

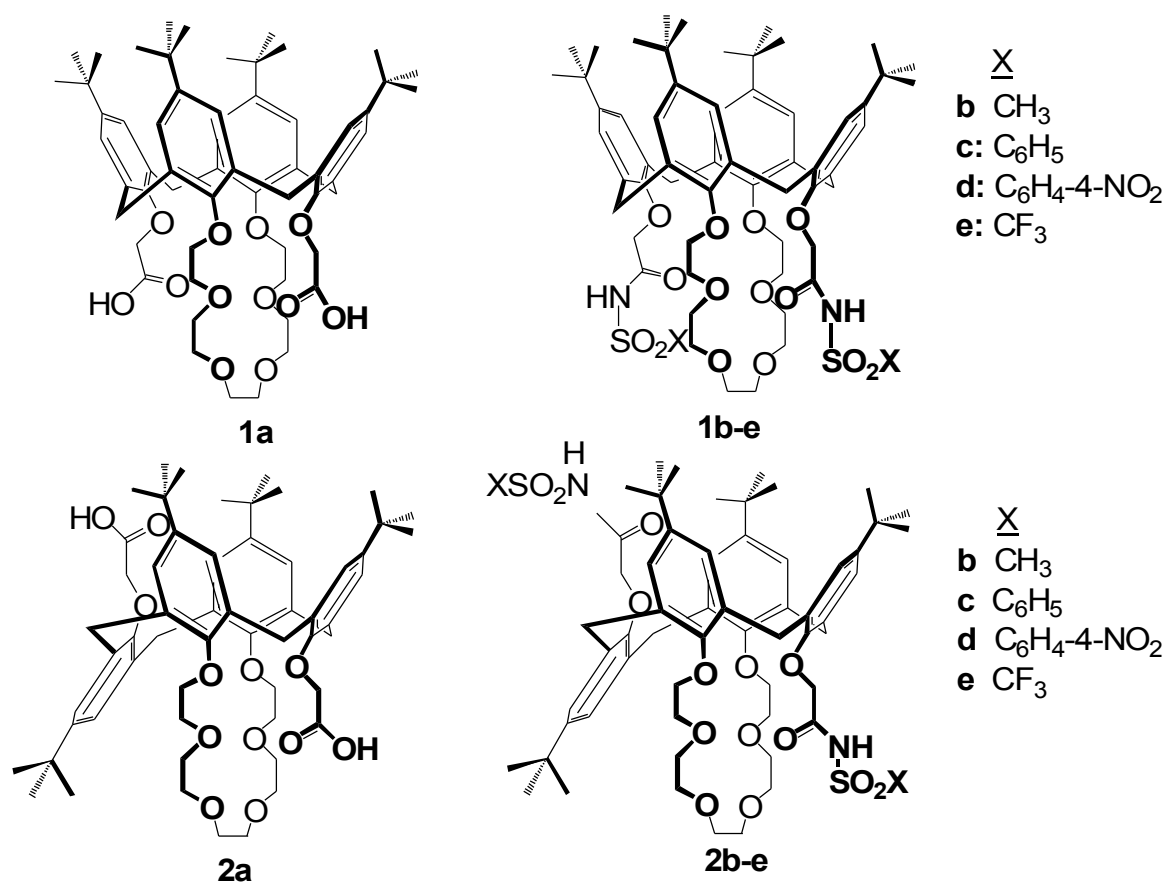
SUPPLEMENTARY INFORMATION

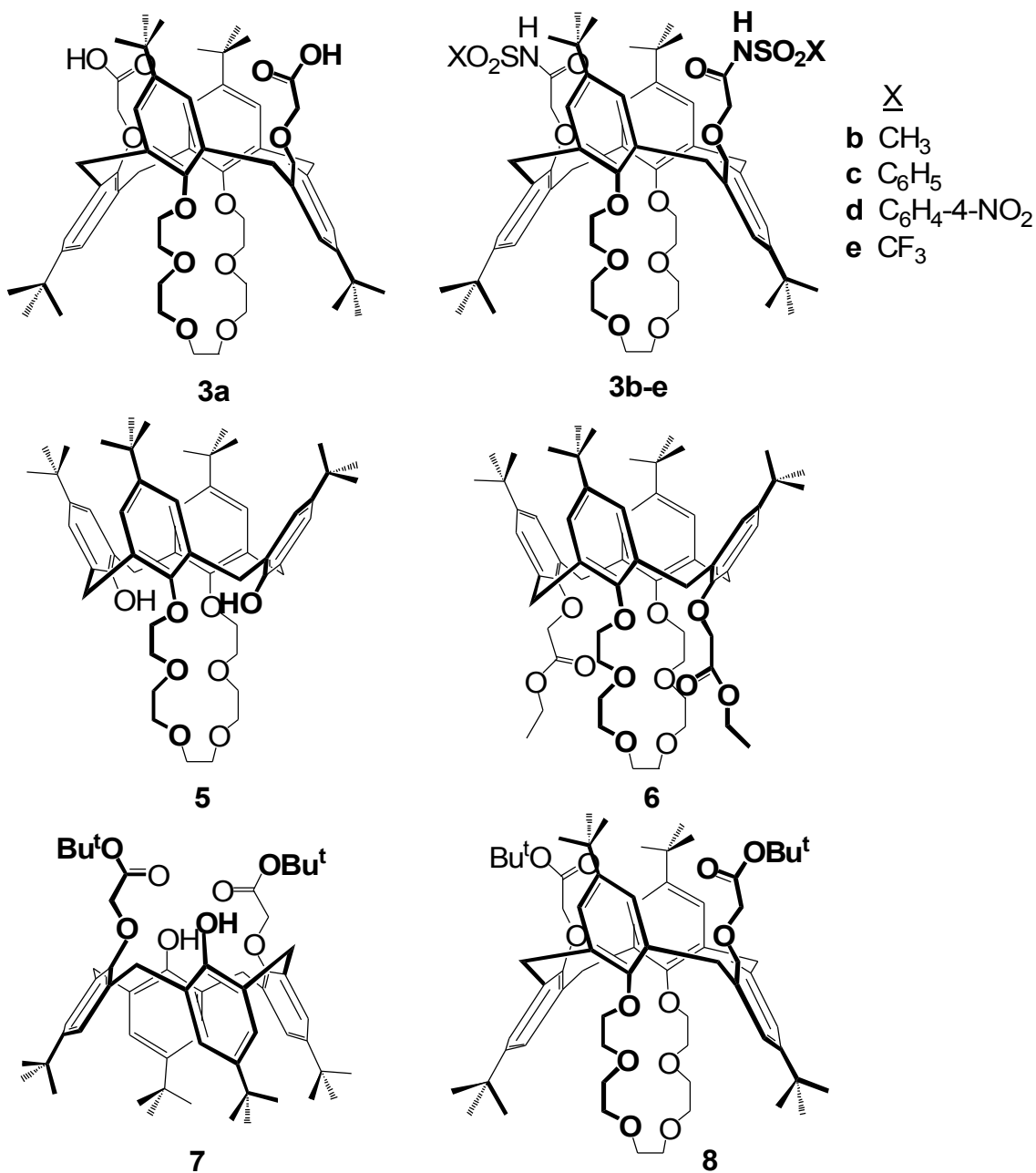
Proton Di-ionizable *p*-*tert*-Butylcalix[4]arene-crown-6 Compounds in Cone, Partial-Cone and 1,3-Alternate Conformations: Synthesis and Alkaline Earth Metal Cation Extraction

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IR, ^1H NMR, and ^{13}C NMR spectra for compounds **1a-e**, **2a-e**, **3a-e**, and **5-7** follow.





Cone **5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)calix[4]arene-crown-6 (1a).** $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3233 (COOH), 1756 (C=O). δ_{H} 10.94 (2 H, bs, CO₂H), 7.13 (4 H, s, ArH), 6.54 (4 H, s, ArH), 4.97 (4 H, s, OCH₂CO), 4.47 (4 H, d, J 12.9, ArCH₂Ar), 3.93 (4 H, m, OCH₂CH₂O), 3.87 (4 H, m, OCH₂CH₂O), 3.79 (8 H, s, OCH₂CH₂O), 3.75 (4 H, m, OCH₂CH₂O), 3.22 (4H, d, J 12.9, ArCH₂Ar), 1.34 (18 H, s, C(CH₃)₃), 0.83 (18 H, s, C(CH₃)₃). δ_{C} 171.11, 153.13, 151.20, 146.11, 145.38, 134.94, 131.96, 125.82, 125.09, 75.61, 71.74, 70.53, 70.51, 70.47, 69.93, 34.09, 33.63, 31.62, 31.29, 30.99.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(methanesulfonyl)carbamoyl]calix[4]arene-crown-6 (1b). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2800-3300 cm^{-1} (N-H); 1734, 1718 cm^{-1} (C=O). δ_{H} 10.57 (2 H, s, NH), 7.11 (4 H, s, ArH), 6.45 (4 H, s, ArH), 5.17 (4 H, s, OCH₂CO), 4.58 (4 H, *d*, *J* 12.9, ArCH₂Ar), 3.92 (8 H, *q*, OCH₂CH₂O), 3.85 (4 H, *d*, OCH₂CH₂O), 3.81 (8 H, s, OCH₂CH₂O), 3.23 (4 H, *d*, *J* 12.9, ArCH₂Ar), 3.18 (6 H, s, CH₃SO₂), 1.33 (18 H, s, C(CH₃)₃), 0.82 (18 H, s, C(CH₃)₃). δ_{C} 170.62, 152.37, 152.20, 145.59, 144.87, 135.31, 131.57, 125.77, 124.72, 73.96, 70.41, 70.23, 69.97, 69.28, 41.35, 34.02, 33.53, 32.09, 31.61, 31.01.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(benzenesulfonyl)carbamoyl]calix[4]arene-crown-6 (1c). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2800-3300 cm^{-1} (N-H); 1721 cm^{-1} (C=O). δ_{H} 10.80 (2 H, s, NH), 8.07 (4 H, *m*, PhH), 7.59 (2 H, *m*, PhH), 7.47 (4 H, *m*, PhH), 6.94 (4 H, s, ArH), 6.38 (4 H, s, ArH), 5.02 (4 H, s, OCH₂CO), 4.38 (4 H, *d*, *J* 12.9, ArCH₂Ar), 3.87 (4 H, *m*, OCH₂CH₂O), 3.81 (4 H, *m*, OCH₂CH₂O), 3.75 (8 H, s, OCH₂CH₂O), 3.67 (4 H, *m*, OCH₂CH₂O), 3.04 (4 H, *d*, *J* 12.9, ArCH₂Ar), 1.29 (18 H, s, C(CH₃)₃), 0.78 (18 H, s, C(CH₃)₃). δ_{C} 168.80, 152.39, 151.79, 145.16, 144.74, 139.32, 134.98, 133.44, 131.59, 128.62, 128.38, 125.65, 124.63, 73.93, 70.57, 70.48, 70.16, 69.92, 69.54, 33.94, 33.49, 31.99, 31.59, 30.98.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(*p*-nitrobenzenesulfonyl)carbamoyl]calix[4]arene-crown-6 (1d). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3104 cm^{-1} (N-H); 1737, 1731 cm^{-1} (C=O). δ_{H} 10.95 (2 H, s, NH), 8.27 (4 H, *m*, PhH), 8.21 (4 H, *m*, PhH), 6.95 (4 H, s, ArH), 6.37 (4 H, s, ArH), 5.07 (4 H, s, OCH₂CO), 4.38 (4 H, *d*, *J* 12.8, ArCH₂Ar), 3.90 (8 H, *q*, OCH₂CH₂O), 3.81 (12 H, *m*, OCH₂CH₂O), 3.08 (4 H, *d*, *J* 13.1, ArCH₂Ar), 1.26 (18 H, s, C(CH₃)₃), 0.77 (18 H, s, C(CH₃)₃). δ_{C} 169.08, 152.35, 151.73, 150.46, 145.72, 145.04, 144.53, 134.96, 131.29, 129.88, 125.73, 124.73, 123.82, 73.92, 70.46, 70.39, 70.22, 69.85, 69.40, 33.94, 33.53, 32.03, 31.54, 30.98.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(trifluoromethanesulfonyl)carbamoyl]calix[4]arene-crown-6 (1e). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2800-3200 cm^{-1} (N-H); 1770 cm^{-1} (C=O). δ_{H} 10.97 (2 H, s, NH), 7.09 (4 H, s, ArH), 6.45 (4 H, s, ArH), 5.23 (4 H, s, OCH₂CO), 4.51 (4 H, *d*, *J* 12.9, ArCH₂Ar), 3.84-3.93 (20 H, *m*, OCH₂CH₂O), 3.23 (4 H, *d*, *J* 12.9, ArCH₂Ar), 1.33 (18 H, s, C(CH₃)₃), 0.81 (18 H, s, C(CH₃)₃). δ_{C} 168.08, 152.46, 151.45, 145.82, 145.01, 135.07, 131.48, 125.85, 124.71, 73.33, 70.35, 70.08, 69.84, 68.55, 34.04, 33.57, 32.03, 31.59, 31.00.

Partial cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)calix[4]arene-crown-6 (2a). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2700-3300 (COOH), 1758 (C=O). δ_{H} 7.5-9.0 (2 H, *bs*, COOH), 7.23 (2 H, s, ArH), 7.14 (2 H, s, ArH), 6.98 (2 H, *d*, *J* 2.44, ArH), 6.77 (2 H, *d*, *J* 2.32, ArH), 4.87 (2 H, s, OCH₂CO), 4.57 (2 H, *d*, *J* 12.6, ArCH₂Ar), 4.21 (2 H, *m*, OCH₂CH₂O), 3.88 (2 H, *d*, *J* 15.5, ArCH₂Ar), 3.79 (2 H, s, OCH₂CO), 3.64-3.77 (8 H, *m*, OCH₂CH₂O, ArCH₂Ar), 3.54-3.64 (6 H, *m*, OCH₂CH₂O), 3.45-3.52 (2 H, *m*, OCH₂CH₂O), 3.34-3.45 (4 H, *m*, OCH₂CH₂O), 3.12 (2 H, *d*, *J* 12.6, ArCH₂Ar), 1.50 (9 H, s, C(CH₃)₃), 1.33 (9 H, s, C(CH₃)₃), 1.10 (18 H, s, C(CH₃)₃). δ_{C} 170.34, 168.47, 152.26, 150.89, 149.79, 148.03, 146.90, 146.48, 135.66, 134.66, 133.14, 132.39, 128.03, 127.25, 125.69, 124.34, 73.64, 71.06, 70.77, 70.73, 70.55, 69.36, 66.13, 38.56, 34.34, 34.12, 33.91, 31.58, 31.52, 30.91, 30.63.

Partial cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(methanesulfonyl)carbamoyl]calix[4]arene-crown-6 (2b). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2800-3200 cm^{-1} (N-H); 1721 cm^{-1} (C=O). δ_{H}

10.62 (1 H, s, NH), 8.46 (1 H, s, NH), 7.22 (2 H, s, ArH), 7.09 (2 H, d, ArH), 6.98 (2 H, s, ArH), 6.91 (2 H, d, ArH), 4.70 (2 H, s, OCH₂CO), 4.54 (2 H, d, *J* 12.4, ArCH₂Ar), 3.93 (2 H, m, OCH₂CH₂O), 3.64-3.89 (14 H, m, ArCH₂Ar, OCH₂CH₂O), 3.60 (2 H, m, OCH₂CH₂O), 3.48 (2 H, m, OCH₂CH₂O), 3.25 (2 H, d, *J* 12.6, ArCH₂Ar), 3.05 (3 H, s, CH₃SO₂), 3.02 (3 H, s, CH₃SO₂), 2.08 (2 H, s, OCH₂CO), 1.42 (9 H, s, C(CH₃)₃), 1.17 (27 H, d, C(CH₃)₃). δ_{C} 170.13, 166.54, 152.46, 151.98, 151.66, 146.45, 146.06, 145.25, 136.20, 133.41, 133.09, 131.97, 127.19, 126.26, 125.54, 125.49, 74.32, 71.98, 70.94, 70.43, 70.07, 70.04, 68.85, 41.24, 40.60, 38.15, 34.07, 33.92, 33.90, 31.65, 31.20, 31.16, 30.97.

Partial cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(benzenesulfonyl)carbamoyl]-calix[4]arene-crown-6 (2c). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2800-3300 cm^{-1} (N-H); 1742, 1723 cm^{-1} (C=O). δ_{H} 11.00 (1 H, s, NH), 8.52 (1 H, s, NH), 8.07 (2 H, m, PhH), 7.83 (2 H, m, PhH), 7.58 (1 H, m, PhH), 7.52 (1 H, m, PhH), 7.45 (2 H, m, PhH), 7.36 (2 H, m, PhH), 7.17 (2 H, s, ArH), 7.02 (2 H, d, ArH), 6.85 (2 H, d, ArH), 6.75 (2 H, s, ArH), 4.53 (2 H, s, OCH₂CO), 4.27 (2 H, d, *J* 12.4, ArCH₂Ar), 3.76-3.94 (8 H, m, OCH₂CH₂O, ArCH₂Ar), 3.70 (4 H, m, OCH₂CH₂O), 3.61 (4 H, m, OCH₂CH₂O), 3.55 (2 H, m, OCH₂CH₂O), 3.47 (2 H, m, OCH₂CH₂O), 3.32-3.42 (4 H, m, OCH₂CH₂O), 2.90 (2 H, d, *J* 12.4, ArCH₂Ar), 1.47 (2 H, s, OCH₂CO), 1.40 (9 H, s, C(CH₃)₃), 1.09 (18 H, s, C(CH₃)₃), 1.01 (9 H, s, C(CH₃)₃). δ_{C} 168.73, 164.44, 152.16, 152.01, 151.68, 146.62, 145.70, 145.40, 139.26, 138.46, 136.87, 133.65, 133.36, 133.29, 131.89, 131.80, 128.49, 128.47, 128.42, 128.33, 126.55, 126.13, 125.86, 125.52, 75.60, 71.64, 70.85, 70.32, 70.04, 69.64, 68.26, 38.16, 34.08, 33.82, 33.81, 31.61, 31.1, 30.98, 30.46.

Partial cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(*p*-nitrobenzenesulfonyl)carbamoyl]calix[4]arene-crown-6 (2d). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2800-3300 cm^{-1} (N-H); 1743, 1727 cm^{-1} (C=O). δ_{H} 11.26 (1 H, s, NH), 8.61 (1 H, s, NH), 8.25-8.33 (4 H, m, PhH), 8.18-8.25 (2 H, m, PhH), 8.00-8.06 (2 H, m, PhH), 7.19 (2 H, s, ArH), 7.04 (2 H, d, ArH), 6.84 (2 H, d, ArH), 6.76 (2 H, s, ArH), 4.56 (2 H, s, OCH₂CO), 4.29 (2 H, d, *J* 12.3, ArCH₂Ar), 3.77-3.92 (8 H, m, ArCH₂Ar, OCH₂CH₂O), 3.74 (4 H, m, OCH₂CH₂O), 3.59 (6 H, m, OCH₂CH₂O), 3.49 (2 H, m, OCH₂CH₂O), 3.30-3.42 (4 H, m, OCH₂CH₂O), 2.94 (2 H, d, *J* 12.4, ArCH₂Ar), 1.44 (2 H, s, OCH₂CO), 1.41 (9 H, s, C(CH₃)₃), 1.07 (18 H, s, C(CH₃)₃), 1.01 (9 H, s, C(CH₃)₃). δ_{C} 169.12, 164.84, 151.95, 151.92, 151.70, 146.93, 146.07, 145.81, 144.77, 143.86, 137.02, 133.78, 131.92, 131.86, 130.11, 129.97, 126.70, 126.25, 125.82, 125.62, 123.67, 123.61, 75.51, 71.62, 70.87, 70.33, 70.12, 69.67, 68.16, 38.28, 34.19, 33.89, 33.87, 31.67, 31.07, 30.98, 30.56.

Partial cone 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(trifluoromethanesulfonyl)carbamoyl]calix[4]arene-crown-6 (2e). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2800-3200 cm^{-1} (N-H); 1773, 1750 cm^{-1} (C=O). δ_{H} 11.47 (1 H, bs, NH), 8.64 (1 H, s, NH), 7.24 (2 H, d, ArH), 7.22 (2 H, s, ArH), 6.96 (2 H, s, ArH), 6.92 (2 H, d, ArH), 4.76 (2 H, s, OCH₂CO), 4.52 (2 H, d, *J* 12.4, ArCH₂Ar), 3.81-4.00 (8 H, m, ArCH₂Ar, OCH₂CH₂O), 3.71-3.81 (4 H, m, OCH₂CH₂O), 3.42-3.71 (12 H, m, OCH₂CH₂O), 3.28 (2 H, d, *J* 12.3, ArCH₂Ar), 1.60 (2 H, s, OCH₂CO), 1.41 (9 H, s, C(CH₃)₃), 1.22 (18 H, s, C(CH₃)₃), 1.12 (9 H, s, C(CH₃)₃). δ_{C} 168.71, 162.90, 151.91, 151.60, 151.45, 147.47, 146.68, 146.21, 137.50, 134.09, 131.96, 131.79, 126.81, 126.59, 125.93, 125.68, 76.12, 71.51, 71.01, 70.58, 70.03, 69.58, 68.28, 38.46, 34.23, 34.06, 34.02, 31.65, 31.15, 31.03, 30.59.

1,3-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)calix[4]arene-crown-6 (3a). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3416 (CO₂H), 1760 (C=O). δ_{H} 7.67 (2 H, bs, COOH),

7.10 (4 H, s, ArH), 7.03 (4 H, s, ArH), 4.07 (4 H, s, OCH₂CO), 3.96 (4 H, d, *J* 16.9, ArCH₂Ar), 3.90 (4 H, d, *J* 16.9, ArCH₂Ar), 3.55 (4 H, s, OCH₂CH₂O), 3.50 (8 H, s, OCH₂CH₂O), 3.34 (4 H, t, OCH₂CH₂O), 3.03 (4 H, t, OCH₂CH₂O), 1.35 (18 H, s, C(CH₃)₃), 1.23 (18 H, s, C(CH₃)₃). δ_{C} 169.27, 169.24, 153.63, 151.98, 146.60, 146.31, 146.30, 132.75, 132.42, 126.20, 126.09, 71.19, 71.09, 70.98, 70.03, 68.41, 67.26, 38.61, 34.10, 33.86, 31.54, 31.16.

1,3-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(methanesulfonyl)carbamoyl]calix[4]arene-crown-6 (3b). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3200 cm⁻¹ (N-H); 1706 cm⁻¹ (C=O). δ_{H} 8.81 (2 H, s, NH), 7.12 (4 H, s, ArH), 7.11 (4 H, s, ArH), 3.93-4.00 (8 H, t, ArCH₂Ar), 3.54 (4 H, s, OCH₂CO), 3.50-3.54 (12 H, m, OCH₂CH₂O), 3.43 (4 H, m, OCH₂CH₂O), 3.16 (6 H, s, CH₃SO₂), 2.69 (4 H, m, OCH₂CH₂O), 1.35 (18 H, s, C(CH₃)₃), 1.27 (18 H, s, C(CH₃)₃). δ_{C} 169.64, 154.08, 153.39, 146.70, 146.19, 132.92, 132.26, 126.77, 126.54, 71.45, 70.66, 70.64, 70.25, 69.31, 68.55, 41.25, 38.72, 34.11, 34.06, 31.46, 31.22.

1,3-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(benzenesulfonyl)carbamoyl]calix[4]arene-crown-6 (3c). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3345 cm⁻¹ (N-H); 1726, 1711 cm⁻¹ (C=O). δ_{H} 9.20 (2 H, s, NH), 8.01 (4 H, m, PhH), 7.60 (2 H, m, PhH), 7.49 (4 H, m, PhH), 7.08 (4 H, s, ArH), 7.03 (4 H, s, ArH), 3.92 (8 H, t, ArCH₂Ar), 3.57 (4 H, s, OCH₂CH₂O), 3.52 (8 H, m, OCH₂CH₂O), 3.42 (4 H, m, OCH₂CH₂O), 3.16 (4 H, s, OCH₂CO), 2.69 (4 H, t, OCH₂CH₂O), 1.33 (18 H, s, C(CH₃)₃), 1.11 (18 H, s, C(CH₃)₃). δ_{C} 168.62, 153.91, 153.28, 146.88, 146.02, 138.61, 133.77, 133.09, 132.47, 128.94, 128.33, 126.82, 126.68, 71.47, 71.08, 70.72, 70.29, 69.16, 68.64, 38.83, 34.06, 33.94, 31.48, 31.07.

1,3-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(*p*-nitrobenzenesulfonyl)carbamoyl]calix[4]arene-crown-6 (3d). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2800-3300 cm⁻¹ (N-H); 1727, 1714 cm⁻¹ (C=O). δ_{H} 9.43 (2 H, s, NH), 8.34 (4 H, m, PhH), 8.23 (4 H, m, PhH), 7.11 (4 H, s, ArH), 7.02 (4 H, s, ArH), 3.88 (4 H, *d*, *J* 17.0, ArCH₂Ar), 3.94 (4 H, *d*, *J* 17.0, ArCH₂Ar), 3.57 (4 H, s, OCH₂CH₂O), 3.52 (8 H, m, OCH₂CH₂O), 3.42 (4 H, m, OCH₂CH₂O), 3.21 (4 H, bs, OCH₂CO), 2.70 (4 H, m, OCH₂CH₂O), 1.34 (18 H, s, C(CH₃)₃), 1.13 (18 H, s, C(CH₃)₃). δ_{C} 169.10, 153.97, 153.31, 150.76, 146.92, 146.51, 143.97, 133.24, 132.53, 129.77, 126.87, 126.73, 124.27, 71.50, 71.19, 70.73, 70.35, 69.43, 68.53, 38.70, 34.11, 33.98, 31.46, 31.01.

1,3-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[*N*-(trifluoromethanesulfonyl)carbamoyl]calix[4]arene-crown-6 (3e). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2800-3300 cm⁻¹ (N-H); 1760 cm⁻¹ (C=O). δ_{H} 9.35 (2 H, bs, NH), 7.12, 7.10 (8 H, s, ArH), 3.98 (8 H, q, ArCH₂Ar), 3.58 (4 H, s, OCH₂CH₂O), 3.53 (8 H, m, OCH₂CH₂O), 3.45 (8 H, m, OCH₂CH₂O, OCH₂CO), 2.74 (4 H, m, OCH₂CH₂O), 1.35 (18 H, s, C(CH₃)₃), 1.25 (18 H, s, C(CH₃)₃). δ_{C} 167.54, 153.99, 152.75, 147.07, 146.53, 133.16, 132.59, 126.83, 71.46, 70.76, 70.38, 69.12, 68.72, 38.84, 34.11, 33.99, 31.47, 31.02.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-calix[4]arene-crown-6 (5). $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3405 (OH). δ_{H} 7.06 (4 H, s, ArH), 6.98 (2 H, s, OH), 6.73 (4 H, s, ArH), 4.35 (2 H, *d*, *J* 13.1, ArCH₂Ar), 4.10 (4 H, m, OCH₂CH₂O), 4.00 (4 H, m, OCH₂CH₂O), 3.93 (4 H, m, OCH₂CH₂O), 3.84 (4 H, m, OCH₂CH₂O), 3.76 (4 H, s, OCH₂CH₂O), 3.28 (2 H, *d*, *J* 13.1, ArCH₂Ar), 1.31 (18 H, s, C(CH₃)₃), 0.91 (18 H, s, C(CH₃)₃). δ_{C} 150.65, 149.92, 146.73, 141.19,

132.36, 127.79, 125.40, 124.96, 76.26, 71.67, 71.05, 70.10, 69.93, 33.82, 33.79, 31.70, 31.28, 30.95.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[(ethoxycarbonylmethoxy)calix[4]-arene-crown-6 (6). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1760, 1735 cm^{-1} (C=O). δ_{H} 7.01 (4 H, s, ArH), 6.55 (4 H, s, ArH), 4.59 (4 H, s, OCH₂CO), 4.52 (4 H, d, *J* 12.6, ArCH₂Ar), 4.24 (8 H, m, OCH₂(CH₃), OCH₂CH₂O), 4.15 (4 H, t, OCH₂CH₂O), 3.74-3.82 (8 H, m, OCH₂CH₂O), 3.73 (4 H, s, OCH₂CH₂O), 3.16 (4 H, d, *J* 12.8, ArCH₂Ar), 1.27-1.32 (6 H, m, (OCH₂)CH₃), 1.25 (18 H, s, C(CH₃)₃), 0.89 (18 H, s, C(CH₃)₃). δ_{C} 169.86, 167.23, 154.28, 152.18, 144.98, 144.78, 134.87, 132.23, 125.44, 124.88, 72.72, 71.93, 70.98, 70.75, 70.52, 69.93, 62.32, 60.65, 33.98, 33.64, 31.61, 31.26, 31.14, 25.93, 14.23, 13.99.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-bis(*p*-*tert*-butoxycarbonylmethoxy)calix[4]-arene (7). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3438 cm^{-1} (OH), 1754, 1732 cm^{-1} (C=O). δ_{H} 7.14 (2 H, s, OH), 7.02 (4 H, s, ArH), 6.79 (4 H, s, ArH), 4.58 (4 H, s, OCH₂CO), 4.44 (4 H, d, *J* 13.1, ArCH₂Ar), 3.29 (4 H, d, *J* 13.2, ArCH₂Ar), 1.54 (18 H, s, C(CH₃)₃), 1.27 (18 H, s, OC(CH₃)₃), 0.91 (18 H, s, C(CH₃)₃). δ_{C} 168.23, 150.81, 150.47, 146.85, 141.18, 132.39, 127.75, 125.61, 124.99, 82.20, 73.08, 33.87, 33.77, 31.80, 31.66, 31.00, 28.14.

1,3-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(*tert*-butoxycarbonyl-methoxy)calix[4]arene-crown-6 (8). $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1756, 1727 cm^{-1} (C=O); δ_{H} 7.14 (4 H, s, ArH), 7.04 (4 H, s, ArH), 4.08 (4 H, d, *J* 15.9, ArCH₂Ar), 3.84 (4 H, s, OCH₂CO), 3.83 (4 H, d, *J* 16.0, ArCH₂Ar), 3.53-3.60 (12 H, m, OCH₂CH₂O), 3.02 (4 H, t, OCH₂CH₂O), 2.89 (4 H, t, OCH₂CH₂O), 1.36 (18 H, s, C(CH₃)₃), 1.33 (18 H, s, C(CH₃)₃), 1.24 (18 H, s, C(CH₃)₃); δ_{C} 169.23, 154.42, 153.76, 144.24, 143.80, 133.23, 133.16, 127.30, 126.35, 80.69, 77.26, 77.00, 76.75, 71.48, 71.11, 70.80, 70.76, 69.00, 68.95, 38.62, 33.90, 33.76, 31.55, 31.38, 27.97.