The Journal of Organic Chemistry

Subscriber access provided by Bethel University

Article

Synthesis of 1-Cyano-3-acylnaphthalenes via Formal [4+2] Benzannulations of 2-(2-Alkynylphenyl)acetonitriles and Alkynones

Lu-Lu Chen, Jing-Wen Zhang, Wan-Wan Yang, Ji-Ya Fu, Jun-Yan Zhu, and Yan-Bo Wang

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00948 • Publication Date (Web): 29 May 2019

Downloaded from http://pubs.acs.org on May 30, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W.,
Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works
produced by employees of any Commonwealth realm Crown government in the course
of their duties.

Synthesis of 1-Cyano-3-acylnaphthalenes *via* Formal [4+2] Benzannulations of 2-(2-Alkynylphenyl)acetonitriles and Alkynones

Lu-Lu Chen, Jing-Wen Zhang, Wan-Wan Yang, Ji-Ya Fu, Jun-Yan Zhu and Yan-Bo Wang*

Institute of Functional Organic Molecular Engineering, Henan Engineering Laboratory of Flame-Retardant and Functional Materials, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, China.

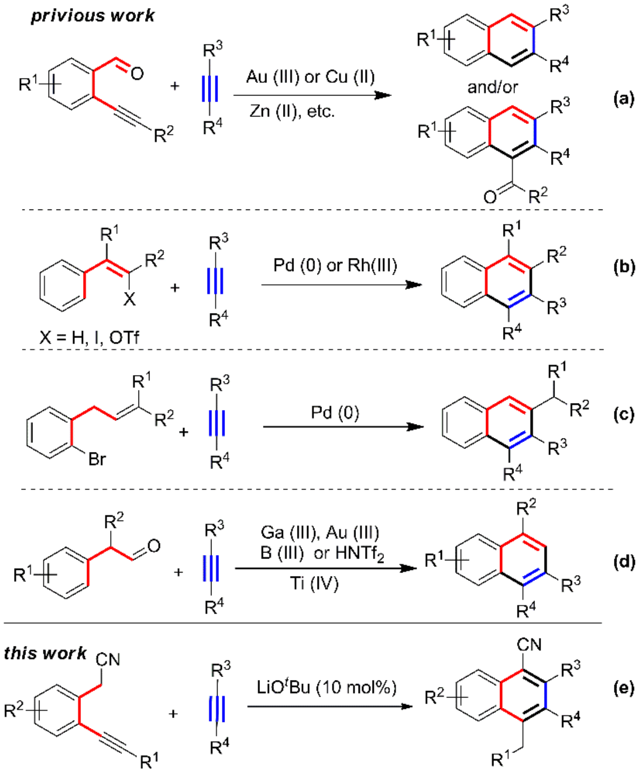
Supporting Information

ABSTRACT: An effective transition-metal-free formal [4+2] benzannulations for the preparation of 1-cyano-3-acylnaphthalenes from 2-(2-alkynylphenyl)acetonitriles and alkynones through a sequential C-C bond coupling has been developed. This protocol is characterized by mild conditions, excellent functional group tolerance, complete regioselectivity and atom economy. The plausible mechanism, gram scale synthesis and further transformations of product were studied.

INTRODUCTION

Polysubstituted naphthalenes have attracted much attention owing to the fact that they are an important structural motif with broad applications in optical and electronic materials.[1] Furthermore, they are also critical skeletons exciting in many biologically active compounds.[2] Therefore, various methods for the synthesis of the naphthalene skeleton using alkynes,[3] arynes,[4] olefins [5] or other reagents [6] have been reported. Among the reported methodologies, an efficient approach for the formal [4+2] benzannulations using alkyne as a two-carbon unit to synthesize the naphthalene derivatives is of significant interest.[7–10] For examples, a seminal work for benzannulation of alkynes with 2-alkynylbenzaldehydes was reported by Asao and Yamamoto.[7a] Subsequently, various catalytic systems suitable for benzannulation of alkynes with 2-alkynylbenzaldehydes were also reported (Scheme 1a).[7b-7i] Transition-metal-catalyzed benzannulation of arene-containing vinylic iodides and triflates or β-enaminonitriles with alkynes was described, respectively (Scheme 1b).[8] Pallaium(0)-catalyzed annulation of 1-allyl-2-bromobenzenes with alkynes has been demonstrated (Scheme 1c).[9] Additionally, naphthalene derivatives could also be synthesized by the condensation of phenylacetaldehydes with alkynes using the Lewis acids or Brønsted-acid as catalysts (Scheme 1d).[10] Besides the above examples, other formal [4+2] benzannulations using alkyne have been reported.[11] However, these catalytic systems usually need transition-metals, Lewis acids or Brønsted-acid as catalysts and demand dehalogenation or dehydration to run smoothly. To the best of our knowledge, base-mediated [4+2] benzannulation involving alkynes for the synthesis of polysubstituted naphthalenes has not been reported. Due to the cyano and acyl substituents as important functional groups, it is of critical interest to explore convenient and efficient access to the construction of naphthalene ring with diverse cyano and acyl groups. As a continuation of our interest in the catalytic transition of alkyne, [12] herein we firstly report an efficient base-catalyzed method for the synthesis of 1-cyano-3-acylnaphthalene derivatives from 2-(2-alkynylphenyl) acetonitriles and alkynones vis a sequential C-C bond coupling with complete regioselectivity and atom economy under mild conditions (Scheme 1e).

Scheme 1. Synthesis of Polysubstituted Naphthalene Derivatives via Formal [4+2] Benzannulation Reaction Involving Alkynes



RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions [a]

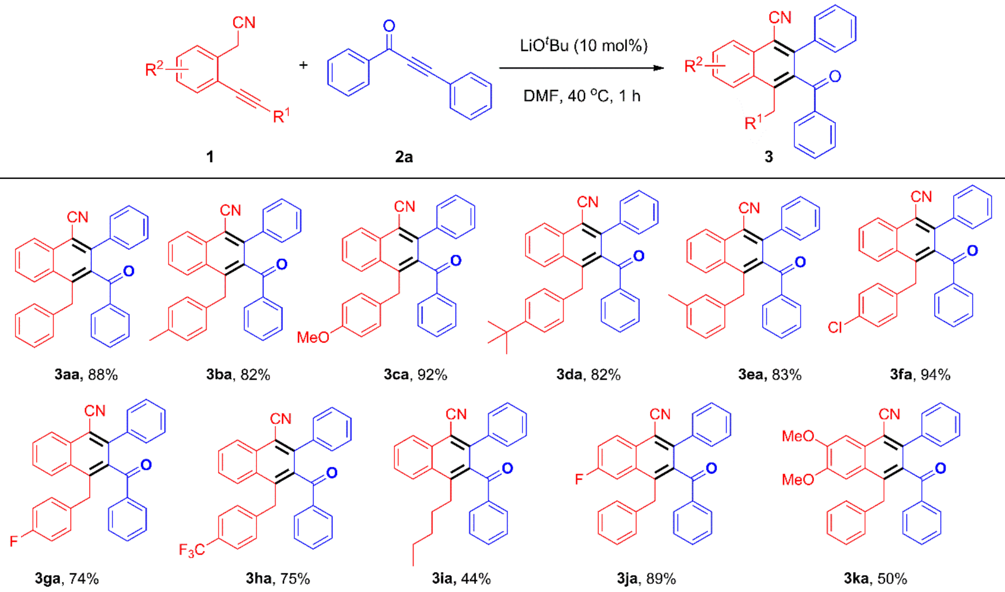
Entry	base	Solvent	Yield [b] (%)
1	K_2CO_3	DMF	56
2	Cs_2CO_3	DMF	76
3	KO^{t}Bu	DMF	65
4	NaO^{t}Bu	DMF	72
5	LiO^{t}Bu	DMF	88
6	NaOH	DMF	76
7	KOH	DMF	74
8	Et_3N	DMF	-
9	DBU	DMF	54
10[c]	LiO^{t}Bu	DMF	77
11	LiO^{t}Bu	NMP	78
12	LiO^{t}Bu	DMSO	86
13	LiO^{t}Bu	CH_3CN	trace
14	LiO^{t}Bu	1,4-dioxane	-
15	LiO^{t}Bu	THF	-
16	LiO^{t}Bu	CH_2Cl_2	-

[a] Reaction conditions: **1a** (0.30 mmol), **2a** (0.30 mmol), base (0.03 mmol) and solvent (1.5 mL) at 40 ºC for 1 h. [b] Isolated yields. [c] **1a** (0.30 mmol), **2a** (0.30 mmol) and base (0.015 mmol) was used.

Initially, we choose 2-(2-(phenylethynyl)phenyl)acetonitrile **1a** and alkynone **2a** as model substrates and the experimental results are summarized in Table 1. To our delight, when the reaction of 2-(2-(phenylethynyl)phenyl)acetonitrile **1a** and alkynone **2a** using 0.1 equiv. amount of K_2CO_3 as catalyst in DMF under 40 ℃ was attempted, desired product **3aa** was obtained in 56% yield (Table 1, entry 1). The structure of **3aa** was unambiguously determined by X-ray crystallography (see Supporting Information). Next, different inorganic bases were screening and the experimental results revealed that LiO^{t}Bu was superior, leading to a higher yield (entries 2−7). However, it failed to deliver product **3aa** by the usage of Et_3N as catalyst (Table 1, entry 8). When DBU was used as catalyst, the product **3aa** was afforded in 54% yield. A decline in the yield of **3aa** appeared when the loading of LiO^{t}Bu was decreased from 0.1 to 0.05 equiv. (Table 1, entry 10). Further condition optimization of reaction solvents was conducted. Solvent including NMP or DMSO proved to be less effective (entries 11−12). However, other solvent such as CH_3CN, 1,4-dioxane, THF or CH_2Cl_2 afforded the product **3aa** in trace or no yields (Table 1, entries 13-16).

Having identified the optimal conditions for this benzannulations reaction, the scope of 2-(2-alkynylphenyl) acetonitriles was then tested (Table 2). The electronic effect of substituents at the 4-position of phenyl ring in the R^1 group has little influence on the reaction reactivity. Both electron-donating (4-Me **1b**, 4-OMe **1c**, 4-^{t}Bu **1d**) and electron-withdrawing (4-Cl **1f**, 4-F **1g**, 4-CF_3 **1h**) substituents could be smoothly transformed into the corresponding products with moderate to excellent yields. Substrate **1e** with 3-Me group could give good yield. Furthermore, 2-(2-(hex-1-yn-1-yl)phenyl)acetonitrile **1i** as substrate was also suitable to this reaction, affording the product **3ia** in 44% yield. The low yield of the desired product **3ia** may be affected by the conjugation effect. In addition, substrate **1j** with 5-F group was also competent in this reaction. However, **1k** with more electron-donating substituent (4,5-dimethoxy group) may go against this cyclization reaction to give the moderate yield.

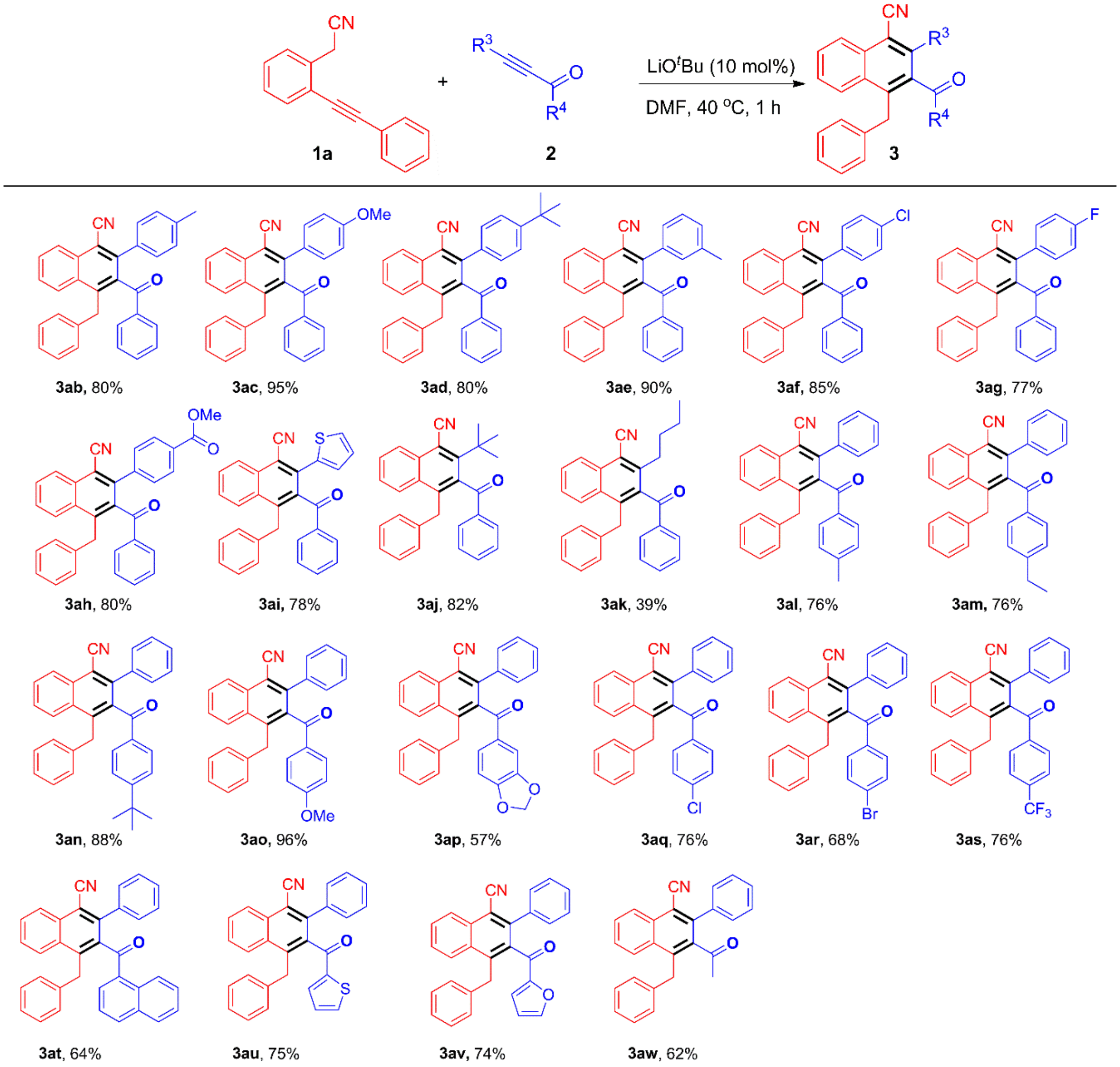
Table 2. Benzannulation Reaction of Various 2-(2-Alkynylphenyl)acetonitriles 1 with Alkynone 2a [a]



[a]Reaction conditions: **1** (0.30 mmol), **2a** (0.30 mmol), Li^{t}OBu (0.03 mmol) and DMF (1.5 mL) at 40 °C for 1 h.

After successful catalytic transition of 2-(2-alkynylphenyl) acetonitriles **1** into the 1-cyano-3-acylnaphthalenes **3**, we next investigated the generality of various alkynones **2** with 2-(2-(phenylethynyl)phenyl)acetonitrile **1a**. This catalytic system exhibits broad substrate tolerance and various of 1-cyano-3-acylnaphthalenes **3** were obtained in moderate to excellent yields as depicted in Table 3. The R^3 groups at the 3-positions of alkynones were firstly studied. Using 3-aryl substituted alkynones with different electron-rich (4-Me **2b**, 4-OMe **2c**, 4-^{t}Bu **2d**), electron-withdrawing (4-Cl **2f**, 4-F **2g**, 4-CO_2Me **2h**) or heteroaromatic derivative (**2i**) as substrates, the corresponding products could be smoothly generated. Substrate **2e** with 3-Me on the phenyl ring was suitable to this reaction in 90% yield. Additionally, the substrate **2j** bearing *t*-butyl-substitution could also provide the product **3aj** in 82% yield. Different from the substrate **2j**, alkynone **2k** with *n*-butyl substitution give the desired product **3ak** in only 39% yield due to the existence of unknown by-products. Furthermore, The R^4 groups at the 1-positions of alkynones were next explored. Similar to the R^3 groups, common substituent containing alkyl (**2l-2n**), ether (**2o-2p**), halo (**2q-2r**), or trifluoromethyl (**2s**) group at *para* position of the phenyl ring, was all tolerated in this reaction. Alkynone with naphthyl (**2t**) or heteroaromatic (**2u-2v**) substrates were compatible with this reaction. Notably, this protocol could also be extended to methyl substrate **2w**, leading to the product **3aw** in 62% yield.

Table 3. Benzannulation Reaction of 2-(2-Alkynylphenyl)acetonitrile 1a with Various Alkynones 2 [a]



3ab, 80% **3ac**, 95% **3ad**, 80% **3ae**, 90% **3af**, 85% **3ag**, 77%

3ah, 80% **3ai**, 78% **3aj**, 82% **3ak**, 39% **3al**, 76% **3am**, 76%

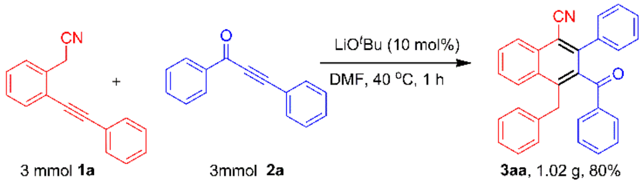
3an, 88% **3ao**, 96% **3ap**, 57% **3aq**, 76% **3ar**, 68% **3as**, 76%

3at, 64% **3au**, 75% **3av**, 74% **3aw**, 62%

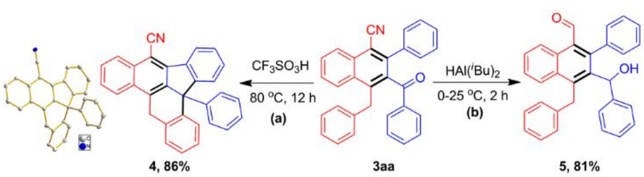
[a]Reaction conditions: **1a** (0.30 mmol), **2** (0.30 mmol), Li^{t}OBu (0.03 mmol) and DMF (1.5 mL) at 40 °C for 1 h.

For the practicability and effectiveness of this new method to be demonstrated, this reaction proceeded smoothly to give the desired product **3aa** in 80% isolated yield under the optimal conditions, when we carried out a gram scale experiment (Scheme 2). To further investigate application of this 1-cyano-3-acylnaphthalenes for constructing functionalized compounds, the product **4** was given by the cyclization of **3aa** in the presence of CF_3SO_3H (Scheme 3a), the structure of which was characterized by X-ray crystallography (see Supporting Information). **3aa** was also reduced to deliver the product **5** in the presence of $HAl(^iBu)_2$ (Scheme 3b).

Scheme 2. Gram-Scale Reaction for Synthesis of Product 3aa

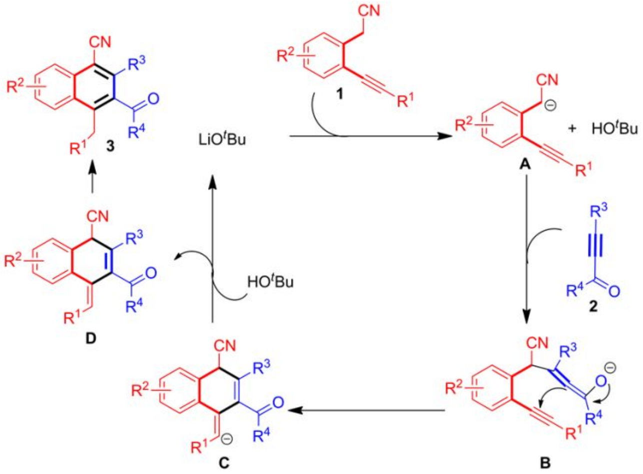


Scheme 3. The Further Transformation of Product 3aa



Scheme 4. Control Experiment

Scheme 5. Plausible Mechanisms for the Synthesis of 1-Cyano-3-acylnaphthalenes Naphthalenes.



To exclude a radical mechanism for this present method, we conducted control experiment under the radical scavenger such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), and the reaction could smoothly run to give the product **3aa** in 61% yield under standard conditions (Scheme 4). On the basis of the above results and previous literatures, [13] a plausible mechanism was proposed and shown in Scheme 5. For the first step, intermediate **A** could be produced by deprotonation of 2-(2-alkynylphenyl)acetonitriles in the presence of LiO^{t}Bu. Then, intermediate **A** added to triple bond of alkynones by nucleophilic attack to obtain intermediate **B**. Subsequently, the new intermediate **C** could be generated by intramolecular cyclization. Usually, carbon anion could attack the triple bond of terminal alkyne.[14] However, this is rare example that carbon anion directly adds to triple bond of internal alkyne without electron-withdrawing group in absence of transition-metal or Lewis acids.[14d] Intermediate **C** was transmitted into intermediate **D** by capturing hydrogen proton. Finally, the products **3** were released by the aromatization.

CONCLUSION

In summary, we have demonstrated a convenient base-mediated approach for the synthesis of 1-cyano-3-acylnaphthalenes from 2-(2-alkynylphenyl)acetonitriles and alkynones through a sequential C-C bond coupling with complete regioselectiviy and atom economy under mild conditions. This strategy provides an efficient and transition-metal-free method and various of the functional products were prepared in moderate to excellent yields. This reaction mays undergo a rare process that carbon anion directly attacks the triple bond of internal alkynes without electron-withdrawing groups in the absence of transition-metals and Lewis acids. What's more, the suitability for gram-scale reaction and facile further transformation of 1-cyano-3-acylnaphthalenes enhance the utility of this new method.

EXPERIMENTAL SECTION

General Information. Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen atmosphere. NMR spectra were recorded with tetramethylsilane as the internal standard. NMR spectrawere recorded on a BrukerAvanceII400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) was measured using a Nicolet NEXUS FT-IR spectrophotometer. CH_2Cl_2, DMSO and DMF were distilled from calcium hydride under N_2 atmosphere. Acetonitrile was distilled from phosphorus pentoxide under N_2 atmosphere. Tetrahydrofuran and 1,4-dioxane were distilled from sodium/benzophenone under N_2 atmosphere. The substrates **1** were synthesized from 2-(2-bromophenyl)acetonitriles and terminal alkynes according the literatures. [15] The substrates **2** were prepared by the Sonogashira coupling of acyl chlorides with terminal alkynes. [16]

Representative Experimental Procedure for Benzannulations of 2-(2-Alkynylphenyl)acetonitriles and Alkynones. A 10 mL oven-dried Schlenck tube was charged with 2-(2-(phenylethynyl)phenyl)acetonitriles **1** (0.30 mmol), alkynones **2** (0.30 mmol) and DMF (1.5 mL), then LiO^{t}Bu (2.4

mg, 0.03 mmol) was added into reaction solution. The tube was sealed and the reaction mixture was stirred at 40 ℃ using oil bath for 1 h. After completion of this reaction, the resulting mixture was diluted with ethyl acetate (10 mL) and washed with H_2O (10 mL). The aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were then washed with brine (10 mL) and dried over anhydrous Na_2SO_4, filtered and concentrated in-vacuo. The crude reaction mixture was purified by column chromatography on silica gel (PE/EtOAc) to give products **3**.

3-Benzoyl-4-benzyl-2-phenyl-1-naphthonitrile (3aa): white solid (111.8 mg, 88% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 258.5–260.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.41 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.61 (dd, *J* = 11.4, 4.0 Hz, 1H), 7.45–7.09 (m, 15H), 4.42 (q, *J* = 15.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.5, 143.7, 139.2, 139.1, 138.7, 137.3, 136.3, 133.6, 133.0, 131.3, 129.4, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 126.5, 126.5, 126.2, 116.8, 110.2,36.4; IR (KBr, cm^{-1}): 3436, 3080, 3061, 3027, 2929, 2222, 1669, 1594, 1579, 1498, 1449; HRMS (ESI-TOF) calcd for $C_{31}H_{22}NO^+$ ([M+H]$^+$): 424.1696, found: 424.1699.

3-Benzoyl-4-(4-methylbenzyl)-2-phenyl-1-naphthonitrile (3ba): white solid (107.6 mg, 82% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 234.1–236.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.48–6.88 (m, 14H), 4.37 (dd, *J* = 66.3, 15.7 Hz, 2H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 143.6, 139.5, 138.6, 137.3, 136.3, 136.0, 133.5, 133.0, 131.3, 129.3, 129.3, 129.23, 128.8, 128.3, 128.3, 128.3, 128.1, 126.4, 126.2, 116.8, 110.1, 36.0, 21.0; IR (KBr, cm^{-1}): 3054, 2927, 2222 ， 1669, 1595, 1579, 1448; HRMS (ESI-TOF) calcd for $C_{32}H_{24}NO^+$ ([M+H]$^+$): 438.1852, found: 438.1856.

4-(4-Methoxybenzyl)-3-benzoyl-2-phenyl-1-naphthonitrile (3ca): white solid (125.2 mg, 92% yield); eluent: petroleum ether/ethyl acetate (20:1); mp 189.9–190.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.38 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.71 (dd, *J* = 11.3, 3.9 Hz, 1H), 7.62–7.55 (m, 1H), 7.46–6.62 (m, 14H), 4.32 (dd, *J* = 64.2, 15.6 Hz, 2H), 3.67 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.5, 158.2, 143.6, 139.6, 138.5, 137.3, 136.3, 133.5, 133.0, 131.2, 131.1, 129.4, 129.3, 128.8, 128.3, 128.3, 128.1, 126.4, 126.2, 116.8, 114.0, 110.0, 55.2, 35.5; IR (KBr, cm^{-1}): 3064, 2997, 2834, 2223, 1676, 1608, 1581, 1509, 1448; HRMS (ESI-TOF) calcd for $C_{32}H_{24}NO_2^+$ ([M+H]$^+$): 454.1802, found: 454.1805.

4-(4-Tert-butylbenzyl)-3-benzoyl-2-phenyl-1-naphthonitrile (3da): white solid (118.0 mg, 82% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 218.9–220.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.67–7.60 (m, 1H), 7.47–6.92 (m, 14H), 4.38 (q, *J* = 15.5 Hz, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.4, 149.2, 143.6, 139.6, 138.5, 137.3, 136.3, 135.8, 133.4, 133.0, 131.3, 129.3, 128.7, 128.3, 128.2, 128.1, 126.4, 126.2, 125.4, 116.8, 110.0, 35.7, 34.3, 31.3; IR (KBr, cm^{-1}): 3058, 2962, 2869, 2222, 1672, 1595, 1578, 1563, 1450; HRMS (ESI-TOF) calcd for $C_{35}H_{30}NO^+$ ([M+H]$^+$): 480.2322, found: 480.2325.

3-Benzoyl-4-(3-methylbenzyl)-2-phenyl-1-naphthonitrile (3ea): yellow solid (108.9 mg, 83% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 245.8–247.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.48–6.83 (m, 14H), 4.38 (q, *J* = 15.4 Hz, 2H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.5, 143.6, 139.4, 139.0, 138.7, 138.2, 137.3, 136.3, 133.6, 133.0, 131.4, 129.4, 129.4, 129.3, 128.8, 128.5, 128.3, 128.2, 127.3, 126.5, 126.3, 125.5, 116.9, 110.1, 36.3, 21.5; IR (KBr, cm^{-1}): 3084, 3030, 2925, 2223, 1666, 1595, 1565, 1450; HRMS (ESI-TOF) calcd for $C_{32}H_{24}NO^+$ ([M+H]$^+$): 438.1852, found: 438.1856.

4-(4-Chlorobenzyl)-3-benzoyl-2-phenyl-1-naphthonitrile (3fa): white solid (129.1 mg, 94% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 189.1–190.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.44–7.05 (m, 14H), 4.37 (dd, *J* = 71.3, 15.7 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.4, 143.6, 138.7, 138.5, 137.5, 137.1, 136.1, 133.7, 133.0, 132.4, 131.1, 129.8, 129.5, 129.3, 128.9, 128.7, 128.5, 128.4, 128.2, 126.6, 125.9, 116.7, 110.4, 35.7; IR (KBr, cm^{-1}): 3436, 3084, 3065, 3036, 2933, 2227, 1664, 1596, 1492, 1450; HRMS (ESI-TOF) calcd for $C_{31}H_{21}ClNO^+$ ([M+H]$^+$): 458.1306, found: 458.1308.

4-(4-Fluorobenzyl)-3-benzoyl-2-phenyl-1-naphthonitrile (3ga): white solid (98.0 mg, 74% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 246.9–247.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.02 (m, 12H), 6.86 (t, *J* = 8.6 Hz, 2H), 4.38 (dd, *J* = 70.7, 15.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.4, 161.5 (d, $J_{C\text{-}F}$= 245.0 Hz), 143.6, 138.9, 138.6, 137.2, 136.1, 134.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 133.7, 133.0, 131.1, 129.9 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.4, 129.3, 128.8, 128.4, 128.3, 128.2, 126.5, 125.9, 116.7, 115.4 (d, *J* = 21.4 Hz), 110.3, 35.5; IR (KBr, cm^{-1}): 3436, 3060, 2931, 2223, 1666, 1605, 1579, 1511, 1448, 1411; HRMS (ESI-TOF) calcd for $C_{31}H_{21}FNO^+$ ([M+H]$^+$): 442.1602, found: 442.1606.

4-(4-(Trifluoromethyl)benzyl)-3-benzoyl-2-phenyl-1-

naphthonitrile (3ha): white solid (110.6 mg, 75% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 210.9–202.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.45 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.66 (dd, *J* = 11.4, 4.1 Hz, 1H), 7.50–7.12 (m, 14H), 4.47 (dd, *J* = 70.2, 15.7 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 197.5, 143.6, 143.1 (q, $J_{\text{C-F}}$ = 1.2 Hz), 138.9, 138.0, 137.0, 136.1, 133.8, 133.1, 131.0, 129.6, 129.3, 129.1, 128.9, 128.8, 128.7, 128.4, 128.3, 126.7, 125.7, 125.6 (q, $J_{\text{C-F}}$ = 3.7 Hz), 124.2 (q, $J_{\text{C-F}}$ =270.3Hz), 116.7, 110.6, 36.1; IR (KBr, cm^{-1}): 3059, 2929, 2226, 1667, 1596, 1565, 1449; HRMS (ESI-TOF) calcd for $C_{32}H_{21}F_3NO^+$ ([M+H]$^+$): 492.1570, found: 492.1572.

3-Benzoyl-4-pentyl-2-phenyl-1-naphthonitrile: (**3ia**): white solid (53.3 mg, 44% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 172.5–173.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, *J* = 7.4 Hz, 1H), 7.58–7.42 (m, 2H), 7.42–7.30 (m, 2H), 7.28–6.95 (m, 9H), 3.31 (d, *J* = 133.8 Hz, 2H), 2.33 (t, *J* = 7.7 Hz, 2H), 1.64 (s, 2H), 1.32–1.14 (m, 2H), 0.90–0.75 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 195.4, 153.8, 152.9, 139.2, 138.3, 137.3, 133.9, 133.3, 133.1, 132.7, 130.5, 130.2, 129.4, 128.4, 128.4, 128.1, 128.0, 127.4, 127.1, 119.0, 114.1, 39.4, 35.8, 30.9, 22.8, 13.9; IR (KBr, cm^{-1}): 2958, 2930, 2871, 2212, 1661, 1593, 1448; HRMS (ESI-TOF) calcd for $C_{29}H_{26}NO^+$ ([M+H]$^+$): 404.2009, found: 404.2012.

3-Benzoyl-4-benzyl-6-fluoro-2-phenyl-1-naphthonitrile (3ja): white solid (117.9 mg, 89% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 227.8–229.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (dd, *J* = 9.1, 5.5 Hz, 1H), 7.73 (dd, *J* = 10.5, 2.2 Hz, 1H), 7.57–7.47 (m, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.24–7.11 (m, 10H), 4.34 (q, *J* = 15.7 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.1, 161.9 (d, $J_{\text{C-F}}$= 250.5 Hz), 143.0 (d, *J* = 2.8 Hz), 139.6, 138.5 (d, $J_{\text{C-F}}$ = 5.6 Hz), 138.5, 137.1, 136.0, 133.7, 132.7 (d, $J_{\text{C-F}}$ = 9.0 Hz), 129.9, 129.3, 129.2 (d, $J_{\text{C-F}}$ = 9.2 Hz), 128.9, 128.8, 128.4, 128.4, 128.2, 126.7, 119.7 (d, $J_{\text{C-F}}$ = 25.4 Hz), 116.6, 110.3 (d, $J_{\text{C-F}}$ = 22.4 Hz), 110.2 (d, $J_{\text{C-F}}$ = 1.2Hz), 36.6; IR (KBr, cm^{-1}): 3085, 3061, 3028, 2924, 2225, 1669, 1594, 1579, 1503, 1409; HRMS (ESI-TOF) calcd for $C_{31}H_{21}FNO^+$ ([M+H]$^+$): 442.1602, found: 442.1604.

3-Benzoyl-4-benzyl-6,7-dimethoxy-2-phenyl-1-naphthonitrile (3ka): white solid (72.5 mg, 50% yield); eluent: petroleum ether/ethyl acetate (5:1); mp 319.3–320.1℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.41–7.06 (m, 14H), 4.32 (d, *J* = 11.8 Hz, 2H), 4.06 (s, 3H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 198.0, 152.2, 150.9, 141.5, 139.3, 137.6, 137.5, 137.0, 136.7, 133.5, 129.9, 129.4, 128.7, 128.6, 128.5, 128.3, 128.1, 127.1, 126.6, 117.4, 108.2, 105.1, 104.8, 56.4, 56.0, 37.1; IR (KBr, cm^{-1}): 3023, 2999, 2834, 2219, 1669, 1594, 1570, 1509, 1498, 1470, 1433; HRMS (ESI-TOF) calcd for $C_{33}H_{26}NO_3^+$ ([M+H]$^+$): 484.1907, found: 484.1908.

3-Benzoyl-4-benzyl-2-p-tolyl-1-naphthonitrile (3ab): white solid (105.0 mg, 80% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 234.8–236.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31–6.76 (m, 11H), 4.38 (dd, *J* = 56.9, 15.7 Hz, 2H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 197.5, 143.8, 139.0, 139.0, 138.7, 138.7, 137.3, 133.6, 133.3, 133.0, 131.2, 129.4, 129.3, 128.9, 128.6, 128.4, 128.3, 128.2, 126.5, 126.4, 126.1, 116.9, 110.22, 36.4, 21.3; IR (KBr, cm^{-1}): 3063, 3029, 2921, 2221, 1671, 1594, 1497, 1448; HRMS (ESI-TOF) calcd for $C_{32}H_{24}NO^+$ ([M+H]$^+$): 438.1852, found: 438.1859.

3-Benzoyl-4-benzyl-2-(4-methoxyphenyl)-1-naphthonitrile (3ac): yellow solid (129.3 mg, 95% yield); eluent: petroleum ether/ethyl acetate (10:1); mp 219.2–221.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30–7.06 (m, 9H), 6.76 (s, 2H), 4.39 (dd, *J* = 58.1, 15.9 Hz, 2H), 3.70 (d, *J* = 17.4 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm): 197.6, 159.8, 143.4, 139.0, 138.8, 137.2, 133.6, 133.0, 131.1, 129.3, 129.3, 128.6, 128.4, 128.4, 128.4, 128.2, 126.5, 126.3, 126.1, 117.0, 113.7, 110.2, 55.2, 36.4; IR (KBr, cm^{-1}): 3060, 3030, 2969, 2939, 2222, 1670, 1608, 1594, 1569, 1516, 1497, 1449; HRMS (ESI-TOF) calcd for $C_{32}H_{24}NO_2^+$ ([M+H]$^+$): 454.1802, found: 454.1804.

3-Benzoyl-4-benzyl-2-(4-(tert-butyl)phenyl)-1-naphthonitrile (3ad) : yellow solid (115.1 mg, 80% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 189.0–190.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H),7.37–7.12 (m, 14H), 4.44 (dd, *J* = 55.2, 15.5 Hz, 2H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (75MHz, $CDCl_3$) δ (ppm): 197.6, 159.8, 143.4, 139.0, 138.8, 137.2, 133.6, 133.0, 131.1, 129.3, 129.3, 128.6, 128.4, 128.4, 128.4, 128.12, 126.5, 126.3, 126.1, 117.0, 113.7, 110.2, 55.2, 36.4; IR (KBr, cm^{-1}): 3062, 2956, 2869, 2219, 1667, 1598, 1581, 1496, 1451; HRMS (ESI-TOF) calcd for$C_{35}H_{30}NO^+$ ([M+H]$^+$): 480.2322, found: 480.2325.

3-Benzoyl-4-benzyl-2-m-tolyl-1-naphthonitrile (3ae): yellow solid (118.1 mg, 90% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 225.8–226.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31–6.83 (m, 11H)., 4.41 (dd, *J* = 58.4, 14.9 Hz, 2H), 2.20 (d, *J* = 86.3 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm): 197.5, 143.9, 139.1, 139.1, 138.7, 137.4, 136.2, 133.5, 133.0, 131.2, 129.5, 129.3, 128.6, 128.4, 128.3, 128.2, 128.0, 126.5, 126.4, 126.2, 116.8, 110.1, 36.4, 21.3; IR (KBr, cm^{-1}): 3084, 3060, 3031, 2925, 2217, 1665, 1596, 1567, 1496, 1450; HRMS (ESI-TOF) calcd for C$_{32}$H$_{24}$NO$^+$ ([M+H]$^+$): 438.1852, found: 438.1856.

3-Benzoyl-4-benzyl-2-(4-chlorophenyl)-1-naphthonitrile (3af): yellow solid (116.8 mg, 85% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 242.5–243.8 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.40 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.52–6.75 (m, 14H), 4.41 (q, *J* = 16.0 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ (ppm): 197.3, 142.2, 139.4, 138.9, 138.4, 137.1, 135.1, 134.7, 133.9, 132.9, 131.3, 129.5, 129.3, 128.6, 128.6, 128.5, 128.4, 126.6, 126.4, 126.2, 116.6, 110.2, 36.4; IR (KBr, cm^{-1}): 3756, 2380, 2345, 2225, 1668, 1511, 1594, 1497, 1404; HRMS (ESI-TOF) calcd for C$_{31}$H$_{21}$ClNO$^+$ ([M+H]$^+$): 458.1306, found: 458.1309.

3-Benzoyl-4-benzyl-2-(4-fluorophenyl)-1-naphthonitrile (3ag): yellow solid (102.0 mg, 77% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 228.6–229.5 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.34 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46–7.00 (m, 14H), 4.35 (q, *J* = 15.7 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ (ppm): 197.4, 162.8 (d, *J* = 249.2 Hz), 142.4, 139.3, 138.9, 138.6, 137.1, 133.8, 132.9, 132.2 (d, *J* = 3.5 Hz), 131.3, 129.4, 129.3, 128.6, 128.5, 128.4, 126.5, 126.4, 126.1, 116.7, 115.3 (d, *J* = 22.2 Hz), 110.3, 36.3; IR (KBr, cm^{-1}): 3435, 2929, 2223, 1669, 1595, 1494, 1448, 1314; HRMS (ESI-TOF) calcd for C$_{31}$H$_{21}$FNO$^+$ ([M+H]$^+$): 442.1602, found: 442.1604.

Methyl 4-(3-benzoyl-4-benzyl-1-cyanonaphthalen-2-yl)benzoate (3ah): yellow solid (115.6 mg, 80% yield); eluent: petroleum ether/ethyl acetate (10:1); mp 203.5–204.8; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.33 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.00–7.65 (m, 3H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.42–6.96 (m, 12H), 4.34 (q, *J* = 15.7 Hz, 2H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ (ppm): 197.1, 166.5, 142.4, 140.8, 139.4, 138.8, 138.1, 137.0, 133.9, 132.8, 131.4, 130.3, 129.5, 129.3, 128.6, 128.6, 128.5, 128.4, 126.6, 126.5, 126.2, 116.5, 110.1, 52.3, 36.4; IR (KBr, cm^{-1}): 3400, 2344, 2224, 1725, 1665, 14978, 1449, 1433, 1404; HRMS (ESI-TOF) calcd for C$_{33}$H$_{24}$NO$_3^+$ ([M+H]$^+$): 482.1751, found: 482.1755.

3-Benzoyl-4-benzyl-2-(thiophen-2-yl)-1-naphthonitrile (3ai): yellow solid (100.5 mg, 78% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 219.1–220.1 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.39 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.63–7.36 (m, 4H), 7.30–6.98 (m, 9H), 6.88 (t, *J* = 4.2 Hz, 1H), 4.38 (dd, *J* = 51.7, 16.0 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ (ppm): 197.2, 139.2, 139.1, 138.9, 137.0, 136.2, 135.8, 133.8, 133.0, 131.6, 131.2, 129.5, 129.5, 128.7, 128.6, 128.5, 128.4, 127.2, 126.6, 126.6, 126.2, 116.7, 111.4, 36.4; IR (KBr, cm^{-1}): 3102, 3078, 3061, 3027, 2222, 1669, 1596, 1569, 1497; HRMS (ESI-TOF) calcd for C$_{29}$H$_{20}$NOS$^+$ ([M+H]$^+$): 430.1260, found: 430.1263.

3-Benzoyl-4-benzyl-2-tert-butyl-1-naphthonitrile (3aj) : white solid (99.3 mg, 82% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 169.2–170.1; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.73 (d, *J* = 7.8 Hz, 1H), 7.57– 7.31 (m, 6H), 7.30 – 7.06 (m, 7H), 6.47 (d, *J* = 294.8 Hz, 2H), 1.46 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ (ppm): 193.3, 162.7, 136.8, 134.8, 133.4, 133.1, 132.2, 132.1, 131.6, 129.2, 129.1, 128.8, 128.7, 128.6, 128.4, 128.0, 125.1, 123.8, 117.8, 111.8, 48.6, 37.8, 30.0; IR (KBr, cm^{-1}): 3368, 3063, 2997, 2958, 2909, 2216, 1688, 1639, 1596, 1481, 1448; HRMS (ESI-TOF) calcd for C$_{29}$H$_{26}$NO$^+$ ([M+H]$^+$): 404.2009, found: 404.2012.

3-Benzoyl-4-benzyl-2-butyl-1-naphthonitrile (3ak) : white solid (47.2 mg, 39% yield); eluent: petroleum ether/ethyl acetate (100:1); mp 154–155.3 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.32 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.81–7.64 (m, 3H), 7.63–7.48 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.11 (ddd, J = 22.7, 14.5, 6.9 Hz, 5H), 4.29 (q, *J* = 16.1 Hz, 2H), 3.20–2.46 (m, 2H), 1.88– 1.46 (m, 2H), 1.33 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ (ppm): 197.8, 144.4, 138.9, 138.5, 138.5, 137.0, 134.4, 133.2, 130.5, 129.6, 129.0, 128.9, 128.6, 128.3, 127.6, 126.5, 125.9, 116.9, 109.9, 36.5, 33.5, 33.5, 22.9, 13.6; IR (KBr, cm^{-1}): 3434, 3028, 2930, 2221, 1670, 1595, 1577, 1498, 1449; HRMS (ESI-TOF) calcd for C$_{29}$H$_{26}$NO$^+$ ([M+H]$^+$): 404.2009, found: 404.2012.

4-Benzyl-3-(4-methylbenzoyl)-2-phenyl-1-naphthonitrile (3al): white solid (99.8 mg, 76% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 189.1–191.1 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.39 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.37–7.09 (m, 12H), 6.98 (d, J = 7.9 Hz, 1H), 4.37 (dd, *J* = 56.0, 16.0 Hz, 2H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm): 196.9, 144.7, 143.7, 139.1, 138.9, 138.9, 136.4, 134.9, 133.0, 131.3, 129.6, 129.2, 129.1, 128.8, 128.6, 128.4, 128.2, 128.2, 126.4, 126.4, 126.2, 116.8, 110.2, 36.5, 21.8; IR (KBr, cm^{-1}): 3062, 3028, 2223, 1665, 1602, 1496, 1446, 1415; HRMS (ESI-TOF) calcd for C$_{32}$H$_{24}$NO$^+$ ([M+H]$^+$): 438.1852, found: 438.1856.

4-Benzyl-3-(4-ethylbenzoyl)-2-phenyl-1-naphthonitrile (3am): yellow solid (103.0 mg, 76% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 201.5–202.3 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.41 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47–

7.32 (m, 3H), 7.17 (dt, *J* = 12.3, 9.9 Hz, 11H), 4.41 (q, *J* = 16.0 Hz, 2H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ (ppm): 197.6, 144.8, 143.8, 139.1, 138.8, 137.3, 133.5, 133.0, 131.1, 129.3, 128.6, 128.4, 128.3, 128.2, 127.7, 126.5, 126.4, 126.1, 117.0, 110.1, 36.3, 28.6, 15.2; IR (KBr, cm^{-1}): 3031, 2969, 2923, 2853, 2220, 1670, 1595, 1567, 1514, 1497, 1450, 1408; HRMS (ESI-TOF) calcd for $C_{33}H_{26}NO^+$ ([M+H]$^+$): 452.2009, found: 452.2011.

4-Benzyl-3-(4-tert-butylbenzoyl)-2-phenyl-1-naphthonitrile (3an): yellow solid (126.6 mg, 88% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 211.6–212.5 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7 8.39 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.44–6.93 (m, 14H), 4.38 (q, *J* = 15.7 Hz, 2H), 1.22 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$) δ (ppm): 197.0, 157.5, 143.8, 139.1, 138.9, 136.4, 134.8, 132.9, 131.3, 129.4, 129.2, 128.7, 128.6, 128.4, 128.2, 128.1, 126.4, 126.1, 125.3, 116.8, 110.2, 36.5, 35.2, 31.0; IR (KBr, cm^{-1}):3316, 3085, 3060, 2968, 2873, 2224, 1665, 1601, 1567, 1454, 1446; HRMS (ESI-TOF) calcd for $C_{35}H_{30}NO^+$ ([M+H]$^+$): 480.2322, found: 480.2325.

4-Benzyl-3-(4-methoxybenzoyl)-2-phenyl-1-naphthonitrile (3ao): yellow solid (130.6 mg, 96% yield); eluent: petroleum ether/ethyl acetate (20:1); mp 181.2–183 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.37 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.48–7.04 (m, 12H), 6.68 (t, *J* = 16.9 Hz, 2H), 4.36 (q, *J* = 16.0 Hz, 2H), 3.74 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ (ppm): 195.7, 163.9, 143.7, 139.2, 138.9, 138.9, 136.4, 132.9, 131.9, 131.3, 130.4, 129.2, 128.8, 128.6, 128.4, 128.3, 128.2, 126.5, 126.4, 126.1, 116.9, 113.7, 110.1, 55.5, 36.5; IR (KBr, cm^{-1}):3066, 3028, 2970, 2367, 2218, 1660, 1591, 1507, 1496, 1445; HRMS (ESI-TOF) calcd for $C_{32}H_{24}NO_2^+$ ([M+H]$^+$): 454.1802, found: 454.1806.

3-(Benzo[d][1,3]dioxole-5-carbonyl)-4-benzyl-2-phenyl-1-naphthonitrile (3ap): white solid (79.9 mg, 57% yield); eluent: petroleum ether/ethyl acetate (10:1); mp 200.0–201.6 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.40 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.35–7.07 (m, 10H), 7.04 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 5.94 (d, *J* = 3.5 Hz, 2H), 4.39 (q, *J* = 16.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ (ppm): 195.2, 152.3, 148.1, 143.6, 139.1, 138.9, 138.7, 136.3, 132.9, 132.2, 131.2, 129.3, 128.8, 128.6, 128.4, 128.3, 128.2, 127.1, 126.5, 126.4, 126.1, 116.8, 110.1, 108.2, 107.7, 102.0, 36.4; IR (KBr, cm^{-1}): 3433, 3027, 2907, 2221, 1653, 1600, 1567, 1485, 1442, 1358 ; HRMS (ESI-TOF) calcd for $C_{32}H_{22}NO_3^+$ ([M+H]$^+$): 468.1594, found: 468.1598.

4-(4-Chlorobenzyl)-3-benzoyl-2-phenyl-1-naphthonitrile (3aq): yellow solid (104.4 mg, 76% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 199.7–202.3 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.44 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.35–7.27 (m, 5H), 7.26–7.03 (m, 9H), 4.53–4.32 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$) δ (ppm): 196.3, 143.3, 139.6, 138.7, 137.9, 136.0, 134.5, 133.3, 133.1, 131.2, 129.6, 129.6, 129.0, 129.0, 128.6, 128.5, 128.4, 128.3, 127.3, 126.6, 126.5, 126.2, 116.7, 110.2, 36.1; IR (KBr, cm^{-1}): 3433, 3065, 2928, 2345, 2225, 1668, 1597, 1511, 1449, 1408, 1315; HRMS (ESI-TOF) calcd for $C_{31}H_{21}ClNO^+$ ([M+H]$^+$): 458.1306, found: 458.1304.

4-Benzyl-3-(4-bromobenzoyl)-2-phenyl-1-naphthonitrile (3ar) : white solid (102.5 mg, 68% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 191.2–193 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.40 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.38–6.99 (m, 14H), 4.40 (q, *J* = 14.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$) δ (ppm): 196.5, 143.4, 139.4, 138.8, 138.0, 136.0, 136.0, 133.1, 131.7, 131.2, 130.7, 129.5, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 126.6, 126.45, 126.1, 116.7, 110.2, 36.2; IR (KBr, cm^{-1}): 3065, 3039, 2927, 2222, 1673, 1583, 1584, 1568, 1496, 1446, 1409; HRMS (ESI-TOF) calcd for $C_{31}H_{21}BrNO^+$ ([M+H]$^+$): 502.0801, found: 502.0805.

4-Benzyl-2-phenyl-3-(4-(trifluoromethyl)benzoyl)-1-naphthonitrile (3as): yellow solid (112.1 mg, 76% yield); eluent: petroleum ether/ethyl acetate (50:1); mp 183.8–184.2 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.43 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56–6.98 (m, 14H), 4.44 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$) δ (ppm): 196.7, 143.3, 139.9, 139.7, 138.6, 137.8, 135.9, 134.4 (q, $J_{C\text{-}F}$= 32.6 Hz), 133.1, 131.3, 129.7, 129.3, 129.0, 128.6, 128.5, 128.4, 128.3, 126.6, 126.5, 126.1, 125.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.1Hz), 116.5, 110.3, 35.9; IR (KBr, cm^{-1}): 3064, 3028, 2946, 2874, 2225, 1673, 1581, 1566, 1495, 1446, 1415; HRMS (ESI-TOF) calcd for $C_{32}H_{21}F_3NO^+$ ([M+H]$^+$): 492.1570, found: 492.1572.

3-(1-Naphthoyl)-4-benzyl-2-phenyl-1-naphthonitrile (3at): yellow solid (90.9 mg, 64% yield); eluent: petroleum ether/ethyl acetate (10:1); mp 203.6–204.7 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.74 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.91–6.78 (m, 18H), 4.56 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$) δ (ppm): 199.0, 144.1, 140.2, 139.5, 139.3, 136.4, 134.4, 134.2, 133.7, 133.0, 132.3, 131.4, 130.3, 129.9, 129.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 126.6, 126.5, 126.4, 126.4, 126.0, 123.8, 116.8, 110.3, 36.3; IR (KBr, cm^{-1}): 3084, 3063, 2222, 1659, 1621, 1592, 1508, 1494, 1454; HRMS (ESI-TOF) calcd for $C_{35}H_{24}NO^+$ ([M+H]$^+$): 474.1852, found: 474.1856.

4-Benzyl-3-(4-methylbenzoyl)-2-phenyl-1-naphthonitrile (3au): yellow solid (96.6 mg, 75% yield); eluent: petroleum ether/ethyl acetate (10:1); mp 219.3–220.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.38 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.82–6.97 (m, 14H), 6.81 (s, 1H), 4.46 (q, *J* = 16.1 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 189.1, 144.8, 143.5, 139.2, 139.1, 138.6, 136.3, 135.6, 135.1, 133.1, 131.2, 129.5, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 126.5, 126.4, 126.2, 116.8, 110.2, 36.5; IR (KBr, cm^{-1}): 3059, 3027, 2220, 1651, 1602, 1567, 1496, 1410; HRMS (ESI-TOF) calcd for $C_{29}H_{20}NOS^+$ ($[M+H]^+$): 430.1260, found: 430.1263.

4-Benzyl-3-(furan-2-carbonyl)-2-phenyl-1-naphthonitrile (3av): yellow solid (91.8 mg, 74% yield); eluent: petroleum ether/ethyl acetate (10:1); mp 193.5–194.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 13.5 Hz, 6H), 7.20–7.08 (m, 5H), 6.75 (d, *J* = 3.0 Hz, 1H), 6.34–6.26 (m, 1H), 4.50 (q, *J* = 16.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ (ppm): 184.5, 152.9, 147.3, 143.7, 139.6, 139.0, 137.6, 136.2, 133.0, 131.2, 130.3, 129.5, 128.9, 128.5, 128.3, 128.3, 126.4, 126.4, 126.2, 120.0, 116.8, 112.6, 110.0, 36.0; IR (KBr, cm^{-1}): 3126, 3062, 3028, 2219, 1662, 1601, 1559, 1497, 1459, 1414; HRMS (ESI-TOF) calcd for $C_{29}H_{20}NO_2^+$ ($[M+H]^+$): 414.1489, found: 414.1492.

3-Acetyl-4-benzyl-2-phenyl-1-naphthonitrile (3aw): yellow solid (67.2 mg, 62% yield); eluent: petroleum ether/ethyl acetate (100:1); mp 162.4–163 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.38 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.64–7.58 (m, 1H), 7.50 (s, 5H), 7.30–7.07 (m, 5H), 4.50 (s, 2H), 1.77 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ (ppm): 205.6, 141.9, 141.4, 139.1, 137.5, 136.4, 132.7, 131.3, 130.1, 129.4, 129.4, 128.9, 128.8, 128.4, 128.4, 126.6, 126.4, 126.1, 116.8, 110.0, 35.3, 32.4; IR (KBr, cm^{-1}): 3381, 3027, 2218, 1701,1600, 1566, 1450,1407; HRMS (ESI-TOF) calcd for $C_{26}H_{20}NO^+$ ($[M+H]^+$): 362.1539, found: 362.1542.

General Procedure for Product 4. A 10 mL oven-dried Schlenck tube was successively charged with 0.30 mmol **3aa**, 1.5 mL DCE and 0.3 mmol CF_3SO_3H. The tube was sealed and the reaction mixture was stirred at 80 °C for 12 h. After completion of this reaction, the mixture was diluted with dichloromethane (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in-vacuo. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give product **4**.

14b-Phenyl-5,14b-dihydroindeno[1,2,3-gh]tetraphene-10-carbonitrile (4): white solid (104.6 mg, 86% yield); eluent: petroleum ether/ethyl acetate (100:1); mp 285.1–286.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.67 (dd, *J* = 5.6, 3.1 Hz, 1H), 8.49–8.31 (m, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.85–7.76 (m, 1H), 7.73–7.58 (m, 2H), 7.57–7.51 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.11–7.00 (m, 3H), 6.77 (dd, *J* = 6.4, 2.9 Hz, 2H), 4.49 (d, *J* = 17.3 Hz, 1H), 3.74 (d, *J* = 17.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ (ppm): 151.3, 147.3, 142.4, 141.5, 139.6, 138.8, 138.0, 137.8, 133.4, 130.3, 128.9, 128.4, 127.9, 127.7, 127.0, 126.8, 126.8, 126.7, 126.5, 126.1, 125.6, 124.2, 123.8, 117.7, 98.5, 59.5, 32.6; IR (KBr, cm^{-1}): 3644, 3057, 2857, 2214, 1596, 1513, 1476, 1443, 1417; HRMS (ESI-TOF) calcd for $C_{31}H_{20}N^+$ ($[M+H]^+$): 406.1590, found: 406.1588.

General Procedure for Product 5: To a solution of **3aa** (0.30 mmol) in $PhCH_3$ (3 mL) at 0 °C under N_2 was added $^{i}Bu_2AlH$ (0.6 mL, 1.5 M in toluene) dropwise. The mixture was stirred at 0 °C for 5 min and then warmed to 25 °C for 2 h. After completion of this reaction, the reaction mixture was quenched with brine. Then, the mixture was diluted with EtOAc (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in-vacuo. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give product **5**.

4-Benzyl-3-(hydroxy(phenyl)methyl)-2-phenyl-1-naphthaldehyde (5): white solid (104.1 mg, 81% yield); eluent: petroleum ether/ethyl acetate (20:1); mp 185.5–187.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.98 (s, 1H), 9.23 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.73–7.58 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.43–7.35 (m, 4H), 7.30 (d, *J* = 6.8 Hz, 1H), 7.24–7.07 (m, 8H), 6.92 (d, *J* = 7.1 Hz, 2H), 6.11 (d, *J* = 5.9 Hz, 1H), 4.58 (dd, *J* = 39.1, 16.9 Hz, 2H), 2.36 (d, *J* = 6.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 195.2, 147.7, 143.6, 142.9, 140.4, 138.7, 137.3, 133.6, 130.1, 130.1, 130.1, 129.6, 129.0, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.1, 126.7, 126.0, 125.8, 125.6, 125.4, 71.7, 36.0; IR (KBr, cm^{-1}): 3457, 3081, 3027, 2872, 2782, 1681, 1601, 1555, 1494, 1450, 1401; HRMS (ESI-TOF) calcd for $C_{31}H_{25}O_2^+$ ($[M+H]^+$): 429.1849, found: 429.1848.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic file in CIF format for the structure determination of products **3aa** and **4**; Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

Email: wangyanbokf@henu.edu.cn

ORCID: 0000-0002-5676-1437

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was financially supported by the National Natural Science Foundation of China (No. U1504205), the Key Research Project of Education Department of Henan Province (No. 17A150002) and Henan University (yqpy20170009).

REFERENCES

(1) (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. Selective Palladium-Catalyzed Cocyclotrimerization of Arynes with Dimethyl Acetylenedicarboxylate: A Versatile Method for the Synthesis of Polycyclic Aromatic Hydrocarbons. *J. Org. Chem.* **2000**, *65*, 6944−6950. (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. Big Is Beautiful−"Aromaticity" Revisited from the Viewpoint of Macromolecular and Supramolecular Benzene Chemistry. *Chem. Rev.* **2001**, *101*, 1267−1300. (c) Lee, J. J.; Noll, B. C.; Smith, B. D. Fluorescent Chemosensor for Chloroalkanes. *Org. Lett.* **2008**, *10*, 1735−1738.

(2) (a) Katritzky, A. R.; Zhang, G.; Xie, L. Benzotriazole-Assisted Aromatic Ring Annulation: Efficient and General Syntheses of Polysubstituted Naphthalenes and Phenanthrenes. *J. Org. Chem.* **1997**, *62*, 721−725. (b) Ukita, T.; Nakamura, Y.; Kubo, A.; Yamamoto, Y.; Takahashi, M.; Kotera, J.; Ikeo, T. 1-Arylnaphthalene Lignan: A Novel Scaffold for Type 5 Phosphodiesterase Inhibitor. *J. Med. Chem.* **1999**, *42*, 1293−1305. (c) Krohn, K.; Kouam, S. F.; Cludius-Brandt, S.; Draeger, S.; Schulz, B. Bioactive Nitronaphthalenes from an Endophytic Fungus, *Coniothyrium* sp., and Their Chemical Synthesis. *Eur. J. Org. Chem.* **2008**, *2008*, 3615−3618. (d) Bringmann, G.; Lombe, B. K.; Steinert, C.; Ioset, K. N.; Brun, R.; Turini, F.; Heubl, G.; Mudogo, V. Mbandakamines A and B, Unsymmetrically Coupled Dimeric Naphthylisoquinoline Alkaloids, from a Congolese Ancistrocladus Species. *Org. Lett.* **2013**, *15*, 2590−2593.

(3) For selected references, see: (a) Fukutani, T.; Hirano, K.; Satoh, T.; Miura, M. Synthesis of Highly Substituted Naphthalene and Anthracene Derivatives by Rhodium-Catalyzed Oxidative Coupling of Arylboronic Acids with Alkynes. *Org. Lett.* **2009**, *11,* 5198−5201. (b) Feng, C.; Loh, T.-P. Palladium-Catalyzed Bisolefination of C−C Triple Bonds: A Facile Method for the Synthesis of Naphthalene Derivatives. *J. Am. Chem. Soc.* **2010**, *132*, 17710−17712. (c) Wang, S.; Zhang, L.; Ding, X.; Zhou, Y.; Wang, J.; Jiang, H.; Liu, H. Synthesis of 2-Phenylnaphthalenes through Gold-Catalyzed Dimerization via a Highly Selective Carbon Nucleophile Pathway. *J. Org. Chem.* **2011**, *76*, 4514–4521. (d) Chen, Z.; Zeng, W.; Jiang, H.; Liu, L. Cu(II)-Catalyzed Synthesis of Naphthalene-1,3-diamine Derivatives from Haloalkynes and Amines. *Org. Lett.* **2012**, *14,* 5385−5387.

(4) For selected references, see: (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. Palladium-Catalyzed Cocyclization of Arynes with Alkynes: Selective Synthesis of Phenanthrenes and Naphthalenes. *J. Am. Chem. Soc.* **1999**, *121*, 5827−5828. (b) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. Palladium-Catalyzed Controlled Carbopalladation of Benzyne. *J. Am. Chem. Soc.* **2000,** *122,* 7280−7286. (c) Yoshikawa, E.; Yamamoto, Y. Palladium-Catalyzed Intermolecular Controlled Insertion of Benzyne-Benzyne-Alkene and Benzyne-Alkyne-Alkene-Synthesis of Phenanthrene and Naphthalene Derivatives. *Angew. Chem. Int. Ed.* **2000**, *39,* 173−175.

(5) For selected references, see: (a) Reddy, C. R.; Dilipkumar, U.; Reddy, M. D. Novel [4+2]-Benzannulation To Access Substituted Benzenes and Polycyclic Aromatic and Benzene-Fused Heteroaromatic Compounds. *Org. Lett.* **2014**, *16*, 3792−3795. (b) Chang, M.-Y.; Cheng, Y.-C. Synthesis of 1-Aryltetralins and 1-Arylnaphthalenes via (4+ 2) Annulation of β-Ketosulfones with Styryl Bromides. *Org. Lett.* **2016**, *18,* 1682−1685. (c) Chan, C.-K.; Chen, Y.-H.; Tsai, Y.-L.; Chang, M.-Y. Synthesis of Substituted 1,6-Diarylnaphthalenes via a Tandem Claisen Rearrangement and Ene Reaction Protocol. *J. Org. Chem.* **2017**, *82*, 3317−3326.

(6) For selected references, see: (a) Shao, L.-X.; Zhang, Y.-P.; Qi, M.-H.; Shi, M. Lewis Acid Catalyzed Rearrangement of Vinylcyclopropenes for the Construction of Naphthalene and Indene Skeletons. *Org. Lett.* **2007**, *9,* 117−120. (b) Glass, A. C.; Morris, B. B.; Zakharov, L. N.; Liu, S.-Y. Synthesis of Substituted Naphthalenes via A Catalytic Ring-Expansion Rearrangement. *Org. Lett.* **2008**, *10,* 4855−4857. (c) Boeck, F.; Kribber, T.; Xiao, L.; Hintermann, L. Mixed Phosphane η^5-CpRuCl(PR$_3$)$_2$ Complexes as Ambifunctional Catalysts for Anti-Markovnikov Hydration of Terminal Alkynes. *J. Am. Chem. Soc.* **2011**, *133*, 8138−8141. (d) Wang, J.-G.; Wang, M.; Xiang, J.-C.; Zhu, Y.-P.; Xue, W.-J.; Wu, A.-X. Direct Synthesis of Substituted Naphthalenes from 1,3-Dicarbonyl Compounds and 1,2-Bis(halomethyl)benzenes Including a Novel Rearrangement Aromatization of Benzo[*c*]oxepine. *Org. Lett.* **2012**, *14,* 6060−6063.

(7) For selected references, see: (a) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. AuCl$_3$-Catalyzed Benzannulation: Synthesis of Naphthyl Ketone Derivatives from *o*-Alkynylbenzaldehydes with Alkynes. *J. Am. Chem. Soc.* **2002**, *124*, 12650−12651. (b) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. Lewis Acid-Catalyzed Benzannulation via Unprecedented [4+2] Cycloaddition of o-Alkynyl(oxo)benzenes and Enynals with Alkynes. *J. Am. Chem. Soc.* **2003**, *125*, 10921−10925. (c) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González. J. M. Regioselective Synthesis of Substituted Naphthalenes: A Novel de Novo Approach Based on a Metal-Free Protocol for Stepwise Cycloaddition of o-Alkynylbenzaldehyde Derivatives with either Alkynes or Alkenes *Org. Lett.* **2003**, *5*, 4121−4123. (d) Asao, N.; Sato, K.; Menggenbateer; Yamamoto, Y. AuBr$_3$- and Cu(OTf)$_2$-Catalyzed Intramolecular [4 +2] Cycloaddition of Tethered Alkynyl and Alkenyl Enynones and Enynals: A New Synthetic Method for Functionalized Polycyclic hydrocarbons. *J. Org. Chem.* **2005**, *70*, 3682−3685. (e) Hildebrandt, D.; Hüggenberg, W.; Kanthak, M.; Plöger, T.; Müller, I. M.; Dyker, G. A platinum-catalyzed annulation reaction leading to medium-sized rings. *Chem. Commun.* **2006**, *696*, 2260−2261. (f) Yamamoto, Y.; Gridnev, I. D.; Patil, N. T.; Jin, T. Alkyne activation with Brønsted acids, iodine, or gold complexes, and its fate leading to synthetic application. *Chem. Commun*. **2009**, 5075−5087. (g) Umeda, R.; Kaiba, K.; Morishita, S.; Nishiyama, Y. Rhenium-Catalyzed Benzannulation of o-Alkynylbenzaldehyde with Alkynes to Multiple 2,3-Disubstituted Naphthalenes. *ChemCatChem* **2011**, *3*, 1743−1746. (h) Asao, N.; Menggenbateer; Seya, Y.; Yamamoto, Y.; Chen, M.; Zhang, W.; Inoue, A. Nanoporous Gold-Catalyzed [4+2] Benzannulation between *ortho*-Alkynylbenzaldehydes and Alkynes. *Synlett* **2012**, *23*, 66–69. (i) Manojveer, S.; Balamurugan, R. A facile access to substituted benzo[a]fluorenes from o-alkynylbenzaldehydes via in situ formed acetals. *Chem. Commun.* **2014**, *50*, 9925−9928.

(8) (a) Larock, R. C.; Doty, M. J.; Tian, Q.; Zenner, J. M. Synthesis of Polycyclic Aromatic Hydrocarbons by the Pd-Catalyzed Annulation of Alkynes. *J. Org. Chem.* **1997**, *62*, 7536−7537. (b) Larock, R. C.; Tian, Q. Palladium-Catalyzed Annulation of Internal Alkynes by Arene-Containing Vinylic Iodides and Triflates. *J. Org. Chem.* **1998**, *63*, 2002−2009. (c) Larock, R. C. *J. Organomet. Chem.* **1999**, *576*, 111−124. (d) Ohno, H.; Yamamoto, M.; Iuchi, M.; Tanaka, T. Palladium-Catalyzed Tandem Cyclization of Bromoenynes through Aromatic C−H Bond Functionalization. *Angew. Chem., Int. Ed.* **2005**, *44*, 5103−5106. (e) Ohno, H.; Yamamoto, M.; Iuchi, M.; Fujii, N.; Tanaka, T. Palladium-Catalyzed Construction of Polycyclic Heterocycles by an Alkyne Insertion and Direct Arylation Cascade. *Synthesis* **2011**, 2567−2578. (f) Wang, H.; Xu, H.; Li, B.; Wang, B. Annulation of *β*-Enaminonitriles with Alkynes via Rh^{III}-Catalyzed

C−H Activation: Direct Access to Highly Substituted 1-Naphthylamines and Naphtho[1,8-bc]pyridines *Org. Lett.* **2018**, *20*, 5640−5643.

(9) (a) Huang, Q.; Larock, R. C. Synthesis of Substituted Naphthalenes by the Palladium-Catalyzed Annulation of Internal Alkynes. *Org. Lett.* **2002**, *4*, 2505−2508. (b) Watanabe, K.; Mino, T.; Hatta, C.; Itoa, S.; Sakamoto, M. Hydrazone–palladium catalyzed annulation of 1-allyl-2-bromobenzene derivatives with internal alkynes. *Org. Biomol. Chem.* **2015**, *13*, 11645–11650.

(10) For selected references, see: (a) Viswanathan, G. S.; Wang, M.; Li, C.-J. A Highly Regioselective Synthesis of Polysubstituted Naphthalene Derivatives through Gallium Trichloride Catalyzed Alkyne-Aldehyde Coupling. *Angew. Chem. Int. Ed.* **2002**, *41*, 2138−2141. (b) Kabalka, G. W.; Ju, Y.; Wu, Z. A New Titanium Tetrachloride Mediated Annulation of r-Aryl-Substituted Carbonyl Compounds with Alkynes: A Simple and Highly Efficient Method for the Regioselective Synthesis of Polysubstituted Naphthalene Derivatives. *J. Org. Chem.* **2003**, *68*, 7915−7917. (c) Balamurugan, R.; Gudla, V. Gold-Catalyzed Electrophilic Addition to Arylalkynes. A Facile Method for the Regioselective Synthesis of Substituted Naphthalenes. *Org. Lett.* **2009**, *11*, 3116−3119. (d) Gulda, V.; Balmamurugan, R. Synthesis of Arylnaphthalene Lignan Scaffold by Gold-Catalyzed Intramolecular Sequential Electrophilic Addition and Benzannulation. *J. Org. Chem.* **2011**, *76*, 9919−9933. (e) Xiang, S.; Hu, H.; Ma, J.; Li, Y.; Wang, B.; Feng, C.; Zhao, K.; Hu, P.; Chen, X. Synthesis of naphthalene derivatives through inexpensive $BF_3 \cdot Et_2O$-catalyzed annulation reaction of arylacetaldehydes with arylalkynes. *Sci. China Chem.* **2013**, *56*, 945−951. (f) Ponra, S.; Vitale, M. R.; Michelet, V.; Ratovelomanana-Vidal, V. $HNTf_2$-Catalyzed Regioselective Preparation of Polysubstituted Naphthalene Derivatives Through Alkyne−Aldehyde Coupling. *J. Org. Chem.* **2015**, *80*, 3250−3257.

(11) For selected references, see: (a) Viswanathan, G. S.; Li, C.-J. Synthesis of naphthalene derivatives via a novel Gallium trichloride catalyzed cross-coupling of epoxides with alkynes. *Synlett* **2002**, 1553−1555. (b) Tian, Q.; Pletnev, A. A.; Larock, R. C. Carbopalladation of Nitriles: Synthesis of 3,4-Disubstituted 2-Aminonaphthalenes and 1,3-Benzoxazine Derivatives by the Palladium-Catalyzed Annulation of Alkynes by (2-Iodophenyl)acetonitrile. *J. Org. Chem.* **2003**, *68*, 339−347. (c) Tan, X.; Liu, B.; Li, X.; Li, B.; Xu, S.; Song, H.; Wang, B. Rhodium-Catalyzed Cascade Oxidative Annulation Leading to Substituted Naphtho[1,8-*bc*]pyrans by Sequential Cleavage of C(sp^2)–H/C(sp^3)–H and C(sp^2)–H/O–H Bonds. *J. Am. Chem. Soc.* **2012**, *134*, 16163−16166. (d) Zhu, S.; Xiao, Y.; Guo, Z.; Jiang, H. Iron-Catalyzed Benzannulation Reactions of 2-Alkylbenzaldehydes and Alkynes Leading to Naphthalene Derivatives. *Org. Lett.* **2013**, *15*, 898−901. (e) Gao, P.; Liu, J.; Wei, Y. Hypervalent Iodine(III)-Mediated Benzannulation of Enamines with Alkynes for the Synthesis of Polysubstituted Naphthalene Derivatives. *Org. Lett.* **2013**, *15*, 2872−2875. (f) Zhou, S.; Wang, J.; Wang, L.; Song, C.; Chen, K.; Zhu, J. Enaminones as Synthons for a Directed C−H Functionalization: Rh^{III}-Catalyzed Synthesis of Naphthalenes. *Angew. Chem., Int. Ed.* **2016**, *55*, 9384-9388. (g) Zhang, C.; Chen, L.; Chen, K.; Jiang, H.; Zhu, S. Iron/zinc-catalyzed benzannulation reactions of 2-(2-oxo-alkyl)benzketones leading to naphthalene and isoquinoline derivatives. *Org. Chem. Front.* **2018**, *5*, 1028–1033.

(12) (a) Wang, Y.-B.; Wang, Y.-M.; Zhang, W.-Z.; Lu, X.-B. Fast CO_2 Sequestration, Activation, and Catalytic Transformation Using N-Heterocyclic Olefins. *J. Am. Chem. Soc.* **2013**, *135*, 11996−12003; (b) Wang, Y.-B.; Sun, D.-S.; Zhou, H.; Zhang, W.-Z.; Lu, X.-B. Alkoxide-functionalized imidazolium betaines for CO_2 activation and catalytic transformation. *Green Chem.*, **2014**, *16*, 2266−2272. (c) Zhang, S.; Bai, X.-T.; Chen, D.-Y.; Chen, P.; Zhang, Q.-Q.; Wang, Y.-B. Water-assisted metal-free catalyzed cyclization of 2-alkynylarylketones: a facile approach to indenones. *RSC Adv.* **2017**, *7*, 31142−31147. (d) Bai, X.-T.; Zhang, Q.-Q.; Zhang, S.; Chen, D.-Y.; Fu, F.-J.; Zhu, J.-Y.; Wang, Y.-B.; Tang, Y.-T. Carbonyl-Oxygen-Assisted KOMe-Mediated Formal Hydration of 4-Alkynones: Complete Regioselectivity in the One-Pot Synthesis of 1,4-Diketones under Mild Conditions. *Eur. J. Org. Chem.* **2018**, *2018*, 1581−1588. (e) Chen, P.; Zhang, Q.-Q.; Guo, J.; Chen, L.-L.; Wang, Y.-B.; Zhang, X. An effective preparation of both 1,3-diketones and nitriles from alkynones with oximes as hydroxide sources. *Org. Biomol. Chem.*, **2018**, *16*, 8336−8344. (f) Chen, L.-L.; Zhang, J.-W.; Yang, W.-W.; Chen, P.; Chen, D.-Y.; Wang, Y.-B. An efficient preparation of β-ketophosphine oxides from alkynylphosphine oxides with benzaldehyde oxime as a hydroxide source *Org. Biomol. Chem.* **2019**, *17*, 3003−3009.

(13) (a) Cheng, X.; Zhou, Y.; Zhang, F.; Zhu, K.; Liu, Y.; Li, Y. Base-Promoted Tandem Reaction Involving Insertion into Carbon-Carbon σ-Bonds: Synthesis of Xanthone and Chromone Derivatives. *Chem. Eur. J.* **2016**, *22*, 12655–12659. (b) Zhou, Y.; Tao, X.; Yao, Q.; Zhao, Y.; Li, Y. Insertion of Isolated Alkynes into Carbon-Carbon σ-Bonds of Unstrained Cyclic β-Ketoesters via Transition-Metal-Free Tandem Reactions: Synthesis of Medium-Sized Ring Compounds. *Chem. Eur. J.* **2016**, *22*, 17936–17939. (c) Wang, M.; Kong, L.; Wang, Y.; Song, B.; Sun, Y.; Tang, R.; Li, Y. Sequential C–C σ-Bond Cleavage/(sp^2) C–O Bond Formation via C–H Functionalization toward Pyranoindolones Fused with Medium-Sized Rings. *Org. Lett.* **2018,** *20,* 6130–6134. (d) Singh, S.; Samineni, R.; Pabbaraja, S.; Mehta, G. Nitromethane as a Carbanion Source for Domino Benzoannulation with Ynones: One-Pot Synthesis of Polyfunctional Naphthalenes and a Total Synthesis of Macarpine. *Angew. Chem., Int. Ed.* **2018**, *57*, 16847–16851. (e) Yao, Q.; Kong, L.; Wang, M.; Yuan, Y.; Sun, R.; Li, Y. Transition-Metal-Free Ring Expansion Reactions of Indene-1,3-dione: Synthesis of Functionalized Benzoannulated Seven-Membered Ring Compounds. *Org. Lett.* **2018**, *20*, 1744−1747. (f) Kong, L.; Wang, M.; Wang, Y.; Song, B.; Yang, Y.; Yao, Q.; Li, Y. Merging base-promoted C–C bond cleavage and iron-catalyzed skeletal rearrangement involving C–C/C–H bond activation: synthesis of highly functionalized carbazoles. *Chem. Commun.* **2018**, *54*, 11009–11012.

(14) (a) Trofimov, B. A.; Schmidt, E. Y.; Ushakov, I. A. Zorina, N. V.; Skital'tseva, E. V.; Protsuk, N. I.; Mikhaleva, A. I. Base-Catalyzed Stereoselective Vinylation of Ketones with Arylacetylenes: A New C(sp^3)-C(sp^2) Bond-Forming Reaction. *Chem. Eur. J.* **2010**, *16*, 8516–8521. (b) Trofimov, B. A.; Schmidt, E. Y.; Zorina, N. V.; Ivanova, E. V.; Ushakov, I. A. Transition-Metal-Free Superbase-Promoted Stereoselective α-Vinylation of Ketones with Arylacetylenes: A General Strategy for Synthesis of β,γ-Unsaturated Ketones. *J. Org. Chem.* **2012**, *77*, 6880–6886. (c) Ouyang, L.; Qi, C.; He, H.; Peng, Y.; Xiong, W.; Ren, Y.; Jiang, H. Base-Promoted Formal [4+3] Annulation between 2-Fluorophenylacetylenes and Ketones: A Route to Benzoxepines. *J. Org. Chem.* **2016**, *81*, 912−919. (d) Qi, C.; Peng, Y.; Ouyang, L.; Ren, Y.; Jiang, H. Base-Promoted Addition of Arylacetonitriles to Terminal Alkynes: Regio-and Stereoselective Access to Disubstituted Acrylonitriles. *Adv. Synth. Catal.* **2017**, *359*, 1339–1350.

(15) (a) Shen, H.; Xie, Z. Atom-Economical Synthesis of N-Heterocycles via Cascade Inter-/Intramolecular C−N Bond-Forming Reactions Catalyzed by Ti Amides. *J. Am. Chem. Soc.* **2010**, *132*, 11473–11480. (b) Chen, X.; He, Q.; Xie, Y.; Yang, C. Palladium (II)-catalyzed synthesis of functionalized indenones via oxidation and cyclization of 2-(2-arylethynylphenyl) acetonitriles. *Org. Biomol. Chem.* **2013**, *11*, 2582–2585.

(16) (a) Alonso, D. A.; Najera, C.; Pacheco, M. C. Synthesis of Ynones by Palladium-Catalyzed Acylation of Terminal Alkynes with Acid Chlorides. *J. Org. Chem.* **2004**, *69*, 1615–1619. (b) Cox, R.; Ritson, D.; Dane, T.; Berge, J.; Charmant, J.; Kantacha, A. Room temperature palladium catalysed coupling of acyl chlorides with terminal alkynes. *Chem. Commun.* **2005**, 1037–1039. (c) Baxendale, I. R.; Schou, S. C.; Sedelmeier, J.; Ley, S. V. Multi-Step Synthesis by Using Modular Flow Reactors: The Preparation of Yne-Ones and Their Use in Heterocycle Synthesis. *Chem. Eur. J.* **2010**, *16*, 89–94. (d) Bhosale, M. A.; Sasaki, T.; Bhanage, B. M. A facile and rapid route for the synthesis of Cu/Cu_2O nanoparticles and their application in the

Sonogashira coupling reaction of acyl chlorides with terminal alkyne. *Catal. Sci. Technol.* **2014**, *4,* 4274–4280. (e) Shiroodi, R. K.; Soltani, M.; Gevorgyan, V. Gold-Catalyzed 1,3-Transposition of Ynones. *J. Am. Chem. Soc.* **2014**, *136*, 9882–9885. (f) Pan, C.; Huang, B.; Hu, W.; Feng, X.; Yu, J.-T. Metal-Free Radical Oxidative Annulation of Ynones with Alkanes To Access Indenones. *J. Org. Chem.* **2016**, *81*, 2087–2093.