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芳基乙烯基硅烷与芳基卤代物的 Hiyama 偶联反应

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摘要 Hiyama 偶联反应已经发展成为一种构筑 C—C 键的常用方法, 尤其是在芳基-芳基和芳基-烯基偶联反应领域. Hiyama 偶联反应通常需要使用 R—SiF_3、R—$Si(OMe)_3$等活性高但稳定性差的有机硅试剂, 发展基于稳定硅烷的 Hiyama 偶联反应是该领域重要的研究方向. 报道了一类钯催化芳基乙烯基硅烷和芳基卤代物的交叉偶联反应, 利用芳基乙烯基硅烷实现芳基化反应. 反应具有较好的官能团兼容性, 为制备二芳基类化合物提供了一种简便高效的途径.

关键词 Hiyama 反应; 偶联反应; 芳基乙烯基硅烷; 芳基化; 二芳基化合物

Hiyama Cross-Coupling Reaction of Aryl Vinylsilanes and Aryl Halides

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Abstract The Hiyama coupling reaction has emerged as a wildly used method for the construction of C—C bonds, especially in the fields of aryl-aryl and aryl-alkenyl coupling reactions. In general, this protocol highly relies on reactive but unstable silicon reagents such as R—SiF_3 and R—$Si(OMe)_3$. The development of Hiyama coupling reaction involving stable organosilanes is in high demand. In this manuscript, a palladium-catalyzed cross-coupling reaction of aryl vinylsilanes and aryl halides is reported, leading to the formation of Ar—Ar bonds. The reaction has shown good functional group compatibility and offered convenient access to biaryl compounds.

Keywords Hiyama reaction; cross-coupling reaction; aryl vinylsilanes; arylation; biaryl compounds

1 Introduction

Biaryl scaffolds are the prevailing structures that exist in numerous natural products, sensors, pharmaceuticals, ligands, polymers, agrochemicals, organocatalysts, and fine chemicals, and they are valuable intermediates in organic synthesis.[1] Among various cross-coupling reactions catalyzed by transition metals, the Hiyama coupling has received considerable attention.[2] The mild reaction conditions and good functional group compatibility make this method a promising tool for the construction of C—C bonds.[3] Since the initial report of this reaction by Hiyama in 1988, a wide range of organosilicon reagents and electrophilic coupling partners have been developed over the past 30 years.[4] In general, these reactions require highly reactive but unstable silicon reagents, such as silfluoride, silchloride, silanol, siloxane, and silicate (Scheme 1a). The development of reactions involving stable organosilanes is in high demand but remains largely undeveloped.[5]

Very recently, our group[6] reported a convenient method for the synthesis of Ar—Si(vinyl)R_2 from readily available aryl electrophiles and Cl—Si(vinyl)R_2. This class of compounds is easy to handle, has shown high stability, and is compatible with various functional groups. Historically, the reaction of heteroaryl vinylsilanes proceeds through vinyl—Si cleavage to form vinylation products (Scheme 1b).[7] Our preliminary studies revealed that the Ar—Si bond could be selectively cleaved over vinyl—Si bond to produce Ar—Ar.[6a] In this manuscript, we extensively investigated this reaction and demonstrated the Ar—Ar

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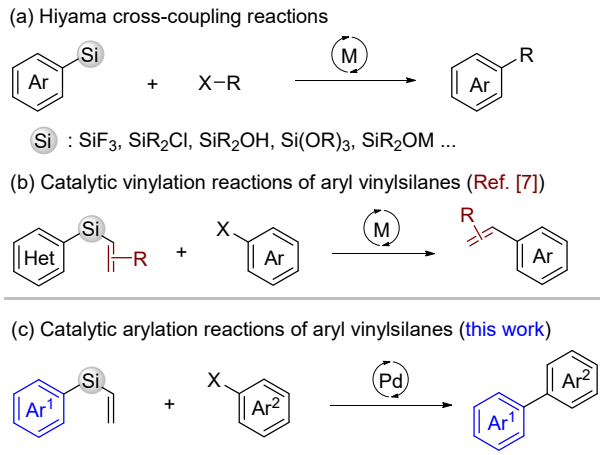
coupling of Ar—Si(vinyl)R_2 with aryl iodides, bromides, and chlorides (Scheme 1c).

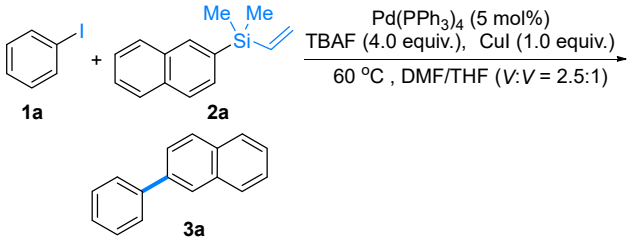


Scheme 1 Transition-metal-catalyzed cross-coupling of organosilanes

2 Results and discussion

We started our investigations by studying the reaction of iodobenzene **1a** with aryl vinylsilane **2a** (Table 1). The best result was obtained by a combination of $Pd(PPh_3)_4$ (5 mol%), tetrabutylammoniumfluoride (TBAF) (4.0 equiv.), and CuI (1.0 equiv.) in *N*,*N*-dimethylformamide (DMF) at 60 ℃, leading to the formation of **3a** in 85% isolated yield (Entry 1). The reaction with $Pd(PPh_3)Cl_2$ gave a 60% yield of the desired product (Entry 2). The use of $Pd(dba)_2$ or $PdCl_2$ as a catalyst leads to a significant decrease in the yield (Entries 3～4). An additive of CuI is critical to increasing the reaction efficiency (Entries 5～6). The use of CsF or KF instead of TBAF as a fluoride source gave **3a** in lower yields (Entries 7～8). In the absence of a palladium catalyst, fluoride source, or copper salt, no reaction was observed and aryl vinylsilane remained intact (Entry 9). The reaction with bromobenzene afforded **3a** in 88% isolated yield (Entry 10).

Table 1 Optimization of reaction conditions[a]



Entry	Change of conditions	Yield/% of **3a**
1	None	89 (85)[c]
2	$Pd(PPh_3)_2Cl_2$[b]	60
3	$Pd(dba)_2$[b]	35
4	$PdCl_2$[b]	15
5	CuCl	28
6	CuF_2	22
7	CsF	51
8	KF	19
9	No Pd, F, or Cu	0
10	PhBr was used[d]	88[c]

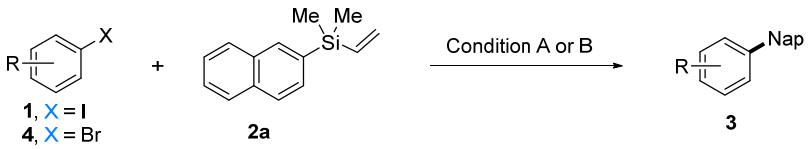
[a] **1a** (0.2 mmol) and **2a** (0.4 mmol) were used, the yields were determined by GC analysis with dodecane as an internal standard. [b] 10 mol% PPh_3 was used. [c] Isolated yield is given. [d] Anisole was used instead of DMF/THF, and reaction at 80 ℃.

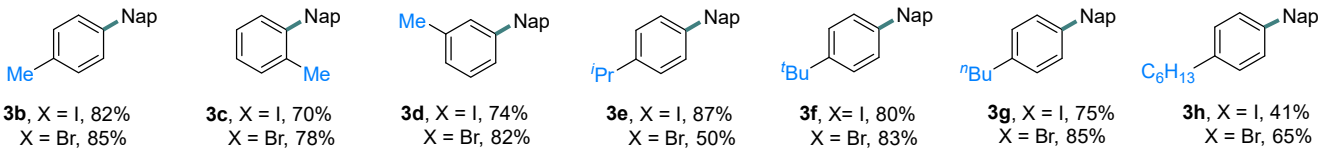
With optimized reaction conditions in hand, the scope of this reaction with respect to aryl iodides and bromides was then investigated (Table 2). Electron-neutral, electron-rich, and electron-poor aryl halides all coupled well with arylsilane **2a** (**3b**～**3s**). The methyl group placed at *para*-, *ortho*-, and *meta*-positions of aryl halides delivered **3b**～**3d** in good yields. Comparable results were obtained by incorporating other aliphatic substituents (**3e**～**3h**). Functionalities such as ether (**3i**), amine (**3j**), trifluoromethyl group (**3k**), ester (**3l**), nitrile (**3m**), ketone (**3n**), aldehyde (**3o**), aryl fluoride (**3p** and **3q**) and chloride (**3r**) are tolerated. While both iodide and bromide undergo the coupling reactions, selective functionalization of iodide over bromide to form biaryl **3s** is operative. Orthogonal reactivity of aryl iodide and bromide was observed for the reactions that produce biaryls **3t** and **3w**. The reactions of heteroaryl halides, including dibenzofuran (**3v**), pyridine (**3x** and **3y**), pyrimidine (**3z**), quinoline (**3aa**), and thiophene (**3ab** and **3ac**), afforded the corresponding products in good yields. In these cases, aryl bromides generally gave better results than aryl iodide, because the higher reactivity of iodides always leads to the increased amount of aryl homo-coupling byproducts.

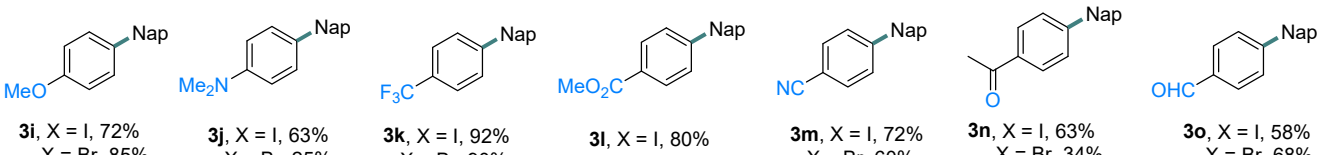
The substrate scope of arylsilanes is shown in Table 3. Both electron-rich and electron-poor substituents were tolerated. Electron-poor arylsilanes generally gave better results than electron-rich derivatives (**3ad**～**3ag** *vs* **3ah**～**3ai**). The reactions tolerated several functional groups such as ethers (**3af** and **3ag**), trifluoromethyl group (**3ah**), ester (**3ai** and **3am**), fluoride (**3aj** and **3ak**), and chloride (**3al**). The vinyl group is essential to the success of this coupling reaction, the reaction has shown high selectivity for the cleavage of Ar—Si(vinyl)Me_2 over Ar—$SiMe_3$ bonds (**3an**).

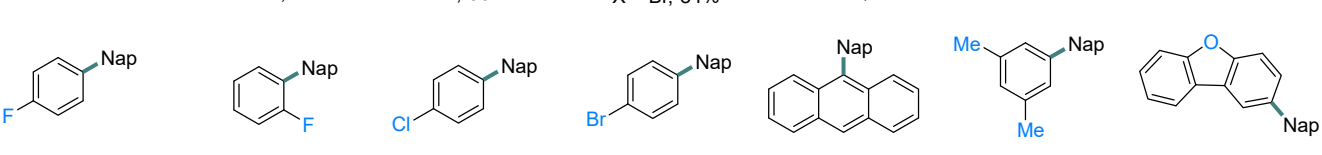
The cross-coupling involving aryl chloride is synthetically appealing but remains a challenging subject.[8] Indeed, under the standard conditions for the reactions with bromides and iodides, aryl chloride did not produce any desired product. Further optimization of reaction conditions revealed that the combination of $Pd(OAc)_2$ and strong electron-donating ligand PCy_3 yielded biaryls in moderate yields (Table 4). $ZnCl_2$ (1.0 equiv.) may act as a Lewis acid to activate Ar—Cl, leading to an increase in the yield of **3ap** from 9% to 42%. At present, the reactions are generally effective to electron-poor aryl chlorides (**3ap**～**3ar**, **3aj**). In the case of reactions for **3ap** and **3aq**, significant amounts of aryl-vinyl coupling byproducts were observed with yields less than 10%. Selective cleavage of Ar—Si(vinyl)Me_2 over Ar—$SiMe_3$ is also operative (**3an**). The reaction of chloroquinoline afforded **3as** in a decreased yield.

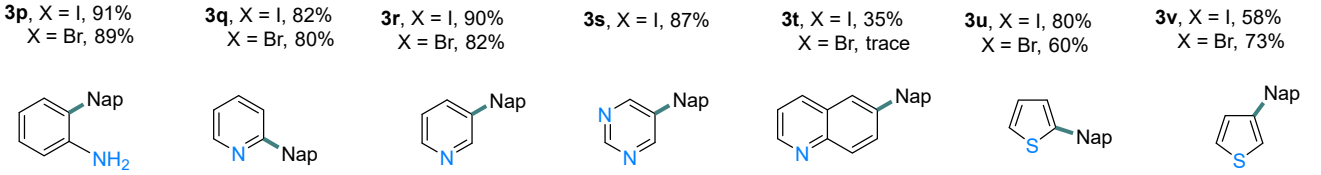
Table 2 Substrates scope of aryl iodides and bromides[a]





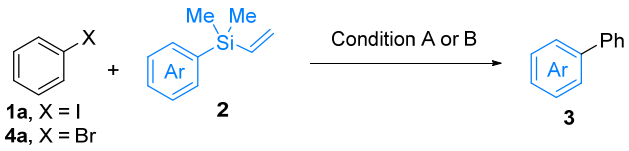


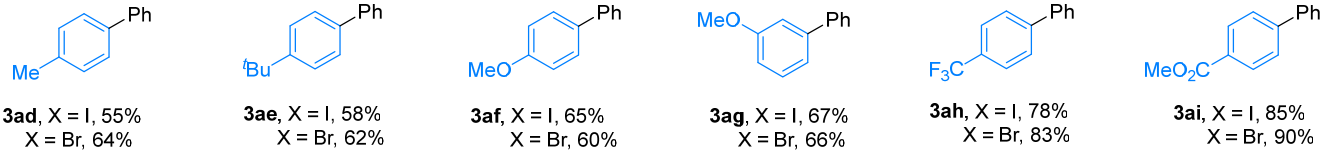


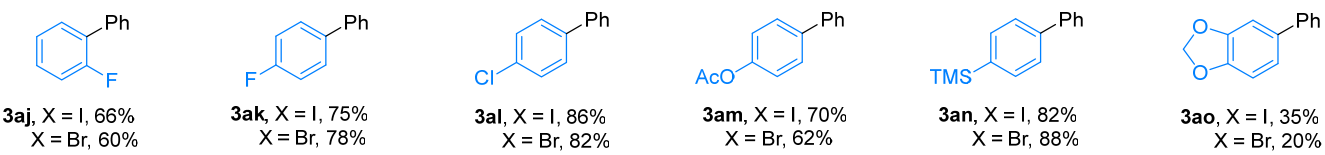


[a] Conditions A and B were used for the reactions with Ar—I and Ar—Br, respectively; isolated yields are given. Conditions A: iodides **1** (0.2 mmol), **2a** (0.4 mmol), $Pd(PPh_3)_4$ (5 mol%), TBAF (4.0 equiv.), and CuI (1.0 equiv.) in DMF/THF (V∶V=2.5∶1) at 60 ℃ for 12 h. Conditions B: aryl bromides **4** (0.2 mmol), arylsilane **2a** (0.4 mmol), $Pd(PPh_3)_4$ (5 mmol%), CuI (1.0 equiv.), and TBAF•$3H_2O$ (4.0 equiv.) in anisole (2 mL, 0.2 mol/L) at 80 ℃ for 12 h.

Table 3 Substrate scope of aryl vinylsilanes[a]



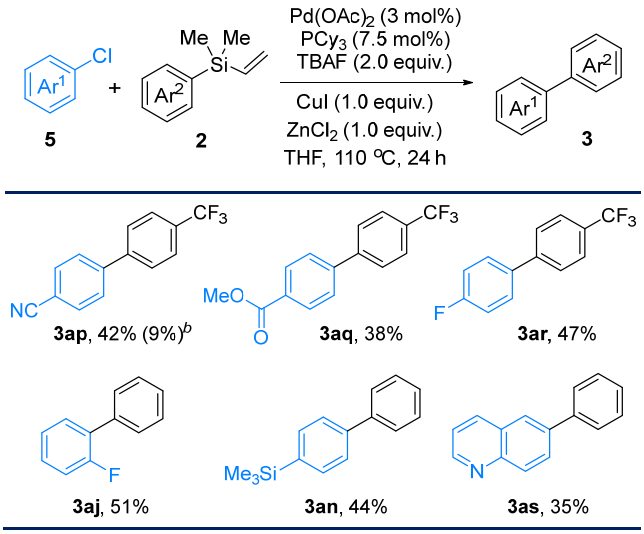




[a] Conditions A and B were used for the reactions with Ar—I and Ar—Br, respectively; isolated yields are given. Conditions A: aryl iodide **1a** (0.2 mmol), **2** (0.4 mmol), $Pd(PPh_3)_4$ (5 mol%), TBAF (4.0 equiv.), and CuI (1.0 equiv.) in DMF/THF (V∶V=2.5∶1) at 60 ℃ for 12 h. Conditions B: aryl bromide **4a** (0.2 mmol), arylsilanes **2** (0.4 mmol), $Pd(PPh_3)_4$ (5% mmol), CuI (1.0 equiv.), and TBAF•$3H_2O$ (4.0 equiv.) in anisole (2 mL, 0.2 mol/L) at 80 ℃ for 12 h.

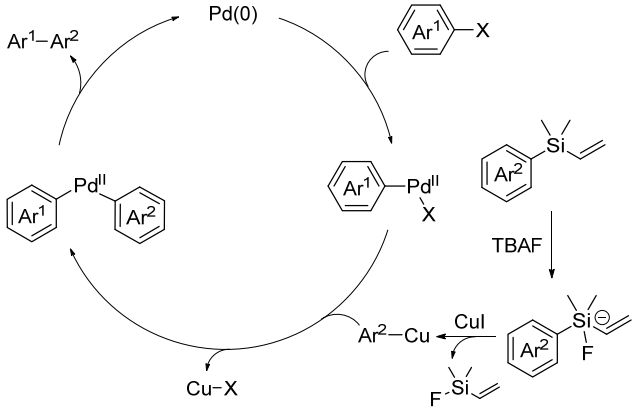
The mechanism of this reaction is proposed as analog to the classic Hiyama reaction (Scheme 2).[2] The oxidative addition of aryl halides to Pd(0) generates Ar^1—Pd(II)—X, which undergoes transmetallation with Ar^2—Cu to afford Ar^1—Pd(II)—Ar^2. Reductive elimination of this species gives the coupling product and regenerates Pd(0). Additive CuI is considered to facilitate the transmetallation process by transferring five-coordinative Ar—Si to Ar—Cu.[9] At

Table 4 Reactions with aryl chlorides[a]



[a] Aryl chloride **5** (0.2 mmol) and arylsilanes **2** (0.4 mmol), isolated yields. [b] Reaction in the absence of $ZnCl_2$.

present, the intrinsic mechanism of selectively transferring an aryl over a vinyl group remains unclear.



Scheme 2 Proposed mechanism

3 Conclusions

In summary, the arylation reactions of Ar—Si(vinyl)R_2 have been reported and the results of their reactions with aryl iodides, bromides, and chlorides have been demonstrated. The reaction has shown high selectivity for the cleavage of the Ar—Si over vinyl—Si bonds, offering access to diaryl compounds. The protocol is distinguished by its broad substrate scope, and it tolerates a wide range of functional groups. The ready availability and easy handle of Ar—Si(vinyl)R_2 make this method a useful synthetic tool for the construction of Ar—Ar bonds.

4 Experimental section

4.1 Instruments and reagents

^{1}H NMR and ^{13}C NMR spectra were collected on Bruker AVANCE III 400MHz, JEOL JNM-ECS 400M and Bruker AVANCE III 600 MHz spectrometer at room temperature. ^{1}H NMR spectra were referenced to the signal of TMS (δ 0). ^{13}C NMR spectra were reported relative to residual $CHCl_3$ (δ 77.00). ^{19}F NMR spectra were also collected on a Bruker AVANCE III 400 MHz spectrometers at room temperature. GC analysis was performed on a Thermo Scientific TRACE 1300.

All reactions were carried out under an atmosphere of argon in sealed tube with magnetic stirring. Dry DMF and THF were purified using a solvent-purification system that contained activated alumina and molecular sieves. Palladium catalysts were purchased from Acros, Alfa Aesar, Ark Pharm. Other chemicals and ligands were purchased from TCI, Adamas, Aldrich, J&K scientific and Energy chemicals, and were directly used without further purifications.

4.2 Preparation of aryl vinylsilanes

Methyl 4-(dimethyl(vinyl)silyl)benzoate (**2g**) was prepared according to the procedure reported in reference [6a]. The rest aryl vinylsilanes (**2a**～**2f** and **2h**～**2m**) were prepared according to the procedure reported in reference [10a]. All of these aryl vinylsilanes are known compounds.[6a,10b]

4.3 General procedure for the coupling reactions with aryl iodides

To a reaction tube equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (11.5 mg, 0.010 mmol), CuI (38.1 mg, 0.2 mmol), TBAF (1.0 mol/L in THF, 0.8 mL, 0.8 mmol), and DMF (2 mL, 0.2 mol/L). Aryl iodides **1** (0.2 mmol) and aryl vinylsilanes **2** (0.4 mmol, 2.0 equiv.) were then added in sequence. The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 60 ℃ for 12 h. The reaction was quenched with water (10.0 mL) and extracted with ethyl acetate (15.0 mL×3). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

4.4 General procedure for the coupling reactions with aryl bromides

To a reaction tube equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (11.5 mg, 0.010 mmol), CuI (38.1 mg, 0.2 mmol), TBAF•$3H_2O$ (0.8 mL, 0.8 mmol), and anisole (2 mL, 0.2 mol/L). Aryl bromides **4** (0.2 mmol) and aryl vinylsilanes **2** (0.4 mmol, 2.0 equiv.) were then added in sequence. The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 80 ℃ for 12 h. The reaction was quenched with water (10.0 mL) and extracted with ethyl acetate (15.0 mL×3). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

4.5 General procedure for the coupling reactions with aryl chlorides

To a reaction tube equipped with a magnetic stir bar was

charged with $Pd(OAc)_2$ (1.3 mg, 0.006 mmol), PCy_3 (0.4 mg, 0.0015 mmol), CuI (38.1 mg, 0.2 mmol), $ZnCl_2$ (27.2 mg, 0.2 mmol), TBAF (1.0 mol/L in THF, 0.8 mL, 0.8 mmol), and THF (2 mL, 0.2 mol/L). Aryl chloride **5** (0.2 mmol) and aryl vinylsilanes **2** (0.4 mmol, 2.0 equiv.) were then added in sequence. The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 110 ℃ for 24 h. The reaction was quenched with water (10.0 mL) and extracted with ethyl acetate (15.0 mL×3). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

2-Phenylnaphthalene (**3a**):[11] 85% yield (34.7 mg) for aryl iodide; 88% yield (35.9 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (s, 1H), 7.85～7.82 (m, 3H), 7.74～7.65 (m, 3H), 7.49～7.38 (m, 4H), 7.34 (t, J=7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.1, 138.5, 133.7, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.2, 125.9, 125.8, 125.5.

2-(*p*-Tolyl)naphthalene (**3b**):[11] 82% yield (35.8 mg) for aryl iodide; 85% yield (37.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99～7.93 (m, 1H), 7.87～7.75 (m, 3H), 7.68 (dd, J=8.6, 1.8 Hz, 1H), 7.57 (d, J=8.0 Hz, 2H), 7.47～7.36 (m, 2H), 7.23 (d, J=7.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.4, 138.1, 137.0, 133.7, 132.5, 129.5, 128.3, 128.1, 127.6, 127.2, 126.2, 125.7, 125.5, 125.4, 21.1.

2-(*o*-Tolyl)naphthalene (**3c**):[11] 70% yield (30.6 mg) for aryl iodide; 78% yield (34.0 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (t, J=8.0 Hz, 3H), 7.75～7.72 (m, 1H), 7.47～7.41 (m, 3H), 7.33～7.28 (m, 1H), 7.28～7.22 (m, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.8, 139.5, 135.5, 133.3, 132.2, 130.3, 129.98, 128.0, 127.7, 127.7, 127.6, 127.5, 127.3, 126.1, 125.8, 125.8, 20.5.

2-(*m*-Tolyl)naphthalene (**3d**):[11] 74% yield (32.3 mg) for aryl iodide; 82% yield (35.8 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=1.8 Hz, 1H), 7.87～7.84 (m, 3H), 7.71 (dd, J=8.6, 2.0 Hz, 1H), 7.52～7.43 (m, 4H), 7.34 (t, J=7.6 Hz, 1H), 7.16 (d, J=7.5 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.1, 138.6, 138.4, 133.7, 132.6, 128.7, 128.3, 128.2, 128.1, 128.1, 127.6, 126.2, 125.8, 125.7, 125.6, 124.5, 21.5.

2-(4-Isopropylphenyl)naphthalene (**3e**):[12] 87% yield (42.9 mg) for aryl iodide; 50% yield (24.6 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=1.8 Hz, 1H), 7.89～7.82 (m, 3H), 7.73 (dd, J=8.6, 2.0 Hz, 1H), 7.67～7.61 (m, 2H), 7.48～7.45 (m, 2H), 7.33 (d, J=8.2 Hz, 2H), 2.97～2.96 (m, 1H), 1.30 (d, J=7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.2, 138.7, 138.6, 133.8, 132.6, 128.4, 128.2, 127.7, 127.4, 127.0, 126.3, 125.8, 125.7, 125.5, 33.9, 24.1.

2-(4-(*tert*-Butyl)phenyl)naphthalene (**3f**):[12] 80% yield (41.7 mg) for aryl iodide; 83% yield (43.2 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.81 (dd, J=14.2, 8.0 Hz, 3H), 7.70 (d, J=8.5 Hz, 1H), 7.62 (d, J=7.8 Hz, 2H), 7.44～7.41 (m, 4H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.3, 138.3, 138.1, 133.7, 132.5, 128.3, 128.1, 127.6, 127.0, 126.2, 125.8, 125.7, 125.5, 125.4, 34.5, 31.4.

2-(4-Butylphenyl)naphthalene (**3g**):[11] 75% yield (39.0 mg) for aryl iodide; 85% yield (44.3 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 1H), 7.87～7.77 (m, 3H), 7.68 (dd, J=8.6, 1.6 Hz, 1H), 7.62 (d, J=8.6 Hz, 2H), 7.45～7.42 (m, 2H), 6.97 (d, J=8.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.1, 138.5, 138.3, 133.7, 132.5, 128.9, 128.3, 128.1, 127.6, 127.2, 126.1, 125.7, 125.5, 125.4, 35.3, 33.6, 22.4, 14.0.

2-(4-Hexylphenyl)naphthalene (**3h**): 41% yield (23.7 mg) for aryl iodide; 65% yield (37.5 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J=4.0 Hz, 1H), 7.87～7.78 (m, 3H), 7.70 (dd, J=8.0, 4.0 Hz, 1H), 7.63～7.57 (m, 2H), 7.44～7.42 (m, 2H), 7.28～7.21 (m, 2H), 2.69～2.56 (m, 2H), 1.64～1.63 (m, 2H), 1.39～1.27 (m, 6H), 0.88 (t, J=4.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.2, 138.5, 138.3, 133.7, 132.5, 128.9, 128.3, 128.1, 127.6, 127.2, 126.2, 125.7, 125.5, 125.4, 35.6, 31.8, 31.5, 29.1, 22.6, 14.1.

2-(4-Methoxyphenyl)naphthalene (**3i**):[13] 72% yield (33.7 mg) for aryl iodide; 85% yield (39.8 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 1H), 7.87～7.77 (m, 3H), 7.68 (dd, J=8.6, 1.6 Hz, 1H), 7.62 (d, J=8.6 Hz, 2H), 7.45～7.43 (m, 2H), 6.97 (d, J=8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.2, 138.1, 133.7, 133.5, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.3.

N,*N*-Dimethyl-4-(naphthalen-2-yl)aniline (**3j**):[11] 63% yield (31.2 mg) for aryl iodide; 25% yield (12.4 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (s, 1H), 7.89～7.80 (m, 3H), 7.73 (dd, J=8.6, 1.8 Hz, 1H), 7.67～7.60 (m, 2H), 7.48～7.38 (m, 2H), 6.87～6.80 (m, 2H), 3.00 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.0, 138.5, 133.9, 132.0, 129.0, 128.2, 127.9, 127.9, 127.6, 126.0, 125.3, 125.2, 124.1, 112.8, 40.6.

2-(4-(Trifluoromethyl)phenyl)naphthalene (**3k**):[11] 92% yield (50.1 mg) for aryl iodide; 90% yield (49.0 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03～7.98 (m, 1H), 7.92～7.81 (m, 3H), 7.76 (d, J=8.2 Hz, 2H), 7.68 (dd, J=8.0, 6.0 Hz, 3H), 7.54～7.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.6, 137.0, 133.5, 133.0, 129.5 (q, J_{C-F}=32.0 Hz), 128.7, 128.3, 127.7, 127.6, 126.6, 126.5, 126.3, 125.7 (q, J_{C-F}=4.0 Hz), 125.1, 124.1 (q, J_{C-F}=230.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.27.

Methyl 4-(naphthalen-2-yl)benzoate (**3l**):[14] 80% yield (42.0 mg) for aryl iodide; 84% yield (44.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J=8.2 Hz, 2H), 8.03 (s, 1H), 7.93～7.77 (m, 3H), 7.71 (dd, J=14.2, 9.0 Hz, 3H), 7.53～7.42 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.9, 145.4, 137.1, 133.5, 132.9, 130.1, 128.8, 128.6, 128.3, 127.6, 127.2, 126.4, 126.3, 126.2, 125.1, 52.1.

4-(Naphthalen-2-yl)benzonitrile (**3m**):[15] 72% yield

(33.0 mg) for aryl iodide; 60% yield (27.5 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.91～7.79 (m, 3H), 7.66～7.63 (m, 5H), 7.53～7.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.2, 136.1, 133.3, 133.0, 132.4, 128.8, 128.2, 127.7, 127.6, 126.7, 126.6, 126.3, 124.6, 118.8, 110.7.

1-(4-(Naphthalen-2-yl)phenyl)ethan-1-one (**3n**):[16] 63% yield (31.0 mg) for aryl iodide; 34% yield (16.7 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (dd, J=8.6, 2.0 Hz, 3H), 7.96～7.85 (m, 3H), 7.84～7.78 (m, 2H), 7.75 (dd, J=8.6, 1.8 Hz, 1H), 7.55～7.48 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.8, 145.7, 137.1, 135.8, 133.5, 133.0, 129.0, 128.7, 128.3, 127.7, 127.4, 126.5, 126.5, 126.4, 125.1, 26.7.

4-(Naphthalen-2-yl)benzaldehyde (**3o**):[17] 58% yield (26.9 mg) for aryl iodide; 68% yield (31.6 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.08 (s, 1H), 8.10 (d, J=1.8 Hz, 1H), 8.01～7.97 (m, 2H), 7.97～7.90 (m, 2H), 7.90～7.85 (m, 3H), 7.76 (dd, J=8.6, 1.8 Hz, 1H), 7.57～7.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.9, 147.1, 137.0, 135.2, 133.5, 133.1, 130.3, 128.8, 128.4, 127.9, 127.7, 126.6, 126.6, 125.1.

2-(4-Fluorophenyl)naphthalene (**3p**):[13] 91% yield (40.4 mg) for aryl iodide; 89% yield (39.5 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95～7.90 (m, 1H), 7.88～7.78 (m, 3H), 7.66～7.56 (m, 3H), 7.51～7.39 (m, 2H), 7.16～7.08 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.5 (d, $J_{C\text{-}F}$=245 Hz), 137.5, 137.1 (d, $J_{C\text{-}F}$=3.0 Hz), 133.6, 132.5, 128.9 (d, $J_{C\text{-}F}$=8.0 Hz), 128.5, 128.1, 127.6, 126.4, 126.0, 125.6, 125.3, 115.7 (d, $J_{C\text{-}F}$=21.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.47.

2-(2-Fluorophenyl)naphthalene (**3q**):[18] 82% yield (36.4 mg) for aryl iodide; 80% yield (35.5 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (s, 1H), 7.92～7.78 (m, 3H), 7.70～7.59 (m, 1H), 7.57～7.41 (m, 3H), 7.33～7.31 (m, 1H), 7.24～7.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.9 (d, $J_{C\text{-}F}$=246.0 Hz), 133.3, 133.2, 132.7, 131.0 (d, $J_{C\text{-}F}$=3.0 Hz), 129.0 (d, $J_{C\text{-}F}$=8.0 Hz), 128.2, 128.0 (d, $J_{C\text{-}F}$=3.0 Hz), 127.9, 127.6, 127.0 (d, $J_{C\text{-}F}$=3.0 Hz), 126.2 (d, $J_{C\text{-}F}$=1.0 Hz), 124.4 (d, $J_{C\text{-}F}$=4.0 Hz), 116.1 (d, $J_{C\text{-}F}$=23.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −117.60.

2-(4-Chlorophenyl)naphthalene (**3r**):[19] 90% yield (43.0 mg) for aryl iodide; 82% yield (39.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.81 (t, J=6.8 Hz, 3H), 7.64～7.57 (m, 1H), 7.54 (d, J=8.4 Hz, 2H), 7.46～7.45 (m, 2H), 7.37 (d, J=8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.4, 137.2, 133.5, 133.4, 132.6, 128.9, 128.5, 128.1, 127.6, 126.4, 126.1, 125.6, 125.1.

2-(4-Bromophenyl)naphthalene (**3s**):[20] 87% yield (49.2 mg) for aryl iodide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=1.8 Hz, 1H), 7.86～7.84 (m, 3H), 7.65 (dd, J=8.6, 1.8 Hz, 1H), 7.60～7.52 (m, 4H), 7.52～7.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.0, 137.2, 133.6, 132.7, 131.9, 128.9, 128.6, 128.2, 127.6, 126.4, 126.1, 125.7, 125.1, 121.6.

9-(Naphthalen-2-yl)anthracene (**3t**):[21] 35% yield (21.3 mg) for aryl iodide; trace for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (s, 1H), 8.09～7.84 (m, 8H), 7.68 (d, J=8.8 Hz, 2H), 7.62～7.42 (m, 6H), 7.36～7.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.4, 136.8, 136.3, 133.4, 132.7, 131.4, 130.4, 130.1, 129.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.9, 127.7, 126.9, 126.7, 126.4, 126.2, 126.1, 126.0, 125.7, 125.4, 125.1.

2-(3,5-Dimethylphenyl)naphthalene (**3u**):[11] 80% yield (37.2 mg) for aryl iodide; 60% yield (27.9 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.78～7.76 (m, 3H), 7.66 (dd, J=8.6, 1.4 Hz, 1H), 7.44～7.33 (m, 2H), 7.28 (s, 2H), 6.94 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.0, 138.7, 138.2, 133.7, 132.5, 128.9, 128.2, 128.1, 127.5, 126.1, 125.7, 125.6, 125.6, 125.3, 21.4.

2-(Naphthalen-2-yl)dibenzo[*b*,*d*]furan (**3v**):[22] 58% yield (34.1 mg) for aryl iodide; 73% yield (43.0 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, J=1.6 Hz, 1H), 8.10 (s, 1H), 8.05～7.97 (m, 1H), 7.93 (t, J=8.8 Hz, 2H), 7.90～7.85 (m, 1H), 7.85～7.76 (m, 2H), 7.64～7.63 (m, 2H), 7.55～7.44 (m, 3H), 7.38～7.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.7, 155.8, 138.6, 136.3, 133.7, 132.5, 128.5, 128.1, 127.7, 127.3, 126.9, 126.3, 125.9, 125.9, 124.8, 124.2, 122.8, 120.7, 119.4, 111.9, 111.8.

2-(Naphthalen-2-yl)aniline (**3w**):[23] Trace for aryl iodide; 45% yield (19.7 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89～7.84 (m, 2H), 7.83～7.79 (m, 2H), 7.55 (dd, J=8.4, 1.6 Hz, 1H), 7.49～7.41 (m, 2H), 7.22～7.11 (m, 2H), 6.84～6.83 (m, 1H), 6.73 (dd, J=8.0, 1.2 Hz, 1H), 3.65 (brs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.6, 136.9, 133.5, 132.3, 130.6, 128.5, 128.3, 127.9, 127.7, 127.6, 127.4, 127.3, 126.2, 125.9, 118.7, 115.6.

2-(Naphthalen-2-yl)pyridine (**3x**):[24] 71% yield (29.1 mg) for aryl iodide; 78% yield (32.0 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72～8.69 (m, 1H), 8.50～8.40 (m, 1H), 8.10 (dd, J=8.6, 1.8 Hz, 1H), 7.89 (dd, J=9.0, 5.2 Hz, 2H), 7.85～7.78 (m, 1H), 7.78～7.71 (m, 1H), 7.65～7.63 (m, 1H), 7.48～7.38 (m, 2H), 7.16～7.13 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.0, 149.6, 136.6, 136.5, 133.5, 133.3, 128.6, 128.3, 127.5, 126.4, 126.1, 124.4, 122.0, 120.6.

3-(Naphthalen-2-yl)pyridine (**3y**):[25] 58% yield (23.8 mg) for aryl iodide; 71% yield (29.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (d, J=2.4 Hz, 1H), 8.60 (dd, J=4.8, 1.6 Hz, 1H), 7.98 (d, J=1.8 Hz, 1H), 7.94～7.87 (m, 2H), 7.87～7.81 (m, 2H), 7.65 (dd, J=8.4, 1.8 Hz, 1H), 7.53～7.43 (m, 2H), 7.35～7.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.4, 148.4, 136.4, 134.9, 134.4, 133.4, 132.7, 128.7, 128.1, 127.6, 126.4, 126.3, 126.0, 124.8, 123.4.

5-(Naphthalen-2-yl)pyrimidine (**3z**):[26] 20% yield (8.3 mg) for aryl iodide; 85% yield (35.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.23 (s, 1H), 9.03 (s, 2H), 8.01～7.91 (m, 2H), 7.90～7.82 (m, 2H), 7.62 (dd, J=8.6, 1.8 Hz, 1H), 7.56～7.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 154.9, 134.0, 133.3, 133.0, 131.3, 129.2,

128.1, 127.6, 126.8, 126.7, 126.1, 124.1.

6-(Naphthalen-2-yl)quinoline (**3aa**):[26] 52% yield (26.5 mg) for aryl iodide; 72% yield (36.8 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (dd, J=4.2, 1.6 Hz, 1H), 8.19 (d, J=8.8 Hz, 1H), 8.17～8.09 (m, 2H), 8.09～8.00 (m, 2H), 7.95～7.87 (m, 2H), 7.85 (dd, J=7.6, 1.8 Hz, 1H), 7.79 (dd, J=8.4, 1.8 Hz, 1H), 7.54～7.44 (m, 2H), 7.36 (dd, J=8.2, 4.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.3, 147.6, 139.0, 137.4, 136.1, 133.5, 132.7, 129.9, 129.2, 128.6, 128.4, 128.2, 127.6, 126.4, 126.2, 126.2, 125.6, 125.4, 121.4.

2-(Naphthalen-2-yl)thiophene (**3ab**):[20] 70% yield (29.4 mg) for aryl iodide; 86% yield (36.2 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.80～7.72 (m, 3H), 7.68 (dd, J=8.6, 1.8 Hz, 1H), 7.44～7.33 (m, 3H), 7.24 (dd, J=5.0, 1.2 Hz, 1H), 7.04 (dd, J=5.0, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.4, 133.6, 132.6, 131.7, 128.5, 128.1, 127.9, 127.6, 126.5, 125.9, 125.0, 124.3, 124.1, 123.4.

3-(Naphthalen-2-yl)thiophene (**3ac**):[27] 75% yield (31.5 mg) for aryl iodide; 84% yield (35.3 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (s, 1H), 7.84 (t, J=9.8 Hz, 3H), 7.77～7.70 (m, 1H), 7.59～7.37 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.2, 133.7, 133.2, 132.6, 128.4, 128.0, 127.6, 126.4, 126.3, 125.7, 125.0, 124.8, 120.6.

4-Methyl-1,1'-biphenyl (**3ad**):[28] 55% yield (18.5 mg) for aryl iodide; 64% yield (21.5 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57～7.50 (m, 2H), 7.48～7.40 (m, 2H), 7.40～7.33 (m, 2H), 7.28～7.23 (m, 1H), 7.21～7.11 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.1, 138.3, 136.9, 129.4, 128.7, 128.7, 126.9, 126.9, 21.0.

4-(*tert*-Butyl)-1,1'-biphenyl (**3ae**):[28] 58% yield (23.1 mg) for aryl iodide; 62% yield (26.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59～7.55 (m, 2H), 7.54～7.49 (m, 2H), 7.47～7.42 (m, 2H), 7.39 (dd, J=8.4, 6.8 Hz, 2H), 7.31～7.26 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.2, 141.0, 138.3, 128.7, 128.6, 127.2, 127.1, 127.0, 126.9, 126.8, 125.7, 34.5, 31.4.

4-Methoxy-1,1'-biphenyl (**3af**):[28] 65% yield (24.0 mg) for aryl iodide; 60% yield (22.1 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54～7.50 (m, 4H), 7.39 (dd, J=8.4, 6.8 Hz, 2H), 7.31～7.23 (m, 1H), 6.99～6.91 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2.

3-Methoxy-1,1'-biphenyl (**3ag**):[29] 67% yield (24.7 mg) for aryl iodide; 66% yield (24.3 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60～7.52 (m, 2H), 7.40 (dd, J=8.6, 6.8 Hz, 2H), 7.35～7.30 (m, 2H), 7.16 (dt, J=7.6, 1.2 Hz, 1H), 7.12 (t, J=2.0 Hz, 1H), 6.89～6.84 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.9, 142.7, 141.0, 129.7, 128.7, 127.4, 127.1, 119.6, 112.8, 112.6, 55.2.

4-(Trifluoromethyl)-1,1'-biphenyl (**3ah**):[28] 78% yield (34.6 mg) for aryl iodide; 83% yield (35.5 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (s, 4H), 7.59～7.54 (m, 2H), 7.47～7.41 (m, 2H), 7.41～7.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.7, 139.7, 129.3 (q, $J_{C\text{-}F}$=32.0 Hz), 129.0, 128.2, 127.4, 127.2, 125.7 (q, $J_{C\text{-}F}$=4.0 Hz), 124.3 (q, $J_{C\text{-}F}$=268.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.33.

Methyl [1,1'-biphenyl]-4-carboxylate (**3ai**):[28] 85% yield (36.1 mg) for aryl iodide; 90% yield (38.2 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12～8.04 (m, 2H), 7.66～7.55 (m, 4H), 7.46～7.40 (m, 2H), 7.40～7.32 (m, 1H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.8, 145.5, 139.8, 130.0, 128.8, 128.8, 128.0, 127.1, 126.9, 52.0.

2-Fluoro-1,1'-biphenyl (**3aj**):[30] 66% yield (22.7 mg) for aryl iodide; 60% yield (20.7 mg) for aryl bromide; 51% yield (17.5 mg) for aryl chloride. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59～7.49 (m, 2H), 7.45～7.37 (m, 3H), 7.37～7.30 (m, 1H), 7.28～7.24 (m, 1H), 7.19～7.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.7 (d, $J_{C\text{-}F}$=247.0 Hz), 135.8, 130.7 (d, $J_{C\text{-}F}$=4.0 Hz), 129.0 (d, $J_{C\text{-}F}$=3.0 Hz), 128.9, 128.8, 128.4, 127.6, 124.3 (d, $J_{C\text{-}F}$=4.0 Hz), 116.1 (d, $J_{C\text{-}F}$=23.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −117.90.

4-Fluoro-1,1'-biphenyl (**3ak**):[28] 75% yield (25.8 mg) for aryl iodide; 78% yield (26.9 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55～7.47 (m, 4H), 7.43～7.37 (m, 2H), 7.35～7.28 (m, 1H), 7.13～7.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.4 (d, $J_{C\text{-}F}$=245.0 Hz), 140.2, 137.3 (d, $J_{C\text{-}F}$=4.0 Hz), 128.8, 128.6 (d, $J_{C\text{-}F}$=8.0 Hz), 127.2, 127.0, 115.6 (d, $J_{C\text{-}F}$=21.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.71.

4-Chloro-1,1'-biphenyl (**3al**):[28] 86% yield (32.4 mg) for aryl iodide; 82% yield (30.9 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56～7.47 (m, 4H), 7.45～7.40 (m, 3H), 7.39～7.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.0, 139.6, 133.3, 128.9, 128.8, 128.4, 127.6, 127.0.

[1,1'-Biphenyl]-4-yl acetate (**3am**):[31] 70% yield (29.7 mg) for aryl iodide; 62% yield (26.3 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59～7.46 (m, 4H), 7.38 (t, J=7.6 Hz, 2H), 7.30 (t, J=7.2 Hz, 1H), 7.17～7.03 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.3, 149.9, 140.2, 138.8, 128.6, 128.0, 127.2, 126.9, 121.7, 20.9.

[1,1'-Biphenyl]-4-yltrimethylsilane (**3an**):[32] 82% yield (37.1 mg) for aryl iodide; 88% yield (39.8 mg) for aryl bromide; 44% yield (20.0 mg) for aryl chloride. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59～7.56 (m, 6H), 7.40 (dd, J=8.4, 6.8 Hz, 2H), 7.33～7.28 (m, 1H), 0.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.6, 141.2, 139.2, 133.8, 128.7, 127.3, 127.1, 126.5, −1.1.

5-Phenylbenzo[*d*][1,3]dioxole (**3ao**):[32] 35% yield (13.9 mg) for aryl iodide; 20% yield (7.9 mg) for aryl bromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51～7.44 (m, 4H), 7.36 (dd, J=8.6, 6.8 Hz, 4H), 7.30～7.23 (m, 2H), 7.07～6.98 (m, 4H), 6.83 (d, J=8.0 Hz, 2H), 5.91 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.0, 147.0, 140.8, 135.5, 128.6, 126.8, 126.8, 120.5, 108.5, 107.6, 101.0.

4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (**3ap**):[33] 42% yield (20.7 mg) for aryl chloride. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78～7.74 (m, 4H), 7.71～7.69 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.2, 142.7, 132.8, 130.8 (q, J_{C-F}=30.0 Hz), 128.0, 127.6, 126.1, 124.0 (q, J_{C-F}=270.0 Hz), 118.6, 112.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.6.

Methyl 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (**3aq**):[34] 38% yield (21.3 mg) for aryl chloride. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J=8.4 Hz, 2H), 7.63 (s, 4H), 7.57 (d, J=8.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9, 143.2, 142.7, 129.3 (q, J_{C-F}=33.4 Hz), 128.9, 126.7, 126.4, 125.0 (q, J_{C-F}=3.0 Hz), 123.3 (q, J_{C-F}=272.8 Hz), 51.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.5.

4-Fluoro-4'-(trifluoromethyl)-1,1'-biphenyl (**3ar**):[35] 47% yield (22.6 mg) for aryl chloride. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (t, J=8.4 Hz, 2H), 7.56 (t, J=6.2 Hz, 2H), 7.76～7.63 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.8 (d, J_{C-F}=246.3 Hz), 143.8, 136.0, 129.5 (d, J_{C-F}=32.4 Hz), 129.1 (d, J_{C-F}=8.1 Hz), 127.8, 127.4, 125.9 (d, J_{C-F}=3.5 Hz), 116.1 (d, J_{C-F}=21.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.2, −113.9.

6-Phenylquinoline (**3as**):[36] 35% yield (14.4 mg) for aryl chloride. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (dd, J=4.2, 1.8 Hz, 1H), 8.22～8.15 (m, 2H), 8.03～7.95 (m, 2H), 7.75～7.67 (m, 2H), 7.55～7.46 (m, 2H), 7.43～7.37 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.3, 147.6, 140.2, 139.2, 136.1, 129.8, 129.1, 128.9, 128.4, 127.7, 127.4, 125.4, 121.4.

Supporting Information The synthetic method of the starting materials **2** and the copies of NMR spectra of product **3**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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