Water-Soluble Calixarenes as New Inverse Phase-Transfer Catalysts. Their Scope in Aqueous Biphasic Alkylations and Mechanistic Implications

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Dedicated to Professor Howard Alper on the occasion of his 60th birthday

Abstract: Alkylation reactions of active methylene compounds, alcohols and phenols with alkyl halides in aqueous NaOH solution can be carried out without the need for any added organic solvents in most cases. The water-soluble calix[*n*]arenes, which contain trimethylammoniomethyl groups on the upper rim, were used as inverse phase-transfer catalysts, resulting in the corresponding alkylated products in good to high yields. The scope of this methodology in aqueous biphasic alkylation reactions and the mechanistic implications are discussed.

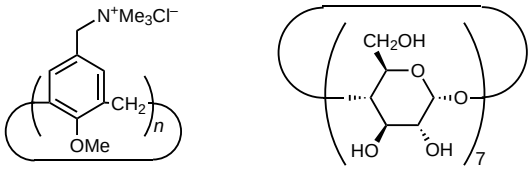
Keywords: alkylation; biphasic catalysis; calixarenes; host-guest systems; water as solvent

Introduction

The 'greening' of global chemical processes has become a major issue in the chemical industry.[1,2] Biphasic catalysis has many advantages as a methodology for organic reactions from the vantage points of the effective two-phase separation of a catalyst and product, as well as catalyst recycling.[2] Thus, the catalyst is immobilized in a liquid phase which can be separated from the product-containing phase. Among some of the possibilities, e.g., fluorous phases[3] and non-aqueous ionic liquids,[4] aqueous biphasic reaction systems are appealing because of the 'green' nature of water as a solvent and the fact that it is inexpensive.[5] However, its application is limited generally to substrates which have appreciable water solubility. To solve this problem, polar water-miscible organic solvents (co-solvents)[6] or surfactants[7,8] are frequently used. On the other hand, use of these additives usually complicates work-up procedures, particularly in regard to product separation and the recovery of the catalyst and additive itself.

In order to circumvent this dilemma, we recently developed a new reaction system,[9-13,14] which is based on the inverse phase-transfer catalysis (IPTC)[15,16] of water-soluble calix[*n*]arenes.[17,18] For example, *C*-alkylation reactions of active methylene compounds with alkyl halides proceed smoothly in aqueous NaOH solution without the need for any added organic solvent using water-soluble calix[*n*]arenes, *p*-(trimethylammoniomethyl)calix[*n*]arene methyl ethers ($n = 4$, 6, and 8; TAC_nM, see Scheme 1) as catalysts,[10] as do the aldol-type condensation and Michael addition reactions of activated methyl and methylene compounds.[11] We have also reported that rhodium complexes with water-soluble calix[4]arenes which contain two phosphine moieties on the upper rim are able to function not only as homogeneous metal catalysts but also as inverse phase-transfer catalysts in aqueous biphasic hydroformylation reactions.[12,13]

We describe herein the scope of this methodology in which TAC_nM is used in aqueous biphasic *C*- and *O*-alkylations of active methylene compounds, alcohols



TAC_nM (n = 4, 6, 8) β-CD

Scheme 1. The structures of the water soluble calix[*n*]arenes, TAC_nM, and β-cyclodextrin.

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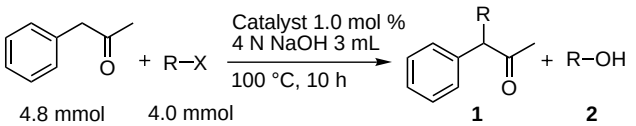
and phenols with alkyl halides.[10] In this biphasic system which employs aqueous NaOH solutions, the TAC_nM catalysts exhibit a selectivity for the size and/or shape of the acidic reactants, and the selective monoalkylations of active methylene compounds and aromatic diols can be achieved. Finally, the mechanistic implications of biphasic alkylation reactions are briefly discussed on the basis of these remarkable features.

Results and Discussion

The activity and selectivity of water-soluble calix[*n*]arenes $TAC_nM \cdot nH_2O$ ($n = 4$, 6 and 8) were first tested in model alkylation reactions of phenylacetone with alkyl halides in aqueous NaOH solution, and these results are summarized in Table 1. The treatment of phenylacetone with octyl bromide in 4 N aqueous NaOH solution for 10 h at 100 °C afforded only trace amounts of 3-phenyl-2-undecanone and octyl alcohol, along with the recovery of the starting material in 85% yield (entry 1). The addition of β-cyclodextrin (β-CD) as an inverse phase-transfer catalyst gave poor yields of 3-phenyl-2-undecanone (entry 2). However, when the same reaction was carried out in the presence of the water-soluble calix[4]-arene TAC_4M, the yield increased to 86% (entry 6). For the sake of comparison, we examined reactions in which tetrabutylammonium bromide (TBAB) and hexadecyltributylphosphonium bromide (HTPB) were employed as normal phase-transfer catalysts,[19,20] and found that there were significant increases in the yields of *O*-alkylated products (entries 4 and 5).[21] When using TBAB with dibutyl ether or HTPB, the reaction largely takes place in the organic phase in which the hydration of the oxygen of the enolate is depressed. The data clearly show that the TAC_4M catalyst is more efficient than TBAB and HTPB in terms of alkylation/hydrolysis and *C*-/*O*-alkylation selectivities in addition to the two major advantages of IPTC, *viz.* ease of separation of the aqueous catalyst solution and no necessity of using an organic solvent. The observed order of reactivity of the alkyl halides is I ≈ Br ≫ Cl (entries 6 – 8). This order suggests that alkyl iodides can be used as alkylating reagents in IPTC reaction systems, which is contrary from that in normal PTC reaction systems. This is presumably the result of a drop in the affinity of the iodide ion for the quaternary cation in aqueous media, that is, a diminished level of catalyst poisoning.[22] The difference in reactivity between alkyl bromide and chloride was confirmed by the reactions with 1-bromo-4-chlorobutane and 1,4-dibromobutane, in which 7-chloro-3-phenyl-2-heptanone and 1-(1-phenylcyclopentyl)ethanone were obtained, respectively, as major products (entries 9 and 10). When activated organic halides, such as 4-*tert*-butylbenzyl, 4-bromobenzyl and 2-naphthylmethyl bromides, were used as alkylating reagents, high to excellent yields were obtained, even at 60 °C (entries 13 – 15).

Some examples of TAC_nM-catalyzed alkylation reactions of active methylene compounds are summarized in Table 2. In all cases, the reactions proceeded smoothly in aqueous NaOH solution to afford the corresponding alkylated products in good to high yields. When 2,4-pentanedione and benzoylacetonitrile were used as substrates, an aqueous 2 N NaOH solution is sufficiently basic to generate the corresponding carbanions to give high yields of alkylated products (entries 3 and 4). In the reaction of phenylacetonitrile, the monoalkylated product was formed with excellent selectivity compared to that for a normal PTC reaction (entry 6).[23] With 2-chlorophenylacetonitrile and 1-naphthylacetonitrile, complete selectivity for monoalkylation was achieved (entries 8 and 14). Furthermore, the alkylation of indene selectively gave the monoalkylated product 3-(1-naphthylmethyl)indene[24] even though it is known that dialkylation takes place to a considerable extent under PTC conditions in the case of highly activated organic

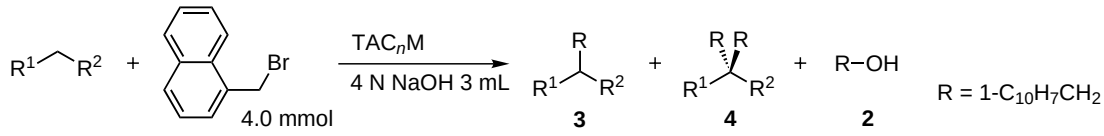
Table 1. *C*-Alkylations of phenylacetone in aqueous NaOH solution.



Entry	Catalyst	R-X	Isolated yield [%] 1	2
1	none	$CH_3(CH_2)_7Br$	trace	trace
2	β-CD[a]	$CH_3(CH_2)_7Br$	14	trace
3	TBAB[b]	$CH_3(CH_2)_7Br$	76 (+trace)[c]	17
4[d]	TBAB[b]	$CH_3(CH_2)_7Br$	73 (+5)[c]	8
5	HTPB[e]	$CH_3(CH_2)_7Br$	71 (+8)[c]	2
6	TAC_4M	$CH_3(CH_2)_7Br$	86	6
7	TAC_4M	$CH_3(CH_2)_7Cl$	12	trace
8	TAC_4M	$CH_3(CH_2)_7I$	84	4
9	TAC_4M	$Cl(CH_2)_4Br$	65[f]	(9)[g]
10	TAC_4M	$Br(CH_2)_4Br$	8 (+63)[h]	(trace)[g]
11	TAC_4M	$CH_2=CH(CH_2)_3Br$	75	0
12[i]	TAC_4M	*c*-$C_6H_{11}CH_2Br$	91	0
13[j]	TAC_4M	4-*t*-$BuC_6H_4CH_2Br$	94	trace
14[j]	TAC_4M	4-$BrC_6H_4CH_2Br$	92	0
15[j]	TAC_4M	2-$C_{10}H_7CH_2Br$	87	0

[a] β-Cyclodextrin.
[b] Tetrabutylammmonium bromide 4.0 mol %.
[c] 2-Methyl-3-oxa-1-phenyl-1-undecene was also formed as an *O*-alkylated product.
[d] Dibutyl ether (3 mL) was used as a solvent.
[e] Hexadecyltributylphosphonium bromide 4.0 mol %.
[f] 7-Chloro-3-phenyl-2-heptanone was formed selectively.
[g] 7-Hydroxy-3-phenyl-2-heptanone.
[h] 1-(1-Phenylcyclopentyl)ethanone.
[i] Reaction time 20 h.
[j] Reaction temperature 60 °C.

Table 2. *C*-Alkylations of various active methylene compounds in aqueous NaOH solution.



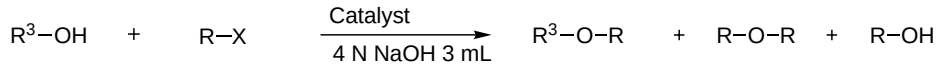
Entry	R^1–CH_2–R^2 [mmol]	Catalyst [mol%]	Conditions	Isolated yield [%]		
				3	**4**	**2**
1[a]	$CH_3COCH_2COCH_3$ (12.0)	none	60 °C, 0.5 h	11 (+trace)[b]	0	0
2[a]	$CH_3COCH_2COCH_3$ (12.0)	TAC_6M (1.0)	60 °C, 0.5 h	50 (+2)[b]	trace	0
3[a]	$CH_3COCH_2COCH_3$ (12.0)	TAC_6M (1.0)	60 °C, 2 h	88 (+3)[b]	3	0
4[a]	$C_6H_5COCH_2CN$ (12.0)	TAC_6M (1.0)	60 °C, 2 h	82	12	(trace)[c]
5[a]	$C_6H_5COCH_2CN$ (4.8)	TAC_6M (1.0)	60 °C, 2 h	69	22	(trace)[c]
6	$C_6H_5CH_2CN$ (12.0)	TAC_4M (1.0)	70 °C, 10 h	90	8	0
7	$C_6H_5CH_2CN$ (4.8)	TAC_4M (1.0)	70 °C, 10 h	68	19	13
8	2-$ClC_6H_4CH_2CN$ (4.8)	TAC_4M (1.0)	60 °C, 10 h	84	0	0
9	C_6H_4-1,2-(–CH=CH–CH_2–) (4.8)	TAC_4M (1.0)	70 °C, 10 h	74[d]	trace[e]	4 (+6)[c]
10[f]	1-$C_{10}H_7CH_2CN$ (4.8)	none	70 °C, 2 h	21	0	0
11[f]	1-$C_{10}H_7CH_2CN$ (4.8)	TAC_4M (1.5)	70 °C, 2 h	58	0	trace
12[f]	1-$C_{10}H_7CH_2CN$ (4.8)	TAC_6M (1.0)	70 °C, 2 h	66	0	trace
13[f]	1-$C_{10}H_7CH_2CN$ (4.8)	TAC_8M (0.75)	70 °C, 2 h	78	0	trace
14[f]	1-$C_{10}H_7CH_2CN$ (4.8)	TAC_6M (1.0)	70 °C, 5 h	91	0	trace

[a] 2 N Aqueous NaOH was used in the place of 4 N aqueous NaOH.
[b] 6-(1-Naphthyl)-2,4-hexanedione was isolated as a mixture with 3-(1-naphthylmethyl)-2,4-pentanedione.
[c] Bis(1-naphthylmethyl) ether.
[d] 3-(1-Naphthylmethyl)indene.
[e] 1,3-Bis(1-naphthylmethyl)indene.
[f] Dipropyl ether (3 mL) was used as a solvent.

halides, such as benzyl and allyl chlorides (entry 9).[25] The formation of 3-(1-naphthylmethyl)indene can be ascribed to the basic isomerization of the initially formed 1-alkylindene.[25] Taking into account the molar amounts of catalysts added, the activities of catalysts TAC_nM increase in the order of $TAC_4M < TAC_6M < TAC_8M$ for the alkylation reactions of 1-naphthylacetonitrile (entries 11 – 13). This may be a reflection of the following interfacial mechanism, because the distribution of TAC_nM in the organic phase was negligible.[9] In the aqueous phase near the interface, the water-soluble calix[*n*]arenes TAC_nM would form host-guest complexes with a carbanion, produced *via* the deprotonation of the active methylene compound by hydroxide ions, and nucleophilic attack by the anion on an alkyl halide would take place at the interface.

The water-soluble calix[*n*]arenes TAC_nM were also examined with respect to *O*-alkylation reactions of alcohols and phenols with alkyl halides in aqueous NaOH solution, and the results are summarized in Table 3. Treatment of 1-hexanol with 4-*tert*-butylbenzyl bromide in 4 N aqueous NaOH solution for 3 h at 60 °C afforded the 4-*tert*-butylbenzyl hexyl ether in 22% yield (entry 1). However, when the same reaction was carried out in the presence of the water-soluble calix[6]arene TAC_6M, the yield increased to 75% (entry 3). When cetyltrimethylammonium bromide (hexadecyltrimethylammonium bromide, CTAB) was used, in place of TAC_6M as a cationic surfactant, the yield of desired unsymmetrical ether was diminished to 56% (entry 2) accompanied by the formation of an emulsion during the work-up. The TAC_6M catalyst is superior to CTAB in terms of yield, selectivity and product separation. A secondary alkyl halide was found to be unsuitable as an alkylating reagent (entry 6). In all other cases where TAC_nM was used, the reactions proceeded smoothly to afford the corresponding *O*-alkylated products in good to high yields. When 1-bromo-4-chlorobutane is used, the butoxide ion reacts predominantly with the bromide substituent. Thus, 1-butoxy-4-chlorobutane is selectively obtained as a monoether (entry 5). When phenol and 4-methylphenol were used instead of alcohols, the reaction afforded *O*-alkylated products in good yields (entries 9 and 10). The selective formation of *O*-alkylated products in our system is in sharp contrast to the reported reactions of allyl and benzyl halides with sodium phenoxide in water.[26] In the case of an aromatic diol, 1,4-benzenedimethanol, good selectivity for the

Table 3. *O*-Alkylations of various alcohols and phenols in aqueous NaOH solution.



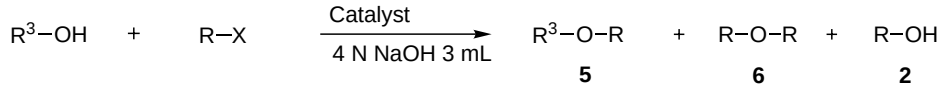
Entry	R^3–OH [mmol]	R–X [4.0 mmol]	Catalyst [mol %]	Conditions	Isolated yield [%] 5	6	2
1	$CH_3(CH_2)_5OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$	none	60 °C, 3 h	22	trace	trace
2	$CH_3(CH_2)_5OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$	CTAB[a] (0.50)	60 °C, 3 h	56	12	5
3	$CH_3(CH_2)_5OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$	TAC_6M (0.50)	60 °C, 3 h	75	trace	3
4	$CH_3(CH_2)_3OH$ (12.0)	4-$BrC_6H_4CH_2Br$	TAC_4M (0.50)	60 °C, 2 h	87	0	3
5	$CH_3(CH_2)_3OH$ (12.0)	$Cl(CH_2)_4Br$	TAC_4M (1.0)	100 °C, 8 h	79[b] (+8)[c]	0	0
6	$CH_3(CH_2)_3OH$ (12.0)	$CH_3(CH_2)_5CHBrCH_3$	TAC_4M (1.0)	100 °C, 10 h	17	0	6 (+6)[d]
7	CH_2=$CHCH_2OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$	TAC_4M (0.50)	60 °C, 2 h	86	4	5
8	$CH_3CHOMe(CH_2)_2OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$	TAC_4M (0.50)	60 °C, 3 h	78	4	6
9[e]	C_6H_5OH (4.8)	4-*t*-$BuC_6H_4CH_2Br$	TAC_4M (0.50)	60 °C, 7 h	82 (+trace)[f]	0	8
10[e]	4-MeC_6H_4OH (4.8)	4-*t*-$BuC_6H_4CH_2Br$	TAC_6M (0.50)	60 °C, 7 h	82 (+9)[g]	0	trace
11	$C_6H_5CH_2OH$ (12.0)	$CH_3(CH_2)_7Br$	TAC_4M (1.0)	100 °C, 2 h	83	0	3
12	C_6H_4-1,4-$(-CH_2OH)_2$ (8.0)	$CH_3(CH_2)_5Br$	HTPB[h] (1.0)	100 °C, 2 h	21 (+47)[i]	trace	13
13	C_6H_4-1,4-$(-CH_2OH)_2$ (8.0)	$CH_3(CH_2)_5Br$	TAC_6M (1.0)	100 °C, 2 h	49 (+12)[i]	trace	21

[a] Cetyltrimethylammonium bromide (hexadecyltrimethylammonium bromide).
[b] 1-Butoxy-4-chlorobutane.
[c] 1,4-Dibutoxybutane.
[d] 2-Octene.
[e] 1 N Aqueous NaOH was used in the place of 4 N aqueous NaOH.
[f] 2-(4-*tert*-Butylbenzyl)phenol.
[g] 2-(4-*tert*-Butylbenzyl)-4-methylphenol.
[h] Hexadecyltributylphosphonium bromide.
[i] 1,4-Bis(hexyloxymethyl)benzene.

mono-*O*-alkylated product was achieved by using TAC_6M (entry 13). The monoether/diether ratio of 4.1 is 9.1 times larger than that (0.45) observed in the presence of HTPB. This selectivity of TAC_6M as an inverse phase-transfer catalyst, which is opposite to HTPB as a phase-transfer catalyst, is of interest.

For mechanistic considerations, the effects of size and/or shape of alcohol molecules and catalyst cavities on *O*-alkylations in aqueous NaOH solution were examined, and the results are summarized in Table 4. The efficiency of the TAC_4M catalyst in terms of yield of desired unsymmetrical ether increases with an increase in the molecular size of alcohols from methanol to butanol (entries 1 – 4), whereas it decreases in the case of a reaction of hexanol (entry 5). In the reactions of methanol to butanol, the efficiency increases with a decrease in the solubility of alcohols in water. Taking into account the molar amounts of catalysts added, the activities of the TAC_nM catalysts increase in the order of $TAC_4M < TAC_6M < TAC_8M$ for an alkylation reaction using 2-(hydroxymethyl)naphthalene (entries 7 – 9). These results show that the mechanism for the *O*-alkylation reaction is similar to that for the *C*-alkylation reaction. In the aqueous phase near the interface, the water-soluble calix[*n*]arenes TAC_nM form host-guest complexes with alkoxide anions, and a nucleophilic attack by the anion on an alkyl halide takes place at the interface. This is somewhat different from the interfacial mechanism of normal phase-transfer catalysis as proposed by Makosza, which involves a C-C bond-forming reaction within the bulk organic phase.[23] In the case of reactions of aliphatic alcohols, the size of the TAC_4M cavity may be sufficiently large to accommodate methanol to butanol, but may be somewhat small to accommodate hexanol. In the case of reactions of 2-(hydroxymethyl)naphthalene, the size of the TAC_8M cavity may be sufficiently large to accommodate the naphthyl ring, but those of TAC_4M and TAC_6M may be too small. This is reminiscent of the result where relatively good selectivity for the mono-*O*-alkylated product was achieved by using TAC_6M in the reaction of 1,4-benzenedimethanol, indicating that the size of the TAC_6M cavity might be too small to accommodate the mono-*O*-alkylated product, 1-(hexyloxymethyl)-4-hy-

Table 4. Effects of size and/or shape of alcohol molecules and catalyst cavities on *O*-alkylations in aqueous NaOH solution.



Entry	R^3–OH [mmol]	R–X [mmol]	Catalyst [mol %]	Conditions	Isolated yield [%] 5	6	2
1	CH_3OH (12.0)	4-*t*-$BuC_6H_4CH_2Br$ (4.0)	TAC_4M (0.50)	60 °C, 3 h	32	5	trace
2	CH_3CH_2OH (12.0)	4-*t*-$BuC_6H_4CH_2Br$ (4.0)	TAC_4M (0.50)	60 °C, 3 h	48	9	trace
3	$CH_3(CH_2)_2OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$ (4.0)	TAC_4M (0.50)	60 °C, 3 h	73	5	6
4	$CH_3(CH_2)_3OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$ (4.0)	TAC_4M (0.50)	60 °C, 3 h	81	3	4
5	$CH_3(CH_2)_5OH$ (12.0)	4-*t*-$BuC_6H_4CH_2Br$ (4.0)	TAC_4M (0.50)	60 °C, 3 h	62	trace	trace
6	2-$C_{10}H_7CH_2OH$ (12.0)	$CH_3(CH_2)_7Br$ (4.0)	none	100 °C, 2 h	19	0	trace
7	2-$C_{10}H_7CH_2OH$ (12.0)	$CH_3(CH_2)_7Br$ (4.0)	TAC_4M (1.0)	100 °C, 2 h	68	0	trace
8	2-$C_{10}H_7CH_2OH$ (12.0)	$CH_3(CH_2)_7Br$ (4.0)	TAC_6M (0.67)	100 °C, 2 h	72	0	trace
9	2-$C_{10}H_7CH_2OH$ (12.0)	$CH_3(CH_2)_7Br$ (4.0)	TAC_8M (0.50)	100 °C, 2 h	81	0	trace
10	none	$C_6H_5CH_2Br$ (8.0)	none	60 °C, 5 h	–	trace	21
11	none	$C_6H_5CH_2Br$ (8.0)	β-CD[a] (0.25)	60 °C, 5 h	–	8	27
12	none	$C_6H_5CH_2Br$ (8.0)	TAC_4M (0.25)	60 °C, 5 h	–	62	17

[a] β-Cyclodextrin.

droxymethylbenzene. Thus, the efficiency of the TAC_nM catalyst varies depending on the size and/or shape of the acidic substrate molecules, but not the alkyl halide molecules. This mechanistic consideration is supported by the finding that the selective formation of dibenzyl ether was observed in the reaction of benzyl bromide in aqueous NaOH solution (entry 12).

Conclusion

The water-soluble calix[*n*]arene TAC_nM was found to catalyze alkylation reactions of active methylene compounds, alcohols, and phenols with alkyl halides smoothly in aqueous NaOH solution. This water-soluble catalytic system employing TAC_nM provides additional options in aqueous biphasic reactions, in terms of synthetic chemistry and process engineering.

Experimental Section

General Remarks

Melting points were determined on a Yazawa BY-1 micro melting-point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-EX90 spectrometer at 89.5 and 22.5 MHz, a JEOL JNM–GX67S spectrometer at 270 and 67.9 MHz, or Bruker Avance-400 at 400 and 100 MHz, respectively. IR spectra were recorded on a Bio-Rad FTS-60A spectrometer. Mass spectra were obtained on a JEOL JMS-AX500 mass spectrometer (EI, 70 eV) using an interfaced GC-MS or a direct-insertion probe. Microanalyses were performed on a Perkin-Elmer 240C or 2400II elemental analyzer. Gas-liquid chromatography (GC) was performed with a Hewlett-Packard GC 5890A using capillary columns (DB-1701 and DB-WAX, 30 m × 0.25 mm). Preparative gel-permeation chromatography (GPC) was done with a JAI model 908 liquid chromatograph using JAIGEL-1H and 2H columns. Preparative thin layer chromatography (TLC) and flash chromatography were carried out on precoated silica gel 60 F_{254} plates (20 cm × 20 cm × 2 mm, E. Merck) and with silica gel 60 (spherical 0.040 – 0.100 mm, Kanto), respectively. Tetrahydrofuran (THF) was freshly distilled from Na-benzophenone. The 1-(bromomethyl)naphthalene used herein was prepared by the reaction of 1-(chloromethyl)naphthalene with $CaBr_2$ in the presence of tetrabutylammonium bromide, and purified by recrystallization from hexane-diethyl ether. Unless otherwise noted, starting materials and substrates were commercially available materials and were used without further purification.

Catalyst Preparation

p-tert-Butylcalix[*n*]arenes ($n = 4$, 6, and 8)[27] were prepared following literature methods.[28] They were debutylated by treatment with $AlCl_3$ and phenol in toluene.[29] The calix[*n*]arenes ($n = 4$, 6, and 8) thus obtained were converted to their methyl ether derivatives by treatment with CH_3I and NaH.[29,30] The methyl ether of the tetramer, 25,26,27,28-tetramethoxycalix[4]arene, was treated with paraformaldehyde, acetic acid, concentrated HCl, and 85% phosphoric acid in dioxane to give the chloromethyl derivative, 5,11,17,23-tetrakis(chloromethyl)-25,26,27,28-tetramethoxycalix[4]arene, according to a procedure developed by Shinkai et al.[31] The chloromethyl derivatives of the hexamer and octamer were prepared from the corresponding methyl ethers by treatment with chloromethyl methyl ether and $ZnCl_2$ in CS_2-CH_2Cl_2.[32]

25,26,27,28-Tetramethoxy-5,11,17,23-tetrakis(trimethylammoniomethyl)calix[4]arene Tetrachloride Tetrahydrate ($TAC_4M \cdot 4\,H_2O$)

The procedure used for this material was analogous to the literature method,[31] with minor modifications. Through a stirred DMF solution (80 mL) of the chloromethylated tetramer, 5,11,17,23-tetrakis(chloromethyl)-25,26,27,28-tetramethoxycalix[4]arene, (4.00 g, 5.9 mmol) was bubbled gaseous trimethylamine for 6 h at room temperature, which essentially follows the established method. The precipitate was collected by filtration, washed with diethyl ether, recrystallized from ethanol-diethyl ether (11:4), and dried under vacuum to give TAC_4M as a white powder; yield: 4.27 g (4.3 mmol, 73%); mp (decomp) $>$ 253 °C [anhydrous TAC_4M; lit.[31] mp (decomp) $>$ 270 °C]; ^{1}H NMR (89.5 MHz, TSP, D_2O): $\delta = 7.40$ (s, 8H), 4.48 (s, 8H), 3.85 (s, 8H), 3.68 (s, 12H), 3.08 (s, 36H); IR (KBr): $\nu = 3430,\ 873\ cm^{-1}$; anal. calcd. for $C_{48}H_{72}Cl_4N_4O_4 \cdot 4\,H_2O$: C 58.65, H 8.20, N 5.70; found: C 58.67, H 8.22, N 5.68.

37,38,39,40,41,42-Hexamethoxy-5,11,17,23,29,35-hexakis(trimethylammoniomethyl)calix[6]arene Hexachloride Hexahydrate ($TAC_6M \cdot 6\,H_2O$)

This compound was prepared from the chloromethylated hexamer (4.0 g, 4.0 mmol) following the procedure described above for TAC_4M and was obtained as a white powder from ethanol-diethyl ether (4:3); yield: 3.12 g (2.1 mmol, 53%); mp (decomp) $>$ 248 °C; ^{1}H NMR (89.5 MHz, TSP, D_2O): $\delta = 7.29$ (s, 12H), 4.42 (s, 12H), 4.1 (s, 12H), 3.50 (s, 18H), 3.10 (s, 54H); IR (KBr): $\nu = 3410,\ 874\ cm^{-1}$; anal. calcd. for $C_{72}H_{108}Cl_6N_6O_6 \cdot 6\,H_2O$: C 58.65, H 8.20, N 5.70; found: C 58.46, H 8.43, N 5.35.

49,50,51,52,53,54,55,56-Octamethoxy-5,11,17,23,29,35,41,47-octakis(trimethylammoniomethyl)calix[8]arene Octachloride Octahydrate ($TAC_8M \cdot 8\,H_2O$)

This compound was prepared from the chloromethylated octamer (4.0 g, 3.0 mmol) following the procedure described above for TAC_4M and was obtained as a white powder from methanol-ethanol-diethyl ether (7:3:5); yield: 3.26 g (1.7 mmol, 56%); mp (decomp) $>$ 255 °C; ^{1}H NMR (89.5 MHz, TSP, D_2O): $\delta = 7.37$ (br s, 16H), 4.49 (br s, 16H), 4.06 (br s, 16H), 3.37 (s, 24H), 3.08 (s, 72H); IR (KBr): $\nu = 3410,\ 875\ cm^{-1}$; anal. calcd. for $C_{96}H_{144}Cl_8N_8O_8 \cdot 8\,H_2O$: C 58.65, H 8.20, N 5.70; found: C 58.59, H 8.47, N 5.16.

Typical Procedure for *C*- and *O*-Alkylations under Aqueous Biphasic Conditions

A mixture of active methylene compound (4.8 mmol), alkyl halide (4.0 mmol), a catalytic amount (1.0 mol %) of $TAC_n M \cdot nH_2O$, and aqueous 4 N NaOH (3 mL) was heated to 60 – 100 °C for 0.5 – 10 h and stirred with a magnetic stirring bar (∅4 × 10 mm) at 1000 rpm. After the addition of water (5 mL), the resulting mixture was extracted with chloroform (10 mL × 4).[33] The combined extracts were dried over anhydrous Na_2SO_4 and evaporated. The products were purified by preparative GPC and/or TLC and the isolated yields were determined.

3-Phenyl-2-undecanone:[20] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.19 - 7.34$ (m, 5H), 3.59 (t, $J = 7.4$ Hz, 1H), 2.04 (s, 3H), 1.13 – 1.27 (m, 14H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 208.65, 139.17, 128.86, 128.24, 127.16, 59.82, 31.85, 31.80, 29.55, 29.39, 29.24, 29.02, 27.46, 22.65, 14.10$; IR (KBr): $\nu = 2926, 2855, 1715, 1455, 1354, 1159, 757, 701\ cm^{-1}$; MS (EI, 70 eV): $m/z = 246$ (M^+, 1), 203 (19), 147 (8), 134 (29), 119 (14), 105 (23), 91 (100), 69 (4), 57 (7), 43 (16).

2-Methyl-3-oxa-1-phenyl-1-undecene: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 7.5$ Hz, 2H), 7.1 – 7.5 (m, 3H), 5.33 (s, 1H), 3.94 (t, $J = 6.6$ Hz, 2H), 2.07 (s, 3H), 0.89 – 1.78 (m, 15H); MS (EI, 70 eV): $m/z = 246$ (M^+, 13), 155 (8), 134 (100), 117 (8), 116 (7), 115 (8), 105 (7), 91 (23), 43 (35).

3-Phenyl-7-octene-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.19 – 7.34 (m, 5H), 5.69 – 5.79 (ddt, $J = 17.0, 10.3, 6.7$ Hz, 1H), 4.90 – 5.01 (m, 2H), 3.60 (t, $J = 7.4$ Hz, 1H), 2.01 – 2.07 (m, 6H), 1.66 – 1.75 (m, 1H), 1.18 – 1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 208.54, 138.96, 138.38, 128.98, 128.95, 128.91, 128.22, 127.24, 114.70, 59.64, 33.62, 31.22, 29.02, 26.71$; IR (KBr): $\nu = 3029, 2937, 2861, 1641, 1713, 1355, 1160, 912, 757, 702\ cm^{-1}$; MS (EI, 70 eV): $m/z = 202$ (M^+, 6), 159 (17), 134 (9), 117 (24), 91 (100), 81 (19), 43 (27).

4-(4-*tert*-Butylphenyl)-3-phenyl-2-butanone: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.19 - 7.31$ (m, 7H), 6.99 – 7.01 (m, 2H), 3.93 (t, $J = 7.3$ Hz, 1H), 3.42 (dd, $J = 13.9, 8.0$ Hz, 1H), 2.86 (dd, $J = 13.9, 6.6$ Hz, 1H), 2.00 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 207.72, 148.80, 138.68, 136.63, 128.86, 128.55, 128.27, 127.31, 125.12, 61.37, 37.75, 34.28, 31.33, 29.50$; IR (KBr): $\nu = 2923, 2869, 1715, 1493, 1356, 1155, 825, 751, 701\ cm^{-1}$; MS (EI, 70 eV): $m/z = 280$ (M^+, 23), 265 (5), 237 (39), 147 (100), 132 (10), 117 (9), 105 (6), 91 (7), 57 (48).

4-(4-Bromophenyl)-3-phenyl-2-butanone: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.23 - 7.33$ (m, 5H), 7.13 – 7.15 (m, 2H), 6.88 – 6.91 (m, 2H), 3.85 (t, $J = 7.4$ Hz, 1H), 3.36 (dd, $J =$ 13.9, 7.2 Hz, 1H), 2.84 (dd, $J = 13.9, 7.5$ Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 207.28, 138.67, 138.02, 131.28, 130.77, 129.00, 128.32, 127.54, 119.97, 61.36, 37.69, 29.45$; IR (KBr): $\nu = 2910, 1716, 1486, 1354, 1219, 1154, 1008, 818, 741, 705\ cm^{-1}$; MS (EI, 70 eV): $m/z = 304$ (27), 302 (28), 261 (51), 259 (54), 223 (11), 180 (100), 171 (30), 169 (34), 165 (16), 90 (13), 89 (13), 77 (14), 43 (47).

4-(2-Naphthyl)-3-phenyl-2-butanone: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.66 - 7.76$ (m, 3H), 7.49 (s, 1H), 7.36 – 7.42 (m, 2H), 7.16 – 7.30 (m, 6H), 4.00 (t, $J = 7.3$ Hz, 1H), 3.59 (dd, $J =$ 13.8, 7.5 Hz, 1H), 3.05 (dd, $J = 13.8, 7.2$ Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 207.59, 138.40, 137.23, 133.42, 132.02, 128.92, 128.34, 127.77, 127.52, 127.49, 127.40, 127.39, 125.84, 125.28, 61.47, 38.49, 29.55$; IR (KBr): $\nu = 2933, 1710, 1492, 1357, 1223, 1155, 961, 814, 751, 697\ cm^{-1}$; MS (EI, 70 eV): $m/z = 274$ (M^+, 31), 231 (26), 215 (7), 153 (23), 141 (100), 115 (8), 103 (5), 77 (5), 43 (7).

7-Chloro-3-phenyl-2-heptanone: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.31 - 7.35$ (m, 2H), 7.24 – 7.28 (m, 1H), 7.19 – 7.21 (m, 2H), 3.60 (t, $J = 7.4$ Hz, 1H), 3.46 – 3.49 (m, 2H), 2.00 – 2.09 (m, 4H), 1.66 – 1.82 (m, 3H), 1.22 – 1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 208.21, 138.75, 128.99, 128.19, 127.36, 59.57, 44.73, 32.48, 31.00, 29.09, 24.75$; IR (KBr): $\nu = 2942, 2865, 1712, 1454, 1356, 1164, 755, 702\ cm^{-1}$; MS (EI, 70 eV): $m/z =$ 224 (M^+, 1), 181 (20), 145 (16), 91 (100).

7-Hydroxy-3-phenyl-2-heptanone: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 – 7.35 (m, 5H), 3.59 – 3.63 (m, 2H), 2.05 (s, 3H), 1.22 – 1.75 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.51, 138.93, 128.97, 128.22, 127.31, 62.65, 59.76, 32.56, 31.49, 29.12, 23.66; IR (KBr): ν = 3405, 2932, 2861, 1710, 1453, 1355, 1159, 1069, 753, 701 cm^{-1}; MS (EI, 70 eV): *m/z* = 206 (M^+, 5), 188 (9), 161 (26), 145 (49), 117 (58), 105 (44), 91 (100), 77 (44), 43 (74).

7-Bromo-3-phenyl-2-heptanone: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 – 7.36 (m, 5H), 3.60 (t, *J* = 7.4 Hz, 1H), 3.36 (t, *J* = 6.8 Hz, 2H), 2.05 (s, 3H), 1.66 – 1.93 (m, 4H), 1.22 – 1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.23, 138.73, 129.01, 128.20, 127.38, 59.57, 33.49, 32.65, 30.87, 29.11, 26.03; IR (KBr): ν = 2940, 2863, 1713, 1454, 1355, 1162, 753, 702 cm^{-1}; MS (EI, 70 eV): *m/z* = 227 (15), 225 (15), 145 (25), 134 (21), 91 (100), 77 (6), 43 (30).

3-(1-Naphthylmethyl)-2,4-pentanedione: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 – 8.13 (m, 7H), 4.06 (s, 2H), 2.03 – 2.09 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.30, 134.70, 133.77, 131.90, 128.93, 127.13, 126.20, 125.82, 125.72, 123.35, 122.68, 106.92, 29.63, 23.01; IR (KBr): ν = 3051, 2919, 1726, 1700, 1596, 1357, 1149, 795, 776 cm^{-1}; MS (EI, 70 eV): *m/z* = 240 (M^+, 22), 222 (9), 197 (74), 179 (57), 153 (17), 141 (43), 128 (12), 115 (14), 43 (100).

6-(1-Naphthyl)-2,4-hexanedione: MS (EI, 70 eV): *m/z* = 240 (M^+, 1), 197 (3), 179 (6), 141 (100), 115 (14), 43 (6).

3,3-Bis(1-naphthylmethyl)-2,4-pentanedione: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.42 (m, 8H), 3.91 (s, 4H), 2.00 (s, 6H);); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.35, 133.80, 132.61, 132.51, 128.78, 127.64, 126.45, 126.02, 125.67, 125.19, 123.38, 71.10, 33.25, 28.41; IR (KBr): ν = 3049, 1717, 1696, 1510, 1356, 1178, 797, 779 cm^{-1}; MS (EI, 70 eV): *m/z* = 380 (M^+, 31), 337 (12), 239 (39), 209 (52), 141 (100), 115 (50).

2-Benzoyl-3-(1-naphthyl)propanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.92 (m, 4H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.61 (m, 7H), 4.68 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.90 (dd, *J* = 14.4, 5.9 Hz, 1H), 3.63 (dd, *J* = 14.4, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.19, 134.59, 134.14, 133.98, 131.69, 131.16, 129.34, 129.03, 128.79, 128.51, 128.10, 126.75, 125.93, 125.59, 122.44, 117.06, 40.31, 32.42; IR (KBr): ν = 3060, 2244, 1693, 1597, 1449, 1266, 779 cm^{-1}; MS (EI, 70 eV): *m/z* = 285 (M^+, 33), 152 (7), 141 (74), 128 (7), 115 (12), 105 (100), 77 (44).

2-Benzoyl-3-(1-naphthyl)-2-(1-naphthylmethyl)propanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.55 (m, 8H), 7.27 – 7.31 (m, 1H), 7.05 – 7.12 (m, 4H), 4.10 (d, *J* = 14.2 Hz, 1H), 3.87 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.02, 136.60, 133.91, 132.64, 132.34, 130.73, 129.02, 128.78, 128.66, 128.30, 127.79, 126.31, 125.86, 125.24, 123.94, 121.44, 55.38, 40.12; IR (KBr): ν = 3051, 2936, 2232, 1682, 1597, 1447, 1232, 778 cm^{-1}; MS (EI, 70 eV): *m/z* = 425 (M^+, 9), 285 (6), 141 (100), 115 (10), 105 (42), 77 (17).

2-(2-Chlorophenyl)-3-(1-naphthyl)propanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.89 (m, 2H), 7.40 – 7.59 (m, 6H), 7.24 – 7.32 (m, 2H), 4.73 (dd, *J* = 9.9, 5.3 Hz, 1H), 3.71 (dd, *J* = 14.0, 5.3 Hz, 1H), 3.46 (dd, *J* = 14.0, 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.88, 133.47, 132.71, 131.95, 131.64, 130.04, 129.74, 129.22, 129.05, 128.46, 128.25, 127.77, 126.42, 125.78, 125.46, 122.85, 119.76, 37.49, 36.34; IR (KBr): ν = 3062, 2941, 2244, 1511, 1476, 1443, 1038, 791, 757cm^{-1}; MS (EI, 70 eV): *m/z* = 293 (2), 291 (M^+,7), 141 (100), 115 (16), 91 (2), 63 (3).

2,3-Bis(1-naphthyl)propanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.97 (m, 14H), 4.89 (t, *J* = 7.3 Hz, 1H), 3.77 – 3.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): ν = 134.01, 133.93, 132.50, 131.50, 131.46, 130.14, 129.34, 129.20, 129.18, 128.30, 127.86, 126.95, 126.44, 126.14, 126.01, 125.79, 125.51, 125.48, 122.67, 122.06, 120.78, 37.88, 35.51; IR (KBr) 3059, 3051, 2936, 2241, 1598, 1512, 1397, 797, 776 cm^{-1}; MS (EI, 70 eV): *m/z* = 307 (M^+, 9), 141 (100), 115 (11).

3-(1-Naphthylmethyl)indene: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.70 – 7.98 (m, 3H), 7.17 – 7.45 (m, 8H), 5.84 (s, 1H), 4.27 (s, 2H), 3.24 (s, 2H); ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.6 – 8.1 (m, 3H), 7.1 – 7.5 (m, 8H), 5.86 (t, *J* = 2.0 Hz, 1H), 4.29 (d, *J* = 2.2 Hz, 2H), 3.26 (d, *J* = 2.2 Hz, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 145.21, 144.42, 143.00, 135.33, 133.80, 132.20, 130.44, 128.57, 127.03, 126.88, 126.07, 125.77, 125.54, 125.46, 124.67, 124.31, 123.76, 119.08, 37.70, 31.57; IR (KBr): ν = 3064, 2896, 2885, 1509, 1461, 1396, 968, 772, 717 cm^{-1}; MS (EI, 70 eV): *m/z* = 256 (M^+, 33), 239 (5), 141 (100), 128 (12), 115 (18).

1,3-Bis(1-naphthylmethyl)indene: ^{1}H NMR (89.5 MHz, $CDCl_3$): = δ 7.6 – 8.1 (m, 6H), 7.1 – 7.5 (m, 12H), 5.79 (d, *J* = 1.7 Hz, 1H), 4.27 (s, 2H), 2.8 – 4.0 (m, 2H); IR (KBr): ν = 3062, 3043, 2927, 1712, 1597, 1510, 1460, 1397, 1018, 789, 776 cm^{-1}; MS (EI, 70 eV): *m/z* = 396 (M^+, 14), 255 (25), 237 (9), 141 (100), 111 (11), 97 (22), 83 (25), 75 (23), 64 (24), 59 (31).

4-*tert*-Butylbenzyl hexyl ether: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.38 (m, 2H), 7.26 – 7.28 (m, 2H), 4.47 (s, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 1.61 (quint, *J* = 7.1 Hz, 2H), 1.27 – 1.38 (m, 15H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.41, 135.68, 127.50, 125.26, 72.68, 70.51, 34.51, 31.73, 31.37, 29.77, 25.90, 22.65, 14.08; IR (KBr): ν = 2960, 2932, 2859, 1515, 1464, 1362, 1269, 1105, 1019, 817 cm^{-1}; MS (EI, 70 eV): *m/z* = 248 (M^+, 23), 233 (91), 191 (10), 147 (100), 133 (30), 117 (18), 92 (57), 57 (36), 43 (31).

4-*tert*-Butylbenzyl 3-methoxybutyl ether: ^{1}H NMR (89.5 MHz, $CDCl_3$): δ = 7.2 – 7.5 (m, 4H), 4.46 (s, 2H), 3.4 – 3.7 (m, 2H), 3.30 (s, 3H), 1.6 – 1.9 (m, 2H), 1.31 (s, 9H), 1.14 (d, *J* = 6.2 Hz, 3H); IR (KBr): ν = 2966, 2868, 1514, 1464, 1364, 1269, 1092, 1019, 817 cm^{-1}; MS (EI, 70 eV): *m/z* = 250 (M^+, 9), 203 (8), 176 (17), 163 (100), 161 (36), 147 (78), 131 (16), 117 (17), 91 (15), 59 (48).

4-*tert*-Butylbenzyl 4-methylphenyl ether: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.41 (m, 4H), 7.06 – 7.08 (m, 2H), 6.86 – 6.89 (m, 2H), 4.98 (s, 2H), 2.28 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.81, 150.88, 134.17, 129.99, 129.87, 127.41, 125.49, 114.62, 69.89, 34.56, 31.34, 20.47; IR (KBr): ν = 3031, 2969, 2871, 1612, 1513, 1364, 1237, 1176,1121, 1110, 1004, 825, 806 cm^{-1}; MS (EI, 70 eV): *m/z* = 254 (M^+, 14), 239 (9), 147 (100), 132 (14), 117 (10), 105 (7), 91 (6), 77 (3).

2-(4-*tert*-Butylbenzyl)-4-methylphenol: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.31 (m, 2H), 7.14 – 7.16 (m, 2H), 6.89 – 6.94 (m, 2H), 6.65 – 6.67 (m, 1H), 4.70 (br s, 1H), 3.92 (s, 2H), 2.24 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.52, 149.11, 136.80, 131.54, 130.03, 128.20, 128.16, 126.75, 125.56, 115.65, 35.92, 34.36, 31.36, 20.51; IR (KBr): ν = 3530, 2963, 2868, 1611, 1510, 1363, 1264, 1203, 1115, 1099, 1020, 919, 812 cm^{-1}; MS (EI, 70 eV): *m/z* = 254 (M^+, 49), 239 (100), 198 (19), 197 (12), 121 (35), 120 (15), 106 (14), 91 (14), 77 (7), 57 (12).

1-(Hexyloxymethyl)-4-hydroxymethylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 4H), 4.61 (s, 2H), 4.47 (s, 2H), 3.44 (t, J = 6.7 Hz, 2H), 2.48 (br s, 1H), 1.56 – 1.63 (m, 2H), 1.24 – 1.38 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.26, 137.91, 127.84, 127.00, 72.57, 70.50, 64.89, 31.69, 29.68, 25.85, 22.63, 14.07; IR (KBr). ν = 3377, 3009, 2956, 2932, 2860, 1515, 1421, 1362, 1214, 1099, 1050, 1018, 807, 757 cm^{-1}; MS (EI, 70 eV): m/z = 222 (M^+, 8), 191 (6), 137 (6), 121 (100), 104 (59), 92 (50), 77 (17), 56 (9), 43 (41).

1,4-Bis(hexyloxymethyl)benzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 4H), 4.49 (s, 4H), 3.45 (t, J = 6.7 Hz, 4H), 1.57 – 1.67 (m, 4H), 1.25 – 1.39 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.95, 127.68, 72.64, 70.46, 31.71, 29.75, 25.88, 22.64, 14.07; IR (KBr): ν = 2957, 2932, 2859, 1467, 1360, 1216, 1099, 1021, 807, 758 cm^{-1}; MS (EI, 70 eV): m/z = 306 (M^+, 7), 221 (4), 205 (41), 191 (16), 121 (39), 107 (44), 104 (100), 85 (55), 58 (15), 43 (68).

4-*tert*-Butylbenzyl ethyl ether: ^{1}H NMR (89.5 MHz, $CDCl_3$): δ = 7.2 – 7.5 (m, 4H), 4.47 (s, 2H), 3.53 (q, J = 6.9 Hz, 3H), 1.1 – 1.4 (m, 12H); IR (KBr): ν = 2966, 2867, 2806, 1365, 1269, 1191, 1107, 1019, 825 cm^{-1}; MS (EI, 70 eV): m/z = 192 (M^+, 29), 177 (100), 147 (16), 135 (21), 117 (9), 107 (12), 92 (15), 91 (15), 59 (12), 57 (15).

4-*tert*-Butylbenzyl propyl ether: ^{1}H NMR (89.5 MHz, $CDCl_3$): δ = 7.2 – 7.5 (m, 4H), 4.47 (s, 2H), 3.43 (t, J = 7.1 Hz, 2H), 1.4 – 1.8 (m, 2H), 1.31 (s, 9H), 0.93 (t, J = 7.5 Hz, 3H); IR (KBr): ν = 2964, 2872, 1459, 1363, 1271, 1106, 824 cm^{-1}; MS (EI, 70 eV): m/z = 206 (M^+, 25), 191 (100), 163 (4), 147 (56), 132 (16), 117 (15), 107 (31), 92 (32), 57 (28), 43 (27).

Butyl 4-*tert*-butylbenzyl ether: ^{1}H NMR (89.5 MHz, $CDCl_3$): δ = 7.2 – 7.5 (m, 4H), 4.46 (s, 2H), 3.47 (t, J = 6.1 Hz, 2H), 1.2 – 1.7 (m, 13H), 0.91 (t, J = 6.5 Hz, 3H); IR (KBr): ν = 2961, 2935, 2868, 1515, 1463, 1362, 1269, 1101, 1019, 818 cm^{-1}; MS (EI, 70 eV): m/z = 220 (M^+, 22), 205 (100), 163 (19), 147 (57), 132 (16), 117 (18), 107 (38), 92 (48), 57 (50).

2-Naphthylmethyl octyl ether: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.82 (m, 4H), 7.42 – 7.47 (m, 3H), 4.65 (s, 2H), 3.49 (t, J = 6.7 Hz, 2H), 1.63 (quint, J = 7.1 Hz, 2H), 1.26 – 1.40 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.22, 133.31, 132.94, 128.09, 127.84, 127.67, 126.24, 126.00, 125.75, 125.72, 72.93, 70.54, 31.84, 29.81, 29.46, 29.29, 26.23, 22.67, 14.11; IR (KBr): ν = 3055, 2928, 2855, 1458, 1373, 1101, 853, 815, 748 cm^{-1}; MS (EI, 70 eV): m/z = 270 (M^+, 14), 158 (6), 142 (100), 129 (10), 115 (9), 69 (4), 43 (4).

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