2-Cyanomethylbenzaldehyde – useful substrate for preparation of some 1,3-di- and 1,2,3-trisubstituted naphthalenes or substituted 1-cyanobenzobicyclo[2.2.2]octenes

Marek Panasiewicz, Tadeusz Zdrojewski, Krzysztof Chrulski, Anna Wojtasiewicz, and Andrzej Jończyk*

Warsaw University of Technology, Faculty of Chemistry
Noakowskiego St. 3, 00-664 Warsaw, Poland
E-mail: anjon@ch.pw.edu.pl

Abstract

2-Cyanomethylbenzaldehyde reacts in the presence of concentrated aqueous solution of sodium hydroxide or powdered potassium carbonate and a quaternary ammonium salt as a catalyst in benzene (phase-transfer catalysis) with 2-chloroethyl aryl ketones or electrophilic alkenes affording 1-cyano-3-acylnaphthalenes, 1-(2-cyano)- and 1-(2-phenylsulfonyl)ethyl-3-substituted naphthalenes or 1-cyano-5,8-diaroyl-benzobicyclo[2.2.2]octenes. Further cyclization of the corresponding 5,8-diacetyl derivative of 1-cyanobenzobicyclooctene gives 1-cyano-10-methyltetracyclo[7.5.1.$0^{2,7}$.$0^{8,13}$]pentadeca-2,4,6,10-tetraen-12-one. Formation of these products is rationalized.

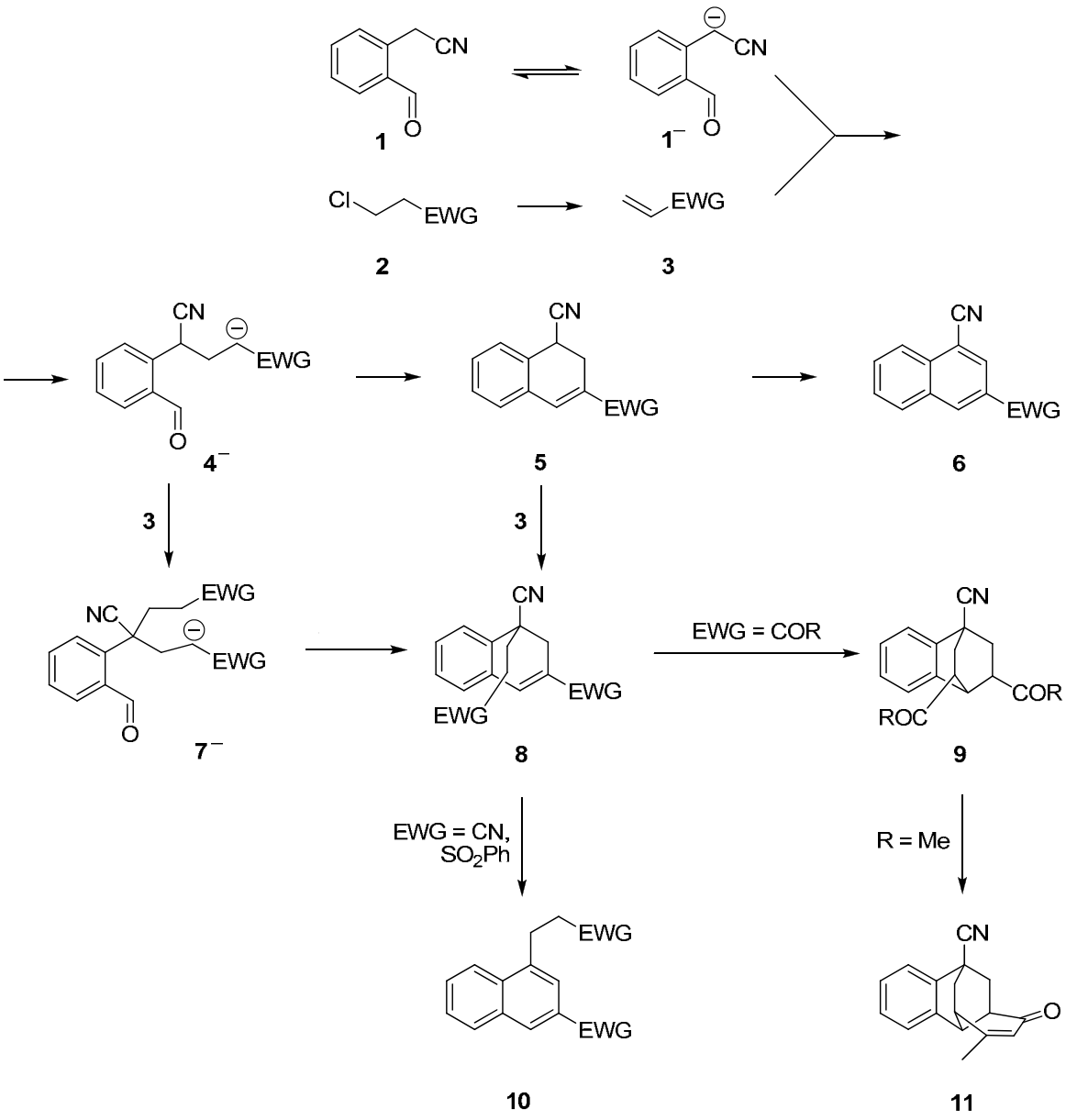
Keywords: Phase-transfer catalysis, Michael reaction, annulation, cyclization, carbocycles, redox reaction

Introduction

The cyanomethyl group together with the adjoining formyl group are suitably arranged in a molecule of 2-cyanomethylbenzaldehyde (**1**)[1] to participate in the formation of fused-ring compounds. Indeed, the reaction of aldehyde **1** with ammonia, primary or secondary amines, catalyzed by trifluoroacetic acid, gives 3-amino substituted isoquinolines, usually in good yields.[2] In this case, amidines formed by the addition of ammonia or amines to the cyano group in **1** undergo cyclization with the formyl group. We expected that in an analogous process, anions $\mathbf{4}^{-}$ generated in Michael reaction of $\mathbf{1}^{-}$ with electrophilic alkenes **3** (where EWG is an electron withdrawing group), should be intercepted by the formyl group forming dihydronaphthalene derivatives **5**.

Results and Discussion

However, the reaction of **1** with equimolar amounts (or slight excess) of 2-chloroethyl aryl ketones **2**, aryl or alkyl vinyl ketones **3**, carried out under phase-transfer catalysis conditions, (PTC[3-6]), i.e. in the presence of 50% aqueous sodium hydroxide and benzyltriethylammonium chloride (TEBAC) as a catalyst (system A) or powdered potassium carbonate and Aliquat 336 as a catalyst (system B), afforded 1-cyano-3-acylnaphthalenes **6a-g**, in 53-73% yield (Scheme 1, Table 1).



Scheme 1. Formation of fused-ring products **6**, **9**, **10** and **11**.

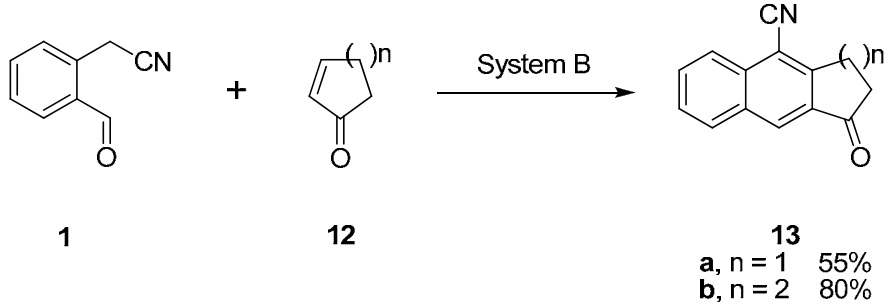
Table 1. Products **6**, **9** and **10** prepared

No.	**2** or **3**; EWG	System[a]	(**2** or **3**)/**1** (mol/mol)	Yield [%] **6**	**9**	**10**
1	**2a**; C_6H_5CO	A	1.0	68	-	-
			2.1	5	60	-
	3a; C_6H_5CO	A	1.0	41[b]	-	-
2	**2b**; 4-MeC_6H_4CO	A	1.0	53	-	-
			2.1	-	52	-
3	**2c**; 4-ClC_6H_4CO	A	1.0	55	-	-
			2.1	-	78	-
4	**2d**; 4-BrC_6H_4CO	A	1.0	73	-	-
			2.1	-	50	-
5	**2e**; 3,4-$(MeO)_2C_6H_3CO$	A	1.0	54	-	-
			2.1	5	47	-
6	**3f**; CH_3CO	A	1.0	11[b]	-	-
		B	1.0	72	-	-
7	**3g**; C_2H_5CO	A	1.0	38[b]	-	-
		B	1.0	60	-	-
8	**3h**; CN	A	2.2	-	-	34
9	**3i**; SO_2Ph	A	2.2	-	-	78

[a]A: 50% aq. NaOH, cat. TEBAC; B: powd. K_2CO_3, cat. Aliquat 336. [b]A lot of tars were formed.

The reaction of **1** with one equivalent of phenyl vinyl ketone **3a** (EWG = Bz) afforded naphthalene **6a**, however in a lower yield comparing to the one where ketone **2a** was used (Table 1; No.1). Aryl vinyl ketones are unstable, easily decomposed when treated with a base, hence the use of their precursors, ketones **2**, in more basic System A is advisable.

Structurally related products **13** were also formed from the reaction of **1** with cyclic ketones **12a,b** (used in significant excess). In this case the best results gave the solid-liquid PTC system B (Scheme 2).

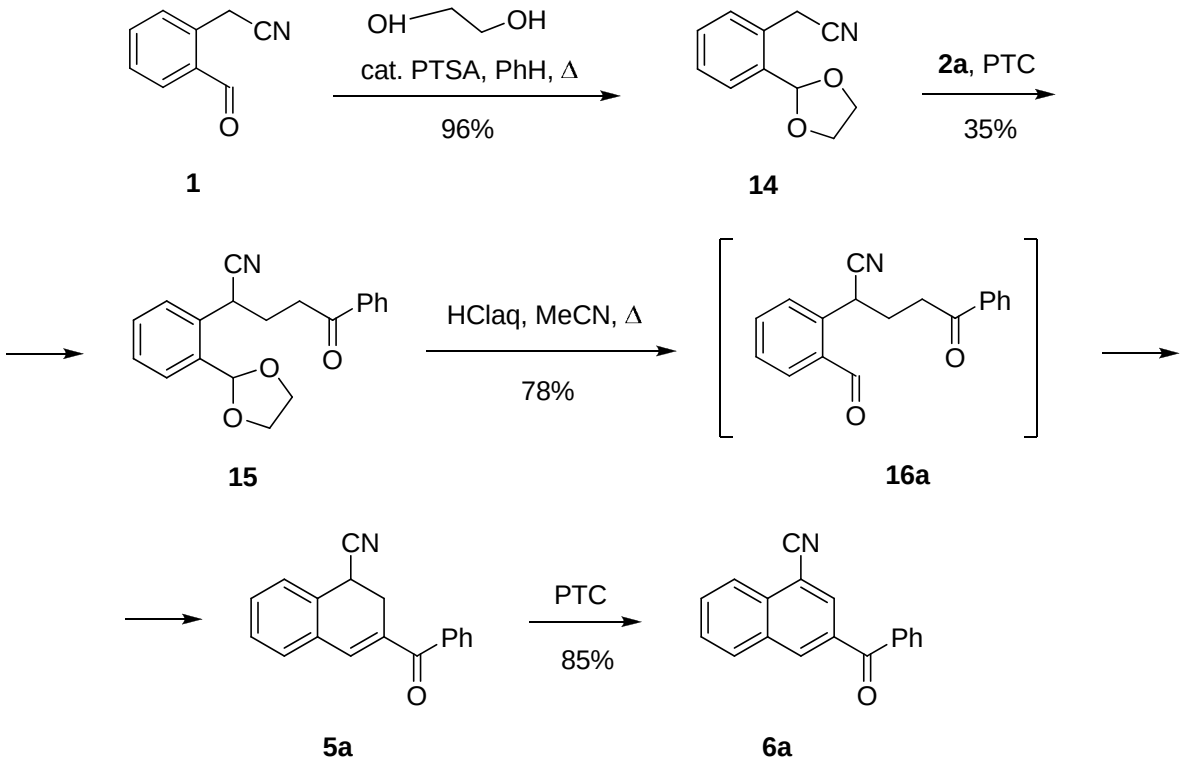


Scheme 2. Reaction of aldehyde **1** with cyclic ketones **12**.

Products **6** and **13** are not described in the literature. Synthesis of naphthalenes substituted at C-1 and C-3 with EWG-s is not easily realized, and such products were often obtained in low yields, usually by processes other than aromatic electrophilic substitution (e.g. 1,3-dinitro-,[7,8] 1,3-dicyano-,[9] 1-nitro-3-acyl-,[10] 3-cyano-1-methoxycarbonyl-[11] or 1-cyano-3-methoxycarbonylnaphthalene[12]). Recently, the synthesis and transformations of fused bicyclo[2.2.2]octenes have been reviewed.[13]

A possible route leading to products **6** is presented on Scheme 1. Carbanion $\mathbf{1}^-$ generated from **1** reacted with ketone **2** or **3** (in the case of chloroketones **2** most likely via aryl vinyl ketone **3**), forming anion $\mathbf{4}^-$. Intramolecular aldol condensation of the latter followed by the elimination of water produces dihydronaphthalene **5**, which is dehydrogenated to the final naphthalene **6**. Conversion of **5** into **6** (Scheme 1) requires comments. It is well established that PTC oxidation of α-arylalkanenitriles with dioxygen leads to the formation of corresponding phenones.[14-16] In the case of **5**, this reaction should give 3-aroyl-1-naphthols (by an oxidation-tautomerization route), which in fact were not formed. On the other hand, 2-substituted derivatives of 1,4-dicyano-1,2-dihydronaphthalene treated with 5% ethanolic potassium hydroxide were dehydrogenated into 1,4-dicyanonaphthalenes in low yield, but aromatization comprised mainly elimination of hydrogen cyanide.[17] Partially unsaturated, cyano-substituted fused aromatic compounds were dehydrogenated with DDQ.[18-20]

Therefore, we undertook the independent synthesis of **5a** (Scheme 3) to investigate its transformation into **6a**.



Scheme 3. Independent synthesis of **5a** and its transformation into **6a** in PTC system A.

Acetalization of **1** gave quantitatively **14** which under PTC conditions reacted sluggishly with ketone **2a** affording the Michael adduct **15**. The reaction progress monitored by GC revealed total conversion of **14**, but column chromatography allowed isolation of **15** in ca. 35% yield, at best. Attempted deacetalization of **15** with hydrochloric acid in acetonitrile led directly to **5a**, instead of **16a**.

Next, the key intermediate **5a** was stirred in the PTC system under air, under inert gas or in the stream of bubbled oxygen. Under the two first conditions, the process led to product **6a**, but at a much higher rate under atmosphere of air, while passing oxygen into the reaction gave a complex mixture of products. The results testify to the spontaneous character of **5** into **6** transformation, difficult to control. Interestingly, we did not observe the formation of a dehydrocyanation product, i.e. 2-benzoylnaphthalene.

The reaction of methylene compounds with electrophilic alkenes often led to substitution of both acidic hydrogen atoms, particularly when an excess of the anion acceptor was applied.[21-23] A similar process, additionally involving the formyl group in **1**, was observed. Thus, stirring of **1** with more than two molar equivalents of ketones **2** produced tricyclic derivatives **9** in a 47-78% yield (Scheme 1, Table 1). The reaction of **1** with an excess of methyl vinyl ketone (**3a)** gave intermediate **9** which possesses an active methyl group hence it reacted further giving polycyclic products **11**.

Concerning tricyclic structure **9**, the parent hydrocarbon, i.e. benzobicyclo[2.2.2]octane[24-28] and some of its derivatives (e.g. 1-hydroxy-,[24,29,30] 1-methoxy-,[25,30,31] 1-chloro-,[25,29] 1-bromo- and 1-acetoxy-,[25] 2-cyano-,[32,33] 2,3-dimethoxycarbonyl-[32] or 2,7-dibromo-[34]) were prepared by multistep procedures, usually in low yields, while compounds listed in Table 1 are not described in the literature.

When an excess of ketone **2** was present in the system, the α-cyanobenzyl carbanion generated from $\mathbf{4}^{-}$ via [1,3] hydrogen shift reacted with the vinyl ketone **3** to give the anion of diadduct $\mathbf{7}^{-}$, which via a series of intramolecular reactions afforded the final structure **9** (Scheme 1). Alternatively, intermediate diketone **8** may be also produced by the reaction of an anion from cyanodihydronaphthalene **5** with vinyl ketone **3**.

Compounds **9a**,**c**-**e** were isolated as pure diastereoisomers, possessing the same relative configuration at the carbon atoms bearing the aroyl groups (**A** and its mirror image; Figure 1). Their structure was fully confirmed by ^{13}C NMR spectra (two signals of carbonyl carbons). Surprisingly, the ^{13}C NMR spectrum of the product of the reaction of aldehyde **1** with ketone **2b** confirms the identically arranged aroyl groups in **9b** (diastereoisomer **B** or **C**; Figure 1). Attempted equilibration of product **9b** (stirring with 50% aq. sodium hydroxide in benzene with TEBAC catalyst for 2 h) failed since it decomposed.

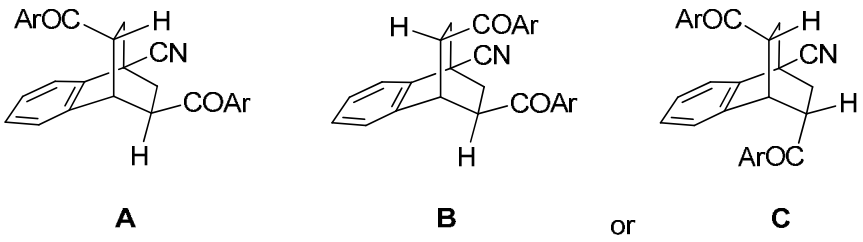


Figure 1. Possible orientation of aroyl groups in compounds **9**.

Still other products were formed from **1** and electrophlic alkenes **3h**,**i.** In these cases, anions from **8** were not prone to cyclize but eliminated hydrogen cyanide giving naphthalene derivatives **10h**,**i.**

Conclusions

We have described a simple approach to derivatives of cyanonaphthalenes **6** and cyanobenzobicyclo[2,2,2]octenes **9** from available aldehyde **1** and ketones **2** or **3**, under convenient PTC conditions. Furthermore, we have indicated that suitably substituted 1-cyano-1,2-dihydronaphthalenes **5** entered under PTC conditions spontaneous dehydrogenation into 1-cyanonaphthalene derivatives **6**. The intermediate tricyclic structure **9f** [produced from **1** and methyl vinyl ketone (**3f**)] reacted further giving the fused-ring product **11**. On the other hand, the PTC reaction of **1** with electrophilic alkenes **3h**,**i** afforded 1,3-disubstituted naphthalenes **10h**,**i**. The formation of these products is rationalized.

Experimental Section

General Procedures. Column chromatography was performed on Merck silica gel (240÷400 mesh) using AcOEt-hexane (gradient) as eluent, and gas chromatography (GC) on an Agilent 6850 Series GC System fitted with HP-50+ (30 m) column. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra were measured on a Varian Mercury 400BB spectrometer, if not indicated otherwise; chemical shifts (δ) are given in ppm related to tetramethylsilane (TMS), coupling constants *J* in Hz. IR spectra were recorded on a Specord M-80 spectrophotometer in KBr; ν are given in cm^{-1}. Elemental analyses were performed on a Perkin Elmer 2400 Ser. II CHNS/O microanalyser. Melting points were measured on a capillary apparatus, and were not corrected.

Aldehyde **1**,[1] chloroethyl aryl ketones **2a-d**[35] and **2e**[36] were obtained according to literature procedures.

General procedure for preparation of 1-cyano-3-aroylnaphthalenes 6a-e in system A

To the stirred solution of aldehyde **1** (0.29 g, 2.0 mmol), chloroketone **2a-e** (2.0 mmol) and TEBAC (0.023 g, 0.1 mmol) in benzene (30 mL), 50%$_{aq}$ NaOH (1 mL, 19.1 mmol) was added. When aldehyde **1** was no longer detected by GC (1-2 h), the reaction mixture was diluted with water (50 mL). The organic phase was separated and the water phase was extracted with $CHCl_3$ (3×20 mL). Combined organic phases were washed with water (30 mL) and dried ($MgSO_4$). After the solvent was evaporated, the crude mixture was purified by column chromatography (Table 1). The products were recrystallized to give analytical samples of **6a-e**.

1-Cyano-3-benzoylnaphthalene (6a). Mp 155-156 °C (MeOH). Yield: 350 mg (68 %). ^{1}H NMR: δ = 7.53-7.57 (m, 2 H, CH_{Ar}), 7.65-7.69 (m, 2 H, CH_{Ar}), 7.70-7.74 (m, 1 H, CH_{Ar}), 7.82-7.86 (m, 2 H, CH_{Ar}), 8.03 (d, *J* = 8.0, 1 H, CH_{Ar}), 8.31 (dd, *J* = 8.0, *J* = 1.6, 1 H, CH_{Ar}), 8.37 (d, *J* = 1.6, 1 H, CH_{Ar}), 8.50 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 111.0, 117.0, 125.2, 128.5, 128.7, 130.0, 130.9, 132.0, 132.6, 133.1, 133.7, 134.1, 135.9, 136.7, 194.4 ppm. IR: ν = 3060, 2224, 1640, 1596, 1300, 916, 716 cm^{-1}. $C_{18}H_{11}NO$ (257.3): calcd. C 84.03, H 4.31, N 5.44; found: C 83.89, H 4.28, N 5.36.

1-Cyano-3-(4-methylbenzoyl)-naphthalene (6b). Mp 159-160 °C (MeOH). Yield: 289 mg (53 %). ^{1}H NMR: δ = 2.49 (s, 3 H, CH_3), 7.35 (d, *J* = 8.0, 2 H, CH_{Ar}), 7.70-7.76 (m, 3 H, CH_{Ar}), 7.82-7.86 (m, 1 H,CH_{Ar}), 8.03 (d, *J* = 8.0, 1 H, CH_{Ar}), 8.32 (d, *J* = 8.0, 1 H, CH_{Ar}), 8.36 (d, *J* = 1.6, 1 H, CH_{Ar}), 8.49 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 21.8, 110.8, 117.1, 125.3, 128.5, 129.4,130.1, 130.2, 130.8, 132.0, 132.7, 133.6, 134.0, 134.5, 135.8, 144.1, 194.2 ppm. IR: ν = 3068, 2220, 1644, 1604, 1292, 764 cm^{-1}. $C_{19}H_{13}NO$ (271.3): calcd. C 84.11, H 4.83, N 5.16; found: C 83,85, H 4.70, N 5.13.

1-Cyano-3-(4-chlorobenzoyl)-naphthalene (6c). Mp 137-138 °C (MeOH). Yield: 321 mg (55 %). ^{1}H NMR: δ = 7.52-7.55 (m, 2 H, CH_{Ar}), 7.71-7.76 (m, 1 H, CH_{Ar}), 7.78-7.81 (m, 2 H, CH_{Ar}), 7.84-7.88 (m, 1 H, CH_{Ar}), 8.03 (d, *J* = 8.4, 1 H, CH_{Ar}), 8.33 (dd, *J* = 8.4, *J* = 1.6, 1 H, CH_{Ar}), 8.35 (d, *J* = 1.6, 1 H, CH_{Ar}), 8.47 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 111.1, 116.9, 125.2, 128,8, 129.0, 130,1, 131,2, 131.3, 131.9, 132.3, 133.6, 133.7, 134.9, 135.8, 139.6, 193.2 ppm. IR: ν = 3068, 2224, 1652, 1584, 1300, 1092, 768 cm^{-1}. $C_{18}H_{10}ClNO$ (291.7): calcd. C 74.11, H 3.45, N 4.80, Cl 12.15; found: C 74.13, H 3.25, N 4.78, Cl 12.08.

1-Cyano-3-(4-bromobenzoyl)-naphthalene (6d). Mp 131-132 °C (MeOH). Yield: 491 mg (73 %). ^{1}H NMR: δ = 7.66-7.75 (m, 5 H, CH_{Ar}), 7.83-7.87 (m, 1 H, CH_{Ar}), 8.03 (d, *J* = 8.4, 1 H, CH_{Ar}), 8.31 (d, *J* = 8.4, 1 H, CH_{Ar}), 8.34 (d, *J* = 1.6, 1 H, CH_{Ar}), 8.46 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 111.1, 116.9, 125.2, 128.2, 128.6, 130.1, 131.0, 131.4, 131.9, 132.0, 132.3, 133.60, 133.62, 135.3, 135.8, 193.3 ppm. IR: ν = 3064, 2224, 1652, 1584, 1292, 1068, 764 cm^{-1}. $C_{18}H_{10}BrNO$ (336.2): calcd. C 64.31, H 3.00, N 4.17, Br 23.77; found: C 64.47, H 2.82, N 3.99, Br 23.69.

1-Cyano-3-(3,4-dimethoxybenzoyl)-naphthalene (6e). Mp 169-170 °C (MeOH). Yield: 343 mg (54 %). ^{1}H NMR: δ = 3.89 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 6.88 (d, *J* = 8.4, 1 H, CH_{Ar}), 7.32 (dd, *J* = 8.4, *J* = 1.6, 1 H, CH_{Ar}), 7.46 (d, *J* = 1.6, 1 H, CH_{Ar}), 7.63-7.69 (m, 1 H, CH_{Ar}), 7.73-7.75 (m, 1 H, CH_{Ar}), 7.97 (d, *J* = 8.4, 1 H, CH_{Ar}), 8.19 (d, *J* = 8.4, 1 H, CH_{Ar}), 8.22 (d, *J* =

1.6, 1 H, CH_{Ar}), 8.40 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 55.9, 56.0, 109.7, 110.4, 111.7, 116.9, 124.9, 125.3, 128.2, 129.1, 129.8, 130.4, 131.7, 132.4, 133.1, 134.5, 149.1, 153.3, 192.8, ppm. IR: ν = 3084, 2964, 2840, 2236, 1664, 1512, 1260, 1152, 1020, 768 cm^{-1}. $C_{20}H_{15}NO_3$ (317.3): calcd. C 75.70, H 4.76, N 4.41; found: C 75.56, H 4.81, N 4.32.

General procedure for preparation of 1-cyano-3-acylnaphthalenes 6f,g in system A

The solution of aldehyde **1** (0.29 g, 2.0 mmol) and ketone **3f,g** (2.0 mmol) in benzene (4 mL) was added dropwise to the stirred mixture of 50%$_{aq}$ NaOH (1 mL, 19.1 mmol), TEBAC (0.023 g, 0.1 mmol) and benzene (6 mL). When aldehyde **1** was no longer detected by GC (1 h), the reaction mixture was diluted with water (50 mL). The organic phase was separated and the water phase was extracted with $CHCl_3$ (3×20 mL). Combined organic phases were washed with water (30 mL) and dried ($MgSO_4$). After the solvent was evaporated, the crude dark mixture was purified by column chromatography and naphthalenes **6f,g** (characterized below) were obtained, however in a much lower yield (Table 1) than in system B.

General procedure for preparation of 1-cyano-3-acylnaphthalenes 6f,g in system B

To the stirred solution of aldehyde **1** (0.29 g, 2.0 mmol), vinyl ketone **3f**,**g** (2.0 mmol) and Aliquat 336 (0.040 g, 0.1 mmol) in benzene (30 mL), K_2CO_3 (0.138 g, 10.0 mmol) was added. When aldehyde **1** was no longer detected by GC (ca 2 h), the reaction mixture has been worked up as described in General procedure for **6a-e** in system A. The crude mixture was purified by column chromatography (Table 1) and the products were recrystallized to give analytical samples of **6f,g**.

1-Cyano-3-acetylnaphthalene (6f). M.p. 156-157 °C (benzene/cyclohexane). Yield: 281 mg (72 %). ^{1}H NMR: δ = 2.74 (s, 3 H, CH_3), 7.68-7.87 (m, 2 H, CH_{Ar}), 8.08 (d, *J* = 8.0, 1 H, CH_{Ar}), 8.28 (d, *J* = 8.0, 1 H, CH_{Ar}), 8.47 (d, *J* = 1.6, 1 H, CH_{Ar}), 8.66 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 26.5, 111.1, 117.02, 125.2, 128.5, 130.3, 130.9, 131.1, 132.2, 133.6, 133.9, 134.4, 195.8 ppm. IR: ν = 3072, 2220, 1680, 1620, 1292, 900, 752 cm^{-1}. $C_{13}H_9NO$ (195.2): calcd. C 79.98, H 4.65, N 7.17; found: C 79.89, H 4.71, N 7.05.

1-Cyano-3-propionylnaphthalene (6g). Mp 104-105 °C (AcOEt). Yield: 289 mg (60 %).^{1}H NMR: δ = 1.30 (t, *J* = 7.2, 3 H, CH_3), 3.14 (q, *J* = 7.2, 2 H, CH_2), 7.66-7.85 (m, 3 H, CH_{Ar}), 8.06 (d, *J* = 7.6, 1 H, CH_{Ar}), 8.26 (d, *J* = 7.6, 1 H, CH_{Ar}), 8.45 (d, *J* = 1.6, 1 H, CH_{Ar}), 8.67 (br. s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 8.09, 31.9, 111.1, 117.1, 125.2, 128.4, 130.3, 130.89, 130.90, 132.3, 133.4, 133.8, 133.9, 198.5 ppm. IR: ν = 3064, 2980, 2220, 1696, 1620, 1184, 748 cm^{-1}. $C_{14}H_{11}NO$ (209.2): calcd. C 80.36, H 5.30, N 6.69; found: C 80.23, H 5.55, N 6.66.

General procedure for preparation of 1-substituted-3-cyanonaphthalenes 10h, i

To the stirred solution of aldehyde **1** (0.29 g, 2.0 mmol), acrylonitrile (**3h**, 0.11 g, 2.0 mmol) or phenyl vinyl sulfone (**3i**, 0.739 g, 4.4 mmol) and TEBAC (0.023 g, 0.1 mmol) in benzene (30 mL), 50%$_{aq}$ NaOH (1 mL, 19.1 mmol) was added. When aldehyde **1** was no longer detected by GC (2 h), the reaction mixture has been worked up as described for compounds **6f,g** and the

crude mixture was purified by column chromatography (Table 1). The products were recrystallized to give analytical samples of **10h,i**.

1-(2-Cyanoethyl)-3-cyanonaphthalene (10h). Mp 93-94 °C (AcOEt). Yield: 140 mg (34 %). ^{1}H NMR: δ = 2.80 (t, *J* = 12.6, 2 H, CH_2), 3.46 (t, *J* = 12.6, 2 H, CH_2), 7.53 (d, *J* = 0.8, 1 H, CH_{Ar}), 7.63-7.68 (m, 1 H, CH_{Ar}), 7.72-7.76 (m, 1 H, CH_{Ar}), 7.95 (d, *J* = 5.2, 1 H, CH_{Ar}), 8.37 (d, *J* = 5.2, 1 H, CH_{Ar}), 8.19 (br. s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 18.1, 28.3, 109.1, 118.4, 118.8, 122.9, 126.5, 127.6, 129.7, 132.5, 132.7, 134.1, 135.8 ppm. IR: ν = 3064, 2948, 2248, 2220, 1600, 1224, 884, 752 cm^{-1}. $C_{14}H_{10}N_2$ (206.2): calcd. C 81.53, H 4.89, N 13.58; found: C 81.16, H 5.21, N 13.33.

1-(2-Phenylsulfonylethyl)-3-(phenylsulfonyl)naphthalene (10i). Mp 185-186 °C (acetone). Yield: 680 mg (78 %); ^{1}H NMR: δ = 3.41-3.46 (m, 2 H, CH_2), 3.50-3.55 (m, 2 H, CH_2), 7.45-7.72 (m, 10 H, CH_{Ar}), 7.87-8.01 (m, 5 H,CH_{Ar}), 8.44 (d, *J* = 1.6, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 26.0, 56.0, 122.7, 123.0, 127.6, 128.0, 128.9, 129.3, 129.4, 130.6, 132.7, 132.9, 133.3, 134.0, 135.9, 138.0, 138.7, 141.2 ppm. IR: ν = 3060, 2968, 1584, 1444, 1304, 1132, 752 cm^{-1}. $C_{24}H_{20}O_4S_2$ (436.6): calcd. C 66.02, H 4.63, S 14.69; found: C 65.85, H 4.41, S 14.59.

Preparation of 1-cyano-10-methyltetracyclo[7.5.1.0^{2,7}.0^{8,13}]pentadeca-2,4,6,10-tetraen-12-one (11). To the stirred solution of aldehyde **1** (0.29 g, 2.0 mmol), methyl vinyl ketone (**3f**, 0.42 g, 6.0 mmol) and TEBAC (0.023 g, 0.1 mmol) in benzene (30 mL), 50%$_{aq}$ NaOH (1 mL, 19.1 mmol) was added. The stirring was continued at rt for 3 h. The reaction mixture was diluted with water (50 mL) and has been worked up as described for naphthalenes **6f,g.** After the solvent was evaporated, the crude mixture was purified by column chromatography. The product was recrystallized to give analytical sample of **11**. Mp 109-110 °C (cyclohexane). Yield: 448 mg (90 %). ^{1}H NMR: δ = 1.95-2.18 (m, 4 H, 2×CH_2), 2.05 (d, *J* = 1.0, 3 H, CH_3), 2.28-2.38 (m, 2 H, 2×CH), 3.55 (t, *J* = 3.0, 1H, CH), 5.80 (br.s, 1 H, =CH), 7.27-7.30 (m, 1 H, CH_{Ar}), 7.35-7.42 (m, 2 H, CH_{Ar}), 7.60 (dd, *J* = 7.0, *J* = 1.0, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 23.5, 32.5, 35.3, 36.6, 37.0, 39.9, 41.5, 120.3, 121.4, 122.2, 124.9, 127.8, 128.3, 136.7, 138.4, 166.8, 200.1 ppm. IR: ν = 3032, 2940, 2240, 1672, 1436, 1380, 880, 760 cm^{-1}. $C_{17}H_{15}NO$ (249.3): calcd. C 81.90, H 6.06, N 5.62; found: C 81.84, H 6.09, N 5.59.

General procedure for preparation of cyanoketones 13a,b

These compounds were obtained according to General procedure in system B, starting from aldehyde 1 (0.29 g, 2.0 mmol), cyclic ketone **12a,b** (8.0 mmol), Aliquat 336 (0.040 g, 0.1 mmol), benzene (30 mL) and powdered K_2CO_3 (0.138 g, 10.0 mmol). The crude mixture was purified by column chromatography and the products were recrystallized to give analytical samples of **13a,b**.

4-Cyano-2,3-dihydro-cyclopenta[*b*]naphthalene-1-one (13a). Mp 207 °C (decomp.) (AcOEt). Yield: 228 mg (55 %). ^{1}H NMR: δ = 2,88-2,92 (m, 2 H, CH_2), 3,51-3,54 (m, 2 H, CH_2), 7.64-7.68 (m, 1 H, CH_{Ar}), 7.81-7.85 (m, 1 H, CH_{Ar}), 8.08 (d, *J* = 8.4, 1H, CH_{Ar}), 8.27 (d, *J* = 8.4, 1 H, CH_{Ar}), 8.50 (s, 1 H, CH_{Ar}), 8.50 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 25.4, 36.3, 107.6, 115.5, 125.0, 127.7, 129.3, 131.3, 131.4, 132.0, 134.4, 135.8, 154.5, 204.7 ppm. IR: ν = 3060, 2924,

2220, 1712, 1620, 1172, 764 cm^{-1}. $C_{14}H_9NO$ (207.2): calcd. C 81.14, H 4.38, N 6.76; found: C 80.59, H 4.50, N 6.63.

10-Cyano-3,4-dihydro-2*H*-anthracen-1-one (13b). Mp 143-145 °C (AcOEt). Yield: 354 mg (80 %). ^{1}H NMR (200 MHz): δ = 2.15-2.34 (m, 2 H, CH_2), 2.77-2.83 (m, 2 H, CH_2), 3.37-3.43 (m, 2 H, CH_2), 7.58-7.7.66 (m, 1 H, CH_{Ar}), 7.74-7.83 (m, 1 H, CH_{Ar}), 8.04 (d, *J* = 8.2, 1 H, CH_{Ar}), 8.22 (d, *J* = 8.2, 1 H, CH_{Ar}), 8.81 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 22.3, 29.0, 38.9, 109.2, 124.9, 127.6, 128.3, 130.2, 130.8, 131.1, 131.3, 133.6, 134.9, 146.0, 196.5 ppm. IR: ν = 3056, 2948, 2216, 1688, 1620, 1176, 748 cm^{-1}. $C_{15}H_{11}NO$ (221.3): calcd. C 81.43, H 5.01, N 6.33; found: C 81.28, H 5.08, N 6.40.

General procedure for preparation of 1-cyano-5,8-diaroylbenzobicyclo[2.2.2]octenes 9a-e

The reactions were carried out as described for **6** in General procedure in system A, starting from aldehyde **1** (0.29 g, 2.0 mmol), chloroketone **2a-e** (4.2 mmol), TEBAC (0.023 g, 0.1 mmol), benzene (30 mL) and 50%$_{aq}$ NaOH (1 mL, 19.1 mmol). The crude mixtures were purified by column chromatography and the products **9a-e** were recrystallized. In case of the reactions of **2a** and **2e**, minute amounts (ca. 5%) of the corresponding naphthalenes **3a** and **3e** were isolated (Table 1).

1-Cyano-5,8-dibenzoyl-benzobicyclo[2.2.2]octene (9a). Mp 165 °C (AcOEt). Yield: 470 mg (60 %). ^{1}H NMR: δ = 2.08-2.14 (m, 1H, CH_2), 2.36-2.48 (m, 2 H, CH_2), 2.82 (dd, *J* = 12.8, *J* = 6.4, 1 H, CH_2), 3.59 (ddd, *J* = 11.2, *J* = 6.4, *J* = 2.4, 1 H, CH), 3.73 (m, 1 H, CH), 4.14 (ddd, *J* = 9.6, *J* = 5.6, *J* = 2.0, 1 H, CH), 7.00 (d, *J* = 7.2, 1 H, CH_{Ar}), 7.26-7.42 (m, 5 H, CH_{Ar}), 7.49-7.70 (m, 4 H, CH_{Ar}), 7.73 (d, *J* = 8.0, 2 H, CH_{Ar}), 8.00 (d, *J* = 8.0, 2 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 32.6, 32.7, 36.5, 39.4, 40.0, 44.4, 120.7, 122.3, 125.0, 127.96, 128.0, 128.18, 128.23, 128.3, 129.0, 133.0, 133.8, 135.2, 135.6, 136.4, 136.6, 198.0, 199.6 ppm. IR: ν = 3060, 2948, 2240, 1672, 1448, 1220, 1016, 756 cm^{-1}. $C_{27}H_{21}NO_2$ (391.5): calcd. C 82.84, H 5.41, N 3.58; found: C 82.93, H 5.45, N 3.57.

1-Cyano-5,8-di-(4-methylbenzoyl)-benzobicyclo[2.2.2]octene (9b). Mp 223-225 °C (AcOEt). Yield: 436 mg (52 %). ^{1}H NMR: δ = 2.37-2.52 (m, 4 H, 2×CH_2), 2.42 (s, 6 H, 2×CH_3), 3.80 (s, 1 H, CH), 4.04-4.07 (m, 2 H, CH), 6.76 (d, *J* = 7.4, 1 H, CH_{Ar}), 7.15-7.19 (m, 1 H, CH_{Ar}), 7.27 (d, *J* = 7.4, 4 H, CH_{Ar}), 7.30-7.34 (m, 1 H, CH_{Ar}), 7.53 (d, *J* = 8.0, 1 H, CH_{Ar}), 7.73 (d, *J* = 8.0, 4 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 21.6, 33.3, 36.2, 40.4, 44.6, 120.8, 121.7, 126.7, 127.8, 127.9, 128.3, 129.5, 133.0, 133.6, 144.2, 197.1 ppm. IR: ν = 2944, 2240, 1664, 1604, 1236, 984, 768 cm^{-1}. $C_{29}H_{25}NO_2$ (419.5): calcd. C 83.03, H 6.01, N 3.34; found: C 83.13, H 6.18, N 3.22.

1-Cyano-5,8-di-(4-chlorobenzoyl)-benzobicyclo[2.2.2]octene (9c). Mp 203-206 °C (AcOEt). Yield: 718 mg (78 %). ^{1}H NMR (Varian Gemini 200BB, 200 MHz, $CDCl_3$): δ = 2.11-2.30 (m, 1 H, CH_2), 2.36-2.45 (m, 2 H, CH_2), 2.66 (dd, *J* = 12.7, *J* = 6.5, 1 H, CH_2), 3.50 (ddd, *J* = 11.2, *J* = 6.4, *J* = 2.1, 1 H, CH), 3.65 (m, 1 H, CH), 4.17 (ddd, *J* = 9.0, *J* = 6.5, *J* = 2.0, 1 H, CH), 6.99 (d, *J* = 7.2, 1 H, CH_{Ar}), 7.25-7.44 (m, 4 H, CH_{Ar}), 7.52 (d, *J* = 8.6, 2 H, CH_{Ar}), 7.61 (d, *J* = 7.2, 1 H, CH_{Ar}), 7.77 (d, *J* = 8.6, 2 H, CH_{Ar}), 7.90 (d, *J* = 8.6, CH_{Ar}) ppm. ^{13}C NMR: δ = 33.1, 36.6, 39.4, 39.7, 44.5, 120.5, 122.6, 125.0, 128.2, 128.3, 129.0, 129.5, 129.78, 129.83, 133.6, 133.9, 136.2,

136.5, 139.7, 140.5, 197.0, 198.7 ppm. IR: ν = 3070, 2956, 2240, 1680, 1588, 1400, 1224, 1092, 764 cm^{-1}. $C_{27}H_{19}NO_2Cl_2$ (460.4): calcd. C 70.44, H 4.16, N 3.04, Cl 15.40; found: C 70.25, H 4.34, N 2.85, Cl 15.20.

1-Cyano-5,8-di-(4-bromobenzoyl)-benzobicyclo[2.2.2]octene (9d). Mp 232-235 °C (AcOEt). Yield: 549 mg (50 %). ^{1}H NMR: δ = 2.14-2.21 (m, 1 H, CH_2), 2.33-2.44 (m, 2 H, CH_2), 2.65 (dd, *J* = 13.0, *J* = 6.6, 1 H, CH_2), 3.49 (ddd, *J* = 11.5, *J* = 6.6, *J* = 2.4, 1 H, CH), 3.65 (m, 1 H, CH), 4.15 (ddd, *J* = 9.8, *J* = 5.8, *J* = 1.6, 1 H, CH), 6.99 (d, *J* = 7.4, 1 H, CH_{Ar}), 7.29 (dd, *J* = 7.4, *J* = 7.6, 1 H, CH_{Ar}), 7.40 (dd, *J* = 7.4, *J* = 7.6, 1 H, CH_{Ar}), 7.53 (d, *J* = 8.4, 2 H, CH_{Ar}), 7.61 (d, *J* = 7.6, 1 H, CH_{Ar}), 7.69 (d, *J* = 8.4, 4 H, CH_{Ar}), 7.82 (d, *J* = 8.4, 2 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 33.0, 33.1, 36.6, 39.4, 39.7, 44.4, 120.5, 122.6, 125.0, 128.3, 128.5, 129.3, 129.88, 129.94, 132.1, 132.5, 134.0, 134.2, 136.2, 136.4, 197.2, 198.9 ppm. IR: ν = 3072, 2956, 2240, 1672, 1584, 1392, 1228, 1068, 760 cm^{-1}. $C_{21}H_{19}BrNO_2$ (397.3): calcd. C 59.04, H 3.49, N 2.55, Br 29.10; found: C 58.73, H 3.54, N 2.45, Br 29.18.

1-Cyano-5,8-di-(3,4-dimethoxybenzoyl)-benzobicyclo[2.2.2]octene (9e). Mp 134-138 °C (AcOEt). Yield: 481 mg (47 %). ^{1}H NMR: δ = 2.09-2.16 (m, 1 H, CH_2), 2.34-2.40 (m, 2 H, CH_2), 2.71 (dd, *J* = 12.8, *J* = 6.4, 1 H, CH_2), 3.50-3.55 (m, 1 H, CH), 3.71 (s, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 4.18-4.23 (m, 1 H, CH), 6.78 (d, *J* = 8.4, 1 H, CH_{Ar}), 6.91 (d, *J* = 8.4, 1 H, CH_{Ar}), 7.03 (d, *J* = 7.2, 1H, CH_{Ar}), 7.29 (d, *J* = 7.2, 1 H, CH_{Ar}), 7.36-7.40 (m, 2 H, CH_{Ar}), 7.49-7.53 (m, 2 H, CH_{Ar}), 7.59-7.60 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 33.2, 33.4, 36.6, 38.9, 40.7, 44.1, 55.8, 56.0, 56.1, 56.2, 110.0, 110.3, 110.4, 110.7, 120.8, 122.4, 122.9, 123.0, 125.0, 127.9, 128.0, 128.4, 128.7, 136.4, 137.1, 148.9, 149.4, 153.2, 153.8, 196.8, 198.1 ppm. IR: ν = 3084, 2996, 2224, 1640, 1512, 1264, 1024, 772 cm^{-1}. $C_{31}H_{29}NO_6$ (511.6): calcd. C 72.78, H 5.71, N 2.74; found: C 72.89, H 5.88, N 2.70.

Preparation of 1-cyano-3-benzoyl-1,2-dihydronaphthalene (5a) and its dehydrogenation into 1-cyano-3-benzoylnaphthalene (6a)

[2-(2,5-Dioxacyclopentyl)-phenyl]-acetonitrile (14). The mixture of aldehyde **1** (3.05 g, 21.0 mmol), ethylene glycol (1.93 g, 31.5 mmol), *p*-toluenesulfonic acid (0.21 g, 1.1 mmol) in benzene (50 mL) was refluxed for 6 h and water was removed by Dean-Stark trap. Then the reaction mixture was cooled, washed with saturated aq. solution of $NaHCO_3$ (2×30 mL), water (2×20 mL), dried ($MgSO_4$) and the solvent was evaporated to give product **14** as pale yellow, sticky oil (yield 3.81 g, 96%). ^{1}H NMR: δ = 3.96 (s, 2H, CH_2CN), 4.02-4.16 (m, 4H, CH_2CH_2), 5.85 (s, 1H, OCHO), 7.30-7.58 (m, 4H, CH_{Ar}) ppm. ^{13}C NMR: δ = 20.7, 64.9, 102.5, 117.8, 127.6, 127.8, 128.7, 129.1, 129.6, 134.5 ppm. IR: ν = 2956, 2892, 2248, 1404, 1224, 1080, 760 cm^{-1}. $C_{11}H_{11}NO_2$ (189.2): calcd. C 69.83, H 5.86, N 7.40; found: C 69.84, H 5.85, N 7.43.

α-[(3-Oxo-3-phenyl)-propyl]-α-[2-(2,5-dioxacyclopentyl)phenyl]-acetonitrile (15). To the stirred solution of nitrile **14** (0.38 g, 2.0 mmol), ketone **2a** (0.34 g, 2.0 mmol) and TEBAC (0.023 g, 0.1 mmol) in benzene (30 mL), 50%$_{aq}$ NaOH (1 mL, 19.1 mmol) was added. The reaction was carried out for 2.0 h, worked up as described for **6** in General procedure in system A, and the crude mixture was purified by column chromatography. The product **15** was obtained as

transparent, colourless oil (yield 0.22 g, 35%), which after being treated with EtOH, afforded crystals (m.p. 58-61 °C; 17%). ^{1}H NMR: δ = 2.28-2.46 (m, 2 H, CH_2), 3.20 (t, *J* = 6.4; 2 H, $COCH_2$), 3.97-4.15 (m, 4 H, OCH_2CH_2O), 4.59 (dd, *J* = 9.2, *J* = 6.4, 1 H, CHCN), 5.94 (s, 1 H, CHO_2), 7.34-7.38 -7.61 (m, 9 H, CH_{Ar}), 7.94 (d, *J* = 1.2, 1 H, CH_{Ar}), 7.96 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR: δ = 30.0, 32.1, 35.4, 65.2, 102.1, 121.3, 127.8, 128.0, 128.3, 128.4, 128.7, 130.1, 133.4, 134.6, 134.8, 136.6, 198.3 ppm. IR: ν = 3060, 2224, 1644, 1596, 1444, 1300, 716 cm^{-1}. $C_{20}H_{19}NO_3$ (321.4): calcd. C 74.75, H 5.96, N 4.36; found: C 74.50, H 6.28, N 4.37.

1-Cyano-3-benzoyl-1,2-dihydronaphthalene (5a). The suspension of nitrile **15** (0.41 g, 1.32 mmol) in a mixture of acetonitrile (6 mL) and 3% HCl (16 mL) was refluxed for 2 h, then cooled and diluted with water (30 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL), the combined organic phases were washed with water (2×20 mL) and dried ($MgSO_4$). The solvents were evaporated and the crude mixture was purified by column chromatography to give the product **5a** as transparent, colourless oil (yield 0.27 g, 78%). ^{1}H NMR: δ = 3.02 (part A of ABMX, J_{AB} = 17.0, J_{AM} = 10.4, J_{AX} = 1.6, 1H, CH_2), 3.18 (part B of ABMX, J_{AB} = 17.0, J_{BM} = 7.2, J_{BX} = 0.8, 1H, CH_2), 4.18 (part M of ABMX, J_{AM} = 10.4, J_{BM} = 7.2, 1H, CHCN), 7.23 (part X of ABMX, br.s, 1H, =CH), 7.25 (dd, $J_{H,H}$ = 7.2, 1.0, 1H, CH_{Ar}), 7.35-7.40 (m, 1H, CH_{Ar}), 7.41-7.46 (m, 1H, CH_{Ar}), 7.48-7.56 (m, 3H, CH_{Ar}), 7.57-7.62 (m 2H, CH_{Ar}), 7.75-7.77 (m, 1H, CH_{Ar}) ppm. ^{13}C NMR: δ = 27.0, 30.2, 119.6, 127.2, 128.6 (two C), 129.3 (three C), 129.6, 130.0, 131.0, 131.5, 132.2, 134.4, 137.4, 139.4, 196.0 ppm. IR: ν = 3058, 2224, 1644, 1596, 1444, 1228, 752, 716 cm^{-1}. $C_{18}H_{13}NO$ (259.3): calcd. C 83.38, H 5.05, N 5.40; found: C 83.29, H 5.25, N 5.40.

1-Cyano-3-benzoylnaphthalene (6a). To the stirred solution of dihydronaphthalene **5a** (0.27 g, 1.03 mmol) and TEBAC (0.02 g, 0.05 mmol) in benzene (15 mL), 50%$_{aq}$ NaOH (0.5 mL, 9.5 mmol) was added. The reaction was carried out for 2.0 h, the mixture was diluted with water (25 mL), the organic phase was separated, and the water phase was extracted with $CHCl_3$ (3×15 mL). The combined organic phases were washed with water (20 mL) and dried ($MgSO_4$). The solvent was evaporated, the residue was purified by column chromatography and the product **6a** was obtained as transparent colourless oil, which solidified. Recrystallization from methanol afforded the product, which exhibited physical and spectral properties the same as described for **6a** obtained according to the General procedure in system A, (yield 0.23 g, 85%).

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