Synthesis of 1-Aminonaphthalene-2-carbonitrile Derivatives by the Reaction of 2-Vinylbenzonitriles with 2-Lithioacetonitrile

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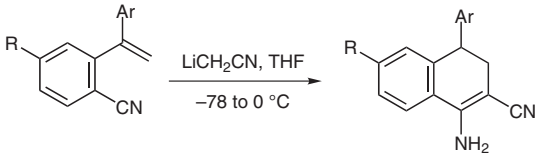
Abstract: A new and simple method for the preparation of 1-aminonaphthalene-2-carbonitrile derivatives has been developed. When 2-(1-arylethenyl)benzonitriles are treated with 2-lithioacetonitrile, 1-amino-4-aryl-3,4-dihydronaphthalene-2-carbonitriles are obtained in good yields. The reaction of 2-(1-aryl-2-methoxyethenyl)benzonitriles with 2-lithioacetonitrile leads to the formation of 1-amino-4-arylnaphthalene-2-carbonitriles in fair-to-good yields.

Key words: arenes, carbanions, nitriles, ring closure, tandem reaction

In previous papers, we reported a new short-step general synthesis of 4-aryl-3,4-dihydroisoquinoline derivatives based on the reaction of 2-(1-arylethenyl)benzonitriles with organolithiums.[1] Subsequently, we decided to examine the reaction of 2-(1-arylethenyl)benzonitriles **1** with 2-lithioacetonitrile, and found that it gave 1-amino-4-aryl-3,4-dihydronaphthalene-2-carbonitriles **2**. On the other hand, it was noted that the reaction using 2-(1-aryl-2-methoxyethenyl)benzonitriles **3** in place of **1** afforded 1-aminonaphthalene-2-carbonitriles **4**. In this paper we wish to describe the results of these studies. Compounds having an enamino nitrile moiety have already proven to be useful precursors for the synthesis of a variety of heterocycles,[2] some of which have reported to be of biological importance. However, only a few general synthetic methods of 1-aminonaphthalene-2-carbonitrile derivatives have been developed.[3,4]

The preparation of 1-amino-4-aryl-3,4-dihydronaphthalene-2-carbonitriles **2** was carried out as shown in Scheme 1. Thus, treatment of 2-(1-arylethenyl)benzonitriles **1** with two molar amounts of 2-lithioacetonitrile, generated by treatment of acetonitrile with butyllithium in THF at –78 °C,[5] at the same temperature followed by raising reaction temperature to 0 °C, resulted in the efficient production of the desired products **2**, after aqueous work-up. Scheme 1 also shows the yields of the products, which are generally good independent of the α-aryl substituents and the 4-methoxy group of the starting nitriles **1**.

It was envisioned that the use of 2-(1-aryl-2-methoxyethenyl)benzonitriles **3** in the place of **1** would be capable of affording 1-amino-4-arylnaphthalene-2-carbonitriles **4**.

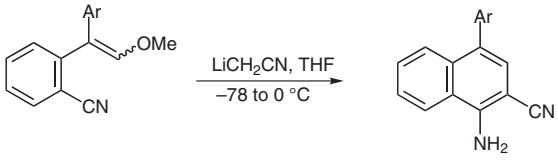


1

a	Ar = Ph, R = H	**2a**	77%
b	Ar = 3-MeC_6H_4, R = H	**2b**	86%
c	Ar = 4-MeC_6H_4, R = H	**2c**	83%
d	Ar = 4-$MeOC_6H_4$, R = H	**2d**	86%
e	Ar = 1-naphthyl, R = H	**2e**	82%
f	Ar = Ph, R = OMe	**2f**	86%

Scheme 1

As expected, subjecting **3** to the reaction with two molar amounts of 2-lithioacetonitrile under the same conditions as described for the preparation of **2** gave the desired products **4**, but the yields were somewhat lower than those of **2**, as illustrated in Scheme 2. When lithium enolates of *tert*-butyl acetate and *N*,*N*-dimethylacetamide were used, the starting nitrile was recovered almost quantitatively in each case.



3

a	Ar = Ph	**4a**	66%
b	Ar = 3-MeC_6H_4	**4b**	65%
c	Ar = 4-MeC_6H_4	**4c**	74%
d	Ar = 4-$MeOC_6H_4$	**4d**	71%
e	Ar = 1-naphthyl	**4e**	66%

Scheme 2

The mechanistic rationale, depicted in Scheme 3, begins with coupling of the first molecule of 2-lithioacetonitrile with the nitrile of 2-vinylbenzonitrile derivatives **1** and **3** to give the adduct **5**. Abstraction of a hydrogen α to the nitrile of this adduct by the second molecule of 2-lithioacetonitrile gives the dianionic intermediate **6**, which undergoes an intramolecular ring closure to give the benzylic anion intermediate **7**. The intermediate **7** (X = H) gives **2** through successive tautomerization via the intermediate **8**, and protonation (or in the inverse order). On the other hand, the intermediate **8** (X = OMe) loses methoxide after the tautomerization (or in the inverse order) to

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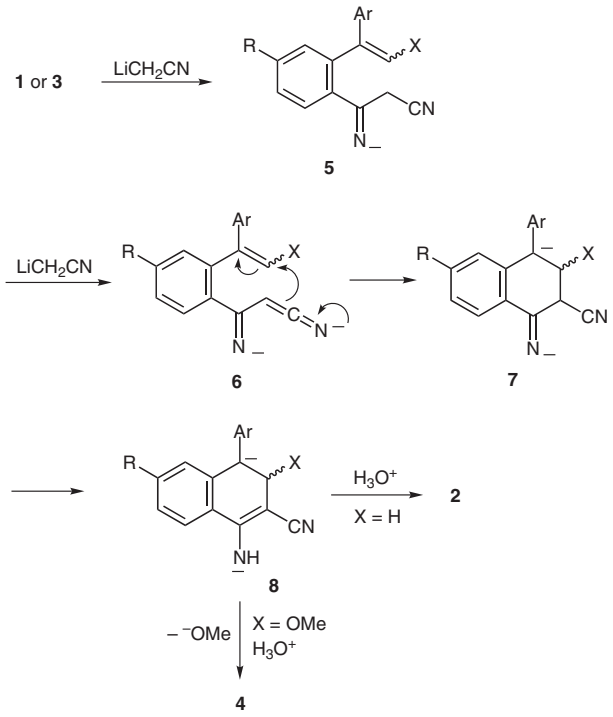
provide **4** as the result of protonation. Although the possibility of anion-promoted electrocyclic reaction of the enamido form of the intermediate **5** for the present ring closure cannot be excluded, the mechanism depicted in Scheme 3 may explain the necessity of two molar amounts of 2-lithioacetonitrile for the satisfactory production of the desired products **2** and **4**. It is noteworthy that no products arising from the addition of imino anion of the adduct **5** to the β-carbon atom of the vinyl moiety were isolated.



Scheme 3

In conclusion, we have developed a new method for preparing 1-aminonaphthalene-2-carbonitrile derivatives. The present procedure may find some value in organic synthesis, because it has some advantages over the previously reported methods; simple manipulations as well as ready availability of the starting materials.

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference using a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or JEOL GX270 FT NMR spectrometer operating at 270 MHz. The ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference on a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were measured using a JEOL AUTOMASS 20 spectrometer. TLC was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

2-(1-Phenylethenyl)benzonitrile (**1a**),[1] 2-benzoylbenzonitrile,[1,6] 2-bromo-3-methylbenzophenone,[7] 2-bromo-4-methylbenzophenone,[7] 2-[1-(4-methoxyphenyl)ethenyl]benzonitrile (**1d**),[8] and 2-bromophenyl(1-naphthyl)methanone[9] were prepared by reported methods. All other chemicals used in this study were commercially available.

2-(2-Methoxy-1-phenylethenyl)benzonitrile (3a)[10]

To a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (3.4 g, 9.9 mmol) in 1,2-dimethoxyethane (DME, 70 mL) at 0 °C under argon was added dropwise BuLi (1.6 M in hexane; 6.2 mL, 9.9 mmol). After 5 min, the resulting ylide was treated with a solution of 2-benzoylbenzonitrile[1,6] (1.6 g, 7.5 mmol) in DME (15 mL) and stirring was continued for an additional 10 min at the same temperature. H_2O (30 mL) was added and the mixture was extracted with Et_2O (2 × 30 mL). The combined extracts were washed with H_2O (20 mL) and brine (20 mL), dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography on silica gel (hexane–Et_2O, 2:1) to give **3a**. Yield: 1.3 g (73%); yellow oil; mixture of stereoisomers (*E*/*Z* = ~1:1); R_f = 0.36 (hexane–Et_2O, 2:1).

IR (neat): 2225, 1634 cm^{-1}.

^{1}H NMR (270 MHz): δ = 3.82 and 3.84 (2 s, 3 H), 6.49 (s, 0.5 H), 6.69 (s, 0.5 H), 7.11 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.20–7.40 (m, 6 H), 7.45–7.60 (m, 1 H), 7.72 (d, *J* = 8.6 Hz, 0.5 H) and 7.76 (d, *J* = 7.9 Hz, 0.5 H).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.46; H, 5.52; N, 5.90.

2-(3-Methylbenzoyl)benzonitrile

This compound was prepared from 2-bromo-4-methylbenzophenone[7] and CuCN under the conditions reported by Friedman et al.[11] Yield: 61%; white solid; mp 53–55 °C (hexane–CH_2Cl_2). IR (KBr): 2228, 1663 cm^{-1}.

^{1}H NMR (500 MHz): δ = 2.43 (s, 3 H), 7.38 (t, *J* = 7.8 Hz, 1 H), 7.46 (d, *J* = 7.3 Hz, 1 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.64–7.71 (m, 4 H), 7.85 (dd, *J* = 7.8, 1.4 Hz, 1 H).

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.36; H, 5.15; N, 6.36.

2-[1-(3-Methylphenyl)ethenyl]benzonitrile (1b)

This compound was prepared by treating 2-(3-methylbenzoyl)benzonitrile with methylenetriphenylphosphorane under conditions for the preparation of **1a** reported by us.[1] Yield: 64%; yellow oil; R_f = 0.41 (THF–hexane, 1:10).

IR (neat): 2226, 1614, 1601 cm^{-1}.

^{1}H NMR (500 MHz): δ = 2.33 (s, 3 H), 5.47 (s, 1 H), 5.86 (s, 1 H), 7.05 (d, *J* = 7.8 Hz, 1 H), 7.08 (s, 1 H), 7.13 (d, *J* = 7.8 Hz, 1 H), 7.22 (dd, *J* = 7.8, 7.3 Hz, 1 H), 7.36 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.42 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1 H), 7.57 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 1 H), 7.71 (dd, *J* = 7.8, 0.9 Hz, 1 H).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.49; H, 6.11; N, 6.38.

2-[2-Methoxy-1-(3-methylphenyl)ethenyl]benzonitrile (3b)

This compound was prepared by treating 2-(3-methylbenzoyl)benzonitrile with (methoxymethylene)triphenylphosphorane as described for the preparation of **3a**. Yield: 74%; mixture of stereoisomers (*E*/*Z* = ~8:2); colorless oil; R_f = 0.44 (CH_2Cl_2–hexane, 1:1).

IR (neat): 2226, 1637, 1601 cm^{-1}.

^{1}H NMR (500 MHz): δ = 2.30 and 2.31 (2 s, 3 H), 3.82 (s, 2.4 H), 3.84 (s, 0.6 H), 6.48 (s, 0.2 H), 6.68 (s, 0.8 H), 6.91 (d, *J* = 7.8 Hz, 1 H), 6.93 (s, 1 H), 7.04 (d, *J* = 7.3 Hz, 0.8 H), 7.14 (d, *J* = 7.8 Hz, 0.2 H), 7.16 (dd, *J* = 7.8, 7.3 Hz, 0.8 H), 7.21 (dd, *J* = 7.8, 7.3 Hz, 0.2 H), 7.27 (dd, *J* = 7.8, 0.9 Hz, 0.8 H), 7.29 (dd, *J* = 7.8, 0.9 Hz,

0.2 H), 7.34 (td, *J* = 7.8, 0.9 Hz, 0.2 H), 7.36 (td, *J* = 7.8, 0.9 Hz, 0.8 H), 7.50 (td, *J* = 7.8, 1.4 Hz, 0.2 H), 7.55 (td, *J* = 7.8, 0.9 Hz, 0.8 H), 7.67 (dd, *J* = 7.8, 1.4 Hz, 0.2 H), 7.72 (dd, *J* = 7.8, 0.9 Hz, 0.8 H).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.80; H, 6.08; N, 5.37.

2-(4-Methylbenzoyl)benzonitrile

This compound was prepared from 2-bromo-4-methylbenzophenone[7] and CuCN under the conditions reported by Friedman et al.[11] Yield: 48%; pale-yellow solid; mp 111–113 °C (hexane–CH_2Cl_2).

IR (KBr): 2228, 1661, 1601 cm^{-1}.

^1H NMR (500 MHz): δ = 2.45 (s, 3 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.63–7.69 (m, 3 H), 7.71 (d, *J* = 8.2 Hz, 2 H), 7.83 (dd, *J* = 7.8, 1.4 Hz, 1 H).

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.38; H, 5.02; N, 6.21.

2-[1-(4-Methylphenyl)ethenyl]benzonitrile (1c)

This compound was prepared by treating 2-(4-methylbenzoyl)benzonitrile with methylenetriphenylphosphorane under conditions for the preparation of **1a** reported by us.[1] Yield: 63%; yellow oil; R_f = 0.50 (Et_2O–hexane, 1:1).

IR (neat): 2226, 1615 cm^{-1}.

^1H NMR (500 MHz): δ = 2.35 (s, 3 H), 5.42 (s, 1 H), 5.84 (s, 1 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 7.8 Hz, 1 H), 7.41 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.56 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.70 (dd, *J* = 7.8, 1.4 Hz, 1 H).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.60; H, 6.07; N, 6.18.

2-[2-Methoxy-1-(4-methylphenyl)ethenyl]benzonitrile (3c)

This compound was prepared by treating 2-(4-methylbenzoyl)benzonitrile with (methoxymethylene)triphenylphosphorane as described for the preparation of **3a**. Yield: 74%; mixture of stereoisomers (~1:1); colorless oil; R_f = 0.40 (Et_2O–hexane, 1:1).

IR (neat): 2224, 1634 cm^{-1}.

^1H NMR (500 MHz): δ = 2.32 (s, 1.5 H), 2.33 (s, 1.5 H), 3.81 (s, 1.5 H), 3.83 (s, 1.5 H), 6.45 (s, 0.5 H), 6.65 (s, 0.5 H), 7.01 (d, *J* = 8.2 Hz, 1 H), 7.08 (d, *J* = 8.2 Hz, 1 H), 7.12 (d, *J* = 8.2 Hz, 1 H), 7.23 (d, *J* = 8.2 Hz, 1 H), 7.27 (d, *J* = 7.8 Hz, 0.5 H), 7.30 (d, *J* = 7.8 Hz, 0.5 H), 7.34 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 0.5 H), 7.35 (ddd, *J* = 7.8, 7.3, 0.9 Hz, 0.5 H), 7.50 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 0.5 H), 7.54 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 0.5 H), 7.66 (dd, *J* = 7.8, 0.9 Hz, 0.5 H), 7.70 (dd, *J* = 7.8, 0.9 Hz, 0.5 H).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.87; H, 6.45; N, 5.57.

2-[2-Methoxy-1-(4-methoxyphenyl)ethenyl]benzonitrile (3d)

This compound was prepared by treating 2-(4-methoxybenzoyl)benzonitrile[8] with (methoxymethylene)triphenylphosphorane as described for the preparation of **3a**. Yield: 54%; mixture of stereoisomers (*E*/*Z* = ~6:4); pale-yellow oil; R_f = 0.45 (CH_2Cl_2–hexane, 2:1).

IR (KBr): 2226, 1634, 1607 cm^{-1}.

^1H NMR (500 MHz): δ = 3.79 and 3.80 (2 s, 4.8 H), 3.83 (s, 1.2 H), 6.41 (s, 0.4 H), 6.59 (s, 0.6 H), 6.81 (d, *J* = 8.7 Hz, 1.2 H), 6.85 (d, *J* = 8.7 Hz, 0.8 H), 7.04 (d, *J* = 8.7 Hz, 1.2 H), 7.26–7.37 (m, 2.8 H), 7.51 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 0.4 H), 7.54 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 0.6 H), 7.66 (d, *J* = 7.8 Hz, 0.4 H), 7.70 (dd, *J* = 7.8, 0.9 Hz, 0.6 H).

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.98; H, 5.70; N, 5.28. Found: C, 76.96; H, 5.99; N, 5.21.

2-(1-Naphthoyl)benzonitrile

This compound was prepared from 2-bromophenyl(1-naphthyl)methanone[9] and CuCN under the conditions reported by Friedman et al.[11] Yield: 40%; pale-yellow solid; mp 94–95 °C (hexane–CH_2Cl_2).

IR (KBr): 2230, 1651 cm^{-1}.

^1H NMR (500 MHz): δ = 7.50 (dd, *J* = 8.2, 7.3 Hz, 1 H), 7.57–7.69 (m, 6 H), 7.88 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.95 (dd, *J* = 7.8, 1.8 Hz, 1 H), 8.08 (d, *J* = 8.2 Hz, 1 H), 8.45 (dd, *J* = 7.8, 1.4 Hz, 1 H).

Anal. Calcd for $C_{18}H_{11}NO$: C, 84.03; H, 4.31; N, 5.44. Found: C, 84.01; H, 4.71; N, 5.28.

2-[1-(1-Naphthyl)ethenyl]benzonitrile (1e)

This compound was prepared by treating 2-(1-naphthoyl)benzonitrile with methylenetriphenylphosphorane under conditions for the preparation of **1a** reported by us.[1] Yield: 57%; yellow viscous oil; R_f = 0.52 (THF–hexane, 1:4).

IR (neat): 2224 cm^{-1}.

^1H NMR (500 MHz): δ = 5.84 (s, 1 H), 6.12 (s, 1 H), 7.18 (d, *J* = 7.8 Hz, 1 H), 7.34 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 1 H), 7.37–7.46 (m, 4 H), 7.49 (dd, *J* = 7.8, 7.3 Hz, 1 H), 7.74 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.80 (d, *J* = 8.7 Hz, 1 H), 7.87 (d, *J* = 8.2 Hz, 2 H).

Anal: Calcd for $C_{19}H_{13}N$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.58; H, 5.36; N, 5.20.

2-[2-Methoxy-1-(1-naphthyl)ethenyl]benzonitrile (3e)

This compound was prepared by treating 2-(1-naphthoyl)benzonitrile with (methoxymethylene)triphenylphosphorane as described for the preparation of **3a**. Yield: 72%; mixture of stereoisomers (~1:1); colorless viscous oil; R_f = 0.31 (THF–hexane, 1:4).

IR (neat): 2224, 1639 cm^{-1}.

^1H NMR (500 MHz): δ = 3.77 (s, 1.5 H), 3.89 (s, 1.5 H), 6.55 (s, 0.5 H), 7.04 (dd, *J* = 8.2, 0.9 Hz, 0.5 H), 7.07 (s, 0.5 H), 7.10 (dd, *J* = 7.8, 0.9 Hz, 0.5 H), 7.21–7.27 (m, 1 H), 7.32 (td, *J* = 7.8, 1.4 Hz, 0.5 H), 7.35–7.52 (m, 4.5 H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 0.5 H), 7.72 (*J* = 7.8, 0.9 Hz, 0.5 H), 7.81–7.89 (m, 3 H).

Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.07; H, 5.51; N, 4.72.

2-Benzoyl-4-methoxybenzonitrile[10]

This compound was prepared from 2-bromo-5-methoxybenzophenone[12] and CuCN under the conditions reported by Friedman et al.[11] Yield: 40%; white solid; mp 130–131 °C (hexane–THF). IR (KBr): 2226, 1665 cm^{-1}.

^1H NMR (270 MHz): δ = 3.89 (s, 3 H), 7.05–7.15 (m, 2 H), 7.50 (dd, *J* = 7.9, 7.3 Hz, 2 H), 7.65 (tt, *J* = 7.3, 1.3 Hz, 1 H), 7.74 (d, *J* = 9.2 Hz, 1 H), 7.83 (dd, *J* = 7.9, 1.3 Hz, 2 H).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 76.04; H, 4.65; N, 5.84.

4-Methoxy-2-(1-phenylethenyl)benzonitrile (1f)

This compound was prepared by treating 4-methoxy-2-benzoylbenzonitrile[10] with methylenetriphenylphosphorane under conditions for the preparation of **1a** reported by us.[1] Yield: 53%; yellow oil; R_f = 0.43 (THF–hexane, 1:4).

IR (neat): 2222 cm^{-1}.

^1H NMR (500 MHz): δ = 3.84 (s, 3 H), 5.48 (s, 1 H), 5.86 (s, 1 H), 6.84 (d, *J* = 2.3 Hz, 1 H), 6.92 (dd, *J* = 8.7, 2.3 Hz, 1 H), 7.27–7.35 (m, 5 H), 7.63 (d, *J* = 8.7 Hz, 1 H).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.54; H, 5.51; N, 5.75.

1-Amino-4-phenyl-3,4-dihydronaphthalene-2-carbonitrile (2a); Typical Procedure

To a stirred solution of MeCN (0.21 g, 5.2 mmol) in THF (10 mL) at –78 °C was added *n*-BuLi (1.6 M in hexane; 3.3 mL, 5.3 mmol). After 15 min, a solution of **1a** (0.54 g, 2.6 mmol) in THF (5 mL) was added and the temperature was gradually raised to 0 °C. The resulting mixture was quenched with sat. aq NH_4Cl (15 mL) and extracted with Et_2O (3 × 15 mL). The combined extracts were washed with brine (15 mL), dried (Na_2SO_4), and evaporated. The residue was subjected to column chromatography on silica gel to give **2a**. Yield: 0.50 g (77%); light-gray solid; mp 182–184 °C (hexane–CH_2Cl_2).

IR (KBr): 3456, 3354, 3238, 2174, 1661, 1649 cm^{-1}.

^1H NMR (500 MHz): δ = 2.74 (d, *J* = 7.8 Hz, 2 H), 4.13 (t, *J* = 7.8 Hz, 1 H), 4.65 (br s, 2 H), 6.96 (d, *J* = 7.3 Hz, 1 H), 7.15 (dd, *J* = 7.3, 1.4 Hz, 2 H), 7.25–7.36 (m, 5 H), 7.46 (dd, *J* = 7.8, 1.4 Hz, 1 H).

^{13}C NMR (125 MHz): δ = 30.60, 43.94, 74.69, 120.39, 122.01, 126.97, 127.17, 128.31, 128.62, 128.75, 129.08, 130.46, 140.76, 142.12, 151.61.

MS: *m*/*z* (%) = 246 (100, $[M^+]$).

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found; C, 82.81; H, 5.77; N, 11.34.

1-Amino-4-(3-methylphenyl)-3,4-dihydronaphthalene-2-carbonitrile (2b)

Pale-yellow solid; mp 108–110 °C (hexane–Et_2O).

IR (KBr): 3441, 3346, 3258, 2181, 1662, 1645, 1605 cm^{-1}.

^1H NMR (500 MHz): δ = 2.33 (s, 3 H), 2.71 (dd, *J* = 15.1, 7.3 Hz, 1 H), 2.73 (dd, *J* = 15.1, 8.7 Hz, 1 H), 4.09 (dd, *J* = 8.7, 7.3 Hz, 1 H), 4.65 (br s, 2 H), 6.92 (d, *J* = 7.8 Hz, 1 H), 6.94 (dd, *J* = 7.3, 1.4 Hz, 1 H), 6.97 (s, 1 H), 7.08 (d, *J* = 7.3 Hz, 1 H), 7.20 (dd, *J* = 7.8, 7.3 Hz, 1 H), 7.28–7.34 (m, 2 H), 7.45 (dd, *J* = 7.3, 1.8 Hz, 1 H).

MS: *m*/*z* (%) = 260 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found; C, 82.97; H, 6.18; N, 10.53.

1-Amino-4-(4-methylphenyl)-3,4-dihydronaphthalene-2-carbonitrile (2c)

Light-gray solid; mp 111–112 °C (hexane–CH_2Cl_2).

IR (KBr): 3460, 3364, 3260, 2181, 1633 cm^{-1}.

^1H NMR (500 MHz): δ = 2.34 (s, 3 H), 2.72 (d, *J* = 7.8 Hz, 2 H), 4.09 (t, *J* = 7.8 Hz, 1 H), 4.64 (br s, 2 H), 6.96 (dd, *J* = 7.3, 0.9 Hz, 1 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.28–7.34 (m, 2 H), 7.45 (dd, *J* = 7.8, 1.4 Hz, 1 H).

MS: *m*/*z* (%) = 260 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found; C, 83.02; H, 6.22; N, 10.65.

1-Amino-4-(4-methoxphenyl)-3,4-dihydronaphthalene-2-carbonitrile (2d)

Yellow solid; mp 173–176 °C (hexane–Et_2O–CH_2Cl_2).

IR (KBr): 3439, 3342, 3258, 2181, 1660, 1645, 1615 cm^{-1}.

^1H NMR (500 MHz): δ = 2.70 (d, *J* = 7.8 Hz, 2 H), 3.80 (s, 3 H), 4.08 (t, *J* = 7.8 Hz, 1 H), 4.64 (br s, 2 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 6.96 (dd, *J* = 7.3, 1.4 Hz, 1 H), 7.06 (d, *J* = 8.7 Hz, 2 H), 7.28–7.34 (m, 2 H), 7.45 (dd, *J* = 7.8, 1.4 Hz, 1 H).

MS: *m*/*z* (%) = 276 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found; C, 78.15; H, 6.05; N, 9.93.

1-Amino-4-(1-naphthyl)-3,4-dihydronaphthalene-2-carbonitrile (2e)

Pale-yellow solid; mp 181–182 °C (hexane–CH_2Cl_2).

IR (KBr): 3464, 3356, 3258, 2174, 1655, 1647, 1604 cm^{-1}.

^1H NMR (500 MHz): δ = 2.85 (dd, *J* = 15.3, 6.7 Hz, 1 H), 2.96 (dd, *J* = 15.3, 8.6 Hz, 1 H), 4.71 (br s, 2 H), 4.97 (dd, *J* = 8.6, 6.7 Hz, 1 H), 6.89 (d, *J* = 7.3 Hz, 1 H), 7.03 (d, *J* = 7.3 Hz, 1 H), 7.25–7.38 (m, 3 H), 7.50–7.53 (m, 3 H), 7.78 (d, *J* = 8.6 Hz, 1 H), 7.91–8.03 (m, 2 H).

^{13}C NMR (125 MHz): δ = 29.78, 39.89, 75.08, 120.37, 121.99, 123.43, 125.40, 125.60, 126.16 (2 C), 127.24, 127.72, 129.04, 129.24, 129.50, 130.64, 131.41, 134.19, 137.51, 140.57, 151.59

MS: *m*/*z* (%) = 296 (100, $[M^+]$).

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found; C, 85.05; H, 5.46; N, 9.38.

1-Amino-6-methoxy-4-phenyl-3,4-dihydronaphthalene-2-carbonitrile (2f)

Pale-yellow solid; mp 115–117 °C (hexane–CH_2Cl_2).

IR (KBr): 3449, 3337, 3256, 2170, 1647, 1609 cm^{-1}.

^1H NMR (500 MHz): δ = 2.70 (dd, *J* = 15.1, 7.8 Hz, 1 H), 2.72 (dd, 15.1, 7.3 Hz, 1 H), 3.73 (s, 3 H), 4.07 (dd, *J* = 7.8, 7.3 Hz, 1 H), 4.58 (br s, 2 H), 6.48 (dd, *J* = 2.7, 0.9 Hz, 1 H), 6.83 (dd, *J* = 8.7, 2.7 Hz, 1 H), 7.14 (dd, *J* = 7.3, 1.4 Hz, 2 H), 7.26 (tt, *J* = 7.3, 1.4 Hz, 1 H), 7.31 (t, *J* = 7.3 Hz, 2 H), 7.40 (d, *J* = 8.7 Hz, 1 H).

MS: *m*/*z* (%) = 276 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found; C, 78.02; H, 5.86; N, 9.91.

1-Amino-4-phenylnaphthalene-2-carbonitrile (4a)

Pale-yellow solid; mp 95–97 °C (hexane–Et_2O).

IR (KBr): 3474, 3377, 3254, 2206, 1634 cm^{-1}.

^1H NMR (500 MHz): δ = 5.13 (br s, 2 H), 7.30 (s, 1 H), 7.40–7.44 (m, 3 H), 7.46–7.49 (m, 2 H), 7.53–7.59 (m, 2 H), 7.86–7.89 (m, 2 H).

MS: *m*/*z* (%) = 244 (100, $[M^+]$).

Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found; C, 83.54; H, 4.96; N, 11.25.

1-Amino-4-(3-methylphenyl)naphthalene-2-carbonitrile (4b)

Pale-yellow solid; mp 157–158 °C (hexane–CH_2Cl_2).

IR (KBr): 3474, 3377, 3254, 2206, 1641 cm^{-1}.

^1H NMR (500 MHz): δ = 2.43 (s, 3 H), 5.11 (br s, 2 H), 7.20–7.24 (m, 4 H), 7.28 (s, 1 H), 7.53–7.58 (m, 2 H), 7.86–7.90 (m, 2 H).

^{13}C NMR (125 MHz): δ = 21.46, 89.43, 118.58, 121.32, 122.08, 126.15, 126.50, 127.18, 127.27, 128.11, 128.26, 128.85, 130.78, 131.38, 134.29, 138.09, 139.25, 147.49.

MS: *m*/*z* (%) = 258 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found; C, 83.64; H, 5.49; N, 10.60.

1-Amino-4-(4-methylphenyl)naphthalene-2-carbonitrile (4c)

Pale-yellow solid; mp 130–132 °C (hexane–Et_2O).

IR (KBr): 3443, 3319, 3233, 2208, 1651 cm^{-1}.

^1H NMR (500 MHz): δ = 2.44 (s, 3 H), 5.10 (br s, 2 H), 7.277 (s, 1 H), 7.284 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.52–7.58 (m, 2 H), 7.87–7.90 (m, 2 H).

MS: *m*/*z* (%) = 258 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found; C, 83.39; H, 5.60; N, 10.70.

1-Amino-4-(4-methoxyphenyl)naphthalene-2-carbonitrile (4d)
Yellow solid; mp 195–198 °C (hexane–Et_2O–CH_2Cl_2).

IR (KBr): 3466, 3379, 3246, 2201, 1636, 1604 cm^{-1}.

^1H NMR (500 MHz): δ = 3.89 (s, 3 H), 5.10 (br s, 2 H), 7.01 (d, *J* = 8.7 Hz, 2 H), 7.27 (s, 1 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 7.53–7.57 (m, 2 H), 7.86–7.89 (m, 2 H).

MS: *m*/*z* (%) = 274 (100, $[M^+]$).

Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found; C, 78.76; H, 5.03; N, 10.11.

1-Amino-4-(1-naphthyl)naphthalene-2-carbonitrile (4e)
Pale-yellow solid; mp 165–167 °C (dec.) (hexane–CH_2Cl_2).

IR (KBr): 3476, 3375, 3260, 2210, 1645 cm^{-1}.

^1H NMR (500 MHz): δ = 5.20 (br s, 2 H), 7.29–7.59 (m, 9 H), 7.91–7.96 (m, 3 H).

MS: *m*/*z* (%) = 294 (100, $[M^+]$).

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52. Found; C, 85.67; H, 4.67; N, 9.46.

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