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

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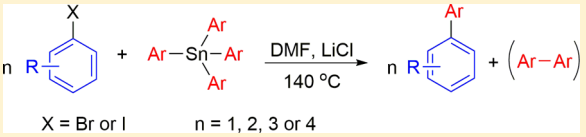
Supporting Information

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 organomagnesium (Kumada), organozinc (Negishi), organoboron (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 organoaluminum[17] 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 $S_{RN}1$,[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 reagents[33] and enhances their reactivity toward transmetalation[34] 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-

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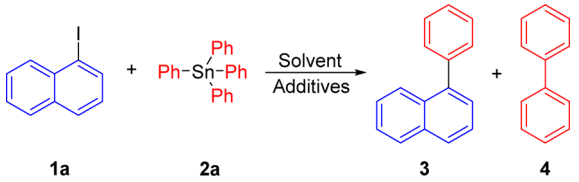
Table 1. Optimization of the LiCl-Promoted Cross-Coupling between Iodonaphthalene 1a and Tetraphenyltin 2a[a]



1a 2a 3 4

		additives					
entry	solvent	salts	equiv	T/°C	time/h	yield (%),[b,c] 3	ratio[b] 3:4
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]

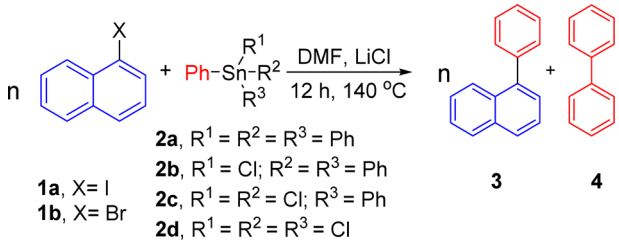
[a]Couplings were performed on 0.20 mmol scale of **2a** (0.05 M) with 1 equiv of **1a**. [b]Determined by GC/MS and/or ^{1}H NMR. [c]Isolated yield in parentheses. [d]Product **3** was not detected. [e]Homocoupling byproduct **4** was observed. [f]Not determined. [g]Coupling in 5, 6, or 12 h yielded **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]



2a, $R^1 = R^2 = R^3 = Ph$
2b, $R^1 = Cl$; $R^2 = R^3 = Ph$
2c, $R^1 = R^2 = Cl$; $R^3 = Ph$
2d, $R^1 = R^2 = R^3 = Cl$

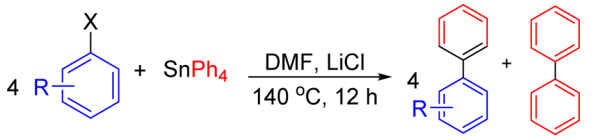
1a, X= I
1b, X= Br

3 4

	halides				
entry	1	equiv (n)	stannanes	yield (%)[b] 3	ratio[c] 3:4
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

[a]Couplings were performed on 0.20 mmol scale of **2a–2d** (0.05 M) with 5 equiv of LiCl at 140 °C for 12 h. [b]Yields 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. [c]Determined by ^{1}H NMR. [d]Heated for 4 h. [e]**3** 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]



5a-5k **2a** **6a-6k** **4**

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

[a]Couplings 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. [b]Calculated based on transferring four phenyl groups from **2a**. [c]Determined by ^{1}H 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

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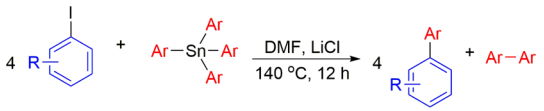
reactive with the electrophilic substituents, such as cyano, ester, or ketone,[12] the organostannane coupling described here demonstrates higher functional group tolerance, similarly to the reactions with arylzinc reagents.[15] The aryl bromide **5k** also undergoes coupling with **2a** to give **6k**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



5a-5j **7-9** **10-12** **13-15**

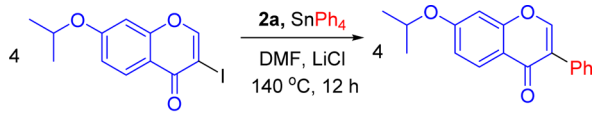
entry	halides		stannane		product	yield (%)[b]	ratio[c]
	R	5	Ar-	7-9			
1	4-$COOCH_3$	**5a**			**10a**	71	15:2
2	4-CN	**5c**			**10c**	48	3:2
3	4-OCH_3	**5d**		**7**	**10d**	26	5:4
4	2-CH_3	**5g**			**10g**	25	2:1
5	3-CF_3	**5i**			**10i**	63	8:1
6	4-$COCH_3$	**5b**		**8**	**11b**	55	7:1
7	3-CH_3	**5j**			**11j**	34	3:1
8	4-$COCH_3$	**5b**			**12b**	65	20:1
9	4-OCH_3	**5d**			**12d**	42	5:2
10	2-CF_3	**5f**		**9**	**12f**	82	50:1
11	3-CN	**5h**			**12h**	79	15:1
12	3-CH_3	**5j**			**12j**	38	5:3

[a]Couplings 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. [b]Calculated based on transferring four aryl groups from tin reagents **7–9**. [c]Ratio of **10**:**13**, **11**:**14**, or **12**:**15** was determined by ^{1}H 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 Ar_4Sn 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



16 **17**

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 arylzinc[15] 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 germane[38] 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 N_2 vs atmospheric conditions vs oxygen introduced by syringe did not improve the yields of coupling products and their selectivity to homocoupling[49] byproducts. It is noteworthy that the best results were obtained when the reaction suspension was heated with a drying tube, filled with anhydrous $CaCl_2$, 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

^{1}H NMR spectra at 300 MHz and proton-decoupled $^{13}C\{^1H\}$ NMR data at 75 MHz were determined with solutions in $CDCl_3$. TLC was performed on Merck kieselgel 60-F_{254}, and products were detected with 254 nm light or by development of color with I_2. Merck kieselgel 60 (230–400 mesh) was used for column chromatography. Purity, yields, and ratio of the products (crude and/or purified) were

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established with GC/MS [EI; capillary column RTX-1MS (30 m × 0.25 mm × 25 μm)] using calibrated standards. HRMS data were recorded by electrospray ionization with a TOF mass analyzer. LiCl (catalog number 449881, ≥ 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 (~5 min), DMF (4 mL) and 1-iodonaphthalene **1a** (116.8 μL, 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 °C (oil bath) for 12 h. Volatiles were evaporated and the residue was partitioned (H_2O/EtOAc). The organic layer was dried (Na_2SO_4), evaporated and purified by column chromatography (hexane) to give **3**[38] (61.3 mg, 75%): ^{1}H 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, $[M]^+$). 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, $[M]^+$) and (t_R 5.8 min, **4**) *m*/*z* 154 (100, $[M]^+$). HRMS $[M + H]^+$ for $C_{16}H_{13}$: 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, 0.20 mmol) with methyl 4-iodobenzoate **5a** (209.6 mg, 0.80 mmol) by the *Typical Procedure* gave **6a**[50] (128.9 mg, 76%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{14}H_{13}O_2$: calcd, 213.0910; found, 213.0911.

4-Acetylbiphenyl (6b). Treatment of **2a** (85.4 mg, 0.20 mmol) with 4-iodoacetophenone **5b** (196.8 mg, 0.8 mmol) by the *Typical Procedure* gave **6b**[50] (94.1 mg, 60%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{14}H_{13}O$: calcd, 197.0961; found, 197.0963.

4-Cyanobiphenyl (6c). Treatment of **2a** (85.4 mg, 0.20 mmol) with 1-cyano-4-iodobenzene **5c** (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave **6c**[50] (103.1 mg, 72%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{10}N$: calcd, 180.0808; found, 180.0810.

4-Methoxybiphenyl (6d). Treatment of **2a** (85.4 mg, 0.20 mmol) with 4-iodo-1-methoxybenzene **5d** (187.2 mg, 0.8 mmol) by the *Typical Procedure* gave **6d**[51] (45.6 mg, 31%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{13}O$: calcd, 185.0961; found, 185.0961.

2-Nitrobiphenyl (6e). Treatment of **2a** (85.4 mg, 0.20 mmol) with 2-iodo-1-nitrobenzene **5e** (199.2 mg, 0.80 mmol) by the *Typical Procedure* gave **6e**[37] (127.4 mg, 80%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{12}H_{10}NO_2$: calcd, 200.0706; found, 200.0707.

2-(Trifluoromethyl)biphenyl (6f). Treatment of **2a** (85.4 mg, 0.20 mmol) with 2-iodo-1-trifluoromethylbenzene **5f** (112.2 μL, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave **6f**[52] (140.3 mg, 79%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{10}F_3$: calcd, 223.0729; found, 223.0731.

2-Methylbiphenyl (6g). Treatment of **2a** (85.4 mg, 0.20 mmol) with 2-iodo-1-methylbenzene **5g** (101.8 μL, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **6g**[50] (59.1 mg, 44%?): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{13}$: calcd, 169.1012; found, 169.1011.

3-Cyanobiphenyl (6h). Treatment of **2a** (85.4 mg, 0.20 mmol) with 1-cyano-3-iodobenzene **5h** (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave **6h**[37] (88.8 mg, 62%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{10}N$: calcd, 180.0808; found, 180.0812.

3-(Trifluoromethyl)biphenyl (6i). Treatment of **2a** (85.4 mg, 0.20 mmol) with 3-iodo-1-trifluoromethylbenzene **5i** (115.3 μL, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave **6i**[38] (133.2 mg, 75%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{10}F_3$: calcd, 223.0729; found, 223.0730.

3-Methylbiphenyl (6j). Treatment of **2a** (85.4 mg, 0.20 mmol) with 3-iodo-1-methylbenzene **5j** (102.7 μL, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **6j**[50] (53.8 mg, 40%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{13}$: calcd, 169.1012; found, 169.1014.

2-Cyanobiphenyl (6k). Treatment of **2a** (85.4 mg, 0.20 mmol) with 1-cyano-2-bromobenzene **5k** (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave **6k**[37] (51.6 mg, 36%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{13}H_{10}N$: calcd, 180.0808; found, 180.0810.

3,4′-Dimethylbiphenyl (10a). Treatment of *tetra*-(*p*-methylphenyl)tin **7** (96.6 mg, 0.20 mmol) with 1-methyl-3-iodobenzene **5a** (102.7 μL, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **10a**[53] (36.4 mg, 25%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{15}H_{15}O_2$: calcd, 227.1067; found, 227.1071.

4-Cyano-4′-methybiphenyl (10c). Treatment of **7** (96.6 mg, 0.20 mmol) with 1-cyano-4-iodo-benzene **5c** (183.2 mg, 0.8 mmol) by the *Typical Procedure* gave **10c**[53] (74.1 mg, 48%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{14}H_{12}N$: calcd, 194.0964; found, 194.0969.

4-Methoxyl-4′-methybiphenyl (10d). Treatment of **7** (96.6 mg, 0.20 mmol) with 4-iodo-1-methoxylbenzene **5d** (187.2 mg, 0.8 mmol) by the *Typical Procedure* gave **10d**[53] (41.2 mg, 26%): ^{1}H 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, M^+). HRMS $[M + H]^+$ for $C_{14}H_{15}O$: calcd, 199.1117; found, 199.1120.

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3′,4-Dimethybiphenyl (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%): ^{1}H 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); ^{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, M$^+$). HRMS [M + Na]$^+$ for $C_{14}H_{14}Na$: 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 μL, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave **10i**[54] (118.9 mg, 63%): ^{1}H 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); ^{13}C NMR δ 21.3, 123.77 (q, ^3J = 3.0 Hz), 123.86 (q, ^3J = 3.0 Hz), 124.4 (q, ^1J = 271.5 Hz), 127.1, 129.3, 129.9, 130.3, 131.3 (q, ^2J = 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 $C_{14}H_{12}F_3$: calcd, 237.0886; found, 237.0889.

4′-Acetyl-3-methoxylbiphenyl (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%): ^{1}H 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); ^{13}C 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 $C_{15}H_{15}O_2$: calcd, 227.1067; found, 227.1069.

3-Methoxyl-3′-methylbiphenyl (11j). Treatment of **8** (109.4 mg, 0.20 mmol) with 3-iodo-1-methylbenzene **5j** (102.7 μL, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **11j**[56] (53.9 mg, 34%): ^{1}H 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); ^{13}C 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 $C_{14}H_{15}O$: 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%): ^{1}H 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); ^{13}C 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 $C_{14}H_{12}ClO$: calcd, 231.0571; found, 231.0572.

4-Methoxyl-4′-chlorobiphenyl (12d). Treatment of **9** (113 mg, 0.20 mmol) with 4-iodo-1-methoxylbenzene **5d** (187.2 mg, 0.8 mmol) by the *Typical Procedure* gave **12d**[57] (73.2 mg, 42%): ^{1}H 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); ^{13}C 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 $C_{13}H_{12}ClO$: 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 μL, 217.6 mg, 0.8 mmol) by the *Typical Procedure* gave **12f** (167.9 mg, 82%): ^{1}H 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); ^{13}C NMR δ 131.2 (q, ^1J = 272 Hz), 125.2 (q, ^3J = 5.0 Hz), 126.7, 127.0, 127.3 (q, ^2J = 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 $C_{13}H_9ClF_3$: 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%): ^{1}H 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);^{13}C 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 $C_{13}H_9ClN$: 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 μL, 174.4 mg, 0.8 mmol) by the *Typical Procedure* gave **12j**[59] (61.4 mg, 38%): ^{1}H 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); ^{13}C 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 $C_{13}H_{12}Cl$: 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; ^{1}H 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); ^{13}C 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 $C_{18}H_{16}O_3Na$: 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.

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

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Notes

The authors declare no competing financial interest.

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