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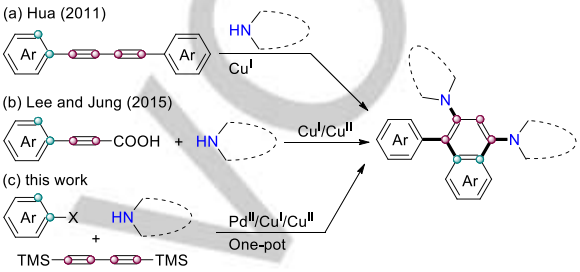
Cooperative Palladium and Copper Catalysis: One-pot Synthesis of Diamino-Substituted Naphthalenes from Aryl Halides, 1,4-Bis(trimethylsilyl)butadiyne and Amines

Yuan Li[a], Shaozhong Qiu[a], Ling Fan[a], and Guodong Yin*[a]

A one-pot method for the preparation of diamino-substituted naphthalene derivatives from easily available starting materials aryl halides, 1,4-bis(trimethylsilyl)butadiyne and amines is developed. Two C–N bonds, three C–C bonds and one aromatic ring are formed in this domino process. This transformation is achieved by the cooperative catalysis of $Pd(OAc)_2$, Cu(Xantphos)I and $Cu(OTf)_2$. A possible double Sonogashira coupling/hydroamination/benzannulation reaction route is proposed.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic conjugated molecules, which are widely used for luminescent materials and molecular devices because of their fascinating optical and electronic properties.[1] Development of a new synthetic route to aromatic cores is crucial for obtaining functionalized PAHs.[2] In recent years, much attention has been paid to alkyne benzannulation as an effective approach to construct aromatic cores.[3] 1,3-Diynes, as key building blocks in organic synthesis,[4] can be attacked by nucleophiles to form a variety of heterocycles,[5] including isoxazoles,[6] furans,[7] pyrroles,[8] thiophenes,[9] pyridines,[10]pyrazoles,[11] pyrimidines,[12] siloles,[13] and germoles.[14] However, few examples have been reported for construction of a non-heteroaromatic ring system using the four unsaturated carbon atoms of a 1,3-diyne.[15] Hua was first to report the formation of diamino-substituted naphthalene derivatives from diaryl 1,3-diynes and secondary amines (Scheme 1a).[16] The reaction is limited to cyclic amines, and excess amine is required because of its dual role of reactant and solvent. Lee and co-workers found that diamino-substituted naphthalenes could be prepared by the copper-catalyzed reaction of aryl alkynyl carboxylic acids and amines (Scheme 1b).[17] These reported methods require the preparation of diaryl 1,3-diynes or aryl alkynyl carboxylic acids, respectively, as the substrates. Accordingly, a new synthetic route to functionalized diamino-substituted naphthalenes from easily available starting materials is still desired. Recently, we found that 1,4-bis(trimethylsilyl)butadiyne could be used as a linear linker to 1,4-diaryl-1,3-diynes catalyzed by the combination of $Pd(OAc)_2$ and Cu(Xantphos)I.[18] In a continuation of our efforts to construct PAHs,[19] herein we report a one-pot, five-component route to diamino-substituted naphthalenes from aryl halides, 1,4-bis(trimethylsilyl)butadiyne and amines (Scheme 1c).



Scheme 1. Routes to functionalized diamino-substituted naphthalene derivatives.

Results and Discussion

Based on our previous results,[18a] when 4-bromobenzonitrile (**1a**) was reacted with 1,4-bis(trimethylsilyl)buta-1,3-diyne (**2**) using diethylamine (**3a**) as the base in the presence of $Pd(OAc)_2$ and Cu(Xantphos)I, an unexpected polycyclic aromatic hydrocarbon, 8-(4-cyanophenyl)-5,7-bis(diethylamino)-2-naphthonitrile (**4a**), was obtained in 27% yield (Table 1, entry 1). It can be seen that the four unsaturated carbon atoms of **2** participated in the formation of the benzene ring fragment. An electron-withdrawing group (-CN) and electron-donating group ($-NEt_2$) were introduced into this conjugated molecule. Molecules bearing these two classes of groups are widely used for fluorescent materials.[20] A literature survey showed that copper salts can facilitate both hydroamination and this cyclization process.[16,17,21] After screening several commonly used copper salts including CuCl, CuBr, CuI and $Cu(OTf)_2$, a 59% NMR yield of **4a** was obtained when $Cu(OTf)_2$ was used (entries 2–5). If the amount of Cu(Xantphos)I and $Cu(OTf)_2$ was increased, the yield reached 72% (entries 6–8). Increasing or decreasing the amount of **3a** was not conducive to this transformation (entries 9, 10).

With the optimized reaction conditions in hand (Table 1, entry 8), the scope of aryl halides and amines was further investigated (Table 2). Substrates bearing electron-withdrawing groups (COMe, COOMe, COOEt, SO_2Me, NO_2, CF_3) on the *para*-position of the phenyl ring gave the corresponding diamino-substituted naphthalenes **4b–4g** in 40–63% yields. The structure of **4e** was confirmed by X-ray single crystal diffraction (Table 2, CCDC 1949108). However, only a trace amount of product **4h** was observed when using 1-bromo-4-methoxybenzene as the substrate, delivering the double Sonogashira coupling product 1,4-bis(4-methoxyphenyl)buta-1,3-diyne as the main product. The possible reason is that the 1,3-diyne intermediate bearing electron-donating group on the phenyl ring is unfavorable for the nucleophilic addition of diethylamine to carbon-carbon triple

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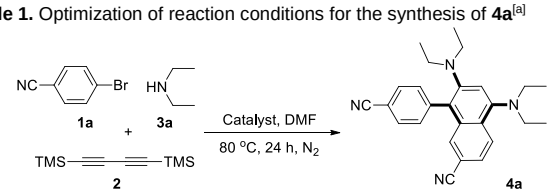
bond.[21] 3-Bromobenzonitrile selectively gave **4i** in 56% yield, whose structure was also confirmed by X-ray single crystal diffraction (Table 2, CCDC 1949109). 5-Bromo-1,2,3-trifluorobenzene and 3-bromoquinoline were also suitable for this reaction, giving **4j** and **4k** in moderate yields. When dipropylamine (**3b**), dibutylamine (**3c**), piperidine (**3d**) and morpholine (**3e**) were examined, **4l–4p** were isolated in 36–58% yields. Notably, for cyclic amines **3c** and **3d**, the corresponding aryl iodides were used as the substrates in a two-step one-pot procedure.

Table 1. Optimization of reaction conditions for the synthesis of **4a**[a]



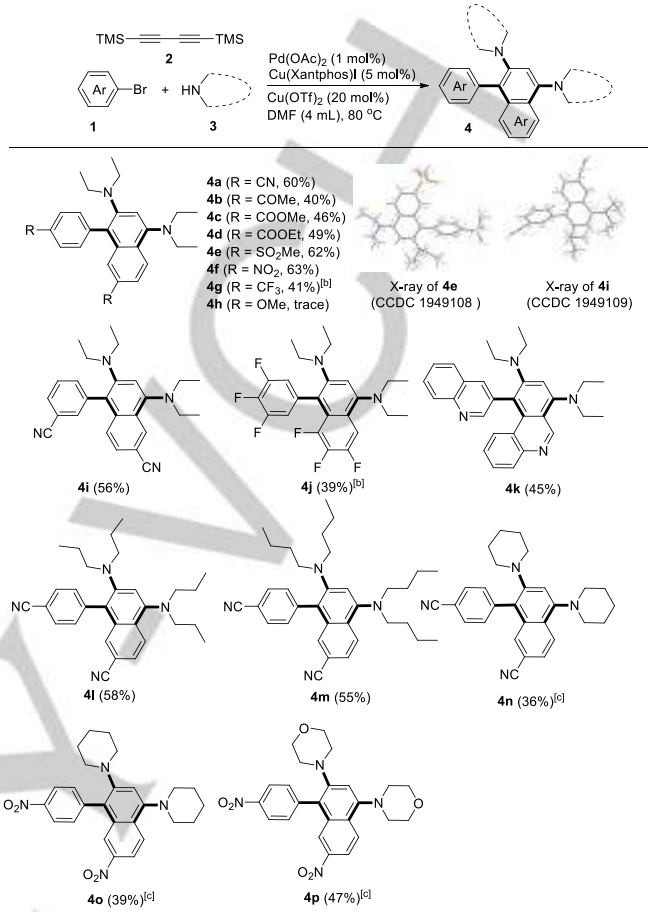
Entry	$Pd(OAc)_2$ (mol%)	Cu(Xantphos)I (mol%)	[Cu] (mol%)	Yield[b] (%)
1	1	1	none	27[c]
2	1	1	CuCl (5)	37
3	1	1	CuBr (5)	45
4	1	1	CuI (5)	53
5	1	1	$Cu(OTf)_2$ (5)	59
6	1	1	$Cu(OTf)_2$ (10)	66
7	1	1	$Cu(OTf)_2$ (20)	69
8	1	5	$Cu(OTf)_2$ (20)	72/60[c]
9	1	5	$Cu(OTf)_2$ (20)	56[d]
10	1	5	$Cu(OTf)_2$ (20)	49[e]

[a] The reactions were carried out using **1a** (1.0 mmol), **2** (0.8 mmol) and **3a** (4.0 mmol) in DMF (4.0 mL) at 80 °C.
[b] NMR yield using 1,3,5-trimethoxybenzene as the internal standard.
[c] Isolated yield.
[d] 6.0 mmol of **3a** was used.
[e] 2.0 mmol of **3a** was used.

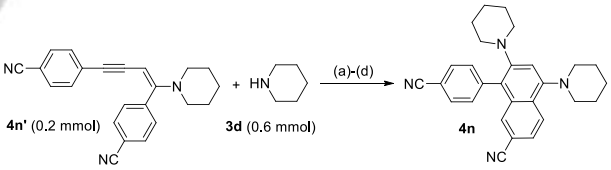
During the synthesis of **4n**, mono-amino substituted eneyne **4n′** was isolated in 15% yield. Subsequently, in an attempted reaction of **4n′** with **3d** in the presence of Cu(Xantphos)I, the cyclization product **4n** was obtained in 40% yield (Scheme 2a). For this cyclization, $Cu(OTf)_2$ was found to be a more effective catalyst (Scheme 2b). The use of $Pd(OAc)_2$ provided a similar yield to $Cu(OTf)_2$ for this cyclization (Scheme 2c). However, the combination of Cu(Xantphos)I and $Cu(OTf)_2$ effectively promoted the formation of the product compared with the use of a single catalyst (Scheme 2d).

On the basis of these results and previously reported work, a preliminary reaction route was proposed using the synthesis of **4n** as an example (Scheme 3). Initially, a double Sonogashira coupling reaction of **1a** with **2** gave the intermediate 4,4′-(buta-1,3-diyne-1,4-diyl)dibenzonitrile (**A**) catalyzed by $Pd(OAc)_2$ and Cu(Xantphos)I.[18] Then an intermolecular hydroamination reaction[16,17] occurred between **A** and **3d** in the presence of Cu(Xantphos)I and $Cu(OTf)_2$, leading to the mono-amino substituted eneyne **4n′** intermediate. The subsequent hydroamination/benzannulation reaction furnished the target product **4n**.

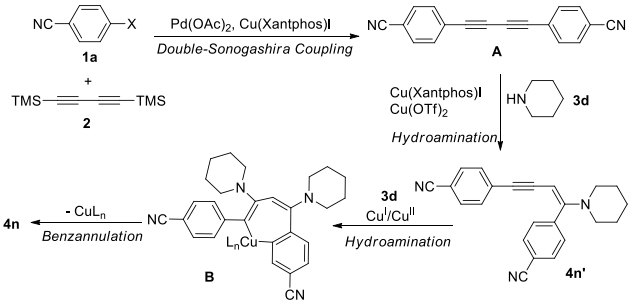
Table 2. The scope of aryl halides and amines[a]



[a] The reactions were carried out using **1** (1.0 mmol), **2** (0.8 mmol), **3** (4.0 mmol), $Pd(OAc)_2$ (0.01 mmol), Cu(Xantphos)I (0.05 mmol) and $Cu(OTf)_2$ (0.2 mmol) in DMF (4.0 mL) at 80 °C for 24 h; Isolated yield based on aryl halides.
[b] 8.0 mmol of **3a** at 100 °C.
[c] Two-step reactions from aryl iodides in the presence of Cs_2CO_3.



(a) Cu(Xantphos)I (5% mmol), DMF (2.0 mL), 100 °C, N_2, 24 h, 40%. (b) $Cu(OTf)_2$ (20% mmol), DMF (2.0 mL), 100 °C, N_2, 24 h, 60%. (c) $Pd(OAc)_2$ (1% mmol), $Cu(OTf)_2$ (20% mmol), DMF (2.0 mL), 100 °C, N_2, 24 h, 61%. (d) Cu(Xantphos)I (5% mmol), $Cu(OTf)_2$ (20% mmol), DMF (2.0 mL), 100 °C, N_2, 24 h, 82%.
Scheme 2. Controlled experiments.



Scheme 3. Proposed reaction route.

Conclusions

In summary, we have described a one-pot, five-component reaction for the synthesis of diamino-substituted naphthalene derivatives form aryl halides, 1,4-bis(trimethylsilyl)butadiyne and amines. The four unsaturated carbon atoms of 1,4-bis(trimethylsilyl)butadiyne participate in the formation of the benzene ring fragment. Two C–N bonds and three C–C bonds form in this domino process. The transformation is achieved through cooperative catalysis of $Pd(OAc)_2$, Cu(Xantphos)I and $Cu(OTf)_2$. A possible double Sonogashira coupling/ hydroamination/benzannulation reaction route is proposed. Electron-withdrawing groups and electron-donating amino groups are simultaneously introduced into these functionalized conjugated molecules. Both cyclic and acyclic secondary amines are suitable for this kind of reaction. Compared with the reported methods, although the reaction yield is relatively low and the substrate is limited to aryl halides bearing electron-withdrawing group on the aromatic ring, the advantage of easy operation and easily available starting materials is still meaningful for this one-pot multi-component reaction.

Experimental Section

GeneralInformation

The chemicals were commercially available without further purification. ^{1}H NMR and ^{13}C NMR ($CDCl_3$ as the solvent) were recorded on Bruker Avance II 300 MHz spectrometers at 300 MHzand 75 MHz respectively. Chemical shifts are reported relative to tetramethylsilane (internal standard). High resolution mass spectra were recorded on Solanx70 FT-MS or Bruker ultrafleXtreme MALDI-TOF/TOF (HCCA matrix). Infrared spectra were recorded on a Nicolet 5700 FTIR spectrometer using KBr pellet samples. Column chromatography was performed on 200–300 mesh silica gel. Melting points were recorded on an uncorrected X-4 apparatus. The X-ray single crystal diffraction was recorded on a Bruker Smart APEX CCD system.

General one-pot procedure for the synthesis of 4a–4m. A mixture of aryl bromides **1** (1.0 mmol) and 1,4-bis(trimethylsilyl)butadiyne **2** (0.8 mmol) and amines **3** (4.0 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.3 mg), Cu(Xantphos)I (0.05 mmol, 38.5 mg), $Cu(OTf)_2$ (0.2 mmol, 72 mg) in anhydrous DMF (4.0 mL) was stirred at 80 ºC for 24 h under nitrogen atmosphere. When the reactions were completed, the solvent DMF was evaporated under reduced pressure. Then the mixture was extracted three times with EA (3×15 mL), and the combined organic layers were dried over anhydrous magnesium sulfate and filtered. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using PE or the mixture of EA/PE (1:100 to 1:1) as the eluent to deliver the target products.

8-(4-Cyanophenyl)-5,7-bis(diethylamino)-2-naphthonitrile (4a)

Yellow solid; yield 60%, 119 mg; m.p. 138–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 1.2 Hz, 1H), 7.49–7.44 (m, 3H), 7.20 (s, 1H), 3.24 (q, *J* = 7.1 Hz, 4H), 2.88 (q, *J* = 7.1 Hz, 4H), 1.10 (t, *J* = 7.1 Hz, 6H), 0.85 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 148.1, 143.4, 133.3, 132.2 (2C), 131.1, 129.3, 127.5, 125.7, 124.1, 119.6, 119.0, 117.0, 110.8, 109.7, 47.6, 47.2, 12.6, 12.1; IR (KBr) *v*: 757, 785, 838, 970, 1048, 1096, 1171, 1225, 1336, 1352, 1401, 1481, 1582, 1607, 1632, 1725, 2223, 2849, 2928, 2963 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{26}H_{29}N_4$: 397.2387, found: 397.2393 $[M+H]^+$.

1-(4-(7-Acetyl-2,4-bis(diethylamino)naphthalen-1-yl)phenyl)ethan-1-one (4b)

Green solid; yield 40%, 86 mg; m.p. 116–118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 8.11–8.08 (m, 3H), 7.89 (dd, J_1 = 8.8, J_2 = 1.7 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.20 (s, 1H), 3.25 (q, *J* = 7.1 Hz, 4H), 2.89 (q, *J* = 7.1 Hz, 4H), 2.71 (s, 3H), 2.47 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 6H), 0.86 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 198.1, 148.0, 147.1, 144.3, 135.5, 134.6, 133.6, 131.8, 130.3, 130.0, 128.2, 127.8, 124.8, 121.5, 116.7, 47.6, 47.4, 26.7, 26.6, 12.6, 12.2; IR (KBr) *v*: 837, 1163, 1223, 1267, 1355, 1601, 1675, 2970 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{28}H_{35}N_2O_2$:431.2693, found: 431.2694 $[M+H]^+$.

Methyl 5,7-bis(diethylamino)-8-(4-(methoxycarbonyl)phenyl)-2-naphthoate (4c)

Yellow solid; yield 46%, 106 mg; m.p. 106–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 8.20–8.15 (m, 3H), 7.92 (dd, J_1 = 1.6 Hz, J_2 = 8.8 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.19 (s, 1H), 3.97 (s, 3H), 3.85 (s, 3H), 3.24 (q, *J* = 7.1 Hz, 4H), 2.87 (q, *J* = 7.1 Hz, 4H), 1.10 (t, *J* = 7.0 Hz, 6H), 0.85 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 167.3, 147.9, 147.0, 144.0, 133.6, 131.6, 130.2, 129.9, 129.4, 128.4, 128.3, 127.4, 124.5, 122.9, 116.4, 52.0, 47.6, 47.3, 12.6, 12.1; IR (KBr) *v*: 762, 999, 1020, 1101, 1175, 1239, 1275, 1353, 1400, 1436, 1605, 1632, 1725, 2852, 2923, 2965 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{28}H_{35}N_2O_4$: 463.2591, found: 463.2595 $[M+H]^+$.

Ethyl 5,7-bis(diethylamino)-8-(4-(ethoxycarbonyl)phenyl)-2-naphthoate (4d)

Yellow liquid; yield 49%, 120 mg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 1H), 8.22 (s, 1H), 8.16 (d, *J* = 7.1 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.18 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.24 (q, *J* = 6.9 Hz, 4H), 2.88 (q, *J* = 6.9 Hz, 4H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 6.9 Hz, 6H), 0.86 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 166.9, 147.9, 146.9, 143.9, 133.6, 131.6, 130.2, 130.0, 129.3, 128.6, 128.5, 127.8, 124.4, 122.9, 116.4, 60.9, 60.8, 47.6, 47.4, 14.4, 14.3, 12.6, 12.2; IR (KBr) *v*: 711, 778, 860, 1022, 1068, 1100, 1175, 1239, 1275, 1367, 1400, 1446, 1558, 1606, 1632, 1719, 2851, 2927, 2971 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{30}H_{39}N_2O_4$: 491.2904, found: 491.2910 $[M+H]^+$.

***N*^{1},*N*^{1},*N*^{3},*N*^{3}-Tetraethyl-6-(methylsulfonyl)-4-(4-(methylsulfonyl)-phenyl)naphthalene-1,3-diamine (4e)**

Yellow solid; yield 62%, 156 mg; m.p. 191–193 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.9 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H), 8.09 (s, 1H), 8.06 (s, 1H), 7.78 (dd, J_1 = 1.8 Hz, J_2 = 8.9 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.24 (s, 1H), 3.26 (q, *J* = 7.1 Hz, 4H), 3.21 (s, 3H), 3.03 (s, 3H), 2.86 (q, *J* = 7.1 Hz, 4H), 1.11 (t, *J* = 7.1 Hz, 6H), 0.85 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 148.5, 144.3, 139.0, 137.8, 133.2, 132.4, 130.0, 128.3, 127.5, 126.4, 125.6, 119.8, 117.3, 47.7, 47.0, 44.6, 44.4, 12.4, 12.1; IR (KBr) *v*: 768, 954, 1089, 1125, 1152, 1226, 1314, 1401, 1581, 1593, 1631, 2811, 2929, 2973, 3203 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{26}H_{35}N_2O_4S_2$: 503.2033, found: 503.2036 $[M+H]^+$.

***N*^{1},*N*^{1},*N*^{3},*N*^{3}-Tetraethyl-6-nitro-4-(4-nitrophenyl)naphthalene-1,3-diamine (4f)**

Red solid; yield 63%, 137 mg; m.p. 116–117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42–8.38 (m, 3H), 8.34 (d, *J* = 2.1 Hz, 1H), 8.11–8.07 (m, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.24 (s, 1H), 3.27 (q, *J* = 7.1 Hz, 4H), 2.90 (q, *J*

= 7.1 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 6H), 0.88 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 148.6, 146.9, 146.1, 145.4, 133.1, 132.4, 130.4, 128.3, 126.3, 123.7, 121.4, 117.6, 116.9, 47.6, 47.1, 12.5, 12.1; IR (KBr) *v*: 706, 861, 1063, 1165, 1237, 1342, 1401, 1532, 1631, 2925, 2966 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{24}H_{29}N_4O_4$: 437.2183, found: 437.2189 $[M+H]^+$.

***N*^{1},*N*^{1},*N*^{3},*N*^{3}-Tetraethyl-6-(trifluoromethyl)-4-(4-(trifluoromethyl)-phenyl)naphthalene-1,3-diamine (4g)**

Yellow solid; yield 41%, 99 mg; m.p. 94–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.8 Hz, 1H), 7.76–7.72 (m, 3H), 7.53–7.46 (m, 3H), 7.20 (s, 1H), 3.25 (q, *J* = 7.1 Hz, 4H), 2.88 (q, *J* = 7.1 Hz, 4H), 1.10 (t, *J* = 7.0 Hz, 6H), 0.85 (t, *J* = 7.1 Hz, 6H);^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 147.7, 142.5, 133.4, 131.8, 129.2 (q, $J_{C\text{-}F}$ = 38.7 Hz), 127.9 (q, $J_{C\text{-}F}$ = 31.2 Hz), 125.6, 125.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 124.5 (q, $J_{C\text{-}F}$ = 270.4 Hz), 122.9, 122.8, 119.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 116.2, 47.7, 47.4, 12.6, 12.2; IR (KBr) *v*: 588, 700, 735, 834, 962, 1020, 1067, 1119, 1158, 1261, 1311, 1325, 1370, 1588, 1616, 1631, 1801, 1922, 2847, 2933, 2974 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{26}H_{29}F_6N_2$: 483.2229, found: 483.2225 $[M+H]^+$.

5-(3-Cyanophenyl)-6,8-bis(diethylamino)-2-naphthonitrile (4i)

Yellow solid; yield 56%, 111 mg; m.p. 135–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.72–7.65 (m, 2H), 7.61–7.59 (m, 2H), 7.41 (s, 2H), 7.13 (s, 1H), 3.25 (q, *J* = 7.1 Hz, 4H), 2.90 (q, *J* = 7.1 Hz, 4H), 1.11 (t, *J* = 7.1 Hz, 6H), 0.86 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 149.1, 139.8, 136.1, 135.8, 135.1, 130.9, 130.4, 129.2, 126.8, 126.7, 125.9, 125.7, 120.0, 118.9, 115.4, 112.5, 106.4, 47.7, 46.9, 12.5, 12.1; IR (KBr) *v*: 788, 810, 920, 1068, 1084, 1199, 1218, 1235, 1333, 1374, 1402, 1452, 1573, 1609, 1631, 2221, 2827, 2931, 2970, 3213 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{26}H_{29}N_4$: 397.2387, found: 397.2381 $[M+H]^+$.

***N*^{1},*N*^{1},*N*^{3},*N*^{3}-Tetraethyl-5,6,7-trifluoro-4-(3,4,5-trifluorophenyl)-naphthalene-1,3-diamine (4j)**

Yellow solid; yield 39%, 89 mg; m.p. 68–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.89 (m, 1H), 7.12 (s, 1H), 6.94–6.86 (m, 2H), 3.16 (q, *J* = 7.1 Hz, 4H), 2.84 (q, *J* = 7.1 Hz, 4H), 1.06 (t, *J* = 7.1 Hz, 6H), 0.85 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 150.4, 148.9, 148.3, 145.1, 140.9, 140.2, 136.9, 136.0, 129.9, 126.6, 125.0, 121.8, 116.1, 114.7, 114.4, 105.5, 105.2, 47.8, 47.7, 12.7, 12.1; IR (KBr) *v*: 766, 869, 1037, 1115, 1221, 1236, 1379, 1471, 1534, 1613, 1631, 2849, 2918, 2973 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{24}H_{25}F_6N_2$: 455.1916, found: 455.1920 $[M+H]^+$.

***N*^{7},*N*^{7},*N*^{9},*N*^{9}-Tetraethyl-10-(quinolin-3-yl)phenanthridine-7,9-diamine (4k)**

Yellow solid; yield 45%, 101 mg; m.p. 144–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (s, 1H), 9.00 (d, *J* = 2.1 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 1H), 8.08–8.03 (m, 2H), 7.80–7.75 (m, 2H), 7.59–7.57 (m, 1H), 7.54–7.43 (m, 1H), 7.29–7.26 (m, 2H), 6.93–6.87 (m, 1H), 3.36 (q, *J* = 7.1 Hz, 4H), 2.82–2.79 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 6H), 0.82 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 153.6, 150.7, 150.4, 146.6, 146.2, 137.2, 134.3, 134.0, 129.5, 129.2 (2C), 128.2, 127.8, 127.7, 127.3, 126.5, 126.3, 124.9, 124.2, 120.8, 115.7, 48.3, 47.1, 12.3, 12.2; IR (KBr) *v*: 768, 1047, 1108, 1172, 1222, 1353, 1401, 1579, 1631, 2813, 2926, 2967, 3177 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{30}H_{33}N_4$: 449.2700, found: 449.2701 $[M+H]^+$.

8-(4-Cyanophenyl)-5,7-bis(dipropylamino)-2-naphthonitrile (4l)

Yellow liquid; yield 58%, 131 mg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 1.1 Hz, 1H), 7.48–7.45 (m, 3H), 7.23 (s, 1H), 3.16–3.11 (m, 4H), 2.80–2.75 (m, 4H), 1.62–1.49 (m, 4H), 1.35–1.22 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H), 0.71 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 148.8, 143.6, 133.4, 132.3, 132.2, 130.9, 128.8, 126.2, 125.6, 123.9, 119.6, 118.9, 116.6, 110.8, 109.6, 55.9, 55.2, 20.7, 20.1, 11.7, 11.5; IR (KBr) *v*: 756, 831, 943, 1068, 1125, 1219, 1299, 1400, 1589, 1631, 2227, 2873, 2965, 3208 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{30}H_{37}N_4$: 453.3013, found: 453.3017 $[M+H]^+$.

8-(4-Cyanophenyl)-5,7-bis(dibutylamino)-2-naphthonitrile (4m)

Yellow liquid; yield 55%, 140 mg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 1.2 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 3H), 7.22 (s, 1H), 3.16 (t, *J* = 7.5 Hz, 4H), 2.81 (t, *J* = 7.7 Hz, 4H), 1.56–1.46 (m, 4H), 1.34–1.08 (m, 12H), 0.91–0.85 (m, 6H), 0.80 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 148.7, 143.6, 133.3, 132.2 (2C), 130.9, 128.7, 126.1, 125.5, 123.8, 119.5, 118.9, 116.6, 110.7, 109.6, 53.8, 53.0, 29.6, 29.1, 20.4, 20.2, 13.9, 13.8; IR (KBr) *v*: 557, 756, 831, 1124, 1212, 1262, 1400, 1587, 1631, 2227, 2860, 2929, 2959 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{34}H_{45}N_4$: 509.3639, found: 509.3641 $[M+H]^+$.

General one-pot procedure for the synthesis of 4n–4p. A mixture of aryl iodides **1** (1.0 mmol), 1,4-bis(trimethylsilyl)butadiyne **2** (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.3 mg), Cu(Xantphos)I (0.05 mmol, 38.5 mg) and Cs_2CO_3 (2.0 mmol, 652 mg) in anhydrous DMF (4.0 mL) was stirred at room temperature for 16 h under nitrogen atmosphere. Then amines **3** (10.0 mmol) and $Cu(OTf)_2$ (0.2 mmol, 72 mg) were added and the temperature was increased to 100 °C for 24 h. When the reactions were completed, the solvent DMF was evaporated under reduced pressure. Then the mixture was extracted three times with EA (3×15 mL), and the combined organic layers were dried over anhydrous magnesium sulfate and filtered. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using PE or the mixture of EA/PE (1:100 to 1:1) as the eluent to deliver the target products.

8-(4-Cyanophenyl)-5,7-di(piperidin-1-yl)-2-naphthonitrile (4n)

Yellow solid; yield 36%, 76 mg; m.p. 270–272 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 1H), 7.82–7.79 (m, 3H), 7.52–7.44 (m, 3H), 7.09 (s, 1H), 3.08 (s, 3H), 2.81 (t, *J* = 5.4 Hz, 4H), 1.86 (q, *J* = 5.4 Hz, 4H), 1.42–1.29 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 151.1, 143.2, 132.8, 132.4, 132.2, 131.0, 126.9, 125.4, 124.5, 123.8, 119.6, 119.0, 111.9, 110.7, 109.8, 54.6, 53.0, 26.5, 26.0, 24.4, 24.0; IR (KBr) *v*: 829, 857, 1036, 1093, 1112, 1224, 1261, 1361, 1381, 1439, 1503, 1586, 1601, 1655, 2225, 2854, 2929 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{28}H_{29}N_4$: 421.2387, found: 421.2396 $[M+H]^+$.

***(E)*-4,4'-(1-(Piperidin-1-yl)but-1-en-3-yne-1,4-diyl)dibenzonitrile (4n')**

Gray solid; yield 15%, 25 mg; m.p. 158–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.51 (m, 4H), 7.47–7.41 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.14 (s, 1H), 3.99 (t, *J* = 5.5 Hz, 2H), 3.81 (s, 2H), 2.72 (t, *J* = 6.2 Hz, 2H), 1.92–1.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 137.6, 132.2, 130.5, 129.5, 129.3, 127.8, 119.2, 117.0, 111.0, 109.6, 109.0, 45.4, 32.3, 23.8, 22.3, 20.4; IR (KBr) *v*: 805, 1144, 1384, 1513, 1601, 2218 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_3$: 338.1651, found: 338.1645 $[M+H]^+$.

1,1'-(6-Nitro-4-(4-nitrophenyl)naphthalene-1,3-diyl)dipiperidine (4o)

Yellow solid; yield 39%, 90 mg; m.p. 267–269 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.0 Hz, 2H), 8.38 (s, 1H), 8.27 (d, *J* = 9.2 Hz, 1H), 8.06 (dd, J_1 = 2.2 Hz, J_2 = 9.2 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.14 (s, 1H), 3.11 (s, 4H), 2.84 (t, *J* = 5.3 Hz, 4H), 1.91–1.85 (m, 4H), 1.71 (s, 2H), 1.42–1.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 151.7, 146.8, 146.2, 145.3, 132.8, 132.5, 128.1, 126.0, 125.4, 123.7, 121.4, 116.6, 112.5, 54.6, 53.0, 26.5, 26.0, 24.4, 24.0; IR (KBr) *v*: 809, 857, 1011, 1103, 1213, 1341, 1386, 1440, 1518, 1587, 1631, 2813, 2851, 2937 cm^{-1};

HRMS *m/z* (ESI) calcd for $C_{26}H_{29}N_4O_4$: 461.2183, found: 461.2190 $[M+H]^+$.

4,4'-(6-Nitro-4-(4-nitrophenyl)naphthalene-1,3-diyl)dimorpholine (4p) Red solid; yield 47%, 109 mg; m.p. 223–224 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.42 (d, *J* = 1.8 Hz, 2H), 8.34 (d, *J* = 9.2 Hz, 1H), 8.13 (dd, J_1 = 2.2 Hz, J_2 = 9.2 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.19 (s, 1H), 4.04 (t, *J* = 4.3 Hz, 4H), 3.52 (t, *J* = 4.3 Hz, 4H), 3.19 (t, *J* = 4.3 Hz, 4H), 2.91 (t, *J* = 4.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 149.9, 147.1, 146.4, 144.3, 132.9, 132.3, 128.0, 126.5, 125.7, 123.9, 121.6, 117.3, 111.9, 67.1, 66.7, 53.4, 51.7; IR (KBr) *v*: 704, 759, 828, 880, 1006, 1069, 1112, 1226, 1262, 1308, 1345, 1443, 1522, 1582, 1631, 2847, 2917, 2962 cm^{-1}; HRMS m/z (ESI) calcd for $C_{24}H_{25}N_4O_6$: 465.1769, found: 465.1784 $[M+H]^+$.

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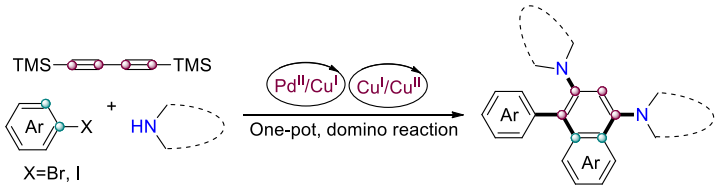

Cooperative catalysis: The diamino-substituted naphthalene derivatives are synthesized from easily available starting materials aryl halides, 1,4-bis(trimethylsilyl)butadiyne and amines in a one-pot procedure by the cooperative action of $Pd(OAc)_2$, Cu(Xantphos)I and $Cu(OTf)_2$.

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1–5

Cooperative Palladium and Copper Catalysis: One-pot Synthesis of Diamino-Substituted Naphthalenes from Aryl Halides, 1,4-Bis(trimethylsilyl)butadiyne and Amines