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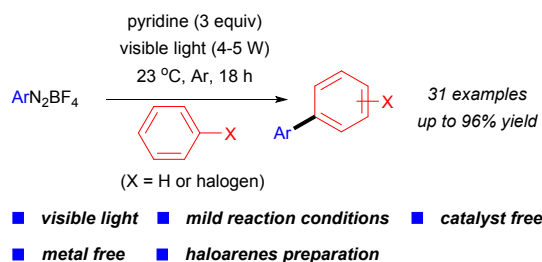
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# Visible-Light-Promoted, Catalyst-Free Gomberg-Bachmann Reaction: Synthesis of Biaryls

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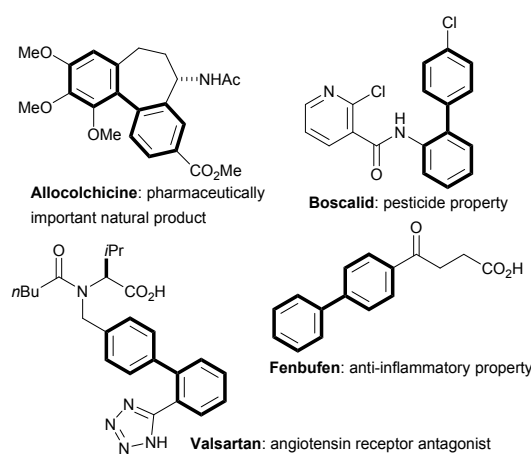
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**Abstract:** Biaryls were synthesized via a novel visible-light-promoted Gomberg-Bachmann reaction that does not require a photosensitizer or any metal reagents. The formation of an electron donor-acceptor complex between aryl diazonium salts and pyridine allows, under visible light irradiation, the synthesis of biaryls in moderate-to-high yields.

The biaryl scaffold, which is frequently found in natural products and commercially available pharmaceuticals, exhibits important bioactivities across a wide range of therapeutic classes, including anti-hypertensive, anti-fungal, anti-tumor, anti-rheumatic, and anti-inflammatory agents (Figure 1).<sup>1</sup> Given the importance of biaryl moieties, their synthesis has received significant attention from the synthetic community. The most common approaches for their preparation include well-known named reactions like Suzuki, Negishi, Ullmann, Stille, and Kumada coupling reactions, which employ transition metal catalysts.<sup>2</sup>

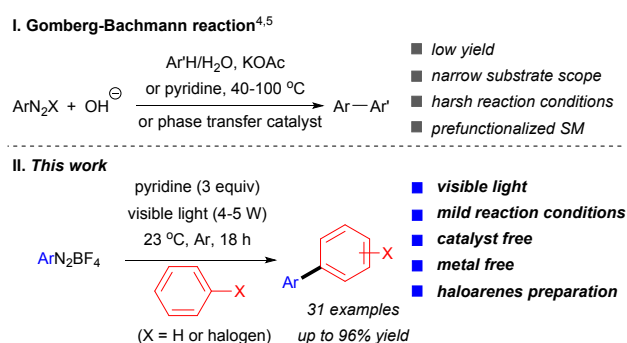


**Figure 1. Bioactive molecules containing a biaryl moiety.**

However, there are certain concerns regarding the use of toxic and expensive transition metal catalysts

and/or reagents. In addition, most of the abovementioned processes employ harsh reaction conditions and require the use of functionalized reactants such as boronic acid, halide, silane, mesylate, triflate, etc. Therefore, the development of environmentally benign and efficient cross-coupling reactions is highly desired. Several previously reported mild approaches have been revisited in recent years.<sup>3</sup> One of these, the Gomberg-Bachmann reaction is a classical method for the synthesis of biaryls that employs aryl diazonium salts and metal-free conditions.<sup>4</sup> This approach has been frequently used in various studies, with some modifications also being introduced.<sup>5</sup> Although these reports provide powerful tools for the synthesis of biaryls, they still have some limitations, such as low yield, harsh reaction conditions, and the use of pre-functionalized starting compounds (Scheme 1).

**Scheme 1. General scheme of the Gomberg-Bachmann reaction (I) and the reaction developed through this work (II)**

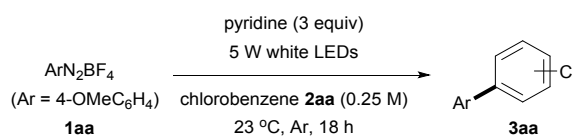


Recently, visible-light-mediated processes have been incorporated in various reactions.<sup>6</sup> For example, photoredox catalysis has been introduced in C-H arylation reactions using aryl diazonium salts.<sup>7</sup> In view of the above and with respect to our continued interest in photo-induced reactions,<sup>8</sup> we envisioned that mild Gomberg-Bachmann reaction could be realized via a visible-light-mediated process. Herein, we report a novel visible-light-induced Gomberg-Bachmann reaction, which employs mild reaction conditions. Notably, the method presents the preparation of haloarenes, which could be used as key intermediates for the synthesis of bioactive compounds.

After choosing 4-methoxybenzenediazonium tetrafluoroborate (**1aa**) and chlorobenzene (**2aa**) as model substrates, we performed a reaction condition optimization, selected examples of which are presented in Table 1. We found that the C-H arylation product **3aa** was obtained in 91% yield in the presence of 3 equiv. of pyridine in chlorobenzene at room temperature under white LED light irradiation in Ar environment (Table 1, entry 1). We discovered that chlorobenzene (**2aa**) acts simultaneously as a solvent and reagent. In addition, while a photoredox catalyst such as eosin Y did not improve the reaction yield (entry 2), the reaction did not take place without light or pyridine (entries 3 and 4). Interestingly, however, varying the amount of pyridine did not improve the reaction yield (entries 1, 5, and 6). In addition, employing different bases such as TEA, DIPEA, and K<sub>2</sub>CO<sub>3</sub> instead of pyridine

caused the reaction yield to diminish significantly (entries 7–9). These results indicate that pyridine was mainly involved in the formation of an electron-donor-acceptor (EDA) complex.<sup>9</sup> Furthermore, changing the light source diminished the reaction yield, giving the desired biaryl (**3aa**) in 18–85% yield (entries 10–13). Finally, the reaction yield decreased when the transformation was performed at higher reaction concentrations (entry 14) and under air (entry 15).

**Table 1. Optimization of the reaction conditions<sup>a</sup>**

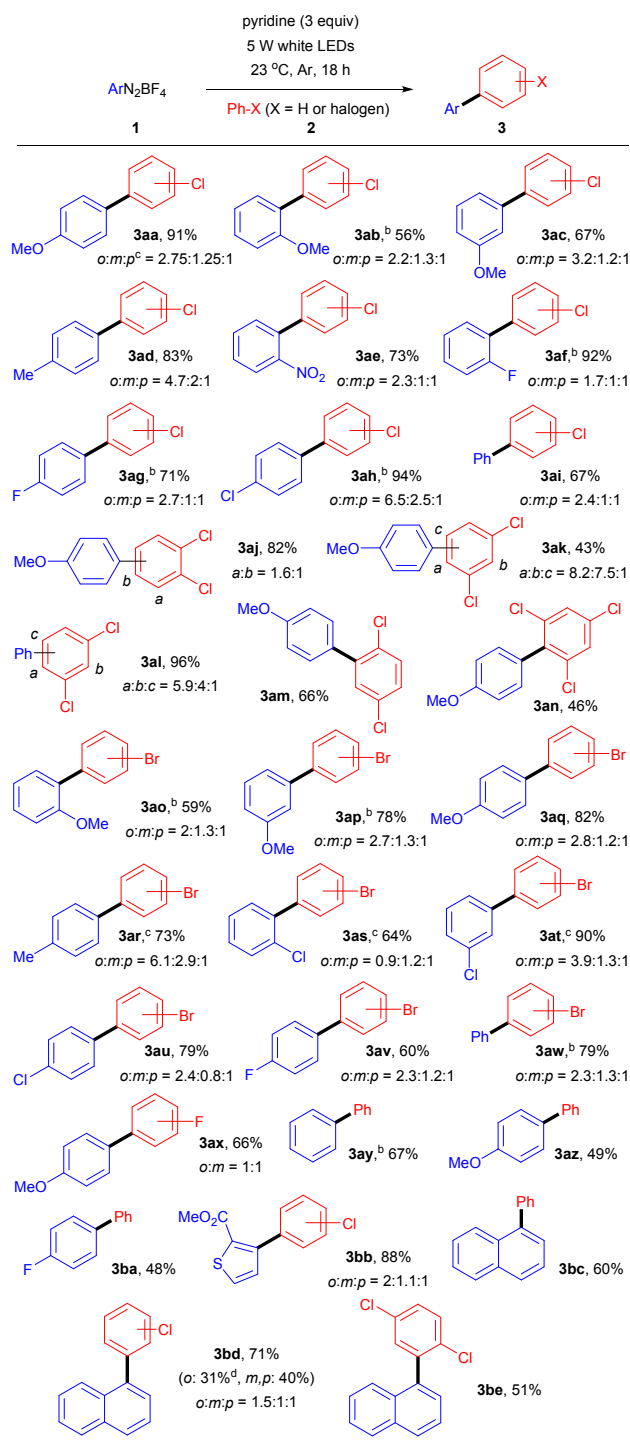


Entry	Variations in the reaction conditions	Yield of <b>3aa</b> (%) <sup>b,c</sup>
1	none	91
2	with eosin Y	90
3	without light	trace
4	without pyridine	trace
5	with 2.0 equiv of pyridine	82
6	with 4.0 equiv of pyridine	89
7	TEA instead of pyridine	16
8	DIPEA instead of pyridine	17
9	K <sub>2</sub> CO <sub>3</sub> instead of pyridine	10
10	green LEDs instead of white LEDs	85
11	blue LEDs instead of white LEDs	79
12	20 W CFL instead of white LEDs	76
13	sunlight instead of white LED	18
14	0.5 M of 4-chlorobenzene	71
15	under air	43

<sup>a</sup>Conditions: **1aa** (0.6 mmol, 1.0 equiv), pyridine (3.0 equiv) in PhCl (2.4 mL, 0.25 M), irradiation with 5 W white LEDs at 23 °C for 18 h under Ar. <sup>b</sup>Isolated yield after column chromatography. <sup>c</sup>Mixture of isomers (*o:m:p* = 2.75:1.25:1). The ratio of isomers was determined by GC-MS after comparison with authentic samples.

With the optimized reaction conditions in hand, we next explored the substrate scope of the synthesis of biaryls. Notably, the transformation proved to be tolerant to various aryl diazonium salts (Table 2).

**Table 2. Substrate scope<sup>a</sup>**



<sup>a</sup>Conditions: **1** (0.6 mmol, 1.0 equiv), pyridine (3.0 equiv) in (halo)benzene (2.4 mL, 0.25 M), irradiation with 5 W white LEDs at 23 °C for 18 h under Ar. Isolated yield after column chromatography. The ratio of isomers was determined by GC-MS. <sup>b</sup>Irradiation with 4 W blue LEDs (455 nm). <sup>c</sup>Irradiation with 4 W green LEDs (530 nm). <sup>d</sup>Separated by column chromatography.

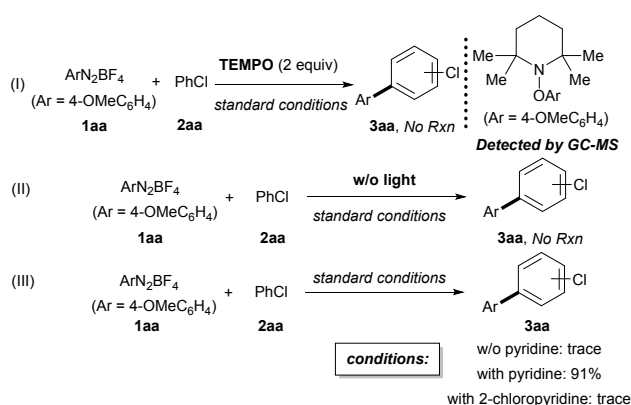
More specifically, aryl diazonium salts with either electron-donating (**3aa–3ad**, **3aj**, **3ak**, **3am–3ar**, **3ax**, **3az**) or electron-withdrawing (**3ae–3ah**, **3as–3av**, **3ba**) groups provided the desired products in

43–94% yields. Additionally, the reaction with heteroaryl diazonium salt **1bb** successfully provided the desired product **3bb** in 88% yield. The use of naphthyl diazonium salts also gave the desired products in 51–71% yields (**3bc–3be**). Furthermore, the products derived from the *ortho*-, *meta*-, and *para*-substituted aryl diazonium salts (**3aa–3ac**, **3ao–3aq**, **3as–3au**) were obtained in moderate-to-high yields (56–91%). However, a noticeable electronic effect of these substituents was not observed.

Importantly, halobenzenes or benzene also acted as solvents under the reaction conditions. However, in the case of solid halobenzenes (**2am**, **2an**, **2be**), DMSO was employed as a solvent, which resulted in lowered reaction yields (46–66%). The further decrease in the yield of **3an** would be due to the steric effect of 1,3,5-trichlorobenzene (**2an**). Previous studies have reported that mixtures of isomers (*ortho*-, *meta*-, and *para*-biarene) are obtained when mono- or di-substituted halobenzenes are used.<sup>4-5</sup> Moreover, the *ortho* isomer is formed predominantly when a mono-halobenzene is used.<sup>5b</sup> Similar results were observed in this transformation in terms of selectivity (**3aa–3ai**, **3ao–3aw**, **3bb**).

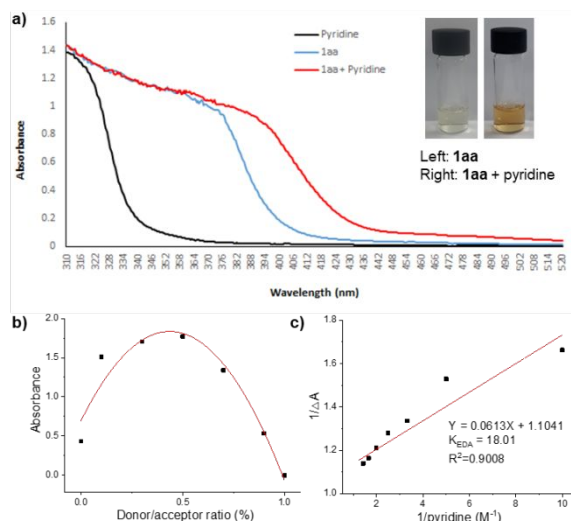
In order to gain a mechanistic insight into this transformation, we performed various control experiments (Scheme 2). Notably, employing TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as a radical inhibitor did not afford the desired product, indicating that the reaction mechanism includes a radical pathway. Additionally, the fact that no desired product was observed in the dark implies that visible light plays an important role in the reaction. Furthermore, since the reaction did not proceed in the absence of pyridine, we assumed that an EDA complex was formed between the aryl diazonium salts and pyridine. The fact that only trace amounts of the desired product were obtained when 2-chloropyridine was used instead proves that pyridine might act as an electron donor in the EDA complex.

### Scheme 2. Control experiments



To gain further insight into the reaction mechanism, we investigated the formation of the proposed EDA complex between the aryl diazonium salt **1aa** and pyridine by UV-vis absorption spectroscopy. When a solution of **1aa** in CH<sub>3</sub>CN was treated with pyridine, the mixture turned yellow and a bathochromic shift was observed in the UV-vis spectrum, which is diagnostic of an EDA complex (Figure 2a).<sup>9</sup> Next,

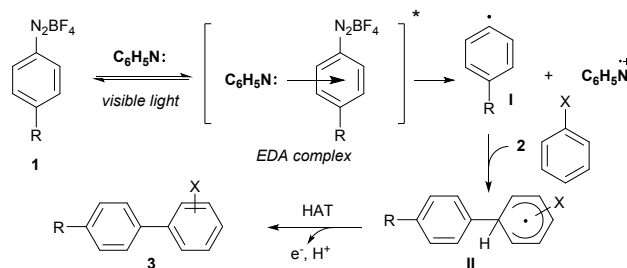
the stoichiometry of the donor-acceptor complex was investigated by constructing a Job plot of the UV-vis spectroscopy results,<sup>10</sup> which yielded a 1:1 ratio of **1aa**/pyridine in the EDA complex (Figure 2b). Finally, the association constant  $K_{EDA}$  ( $K_{EDA}=18.01$ ) for the formation of the EDA complex was determined through the Benesi-Hildebrand method (Figure 2c, see the Supporting Information for details).<sup>11</sup>



**Figure 2.** Mechanistic studies. a) UV-vis absorption spectra of pyridine, **1aa**, and a mixture of pyridine and **1aa** (0.2 M in CH<sub>3</sub>CN). b) Job plot of **1aa** and pyridine in CH<sub>3</sub>CN c) Scott plot.

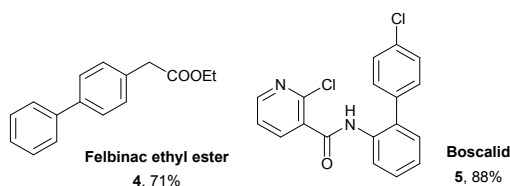
Considering the results from the present study and previous reports,<sup>7b,7i,12</sup> a reaction pathway was proposed (Scheme 3). We believe that the reaction starts with the formation of an EDA complex between pyridine and aryl diazonium salt **1**. Next, a photo-excitation of the EDA complex triggers a SET to generate aryl radical **I**, which then reacts with **2**, affording radical intermediate **II**. Finally, a hydrogen atom transfer (HAT) takes place, regenerating the aromaticity and affording the desired product (**3**).

### Scheme 3. Proposed reaction pathway



The applicability of this transformation was demonstrated by employing *p*-**3ae** and *p*-**3ai** as starting materials to synthesize bioactive compounds containing biaryl moieties.<sup>13</sup> The desired products **4** and

5 were obtained in good to high yields under the reaction conditions (Figure. 3, see the Experimental Section for details).



**Figure 3. Synthesis of bioactive compounds**

In conclusion, we developed a catalyst-free, visible-light-mediated Gomberg-Bachmann reaction for the synthesis of biaryls. The desired products were obtained under mild reaction conditions and without the need of a catalyst or metal reagents. In addition, this method provides a straightforward access to haloarenes, which are important scaffolds of many bioactive compounds and other key synthetic intermediates.

## EXPERIMENTAL SECTION

**General experimental information:** Reactions were performed in a well-dried flask under Ar atmosphere. Unless otherwise mentioned, all solvents and reagents were commercially available and utilized without further purification. Column chromatography was performed with silica gel 60 (70 – 230 mesh) using a mixture of EtOAc/hexane as eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were, respectively, recorded on an Agilent 400 MHz (<sup>1</sup>H NMR), 101 MHz (<sup>13</sup>C NMR) spectrometer in deuterated chloroform (CDCl<sub>3</sub>) with tetramethylsilane (TMS) as an internal reference. Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, coupling constant (Hz), and integration). High-resolution mass spectroscopy was performed using a magnetic sector analyser. Spotlight-type LED bulbs purchased from CR LIGHTING TECHNOLOGY (Model Number: CR-MR16-5W Cool White LED Bulb, CR-MR16-4W Green LED Bulb, and CR-MR16-4W-B Blue LED Bulb), and OSRAM 20W CFL (Model Number – Duluxstar compact 20W/865) were used without using filters. Borosilicate glass irradiation vessels were used. When the reaction was carried out, the distance from the light source to the irradiation vessel was 5.0 cm.

*General procedure for the synthesis of biaryls (A):* Aryl diazonium salt **1** (0.6 mmol, 1.0 equiv), and pyridine (1.8 mmol, 3.0 equiv) were dissolved in dry aryl halide or benzene (0.25 M). The reaction mixture was stirred and irradiated by 4 W green LEDs (530 nm) or 4 W blue LEDs (460 nm) or 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by flash chromatography with EtOAc/hexane afforded the corresponding product.



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*General procedure for the synthesis of biaryls (B):* Aryl diazonium salt **1** (0.6 mmol, 1.0 equiv), pyridine (1.8 mmol, 3.0 equiv) and halobenzene **3** (30 mmol, 50.0 equiv) were dissolved in dry DMSO (0.25 M). The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h to 72 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by flash chromatography with EtOAc/hexane afforded the corresponding product.

n-Chloro-4'-methoxy-1,1'-biphenyl (**3aa**).<sup>14</sup> Prepared according to the general procedure **A** using chlorobenzene and 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 119 mg (91% yield, *ortho* (*o*) : *meta* (*m*) : *para* (*p*) = 2.75 : 1.25 : 1) of product as a yellow oil. Total yield was calculated by taking weight of obtained mixture of products (*ortho*, *meta*, and *para* compounds). The ratio of isomers was determined by GC-MS after comparison with authentic samples. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.42 (m, 6H), 7.42 – 7.35 (m, 5H), 7.35 – 7.30 (m, 3H), 7.30 – 7.22 (m, 4H), 6.99 – 6.95 (m, 6H), 3.85 (s, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.1, 140.1, 134.6, 132.6, 132.3, 131.8, 131.4, 130.6, 129.9, 128.8, 128.2, 128.1, 128.0, 127.9, 126.8, 126.8, 126.6, 124.8, 114.3, 113.5, 55.4, 55.3; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>ClO [M]<sup>+</sup>: 218.0; found 218.0.

n-Chloro-2'-methoxy-1,1'-biphenyl (**3ab**).<sup>14a</sup> Prepared according to the general procedure **A** using chlorobenzene and 2-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 74 mg (56% yield, *o* : *m* : *p* = 2.2 : 1.3 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.42 (m, 3H), 7.41 – 7.33 (m, 4H), 7.32 – 7.23 (m, 9H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.17 (d, *J* = 1.7 Hz, 1H), 7.03 – 6.99 (m, 3H), 6.98 – 6.95 (m, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 156.7, 156.3, 140.3, 137.7, 136.9, 133.9, 133.7, 132.8, 131.6, 130.9, 130.8, 130.7, 130.6, 129.6, 129.4, 129.3, 129.2, 129.1, 128.9, 128.5, 128.4, 128.1, 127.7, 126.9, 126.4, 120.9, 120.8, 120.3, 111.3, 111.2, 110.9, 55.6, 55.5, 55.4; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>ClO [M]<sup>+</sup>: 218.0; found 218.0.

n-Chloro-3'-methoxy-1,1'-biphenyl (**3ac**).<sup>15</sup> Prepared according to the general procedure **A** using chlorobenzene and 3-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 88 mg (67% yield, *o* : *m* : *p* = 3.2 : 1.2 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.43 (m, 4H), 7.41 – 7.31 (m, 7H), 7.31 – 7.23 (m, 4H), 7.16 – 7.11 (m, 1H), 7.10 – 7.06 (m, 1H), 7.04 – 7.00 (m, 2H), 7.00 – 6.96 (m, 2H), 6.95 – 6.93 (m, 1H), 6.93 – 6.88 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 160.0, 159.2, 142.9, 141.5, 141.3, 140.7, 140.4,

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4 139.5, 134.6, 134.5, 133.5, 132.4, 131.3, 129.9, 129.8, 129.0, 128.9, 128.5, 128.4, 127.4, 127.3, 126.8,  
5 125.3, 121.9, 119.6, 119.4, 115.1, 113.3, 113.2, 112.9, 112.8, 112.7, 55.3, 55.2; LRMS (EI); Mass calcd  
6 for C<sub>13</sub>H<sub>11</sub>ClO [M]<sup>+</sup>: 218.0; found 218.0.

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9 n-Chloro-4'-methyl-1,1'-biphenyl (**3ad**).<sup>14</sup> Prepared according to the general procedure A using  
10 chlorobenzene and 4-methylbenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
11 irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The  
12 reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 101 mg (83%  
13 yield, *o* : *m* : *p* = 4.7 : 2 : 1) of product as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (t, *J* =  
14 1.9 Hz, 1H), 7.53 – 7.44 (m, 5H), 7.42 – 7.33 (m, 7H), 7.32 – 7.29 (m, 3H), 7.29 – 7.27 (m, 5H), 7.27  
15 – 7.25 (m, 3H), 2.43 (s, 3H), 2.41 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 142.9, 140.4, 139.5,  
16 137.7, 137.4, 137.3, 137.0, 136.9, 136.5, 134.6, 133.0, 132.5, 131.3, 129.9, 129.8, 129.6, 129.5, 129.3,  
17 128.8, 128.7, 128.3, 128.1, 127.0, 126.9, 126.8, 126.7, 125.0, 21.2, 21.1; LRMS (EI); Mass calcd for  
18 C<sub>13</sub>H<sub>11</sub>Cl [M]<sup>+</sup>: 202.0; found 202.0.

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25 n-Chloro-2-nitro-1,1'-biphenyl (**3ae**).<sup>16</sup> Prepared according to the general procedure A using  
26 chlorobenzene and 2-nitrobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
27 irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The  
28 reaction mixture was purified by flash chromatography using 20% EtOAc/hexane to afford 103 mg  
29 (73% yield, *o* : *m* : *p* = 2.3 : 1 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (dd, *J*  
30 = 8.2, 1.3 Hz, 1H), 7.88 (td, *J* = 8.7, 1.2 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.64 – 7.59 (m, 2H), 7.58 – 7.54  
31 (m, 1H), 7.54 – 7.52 (m, 1H), 7.52 – 7.48 (m, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.36 (m, 4H), 7.36 –  
32 7.31 (m, 5H), 7.29 – 7.21 (m, 3H), 7.19 – 7.15 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 149.0,  
33 148.9, 148.5, 139.2, 137.1, 135.8, 135.1, 134.9, 134.4, 134.3, 134.2, 133.0, 132.6, 132.5, 132.4, 132.3,  
34 131.8, 131.7, 129.8, 129.4, 129.3, 129.2, 128.9, 128.8, 128.7, 128.5, 128.3, 128.0, 126.9, 126.1, 124.3,  
35 124.2; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>8</sub>ClNO<sub>2</sub> [M]<sup>+</sup>: 233.0; found 233.0.

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42 n-Chloro-2'-fluoro-1,1'-biphenyl (**3af**).<sup>17</sup> Prepared according to the general procedure A using  
43 chlorobenzene and 2-fluorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
44 irradiated by 4 W blue LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction  
45 mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 114 mg (92% yield,  
46 *o* : *m* : *p* = 1.7 : 1 : 1) of product as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.52 (m,  
47 1H), 7.51 – 7.45 (m, 3H), 7.44 – 7.34 (m, 7H), 7.33 – 7.28 (m, 7H), 7.23 – 7.19 (m, 3H), 7.18 – 7.16  
48 (m, 1H), 7.16 – 7.11 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6 (d, *J* = 247.9 Hz), 159.6 (d, *J*  
49 = 248.5 Hz), 159.6 (d, *J* = 247.6 Hz), 137.5, 134.9, 134.3, 133.7, 131.6 (d, *J* = 1.1 Hz), 131.5 (d, *J* =  
50 3.2 Hz), 130.6 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 3.4 Hz), 130.3 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 8.0 Hz), 129.7,  
51 129.6, 129.5, 129.3, 129.2, 129.1, 128.6, 127.8, 127.7, 127.6, 127.2 (d, *J* = 3.1 Hz), 127.1, 126.9, 124.5  
52 (d, *J* = 3.7 Hz), 124.4 (d, *J* = 3.8 Hz), 123.8 (d, *J* = 3.8 Hz), 116.2 (d, *J* = 22.6 Hz), 115.6 (d, *J* = 22.1  
53 Hz); LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>8</sub>ClF [M]<sup>+</sup>: 206.0; found 206.0.

n-Chloro-4'-fluoro-1,1'-biphenyl (**3ag**).<sup>14a</sup> Prepared according to the general procedure A using chlorobenzene and 4-fluorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 88 mg (71% yield, *o* : *m* : *p* = 2.7 : 1 : 1) of product as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.49 (m, 3H), 7.49 – 7.44 (m, 3H), 7.44 – 7.38 (m, 5H), 7.37 – 7.34 (m, 1H), 7.33 – 7.27 (m, 6H), 7.16 – 7.09 (m, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 162.7 (d, *J* = 247.5 Hz), 162.6 (d, *J* = 247.0 Hz), 162.3 (d, *J* = 247.0 Hz), 142.0, 139.5, 138.7, 136.1 (d, *J* = 3.4 Hz), 136.0 (d, *J* = 3.2 Hz), 135.3 (d, *J* = 3.5 Hz), 134.7, 133.4, 132.5, 131.3, 131.1 (d, *J* = 8.1 Hz), 130.0, 129.9, 128.9, 128.7, 128.6, 128.5 (d, *J* = 8.1 Hz), 128.2, 127.3, 127.1, 126.9, 125.1, 115.8 (d, *J* = 21.5 Hz), 115.7 (d, *J* = 21.5 Hz), 115.0 (d, *J* = 21.5 Hz); LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>8</sub>ClF [M]<sup>+</sup>: 206.0; found 206.0.

n-Chloro-4'-chloro-1,1'-biphenyl (**3ah**).<sup>17</sup> Prepared according to the general procedure A using chlorobenzene and 4-chlorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 126 mg (94% yield, *o* : *m* : *p* = 6.5 : 2.5 : 1) of product as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.48 – 7.44 (m, 4H), 7.42 – 7.38 (m, 7H), 7.39 – 7.34 (m, 5H), 7.33 – 7.26 (m, 7H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7, 139.3, 138.4, 138.2, 137.7, 134.7, 134.0, 133.7, 132.4, 131.2, 130.8, 130.1, 130.0, 129.1, 129.0, 128.8, 128.3, 128.2, 128.1, 127.6, 127.1, 126.9, 125.1; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub> [M]<sup>+</sup>: 222.0; found 222.0.

n-Chloro-1,1'-biphenyl (**3ai**).<sup>14a</sup> Prepared according to the general procedure A using chlorobenzene and benzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 76 mg (67% yield, *o* : *m* : *p* = 2.4 : 1 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.50 (m, 4H), 7.50 – 7.48 (m, 1H), 7.48 – 7.46 (m, 2H), 7.46 – 7.42 (m, 10H), 7.41 – 7.37 (m, 3H), 7.36 – 7.33 (m, 3H), 7.32 – 7.29 (m, 3H), 7.29 – 7.27 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 143.0, 140.5, 139.9, 139.8, 139.6, 139.4, 134.6, 133.3, 132.5, 131.3, 130.0, 129.9, 129.4, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 127.6, 127.3, 127.2, 127.1, 126.9, 126.8, 125.3; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>9</sub>Cl [M]<sup>+</sup>: 188.0; found 188.0.

2,3-Dichloro-4'-methoxy-1,1'-biphenyl/ 3,4-Dichloro-4'-methoxy-1,1'-biphenyl (**3aj**).<sup>18</sup> Prepared according to the general procedure A using 1,2-dichlorobenzene and 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 125 mg (82% yield, *a* : *b* = 1.6 : 1) of product as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 2.1 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.38 – 7.32 (m, 3H), 7.23 – 7.19 (m, 3H), 6.99 – 6.96 (m, 2H), 6.96 – 6.94 (m, 2H), 3.85 (s, 3H), 3.84 (s, 3H);

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.7, 159.3, 142.5, 140.8, 133.5, 132.7, 131.6, 131.2, 131.1, 130.6, 130.5, 130.4, 129.5, 129.0, 128.4, 128.0, 127.0, 125.8, 114.4, 113.5, 55.3, 55.2; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>O [M]<sup>+</sup>: 252.0; found 252.0.

2,4-Dichloro-4'-methoxy-1,1'-biphenyl/ 2,6-Dichloro-4'-methoxy-1,1'-biphenyl/ 3,5-Dichloro-4'-methoxy-1,1'-biphenyl (**3ak**).<sup>19</sup> Prepared according to the general procedure **A** using 1,3-dichlorobenzene and 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 65 mg (43% yield, *a* : *b* : *c* = 8.2 : 7.5 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.46 (m, 2H), 7.42 – 7.41 (m, 1H), 7.41 – 7.37 (m, 2H), 7.37 – 7.33 (m, 3H), 7.30 – 7.24 (m, 3H), 7.23 – 7.17 (m, 4H), 7.02 – 6.95 (m, 6H), 3.87 (s, 3H), 3.86 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.3, 159.2, 139.2, 138.7, 135.3, 135.1, 133.3, 133.2, 132.0, 130.8, 130.6, 130.5, 129.6, 129.2, 128.8, 128.1, 128.0, 127.1, 126.4, 125.1, 114.4, 113.6, 55.3, 55.2; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>O [M]<sup>+</sup>: 252.0; found 252.0.

2,4-Dichloro-1,1'-biphenyl/ 2,6-Dichloro-1,1'-biphenyl/ 3,5-Dichloro-1,1'-biphenyl (**3al**).<sup>20</sup> Prepared according to the general procedure **A** using 1,3-dichlorobenzene and benzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 129 mg (96% yield, *a* : *b* : *c* = 5.9 : 4 : 1) of product as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.51 (m, 1H), 7.50 – 7.47 (m, 2H), 7.47 – 7.42 (m, 4H), 7.42 – 7.38 (m, 8H), 7.38 – 7.35 (m, 1H), 7.34 – 7.30 (m, 1H), 7.29 – 7.27 (m, 3H), 7.26 – 7.20 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.2, 139.5, 139.0, 138.5, 138.3, 137.0, 135.2, 135.0, 134.9, 133.6, 133.2, 132.1, 130.4, 129.7, 129.5, 129.3, 129.0, 128.9, 128.7, 128.4, 128.2, 128.1, 128.0, 127.9, 127.1, 127.0, 126.9, 125.6; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub> [M]<sup>+</sup>: 222.0; found 222.0.

2,5-Dichloro-4'-methoxy-1,1'-biphenyl (**3am**). Prepared according to the general procedure **B** using 1,4-dichlorobenzene and 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 100 mg (66% yield) of product as a white solid. mp 51–52 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.33 (m, 3H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.99 – 6.94 (m, 2H), 3.85 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.4, 141.6, 132.5, 131.1, 131.0, 130.9, 130.5, 130.4, 128.0, 113.6, 55.3; HRMS (EI); Mass calcd for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>O [M]<sup>+</sup>: 252.0109; found 252.0106.

2,4,6-Trichloro-4'-methoxy-1,1'-biphenyl (**3an**). Prepared according to the general procedure **B** using 1,3,5-trichlorobenzene and 4-methoxy benzenediazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 72 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford

80 mg (46% yield) of product as a white solid. mp 79–80 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.39 (m, 2H), 7.20 – 7.13 (m, 2H), 7.02 – 6.95 (m, 2H), 3.86 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.4, 137.9, 135.8, 133.5, 130.8, 128.1, 128.0, 113.7, 55.2; HRMS (EI); Mass calcd for C<sub>13</sub>H<sub>9</sub>Cl<sub>3</sub>O [M]<sup>+</sup>: 285.9719; found 285.9722.

*n*-Bromo-2'-methoxy-1,1'-biphenyl (**3ao**).<sup>21</sup> Prepared according to the general procedure A using bromobenzene and 2-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 93 mg (59% yield, *o* : *m* : *p* = 2 : 1.3 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (t, *J* = 1.8 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 7.29 – 7.24 (m, 4H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 7.04 – 6.99 (m, 3H), 6.98 – 6.95 (m, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 156.5, 156.3, 156.2, 140.6, 139.8, 137.3, 132.4, 131.5, 131.1, 131.0, 130.8, 130.7, 130.5, 130.2, 129.8, 129.4, 129.3, 129.2, 129.0, 128.9, 128.6, 128.1, 127.0, 124.2, 122.0, 121.0, 120.9, 120.8, 120.2, 111.2, 111.1, 110.9, 55.5, 55.4, 55.3; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>BrO [M]<sup>+</sup>: 262.0; found 262.0.

*n*-Bromo-3'-methoxy-1,1'-biphenyl (**3ap**).<sup>22</sup> Prepared according to the general procedure A using bromobenzene and 3-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 124 mg (78% yield, *o* : *m* : *p* = 2.7 : 1.3 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 – 7.71 (m, 1H), 7.68 – 7.63 (m, 2H), 7.58 – 7.41 (m, 4H), 7.38 – 7.25 (m, 7H), 7.24 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 7.08 – 7.05 (m, 1H), 7.01 – 6.87 (m, 6H), 3.87 – 3.83 (m, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 160.0, 159.1, 143.2, 142.4, 142.3, 141.4, 141.1, 139.9, 133.1, 131.8, 131.2, 130.3, 130.2, 130.1, 129.9, 128.9, 128.7, 127.3, 125.8, 122.8, 122.5, 121.8, 119.5, 119.4, 115.0, 113.3, 113.2, 112.9, 112.8, 112.7, 55.3, 55.2, 55.2; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>BrO [M]<sup>+</sup>: 262.0; found 262.0.

*n*-Bromo-4'-methoxy-1,1'-biphenyl (**3aq**).<sup>23</sup> Prepared according to the general procedure A using bromobenzene and 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 129 mg (82% yield, *o* : *m* : *p* = 2.8 : 1.2 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (t, *J* = 1.9 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.54 – 7.45 (m, 4H), 7.45 – 7.41 (m, 1H), 7.41 – 7.38 (m, 1H), 7.36 – 7.22 (m, 7H), 7.18 – 7.13 (m, 2H), 6.98 – 6.94 (m, 6H), 3.84 (s, 3H), 3.83 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6, 159.4, 159.1, 142.9, 142.2, 139.7, 133.5, 133.1, 132.4, 132.1, 131.8, 131.3, 130.5, 130.2, 129.7, 129.5, 128.4, 128.3, 128.1, 127.9, 127.3, 125.3, 122.9, 122.8, 120.8, 114.3, 113.3, 55.3, 55.2; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>BrO [M]<sup>+</sup>: 262.0; found 262.0.

*n*-Bromo-4'-methyl-1,1'-biphenyl (**3ar**).<sup>24</sup> Prepared according to the general procedure A using

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4 bromobenzene and 4-methylbenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
5 irradiated by 4 W green LEDs (530 nm) at room temperature under Ar atmosphere for 18 h. The reaction  
6 mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 108 mg (73% yield,  
7  $o : m : p = 6.1 : 2.9 : 1$ ) of product as a colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (t,  $J = 1.8$  Hz,  
8 1H), 7.67 – 7.63 (m, 2H), 7.55 – 7.51 (m, 1H), 7.50 – 7.46 (m, 1H), 7.46 – 7.40 (m, 3H), 7.36 – 7.26  
9 (m, 8H), 7.26 – 7.20 (m, 6H), 7.20 – 7.13 (m, 2H), 2.40 (s, 6H), 2.39 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  
10  $\text{CDCl}_3$ )  $\delta$  143.2, 142.5, 140.0, 138.2, 137.7, 137.4, 137.3, 137.0, 136.8, 133.0, 131.8, 131.3, 130.2,  
11 129.9, 129.8, 129.6, 129.2, 128.7, 128.5, 127.3, 126.9, 126.7, 125.5, 122.8, 122.7, 121.1, 21.2, 21.1;  
12 LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{11}\text{Br}$   $[\text{M}]^+$ : 246.0; found 246.0.

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18 n-Bromo-2'-chloro-1,1'-biphenyl (**3as**).<sup>25</sup> Prepared according to the general procedure A using  
19 bromobenzene and 2-chlorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
20 irradiated by 4 W green LEDs (530 nm) at room temperature under Ar atmosphere for 18 h. The reaction  
21 mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 103 mg (64% yield,  
22  $o : m : p = 0.9 : 1.2 : 1$ ) of product as a pale yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.65 (m,  
23 1H), 7.58 (t,  $J = 1.8$  Hz, 1H), 7.57 – 7.53 (m, 2H), 7.53 – 7.49 (m, 1H), 7.49 – 7.44 (m, 3H), 7.39 – 7.34  
24 (m, 2H), 7.34 – 7.32 (m, 1H), 7.32 – 7.27 (m, 9H), 7.27 – 7.22 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  
25  $\text{CDCl}_3$ )  $\delta$  141.3, 140.3, 139.9, 139.2, 138.9, 138.2, 133.3, 132.5, 132.3, 132.2, 131.5, 131.2, 131.1,  
26 131.1, 131.0, 131.0, 130.6, 130.0, 129.9, 129.5, 129.4, 129.3, 129.2, 129.0, 128.8, 128.1, 127.1, 126.9,  
27 126.8, 126.4, 123.6, 122.0, 121.9; LRMS (EI); Mass calcd for  $\text{C}_{12}\text{H}_8\text{BrCl}$   $[\text{M}]^+$ : 265.9; found 266.0.

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34 n-Bromo-3'-chloro-1,1'-biphenyl (**3at**).<sup>26</sup> Prepared according to the general procedure A using  
35 bromobenzene and 3-chlorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
36 irradiated by 4 W green LEDs (530 nm) at room temperature under Ar atmosphere for 18 h. The reaction  
37 mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 144 mg (90% yield,  
38  $o : m : p = 3.9 : 1.3 : 1$ ) of product as a pale yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (t,  $J = 1.9$   
39 Hz, 1H), 7.65 (dd,  $J = 8.0, 1.3$  Hz, 2H), 7.57 – 7.53 (m, 1H), 7.53 – 7.50 (m, 1H), 7.50 – 7.44 (m, 1H),  
40 7.43 – 7.36 (m, 4H), 7.36 – 7.30 (m, 8H), 7.30 – 7.24 (m, 4H), 7.24 – 7.17 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101  
41 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 141.8, 141.7, 141.4, 141.1, 138.6, 134.8, 133.8, 133.2, 132.0, 131.1, 130.8, 130.4,  
42 130.1, 130.0, 129.4, 129.2, 129.1, 128.6, 127.9, 127.7, 127.6, 127.6, 127.4, 127.2, 127.0, 125.7, 125.2,  
43 125.0, 123.0, 122.4, 122.2; LRMS (EI); Mass calcd for  $\text{C}_{12}\text{H}_8\text{BrCl}$   $[\text{M}]^+$ : 265.9; found 266.0.

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50 n-Bromo-4'-chloro-1,1'-biphenyl (**3au**).<sup>17</sup> Prepared according to the general procedure A using  
51 bromobenzene and 4-chlorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
52 irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The  
53 reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 127 mg (79%  
54 yield,  $o : m : p = 2.4 : 0.8 : 1$ ) of product as a pale yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (t,  $J$   
55 = 1.8 Hz, 1H), 7.65 (dd,  $J = 8.0, 1.2$  Hz, 2H), 7.57 – 7.52 (m, 1H), 7.51 – 7.43 (m, 4H), 7.42 – 7.36 (m,  
56 6H), 7.35 – 7.30 (m, 5H), 7.30 – 7.26 (m, 2H), 7.25 – 7.16 (m, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  
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4  $\delta$  142.0, 141.3, 139.4, 138.8, 138.4, 138.1, 134.0, 133.8, 133.7, 133.2, 132.0, 131.1, 130.7, 130.5, 130.3,  
5 130.0, 129.0, 128.5, 128.3, 128.2, 128.1, 127.5, 125.5, 123.0, 122.5, 121.9; LRMS (EI); Mass calcd for  
6  $C_{12}H_8BrCl [M]^+$ : 265.9; found 266.0.

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9 n-Bromo-4'-fluoro-1,1'-biphenyl (**3av**).<sup>27</sup> Prepared according to the general procedure A using  
10 bromobenzene and 4-fluorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and  
11 irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The  
12 reaction mixture was purified by flash chromatography using 2% EtOAc/hexane to afford 90 mg (60%  
13 yield, *o* : *m* : *p* = 2.3 : 1.2 : 1) of product as a pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 – 7.62  
14 (m, 2H), 7.56 – 7.52 (m, 1H), 7.52 – 7.46 (m, 3H), 7.46 – 7.42 (m, 1H), 7.41 – 7.32 (m, 6H), 7.31 –  
15 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 7.15 – 7.07 (m, 6H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.7 (d,  
16  $J_{CF}$  = 247.3 Hz), 162.6 (d,  $J_{CF}$  = 247.1 Hz), 162.3 (d,  $J_{CF}$  = 246.9 Hz), 142.3, 141.5, 139.1, 137.0 (d,  $J$   
17 = 3.4 Hz), 136.1 (d,  $J$  = 3.2 Hz), 135.8 (d,  $J$  = 3.5 Hz), 133.1, 131.9, 131.2, 131.0 (d,  $J$  = 8.1 Hz), 130.3,  
18 130.2, 130.0, 128.8, 128.7 (d,  $J$  = 8.0 Hz), 128.6, 128.5, 128.4, 127.4, 125.6, 122.9, 122.7, 121.5, 115.8  
19 (d,  $J$  = 21.4 Hz), 114.9 (d,  $J$  = 21.3 Hz); LRMS (EI); Mass calcd for  $C_{12}H_8BrF [M]^+$ : 249.9; found 250.0.

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22 n-Bromo-1,1'-biphenyl (**3aw**).<sup>28</sup> Prepared according to the general procedure A using bromobenzene  
23 and benzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue  
24 LEDs (460 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified  
25 by flash chromatography using 2% EtOAc/hexane to afford 111 mg (79% yield, *o* : *m* : *p* = 2.3 : 1.3 :  
26 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (t,  $J$  = 1.8 Hz, 1H), 7.67 – 7.64 (m,  
27 2H), 7.56 – 7.51 (m, 3H), 7.51 – 7.46 (m, 1H), 7.46 – 7.42 (m, 5H), 7.41 – 7.33 (m, 9H), 7.33 – 7.25  
28 (m, 4H), 7.23 – 7.16 (m, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.3, 142.5, 141.0, 140.0, 139.9,  
29 139.6, 133.0, 131.8, 131.5, 131.2, 130.2, 130.1, 130.1, 130.0, 129.3, 128.8, 128.7, 128.6, 127.9, 127.8,  
30 127.6, 127.5, 127.3, 127.0, 126.9, 126.8, 125.7, 122.9, 122.6, 122.5, 121.5; LRMS (EI); Mass calcd for  
31  $C_{12}H_9Br [M]^+$ : 232.0; found 232.0.

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42 n-Fluoro-4'-methoxy-1,1'-biphenyl (**3ax**).<sup>29</sup> Prepared according to the general procedure A using  
43 fluorobenzene and 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred  
44 and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h.  
45 The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 80 mg  
46 (66% yield, *o* : *m* = 1 : 1) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.44 (m, 5H),  
47 7.42 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.31 – 7.21 (m, 2H), 7.20 – 7.16 (m, 1H), 7.16 – 7.11 (m,  
48 1H), 7.11 – 7.05 (m, 1H), 6.99 – 6.95 (m, 4H), 3.83 (s, 6H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.2,  
49 163.0, 162.2, 161.0, 160.7, 159.5, 159.2, 159.1, 158.7, 143.0 (d,  $J$  = 7.8 Hz), 136.9 (d,  $J$  = 3.0 Hz),  
50 132.7, 132.3 (d,  $J$  = 1.9 Hz), 130.4 (d,  $J$  = 3.6 Hz), 130.1, 130.0, 128.6 (d,  $J$  = 13.1 Hz), 128.3 (d,  $J$  =  
51 8.2 Hz), 128.1, 128.0, 127.9, 126.6 (d,  $J$  = 5.5 Hz), 124.2 (d,  $J$  = 3.7 Hz), 122.2 (d,  $J$  = 2.6 Hz), 116.1,  
52 115.9, 115.4 (d,  $J$  = 21.3 Hz), 114.2, 114.1, 113.9, 113.4 (d,  $J$  = 21.9 Hz), 113.3 (d,  $J$  = 21.1 Hz); LRMS  
53 (EI); Mass calcd for  $C_{13}H_{11}FO [M]^+$ : 202.0; found 202.0.

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4 1,1'-Biphenyl (**3ay**).<sup>30</sup> Prepared according to the general procedure **A** using benzene and benzene  
5 diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 4 W blue LEDs (460  
6 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash  
7 chromatography using 2% EtOAc/hexane to afford 62 mg (67% yield) of product as a white solid. mp  
8 67–68 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.56 (m, 4H), 7.47 – 7.40 (m, 4H), 7.37 – 7.31 (m,  
9 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 141.2, 128.7, 127.2, 127.1; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>10</sub>  
10 [M]<sup>+</sup>: 154.0; found 154.0.

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15 4-Methoxy-1,1'-biphenyl (**3az**).<sup>31</sup> Prepared according to the general procedure **A** using benzene and  
16 4-methoxybenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5  
17 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture  
18 was purified by flash chromatography using 10% EtOAc/hexane to afford 54 mg (49% yield) of product  
19 as a white solid. mp 87–88 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.49 (m, 4H), 7.45 – 7.38 (m, 2H),  
20 7.34 – 7.27 (m, 1H), 7.01 – 6.95 (m, 2H), 3.84 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 159.1,  
21 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>12</sub>O [M]<sup>+</sup>: 184.0;  
22 found 184.0.

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28 4-Fluoro-1,1'-biphenyl (**3ba**).<sup>32</sup> Prepared according to the general procedure **A** using benzene and 4-  
29 fluorobenzene diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W  
30 white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture  
31 was purified by flash chromatography using 2% EtOAc/hexane to afford 50 mg (48% yield) of product  
32 as a white solid. mp 73–74 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.51 (m, 4H), 7.46 – 7.39 (m, 2H),  
33 7.37 – 7.31 (m, 1H), 7.16 – 7.08 (m, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 162.4 (d, *J* = 246.3 Hz),  
34 140.2, 137.3 (d, *J* = 3.3 Hz), 129.8, 128.7 (d, *J* = 8.0 Hz), 127.2, 127.0, 115.6 (d, *J* = 21.3 Hz); LRMS  
35 (EI); Mass calcd for C<sub>12</sub>H<sub>9</sub>F [M]<sup>+</sup>: 172.0; found 172.0.

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41 Methyl 3-(*n*-chlorophenyl)thiophene-2-carboxylate (**3bb**).<sup>33</sup> Prepared according to the general  
42 procedure **A** using chlorobenzene and 2-(methoxycarbonyl)-3-thiophene diazonium tetrafluoroborate.  
43 The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature  
44 under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 20%  
45 EtOAc/hexane to afford 134 mg (88% yield, *o* : *m* : *p* = 2 : 1.1 : 1) of product as a colorless oil. <sup>1</sup>H NMR  
46 (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.48 (m, 3H), 7.47 – 7.42 (m, 2H), 7.40 – 7.34 (m, 3H), 7.34 – 7.30 (m,  
47 3H), 7.30 – 7.26 (m, 4H), 7.06 – 7.03 (m, 1H), 7.03 – 7.01 (m, 2H), 3.77 (s, 6H), 3.72 (s, 3H); <sup>13</sup>C {<sup>1</sup>H}  
48 NMR (101 MHz, CDCl<sub>3</sub>) δ 162.2, 162.1, 161.9, 147.2, 146.8, 144.9, 137.2, 135.1, 133.9, 133.8, 133.5,  
49 132.9, 131.2, 131.1, 131.0, 130.7, 130.5, 130.4, 130.1, 129.2, 129.1, 129.0, 128.9, 127.9, 127.8, 127.5,  
50 127.4, 127.0, 126.2, 51.9, 51.8; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>9</sub>ClO<sub>2</sub>S [M]<sup>+</sup>: 252.0; found 252.0.

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56 1-Phenylnaphthalene (**3bc**).<sup>34</sup> Prepared according to the general procedure **A** using benzene and  
57 naphthalene-1-diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W  
58 white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture  
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was purified by flash chromatography using 5% CH<sub>2</sub>Cl<sub>2</sub>/hexane to afford 74 mg (60% yield) of product as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.87 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.45 (m, 6H), 7.43 – 7.39 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 140.7, 140.2, 133.8, 131.6, 130.0, 128.2, 128.2, 127.6, 127.2, 126.9, 126.0, 126.0, 125.7, 125.3; LRMS (EI); Mass calcd for C<sub>16</sub>H<sub>12</sub> [M]<sup>+</sup>: 204.1; found 204.0.

1-(*n*-Chlorophenyl)naphthalene (**3bd**).<sup>35</sup> Prepared according to the general procedure **A** using chlorobenzene and naphthalene-1-diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 5% CH<sub>2</sub>Cl<sub>2</sub>/hexane to afford 101 mg (71% yield, *o* : *m* : *p* = 1.5 : 1 : 1) of product.

*o*-**3bd** white solid. mp 54–56 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.89 (m, 2H), 7.55 – 7.51 (m, 2H), 7.50 – 7.46 (m, 2H), 7.42 – 7.35 (m, 5H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 139.3, 137.4, 134.1, 133.4, 132.1, 131.6, 129.5, 128.9, 128.2, 128.2, 127.1, 126.6, 126.1, 125.9, 125.8, 125.2; LRMS (EI); Mass calcd for C<sub>16</sub>H<sub>11</sub>Cl [M]<sup>+</sup>: 238.1; found 238.0.

*m,p*-**3bd** colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.82 (m, 3H), 7.53 – 7.35 (m, 8H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 142.5, 139.1, 138.9, 138.7, 134.1, 133.8, 133.7, 133.3, 131.4, 131.3, 130.0, 129.5, 128.5, 128.3, 128.3, 128.1, 128.0, 127.4, 126.9, 126.9, 126.3, 126.2, 125.9, 125.9, 125.6, 125.6, 125.3, 125.3; LRMS (EI); Mass calcd for C<sub>16</sub>H<sub>11</sub>Cl [M]<sup>+</sup>: 238.1; found 238.0.

1-(2,5-Dichlorophenyl)naphthalene (**3be**). Prepared according to the general procedure **B** using 1,4-dichlorobenzene and naphthalene-1-diazonium tetrafluoroborate. The reaction mixture was stirred and irradiated by 5 W white LEDs (430 – 660 nm) at room temperature under Ar atmosphere for 18 h. The reaction mixture was purified by flash chromatography using 5% CH<sub>2</sub>Cl<sub>2</sub>/hexane to afford 83 mg (51% yield) of product as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.91 (m, 2H), 7.56 – 7.43 (m, 5H), 7.38 – 7.35 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 140.9, 136.1, 133.4, 132.5, 132.4, 131.9, 131.3, 130.6, 129.0, 128.7, 128.4, 127.1, 126.4, 126.0, 125.5, 125.2; HRMS (EI); Mass calcd for C<sub>16</sub>H<sub>10</sub>Cl<sub>2</sub> [M]<sup>+</sup>: 272.0160; found 272.0162.

Ethyl 2-(biphenyl-4-yl)acetate (**4**).<sup>36</sup> A frame dried rbf equipped with a magnetic bar was charged with Pd catalyst (2 mol%), Ru-Phos (6 mol%), DMAP (10 mol%), and ethyl potassium malonate (1.5 eq.). The flask was evacuated and backfilled with argon three times. Under the argon, 4-chlorobiphenyl (0.77 mmol) and solvent (mesitylene, 1.5 mL) were added by syringe. The flask was sealed and stirred at room temperature for 10 min. Then the flask was stirred in a preheated oil bath (140 – 150 °C) for 20 hours. Upon completion of the reaction, the mixture was cooled to room temperature and extracted by diethyl ether (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The reaction mixture was purified by flash chromatography using 1% MeOH/DCM to afford 132 mg (71% yield) of product as a yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.52 (m, 4H), 7.41 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.34 (dd, *J* = 4.8, 3.5 Hz, 3H), 4.16 (q, *J* = 7.1 Hz,

2H), 3.64 (s, 2H), 1.26 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.5, 140.7, 139.9, 133.1, 129.6, 128.7, 127.2, 127.1, 127.0, 60.9, 40.9, 14.1; LRMS (EI); Mass calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_2$  [ $\text{M}$ ] $^+$ : 240.1; found 240.0.

2-Chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide (**5**).<sup>37</sup> A frame dried rbf equipped with a magnetic bar was charged with Fe powder (3 eq.) and ammonium chloride (0.6 eq). Under the argon, 4-chloro-2'-nitrobiphenyl (0.6 mmol) and solvent (Ethyl alcohol:  $\text{H}_2\text{O} = 1.8$  mL: 0.6 mL) were added by syringe. The flask was sealed and stirred in an oil bath (85 °C) for 1 hour. Upon completion of the reaction, the mixture was cooled to room temperature and extracted by DCM (3 x 20 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting amine (4'-chloro-[1,1'-biphenyl]-2-amine) was used in the next step without further purification. Next, A frame dried rbf equipped with a magnetic bar was charged with 4'-chloro-[1,1'-biphenyl]-2-amine (0.6 mmol), 2-chloronicotinoyl chloride (1.6 eq.) and  $\text{Et}_3\text{N}$  (2.0 eq.) in dry THF (6.9 mL). The flask was evacuated and backfilled with argon three times. The flask was sealed and stirred at room temperature for 1 hour. Upon completion of the reaction, the mixture was concentrated under reduced pressure. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 181 mg (88% yield for two steps) of product as a white solid. mp 144–146 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (dd,  $J = 4.8, 2.0$  Hz, 1H), 8.35 (d,  $J = 8.2$  Hz, 1H), 8.21 (s, 1H), 8.07 (dd,  $J = 7.7, 2.0$  Hz, 1H), 7.47 – 7.38 (m, 3H), 7.32 (dq,  $J = 7.3, 2.5$  Hz, 3H), 7.28 – 7.23 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 151.1, 146.6, 139.9, 136.2, 134.2, 134.1, 132.3, 131.0, 130.7, 130.1, 129.1, 128.8, 125.3, 122.8, 122.2; LRMS (ESI+); Mass calcd for  $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}$  [ $\text{M}+\text{H}$ ] $^+$ : 343.0; found 343.0. Supporting Information:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **3–5**, and the mechanistic studies of the reactions

## Notes

The authors declare no competing financial interest.

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