Synthesis Y. Inai et al. Special Topic

Synthesis of Benzo-Fused Cyclic Compounds via Rhodium-Catalyzed Decarboxylative Coupling of Aromatic Carboxylic Acids with Alkynes

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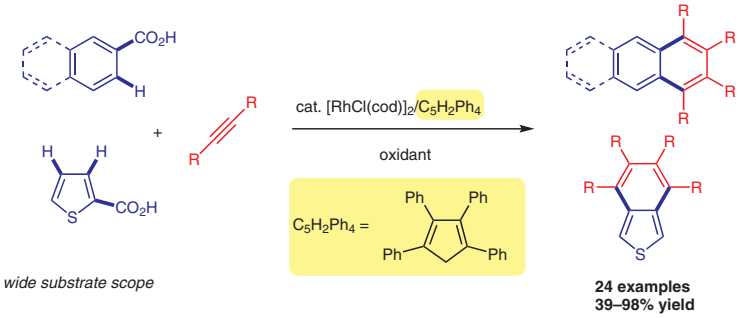

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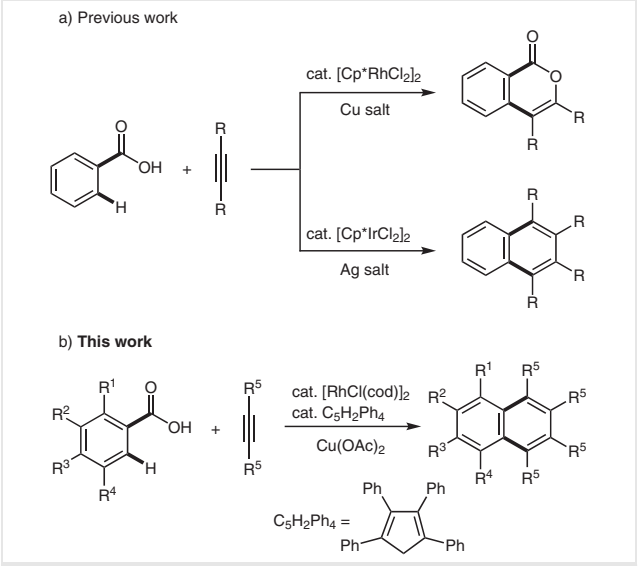
Abstract The decarboxylative coupling of diversely substituted benzoic acids with internal alkynes proceeds smoothly in the presence of a $[RhCl(cod)]_2$/1,2,3,4-tetraphenyl-1,3-cyclopentadiene catalyst system to selectively produce highly substituted naphthalene derivatives. The catalyst system is applicable to constructing anthracene and benzo[c]thiophene frameworks through reactions of naphthoic and thiophene-2-carboxylic acids, respectively.

Key words C–H functionalization, carboxylic acids, decarboxylative coupling, homologation, rhodium catalysis

Aromatic and heteroaromatic carboxylic acids have been recognized as promising building blocks in the field of organic synthesis because of their ready availability. Moreover, their carboxy function acts as a directing group[1] to bring about regioselective C–H functionalization[2] at the neighboring positions under transition-metal catalysis. Our group has reported that benzoic acids undergo dehydrogenative coupling with internal alkynes through *ortho* C–H bond cleavage upon treatment with a $[Cp^*RhCl_2]_2$ catalyst and a copper salt oxidant to produce isocoumarins (Scheme 1, a).[3] Meanwhile, treatment of the same starting materials with a $[Cp^*IrCl_2]_2$ catalyst and a silver salt oxidant induces decarboxylative 1:2 coupling to give 1,2,3,4-tetrasubstituted naphthalene derivatives.[4] The latter aromatic homologation[5] is of particular interest because of its utility for constructing benzo-fused cyclic compounds such as acenes and benzoheteroles. Recently, the groups of Tanaka[6] and Loginov[7] reported that homologation can be conducted smoothly by using $[Cp^ERhCl_2]_2$ and $[CpRhI_2]_2$, respectively, as catalysts [Cp^E = 1,3-bis(ethoxycarbonyl)-2,4,5-trimethylcyclopentadienyl]. Despite this progress, the substrate scope is still limited.

During our further studies on such homologation, we found that the catalyst system $[RhCl(cod)]_2/C_5H_2Ph_4$ ($C_5H_2Ph_4$ = 1,2,3,4-tetraphenyl-1,3-cyclopentadiene)[3b,5c,8] was effective for the reaction of diversely substituted benzoic acids with alkynes to produce highly substituted naphthalenes selectively (Scheme 1, b). This catalyst system was also found to be applicable to the homologation of naph-



Scheme 1 Dehydrogenative coupling of benzoic acids with alkynes

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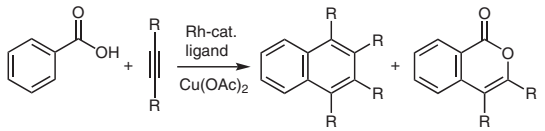
Table 1 Reaction of Benzoic Acid (**1a**) with Diphenylacetylene (**2a**) or 8-Hexadecyne (**2b**)[a]



1a **2a** (R = Ph) **2b** (R = *n*-C_7H_{15}) **3aa** (R = Ph) **3ab** (R = *n*-C_7H_{15}) **4aa** (R = Ph) **4ab** (R = *n*-C_7H_{15})

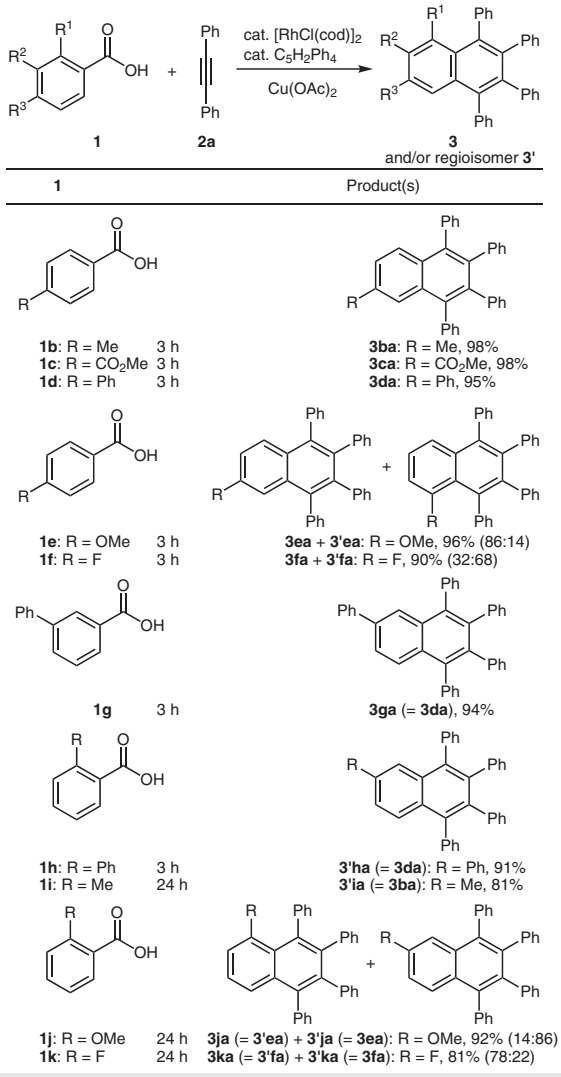
Entry	R	Rh-cat.	Ligand	Yield (%)[b]	
				3	**4**
1	Ph	$[Cp^*RhCl_2]_2$	–	8	92 (91)
2	Ph	$[Cp^*RhCl_2]_2$	cod	0	10
3	Ph	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	97 (96)	3
4	Ph	$[RhCl(cod)]_2$	C_5HPh_5	0	1
5	Ph	$[RhCl(cod)]_2$	–	3	1
6[c]	Ph	$RhCl_3{\cdot}3H_2O$	–	0	0
7[c]	Ph	$RhCl_3{\cdot}3H_2O$	$C_5H_2Ph_4$	0	0
8[d]	Ph	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	74	21
9[e]	Ph	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	23	1
10	*n*-C_7H_{15}	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	(60)	20

[a] Reaction conditions: **1a** (0.38 mmol), **2a** (0.5 mmol), Rh-cat. (0.005 mmol), ligand (0.02 mmol), $Cu(OAc)_2$ (1 mmol), *o*-xylene (2.5 mL), 160 °C, Ar (1 atm), 24 h.
[b] GC yield based on the amount of **2a** used. Value in parentheses indicates the yield of isolated product after purification.
[c] $RhCl_3{\cdot}3H_2O$ (0.01 mmol) was used.
[d] $Cu(OAc)_2$ (0.025 mmol) was used under air (1 atm).
[e] Reaction at 120 °C.

thoic acids and thiophene-2-carboxylic acid to form anthracene and benzo[*c*]thiophene frameworks, respectively. These findings are described herein.

In an initial attempt, benzoic acid (**1a**) (0.38 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) under conditions similar to those described in our previous report. Thus, in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and $Cu(OAc)_2$ (1 mmol) as the catalyst and the oxidant, respectively, in *o*-xylene (2.5 mL) at 160 °C under argon (1 atm), 3,4-diphenyl-1*H*-isochromen-1-one (**4aa**) was formed as the major product, along with a minor amount of 1,2,3,4-tetraphenylnaphthalene (**3aa**) (Table 1, entry 1). Adding cod (cod = 1,5-cyclooctadiene) (0.02 mmol) retarded the reaction (entry 2). In contrast, as described above, the catalyst system of $[RhCl(cod)]_2/C_5H_2Ph_4$ effectively promoted the decarboxylative coupling to give **3aa** in 96% isolated yield (entry 3). The use of C_5HPh_5 (C_5HPh_5 = 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene) in place of $C_5H_2Ph_4$ (entry 4) or the absence of any Cp ligand (entries 5 and 6) led to poor results. It is possible that sterically more hindered C_5HPh_5 did not act as a ligand effectively.[9] The system comprising $RhCl_3{\cdot}3H_2O/C_5H_2Ph_4$ also showed no activity for the coupling (entry 7). The reaction using a catalytic amount of $Cu(OAc)_2$ (0.025 mmol) under air (1 atm) gave **3aa** in a somewhat reduced yield (entry 8). At 120 °C, the reaction was sluggish (entry 9). Under the same conditions as those in entry 3, **1a** also reacted with 8-hexadecyne (**2b**) to give 1,2,3,4-tetra(*n*-heptyl)naphthalene (**3ab**) predominantly, along with a minor amount of 3,4-di(*n*-heptyl)-1*H*-isochromen-1-one (**4ab**) (entry 10).

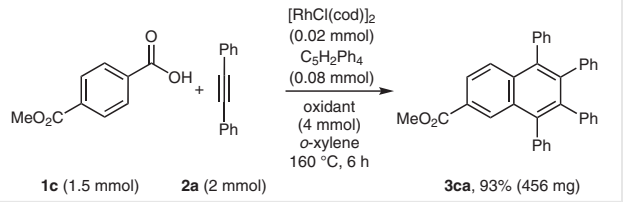
Under the optimized conditions (Table 1, entry 3), the reactions of differently substituted benzoic acids **1b–k** with **2a** were examined (Scheme 2). 4-Methyl- (**1b**) and 4-(methoxycarbonyl)benzoic acids (**1c**) and [1,1′-biphenyl]-4-carboxylic acid (**1d**) coupled with **2a** efficiently to produce the corresponding 6-substituted 1,2,3,4-tetraphenylnaphthalenes **3ba–da** in excellent yields. The reaction



Scheme 2 Reactions of benzoic acids **1** with **2a**. *Reagents and conditions*: **1** (0.38 mmol), **2a** (0.5 mmol), $[RhCl(cod)]_2$ (0.005 mmol), $C_5H_2Ph_4$ (0.02 mmol), $Cu(OAc)_2$ (1 mmol), *o*-xylene (2.5 mL), 160 °C, Ar (1 atm). Yields of isolated products are given. Values in parentheses indicate product ratios determined by ^1H NMR.

of 4-methoxybenzoic acid (**1e**) also proceeded smoothly to give a mixture of regioisomers **3ea** and **3′ea** (86:14, 96% total yield). In the reaction of 4-fluorobenzoic acid (**1f**), the sterically hindered 5-fluoro-1,2,3,4-tetraphenylnaphthalene (**3′fa**) was formed predominantly over the less crowded regioisomer **3fa**. We previously observed the similar predominant formation of a 5-substituted naphthalene derivative in the iridium-catalyzed decarboxylative coupling of 4-hydroxybenzoic acid.[4a] [1,1′-Biphenyl]-3-carboxylic acid (**1g**), [1,1′-biphenyl]-2-carboxylic acid (**1h**), and 2-methylbenzoic acid (**1i**) also underwent the reaction with **2a** to selectively afford 6-substituted 1,2,3,4-tetraphenylnaphthalenes **3ga**, **3′ha**, and **3′ia**, respectively, in good yields. The reactions of 2-methoxy- (**1j**) and 2-fluorobenzoic acids (**1k**) gave similar mixtures of regioisomers **3ja**/**3′ja** and **3ka**/**3′ka**, as in cases with **1e** and **1f**.

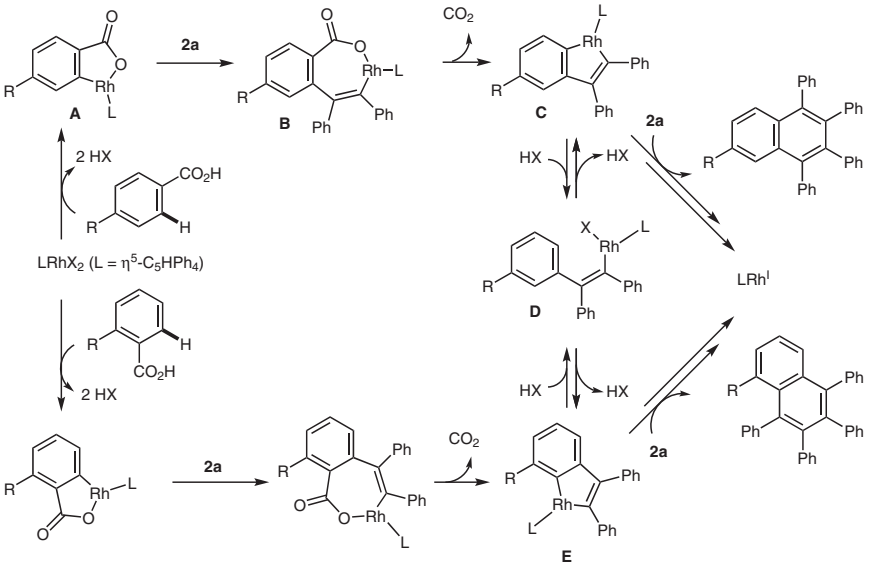
It was confirmed that the present decarboxylative coupling could be scaled up to mmol scale. Thus, the reaction of **1c** (1.5 mmol) with **2a** (2 mmol) gave the desired product **3ca** in a reasonable yield (456 mg, 93%) (Scheme 3).



Scheme 3 A large-scale synthesis of **3ca**

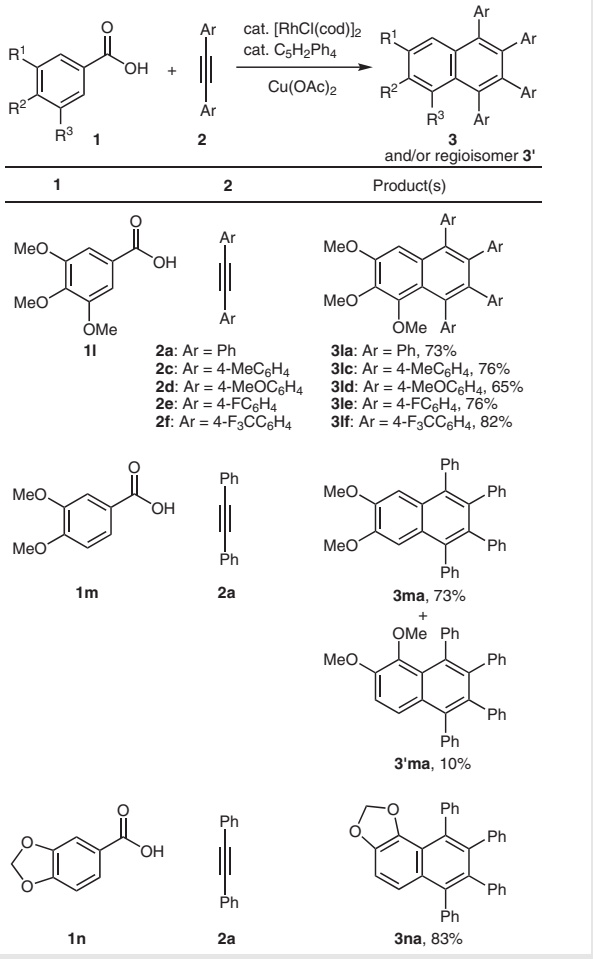
Plausible pathways for the reactions of 4- and 2-substituted benzoic acids with **2a** are depicted in Scheme 4. An active $LRh^{III}X_2$ species (L = η^5-C_5HPh_4) appears to be generated from $[RhCl(cod)]_2$, $C_5H_2Ph_4$, and the Cu salt oxidant. The reaction of 4-substituted benzoic acids appears to proceed in a similar way to that proposed for the previously reported iridium-catalyzed reaction,[4b] through carboxy-group-directed C–H bond cleavage to form **A**, alkyne insertion to form **B**, decarboxylation to form **C**, a second alkyne insertion, and reductive elimination steps to release 6-substituted 1,2,3,4-tetraphenylnaphthalene **3**. The LRh^{I} species generated in the final step appears to be reoxidized by the copper salt oxidant to regenerate the active $LRh^{III}X_2$ species. In the reactions of 4-methoxy- and 4-fluorobenzoic acids, at least some of **C** may isomerize into **E** through **D** to afford 5-substituted 1,2,3,4-tetraphenylnaphthalenes **3′** along with **3**. On the other hand, the reaction of 2-substituted benzoic acids proceeds through *ortho* C–H bond cleavage, alkyne insertion, and decarboxylation to form intermediate **E**. In the cases with 2-phenyl- and 2-methylbenzoic acids (R = Ph, Me), **E** undergoes isomerization into **C** due to steric hindrance, to exclusively form 6-substituted 1,2,3,4-tetraphenylnaphthalene **3′**. The reactions of 2-methoxy- and 2-fluorobenzoic acids gave similar mixtures of 5- and 6-substituted 1,2,3,4-tetraphenylnaphthalene regioisomers as in the cases with 4-methoxy- and 4-fluorobenzoic acids, showing the existence of an equilibrium between intermediates **C** and **E**. The ratio of **C**/**E** may be determined by the electronic and steric properties of these substituents.

It is known that hydroxy- and alkoxy-substituted benzoic acids are widely distributed in plants and are therefore readily available from biomass.[3a,10] We next examined their utilization as promising building blocks for constructing highly substituted naphthalene derivatives (Scheme 5). Under our standard conditions, 3,4,5-trimethoxybenzoic acid (**1l**) reacted with **2a** smoothly to produce 5,6,7-trimethoxy-



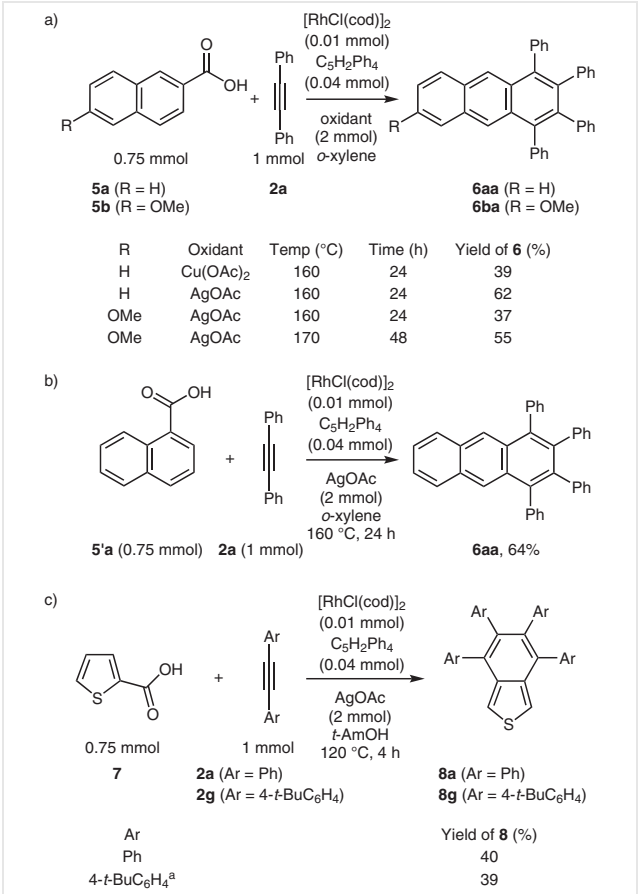
Scheme 4 Plausible pathways for the reactions of 4- and 2-substituted benzoic acids with **2a**

1,2,3,4-tetraphenylnaphthalene (**3la**) in 73% yield. 4-Methyl- (**2c**), 4-methoxy- (**2d**), 4-fluoro- (**2e**), and 4-(trifluoromethyl)- (**2f**) substituted diphenylacetylenes also underwent the coupling with **1l** to give products **3lc–lf** in 64–82% yields. The coupling of 3,4-dimethoxybenzoic acid (**1m**) with **2a** gave separable 6,7-dimethoxy-1,2,3,4-tetraphenylnaphthalene (**3ma**) and 5,6-dimethoxy-1,2,3,4-tetraphenylnaphthalene (**3'ma**) in 73% and 10% yields, respectively. Benzo[*d*][1,3]dioxole-5-carboxylic acid (**1n**) is known to be readily available from piperonal. Interestingly, the homologation of this acid proceeded regioselectively to afford 6,7,8,9-tetraphenylnaphtho[1,2-*d*][1,3]dioxole (**3na**) in 83% yield.[11]



Scheme 5 Reactions of alkoxy-substituted benzoic acids **1** with alkynes **2**. *Reagents and conditions*: **1** (0.38 mmol), **2** (0.5 mmol), $[RhCl(cod)]_2$ (0.005 mmol), $C_5H_2Ph_4$ (0.02 mmol), $Cu(OAc)_2$ (1 mmol), *o*-xylene (2.5 mL), 160 °C, Ar (1 atm), 24 h. Yields of isolated products are given.

Besides naphthalene synthesis, homologation for constructing other benzo-fused cyclic systems was also examined. The reaction of 2-naphthoic acid (**5a**) with **2a** proceeded regioselectively under our standard conditions to form 1,2,3,4-tetraphenylanthracene (**6aa**) in 39% yield (Scheme 6, a). No phenanthrene isomer could be detected.[12] As an oxidant, the use of AgOAc in place of $Cu(OAc)_2$ improved the yield of **6aa** up to 62%. Under similar conditions, 6-methoxy-2-naphthoic acid (**5b**) underwent the reaction with **2a** to produce 6-methoxy-1,2,3,4-tetraphenylanthracene (**6ba**) in 37% yield. The yield of **6ba** was improved to 55% by increasing the temperature of the reaction bath to 170 °C. The anthracene **6aa** could also be obtained in 64% yield from the reaction of 1-naphthoic acid (**5'a**) with **2a** under conditions using AgOAc at 160 °C (Scheme 6, b). Thiophene-2-carboxylic acid (**7**) underwent the coupling with **2a** in the presence of the $[RhCl(cod)]_2/C_5H_2Ph_4$ catalyst system and AgOAc as the oxidant in *t*-AmOH at 120 °C to predominantly produce 4,5,6,7-tetraphenylbenzo[*c*]thiophene (**8a**) in a moderate yield (Scheme 6, c).[13] A similar tetraarylbenzo[*c*]thiophene derivative **8g** could also be prepared by the reaction of **7** with bis(4-*t*-butylphenyl)acetylene (**2g**).



Scheme 6 Reactions of naphthoic acids **5** and thiophene-2-carboxylic acid (**7**) with **2a**. [a] Thiophene-2-carboxylic acid (**7**) (0.38 mmol), **2g** (0.5 mmol), $[RhCl(cod)]_2$ (0.005 mmol), $C_5H_2Ph_4$ (0.02 mmol), and AgOAc (1 mmol) were used.

In conclusion, we have developed the decarboxylative coupling of aromatic carboxylic acids with internal alkynes. For the homologation reactions, the $[RhCl(cod)]_2/C_5H_2Ph_4$ catalyst system was found to be effective. The procedure provides straightforward routes not only to highly substituted naphthalenes, but also to anthracene and benzo[*c*]thiophene derivatives.

Chemicals were either purchased or were purified by standard techniques. Diarylacetylenes **2c–g** were prepared according to published procedures.[14] Column chromatography was performed using silica gel 60 (40–50 μm). GPC (gel permeation chromatography) was performed using a JASCO HPLC system EXTREMA composed of a PU-4086 pump, a UV-4075 detector, and a RV-2002-02 recycle valve unit with a YMC-GPC-T2000 column. Melting points were obtained using a MP-J3 Micro Melting Point Apparatus or a MPA100 OptiMelt Automated Melting Point System. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded at room temperature on a Bruker AV400N spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are quoted relative to TMS, and the coupling constants (*J*) are given in Hz. ^{19}F NMR (282 MHz) spectra were recorded on a Bruker AV 300N spectrometer. Chemical shifts (δ) are quoted relative to external trifluoroacetic acid (TFA) (δ = –76.5). GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC-MS analysis was carried out using a Shimadzu GC-MS-QP2010 Plus mass spectrometer with a CBP-1 capillary column (i.d. 0.25 mm × 25 m). High-resolution mass spectrometry was performed using a JEOL AccuTOF LC-plus 4G mass spectrometer.

Decarboxylative Coupling of 1 with 2; General Procedure

A mixture of benzoic acid **1** (0.38 mmol), alkyne **2** (0.5 mmol), $[Rh(cod)Cl_2]_2$ (2.5 mg, 0.005 mmol), $C_5H_2Ph_4$ (7.4 mg, 0.02 mmol), $Cu(OAc)_2$ (181.6 mg, 1.0 mmol) and 1-methylnaphthalene (ca. 50 mg) as an internal standard in *o*-xylene (2.5 mL) was stirred at 160 °C under Ar (1 atm) for 3–24 h. After the reaction was complete, the mixture was diluted with dichloromethane (100 mL). The organic layer was washed with water (2 × 100 mL) and brine (100 mL), and then dried over Na_2SO_4. After evaporation of the solvents under vacuum, products **3** (and **3′**) were isolated by column chromatography on silica gel using hexane–ethyl acetate as eluent. Further purification by GPC (gel permeation chromatography) was performed, if needed.

1,2,3,4-Tetraphenylnaphthalene (3aa)

Yield: 103.6 mg (96%); white solid; mp 206–207 °C (Lit.[5b] 205–206 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.61 (m, 2 H), 7.41–7.36 (m, 2 H), 7.27–7.16 (m, 10 H), 6.88–6.80 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 139.6, 138.9, 138.4, 132.0, 131.3 (overlapped), 127.5, 127.0, 126.5, 126.4, 125.8, 125.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{25}$: 433.19563; found: 433.19472.

1,2,3,4-Tetraheptylnaphthalene (3ab)[5c]

Yield: 78.6 mg (60%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.94 (m, 2 H), 7.43–7.35 (m, 2 H), 3.07–2.95 (m, 4 H), 2.80–2.69 (m, 4 H), 1.71–1.26 (m, 40 H), 0.96–0.87 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9, 134.2, 131.1, 124.5, 124.4, 31.93, 31.91, 31.6, 31.3, 30.53, 30.48, 30.3 (overlapped), 29.2, 29.1, 22.7 (overlapped), 14.1 (overlapped).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{65}$: 521.50863; found: 521.50870.

6-Methyl-1,2,3,4-tetraphenylnaphthalene (3ba)

Yield: 109.1 mg (98%); white solid; mp 220–221 °C (Lit.[5b] 216–217 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.6 Hz, 1 H), 7.40 (s, 1 H), 7.27–7.16 (m, 11 H), 6.88–6.78 (m, 10 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 140.6, 139.73, 139.72, 138.9, 138.2, 138.0, 137.7, 135.6, 132.1, 131.4, 131.33, 131.31, 131.27, 130.2, 128.1, 127.46 (overlapped), 127.45, 126.9, 126.5 (overlapped), 126.31, 126.29, 125.8, 125.2, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{27}$: 447.21128; found: 447.21113.

6-(Methoxycarbonyl)-1,2,3,4-tetraphenylnaphthalene (3ca)

Yield: 120.2 mg (98%); pale yellow solid; mp 296–297 °C (Lit.[5b] 296–297 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 1.4 Hz, 1 H), 7.95 (dd, *J* = 8.9, 1.8 Hz, 1 H), 7.69 (d, *J* = 8.9 Hz, 1 H), 7.29–7.18 (m, 10 H), 6.90–6.80 (m, 10 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 141.2, 140.08, 140.06, 139.9, 139.8, 139.0, 138.7, 138.4, 134.2, 131.3, 131.19, 131.15 (overlapped), 131.0, 130.0, 127.7, 127.6, 127.31, 127.29, 126.8, 126.6 (overlapped), 125.53, 125.48, 125.1, 52.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{27}O_2$: 491.20110; found: 491.20107.

1,2,3,4,6-Pentaphenylnaphthalene (3da)

Yield: 120.8 mg (95%); white solid; mp 268–269 °C (Lit.[4b] 268–271 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 1.7 Hz, 1 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.65 (dd, *J* = 8.8, 1.8 Hz, 1 H), 7.53 (dd, *J* = 7.8, 1.4 Hz, 2 H), 7.39 (dd, *J* = 7.5, 7.2 Hz, 2 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 7.27–7.16 (m, 10 H), 6.90–6.80 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.51, 140.48, 139.5, 139.4, 139.0, 138.7, 138.4, 138.3, 132.3, 131.3 (overlapped), 131.2, 128.8, 127.57 (overlapped), 127.56, 127.4, 127.2, 126.6 (overlapped), 126.49, 126.46, 125.5, 125.3, 124.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{29}$: 509.22684; found: 509.22684.

6-Methoxy-1,2,3,4-tetraphenylnaphthalene (3ea) and 5-Methoxy-1,2,3,4-tetraphenylnaphthalene (3′ea)

Yield: 111.4 mg (96%); white solid; mp 274–275 °C (Lit.[6b] 272.8–274.8 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 9.2 Hz, 1 H, **3ea**), 7.27–7.15 (m, 10 H, **3ea**), 7.06 (dd, *J* = 9.3, 2.6 Hz, 1 H, **3ea**), 6.95 (d, *J* = 2.5 Hz, 1 H, **3ea**), 6.88–6.75 (m, 10 H, **3ea**), 3.69 (s, 3 H, **3ea**), 3.37 (s, 3 H, **3′ea**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5 (**3ea**), 143.8 (**3′ea**), 140.7 (**3ea**), 140.6 (**3ea**), 140.1 (**3′ea**), 139.8 (**3ea**), 139.7 (**3ea**), 139.4 (**3ea**), 138.3 (**3ea**), 138.2 (**3′ea**), 137.3 (**3ea**), 136.8 (**3ea**), 133.3 (**3ea**), 131.4 (**3ea**), 131.25 (**3ea**), 131.23 (**3ea**), 131.18 (**3ea**), 131.1 (**3′ea**), 129.8 (**3′ea**), 128.7 (**3ea**), 127.6 (**3ea**), 127.5 (overlapped) (**3ea**), 126.5 (**3ea**), 126.4

(**3'ea**), 126.37 (**3ea**), 126.36 (**3ea**), 126.3 (**3'ea**), 126.2 (**3'ea**), 126.0 (**3'ea**), 125.23 (**3ea**), 125.17 (**3ea**), 125.0 (**3'ea**), 124.7 (**3'ea**), 120.1 (**3'ea**), 118.0 (**3ea**), 106.9 (**3'ea**), 105.7 (**3ea**), 55.8 (**3'ea**), 55.1 (**3ea**).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{27}O$: 463.20619; found: 463.20549.

6-Fluoro-1,2,3,4-tetraphenylnaphthalene (3fa) and 5-Fluoro-1,2,3,4-tetraphenylnaphthalene (3'fa)

Yield: 101.3 mg (90%); white solid; mp 254–255 °C (Lit.[6b] 253.4–256.7 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 9.3, 5.9 Hz, 1 H, **3'fa**), 7.43 (d, *J* = 8.5 Hz, 1 H, **3fa**), 7.33–7.02 (m, 12 H, **3fa**), 6.88–6.76 (m, 10 H, **3fa**).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 160.8, 159.5, 158.3, 141.71, 141.67, 140.7, 140.3, 140.2, 140.1, 140.0, 139.93, 139.91, 139.8, 139.5, 139.3, 139.1, 138.5, 138.37, 138.35, 138.2, 137.93, 137.88, 134.89, 134.86, 134.4, 134.3, 133.3, 133.2, 131.3, 131.24, 131.15, 131.12, 131.10, 131.0, 130.00, 129.96, 129.7, 129.6, 129.1, 127.7, 127.6, 126.69, 126.65, 126.59, 126.56, 126.4, 125.9, 125.8, 125.7, 125.44, 125.39, 125.3, 123.42, 123.37, 122.1, 122.0, 116.1, 115.8, 111.6, 111.4, 110.4, 110.2.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –105.8 (**3'fa**); δ = –114.3 (**3fa**).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{24}F$: 451.18620; found: 451.18544.

5,6,7-Trimethoxy-1,2,3,4-tetraphenylnaphthalene (3la)[15]

Yield: 95.0 mg (73%); white solid; mp 285–286 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.13 (m, 7 H), 7.12–7.06 (m, 2 H), 7.04–6.99 (m, 1 H), 6.84–6.73 (m, 11 H), 3.86 (s, 3 H), 3.68 (s, 3 H), 3.25 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 150.1, 142.9, 142.5, 140.7, 140.6, 140.1, 138.9, 138.8, 137.2, 135.9, 131.5, 131.13, 131.10, 130.2, 130.1, 127.6, 126.4 (overlapped), 126.2, 126.1, 125.1, 125.0, 124.9, 122.7, 102.5, 60.8, 60.6, 55.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{37}H_{31}O_3$: 523.22732; found: 523.22725.

5,6,7-Trimethoxy-1,2,3,4-tetrakis(4-methylphenyl)naphthalene (3lc)

Yield: 109.7 mg (76%); white solid; mp 297–298 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07–6.98 (m, 6 H), 6.89 (d, *J* = 7.8 Hz, 2 H), 6.76 (s, 1 H), 6.66–6.58 (m, 8 H), 3.85 (s, 3 H), 3.68 (s, 3 H), 3.23 (s, 3 H), 2.29 (s, 3 H), 2.24 (s, 3 H), 2.061 (s, 3 H), 2.057 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 150.1, 142.4, 140.0, 139.2, 139.0, 138.0, 137.8, 137.22, 137.18, 135.8, 135.5, 134.1, 134.0, 133.8, 131.3, 131.0 (overlapped), 130.4, 129.9, 128.3, 127.1, 126.9, 126.8, 122.8, 102.7, 60.9, 60.8, 55.5, 21.3, 21.2, 21.0 (overlapped).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{39}O_3$: 579.28992; found: 579.28933.

5,6,7-Trimethoxy-1,2,3,4-tetrakis(4-methoxyphenyl)naphthalene (3ld)

Yield: 104.1 mg (65%); white solid; mp 292–293 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 8.6 Hz, 2 H), 7.03 (d, *J* = 8.6 Hz, 2 H), 6.80–6.75 (m, 3 H), 6.69–6.60 (m, 6 H), 6.41–6.35 (m, 4 H), 3.86 (s, 3 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 3.69 (s, 3 H), 3.60 (s, 6 H), 3.26 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 157.0, 156.7, 156.6, 152.2, 150.1, 142.4, 139.3, 139.1, 137.1, 135.7, 135.6, 133.6, 133.4, 132.6, 132.4, 132.11, 132.05, 131.0, 130.6, 122.9, 113.1, 112.0, 111.8, 111.7, 102.6, 60.9, 60.8, 55.5, 55.10, 55.06, 54.86, 54.85.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{39}O_7$: 643.26958; found: 643.26961.

5,6,7-Trimethoxy-1,2,3,4-tetrakis(4-fluorophenyl)naphthalene (3le)

Yield: 112.2 mg (76%); white solid; mp 267–268 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (dd, *J* = 8.3, 5.5 Hz, 2 H), 7.06 (dd, *J* = 8.3, 5.6 Hz, 2 H), 6.95 (dd, *J* = 8.6, 8.6 Hz, 2 H), 6.82 (dd, *J* = 8.7, 8.7 Hz, 2 H), 6.73–6.63 (m, 5 H), 6.61–6.51 (m, 4 H), 3.87 (s, 3 H), 3.71 (s, 3 H), 3.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5 (d, *J* = 244.7 Hz), 160.8 (d, *J* = 242.5 Hz), 160.6 (d, *J* = 243.9 Hz), 160.5 (d, *J* = 243.5 Hz), 152.8, 149.9, 142.8, 138.5 (d, *J* = 3.5 Hz), 138.05, 137.99, 136.7, 136.3 (d, *J* = 3.5 Hz), 136.2 (d, *J* = 3.5 Hz), 135.6 (d, *J* = 3.4 Hz), 135.4, 132.7 (d, *J* = 7.9 Hz), 132.4 (d, *J* = 8.2 Hz), 132.3 (d, *J* = 8.2 Hz), 131.1 (d, *J* = 8.2 Hz), 130.3, 122.8, 114.9 (d, *J* = 21.2 Hz), 113.8 (d, *J* = 21.0 Hz), 113.6 (d, *J* = 22.3 Hz), 113.3 (d, *J* = 21.1 Hz), 102.3, 60.9, 60.6, 55.5.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.3, –116.6, –117.0, –117.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{37}H_{27}F_4O_3$: 595.18963; found: 595.18928.

5,6,7-Trimethoxy-1,2,3,4-tetrakis[4-(trifluoromethyl)-phenyl]naphthalene (3lf)

Yield: 163.1 mg (82%); white solid; mp 295–296 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 6.62 (s, 1 H), 3.88 (s, 3 H), 3.71 (s, 3 H), 3.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 149.8, 143.4, 143.3, 143.2, 143.0, 140.06, 140.05, 136.8, 136.7, 136.4, 135.3, 131.5, 131.2, 131.1, 129.9, 129.4 (q, *J* = 32.7 Hz), 128.3 (q, *J* = 32.7 Hz), 128.1 (q, *J* = 32.7 Hz), 127.9 (q, *J* = 32.5 Hz), 125.0 (q, *J* = 3.2 Hz), 124.3 (q, *J* = 271.9 Hz), 123.98 (q, *J* = 272.1 Hz), 123.97 (q, *J* = 3.3 Hz), 123.82 (q, *J* = 271.9 Hz), 123.79 (q, *J* = 272.1 Hz), 123.5 (q, *J* = 3.4 Hz), 123.3 (q, *J* = 3.3 Hz), 122.7, 102.0, 60.9, 60.5, 55.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.5, –62.6, –62.85, –62.87.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{27}F_{12}O_3$: 795.17686; found: 795.17667.

6,7-Dimethoxy-1,2,3,4-tetraphenylnaphthalene (3ma)

Yield: 89.3 mg (73%); white solid; mp 333–334 °C (Lit.[16] 324 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.15 (m, 10 H), 6.94 (s, 2 H), 6.89–6.78 (m, 10 H), 3.73 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 140.8, 139.9, 137.3, 137.0, 131.4, 131.1, 127.8, 127.6, 126.4, 126.3, 125.1, 105.8, 55.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{29}O_2$: 493.21675; found: 493.21718.

5,6-Dimethoxy-1,2,3,4-tetraphenylnaphthalene (3'ma)

Yield: 11.7 mg (10%); pale yellow solid; mp 229–230 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 9.3 Hz, 1 H), 7.24–7.15 (m, 8 H), 7.11–7.05 (m, 2 H), 7.04–6.98 (m, 1 H), 6.85–6.74 (m, 10 H), 3.90 (s, 3 H), 3.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 144.5, 142.7, 141.1, 140.6 (overlapped), 139.9, 138.4, 137.3, 135.3, 131.4, 131.24, 131.19, 130.3, 129.0, 127.5, 127.3, 126.42, 126.36, 126.2, 126.1, 125.1, 125.0 (overlapped), 123.8, 114.5, 60.4, 56.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{29}O_2$: 493.21675; found: 493.21676.

6,7,8,9-Tetraphenylnaphtho[1,2-*d*][1,3]dioxole (3na)

Yield: 99.2 mg (83%); yellow solid; mp 313–314 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.07 (m, 12 H), 7.85–6.77 (m, 10 H), 5.77 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 142.0, 140.49, 140.47, 140.1, 140.0, 139.9, 138.7, 137.3, 133.6, 131.3 (overlapped), 131.1, 130.8, 129.2, 127.5, 126.5, 126.44 (overlapped), 126.38, 126.0, 125.23, 125.22, 121.8, 119.1, 110.3, 100.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{25}O_2$: 477.18545; found: 477.18564.

3,4-Diphenyl-1*H*-isochromen-1-one (4aa)

Yield: 101.3 mg (91%); white solid; mp 171–172 °C (Lit.[4b] 172–174 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.64 (td, *J* = 8.1, 1.4 Hz, 1 H), 7.52 (td, *J* = 7.7, 1.1 Hz, 1 H), 7.44–7.39 (m, 3 H), 7.36–7.32 (m, 2 H), 7.29–7.16 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 150.9, 138.9, 134.6, 134.3, 132.9, 131.2, 129.5, 129.2, 129.0, 128.9, 128.10, 128.06, 127.8, 125.3, 120.5, 116.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{15}O_2$: 299.10720; found: 299.10711.

Decarboxylative Coupling of 5 or 7 with 2; General Procedure

A mixture of carboxylic acid **5** or **7** (0.75 mmol), alkyne **2** (1 mmol), $[Rh(cod)Cl_2]_2$ (5 mg, 0.01 mmol), $C_5H_2Ph_4$ (14.8 mg, 0.04 mmol), AgOAc (334 mg, 2 mmol) and 1-methylnaphthalene (ca. 80 mg) as an internal standard in o-xylene or *t*-AmOH (5 mL) was stirred at 120–170 °C under Ar (1 atm) for 4–24 h. After the reaction was complete, the mixture was diluted with dichloromethane (100 mL). The organic layer was washed with water (2 x 100 mL) and brine (100 mL), and then dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **6** or **8** was isolated by column chromatography on silica gel using hexane–ethyl acetate as eluent. Further purification by GPC (gel permeation chromatography) was performed, if needed.

1,2,3,4-Tetraphenylanthracene (6aa)

Yield: 149.7 mg (62%); yellow solid; mp 295–296 °C (Lit.[5b] 295–296 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 2 H), 7.85–7.79 (m, 2 H), 7.39–7.34 (m, 2 H), 7.33–7.23 (m, 10 H), 6.90–6.81 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 139.7, 138.5, 138.1, 131.5, 131.4, 131.3, 130.9, 128.3, 127.6, 126.6, 126.5, 125.9, 125.4, 125.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{27}$: 483.21128; found: 483.21029.

6-Methoxy-1,2,3,4-tetraphenylanthracene (6ba)

Yield: 141.0 mg (55%); yellow solid; mp 283–284 °C (Lit.[5b] 284–285 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 8.03 (s, 1 H), 7.71 (d, *J* = 9.2 Hz, 1 H), 7.33–7.22 (m, 10 H), 7.09–7.02 (m, 2 H), 6.90–6.80 (m, 10 H), 3.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 140.7, 140.6, 140.0, 139.8, 138.6, 138.2, 137.6, 137.5, 132.5, 131.5, 131.42, 131.35, 131.3 (overlapped), 130.0, 129.5, 128.0, 127.60, 127.58, 126.52 (overlapped), 126.46, 126.4, 125.9, 125.3, 125.2, 123.8, 120.6, 103.8, 55.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{39}H_{29}O$: 513.22184; found: 513.22145.

4,5,6,7-Tetraphenylbenzo[*c*]thiophene (8a)

Yield: 87.7 mg (40%); pale yellow solid; mp 237–238 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 2 H), 7.29–7.15 (m, 10 H), 6.90–6.81 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1, 139.7, 138.6, 136.4, 132.9, 131.5, 130.5, 127.7, 126.6, 126.5, 125.4, 118.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{23}S$: 439.15205; found: 439.15265.

4,5,6,7-Tetrakis[4-(1,1-dimethylethyl)phenyl]benzo[*c*]thiophene (8g)

Yield: 65.3 mg (39%); pale yellow solid; mp 239–240 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 2 H), 7.19 (q, *J* = 8.2 Hz, 8 H), 6.82 (d, *J* = 8.4 Hz, 4 H), 6.67 (d, *J* = 8.2 Hz, 4 H), 1.27 (s, 18 H), 1.11 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 147.7, 138.7, 137.3, 136.9 (overlapped), 132.5, 131.2, 130.2, 124.3, 123.1, 118.0, 34.4, 34.1, 31.3, 31.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{48}H_{55}S$: 663.40245; found: 663.40252.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1416-6997.

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