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Synthesis of Internal Alkynes by $Pd(PPh_3)_4$/TMEDA-Catalyzed Kumada Cross-Coupling of Alkynyl Halides with Grignard Reagents

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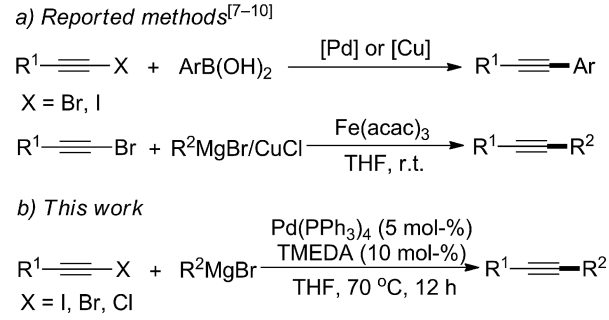
Alkynes serve as prevalent intermediates in the synthesis of natural products and pharmaceuticals. We here described a new and efficient route to internal alkynes by Pd-catalyzed Kumada cross-coupling reactions of alkynyl halides with Grignard reagents. In the presence of $Pd(PPh_3)_4$ and N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (TMEDA), a variety of alkynyl halides underwent Kumada coupling with Grignard reagents, giving the corresponding internal alkynes in moderate to good yields.

Introduction

Alkynes are important building blocks in synthetic chemistry and in materials, biological, and medicinal science.[1–3] Among the reported methods for the preparation of alkynes, the Sonogashira cross-coupling reaction is considered as a premium tool.[4,5] Despite impressive progress in the Sonogashira cross-coupling reaction, it still suffers from difficulties with respect to the introduction of alkyl groups into the carbon–carbon triple bond for the synthesis of internal alkyl alkynes. Therefore, the development of a novel cross-coupling alternative with which to access internal alkynes would be highly desirable.

An efficient alternative to the assembly of internal alkynes is the cross-coupling of alkynyl halides with organometallic reagents; however, transformations reported to date that use this approach are much less abundant (Scheme 1, a).[6–10] For example, the group of Liu and Sun[7] reported Pd-catalyzed Suzuki-type cross-coupling reaction between arylacetylenic iodides and arylboronic acids to afford diarylacetylenes. Subsequently, the groups of Tang[8] and Wang[9] have independently described the Suzuki-type cross-coupling reaction between arylacetylene iodides using Pd or Cu as the catalyst. Recently, the group of Botta[10] developed an iron-catalyzed cross-coupling between alkynyl bromides and Grignard-derived organocuprates. However, this latter transformation required a stoichiometric amount of CuCl to generate Grignard-derived organocuprate reagents in situ. As a continuation of our interest in the cross-coupling of alkynyl halides with organometallic reagents, we here report an efficient $Pd(PPh_3)_4$-catalyzed Kumada cross-coupling reaction between alkynyl halides and Grignard reagents by using N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (TMEDA) as the ligand; this new method is realized by the introduction of aryl or alkyl groups into the existing carbon–carbon triple bond, and provides a new access to internal alkynes through the Kumada cross-coupling strategy (Scheme 1, b).



Scheme 1. Synthesis of internal alkynes.

Results and Discussion

As shown in Table 1, the reaction of (iodoethynyl)benzene (**1a**) with PhMgBr (**2a**) was carried out to establish the optimal reaction conditions. To our delight, treatment of **1a** with **2a**, $Pd(PPh_3)_4$, and TMEDA (**L1**) in tetrahydrofuran (THF) afforded the desired 1,2-diphenylethyne (**3**) in 81% yield (entry 1). Encouraged by the results, a number of other Pd catalysts, including $PdCl_2(MeCN)_2$, $Pd(OAc)_2$,

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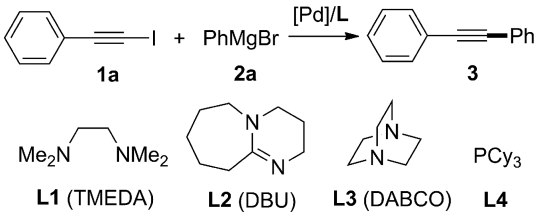
and $PdCl_2$, were tested; however, the results showed that these conditions were less effective than with $Pd(PPh_3)_4$ (entry 1 vs. entries 2–4). Whereas 60% yield of **3** was obtained when $PdCl_2(MeCN)_2$ was used as catalyst (entry 2), a relatively low yield of product **3** was observed when $Pd(OAc)_2$ or $PdCl_2$ were used as catalysts (32 and 25% yields, respectively; entries 3 and 4). However, the absence of palladium catalysts resulted in no detectable product **3** (entry 5). Screening revealed that the amount of $Pd(PPh_3)_4$ affected the reaction: whereas identical results to those obtained with 5 mol-% $Pd(PPh_3)_4$ were achieved by increased loading of $Pd(PPh_3)_4$ (10 mol-%; entry 6), only 51% yield was isolated at 2 mol-% $Pd(PPh_3)_4$ (entry 7). Subsequently, the effect of ligands was examined. Without ligand, only a low yield was isolated (entry 8). Although three other ligands, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (**L2**), 1,4-diazabicyclo[2.2.2]octane (DABCO) (**L3**) and PCy_3 (**L4**), could improve the reaction, they were less effective than TMEDA (**L1**) (entry 1 vs. entries 9–11). Among the reaction temperatures examined, it turned out that the reaction at 70 °C gave the best results (entry 1 vs. entries 12 and 13). We found that three other solvents, including dimethyl sulfoxide (DMSO), toluene, and MeCN, also effected the reaction, but they were inferior to THF (entry 1 vs. entries 14–16).

Table 1. Screening optimal conditions.[a]



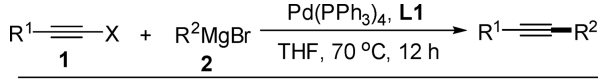
Entry	[Pd] [mol-%]	**L** [mol-%]	Solvent	Isolated yield [%]
1	$Pd(PPh_3)_4$ (5)	**L1** (10)	THF	81
2	$PdCl_2(MeCN)_2$ (5)	**L1** (10)	THF	60
3	$Pd(OAc)_2$ (5)	**L1** (10)	THF	32
4	$PdCl_2$ (5)	**L1** (10)	THF	25
5	–	**L1** (10)	THF	0
6	$Pd(PPh_3)_4$ (10)	**L1** (20)	THF	80
7	$Pd(PPh_3)_4$ (2)	**L1** (4)	THF	51
8	$Pd(PPh_3)_4$ (5)	–	THF	23
9	$Pd(PPh_3)_4$ (5)	**L2** (10)	THF	57
10	$Pd(PPh_3)_4$ (5)	**L3** (10)	THF	75
11	$Pd(PPh_3)_4$ (5)	**L4** (10)	THF	60
12[b]	$Pd(PPh_3)_4$ (5)	**L1** (10)	THF	73
13[c]	$Pd(PPh_3)_4$ (5)	**L1** (10)	THF	64
14	$Pd(PPh_3)_4$ (5)	**L1** (10)	DMSO	60
15	$Pd(PPh_3)_4$ (5)	**L1** (10)	toluene	38
16	$Pd(PPh_3)_4$ (5)	**L1** (10)	MeCN	42

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd], **L** and solvent (2 mL) at 70 °C for 12 h under argon atmosphere. [b] Reaction performed at 90 °C. [c] Reaction performed at 60 °C.

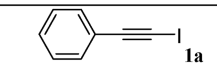
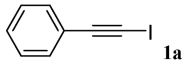
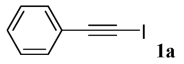
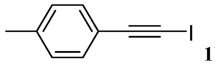
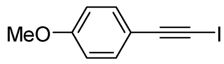
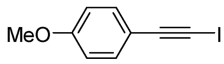
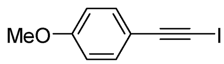
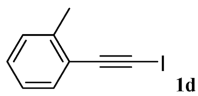
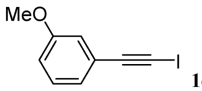
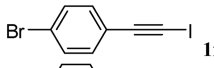
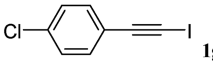
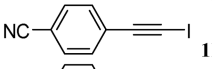
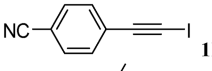
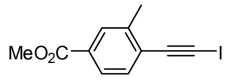
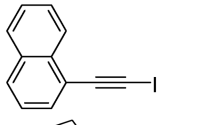
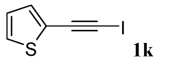
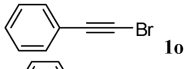
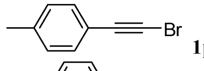
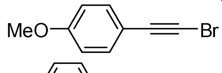
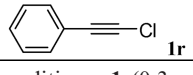
With the optimal conditions in hand, the scope of the Kumada cross-coupling reaction was investigated with a wide range of alkynyl halides (**1**) and Grignard reagents (**2**) (Table 2). Initially, a number of Grignard reagents, such as 4-MeC_6H_4MgBr (**2b**), 4-$MeOC_6H_4MgBr$ (**2c**) and MeMgBr (**2d**), were employed to react with **1a**, $Pd(PPh_3)_4$ and **L1** (entries 1–3). The results demonstrated that both aryl and alkyl Grignard reagents were suitable substrates for the reaction, giving products **4**–**6**. For example, **2b** smoothly underwent the reaction, giving the desired alkyne **4** in 78% yield (entry 1). The reaction of **2c** with substrate **1a** also afforded the internal alkynes **5** in good yield (entry 2). Gratifyingly, the optimal conditions were compatible with **2d**, giving the corresponding product **6** in moderate yield (entry 3). Subsequently, the reactions of various alkynyl halides, including alkynyl iodides **1b**–**n**, alkynyl bromides **1o**–**q**, and alkynyl chloride **1r**, were examined under the optimal conditions (entries 4–23). The results indicated that several substituents, including Me, MeO, Br, Cl, CN, and CO_2Me groups, on the aromatic ring at the terminal alkyne were well tolerated (entries 4–14). Notably, the nature of the substituents including position and electronic properties affected the reaction, and the reactivity order of the substituents was: *para* > *meta* or *ortho* and electron-donating > electron-withdrawing. Whereas substrate **1c**, with a *p*-MeO group, was treated with **2a** or **2c** in the presence of $Pd(PPh_3)_4$ and **L1**, providing the corresponding alkynes **5** and **7** in 87 and 85% yield, respectively (entries 5 and 6), substrate **1e**, with a *m*-MeO group, reacted with **2a** to give the desired product **10** in 69% yield (entry 9). Substrates **1b** and **1d**, with a *p*-Me or an *o*-Me group, furnished products **4** and **9** in 80 and 75% yields, respectively (entries 4 and 8). Although substrate **1h**, with an electron-withdrawing CN group, reacted successfully with aryl or alkyl Grignard reagents **2a** or **2d**, the yields of the corresponding internal alkynes **13** and **14** were lowered to moderate (entries 12 and 13). Similar results were observed for substrate **1i**, having a *p*-CO_2Me group and an *o*-Me group (entry 14). Importantly, halogen functional groups, Cl and Br, were compatible with the optimal conditions, thereby facilitating additional modifications at the halogenated positions (entries 10 and 11). Furthermore, 1-(iodoethynyl)naphthalene (**1j**) reacted with **2a** to deliver product **16** in 75% yield (entry 15). We were pleased to find that heteroaryl alkynyl iodide **1k** was viable for the reaction, providing 2-[(4-methoxyphenyl)ethynyl]thiophene (**17**) in high yield (entry 16). Although the reactivity of aliphatic iodoalkynes **1l** and **1m** was lowered, both delivered the desired products **18** and **19** in moderate yields (entries 17 and 18). It is noted that a $SiMe_3$ group could be tolerated under the optimal conditions (entry 19).

Interestingly, the scope of this Kumada cross-coupling transformation was applicable to alkynyl bromides **1o**–**q** and alkynyl chloride **1r** (entries 20–23). Several alkynyl bromides **1o**–**q** even having Me and MeO groups on the aromatic ring at the terminal alkyne, were compatible with the optimal conditions, although their reactivity was lower than those of alkynyl iodides (entries 20–22). For example, *p*-MeO-substituted substrate **1q** underwent the reaction with **2a**, $Pd(PPh_3)_4$ and **L1** smoothly, giving the desired product **5** in 75% yield (entry 22). It should be noted that moderate yield was still achieved when (chloroethynyl)benzene (**1r**) was used to react with **2a** (entry 23).

Table 2. Pd/**L1**-catalyzed Kumada cross-coupling of alkynyl halide **1** with Grignard reagents **2**.[a]

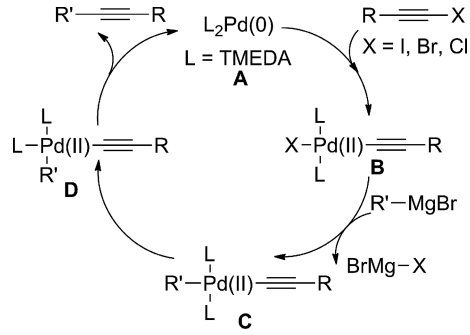


1 2

Entry	Alkynyl halides **1**	R^2	Yield (%)[b]
1	 **1a**	4-MeC_6H_4, **2b**	78 (**4**)
2	 **1a**	4-$MeOC_6H_4$, **2c**	82 (**5**)
3	 **1a**	Me, **2d**	53 (**6**)
4	 **1b**	Ph, **2a**	80 (**4**)
5	 **1c**	Ph, **2a**	87 (**5**)
6	 **1c**	4-$MeOC_6H_4$, **2c**	85 (**7**)
7	 **1c**	Me, **2d**	70 (**8**)
8	 **1d**	Ph, **2a**	75 (**9**)
9	 **1e**	Ph, **2a**	69 (**10**)
10	 **1f**	Ph, **2a**	79 (**11**)
11	 **1g**	Ph, **2a**	73 (**12**)
12	 **1h**	Ph, **2a**	68 (**13**)
13	 **1h**	Me, **2d**	62 (**14**)
14	 **1i**	Ph, **2a**	65 (**15**)
15	 **1j**	Ph, **2a**	75 (**16**)
16	 **1k**	4-$MeOC_6H_4$, **2c**	74 (**17**)
17	n-C_6H_{13}—≡—I **1l**	Ph, **2a**	53 (**18**)
18	n-C_8H_{17}—≡—I **1m**	4-$MeOC_6H_4$, **2c**	55 (**19**)
19	$SiMe_3$—≡—I **1n**	Ph, **2a**	58 (**20**)
20	 **1o**	Ph, **2a**	73 (**3**)
21	 **1p**	Ph, **2a**	71 (**4**)
22	 **1q**	Ph, **2a**	75 (**5**)
23	 **1r**	Ph, **2a**	66 (**3**)

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), $Pd(PPh_3)_4$, TMEDA (10 mol-%), THF (2 mL), 70 °C, 12 h under argon atmosphere. [b] Isolated yield.

On the basis of the present results and on previous reports,[1,6–10] we proposed a reaction mechanism that is outlined in Scheme 2. Initially, insertion of the electron-rich Pd^0 complex **A** into the alkynyl C–X bond of the alkynyl halide affords an alkynyl-Pd^{II} intermediate **B**. Subsequent transmetalation with the Grignard reagent forms intermediate **C**, then isomerization of intermediate **C** leads to *cis* oriented intermediate **D**. Finally, reductive elimination of intermediate **D** releases the cross-coupled product and regenerates the active Pd^0 species **A**.



Scheme 2. Plausible mechanism.

Conclusions

We have developed a new protocol for the synthesis of internal alkynes by palladium-catalyzed Kumada cross-coupling reaction of alkynyl halides with Grignard reagents by using TMEDA (**L1**) as the ligand. This novel method can be applicable to a wide range of alkynyl halides and Grignard reagents (aryl and alkyl Grignard reagents), and provides a mild and general access to internal alkynes with excellent functional group tolerance.

Experimental Section

General Methods: All the materials and solvents were purchased from commercial suppliers and used without additional purification. IR measurements were performed with a FTIR Shimadzu DR-8000 spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX-500 spectrometer (^1H at 500 MHz and ^{13}C at 125 MHz) or with a Bruker DRX-400 spectrometer (^1H at 400 MHz and ^{13}C at 100 MHz). NMR spectroscopic data were obtained in $CDCl_3$ unless otherwise noted. High-resolution mass spectra were recorded with a Bruker microTOF-QII (ESI) spectrometer. Preparative thin-layer chromatography was performed on silica gel plates with PF254 indicator. Flash column chromatography was performed with silica gel 60N unless otherwise noted.

Palladium-Catalyzed Kumada Reactions of Alkynyl Halides with Grignard Reagents. General Procedure: To a Schlenk tube were added alkynyl halide **1** (0.3 mmol), Grignard reagent **2** (0.36 mol), $Pd(PPh_3)_4$ (5 mol-%), TMEDA (10 mol-%), and THF (2 mL) at room temperature under an argon atmosphere. The tube was then stirred at 70 °C for the indicated time until complete consumption of starting material was observed (reaction monitored by TLC and GC–MS analysis). Upon completion of the reaction, the mixture

was diluted in diethyl ether, and washed with brine. The aqueous phase was extracted with diethyl ether and the combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the product. Melting points are uncorrected.

1,2-Diphenylethyne (3):[8c] White solid; m.p. 59.0–61.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 5.6 Hz, 4 H), 7.34 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.6, 128.3, 128.2, 123.2, 89.3 ppm. MS (EI, 70 eV): m/z (%) = 178 (100) [M^+].

1-Methyl-4-(phenylethynyl)benzene (4):[8c] White solid; m.p. 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), 2.37 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5 ppm. MS (EI, 70 eV): m/z (%) = 192 (100) [M^+].

1-Methoxy-4-(phenylethynyl)benzene (5):[8c] White solid; m.p. 57.0–59.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 4 H), 7.32 (d, J = 6.0 Hz, 3 H), 6.88 (d, J = 7.6 Hz, 2 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 133.0, 131.4, 128.3, 127.9, 123.5, 115.3, 113.9, 89.3, 88.0, 55.3 ppm. MS (EI, 70 eV): m/z (%) = 208 (100) [M^+].

Prop-1-ynyl-benzene (6):[11a] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 2 H), 7.30–7.23 (m, 3 H), 2.04 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.4, 128.2, 127.5, 124.0, 85.8, 79.7, 4.3 ppm. MS (EI, 70 eV): m/z (%) = 117 (7) [M^+ + 1], 116 (77) [M^+], 115 (100), 89 (12).

1,2-Bis(4-methoxyphenyl)ethyne (7):[12] White solid; m.p. 143.1–144.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.2 Hz, 4 H), 6.87 (d, J = 7.2 Hz, 4 H), 3.82 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 132.8, 115.7, 113.9, 87.9, 55.3 ppm. MS (EI, 70 eV): m/z (%) = 238 (100) [M^+].

1-Methoxy-4-(prop-1-ynyl)benzene (8):[11a] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 9.2 Hz, 2 H), 6.81 (d, J = 9.6 Hz, 2 H), 3.77 (s, 3 H), 2.02 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 132.7, 116.1, 113.8, 84.1, 79.4, 55.2, 4.2 ppm. MS (EI, 70 eV): m/z (%) = 147 (19) [M^+ + 1], 146 (100) [M^+], 131 (47), 103 (75).

1-Methyl-2-(phenylethynyl)benzene (9):[8c] 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), 2.52 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2, 132.5, 131.8, 131.5, 129.4, 128.4, 128.3, 128.1, 125.6, 123.6, 123.0, 93.4, 88.3, 20.7 ppm. MS (EI, 70 eV): m/z (%) = 192 (100) [M^+].

1-Methoxy-3-(phenylethynyl)benzene (10):[12] White solid; m.p. 79.1–79.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 2 H), 7.31–7.25 (m, 3 H), 7.20 (t, J = 8.0 Hz, 1 H), 7.12 (d, J = 7.6 Hz, 1 H), 7.06 (s, 1 H), 6.85–6.83 (m, 1 H), 3.72 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 131.5, 129.3, 128.2 (2 C), 124.1, 124.0, 123.1, 116.3, 114.8, 89.3, 89.2, 55.0 ppm. MS (EI, 70 eV): m/z (%) = 208 (100) [M^+].

1-Bromo-4-(phenylethynyl)benzene (11):[9] White solid; m.p. 78.0–79.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 2 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.39–7.34 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.0, 131.6, 131.5, 128.5, 128.4, 122.8, 122.4, 122.2, 90.5, 88.3 ppm. MS (EI, 70 eV): m/z (%) = 258 (100) [M^+ + 2], 256 (100) [M^+].

1-Chloro-4-(phenylethynyl)benzene (12):[9] White solid; m.p. 80.1–81.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 2 H), 7.44 (d, J = 8.0 Hz, 2 H), 7.34–7.30 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2, 132.8, 131.5, 128.6, 128.4 (2 C), 122.8, 121.7, 90.3, 88.2 ppm. MS (EI, 70 eV): m/z (%) = 214 (33) [M^+ + 2], 212 (100) [M^+].

4-(Phenylethynyl)benzonitrile (13):[11b] White solid; m.p. 108.4–110.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 10.0 Hz, 6 H), 7.26 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.8, 131.6 (2 C), 129.0, 128.3, 127.9, 122.0, 118.3, 111.2, 93.6, 87.6 ppm. MS (EI, 70 eV): m/z (%) = 203 (100) [M^+].

4-(Prop-1-ynyl)benzonitrile (14):[11a] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.4 Hz, 2 H), 7.45 (d, J = 8.4 Hz, 2 H), 2.08 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.0, 131.9, 129.1, 118.6, 110.8, 91.1, 78.6, 4.5 ppm.

Methyl 3-Methyl-4-(phenylethynyl)benzoate (15): White solid; m.p. 119.4–121.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.80 (t, J = 7.6 Hz, 1 H), 7.52–7.49 (m, 3 H), 7.31 (d, J = 2.8 Hz, 3 H), 3.87 (s, 3 H), 2.51 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 140.0, 131.5, 131.4, 130.2, 129.2, 128.5, 128.2, 127.6, 126.5, 122.8, 96.1, 87.5, 51.9, 20.5 ppm. MS (EI, 70 eV): m/z (%) = 250 (100) [M^+]. HRMS (ESI): m/z calcd. for $C_{17}H_{15}O_2$ [M + H]$^+$ 251.1067; found 251.1061.

1-(Phenylethynyl)naphthalene (16):[12] Light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.4 Hz, 1 H), 7.82–7.30 (m, 3 H), 7.64–7.61 (m, 2 H), 7.59–7.54 (m, 1 H), 7.50–7.46 (m, 1 H), 7.42–7.38 (m, 1 H), 7.37–7.30 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.2 (2 C), 131.6, 130.3, 128.7, 128.4, 128.3 (2 C), 126.7, 126.4, 126.2, 125.2, 123.4, 120.9, 94.3, 87.5 ppm. MS (EI, 70 eV): m/z (%) = 228 (100) [M^+].

2-[(4-Methoxyphenyl)ethynyl]thiophene (17):[12] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 10.8 Hz, 2 H), 7.24 (t, J = 2.4 Hz, 2 H), 6.99 (t, J = 4.4 Hz, 1 H), 6.86 (d, J = 8.8 Hz, 2 H), 3.80 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 132.9, 131.4, 127.0, 126.8, 123.7, 114.9, 114.0, 93.0, 81.2, 55.2 ppm. MS (EI, 70 eV): m/z (%) = 184 (100) [M^+].

Oct-1-ynylbenzene (18):[8c] 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) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.5, 128.2, 127.5, 123.9, 94.2, 84.1, 27.7 (2 C), 27.6 (2 C), 20.4, 18.9 ppm. MS (EI, 70 eV): m/z (%) = 186 (100) [M^+].

1-(Dec-1-ynyl)-4-methoxybenzene (19):[12] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.8 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 2 H), 3.76 (s, 3 H), 2.37 (t, J = 7.2 Hz, 2 H), 1.62–1.54 (m, 2 H), 1.45–1.40 (m, 2 H), 1.32–1.22 (m, 8 H), 0.88 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 132.7, 116.2, 113.6, 88.6, 80.1, 55.0, 31.7, 29.1, 29.0, 28.8 (2 C), 22.5, 19.3, 14.0 ppm.

Trimethyl(phenylethynyl)silane (20):[11c] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 3.2 Hz, 2 H), 7.10 (s, 3 H), 0.07 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.9, 128.4, 128.2, 123.0, 105.1, 94.0, 0 ppm. MS (EI, 70 eV): m/z (%) = 174 (100).

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for internal alkyne products.

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