

Transition-Metal-Free Cross-Coupling of Aryl Halides with Arylstannanes

Qing He,^{†,‡} Liwen Wang,[†] Yong Liang,^{||,§} Zunting Zhang,^{*,†} and Stanislaw F. Wnuk^{*,§}

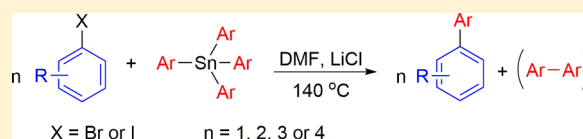
[†]Key Laboratory of the Ministry of Education for Medicinal Resources and Natural Pharmaceutical Chemistry, National Engineering Laboratory for Resource Development of Endangered Crude Drugs in Northwest of China, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, P. R. China

[‡]College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, 325027, P. R. China

[§]Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, United States

S Supporting Information

ABSTRACT: Transition-metal-free LiCl-promoted cross-coupling reactions of tetraphenyltin, trichlorophenyl-, dichlorodiphenyl-, and chlorotriphenylstannanes with aryl halides in DMF provided access to biaryls in good to high yields. Up to four phenyl groups were transferred from the organostannanes substrates. The aryls bearing electron-withdrawing groups in either halides or organotin substrates gave coupling products in higher yields. The methodology has been applied for the efficient synthesis of ipriflavones.



The transition-metal catalyzed cross-coupling of organo-magnesium (Kumada), organozinc (Negishi), organo-boron (Suzuki), organotin (Stille), or organosilicon (Hiyama) with aryl, alkenyl, or alkyl halides is one of the most widely used methods for the formation of new carbon–carbon bonds.^{1,2} In recent years, alternative approaches have begun to compete with these traditional cross-coupling protocols. One such approach is the C–H functionalization based on the coupling of one activated component (e.g., aryl halides) requiring direct C–H bond activation on the counterpart.^{3–5} Cross dehydrogenative-coupling reactions, which require direct activation of C–H bonds on both substrates (e.g., alkene and/or arenes), have been also developed.^{6–8} The combination of transition metal catalysts with oxidants and ligands was found to be crucial for efficient cross-coupling via direct C–H functionalization.

Recently, there has also been a significant effort to develop cross-coupling reactions that avoid the usage of a transition-metal catalyst, in order to facilitate the purification of products and lower the costs.^{9–11} This includes cross-coupling of aryl halides with aryl Grignard,^{12–14} arylzinc,^{15,16} or organo-aluminum¹⁷ reagents, among others.¹¹ The transition-metal-free synthesis of biaryls occurred via homolytic aromatic substitution (HAS),^{18,19} single electron transfer (SET) processes via $\text{S}_{\text{RN}}1$,^{12,15,20–22} or via benzyne-radical initiation.²³

The effect of lithium halides on the transition-metal catalyzed Stille,²⁴ Negishi,^{25,26} Suzuki,^{27,28} and other reactions^{29–32} has been studied. LiCl accelerates the formation of organozinc reagents³³ and enhances their reactivity toward transmetalation³⁴ by forming more nucleophilic lithium zincate complexes.^{33,35} Recently, the effect of LiCl on increasing cross-coupling efficiency of Kumada- or Negishi-type transition-metal-free reactions with aryl or alkenyl halides has also been reported.^{13,15} However, the analogous effect of LiCl in the

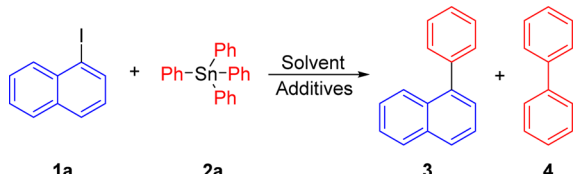
transition-metal-free Stille cross-coupling reaction is still undeveloped. Herein, we report first transition-metal-free LiCl-promoted cross-coupling of aryl halides and arylstannanes to give access to biaryls.

Initially, we examined coupling of tetraphenyltin **2a** with iodonaphthalene **1a** in DMAC in the presence of LiCl. Thus, heating of **2a** with 1 equiv of **1a** in the presence of LiCl (5 equiv) at 140 °C for 4 h produced the biaryl product **3** in 92% yield, along with minor quantities of the reductive homocoupling byproduct **4** (3:4, 40:1; Table 1, entry 1). Coupling also proceeded smoothly in DMF (entry 2), whereas no **3** was formed in refluxing toluene (entry 3). Screening of the LiCl loading showed that 5 equiv of LiCl are required to produce **3** in maximum yield (entries 4–5). Coupling in the absence of LiCl led mainly to the recovery of **1a** with only a trace amount of **3** detected (entry 6). At least 3 h of heating were required to produce **3** in high yield (entries 7–9). Reaction at higher temperature (160 °C) yielded substantial quantities of biphenyl homocoupling byproduct **4** with decreased formation of **3** (32%; entry 10). Interestingly, at lower temperature (120 °C), product **3** was also obtained in lower yield (25%) but with excellent selectivity of **3** over **4** (entry 11). Prolonged reaction time afforded **3** in higher yield with the retention of a good ratio of **3** to **4** (entry 11, footnote). Other lithium salts were less efficient (LiBr or LiI) or failed (LiF) to promote coupling (entries 12–14). The coupling also proceeded less successfully when chloride salts other than LiCl were used; with NaCl giving **3** in good yield, while coupling basically failed in the presence of KCl or CsCl (entries 15–17).

We also examined coupling of **1a** with various equivalents^{36–38} of **2a** to increase the atom efficiency of the LiCl-

Received: July 9, 2016

Published: August 29, 2016

Table 1. Optimization of the LiCl-Promoted Cross-Coupling between Iodonaphthalene 1a and Tetraphenyltin 2a^a


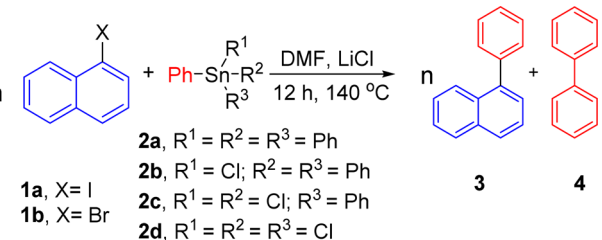
entry	solvent	additives		T/°C	time/h	yield (%) ^{b,c} 3	ratio ^b 3:4
		salts	equiv				
1	DMAC	LiCl	5	140	4	92 (79)	40:1
2	DMF	LiCl	5	140	4	98 (87)	99:1
3	toluene	LiCl	5	110	4	— ^d	— ^e
4	DMF	LiCl	3	140	4	64	50:1
5	DMF	LiCl	1	140	4	45	20:1
6	DMF	LiCl	0	140	4	5	— ^f
7	DMF	LiCl	5	140	1	32	99:1
8	DMF	LiCl	5	140	2	58	50:1
9	DMF	LiCl	5	140	3	96 (82)	80:1
10	DMF	LiCl	5	160	4	32	0.9:1
11	DMF	LiCl	5	120	4	25 ^g	99:1
12	DMF	LiBr	5	140	4	65	2:1
13	DMF	LiI	5	140	4	45	10:1
14	DMF	LiF	5	140	4	— ^d	— ^f
15	DMF	NaCl	5	140	4	76	8:1
16	DMF	KCl	5	140	4	10	— ^f
17	DMF	CsCl	5	140	4	12	— ^f

^aCouplings were performed on 0.20 mmol scale of 2a (0.05 M) with 1 equiv of 1a. ^bDetermined by GC/MS and/or ¹H NMR. ^cIsolated yield in parentheses. ^dProduct 3 was not detected. ^eHomocoupling byproduct 4 was observed. ^fNot determined. ^gCoupling in 5, 6, or 12 h yielded 3 in 32% (80:1), 40% (80:1), or 48% (75:1), respectively.

promoted Stille cross-coupling reactions. Thus, couplings of 2a with 1–4 equiv of 1a gave 3 in excellent yields, indicating transfer of up to four phenyl groups from 2a (Table 2, entries 1–4). Treatment of 2a with less reactive 1-bromonaphthalene 1b gave the coupling product in 48% yield (entry 5).

When chlorotriphenylstannane 2b and dichlorodiphenylstannane 2c were subjected to coupling with different equivalents of 1a, multiple phenyl group transfer was also observed, even though the coupling efficiency was lower compared to 2a (entries 6–10). Less coupling efficiency (25%) was observed for the reaction of trichlorophenylstannane 2d with 1a (entry 11). In general, both the yield and ratio increase with the number of phenyl groups present in the organostannane substrates.

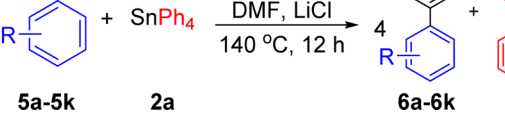
Next, the LiCl-promoted coupling reactions of tetraphenyltin 2a with a series of aryl halides 5a–5k have been examined (Table 3). Coupling of 2a with 4 equiv of aryl iodides 5a–5c, having an electron-withdrawing group (EWG) at the *para*-position, proceeded efficiently in the presence of LiCl (140 °C/12 h) to give biaryls 6a–6c in good yields with transfer of four phenyl groups from the Sn center (entries 1–3, 60–76%). Analogous coupling of 2a with iodide 5d, having an electron-donating group (EDG) at the *para*-position yielded the biaryl 6d in only 31% yield along with large quantities of 4 (entry 4). Similarly, aryl iodides bearing EWGs at the *ortho*-position, 5e and 5f, gave the coupling products in better yields and ratios as compared to those having EDG 5g (entries 5–7). The same trend was also observed for the *meta*-substituted iodides 5h–5j

Table 2. Coupling of Arylstannanes 2 with Different Equivalency of 1-Iodonaphthalene 1a^a


entry	halides		stannanes	yield (%) ^b 3	ratio ^c 3:4
	1	equiv (n)			
1	1a	1	2a	98 ^d	99:1
2	1a	2	2a	92	30:1
3	1a	3	2a	91 (84)	99:1
4	1a	4	2a	83 (75) ^e	99:1
5	1b	4	2a	48	9:1
6	1a	1	2b	78	20:1
7	1a	2	2b	68	30:1
8	1a	3	2b	60 (53)	40:1
9	1a	1	2c	75	40:1
10	1a	2	2c	53	20:1
11	1a	1	2d	25	50:1

^aCouplings were performed on 0.20 mmol scale of 2a–2d (0.05 M) with 5 equiv of LiCl at 140 °C for 12 h. ^bYields for product 3 are based upon transferring four, three, two, or one phenyl groups from tin reagents 2a, 2b, 2c, or 2d respectively. Determined by GC/MS. Isolated yield in the parentheses. ^cDetermined by ¹H NMR. ^dHeated for 4 h. ^e3 was obtained in 26% yield (3:4, 80:1) for 4 h and 50% yield (3:4, 90:1) for 8 h.

Table 3. LiCl-Promoted Couplings of Tetraphenyltin 2a with Different Aryl Halides 5a–5k^a



Reaction scheme showing the synthesis of biaryl compounds **6a-6k** and **4** from tetraphenyltin (**2a**) and aryl halides (**5a-5k**) in DMF with LiCl at 140 °C for 12 h.

entry	halides	X	R	product	yield (%) ^b	ratio (6:4) ^c
1	5a	I	4-COOCH ₃	6a	76	10:1
2	5b	I	4-COCH ₃	6b	60	7:1
3	5c	I	4-CN	6c	72	12:1
4	5d	I	4-OCH ₃	6d	31	4:5
5	5e	I	2-NO ₂	6e	80	50:1
6	5f	I	2-CF ₃	6f	79	15:1
7	5g	I	2-CH ₃	6g	44	5:4
8	5h	I	3-CN	6h	62	8:1
9	5i	I	3-CF ₃	6i	75	13:1
10	5j	I	3-CH ₃	6j	40	5:4
11	5k	Br	2-CN	6k	36	5:2

^aCouplings were performed on 0.20 mmol scale of 2a (0.05 M) with 4.0 equiv of 5a–5k at the presence of LiCl (5 equiv) at 140 °C for 12 h. ^bCalculated based on transferring four phenyl groups from 2a. ^cDetermined by ¹H NMR.

(entries 8–10). In general, both yields of biaryls 6 and ratios of 6 to 4 were higher for aryl halides with an EWG in the phenyl ring. However, the position of the substituent (*o*-, *m*-, *p*-) has less effect. It is noteworthy that compared to the transition-metal-free cross-couplings of Grignard reagents, which are also

reactive with the electrophilic substituents, such as cyano, ester, or ketone,¹² the organostannane coupling described here demonstrates higher functional group tolerance, similarly to the reactions with arylzinc reagents.¹⁵ The aryl bromide **5k** also undergoes coupling with **2a** to give **6k** but in lower yield (entry 11).

The LiCl-promoted Stille coupling is also efficient in transferring phenyl groups substituted with an EDG or EWG from the Sn center. The results for coupling of *tetra*-(*p*-tolyl)tin **7**, *tetra*-(*m*-methoxyphenyl)tin **8**, or *tetra*-(*p*-chlorophenyl)tin **9** with various aryl iodides (4.0 equiv) are presented in Table 4

Table 4. LiCl-Promoted Couplings of Tetraaryltins **7–9** with Different Aryl Halides **5a–5j**^a

entry	halides		stannane		product	yield (%) ^b	ratio ^c
	R	5	Ar-	7–9			
1	4-COCH ₃	5a			10a	71	15:2
2	4-CN	5c	CH ₃		10c	48	3:2
3	4-OCH ₃	5d	CH ₃	7	10d	26	5:4
4	2-CH ₃	5g	CH ₃		10g	25	2:1
5	3-CF ₃	5i			10i	63	8:1
6	4-COCH ₃	5b	MeO	8	11b	55	7:1
7	3-CH ₃	5j			11j	34	3:1
8	4-COCH ₃	5b			12b	65	20:1
9	4-OCH ₃	5d	Cl		12d	42	5:2
10	2-CF ₃	5f	Cl	9	12f	82	50:1
11	3-CN	5h			12h	79	15:1
12	3-CH ₃	5j			12j	38	5:3

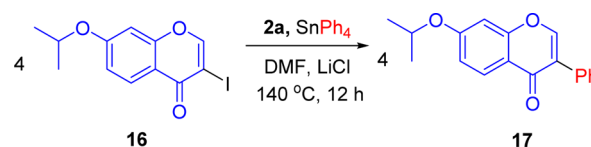
^aCouplings were performed on 0.20 mmol scale of **7–9** (0.05 M) with 4 equiv of **5** in the presence of LiCl (5 equiv) at 140 °C for 12 h.

^bCalculated based on transferring four aryl groups from tin reagents **7–9**. ^cRatio of **10:13**, **11:14**, or **12:15** was determined by ¹H NMR and GC-MS.

(entries 1–12). Coupling of aryltins having EDG **7** or **8** gave better yields and ratios with aryl halides bearing EWGs (**5a–c**, or **5i**) as compared to those with an EDG (**5d**, **5g**, or **5j**), with efficient transfer of up to four aryl groups from organotin substrates (entries 1–7). Coupling of *p*-chloro substituted aryltin **9** yielded products **12** generally in higher yields than when **7** and **8** were used. Again, the products were obtained in higher yields and better ratio with iodides having an EWG (entries 6–10). Atom-efficient Pd-catalyzed Stille couplings with Ar₄Sn are known.^{36–38} However, transfer of multiple Ar groups from a Sn center, in the absence of a Pd-catalyst, has not been reported.

The LiCl-promoted cross-coupling reaction with stannanes was successfully applied for the synthesis of ipriflavone **17**, which is in clinical studies for postmenopausal osteoporosis.³⁹ We found that treatment of 3-iodo-7-isopropoxychromone **16** (1 equiv) with **2a** (0.25 equiv)/LiCl (1.25 equiv) afforded ipriflavone **17** (92%) with the efficient transfer of four phenyl groups (Scheme 1).

Scheme 1. Synthesis of Ipriflavone **17** by LiCl-Promoted Couplings of **2a** with **16**



The LiCl-promoted cross-coupling of aryl halides with arylstannanes might occur via the single electron transfer (SET) induced radical-nucleophilic aromatic substitution (S_{RN}1)⁴⁰ mechanism, similar to the pathway proposed for the transition-metal-free coupling between aryl halides and Grignard^{12,20,22} or arylzinc¹⁵ reagents. This assumption is supported by the fact that (i) no rearranged coupling product was formed, which excludes the aryne mechanistic pathway,^{41,42} and (ii) couplings proceed with aryl halides bearing an EDG, which should eliminate nucleophilic aromatic substitution (S_NAr). The addition of LiCl has been proven to be beneficial for the coupling of organotin with vinyl triflates. The role of the lithium has been explained by the formation of a more reactive palladium complex involving the coordination of a chloride ion.⁴³ Shirakawa et al. attributed enhancement of LiCl on the reactivity of PhZnI in the transition-metal-free coupling with aryl halides on the generation of nucleophilic lithium zincates complexes,³⁵ such as Li⁺[PhZnICl][−].¹⁵ It is noteworthy that hypervalent fluoro tin^{44,45} (e.g., difluorotriphenylstannate), silicon,^{46,47} and germane³⁸ species have been established as active intermediates in Pd-catalyzed couplings.

It is noteworthy that LiCl-promoted coupling requires anhydrous conditions and predried LiCl of high purity for the optimal efficiency. Moreover, it was found that coupling under oxygen-free conditions sometimes led to irreproducible results. Murarka and Studer noted that initiation for the transition-metal-free growth polymerization of haloaryl Grignard reagents can be achieved in the presence of traces of oxygen or by adding the TEMPO radical.^{14,48} Efforts have been made to further optimize conditions. However, experiments under Ar vs N₂ vs atmospheric conditions vs oxygen introduced by syringe did not improve the yields of coupling products and their selectivity to homocoupling⁴⁹ byproducts. It is noteworthy that the best results were obtained when the reaction suspension was heated with a drying tube, filled with anhydrous CaCl₂, attached to the condenser.

In summary, we have demonstrated that aryl halides undergo transition-metal-free LiCl-promoted coupling with tetraaryltins (or chloroarylstannanes) to give biaryls in moderate to high yield with the transfer of all four phenyl groups from the Sn center. This atom-efficient protocol eliminates the usage of a transition-metal catalyst and proceeds without the addition of extra ligands or other additives. In general, the aryls bearing electron-withdrawing groups, either in halides or organotin substrates, give coupling products in better yields. This LiCl-promoted coupling is believed to occur via SET-induced radical-nucleophilic aromatic substitution.

EXPERIMENTAL SECTION

¹H NMR spectra at 300 MHz and proton-decoupled ¹³C{¹H} NMR data at 75 MHz were determined with solutions in CDCl₃. TLC was performed on Merck kieselgel 60-F₂₅₄ and products were detected with 254 nm light or by development of color with I₂. Merck kieselgel 60 (230–400 mesh) was used for column chromatography. Purity, yields, and ratio of the products (crude and/or purified) were

established with GC/MS [EI; capillary column RTX-1MS (30 m \times 0.25 mm \times 25 μ m)] using calibrated standards. HRMS data were recorded by electrospray ionization with a TOF mass analyzer. LiCl (catalog number 449881, \geq 99.9%), tetraphenyltin (T26727, 97%), and phenyltin chlorides [2b, 245712, 95%; 2c, 229202, 96%; 2d, 277231, 98%) as well as anhydrous DMF (227056, 99.8%) were purchased from Aldrich-Sigma Co.

1-(Phenyl)naphthalene (3). *Typical Procedure.* LiCl (42.4 mg, 1 mmol) was placed in a 10 mL round-bottom flask fitted with a septum and was flame-dried under an Ar atmosphere for 1 min. After cooling to an ambient temperature (\sim 5 min), DMF (4 mL) and 1-iodonaphthalene 1a (116.8 μ L, 203.2 mg, 0.8 mmol) were added via syringe followed by tetraphenyltin 2a (85.4 mg, 0.2 mmol). The septum was removed, and the condenser, fitted with a drying tube on top filled with anhydrous CaCl_2 , was quickly attached to the flask. The stirred suspension was heated at 140 $^\circ\text{C}$ (oil bath) for 12 h. Volatiles were evaporated and the residue was partitioned ($\text{H}_2\text{O}/\text{EtOAc}$). The organic layer was dried (Na_2SO_4), evaporated and purified by column chromatography (hexane) to give 3³⁸ (61.3 mg, 75%): ^1H NMR δ 7.40–7.44 (m, 3H), 7.46–7.54 (m, 6H), 7.84–7.86 (m, 1H), 7.87–7.91 (m, 2H); ^{13}C NMR δ 125.4, 125.8, 126.0, 126.9, 127.2, 127.6, 128.3, 130.1, 131.7, 133.8, 140.3, 140.8. GC-MS (t_{R} 10.1 min) m/z 204 (100, $[\text{M}]^+$). GC-MS of the crude reaction mixture showed the ratio of 3:4 as 100 to 1: GC-MS (t_{R} 10.1 min, 3) m/z 204 (100, $[\text{M}]^+$) and (t_{R} 5.8 min, 4) m/z 154 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{16}\text{H}_{13}$: calcd, 205.1012; found, 205.1013.

Note: See Table 1 for the reaction conditions used during optimization studies and Table 2 for the coupling conditions of stannanes 2 with different equivalents of 1-iodonaphthalene 1a.

Methyl Biphenyl-4-carboxylate (6a). Treatment of tetraphenyltin 2a (85.4 mg, 0.2 mmol) with methyl 4-iodobenzoate 5a (209.6 mg, 0.8 mmol) by the *Typical Procedure* gave 6a⁵⁰ (128.9 mg, 76%): ^1H NMR δ 3.94 (s, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 52.3, 127.1, 127.3, 128.2, 128.9, 130.1, 140.0, 145.7, 167.1. GC-MS (t_{R} 10.4 min) m/z 212 (60, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{14}\text{H}_{13}\text{O}_2$: calcd, 213.0910; found, 213.0911.

4-Acetylbiphenyl (6b). Treatment of 2a (85.4 mg, 0.2 mmol) with 4-iodoacetophenone 5b (196.8 mg, 0.8 mmol) by the *Typical Procedure* gave 6b⁵⁰ (94.1 mg, 60%): ^1H NMR δ 2.64 (s, 3H), 7.40 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 26.6, 127.2, 127.3, 128.2, 128.9, 129.0, 136.0, 139.9, 145.8, 197.8; GC-MS (t_{R} 9.8 min) m/z 196 (50, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{14}\text{H}_{13}\text{O}$: calcd, 197.0961; found, 197.0963.

4-Cyanobiphenyl (6c). Treatment of 2a (85.4 mg, 0.2 mmol) with 1-cyano-4-iodobenzene 5c (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave 6c⁵⁰ (103.1 mg, 72%): ^1H NMR δ 7.42 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 110.0, 118.9, 127.2, 127.7, 128.7, 129.1, 132.6, 139.2, 145.7. GC-MS (t_{R} 9.0 min) m/z 179 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{10}\text{N}$: calcd, 180.0808; found, 180.0810.

4-Methoxybiphenyl (6d). Treatment of 2a (85.4 mg, 0.2 mmol) with 4-iodo-1-methoxybenzene 5d (187.2 mg, 0.8 mmol) by the *Typical Procedure* gave 6d⁵¹ (45.6 mg, 31%): ^1H NMR δ 3.84 (s, 3H), 6.97 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 3H), 7.41 (t, J = 8.0 Hz, 2H), 7.51–7.56 (m, 4H); ^{13}C NMR δ 55.4, 114.2, 126.7, 126.8, 128.2, 128.7, 133.8, 140.9, 159.2. GC-MS (t_{R} 8.4 min) m/z 184 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{13}\text{O}$: calcd, 185.0961; found, 185.0961.

2-Nitrobiphenyl (6e). Treatment of 2a (85.4 mg, 0.2 mmol) with 2-iodo-1-nitrobenzene 5e (199.2 mg, 0.8 mmol) by the *Typical Procedure* gave 6e³⁷ (127.4 mg, 80%): ^1H NMR δ 7.32 (d, J = 7.2 Hz, 2H), 7.41–7.50 (m, 2H), 7.61 (t, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 124.1, 127.9, 128.1, 128.2, 128.7, 132.0, 132.2, 136.4, 137.4, 149.4. GC-MS (t_{R} 8.7 min) m/z 199 (20, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{12}\text{H}_{10}\text{NO}_2$: calcd, 200.0706; found, 200.0707.

2-(Trifluoromethyl)biphenyl (6f). Treatment of 2a (85.4 mg, 0.2 mmol) with 2-iodo-1-trifluoromethylbenzene 5f (112.2 μ L, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave 6f⁶² (140.3 mg, 79%): ^1H

NMR δ 7.38–7.48 (m, 7H), 7.53–7.58 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 124.1 (q, 1J = 272.0 Hz), 126.0 (q, 3J = 5.4 Hz), 127.3, 127.6, 127.7, 128.9, 128.4 (q, 2J = 28.5 Hz), 131.3, 132.0, 139.9, 141.5. GC-MS (t_{R} 5.2 min) m/z 222 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{10}\text{F}_3$: calcd, 223.0729; found, 223.0731.

2-Methylbiphenyl (6g). Treatment of 2a (85.4 mg, 0.2 mmol) with 2-iodo-1-methylbenzene 5g (101.8 μ L, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave 6g⁵⁰ (59.1 mg, 44%): ^1H NMR δ 2.27 (s, 3H), 7.25–7.27 (m, 2H), 7.31–7.34 (m, 3H), 7.39–7.45 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 20.5, 125.8, 126.8, 127.2, 127.3, 128.1, 128.8, 129.2, 129.8, 130.3, 135.4, 142.0. GC-MS (t_{R} 6.0 min) m/z 168 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{13}$: calcd, 169.1012; found, 169.1011.

3-Cyanobiphenyl (6h). Treatment of 2a (85.4 mg, 0.2 mmol) with 1-cyano-3-iodobenzene 5h (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave 6h³⁷ (88.8 mg, 62%): ^1H NMR δ 7.39–7.43 (m, 1H), 7.46–7.49 (m, 2H), 7.52–7.56 (m, 3H), 7.62 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H); ^{13}C NMR δ 113.0, 118.8, 127.1, 128.4, 129.1, 129.6, 130.7, 131.5, 138.9, 140.5, 141.9, 142.5. GC-MS (t_{R} 8.8 min) m/z 179 (95, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{10}\text{N}$: calcd, 180.0808; found, 180.0812.

3-(Trifluoromethyl)biphenyl (6i). Treatment of 2a (85.4 mg, 0.2 mmol) with 3-iodo-1-trifluoromethylbenzene 5i (115.3 μ L, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave 6i³⁸ (133.2 mg, 75%): ^1H NMR δ 7.38–7.60 (m, 7H), 7.76 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H); ^{13}C NMR δ 124.95 (q, 3J = 3.2 Hz), 124.98 (q, 3J = 3.2 Hz), 124.3 (q, 1J = 271.0 Hz), 127.2, 128.0, 129.0, 129.2, 130.4, 131.2 (q, 2J = 32.6 Hz), 139.8, 142.1. GC-MS (t_{R} 5.6 min) m/z 222 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{10}\text{F}_3$: calcd, 223.0729; found, 223.0730.

3-Methylbiphenyl (6j). Treatment of 2a (85.4 mg, 0.2 mmol) with 3-iodo-1-methylbenzene 5j (102.7 μ L, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave 6j⁵⁰ (53.8 mg, 40%): ^1H NMR δ 2.41 (s, 3H), 7.14–7.16 (m, 1H), 7.30–7.35 (m, 2H), 7.38–7.45 (m, 4H), 7.57–7.59 (m, 2H); ^{13}C NMR δ 21.6, 124.3, 127.2, 127.3, 128.0, 128.7, 128.7, 128.8, 138.3, 141.3, 141.4. GC-MS (t_{R} 6.8 min) m/z 168 (85, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{13}$: calcd, 169.1012; found, 169.1014.

2-Cyanobiphenyl (6k). Treatment of 2a (85.4 mg, 0.2 mmol) with 1-cyano-2-bromobenzene 5k (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave 6k³⁷ (51.6 mg, 36%): ^1H NMR δ 7.42–7.57 (m, 7H), 7.65 (t, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.51–7.56 (m, 4H); ^{13}C NMR δ 111.3, 118.7, 127.6, 128.73, 128.76, 130.1, 132.8, 133.7, 133.9, 138.2, 145.5. GC-MS (t_{R} 8.2 min) m/z 179 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{13}\text{H}_{10}\text{N}$: calcd, 180.0808; found, 180.0810.

3,4'-Dimethylbiphenyl (10a). Treatment of tetra-(*p*-methylphenyl)tin 7 (96.6 mg, 0.2 mmol) with 1-methyl-3-iodobenzene 5a (102.7 μ L, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave 10a⁵³ (36.4 mg, 25%): ^1H NMR δ 2.41 (s, 3H), 2.43 (s, 3H), 7.16 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 12.7 Hz, 2H), 7.56 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ 20.1, 20.5, 123.1, 125.8, 126.0, 126.7, 126.8, 127.6, 128.4, 135.9, 137.2, 140.1. GC-MS (t_{R} 8.4 min) m/z 182 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{15}\text{H}_{15}\text{O}_2$: calcd, 227.1067; found, 227.1071.

4-Cyano-4'-methylobiphenyl (10c). Treatment of 7 (96.6 mg, 0.2 mmol) with 1-cyano-4-iodobenzene 5c (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave 10c⁵³ (74.1 mg, 48%): ^1H NMR δ 2.41 (s, 3H), 7.28 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H); ^{13}C NMR δ 21.2, 110.6, 119.0, 127.1, 127.5, 129.9, 132.6, 136.3, 138.8, 145.6. GC-MS (t_{R} 10.4 min) m/z 193 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{14}\text{H}_{12}\text{N}$: calcd, 194.0964; found, 194.0969.

4-Methoxy-4'-methylobiphenyl (10d). Treatment of 7 (96.6 mg, 0.2 mmol) with 4-iodo-1-methoxybenzene 5d (187.2 mg, 0.8 mmol) by the *Typical Procedure* gave 10d⁵³ (41.2 mg, 26%): ^1H NMR δ 2.38 (s, 3H), 3.83 (s, 3H), 6.96 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 21.1, 55.4, 114.2, 126.6, 128.0, 129.5, 133.8, 136.4, 138.0, 159.0. GC-MS (t_{R} 9.8 min) m/z 198 (100, $[\text{M}]^+$). HRMS $[\text{M} + \text{H}]^+$ for $\text{C}_{14}\text{H}_{15}\text{O}$: calcd, 199.1117; found, 199.1120.

3',4-Dimethylbiphenyl (10g). Analogous treatment of **7** (96.6 mg, 0.20 mmol) with 2-iodo-1-methylbenzene **5g** (174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **10g**⁵³ (36.4 mg, 25%): ¹H NMR δ 2.41 (s, 3H), 2.42 (s, 3H), 6.96 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H); ¹³C NMR δ 20.1, 20.5, 123.1, 125.8, 126.0, 126.7, 126.8, 127.6, 128.4, 135.9, 137.2, 140.1. GC-MS (t_R 8.4 min) m/z 182 (100, M⁺). HRMS [M + Na]⁺ for C₁₄H₁₄Na: calcd, 205.0988; found, 205.0991.

4'-Methyl-3-(trifluoromethyl)biphenyl (10i). Treatment of **7** (96.6 mg, 0.20 mmol) with 3-iodo-1-trifluoromethylbenzene **5i** (115.3 μ L, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave **10i**⁵⁴ (118.9 mg, 63%): ¹H NMR δ 2.42 (s, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.83 (s, 1H); ¹³C NMR δ 21.3, 123.77 (q, ³ J = 3.0 Hz), 123.86 (q, ³ J = 3.0 Hz), 124.4 (q, ¹ J = 271.5 Hz), 127.1, 129.3, 129.9, 130.3, 131.3 (q, ² J = 31.5 Hz), 137.0, 138.1, 142.1. GC-MS (t_R 7.3 min) m/z 236 (100, M⁺). HRMS [M + H]⁺ for C₁₄H₁₂F₃: calcd, 237.0886; found, 237.0889.

4'-Acetyl-3-methoxybiphenyl (11b). Treatment of tetra-(*m*-methoxyphenyl)tin **8** (109.4 mg, 0.20 mmol) with 4-iodoacetophenone **5b** (196.8 mg, 0.8 mmol) by the *Typical Procedure* gave **11b**⁵⁵ (99.4 mg, 55%): ¹H NMR δ 2.63 (s, 3H), 3.87 (s, 3H), 6.94 (d, J = 8.2 Hz, 1H), 7.12–7.18 (m, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.67 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H); ¹³C NMR, δ 26.64, 55.4, 113.1, 113.6, 119.8, 127.3, 128.9, 130.0, 136.0, 141.4, 145.7, 160.1, 197.7. GC-MS (t_R 12.2 min) m/z 226 (56, M⁺). HRMS [M + H]⁺ for C₁₅H₁₅O₂: calcd, 227.1067; found, 227.1069.

3-Methoxy-3'-methylbiphenyl (11j). Treatment of **8** (109.4 mg, 0.20 mmol) with 3-iodo-1-methylbenzene **5j** (102.7 μ L, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **11j**⁵⁶ (53.9 mg, 34%): ¹H NMR δ 2.44 (s, 3H), 3.88 (s, 3H), 6.90–6.92 (m, 1H), 7.13–7.16 (m, 1H), 7.17–7.22 (m, 2H), 7.33–7.38 (m, 2H), 7.42 (d, J = 8.1 Hz, 2H); ¹³C NMR, δ 20.5, 54.3, 111.6, 111.9, 118.7, 123.3, 127.0, 127.1, 127.6, 128.6, 137.3, 140.1, 141.9. GC-MS (t_R 9.6 min) m/z 198 (100, M⁺). HRMS [M + H]⁺ for C₁₄H₁₅O: calcd, 199.1117; found, 199.1121.

4'-Acetyl-4-chlorobiphenyl (12b). Treatment of tetra-(*p*-chlorophenyl)tin **9** (113 mg, 0.20 mmol) with 4-iodoacetophenone **5b** (196.8 mg, 0.8 mmol) by the *Typical Procedure* gave **12b**⁵⁵ (119.6 mg, 65%): ¹H NMR δ 2.62 (s, 3H), 7.42 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 8.02 (d, J = 8.6 Hz, 2H); ¹³C NMR δ 25.6, 126.0, 127.5, 128.0, 128.1, 133.4, 135.1, 137.3, 143.4, 196.5. GC-MS (t_R 11.8 min) m/z 230 (50, M⁺). HRMS [M + H]⁺ for C₁₄H₁₂ClO: calcd, 231.0571; found, 231.0572.

4-Methoxy-4'-chlorobiphenyl (12d). Treatment of **9** (113 mg, 0.20 mmol) with 4-iodo-1-methoxybenzene **5d** (187.2 mg, 0.8 mmol) by the *Typical Procedure* gave **12d**⁵⁷ (73.2 mg, 42%): ¹H NMR δ 3.84 (s, 3H), 6.96 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.44–7.50 (m, 4H); ¹³C NMR δ 55.4, 114.4, 128.0, 128.0, 128.9, 132.5, 132.7, 139.3, 159.4. GC-MS (t_R 10.6 min) m/z 218 (100, M⁺). HRMS [M + H]⁺ for C₁₃H₁₂ClO: calcd, 219.0571; found, 219.0571.

4-Chloro-2'-(trifluoromethyl)biphenyl (12f). Treatment of **9** (113 mg, 0.20 mmol) with 2-iodo-1-(trifluoromethyl)benzene **5f** (112.2 μ L, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave **12f** (167.9 mg, 82%): ¹H NMR δ 7.27 (d, J = 4.7 Hz, 2H), 7.31 (d, J = 5.1 Hz, 1H), 7.38 (d, J = 5.6 Hz, 2H), 7.49 (t, J = 4.8 Hz, 1H), 7.57 (t, J = 5.0 Hz, 1H), 7.75 (d, J = 5.3 Hz, 1H); ¹³C NMR δ 131.2 (q, ¹ J = 272 Hz), 125.2 (q, ³ J = 5.0 Hz), 126.7, 127.0, 127.3 (q, ² J = 31.3 Hz), 129.3, 130.4, 130.9, 132.8, 137.2, 139.1. GC-MS (t_R 7.5 min) m/z 256 (100, M⁺). HRMS [M + H]⁺ for C₁₃H₉ClF₃: calcd, 257.0339; found, 257.0343.

4-Chloro-3'-cyanobiphenyl (12h). Treatment of **9** (113 mg, 0.20 mmol) with 1-cyano-3-iodobenzene **5h** (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave **12h**⁵⁸ (134.6 mg, 79%): ¹H NMR δ 7.44–7.50 (m, 4H), 7.52–7.57 (m, 1H), 7.60–7.67 (m, 1H), 7.76 (s, 1H), 7.82 (s, 1H); ¹³C NMR δ 113.2, 118.6, 128.3, 129.3, 129.8, 130.5, 131.0, 131.3, 134.7, 137.3, 141.2. GC-MS (t_R 11.0 min) m/z 213 (100, M⁺). HRMS [M + H]⁺ for C₁₃H₉ClN: calcd, 214.0418; found, 214.0421.

4-Chloro-3'-methylbiphenyl (12j). Treatment of **9** (113 mg, 0.20 mmol) with 3-iodo-1-methylbenzene **5j** (102.7 μ L, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **12j**⁵⁹ (61.4 mg, 38%): ¹H NMR δ 2.44 (s, 3H), 7.20 (d, J = 4.7 Hz, 1H), 7.33–7.39 (m, 3H), 7.41 (d, J = 4.7 Hz, 2H), 7.52 (d, J = 5.3 Hz, 2H); ¹³C NMR δ 20.5, 126.7, 127.3, 127.4, 127.8, 127.8, 132.2, 137.5, 138.8, 139.0. GC-MS (t_R 9.2 min) m/z 202 (100, M⁺). HRMS [M + H]⁺ for C₁₃H₁₂Cl: calcd, 203.0622; found, 203.0625.

7-Isopropoxyisoflavone (Ipriflavone, 17). Treatment of tetraphenyltin **2a** (85.4 mg, 0.20 mmol) with 3-iodo-7-isopropylchromone **16**⁶⁰ (174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **17**⁶¹ as a white solid (206 mg, 92%): mp, 121.9–123.0 °C; IR (KBr), ν (cm⁻¹) 3060, 2985, 2972, 2928, 1637, 1592, 1561, 1491, 1439, 1369, 1325, 1261, 1034, 907, 881, 820, 780, 738, 694; ¹H NMR δ 1.40 (d, J = 6.0 Hz, 6H), 4.62–4.70 (m, 1H), 6.83 (s, 1H), 6.95 (dd, J = 9.0, 3.0 Hz, 1H), 7.34–7.45 (m, 3H), 7.56 (d, J = 9.0 Hz, 2H), 7.92 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H); ¹³C NMR 175.6, 162.5, 158.0, 152.6, 132.1, 129.0, 128.4, 128.1, 127.8, 125.2, 118.2, 115.6, 101.6, 70.8, 21.8. HRMS [M + Na]⁺ for C₁₈H₁₆O₃Na: calcd, 303.0997; found, 303.0969.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01648.

¹H and ¹³C NMR spectra for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wnuk@fiu.edu.

*E-mail: zhangzt@snnu.edu.cn.

Present Address

[†]Department of Molecular Medicine, Beckman Research Institute of the City of Hope Duarte, CA 91010

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Z.T.Z. and Y.L. are grateful to the Oversea Scholarship Program of Shaanxi Normal University and FIU University Graduate School for Dissertation Year Fellowship, respectively.

■ REFERENCES

- (1) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004.
- (2) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470.
- (3) Fagnou, K. *Top. Curr. Chem.* **2009**, *292*, 35–56.
- (4) Li, B.; Dixneuf, P. H. *Chem. Soc. Rev.* **2013**, *42*, 5744–5767.
- (5) Liang, Y.; Wnuk, S. F. *Molecules* **2015**, *20*, 4874–4901.
- (6) Dwight, T. A.; Rue, N. R.; Charyk, D.; Josselyn, R.; DeBoef, B. *Org. Lett.* **2007**, *9*, 3137–3139.
- (7) Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 11904–11905.
- (8) Liu, C.; Yuan, J.; Gao, M.; Tang, S.; Li, W.; Shi, R.; Lei, A. *Chem. Rev.* **2015**, *115*, 12138–12204.
- (9) Zhang, H.; Shi, R.; Ding, A.; Lu, L.; Chen, B.; Lei, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 12542–12545.
- (10) Mehta, V. P.; Punji, B. *RSC Adv.* **2013**, *3*, 11957–11986.
- (11) Sun, C.-L.; Shi, Z.-J. *Chem. Rev.* **2014**, *114*, 9219–9280.
- (12) Shirakawa, E.; Hayashi, Y.; Itoh, K.-i.; Watabe, R.; Uchiyama, N.; Konagaya, W.; Masui, S.; Hayashi, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 218–221.
- (13) Shirakawa, E.; Okura, K.; Uchiyama, N.; Murakami, T.; Hayashi, T. *Chem. Lett.* **2014**, *43*, 922–924.

- (14) Murarka, S.; Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 12362–12366.
- (15) Shirakawa, E.; Tamakuni, F.; Kusano, E.; Uchiyama, N.; Konagaya, W.; Watabe, R.; Hayashi, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 521–525.
- (16) Minami, H.; Wang, X.; Wang, C.; Uchiyama, M. *Eur. J. Org. Chem.* **2013**, *2013*, 7891–7894.
- (17) Minami, H.; Saito, T.; Wang, C.; Uchiyama, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 4665–4668.
- (18) Sun, C.-L.; Li, H.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* **2010**, *2*, 1044–1049.
- (19) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2011**, *50*, 5018–5022.
- (20) Uchiyama, N.; Shirakawa, E.; Hayashi, T. *Chem. Commun.* **2013**, *49*, 364–366.
- (21) Shirakawa, E.; Watabe, R.; Murakami, T.; Hayashi, T. *Chem. Commun.* **2013**, *49*, 5219–5221.
- (22) Haines, B. E.; Wiest, O. J. *Org. Chem.* **2014**, *79*, 2771–2774.
- (23) Zhou, S.; Anderson, G. M.; Mondal, B.; Doni, E.; Ironmonger, V.; Kranz, M.; Tuttle, T.; Murphy, J. A. *Chem. Sci.* **2014**, *5*, 476–482.
- (24) Yabe, Y.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Tetrahedron* **2010**, *66*, 8654–8660.
- (25) Moriya, K.; Knochel, P. *Org. Lett.* **2014**, *16*, 924–927.
- (26) McCann, L. C.; Organ, M. G. *Angew. Chem.* **2014**, *126*, 4475–4478.
- (27) Boruah, P. R.; Koiri, M. J.; Bora, U.; Sarma, D. *Tetrahedron Lett.* **2014**, *55*, 2423–2425.
- (28) Hao, X.-Q.; Wang, Y.-N.; Liu, J.-R.; Wang, K.-L.; Gong, J.-F.; Song, M.-P. *J. Organomet. Chem.* **2010**, *695*, 82–89.
- (29) Stathakis, C. I.; Manolikakes, S. M.; Knochel, P. *Org. Lett.* **2013**, *15*, 1302–1305.
- (30) Klier, L.; Bresser, T.; Nigst, T. A.; Karaghiosoff, K.; Knochel, P. *J. Am. Chem. Soc.* **2012**, *134*, 13584–13587.
- (31) Peng, Z.; Li, N.; Sun, X.; Wang, F.; Xu, L.; Jiang, C.; Song, L.; Yan, Z.-F. *Org. Biomol. Chem.* **2014**, *12*, 7800–7809.
- (32) Blumke, T.; Chen, Y. H.; Peng, Z.; Knochel, P. *Nat. Chem.* **2010**, *2*, 313–318.
- (33) Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 6040–6044.
- (34) Ochiai, H.; Jang, M.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 2681–2683.
- (35) Fleckenstein, J. E.; Koszinowski, K. *Organometallics* **2011**, *30*, 5018–5026.
- (36) Fugami, K.; Ohnuma, S.-y.; Kameyama, M.; Saotome, T.; Kosugi, M. *Synlett* **1999**, *1999*, 63–64.
- (37) Zhou, W.-J.; Wang, K.-H.; Wang, J.-X. *J. Org. Chem.* **2009**, *74*, 5599–5602.
- (38) Pitteloud, J.-P.; Zhang, Z.-T.; Liang, Y.; Cabrera, L.; Wnuk, S. F. *J. Org. Chem.* **2010**, *75*, 8199–8212.
- (39) Varga, M.; Batori, S.; Kövári-Rádkai, M.; Prohászka-Német, I.; Vitányi-Morvai, M.; Böcskey, Z.; Bokotey, S.; Simon, K.; Hermecz, I. *Eur. J. Org. Chem.* **2001**, *2001*, 3911–3920.
- (40) Rossi, R. A.; Pierini, A. B.; Peñeñory, A. B. *Chem. Rev.* **2003**, *103*, 71–168.
- (41) Hart, H.; Harada, K.; Du, C. J. F. *J. Org. Chem.* **1985**, *50*, 3104–3110.
- (42) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470.
- (43) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033–3040.
- (44) Garcia Martinez, A.; Osio Barcina, J.; Colorado Heras, M. d. R.; de Fresno Cerezo, A. *Organometallics* **2001**, *20*, 1020–1023.
- (45) Grasa, G. A.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119–122.
- (46) Mowery, M. E.; DeShong, P. J. *J. Org. Chem.* **1999**, *64*, 3266–3270.
- (47) Handy, C. J.; Lam, Y.-F.; DeShong, P. J. *J. Org. Chem.* **2000**, *65*, 3542–3543.
- (48) Acceleration of Pd-catalyzed coupling of tetraorganotin with ArX in which oxidative addition was the rate-determining step has been also reported: Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992–4998.
- (49) Formation of homocoupling byproducts (e.g., **4**) likely involves aryl iodide oxidants as electron acceptors from [Ph–Ph]^{•–} species, as elegantly shown in ref **20** for transition-metal-free coupling of aryl Grignard reagents with aryl halides. Transition-metal-free homocoupling of organomagnesium compounds in the presence of an organic oxidant has also been demonstrated: Krasovskiy, A.; Tishkov, A.; Del Amo, V.; Mayr, H.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 5010–5014.
- (50) Yokoyama, N.; Nakayama, Y.; Nara, H.; Sayo, N. *Adv. Synth. Catal.* **2013**, *355*, 2083–2088.
- (51) Zhang, Z.-T.; Pitteloud, J.-P.; Cabrera, L.; Liang, Y.; Toribio, M.; Wnuk, S. F. *Org. Lett.* **2010**, *12*, 816–819.
- (52) Hafner, A.; Bräse, S. *Adv. Synth. Catal.* **2013**, *355*, 996–1000.
- (53) Chen, X.; Ke, H.; Zou, G. *ACS Catal.* **2014**, *4*, 379–385.
- (54) Xie, L.-G.; Wang, Z.-X. *Chem. - Eur. J.* **2011**, *17*, 4972–4975.
- (55) Traficante, C. I.; Mata, E. G.; Delpiccolo, C. M. L. *RSC Adv.* **2015**, *5*, 26796–26800.
- (56) Marciasini, L.; Richy, N.; Vaultier, M.; Pucheault, M. *Chem. Commun.* **2012**, *48*, 1553–1555.
- (57) Chauhan, P.; Ravi, M.; Singh, S.; Raju, K. S. R.; Bajpai, V.; Kumar, B.; Wahajuddin; Yadav, P. P. *RSC Adv.* **2014**, *4*, 43336–43340.
- (58) Kagiya, N.; Tsurushima, M. Mikuni Seiyaku Kogyo K. K. JP09176104A, 1997 Japan.
- (59) He, Y.; Zhang, X.-Y.; Cui, L.-Y.; Fan, X.-S. *Chem. - Asian J.* **2013**, *8*, 717–722.
- (60) Yang, Q.; Zhang, Z.; Liang, B. J. *Heterocycl. Chem.* **2015**, *52*, 310–316.
- (61) Zhang, Z.; Qiao, J.; Wang, D.; Han, L.; Ding, R. *Mol. Diversity* **2014**, *18*, 245–251.