Supplementary Information (SI):

Efficient Packing of Long Flexible bis-Imidazolium Cations in the Ubiquitous Bilayers of their *p*-Sulfonatocalix[4]arene Salts

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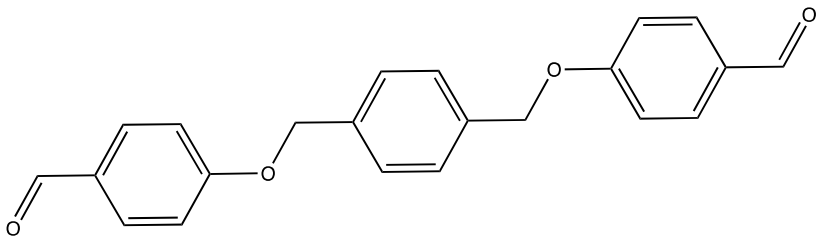
Synthetic procedures and characterization data

General considerations: All reagents were obtained from commercial sources and used without further purification. TLC was performed on pre-coated aluminum plates of Silica Gel 60 F254 (0.25 mm, E. Merck).
^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Differential Scanning Calorimetry (DSC) thermograms were collected using a TA Instrument Q100 DSC, using heating and cooling scan rate of 10 ^{o}C min^{-1} under purging nitrogen gas flow of 50 ml min^{-1}.

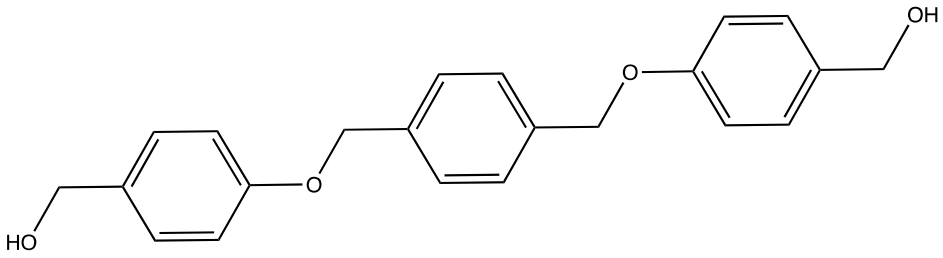
Experimental section

1,4-Benzyloxy-bis-(4-benzaldehyde), 1



To a heterogeneous mixture of α,α'-dibromo-*p*-xylene (5.28 g, 0.02 mol) and sodium carbonate (5.30 g, 0.05 mol) in dry acetone (250 ml), 4-hydroxybenzaldehyde (4.88 g, 0.04 mol) was added portion wise and the mixture was refluxed for 48 hours under continuous stirring. The solvent was then evaporated under reduced pressure and the crude material was washed with methanol followed by 3 × 250 mL water. The precipitate was filtered, dried and re-crystallized from methanol to obtain off-white powder of 1,4-benzyloxy-bis-(4-benzaldehyde). Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.91 [s, 2H, CHO], 7.88 [d, 4H, ArH], 7.49 [s, 4H, ArH], 7.11 [d, 4H, ArH], 5.19 [s, 4H, CH_2]; ^{13}C NMR (400 MHz, $CDCl_3$) δ_C = 190.74, 163.59, 136.16, 132.01, 130.25, 127.83, 115.14, 69.89; HRMS-ESI (*m/z*) : $[M + Na]^+$ calcd for $C_{22}H_{18}O_4Na$, 369.1103, 370.1136; found 369.1116, 370.1150.

4,4'-(1,4-Phenylenebis(methyleneoxy))diphenol, 2



Compound **1** (3.5 g, 0.01 mol) were dissolved in tetrahydrofuran (250ml) and cooled down to 0°C. Lithium aluminum hydride (1.0g, 0.026 mol) was added in small portions carefully in 30 minutes period. The mixture was stirred for 2 hours. The progress of the reaction was monitored using TLC. 1 mL of water was added dropwise to the mixture, followed by addition of 1 mL of 15% aqueous sodium hydroxide and further diluted with 3 mL of water. The mixture was stirred for another 30 min. The white solid was filtered and the solvent was evaporated which affords pure white solid of compound **2**. Recrystallization from a warm aqueous solution affords colorless crystals. Yield 90%; ^{1}H NMR (400 MHz, DMSO) δ_H = 7.45 [s, 4H, ArH], 7.23 [d, 4H, ArH], 6.96 [d, 4H, ArH], 5.09 [s, 4H, CH_2], 5.04 [d, 4H, CH_2], 4.41 [d, 4H, CH_2]; ^{13}C NMR (400 MHz, DMSO) δ_C = 157.60, 137.22, 135.24, 128.39, 128.14, 114.90, 69.35, 62.99; HRMS-ESI (*m/z*) : $[M + Na]^+$ calcd for $C_{22}H_{22}O_4Na$, 373.1416, 374.1449; found 373.1415, 374.1441.

Crystal data for $C_{22}H_{22}O_4$: M = 350.39, colorless plate, 0.36 · 0.15 · 0.03 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 19.6775(18), b = 7.2816(9), c = 6.0174(6) Å, β = 96.137(9)°, V = 857.25(16) Å^3, Z = 2, D_c = 1.357 g/cm^3, μ = 0.748 mm^{-1}. F_{000} = 372, CuKα radiation, λ = 1.54178 Å, T = 100(2)K, $2\theta_{max}$ = 134.4°, 3271 reflections collected, 1505 unique (R_{int} = 0.0474). Final *GooF* = 1.005, *R1* = 0.0554, *wR2* = 0.1322, *R* indices based on 1155 reflections with I > 2σ(I) (refinement on F^2), $|\Delta\rho|_{max}$= 0.24(5) e Å^{-3}, 127 parameters. Lp and absorption corrections applied.

CCDC reference number: 1038273.

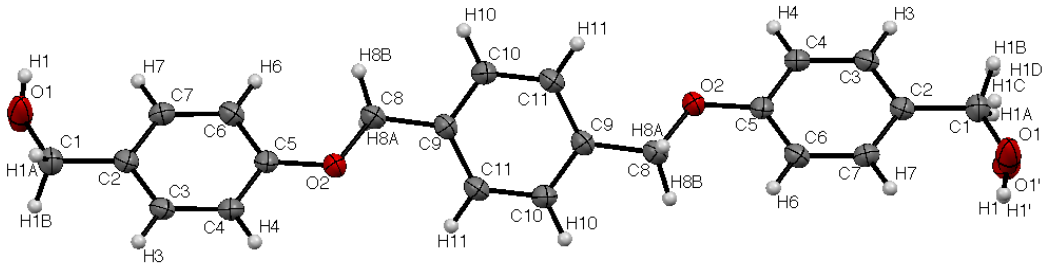
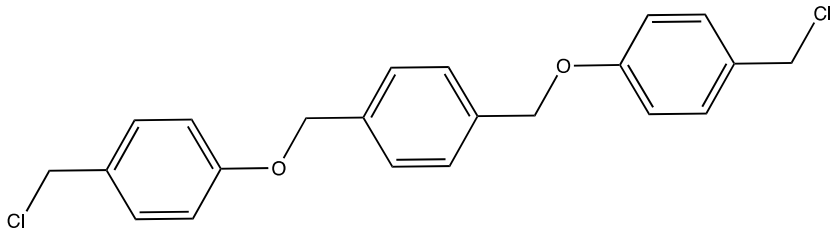


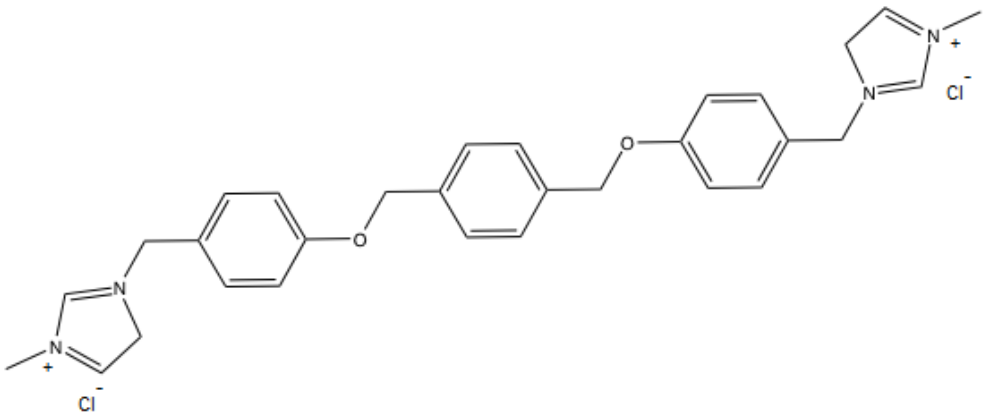
Figure 1: Crystal structure of **2**.

1,4-Benzyloxy-bis-(4-(chloromethyl)benzene), 3



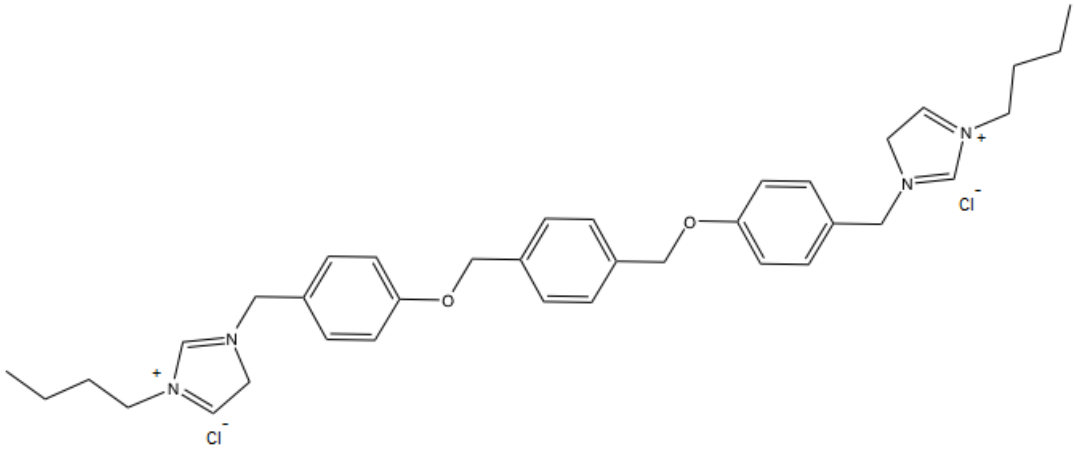
To a stirred solution of **2** (4.0 g; 0.01 mol) in THF (25 mL), hydrochloric acid (4.0 mL; 0.10 mol) was slowly added over a period of 15 min at 0°C. The reaction was to stir for 5-6 hours whilst monitoring its progress by TLC. After the completion of dichlorination, the solvent was removed under reduced pressure affording the crude product **3**. Yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.47 [s, 4H, ArH], 7.33 [d, 4H, ArH], 6.98 [d, 4H, ArH], 5.20 [s, 4H, CH_2], 4.59 [s, 4H, CH_2]; ^{13}C NMR (400 MHz, $CDCl_3$) δ_C = 158.80, 136.65, 130.09, 127.70, 115.07, 69.76, 46.23; HRMS-ESI (*m/z*) : $[M + Na]^+$ calcd for $C_{22}H_{20}O_2Cl_2Na$, 409.0738; found 409.1631.

1,1´-[1,4-phenylenebis(methylene)bis(oxy)bis(4,1-phenylene)bis(methylene)]bis(3-methylimidazolium) dichloride, 4



Compound **3** (4.0 g; 0.01 mol) was dissolved in dried acetonitrile (50 mL) and stirred, followed by dropwise addition of methyl imidazole (1.64 g, 0.02 mol). The mixture was stirred for 24 hours in room temperature. The solvent was removed under reduced pressure and yield white solid of compound **4**. The solid was washed with acetone followed by drying under vacuum for 24 hours to remove traces of solvents and moisture. Yield 90%; T_m = 200-210 ^{o}C; ^{1}H NMR (400 MHz, D_2O) δ_H = 7.38 [s, 4H, ArH], 7.33 [d, 4H, ArH], 7.32 [d, 2H, ArH], 7.29 [d, 2H, ArH], 7.01 [d, 4H, ArH], 5.21 [s, 4H, CH_2], 5.09 [d, 4H, CH_2], 3.76[s, 6H, CH_3]; ^{13}C NMR (400 MHz, D_2O) δ_C = 158.41, 136.47, 130.37, 128.30, 126.47, 123.66, 122.00, 115.76, 69.88, 52.21, 35.61; HRMS-ESI (*m/z*) : $[M + Na]^+$ calcd for $C_{30}H_{32}N_4O_2Cl_2Na$, 480.2525, 481.2559; found 480.2740, 481.2742.

1,1´-[1,4-phenylenebis(methylene)bis(oxy)bis(4,1-phenylene)bis(methylene)]bis(3-butylimidazolium) dichloride, 5



Compound **3** (4.0 g; 0.01 mol) was dissolved in dried acetonitrile (50 mL) and stirred, followed by dropwise addition of butyl imidazole (2.48 g, 0.02 mol). The mixture was stirred for 24 hourrs in room temperature. The solvent was removed under reduced pressure and yield yellow viscous liquid of compound **5**. The solid was washed with acetone followed by drying under vacuum for 24 hours to remove traces of solvents and moisture. Yield 90%; ^{1}H NMR (400 MHz, D_2O) δ_H = 7.32 [d, 4H, ArH], 7.22 [d, 4H, ArH], 7.04 [s, 4H, ArH], 6.76 [d, 4H, ArH], 7.01 [d, 4H, ArH], 5.35 [s, 4H, CH_2], 5.15 [s, 4H, CH_2], 4.00 [m, 4H, CH_2], 1.64[m, 4H, CH_2], 1.13 [m, 4H, CH_2], 0.78 [t, 6H, CH_3]; ^{13}C NMR (400 MHz, D_2O) δ_C = 158.34, 136.30, 120.29, 127.89, 127.05, 126.64, 122.52, 122.04, 115.66, 69.41, 52.22, 49.33, 46.67, 32.13, 31.12, 18.96, 18.60, 12.70, 12.55; HRMS-ESI (*m/z*) : $[M + Na]^+$ calcd for $C_{36}H_{44}N_4O_2Cl_2Na$, 657.2739, 659.2710; found 657.3617, 657.3745.

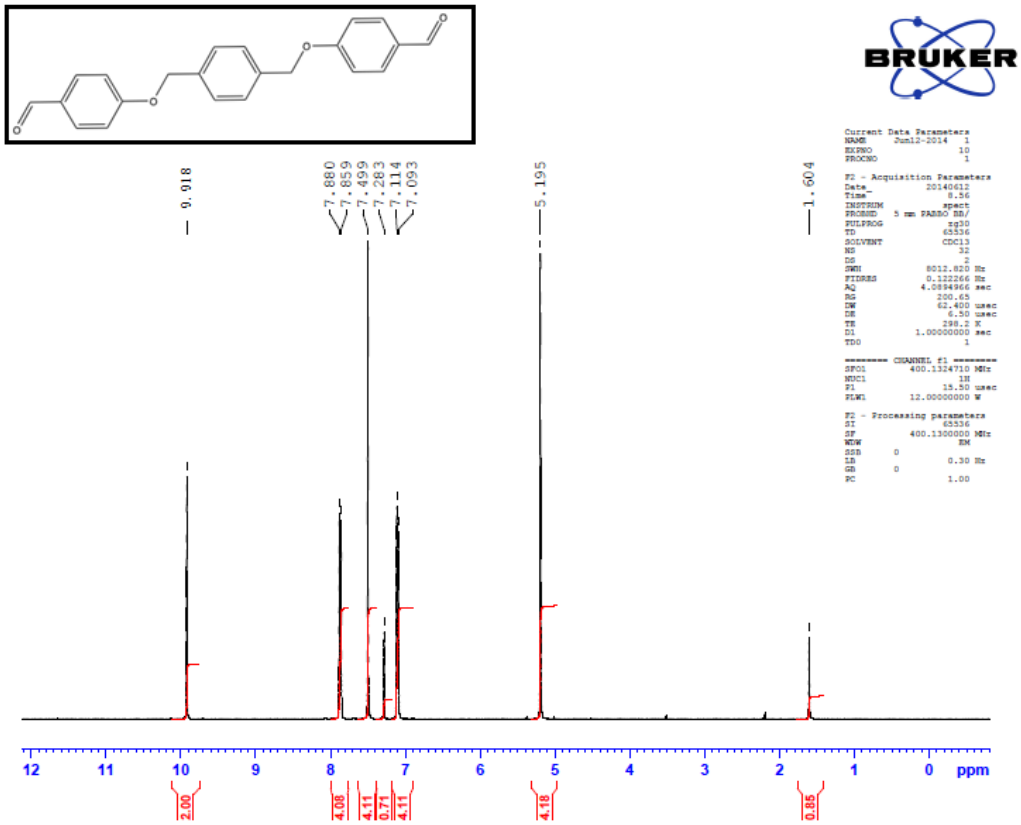


Figure 2: ^{1}H NMR for **1**.

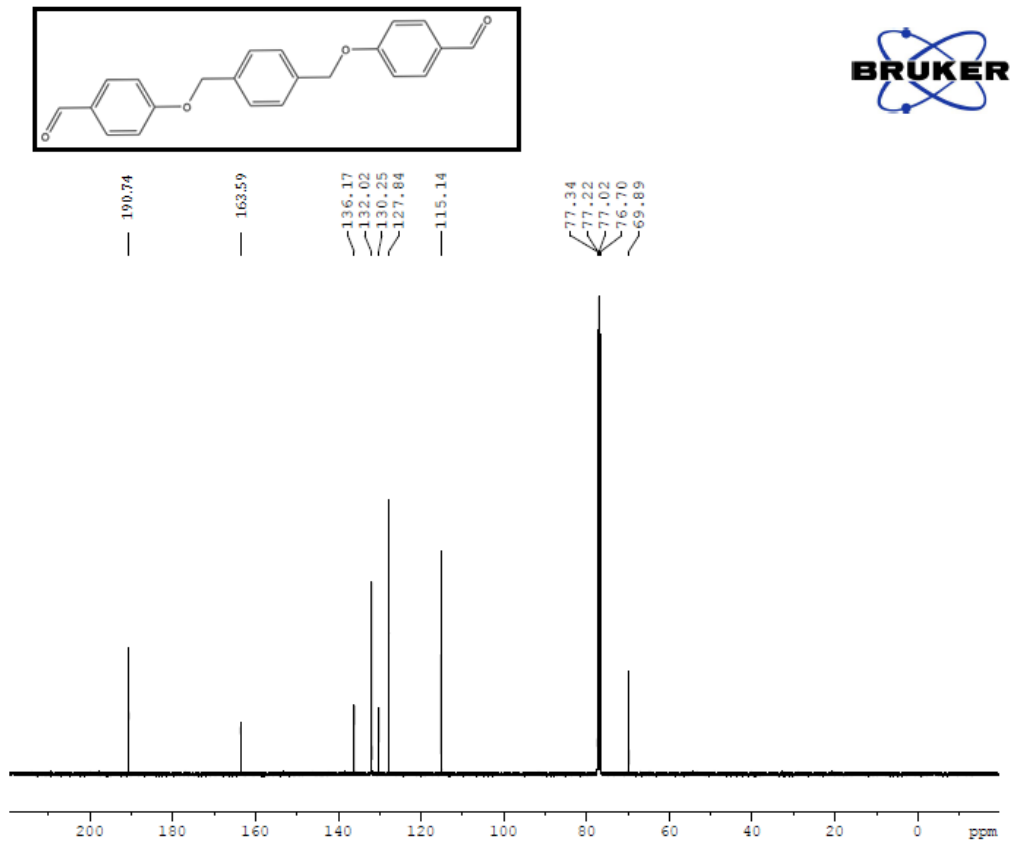


Figure 3: ^{13}C NMR for **1**.

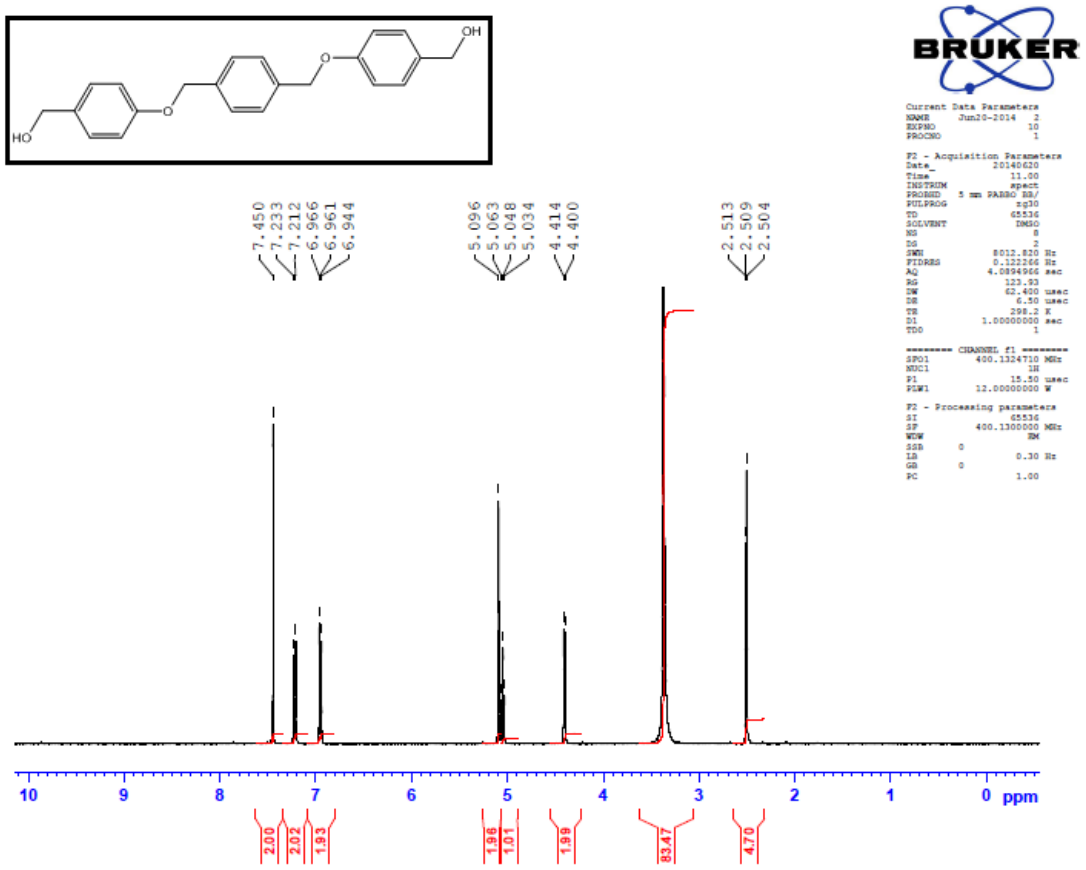


Figure 4: ^{1}H NMR for **2**.

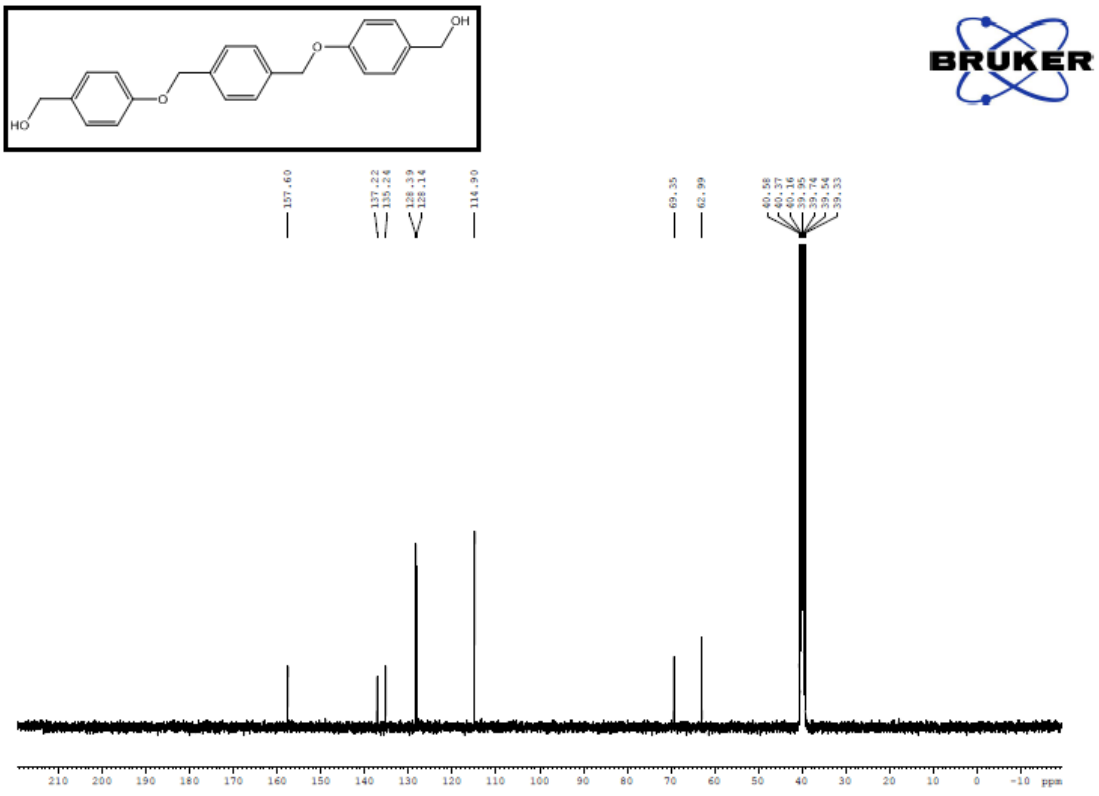


Figure 5: ^{13}C NMR for **2**.

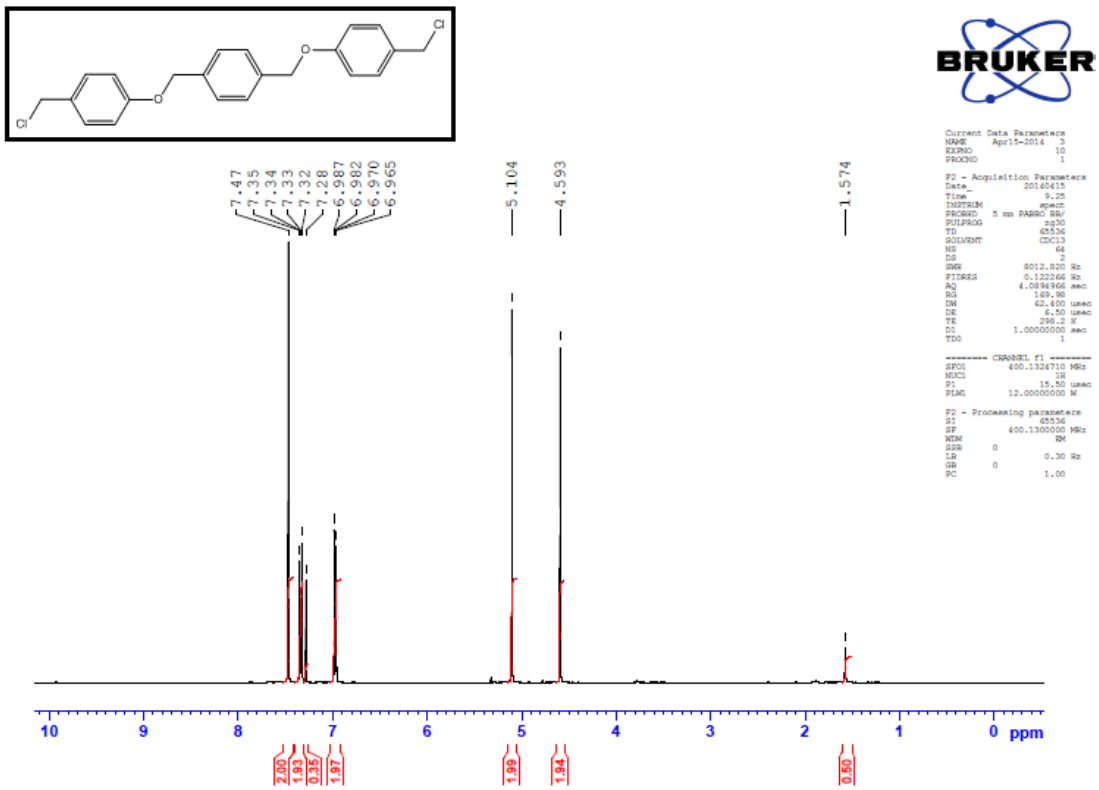


Figure 6: ^{1}H NMR for **3**.

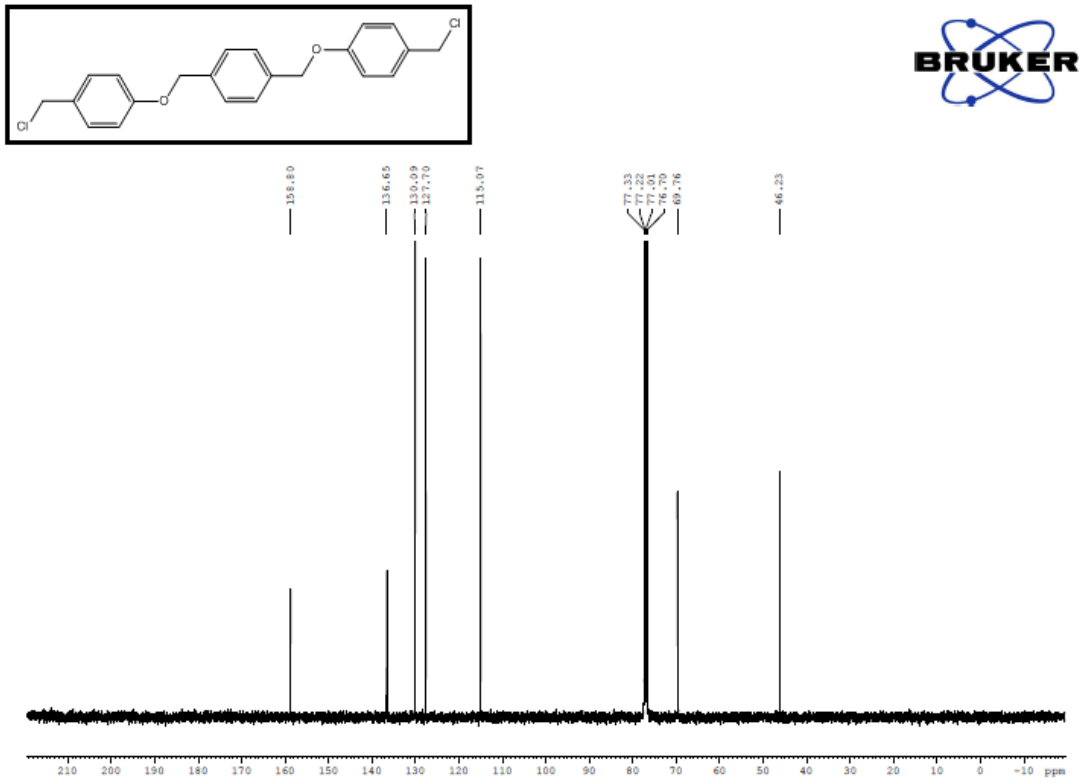


Figure 7: ^{13}C NMR for **3**.

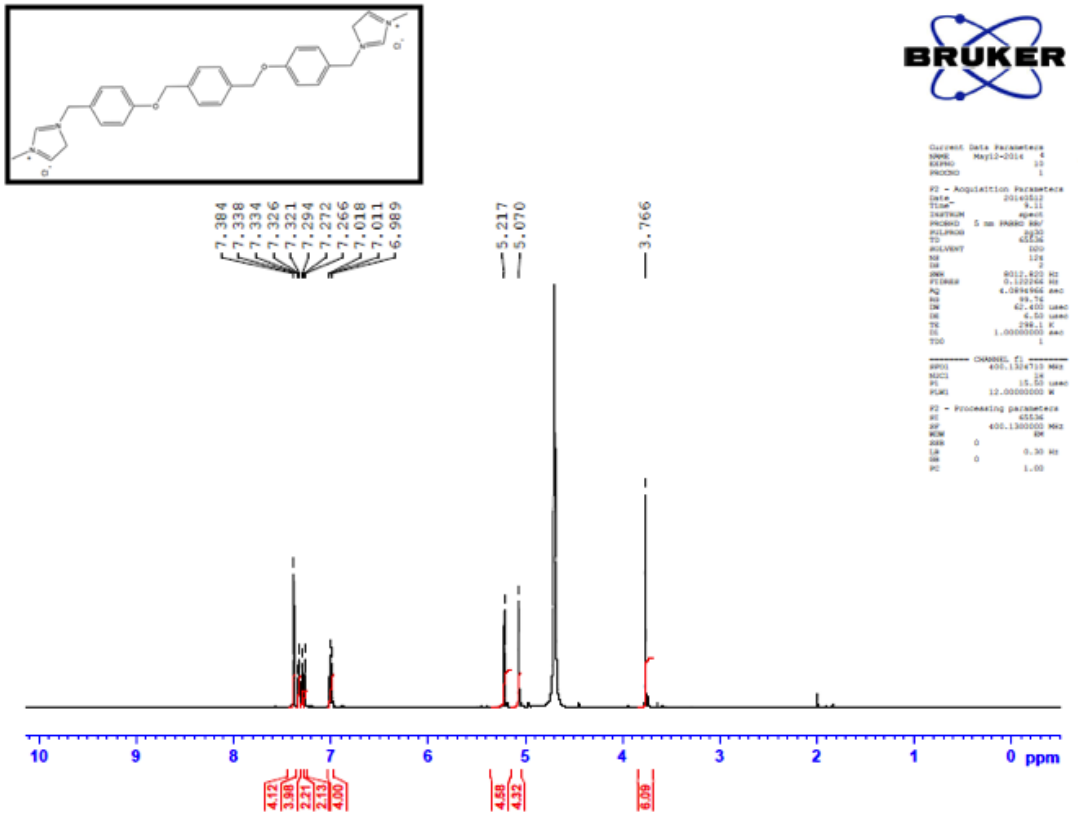


Figure 8: ^{1}H NMR for **4**.

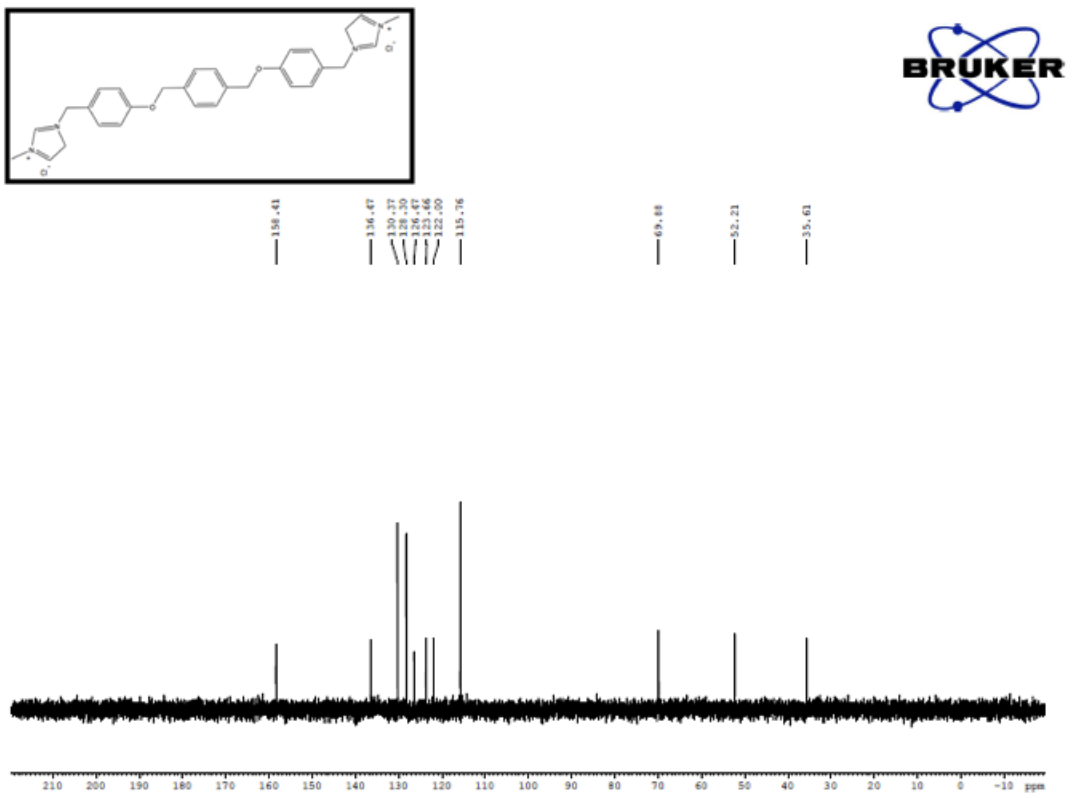


Figure 9: ^{13}C NMR for **4**.

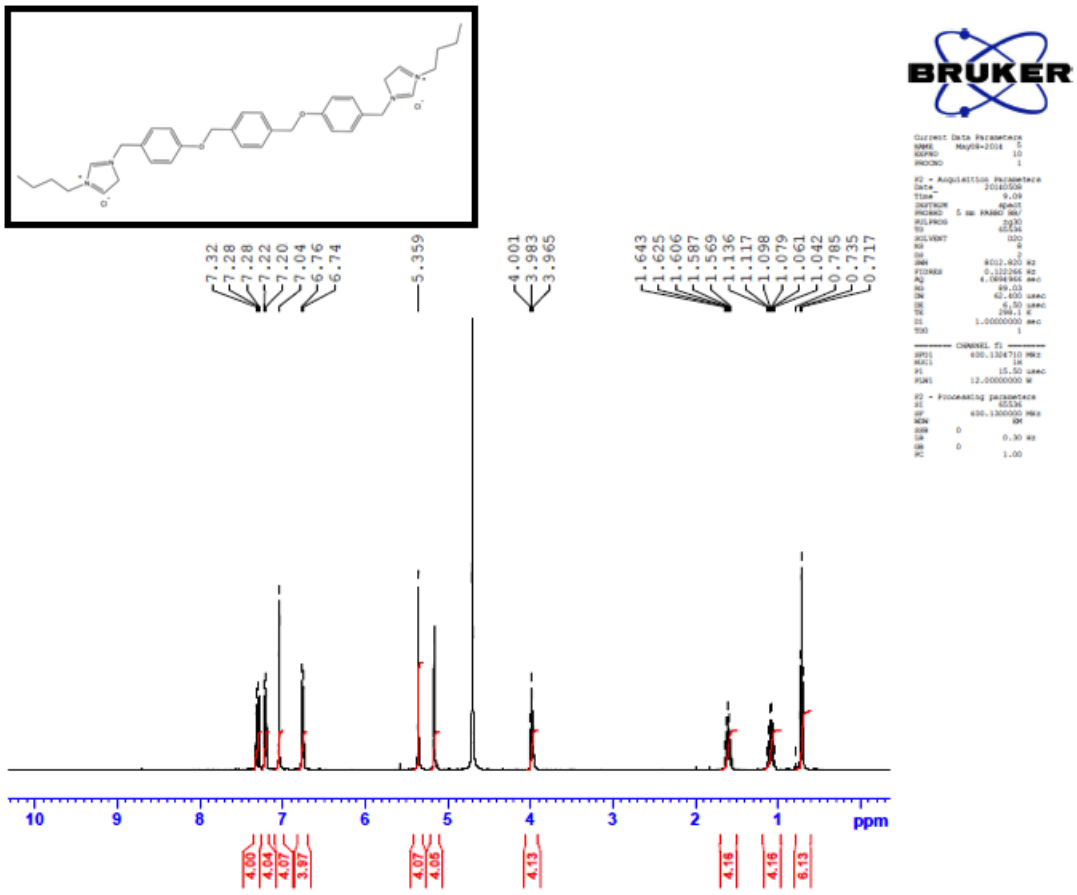


Figure 10: ^{1}H NMR for **5**.

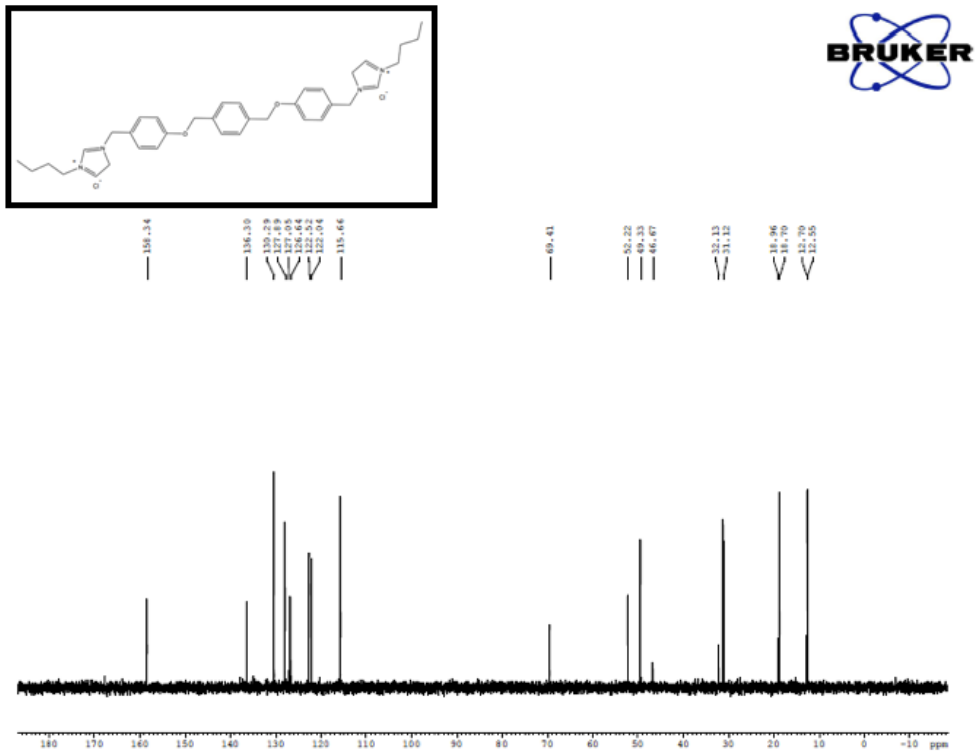


Figure 11: ^{13}C NMR for **5**.

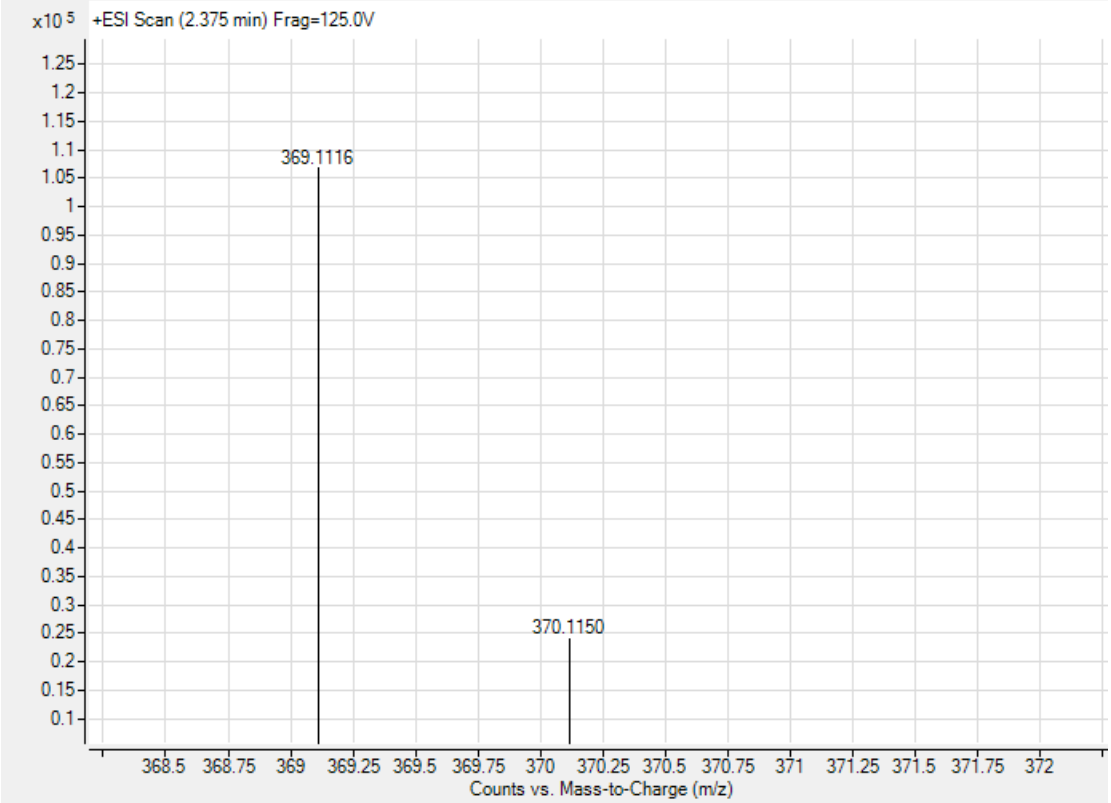


Figure 12: HRMS-ESI for **1**.

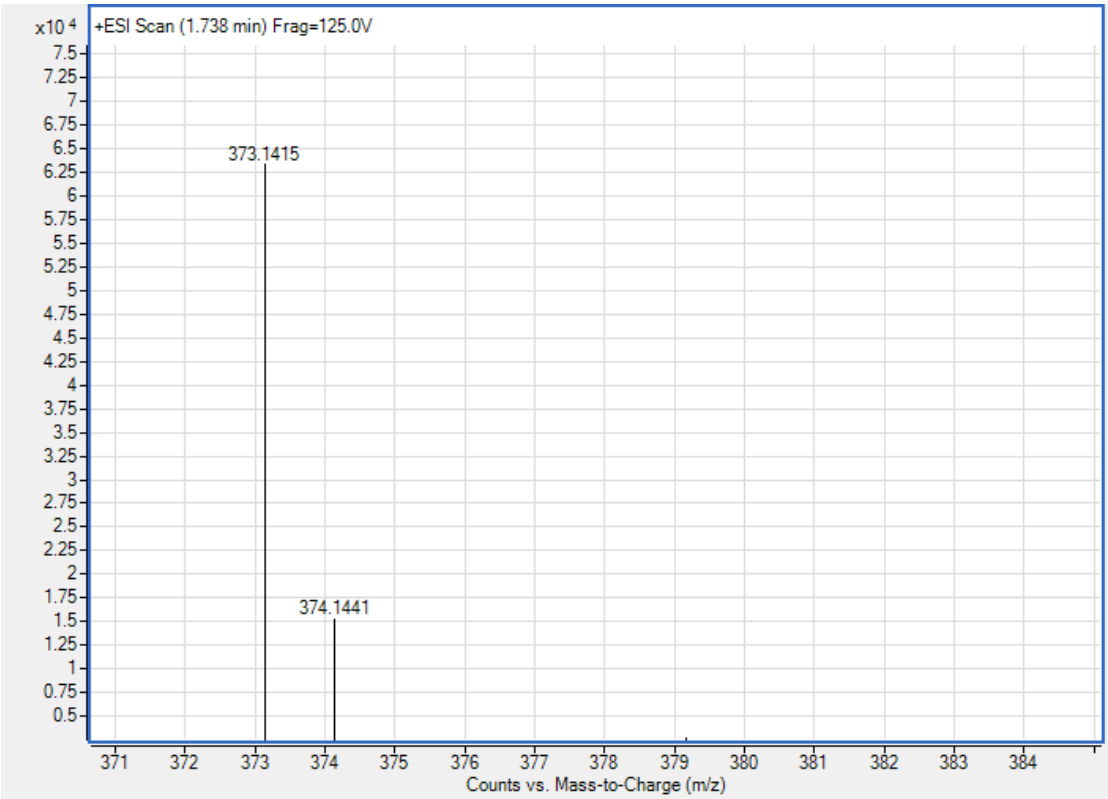


Figure 13: HRMS-ESI for **2**.

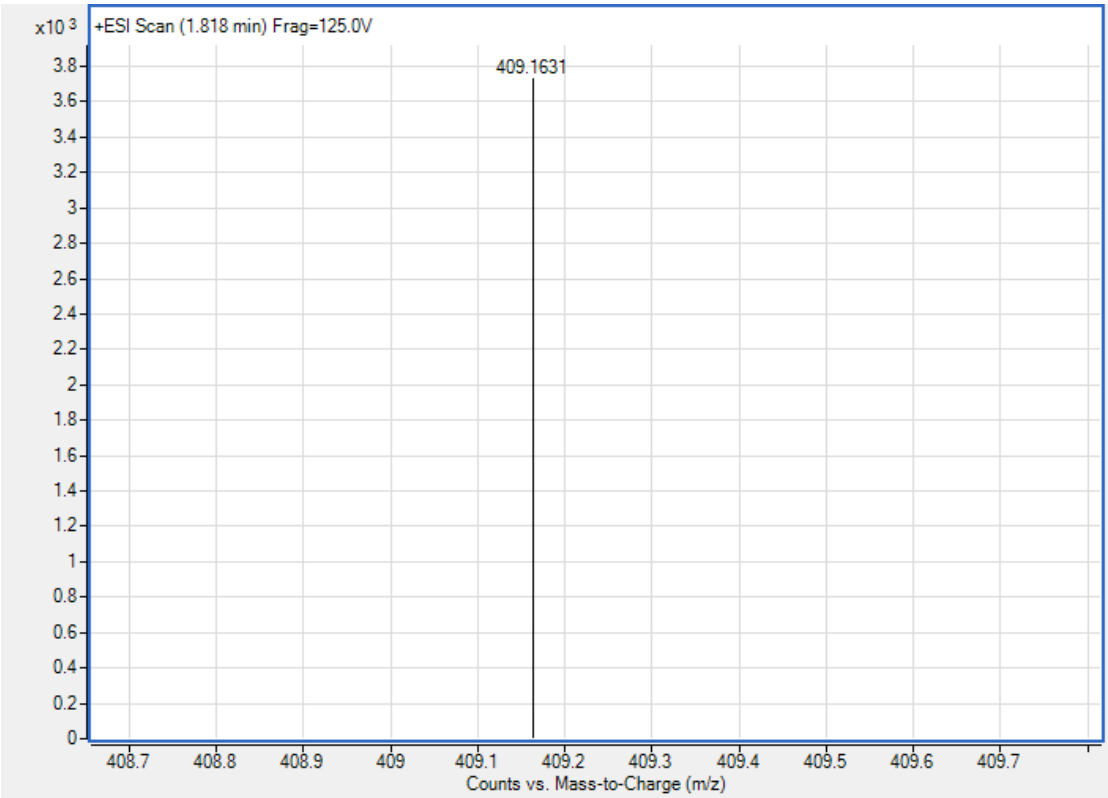


Figure 14: HRMS-ESI for **3**.

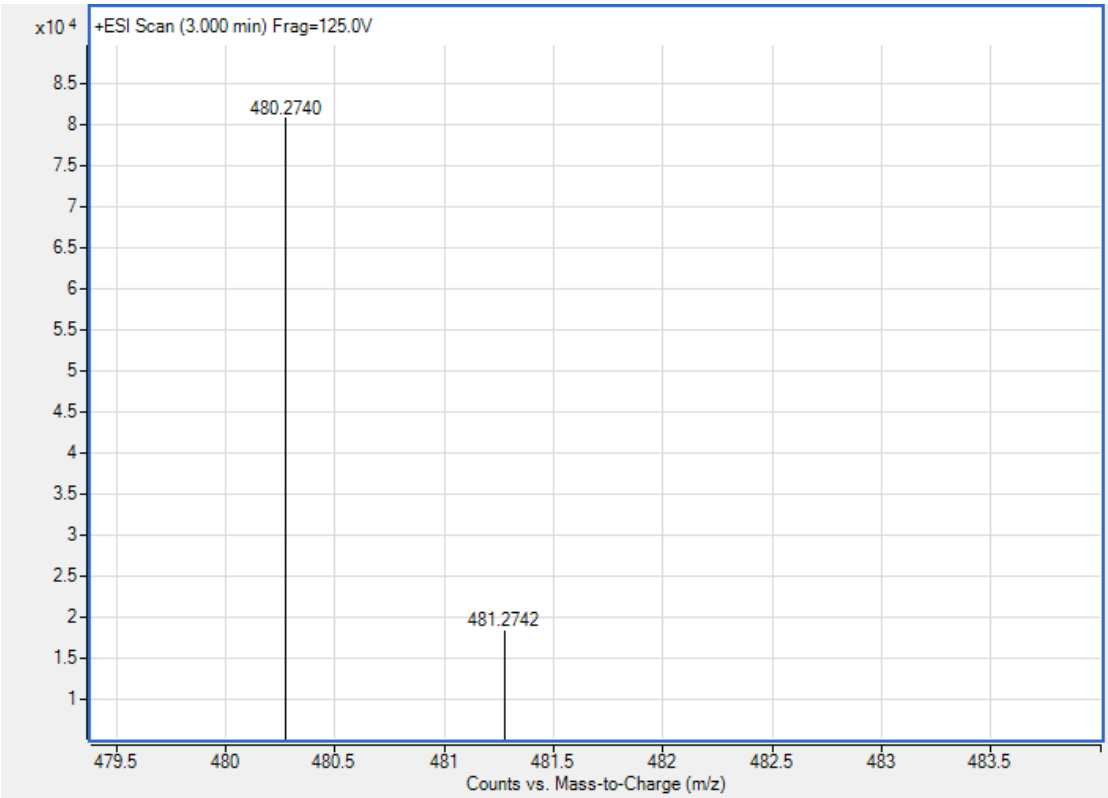


Figure 15: HRMS-ESI for **4**.

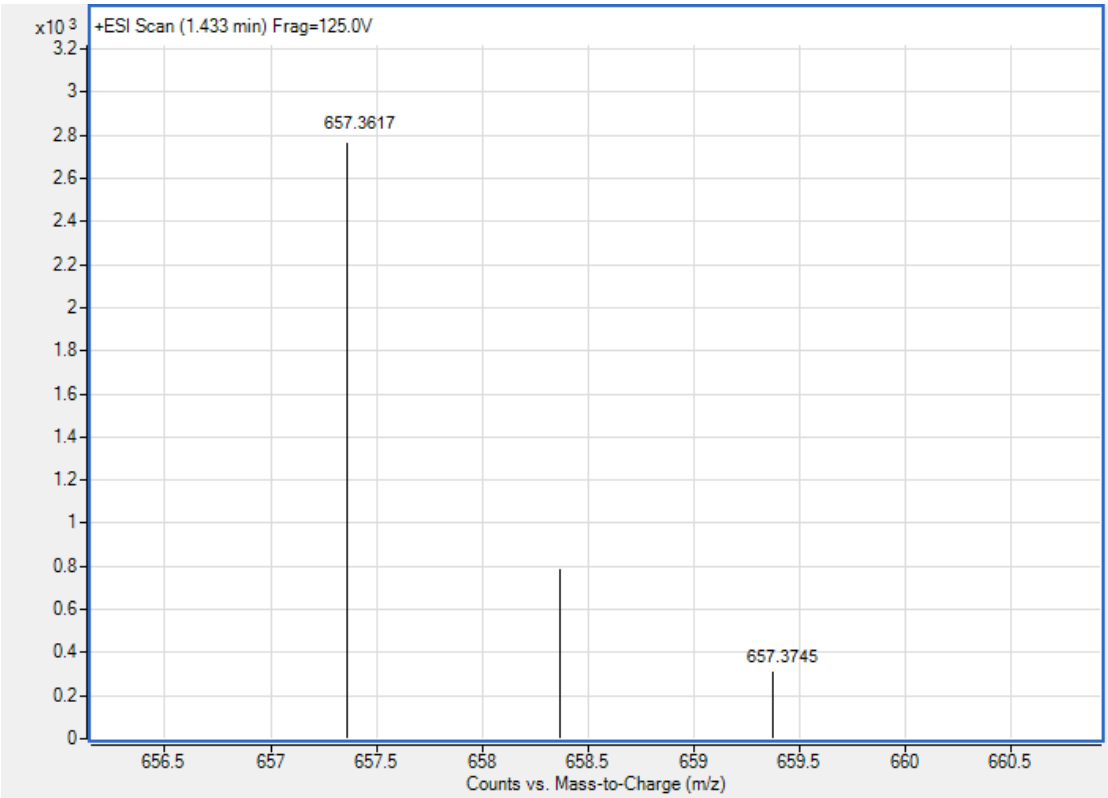


Figure 16: HRMS-ESI for **5**.

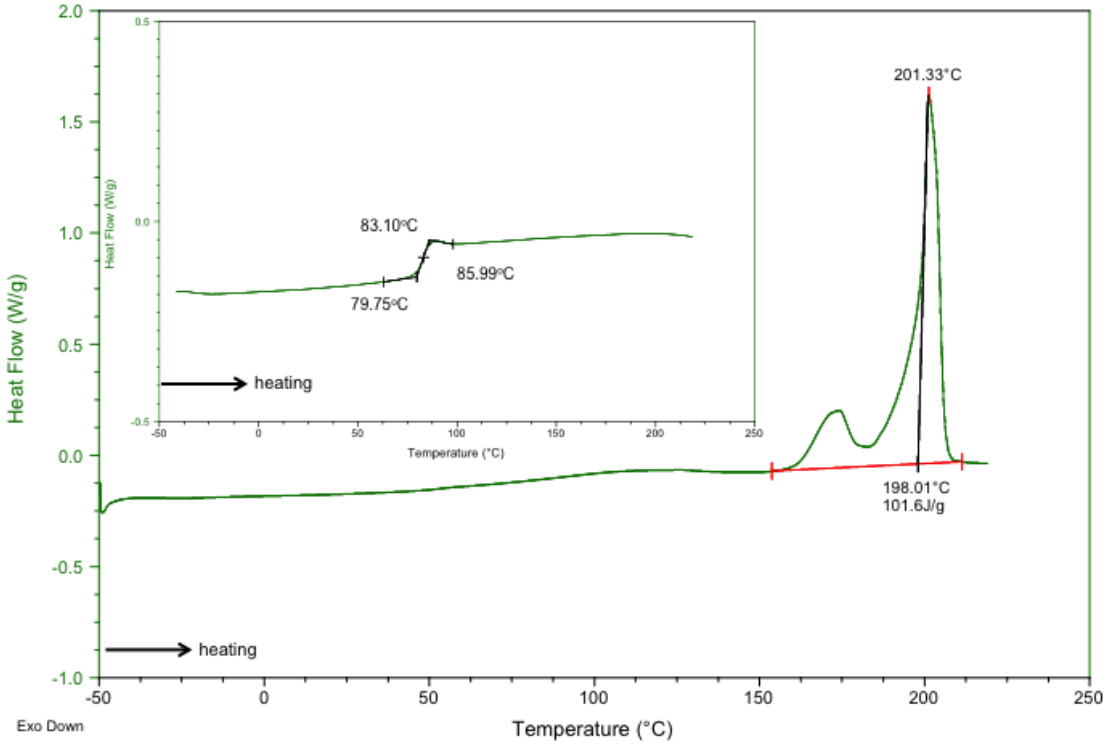


Figure 17: DSC thermogram for **4**.

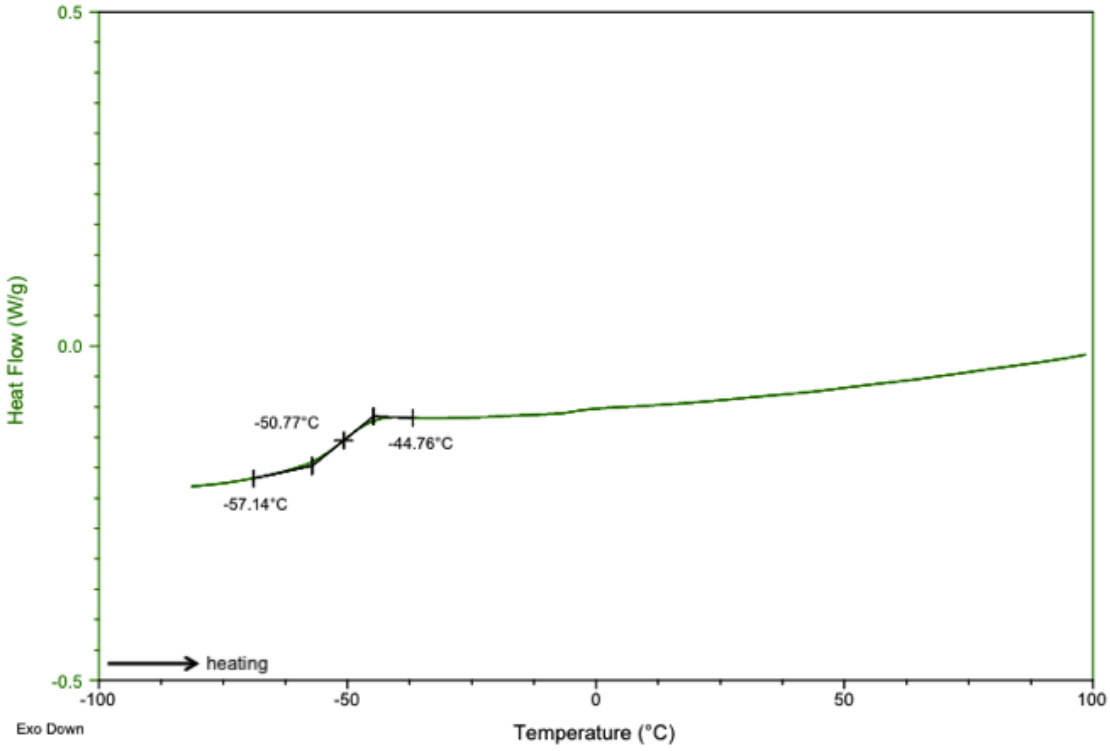


Figure 18: DSC thermogram for **5**.