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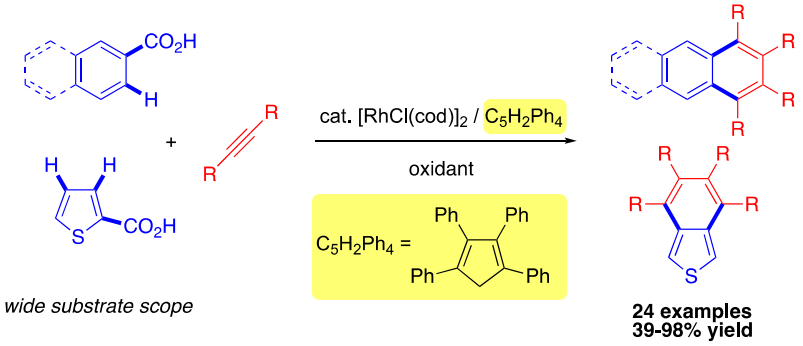

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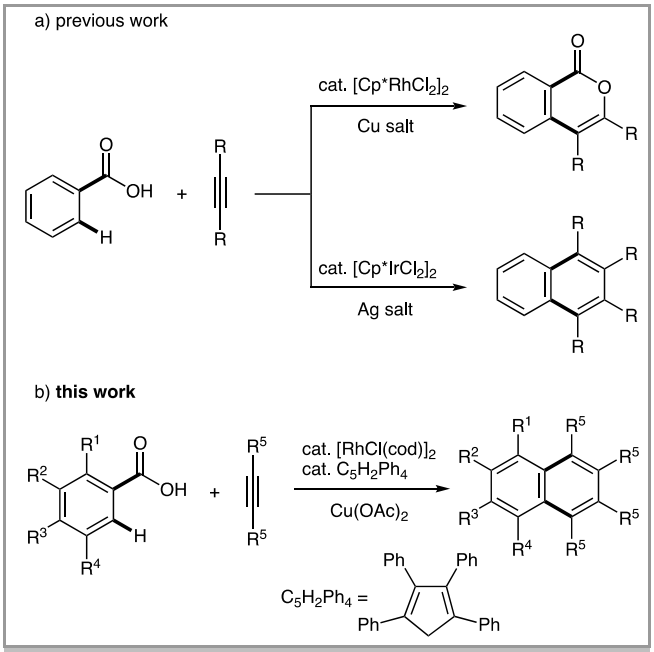
Abstract The decarboxylative coupling of variously substituted benzoic acids with internal alkynes proceeds smoothly in the presence of $[RhCl(cod)]_2$ / 1,2,3,4-tetraphenyl-1,3-cyclopentadiene catalyst system to selectively produce highly substituted naphthalene derivatives. The catalyst system is applicable to constructing anthracene and benzo[*c*]thiophene flameworks through the 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 organic synthesis field 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 $[Cp^*RhCl_2]_2$ catalyst and copper salt oxidant to produce isocoumarins (Scheme 1a).[3] Meanwhile, treatment of the same starting materials with a $[Cp^*IrCl_2]_2$ catalyst and 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, Tanaka's[6] and Loginov's[7] groups reported the 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 these progresses, the substrate scope has been still limited.

During our further study on the homologation, we found that a catalyst system $[RhCl(cod)]_2$ / $C_5H_2Ph_4$ ($C_5H_2Ph_4$ = 1,2,3,4-tetraphenyl-1,3-cyclopentadiene)[5c,8] is effective for the reaction of variously substituted benzoic acids with alkynes to produce highly substituted naphthalenes selectively (Scheme 1b). This catalyst system was also found to be applicable to the homologation of naphthoic acids and thiophene-2-carboxylic acid to form anthracene and benzo[*c*]thiophene flameworks, respectively. These findings are described herein.

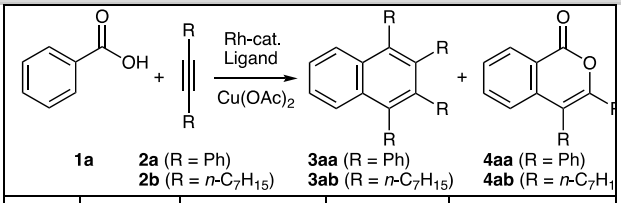


Scheme 1 Dehydrogenative coupling of benzoic acids with alkynes.

In an initial attempt, benzoic acid (**1a**) (0.38 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) under conditions similar to those in our previous report. Thus, in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and $Cu(OAc)_2$ (1 mmol) as catalyst and oxidant, respectively, in *o*-xylene (2.5 mL) at 160 °C under Ar (1 atm), 3,4-diphenyl-1*H*-isochromen-1-one (**4aa**) was

formed as a 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 of $RhCl_3•H_2O$ / $C_5H_2Ph_4$ 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 with 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).

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

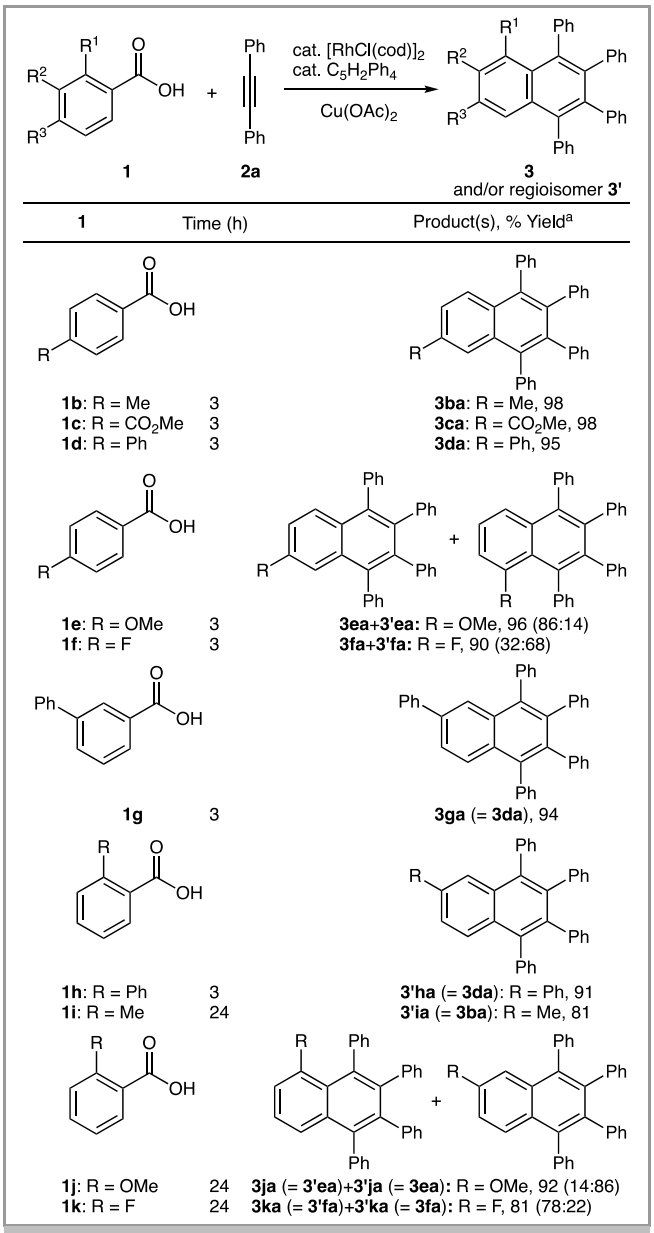


1a **2a** (R = Ph) **2b** (R = *n*-C_7H_{15}) **3aa** (R = Ph) **3ab** (R = *n*-C_7H_{15}) **4aa** (R = Ph) **4ab** (R = *n*-C_7H_{15})

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	$RhCl_3•H_2O$	-	0	0
7[c]	Ph	$RhCl_3•H_2O$	C_5HPh_5	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

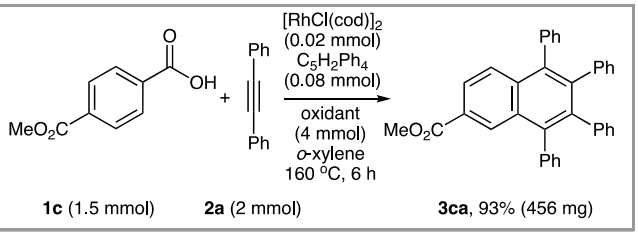
[a] Reaction conditions: **1a** (0.38 mmol), **2a** (0.5 mmol), Rh-cat. (0.005 mmol), Ligand (0.02 mmol), $Cu(OAc)_2$ (1 mmol) in *o*-xylene (2.5 mL) at 160 °C under Ar (1 atm) for 24 h. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates isolated yield after purification.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

Under the optimized conditions (Table 1, entry 3), the reactions of variously 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**-**3da** in excellent yields. The reaction 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 predominantly formed prior to less crowded regioisomer **3fa**. We previously observed similar predominant formation of 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**.



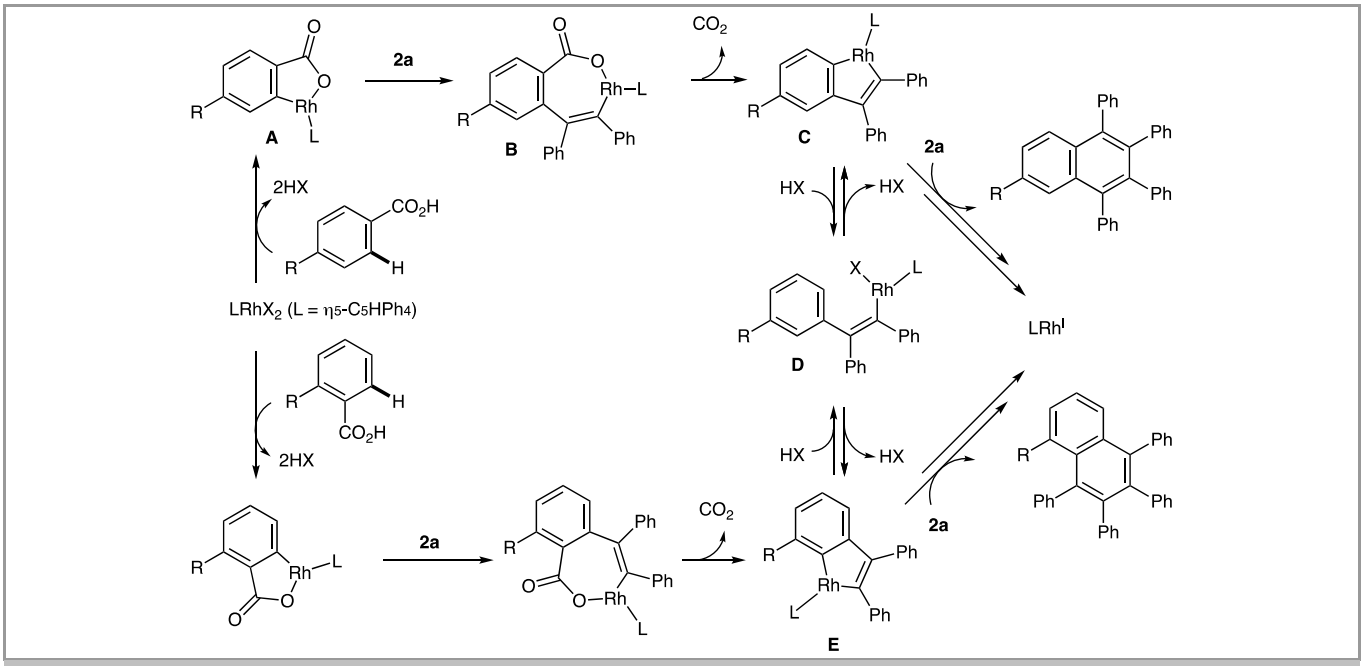
Scheme 2 Reaction of Benzoic Acids **1** with **2a**. Reaction conditions: **1** (0.38 mmol), **2a** (0.5 mmol), $[RhCl(cod)]_2$ (0.005 mmol), $C_5H_2Ph_4$ (0.02 mmol), $Cu(OAc)_2$ (1 mmol) in *o*-xylene (2.5 mL) at 160 °C under Ar (1 atm). [a] Isolated yield. Value in parentheses indicates product ratio determined by ^1H NMR.

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



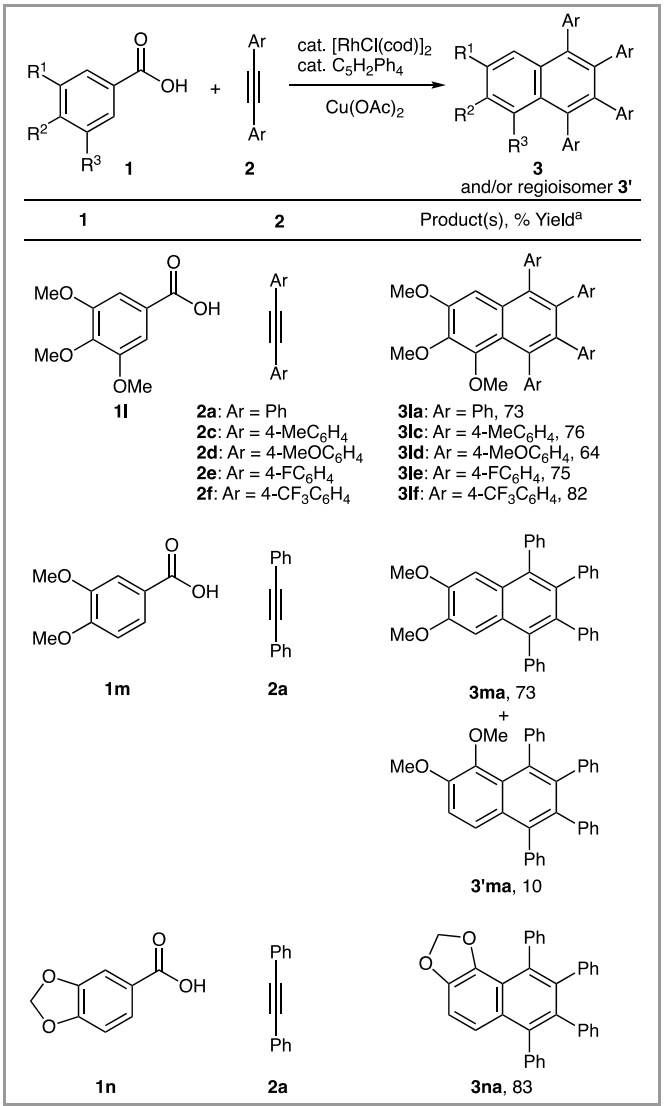
Scheme 3 Large Scale Synthesis of **3ca**.

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 a precursor $[RhCl(cod)]_2$, $C_5H_2Ph_4$, and Cu salt oxidant. The reaction of 4-substituted benzoic acids seems to proceed in a similar way to that proposed for 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**, the second alkyne insertion, and reductive elimination steps to release 6-substituted 1,2,3,4-tetraphenylnaphthalene **3**. The LRh^{I} species generated at the last step seems to be reoxidized by a copper salt oxidant to regenerate an active $LRh^{III}X_2$ species. In the reactions of 4-methoxy- and 4-fluorobenzoic acids, at least part of **C** may isomerize to **E** through **D** to afford 5-substituted 1,2,3,4-tetraphenylnaphthalene **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 to **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 regioisomers 5- and 6-substituted 1,2,3,4-tetraphenylnaphthalenes as in the cases with 4-methoxy- and 4-fluorobenzoic acids, showing the existence of the equilibrium between intermediates **C** and **E**. The ratio of **C**/**E** may be determined by the electronic and steric properties of these substituents.



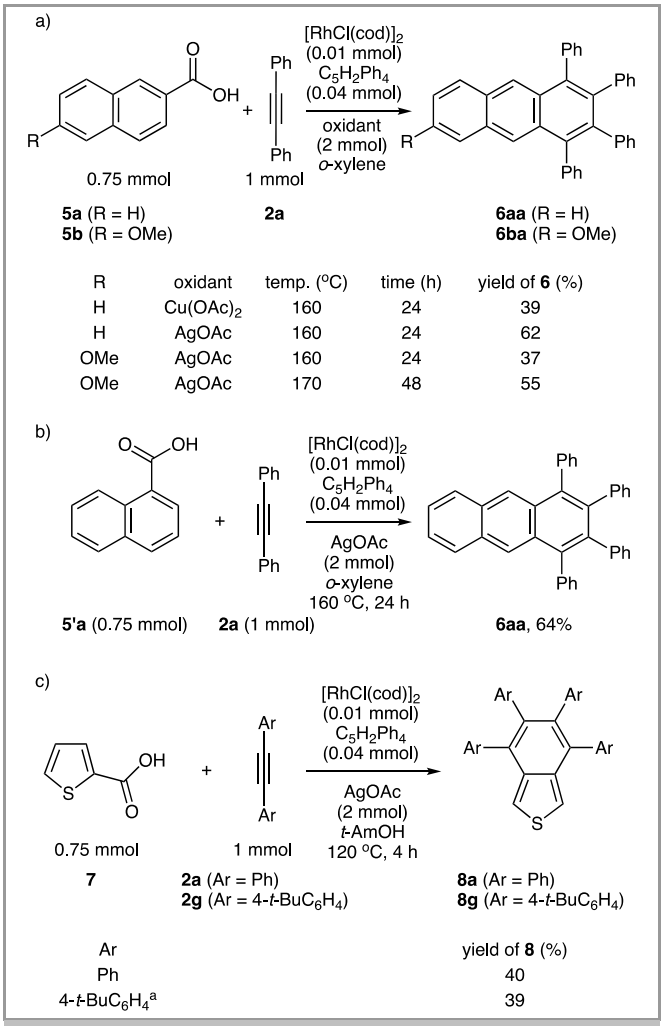
Scheme 4 Plausible Pathways for the Reactions of 4- and 2-substituted benzic acids with **2a**.

It is known that hydroxy- and alkoxy-substituted benzoic acids are widely distributed in plants and 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-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 **3lc**-**3lf** in 64-82% yields. The coupling of 3,4-dimethoxybenzoic acid (**1m**) with **2a** gave sparable 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 regioseletively to afford 6,7,8,9-tetraphenylnaphtho[1,2-*d*][1,3]dioxole (**3na**) in 83% yield.[11]



Scheme 5 Reaction of Alkoxy-Substituted Benzoic Acids **1** with **2**. Reaction 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) in *o*-xylene (2.5 mL) at 160 °C under Ar (1 atm) for 24 h. [a] Isolated yield..

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 6a). No phenanthrene isomer could be detected.[12] As an oxidant, the use of AgOAc in place of $Cu(OAc)_2$ improved the **6aa** yield 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 reaction bath temperature 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 6b). Thiophene-2-carboxylic acid (**7**) underwent the coupling with **2a** in the presence of $[RhCl(cod)]_2$ / $C_5H_2Ph_4$ catalyst system and AgOAc oxidant in t-AmOH at 120 °C to predominantly produce 4,5,6,7-tetraphenylbenzo[*c*]thiophene in a moderate yield (Scheme 6c).[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 Reaction of Naphthoic Acids **5** and Thiophenecarboxylic Acid **7** with **2a**. [a] **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, $[RhCl(cod)]_2$ / $C_5H_2Ph_4$ catalyst system has been found to be effective. The procedure provides straightforward routes not only to highly substituted naphthalenes but also to anthracene and benzo[*c*]thiophene derivatives.

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Chemicals were either purchased or were purified by standard techniques. Diarylacetylene (**2c-2g**) 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 PU-4086, UV-4075, RV-2002-02 and YMC-GPC-T2000. Melting points were obtained using a Micro Melting Point Apparatus MP-J3 or MPA100 OptiMelt Automated Melting Point System. ^1H (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 an external trifluoroacetic acid, TFA (δ -76.5 ppm). GC analysis was carried out using a silicon OV-17 column (i. d.

2.6 mm x 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 x 25 m). High Resolution Mass Spectra were obtained using a JEOL AccuTOF LC-plus 4G mass spectrometer.

General Procedures

A mixture of benzoic acids **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 (1atm) for 3-24 h. After the reaction was complete, the reaction mixture was diluted by dichloromethane (100 mL). The organic layer was washed by water (100 mL, two times) and brine (100 mL) and 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] m.p. 205-206 °C)

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

^{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, 2H), 7.43-7.35 (m, 2H), 3.07-2.95 (m, 4H), 2.80-2.69 (m, 4H), 1.71-1.26 (m, 40H), 0.96-0.87 (m, 12H).

^{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] m.p. 216-217 °C)

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

^{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] m.p. 296-297 °C)

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

^{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] m.p. 268-271 °C)

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

^{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) + 5-Methoxy-1,2,3,4-tetraphenylnaphthalene (3'ea)

Yield: 111.4 mg (96%); white solid; mp 274-275 °C. (lit.[6b] m.p. 272.8-274.8 °C)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 9.2 Hz, 1H, **3ea**), 7.27-7.15 (m, 10H, **3ea**), 7.06 (dd, *J* = 9.3, 2.6 Hz, 1H, **3ea**), 6.95 (d, *J* = 2.5 Hz, 1H, **3ea**), 6.88-6.75 (m, 10H, **3ea**), 3.69 (s, 3H, **3ea**), 3.37 (s, 3H, **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) + 5-Fluoro-1,2,3,4-tetraphenylnaphthalene (3'fa)

Yield: 101.3 mg (90%); white solid; mp 254-255 °C. (lit.[6b] m.p. 253.4-256.7 °C)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 9.3, 5.9 Hz, 1H, **3'fa**), 7.43 (d, *J* = 8.5 Hz, 1H, **3fa**), 7.33-7.02 (m, 12H, **3fa**), 6.88-6.76 (m, 10H, **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, $CDCl_3$): **3'fa**: δ = -105.8; **3fa**: δ = -114.3.

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, 7H), 7.12-7.06 (m, 2H), 7.04-6.99 (m, 1H), 6.84-6.73 (m, 11H), 3.86 (s, 3H), 3.68 (s, 3H), 3.25 (s, 3H).

^{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, 6H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.76 (s, 1H), 6.66-6.58 (m, 8H), 3.85 (s, 3H), 3.68 (s, 3H), 3.23 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 2.061 (s, 3H), 2.057 (s, 3H).

^{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, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.80-6.75 (m, 3H), 6.69-6.60 (m, 6H), 6.41-6.35 (m, 4H), 3.86 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H), 3.60 (s, 6H), 3.26 (s, 3H).

^{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, 2H), 7.06 (dd, *J* = 8.3, 5.6 Hz, 2H), 6.95 (dd, *J* = 8.6, 8.6 Hz, 2H), 6.82 (dd, *J* = 8.7, 8.7 Hz, 2H), 6.73-6.63 (m, 5H), 6.61-6.51(m, 4H), 3.87 (s, 3H), 3.71 (s, 3H), 3.27 (s, 3H).

^{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, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.2, 2H), 7.10 (d, *J* = 8.3Hz, 2H), 6.88 (d, *J* = 8.0, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.24 (s, 3H).

^{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] m.p. 305-307 °C)

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

^{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, 1H), 7.24-7.15 (m, 8H), 7.11-7.05 (m, 2H), 7.04-6.98 (m, 1H), 6.85-6.74 (m, 10H), 3.90 (s, 3H), 3.17 (s, 3H).

^{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, 12H), 7.85-6.77 (m, 10H), 5.77 (s, 2H).

^{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] mp 172-174 °C)

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

^{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.

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

Yield: 149.7 mg (62%); yellow solid; mp 295-296 °C. (lit.[5b] m.p. 295-296 °C)

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

^{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] m.p. 284-285 °C)

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

^{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, 2H), 7.29-7.15 (m, 10H), 6.90-6.81 (m, 10H).

^{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, 2H), 7.19 (q, *J* = 8.2 Hz, 8H), 6.82 (d, J = 8.4 Hz, 4H), 6.67 (d, *J* = 8.2 Hz, 4H), 1.27 (s, 18H), 1.11 (s, 18H).

^{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.

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Supporting Information

YES

Primary Data

NO

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