Aroylation and Acylation of *p*-Cyanomethylcalix[4]arenes[1,2]

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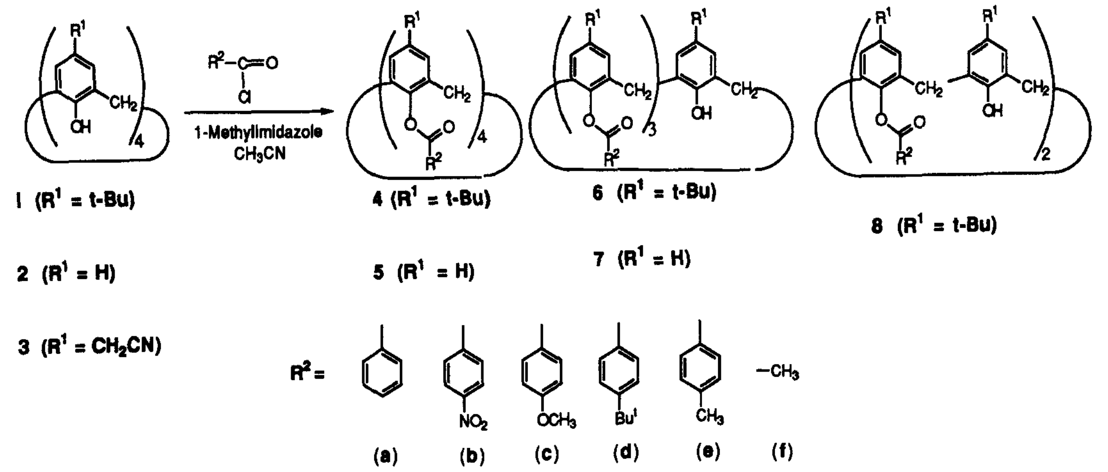
Calix[4]arenes carrying H, *tert*-butyl, and cyanomethyl groups in the *p*-positions are converted into tetraesters by aroylation or acylation in the presence of 1-methylimidazole or sodium hydride. Aroylation or acylation of *p*-cyanomethylcalix[4]arene in the presence of aluminum chloride yield the 1,3-diesters which, upon further aroylation or acylation, provide a variety of tetraesters of mixed functionality.

The calix[4]arenes are basket-shaped molecules that are attractive as metal-ion-complexing agents and as molecule-binders for use as enzyme mimics.[3] In an earlier paper, as part of a series[4] dealing with these compounds, we reported that the aroylation of *p*-*tert*-butylcalix[4]arene (**1**) yields tetraesters either in the cone or 1,3-alternate conformation, depending *inter alia* on the *p*-substituent of the aroylating agent. The present paper expands upon that investigation and includes the aroylation and acylation of *p*-cyanomethylcalix[4]arene[5] (**3**) as part of a program directed to the construction of calixarenes containing mixed functionalities.

The results of the 1-methylimidazole-induced aroylation and acylation of *p*-*tert*-butylcalix[4]arene (**1**) and *p*-H-calix[4]arene (**2**) to yield the tetraesters **4** and **5**, triesters **6** and **7**, or diesters **8** (Scheme 1) are shown in Table 1. Comparison with the NaH-induced aroylations[3] reveal both similarities and differences. In the NaH-induced reactions of **1**, benzoyl chloride and *p*-methoxybenzoyl chloride yield **4a** and **4c** predominately in the cone conformation, whereas in the 1-methylimidazole-induced reaction the cone conformer is formed in only 30 and 45% yields, respectively. In the NaH-induced benzoylation of **2** the 1,3-alternate conformer of **4a** is the sole product, whereas in the 1-methylimidazole-induced reaction the major conformer is the partial cone. In most other instances there is a generally greater similarity in product distribution for the two methods of aroylation.

The compounds of primary interest in the present work are those carrying a cyanomethyl moiety in the *p*-posi-



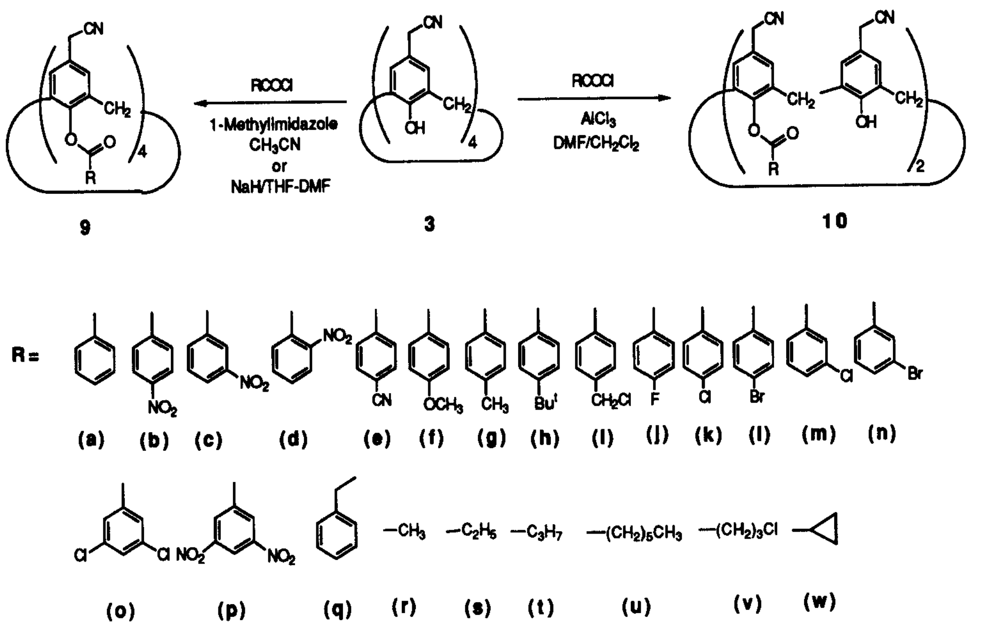
Scheme 1. Aroylation and acylation of *p*-*tert*-butylcalix[4]arene (**1**) and *p*-H-calix[4]arene (**2**)

Table 1. 1-Methylimidazole-induced Reactions of *p*-*tert*-Butylcalix[4]arene (**1**) and *p*-H-Calix[4]arene (**2**) with Aroyl and Acyl Chlorides, R^2COCl

Substrate	R^2 (equiv)	1-Methylimidazole (equiv)	Product Distribution[a] Compound (conformation,[b] % yield)
1	Ph (10)	15	**4** (cone, 30), **4** (partial cone, 20), **6** (cone, 30), **8** (cone, 10)
1	4-$NO_2C_6H_4$ (10)	15	**4** (cone, 80), **6** (cone, 15), **8** (cone, 15)
1	4-$MeOC_6H_4$ (10)	15	**4** (cone, 45), **4** (partial cone, 40), **6** (cone, 8), **8** (cone, 2)
1	4-*t*-BuC_6H_4 (10)	20	**4** (cone, 80), **4** (partial cone, 10), **6** (cone, 5)
1	4-MeC_6H_4 (10)	20	**4** (cone, 70), **4** (partial cone, 5), **6** (cone, 10), **8** (cone, 5)
1	Me (10)	15	**4** (partial cone, 80), **4** (1,3-alternate, 15)
2	Ph (8)	15	**5** (1,3-alternate, 20), **5** (partial cone, 70), **7** (cone, 5)
2	4-$NO_2C_6H_4$ (10)	15	**5** (cone, 80), **7** (cone, 10)
2	4-$MeOC_6H_4$ (10)	15	**5** (1,3-alternate, 80), **5** (partial cone, 10), **7** (cone, 5)
2	4-*t*-BuC_6H_4 (10)	20	**5** (1,3-alternate, 65), **5** (partial cone, 25), **7** (cone, 5)
2	Me (15)	15	**5** (1,3-alternate, 30), **5** (partial cone, 60)

[a] The product distribution was determined from the ^1H NMR spectrum of the crude reaction mixture.

[b] The conformations of the compounds were assigned on the basis of the ^1H and ^{13}C NMR spectra and confirmed by TLC comparison with samples obtained from previously reported reactions.



Scheme 2. Aroylation and acylation of *p*-cyanomethylcalix[4]arene (3).

tion; the cyano group having the potential for conversion into amino, amido, or carboxyl groups. 1-Methylimidazole or NaH-induced aroylation and acylation of cyanomethylcalix[4]arene (**3**) with the various reagents shown in Scheme 2 gave, in all but one instance, high yields of the tetraesters **9** in the 1,3-alternate conformation, the data for which are shown in Table 2. Aroylation with 3,5-dinitrobenzoyl chloride is the sole exception, the product in this case being a mixture of the 1,3-alternate conformers (52 %) and the partial cone conformer. In contrast to **1** and **2**, which produce tetraesters in the cone, partial cone, or 1,3-alternate conformation in varying proportions depending on the aroylating agent, **3** favors the 1,3-alternate conformer of the tetraester in virtually all cases. The reactions of *p*-chloromethylbenzoyl chloride and γ-chlorobutanoyl chloride with **3** to produce **9i** and **9v** represent a potentially useful way for introducing other functional groups via the chloromethyl moiety. The reaction succeeds, however, only when induced by the weak base 1-methylimidazole. When $AlCl_3$ was employed as the catalyst, Friedel–Crafts reactions were promoted, and when the strong base NaH was used alkylation at the carbons α to the CN groups occurred.[6]

The outcome of aroylation and acylation changes when $AlCl_3$ is used to induce the reaction. The products in these cases are 1,3-diestes (probably in a flattened cone conformation), the data for which are shown in Table 3. It should be noted that this method works best when the solvent (typically CH_2Cl_2) contains some DMF (typically 10 %); it is reported that without DMF only intractable mixtures are obtained from **1**[7] and tetraesters from *p*-allylcalix[4]arene.[4] The 1,3-diesters **10** produced in the $AlCl_3$-induced reactions provide the starting materials

Table 2. Physical and Spectroscopic Data of the Tetraesters **9** (1,3-Alternate Conformation) from the 1-Methylimidazole and Sodium Hydride-Induced Reactions of *p*-Cyanomethylcalix[4]arene (**3**) with Aroyl and Acyl Chlorides

Compound (% yields)[a]	mp (°C)	^1H NMR (300 MHz) δ, *J* (Hz)	^{13}C NMR (300 MHz) δ
9a (88, 84)	405–407	($CDCl_3$): 7.82 (t, 4H, *J* = 7.08 and 7.47, ArH), 7.74 (d, 8H, *J* = 7.92, ArH), 7.63 (t, 8H, *J* = 7.92 and 7.41, ArH), 6.68 (s, 8H, ArH), 3.53 (s, 8H, $ArCH_2Ar$), 3.06 (s, 8H, CH_2CN)	($CDCl_3$): 162.75 (C=O), 147.04 (C–O), 133.57, 133.44, 129.48, 129.19, 127.90, 127.53, 125.15 (Ar), 115.46 (CH_2CN), 35.74 ($ArCH_2Ar$), 21.39 (CH_2CN)
9b (82, 77)	> 450 (turns brown)	($DMSO\text{-}d_6$): 8.56 (d, 8H, *J* = 8.61, ArH), 7.86 (d, 8H, *J* = 8.19, ArH), 6.87 (s, 8H, ArH), 3.68 (s, 8H, $ArCH_2Ar$), 3.38 (s, 8H, CH_2CN)	($DMSO\text{-}d_6$): 162.23 (C=O), 151.02 (CNO_2), 147.19 (C–O), 134.02, 133.45, 130.82, 129.84, 127.42, 123.98 (Ar), 117.92 (CH_2CN), 35.41 ($ArCH_2Ar$) 21.68 (CH_2CN)
9c (85, 81)	> 450 (turns brown)	($DMSO\text{-}d_6$): 8.76 (s, 4H, ArH), 8.75 (d, 4H, *J* = 8.07, ArH), 8.17 (t, 4H, *J* = 7.04, ArH), 7.69 (d, 4H, *J* = 7.62, ArH), 6.86 (s, 8H, ArH), 3.59 (s, 8H, $ArCH_2Ar$), 3.43 (s, 8H, CH_2CN)	($DMSO\text{-}d_6$): 162.15 (C=O), 148.36 (CNO_2), 147.25 (C–O), 134.29, 134.02, 130.69, 129.92, 129.87, 129.01, 126.90, 125.33 (Ar), 117.33 (CH_2CN), 35.04 ($ArCH_2Ar$), 21.60 (CH_2CN)
9d (80, 73)	262–264	($DMSO\text{-}d_6$): 8.19 (d, 4H, *J* = 7.95, ArH), 8.10 (t, 4H, *J* = 7.53 and 8.01, ArH), 7.91 (t, 4H, *J* = 7.65 and 7.53, ArH), 7.78 (d, 4H, *J* = 7.50, ArH), 7.09 (s, 8H, ArH), 3.79 (s, 8H, $ArCH_2Ar$), 3.36 (s, 8H, CH_2CN)	($DMSO\text{-}d_6$): 160.94 (C=O), 150.49 (CNO_2), 146.96 (C–O), 135.10, 134.00, 132.17, 129.85, 128.94, 127.87, 125.13, 122.57 (Ar), 117.63 (CH_2CN), 35.07 ($ArCH_2Ar$), 21.27 (CH_2CN)

Table 2. (continued)

Compound (% yields)[a]	mp (°C)	^{1}H NMR (300 MHz) δ, J (Hz)	^{13}C NMR (300 MHz) δ
9f[b] (93, 80)	350–354	($CDCl_3$): 7.75 (d, 8H, J = 8.46, ArH), 7.16 (d, 8H, J = 8.16, ArH), 6.74 (s, 8H, ArH), 4.04 (s, 12H, $ArOCH_3$), 3.60 (s, 8H, $ArCH_2Ar$), 3.22 (s, 8H, CH_2CN)	($CDCl_3$): 164.52 (C=O), 163.56 ($COCH_3$), 148.16 (C–O), 134.57, 132.68, 130.15, 125.91, 120.61, 114.24 (Ar), 116.75 (CH_2CN), 55.90 (OCH_3), 36.78 ($ArCH_2Ar$), 22.64 (CH_2CN)
9g[c] (92, 79)	425–427	(DMSO-d_6): 7.58 (s, 16H, ArH), 6.71 (s, 8H, ArH), 3.52 (s, 8H, $ArCH_2Ar$), 3.31 (s, 8H, CH_2CN), 2.63 (s, 12H, $ArCH_3$)	(DMSO-d_6): 163.56 (C=O), 147.29 (C–O), 145.11 (CCH_3), 133.74, 129.97, 129.82, 129.53, 126.29, 125.43 (Ar), 117.70 (CH_2CN), 35.86 ($ArCH_2Ar$), 21.63 (CH_3), 21.48 (CH_2CN)
9h (90, 82)	436–438	($CDCl_3$): 7.70 (bs, 16H, ArH), 6.66 (s, 8H, ArH), 3.51 (s, 8H, $ArCH_2Ar$), 3.14 (s, 8H, CH_2CN), 1.47 (s, 36H, ArBu-*t*)	($CDCl_3$): 162.90 (C=O), 157.48 (CBu-*t*), 147.15 (C–O), 135.47, 129.56, 129.16, 124.92, 124.85, 124.77 (Ar), 115.37 (CH_2CN), 35.64 ($ArCH_2Ar$), 34.49 (*t*-Bu), 30.29 (*t*-Bu), 21.37 (CH_2CN)
9i (87)	410 (softening)–450 (liquid)	(DMSO-d_6): 7.87 (d, 8H, J = 8.34, ArH), 7.67 (d, 8H, J = 8.07, ArH), 6.76 (s, 8H, ArH), 5.09 (s, 8H, $ArCH_2Cl$), 3.58 (s, 8H, $ArCH_2Ar$), 3.24 (s, 8H, CH_2CN)	
9j (83, 72)	452–454	(DMSO-d_6): 7.82 (bs, 8H, ArH), 7.79 (bs, 8H, ArH), 3.61–3.56 (bs, 16H, $ArCH_2Ar$ and CH_2CN)	(DMSO-d_6): 162.67 (C=O), 147.24 (C–O), 133.84, 132.55, 132.42, 129.92, 126.42, 124.57 (Ar), 117.81 (CH_2CN), 116.65 (CF), 116.35 (CF), 35.49 ($ArCH_2Ar$), 21.27 (CH_2CN)
9k[d] (86, 75)	370–372	(DMSO-d_6): 7.91 (d, 8H, J = 8.46, ArH), 7.68 (d, 8H, J = 8.07, ArH), 6.86 (s, 8H, ArH), 3.56 (bs, 16H, $ArCH_2Ar$ and CH_2CN)	(DMSO-d_6): 162.87 (C=O), 147.19 (C–O), 133.78, 131.32, 131.05, 129.89, 129.35, 128.64, 126.96 (Ar), 117.83 (CH_2CN), 35.41 ($ArCH_2Ar$), 21.63 (CH_2CN)
9m[e] (84, 77)	420–423	(DMSO-d_6): 8.08 (bs, 8H, ArH), 7.95 (t, 4H, J = 8.07 and 8.04, ArH), 7.33 (d, 4H, J = 7.53, ArH), 6.87 (s, 8H, ArH), 3.60 (s, 8H, $ArCH_2Ar$), 3.54 (s, 8H, CH_2CN)	(DMSO-d_6): 162.48 (C=O), 147.22 (C–O), 134.47, 134.14, 133.83, 130.69, 130.22, 130.16, 130.01, 127.30, 126.47 (Ar), 117.59 (CH_2CN), 35.27 ($ArCH_2Ar$), 21.64 (CH_2CN)
9o[f] (82, 78)	408–410	(DMSO-d_6): 8.29 (s, 4H, ArH), 7.80 (s, 8H, ArH), 7.00 (s, 8H, ArH), 3.98 (s, 8H, $ArCH_2Ar$), 3.49 (s, 8H, CH_2CN)	(DMSO-d_6): 161.95 (C=O), 147.12 (C–O), 124.87, 133.94, 133.82, 131.84, 129.73, 128.32, 126.38 (Ar), 117.67 (CH_2CN), 34.30 ($ArCH_2Ar$), 21.82 (CH_2CN)
9p[g] (52)	350–352	(DMSO-d_6): 9.29 (s, 4H, ArH), 8.86 (s, 8H, ArH), 7.07 (s, 8H, ArH), 3.79 (s, 8H, $ArCH_2Ar$), 3.53 (s, 8H, CH_2CN)	(DMSO-d_6): 161.65 (C=O), 148.33 ($C-NO_2$), 147.17 (C–O), 134.20, 131.94, 129.54, 129.48, 127.65, 123.32 (Ar), 118.18 (CH_2CN), 34.44 ($ArCH_2Ar$), 21.38 (CH_2CN)
9r (90, 84)	370–372	(DMSO-d_6): 7.14 (s, 8H, ArH), 3.95 (s, 8H, CH_2CN), 3.60 (s, 8H, $ArCH_2Ar$), 1.57 (s, 12H, CH_3COO)	(DMSO-d_6): 167.33 (C=O), 147.04 (C–O), 133.08, 128.72, 127.83 (Ar), 119.02 (CH_2CN), 36.30 ($ArCH_2Ar$), 21.31 (CH_2CN), 19.87 (CH_3COO)
9s[h] (91, 83)	188–190	(DMSO-d_6): 7.10 (s, 8H, ArH), 3.91 (s, 8H, CH_2CN), 3.60 (s, 8H, $ArCH_2Ar$), 1.75 (q, 8H, J = 7.29 and 6.03, CH_2CH_3), 0.92 (t, 12H, J = 7.11 and 6.59, CH_2CH_3)	(DMSO-d_6): 170.83 (C=O), 147.24 (C–O), 133.28, 128.70, 127.76 (Ar), 118.76 (CH_2CN), 36.41 ($ArCH_2Ar$), 25.74 (CH_2CH_3), 21.36 (CH_2CN), 8.25 (CH_3CH_2)
9t[i] (88, 79)	330–332	(DMSO-d_6): 7.11 (s, 8H, ArH), 3.91 (s, 8H, CH_2CN), 3.62 (s, 8H, $ArCH_2Ar$), 1.61 (t, 8H, J = 5.52, CH_2CH_2), 1.47 (m, 8H, $CH_2CH_2CH_3$), 0.90 (t, 12H, J = 7.10 and 6.50, CH_2CH_3)	(DMSO-d_6): 169.84 (C=O), 147.26 (C–O), 133.17, 128.52, 127.67 (Ar), 118.66 (CH_2CN), 36.56 ($ArCH_2Ar$), 34.08 (CH_2CH_2), 21.41 (CH_2CN), 16.96 (CH_2CH_2), 13.27 (CH_3CH_2)
9u[j] (86, 82)	269–272	($CDCl_3$): 7.03 (s, 8H, ArH), 3.72 (s, 8H, CH_2CN), 3.63 (s, 8H, $ArCH_2Ar$), 1.65 (t, 8H, J = 5.07, $OCOCH_2$), 1.58 (m, 8H, CH_2), 1.32 (bs, 24H, $CH_2CH_2CH_2$), 0.92 (bs, 12H, CH_3)	($CDCl_3$): 170.30 (C=O), 148.10 (C–O), 133.91, 128.58, 126.96 (Ar), 117.08 (CH_2CN), 37.44 ($ArCH_2Ar$), 33.16 (CH_2), 31.85 (CH_2), 29.12 (CH_2), 24.15 (CH_2), 22.75 (CH_2), 22.52 (CH_2CN), 14.06 (CH_3)
9v[k] (79)	318–320	(DMSO-d_6): 7.16 (s, 8H, ArH), 3.95 (s, 8H, CH_2CN), 3.68 (t, 8H, J = 6.42, CH_2Cl), 3.65 (s, 8H, $ArCH_2Ar$), 1.95 (t, 8H, J = 6.15 and 6.87, CH_2), 1.76 (t, 8H, J = 6.57 and 6.45, CH_2)	(DMSO-d_6): 169.09 (C=O), 147.09 (C–O), 133.33, 128.50, 127.97 (Ar), 118.93 (CH_2CN), 44.25 (CH_2Cl), 36.31 ($ArCH_2Ar$), 29.51 (CH_2), 26.55 (CH_2), 21.62 (CH_2CN)

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[a] The second value shown is the yield obtained with NaH.

[b] Anal. calcd. for $C_{68}H_{52}N_4O_{12}$: C, 73.11; H, 4.69; found C, 72.91; H, 4.50.

[c] Anal. calcd. for $C_{68}H_{52}N_4O_8$: C, 77.55; H, 4.98; found C, 77.80; H, 4.81.

[d] Anal. calcd. for $C_{64}H_{40}N_4O_8Cl_4$: C, 67.30; H, 3.55; found C, 67.30; H, 3.35.

[e] Anal. calcd. for $C_{64}H_{40}N_4O_8Cl_4$: C, 67.30; H, 3.55; found C, 67.18; H, 3.32.

[f] Anal. calcd. for $C_{64}H_{36}N_4O_8Cl_8$: C, 60.40; H, 2.85; found C, 60.20; H, 2.74.

[g] A mixture of two products was obtained, separable into an acetone-insoluble fraction (compound **9p**) and an acetone soluble fraction. The acetone-soluble fraction is thought to be the partial cone conformer on the basis of its ^{13}C and ^{1}H NMR spectra.

[h] Anal. calcd. for $C_{48}H_{44}N_4O_8$: C, 71.63; H, 5.51; found C, 71.72; H, 5.48.

[i] Anal. calcd. for $C_{52}H_{52}N_4O_8$: C, 72.54; H, 6.09; found C, 72.84; H, 6.05.

[j] Anal. calcd. for $C_{64}H_{76}N_4O_8$: C, 74.68; H, 7.44; found C, 75.16; H, 7.32.

[k] Anal. calcd. for $C_{52}H_{48}N_4O_8Cl_4$: C, 62.53; H, 4.84; found C, 62.53; H, 4.71.

Table 3. Physical and Spectroscopic Data of the 1,3-Diesters **10** (Cone Conformation) from the Reactions of *p*-Cyanomethylcalix[4]arene (**3**) with Aroyl and Acyl Chlorides

Compound (% yield)	mp (°C)	^{1}H NMR (300 MHz) (DMSO-d_6/TMS) δ, *J* (Hz)	^{13}C NMR (300 MHz) (DMSO-d_6/TMS) δ
10a[a] (90)	362–365	8.06 (d, 4H, *J* = 6.9, ArH), 7.89 (t, 2H, *J* = 6.0, ArH), 7.71 (t, 4H, *J* = 6.0, ArH), 7.15 (s, 4H, ArH), 7.08 (s, 2H, ArOH), 6.74 (s, 4H, ArH), 3.87 (s, 4H, CH$_2$CN), 3.72 (d, 4H, *J* = 14.1, ArCH$_2$Ar), 3.59 (d, 4H, *J* = 14.1, ArCH$_2$Ar), 3.44 (s, 4H, CH$_2$CN)	164.11 (ArCO), 152.63 (COH), 146.16 (COCOAr), 134.18, 132.87, 129.99, 129.42, 129.20, 128.96, 128.88, 128.60, 127.05, 120.11 (Ar), 119.06 (CH$_2$CN), 118.76 (CH$_2$CN), 33.53 (ArCH$_2$Ar), 21.75 (CH$_2$CN), 21.42 (CH$_2$CN)
10b[b] (82)	315–318	8.37 (d, 4H, *J* = 6.45, ArH), 8.31 (d, 4H, *J* = 8.70, ArH), 7.27 (s, 2H, ArOH), 7.13 (s, 4H, ArH), 6.91 (s, 4H, ArH), 3.88 (s, 4H, CH$_2$CN), 3.76 (d, 4H, *J* = 14.1, ArCH$_2$Ar), 3.66 (d, 4H, *J* = 13.83, ArCH$_2$Ar), 3.59 (s, 4H, CH$_2$CN)	163.11 (ArCO), 152.51 (COH), 150.41 (CNO$_2$), 145.55 (COCOAr), 134.41, 133.01, 131.48, 129.26, 129.21, 128.64, 127.80, 123.89, 121.07 (Ar), 119.11 (CH$_2$CN), 118.98 (CH$_2$CN), 32.78 (ArCH$_2$Ar), 21.78 (CH$_2$CN), 21.50 (CH$_2$CN)
10c[c] (87)	305–307	8.86 (s, 2H, ArH), 8.70 (d, 2H, *J* = 8.04, ArH), 8.34 (t, 2H, *J* = 7.53, ArH), 7.94 (t, 2H, *J* = 8.04, ArH), 7.22 (s, 2H, ArOH), 7.14 (s, 4H, ArH), 6.79 (s, 4H, ArH), 3.88 (s, 4H, CH$_2$CN), 3.71 (d, 4H, *J* = 13.98, ArCH$_2$Ar), 3.59 (d, 4H, *J* = 14.49, ArCH$_2$Ar), 3.55 (s, 4H, CH$_2$CN)	162.75 (ArCO), 152.71 (COH), 148.14 (CNO$_2$), 145.90 (COCOAr), 135.54, 132.60, 130.63, 130.25, 129.47, 129.30, 128.59, 128.49, 127.20, 124.83, 120.29 (Ar), 119.06 (CH$_2$CN), 118.85 (CH$_2$CN), 33.24 (ArCH$_2$Ar), 21.72 (CH$_2$CN), 21.37 (CH$_2$CN)
10d[d] (75)	264–266	8.15 (d, 2H, *J* = 8.07, ArH), 8.00 (dd, 4H, *J* = 7.98 and 7.46, ArH), 7.67 (d, 2H, *J* = 7.50, ArH), 7.07 (s, 4H, ArH), 7.01 (s, 4H, ArH), 6.88 (s, 2H, ArOH), 3.85 (s, 4H, CH$_2$CN), 3.70 (d, 4H, *J* = 13.95, ArCH$_2$Ar), 3.68 (d, 4H, *J* = 14.37, ArCH$_2$Ar), 3.50 (s, 4H, CH$_2$CN)	162.19 (ArCO), 152.44 (COH), 149.50 (CNO$_2$), 145.16 (COCOAr), 134.12, 132.93, 132.84, 130.36, 129.50, 129.14, 128.67, 128.17, 124.47, 123.73, 121.36 (Ar), 118.92 (CH$_2$CN), 32.56 (ArCH$_2$Ar), 21.70 (CH$_2$CN), 21.36 (CH$_2$CN)
10e (80)	291–294	8.22 (d, 4H, *J* = 7.41, ArH), 8.11 (d, 4H, *J* = 7.53, ArH), 7.28 (s, 2H, ArOH), 7.16 (s, 4H, ArH), 6.68 (s, 4H, ArH), 3.88 (s, 4H, CH$_2$CN), 3.72 (d, 4H, *J* = 13.98, ArCH$_2$Ar), 3.48 (d, 4H, *J* = 14.25, ArCH$_2$Ar), 3.55 (s, 4H, CH$_2$CN)	162.99 (ArCO), 152.73 (COH), 146.11 (COCOAr), 133.01, 132.63, 132.41, 130.42, 129.63, 129.09, 128.63, 126.96, 119.10, 116.43 (Ar), 119.91 (CH$_2$CN), 118.92 (CN), 118.16 (CH$_2$CN), 33.67 (ArCH$_2$Ar), 21.74 (CH$_2$CN), 21.57 (CH$_2$CN)
10f[e] (92)	305–307	8.06 (d, 4H, *J* = 8.07, ArH), 7.15 (d, 4H, *J* = 8.04, ArH), 7.10 (s, 2H, ArOH), 7.01 (s, 4H, ArH), 6.82 (s, 4H, ArH), 3.93 (s, 6H, ArOCH$_3$), 3.86 (s, 4H, CH$_2$CN), 3.68 (d, 4H, *J* = 13.95, ArCH$_2$Ar), 3.61 (d, 4H, *J* = 12.87, ArCH$_2$Ar), 3.55 (s, 4H, CH$_2$CN)	163.80 (ArCO), 163.68 (COCH$_3$), 152.45 (COH), 145.90 (COCOAr), 132.99, 132.19, 129.12, 128.89, 128.80, 128.15, 127.19, 122.32, 114.35 (Ar), 120.55 (CH$_2$CN), 119.01 (CH$_2$CN, 55.56 (OCH$_3$), 33.03 (ArCH$_2$Ar), 21.73 (CH$_2$CN), 21.53 (CH$_2$CN)
10g (89)	308–310	7.96 (d, 4H, *J* = 7.83, ArH), 7.44 (d, 4H, *J* = 7.65, ArH), 7.12 (s, 4H, ArH), 7.03 (s, 2H, ArOH), 6.78 (s, 4H, ArH), 3.87 (s, 4H, CH$_2$CN), 3.69 (d, 4H, *J* = 13.95, ArCH$_2$Ar), 3.59 (d, 4H, *J* = 13.68, ArCH$_2$Ar), 3.48 (s, 4H, CH$_2$CN), 2.53 (s, 6H, ArCH$_3$)	164.32 (ArCO), 152.44 (COH), 146.04 (COCOAr), 144.38 (CCH$_3$), 132.93, 130.02, 129.59, 129.24, 128.85, 128.75, 127.19, 125.93, 120.44 (Ar), 119.06 (CH$_2$CN), 118.90 (CH$_2$CN), 33.24 (ArCH$_2$Ar), 21.73 (CH$_2$CN), 21.43 (CH$_2$CN), 21.37 (CH$_3$)
10h[f] (86)	385–387	7.99 (d, 4H, *J* = 8.04, ArH), 7.71 (d, 4H, *J* = 7.11, ArH), 7.12 (s, 4H, ArH), 7.05 (s, 2H, ArOH), 6.67 (s, 4H, ArH), 3.86 (s, 4H, CH$_2$CN), 3.70 (d, 4H, *J* = 14.07, ArCH$_2$Ar), 3.50 (d, 4H, *J* = 14.28, ArCH$_2$Ar), 3.44 (s, 4H, CH$_2$CN), 1.42 (s, 18H, *t*-Bu)	163.91 (ArCO), 157.09 (CBu-*t*), 152.68 (COH), 146.34 (COCOAr), 132.72, 130.08, 129.46, 128.89, 128.70, 126.72, 125.91, 125.54, 119.68 (Ar), 119.10 (CH$_2$CN), 118.54 (CH$_2$CN), 34.92 (*t*-Bu), 33.61 (ArCH$_2$Ar), 30.77 (*t*-Bu), 21.67 (CH$_2$CN), 21.31 (CH$_2$CN)
10i (77)	270–272	8.10 (d, 4H, *J* = 7.65, ArH), 7.73 (d, 4H, *J* = 7.65, ArH), 7.13 (s, 4H, ArH), 7.05 (s, 2H, ArOH), 6.80 (s, 4H, ArH), 5.01 (s, 4H, CH$_2$Cl), 3.87 (s, 4H, CH$_2$CN), 3.65–3.69 (bs, 8H, ArCH$_2$Ar), 3.44 (s, 4H, CH$_2$CN)	163.82 (ArCO), 152.60 (COH), 145.94 (COCOAr), 143.63 (CCH$_2$Cl), 132.95, 130.37, 129.25, 129.18, 129.10, 128.89, 128.58, 127.29, 120.51 (Ar), 119.04 (CH$_2$CN), 118.84 (CH$_2$CN), 45.31 (CH$_2$Cl), 33.25 (ArCH$_2$Ar), 21.74 (CH$_2$CN), 21.44 (CH$_2$CN)
10j (82)	328–330	8.09 (t, 4H, *J* = 5.31 and 5.47, ArH), 7.54 (t, 4H, *J* = 8.73 and 8.88, ArH), 7.18 (s, 2H, ArOH), 7.13 (s, 4H, ArH), 6.74 (s, 4H, ArH), 3.88 (s, 4H, CH$_2$CN), 3.70 (d, 4H, *J* = 14.40, ArCH$_2$Ar), 3.57 (s, 4H, CH$_2$CN), 3.52 (d, 4H, *J* = 13.98, ArCH$_2$Ar)	164.00 (ArCO), 163.25 (CF), 152.64 (COH), 146.10 (COCOAr), 132.91, 132.75, 129.40, 129.05, 128.71, 126.94, 125.18, 120.13, 116.36, 116.07 (Ar), 119.06 (CH$_2$CN), 118.88 (CH$_2$CN), 33.45 (ArCH$_2$Ar), 21.76 (CH$_2$CN), 21.50 (CH$_2$CN)
10k[g] (85)	325–327	8.09 (d, 4H, *J* = 8.49, ArH), 7.71 (d, 4H, *J* = 8.46, ArH), 7.17 (s, 2H, ArOH), 7.13 (s, 4H, ArH), 6.82 (s, 4H, ArH), 3.88 (s, 4H, CH$_2$CN), 3.70 (d, 4H, *J* = 13.65, ArCH$_2$Ar), 3.59 (s, 4H, CH$_2$CN), 3.61 (d, 4H, *J* = 13.90, ArCH$_2$Ar)	163.50 (ArCO), 152.50 (COH), 145.79 (COCOAr), 139.11 (CCl), 132.79, 131.73, 129.23, 129.17, 129.03, 128.66, 127.56, 127.20, 120.47 (Ar), 119.02 (CH$_2$CN), 118.94 (CH$_2$CN), 33.11 (ArCH$_2$Ar), 21.74 (CH$_2$CN), 21.41 (CH$_2$CN)
10l (88)	347–349	8.07 (d, 4H, *J* = 8.49, ArH), 7.88 (d, 4H, *J* = 8.55, ArH), 7.16 (s, 6H, ArOH and ArH), 6.89 (s, 4H, ArH), 3.91 (s, 4H, CH$_2$CN), 3.67–3.75 (bs, 8H, ArCH$_2$Ar), 3.63 (s, 4H, CH$_2$CN)	163.73 (ArCO), 152.50 (COH), 145.74 (COCOAr), 132.86, 132.14, 131.87, 129.20, 129.10, 128.68, 128.27, 127.99, 127.34, 120.66 (Ar), 119.04 (CH$_2$CN), 118.98 (CH$_2$CN), 33.03 (ArCH$_2$Ar), 21.76 (CH$_2$CN), 21.41 (CH$_2$CN)

Table 3. (continued)

Compound (% yield)	m$_p$ (°C)	^{1}H NMR (300 MHz) (DMSO-d_6/TMS) δ, J (Hz)	^{13}C NMR (300 MHz) (DMSO-d_6/TMS) δ
10m[h] (84)	292–294	8.26 (s, 2H, ArH), 7.92 (dd, 4H, J = 6.99 and 7.11, ArH), 7.70 (t, 2H, J = 7.95, ArH), 7.16 (s, 2H, ArOH), 7.11 (s, 4H, ArH), 6.76 (s, 4H, ArH), 3.86 (s, 4H, CH_2CN), 3.69 (d, 4H, J = 13.98, $ArCH_2Ar$), 3.58 (s, 4H, CH_2CN), 3.52 (d, 4H, J = 13.31, $ArCH_2Ar$)	163.12 (ArCO), 152.68 (COH), 146.05 (COCOAr), 134.04, 133.77, 132.58, 130.80, 130.61, 129.71, 129.40, 129.22, 128.64, 128.33, 126.95, 120.02 (Ar), 119.08 (CH_2CN), 118.74 (CH_2CN), 33.33 ($ArCH_2Ar$), 21.71 (CH_2CN), 21.44 (CH_2CN)
10n (90)	259–261	8.26 (s, 2H, ArH), 8.07 (d, 2H, J = 8.01, ArH), 7.92 (d, 2H, J = 7.53, ArH), 7.64 (t, 2H, J = 7.62 and 7.68, ArH), 7.15 (s, 2H, ArOH), 7.10 (s, 4H, ArH), 6.76 (s, 4H, ArH), 3.86 (s, 4H, CH_2CN), 3.70 (d, 4H, J = 13.95, $ArCH_2Ar$), 3.58 (s, 4H, CH_2CN), 3.53 (d, 4H, J = 13.95, $ArCH_2Ar$)	163.02 (ArCO), 152.64 (COH), 146.01 (COCOAr), 136.91, 132.58, 131.05, 130.77, 129.35, 129.18, 128.64, 126.96, 122.19, 120.06 (Ar), 119.06 (CH_2CN), 118.78 (CH_2CN), 33.27 ($ArCH_2Ar$), 21.70 (CH_2CN), 21.51 (CH_2CN)
10o (71)	302–304	8.15 (bs, 2H, ArH), 8.04 (bs, 4H, ArH), 7.18 (s, 2H, ArOH), 6.99 (s, 4H, ArH), 6.88 (s, 4H, ArH), 3.81 (s, 4H, CH_2CN), 3.62 (d, 4H, J = 14.4, $ArCH_2Ar$), 3.52 (d, 4H, J = 13.71, $ArCH_2Ar$), 3.32 (s, 4H, CH_2CN)	162.49 (ArCO), 152.59 (COH), 145.86 (COCOAr), 134.85, 133.62, 132.22, 131.99, 129.70, 129.03, 128.39, 128.16, 126.90, 120.35 (Ar), 119.11 (CH_2CN), 118.88 (CH_2CN), 32.69 ($ArCH_2Ar$), 21.73 (CH_2CN), 21.59 (CH_2CN)
10q (81)	235–236	7.45 (s, 2H, ArH), 7.35–7.40 (m, 4H, ArH), 7.23–7.31 (m, 4H, ArH), 7.13 (s, 4H, ArH), 7.11 (s, 2H, ArOH), 7.08 (s, 4H, ArH), 4.04 (s, 4H, CH_2CN), 3.87 (s, 4H, CH_2CN), 3.85 (s, 4H, $ArCH_2$), 3.73 (d, 4H, J = 13.44, $ArCH_2Ar$), 3.63 (d, 4H, J = 13.49, $ArCH_2Ar$)	169.57 (CH_2CO), 152.16 (COH), 145.33 ($COCOCH_2$), 133.58, 133.31, 129.52, 129.29, 128.77, 128.53, 128.47, 128.29, 128.17, 127.12, 121.44 (Ar), 119.51 (CH_2CN), 118.92 (CH_2CN), 32.67 ($ArCH_2Ar$), 21.74 (CH_2CN), 21.55 (CH_2CN)
10r (85)	324–326	7.10 (s, 4H, ArH), 7.05 (s, 2H, ArOH), 6.99 (s, 4H, ArH), 3.91 (s, 4H, CH_2CN), 3.85 (s, 4H, CH_2CN), 3.75 (d, 4H, J = 15.03, $ArCH_2Ar$), 3.62 (d, 4H, J = 14.52, $ArCH_2Ar$), 1.98 (s, 6H, $COCH_3$)	168.14 (CH_3CO), 152.32 (COH), 146.41 ($COCOCH_3$), 133.44, 128.93, 128.66, 128.34, 127.37, 120.79 (Ar), 119.44 (CH_2CN), 119.03 (CH_2CN), 33.48 ($ArCH_2Ar$), 21.76 (CH_2CN), 21.28 (CH_2CN), 20.50 ($COCH_3$)
10s[i] (86)	355–357	7.09 (s, 4H, ArH), 7.03 (s, 4H, ArH), 6.98 (s, 2H, ArOH), 3.89 (s, 4H, CH_2CN), 3.83 (s, 4H, CH_2CN), 3.71 (d, 4H, J = 14.82, $ArCH_2Ar$), 3.63 (d, 4H, J = 14.19, $ArCH_2Ar$), 2.35–2.42 (q, 4H, J = 7.41, CH_2CH_3), 1.14 (t, 6H, J = 7.47 and 7.02, $COCH_2CH_3$)	171.56 (CH_2CO), 152.27 (COH), 145.82 ($COCOCH_2$), 133.37, 128.82, 128.56, 128.33, 127.60, 121.08 (Ar), 119.26 (CH_2CN), 118.94 (CH_2CN), 33.79 ($ArCH_2Ar$), 26.40 (CH_2CH_3), 21.72 (CH_2CN), 21.35 (CH_2CN), 8.56 (CH_2CH_3)
10t (83)	314–316	7.09 (s, 4H, ArH), 7.07 (s, 4H, ArH), 7.00 (s, 2H, ArOH), 3.88 (s, 4H, CH_2CN), 3.85 (s, 4H, CH_2CN), 3.65–3.69 (bs, 8H, $ArCH_2Ar$), 2.44 (t, 4H, J = 7.83 and 7.31, CH_2CO), 1.71 (m, 4H, J = 7.53, 7.50 and 7.53, CH_2), 1.01 (t, 6H, J = 7.29 and 7.49, CH_3)	170.69 (CH_2CO), 152.20 (COH), 145.51 ($COCOCH_2$), 133.38, 128.81, 128.56, 128.40, 127.87, 121.24 (Ar), 119.31 (CH_2CN), 118.95 (CH_2CN), 34.97 (CH_2CO), 33.37 ($ArCH_2Ar$), 21.75 (CH_2CN), 21.45 (CH_2CN), 17.46 (CH_2), 13.50 (CH_2CH_3)
10v (73)	282–284	7.09 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.00 (s, 2H, ArOH), 3.88 (s, 4H, CH_2CN), 3.85 (s, 4H, CH_2CN), 3.67–3.75 (m, 14H, CH_2Cl and $ArCH_2Ar$), 2.54 (m, 4H, CH_2), 2.12 (t, 4H, J = 6.66 and 6.45, CH_2)	170.14 (CH_2CO), 152.28 (COH), 145.70 ($COCOCH_2$), 133.40 (CCH_2Cl), 128.87, 128.54, 128.49, 127.80, 121.16 (Ar), 119.42 (CH_2CN), 118.96 (CH_2CN), 44.49 (CH_2Cl), 33.70 ($ArCH_2Ar$), 30.34 (CH_2CO), 26.91 (CH_2), 21.76 (CH_2CN), 21.52 (CH_2CN)
10w (84)	325–327	7.10 (s, 4H, ArH), 7.03 (s, 2H, ArOH), 6.97 (s, 4H, ArH), 3.90 (s, 4H, CH_2CN), 3.81 (s, 4H, CH_2CN), 3.78 (d, 4H, J = 15.06, $ArCH_2Ar$), 3.47 (d, 4H, J = 14.82, $ArCH_2Ar$), 1.36–1.41 (m, 2H, CH), 1.09–1.12 (m, 4H, CH_2), 1.04 (bs, 4H, CH_2)	172.04 (CHCO), 152.15 (COH), 146.57 (COCOCH), 133.35, 128.93, 128.04, 127.06, 120.38 (Ar), 119.39 (CH_2CN), 118.99 (CH_2CN), 34.52 ($ArCH_2Ar$), 21.75 (CH_2CN), 21.44 (CH_2CN), 12.58 (CH), 9.07 (CH_2)

[a] Anal. calcd. for $C_{50}H_{36}N_4O_6 \cdot 3/4H_2O$: C, 74.85; H, 4.71; found: C, 74.75; H, 4.83.

[b] Anal. calcd. for $C_{50}H_{34}N_6O_{10} \cdot 3/4H_2O$: C, 67.30; H, 4.01; found: C, 67.45; H, 4.18.

[c] Anal. calcd. for $C_{50}H_{34}N_6O_{10} \cdot 3/4H_2O$: C, 67.30; H, 4.01; found: C, 67.03; H, 3.98.

[d] Anal. calcd. for $C_{50}H_{34}N_6O_{10} \cdot 3/4H_2O$: C, 67.30; H, 4.01; found: C, 67.35; H, 4.00.

[e] Anal. calcd. for $C_{52}H_{40}N_4O_8 \cdot 3/4H_2O$: C, 72.42; H, 4.85; found: C, 72.49; H, 5.02.

[f] Anal. calcd. for $C_{58}H_{52}N_4O_6 \cdot 3/4H_2O$: C, 76.17; H, 5.90; found: C, 76.09; H, 5.87.

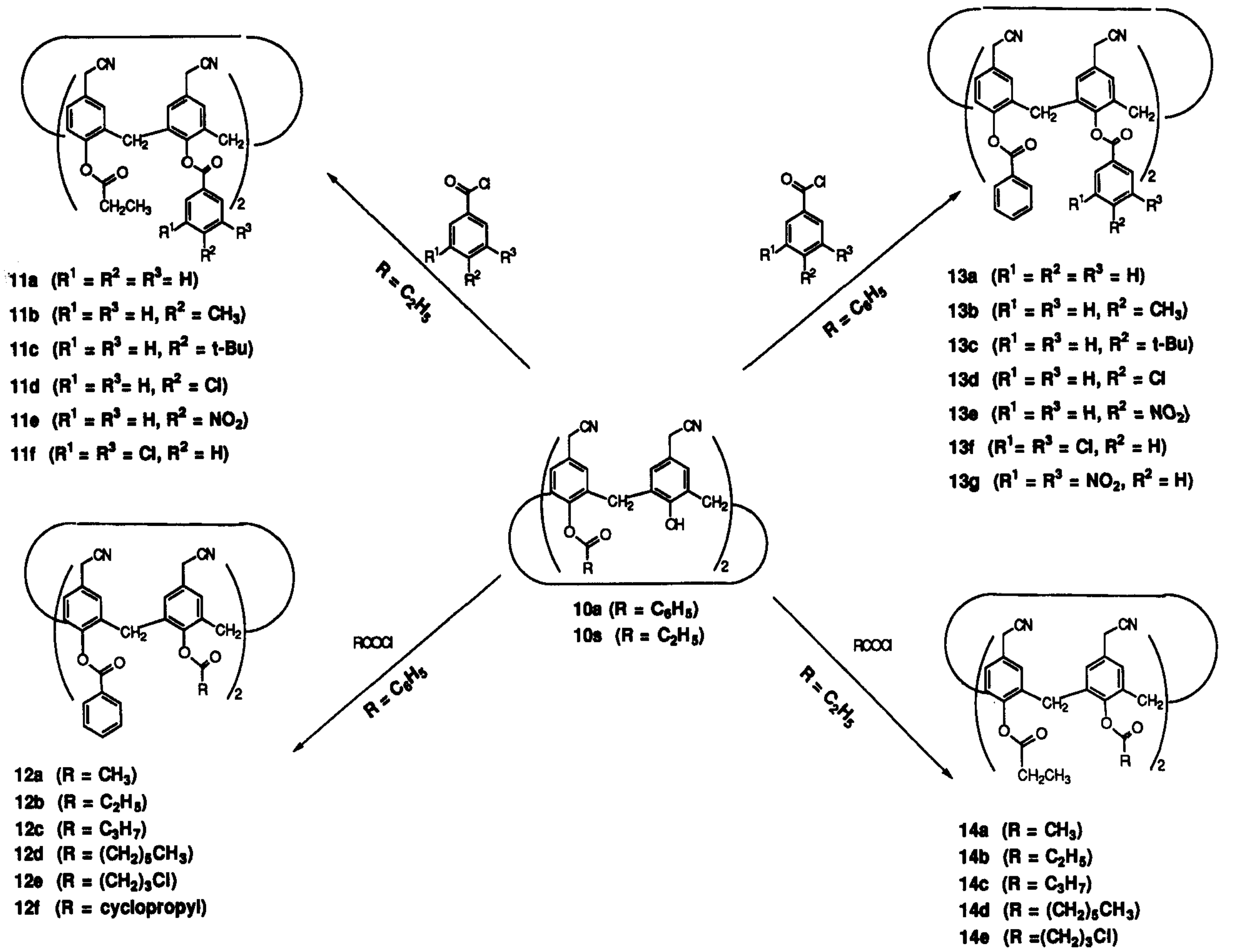
[g] Anal. calcd. for $C_{50}H_{34}N_4O_6Cl_2 \cdot 3/4H_2O$: C, 68.93; H, 4.11; found: C, 68.86; H, 3.98.

[h] Anal. calcd. for $C_{50}H_{34}N_4O_6Cl_2 \cdot 3/4H_2O$: C, 68.93; H, 4.11; found: C, 68.82; H, 4.00.

[i] Anal. calcd. for $C_{40}H_{36}N_4O_6 \cdot 3/4H_2O$: C, 71.43; H, 5.35; found: C, 71.60; H, 5.08.

for the synthesis of the tetraesters of mixed function shown in Scheme 3. Through the use of various combinations of reactants, the 1,3-alternate conformers of the aroyl-aliphatic tetraesters **11** and **12**, all-aroyl tetraesters **13**, and all-aliphatic tetraesters **14** have been prepared, the data for which are shown in Table 4.

Conformational assignments were made on the basis of the NMR spectra. Calix[4]arenes in the cone conformation show a widely separated pair of doublets in the ^{1}H NMR spectrum arising from the $ArCH_2Ar$ protons,[5] whereas those in the 1,3-alternate conformation show either a singlet or a closely separated pair of doublets.



Scheme 3. 1-Methylimidazole-induced aroylation and acylation of 1,3-diesters of *p*-cyanomethylcalix[4]arene (**10**)

Table 4. Physical and Spectroscopic Data of the Mixed Tetraesters **11**, **12**, **13** and **14** (1,3-Alternate Conformation) from the Reactions of the 1,3-Diesters of *p*-Cyanomethylcalix[4]arene (**10a** and **10s**) with Aroyl and Acyl Chlorides

Product (% yield)	mp (°C)	^{1}H NMR (300 MHz) (DMSO-d_6/TMS) δ, *J* (Hz)	^{13}C NMR (300 MHz) (DMSO-d_6/TMS) δ
11a[a] (92)	381–382	7.88 (t, 2H, *J* = 6.57 and 7.41, ArH), 7.66 (t, 4H, *J* = 7.08 and 7.41, ArH), 7.57 (d, 4H, *J* = 7.11, ArH), 7.19 (s, 4H, ArH), 6.65 (s, 4H, ArH), 3.97 (s, 4H, CH_2CN), 3.55 (s, 8H, $ArCH_2Ar$), 3.20 (s, 4H, CH_2CN), 2.25 (q, 4H, *J* = 6.45 and 7.11, CH_2CH_3), 1.14 (t, 6H, *J* = 7.11 and 6.45, CH_3CH_2)	171.22 (CH_3CH_2CO), 163.54 (ArCO), 147.33 (C—O), 147.14 (C—O), 134.25, 133.65, 133.50, 129.61, 129.52, 129.37, 128.88, 128.16, 127.29, 126.29 (Ar), 118.67 (CH_2CN), 117.66 (CH_2CN), 36.03 ($ArCH_2Ar$), 26.31 (CH_2CH_3), 21.39 (CH_2CN), 21.32 (CH_2CN), 8.47 (CH_3CH_2)
11b[b] (93)	335–337	7.40 (d, 8H, *J* = 5.49, ArH), 7.18 (s, 4H, ArH), 6.66 (s, 4H, ArH), 3.96 (s, 4H, CH_2CN), 3.55 (s, 8H, $ArCH_2Ar$), 3.21 (s, 4H, CH_2CN), 2.53 (s, 6H, $ArCH_3$), 2.19 (q, 4H, *J* = 7.11, CH_2CH_3), 1.11 (t, 6H, *J* = 6.99, CH_3CH_2)	171.20 (CH_3CH_2CO), 163.50 (ArCO), 147.30 (C—O), 147.20 (C—O), 144.47 (CCH_3), 133.69, 133.44, 129.59, 129.45, 129.32, 127.27, 126.50, 125.47 (Ar), 118.68 (CH_2CN), 117.80 (CH_2CN), 36.16 ($ArCH_2Ar$), 26.24 (CH_2CH_3), 21.38 (CH_2CN, CH_3), 8.44 (CH_3CH_2)
11c (86)	351–353	7.70 (d, 4H, *J* = 6.96, ArH), 7.58 (d, 4H, *J* = 6.06, ArH), 7.18 (s, 4H, ArH), 6.62 (s, 4H, ArH), 3.97 (s, 4H, CH_2CN), 3.55 (bs, 8H, $ArCH_2Ar$), 3.27 (s, 4H, CH_2CN), 2.33 (q, 4H, *J* = 7.11, CH_2), 1.46 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu), 1.17 (t, 6H, *J* = 7.35 and 7.43, CH_3CH_2)	171.29 (CH_3CH_2CO), 163.57 (ArCO), 157.18 (CBu-*t*), 147.34 (C—O), 147.22 (C—O), 133.60, 133.53, 129.70, 129.63, 129.32, 127.04, 126.00, 125.56, 125.12 (Ar), 118.67 (CH_2CN), 117.46 (CH_2CN), 35.94 ($ArCH_2Ar$), 35.01 (*t*-Bu), 30.83 (*t*-Bu), 26.42 (CH_2CH_3), 21.38 (CH_2CN), 21.30 (CH_2CN), 8.53 (CH_3)
11d (89)	334–335 (brown liquid)	8.27 (d, 4H, *J* = 8.34, ArH), 7.66 (d, 4H, *J* = 8.04, ArH), 7.23 (s, 4H, ArH), 6.78 (s, 4H, ArH), 3.99 (s, 4H, CH_2CN), 3.69 and 3.61 (dd, 8H, *J* = 16.14 and 15.57, $ArCH_2Ar$), 3.33 (s, 4H, CH_2CN), 2.10 (q, 4H, *J* = 7.41, CH_2CH_3), 1.10 (t, 6H, *J* = 6.54 and 6.46, CH_3CH_2)	171.11 (CH_3CH_2CO), 162.15 (ArCO), 150.65 (CCl), 147.44 (C—O), 146.88 (C—O), 133.67, 133.46, 130.54, 129.60, 129.07, 127.98, 127.18, 123.84 (Ar), 118.61 (CH_2CN), 118.08 (CH_2CN), 36.02 ($ArCH_2Ar$), 26.17 (CH_2CH_3), 21.39 (CH_2CN), 8.40 (CH_3CH_2)

Table 4. (continued)

Product (% yield)	mp (°C)	^1H NMR (300 MHz) (DMSO-d_6/TMS) δ, J (Hz)	^{13}C NMR (300 MHz) (DMSO-d_6/TMS) δ
11e (84)	345–347	8.58 (d, 4H, $J = 7.92$, ArH), 7.46 (d, 4H, $J = 7.95$, ArH), 7.20 (s, 4H, ArH), 6.75 (s, 4H, ArH), 3.98 (s, 4H, CH_2CN), 3.59 (bs, 8H, $ArCH_2Ar$), 3.35 (s, 4H, CH_2CN), 2.21 (q, 4H, $J = 7.29$ and 6.69, CH_2CH_3), 1.11 (t, 6H, $J = 6.87$ and 7.11, CH_3CH_2)	171.17 (CH_3CH_2CO), 162.74 (ArCO), 147.37 (C–O), 147.01 (C–O), 139.17 (CNO_2), 133.65, 133.57, 131.07, 129.54, 129.10, 127.62, 127.02, 126.80 (Ar), 118.66 (CH_2CN), 117.88 (CH_2CN), 36.09 ($ArCH_2Ar$), 26.20 (CH_2CH_3), 21.37 (CH_2CN), 8.43 (CH_3CH_2)
11f (78)	291–293	8.02 (s, 2H, ArH), 7.40 (s, 4H, ArH), 7.19 (s, 4H, ArH), 6.92 (s, 4H, ArH), 3.99 (s, 4H, CH_2CN), 3.55–3.66 (dd, 8H, $J = 15.72$, $ArCH_2Ar$), 3.34 (s, 4H, CH_2CN), 2.18 (q, 4H, $J = 4.95$, CH_2CH_3), 1.16 (t, 6H, $J = 6.96$, CH_3CH_2)	171.48 (CH_3CH_2CO), 161.83 (ArCO), 147.47 (C–O), 146.96 (C–O), 134.62, 133.66, 133.54, 133.47, 133.40, 131.54, 129.89, 128.89, 127.97, 127.68, 126.89 (Ar), 118.71 (CH_2CN), 117.97 (CH_2CN), 35.77 ($ArCH_2Ar$), 26.42 (CH_2CH_3), 21.84 (CH_2CN), 21.36 (CH_2CN), 8.52 (CH_3CH_2)
12a (95)	352–354	7.89 (t, 2H, $J = 7.11$, ArH), 7.67 (t, 4H, $J = 7.50$ and 7.53, ArH), 7.57 (d, 4H, $J = 7.53$, ArH), 7.25 (s, 4H, ArH), 6.65 (s, 4H, ArH), 4.00 (s, 4H, CH_2CN), 3.55 (s, 8H, $ArCH_2Ar$), 3.22 (s, 4H, CH_2CN), 2.03 (s, 6H, CH_3)	167.83 (CH_3CO), 163.51 (ArCO), 147.29 (C–O), 147.01 (C–O), 134.27, 133.46, 133.42, 129.79, 129.53, 129.27, 128.87, 128.15, 127.26, 126.36 (Ar), 118.94 (CH_2CN), 117.66 (CH_2CN), 35.92 ($ArCH_2Ar$), 21.34 (CH_2CN), 20.76 (CH_3COO)
12b[c] (94)	381–382	7.88 (t, 2H, $J = 6.57$ and 7.41, ArH), 7.66 (t, 4H, $J = 7.08$ and 7.41, ArH), 7.57 (d, 4H, $J = 7.11$, ArH), 7.19 (s, 4H, ArH), 6.65 (s, 4H, ArH), 3.97 (s, 4H, CH_2CN), 3.55 (s, 8H, $ArCH_2Ar$), 3.20 (s, 4H, CH_2CN), 2.25 (q, 4H, $J = 6.45$ and 7.11, CH_2CH_3), 1.14 (t, 6H, $J = 7.11$ and 6.45, CH_3CH_2)	171.22 (CH_3CH_2CO), 163.54 (ArCO), 147.33 (C–O), 147.14 (C–O), 134.25, 133.65, 133.50, 129.61, 129.52, 129.37, 128.88, 128.16, 127.29, 126.29 (Ar), 118.67 (CH_2CN), 117.66 (CH_2CN), 36.03 ($ArCH_2Ar$), 26.31 (CH_2CH_3), 21.39 (CH_2CN), 21.32 (CH_2CN), 8.47 (CH_3CH_2)
12c (90)	382–384	7.90 (t, 2H, $J = 6.87$, ArH), 7.68 (t, 4H, $J = 7.87$ and 7.41, ArH), 7.59 (d, 4H, $J = 7.62$, ArH), 7.20 (s, 4H, ArH), 6.65 (s, 4H, ArH), 3.97 (s, 4H, CH_2CN), 3.54 (s, 8H, $ArCH_2Ar$), 3.23 (s, 4H, CH_2CN), 2.27 (t, 4H, $J = 6.99$, CH_2CO), 1.68 (m, 4H, $CH_2CH_2CH_3$), 1.07 (t, 6H, $J = 5.91$ and 7.53, CH_3CH_2)	170.38 (CH_2CH_2CO), 163.52 (ArCO), 147.31 (C–O), 147.14 (C–O), 134.30, 133.56, 133.49, 129.65, 129.55, 129.43, 128.90, 128.14, 127.12, 126.24 (Ar), 118.65 (CH_2CN), 117.66 (CH_2CN), 36.03 ($ArCH_2Ar$), 34.63 (CH_2CO), 21.40 (CH_2CN), 21.35 (CH_2CN), 17.27 (CH_2CH_3), 13.46 (CH_3CH_2)
12d (86)	306–308	7.89 (t, 2H, $J = 6.96$ and 6.99, ArH), 7.68 (t, 4H, $J = 7.08$ and 7.56, ArH), 7.59 (d, 4H, $J = 7.44$, ArH), 7.19 (s, 4H, ArH), 6.65 (s, 4H, ArH), 3.94 (s, 4H, CH_2CN), 3.53 (s, 8H, $ArCH_2Ar$), 3.23 (s, 4H, CH_2CN), 2.25 (t, 4H, $J = 7.38$ and 7.41, CH_2CO), 1.67 (m, 4H, CH_2), 1.37–1.46 (m, 12H, $CH_2CH_2CH_2$), 0.93 (bs, 6H, CH_3CH_2)	170.51 (CH_2CH_2CO), 163.51 (ArCO), 147.31 (C–O), 147.14 (C–O), 134.30, 133.56, 133.48, 129.62, 129.56, 129.42, 128.90, 128.13, 126.99, 126.24 (Ar), 118.54 (CH_2CN), 117.64 (CH_2CN), 36.00 ($ArCH_2Ar$), 33.00 (CH_2CO), 31.29 (CH_2), 28.30 (CH_2), 24.00 (CH_2), 22.03 (CH_2), 21.42 (CH_2CN), 21.35 (CH_2CN), 13.86 (CH_3CH_2)
12e (84)	356–358	7.89 (t, 2H, $J = 7.32$ and 6.09, ArH), 7.67 (t, 4H, $J = 7.77$ and 7.95, ArH), 7.57 (d, 4H, $J = 8.07$, ArH), 7.24 (s, 4H, ArH), 6.65 (s, 4H, ArH), 3.99 (s, 4H, CH_2CN), 3.82 (t, 4H, $J = 6.63$ and 6.66, CH_2Cl), 3.56 (s, 8H, $ArCH_2Ar$), 3.22 (s, 4H, CH_2CN), 2.36 (t, 4H, $J = 7.11$ and 7.53, CH_2CO), 2.13 (t, 4H, $J = 6.99$ and 6.87, CH_2CH_2)	169.58 (CH_2CH_2CO), 163.54 (ArCO), 147.21 (C–O), 147.17 (C–O), 134.29, 133.75, 133.53, 129.54, 129.46, 128.89, 128.12, 127.25, 126.46 (Ar), 118.85 (CH_2CN), 117.63 (CH_2CN), 44.43 (CH_2Cl), 35.95 ($ArCH_2Ar$), 30.25 (CH_2CO), 26.85 (CH_2CH_2), 21.58 (CH_2CN), 21.35 (CH_2CN)
12f[d] (91)	403–405	7.91 (t, 2H, $J = 6.99$ and 7.53, ArH), 7.72 (t, 4H, $J = 7.31$ and 7.65, ArH), 7.59–7.64 (m, 4H, ArH), 7.17 (s, 4H, ArH), 6.63 (s, 4H, ArH), 4.00 (s, 4H, CH_2CN), 3.56 and 3.47 (dd, 8H, $J = 15.45$ and 15.57, $ArCH_2Ar$), 3.23 (s, 4H, CH_2CN), 1.21 (bs, 6H, CH and CH_2), 1.10 (bs, 4H, CH_2)	171.92 (CHCO), 163.47 (ArCO), 147.46 (C–O), 146.73 (C–O), 135.06, 134.40, 133.46, 133.27, 130.30, 129.85, 129.57, 129.26, 129.19, 128.86, 128.12, 127.01, 126.26 (Ar), 118.90 (CH_2CN), 117.61 (CH_2CN), 35.89 ($ArCH_2Ar$), 21.57 (CH_2CN), 21.39 (CH_2CN), 12.63 ($CHCH_2$), 9.59 (CH_2CH)
13a (94)	405–407	7.82 (t, 4H, $J = 7.08$ and 7.47, ArH), 7.74 (d, 8H, $J = 7.92$, ArH), 7.63 (t, 8H, $J = 7.92$ and 7.41, ArH), 6.68 (s, 8H, ArH), 3.53 (s, 8H, $ArCH_2Ar$), 3.06 (s, 8H, CH_2CN)	162.75 (C=O), 147.04 (C–O), 133.57, 133.44, 129.48, 129.19, 127.90, 127.53, 125.15 (Ar), 115.46 (CH_2CN), 35.74 ($ArCH_2Ar$), 21.39 (CH_2CN)
13b[e] (90)	441–443	7.98 (d, 2H, $J = 7.11$, ArH), 7.84 (t, 4H, $J = 7.50$ and 6.99, ArH), 7.71 (d, 4H, $J = 6.99$, ArH), 7.60 (s, 8H, ArH), 6.72 (s, 8H, ArH), 3.53 (s, 8H, $ArCH_2Ar$), 3.34 (s, 4H, CH_2CN), 3.30 (s, 4H, CH_2CN), 2.64 (s, 6H, $ArCH_3$)	163.48 (ArCO), 147.34 (C–O), 147.26 (C–O), 145.12 (CCH_3), 134.61, 133.77, 133.72, 130.00, 129.81, 129.74, 129.51, 129.17, 128.99, 128.09, 126.35, 126.15, 125.39 (Ar), 117.62 (CH_2CN), 117.52 (CH_2CN), 35.78 ($ArCH_2Ar$), 21.64 (CH_2CN), 21.51 (CH_2CN), 21.45 (CH_3)
13c (89)	431–433	7.96 (bs, 2H, ArH), 7.82 (bs, 4H, ArH), 7.75 (s, 4H, ArH), 7.72 (bs, 8H, ArH), 3.54 (s, 8H, $ArCH_2Ar$), 3.38 (s, 4H, CH_2CN), 3.34 (s, 4H, CH_2CN), 1.48 (s, 18H, *t*-Bu)	163.46 (ArCO), 157.40 (CBu-*t*), 147.39 (C–O), 147.32 (C–O), 134.65, 133.79, 130.01, 129.88, 129.76, 129.00, 128.07, 126.12, 126.08, 125.63, 125.54 (Ar), 117.51 (CH_2CN), 117.33 (CH_2CN), 35.70 ($ArCH_2Ar$), 35.01 (*t*-Bu), 30.81 (*t*-Bu), 21.54 (CH_2CN), 21.45 (CH_2CN)

Table 4. (continued)

Product (% yield)	mp (°C)	^{1}H NMR (300 MHz) (DMSO-d_6/TMS) δ, *J* (Hz)	^{13}C NMR (300 MHz) (DMSO-d_6/TMS) δ
13d (87)	444–446	8.15 (d, 2H, *J* = 7.11, ArH), 7.85–7.95 (m, 8H, ArH), 7.61–7.72 (m, 6H, ArH), 7.57 (d, 2H, *J* = 7.41, ArH), 6.79 (s, 4H, ArH), 6.72 (s, 4H, ArH), 3.53 (s, 8H, ArCH$_2$Ar), 3.47 (s, 4H, CH$_2$CN), 3.34 (s, 4H, CH$_2$CN)	163.50 (ArCO), 162.84 (ArCO), 147.38 (C–O), 147.12 (C–O), 139.71 (CCl), 134.61, 134.66, 133.89, 133.74, 131.28, 131.05, 130.11, 129.78, 129.40, 129.05, 128.64, 128.08, 126.99, 126.40 (Ar), 117.73 (CH$_2$CN), 117.55 (CH$_2$CN), 35.63 (ArCH$_2$Ar), 21.66 (CH$_2$CN), 21.55 (CH$_2$CN)
13e (83)	395–397	8.57 (d, 4H, *J* = 8.07, ArH), 7.99 (t, 2H, *J* = 7.83 and 6.45, ArH), 7.84 (t, 8H, *J* = 8.07 and 7.53, ArH), 7.70 (d, 4H, *J* = 7.50, ArH), 6.81 (s, 4H, ArH), 6.76 (s, 4H, ArH), 3.64 and 3.57 (dd, 8H, *J* = 15.57 and 15.45, ArCH$_2$Ar), 3.36 (bs, 8H, CH$_2$CN)	163.54 (ArCO), 162.18 (ArCO), 151.06 (CNO$_2$), 147.53 (C–O), 147.02 (C–O), 134.67, 134.11, 133.72, 133.47, 130.86, 130.21, 129.74, 129.06, 128.81, 128.11, 126.88, 126.80, 123.96 (Ar), 117.91 (CH$_2$CN), 117.53 (CH$_2$CN), 35.59 (ArCH$_2$Ar), 21.71 (CH$_2$CN), 21.53 (CH$_2$CN)
13f (82)	380–382	8.22 (s, 2H, ArH), 8.00 (d, 2H, *J* = 6.50, ArH), 7.92 (t, 4H, *J* = 6.60 and 5.88, ArH), 7.82 (d, 4H, *J* = 6.45, ArH), 7.72 (s, 4H, ArH), 7.00 (s, 4H, ArH), 6.73 (s, 4H, ArH), 3.82 (s, 4H, CH$_2$CN), 3.61 (d, 4H, *J* = 14.94, ArCH$_2$Ar), 3.47 (s, 4H, CH$_2$CN), 3.45 (d, 4H, *J* = 12.57, ArCH$_2$Ar)	163.52 (ArCO), 162.13 (ArCO), 147.52 (C–O), 147.02 (C–O), 134.75, 133.94, 133.68, 133.60, 131.90, 130.38, 129.94, 129.88, 129.60, 129.21, 128.18, 128.03, 126.42, 126.34 (Ar), 117.66 (CH$_2$CN), 35.15 (ArCH$_2$Ar), 21.68 (CH$_2$CN)
13g (80)	370 (decomposed)	9.23 (s, 2H, ArH), 8.76 (s, 4H, ArH), 8.02 (t, 2H, *J* = 6.87, ArH), 7.87–7.92 (m, 4H, ArH), 7.76 (d, 4H, *J* = 7.92, ArH), 7.02 (s, 4H, ArH), 6.77 (s, 4H, ArH), 3.84 and 3.54 (dd, 8H, *J* = 15.03 and 15.06, ArCH$_2$Ar), 3.36 (s, 4H, CH$_2$CN), 3.34 (s, 4H, CH$_2$CN)	163.60 (ArCO), 161.62 (ArCO), 148.26 (CNO$_2$), 147.76 (C–O), 146.85 (C–O), 134.79, 134.29, 133.70, 131.92, 130.53, 129.85, 129.52, 129.24, 129.16, 128.12, 127.34, 126.69, 123.25 (Ar), 118.76 (CH$_2$CN), 117.55 (CH$_2$CN), 35.24 (ArCH$_2$Ar), 21.59 (CH$_2$CN), 21.37 (CH$_2$CN)
14a (93)	381–383	7.12 (s, 4H, ArH), 7.11 (s, 4H, ArH), 3.96 (s, 4H, CH$_2$CN), 3.91 (s, 4H, CH$_2$CN), 3.61 (s, 8H, ArCH$_2$Ar), 1.80 (q, 4H, *J* = 7.41, 7.23 and 7.29, CH$_2$CH$_3$), 1.58 (s, 6H, COCH$_3$), 0.89 (t, 6H, *J* = 7.41 and 7.20, CH$_3$CH$_2$)	170.80 (CH$_3$CH$_2$CO), 167.35 (CH$_3$CO), 147.14 (C–O), 134.30, 133.22, 133.16, 128.80, 128.65, 127.89, 127.71 (Ar), 119.02 (CH$_2$CN), 118.77 (CH$_2$CN), 36.37 (ArCH$_2$Ar), 25.77 (CH$_2$CO), 21.37 (CH$_2$CN), 21.30 (CH$_2$CN), 19.95 (COCH$_3$), 8.25 (CH$_3$)
14b[f] (93)	188–190	7.10 (s, 8H, ArH), 3.91 (s, 8H, CH$_2$CN), 3.60 (s, 8H, ArCH$_2$Ar), 1.75 (q, 8H, *J* = 7.29 and 6.03, CH$_2$CH$_3$), 0.92 (t, 12H, *J* = 7.11 and 6.59, CH$_3$CH$_2$)	170.83 (C=O), 147.24 (C–O), 133.28, 128.70, 127.76 (Ar), 118.76 (CH$_2$CN), 36.41 (ArCH$_2$Ar), 25.74 (CH$_2$CH$_3$), 21.36 (CH$_2$CN), 8.25 (CH$_3$CH$_2$)
14c (90)	360–362	7.10 (bs, 8H, ArH), 3.92 (bs, 8H, CH$_2$CN), 3.61 (bs, 8H, ArCH$_2$Ar), 1.63–1.73 (m, 8H, CH$_2$CO), 1.43–1.49 (m, 4H, CH$_2$CH$_3$), 0.87–0.93 (m, 12H, CH$_3$CH$_2$)	170.86 (CH$_3$CH$_2$CO), 169.81 (CH$_3$CO), 147.25 (C–O), 133.22, 128.71, 128.52, 127.86, 127.61 (Ar), 118.77 (CH$_2$CN), 118.70 (CH$_2$CN), 36.49 (ArCH$_2$Ar), 34.10 (CH$_2$), 25.71 (CH$_2$), 21.41 (CH$_2$CN), 16.94 (CH$_2$), 13.29 (CH$_3$), 8.26 (CH$_3$)
14d (86)	262–265 (sharp melting point)	–[g]	170.86 (C=O), 169.90 (C=O), 147.25 (C–O), 147.19 (C–O), 133.17, 129.06, 128.68, 128.45, 127.86, 127.46 (Ar), 118.78 (CH$_2$CN), 118.54 (CH$_2$CN), 36.46 (ArCH$_2$Ar), 32.38 (CH$_2$CO), 31.28 (CH$_2$CO), 28.20 (CH$_2$), 25.69 (CH$_2$), 23.72 (CH$_2$), 21.96 (CH$_2$), 21.42 (CH$_2$CN), 21.34 (CH$_2$CN), 13.80 (CH$_3$), 8.23 (CH$_3$)
14e (81)	154 (softening) 210–212 (liquid)	7.14 (s, 4H, ArH), 7.12 (s, 4H, ArH), 3.95 (s, 4H, CH$_2$CN), 3.93 (s, 4H, CH$_2$CN), 3.71 (t, 4H, *J* = 6.75 and 6.15, CH$_2$Cl), 3.62 (bs, 8H, ArCH$_2$Ar), 1.95 (t, 4H, *J* = 6.87 and 6.69, CH$_2$), 1.76 (m, 8H, CH$_2$), 0.92 (t, 6H, *J* = 7.35, CH$_2$)	170.76 (CO), 169.06 (CO), 147.23 (C–O), 147.02 (C–O), 133.29, 133.22, 128.70, 128.43, 127.97, 127.66 (Ar), 118.89 (CH$_2$CN), 118.69 (CH$_2$CN), 44.22 (CH$_2$Cl), 36.32 (ArCH$_2$Ar), 29.50 (CH$_2$), 26.52 (CH$_2$), 25.67 (CH$_2$), 21.58 (CH$_2$CN), 21.31 (CH$_2$CN), 8.19 (CH$_3$)

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[a] Anal. calcd. for $C_{56}H_{44}N_4O_8$: C, 74.65; H, 4.92; found: C, 74.51; H, 4.75.

[b] Anal. calcd. for $C_{58}H_{48}N_4O_8$: C, 74.98; H, 5.21; found: C, 74.96; H, 5.00.

[c] Anal. calcd. for $C_{56}H_{44}N_4O_8$: C, 74.65; H, 4.92; found: C, 74.51; H, 4.75.

[d] Anal. calcd. for $C_{58}H_{44}N_4O_8$: C, 75.31; H, 4.79; found: C, 75.38; H, 4.55.

[e] Anal. calcd. for $C_{66}H_{48}N_4O_8$: C, 77.33; H, 4.72; found: C, 77.18; H, 4.50.

[f] Anal. calcd. for $C_{48}H_{44}N_4O_8$: C, 71.63; H, 5.51; found: C, 71.72; H, 5.48.

[g] Mixture of conformers. Minor product (partial cone conformer): $\delta = 7.37, 7.32, 6.93, 6.54$. Major product (1,3-alternate conformer): $\delta = 7.12$.

In the ^{13}C NMR spectra the resonance associated with the ArCH$_2$Ar methylene carbon appears near $\delta = 31$ for calix[4]arenes in the cone conformation and near $\delta = 37$ for those in the 1,3-alternate conformation.[8] Thus, the tetraesters **9a–p** show a ^{1}H NMR singlet at $\delta = 3.60 \pm 0.10$ (except for **9o** with $\delta = 3.98$) and a ^{13}C NMR line at $\delta = 35.45 \pm 0.4$ (except for **9f** with $\delta = 36.78$, **9o** with $\delta = 34.30$, and **9p** with $\delta = 34.44$) characteristic of a 1,3-alternate conformation. Similarly, tetraesters **9r–v** (all four R groups identical alkyl moieties) show a ^{1}H NMR singlet at $\delta = 3.62 \pm 0.03$ and a ^{13}C NMR line at $\delta = 36.43 \pm 0.13$ (except **9u** at $\delta = 37.44$). In theory, all of the mixed tetraesters **11–14** in a 1,3-alternate conformation should show a close lying pair of doublets for the $ArCH_2Ar$ protons. In fact, however, only compounds **11d, 11f, 12f, 13e, 13f and 13g** display this feature ($\Delta\delta = 0.09 \pm 0.02$ except for **13f** and **13g** for which it is 0.20 and 0.30, respectively), all the remaining compounds of this series showing only a singlet at $\delta = 3.57 \pm 0.06$. The ^{13}C NMR spectra of these compounds have a resonance in the region $\delta = 36.19 \pm 0.30$.

The conformational assignments of the 1,3-diesters **10a–w** is less secure. They all show a pair of doublets in the ^1H NMR spectra with $\Delta\delta$ values ranging from 0.04 to 0.33 ppm but in most cases falling near 0.10 ppm. If these compounds were in a true cone conformation the $\Delta\delta$ values would be expected to be closer to 1.0 ppm.[5] In the ^{13}C NMR spectra the resonance associated with the $ArCH_2Ar$ methylene carbon falls in most cases at $\delta = 33.4 \pm 0.4$, which is somewhat closer to that expected for a cone than for a 1,3-alternate conformer. Only compounds **10b** and **10d** show a resonance at lower field ($\delta = 32.78$ and 32.56) while compound **10w** shows it at higher field ($\delta = 34.52$). It is concluded that these data are best interpreted as indicating a flattened cone conformation for the 1,3-diesters.

In contrast to *p-tert*-butylcalix[4]arene **(1)** and *p*-H-calix[4]arene **(2)** in which the conformational outcome is dependent on the aroylating agent, *p*-cyanomethylcalix[4]arene **(3)** appears to be insensitive to this feature, producing tetraesters in only the 1,3-alternate conformation with all of the monosubstituted benzoyl chlorides. The reactions are less clean with certain disubstituted benzoyl chlorides, particularly with 3,5-dinitrobenzoyl chloride which affords the tetraester in the 1,3-alternate conformation in only 52% yield accompanied by the partial cone conformer. Also, attempts to obtain the 1,3-diester **10p** from **3** and 3,5-dinitrobenzoyl chloride via the $AlCl_3$ method or with 3,5-dinitrobenzoic acid via the phenyl dichlorophosphate method were completely unavailing, although the latter procedure works smoothly with **1**.[9]

Most reagents were purchased from Aldrich Chemical Co. and were used without further purification. THF was freshly distilled from K-benzophenone; DMF, MeCN and acetone were distilled and stored over 3 and 4 Å Linde sieves for at least 10 d. Flash chromatography employed J. T. Baker 40 µm silica gel; column chromatography employed Aldrich 70–230 mesh, 60 Å silica gel. TLC was performed on 250 µm silica gel plates, and preparative TLC (PTLC) on 1000 µm silica gel plates containing a fluorescent indicator. Melting points (uncorrected) were taken in sealed and evacuated capillary tubes on a MEL-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 500 °C thermometer calibrated against a thermocouple. NMR spectra were recorded at 20 ± 1 °C on a Varian XL-300 spectrometer, and the chemical shifts are reported as δ values referenced to tetramethylsilane (TMS) at $\delta = 0.00$ as an internal standard. ^{13}C NMR spectra are referenced to either $CDCl_3$ ($\delta = 77.00$), DMSO ($\delta = 40.0$ ppm) or to TMS ($\delta = 0.00$ ppm) and were also recorded at 20 ± 1 °C. All the reagents used for crystallizations were strictly anhydrous. Microanalytical samples were dried for 36–72 h at 111 °C using toluene or at 140 °C using xylene at 1–2 mmHg. Analyses were carried out by Desert Laboratories, Tucson, AZ. Solvent of crystallization was retained in some of the analytical samples and affected the elemental analysis.[10] In such cases, best fits between the analytical values and appropriate increments of solvents were used.

1,3-Diesters 10 via $AlCl_3$; General Method:

In a 250 mL 3-necked round-bottomed flask was placed 6.70 g (50 mmol) of white, powdered, anhydr. $AlCl_3$, and 60 mL of a CH_2Cl_2–DMF (5:1) mixture was carefully added (white fumes). The flask was cooled in an ice bath, the reaction mixture was stirred for 10 min in an N_2 atmosphere, and 0.58 g (1.0 mmol) of *p*-cyanomethylcalix[4]arene **(3)** was added in portions. A solution of the aroyl or acyl halide (6–10 mmol) in 5 mL of CH_2Cl_2 was then added dropwise over 20 min to the stirred reaction mixture. The flask was allowed to warm to r.t. (22–25 °C) and stirred for an additional 16–24 h. On completion of the reaction (as indicated by TLC), 50 mL of ice-cold water was added slowly with stirring followed by 10% HCl (ca. 40–60 mL) to destroy the unreacted $AlCl_3$. The organic layer was separated, and the water layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined extract was evaporated under reduced pressure on a rotary evaporator to leave a viscous residue which was stirred first with hexane (2 × 50 mL) and then with MeOH (3 × 50 mL) to give a white or gray solid. The product was purified by trituration with acetone to afford the product as a white powder. In some cases the product was soluble in acetone, in which case a small amount of acetone was used to dissolve the product, and 100 mL of a mixture of hexane–methanol (2:3 ratio) was added dropwise until a white precipitate formed which was separated by filtration.

Tetraesters 4, 5, and 9 of Uniform Functionality via 1-Methylimidazole; General Method:

In a 250 mL 3-necked round-bottomed flask was placed a mixture of 1–2 mL of 1-methylimidazole and 60–90 mL of freshly distilled and dried MeCN to which the aroyl or acyl chloride (10–20 mmol) was added dropwise over 5–10 min. The flask was cooled in an ice bath, and the contents were stirred for 20 min in an atmosphere of N_2. To the stirred solution, 1.00 mmol of freshly dried *p-tert*-butylcalix[4]arene **(1)**, *p*-H-calix[4]arene **(2)**, or *p*-cyano-methylcalix[4]arene **(3)** was added in portions. The flask was allowed to warm to r.t (22–25 °C), and the contents were stirred an additional 10–18 h. On completion of the reaction, the solvent was removed under reduced pressure on a rotary evaporator, and the residue was poured into ice-cold 10% HCl (ca. 30–40 mL) to give a white or light-yellow precipitate. In some cases a semi-solid was obtained which was extracted into CH_2Cl_2 (3 × 50 mL), the solvent then removed under reduced pressure to leave a viscous residue, and the residue poured, with stirring, into 50 mL of MeOH to give a white or light-yellow solid. The product was purified by triturating with an appropriate solvent or solvent mixture to afford the purified product.

Tetraesters 4, 5, and 9 of Uniform Functionality via Sodium Hydride; General Method:

A 1.25 g (30 mmol) sample of NaH (60% in oil dispersion) was placed in a 250 mL 3-necked round-bottomed flask and 50–100 mL of freshly distilled THF–DMF (4:1 or 5:1 ratio) was added. The mixture was stirred for 5 min, and 1.0 mmol of **1**, **2**, or **3** was added in portions over 30 min. A solution of the aroyl or acyl chloride (10–20 equiv) in THF was added dropwise over 5–10 min, considerable frothing occurring at this stage. The flask was then placed in an oil bath, and the contents were refluxed for an additional 10–28 h (in some cases the reactions were carried out at r.t.) in an atmosphere of N_2. On completion of the reaction, solvent (THF) was removed under reduced pressure using a rotary evaporator, the residue was poured into stirred ice-cold 10% HCl (ca. 40–60 mL) to destroy unreacted NaH, and the product was worked up as described above for the 1-methylimidazole method.

Tetraesters 11, 12, 13, and 14 of Mixed Functionality via 1-Methylimidazole; General Method:

A solution of 1 mL of 1-methylimidazole in 50 mL of dry MeCN was placed in a 150 mL 3-necked round-bottomed flask filled with N_2, cooled in an ice bath, and treated dropwise with 10–15 equiv of the appropriate aroyl or acyl chloride over 10–15 min. After 20 min of stirring 0.23 g (0.33 mmol) of 5,11,17,23-tetracyanomethyl-25,27-bis(propionyloxy)-26,28-dihydroxycalix[4]arene **(10s)** was added in portions. The flask was allowed to warm to r.t., stirred for an additional 10–18 h, and worked up as described above to give products **11a–f** and **14a–e** as white solids.

The mixed tetraesters **12a–f** and **13a–g** were prepared in a similar fashion using 0.27 g (0.33 mmol) of 5,11,17,23-tetracyanomethyl-25,27-bis(benzoyloxy)-26,28-dihydroxycalix[4]arene **(10a)**.

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(1) Paper number 35 in a series entitled *Calixarenes*. For paper number 34 see:
Sharma, S. K.; Gutsche, C. D. *Tetrahedron Lett.* **1993**, *34*, 5389.

(2) The term "calixarene" is variously employed in different contexts. In colloquial usage (as employed in a discussion section), it implies the presence of hydroxy groups as, for instance, in "*p-tert*-butylcalix[4]arene" for **1** and "*p*-H-calix[4]arene" for **2**. In the more precise and complete specification of a compound (as used in an experimental section) it implies only the basic skeleton to which the substituents, including the OH groups, are attached at positions designated by appropriate numbers.

(3) Gutsche, C. D. *Calixarenes*; Monographs in Supramolecular Chemistry; Stoddart, J. F., Ed.; Royal Society of Chemistry: London, 1989.

(4) Iqbal, M.; Mangiafico, T.; Gutsche, C. D. *Tetrahedron* **1987**, *43*, 4917.

(5) Gutsche, C. D.; Nam, K. C. *J. Am. Chem. Soc.* **1988**, *110*, 6153.

(6) Sharma, S. K.; Gutsche, C. D. *Tetrahedron Lett.* **1993**, 5389.

(7) See, K. A.; Ph. D. Thesis, Washington University, 1991, p 13.

(8) Jaime, C.; deMendoza, J.; Prados, P.; Nieto, P. M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.

(9) See, K. A.; Fronczek, F. R.; Watson, W. H.; Kashyap, R. P.; Gutsche, C. D. *J. Org. Chem.* **1991**, *56*, 7256.

(10) It is interesting to note that strong solvent retention occurs only with the 1,3-diesters in the cone conformation. It is not known whether this a consequence of the free phenolic groups, the cone conformation, or both. The elemental analyses for these compounds, listed in Table 3, all show values for C and H that are lower than the calculated values even after long drying of the compounds at elevated temperature under vacuum. Elemental analyses show that the amount of Cl present in the samples is less than 0.05 %, indicating that the occluded solvent is neither $CHCl_3$ nor CH_2Cl_2. That it is H_2O is indicated by a ^1H NMR spectral analysis which shows that the integration ratio of the $H_2O/CHCl_3$ peaks changes from 2:1 for $CDCl_3$ alone to ca. 3:1 when the calixarene is dissolved in the $CDCl_3$. Concomitantly, the H_2O resonance changes from a sharp line to a considerably broadened resonance. When 3/4 of a mole of H_2O is added to the molecular formulas of the compounds analyzed, the found values agree very closely with the calculated values in every case, providing reassurance that H_2O is, indeed, the occluded molecule.