + Na]^+$, $C_{450}H_{398}N_{32}O_{128}S_{64}Na$ requires 10379.8; elemental analysis calcd (%) for $C_{450}H_{398}N_{32}O_{128}S_{64}$ (10354.27): C 52.20, H 3.87, N 4.33, S 19.82; found C 52.24, H 3.96, N 4.21, S 19.67.

Preparation and isolation of compounds 10 and 11. 2.5 g (9.3 mmol) of dansyl chloride and 3.5 mL of triethylamine were added to a solution of 0.5 g (1.1 mmol) of diamine **2** in 25 mL of dichloromethane. The reaction mixture was stirred at reflux for 24

hrs then the solvent was evaporated and the solid residue was dried in vacuum and subjected to a column chromatography on silica gel with $CHCl_3$/ethyl acetate 5:1. The chromatography resulted in three fractions: compound **10** (135 mg, 18%), compound **11** (200 mg, 20%) and the starting diamine **2** (250 mg, 50%).

Compound 10. The compound was isolated as the second eluted fraction in the chromatographic separation (R_f = 0.32); intensely yellow viscous solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.23 (m, 10 H, $(CH_2)_5$), 1.67 (br. s, 2 H, CH_2), 2.89 (s, 6 H, CH_3), 3.56 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, CH_2), 4.25 (s, 2 H, NH_2), 6.58 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 7.12 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.20 (d, $^3J_{H,H}$ = 9 Hz, 1 H, ArH), 7.56 (m, 2 H, ArH), 7.66 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H), 7.77 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 8.34 (m, 2 H, ArH+NH), 8.58 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.53, 23.03, 27.00, 29.35, 29.53, 30.50, 32.12, 45.79, 49.81, 114.03, 115.95, 118.57, 118.66, 123.55, 127.04, 129.46, 129.83, 129.95, 130.30, 130.78, 131.00, 132.06, 133.99, 135.14, 142.26, 152.24, 152.59 ppm; MS (HiRes ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 695.2002 [*M* + Na]$^+$, calcd monoisotopic peak ($^{12}C_{32}{}^1H_{40}{}^{14}N_4{}^{16}O_6{}^{32}S_3Na$) 695.2008; elemental analysis calcd (%) for $C_{32}H_{40}N_4O_6S_3$ (672.88): C 55.12, H 5.99, N 8.33, S 14.30; found C 55.21, H 5.85, N 8.14, S 14.38.

Compound 11. The compound was isolated as the first eluted fraction in the chromatographic separation (R_f = 0.56); yellow solid m.p. 107 – 109 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.23 (m, 10 H, $(CH_2)_5$), 1.65 (br, 2 H, CH_2), 2.87 (s, 12 H, CH_3), 3.56 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 4.27 (s, 2 H, NH_2), 6.62 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 7.09 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.17-7.22 (m, 4 H, ArH), 7.49 (m, 2 H, ArH), 7.63 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.76 (m, 4 H, ArH), 8.28 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 8.59 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.28, 22.79, 26.81, 29.14, 29.32, 30.21, 31.90, 45.62, 49.64, 113.89, 115.61, 118.82, 123.29, 126.82, 128.71, 128.78, 129.73, 130.06, 130.69, 132.70, 132.98, 133.26, 133.52, 138.38, 141.86, 152.07 ppm; MS (HiRes ESI pos., CH_2Cl_2/CH_3OH): *m/z* = 928.2512 [*M* + Na]$^+$, calcd monoisotopic peak ($^{12}C_{44}{}^1H_{51}{}^{14}N_5{}^{16}O_8{}^{32}S_4Na$) 958.2518; elemental analysis calcd (%) for $C_{44}H_{51}N_5O_8S_4$ (906.16): C 58.32, H 5.67, N 7.73, S 14.15; found C 58.27, H 5.64, N 7.75, S 14.19.

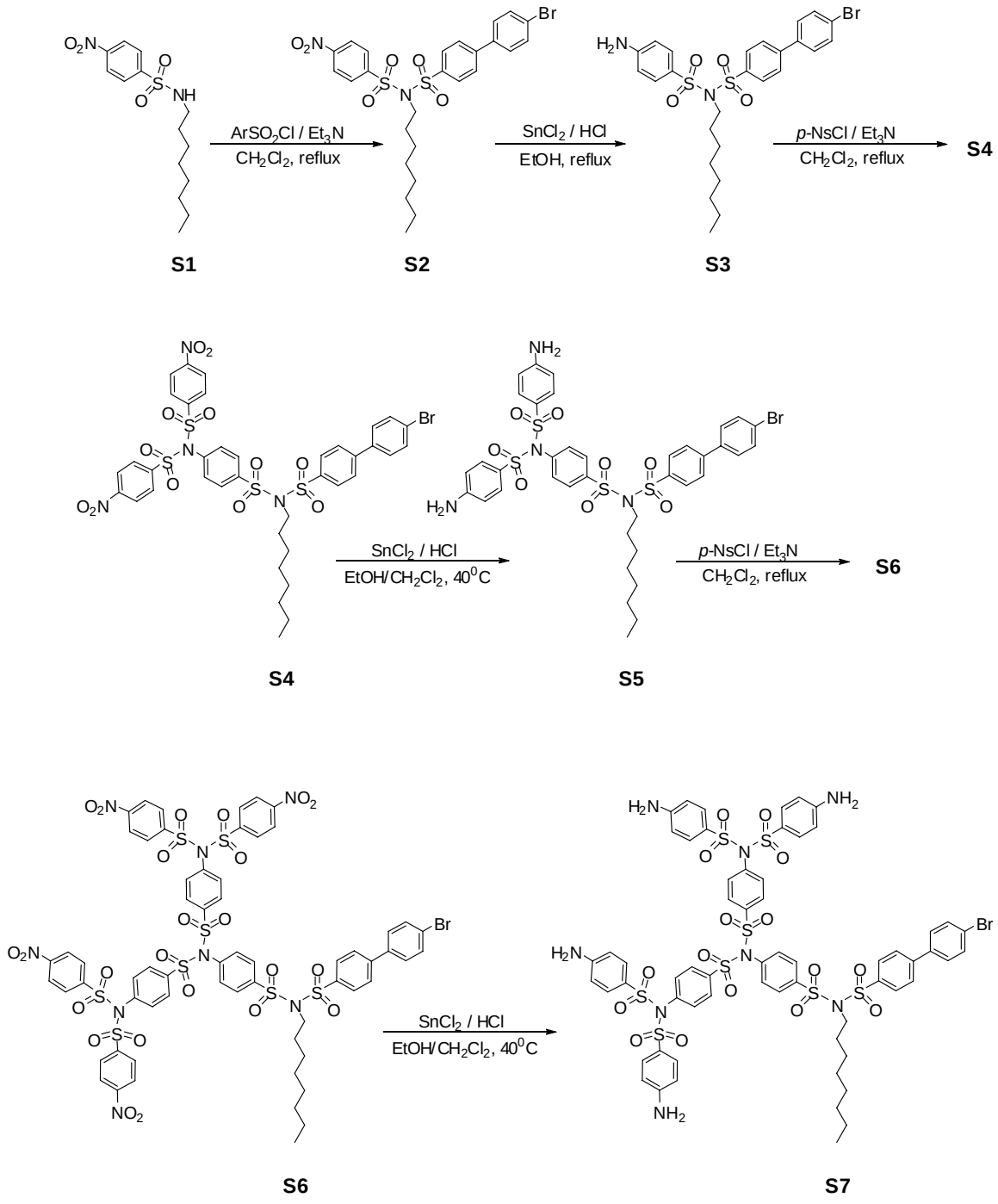
Compound 12. The compound was isolated from the raw product of the synthesis of **3e** in a yield of 3%. Separated by column chromatography (silica gel, CH_2Cl_2, R_f = 0.38); yellowish solid; m.p. 270 – 272 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.84 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.19 (m, 10 H, $(CH_2)_5$), 1.55 (m, 2 H, CH_2), 3.62 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, CH_2), 6.42 (s, 2 H, NH_2), 6.64 (d, $^3J_{H,H}$ = 9 Hz, 2 H, ArH), 7.44 (m, 4 H, ArH), 7.77 (m, 8 H, ArH), 7.95 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H) 8.01-8.06 (m, 6 H, ArH); ^{13}C NMR (125.75 MHz, DMSO-d_6): δ = 14.54, 22.70, 26.55, 29.03, 29.18, 30.05, 31.80, 49.39, 113.14, 122.67, 123.39, 128.27, 129.52, 129.60, 129.89, 130.67, 132.67, 132.83, 137.68, 137.69, 138.55, 142.33, 145.63, 155.08 ppm; MS (ESI pos., $CHCl_3$/MeOH): *m/z* = 1052.0 [*M* + Na]$^+$, elemental analysis calcd (%) for $C_{44}H_{43}N_3O_8S_4Br_2$ (1029.90): C 51.31, H 4.21, N 4.08; found C 51.31, H 4.17, N 4.00.

Compound 13. The compound was isolated from the raw product of the synthesis of **3g** in a yield of 2%. Separated by column chromatography (silica gel, CH_2Cl_2, R_f = 0.07); orange solid; m.p. 197 – 199 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.27 (m, 10 H, CH_2), 1.67 (m. 2 H, CH_2), 3.67 (m, 2 H, CH_2), 7.31 (m, 4 H,

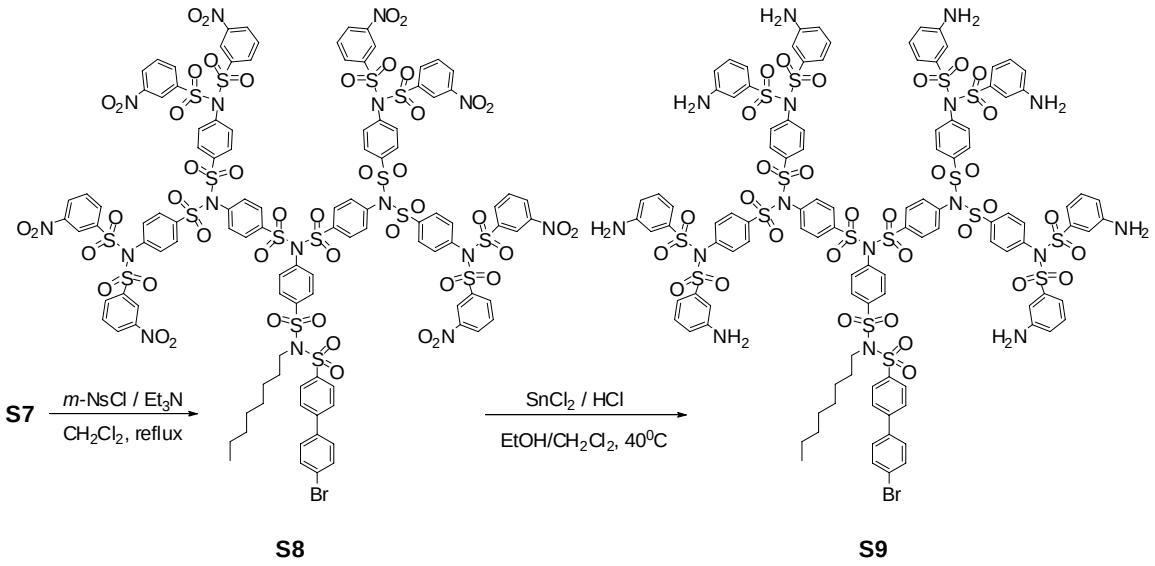
ArH), 7.59 (s, 1 H, NH), 7.76 (t, $^{3}J_{H,H}$ = 8.1 Hz, 1 H, ArH), 7.92 (m, 4 H, ArH), 8.10 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, ArH), 8.20 (d, $^{3}J_{H,H}$ = 8.1 Hz, 1 H, ArH), 8.28 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2 H, ArH), 8.46 (d, $^{3}J_{H,H}$ = 8.1 Hz, 1 H, ArH), 8.61 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H, ArH), 8.78 (s, 1 H, ArH), 8.81 (s, 3 H, ArH); MS (HiRes ESI pos.,$CHCl_3/CH_3OH$): *m/z* = 1017.0859 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{38}{}^{1}H_{38}{}^{14}N_6{}^{16}O_{16}{}^{32}S_5Na$) 1017.0846; elemental analysis calcd (%) for $C_{38}H_{38}N_6O_{16}S_5$ (995.06): C 45.87, H 3.85, N 8.45, S 16.11; found C 45.89, H 3.81, N 8.26, S 16.00.

Compound 14. The compound was isolated from the raw product of the synthesis of **3g** in a yield of 16%. Separated by column chromatography (R_f = 0.25, silica gel, CH_2Cl_2/ethyl acetate 10:1). Colorless solid; m.p. 147 – 149 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, $^{3}J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.25 (m, 10 H, CH_2), 1.71 (m. 2H, CH_2), 3.69 (m, 2 H, CH_2), 4.33 (s, 2 H, NH_2), 6.60 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2 H, ArH), 6.97-7.01 (m, 12 H, ArH), 7.14 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.19-7.22 (m, 8 H, ArH), 7.48 (d, $^{3}J_{H,H}$ = 9 Hz, 2 H, ArH), 7.72 (d, $^{3}J_{H,H}$ = 8.5 Hz, 4 H, ArH), 7.81-7.85 (m, 14 H, ArH), 7.89 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.96 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2 H, ArH) ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 2102.08 $[M + Na]^+$; elemental analysis calcd (%) for $C_{86}H_{85}N_7O_{30}S_{12}$ (2081.40): C 49.63, H 4.12, N 4.71, S 18.49; found C 49.56, H 4.10, N 4.89, S 18.71.

Experimental and characterization data for the compounds S2-S9



Scheme S1. Syntheses of intermediates for the preparation of the dendron **8**



Scheme S1. (Continuation)

Compound S2. A solution containing 5 g (16 mmol) of compound **S1**,[2] 10 g (30 mmol) of 4-biphenylsulfonyl chloride,[3] and 10 mL of triethylamine in 100 mL of dichloromethane was stirred at reflux for 2 hrs. The solvent was removed under reduced pressure and the solid residue was recrystallized from 100 mL of acetonitrile and dried in vacuum affording 6.8 g (70%) of **S2**. Colorless solid; m.p. 181°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^{3}J_{H,\,H}$ = 6.5 Hz, 3 H, CH_3), 1.26 (br. s, 10 H, CH_2), 1. 74 (m. 2H, CH_2), 3.78 (m, 2 H, CH_2), 7.51 (d, $^{3}J_{H,\,H}$ = 9 Hz, 2 H, ArH), 7.66 (d, $^{3}J_{H,\,H}$ = 8.4 Hz, 2 H, ArH), 7.77 (d, $^{3}J_{H,\,H}$ = 8.4 Hz, 2 H, ArH), 8.15 (d, $^{3}J_{H,\,H}$ = 8.4 Hz, 2 H, ArH), 8.29 (d, $^{3}J_{H,\,H}$ = 9 Hz, 2 H, ArH) 8.45 (d, $^{3}J_{H,\,H}$ = 8.4 Hz, 2 H, ArH) ppm; ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.07, 22.60, 26.53, 28.93, 29.09, 29.95, 31.69, 50.06, 123.43, 124.31, 127.61, 128.96, 128.97, 129.54, 132.34, 137.78, 138.35, 145.74, 145.87, 150.59 ppm; MS (HiRes. ESI pos.,): 633.0525 *m/z* = $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{26}{}^{1}H_{29}{}^{14}BrN_2{}^{16}O_6{}^{32}S_2Na$) 633.0528; elemental analysis calcd (%) for $C_{26}H_{29}BrN_2O_6S_2$ (609.55): C 51.23, H 4.80, N 4.60; found C 51.51, H 4.72, N 4.60.

Compound S3. Compound **S2** (6 g, 10 mmol) was added to a stirred solution of $SnCl_2$ (24 g), and concentrated hydrochloric acid (20 mL) in 200 mL of ethanol. The reaction mixture was stirred at 80 °C for 4 hrs then poured into 600 mL of cold deionized water and extracted with CH_2Cl_2 (3x300 mL). The combined organic layers were washed with deionized water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resinous residue was dried in vacuum. Colorless solid; yield 5.18 g (91%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, $^{3}J_{H,\,H}$ = 6.4 Hz, 3 H, CH_3), 1.21 (m, 10 H, CH_2), 1.67 (m. 2H, CH_2), 3.63 (m, 2 H, CH_2), 4.25 (s, 2 H, NH_2), 6.65 (d, $^{3}J_{H,\,H}$ = 8.5 Hz, 2 H, ArH), 7.45 (d, $^{3}J_{H,\,H}$ = 8.5 Hz, 2 H, ArH), 7.59 (d, $^{3}J_{H,\,H}$ = 8.5 Hz, 2 H, ArH), 7.66 (d, $^{3}J_{H,\,H}$ = 8.5 Hz, 2 H, ArH), 7.78 (d, $^{3}J_{H,\,H}$ = 8.5 Hz, 2 H, ArH) 8.05 (d, $^{3}J_{H,\,H}$ = 8.5 Hz, 2 H, ArH) ppm; MS (Hi-Res. ESI pos.,): *m/z* = 601.0802 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{26}{}^{1}H_{31}{}^{14}BrN_2{}^{16}O_4{}^{32}S_2Na$) 601.0806.

Compound S4. Amine **S3** (2 g, 3.4 mmol) was dissolved in a mixture of 50 mL of CH_2Cl_2 and 5 mL triethylamine. Then 4-nitrobenzenesulfonyl chloride (4 g, 18 mmol) was added at stirring and the reaction mixture was refluxed for 4 hrs. The solvent was

removed under reduced pressure and the residue was triturated with methanol. The brownish precipitate was filtered and recrystallized from methanol-dichloromethane affording 1.95 g (60%) of yellowish crystalline powder. M.p. 185 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^{3}J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.27 (m, 10 H, CH_2), 1.75 (m. 2H, CH_2), 3.77 (m, 2 H, CH_2), 7.28 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.52 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.66 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.78 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H, ArH), 8.12-8.20 (m, 8 H, ArH), 8.48 (d, $^{3}J_{H,H}$ = 9 Hz, 2 H, ArH) ppm; ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 14.23, 22.76, 26.71, 29.13, 29.27, 30.13, 31.86, 50.15, 123.57, 124.79, 127.77, 129.06, 129.11, 129.79, 130.29, 132.13, 132.50, 137.80, 137.95, 138.51, 142.90, 143.88, 146.00, 151.32 ppm; MS (Hi-Res. ESI pos.,): *m/z* = 971.0368 $[M + Na]^+$ calcd monoisotopic peak ($^{12}C_{37}{}^{1}H_{37}{}^{14}BrN_4{}^{16}O_{12}{}^{32}S_4Na$) 971.0372; elemental analysis calcd (%) for $C_{38}H_{37}BrN_4O_{12}S_4$ (949.88): C 48.05, H 3.93, Br 8.41, N 5.90, S 13.50; found C 48.08 H 3.94, Br 8.54, N 5.70, S 13.48.

Compound S5. A solution of compound **S4** (1.5 g, 1.6 mmol) in 80 mL of CH_2Cl_2 was poured into a stirred solution of $SnCl_2$ (9 g), and concentrated hydrochloric acid (4 mL) in 100 mL of ethanol. The reaction mixture was stirred at 50 °C for 4 hrs then poured into 400 mL of deionized water and extracted with CH_2Cl_2 (2x200 mL). The combined organic layers were washed with deionized water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting solid residue was dried in vacuum. Yield 1.37 g (98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^{3}J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.27 (m, 10 H, CH_2), 1.75 (m. 2H, CH_2), 3.72 (m, 2 H, CH_2), 6.70 (d, $^{3}J_{H,H}$ = 9 Hz, 4 H, ArH), 7.28 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.51 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.64-7.69 (m, 6 H, ArH), 7.35 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H, ArH), 8.00-8.05 (m, 4 H, ArH) ppm; MS (Hi-Res. ESI pos.,): *m/z* = 911.0878 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{38}{}^{1}H_{41}{}^{14}BrN_4{}^{16}O_8{}^{32}S_4Na$) 911.0888.

Compound S6. 1.3 g of **S5** was used in the reaction. The raw product was recrystallized from THF/methanol yielding 1.32 g (55%) of the yellowish crystalline powder. M.p. 249 °C; ^{1}H NMR (500 MHz, DMSO[d_6]): δ = 0.77 (t, $^{3}J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.13 (m, 10 H, CH_2), 1.58 (m. 2H, CH_2), 3.78 (m, 2 H, CH_2), 7.43 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, ArH), 7.48 (d, $^{3}J_{H,H}$ = 8.5 Hz, 4 H, ArH), 7.72 (m, 4 H, ArH), 7.90 (d, $^{3}J_{H,H}$ = 8.5 Hz, 4 H, ArH), 7.96-8.03 (m, 4 H, ArH), 8.11 (d, $^{3}J_{H,H}$ = 8 Hz, 2 H, ArH), 8.15 (d, $^{3}J_{H,H}$ = 8.5 Hz, 8 H, ArH), 8.50 (d, $^{3}J_{H,H}$ = 8.5 Hz, 8 H, ArH) ppm; ^{13}C NMR (125.75 MHz, DMSO-d_6): δ = 14.48, 22.61, 26.39, 28.94, 29.10, 30.00, 31.72, 50.11, 123.32, 123.93, 125.78, 127.53, 128.29, 129.14, 129.93, 130.63, 130.72, 132.73, 133.20, 133.55, 137.73, 138.11, 138.42, 138.73, 140.22, 142.21, 143.04, 145.30, 151.75 ppm; elemental analysis calcd (%) for $C_{62}H_{53}BrN_8O_{24}S_8$ (1630.55): C 45.67, H 3.28, Br 4.90, N 6.87, S 15.73; found C 45.85 H 3.34, Br 4.88, N 6.89, S 15.97.

Compound S7. 1 g of **S6** was used in the reaction. Yellowish solid; yield 0.88 g (95%); ^{1}H NMR (300 MHz, DMSO[d_6]): δ = 0.81 (t, $^{3}J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.18 (m, 10 H, CH_2), 1.60 (m. 2H, CH_2), 3.81 (m, 2 H, CH_2), 6.42 (s, 8 H, NH_2), 6.64 (d, $^{3}J_{H,H}$ = 8.7 Hz, 8 H, ArH), 7.31 (d, $^{3}J_{H,H}$ = 8.1 Hz, 4 H, ArH), 7.36-7.39 (m, 10 H, ArH), 7.75 (br. s, 4 H, ArH), 7.83 (d, $^{3}J_{H,H}$ = 8.1 Hz, 4 H, ArH), 7.97-8.04 (m, 4 H, ArH), 8.11 (d, $^{3}J_{H,H}$ = 7.2 Hz, 2 H, ArH) ppm; MS (Hi-Res. ESI pos.,): *m/z* = 1531.1050 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{62}{}^{1}H_{61}{}^{14}BrN_8{}^{16}O_{16}{}^{32}S_8Na$) 1531.1052.

Compound S8. 0.8 g of **S7** was used in the reaction. The raw product was purified by column chromatography on silica gel (R_f = 0.5, CH_2Cl_2/ethylacetate 50/1) affording 0.82

g (52%) of the product as a yellowish solid. M.p. 212-214°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, $^3J_{H,\,H}$ = 6.4 Hz, 3 H, CH_3), 1.18 (m, 10 H, CH_2), 1.63 (m. 2H, CH_2), 3.64 (m, 2 H, CH_2), 7.21-7.25 (m, 6 H, ArH), 7.28 (d, $^3J_{H,\,H}$ = 8 Hz, 8 H, ArH), 7.45 (d, $^3J_{H,\,H}$ = 8 Hz, 2 H, ArH), 7.59 (d, $^3J_{H,\,H}$ = 8 Hz, 2 H, ArH), 7.68 (d, $^3J_{H,\,H}$ = 8 Hz, 2 H, ArH), 7.81-7.85 (m, 12 H, ArH), 7.89-7.93 (m, 10 H, ArH), 8.06 (d, $^3J_{H,\,H}$ = 8 Hz, 2 H, ArH), 8.26 (d, $^3J_{H,\,H}$ = 7.5 Hz, 8 H, ArH), 8.54 (d, $^3J_{H,\,H}$ = 8 Hz, 2 H, ArH), 8.71 (s, 8 H, ArH) ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 3014.80 $[M + Na]^+$; elemental analysis calcd (%) for $C_{110}H_{85}BrN_{16}O_{48}S_{16}$ (2991.87): C 44.16, H 2.86, Br 2.67, N 7.49, S 17.15; found C 44.46, H 2.98, Br 2.84, N 7.32, S 17.03.

Compound S9. 0.8 g of **S8** was used in the reaction. Yellowish solid; yield 0.65 g (89%); ^{1}H NMR (500 MHz, DMSO[d_6]): δ = 0.76 (t, $^3J_{H,\,H}$ = 6.4 Hz, 3 H, CH_3), 1.11 (m, 10 H, CH_2), 1.55 (br. s, 2H, CH_2), 3.75 (br. s, 2 H, CH_2), 5.77 (s, 16 H, NH_2), 6.85 (d, $^3J_{H,\,H}$ = 7.5 Hz, 8 H, ArH), 6.89 (d, $^3J_{H,\,H}$ = 7.5 Hz, 8 H, ArH), 7.05 (s, 8 H, ArH), 7.23 (m, 8 H, ArH), 7.36 (d, $^3J_{H,\,H}$ = 8 Hz, 8 H, ArH), 7.44-7.47 (m, 6 H, ArH), 7.71 (br. s, 4 H, ArH), 7.87 (d, $^3J_{H,\,H}$ = 8 Hz, 8 H, ArH), 7.97 (m, 4 H, ArH), 8.07 (d, $^3J_{H,\,H}$ = 8 Hz, 4 H, ArH), 8.11 (d, $^3J_{H,\,H}$ = 8 Hz, 2 H, ArH) ppm; MS (MALDI-TOF, dithranol+Na-TFA): *m/z* = 2774.80 $[M + Na]^+$.

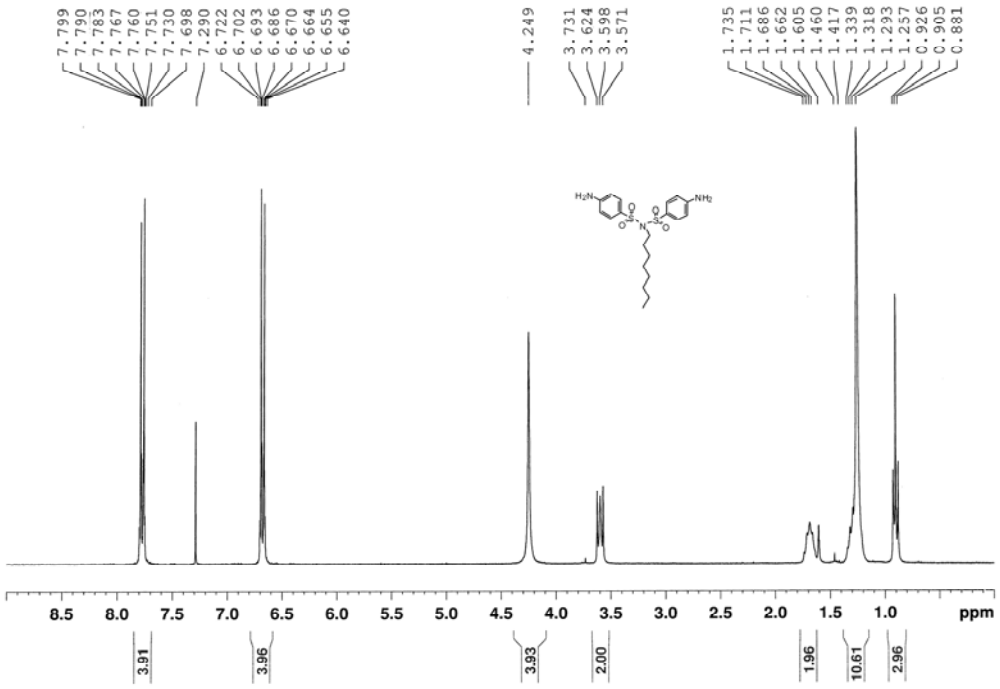
References

(1) Kandre, R.; Feldman, K.; Meijer, H. E. H.; Smith, P.; Schlüter, A. D. *Angew. Chem. Int. Ed.* **2007**, *46*, 4956-4959.

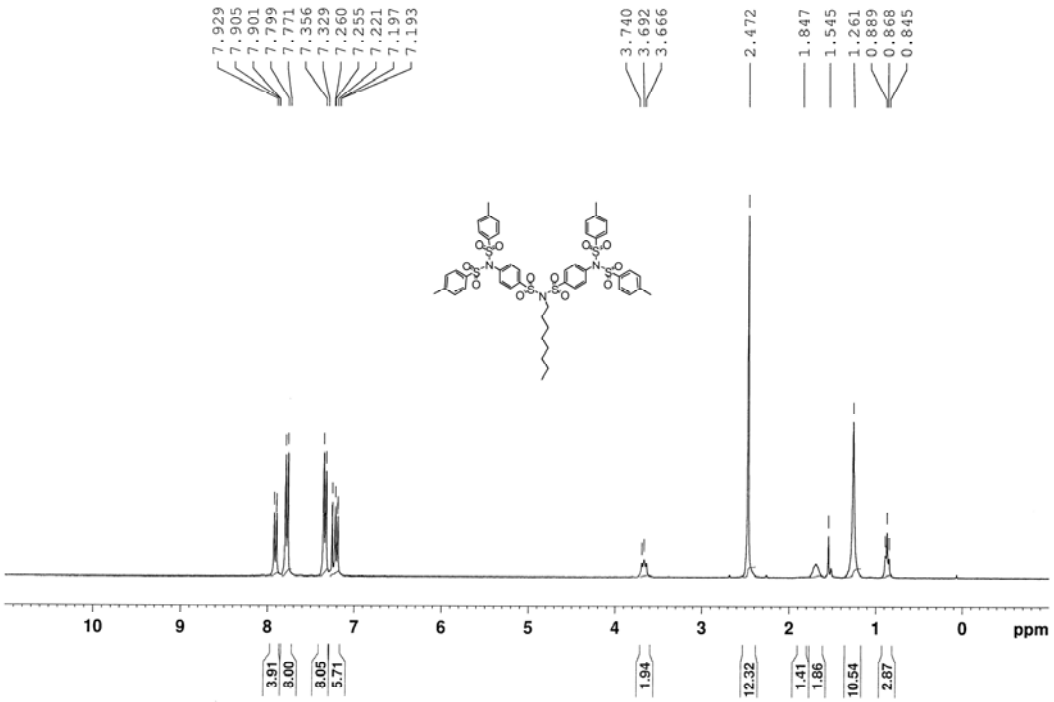
(2) Lukin, O.; Gramlich, V.; Kandre, R.; Zhun, I.; Felder, T.; Schalley, C. A.; Dolgonos, G. *J. Am. Chem. Soc*. **2006**, *128*, 8964-8974.

(3) O'Brien, P. M.; Ortwine, D. F.; Pavlovsky, A. G.; Picard, J. A.; Sliskovic, D. R.; Roth, B. D.; Dyer, R. D.; Man, C. F.; Hallak, H. *J. Med. Chem*. **2000**, *43*, 156-166.

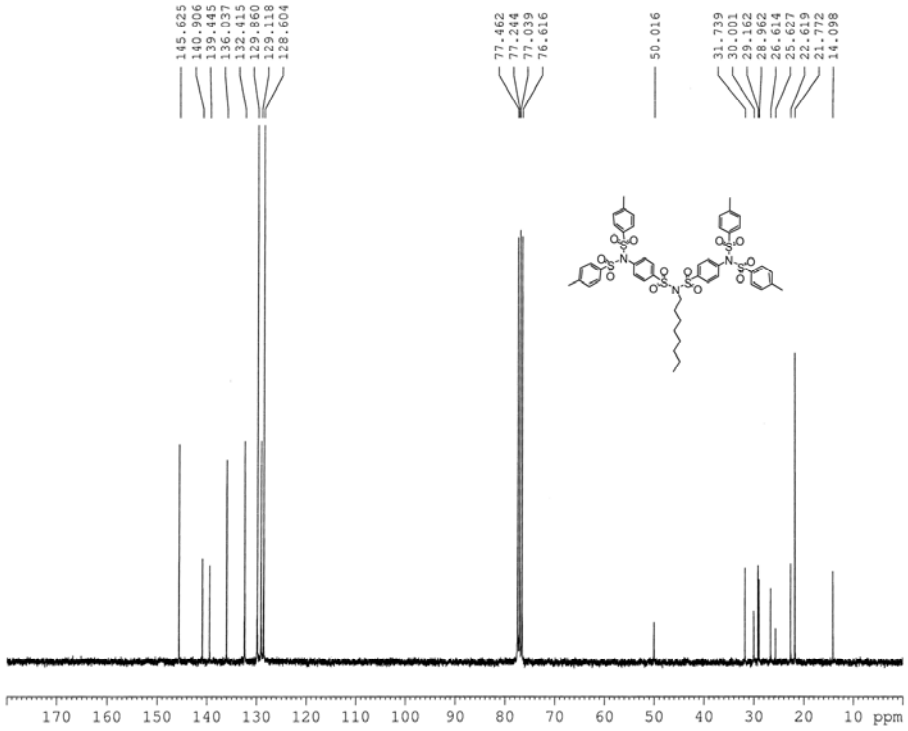
Compound **2**: 1H NMR, 300 MHz, CDCl3



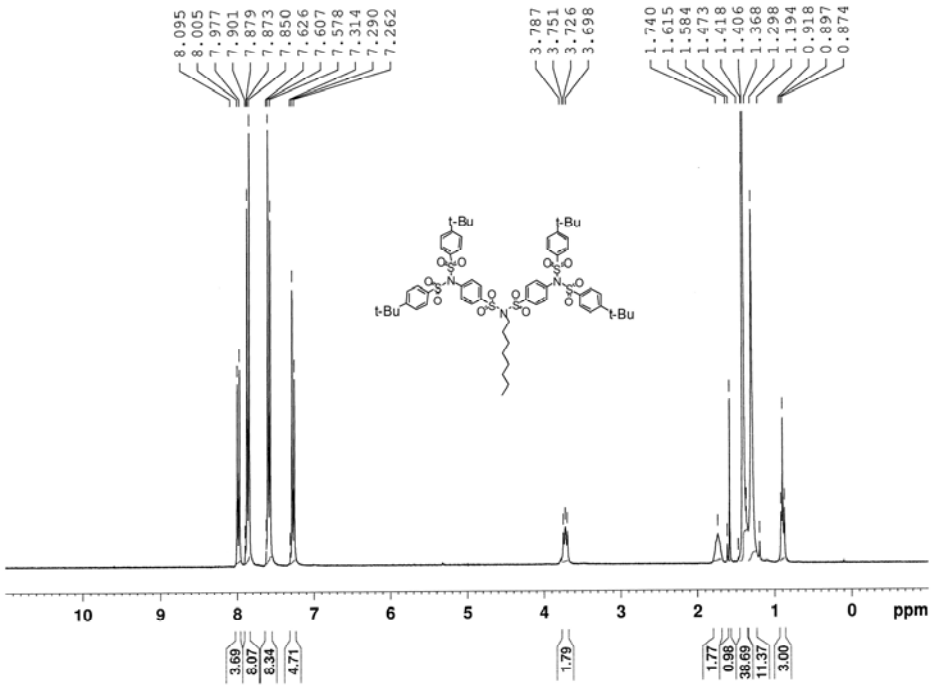
Compound **3a**: 1H NMR, 300 MHz, CDCl3



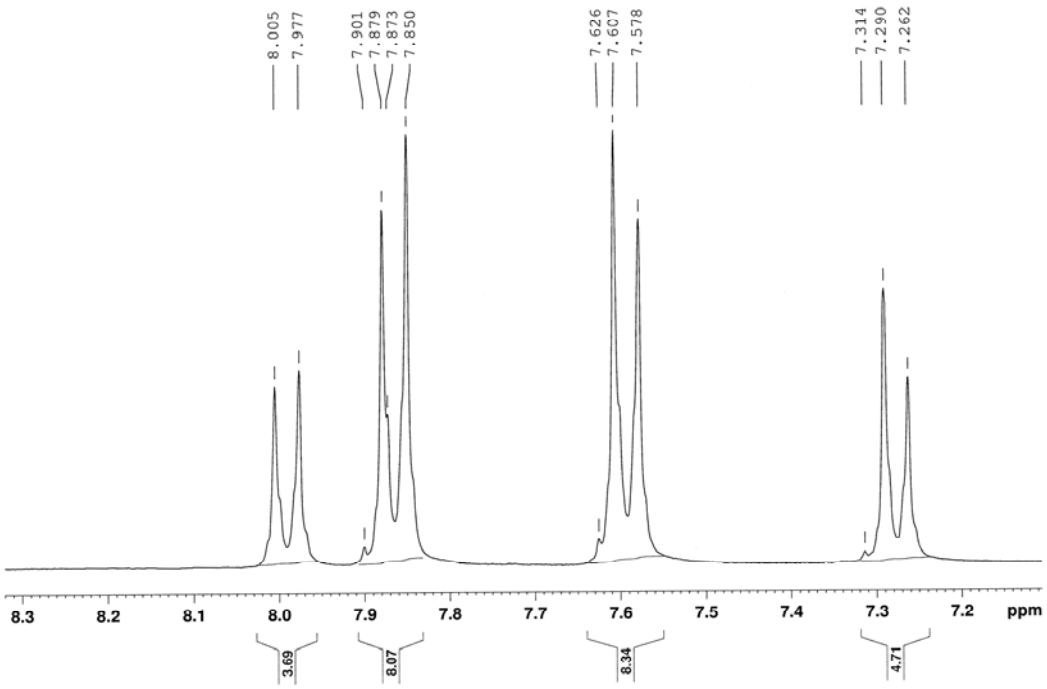
Compound **3a**: 13C NMR, 75 MHz, CDCl3



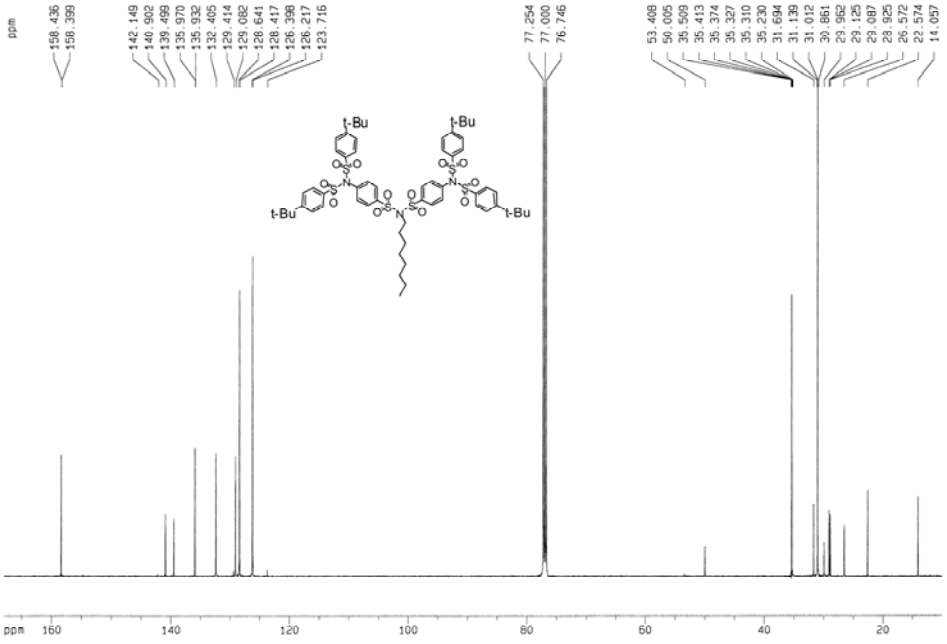
Compound **3b**: 1H NMR, 300 MHz, CDCl3



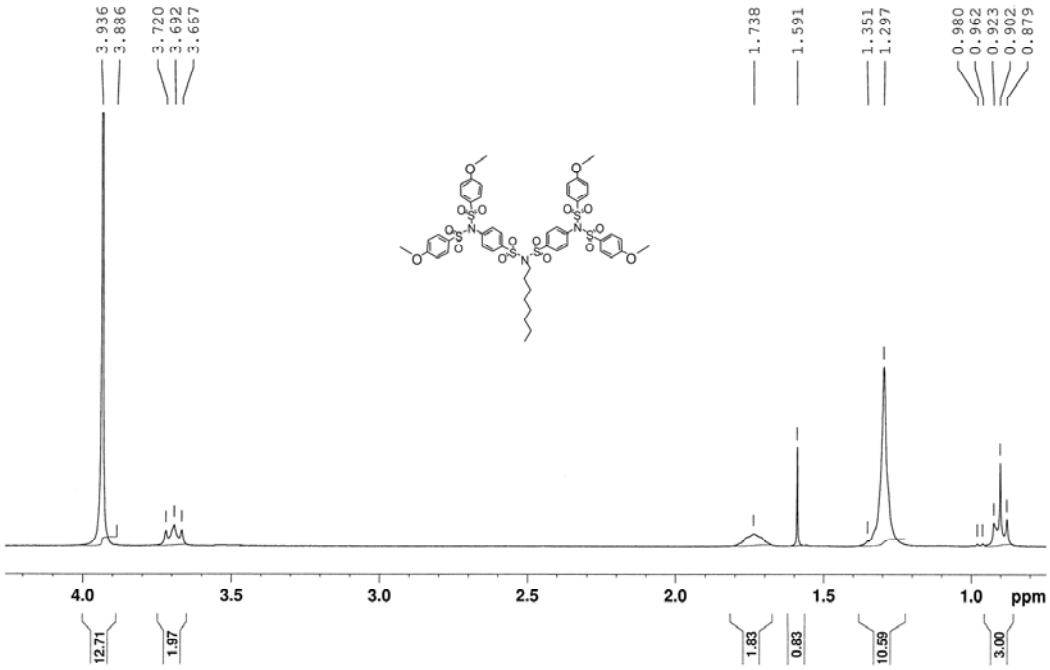
Compound **3b**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



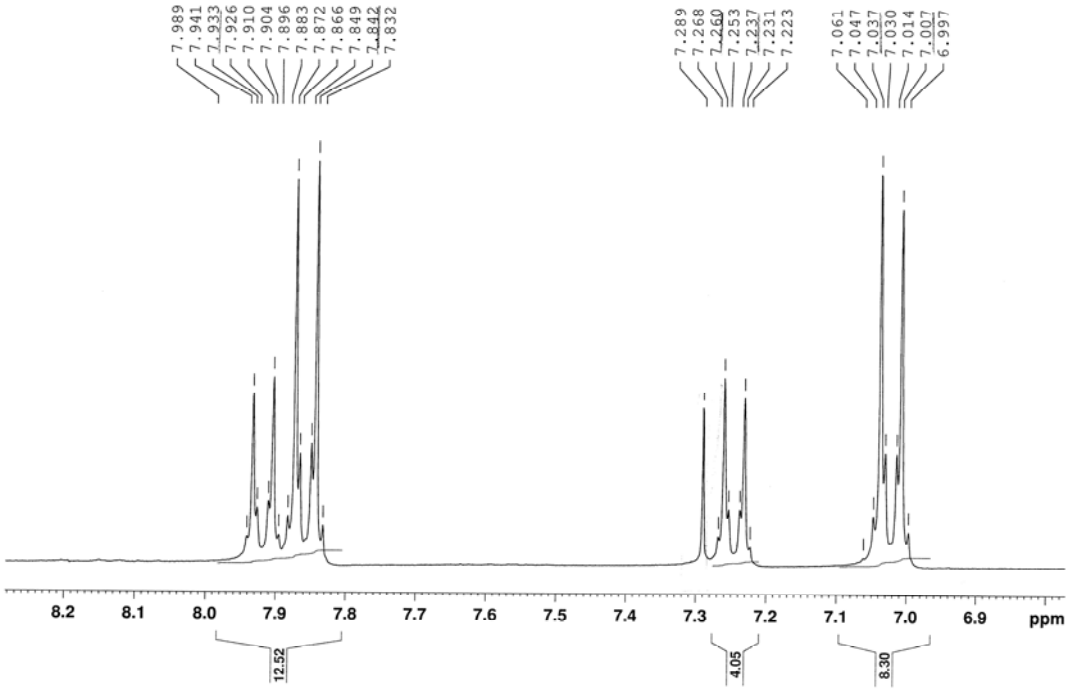
Compound **3b**: 13C NMR, 125 MHz, CDCl3



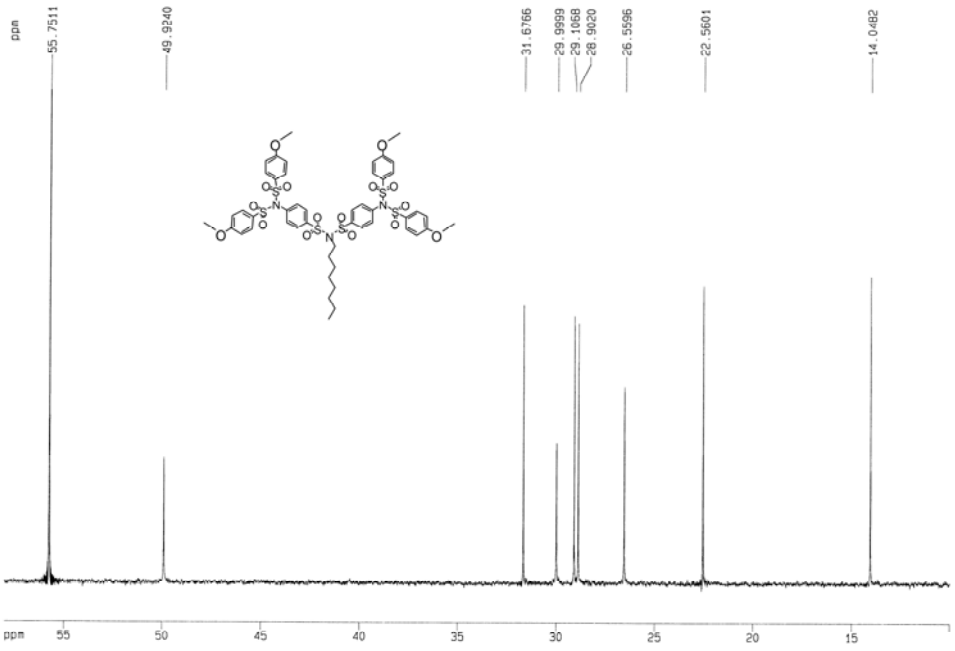
Compound **3c**: 1H NMR, 300 MHz, CDCl3 (Aliphatic region)



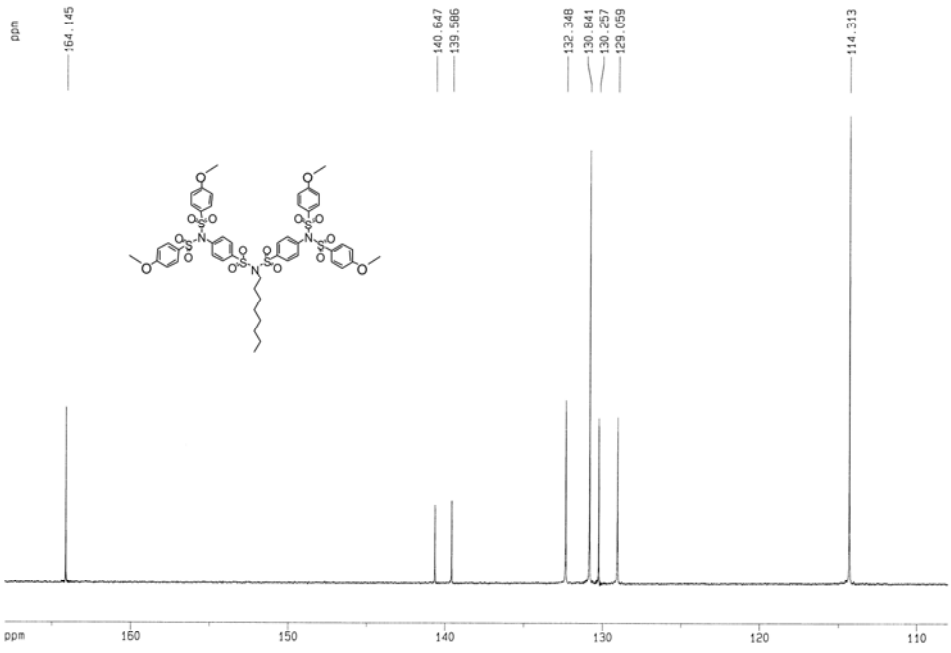
Compound **3c**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



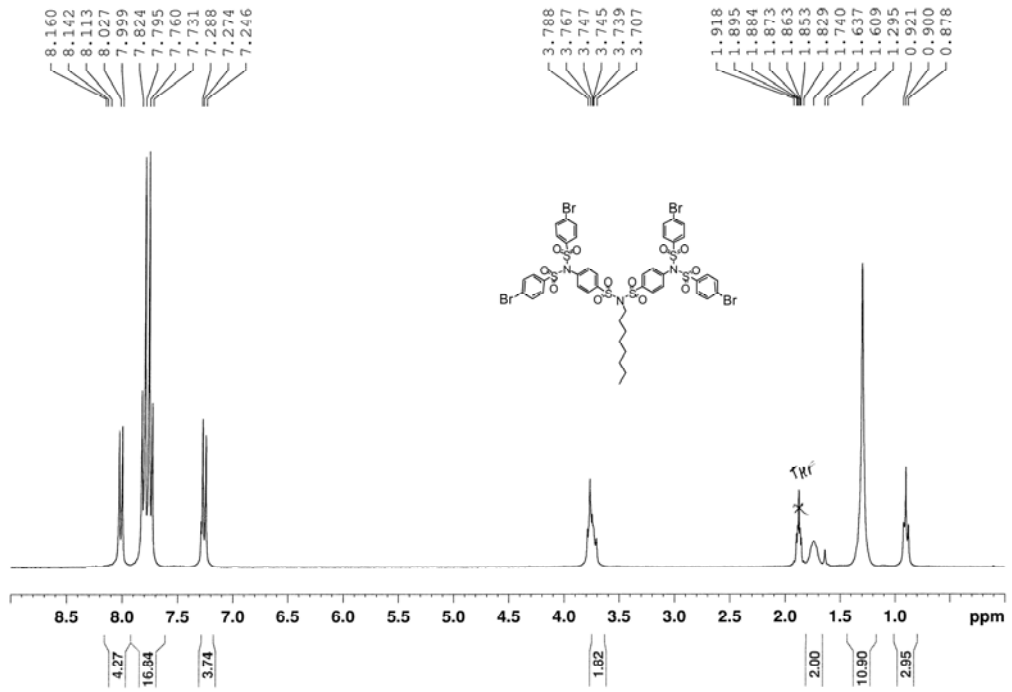
Compound **3c**: 13C NMR, 125 MHz, CDCl3 (Aliphatic region)



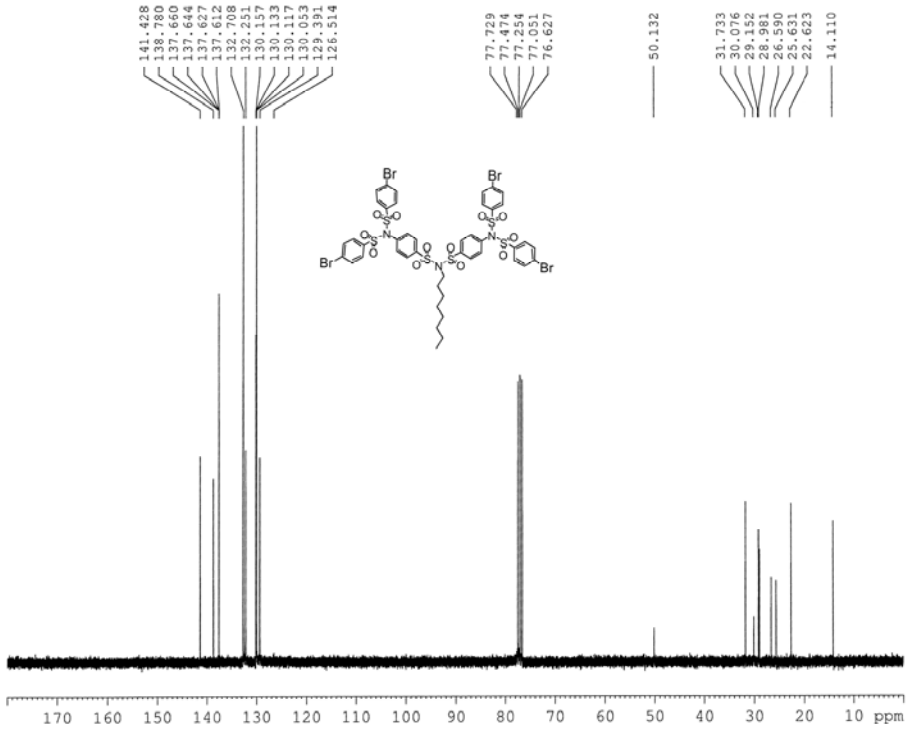
Compound **3c**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



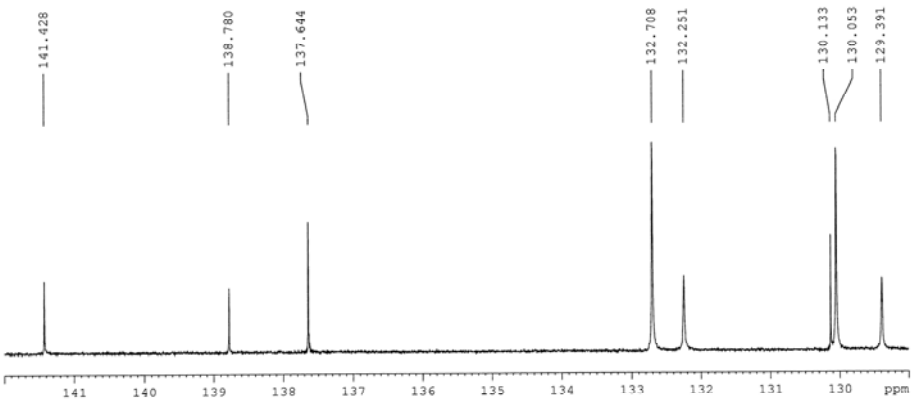
Compound **3d**: 1H NMR, 300 MHz, CDCl3



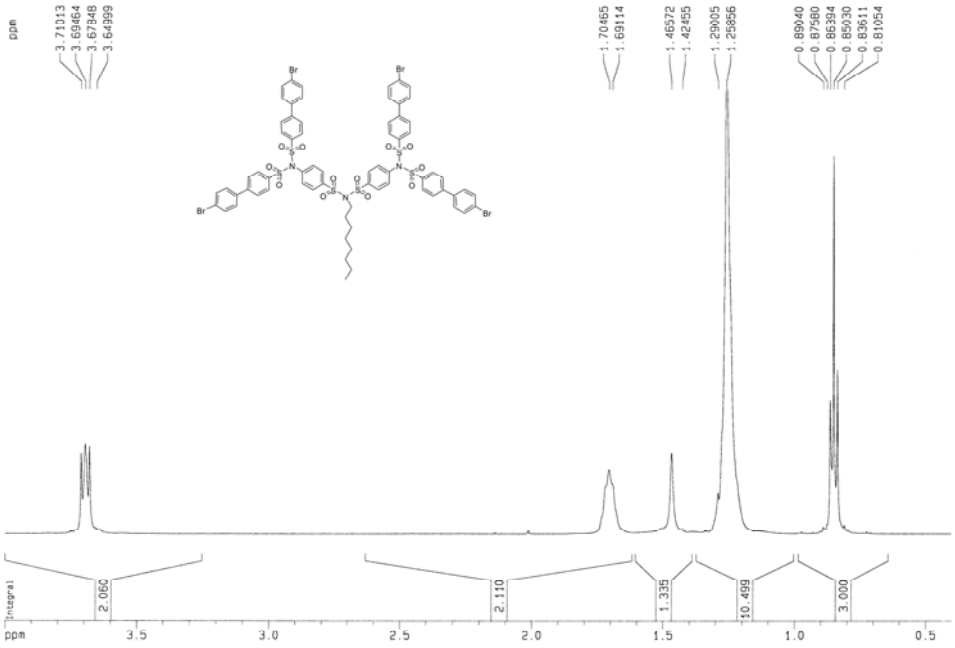
Compound **3d**: 13C NMR, 75 MHz, CDCl3



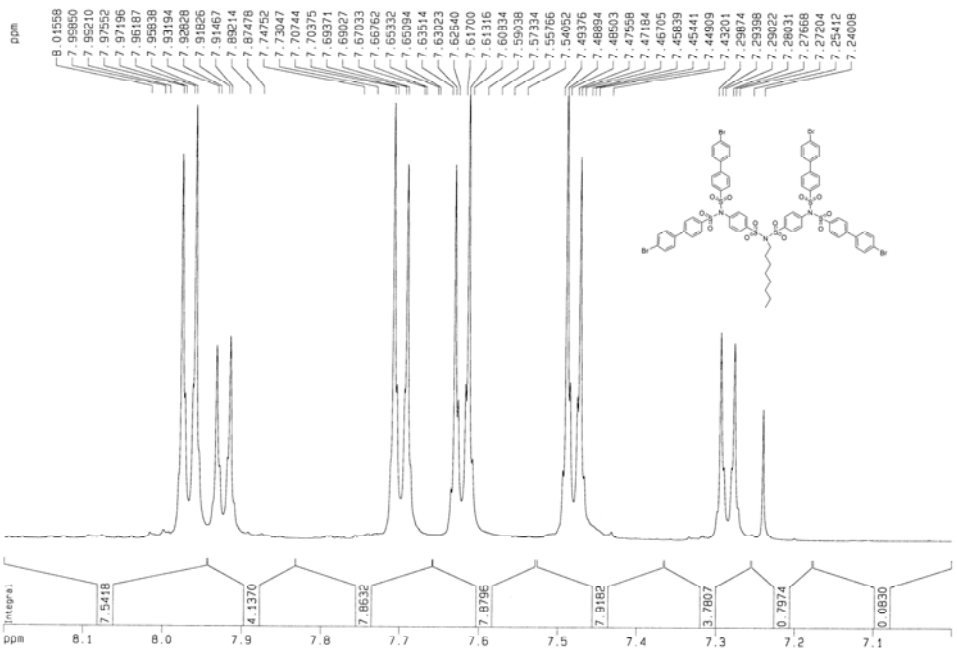
Compound **3d**: 13C NMR, 75 MHz, CDCl3 (Aromatic region)



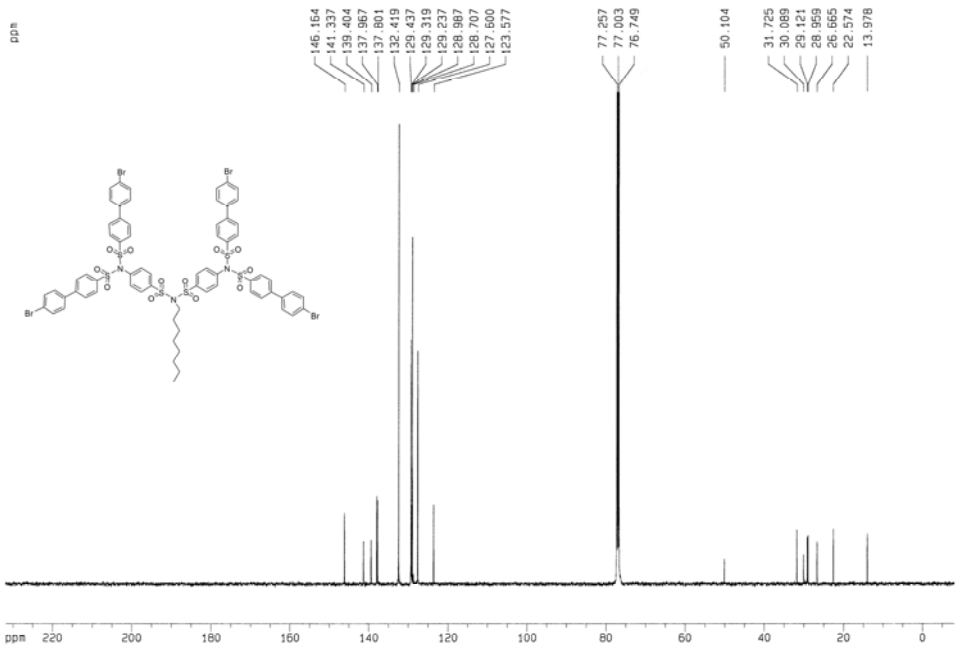
Compound **3e**: 1H NMR, 500 MHz, CDCl3 (Aliphatic region)



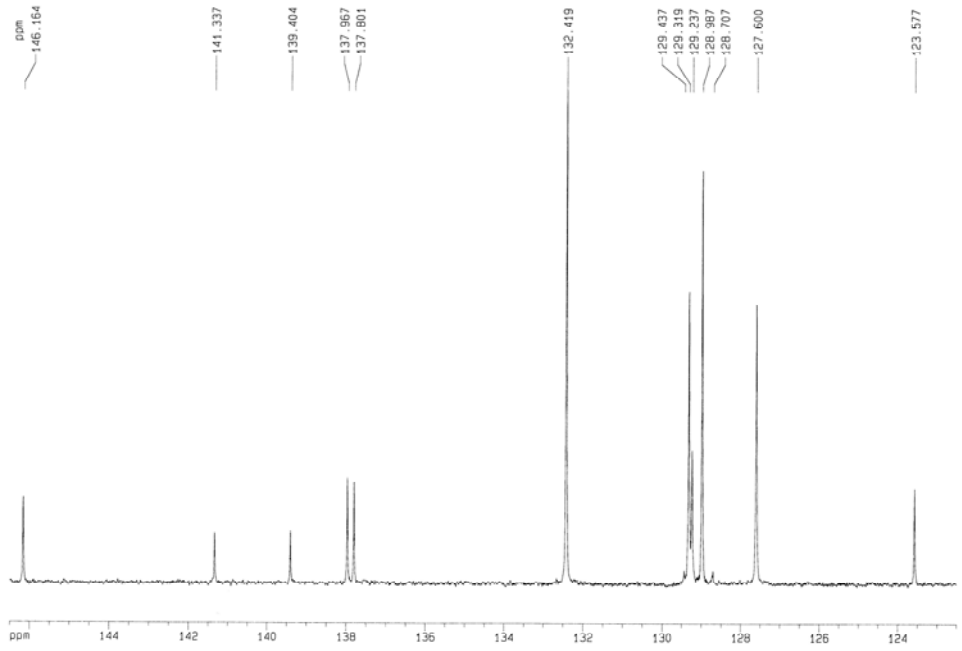
Compound **3e**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



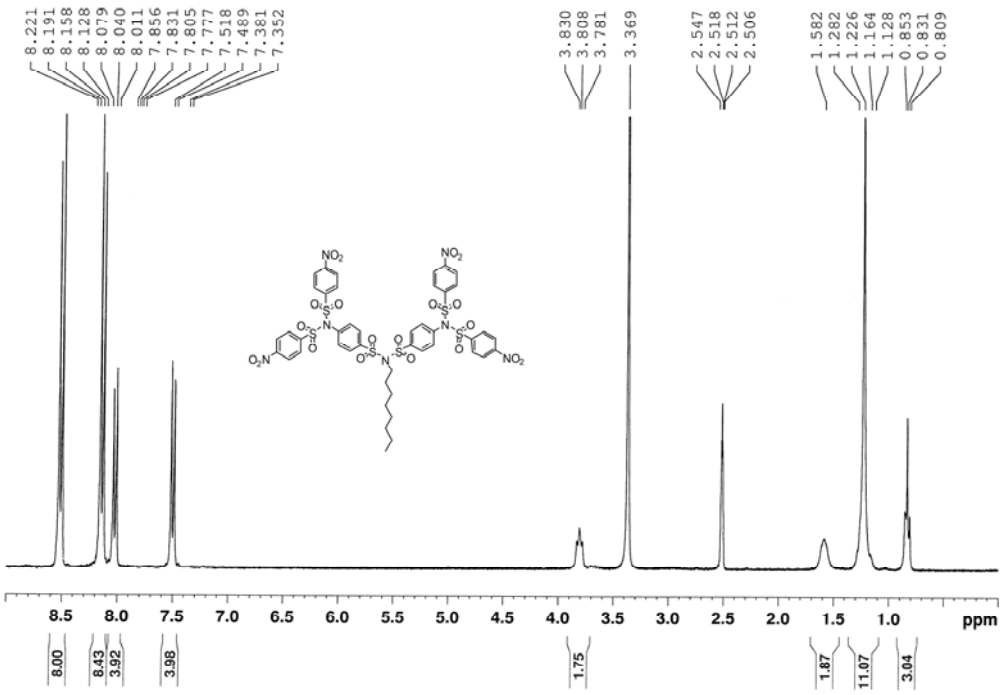
Compound **3e**: 13C NMR, 125 MHz, CDCl3



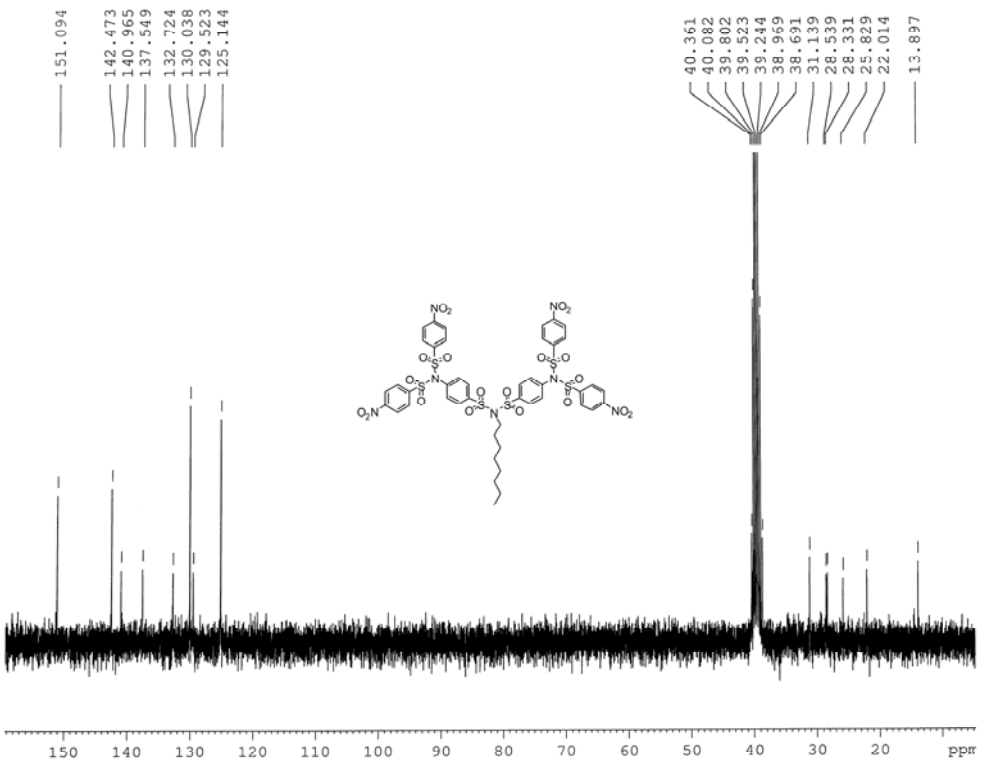
Compound **3e**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



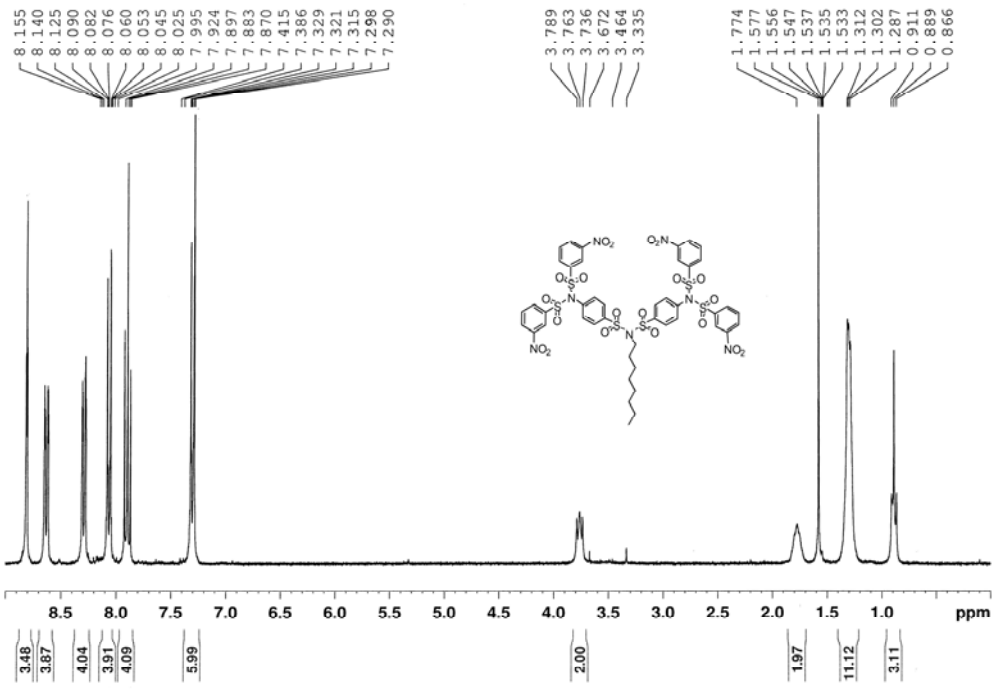
Compound **3f**: 1H NMR, 300 MHz, DMSO-d6



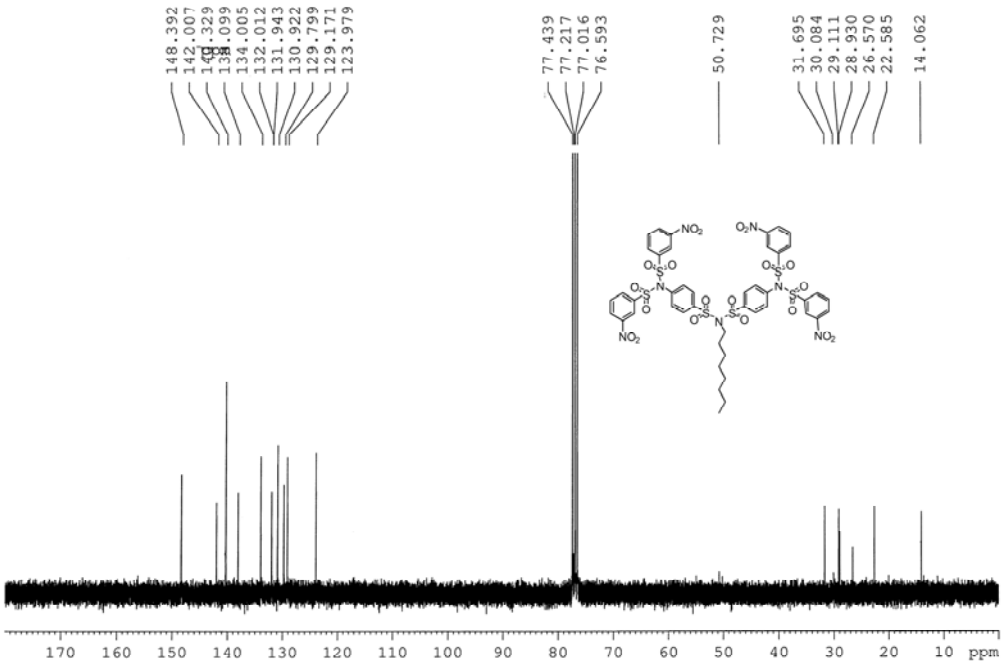
Compound **3f**: 13C NMR, 75 MHz, DMSO-d6



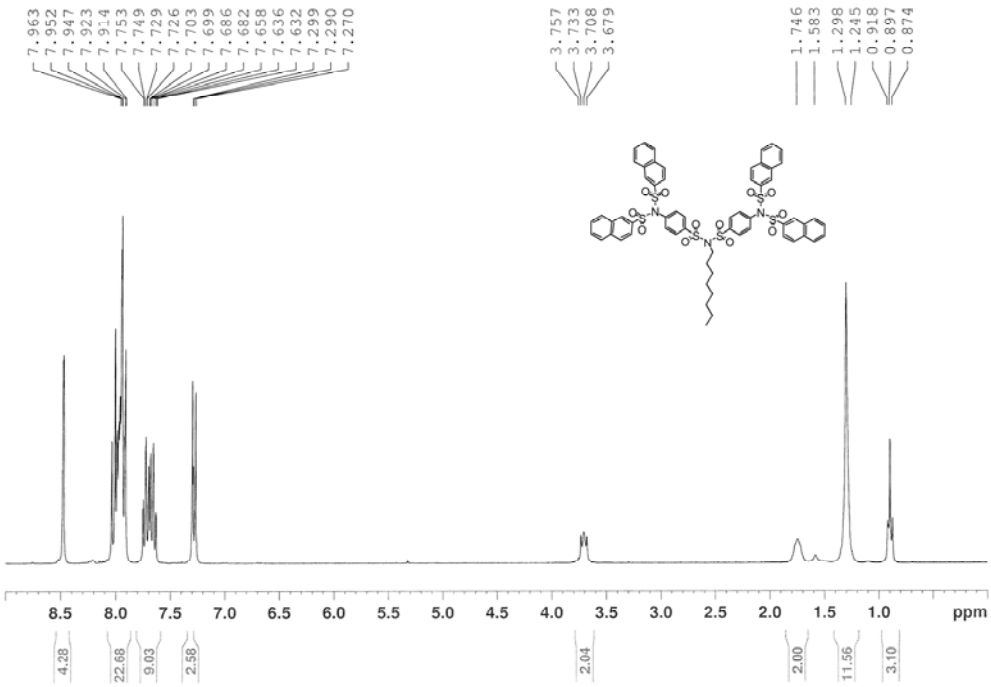
Compound **3g**: 1H NMR, 300 MHz, CDCl3



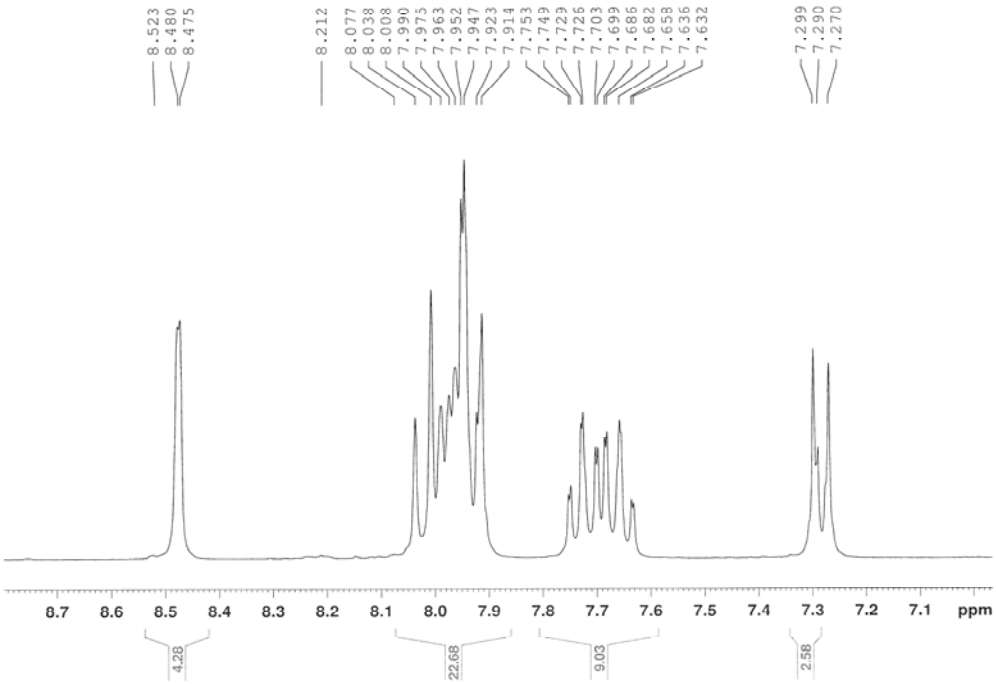
Compound **3g**: 13C NMR, 75 MHz, CDCl3



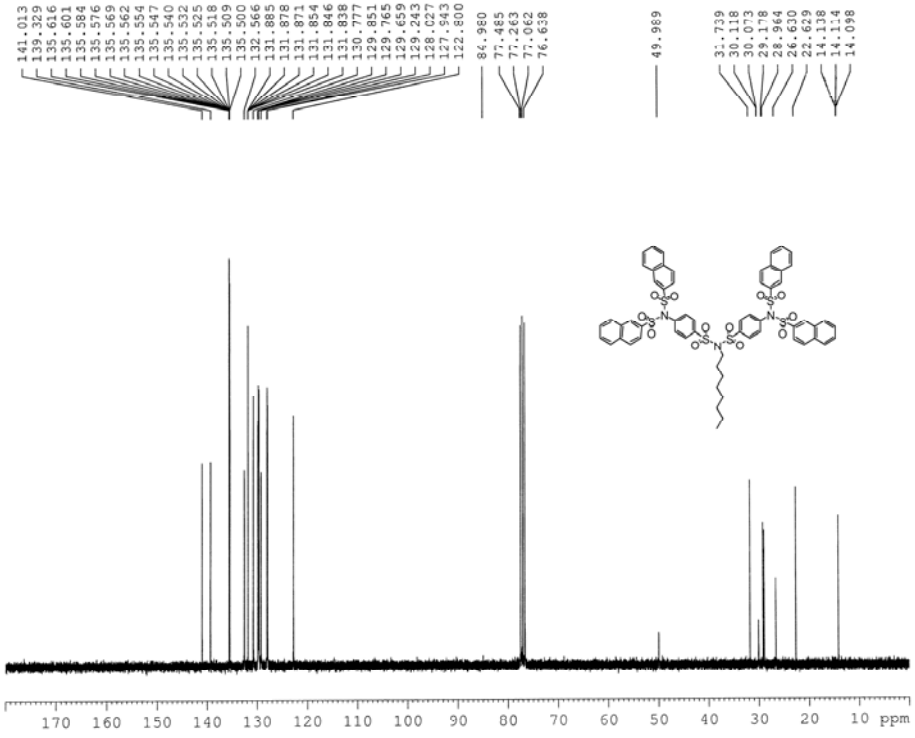
Compound **3h**: 1H NMR, 300 MHz, CDCl3



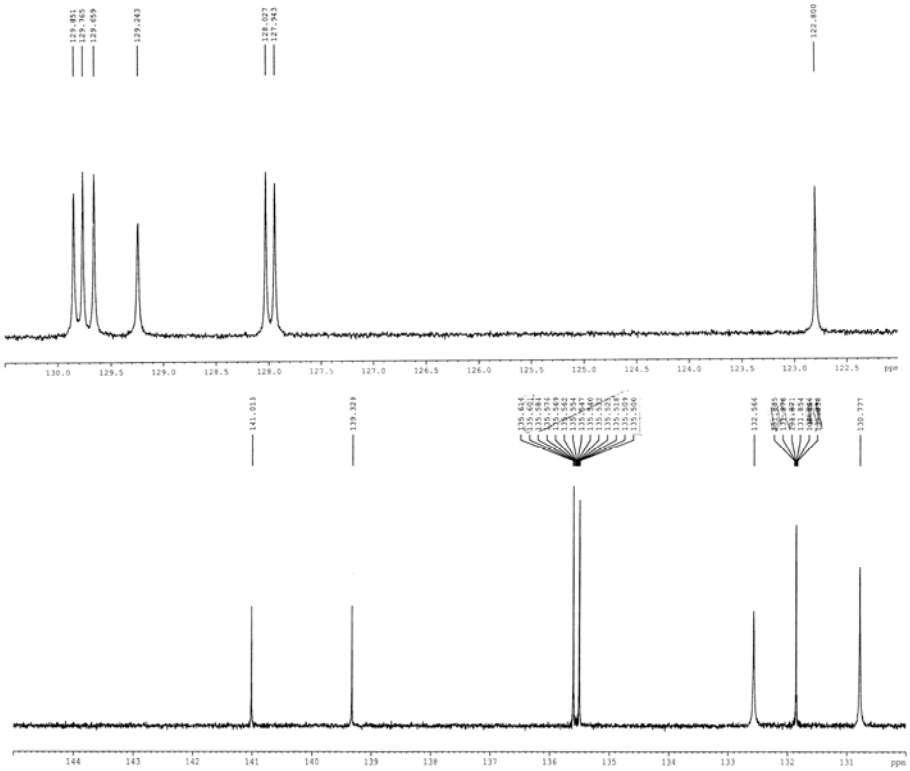
Compound **3h**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



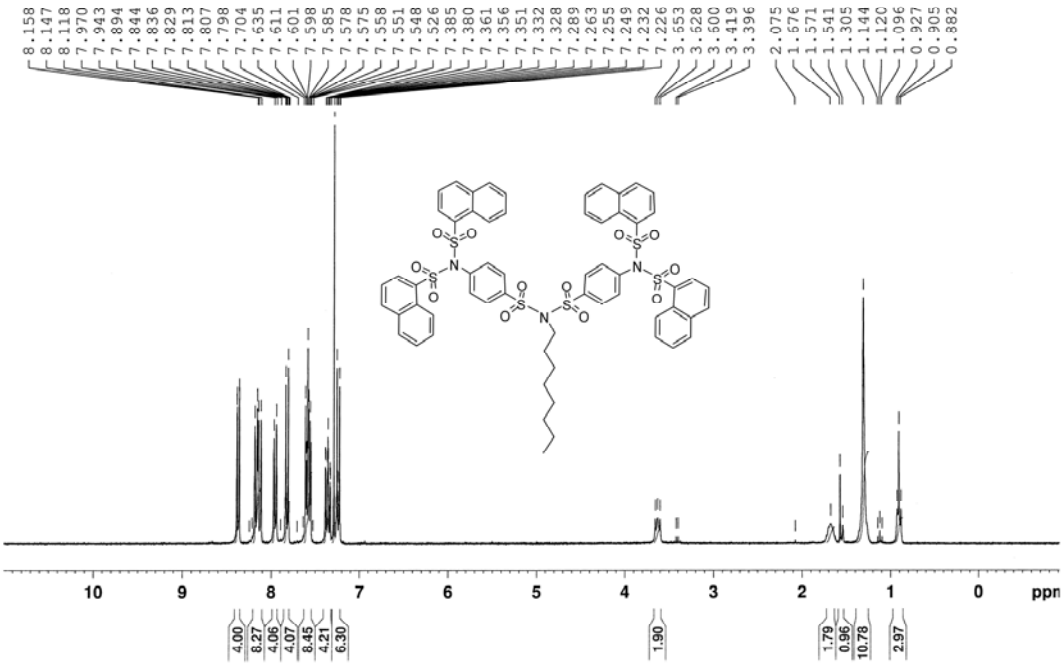
Compound **3h**: 13C NMR, 75 MHz, CDCl3



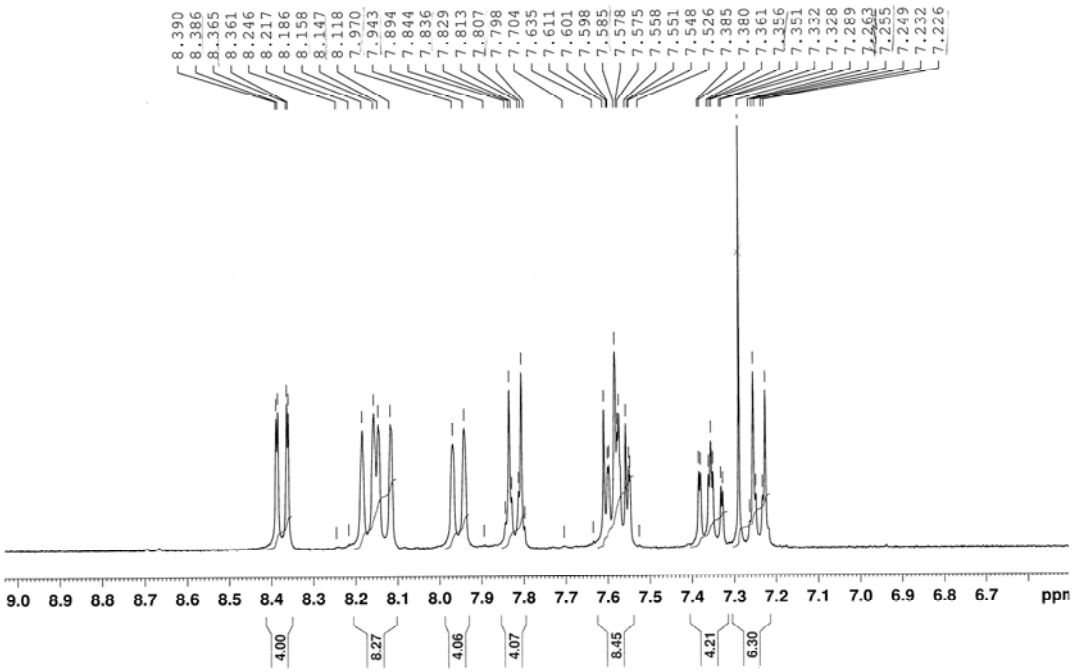
Compound **3h**: 13C NMR, 75 MHz, CDCl3 (Aromatic region)



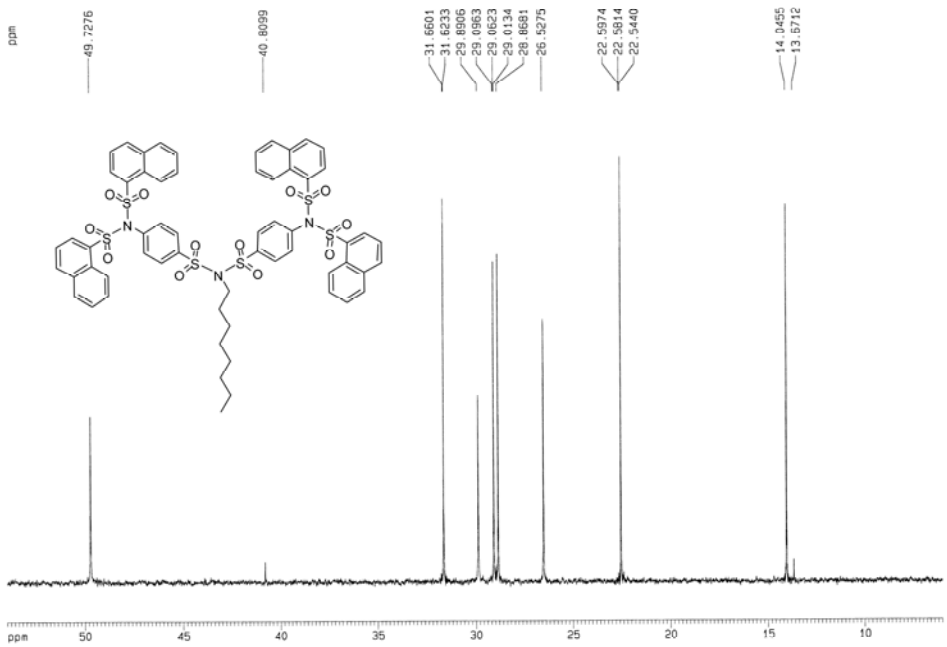
Compound **3i**: 1H NMR, 300 MHz, CDCl3



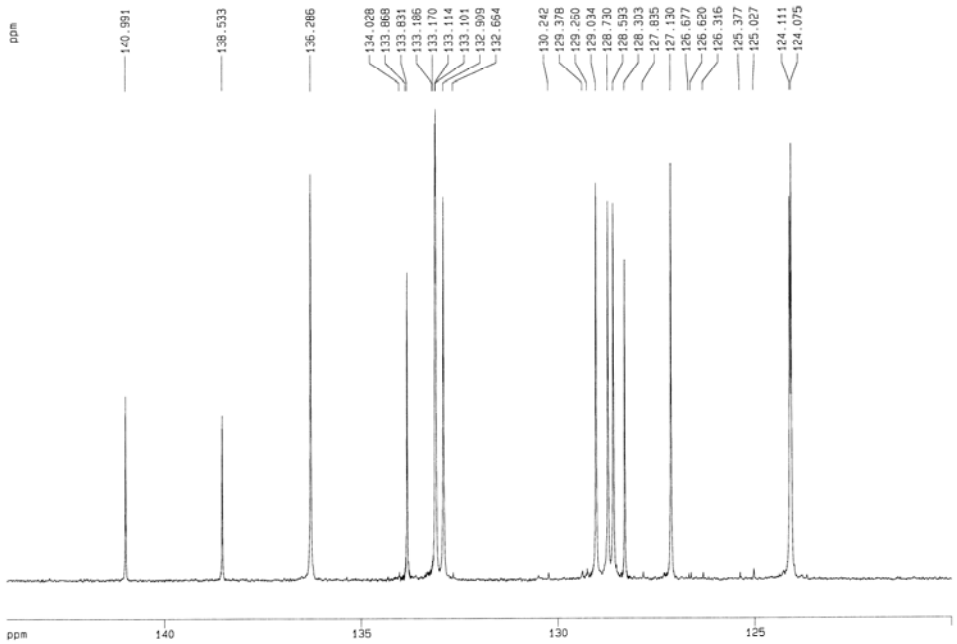
Compound **3i**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



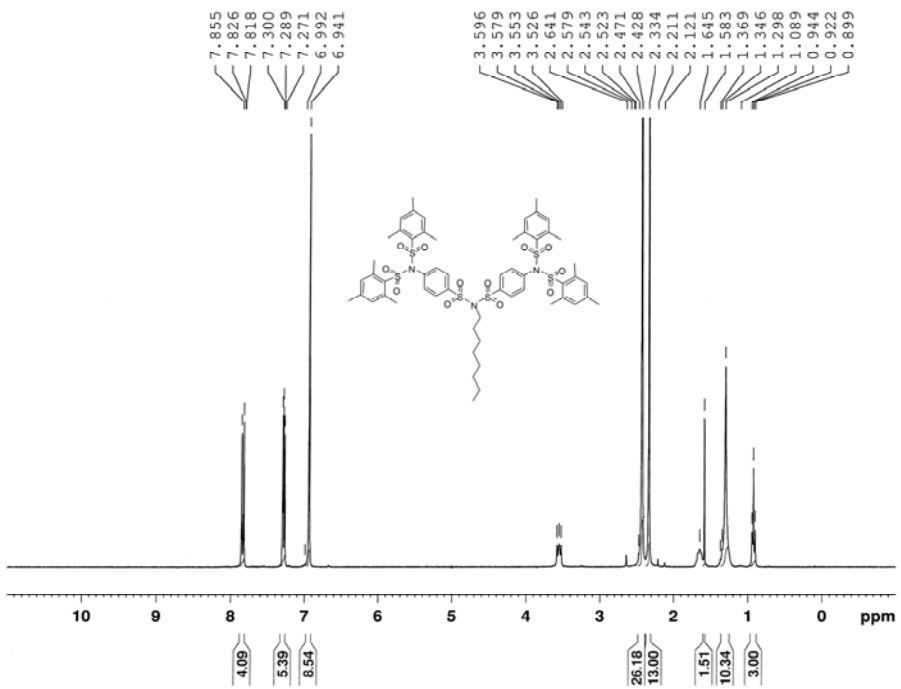
Compound **3i**: 13C NMR, 75 MHz, CDCl3 (Aliphatic region)



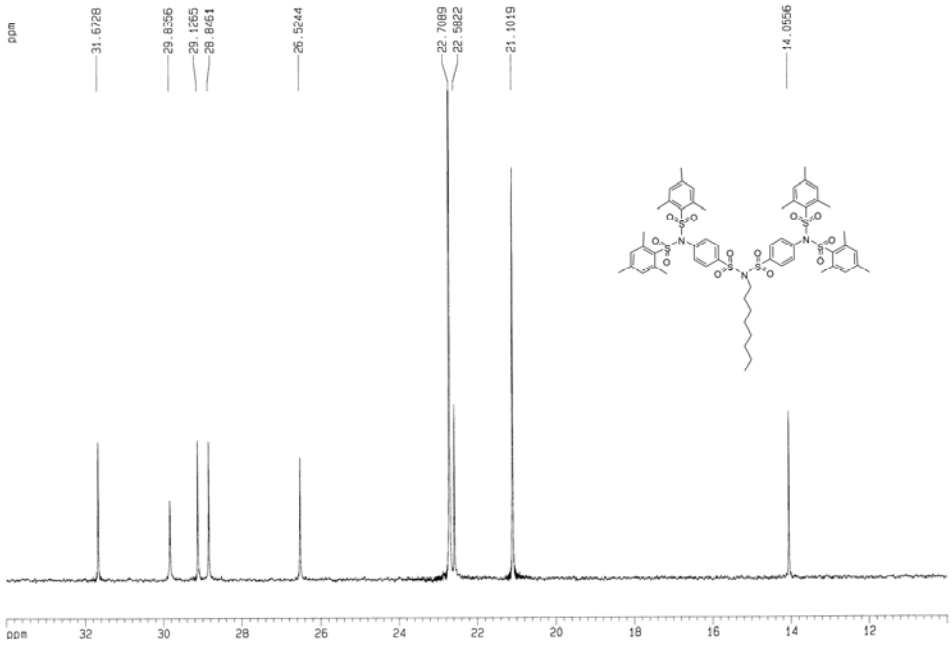
Compound **3i**: 13C NMR, 75 MHz, CDCl3 (Aromatic region)



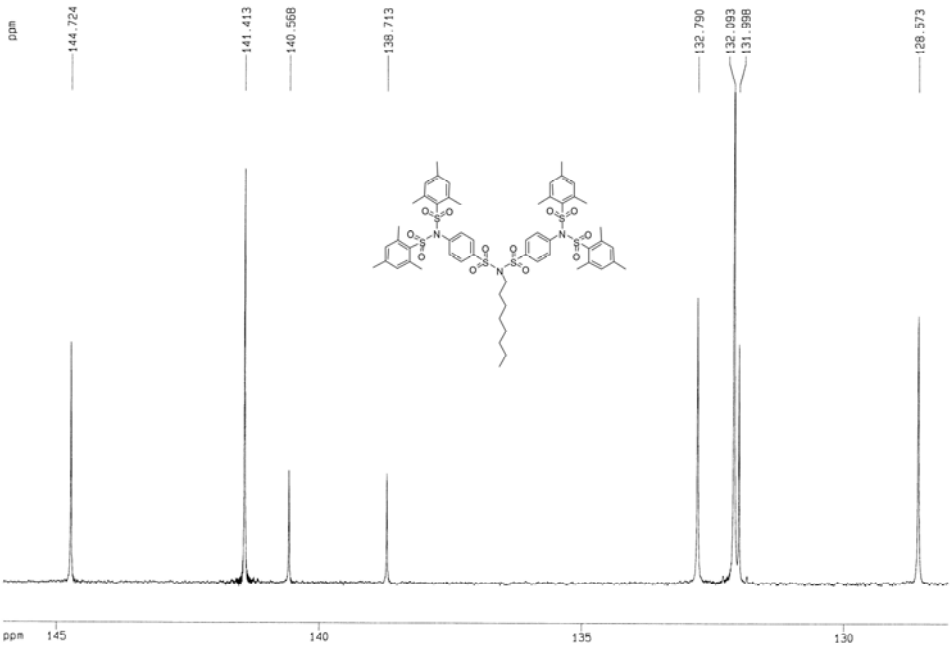
Compound **3j**: 1H NMR, 300 MHz, CDCl3



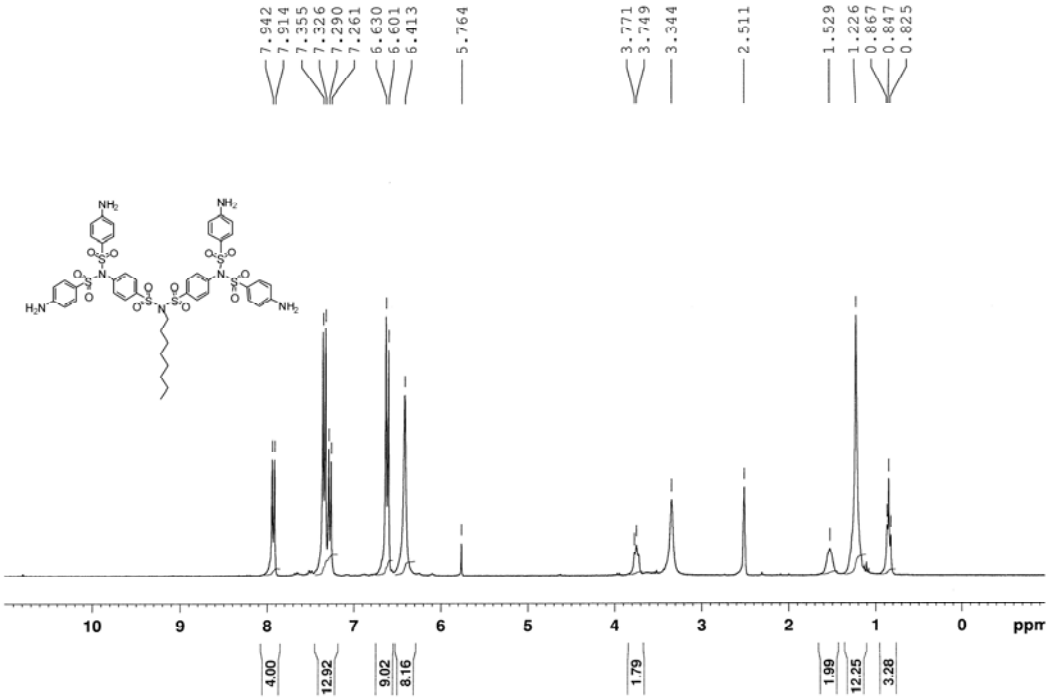
Compound **3j**: 13C NMR, 75 MHz, CDCl3 (Aliphatic region)



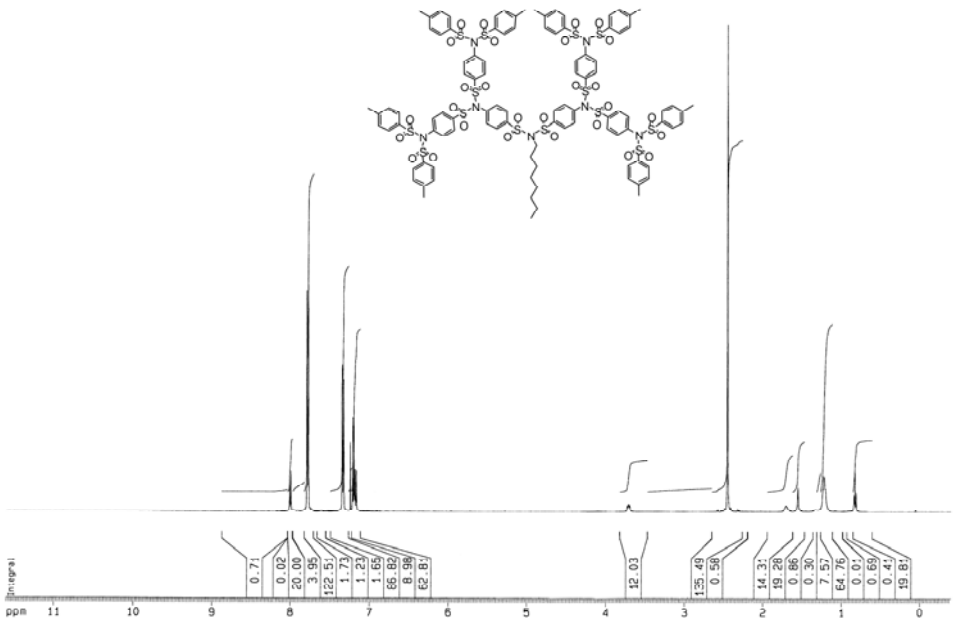
Compound **3i**: 13C NMR, 75 MHz, CDCl3 (Aromatic region)



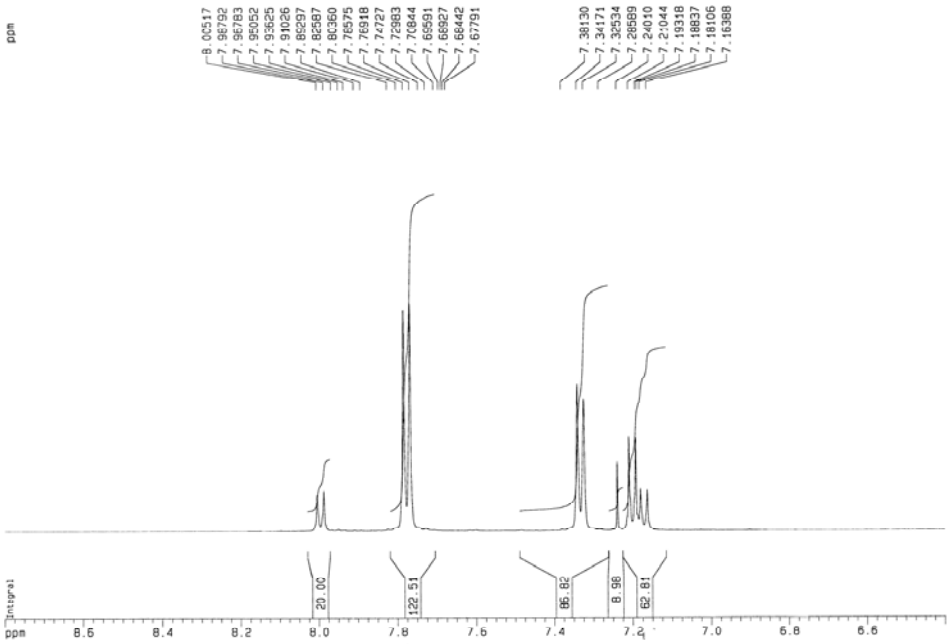
Compound **4**: 1H NMR, 300 MHz, DMSO-d6



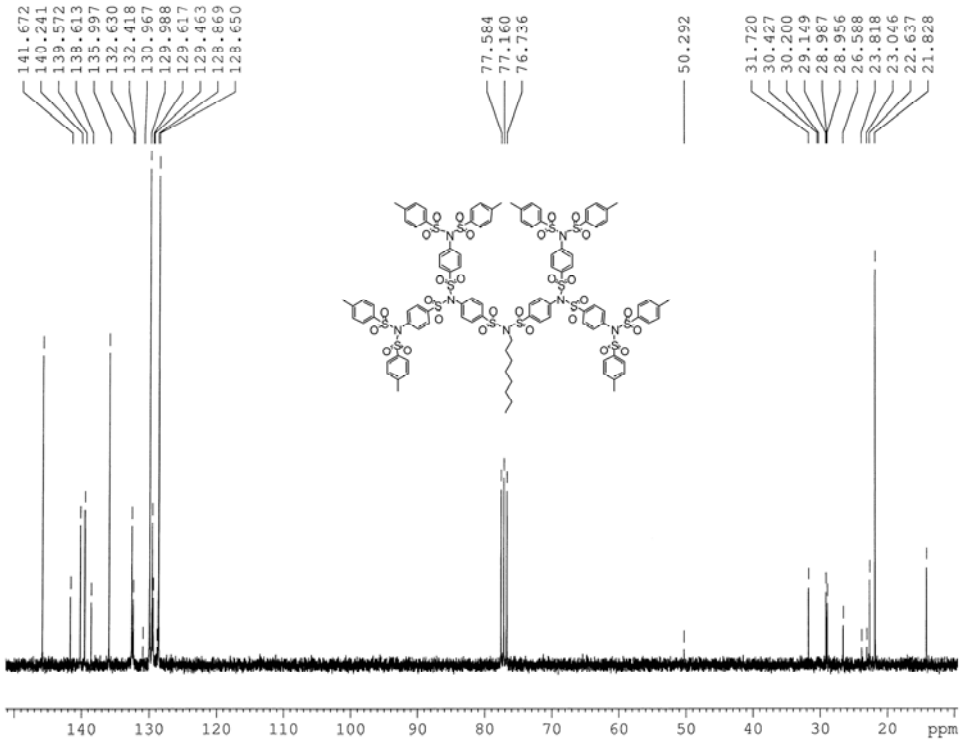
Compound **5a**: 1H NMR, 500 MHz, CDCl3



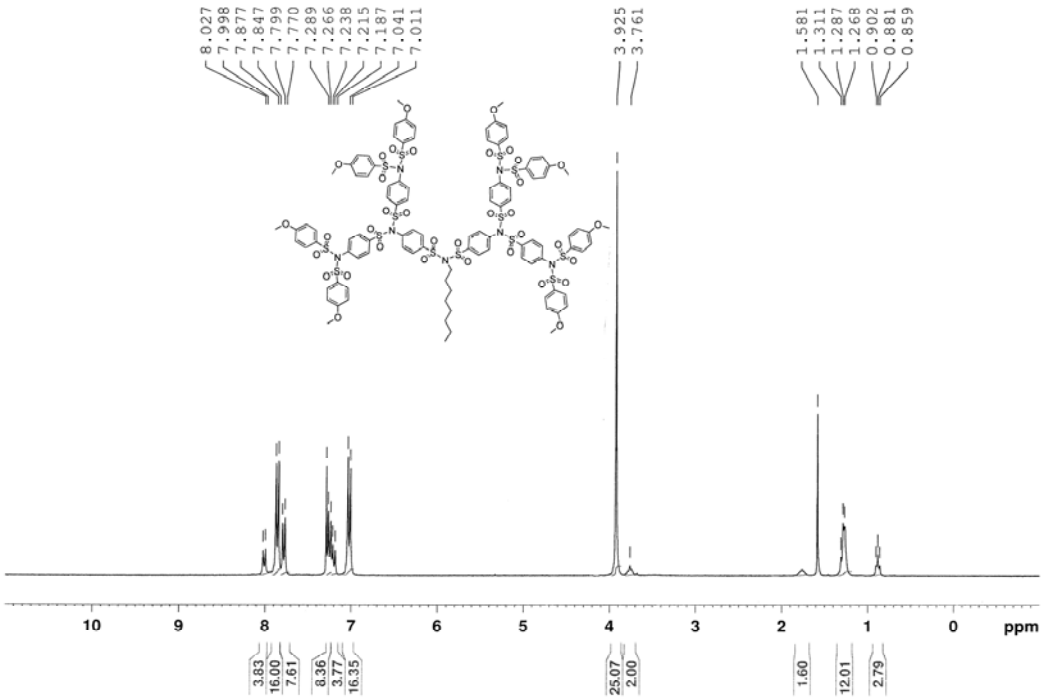
Compound **5a**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



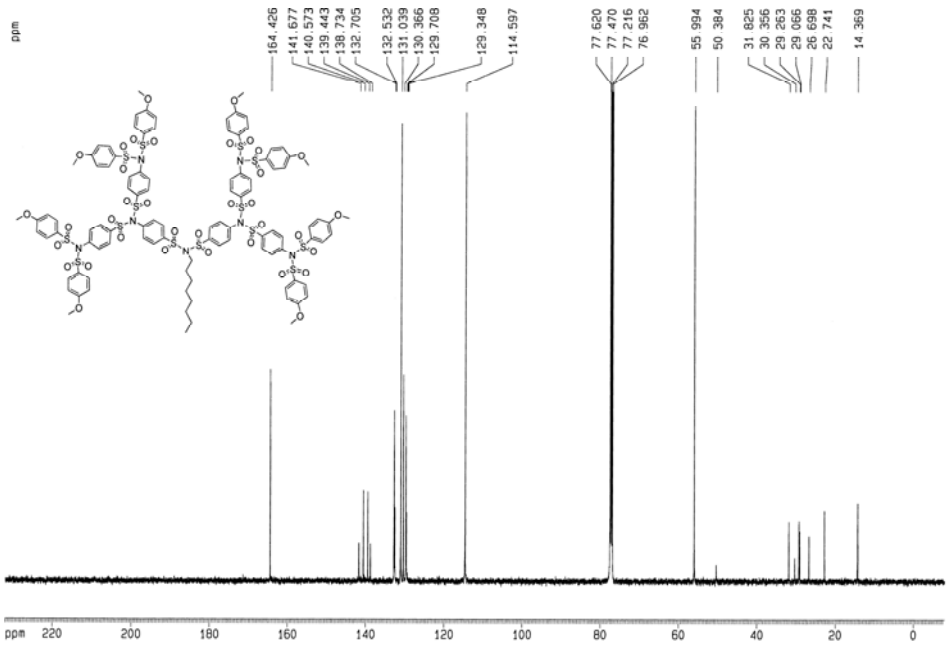
Compound **5a**: 13C NMR, 75 MHz, CDCl3



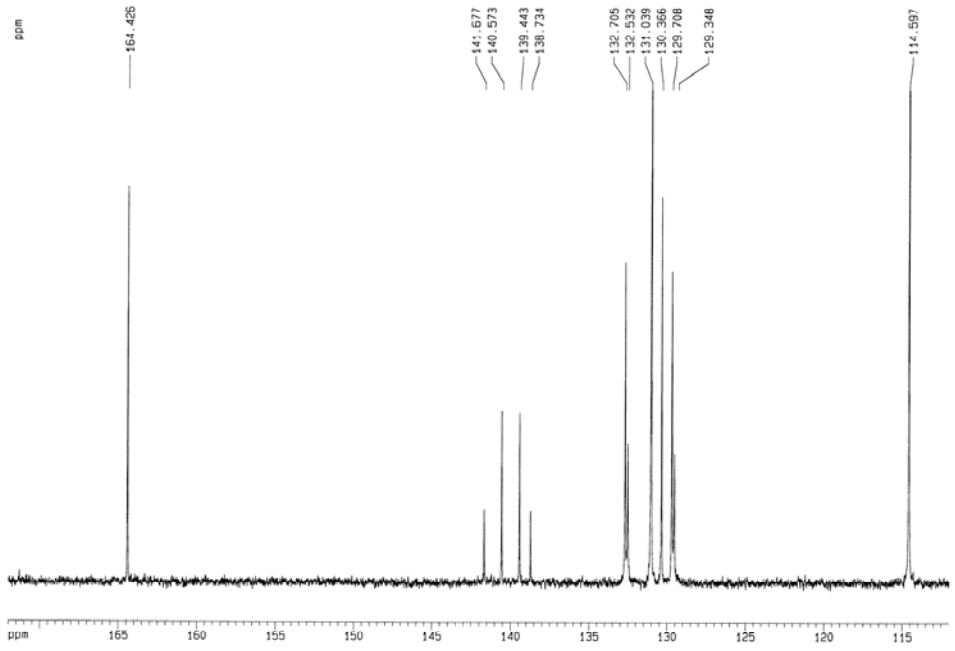
Compound **5b**: 1H NMR, 300 MHz, CDCl3



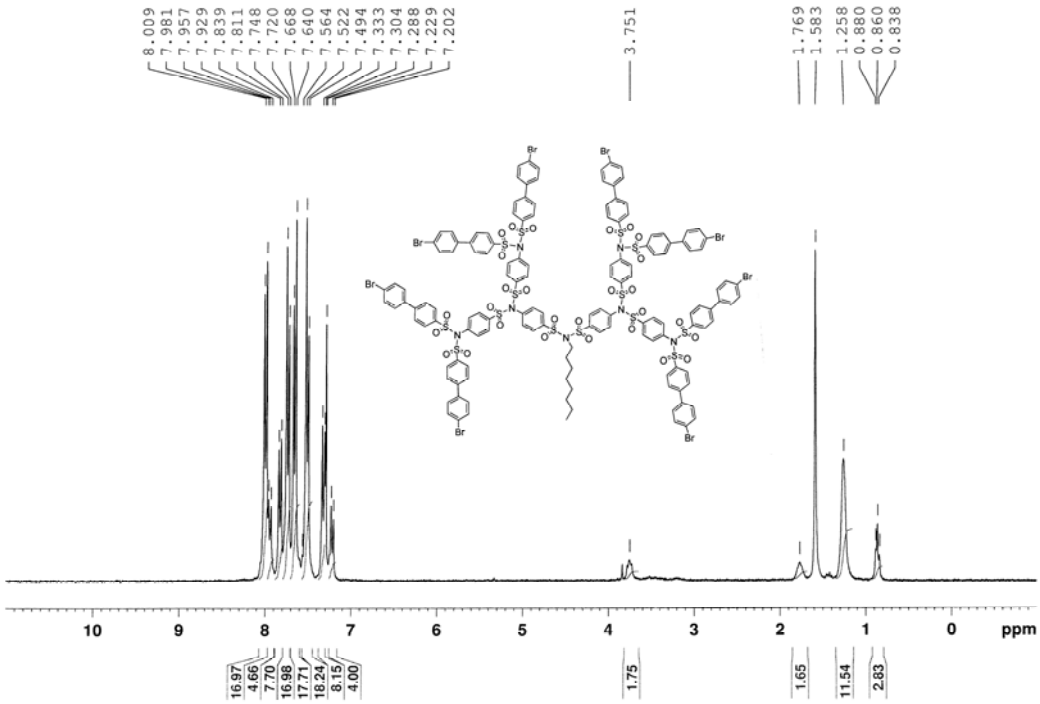
Compound **5b**: 13C NMR, 125 Mhz, CDCl3



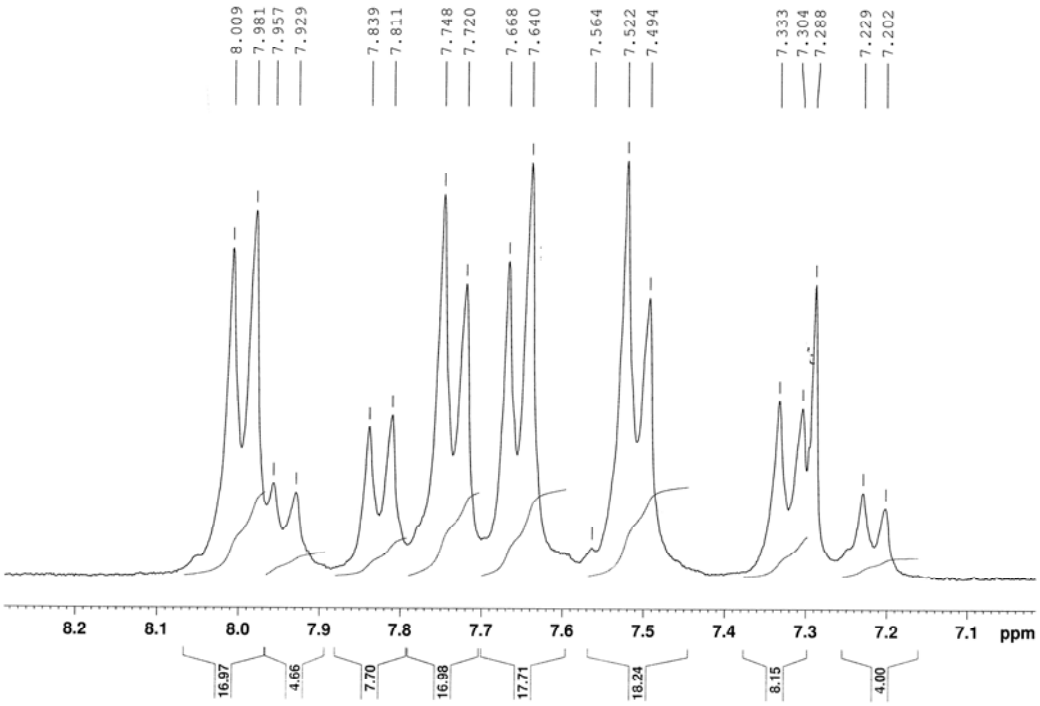
Compound **5b**: 13C NMR, 125 Mhz, CDCl3 (Aromatic region)



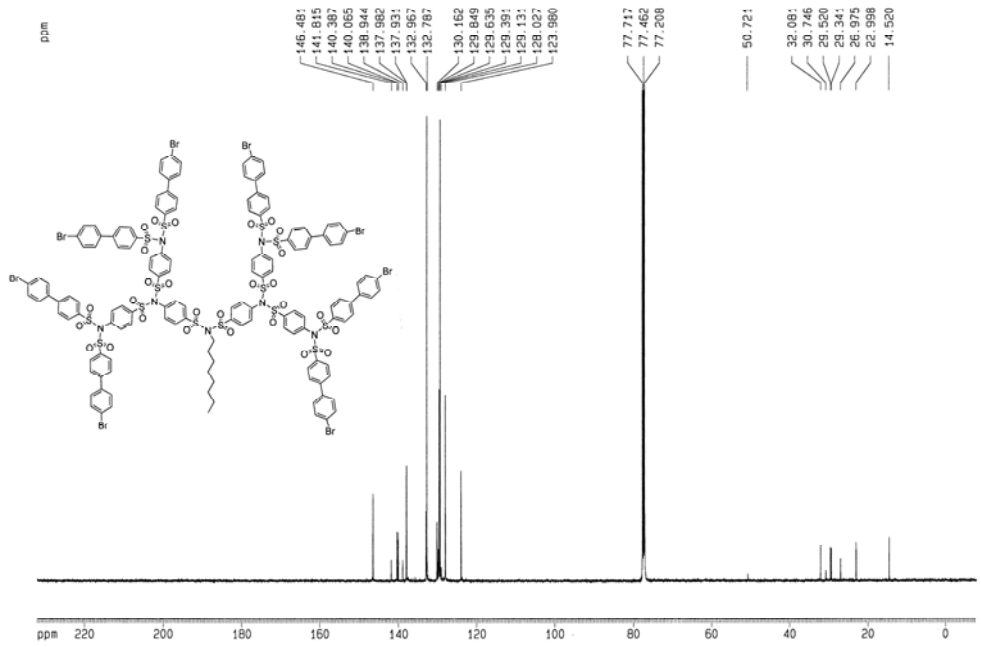
Compound **5c**: 1H NMR, 300 MHz, CDCl3



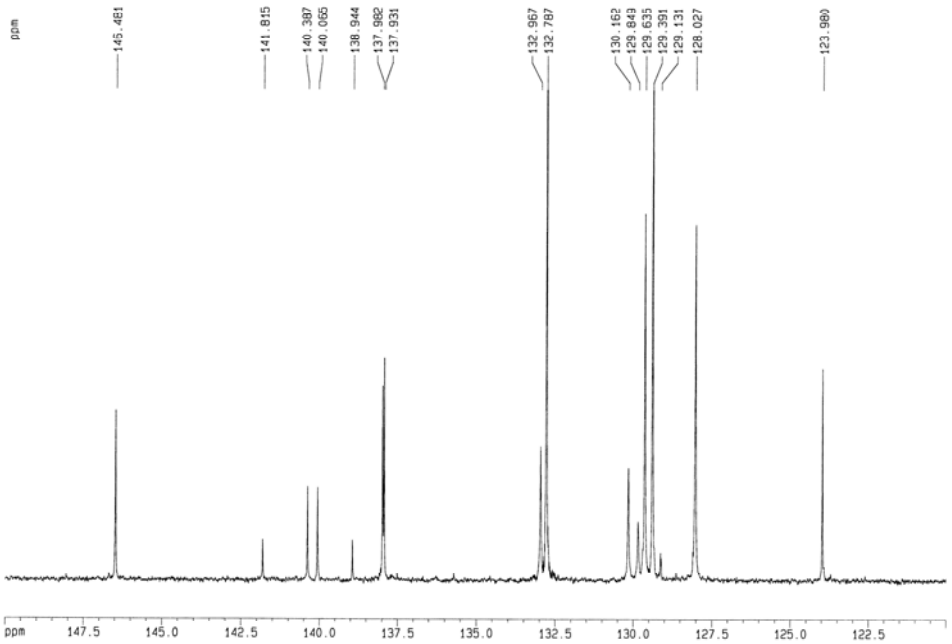
Compound **5c**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



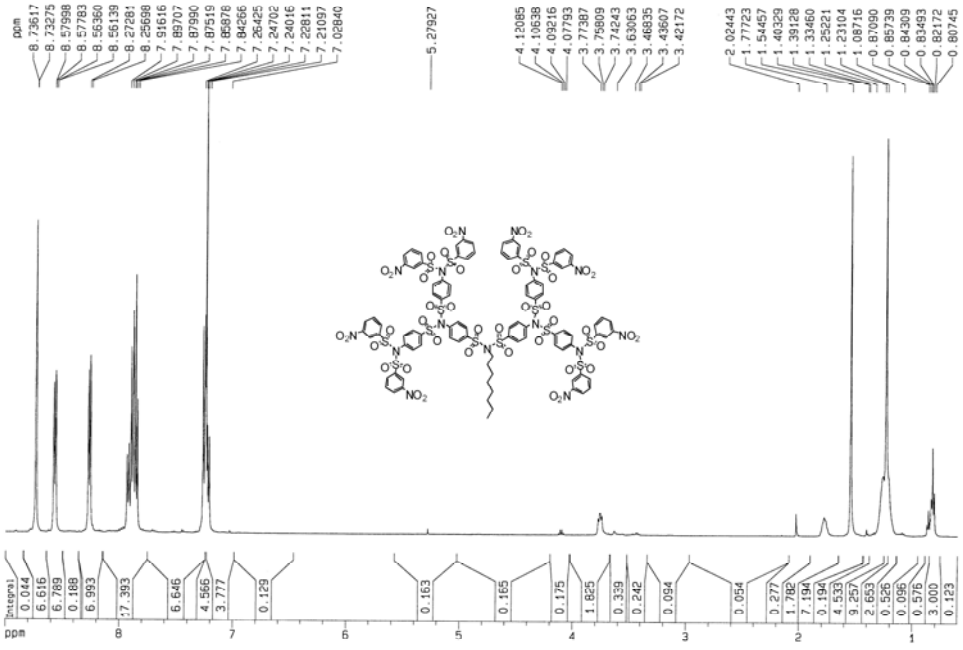
Compound **5c**: 13C NMR, 125 MHz, CDCl3



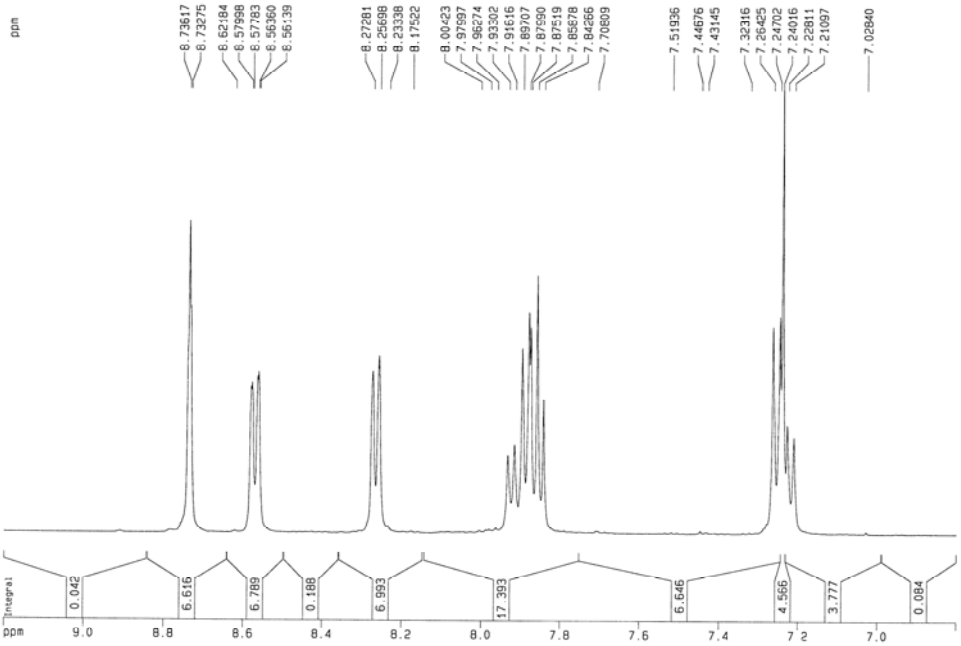
Compound **5c**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



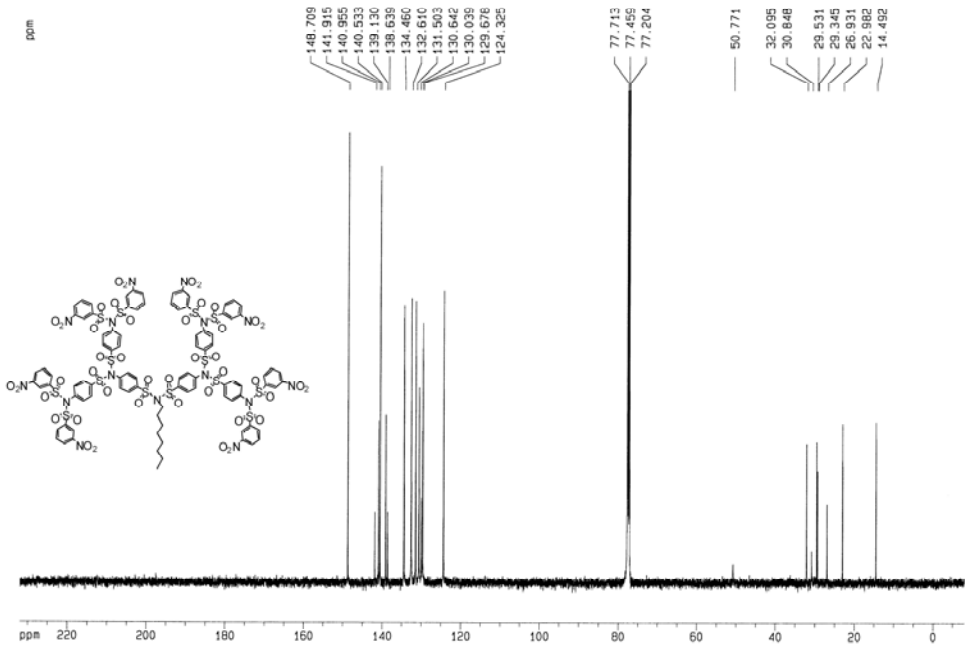
Compound **5d**: 1H NMR, 500 MHz, CDCl3



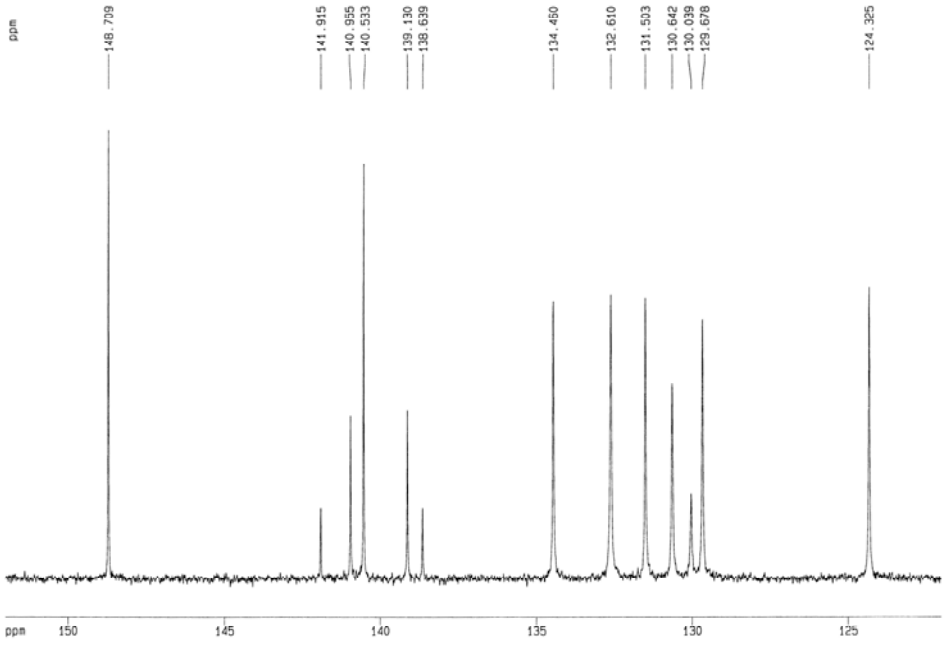
Compound **5d**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



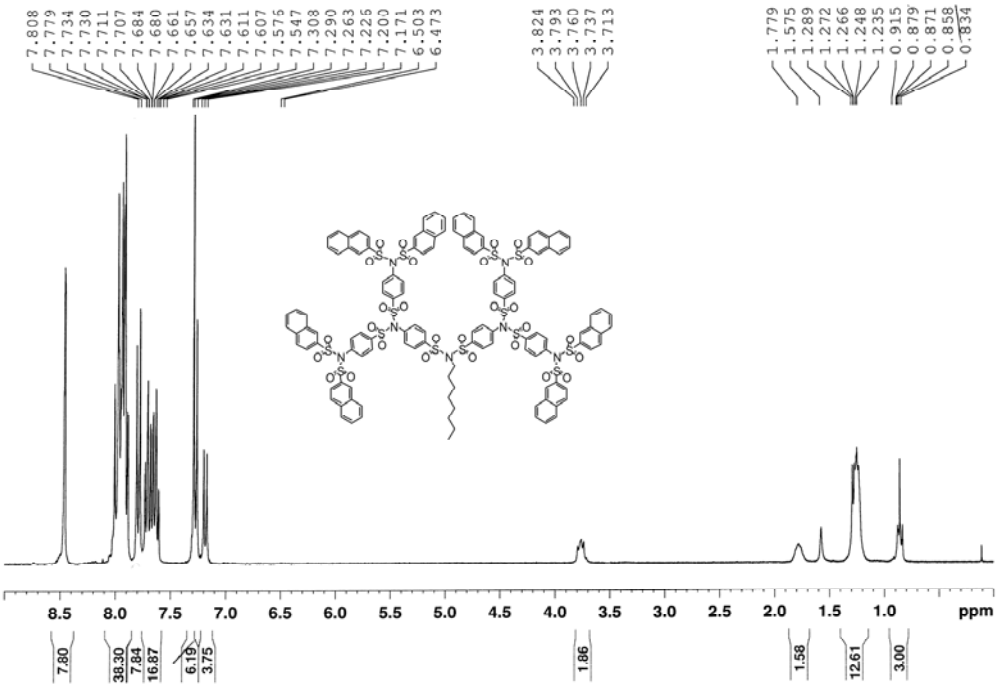
Compound **5d**: 13C NMR, CDCl3, 125 MHz



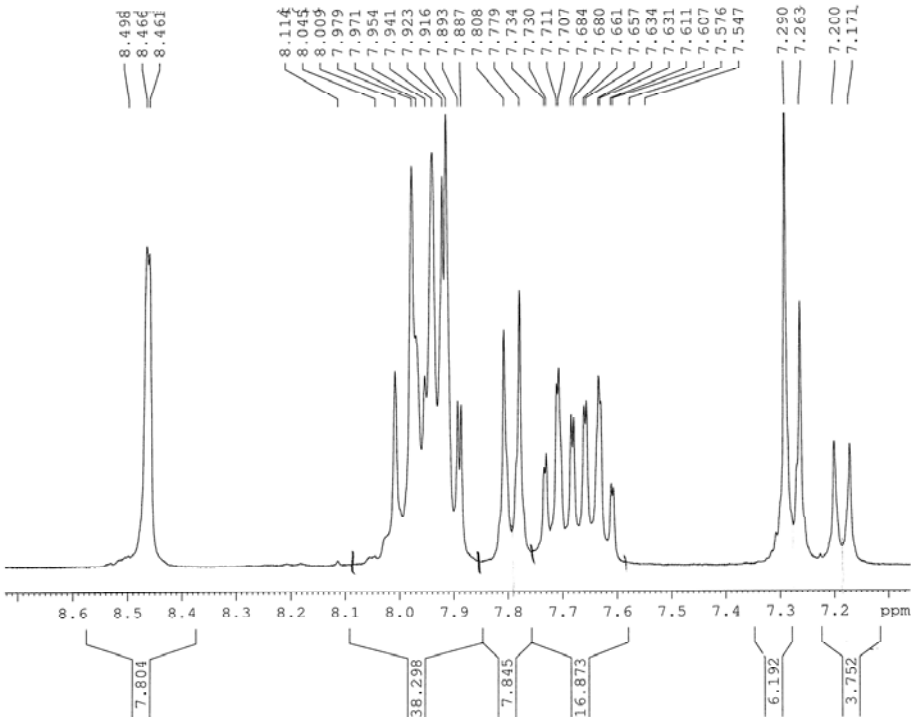
Compound **5d**: 13C NMR, CDCl3, 125 MHz (Aromatic region)



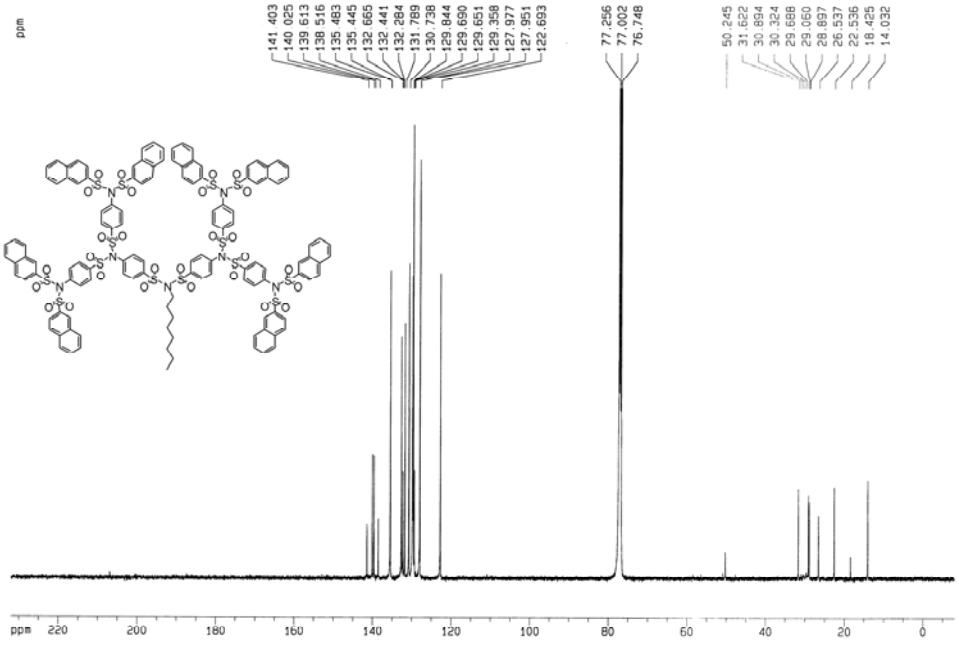
Compound **5e**: 1H NMR, 300 MHz, CDCl3



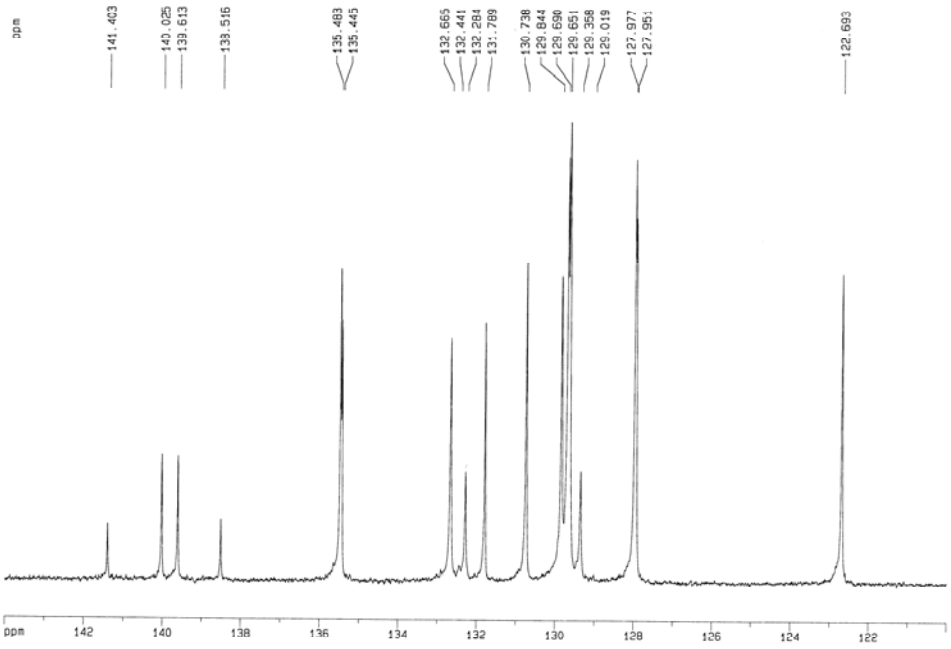
Compound **5e**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



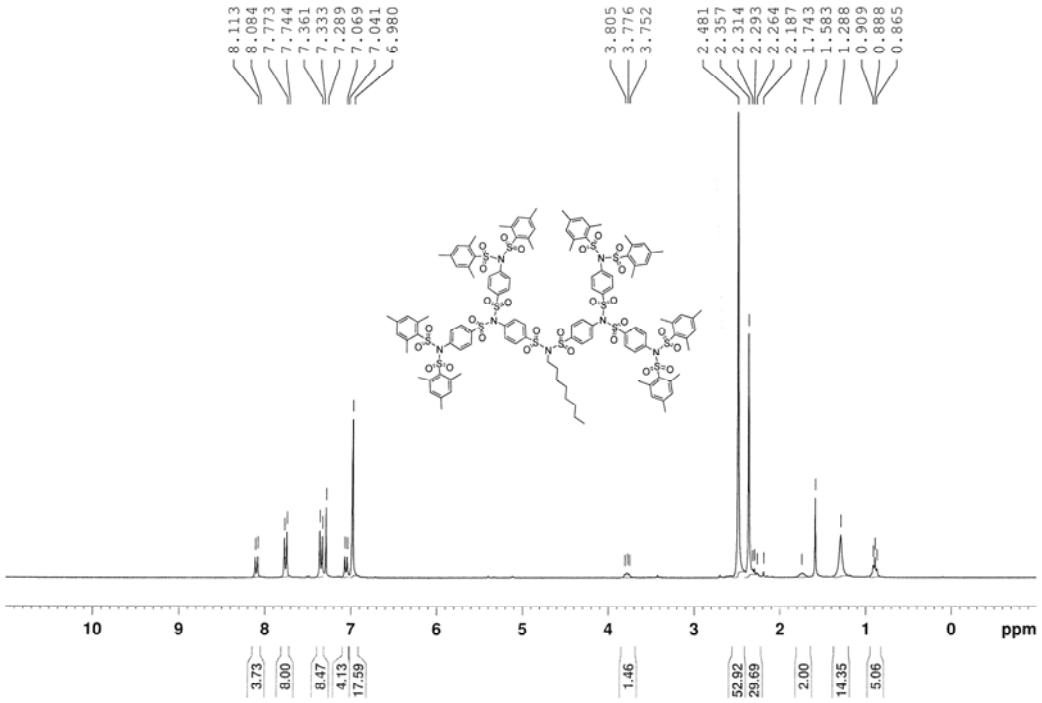
Compound **5e**: 13C NMR, 125 MHz, CDCl3



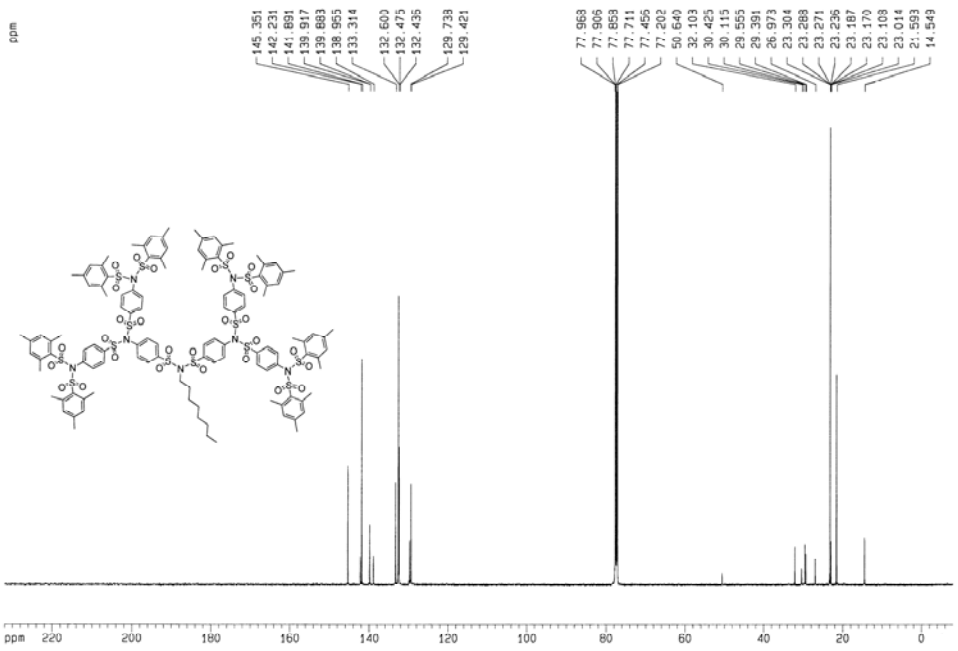
Compound **5e**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



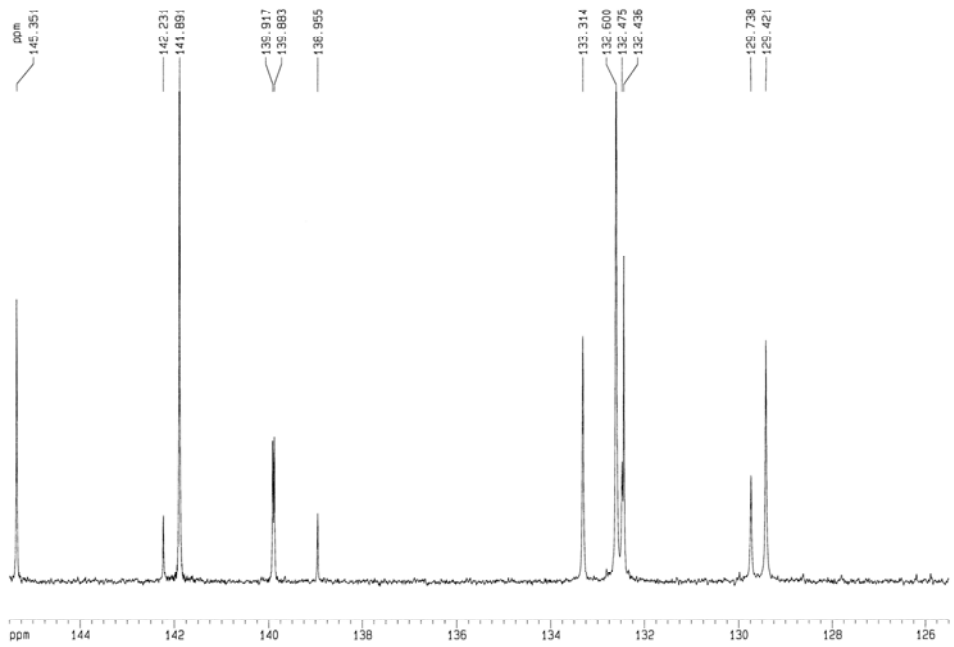
Compound **5f**: 1H NMR, 300 MHz, CDCl3



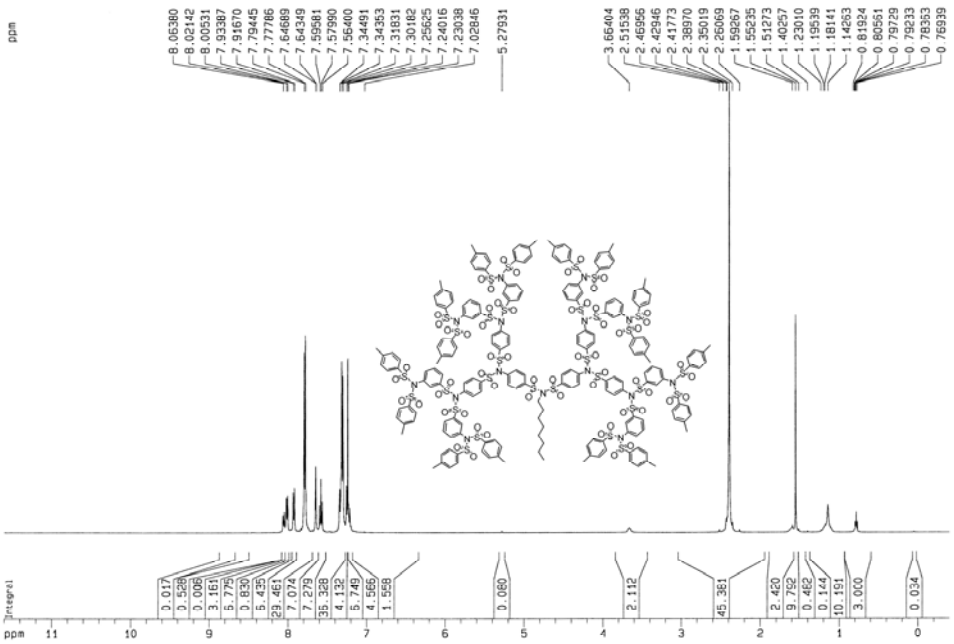
Compound **5f**: 13C NMR, 125 MHz, CDCl3



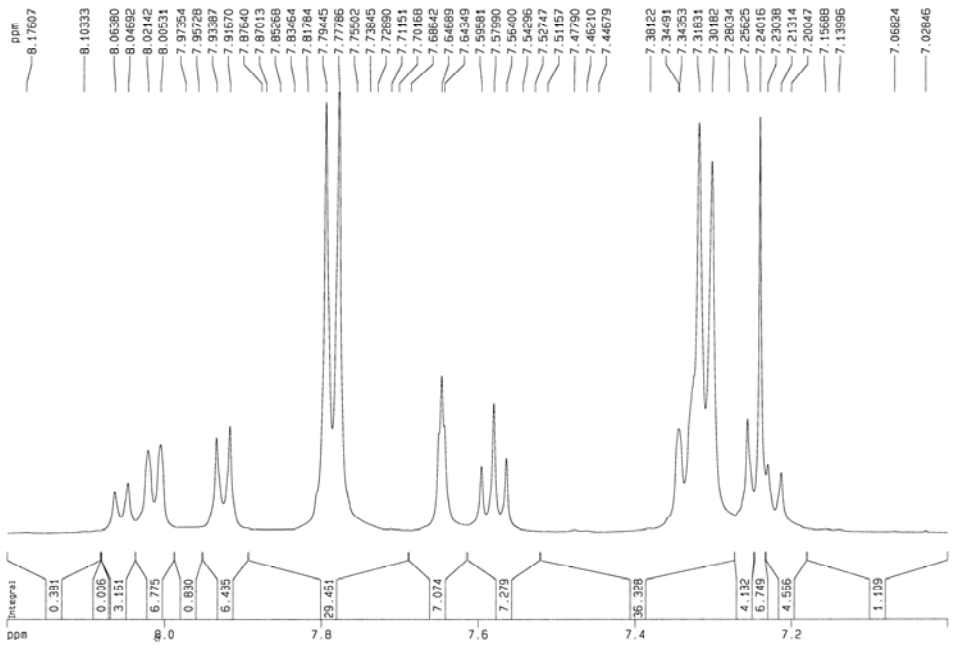
Compound **5f**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



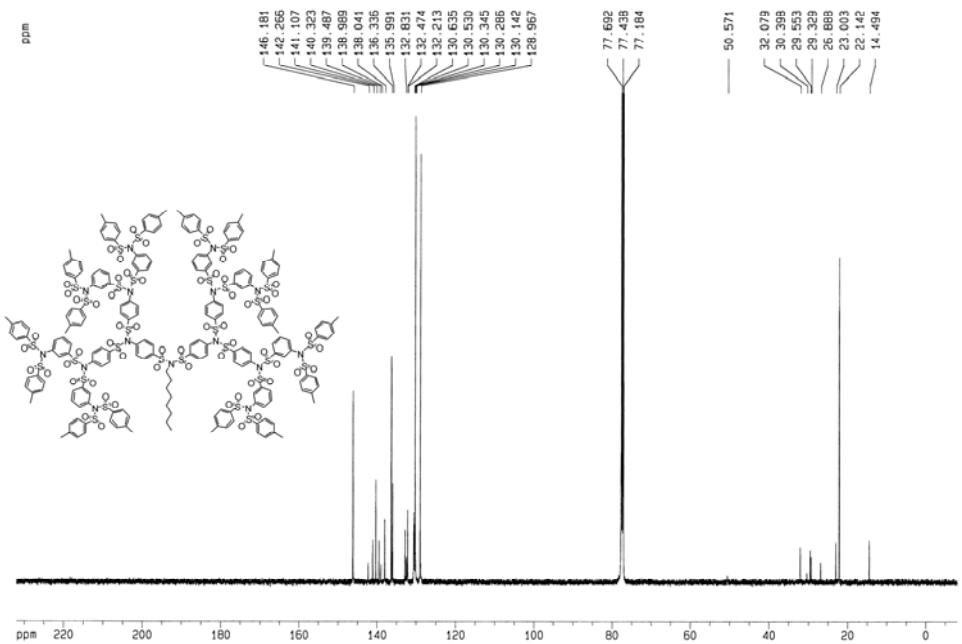
Compound **6**: 1H NMR, 500 MHz, CDCl3



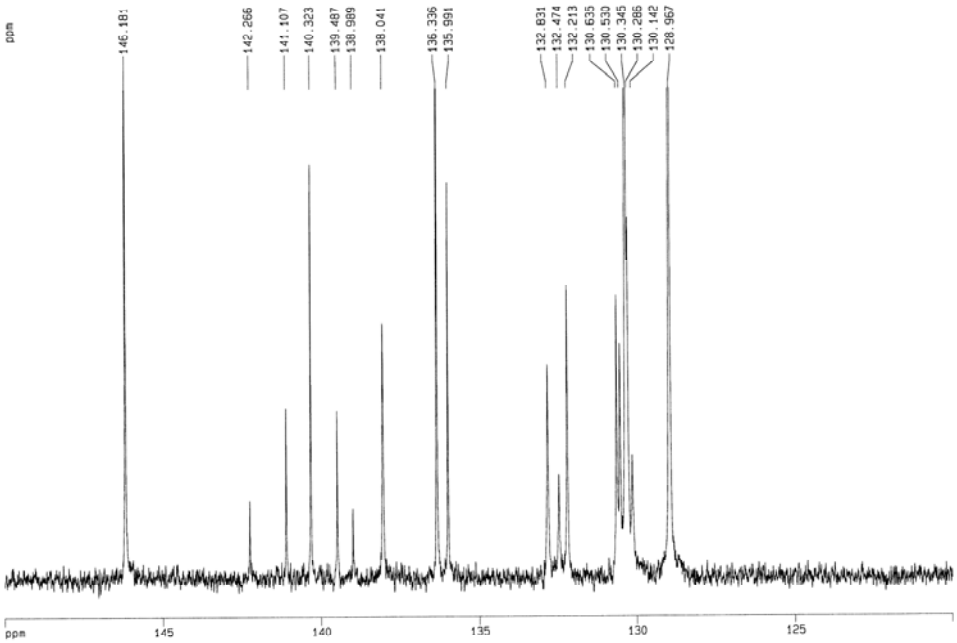
Compound **6**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



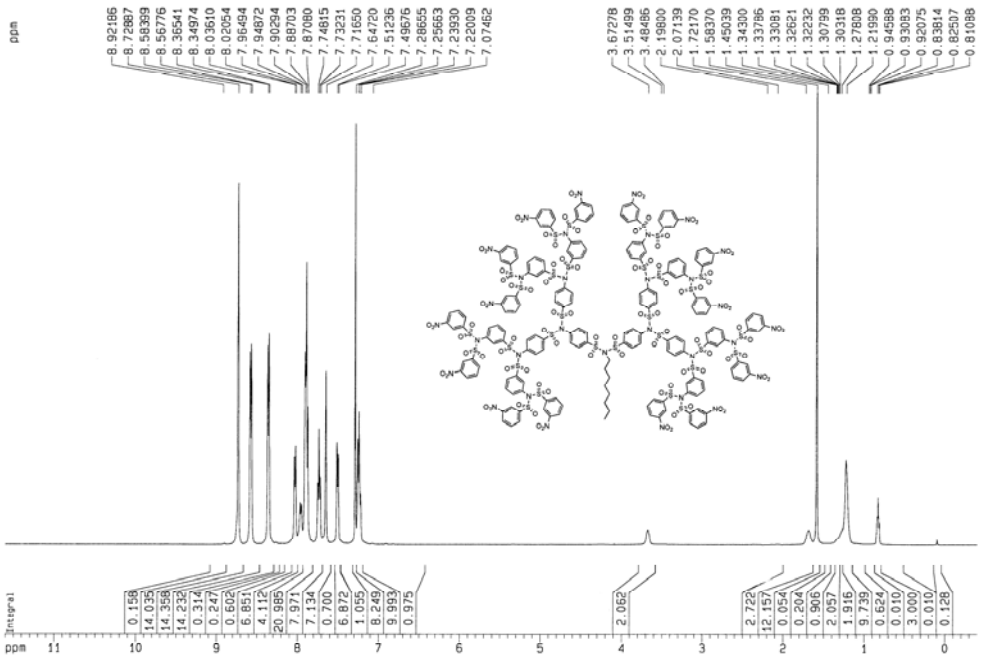
Compound **6**: 13C NMR, 125 MHz, CDCl3



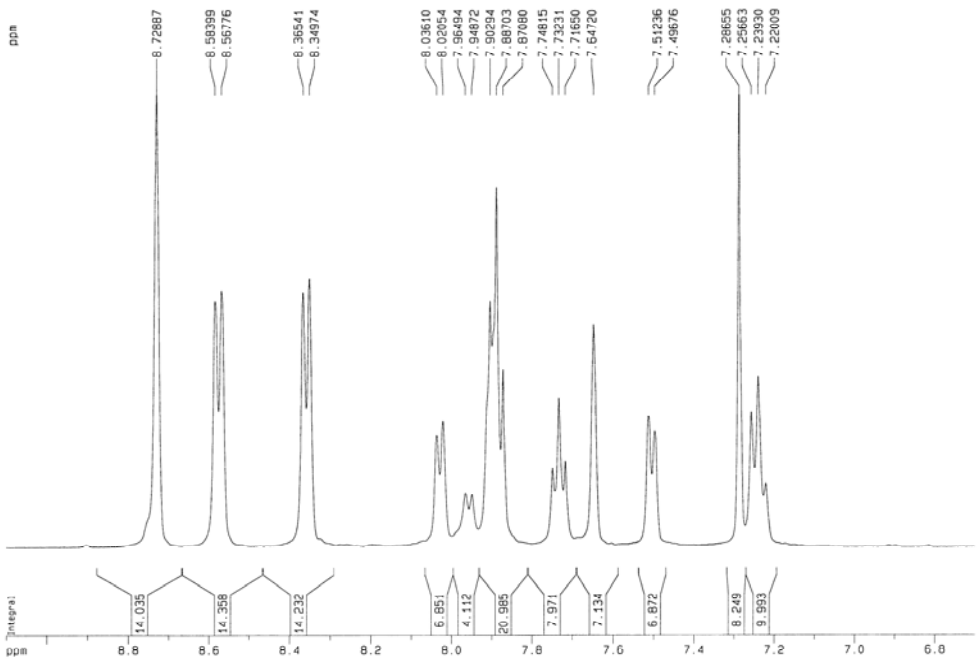
Compound **6**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



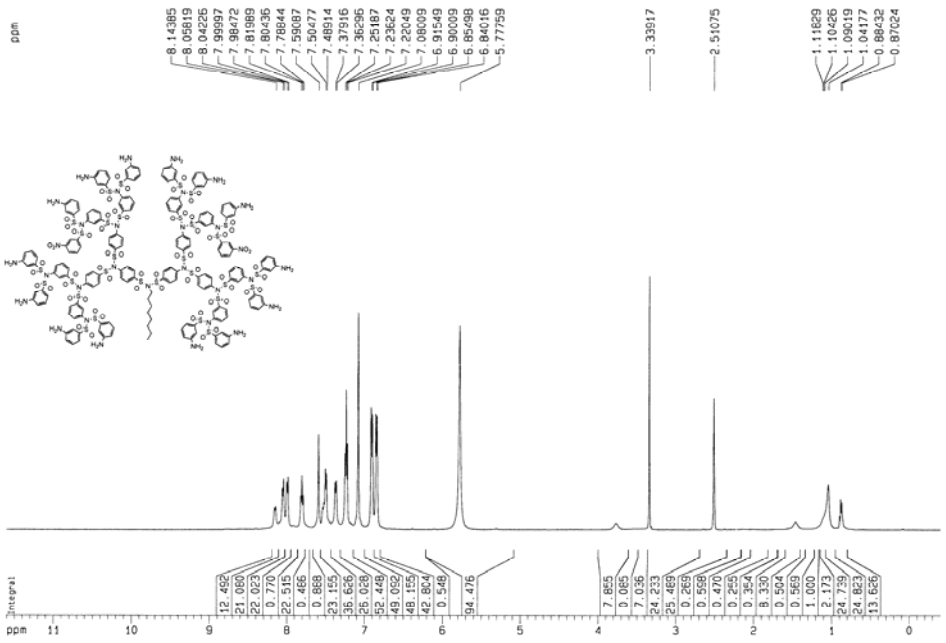
Compound **7a**: 1H NMR, 500 MHz, CDCl3



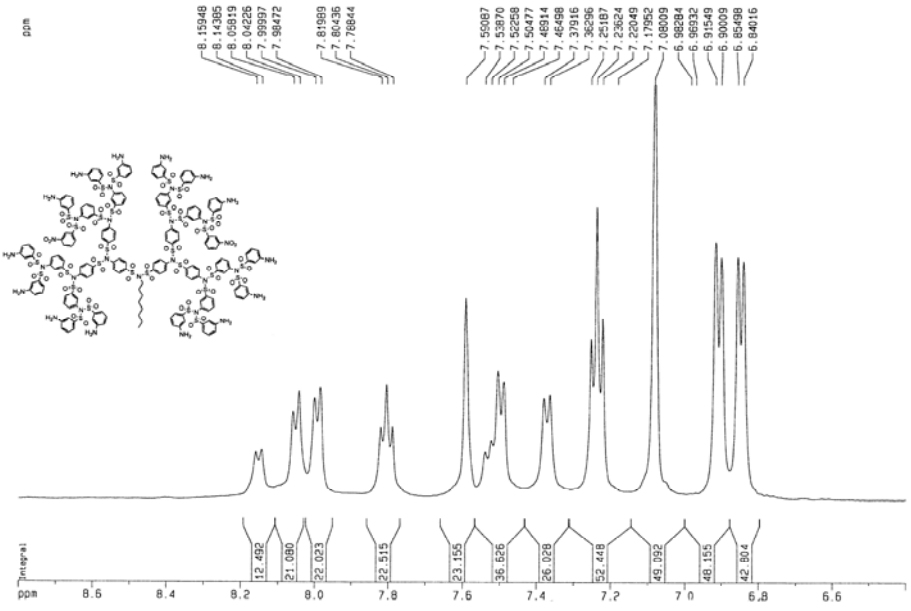
Compound **7a**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



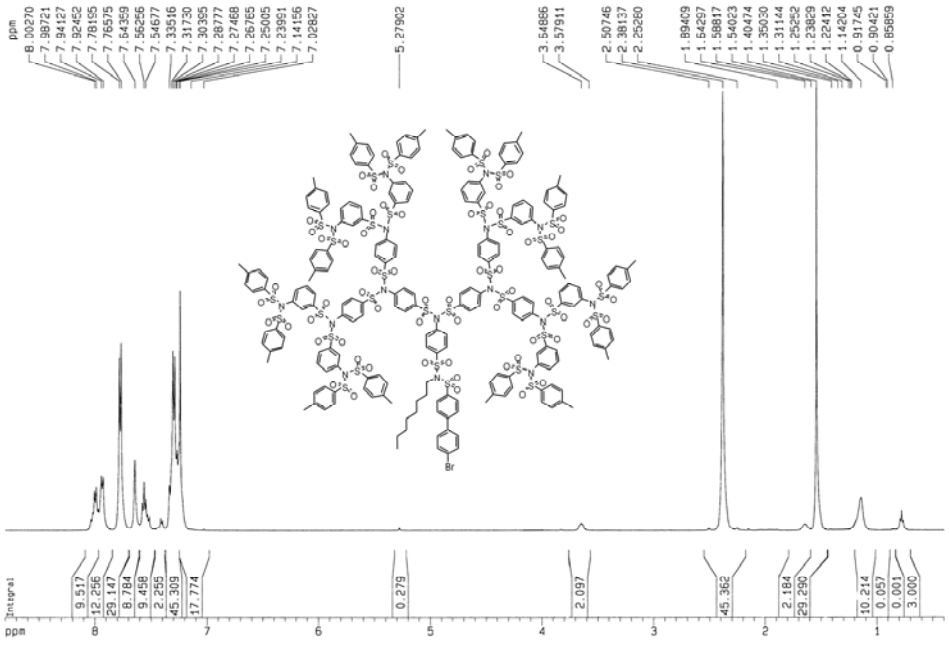
Compound **7b**: 1H NMR, 500 MHz, DMSO-d6



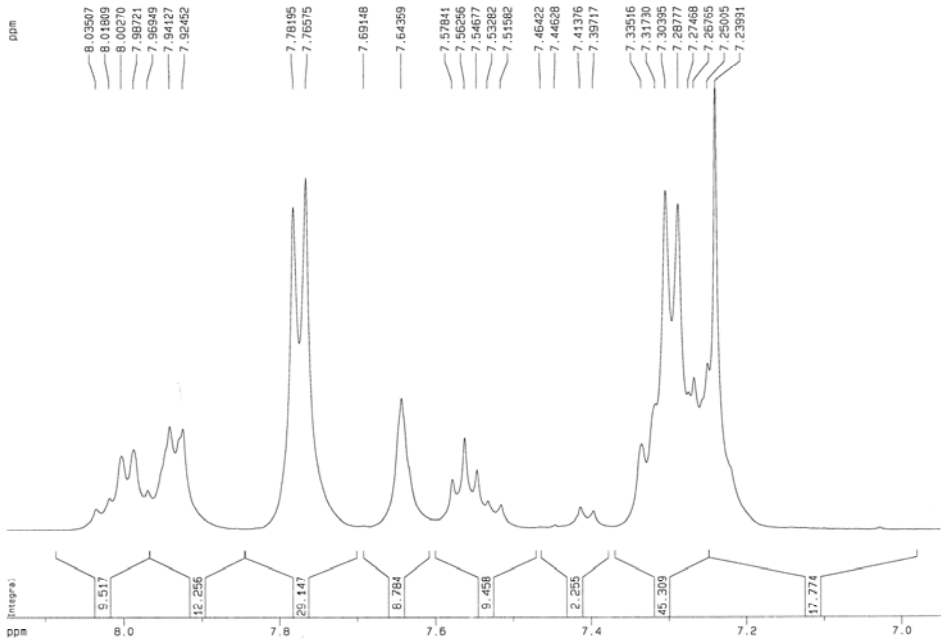
Compound **7b**: 1H NMR, 500 MHz, DMSO-d6 (Aromatic region)

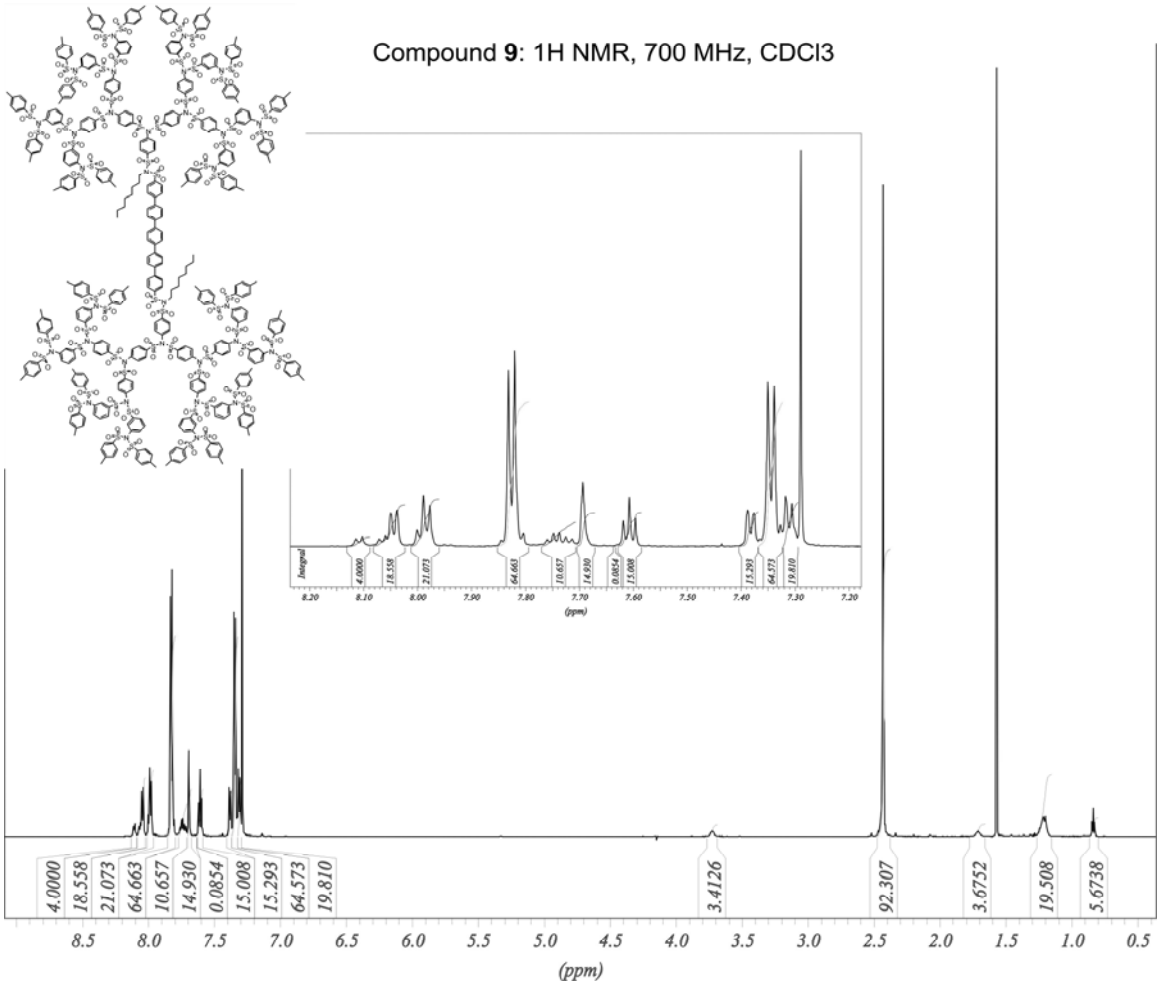


Compound **8**: 1H NMR, 500 MHz, CDCl3

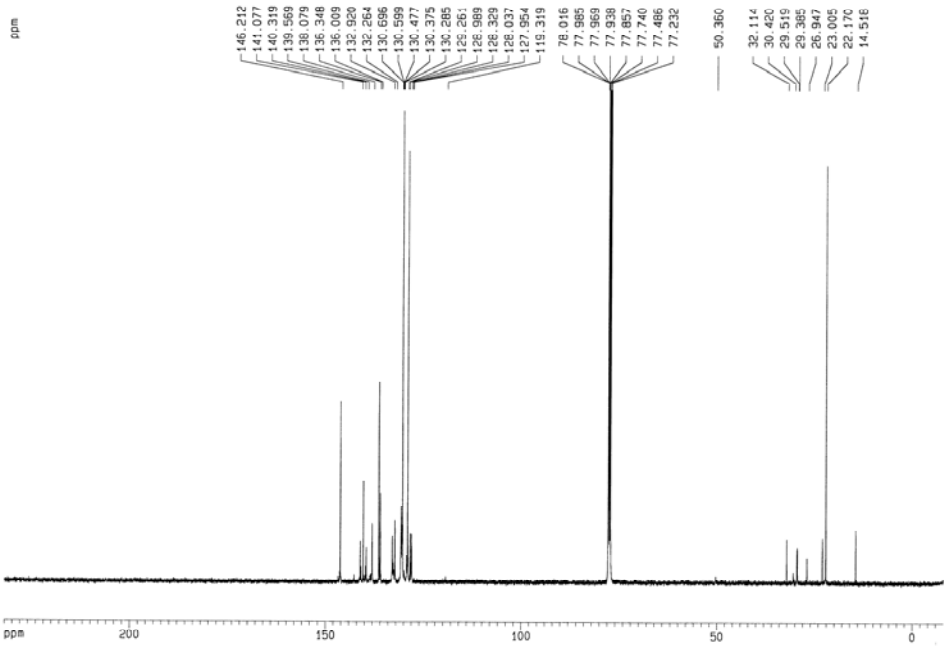


Compound **8**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)

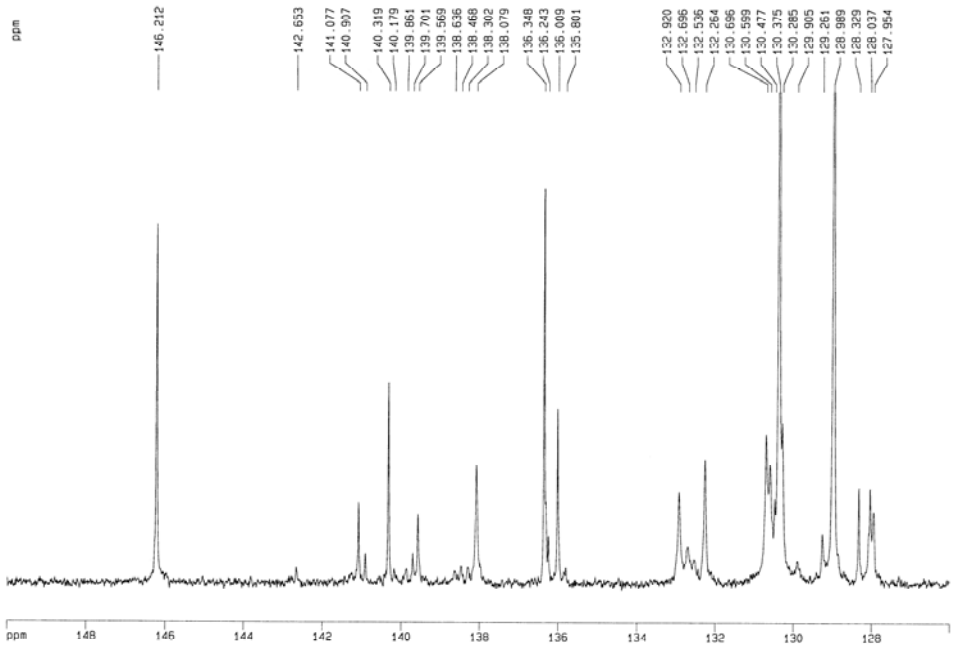



Compound 9: 1H NMR, 700 MHz, CDCl3
4.0000
18.558
21.073
64.663
10.657
14.930
0.0854
15.008
15.293
64.573
19.810
3.4126
92.307
3.6752
19.508
5.6738
(ppm)

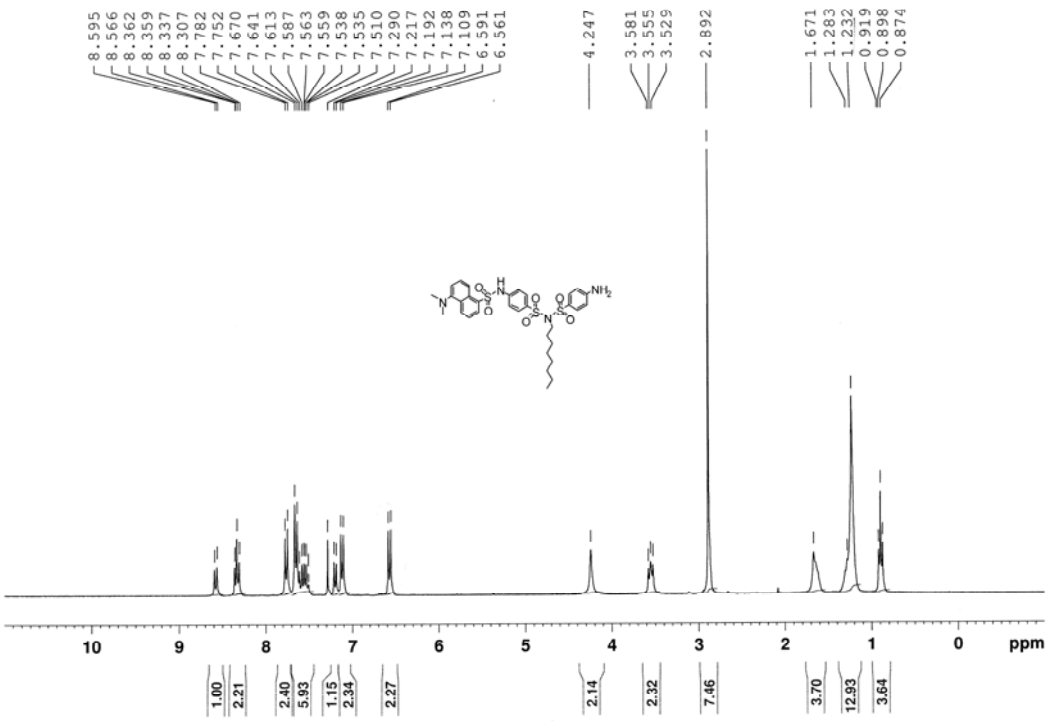
Compound **9**: 13C NMR, 125 MHz, CDCl3



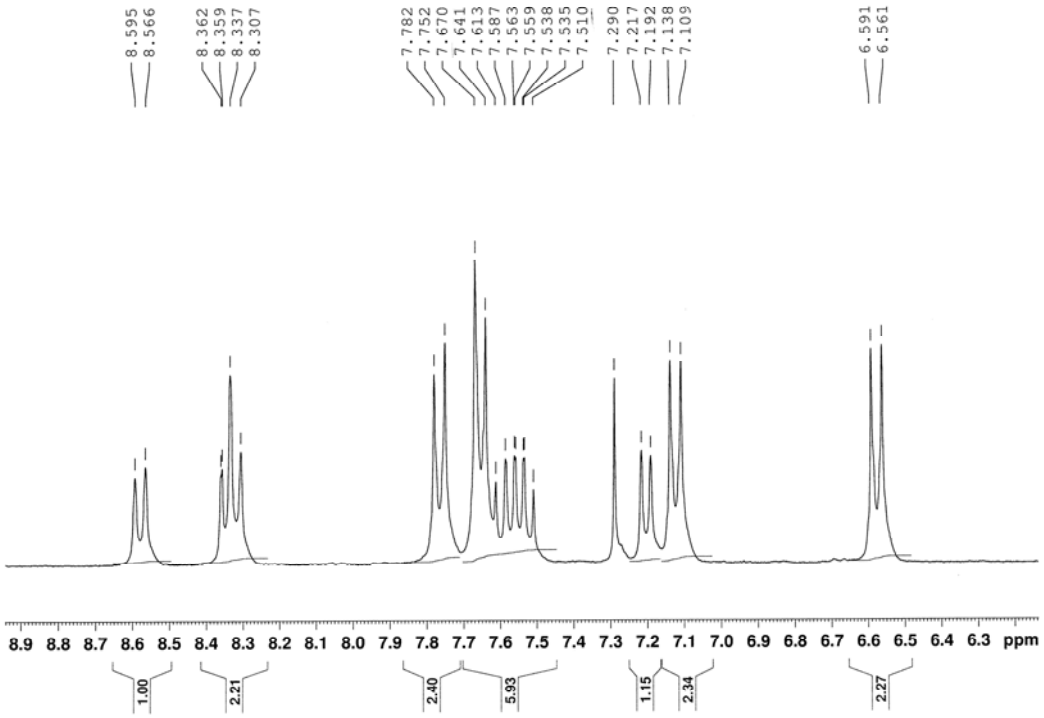
Compound **9**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



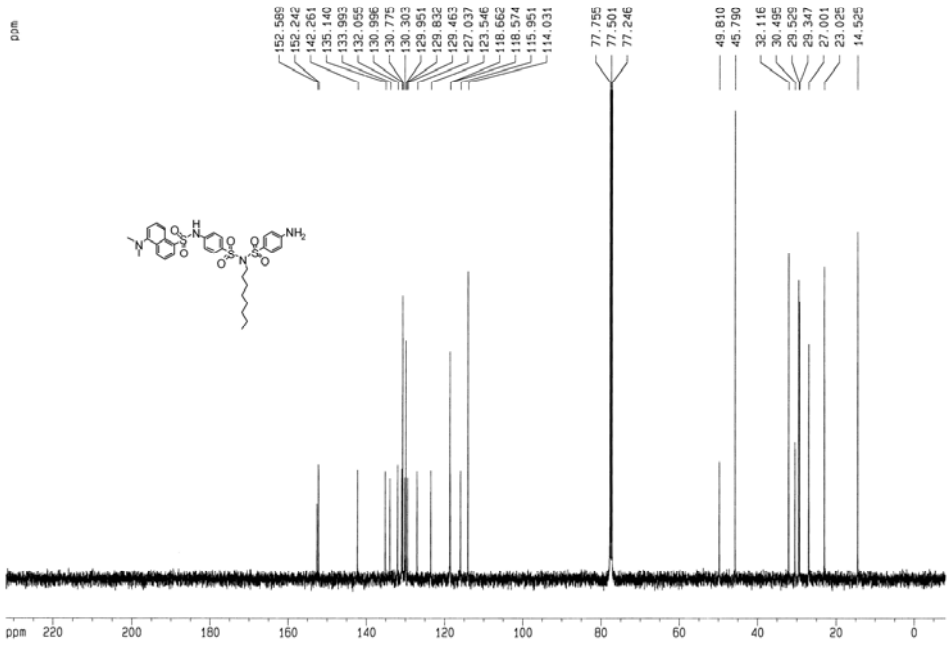
Compound **10**: 1H NMR, 300 MHz, CDCl3



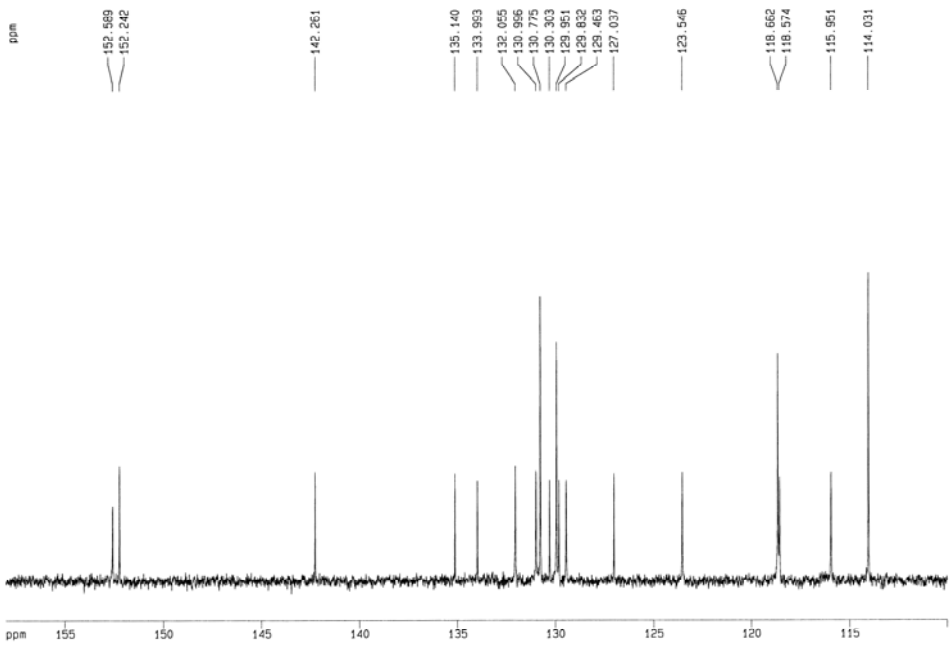
Compound **10**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



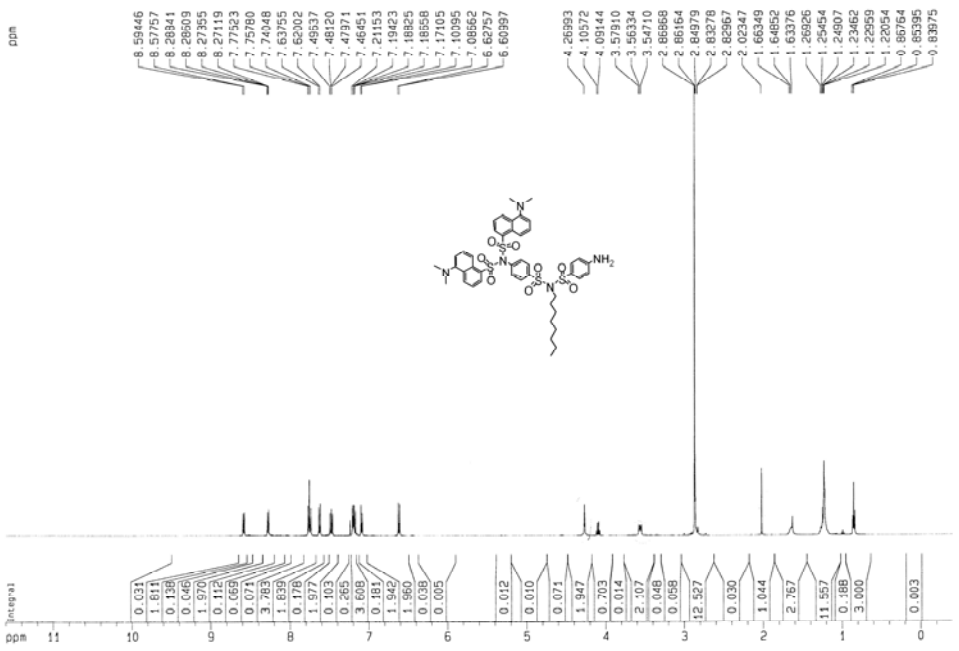
Compound **10**: 13C NMR, 125 MHz, CDCl3



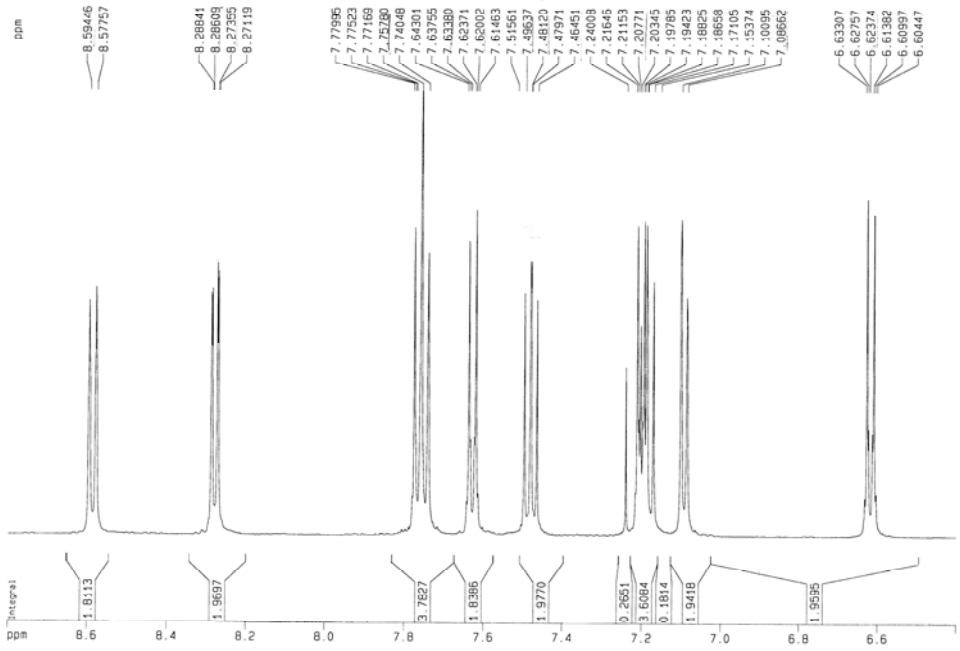
Compound **10**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



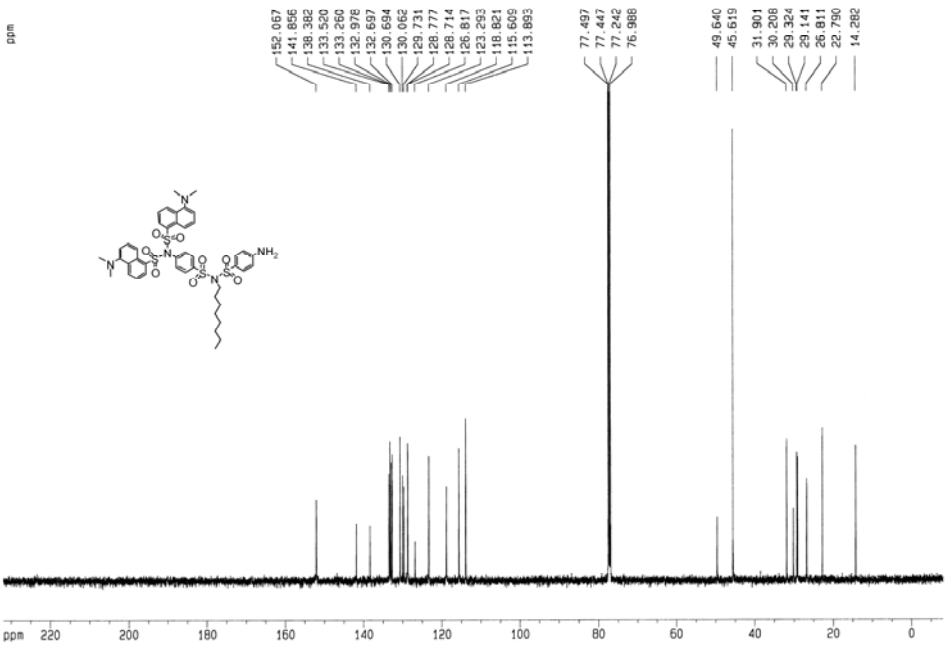
Compound **11**: 1H NMR, 500 MHz, CDCl3



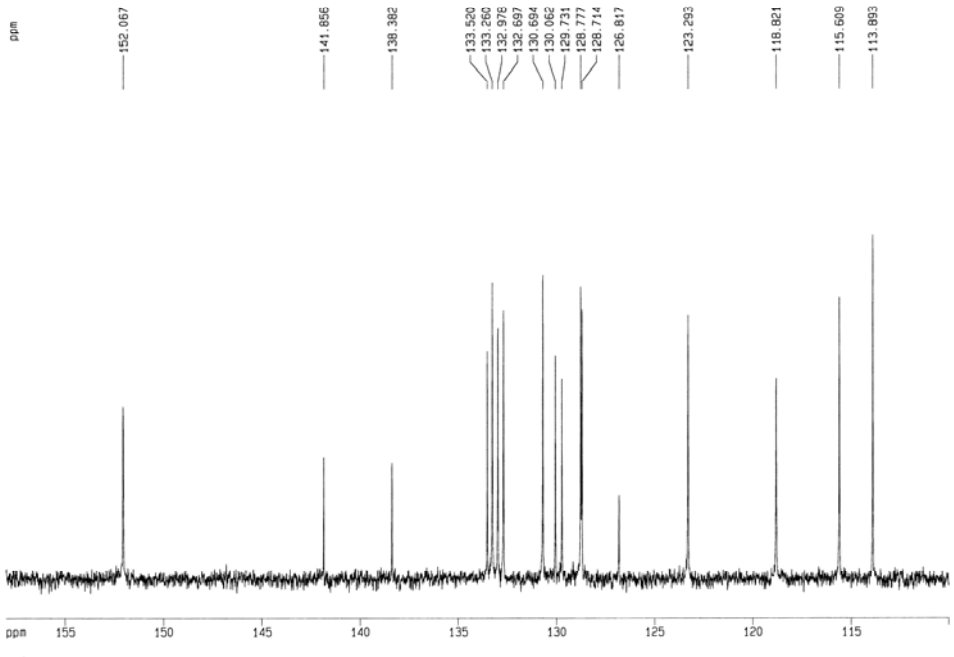
Compound **11**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



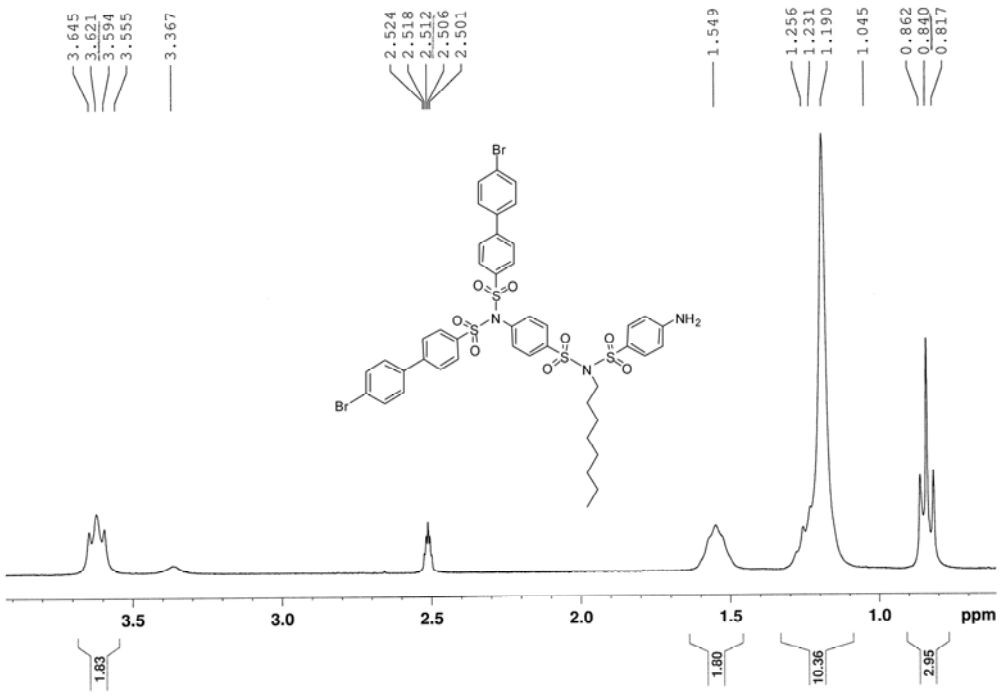
Compound **11**: 13C NMR, 125 MHz, CDCl3



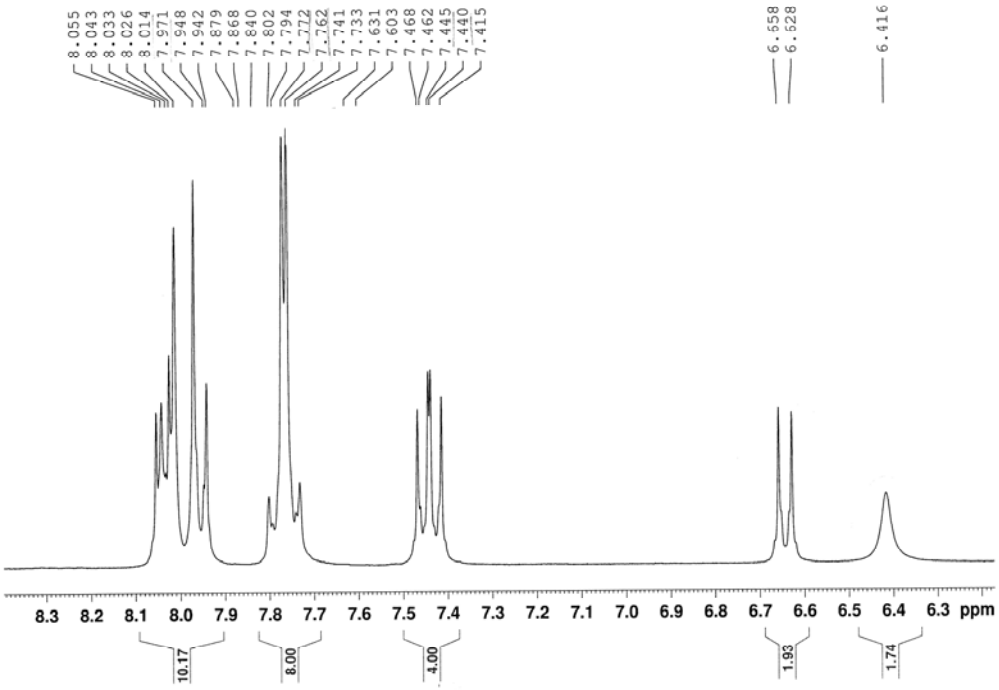
Compound **11**: 13C NMR, 125 MHz, CDCl3 (Aromatic region)



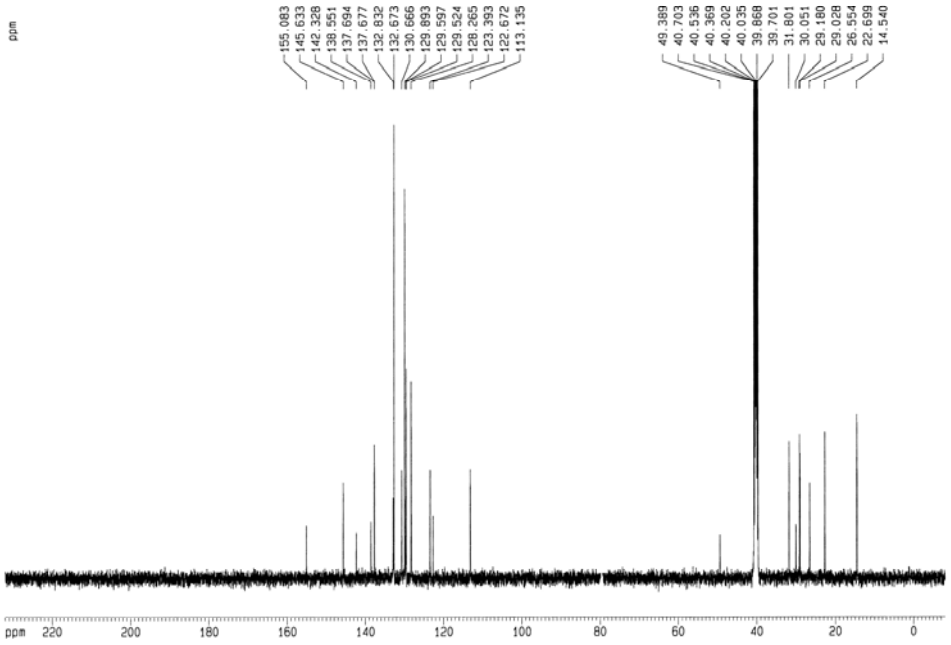
Compound **12**: 1H NMR, 300 MHz, CDCl3 (Aliphatic region)



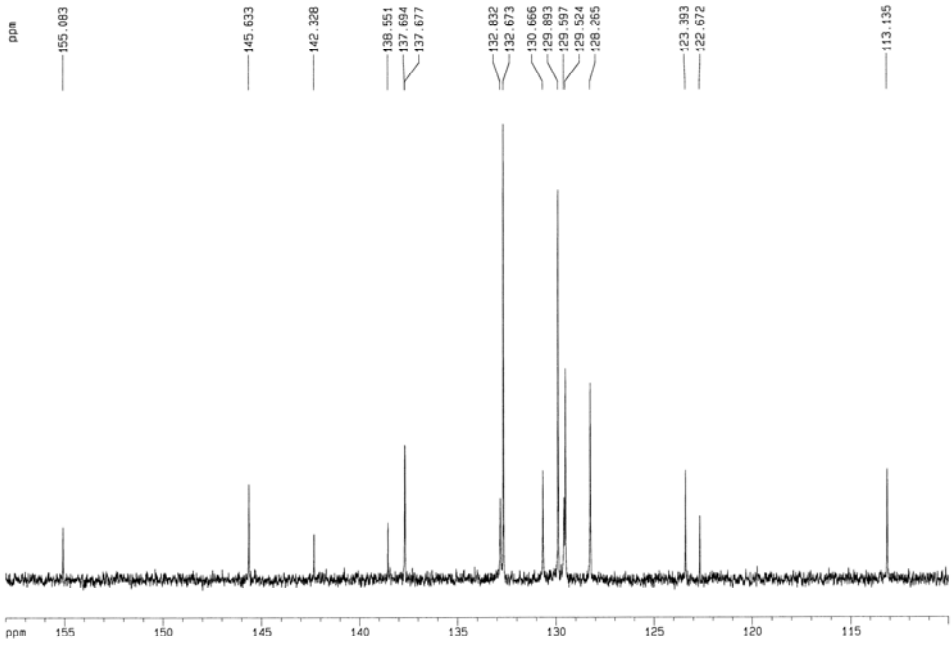
Compound **12**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



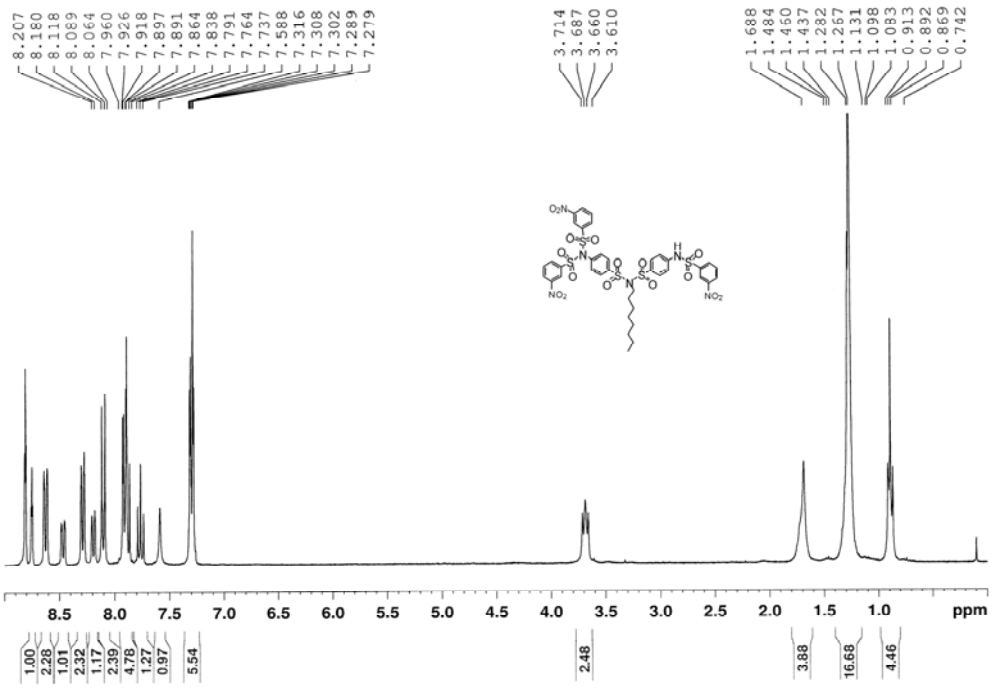
Compound **12**: 13C NMR, 125 MHz, DMSO-d6



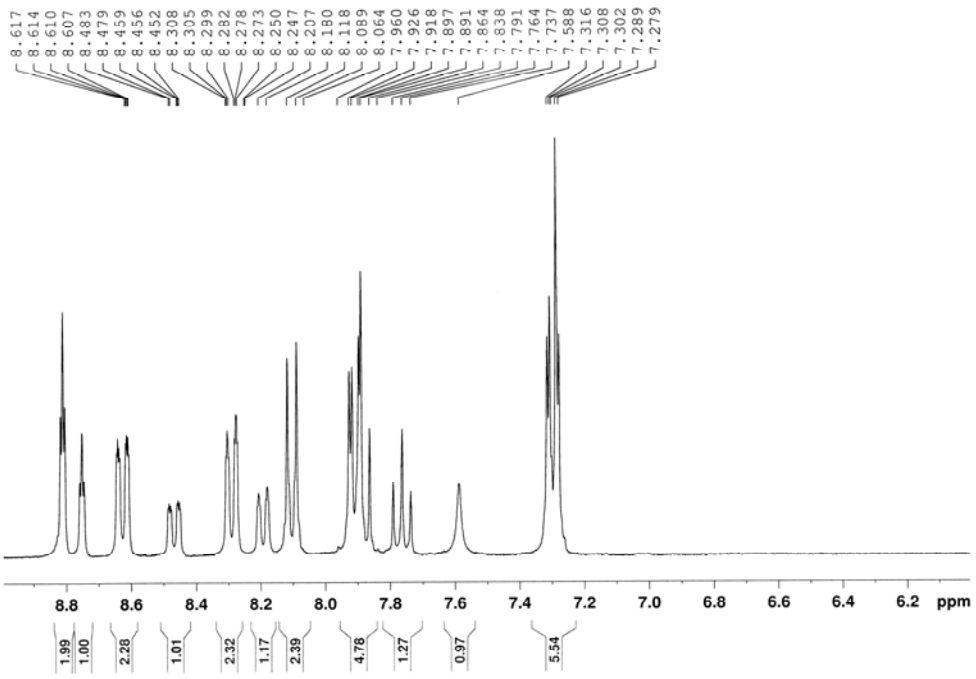
Compound **12**: 13C NMR, 125 MHz, DMSO-d6 (Aromatic region)



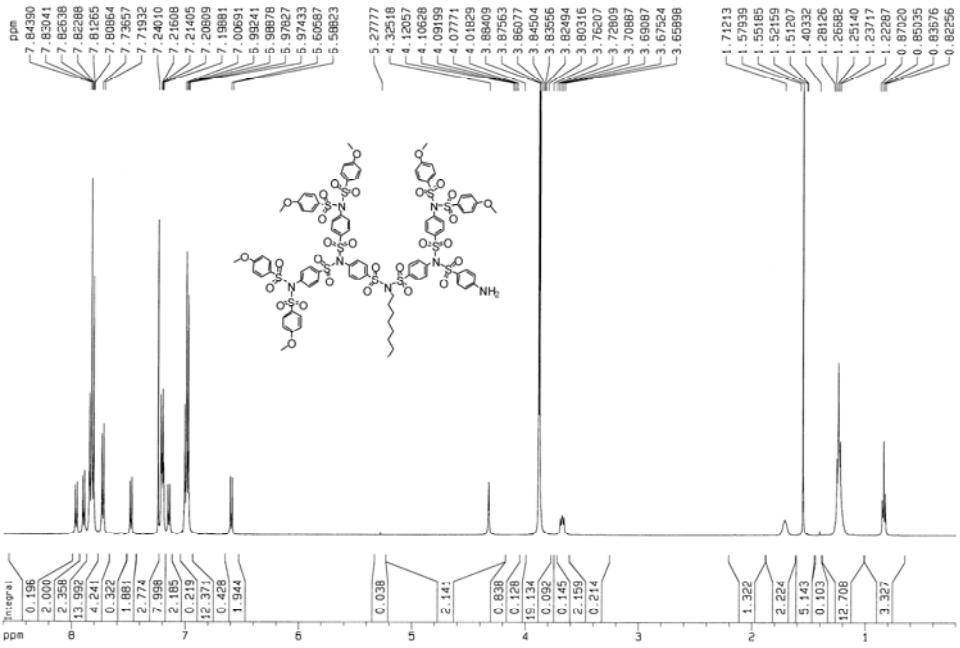
Compound **13**: 1H NMR, 300 MHz, CDCl3



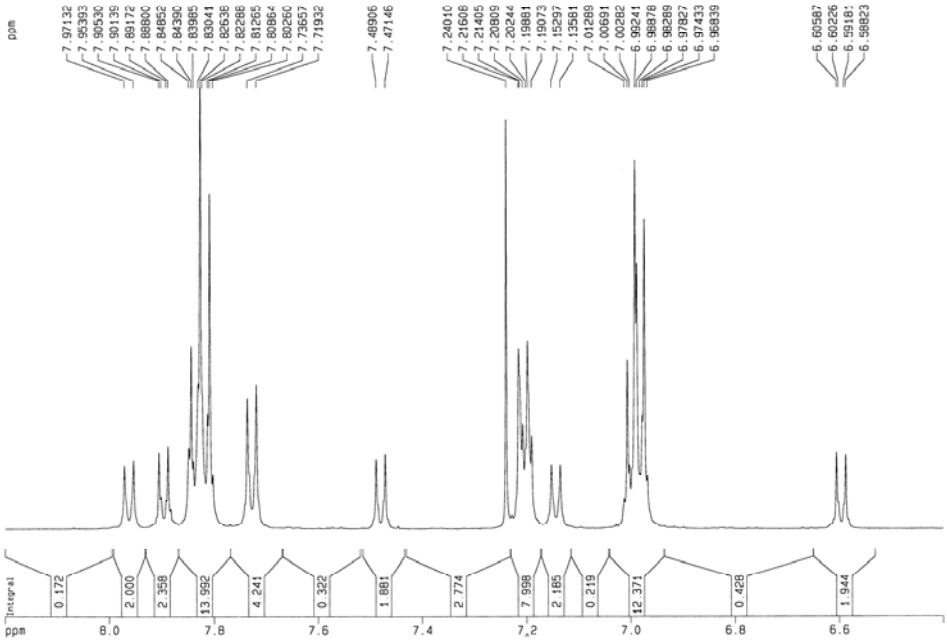
Compound **13**: 1H NMR, 300 MHz, CDCl3 (Aromatic region)



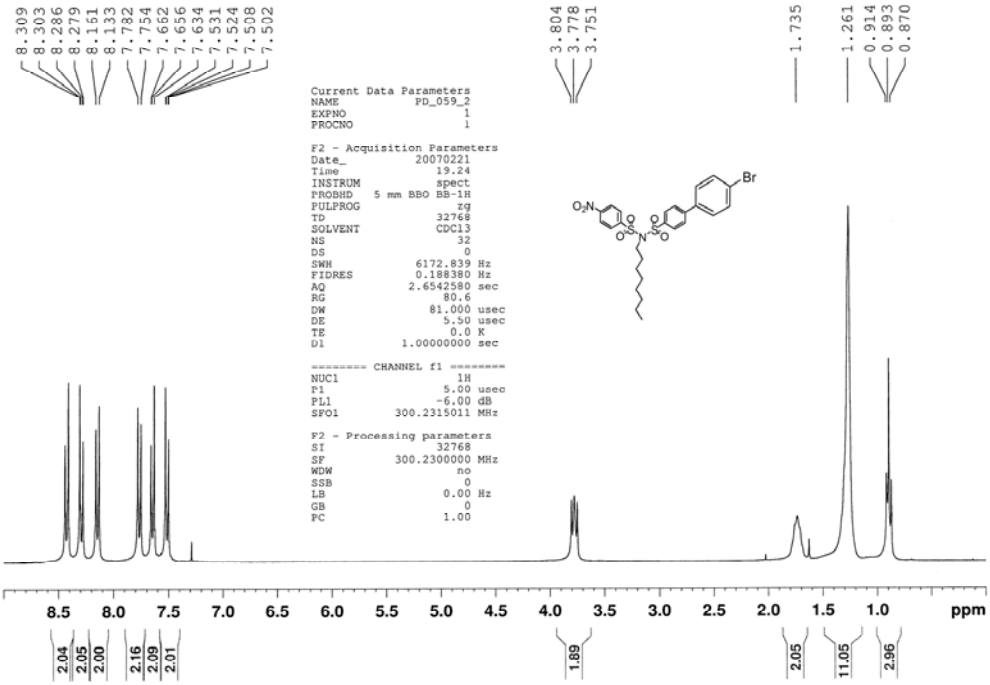
Compound **14**: 1H NMR, 500 MHz, CDCl3



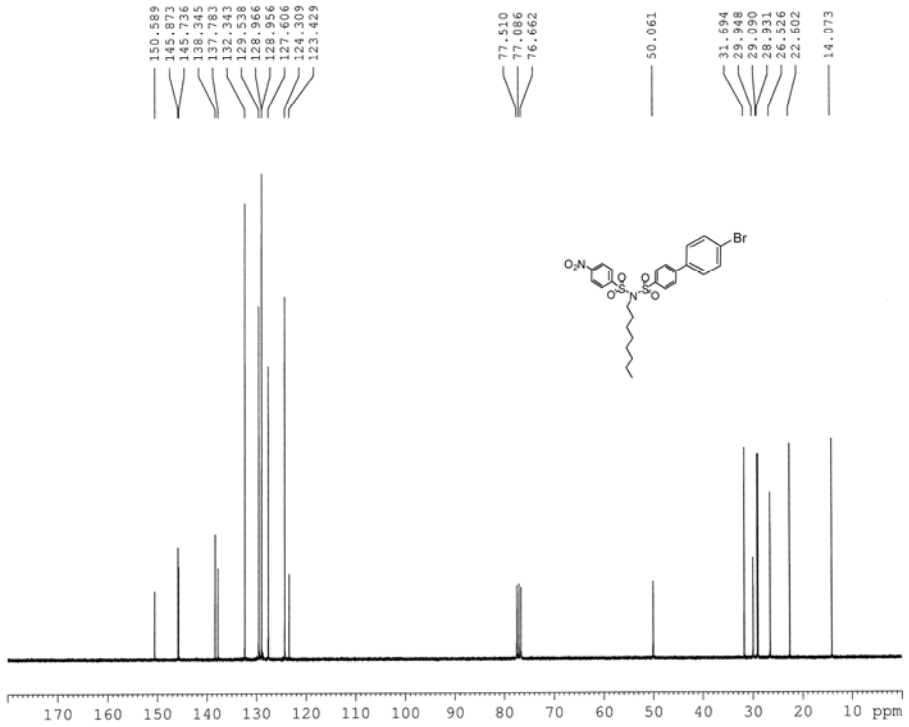
Compound **14**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



Compound **S2**: 1H NMR, 300 MHz, CDCl3

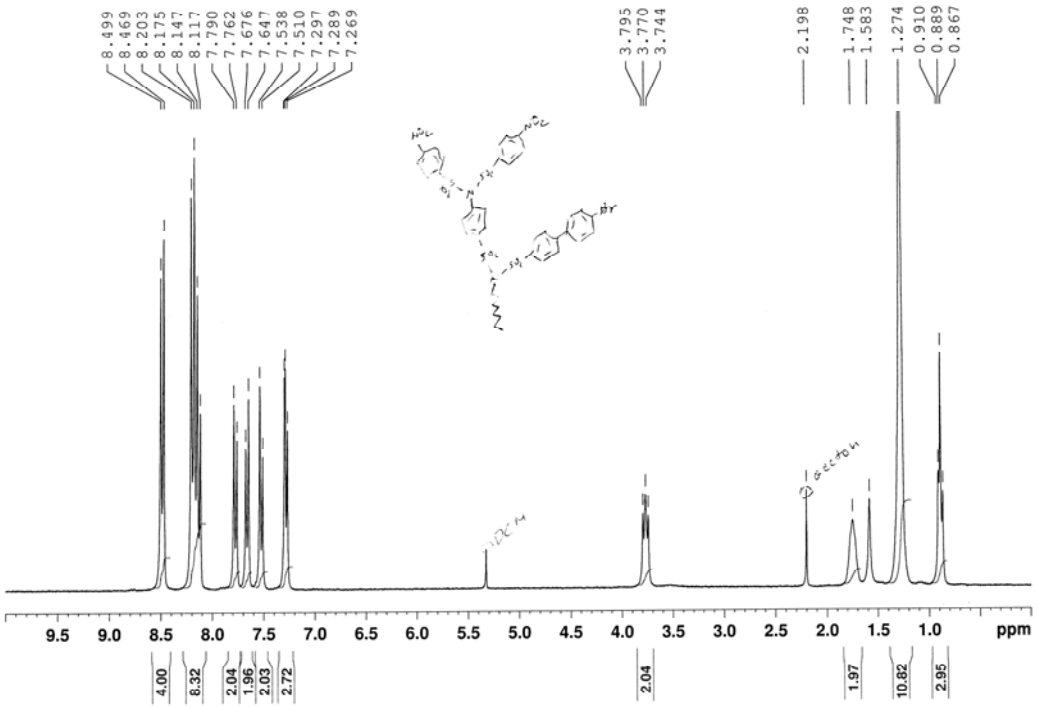


Compound **S2**: 13C NMR, 75 MHz, CDCl3

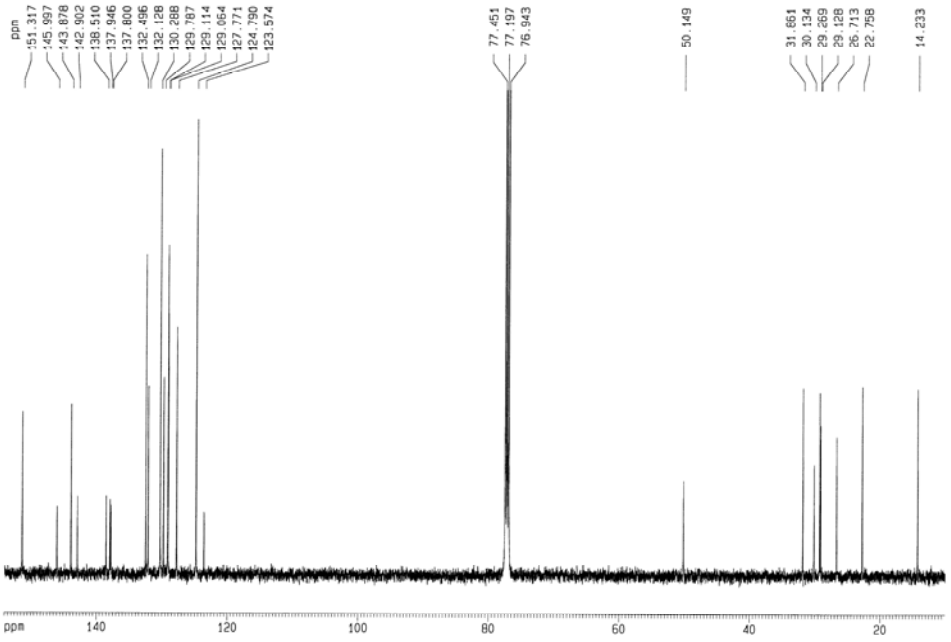


Compound **S3**: 1H NMR, 500 MHz, CDCl3

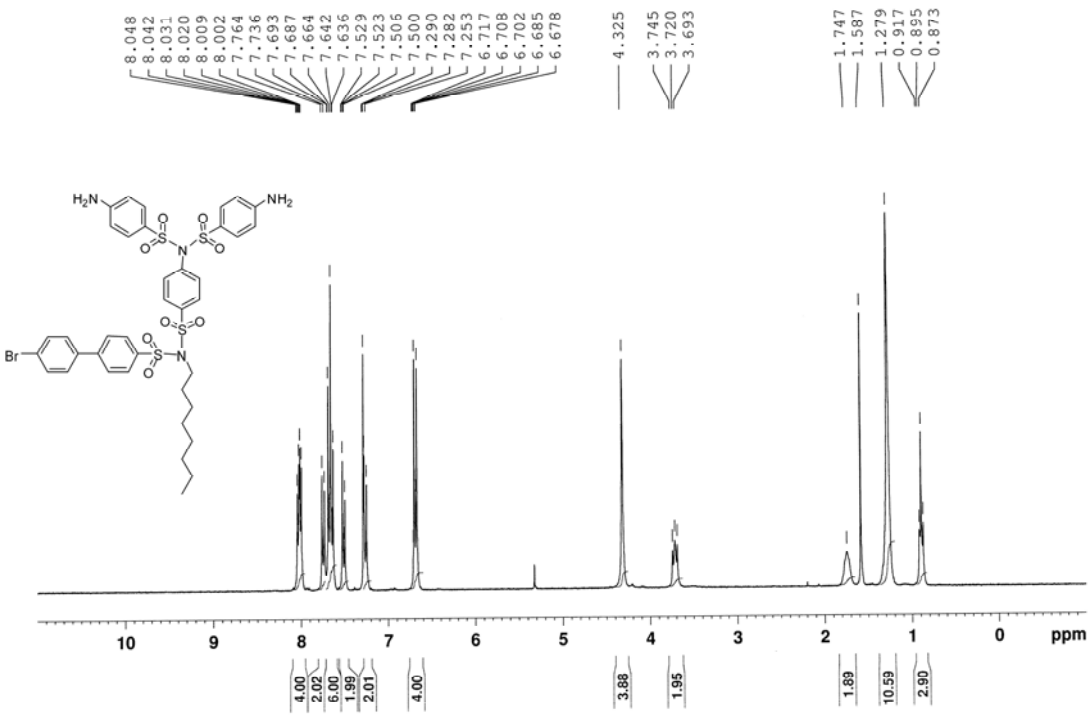
Compound **S4**: 1H NMR, 300 MHz, CDCl3



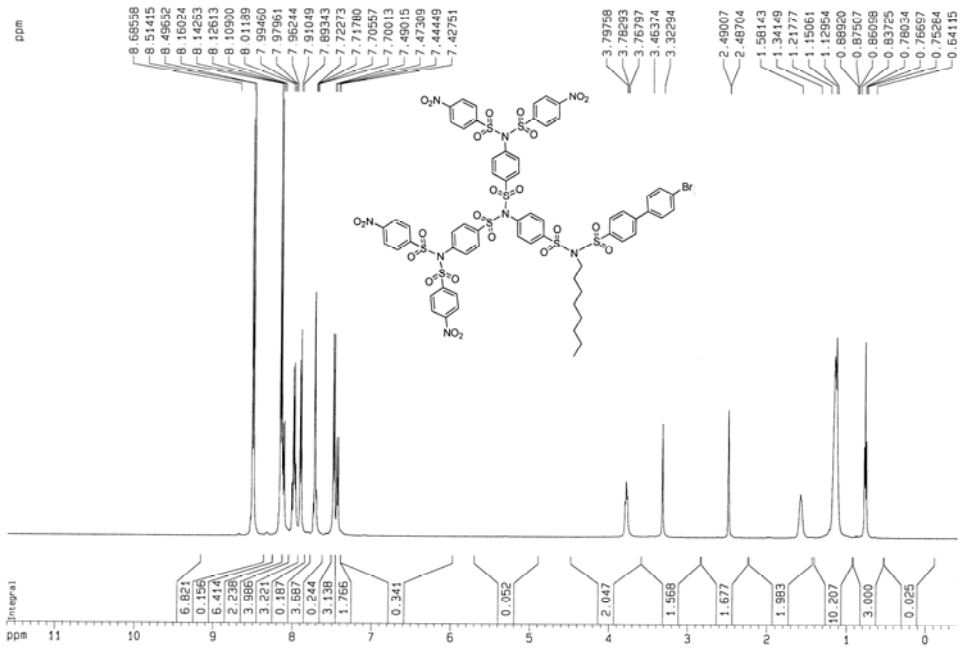
Compound **S4**: 13C NMR, 125 MHz, CDCl3



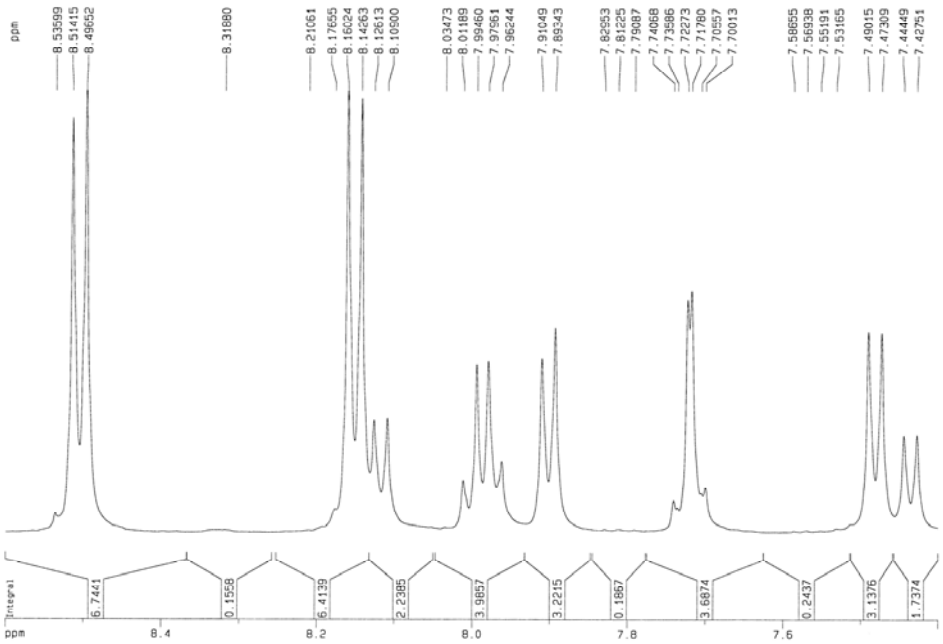
Compound **S5**: 1H NMR, 300 MHz, CDCl3



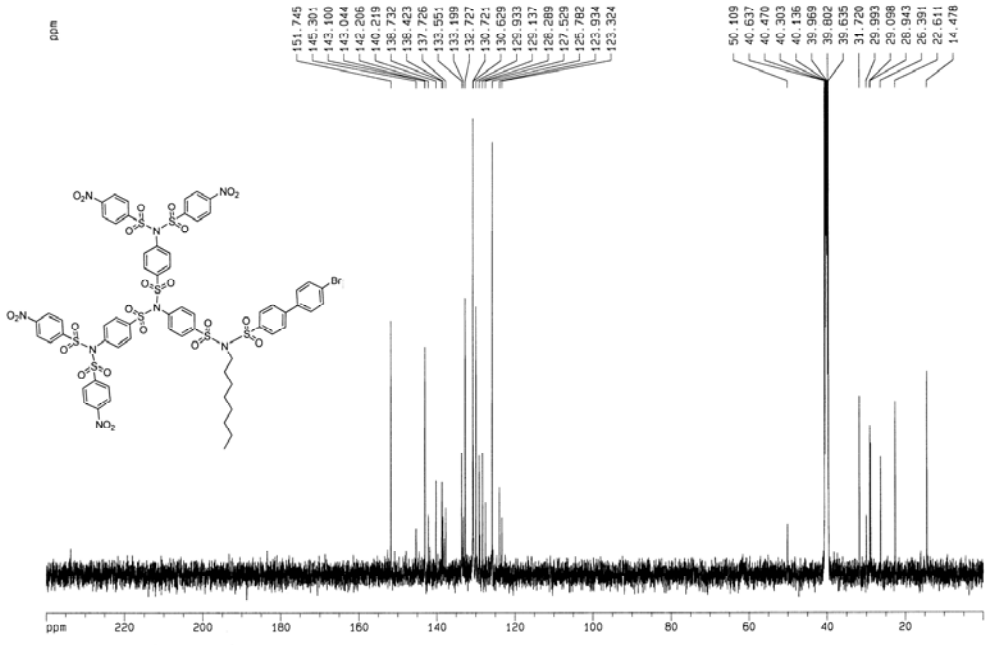
Compound **S6**: 1H NMR, 500 MHz, DMSO-d6



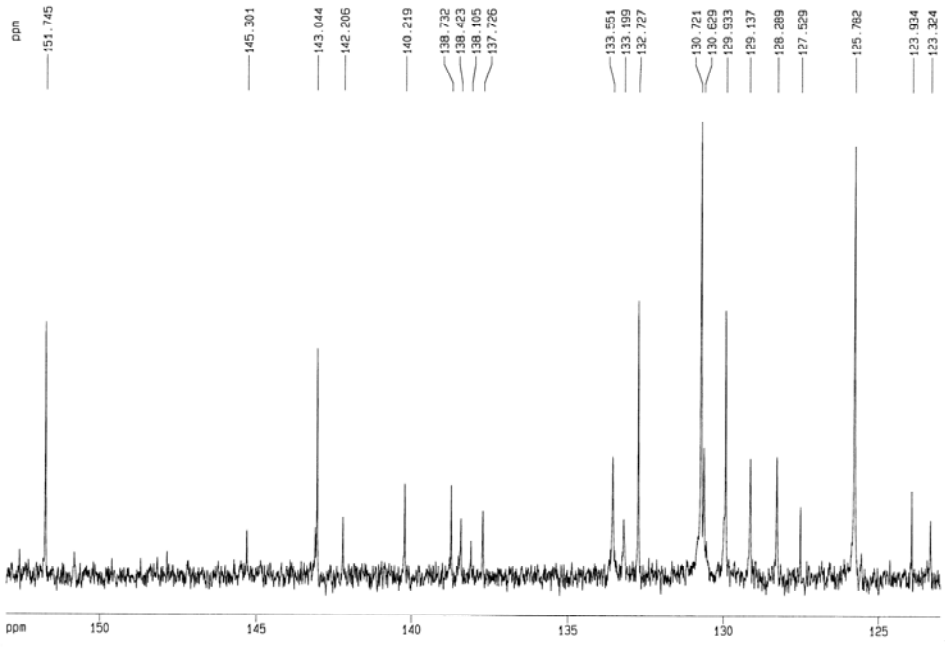
Compound **S6**: 1H NMR, 500 MHz, DMSO-d6 (Aromatic region)



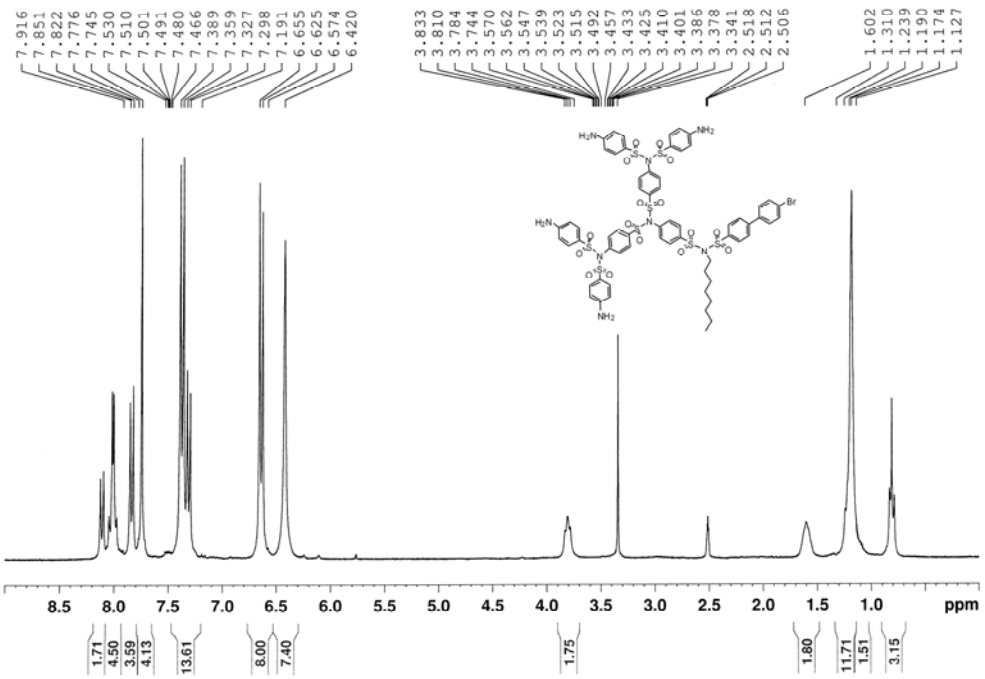
Compound **S6**: 13C NMR, 125 MHz, DMSO-d6



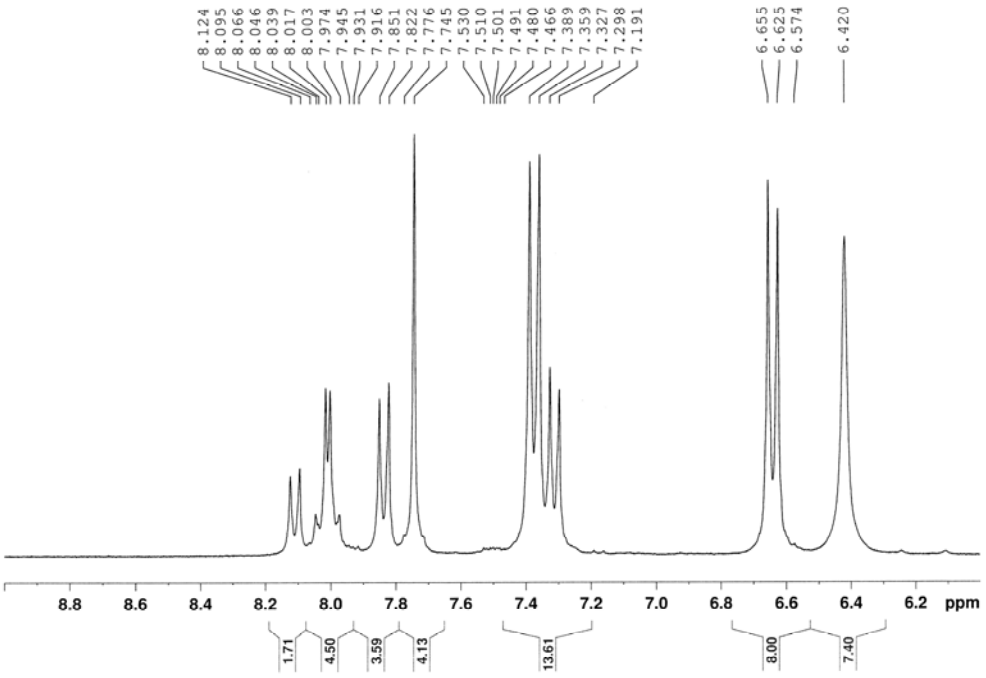
Compound **S6**: 13C NMR, 125 MHz, DMSO-d6 (Aromatic region)



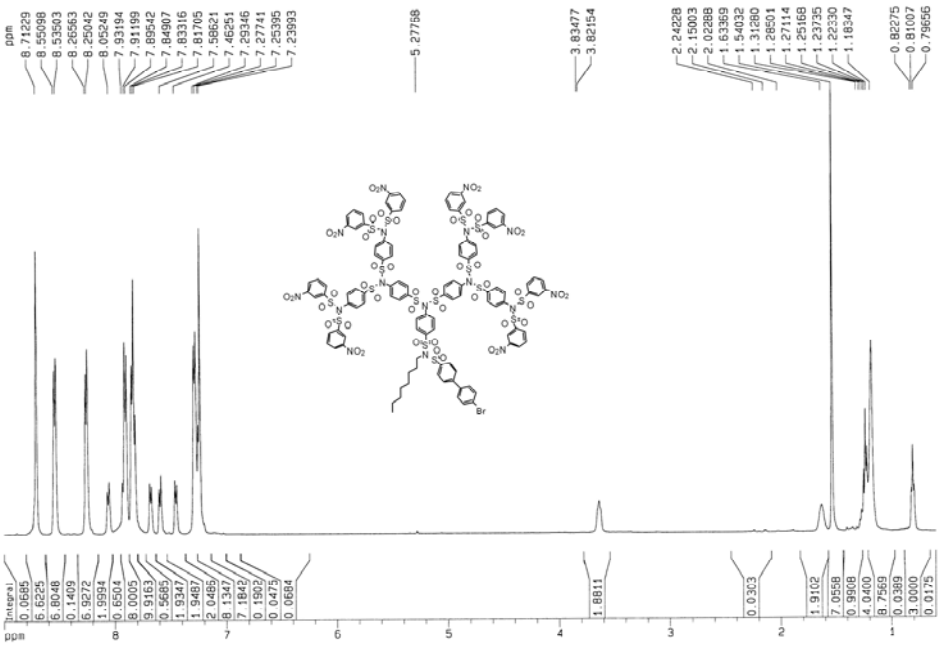
Compound **S7**: 1H NMR, 300 MHz, DMSO-d6



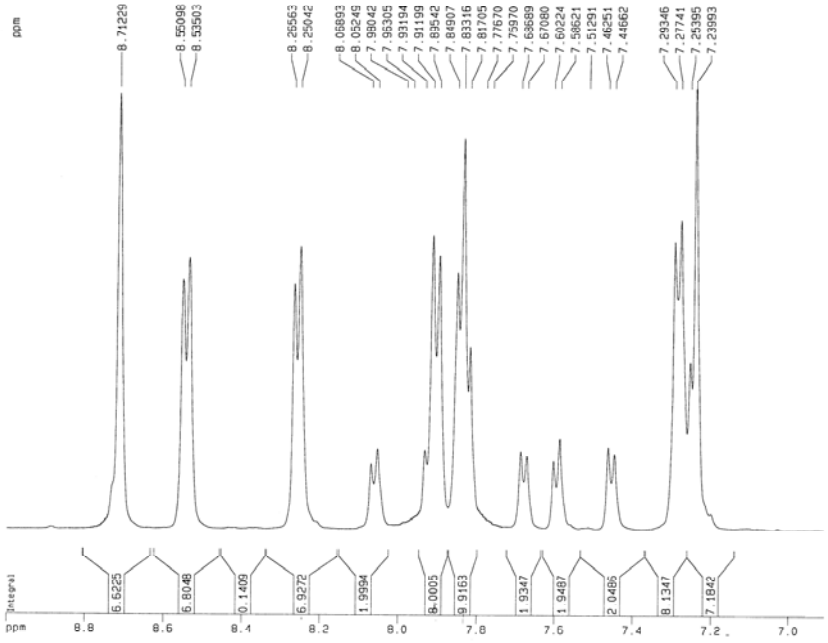
Compound **S7**: 1H NMR, 300 MHz, DMSO-d6 (Aromatic region)



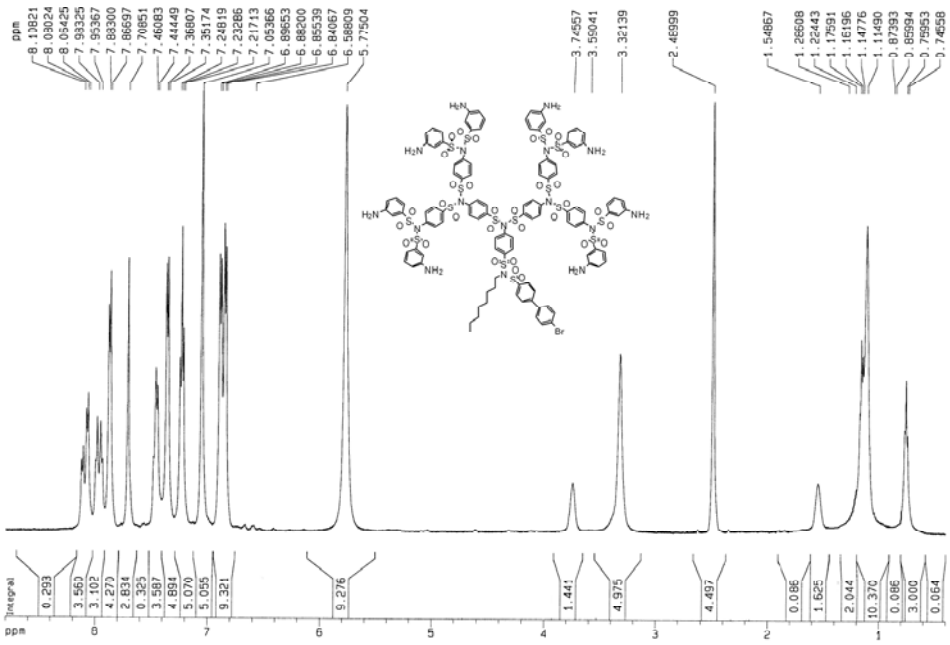
Compound **S8**: 1H NMR, 500 MHz, CDCl3



Compound **S8**: 1H NMR, 500 MHz, CDCl3 (Aromatic region)



Compound **S9**: 1H NMR, 500 MHz, DMSO-d6



Compound **S9**: 1H NMR, 500 MHz, DMSO-d6 (Aromatic region)