Selective Mono-O-acylation of the C_{2V}-Symmetrical Calix[4]arenediols with Acylisocyanates

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5,11,17,23-Tetrakis-*tert*-butyl-25,27-dimethoxy-26-trifluoroacetylaminocarbonyl-28-hydroxycalix[4]arene (4a). Yield 75 %. M. p. 130-134 °C. ^{1}H NMR (300 MHz, *$CDCl_3$*), δ, ppm: 0.76 (s, 18H), 1.28 (s, 9H), 1.30 (s, 9H), 3.31 (d, *J* = 13.5 Hz, 2H), 3.33 (d, *J* = 13.2 Hz, 2H), 3.74 (s, 6H), 4.14 (d, *J* =13.5 Hz, 2H), 4.17 (d, *J* = 13.2 Hz, 2H), 6.51 (d, $J^4_{H\text{-}H}$ = 4.3 Hz, 2H), 6.55 (d, *J* = 4.3 Hz, 2H), 6.85 (s, 1H), 7.05 (s, 2H), 7.17 (s, 2H), 10.76 (s, 1H). ^{19}F NMR (*CH_2Cl_2*), δ, ppm.: -76.9. IR (CCl_4), cm^{-1}: 1745 (CF_3C=O), 1815 (O-C=O), 3245, 3410 (NH), 3300 (ass OH). Calculated for $C_{49}H_{60}F_3NO_6$: C 72.12, H 7.41, found: C 72.09, H 7.42.

5,11,17,23-Tetrakis-*tert*-butyl-25,27-dimethoxy-26-benzoylaminocarbonyl-28-hydroxycalix[4]arene (4c). Yield 50%. M. p. 195 °C (decomp.). ^{1}H NMR (300 MHz, *DMSO-d_6*), δ, ppm: 0.80 (s, 18H), 1.21 (s, 9H), 1.26 (s, 9H), 3.37 (d, *J* = 12.6 Hz, 2H), 3.38 (d, *J* = 13.5 H, 2H), 3.55 (s, 6H), 3.97 (d, *J* = 12.6 Hz, 2H), 4.06 (d, *J* = 13.5 Hz, 2H), 6.68 (d, *J* = 4.2 Hz, 2H), 6.70 (d, *J* = 4.2 Hz, 2H), 7.13 (s, 2H), 7.35 (s, 2H), 7.49 (s, 1H), 7.62 (m, 3H), 8.32 (d, 2H), 10.40 (s, 1H). IR (CCl_4), cm^{-1}: 1701 (Ph-C=O), 1794 (O-C=O), 3365 (NH and OH). Calculated for $C_{54}H_{65}NO_6$: C 78.70, H 7.95, N 1.70, found: C 79.09, H 7.72, N 2.20.

5,11,17,23-Tetrakis-*tert*-butyl-25,27-dimethoxy-26-(*p*-tolyl)sulfonylaminocarbonyl-28-hydroxycalix[4]arene (4d). Yield 44%. M. p. 251-254 °C. ^{1}H NMR (300 MHz, *CDCl$_3$*), δ, ppm: 0.80 (s, 18H, t-Bu), 1.31 (s, 9H), 1.37 (s, 9H), 2.45 (s, 3H), 3.24 (d, *J* = 12.9 Hz, 2H), 3.33 (d, *J* = 13.4 Hz, 2H), 3.80 (s, 6H), 4.07 (d, *J* = 12.9 Hz, 2H), 4.27 (d, *J* =13.4 Hz, 2H), 6.52 (d, *J* = 1.7 Hz, 2H), 6.60 (d, *J* = 1.7 Hz, 2H), 7.09 (s, 2H), 7.15 (s, 1H), 7.16 (s, 2H). 7.37 and 8.15 (d, *J* = 8.1 Hz, 2H each), 9.93 (s, 1H). IR (CCl_4), cm^{-1}: 1765 (O-C=O), 3240 (NH), 3300 (OH). Calculated for $C_{54}H_{67}NO_7S$: C 74.19, H 7.73, N 1.60, found: C 74.62, H 8.03, N 1.98.

5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxy-26-trifluoroacetylaminocarbonyloxy-28-hydroxycalix[4]arene (4e). To a solution of calixarene **3b** (0.4 g, 0.546 mmol) in 5 ml of dried benzene was added drop wise a solution of trifluoroacetylisocyanate (0.45 g, 3.276 mmol) in 3 ml of benzene and 2 drops of Et_3N. The reaction mixture was stirred overnight at room temperature. Then the solution was evaporated *in vacuo*. The product was crystallized from acetonitrile-methanol mixture. The compound **4e** (colorless crystals) was filtered off and dried *in vacuo*. Yield 55%. ^{1}H NMR (*CDCl$_3$*), δ, ppm.: 0.81 (s, 18H), 0.95 (t, J = 7.8 Hz, 6H), 1.35 (s, 9H), 1.36 (s, 9H), 1.78 (m, 4H), 3.297 and 3.34 (2d, *J* =13.4 Hz, 2H each), 3.78 (t, J = 7.8 Hz, 4H) 4.14 and 4.24 (2d, *J* = 13.4 Hz, 2H each), 6.53 and 6.55 (2bs, 2H each), 6.88 (s, 1H), 7.12 (bs, 2H), 7.23 (bs, 2H), 10.50 (bs, 1H).

25,27-dimethoxy-26-trifluoroacetylaminocarbonyloxy-28-hydroxycalix[4]arene 4f. To a solution of calixarene **3c** (0.120 g, 0.265 mmol) in 5 ml of dried dichloromethane was added drop wise a solution of trifluoroacetylisocyanate (0.29 g, 0.212 mmol) in 3 ml of CH_2Cl_2 and 2 drops of Et_3N. The reaction mixture was stirred overnight at room temperature. Then the solution was evaporated *in vacuo*. The obtained residue was dissolved in minimal volume of

dichloromethane on precipitated with diethyl ether. The compound **4f** (colorless crystals) was filtered off and dried *in vacuo*. Yield 50%. M.p. decomp > 120°. ^{1}H NMR (*$CDCl_3$*), δ, ppm.: 3.40 and 3.41 (2d, *J* =13.4 Hz, 2H each), 3.81 (s, 6H), 4.23 (d, *J* =13.7 Hz, 4H), 6.55-6.80 (m, 7H) , 7.01 (s, 1H), 7.11 (bs, 1H), 7.13 (bs, 1H), 7.24 (bs, 1H), 7.26 (bs, 1H), 7.35 (bs, 1H) 10.94 (bs, 1H). ^{19}F NMR (*$CDCl_3$*), δ, ppm.: -77.56.