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Direct Assembly of Polysubstituted Naphthalenes via a Tandem Reaction of Benzynes and α-Cyano-β-methylenones

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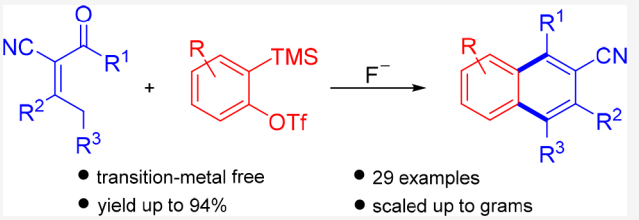
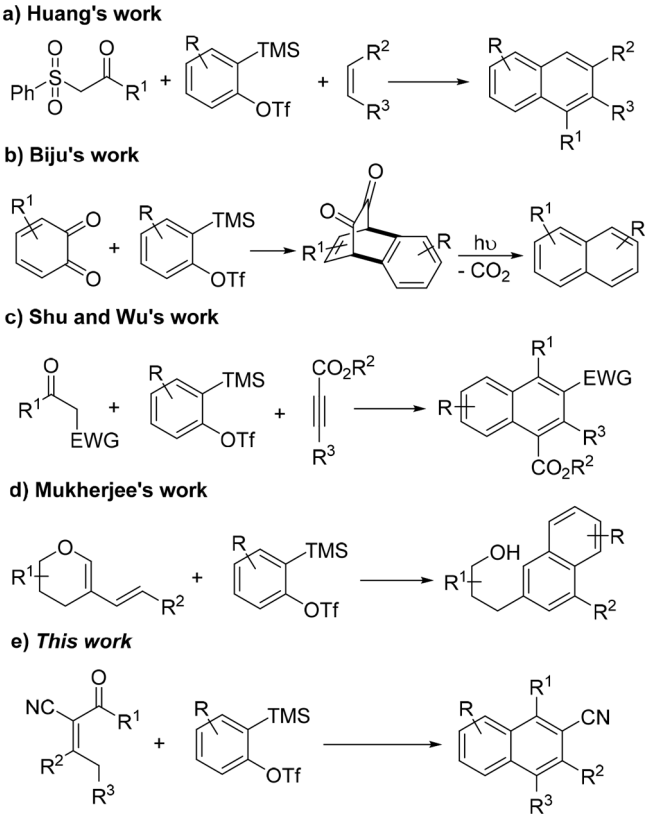
ABSTRACT: A mild and transition-metal-free benzannulation reaction for the construction of the naphthalene skeleton has been described. Benzynes react with α-cyano-β-alkylenones through a tandem nucleophilic addition/cyclization/aromatization process to afford polysubstituted naphthalenes in 50−94% yields.



Polysubstituted naphthalenes are privileged structural motifs found in many natural products, biologically active compounds, pharmaceuticals, and functional organic materials.[1] Due to their importance, tremendous efforts have been exerted to develop efficient methods for the synthesis of these ubiquitous frameworks.[2] In the past decade, the transition-metal-catalyzed Diels−Alder reaction,[3] Dötz reaction,[4] and other cyclizations[5] have been extensively studied for the construction of naphthalene scaffolds. On the other hand, benzynes[6] are highly reactive intermediates that have been used widely in the synthesis of various carbocycles and heterocycles.[7] In particular, the annulation of benzynes provides facile access to different polyaromatic hydrocarbons.[8] As one of the most convenient methods, transition-metal-catalyzed [2+2+2] cycloaddition reactions[9] of benzynes have been well established, which provide rapid construction of polysubstituted naphthalenes. However, this method often suffers from the use of expensive transition-metal catalysts and the difficulty in controlling chemo- and regioselectivity.

In 2007, Huang and Xue described a transition-metal-free multicomponent reaction of benzynes, β-ketosulfones, and activated alkenes, affording polysubstituted naphthols and naphthalenes (Scheme 1a).[10] In 2012, Biju and co-workers reported an interesting Diels−Alder reaction of 1,2-benzoquinones and benzynes to produce dioxobenzobicyclooctadienes, which can be further transformed to naphthalenes via irradiation at 254 nm (Scheme 1b).[11] Recently, Wu, Shu, and co-workers reported a formal [2+2+2] cycloaddition of benzynes, ketones, and alkynoates, which provided a novel method for the synthesis of functionalized naphthalenes (Scheme 1c).[12] Subsequently, the same group further developed a tandem σ-bond insertion/benzannulation reaction of benzynes to give two classes of polysubstituted naphthalenes.[13] Very recently, Mukherjee and co-workers reported an impressive Diels−Alder reaction of benzynes and glycal-derived dienes to

Scheme 1. Transition-Metal-Free Synthesis of Naphthalenes Involving Benzynes



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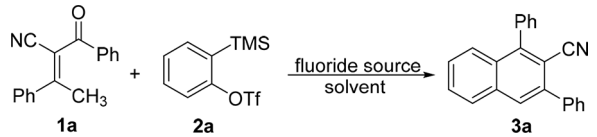
construct meta-disubstituted naphthalenes with a chiral side chain (Scheme 1d).[14] Despite significant advances made in this research field, the development of novel protocols for the synthesis of polysubstituted naphthalene derivatives with unprecedented C4 synthons is still highly significant.

In line with our continued interest in benzyne chemistry,[15] we hypothesized that α-cyano-β-methylenones, which have been used successfully by Ye,[16a−c] Wang,[16d] and Shi[16e] as C4 synthon partners in the synthesis of polysubstituted benzenes, may undergo benzannulation with benzynes to form polysubstituted naphthalenes (Scheme 1e). Herein, we report our development on the construction of polysubstituted naphthalenes. As shown in Table 1, our study commenced by

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

entry	additives	time (h)	solvent	yield (%)[b]
1	CsF (4.5 equiv)	24	CH_3CN	37
2	KF/18-crown-6 (4.5 equiv)	24	CH_3CN	39
3	TBAF (4.5 equiv)	24	CH_3CN	40
4	TMAF (4.5 equiv)	24	CH_3CN	47
5	TBAT (4.5 equiv)	24	CH_3CN	81
6	TBAT (4.5 equiv)	24	THF	55
7	TBAT (4.5 equiv)	24	DME	65
8	TBAT (4.5 equiv)	24	1,4-dioxane	51
9	TBAT (4.5 equiv)	24	CH_2Cl_2	62
10	TBAT (4.5 equiv)	24	$ClCH_2CH_2Cl$	48
11	TBAT (4.5 equiv)	48	toluene	17
12	TBAT (4.5 equiv)	48	DMF	21
13	TBAT (4.5 equiv)	48	DMSO	18
14[c]	TBAT (6.0 equiv)	24	CH_3CN	94
15[d]	TBAT (7.5 equiv)	24	CH_3CN	95

[a]Standard conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), 1.0 mL of the solvent, room temperature. [b]Isolated yield. [c]**1a** (0.10 mmol), **2a** (0.20 mmol), and TBAT (0.60 mmol). [d]**1a** (0.10 mmol), **2a** (0.25 mmol), TBAT (0.75 mmol). TBAT: tetrabutylammonium difluorotriphenylsilicate.

selecting readily available α-cyano-β-methylenone **1a** and Kobayashi's reagent[17] **2a** as the model substrates for optimization of the reaction conditions. With 4.5 equiv of CsF as a fluoride source, the benzannulation smoothly proceeded in acetonitrile at room temperature to afford the desired polysubstituted naphthalene **3a** in 37% yield (Table 1, entry 1). Encouraged by this success, several other fluoride sources were subsequently investigated for the reaction. KF/18-crown-6 gave the desired product in a 39% isolated yield (Table 1, entry 2). TBAF and TMAF promoted the reaction in moderate yield (Table 1, entries 3 and 4). Gratifyingly, when tetrabutylammonium difluorotriphenylsilicate (TBAT) was used as the fluoride source, the yield was dramatically improved to 81% (Table 1, entry 5). A brief screening of the reaction solvent showed that acetonitrile was optimal (Table 1, entries 6−13). Increasing the amount of benzyne precursor to 2.0 equiv led to a higher reaction yield (Table 1, entry 14). However, a further increase of the benzyne precursor to 2.5 equiv did not give a significant change in the reaction yield (Table 1, entry 15).

With the optimized reaction conditions in hand, the generality of the reaction was next examined, and the results are summarized in Scheme 2. Both electron-withdrawing substituents (R^2 = 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4) and electron-donating substituents (R^2 = 4-MeC_6H_4, 4-$MeOC_6H_4$) substituted β-arylenones participated in the benzannulation well, producing the corresponding naphthalenes in high yields (Scheme 2, **3b−3f**). The electronic properties and position of the substituents on the β-aryl ring have little influence on the reaction yield (Scheme 2, **3g−3l**). A bulky naphthyl-derived enone performed smoothly to give the desired naphthalene **3m** in 84% yield (Scheme 2, **3m**). In addition, β-heteroarylenone (R^2 = 2-thienyl) **1n** was proved to be a successful candidate for the annulation, affording **3n** in 68% yield (Scheme 2, **3n**). Interestingly, β-ethyl-β-phenyl-substituted enone coupled with benzyne provided tetrasubstituted naphthalene **3o** in a 61% yield (Scheme 2, **3o**). The bulky isopropyl-substituted enone **1p** underwent the reaction to afford **3p** in a 60% yield (Scheme 2, **3p**). However, when β,β-dimethyl-substituted enone **1q** was used to couple with benzyne, it gave a complex reaction mixture, and no desired product was obtained under the standard conditions (Scheme 2, **3q**). This may be due to the instability of the dienolate intermediate[16e] shown in Scheme 5. β-Arylenones containing electron-deficient groups (R^1 = 4-FC_6H_4, 4-$MeO_2C-C_6H_4$) or electron-rich groups (R^1 = 4-MeC_6H_4, 4-$MeOC_6H_4$) underwent the reaction to furnish the corresponding products in high yields (Scheme 2, **3r−3u**). Furthermore, heteroaryl-substituted β-arylenones **1v** and **1w** (R^1 = 2-furyl, 2-thienyl) reacted with benzyne to afford **3v** and **3w** in 71% and 76% yields, respectively (Scheme 2, **3v** and **3w**). Notably, alkyl-substituted enone **1x** was also suitable for the reaction, giving **3x** in 50% yield (Scheme 2, **3x**).

Other different types of enones and enoates were also prepared and tested for the tandem reaction. As shown in Scheme 3, when substrates **1y**, **1z**, and **1aa** that have no phenyl group at the β-position were used for the reaction, these enones were consumed completely within 24 h. However, the reactions were very complex, and no desired products were obtained. We attributed this result to a similar reason as that of **3q** (Scheme 2, **3q**). Substrates **4a−4d** did not react with benzyne, and the starting materials were recovered in high yields. We concluded that the acidity of the methyl protons of these tested enones and enoates is weaker than that of enone **1a**. Therefore, they could be difficult to generate the dienolate intermediate **I** shown in Scheme 5 and trigger the following cyclization.

Substituted benzyne precursors were also tested for the reaction. The symmetrical benzynes derived from precursors **2b**, **2c**, and **2d** smoothly underwent the benzannulation with enone **1a** to afford the corresponding polysubstituted naphthalenes in good yields (Scheme 4, **3y−3aa**). Interestingly, the polysubstituted anthracene **3ab** was obtained in 56% yield when the symmetrical 2,3-naphthalyne **2e** was introduced to the reaction (Scheme 4, **3ab**). Unsymmetrical 3-methoxybenzyne and 3-methylbenzyne derived from **2f** and **2g** performed smoothly in the reaction to give **3ac** and **3ad** in 74% and 80% yields with excellent regioselectivity (Scheme 4, **3ac** and **3ad**). Notably, the benzannulation reaction can be conducted on a gram-scale, and a high yield can be maintained (Scheme 4, **3ad**).

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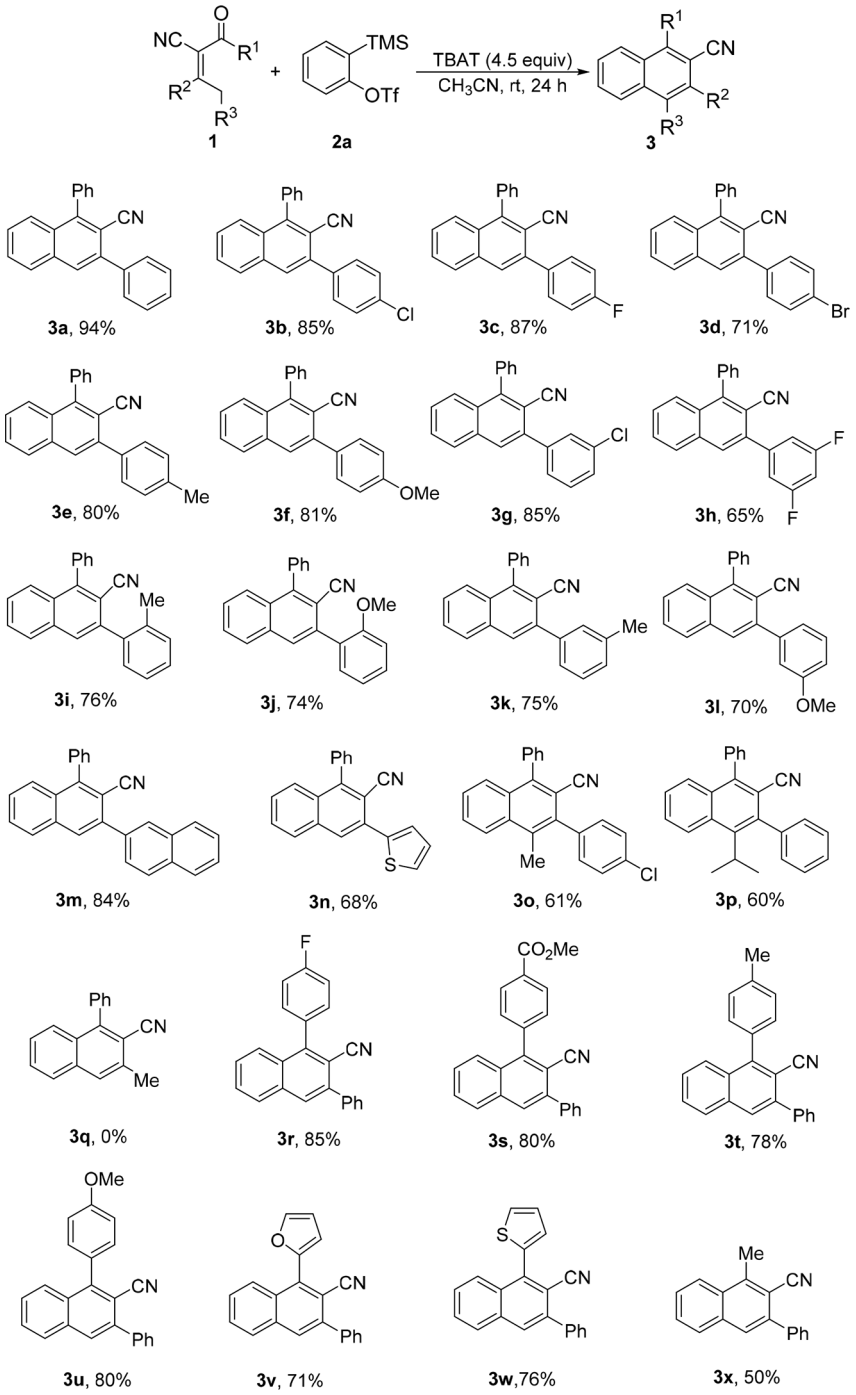
Scheme 2. Scope of α-Cyano-β-methylenones[a]



[a]General conditions: **1a** (0.10 mmol), **2a** (0.20 mmol), TBAT (0.60 mmol), CH_3CN (1.0 mL), room temperature, 24 h. The yields reported are isolated yields.

The products **3a** and **3ad** were crystallized from tetrahydrofuran and *n*-hexane, and their structure was clearly confirmed by single-crystal X-ray analysis.[18]

Based on the pioneering work on the nucleophilic addition-cyclization reactions of benzynes[7,10] and the transformations of α-cyano-β-methylenones,[16] a plausible reaction mechanism was proposed in Scheme 5. In the presence of basic fluoride, α-cyano-β-methylenone undergoes deprotonation to generate dienolate intermediate **I**. Subsequent cyclization of intermediate **I** and benzyne lead to intermediate **II**. Protonation of intermediate **II** results in the formation of compound **III**. Finally, the aromatization of **III** (via dehydration) leads to the formation of the desired product.

In summary, we have demonstrated a benzannulation reaction of benzynes and readily available α-cyano-β-methylenones. The transition-metal-free and mild conditions, simple procedure, and generally high yields provide a novel, useful protocol for the synthesis of polysubstituted naphthalenes. Further studies of a broader substrate scope and the

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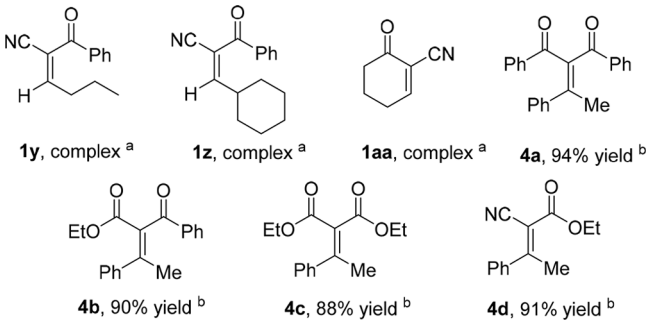
Scheme 3. Unsuccessful Substrates



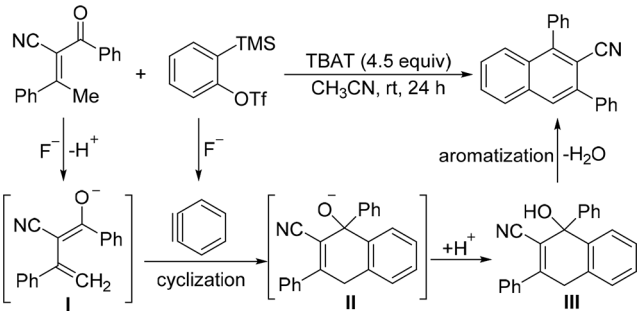
[a]The reaction is very complex, indicated by TLC. [b]The recovery yield of the starting enones or enoates.

synthetic applications of this method are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Experimental Methods. Unless otherwise indicated, all reactions were conducted under a nitrogen atmosphere in oven-dried glassware. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), and ^{19}F NMR (376 MHz) spectra are reported in ppm (δ). High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometer equipped with an ESI source from Thermo Scientific at Keeclound Biotech in Shanghai. The X-ray diffraction study for products **3a** and **3ad** was carried out on a Bruker D8 VENTURE photon II diffractometer with an Iμs 3.0 microfocus X-ray source using the APEX III program. Benzyne precursors were obtained from commercial suppliers and used without purification. Benzyne precursors **2b**,[19] **2c**,[19] α-cyano-β-methylenones **1a**−**1x**,[16] **1y**-**1z**,[20] **1aa**,[21] **4a**,[22] **4b**,[23] **4c**,[24] and **4d**[25] were prepared according to literature procedures. Anhydrous THF, 1,4-dioxane, toluene, and DME were distilled from sodium and benzophenone prior to use. CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, DMF, and DMSO were distilled from calcium hydride prior to use. Petroleum ether (PE), where used, has a boiling point range of 60−90 °C.

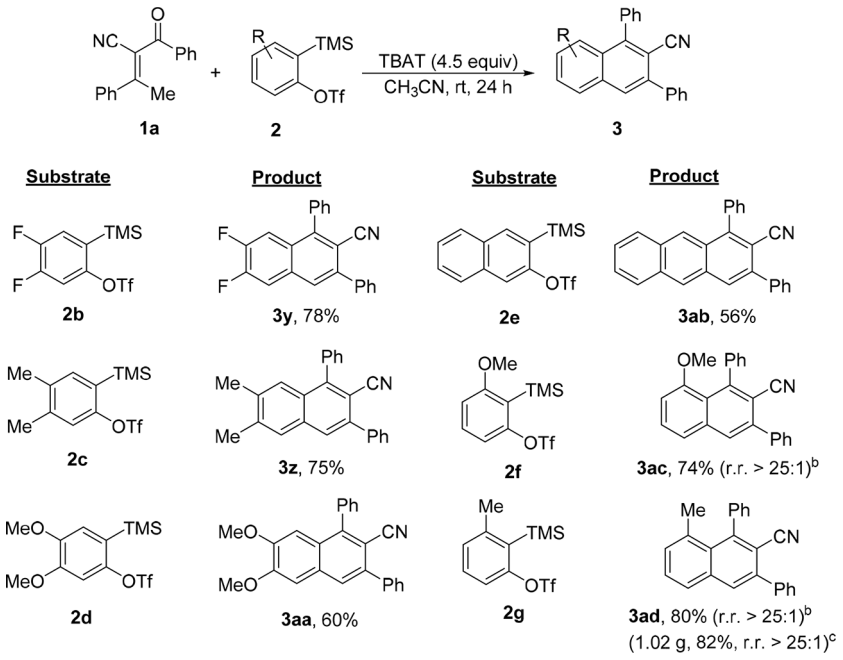
Scheme 5. Proposed Mechanism



Typical Procedure for the Tandem Reaction of Benzyne and α-Cyano-β-methylenone. To a mixture of α-cyano-β-methylenone **1a** (0.10 mmol, 24.7 mg) and TBAT (0.60 mmol, 323.9 mg) in anhydrous acetonitrile (1.0 mL) was added 2-(trimethylsilyl) aryl triflate **2a** (0.20 mmol, 60.0 mg) under a nitrogen atmosphere. The mixture was stirred at room temperature until full consumption of the starting enone was indicated by TLC. The reaction mixture was then diluted with ethyl acetate, filtered through a short pad of silica gel, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the desired product **3a**.

Scale-up Experiment. To a mixture of α-cyano-β-methylenone **1a** (3.92 mmol, 0.97g) and TBAT (23.52 mmol, 12.7 g) in anhydrous acetonitrile (40.0 mL) was added 2-(trimethylsilyl) aryl triflate **2g** (7.84 mmol, 2.45g) under a nitrogen atmosphere. The mixture was stirred at room temperature until full consumption of the starting enone was indicated by TLC. The reaction mixture was then diluted with ethyl acetate, filtered through a short pad of silica gel, washed with ethyl acetate, and concentrated. The crude product was purified

Scheme 4. Scope of Benzynes[a]



[a]General conditions: **1a** (0.10 mmol), **2** (0.20 mmol), TBAT (0.60 mmol), CH_3CN (1.0 mL), room temperature, 24 h. The yields reported are isolated yields. [b]The regioisomeric ratio (rr) was determined by ^{1}H NMR analysis. [c]**1a** (3.92 mmol), **2g** (7.84 mmol), TBAT (23.52 mmol), CH_3CN (40.0 mL), room temperature, 48 h.

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by flash column chromatography on silica gel (petroleum ether) to give **3ad** in 82% yield (1.02 g)

*1,3-Diphenyl-2-naphthonitrile (**3a**):* white solid (28.7 mg, 94% yield); mp 144.3−144.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3043, 2222, 1619, 1580, 1488, 1444, 1410, 1371, 1332, 1182, 1075, 1026, 895, 793, 696, 613, 516; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96−7.90 (m, 2H), 7.69−7.61 (m, 4H), 7.60−7.41 (m, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.9, 139.9, 138.8, 136.9, 134.7, 130.8, 130.1, 129.3, 129.1, 128.9, 128.7, 128.63, 128.61, 128.5, 128.3, 127.39, 127.37, 118.0, 110.0; HRMS (ESI) m/z calcd for $C_{23}H_{16}N^+[M + H]^+$ 306.1277, found 306.1278.

*3-(4-Chlorophenyl)-1-phenyl-2-naphthonitrile (**3b**).* white solid (28.8 mg, 85% yield); mp 173.2−173.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3438, 3055, 2225, 1616, 1596, 1566, 1492, 1442, 1330, 1093, 1014, 900, 831, 754, 702, 613; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95−7.89 (m, 2H), 7.67−7.53 (m, 7H), 7.53−7.46 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.2, 138.6, 137.2, 136.7, 134.8, 134.6, 130.9, 130.6, 130.0, 129.3, 129.0, 128.9, 128.67, 128.65, 128.3, 127.6, 127.4, 117.8, 109.7; HRMS (ESI) m/z calcd for $C_{23}H_{15}ClN^+$ $[M + H]^+$ 340.0888, found 340.0885.

*3-(4-Fluorophenyl)-1-phenyl-2-naphthonitrile (**3c**):* white solid (28.1 mg, 87% yield); mp 146.9−147.6 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3060, 2227, 1600, 1508, 1487, 1442, 1228, 1161, 850, 835, 784, 700, 609; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96−7.91 (m, 1H), 7.90−7.88 (m, 1H), 7.68−7.61 (m, 4H), 7.60−7.53 (m, 3H), 7.52−7.46 (m, 3H), 7.23−7.15 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 163.0 (d, J = 246.0 Hz), 148.0, 138.8, 136.8, 134.8 (d, J = 4.0 Hz), 134.7, 131.0 (d, J = 8.0 Hz), 130.9, 130.0, 129.2, 128.9, 128.7, 128.3, 127.5, 127.4, 117.9, 115.7 (d, J = 21.7 Hz), 109.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) −113.46; HRMS (ESI) m/z calcd for $C_{23}H_{15}FN^+$ $[M + H]^+$ 324.1183, found 324.1182.

*3-(4-Bromophenyl)-1-phenyl-2-naphthonitrile (**3d**):* white solid (27.2 mg, 71% yield); mp 184.8−185.5 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3053, 2214, 1590, 1491, 1446, 1377, 1332, 1297, 1149, 1104, 1069, 1005, 990, 915, 831, 752, 702, 613, 524; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91−7.81 (m, 2H), 7.63−7.55 (m, 4H), 7.52−7.39 (m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.2, 138.6, 137.6, 136.7, 134.6, 131.8, 130.94, 130.86, 130.0, 129.3, 129.0, 128.7, 128.6, 128.3, 127.6, 127.4, 123.0, 117.8, 109.6; HRMS (ESI) m/z calcd for $C_{23}H_{15}NBr^+$ $[M + H]^+$ 384.0382, found 384.0380.

*1-Phenyl-3-p-tolyl-2-naphthonitrile (**3e**):* white solid (25.5 mg, 80% yield); mp 149.0−149.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3049, 2219, 1616, 1512, 1485, 1440, 1373, 1330, 1186, 1026, 896, 815, 756, 702, 621, 522; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95−7.87 (m, 2H), 7.65−7.52 (m, 7H), 7.51−7.42 (m, 3H), 7.35−7.29 (m, 2H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.9, 140.0, 138.3, 136.9, 135.9, 134.7, 130.7, 130.0, 129.3, 129.1, 129.0, 128.8, 128.6, 128.5, 128.2, 127.3, 127.2, 118.1, 110.1, 21.3; HRMS (ESI) m/z calcd for $C_{24}H_{18}N^+$ $[M + H]^+$ 320.1434, found 320.1433.

*3-(4-Methoxyphenyl)-1-phenyl-2-naphthonitrile (**3f**):* white solid (27.1 mg, 81% yield); mp 128.3−129.1 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3047, 2839, 2221, 1610, 1571, 1514, 1465, 1286, 1245, 1180, 1028, 833, 756, 702, 613; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96−7.86 (m, 2H), 7.65−7.53 (m, 7H), 7.51−7.44 (m, 3H), 7.06−7.03 (m, 2H), 3.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 159.9, 147.9, 139.6, 136.9, 134.8, 131.1, 130.6, 130.5, 130.0, 129.0, 128.8, 128.6, 128.4, 128.2, 127.3, 127.2, 118.1, 114.1, 110.1, 55.4; HRMS (ESI) m/z calcd for $C_{24}H_{18}NO^+$ $[M + H]^+$ 336.1383, found 336.1380.

*3-(3-Chlorophenyl)-1-phenyl-2-naphthonitrile (**3g**):* white solid (28.8 mg, 85% yield); mp 132.0−132.7 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3055, 2218, 1595, 1562, 1477, 1446, 1332, 1080, 881, 786, 756, 709; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 8.6, 1.2 Hz, 1H), 7.92 (s, 1H), 7.69−7.63 (m, 3H), 7.61−7.42 (m, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.2, 140.5, 138.4, 136.6, 134.6, 134.5, 131.0, 130.0, 129.8, 129.34, 129.29, 129.0, 128.8, 128.7, 128.6, 128.3, 127.7, 127.5, 127.4, 117.6, 109.7; HRMS (ESI) m/z calcd for $C_{23}H_{15}ClN^+$ $[M + H]^+$ 340.0888, found 340.0886.

*3-(3,5-Difluorophenyl)-1-phenyl-2-naphthonitrile (**3h**):* white solid (22.1 mg, 65% yield); mp 118.1−118.9 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3436, 3053, 2214, 1625, 1593, 1448, 1344, 1118, 989, 864, 757, 717; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (dd, J = 8.6, 1.3 Hz, 1H), 7.92 (s, 1H), 7.71−7.65 (m, 2H), 7.62−7.45 (m, 6H), 7.22−7.18 (m, 2H), 6.95−6.88 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 162.9 (dd, J = 248.0, 13.0 Hz), 148.4, 141.8 (t, J = 9.6 Hz), 137.4 (t, J = 2.5 Hz), 136.5, 134.5, 131.2, 130.0, 129.5, 129.1, 128.8, 128.7, 128.4, 128.0, 127.5, 117.4, 112.5 (dd, J = 18.8, 7.3 Hz), 109.3, 103.9 (t, J = 25.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) −108.96 (s, 2F); HRMS (ESI) m/z calcd for $C_{23}H_{14}F_2N^+$ $[M + H]^+$ 342.1089, found 342.1086.

*1-Phenyl-3-o-tolyl-2-naphthonitrile (**3i**):* white solid (24.2 mg, 76% yield); mp 119.8−120.6 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3047, 2920, 2223, 1618, 1587, 1487, 1444, 1149, 1028, 900, 794, 757, 729, 700, 615; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 8.2 Hz, 1H), 7.82 (s, 1H), 7.72−7.61 (m, 2H), 7.58−7.48 (m, 6H), 7.38−7.29 (m, 4H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.1, 140.0, 138.6, 136.7, 136.2, 134.6, 130.8, 130.3, 130.1, 129.9, 129.0, 128.84, 128.78, 128.7, 128.6, 128.2, 127.4, 127.3, 125.8, 117.5, 111.3, 20.1; HRMS (ESI) m/z calcd for $C_{24}H_{18}N^+$ $[M + H]^+$ 320.1434, found 320.1432.

*3-(2-Methoxyphenyl)-1-phenyl-2-naphthonitrile (**3j**):* white solid (24.8 mg, 74% yield); mp 190.3−190.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3448, 3057, 2923, 2837, 2229, 1600, 1587, 1490, 1465, 1249, 1110, 1022, 891, 763, 702; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (d, J = 8.2 Hz, 1H), 7.88 (s, 1H), 7.69−7.41 (m, 9H), 7.38 (dd, J = 7.5, 1.8 Hz, 1H), 7.10 (dd, J = 7.5, 1.0 Hz, 1H), 7.08−7.03 (m, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 156.9, 146.6, 137.2, 136.9, 134.8, 131.2, 130.8, 130.24, 130.15, 129.1, 128.7, 128.6, 128.5, 128.2, 127.9, 127.3, 127.2, 120.8, 117.9, 112.0, 111.3, 55.6; HRMS (ESI) m/z calcd for $C_{24}H_{18}NO^+$ $[M + H]^+$ 336.1383, found 336.1380.

*1-Phenyl-3-m-tolyl-2-naphthonitrile (**3k**):* white solid (23.9 mg, 75% yield); mp 109.7−110.5 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3438, 3049, 2219, 1610, 1583, 1485, 1442, 1334, 1149, 892, 792, 754, 700; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 7.2 Hz, 2H), 7.69−7.62 (m, 2H), 7.61−7.54 (m, 3H), 7.52−7.46 (m, 5H), 7.44−7.38 (m, 1H), 7.28 (d, J = 7.8 Hz, 1H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.9, 140.1, 138.7, 138.2, 136.9, 134.7, 130.8, 130.1, 130.0, 129.2, 129.0, 128.8, 128.6, 128.5, 128.3, 127.4, 127.3, 126.4, 118.0, 110.1, 21.5; HRMS (ESI) m/z calcd for $C_{24}H_{18}N^+$ $[M + H]^+$ 320.1434, found 320.1431.

*3-(3-Methoxyphenyl)-1-phenyl-2-naphthonitrile (**3l**):* white solid (23.5 mg, 70% yield); mp 93.0−93.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3051, 2964, 2831, 2221, 1579, 1490, 1452, 1433, 1282, 1255, 1224, 1155, 1053, 873, 773, 752, 700; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97−7.90 (m, 2H), 7.67−7.62 (m, 2H), 7.60−7.52 (m, 3H), 7.52−7.45 (m, 3H), 7.45−7.38 (m, 1H), 7.24−7.23 (m, 1H), 7.21−7.19 (m, 1H), 7.02−6.98 (m, 1H), 3.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 159.6, 147.9, 140.1, 139.8, 136.9, 134.6, 130.9, 130.0, 129.7, 129.1, 128.8, 128.6, 128.3, 127.42, 127.37, 121.7, 117.9, 114.8, 114.3, 110.0, 55.4; HRMS (ESI) m/z calcd for $C_{24}H_{18}NO^+$ $[M + H]^+$ 336.1383, found 336.1381.

*3-(Naphthalen-2-yl)-1-phenyl-2-naphthonitrile (**3m**):* white solid (29.8 mg, 84% yield); mp 172.1−172.9 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3440, 3043, 2223, 1616, 1585, 1442, 1317, 1128, 889, 860, 815, 744, 702; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14 (s, 1H), 8.04 (s, 1H), 8.01−7.89 (m, 4H), 7.80 (d, J = 8.5 Hz, 1H), 7.71−7.63 (m, 2H),

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7.62−7.48 (m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.1, 139.9, 136.9, 136.2, 134.7, 133.3, 133.1, 130.9, 130.1, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 127.8, 127.44, 127.41, 127.0, 126.6, 126.5, 118.0, 110.2; HRMS (ESI) m/z calcd for $C_{27}H_{18}N^+$ $[M + H]^+$ 356.1434, found 356.1431.

*1-Phenyl-3-(thiophen-2-yl)-2-naphthonitrile (**3n**):* white solid (21.2 mg, 68% yield); mp 154.7−155.5 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3047, 2229, 1620, 1583, 1485, 1444, 1377, 1319, 1153, 1070, 954, 885, 854, 837, 756, 705; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.67−7.53 (m, 6H), 7.51−7.41 (m, 4H), 7.19 (dd, J = 5.1, 3.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.6, 139.8, 136.7, 134.6, 132.0, 130.9, 130.0, 129.3, 128.9, 128.69, 128.66, 128.3, 128.2, 127.9, 127.6, 127.4, 126.8, 118.0, 109.3; HRMS (ESI) m/z calcd for $C_{21}H_{14}NS^+$ $[M + H]^+$ 312.0842, found 312.0841.

*3-(4-Chlorophenyl)-4-methyl-1-phenyl-2-naphthonitrile (**3o**):* white solid (21.6 mg, 61% yield); mp 198.1−198.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ3057, 2225, 1610, 1598, 1488, 1400, 1365, 1161, 1087, 1014, 1001, 842, 765, 700, 657, 624; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18−8.14 (m, 1H), 7.75−7.66 (m, 2H), 7.57−7.41 (m, 8H), 7.36−7.29 (m, 2H), 2.53 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 145.3, 137.5, 137.4, 136.9, 134.3, 134.2, 133.0, 131.14, 131.13, 130.1, 129.1, 128.83, 128.75, 128.6, 128.2, 127.1, 124.8, 117.8, 111.2, 16.8; HRMS (ESI) m/z calcd for $C_{24}H_{17}ClN^+$ $[M + H]^+$ 354.1044, found 354.1046.

*4-Isopropyl-1,3-diphenyl-2-naphthonitrile (**3p**):* white solid (42 mg, 60% yield); mp 214.2−214.7 °C; R_f (petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3059, 2221, 1484, 1441, 1332, 1365, 1332, 1241, 1152, 1091, 1071, 1025, 762, 699, 676; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30−8.24 (m, 1H), 7.65−7.57 (m, 1H), 7.55−7.47 (m, 6H), 7.43−7.38 (m, 3H), 7.32−7.29 (m, 2H), 7.27−7.22 (m, 1H), 3.21−3.12 (m, 1H), 0.89 (d, J = 3.8 Hz, 3H), 0.87 (d, J = 3.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.6, 144.0, 141.9, 139.5, 139.1, 133.0, 130.6, 130.2, 129.7, 128.4, 128.14, 128.12, 127.9, 127.7, 127.5, 127.0, 125.1, 117.1, 112.1, 32.1, 23.0, 22.9; HRMS (ESI) m/z calcd for $C_{26}H_{22}N^+$ $[M + H]^+$ 348.1752, found 348.1748.

*1-(4-Fluorophenyl)-3-phenyl-2-naphthonitrile (**3r**):* white solid (27.5 mg, 85% yield); mp 178.8−179.6 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3057, 2223, 1606, 1514, 1490, 1218, 1161, 896, 844, 763, 752, 698; ^1H NMR (400 MHz, $CDCl_3$):δ (ppm) 7.97−7.92 (m, 2H), 7.70−7.59 (m, 4H), 7.56−7.43 (m, 6H), 7.30−7.26 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 163.1 (d, J = 248.4 Hz), 146.8, 139.9, 138.6, 134.7, 132.7 (d, J = 3.5 Hz), 131.9 (d, J = 8.3 Hz), 130.9, 129.23, 129.18, 128.9, 128.6, 128.5, 128.4, 127.6, 127.1, 117.9, 115.9 (d, J = 21.7 Hz), 110.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) −112.54; HRMS (ESI) m/z calcd for $C_{23}H_{15}NF^+$ $[M + H]^+$ 324.1183, found 324.1181.

*Methyl 4-(2-Cyano-3-phenylnaphthalen-1-yl)benzoate (**3s**):* white solid (29.0 mg, 80% yield); mp 183.4−184.3 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3429, 3060, 2948, 2221, 1716, 1614, 1492, 1434, 1278, 1107, 867, 763, 707; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.28−8.24 (m, 2H), 7.96 (d, J = 9.1 Hz, 2H), 7.70−7.62 (m, 3H), 7.62−7.44 (m, 7H), 3.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.7, 146.7, 141.6, 139.9, 138.5, 134.7, 130.6, 130.4, 130.3, 130.0, 129.3, 129.24, 129.16, 128.7, 128.6, 128.4, 127.7, 126.9, 117.7, 109.8, 52.3; HRMS (ESI) m/z calcd for $C_{25}H_{18}NO_2^+$ $[M + H]^+$ 364.1332, found 364.1333.

*3-Phenyl-1-p-tolyl-2-naphthonitrile (**3t**):* white solid (24.9 mg, 78% yield); mp 119.3−120.2 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3025, 2221, 1613, 1584, 1513, 1489, 1446, 1375, 1332, 1294, 1184, 1151, 1113, 1070, 1023, 899, 832, 790, 699, 652; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, J = 9.2 Hz, 2H), 7.71−7.58 (m, 4H), 7.54−7.45 (m, 4H), 7.38 (s, 4H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.1, 139.9, 138.8, 138.7, 134.7, 133.9, 131.0, 129.9, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 128.3, 127.5, 127.3, 118.1, 110.0, 21.5; HRMS (ESI) m/z calcd for $C_{24}H_{18}N^+$ $[M + H]^+$ 320.1434, found 320.1431.

*1-(4-Methoxyphenyl)-3-phenyl-2-naphthonitrile (**3u**):* white solid (26.8 mg, 80% yield); mp 161.5−162.3 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3062, 2933, 2223, 1610, 1575, 1514, 1492, 1382, 1249, 1031, 837, 773, 703; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95−7.90 (m, 2H), 7.74−7.60 (m, 4H), 7.56−7.40 (m, 6H), 7.13−7.07 (m, 2H), 3.92 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 160.0, 147.8, 140.0, 138.8, 134.7, 131.4, 131.1, 129.3, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 127.4, 127.3, 118.2, 114.1, 110.2, 55.3; HRMS (ESI) m/z calcd for $C_{24}H_{18}NO^+$ $[M + H]^+$ 336.1383, found 336.1381.

*1-(Furan-2-yl)-3-phenyl-2-naphthonitrile (**3v**):* white solid (21.0 mg, 71% yield); mp 145.3−150.1 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3052, 2221, 1618, 1495, 1451, 1363, 1327, 1301, 1147, 1081, 1011, 901, 821, 760, 729, 694, 632; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 11.2 Hz, 2H), 7.75 (dd, J = 1.8, 0.6 Hz, 1H), 7.69−7.62 (m, 3H), 7.62−7.56 (m, 1H), 7.55−7.44 (m, 3H), 6.95 (dd, J = 3.4, 0.6 Hz, 1H), 6.69 (dd, J = 3.4, 1.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.6, 144.0, 140.3, 138.5, 136.0, 134.8, 130.6, 129.9, 129.3, 128.62, 128.55, 128.4, 127.9, 126.9, 117.9, 113.6, 111.6, 110.3; HRMS (ESI) m/z calcd for $C_{21}H_{14}NO^+$ $[M + H]^+$ 296.1069, found 296.1068.

*3-Phenyl-1-(thiophen-2-yl)-2-naphthonitrile (**3w**):* white solid (23.6 mg, 76% yield); mp 125.3−126.0 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3064, 2219, 1614, 1589, 1488, 1440, 1369, 1326, 1288, 1224, 1145, 1072, 902, 846, 767, 700, 624; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (s, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.68−7.62 (M, 3H), 7.60 (dd, J = 5.1, 1.2 Hz, 1H), 7.57−7.43 (m, 4H), 7.31 (dd, J = 3.5, 1.1 Hz, 1H), 7.27−7.25 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 140.3, 140.0, 138.5, 136.4, 134.5, 131.9, 129.9, 129.6, 129.27, 129.26, 128.7, 128.6, 128.2, 127.9, 127.8, 127.4, 127.1, 117.6, 111.9; HRMS (ESI) m/z calcd for $C_{21}H_{14}NS^+$ $[M + H]^+$ 312.0842, found 312.0840.

*1-Methyl-3-phenyl-2-naphthonitrile (**3x**):* white solid (12.2 mg, 50% yield); mp 112.1−112.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3058, 2219, 1625, 1586, 1494, 1445, 1410, 1379, 1326, 1181, 1072, 1028, 927, 883, 777, 764, 751, 698, 676, 615; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (m, 1H), 7.91−7.84 (m, 1H), 7.77 (s, 1H), 7.68−7.58 (m, 4H), 7.54−7.40 (m, 3H), 3.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 142.8, 139.8, 139.0, 134.4, 130.7, 129.2, 128.94, 128.87, 128.6, 128.4, 127.5, 127.3, 124.9, 118.4, 110.2, 18.1; HRMS (ESI) m/z calcd for $C_{18}H_{14}N^+$ $[M + H]^+$ 244.1121, found 244.1121.

*6,7-Difluoro-1,3-diphenyl-2-naphthonitrile (**3y**):* white solid (26.6 mg, 78% yield); mp 175.1−175.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3070, 2216, 1724, 1598, 1580, 1515, 1493, 1458, 1441, 1388, 1306, 1275, 1253, 1201, 1311, 1075, 1035, 905, 870, 822, 761, 739, 700, 613, 569, 508; ^1H NMR (400 MHz, $CDCl_3$):δ (ppm) 7.86 (s, 1H), 7.67 (dd, J = 10.4, 7.8 Hz, 1H), 7.65−7.62 (m, 2H), 7.61−7.56 (m, 3H), 7.55−7.44 (m, 5H), 7.39 (dd, J = 11.7, 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$):δ (ppm) 151.9 (dd, J = 255.0, 16.0 Hz), 150.7 (dd, J = 251.5, 15.4 Hz), 147.2 (dd, J = 5.7, 2.1 Hz), 140.7 (d, J = 2.2 Hz), 138.2, 136.2, 132.0 (dd, J = 7.9, 1.0 Hz), 129.8, 129.3, 129.2, 128.9, 128.74, 128.71, 128.1 (d, J = 6.8 Hz), 127.8 (dd, J = 4.9, 1.8 Hz), 117.4, 114.1 (d, J = 17.0 Hz), 113.9 (d, J = 18.5 Hz), 110.6 (d, J = 2.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.66 (d, J = 20.8 Hz), −133.10 (d, J = 20.8 Hz); HRMS (ESI) m/z calcd for $C_{23}H_{14}F_2N^+$ $[M + H]^+$ 342.1089, found 342.1090.

*6,7-Dimethyl-1,3-diphenyl-2-naphthonitrile (**3z**):* white solid (25.0 mg, 75%, yield); mp 173.4−174.2 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3440, 3060, 2916, 2219, 1623, 1591, 1494, 1450, 1375, 1024, 902, 761, 698, 613; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (s, 1H),

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7.69−7.63 (m, 3H), 7.61−7.40 (m, 8H), 7.36 (s, 1H), 2.46 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.0, 139.5, 139.13, 139.06, 137.6, 137.2, 133.7, 130.0, 129.6, 129.3, 128.7, 128.6, 128.5, 128.2, 127.8, 127.7, 126.6, 118.3, 108.9, 20.4, 20.3; HRMS (ESI) m/z calcd for $C_{25}H_{20}N^+$ $[M + H]^+$ 334.1590, found 334.1590.

*6,7-Dimethoxy-1,3-diphenyl-2-naphthonitrile (**3aa**):* white solid (21.9 mg, 60%, yield); mp 176.9−177.4 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3019, 2221, 1617, 1571, 1506, 1460, 1428, 1248, 1225, 1142, 1073, 1031, 1013, 888, 851, 824, 768, 745, 704; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (s, 1H), 7.67−7.62 (m, 2H), 7.60−7.46 (m, 7H), 7.46−7.40 (m, 1H), 7.19 (s, 1H), 6.88 (s, 1H), 4.04 (s, 3H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 151.9, 150.4, 145.7, 139.1, 139.0, 137.4, 131.4, 129.9, 129.2, 128.8, 128.7, 128.5, 128.2, 127.0, 126.7, 118.4, 107.9, 106.4, 105.5, 56.1, 55.8; HRMS (ESI) m/z calcd for $C_{25}H_{20}NO_2^+$ $[M + H]^+$ 366.1489, found 366.1489.

*1,3-Diphenylanthracene-2-carbonitrile (**3ab**):* yellow solid (19.9 mg, 56% yield); mp 174.5−175.2 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3049, 2219, 1602, 1495, 1442, 1362, 1282, 1074, 1025, 998, 909, 772, 745, 697, 603; ^1H NMR (400 MHz, $CDCl_3$):δ (ppm) 8.49 (s, 1H), 8.21 (s, 1H), 8.07 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.74−7.67 (m, 2H), 7.66−7.41 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 149.3, 138.8, 137.9, 137.1, 133.3, 132.3, 131.7, 130.1, 129.3, 129.03, 129.00, 128.78, 128.77, 128.6, 128.4, 127.9, 127.5, 127.4, 126.9, 126.3, 118.1, 109.7; HRMS (ESI) m/z calcd for $C_{27}H_{18}N^+$ $[M + H]^+$ 356.1434, found 356.1432.

*8-Methoxy-1,3-diphenyl-2-naphthonitrile (**3ac**):* white solid (24.8 mg, 74% yield); mp 182.9−183.6 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3001, 2218, 1614, 1558, 1496, 1454, 1369, 1348, 1292, 1259, 1109, 777, 744, 702; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (s, 1H), 7.67−7.61 (m, 2H), 7.59−7.39 (m, 8H), 7.37−7.32 (m, 2H), 6.81 (dd, J = 7.5, 1.2 Hz, 1H), 3.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 157.1, 146.7, 141.6, 140.1, 138.6, 136.5, 129.8, 129.2, 128.7, 128.5, 128.4, 128.3, 127.4, 127.3, 122.5, 121.0, 117.8, 111.4, 107.3, 55.5; HRMS (ESI) m/z calcd for $C_{24}H_{18}NO^+$ $[M + H]^+$ 336.1383, found 336.1382.

*8-Methyl-1,3-diphenyl-2-naphthonitrile (**3ad**):* white solid (25.5 mg, 80% yield); mp 138.1−138.8 °C; R_f (silica, petroleum ether/EtOAc/methanol, 100:1:1) = 0.3; IR (KBr, cm^{-1}) υ 3062, 2223, 1591, 1479, 1446, 1380, 1325, 1311, 1178, 1074, 1028, 889, 811, 769, 759, 742, 700, 646, 586, 540, 514; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (s, 1H), 7.72−7.64 (m, 2H), 7.60−7.41 (m, 10H), 7.37 (dd, J = 8.5, 7.0 Hz, 1H), 2.75 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 148.3, 139.7, 139.2, 137.3, 134.8, 133.9, 131.1, 130.0, 129.8, 129.4, 128.8, 128.61, 128.56, 128.4, 127.0, 125.8, 125.1, 118.0, 109.8, 19.7; HRMS (ESI) m/z calcd for $C_{24}H_{18}N^+$ $[M + H]^+$ 320.1434, found 320.1433.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01975.

^1H, ^{13}C, and ^{19}F NMR spectra for all products and the single-crystal X-ray structure analysis of products **3a** and **3ad** (PDF)

Accession Codes

CCDC 1960284 and 1962437 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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