Synthesis B. V. Moreira et al. Paper

Synthesis of Silylbiaryl Triflates by Chemoselective Suzuki Reaction

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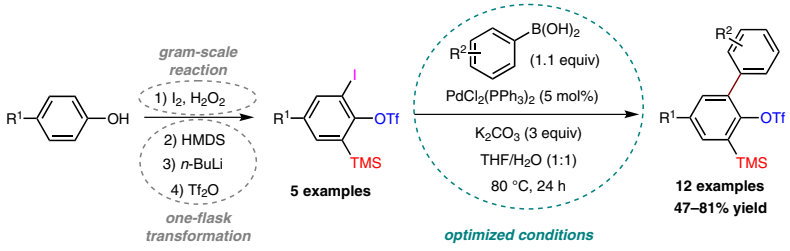

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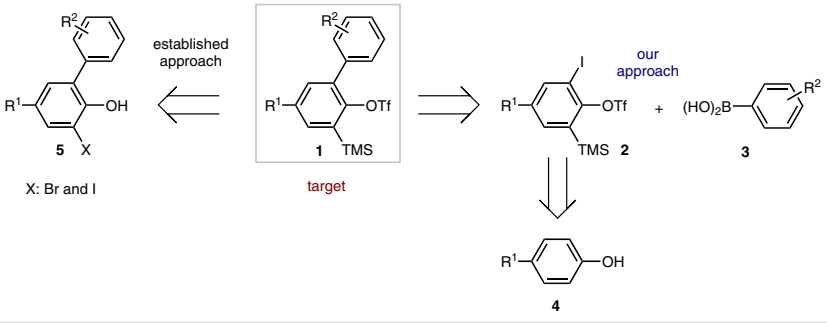
Abstract A modular approach for the synthesis of functionalized silylbiaryl triflates has been developed. Iodinated silylaryl triflates were prepared via a gram-scale diiodination reaction, followed by a one-flask transformation, in 42–52% overall yield. The iodinated silylaryl triflates were subjected to a novel chemoselective Suzuki reaction with arylboronic acids, using $PdCl_2(PPh_3)_2$ as catalyst and K_2CO_3 as base in THF/H_2O (1:1) at 80 °C for 24 hours, which afforded silylbiaryl triflates in 47–81% yield.

Key words iodinated silylaryl triflates, chemoselective cross-coupling, Suzuki reaction, silylbiaryl triflates, benzyne chemistry

Over the last years, silylaryl triflates have expanded benzyne chemistry applications in preparative organic chemistry.[1] In this context, arynes generated from silylaryl triflates have been employed in total syntheses of natural products[2] and preparations of functional materials.[3] Presumably, the dissemination of silylaryl triflates as aryne precursors in organic preparations[1–3] is related to some advantages, including mild conditions involved in the reactions[1,4] and well-established routes for the production of silylaryl triflates.[4,5] However, a critical evaluation reveals that the approaches for the syntheses of silylaryl triflates have limitations, which are responsible for the restriction of structural diversity associated with the silylaryl triflates eventually produced. Currently, for instance, silylbiaryl triflates **1** have been synthesized exclusively from halogenated phenylphenols **5**.[6] This approach restricts the substitution pattern of the silylbiaryl triflates **1** to a limited number of commercially available halo(phenyl)phenols **5** (Scheme 1).

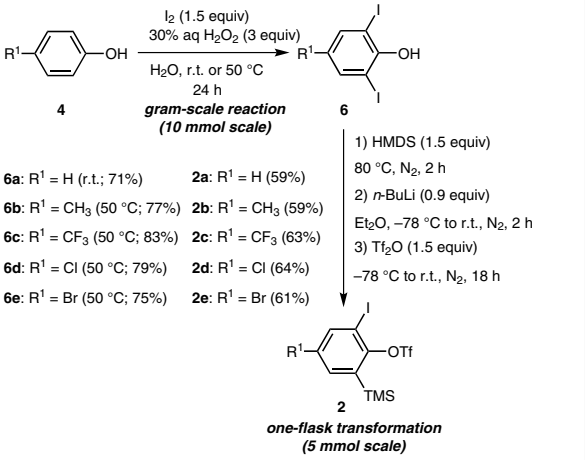
Seeking advances for the synthesis of silylaryl triflates, we conceived the possibility of achieving silylbiaryl triflates **1** through a modular approach involving the preparation of iodinated silylaryl triflates **2** from their corresponding phenols **4**, employing known transformations,[7,8] followed by a novel chemoselective Suzuki cross-coupling[9] between the iodinated silylaryl triflates **2** and arylboronic acids **3**, with the aim of producing functionalized silylbiaryl triflates **1** (Scheme 1).

In order to accomplish our goals, we subjected phenols **4** to a gram-scale reaction with I_2 and 30% H_2O_2 in water, employing mechanical stirring at room temperature or



Scheme 1 Approaches to produce silylbiaryl triflates **1**

50 °C for 24 hours, promoting the formation of diiodinated phenols **6** in 71–83% yield (Scheme 2).[7]



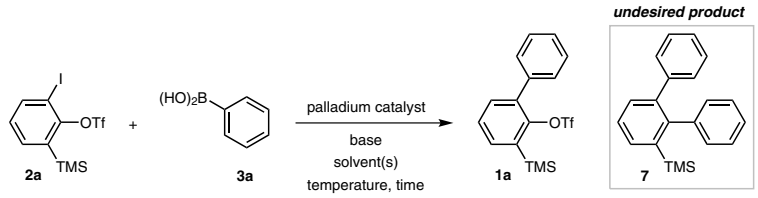
Scheme 2 Route for the synthesis of iodinated silylaryl triflates **2**

The sequence of the subsequent one-flask transformation was optimized employing 2,6-diiodophenol (**6a**), varying the amount of *n*-BuLi (0.9 to 1.1 equiv) and the solvent (THF and Et_2O) for the iodine–lithium exchange reaction, and the time for the reaction with triflic anhydride (0.5 to 18 h). Thereafter, five iodinated silylaryl triflates **2**, containing an electron-donating or -withdrawing group, or a halogen (Cl and Br) in their structures, were obtained in 59–64% isolated yield (Scheme 2).[8]

Next, optimization of the chemoselective Suzuki reaction was carried out employing the iodinated silylaryl triflate **2a** and phenylboronic acid (**3a**), evaluating several palladium catalysts, bases, and solvents or mixtures, and different temperatures and times, providing the silylbiaryl triflate **1a** (Table 1).

Allowing iodinated silylaryl triflate **2a** to react with phenylboronic acid (**3a**) using $Pd(PPh_3)_4$ as catalyst and K_2CO_3 as base in toluene/water (1:1) at 80 °C for 24 hours, we obtained silylbiaryl triflate **1a** in 15% isolated yield (Table 1, entry 1). In an attempt to improve the yield, we performed the microwave-assisted reaction between compounds **2a** and **3a** employing $Pd(PPh_3)_4$ as catalyst and

Table 1 Chemoselective Suzuki Cross-Coupling for the Preparation of Silylbiaryl Triflate **1a**[a]



Entry	Palladium catalyst (% mol)	Base (equiv)	Solvent(s)	Temp (°C)	Time (h)	Isolated yield (%) of **1a**
1	$Pd(PPh_3)_4$ (5)	K_2CO_3 (3)	toluene/H_2O (1:1)	80	24	15
2	$Pd(PPh_3)_4$ (5)	K_2CO_3 (3)	toluene/H_2O (1:1)	150 (MO)[b]	3	25
3	$Pd(PPh_3)_4$ (10)	K_2CO_3 (3)	toluene/H_2O (1:1)	150 (MO)[b]	3	25
4	$Pd(OAc)_2$ (2.5)	K_2CO_3 (2.5)	acetone/H_2O (1:1)	reflux	24	15[c]
5	$Pd(OAc)_2$ (2.5)	K_2CO_3 (2.5)	acetone/H_2O (1:1)	reflux	2	20[c]
6	$Pd(OAc)_2$ (2.5)	K_2CO_3 (2.5)	acetone/H_2O (1:1)	r.t.	2	6[c]
7	10% Pd/C (5)	K_2CO_3 (2)	H_2O	r.t.	24	0[d]
8	10% Pd/C (5)	K_2CO_3 (2)	MeOH	r.t.	24	0[d]
9	$PdCl_2(PPh_3)_2$ (5)	K_2CO_3 (3)	toluene/H_2O (1:1)	80	24	60
10	$PdCl_2(PPh_3)_2$ (5)	K_2CO_3 (3)	toluene/H_2O (1:1)	150 (MO)[b]	3	36
11	$PdCl_2(PPh_3)_2$ (10)	K_2CO_3 (3)	toluene/H_2O (1:1)	150 (MO)[b]	3	44
12	$PdCl_2(PPh_3)_2$ (5)	KOH (3)	toluene/H_2O (1:1)	80	24	52
13	$PdCl_2(PPh_3)_2$ (5)	*t*-BuOK (3)	toluene/H_2O (1:1)	80	24	42
14	$PdCl_2(PPh_3)_2$ (5)	K_2CO_3 (3)	THF/H_2O (1:1)	80	24	80
15	$PdCl_2(PPh_3)_2$ (5)	K_2CO_3 (3)	EtOH/H_2O (1:1)	80	24	56

[a] Reaction conditions: **2a** (1 mmol), **3a** (1.1 mmol), palladium catalyst, base, solvent(s) (3 mL), with stirring.
[b] Reaction performed in a sealed tube under microwave heating.
[c] Compound **7** was obtained as the major product, according to GC/MS analysis.
[d] Compound **1a** was not obtained and the starting material **2a** was partially recovered.

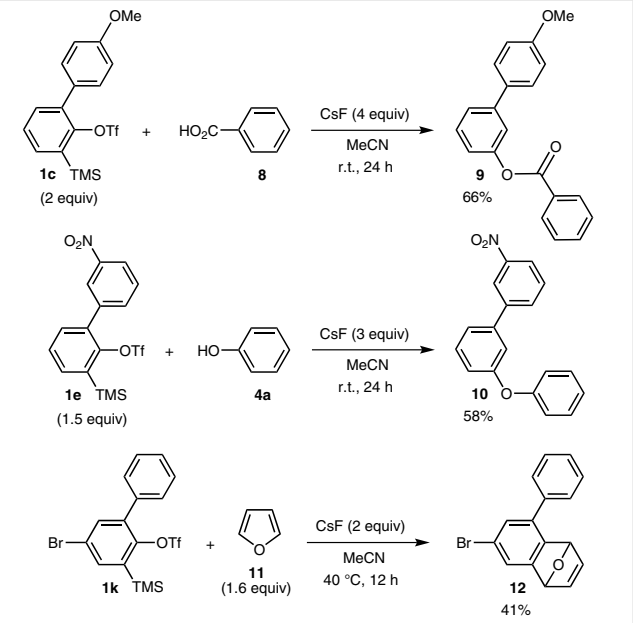
K_2CO_3 as base in toluene/water (1:1) at 150 °C for 3 hours, which provided compound **1a** in 25% yield (Table 1, entry 2). When the same transformation was carried out with a higher load of $Pd(PPh_3)_4$, no improvement in yield was observed (Table 1, entry 3). When the reaction between iodinated aryne precursor **2a** and boronic acid **3a** was performed using $Pd(OAc)_2$ as catalyst and K_2CO_3 as base in acetone/water (1:1) under reflux for 24 hours, triflate **1a** was obtained in 15% yield (Table 1, entry 4). For all reactions using $Pd(OAc)_2$ as catalyst, compound **7** was obtained as the major product, according to GC/MS analysis, which could not be avoided even with reduced reaction time and temperature (Table 1, entries 4–6). The desired product **1a** was not obtained when 10% Pd/C was employed as catalyst and the starting material **2a** was partially recovered, according to GC/MS analysis (Table 1, entries 7 and 8). Treatment of **2a** with **3a** using $PdCl_2(PPh_3)_2$ as catalyst and K_2CO_3 as base in toluene/water (1:1) at 80 °C for 24 hours gave triflate **1a** in 60% yield (Table 1, entry 9). The microwave-assisted reaction between **2a** and **3a** using $PdCl_2(PPh_3)_2$ as catalyst and K_2CO_3 as base in toluene/water (1:1) at 150 °C for 3 hours led to **1a** in 36% yield (Table 1, entry 10). When the same reaction was carried out with a higher load of $PdCl_2(PPh_3)_2$, the desired product **1a** was isolated in 44% yield (Table 1, entry 11). Allowing compound **2a** to react with **3a** using $PdCl_2(PPh_3)_2$ as catalyst and KOH as base in toluene/water (1:1) at 80 °C for 24 hours, we obtained **1a** in 52% yield (Table 1, entry 12). When the reaction was performed with *t*-BuOK instead of KOH, silylbiaryl triflate **1a** was isolated in 42% yield (Table 1, entry 13). The reaction between **2a** and **3a** using $PdCl_2(PPh_3)_2$ as catalyst and K_2CO_3 as base in THF/water (1:1) at 80 °C for 24 hours gave **1a** in 80% yield (Table 1, entry 14). Finally, when the reaction was carried out in ethanol/water (1:1), **1a** was isolated in 56% yield (Table 1, entry 15).

Employing the optimal conditions (Table 1, entry 14), we examined the scope of the transformation using various iodinated aryne precursors **2** and arylboronic acids **3** (Table 2). When iodinated silylaryl triflate **2a** was allowed to react with arylboronic acids **3b** and **3c**, which contain an electron-donating group, silylbiaryl triflates **1b** and **1c** were obtained in 60% and 61% yield, respectively (Table 2, entries 2 and 3). The reaction between **2a** and 4-chlorophenylboronic acid (**3d**) gave compound **1d** in 50% isolated yield (Table 2, entry 4). Treatment of **2a** with arylboronic acid **3e**, which contains an electron-withdrawing group, gave **1e** in 81% yield (Table 2, entry 5). The reaction between **2a** and 2-hydroxyphenylboronic acid (**3f**) led to compound **1f** in 53% isolated yield (Table 2, entry 6). Treatment of iodinated silylaryl triflates **2b** and **2c**, containing an electron-donating and -withdrawing group, with phenylboronic acid (**3a**) gave silylbiaryl triflates **1g** and **1h** in 60% and 58% yield, respectively (Table 2, entries 7 and 8).

When the chloro-substituted aryne precursor **2d** was subjected to reactions with phenylboronic acid (**3a**) and 3-nitrophenylboronic acid (**3e**), silylbiaryl triflates **1i** and **1j** were obtained in 56% and 64% yield, respectively (Table 2, entries 9 and 10). Remarkably, even when the bromo-substituted aryne precursor **2e** was treated with phenylboronic acid (**3a**) and 3-methylphenylboronic acid (**3b**), we obtained silylbiaryl triflates **1k** and **1l** in reasonable yields of 55% and 47%, respectively (Table 2, entries 11 and 12).

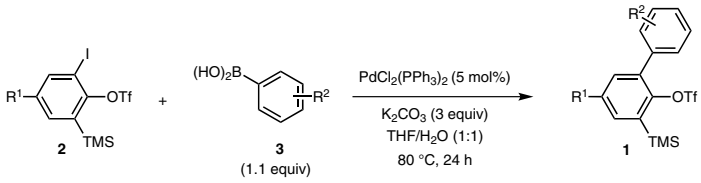
The reactions that resulted in compounds **1** (Table 2) did not promote the formation of byproducts corresponding to compound **7** (Table 1), according to GC/MS analysis. The development of this highly selective reaction to produce silylbiaryl triflates **1** was only possible based on the prior extensive optimization of the Suzuki cross-coupling conditions (Table 1).

Silylbiaryl triflates **1** are versatile reagents in organic synthesis, which can find application, for example, in nucleophilic additions[10] and cycloaddition reactions.[4,11] Accordingly, we subjected silylbiaryl triflates **1c** and **1e** to nucleophilic couplings with benzoic acid (**8**) and phenol (**4a**), respectively, in the presence of cesium fluoride and regioselectively obtained the benzoate **9** in 66% yield and the diaryl ether **10** in 58% yield (Scheme 3). In addition, when silylbiaryl triflate **1k** was allowed to react with furan (**11**) and cesium fluoride, the Diels–Alder adduct **12** was obtained in a moderate 41% yield.



Scheme 3 Reactions employing silylbiaryl triflates **1**

Table 2 Silylbiaryl Triflates **1** Prepared by the Chemoselective Suzuki Reaction[a]



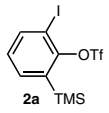
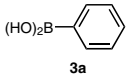
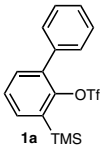
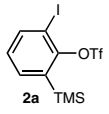
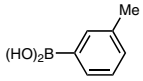
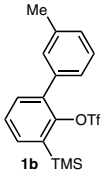
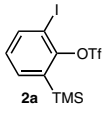
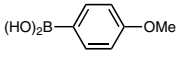
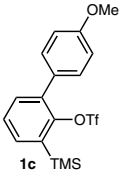
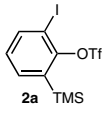
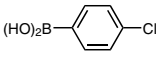
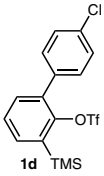
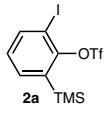
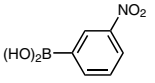
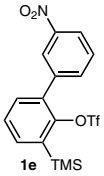
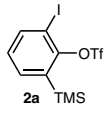
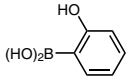
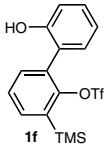
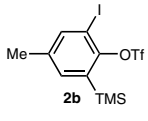
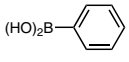
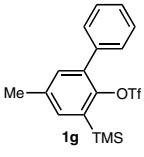
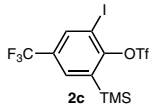
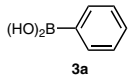
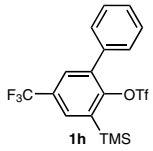
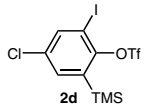
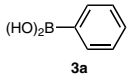
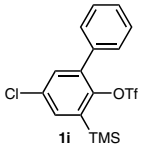
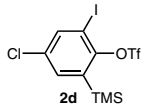
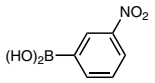
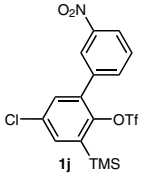
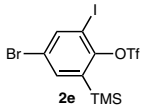
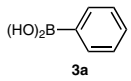
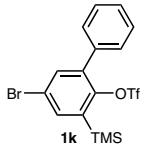
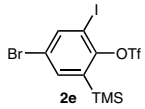
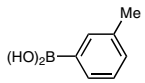
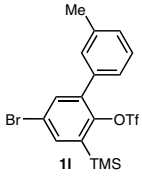
Entry	Iodinated silylaryl triflate **2**	Arylboronic acid **3**	Silylbiaryl triflate **1**	Isolated yield (%)
1	 **2a**	 **3a**	 **1a**	80
2	 **2a**	 **3b**	 **1b**	60
3	 **2a**	 **3c**	 **1c**	61
4	 **2a**	 **3d**	 **1d**	50
5	 **2a**	 **3e**	 **1e**	81
6	 **2a**	 **3f**	 **1f**	53
7	 **2b**	 **3a**	 **1g**	60

Table 2 (continued)

Entry	Iodinated silylaryl triflate **2**	Arylboronic acid **3**	Silylbiaryl triflate **1**	Isolated yield (%)
8	 **2c**	 **3a**	 **1h**	58
9	 **2d**	 **3a**	 **1i**	56
10	 **2d**	 **3e**	 **1j**	64
11	 **2e**	 **3a**	 **1k**	55
12	 **2e**	 **3b**	 **1l**	47

[a] Reaction conditions: **2** (1 mmol), **3** (1.1 mmol), $PdCl_2(PPh_3)_2$ (5 mol%), K_2CO_3 (3 mmol), THF/H_2O (1:1) (3 mL), 80 °C, 24 h, with stirring.

The structures of compounds **6a–e** are supported by their ^{1}H NMR, ^{13}C NMR, and mass spectra. The structures of compounds **2a–e**, **1a–l**, **9**, **10**, and **12** were assigned according to their IR, ^{1}H NMR, ^{13}C NMR, and mass spectra. All new compounds (**2b–e**, **1b–l**, **9**, **10**, and **12**) provided HRMS data that are in agreement with the proposed structures.

In summary, a modular approach for the synthesis of functionalized silylbiaryl triflates was developed. Iodinated silylaryl triflates were synthesized via a gram-scale diiodination reaction, followed by a one-flask transformation, in 42–52% overall yield. A novel chemoselective Suzuki reaction involving the iodinated silylaryl triflates and arylboronic acids then provided functionalized silylbiaryl triflates in 47–81% yield. The described synthetic route provides an alternative method for the preparation of silylbiaryl triflates and should find use in the construction of molecules with interesting biological properties and applications in materials science.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Ultrashield 300 spectrometer operating at 300 MHz and 75 MHz, respectively. The ^{1}H NMR chemical shifts are given in ppm with respect to TMS used as internal standard, and the ^{13}C NMR chemical shifts are given in ppm with respect to the deuterated solvent used as reference. IR spectra were obtained on a Shimadzu IRPrestige-21 spectrophotometer using attenuated total reflectance (ATR) or KBr pellets, in the 4000–400 cm^{-1} region. Mass spectra were recorded employing a Shimadzu GC-2010 gas chromatograph connected to a Shimadzu GCMS-QP2010 Plus mass spectrometer using electron impact ionization at 70 eV. High-resolution mass spectra were obtained using a Bruker micrOTOF-Q II time-of-flight mass spectrometer. Melting point values are uncorrected. Column chromatographic separations were carried out using 70–230 mesh silica gel. Preparative thin-layer chromatographic separations were carried out using a silica gel matrix with inorganic binder and fluorescent indicator. Commercially obtained reagents were employed without further purification. High-purity CsF (99.99%) was used. THF and Et_2O were distilled from sodium/benzophenone under N_2 atmosphere before use.[12] MeCN was distilled from CaH_2 under anhydrous conditions prior to use.[12] *n*-BuLi was titrated against *s*-BuOH using 1,10-phenanthroline as indicator under N_2 at-

mosphere.[13] Solvents were treated, when necessary, according to literature methods.[12]

Diiodinated Phenols 6a–e; General Procedure

To a suspension of the appropriate phenol **4a–e** (10 mmol) and I_2 (3.81 g, 15 mmol) in distilled H_2O (50 mL) was added 30% (w/v) aqueous H_2O_2 (3.1 mL, 30 mmol). The mixture was maintained under mechanical stirring at r.t. or 50 °C for 24 h. Next, a saturated aqueous solution of sodium thiosulfate (25 mL) was added to the reaction mixture, which was then extracted with EtOAc (3 × 50 mL). The combined organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane), affording the corresponding diiodinated phenol **6a–e**.

2,6-Diiodophenol (6a)[7b]

Reaction temperature: r.t.; yield: 2.46 g (71%); off-white solid; mp 67.6–68.2 °C.

R_f = 0.24 (hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.9 Hz, 2 H), 6.41 (t, *J* = 7.9 Hz, 1 H), 5.78 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 139.3, 124.1, 82.4.

MS (EI): *m*/*z* (%) = 346 (100.0), 152 (0.2), 129 (3.8), 127 (3.3), 92 (43.1), 63 (22.0).

2,6-Diiodo-4-methylphenol (6b)[14]

Reaction temperature: 50 °C; yield: 2.77 g (77%); off-white solid; mp 60.5–61.0 °C.

R_f = 0.35 (hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (s, 2 H), 5.49 (s, 1 H), 2.13 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3, 139.5, 133.8, 81.9, 19.4.

MS (EI): *m*/*z* (%) = 360 (100.0), 233 (28.7), 180 (2.4), 106 (23.9), 74 (3.2), 52 (9.1).

2,6-Diiodo-4-(trifluoromethyl)phenol (6c)[15]

Reaction temperature: 50 °C; yield: 3.44 g (83%); off-white solid; mp 104.2–104.5 °C.

R_f = 0.26 (hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (s, 2 H), 6.00 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4 (q, *J* = 0.96 Hz), 136.4 (q, *J* = 3.7 Hz), 126.2 (q, *J* = 33.5 Hz), 121.9 (q, *J* = 270.9 Hz), 81.8.

MS (EI): *m*/*z* (%) = 414 (100.0), 160 (32.0), 141 (5.6), 132 (19.8), 131 (8.4), 61 (4.5).

4-Chloro-2,6-diiodophenol (6d)[7b]

Reaction temperature: 50 °C; yield: 3.00 g (79%); off-white solid; mp 103.8–104.9 °C.

R_f = 0.17 (hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (s, 2 H), 5.64 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.7, 138.2, 126.7, 81.7.

MS (EI): *m*/*z* (%) = 382 (31.8), 380 (100.0), 252 (4.6), 199 (0.2), 126 (31.4), 73 (1.8), 62 (13.9).

4-Bromo-2,6-diiodophenol (6e)[16]

Reaction temperature: 50 °C; yield: 3.19 g (75%); off-white solid; mp 128.6–129.8 °C.

R_f = 0.26 (hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 2 H), 5.66 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 140.8, 113.5, 82.4.

MS (EI): *m*/*z* (%) = 426 (91.6), 424 (100.0), 292 (3.3), 218 (3.2), 170 (20.1), 91 (12.3), 62 (37.0).

Iodinated Silylaryl Triflates 2a–e; General Procedure

To the appropriate diiodinated phenol **6a–e** (5 mmol) was added HMDS (1.6 mL, 1.21 g, 7.5 mmol). The mixture was maintained under magnetic stirring and N_2 atmosphere at 80 °C for 2 h. Then, the volatile residues were removed under reduced pressure for 30 min. In the same round-bottomed flask, Et_2O (50 mL) was added using a syringe and needle under anhydrous conditions. The solution was cooled to –78 °C under magnetic stirring and N_2 atmosphere. After that, 1.9 M *n*-BuLi in hexane (2.4 mL, 4.5 mmol) was added dropwise using a syringe and needle. The mixture was heated to r.t. and maintained under magnetic stirring and N_2 atmosphere for 2 h. Then, the reaction mixture was cooled to –78 °C and Tf_2O (1.3 mL, 2.12 g, 7.5 mmol) was added. The mixture was heated to r.t. and maintained under magnetic stirring and N_2 atmosphere for 18 h. Next, a 10% (w/v) aqueous solution of sodium bicarbonate (50 mL) was added to the reaction mixture, which was then extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to afford the corresponding iodinated silylaryl triflate **2a–e**.

2-Iodo-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (2a)[8a]

Yield: 1.25 g (59%); colorless oil.

R_f = 0.44 (hexane).

IR (ATR): 3457 (w), 3059 (w), 3005 (w), 2955 (w), 1402 (m), 1383 (m), 1358 (s), 1155 (s), 1072 (s), 868 (m), 569 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.24 (dd, *J* = 7.4, 1.7 Hz, 1 H), 6.77 (t, *J* = 7.6 Hz, 1 H), 0.89 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1, 142.5, 137.4, 136.8, 129.3, 118.5 (q, *J* = 318.8 Hz), 89.9, 0.2.

MS (EI): *m*/*z* (%) = 409 (100.0), 339 (0.61), 291 (14.1), 149 (44.2), 109 (0.53), 75 (4.3).

2-Iodo-4-methyl-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (2b)

Yield: 1.27 g (59%); colorless oil.

R_f = 0.50 (hexane).

IR (ATR): 3231 (w), 3154 (w), 2496 (w), 2313 (w), 2110 (w), 1400 (s), 1379 (m), 1204 (s), 1134 (s), 764 (m), 633 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 1.9 Hz, 1 H), 7.12 (d, *J* = 1.5 Hz, 1 H), 2.15 (s, 3 H), 0.20 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 143.9, 140.6, 138.6, 137.8, 119.6 (q, *J* = 318.7 Hz), 90.7, 21.4, 1.3.

MS (EI): *m*/*z* (%) = 423 (100.0), 290 (73.2), 163 (47.3), 149 (4.7), 73 (15.5), 53 (5.0).

HRMS (ESI): *m*/*z* [M – Me]$^+$ calcd for $C_{10}H_{11}F_3IO_3SSi$: 422.9189; found: 422.9195.

2-Iodo-4-(trifluoromethyl)-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (2c)

Yield: 1.55 g (63%); colorless oil.

R_f = 0.55 (hexane).

IR (ATR): 3292 (w), 3036 (w), 2957 (w), 2872 (w), 2623 (w), 1408 (m), 1311 (s), 1211 (s), 1128 (s), 766 (m), 717 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 1.8 Hz, 1 H), 7.55 (d, *J* = 1.6 Hz, 1 H), 0.20 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5 (q, *J* = 1.4 Hz), 139.4 (q, *J* = 3.6 Hz), 138.9, 133.6 (q, *J* = 3.6 Hz), 131.3 (q, *J* = 32.8 Hz), 122.4 (q, *J* = 271.8 Hz), 118.4 (q, *J* = 318.9 Hz), 90.2, –0.02.

MS (EI): *m*/*z* (%) = 477 (100.0), 344 (76.4), 217 (30.5), 81 (8.4), 73 (14.8), 69 (9.5).

HRMS (ESI): *m*/*z* [M – Me]$^+$ calcd for $C_{10}H_8F_6IO_3SSi$: 476.8907; found: 476.8908.

4-Chloro-2-iodo-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (2d)

Yield: 1.47 g (64%); colorless oil.

R_f = 0.54 (hexane).

IR (ATR): 3456 (w), 3062 (w), 2957 (w), 2907 (w), 1537 (m), 1401 (s), 1362 (m), 1132 (s), 1051 (s), 725 (m), 619 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 2.5 Hz, 1 H), 7.17 (d, *J* = 2.5 Hz, 1 H), 0.09 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 141.4, 139.0, 136.3, 134.5, 118.4 (q, *J* = 318.8 Hz), 90.4, 0.02.

MS (EI): *m*/*z* (%) = 445 (41.4), 443 (100.0), 312 (33.6), 310 (91.0), 183 (24.4), 147 (5.3), 73 (26.2).

HRMS (ESI): *m*/*z* [M – Me]$^+$ calcd for $C_9H_8ClF_3IO_3SSi$: 442.8643; found: 442.8650.

4-Bromo-2-iodo-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (2e)

Yield: 1.53 g (61%); yellowish oil.

R_f = 0.50 (hexane).

IR (ATR): 3219 (w), 3038 (w), 2955 (w), 2901 (w), 2812 (w), 1529 (m), 1404 (s), 1358 (m), 1132 (s), 1049 (s), 723 (m), 656 (s), 609 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 2.4 Hz, 1 H), 7.41 (d, *J* = 2.4 Hz, 1 H), 0.20 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 144.1, 139.6, 139.2, 122.2, 118.4 (q, *J* = 318.9 Hz), 90.9, 0.03.

MS (EI): *m*/*z* (%) = 489 (100.0), 487 (91.0), 356 (80.6), 226 (9.9), 153 (1.0), 148 (17.7), 73 (48.1).

HRMS (ESI): *m*/*z* [M – Me]$^+$ calcd for $C_9H_8BrF_3IO_3SSi$: 486.8138; found: 486.8145.

Functionalized Silylbiaryl Triflates 1a–l; General Procedure

To a vial were added the appropriate iodinated silylaryl triflate **2a–e** (1 mmol), the appropriate arylboronic acid **3a–f** (1.1 mmol), $PdCl_2(PPh_3)_2$ (35.1 mg, 0.05 mmol), K_2CO_3 (415 mg, 3 mmol), and THF/H_2O (1:1) (3 mL). The vial was sealed using a cap, and the mixture was maintained under magnetic stirring at 80 °C for 24 h. Next, brine (10 mL) was added to the reaction mixture, which was then extracted with Et_2O (3 × 20 mL). The combined organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel (hexane or hexane/EtOAc, 9:1), affording the corresponding silylbiaryl triflate **1a–l**.

3-(Trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1a)[6a]

Yield: 299 mg (80%); yellowish oil.

R_f = 0.36 (hexane).

IR (ATR): 3499 (w), 2955 (w), 2766 (w), 2515 (w), 1400 (s), 1389 (m), 1202 (s), 1134 (s), 762 (m), 737 (m), 698 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 1 H), 7.35–7.29 (m, 7 H), 0.37 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 136.8, 136.2, 135.8, 135.7, 135.5, 129.6, 128.3, 128.0, 127.9, 117.9 (q, *J* = 318.6 Hz), 0.2.

MS (EI): *m*/*z* (%) = 359 (69.5), 225 (49.4), 211 (16.9), 195 (8.8), 141 (100.0), 139 (3.9), 73 (53.4).

3′-Methyl-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1b)

Yield: 233 mg (60%); yellowish oil.

R_f = 0.60 (hexane).

IR (ATR): 3503 (w), 2955 (w), 2903 (w), 2856 (w), 1400 (s), 1389 (m), 1201 (s), 1136 (s), 800 (m), 773 (m), 704 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.44 (m, 1 H), 7.34–7.10 (m, 6 H), 2.31 (s, 3 H), 0.36 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 137.9, 136.7, 136.2, 135.8, 135.6, 133.6, 130.2, 128.6, 128.3, 128.0, 126.7, 118.0 (q, *J* = 318.6 Hz), 21.3, 0.2.

MS (EI): *m*/*z* (%) = 373 (59.9), 239 (37.8), 225 (11.2), 165 (21.3), 141 (100.0), 119 (9.2), 73 (74.1).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{23}F_3NO_3SSi$: 406.1115; found: 406.1115.

4′-Methoxy-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1c)

Yield: 246 mg (61%); yellowish solid; mp 59.8–59.9 °C.

R_f = 0.40 (hexane).

IR (KBr): 3518 (w), 3044 (w), 2999 (w), 2902 (w), 1402 (s), 1385 (m), 1205 (s), 1138 (s), 839 (s), 810 (m), 771 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 3 H), 6.94–6.84 (m, 4 H), 3.74 (s, 3 H), 0.35 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 135.8, 135.7, 135.3, 133.5, 130.8, 128.0, 127.7, 118.0 (q, *J* = 318.6 Hz), 114.8, 113.8, 55.2, 0.2.

MS (EI): *m*/*z* (%) = 404 (11.9), 398 (2.9), 271 (7.9), 152 (3.0), 141 (15.6), 120 (4.9), 73 (100.0).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{23}F_3NO_4SSi$: 422.1064; found: 422.1064.

4′-Chloro-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1d)

Yield: 205 mg (50%); yellowish solid; mp 58.0–58.5 °C.

R_f = 0.52 (hexane).

IR (KBr): 3528 (w), 2955 (w), 2924 (w), 2901 (w), 1404 (s), 1381 (m), 1209 (s), 1138 (s), 847 (s), 791 (m), 771 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 7.0, 2.2 Hz, 1 H), 7.45–7.34 (m, 6 H), 0.44 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 136.2, 136.1, 135.4, 135.1, 134.2, 133.3, 130.9, 128.6, 128.2, 118.0 (q, *J* = 318.6 Hz), 0.2.

MS (EI): *m*/*z* (%) = 408 (4.7), 393 (50.3), 259 (35.6), 165 (23.7), 141 (100.0), 112 (5.3), 73 (62.8).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{20}ClF_3NO_3SSi$: 426.0568; found: 426.0575.

3′-Nitro-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1e)

Yield: 339 mg (81%); yellowish solid; mp 62.8–63.2 °C.

R_f = 0.48 (hexane).

IR (KBr): 3447 (w), 3074 (w), 2957 (w), 2903 (w), 1398 (m), 1350 (s), 1203 (s), 1136 (s), 839 (s), 810 (m), 771 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32–8.26 (m, 2 H), 7.80–7.44 (m, 5 H), 0.46 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 148.1, 138.7, 137.1, 136.6, 135.7, 134.0, 133.2, 129.4, 128.5, 124.5, 122.9, 117.9 (q, *J* = 318.4 Hz), 0.1.

MS (EI): *m*/*z* (%) = 404 (94.1), 389 (5.9), 270 (50.6), 225 (54.5), 151 (12.3), 141 (100.0), 73 (52.7).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{20}F_3N_2O_5SSi$: 437.0809; found: 437.0813.

2′-Hydroxy-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1f)

Yield: 207 mg (53%); yellowish oil.

R_f = 0.25 (hexane/EtOAc, 9:1).

IR (ATR): 3555 (w), 3493 (w), 2955 (w), 2903 (w), 2855 (w), 1391 (s), 1350 (m), 1202 (s), 1136 (s), 833 (s), 793 (m), 773 (m), 716 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.59 (m, 1 H), 7.49–7.43 (m, 2 H), 7.32–7.16 (m, 3 H), 7.00–6.98 (m, 1 H), 5.00 (s, 1 H), 0.44 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.9, 150.2, 136.7, 136.1, 134.2, 131.4, 130.1, 128.3, 123.4, 120.7, 118.0 (q, *J* = 318.6 Hz), 116.6, 115.2, 0.3.

MS (EI): *m*/*z* (%) = 390 (11.0), 375 (19.8), 241 (8.2), 225 (80.8), 165 (24.3), 141 (25.9), 77 (100.0), 73 (95.3).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{21}F_3NO_4SSi$: 408.0907; found: 408.0919.

5-Methyl-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1g)

Yield: 233 mg (60%); yellowish solid; mp 77.6–78.0 °C.

R_f = 0.32 (hexane).

IR (KBr): 3495 (w), 3035 (w), 2955 (w), 2901 (w), 1402 (s), 1251 (m), 1206 (s), 1138 (s), 910 (m), 845 (s), 777 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.12 (m, 5 H), 7.09–6.98 (m, 2 H), 2.15 (s, 3 H), 0.20 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 137.8, 137.0, 136.2, 135.8, 135.4, 134.2, 129.6, 128.3, 127.9, 118.0 (q, *J* = 318.6 Hz), 20.8, 0.2.

MS (EI): *m*/*z* (%) = 388 (5.9), 373 (46.1), 239 (29.1), 225 (9.4), 166 (5.4), 141 (74.6), 73 (100.0).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{23}F_3NO_3SSi$: 406.1115; found: 406.1113.

5-(Trifluoromethyl)-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1h)

Yield: 256 mg (58%); yellowish solid; mp 66.3–66.9 °C.

R_f = 0.54 (hexane).

IR (KBr): 3491 (w), 3036 (w), 2957 (w), 2903 (w), 1408 (s), 1284 (m), 1211 (s), 1134 (s), 887 (s), 783 (m), 725 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.59 (m, 2 H), 7.37–7.32 (m, 5 H), 0.38 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7, 137.8, 137.2, 135.6, 132.4 (q, *J* = 3.6 Hz), 130.6 (q, *J* = 3.7 Hz), 129.5, 128.7, 128.6, 127.2, 123.5 (q, *J* = 272.1 Hz), 117.9 (q, *J* = 318.8 Hz), 0.01.

MS (EI): *m*/*z* (%) = 442 (2.3), 427 (97.3), 293 (83.4), 279 (32.3), 217 (59.3), 141 (100.0), 73 (50.3).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{20}F_6NO_3SSi$: 460.0832; found: 460.0840.

5-Chloro-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1i)

Yield: 229 mg (56%); yellowish solid; mp 75.5–76.0 °C.

R_f = 0.72 (hexane).

IR (KBr): 3491 (w), 2957 (w), 2922 (w), 2851 (w), 1406 (s), 1387 (m), 1207 (s), 1138 (s), 879 (s), 777 (m), 739 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.50 (m, 1 H), 7.46–7.42 (m, 6 H), 0.48 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9, 138.4, 137.9, 135.7, 135.1, 134.0, 133.1, 129.4, 128.7, 128.5, 117.9 (q, *J* = 318.8 Hz), 0.4.

MS (EI): *m*/*z* (%) = 408 (4.2), 393 (41.5), 263 (2.4), 259 (30.1), 245 (13.2), 141 (76.4), 73 (100.0).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{20}ClF_3NO_3SSi$: 426.0568; found: 426.0575.

5-Chloro-3′-nitro-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1j)

Yield: 291 mg (64%); yellowish solid; mp 127.6–127.9 °C.

R_f = 0.56 (hexane).

IR (KBr): 3372 (w), 2957 (w), 2903 (w), 2853 (w), 1404 (m), 1350 (s), 1215 (s), 1138 (s), 878 (s), 766 (m), 733 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30–8.27 (m, 2 H), 7.78–7.74 (m, 1 H), 7.67–7.62 (m, 1 H), 7.57–7.43 (m, 2 H), 0.46 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 146.9, 139.2, 137.4, 136.4, 135.6, 135.5, 134.5, 132.7, 129.6, 124.3, 123.3, 117.9 (q, *J* = 318.6 Hz), 0.04.

MS (EI): *m*/*z* (%) = 453 (0.3), 338 (62.1), 304 (41.3), 259 (48.6), 245 (5.4), 141 (100.0), 73 (35.3).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{19}ClF_3N_2O_5SSi$: 471.0419; found: 471.0421.

5-Bromo-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1k)

Yield: 249 mg (55%); yellowish solid; mp 99.8–100.2 °C.

R_f = 0.48 (hexane).

IR (KBr): 3489 (w), 2955 (w), 2936 (w), 2920 (w), 1404 (s), 1387 (m), 1206 (s), 1138 (s), 876 (s), 777 (m), 739 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.29 (m, 2 H), 7.17–7.12 (m, 5 H), 0.19 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 138.9, 138.2, 138.0, 136.0, 135.6, 129.4, 128.5, 128.4, 122.3, 117.9 (q, *J* = 318.8 Hz), 0.04.

MS (EI): *m*/*z* (%) = 454 (1.4), 437 (15.1), 303 (9.3), 246 (1.1), 190 (4.5), 141 (66.9), 73 (100.0).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{16}H_{20}BrF_3NO_3SSi$: 470.0063; found: 470.0063.

5-Bromo-3′-methyl-3-(trimethylsilyl)-1,1′-biphenyl-2-yl Trifluoromethanesulfonate (1l)

Yield: 219 mg (47%); yellowish oil.

R_f = 0.60 (hexane).

IR (ATR): 3530 (w), 2955 (w), 2922 (w), 2902 (w), 1402 (s), 1380 (m), 1202 (s), 1130 (s), 872 (s), 787 (s), 760 (m), 741 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 7.3, 2.6 Hz, 2 H), 7.08–6.94 (m, 4 H), 2.14 (s, 3 H), 0.20 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5, 138.8, 138.4, 138.1, 137.9, 136.0, 135.4, 130.0, 129.2, 128.4, 126.5, 122.2, 117.9 (q, *J* = 318.8 Hz), 21.3, 0.03.

MS (EI): *m*/*z* (%) = 468 (2.7), 451 (11.9), 318 (6.5), 239 (6.9), 165 (10.2), 141 (53.7), 73 (100.0).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{22}BrF_3NO_3SSi$: 484.0220; found: 484.0217.

4′-Methoxy-1,1′-biphenyl-3-yl Benzoate (9)

To a vial were added benzoic acid (**8**) (9.8 mg, 0.08 mmol), silylbiaryl triflate **1c** (64.7 mg, 0.16 mmol), MeCN (3 mL), and CsF (48.6 mg, 0.32 mmol). The vial was sealed using a cap, and the mixture was maintained under magnetic stirring at r.t. for 24 h. Next, brine (10 mL) was added to the reaction mixture, which was then extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel (hexane/EtOAc, 19:1) to afford the desired product **9**.

Yield: 16.1 mg (66%); off-white solid; mp 84.5–87.0 °C.

R_f = 0.28 (hexane/EtOAc, 19:1).

IR (KBr): 3061 (w), 2924 (w), 2851 (w), 1734 (s), 1605 (m), 1521 (m), 1479 (m), 1246 (s), 1177 (m), 787 (m), 698 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24–8.21 (m, 2 H), 7.67–7.62 (m, 1 H), 7.55–7.45 (m, 6 H), 7.40–7.39 (m, 1 H), 7.18–7.14 (m, 1 H), 6.99–6.96 (m, 2 H), 3.85 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 159.4, 151.3, 142.5, 133.6, 132.7, 130.2, 129.7, 129.6, 128.6, 128.2, 124.2, 120.0, 119.8, 114.2, 55.3.

MS (EI): *m*/*z* (%) = 304 (28.2), 171 (3.4), 128 (4.4), 106 (8.2), 105 (100.0), 77 (28.7).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}O_3$: 305.1172; found: 305.1174.

3-Nitro-3′-phenoxy-1,1′-biphenyl (10)

To a vial were added phenol (**4a**) (10.0 mg, 0.11 mmol), silylbiaryl triflate **1e** (67.0 mg, 0.16 mmol), MeCN (3 mL), and CsF (50.1 mg, 0.33 mmol). The vial was sealed using a cap, and the mixture was maintained under magnetic stirring at r.t. for 24 h. Next, brine (10 mL) was added to the reaction mixture, which was then extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel (hexane), affording the desired product **10**.

Yield: 18.5 mg (58%); colorless oil.

R_f = 0.12 (hexane).

IR (KBr): 3074 (w), 2938 (w), 2851 (w), 1528 (s), 1489 (s), 1350 (s), 1412 (w), 1221 (s), 1163 (m), 737 (m), 684 (m) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (t, *J* = 2.0 Hz, 1 H), 8.20 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1 H), 7.87 (ddd, *J* = 7.8, 1.5, 1.1 Hz, 1 H), 7.59 (t, *J* = 8.0 Hz, 1 H), 7.45 (t, *J* = 7.9 Hz, 1 H), 7.40–7.33 (m, 3 H), 7.28 (t, *J* = 2.0 Hz, 1 H), 7.17–7.12 (m, 1 H), 7.08–7.03 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 156.8, 148.7, 142.2, 140.5, 133.0, 130.5, 129.9, 129.7, 123.7, 122.3, 122.0, 121.9, 119.0, 118.6, 117.5.

MS (EI): *m*/*z* (%) = 292 (20.0), 291 (100.0), 263 (8.7), 215 (9.5), 202 (8.7), 152 (43.4), 139 (10.7).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{14}NO_3$: 292.0968; found: 292.0976.

7-Bromo-1,4-dihydro-5-phenyl-1,4-epoxynaphthalene (12)

To vial were added furan (**11**) (19.0 µL, 17.7 mg, 0.26 mmol), silylbiaryl triflate **1k** (72.3 mg, 0.16 mmol), MeCN (3 mL), and CsF (48.6 mg, 0.32 mmol). The vial was sealed using a cap, and the mixture was maintained under magnetic stirring at 40 °C for 12 h. Then, the reaction mixture was cooled to r.t., filtered, and the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel (hexane) to afford the desired product **12**.

Yield: 19.4 mg (41%); brownish oil.

R_f = 0.25 (hexane).

IR (KBr): 3019 (w), 2922 (w), 2851 (w), 1593 (m), 1425 (m), 1279 (m), 1098 (m), 854 (s), 767 (m), 698 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 2 H), 7.42–7.37 (m, 2 H), 7.34–7.31 (m, 2 H), 7.24 (d, *J* = 1.6 Hz, 1 H), 7.16 (dd, *J* = 5.6, 1.8 Hz, 1 H), 7.09 (dd, *J* = 5.6, 1.8 Hz, 1 H), 5.79–5.78 (m, 1 H), 5.73–5.72 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.8, 146.1, 142.9, 142.9, 138.3, 136.2, 128.9, 127.9, 127.6, 122.8, 119.0, 82.1, 81.7.

MS (EI): *m*/*z* (%) = 298 (8.8), 272 (18.4), 219 (2.7), 191 (100.0), 165 (26.0), 94 (11.2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{12}BrO$: 299.0066; found: 299.0058.

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Supporting Information

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