Selective Arylmethylation, Arylmethenylation and Aroylation of Mono- and Tetra-*p*-Cyanomethylcalix[4]arene[1]

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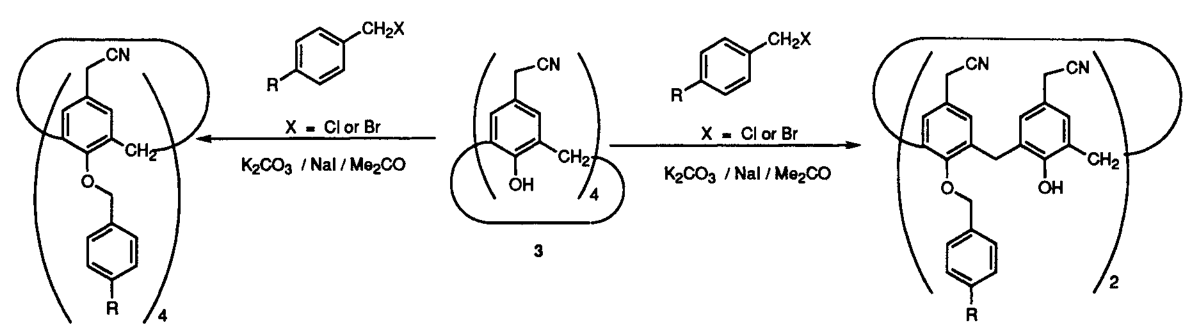
Tetra-*p*-cyanomethylcalix[4]arene (**3**) is selectively converted to its tetrabenzyl ethers **4** (1,3-alternate conformer) and 1,3-dibenzyl ethers **5** (cone conformer) by reaction with benzyl halides in the presence of variable amounts of potassium carbonate. Mono-*p*-cyanomethylcalix[4]arene (**6**) gives exclusively the cone conformer of the 1,3-disubstituted product **7** (benzyl moiety attached to the unsubstituted rings). Aroylation of **6** in the presence of sodium hydride gives tetrasubstituted product **9**, whereas with aluminum chloride it produces an easily separable mixture of 1,3-disubstituted compounds **10** and **11**. Surprisingly, no regioselectivity is achieved using 1-methylimidazole as the base. On the other hand, **6** reacts with 4-bromobenzenesulfonyl chloride under the same reaction conditions to produce the cone conformer of the tetrasubstituted product **12**. Reactions of **6** with benzyl halides or benzaldehydes using sodium hydride as a base give the fully benzylated compounds **8** or the benzal derivatives **13**, respectively.

p-tert-Butylcalix[4]arene,[2,3] easily prepared in good yield by a one-pot reaction of *p-tert*-butylphenol and formaldehyde,[4] can be converted to *p*-cyanomethylcalix[4]arene (**3**) in a four-step sequence.[5] Compound **3** and its monosubstituted analog **6**[6] are useful precursors to carboxylic acids and amines and can also undergo benzylation[7] and arylmethenylation[8] at the carbons α to the cyano groups. The present work extends these investigations and includes studies of the di- and tetra-*O*-benzylation of **3** and **6**, the di- and tetra-*O*-aroylation of **6**, and the arylmethenylation of **6**.

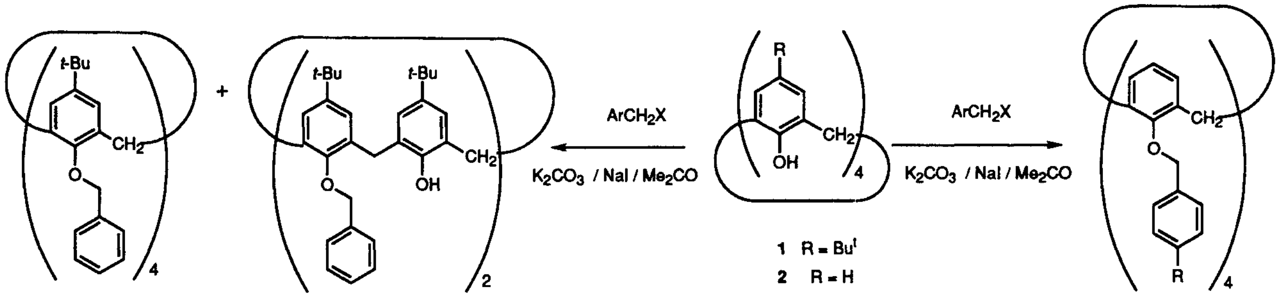
Reactions of *p*-cyanomethylcalix[4]arene (**3**) with benzyl halides in the presence of a 50-fold excess of potassium carbonate yields tetra-*O*-benzylated products **4a–e** in the 1,3-alternate conformation. Increasing the quantity of potassium carbonate (50–100 equiv) reduces the necessary reaction time except in the case of *p*-nitrobenzyl halide in which case product decomposition occurs. The 1,3-dibenzyl ethers **5a–h** were obtained by using only 2–3 equivalents of potassium carbonate with 2.3 equivalents of benzyl halide, carrying out the reaction at room temperature for shorter times to give 60–85% of the desired product along with the starting material which is easily recovered by column chromatography. The rates of these reactions are dependent on the *p*-substituent of the benzylating agent, electron-withdrawing groups such



3

4a. R = H
4b. R = F
4c. R = CH_3
4d. R = Bu^t
4e. R = NO_2

5a. R = H
5b. R = F
5c. R = Br
5d. R = CH_3
5e. R = OCH_3
5f. R = CN
5g. R = NO_2
5h. R = Bu^t



16

17

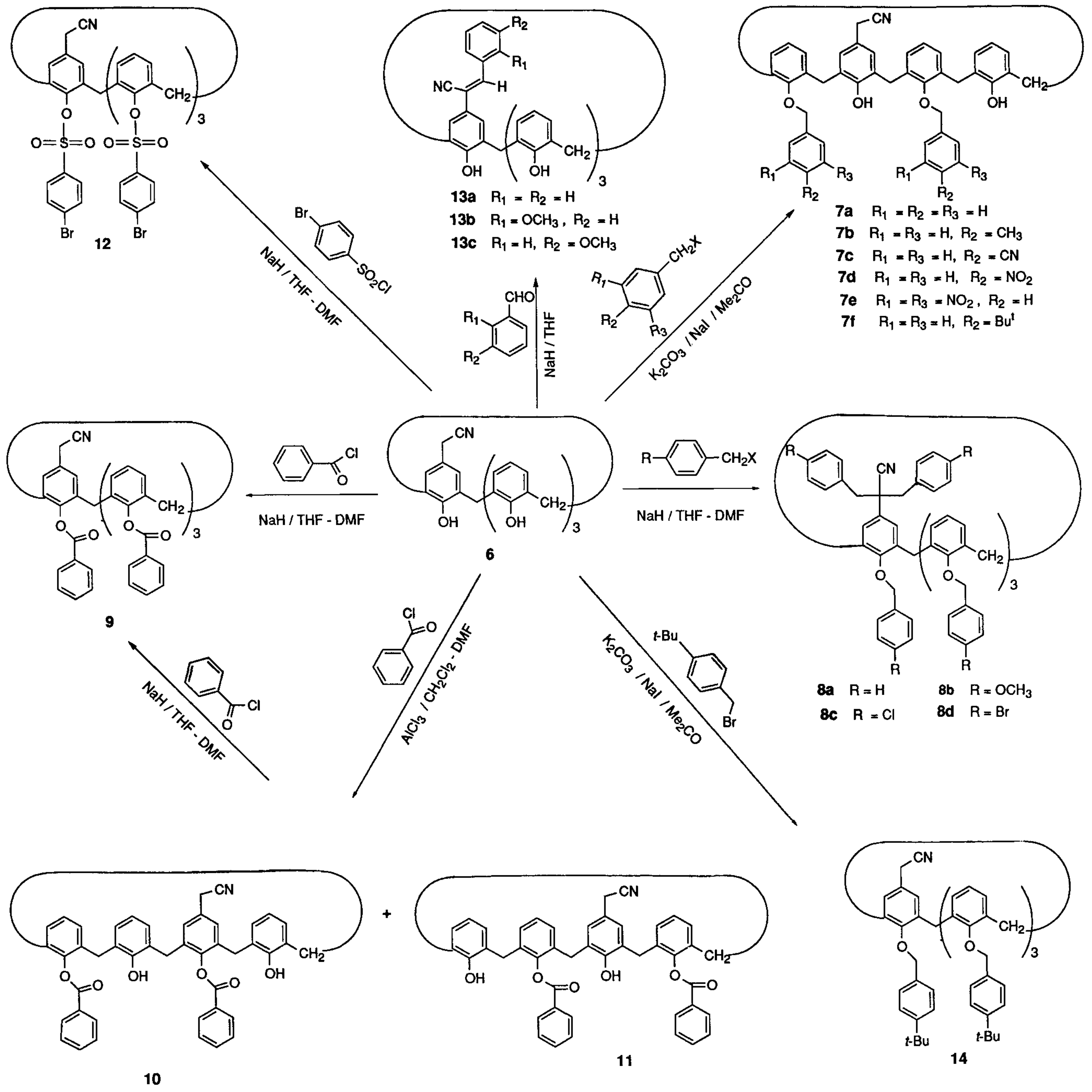
1 R = Bu^t
2 R = H

15a R_1 = H
15b R = Bu^t

as nitro facilitating the reaction and electron-releasing groups such as alkyl and methoxyl slowing it down. Benzyl bromides react more rapidly than benzyl chlorides, and in the latter case it is advisable to add sodium iodide to the reaction mixture.

In contrast to the tetracyanomethyl compound **3**, the monocyanomethyl compound **6** presents the possibility of regioisomeric 1,3-di-*O*-substitution. Treatment of **6** with various benzyl halides in the presence of potassium carbonate yields 1,3-diethers **7** in which both benzyl moieties are attached to *p*-H-phenolic residues, indicating that in the calix[4]arene the pK_a of *p*-H-phenol rings is lower than that of *p*-cyanomethylphenol rings. When *p*-H-calix[4]arene (**2**) is benzylated in the presence of a large excess of potassium carbonate under the condition used for the preparation of **4** (either at room temperature or reflux), it gives the tetrasubstituted products **15a** and **15b** in the 1,3-alternate conformation. On the other hand, *p*-*tert*-butylcalix[4]arene (**1**) under the same conditions gives a mixture of 1,3-di- and tetrasubstituted products **17** and **16** in a 1 : 1 ratio at room temperature. Thus, the reactivity sequence for *O*-benzylation in the calix[4]arenes appears to be *p*-H-phenol > *p*-cyanomethylphenol > *p*-*tert*-butylphenol.

In esterification reactions **6** behaves like **1** and **2**.[9] Thus, benzoyl chloride in the presence of 1-methylimidazole as a base gives a mixture of products, while sodium hydride gives the tetrasubstituted product **9** in the 1,3-alternate



conformation. When aluminum chloride in dimethylformamide/dichloromethane is used, a mixture of **10** (major product) and **11** (minor product) in the cone conformations is produced. Treatment of **6** with *p*-bromobenzenesulfonyl chloride in the presence of sodium hydride produces the tetrasubstituted product **12** which, surprisingly, is in the cone conformation.

In arylmethylation[7] and arylmethenylation[8] reactions **6** behaves like **3**, *viz.* treatment with benzyl halides introduces arylmethyl groups onto the carbons α to the cyano groups to produce **8**, and treatment with benzaldehydes introduces arylmethenyl groups at these same positions to produce **13**.

Structures for the various products were established on the basis of ^{1}H and ^{13}C NMR spectroscopy, taking advantage of the characteristic patterns arising from the $ArCH_2Ar$ methylenes in the proton spectrum[3a] and the position of the resonance in the carbon spectrum.[10] For example, the tetrabenzyl ethers **4a–d** show a ^{1}H NMR singlet at $\delta = 3.55 \pm 0.04$ and a ^{13}C resonance at $\delta = 37$, commensurate with a 1,3-alternate conformation. The 1,3-dibenzyl ethers **5a–h**, on the other hand, show a pair of doublets in the $\delta = 3.27–3.43$ and 4.20–4.25 region of the ^{1}H NMR spectrum and a singlet at ca. $\delta = 31$ in the ^{13}C NMR spectrum commensurate with a cone conformation. Similar, but more complex, patterns are observed for the benzyl ethers obtained from **6** where, because of the lower symmetry of the molecules, the $ArCH_2Ar$ methylenes can give rise to four doublets in the ^{1}H NMR spectrum. Due to accidental overlap, however, fewer lines are sometimes observed as in the case of dibenzyl ether **7a** which shows only three doublets (ratio 2 : 1 : 1). In the arylmethylated products **8a–d** the $ArCH_2Ar$ methylenes appear as four well-resolved doublets, and the $ArCH_2O$ protons appear as two sharp singlets and a well-resolved pair of doublets. The diastereomeric $ArCH_2[CN]$ protons appear as an accidental singlet in **8a** and a well-resolved pair of doublets in **8b–d**. The ^{13}C NMR spectra of **8a–d** are commensurate with a cone conformation.

Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. THF was always freshly distilled from Na-benzophenone, and DMF and MeCN were stored over 3 Å and 4 Å Linde molecular sieves for at least 10 d. Flash chromatography was carried out with J.T. Baker 40 μm silica gel, and colum chromatography with Aldrich 70–230 mesh, 60 Å silica gel. TLC was performed on 250 μm silica gel plates, and preparative TLC on 1000 μm silica gel plates containing a fluorescent indicator. Melting points are uncorrected and were taken in sealed and evacuated melting point capillary tubes on a MEL-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 500 °C thermometer calibrated against a thermocouple. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer, and the chemical shifts are reported as δ values with units of ppm. ^{1}H NMR spectra are referenced to TMS at 0.00 ppm as an internal standard and recorded at r.t., and ^{13}C NMR spectra are referenced to either $CDCl_3$ (77.00 ppm), DMSO-d_6 (40.0 ppm) or to TMS (0.00 ppm) and also recorded at r.t. Microanalytical samples were dried for at least 72 h at 111 °C (toluene) or at 140 °C (xylene) at 1–2 mm, and the analyses were carried out by Desert Laboratories, Tucson, AZ. A half molecule of water was retained in some of the analytical samples even after prolonged drying, affecting the elemental analysis.[11]

Tetrabenzyl Ethers 4, 14 and 15 (1,3-Alternate Conformers); General Procedure:

Anhydrous, finely powdered K_2CO_3 (6.90 g, 50 mmol, 50 equiv) and NaI (0.5 g) were suspended in anhydr. acetone (100 mL) in a 250 mL round-bottomed flask and treated portionwise with 1 mmol of one of the following calixarenes: *p-tert*-butylcalix[4]arene **(1)** (0.64 g), calix[4]arene **(2)** (0.42 g), tetra-*p*-cyanomethylcalix[4]arene **(3)** (0.58 g), or mono-*p*-cyanomethylcalix[4]arene **(6)** (0.46 g). The reaction mixture was stirred in an atmosphere of N_2 for 10 min, and a solution of benzyl halide (15–20 equiv) in acetone (10 mL) was added slowly from a dropping funnel. The mixture was allowed to stir under reflux or at r.t., filtered, and the residue throughly washed with anhydr. acetone (100 mL). The combined acetone filtrate was concentrated under reduced pressure and poured into hexane or Et_2O (150 mL) to give a white to light yellow precipitate (in some cases a semisolid which was extracted with CH_2Cl_2) which was removed by filtration and washed with hexane. The product was stirred with MeOH (3 × 100 mL) for 30 min to remove unreacted benzyl halide, filtered and purified by column chromatography using $CHCl_3$ or CH_2Cl_2. An analytical sample was obtained by crystallization from $CHCl_3$ or CH_2Cl_2 either alone or in combination with hexane followed by stirring with anhydr. MeOH to remove solvent of crystallization, affording pure products **4a–e, 14** and **15a–b**. The physical and spectroscopic data are given in the Table.

1,3-Dibenzyl Ethers 5a–h (Cone Conformers); General Procedure:

To a suspension of anhydr. freshly powdered K_2CO_3 (0.30 g, 2.3 mmol, 2.3 equiv) and NaI (0.3 g) in anhydr. acetone (100 mL) in a 250 mL round-bottomed flask was added *p*-cyanomethylcalix[4]arene **(3)** (0.58 g, 1 mmol). The mixture was stirred in an atmosphere of N_2 for 10 min, and a solution of benzyl halide (2.3 equiv) in acetone (5 mL) was added slowly from a dropping funnel. The mixture was allowed to stir in a tightly sealed flask at r.t. and worked up according to the procedure described above to afford a mixture of the desired product and starting material. The product was separated by column chromatography via elution with $CHCl_3$ or CH_2Cl_2. The starting material was recovered by eluting with acetone or MeCN. An analytical sample was obtained by crystallization from $CHCl_3$ or CH_2Cl_2 to gave pure **5a–h**. The physical and spectroscopic data are given in the Table.

1,3-Dibenzyl Ethers 7a–f (Cone Conformers); General Procedure:

Anhydrous, finely powdered K_2CO_3 (1.38 g, 10 mmol, 10 equiv) and NaI (0.3 g) were suspended in anhydr. acetone (100 mL) in a 250 mL round-bottomed flask and mono-*p*-cyanomethylcalix[4]arene (**6**; 0.46 g, 1 mmol) was added. The mixture was stirred in an atmosphere of N_2 for 10 min, and a solution of benzyl halide (8–10 equiv) in acetone (10 mL) was added slowly from a dropping funnel. The mixture was allowed to stir at r.t. for 24 h and worked up as described above to give a single product (as confirmed by TLC) which were purified by column chromatography, eluting with $CHCl_3$ or CH_2Cl_2 followed by crystallization. The physical and spectroscopic data are given in the Table.

***C*- and *O*-Arylmethylated Compounds 8a–d; General Procedure:**

NaH (1.0 g, 25 mmol, 25 equiv, 60 % in oil dispersion) was placed in a 150 mL 3-necked round-bottomed flask followed by a mixture of THF/DMF (60 mL, 5 : 1), and the flask was purged with N_2. The flask was placed in an ice bath, maintaining the temperature at ca. 2–3 °C, and **6** (0.46 g, 1 mmol) was added. The flask was allowed to warm to r.t., and the contents were stirred for 10 min under a stream of N_2. A solution of benzyl halide (20 equiv) in anhydr. THF (10 mL) was added dropwise over a period of 30 min, and the mixture was allowed to stir at r.t. for 8 h. The solvent was removed under reduced pressure on a rotary evaporator, and the concentrated residue was neutralized with ice cold 10 % HCl to produce a light yellow precipitate (in some cases semisolid material, which was extracted with CH_2Cl_2). This was separated by filtration and triturated for 30 min with MeOH (100 mL) followed by hexane to leave a white solid. The product was purified by column chromatography using $CHCl_3$ as an eluent followed by recrystallization. The physical and spectroscopic data are given in the Table.

Table. Compounds **4, 5, 7–15** Prepared

Product[a]	Yield (%)	mp (°C)	^{1}H NMR (300 MHz) (CDCl$_3$/TMS) δ, J (Hz)	^{13}C NMR (75 MHz) (CDCl$_3$/TMS) δ
4a[b]	91	188–190	7.40–7.36 (m, 12 H, ArH), 7.02 (d, 8 H, ArH), 6.65 (s, 8 H, ArH), 4.75 (s, 8 H, Ar$\underline{C}\underline{H}_2$O), 3.59 (s, 8 H, Ar$\underline{C}\underline{H}_2$Ar), 2.93 (s, 8 H, CH$_2$CN)	155.48 ($\underline{C}$-OCH$_2$), 137.47, 134.39, 130.09, 128.31, 127.69, 127.16, 123.95 (ArC), 118.22 (CN), 72.29 (ArCH$_2$O), 37.18 (Ar$\underline{C}$H$_2$Ar), 22.18 ($\underline{C}$H$_2$CN)
4b	84	233–234	7.05–7.00 (m, 16 H, F-ArH), 6.68 (s, 8 H, ArH), 4.07 (s, 8 H, Ar$\underline{C}\underline{H}_2$O), 3.51 (s, 8 H, Ar$\underline{C}\underline{H}_2$Ar), 3.06 (s, 8 H, CH$_2$CN)	155.30 ($\underline{C}$-OCH$_2$), 134.25, 132.93, 129.84, 129.20, 124.00, 115.40, 115.11 (ArC), 118.07 (CN), 71.94 (ArCH$_2$O), 37.03 (Ar$\underline{C}$H$_2$Ar), 22.33 ($\underline{C}$H$_2$CN)
4c	80	212–213	7.17 (d, 8 H, J = 7.95, H$_3$C-$\underline{Ar}\underline{H}$), 6.93 (d, J = 7.68, H$_3$C-$\underline{Ar}\underline{H}$), 6.65 (s, 8 H, ArH), 4.70 (s, 8 H, ArCH$_2$O), 3.57 (s 8 H, Ar$\underline{C}\underline{H}_2$Ar), 2.94 (s, 8 H, CH$_2$CN), 2.45 (s, 12 H, CH$_3$)	155.40 ($\underline{C}$-OCH$_2$), 137.23, 134.50, 134.42, 130.17, 129.33, 127.04, 123.72 (ArC), 118.04 (CN), 73.32 (Ar$\underline{C}$H$_2$O), 37.12 (Ar$\underline{C}$H$_2$Ar), 22.17 ($\underline{C}$H$_2$CN), 21.32 (CH$_3$)
4d	82	276–278	7.49 (d, 8 H, J = 8.40, t-C$_4$H$_9$-$\underline{Ar}\underline{H}$), 7.03 (d, J = 8.10, t-C$_4$H$_9$-$\underline{Ar}\underline{H}$), 6.62 (s, 8 H, ArH), 4.75 (s, 8 H, Ar$\underline{C}\underline{H}_2$O), 3.54 (s, 8 H, Ar$\underline{C}\underline{H}_2$Ar), 3.00 (s, 8 H, CH$_2$CN), 1.44 (s, 36 H, t-C$_4H_9$)	155.75 ($\underline{C}$-OCH$_2$), 150.69 ($\underline{C}$-C$_4$H$_9$-t), 134.75, 134.39, 130.40, 126.78, 125.17, 123.50 (ArC), 118.17 (CN), 72.32 (ArCH$_2$O), 37.04 (Ar$\underline{C}$H$_2$Ar), 34.70 (t-C$_4$H$_9$), 31.56 (t-C$_4$H$_9$), 22.34 ($\underline{C}$H$_2$CN)
4e	76	175 (Softening) 295 (decomp)	8.16 (d, 8 H, J = 8.73, O$_2$N-ArH), 7.23 (d, 8 H, J = 8.58, O$_2$N-ArH), 6.72 (s 8 H, ArH), 4.87 (s, 8 H, Ar$\underline{C}\underline{H}_2$O), 3.77 (s, 8 H, Ar$\underline{C}\underline{H}_2$Ar), 3.08 (s, 8 H, CH$_2$CN)[c]	154.68 ($\underline{C}$-OCH$_2$), 146.79, 144.86, 134.17, 129.10, 127.87, 124.35, 122.91 (ArC), 118.20 (CN), 70.61 (Ar$\underline{C}$H$_2$O), 36.08 (Ar$\underline{C}$H$_2$Ar), 21.30 ($\underline{C}$H$_2$C)[c]
5a	83	291–293	7.86 (s, 2 H, ArOH), 7.55 (m, 4 H, ArH), 7.35 (m, 6 H, ArH), 7.02 (s, 4 H, ArH), 6.82 (s, 4 H, ArH), 5.03 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.25 (d, 4 H, J = 13.29, Ar$\underline{C}\underline{H}_2$Ar), 3.63 (s, 4 H, CH$_2$CN), 3.39 (s, 4 H, CH$_2$CN), 3.31 (d, 4 H, J = 13.44, Ar$\underline{C}\underline{H}_2$Ar)	153.04 ($\underline{C}$-OCH$_2$), 151.71 (C-OH), 135.92, 133.80, 128.85, 128.76, 128.43, 128.17, 127.83, 127.70, 126.83, 120.22 (ArC), 118.23 (CN), 117.91 (CN), 78.76 (Ar$\underline{C}$H$_2$O), 31.35 (ArCH$_2$Ar), 22.92 (CH$_2$CN), 22.73 (CH$_2$CN)
5b	80	240–242	7.79 (s, 2 H, ArOH), 7.56–7.52 (m, 4 H, ArH), 7.08–7.03 (m, 8 H, ArH), 6.84 (s, 4 H, ArH), 4.99 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.23 (d, 4 H, J = 13.32, Ar$\underline{C}\underline{H}_2$Ar), 3.65 (s, 4 H, CH$_2$CN), 4.35 (s, 4 H, CH$_2$CN), 3.33 (d, 4 H, J = 13.29, Ar$\underline{C}\underline{H}_2$Ar	152.95 ($\underline{C}$-OCH$_2$), 151.47 (C-OH), 133.80, 129.81, 129.70, 128.86, 128.68, 128.26, 128.08, 127.02, 120.42, 115.96, 115.67 (ArC), 118.47 (CN), 117.92 (CN), 78.05 (Ar$\underline{C}$H$_2$O), 31.38 (Ar$\underline{C}$H$_2$Ar), 23.01 ($\underline{C}$H$_2$CN), 22.77 ($\underline{C}$H$_2$CN)
5c	76	153 (Softening) 230–232	7.71 (s, 2 H, ArOH), 7.54, 7.47 (dd, 8 H, J = 8.49, 8.46, Br-ArH), 7.03 (s, 4 H, ArH), 6.84 (s, 4 H, ArH), 4.98 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.22 (d, 4 H, J = 13.20, Ar$\underline{C}\underline{H}_2$Ar), 3.66 (s, 4 H, CH$_2$CN), 3.46 (s, 4 H, CH$_2$CN), 3.35 (d, 4 H, J = 13.38, Ar$\underline{C}\underline{H}_2$Ar)	152.93 ($\underline{C}$-OCH$_2$), 151.52 (C-OH), 134.91, 133.67, 132.10, 129.23, 128.90, 128.29, 128.01, 127.08, 122.67, 120.45 (ArC), 118.45 (CN), 117.87 (CN), 77.94 (Ar$\underline{C}$H$_2$O), 31.37 (Ar$\underline{C}$H$_2$Ar), 23.01 ($\underline{C}$H$_2$CN), 22.78 ($\underline{C}$H$_2$CN)
5d	84	241–243	7.90 (s, 2 H, ArOH), 7.54 (d, 4 H, J = 7.50, H$_3$C-ArH), 7.19 (d, 4 H, J = 7.53, H$_3$C-ArH), 7.00 (s, 4 H, ArH), 6.83 (s, 4 H, ArH), 5.01 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.24 (d, 4 H, J = 13.41, Ar$\underline{C}\underline{H}_2$Ar), 3.64 (s, 4 H, CH$_2$CN), 3.45 (s, 4 H, CH$_2$CN), 3.29 (d, 4 H, J = 13.29, Ar$\underline{C}\underline{H}_2$Ar), 2.42 (s, 12 H, CH$_3$)	153.09, $\underline{C}$-OCH$_2$), 151.78 (C-OH), 138.18, 133.94, 132.98, 129.52, 128.73, 128.22, 128.14, 127.91, 126.71, 120.15 (ArC), 118.49 (CN), 117.94 (CN), 78.74 (Ar$\underline{C}$H$_2$O), 31.43 (Ar$\underline{C}$H$_2$Ar), 23.00 ($\underline{C}$H$_2$CN), 22.77 ($\underline{C}$H$_2$CN), 21.38 (CH$_3$)
5e	81	150 (Softening) 195–196	7.91 (s, 2 H, ArOH), 7.45 (d, 4 H, J = 8.64, ArH), 7.00 (s, 4 H, ArH), 6.91 (d, 4 H, J = 8.61, ArH), 6.82 (s, 4 H, ArH), 4.99 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.22 (d, 4 H, J = 13.29, Ar$\underline{C}\underline{H}_2$Ar), 3.85 (s, 12 H, OCH$_3$), 3.63 (s, 4 H, CH$_2$CN), 3.45 (s, 4 H, CH$_2$CN), 3.27 (d, 4 H, J = 13.35, Ar$\underline{C}\underline{H}_2$Ar)	159.83 ($\underline{C}$-OCH$_3$), 153.04 ($\underline{C}$-OCH$_2$), 151.67 (C-OH), 134.04, 129.66, 128.71, 128.28, 128.13, 128.02, 126.70, 120.20, 114.16 (ArC), 118.52 (CN), 117.99 (CN), 78.59 (Ar$\underline{C}$H$_2$O), 55.28 (OCH$_3$), 31.45 (Ar$\underline{C}$H$_2$Ar), 23.01 ($\underline{C}$H$_2$CN), 22.76 (CH$_2$CN)
5e	80	151–152	7.75 (d, 4 H, J = 8.04, NC-ArH), 7.65 (d, 4 H, J = 7.95, NC-ArH), 7.55 (s, 2 H, ArOH), 7.05 (s, 4 H, ArH), 6.85 (s, 4 H, ArH), 5.11 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.20 (d, 4 H, J = 13.44, ArCH$_2$Ar), 3.67 (s, 4 H, CH$_2$CN), 3.46 (s, 4 H, CH$_2$CN), 3.37 (d, 4 H, J = 13.41, Ar$\underline{C}\underline{H}_2$Ar)	152.73 ($\underline{C}$-OCH$_2$), 151.34 (C-OH), 141.16 ($\underline{C}$-CN), 133.47, 132.67, 129.17, 129.07, 128.42, 127.84, 127.46, 120.81, 112.52 (ArC), 118.38 (CN), 118.27 (CN), 117.78 (CN), 77.45 (Ar$\underline{C}$H$_2$O), 31.32 (Ar$\underline{C}$H$_2$Ar), 23.00 ($\underline{C}$H$_2$CN), 22.78 ($\underline{C}$H$_2$CN)
5g	82	152–153	8.17 (d, 4 H, J = 8.70, O$_2$N-ArH), 7.89 (d, 4 H, J = 8.61, O$_2$N-ArH), 7.67 (s, 2 H, ArOH), 7.08 (s, 4 H, ArH), 6.88 (s, 4 H, ArH), 5.17 (s, 4 H, Ar$\underline{C}\underline{H}_2$O), 4.25 (d, 4 H, J = 13.26, Ar$\underline{C}\underline{H}_2$Ar), 3.68 (s, 4 H, CH$_2$CN), 3.48 (s, 4 H, CH$_2$CN), 3.43 (d, 4 H, J = 13.29, Ar$\underline{C}\underline{H}_2$Ar)	152.77 ($\underline{C}$-OCH$_2$), 151.27 (C-OH), 147.75, 143.26, 133.48, 129.16, 128.49, 127.81, 127.63, 124.10, 120.88 (ArC), 118.43 (CN), 117.82 (CN), 77.12 (Ar$\underline{C}$H$_2$-Ar), 23.02 (CH$_2$CN), 22.77 ($\underline{C}$H$_2$CN)
5h	76	155 (Softening) 180–181	7.88 (s, 2 H, ArOH), 7.48 (bs, 8 H, t-C$_4$H$_9$-ArH), 6.98 (s, 4 H, ArH), 6.81 (s, 4 H, ArH), 5.06 (s, 4 H, ArCH$_2$O), 4.20 (d, 4 H, J = 13.02, Ar$\underline{C}\underline{H}_2$Ar), 3.63 (s, 4 H, CH$_2$CN), 3.45 (s, 4 H, CH$_2$CN), 3.25 (d, 4 H, J = 13.32, Ar$\underline{C}\underline{H}_2$Ar)	153.01 ($\underline{C}$-OCH$_2$), 151.97 (C-OH), 151.71 ($\underline{C}$-C$_4$H$_9$-t), 134.03, 133.01, 128.71, 128.39, 128.12, 127.84, 126.65, 125.66, 120.20 (ArC), 118.52 (CN), 118.00 (CN), 78.68 (Ar$\underline{C}$H$_2$O), 34.72 (t-C$_4$H$_9$), 31.43 (t-C$_4$H$_9$), 31.25 (Ar$\underline{C}$H$_2$Ar), 23.00 ($\underline{C}$H$_2$CN), 22.77 ($\underline{C}$H$_2$CN)

Table. (continued)

Product[a]	Yield (%)	mp (°C)	^{1}H NMR (300 MHz) ($\mathrm{CDCl_3/TMS}$) δ, J (Hz)	^{13}C NMR (75 MHz) ($\mathrm{CDCl_3/TMS}$) δ
7a	70	260–262	7.83 (s, 2H, ArOH), 7.63 (bs, 4H, ArH), 7.42–7.34 (m, 6H, ArH), 7.09–7.04 (m, 4H, ArH), 6.82 (s, 2H, ArH), 6.91–6.74 (m, 2H, ArH), 6.69 (t, 2H, $J = 7.2, 7.8$, ArH), 6.57 (t, 1H, $J = 4.5$, ArH), 5.06 (s, 4H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.31 (d, 4H, $J = 13.02$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.35 (d, 2H, $J = 13.90$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.34 (s, 2H, $\mathrm{CH_2CN}$), 3.33 (d, 2H, $J = 13.90$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$)	153.43 ($\mathrm{\underline{C}\text{-}OCH_2}$), 151.73 (C-OH), 151.68 (C-OH), 136.62, 136.42, 134.19, 132.88, 129.33, 129.02, 128.81, 128.75, 128.45, 128.21, 128.12, 127.93, 127.57, 127.50, 126.69, 125.47, 119.14 (ArC), 118.12 (CN), 127.93, 127.57, 127.50, 126.69, 125.47, 119.14 (ArC), 118.12 (CN), 76.61 ($\mathrm{Ar\underline{C}H_2O}$), 78.48 ($\mathrm{Ar\underline{C}H_2O}$), 31.46 ($\mathrm{Ar\underline{C}H_2Ar}$), 22.74 ($\mathrm{\underline{C}H_2CN}$)
7b	65	153–154	7.89 (s, 1H, ArH), 7.54–7.49 (m, 4H, ArH), 7.19 (d, 4H, $J = 7.7$, ArH), 7.07–7.03 (m, 4H, ArH), 7.89–7.82 (m, 5H, ArH), 7.69–7.63 (m, 3H, ArH), 5.02 (s, 2H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 5.01 (s, 2H, $\mathrm{ArCH_2O}$), 4.30 (d, 2H, $J = 13.20$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 4.28 (d, 2H, $J = 13.02$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.39 (s, 2H, $\mathrm{CH_2CN}$), 3.34 (d, 2H, $J = 12.90$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.31 (d, 2H, $J = 12.90$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 2.42 (s, 6H, $\mathrm{CH_3}$)	153.43 ($\mathrm{\underline{C}\text{-}OCH_2}$), 151.92 (C-OH), 151.71 (C-OH), 137.74, 134.68, 134.28, 133.72, 133.68, 133.45, 133.08, 129.47, 128.97, 128.70, 128.58, 128.26, 127.97, 127.70, 125.48, 125.39, 119.09 (ArC), 119.02 (CN), 78.55 ($\mathrm{Ar\underline{C}H_2O}$), 78.43 ($\mathrm{Ar\underline{C}H_2O}$), 31.49 ($\mathrm{Ar\underline{C}H_2Ar}$), 22.80 ($\mathrm{\underline{C}H_2CN}$), 21.42 ($\mathrm{CH_3}$)
7c	71	165 (Softening) 203–205	7.82–7.79 (m, 4H, ArH), 7.63–7.57 (m, 5H, ArH), 7.10–7.02 (m, 5H, ArH), 6.92–6.78 (m, 4H, ArH), 6.73–6.66 (m, 3H, ArH), 5.12 (s, 4H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.22 (d, 4H, $J = 13.20$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.38 (d, 2H, $J = 13.02$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.39 (s, 2H, $\mathrm{CH_2CN}$), 3.37 (d, 2H, $J = 13.02$, $\mathrm{Ar\underline{C}H_2Ar}$)	153.03 ($\mathrm{\underline{C}\text{-}OCH_2}$), 151.43 (C-OH), 151.28 (C-OH), 141.86, 141.63, 133.91, 132.97, 132.57, 132.28, 129.53, 129.24, 129.15, 128.95, 128.82, 128.15, 127.74, 127.60, 125.99, 125.86, 119.60 (ArC), 118.44 (CN), 118.40 (CN), 77.16 ($\mathrm{Ar\underline{C}H_2O}$), 31.42 ($\mathrm{Ar\underline{C}H_2Ar}$), 22.81 ($\mathrm{\underline{C}H_2CN}$)
7d	78	220–222	8.15–8.12 (m, 4H, ArH), 7.96–7.83 (m, 4H, ArH), 7.68 (m, 2H, ArH), 7.16–7.07 (m, 4H, ArH), 6.90–6.82 (m, 4H, ArH), 6.74–6.62 (m, 3H, ArH), 5.18 (bs, 4H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.28 (d, 4H, $J = 13.29$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.43 (d, 4H, $J = 13.23$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.41 (s, 2H, $\mathrm{CH_2CN}$)	
7e	60	161–163	9.16 (bs, 4H, ArH), 8.86 (bs, 2H, ArH), 7.82 (s, 2H, ArOH), 7.08 (m, 4H, ArH), 7.04–6.90 (m, 4H, ArH), 6.82–6.74 (t, 1H, ArH), 6.71 (t, 2H, ArH), 5.37 (s, 4H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.24 (d, 4H, $J = 13.29$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.48 (d, 4H, $J = 12.90$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.47 (s, 2H, $\mathrm{CH_2CN}$)	
7f	68	266–268	7.85 (s, 2H, ArOH), 7.56–7.46 (m, 8H, ArH), 7.05–7.01 (m, 4H, ArH), 6.86–6.80 (m, 4H, ArH), 6.67–6.65 (m, 3H, ArH), 5.09 (s, 4H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.27 (d, 2H, $J = 13.29$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 4.22 (d, 2H, $J = 13.32$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.39 (s, 2H, $\mathrm{CH_2CN}$), 3.27 (t, 4H, $J = 11.83, 12.36$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$)	152.57 ($\mathrm{\underline{C}\text{-}OCH_2}$), 152.00 ($\mathrm{\underline{C}\text{-}OH}$), 151.52 ($\mathrm{\underline{C}\text{-}OH}$), 150.50 ($\mathrm{\underline{C}\text{-}C_4H_9\text{-}}t$), 134.21, 133.70, 133.61, 128.97, 128.60, 128.49, 128.40, 128.18, 127.86, 127.49, 127.49, 127.37, 127.31, 127.22, 125.12, 119.19 (ArC), 119.00 (CN), 78.03 ($\mathrm{Ar\underline{C}H_2O}$), 77.96 ($\mathrm{Ar\underline{C}H_2O}$), 34.29 ($t\text{-}\mathrm{C_4H_9}$), 31.09 ($t\text{-}\mathrm{C_4H_9}$), 30.61 ($\mathrm{Ar\underline{C}H_2Ar}$), 21.77 ($\mathrm{\underline{C}H_2CN}$)
8a	91	170–172	7.36 (bs, 10H, ArH), 7.22–7.18 (m, 12H, ArH), 7.12–7.05 (m, 10H, ArH), 6.98 (m, 1H, ArH), 6.84 (s, 2H, ArH), 6.28 (t, 2H, $J = 7.53, 7.53$, ArH), 6.14 (d, 2H, $J = 6.45$, ArH), 5.82 (d, 2H, $J = 6.99$, ArH), 5.16 (s, 2H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 5.09 (s, 2H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.72 (d, 2H, $J = 11.34$, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.67 (d, 2H, $J = 11.34$ ($\mathrm{ArCH_2O}$), 4.24 (d, 2H, $J = 13.94$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 4.04 (d, 2H, $J = 13.68$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.32 (s, 4H, $\mathrm{ArCH_2}$), 2.95 (d, 2H, $J = 13.74$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 2.77 (d, 2H, $J = 13.47$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$)	156.00, $\mathrm{\underline{C}\text{-}OCH_2}$), 155.01 ($\mathrm{\underline{C}\text{-}OCH_2}$), 154.81 ($\mathrm{\underline{C}\text{-}OCH_2}$), 137.97, 137.67, 137.63, 137.33, 137.12 , 135.42, 133.55, 133.10, 130.48, 130.27, 130.05, 129.00, 128.95, 128.41, 128.09, 128.04, 127.93, 127.93, 127.83, 127.75, 127.67, 127.36, 127.15, 122.36, 122.19, 121.79 (ArC), 77.24 ($\mathrm{Ar\underline{C}H_2O}$), 75.83 ($\mathrm{Ar\underline{C}H_2O}$), 75.43 ($\mathrm{Ar\underline{C}H_2O}$), 50.70 ($\mathrm{\underline{C}\text{-}CN}$), 47.16 ($\mathrm{Ar\underline{C}H_2}$), 31.48 ($\mathrm{Ar\underline{C}H_2Ar}$), 31.37 ($\mathrm{Ar\underline{C}H_2Ar}$)
8b	86	106–107	7.27 (m, 6H, $J = 8.70$, ArH), 7.14 (d, 2H, $J = 8.70$, ArH), 7.05–6.99 (m, 7H, ArH), 6.87 (s, 2H, ArH), 6.84 (s, 2H, ArH), 6.84 (s, 4H, $J = 8.70$, ArH), 6.76 (d, 4H, $J = 8.70$, ArH), 6.65–6.59 (m, 4H, ArH), 6.28 (t, 2H, $J = 7.50, 7.50$, ArH), 6.14 (d, 2H, $J = 6.90$, ArH), 5.85 (d, 2H, $J = 7.20$, ArH), 5.08 (s, 2H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 5.01 (s, 2H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.68 (d, 2H, $J = 11.40$, $\mathrm{ArCH_2O}$), 4.61 (d, 2H, $J = 11.40$, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.20 (d, 2H, $J = 13.50$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 4.05 (d, 2H, $J = 13.50$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.87 (s, 6H, $\mathrm{OCH_3}$), 3.77 (s, 9H, $\mathrm{OCH_3}$), 3.74 (s, 3H), $\mathrm{OCH_3}$), 3.25 (s, 4H, $\mathrm{Ar\underline{C}\underline{H}_2}$), 2.95 (d, 2H, $J = 13.80$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 2.78 (d, 2H, $J = 13.50$, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$)	159.40 ($\mathrm{\underline{C}\text{-}OCH_3}$), 159.25 ($\mathrm{\underline{C}\text{-}OCH_3}$), 159.20 ($\mathrm{\underline{C}\text{-}OCH_3}$), 158.73 ($\mathrm{\underline{C}\text{-}OCH_3}$), 156.03 ($\mathrm{\underline{C}\text{-}OCH_2}$), 154.92 ($\mathrm{\underline{C}\text{-}OCH_2}$), 154.84 ($\mathrm{\underline{C}\text{-}OCH_2}$), 137.76, 137.30, 133.62, 133.20, 131.85, 131.66, 131.45, 130.48, 130.27, 130.20, 130.07, 129.85, 128.89, 127.75, 127.67, 127.60, 127.33, 122.25, 122.07, 113.69, 113.44, 113.24, 113.09, 112.96 (ArC), 76.78 ($\mathrm{Ar\underline{C}H_2O}$), 75.20 ($\mathrm{Ar\underline{C}H_2O}$), 74.62 ($\mathrm{Ar\underline{C}H_2O}$), 55.30 ($\mathrm{OCH_3}$), 55.17 ($\mathrm{OCH_3}$), 51.32 ($\mathrm{\underline{C}\text{-}CN}$), 46.30 ($\mathrm{Ar\underline{C}H_2}$), 31.59 ($\mathrm{Ar\underline{C}H_2Ar}$), 31.43 ($\mathrm{Ar\underline{C}H_2Ar}$), 31.43 ($\mathrm{Ar\underline{C}H_2Ar}$)

Table. (continued)

Product^{a}	Yield (%)	mp (°C)	^{1}H NMR (300 MHz) (CDCl$_3$/TMS) δ, *J* (Hz)	^{13}C NMR (75 MHz) (CDCl$_3$/TMS) δ
8c	84	114–115	7.34–7.30 (m, 4H, ArH), 7.24–7.12 (m, 12H, ArH), 7.08–6.90 (m, 13H, ArH), 6.80 (s, 2H, ArH), 6.34 (t, 2H, *J* = 7.41, ArH), 6.17 (d, 2H, *J* = 7.65, ArH), 5.76 (d, 2H, *J* = 7.53, ArH), 5.04 (s, 2H, Ar$\underline{\mathrm{CH}}_2$O), 4.99 (s, 2H, Ar$\underline{\mathrm{CH}}_2$O), 4.68 (d, 2H, *J* = 11.28, Ar$\underline{\mathrm{CH}}_2$O), 4.60 (d, 2H, *J* = 11.28, Ar$\underline{\mathrm{CH}}_2$), 3.25 (d, 2H, *J* = 13.56, Ar$\underline{\mathrm{CH}}_2$), 2.97 (d, 2H, *J* = 13.41, Ar$\underline{\mathrm{CH}}_2$Ar), 2.78 (d, 2H, *J* = 13.56, Ar$\underline{\mathrm{CH}}_2$Ar)	155.82 ($\underline{\mathrm{C}}$-OCH$_2$), 154.88 ($\underline{\mathrm{C}}$-OCH$_2$), 154.34 ($\underline{\mathrm{C}}$-OCH$_2$), 137.65, 136.75, 136.05, 135.73, 135.50, 134.22, 134.18, 133.64, 133.38, 133.33, 132.61, 131.69, 131.55, 131.40, 130.81, 130.53, 129.62, 129.23, 128.70, 128.32, 128.14, 128.08, 127.54, 127.43, 122.74, 121.38 (ArC), 76.53 (Ar$\underline{\mathrm{C}}$H$_2$O), 75.14 (Ar$\underline{\mathrm{C}}$H$_2$O), 74.38 (Ar$\underline{\mathrm{C}}$H$_2$O), 50.64 ($\underline{\mathrm{C}}$-CN), 46.33 (Ar$\underline{\mathrm{C}}$H$_2$), 31.53 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 31.31 (Ar$\underline{\mathrm{C}}$H$_2$Ar)
8d	82	119–120	7.50 (d, 4H, *J* = 8.19, ArH), 7.33 (d, 4H, *J* = 8.31, ArH), 7.25–7.20 (m, 2H, ArH), 7.16 (4H, *J* = 8.28, ArH), 7.03 (d, 4H, *J* = 6.93, ArH), 6.96–6.87 (m, 6H, ArH), 6.82 (s, 2H, ArH), 6.34 (t, 2H, *J* = 7.65, 7.53, ArH), 6.17 (d, 2H, *J* = 7.53, ArH), 5.76 (d, 2H, *J* = 6.45, ArH), 5.02 (s, 2H, Ar$\underline{\mathrm{CH}}_2$O), 4.96 (s, 2H, Ar$\underline{\mathrm{CH}}_2$O), 4.65 (d, 2H, *J* = 11.22, ArCH$_2$O), 4.58 (d, 2H, *J* = 11.34, Ar$\underline{\mathrm{CH}}_2$O), 4.10 (d, 2H, *J* = 13.41, Ar$\underline{\mathrm{CH}}_2$Ar), 3.96 (d, 2H, *J* = 13.86, Ar$\underline{\mathrm{CH}}_2$Ar), 3.31 (d, 2H, *J* = 13.62, Ar$\underline{\mathrm{CH}}_2$), 3.24 (d, 2H, *J* = 13.53, Ar$\underline{\mathrm{CH}}_2$), 2.97 (d, 2H, *J* = 13.50, Ar$\underline{\mathrm{CH}}_2$Ar), 2.80 (d, 2H, *J* = 13.95, Ar$\underline{\mathrm{CH}}_2$Ar)	155.91 ($\underline{\mathrm{C}}$-OCH$_2$), 154.89 ($\underline{\mathrm{C}}$-OCH$_2$), 154.29 ($\underline{\mathrm{C}}$-OCH$_2$), 137.61, 136.68, 136.47, 136.15, 135.89, 134.05, 133.33, 132.55, 132.09, 132.00, 131.79, 131.66, 131.45, 131.26, 131.09, 130.95, 130.81, 129.55, 129.22, 128.13, 127.50, 127.42, 122.76, 122.65, 122.40, 122.29, 121.49, 121.29 (ArC), 76.63 (Ar$\underline{\mathrm{C}}$H$_2$O), 75.20 (Ar$\underline{\mathrm{C}}$H$_2$O), 74.42 (Ar$\underline{\mathrm{C}}$H$_2$O), 50.49 ($\underline{\mathrm{C}}$-CN), 46.39 (Ar$\underline{\mathrm{C}}$H$_2$), 31.50 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 31.27 (Ar$\underline{\mathrm{C}}$H$_2$Ar)
9	90	386–388	7.94–7.81 (m, 12H, ArH), 7.71–7.63 (m, 8H, ArH), 6.81 (s, 2H, ArH), 6.78–6.66 (m, 9H, ArH), 3.61 (s, 4H, Ar$\underline{\mathrm{CH}}_2$Ar), 3.59 (s, 4H, Ar$\underline{\mathrm{CH}}_2$Ar), 3.07 (s, 2H, CH$_2$CN)	164.30 (C=O), 164.14 (C=O), 164.07 (C=O), 148.39 ($\underline{\mathrm{C}}$-OCO), 148.16 ($\underline{\mathrm{C}}$-OCO), 148.10 ($\underline{\mathrm{C}}$-OCO), 134.70, 134.24, 134.11, 133.69, 133.44, 132.99, 131.60, 131.53, 131.35, 131.11, 130.10, 128.91, 128.79, 128.73, 128.48, 128.24, 125.58, 124.80, 124.73 (ArC), 116.63 (CN), 36.98, 36.87 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 22.40 ($\underline{\mathrm{C}}$H$_2$CN)
10	51	296–297	8.39 (d, 4H, *J* = 8.40, ArH), 7.72 (m, 2H, ArH), 7.54 (t, 4H, *J* = 7.80, 7.50, ArH), 7.09 (m, 4H, ArH), 6.86 (s, 2H, ArH), 6.74 (m, 4H, ArH), 6.58 (m, 1H, ArH), 5.65 (s, 2H, ArOH), 4.02 (d, 2H, *J* = 14.16, Ar$\underline{\mathrm{CH}}_2$Ar), 4.01 (d, 2H, *J* = 14.25, Ar$\underline{\mathrm{CH}}_2$Ar), 3.53 (d, 2H, *J* = 4.19, Ar$\underline{\mathrm{CH}}_2$Ar), 3.52 (d, 2H, *J* = 14.07, Ar$\underline{\mathrm{CH}}_2$Ar), 3.39 (s, 2H, CH$_2$CN)	164.95 (C=O), 164.88 (C=O), 152.78 (C-OH), 144.76 ($\underline{\mathrm{C}}$-OCO), 144.59 ($\underline{\mathrm{C}}$-OCO), 134.16, 134.01, 133.22, 131.46, 130.54, 130.46, 130.14, 129.41, 129.19, 129.13, 129.02, 128.94, 128.79, 127.87, 127.44, 127.20, 120.16 (ArC), 117.57 (CN), 32.22 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 32.06 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 22.49 ($\underline{\mathrm{C}}$H$_2$CN)
11	34	280–282	8.34 (m, 4H, ArH), 7.76 (m, 2H, ArH), 7.56 (m, 4H, ArH), 7.07 (d, 2H, *J* = 7.5, ArH), 6.97 (s, 2H, ArH), 6.95–6.90 (m, 5H, ArH), 6.85–6.80 (m, 2H, ArH), 5.54 (s, 1H, ArOH), 5.51 (s, 1H, ArOH), 3.99 (d, 2H, *J* = 14.1, Ar$\underline{\mathrm{CH}}_2$Ar), 3.97 (d, 2H, *J* = 14.4, ArCH$_2$Ar), 3.55 (d, 2H, *J* = 14.4, Ar$\underline{\mathrm{CH}}_2$Ar), 3.53 (d, 2H, *J* = 14.4, Ar$\underline{\mathrm{CH}}_2$Ar), 3.49 (s, 2H, CH$_2$CN)	164.71 (C=O), 152.79 (C-OH), 152.65 (C-OH), 145.54 ($\underline{\mathrm{C}}$-OCO), 134.04, 132.52, 131.83, 130.50, 129.48, 129.30, 129.14, 129.04, 128.93, 128.84, 128.63, 128.01, 126.81, 120.81, 120.18, 120.00 (ArC), 32.76 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 32.44 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 22.63 ($\underline{\mathrm{C}}$H$_2$CN)
12	86	175 (Softening) 187–188	7.79–7.70 (m, 16H, ArH), 6.84 (t, 2H, *J* = 7.50, ArH), 6.67–6.59 (m, 5H, ArH), 6.39 (d, 2H, *J* = 7.80, ArH), 6.28 (s, 2H, ArH), 3.79 (d, 2H, *H* = 14.40, Ar$\underline{\mathrm{CH}}_2$Ar), 3.75 (d, 2H, *J* = 14.40, Ar$\underline{\mathrm{CH}}_2$Ar), 3.33 (s, 2H, CH$_2$CN), 2.56 (d, 2H, *J* = 14.40, Ar$\underline{\mathrm{CH}}_2$Ar), 2.53 (d, 2H, *J* = 14.70, Ar$\underline{\mathrm{CH}}_2$Ar)	145.25 (C-OSO$_2$), 144.75 (C-OSO$_2$), 144.51 (C-OSO$_2$), 136.22, 136.07, 135.38, 125.11, 134.32, 132.77, 132.65, 132.50, 132.40, 130.97, 130.82, 130.76, 129.70, 129.52, 129.35, 129.13, 128.39, 127.53, 126.45, 125.71, (ArC), 117.20 (CN), 31.38 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 31.32 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 22.89 ($\underline{\mathrm{C}}$H$_2$CN)
13a	81	251–253 (brown liquid)	10.20 (bs, 4H, ArOH), 7.80 (d, 2H, *J* = 6.33, ArH), 7.41–7.44 (m, 3H, ArH), 7.35 (s, 2H, ArH), 7.31 (s, 1H, CH=CCN), 7.13–7.04 (m, 6H, ArH), 6.80 (m, 3H, ArH), 4.28 (bs, 4H, Ar$\underline{\mathrm{CH}}_2$Ar), 3.58 (bs, 4H, Ar$\underline{\mathrm{CH}}_2$Ar)	150.11 (C-OH), 148.74 (C-OH), 148.67 (C-OH), 140.84, 133.85, 130.25, 129.29, 129.16, 129.09, 129.06, 128.91, 128.44, 128.13, 127.60, 126.78, 122.52, 122.44 (ArC), 118.04 (CN), 111.14 ($\underline{\mathrm{C}}$=CH), 31.83 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 31.70 (Ar$\underline{\mathrm{C}}$H$_2$Ar)
13b	76	276–278	10.20 (bs, 4H, ArOH), 7.99 (d, 1H, *J* = 7.80, ArH), 7.69 (s, 1H, ArH), 7.38–7.35 (m, 3H, ArH), 7.13–7.00 (m, 7H, ArH), 6.92 (m, 1H, ArH), 6.89–6.71 (m, 3H, ArH), 4.25 (bs, 4H, Ar$\underline{\mathrm{CH}}_2$Ar), 3.85 (s, 3H, OCH$_3$), 3.53 (bs, 4H, Ar$\underline{\mathrm{CH}}_2$Ar)	157.76 (C-OCH$_3$), 149.90 (C-OH), 148.78 (C-OH), 148.70 (C-OH), 136.41, 131.71, 129.43, 129.15, 129.08, 128.80, 128.72, 128.46, 128.16, 127.53, 126.87, 123.28, 122.50, 120.82, 118.18, 110.79, 110.68 (ArC), 55.61 (OCH$_3$), 31.82 (Ar$\underline{\mathrm{C}}$H$_2$Ar), 31.72 (Ar$\underline{\mathrm{C}}$H$_2$Ar)

Table. (continued)

Product[a]	Yield (%)	mp (°C)	^{1}H NMR (300 MHz) ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR (75 MHz) ($CDCl_3$/TMS) δ
13c	73	165 (Softening) 190–191	10.20 (bs, 4 H, ArOH), 7.80 (d, 1 H, ArH), 7.31 (s, 1 H, ArH), 7.22 (m, 1 H, ArH), 7.10–6.90 (m, 9 H, ArH), 6.72 (m, 4 H, ArH), 4.24 (bs, 4 H, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.84 (s, 3 H, OCH_3), 3.48 (bs, 4 H, $\mathrm{Ar\underline{C}H_2Ar}$)	161.19 ($\mathrm{\underline{C}\text{-}OCH_3}$), 149.73 (C-OH), 148.85 (C-OH), 148.76 (C-OH), 140.60, 131.86, 130.99, 129.54, 129.45, 129.28, 128.44, 128.17, 127.69, 126.56, 122.45, 122.52, 122.33, 118.62, 114.36 (ArC), 55.40 (OCH_3), 31.85 ($\mathrm{Ar\underline{C}H_2Ar}$), 31.71 ($\mathrm{Ar\underline{C}H_2Ar}$)
14	70	212–214	7.52–7.47 (m, 8 H, ArH), 7.16–7.10 (m, 8 H, ArH), 6.87 (d, 2 H, ArH), 6.68 (m, 5 H, ArH), 6.49–6.42 (m, 4 H, ArH), 4.93 (d, 2 H, J = 12.36, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.85 (d, 4 H, J = 12.90, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 4.72 (d, 2 H, J = 12.36, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 3.62 (s, 4 H, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 3.52 (s, 4 H, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 2.83 (s, 2 H, CH_2CN), 1.46 (s, 18 H, $t\text{-}C_4H_9$), 1.45 (s, 9 H, $t\text{-}C_4H_9$), 1.44 (s, 9 H, $t\text{-}C_4H_9$)	155.91 ($\mathrm{\underline{C}\text{-}OCH_2}$), 155.87 ($\mathrm{\underline{C}OCH_2}$), 150.16 ($\mathrm{\underline{C}\text{-}C_4H_9}\text{-}t$), 149.96 ($\mathrm{\underline{C}\text{-}C_4H_9}\text{-}t$), 135.44, 135.20, 135.06, 134.65, 134.22, 133.79, 133.38, 131.38, 131.13, 131.03, 130.85, 126.79, 126.73, 126.63, 124.89, 124.75, 124.65, 122.66, 122.22 (ArC), 118.32 (CN), 72.24 ($\mathrm{Ar\underline{C}H_2O}$), 71.96 ($\mathrm{Ar\underline{C}H_2O}$), 37.28 ($\mathrm{Ar\underline{C}H_2Ar}$), 37.01 ($\mathrm{Ar\underline{C}H_2Ar}$), 34.67 ($t\text{-}C_4H_9$), 31.65 ($t\text{-}C_4H_9$), 31.54 ($t\text{-}C_4H_9$), 31.49 ($t\text{-}C_4H_9$) 31.45, ($t\text{-}C_4H_9$), 22.33 ($\mathrm{\underline{C}H_2CN}$)
15a	88	191–193	7.47–7.39 (m, 12 H, ArH), 7.20 (d, 8 H, J = 6.90 (ArH), 6.70 (d, 8 H, J = 7.20, ArH), 6.47 (t, 4 H, J = 7.50 and 7.50, ArH), 4.89 (s, 8 H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 3.60 (s, 8 H, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$)	155.87 ($\mathrm{\underline{C}\text{-}OCH_2}$), 138.18, 133.89, 131.28, 127.86, 127.03, 126.84, 122.22 (ArC), 71.86 ($\mathrm{Ar\underline{C}H_2O}$), 37.27 ($\mathrm{Ar\underline{C}H_2Ar}$)
15b	81	230–232	7.49 (d, 8 H, J = 8.40, ArH), 7.17 (d, 8 H, J = 8.10, ArH), 6.67 (d, 8 H, J = 7.50, ArH), 6.46 t, 4 H, J = 7.20, ArH), 4.86 (s, 8 H, $\mathrm{Ar\underline{C}\underline{H}_2O}$), 3.57 (s, 8 H, $\mathrm{Ar\underline{C}\underline{H}_2Ar}$), 1.46 (s, 36 H, $t\text{-}C_4H_9$)	156.08 ($\mathrm{\underline{C}\text{-}OCH_2}$), 149.95 ($\mathrm{\underline{C}\text{-}C_4H_9}\text{-}t$), 135.38, 133.88, 131.22, 126.78, 124.68, 122.05 (ArC), 71.99 ($\mathrm{Ar\underline{C}H_2O}$), 37.19 ($\mathrm{Ar\underline{C}H_2Ar}$), 34.66 ($\mathrm{C\text{-}C_4H_9}\text{-}t$), 31.54 ($t\text{-}C_4H_9$)

[a] Satisfactory microanalyses obtained: C ± 0.48, H ± 0.28.

[b] Reported in literature.[7]

[c] Recorded in DMSO-d_6.

Tetrabenzoyl Ester 9 (1,3-Alternate Conformer) and Tetra-4-bromobenzenesulfonyl Ester 12 (Cone Conformer):

A mixture of **6** (0.47 g, 1 mmol) NaH (60 % in oil dispersion 1.0 g, 25 equiv) and freshly distilled and dried THF/DMF (60 mL, 5:1) was placed in a 250 mL 3-necked round-bottomed flask. The mixture was stirred for 5 min under N_2, and benzoyl chloride (1.40 g, 10 equiv) or 4-bromobenzenesulfonyl chloride (1.50 g, 12 equiv) in THF (5 mL) was added. The mixture was stirred for 18 h at r.t. On completion of the reaction, as monitored by TLC, the solvent was removed under reduced pressure on a rotary evaporator, and the residue was poured over ice cold 10 % HCl to give a semisolid. This was dissolved in CH_2Cl_2 and treated with MeOH to precipitate compounds **9** and **12**, respectively. An analytical sample was obtained by triturating this material with MeOH.

1,3-Dibenzoyl Esters 10 and 11 (Cone Conformers); General Procedure:

In a 250 mL 3-necked round-bottomed flask, white, finely powdered, anhydr. $AlCl_3$ (2.70 g, 20 mmol) was added to a mixture of CH_2Cl_2/DMF (60 mL, 5:1), stirred for 2 min, and **6** (0.46 g, 1.0 mmol) was then added. The mixture was stirred for 5 min, benzoyl chloride (1.40 g, 10 mmol) was added, and stirring at r.t. was continued 16 h. The mixture was poured over ice cold water followed by 10 % HCl to destroy the unreacted $AlCl_3$. The organic layer was separated, and the water layer was extracted with CH_2Cl_2. The combined organic extract was concentrated under reduced pressure to leave a viscous residue which was stirred with MeOH (50 mL) to give a white precipitate. The product mixture (TLC) was removed by filtration, dried, and stirred with cold acetone which dissolved only one of the components. The acetone soluble product was purified by recrystallization to yield **11** (minor product) and from the acetone insoluble fraction **10** (major product) was obtained and purified by recrystallization. An analytical sample was prepared by triturating the recrystallized material with MeOH (50 mL) to remove solvent of crystallization followed by drying.

Arylmethenylation of 6 to 13a–c (Cone Conformers); General Procedure:

NaH (1.2 g, 30 equiv, 60 % in oil dispersion) was placed in a 150 mL 3-necked round-bottomed flask followed by freshly distilled anhydr. THF (60 mL), and the air in the flask was replaced with N_2. The flask was placed in an ice bath, maintaining the temperature at ca. 2–3 °C, and **6** (0.47 g, 1 mmol) was added. The mixture was allowed to warm to r.t., and the contents were stirred for 10 min under a stream of N_2. A solution of benzaldehyde (10 equiv) in anhydr. THF (10 mL) was added dropwise, and the mixture was stirred at r.t. for 18 h. The solvent was removed under reduced pressure on a rotary evaporator, and the residue was neutralized with ice cold 10 % HCl to produce a light yellow precipitate. This was separated by filtration and triturated for 30 min with MeOH (100 mL) followed by hexane (100 mL) to leave a white solid. The product was purified by column chromatography using $CHCl_3$ as an eluent followed by recrystallization.

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(1) Paper No. 41 in a series entitled "Calixarenes". For paper No. 40, see: Sharma, S.K.; Gutsche, C.D. *J. Org. Chem.* **1994**, *59*, 6030.

(2) The term "calixarene" is variously employed in different contexts. In colloquial usage, as employed in the Discussion Section, it implies the presence of OH groups (e.g. "*p-tert*-butylcalix[4]arene for **1**, *p*-H-calix[4]arene for **2**, *p*-cyanomethylcalix[4]arene for **3**). In the more precise and complete specification, as used in the 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) (a) Gutsche, C.D. *Calixarenes*; Stoddart, F.J., Ed.; Monographs in Supramolecular Chemistry: The Royal Society of Chemistry: Cambridge, England, 1989.
(b) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J.; Böhmer, V. Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(4) Gutsche, C.D.; Iqbal, M. *Org. Synth.* **1990**, *68*, 234.

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(6) Alam, I.; Sharma, S.K.; Gutsche, C.D. *J. Org. Chem.* **1994**, *59*, 3716.

(7) (a) Sharma, S.K.; Gutsche, C.D. *Tetrahedron Lett.* **1993**, *34*, 5389.
(b) Sharma, S.K. Gutsche, C.D. *Tetrahedron* **1994**, *50*, 4087.

(8) Sharma, S.K.; Gutsche, C.D. *J. Org. Chem.* **1994**, *59*, 6030.

(9) Sharma, S.K.; Gutsche, C.D. *Synthesis* **1994**, 813.

(10) Jaime, C.; de Mendoza, J.; Prados, P.; Nieto, P.M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.

(11) The presence of a water molecule inside the cavity was qualitatively supported by the appearance of a broad signal at δ 1.5 (in $CDCl_3$) or δ 3.4 (in DMSO-d_6) in the ^1H NMR spectrum.