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Water-soluble calixarenes as new inverse phase-transfer catalysts. Their application to aldol-type condensation and Michael addition reactions in water

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Abstract—Aldol-type condensation and Michael addition reactions of activated methyl and methylene compounds in aqueous NaOH solution have been developed without the need for any added organic solvents. 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 products in good to excellent yields. © 2001 Elsevier Science Ltd. All rights reserved.

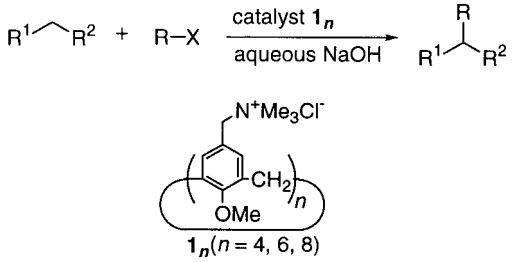
1. Introduction

The use of water as a medium for organic reactions has a number of potential advantages: (i) it is the cheapest solvent available on earth; (ii) it is non-hazardous to the environment and non-toxic; (iii) isolation of the organic products can be performed by simple phase separation.[1] There are beneficial effects of aqueous solvents on rates and selectivities of important organic transformations, e.g. Diels–Alder reactions, aldol reactions and Michael additions.[1,2] In some cases, polar water-miscible organic solvents (co-solvents)[3] or surfactants[4–6] are used when the solubility of substrate in water is not sufficiently high, but their use usually complicates workup procedures particularly in regard to catalyst recovery.[7] The use of inverse phase-transfer catalysts has the potential to solve this dilemma,[8] since they would facilitate reactions between two immiscible reactants via the transport of an organic substrate into an aqueous solution of a second reactant in which reactions would take place. One advantage of water-soluble catalysts is that they can be reused after simple decantation or extraction of the water-insoluble products.

We recently discovered that, by using water-soluble calix[*n*]arenes,[9] *p*-(trimethylammoniomethyl)calix[*n*]arene methyl ethers **1**$_n$ (*n*=4, 6 and 8), as inverse phase-transfer catalysts, nucleophilic substitution reactions of alkyl halides with simple nucleophiles such as sodium cyanide proceed smoothly in an aqueous environment to afford the desired products,[10] as do the alkylation reactions of active methylene compounds with alkyl halides in aqueous NaOH solution (Scheme 1).[11] We have also reported that metal 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 that the water-soluble calix[*n*]arenes as the inverse phase-transfer catalysts can be applied to aldol-type condensation and Michael addition reactions in aqueous NaOH solution. In these reactions, only the desired compound is formed as a product and the catalyst in the aqueous phase can be recycled after the separation of organic products.

2. Results and discussion

The activity and selectivity of the water-soluble calix[*n*]-arenes **1**$_n$ was first tested for the case of aldol-type condensation reactions of indene and acetophenone with aromatic



Scheme 1. R^1=C_6H_5, CH_3CO, C_6H_5CO, 2-ClC_6H_4, 1-$C_{10}H_7$; R^2=CH_3CO, CN; R=C_8H_{17}, 4-*t*-$BuC_6H_4CH_2$, $Cl(CH_2)_4$, 1-$C_{10}H_7CH_2$; X=Br, I.

Keywords: calixarenes; catalysis; water; aldol reactions.

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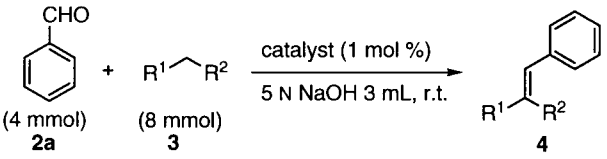
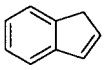
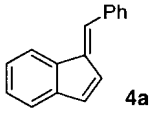
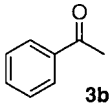
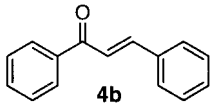
Table 1. Aldol-type condensations in aqueous NaOH solution

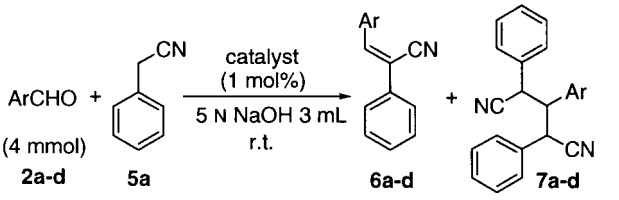


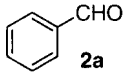
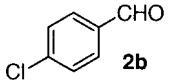
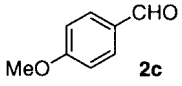
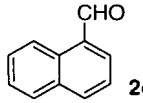
Entry	3	Catalyst	Time (h)	4	Yield (%)
1		None	1.5		0
2		β-CD[a]	1.5		0
3		CTAB[b]	1.5		82
4	**3a**	$\mathbf{1}_4$	1.5	**4a**	90
5		None	0.5		25
6		β-CD[a]	0.5		53
7		CTAB[b]	0.5		83
8	**3b**	$\mathbf{1}_4$	0.5	**4b**	92

[a] β-Cyclodextrin.
[b] Cetyltrimethylammonium bromide 10 mol%.

aldehydes in aqueous NaOH solutions, and the results are summarized in Table 1. The treatment of indene **3a** with benzaldehyde **2a** in 5N aqueous NaOH solution for 1.5 h at room temperature resulted in no reaction product being produced (entry 1). No acceleration effect was observed when β-cyclodextrin as an inverse phase-transfer catalyst was added to the reaction mixture (entry 2). In contrast, the addition of the water-soluble calix[*n*]arenes $\mathbf{1}_n$ resulted in an excellent yield of aldol-type condensation product, *E*-1-benzylidene-1*H*-indene **4a** (entry 4). Neither products derived from non-dehydration nor bis-condensation was formed. For the sake of comparison, the same reaction was also conducted in aqueous micelles using the well-known cationic surfactant,[5,6,14] cetyltrimethylammonium bromide (CTAB) (entry 3). Although the micellar reaction gave a similar selectivity and product yield,[6] the catalyst $\mathbf{1}_4$ was superior to CTAB in terms of product separation and catalyst recovery. The workup procedure for the reaction using $\mathbf{1}_4$ was extremely simple, compared with that of CTAB, because the distribution of $\mathbf{1}_n$ into the organic phase was negligible[10] and no emulsion was observed during the reaction and workup. The aldol condensation of acetophenone **3b** with **2a** also proceeded efficiently in the presence of $\mathbf{1}_4$ to afford the α,β-unsaturated ketone **4b** (entry 8).

Table 2. Aldol-type condensations of phenylacetonitrile with various aromatic aldehydes in aqueous NaOH solution



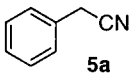
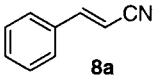
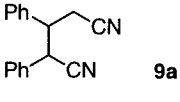
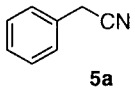
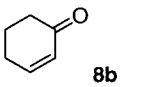
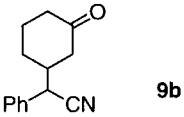
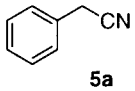
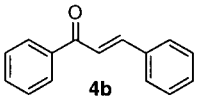
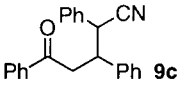
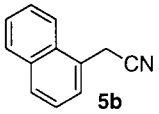
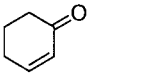
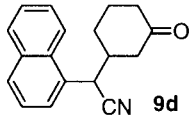
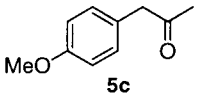
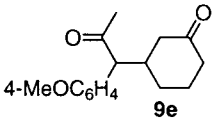
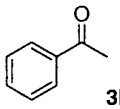
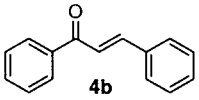
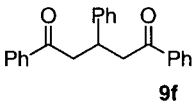
Entry	2	Catalyst	5a/2	Time (h)	Yield (%)	
					6	7[a]
1		None	5.0	1.0	36	38
2		$\mathbf{1}_4$	5.0	1.0	5	90
3	**2a**	None	2.0	0.5	14	0
4		$\mathbf{1}_4$	2.0	0.5	23	67
5		$\mathbf{1}_4$	1.1	0.5	76	10
6[b]		None	0.5	2.0	62	Trace
7[b]		CTAB[c]	0.5	2.0	76	3
8[b]		$\mathbf{1}_4$	0.5	2.0	91	3
9		None	5.0	2.0	53	4
10		$\mathbf{1}_4$	5.0	2.0	3	94
11		None	1.1	1.0	48	Trace
12	**2b**	$\mathbf{1}_4$	1.1	1.0	84	12
13		$\mathbf{1}_4$	5.0	2.0	11	87
14		None	1.1	1.0	19	Trace
15	**2c**	$\mathbf{1}_4$	1.1	1.0	47	16
16		None	1.1	1.0	35	Trace
17	**2d**	$\mathbf{1}_4$	1.1	1.0	87	Trace

[a] The α,γ-nitriles **7a–c** were isolated as a mixture of *syn*/*syn*, *syn*/*anti*, and *anti*/*anti* diastereomers. The ratios were determined by ^{1}H NMR.
[b] An 8 mmol amount of **2a** was used, and yields were based on 4.0 mmol amount of **5a**.
[c] Cetyltrimethylammonium bromide 10 mol%.

Some examples of the reaction of phenylacetonitrile with aromatic aldehydes in aqueous NaOH solution are shown in Table 2. In all cases, along with aldol-type condensation, a Michael addition of phenylacetonitrile to the first condensation product **6** took place to give the α,γ-dinitrile compound **7**. The configuration of products **6a–d** is exclusively *Z*, because the chemical shift of the aromatic protons in the ^{1}H NMR spectra indicates that the aromatic rings are coplanar with the double bond.[15] However, in the presence of the catalyst $\mathbf{1}_4$ the reactions proceeded with good selectivity. The product selectivity was highly dependent on the molar ratio of **5a** to **2**. Thus, the α,β-unsaturated nitrile **6a** was obtained as the major product in the reaction of **5a** with **2a** at a lower molar ratio (entry 8), while α,γ-dinitrile **7a** was obtained at a higher molar ratio (entry 2). Similarly, good to high selectivity was observed for 4-chlorobenzaldehyde **2b** (entries 10 and 12), and 1-naphthaldehyde **2d** (entry 17).

Encouraged by the above observations, we also examined the Michael addition reactions of activated methyl and methylene compounds to α,β-unsaturated ketones and nitriles in aqueous NaOH solution. The results are summarized in Table 3. With the exception of acetophenone, the

Table 3. Michael additions of activated methyl and methylene compounds to α,β-unsaturated ketones and nitrile in aqueous NaOH solution

Entry	Donor (8 mmol)	Acceptor (4 mmol)	Catalyst (1 mol%)	Conditions[a] (°C, h)	Product	Yield[b] (%)
1	 **5a**	 **8a**	none	rt, 2 h	 **9a**	19
2			$\mathbf{1}_4$	rt, 2 h		69
3			$\mathbf{1}_6$ (1st use)	rt, 2 h		79
4			$\mathbf{1}_6$ (2nd use)[c]	rt, 2 h		52
5	 **5a**	 **8b**	none	rt, 0.5 h	 **9b**	49
6			$\mathbf{1}_4$	rt, 0.5 h		93
7	 **5a**	 **4b**	none	rt, 0.2 h	 **9c**	79
8			$\mathbf{1}_4$	rt, 0.2 h		98
9	 **5b**	 **8b**	none	40°C, 0.5 h	 **9d**	12
10			$\mathbf{1}_4$	40°C, 0.5 h		61
11			$\mathbf{1}_6$	40°C, 0.5 h		65
12			$\mathbf{1}_8$	40°C, 0.5 h		84
13	 **5c**	 **8b**	none	rt, 0.5 h	 **9e**	3
14			$\mathbf{1}_6$	rt, 0.5 h		79
15	 **3b**	 **4b**	none	60°C, 10 h	 **9f**	9
16			$\mathbf{1}_4$	60°C, 10 h		35

[a] An aqueous 5N NaOH solution (3 mL) was used.
[b] The Michael adducts **9a–e** were isolated as a mixture of *syn* and *anti* diastereomers. The ratios were determined by ^{1}H NMR.
[c] Aqueous layer used in entry 3.

reactions proceeded efficiently in the presence of a catalytic amount (1 mol%) of $\mathbf{1}_n$ to afford the corresponding Michael adducts. For instance, in the reaction of phenylacetonitrile **5a** with cinnamonitrile **8a** the yield of Michael adduct **9a** was increased from 19% to 79% by the addition of $\mathbf{1}_6$ (entry 3). Unfortunately, however, the catalytic activity was reduced to approximately 66% with reuse of the aqueous layer, which contained the catalyst (entry 4). The use of the catalyst $\mathbf{1}_6$ in the reaction of 4-methoxyphenylacetone **5c** and 2-cyclohexen-1-one **8b** increased the yield of **9e** to 79%, that is, 26 times larger than that observed in its absence (entries 13 and 14). Treatment of **3b** with **4b** at 60°C for 10 h afforded the 1,4-adduct **9f** in 35% yield (entry 16). This result suggests that a one-pot synthesis of **9f** from **3b** and **2a** can be achieved by controlling the molar ratios of reactants and the reaction temperature. Indeed, the reaction of **3b** with **2a** at room temperature gave **4b** in an excellent yield (entry 8 in Table 1). In the reaction of 1-naphthylacetonitrile **5b** with **8b**, the activities of the catalysts **1** increase in the order of $\mathbf{1}_4 \leq \mathbf{1}_6 < \mathbf{1}_8$ (entries 10–12).[10,11] This result may be a reflection of the following interfacial mechanism.[11] In the aqueous phase near the interface, the water-soluble calix[*n*]arenes $\mathbf{1}_n$ would be expected to form host-guest complexes with the carbanion which arises via the deprotonation of Michael donor with hydroxide ions, and the nucleophilic attack of the anion on the Michael acceptor would take place at the interface. This is somewhat different from the Makosza interfacial mechanism of normal phase-transfer catalysis, which involves C–C bond-forming reaction within balk organic phase as a final step.[16] The size of the cavity of $\mathbf{1}_8$ may be sufficiently large to accommodate the naphthyl ring, but those of $\mathbf{1}_4$ and $\mathbf{1}_6$ may be somewhat small. Thus, the efficiency of the catalyst $\mathbf{1}_n$ varies depending on the size of the Michael donor molecules, but not the Michael acceptor molecules. Aldol-type condensation reactions using catalysts $\mathbf{1}_n$ also most likely proceed via this mechanism.

In conclusion, water-soluble calix[*n*]arene derivatives $\mathbf{1}_n$ were found to catalyze aldol-type condensation and Michael addition reactions of activated methyl and methylene compounds smoothly in aqueous NaOH solution. This water-soluble catalytic system employing $\mathbf{1}_n$ provides powerful options in aqueous biphasic reactions for synthetic chemistry and process engineering.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400s spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ with tetramethylsilane as an internal standard and *J* values are given in Hz. The MS spectra were measured on a JEOL JMS-AX500 mass spectrometer

(EI, 70 eV) using GC–MS coupling. IR spectra were recorded on a Bio-Rad FTS-60A spectrometer. Preparative gel-permeation chromatography (GPC) was done with a JAI model 908 liquid chromatograph with a couple of JAIGEL-1H and 2H columns.

3.2. Materials

The water-soluble calix[*n*]arenes $\mathbf{1}_n{\cdot}n\mathrm{H_2O}$ (n=4, 6 and 8) were prepared by following literature methods[17] and identified by IR and NMR spectroscopy as well as elemental analysis. Cetyltrimethylammonium bromide and β-cyclodextrin were purchased from Tokyo Kasei Kogyo, and used without further purification.

3.3. Typical procedure for the aldol-type condensation and Michael addition

To a 10 mL three-necked flask containing $\mathbf{1}_n{\cdot}n\mathrm{H_2O}$ (1 mol%) was added an aqueous 5N NaOH solution (3 mL). An activated methyl or methylene compound and aldehyde or enone were then introduced. The reaction mixture was stirred with a magnetic stirring bar at 800 rpm for 0.2–2 h at rt−60°C (depending on the substrates). After addition of water (5 mL), the resulting mixture was extracted with chloroform (10 mL×3). The combined extracts were dried with anhydrous Na_2SO_4 and evaporated. The products were purified by preparative GPC and the isolated yields were determined.

3.3.1. *E*-1-Benzylidene-1*H*-indene (4a).[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–6.98 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.08, 140.09, 137.44, 136.93, 134.56, 130.24, 128.72, 128.69, 128.34, 127.56, 126.11, 125.16, 120.96, 119.15; IR (KBr) 3062, 1443, 795, 762, 694, 505 cm^{-1}; MS (EI) *m/z* 204 (M^+, 100), 203 (95), 202 (62), 101 (27), 89 (10), 76 (6).

3.3.2. Benylideneacetophenone (4b).[5b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.39 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.58, 144.86, 138.22, 134.89, 132.79, 130.56, 128.97, 128.64, 128.51, 128.46, 122.10; IR (KBr) 3081, 2917, 1664, 1605, 1576, 1449, 1336, 1215, 1016, 747, 689 cm^{-1}; MS (EI) *m/z* 208 (M^+, 100), 207 (97), 179 (16), 131 (41), 105 (21), 103 (22), 77 (58), 51 (16).

3.3.3. α-Phenylcinnamonitrile (6a).[15b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.69–7.67 (m, 2H), 7.54 (s, 1H), 7.50–7.38 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.24, 134.43, 133.69, 130.52, 129.25, 129.19, 129.05, 128.94, 125.97, 117.99, 111.64; IR (KBr) 3032, 2019, 1447, 938, 908, 761, 744, 692, 518 cm^{-1}; MS (EI) *m/z* 205 (M^+, 100), 204 (71), 190 (31), 177 (16), 102 (10), 89 (19).

3.3.4. β-(4-Chlorophenyl)-α-pheylacrylonitrile (6b).[15a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.68–7.66 (m, 2H), 7.48–7.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.58, 136.39, 134.09, 132.13, 130.45, 129.41, 129.20, 129.10, 125.96, 117.73, 112.22; IR (KBr) 3057, 3036, 2220, 1589, 1493, 1448, 1092, 829, 762, 691, 522 cm^{-1}; MS (EI) *m/z* 241 ($[M+2]^+$, 29), 239 (M^+, 89), 204 (100), 177 (20), 101 (13), 88 (26).

3.3.5. β-(4-Methoxyphenyl)-α-pheylacrylonitrile (6c).[15a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.87 (m, 2H), 7.66–7.64 (m, 2H), 7.46–7.36 (m, 4H), 6.99–6.96 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.39, 141.85, 134.80, 131.18, 128.98, 128.72, 126.48, 125.74, 118.54, 114.36, 108.58, 55.40; IR (KBr) 3016, 2844, 2210, 1603, 1595, 1512, 1255, 1180, 1027, 832, 694 cm^{-1}; MS (EI) *m/z* 235 (M^+, 100), 204 (8), 190 (10), 165 (16).

3.3.6. β-Naphthylmethyl-α-pheylacrylonitrile (6d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.08 (d, 1H, J=7.2 Hz), 7.98–7.89 (m, 3H), 7.78–7.76 (m, 2H), 7.59–7.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.22, 134.40, 133.70, 131.71, 131.27, 130.75, 129.48, 129.20, 129.02, 127.07, 126.99, 126.45, 126.30, 125.57, 123.43, 117.63, 115.57; IR (KBr) 3041, 2219, 1448, 890, 781, 758, 685 cm^{-1}; MS (EI) *m/z* 255 (M^+, 100), 254 (66), 240 (18), 228 (15), 177 (13), 127 (12), 113 (13).

3.3.7. 1,2,3-Triphenyl-1,3-propanedicarbonitrile (7a). (Diastereomer ratio: **A/B/C**=62/32/6) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–6.64 (m, 15H), 4.82 (d, 0.32H, J=5.2 Hz, for **B**), 4.45 (d, 0.32H, J=10.6 Hz, for **B**), 4.41 (d, 0.12H, J=7.7 Hz, for **C**), 4.13 (d, 1.24H, J=8.1 Hz, for **A**), 3.86 (t, 0.06H, J=7.7 Hz, for **C**), 3.45 (dd, 0.32H, J=10.6, 5.2 Hz, for **B**), 3.37 (t, 0.62H, J=8.1 Hz, for **A**); IR (KBr) 3065, 3033, 2245, 1495, 1455, 757, 747, 701 cm^{-1}; MS (EI) *m/z* 322 (M^+), 206 (100), 179.

3.3.8. 2-(4-Chlorophenyl)-1,3-diphenyl-1,3-propanedicarbonitrile (7b). (Diastereomer ratio: **A/B/C**=64/27/9) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–6.55 (m, 14H), 4.82 (d, 0.27H, J=5.0 Hz, for **B**), 4.40 (d, 0.27H, J=10.7 Hz, for **B**), 4.37 (d, 0.18H, J=7.7 Hz, for **C**), 4.11 (d, 1.28H, J=8.1 Hz, for **A**), 3.86 (t, 0.09H, J=7.7 Hz, for **C**), 3.45 (dd, 0.27H, J=10.7, 5.0 Hz, for **B**), 3.37 (t, 0.64H, J=8.1 Hz, for **A**); IR (KBr) 3066, 3035, 2244, 1495, 1456, 1095, 1015, 755, 733, 700 cm^{-1}; MS (EI) *m/z* 358 ($[M+2]^+$), 356 (M^+), 240 (100), 213, 205, 178, 117.

3.3.9. 2-(4-Methoxyphenyl)-1,3-diphenyl-1,3-propanedicarbonitrile (7c). (Diastereomer ratio: **A/B/C**=64/28/8) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–6.53 (m, 14H), 4.78 (d, 0.28H, J=5.1 Hz, for **B**), 4.39 (d, 0.28H, J=10.5 Hz, for **B**), 4.36 (d, 0.16H, J=7.7 Hz, for **C**), 4.09 (d, 1.28H, J=8.0 Hz, for **A**), 3.85–3.81 (t, 0.08H, for **C**), 3.78 (s, 1.92H, for **A**), 3.70 (s, 0.24H, for **C**), 3.69 (s, 0.84H, for **B**), 3.41 (dd, 0.28H, J=10.5, 5.1 Hz, for **B**), 3.33 (t, 0.64H, J=8.0 Hz, for **A**); IR (KBr) 3002, 2965, 2839, 2241, 1516, 1455, 1254, 1181, 1032, 760, 743, 699 cm^{-1}; MS (EI) *m/z* 352 (M^+), 236 (100).

3.3.10. 2-(1-Naphthyl)-1,3-diphenyl-1,3-propanedicarbonitrile (7d). This compound has not been isolated because of its trace amount. MS (EI) *m/z* 372 (M^+), 256, 178 (100).

3.3.11. 1,2-Diphenyl-1,3-propanedicarbonitrile (9a). (Diastereomer ratio: **A/B**=60/40) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.17 (m, 10H), 4.29 (d, 0.6H, J=8.0 Hz, for **A**), 4.17 (d, 0.4H, J=6.8 Hz, for **B**), 3.50–3.38 (m, 1H), 2.98 (dd, 0.4H, J=16.8, 9.6 Hz, for **B**), 2.88–2.78 (m, 1H), 2.98 (dd, 0.6H, J=16.9, 7.3 Hz, for **A**); IR (KBr) 3065, 3035, 2924, 2245, 1601, 1494, 1456, 1422, 760, 701 cm^{-1}; MS (EI) *m/z* 246 (M^+), 130 (100), 117, 103, 77.

3.3.12. α-(3-Oxocyclohexyl)phenylacetonitrile (9b). (Diastereomer ratio: **A/B**=50/50) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.27 (m, 5H), 3.92 (d, 0.5H, *J*=4.5 Hz, for **A**), 3.76 (d, 0.5H, *J*=5.8 Hz, for **B**), 2.43–1.59 (m, 9H); IR (KBr) 2945, 2870, 2240, 1712, 1453, 1228, 762, 702 cm^{-1}; MS (EI) *m/z* 213 (M^+), 117, 97 (100), 69.

3.3.13. 3-Benzoyl-1,2-diphenylpropanecarbonitrile (9c). (Diastereomer ratio: **A/B**=50/50) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.86 (m, 2H), 7.42–7.07 (m, 13H), 4.50 (d, 0.5H, *J*=5.3 Hz, for **A**), 4.22 (d, 0.5H, *J*=6.0 Hz, for **B**), 3.94–3.70 (m, 2H), 3.52 (dd, 0.5H, *J*=17.9, 5.0 Hz), 3.38 (dd, 0.5H, *J*=17.4, 4.8 Hz); IR (KBr) 3063, 3032, 2240, 1684, 1452, 1212, 754, 733, 700 cm^{-1}; MS (EI) *m/z* 325 (M^+), 209, 205, 105 (100), 77.

3.3.14. α-(3-Oxocyclohexyl)-1-naphtylacetonitrile (9d). (Diastereomer ratio: **A/B**=50/50) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.49 (m, 7H), 4.75 (d, 0.5H, *J*=4.0 Hz, for **A**), 4.56 (d, 0.5H, *J*=4.7 Hz, for **B**), 2.54–1.41 (m, 9H); IR (KBr) 3054, 2946, 2869, 2241, 1713, 1228, 802, 780 cm^{-1}; MS (EI) *m/z* 263 (M^+), 167, 97 (100), 69.

3.3.15. 1-(3-Oxocyclohexyl)-1-(4-methoxyphenyl)-2-propanone (9e). (Diastereomer ratio: **A/B**=50/50) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.05 (m, 2H), 6.89–6.84 (m, 2H), 3.85 (s, 1.5H), 3.80 (s, 1.5H), 3.48 (d, 0.5H, *J*=2.6 Hz, for **A**), 3.46 (d, 0.5H, *J*=1.8 Hz, for **B**), 2.66–1.12 (m, 12H); IR (KBr) 2953, 1711, 1511, 1253 cm^{-1}; MS (EI) *m/z* 260 (M^+), 217 (100), 121.

3.3.16. 1,3,5-Triphenyl-1,5-pentanedione (9f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 4H, *J*=7.4 Hz), 7.55 (t, 2H, *J*=7.1 Hz), 7.44 (t, 4H, *J*=7.7 Hz), 7.29–7.25 (m, 4H), 7.20–7.16 (m, 1H), 4.09–4.04 (m, 1H), 3.50 (dd, 2H, *J*=16.6, 7.0 Hz), 3.36 (dd, 2H, *J*=16.6, 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.56, 143.98, 137.28, 132.99, 128.65, 128.60, 128.18, 127.55, 126.72, 44.98, 37.46; IR (KBr) 3063, 3029, 2899, 1695, 1678, 759, 698 cm^{-1}; MS (EI) *m/z* 328 (M^+), 209 (77), 105 (100), 77 (77).

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