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Palladium-Catalyzed Hiyama Cross-Coupling of Aryltrifluorosilanes with Aryl and Heteroaryl Chlorides

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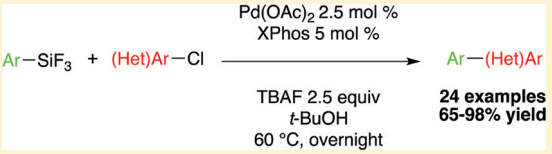
Supporting Information

ABSTRACT: An efficient, palladium-catalyzed Hiyama cross-coupling reaction of aryltrifluorosilanes with aryl chlorides has been developed. A wide variety of functionalized biaryl derivatives were isolated in good to excellent yields. The scope of this reaction has also been extended to heteroaryl chlorides, affording the corresponding heterobiaryl compounds in high yields.



Metal-mediated cross-coupling reactions are among the most powerful methods of creating carbon−carbon bonds in organic chemistry. In the past 40 years, organomagnesium (Kumada−Corriu), organoboron (Suzuki−Miyaura), organotin (Stille), organozinc (Negishi), and organosilane (Hiyama) derivatives have been developed as nucleophilic partners for cross-coupling reactions.[1−5] Each of these classes has its own limitations, often because of the instability or toxicity of the reagent. In this context, organosilicon derivatives, known to be easy to handle, stable (toward air and moisture), and less toxic compared to other organometallic reagents such as organostannanes, appeared as interesting partners for the development of cross-coupling reactions.[5]

Previously, silane derivatives have been seen as poor cross-coupling partners because of the weak polarization of the carbon−silicon bond. This limitation has been overcome through the generation of a pentacoordinate silicon intermediate in situ,[6] using a fluoride activator[7] such as tetra-*n*-butylammonium fluoride (TBAF) or an inorganic base.[8−12] Subsequently, efficient partners for Hiyama cross-coupling such as organo(trialkoxy)silanes,[13−19] organosilanolates,[20−23] organobis(catechol)silicates,[24] organosilatranes,[25] and organohalosilanes[26−32] have been developed.

Among these types of organosilanes, organotrifluorosilanes are interesting because of their stability to heat, air, and moisture, easy handling, and facile accessibility from commercially available trichlorosilanes.[33] Surprisingly, although they have been used in a wide range of metal-mediated reactions as efficient partners,[34−39] only a few examples of Hiyama cross-coupling reactions of trifluorosilanes have been reported. The first report came from Hiyama and co-workers, who achieved the cross-coupling reaction of alkyltrifluorosilanes with a variety of aryl iodides and bromides using a catalytic amount of $Pd(PPh_3)_4$, but a large excess of TBAF.[29,30] More recently, Fu has developed a nickel-catalyzed Hiyama cross-coupling of aryltrifluorosilanes with secondary alkyl halides (iodides, bromides, and chlorides).[31,32] To the best of our knowledge, there are no examples of aryltrifluorosilane cross-couplings with aryl chlorides. Therefore, we were intrigued to see if they could be suitable partners for this transformation.

Herein, we describe an efficient palladium-catalyzed Hiyama cross-coupling of aryltrifluorosilanes with both aryl and heteroaryl chlorides for the synthesis of biaryls and heterobiaryls. The catalytic system was first optimized on a model reaction between phenyltrifluorosilane **1a** and 4-chloroanisole in the presence of 2.5 mol % of $Pd(OAc)_2$ as catalyst. After a ligand screen with various ligands (Figure 1)

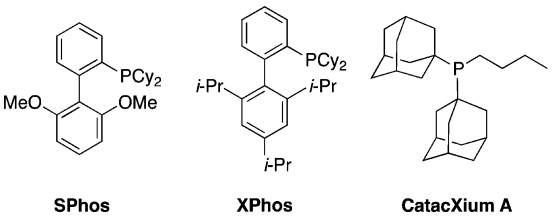


Figure 1. Ligands utilized in optimization studies.

was performed in *t*-BuOH as solvent (Table 1, entries 1−3), XPhos emerged as the most efficient, yielding **2a** in 71% yield.

Other solvents were tested (Table 1, entries 4 and 5), but all of them led to a decrease in reaction yield. When TBAF was replaced with various inorganic bases (Table 1, entries 6−8), no reaction occurred. Finally, the ratio of aryltrifluorosilane **1a** and TBAF was studied, and **2a** was isolated in 78% yield by employing 1.5 equiv of **1a** and 2.5 equiv of TBAF at 60 °C.

We then chose to investigate the electrophile compatibility in this palladium-catalyzed Hiyama cross-coupling reaction under the conditions previously optimized. The iodide, bromide, and triflate provided the desired product in 95, 88, and 86% yields, respectively (Table 2, entries 1, 2, and 4). The aryl chloride afforded a slightly lower yield (78%) (Table 2, entry 3). On the

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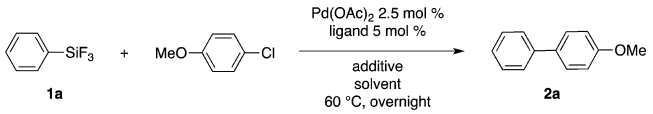
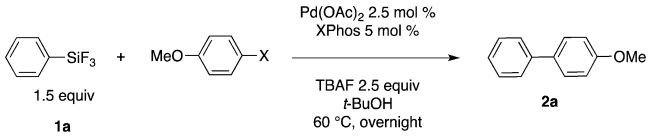
Table 1. Optimization



1a 2a

entry	1a equiv	ligand	additive (equiv)	solvent	% isolated yield
1	1	SPhos	TBAF (2)	*t*-BuOH	53
2	1	CatacXiumA	TBAF (2)	*t*-BuOH	38
3	1	XPhos	TBAF (2)	*t*-BuOH	71
4	1	XPhos	TBAF (2)	THF	51
5	1	XPhos	TBAF (2)	toluene	47
6	1	XPhos	CsF (3)	*t*-BuOH	0
7	1	XPhos	NaOH (3)	*t*-BuOH	0
8	1	XPhos	KF (3)	*t*-BuOH	0
9	1	XPhos	TBAF (2)	*t*-BuOH	73
10	1.5	XPhos	TBAF (2.5)	*t*-BuOH	78

Table 2. Electrophile Compatibility



1.5 equiv 1a 2a

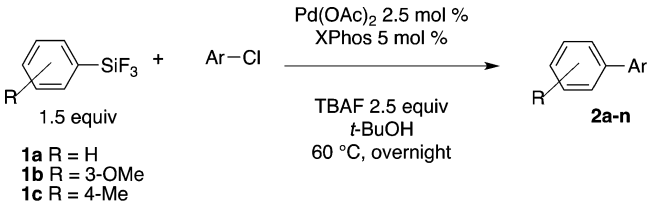
entry	X	% isolated yield
1	I	95
2	Br	88
3	Cl	78
4	OTf	86
5	OTs	16
6	OMs	24

other hand, the tosylate and mesylate were not effective coupling partners under these conditions, affording the cross-coupled product in low yields. Given the low price and wide range of commercially available aryl chlorides, we used them as the electrophiles of choice.

We were pleased to find that a wide variety of substituted aryl chlorides provided the expected biaryl derivatives in good to excellent yields (Table 3). Even the hindered 1-chloro-4-methoxy-2,6-dimethylbenzene could be used with phenyltrifluorosilane **1a** to give the coupling product **2d** with an excellent yield of 97% by simply increasing the temperature to 100 °C (Table 3, entry 4). We were delighted to observe the compatibility of this reaction with both electron-rich (Table 3, entries 1−5) and electron-poor (Table 3, entries 6−12) aryl chlorides. Notably, a large functional group array including ether, amine, nitrile, nitro, ester, aldehyde, and ketone functional groups was tolerated. Substituted 3-methoxy- and 4-methylbenzenetrifluorosilanes **1b** and **1c** were also suitable partners in this process, affording the corresponding products **2m** and **2n** in 80 and 81% yields, respectively (Table 3, entries 13 and 14). Interestingly, scaling the reaction up to 6.4 mmol of 4-chloroacetophenone allowed a reduction in the catalyst loading to 2 mol % of palladium and 4 mol % of ligand, yielding the biaryl **2l** in 96% yield.

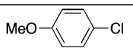
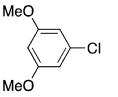
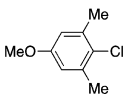
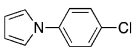
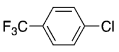
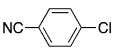
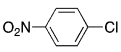
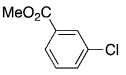
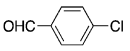
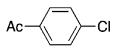
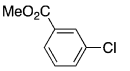
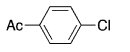
To expand the scope of this transformation even further, heteroaryl chlorides were next examined. 3-Arylpyridines **3a−e** were obtained in yields ranging from 74 to 94% (Table 4, entries 1−5). 4-Chloroquinaldine was coupled with phenyltrifluorosilane **1a**, providing the corresponding heterobiaryl **3f** in moderate yield (Table 4, entry 6). Thienyl and furanyl

Table 3. Scope of Aryl Chlorides



1.5 equiv

1a R = H
1b R = 3-OMe
1c R = 4-Me

entry	silane	Ar-Cl	product	%isoltd yield
1	**1a**		**2a**	78
2	**1a**		**2b**	90
3	**1a**		**2c**	70
4	**1a**		**2d**	97[a]
5	**1a**		**2e**	90
6	**1a**		**2f**	75
7	**1a**		**2g**	89
8	**1a**		**2h**	73
9	**1a**		**2i**	91
10	**1a**		**2j**	98
11	**1a**		**2k**	85
12	**1a**		**2l**	86 (96)[b]
13	**1b**		**2m**	80
14	**1c**		**2n**	81

[a]100 °C. [b]Reaction performed on a 6.4 mmol scale using 2 mol % of $Pd(OAc)_2$, 4 mol % of XPhos, 1.5 equiv of **1a**, and 2.5 equiv of TBAF.

chlorides also reacted, affording coupled products **3g** and **3h** in 90 and 74% yields, respectively (Table 4, entries 7 and 8). As before, sensitive functional groups such as aldehydes were tolerated under the reaction conditions. In addition, 6-chloroisoquinoline gave the desired heterobiaryl derivatives **3i** and **3j** in good yields, although it required a higher temperature

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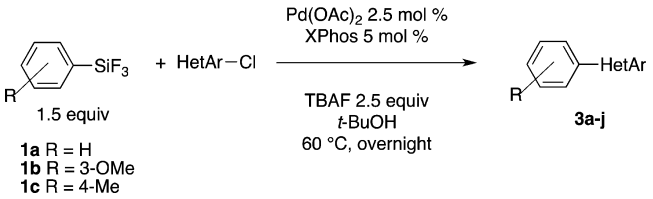
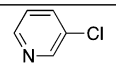
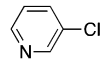
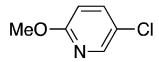
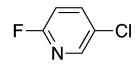
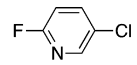
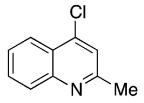
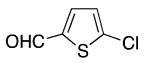
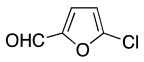
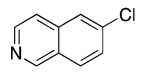
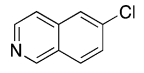
Table 4. Scope of Heteroaryl Chlorides



entry	silane	HetAr-Cl	product	% isoltd yield
1	**1a**		**3a**	74
2	**1b**		**3b**	76
3	**1a**		**3c**	78
4	**1a**		**3d**	84
5	**1c**		**3e**	94
6	**1a**		**3f**	65
7	**1a**		**3g**	90
8	**1a**		**3h**	74
9	**1a**		**3i**	85[a]
10	**1b**		**3j**	71[a]

[a]100 °C.

to cross-couple (Table 3, entries 9 and 10). Moreover, substituted trifluorosilanes **1b** and **1c** performed as efficient partners in Hiyama cross-coupling with heteroaryls, leading to the expected products **3b** and **3e** with good yields (Table 4, entries 2 and 5).

In summary, we have demonstrated that aryltrifluorosilanes can be cross-coupled with a wide variety of substituted aryl and heteroaryl chlorides. The corresponding cross-coupled products were obtained in good to excellent yields.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an argon atmosphere. $Pd(OAc)_2$, XPhos, and TBAF were used as received. Phenyltrichlorosilane and trichloro(4-methylphenyl)silane were purchased and used as received. Trichloro(3-methoxyphenyl)-silane was prepared as described in the literature.[40] Solvents were degassed with argon each time prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500 MHz spectrometer. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant J (Hz), and integration. Analytical thin-layer chromatography (TLC) was performed on TLC silica or alumina gel plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures were followed using 32−63 μm silica gel. Visualization was effected with ultraviolet light.

General Procedure for Preparation of Organotrifluorosilanes. The organotrichlorosilane (1 equiv) and Na_2SiF_6 (2 equiv) were heated to 200 °C for 1 h.[33] After being cooled to rt, the crude mixture was purified by distillation, affording the desired organotrifluorosilane.

Phenyltrifluorosilane (1a).[31] Following the general procedure for preparation of organotrifluorosilane, **1a** was obtained as a colorless oil (2.95 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (t, J = 7.5 Hz, 2 H), 7.64−7.67 (m, 1 H), 7.76−7.78 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.3, 128.8, 133.5, 134.7. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −141.1. IR (neat): $\tilde{\nu}_{max}$ = 1537, 1589, 3078 cm^{-1}.

Trifluoro(3-methoxyphenyl)silane (1b).[40] Following the general procedure for preparation of organotrifluorosilane, **1b** was obtained as a colorless oil (1.29 g, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 7.15−7.17 (m, 1 H), 7.22−7.23 (m, 1 H), 7.30−7.32 (m, 1 H), 7.41−7.45 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 119.4, 119.6, 121.4, 126.8, 130.3, 159.6. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −141.0. IR (neat): $\tilde{\nu}_{max}$ = 1267, 1507, 1567, 3089 cm^{-1}.

Trifluoro(*p*-tolyl)silane (1c).[31] Following the general procedure for preparation of organotrifluorosilane, **1c** was obtained as a colorless oil (2.06 g, 42%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 7.33 (d, J = 8.0 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.9, 116.8, 117.0, 129.6, 133.3, 134.7, 144.2. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −140.9. IR (neat): $\tilde{\nu}_{max}$ = 1540, 1609, 3056 cm^{-1}.

General Procedure for Hiyama Cross-Coupling with Aryltrifluorosilanes. $Pd(OAc)_2$ (0.17 mmol, 3.9 mg) and XPhos (0.35 mmol, 17 mg) were added under argon to a solution of aryltrifluorosilane **1a−c** (1.05 mmol) in *t*-BuOH (1 mL) in a Biotage microwave vial. TBAF was added and the vial sealed with a cap lined with a disposable Teflon septum. After being stirred for 5 min at rt, a solution of aryl chloride (0.7 mmol) in *t*-BuOH (1 mL) was added and the reaction mixture heated conventionally to 60 °C overnight. After being cooled to rt, the crude mixture was filtered through a pad of silica, concentrated in vacuo, and purified by flash column chromatography using a gradient mixture of hexanes and EtOAc as eluent.

4-Methoxybiphenyl (2a).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2a** was obtained as a white solid directly from the chromatographic solvent. Mp: 84−86 °C (100 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 6.69 (d, J = 8.5 Hz, 2 H), 7.32 (t, J = 7.2 Hz, 1 H), 7.43 (t, J = 7.5 Hz, 2 H), 7.54−7.58 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 114.3, 126.7, 126.8, 128.2, 128.8, 133.9, 140.9, 159.2. IR (neat): $\tilde{\nu}_{max}$ = 1290, 1579, 3098 cm^{-1}. HRMS: calcd for $C_{13}H_{13}O$ $[M + H]^+$ 185.0966, found 185.0970.

3,5-Dimethoxybiphenyl (2b).[42] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2b** was obtained as a yellow oil (135 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.85 (s, 6 H), 6.48 (t, J = 2.0 Hz, 1 H), 6.75 (d, J = 2.0 Hz, 2 H), 7.34−7.36 (m, 1 H), 7.42−7.45 (m, 2 H), 7.58−7.59 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 99.4, 105.6, 127.3, 127.6, 128.8, 141.3, 143.6, 161.1. IR (neat): $\tilde{\nu}_{max}$ = 1167, 1534, 1589, 3045 cm^{-1}. HRMS: calcd for $C_{14}H_{15}O_2$ $[M + H]^+$ 215.1072, found 215.1077.

2-Methoxybiphenyl (2c).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilane, **2c** was obtained as a colorless oil (90 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.99−7.01 (m, 1 H), 7.04 (t, J = 7.5 Hz, 1 H), 7.32−7.35 (m, 3 H), 7.42 (t, J = 7.5 Hz, 2 H), 7.55 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (125

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MHz, $CDCl_3$): δ = 55.6, 111.3, 120.9, 127.7, 128.1, 128.7, 129.6, 130.8, 131.0, 138.6, 156.5. IR (neat): $\tilde{\nu}_{max}$ = 1178, 1508, 1567, 3029 cm^{-1}. HRMS: calcd for $C_{13}H_{12}O$ $[M]^+$ 184.0888, found 184.0889.

2-Phenyl-5-methoxy-1,3-dimethylbenzene (2d). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilane, **2d** was obtained as a colorless oil (143 mg, 97%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, 6 H), 3.90 (s, 3 H), 6.78 (s, 2 H), 7.23 (d, J = 7.5 Hz, 2 H), 7.40 (t, J = 7.5 Hz, 1 H), 7.49 (t, J = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 55.1, 112.6, 126.5, 128.4, 129.7, 134.6, 137.4, 140.9, 158.3. IR (neat): $\tilde{\nu}_{max}$ = 1234, 1567, 1590, 3028 cm^{-1}. HRMS: calcd for $C_{15}H_{16}O$ $[M]^+$ 212.1201, found 212.1210.

4-Phenyl-1*H*-benzopyrrole (2e). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2e** was obtained as a white solid directly from the chromatographic solvent. Mp: 185−186 °C (139 mg, 90%). ^1H NMR (500 MHz, $CDCl_3$): δ = 6.39 (t, J = 2.0 Hz, 2 H), 7.15 (t, J = 2.0 Hz, 2 H), 7.38 (t, J = 7.5 Hz, 1 H), 7.46−7.49 (m, 4 H), 7.62 (d, J = 8.0 Hz, 2 H), 7.66 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 110.6, 119.3, 120.7, 126.9, 127.4, 128.2, 128.9, 138.5, 139.9, 140.2. IR (neat): $\tilde{\nu}_{max}$ = 1123, 1597, 1690, 3043, cm^{-1}. HRMS: calcd for $C_{16}H_{14}N$ $[M + H]^+$ 220.1126, found 220.1126.

1-Phenylnaphthalene (2f).[43] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2f** was obtained as a colorless oil (107 mg, 75%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44−7.47 (m, 3 H), 7.50−7.57 (m, 6 H), 7.89 (d, J = 8.5 Hz, 1 H), 7.94 (d, J = 9.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 125.4, 125.8, 126.1 (2C), 127.0, 127.3, 127.7, 128.3, 130.1, 131.7, 133.9, 140.3, 140.8. IR (neat): $\tilde{\nu}_{max}$ = 1578, 1590, 3067, 3090 cm^{-1}. HRMS: calcd for $C_{16}H_{13}$ $[M + H]^+$ 205.1017, found 205.1012.

4-(Trifluoromethyl)biphenyl (2g).[44] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2g** was obtained as a white solid directly from the chromatographic solvent. Mp: 65−67 °C (138 mg, 89%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43−7.46 (m, 1 H), 7.51 (t, J = 7.5 Hz, 2 H), 7.63 (d, J = 7.5 Hz, 2 H), 7.70−7.74 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 123.4 (q, J = 272.1 Hz), 125.8 (q, J = 3.7 Hz), 127.4, 127.5, 128.3, 128.8, 129.1 (q, J = 32.2 Hz), 139.9, 144.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −62.3. IR (neat): $\tilde{\nu}_{max}$ = 1545, 1607, 3067 cm^{-1}. HRMS: calcd for $C_{13}H_9F_3$ $[M]^+$ 222.0656, found 222.0648.

4-Phenylbenzonitrile (2h).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2h** was obtained as a white solid directly from the chromatographic solvent. Mp: 85−87 °C (91 mg, 73%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41−7.44 (m, 1 H), 7.47−7.50 (m, 2 H), 7.58−7.59 (m, 2 H), 7.66−7.72 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 110.8, 118.9, 127.2, 127.7, 128.7, 129.1, 132.6, 139.1, 145.6. IR (neat): $\tilde{\nu}_{max}$ = 1567, 1601, 2307, 3110 cm^{-1}. HRMS: calcd for $C_{13}H_9N$ $[M]^+$ 179.0735, found 179.0743.

4-Nitrobiphenyl (2i).[45] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2i** was obtained as a yellow solid directly from the chromatographic solvent. Mp: 100−102 °C (127 mg, 91%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43−7.46 (m, 1 H), 7.49−7.52 (m, 2 H), 7.63 (d, J = 8.0 Hz, 2 H), 7.72−7.74 (m, 2 H), 8.28−8.30 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.2, 127.4, 127.8, 129.0, 129.2, 138.8, 147.1, 147.7. IR (neat): $\tilde{\nu}_{max}$ = 1343, 1508, 1643, 3078 cm^{-1}. HRMS: calcd for $C_{12}H_9NO_2$ $[M]^+$ 199.0633, found 199.0639.

3-Phenylmethylbenzoate (2j).[46] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2j** was obtained as a colorless oil (146 mg, 98%). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.94 (s, 3 H), 7.36−7.39 (m, 1 H), 7.44−7.53 (m, 3 H), 7.61−7.63 (m, 2 H), 7.78−7.79 (m, 1 H), 8.02 (d, J = 7.5 Hz, 1 H), 8.28 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.3, 127.3, 127.8, 128.4 (2C), 128.9, 129.0, 130.8, 131.6, 140.2, 141.6, 167.2. IR (neat): $\tilde{\nu}_{max}$ = 1234, 1576, 1705, 3090 cm^{-1}. HRMS: calcd for $C_{14}H_{13}O_2$ $[M + H]^+$ 213.0916, found 213.0911.

Biphenyl-4-carboxaldehyde (2k).[43] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2k** was obtained as a yellow solid directly from the chromatographic solvent. Mp: 182−184 °C (108 mg, 85%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.43 (m, 1 H), 7.46−7.49 (m, 2 H), 7.62−7.64 (m, 2 H), 7.73−7.74 (m, 2 H), 7.93−7.95 (m, 2 H), 10.05 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.3, 127.6, 128.5, 129.0, 130.2, 135.2, 139.7, 147.1, 191.8. IR (neat): $\tilde{\nu}_{max}$ = 1527, 1604, 1689, 3087 cm^{-1}. HRMS: calcd for $C_{13}H_{10}O$ $[M]^+$ 182.0732, found 182.0732.

4-Acetylbiphenyl (2l).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2l** was obtained as a white solid directly from the chromatographic solvent. Mp: 118−120 °C (118 mg, 86%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.62 (s, 3 H), 7.38−7.41 (m, 1 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.62 (d, J = 7.5 Hz, 2 H), 7.67 (d, J = 8.0 Hz, 2 H), 8.02 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.6, 127.1, 127.2, 128.2, 128.8, 128.9, 135.8, 139.7, 145.6, 197.6. IR (neat): $\tilde{\nu}_{max}$ = 1549, 1579, 1721, 3023 cm^{-1}. HRMS: calcd for $C_{14}H_{13}O$ $[M + H]^+$ 197.0966, found 197.0968.

3-(3-Methoxybenzene)methylbenzoate (2m). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2m** was obtained as a yellow oil (136 mg, 80%). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.94 (s, 3 H), 6.91−6.93 (m, 1 H), 7.16 (s, 1 H), 7.21 (d, J = 8.0 Hz, 1 H), 7.37 (t, J = 7.7 Hz, 1 H), 7.49 (t, J = 7.7 Hz, 1 H), 7.77 (d, J = 7.5 Hz, 1 H), 8.03 (d, J = 7.5 Hz, 1 H), 8.29 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.1, 55.3, 112.9, 113.1, 119.6, 128.2, 128.5, 128.8, 129.9, 130.6, 131.5, 141.3, 141.6, 160.0, 167.0. IR (neat): $\tilde{\nu}_{max}$ = 1178, 1230, 1567, 1609, 1715, 3067 cm^{-1}. HRMS: calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1015.

4-Methyl-4-acetylbiphenyl (2n).[47] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **2n** was obtained as a white solid directly from the chromatographic solvent. Mp: 116−118 °C (120 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.62 (s, 3 H), 7.28 (d, J = 7.5 Hz, 2 H), 7.53 (d, J = 7.5 Hz, 2 H), 7.66 (d, J = 7.5 Hz, 2 H), 8.01 (d, J = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 26.5, 126.8, 127.0, 128.8, 129.6, 135.5, 136.8, 138.1, 145.6, 197.6. IR (neat): $\tilde{\nu}_{max}$ = 1534, 1605, 1708, 3026 cm^{-1}. HRMS: calcd for $C_{15}H_{15}O$ $[M + H]^+$ 211.1123, found 211.1126.

3-Phenylpyridine (3a).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3a** was obtained as a colorless oil (80 mg, 74%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.33−7.38 (m, 1 H), 7.39−7.41 (m, 1 H), 7.45−7.48 (m, 2 H), 7.56−7.58 (m, 2 H), 7.85 (d, J = 8.0 Hz, 1 H), 8.59 (d, J = 5.0 Hz, 1 H), 8.85 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 123.6, 127.2, 128.1, 129.1, 134.4, 136.6, 137.9, 148.4, 148.5. IR (neat): $\tilde{\nu}_{max}$ = 1534, 1569, 3089 cm^{-1}. HRMS: calcd for $C_{11}H_{10}N$ $[M + H]^+$ 156.0813, found 156.0811.

3-(3-Methoxyphenyl)pyridine (3b).[48] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3b** was obtained as a yellow oil (98 mg, 76%). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.91 (d, J = 7.5 Hz, 1 H), 7.07 (s, 1 H), 7.12 (d, J = 7.0 Hz, 1 H), 7.29−7.31 (m, 1 H), 7.35 (t, J = 8.0 Hz, 1 H), 7.81 (d, J = 7.5 Hz, 1 H), 8.56 (s, 1 H), 8.82 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.2, 112.9, 113.3, 119.5, 123.4, 130.1, 134.3, 136.4, 139.2, 148.3, 148.5, 160.1. IR (neat): $\tilde{\nu}_{max}$ = 1178, 1549, 1590, 3034 cm^{-1}. HRMS: calcd for $C_{12}H_{12}NO$ $[M + H]^+$ 186.0919, found 186.0911.

6-Methoxy-3-phenylpyridine (3c).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3c** was obtained as a yellow oil (100 mg, 78%). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.99 (s, 3 H), 6.82 (d, J = 8.5 Hz, 1 H), 7.34−7.37 (m, 1 H), 7.45 (t, J = 8.2 Hz, 2 H), 7.52−7.54 (m, 2 H), 7.79 (dd, J = 8.5, 2.5 Hz, 1 H), 8.40−8.41 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.5, 110.8, 126.7, 127.3, 129.0, 130.1, 137.5, 137.9, 145.0, 163.6. IR (neat): $\tilde{\nu}_{max}$ = 1290, 1508, 1567, 3045 cm^{-1}. HRMS: calcd for $C_{12}H_{12}NO$ $[M + H]^+$ 186.0919, found 186.0914.

6-Fluoro-3-phenylpyridine (3d). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3d** was obtained as a yellow oil (101 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.00 (dd, J = 8.5, 2.5 Hz, 1 H), 7.39−7.42 (m, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.52−7.53 (m, 2 H), 7.96 (dt, J = 8.0, 2.5 Hz, 1 H), 8.41 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 109.3, 109.6, 127.1, 128.2, 129.2, 134.9, 136.7, 139.7, 145.8, 162.2, 164.1. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −71.06. IR (neat): $\tilde{\nu}_{max}$ = 1567, 3089 cm^{-1}. HRMS: calcd for $C_{11}H_8FN$ $[M]^+$ 173.0641, found 173.0640.

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3-(4-Methylbenzene)-6-fluoropyridine (3e). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3e** was obtained as a white solid directly from the chromatographic solvent. Mp: 55−57 °C (122 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 6.97−6.99 (m, 1 H), 7.28 (d, J = 7.5 Hz, 2 H), 7.43 (d, J = 6.5 Hz, 2 H), 7.92−7.96 (m, 1 H), 8.40 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 109.3, 109.6, 127.0, 129.9, 133.9, 134.9, 138.2, 139.6, 145.7, 162.1, 164.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ = −71.0. IR (neat): $\tilde{\nu}_{max}$ = 1569, 1607, 3032 cm^{-1}. HRMS: calcd for $C_{12}H_{11}NF$ $[M + H]^+$ 188.0876, found 188.0879.

4-Phenyl-2-methoxyquinoline (3f).[49] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3f** was obtained as a yellow oil (100 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.76 (s, 3 H), 7.20 (s, 1 H), 7.40 (t, J = 7.5 Hz, 1 H), 7.46−7.50 (m, 5 H), 7.66 (t, J = 7.5 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 8.10 (d, J = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.3, 122.2, 125.1, 125.6, 125.7, 128.3, 128.5, 129.0, 129.3, 129.5, 138.1, 148.4, 148.5, 158.5. IR (neat): $\tilde{\nu}_{max}$ = 1567, 1609, 3065, 3089 cm^{-1}. HRMS: calcd for $C_{16}H_{14}N$ $[M + H]^+$ 220.1126, found 220.1130.

5-Phenylthiophene-2-carboxaldehyde (3g).[41] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3g** was obtained as an orange solid directly from the chromatographic solvent. Mp: 92−94 °C (118 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36−7.41 (m, 4 H), 7.62−7.64 (m, 2 H), 7.70 (d, J = 4.0 Hz, 1 H), 9.86 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.1, 126.3, 129.1, 129.4, 132.9, 137.5, 142.3, 154.1, 182.8. IR (neat): $\tilde{\nu}_{max}$ = 1534, 1609, 1789, 3023 cm^{-1}. HRMS: calcd for $C_{11}H_9OS$ $[M + H]^+$ 189.0374, found 189.0383.

5-Phenylfuran-2-carboxaldehyde (3h).[50] Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3h** was obtained as a yellow oil (89 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.80 (d, J = 3.5 Hz, 1 H), 7.28 (d, J = 3.5 Hz, 1 H), 7.35−7.42 (m, 3 H), 7.78 (m, 2 H), 9.60 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 107.7, 125.2, 128.9, 129.6, 151.9, 159.3, 177.2. IR (neat): $\tilde{\nu}_{max}$ = 1567, 1602, 1712, 3078 cm^{-1}. HRMS: calcd for $C_{11}H_9O_2$ $[M + H]^+$ 173.0603, found 173.0607.

6-Phenylisoquinoline (3i). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3i** was obtained as a colorless oil (122 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45−7.53 (m, 5 H), 7.67 (d, J = 4.5 Hz, 2 H), 7.73 (d, J = 5.5 Hz, 1 H), 7.99 (t, J = 4.5 Hz, 1 H), 8.49 (d, J = 6.0 Hz, 1 H), 9.31 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.9, 127.2, 127.9, 128.6, 129.9, 131.0, 134.2, 139.1, 139.3, 143.5, 153.0. IR (neat): $\tilde{\nu}_{max}$ = 1589, 1609, 3034 cm^{-1}. HRMS: calcd for $C_{15}H_{12}N$ $[M + H]^+$ 206.0970, found 206.0971.

6-(3-Methoxybenzene)isoquinoline (3j). Following the general procedure for Hiyama cross-coupling with aryltrifluorosilanes, **3j** was obtained as a yellow solid directly from the chromatographic solvent. Mp: 71−73 °C (117 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.96−7.02 (m, 3 H), 7.38 (t, J = 7.7 Hz, 1 H), 7.57−7.62 (m, 2 H), 7.73 (d, J = 6.0 Hz, 1 H), 7.92 (d, J = 7.5 Hz, 1 H), 8.46 (d, J = 6.0 Hz, 1H), 9.27 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.2, 113.1, 115.5, 118.5, 122.2, 126.7, 127.1, 128.9, 129.5, 130.7, 134.0, 139.0, 140.3, 143.3, 152.8, 159.6. IR (neat): $\tilde{\nu}_{max}$ = 1230, 1524, 1589, 3078 cm^{-1}. HRMS: calcd for $C_{16}H_{14}NO$ $[M + H]^+$ 236.1075, found 236.1079.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectral data for compounds **1a−c**, **2a−n** and **3a−j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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