Supplementary material (ESI) for Organic & Biomolecular Chemistry

SUPPLEMENTARY INFORMATION

"Di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in cone and 1,2-alternate conformations: synthesis and metal ion extraction"

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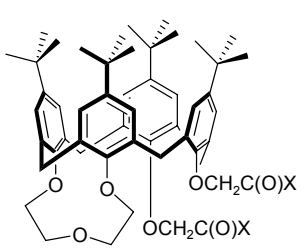
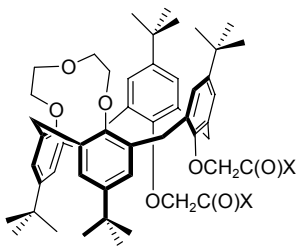
Included in this Supplementary Information are IR, ^{1}H NMR and ^{13}C NMR spectral data for compounds **4**-**7** and **9**-**12**.





	X	
4	$NHSO_2CH_3$	**9**
5	$NHSO_2C_6H_5$	**10**
6	$NHSO_2C_6H_4$-4-NO_2	**11**
7	$NHSO_2CF_3$	**12**

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(methane)sulfonyl carbamoyl-methoxy]calix[4]arene-25,26-crown-3 (4). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3218 (N-H), 1721 (C=O), 1346 and 1153 (S=O), 1202 and 1124 (C-O); ^{1}H NMR ($CDCl_3$): δ 1.03 (s, 18 H, CH_3), 1.14 (s, 18 H, CH_3), 3.11, (d, *J*= 12.0 Hz, 1 H, $ArCH_2Ar$), 3.31 (d, *J*= 13.0 Hz, 2 H, $ArCH_2Ar$), 3.38 (d, *J*= 12.5 Hz, 1 H, $ArCH_2Ar$), 3.42 (s, 6 H, SO_2CH_3), 3.82-3.93 (m, 2 H, OCH_2CH_2O), 3.93-4.03 (m, 2 H, OCH_2CH_2O), 4.18 (d, *J*= 12.0 Hz, 2 H, $ArCH_2Ar$), 4.22-4.35 (m, 4 H, OCH_2CH_2O), 4.39 (d, *J*= 16.0 Hz, 2 H, OCH_2CO), 4.53 (d, *J*= 13.0 Hz, 1 H, $ArCH_2Ar$), 5.06 (d, *J*= 12.5 Hz, 1 H, $ArCH_2Ar$), 5.16 (d, *J*= 16.0 Hz, 2 H, OCH_2CO), 6.80 (d, *J*= 2.5 Hz, 2 H, ArH), 6.82 (d, *J*= 2.5 Hz, 2 H, ArH), 6.87 (d, *J*= 2.5 Hz, 2 H, ArH), 6.97 (d, *J*= 2.5, 2 H, ArH), 9.52 (s, 2 H, NH); ^{13}C NMR ($CDCl_3$): δ 30.90, 31.03, 31.12,

31.33, 31.55, 33.90, 33.94, 41.75, 73.93, 74.60, 76.09, 124.52, 125.60, 126.15, 126.75, 132.18, 132.55, 133.12, 134.68, 145.47, 146.47, 152.50, 152.71, 169.33.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(benzene)sulfonyl-carbamoyl-methoxy]calix[4]arene-25,26-crown-3 (5) . IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3246 (N-H), 1717 (C=O), 1360 and 1163 (S=O), 1202 and 1124 (C-O); ^1H NMR ($CDCl_3$): δ 1.00 (s, 18 H, CH_3), 1.13 (s, 18 H, CH_3), 3.09, (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 3.13 (d, J= 13.0 Hz, 1 H, $ArCH_2Ar$), 3.22 (d, J= 13.0 Hz, 2 H, $ArCH_2Ar$), 3.82-3.89 (m, 2 H, OCH_2CH_2O), 3.89-3.97 (m, 2 H, OCH_2CH_2O), 4.06-4.12 (m, 2 H, OCH_2CH_2O), 4.20-4.32 (m, 7 H, $ArCH_2Ar$, OCH_2CO, OCH_2CH_2O), 5.03 (d, J= 15.5 Hz, 2 H, OCH_2CO), 5.05 (d, J= 12.5 Hz, 1 H, $ArCH_2Ar$), 6.69 (d, J= 2.5 Hz, 2 H, ArH), 6.76 (d, J= 2.5 Hz, 2 H, ArH), 6.82 (d, J= 2.5 Hz, 2 H, ArH), 6.95 (d, J= 2.5, 2 H, ArH), 7.48-7.56 (m, 6 H, ArH), 8.06-8.12 (m, 4 H, ArH), 9.75 (s, 2 H, NH); ^{13}C NMR ($CDCl_3$): δ 31.06, 31.43, 33.86, 33.92, 73.65, 74.56, 75.97, 124.54, 125.49, 126.05, 126.42, 126.69, 128.60, 129.00, 129.16, 132.15, 132.47, 132.81, 133.09, 134.09, 134.63, 138.37, 145.33, 146.25, 152.29, 152.77, 168.08.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(4-nitrobenzene)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (6). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3237 (N-H), 1722 (C=O), 1350 and 1161 (S=O), 1200 and 1124 (C-O); ^1H NMR ($CDCl_3$): δ 1.00 (s, 18 H, CH_3), 1.13 (s, 18 H, CH_3), 3.11, (d, J= 12.5 Hz, 1 H, $ArCH_2Ar$), 3.17 (d, J= 13.5 Hz, 1 H, $ArCH_2Ar$), 3.24 (d, J= 13.0 Hz, 2 H, $ArCH_2Ar$), 3.84-3.98 (m, 4 H, OCH_2CH_2O), 4.10-4.34 (m, 8 H, $ArCH_2Ar$, OCH_2CO, OCH_2CH_2O), 4.44 (d, J= 13.0 Hz, 1 H, $ArCH_2Ar$), 5.04 (d, J= 12.5 Hz, 1 H, $ArCH_2Ar$), 5.23 (d, J= 16.0 Hz, 2 H, OCH_2CO), 6.70 (d, J= 2.5 Hz, 2 H, ArH), 6.78 (d, J= 2.5 Hz, 2 H, ArH), 6.83 (d, J= 2.5 Hz, 2 H, ArH), 6.96 (d, J= 2.5, 2 H, ArH), 8.27-8.33 (m, 4 H, ArH), 8.34-8.40 (m, 4 H, ArH), 9.76 (s, 2 H, NH); ^{13}C NMR ($CDCl_3$): δ 31.06, 31.60, 33.88, 33.94, 53.42, 73.59, 74.36, 75.88, 124.16, 124.45, 124.49, 125.52, 126.21, 126.91, 127.88, 130.20, 132.10, 132.33, 132.90, 134.62, 143.63, 145.57, 146.54, 150.83, 152.42, 152.67, 168.43.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(trifluoromethane)-sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (7). IR (deposit from CH_2Cl_2 solution on a

NaCl plate) ν_{max}/cm^{-1} 3235 (N-H), 1751 (C=O), 1363 and 1154 (S=O), 1203 and 1131 (C-O); ^{1}H NMR ($CDCl_3$): δ 1.03 (s, 18 H, CH_3), 1.14 (s, 18 H, CH_3), 3.13, (d, J= 12.5 Hz, 1 H, $ArCH_2Ar$), 3.32 (d, J= 13.0 Hz, 2 H, $ArCH_2Ar$), 3.42 (d, J= 13.0 Hz, 1 H, $ArCH_2Ar$), 3.84-4.02 (m, 4 H, OCH_2CH_2O), 4.12-4.32 (m, 6 H, $ArCH_2Ar$, OCH_2CH_2O), 4.46-4.58 (m, 3 H, $ArCH_2Ar$, OCH_2CO), 5.04 (d, J= 11.5 Hz, 1 H, $ArCH_2Ar$), 5.29 (d, J= 15.5 Hz, 2 H, OCH_2CO), 6.74-6.92 (m, 6 H, ArH), 6.94-7.02 (m, 2 H, ArH), 9.54 (s, 2 H, NH); ^{13}C NMR ($CDCl_3$): δ 30.91, 30.98, 31.05, 31.23, 31.36, 31.53, 31.62, 33.93, 33.96, 73.61, 74.28, 75.99, 96.11, 120.43, 124.62, 125.74, 126.26, 126.92, 132.21, 132.83, 134.63, 145.61, 146.75, 152.22, 152.68, 167.44.

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(methane)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (9). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3258 (N-H), 1723 (C=O), 1348 and 1153 (S=O), 1207 and 1124 (C-O); ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 18 H, CH_3), 1.34 (s, 18 H, CH_3), 2.20 (t, J= 11.0 Hz, 2 H, OCH_2CH_2O), 3.05 (s, 6 H, SO_2CH_3), 3.16 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 3.36 (t, J= 10.0 Hz, 2 H, OCH_2CH_2O), 3.43-3.52 (m, 3 H, $ArCH_2Ar$, OCH_2CH_2O), 3.59 (d, J= 12.0 Hz, 2 H, OCH_2CH_2O), 3.90 (d, J= 17.5 Hz, 2 H, $ArCH_2Ar$), 4.03 (d, J= 17.5 Hz, 2 H, $ArCH_2Ar$), 4.15 (d, J= 15.5 Hz, 2 H, OCH_2CO), 4.27 (d, J= 15.5 Hz, 2 H, OCH_2CO), 4.34 (d, J= 13.0 Hz, 1 H, $ArCH_2Ar$), 4.43 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 7.00 (d, J= 2.0 Hz, 2 H, ArH), 7.10 (d, J= 2.0 Hz, 2 H, ArH), 7.26 (d, J= 2.5 Hz, 2 H, ArH), 7.46 (d, J= 2.5 Hz, 2 H, ArH), 8.61 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ 29.20, 30.08, 31.60, 34.21, 34.23, 38.88, 41.51, 71.93, 73.06, 74.94, 125.19, 125.53, 125.62, 126.09, 131.89, 131.93, 132.80, 134.93, 146.21, 146.40, 152.64, 152.71, 168.42.

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(benzene)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (10). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3250 (N-H), 1724 (C=O), 1335 and 1160 (S=O), 1204 and 1125 (C-O); ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 18 H, CH_3), 1.33 (s, 18 H, CH_3), 2.30 (t, J= 11.0, 2 H, OCH_2CH_2O), 3.17 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 3.34-3.46 (m, 3 H, OCH_2CH_2O, $ArCH_2Ar$), 3.53 (d, J= 10.0 Hz, 2 H, OCH_2CH_2O), 3.62 (d, J= 12.5 Hz, 2 H, OCH_2CH_2O), 3.69 (d, J= 15.5 Hz, 2 H, OCH_2CO), 3.79-3.97 (m, 5 H, OCH_2CH_2O, OCH_2CO, $ArCH_2Ar$), 4.05 (d, J= 17.0 Hz, 2 H, $ArCH_2Ar$), 4.49 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 7.00 (d, J= 2.0 Hz, 2 H, ArH), 7.13 (d, J= 2.0 Hz, 2 H, ArH), 7.32 (d, J= 2.0 Hz, 2 H, ArH), 7.40 (t, J= 8.0 Hz, 4 H, ArH), 7.46 (d, J= 2.5 Hz, 2 H, ArH), 7.49-7.57 (m, 2 H, ArH), 7.87-7.98 (m, 4 H, ArH), 8.61 (s, 2 H, NH); ^{13}C NMR

($CDCl_3$): δ 28.94, 29.57, 31.07, 31.43, 31.61, 34.19, 38.88, 72.51, 73.24, 74.83, 125.39, 125.61, 125.99, 126.10, 126.44, 128.66, 128.77, 129.16, 132.38, 132.56, 132.70, 132.82, 133.79, 135.17, 138.19, 146.14, 146.78, 152.52, 167.41.

1,2-Alternate 5,11,17,23-Tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(4-nitrobenzene)-sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (11). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3277 (N-H), 1729 (C=O), 1349 and 1162 (S=O), 1203 and 1125 (C-O); ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 18 H, CH_3), 1.34 (s, 18 H, CH_3), 2.31 (t, J= 11.0 Hz, 2 H, OCH_2CH_2O), 3.17 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 3.34-3.45 (m, 3 H, OCH_2CH_2O, $ArCH_2Ar$), 3.49-3.67 (m, 6 H, OCH_2CH_2O, OCH_2CO), 3.80-4.03 (m, 7 H, $ArCH_2CH_2Ar$, OCH_2CO), 4.50 (d, J= 12.5Hz, 1 H, $ArCH_2Ar$), 7.02 (d, J= 2.5 Hz, 2 H, ArH), 7.05 (d, J= 2.0 Hz, 2 H, ArH), 7.30 (d, J= 2.0 Hz, 2 H, ArH), 7.46 (d, J= 2.0 Hz, 2 H, ArH), 8.10-8.18 (m, 4 H, ArH), 8.25-8.30 (m, 4 H, ArH), 8.95 (s, 2 H, NH); ^{13}C NMR ($CDCl_3$): δ 28.77, 29.42, 31.35, 31.49, 31.59, 34.13, 34.23, 38.89, 72.05, 73.39, 74.69, 123.90, 124.43, 125.28, 125.84, 126.14, 126.18, 127.89, 130.28, 132.51, 132.66, 135.40, 143.40, 146.48, 146.79, 150.76, 152.16, 152.60, 167.65.

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(trifluoromethane)-sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (12). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3277 (N-H), 1758 (C=O), 1364 and 1170 (S=O), 1206 and 1133 (C-O); ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 18 H, CH_3), 1.34 (s, 18 H, CH_3), 2.19-2.36 (m, 2 H, OCH_2CH_2O), 3.17 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 3.35-3.47 (m, 3 H, OCH_2CH_2O, $ArCH_2Ar$), 3.47-3.56 (m, 2 H, OCH_2CH_2O), 3.61 (d, J= 12.0, 2 H, OCH_2CH_2O), 3.92 (s, 4 H, $ArCH_2Ar$), 3.98-4.18 (m, 2 H, OCH_2CO), 4.21-4.40 (m, 2 H, OCH_2CO), 4.47 (d, J= 12.0 Hz, 1 H, $ArCH_2Ar$), 4.54 (d, J= 12.5 Hz, 1 H, $ArCH_2Ar$), 6.97-7.12 (m, 4 H, ArH), 7.34 (s, 2 H, ArH), 7.46 (s, 2 H, ArH), 7.46 (d, J= 2.5 Hz, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 28.73, 29.57, 31.09, 31.29, 31.37, 31.60, 34.19, 34.23, 38.95, 71.46, 73.12, 74.78, 117.62, 120.18, 124.75, 125.84, 126.06, 126.40, 131.66, 132.12, 133.17, 135.12, 146.60, 146.93, 152.38, 167.01.