The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01207 • Publication Date (Web): 07 Jun 2018

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Sequential σ-Bond Insertion/Benzannulation Involving Arynes: Selective Synthesis of Polysubstituted Naphthalenes

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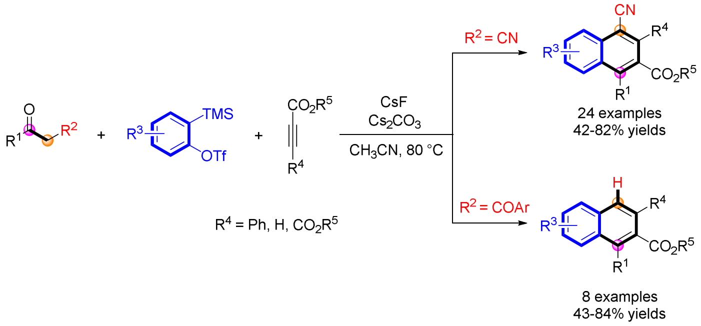


ABSTRACT: An interesting σ-bond insertion/benzannulation reaction for the synthesis of polysubstituted naphthalene derivatives has been developed from readily accessible ketones, arynes, and alkynoates. This practical and transition-metal-free method provides a novel route to diverse naphthalenes through a substrate-controlled rearrangement reaction with the cleavage of C-C bonds.

INTRODUCTION

Substituted naphthalenes are important motifs widely found in natural products, pharmaceuticals, and biologically active molecules, such as parvinaphthol B, justicidin B, and amonafide (Figure 1).[1] In addition, they have numerous applications in supramolecular chemistry and materials science.[2]

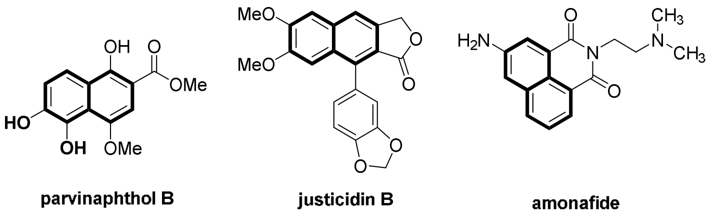
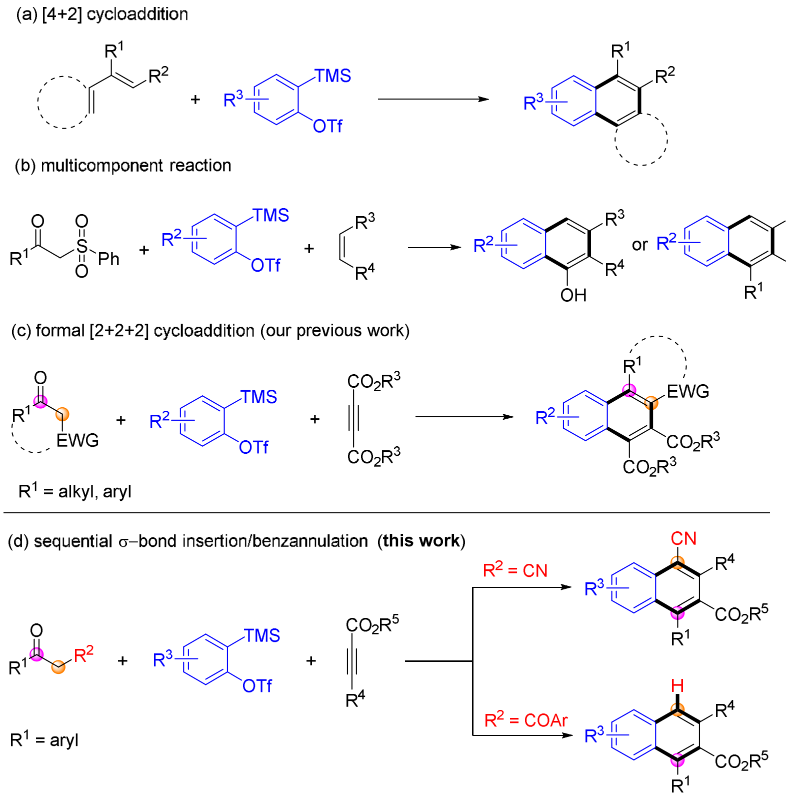


Figure 1. Selected examples of activated naphthalenes.

Accordingly, much effort has been devoted to their regioselective synthesis over recent years, and many useful synthetic methods to this field were accomplished.[3] These strategies include Diels−Alder reactions,[4] transition-metal or Lewis acid catalyzed annulations,[5] and rearrangements of strained rings.[6] Despite some progress in this area, these methods cannot directly synthesize α–CN substituted naphthalene derivatives. As the cyano group is easily converted into various different functional groups, it is of significant interest to develop efficient and direct methods for the construction of naphthalene ring with a versatile cyano group at the α position.[7]

Arynes are indispensable reactive intermediates in organic synthesis and have received considerable attention over recent years.[8] Due to their high reactivity and ease of preparation (only in the presence of fluoride),[9] they have the potential to take part in a large number of novel reactions to construct various organic compounds.[10] In particular, the annulation of benzynes has been shown to be one of the most powerful and reliable approaches for preparing naphthalene derivatives.[11] For example, the Diels–Alder reaction of arynes and conjugated dienes can directly and efficiently afford a variety of promising natural products and useful naphthalene skeletons (Scheme 1a).[12] Huang and coworkers reported a novel multicomponent reaction of arynes, α-keto sulfones, and Michael-type acceptors for the synthesis of polysubstituted naphthols and naphthalenes (Scheme 1b).[13] Recently, our group developed a novel formal [2+2+2] cycloaddition reaction involving arynes for the efficient and convenient synthesis of naphthalene derivatives from simple available substances under mild conditions (Scheme 1c).[14] With our continued interest in arynes, we herein report a sequential σ-bond insertion/annulation reaction for the direct synthesis of α–CN naphthalenes. In addition, interesting naphthalene derivatives with acyl group abscission were also obtained (Scheme 1d).

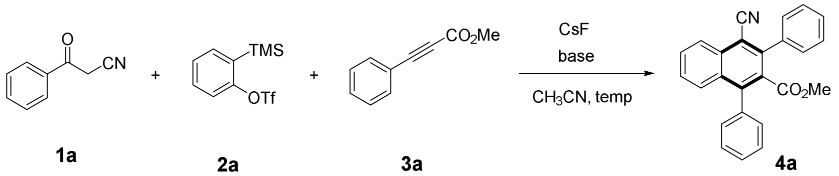
Scheme 1. Methods for Accessing Polysubstituted Naphthalenes Involving Arynes.



RESULTS AND DISCUSSION

Initially, we tested the combination of benzoylacetonitrile (**1a**), 2-(trimethylsilyl)phenyl triflate (**2a**), methyl phenylpropargylate (**3a**) and CsF in CH_3CN as the model reaction, and the results are summarized in Table 1. To our delight, desired product **4a** was furnished with 43% yield in the absence of base (entry 1). Subsequently, the influence of base (such as K_2CO_3, Na_2CO_3, Cs_2CO_3, $NaHCO_3$, NaOH, KOH, K_3PO_4, and NaOEt) in the reaction was examined (entries 2–9). Pleasingly, Cs_2CO_3 worked well in this transformation, affording the product in 74% yield (entry 4). Then, different solvents were evaluated and CH_3CN was found to be the most efficient solvent for this reaction (entries 10–15). Following the above investigation, the ratio of substrates was evaluated (entries 16–18), and a higher yield was observed with the ratio 1:1:1.2 (entry 16). Moreover, decreased yields were observed at lower reaction temperatures (entries 19 and 20). Thus, the optimized conditions were established as follows: benzoylacetonitrile **1a** (0.1 mmol), 2-(trimethylsilyl)phenyl triflate **2a** (0.1 mmol), and methyl phenylpropargylate **3a** (0.12 mmol) in the presence of CsF (3.0 equiv) and Cs_2CO_3 (3.0 equiv) in CH_3CN at 80 °C for 15 h.

Table 1. Optimization of the Reaction Conditions[a]



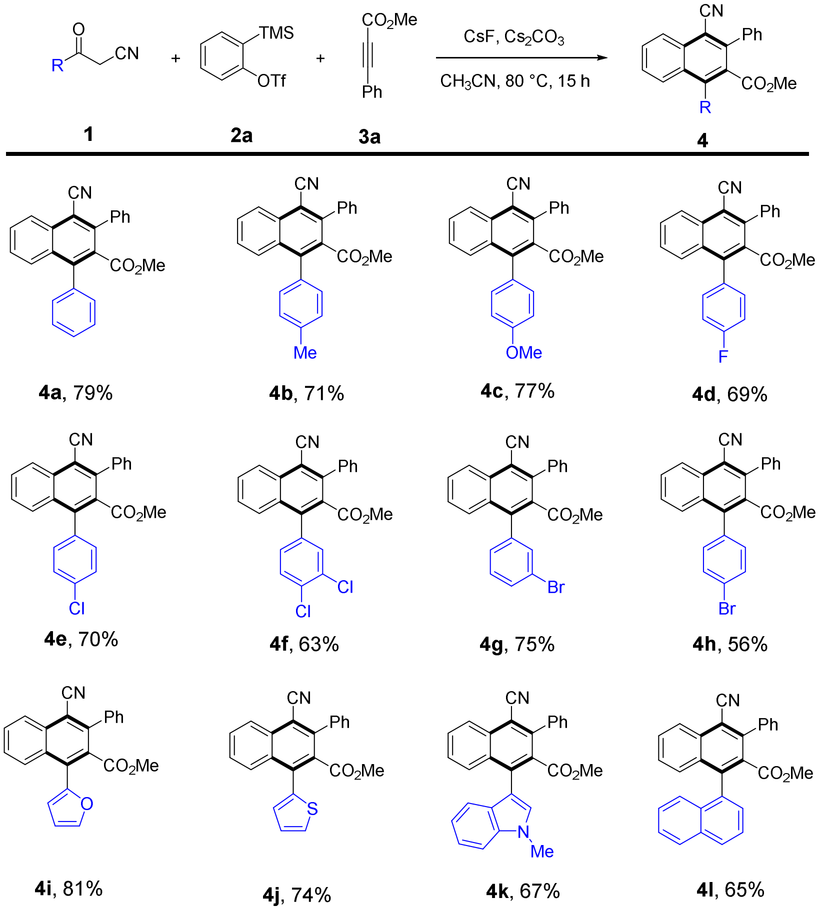
entry	solvent	base	temp (°C)	ratio of **1a**:**2a**:**3a**	yield[b] (%)
1	CH_3CN	-	80	1:1:1	43
2	CH_3CN	K_2CO_3	80	1:1:1	70
3	CH_3CN	Na_2CO_3	80	1:1:1	39
4	CH_3CN	Cs_2CO_3	80	1:1:1	74
5	CH_3CN	$NaHCO_3$	80	1:1:1	0
6	CH_3CN	NaOH	80	1:1:1	68
7	CH_3CN	KOH	80	1:1:1	43
8	CH_3CN	K_3PO_4	80	1:1:1	38
9	CH_3CN	NaOEt	80	1:1:1	45
10	toluene	Cs_2CO_3	80	1:1:1	0
11	THF	Cs_2CO_3	80	1:1:1	32
12	DCE	Cs_2CO_3	80	1:1:1	0
13	EtOAc	Cs_2CO_3	80	1:1:1	67
14	EtOH	Cs_2CO_3	80	1:1:1	0
15	dioxane	Cs_2CO_3	80	1:1:1	0
16	**CH_3CN**	**Cs_2CO_3**	**80**	**1:1:1.2**	**79**
17	CH_3CN	Cs_2CO_3	80	1:1:1.5	76
18	CH_3CN	Cs_2CO_3	80	2:1:1	64
19	CH_3CN	Cs_2CO_3	60	1:1:1.2	43
20	CH_3CN	Cs_2CO_3	70	1:1:1.2	60

[a] Reaction conditions: CsF (3.0 equiv), base (3.0 equiv), and solvent (2 mL) for 15 h.

[b] Isolated yields.

With the optimized reaction conditions in hand, a wide variety of α-cyanoacetophenones (**1**) were then explored, as shown in Scheme 2. The results demonstrated that α-cyanoacetophenones bearing various electron-neutral (H), electron-donating (3–Me, 3–OMe), and halogen (4–F, 4–Cl, 3, 4–2Cl, 3–Br, and 4–Br) substituents attached to the benzene ring all reacted smoothly with **2a** and **3a**, to afford various polysubstituted naphthalene derivatives in 56%–79% yields (**4a**–**4h**). Furthermore, moderate to good yields were also obtained for heteroaromatic (2-furyl, 2-thienyl and 3-(1-methyl-1*H*-indol)-yl) group substrates (67%–81%; **4i**–**4k**). Much to our satisfaction, even when the substrate contained a sterically hindered 1-naphthyl group, the expected product (**4l**) was obtained in 65% yield. The structure of **4a** was identified by single-crystal X-ray diffraction (see Supporting Information (SI)).

Scheme 2. Scope of α-Cyano Ketones[a]

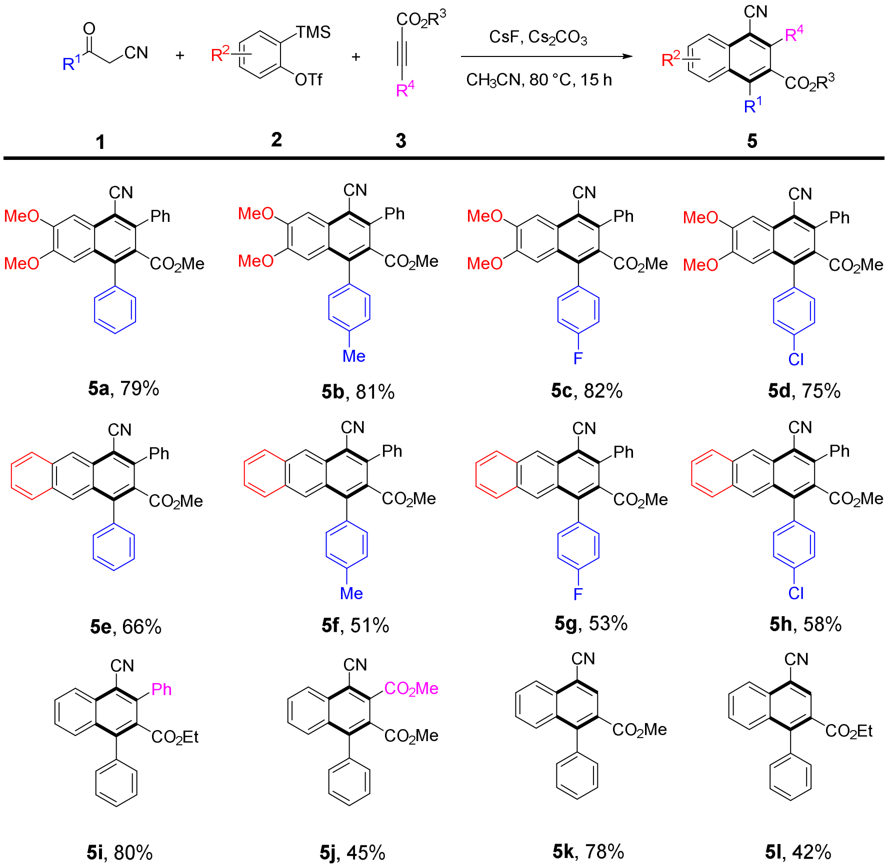


[a]Reactions were carried out with **1** (0.5 mmol, 1.0 equiv), **2a** (0.5 mmol, 1.0 equiv), **3a** (0.6 mmol, 1.2 equiv), CsF (3.0 equiv) and Cs_2CO_3 (3.0 equiv) in the CH_3CN (5mL) at 80 °C for 15 h. Isolated yields are shown.

Encouraged by the above results, we then examined the scope of the 2-(trimethylsilyl)aryl triflates (**2**) (Scheme 3). Symmetrically substituted 2,3-naphthalyne and 4,5-dimethoxybenzyne precursors were explored, and the corresponding products were obtained in moderate to good yields (51%–82%; **5a**–**5h**). The generality of alkynoates (**3**) was investigated next, and ethyl phenylpropargylate was also tolerated in the reaction, leading to the expected product **5i** in 80% yield.

Much to our satisfaction, dimethyl acetylenedicarboxylate also participated in the annulation reaction, affording the naphthalene product **5j** in 45% yield. The structure of **5j** was further confirmed by single-crystal X-ray (see SI). Moreover, methyl and ethyl propiolate were also tolerated in this annulation to afford the corresponding products **5k** and **5l** in 78% and 42% yields, respectively.

Scheme 3. Scope of 2-(Trimethylsilyl)aryl Triflates, and Alkynoates[a]

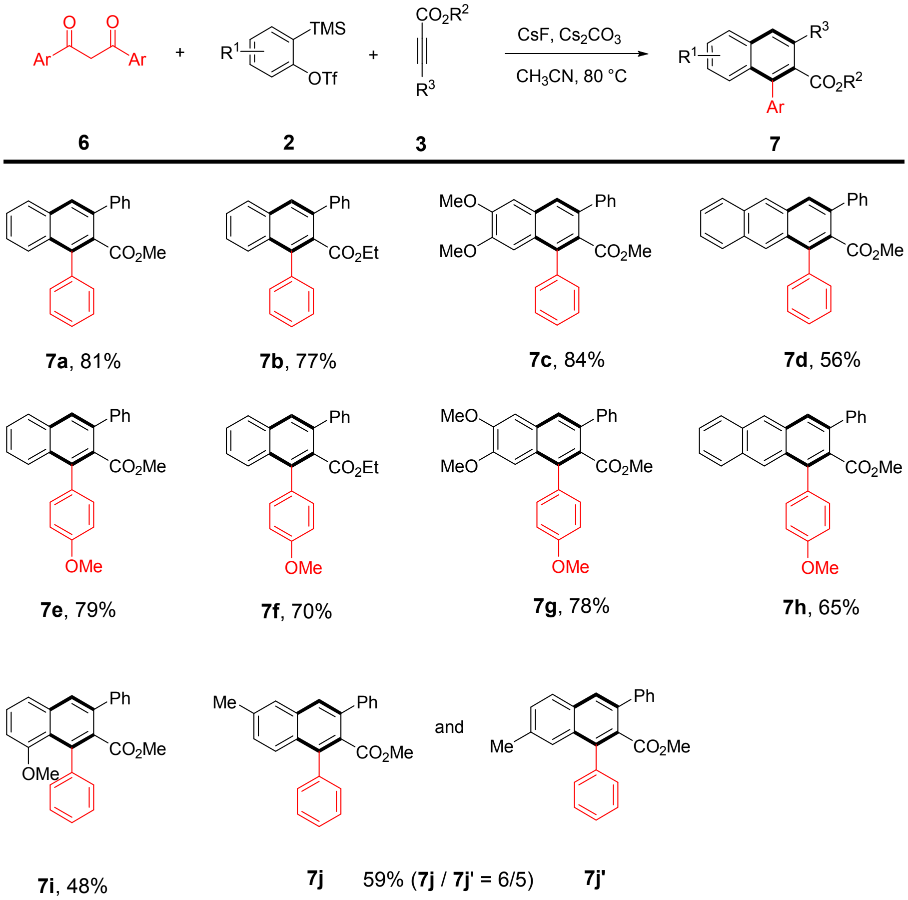


[a]Isolated yields.

Interestingly, when using 1,3-diketones (**6**) instead of α-cyanoacetophenones in the reaction, an unexpected product was observed (Scheme 4). We afforded different naphthalene derivatives, lacking the benzoyl group at the α-position of the product.

Subsequently, the scope of the 2-(trimethylsilyl)aryl triflates (**2**) and alkynoates (**3**) were examined. To our delight, symmetrically substituted benzyne precursors were all compatible in the current reaction system, giving the corresponding products in 56%–84% yields (**7a**–**7d**). 1,3-Bis(4-methoxyphenyl)propane-1,3-dione (**6b**) was also a viable substrate in this transformation, furnishing the desired products **7e**–**7h** in moderate to good yields (65%–79%). Moreover, nonsymmetrical arynes derived from precursors were investigated in the annulation. When the 4-methylbenzyne precursor involved in the reaction, we afforded a mixture of products **7j**/**7j′** in 59% yield. But the sole product **7i** gained in 48% yield by using 3-methoxybenzyne precursor as substrate. Furthermore, the structure of **7f** was determined by X-ray crystallographic analysis (see SI).

Scheme 4. Scope of dibenzoylmethanes[a]



7a, 81% **7b**, 77% **7c**, 84% **7d**, 56%

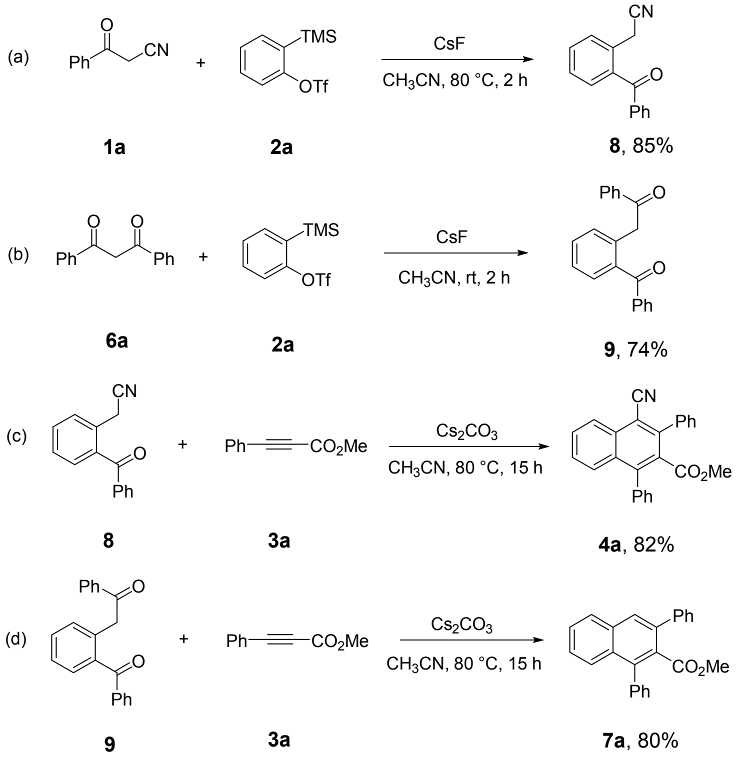
7e, 79% **7f**, 70% **7g**, 78% **7h**, 65%

7i, 48% **7j** 59% (**7j** / **7j'** = 6/5) **7j'**

[a]Isolated yields.

To provide some insights into the reaction mechanism, a series of control experiments was carried out (Scheme 5). When the reaction of ketone **1a** and 2-(trimethylsilyl)phenyl triflate **2a** was carried out in the presence of CsF in CH_3CN at 80 °C for 2 h, product **8**[15] was afforded in 85% yield (Scheme 5a). Similarly, dibenzoylmethane **6a** reacted with benzyne precursor **2a** to give compound **9**[16] at room temperature (Scheme 5b). Much to our satisfaction, compounds **8** and **9** were transformed into the desired products **4a** and **7a** in the presence of Cs_2CO_3 in excellent yields (Scheme 5c and 5d). These results indicate that compounds **8** and **9** are the intermediates in the annulation reaction.

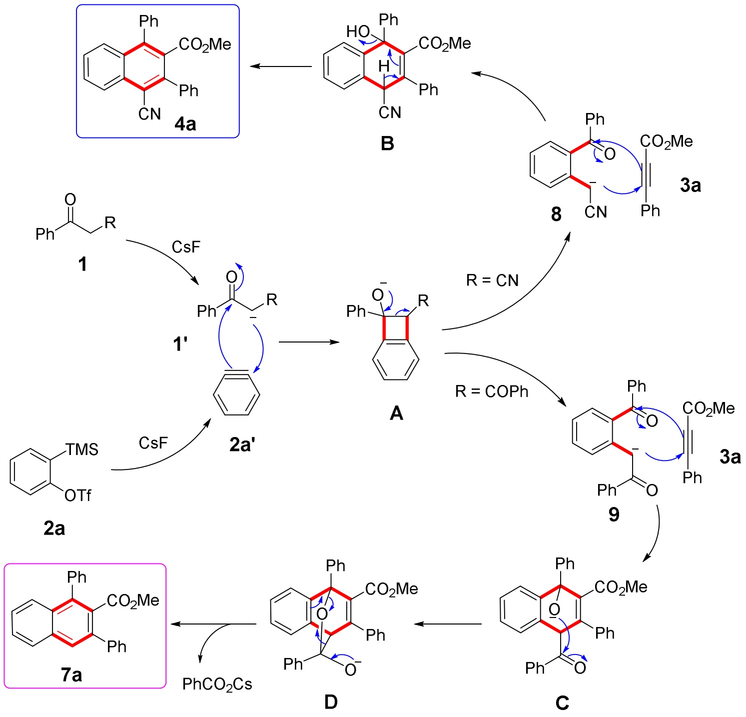
Scheme 5. Control Experiments[a]



[a]Isolated products.

On the basis of the abovementioned experimental results, a possible mechanism for this reaction is shown in Scheme 6 (using **4a** and **7a** as examples). Initially, ketone **1** transformed into anion **1′** in the presence of CsF, which subsequently reacted with benzyne **2a′** (generated in situ generated from 2-(trimethylsilyl)phenyl triflate **2a**) to afford cyclobutane intermediate **A**.[10b, 17] Subsequent cleavage of the benzylic C-C bond then afforded compounds **8** and **9** via intermediate A.[18] Intermediates **8** and **9** then underwent a coupling annulation with methyl 3-phenylpropiolate **3a** giving intermediates **B** and **C**, respectively. Finally, intermediate **B** was transformed to the desired product **4a** via an aromatization reaction with elimination of H_2O. Intermediate **C** was transformed into intermediate **D**, which was subsequently converted to product **7a** by the rearrangement-aromatization process, with loss of cesium benzoate.[19]

Scheme 6. A Possible Mechanism



CONCLUSION

In summary, we have developed a novel sequential σ-bond insertion/benzannulation reaction of ketones, arynes, and alkynoates to synthesize two classes of naphthalene derivatives under mild conditions. A detailed study of the mechanism demonstrated that the ketone substituent plays a key role in the reactivity of the subsequent annulation process to give different naphthalene products. Further studies on these practical methods for the construction of natural products and functional organic molecules are in progress in our laboratory.

EXPERIMENTAL SECTION

General Information. All substrates and reagents were commercial and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^{1}H NMR spectra were determined at 25 °C on a Varian Mercury 400 or 600 MHz spectrometer. Chemical shifts are given in ppm relative to the internal standard of tetramethylsilane (TMS). ^{13}C spectra were recorded in $CDCl_3$ or DMSO-d_6 on 100/150 MHz NMR spectrometers and resonances (δ) in ppm. HRMS were obtained on an Apex-Ultra MS equipped with an atmospheric-pressure chemical ionization source or electrospray ionization (ESI) source. The melting points were determined using XT-4 apparatus and recorded without correction. The X-ray crystal-structures were obtained on a Bruker APEX DUO CCD system.

General Procedure for the Synthesis of 4a-4l, 5a-5l 7a-7i, and 7j/7j′ (4a as example). The mixture of benzoyl acetonitrile **1a** (72.6 mg, 0.5 mmol), 2-trimethylsilylphenyl triflate **2a** (149.2 mg, 0.5 mmol), methyl 3-phenylpropiolate **3a** (96.1 mg, 0.6 mmol) was added in CH_3CN (5 mL). Then, added CsF (227.9 mg, 3.0

mmol) and Cs_2CO_3 (488.7 mg, 3.0 mmol) in the solvent and the resulting mixture was stirred at reflux for 15 h. After the reaction completed, and then added 100 mL water to the mixture, extracted with EtOAc three times (3 × 100 mL). Dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the desired product **4a**.

methyl 4-cyano-1,3-diphenyl-2-naphthoate (**4a**): Yield 79% (143.5 mg); white solid; m.p. 171–172 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.39 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.54–7.44 (m, 8H), 7.39 (d, J = 6.0 Hz, 2H), 3.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.8, 143.0, 142.6, 136.7, 136.3, 132.7, 131.0, 129.6, 129.1, 129.0, 128.5, 128.4, 128.2, 128.0, 127.8, 125.7, 116.7, 110.1, 51.9; IR (KBr, cm^{-1}): 2357, 2221,1734, 1638, 1566, 1488, 1441, 1384, 1305, 1230, 1185, 1152, 1117, 1045, 1016, 984, 845, 818, 765, 700, 605, 569, 486; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{18}NO_2$: 364.1332; found: 364.1327.

methyl 4-cyano-3-phenyl-1-(p-tolyl)-2-naphthoate (**4b**): Yield 71% (134.0 mg); white solid; m.p. 145–146 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.52–7.46 (m, 5H), 7.28 (q, J = 7.2 Hz, 4H), 3.25 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.6, 142.8, 142.5, 138.1, 136.6, 133.0, 132.5, 132.5, 130.9, 129.4, 129.3, 128.9, 128.8, 128.8, 128.2, 127.7, 127.6, 125.4, 116.5, 109.7, 51.9, 21.5; IR (KBr, cm^{-1}): 1734, 1638, 1493, 1429, 1384, 1304, 1226, 1185, 1151, 1117, 1044, 1016, 816, 767, 690, 621, 570; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{19}NNaO_2$: 400.1308; found: 400.1307.

methyl 4-cyano-1-(4-methoxyphenyl)-3-phenyl-2-naphthoate (**4c**): Yield 77% (151.5 mg); yllow solid; m.p. 179–180 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.4 Hz, 1H), 7.78–7.70 (m, 2H), 7.61–7.53 (m, 1H), 7.53–7.43 (m, 5H), 7.31 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H), 3.27 (s, 3H); ^{13}C NMR

(150 MHz, $CDCl_3$): δ (ppm) 167.9, 159.6, 143.0, 142.4, 136.8, 132.9, 132.7, 131.3, 130.9, 129.6, 129.1, 129.0, 128.4, 128.3, 127.9, 127.8, 125.7, 116.7, 113.7, 109.8, 55.3, 52.0; IR (KBr, cm^{-1}): 2219, 1726, 1639, 1609, 1514, 1493, 1431, 1383, 1294, 1245, 1181, 1155, 1119, 1022, 992, 843, 818, 765, 694, 622, 575, 529, 482; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{19}NNaO_3$: 416.1257; found: 416.1252.

methyl 4-cyano-1-(4-fluorophenyl)-3-phenyl-2-naphthoate (**4d**): Yield 69% (131.6 mg); white solid; m.p. 156–158 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.40 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.51–7.47 (m, 5H), 7.38–7.36 (m, 2H), 7.20 (t, J = 8.6 Hz, 2H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.3, 162.5 (d, J_{C-F} = 230 Hz), 142.7, 141.2, 136.4, 132.7 (d, J_{C-F} = 27.8 Hz), 131.9 (d, J_{C-F} =3.5 Hz), 131.4, 131.3, 130.8, 129.6, 129.5, 128.9, 128.9, 128.3, 127.9, 127.3, 125.6, 116.3, 115.3 (d, J_{C-F} =21.5 Hz), 110.2, 52.0; IR (KBr, cm^{-1}):2222, 1733, 1638, 1605, 1512, 1494, 1433, 1383, 1304, 1228, 1186, 1154, 1116, 1044, 1016, 989, 903, 847, 819, 798, 767, 692, 622, 573, 537; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{17}FNO_2$: 382.1238; found: 382.1234.

methyl 1-(4-chlorophenyl)-4-cyano-3-phenyl-2-naphthoate (**4e**): Yield 70% (139.3 mg); white solid; m.p. 193–194 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.40 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.53–7.43 (m, 7H), 7.34 (d, J = 8.4 Hz, 2H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 142.7, 140.9, 136.3, 134.5, 134.5, 132.6, 132.5, 130.9, 130.6, 129.6, 128.9, 128.9, 128.4, 128.2, 128.0, 127.2, 125.6, 116.3, 110.3, 52.1; IR (KBr, cm^{-1}): 2225, 1734, 1634, 1487, 1434, 1306, 1233, 1185, 1153, 1118, 1044, 1015, 989, 903, 843, 817, 769, 730, 699, 622, 571, 517; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{16}ClNNaO_2$: 420.0762; found: 420.0755.

methyl 4-cyano-1-(3,4-dichlorophenyl)-3-phenyl-2-naphthoate (**4f**): Yield 63% (136.2 mg); white solid; m.p. 140–141 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.41 (d, J = 8.4 Hz, 1H), 7.82–7.79 (m, 1H), 7.65–7.61 (m, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.53–7.51 (m, 1H), 7.51–7.46 (m, 5H), 7.25–7.24 (m, 1H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.0, 142.7, 139.4, 136.2, 135.9, 132.9, 132.6, 132.5, 132.4, 131.4, 130.3, 130.2, 129.7, 129.0, 128.8, 128.3, 128.3, 126.9, 125.7, 116.1, 110.7, 52.2; IR (KBr, cm^{-1}): 2221, 1731, 1638, 1496, 1408, 1384, 1307, 1222, 1186, 1153, 1122, 1044, 1016, 958, 902, 818, 766, 690, 623, 569; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{25}H_{15}Cl_2NNaO_2$: 454.0372; found: 454.0366.

methyl 1-(3-bromophenyl)-4-cyano-3-phenyl-2-naphthoate (**4g**): Yield 75% (165.9 mg); white solid; m.p. 153–155 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.40 (d, J = 8.4 Hz, 1H), 7.79–7.77 (m, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.63–7.59 (m, 2H), 7.58–7.56 (m, 1H), 7.52–7.47 (m, 5H), 7.38 (t, J = 7.8 Hz, 1H), 7.35–7.33 (m, 1H), 3.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.5, 143.0, 140.7, 138.3, 136.5, 132.7, 132.7, 132.5, 131.7, 130.6, 129.8, 129.1, 129.0, 128.5, 128.4, 128.3, 127.4, 125.8, 122.3, 116.4, 110.6, 52.1; IR (KBr, cm^{-1}): 2221, 1725, 1638, 1556, 1496, 1437, 1412, 1307, 1232, 1187, 1154, 1120, 1075, 1044, 1016, 993, 955, 917, 849, 802, 764, 722, 699, 636, 576; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{25}H_{16}BrNNaO_2$: 464.0257; found: 464.0251.

methyl 1-(4-bromophenyl)-4-cyano-3-phenyl-2-naphthoate (**4h**): Yield 56% (123.8 mg); white solid; m.p. 207–207 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.40 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.65–7.63 (m, 3H), 7.59 (t, J = 7.8 Hz, 1H), 7.49–7.47 (m, 5H), 7.27 (d, J = 7.8 Hz, 2H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.3, 142.8, 141.0, 136.4, 135.0, 132.6, 131.4, 131.2, 130.6, 129.6, 129.0, 128.9, 128.3, 128.1, 127.3, 125.7, 122.9, 116.4, 110.4, 52.2; IR (KBr, cm^{-1}): 1733, 1638, 1619, 1431, 1385, 1305, 1185, 1151, 1118, 1044, 1013, 816, 768, 726, 689, 618; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{25}H_{16}BrNNaO_2$: 464.0257; found: 464.0251.

methyl 4-cyano-1-(furan-2-yl)-3-phenyl-2-naphthoate (**4i**): Yield 81% (143.1 mg); yellow solid; m.p. 119–120 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.67 (s, 1H), 7.51–7.45 (m, 5H), 6.74 (d, J = 3.6 Hz, 1H), 6.64–6.61 (m, 1H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.5, 148.1, 143.8, 142.9, 136.2, 132.7, 132.6, 130.9, 130.1, 129.6, 128.9, 128.8, 128.3, 128.2, 127.0, 125.6, 116.2, 113.0, 111.5, 111.0, 52.3; IR (KBr, cm^{-1}): 1738, 1638, 1410, 1385, 1305, 1185, 1151, 1119, 1044, 1016, 957, 816, 762, 690, 620, 568; HRMS (ESI): m/z [M+Na]$^+$ calcd for

$C_{23}H_{15}NNaO_3$: 376.0944; found: 376.0940.

methyl 4-cyano-3-phenyl-1-(thiophen-2-yl)-2-naphthoate (**4j**): Yield 74% (136.7 mg); white solid; m.p. 165–166 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 8.4 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.55 (t, J = 3.6 Hz, 1H), 7.51–7.47 (m, 5H), 7.18 (d, J = 3.0 Hz, 2H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 142.6, 136.3, 135.6, 135.0, 134.1, 132.4, 131.7, 129.6, 129.6, 128.9, 128.9, 128.3, 128.1, 127.6, 127.3, 126.9, 125.5, 116.3, 110.9, 52.1; IR (KBr, cm^{-1}): 2224, 1735, 1638, 1493, 1434, 1385, 1304, 1223, 1185, 1152, 1126, 1044, 1016, 982, 846, 816, 762, 694, 618, 568; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{16}NO_2S$: 370.0896; found: 370.0891.

methyl 4-cyano-1-(1-methyl-3a,7a-dihydro-1H-indol-3-yl)-3-phenyl-2-naphthoate (**4k**): Yield 67% (139.5 mg); yellow solid; m.p. 237–239 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.52–7.44 (m, 8H), 7.32 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 3.95 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.3, 142.2, 138.3, 137.1, 136.7, 131.3, 131.3, 130.8, 129.9, 129.9, 129.1, 128.6, 128.5, 128.2, 127.8, 127.2, 125.2, 122.2, 120.2, 120.0, 117.8, 111.6, 110.1, 109.7, 52.5, 33.4.; IR (KBr, cm^{-1}): 1729, 1638, 1407, 1385, 1299, 1222, 1185, 1151, 1125, 1044, 1015, 816, 757, 690, 620, 569; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{21}N_2O_2$: 417.1598; found: 417.1599.

methyl 4-cyano-3-phenyl-[1,1'-binaphthalene]-2-carboxylate (**4l**): Yield 65% (134.4 mg); white solid; m.p. 167–168 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.44 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.57 (t, J = 7.8 Hz, 3H), 7.50–7.41 (m, 6H), 7.36–7.34 (m, 2H), 7.28 (d, J = 8.4 Hz, 1H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 143.0, 141.2, 136.6, 133.7, 133.4, 133.0, 132.4, 132.1, 131.4, 129.6, 129.0, 128.9, 128.9, 128.3, 128.0, 127.9, 127.9, 127.7, 126.4, 126.0, 126.0, 125.6, 124.9, 116.6, 110.4, 51.8; IR (KBr, cm^{-1}): 1729, 1637, 1408, 1385, 1303, 1185, 1151, 1125, 1044, 1015, 957, 816, 762, 688, 621, 567; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{20}NO_2$: 414.1489; found: 414.1483.

methyl 4-cyano-6,7-dimethoxy-1,3-diphenyl-2-naphthoate (**5a**): Yield 79% (167.3 mg); white solid; m.p. 220–221 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.60 (s, 1H), 7.52 – 7.43 (m, 7H), 7.41 – 7.36 (m, 2H), 6.91 (s, 1H), 4.10 (s, 3H), 3.76 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8, 152.3, 150.5, 140.8, 140.6, 136.9, 136.7, 130.9, 129.6, 129.3, 129.0, 128.6, 128.3, 128.2, 126.6, 117.1, 108.0, 105.9, 104.0, 56.4, 55.8, 51.9; IR (KBr, cm^{-1}): 2221, 1726, 1620, 1570, 1508, 1469, 1430, 1385, 1342, 1265, 1242, 1213, 1186, 1127, 1033, 1011, 979, 880, 841, 765, 728, 703; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{22}NO_4$: 424.1543; found: 424.1543.

methyl 4-cyano-6,7-dimethoxy-3-phenyl-1-(p-tolyl)-2-naphthoate (**5b**): Yield 81% (177.2 mg); white solid; m.p. 235–236 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.59 (s, 1H), 7.51–7.42 (m, 5H), 7.30–7.26 (m, 4H), 6.96 (s, 1H), 4.10 (s, 3H), 3.78 (s, 3H), 3.23 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.0, 152.2, 150.4, 140.8, 138.0, 137.0, 133.6, 131.0, 129.6, 129.2, 129.0, 128.9, 128.6, 128.2, 126.8, 117.2, 107.8, 106.0, 104.0, 56.4, 55.9, 51.9, 21.6; IR (KBr, cm^{-1}): 2215, 1732, 1620, 1572, 1510, 1470, 1432, 1385, 1340, 1264, 1240, 1214, 1183, 1152, 1127, 1042, 1018, 983, 882, 838, 816, 759, 732, 703, 568, 527; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{28}H_{23}NNaO_4$: 460.1519; found: 460.1516.

methyl 4-cyano-1-(4-fluorophenyl)-6,7-dimethoxy-3-phenyl-2-naphthoate (**5c**): Yield 82% (181.0 mg); white solid; m.p. 239–240 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.60 (s, 1H), 7.51–7.43 (m, 4H), 7.41–7.33 (m, 2H), 7.20 (t, J = 8.4 Hz, 2H), 6.85 (s, 1H), 4.11 (s, 3H), 3.78 (s, 3H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8, 162.4 (d, $J_{C,F}$ = 246 Hz), 152.4, 150.7, 140.8, 139.4, 136.8, 132.6 (d, $J_{C,F}$ = 3.5 Hz), 131.2 (d, $J_{C,F}$ = 8.1 Hz), 129.6, 129.0, 128.7, 128.2, 126.7, 117.0, 115.4 (d, $J_{C,F}$ = 21.4 Hz), 108.2, 105.5, 104.1, 56.4, 55.9, 52.0; IR (KBr, cm^{-1}): 2217, 1735, 1622, 1508, 1469, 1432, 1385, 1343, 1265, 1243, 1216, 1186, 1128, 1046, 1015, 983, 880, 845, 817, 796, 757, 730, 698, 568, 527; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{27}H_{20}FNNaO_4$: 464.1269; found: 464.1269.

methyl 1-(4-chlorophenyl)-4-cyano-6,7-dimethoxy-3-phenyl-2-naphthoate (**5d**): Yield 75% (171.7 mg); white solid; m.p. 242–243 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.60 (s, 1H), 7.52–7.43 (m, 7H), 7.34 (d, J = 8.4 Hz, 2H), 6.84 (s, 1H), 4.10 (s, 3H), 3.79 (s, 3H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 167.7, 152.4, 150.7, 140.8, 139.2, 136.8, 135.1, 134.4, 130.9, 130.7, 129.6, 129.0, 128.7, 128.5, 128.2, 126.5, 116.9, 108.4, 105.4, 104.1, 56.4, 56.0, 52.0; IR (KBr, cm^{-1}): 2359, 2217, 1738, 1619, 1572, 1503, 1469, 1431, 1384, 1343, 1243, 1242, 1213, 1186, 1128, 1046, 1016, 880, 845, 815, 756, 727, 699, 574; HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{27}H_{21}ClNO_4$: 458.1154; found: 458.1151.

methyl 4-cyano-1,3-diphenylanthracene-2-carboxylate (**5e**): Yield 66% (136.5 mg); yellow solid; m.p. 318–319 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 8.97 (s, 1H), 8.26 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.59–7.54 (m, 5H), 7.54–7.49 (m, 4H), 7.49–7.45 (m, 2H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 167.6, 143.4, 142.8, 136.8, 136.4, 133.1, 132.3, 131.6, 129.6, 129.1, 128.9, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.5, 126.7, 124.6, 116.9, 109.9, 52.0; IR (KBr, cm^{-1}): 2361, 2225, 1738, 1638, 1428, 1385, 1288, 1186, 1126, 1043, 1014, 815, 757, 702, 618, 568, 546; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{29}H_{19}NNaO_2$: 436.1308; found: 436.1308.

methyl 4-cyano-3-phenyl-1-(p-tolyl)anthracene-2-carboxylate (**5f**): Yield 51% (109.0 mg); yellow solid; m.p. 298–301 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 8.95 (s, 1H), 8.29 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.57–7.55 (m, 2H), 7.54–7.48 (m, 4H), 7.35 (s, 4H), 3.27 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 167.7, 143.4, 143.0, 138.3, 136.8, 133.3, 133.1, 132.2, 131.6, 129.5, 129.3, 129.1, 128.9, 128.9, 128.8, 128.4, 128.3, 128.0, 127.8, 127.5, 126.6, 124.6, 117.0, 109.7, 52.0, 21.6; IR (KBr, cm^{-1}): 1738, 1638, 1427, 1385, 1290, 1218, 1185, 1152, 1118, 1043, 1015, 815, 755, 690, 621, 567; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{30}H_{21}NNaO_2$: 450.1465; found: 450.1459.

methyl 4-cyano-1-(4-fluorophenyl)-3-phenylanthracene-2-carboxylate (**5g**): Yield 53% (114.3 mg); yellow solid; m.p. 298–299 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 8.96 (s, 1H), 8.20 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.58–7.54 (m, 3H), 7.53–7.49 (m, 3H), 7.46–7.44 (m, 2H), 7.27–7.24 (m, 2H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 167.5, 162.6 (d, $J_{C,F}$ = 246.3 Hz), 143.2, 141.6, 136.6, 133.1, 132.3, 132.1 (d, $J_{C,F}$ = 3.5 Hz), 131.8, 131.4 (d, $J_{C,F}$ = 8.2 Hz), 129.0, 128.9, 128.7, 128.6, 128.3, 128.3, 128.1, 128.0, 127.6, 127.4, 126.8, 124.7, 116.8, 115.4 (d, $J_{C,F}$ = 21.4 Hz), 110.1, 52.1; IR (KBr, cm^{-1}): 2222, 1737, 1640, 1604, 1508, 1431, 1383, 1287, 1231, 1186, 1155, 1116, 1043, 1014, 985, 885, 850, 815, 755, 704, 600, 554; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{29}H_{18}FNNaO_2$: 454.1214; found: 454.1200.

methyl 1-(4-chlorophenyl)-4-cyano-3-phenylanthracene-2-carboxylate (**5h**): Yield 58% (129.9 mg); yellow solid; m.p. 310–311 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.96 (s, 1H), 8.19 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.63 (t, J = 8.4 Hz, 1H), 7.57–7.49 (m, 8H), 7.42 (d, J = 7.8 Hz, 2H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.4, 143.2, 141.3, 136.6, 134.7, 134.7, 133.1, 132.3, 131.7, 131.0, 129.0, 129.0, 128.9, 128.5, 128.4, 128.3, 128.0, 127.7, 127.3, 126.9, 124.8, 116.7, 110.2, 52.1; IR (KBr, cm^{-1}): 2362, 2227, 1736, 1639, 1488, 1430, 1289, 1195, 1167, 1105, 1041, 1015, 987, 858, 816, 753, 701, 549; HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{29}H_{18}ClNNaO_2$: 470.0918; found: 470.0914.

ethyl 4-cyano-1,3-diphenyl-2-naphthoate (**5i**): Yield 80% (151.0 mg); white solid; m.p. 94–95 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.39 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.54 –7.52 (m, 2H), 7.51–7.47 (m, 6H), 7.1–7.39 (m, 2H), 3.72 (q, J = 7.2 Hz, 2H), 0.72 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.9, 142.8, 142.2, 136.6, 136.1, 132.7, 132.5, 130.8, 129.6, 129.4, 129.0, 128.8, 128.3, 128.2, 128.0, 127.7, 127.5, 125.5, 116.5, 110.0, 61.2, 13.5; IR (KBr, cm^{-1}): 1729, 1637, 1409, 1384, 1305, 1226, 1182, 1151, 1117, 1044, 1013, 817, 763, 690, 622, 569; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{26}H_{19}NNaO_2$: 400.1308; found: 400.1305.

dimethyl 1-cyano-4-phenylnaphthalene-2,3-dicarboxylate (**5j**): Yield 51% (88.0 mg); white solid; m.p. 162–164 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.48 (d, J = 8.4 Hz, 1H), 7.86–7.78 (m, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.65–7.63 (m, 1H), 7.52–7.49 (m, 3H), 7.33–7.31 (m, 2H), 4.06 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.4, 165.3, 144.0, 135.7, 132.9, 132.4, 130.4, 130.2, 129.7, 129.5, 128.7, 128.3, 128.0, 126.5, 115.4, 110.6, 53.5, 52.5; IR (KBr, cm^{-1}): 2362, 1728, 1638, 1432, 1384, 1306, 1260, 1220, 1185, 1128, 1044, 1015, 972, 815, 762, 691, 610, 570; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{15}NNaO_4$: 368.0893; found: 368.0897.

methyl 4-cyano-1-phenyl-2-naphthoate (**5k**): Yield 78% (112.0 mg); white solid; m.p. 154–156 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.41 (s, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.78–7.76 (m, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.57–7.55 (m, 1H), 7.53–7.50 (m, 3H), 7.28–7.24 (m, 2H), 3.66 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.6, 146.8, 137.3, 133.2, 132.6, 132.4, 130.0, 129.0, 128.7, 128.1, 128.1, 127.4, 125.2, 117.1, 110.1, 52.4; IR (KBr, cm^{-1}): 1638, 1411, 1385, 1302, 1220, 1185, 1151, 1125, 1044, 1015, 816, 765, 689, 621, 569; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{13}NNaO_2$: 310.0839; found: 310.0838.

ethyl 4-cyano-1-phenyl-2-naphthoate (**5l**): Yield 42% (65.2 mg); white solid; m.p. 118–119 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.40 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.52–7.46 (m, 3H), 7.29–7.26 (m, 2H), 4.09 (q, J = 7.2 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 166.5, 146.4, 137.6, 133.2, 132.6, 132.5, 129.9, 129.1, 128.7, 128.1, 128.1, 128.0, 125.2, 117.2, 110.1, 61.5, 13.6; IR (KBr, cm^{-1}):1708, 1638, 1414, 1379, 1338, 1256, 1220, 1184, 1151, 1117, 1044, 1018, 901, 864, 816, 763, 691, 622, 571, 529; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{15}NNaO_2$: 324.0995; found: 324.0990.

methyl 1,3-diphenyl-2-naphthoate (**7a**): Yield 81% (137.1 mg); oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.90 (d, J = 8.4 Hz, 1H), 7.87 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.39–7.44 (m, 6H), 7.36 (t, J = 7.8 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.6, 140.6, 138.3, 137.7, 136.6, 133.4, 131.8, 131.1, 130.1, 128.5, 128.4, 128.3, 128.05, 128.0, 127.7, 127.5, 127.1, 126.8, 126.6, 51.7; IR (KBr, cm^{-1}):1732, 1640, 1492, 1433, 1384, 1303, 1267, 1226, 1184, 1151, 1129, 1110, 1043, 1016, 959, 894, 817, 795, 757, 700, 604, 575; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{18}NaO_2$: 361.1199; found: 361.1199.

ethyl 1,3-diphenyl-2-naphthoate (**7b**): Yield 77% (135.7 mg); yellow solid; m.p. 68–69 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.90 (d, J = 8.4 Hz, 1H), 7.87 (s, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 3H), 7.50–7.44 (m, 2H), 7.44–7.39 (m, 5H), 7.37 (t, J = 7.2 Hz, 1H), 3.79 (q, J = 7.2 Hz, 2H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.0, 140.7, 138.2, 137.8, 136.7, 133.4, 131.9, 131.2, 130.2, 128.7, 128.4, 128.2, 128.0, 127.9, 127.7, 127.4, 127.1, 126.8, 126.6, 60.8, 13.4; IR (KBr, cm^{-1}):1726, 1491, 1446, 1420, 1384, 1301, 1264, 1227, 1184, 1152, 1131, 1107, 1039, 1015, 891, 855, 815, 796, 756, 701, 604, 578; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{25}H_{20}NaO_2$: 375.1356; found: 375.1358.

methyl 6,7-dimethoxy-1,3-diphenyl-2-naphthoate (**7c**): Yield 84% (167.4 mg); white solid; m.p. 142–144 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.72 (s, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.44–7.37 (m, 5H), 7.35 (t, J = 7.8 Hz, 1H), 7.17 (s, 1H), 6.86 (s, 1H), 4.01 (s, 3H), 3.74 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.6, 150.2, 149.7, 140.7, 138.1, 136.7, 135.1, 130.0, 129.7, 129.5, 128.4, 128.1, 127.9, 127.5, 127.1, 126.7, 106.2, 105.3, 56.0, 55.7, 51.6; IR (KBr, cm^{-1}):1732, 1624, 1501, 1466, 1429, 1311, 1244, 1220, 1188, 1144, 1113, 1037, 1012, 899, 816, 752, 703, 621, 569; HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{26}H_{22}NaO_4$: 421.1410; found: 421.1414.

methyl 1,3-diphenylanthracene-2-carboxylate (**7d**): Yield 56% (108.8 mg); yellow solid; m.p. 130–131 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.49 (s, 1H), 8.15 (s, 1H), 8.04 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.57–7.55 (m, 2H), 7.52 (t, J = 7.2 Hz, 2H), 7.50 (d, J = 7.2 Hz, 3H), 7.48–7.42 (m, 3H), 7.41–7.37 (m, 1H), 3.3 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.7, 140.7, 138.6, 137.9, 136.0, 132.3, 132.0, 131.4, 131.3, 130.2, 129.6, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.5, 126.6, 126.4, 126.3, 125.7, 51.7; IR (KBr, cm^{-1}):1729, 1638, 1411, 1385, 1301, 1184, 1150, 1126, 1044, 1015, 957, 816, 757, 691, 620, 567; HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{28}H_{21}O_2$: 389.1536; found: 389.1538.

methyl 1-(4-methoxyphenyl)-3-phenyl-2-naphthoate (**7e**): Yield 79% (145.5 mg); yellow solid; m.p. 144–145 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.89 (d, J = 8.4 Hz, 1H), 7.85 (s, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.55–7.50 (m, 3H), 7.42 (t, J = 7.2 Hz, 3H), 7.36 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 3.87 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5, 158.9, 140.5, 137.8, 136.4, 133.3, 131.9, 131.3, 131.1, 129.7, 128.4, 128.1, 128.1, 127.9, 127.3, 126.9, 126.7, 126.4, 113.4, 55.3, 51.8; IR (KBr, cm^{-1}):1732, 1607, 1513, 1493, 1435, 1384, 1288, 1249, 1183, 1152, 1133, 1109, 1039, 995, 965, 894, 860, 841, 795, 753, 704, 605, 578; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{20}NaO_3$: 391.1305; found: 391.1308.

ethyl 1-(4-methoxyphenyl)-3-phenyl-2-naphthoate (**7f**): Yield 70% (133.9 mg); white solid; m.p. 122–123 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.88 (d, J = 8.4 Hz, 1H), 7.85 (s, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.53–7.51 (m, 3H), 7.41 (t, J = 7.2 Hz, 3H), 7.37 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 3.82 (q, J = 7.2 Hz, 2H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.8, 158.9, 140.5, 137.7, 136.5, 133.2, 132.1, 131.4, 131.2, 129.8, 128.6, 128.1, 128.0, 127.9, 127.2, 126.8, 126.7, 126.3, 113.3, 60.8, 55.3, 13.7; IR (KBr, cm^{-1}):1729, 1638, 1608, 1513, 1493, 1422, 1384, 1289, 1245, 1226, 1182, 1151, 1130, 1110, 1039, 1015, 887, 839, 816, 753, 702, 605, 577; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{23}O_3$: 383.1642; found: 383.1646.

methyl 6,7-dimethoxy-1-(4-methoxyphenyl)-3-phenyl-2-naphthoate (**7g**): Yield 78% (167.1 mg); yellow solid; m.p. 175–177 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.70 (s, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.17 (s, 1H), 7.00 (d, J = 9.0 Hz, 2H), 6.90 (s, 1H), 4.02 (s, 3H), 3.89 (s, 3H), 3.77 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.8, 158.7, 150.2, 149.7, 140.8, 136.4, 135.0, 130.9, 130.2, 130.2, 129.5, 128.4, 128.1, 127.0, 126.5, 113.4, 106.2, 105.3, 56.0, 55.8, 55.3, 51.7; IR (KBr, cm^{-1}):2362, 2339, 1737, 1623, 1504, 1465, 1428, 1290, 1245, 1221, 1182, 1148, 1112, 1039, 1013, 898, 850, 815, 763, 688, 570; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{25}O_5$: 429.1697; found: 429.1698.

methyl 1-(4-methoxyphenyl)-3-phenylanthracene-2-carboxylate (**7h**): Yield 65% (136.0 mg); yellow solid; m.p. 182–184 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H), 8.19 (s, 1H), 8.01–7.99 (m, 2H), 7.85 (d, J = 9.0 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H), 3.36 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ (ppm) 169.5, 159.0, 140.6, 138.1, 135.9, 132.1, 131.8, 131.5, 131.2, 131.2, 129.9, 129.8, 128.6, 128.4, 128.2, 128.2, 127.7, 127.3, 126.4, 126.3, 126.1, 125.5, 113.5, 55.3, 51.8; IR (KBr, cm^{-1}):1730, 1637, 1504, 1425, 1385, 1288, 1224, 1183, 1149, 1126, 1043, 1015, 957, 898, 816, 753, 689, 621, 570; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{23}O_3$: 419.1642; found: 419.1642.

methyl 8-methoxy-1,3-diphenyl-2-naphthoate (**7i**): Yield 48% (88.4 mg); yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 1H), 7.49 (t, J = 8.4 Hz, 3H), , 7.44 (t, J = 7.8 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 6.6 Hz, 2H), 7.31 (s, 4H), 6.77 (d, J = 7.8 Hz, 1H), 3.40 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.6, 157.2, 141.7, 140.3, 136.6, 136.5, 135.4, 133.2, 128.9, 128.6, 128.5, 128.2, 127.5, 126.4, 126.2, 122.5, 121.0, 106.9, 55.5, 51.5; IR (KBr, cm^{-1}):1727, 1563, 1435, 1266, 1251, 1119, 1108, 772, 758, 702; HRMS (ESI): $C_{25}H_{21}O_3$: m/z $[M+H]^+$ calcd for: 369.1485; found: 369.1486.

methyl 6-methyl-1,3-diphenyl-2-naphthoate (**7j**)/*methyl 7-methyl-1,3-diphenyl-2-naphthoate* (**7j'**): Yield 59% (103.9 mg); yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.82 (s, 1H), 7.80–7.78 (m, 2H), 7.66 (s, 1H), 7.51–7. 48 (m, 6H), 7.47–7.43 (m, 5H), 7.43–7.40 (m, 9H), 7.37–7.35 (m, 5H), 7.25–7.22 (m, 2H), 3.29 (s, 6H), 2.50 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 169.7, 140.7, 140.7, 138.2, 137.9, 137.6, 137.0, 136.6, 136.5, 135.6, 133.7, 131.8, 131.7, 131.2, 130.9, 130.1, 130.0, 129.4, 129.3, 128.9, 128.5, 128.5, 128.5, 128.5, 128.3, 128.2, 127.9, 127.9, 127.8, 127.6, 127.4, 127.3, 127.0, 126.6, 125.6, 51.6, 21.9, 21.6; IR (KBr, cm^{-1}):1729, 1568, 1429, 1266, 1108, 774, 701; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{21}O_2$: 353.1536; found: 353.1535.

2-(2-benzoylphenyl)acetonitrile (**8**): Yield 83% (91.0 mg); oil; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.2 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.49–7.46 (m, 3H), 7.41 (t, J = 7.8 Hz, 1H), 3.99 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 197.0, 137.1, 136.6, 133.4, 131.6, 130.6, 130.2, 130.1, 129.8, 128.5, 127.4, 117.7, 21.8; IR (KBr, cm^{-1}):1713, 1667, 1493, 1433, 1384, 1329, 1285, 1186, 1151, 1125, 1044, 1016, 954, 816, 781, 756, 727, 689, 622, 570; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{12}NO$: 222.0913;

found: 222.0915.

2-(2-benzoylphenyl)-1-phenylethan-1-one (**9**): Yield 77% (115.7 mg); yellow solid; m.p. 50–51 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.06 (d, J = 9.0 Hz, 1H), 8.27 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 8.4, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.30–7.27 (m, 2H), 7.26–7.22 (m, 4H), 4.01 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 198.0, 167.4, 143.1, 137.4, 136.8, 135.8, 133.0, 132.6, 132.0, 130.5, 129.7, 128.6, 128.5, 128.1, 127.9, 127.5, 127.0, 126.6, 125.9, 52.4; IR (KBr, cm^{-1}):1732, 1665, 1598, 1493, 1431, 1384, 1340, 1286, 1231, 1184, 1151, 1130, 1113, 1044, 1018, 951, 882, 841, 816, 753, 702, 629, 571, 533; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{16}NaO_2$: 323.1043; found: 323.1043.

Supporting Information

Crystallographic data, and copies of ^{1}H and ^{13}C NMR spectra of compounds **4a-4l, 5a-5l** and **7a-7j**. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (Grants 21472056, 21772051), and the Doctoral Scientific Research Startup Foundation of Yangtze University (No. 801090010135) for financial support. This work was also supported by the Yangtze Youth Talents Fund (No. 2016cqn25).

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