JOC The Journal of Organic Chemistry

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Cobalt-Catalyzed Cross-Benzannulation of Conjugated Enynes and Diynes

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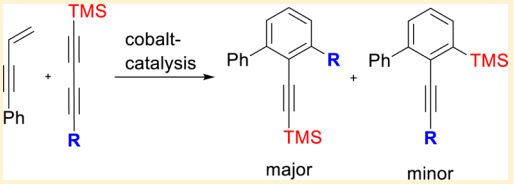
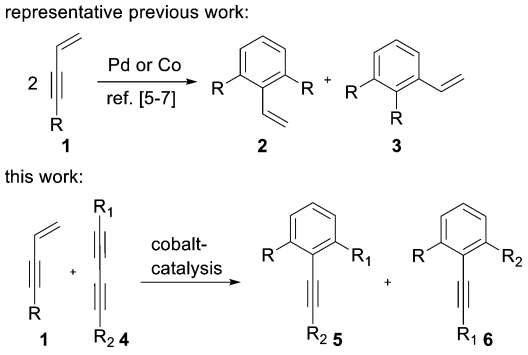
Supporting Information

ABSTRACT: The [4 + 2] cross-benzannulation of conjugated enynes and diynes under cobalt-catalysis led to 1,2,3-trisubstituted benzene derivatives in good yields. The reaction proceeds smoothly in absolute regiospecific control when symmetrical diynes are applied. Moreover, the use of unsymmetrical diynes was investigated, resulting in the formation of the unprecedented regioisomers as major products, which is in contrast to the results obtained in palladium-catalyzed benzannulation reactions. Also, 4-bromophenyl-substituted starting materials could be applied successfully in the cobalt-catalyzed process, which can be problematic in the palladium-catalyzed counterpart.



The regioselective construction of polysubstituted benzene derivatives represents an outstanding topic among organic reactions, and innumerable syntheses have been developed in the recent years.[1] Among those reactions, one of the most prominent approaches can be considered to be the [2 + 2 + 2] cyclotrimerization of alkynes catalyzed by several transition metals.[2] Further approaches are the Diels–Alder reaction of conjugated 1,3-dienes with alkynes,[3] the dehydro-Diels–Alder reaction,[4] and the [4 + 2] benzannulation of conjugated enynes and diynes (Scheme 1). In contrast to the Diels–Alder reaction, benzannulation leads directly to benzene derivatives, requiring no further oxidation of the 1,4-dihydroaromatic compounds.

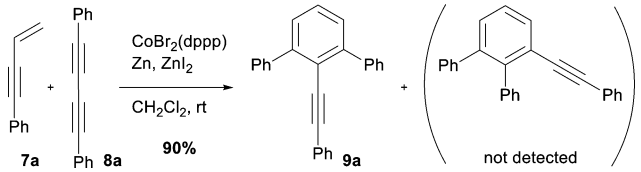
Scheme 1. Palladium- and Cobalt-Catalyzed Cross-Benzannulation



Two transition metal-catalyzed benzannulation reactions of enynes and diynes have been reported thus far: first, the palladium-catalyzed homobenzannulation[5] of two conjugated enynes **1** to symmetric styrenes **2** as well as the cross-benzannulation of enynes **1** and diynes **4** reported by Yamamoto and Gevorgyan;[6] second, the regiodivergent cobalt-catalyzed homobenzannulation of enynes **1** recently reported by our group.[7] In the cobalt-catalyzed reaction, the regioselectivity is strongly solvent-dependent leading to regioisomer **3**, which is not accessible via the palladium-catalyzed reaction.

On the basis of the results in the regiodivergent cobalt-catalyzed homobenzannulation, we extended our study toward the cross-benzannulation of conjugated enynes **1** with symmetrical as well as unsymmetrical diynes of type **4**. To probe the feasibility of the reaction, we initially investigated the reaction of but-3-en-1-yn-1-ylbenzene **7a** with the symmetric 1,4-diphenylbuta-1,3-diyne **8a** in the presence of $CoBr_2$(dppp) (10 mol %),[8] zinc powder (20 mol %), and zinc iodide (20 mol %) in dichloromethane at ambient temperatures (Scheme 2). The

Scheme 2. Cobalt-Catalyzed Cross-Benzannulation



reaction led to the symmetric 1,2,3-trisubstituted benzene derivative **9a** as a single isomer in an excellent yield of 90%. Besides the desired product, the formation of the homobenzannulation reaction of enyne **7a** and cyclotrimerization of diyne **8a** was also observed (~10%).

In contrast to the homobenzannulation, no solvent dependency in terms of regiocontrol could be observed. The use of CH_3CN, THF, DMF, or DMSO led to inferior conversions or unselective homobenzannulation, and cyclotrimerization of the starting materials was encountered. Moreover, reaction temperatures below 15 °C slowed the reaction dramatically, whereas temperatures above 35 °C led to cyclotrimerization preferentially. The use of 1- and 2-substituted enynes was tested, but

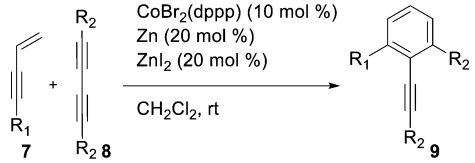
Received: May 29, 2015
Published: June 18, 2015

DOI: 10.1021/acs.joc.5b01198
J. Org. Chem. 2015, 80, 7311–7316

neither homobenzannulation nor cross-benzannulation occurred with these types of substrates.

With the optimized reaction conditions in hand, we first focused our efforts toward the cross-benzannulation of 4-substituted enynes **7** and symmetric diynes **8** (Scheme 3).

Scheme 3. Cobalt-Catalyzed Cross-Benzannulation Using Conjugated Enynes and Symmetric Diynes



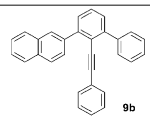
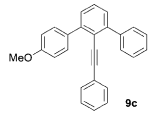
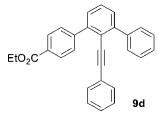
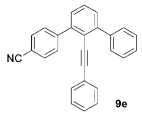
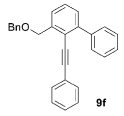
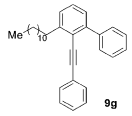
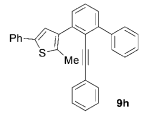
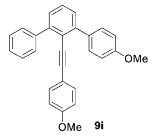
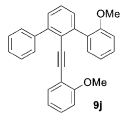
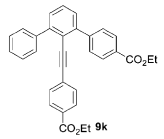
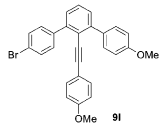
The present reaction tolerated a wide range of enynes with electron-neutral as well as electron-rich and -deficient arenes, affording corresponding terphenyls **9b**–**9e** in yields between 42 and 80% (Table 1, entries 1–4). Alkyl-substituted enynes gave products **9f** and **9g** in moderate yields after a prolonged reaction time (Table 1, entries 5 and 6) and applying either $CoBr_2$(dppp) or $CoBr_2$(dppe) as precatalyst.[8] Also, the sterically hindered thienyl-substituted enyne (Table 1, entry 7) gave product **9h** in a good yield of 56%, and its structure could be verified by X-ray analysis (see Supporting Information).

Moreover, various diynes **8i**–**8k** with electron-donating as well as electron-withdrawing substituents could be applied in good yields (Table 1, entries 8–10). In the case of **9j**, less cyclotrimerization than that with **9i** took place, presumably due to a more sterically hindered diyne moiety. Also of particular interest is bromo-substituted terphenyl **9l**, which could be synthesized in good yield (Table 1, entry 11). In contrast to the palladium-catalyzed benzannulation reactions, under the cobalt-catalyzed reaction conditions, the bromo substituent remained unchanged; neither proto-debromination nor other cross-coupling products could be observed. Accordingly, the scope of the reaction could be expanded so that further modifications will be possible. To our regret, terminal diynes, of the R-C≡C-C≡CH type, as well as diynes with electron-withdrawing substituents led predominantly to the corresponding cyclotrimerization products and led to the desired benzannulation products only in trace amounts.

Moving onward in the investigation, we focused our attention on the regioselective benzannulation reaction utilizing conjugated enynes and unsymmetrical diynes (Scheme 4).

In a first survey applying but-3-en-1-yn-1-ylbenzene **7a** with nona-1,3-diyn-1-ylbenzene **4a**, products **10a** and **11a** could be obtained in 50% yield, and a moderate regioselectivity of **10a**/**11a** (61:39) was detected (Table 2, entry 1). Thereby, terphenyl **10a** containing the phenyl substituent at the annulated ring was predominantly formed. An increased regioselectivity could be observed when TMS-substituted diynes **4b**–**4f** were used. Products **10b**, **10c**, and **10f** could be obtained in 46–60% yield and good regioselectivity (Table 2, entries 2, 3, and 7). Noteworthy is that in the case of the *ortho*- and *para*-methoxyphenyl-substituted diynes **4d** and **4e**, terphenyls **10d** and **10e** could be isolated in 61–69% yield and excellent regioselectivity (Table 2, entries 4 and 5). The divergent nature of the cobalt- versus palladium-catalyst system becomes obvious when diyne **4e** is applied. The palladium-catalyzed benzannulation of **4e** resulted in the exclusive formation of regioisomer

Table 1. Cobalt-Catalyzed Benzannulation of Conjugated Enynes with Symmetric Diynes

no.	product (9)[c]	t / h	yield[a]
1	 **9b**	18	42%
2	 **9c**	22	64%
3	 **9d**	18	80%
4	 **9e**	48	43%
5	 **9f**	48	45%[b]
6	 **9g**	48	45%[b]
7	 **9h**	15	56%
8	 **9i**	14	62%
9	 **9j**	14	72%
10	 **9k**	16	66%
11	 **9l**	20	60%

[a]Reaction conditions: enyne **7** (1.2 equiv), diyne **8** (1.0 equiv), $CoBr_2$(dppp) (10 mol %), Zn powder (20 mol %), ZnI_2 (20 mol %), CH_2Cl_2, rt. [b]$CoBr_2$(dppp) or $CoBr_2$(dppe) can be used as precatalyst. [c]In all reactions, trimerization of the enyne or diyne could be observed (~5–10%).

DOI: 10.1021/acs.joc.5b01198
J. Org. Chem. 2015, 80, 7311–7316

Scheme 4. Cobalt-Catalyzed Cross-Benzannulation Applying Unsymmetrical Diynes

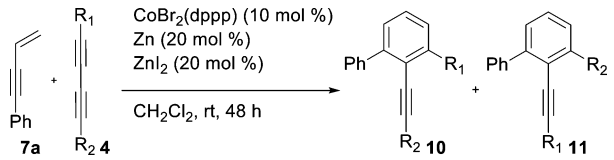
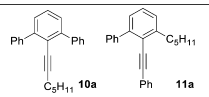
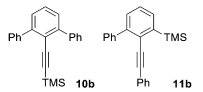
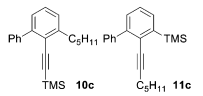
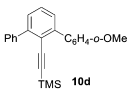
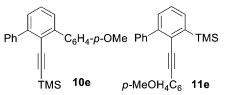
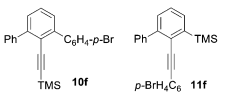


Table 2. Cobalt-Catalyzed Benzannulation of Conjugated Enynes with Unsymmetrical Diynes[a]

no.	product (10 / 11)[d]	ratio 10:11[c]	yield[a]
1		61:39	50%
2		82:18	46%
3		80:20	56%
4		>99:1	69%
5		91:9	61%
6	**10e** **11e**	0:100	58%[b]
7		85:15	60%

[a]Reaction conditions: enyne **7a** (1.8 equiv), diyne **4** (0.5 mmol, 1.0 equiv), Co(dppp)Br_2 (10 mol %), Zn powder (20 mol %), ZnI_2 (20 mol %), CH_2Cl_2, rt, 48 h. [b]Enyne **7a** (1.2 equiv), diyne **4** (1.0 equiv), $Pd(PPh_3)_4$ (5 mol %), NEt_3 (2.0 equiv), toluene, 100 °C, 48 h. [c]The regioisomer ratio was determined by GC analysis. [d]In all reactions, trimerization of the enyne or diyne could be observed (~5−10%).

11e (Table 2, entry 6) with the TMS group at the annulated ring as a single isomer in good yield (Table 2, entry 6). These results illustrate the different behavior of the cobalt- and palladium-catalyst systems and the complementary of the catalyst systems

Finally, we would like to direct attention to product **10f**, which is difficult to generate by palladium-catalyzed benzannulation; the bromo-substituent will afford us the ability to direct further modifications, such as Ullman-type dimerization or cross-coupling reactions.

In conclusion, we described the first cobalt-catalyzed enyne-diyne cross-benzannulation reaction leading to 1,2,3-substituted benzene derivatives. The products could be obtained in absolute regiospecific control and good yields. Several functionalyzed enynes and diynes could be applied, illustrating the high functional group tolerance of this reaction. Furthermore, regioselective cross-benzannulation utilizing unsymmetrical diynes was investigated. The products were formed in moderate to good yields and good regioselectivities, giving the opposite regioisomer from that with the palladium-catalyzed benzannulation reaction as the major product. Consequently, the cobalt-catalyzed transformation broadened the scope of this reaction and led to new products not easily accessible by other methods.

EXPERIMENTAL SECTION

General Methods. All reactions requiring water- or air-sensitive compounds were carried out in vacuum- and flame-dried flasks utilizing Schlenk techniques under an argon atmosphere. DCM was died over P_4O_{10}, and THF was dried over sodium/benzophenone and distilled under a nitrogen atmosphere. ZnI_2 was dried in vacuo at 150 °C prior to use. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, at room temperature utilizing preset pulse programs. The chemical shifts are given relative to tetramethylsilane as an internal standard. The solvent signal was used for calibration (^1H NMR δ ($CHCl_3$) = 7.26 ppm; ^{13}C NMR δ ($CHCl_3$) = 77.16 ppm). The following abbreviations are used to describe the signals: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), and m (multiplet). The coupling constants (J) are given in hertz (Hz). Infrared spectra (IR) were recorded on a FT-IR spectrometer. The absorption bands are given in wave numbers (cm^{-1}). The detected ion masses (m/z) are reported in u corresponding to the intensity of the signals as a percentage of the most intense signal. GC analysis was performed on a gas chromatograph with a flame ionization detector (FID). High-resolution mass spectra (HRMS) were recorded as electron ionization spectra (EI/HRMS) utilizing a quadrupole mass analyzer at an energy of 70 eV or as electron spray ionization (ESI/HRMS) using an LTQ-FT system. The detected ion masses (m/z) are given in u.

General Procedure for the Synthesis of Terminal 1,3-Enynes from Terminal Alkynes. $PdCl_2(PPh_3)_2$ (2 mol %), CuI (2 mol %), and Ph_3P (4 mol %) were suspended in THF (2 mL/mmol). Degassed iPr_2NH or Et_3N (2.30 equiv), the alkyne (1.00 equiv), and vinyl bromide solution (1 M in THF, 1.20 equiv) were added successively. The reaction mixture was stirred at room temperature until complete conversion was determined by TLC and GC-MS analyses. The reaction mixture was concentrated under reduced pressure, and H_2O was added followed by extraction with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, eluent: *n*-pentane/Et_2O) to give the desired product.

Literature known compounds prepared by this method: but-3-en-1-yn-1-ylbenzene **7a**.[9] Yield: 90% (1.15 g, 9.00 mmol). 2-(But-3-en-1-yn-1-yl)naphthalene **7b**.[7] Yield: 66% (232 mg, 1.30 mmol). ((Pent-4-en-2-yn-1-yloxy)methyl)benzene **7f**.[10] Yield: 43% (297 mg, 7.72 mmol). Hexadec-1-en-3-yne **7g**.[11] Yield: 82% (3.24 g, 14.7 mmol). 1-Bromo-4-(but-3-en-1-yn-1-yl)benzene **7h**.[12] Yield: 78% (397 mg, 1.92 mmol).

Ethyl 4-(But-3-en-1-yn-1-yl)benzoate ***7d***. Yield: 86% (579 mg, 2.89 mmol), orange oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96−7.86 (m, 2H), 7.49−7.34 (m, 2H), 5.96 (dd, J = 17.6, 11.1 Hz, 1H), 5.70 (dt, J = 17.7, 2.1 Hz, 1H), 5.52 (dt, J = 11.1, 2.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 166.2, 131.6, 130.1, 129.6, 128.0, 127.9, 117.0, 91.0, 89.4, 61.3, 14.5. IR (ATR) 2982, 1714, 1607, 1404, 1367, 1265, 1173, 1100, 1019, 969, 922, 854, 766, 693. HR MS (EI+) m/z calcd for $C_{13}H_{12}O_2$ ($[M]^+$), 200.0837; found, 200.0824.

4-(But-3-en-1-yn-1-yl)benzonitrile ***7e***. Yield: 86% (579 mg, 2.89 mmol), white solid. mp 63−64 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60−7.57 (m, 2H), 7.51−7.46 (m, 2H), 6.02 (dd, J = 17.5, 11.1 Hz, 1H), 5.79 (dd, J = 17.6, 2.1 Hz, 1H), 5.63 (dd, J = 11.1, 2.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 132.1, 132.1, 128.8, 128.2, 118.5, 116.6, 111.7, 92.4, 88.3. IR (ATR) 3883, 2223, 2153, 2073, 2020, 1979, 1921, 1774, 1717, 1602, 1499, 1442, 1402, 1271, 1179, 1105, 1014, 956, 924, 835, 773, 731, 694, 618, 554, 472, 430. MS (EI+) m/z = 153 (100, $[M]^+$), 147 (20), 139 (36), 130 (48), 127 (60), 102 (20), 75 (24), 69 (24). HR MS (EI+) m/z calcd for $C_{11}H_7N$ ($[M]^+$), 153.0578; found, 153.0570.

General Procedure for the Synthesis of Symmetrically Substituted Buta-1,3-diynes from Acetylenes. Under an oxygen

DOI: 10.1021/acs.joc.5b01198
J. Org. Chem. 2015, 80, 7311−7316

atmosphere, copper(II) chloride dihydrate (0.10 equiv) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.30 equiv) were dissolved in CH_2Cl_2 (1 mL/mmol). The alkyne (1.00 equiv) was added, and the mixture was stirred at room temperature until complete conversion was determined by TLC and GC-MS analyses. H_2O was added, and the organic phase was separated, followed by extraction with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, eluent: *n*-pentane/Et_2O).

Literature known compounds prepared by this method: 1,4-diphenylbuta-1,3-diyne **8a**.[13] Yield: 98% (993 mg, 4.91 mmol). 1,4-Bis(4-methoxyphenyl)buta-1,3-diyne **8b**.[14] Yield: 79% (1.04 g, 3.95 mmol). 1,4-Bis(2-methoxyphenyl)buta-1,3-diyne **8c**.[15] Yield: 55% (721 mg, 2.75 mmol). Diethyl 4,4′-(buta-1,3-diyne-1,4-diyl)dibenzoate **8d**.[6l] Yield: 58% (311 mg, 0.90 mmol).

General Procedure for the Synthesis of Unsymmetrically Substituted Diynes. Following a modified procedure of Tykwinsky,[16] alkyne (1.25 equiv) was dissolved in Et_2O (2 mL/mmol) and cooled to −78 °C. Then, *n*-BuLi (2.5 M in hexane, 1.20 equiv) was added, and the solution was allowed to warm to room temperature over a period of 30 min. The appropriate aldehyde (1.00 equiv) was added, and the solution was stirred at room temperature until complete conversion was determined by TLC and GC-MS analyses. The reaction was quenched with saturated NH_4Cl solution, the organic phase was separated and washed with 3 × 15 mL brine, and the aqueous phase was extracted with 3 × 15 mL Et_2O. The combined organic phases were dried over $MgSO_4$, and the solvent was removed in vacuo. The thus formed alcohol (1.00 equiv) was dissolved in CH_2Cl_2 (4 mL/mmol), PCC (1.10 equiv) was added, and the solution was stirred at room temperature until completion was determined by TLC and GC-MS analyses. The solution was filtered over a plug of silica, and the solvent was removed. PPh_3 (3.60 equiv) was dissolved in CH_2Cl_2 (3 mL/mmol), CBr_4 (1.80 equiv) was added slowly at 0 °C, and the solution was stirred for 15 min. Then, the ketone (1.00 equiv) was added, and the mixture was stirred for 2 h at room temperature. The mixture was concentrated, *n*-pentane was added, the mixture was filtered over a plug of silica (*n*-pentane/CH_2Cl_2 4:1), and the solvent was removed. The dibromo-olefin was dissolved in benzene (1 mL/mmol), and hexane was added (3 mL/mmol). The mixture was cooled to −35 °C, and *n*-BuLi (2.5 M in hexane, 1.00 equiv) was added. The mixture was allowed to warm to room temperature and was stirred until completion was determined by GC-MS analysis. The reaction was quenched with a saturated NH_4Cl solution, the organic phase was separated and washed with 3 × 15 mL brine, and the aqueous phase was extracted with 3 ×15 mL Et_2O. The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, eluent: *n*-pentane/Et_2O).

Literature known compounds prepared by this method: nona-1,3-diyn-1-ylbenzene **4a**.[17] Yield: 32% (576 mg, 3.16 mmol). Trimethyl(phenylbuta-1,3-diyn-1-yl)silane **4b**.[16] Yield: 70% (1.38 g, 6.96 mmol). Trimethyl(nona-1,3-diyn-1-yl)silane **4c**.[16] Yield: 55% (1.06 g, 5.51 mmol). ((2-Methoxyphenyl)buta-1,3-diyn-1-yl)trimethylsilane **4d**.[16] Yield: 53% (1.20 g, 5.25 mmol). ((4-Methoxyphenyl)buta-1,3-diyn-1-yl)trimethylsilane **4e**.[16] Yield: 75% (1.20 g, 7.47 mmol). ((4-Bromophenyl)buta-1,3-diyn-1-yl)trimethylsilane **4f**.[18] Yield: 70% (1.88 g, 6.79 mmol).

General Procedure for the Cobalt-Catalyzed Cross-Benzannulation of 1,3-Enynes with Symmetrical Buta-1,3-diynes. Under argon atmosphere cobaltdibromo(1,3-bis(diphenylphosphino)-propane) [= $CoBr_2$(dppp)] (10 mol %), zinc powder (10 mol %), and zinc iodide (10 mol %) were dissolved in CH_2Cl_2 (2 mL/mmol). The 1,3-enyne (0.60 mmol, 1.20 equiv) and buta-1,3-diyne (0.50 mmol, 1.00 equiv) were added subsequently. The reaction was stirred at room temperature until complete conversion was determined by TLC and GC-MS analyses. After complete reaction, *n*-pentane was added followed by filtration over a plug of silica (eluent: *n*-pentane/Et_2O 1:1). The solvent was removed, and the crude mixture was purified by flash chromatography (silica, eluent: *n*-pentane/Et_2O).

2′-(Phenylethynyl)-1,1′:3′,1″-terphenyl ***9a***.[6e] Yield: 90% (149 mg, 0.45 mmol), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73−7.65 (m, 4H), 7.53−7.35 (m, 9H), 7.22−7.15 (m, 3H), 7.00 (dd, J = 6.4, 3.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.9, 141.0, 130.9, 129.6, 128.3, 128.0, 128.0, 127.8, 127.7, 127.3, 123.5, 120.2, 95.8, 88.9.

2-(2-(Phenylethynyl)-[1,1′-biphenyl]-3-yl)naphthalene ***9b***. Yield: 42% (80 mg, 0.21 mmol), slight yellow solid. mp 58−60 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.92 (dt, J = 12.1, 8.8 Hz, 3H), 7.71 (d, J = 7.7 Hz, 2H), 7.60−7.35 (m, 7H), 7.32−7.20 (m, 2H), 7.20−7.06 (m, 3H), 6.94 (d, J = 7.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 145.3, 144.9, 141.3, 138.7, 133.4, 132.9, 131.6, 131.2, 130.6, 129.9, 128.9, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.2, 126.2, 126.2, 123.6, 120.6, 96.3, 89.1. IR (ATR) 2962, 1413, 1259, 1085, 1015, 864, 795, 699, 662. MS (EI+) m/z = 380 (68, $[M]^+$), 376 (17), 363 (12), 350 (6), 303 (100), 276 (3), 182 (7), 151 (10). HR MS (EI+) m/z calcd for $C_{30}H_{20}$ ($[M]^+$), 380.1565; found, 380.1565.

4-Methoxy-2′-(phenylethynyl)-1,1′:3′,1″-terphenyl ***9c***. Yield: 64% (115 mg, 0.32 mmol), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75−7.62 (m, 4H), 7.53−7.36 (m, 6H), 7.25−7.15 (m, 3H), 7.12−6.98 (m, 4H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.3, 145.3, 144.6, 141.4, 133.7, 131.2, 131.0, 129.8 (2C), 128.5, 128.2, 128.2, 128.0, 127.9, 127.5, 123.8, 120.3, 113.4, 95.9, 89.3, 55.5. IR (ATR) 3055, 2956, 2931, 2834, 1608, 1512, 1491, 1455, 1441, 1290, 1245, 1176, 1029, 910, 835, 802, 755, 691. MS (EI+) m/z = 360 (98, $[M]^+$), 329 (81), 313 (62), 300 (22), 289 (24), 283 (64), 268 (37), 252 (32), 239 (100), 213 (8), 187 (6), 163 (17), 157 (28), 150 (20). HR MS (EI+) m/z calcd for $C_{27}H_{20}O$ ($[M]^+$), 360.1514; found, 360.1496.

Ethyl 2′-(Phenylethynyl)-[1,1′:3′,1″-terphenyl]-4-carboxylate ***9d***. Yield: 80% (162 mg, 0.40 mmol), white solid. mp 89−91 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13−8.03 (m, 2H), 7.73−7.64 (m, 2H), 7.64−7.56 (m, 2H), 7.43−7.29 (m, 6H), 7.15−7.09 (m, 3H), 6.97−6.87 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 166.8, 145.8, 145.4, 143.9, 141.1, 131.2, 129.8, 129.8, 129.6, 129.2, 129.2, 128.5, 128.3, 128.3, 128.3, 128.0, 127.7, 123.5, 120.4, 96.5, 88.6, 61.1, 14.5. IR (ATR) 3055, 2989, 2924, 2856, 1702, 1605, 1449, 1270, 1175, 1270, 1175, 1100, 1018, 754, 694, 513. HR MS (EI+) m/z calcd for $C_{29}H_{22}O_2$ ($[M]^+$), 402,1620; found, 402.1629.

2′-(Phenylethynyl)-[1,1′:3′,1″-terphenyl]-4-carbonitrile ***9e***. Yield: 35% (46 mg, 0.13 mmol), yellow solid. mp 87−89 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76−7.64 (m, 3H), 7.64−7.51 (m, 2H), 7.47−7.33 (m, 5H), 7.33−7.23 (m, 1H), 7.23−7.06 (m, 4H), 6.98−6.81 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 146.0, 145.6, 143.0, 140.8, 131.8, 131.1, 130.6, 129.7, 129.6, 129.3, 128.5, 128.4, 128.2, 128.0, 127.8, 123.2, 120.4, 119.2, 111.4, 96.8, 88.2. IR (ATR) 3055, 2966, 2225, 1949, 1809, 1719, 1601, 1492, 1446, 1396, 1275, 1180, 1073, 1022, 970, 914, 843, 803, 753, 691, 604, 546, 519, 429. MS (EI+) m/z = 355 (100, $[M]^+$), 352 (21), 277 (89), 73 (34), 57 (20). HR MS (EI+) m/z calcd for $C_{27}H_{17}N$ ($[M]^+$), 355.1361; found, 355.1352.

3-((Benzyloxy)methyl)-2-(phenylethynyl)-1,1′-biphenyl ***9f***. Yield: 43% (82 mg, 0.22 mmol), white solid. mp 25−27 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.53 (m, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.41−7.32 (m, 4H), 7.31−7.23 (m, 4H), 7.22−7.12 (m, 7H), 4.83 (s, 2H), 4.63 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.6, 141.0, 141.0, 138.6, 131.6, 131.4, 129.7, 128.7, 128.6, 128.4, 128.4, 128.3, 128.0, 127.8, 127.6, 126.5, 123.6, 120.4, 97.6, 86.9, 73.1, 71.0. IR (ATR) 3058, 3029, 2921, 2854, 1491, 1451, 1356, 1106, 1068, 753, 691. MS (EI+) m/z = 355 (1, $[M]^+$), 283 (37), 265 (100), 239 (27), 105 (8), 91 (15). HR MS (EI+) m/z calcd for $C_{28}H_{22}O$ ($[M]^+$), 374.1671; found, 374,1675.

3-Dodecyl-2-(phenylethynyl)-1,1′-biphenyl ***9g***. Yield: 45% (82 mg, 0.22 mmol), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68−7.58 (m, 2H), 7.48−7.35 (m, 3H), 7.31−7.19 (m, 8H), 2.93 (t, J = 7.8 Hz, 2H), 1.83−1.65 (m, 2H), 1.55−1.11 (m, 18H), 0.87 (t, J = 5.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 145.9, 144.7, 141.4, 131.3, 129.7, 128.9, 128.14, 128.08, 127.9, 127.8, 127.4, 127.1, 124.0, 121.2, 96.4, 88.1, 35.5, 32.1, 31.0, 29.9, 29.8, 29.85 (2C), 29.82 (2C), 29.5, 22.8, 14.3. IR (ATR): 3058, 2922, 2852, 1490, 1459, 1069, 1027, 911, 754, 698, 689. MS (EI+) m/z = 422 (14, $[M]^+$), 267 (60), 252 (51), 202 (35), 178 (38), 154 (9), 127 (14), 101 (16), 85 (29), 57 (100). HR MS (EI+) m/z calcd for $C_{32}H_{38}$ ($[M]^+$), 422.2974; found, 422.2967.

DOI: 10.1021/acs.joc.5b01198
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2-Methyl-5-phenyl-3-(2-(phenylethynyl)-[1,1′-biphenyl]-3-yl)-thiophene ***9h***. Yield: 56% (119 mg, 0.28 mmol), yellow solid. mp 156−158 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.58 (m, 2H), 7.54−7.49 (m, 2H), 7.42−7.35 (m, 2H), 7.35−7.30 (m, 4H), 7.25 (ddd, J = 7.8, 4.8, 1.5 Hz, 3H), 7.17−7.12 (m, 1H), 7.09−7.00 (m, 3H), 6.98−6.91 (m, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.8, 141.0, 140.2, 139.2, 139.1, 136.1, 134.8, 133.5, 131.3, 129.8, 129.0, 128.6, 128.3, 128.1, 128.0, 127.9, 127.6, 127.1, 126.3, 125.6, 123.6, 121.7, 96.2, 88.9, 14.6. IR (ATR) 3024, 2919, 2853, 1593, 1486, 1444, 1414, 1378, 1251, 1152, 1069, 1025, 907, 809, 754, 682. MS (EI+) m/z = 426 (62), 411 (67), 349 (20), 334 (15), 289 (10), 206 (11), 149 (10), 136 (73), 111 (25), 97 (43), 69 (54), 57 (100). HR MS (EI+) m/z calcd for $C_{31}H_{22}S$ ([M]$^+$), 426.1442; found, 426.1440.

4-Methoxy-2′-((4-methoxyphenyl)ethynyl)-1,1′:3′,1″-terphenyl ***9i***. Yield: 62% (121 mg, 0.31 mmol), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73−7.61 (m, 4H), 7.52−7.32 (m, 6H), 7.12−6.92 (m, 4H), 6.83−6.68 (m, 2H), 3.90 (s, 3H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.5, 159.2, 144.9, 144.3, 141.5, 133.8, 132.6, 131.1, 129.9, 128.5, 128.2, 127.8 (2C), 127.4, 120.7, 116.0, 114.0, 113.3, 96.0, 88.0, 55.5, 55.4. IR (ATR) 3053, 3002, 2957, 2834, 2211, 1604, 1571, 1507, 1450, 1288, 1243, 1174, 1027, 829, 803, 758, 698, 576, 529. MS (EI+) m/z = 390 (76, [M]$^+$), 359 (51), 315 (27), 283 (56), 268 (26), 239 (100), 150 (56), 84 (8). HR MS (EI+) m/z calcd for $C_{28}H_{22}O_2$ ([M]$^+$), 390.1620; found, 390.1627.

2-Methoxy-2′-((2-methoxyphenyl)ethynyl)-1,1′:3′,1″-terphenyl ***9j***. Yield: 72% (139 mg, 0.36 mmol), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−7.72 (m, 2H), 7.52−7.31 (m, 8H), 7.14−7.00 (m, 3H), 6.87−6.64 (m, 3H), 3.78 (s, 3H), 3.60 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.0, 157.3, 144.1, 142.4, 141.3, 133.4, 131.7, 130.8, 130.0, 129.2, 129.1, 128.9, 128.5, 127.8, 127.7, 127.2, 122.2, 120.34, 120.32, 113.5, 111.2, 110.9, 92.9, 92.0, 55.9, 55.6. IR (ATR) 3059, 2926, 2841, 1595, 1494, 1460, 1432, 1270, 1245, 1270, 1245, 1157, 1103, 1027, 802, 753, 699. MS (EI+) m/z = 390 (100, [M]$^+$), 375 (28), 359 (51), 344(26), 326 (20), 313 (30), 283(24) 268 (13), 252 (13), 239 (21), 157 (14). HR MS (EI+) m/z calcd for $C_{28}H_{22}O_2$ ([M]$^+$), 390.1620; found, 390.1626.

Ethyl 2′-((4-(Ethoxycarbonyl)phenyl)ethynyl)-[1,1′:3′,1″-terphenyl]-4-carboxylate ***9k***. Yield: 66% (157 mg, 0.33 mmol), yellow solid. mp 124−126 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23−8.10 (m, 2H), 7.92−7.85 (m, 2H), 7.81−7.72 (m, 2H), 7.71−7.61 (m, 2H), 7.56−7.36 (m, 6H), 7.03 (dd, J = 8.4, 1.7 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.7, 166.1, 145.8, 145.6, 144.2, 140.9, 131.0, 129.8, 129.7, 129.4, 129.3, 129.2, 128.9, 128.5, 128.0, 127.9, 127.8, 119.9, 95.6, 91.6, 61.2 (2C), 14.5, 14.4. IR (ATR) 3050, 2985, 2913, 1717, 1603, 1397, 1364, 1267, 1102, 1022, 852, 755, 693. HR MS (ESI+) m/z calcd for $C_{32}H_{26}O_4$ ([M + H]$^+$), 474.1831; found, 474.1842.

4-Bromo-4″-methoxy-2′-((4-methoxyphenyl)ethynyl)-1,1′:3′,1″-terphenyl ***9l***. Yield: 60% (141 mg, 0.30 mmol), brown solid. mp 112−113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72−7.50 (m, 6H), 7.45−7.27 (m, 3H), 7.07−6.94 (m, 4H), 6.84−6.69 (m, 2H), 3.89 (s, 3H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.6, 159.2, 144.4, 143.3, 140.3, 133.5, 132.5, 131.4, 130.9, 130.8, 128.9, 128.7, 127.8, 121.6, 120.4, 115.6, 113.9, 113.2, 96.3, 87.5, 55.4, 55.3. IR (ATR) 3049, 2998, 2924, 2832, 1604, 1505, 1449, 1386, 1290, 1241, 1172, 1103, 1070, 1033, 825, 791, 748, 523. MS (EI+) m/z = 468 (2, [M]$^+$), 433 (23), 419 (46), 404 (8), 389 (18), 374 (55), 357 (15), 341 (21), 327 (16), 281 (64), 207 (100), 73 (71). HR MS (EI+) m/z calcd for $C_{28}H_{21}BrO_2$ ([M]$^+$), 468.0725; found, 468.0730.

General Procedure for the Cobalt-Catalyzed Cross-Benzannulation of 1,3-Enynes with Unsymmetrical Buta-1,3-diynes. Under an argon atmosphere cobaltdibromo(1,3-bis-(diphenylphosphino)propane) [= $CoBr_2$(dppp)] (10 mol %), zinc powder (20 mol %), and zinc iodide (20 mol %) were dissolved in CH_2Cl_2 (2 mL/mmol). But-3-en-1-yn-1-ylbenzene (0.60 mmol, 1.20 equiv) and buta-1,3-diyn (0.50 mmol, 1.00 equiv) were added subsequently. The reaction was monitored by GC-MS analysis. After 50% conversion of the 1,3-enyne, additional but-3-en-1-yn-1-ylbenzene (0.3 equiv) was added. The reaction was stirred at room temperature until complete conversion was determined by TLC and GC-MS analyses. After complete reaction, n-pentane was added, followed by filtration over a plug of silica (n-pentane/Et_2O 1:1). The solvent was removed, and the crude mixture was purified by flash chromatography (silica, eluent: n-pentane/Et_2O).

2′-(Hept-1-yn-1-yl)-1,1′:3′,1″-terphenyl ***10a*** *and 3-Pentyl-2-(phenylethynyl)-1,1′-biphenyl* ***11a***. Yield: 50% (81 mg, 0.25 mmol, **10a**/**11a** = 61:39), yellow oil. Analytical data of **10a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.55 (m, 2H), 7.47−7.29 (m, 4H), 7.29−7.10 (m, 7H), 2.93 (dd, J = 8.9, 6.5 Hz, 2H), 1.87−1.58 (m, 2H), 1.51−1.26 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.9, 144.8, 141.5, 131.3, 129.8, 128.4, 128.14, 128.08, 127.9, 127.8, 127.4, 127.1, 124.0, 121.2, 96.4, 88.2, 35.5, 32.1, 30.7, 22.8, 14.2. IR (ATR) 3057, 2925, 2857, 1943, 1878, 1806, 1597, 1567, 1492, 1455, 1377, 1249, 1177, 1108, 1070, 1026, 972, 913, 841, 801, 755, 694, 634, 623, 577, 520, 485, 411. MS (EI+) m/z = 234 (57, [M]$^+$), 267 (60), 256 (100), 252 (100), 239 (46), 233 (21), 215 (17), 203 (32), 178 (90), 165 (24), 57 (20), 32 (28). HR-MS (EI+) m/z calcd for $C_{25}H_{24}$ ([M]$^+$), 324.1878; found, 324.1865. Analytical data of **11a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.54 (m, 4H), 7.47−7.28 (m, 9H), 2.08 (t, J = 6.9 Hz, 2H), 1.33−1.21 (m, 2H), 1.21−1.13 (m, 2H), 1.13−1.03 (m, 2H), 0.82 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.1, 141.6, 129.7, 128.5, 127.8, 127.32, 127.26, 121.2, 97.7, 79.3, 31.0, 27.9, 22.3, 19.6, 14.0. IR (ATR) 3057, 2927, 2860, 1599, 1569, 1495, 1454, 1422, 1072, 1028, 914, 807, 756, 697. MS (EI+) m/z = 234 (8, [M]$^+$), 281 (15), 267 (30), 253 (100), 239 (13), 207 (25). HR MS (EI+) m/z calcd for $C_{25}H_{24}$ ([M]$^+$), 324.1878; found, 324.1881.

([1,1′:3′,1″-Terphenyl]-2′-ylethynyl)trimethylsilane ***10b*** *and Trimethyl(2-(phenylethynyl)-[1,1′-biphenyl]-3-yl)silane* ***11b***. Yield: 46% (75 mg, 0.23 mmol, **10b**/**11b** = 82:18), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.60 (m, 3H), 7.46−7.32 (m, 10H), −0.04 (s, J = 3.1 Hz, 9H). Analytical data of the resolved signals of the major isomer **10b**: ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.6, 141.1, 129.8, 128.5, 128.3, 127.8, 127.5, 120.4, 103.8, 102.1, −0.5. Analytical data of the resolved signals of the minor isomer **11b**: ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 130.1, 129.9, 128.6, 128.1, 120.4, −0.5. IR (ATR) 3057, 2154, 1600, 1569, 1449, 1412, 1248, 1209, 1074, 1027, 915, 839, 753, 695, 641, 607, 556, 516, 448. MS (EI+) m/z = 326 (43, [M]$^+$), 311 (26), 295 (68), 279 (8), 267 (31), 252 (100), 226 (5), 155 (4), 73 (11). HR MS (EI+) m/z calcd for $C_{23}H_{22}Si$ ([M]$^+$), 326.1491; found, 326.1490.

Trimethyl((3-pentyl-[1,1′-biphenyl]-2-yl)ethynyl)silane ***10c*** *and Trimethyl((3-pentyl-[1,1′-biphenyl]-2-yl)ethynyl)silane* ***11c***. Yield: 56% (90 mg, 0.28 mmol, **10c**/**11c** = 80:20). The major product could be separated after additional column chromatography (eluent: n-pentane) as a colorless oil (71 mg, 0.22 mmol, 44%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.55 (m, 2H), 7.46−7.31 (m, 3H), 7.31−7.25 (m, 1H), 7.21 (ddd, J = 6.7, 5.2, 1.7 Hz, 2H), 2.96−2.76 (m, 2H), 1.82−1.61 (m, 2H), 1.49−1.31 (m, 4H), 0.95 (t, J = 7.3 Hz, 3H), 0.15 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.5, 145.0, 141.2, 129.7, 128.2, 127.71, 127.66, 127.3, 127.0, 121.2, 103.2, 101.9, 35.5, 32.1, 30.6, 22.7, 14.2, −0.2. IR (ATR) 2956, 2927, 2860, 2152, 1457, 1430, 1249, 841, 755, 698, 639, 608. MS (EI+) m/z = 320 (57, [M]$^+$), 305 (41), 246 (100), 231 (64), 217 (89), 212 (67), 191 (84), 165 (11), 73 (52). HR MS (EI+) m/z calcd for $C_{22}H_{28}Si$ ([M]$^+$), 320.1960; found, 320.1968.

((2-Methoxy-[1,1′:3′,1″-terphenyl]-2′-yl)ethynyl)trimethyl-silane ***10d***. Yield: 69% (123 mg, 0.345 mmol), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72−7.63 (m, 2H), 7.47−7.30 (m, 8H), 7.09−6.94 (m, 2H), 3.81 (s, 3H), −0.06 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 157.1, 144.6, 143.1, 141.0, 131.4, 130.6, 129.8, 129.0, 128.9, 128.3, 128.0, 127.7, 127.3, 121.8, 120.2, 111.0, 103.9, 100.7, 55.7, −0.3. IR (ATR) 3059, 2957, 2835, 2156, 1947, 1597, 1496, 1459, 1418, 1246, 1179, 1106, 1030, 863, 755, 699, 642, 612, 567, 488, 425. MS (EI+) m/z = 356 (100, [M]$^+$), 355 (82), 341 (45), 309 (55), 293 (27), 283 (49), 265 (66), 252 (52), 239 (34), 89 (37), 73 (44), 59 (35). HR MS (EI+) m/z calcd for $C_{24}H_{24}OSi$ ([M]$^+$), 356.1596; found, 356.1589.

((4-Methoxy-[1,1′:3′,1″-terphenyl]-2′-yl)ethynyl)trimethyl-silane ***10e*** *and (2-((4-Methoxyphenyl)ethynyl)-[1,1′-biphenyl]-3-yl)-trimethylsilane* ***11e***. Yield: 61% (109 mg, 0.305 mmol, **10e**/**11e** =

DOI: 10.1021/acs.joc.5b01198
J. Org. Chem. 2015, 80, 7311−7316

91:9). Analytical data of major isomer **10e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.57 (m, 4H), 7.49−7.30 (m, 6H), 7.04−6.88 (m, 2H), 3.88 (s, 3H), 0.02 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.2, 145.7, 145.1, 141.1, 133.5, 130.9, 129.7, 128.4, 128.3, 128.1, 127.7, 127.4, 120.2, 113.2, 104.0, 101.9, 55.4, −0.43. IR (ATR) 3288, 3056, 2835, 2153, 1946, 1884, 1608, 1575, 1512, 1453, 1290, 1246, 1178,1110, 1076, 1034, 839, 805, 759, 699, 638, 604, 571, 536, 442. MS (EI+) m/z = 356 (100, $[M]^+$), 325 (29), 283 (62), 268 (21), 252 (46), 239 (76), 73 (15), 59 (15), 32 (100). HR MS (EI+) m/z calcd for $C_{24}H_{24}OSi$ ($[M]^+$), 356.1596; found, 356.1599.

((4-Bromo-[1,1′:3′,1″-terphenyl]-2′-yl)ethynyl)trimethyl-silane ***10f*** *and (2-((4-Bromophenyl)ethynyl)-[1,1′-biphenyl]-3-yl)-trimethylsilane* ***11f***. Yield: 60% (122 mg, 0.30 mmol, **10f**/**11f** = 85:15). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66−7.59 (m, 2H), 7.58−7.50 (m, 3H), 7.47−7.36 (m, 6H), 7.33 (dd, J = 7.2, 1.8 Hz, 1H), −0.09 (s, 9H). Resolved signals of major isomer **10f**: $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 145.6, 144.2, 140.9, 140.0, 131.5, 130.9, 129.7, 128.8, 128.5, 128.2, 127.8, 127.6, 121.8, 120.3, 103.4, 102.7, −0.5. Resolved signals of minor isomer **11f**: $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 130.8, 129.8, 128.3, 127.8, 127.5, 120.2, 100.1. IR (ATR) 2958, 2153, 1491, 1451, 1418, 1388, 1248, 1072, 1009, 835, 804, 754, 697, 650, 602, 515, 449, 415. MS (EI+) m/z = 404 (30, $[M]^+$), 391 (21), 373 (9), 332 (10), 309 (12), 295 (100), 279 (9), 265 (23), 252 (73), 73 (16). HR MS (EI+) m/z calcd for $C_{23}H_{21}BrSi$ ($[M]^+$), 404.0596; found, 404.0596.

■ ASSOCIATED CONTENT

Supporting Information

Detailed X-ray structure of compound **9h** and copies of ^{1}H and ^{13}C NMR spectra of **4a−f**, **7a−g**, **7l**, **8a−d**, **9a−l**, and **10a**/**11a−10f**/**11f**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01198.

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Notes

The authors declare no competing financial interest.

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DOI: 10.1021/acs.joc.5b01198
J. Org. Chem. 2015, 80, 7311−7316