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Synthesis of α-arylnaphthalenes from diphenylacetaldehydes and 1,1-diphenylacetones

Bartłomiej Kozik *, Jarosław Wilamowski, Maciej Góra, Janusz J. Sepioł

Department of Organic Chemistry, Jagiellonian University, Ingardena 3, PL-30-060 Kraków, Poland

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ABSTRACT

Condensation of diphenylacetaldehydes and 1,1-diphenylacetones with malonodinitrile and cyclization of obtained aryl-ylidenemalonodinitriles in concentrated sulfuric acid leads to 1-amino-4-arylnaphthalene-2-carbonitriles. The benzannulation reaction is accompanied by a *quasi*-aromatic rearrangement. Preliminary tests of some synthesized aminonitriles have revealed their considerable biological activity against phytopathogenic fungi.

1. Introduction

Biaryls continue to attract considerable attention. Special interest is focused on 2,2′-disubstituted-1,1′-binaphthyls and their analogues. This is, particularly, due to the presence of a stereogenic axis and the ability of these compounds to form atropoisomers.[1,2] The same properties are exhibited by substituted 1,1′-biphenyls. A third group of compounds possessing a stereogenic axis contains 1-(substituted-phenyl)naphthalenes. These three major groups of biaryls appear to have enormous and steadily increasing applications in chemistry and related areas. First of all, chiral biaryls find important applications as catalysts in the synthesis of chiral products possessing high or very high enantiopurity.[3–5] Hence, there are many recent reports and reviews on biaryl synthesis with control of axial chirality.[4–6] Furthermore, chiral biaryls are employed as building units in a variety of natural products and biologically active compounds.[5,7] They have also many other applications, for example, in synthesis of conducting polymers[8] or liquid crystals.[9]

In a recent communication we reported a synthesis of derivatives of α-(substituted-phenyl)naphthalenes from 2,2-diphenylethanals and 1,1-diphenylpropan-2-ones.[10] The synthetic route involved the condensation of the carbonyl compounds with malonodinitrile and cyclization of the obtained aryl-alkylidenemalonodinitriles in concentrated sulfuric acid. The same strategy was previously applied in syntheses of other aromatic, vicinal aminonitriles, derivatives of alkylated naphthalene[11] or phenanthrene[12] and cycloalkaphenanthrene.[13] In this report we wish to present all details of our approach leading to 4-phenyl- or 4-(substituted-phenyl)-1-aminonaphthalene-2-carbonitriles. Results of the biological tests encourage us to extend the research to the chloro-substituted aminonitriles.

2. Results and discussion

An example of this synthetic strategy is shown in Scheme 1. Starting ketone **1** was condensed with malonodinitrile and afforded the dinitrile **2**. Cyclization of the investigated aryl-alkylidenemalonodinitriles, including **2**, involves the *ipso* electrophilic attack of the protonated nitrile group on the benzene ring with the formation of a spirobenzenium cation **2′**. The alkyl shift (**2″**) gives **2‴**, which after losing the proton tautomerizes to **3** (Scheme 1).

The essential problem of the strategy was an issue of how the ring closure proceeds towards the naphthalene system. In the case of monosubstituted dinitriles (e.g., **2**), the cyclization might involve an annulation to the phenyl or substituted-phenyl group. Depending on the substituent's character, there is also a possibility of simultaneous annulation on both pathways—as outlined in Scheme 2. To study the preferences of the attack of the protonated nitrile group on the benzene system 'A' or 'B' (path 'a' or 'b', respectively) we have synthesized several α,α-diphenyl-substituted acetaldehydes and acetones having methyl groups or chlorine

* Corresponding author. Tel.: +48 126632904; fax: +48 126340515.
E-mail address: kozik@chemia.uj.edu.pl (B. Kozik).

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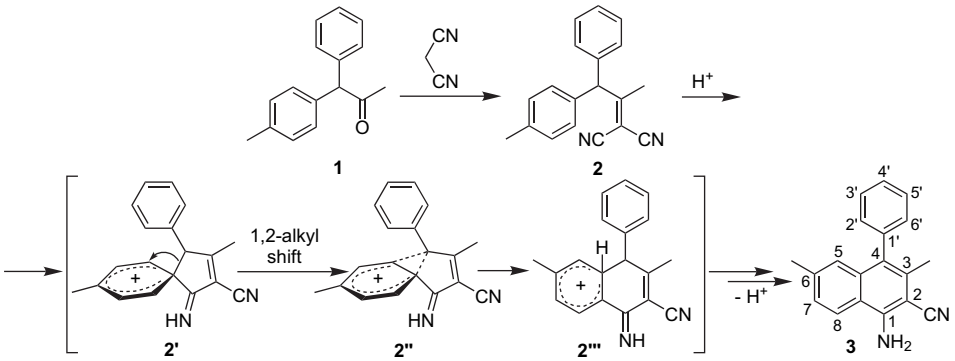
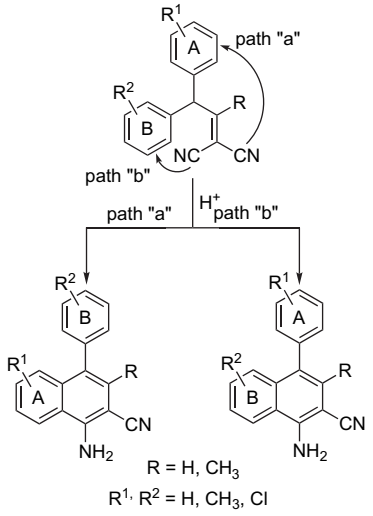


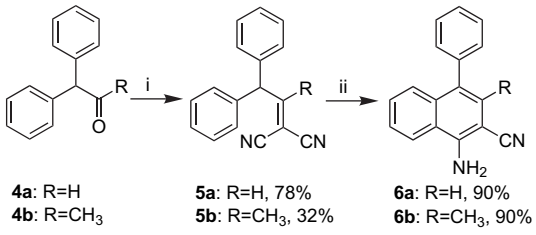
Scheme 1.



Scheme 2.

atoms located exclusively in the *para* position of one or both benzene rings.

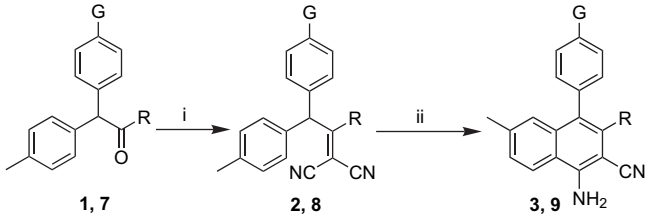
In the beginning we focused on verifying the usefulness of this method in the synthesis of 1-amino-4-phenylnaphthalene-2-carbonitrile system. As starting materials diphenylacetaldehyde (**4a**) and 1,1-diphenylacetone (**4b**) were used (Scheme 3).[14] To the best of our knowledge, with exception of **4a**, there were no other reports on condensation of the carbonyl compounds investigated here with malonodinitrile.[15] The above-mentioned condensation of aldehyde **4a** had been catalyzed by potassium fluoride and gave **5a** in moderate yield.[15] We carried out the same reaction in boiling benzene with continuous removal of water and in the presence of NH_4OAc/AcOH as a catalyst. Due to the difficulties in isolation of dinitrile **5a**, we decided to find a more effective method. Thus, brief heating of diphenylacetaldehyde (**4a**) with malonodinitrile in anhydrous ethanol and with a catalytic amount of piperidine gave **5a** in 78% yield.[10] Previously, we reported the condensation of 1,1-diphenylacetone (**4b**) with NH_4OAc/AcOH as a catalyst.[10] The currently presented reaction of **4b**, carried out with addition of piperidine, did not give much better results (32%). A low yield, in spite of relatively prolonged condensation time under standard conditions, might be caused by the steric hindrance imposed on the carbonyl function by the phenyl group and partial degradation of the product during extended heating time. Cyclization of **5a** and **5b** in concentrated sulfuric acid occurred in a straightforward manner to give aminonitriles **6a** and **6b**, respectively, in high yields. From all aminonitriles reported in this paper, only **6b** was synthesized before.[16] However, the mentioned method seemed to be more complex in comparison with our synthetic strategy.



Scheme 3. Reagents and conditions: (i) $CH_2(CN)_2$, piperidine, EtOH, 5 min (**4a**) or $CH_2(CN)_2$, piperidine–AcOH/NH_4OAc, C_6H_6, 15 h (**4b**); (ii) concd H_2SO_4, −15 °C→ −5 °C, 1 h.

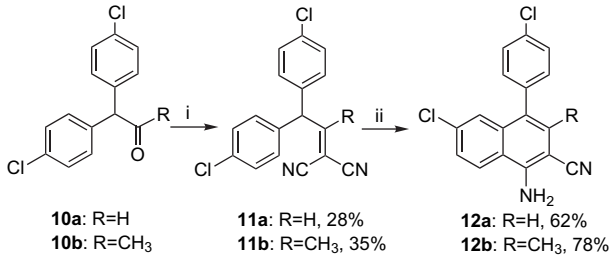
Diphenylacetaldehyde (**4a**) and 1,1-diphenylacetone (**4b**) were the only commercially available substrates. To investigate the scope of the synthesis of 1-amino-4-arylnaphthalene-2-carbonitriles, having the general structure of **6a**,**b**, we obtained methyl (**1**, **7**, Scheme 4) and chloro (**10**, **13**, Scheme 5) derivatives of **4a**,**b**. Unfortunately, the syntheses and purification of these apparently simple compounds encountered unexpected difficulties and required several attempts. We did not manage to work out the general method for synthesis of either the aldehydes **1** and **7** or ketones **10** and **13**.

Monosubstituted aldehydes, which have a methyl group (**7a**) or a chlorine atom (**13a**) in the *para* position of the benzene ring, were prepared by oxidation of 4-methyl- or 4-chlorostilbene, respectively, with perbenzoic acid, followed by rearrangement of the resulting oxiranes using bismuth(III) perchlorate oxide hydrate ($BiOClO_4 \cdot xH_2O$) as a catalyst.[17] Similarly, pinacol rearrangement of 1,2-bis(4-methylphenyl)ethane-1,2-diol in glacial acetic acid,



	G	R	yield 2, 8	yield 3, 9
1-3	H	CH_3	45%	71%
7-9a	H	H	41%	79%
7-9b	CH_3	H	49%	60%
7-9c	CH_3	CH_3	44%	77%

Scheme 4. Reagents and conditions: (i) $CH_2(CN)_2$, piperidine–AcOH/NH_4OAc, C_6H_6, 5–17 h; (ii) concd H_2SO_4, −15 °C→ −5 °C, 60–75 min.



Scheme 5. Reagents and conditions: (i) $CH_2(CN)_2$, piperidine–AcOH/NH_4OAc, C_6H_6, 6 h (**10a**) or 19 h (**10b**); (ii) concd H_2SO_4, −15 °C→−5 °C, ca. 20 h (**11a**) or 2.5 h (**11b**).

catalyzed by sulfuric acid, gave dimethyl derivative **7b** in good yield.[18] 2,2-Bis(4-chlorophenyl)ethanal (**10a**) was obtained from 4,4′-dichlorobenzophenone and ethyl chloroacetate by Darzens synthesis.[19]

Ketones **1** and **13b** were synthesized according to the published procedure, by the α-bromination of phenylacetone followed by Friedel–Crafts reaction with toluene or chlorobenzene, respectively.[20] Diarylpropanones **7c** and **10b** were prepared by pinacol rearrangement[18] of appropriate 1,1-diarylpropane-1,2-diols.[21]

After their preparation, the carbonyl compounds **1**, **7**, **10** and **13** were condensed with malonodinitrile. We employed the standard method for the condensation involving heating of the appropriate aldehyde or ketone with malonodinitrile in benzene in the presence of piperidine–AcOH/NH_4OAc as a catalyst. In contrast to **4b**, similar carbonyl compounds (**1**, **7c**, **10b** and **13b**) in the same conditions were condensed with significantly higher yields. As a solvent we chose benzene instead of toluene to reduce formation of tar substances and other possible side products.

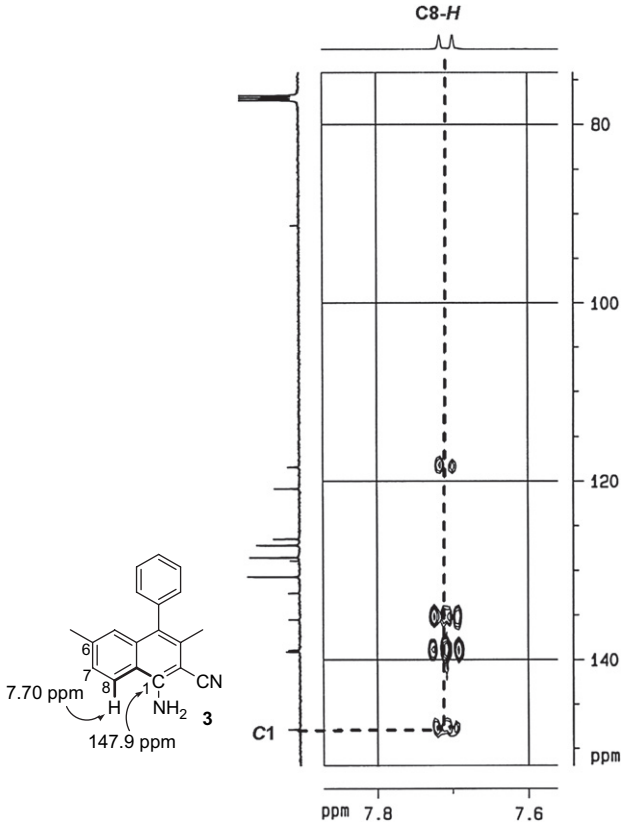


Figure 1. A part of the HMBC spectrum of **3**—correlation between the C8–*H* proton and *C*1 carbon atom.

The condensation step was followed by cyclization of the obtained aryl-ylidenemalonodinitriles in concentrated sulfuric acid. The pathways of ring closure of the dinitriles **2**, **8**, **11** and **14** were more complex in comparison with the straightforward cyclization of dinitriles **5a** and **5b**. The unusual mechanism of the cyclization and *quasi*-aromatic rearrangement has already been shown on Scheme 1. It is similar to the mechanism suggested in our recent reports that had assumed the presence of the *allylic*-type carbocation in the alkyl-shift stage.[11,13] However, rearrangements discussed here appear to be the first example of cyclization involving the *benzylic*-type carbocation. The stability of this carbocation may have contributed to the relatively high yield of obtained aminonitriles. Cyclizations of the methyl- or dimethyl-substituted ylidenemalonodinitriles **8a**–**c** proceeded in the same way as previously discussed cyclization of **2** (Scheme 4). In all cases the reaction involved only annulation of a methyl-substituted benzene ring. We obtained rearranged aminonitriles **3** and **9a**–**c** as single products in good yields.

The position of the methyl group at C-6 of naphthalene moiety **3** was established through 2D NMR experiments. The HMBC spectrum of **3** revealed correlation through three bonds between strongly deshielded C-1 (δ 147.9 ppm) and the proton bonded to the C-8 carbon atom (Fig. 1). This proton appeared at δ 7.70 as a doublet and was coupled to the neighbouring proton connected to C-7 (δ 7.28 ppm) with the coupling constant of 8.5 Hz. Furthermore, the proton bonded to C-7 was also coupled over four bonds to the proton at C-5 (J=1.6 Hz). The signal of the proton at C-5 at δ 7.07 had an unclear multiplet structure and appeared as a broad singlet. All acquired data indicated the location of the methyl group at the '6-position' of **3**. Moreover, the experimental ^{1}H NMR spectrum of **3** was in agreement with the simulated one.[22a] The spin systems involving protons C5–*H*, C7–*H*, C8–*H*, C6–CH_3 and H_{Ph} were simulated with the spectral analysis routine NUMMRIT[22b] using the SpinWorks software.[22c] The exact structures of the aminonitriles **9a**–**c** were determined by 1D or 2D NMR experiments in comparison with the appropriate spectra of **3**.

The second group of ylidenemalonodinitriles investigated included chloro- or dichloro-substituted derivatives (**14** and **11**, respectively). The dinitriles **11** cyclized with rearrangement in a similar way to their dimethyl analogues **8b**,**c** (Scheme 5). In order to obtain **12** in good yields we prolonged the reaction time to 2.5 h in the case of **12b** and approximately to 20 h in the case of cyclization of **11a** to aminonitrile **12a**. The slower progress of the reaction of **11** was primarily caused by the electron withdrawing character of the chlorine atoms. On the other hand, noticeably higher rate of the cyclization of **11b** might have been dependent on the more stable protonated form of the dinitrile **11b**, which was probably due to the presence of the methyl group at the sp^2 carbon atom (Fig. 2). Higher population of the more stable carbocation, hypothetically, could be favourable for its

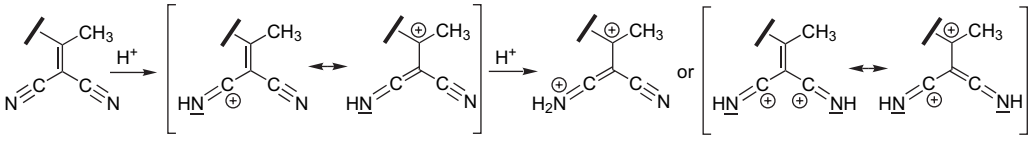
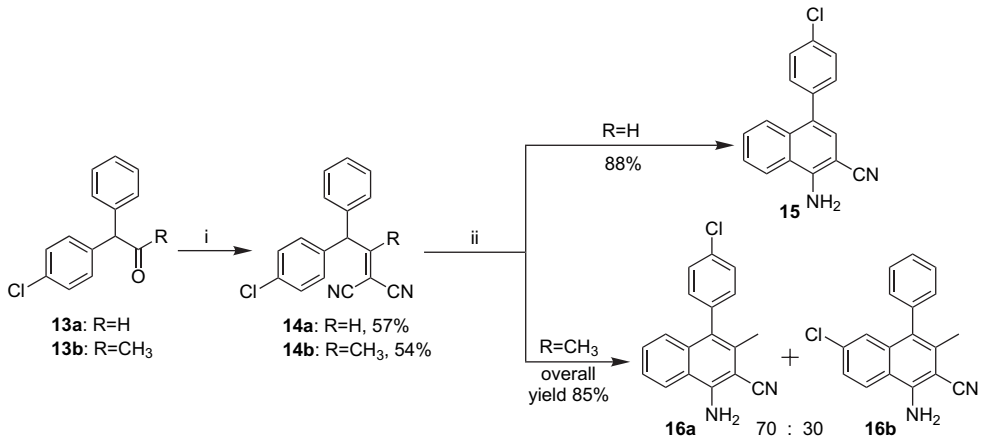


Figure 2. Mono- and diprotonation of dicyanovinyl group.

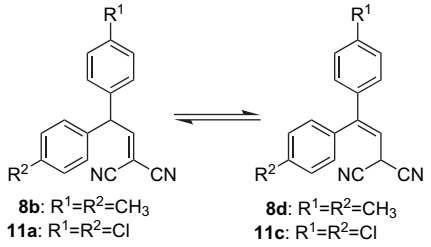


Scheme 6. Reagents and conditions: (i) $CH_2(CN)_2$, piperidine–AcOH/NH_4OAc, C_6H_6, 3 h (**14a**) or $CH_2(CN)_2$, piperidine–AcOH/NH_4OAc, toluene, 9 h (**14b**); (ii) concd H_2SO_4, −15 °C→ −5 °C, 2–3 h.

second protonation. Such a diprotonation of the nitrile group has already been reported in the case of the similar intramolecular Houben–Hoesch reaction.[23]

Cyclizations of dinitriles **14** possessing the chlorine atom only in one of the benzene rings confirmed our previous conclusions about the better stabilized protonated forms of the dinitriles obtained from the ketones (Scheme 6). Stirring **14a** in chilled concentrated sulfuric acid for 3 h led only to one isomer **15** (88% yield). On the contrary, analogous cyclization of the dinitrile **14b** gave two products with comparable overall yield. As expected, the main isomer **16a** was formed by annulation to the unsubstituted benzene ring of **14b**. However, the NMR spectra of the isolated product revealed also the presence of isomer **16b**, having the chlorine atom in the naphthalene system. That indicates the attack of the protonated nitrile function of the dinitrile **14b** on the phenyl group deactivated by the chlorine atom. The less selective cyclization of **14b** suggests higher reaction rate than in case of **14a**. In conclusion, the methyl group at *C*-2 carbon atom of the investigated 3,3-diarylpropene-1,1-dicarbonitriles seems to be the most probable factor increasing the electrophilicity of the protonated nitrile group during the rate determining step of electrophilic substitution. The structure and the ratio of isomers **16a** and **16b** (70:30) were established from the ^{1}H NMR spectrum. Attempts to separate the isomers using chromatographic methods were not successful.

It is also noteworthy that the dinitriles presented in the report, obtained during condensations of aldehydes with malonodinitrile, might occur along with their tautomeric forms (Scheme 7). Coexistence of similar tautomeric forms in solution was earlier observed also by Zimmerman and co-workers.[15] We made an investigation with special consideration of dinitriles **8b** and **11a**, which have the clearest ^{1}H NMR spectra due to the molecule's symmetry. Their isomers, respectively, **8d** and **11c**, arose through the migration of the carbon–carbon double bond (Scheme 7).



Scheme 7. Tautomerism of ylidenemalonodinitriles **8b** and **11a**.

Precise structural and energetic characterization of 3,3-bis(4-chlorophenyl)prop-1-ene-1,1-dicarbonitrile (**11a**) has already been presented in our earlier report.[24] The ratios were estimated from the ^{1}H NMR spectra, recorded in $CDCl_3$. Calculated proportions, **11a**/**11c** (3.8:1) and **8b**/**8d** (6.2:1), indicated a possible relationship between the state of equilibrium and the electron withdrawing character of substituents in the benzene rings. We also noticed that the ratio might be dependent on time, which passed since the sample was dissolved in $CDCl_3$. However, the rough measurements were performed only for **8b** and we did not investigate the subject in more detail. The tautomerism was observed also for monosubstituted dinitriles **8a** and **14a**. In the methyl derivative **8a** the equilibrium was significantly shifted towards the diarylprop-1-ene-1,1-dicarbonitrile structure.

Furthermore, the aminonitriles **3**, **6a**, **9a**–**c**, **12a**–**b** and **15** were evaluated in vitro for growth-inhibiting activity against some phytopathogenic fungi such as *Fusarium culmorum*, *Penicillium expansum*, *Botrytis cinerea* and *Alternaria* species.[25] In connection with our earlier studies on highly active 1-aminonaphthalene-2-carbonitriles possessing short alkyl groups at the '4-position,'[26] we presumed that the analogous 4-phenyl- or 4-aryl-substituted aminonitriles might also exhibit fungicidal activity. Preliminary tests of above-mentioned 4-aryl-1-aminonaphthalene-2-carbonitriles revealed their diverse biological activity against investigated fungi. Aminonitrile **6a** showed relatively the highest fungistatic activity. The results for the **6a** were compared in Table 1 with the activity of a commercial fungicide—Kaptan 50 WP (a.i. captan 50%).[25]

The synthetic strategy presented in this report enables simple, two-stage synthesis of α-arylnaphthalene systems from α,α-diaryl-substituted acetaldehydes or acetones. We investigated the possible ways of ring closure of the diarylalkylidenemalonodinitriles equipped with methyl groups or chlorine atoms in the benzene rings. The presented approach might potentially be employed in the synthesis of some chiral α-arylnaphthalenes having versatile amino and nitrile functions.

Table 1
A comparison of the fungistatic activity of 1-amino-4-phenylnaphthalene-2-carbonitrile (**6a**) and the commercial fungicide—captan

	EC_{50} [mg/dm^3]			
	Fusarium culmorum	*Alternaria brassicicola*	*Botrytis cinerea*	*Penicillium expansum*
6a	93	30	11	20
Captan	743	11	18	45

3. Experimental

3.1. General remarks

Melting points were recorded on Boëtius apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were taken on a Bruker AMX 500 instrument at 500 and 125 MHz, respectively, using tetramethylsilane as internal standard. IR spectra were recorded on Bruker IFS 48FT or Bruker Equinox 55 spectrophotometer. Elemental analysis was performed on a EuroEA Elemental Analyzer. Thin layer chromatography was performed on silica plates (Fluka, 0.2 mm) and column chromatography on silica gel (Fluka, 70–230 mesh).

3.2. Preparation of diarylalkylidenemalonodinitriles 2, 5, 8, 11 and 14

*General procedure for the synthesis of **2**, **5b**, **8**, **11** and **14** (method A).* The carbonyl compounds **1**, **4b**, **7**, **10** or **13**, malonodinitrile, glacial acetic acid, ammonium acetate, piperidine and benzene (or toluene) were heated for 10–17 h (**7b**: 5 h) with continuous water separation (Dean–Stark apparatus). The reaction was monitored by TLC (toluene or chloroform/SiO_2) and, if necessary, further portions of malonodinitrile, ammonium acetate and piperidine were added. The reaction mixture was washed with water, dried with anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The products **2** and **14b** were isolated by vacuum distillation. Other crude dinitriles were purified by column chromatography and were usually recrystallized.

*General procedure for the synthesis of **5a** and **8b** (method B).* A solution of aldehyde **4a** or **7b**, malonodinitrile and catalytic amount of piperidine in anhydrous ethanol was heated to reflux for 5 min and then was slowly cooled in an ice-bath. In case of **5a**, colourless precipitated solid was filtered off and washed with a small amount of chilled ethanol. Dinitrile **8b** was isolated by column chromatography and recrystallized.

3.2.1. 2-Methyl-3-(4-methylphenyl)-3-phenylprop-1-ene-1,1-dicarbonitrile (**2**)

Following the method A, ketone **1** (3.00 g, 13.37 mmol), malonodinitrile (1.02 g, 15.38 mmol), glacial acetic acid (1.50 g, 24.97 mmol), ammonium acetate (0.50 g, 6.49 mmol), piperidine (0.36 g, 4.23 mmol) and benzene (50 mL) were heated for 4.5 h with continuous water separation. Then the additional portions of malonodinitrile (0.30 g, 4.54 mmol), ammonium acetate (0.30 g, 3.89 mmol) and piperidine (0.15 g, 1.76 mmol) were added, and the mixture was heated to reflux for the next 5 h. After standard work-up, the residue was distilled in vacuo to give the dinitrile **2** (1.64 g, yield 45.1%) as a thick, yellow oil. Bp 141–144 °C/1 mmHg. IR (neat) 3061, 3029, 2923, 2232 (CN), 1592, 1511, 1454, 1379, 707 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3H, C–C*H*$_3$), 2.37 (s, 3H, Ar–C*H*$_3$), 5.68 (s, 1H, Ar_2CH), 7.02–7.04 (m, 2H, Ar–*H*), 7.13–7.20 (m, 4H, Ar–*H*), 7.34–7.40 (m, 3H, Ar–*H*). ^{13}C NMR ($CDCl_3$) δ 21.0 (2×CH_3, Ar–*C*H$_3$, =C–*C*H$_3$), 56.7 (Ar_2C), 87.7 ((CN)$_2$*C*=), 111.7 (*C*N), 111.9 (*C*N), 128.0, 128.6 (2×C_{Ar}), 128.7 (2×C_{Ar}), 128.9, 129.0 (2×C_{Ar}), 129.8 (2×C_{Ar}), 134.7, 137.9, 138.0, 181.8 (–*C*(CH$_3$)=). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29%. Found: C, 83.75; H, 5.96; N, 10.27%.

3.2.2. 3,3-Diphenylprop-1-ene-1,1-dicarbonitrile (**5a**)[15]

Following the method B, diphenylacetaldehyde (**4a**) (1.14 g, 5.81 mmol), malonodinitrile (0.38 g, 5.81 mmol), piperidine (34.5 mg, 0.405 mmol) and anhydrous ethanol (5 mL) were heated to reflux for 5 min, and then slowly cooled in an ice-bath. The resulting colourless precipitated solid was washed with a small amount of chilled ethanol. Dinitrile **5a** was obtained as small, white crystals (1.11 g, yield 78.2%). Mp 110–111 °C (Ref. 15: mp 107.5–113 °C). IR (KBr) 3049, 3029, 2929, 2239 (CN), 1599, 1492, 1454, 965, 745, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.34 (d, 1H, *J*=11.1 Hz, Ph_2CH), 7.16–7.18 (m, 4H, Ar–*H*), 7.32–7.41 (m, 6H, Ar–*H*), 7.70 (d, 1H, *J*=11.1 Hz, –C*H*=). ^{13}C NMR ($CDCl_3$) δ 53.3 (Ph_2C), 89.1 ((CN)$_2$*C*=), 110.5 (*C*N), 111.9 (*C*N), 128.1 (4×C_{Ar}), 128.3 (2×C_{Ar}), 129.4 (4×C_{Ar}), 138.2 (2×C_{Ar}), 167.7 (–*C*H=).

3.2.3. 2-Methyl-3,3-diphenylprop-1-ene-1,1-dicarbonitrile (**5b**)

Following the method A, 1,1-diphenylacetone (**4b**) (0.61 g, 2.90 mmol), malonodinitrile (0.21 g, 3.18 mmol), glacial acetic acid (0.33 g, 5.50 mmol), ammonium acetate (0.11 g, 1.43 mmol), piperidine (78 mg, 0.93 mmol) and benzene (11 mL) were heated for 4 h with continuous water separation. Due to the relatively high amount of unreacted ketone **4b** indicated by TLC, additional portions of malonodinitrile (70 mg, 1.06 mmol), ammonium acetate (70 mg, 0.91 mmol) and piperidine (34.5 mg, 0.41 mmol) were added twice during a further 11 h of heating to reflux. After standard work-up, the crude product was purified by column chromatography (toluene/SiO_2) to give the dinitrile **5b** (242 mg, yield 32.3%) as small, white crystals. Mp 100–101 °C. IR (KBr) 3061, 3029, 2916, 2232 (CN), 1580, 1498, 1454, 1367, 745, 714, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3H, –C*H*$_3$), 5.71 (s, 1H, Ph_2CH), 7.14–7.15 (m, 4H, Ar–*H*), 7.33–7.40 (m, 6H, Ar–*H*). ^{13}C NMR ($CDCl_3$) δ 21.1 (–*C*H$_3$), 57.1 (Ph_2C), 88.0 ((CN)$_2$*C*=), 111.6 (*C*N), 111.8 (*C*N), 128.1 (2×C_{Ar}), 128.8 (4×C_{Ar}), 129.1 (4×C_{Ar}), 137.8 (2×C_{Ar}), 181.4 (–*C*(CH$_3$)=). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85%. Found: C, 83.45; H, 5.56; N, 11.09%.

3.2.4. 3-(4-Methylphenyl)-3-phenylprop-1-ene-1,1-dicarbonitrile (**8a**)

Following the method A, ketone **7a** (1.73 g, 8.23 mmol), malonodinitrile (0.60 g, 9.08 mmol), glacial acetic acid (0.42 g, 6.99 mmol), ammonium acetate (0.24 g, 3.11 mmol), piperidine (0.22 g, 2.58 mmol) and benzene (25 mL) were heated for 5 h with continuous water separation. The mixture was diluted with benzene (25 mL) and worked up in the usual manner. The crude product was isolated by column chromatography (CCl_4/SiO_2) and recrystallized from cyclohexane to give dinitrile **8a** (0.88 g, yield 41.3%) as small, white crystals. Mp 95–97 °C. IR (KBr) 3083, 3057, 3034, 2922, 2859, 2237 (CN), 1606, 1595, 1513, 1493, 1451, 946, 775, 736, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H, C*H*$_3$), 5.30 (d, 1H, *J*=11.1 Hz, Ar_2CH), 7.05–7.06 (m, 2H, Ar–*H*), 7.13–7.20 (m, 4H, Ar–*H*), 7.32–7.39 (m, 3H, Ar–*H*), 7.68 (d, 1H, *J*=11.1 Hz, –C*H*=). ^{13}C NMR ($CDCl_3$) δ 21.1 (*C*H$_3$), 53.0 (Ar_2C), 88.8 ((CN)$_2$*C*=), 110.6 (*C*N), 112.0 (*C*N), 128.0 (2×C_{Ar}), 128.1 (2×C_{Ar}), 128.2, 129.4 (2×C_{Ar}), 130.1 (2×C_{Ar}), 135.2, 138.2, 138.5, 167.9 (–*C*H=). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85%. Found: C, 83.61; H, 5.59; N, 10.89%.

3.2.5. 3,3-Bis(4-methylphenyl)prop-1-ene-1,1-dicarbonitrile (**8b**)

Method A. Aldehyde **7b** (1.00 g, 4.46 mmol), malonodinitrile (0.32 g, 4.84 mmol), glacial acetic acid (0.23 g, 3.83 mmol), ammonium acetate (0.19 g, 2.46 mmol), piperidine (112 mg, 1.32 mmol) and benzene (25 mL) were heated for 5 h with continuous water separation. The mixture was diluted with benzene (25 mL) and worked up in the usual manner. The crude product was isolated by column chromatography (toluene/SiO_2) and the obtained yellow thick oil was recrystallized from petroleum ether (bp 60–90 °C) to give dinitrile **8b** (0.59 g, yield 48.6%) as white crystals. Physical and spectroscopic data were in agreement with the values reported below (method B).

Method B. A solution of aldehyde **7b** (0.50 g, 2.23 mmol), malonodinitrile (0.16 g, 2.42 mmol) and piperidine (21.5 mg, 0.252 mmol) in anhydrous ethanol (5 mL) was heated to reflux for 5 min. After removal of the solvent in vacuo, the residue was chromatographed (CCl_4/SiO_2) and the obtained yellow thick oil was crystallized from petroleum ether (bp 60–90 °C) to give dinitrile **8b**

(217.4 mg, yield 35.8%) as white short needles. Mp 110–112 °C. IR (KBr) 3032, 2950, 2919, 2860, 2234 (CN), 1606, 1510, 1450, 1042, 1021, 942, 855, 818, 751 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.35 (s, 6H, 2×CH_3), 5.25 (d, 1H, J=11.1 Hz, Ar_2CH), 7.03–7.05 (m, 4H, Ar–H), 7.17–7.18 (m, 4H, Ar–H), 7.65 (d, 1H, J=11.1 Hz, –CH=). ^{13}C NMR ($CDCl_3$) δ 21.0 (2×CH_3), 52.7 (Ar_2C), 88.5 ($(CN)_2C$=), 110.6 (*C*N), 112.0 (*C*N), 127.9 (4×C_{Ar}), 130.0 (4×C_{Ar}), 135.4 (2×C_{Ar}), 138.1 (2×C_{Ar}), 168.1 (–*C*H=). Tautomer of **8b**: 3,3-bis(4-methylphenyl)prop-2-ene-1,1-dicarbonitrile (**8d**). ^1H NMR ($CDCl_3$) δ 2.35 (s, 6H, 2×CH_3), 4.51 (d, 1H, J=9.5 Hz, –$CH(CN)_2$), 5.98 (d, 1H, J=9.5 Hz, Ar_2C=C*H*), 7.07–7.09 (m, 4H, Ar–H), 7.27–7.29 (m, 4H, Ar–H). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29%. Found: C, 83.94; H, 5.86; N, 10.44%.

3.2.6. 2-Methyl-3,3-bis(4-methylphenyl)prop-1-ene-1,1-dicarbonitrile (*8c*)

Following the method A, ketone **7c** (2.06 g, 8.64 mmol), malonodinitrile (0.63 g, 9.54 mmol), glacial acetic acid (0.44 g, 7.32 mmol), ammonium acetate (0.36 g, 4.67 mmol), piperidine (0.31 g, 3.64 mmol) and benzene (40 mL) were heated for 5.5 h with continuous water separation. Due to the relatively high amount of unreacted ketone **7c**, indicated by TLC, additional portions of malonodinitrile (0.60 g, 9.08 mmol), ammonium acetate (0.42 g, 5.45 mmol) and piperidine (233 mg, 2.74 mmol) were added, and the reaction time was prolonged to 12 h. After standard work-up, tar substances were removed by flash chromatography (toluene/SiO_2) and the crude product was purified by column chromatography (petroleum ether (bp 60–90 °C)–ethyl acetate, 25:1 (v/v)/SiO_2) to give the dinitrile **8c** (1.10 g, yield 44.5%) as very thick, colourless oil. IR (neat) 3027, 3003, 2952, 2924, 2869, 2232 (CN), 1589, 1512, 1449, 1378, 1189, 1121, 1022, 843, 819, 765, 737 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.21 (s, 3H, CCH_3), 2.36 (s, 6H, 2×Ar–CH_3), 5.62 (s, 1H, Ar_2CH), 7.01–7.03 (m, 4H, Ar–H), 7.16–7.18 (m, 4H, Ar–H). ^{13}C NMR ($CDCl_3$) δ 21.0 (2×Ar–*C*H_3, C*C*H_3), 56.4 (Ar_2C), 87.5 ($(CN)_2C$=), 111.7 (*C*N), 111.9 (*C*N), 128.6 (4×C_{Ar}), 129.7 (4×C_{Ar}), 135.0 (2×C_{Ar}), 137.9 (2×C_{Ar}), 182.0 (–*C*(CH_3)=). Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78%. Found: C, 83.86; H, 6.39; N, 9.78%.

3.2.7. 3,3-Bis(4-chlorophenyl)prop-1-ene-1,1-dicarbonitrile (*11a*)[24]

Following the method A, aldehyde **10a** (1.58 g, 5.96 mmol), malonodinitrile (0.47 g, 7.12 mmol), glacial acetic acid (0.34 g, 5.66 mmol), ammonium acetate (0.22 g, 2.85 mmol), piperidine (0.23 g, 2.70 mmol) and benzene (35 mL) were heated for 6 h with continuous water separation. The mixture was diluted with benzene (20 mL) and worked up in the usual manner. The dinitrile **11a** was purified by column chromatography (CCl_4/SiO_2) to give a red oil, which slowly solidified (0.52 g, yield 27.8%). An analytical sample of **11a** was obtained by double recrystallization from petroleum ether (bp 60–90 °C). Mp 101.5–103.5 °C (yellow plates). IR (KBr) 3087, 3055, 3032, 2921, 2853, 2238 (CN), 1909, 1606, 1489, 1405, 1090, 1011, 933, 828, 800, 771, 551, 525, 492 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.28 (d, 1H, J=11.0 Hz, Ar_2CH), 7.07–7.09 (m, 4H, Ar–H), 7.36–7.38 (m, 4H, Ar–H), 7.58 (d, 1H, J=11.0 Hz, –CH=). ^{13}C NMR ($CDCl_3$) δ 52.0 (Ar_2C), 90.1 ($(CN)_2C$=), 110.2 (*C*N), 111.6 (*C*N), 129.3 (4×C_{Ar}), 129.8 (4×C_{Ar}), 134.7 (2×C_{Ar}), 136.4 (2×C_{Ar}), 166.0 (–*C*H=). Tautomer of **11a**: 3,3-bis(4-chlorophenyl)prop-2-ene-1,1-dicarbonitrile (**11c**).[24] ^1H NMR ($CDCl_3$) δ 4.44 (d, 1H, J=9.3 Hz, –$CH(CN)_2$), 6.06 (d, 1H, J=9.3 Hz, Ar_2C=C*H*), 7.14–7.17 (m, 4H, Ar–H), 7.32–7.34 (m, 2H, Ar–H), 7.48–7.50 (m, 2H, Ar–H). ^{13}C NMR ($CDCl_3$) δ 23.0 (–*C*H($CN)_2$), 111.4 (Ar_2C=*C*H), 112.5 (*C*N), 129.0 (2×C_{Ar}), 129.1 (2×C_{Ar}), 129.9 (2×C_{Ar}), 130.3 (2×C_{Ar}), 134.1, 136.0, 136.1, 136.8, 149.6 (Ar_2C=).

3.2.8. 3,3-Bis(4-chlorophenyl)-2-methylprop-1-ene-1,1-dicarbonitrile (*11b*)

Following the method A, ketone **10b** (1.79 g, 6.41 mmol), malonodinitrile (0.47 g, 7.12 mmol), glacial acetic acid (0.34 g, 5.66 mmol), ammonium acetate (0.22 g, 2.85 mmol), piperidine (232 mg, 2.72 mmol) and benzene (35 mL) were heated for 7 h with continuous water separation. Due to the relatively high amount of unreacted ketone **10b** indicated by TLC, additional portions of malonodinitrile (0.24 g, 3.63 mmol), ammonium acetate (0.12 g, 1.16 mmol) and piperidine (121 mg, 1.42 mmol) were added twice during further 12 h of heating to reflux. After standard work-up, the crude product was purified by double column chromatography, using at first toluene/SiO_2, then petroleum ether (bp 60–90 °C)–ethyl acetate, 30:1 (v/v)/SiO_2. The dinitrile **11b** was obtained as a colourless, very thick oil, which partially solidified after a few days (0.74 g, yield 35.2%). An analytical sample of **11b** was obtained by recrystallization from ethanol. Mp 87–88.5 °C (small, white crystals). IR (KBr) 3088, 3067, 3049, 2962, 2922, 2852, 2228 (CN), 1588, 1490, 1406, 1089, 1012, 829, 792, 750, 542, 494 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.20 (s, 3H, CH_3), 5.63 (s, 1H, Ar_2CH), 7.05–7.07 (m, 4H, Ar–H), 7.36–7.39 (m, 4H, Ar–H). ^{13}C NMR ($CDCl_3$) δ 21.0 (*C*H_3), 55.7 (Ar_2C), 88.7 ($(CN)_2C$=), 111.3 (*C*N), 111.5 (*C*N), 129.5 (4×C_{Ar}), 130.0 (4×C_{Ar}), 134.6 (2×C_{Ar}), 135.8 (2×C_{Ar}), 179.7 (–*C*(CH_3)=). Anal. Calcd for $C_{18}H_{12}Cl_2N_2$: C, 66.07; H, 3.70; N, 8.56%. Found: C, 66.20; H, 3.59; N, 8.52%.

3.2.9. 3-(4-Chlorophenyl)-3-phenylprop-1-ene-1,1-dicarbonitrile (*14a*)

Following the method A, aldehyde **13a** (0.67 g, 2.90 mmol), malonodinitrile (0.32 g, 4.84 mmol), glacial acetic acid (0.21 g, 3.50 mmol), ammonium acetate (0.18 g, 2.34 mmol), piperidine (0.20 g, 2.30 mmol) and benzene (20 mL) were heated for 3 h with continuous water separation. The mixture was diluted with benzene (25 mL) and worked up in the usual manner. The dinitrile **14a** was isolated by column chromatography (petroleum ether (bp 60–90 °C)–ethyl acetate, 15:1 (v/v)/SiO_2) as white small crystals (0.46 g, yield 56.8%). Mp 96–98.5 °C. IR (KBr) 3039, 2920, 2853, 2237 (CN), 1606, 1491, 1450, 1408, 1092, 1015, 753, 701 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.30 (d, 1H, J=10.8 Hz, Ar_2CH), 7.09–7.11 (m, 2H, Ar–H), 7.13–7.15 (m, 2H, Ar–H), 7.35–7.41 (m, 5H, Ar–H), 7.63 (d, 1H, J=10.8 Hz, –CH=). ^{13}C NMR ($CDCl_3$) δ 52.6 (Ar_2C), 89.6 ($(CN)_2C$=), 110.4 (*C*N), 111.8 (*C*N), 128.0 (2×C_{Ar}), 128.5, 129.4 (2×C_{Ar}), 129.5 (2×C_{Ar}), 129.6 (2×C_{Ar}), 134.4, 136.8, 137.9, 166.9 (–*C*H=). Anal. Calcd for $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05%. Found: C, 73.07; H, 3.84; N, 10.05%.

3.2.10. 3-(4-Chlorophenyl)-2-methyl-3-phenylprop-1-ene-1,1-dicarbonitrile (*14b*)

Ketone **13b** (5.70 g, 23.3 mmol), malonodinitrile (1.85 g, 28.0 mmol), glacial acetic acid (1.50 g, 25.0 mmol), piperidine (0.85 g, 10.0 mmol) and toluene (20 mL) were heated for 5 h with continuous water separation. Then the additional portions of malonodinitrile (1.85 g, 28.0 mmol) and glacial acetic acid (2.00 g, 33.3 mmol) and also ammonium acetate (1.00 g, 13.0 mmol) were added, and the mixture was heated to reflux for next 4 h. The reaction mixture was washed with water, dried with anhydrous magnesium sulfate and the solvent was evaporated. The residue was distilled in vacuo to give the dinitrile **14b** (3.71 g, yield 54.4%) as a thick, yellow oil. An analytical sample of **14b** was obtained by column chromatography (cyclohexane–ethyl acetate, 15:1 (v/v)/SiO_2). Bp 182–187 °C/2 mmHg. IR (neat) 3029, 2929, 2848, 2232 (CN), 1592, 1492, 1454, 1373, 833, 739, 701 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.22 (s, 3H, –CH_3), 5.67 (s, 1H, Ar_2CH), 7.07–7.10 (m, 2H, Ar–H), 7.11–7.13 (m, 2H, Ar–H), 7.33–7.41 (m, 5H, Ar–H). ^{13}C NMR ($CDCl_3$) δ 21.0 (*C*H_3–), 56.3 (Ar_2C), 88.3 ($(CN)_2C$=), 111.5 (*C*N), 111.7 (*C*N), 128.4, 128.7 (2×C_{Ar}), 129.3 (2×C_{Ar}), 129.4 (2×C_{Ar}), 130.1 (2×C_{Ar}), 134.2, 136.3, 137.3, 180.7 (–*C*(CH_3)=). Anal. Calcd for $C_{18}H_{13}ClN_2$: C, 73.85; H, 4.48; N, 9.57%. Found: C, 73.86; H, 4.45; N, 9.43%.

3.3. Preparation of 1-amino-4-arylnaphthalene-2-carbonitriles 3, 6, 9, 12, 15 and 16

3.3.1. 1-Amino-3,6-dimethyl-4-phenylnaphthalene-2-carbonitrile (**3**)[10]

Dinitrile **2** (0.62 g, 2.28 mmol) was dissolved in chilled concentrated sulfuric acid (9 mL). After stirring at −5 to −15 °C for 1 h, the resulting brown solution was poured onto crushed ice (ca. 80 g). Obtained pink solid was filtered off and washed with saturated $NaHCO_3$ solution. Crude product was purified by column chromatography (toluene/SiO_2) to give aminonitrile **3** (0.44 g, yield 71%) as beige small crystals. An analytical sample of **3** was obtained by crystallization from cyclohexane. Mp 117–119 °C. IR (KBr) 3457, 3372, 3254 (ν_{N-H}), 3054, 3023, 2920, 2851, 2199 (CN), 1652 (δ_{N-H}), 1623, 1574, 1506, 1440, 1369, 1257, 1159, 1071, 815, 776, 722, 695 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H, C3–CH_3), 2.35 (s, 3H, C6–CH_3), 5.08 (br s, 2H, NH_2), 7.07 (mc, 1H, C5–*H*), 7.17–7.20 (m, 2H, C2′–*H*, C6′–*H*), 7.28 (dd, 1H, *J*=8.5, 1.6 Hz, C7–*H*), 7.41–7.45 (m, 1H, C4′–*H*), 7.47–7.51 (m, 2H, C3′–*H*, C5′–*H*), 7.70 (d, 1H, *J*=8.5 Hz, C8–*H*). ^{13}C NMR ($CDCl_3$) δ 19.5 (C3–*C*H_3), 21.9 (C6–*C*H_3), 91.3 (*C*2), 118.4 (*C*N), 118.5, 120.8, 126.5, 127.2 (2×C), 128.6 (2×C_{Ph}), 128.9, 130.7 (2×C_{Ph}), 132.5, 135.5, 138.9, 139.1, 147.9 (*C*1).

3.3.2. 1-Amino-4-phenylnaphthalene-2-carbonitrile (**6a**)

Dinitrile **5a** (113 mg, 0.463 mmol) was dissolved in chilled concentrated sulfuric acid (3 mL). After stirring at 0 °C for 1 h, the resulting brown solution was poured onto crushed ice (ca. 40 g). Precipitated solid was filtered off and washed with saturated $NaHCO_3$ solution to give aminonitrile **6a** (102 mg, yield 90.3%) as small, light yellow crystals. An analytical sample of **6a** was obtained by sublimation in vacuo. Mp 116–117 °C. IR (KBr) 3500, 3356 (ν_{N-H}), 3080, 3049, 3023, 2214 (CN), 1642 (δ_{N-H}), 1601, 1564, 1510, 1450, 1262, 883, 761 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.14 (s, 2H, NH_2), 7.28 (s, 1H, C3–*H*), 7.39–7.43 (m, 3H, H_{Ph}), 7.46–7.48 (m, 2H, H_{Ph}), 7.52–7.57 (m, 2H, C6–*H*, C7–*H*), 7.84–7.90 (m, 2H, C5–*H*, C8–*H*). ^{13}C NMR ($CDCl_3$) δ 89.5 (*C*2), 118.5 (*C*N), 121.4, 122.1, 126.2, 126.6, 127.2, 127.4, 128.4 (2×C_{Ph}), 128.9, 130.1 (2×C_{Ph}), 131.2, 134.3, 139.4, 147.7 (*C*1). Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47%. Found: C, 83.38; H, 5.04; N, 11.32%.

3.3.3. 1-Amino-3-methyl-4-phenylnaphthalene-2-carbonitrile (**6b**)[16]

Dinitrile **5b** (115 mg, 0.445 mmol) was dissolved in chilled concentrated sulfuric acid (3 mL). After stirring at 0 °C for 1 h, the resulting green solution was poured onto crushed ice (ca. 40 g). Precipitated solid was filtered off and washed with saturated $NaHCO_3$ solution to give aminonitrile **6b** (104 mg, yield 90.4%) as small, white crystals. An analytical sample of **6b** was obtained by vacuum sublimation. Mp 169–171 °C (the mp of **6b** is not given in Ref. 16). IR (KBr) 3469, 3375 (ν_{N-H}), 3249, 3055, 3023, 2201 (CN), 1645 (δ_{N-H}), 1601, 1567, 1506, 1440, 1374, 1259, 761, 705, 761 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.30 (s, 3H, CH_3), 5.12 (s, 2H, NH_2), 7.19–7.21 (m, 2H, H_{Ph}), 7.34 (dd, 1H, *J*=8.7, 1.5 Hz, C5–*H*), 7.41–7.50 (m, 5H, C6–*H*, C7–*H*, H_{Ph}), 7.81 (dd, 1H, *J*=8.5, 1.5 Hz, C8–*H*). ^{13}C NMR ($CDCl_3$) δ 19.4 (–*C*H_3), 92.1 (*C*2), 118.1 (*C*N), 120.3, 120.9, 125.1, 127.3, 127.4, 128.6 (2×C_{Ph}), 128.8, 129.5, 130.7 (2×C_{Ph}), 132.4, 135.3, 138.8, 147.4 (*C*1).

3.3.4. 1-Amino-6-methyl-4-phenylnaphthalene-2-carbonitrile (**9a**)

Dinitrile **8a** (309.8 mg, 1.20 mmol) was dissolved in chilled concentrated sulfuric acid (15 mL). After stirring at −5 to −15 °C for 75 min, the resulting brown solution was poured onto crushed ice (ca. 80 g). The obtained suspension was neutralized with aq NaOH, extracted with chloroform, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Crude product was purified by vacuum sublimation to give aminonitrile **9a** (245.3 mg, yield 79.2%) as white, short needles. Mp 172–174 °C. IR (KBr) 3431, 3325, 3237 (ν_{N-H}), 3055, 3036, 2973, 2916, 2208 (CN), 1645 (δ_{N-H}), 1623, 1598, 1569, 1503, 1432, 1247, 1076, 1027, 891, 815, 781, 768, 705, 683, 639 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.42 (s, 3H, CH_3), 5.08 (br s, 2H, NH_2), 7.24 (s, 1H, C3–*H*), 7.38–7.43 (m, 4H, 3×H_{Ph}, C7–*H*), 7.46–7.49 (m, 2H, 2×H_{Ph}), 7.62 (s, 1H, C5–*H*), 7.77 (d, 1H, *J*=8.6 Hz, C8–*H*). ^{13}C NMR ($CDCl_3$) δ 21.8 (*C*H_3), 88.6 (*C*2), 118.7 (*C*N), 120.2, 121.3, 126.3, 126.8, 127.3, 128.2, 128.4 (2×C_{Ph}), 130.1 (2×C_{Ph}), 130.6, 134.4, 139.2, 139.5, 147.6 (*C*1). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85%. Found: C, 83.61; H, 5.59; N, 10.89%.

3.3.5. 1-Amino-6-methyl-4-(4-methylphenyl)naphthalene-2-carbonitrile (**9b**)

Dinitrile **8b** (145.9 mg, 0.536 mmol) was dissolved in chilled concentrated sulfuric acid (7 mL). After stirring at about −15 °C for 1 h, the resulting brown solution was poured onto crushed ice (ca. 60 g). The obtained suspension was neutralized with aq NaOH, diluted with 50 mL of water, extracted with chloroform, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Crude product was purified by column chromatography (toluene/SiO_2) to give aminonitrile **9b** (87.9 mg, yield 60.3%) as white small crystals. An analytical sample of **9b** was obtained by vacuum sublimation. Mp 182.5–183.5 °C (white, short needles). IR (KBr) 3467, 3375, 3251 (ν_{N-H}), 3025, 2923, 2854, 2203 (CN), 1650 (δ_{N-H}), 1569, 1506, 1442, 1244, 1025, 880, 810, 768, 724, 682, 625 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.42 (s, 3H, C6–CH_3), 2.44 (s, 3H, C4′–CH_3), 5.05 (br s, 2H, NH_2), 7.21 (s, 1H, C3–*H*), 7.28 (br s, 4H, Ar–*H*), 7.37 (dd, 1H, *J*=8.5, 1.5 Hz, C7–*H*), 7.63 (mc, 1H, C5–*H*), 7.76 (d, 1H, *J*=8.6 Hz, C8–*H*). ^{13}C NMR ($CDCl_3$) δ 21.2 (C4′–*C*H_3), 21.8 (C6–*C*H_3), 88.8 (*C*2), 118.7 (*C*N), 120.3, 121.3, 126.4, 126.7, 128.2, 129.1 (2×C_{Ar}), 129.9 (2×C_{Ar}), 130.7, 134.6, 136.6, 137.0, 139.1, 147.4 (*C*1). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29%. Found: C, 83.73; H, 6.06; N, 10.26%.

3.3.6. 1-Amino-3,6-dimethyl-4-(4-methylphenyl)naphthalene-2-carbonitrile (**9c**)

A solution of dinitrile **8c** (156.9 mg, 0.548 mmol) in 0.3 mL of acetone was added to chilled concentrated sulfuric acid (6 mL). After stirring at −15 °C for 1 h, the resulting brown solution was poured onto crushed ice (ca. 60 g). The obtained suspension was neutralized with aq NaOH, extracted with chloroform, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Crude product was purified by column chromatography (toluene/SiO_2) to give aminonitrile **9c** (121.2 mg, yield 77.3%) as light beige small crystals. Mp 169.5–170 °C. IR (KBr) 3465, 3372, 3254 (ν_{N-H}), 3028, 2916, 2852, 2199 (CN), 1651 (δ_{N-H}), 1620, 1572, 1503, 1439, 1369, 1252, 1157, 1072, 812, 776, 772, 734 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H, C3–CH_3), 2.35 (s, 3H, C6–CH_3), 2.46 (s, 3H, C4′–CH_3), 5.05 (br s, 2H, NH_2), 7.06–7.08 (m, 2H, Ar–*H*), 7.12 (s, 1H, C5–*H*), 7.26–7.29 (m, 3H, 2×Ar–*H*, C7–*H*), 7.69 (d, 1H, *J*=8.6 Hz, C8–*H*). ^{13}C NMR ($CDCl_3$) δ 19.5 (C3–*C*H_3), 21.3 (C4′–*C*H_3), 21.8 (C6–*C*H_3), 91.4 (*C*2), 118.4 (*C*N), 118.5, 120.8 (*C*8), 126.5, 127.1, 129.0, 129.3 (2×C_{Ar}), 130.6 (2×C_{Ar}), 132.6, 135.7, 135.8, 136.8, 139.0, 147.8 (*C*1). Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78%. Found: C, 83.65; H, 6.52; N, 9.65%.

3.3.7. 1-Amino-6-chloro-4-(4-chlorophenyl)naphthalene-2-carbonitrile (**12a**)

Dinitrile **11a** (153.4 mg, 0.490 mmol) was dissolved in chilled concentrated sulfuric acid (7 mL). Reaction was monitored by TLC (chloroform/SiO_2 and toluene/SiO_2). The mixture was stirred at −15 to −10 °C for 3.5 h, then left overnight at about −15 °C. The resulting solution was poured onto crushed ice (ca. 60 g). The obtained suspension was neutralized with aq NaOH, extracted with chloroform, dried over anhydrous magnesium sulfate and the

solvent was removed under reduced pressure. Crude product was purified by column chromatography (toluene–ethyl acetate, 4:1 (v/v)/SiO_2) to give aminonitrile **12a** (94.7 mg, yield 61.7%) as white small crystals. Mp 264.5–266 °C. IR (KBr) 3466, 3372, 3250 (ν_{N-H}), 3088, 2208 (CN), 1651 (δ_{N-H}), 1607, 1559, 1494, 1440, 1284, 1116, 1091, 1011, 888, 822, 809, 526 cm^{-1}. ^1H NMR (DMSO-d_6) δ 7.11 (br s, 2H, NH_2), 7.33 (s, 1H, C3–*H*), 7.42–7.44 (m, 2H, Ar–*H*), 7.54–7.56 (m, 2H, Ar–*H*), 7.58–7.60 (m, 2H, C5–*H*, C7–*H*), 8.47 (d, 1H, *J*=9.8 Hz, C8–*H*). ^{13}C NMR (DMSO-d_6) δ 86.5 (*C*2), 118.3 (*C*N), 120.3, 124.0, 125.2, 125.8, 126.1, 128.5 (2×C_{Ar}), 129.0, 131.5 (2×C_{Ar}), 132.1, 134.3, 134.4, 137.2, 149.7 (*C*1). Anal. Calcd for $C_{17}H_{10}Cl_2N_2$: C, 65.20; H, 3.22; N, 8.94%. Found: C, 65.45; H, 3.55; N, 8.80%.

3.3.8. 1-Amino-6-chloro-4-(4-chlorophenyl)-3-methylnaphthalene-2-carbonitrile (**12b**)

Dinitrile **11b** (217.0 mg, 0.663 mmol) was dissolved in chilled concentrated sulfuric acid (10 mL). Reaction was monitored by TLC (toluene/SiO_2). The mixture was stirred at −15 to −10 °C for 2.5 h. The resulting solution was poured onto crushed ice (ca. 100 g). The obtained suspension was neutralized with aq NaOH, extracted with chloroform, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Crude product was purified by column chromatography (chloroform/SiO_2) to give aminonitrile **12b** (168.1 mg, yield 77.5%) as white small crystals. An analytical sample of **12b** was obtained by recrystallization from toluene. Mp 194–195.5 °C (white short needles). IR (KBr) 3470, 3370, 3251 (ν_{N-H}), 2958, 2918, 2853, 2204 (CN), 1649 (δ_{N-H}), 1607, 1566, 1494, 1436, 1363, 1280, 1247, 1091, 1014, 942, 878, 815, 765, 731 cm^{-1}. ^1H NMR (DMSO-d_6) δ 2.15 (s, 3H, C3–CH_3), 6.98 (br s, 2H, NH_2), 7.03 (d, 1H, *J*=2.2 Hz, C5–*H*), 7.22–7.25 (m, 2H, C2′–*H*, C6′–*H*), 7.47 (dd, 1H, *J*=8.9, 2.1 Hz, C7–*H*), 7.56–7.58 (m, 2H, C3′–*H*, C5′–*H*), 8.40 (d, 1H, *J*=9.0 Hz, C8–*H*). ^{13}C NMR (DMSO-d_6) δ 19.2 (*C*H_3), 89.0 (*C*2), 117.7, 118.6 (*C*N), 124.0, 124.1, 124.7, 125.7, 128.8 (2×C_{Ar}), 132.3, 132.4 (2×C_{Ar}), 134.1, 134.3, 135.5, 136.6, 150.0 (*C*1). Anal. Calcd for $C_{18}H_{12}Cl_2N_2$: C, 66.07; H, 3.70; N, 8.56%. Found: C, 66.09; H, 3.70; N, 8.46%.

3.3.9. 1-Amino-4-(4-chlorophenyl)naphthalene-2-carbonitrile (**15**)

Dinitrile **14a** (304.5 mg, 1.09 mmol) was dissolved during 1 h in chilled concentrated sulfuric acid (20 mL). Then the mixture was stirred at −10 to −5 °C for next 2 h. The resulting solution was poured onto crushed ice (ca. 120 g). The obtained suspension was neutralized with aq NaOH, extracted with chloroform, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Crude product was purified by column chromatography (chloroform/SiO_2) to give aminonitrile **15** (268.4 mg, yield 88.1%) as beige small crystals. An analytical sample of **15** was obtained by recrystallization from ethanol. Mp 175–178 °C. IR (KBr) 3471, 3385, 3244 (ν_{N-H}), 3082, 3050, 2924, 2853, 2201 (CN), 1645 (δ_{N-H}), 1598, 1563, 1510, 1491, 1439, 1405, 1093, 1011, 890, 826, 778, 762, 718, 682 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.15 (br s, 2H, NH_2), 7.26 (s, 1H, C3–*H*), 7.31–7.35 (m, 2H, Ar–*H*), 7.43–7.46 (m, 2H, Ar–*H*), 7.54–7.59 (m, 2H, C6–*H*, C7–*H*), 7.78–7.81 (m, 1H, C5–*H* or C8–*H*), 7.87–7.89 (m, 1H, C8–*H* or C5–*H*). ^{13}C NMR ($CDCl_3$) δ 89.4 (*C*2), 118.4 (*C*N), 121.5, 122.1, 126.3, 126.7, 126.8, 128.7 (2×C_{Ar}), 129.1, 129.8, 131.4 (2×C_{Ar}), 133.5, 134.1, 137.8, 147.8 (*C*1). Anal. Calcd for $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05%. Found: C, 73.02; H, 3.77; N, 9.90%.

3.3.10. Cyclization of 3-(4-chlorophenyl)-2-methyl-3-phenylprop-1-ene-1,1-dicarbonitrile (**14b**). 1-Amino-4-(4-chlorophenyl)-3-methylnaphthalene-2-carbonitrile (**16a**) and 1-amino-6-chloro-3-methyl-4-phenylnaphthalene-2-carbonitrile (**16b**)

Dinitrile **14b** (203.7 mg, 0.696 mmol) was dissolved in chilled concentrated sulfuric acid (9 mL). The reaction progress was monitored by TLC (toluene/SiO_2). The mixture was stirred at −15 to −10 °C for 2 h. The resulting solution was poured onto crushed ice (ca. 100 g). The obtained suspension was neutralized with aq NaOH, extracted with chloroform, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Crude product was purified by column chromatography (toluene/SiO_2) to give mixture of aminonitriles **16a** and **16b** (70:30, 172.5 mg, overall yield 84.7%) as beige small crystals. IR (KBr) 3450, 3369, 3262 (ν_{N-H}), 3067, 3029, 2848, 2201 (CN), 1649 (δ_{N-H}), 1567, 1498, 1442, 1373, 1254, 827, 764, 701 cm^{-1}. Compound **16a**: ^1H NMR (DMSO-d_6) δ 2.15 (s, 3H, CH_3), 6.84 (br s, 2H, NH_2), 7.12–7.13 (m, 1H, C5–*H*), 7.20–7.23 (m, 2H, H_{Ph}), 7.43–7.49 (m, 2H, C6–*H*, C7–*H*), 7.54–7.56 (m, 2H, H_{Ph}), 8.34–8.35 (m, 1H, C8–*H*). ^{13}C NMR (DMSO-d_6) δ 19.1 (*C*H_3), 88.4 (*C*2), 118.1 (*C*N), 120.1, 123.1 (*C*8), 124.5, 124.9, 125.6 (*C*5), 128.5 (2×C_{Ar}), 129.1, 131.9, 132.1, 132.5 (2×C_{Ar}), 134.4, 137.4, 150.1 (*C*1). **16b**: ^1H NMR (DMSO-d_6) δ 2.15 (s, 3H, CH_3), 6.94 (br s, 2H, NH_2), 7.05 (d, 1H, *J*=2.2 Hz, C5–*H*), 7.19–7.21 (m, 2H, C2′–*H*, C6′–*H*), 7.43–7.49 (m, 2H, C7–*H*, C4′–*H*), 7.50–7.53 (m, 2H, C3′–*H*, C5′–*H*), 8.39 (d, 1H, *J*=9.0 Hz, C8–*H*). ^{13}C NMR (DMSO-d_6) δ 19.2 (*C*H_3), 89.0 (*C*2), 117.8, 118.6 (*C*N), 124.4 (*C*5), 124.6 (*C*7), 125.4, 125.6 (*C*8), 127.4 (*C*4′), 128.7 (2×C_{Ph}), 130.5 (2×C_{Ph}), 133.9, 134.0, 135.7, 137.8, 149.8 (*C*1). Anal. Calcd for $C_{18}H_{13}ClN_2$: C, 73.85; H, 4.48; N, 9.57%. Found: C, 73.64; H, 4.43; N, 9.30%.

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7.09 (dqd, 1H, $^{4}J_{H5-H7}$=1.45 Hz, $^{4}J_{H5-Me}$=0.88 Hz, $^{5}J_{H5-H8}$=0.52 Hz, C5–*H*), 7.19 (dddd, 2H, ^{3}J=7.61 Hz, ^{4}J=1.92 Hz, ^{4}J=1.29 Hz, ^{5}J=0.65 Hz, C2′–*H*, C6′–*H*), 7.28 (ddq, 1H, $^{3}J_{H7-H8}$=8.60 Hz, $^{4}J_{H7-H5}$=1.45 Hz, $^{4}J_{H7-Me}$=0.34 Hz, C7–*H*), 7.43 (tt, 1H, ^{3}J=7.48 Hz, ^{4}J=1.29 Hz, C4′–*H*), 7.48 (dddd, 2H, ^{3}J=7.61 Hz, ^{3}J=7.48 Hz, ^{4}J=1. 37 Hz, ^{5}J=0.65 Hz, C3′–*H*, C5′–*H*), 7.70 (ddq, 1H, $^{3}J_{H8-H7}$=8.60 Hz, $^{5}J_{H8-H5}$=0. 52 Hz, $^{5}J_{H8-Me}$=0.22 Hz, C8–*H*); (b) Quirt, A. R.; Martin, J. S. *J. Magn. Reson.* **1971**, *5*, 318–327; (c) Marat, K. *SpinWorks 2.5.5*; University of Manitoba: Winnipeg, Manitoba, Canada, 2006, http://www.umanitoba.ca/chemistry/nmr/spinworks.

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