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Synthesis of Highly Substituted Acenes through Rhodium-Catalyzed Oxidative Coupling of Arylboron Reagents with Alkynes

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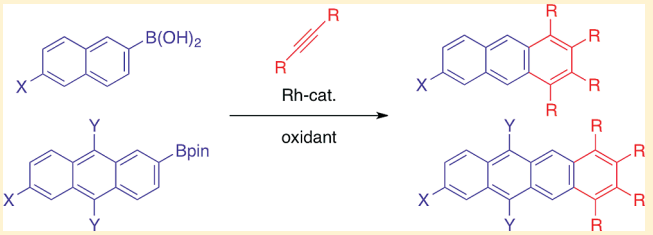
Supporting Information

ABSTRACT: The rhodium-catalyzed oxidative 1:2 coupling reactions of arylboronic acids or their esters with alkynes smoothly proceed to produce the corresponding annulated products. Of special note, highly substituted, readily soluble, and tractable anthracene and tetracene derivatives can be obtained selectively from 2-naphthyl- and 2-anthrylboron reagents, respectively.

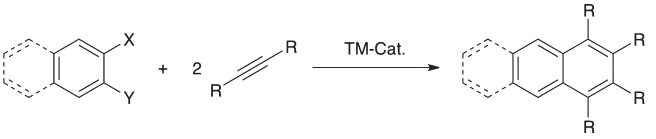


INTRODUCTION

Linearly fused aromatic ring systems, so-called acenes including anthracene and tetracene, have attracted much attention because of their photo- and electrochemical properties and applicability to organic semiconductors and luminescent materials.[1] Highly substituted derivatives around fused aromatic cores are of particular interest due to their stability, solubility, enhanced ability to transport charge, and fluorescent properties in the solid state.[2] One of the most promising strategies for constructing such π-conjugated molecules is the transition metal-catalyzed homologation, such as benzene to naphthalene and naphthalene to anthracene, by the coupling of a given aromatic substrate with two alkyne molecules (Scheme 1).[3] Among such reactions, the catalytic transformations of monofunctionalized aromatic substrates ($X \neq H$, $Y = H$)[4] involving C−H bond cleavage are more attractive from atom- and step-economical points of view[5] than those with difunctionalized ones ($X \neq H$, $Y \neq H$).[3,6] In particular, the reactions of iodobenzenes ($X = I$, $Y = H$)[4c−e] and benzoic acids ($X = CO_2H$, $Y = H$)[4g−i] are of considerable synthetic utility owing to the wide availability of the substrates as aryl sources.

Meanwhile, various arylboronic acids are also commercially available as arylation reagents. Furthermore, the iridium-catalyzed direct borylation[7] of a wide range of aromatic cores including fused polycyclic systems[8] has been developed to provide the corresponding arylboronates in a single step. The catalytic homologation of arylboron reagents has, however, been less explored, and only two examples with *o*-bromophenylboronic acids ($X = B(OH)_2$, $Y = Br$) have been reported.[9] During our study of the catalytic homologation through the oxidative coupling of aromatic substrates with alkynes,[4c,f−l] it has been revealed that simple phenylboronic acids ($X = B(OH)_2$, $Y = H$) undergo the reaction smoothly under rhodium catalysis to efficiently afford 1,2,3,4-tetrasubstituted naphthalenes.[10,11] Interestingly, the reactions of 2-naphthyl- and 2-anthrylboron reagents also proceeded to form the corresponding anthracene and tetracene derivatives selectively. The details of these findings are described herein.

Scheme 1. Transition Metal-Catalyzed Coupling of Aromatic Substrates with Internal Alkynes



RESULTS AND DISCUSSION

In an initial attempt, phenylboronic acid (**1a**) (0.5 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) in the presence of $[(Cp^*RhCl_2)_2]$ (0.005 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) as catalyst and oxidant, respectively, in DMF (3 mL) at 100 °C under N_2 for 2 h. As a result, 1,2,3,4-tetraphenylnaphthalene (**3a**) was formed in 56% yield (entry 1 in Table 1, Cp^* = pentamethylcyclopentadienyl). While the reaction was sluggish in DMSO, *o*-xylene, and dioxane, a comparable result was obtained in NMP (entries 2−5). The reaction was not sensitive to the temperature between 60 and 100 °C (entries 6 and 7). AgOAc could also be used as oxidant (entires 8−11). Thus, with AgOAc, the reaction proceeded smoothly even at room temperature to form **3a** in 67% yield within 2 h (entry 11). $AgOCOCF_3$ gave a better yield (87%, entry 13). To our delight, a comparably good yield was obtained when the reaction was conducted with a catalytic amount of $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol) under air (entry 14). Thus, the aerobic oxidative coupling proceeded efficiently to give **3a** in 86% yield. Phenylboronic acid

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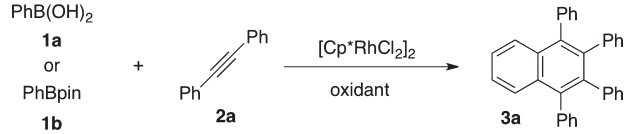
Table 1. Reaction of Phenylboronic Acid (1a) or Its Pinacol Ester (1b) with Diphenylacetylene (2a)[a]



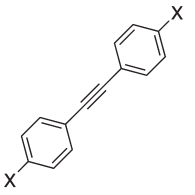
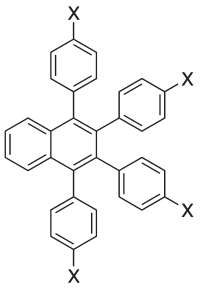
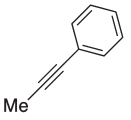
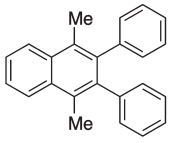
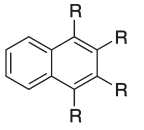
entry	1	oxidant (mmol)	solvent	temp (°C)	% yield of 3a[b]
1	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	DMF	100	56
2	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	DMSO	100	3
3	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	*o*-xylene	100	3
4	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	dioxane	100	22
5	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	NMP	100	50
6	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	DMF	80	53
7	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.5)	DMF	60	53
8	**1a**	AgOAc (0.5)	DMF	100	74
9	**1a**	AgOAc (0.5)	DMF	80	66
10	**1a**	AgOAc (0.5)	DMF	60	67
11	**1a**	AgOAc (0.5)	DMF	rt	67
12	**1a**	Ag_2CO_3 (0.25)	DMF	100	32
13	**1a**	$AgOCOCF_3$ (0.5)	DMF	100	87
14[c]	**1a**	$Cu(OAc)_2 \cdot H_20$ (0.025)	DMF	100	86 (78)
15[c]	**1b**	$Cu(OAc)_2 \cdot H_20$ (0.025)	DMF	100	60
16[d]	**1b**	$Cu(OAc)_2 \cdot H_20$ (0.025)	DMF	100	67
17[d,e]	**1b**	$Cu(OAc)_2 \cdot H_20$ (0.025)	DMF	100	83

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), solvent (3 mL) under N_2 for 2 h. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates the yield after purification. [c] Under air. [d] Under N_2—air (5:1). [e] $[(Cp^*RhCl_2)_2]$ (0.01 mmol) was used.

pinacol ester (**1b**) in place of **1a** also reacted under the same conditions to produce **3a** in 60% yield (entry 15, pin = $OCMe_2CMe_2O$). The product yield with **1b** was significantly improved up to 83% under *diluted* air (N_2:air = 5:1, 1 atm) with the higher loading of the Rh catalyst (0.01 mmol) (entry 17).

Under the conditions employed for entry 14 in Table 1 (conditions A), the couplings of **1a** with various internal alkynes **2a**—**h** were examined (Table 2). Methyl- (**2b**), methoxy- (**2c**), and chloro- (**2d**) substituted diphenylacetylenes reacted smoothly to form the corresponding 1,2,3,4-tetraarylnaphthalenes **3b**—**d** selectively (Table 2, entries 1—3). The reaction of **1a** with bis[4-(trifluoromethyl)phenyl]acetylene (**2e**) proceeded efficiently under the conditions with $AgOCOCF_3$ (0.5 mmol) in place of $Cu(OAc)_2 \cdot H_2O$ under N_2 (entry 4). 1-Phenylpropyne (**2f**) coupled with **1a** to give 1,4-dimethyl-2,3-diphenylnaphthalene (**3f**) in 70% yield along with a small amount (7%) of a separable unidentified isomer (entry 5). In contrast, the reaction of 4-octyne (**2g**) was sluggish under the aerobic conditions to form 1,2,3,4-tetrapropylnaphthalene (**3g**) in only 10% yield (entry 6). The reaction efficiency was improved by using a stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) at 60 °C or room temperature (entries 7 and 8). Finally, the highest yield of **3g** (74%) was obtained at 60 °C with the higher Rh loading (entry 9). While 1-phenyl-2-(trimethylsilyl)acetylene did not couple with **1a** at all, diethyl acetylenedicarboxylate (**2h**) underwent the reaction by using $AgOCOCF_3$ as an oxidant to produce naphthalene **3h** in a moderate yield (entry 10).

Table 2. Reaction of Phenylboronic Acid (1a) with Alkynes 2[a]

entry	2	temp (°C)	product, % yield
			
1	**2b**: X = Me	100	**3b**: X = Me, 80
2	**2c**: X = OMe	100	**3c**: X = OMe, 48
3	**2d**: X = Cl	100	**3d**: X = Cl, 83
4[b]	**2e**: X = CF_3	100	**3e**: X = CF_3, 76
			
5	**2f**	100	**3f**, 70[c]
			
6	**2g**: R = Pr	60	**3g**: R = Pr, (10)[d]
7[e]	**2g**: R = Pr	60	**3g**: R = Pr, (42)[d]
8[e]	**2g**: R = Pr	rt	**3g**: R = Pr, 46 (47)[d]
9[e,f]	**2g**: R = Pr	60	**3g**: R = Pr, 68 (74)[d]
10[b,f]	**2h**: R = CO_2Et	100	**3h**: R = CO_2Et, 41

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol), DMF (3 mL) under air for 2 h. [b] $AgOCOCF_3$ (0.5 mmol) was used in place of $Cu(OAc)_2 \cdot H_2O$ under N_2. [c] A small amount (7%) of a regioisomer was also formed. [d] Value in parentheses indicates GC yield based on the amount of **2** used. [e] $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) was used under N_2. [f] $[(Cp^*RhCl_2)_2]$ (0.01 mmol) was used.

Table 3 summarizes the results for the coupling of a series of substituted phenylboronic acids **1c**—**q** with **2a**. 4-Methyl-, methoxy-, chloro-, fluoro-, and bromophenylboronic acids **1c**—**g** reacted with **2a** smoothly under the aerobic conditions to form 6-substituted 1,2,3,4-tetraphenylnaphthalenes **3i**—**m** in 72—89% yields (entries 1—5). It was found that electron-deficient phenylboronic acids were less reactive in the present reaction. Thus, the reaction of 4-(trifluoromethyl)phenylboronic acid (**1h**) with **2a** under the standard conditions gave the corresponding naphthalene **3n** in only 22% yield (entry 6). In this case, the use of $Cu(OCOCF_3)_2$ (0.025 mmol) in place of $Cu(OAc)_2$ improved the yield to 82% (entry 7). Even under the modified condition with $Cu(OCOCF_3)_2$, the reactions of 4-(methoxycarbonyl)- (**1i**) and 4-formyl- (**1j**) phenylboronic acids were sluggish (entries 8 and 10). In these reactions, $AgOCOCF_3$ was found to be more effective as oxidant. Thus, in the presence of the Ag salt (0.5 mmol) under N_2, naphthalenes **3o** and **3p** were obtained in 9%1 and 79% yields, respectively (entries 9 and 11).

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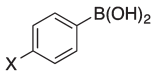
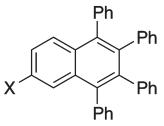
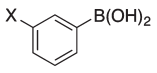
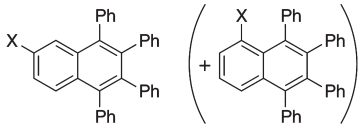
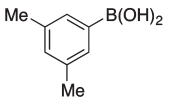
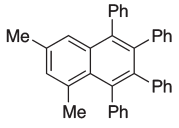
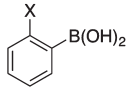
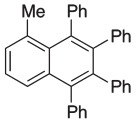
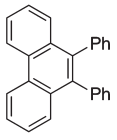
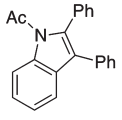
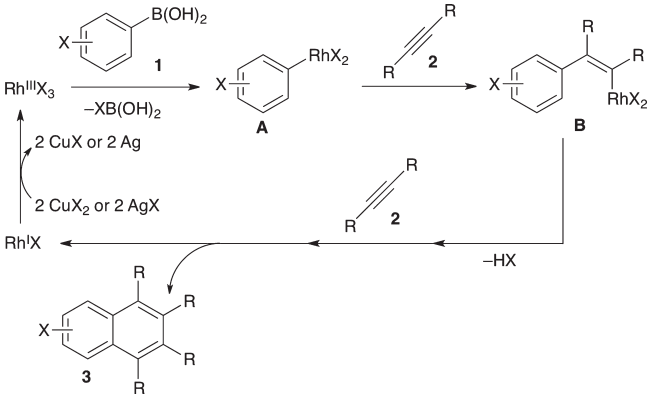
Table 3. Reaction of Arylboronic Acids 1 with Diphenylacetylene (2a)[a]

entry	1	product(s), % yield
		
1	**1c**: X = Me	**3i**: X = Me, 66
2	**1d**: X = OMe	**3j**: X = OMe, 72
3	**1e**: X = Cl	**3k**: X = Cl, 83
4	**1f**: X = F	**3l**: X = F, 82
5	**1g**: X = Br	**3m**: X = Br, 79
6	**1h**: X = CF_3	**3n**: X = CF_3, (22)[b]
7[c]	**1h**: X = CF_3	**3n**: X = CF_3, 82 (82)[b]
8[c]	**1i**: X = CO_2Me	**3o**: X = CO_2Me, (64)[b]
9[d]	**1i**: X = CO_2Me	**3o**: X = CO_2Me, 87 (91)[b]
10[c]	**1j**: X = CHO	**3p**: X = CHO, (59)[b]
11[d]	**1j**: X = CHO	**3p**: X = CHO, 79 (79)[b]
		
12	**1k**: X = Me	**3i**: X = Me, 51
13[d]	**1k**: X = Me	**3i**: X = Me, 71
14[d,e]	**1k**: X = Me	**3i**: X = Me, 96
15[d,e]	**1l**: X = OMe	**3j** / **3'j**: X = OMe, 96 [2.2:1]
16[d,e]	**1m**: X = F	**3l** / **3'l**: X = F, 89 [1:4.2]
		
17[e]	**1n**	**3q**, 58
		
18	**1o**: X = Me	**3r**, 34
		
19[f]	**1p**: X = Ph	**4**, 74
		
20[f]	**1q**: X = NHAc	**5**, 52

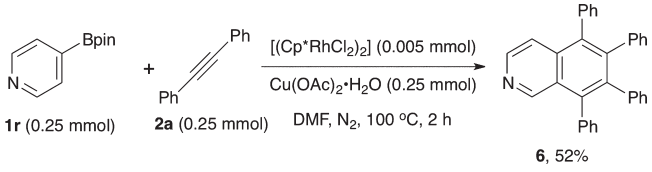
[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), [$(Cp^*RhCl_2)_2$] (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol), DMF (3 mL) under air for 2 h. [b] Value in parentheses indicates GC yield based on the amount of **2a** used. [c] $Cu(OCOCF_3)_2 \cdot nH_2O$ (0.025 mmol) was used in place of $Cu(OAc)_2 \cdot H_2O$. [d] $AgOCOCF_3$ (0.5 mmol) was used in place of $Cu(OAc)_2 \cdot H_2O$ under N_2. [e] DABCO (0.5 mmol) was added. [f] **1** (0.25 mmol) and **2a** (0.25 mmol) were used.

The reaction of 3-methylphenylboronic acid (**1k**) was significantly promoted by addition of DABCO together with the silver salt to afford **3i** exclusively in 96% yield (entry 14, DABCO = 1,4-diazabicyclo[2.2.2]octane). In contrast to **1k**, other 3-substituted phenylboronic acids **1***l* and **1m** reacted with **2a** to give regioisomeric mixtures of the corresponding naphthalenes (**3** and **3**′). In the case with *m*-methoxy-substituted **1***l*, the cyclization occurred at the less hindered ortho-position predominantly (entry 15). Meanwhile, *m*-fluoro-substituted **1m** reacted at the more hindered position to form **3**′***l*** preferentially (entry 16). Treatment of 3,5-dimethyl- (**1n**) and 2-methylboronic acid (**1o**) with **2a** under aerobic conditions gave naphthalenes **3q** and **3r** in moderate yields (entries 17 and 18). Meanwhile, the coupling of 2-phenyl- (**1p**) and 2-(acetylamino)- (**1q**) phenylboronic acids with **2a** took place in a 1:1 manner to produce not naphthalenes but 9,10-diphenylphenanthrene (**4**) and 1-acetyl-2,3-diphenylindole (**5**),[12] respectively (entries 19 and 20).

Scheme 2. Plausible Mechanism for the Reaction of 1 with 2



Scheme 3. Reaction of Pyridin-4-ylboronate 1r with 2a



A plausible mechanism for the reaction of **1** with **2** is illustrated in Scheme 2, in which neutral ligands are omitted. Initial transmetalation of the added $Rh^{III}X_3$ species with **1** gives an arylrhodium intermediate **A**. Then, alkyne insertion occurs to form a vinylrhodium species **B**. Subsequent cyclorhodation, the second alkyne insertion, and reductive elimination afford naphthalene **3**. The direction of cyclorhodation may be influenced by both steric and electronic factors (entries 14−16 in Table 3). The resulting Rh^IX species seems to be oxidized in the presence of a Cu or Ag salt to regenerate $Rh^{III}X_3$. Under aerobic conditions, the Cu^I species formed in the last step may be oxidized by air to Cu^{II}, so that the reaction can also be catalytic in Cu.

Besides phenylboronic acids, pyridin-4-ylboronate **1r** also underwent coupling with **2a** to selectively produce 5,6,7,8-tetraphenylisoquinoline (**6**) (Scheme 3). The reaction with the corresponding pyridin-4-ylboronic acid in place of **1r** under similar conditions gave **6** in a lower yield (28%).

The higher homologations from naphthalene substrates to anthracene derivatives, and anthracene substrates to tetracene

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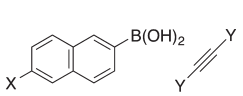
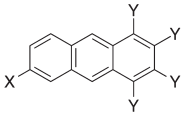
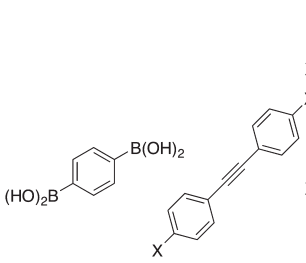
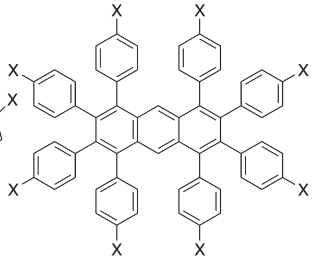
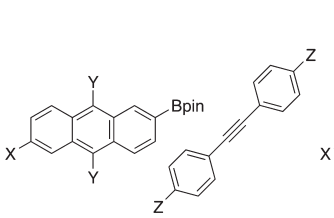
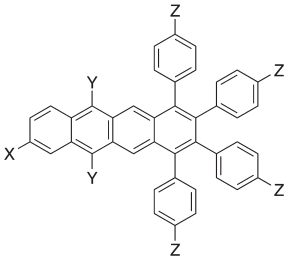
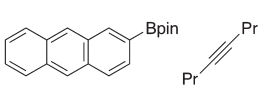
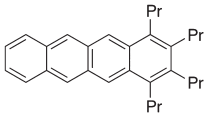
Table 4. Syntheses of Anthracene and Tetracene Derivatives[a]

entry	1	2	conditions	product, % yield
				
1	**1s**: X = H	**2a**: Y = Ph	A	**7a**: X = H; Y = Ph, 67
2	**1t**: X = OMe	**2a**: Y = Ph	A	**7b**: X = OMe; Y = Ph, 72
3	**1s**: X = H	**2g**: Y = Pr	B	**7c**: X = H; Y = Pr, 65
4	**1s**: X = H	**2i**: Y = $C_7H_{15}{}^n$	B	**7d**: X = H; Y = $C_7H_{15}{}^n$, 67
				
5	**1u**	**2j**: X = $C_8H_{17}{}^n$	C	**7e**: X = $C_8H_{17}{}^n$, 48
				
6	**1v**: X = Y = H	**2a**: Z = H	D	**8a**: X = Y = Z = H, 54
7	**1v**: X = Y = H	**2b**: Z = Me	D	**8b**: X = Y = H; Z = Me, 54
8	**1v**: X = Y = H	**2c**: Z = OMe	D	**8c**: X = Y = H; Z = OMe, 45
9	**1v**: X = Y = H	**2d**: Z = Cl	D	**8d**: X = Y = H; Z = Cl, 37
10	**1w**: X = Me, Y = H[b]	**2a**: Z = H	D	**8e**: X = Me; Y = Z = H, 51
11	**1x**: X = H, Y = Me	**2a**: Z = H	D	**8f**: X = Z = H; Y = Me, 53
12	**1y**: X = H, Y = Br	**2a**: Z = H	D	**8g**: X = Z = H; Y = Br, 71
				
13	**1v**	**2g**	E	**8h**, 31

[a] Conditions A: **1** (0.5 mmol), **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol), DMF (3 mL) under air at 100 °C for 2 h. Conditions B: **1** (0.5 mmol), **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol), DMF (3 mL) under N_2 at rt for 2 h. Conditions C: **1** (0.2 mmol), **2** (0.4 mmol), $[(Cp^*RhCl_2)_2]$ (0.004 mmol), $AgOCOCF_3$ (0.4 mmol), DABCO (0.4 mmol), DMF (3 mL) under N_2 at 100 °C for 2 h. Conditions D: **1** (0.2 mmol), **2** (0.2 mmol), $[(Cp^*RhCl_2)_2]$ (0.004 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.01 mmol), DMF (3 mL) under N_2–air (5:1) at 100 °C for 2 h. Conditions E: **1** (0.2 mmol), **2** (0.2 mmol), $[(Cp^*RhCl_2)_2]$ (0.004 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol), DMF (3 mL) under N_2 at 60 °C for 2 h. [b] A 1:1 mixture of 6- and 7-methylanthrylboronic acid pinacol esters was employed.

derivatives were next examined (Table 4). Treatment of 2-naphthylboronic acid (**1s**) with **2a** under the standard aerobic conditions A gave 1,2,3,4-tetraphenylanthracene (**7a**) in 77% yield as a single coupling product. 6-Methoxy-2-naphthylboronic acid (**1t**) also underwent the reaction in a similar manner to afford the corresponding anthracene **7b**. The reaction with dialkylacetylenes proceeded efficiently in the presence of a stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$ as an oxidant to produce 1,2,3,4-tetraalkylanthracenes **7c** and **7d** (entries 3 and 4). It should be noted that the corresponding phenanthrenes were not formed at all, while the mixtures of anthracene and phenanthrene derivatives were usually formed in the previous homologations of iodides[4c] and acid chlorides[4f] by using Pd- and Ir-catalysts, respectively. Thus, the present higher homologation is largely governed by steric factors. 1,4-Phenylenediboronic acid (**1u**) reacted with bis(4-octylphenyl)acetylene (**2j**) in a 1:4 manner under conditions using $AgOCOCF_3$ and DABCO to afford 1,2,3,4,5,6,7,8-octakis(4-octylphenyl)anthracene (**7e**) (entry 5). In this case, double cyclization also took place regioselectively, in which no phenanthrene derivative could be detected.

Various arylboron compounds, including 2-anthrylboronates, are preparable via the direct borylation of their parent arenes under Ir-catalysis.[7,8] Combining our homologation with the borylation, a range of linear acenes appear to be readily available. Actually, anthrylboronates **1v**–**y**, prepared via the direct borylation of substituted anthracenes, coupled with diarylacetylenes **2a**–**d** under the aerobic conditions with the Rh/Cu catalyst system to give the corresponding 1,2,3,4-tetraaryltetracene derivatives **8a**–**g** (entries 6–12). By using the copper salt as a stoichiometric oxidant, **1v** also reacted with 4-octyne (**2g**) to form 1,2,3,4-tetrapropyltetracene (**8h**) in a moderate yield (entry 13). It should be noted that alkylated tetracene derivatives have been traditionally synthesized through complicated multistep routes.[2a–c] Compared with such conventional ones, the present procedure is rather efficient and straightforward.

CONCLUSIONS

In summary, we have demonstrated that the oxidative coupling of substituted phenyl-, pyridyl-, naphthyl-, and anthrylboron compounds with internal alkynes can be performed in the presence of a rhodium/copper catalyst system to selectively give the corresponding highly substituted naphthalene, isoquinoline, anthracene, and tetracene derivatives, respectively. Particularly, the fourth reaction is of interest as the first example, to our knowledge, of the single-step construction of tetracene frameworks by selective linear homologations with monofunctionalized anthryl substrates (X ≠ H, Y = H in Scheme 1).

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. MS data were obtained by EI, unless noted. GC analysis was carried out with a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC-MS analysis was carried out with a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **2b**–**e**,**j**,[13] pyridin-4-ylboronate **1r**,[14] and anthrylboronates **1v**–**y**[8b] were prepared according to published procedures. Other starting materials and reagents were commercially available.

General Procedure for Oxidative Coupling of Arylboronic Acids with Internal Alkynes under Aerobic Conditions (Conditions A). To a 20-mL two-necked flask were added arylboronic acid **1** (0.5 mmol), alkyne **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol, 3 mg), $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol, 5 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (3 mL). The resulting mixture was stirred under air at 100 °C for 2 h. GC and GC-MS analyses of the mixtures confirmed formation of **3** or **7**. Then, the reaction mixture was

cooled to room temperature and extracted with ethyl acetate (100 mL). The organic layer was washed by water (100 mL, three times), and dried over Na_2SO_4. Product **3** or **7** was isolated by column chromatography on silica gel, using hexane−ethyl acetate as eluant.

General Procedure for Tetracene Synthesis from Anthrylboronates (Conditions C in Table 4). To a 20-mL two-necked flask were added anthrylboronate **1** (0.2 mmol), alkyne **2** (0.2 mmol), $[(Cp^*RhCl_2)_2]$ (0.004 mmol, 2 mg), $Cu(OAc)_2 \cdot H_2O$ (0.001 mmol, 2 mg), and DMF (3 mL). After the apparatus was evacuated by pumping, nitrogen (ca. 750 mL) was introduced. Then, air (150 mL) was injected into the flask, and the resulting mixture was stirred at 100 °C for 2 h. Then, the reaction mixture was cooled to room temperature and extracted with dichloromethane (100 mL). The organic layer was washed by water (100 mL, three times), and dried over Na_2SO_4. Product **8** was isolated by column chromatography on silica gel, using hexane−ethyl acetate as eluant, and preparative GPC, using chloroform as eluant.

1,2,3,4-Tetraphenylnaphthalene (3a) (entry 14 in Table 1):[10] mp 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80−6.82 (m, 10H), 7.15−7.25 (m, 10H), 7.36−7.40 (m, 2H), 7.63−7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.3, 125.9, 126.4, 126.6, 127.0, 127.5, 131.3 (overlapped), 132.0, 138.4, 138.9, 139.6, 140.5; HRMS m/z (M^+) calcd for $C_{34}H_{24}$ 432.1878, found 432.1876.

1,2,3,4-Tetrakis(4-methylphenyl)naphthalene (3b) (entry 1 in Table 2):[10] mp 206−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 6H), 2.29 (s, 6H), 6.31−6.72 (m, 8H), 7.01−7.08 (m, 8H), 7.30−7.33 (m, 2H), 7.59−7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.2, 125.5, 126.9, 127.2, 128.2, 131.09, 131.11, 132.2, 134.3, 135.6, 136.8, 137.7, 138.3, 139.1; HRMS m/z (M^+) calcd for $C_{38}H_{32}$ 488.2504, found 488.2498.

1,2,3,4-Tetrakis(4-methoxyphenyl)naphthalene (3c) (entry 2 in Table 2):[10] mp 245−246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 6H), 3.79 (s, 6H), 6.43 (d, J = 8.7 Hz, 4H), 6.71 (d, J = 8.7 Hz, 4H), 6.79 (d, J = 8.7 Hz, 4H), 7.09 (d, J = 8.7 Hz, 4H), 7.35−7.37 (m, 2H), 7.63−7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.9, 55.1, 112., 113.0, 125.6, 126.9, 132.1, 132.2, 132.27, 132.34, 133.3, 138.1, 139.1, 156.9, 157.8; HRMS m/z (M^+) calcd for $C_{38}H_{32}O_4$ 552.2301, found 552.2304.

1,2,3,4-Tetrakis(4-chlorophenyl)naphthalene (3d) (entry 3 in Table 2):[10] mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72−6.74 (m, 4H), 6.89−6.92 (m, 4H), 7.09−7.12 (m, 4H), 7.24−7.27 (m, 4H), 7.42−7.45 (m, 2H), 7.55−7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 126.8, 127.4, 128.1, 131.9, 132.0, 132.26, 132.33, 132.9, 137.4 (overlapped), 137.5, 138.3; HRMS m/z (M^+) calcd for $C_{34}H_{20}Cl_4$ 568.0319, found 568.0314.

1,2,3,4-Tetrakis[4-(trifluoromethyl)phenyl]naphthalene (3e) (entry 4 in Table 2). mp 262−264 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, 4H), 7.18 (d, 4H), 7.34 (d, 4H), 7.48−7.58 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.8 (q, J = 272.4 Hz), 124.0 (q, J = 272.4 Hz), 124.1 (q, J = 3.8 Hz), 124.9 (q, J = 3.8 Hz), 126.8, 127.2, 128.5 (q, J = 32.6 Hz), 129.4 (q, J = 32.5 Hz), 131.3, 131.4, 131.8, 137.0, 137.9, 142.5, 143.2; HRMS m/z (M^+) calcd for $C_{38}H_{20}F_{12}$ 704.1373, found 704.1377.

1,4-Dimethyl-2,3-diphenylnaphthalene (3f) (entry 5 in Table 2):[10] mp 143−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 6H), 6.96−6.98 (m, 4H), 7.07−7.15 (m, 6H), 7.58−7.61 (m, 2H), 8.14−8.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 125.0, 125.76, 125.84, 127.2, 129.4, 130.4, 132.0, 139.4, 141.7; HRMS m/z (M^+) calcd for $C_{24}H_{20}$ 308.1565, found 308.1566.

1,2,3,4-Tetrapropylnaphthalene (3g) (entry 8 in Table 2):[10] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08−1.14 (m, 12H), 1.54−1.73 (m, 8H), 2.71−2.75 (m, 4H), 2.98−3.02 (m, 4H), 7.38−7.41 (m, 2H), 7.97−8.00 (m, 2H); ^{13}C NMR δ 14.9, 15.1, 24.5, 24.9, 31.3, 32.6, 124.4, 124.5, 131.2, 134.2, 136.9; HRMS m/z (M^+) calcd for $C_{22}H_{32}$ 296.2504, found 296.2496.

Tetraethyl naphthalene-1,2,3,4-tetracarboxylate (3h) (entry 10 in Table 2):[4c] mp 94−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J = 7.3 Hz, 6H), 1.42 (t, J = 7.3 Hz, 6H), 4.37 (q, J = 7.3 Hz, 4H), 4.50 (q, J = 7.3 Hz, 4H), 7.68−7.71 (m, 2H), 8.08−8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 62.2, 62.3, 126.1, 127.6, 129.5, 129.9, 133.9, 166.3, 166.8; HRMS m/z (M^+) calcd for $C_{22}H_{24}O_8$ 416.1471, found 416.1469.

6-Methyl-1,2,3,4-tetraphenylnaphthalene (3i) (entry 1 in Table 3):[10] mp 216−217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.79−6.87 (m, 10H), 7.16−7.26 (m, 11H), 7.40 (s, 1H), 7.54 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 125.2, 125.8, 126.30, 126.32, 126.5 (overlapped), 126.9, 127.45, 127.47 (overlapped), 128.1, 130.2, 131.27, 131.30, 131.32, 131.4, 132.1, 135.6, 137.7, 138.0, 138.2, 138.9, 139.7 (overlapped), 140.6, 140.7; HRMS m/z (M^+) calcd for $C_{35}H_{26}$ 446.2034, found 446.2033.

6-Methoxy-1,2,3,4-tetraphenylnaphthalene (3j) (entry 2 in Table 3):[10] mp 258−259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 6.80−6.85 (m, 10H), 6.95 (d, J = 2.7 Hz, 1H), 7.06 (dd, J = 2.7, 9.2 Hz, 1H), 7.15−7.26 (m, 10H), 7.56 (d, J = 9.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 105.6, 118.0, 125.2, 125.2, 126.36, 126.38, 126.5 (overlapped), 127.5, 127.6, 128.7, 131.17, 131.24 (overlapped), 131.4, 133.2, 136.8, 137.3, 138.3, 139.4, 139.68, 139.73, 140.6, 140.7, 157.5; HRMS m/z (M^+) calcd for $C_{35}H_{26}O$ 462.1984, found 462.1979.

6-Chloro-1,2,3,4-tetraphenylnaphthalene (3k) (entry 3 in Table 3):[10] mp 226−227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80−6.88 (m, 10H), 7.17−7.27 (m, 10H), 7.31 (dd, J = 2.1, 9.1 Hz, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.45, 125.48, 125.6, 126.61 (overlapped), 126.63, 126.7, 127.6, 127.7, 128.8, 130.4, 131.11, 131.14, 131.2 (overlapped), 132.0, 132.9, 137.7, 138.4, 138.8, 139.1, 139.2, 140.0, 140.1, 140.2; HRMS m/z (M^+) calcd for $C_{34}H_{23}Cl$ 466.1488, found 466.1486.

6-Fluoro-1,2,3,4-tetraphenylnaphthalene (3*l*) (entry 4 in Table 3):[10] mp 206−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 10H), 7.10−7.28 (m, 12H), 7.61−7.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.3 (d, J = 22.0 Hz), 116.0 (d, J = 24.4 Hz), 125.4, 125.5, 126.59, 126.61 (overlapped), 126.7, 127.6, 127.7, 129.1, 129.7 (d, J = 9.1 Hz), 131.10, 131.12 (overlapped), 131.14, 131.3, 133.2 (d, J = 9.2 Hz), 137.9 (d, J = 5.3 Hz), 138.2 (d, J = 2.4 Hz), 138.5, 139.1, 139.3, 140.0, 140.3, 160.8 (d, J = 245.8 Hz); HRMS m/z (M^+) calcd for $C_{34}H_{23}F$ 450.1784, found 450.1785.

6-Bromo-1,2,3,4-tetraphenylnaphthalene (3m) (entry 5 in Table 3):[10] mp 246−247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81−6.88 (m, 10H), 7.17−7.27 (m, 10H), 7.44 (dd, J = 2.1, 8.7 Hz, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.78 (d, J = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.4, 125.5, 126.61 (overlapped), 126.64, 126.7, 127.6, 127.7, 128.87, 128.91, 129.2, 130.6, 131.10, 131.12, 131.14 (overlapped), 133.3 (overlapped), 137.7, 138.5, 138.8, 139.0, 139.3, 140.0, 140.1 (overlapped); HRMS m/z (M^+) calcd for $C_{34}H_{23}Br$ 510.0983, found 510.0980. Anal. Calcd for $C_{34}H_{23}Br$: C, 79.84; H, 4.53. Found: C, 79.88; H, 4.89.

1,2,3,4-Tetraphenyl-6-(trifluoromethyl)naphthalene (3n) (entry 7 in Table 3):[10] mp 244−246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81−6.90 (m, 10H), 7.19−7.29 (m, 10H), 7.54 (dd, J = 1.8, 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.3 (q, J = 3.0 Hz), 124.4 (q, J = 272.4 Hz), 124.6 (q, J = 4.6 Hz), 125.61, 125.63, 126.7 (overlapped), 126.8, 126.9, 127.1, 127.4, 127.7, 127.8, 128.2, 131.0, 131.10, 131.11, 131.13, 133.3, 138.45, 138.51, 138.9, 139.4, 139.9, 140.0, 140.3, 141.0; HRMS m/z (M^+) calcd for $C_{35}H_{23}F_3$ 500.1752, found 500.1750.

6-(Methoxycarbonyl)-1,2,3,4-tetraphenylnaphthalene (3o) (entry 9 in Table 3):[10] mp 296−297 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.81−6.88 (m, 10H), 7.19−7.28 (m, 10H), 7.69 (d, J = 9.1 Hz, 1H), 7.95 (d, J = 9.1 Hz, 1H), 8.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 125.2, 125.3, 125.5, 125.6, 126.6, 126.8, 127.29,

127.33, 127.65, 127.66, 128.2, 129.0, 130.0, 131.0, 131.17, 131.22, 131.3, 134.2, 138.4, 138.7, 139.1, 139.8, 139.9, 140.07, 140.10, 141.2, 167.3; HRMS m/z (M^+) calcd for $C_{36}H_{26}O_2$ 490.1933, found 490.1931.

6-Formyl-1,2,3,4-tetraphenylnaphthalene (3p) (entry 11 in Table 3):[10] mp 225−226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83−6.89 (m, 10H), 7.18−7.31 (m, 10H), 7.74 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 7.3 Hz, 1H), 8.14 (s, 1H), 9.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.3, 125.6, 125.7, 126.69, 126.71, 126.8, 127.0, 127.7, 127.8, 128.2, 129.0, 130.9, 131.07, 131.10, 131.14, 131.5, 133.9, 134.2, 135.0, 138.5, 138.8, 139.8, 139.9, 140.1, 140.2, 142.1, 192.5; HRMS m/z (M^+) calcd for $C_{35}H_{24}O$ 460.1827, found 460.1826 .

5,7-Dimethyl-1,2,3,4-tetraphenylnaphthalene (3q) (entry 17 in Table 3):[4i] mp 252−254 °C; ^{1}H NMR (400 MHz, CDCl3) δ 2.07 (s, 3H), 2.47 (s, 3H), 6.91−6.94 (m, 10H), 7.24−7.38 (m, 11H), 7.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.2, 124.9, 125.1, 125.2, 126.1, 126.2 (overlapped), 126.4, 126.7, 127.4, 129. 1, 131.1, 131.3, 131.4, 131.6, 132.6, 133.6, 134.88, 135.6, 137.9, 138.4, 138.5, 139.5, 140.4, 140.8 (overlapped), 143.0; HRMS m/z (M^+) calcd for $C_{36}H_{28}$ 460.2191, found 460.2186.

5-Methyl-1,2,3,4-tetraphenylnaphthalene (3r) (entry 18 in Table 3):[10] mp 237−238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 3H), 6.75−6.82 (m, 10H), 7.09−7.28 (m, 12H), 7.51−7.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3, 124.0, 124.2, 124.4, 125.1, 125.2 (overlapped), 125.3, 125.4, 125.8, 126.4, 129.3, 129.9, 130.1, 130.3, 130.4, 130.6, 132.4, 134.9, 137.0, 137.4, 138.0, 139.3, 139.4, 139.6, 139.7, 141.9; HRMS m/z (M^+) calcd for $C_{35}H_{26}$ 446.2034, found 446.2029.

9,10-Diphenylphenanthrene (4) (entry 19 in Table 3):[15] mp 235−236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.25 (m, 10H), 7.46−7.50 (m, 2H), 7.55−7.57 (m, 2H), 7.63−7.67 (m, 2H), 8.80 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.5, 126.4, 126.5, 126.6, 127.6, 127.8, 130.0, 131.0, 131.9, 137.2, 139.6; HRMS m/z (M^+) calcd for $C_{26}H_{18}$ 330.1409, found 330.1405.

1-Acetyl-2,3-diphenylindole (5) (entry 19 in Table 3):[12b] mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 7.21−7.43 (m, 12H), 7.43 (d, J = 7.8 Hz, 1H), 8.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 116.2, 119.5, 123.3, 123.8, 125.5, 126.9, 128. 2, 128.6 (overlapped), 129.2, 130.0, 130.8, 132.9, 133.0, 135.0, 136.8, 171.6; HRMS m/z (M^+) calcd for $C_{22}H_{17}NO$ 311.1310, found 311.1305.

5,6,7,8-Tetraphenylisoquinoline (6) (Scheme 3):[16] mp 215−217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82−6.90 (m, 10H), 7.17−7.28 (m, 10H), 7.43 (d, J = 6.0 Hz, 1H), 8.45 (d, J = 6.0 Hz, 1H), 9.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.0, 125.7, 125.8, 126.8 (overlapped), 126.9, 127.0, 127.7, 127.8, 130.9, 131.05, 131.12, 131.2, 134.7 (overlapped), 137.37, 137.44, 138.0, 139.0, 139.4, 139.6, 140.3, 143.0 (overlapped), 151.9; HRMS m/z (M^+) calcd for $C_{33}H_{23}N$ 433.1830, found 433.1833.

1,2,3,4-Tetraphenylanthracene (7a) (entry 1 in Table 4):[10] mp 295−296 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (m, 10H), 7.22−7.38 (m, 12H), 7.80−7.83 (m, 2H), 8.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.3, 125.4, 125.9, 126.5, 126.6, 127.6, 128.3, 130.9, 131.3, 131.42, 131.44, 138.1, 138.5, 139.7, 140.6; HRMS m/z (M^+) calcd for $C_{38}H_{26}$ 482.2034, found 482.2036.

6-Methoxy-1,2,3,4-tetraphenylanthracene (7b) (entry 2 in Table 4):[10] mp 284−285 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.82−6.88 (m, 10H), 7.02−7.08 (m, 2H), 7.22−7.31 (m, 10H), 7.71 (d, J = 9.2 Hz, 1H), 8.03 (s, 1H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 103.8, 120.6, 123.8, 125.25, 125.28, 125.9, 126.4, 126.47, 126.53 (overlapped), 127.59, 127.61, 128.0, 129.5, 130.0, 131.3 (overlapped), 131.36, 131.42, 131.5, 132.5, 137.5, 137.6, 138.2, 138.6, 139.8, 140.0, 140.65, 140.69, 157.3; HRMS m/z (M^+) calcd for $C_{39}H_{28}O$ 512.2140, found 512.2134.

1,2,3,4-Tetrapropylanthracene (7c) (entry 3 in Table 4):[4f] mp 113−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.3 Hz, 6H), 1.18 (t, J = 7.3 Hz, 6H), 1.67−1.58 (m, 4H), 1.83−1.73 (m, 4H), 2.80−2.75 (m, 4H), 3.17−3.13 (m, 4H), 7.97 (dd, J = 3.3, 6.6 Hz, 2H), 7.40 (dd, J = 3.3, 6.6 Hz, 2H), 8.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 15.1, 24.4, 24.9, 31.5, 32.8, 122.8, 124.7, 128.2, 130.3, 130.7, 133.6, 136.6; HRMS m/z (M^+) calcd for $C_{26}H_{34}$ 346.2661, found 346.2662.

1,2,3,4-Tetraheptylanthracene (7d) (entry 4 in Table 4). oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (m, 12H), 1.35−1.75 (m, 40H), 2.77−2.81 (m, 4H), 3.14−3.18 (m, 4H), 7.39−7.41 (m, 2H), 7.96−7.99 (m, 2H), 8.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.14, 14.16, 22.73, 22.74, 29.1, 29.2, 29.3, 30.5, 30.6, 31.1, 31.6, 31.9, 122.8, 124.7, 128.2, 130.3, 130.7, 133.7, 136.6; HRMS m/z (M^+) calcd for $C_{42}H_{66}$ 570.5164, found 570.5164.

1,2,3,4,5,6,7,8-Octakis(4-octylphenyl)anthracene (7e) (entry 5 in Table 4). oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85−0.92 (m, 24H), 1.10−1.51 (m, 96H), 2.30−2.34 (m, 8H), 2.44−2.48 (m, 8H), 6.57−6.61 (m, 8H), 6.65−6.67 (m, 8H), 6.82−6.84 (m, 8H), 6.91−6.95 (m, 8H), 8.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (overlapped), 22.7 (overlapped), 28.9, 29.4 (overlapped), 29.46, 29.48, 29.6, 31.2, 31.4, 31.96, 31.98, 35.3, 35.7, 126.4, 127.0, 130.6, 131.1, 131.3, 136.6, 138.1, 138.3, 138.5, 139.1, 140.0, 140.5; HRMS (TOF) m/z (M^+) calcd for $C_{126}H_{170}$ 1683.3303, found 1683.3297.

1,2,3,4-Tetraphenyltetracene (8a) (entry 6 in Table 4). mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82−6.91 (m, 10H), 7.25−7.35 (m, 12H), 7.88−7.91 (m, 2H), 8.43 (s, 2H), 8.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.1, 125.4, 126.4, 126.6 (overlapped), 127.7, 128.3, 130.0, 131.1, 131.3, 131.5, 131.6, 138.0, 138.3, 139.7, 140.6; HRMS m/z (M^+) calcd for $C_{42}H_{28}$ 532.2191, found 532.2186.

1,2,3,4-Tetrakis(4-methylphenyl)tetracene (8b) (entry 7 in Table 4). mp 274−276 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 6H), 2.37 (s, 6H), 6.68 (d, J = 7.8 Hz, 4H), 6.74−6.76 (m, 4H), 7.12 (d, J = 7.4 Hz, 4H), 7.18−7.20 (m, 4H), 7.30−7.32 (m, 2H), 7.85−7.88 (m, 2H), 8.39 (s, 2H), 8.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.3, 124.9, 126.5, 126.6, 127.3, 128.3, 128.4, 129.9, 131.1, 131.3, 131.37, 131.43, 134.4, 135.8, 136.9, 137.8 (overlapped), 138.6; HRMS m/z (M^+) calcd for $C_{46}H_{36}$ 588.2817, found 588.2811.

1,2,3,4-Tetrakis(4-methoxyphenyl)tetracene (8c) (entry 8 in Table 4). mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 6H), 3.86 (s, 6H), 6.45−6.47 (m, 4H), 6.75−6.78 (m, 4H), 6.87−6.89 (m, 4H), 7.21−7.23 (m, 4H), 7.32−7.35 (m, 2H), 7.88−7.91 (m, 2H), 8.42 (s, 2H), 8.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 55.1, 112.1, 113.1, 124.9, 126.1, 126.5, 128.2, 129.9, 131.4, 131.5, 132.17, 132.20, 132.4, 133.3, 137.6, 138.5, 156.8, 157.9; HRMS m/z (M^+) calcd for $C_{46}H_{36}O_4$ 652.2614, found 652.2619.

1,2,3,4-Tetrakis(4-chlorophenyl)tetracene (8d) (entry 9 in Table 4). mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77−6.79 (m, 4H), 6.92−6.94 (m, 4H), 7.21−7.24 (m, 4H), 7.34−7.39 (m, 6H), 7.92−7.93 (m, 2H), 8.34 (s, 2H), 8.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.5, 126.4, 126.7, 127.4, 128.2, 128.3, 130.0, 130.5, 131.87, 131.93, 132.2, 132.5, 133.0, 136.7, 137.5, 137.6, 138.4; HRMS m/z (M^+) calcd for $C_{42}H_{24}Cl_4$ 668.0632, found 668.0625.

8-Methyl-1,2,3,4-tetraphenyltetracene (8e) (entry 10 in Table 4). mp 186−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 6.84−6.90 (m, 10H), 7.16−7.19 (m, 1H), 7.26−7.35 (m, 10H), 7.62 (s, 1H), 7.80 (d, J = Hz, 1H), 8.37−8.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 125.3 (overlapped), 126.1, 126.3, 126.4, 126.55, 126.57 (overlapped), 127.7 (overlapped), 127.8, 127.9, 128.1, 128.2, 129.7, 130.2, 130.4, 130.7, 130.1, 131.3 (overlapped), 131.45, 131.47, 131.9, 134.7, 137.9, 138.0, 138.1, 138.2, 139.7, 140.6; HRMS m/z (M^+) calcd for $C_{43}H_{30}$ 546.2347, found 546.2343.

6,11-Dimethyl-1,2,3,4-tetraphenyltetracene (8f) (entry 11 in Table 4). mp 228−230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92

(s, 6H), 6.84−6.92 (m, 10H), 7.24−7.39 (m, 12H), 8.22−8.25 (m, 2H), 8.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 123.8, 124.4, 125.3, 125.5, 126.58, 126.59, 127.7, 128.5, 128.7, 129.4, 130.3, 131.3, 131.5, 138.15, 138.17, 139.7, 140.7; HRMS m/z (M^+) calcd for $C_{44}H_{32}$ 560.2504, found 560.2502.

6,11-Dibromo-1,2,3,4-tetraphenyltetracene (8g) (entry 12 in Table 4). mp 227−229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86−6.90 (m, 10H), 7.23−7.45 (m, 12H), 8.41−8.45 (m, 2H), 9.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.7, 125.6, 126.7, 126.8, 127.0, 127.5, 127.8, 128.2, 128.9, 130.6, 131.2, 131.4, 132.2, 139.1, 139.6, 140.3 (overlapped); HRMS m/z (M^+) calcd for $C_{42}H_{26}Br_2$ 688.0401, found 688.0396.

1,2,3,4-Tetrapropyltetracene (8h) (entry 13 in Table 4). mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10−1.15 (m, 6H), 1.20−1.25 (m, 6H), 1.61−1.67 (m, 4H), 1.80−1.86 (m, 4H), 2.75−2.79 (m, 4H), 3.16−3.20 (m, 4H), 7.34−7.37 (m, 2H), 7.96−7.99 (m, 2H), 8.64 (s, 2H), 8.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 15.1, 24.3, 24.8, 31.6, 32.8, 122.7, 124.7, 126.2, 128.3, 129.6, 130.4, 131.3, 133.3, 136.5; HRMS m/z (M^+) calcd for $C_{30}H_{36}$ 396.2817, found 396.2815.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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