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Investigation of the reaction of 2-bromo-1-naphthol with arylacetonitriles and LiTMP: facile synthesis of 3-arylmethyl-1-hydroxynaphthalene-2-carbonitriles

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2-Bromo-1-naphthol reacts with arylacetonitriles and 3-thienylacetonitrile in the presence of LiTMP to give the rearranged 3-benzyl-1-hydroxynaphthalene-2-carbonitriles and 11-amino-5*H*-anthra[2,3-*b*]thiophen-10-one, respectively. The reactions proceed *via* a tandem addition–rearrangement pathway involving a non-synchronous [2 + 2] cycloaddition of an *N*-lithiated ketenimine and 2,3-didehydronaphthalene 1-oxide. An explanation of the orientation to and reactivity of the aforementioned aryne is presented in terms of chelation between the OLi group and the attacking nitrile nucleophile. Support for the intermediacy of 2,3-didehydronaphthalene 1-oxide was accomplished by obtaining 3-amino-1-naphthols from the reaction of 2-bromonaphthol and the appropriate lithium amide. Alternate non-aryne mechanisms were addressed, but were rejected based on experimental results.

Introduction

Potassium and sodium amides in liquid ammonia generate didehydrophenoxides from halophenols reluctantly.[1] However, we[2] have shown that lithium 2,2,6,6-tetramethylpiperidide (LiTMP) can readily convert 2-bromophenol to 2,3-didehydrophenoxide. This aryne can be trapped by lithiated arylacetonitriles to give 2-arylmethyl-6-hydroxybenzenecarbonitriles, after proton quench. The benzonitrile products are most likely formed *via* a tandem addition–rearrangement pathway (*vide infra*).[3] The key step in the process involves a [2 + 2] non-synchronous cycloaddition in which the C1 and C2 carbons of a nitrile derived *N*-lithiated ketenimine [$ArC_2H{=}C_1{=}N{-}Li$] add regioselectively to the respective C2 and C3 positions of 2,3-didehydrophenoxide to form a *N*-lithiated benzocyclobutanimine intermediate. The observed regioselectivity indicates that the bonding in the transition state between the C3 of the aryne and C2 of the ketenimine is further along in its formation than that between C2 of the aryne and C1 of the ketenimine. In such a transition state, a partial negative charge is developed at C2 of the aryne, whereas in the transition state for the opposition mode of cycloaddition the partial negative charge is developed at C3 of the aryne. Accordingly, the partial negative charge at C2 in the former transition state would be stabilized to a greater extent than that at C3 in the latter due to its closer proximity to the electron-withdrawing OLi group at C1, and this favors the observed products.[4] These arguments are supported by density functional theory (DFT) calculations.[5,6]

Our orientation–reactivity studies of the OLi group have been extended to include the 2,3-didehydronaphthalene 1-oxide intermediate. Previously, it was shown that 1,4-dimethoxy-2,3-didehydronaphthalene reacts with arylacetonitrile anions to give only simple addition products *via* the usual aryne pathway.[7] On the other hand, 3,6-dimethylbenzyne reacts with arylacetonitrile anions to give rearranged nitriles exclusively. Semi-empirical AM1 calculations showed that 2,3-didehydronaphthalene was less stable by 0.72 kcal mol^{-1} than benzyne itself due to the difficulty of 2,3-didehydronaphthalene to accommodate a shorter dehydro-bond at C2–C3.[8] Because of the increase in energy, nitrile anion addition to 1,4-dimethoxy-2,3-didehydronaphthalene is, therefore, expected to proceed through an earlier transition state than that for nitrile anion addition to 3,6-dimethylbenzyne. In such a transition state, the bonding between the nitrile anion and the 2,3-didehydronaphthalene would be weaker than that between the nitrile and 3,6-dimethylbenzyne. Therefore the former transition state would be expected to collapse to give the usual aryne–nitrile anion adduct[9] rather than undergo a [2 + 2] process.

The OLi group has been shown to promote the key [2 + 2] cycloaddition pathway in reactions involving 2,3-didehydrophenoxide. To see if the OLi group could also influence reactions involving 2,3-didehydronaphthlene 1-oxide in a similar way, a study of the reaction of 2-bromo-1-naphthol with certain arylacetonitriles in the presence of lithium amide bases was initiated. If this were to be the case, then the 2 + 2 cycloaddition–aryne reaction would provide a ready access to novel 3-arylmethyl-1-hydroxynaphthlene-2-carbonitriles using readily available starting materials.

Results and discussion

2-Bromo-1-naphthol **1** was chosen as the 2,3-didehydronaphthalene 1-oxide precursor, due to its ease of preparation.[10] Compound **1** reacted with a variety of arylacetonitriles (**2a**–**e**) and 3-thienylacetonitrile (**2f**) in presence of LiTMP in THF at room temperature to give the corresponding 3-arylmethyl-1-hydroxynaphthalene-2-carbonitriles **3a**–**e** (eqn. (1)) in yields ranging from 44 to 85%. However, the reaction of **1** with 3-thienylacetonitrile **2f** afforded 11-amino-5*H*-anthra[2,3-*b*]-thiophen-10-one **4** in 44% yield (see eqn. (2)).

The reactions were carried out by first adding LiTMP to a solution of **1** followed by the addition of nitriles **2a**–**f**. The order of the addition is the reverse of that generally used in aryne reactions. GC monitoring of the reaction mixtures indicated that the reaction did not commence until the addition of **2a**–**f**. During the addition of **2a**–**f**, the solution immediately developed a red color, which gradually deepened over the course of the reaction. We have found throughout our extensive studies of aryne reactions over the past forty years that, without exception, such color changes are indicative of products formed from a base-mediated aryne reaction.[11] The red color in these reaction solutions is thought to be due to the formation of

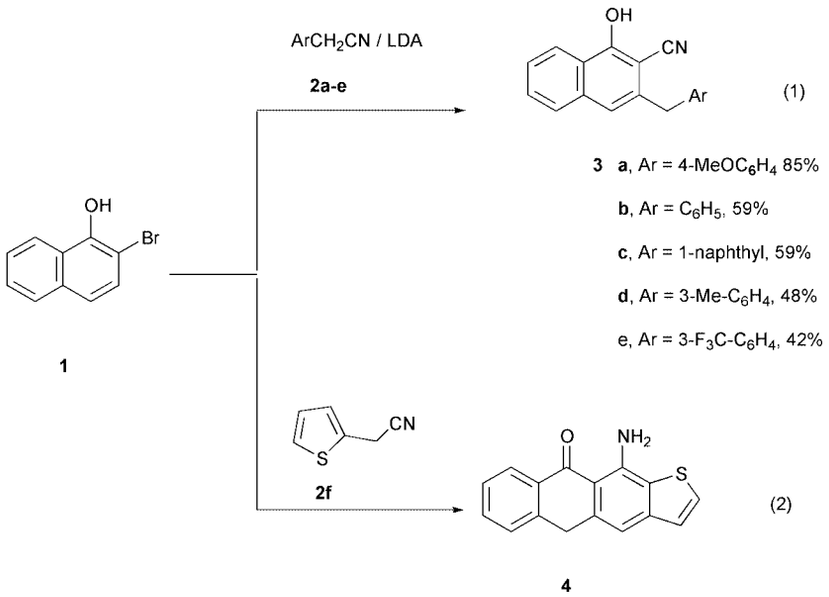


Table 1 Physical properties of 3-arylmethyl-1-hydroxynaphthalene-2-carbonitriles **3a**–**e**, 11-amino-5*H*-anthra[2,3-*b*]thiophen-10-one **4**, and amines **15** and **16**

Compound (Formula)	Yield (%)	Mp/°C[a]	Found (%) (Required) C	H	N
3a	85	Viscous liquid	78.9	5.2	4.8
$C_{19}H_{15}NO_2$			(78.4)	(5.3)	(4.7)
3b	59	Viscous liquid	75.4	5.3	5.5
$C_{18}H_{13}NO$			(75.3)	(5.5)	(5.4)
3c	59	215–216	85.4	4.9	4.5
$C_{22}H_{15}NO$			(85.3)	(4.8)	(4.4)
3d	48	Viscous liquid	83.4	5.4	5.3
$C_{19}H_{15}NO$			(83.5)	(5.5)	(5.1)
3e	42	138–140	69.4	3.8	4.3
$C_{19}H_{12}NOF_3$			(69.7)	(3.7)	(4.2)
4	57	160 (decomp.)	72.5	4.3	5.2[b]
$C_{14}H_{13}NOS$			(72.4)	(4.2)	(5.3)
15	45	Viscous liquid	79.8	9.4	5.1
$C_{18}H_{25}NO$			(79.7)	(9.3)	(5.2)
16	15	Viscous liquid	79.4	7.6	6.3
$C_{15}H_{17}NO$			(79.3)	(7.5)	(6.2)

[a] All solid products were recrystallized from 80% hexane–20% ethyl acetate. [b] S 12.2% (12.1)

resonance delocalized *α*-lithiated derivatives of **3a**–**f**. The fact that nitriles **6a**–**f** must be present for aryne generation to occur is consistent with previous studies involving the generation of other arynes possessing charged substituents.[11,2] It has been suggested[12] that nitriles accelerate the rate of aryne generation by increasing the strength of the base involved in the rate determining hydrogen abstraction step of the aryne reaction.[9]

When the usual procedure was used, the yields of **3a**–**e** and **4** were markedly lower due to significant amounts of dimeric and polymeric side products. The use of the less expensive LDA as an aryne generating base was explored as an alternate to the considerably more expensive LiTMP. However, nitriles **3a**–**e** were formed in lower yields in these reactions due to the formation of high molecular weight tars and the reduction of **1** to 1-naphthol by LDA.[13]

The identity of the structures of **3a**–**e** and **4** was determined by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy. The spectral data are presented in the Experimental section and the melting points and elemental analyses are shown in Table 1. Single-crystal X-ray diffractometry further aided in the identification of the structure of **4**. An ORTEP[14] drawing of **4** is shown in Fig. 1. NMR spectroscopy confirmed that **4** exists exclusively as

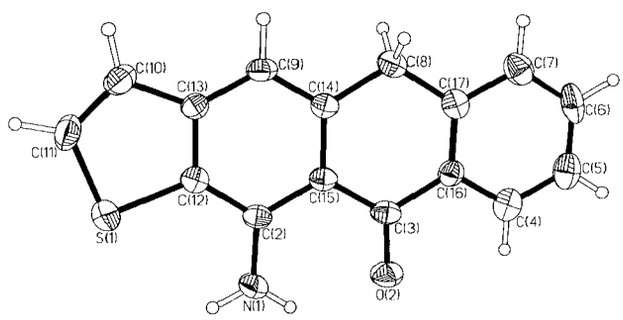


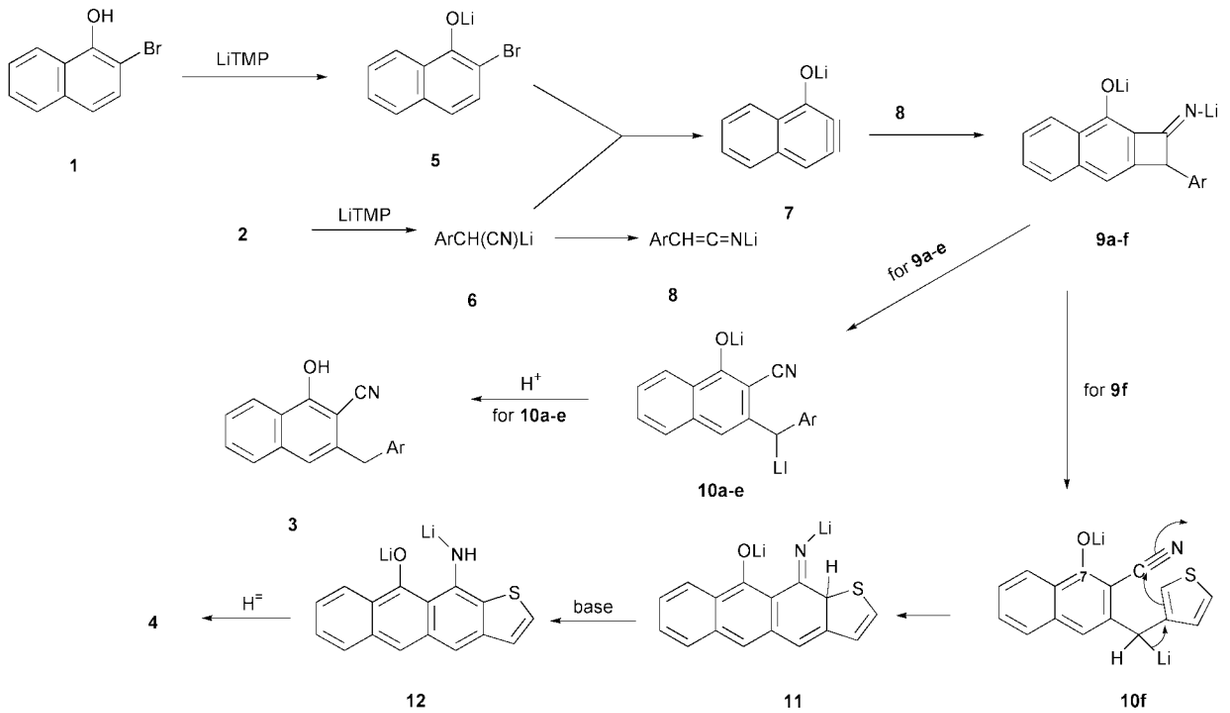
Fig. 1 ORTEP diagram of compound **4**.

the 11-amino-10-keto tautomer, which is presumably stabilized by intramolecular H-bonding between the 11-amino and 10-carbonyl group.

The products **3a**–**e** and **4** are most likely formed *via* a tandem addition–rearrangement pathway[3] as shown in Scheme 1. In this reaction sequence, reactant **1** reacts with LiTMP to give the lithiated 2-bromonaphthalene 1-oxide **5**. The nitriles **2a**–**f** are then added and react with LiTMP to give *N*-lithiated ketenimines **8a**–**f** *via* the lithiated arylacetonitriles **6a**–**f**. In the presence of LiTMP and **8a**–**f**, **5** is converted to 2,3-didehydronaphthalene 1-oxide **7**. The ketenimines **8a**–**f** then add regioselectively to **7** to produce lithiated benzocyclobutanimines **9a**–**f**, which in turn fragment to *α*-lithiated benzylbenzonitriles **10a**–**e** and thienylmethylbenzonitrile **10f**. With the exception of **10f**, the naphthalene-2-carbonitriles **10a**–**e** are converted to **3a**–**e** during acidic aqueous work up. In the exceptional case, the thienyl derivative **10f** cyclizes by a Stork type mechanism to the tetracyclic compound **11**, which can be converted to **4** *via* the dilithiated intermediate **12**. The lithiated derivative of 3-thienylacetonitrile **2h** has been found to react with 2,3-didehydrobenzyl oxide in a similar fashion to give 9-aminonaphtho[2,3-*b*]-thiophen-8-ylmethanol.[15]

The fact that **7**, unlike 1,4-dimethyl-2,3-didehydronaphthalene, proceeds *via* a [2 + 2] cycloaddition pathway rather than the usual aryne addition pathway is most likely the result of a favorable interaction between the lithium of the OLi group in **7** and the nitrogen atom of the cyano group of the attacking nucleophile **8a**–**f**. Such an interaction, shown in Fig. 2, presumably overcomes the inherent instability of the 2,3-didehydronaphthalene ring by bringing the bonding *loci* sufficiently close in the transition state for the 2 + 2 cycloaddition step.

Since benzynes are reluctantly formed from the reaction of alkali metals and halophenols, it could be argued that benzyne



Scheme 1

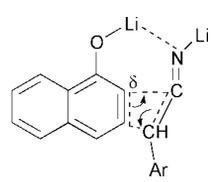
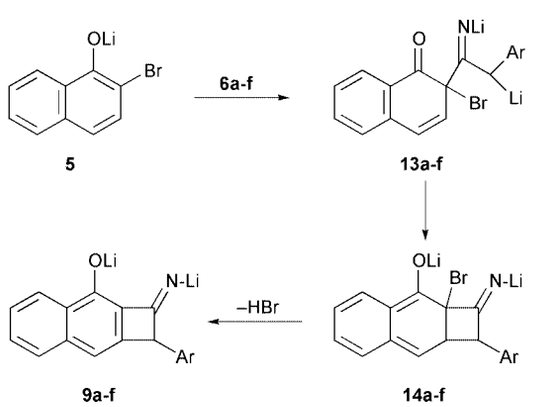


Fig. 2 Possible transition state involving cycloaddition of lithiated ketenimine **8** to aryne **7**.

formation from 2-halo-1-naphthol should be even more difficult given the increased C2–C3 bond length of the naphthalene system. Thus, it was prudent that other non-aryne pathways for the formation of nitriles **3a**–**f** be addressed. A possible alternate non-benzyne mechanism, shown in Scheme 2,

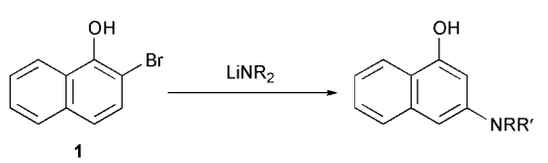


Scheme 2

suggests that the lithiated benzocyclobutanimines **9** could be formed by an initial attack of the cyano group of the α-lithiated arylacetonitrile **6** on C-2 of the naphthalene-1 oxide **5** by the cyano group of the (enolate type mechanism) affording adduct **13**. Cyclization of **13** (Michael type addition) and loss of HBr from the resulting adduct **14** would then give **9**.

To test the validity of this alternative pathway, 2-bromonaphthalene 1-oxide **5** was treated with α-lithiophenylacetonitrile **6b** under conditions similar to those used in the LiTMP-mediated reactions of **1**, but with the absence of LiTMP. GC-MS analysis of the reaction mixture, however, did not detect benzonitrile **3a**, but rather revealed the presence of starting materials **1** (62%) and **2a** (98%) as well as 1-naphthol (38%). In fact, **5** did not react with phenylacetonitrile **2a**, whose cyano group is even more electrophilic than that of **6a**. Thus, this alternate mechanism is unlikely. Haloarenes occasionally react with certain nucleophiles under aryne-forming conditions by a $S_{RN}1$[16] pathway. However, this mechanism can also be discarded since it would predict, incorrectly, a direct displacement of the 2-bromo group by the α-carbon of **6**.

Although these negative results add credence to the intermediacy of **7** in these reactions, we were able to obtain additional support by treating **1** with lithium di-*n*-butylamide and lithium piperidide in the absence of arylnitrile for 2 days. As shown in eqn. (3), these amides reacted with **1** to give 3-di-*n*-



(3)

butylamino-1-naphthol **15** and 3-(piperidin-1-yl)-1-naphthol **16** in 45% and 15%, respectively. The fact that *cine* substituted products (*i.e.* substitution at the carbon adjacent to the debromo carbon) were obtained in these reactions argues strongly for the intermediacy of **7**.[4] Under these conditions, LiTMP did not react with **1** and LDA reduced **1** to 1-naphthol (38% yield).

In conclusion, a facile, one-step preparation of 3-benzyl-1-hydroxynaphthalene-2-carbonitriles **3a**–**e**, 11-amino-5*H*-anthra[2,3-*b*]thiophen-10-one **4** and 3-amino-1-naphthols **15** and **16** *via* 2,3-didehydronaphthalene 1-oxide **7** has been described. Preparations of these 1,2,3-trisubstitued naphthalenes by conventional non-arynic methodology would be difficult.

Experimental

General data

Melting points were taken on a Mel-Temp II capillary

apparatus and are uncorrected with respect to stem correction. IR spectra were recorded on a Nicolet Magna-IR™ 550 FTIR spectrometer, and the ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCE DRX-400 multi-nuclear NMR spectrometer; chemical shifts were referenced to TMS as internal standard. Elemental analyses were obtained from SMU Analytical Laboratories. 1-Naphthol, arylacetonitriles, 2,2,6,6-dimethylpiperidine, diisopropylamine, and *n*-BuLi were purchased from Aldrich Chemical Company. Diisopropylamine and 2,2,6,6-dimethylpiperidine were refluxed over and distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from Na–benzophenone immediately prior to use. The glassware was heated at 125 °C in an oven overnight prior to use. All benzyne reactions were done under an atmosphere of dry O_2-free N_2 *via* balloon.

General procedure for the reaction of 1 with arylacetonitriles

In a flame-dried flask flushed with nitrogen, fresh LiTMP or LDA (10 mmol) was prepared by adding *n*-BuLi (10 mmol, 2.5 M in hexane) to a solution of 2,2,6,6-tetramethylpiperidine (1.8 g, 10 mmol) or diisopropylamine (1.0 g, 10 mmol) in THF (50 mL) at rt. After stirring for 10 min, 2-bromo-1-naphthol (0.45 g, 2 mmol) was added slowly and the stirring continued for 10 min. The appropriate nitrile (2 mmol) was then added, and the resulting solution immediately developed a dark red color. After stirring overnight, the reaction mixture was quenched with saturated NH_4Cl solution (30 mL), and then extracted with methylene chloride. The combined extracts were washed with dilute HCl, dried (Na_2SO_4), and concentrated (rotary evaporator) to give a crude oily material. Chromatography of this material on silica gel (hexane–ethyl acetate, 9 : 1) gave the pure product **3a**–**e**, and **4**. The yields, mp and elemental analyses for these compounds are presented in Table 1 and the spectral data are given below.

1-Hydroxy-3-(4-methoxyphenylmethyl)naphthalene-2-carbonitrile 3a. ν_{max}/cm^{-1} 2220 (aromatic CN), 3423 (phenolic OH); δ_H(400 MHz; $CDCl_3$) 3.81 (s, 3 H), 4.18 (s, 2 H), 6.89 (dd J = 6.4 Hz, 1.6 Hz, 3 H), 7.23 (d, J = 8.4 Hz, 2 H), 7.53 (t, J = 8.2 Hz, 1 H), 7.62 (t, J = 8.2 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 8.24 (d, J = 8.4 Hz, 1 H).

1-Hydroxy-3-(phenylmethyl)naphthalene-2-carbonitrile 3b. ν_{max}/cm^{-1} 2216 (aromatic CN), 3389 (phenolic OH); δ_H(400 MHz; $CDCl_3$) 4.25 (s 2 H), 7.22 (s, 1 H), 7.33–7.28 (m, 5 H), 7.54 (d, J = 8.2 Hz, 1 H), 7.62 (t, J = 8.2 Hz, 1 H), 7.74 (d, J = 8.2 Hz), 8.25 (d, J = 8.4 Hz, 1 H).

1-Hydroxy-3-(1-naphthylmethyl)naphthalene-2-carbonitrile 3c. ν_{max}/cm^{-1} 2220 (aromatic CN), 3390 (phenolic OH); δ_H(400 MHz; $CDCl_3$) 4.71 (s, 1 H), 6.90 (s, 1 H), 7.36 (d, J = 8.2 Hz, 1H), 7.54–7.48 (m, 5 H), 7.61 (d, J = 8 Hz, 1 H), 7.91–7.95 (m, 3 H), 8.25 (d, J = 8.2 Hz, 1 H); δ_C(400 MHz; $CDCl_3$) 37.7, 95.8, 117.5, 120.2, 123.3, 123.8, 124.4, 125.9, 125.9, 126.0, 126.1, 126.5, 127.9, 129.0, 129.4, 132.4, 134.2, 135.1, 136.2, 138.1.

1-Hydroxy-3-(3-methylphenylmethyl)naphthalene-2-carbonitrile 3d. ν_{max}/cm^{-1} 2225 (aromatic CN), 3410 (phenolic OH); δ_H(400 MHz; $CDCl_3$) 2.35 (s, 3 H), 4.21(s, 2 H), 7.09–7.10 (m, 2 H), 7.23 (d, J = 7.6 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H), 7.62 (t, J = 8 Hz, 1 H), 7.74 (d, J = 8 Hz, 1 H), 8.26 (d, J = 8.4 Hz, 1 H); δ_C(400 MHz; $CDCl_3$) 21.8, 40.6, 94.5, 116.79, 116.8, 121.3, 122.7, 123.1, 126.5, 127.9, 127.8, 128.0 130.1, 130.3, 136.5, 138.1, 138.7, 138.9, 158.6.

1-Hydroxy-3-(3-trifluromethylphenylmethyl)naphthalene-2-carbonitrile 3e. ν_{max}/cm^{-1} 2215 (aromatic CN), 3415 (phenolic OH); δ_H(400 MHz; $CDCl_3$) 4.25 (s, 2 H), 7.13 (s, 1 H), 7.41–7.53 (m, 5H), 7.60 (t, J = 8 Hz, 1 H), 7.70 (d, J = 8 Hz, 1 H), 8.28 (d, J = 8.4 Hz, 1 H); δ_C(400 MHz; $CDCl_3$) 40.7, 94.0, 117.2, 121.0, 123.5, 124.0, 124.1, 126.2, 126.5, 126.7, 127.9, 129.5, 130.4, 133.0, 136.5, 136.9, 140.1, 160.1.

11-Amino-5*H*-anthra[2,3-*b*]thiophen-10-one 4. δ_H(400 MHz; $CDCl_3$) 4.43 (s, 2 H), 7.21 (br, 2 H), 7.29 (s, 1 H), 7.31 (d, J = 6 Hz, 1 H), 7.45 (t, J = 8 Hz, 1 H), 7.56 (d, J = 8.8 Hz, 1 H), 7.61 (d, J = 5.2 Hz, 1 H), 8.33 (d, J = 7.6 Hz, 1 H); δ_C(400 MHz; $CDCl_3$) 33.8, 110.4, 111.8, 124.7, 125.2, 127.0, 127.3, 128.1, 129.6, 132.5, 133.5, 138.2, 140.2, 143.9, 147.4, 187.6.

General procedure for the reaction of 1 with lithium amides

In a flame-dried flask flushed with nitrogen, the lithium amide (10 mmol) was prepared by adding *n*-BuLi (10 mmol, 2.5 M in hexane) to a solution of the appropriate amine (10 mmol) in THF (50 mL) at rt. The appropriate aryne precursor (2 mmol) was then added and the resulting mixture stirred for 48 h. At this point the reactions were worked up in the same manner described above for the reaction involving arylacetonitriles. The spectral properties of **15** and **16** are given below.

3-Di-*n*-butylamino-1-naphthol 15. δ_H(400 MHz; $CDCl_3$) 0.96 (t, J = 7.6 Hz, 6 H), 1.33–1.39 (m, 4 H), 1.63–1.68 (m, 4 H), 3.45 (t, J = 8.0 Hz, 4 H), 5.8 (s, 1 H), 7.24 (s, 1 H), 7.57–7.59 (m, 1 H), 7.65–7.67 (m, 1 H), 7.93–7.96 (m, 1 H), 8.01 (d, J = 1.2 Hz, 1 H), 8.23 (d, J = 1.2 Hz, 1 H); δ_C(400 MHz; $CDCl_3$) 14.2, 20.6, 30.0, 53.2, 106.4, 125.6, 126.8, 132.2, 133.3, 134.1, 134.2, 151.6, 183.1, 183.3.

3-(Piperidin-1-yl)-1-naphthol 16. δ_H(400 MHz; $CDCl_3$) 0.96 (t, J = 7.6 Hz, 6 H), 1.33–1.39 (m, 4 H), 1.63–1.68 (m, 4 H), 3.45 (t, J = 8.0 Hz, 4 H), 5.8 (s, 1 H), 7.24 (s, 1 H), 7.57–7.59 (m, 1 H), 7.65–7.67 (m, 1 H), 7.93–7.96 (m, 1 H), 8.01 (d, J = 1.2 Hz, 1 H), 8.23 (d, J = 1.2 Hz, 1 H).

X-Ray analysis of 11-amino-5*H*-anthra[2,3-*b*]thiophen-10-one 4

X-ray analysis of crystals of **4** ($C_{16}H_{11}NOS$, M 265.32) was carried out on a Brucker AXS P4 diffractometer at 228 K. The crystal was orthorhombic, space group $PZ_1Z_1Z_1$ with unit cell a = 7.131(1), b = 12.598(2), c = 13.699(2) Å, β = 90.00°, V = 1230.9(3) Å, Z = 4, D_x = 1.432 g cm^{-3}, μ = 0.252 mm^{-1}. Mo-Kα radiation (λ = 0.71073 Å), 903 reflections measured, 863 unique, 2409 with $F \geq 2\sigma(F)$ gave R_1 = 0.032 in a full matrix least squares refinement[17] with 173 parameters. CCDC reference number 207/461. See http://www.rsc.org/suppdata/p1/b0/b003935g/ for crystallographic files in .cif format.

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