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## Direct C–H bond arylation of fluorenes with aryl chlorides catalyzed by N-heterocyclic carbene–palladium(II)–1-methylimidazole complex and further transformation of the products in a one-pot procedure†

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We report here the NHC–Pd(II)–Im complex **1**-catalyzed direct C–H bond functionalization of the C9 position of fluorenes with aryl chlorides and further transformation of the resulting products in a one-pot procedure. Under the optimal conditions, arylated fluorenes can be obtained in moderate to almost quantitative yields using various activated and unactivated (hetero)aryl chlorides as the arylating reagents. Furthermore, if the mixture from the arylation reaction is exposed to air, the C9-oxidized products can be obtained in acceptable to good yields in a one-pot procedure. In addition, alkyl groups can also be efficiently introduced to the above mixture from the arylation reaction, producing further C9-alkylated products in good to almost quantitative yields in a one-pot procedure, thus providing an expedient, inexpensive and practical strategy for the mono- and di-functionalization of fluorenes.

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### Introduction

The direct C–H bond functionalization reactions, which at least can avoid additional pre-functionalization of one of the reaction partners, have been an expedient, economical, and beneficial alternative to the traditional coupling reactions between organic electrophiles and organometallic nucleophiles.<sup>1</sup> During the past decade, in contrast to the abundant applications of N-heterocyclic carbene (NHC)-metal complex-catalyzed traditional coupling reactions,<sup>2</sup> only slight attention was paid to their applications toward direct C–H bond functionalizations,<sup>3</sup> indicating that much room still remains in this field using NHC–metal complexes as the catalysts.

Recently, from easily available starting materials such as the imidazolium salt [1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, IPr·HCl], PdCl<sub>2</sub> and 1-methylimidazole, we have developed a N-heterocyclic carbene–palladium(II)–1-methylimidazole [NHC–Pd(II)–Im] complex **1** under mild conditions,

and have found that it showed efficient catalytic activity toward traditional C–C and C–N coupling reactions using easily available and cost-effective aryl chlorides as the substrates under suitable conditions.<sup>4</sup> In addition, very recently, we found that the NHC–Pd(II)–Im complex **1** was also a good catalyst for the direct C–H bond arylation of (benz)oxazoles and (benz)imidazoles using aryl chlorides as the arylating reagents.<sup>5</sup> These results thus prompted us to further investigate its application toward other direct C–H bond arylation reactions using aryl chlorides as the arylating reagents. In this case, fluorenes were chosen as the other partners, because functionalized fluorenes are very important moieties for various organic materials.<sup>6</sup> In 2012 and 2013, Wu *et al.*<sup>7</sup> and Song, Xie and Huang *et al.*<sup>8</sup> have independently reported the Pd-catalyzed direct C–H bond arylation of the C9 position of fluorenes in the presence of phosphine ligands. However, in most cases, only aryl bromides can be used as the coupling partners. For instance, only very few examples involving aryl chlorides were reported,<sup>7</sup> implying that great challenges still remain in using the less active, while cheaper and more easily available aryl chlorides as the arylating reagents in such a transformation. One may draw the conclusion that efficient direct C–H bond arylation of fluorenes with aryl chlorides has been far from well investigated to date. Here, we reported the first example of phosphine-free, NHC–Pd(II)–Im complex **1**-catalyzed direct C–H bond arylation of fluorenes at the C9 position with various aryl chlorides and further functionalization of the products in a one-pot procedure.

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## Results and discussion

We began our investigation by using fluorene **2a** (1.0 mmol) and chlorobenzene **3a** (0.75 mmol) as model substrates in the presence of NHC–Pd(II)–Im complex **1** (1.0 mol%) at 120 °C for 12 h for the optimization of the reaction conditions. It was found that both the solvent and the base played important roles in this reaction. For example, in the first round, dioxane was chosen as solvent, and KO<sup>t</sup>Bu showed the best result, giving the desired arylated product **4a** in 99% yield (Table 1, entry 1).<sup>9</sup> However, in the presence of other bases such as NaO<sup>t</sup>Bu, KOH, NaOH, Na<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, no desired product was detected (Table 1, entries 2–7). In the second round, solvent screening showed that dioxane was the best, surpassing THF (82%) and toluene (73%) (Table 1, entries 8 and 9). In addition, no product was observed when using CH<sub>3</sub>CN as solvent in the reaction (Table 1, entry 10).

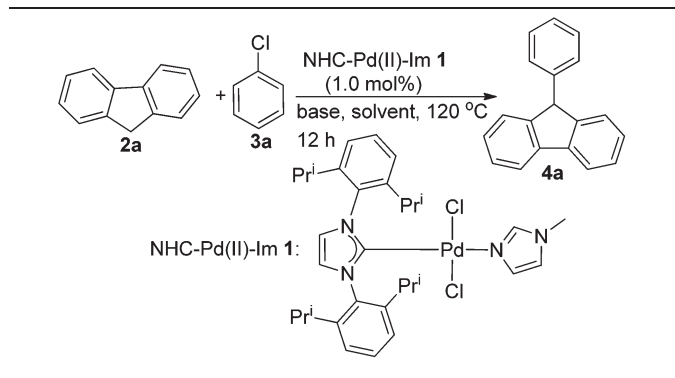
With the optimal conditions established (Table 1, entry 1), the reaction was then first tested by the treatment of fluorene **2a** with a variety of aryl chlorides **3** (Table 2). All reactions proceeded smoothly to give the desired C–H bond arylated products **4** in moderate to almost quantitative yields. As can be seen from Table 2, the substituents on the aryl chlorides **3** did not affect the reactions significantly in most cases. For example, when electron-rich substituents, such as methoxy, methyl and dimethylamino groups, or electron-poor groups, such as fluorine atoms, were attached to the phenyl rings of aryl chlorides **3**, respectively, all reactions proceeded well

**Table 2** NHC–Pd(II)–Im complex **1** catalyzed reactions between fluorene **2a** and aryl chlorides **3**

Entry <sup>a</sup>	3 (R')	Yield <sup>b</sup> (%)
1	<b>3b</b> (2-OMe)	<b>4b</b> , 94
2	<b>3c</b> (3-OMe)	<b>4c</b> , 96
3	<b>3d</b> (4-OMe)	<b>4d</b> , 94
4	<b>3e</b> (2-Me)	<b>4e</b> , 99 <sup>c</sup>
5	<b>3f</b> (3-Me)	<b>4f</b> , 93
6	<b>3g</b> (4-Me)	<b>4g</b> , 96
7	<b>3h</b> (2-F)	<b>4h</b> , 80
8	<b>3i</b> (3-F)	<b>4i</b> , 78
9	<b>3j</b> (4-F)	<b>4j</b> , 93
10	<b>3k</b> (2,6-Me <sub>2</sub> )	<b>4k</b> , 91
11	<b>3l</b> (4-NMe <sub>2</sub> )	<b>4l</b> , 82
12	<b>3m</b>	<b>4m</b> , 74
13	<b>3n</b>	<b>4n</b> , 65

<sup>a</sup> All reactions were carried out using **2a** (1.0 mmol), **3** (0.75 mmol), **1** (1.0 mol%), KO<sup>t</sup>Bu (1.5 equiv.) in dioxane (2.0 mL) at 120 °C for 12 h. <sup>b</sup> Isolated yields. <sup>c</sup> The ratio (*syn/anti* = 63/37) was determined by <sup>1</sup>H NMR.

**Table 1** Optimization for the reaction conditions



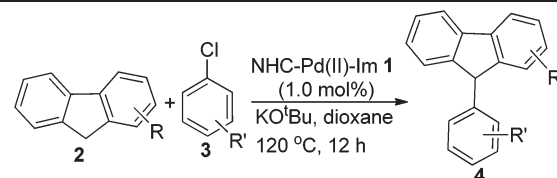
Entry <sup>a</sup>	Solvent	Base	Yield <sup>b</sup> (%)
1	Dioxane	KO <sup>t</sup> Bu	99
2	Dioxane	NaO <sup>t</sup> Bu	ND
3	Dioxane	KOH	ND
4	Dioxane	NaOH	ND
5	Dioxane	Na <sub>2</sub> CO <sub>3</sub>	ND
6	Dioxane	Cs <sub>2</sub> CO <sub>3</sub>	ND
7	Dioxane	K <sub>2</sub> CO <sub>3</sub>	ND
8	THF	KO <sup>t</sup> Bu	82
9	Toluene	KO <sup>t</sup> Bu	73
10	CH <sub>3</sub> CN	KO <sup>t</sup> Bu	ND

<sup>a</sup> All reactions were carried out using **2a** (1.0 mmol), **3a** (0.75 mmol), **1** (1.0 mol%), base (1.5 equiv.) in solvent (2.0 mL) at 120 °C for 12 h. <sup>b</sup> Isolated yields. ND = not detected.

enough (Table 2, entries 1–11). Sterically hindering substituents, such as 2-methoxy, 2-methyl, 2-fluoro and even 2,6-dimethyl groups attached to the phenyl rings of aryl chlorides **3**, were all tolerated to give the expected products **4b**, **4e**, **4h** and **4k** in good to almost quantitative yields, respectively (Table 2, entries 1, 4, 7 and 10). In addition, heteroaryl chlorides such as 2-chloropyridine **3m** and 3-chloropyridine **3n** were also good substrates, giving the arylated products **4m** and **4n** in satisfactory yields, respectively (Table 2, entries 12 and 13).

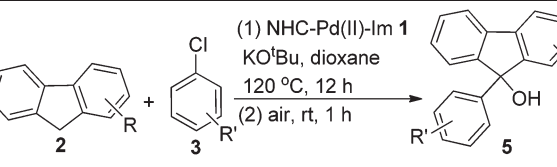
Encouraged by these results, the reactions of various other fluorenes **2** and aryl chlorides **3** were further investigated under the optimal conditions. As can be seen from Table 3, all reactions can give the desired arylated products **4** in good to almost quantitative yields, regardless of whether electron-rich or -poor or sterically hindering substituents were attached on the phenyl rings of either substrate. For instance, aryl chlorides possessing sterically hindering substituents reacted very well to give the corresponding products **4p** and **4ac** in good to almost quantitative yields (Table 3, entries 2 and 15).

It seems that products **4** are liable to be oxidized if the reaction mixture is exposed to air. For example, when the reactions between fluorenes **2** and aryl chlorides **3** were finished and then the mixture was exposed to air at room temperature for another 1 h, 9-aryl-9-hydroxyfluorenes **5** can be obtained in acceptable to good yields (Table 4). Therefore, once the C–H bond arylation reaction is completed, the work-up should be carried out as soon as possible in order to achieve satisfactory

**Table 3** NHC–Pd(II)–Im complex **1** catalyzed reactions between fluorenes **2** and aryl chlorides **3**


Entry <sup>a</sup>	2 (R)	3 (R')	Yield <sup>b</sup> (%)
1	<b>2b</b> (2-Me)	<b>3a</b> (H)	<b>4o</b> , 99
2	<b>2b</b>	<b>3b</b> (2-OMe)	<b>4p</b> , 99
3	<b>2b</b>	<b>3d</b> (4-OMe)	<b>4q</b> , 89
4	<b>2b</b>	<b>3f</b> (3-Me)	<b>4r</b> , 89
5	<b>2b</b>	<b>3g</b> (4-Me)	<b>4s</b> , 88
6	<b>2b</b>	<b>3j</b> (4-F)	<b>4t</b> , 80
7	<b>2b</b>	<b>3l</b> (4-NMe <sub>2</sub> )	<b>4u</b> , 87
8	<b>2c</b> (4-Me)	<b>3a</b>	<b>4v</b> , 85
9	<b>2c</b>	<b>3d</b>	<b>4w</b> , 92
10	<b>2c</b>	<b>3g</b>	<b>4x</b> , 87
11	<b>2c</b>	<b>3j</b>	<b>4y</b> , 76
12	<b>2c</b>	<b>3l</b>	<b>4z</b> , 86
13	<b>2d</b> (2-F)	<b>3c</b> (3-OMe)	<b>4aa</b> , 92
14	<b>2d</b>	<b>3d</b>	<b>4ab</b> , 82
15	<b>2d</b>	<b>3e</b> (2-Me)	<b>4ac</b> , 83 <sup>c</sup>
16	<b>2d</b>	<b>3g</b>	<b>4ad</b> , 83
17	<b>2d</b>	<b>3l</b>	<b>4ae</b> , 93

<sup>a</sup> All reactions were carried out using **2** (1.0 mmol), **3** (0.75 mmol), **1** (1.0 mol%), KO<sup>t</sup>Bu (1.5 equiv.) in dioxane (2.0 mL) at 120 °C for 12 h. <sup>b</sup> Isolated yields. <sup>c</sup> The ratio (*syn/anti* = 64/36) was determined by <sup>1</sup>H NMR.

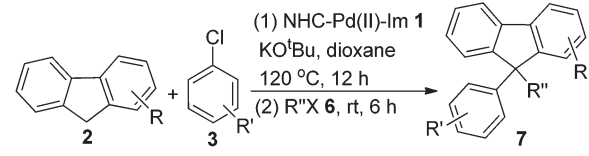
**Table 4** NHC–Pd(II)–Im complex **1** catalyzed reactions of fluorenes **2** with aryl chlorides **3** and further oxidation in a one-pot procedure


Entry <sup>a</sup>	2 (R)	3 (R')	Yield <sup>b</sup> (%)
1	<b>2a</b> (H)	<b>3a</b> (H)	<b>5a</b> , 64
2	<b>2a</b>	<b>3b</b> (2-OMe)	<b>5b</b> , 84
3	<b>2a</b>	<b>3c</b> (3-OMe)	<b>5c</b> , 72
4	<b>2a</b>	<b>3d</b> (4-OMe)	<b>5d</b> , 69
5	<b>2a</b>	<b>3g</b> (4-Me)	<b>5e</b> , 65
6	<b>2a</b>	<b>3h</b> (2-F)	<b>5f</b> , 68
7	<b>2a</b>	<b>3i</b> (3-F)	<b>5g</b> , 60
8	<b>2a</b>	<b>3j</b> (4-F)	<b>5h</b> , 68
9	<b>2a</b>	<b>3n</b> (4-Cl)	<b>5i</b> , 53
10	<b>2b</b> (2-Me)	<b>3d</b>	<b>5j</b> , 75
11	<b>2b</b>	<b>3g</b>	<b>5k</b> , 75
12	<b>2d</b> (2-F)	<b>3d</b>	<b>5l</b> , 69
13	<b>2d</b>	<b>3g</b>	<b>5m</b> , 70

<sup>a</sup> All reactions were carried out using **2** (1.0 mmol), **3** (0.75 mmol), **1** (1.0 mol%), KO<sup>t</sup>Bu (1.5 equiv.) in dioxane (2.0 mL) at 120 °C for 12 h, then the mixture was stirred at rt under air for another 1 h. <sup>b</sup> Isolated yields.

yields of products **4**. As can be seen from Table 4, it seems that the substituents on the fluorenes **2** and aryl chlorides **3** did not affect the reactions significantly. For instance, aryl chlorides **3** having electron-rich, -neutral or -poor groups or sterically hindering substituents were all tolerated to give the corresponding products **5** in moderate to good yields. The reaction of a heteroaryl chloride such as 3-chloropyridine **3n** also proceeded smoothly in a one-pot procedure, giving product **5i** in an acceptable yield (Table 4, entry 9).

Since the normal direct C–H bond arylated products **4** are liable to be oxidized once the reaction mixture is exposed to air (Table 4), which may be partially due to the acidic hydrogen on the C9 position, therefore we then turned our interest attention to the further functionalization of the acidic hydrogen of products **4** by alkylation in a one-pot procedure. To our satisfaction, when the amount of KO<sup>t</sup>Bu was increased to 2.5 equiv. in the first step of the arylation reaction under identical con-

**Table 5** NHC–Pd(II)–Im complex **1** catalyzed reactions of fluorenes **2** with aryl chlorides **3** and further alkylation in a one-pot procedure


Entry <sup>a</sup>	2 (R)	3 (R')	6 (R''/X)	Yield <sup>b</sup> (%)
1	<b>2a</b> (H)	<b>3a</b> (H)	<b>6a</b> (benzyl/Cl)	<b>7a</b> , 99
2	<b>2a</b>	<b>3c</b> (3-OMe)	<b>6a</b>	<b>7b</b> , 99
3	<b>2a</b>	<b>3d</b> (4-OMe)	<b>6a</b>	<b>7c</b> , 98
4	<b>2a</b>	<b>3f</b> (3-Me)	<b>6a</b>	<b>7d</b> , 99
5	<b>2a</b>	<b>3g</b> (4-Me)	<b>6a</b>	<b>7e</b> , 99
6	<b>2a</b>	<b>3i</b> (3-F)	<b>6a</b>	<b>7f</b> , 98
7	<b>2a</b>	<b>3j</b> (4-F)	<b>6a</b>	<b>7g</b> , 98
8	<b>2a</b>	<b>3l</b> (4-NMe <sub>2</sub> )	<b>6a</b>	<b>7h</b> , 83
9	<b>2a</b>	<b>3a</b>	<b>6b</b> (Et/Br)	<b>7i</b> , 94 <sup>c</sup>
10	<b>2a</b>	<b>3a</b>	<b>6c</b> (allyl/Cl)	<b>7j</b> , 93
11	<b>2a</b>	<b>3a</b>	<b>6d</b> (Me/I)	<b>7k</b> , 94 <sup>d</sup>
12	<b>2a</b>	<b>3m</b> (4-Cl)	<b>6a</b>	<b>7l</b> , 81
13	<b>2a</b>	<b>3n</b> (4-Cl)	<b>6a</b>	<b>7m</b> , 89
14	<b>2b</b> (2-Me)	<b>3a</b>	<b>6a</b>	<b>7n</b> , 99
15	<b>2b</b>	<b>3d</b>	<b>6a</b>	<b>7o</b> , 99
16	<b>2b</b>	<b>3g</b>	<b>6a</b>	<b>7p</b> , 96
17	<b>2b</b>	<b>3l</b>	<b>6a</b>	<b>7q</b> , 99
18	<b>2c</b> (4-Me)	<b>3a</b>	<b>6a</b>	<b>7r</b> , 93
19	<b>2c</b>	<b>3d</b>	<b>6a</b>	<b>7s</b> , 84
20	<b>2c</b>	<b>3g</b>	<b>6a</b>	<b>7t</b> , 99
21	<b>2c</b>	<b>3j</b>	<b>6a</b>	<b>7u</b> , 94
22	<b>2c</b>	<b>3l</b>	<b>6a</b>	<b>7v</b> , 86
23	<b>2d</b> (2-F)	<b>3a</b>	<b>6a</b>	<b>7w</b> , 99
24	<b>2d</b>	<b>3g</b>	<b>6a</b>	<b>7x</b> , 99
25	<b>2d</b>	<b>3l</b>	<b>6a</b>	<b>7y</b> , 91

<sup>a</sup> All reactions were carried out using **2** (1.0 mmol), **3** (0.75 mmol), **1** (1.0 mol%), KO<sup>t</sup>Bu (2.5 equiv.) in dioxane (2.0 mL) at 120 °C for 12 h, then **6** (1.0 mmol) was added and the mixture was stirred at rt for another 6 h. <sup>b</sup> Isolated yields. <sup>c</sup> The ratio (*syn/anti* = 83/17) was determined by <sup>1</sup>H NMR. <sup>d</sup> The ratio (*syn/anti* = 87/13) was determined by <sup>1</sup>H NMR.

ditions, then alkyl scaffolds can be efficiently introduced, giving the final products **7** in good to almost quantitative yields (Table 5). It seems that better yields can be achieved in these two-step, one-pot procedures in most cases, which also indicates the instability of the arylated products **4** obtained from the first step.

## Conclusions

In conclusion, the first example of phosphine ligand-free direct C–H bond arylation of the C9 position of fluorenes using various activated and unactivated (hetero)aryl chlorides as the arylating reagents was achieved in the presence of a well-defined, easily available NHC–Pd(II) complex.<sup>10</sup> Under the optimal conditions, various fluorenes and aryl chlorides can react sufficiently to give the expected arylated products in good to almost quantitative yields. Electron-rich, neutral, electron-poor and sterically hindered substituents on both substrates are tolerated. In addition, the arylated products can be further oxidized or alkylated in a one-pot procedure to give di-functionalized fluorenes in good to almost quantitative yields. The methodology reported in this paper will become a beneficial supplement to traditionally reported methods for the functionalization of fluorenes in organic synthesis.

## Experimental

### General remarks

Melting points are uncorrected. NMR spectra were recorded at 300/500/600 (for <sup>1</sup>H NMR) or 75/125/150 MHz (for <sup>13</sup>C NMR), respectively. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra recorded in CDCl<sub>3</sub> solutions were referenced to TMS (0.00 ppm) and the residual solvent peak (77.0 ppm), respectively. *J*-values are in Hz. Organic solvents used were dried by standard methods. The mass analyzer type for the high-resolution mass spectra was EI (70 eV) and ESI (quadrupole). Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel.

### General procedure for the NHC–Pd(II)–Im complex-catalyzed reactions of fluorenes with aryl chlorides

Under a N<sub>2</sub> atmosphere, fluorenes **2** (1.0 mmol), NHC–Pd(II)–Im complex **1** (0.01 mmol), KO<sup>t</sup>Bu (1.125 mmol), dioxane (2.0 mL) and aryl chlorides **3** (0.75 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at 120 °C for 12 h, then it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>) (eluent: petroleum ether; petroleum ether–ethyl acetate = 10 : 1 for products derived from 4-dimethylaminophenyl chloride) to give the pure products **4**.

### General procedure for the NHC–Pd(II)–Im complex-catalyzed reactions of fluorenes with aryl chlorides and further oxidation in a one-pot procedure

Under a N<sub>2</sub> atmosphere, fluorenes **2** (1.0 mmol), NHC–Pd(II)–Im complex **1** (0.01 mmol), KO<sup>t</sup>Bu (1.125 mmol), dioxane (2.0 mL) and aryl chlorides **3** (0.75 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at 120 °C for 12 h, and then it was cooled to room temperature and stirred for another 1 h under an atmosphere of air. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO<sub>2</sub>) (eluent: petroleum ether–ethyl acetate = 10 : 1) to obtain the pure product **5**.

### General procedure for the NHC–Pd(II)–Im complex-catalyzed reactions of fluorenes with aryl chlorides and further alkylation in a one-pot procedure

Under a N<sub>2</sub> atmosphere, fluorenes **2** (1.0 mmol), NHC–Pd(II)–Im complex **1** (0.01 mmol), KO<sup>t</sup>Bu (1.875 mmol), dioxane (2.0 mL) and aryl chlorides **3** (0.75 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at 120 °C for 12 h. After the reaction mixture was cooled to room temperature, alkyl halides **6** (1.0 mmol) were added. The resulting mixture was stirred vigorously at room temperature for another 6 h, then it was cooled to room temperature and concentrated under reduced pressure, and the residue was purified by flash column chromatography (SiO<sub>2</sub>) (eluent: petroleum ether; petroleum ether–ethyl acetate = 10 : 1 for products derived from 4-dimethylaminophenyl chloride) to obtain the pure product **7**.

Compound **4a**:<sup>11</sup> white solid (179.7 mg, 99%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.37–7.21 (m, 9H), 7.07–7.05 (m, 2H), 5.04 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.9, 141.6, 141.0, 128.7, 128.3, 127.3, 126.8, 125.3, 119.8, 54.4.

Compound **4b**:<sup>12</sup> white solid (191.8 mg, 94%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.34–7.30 (m, 4H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.58 (s, 1H), 5.65 (s, 1H), 3.89 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.0, 148.2, 141.3, 130.4, 128.5, 127.8, 127.1, 127.0, 125.2, 120.9, 119.7, 111.1, 55.7, 47.6.

Compound **4c**: white solid (196.0 mg, 96%); mp: 89–90 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.32–7.28 (m, 4H), 7.22–7.11 (m, 3H), 6.74–6.61 (m, 3H), 4.96 (s, 1H), 3.63 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.7, 147.6, 143.1, 140.9, 129.6, 127.25, 127.22, 125.2, 120.7, 119.8, 114.1, 111.8, 55.0, 54.3; MS (EI, %) *m/z* 272 (M<sup>+</sup>, 100), 241 (32), 227 (23), 165 (30), 115 (28); HRMS (EI) calcd for C<sub>20</sub>H<sub>16</sub>O: 272.1201, found: 272.1197.

Compound **4d**:<sup>11</sup> white solid (192.0 mg, 94%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.33–7.16 (m, 6H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.93 (s, 1H), 3.66 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 158.5, 148.1, 140.8, 133.4, 129.2, 127.2, 127.1, 125.2, 119.7, 114.0, 55.0, 53.6.



Compound **4e**:<sup>7</sup> white solid (mixture of two rotamers, *syn/anti* = 63/37) (190.1 mg, 99%); (*syn*-rotamer) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 6.6 Hz, 3H), 7.27–7.17 (m, 7H), 5.37 (s, 1H), 2.72 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 148.4, 141.1, 140.1, 138.4, 136.0, 132.6, 130.3, 127.2, 127.1, 125.0, 124.6, 119.9, 49.9, 20.4; (*anti*-rotamer) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.56 (d, *J* = 6.9 Hz, 2H), 7.07 (t, *J* = 6.9 Hz, 3H), 6.94–6.84 (m, 4H), 6.36 (d, *J* = 7.5 Hz, 3H), 4.97 (s, 1H), 1.12 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 146.8, 140.8, 140.1, 137.3, 136.0, 131.6, 127.5, 126.6, 126.5, 125.7, 124.6, 119.9, 56.2, 18.2.

Compound **4f**:<sup>13</sup> white solid (178.7 mg, 93%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.37–7.11 (m, 7H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 4.98 (s, 1H), 2.23 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.9, 141.4, 140.9, 138.2, 128.8, 128.5, 127.6, 127.24, 127.21, 125.5, 125.3, 119.8, 54.4, 21.4.

Compound **4g**:<sup>11</sup> white solid (184.4 mg, 96%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.36–7.18 (m, 6H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.98 (s, 1H), 2.27 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 148.0, 140.9, 138.5, 136.3, 129.3, 128.1, 127.24, 127.18, 125.2, 119.8, 54.0, 21.0.

Compound **4h**: white solid (156.0 mg, 80%); mp: 102–103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.38–7.34 (m, 4H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.18–7.10 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 7.5 Hz, 1H), 5.47 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.5 (d, *J*<sub>C-F</sub> = 243.6 Hz), 146.8, 141.1, 129.2 (d, *J*<sub>C-F</sub> = 4.0 Hz), 128.6 (d, *J*<sub>C-F</sub> = 14.9 Hz), 128.3 (d, *J*<sub>C-F</sub> = 8.0 Hz), 127.4 (d, *J*<sub>C-F</sub> = 7.5 Hz), 125.2, 124.3 (d, *J*<sub>C-F</sub> = 3.5 Hz), 119.9, 115.5 (d, *J*<sub>C-F</sub> = 22.1 Hz), 46.9; MS (EI, %) *m/z* 260 (M<sup>+</sup>, 100), 165 (25), 120 (19); HRMS (EI) calcd for C<sub>19</sub>H<sub>13</sub>F: 260.1001, found: 260.0999.

Compound **4i**:<sup>14</sup> white solid (152.1 mg, 78%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.28–7.12 (m, 5H), 6.90–6.84 (m, 2H), 6.72 (dt, *J* = 9.6, 1.8 Hz, 1H), 4.97 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.0 (d, *J*<sub>C-F</sub> = 244.6 Hz), 147.1, 144.2 (d, *J*<sub>C-F</sub> = 6.9 Hz), 141.0, 130.0 (d, *J*<sub>C-F</sub> = 8.1 Hz), 127.4 (d, *J*<sub>C-F</sub> = 17.9 Hz), 125.2, 124.0, 119.9, 115.0 (d, *J*<sub>C-F</sub> = 21.4 Hz), 113.7 (d, *J*<sub>C-F</sub> = 22.3 Hz), 54.0.

Compound **4j**:<sup>11</sup> white solid (181.3 mg, 93%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.36–7.31 (m, 2H), 7.25–7.18 (m, 4H), 7.01–6.97 (m, 2H), 6.93–6.87 (m, 2H), 4.95 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.8 (d, *J*<sub>C-F</sub> = 243.5 Hz), 147.7, 140.9, 137.3 (d, *J*<sub>C-F</sub> = 3.1 Hz), 129.7 (d, *J*<sub>C-F</sub> = 7.9 Hz), 127.4 (d, *J*<sub>C-F</sub> = 8.9 Hz), 125.2, 119.9, 115.5 (d, *J*<sub>C-F</sub> = 21.1 Hz), 53.6.

Compound **4k**:<sup>7</sup> white solid (185.0 mg, 91%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.25–7.17 (m, 5H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 5.51 (s, 1H), 2.69 (s, 3H), 1.11 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.9, 140.9, 138.0, 137.7, 136.9, 129.7, 128.0, 127.2, 126.83, 126.79, 124.1, 120.0, 50.0, 21.8, 18.7.

Compound **4l**:<sup>15</sup> yellow solid (175.3 mg, 82%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.25–7.22 (m, 2H), 6.96 (d,

*J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.97 (s, 1H), 2.89 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.5, 148.6, 140.9, 128.9, 127.2, 127.0, 125.3, 119.7, 112.9, 53.6, 40.7.

Compound **4m**:<sup>16</sup> pale yellow solid (134.9 mg, 74%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 8.60 (dq, *J* = 5.1, 0.9 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.43–7.34 (m, 5H), 7.24 (dt, *J* = 7.5, 1.2 Hz, 2H), 7.08 (ddd, *J* = 7.5, 5.1, 1.2 Hz, 1H), 6.65 (dt, *J* = 7.5, 1.2 Hz, 1H), 5.35 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 161.4, 149.2, 146.1, 141.1, 136.7, 127.5, 127.2, 125.3, 121.8, 121.4, 119.9, 56.4.

Compound **4n**: pale yellow solid (118.5 mg, 65%); mp: 139–140 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ 8.59 (s, 1H), 8.48 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.40–7.35 (m, 2H), 7.25–7.21 (m, 4H), 7.13–7.06 (m, 2H), 5.01 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 149.8, 148.3, 146.7, 140.9, 137.3, 135.2, 127.6, 127.4, 125.1, 123.6, 119.9, 51.4; MS (EI, %) *m/z* 243 (M<sup>+</sup>, 100), 165 (35); HRMS (EI) calcd for C<sub>18</sub>H<sub>13</sub>N: 243.1048, found: 243.1049.

Compound **4o**:<sup>17</sup> white solid (190.1 mg, 99%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.24–7.13 (m, 6H), 7.09–7.05 (m, 3H), 4.95 (s, 1H), 2.30 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.1, 147.7, 141.8, 141.1, 138.3, 137.1, 128.6, 128.3, 128.1, 127.2, 126.8, 126.7, 125.9, 125.2, 119.6, 119.5, 54.3, 21.6.

Compound **4p**: yellow solid (212.4 mg, 99%); mp: 84–85 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.18–7.14 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.71 (t, *J* = 7.2 Hz, 2H), 6.59 (s, 1H), 5.61 (s, 1H), 3.92 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.0, 148.5, 148.2, 141.4, 138.7, 136.9, 130.7, 128.6, 127.9, 127.7, 126.9, 126.6, 125.9, 125.2, 121.0, 119.5, 119.4, 111.1, 55.8, 47.4, 21.6; MS (EI, %) *m/z* 286 (M<sup>+</sup>, 100), 271 (70), 255 (44), 239 (35), 178 (26); HRMS (EI) calcd for C<sub>21</sub>H<sub>18</sub>O: 286.1358, found: 286.1356.

Compound **4q**: pale yellow solid (190.9 mg, 89%); mp: 102–103 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 4.92 (s, 1H), 3.72 (s, 3H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.4, 148.4, 148.0, 140.9, 138.2, 137.1, 133.7, 129.3, 128.0, 127.1, 126.7, 125.8, 125.2, 119.5, 119.4, 114.0, 55.1, 53.5, 21.6; MS (EI, %) *m/z* 286 (M<sup>+</sup>, 100), 271 (84), 255 (29), 239 (22), 226 (23); HRMS calcd for C<sub>21</sub>H<sub>18</sub>O: 286.1358, found: 286.1355.

Compound **4r**: white solid (180.2 mg, 89%); mp: 68–69 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.20–7.10 (m, 4H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 4.93 (s, 1H), 2.31 (s, 3H), 2.23 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.2, 147.8, 141.6, 141.0, 138.3, 138.2, 137.1, 128.9, 128.5, 128.1, 127.6, 127.1, 126.7, 125.9, 125.5, 125.2, 119.5, 119.4, 54.2, 21.6, 21.4; MS (EI, %) *m/z* 270 (M<sup>+</sup>, 96), 255 (100), 239 (27), 178 (23); HRMS (EI) calcd for C<sub>21</sub>H<sub>18</sub>: 270.1409, found: 270.1410.

Compound **4s**: white solid (179.0 mg, 88%); mp: 102–105 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ 7.71 (d, *J* = 7.5

Hz, 1H), 7.64 (d,  $J = 8.0$  Hz, 1H), 7.31 (t,  $J = 7.5$  Hz, 1H), 7.25 (d,  $J = 7.5$  Hz, 1H), 7.17 (t,  $J = 7.5$  Hz, 1H), 7.14 (d,  $J = 8.0$  Hz, 1H), 7.09 (s, 1H), 7.05 (d,  $J = 8.0$  Hz, 2H), 6.95 (d,  $J = 8.0$  Hz, 2H), 4.93 (s, 1H), 2.30 (s, 3H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 147.9, 141.0, 138.7, 138.3, 137.1, 136.2, 129.3, 128.2, 128.1, 127.1, 126.7, 125.9, 125.2, 119.5, 119.4, 53.9, 21.6, 21.0; MS (EI, %)  $m/z$  270 ( $\text{M}^+$ , 94), 255 (100), 239 (27), 178 (18); HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{18}$ : 270.1409, found: 270.1414.

Compound **4t**: white solid (164.4 mg, 80%); mp: 80–81 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.71 (d,  $J = 7.5$  Hz, 1H), 7.64 (d,  $J = 7.5$  Hz, 1H), 7.32 (t,  $J = 7.5$  Hz, 1H), 7.22–7.12 (m, 3H), 7.06 (s, 1H), 7.01–6.98 (m, 2H), 6.91 (t,  $J = 8.5$  Hz, 2H), 4.92 (s, 1H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8 (d,  $J_{\text{C-F}} = 243.3$  Hz), 148.0, 147.6, 141.0, 138.2, 137.5 (d,  $J_{\text{C-F}} = 3.1$  Hz), 137.3, 129.8, 129.7, 128.3, 127.3, 126.8, 125.8, 125.1, 119.6 (d,  $J_{\text{C-F}} = 9.3$  Hz), 115.5 (d,  $J_{\text{C-F}} = 21.4$  Hz), 53.4, 21.6; MS (EI, %)  $m/z$  274 ( $\text{M}^+$ , 86), 259 (100); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{15}\text{F}$ : 274.1158, found: 274.1156.

Compound **4u**: yellow solid (195.1 mg, 87%); mp: 149–150 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.72 (d,  $J = 7.5$  Hz, 1H), 7.65 (d,  $J = 8.0$  Hz, 1H), 7.33–7.28 (m, 2H), 7.21–7.13 (m, 3H), 6.95 (d,  $J = 8.5$  Hz, 2H), 6.64 (d,  $J = 8.5$  Hz, 2H), 4.91 (s, 1H), 2.88 (s, 6H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.5, 148.8, 148.5, 141.0, 138.2, 137.0, 129.4, 129.0, 127.9, 126.9, 126.7, 125.9, 125.2, 119.44, 119.36, 112.8, 53.5, 40.6, 21.6; MS (ESI): 300  $[\text{M} + \text{H}]^+$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{22}\text{N}$   $[\text{M} + \text{H}]^+$ : 300.1747, found: 300.1752.

Compound **4v**: white solid (163.0 mg, 85%); mp: 106–107 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.89 (d,  $J = 7.5$  Hz, 1H), 7.34 (t,  $J = 7.5$  Hz, 1H), 7.28 (d,  $J = 7.0$  Hz, 1H), 7.22–7.15 (m, 4H), 7.12–7.11 (m, 3H), 7.03 (d,  $J = 7.5$  Hz, 2H), 4.95 (s, 1H), 2.71 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.31, 148.27, 141.93, 141.91, 139.0, 132.9, 129.5, 128.6, 128.3, 127.1, 126.9, 126.7, 126.6, 125.2, 123.0, 122.8, 54.3, 21.0; MS (EI, %)  $m/z$  256 ( $\text{M}^+$ , 85), 241 (100); HRMS calcd for  $\text{C}_{20}\text{H}_{16}$ : 256.1252, found: 256.1254.

Compound **4w**: pale yellow solid (198.0 mg, 92%); mp: 102–103 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.88 (d,  $J = 8.0$  Hz, 1H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.27 (d,  $J = 7.5$  Hz, 1H), 7.19 (dt,  $J = 7.5$ , 0.5 Hz, 1H), 7.09–7.11 (m, 3H), 6.94 (d,  $J = 8.5$  Hz, 2H), 6.74 (d,  $J = 8.5$  Hz, 2H), 4.90 (s, 1H), 3.66 (s, 3H), 2.70 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 148.58, 148.55, 141.8, 133.8, 129.4, 129.3, 127.0, 126.9, 126.5, 125.1, 122.9, 122.7, 114.0, 55.0, 53.5, 21.0; MS (EI, %)  $m/z$  286 ( $\text{M}^+$ , 100), 271 (99); HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{18}\text{O}$ : 286.1358, found: 286.1357.

Compound **4x**: white solid (176.2 mg, 87%); mp: 100–101 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.89 (d,  $J = 7.5$  Hz, 1H), 7.34 (t,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 7.0$  Hz, 1H), 7.20 (dt,  $J = 7.5$ , 1.0 Hz, 1H), 7.14–7.10 (m, 3H), 7.03 (d,  $J = 8.0$  Hz, 2H), 6.93 (d,  $J = 8.0$  Hz, 2H), 4.93 (s, 1H), 2.71 (s, 3H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.51, 148.47, 141.9, 138.9, 138.8, 136.2, 132.9, 129.4, 129.3, 128.2, 127.1, 126.9, 126.5, 125.2, 123.0, 122.8, 54.0, 21.03, 21.02; MS (EI, %)  $m/z$  270 ( $\text{M}^+$ , 90), 255 (100), 239 (24), 178 (31); HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{18}$ : 270.1409, found: 270.1406.

Compound **4y**: white solid (156.2 mg, 76%); mp: 98–99 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.90 (d,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 7.5$  Hz, 1H), 7.26 (d,  $J = 7.5$  Hz, 1H), 7.21 (dt,  $J = 7.5$ , 1.0 Hz, 1H), 7.13–7.12 (m, 2H), 7.09 (dd,  $J = 8.5$ , 4.0 Hz, 1H), 6.98 (dd,  $J = 8.5$ , 5.5 Hz, 2H), 6.90 (t,  $J = 8.5$  Hz, 2H), 4.92 (s, 1H), 2.72 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8 (d,  $J_{\text{C-F}} = 243.3$  Hz), 148.1 (d,  $J_{\text{C-F}} = 3.5$  Hz), 141.9, 138.9, 137.6 (d,  $J_{\text{C-F}} = 3.1$  Hz), 133.0, 129.8 (d,  $J_{\text{C-F}} = 7.8$  Hz), 129.6, 127.3, 127.0, 126.6, 125.1, 123.1, 122.7, 115.4 (d,  $J_{\text{C-F}} = 21.4$  Hz), 53.5, 21.0; MS (EI, %)  $m/z$  274 ( $\text{M}^+$ , 80), 259 (100); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{15}\text{F}$ : 274.1158, found: 274.1161.

Compound **4z**: yellow solid (192.9 mg, 86%); mp: 141–142 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.92 (d,  $J = 8.0$  Hz, 1H), 7.38–7.33 (m, 2H), 7.25–7.22 (m, 1H), 7.18–7.11 (m, 3H), 6.95 (d,  $J = 8.5$  Hz, 2H), 6.65 (d,  $J = 8.5$  Hz, 2H), 4.94 (s, 1H), 2.90 (s, 6H), 2.76 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.03, 148.99, 141.9, 138.9, 132.8, 129.3, 129.0, 126.93, 126.85, 126.5, 125.2, 122.9, 122.8, 113.0, 53.6, 40.7, 21.0; MS (ESI): 300  $[\text{M} + \text{H}]^+$ ; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{22}\text{N}$ :  $[\text{M} + \text{H}]^+$ : 300.1746, found: 300.1752.

Compound **4aa**: yellow solid (200.1 mg, 92%); mp: 67–68 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.69–7.65 (m, 2H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.28 (d,  $J = 7.5$  Hz, 1H), 7.20 (dt,  $J = 7.5$ , 1.0 Hz, 1H), 7.16 (t,  $J = 7.5$  Hz, 1H), 7.05–6.99 (m, 2H), 6.75 (dd,  $J = 8.5$ , 2.5 Hz, 1H), 6.65 (d,  $J = 7.5$  Hz, 1H), 6.59 (t,  $J = 2.0$  Hz, 1H), 4.93 (s, 1H), 3.67 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6 (d,  $J_{\text{C-F}} = 244.0$  Hz), 159.8, 149.7 (d,  $J_{\text{C-F}} = 8.1$  Hz), 147.4 (d,  $J_{\text{C-F}} = 1.9$  Hz), 142.4, 140.1, 136.9 (d,  $J_{\text{C-F}} = 2.3$  Hz), 129.7, 127.4, 126.9, 125.2, 120.8 (d,  $J_{\text{C-F}} = 8.8$  Hz), 120.6, 119.5, 114.5 (d,  $J_{\text{C-F}} = 22.9$  Hz), 114.1, 112.5 (d,  $J_{\text{C-F}} = 22.9$  Hz), 112.0, 55.0, 54.3 (d,  $J_{\text{C-F}} = 2.1$  Hz); MS (EI, %)  $m/z$  290 ( $\text{M}^+$ , 100), 259 (37), 183 (28); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{15}\text{FO}$ : 290.1107, found: 290.1111.

Compound **4ab**: yellow solid (179.0 mg, 82%); mp: 99–100 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.70–7.66 (m, 2H), 7.34 (t,  $J = 7.5$  Hz, 1H), 7.26 (d,  $J = 7.5$  Hz, 1H), 7.21 (dt,  $J = 7.5$ , 1.0 Hz, 1H), 7.04 (dt,  $J = 9.0$ , 2.0 Hz, 1H), 6.98–6.95 (m, 3H), 6.79 (d,  $J = 8.5$  Hz, 2H), 4.92 (s, 1H), 3.72 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6 (d,  $J_{\text{C-F}} = 243.9$  Hz), 158.6, 150.3 (d,  $J_{\text{C-F}} = 8.0$  Hz), 148.0 (d,  $J_{\text{C-F}} = 1.8$  Hz), 140.0, 136.8 (d,  $J_{\text{C-F}} = 2.1$  Hz), 132.7, 129.2, 127.3, 126.9, 125.2, 120.7 (d,  $J_{\text{C-F}} = 8.8$  Hz), 119.5, 114.4 (d,  $J_{\text{C-F}} = 22.9$  Hz), 114.1, 112.5 (d,  $J_{\text{C-F}} = 22.8$  Hz), 55.1, 53.6; MS (EI, %)  $m/z$  290 ( $\text{M}^+$ , 100), 259 (42); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{15}\text{FO}$ : 290.1107, found: 290.1108.

Compound **4ac**: colorless liquid (170.6 mg, 83%); (mixture of two rotamers, *syn/anti* = 64/36) (*syn*-rotamer)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.72–7.66 (m, 3H), 7.35–7.32 (m, 1H), 7.28–7.25 (m, 1H), 7.20–7.15 (m, 2H), 7.10–7.07 (m, 1H), 6.96–6.93 (m, 2H), 6.35 (d,  $J = 7.5$  Hz, 1H), 5.32 (s, 1H), 2.71 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6 (d,  $J_{\text{C-F}} = 243.9$  Hz), 150.5 (d,  $J_{\text{C-F}} = 8.1$  Hz), 148.2, 140.2, 139.4, 136.0, 132.5, 131.7, 130.4, 127.4, 127.3, 126.9, 126.8, 126.5, 125.0, 120.8, 119.6, 114.3 (d,  $J_{\text{C-F}} = 22.9$  Hz), 112.3 (d,  $J_{\text{C-F}} = 22.8$  Hz), 49.9, 20.4; (*anti*-rotamer)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.72–7.66 (m, 3H), 7.53 (d,  $J = 7.5$  Hz, 1H), 7.35–7.32 (m, 1H), 7.28–7.25 (m, 1H), 7.20–7.15 (m, 2H), 7.05–7.03 (m, 1H), 6.91–6.88 (m, 2H),

4.92 (s, 1H), 1.15 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 (d,  $J_{\text{C-F}} = 244.1$  Hz), 149.0 (d,  $J_{\text{C-F}} = 8.0$  Hz), 146.7, 139.9, 137.7, 137.2, 137.1, 136.8, 130.4, 127.5, 127.2, 126.9, 126.8, 125.8, 125.0, 124.6, 120.8, 119.6, 114.3 (d,  $J_{\text{C-F}} = 22.9$  Hz), 112.0 (d,  $J_{\text{C-F}} = 22.8$  Hz), 56.1, 18.2; MS (EI, %)  $m/z$  274 ( $\text{M}^+$ , 100), 259 (42), 183 (43); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{15}\text{F}$ : 274.1158, found: 274.1154.

**Compound 4ad**: white solid (170.6 mg, 83%); mp: 132–133 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.69 (d,  $J = 7.5$  Hz, 1H), 7.66 (dd,  $J = 8.0, 5.0$  Hz, 1H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.26 (d,  $J = 7.5$  Hz, 1H), 7.20 (t,  $J = 7.5$  Hz, 1H), 7.06 (d,  $J = 7.5$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 1H), 6.98 (d,  $J = 7.5$  Hz, 1H), 6.94 (d,  $J = 7.5$  Hz, 2H), 4.93 (s, 1H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6 (d,  $J_{\text{C-F}} = 244.0$  Hz), 150.2 (d,  $J_{\text{C-F}} = 8.0$  Hz), 147.9, 140.1, 137.8, 136.9 (d,  $J_{\text{C-F}} = 2.0$  Hz), 136.6, 129.5, 128.1, 127.4, 126.9, 125.2, 120.7 (d,  $J_{\text{C-F}} = 8.8$  Hz), 119.5, 114.4 (d,  $J_{\text{C-F}} = 22.9$  Hz), 112.5 (d,  $J_{\text{C-F}} = 22.9$  Hz), 54.1 (d,  $J_{\text{C-F}} = 1.9$  Hz), 21.0; MS (EI, %)  $m/z$  274 ( $\text{M}^+$ , 100), 259 (58), 183 (22); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{15}\text{F}$ : 274.1158, found: 274.1154.

**Compound 4ae**: red solid (211.4 mg, 93%); mp: 131–132 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.72–7.68 (m, 2H), 7.35 (t,  $J = 7.5$  Hz, 1H), 7.30 (d,  $J = 7.5$  Hz, 1H), 7.22 (t,  $J = 7.5$  Hz, 1H), 7.07–7.00 (m, 2H), 6.95 (d,  $J = 8.5$  Hz, 2H), 6.67 (d,  $J = 8.5$  Hz, 2H), 4.94 (s, 1H), 2.91 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 (d,  $J_{\text{C-F}} = 243.6$  Hz), 150.8 (d,  $J_{\text{C-F}} = 8.0$  Hz), 149.6, 148.4, 140.1, 136.8 (d,  $J_{\text{C-F}} = 2.1$  Hz), 135.0, 128.9, 128.8, 127.2, 126.9, 125.3, 120.6 (d,  $J_{\text{C-F}} = 8.8$  Hz), 119.4, 114.3 (d,  $J_{\text{C-F}} = 22.9$  Hz), 113.7, 113.0, 112.6 (d,  $J_{\text{C-F}} = 22.8$  Hz), 53.7 (d,  $J_{\text{C-F}} = 2.1$  Hz), 40.7; MS (ESI): 304 [ $\text{M} + \text{H}$ ] $^+$ ; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{19}\text{FN}$  304 [ $\text{M} + \text{H}$ ] $^+$ : 304.1500, found: 304.1502.

**Compound 5a**<sup>18</sup>: yellow solid (123.9 mg, 64%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.61 (d,  $J = 7.5$  Hz, 2H), 7.34–7.29 (m, 4H), 7.25 (d,  $J = 7.0$  Hz, 2H), 7.22–7.15 (m, 5H), 2.52 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.4, 143.1, 139.5, 129.0, 128.4, 128.1, 127.1, 125.3, 124.7, 120.0, 83.5.

**Compound 5b**: white solid (181.4 mg, 84%); mp: 74–75 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.60 (d,  $J = 7.5$  Hz, 2H), 7.44 (d,  $J = 7.5$  Hz, 2H), 7.29 (td,  $J = 7.5, 1.0$  Hz, 2H), 7.21–7.15 (m, 3H), 7.11–7.03 (m, 1H), 6.84 (d,  $J = 8.0$  Hz, 1H), 6.77 (t,  $J = 7.5$  Hz, 1H), 4.87 (br, 1H), 3.66 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 149.9, 139.7, 131.5, 128.64, 128.63, 127.9, 127.2, 124.2, 120.8, 119.7, 111.9, 84.0, 55.5; MS (ESI): 327 [ $\text{M} + \text{K}$ ] $^+$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{16}\text{KO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 327.0787, found: 327.0779.

**Compound 5c**: white solid (155.6 mg, 72%); mp: 71–72 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.57 (d,  $J = 7.5$  Hz, 2H), 7.29–7.25 (m, 4H), 7.16 (td,  $J = 7.5, 1.0$  Hz, 2H), 7.07 (t,  $J = 8.0$  Hz, 1H), 7.00 (t,  $J = 2.0$  Hz, 1H), 6.81 (d,  $J = 8.0$  Hz, 1H), 6.68 (dd,  $J = 8.5, 3.5$  Hz, 1H), 3.64 (s, 3H), 2.68 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 150.2, 144.9, 139.5, 129.1, 128.9, 128.3, 124.6, 119.9, 117.9, 112.3, 111.3, 83.4, 55.0; MS (ESI): 271 [ $\text{M} + \text{H} - \text{H}_2\text{O}$ ] $^+$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{15}\text{O}$  [ $\text{M} + \text{H} - \text{H}_2\text{O}$ ] $^+$ : 271.1123, found: 271.1108.

**Compound 5d**<sup>19</sup>: white solid (149.0 mg, 69%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.58 (d,  $J = 7.5$  Hz, 2H), 7.30–7.23 (m,

6H), 7.17 (t,  $J = 7.5$  Hz, 2H), 6.71 (d,  $J = 9.0$  Hz, 2H), 3.65 (s, 3H), 2.68 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 150.5, 139.4, 135.3, 128.9, 128.3, 126.5, 124.6, 119.9, 113.5, 83.2, 55.0.

**Compound 5e**<sup>20</sup>: white solid (132.6 mg, 65%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.59 (d,  $J = 7.5$  Hz, 2H), 7.29 (td,  $J = 7.5, 1.5$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.21 (d,  $J = 7.5$  Hz, 2H), 7.17 (td,  $J = 7.5, 1.0$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 2.49 (s, 1H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 140.2, 139.5, 136.7, 128.9, 128.8, 128.3, 125.2, 124.7, 120.0, 83.4, 21.0.

**Compound 5f**: white solid (140.7 mg, 68%); mp: 94–95 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.91 (td,  $J = 8.0, 1.5$  Hz, 1H), 7.65 (d,  $J = 7.5$  Hz, 2H), 7.35 (t,  $J = 7.0$  Hz, 2H), 7.28 (d,  $J = 7.5$  Hz, 2H), 7.23–7.15 (m, 4H), 6.83 (dd,  $J = 11.0, 8.0$  Hz, 1H), 2.62 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7 (d,  $J_{\text{C-F}} = 247.3$  Hz), 149.1, 139.8, 130.2 (d,  $J_{\text{C-F}} = 10.8$  Hz), 129.2, 129.1 (d,  $J_{\text{C-F}} = 8.4$  Hz), 128.3, 127.9 (d,  $J_{\text{C-F}} = 3.3$  Hz), 124.0, 123.8 (d,  $J_{\text{C-F}} = 3.5$  Hz), 120.1, 115.8 (d,  $J_{\text{C-F}} = 21.8$  Hz), 81.2; MS (ESI): 299 [ $\text{M} + \text{Na}$ ] $^+$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{13}\text{FNaO}$  [ $\text{M} + \text{H}$ ] $^+$ : 299.0830, found: 299.0848.

**Compound 5g**: pale yellow liquid (124.2 mg, 60%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.61 (d,  $J = 7.5$  Hz, 2H), 7.31 (td,  $J = 7.5, 1.0$  Hz, 2H), 7.23 (d,  $J = 7.0$  Hz, 2H), 7.19 (td,  $J = 7.5, 1.0$  Hz, 2H), 7.15–7.11 (m, 2H), 7.01 (dt,  $J = 9.0, 1.0$  Hz, 1H), 6.88–6.84 (m, 1H), 2.59 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $J_{\text{C-F}} = 243.8$  Hz), 149.9, 146.0 (d,  $J_{\text{C-F}} = 7.0$  Hz), 139.5, 129.6 (d,  $J_{\text{C-F}} = 8.1$  Hz), 129.2, 128.5, 124.6, 121.1 (d,  $J_{\text{C-F}} = 2.8$  Hz), 120.1, 114.0 (d,  $J_{\text{C-F}} = 21.0$  Hz), 112.7 (d,  $J_{\text{C-F}} = 22.8$  Hz), 83.1 (d,  $J_{\text{C-F}} = 1.9$  Hz); MS (ESI): 259 [ $\text{M} + \text{H} - \text{H}_2\text{O}$ ] $^+$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{12}\text{F}$  [ $\text{M} + \text{H} - \text{H}_2\text{O}$ ] $^+$ : 259.0923, found: 259.0919.

**Compound 5h**<sup>20</sup>: white solid (140.7 mg, 68%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.59 (d,  $J = 7.5$  Hz, 2H), 7.29 (td,  $J = 7.0, 1.5$  Hz, 2H), 7.27–7.23 (m, 2H), 7.20–7.15 (m, 4H), 6.88–6.84 (m, 2H), 2.65 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 (d,  $J_{\text{C-F}} = 243.8$  Hz), 150.1, 139.4, 138.9 (d,  $J_{\text{C-F}} = 3.0$  Hz), 129.1, 128.4, 127.1 (d,  $J_{\text{C-F}} = 8.1$  Hz), 124.6, 120.1, 114.9 (d,  $J_{\text{C-F}} = 21.3$  Hz), 83.1.

**Compound 5i**<sup>21</sup>: white solid (103.0 mg, 53%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.16 (d,  $J = 1.5$  Hz, 1H), 8.02 (d,  $J = 5.5$  Hz, 1H), 7.66 (d,  $J = 8.0$  Hz, 1H), 7.53 (d,  $J = 7.5$  Hz, 2H), 7.29–7.25 (m, 2H), 7.18–7.13 (m, 4H), 7.03 (dd,  $J = 8.0, 5.0$  Hz, 1H), 5.16 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 147.4, 146.6, 139.6, 139.4, 133.4, 129.1, 128.3, 124.7, 122.9, 120.0, 81.9.

**Compound 5j**: purple liquid (169.9 mg, 75%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.54 (d,  $J = 7.5$  Hz, 1H), 7.46 (d,  $J = 7.5$  Hz, 1H), 7.28–7.21 (m, 4H), 7.14 (t,  $J = 7.5$  Hz, 1H), 7.09 (d,  $J = 9.0$  Hz, 2H), 6.72 (d,  $J = 9.0$  Hz, 2H), 3.65 (s, 3H), 2.60 (s, 1H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 150.7, 150.5, 139.5, 138.3, 136.7, 135.5, 129.6, 128.8, 127.8, 126.5, 125.3, 124.5, 119.7, 119.6, 113.5, 83.1, 55.0, 21.5; MS (ESI): 341 [ $\text{M} + \text{K}$ ] $^+$ ; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{18}\text{KO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 341.0944, found: 341.0933.

**Compound 5k**: brown liquid (160.9 mg, 75%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.54 (d,  $J = 7.5$  Hz, 1H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.26 (t,  $J = 7.5$  Hz, 1H), 7.23–7.20 (m, 3H), 7.13



(t,  $J = 7.5$  Hz, 1H), 7.09–7.07 (m, 2H), 7.01 (d,  $J = 8.0$  Hz, 2H), 2.47 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.7, 140.6, 139.8, 138.5, 137.0, 136.8, 129.8, 129.0, 128.0, 125.50, 125.49, 124.8, 119.9, 119.8, 83.5, 21.7, 21.2; MS (ESI): 325  $[\text{M} + \text{K}]^+$ ; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{18}\text{KO} [\text{M} + \text{K}]^+$ : 325.0995, found: 325.0994.

Compound **5l**: colorless liquid (158.4 mg, 69%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.54–7.51 (m, 2H), 7.29 (t,  $J = 7.5$  Hz, 1H), 7.25–7.21 (m, 3H), 7.17 (t,  $J = 7.5$  Hz, 1H), 7.00–6.95 (m, 2H), 6.73 (d,  $J = 9.0$  Hz, 2H), 3.67 (s, 3H), 2.76 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (d,  $J_{\text{C-F}} = 245.9$  Hz), 158.8, 152.9 (d,  $J_{\text{C-F}} = 7.3$  Hz), 150.4 (d,  $J_{\text{C-F}} = 1.9$  Hz), 138.6, 135.2 (d,  $J_{\text{C-F}} = 2.6$  Hz), 134.7, 129.1, 128.0, 126.5, 124.7, 121.1 (d,  $J_{\text{C-F}} = 8.5$  Hz), 119.7, 115.8 (d,  $J_{\text{C-F}} = 23.0$  Hz), 113.6, 112.2 (d,  $J_{\text{C-F}} = 23.1$  Hz), 83.0 (d,  $J_{\text{C-F}} = 1.9$  Hz), 55.1; MS (ESI): 289  $[\text{M} + \text{H} - \text{H}_2\text{O}]^+$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{14}\text{FO} [\text{M} + \text{H} - \text{H}_2\text{O}]^+$ : 289.1029, found: 289.1022.

Compound **5m**: pale yellow liquid (152.3 mg, 70%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.54–7.51 (m, 2H), 7.29 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.22 (d,  $J = 7.5$  Hz, 1H), 7.19–7.14 (m, 3H), 7.02 (d,  $J = 8.0$  Hz, 2H), 6.98 (dt,  $J = 8.0, 2.5$  Hz, 1H), 6.94 (dd,  $J = 8.0, 2.5$  Hz, 1H), 2.61 (s, 1H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (d,  $J_{\text{C-F}} = 245.9$  Hz), 152.8 (d,  $J_{\text{C-F}} = 7.4$  Hz), 150.4 (d,  $J_{\text{C-F}} = 2.0$  Hz), 139.6, 138.7, 137.0, 135.2 (d,  $J_{\text{C-F}} = 2.5$  Hz), 129.1, 129.0, 128.0, 125.2, 124.7, 121.1 (d,  $J_{\text{C-F}} = 8.5$  Hz), 119.7, 115.9 (d,  $J_{\text{C-F}} = 23.0$  Hz), 112.3 (d,  $J_{\text{C-F}} = 23.1$  Hz), 83.2 (d,  $J_{\text{C-F}} = 1.9$  Hz), 21.0; MS (ESI): 273  $[\text{M} + \text{H} - \text{H}_2\text{O}]^+$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{14}\text{F} [\text{M} + \text{H} - \text{H}_2\text{O}]^+$ : 273.1080, found: 273.1061.

Compound **7a**:<sup>22</sup> white solid (246.5 mg, 99%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.43–7.41 (m, 2H), 7.31–7.28 (m, 4H), 7.22–7.14 (m, 7H), 6.83 (t,  $J = 7.5$  Hz, 1H), 6.74 (t,  $J = 7.5$  Hz, 2H), 6.42 (d,  $J = 7.5$  Hz, 2H), 3.77 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 144.5, 140.8, 136.4, 129.9, 128.4, 127.1, 127.0, 126.8, 126.7, 126.5, 125.6, 125.0, 119.7, 59.9, 43.9.

Compound **7b**: white solid (268.8 mg, 99%); mp: 118–119 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.49–7.45 (m, 2H), 7.37–7.33 (m, 2H), 7.26–7.22 (m, 4H), 7.18 (t,  $J = 8.0$  Hz, 1H), 6.90–6.86 (m, 3H), 6.79–6.74 (m, 3H), 6.43 (d,  $J = 7.5$  Hz, 2H), 3.77 (s, 2H), 3.72 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 150.3, 146.3, 140.8, 136.4, 129.9, 129.2, 127.1, 127.0, 126.7, 125.6, 124.9, 119.7, 119.4, 113.6, 111.0, 59.9, 55.0, 44.0; MS (EI, %)  $m/z$  362 ( $\text{M}^+$ , 4), 271 (100); HRMS (EI) calcd for  $\text{C}_{27}\text{H}_{22}\text{O}$ : 362.1671, found: 362.1670.

Compound **7c**: white solid (266.1 mg, 98%); mp: 142–143 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.44–7.42 (m, 2H), 7.30–7.29 (m, 2H), 7.21–7.19 (m, 6H), 6.84–6.75 (m, 5H), 6.42 (d,  $J = 7.2$  Hz, 2H), 3.73 (s, 2H), 3.68 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 150.8, 140.7, 136.6, 130.0, 127.9, 127.1, 127.0, 126.7, 125.6, 124.9, 119.7, 113.7, 59.3, 55.1, 44.2; MS (EI, %)  $m/z$  362 ( $\text{M}^+$ , 2), 271 (100); HRMS (EI) calcd for  $\text{C}_{27}\text{H}_{22}\text{O}$ : 362.1671, found: 362.1673.

Compound **7d**: white solid (256.9 mg, 99%); mp: 93–94 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.40–7.38 (m, 2H), 7.30–7.29 (m, 2H), 7.17–7.16 (m, 4H), 7.11–7.07 (m, 3H), 6.97 (s, 1H), 6.80 (t,  $J = 7.5$  Hz, 1H), 6.72 (t,  $J = 7.5$  Hz, 2H), 6.40 (d,

$J = 7.5$  Hz, 2H), 3.75 (s, 2H), 2.20 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 144.5, 140.8, 137.8, 136.5, 129.9, 128.2, 127.5, 127.4, 127.1, 127.0, 126.7, 125.6, 125.0, 123.9, 119.7, 59.9, 44.1, 21.6; MS (EI, %)  $m/z$  346 ( $\text{M}^+$ , 4), 255 (100), 239 (24); HRMS (EI) calcd for  $\text{C}_{27}\text{H}_{22}$ : 346.1722, found: 346.1720.

Compound **7e**: white solid (257.0 mg, 99%); mp: 132–133 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.42–7.39 (m, 2H), 7.31–7.29 (m, 2H), 7.19–7.16 (m, 7H), 7.02 (d,  $J = 7.8$  Hz, 2H), 6.88–6.63 (m, 2H), 6.42 (d,  $J = 7.5$  Hz, 2H), 3.75 (s, 2H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 141.6, 140.8, 136.6, 136.1, 130.0, 129.1, 127.1, 127.0, 126.8, 126.7, 125.6, 125.0, 119.7, 59.7, 44.1, 20.9; MS (EI, %)  $m/z$  346 ( $\text{M}^+$ , 2), 255 (100), 239 (19); HRMS calcd for  $\text{C}_{27}\text{H}_{22}$ : 346.1722, found: 346.1724.

Compound **7f**: white solid (257.3 mg, 98%); mp: 153–156 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.45–7.44 (m, 2H), 7.31–7.30 (m, 2H), 7.23–7.15 (m, 5H), 7.07–7.00 (m, 2H), 6.89–6.84 (m, 2H), 6.76 (t,  $J = 7.5$  Hz, 2H), 6.41 (d,  $J = 7.5$  Hz, 2H), 3.74 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $J_{\text{C-F}} = 243.9$  Hz), 149.9, 147.4 (d,  $J_{\text{C-F}} = 6.8$  Hz), 140.8, 136.0, 130.0, 129.7 (d,  $J_{\text{C-F}} = 8.3$  Hz), 127.4, 127.2, 126.8, 125.8, 124.9, 122.6, 119.8, 114.1 (d,  $J_{\text{C-F}} = 22.3$  Hz), 113.4 (d,  $J_{\text{C-F}} = 20.9$  Hz), 59.7, 43.9; MS (EI, %)  $m/z$  350 ( $\text{M}^+$ , 5), 259 (100); HRMS calcd for  $\text{C}_{26}\text{H}_{19}\text{F}$ : 350.1471, found: 350.1472.

Compound **7g**: white solid (257.5 mg, 98%); mp: 137–138 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.43–7.38 (m, 2H), 7.28–7.17 (m, 8H), 6.90–6.80 (m, 3H), 6.73 (t,  $J = 7.5$  Hz, 2H), 6.39 (d,  $J = 6.9$  Hz, 2H), 3.71 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5 (d,  $J_{\text{C-F}} = 243.9$  Hz), 150.4, 140.7, 140.3 (d,  $J_{\text{C-F}} = 3.1$  Hz), 136.2, 129.9, 128.4 (d,  $J_{\text{C-F}} = 7.8$  Hz), 127.3, 127.1, 126.8, 125.8, 124.8, 119.8, 115.1 (d,  $J_{\text{C-F}} = 20.9$  Hz), 59.4, 44.1; MS (EI, %)  $m/z$  350 ( $\text{M}^+$ , 2), 259 (100); HRMS calcd for  $\text{C}_{26}\text{H}_{19}\text{F}$ : 350.1471, found: 350.1474.

Compound **7h**: pale yellow solid (233.4 mg, 83%); mp: 178–179 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.45–7.44 (m, 2H), 7.35–7.33 (m, 2H), 7.23–7.17 (m, 6H), 6.85 (t,  $J = 7.5$  Hz, 1H), 6.76 (t,  $J = 7.5$  Hz, 2H), 6.63 (d,  $J = 7.5$  Hz, 2H), 6.43 (d,  $J = 7.5$  Hz, 2H), 3.74 (s, 2H), 2.87 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.1, 149.2, 140.7, 136.9, 132.2, 130.0, 127.5, 126.92, 126.89, 126.7, 125.5, 125.0, 119.6, 112.5, 59.3, 44.3, 40.5; MS (ESI): 376  $[\text{M} + \text{H}]^+$ ; HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{26}\text{N} [\text{M} + \text{H}]^+$ : 376.2065, found: 376.2065.

Compound **7i**: white solid (190.3 mg, 94%); mp: 78–79 °C; (mixture of two rotamers, *syn/anti* = 83/17) (*syn*-rotamer)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.73 (d,  $J = 7.5$  Hz, 2H), 7.32–7.28 (m, 2H), 7.23–7.17 (m, 9H), 2.50 (q,  $J = 7.5$  Hz, 2H), 0.41 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.5, 145.0, 140.9, 128.2, 127.5, 127.3, 127.1, 126.7, 124.3, 119.8, 59.2, 30.5; (*anti*-rotamer)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.78 (d,  $J = 7.5$  Hz, 2H), 7.36–7.33 (m, 2H), 7.23–7.17 (m, 3H), 7.14–7.10 (m, 4H), 7.07–7.05 (m, 2H), 2.50 (q,  $J = 7.5$  Hz, 2H), 0.41 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 141.5, 140.9, 128.6, 128.3, 127.3, 126.8, 126.3, 125.3, 119.8, 54.4, 8.5; MS (EI, %)  $m/z$  270 ( $\text{M}^+$ , 17), 241 (100); HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{18}$ : 270.1409, found: 270.1413.

Compound **7j**: white solid (196.7 mg, 93%); mp: 97–98 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.71 (d,  $J = 7.5$  Hz, 2H), 7.29



(dt,  $J = 7.5, 1.5$  Hz, 2H), 7.24–7.10 (m, 9H), 5.23–5.15 (m, 1H), 4.80 (d,  $J = 17.0$  Hz, 1H), 4.69 (d,  $J = 10.0$  Hz, 1H), 3.20 (d,  $J = 6.5$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.1, 144.2, 140.5, 133.5, 128.3, 127.4, 127.2, 126.6, 126.4, 124.6, 119.8, 117.8, 58.4, 42.2; MS (EI, %)  $m/z$  282 ( $\text{M}^+$ , 3), 241 (100); HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{18}$ : 282.1409, found: 282.1411.

Compound **7k**:<sup>23</sup> white solid (180.5 mg, 94%); (mixture of two rotamers, *syn/anti* = 87/13) (*syn*-rotamer)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.73 (d,  $J = 7.5$  Hz, 2H), 7.34–7.27 (m, 2H), 7.20–7.04 (m, 9H), 1.84 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 144.9, 139.7, 128.2, 127.6, 127.1, 126.4, 126.3, 124.0, 120.0, 54.6, 25.2; (*anti*-rotamer)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.76 (d,  $J = 7.5$  Hz, 2H), 7.34–7.27 (m, 2H), 7.20–7.04 (m, 9H), 1.84 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 141.5, 141.0, 128.6, 128.3, 127.3, 126.8, 126.4, 125.3, 119.8, 54.4, 25.2.

Compound **7l**: yellow solid (202.3 mg, 81%); mp: 143–145 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.72 (dq,  $J = 4.8, 0.9$  Hz, 1H), 7.52–7.43 (m, 4H), 7.27–7.18 (m, 5H), 7.05–7.01 (m, 1H), 6.90–6.78 (m, 3H), 6.64 (d,  $J = 7.8$  Hz, 1H), 6.56 (d,  $J = 6.9$  Hz, 2H), 3.98 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 149.0, 148.9, 140.7, 137.6, 136.1, 130.2, 127.4, 126.9, 126.8, 125.62, 125.57, 121.6, 121.4, 119.8, 62.4, 43.9; MS (EI, %)  $m/z$  333 ( $\text{M}^+$ , 25), 242 (100); HRMS (EI) calcd for  $\text{C}_{25}\text{H}_{19}\text{N}$ : 333.1517, found: 333.1512.

Compound **7m**: yellow solid (222.3 mg, 89%); mp: 181–182 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.72 (d,  $J = 2.1$  Hz, 1H), 8.42 (dd,  $J = 4.5, 1.2$  Hz, 1H), 7.46–7.41 (m, 3H), 7.32–7.21 (m, 6H), 7.07 (dd,  $J = 8.1, 4.5$  Hz, 1H), 6.85 (t,  $J = 7.2$  Hz, 1H), 6.76 (t,  $J = 7.2$  Hz, 2H), 6.43 (d,  $J = 7.5$  Hz, 2H), 3.78 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.3, 148.3, 147.8, 140.7, 140.2, 135.6, 134.5, 129.8, 127.5, 127.2, 126.7, 125.8, 124.8, 123.1, 119.8, 58.3, 43.4; MS (EI, %)  $m/z$  333 ( $\text{M}^+$ , 11), 242 (100); HRMS calcd for  $\text{C}_{25}\text{H}_{19}\text{N}$ : 333.1517, found: 333.1520.

Compound **7n**: white solid (256.9 mg, 99%); mp: 137–138 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.39–7.38 (m, 1H), 7.33–7.14 (m, 9H), 7.11 (s, 1H), 7.01 (d,  $J = 7.5$  Hz, 1H), 6.84 (t,  $J = 7.5$  Hz, 1H), 6.76 (t,  $J = 7.5$  Hz, 2H), 6.43 (d,  $J = 7.0$  Hz, 2H), 3.75 (s, 2H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 150.4, 144.8, 140.9, 138.2, 136.8, 136.5, 130.0, 128.3, 128.0, 127.1, 126.9, 126.7, 126.50, 126.46, 125.6, 125.5, 125.0, 119.43, 119.35, 59.7, 43.9, 21.7; MS (EI, %)  $m/z$  346 ( $\text{M}^+$ , 4), 255 (100); HRMS calcd for  $\text{C}_{27}\text{H}_{22}$ : 346.1722, found: 346.1718.

Compound **7o**: white solid (279.2 mg, 99%); mp: 134–135 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.42–7.41 (m, 1H), 7.34 (d,  $J = 7.5$  Hz, 1H), 7.28–7.19 (m, 5H), 7.12 (s, 1H), 7.04 (d,  $J = 7.5$  Hz, 1H), 6.88 (t,  $J = 7.5$  Hz, 1H), 6.81–6.77 (m, 4H), 6.43 (d,  $J = 7.5$  Hz, 2H), 3.75 (s, 3H), 3.72 (s, 2H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 151.0, 150.6, 140.8, 138.1, 136.8, 136.73, 136.66, 130.0, 127.9, 127.0, 126.7, 126.5, 125.6, 125.5, 124.9, 119.4, 119.3, 113.7, 59.1, 55.1, 44.2, 21.8; MS (EI, %)  $m/z$  376 ( $\text{M}^+$ , 2), 285 (100); HRMS calcd for  $\text{C}_{28}\text{H}_{24}\text{O}$ : 376.1827, found: 376.1831.

Compound **7p**: white solid (259.2 mg, 96%); mp: 114–115 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.39–7.37 (m, 1H), 7.31 (d,  $J = 7.5$  Hz, 1H), 7.27–7.25 (m, 1H), 7.19–7.15 (m,

4H), 7.12 (s, 1H), 7.04 (d,  $J = 8.5$  Hz, 2H), 7.01 (d,  $J = 7.5$  Hz, 1H), 6.84 (t,  $J = 7.5$  Hz, 1H), 6.76 (t,  $J = 8.0$  Hz, 2H), 6.43 (d,  $J = 7.5$  Hz, 2H), 3.73 (s, 2H), 2.33 (s, 3H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.5, 141.7, 140.9, 138.1, 136.8, 136.6, 136.0, 130.0, 129.1, 127.9, 127.0, 126.8, 126.7, 126.5, 125.6, 125.5, 124.9, 119.4, 119.3, 59.4, 44.0, 21.8, 20.9; MS (EI, %)  $m/z$  360 ( $\text{M}^+$ , 3), 269 (100); HRMS (EI) calcd for  $\text{C}_{28}\text{H}_{24}$ : 360.1878, found: 360.1880.

Compound **7q**: yellow solid (288.8 mg, 99%); mp: 145–146 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.40–7.28 (m, 3H), 7.18–7.14 (m, 5H), 7.01 (d,  $J = 7.0$  Hz, 1H), 6.85 (t,  $J = 7.0$  Hz, 1H), 6.78–6.75 (m, 2H), 6.63 (d,  $J = 7.0$  Hz, 2H), 6.44 (s, 2H), 3.71 (s, 2H), 2.87 (s, 6H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 150.9, 149.1, 140.8, 138.1, 137.0, 136.6, 132.4, 130.0, 127.8, 127.5, 126.8, 126.6, 126.4, 125.6, 125.5, 125.0, 119.3, 119.2, 112.5, 59.1, 44.3, 40.5, 21.7; MS (ESI): 390  $[\text{M} + \text{H}]^+$ ; HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{28}\text{N}$   $[\text{M} + \text{H}]^+$ : 390.2219, found: 390.2222.

Compound **7r**: white solid (241.3 mg, 93%); mp: 116–117 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.59–7.55 (m, 1H), 7.30–7.29 (m, 1H), 7.25 (d,  $J = 7.5$  Hz, 2H), 7.20–7.12 (m, 6H), 7.09 (t,  $J = 7.5$  Hz, 1H), 6.96 (d,  $J = 7.5$  Hz, 1H), 6.80 (t,  $J = 7.5$  Hz, 1H), 6.72 (t,  $J = 7.5$  Hz, 2H), 6.38 (d,  $J = 7.5$  Hz, 2H), 3.75 (s, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.03, 151.02, 144.9, 141.9, 138.9, 136.4, 132.6, 129.9, 129.4, 128.3, 127.0, 126.9, 126.7, 126.6, 126.4, 126.3, 125.6, 124.9, 122.8, 122.5, 59.4, 44.1, 20.8; MS (EI, %)  $m/z$  346 ( $\text{M}^+$ , 4), 255 (100); HRMS (EI) calcd for  $\text{C}_{27}\text{H}_{22}$ : 346.1722, found: 346.1726.

Compound **7s**: white solid (236.9 mg, 84%); mp: 137–138 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.58–7.57 (m, 1H), 7.31–7.29 (m, 1H), 7.21–7.09 (m, 6H), 6.98 (d,  $J = 7.0$  Hz, 1H), 6.83 (t,  $J = 7.5$  Hz, 1H), 6.76–6.72 (m, 4H), 6.38 (d,  $J = 7.5$  Hz, 2H), 3.72 (s, 2H), 3.68 (s, 3H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 151.23, 151.21, 141.8, 138.8, 136.9, 136.5, 132.6, 129.9, 129.3, 127.9, 126.9, 126.7, 126.6, 126.3, 125.5, 124.8, 122.7, 122.4, 113.6, 58.9, 55.1, 44.4, 20.8; MS (EI, %)  $m/z$  376 ( $\text{M}^+$ , 2), 285 (100); HRMS calcd for  $\text{C}_{28}\text{H}_{24}\text{O}$ : 376.1827, found: 376.1825.

Compound **7t**: white solid (267.3 mg, 99%); mp: 138–139 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.57–7.55 (m, 1H), 7.31–7.29 (m, 1H), 7.21–7.18 (m, 2H), 7.17–7.14 (m, 3H), 7.10 (t,  $J = 7.5$  Hz, 1H), 7.02 (d,  $J = 8.0$  Hz, 2H), 6.96 (d,  $J = 7.5$  Hz, 1H), 6.81 (t,  $J = 7.5$  Hz, 1H), 6.72 (t,  $J = 7.5$  Hz, 2H), 6.38 (d,  $J = 7.0$  Hz, 2H), 3.73 (s, 2H), 2.45 (s, 3H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.17, 151.16, 141.9, 141.8, 138.9, 136.5, 135.9, 132.6, 129.9, 129.3, 129.0, 127.0, 126.9, 126.8, 126.7, 126.6, 126.3, 125.5, 124.9, 122.7, 122.4, 59.2, 44.2, 20.9, 20.8; MS (EI, %)  $m/z$  360 ( $\text{M}^+$ , 3), 269 (100), 255 (37); HRMS (EI) calcd for  $\text{C}_{28}\text{H}_{24}$ : 360.1878, found: 360.1874.

Compound **7u**: white solid (256.6 mg, 94%); mp: 142–143 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.58 (d,  $J = 5.5$  Hz, 1H), 7.28–7.12 (m, 7H), 7.00 (s, 1H), 6.90 (t,  $J = 8.5$  Hz, 2H), 6.83 (t,  $J = 7.0$  Hz, 1H), 6.74 (t,  $J = 7.0$  Hz, 2H), 6.36 (d,  $J = 7.0$  Hz, 2H), 3.71 (s, 2H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5 (d,  $J_{\text{C-F}} = 243.6$  Hz), 150.8 (d,  $J_{\text{C-F}} = 2.9$  Hz), 141.8, 140.6 (d,  $J_{\text{C-F}} = 3.1$  Hz), 138.8, 136.2, 132.8, 129.9, 129.5, 128.5

(d,  $J_{C-F} = 7.6$  Hz), 127.2, 126.8, 126.7, 126.4, 125.7, 124.8, 122.9, 122.3, 115.0 (d,  $J_{C-F} = 20.9$  Hz), 58.9, 44.3, 20.8; MS (EI, %)  $m/z$  364 ( $M^+$ , 3), 273 (100); HRMS (EI) calcd for  $C_{27}H_{21}F$ : 364.1627, found: 364.1629.

Compound **7v**: yellow solid (250.9 mg, 86%); mp: 142–143 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS)  $\delta$  7.60–7.58 (m, 1H), 7.35–7.33 (m, 1H), 7.23–7.11 (m, 6H), 6.99 (d,  $J = 7.5$  Hz, 1H), 6.85 (t,  $J = 7.5$  Hz, 1H), 6.75 (t,  $J = 7.5$  Hz, 2H), 6.64 (d,  $J = 8.5$  Hz, 2H), 6.39 (d,  $J = 8.5$  Hz, 2H), 3.73 (s, 2H), 2.89 (s, 6H), 2.50 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  151.6, 149.1, 141.8, 138.8, 136.9, 132.5, 129.9, 129.1, 127.6, 126.8, 126.6, 126.2, 125.5, 124.9, 122.7, 122.5, 112.5, 58.8, 44.5, 40.5, 20.8; MS (ESI): 390 [ $M + H$ ] $^+$ ; HRMS (ESI) calcd for  $C_{29}H_{28}N$  [ $M + H$ ] $^+$ : 390.2213, found: 390.2222.

Compound **7w**: pale yellow solid (259.9 mg, 99%); mp: 170–171 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS)  $\delta$  7.37–7.19 (m, 10H), 7.02 (dd,  $J = 7.5, 2.5$  Hz, 1H), 6.91–6.85 (m, 2H), 6.78 (t,  $J = 7.5$  Hz, 2H), 6.44 (d,  $J = 7.5$  Hz, 2H), 3.77 (d,  $J = 12.5$  Hz, 1H), 3.74 (d,  $J = 12.5$  Hz, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  162.4 (d,  $J_{C-F} = 243.8$  Hz), 152.9 (d,  $J_{C-F} = 7.5$  Hz), 150.5, 143.9, 139.9, 136.8, 136.0, 129.9, 128.5, 127.3, 126.9, 126.81, 126.77, 125.8, 125.0, 120.7 (d,  $J_{C-F} = 8.8$  Hz), 119.4, 114.4 (d,  $J_{C-F} = 23.0$  Hz), 112.2 (d,  $J_{C-F} = 22.8$  Hz), 60.0, 43.8; MS (EI, %)  $m/z$  350 ( $M^+$ , 5), 259 (100); HRMS (EI) calcd for  $C_{26}H_{19}F$ : 350.1471, found: 350.1468.

Compound **7x**: white solid (270.3 mg, 99%); mp: 149–150 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS)  $\delta$  7.38–7.29 (m, 3H), 7.21–7.19 (m, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 7.01 (dd,  $J = 9.0, 2.5$  Hz, 1H), 6.95–6.85 (m, 2H), 6.78 (t,  $J = 7.5$  Hz, 2H), 6.44 (d,  $J = 7.0$  Hz, 2H), 3.75 (d,  $J = 13.0$  Hz, 1H), 3.71 (d,  $J = 13.0$  Hz, 1H), 2.28 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  162.4 (d,  $J_{C-F} = 243.9$  Hz), 153.0 (d,  $J_{C-F} = 7.5$  Hz), 150.6, 140.9, 139.9, 136.7 (d,  $J_{C-F} = 2.0$  Hz), 136.4, 136.1, 129.9, 129.2, 127.3, 126.8, 126.7, 126.6, 125.8, 124.9, 120.7 (d,  $J_{C-F} = 8.8$  Hz), 119.4, 114.3 (d,  $J_{C-F} = 23.0$  Hz), 112.2 (d,  $J_{C-F} = 22.6$  Hz), 59.8 (d,  $J_{C-F} = 1.6$  Hz), 44.0, 20.9; MS (EI, %)  $m/z$  364 ( $M^+$ , 3), 273 (100); HRMS (EI) calcd for  $C_{27}H_{21}F$ : 364.1627, found: 364.1628.

Compound **7y**: yellow solid (268.2 mg, 91%); mp: 139–140 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS)  $\delta$  7.41–7.31 (m, 3H), 7.24–7.20 (m, 2H), 7.16 (d,  $J = 9.0$  Hz, 2H), 7.03 (dd,  $J = 9.0, 2.0$  Hz, 1H), 6.93–6.87 (m, 2H), 6.79 (t,  $J = 7.5$  Hz, 2H), 6.65 (d,  $J = 8.0$  Hz, 2H), 6.45 (d,  $J = 8.0$  Hz, 2H), 3.74 (d,  $J = 13.0$  Hz, 1H), 3.71 (d,  $J = 13.0$  Hz, 1H), 2.91 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  162.5 (d,  $J_{C-F} = 243.5$  Hz), 153.5 (d,  $J_{C-F} = 7.4$  Hz), 151.0, 149.4, 139.9, 136.7, 136.5, 131.4, 129.9, 127.4, 127.1, 126.8, 126.6, 125.7, 125.0, 120.6 (d,  $J_{C-F} = 8.8$  Hz), 119.3, 114.1 (d,  $J_{C-F} = 22.9$  Hz), 112.5, 112.2 (d,  $J_{C-F} = 22.6$  Hz), 59.4, 44.3, 40.5; MS (ESI): 394 [ $M + H$ ] $^+$ ; HRMS (ESI) calcd for  $C_{28}H_{25}NF$  [ $M + H$ ] $^+$ : 394.1965, found: 394.1971.

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