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Iron-catalyzed annulation reaction of arylindium reagents and alkynes to produce substituted naphthalenes

Laksmikanta Adak, Naohiko Yoshikai *

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

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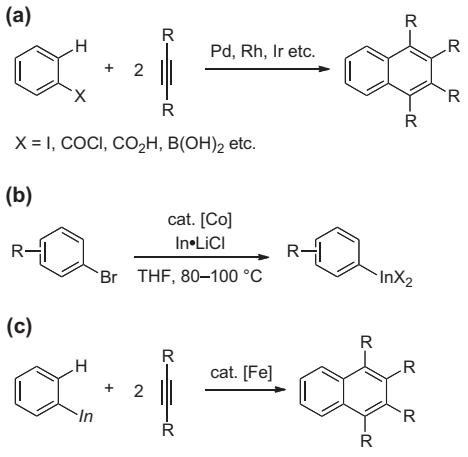
ABSTRACT

We report here an iron–bisphosphine complex-catalyzed annulation reaction of an arylindium reagent and two alkyne molecules that affords a substituted naphthalene derivative in moderate to good yield. The reaction represents a new example of iron-catalyzed C–C bond forming reactions via C–H bond functionalization.

1. Introduction

Efficient and selective construction of naphthalenes and other polycyclic aromatic hydrocarbons has been an important subject in organic synthesis because of their potential utility as π-conjugated functional materials.[1] Among various synthetic methods for naphthalenes,[2] metal-mediated or -catalyzed annulation of a mono- or difunctionalized aromatic substrate with two alkyne molecules has attracted significant attention because of flexible and modular nature of the approach.[3–5] The use of monofunctionalized aromatic substrates is not only synthetically attractive from atom economy and structural diversity points of view but also mechanistically intriguing because the reaction involves functionalization of the *ortho* C–H bond.[6] Thus far, a variety of monofunctionalized aromatic substrates have been shown to participate in such annulation reactions, including iodoarenes,[3c-e] aroyl chlorides,[3f] benzoic acids,[3g–i] and arylboronic acids,[3n,o] while in all cases expensive transition metals, such as palladium, rhodium, and iridium have been used as catalysts (Scheme 1a).

Recently, we developed a preparative method for arylindium reagents from the corresponding aryl bromides and indium metal using a cobalt–bathophenanthroline complex and LiCl as a catalyst and a promoter, respectively (Scheme 1b).[7–9] The thus-formed arylindium reagents participate in palladium-catalyzed biaryl cross-coupling reactions without interference from the cobalt catalyst. On our way to expand the scope of synthetic applications of the arylindium reagents, we became interested in their use in an iron-catalyzed reaction with alkynes because of the prominent reactivity of iron catalysts in carbometalation of alkynes.[10] Contrary to our initial expectation, we have found an iron-catalyzed annulation reaction of an arylindium reagent and two alkyne molecules to afford a naphthalene derivative, which is reported herein



Scheme 1.

* Corresponding author. Tel.: +65 6592 7768; fax: +65 6791 1961; e-mail address: nyoshikai@ntu.edu.sg (N. Yoshikai).

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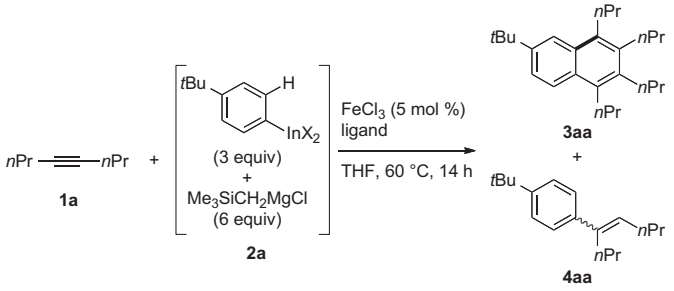
(Scheme 1c). The reaction represents an interesting new example of iron-catalyzed C–C bond formation via C–H bond cleavage.[11,12]

2. Results and discussion

At the outset of our investigation, we examined the reaction of 4-octyne **1a** with a 4-*tert*-butylphenylindium reagent prepared by our indium insertion reaction of 1-bromo-4-*tert*-butylbenzene. After initial experiments using a few different iron catalysts, it became clear that the as prepared indium reagent is too unreactive to give any addition products. In analogy to the reactivity of arylzinc reagents in iron-catalyzed cross-coupling reactions,[13] we envisioned that the reactivity of the arylindium reagent might be enhanced by transmetalation with a Grignard reagent bearing a nontransferable trimethylsilylmethyl group. Thus, systematic screening experiments were performaed on the reaction of **1a** with an arylindium reagent **2a**, which was generated from the 4-*tert*-butylphenylindium reagent (3 equiv) and Me_3SiCH_2MgCl (6 equiv) (Table 1). With $FeCl_3$ (5 mol %) as the precatalyst, we obtained a naphthalene derivative **3aa** and an olefin product **4aa** (*E*/*Z*=ca. 6:4) albeit in low yields (entry 1), whereas none of those products was obtained in the absence of $FeCl_3$ (entry 2).

Table 1
Screening of reaction conditions[a]

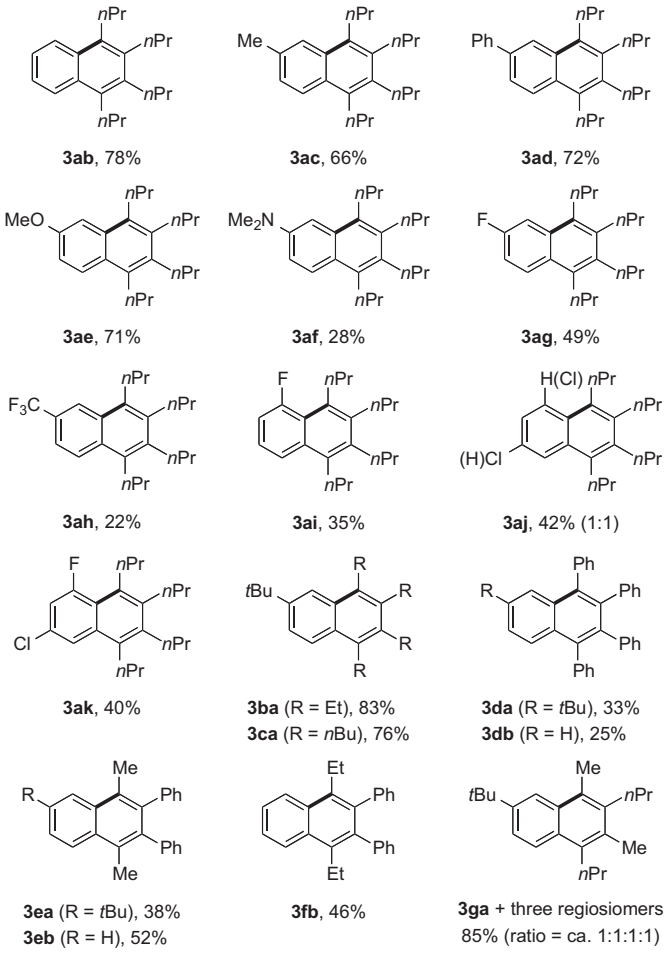


Entry	Ligand (mol %)	Yield (%)[b]	
		3aa	**4aa**[c]
1	—	3	5
2[d]	—	0	0
3	dppbz (10)	80[e]	0
4	dppe (10)	20	3
5	dppp (10)	5	2
6	dppf (10)	7	9
7	DPEphos (10)	3	8
8	Xantphos (10)	3	12
9	PCy_3 (20)	3	7
10	1,10-Phenanthroline (10)	5	8
11	IPr•HCl (20)	0	5
12	dppbz (5)	27	0
13[f]	dppbz (10)	55	0
14[g]	dppbz (10)	0	41

[a] Reaction was performed on a 0.3 mmol scale.
[b] Determined by GC using *n*-tridecane as an internal standard.
[c] The *E*/*Z* ratio was 6:4 as determined by GC and ^1H NMR.
[d] $FeCl_3$ was omitted from the reaction.
[e] Isolated yield.
[f] $Fe(acac)_3$ was used instead of $FeCl_3$.
[g] 3 equiv of Me_3SiCH_2MgCl was used.

Subsequent screening of ligands led us to find that a diphosphine ligand 1,2-bis(diphenylphosphino)benzene (dppbz) (10 mol %) significantly promotes the annulation reaction to afford **3aa** in 80% yield with no formation of **4aa** (entry 3). It is interesting to note that no external oxidant is necessary for the catalytic turnover, while the overall transformation appears to be an oxidative coupling of the arylindium reagent and the alkyne. None of other bidentate phosphine ligands including dppe, dppp, dppf, DPEphos, and Xantphos exhibited comparable catalytic activity (entries 4–8).[14] Other types of ligands, such as PCy_3, 1,10-phenanthroline, and IPr•HCl[14] were also ineffective (entries 9–11). The metal/ligand ratio of 2 was crucial as the use of 5 mol % of dppbz resulted in a significant decrease in the product yield (entry 12). $Fe(acac)_3$ was an inferior precatalyst compared with $FeCl_3$ (entry 13). The use of a smaller amount of Me_3SiCH_2MgCl led to exclusive formation of the alkenylation product **4aa** (entry 14). Note that aryl Grignard and zinc reagents did not produce the annulation product at all under the optimized conditions shown in entry 3.

With the optimized catalytic system in hand, we explored the scope of the present annulation reaction (Scheme 2). Arylindium reagents bearing electron-neutral or electron-donating substituents at the *para* position participated smoothly in the reaction with **1a** to afford naphthalene derivatives **3ab**–**3ae** in 66–78% yields, except that a strongly donating dimethylamino substituent caused adverse effects (see **3af**). On the other hand, electron-withdrawing fluoro and trifluoromethyl groups at the *para* position slowed down the reaction, resulting in modest yields of products **3ag** and **3ah**, respectively. The reaction of *meta*-fluorophenylindium reagent afforded an annulation product **3ai** via regioselective functionalization of the C–H bond *ortho* to the fluorine atom. The same sense of regioselectivity has been observed for rhodium-catalyzed annulation of *meta*-fluorophenylboronic acid and diphenylacetylene,[3o] which may be ascribed to the ability of fluorine to strengthen a metal–carbon bond at the *ortho*

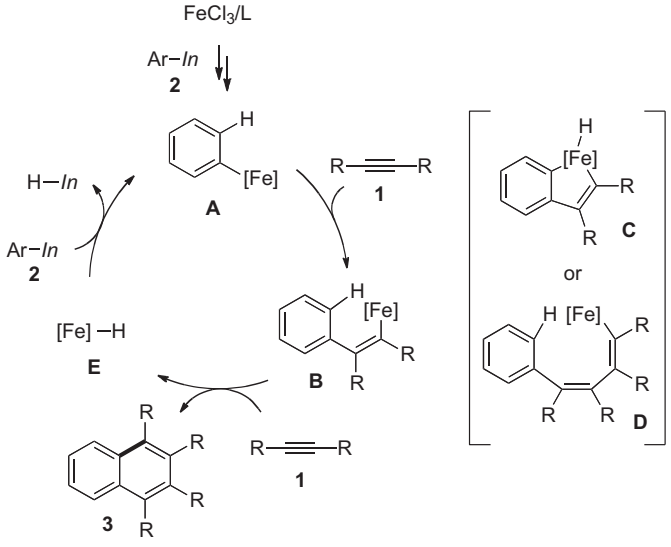


Scheme 2. Scope of iron-catalyzed annulation of arylindium reagents and alkynes. The bond indicated by a bold line refer to the C–C bond formed via C–H bond cleavage.

position.[15] In contrast, no regioselectivity in the C–H bond functionalization was observed for the reaction of *meta*-chlorophenylindium reagent (see **3aj**). When both chloro and fluoro substituents were present at the *meta* positions, exclusive functionalization of the C–H bond proximal to the fluorine atom took place (see **3ak**).

Not unexpectedly, other dialkylacetylenes, such as 3-hexyne and 5-decyne took part in the annulation reaction to afford products **3ba** and **3ca** in good yields. On the other hand, the reaction of diphenylacetylene was rather sluggish, and the corresponding annulation products were obtained only in modest yields (**3da** and **3db**). 1-Phenyl-1-propyne and 1-phenyl-1-butyne regioselectively afforded 1,4-dialkyl-2,3-diphenylnaphthalene derivatives **3ea**, **3eb**, and **3fb** in moderate yields. Note that this regioselectivity is the same as that observed for rhodium-catalyzed annulation reactions using phenylpyrazole and phenylboronic acid.[3k,o] On the other hand, the reaction of 2-hexyne was efficient but not regioselective, producing an equimolar mixture of four regioisomers including **3ga** in 85% overall yield.

While the mechanism of the present reaction is not clear at present, we may suggest a possible catalytic cycle as illustrated in Scheme 3. The iron precatalyst and the arylindium reagent would generate an aryliron species **A**, which would undergo insertion of the alkyne to give an alkenyliron species **B**.[10] The subsequent reaction pathway of the species **B** may be relevant to that of a putative 2-biarylliron species proposed for the iron-catalyzed reaction of a 2-biaryl Grignard reagent with an alkyne to produce a phenanthrene derivative by Nakamura et al.[12c] Thus, it may undergo intramolecular *ortho* C–H bond activation to give a ferracycle **C** followed by insertion of the second alkyne molecule to afford the naphthalene product **3**. An alternative route to **3** may involve insertion of the second alkyne molecule to the species **B** to form a dienyliron species **D**, which then undergoes intramolecular C–H bond functionalization. Judging from the regioselectivity observed for the reactions of 1-phenyl-1-propyne (**3ea** and **3eb**) and 1-phenyl-1-butyne (**3fb**), the former pathway appears more likely. The formation of naphthalene **3** is formally accompanied by generation of an iron hydride species **E**. Because the present reaction does not require an external oxidant, we speculate that the aryliron species **A** is regenerated through transmetalation between the iron hydride species **E** and the arylindium reagent.



Scheme 3. A possible catalytic cycle.

3. Conclusion

In summary, we have developed an iron-catalyzed annulation reaction of arylindium reagents and internal alkynes to afford substituted naphthalene derivatives. The reaction represents an intriguing new example of iron-catalyzed aromatic C–H bond functionalization. Further effort will focus on the investigation of mechanistic details including the origin of the ligand effect,[16] and the extension of iron catalysis of organoindium reagents.

4. Experimental section

4.1. General

All reactions dealing with air- and moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40–63 μm silica gel (Si 60, Merck). 1H and 13C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-400 (400 MHz) spectrometer, and are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CHCl_3$ (77 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d.×30 m, 0.25 μm film thickness). High-resolution mass spectra (HRMS) were recorded with a Q-TOf Premier LC HR mass spectrometer. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Cobalt(II) bromide (99%) and indium powder (99.99% trace metals basis; contain ~1% Mg as anticaking agent) were purchased from Aldrich. Bathophenanthroline, iron(III) chloride (>98%), and 1,2-bis(diphenylphosphino)benzene were purchased from Alfa Aesar, Merck, and Strem Chemicals, respectively. THF was distilled over Na/benzophenone before use.

4.2. General procedure for iron-catalyzed annulation of arylindium reagents and alkynes

An arylindium reagent was prepared in a 10 mL Schlenk tube according to our procedure (typically 0.90 mmol in 1 mL THF).[7] The reagent solution was carefully transferred to another Schlenk tube via cannula while leaving insoluble materials including excess indium powder. To the arylindium solution was added Me_3SiCH_2MgCl (0.90 M in THF, 2 mL, 1.8 mmol) over 5 min at 0 °C. After stirring for 1 h at 0 °C and 45 min at room temperature, 1,2-bis(diphenylphosphino)benzene (13.4 mg, 0.030 mmol), 4-octyne (44 μL, 0.30 mmol), and $FeCl_3$ (2.5 mg, 0.015 mmol) were sequentially added. The resulting mixture was stirred at 60 °C for 14 h, and then allowed to room temperature, diluted with ethyl acetate (5 mL), and quenched with H_2O (1 mL). The aqueous layer was extracted with ethyl acetate (3 x 10 mL), and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford the naphthalene product.

*4.2.1. 6-(tert-Butyl)-1,2,3,4-tetrapropylnaphthalene (**3aa**).* Colorless liquid; R_f 0.65 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12–1.20 (m, 12H), 1.46 (s, 9H), 1.58–1.65 (m, 4H), 1.70–1.79 (m, 4H), 2.75–2.80 (m, 4H), 3.02–3.09 (m, 4H), 7.49 (dd, J=6.8, 3.2 Hz, 2H), 8.09 (dd, J=6.6, 3.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 15.2, 15.3 (2C), 24.7, 24.8, 25.2 (2C), 31.5 (5C), 32.7, 32.9, 35.0, 119.8, 123.4, 124.5, 129.5, 131.0, 134.1, 134.2, 136.4, 137.1, 146.8; HRMS (ESI+) Calcd for

$C_{26}H_{40}$ $[M+H]^+$ 353.3208, found 353.3209. The ^1H and ^{13}C NMR spectra were in agreement with the literature data.[3f]

*4.2.2. 1,2,3,4-Tetrapropylnaphthalene (**3ab**).* Colorless liquid; R_f 0.64 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.18–1.24 (m, 12H), 1.66–1.72 (m, 4H), 1.74–1.82 (m, 4H), 2.81–2.86 (m, 4H), 3.09–3.13 (m, 4H), 7.47–7.50 (m, 2H), 8.07–8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2 (2C), 15.3 (2C), 24.8 (2C), 25.2 (2C), 31.5 (2C), 32.8 (2C), 124.7 (2C), 124.8 (2C), 131.4 (2C), 134.4 (2C), 137.1 (2C); HRMS (ESI+) Calcd for $C_{22}H_{32}$ $[M+H]^+$ 297.2582, found 297.2581. The ^1H and ^{13}C NMR spectra were in agreement with the literature data.[3f]

*4.2.3. 6-Methyl-1,2,3,4-tetrapropylnaphthalene (**3ac**).* Colorless liquid; R_f 0.67 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.07–1.14 (m, 12H), 1.53–1.60 (m, 4H), 1.62–1.71 (m, 4H), 2.50 (s, 3H), 2.69–2.73 (m, 4H), 2.96–3.00 (m, 4H), 7.23 (d, J=8.7 Hz, 1H), 7.73 (s, 1H), 7.88 (d, J=8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 15.2, 15.3 (2C), 22.2, 24.7, 24.8, 25.1, 25.2, 31.4, 31.5, 32.7, 32.9, 123.8, 124.7, 126.8, 129.6, 131.5, 133.7, 133.9, 134.2, 136.1, 137.2; HRMS (ESI+) Calcd for $C_{23}H_{34}$ $[M+H]^+$ 311.2739, found 311.2730. The ^1H and ^{13}C NMR spectra were in agreement with the literature data.[3f]

*4.2.4. 6-Phenyl-1,2,3,4-tetrapropylnaphthalene (**3ad**).* Colorless liquid; R_f 0.59 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.09–1.15 (m, 12H), 1.57–1.63 (m, 4H), 1.68–1.76 (m, 4H), 2.73–2.77 (m, 4H), 3.00–3.08 (m, 4H), 7.36 (t, J=7.6 Hz, 1H), 7.48 (t, J=7.8 Hz, 2H), 7.65 (dd, J=9.1, 1.8 Hz, 1H), 7.71 (dd, J=8.2, 1.4 Hz, 2H), 8.06 (d, J=9.1 Hz, 1H), 8.17 (d, J=1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 15.2, 15.3 (2C), 24.8, 24.9, 25.2 (2C), 31.5 (2C), 32.8, 32.9, 123.0, 124.3, 125.4, 127.2, 127.7 (2C), 129.0 (2C), 130.6, 131.5, 134.3, 134.6, 137.2, 137.4, 137.7, 142.2; HRMS (ESI+) Calcd for $C_{28}H_{36}$ $[M+H]^+$ 373.2895, found 373.2894.

*4.2.5. 6-Methoxy-1,2,3,4-tetrapropylnaphthalene (**3ae**).* Colorless liquid; R_f 0.54 (hexane/EtOAc=99/1); ^1H NMR (400 MHz, $CDCl_3$): δ 1.07–1.14 (m, 12H), 1.54–1.61 (m, 4H), 1.63–1.72 (m, 4H), 2.67–2.73 (m, 4H), 2.94–2.99 (m, 4H), 3.92 (s, 3H), 7.09 (dd, J=9.2, 2.7 Hz, 1H), 7.28 (d, J=2.3 Hz, 1H), 7.91 (d, J=9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 15.2, 15.3 (2C), 24.2, 24.9, 25.1, 25.2, 31.6, 31.7, 32.6, 32.9, 55.4, 104.1, 116.3, 126.5, 126.8, 132.5, 133.2, 134.4, 134.9, 137.8, 156.7; HRMS (ESI+) Calcd for $C_{23}H_{34}O$ $[M+H]^+$ 327.2688, found 327.2681. The ^1H and ^{13}C NMR spectra were in agreement with the literature data.[3f]

*4.2.6. N,N-Dimethyl-5,6,7,8-tetrapropylnaphthalen-2-amine (**3af**).* Pale yellow liquid; R_f 0.29 (hexane/EtOAc=99/1); ^1H NMR (400 MHz, $CDCl_3$): δ 1.05–1.13 (m, 12H), 1.54–1.71 (m, 8H), 2.65–2.71 (m, 4H), 2.88–2.97 (m, 4H), 3.02 (s, 6H), 7.06 (d, J=2.3 Hz, 1H), 7.11 (dd, J=9.6, 2.3 Hz, 1H), 7.86 (d, J=9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 15.3 (3C), 23.9, 24.9, 25.2, 25.3, 31.5, 31.7, 32.6, 32.9, 41.4 (2C), 104.8, 115.5, 124.8, 125.7, 127.1, 132.4, 132.5, 134.1, 137.4, 147.9; HRMS (ESI+) Calcd for $C_{24}H_{38}N$ $[M+H]^+$ 340.3004, found 340.3008.

*4.2.7. 6-Fluoro-1,2,3,4-tetrapropylnaphthalene (**3ag**).* Colorless liquid; R_f 0.72 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.11–1.16 (m, 12H), 1.56–1.71 (m, 8H), 2.71–2.76 (m, 4H), 2.93–3.03 (m, 4H), 7.17–7.21 (m, 1H), 7.59 (dd, J=11.9, 2.7 Hz, 1H), 7.99 (dd, J=9.2, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1(2C), 15.3 (2C), 24.5, 24.8, 25.1, 25.2, 31.7 (2C), 32.7, 32.9, 108.2 (d, $^2J_{C-F}$=20.0 Hz), 114.5 (d, $^2J_{C-F}$=24.8 Hz), 127.2 (d, $^3J_{C-F}$=8.6 Hz), 128.4, 132.5 (d, $^3J_{C-F}$=8.6 Hz), 133.8 (d, $^4J_{C-F}$=5.7 Hz), 134.6, 136.4, 138.5, 160.4 (d, $^1J_{C-F}$=242.3 Hz); HRMS (ESI+) Calcd for $C_{22}H_{31}F$ $[M+H]^+$ 315.2488, found 315.2483.

*4.2.8. 1,2,3,4-Tetrapropyl-6-(trifluoromethyl)naphthalene (**3ah**).* Colorless liquid; R_f 0.72 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.09–1.15 (m, 12H), 1.56–1.62 (m, 4H), 1.64–1.71 (m, 4H), 2.73–2.77 (m, 4H), 3.00–3.05 (m, 4H), 7.56 (dd, J=9.2, 1.8 Hz, 1H), 8.08 (d, J=9.2 Hz, 1H), 8.27 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 15.1, 15.3 (2C), 24.8, 24.9, 25.1 (2C), 31.3, 31.4, 32.8, 32.9, 120.1 (q, $^3J_{C-F}$=2.9 Hz), 122.4 (q, $^3J_{C-F}$=4.1 Hz), 125.1 (q, $^1J_{C-F}$=270.6 Hz), 125.8, 126.3 (q, $^2J_{C-F}$=31.0 Hz), 130.4, 132.7, 134.6, 135.4, 138.7, 139.6; HRMS (ESI+) Calcd for $C_{23}H_{31}F_3$ $[M+H]^+$ 365.2456, found 365.2452.

*4.2.9. 5-Fluoro-1,2,3,4-tetrapropylnaphthalene (**3ai**).* Colorless liquid; R_f 0.75 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.02–1.13 (m, 12H), 1.50–1.69 (m, 8H), 2.45–2.49 (m, 2H), 2.70–2.74 (m, 4H), 2.95–3.00 (m, 1H), 3.08 (br, 1H), 6.99–7.06 (m, 1H), 7.25–7.31 (m, 1H), 7.76 (d, J=8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 15.2, 15.3, 15.5, 24.5, 25.0, 25.1, 25.7 (d, $^5J_{C-F}$=4.8 Hz), 32.1, 32.4 (d, $^5J_{C-F}$=12.4 Hz), 33.0, 33.8 (d, $^4J_{C-F}$=14.4 Hz), 110.5 (d, $^2J_{C-F}$=25.9 Hz), 120.8 (d, $^4J_{C-F}$=3.8 Hz), 122.1 (d, $^3J_{C-F}$=9.6 Hz), 124.3 (d, $^2J_{C-F}$=10.5 Hz), 133.4 (d, $^3J_{C-F}$=5.8 Hz), 134.1 (d, $^3J_{C-F}$=4.8 Hz), 136.9, 138.2, 138.7, 160.6 (d, $^1J_{C-F}$=253.9 Hz); HRMS (ESI+) Calcd for $C_{22}H_{31}F$ $[M+H]^+$ 315.2488, found 315.2489.

*4.2.10. 6-Chloro-1,2,3,4-tetrapropylnaphthalene (**3aj**) and 5-chloro-1,2,3,4-tetrapropylnaphthalene (**3aj'**).* Colorless liquid; R_f 0.72 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.03–1.14 (m, 24H), 1.53–1.71 (m, 16H), 2.70–2.77 (m, 8H), 2.93–3.00 (m, 8H), 7.21–7.25 (m, 2H), 7.32 (dd, J=9.3, 2.0 Hz, 1H), 7.49 (d, J=7.4 Hz, 1H), 7.90–7.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 15.1 (3C), 15.3 (4C), 24.6, 24.7, 24.8, 24.9, 25.1 (2C), 26.3 (2C), 31.4, 31.5, 32.2, 32.5, 32.7, 32.8, 32.9, 33.1, 123.7, 124.1, 124.4, 125.3, 126.6, 129.2, 129.4, 129.7, 130.6, 131.1, 132.4, 133.7, 134.2, 134.5, 134.9, 135.0, 137.5, 138.0, 138.5, 140.2; HRMS (ESI+) Calcd for $C_{22}H_{31}Cl$ $[M+H]^+$ 331.2193, found 331.2188. The ^1H NMR spectra indicated ca. 1:1 ratio of the two regioisomers.

*4.2.11. 7-Chloro-5-fluoro-1,2,3,4-tetrapropylnaphthalene (**3ak**).* Colorless liquid; R_f 0.75 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.08–1.15 (m, 12H), 1.55–1.68 (m, 8H), 2.69–2.75 (m, 4H), 2.91–2.95 (m, 2H), 3.04–3.07 (br, 2H), 7.05 (dd, J=14.2, 2.3 Hz, 1H), 7.74 (d, J=1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 15.1, 15.3 (2C), 24.5, 24.9, 25.1, 25.7 (d, $^5J_{C-F}$=3.8 Hz), 31.9, 32.2 (d, $^5J_{C-F}$=11.5 Hz), 33.0, 33.6 (d, $^4J_{C-F}$=13.4 Hz), 111.7 (d, $^2J_{C-F}$=30.5 Hz) 120.0 (d, $^3J_{C-F}$=3.8 Hz), 120.7 (d, $^3J_{C-F}$=9.5 Hz), 129.4 (d, $^2J_{C-F}$=12.4 Hz), 133.6, 133.7, 134.4 (d, $^3J_{C-F}$=5.7 Hz), 139.1, 139.6, 160.5 (d, $^1J_{C-F}$=255.6 Hz); HRMS (ESI+) Calcd for $C_{22}H_{30}ClF$ $[M+H]^+$ 349.2098, found 349.2099.

*4.2.12. 6-(tert-Butyl)-1,2,3,4-tetraethylnaphthalene (**3ba**).* Colorless liquid; R_f 0.65 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.25–1.29 (m, 6H), 1.32–1.39 (m, 6H), 1.46 (s, 9H), 2.84–2.91 (m, 4H), 3.10–3.19 (m, 4H), 7.55 (dd, J=9.2, 1.8 Hz, 1H), 8.01–8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.6, 15.8, 16.1 (2C), 21.9 (2C), 22.9, 23.0, 31.6 (3C), 35.0, 119.8, 123.4, 124.4, 129.3, 130.9, 135.3, 135.4, 137.3, 137.9, 146.9; HRMS (ESI+) Calcd for $C_{22}H_{32}$ $[M+H]^+$ 297.2582, found 297.2589.

*4.2.13. 6-(tert-Butyl)-1,2,3,4-tetrabutylnaphthalene (**3ca**).* Colorless liquid; R_f 0.70 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.00–1.07 (m, 12H), 1.42 (s, 9H), 1.53–1.67 (m, 16H), 2.73–2.78 (m, 4H), 2.99–3.07 (m, 4H), 7.50 (dd, J=9.2, 1.8 Hz, 1H), 7.94–7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (2C), 14.3 (2C), 23.7 (2C), 23.8 (2C), 28.8, 28.9, 30.0, 30.1, 31.5 (3C), 33.5, 33.7, 34.0 (2C), 35.0, 119.8, 123.3, 124.5, 129.5, 131.0, 134.1, 134.2, 136.4, 137.1, 146.8; HRMS (ESI+) Calcd for $C_{30}H_{48}$ $[M+H]^+$ 409.3834, found 409.3838.

*4.2.14. 6-(tert-Butyl)-1,2,3,4-tetraphenylnaphthalene (**3da**).* Yellow solid; Mp=250–251 °C; R_f 0.22 (hexane/EtOAc=99/1); ^1H NMR

(400 MHz, $CDCl_3$): δ 1.18 (s, 9H), 6.74–6.79 (m, 10H), 7.09–7.17 (m, 10H), 7.41 (dd, J=8.9, 2.0 Hz, 1H), 7.51–7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.3 (3C), 35.1, 122.3, 124.9, 125.4 (2C), 126.5 (2C), 126.7 (4C), 126.9, 127.6 (2C), 127.7 (2C), 130.4, 131.5 (4C), 131.6 (4C), 132.0, 138.2, 138.4, 138.6, 139.1, 139.8, 139.9, 140.8, 140.9, 148.7; HRMS (ESI+) Calcd for $C_{38}H_{32}$ $[M+H]^+$ 489.2582, found 489.2581.

*4.2.15. 1,2,3,4-Tetraphenylnaphthalene (**3db**).* Yellow solid; Mp=201–203 °C; R_f 0.21 (hexane/EtOAc=99/1); ^1H NMR (400 MHz, $CDCl_3$): δ 6.82–6.86 (m, 10H), 7.16–7.25 (m, 10H), 7.39 (dd, J=6.6, 3.4 Hz, 2H), 7.64 (dd, J=6.6, 3.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.5 (2C), 126.1 (2C), 126.6 (2C), 126.8 (4C), 127.2 (2C), 127.7 (4C), 127.8 (2C), 131.5 (6C), 132.2 (2C), 138.6 (2C), 139.1 (2C), 139.8 (2C), 140.7 (2C); HRMS (ESI+) Calcd for $C_{34}H_{24}$ $[M+H]^+$ 433.1956, found 433.1955. The ^1H and ^{13}C NMR spectra were in agreement with the literature data.[3n]

*4.2.16. 6-(tert-Butyl)-1,4-dimethyl-2,3-diphenylnaphthalene (**3ea**).* White solid; Mp=157–159 °C; R_f 0.27 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 9H), 2.42 (s, 3H), 2.44 (s, 3H), 6.94–6.97 (m, 4H), 7.06–7.14 (m, 6H), 7.69 (dd, J=8.9, 2.0 Hz, 1H), 8.08–8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 17.0, 31.6 (3C), 35.3, 120.2, 124.7, 125.0, 125.9 (2C), 127.4 (4C), 129.3, 129.4, 130.3, 130.6 (2C), 130.7 (2C), 131.9, 139.0, 139.7, 142.0, 142.1, 148.6; HRMS (ESI+) Calcd for $C_{28}H_{28}$ $[M+H]^+$ 365.2269, found 365.2263.

*4.2.17. 1,4-Dimethyl-2,3-diphenylnaphthalene (**3eb**).* White solid; Mp=166–167 °C; R_f 0.26 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 6H), 6.95–6.97 (m, 4H), 7.06–7.14 (m, 6H), 7.57 (dd, J=6.4, 3.2 Hz, 2H), 8.13 (dd, J=6.4, 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1 (2C), 125.2 (2C), 125.9 (2C), 126.0 (2C), 127.4 (4C), 129.6 (2C), 130.6 (4C), 132.2 (2C), 139.6 (2C), 141.9 (2C); HRMS (ESI+) Calcd for $C_{24}H_{20}$ $[M+H]^+$ 309.1643, found 309.1640. The ^1H and ^{13}C NMR spectra were in agreement with the literature data.[3n]

*4.2.18. 1,4-Diethyl-2,3-diphenylnaphthalene (**3fb**).* Colorless viscous liquid; R_f 0.33 (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, J=7.6 Hz, 6H), 2.86 (q, J=7.6 Hz, 4H), 6.99 (d, J=6.8 Hz, 4H), 7.05–7.13 (m, 6H), 7.55–7.58 (m, 2H), 8.16–8.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9 (2C), 23.5 (2C), 125.4 (2C), 125.8 (2C), 126.0 (2C), 127.4 (4C), 130.3 (4C), 131.5 (2C), 135.9 (2C), 139.3 (2C), 141.7 (2C); HRMS (ESI+) Calcd for $C_{26}H_{25}$ $[M+H]^+$ 337.1956, found 337.1943.

*4.2.19. 6-(tert-Butyl)-2,4-dimethyl-1,3-dipropylnaphthalene (**3ga**) and its three regioisomers.* Colorless liquid; R_f 0.64 (hexane); GC analysis indicated the presence of four regioisomers in an approximate ratio of 1:1:1:1; ^1H NMR (400 MHz, $CDCl_3$): δ 1.08–1.17 (m), 1.46 (s), 1.55–1.61 (m), 1.66–1.75 (m), 2.43 (s), 2.44 (s), 2.47 (s), 2.48 (s), 2.65 (s), 2.68 (s), 2.79–2.88 (m), 3.05–3.13 (m), 7.53–7.58 (m), 7.98–8.02 (m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 14.9, 15.0, 15.1, 15.2, 16.4, 16.6, 17.1, 17.2, 23.6, 23.8, 23.9, 24.5,31.5, 31.6, 33.0, 33.1, 33.3, 33.4, 35.0, 35.1, 119.6, 119.7, 123.2, 123.3, 123.5, 123.6, 124.2, 124.3, 124.4, 128.7, 128.8, 129.0, 129.2, 129.9, 130.0, 130.6, 130.8, 131.5, 131.6, 131.7, 132.2, 132.3, 132.9, 133.7, 133.9, 134.0, 134.2, 136.7, 137.2, 137.5, 137.9, 146.7, 146.9, 147.0, 147.2; HRMS (ESI+) Calcd for $C_{22}H_{33}$ $[M+H]^+$ 297.2582, found 297.2581.

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Supplementary data

Copies of ^1H and ^{13}C NMR spectra for all the naphthalene products. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.04.004.

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