SUPPORTING INFORMATION

for

An efficient organocatalytic method for constructing biaryls through aromatic C-H activation

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Contents

Table of Contents S1.
General Experimental Section S2.
Supporting Data of Extra Experiments S3-S10.
General Experimental Procedures and Characterization Data S11-S23.
NMR Spectra of Products S24-S55.
General Experimental Section:

**Analytic methods.** All the analytic methods, GC, MS, IR, IR-online, and ICP were performed by the State- Authorized Analytical Center at Peking University. The data GC-yields were obtained after amendment by standard curve, with the n-dodecane as the internal standard. $^1$H NMR and $^{13}$C NMR data were obtained on Varian 200 M and 300 M nuclear resonance spectrometers with CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H NMR spectrum as 0.00 ppm (chloroform, 7.26 ppm). Data were reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiplet and $br$ = broad), coupling constant ($J$ values) in Hz and integration. Chemical shifts for $^{13}$C NMR spectra were recorded in ppm from tetramethylsilane using the central peak of CDCl$_3$ (77.0 ppm) as the internal standard. Flash column chromatography was performed using 200-300 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm).

**General preparation for chemicals.** All the transition metal salts and all the substrates aryl iodides/bromides were purchased from Alfa Aesar China (Tianjin) Chemical Co., Ltd. without any further purification. KO'Bu and ligands were purchased from different chemical companies. KO'Bu was further purified by sublimation under reduced pressure. All the reagents and solvents were anhydrous.
Supporting Data of Extra Experiments

**GC-yield Standard Curve**

The response peak area ratios of product 4-methoxybiphenyl and internal standard \( n \)-dodecane (\( \frac{A_p}{A_d} \)) were obtained from Agilent G2095AA GC spectrometer. All the GC-yields were calculated by the formula of curve fitting.

**Figure S1.** GC-Yield Standard Curve.

\[
y = 1.786 \times x - 0.075
\]

<table>
<thead>
<tr>
<th>( \frac{A_p}{A_d} )</th>
<th>0.1916</th>
<th>0.3259</th>
<th>0.3734</th>
<th>0.4873</th>
<th>0.5482</th>
<th>0.5931</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yields</td>
<td>0.30</td>
<td>0.45</td>
<td>0.60</td>
<td>0.80</td>
<td>0.90</td>
<td>1.00</td>
</tr>
</tbody>
</table>
ICP data and other relative experiments

The commercial available KOtBu and 1,10-phenanthroline from different chemicals companies were examined by ICP-AES experiments. Possible critical transition metals, including Fe, Co, Ni, Cu, Mo, Pd, Rh, Ru were tested. The results were as Table S1.

Table S1. ICP-AES (Inductively Coupled Plasma-Mass Spectroscopy) Analysis of Various Metals in Reagents.

<table>
<thead>
<tr>
<th>Element</th>
<th>KOtBu sublimated</th>
<th>KOtBu Alfa Aesar</th>
<th>KOtBu Acros</th>
<th>phen Aldrich</th>
<th>phen Alfa Aesar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0391</td>
<td>ND</td>
<td>0.595</td>
<td>0.275</td>
<td>ND</td>
</tr>
<tr>
<td>Fe</td>
<td>2.83</td>
<td>8.04</td>
<td>1.84</td>
<td>1.86</td>
<td>1.81</td>
</tr>
<tr>
<td>Mg</td>
<td>3.04</td>
<td>2.49</td>
<td>1.09</td>
<td>ND</td>
<td>0.295</td>
</tr>
<tr>
<td>Mo</td>
<td>ND</td>
<td>ND</td>
<td>0.154</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ni</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Pd</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Rh</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ru</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Unit: $\mu g/g$ (ppm), ND: Not detected.
We further analyzed the various metals in the base, catalyst as well as the reaction mixture after the reaction is finished. All the metals, which showed good catalytic ability in the corresponding cross coupling reactions and direct C-H transformations, were detected in the ppb level by IPC-MS. We found that all the samples, even the sublimated KOtBu from Aldrich, contained most of these metals more or less in the ppb to ppm level (Table S2).

**Table S2.** ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) Analysis of Various Metals in Reagents and the Final Reaction Mixture.

<table>
<thead>
<tr>
<th>Element</th>
<th>KOtBu (Aldrich Sublimated)</th>
<th>KOtBu (Acros)</th>
<th>phenanthroline (Alfa Aesar)</th>
<th>phenanthroline (Aldrich)</th>
<th>Reaction Mixture*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.584</td>
<td>7.536</td>
<td>0.010</td>
<td>0.812</td>
<td>2.462</td>
</tr>
<tr>
<td>Cu</td>
<td>2.636</td>
<td>29.896</td>
<td>7.786</td>
<td>12.916</td>
<td>273.396</td>
</tr>
<tr>
<td>Fe</td>
<td>187.7</td>
<td>589.6</td>
<td>13.6</td>
<td>597.0</td>
<td>432.4</td>
</tr>
<tr>
<td>Ni</td>
<td>0.606</td>
<td>133.149</td>
<td>3.151</td>
<td>101.249</td>
<td>62.129</td>
</tr>
<tr>
<td>Pd</td>
<td>3.959</td>
<td>17.082</td>
<td>3.028</td>
<td>3.697</td>
<td>1.297</td>
</tr>
<tr>
<td>Rh</td>
<td>0.045</td>
<td>0.358</td>
<td>ND</td>
<td>0.099</td>
<td>0.158</td>
</tr>
<tr>
<td>Ru</td>
<td>2.243</td>
<td>5.642</td>
<td>ND</td>
<td>5.460</td>
<td>4.613</td>
</tr>
</tbody>
</table>

Unit: ng/g (ppb), ND: Not detected.

*In the reaction mixture, chemical KOtBu (Aldrich sublimated) and 1,10-phenanthroline (Alfa Aesar) were used.*
To exclude the effect of the transition metal species, the kinetic studies with/without the additional metal species were systematically studied with all these metal sources. We are happy to learn that kinetic data was not significantly changed after we added 10 ppm of various metal salts, which have been most frequently used in the cross couplings. Recently, Fe and Cu were found as an efficient catalyst for similar reaction, we also tested the different amount of Fe and Cu catalysts. We found the kinetic data indicated that the reactions were not significantly affected by such additions based on both the conversion of starting material and the formation of coupling product. In some cases, the efficacy was even lowered by the addition of the corresponding metal salts (Figures S2, S3).

The procedure of experiments as follow:
1,10-Phenanthroline (0.4 mmol, 40 mol %) was added into Schlenk tubes (dried by heat gun). KOtBu (3.0 mmol, 3.0 equiv) was added in Schlenk tubes in glove box. Benzene (8 mL), n-dodecane (1.0 mmol, 1.0 equiv), and 4-bromoanisole (1.0 mmol) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at 100 °C for 20 h. In the reactions with additional transition metal salts, 10⁻⁵ mmol transition metal salts were added as this way: 10 ppm metal, 0.01 equiv metal salts and 0.03 equiv 1,10-Phenanthroline were weighed exactly on balance and solved in 10 mL benzene, and then 10 µL of the solution was added. The transition metals used were Co(acac)₃, Ni(acac)₂, Pd(OAc)₂, [Ru(COD)Cl]₂, [Rh(COD)Cl]₂. The reaction mixture samples were taken out by syringe every 1 or 2 hours.

The following figures are the conversion-time curves and yield-time curves with different amounts of additional metal salts in reactions.

The procedure of experiments as follow:
1,10-Phenanthroline (0.4 mmol, 40 mol %) was added into Schlenk tubes (dried by heat gun). KOtBu (3.0 mmol, 3.0 equiv) was added in Schlenk tubes in glove box. Benzene (8 mL), n-dodecane (1.0 mmol, 1.0 equiv), and 4-bromoanisole (1.0 mmol) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at 100 °C for 20 h. In the reactions with additional transition metal salts, 10⁻⁵ mmol Fe(OAc)₂ was added as this way: 10 ppm Fe, 0.01 equiv iron and 0.03 equiv 1,10-Phenanthroline were weighed exactly on balance and solved in 10 mL benzene, and then 10 µL of the solution was added. Other amounts of additional metal salts as added in the same way as 10 ppm Fe. The reaction mixture samples were taken out by syringe every 1 or 2 hours.

The following figures are the conversion-time curves and yield-time curves with different amounts of additional metal salts in reactions.
**Figure S2.** Kinetic Experiments with Additional Transition Metals Based on the Conversion of Starting Materials.

**Figure S3.** Kinetic Experiments with Additional Transition Metals Based on the Formation of Desired Products.
Moreover, we also added the general reaction partners in traditional cross couplings to the reaction mixture, for instance, ArB(OH)₂, ArZnCl, ArSi(OR)₃ and ArSnBu₃ as reviewer #4 suggested. However, no corresponding desired traditional cross coupling products were observed, which indicated that the late transition metal species contained in material might not play the role to facilitate the desired cross coupling. In fact, the addition of arylboronic acid, arylzinc chloride and aryltin reagents did not terminated our desired cross coupling and the desired products were isolated in good yield respectively (equation 1, 3, and 4). However, the addition of TBAF terminated the desired coupling (equation 2).

\[
\begin{align*}
\text{MeO-} & \quad \text{Br} + \quad \text{Me-} \quad \text{B(OH)₂} \quad \xrightarrow{\text{phen, 40 mol % KOtBu, 3.0 eq, PhH, 100 °C}} \quad \text{MeO-} \quad \text{Ph} + \quad \text{Me-O-} \quad \text{Me} & \quad (1) \\
\text{MeO-} & \quad \text{Br} + \quad \text{tBu-} \quad \text{Si(OEt)₃} \quad \xrightarrow{\text{phen, 40 mol % KOtBu, 3.0 eq, TBAF 1.0 eq, PhH, 100 °C}} \quad \text{MeO-} \quad \text{Ph} + \quad \text{Me-O-} \quad \text{Bu} & \quad \text{Not Observed!} \\
\text{MeO-} & \quad \text{Br} + \quad \text{Me-} \quad \text{ZnCl} \quad \xrightarrow{\text{phen, 40 mol % KOtBu, 3.0 eq, PhH, 100 °C}} \quad \text{MeO-} \quad \text{Ph} + \quad \text{Me-O-} \quad \text{Me} & \quad (3) \\
\text{MeO-} & \quad \text{Br} + \quad \text{Me-} \quad \text{SnBu₃} \quad \xrightarrow{\text{phen, 40 mol % KOtBu, 3.0 eq, PhH, 100 °C}} \quad \text{MeO-} \quad \text{Ph} + \quad \text{Me-O-} \quad \text{Me} & \quad (4)
\end{align*}
\]
Experimental data for the reaction mechanism

To further understand the proposed radical pathway. We further tested such a transformation in the presence of various radical scavengers according to the reviewer #2’s comments. We found that, 1) in the presence of TEMPO and SmI₂, the cross coupling was completely inhibited (equation 5); 2) in the presence of 2.0 equivalent of 1,1-diphenylethylene, the product was detected in an 18% yield with a considerable amount of addition product 1,1-diphenyl-2-(4-methoxyphenyl)ethylene as byproduct (equation 6); 3) in the presence of 1.0 equivalent of Bu₃SnH, 16% yield of desired coupling product was observed with a large amount of reductive product anisole from 4-bromoanisole (equation 7); 4) with the use of AIBN and Bu₃SnH as the radical initiator in the absence of the base and catalyst, the desired coupling product was also observed in spite of lower efficiency (equation 8). Based on all these studies, we are quite sure that this transformation goes through the radical key intermediate. All the data above mentioned have been added to the supporting information of the revised manuscript.

![Chemical reactions](image-url)
Kinetic isotopic effects of the reactions

Table S3. Kinetic Isotopic Effects of the Model Reactions, as Well as the Reactions with Additional Fe and Cu Salts.

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>kD/kH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OAc)₂</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAc)₂</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Procedure:

1,10-Phenanthroline (0.2 mmol, 40 mol %) was added into Schlenk tubes (dried by heat gun). KO'Bu (1.5 mmol, 3.0 equiv) and additive (0.005 mmol, 1 mol %, if any) were added in Schlenk tubes in glove box. Benzene (2 mL), benzene-D₆ (2 mL), and 4-bromanisole (0.5 mmol) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at 100 °C for 18 h. The work up procedure was the same as model reaction.

This result suggested that the step of cleavage of C-H bond on benzene ring was NOT the rate-determining step, and also the additional transition metal salts, such as Fe(OAc)₂ and Cu(OAc)₂, did not change the pathway of C-H bond activation step.

NMR spectrum of product in entry 1.
SUPPLEMENTARY INFORMATION

General Experimental Procedures and Characterization Data:

General experimental procedures for cobalt-catalyzed arylation of aryl C-H with aryl bromides/iodides:

Cobalt salt (0.05 mmol, 10 mol %) and KO'Bu (1.5 mmol, 3.0 equiv) (and also ligands (0.15 mmol, 40 mol %), if solid; as well as 4-idoanisole (0.5 mmol) in entry 1 and 2 of Table 1) were added into Schlenk tubes in glove box. Benzene (4 mL) was added by syringe. 4-Bromoanisole (1.0 equiv, 0.5 mmol) (and also ligands (0.15 mmol, 30 mol %), if liquid) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at corresponding temperature. The reaction was cooled down to room temperature and quenched by water. The yields were determined by GC with the use of n-dodecane as an internal standard.

General experimental procedures for cross-coupling of aryl iodides with benzene:

Aryl iodides (0.2 mmol, if solid) and 1,10-phenanthroline (0.04 mmol, 20 mol %) were added in Schlenk tubes dried by heat gun. KO'Bu (0.4 mmol, 2.0 equiv) was added in glove box. Benzene (2 mL) and aryl iodides (0.2 mmol, if liquid) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at 100 °C for 24 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200-300 mesh silica gel with petroleum ether/ethyl acetate as eluent.

Characterization of Products in details:

(3aa) 4-Methoxybiphenyl.

The title compound was prepared according to the general procedure described above using 4-idoanisole with benzene, and purified by flash column chromatography as white solid (30.5 mg, 83%). Rf = 0.15 (100% petroleum ether 60-90). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3H), 6.94 (d, J = 8.7, 2H), 7.27-7.54 (m, 7H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.2, 114.1, 126.6, 128.1, 128.7, 133.6, 140.7, 159.0. MS (EI): found: 184(M⁺), calcd for C₁₂H₁₀ (M⁺): 184.09. IR: 1607 cm⁻¹, 1486 cm⁻¹, 1247 cm⁻¹, 908 cm⁻¹, 833 cm⁻¹,
760 cm⁻¹, 734 cm⁻¹.

(3ba) 3-Methoxybiphenyl.

The title compound was prepared according to the general procedure described above using 3-iodoanisole with benzene, and purified by flash column chromatography as white solid (29.8 mg, 81%). Rf = 0.20 (100% petroleum ether 60-90). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.88-6.91 (m, 1H), 7.12-7.19 (m, 2H), 7.33-7.46 (m, 4H), 7.58-7.60 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.2, 112.6, 112.9, 119.7, 127.2, 127.4, 128.7, 129.7, 141.0, 142.7, 159.9. MS (EI): found: 184(M⁺), calcd for C₁₂H₁₀ (M⁺): 184.09. IR: 1599 cm⁻¹, 1479 cm⁻¹, 1296 cm⁻¹, 1213 cm⁻¹, 789 cm⁻¹, 756 cm⁻¹.

(3ca) 2-Methoxybiphenyl.

The title compound was prepared according to the general procedure described above using 2-iodoanisole with benzene, and purified by flash column chromatography as white solid (27.2 mg, 74%). Rf = 0.15 (100% petroleum ether 60-90). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 3.81 (s, 3H), 6.97-7.04 (m, 2H), 7.25-7.44 (m, 5H), 7.51-7.55 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.5, 111.1, 120.8, 126.9, 128.0, 128.6, 129.5, 130.9, 138.5, 148.2, 156.4. MS (EI): found: 184(M⁺), calcd for C₁₂H₁₀ (M⁺): 184.09. IR: 1483 cm⁻¹, 1429 cm⁻¹, 1259 cm⁻¹, 732 cm⁻¹.

(3ea) 4-Methylbiphenyl.

The title compound was prepared according to the general procedure described above using 4-iodotoluene with benzene, and purified by flash column chromatography as white solid (23.2 mg, 69%). Rf = 0.47 (100% petroleum ether 60-90). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 2.41 (s, 3H), 7.25-7.36 (m, 3H), 7.41-7.46 (m, 2H), 7.51-7.62 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ = 21.1, 126.9, 128.7, 129.4, 136.9, 138.3, 141.1. MS (EI): found: 168(M⁺), calcd for C₁₂H₁₀ (M⁺): 168.09. IR: 1487 cm⁻¹, 909 cm⁻¹, 822 cm⁻¹, 755 cm⁻¹.

(3ga) 2-Methylbiphenyl.

The title compound was prepared according to the general procedure described above using 2-iodotoluene with benzene, and purified by flash column chromatography as colorless oil (17.5 mg, 52%). Rf = 0.40 (100% petroleum ether 60-90). The observed characterization data (¹H) was
consistent with that previously reported in the literature. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.28\) (s, 3H), 7.24-7.43 (m, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 20.5, 125.7, 126.7, 127.1, 127.2, 128.0, 129.2, 129.8, 130.3, 135.3, 141.9\). MS (EI): found: 168(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 168.09. IR: 1480 cm\(^{-1}\), 749 cm\(^{-1}\), 702 cm\(^{-1}\).

**3ha 3,5-Dimethylbiphenyl.**

The title compound was prepared according to the general procedure described above using 5-iodo-\(m\)-xylene with benzene, and purified by flash column chromatography as colorless oil (26.9 mg, 74%). Rf = 0.42 (100% petroleum ether 60-90). The observed characterization data (\(^1\)H) was consistent with that previously reported in the literature. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.37\) (s, 6H), 6.99 (s, 1H), 7.21 (s, 2H), 7.32-7.44 (m, 3H), 7.56-7.58 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 21.4, 125.0, 125.1, 127.0, 127.2, 128.6, 138.2, 141.2, 141.4\). MS (EI): found: 182(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 182.11. IR: 1604 cm\(^{-1}\), 849 cm\(^{-1}\), 760 cm\(^{-1}\), 698 cm\(^{-1}\).

**3ja \(\sigma\)-Terphenyl.**

The title compound was prepared according to the general procedure described above using 4-iodo-biphenyl with benzene, and purified by flash column chromatography as white solid (40.9 mg, 89%). Rf = 0.60 (100% petroleum ether 60-90). The observed characterization data (\(^1\)H) was consistent with that previously reported in the literature. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.34-7.39\) (m, 2H), 7.44-7.49 (m, 4H), 7.63-7.68 (m, 8H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 127.0, 127.3, 127.5, 128.8, 140.1, 140.7\). MS (EI): found: 230(M\(^+\)), calcd for C\(_{13}\)H\(_{10}\) (M\(^+\)): 230.11. IR: 1480 cm\(^{-1}\), 1455 cm\(^{-1}\), 1404 cm\(^{-1}\), 1004 cm\(^{-1}\), 838 cm\(^{-1}\), 745 cm\(^{-1}\).

**3ka 4-Trifluoromethoxybiphenyl.**

The title compound was prepared according to the general procedure described above using 4-trifluoromethoxyiodo-benzene with benzene, and purified by flash column chromatography as white solid (42.4 mg, 89%). Rf = 0.40 (98% petroleum ether 60-90/2% ethyl acetate). The observed characterization data (\(^1\)H) was consistent with that previously reported in the literature. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.23-7.29\) (m, 2H), 7.36-7.47 (m, 3H), 7.54-7.60 (m, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 118.7, 121.2, 122.2, 127.1, 127.6, 128.4, 128.9, 139.8, 139.9, 148.6\). MS (EI): found: 238(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 238.06. IR: 1487 cm\(^{-1}\), 1258 cm\(^{-1}\), 1209 cm\(^{-1}\), 1157 cm\(^{-1}\), 1007 cm\(^{-1}\), 852 cm\(^{-1}\), 765 cm\(^{-1}\), 737 cm\(^{-1}\).
**SUPPLEMENTARY INFORMATION**

(3la) 4-Fluorobiphenyl.
The title compound was prepared according to the general procedure described above using 4-fluoro-1-iodobenzene with benzene, and purified by flash column chromatography as white solid (26.8 mg, 78%). Rf = 0.40 (99% petroleum ether 60-90/1% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): δ = 7.09-7.14 (m, 2H), 7.31-7.55 (m, 7H). 13C NMR (75 MHz, CDCl3): δ = 115.6 (d, J = 22.4 Hz), 127.0, 127.2, 128.6 (d, J = 7.1 Hz), 128.8, 137.3 (d, J = 3.3 Hz), 140.2, 162.4 (d, J = 244.3 Hz). MS (EI): found: 172(M+), calcd for C12H10 (M+): 172.07. IR: 2928 cm⁻¹, 1486 cm⁻¹, 1238 cm⁻¹, 837 cm⁻¹, 758 cm⁻¹.

(3ma) 4-Chlorobiphenyl.
The title compound was prepared according to the general procedure described above using 4-chloro-1-iodobenzene with benzene, and purified by flash column chromatography as white solid (31.1 mg, 82%). Rf = 0.35 (99% petroleum ether 60-90/1% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): δ = 7.35-7.46 (m, 5H), 7.49-7.56 (m, 4H). 13C NMR (75 MHz, CDCl3): δ = 126.9, 127.6, 128.3, 128.6, 133.3, 139.6, 139.9, 143.5. MS (EI): found: 188(M+), 100%), calcd for C12H10 (M+): 188.04. IR: 1479 cm⁻¹, 1094 cm⁻¹, 904 cm⁻¹, 758 cm⁻¹, 738 cm⁻¹, 705 cm⁻¹.

(3na) 3-Trifluoromethylbiphenyl.
The title compound was prepared according to the general procedure described above using 3-trifluoromethyliodobenzene with benzene, and purified by flash column chromatography as white solid (18.6 mg, 42%). Rf = 0.20 (90% petroleum ether 60-90/10% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): δ = 7.40-7.50 (m, 3H), 7.55-7.61 (m, 4H), 7.75-7.78 (m, 1H), 7.84 (s, 1H). 13C NMR (75 MHz, CDCl3): δ = 124.2 (q, J = 270.7 Hz), 123.9 (q, J = 4.4 Hz), 127.2, 128.0, 129.0, 129.2, 130.4, 130.9, 131.3, 139.7, 141.9. MS (EI): found: 222(M+), calcd for C12H10 (M+): 222.07. IR: 1334 cm⁻¹, 1261 cm⁻¹, 1166 cm⁻¹, 1124 cm⁻¹, 758 cm⁻¹.

(3oa) 4-Cyanobiphenyl.
The title compound was prepared according to the general procedure described above using 4-iodobenzonitrile with benzene, and purified by flash column chromatography as white.
solid (12.9 mg, 36%). Rf = 0.45 (90% petroleum ether 60-90/10% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): \( \delta = 7.35-7.49 \) (m, 4H), 7.56-7.58 (m, 2H), 7.63-7.71 (m, 3H). 13C NMR (75 MHz, CDCl3): \( \delta = 110.7, 118.9, 127.1, 127.6, 128.5, 129.0, 132.4, 139.0, 145.5. \) MS (EI): found: 179(M+), calcd for C12H10 (M+): 179.07. IR: 1606 cm\(^{-1}\), 1489 cm\(^{-1}\), 1392 cm\(^{-1}\), 848 cm\(^{-1}\), 768 cm\(^{-1}\), 697 cm\(^{-1}\).

\[ \text{Ph} \]

**(3qa) 1-Phenynaphthalene.**

The title compound was prepared according to the general procedure described above using 1-iodonaphthalene with benzene, and purified by flash column chromatography as white solid (26.5 mg, 65%). Rf = 0.30 (100% petroleum ether 60-90). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): \( \delta = 7.41-7.56 \) (m, 9H), 7.84-7.92 (m, 3H). 13C NMR (75 MHz, CDCl3): \( \delta = 125.3, 125.7, 126.0, 126.89, 126.91, 127.1, 127.2, 127.6, 128.2, 130.0, 131.5, 133.7, 140.2, 140.7. \) MS (EI): found: 204(M+), calcd for C12H10 (M+): 204.08. IR: 1489 cm\(^{-1}\), 1391 cm\(^{-1}\), 778 cm\(^{-1}\), 760 cm\(^{-1}\), 705 cm\(^{-1}\).

\[ \text{Ph} \]

**(3ra) 2-Phenylpyrazine.**

The title compound was prepared according to the general procedure described above using 2-iodopyrazine with benzene, and purified by flash column chromatography as white solid (22.5 mg, 72%). Rf = 0.25 (80% petroleum ether 60-90/20% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): \( \delta = 7.50-7.53 \) (m, 3H), 8.00-8.04 (m, 2H), 8.51-8.65 (m, 2H), 9.04 (s, 1H). 13C NMR (75 MHz, CDCl3): \( \delta = 126.9, 129.0, 129.9, 136.3, 142.3, 142.9, 144.2, 152.8. \) MS (EI): found: 156(M+), calcd for C12H10 (M+): 156.07. IR: 1475 cm\(^{-1}\), 1444 cm\(^{-1}\), 1402 cm\(^{-1}\), 1079 cm\(^{-1}\), 1018 cm\(^{-1}\), 697 cm\(^{-1}\), 692 cm\(^{-1}\).

**General experimental procedures for cross-coupling of 4-idoanisole with arenes:**

1,10-Phenanthroline (0.04 mmol, 20 mol %) and arenes (16 mmol, 80 equiv, if solid) were added into Schlenk tubes (dried by heat gun). KO\(^{t}\)Bu (0.4 mmol, 2.0 equiv) was added in Schlenk tubes in glove box. Arenes (2 mL, if liquid) and 4-idoanisole (0.2 mmol) were added into tubes by syringe. The mixture was stirred under N\(_2\) atmosphere in sealed Schlenk tubes at 100 °C for 24 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200-300 mesh silica.
gel with petroleum ether/ethyl acetate as eluent.

(3ab) 4'-methoxy-2,4,6-trimethylbiphenyl.
The title compound was prepared according to the general procedure described above using mesitylene as solvent, and purified by flash column chromatography as a white solid (30.5 mg, 27%). Rf = 0.45 (98% petroleum ether 60-90/2% ethyl acetate). \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.01 \) (s, 6H), 2.32 (s, 3H), 3.84 (s, 3H), 6.93-6.96 (m, 4H), 7.04-7.07 (m, 2H). \( ^{13} \)C NMR (50 MHz, CDCl\(_3\)): \( \delta = 20.8, 21.0, 55.1, 113.7, 128.0, 130.3, 133.3, 136.4, 138.6, 158.1. MS (EI): found: 226(M\(^+\)), calcd for C\(_{16}\)H\(_{18}\)O (M\(^+\)): 226.14. IR: 2916 cm\(^{-1}\), 1609 cm\(^{-1}\), 1511 cm\(^{-1}\), 1465 cm\(^{-1}\), 1285 cm\(^{-1}\), 1243 cm\(^{-1}\), 1042 cm\(^{-1}\), 831 cm\(^{-1}\).

(3ac) 2,5-difluoro-4'-methoxybiphenyl.
The title compound was prepared according to the general procedure described above using 1,4-difluorobenzene as solvent, and purified by flash column chromatography as a light yellow solid (35.6 mg, 81%). Rf = 0.30 (98% petroleum ether 60-90/2% ethyl acetate). \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 3.80 \) (s, 3H), 6.94-7.07 (m, 5H), 7.44-7.46 (m, 2H). MS (EI): found: 220(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 220.07. IR: 1610 cm\(^{-1}\), 1519 cm\(^{-1}\), 1490 cm\(^{-1}\), 1254 cm\(^{-1}\), 1176 cm\(^{-1}\), 1040 cm\(^{-1}\), 833 cm\(^{-1}\), 762 cm\(^{-1}\).

(3ae) 2,5-dimethyl-4'-methoxybiphenyl.
The title compound was prepared according to the general procedure described above using p-xylene as solvent, and purified by flash column chromatography as light yellow oil (51.9 mg, 49%). Rf = 0.40 (98% petroleum ether 60-90/2% ethyl acetate). \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.23 \) (s, 3H), 2.34 (s, 3H), 3.84 (s, 3H), 6.93-7.26 (m, 7H). \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 20.0, 20.9, 55.2, 113.4, 127.6, 130.2, 130.6, 130.7, 132.2, 134.4, 135.1, 141.3, 158.4. MS (EI): found: 212(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 212.12. IR: 2923 cm\(^{-1}\), 1609 cm\(^{-1}\), 1516 cm\(^{-1}\), 1496 cm\(^{-1}\), 1245 cm\(^{-1}\), 1176 cm\(^{-1}\), 1032 cm\(^{-1}\), 834 cm\(^{-1}\).

(3ah) Mixture of 4'-methoxy-2-methylbiphenyl, 4'-methoxy-3-methylbiphenyl, 4'-methoxy-4-methylbiphenyl.
The title compounds were prepared according to the general procedure described above using toluene as solvent,
and purified by flash column chromatography as white solid (57.4 mg, 58%). \( R_f = 0.35 \)
(98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 198(M⁺), calcd for C₁₂H₁₀
(M⁺): 198.10. IR: 2913 cm⁻¹, 1608 cm⁻¹, 1514 cm⁻¹, 1246 cm⁻¹, 1174 cm⁻¹, 1032 cm⁻¹, 832
cm⁻¹, 736 cm⁻¹.

(3af) Mixture of 4'-methoxy-2-fluoro-5-methylbiphenyl, 4'-methoxy-2-methyl-5-fluorobiphenyl.
The title compounds were prepared according to the general procedure described above using 4-fluorotoluene as solvent, and purified by flash column chromatography as light yellow solid (67.0 mg, 62%). \( R_f = 0.30 \)
(98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 216(M⁺), calcd for C₁₂H₁₀
(M⁺): 216.10. IR: 2928 cm⁻¹, 2360 cm⁻¹, 1611 cm⁻¹, 1493 cm⁻¹, 1246 cm⁻¹, 1176 cm⁻¹, 1043 cm⁻¹, 833 cm⁻¹.

(3ad) Mixture of 4',5-dimethoxy-2-fluorobiphenyl, 2,4'-dimethoxy-5-fluorobiphenyl
The title compounds were prepared according to the general procedure described above using 4-fluoroanisole as solvent, and purified by flash column chromatography as light yellow oil (85.4 mg, 74%). \( R_f = 0.20 \)
(98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 232(M⁺), calcd for C₁₄H₁₃FO₂
(M⁺): 232.09. IR: 2917 cm⁻¹, 2849 cm⁻¹, 1519 cm⁻¹, 1494 cm⁻¹, 1248 cm⁻¹, 1179 cm⁻¹, 1041 cm⁻¹, 833 cm⁻¹.

(3ag) Mixture of 2,4'-dimethoxybiphenyl, 3,4'-dimethoxybiphenyl, 4,4'-dimethoxybiphenyl
The title compounds were prepared according to the general procedure described above using anisole as solvent, and purified by flash column chromatography as a white solid (74.3 mg, 70%). \( R_f = 0.38 \)
(98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 214(M⁺), calcd for C₁₄H₁₄O₂
(M⁺): 214.10. IR: 2916 cm⁻¹, 2832 cm⁻¹, 1610 cm⁻¹, 1487 cm⁻¹, 1245 cm⁻¹, 1178 cm⁻¹, 1040
cm⁻¹, 831 cm⁻¹, 753 cm⁻¹.

(3ai) Mixture of 2-fluoro-4'-methoxybiphenyl, 3-fluoro-4'-methoxybiphenyl, 4-fluoro-4'-methoxybiphenyl
The title compounds were prepared according to the general procedure described above using fluoro benzene as solvent, and purified by flash column chromatography as a colorless solid (73.8 mg, 74%). \( R_f = 0.45 \)
(98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 202(M⁺), calcd for
C_{13}H_{11}FO (M^+): 202.08. IR: 1606 cm\(^{-1}\), 1522 cm\(^{-1}\), 1486 cm\(^{-1}\), 1247 cm\(^{-1}\), 1177 cm\(^{-1}\), 1043 cm\(^{-1}\), 832 cm\(^{-1}\), 762 cm\(^{-1}\).

**3aj** Mixture of 4'-methoxy-2-trifluoromethylbiphenyl, 4'-methoxy-3-trifluoromethylbiphenyl, 4'-methoxy-4-trifluoromethylbiphenyl

The title compounds were prepared according to the general procedure described above using trifluoromethylbenzene as solvent, and purified by flash column chromatography as a white solid (75.4 mg, 60%). R\(_f\) = 0.35 (98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 252(M^+), calcd for C_{14}H_{11}F_{3}O (M^+): 252.08. IR: 2916 cm\(^{-1}\), 2847 cm\(^{-1}\), 1610 cm\(^{-1}\), 1522 cm\(^{-1}\), 1335 cm\(^{-1}\), 1262 cm\(^{-1}\), 1167 cm\(^{-1}\), 1126 cm\(^{-1}\), 1074 cm\(^{-1}\), 1045 cm\(^{-1}\), 833 cm\(^{-1}\), 800 cm\(^{-1}\).

**3ak** Mixture of 1-(4-anisyl)-naphthalene, 2-(4-anisyl)-naphthalene.

The title compounds were prepared according to the general procedure described above using naphthalene as solvent, and purified by flash column chromatography as a yellow solid (28.1 mg, 60%). R\(_f\) = 0.35 (98% petroleum ether 60-90/2% ethyl acetate). MS (EI): found: 234(M^+), calcd for C_{12}H_{10} (M^+): 234.10. IR: 2360 cm\(^{-1}\), 1608 cm\(^{-1}\), 1515 cm\(^{-1}\), 1246 cm\(^{-1}\), 1174 cm\(^{-1}\), 1032 cm\(^{-1}\), 800 cm\(^{-1}\), 780 cm\(^{-1}\).

**3al** 1-methyl-2-(4-anisyl)-pyrrole

The title compound was prepared according to the general procedure described above using 1-methylpyrrole as solvent, and purified by flash column chromatography as a yellow oil (24.3 mg, 26%). R\(_f\) = 0.30 (98% petroleum ether 60-90/2% ethyl acetate). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.62\) (s, 3H), \(3.83\) (s, 3H), \(6.15-6.18\) (m, 2H), \(6.68-6.69\) (m, 1H), \(6.93\) (d, \(J = 2.3\) Hz, 2H), \(7.20\) (d, \(J = 2.3\) Hz, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 34.9, 55.2, 107.5, 107.9, 113.7, 123.0, 125.8, 130.0, 134.3, 158.5\). MS (EI): found: 187(M^+), calcd for C_{12}H_{13}NO (M^+): 187.10. IR: 2954 cm\(^{-1}\), 2832 cm\(^{-1}\), 1506 cm\(^{-1}\), 1289 cm\(^{-1}\), 1249 cm\(^{-1}\), 1177 cm\(^{-1}\), 1029 cm\(^{-1}\), 834 cm\(^{-1}\).
General experimental procedures for cross-coupling of aryl bromides with benzene:

1,10-Phenanthroline (0.2 mmol, 40 mol %) and aryl bromides (0.5 mmol, if solid) were added into Schlenk tubes (dried by heat gun). KO'Bu (1.5 mmol, 3.0 equiv) was added in Schlenk tubes in glove box. Benzene (4 mL) and aryl bromides (0.5 mmol, if liquid) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at 100 °C for 18 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200-300 mesh silica gel with petroleum ether/ethyl acetate as eluent.

Characterization of Products in details:

(3aa) 4-Methoxybiphenyl.
The title compound was prepared according to the general procedure described above using 4-bromoanisole with benzene, and purified by flash column chromatography as white solid (78.6 mg, 86%). Rf = 0.15 (100% petroleum ether 60-90). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3H), 6.94 (d, J = 8.7, 2H), 7.27-7.54 (m, 7H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.2, 114.1, 126.6, 128.1, 128.7, 133.6, 140.7, 159.0. MS (EI): found: 184(M⁺), calcd for C₁₂H₁₀ (M⁺): 184.09. IR: 1607 cm⁻¹, 1486 cm⁻¹, 1247 cm⁻¹, 908 cm⁻¹, 833 cm⁻¹, 760 cm⁻¹, 734 cm⁻¹.

(3da) Biphenyl.
The title compound was prepared according to the general procedure described above using bromobenzene with benzene, and purified by flash column chromatography as white solid (57.0 mg, 74%). Rf = 0.42 (100% petroleum ether 60-90). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 7.31-7.43 (m, 6H), 7.56-7.60 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ = 127.1, 127.2, 128.7, 141.1. MS (EI): found: 154(M⁺), calcd for C₁₂H₁₀ (M⁺): 154.08. IR: 1480 cm⁻¹, 907 cm⁻¹, 728 cm⁻¹.

(3ea) 4-Methylbiphenyl.
The title compound was prepared according to the general procedure described above using 4-bromotoluene with benzene, and purified by flash column chromatography as white solid
(74.5 mg, 89%). \( \text{Rf} = 0.47 \) (100% petroleum ether 60-90). The observed characterization data \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.41 \) (s, 3H), 7.25-7.36 (m, 3H), 7.41-7.46 (m, 2H), 7.51-7.62 (m, 4H). \(^13\text{C}\) NMR (75 MHz, CDCl\(_3\)): \( \delta = 21.1, 126.9, 128.7, 129.4, 136.9, 138.3, 141.1. \) MS (EI): found: 168(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 168.09. IR: 1487 cm\(^{-1}\), 909 cm\(^{-1}\), 822 cm\(^{-1}\), 755 cm\(^{-1}\).

(3fa) 3-Methylbiphenyl.

The title compound was prepared according to the general procedure described above using 3-bromotoluene with benzene, and purified by flash column chromatography as white solid (68.6 mg, 82%). \( \text{Rf} = 0.43 \) (100% petroleum ether 60-90). The observed characterization data \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.38 \) (s, 3H), 7.12-7.14 (m, 1H), 7.27-7.42 (m, 6H), 7.55-7.57 (m, 2H). \(^13\text{C}\) NMR (75 MHz, CDCl\(_3\)): \( \delta = 21.5, 124.2, 127.1, 127.9, 128.6, 138.2, 141.1, 141.3. \) MS (EI): found: 168(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 168.09. IR: 1482 cm\(^{-1}\), 792 cm\(^{-1}\), 753 cm\(^{-1}\), 698 cm\(^{-1}\).

(3ga) 2-Methylbiphenyl.

The title compound was prepared according to the general procedure described above using 2-bromotoluene with benzene, and purified by flash column chromatography as colorless oil (37.3 mg, 44%). \( \text{Rf} = 0.40 \) (100% petroleum ether 60-90). The observed characterization data \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.28 \) (s, 3H), 7.24-7.43 (m, 9H). \(^13\text{C}\) NMR (75 MHz, CDCl\(_3\)): \( \delta = 20.5, 125.7, 126.7, 127.1, 127.2, 128.0, 129.2, 129.8, 130.3, 135.3, 141.9. \) MS (EI): found: 168(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 168.09. IR: 1480 cm\(^{-1}\), 749 cm\(^{-1}\), 702 cm\(^{-1}\).

(3ha) 3,5-Dimethylbiphenyl.

The title compound was prepared according to the general procedure described above using 5-bromo-m-xylene with benzene, and purified by flash column chromatography as colorless oil (51.0 mg, 57%). \( \text{Rf} = 0.42 \) (100% petroleum ether 60-90). The observed characterization data \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.37 \) (s, 6H), 6.99 (s, 1H), 7.21 (s, 2H), 7.32-7.44 (m, 3H), 7.56-7.58 (m, 2H). \(^13\text{C}\) NMR (75 MHz, CDCl\(_3\)): \( \delta = 21.4, 125.0, 125.1, 127.0, 127.2, 128.6, 138.2, 141.2, 141.4. \) MS (EI): found: 182(M\(^+\)), calcd for C\(_{12}\)H\(_{10}\) (M\(^+\)): 182.11. IR: 1604 cm\(^{-1}\), 849 cm\(^{-1}\), 760 cm\(^{-1}\), 698 cm\(^{-1}\).
(3ia) 4-Methoxy-3,5-dimethylbiphenyl.

The title compound was prepared according to the general procedure described above using 4-bromo-2,6-dimethylanisole with benzene, and purified by flash column chromatography as yellow oil (80.9 mg, 77%). Rf = 0.50 (98% petroleum ether 60-90/2% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): δ = 2.34 (s, 6H), 3.75 (s, 3H), 7.23-7.32 (m, 3H), 7.37-7.42 (m, 2H), 7.52-7.55 (m, 2H). 13C NMR (75 MHz, CDCl3): δ = 16.2, 59.7, 126.8, 126.9, 127.5, 128.6, 131.1, 136.7, 140.9, 156.5. MS (EI): found: 212(M⁺), calcd for C12H10 (M⁺): 212.12. IR: 1478 cm⁻¹, 1239 cm⁻¹, 1165 cm⁻¹, 1015 cm⁻¹, 874 cm⁻¹, 697 cm⁻¹.

(3oa) 4-Cyanobiphenyl.

The title compound was prepared according to the general procedure described above using 4-bromobenzonitrile with benzene, and purified by flash column chromatography as white solid (56.1 mg, 72%). Rf = 0.45 (90% petroleum ether 60-90/10% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): δ = 7.35-7.49 (m, 4H), 7.56-7.58 (m, 2H), 7.63-7.71 (m, 3H). 13C NMR (75 MHz, CDCl3): δ = 110.7, 118.9, 127.1, 127.6, 128.5, 129.0, 132.4, 139.0, 145.5. MS (EI): found: 179(M⁺), calcd for C12H10 (M⁺): 179.07. IR: 1606 cm⁻¹, 1484 cm⁻¹, 1397 cm⁻¹, 1179 cm⁻¹, 848 cm⁻¹, 768 cm⁻¹, 697 cm⁻¹.

(3pa) 4-Benzoylbiphenyl.

The title compound was prepared according to the general procedure described above using 4-bromobenzophenone with benzene, and purified by flash column chromatography as yellow solid (87.5 mg, 68%). Rf = 0.50 (90% petroleum ether 60-90/10% ethyl acetate). The observed characterization data (1H) was consistent with that previously reported in the literature. 1H NMR (300 MHz, CDCl3): δ = 7.37-7.49 (m, 5H), 7.55-7.69 (m, 5H), 7.79-7.89 (m, 4H). 13C NMR (75 MHz, CDCl3): δ = 126.8, 127.1, 128.1, 128.8, 129.8, 129.9, 130.6, 132.2, 136.0, 137.5, 139.7, 145.0, 196.1. MS (EI): found: 258(M⁺), calcd for C12H10 (M⁺): 258.10. IR: 1657 cm⁻¹, 1599 cm⁻¹, 1316 cm⁻¹, 1279 cm⁻¹, 1149 cm⁻¹, 938 cm⁻¹, 736 cm⁻¹, 697 cm⁻¹.

(3sa) 4-Phenylisoquinoline.

The title compound was prepared according to the general procedure described above using 4-bromoisoquinoline with benzene, and purified by flash column chromatography as yellow
oil (69.8 mg, 68%). Rf = 0.15 (90% petroleum ether 60-90/10% ethyl acetate). The observed characterization data ($^1$H) was consistent with that previously reported in the literature. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.41-7.61 (m, 7H), 7.85-7.97 (m, 2H), 8.46 (s, 1H), 9.21 (s, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 124.5, 127.0, 127.6, 127.7, 128.2, 128.4, 129.9, 130.3, 133.0, 133.9, 136.7, 142.6, 151.8. MS (EI): found: 205(M$^+$), calcd for C$_{12}$H$_{10}$ (M$^+$): 205.09. IR: 1619 cm$^{-1}$, 1568 cm$^{-1}$, 1524 cm$^{-1}$, 1390 cm$^{-1}$, 965 cm$^{-1}$, 897 cm$^{-1}$, 788 cm$^{-1}$, 760 cm$^{-1}$.

(3ta) 2-Methyl-6-phenylquinoline.

The title compound was prepared according to the general procedure described above using 6-bromo-2-methylquinoline with benzene, and purified by flash column chromatography as yellow solid (56.8 mg, 52%). Rf = 0.45 (80% petroleum ether 60-90/20% ethyl acetate). The observed characterization data ($^1$H) was consistent with that previously reported in the literature. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 2.73 (s, 3H), 7.22-7.24 (m, 1H), 7.34-7.47 (m, 3H), 7.65-7.68 (m, 2H), 7.89-7.93 (m, 2H), 7.98-8.09 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 25.3, 122.2, 122.3, 125.1, 126.4, 127.2, 127.4, 128.8, 128.9, 136.2, 138.2, 140.2, 147.1, 158.8. MS (EI): found: 219(M$^+$), calcd for C$_{12}$H$_{10}$ (M$^+$): 219.10. IR: 1597 cm$^{-1}$, 1490 cm$^{-1}$, 1372 cm$^{-1}$, 1224 cm$^{-1}$, 893 cm$^{-1}$, 842 cm$^{-1}$, 816 cm$^{-1}$, 783 cm$^{-1}$, 766 cm$^{-1}$.

General experimental procedures for cross-coupling of 4-bromoanisole with arenes:

1,10-Phenanthroline (0.2 mmol, 40 mol %) and arenes (40 mmol, 80 equiv, if solid) were added into Schlenk tubes (dried by heat gun). KOtBu (1.5 mmol, 3.0 equiv) was added in Schlenk tubes in glove box. Arenes (4 mL, if liquid) and 4-bromoanisole (0.5 mmol) were added into tubes by syringe. The mixture was stirred under N$_2$ atmosphere in sealed Schlenk tubes at 100 °C for 18 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200-300 mesh silica gel with petroleum ether/ethyl acetate as eluent.

(3ac) 2,5-difluoro-4'-methoxybiphenyl.

The title compound were prepared according to the general procedure described above using 1,4-difluorobenzene as solvent, and purified by flash column chromatography as light yellow solid (88.2 mg, 81%). Rf = 0.30 (98% petroleum ether 60-90/2% ethyl acetate). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.80 (s, 3H), 6.94-7.07 (m, 5H), 7.44-7.46 (m, 2H). MS (EI): found: 220(M$^+$), calcd for C$_{12}$H$_{10}$ (M$^+$): 220.07. IR: 1610 cm$^{-1}$, 1519 cm$^{-1}$, 1490 cm$^{-1}$, 1254 cm$^{-1}$, 1176 cm$^{-1}$, 1040 cm$^{-1}$, 833 cm$^{-1}$, 762 cm$^{-1}$.
Experimental procedures for intramolecular reaction:

1,10-Phenanthroline (0.2 mmol, 40 mol %) was added into Schlenk tubes (dried by heat gun). KOtBu (1.5 mmol, 3.0 equiv) was added in Schlenk tubes in glove box. Mesitylene (4 mL) and 1-(benzyloxy)-2-bromobenzene (0.5 mmol) were added into tubes by syringe. The mixture was stirred under N₂ atmosphere in sealed Schlenk tubes at 100 °C for 20 h. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200-300 mesh silica gel with petroleum ether/ethyl acetate as eluent.

(5) 6H-benzo[c]chromene

The title compound was prepared according to the procedure described above and purified by flash column chromatography as colorless oil (66.0 mg, 73%). Rf = 0.32 (99% petroleum ether 60-90/1% ethyl acetate). The observed characterization data (¹H) was consistent with that previously reported in the literature. ¹H NMR (300 MHz, CDCl₃): δ = 5.09 (s, 2H), 6.97-7.13 (m, 3H), 7.20-7.35 (m, 3H), 7.66-7.73 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 68.4, 117.3, 122.0, 122.1, 123.3, 124.6, 127.4, 127.6, 128.4, 129.4, 130.0, 131.4, 154.7. MS (El): found: 182(M⁺), calcd for C₁₂H₁₀ (M⁺): 182.07.
NMR Spectra of Products:

(3aa) 4-Methoxybiphenyl
(3ba) 3-Methoxybiphenyl
(3ca) 2-methoxybiphenyl

\[ \text{Ph} \quad \text{OMe} \]
(3da) Biphenyl
(3ea) 4-Methylbiphenyl
(3fa) 3-Methylbiphenyl

![Chemical structure of 3-Methylbiphenyl](image)

![NMR spectra of 3-Methylbiphenyl](image)
(3ga) 2-Methylbiphenyl
(3ha) 3,5-Dimethylbiphenyl

[Chemical structure image]

[Graphs and charts showing NMR spectra]

[Additional NMR spectra images]

[Data and peak assignments]
(3ia) 4-Methoxy-3,5-dimethylbiphenyl

![Chemical Structure](image)

![NMR Spectra](image)
(3ja) p-Terphenyl
(3ka) 4-trifluoromethoxybiphenyl
(3la) 4-Fluorobiphenyl
(3ma) 4-Chlorobiphenyl
(3na) 3-Trifluoromethylbiphenyl

![Chemical Structure of 3-Trifluoromethylbiphenyl]
(3oa) 4-Cyanobiphenyl
(3pa) 4-Benzoylbiphenyl

[Chemical structure image]

[Spectroscopic data graphs]
(3qa) 1-Phenylnaphthalene

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(3ra) 2-Phenylpyrazine
(3sa) 4-Phenylisoquinoline
(3ta) 2-Methyl-6-phenylquinoline
(3ab) 4'-methoxy-2,4,6-trimethylbiphenyl

\[
\begin{align*}
&\text{Me} & & \text{Me} \\
&\text{Me} & & \text{Me} \\
&\text{MeO} & & \\
\end{align*}
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(3ac) 2,5-difluoro-4′-methoxybiphenyl
(3ad) Mixture of 4',5-dimethoxy-2-fluorobiphenyl, 2,4'-dimethoxy-5-fluorobiphenyl
(3ae) 2,5-dimethyl-4'-methoxybiphenyl
(3af) Mixture of 2-fluoro-4'-methoxy-5-methylbiphenyl, 5-fluoro-4'-methoxy-2-methylbiphenyl
(3ag) Mixture of 2,4'-dimethoxybiphenyl, 3,4'-dimethoxybiphenyl, 4,4'-dimethoxybiphenyl
(3ah) Mixture of 4’-methoxy-2-methylbiphenyl, 4’-methoxy-3-methylbiphenyl, 4’-methoxy-4-methylbiphenyl.

Mixture from the reaction of 4-iodoanisole and m-xylene.
(3ai) Mixture of 2-fluoro-4'-methoxybiphenyl, 3-fluoro-4'-methoxybiphenyl, 4-fluoro-4'-methoxybiphenyl
(3aj) Mixture of 4’-methoxy-2-trifluoromethylbiphenyl, 4’-methoxy-3-trifluoromethylbiphenyl, 4’-methoxy-4-trifluoromethylbiphenyl
(3ak) Mixture of 1-(4-anisyl)-naphthalene, 2-(4-anisyl)-naphthalene.
(3al) 1-methyl-2-(4-anisyl)-pyrrole
(5) $6H$-benzo[c]chromene