Synthesis of Tri- and Diaryloxybenzenes by Rhodium-Catalyzed Complete Intermolecular [2+2+2] Cycloaddition of Aryl Ethynyl Ethers

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Abstract: We have established that a cationic rhodium(I)–H_8-BINAP complex catalyzes the complete intermolecular homo-[2+2+2] cycloaddition of aryl ethynyl ethers and cross-[2+2+2] cycloaddition of aryl ethynyl ethers with electron-deficient monoalkynes, leading to tri- and diaryloxybenzenes, respectively, at room temperature.

Key words: alkynes, aryl ethynyl ethers, [2+2+2] cycloaddition, H_8-BINAP, rhodium

The transition-metal-catalyzed complete intermolecular [2+2+2] cycloaddition of monoalkynes has been widely examined for the atom economical and convergent synthesis of substituted benzenes.[1] Electronically and sterically diverse arrays of monoalkynes have been employed for this reaction, while alkynyl ethers have been scarcely examined despite of their potential utility for the synthesis of aryl ethers.[2–7] An iron carbonyl complex is able to mediate the homo-[2+2+2] cycloaddition of an alkynyl ether, but a reported substrate is limited to di-*tert*-butoxyacetylene.[2] The regioselective cross-[2+2+2] cycloadditions of cyclohexyl trimethylsilylethynyl ether with ethynyl tolyl sulfone[3] and ethyl ethynyl ether with 3-hexyne[4] were reported, but these reactions require a stoichiometric amount of a titanium or zirconium complex. On the other hand, our research group recently reported the rhodium-catalyzed complete intermolecular cross-[2+2+2] cycloaddition of aryl ethynyl ethers with nitriles or isocyanates, leading to substituted diaryloxypyridines or diaryloxy-2-pyridones, respectively.[8,9] In this paper, we describe the rhodium-catalyzed complete intermolecular homo-[2+2+2] cycloaddition of aryl ethynyl ethers and cross-[2+2+2] cycloaddition of aryl ethynyl ethers with electron-deficient internal monoalkynes, leading to tri- and diaryloxybenzenes,[10] respectively, at room temperature (Scheme 1).

We first investigated the homo-[2+2+2] cycloaddition of ethynyl 2-naphthyl ether (**1a**)[11] in the presence of the cationic rhodium(I)–BIPHEP complex (10 mol%) as a catalyst. Pleasingly, the desired homo-[2+2+2] cycloaddition proceeded at room temperature for only 1 hour to give 1,3,5- and 1,2,4-triaryloxybenzenes **2a** and **3a** in good yield (Table 1, entry 1). The effect of biaryl bisphosphine ligands was then examined (entries 1–4), which revealed that the use of H_8-BINAP (Figure 1) furnished **2a** and **3a** in the highest yield, and 1,3,5-triaryloxybenzene **2a** was

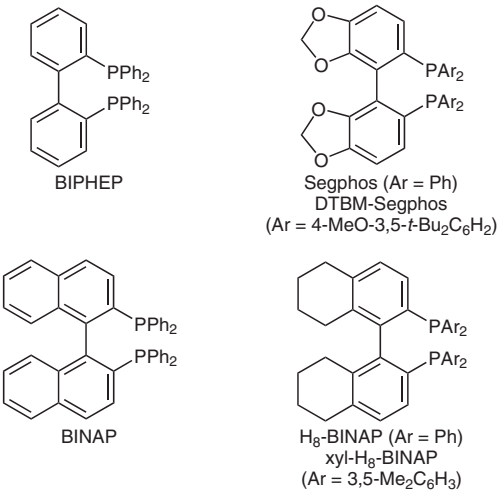
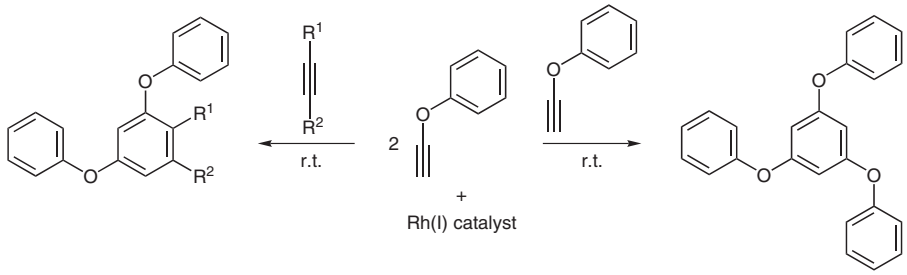


Figure 1



Scheme 1

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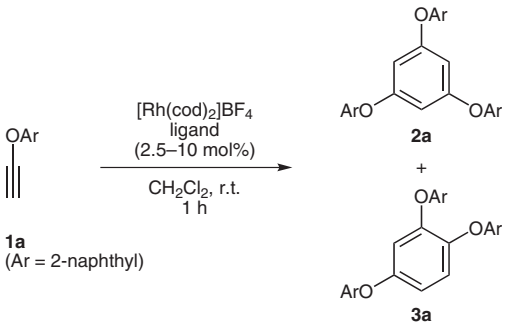
Table 1 Screening of Ligands for Rh-Catalyzed Homo-[2+2+2] Cycloaddition of Aryl Ethynyl Ether **1a**



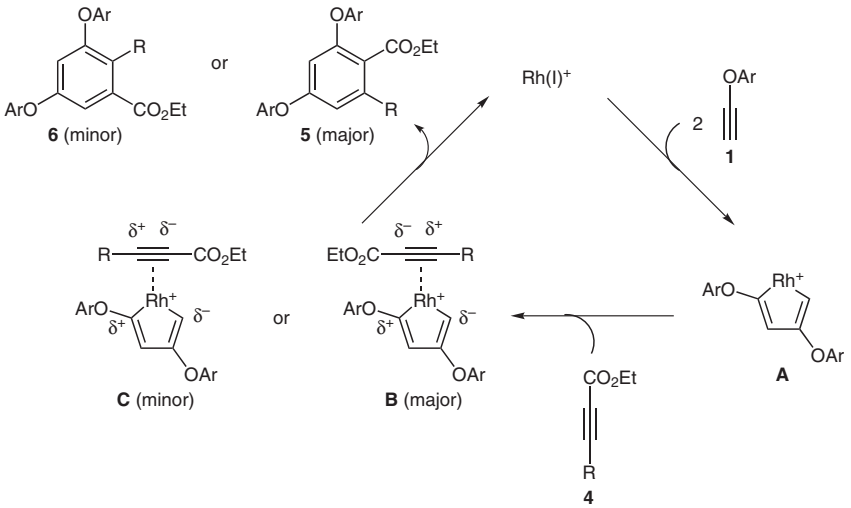
Entry	Ligand	Catalyst (mol%)	Yield (%)[a]	**2a/3a**[b]
1	BIPHEP	10	75	48:52
2	Segphos	10	74	47:53
3	BINAP	10	72	58:42
4	H_8-BINAP	10	92	63:37
5	xyl-H_8-BINAP	10	73	41:59
6	DTBM-Segphos	10	57	44:56
7	H_8-BINAP	5	85	60:40
8	H_8-BINAP	2.5	78	62:38

[a] Isolated yield.
[b] Determined by ^{1}H NMR.

obtained as a major regioisomer (entry 4). The use of sterically demanding biaryl bisphosphine ligands decreased the product yields (entries 5 and 6). The catalyst loading could be reduced to 5 mol% or 2.5 mol% with slight loss of the product yield (entries 7 and 8).

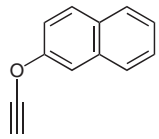
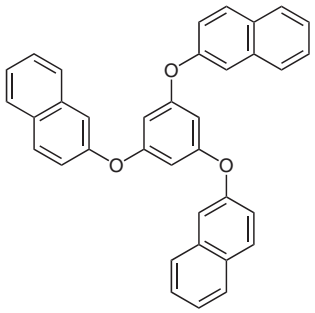
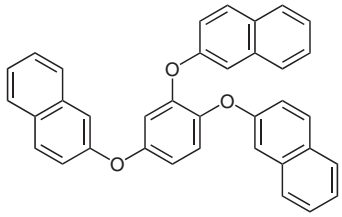
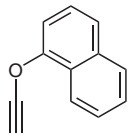
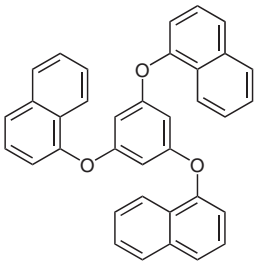
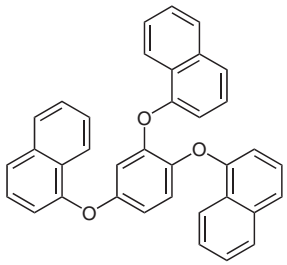
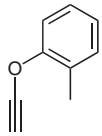
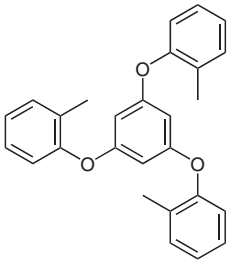
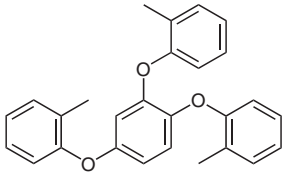
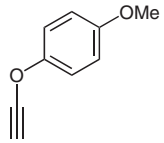
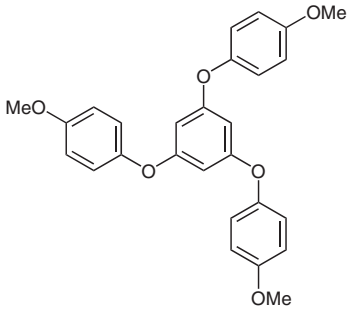
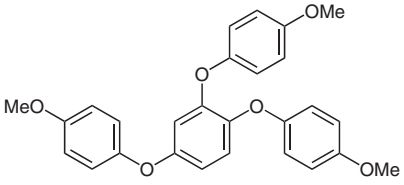
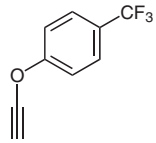
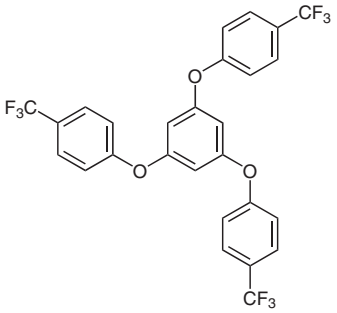
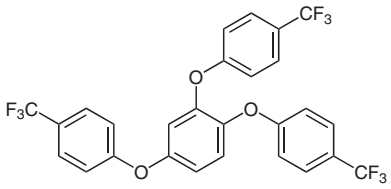
The scope of the triaryloxybenzene synthesis was then examined under the above optimal reaction conditions (Table 2).[12] Not only ethynyl 2-naphthyl ether (**1a**, entry 1) but also sterically and electronically diverse aryl ethynyl ethers **1b–e** could be employed for this reaction to give the corresponding triaryloxybenzenes in good to high yields (entries 2–5). The reaction of sterically demanding ethynyl 2-methylphenyl ether (**1c**, entry 3) improved the regioselectivity of 1,3,5-triaryloxybenzene **2c** over 1,2,4-triaryloxybenzene **3c**. Although regioselectivities of the present homo-[2+2+2] cycloaddition reactions of aryl ethynyl ethers **1a–e** were moderate, two regioisomers could be readily separated by a silica gel chromatography.

Our research group reported that the cationic rhodium(I)–H_8-BINAP complex catalyzes the complete intermolecular cross-[2+2+2] cycloaddition of electron-rich terminal monoalkynes with highly electron-deficient internal monoalkynes (dialkyl acetylenedicarboxylates) to give 3,6-disubstituted phthalates in high yields with excellent regioselectivity.[13,14] In a previous report, we attempted the complete intermolecular cross-[2+2+2] cycloaddition of ethynyl 2-naphthyl ether (**1a**) with diethyl acetylenedicarboxylate in the presence of the cationic rhodium(I)–H_8-BINAP catalyst, however, the desired 3,6-diaryloxyphthalate was obtained in very low yield.[8] Thus moderately electron-deficient internal monoalkynes [ethyl 2-butynoate (**4a**)] was used instead of diethyl acetylenedicarboxylate. Pleasingly, the desired cross-[2+2+2] cycloaddition proceeded at room temperature for one hour to give diaryloxybenzenes **5aa** and **6aa** with moderate yield and regioselectivity (Table 3, entry 1). Importantly, regioisomeric diaryloxybenzenes **7aa** and **8aa** were not detected at all in the crude reaction mixture. In the present cross-[2+2+2] cycloaddition, the use of H_8-BINAP as a ligand is of critical importance. The use of BINAP, Segphos, and BIPHEP dramatically decreased the yield of diaryloxybenzenes **5aa** and **6aa** due to the rapid homo-[2+2+2] cycloaddition of **1a** (entries 2–4). Increasing the amount of **4a** to 1.0 equivalent significantly increased the yield of **5aa** and **6aa**, while further increase the amount of **4a** to 2.0 equivalents furnished **5aa** and **6aa** in only slight improved yield.



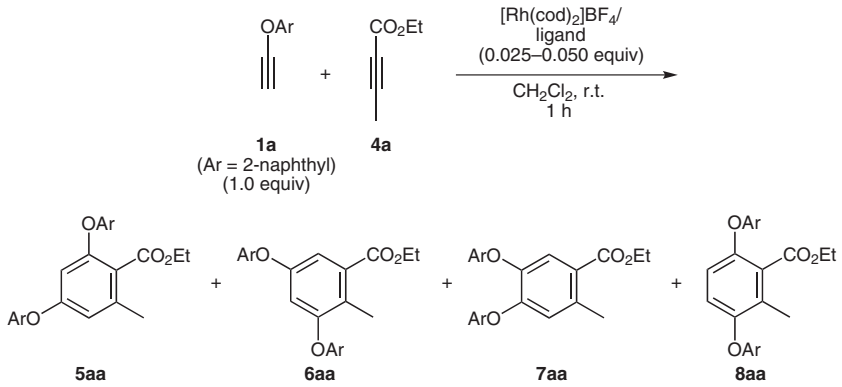
Scheme 2

Table 2 Synthesis of Triaryloxybenzenes **2** and **3** by Rh-Catalyzed Homo-[2+2+2] Cycloaddition of Aryl Ethynyl Ethers **1a–e**[a]

Entry	**1**	Yield of **2** (%)[b]	Yield of **3** (%)[b]
1	 **1a**	 **2a** 51	 **3a** 34
2	 **1b**	 **2b** 40	 **3b** 26
3	 **1c**	 **2c** 46	 **3c** 16
4	 **1d**	 **2d** 51	 **3d** 25
5	 **1e**	 **2e** 54	 **3e** 35

[a] Reactions were conducted using **1a–e**, $[Rh(cod)_2BF_4$ (5 mol%), H_8-BINAP (5 mol%) in CH_2Cl_2 at r.t. for 1 h.
[b] Isolated yield.

Table 3 Screening of Ligands for Rh-Catalyzed Cross-[2+2+2] Cycloaddition of Aryl Ethynyl Ether **1a** with Electron-Deficient Internal Monoalkyne **4a**



Entry	Ligand	**4a** (equiv)	Rh (equiv)	Yield (%)[a]	**5aa/6aa/7aa/8aa**[b]
1	H_8-BINAP	0.5	0.025	40	73:27:0.0
2	BINAP	0.5	0.050	8	76:24:0.0
3	Segphis	0.5	0.050	3	70:30:0.0
4	BIPHEP	0.5	0.050	4	67:33:0.0
5	H_8-BINAP	1.0	0.025	81	74:26:0.0
6	H_8-BINAP	2.0	0.025	83	73:27:0.0

[a] Isolated yield of **5**–**8**.
[b] Determined by ^{1}H NMR.

Table 4 Synthesis of Diaryloxybenzenes **5** and **6** by Rh-Catalyzed Cross-[2+2+2] Cycloaddition of Aryl Ethynyl Ethers **1a**–**e** with Electron-Deficient Internal Monoalkynes **4a**–**c**[a]

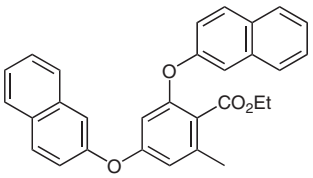
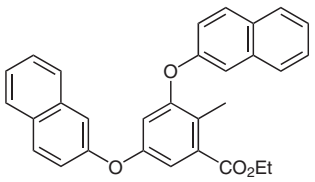
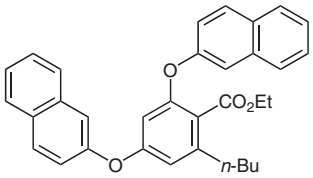
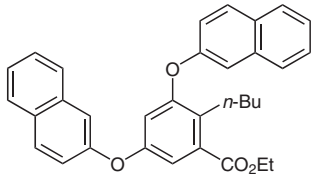
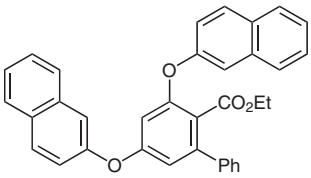
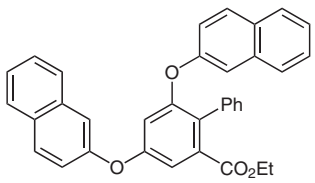
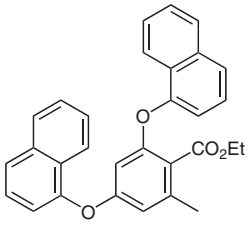
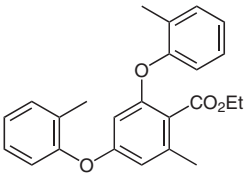
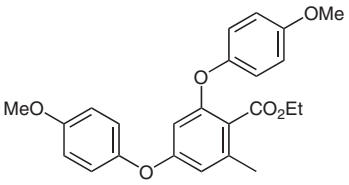
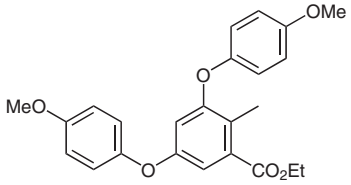
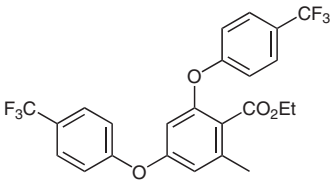
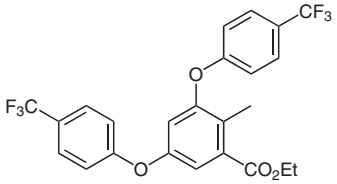
Entry	**1**	**4**	Yield of **5** and **6** (%)[b]	
1	**1a**	 **4a**	 **5aa** 60	 **6aa** 21
2	**1a**	 **4b**	 **5ab** 45	 **6ab** 10
3	**1a**	 **4c**	 **5ac** 42[c] (**5ac**/**6ac** = 87:13)	 **6ac**

Table 4 Synthesis of Diaryloxybenzenes **5** and **6** by Rh-Catalyzed Cross-[2+2+2] Cycloaddition of Aryl Ethynyl Ethers **1a–e** with Electron-Deficient Internal Monoalkynes **4a–c**[a] (continued)

Entry	1	4	Yield of **5** and **6** (%)[b]
4	**1b**	 **4a**	 **5ba** 37
5	**1c**	 **4a**	 **5ca** 19
6	**1d**	 **4a**	 **5da** 46  **6da** 24
7	**1e**	 **4a**	 **5ea** 54  **6ea** 25

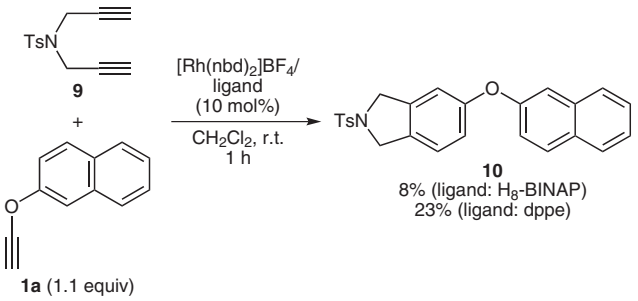
[a] Reactions were conducted using **1a–e** (1.0 equiv), **4a–c** (1.0 equiv), $[Rh(cod)_2BF_4$ (0.025 equiv), H_8-BINAP (0.025 equiv) in CH_2Cl_2 at r.t. for 1 h.
[b] Isolated yield.
[c] Isolated as a mixture of **5ac** and **6ac**.

The scope of the diaryloxybenzene synthesis was then examined under the above optimal reaction conditions (Table 4).[15] Not only ethyl 2-butynoate (**4a**, entry 1) but also sterically demanding ethyl 2-heptynoate (**4b**, entry 2) and ethyl phenylpropiolate (**4c**, entry 3) could be employed for this reaction to give the corresponding diaryloxybenzenes in moderate to good yields with improved regioselectivity of **5** over **6** (entries 2 and 3). With respect to aryl ethynyl ethers, the use of sterically demanding ethynyl 1-naphthyl ether (**1b**, entry 4) and ethynyl 2-methylphenyl ether (**1c**, entry 5) furnished the corresponding diaryloxybenzenes **5ba** and **5ca**, respectively, with excellent regioselectivity, although the product yields decreased. On the other hand, electronic nature of aryl ethynyl ethers showed a small impact on both the product yields and regioselectivity (entries 6 and 7).

Scheme 2 depicts a possible mechanism for the rhodium-catalyzed complete intermolecular cross-[2+2+2] cycloaddition of aryl ethynyl ethers **1** with electron-deficient internal monoalkynes **4**. The regioselective oxidative coupling of two aryl ethynyl ethers **1** with rhodium forms rhodacyclopentadiene intermediate **A**. Subsequent regioselective coordination of **4** with intermediate **A** forms intermediate **B** over intermediate **C**, which results in the observed regioselective formation of **5** over **6**. Although the chemoselective [2+2+2] cycloaddition between two molecules of **1** and one molecule of **4** is not clear, the regioselective formation of **5** over **6** might be electronic control. The C–C bond formation between electropositive alkyne carbon of **4** and the electronegative rhodacycle carbon α to rhodium exhibits the observed regioselectivity. The homo-[2+2+2] cycloaddition of **1**, leading to triaryloxybenzenes **2** and **3**, was the sole side reaction in the rhodium-catalyzed reaction between **1** and **4**, which supports the initial formation of rhodacyclopentadiene intermediate **A**.

Finally, the monoaryloxybenzene synthesis by the rhodium-catalyzed [2+2+2] cycloaddition of 1,6-diyne **9** with aryl ethynyl ether **1a** was also examined.[16] However, the cationic rhodium(I)–H_8-BINAP catalyst was ineffective

due to the rapid homo-[2+2+2] cycloaddition of **1a**. After screening phosphine ligands, the best result was obtained by using dppe [1,2-bis(diphenylphosphino)ethane] as a ligand, although the yield of the corresponding monoaryloxybenzene **10**[17] was still low (Scheme 3).



Scheme 3

In conclusion, we have established that a cationic rhodium(I)–H_8-BINAP complex catalyzes the complete intermolecular homo-[2+2+2] cycloaddition of aryl ethynyl ethers and cross-[2+2+2] cycloaddition of aryl ethynyl ethers with electron-deficient internal monoalkynes, leading to tri- and diaryloxybenzenes, respectively, at room temperature. Future studies will focus on the further utilization of aryl ethynyl ethers in rhodium-catalyzed reactions.

Acknowledgment

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References and Notes

(1) For recent reviews of the transition-metal-catalyzed [2+2+2] cycloaddition reactions, see: (a) Galan, B. R.; Rovis, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 2830. (b) Tanaka, K. *Chem. Asian J.* **2009**, *4*, 508. (c) Varela, J. A.; Saá, C. *Synlett* **2008**, 2571. (d) Shibata, T.; Tsuchikama, K. *Org. Biomol. Chem.* **2008**, 1317. (e) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085. (f) Agenet, N.; Buisine, O.; Slowinski, F.; Gandon, V.; Aubert, C.; Malacria, M. *Organic Reactions*, Vol. 68; RajanBabu, T. V., Ed.; John Wiley and Sons: Hoboken, **2007**, 1. (g) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307. (h) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209. (i) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741. (j) Gandon, V.; Aubert, C.; Malacria, M. *Curr. Org. Chem.* **2005**, *9*, 1699. (k) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503.

(2) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.

(3) Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2001**, *123*, 7925.

(4) Takahashi, T. JP 11263737, **1999**; *Chem. Abstr.* **1999**, *131*, 228541.

(5) For the transition-metal-mediated intermolecular [4+2]-benzannulation reactions using alkynyl ethers, see: (a) Darbasie, N. D.; Schnatter, W. F. K.; Warner, K. F.; Manolache, N. *Tetrahedron Lett.* **2006**, *47*, 963. (b) Dudley, G. B.; Takaki, K. S.; Cha, D. D.; Danheiser, R. L. *Org. Lett.* **2000**, *2*, 3407. (c) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 568. (d) Morris, K. G.; Saberi, S. P.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1993**, 209. (e) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093. (f) Danheiser, R. L.; Gee, S. K.; Perez, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 806.

(6) For the nickel-catalyzed complete intermolecular cross-[2+2+2] cycloaddition of two ethyl ethynyl ethers and carbon dioxide, see: (a) Tsuda, T.; Kunisada, K.; Nagahama, N.; Morikawa, S.; Saegusa, T. *Synth. Commun.* **1989**, *19*, 1575. (b) For the rhodium-catalyzed complete intermolecular cross-[2+2+2] cycloaddition of two ethyl ethynyl ethers with an isocyanate, see: Oberg, K. M.; Lee, E. E.; Rovis, T. *Tetrahedron* **2009**, *65*, 5056.

(7) For the nickel-catalyzed complete intermolecular cross-[3+2+2] cycloaddition of ethyl cyclopropylideneacetate, an internal 1,3-diyne, and an alkynyl ether, see: Yamasaki, R.; Terashima, N.; Sotome, I.; Komagawa, S.; Saito, S. *J. Org. Chem.* **2010**, *75*, 480.

(8) Komine, Y.; Tanaka, K. *Org. Lett.* **2010**, *12*, 1312.

(9) For the rhodium-catalyzed [2+2+2] cycloadditions of phenol-linked 1,6-diynes with alkynes and nitriles, leading to substituted dibenzofurans and azadibenzofurans, see: Komine, Y.; Kamisawa, A.; Tanaka, K. *Org. Lett.* **2009**, *11*, 2361.

(10) Tri- and diaryloxybenzenes are useful compounds in material sciences. For selected recent examples, see: (a) Pei, S.; Chen, X.; Jiang, Z.; Peng, W. *J. Appl. Polym. Sci.* **2010**, *117*, 2069. (b) Yamanaka, M.; Fujii, H. *J. Org. Chem.* **2009**, *74*, 5390. (c) Chen, X.; Zhang, Y.; Liu, B.; Zhang, J.; Wang, H.; Zhang, W.; Chen, Q.; Pei, S.; Jiang, Z. *J. Mater. Chem.* **2008**, *18*, 5019. (d) Rao, X.; Dang, G.; Zhou, H.; Yang, W.; Cui, G.; Chen, C.; Yokota, R. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4844.

(11) Aryl ethynyl ethers are stable compounds and can be readily handled and purified without any special precautions. For the synthesis of aryl ethynyl ethers **1a–e**, see ref. 8.

(12) **Typical Procedure (Table 2, Entry 1)**
Under an argon atmosphere, H_8-BINAP (6.3 mg, 0.010 mmol) and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (1.0 mL), and the mixture was stirred for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at r.t. for 0.5 h, the resulting mixture was concentrated to dryness. To a CH_2Cl_2 (0.5 mL) solution of the residue was added a CH_2Cl_2 (1.5 mL) solution of **1a** (67.3 mg, 0.400 mmol). The mixture was stirred at r.t. for 1 h. The resulting mixture was concentrated and purified on a preparative TLC (*n*-hexane–toluene = 4:1), which furnished **2a** (34.2 mg, 0.0678 mmol, 51% yield) and **3a** (23.0 mg, 0.0456 mmol, 34% yield).
Compound **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.76 (m, 6 H), 7.72–7.70 (m, 3 H), 7.47–7.35 (m, 9 H), 7.27–7.23 (m, 3 H), 6.53 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.6, 153.9, 134.2, 130.4, 130.0, 127.7, 127.2, 126.6, 125.0, 119.9, 115.0, 103.9. ESI-HRMS: *m/z* calcd for $C_{36}H_{24}O_3Na$ $[M + Na]^+$: 527.1618; found: 527.1635.
Compound **3a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84–7.64 (m, 9 H), 7.45–7.33 (m, 7 H), 7.30–7.13 (m, 6 H), 6.93–6.86 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 154.7, 154.6, 154.1, 149.0, 142.9, 134.22, 134.19, 134.10, 130.3, 130.1, 130.0, 129.9, 129.7, 129.6, 127.73, 127.68, 127.66, 127.13, 127.08, 127.00, 126.6, 126.45, 126.43, 124.9, 124.6, 124.4, 123.1, 119.7, 119.1, 118.8, 114.8, 114.1, 113.2, 112.5, 111.7. ESI-HRMS: *m/z* calcd for $C_{36}H_{24}O_3Na$ [M +

Na]$^+$: 527.1618; found: 527.1617.
Compound **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11–8.08 (m, 3 H), 7.84–7.81 (m, 3 H), 7.61–7.58 (m, 3 H), 7.51–7.44 (m, 6 H), 7.38–7.33 (m, 3 H), 7.07–7.05 (m, 3 H), 6.45 (s, 3 H).
Compound **3b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21–8.18 (m, 1 H), 8.00–7.97 (m, 1 H), 7.86–7.83 (m, 2 H), 7.74–7.69 (m, 2 H), 7.61–7.58 (m, 1 H), 7.51–7.49 (m, 4 H), 7.40–7.21 (m, 7 H), 7.16–7.14 (m, 1 H), 7.01–6.97 (m, 2 H), 6.92–6.90 (m, 2 H), 6.82–6.78 (m, 1 H).
Compound **2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.12 (m, 6 H), 7.07–7.01 (m, 3 H), 6.95–6.92 (m, 3 H), 6.12 (s, 3 H), 2.20 (s, 9 H).
Compound **3c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.18 (m, 1 H), 7.16–6.89 (m, 10 H), 6.81–6.78 (m, 1 H), 6.74–6.72 (m, 1 H), 6.60–6.56 (m, 2 H), 2.24 (s, 3 H), 2.05 (s, 3 H), 1.98 (s, 3 H).
Compound **2d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.98–6.94 (m, 6 H), 6.88–6.82 (m, 6 H), 6.19 (s, 3 H), 3.78 (s, 9 H).
Compound **3d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96–6.80 (m, 13 H), 6.61–6.54 (m, 2 H), 3.78 (s, 3 H), 3.77 (s, 6 H).
Compound **2e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.60 (m, 6 H), 7.12–7.10 (m, 6 H), 6.51 (s, 3 H).
Compound **3e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.61 (m, 2 H), 7.54–7.51 (m, 4 H), 7.23–7.20 (m, 1 H), 7.13–7.10 (m, 2 H), 6.95–6.90 (m, 6 H).

(13) (a) Tanaka, K.; Shirasaka, K. *Org. Lett.* **2003**, *5*, 4697. (b) Tanaka, K.; Toyoda, K.; Wada, A.; Shirasaka, K.; Hirano, M. *Chem. Eur. J.* **2005**, *11*, 1145.

(14) For our account of the cationic rhodium(I)–biaryl bisphosphine-complex-catalyzed [2+2+2]-cycloaddition reactions, see: Tanaka, K. *Synlett* **2007**, 1977.

(15) **Typical Procedure (Table 4, Entry 1)**
Under an argon atmosphere, H_8-BINAP (6.3 mg, 0.010 mmol) and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (1.0 mL), and the mixture was stirred for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at r.t. for 0.5 h, the resulting mixture was concentrated to dryness. To a CH_2Cl_2 (0.5 mL) solution of the residue and **4a** (44.9 mg, 0.400 mmol) was added a CH_2Cl_2 (1.5 mL) solution of **1a** (67.3 mg, 0.400 mmol). The mixture was stirred at r.t. for 1 h. The resulting mixture was concentrated and purified on a preparative TLC (*n*-hexane–EtOAc = 15:1), which furnished **5aa** (53.9 mg, 0.120 mmol, 60% yield) and **6aa** (18.5 mg, 0.0412 mmol, 21% yield).
Compound **5aa**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.77 (m, 4 H), 7.72–7.69 (m, 2 H), 7.47–7.37 (m, 4 H), 7.34–7.33 (m, 2 H), 7.27–7.23 (m, 1 H), 7.21–7.18 (m, 1 H), 6.66 (d, *J* = 1.8 Hz, 1 H), 6.56 (d, *J* = 1.8 Hz, 1 H), 4.28 (q, *J* = 7.1 Hz, 2 H), 2.38 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 158.92, 158.91, 155.6, 154.7, 153.8, 139.40, 139.38, 134.1, 130.4, 130.1, 130.0, 129.8, 127.7, 127.6, 127.1, 126.6, 126.5, 125.0, 124.7, 121.6, 119.8, 119.4, 115.3, 114.9, 113.9, 107.6, 61.2, 19.8, 14.1. ESI-HRMS: *m/z* calcd for $C_{30}H_{24}O_4Na$ [M + Na]$^+$: 471.1567; found: 471.1575.
Compound **6aa**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.77 (m, 4 H), 7.70–7.65 (m, 2 H), 7.47–7.34 (m, 5 H), 7.30 (d, *J* = 2.4 Hz, 1 H), 7.24–7.20 (m, 2 H), 7.13–7.12 (m, 1 H), 6.90 (d, *J* = 2.4 Hz, 1 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 2.48 (s, 3 H), 1.37 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 155.9, 155.2, 154.5, 134.23, 134.20, 133.6, 130.2, 130.08, 130.04, 129.9, 127.7, 127.1, 127.0, 126.8, 126.6, 124.8, 124.6, 119.5, 118.8, 116.5, 114.6, 113.9, 112.1, 61.2, 14.2, 12.9. ESI-HRMS: *m/z* calcd for $C_{30}H_{24}O_4Na$ [M + Na]$^+$: 471.1567; found: 471.1567.
Compound **5ab**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.77 (m, 4 H), 7.71–7.68 (m, 2 H), 7.46–7.32 (m, 6 H), 7.27–7.17 (m, 2 H), 6.69 (d, *J* = 1.8 Hz, 1 H), 6.54 (d, *J* = 1.8 Hz, 1 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 2.66 (t, *J* = 7.4 Hz, 2 H), 1.65–1.55 (m, 2 H), 1.43–1.30 (m, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 0.91 (t, *J* = 7.4 Hz, 3 H).
Compound **6ab**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.78 (m, 4 H), 7.70–7.68 (m, 2 H), 7.47–7.35 (m, 4 H), 7.31–7.30 (m, 2 H), 7.25–7.19 (m, 3 H), 6.84 (d, *J* = 2.7 Hz, 1 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 2.94 (t, *J* = 7.5 Hz, 2 H), 1.61–1.51 (m, 2 H), 1.47–1.35 (m, 5 H), 0.90 (t, *J* = 7.5 Hz, 3 H).
Compound **5ac**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.61 (m, 6 H), 7.54–7.13 (m, 13 H), 6.81 (d, *J* = 2.4 Hz, 1 H), 6.70 (d, *J* = 2.4 Hz, 1 H), 4.06 (q, *J* = 7.2 Hz, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H). An aromatic proton of the tetrasubstituted benzene moiety of minor isomer **6ac**: 6.93 (d, *J* = 2.4 Hz, 1 H). Ethoxy protons of minor isomer **6ac**: 3.99 (q, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3 H).
Compound **5ba**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23–8.20 (m, 1 H), 8.02–7.99 (m, 1 H), 7.84–7.81 (m, 2 H), 7.62–7.57 (m, 2 H), 7.52–7.41 (m, 4 H), 7.37–7.32 (m, 2 H), 7.01–6.96 (m, 2 H), 6.53 (d, *J* = 2.4 Hz, 1 H), 6.45 (d, *J* = 2.4 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 2.34 (s, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H).
Compound **5ca**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–6.99 (m, 6 H), 6.95–6.85 (m, 2 H), 6.31 (d, *J* = 2.1 Hz, 1 H), 6.17 (d, *J* = 2.1 Hz, 1 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 2.30 (s, 3 H), 2.23 (s, 3 H), 2.15 (s, 3 H), 1.27 (t, *J* = 7.2 Hz, 3 H).
Compound **5da**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.98–6.90 (m, 4 H), 6.88–6.83 (m, 4 H), 6.39 (d, *J* = 2.0 Hz, 1 H), 6.29 (d, *J* = 2.0 Hz, 1 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 2.30 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H).
Compound **6da**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 2.7 Hz, 1 H), 6.94–6.90 (m, 2 H), 6.87–6.83 (m, 6 H), 6.61 (d, *J* = 2.7 Hz, 1 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 2.42 (s, 3 H), 1.36 (t, *J* = 7.1 Hz, 3 H).
Compound **5ea**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.56 (m, 4 H), 7.08–7.03 (m, 4 H), 6.72 (d, *J* = 2.1 Hz, 1 H), 6.52 (d, *J* = 2.1 Hz, 1 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 2.39 (s, 3 H), 1.18 (t, *J* = 7.2 Hz, 3 H).
Compound **6ea**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 4 H), 7.43 (d, *J* = 2.4 Hz, 1 H), 7.06–7.03 (m, 2 H), 6.97–6.94 (m, 2 H), 6.84 (d, *J* = 2.4 Hz, 1 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 2.41 (s, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H).

(16) For the rhodium(I)-catalyzed [2+2+2] cycloaddition of diynes with internal alkynyl ethers, see: (a) Alayrac, C.; Schollmeyer, D.; Witulski, B. *Chem. Commun.* **2009**, 1464. (b) Clayden, J.; Moran, W. J. *Org. Biomol. Chem.* **2007**, *5*, 1028.

(17) Compound **10**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.72 (m, 4 H), 7.72–7.63 (m, 1 H), 7.49–7.37 (m, 3 H), 7.37–7.29 (m, 2 H), 7.22–7.17 (m, 1 H), 7.16–7.10 (m, 1 H), 6.98–6.91 (m, 1 H), 6.87–6.81 (m, 1 H), 4.60 (s, 2 H), 4.58 (s, 2 H), 2.42 (s, 3 H).