Dichloro[(2-dimethylamino)propyldiphenylphosphine]palladium(II) ($PdCl_2$(alaphos)): An Efficient Catalyst for Cross-Coupling of Aryl Triflates with Alkynyl Grignard Reagents[1]

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Dichloro[(2-dimethylamino)propyldiphenylphosphine]palladium ($PdCl_2$(alaphos)) was found to be much more effective as catalyst than other palladium complexes for cross-coupling of aryl triflates with alkynyl Grignard reagents. Reaction of bromoaryl triflates with alkynyl Grignard reagents in the presence of $PdCl_2$(alaphos) catalyst gave high yields of alkynyl arene bromides, which were formed by selective replacement of triflate by alkynyl group.

Introduction

Alkynyl arenes are very useful materials for π-conjugated polymers, liquid crystals, and so on.[2] For the carbon−carbon bond formation between aryl and alkynyl groups, the Sonogashira reaction[3] has been often used.[4] Although alkynylmetal reagents of magnesium,[5] zinc,[6] and tin[7] have been also conveniently used for the preparation of alkynylarenes from aryl bromides and iodides, few reports have appeared, to our knowledge, on the successful alkynylation of aryl triflates, which are readily available from the corresponding phenols, with alkynyl Grignard reagents.[8,9] During our studies on the enantioposition-selective cross-coupling of aryl triflates with the Grignard reagents,[10,11] it was found that palladium complexes coordinated with β-(dimethylamino)-alkyldiphenylphosphines are highly catalytically active as well as enantioselective. Here we wish to report that $PdCl_2$(alaphos),[12] where alaphos stands for (2-dimethylamino)propyldiphenylphosphine, is a unique catalyst which efficiently catalyzes the cross-coupling of aryl triflates with alkynyl Grignard reagents forming alkynylarenes in high yields. It is also described that the selective replacement of triflate by alkynyl groups occurred in the reaction of arenes containing both the bromide and triflate groups with alkynyl Grignard reagents catalyzed by $PdCl_2$(alaphos) to give alkynyl arene bromides in high yields.

Results and Discussion

Effects of phosphine ligands on the catalytic activity were examined for the palladium-catalyzed cross-coupling of 2-phenylphenyl triflate (**1**) with phenylethynylmagnesium bromide (Scheme 1), which was generated by the reaction of phenylethyne with ethylmagnesium bromide. The cross-coupling was carried out with 2 equiv of the Grignard reagent in the presence of 1 equiv of LiBr and 5 mol % of palladium catalyst at 30 °C. The results are summarized in Table 1. It was found that $PdCl_2$-(alaphos) is by far the most effective of the palladium and nickel catalysts examined, giving a 93% yield of 2-phenylethynylbiphenyl (**2a**) in the reaction carried out for 6 h (entry 1). The second best catalyst was $PdCl_2$-$(PPh_3)_2$, but the reaction was much slower, 30% of **2a** being formed after 24 h (entry 2). $PdCl_2$(dppp), which is one of the most active catalytsts for the cross-coupling of aryl triflates with the aryl Grignard reagents,[1] is not effective at all for the present cross-coupling with the alkynyl Grignard reagent (entry 3). $PdCl_2$(dppf) and $NiCl_2(PPh_3)_2$ were much less catalytically active than $PdCl_2$(alaphos) for the alkynylation (entries 4 and 5). The reaction with triphenylsilylethynylmagnesium bromide also proceeded efficiently to give 2-(triphenylsilylethynyl)-biphenyl (**2b**) in 99% yield (entry 6).

It would be very useful if aromatic compounds bearing both bromide and triflate underwent the selective replacement of either bromide or triflate by an alkynyl group. Unfortunately, there have been no examples of the chemoselective alkynylation of bromoaryl triflates by palladium-catalyzed cross-coupling type reactions,[8,13] probably because of the difficulty in controlling the reactivity of the bromide and triflate groups at the oxidative addition to a palladium(0) species.[14,15] In the

(1) Part of this paper appeared previously: Kamikawa, T.; Hayashi, T. *Synlett* **1997**, 163.

(2) For examples, see the following. (a) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956. (b) Ley, K. D.; Whittle, E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423. (c) Manna, J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Smith, R. D. *J. Am. Chem. Soc.* **1996**, *118*, 8731.

(3) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(4) For reviews, see the following. (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1995. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(5) Rossi, R.; Capita, A.; Lezzi, A. *Tetrahedron* **1984**, *40*, 2773.

(6) Yoneda, N.; Matsuoka, S.; Miyaura, N.; Fukuhara, T.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2124.

(7) Sakamoto, T.; Yasuhara, A.; Kondo, Y.; Yamanaka, H. *Synlett* **1992**, 746.

(8) For palladium-catalyzed cross-coupling of aryl triflates with alkynyltin, see: Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(9) For nickel-catalyzed cross-coupling of alkynyl Grignard reagents with alkenyl carbamates, see: Madoc, D.; Pujol, S.; Henryon, V.; Ferezou, J. P. *Synlett* **1995**, 435.

(10) Hayashi, T.; Niizuma, S.; Kamikawa, T.; Suzuki, N.; Uozumi, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9101.

(11) Kamikawa, T.; Uozumi, Y.; Hayashi, T. *Tetrahedron Lett.* **1996**, *37*, 3161.

(12) Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195.

(13) Selective alkenylation or carbonylation has been reported in the palladium-catalyzed reactions of 4-bromophenyl triflate: (a) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 3931. (b) Oh-e, T.; Miyaura, N.; Suzuki, A. *Synlett* **1990**, 221. (c) Saá, J. M.; Martorell, G. *J. Org. Chem.* **1993**, *58*, 1963.

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Scheme 1

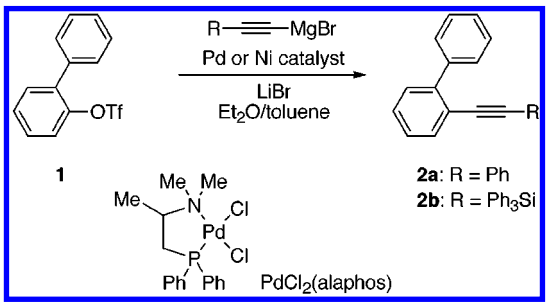


Table 1. Effects of Phosphine Ligands on the Cross-Coupling of Aryl Triflate 1 with the Alkynyl Grignard Reagents[a]

entry	catalyst[b]	Grignard	time (h)	yield (%) of **2**[c]
1	$PdCl_2$(alaphos)	PhC≡CMgBr	6	93 (**2a**)
2	$PdCl_2(PPh_3)_2$	PhC≡CMgBr	24	30 (**2a**)
3	$PdCl_2$(dppp)	PhC≡CMgBr	6	0 (**2a**)
4	$PdCl_2$(dppf)	PhC≡CMgBr	24	3 (**2a**)
5	$NiCl_2(PPh_3)_2$	PhC≡CMgBr	6	0 (**2a**)
6	$PdCl_2$(alaphos)	Ph_3SiC≡CMgBr	10	99 (**2b**)

[a] The cross-coupling was carried out with 2 equiv of Grignard reagent in the presence of 1 equiv of LiBr and 5 mol % of palladium catalyst in ether/toluene (3:1) at 30 °C. [b] The ligands, alaphos, dppp, and dppf stand for (2-dimethylamino)propyldiphenylphosphine, 1,3-bis(diphenylphosphino)propane, and 1,1′-bis(diphenylphosphino)ferrocene, respectively. [c] Isolated yield by silica gel chromatography.

present alkynylation of 4-bromophenyl triflate (**3**) with phenylethynylmagnesium bromide catalyzed by $PdCl_2$(alaphos), it was found that the triflate group is selectively replaced by the alkynyl group (Scheme 2). Thus, the reaction of **3** with 2 equiv of phenyethynylmagnesium bromide in the presence of 1 equiv of lithium bromide and 5 mol % of $PdCl_2$(alaphos) at 20 °C for 3 h gave a 96% yield of 1-bromo-4-(phenylethynyl)benzene (**4a**) together with a small amount (2%) of 1,4-di(phenylethynyl)benzene (**6a**) (entry 1 in Table 2). None of 1-phenylethynyl-4-trifluoromethanesulfonyloxybenzene (**5a**), which would be formed by the alkynylation of bromide, was

Scheme 2

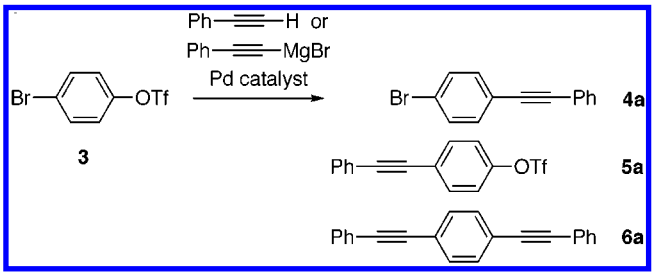


Table 2. Palladium-Catalyzed Cross-Coupling of 4-Bromophenyl Triflate (3) with (Phenylethynyl)magnesium Bromide or Phenylethyne

entry	catalyst	reagent (equiv)	time (h)	recovd (%)[a] **3**	yield (%)[a] of **4a**	**5a**	**6a**
1[b]	$PdCl_2$(alaphos)	PhC≡CMgBr (2)	3	0	96	0	2
2[b,c]	$PdCl_2$(alaphos)	PhC≡CMgBr (2)	3	5	92	0	2
3[d]	$PdCl_2(PPh_3)_2$	PhC≡CH (2)	40	10	8	73	8

[a] Isolated yield by silica gel chromatography. [b] The reaction was carried out in the presence of 1 equiv of LiBr and 5 mol % of palladium catalyst in ether/toluene (3:1) at 20 °C. [c] The reaction in the absence of LiBr. [d] The reaction was carried out in the presence of 10 mol % of CuI and 10 mol % of palladium catalyst in THF/Et_3N (4:1).

Scheme 3

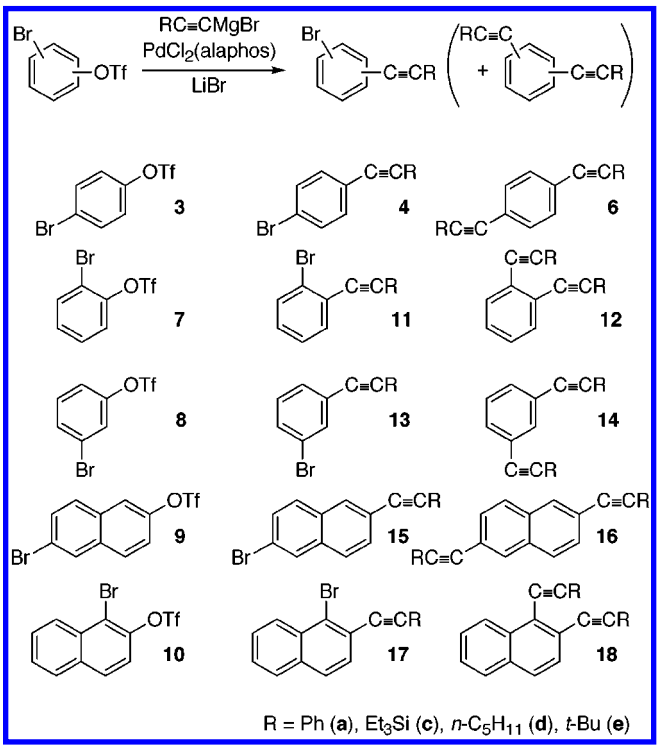


Table 3. Cross-Coupling of Bromoaryl Triflates with Alkynyl Grignard Reagents[a]

entry	triflate	R in RC≡CMgBr	temp (°C)	time (h)	yield (%)[b] of alkyne[c]	yield (%)[b] of diyne
1	**3**	Et_3Si	20	1	99 (**4c**)	2 (**6c**)
2	**3**	n-C_5H_{11}	30	12	92 (**4d**)	5 (**6d**)
3	**3**	t-Bu	30	20	90 (**4e**)	8 (**6e**)
4	**7**	Ph	20	4	92 (**11a**)	2 (**12a**)
5	**7**	Et_3Si	30	4	91 (**11c**)	3 (**12c**)
6	**8**	Ph	20	1	99 (**13a**)	0
7	**8**	Et_3Si	20	1	93 (**13c**)	2 (**14c**)
8	**9**	Ph	20	12	95 (**15a**)	2 (**16a**)
9	**9**	Et_3Si	20	4	92 (**15c**)	5 (**16c**)
10	**10**	Ph	40	4	94 (**17a**)	0
11	**10**	Et_3Si	40	6	90 (**17c**)	5 (**18c**)

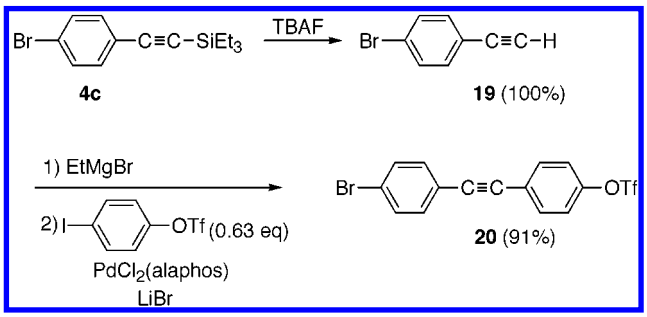
[a] The reaction was carried out with 2 equiv of Grignard reagent in the presence of 1 equiv of LiBr and 5 mol % of palladium catalyst in ether/toluene (3:1). In no cases were starting materials or alkynylarene triflates detected. [b] Isolated yield by silica gel chromatography. [c] Monoalkynylation product at triflate.

detected at all. In the absence of lithium bromide, the alkynylation was slower but the selectivity in forming **4a** was kept high (entry 2), indicating that lithium bromide is not responsible for the high triflate selectivity.[16] Under the standard Sonogashira conditions,[3,4] preferential substitution of bromide was observed, though the selectivity was lower (entry 3).

In the presence of $PdCl_2$(alaphos) as catalyst, 4-bromophenyl triflate (**3**) underwent the selective replacement of the triflate group by several alkynyl Grignard reagents to give the corresponding monoalkynylation products **4** in high yields together with a minor amount of dialkynylation products **6** (entries 1−3 in Table 3). The selective substitution of triflate with an alkynyl group was also successful in the reaction of benzene and

(14) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810.
(15) Kamikawa, T.; Hayashi, T. *Tetrahedron Lett.* **1997**, *38*, 7087.
(16) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531.

Scheme 4



naphthalene derivatives bearing both triflate and bromide (**7**−**10**). The triflate selectivities are all high, with monoalkynylation products at triflate, namely, alkynylarene bromides, being obtained in over 90% isolated yields. Monoalkynylation products resulting from replacement of bromide were not observed in any case.

The monoalkynylation product, 1-bromo-4-(triethylsilylethynyl)benzene (**4c**), obtained selectively by the reaction of **3** with the triethylsilylethynyl Grignard reagent in the presence of $PdCl_2$(alaphos), was converted into terminal acetylene **19** by desilylation with tetrabutylammonium fluoride, and it was submitted to the second cross-coupling. The alkynyl Grignard reagent generated from **19** was allowed to react with 4-iodophenyl triflate by use of $PdCl_2$(alaphos) as a catalyst. Selective substitution of iodide took place to give 1-(4-bromophenyl)-2-[(4-trifluoromethanesulfonyloxy)phenyl]ethyne (**20**) with high selectivity. These results indicate that the order of reactivity of the leaving groups on an aromatic ring is iodide > triflate > bromide in the Grignard cross-coupling catalyzed $PdCl_2$(alaphos). The present selective alkynylation method provides an efficient route to various types of conjugated aromatic compounds substituted with alkynyl groups.

Experimental Section

Materials. PPh_3, dppf, and dppp from Aldrich Chemical Co., Inc., were commercially available. Palladium complex $PdCl_2$(alaphos) was prepared according to the reported procedures.[12] Aryl triflates were prepared by triflation of phenols with triflluoromethanesulfonic anhydride and pyridine. Ether and toluene were distilled from sodium benzophenone ketyl under nitrogen.

Synthesis of Alkynylmagnesium Bromide. Typical Procedure. To a solution of phenylacetylene (510 mg, 4.99 mmol) in 1.4 mL of toluene was added ethylmagnesium bromide (2.7 mL, 2 M ether solution, 5.5 mmol). The mixture was heated at 50 °C for 30 min. Other alkynylmagnesium bromides were prepared in a similar manner.

Grignard Cross-Coupling of Aryl Triflates (1) with Alkynyl Grignard Reagents Catalyzed by $PdCl_2$(alaphos). Typical Procedure. To a mixture of triflate **1** (60.4 mg, 0.2 mmol), dichloro[(2-dimethylamino)propyldiphenylphosphine]-palladium ($PdCl_2$(alaphos)) (4.4 mg, 0.01 mmol), and lithium bromide (17.2 mg, 0.2 mmol) in 100 μL of ether was added (phenylethynyl)magnesium bromide (290 μL, 1.4 M, 0.4 mmol) in ether/toulene (2/1) at room temperature, and the mixture was stirred at 30 °C until **1** was not detected by silica gel TLC (hexane/benzene = 3/1). The reaction mixture was quenched with water and extracted with 100 mL of ether. Combined ether extracts were washed with brine (2 × 20 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane/benzene = 3/1) to give 44.6 mg (93% yield) of 2-phenylethynylbiphenyl (**2a**). The reaction conditions and results are summarized in Table 1.

Sonogashira Reaction of Bromophenyl Triflate (3) with Phenylacetylene Catalyzed by $PdCl_2(PPh_3)_2$. To a mixture of bromophenyl triflate (**3**) (60.4 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.020 mmol), copper(I) iodide (3.8 mg, 0.020 mmol), and 0.25 mL of triethylamine in 1 mL of THF was added phenylacetylene (32 μL, 0.29 mmol), and the mixture was stirred at 40 °C for 12 h. The mixture was quenched with 10% hydrochloric acid and extracted with 100 mL of ethyl acetate. The organic layer was washed with brine (2 × 20 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give 47.6 mg (73% yield) of 4-trifluoromethanesulfonyloxy(phenylethynyl)benzene (**5a**), 4.1 mg (8% yield) of 4-phenylethynylbromobenzene (**4a**), and 4.4 mg (8% yield) of 1,4-di(phenylethynyl)benzene (**6a**).

Grignard Cross-Coupling of Bromoaryl Triflates with Alkynyl Grignard Reagents Catalyzed by $PdCl_2$(alaphos). Grignard cross-goupling of bromoaryl triflates with alkynyl Grignard reagents catalyzed by $PdCl_2$(alaphos) was carried out in a manner similar to that of aryl triflate **1** shown above. The results are summarized in Tables 2 and 3.

Spectral and analytical data for the alkynylation products are shown below. **2-Phenylethynylbiphenyl (2a):**[17] ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.25−7.49 (m, 11 H), 7.63−7.68 (m, 3H). **2-Triphenylsilylethynylbiphenyl (2b):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28−7.42 (m, 17 H), 7.53 (dd, J = 1.5, 7.8 Hz, 6H), 7.71 (d, J = 7.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 92.10, 109.09, 121.17, 126.92, 127.40, 127.86, 129.15, 129.35, 129.45, 129.74, 133.52, 133.70, 135.53, 135.96, 140.26, 144.74. Anal. Calcd for $C_{32}H_{24}Si$: C, 88.03; H, 5.54. Found: C, 87.83; H, 5.57. **4-Phenylethynylbromobenzene (4a):**[18] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 (s, 7H), 7.39 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 7.52 (s, 2H). **4-Trifluoromethanesulfonyloxy(phenylethynyl)benzene (5a):** mp 55 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27−7.61 (m, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 87.30, 91.27, 118.73 (q, J = 318.8 Hz), 121.47, 122.52, 124.01, 128.44, 128.79, 131.67, 133.37, 148.89; EI-MS m/z, 326 (M^+, 27), 193 (100). Anal. Calcd for $C_{15}H_9O_3F_3S$: C, 55.22; H, 2.78. Found: C, 55.52; H, 2.77. **1,4-Di(phenylethynyl)benzene (6a):**[19] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.36 (m, 6H), 7.50−7.54 (m, 8H). **4-(Triethylsilylethynyl)-bromobenzene (4c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.67 (q, J = 7.9 Hz, 6H), 1.04 (t, J = 7.9 Hz, 9H), 7.32 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.38, 7.46, 93.76, 104.86, 123.25, 131.79; EI-MS m/z, 296 (M^+ + 2, 11), 294 (M^+, 11), 209 (100). Anal. Calcd for $C_{14}H_{19}BrSi$: C, 56.94; H, 6.49. Found: C, 57.11; H, 6.60. **1,4-Bis-(triethylsilylethynyl)benzene (6c):** mp 36−38 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.67 (q, J = 8.3 Hz, 12H), 1.04 (t, J = 8.3 Hz, 18H), 7.38 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.38, 7.46, 93.76, 105.86, 123.25, 131.79; EI-MS m/z, 354 (M^+, 25), 325 (100). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.25; H, 9.92. **4-Heptynylbromobenzene (4d):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, J = 7.0 Hz, 3H), 1.37 (sextet, J = 7.0 Hz, 2H), 1.43 (tt, J = 7.0, 7.5 Hz, 2H), 1.60 (quint, J = 7.0 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 7.29 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.97, 19.40, 22.21, 28.33, 31.11, 79.55, 91.78, 121.50, 123.10, 131.39, 133.01; EI-MS m/z, 252 (M^+ + 2, 26), 250 (M^+, 26), 116 (100). Anal. Calcd for $C_{13}H_{15}Br$: C, 62.17; H, 6.02. Found: C, 62.38; H, 6.07. **1,4-Diheptynylbenzene (6d):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, J = 7.0 Hz, 6H), 1.37 (sextet, J = 7.0 Hz, 4H), 1.43 (tt, J = 7.0, 7.5 Hz, 4H), 1.60 (quint, J = 7.0 Hz, 4H), 2.38 (t, J = 7.5 Hz, 4H), 7.24 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.97, 19.43, 22.21, 28.41, 31.11, 80.36, 91.92, 123.17, 131.31; EI-MS m/z, 266 (M^+, 85), 141 (100). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.33; H, 9.93. **4-(*tert*-Butylethynyl)bromobenzene (4e):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 (s, 9H), 7.23 (d, J = 8.3 Hz, 2H), 7.39 (d, J =

(17) Bookham, J. L.; Smithies, D. M.; Wright, A.; Thornton-Pett, M.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1998**, 811.
(18) Hellwinkel, D.; Fritsch, H. *Chem. Ber.* **1989**, *122*, 2315.
(19) Nakatsuji, S.; Matsuda, K.; Uesugi, Y.; Nakashima, K.; Akiyama, S.; Fabin, W. *J. Chem. Soc., Perkin Trans. 1* **1992**, 755.

8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.95, 30.92, 78.07, 99.71, 121.42, 123.07, 131.29, 133.02; EI-MS *m*/*z*, 238 (M^+ + 2, 30), 236 (M^+, 32), 142 (100). Anal. Calcd for $C_{12}H_{13}Br$: C, 60.78; H, 5.53. Found: C, 60.57; H, 5.53. **1,4-Di(*tert*-Butylethynyl)benzene (6e):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 (s, 18H), 7.28 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.97, 30.98, 78.90, 99.81, 123.05, 131.28; EI-MS *m*/*z*, 238 (M^+, 55), 223 (100). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.70; H, 9.53. **2-(Phenylethynyl)bromobenzene (11a):**[20] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38−7.63 (m, 6H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H). **1,2-Di(phenylethynyl)benzene (12a):**[21] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35−7.37 (m, 7H), 7.51−7.54 (m, 7H). **2-(Triethylsilylethynyl)bromobenzene (11c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.70 (q, *J* = 8.0 Hz, 6H), 1.07 (t, *J* = 8.0 Hz, 9H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.38, 7.50, 97.26, 104.11, 125.46, 125.74, 126.82, 129.43, 132.33, 133.73; EI-MS *m*/*z*, 296 (M^+ + 2, 6), 294 (M^+, 5), 267 (100). Anal. Calcd for $C_{14}H_{19}BrSi$: C, 56.94; H, 6.49. Found: C, 56.93; H, 6.42. **1,2-Bis(triethylsilylethynyl)-benzene (12c):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (q, *J* = 8.0 Hz, 12H), 1.06 (t, *J* = 8.0 Hz, 18H), 7.23 (dd, *J* = 2.5, 6.5 Hz, 2H), 7.47 (dd, *J* = 2.5, 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.43, 7.56, 95.86, 104.59, 125.75, 127.88, 132.89; EI-MS *m*/*z*, 354 (M^+, 28), 297 (100). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.44; H, 9.91. **3-(Phenylethynyl)-bromobenzene (13a):**[22] ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.02−7.53 (m, 8H), 7.69 (s, 1H). **3-(Triethylsilylethynyl)bromobenzene (13c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.67 (q, *J* = 7.8 Hz, 6H), 1.04 (t, *J* = 7.8 Hz, 9H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.61 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.35, 7.45, 93.42, 104.54, 122.00, 125.33, 129.59, 130.53, 131.51, 134.74; EI-MS *m*/*z*, 296 (M^+ + 2, 5), 294 (M^+, 5), 129 (100). Anal. Calcd for $C_{14}H_{19}BrSi$: C, 56.94; H, 6.49. Found: C, 57.17; H, 6.60. **1,3-Bis(triethylsilylethynyl)benzene (14c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.67 (q, *J* = 7.8 Hz, 12H), 1.04 (t, *J* = 7.8 Hz, 18H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 1.5, 8.0 Hz, 2H), 7.57 (t, *J* = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.38, 7.48, 92.36, 105.35, 123.53, 128.13, 131.85, 135.40; EI-MS *m*/*z*, 354 (M^+, 11), 325 (100). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.51; H, 9.80. **2-Bromo-6-(phenylethynyl)-naphthalene (15a):** mp 131−133 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.34−7.37 (m, 2H), 7.54−7.57 (m, 3H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.72 (t, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 89.36, 90.35, 120.68, 121.12, 123.07, 127.06, 128.39, 128.44, 129.31, 129.48, 129.84, 129.96, 131.23, 131.41, 131.65, 133.70; EI-MS *m*/*z*, 308 (M^+ + 2, 100), 306 (M^+, 99). Anal. Calcd for $C_{18}H_{11}Br$: C, 70.38; H, 3.61. Found: C, 70.09; H, 3.39. **2,6-Di(phenylethynyl)naphthalene (16a):** mp 200−201 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.40 (m, 6H), 7.52−7.61 (m, 6H), 7.79 (d, *J* = 8.5 Hz, 2H), 8.03 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 89.63, 90.47, 121.44, 123.17, 127.83, 128.41, 129.17, 131.19, 131.69, 131.72, 132.38. Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.69; H, 4.94. **2-Bromo-6-(triethylsilylethynyl)naphthalene (15c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.71 (q, *J* = 8.0 Hz, 6H), 1.07 (t, *J* = 8.0 Hz, 8H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 7.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.43, 7.50, 92.86, 106.19, 120.71, 121.16, 126.87, 129.28, 129.81, 129.92, 131.28, 131.79, 133.57; EI-MS *m*/*z*, 346 (M^+ + 2, 27), 344 (M^+, 26), 259 (100). Anal. Calcd for $C_{18}H_{21}BrSi$: C, 62.60; H, 6.13. Found: C, 62.47; H, 6.10. **2,6-Bis(triethylsilylethynyl)naphthalene (16c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.71 (q, *J* = 7.5 Hz, 12H), 1.07 (t, *J* = 7.5 Hz, 8H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.94 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.45, 7.51, 92.91, 106.44, 121.45, 127.62, 129.41, 131.70, 132.28; EI-MS *m*/*z* 404 (M^+, 31), 117 (100). Anal. Calcd for $C_{26}H_{36}Si_2$: C, 77.16; H, 8.97. Found: C, 76.90; H, 9.09. **1-Bromo-2-(phenylethynyl)naphthalene (17a):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.18−7.35 (m, 6H), 7.58 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 89.36, 90.35, 120.69, 121.16, 123.08, 127.07, 128.41, 128.46, 129.35, 129.51, 129.86, 129.99, 131.24, 131.44, 131.61, 133.73; EI-MS *m*/*z*, 306 (M^+ + 2, 98), 304 (M^+, 100). Anal. Calcd for $C_{18}H_{11}Br$: C, 70.38; H, 3.61. Found: C, 70.17; H, 3.38. **1-Bromo-2-(triethylsilylethynyl)naphthalene (17c):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (q, *J* = 8.0 Hz, 6H), 1.09 (t, *J* = 8.0 Hz, 9H), 7.51 (t, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.43, 7.56, 98.21, 105.40, 123.50, 126.71, 127.12, 127.29, 127.80, 127.90, 128.13, 129.35, 132.17, 133.67; EI-MS *m*/*z*, 346 (M^+ + 2, 27), 344 (M^+, 26), 179 (100). Anal. Calcd for $C_{18}H_{21}BrSi$: C, 62.60; H, 6.13. Found: C, 62.37; H, 6.09. **1,2-Bis(triethylsilylethynyl)naphthalene (18c):** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.72 (q, *J* = 8.0 Hz, 6H), 0.78 (q, *J* = 8.0 Hz, 6H), 1.09 (t, *J* = 8.0 Hz, 9H), 1.13 (t, *J* = 8.0 Hz, 9H), 7.50 (t, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.57 (t, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.48, 4.56, 7.63, 7.71, 97.09, 102.23, 102.50, 105.60, 123.74, 124.39, 126.59, 126.87, 127.32, 128.06, 129.07, 132.40, 133.42; EI-MS *m*/*z*, 404 (M^+, 100). Anal. Calcd for $C_{26}H_{36}Si_2$: C, 77.16; H, 8.97. Found: C, 76.93; H, 9.12.

4-Ethynylbromobenzene (19). To a solution of 4-(triethylsilylethynyl)bromobenzene (**5c**) (200 mg, 0.738 mmol) in 2 mL of THF was added aqueous tetrabutylammonium fluoride (0.5 mL) at room temperature. The reaction mixture was stirred for 30 min and then concentrated under reduced pressure and extracted with 100 mL of ether. The organic layer was washed with water (2 × 50 mL), dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give 75 mg (quantitative yield) of **19**:[23] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.12 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H).

1-(4-Bromophenyl)-2-[(4-trifluoromethanesulfonyloxy)-phenyl]ethyne (20). To a solution of **19** (36.2 mg, 0.20 mmol) in 100 mL of ether and 100 mL of toluene was added ethylmagnesium bromide (1.6 M, 130 mL, 0.21 mmol) at room temperature, and the mixture was stirred at 50 °C for 30 min. To a mixture of 4-iodophenyl triflate (41 mg, 0.12 mmol), lithium bromide (10 mg, 0.12 mmol), and $PdCl_2$(alaphos) (2.4 mg, 0.006 mmol) was added the Grignard reagent. The mixture was stirred at 30 °C for 2 h, quenched with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give 44.3 mg (91% yield) of **20**: mp 152−153 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 88.39, 90.15, 118.73 (q, *J* = 321.3 Hz), 121.57, 123.13, 123.66, 130.47, 131.75, 133.07, 133.40, 149.06; EI-MS *m*/*z* 406 (M^+ + 2, 20), 404 (M^+, 21), 271 (100). Anal. Calcd for $C_{24}H_{17}O_3BrF_3S$: C, 44.46; H, 1.99. Found: C, 44.42; H, 1.91.

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(20) Mulvaney, J. E.; Carr, L. J. *J. Org. Chem.* **1968**, *33*, 3286.
(21) John, J. A.; Tour, J. M. *Tetrahedron* **1997**, *53*, 15515.
(22) Martelli, G.; Spagnolo, P.; Tiecco, M. *J. Chem. Soc. B* **1970**, 1413.
(23) Okuhara, K.; *J. Org. Chem.* **1976**, *41*, 1487.