Efficient Palladium-Catalyzed Cross-Coupling Reaction of Alkynyl Halides with Organoboronic Acids under Aerobic Conditions

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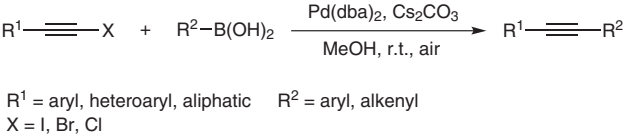
Abstract: Ligand-free palladium-catalyzed cross-coupling reaction of alkynyl halides with organoboronic acids under aerobic conditions has been developed. In the presence of bis(dibenzylideneacetone)palladium(0) and cesium carbonate, a variety of alkynyl halides (I, Br, and Cl) underwent the Suzuki–Miyaura cross-coupling reaction with organoboronic acids at room temperature to afford the corresponding unsymmetrical diarylalkynes in moderate to good yields. It is noteworthy that this is first report on the reaction of alkynyl chlorides with arylboronic acids.

Key words: palladium, alkynyl halides, organoboronic acids, cross-coupling reaction, alkynes

The acetylenic subunit is a useful building block in organic synthesis and a commonly found motif in many natural products.[1] Among the methods for the synthesis of alkynes, the traditional Sonogashira cross-coupling reaction has proven to be the most commonly used tool.[2] However, it does not work well for electron-poor alkynes. Therefore, the development of a novel cross-coupling alternative to these alkynes synthesis is of interest.[3–5] Recently, Sun and co-workers reported a palladium(II) chloride catalyzed cross-coupling reaction of arylalkyne iodides with arylboronic acids to afford moderate to good yields of the corresponding products.[5b] However, the reaction required a high loading of palladium(II) chloride (1–5 mol%), and no reactions involving the synthesis of arylalkyne analogues were reported. Subsequently, Wang and co-workers extended the scope to organoboronic acids using a magnetic-nanoparticle-supported palladium(II) and only examples of alkynyl bromides were described.[5d] Very recently, we also reported a modified protocol for the synthesis of internal alkynes, such as *N*,3-diarylphenylpropiolamides, by palladium(II) acetate catalyzed Suzuki–Miyaura cross-coupling reaction of alkynyl iodides with arylboronic acids.[5c] To the best of our knowledge, no reactions involving the synthesis of alkynyl chlorides with arylboronic acids have been reported. As an extension of our work, we report here a simple system such as bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] and cesium carbonate for the general Suzuki–Miyaura cross-coupling reaction of a wide range of alkynyl halides (I, Br, and Cl) with organoboronic acids under aerobic and ligand-free conditions (Scheme 1).



Scheme 1 Palladium-catalyzed synthesis of unsymmetrical diarylalkynes

The reaction between (iodoethynyl)benzene (**1a**) and 4-methoxyphenylboronic acid (**2a**) was chosen as a model reaction to screen the optimal reaction conditions, and the results are summarized in Table 1. Initially, the effect of the palladium catalyst was examined. The results showed that treatment of iodoalkyne **1a** with **2a** using 0.1 mol% palladium catalyst and two equivalents of cesium carbonate in methanol under air atmosphere for 12 hours afforded the desired product **3** in 78, 60, 48, 83, and 90% yield, respectively (Table 1, entries 1–5). $Pd(dba)_2$ turned out to be the best catalyst in terms of yields, and the amount of $Pd(dba)_2$ also affected the yield to some extent (entries 5 and 6). No cross-coupling product was generated in a control experiment without the palladium catalyst (entry 7). A set of bases, such as cesium carbonate, potassium carbonate, potassium acetate, sodium methoxide, potassium phosphate, and triethylamine were then investigated, and cesium carbonate gave the best result (entries 5 and 8–12). Finally, some solvents, including methanol, ethanol, isopropanol, tetrahydrofuran, *N*,*N*-dimethylformamide, and acetonitrile were also tested, and methanol provided the highest yield (entries 5 and 13–17).

With the optimal reaction conditions in hand, the scope of alkynyl halides with organoboronic acids was investigated (Table 2). Initially, a variety of organoboronic acids **2b–j** were investigated by reacting with (iodoethynyl)benzene (**1a**) (Table 2, entries 1–9). The results demonstrated that the optimal conditions were general for arylboronic acids and styrylboronic acid, and compatible with several functional groups, including methyl, methoxy, chloro, acetyl, nitro, and cyano groups on the aryl moiety. For example, phenylboronic acid (**2b**) or the methyl-substituted arylboronic acids **2c–e** smoothly underwent the reaction with substrate **1a**, 0.1 mol% $Pd(dba)_2$, and two equivalents of cesium carbonate under air atmosphere in good yields, although the *ortho*-substi-

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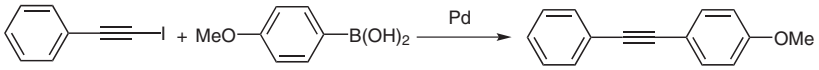
Table 1 Screening Optimal Conditions[a]



1a 2a 3

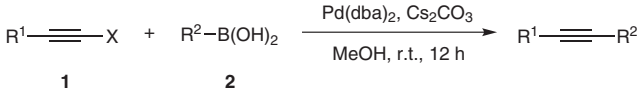
Entry	Pd catalyst	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	Cs_2CO_3	MeOH	78
2	$PdCl_2$	Cs_2CO_3	MeOH	60
3	$PdCl_2(MeCN)_2$	Cs_2CO_3	MeOH	48
4	$Pd(PPh_3)_4$	Cs_2CO_3	MeOH	83
5	$Pd(dba)_2$	Cs_2CO_3	MeOH	90
6[c]	$Pd(dba)_2$	Cs_2CO_3	MeOH	47
7	–	Cs_2CO_3	MeOH	0
8	$Pd(dba)_2$	K_2CO_3	MeOH	61
9	$Pd(dba)_2$	KOAc	MeOH	32
10	$Pd(dba)_2$	NaOMe	MeOH	59
11	$Pd(dba)_2$	K_3PO_4	MeOH	36
12	$Pd(dba)_2$	Et_3N	MeOH	32
13	$Pd(dba)_2$	Cs_2CO_3	EtOH	88
14	$Pd(dba)_2$	Cs_2CO_3	*i*-PrOH	32
15	$Pd(dba)_2$	Cs_2CO_3	THF	11
16	$Pd(dba)_2$	Cs_2CO_3	DMF	25
17	$Pd(dba)_2$	Cs_2CO_3	MeCN	19

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), Pd catalyst (0.1 mol%), base (2 equiv), solvent (2 mL), 12 h, r.t., air atmosphere.
[b] Yield of isolated product.
[c] Pd catalyst (0.01 mol%), for 60 h; the conversion of **1a** was 62% (determined by GC analysis).

tution on the arene ring decreased the substrates activity (entries 1–4). The optimal conditions were compatible with chloro-substituted substrate **2f** (entry 5). Gratifyingly, substrates **2g–i** with the activation group, such as acetyl, nitro, or cyano group, was tolerated well (entries 6–8). Alkenylboronic acid **2j** was also a suitable substrate providing moderate yield (entry 9). Subsequently, a number of alkynyl iodides, were examined in the presence of arylboronic acid, $Pd(dba)_2$, and cesium carbonate (entries 10–16). Substituted iodoalkynes **1b–d** successfully reacted with phenylboronic acid (**2b**) in moderate to good yields (entries 10, 11, 13). Using heteroaryl iodoalkyne (**1e**), a good yield of the product was achieved under the same conditions (entry 14). Although the activity was reduced for the reaction, aliphatic iodoalkynes **1f** and **1g** were also suitable substrates leading to the desired products **16** and **17** smoothly in moderate yields (entries 15 and 16).

Under the same reaction conditions, the couplings of alkynyl bromide and heteroaryl bromoalkyne with arylboronic acids were also proceeded efficiently to give the corresponding cross-coupled products in moderate to good yields (entries 17–21). For example, treatment of **1h** with arylboronic acids **2a**, **2b**, and **2c** gave the corresponding products **3**, **4**, and **5** in 92, 91, and 91% yield, respectively (entries 17–19). A moderate yield of the desirable product **12** was isolated from the reaction of substrate **1h** with alkenyl boronic acid **2j** (entry 20). The reaction of heteroaryl bromoalkyne **1i** with phenylboronic acid (**2b**) also proceeded smoothly to produce 94% yield of the corresponding product **15** under the same conditions (entry 21). It is worth mentioning that the system was still effective for the coupling of the alkynyl chlorides, including activated and deactivated alkynyl chlorides. In the presence of 0.1 mol% $Pd(dba)_2$ and two equivalents of cesium carbonate, treatment of **1j** with phenylboronic acid (**2b**) by prolonging the reaction time to 36 hours afforded the desired product in good yield whereas the reactions of alkynyl chloride **1k** with arylboronic acids **2a–c** were conducted smoothly in moderate yields (entries 23–25).

Table 2 Palladium-Catalyzed Cross-Coupling Reaction of Alkynyl Halides **1** with Organoboronic Acids **2**[a]



1 **2**

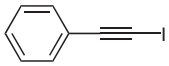
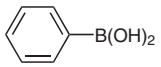
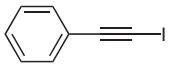
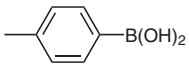
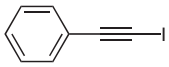
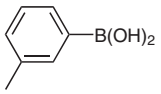
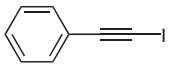
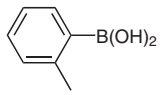
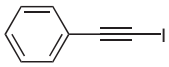
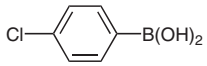
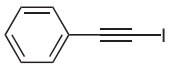
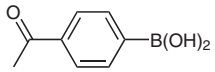
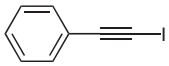
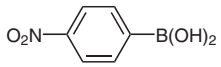
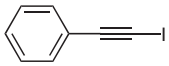
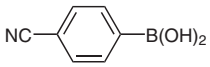
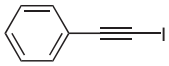
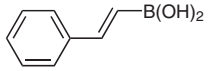
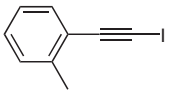
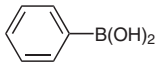
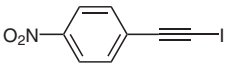
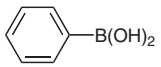
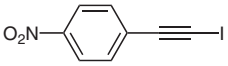
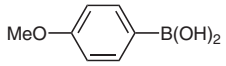
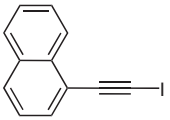
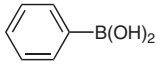
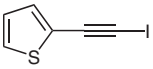
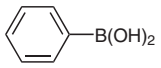
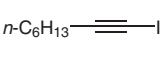
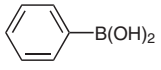
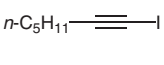
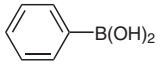
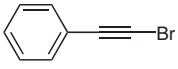
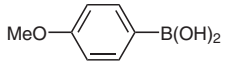
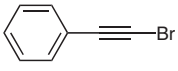
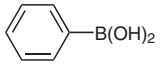
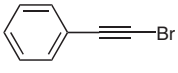
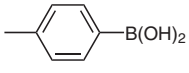
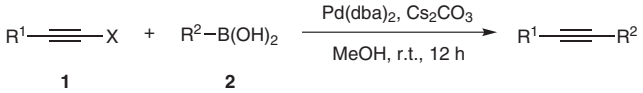
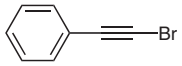
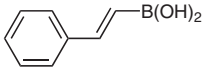
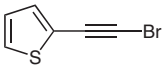
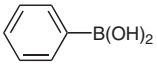
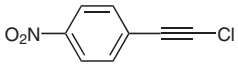
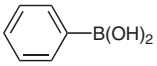
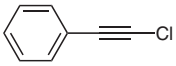
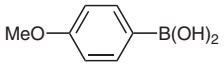
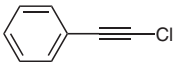
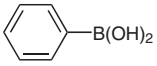
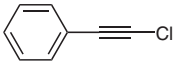
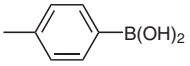
Entry	Alkynyl halide **1**		Organoboronic acid **2**		Yield (%)[b] (Product)
1	**1a**		**2b**		90 (**4**)
2	**1a**		**2c**		94 (**5**)
3	**1a**		**2d**		84 (**6**)
4	**1a**		**2e**		76 (**7**)
5	**1a**		**2f**		83 (**8**)
6	**1a**		**2g**		80 (**9**)
7	**1a**		**2h**		78 (**10**)
8	**1a**		**2i**		84 (**11**)
9	**1a**		**2j**		68 (**12**)
10	**1b**		**2b**		80 (**7**)
11	**1c**		**2b**		82 (**10**)
12	**1c**		**2a**		91 (**13**)
13	**1d**		**2b**		74 (**14**)
14	**1e**		**2b**		95 (**15**)
15	**1f**		**2b**		63 (**16**)
16	**1g**		**2b**		68 (**17**)
17	**1h**		**2a**		92 (**3**)
18	**1h**		**2b**		91 (**4**)
19	**1h**		**2c**		91 (**5**)

Table 2 Palladium-Catalyzed Cross-Coupling Reaction of Alkynyl Halides **1** with Organoboronic Acids **2**[a] (continued)



Entry	Alkynyl halide **1**		Organoboronic acid **2**		Yield (%)[b] (Product)
20	**1h**		**2j**		67 (**12**)
21	**1i**		**2b**		94 (**15**)
22[c]	**1j**		**2b**		78 (**10**)
23[c]	**1k**		**2a**		56 (**3**)
24[c]	**1k**		**2b**		54 (**4**)
25[c]	**1k**		**2c**		55 (**5**)

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), $Pd(dba)_2$ (0.1 mol%), Cs_2CO_3 (2 equiv), MeOH (2 mL), 12 h, r.t., air atmosphere.
[b] Isolated yield.
[c] Reaction performed for 36 h.

In summary, we have developed a mild, efficient, and general protocol for the synthesis of unsymmetrical diarylalkynes by palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of alkynyl halides with organoboronic acids under aerobic and ligand-free conditions. The protocol can provide good yields for alkynyl bromides and alkynyl iodides containing different functional groups using a relatively lower loading of palladium catalysts and is also extended to deactivated alkynyl chlorides with moderate to good yields. Currently, further efforts to apply these methods in other transformations are underway in our laboratory.

All chemicals were purchased from commercial suppliers (Aldrich, USA, and Changsha Chemical Company, China) and used without purification prior to use. Alkynyl halides **1** were respectively synthesized via iodination, bromination, or chlorination of terminal alkynes according to the literature.[5a,6,7] NMR spectroscopy was performed on a Bruker 500 spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). TMS was used an internal standard and $CDCl_3$ as the solvent. Mass spectrometric analysis was performed on GC-MS analysis (Shimadzu GCMS-QP2010 plus). Melting points were measured on a Kolfler micromelting point hot stage apparatus and are uncorrected.

Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of Alkynyl Halides 1 with Organoboronic Acids 2; General Procedure

Alkynyl halide **1** (0.3 mmol), organoboronic acid **2** (0.36 mmol), $Pd(OAc)_2$ (0.1 mol%), Cs_2CO_3 (2 equiv), and MeOH (2 mL) were successively added to a Schlenk tube. Then, the mixture was stirred at r.t. for the indicated time (12 h) until complete consumption of starting material was observed [reaction monitored by TLC (eluent: hexane–EtOAc, 60:1) and GC-MS analysis]. The mixture was washed with brine (3 × 3 mL), extracted with Et_2O (3 × 5 mL), dried (Na_2SO_4), and evaporated in vacuum. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc) to afford the desired product (Table 2).

1-Methoxy-4-(phenylethynyl)benzene (3)[2j]

Yield starting from alkynyl iodide **1a**: 56.2 mg (90%), from alkynyl bromide **1h**: 57.4 mg (92%), from alkynyl chloride **1k**: 34.9 mg (56%); white solid; mp 57.1–59.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 2.0 Hz, 2 H), 7.50 (d, *J* = 1.0 Hz, 2 H), 7.35–7.29 (m, 3 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 3.82 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

MS (EI, 70 eV): *m*/*z* (%) = 208 (100, $[M]^+$).

1, 2-Diphenylethyne (4)[2j]

Yield starting from alkynyl iodide **1a**: 48 mg (90%), from alkynyl bromide **1h**: 48.6 mg (91%), from alkynyl chloride **1k**: 28.8 mg (54%); white solid; mp 59.4–60.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 4 H), 7.34 (d, *J* = 6.5 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.6, 128.3, 128.2, 123.3, 89.4.

MS (EI, 70 eV): *m*/*z* (%) = 178 (100, $[M]^+$).

1-Methyl-4-(phenylethynyl)benzene (5)[2j]

Yield starting from alkynyl iodide **1a**: 54.1 mg (94%), from alkynyl bromide **1h**: 52.4 mg (91%), from alkynyl chloride **1k**: 31.7 mg (55%); white solid; mp 70.1–72.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.35–7.31 (m, 3 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 2.36 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.4, 131.6, 131.5, 129.1, 128.3, 128.0, 123.5, 120.2, 89.6, 88.7, 21.5.

MS (EI, 70 eV): *m*/*z* (%) = 192 (100, $[M]^+$).

1-Methyl-3-(phenylethynyl)benzene (6)[3b]
Yield: 48.4 mg (84%); white solid; mp 71.1–73.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2 H), 7.36–7.30 (m, 5 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 2.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.0, 132.2, 131.6, 129.1, 128.7, 128.3, 128.2, 128.1, 123.4, 123.1, 89.6, 89.0, 21.2.

MS (EI, 70 eV): *m*/*z* (%) = 192 (100, $[M]^+$).

1-Methyl-2-(phenylethynyl)benzene (7)[2j]
Yield starting from alkynyl iodide **1a**: 43.8 mg (76%), from alkynyl bromide **1b**: 46 mg (80%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.5 Hz, 2 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.35–7.32 (m, 3 H), 7.22 (d, *J* = 4.0 Hz, 2 H), 7.22–7.14 (m, 1 H), 2.51 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2, 131.8, 131.5, 129.4, 128.3, 128.3, 128.1, 125.6, 123.6, 123.0, 88.3, 20.7.

MS (EI, 70 eV): *m*/*z* (%) = 192 (100, $[M]^+$).

1-Chloro-4-(phenylethynyl)benzene (8)[5d]
Yield: 52.8 mg (83%); white solid; mp 80.1–81.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.58 (m, 4 H), 7.54–7.53 (m, 2 H), 7.38–7.36 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.3, 132.8, 131.6, 128.7, 128.5, 128.4, 123.0, 121.8, 90.3, 88.2.

MS (EI, 70 eV): *m*/*z* (%) = 212 (100, $[M]^+$).

1-(4-(Phenylethynyl)phenyl)ethanone (9)[5c]
Yield: 52.8 mg (80%); pale yellow solid; mp 99.2–101.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.5 Hz, 2 H), 7.59 (d, *J* = 7.5 Hz, 2 H), 7.56–7.54 (m, 2 H), 7.36 (d, *J* = 3.5 Hz, 3 H), 2.60 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.2, 136.2, 131.7, 131.6, 128.8, 128.4, 128.3, 128.2, 122.6, 92.7, 88.6, 26.5.

MS (EI, 70 eV): *m*/*z* (%) = 220 (100, $[M]^+$).

1-Nitro-4-(phenylethynyl)benzene (10)[2j]
Yield starting from alkynyl iodide **1a**: 52.2 mg (78%), from alkynyl bromide **1c**: 54.9 mg (82%), from alkynyl chloride **1j**: 52.2 mg (78%); yellow solid; mp 120.3–122.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 9.0 Hz, 2 H), 7.66 (d, *J* = 8.5 Hz, 2 H), 7.57–7.55 (m, 2 H), 7.41–7.36 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.0, 132.3, 131.8, 130.3, 129.3, 128.5, 123.6, 122.1, 94.7, 87.5.

MS (EI, 70 eV): *m*/*z* (%) = 223 (100, $[M]^+$).

4-(Phenylethynyl)benzonitrile (11)[8]
Yield: 51.2 mg (84%); white solid; mp 108.4–110.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 4.0 Hz, 2 H), 7.46 (t, *J* = 9.0 Hz, 2 H), 7.35–7.31 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.0, 131.9, 131.7, 129.1, 128.5, 128.2, 122.2, 118.4, 111.4, 93.7, 87.7.

MS (EI, 70 eV): *m*/*z* (%) = 203 (100, $[M]^+$).

(*E*)-But-1-en-3-yne-1,4-diyldibenzene (12)[9]
Yield starting from alkynyl iodide **1a**: 41.6 mg (68%), from alkynyl bromide **1h**: 41 mg (67%); light yellow solid; mp 97.1–98.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.45 (m, 2 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 7.33–7.23 (m, 6 H), 7.08 (d, *J* = 16.0 Hz, 1 H), 6.38 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2, 136.3, 131.5, 128.7, 128.6, 128.3, 126.3, 123.4, 91.8, 88.9.

MS (EI, 70 eV): *m*/*z* (%) = 204 (100, $[M]^+$).

1-Methoxy-4-[(4-nitrophenyl)ethynyl]benzene (13)[9]
Yield: 69.0 mg (91%); yellow solid; mp 120.5–122.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 6.0 Hz, 2 H), 7.62 (d, *J* = 11.0 Hz, 2 H), 7.60 (d, *J* = 10.5 Hz, 2 H), 6.90 (d, *J* = 10.5 Hz, 2 H), 3.84 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4, 146.7, 134.0, 133.4, 132.0, 123.6, 114.2, 114.1, 95.1, 86.6, 55.3.

MS (EI, 70 eV): *m*/*z* (%) = 253 (100, $[M]^+$).

1-(Phenylethynyl)naphthalene (14)[5d]
Yield: 50.6 mg (74%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.0 Hz, 1 H), 7.88–7.86 (m, 2 H), 7.85–7.82 (m, 1 H), 7.77–7.75 (m, 2 H), 7.73 (d, *J* = 7.0 Hz, 1 H), 7.66–7.64 (m, 1 H), 7.59–7.58 (m, 1 H), 7.45–7.34 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.2, 133.1, 131.7, 130.4, 129.3, 128.4, 128.3, 127.2, 126.9, 126.4, 126.1, 125.3, 123.4, 120.9, 94.3, 87.5.

MS (EI, 70 eV): *m*/*z* (%) = 228 (100, $[M]^+$).

2-(Phenylethynyl)thiophene (15)[10]
Yield starting from alkynyl iodide **1e**: 52.4 mg (95%), from alkynyl bromide **1i**: 51.9 mg (94%); white solid; mp 49.1–50.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 2 H), 7.34–7.31 (m, 3 H), 7.26–7.24 (m, 2 H), 6.98–6.97 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.8, 131.4, 128.4, 128.3, 127.2, 127.0, 123.3, 122.9, 93.0, 82.6.

MS (EI, 70 eV): *m*/*z* (%) = 184 (100, $[M]^+$).

Oct-1-ynylbenzene (16)[3a]
Yield: 35.2 mg (63%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.38 (m, 2 H), 7.27–7.25 (m, 3 H), 2.43 (t, *J* = 3.5 Hz, 5 H), 2.27–2.24 (m, 2 H), 1.73–1.69 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.5, 128.2, 127.5, 123.9, 94.2, 84.1, 27.7, 27.7, 27.6, 27.6, 20.4, 18.0.

MS (EI, 70 eV): *m*/*z* (%) = 186 (100, $[M]^+$).

1-(Hept-1-ynyl)-4-methylbenzene (17)[5c]
Yield: 37.9 mg (68%); colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 2.38 (t, *J* = 7.5 Hz, 2 H), 2.31 (s, 3 H), 1.60 (t, *J* = 7.5 Hz, 2 H), 1.44–1.41 (m, 4 H), 0.92 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3, 131.4, 128.9, 121.0, 89.6, 80.5, 31.1, 28.5, 22.2, 21.3, 19.4, 14.0.

MS (EI, 70 eV): *m*/*z* (%) = 186 (33, $[M]^+$), 157 (33), 142 (38), 131(69), 129 (100).

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