Electronic Supplementary Material (ESI) for ChemComm.

Selective Monoalkylations of *tert*-butylcalix-[4]-arene in a Methyl Carbonate Ionic Liquid

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Supplementary Data

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1. Supporting figures and information

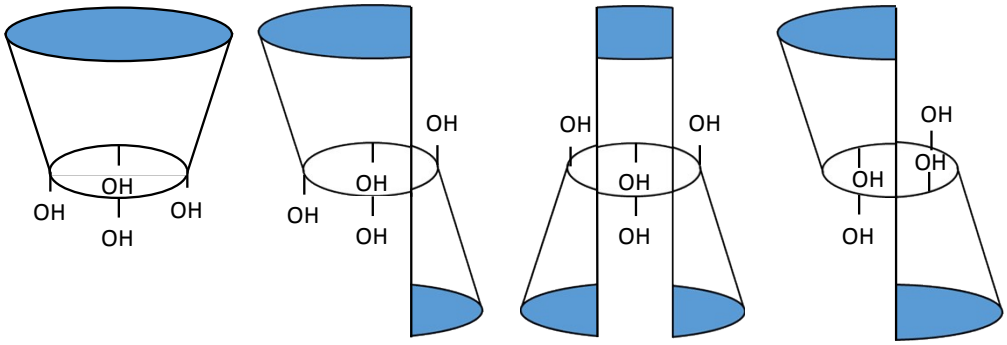


Figure 1. Conformers of TBC (L-R) cone, partial cone, 1, 3-alternate and 1, 2-alternate.

Note on the IL obtained as a by-product of the alkylation reactions:

The methyl carbonate ionic liquid acts as a reagent to form a calixarate ionic salt for application to selective mono-alkylations reactions of the TBC motif. As a result of the alkylation reactions a new ionic liquid is obtained, specifically as an iodide or as a dialkyl sulfate anion containing IL depending on the alkylating agent selected. This new IL can be obtained from the reaction mixture (after precipitation and removal of the TBC-R product) as they are water soluble ILs and can be extracted *via* the water washing step of the work up. The new ILs can be purified *via* cyclohexane washes and utilised.

2. Experimental Procedures

(a) General information

p-tert-Butylcalix-[4]-arene was obtained in 99% purity from Alfa Aesar. All solvents used were obtained from Honeywell and were of analytical purity. All alkylating agents were obtained from Sigma Aldrich with a minimum purity of 99%.

p-tert-Butylcalix-[4]-arene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34(s, 4H, 4xOH), 7.05 (s, 8H, 8xAr-**H**), 4.26 (d, *J* = 19.4 Hz, 3.98H, 2xAr-C**H**$_2$-Ar), 3.49 (d, *J* = 13.3 Hz, 3.91H, 2xAr-C**H**$_2$-Ar), 1.55 (s, 35.64H, 4xt-C(**CH$_3$**)$_3$).
Note: *dichloromethane impurities are evident in this commercial sample from the ^{1}H NMR.

(b) Synthesis of mono-calixarate salts

Triethylmethylammonium calixarate,[N$_{2\ 2\ 2\ 1}$][TBC]: Equimolar amounts of triethylmethylammonium methyl carbonate (2.5 g, 13.07 mmol) and *tert*-butylcalix-[4]-arene (8.48 g, 13.07 mmol) were mixed together in acetonitrile (75 mL) and sonicated for 45 minutes until effervescence had ceased. The solution is concentrated under vacuum to form a white crystalline solid (9.76 g, 12.88 mmol, 98.0 %). This salt was used for other experiments without further purification.

^{1}H NMR (400 MHz, CD_3CN) δ 12.90 (s, 3H, 3xAr-O**H**), 6.99 (s, 8H,8xAr-**H**), 4.34 (d, *J* = 11.7 Hz, 4H,2x Ar-C**H**$_2$-Ar), 3.21 – 3.05 (m, 10 H, 2x Ar-C**H**$_2$-Ar and 3xN-C**H**$_2$-R), 2.87 (s, 3H,N-C**H**$_3$), 1.69 – 1.59 (m, 6.20H, 3xN-CH$_2$-C**H**$_2$-R), 1.40 – 1.31 (m, 6.08H,3xN-CH$_2$- CH$_2$-C**H**$_2$-R), 1.16 (s, 34.10H,4x t-C(**CH$_3$**)$_3$), 1.00 – 0.93 (m, 9.04H, 3xN-CH$_2$-CH$_2$ CH$_2$-C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.50, 140.57, 130.27, 124.95, 116.53, 77.48, 77.36, 77.16, 76.84, 56.08, 47.05, 34.23, 33.89, 31.81, 8.10, 1.47, 0.12.

Tributylmethylammonium calixarate, [N$_{4\ 4\ 4\ 1}$][TBC]: Equimolar amounts of tributylmethylammonium methyl carbonate, [N$_{4\,4\,4\,1}$][CO_3Me] (0.25 g, 0.908 mmol) and *tert*-Butylcalix[4]arene, TBC (0.589 g, 0.908 mmol) are mixed in acetonitrile(15 ml) at 60 ^{o}C for 24 hours. Small amounts of residual TBC are removed *via* filtration through glass wool

and the filtrate is concentrated to ¼ of its initial volume and from which colourless cubic crystals are obtained (0.656 g, 0.774 mmol, 85.23 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (14.34 3xAr-O**H**), 6.97 (s, 8H, 8xAr-**H**), 4.41 (d, *J* = 12.1 Hz, 4H, 2x Ar-C$\mathbf{H}_2$-Ar), 3.55 – 3.41 (m, *J* = 30.0 Hz, 6.30H, 3xN-C$\mathbf{H}_2$-R), 3.26 (d, *J* = 12.4 Hz, 3.98H, 2x Ar-C$\mathbf{H}_2$-Ar), 1.90 (s, 2.97H, N-C$\mathbf{H}_3$),1.40(s, 8.99 H, 3xN-CH_2-C$\mathbf{H}_3$) 1.33 – 1.01 (m, 35.68H, 4x t-C(**CH_3**)$_3$).

(c) <u>Mono-alkylations of mono-calixarate salts</u>

General procedure: To a concentrated solution of [cation][TBC] (0.262 mmol) in chloroform (2.5 mL), dialkylsulfate/alkyl iodide (0.2882 mmol) was added and stirred for 72 hours at room temperature. The reaction mixture was washed with water (4x2 mL) and the organic layer was separated. The residual chloroform is removed under vacuum, affording off white solid.

The yields obtained for all alkylations are given in Table 1 below.

Table 1- Yields obtained from mono-alkylations of mono-anion calixarate salts

		Mass Spectrometry data of isolated product				
Alkylating agent	Calculated mass	Exact Mass	$[M+H]^+$	$[M+Na]^+$	$[M+NH_4]^+$	$[M+K]^+$
Me_2SO_4	663.4413	663.4413	663.4413		680.4679	
Et_2SO_4	677.4570	677.4595	677.4595	699.4402		
Pr_2SO_4	691.4726	691.0090	691.4727	713.4546	708.4992	
Bu_2SO_4	705.4883	705.4869	705.4883	727.4702	722.5140	743.4442
MeI	663.4413	663.4423	664.4454	685.4233		
EtI	677.4570	677.4570	678.4620	699.4389	694.4835	715.4128
PrI	691.4726	691.4733	691.4727	713.4546	708.4992	
BuI	705.4883	705.4861	705.4883	727.4702	722.5148	743.4442

NMR Spectroscopic data

Methylated *via* dimethyl sulfate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 0.52H, Ar-O**H**), 10.14 (s, 0.76H, Ar-O**H**), 9.55 (s, 1.47H, Ar-O**H**), 7.15 – 6.67 (m, *J* = 112.2, 54.2, 51.0 Hz, 8H,8xAr-**H**), 4.41 – 4.21 (m, *J* = 35.1, 13.3 Hz, 3.99H, 2x Ar-C**H**$_2$-Ar), 4.12 -3.94(s, 2.38H+0.62H, Ar-O-C**H**$_3$), 3.43 (m, *J* = 13.4 Hz, 4H, 2x Ar-C**H**$_2$-Ar), 1.41 – 0.78 (m, 35.94H, 4x t-C(**CH$_3$**)$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.25, 150.79, 148.65, 147.01, 143.94, 143.53, 133.74, 128.50, 128.22, 128.03, 126.81, 126.27, 126.11, 126.03, 125.98, 78.84, 77.66, 77.55, 77.35, 77.03, 63.56, 52.16, 34.57, 34.25, 33.33, 32.95, 32.45, 32.04, 31.81, 31.73, 31.58, 31.33, 31.25, 30.63, 11.99, 0.33.

With D_2O shake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 6.71 (m,8H,8xAr-**H**), 4.39 – 4.20 (m, 4.12H, 2x Ar-C**H**$_2$-Ar), 4.12 -3.94(s, 2.35H+0.64H, Ar-O-C**H**$_3$), 3.45-3.28 (m, 4.06H, 2x Ar-C**H**$_2$-Ar), 1.41 – 0.78 (m, 35.98H, 4x t-C(**CH$_3$**)$_3$).

Ethylated *via* diethyl sulfate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 0.17H, Ar-O**H**), 10.23 (s, 0.87H, Ar-O**H**), 9.65 (s, 1.69H, Ar-O**H**), 7.77 (s, 0.23H, Ar-O**H**), 7.17 – 6.76 (m, J = 74.7, 38.2, 35.9 Hz, 8H, 8xAr-**H**), 4.39 – 4.04 (m, 6.21H, 2xAr-C**H**$_2$-Ar and Ar-O-C**H**$_2$-R), 3.49 – 3.25 (m, 4.02H, 2xAr-C**H**$_2$-Ar), 1.69 (dt, J = 54.6, 7.0 Hz, 2.29+0.73H, Ar-O-CH$_2$-C**H**$_3$), 1.39 – 0.96 (m, 35.96H, 4x t-C(**CH$_3$**)$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.27, 148.40, 148.13, 147.90, 143.57, 143.14, 133.68, 133.01, 128.27, 128.24, 128.11, 127.88, 126.35, 125.74, 125.71, 125.65, 125.48, 125.08, 77.33, 77.22, 77.02, 76.70, 72.40, 34.24, 33.99, 33.92, 33.04, 32.32, 31.98, 31.69, 31.49, 31.27, 31.10, 30.92, 15.27, 0.00.

With D_2Oshake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 6.76 (m,8H, 8xAr-**H**), 4.38 – 4.05 (m, 6.09H, 2xAr-C**H**$_2$-Ar and Ar-O-C**H**$_2$-R), 3.48 – 3.28 (m, 3.99H, 2xAr-C**H**$_2$-Ar), 1.75 -1.62(dt, *J* = 7.1 Hz, , 2.28+0.78H, Ar-O-CH$_2$-C**H**$_3$), , 1.34 – 0.98 (m, 36.09H, 4x t-C(**CH$_3$**)$_3$).

Propylated *via* dipropyl sulfate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 0.20H, Ar-O**H**), 10.20 (s, 0.86H, Ar-O**H**), 9.61 (s, 1.68H, Ar-O**H**), 7.86 (s, 0.21H, Ar-O**H**), 7.01 (m, 8H, 8xAr-**H**), 4.40 – 4.21,4.10 (m, t, *J* = 7.0 Hz, 4.80H+1.71H, 2xAr-C**H**$_2$-Ar and Ar-O-C**H**$_2$-R), 3.50 – 3.25 (m, 4.01H, 2xAr-C**H**$_2$-Ar), 2.36 – 1.62 (m, 3.77H, Ar-O-CH$_2$-C**H**$_2$-R, NB: acetone impurities), 1.31 – 0.98 (m, 40.69H, 4x t-C(**CH$_3$**)$_3$ and Ar-O-R-C**H**$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.73, 148.46, 143.47, 134.01, 128.60, 128.57, 128.21, 126.68, 126.28, 126.07, 126.04, 125.98, 77.67, 77.55, 77.35, 77.03, 72.73, 34.57, 34.32, 34.25, 33.36, 32.65, 31.81, 31.74, 31.60, 31.25, 15.60, 1.36, 0.33.

With D_2O shake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.79 (m, 8H, 8xAr-**H**), 4.40 – 4.20,4.10 (m,t, *J* = 31.8, 13.1, 4.9 Hz, 4.74H+1.73H, 2xAr-C**H**$_2$-Ar and Ar-O-C**H**$_2$-R), 3.50 – 3.25 (m, 3.45H, 2xAr-C**H**$_2$-Ar), 2.25 – 1.74 (dq, 3.44H, Ar-O-CH$_2$-C**H**$_2$-R), 1.31 – 0.98 (m, 39.79H, 4x t-C(**CH$_3$**)$_3$ and Ar-O-R-C**H**$_3$).

Butylated *via* dibutylsulfate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1.06H, Ar-O**H**), 10.19 (s, 0.55H, Ar-O**H**), 9.60 (s, 1.03H, Ar-O**H**), 7.84 (s, 0.49H, Ar-O**H**), 7.12 – 6.79 (m, 8H, 8xAr-**H**), 4.40 – 3.94 (m, 6.44H, 2xAr-C**H**$_2$-Ar and Ar-O-C**H**$_2$-R), 3.41 (ddd, *J* = 52.0, 34.8, 13.3 Hz, 4.08H, 2xAr-C**H**$_2$-Ar), 2.14 – 1.90,1.71 (m, 1.91H, Ar-O- CH$_2$-C**H**$_2$-R), 1.71 (ddd, *J* = 22.5, 15.1, 7.6 Hz, 2.04H, Ar-O- CH$_2$- CH$_2$-C**H**$_2$-R), 1.45 – 0.76 (m, 39.55H, Ar-O-R-C**H**$_3$ and 4x t-C(**CH$_3$**)$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.42, 147.98, 146.62, 144.32, 143.03, 133.47, 128.29, 128.11, 127.73, 127.64, 126.34, 125.89, 125.64, 125.57, 125.41, 124.98, 77.27, 77.16, 76.96, 76.64, 34.17, 33.96, 33.86, 32.97, 32.57, 32.20, 31.82, 31.65, 31.44, 31.35, 31.20, 31.03, 19.15, 13.95, 0.97, -0.06.

With D_2O shake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.75 (m, 8H8xAr-**H**), 4.39 – 3.95 (m, 6.29H, 2xAr-C**H**$_2$-Ar and Ar-O-C**H**$_2$-R), 3.55 – 3.27 (m, 4.16H, 2xAr-C**H**$_2$-Ar), 2.16 – 1.94 (m, 2.07H, Ar-O- CH_2-C**H**$_2$-R), 1.71 (ddd, *J* = 22.4, 14.9, 7.5 Hz, 1.98H, Ar-O- CH_2- CH_2-C**H**$_2$-R), 1.43 – 0.78 (m, 38.95H, Ar-O-R-C**H**$_3$ and 4x t-C(**CH$_3$**)$_3$).

Methylated *via* methyl iodide:

^{1}H NMR (400 MHz, $CDCl_3$) δ[10.34 (s, 0.55H), 10.15 (s, 0.94H), 9.55 (s, 1.50H) 3xAr-O**H**], 7.14 – 6.69 (m, *J* = 113.1, 54.6, 51.4 Hz, 8H, 8XAr-**H**), 4.42 – 4.19 (m, 4H, 2xAr-C**H$_2$**-Ar), 4.13-3.95 (s, s,2.33H,0.67H, Ar-O-C**H**$_3$), 3.38 (dd, *J* = 42.3, 13.3 Hz, 3.99H,2xAr-C**H$_2$**-Ar), 1.44 – 0.82 (m, 35.66H, t-C(**CH$_3$**)$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.46, 148.33, 147.81, 143.22, 133.43, 132.30, 128.19, 127.91, 126.49, 125.71, 125.66, 125.07, 77.35, 77.03, 76.71, 33.94, 33.01, 32.13, 31.73, 31.49, 31.41, 31.27, 31.02.

With D_20 shake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.91 (m, 8H, 8X Ar-**H**), 4.31 (dd, *J* = 35.6, 13.3 Hz, 9H, 2xAr-C**H$_2$**-Ar), 4.12-3.65 (M, 2.30H+1.86H, Ar-O-C**H**$_3$), 3.43 (d, *J* = 13.6 Hz, 3.98H, 2xAr-C**H$_2$**-Ar), 1.28 – 1.12 (m, 36.33H, t-C(**CH$_3$**)$_3$).

Ethylated with ethyl iodide:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 0.54, Ar-O**H**), 10.14 (s, 0.80H, Ar-O**H**), 9.55 (s, 1.72H, Ar-O**H**), 7.16 – 6.65 (m, *J* = 113.1, 54.6, 51.4 Hz, 8H, 8xAr-**H**), 4.46 – 4.17 (m, 4H, 2xAr-C**H$_2$**-Ar), 3.73-3.71(q, 2.04H, Ar-O-C**H$_2$**-R) 3.50 – 3.27 (m, 4.02H, 2xAr-C**H$_2$**-Ar), 1.31 – 0.91 (m, 39.32H, 4xt-C(**CH$_3$**)$_3$ and Ar-O-R-C**H**$_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.80, 148.67, 148.63, 148.16, 148.07, 147.19, 143.95, 143.55, 141.87, 133.76, 132.63, 128.54, 128.53, 128.24, 126.83, 126.29, 126.13, 126.05, 126.00, 125.89, 125.41, 77.58, 77.37, 77.16, 63.87, 63.59, 58.85, 34.60, 34.35, 34.28, 34.25, 33.35, 32.97, 32.47, 32.07, 31.83, 31.76, 31.60, 31.36, 18.80, 1.38, 0.36.

With D_2O shake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 6.65 (m, *J* = 113.1, 54.6, 51.4 Hz, 8H, 8xAr-**H**), 4.46 – 4.17 (m, 4.09H, 2xAr-C**H$_2$**-Ar), 3.73-3.71(q, 2.08H, Ar-O-C**H$_2$**-R) 3.50 – 3.27 (m, 4.11H, 2xAr-C**H$_2$**-Ar), 1.31 – 0.91 (m, 40.19H, 4xt-C(**CH$_3$**)$_3$ and Ar-O-R-C**H**$_3$).

Propylated with propyl iodide:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 0.23H, Ar-O**H**), 10.22 (s, 0.79H, Ar-O**H**), 9.62 (s,1.58H, Ar-O**H**), 7.77 (s, 0.39H, Ar-O**H**), 7.17 – 6.73 (m, 8H, 8xAr-**H**), 4.40 – 4.06 (m, 6.08H, 2xAr-C**H$_2$**-Ar and Ar-O-C**H$_2$**-R), 3.70 (dd, *J* = 16.7, 10.7 Hz, 2H, Ar-O-CH_2-C**H$_2$**-R), 3.50 – 3.26 (m, 4H, 2xAr-C**H$_2$**-Ar), 1.76 -1.32(dt, *J* = 7.1 Hz, 2H+1.01H, Ar-O-R-C**H$_3$**),1.43 – 0.85 (m, 37.6H,4x t-C(**CH$_3$**)$_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.42, 150.57, 150.05, 149.24, 148.38, 148.12, 147.89, 147.78, 143.55, 143.13, 140.52, 133.66, 133.02, 132.07, 128.25, 128.23, 128.10, 127.87, 126.34, 125.94, 125.73, 125.70, 125.64, 125.47, 125.08, 77.22, 77.01, 76.80, 72.40, 71.91, 58.50, 34.23, 33.98, 33.92, 33.81, 33.02, 32.30, 31.98, 31.68, 31.47, 31.40, 31.26, 31.10, 18.44, 15.27, 1.02.

With D_2O shake

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (m, *J* = 77.5, 38.7, 36.3 Hz, 8H, 8xAr-**H**), 4.46 – 4.13 (m, 5.58H, 2xAr-C**H$_2$**-Ar + Ar-O-C**H$_2$**-R), 4.08-3.62 (m, 1.07H+0.94H, Ar-O-R-C**H$_2$**-R), 3.49 – 3.26 (m, 4.01H, 2xAr-C**H$_2$**-Ar), 1.75-1.62 (dt, *J* = 7.1 Hz, 2.04H+1.08H), 1.33 – 0.98 (m, 36H, 4x t-C(**CH$_3$**)$_3$).

Butylated with butyl iodide:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1.06H, Ar-O**H**), 10.19 (s, 0.55H, Ar-O**H**), 9.60 (s, 1.14H, Ar-O**H**), 7.84 (s, 0.49H, Ar-O**H**), 7.12 – 6.79 (m, 8H, 8xAr-**H**), 4.39 – 4.21 (m, 3.96H, 2xAr-C$\mathbf{H_2}$-Ar), 4.05 (dt, *J* = 13.0, 6.8 Hz, 2.17H, Ar-O-C$\mathbf{H_2}$-R), 3.41 (ddd, *J* = 52.0, 34.8, 13.3 Hz, 4.26H, 2xAr-C$\mathbf{H_2}$-Ar), 2.15 – 1.95 (m, 2.02H, Ar-O-R-C$\mathbf{H_2}$-R), 1.71 (ddd, *J* = 22.5, 15.1, 7.6 Hz, 2.04H, Ar-O-R-C$\mathbf{H_2}$-R), 1.41 – 0.95 (m, 38.32H, Ar-O-R-C$\mathbf{H_3}$ and 4x t-C($\mathbf{CH_3}$)$_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.42, 150.57, 150.05, 149.24, 148.38, 148.12, 147.89, 147.78, 143.55, 143.13, 140.52, 133.66, 133.02, 132.07, 128.25, 128.23, 128.10, 127.87, 126.34, 125.94, 125.73, 125.70, 125.64, 125.47, 125.08, 77.22, 77.01, 76.80, 72.40, 71.91, 58.50, 34.23, 33.98, 33.92, 33.81, 33.02, 32.30, 31.98, 31.68, 31.47, 31.40, 31.26, 31.10, 18.44, 15.27, 1.02.

1. Nuclear magnetic resonance spectroscopic data

(a) *p-tert*-Butylcalix-[4]-arene-commerical sample

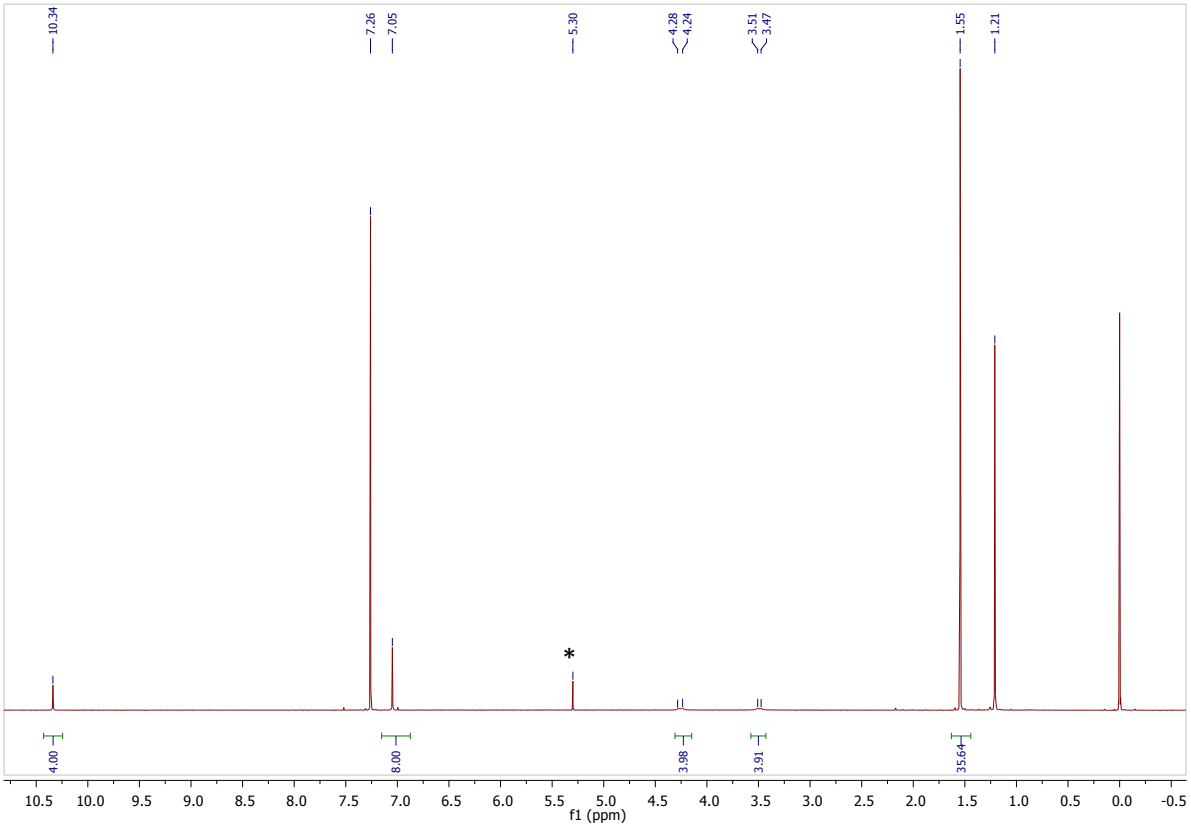


Figure 2-^{1}H NMR spectrum of a commercial sample of *tert*-butylcalix-[4]-arene

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34(s, 4H, 4xOH), 7.05 (s, 8H, 8xAr-**H**), 4.26 (d, *J* = 19.4 Hz, 3.98H, 2xAr-C**H**$_2$-Ar), 3.49 (d, *J* = 13.3 Hz, 3.91H, 2xAr-C**H**$_2$-Ar), 1.55 (s, 35.64H, 4xt-C(**CH**$_3$)$_3$).

Note: *dichloromethane impurities are evident in this commercial sample from the ^{1}H NMR.

(b) Mono-anion calixarate salts

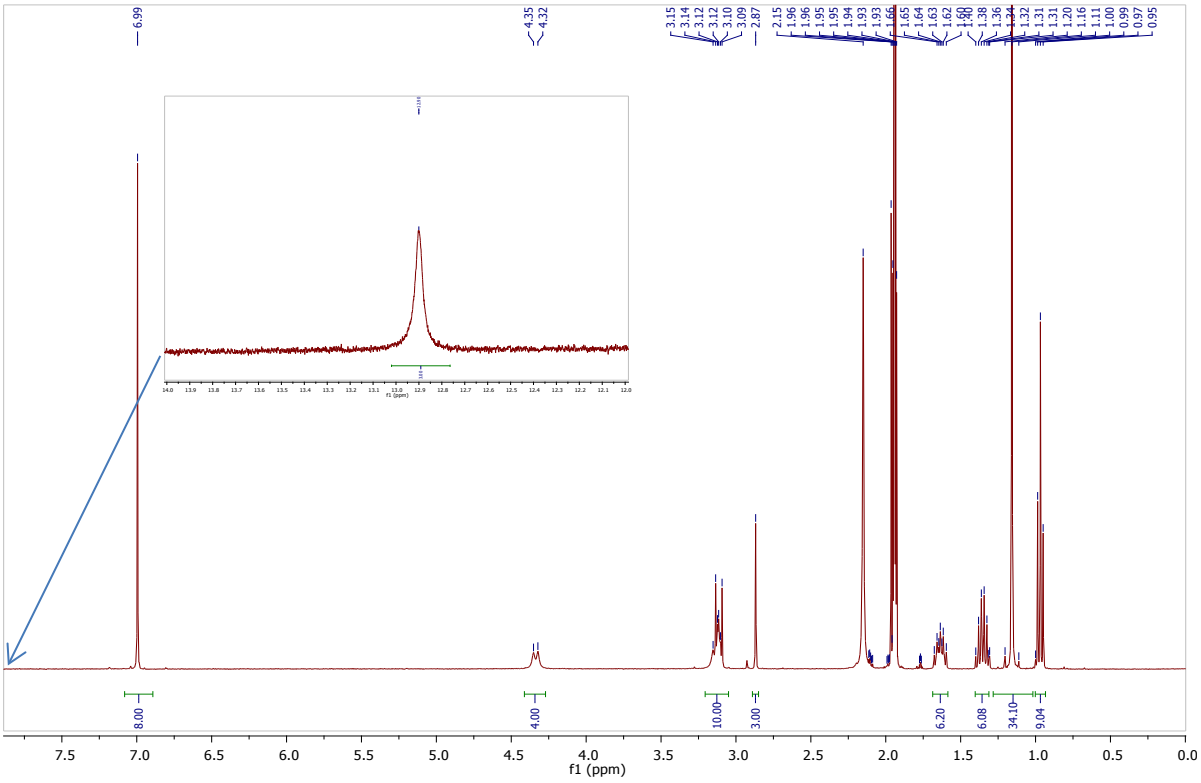


Figure 3-^{1}H NMR spectrum of Tributylmethylammonium *tert*-butylcalix-4-arate salt

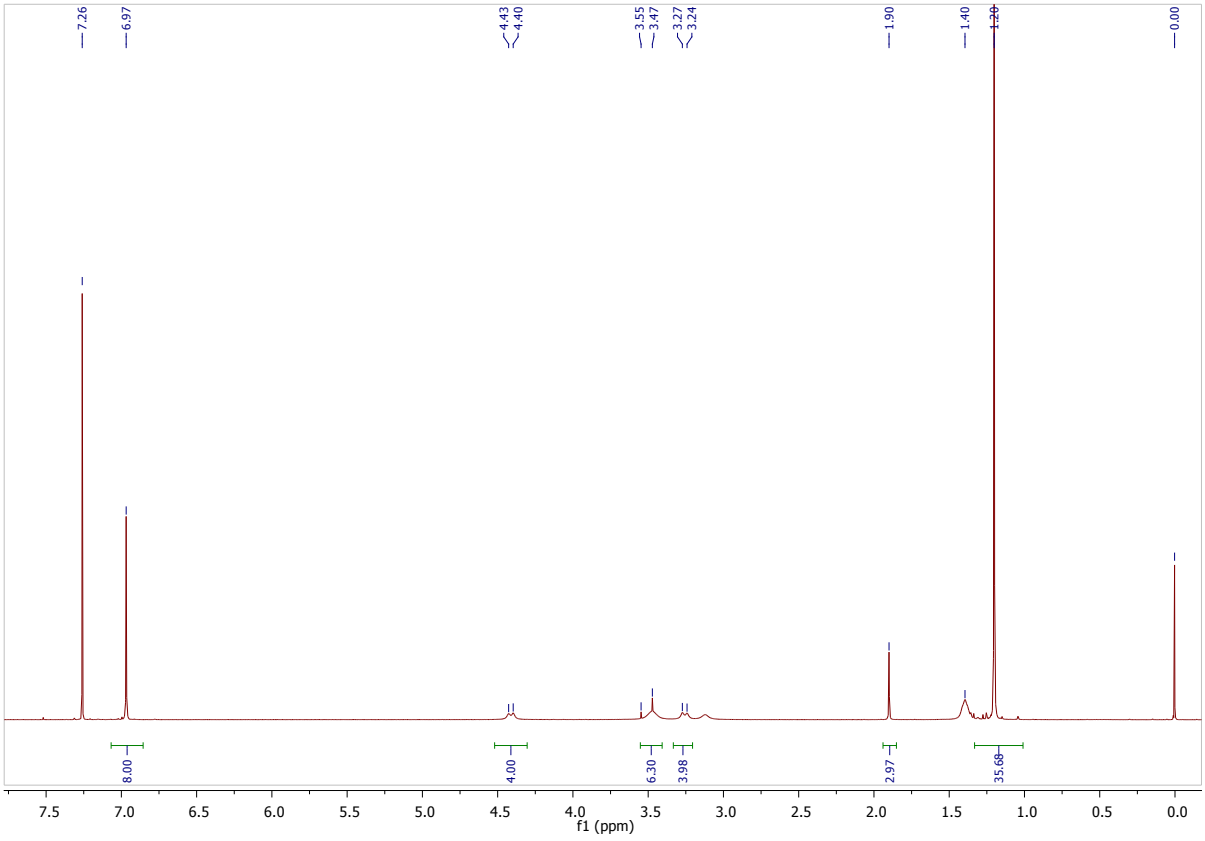


Figure 4-^{1}H NMR spectrum of Triethylmethylammonium *tert*-butylcalix-[4]-arate salt

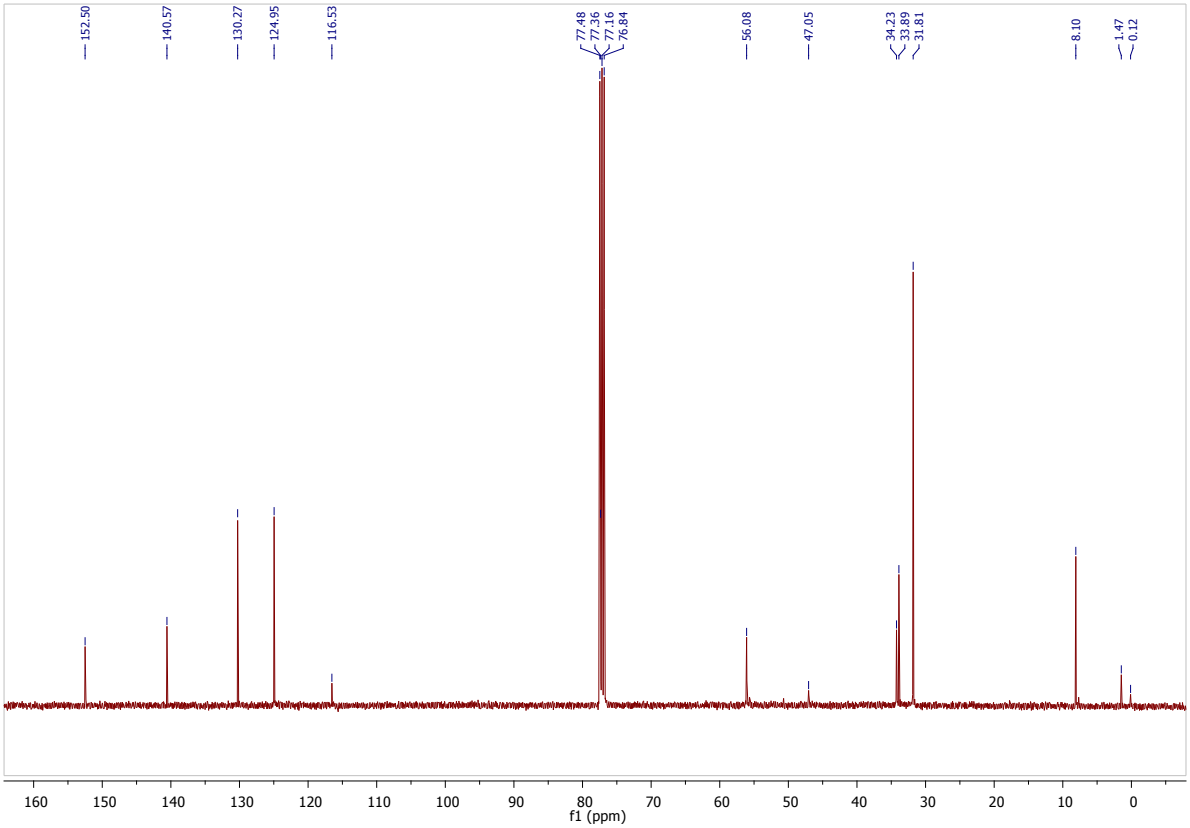


Figure 5-^{13}C NMR spectrum of Triethylmethylammonium *tert*-butylcalix-[4]-arate salt

(c) Mono-alkylations *via* dialkyl sulfates

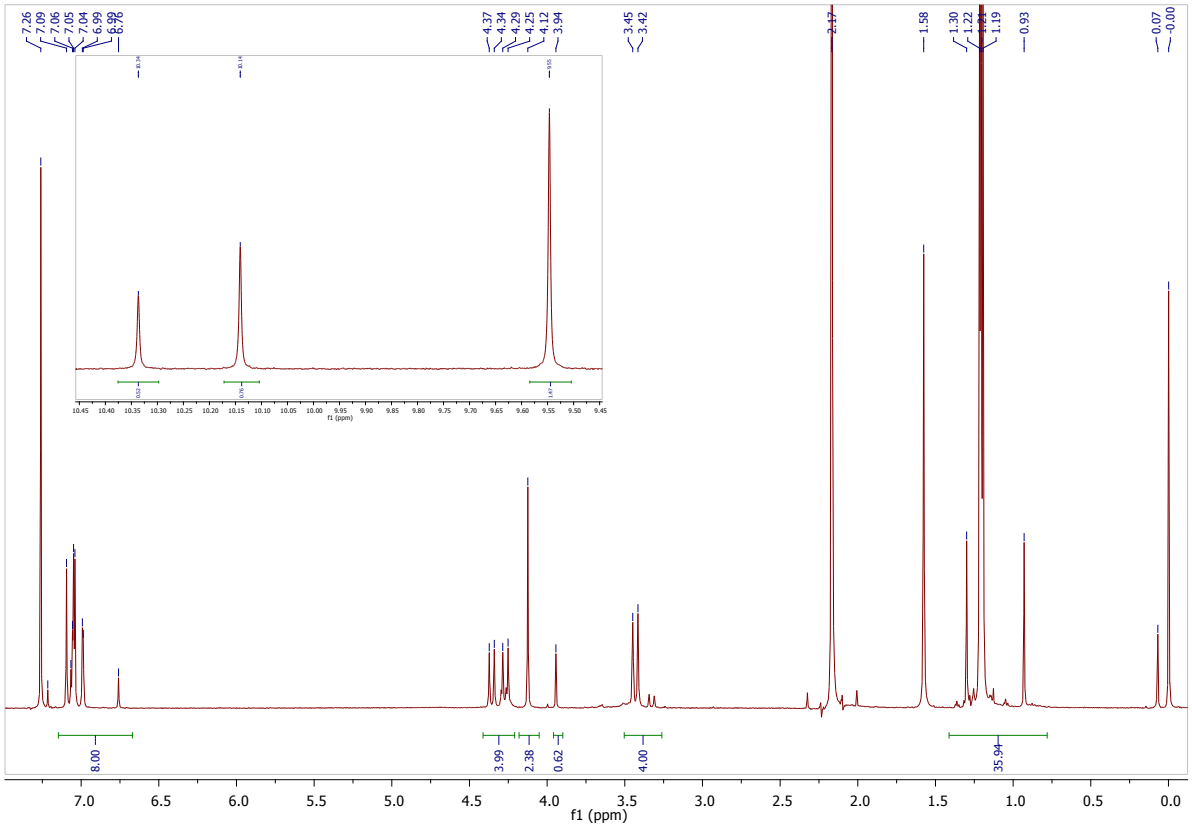


Figure 6-^{1}H NMR of methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate

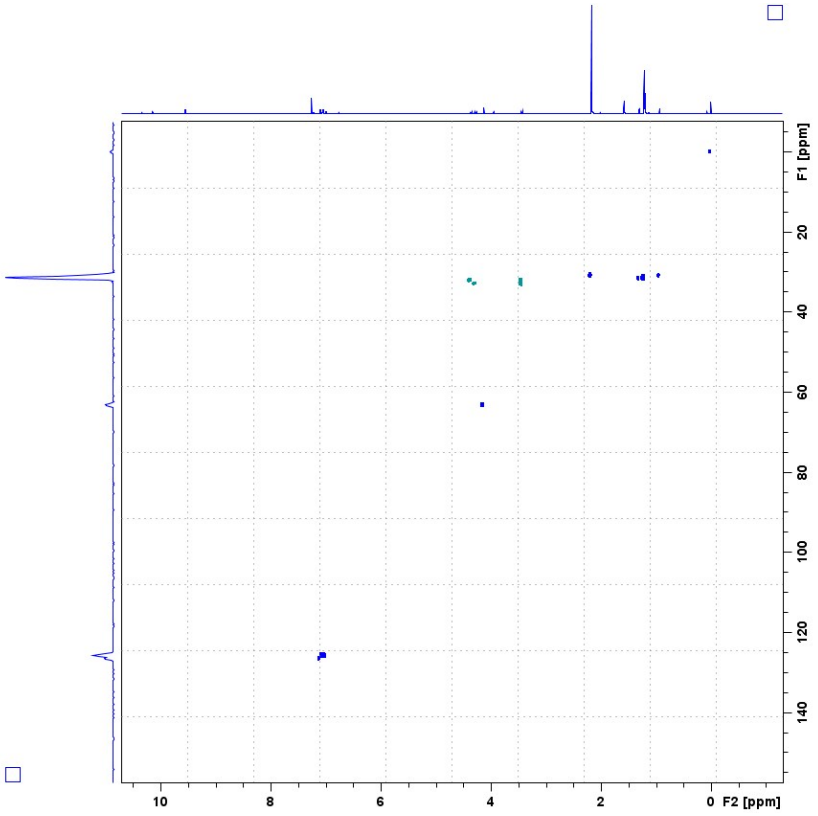


Figure 7-HSQC of methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate

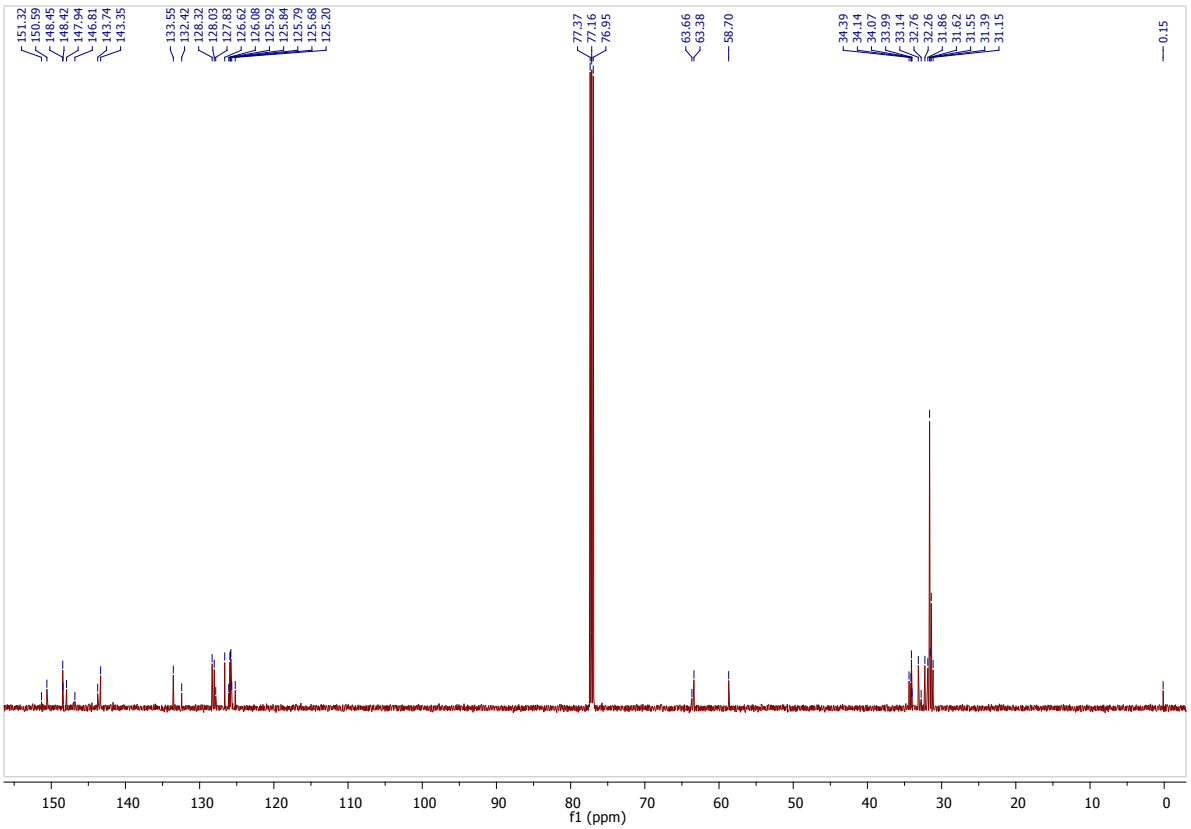


Figure 9-^{13}C NMR of methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate

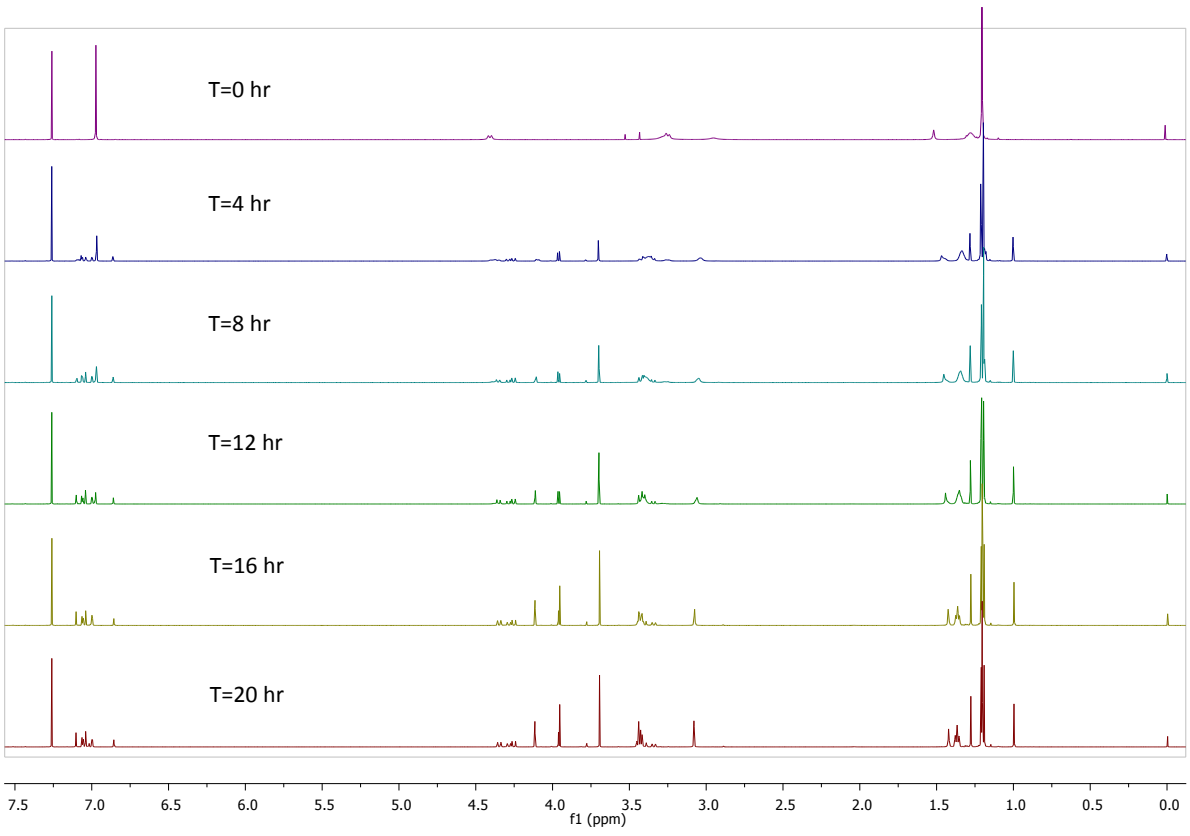


Figure 8-^{1}H NMR of methylated *tert*-butylcalix-4-arene via dimethyl sulfate as a function of time. (600 MHz NMR $CDCl_3$)

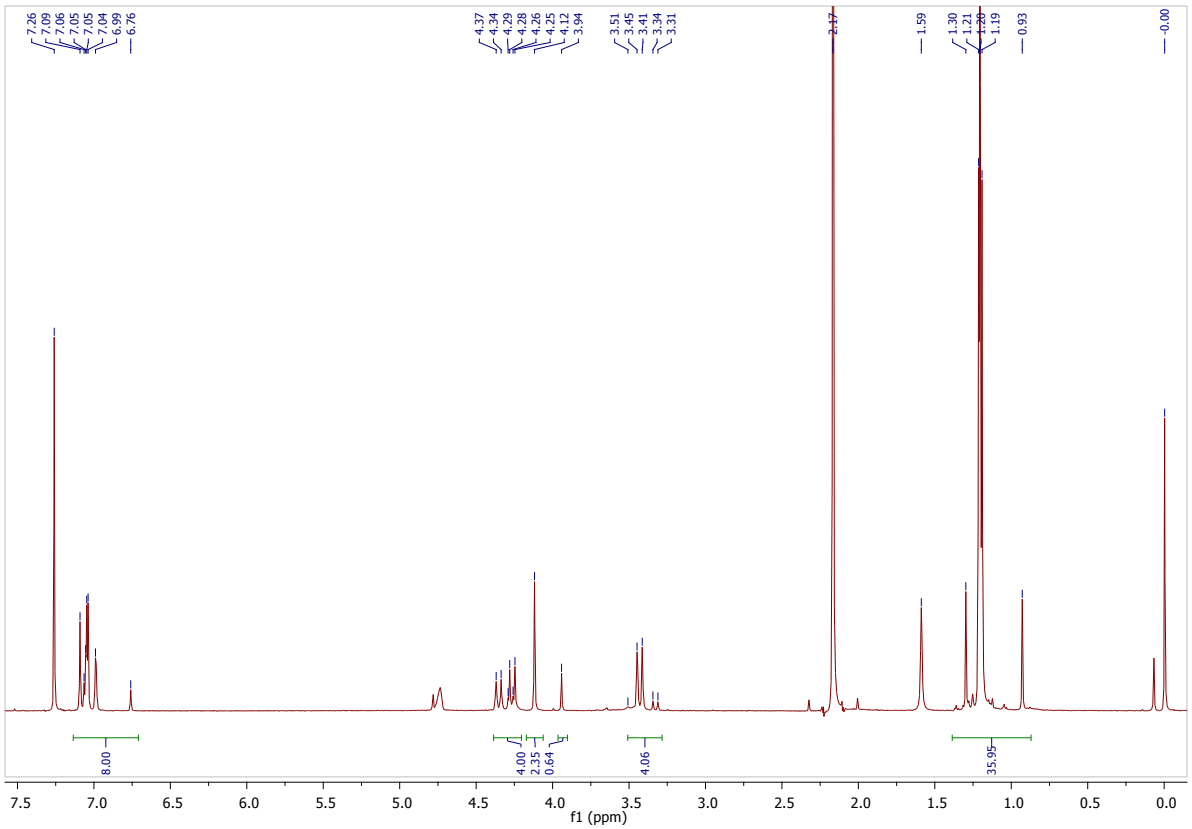


Figure 10-^{1}H NMR of methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate with a drop of D_2O

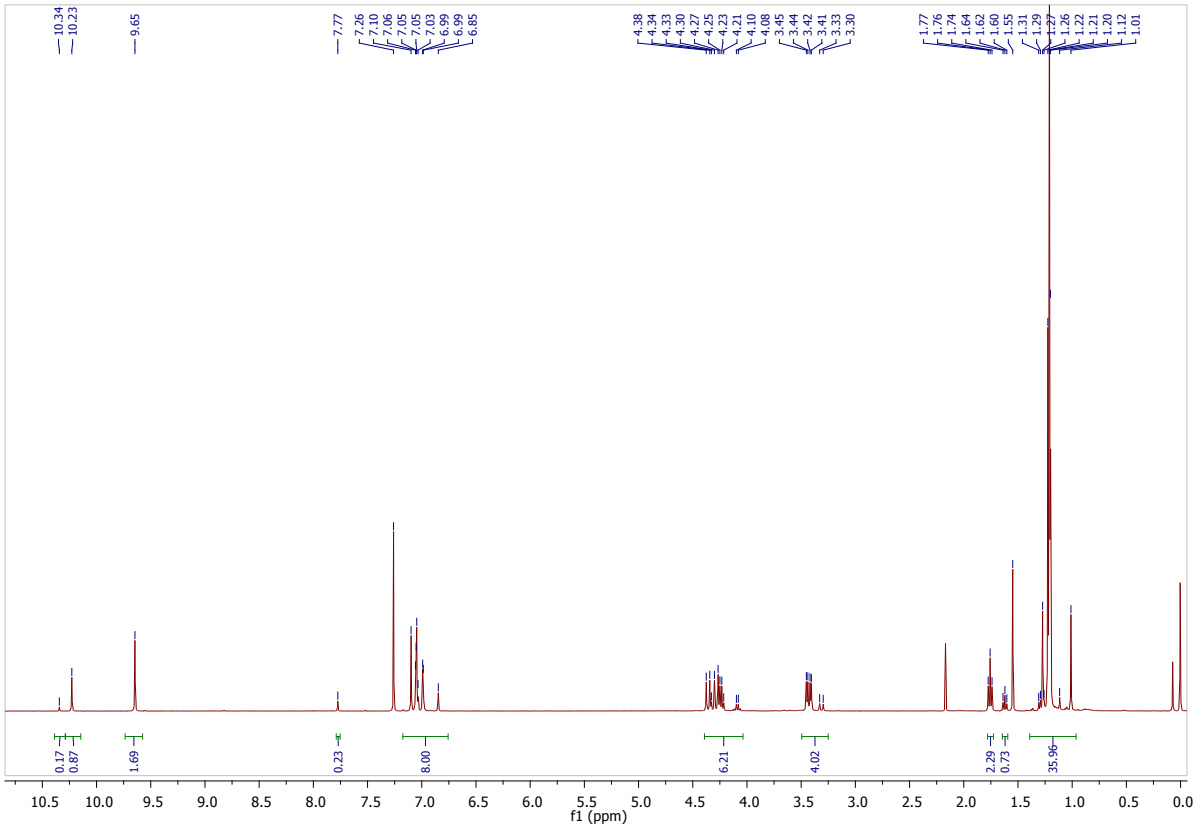


Figure 11-^{1}H NMR of ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate

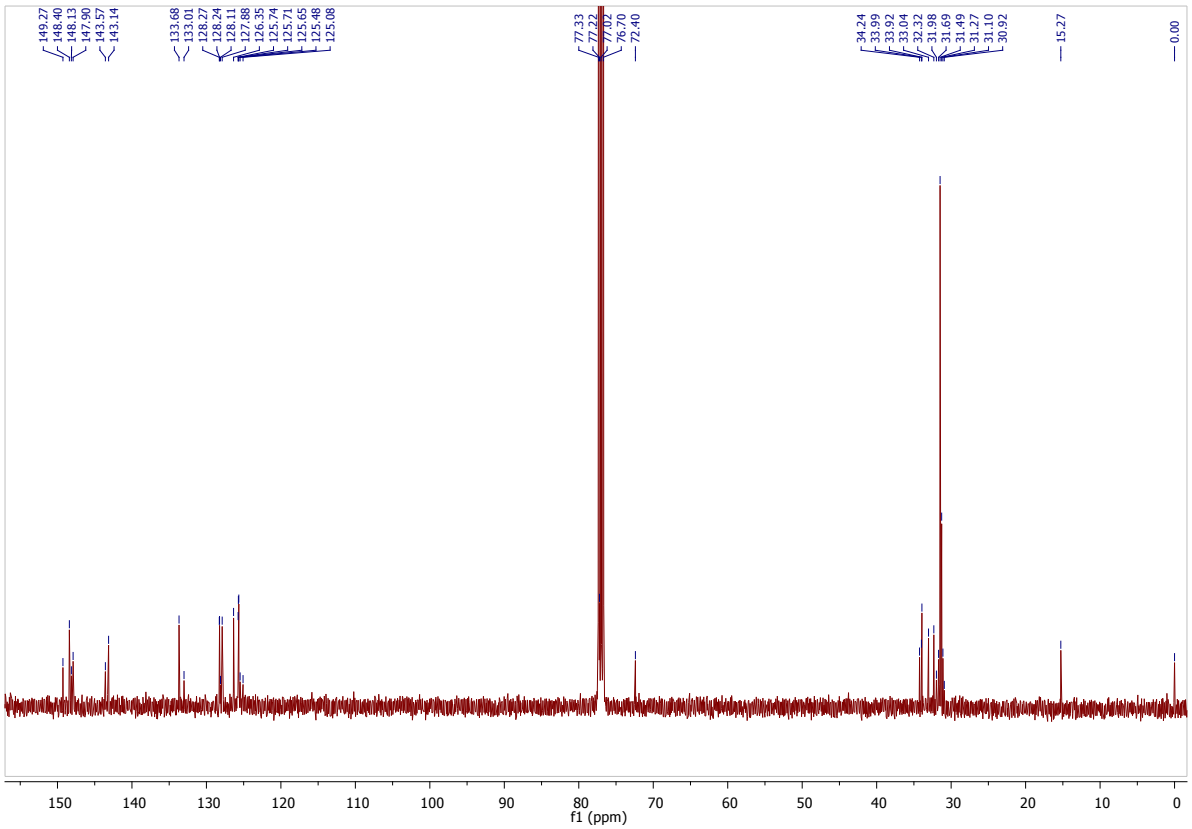


Figure 12-^{13} C NMR ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate

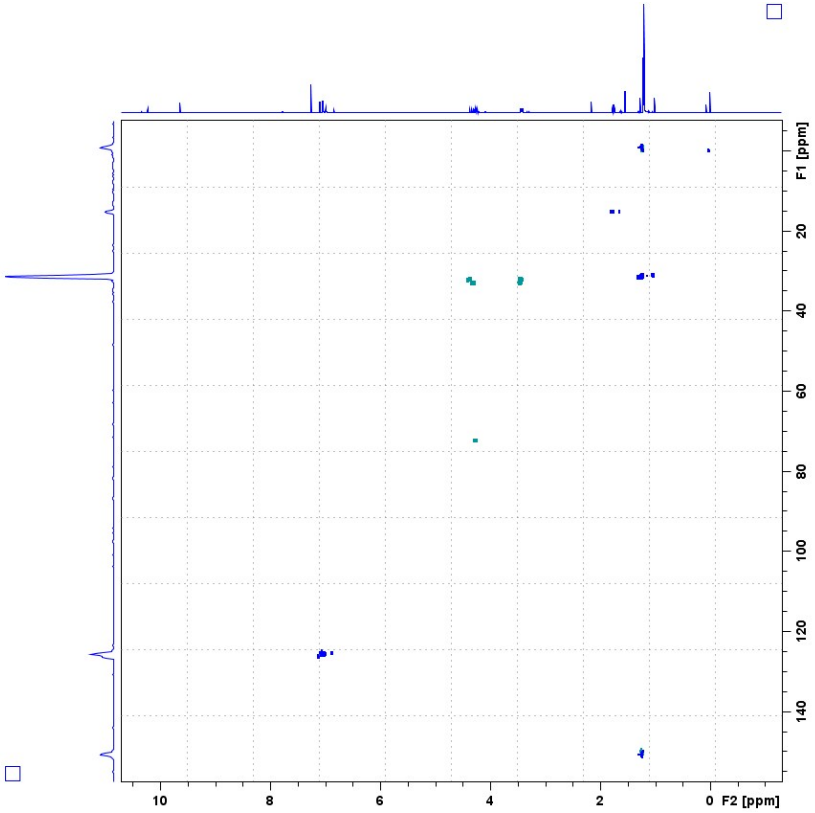


Figure 13-HSQC of ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate

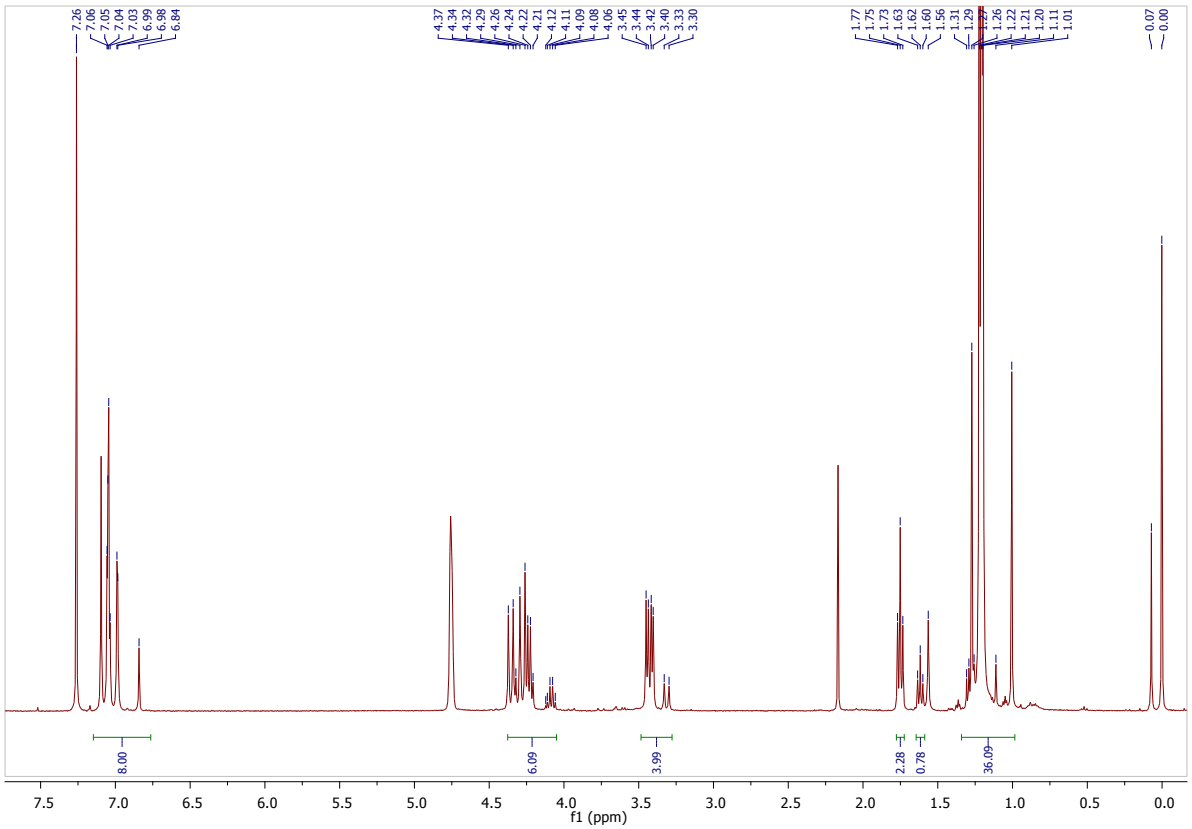


Figure 14-^{1}H NMR of ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate with a D_2O shake

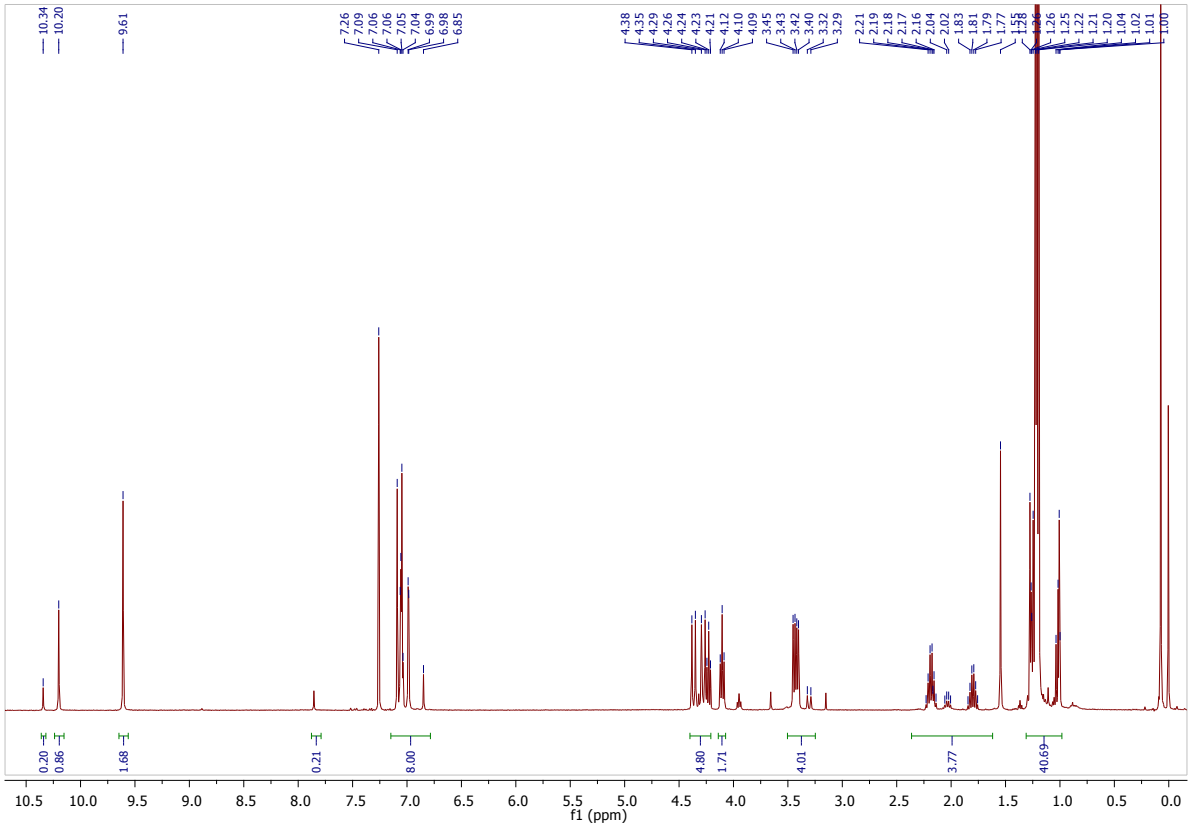


Figure 15-^{1}H NMR of propylated *tert*-butylcalix-[4]-arene *via* dipropyl sulfate

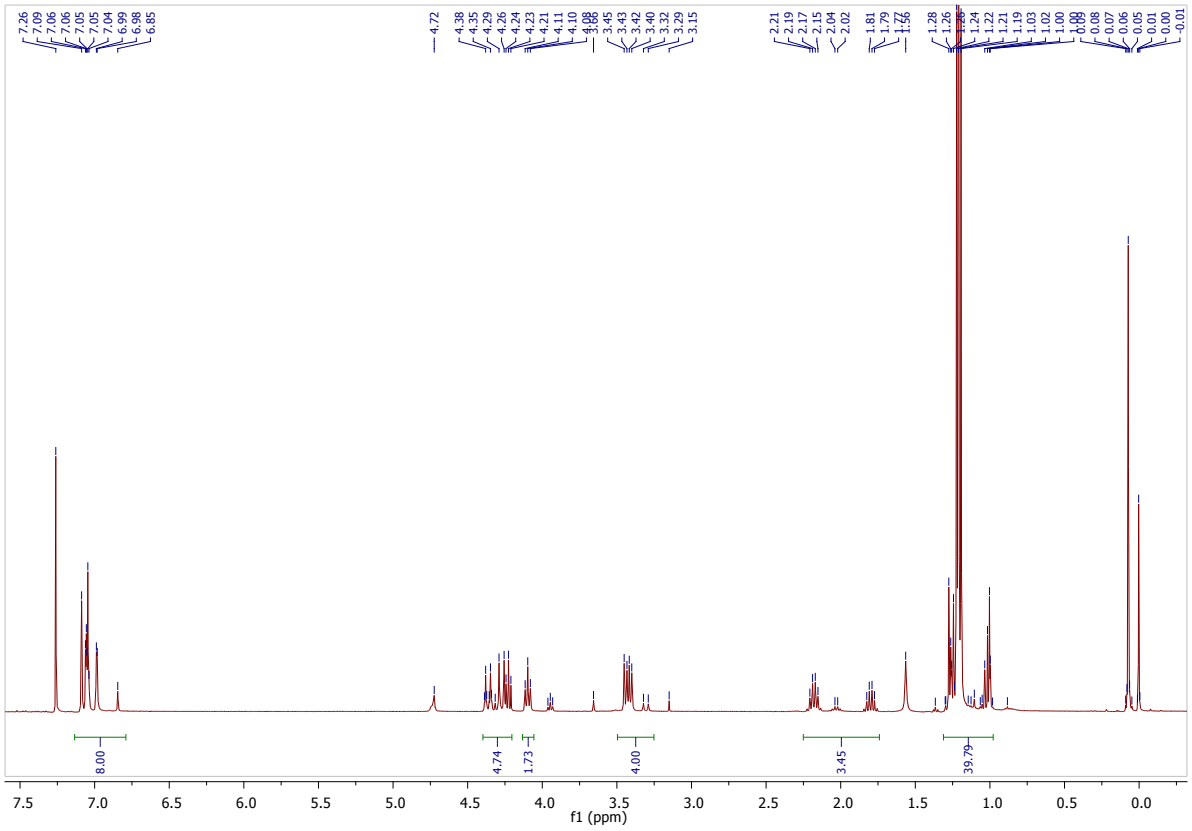


Figure 16-^{1}H NMR of propylated *tert*-butylcalix-[4]-arene *via* dipropyl sulfate with D_2O shake

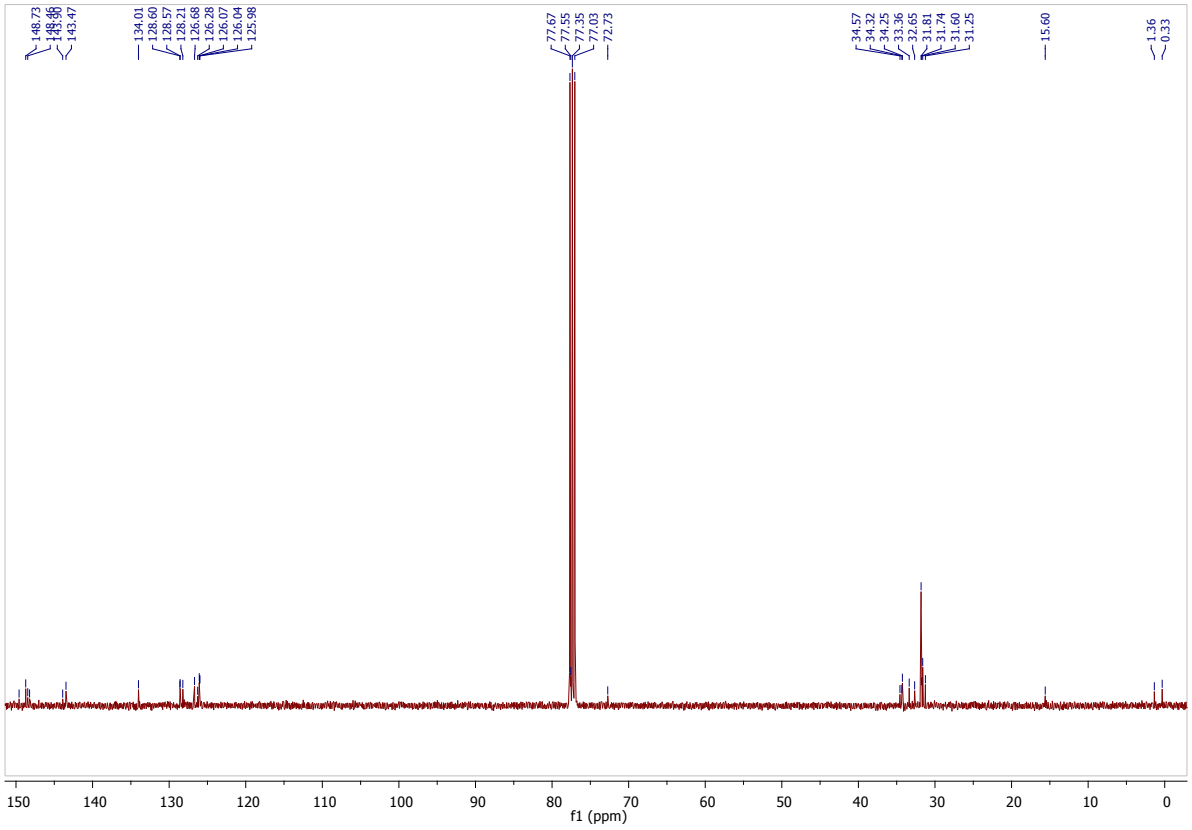


Figure 17-^{13}C NMR of propylated tert-butylcalix-[4]-arene *via* dipropyl sulfate with D2O shake

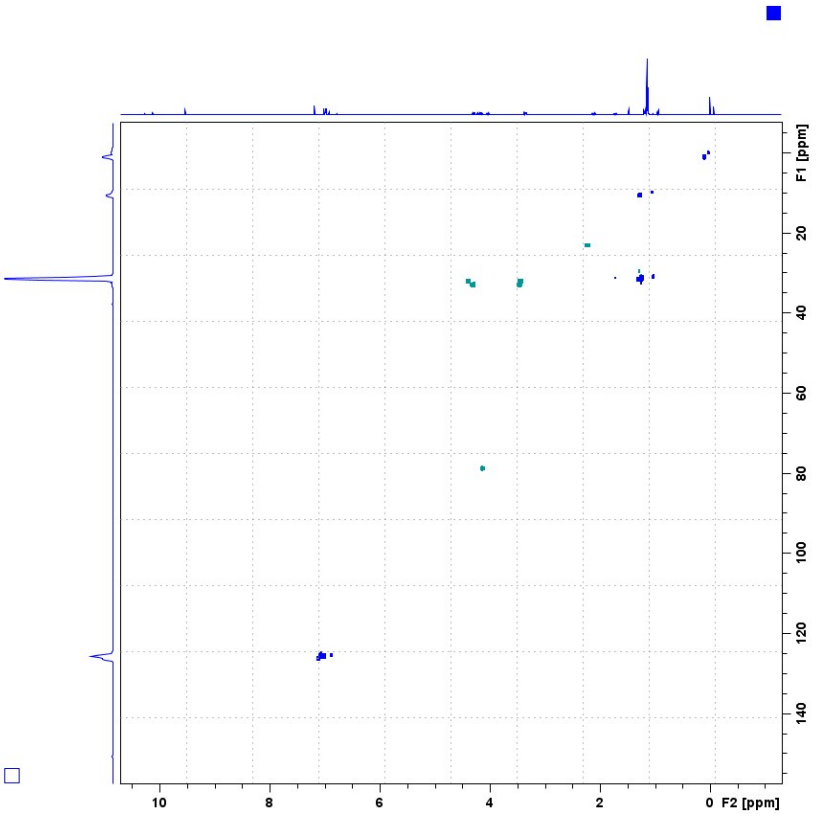


Figure 18-HSQC of propylated *tert*-butylcalix-[4]-arene *via* dipropyl sulfate

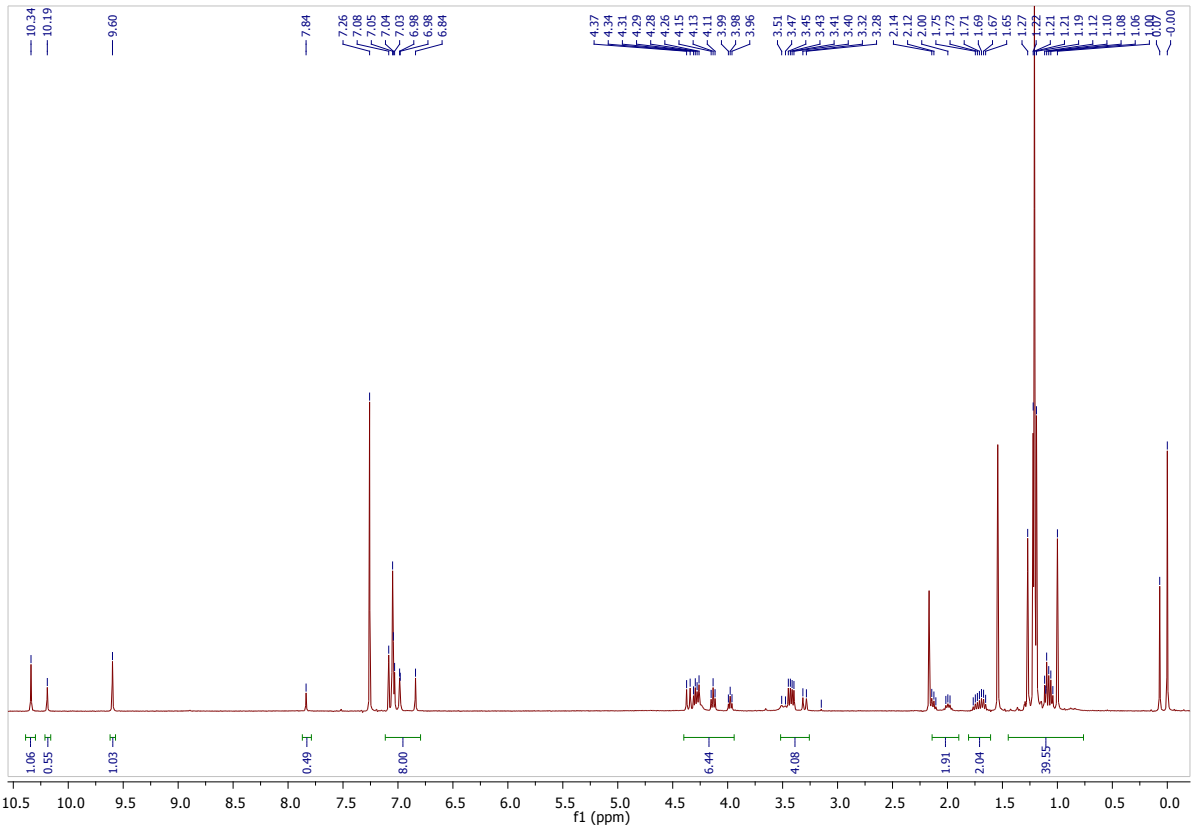


Figure 19-^{1}H NMR of butylated *tert*-butylcalix-[4]-arene *via* dibutyl sulfate

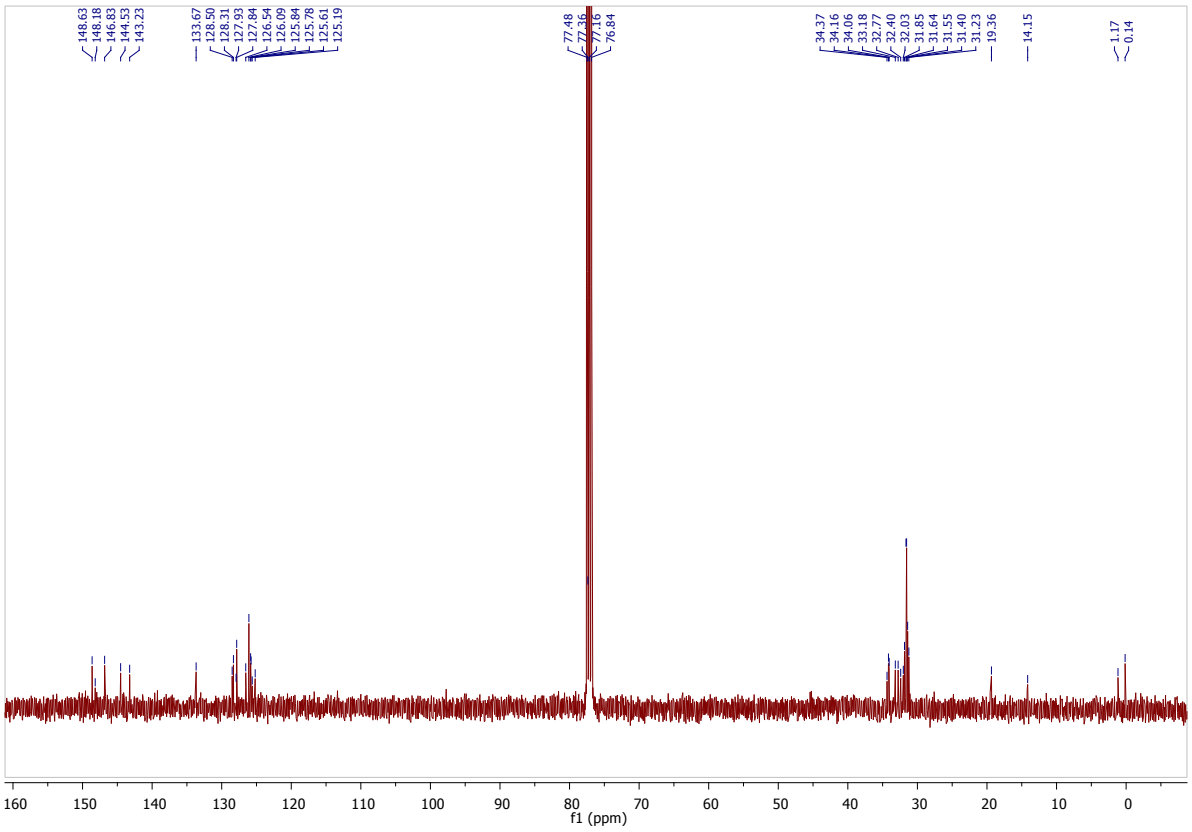


Figure 20-^{13}C NMR of butylated *tert*-butylcalix-[4]-arene *via* dibutyl sulfate

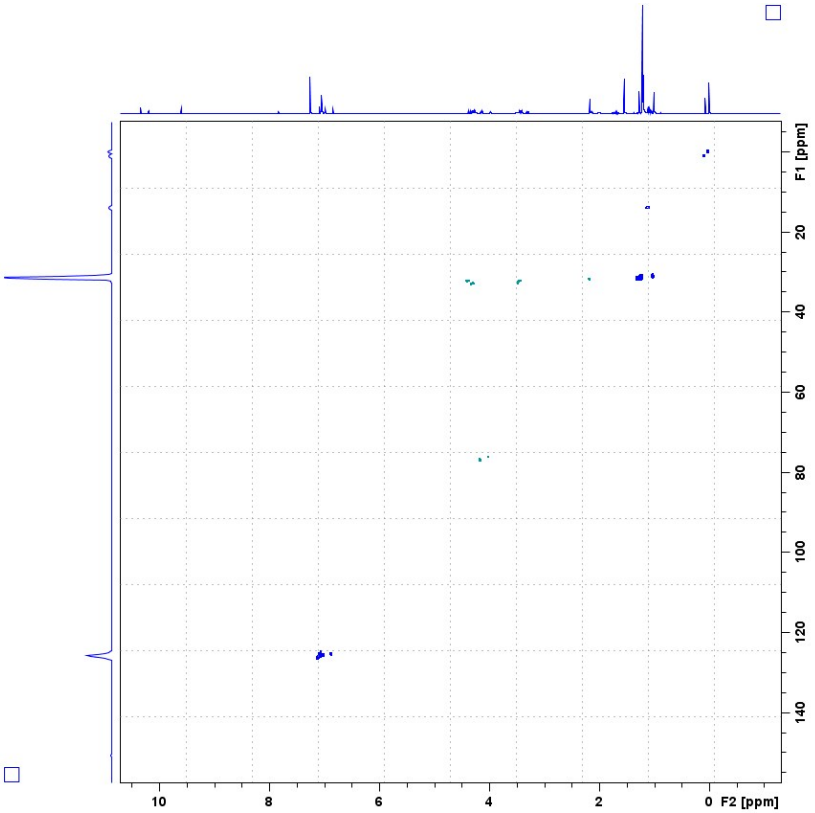


Figure 21-HSQC of butylated *tert*-butylcalix-[4]-arene *via* dibutyl sulfate

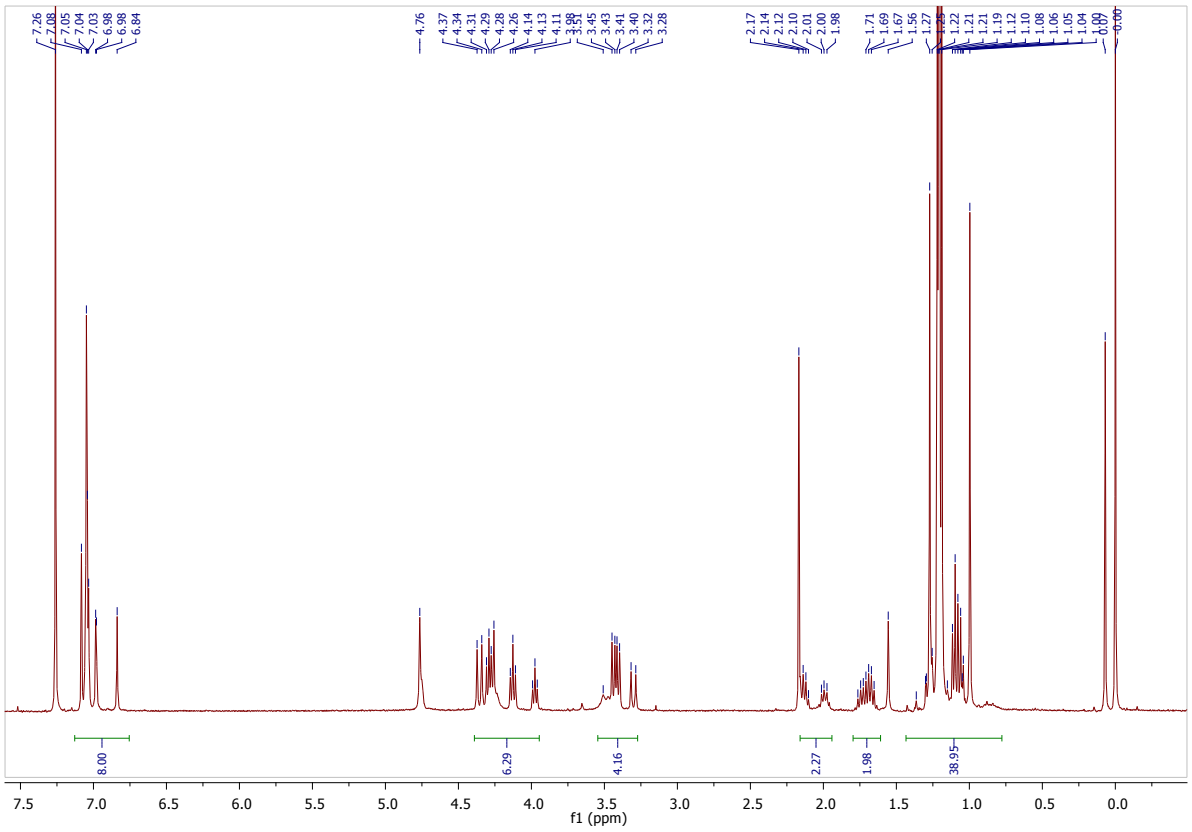


Figure 22-^{1}H NMR of butylated *tert*-butylcalix-[4]-arene *via* dibutyl sulfate with D_2O shake

(d) Alkylations *via* alkyl iodides

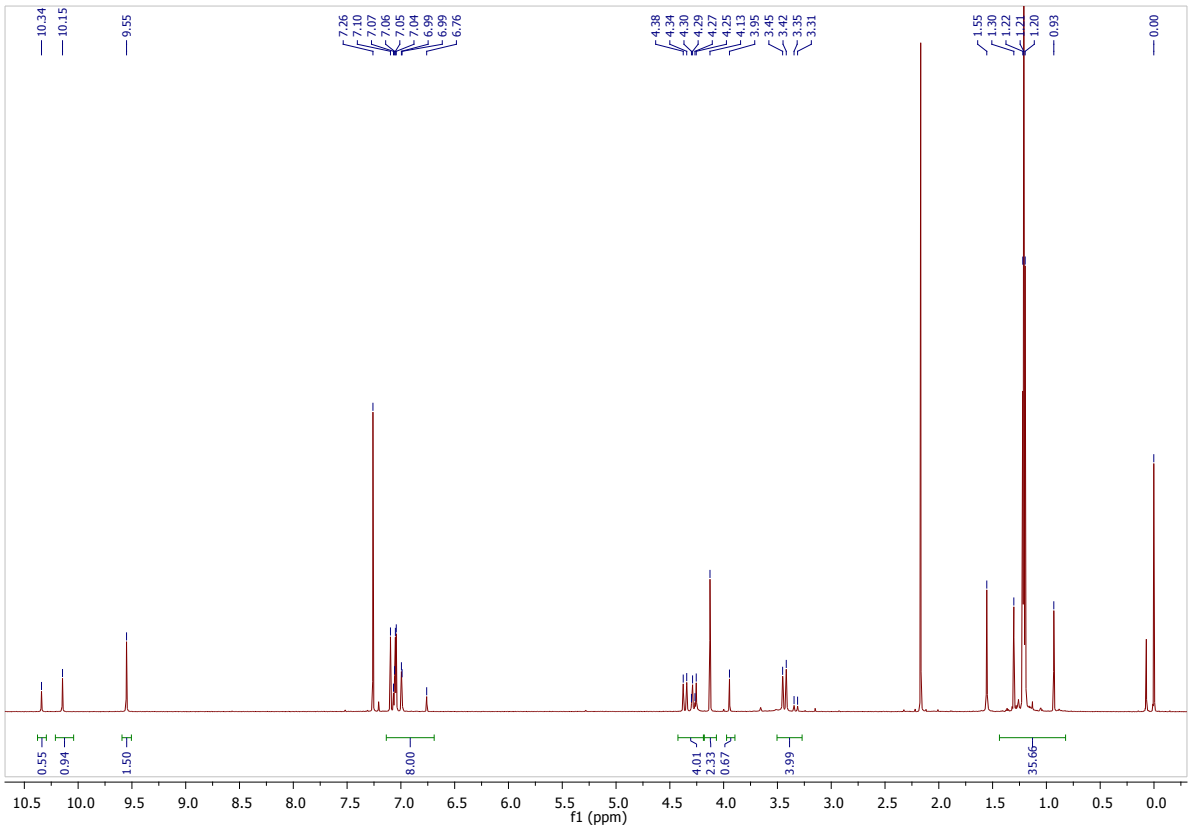


Figure 23-^{1}H NMR of methylated *tert*-butylcalix-[4]-arene *via* methyl iodide

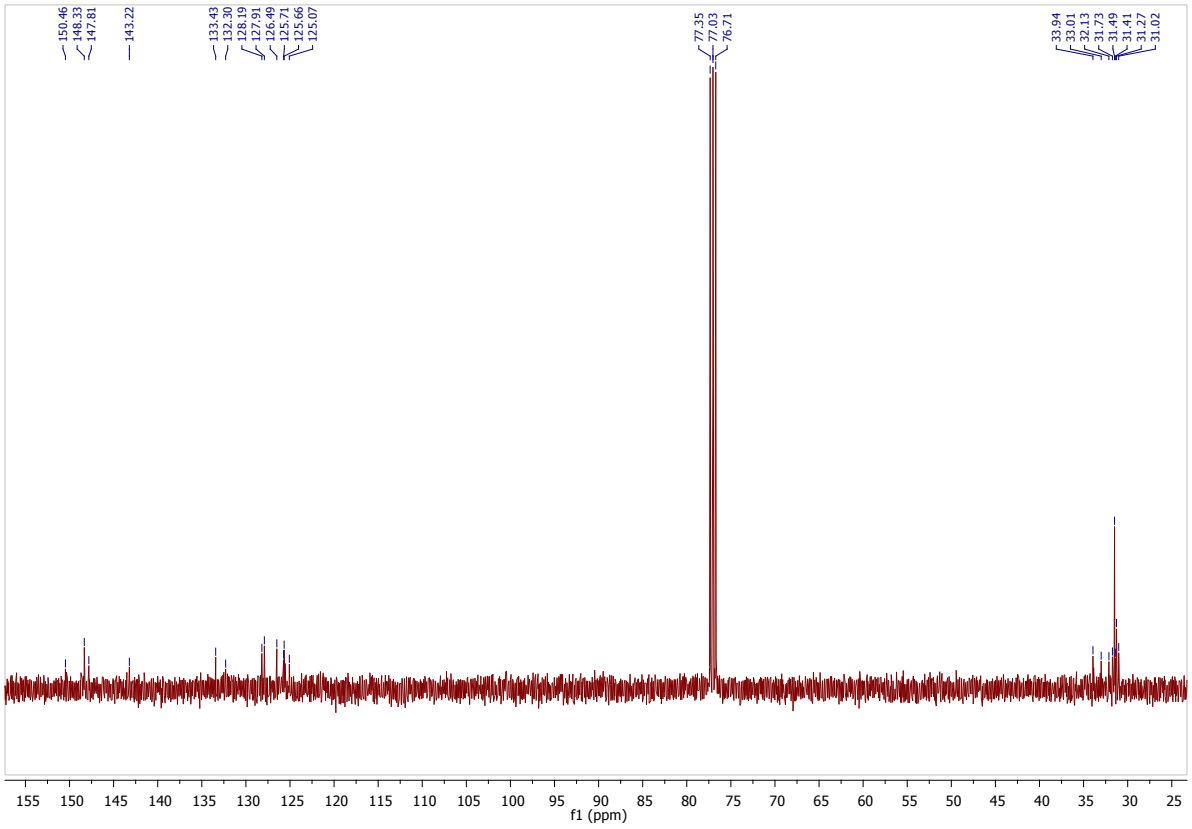


Figure 24-^{13}C NMR of methylated *tert*-butylcalix-[4]-arene *via* methyl iodide

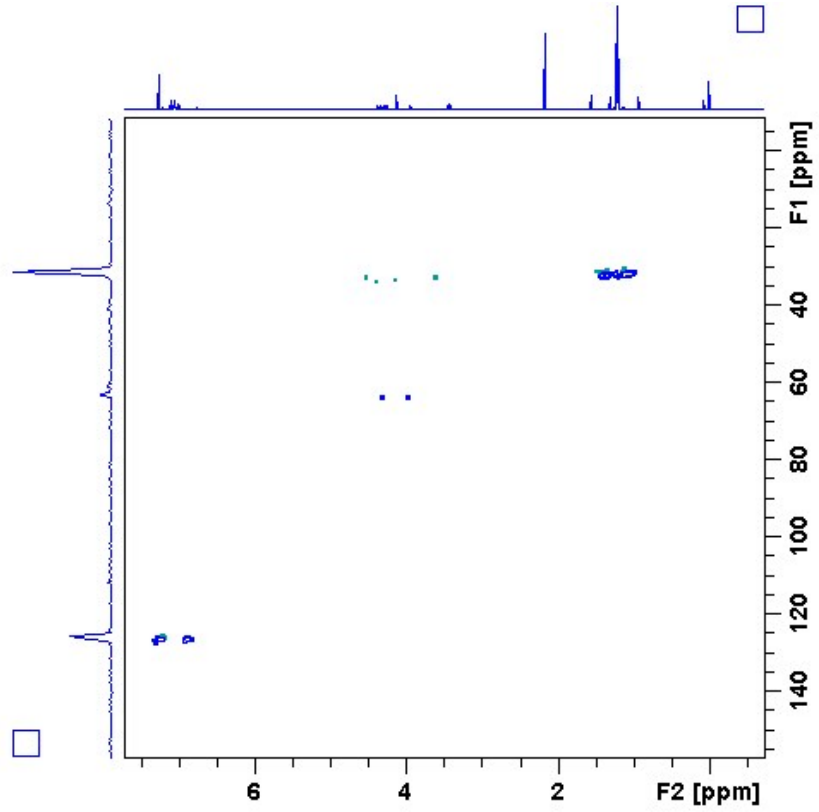


Figure 25-HSQC of methylated *tert*-butylcalix-[4]-arene *via* methyl iodide

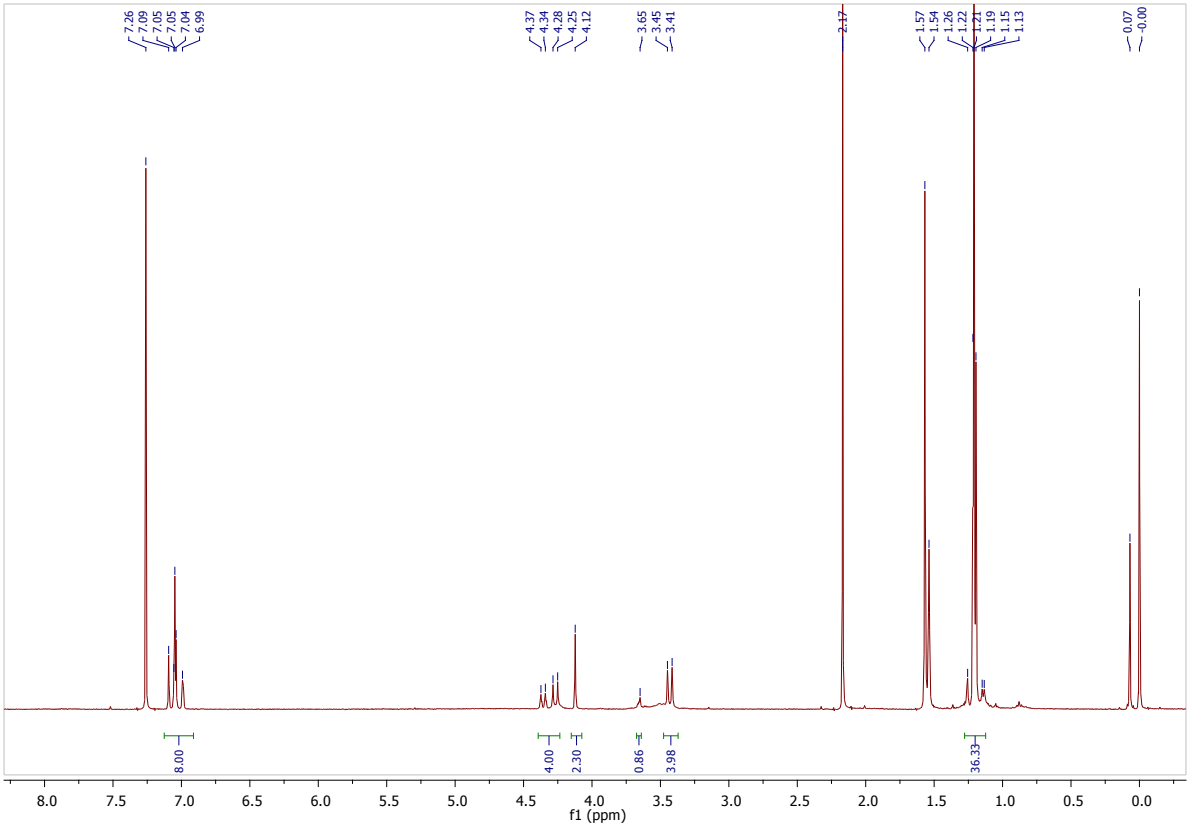


Figure 26-^{1}H NMR of methylated *tert*-butylcalix-[4]-arene *via* methyl iodide with D_2O shake

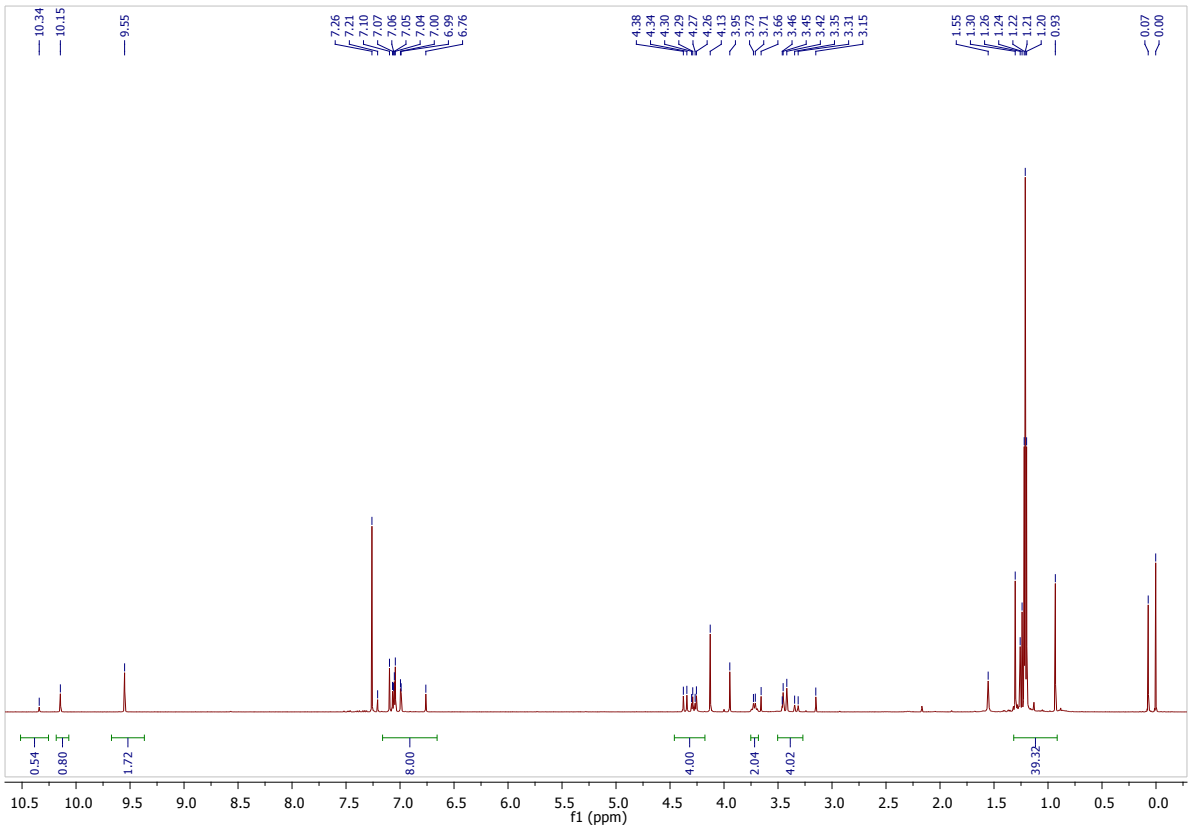


Figure 27-^{1}H NMR of ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide

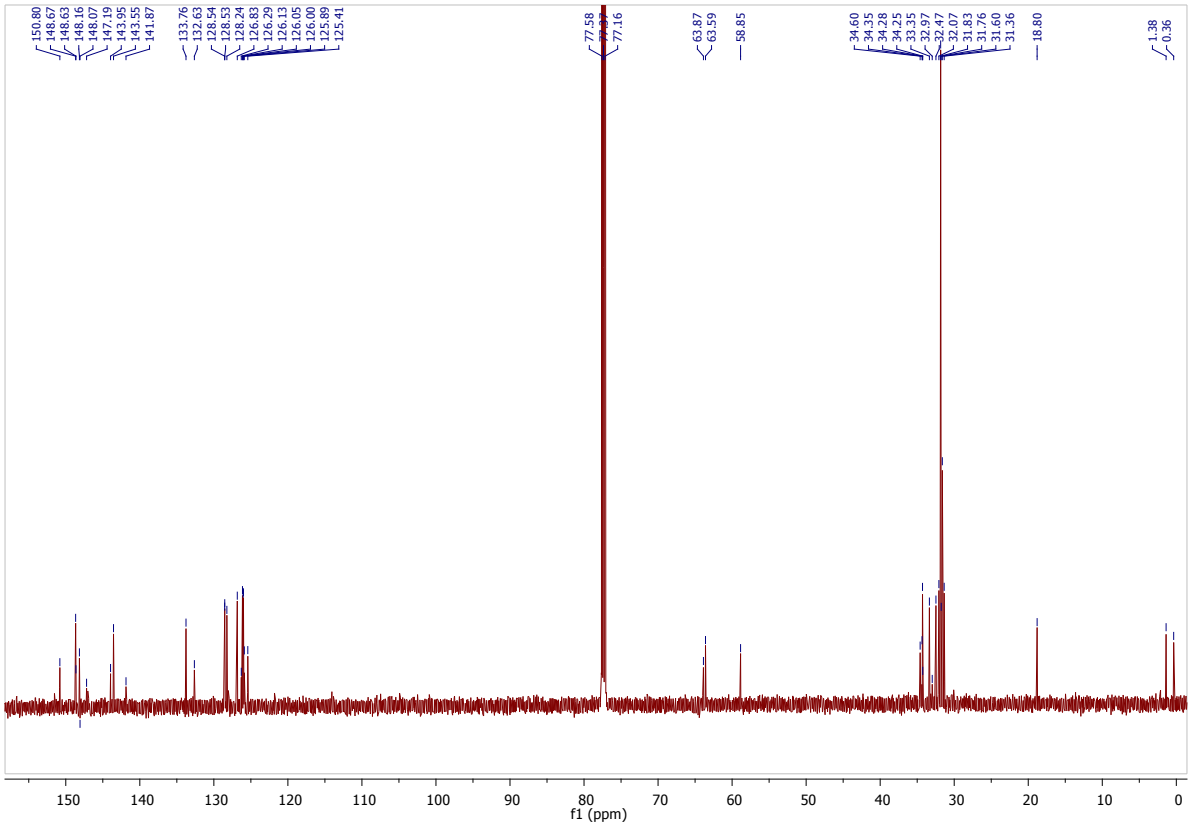


Figure 28-^{13}C NMR of ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide

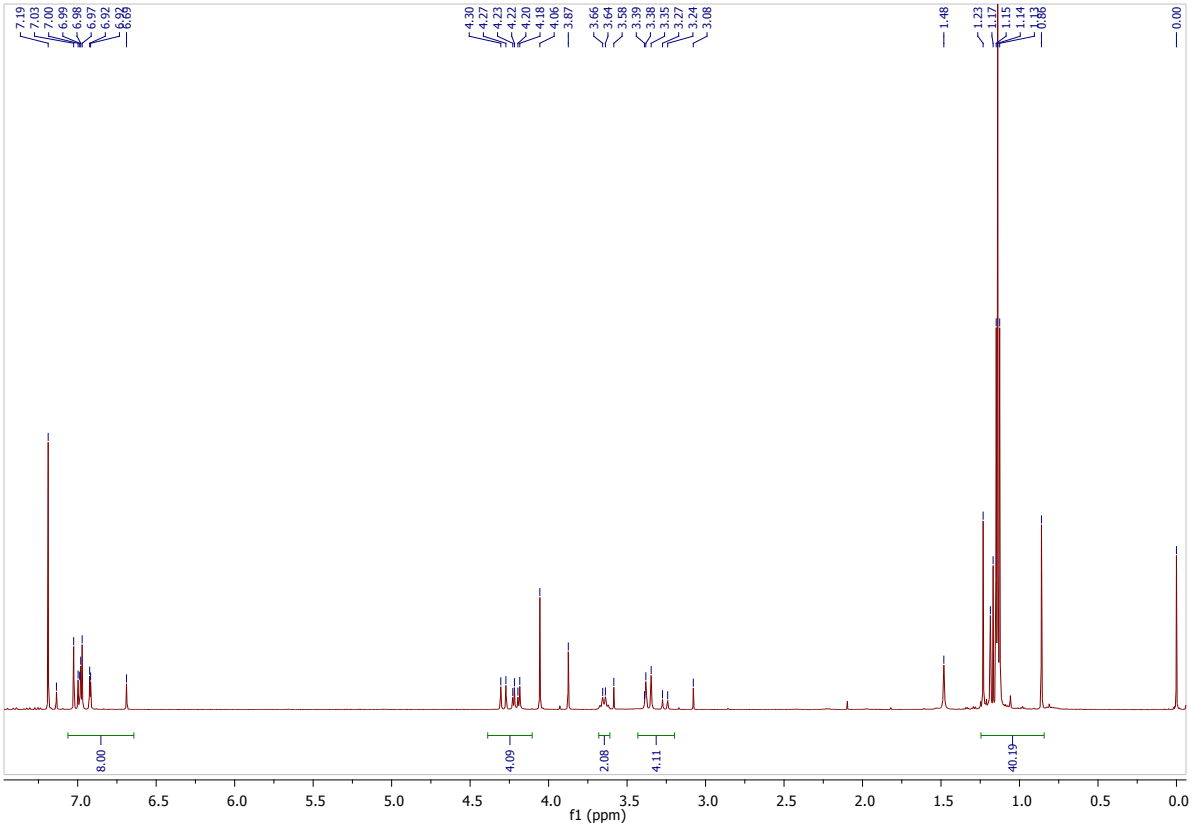


Figure 29-^{1}H NMR of ethylated tert-butylcalix-[4]-arene *via* ethyl iodide with a D_2O shake

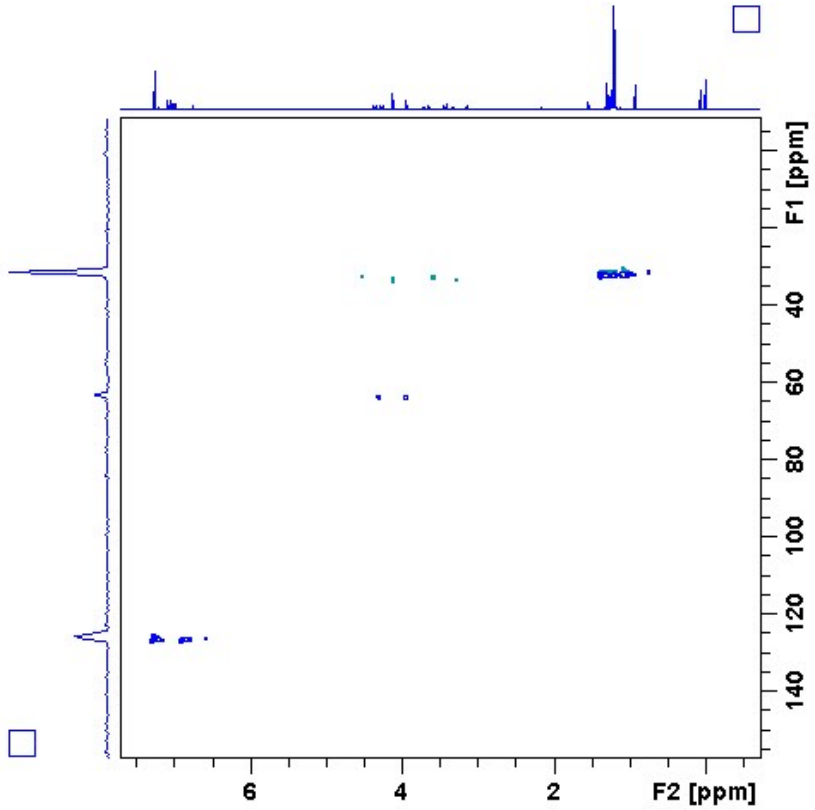


Figure 30-HSQC of ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide

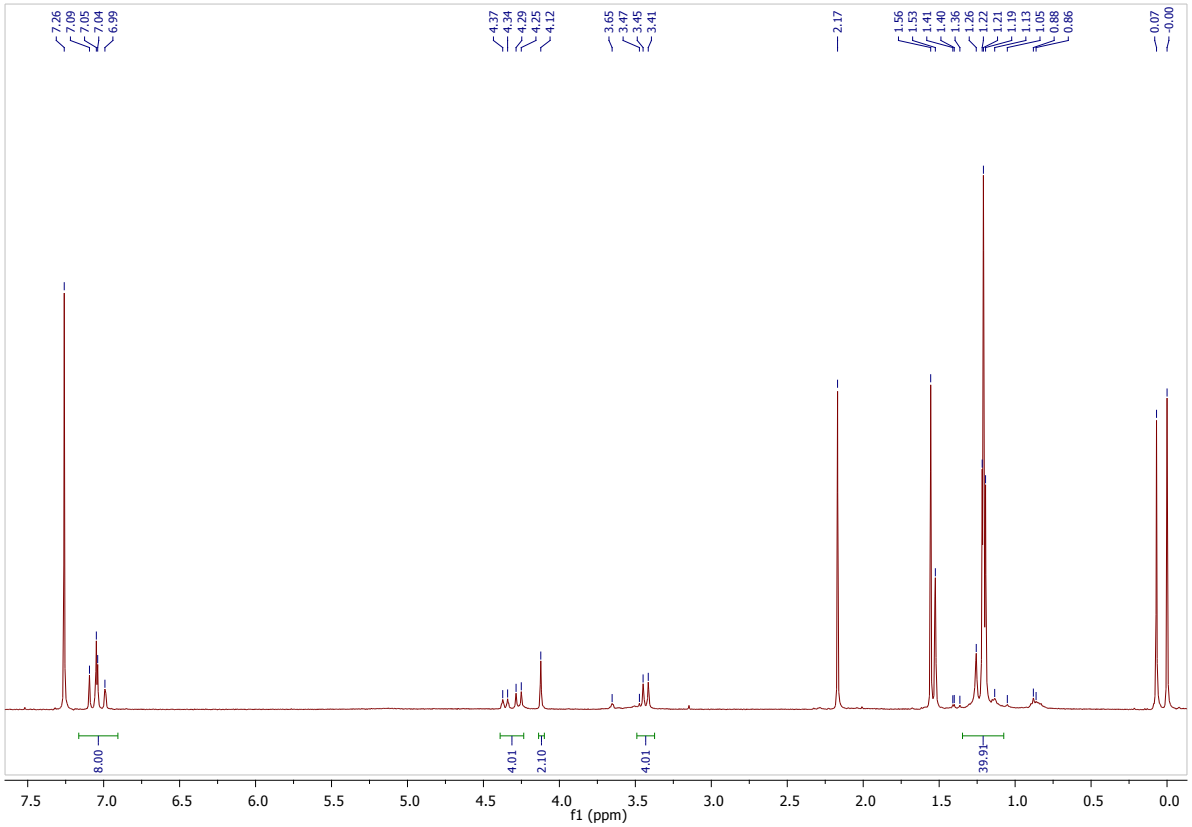


Figure 31-^{1}H NMR of ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide with D_2O

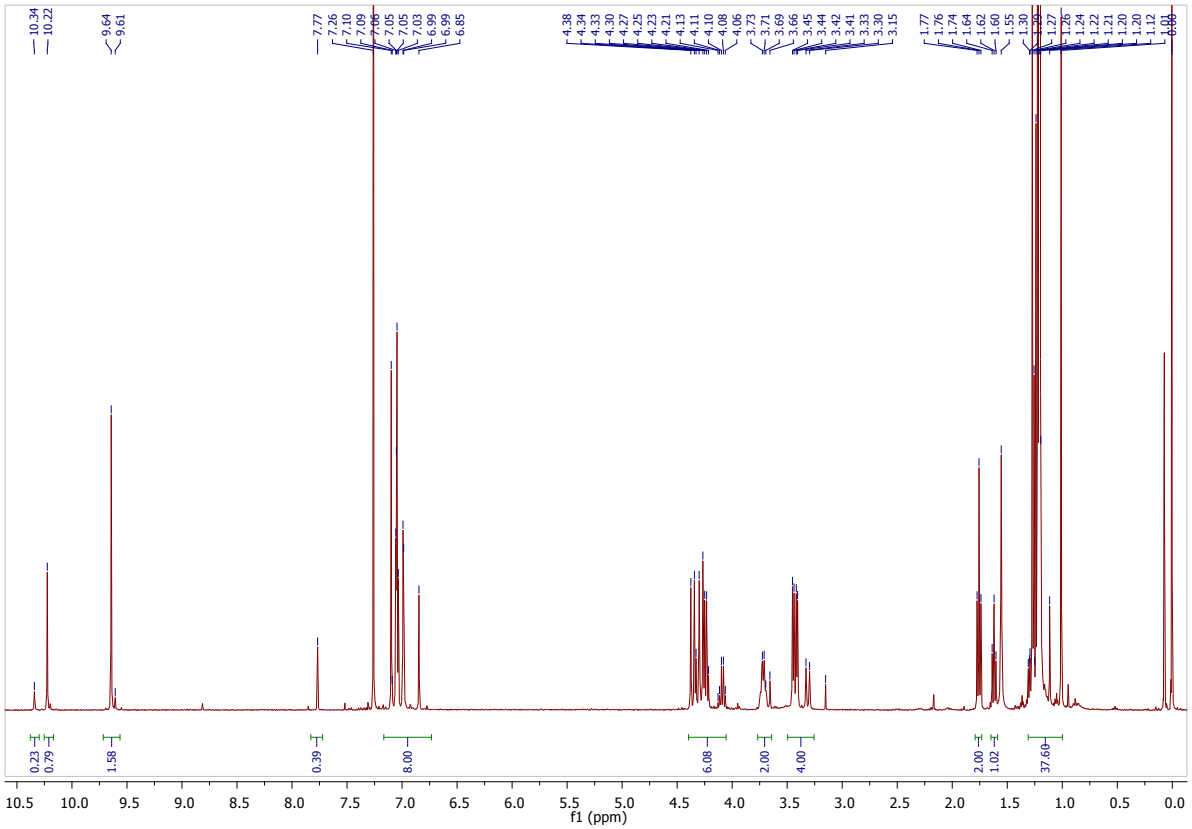


Figure 32- ^{1}H NMR of propylated *tert*-butylcalix-[4]-arene *via* propyl iodide

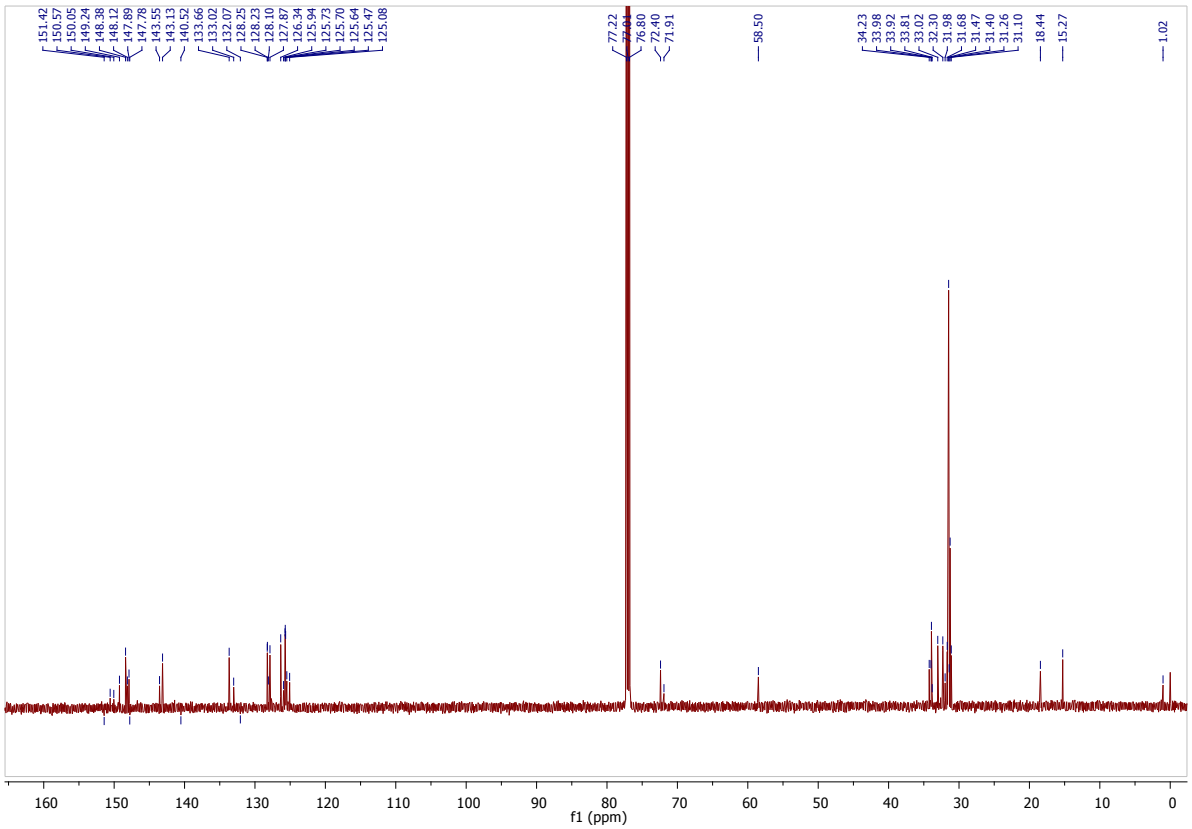


Figure 33-^{13}C NMR of propylated *tert*-butylcalix-[4]-arene *via* propyl iodide

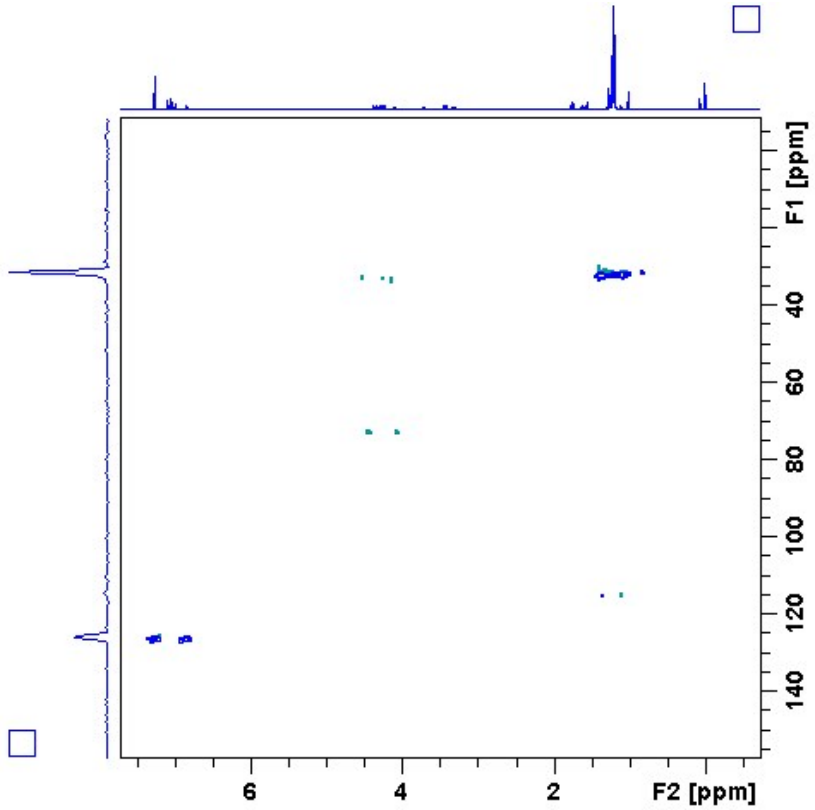


Figure 34-HSQC of propylated *tert*-butylcalix-[4]-arene *via* propyl iodide

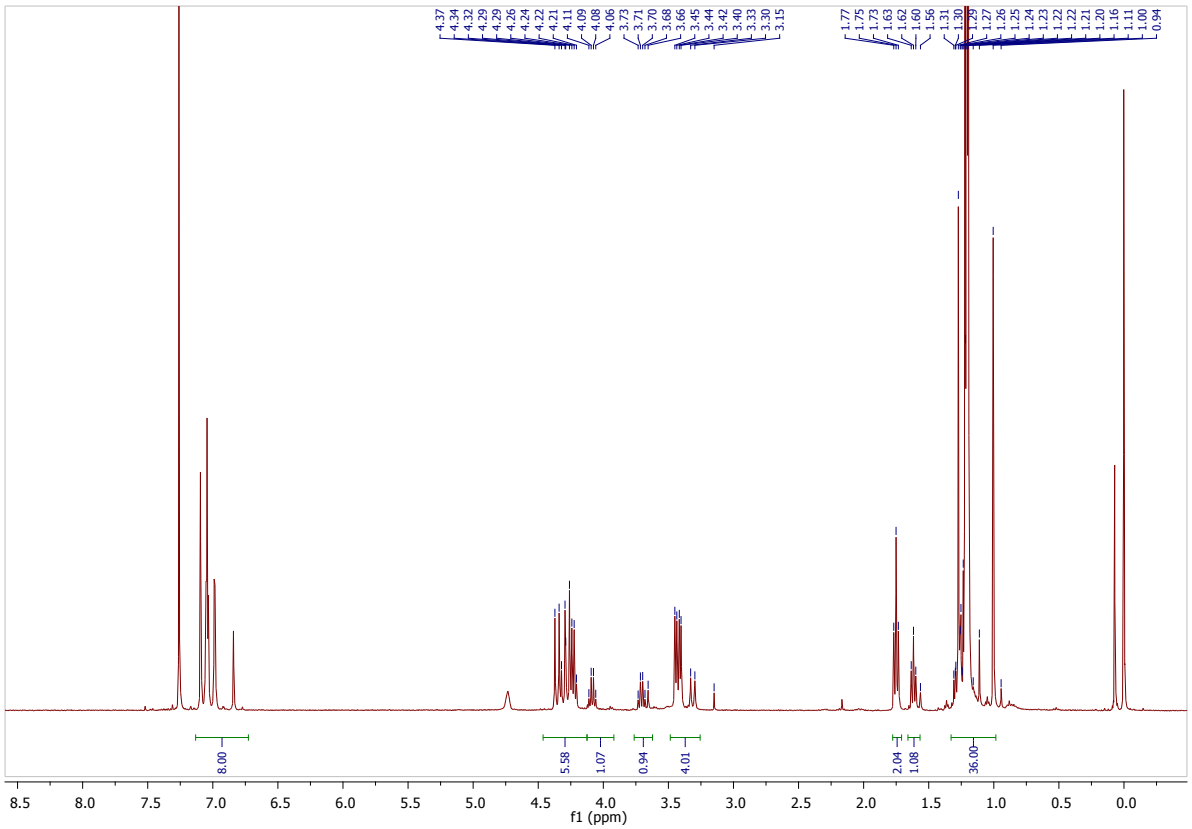


Figure 35-^{1}H NMR of propylated *tert*-butylcalix-[4]-arene *via* propyl iodide with D_2O shake

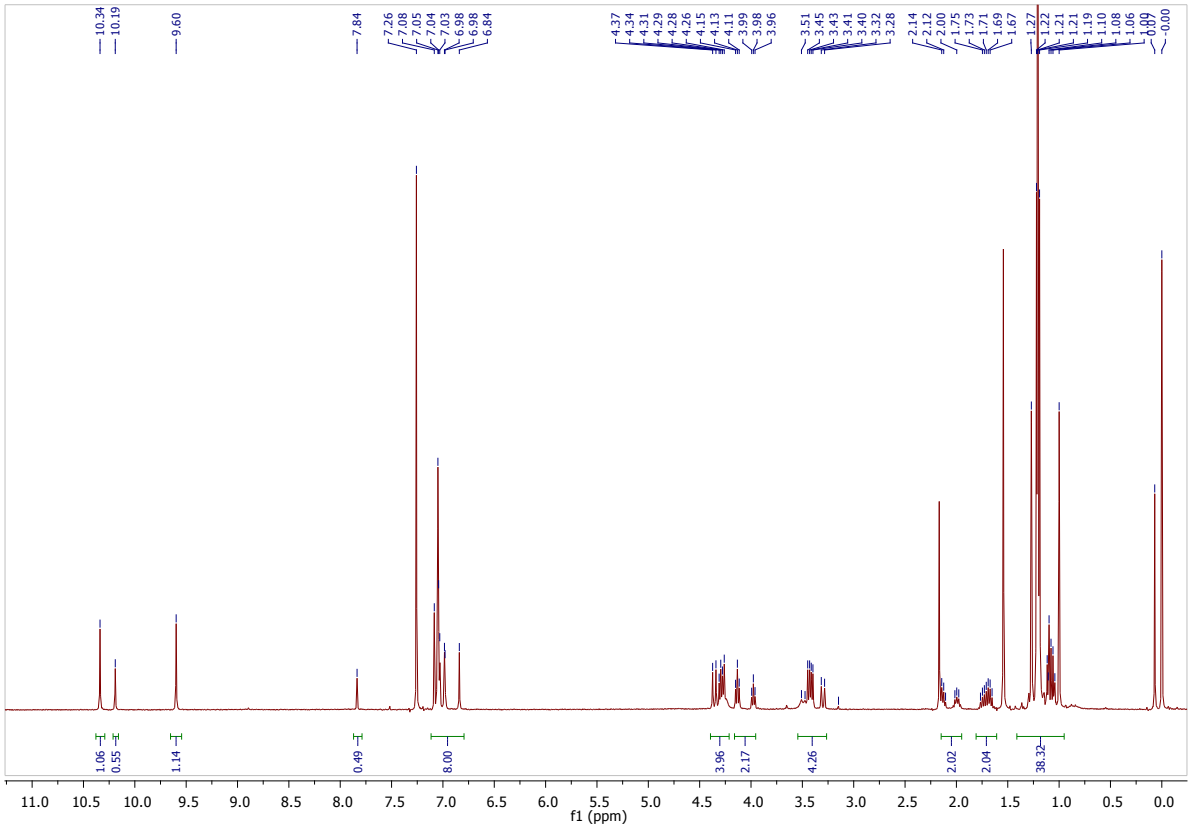


Figure 36-^{1}H NMR of butylated *tert*-butylcalix-[4]-arene *via* butyl iodide

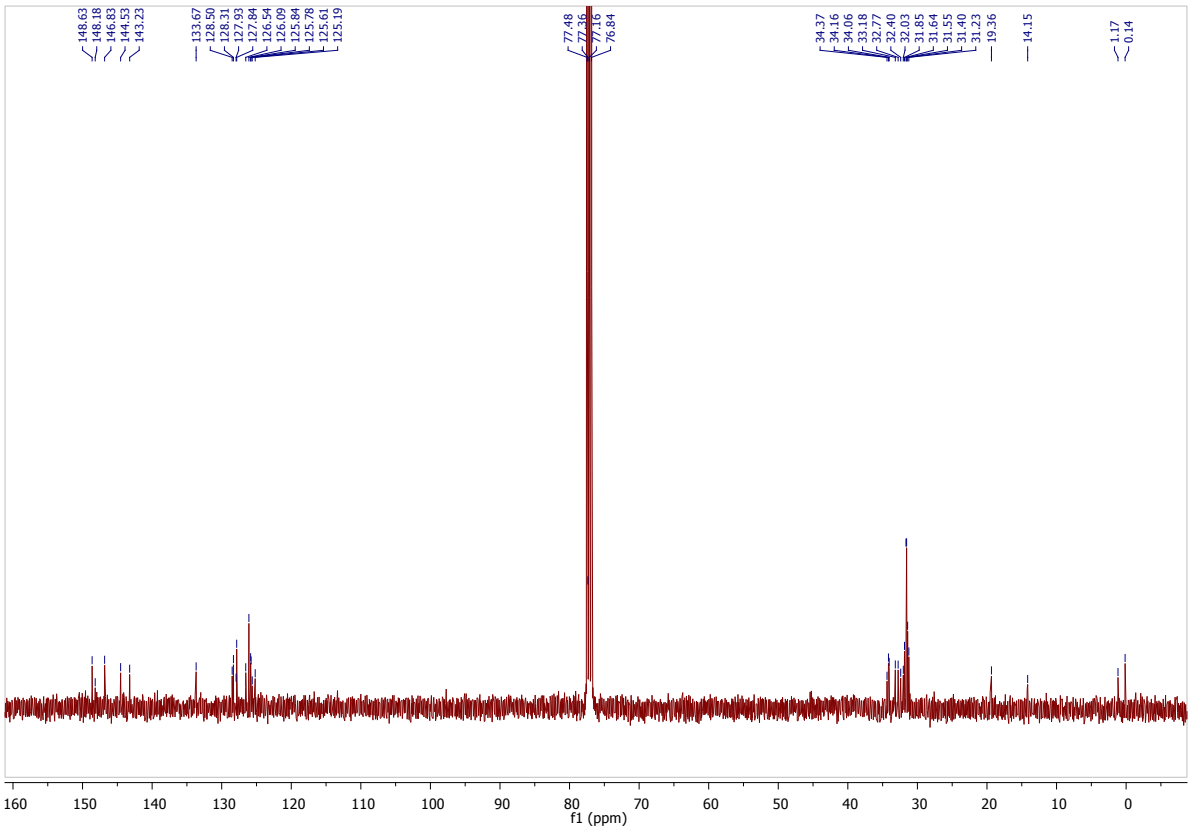


Figure 37-^{13}C NMR of butylated *tert*-butylcalix-[4]-arene *via* butyl iodide

2. Single Crystal Diffraction Data

Triethylmethylammonium *tert*-butylcalix-[4]-arene, [$N_{2\,2\,2\,1}$] [TBC]

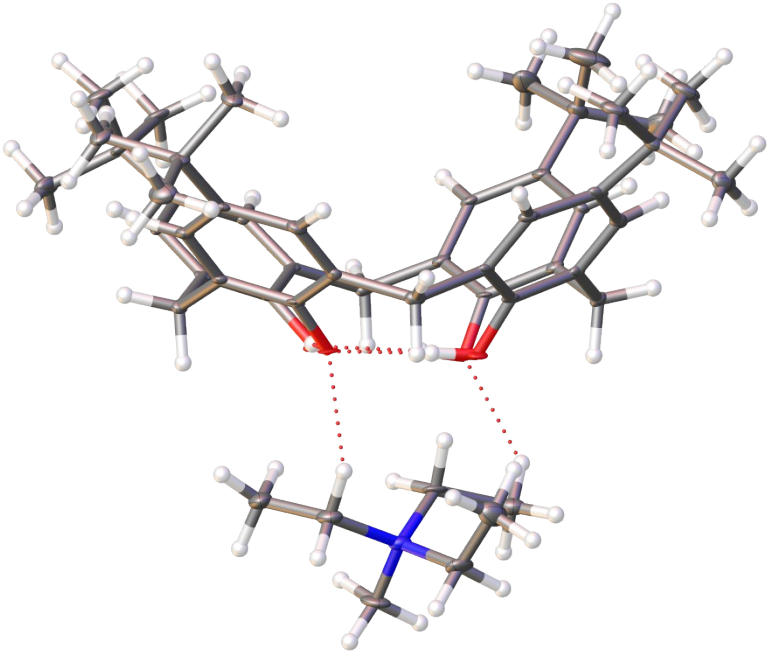


Figure 38-Structure of triethylmethylammonium *tert*-butyl calixarene

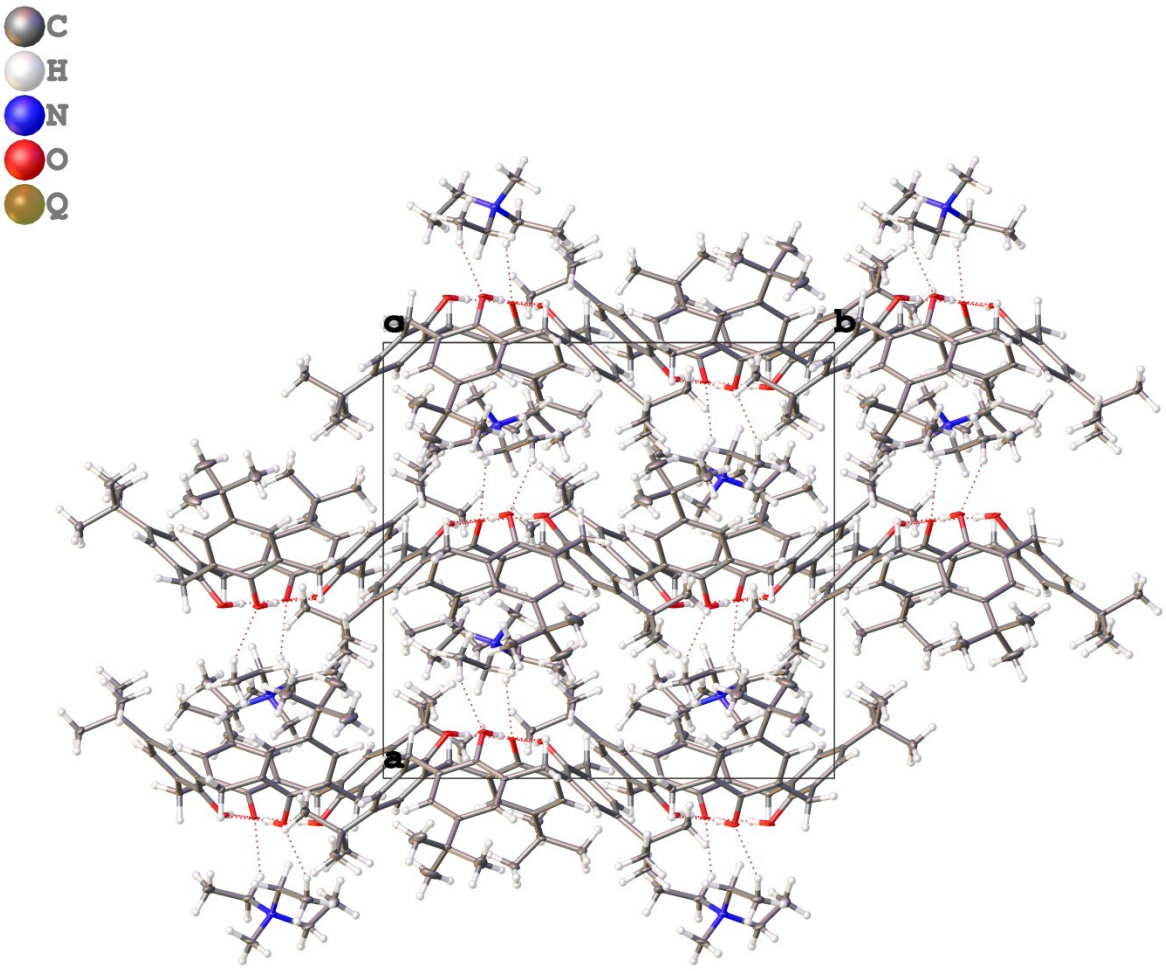


Figure 39-Packing of triethylmethylammonium calixarate, [N_{2221}][TBC]

Table 2-Table of Structural data for trethylmethylammonium tert-butylcalixarate

Identification code	N2221CALIX
Empirical formula	$C_{44}H_{55}O_4N$
Formula weight	764.10
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	15.4381(2)
b/Å	15.9969(2)
c/Å	18.31405(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4522.86(9)
Z	20
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.651
F(000)	1820.0
Crystal size/mm^3	0.168 × 0.085 × 0.067
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.338 to 178.274
Index ranges	-20 ≤ h ≤ 20, -19 ≤ k ≤ 19, -16 ≤ l ≤ 18
Reflections collected	40528
Independent reflections	8049 [R_{int} = 0.0404, R_{sigma} = 0.0309]
Data/restraints/parameters	8049/49/525
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0608, wR_2 = 0.1673
Final R indexes [all data]	R_1 = 0.0622, wR_2 = 0.1692
Largest diff. peak/hole / e Å^{-3}	0.48/-0.40
Flack parameter	0.05(7)

Tetrabutylmethylammonium *tert*-butylcalix-[4]-arene, [N_{4441}] [TBC]

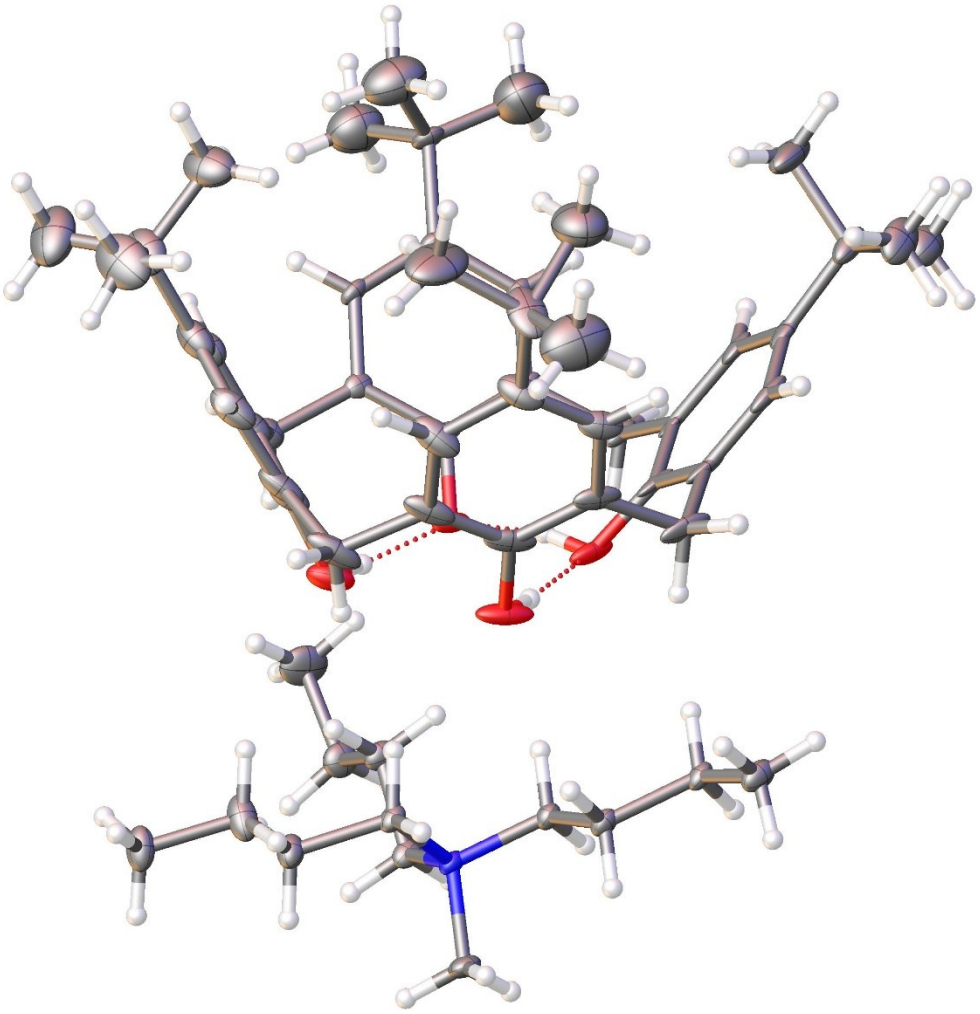


Figure 40: Tetrabutylmethylammonium *tert*-butylcalix-[4]-arene, [N_{4441}] [TBC]

Table 3-Table of Structural data for tetrabutylmethylammonium tert-butylcalixarate

Identification code	RW011720A_100K
Empirical formula	$C_{64}H_{100}N_3O_4$
Formula weight	975.47
Temperature/K	100.00(18)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.3846(2)
b/Å	15.7251(2)
c/Å	24.2062(3)
α/°	90
β/°	105.0730(10)
γ/°	90
Volume/Å^3	5654.59(13)
Z	4
ρ_{calc}g/cm^3	1.093
μ/mm^{-1}	0.515
F(000)	2040.0
Crystal size/mm^3	6.437 × 0.732 × 0.424
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.564 to 144.524

Index ranges	$-19 \leq h \leq 18, -19 \leq k \leq 19, -28 \leq l \leq 29$
Reflections collected	54073
Independent reflections	11067 [R_{int} = 0.0387, R_{sigma} = 0.0234]
Data/restraints/parameters	11067/0/681
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0840, wR_2 = 0.2540
Final R indexes [all data]	R_1 = 0.0882, wR_2 = 0.2590
Largest diff. peak/hole / e $Å^{-3}$	0.70/-1.10

3. Mass Spectrometry Data

Mass spectrometry data is summarised in the table below

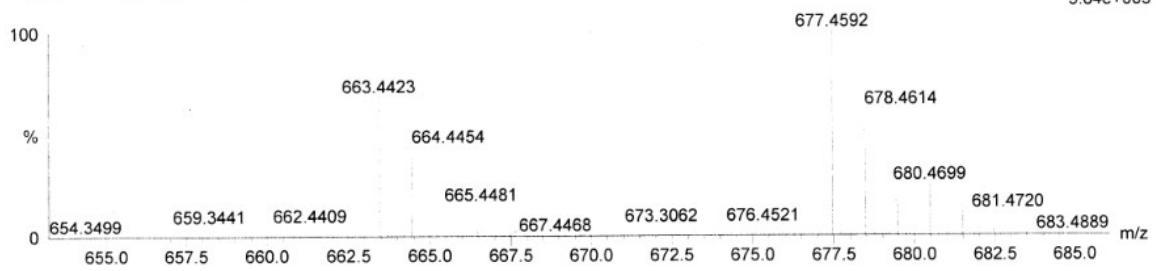
Table 4-Mass spectrometry data for alkylated *tert*-butylcalix-[4]-arene

	Mass Spectrometry data				
Alkylating agent	Exact Mass	$[M+H]^+$	$[M+Na]^+$	$[M+NH_4]^+$	$[M+K]^+$
Me_2SO_4	662.9550	663.4413		680.4679	
Et_2SO_4	676.4491	677.4595	699.4402		
Pr_2SO_4	691.0090	691.4727	713.4546	708.4992	
Bu_2SO_4	704.4804	705.4883	727.4702	722.5140	743.4442
MeI	662.9550	663.4413	685.4233		
EtI	676.4491	677.4570	699.4389	694.4835	715.4128
PrI	691.0090	691.4727	713.4546	708.4992	
BuI	704.4804	705.4883	727.4702	722.5148	

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
173 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 0-150 O: 0-10 Na: 0-1
RW081704B
asep__03JULY_2017_118 10 (0.468) Cm (9:14)



Minimum:				-1.5		
Maximum:		5.0	4.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
663.4423	663.4413	1.0	1.5	16.5	1166.6	C45 H59 O4
	663.4448	-2.5	-3.8	4.5	9629.2	C36 H64 O9 Na

Figure 41-Mass spectrometry report for methylated *tert*-butylcalix-[4]-arene *via* methyl iodide

RW081704B
asep__03JULY_2017_118 (0.075) Is (1.00,1.00) C45H58O4Na

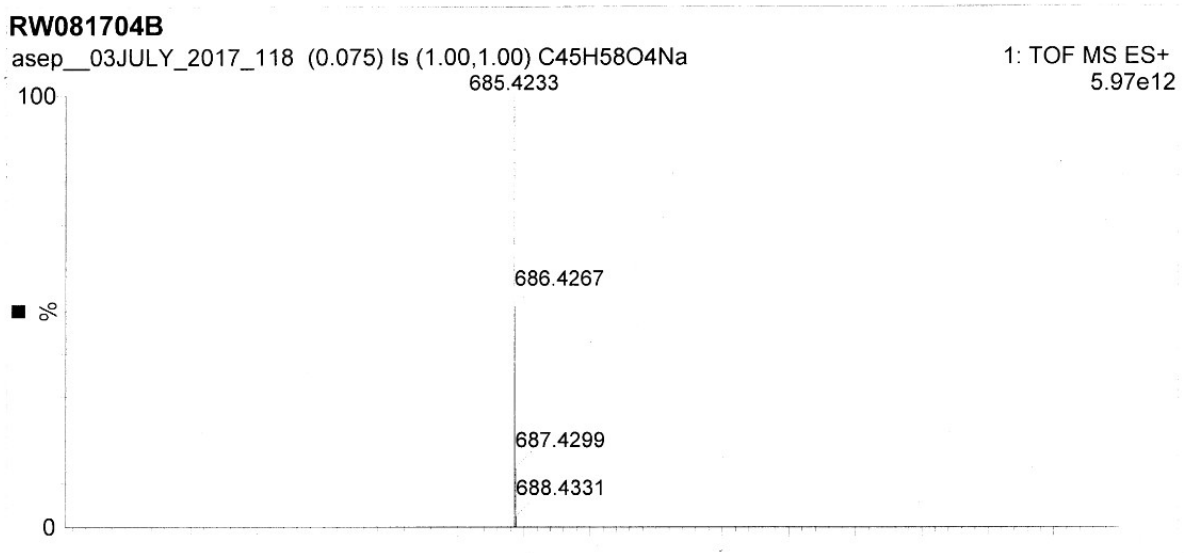


Figure 42-Mass spectrometry report for methylated *tert*-butylcalix-[4]-arene *via* methyl iodide $[M+Na]^+$

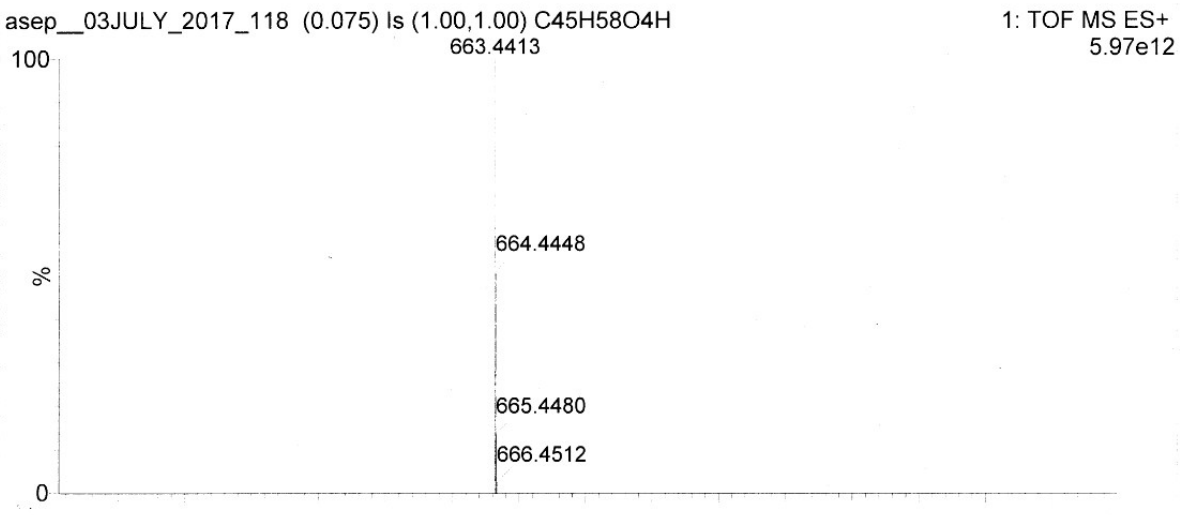
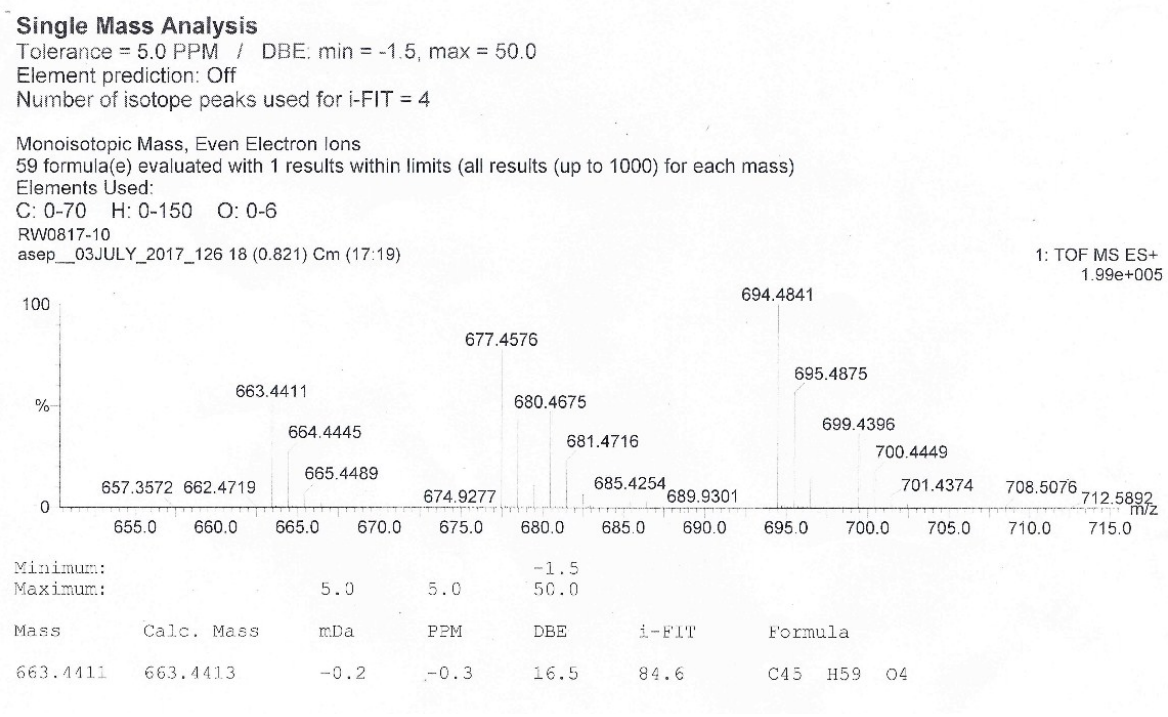


Figure 43- Mass spectrometry report for methylated tert-butylcalix-[4]-arene *via* methyl iodide $[M+H]^+$



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
663.4411	663.4413	-0.2	-0.3	16.5	84.6	C45 H59 O4

Figure 44- Mass spectrometry report for methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate

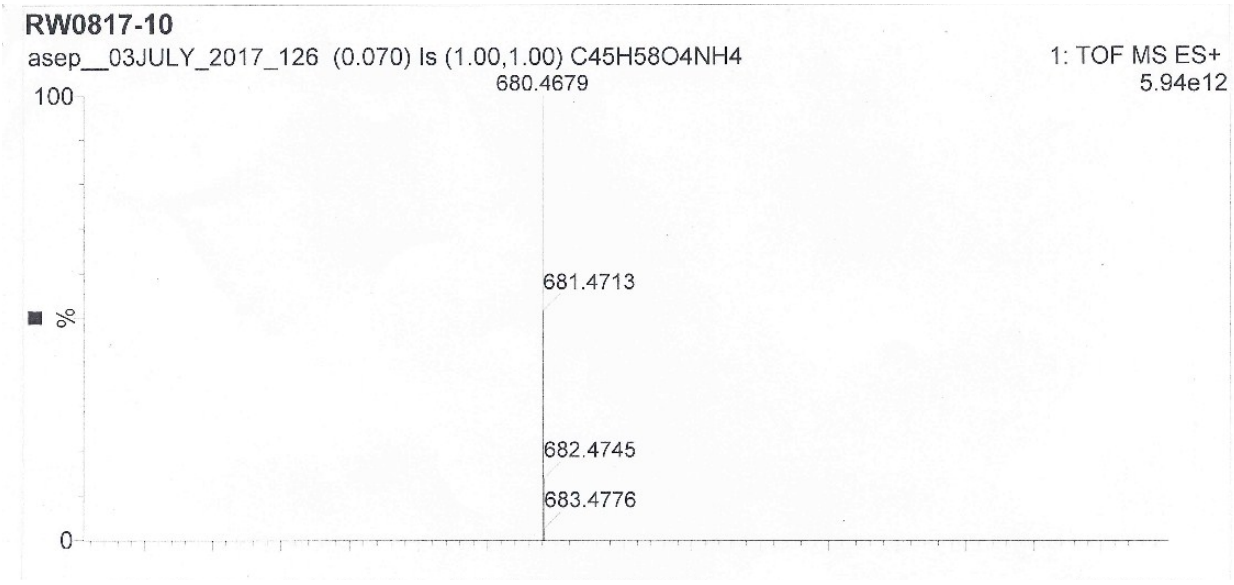


Figure 45- Mass spectrometry report for methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate $[M+NH_4]^+$

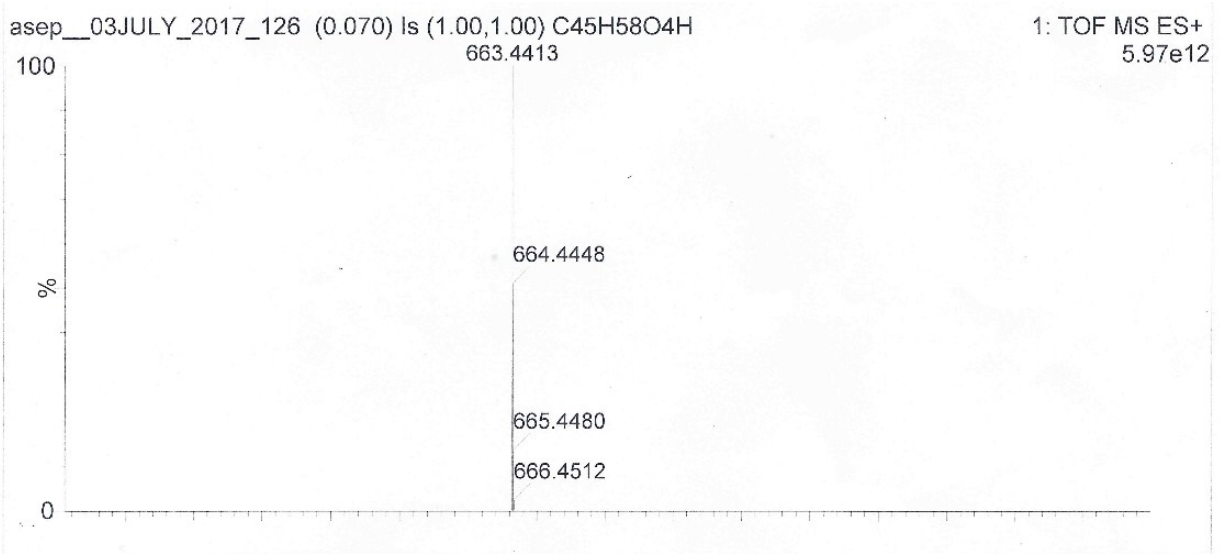
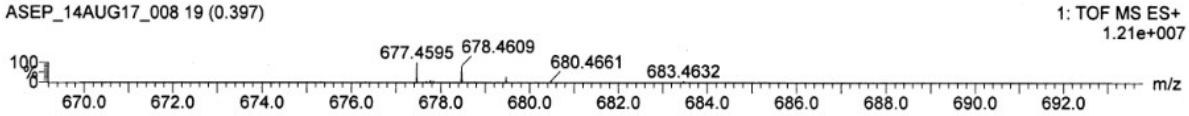


Figure 46- Mass spectrometry report for methylated *tert*-butylcalix-[4]-arene *via* dimethyl sulfate $[M+H]^+$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 44-48 H: 55-65 O: 2-6
RW081707A
ASEP_14AUG17_008 19 (0.397)



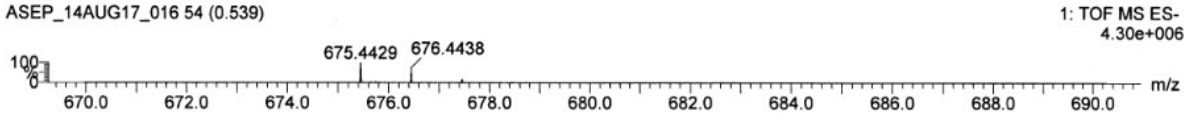
Minimum:				-1.5	
Maximum:		5.0	10.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
677.4595	677.4570	2.5	3.7	16.5	C46 H61 O4

Figure 47- Mass spectrometry report for ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate $[M+H]^+$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 44-48 H: 55-65 O: 2-6
RW081707A
ASEP_14AUG17_016 54 (0.539)



Minimum:				-1.5	
Maximum:		5.0	10.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
675.4429	675.4413	1.6	2.4	17.5	C46 H59 O4

Figure 48- Mass spectrometry report for ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate $[M-H]^-$

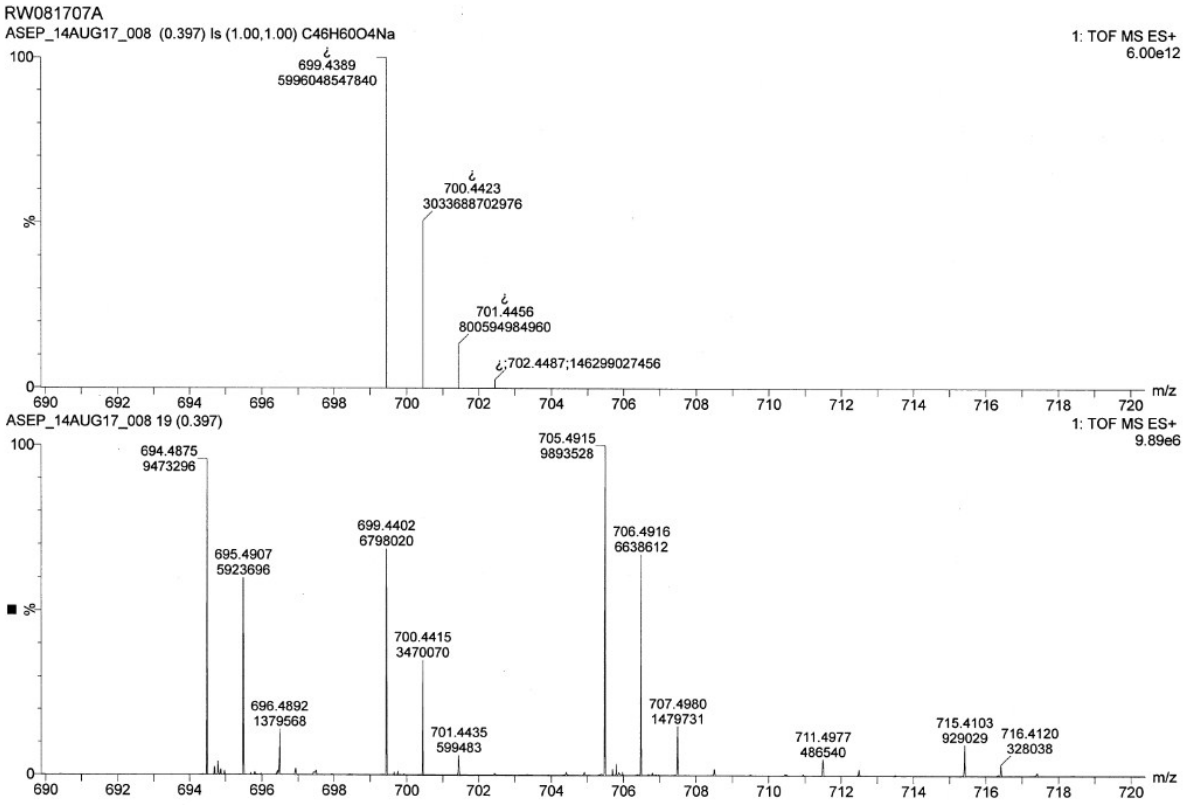
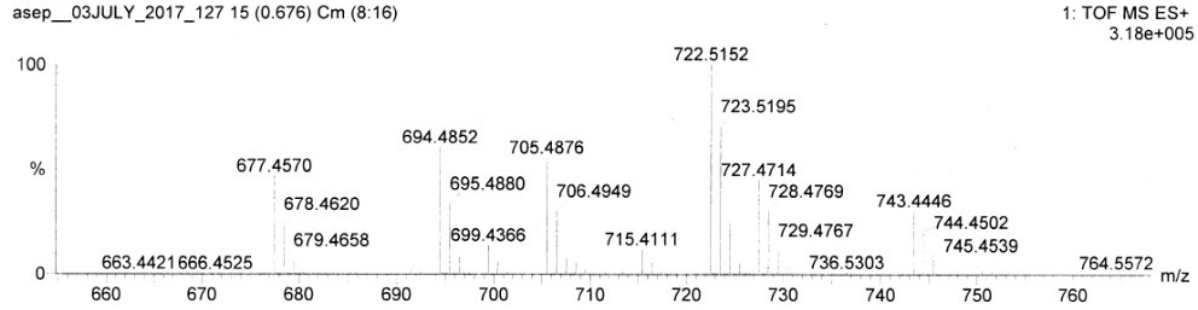


Figure 49- Mass spectrometry report for ethylated *tert*-butylcalix-[4]-arene *via* diethyl sulfate $[M+Na]^+$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
59 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 0-150 O: 0-6
RW0817-12
asep__03JULY_2017_127 15 (0.676) Cm (8:16)



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
677.4570	677.4570	0.0	0.0	16.5	442.5	C46 H61 O4

Figure 50-Mass spectrometry report for ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide

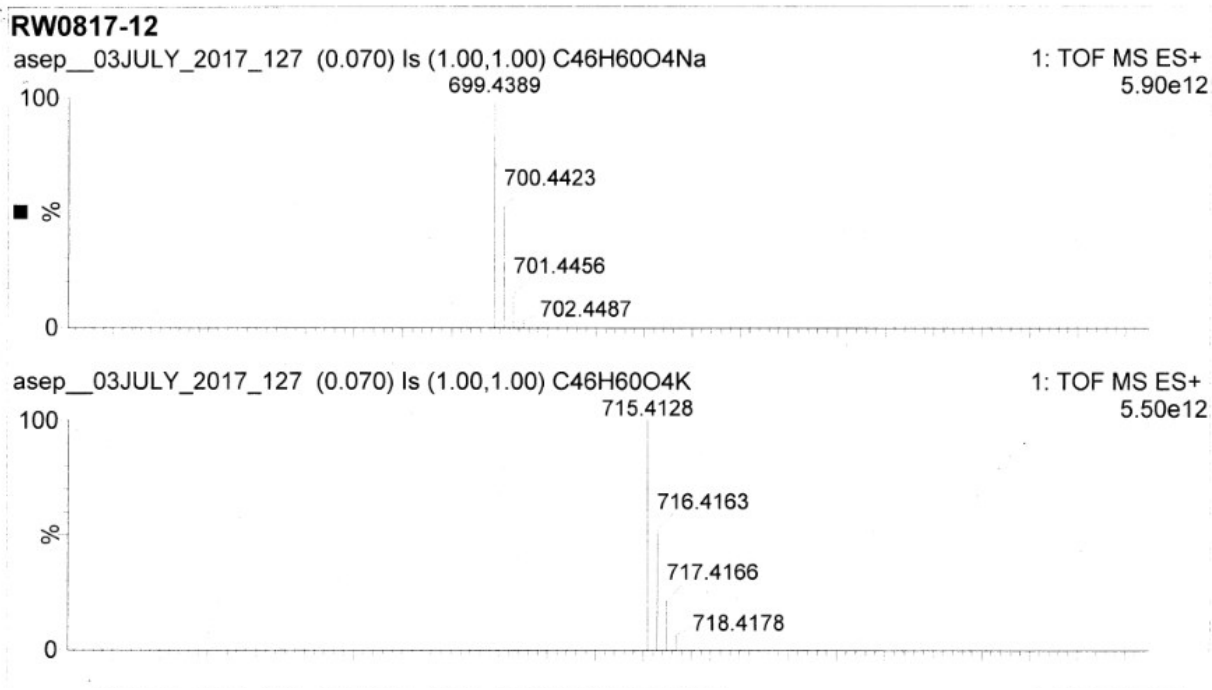


Figure 51- Mass spectrometry report for ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide $[M+Na]^+$ and $[M+K]^+$

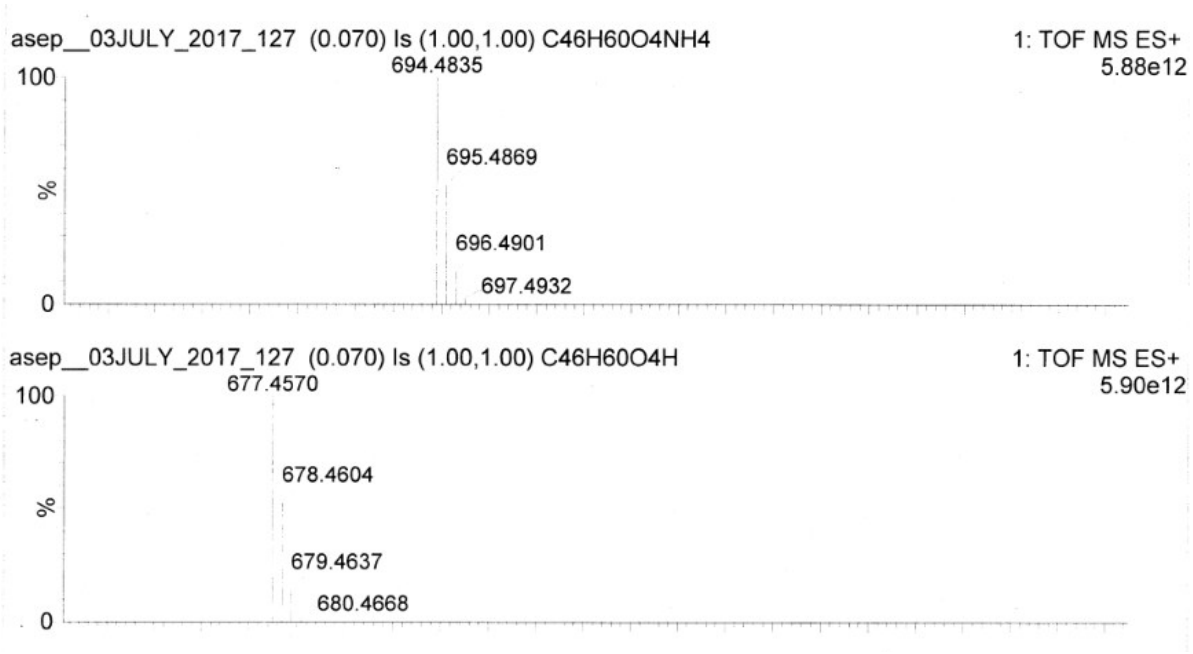


Figure 52- Mass spectrometry report for ethylated *tert*-butylcalix-[4]-arene *via* ethyl iodide $[M+NH_4]^+$ and $[M+H]^+$

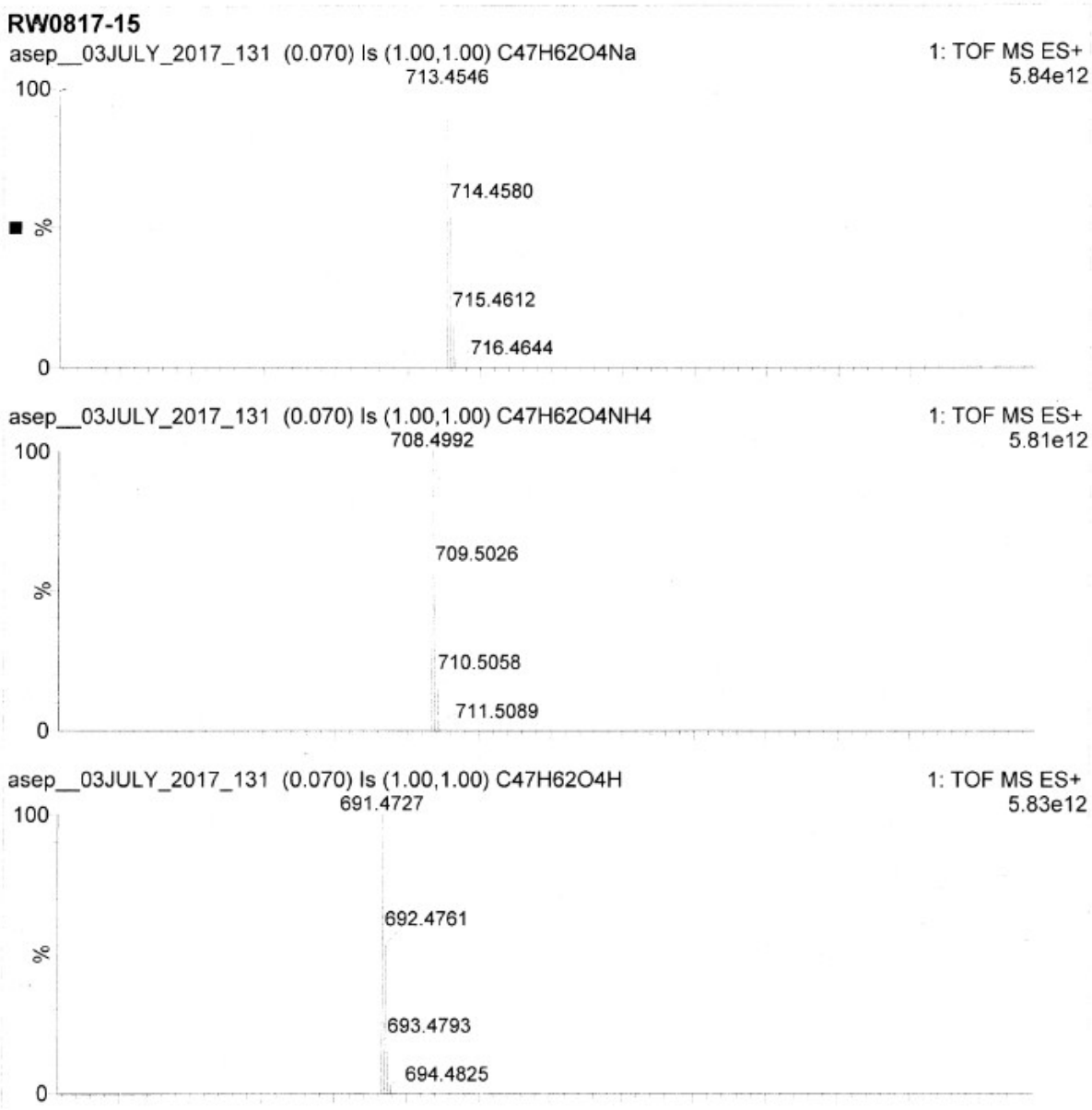


Figure 53- Mass spectrometry report for propylated *tert*-butylcalix-[4]-arene *via* propyl iodide, $[M+Na]^+$, $[M+NH_4]^+$, $[M+H]^+$

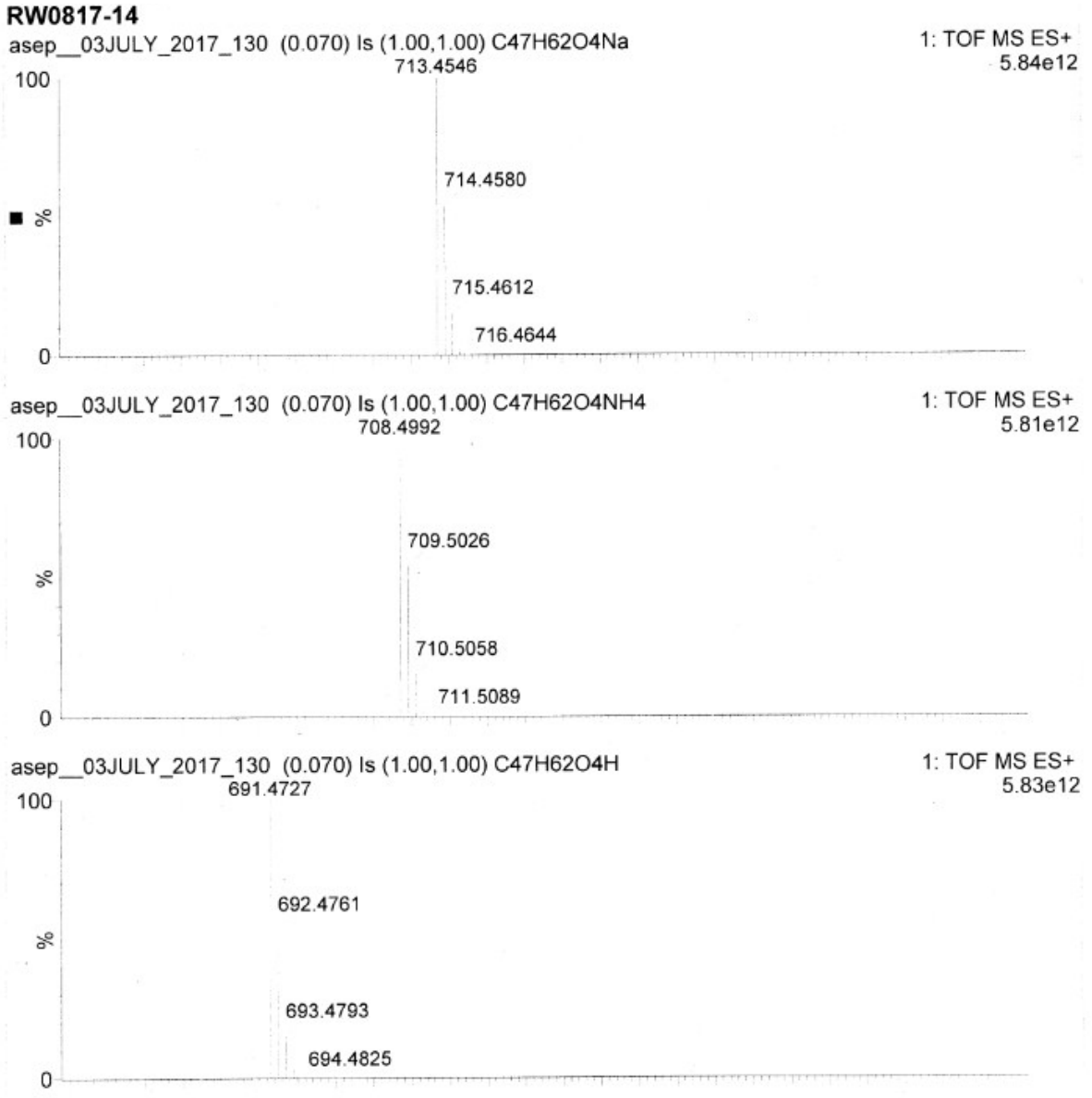


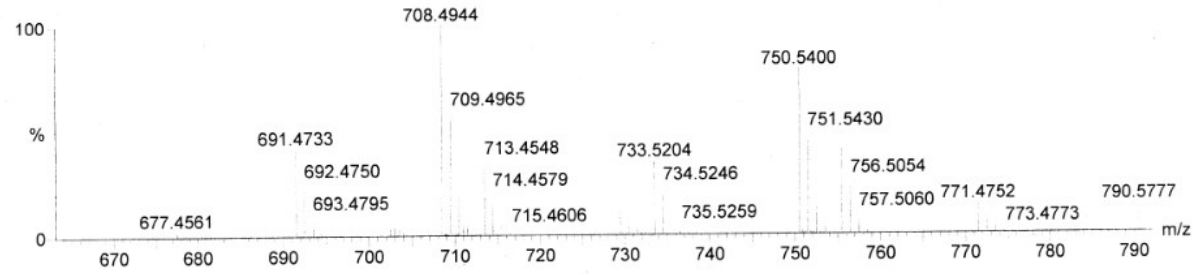
Figure 54-Mass spectrometry report for propylated *tert*-butylcalix-[4]-arene *via* dipropyl sulfate, $[M+Na]^+$, $[M+NH4]^+$, $[M+H]^+$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
61 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 0-150 O: 0-6
RW0817-14
asep__03JULY_2017_130 19 (0.856) Cm (14:21)

1: TOF MS ES+
5.26e+004



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
691.4733	691.4726	0.7	1.0	16.5	10.6	C47 H63 O4

Figure 55-Mass spectrometry report for propylated *tert*-butylcalix-[4]-arene *via* dipropyl sulfate

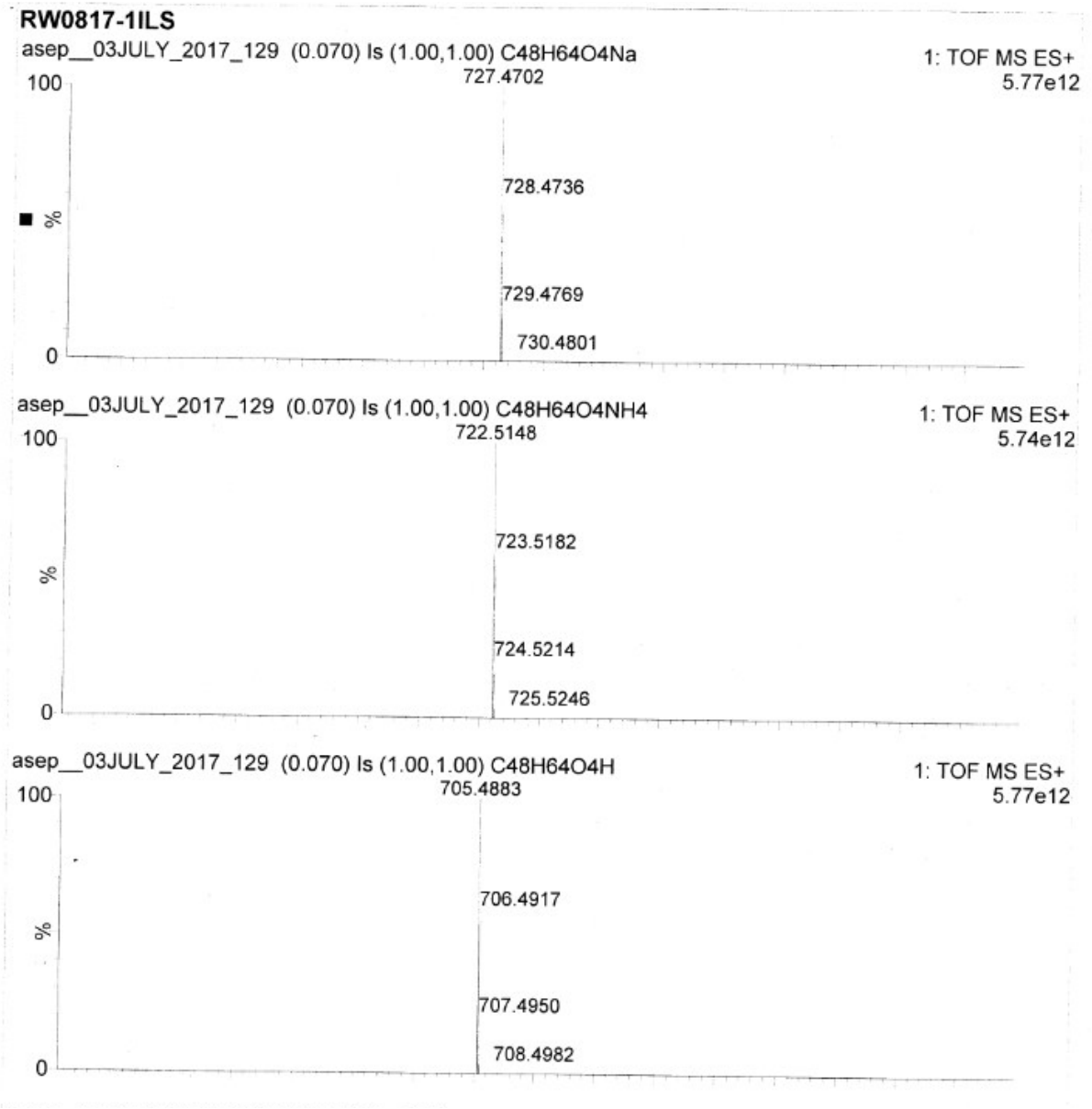
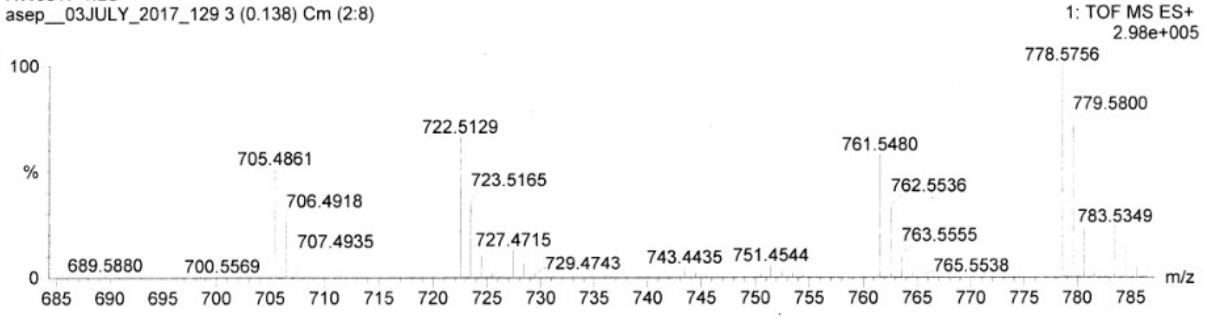


Figure 56- Mass spectrometry report for butylated *tert*-butylcalix-[4]-arene *via* butyl iodide, $[M+Na]^+$, $[M+NH4]^+$, $[M+H]^+$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
61 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 0-150 O: 0-6
RW0817-1ILS
asep__03JULY_2017_129 3 (0.138) Cm (2:8)



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
705.4861	705.4883	-2.2	-3.1	16.5	148.0	C48 H65 O4

Figure 57-Mass spectrometry report for butylated *tert*-butylcalix-[4]-arene *via* butyl iodide

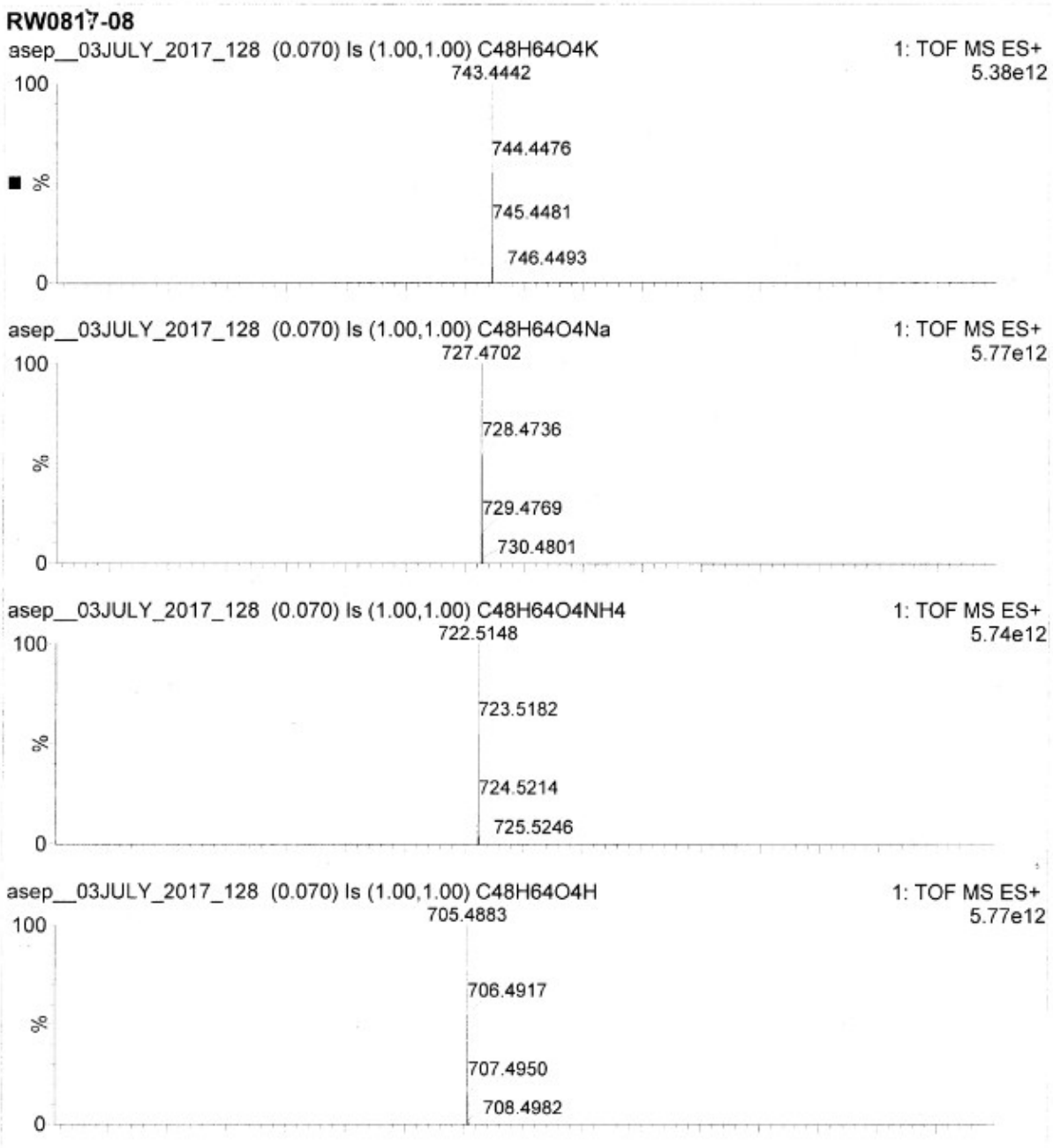


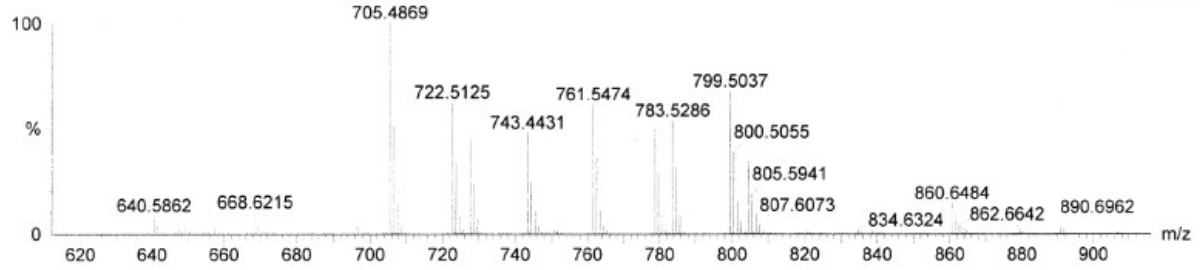
Figure 58-Mass spectrometry report for butylated *tert*-butylcalix-[4]-arene *via* dibutyl sulfate,$[M+K]^+$, $[M+Na]^+$, $[M+NH_4]^+$, $[M+H]^+$

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
61 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 0-150 O: 0-6
RW0817-08
asep__03JULY_2017_128 6 (0.283) Cm (6:8)

1: TOF MS ES+
6.78e+003



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
705.4869	705.4883	-1.4	-2.0	16.5	6.3	C48 H65 O4

Figure 59- Mass spectrometry report for butylated *tert*-butylcalix-[4]-arene *via* dibutylsulfate