Oxovanadium(V)-Induced Cross-Coupling Reaction between Two Ligands of Organozinc Compounds

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Oxovanadium(V) compounds such as $VO(OEt)Cl_2$ serve as useful oxidants for organozinc compounds, providing the corresponding cross-coupling products derived from two ligands of organozinc compounds. In particular, triorganozincates undergo selective cross-coupling smoothly by the action of oxovanadium(V).

Introduction

Organozinc compounds, which can tolerate a broad range of functionalities,[1] are useful synthetic intermediates, and their chemistry has been developed intensively in recent years.[2] In particular, cross-coupling reactions of organozinc reagents catalyzed by transition metal salts provide versatile synthetic tools in organic syntheses.[3] In these reactions, the substituents on zinc couple with electrophilic species such as organic halides; however, examples of the selective cross-coupling of two ligands of organozinc compounds are limited to a few cases, which include effective carbon−carbon bond forming reaction via 1,2-migration of zincate carbenoids and intramolecular coupling reaction of organozinc compounds by organocopper reagents.[4] Thus, the development of such a selective coupling of the ligands of zinc reagents is one of the most challenging subjects in organozinc chemistry. To accomplish this transformation, oxidation of organozinc compounds has been investigated in detail, and the desired coupling of organozinc compounds, which was found to take place by the action of oxovanadium(V) compounds as the oxidants (Scheme 1), is described in this paper.

Results and Discussion

Cross-Coupling Reaction of Organozinc Compounds 2 with Oxidants. Table 1 represents the results of the reaction of the organozinc compound **2a** with a variety of oxidants. Owing to the property that organozinc compounds are subject to undergo the Schlenk equilibrium,[5] isolation of mixed diorganozinc compounds such as **2a** was very difficult, and therefore the organozinc compound was prepared in situ by transmetalation of the corresponding alkylzinc halide with the aryllithium. The reaction of (2-methoxyphenyl)methylzinc (**2a**) with Cp_2FePF_6 afforded the homo-coupling

Scheme 1

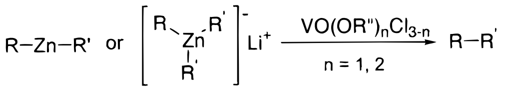
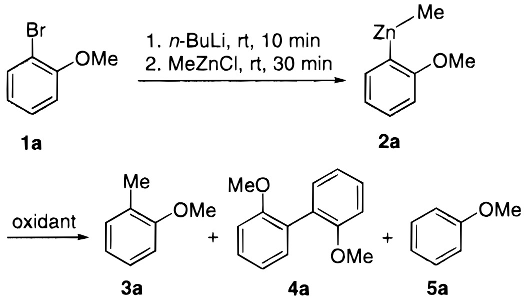


Table 1. Coupling Reaction of Organozinc Compound 2a with Oxidants



entry	oxidant [a]	yield of **3 + 4** (%)[b]	selectivity[b] **3 / 4**
1	Cp_2FePF_6	33	0 / 100
2	TCNQ	0	
3	DDQ	0	
4	CAN	0	
5	$Mn(OAc)_3$	0	
6	CrO_3	0	
7	$AgBF_4$[c]	55	31 / 69
8	$VO(OEt)Cl_2$	82	68 / 32

[a] Oxidant (3.0 equiv) was used unless otherwise stated. [b] Determined by ^1H NMR of the reaction mixture. [c] $AgBF_4$ (6.0 equiv) was used.

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(1) (a) Guijarro, A.; Rosenberg, D. M.; Rieke, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 4155. (b) Thorn, S. N.; Gallagher, T. *Synlett* **1996**, 185. (c) Lipshutz, B. H.; Wood, M. R.; Tiroda, R. *J. Am. Chem. Soc.* **1995**, *117*, 6126.

(2) For recent reviews of syntheses of organozinc compounds, see: (a) Knochel, P.; Langer, F.; Longeau, A.; Rottländer, M.; Stüdemann, T. *Chem. Ber.* **1997**, *130*, 1021. (b) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117.

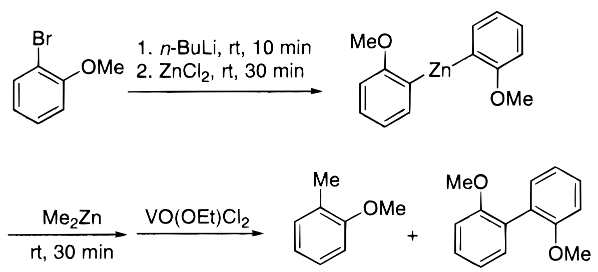
(3) (a) Oshima, K. Transition Metal Catalyzed Reactions of Organozinc Compounds, In *Advance in Organometallic Chemistry*; Liebiskind, L. S., Ed.; JAI Press: London, 1991; Vol. 2, p 101. (b) Erdik, E. *Tetrahedron* **1992**, *48*, 9577.

(4) (a) Iyoda, M.; Kabir, S. M. H.; Vorasingha, A.; Kuwatani, Y.; Yosihda, M. *Tetrahedron Lett.* **1998**, *39*, 5393. For coupling reactions of substituents on zinc via 1,2-migration of zincate carbenoids, see: (b) Harada, T.; Iwazaki, K.; Hara, D.; Hattori, K.; Oku, A. *J. Org. Chem.* **1997**, *62*, 8966. (c) Harada, T.; Katsuhira, T.; Katsuhira, T.; Osada, A.; Iwazaki, K.; Maejima, K.; Oku, A. *J. Am. Chem. Soc.* **1996**, *118*, 11377 and references therein.

(5) For discussion of the Schlenk equilibrium of organozinc compounds, see: (a) Charette, A. B.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1996**, *118*, 4539 and references therein. (b) André, B. C.; André B.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1998**, *120*, 5114.

10.1021/jo9919106 CCC: $19.00

Scheme 2



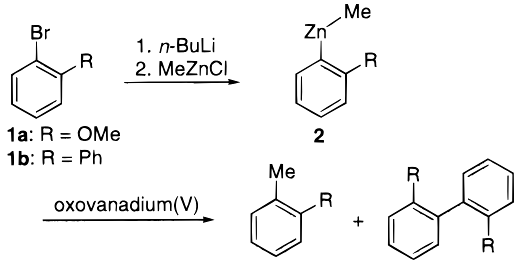
3a 51% **4a** 10%

compound **4a** selectively. The result prompted us to investigate the coupling by use of other oxidants. Among the oxidants employed, $AgBF_4$ served as a useful oxidizing agent to give the desired cross-coupling compound **3a**, probably via a one-electron oxidation process. More interestingly, the use of $VO(OEt)Cl_2$[6] instead of $AgBF_4$ dramatically improved the yield of **3a** (Table 1). The present coupling reaction of organic ligands of organozinc compounds also proceeded successfully in the Schlenk equilibrium between two kinds of diorganozinc compounds (Scheme 2). Whether this reaction occurs by intramolecular or intermolecular process is not clear, but this result indicates that the cross-coupling reaction proceeds in preference to the homo-coupling one.

Oxovanadium(V)-Induced Cross-Coupling Reaction of Diorganozinc Compounds 2. The oxidative coupling of organozinc compounds **2a** and **2b** was examined by using oxovanadium(V) compounds. In the case of the reaction of **2** with $VO(OEt)Cl_2$, the cross-coupling compound **3** was obtained as the major product with high selectivity (Table 2, entry 3). Moreover, when 3.0 equiv of $VO(OEt)Cl_2$ was used, the best yield of **3** was attained, whereas the reaction using isopropoxy oxovanadium(V) reagents was accompanied by the formation of the homo-coupling product **4** (entries 4 and 5). The oxidative reaction with a combination of $VO(OEt)Cl_2$ and Me_3SiOTf[7] gave a complex mixture, and the coupling compound **3** was produced in a lower yield (entry 6).

This method was successfully applied to various organozinc compounds, affording the corresponding coupling products in good yields (Table 3). The coupling reaction of organozinc compounds bearing an *o*-methoxy, *o*-phenyl, or *o*-methylthio group on the arene ring proceeded smoothly at room temperature to give good yields of the cross-coupling products (Table 3, entries 1, 2, 5, and 9). In contrast, *o*-cyano-substituted aryl alkylzinc compound **2d** exhibited lower reactivity toward the oxidative coupling with $VO(OEt)Cl_2$ (entry 6). However, while an organoaluminum compound having an electron-withdrawing substituent did not undergo oxidative coupling with oxovanadium(V), the corresponding organozinc compound was oxidized to the cross-coupling compound **3d** exclusively. The cross-coupling reaction of organozinc compounds having an *ortho*-substituent proceeded efficiently, whereas the oxidative reaction of **2e** and **2i**, with less steric hindrance, preferentially gave a substantial amount of the homo-coupling compounds **4e** and **4i**, respectively (entries 7 and 13). The reaction of **2f** having an *m*-methoxy group led to the recovery of the starting material, because the bromine−lithium exchange reaction did not take place and the corresponding organozinc compound could not be prepared (entry 8). It should be noted that, in addition to the methyl group, an *n*-butyl or 1-alkynyl group could couple with the aryl group successfully, as shown in Table 3 (entries 3, 4, 10, and 11). On the other hand, the cross-coupling with a vinyl group was inefficient, and sterically hindered *sec*- and *tert*-butyl groups could not couple with aryl groups at all.

Table 2. Coupling Reaction of Organozinc Compounds 2 with Oxovanadium(V) Compounds



1a: R = OMe
1b: R = Ph
2
3 **4**

entry	oxovanadium(V)[a]	yield of **3** + **4** (%)[b], (selectivity, **3** / **4**)[b]	
		from **1a**	**1b**
1	$VO(OEt)Cl_2$ (1.0 equiv)	-	34 (94 / 6)
2	$VO(OEt)Cl_2$ (2.0 equiv)	-	58 (96 / 4)
3	$VO(OEt)Cl_2$ (3.0 equiv)	82 (68 / 32)	81 (90 / 10)
4	$VO(OPr\text{-}i)Cl_2$	68 (54 / 46)	67 (94 / 6)
5	$VO(OPr\text{-}i)_2Cl$	54 (52 / 48)	34 (90 / 10)
6	$VO(OEt)Cl_2$-$2Me_3SiOTf$	26 (38 / 62)	13 (85 / 15)
7	-[c]	0	0

[a] Oxovanadium (3.0 equiv) was used unless otherwise stated. [b] Determined by ^1H NMR of the reaction mixture. [c] Without oxovanadium(V).

Oxidative Cross-Coupling Reaction of Triorganozincates 6. It is expected that triorganozincates **6** may undergo the more facile oxidation with oxovanadium(V) compounds, compared with diorganozinc compounds **2**. Actually, as shown in Table 4, the cross-coupling reaction of triorganozincates using $VO(OEt)Cl_2$ proceeded very smoothly to give the corresponding cross-coupling compounds **3** in high yields. When diethylzinc was used, gas evolution was observed with the moderate yield of **3**. Selective cross-coupling reaction between alkyl groups and *o*-methoxy-substituted aryl groups occurred when 6.0 equiv of $AgBF_4$ was used instead of the oxovanadium(V) compound. In this case, an excess of $AgBF_4$ seems to be essential because $AgBF_4$ is less soluble in ether. After the reaction was complete, Ag(0) was detected in the reaction mixture. The result suggests that the cross-coupling reaction is induced by one-electron oxidation with Ag(I).

More interestingly, the preparation of the zincate complexes by the halogen−zinc exchange reaction with triorganozincates[8] dramatically improved the product selectivity: when zincate complex **6**, prepared by iodine−zinc exchange reaction with Me_3−ZnLi, was oxidized by

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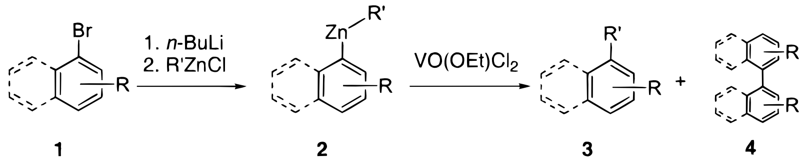
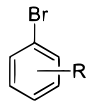
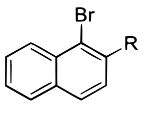
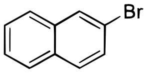
(6) (a) Ishikawa, T.; Ogawa, A.; Hirao, T. *J. Am. Chem. Soc.* **1998**, *120*, 5124. (b) Ishikawa, T.; Nonaka, S.; Ogawa, A.; Hirao, T. *Chem. Commun.* **1998**, 1209. (c) Ishikawa, T.; Ogawa, A.; Hirao, T. *J. Organomet. Chem.* **1999**, *575*, 76.

(7) The order of the reactivity of vanadium reagents is $VO(OR)Cl_2$−AgOTf or Me_3SiOTf > $VO(OR)Cl_2$ > $VO(OR)_3$ > $VO(acac)_2$. Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399. Hirao, T.; Mori, M.; Ohshiro, Y. *J. Org. Chem.* **1990**, *55*, 358. Hirao, T.; Mori, M.; Ohshiro, Y. *Chem. Lett.* **1991**, 783.

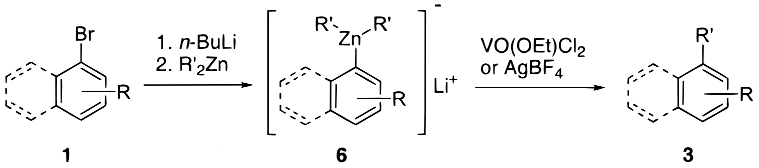
Table 3. Cross-Coupling Reaction of Organozinc Compounds 2 with VO(OEt)Cl$_2$[a]

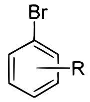
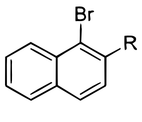
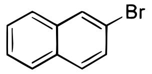


entry	1	R	2	R'	temp.	time (h)[b]	yield of 3 (%)[c]	yield of 4 (%)[c]
1		**1a** *o*-OMe	**2a**	Me	rt	3	**3a** 52	**4a** 25
2		**1b** *o*-Ph	**2b**	Me	rt	10	**3b** 72	**4b** 6
3		**1b** *o*-Ph	**2j**	$\equiv$–^{n}Hex	rt	16	**3j** 52	-
4		**1b** *o*-Ph	**2k**	$\equiv$–SiMe$_3$	rt	16	**3k** 49	-
5		**1c** *o*-SMe	**2c**	Me	rfx	2	**3c** 50	-
6		**1d** *o*-CN	**2d**	Me	rt	3	**3d** 24	-
7		**1e** *p*-OMe	**2e**	Me	rt	10	**3e** 32	**4e** 43
8		**1f** *m*-OMe	**2f**	Me	rt	10	**3f** -	-
9		**1g** OMe	**2g**	Me	rt	3	**3g** 92	-
10		**1g** OMe	**2l**	^{n}Bu	rt	5	**3l** 43	-
11		**1g** OMe	**2m**	$\equiv$–^{n}Hex	rt	16	**3m** 63	-
12		**1h** H	**2h**	Me	rt	3	**3h** 49	**4h** 10
13		**1i**	**2i**	Me	rt	10	**3i** 30	**4i** 62

[a] VO(OEt)Cl$_2$ (3.0 equiv) was used. [b] Reactions conditions for the oxidation with VO(OEt)Cl$_2$. [c] Isolated yield.

Table 4. Cross-Coupling Reaction of Triorganozincates 6 with VO(OEt)Cl$_2$ or AgBF$_4$

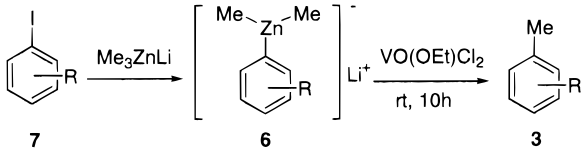


entry	1	R	6	R'	oxidant[a]	time (h)[b]	yield of 3 (%)[c]	yield of 4 (%)[c]
1		**1a** *o*-OMe	**6a**	Me	A	3	**3a** 59	**4a** 22
2		**1a** *o*-OMe	**6n**	Et	A	3	**3n** 44	**4a** 30
3		**1a** *o*-OMe	**6n**	Et	B	2	**3n** 70	**4a** 4
4		**1a** *o*-OMe	**6o**	^{n}Bu	A	10	**3o** 31	**4a** 60
5		**1b** *o*-Ph	**6b**	Me	A	10	**3b** 84	**4b** -
6		**1c** *o*-SMe	**6c**	Me	A	16	**3c** 72	**4c** -
7		**1d** *o*-CN	**6d**	Me	A	3	**3d** 59	**4d** 28
8		**1e** *p*-OMe	**6e**	Me	A	3	**3e** 45	**4e** 38
9		**1f** *m*-OMe	**6f**	Me	A	3	**3f** -	**4f** -
10		**1g** OMe	**6g**	Me	A	3	**3g** 92	**4g** -
11		**1g** OMe	**6p**	Et	B	10	**3p** 55	**4g** -
12		**1g** OMe	**6l**	^{n}Bu	A	10	**3l** 52	**4g** -
13		**1h** H	**6h**	Me	A	3	**3h** 73	**4h** -
14		**1i**	**6i**	Me	A	10	**3i** 46	**4i** 40

[a] A: VO(OEt)Cl$_2$ (3.0 equiv); B: AgBF$_4$ (6.0 equiv). [b] Reaction time for the oxidation with VO(OEt)Cl$_2$ or AgBF$_4$ at room temperature. [c] Isolated yield.

VO(OEt)Cl$_2$, the corresponding cross-coupling compound was obtained exclusively in high yield without formation of any homo-coupling products (Table 5). This reaction does not involve the aryllithium derivatives as starting reagents in the preparation step of the zincates **6**. When the organozinc compounds were prepared from organolithiums and zinc halides or dialkylzincs, most probably, the homo-coupling may proceed via the oxidation of

Table 5. Cross-Coupling Reaction of Triorganozincates 6 Prepared from Aryl Iodides 7 with $VO(OEt)Cl_2$[a]



entry	7	R	temp. (°C)	time (h)[b]	yield of 3 (%)[c]
1	**7a**	*o*-OMe	0	2	86 (83)
2	**7q**	*o*-CO_2Pr^i	-78	1	66 (55)
3	**7r**	*p*-NO_2	-78	1	49 (48)

[a] $VO(OEt)Cl_2$ (3.0 equiv) was used. [b] Reactions conditions in zincation with Me_3ZnLi. [c] Determined by ^1H NMR. Isolated yields are shown in parentheses.

organolithium compounds remaining in situ.[9] Thus, the selective synthesis of cross-coupling compounds was accomplished, where the coupling reaction of aryl compounds having functional groups such as isopropoxycarbonyl and nitro groups was found to proceed efficiently.

Conclusion

In summary, we have demonstrated that organozinc compounds undergo oxovanadium(V)-promoted cross-coupling reactions. This novel approach for selective cross-coupling of organozinc compounds realizes the carbon−carbon bond formation between sp^2 carbon (aryl group) and sp carbon (alkynyl group) or sp^3-carbon (alkyl group). Although the mechanism of these coupling reactions is still ambiguous, we are presuming that the reactions proceed by either a process of one-electron transfer between organozinc compounds and oxovanadium(V) or transmetalation. We are currently developing the application of these reactions to some other organometallics and investigating several reactions for considering the reaction mechanism.

Experimental Section

General Methods. All reagents are of commercial quality. All solvents were freshly distilled under argon over an appropriate drying agent before use. The bromonaphthalene derivative **1g** was prepared according to the standard procedure.[10]

General Procedure for Preparation of Oxovanadium(V) Compounds.[11] To a 200 mL round-bottomed flask equipped with a condenser, magnetic stirring bar, and septum was added hexane (20 mL) under argon, followed by trichlorooxovanadium(V) (100 g, 54.3 mL, 0.58 mol). Then, the dry corresponding alcohol (1.1 or 2.2 equiv) was added dropwise to the solution. During the addition, argon was flowed to remove HCl evolved from the reaction. After the addition was complete, the mixture was stirred for 1 h. The condenser was then quickly replaced with a distillation head, and the solvent was removed at atmospheric pressure. The product was distilled under reduced pressure to give the corresponding oxovanadium(V) compound as a yellow/orange liquid.

Dichloro(ethoxy)oxovanadium(V), 78%, bp 55−60 °C/5 mmHg [1801-77-0]; **dichloro(isopropoxy)oxovanadium(V)**, 75%, bp 59−62 °C/3 mmHg [1636-01-7]; **chloro(diisopropoxy)oxovanadium(V)**, 83%, bp 55−58 °C/1 mmHg [1636-00-6].

Preparation of 2-Methoxy-1-methylnaphthalene (1g). To a solution of 1-bromo-2-naphthol (2.23 g, 10.0 mmol) in dry THF (50 mL) was added sodium hydride (0.36 g, 15.0 mmol) followed by methyl iodide (5.7 g, 40.0 mmol) at room temperature. The mixture was stirred for 24 h at room temperature, the reaction mixture was quenched with water. The mixture was extracted with ether, which was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel eluting with hexane−ether (9:1) to give **1g** (1.70 g, 72%, $R_f = 0.7$).

Representative Procedure for Oxidative Coupling Reaction of Diorganozinc Derivative 2 (Table 3). To a stirred solution of the aryl bromide **1a** (187 mg, 1.0 mmol) in dry ether (2.0 mL) under argon at room temperature was added *n*-BuLi (1.1 mmol, 0.71 mL, 1.54 M in hexane) to generate the corresponding aryllithium. After the mixture stirred for 10 min at room temperature, MeZnCl (1.5 mmol, 0.75 mL, 2.0 M in THF) was added dropwise to the resulting solution at 0 °C. After stirring for 30 min at 0 °C, the resulting solution of **2a** was added to a solution of $VO(OEt)Cl_2$ (549 mg, 3.0 mmol) in dry ether (2.0 mL) at room temperature. The mixture was stirred for 3 h at room temperature, and then ether and 1.5 M aqueous HCl were added to the reaction mixture. After extraction with ether, the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane−ether (4:1) to give **3a** (63 mg, 52%, $R_f = 0.6$) and **4a** (27 mg, 25%, $R_f = 0.4$). The products were identified by comparison of spectral data with those of the authentic samples. 1-Octynylzinc chloride was prepared from 1-octynyllithium (1.1 mmol), which was prepared from 1-octyne (121 mg, 1.1 mmol) and *n*-BuLi (1.1 mmol, 0.71 mL, 1.54 M in hexane) in dry ether (2.0 mL), and $ZnCl_2$ (217 mg, 1.5 mmol) in dry THF (1.0 mL). Trimethylsilylethynylzinc chloride was similarly prepared. *n*-Butylzinc chloride was prepared from *n*-BuLi (1.5 mmol, 0.97 mL, 1.54 M in hexane) and $ZnCl_2$ (217 mg, 1.5 mmol) in dry THF (1.0 mL).

2-Methylanisole (3a), [578-58-5]; **2,2′-dimethoxybiphenyl (4a)**, [4877-93-4]; **2-phenyltoluene (3b)**, [643-58-3]; ***o*-quaterphenyl (4b)**, [641-96-3]; **1-methyl-2-(methylthio)benzene (3c)**, [14092-00-3]; ***o*-tolunitrile (3d)**, [529-19-1]; **4-methyl-anisole (3e)**, [104-93-8]; **4,4′-dimethoxybiphenyl (4e)**, [2132-39-0]; **2-methoxy-1-methylnaphthalene (3g)**, [1130-80-9]; **1-methylnaphthalene (3h)**, [90-12-0]; **1,1′-binaphthyl (4h)**, [604-53-5]; **2-methylnaphthalene (3i)**, [91-57-6]; **2,2′-binaphthyl (4i)**, [612-78-2]. **2-(1-Octynyl)-1-phenylbenzene (3j)**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58−7.62 (m, 2 H), 7.51−7.54 (m, 1 H), 7.24−7.45 (m, 6 H), 2.23 (t, 2 H, $J = 6.9$ Hz), 1.43−1.52 (m, 2 H), 1.19−1.35 (m, 6 H), 0.90 (t, 3 H, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 143.6, 140.8, 133.0, 129.4, 129.3, 127.7, 127.6, 127.2, 126.9, 122.4, 93.5, 80.2, 31.6, 28.7, 28.6, 22.7, 19.7, 14.3; IR (neat) 2227 cm^{-1}; MS (EI) *m/z* 262 (94, M^+), 191 (100), 178 (48). Anal. Calcd for $C_{20}H_{22}$: C, 91.28; H, 8.33. Found: C, 91.55; H, 8.45. **1-Phenyl-2-{2-(trimethylsilyl)ethynyl}benzene (3k)**, [147492−79−2]; **1-butyl-2-methoxynaphthalene (3l)**, [99287−89−5]. **2-Methoxy-1-(1-octynyl)naphthalene (3m)**: pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17−8.21 (m, 1 H), 7.67−7.70 (m, 2 H), 7.41−7.46 (m, 1 H), 7.25−7.31 (m, 1 H), 7.15 (d, 1 H, $J = 9.0$ Hz), 3.93 (s, 3 H), 2.56 (t, 2 H, $J = 6.9$ Hz), 1.62−1.71 (m, 2 H), 1.45−1.54 (m, 2 H), 1.26−1.32 (m, 4 H), 0.83−0.87 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 158.4, 134.8, 129.1, 128.6, 128.0, 127.0, 125.4, 124.0, 112.7, 107.2, 100.5, 74.7, 56.7, 31.6, 29.2, 28.9, 22.8, 20.4, 14.3; IR (neat) 2223, 1272, 1065 cm^{-1}; MS (EI) *m/z* 266 (100, M^+), 251 (4), 197 (32), 181 (11), 158

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(8) For the preparation of zincate complex by halogen−zinc exchange reactions, see: Kondo, Y.; Takazawa, N.; Yamazaki, C.; Sakamoto, T. *J. Org. Chem.* **1994**, *59*, 4717.

(9) Ishikawa, T.; Ogawa, A.; Hirao, T. *Organometallics*, **1998**, *17*, 5713.

(10) Onoda, M.; Kawai, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1761.

(11) (a) Funk, H.; Weiss, W.; Zeising, M. *Z. Anorg. Allg. Chem.* **1958**, *36*, 296. (b) Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399.

(13). Anal. Calcd for $C_{19}H_{22}O$: C, 84.81; H, 8.32. Found: C, 84.67; H, 8.42.

Representative Procedure for Oxidative Coupling Reactions of Diorganozinc Derivative 6 (Table 4). To a stirred solution of the aryl bromide **1a** (187 mg, 1.0 mmol) in dry ether (2.0 mL) under argon at room temperature was added *n*-BuLi (1.1 mmol, 0.71 mL, 1.54 M in hexane) to generate the corresponding aryllithium. After the solution stirred for 10 min at room temperature, Me_2Zn (1.2 mmol, 1.2 mL, 1.0 M in hexane) was added dropwise to the resulting solution at 0 °C. After stirring for 30 min at 0 °C, the resulting solution of **6a** was added to a solution of $VO(OEt)Cl_2$ (549 mg, 3.0 mmol) in dry ether (2.0 mL) at room temperature. The mixture was stirred for 3 h at room temperature, and then ether and 1.5 M aqueous HCl were added to the reaction mixture. After extraction with ether, the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–ether (4:1) to give **3a** (72 mg, 59%) and **4a** (23 mg, 22%). The products were identified by comparison of spectral data with those of the authentic samples. Di-*n*-butylzinc was prepared from *n*-BuLi (2.2 mmol, 1.4 mL, 1.5 M in hexane) and $ZnCl_2$ (136 mg, 1.0 mmol) in dry THF (2.0 mL).

Biphenyl-2,2′-dicarbonitrile (4d), [4341-02-0]; **2-butylanisole (3o)**, [18272-72-5].

Representative Procedure for Oxidative Coupling Reaction with $AgBF_4$. To a stirred solution of the aryl bromide **1a** (0.68 mmol) in dry ether (1.4 mL) under argon at room temperature was added *n*-BuLi (0.75 mmol, 0.49 mL, 1.54 M in hexane) to generate the corresponding aryllithium. After the solution stirred for 10 min at room temperature, Et_2Zn (0.75 mmol, 0.75 mL, 1.0 M in hexane) was added dropwise to the resulting solution at 0 °C. After stirring for 10 min at 0 °C, the resulting solution of **6n** was added to a solution of $AgBF_4$ (801 mg, 4.1 mmol, 6.0 equiv) in dry ether at 0 °C. The mixture was stirred for 2 h at room temperature, and then ether and 1.5 M aqueous HCl were added to the reaction mixture. After extraction with ether, the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–ether (3:1) to give **3n** (65 mg, 70%, $R_f = 0.7$, [14804-32-1]) and **4a** (3 mg, 4%).

1-Ethyl-2-methoxynaphthalene (3p), [17295-03-3].

Representative Procedure for Oxidative Coupling Reaction of Triorganozincate 6 Prepared from Aryl Iodide 7 (Table 5). To a stirred solution of the aryl iodide **7a** (117 mg, 0.5 mmol) in dry THF (1.0 mL) under argon at 0 °C was added Me_3ZnLi, which was prepared from MeLi (2.25 mmol, 2.25 mL, 1.02 M in ether) and $ZnCl_2$ (102 mg, 0.75 mmol) in dry THF (1.0 mL). After stirring for 2 h at 0 °C, $VO(OEt)Cl_2$ (549 mg, 3.0 mmol) was added to the resulting solution of **6a** at 0 °C. The mixture was stirred for 10 h at room temperature, and then ether and 1.5 M aqueous HCl were added to the reaction mixture. After extraction with ether, the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane–ether (4:1) to give **3a** (101 mg, 83%, $R_f = 0.5$). The products were identified by comparison of spectral data with those of the authentic samples.

Isopropyl 2-methylbenzoate (3q), [943-13-2]; **4-nitrotoluene (3r)**, [99-99-0].

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