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N-Heterocyclic Carbene-Palladium(II)-1-Methylimidazole Complex-Catalyzed Direct C−H Bond Arylation of (Benz)imidazoles with Aryl Chlorides

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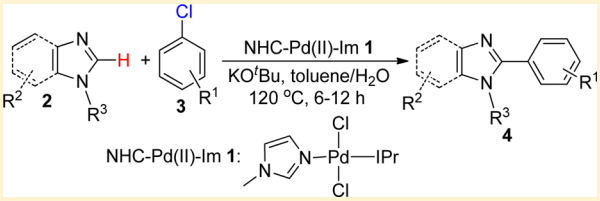
Supporting Information

ABSTRACT: (Benz)imidazoles can be efficiently functionalized by (hetero)aryl chlorides via direct C−H bond arylation in the presence of a well-defined NHC-Pd(II)-Im complex. Under the optimal conditions, various activated, unactivated, and deactivated (hetero)aryl chlorides were successfully applied as the arylating reagents to achieve the 2-(hetero)aryl (benz)imidazoles in acceptable to high yields, giving a facile and alternative methodology for the direct C−H bond arylation of (benz)imidazoles.



INTRODUCTION

C2-arylated (benz)imidazoles are frequently found in various pharmaceuticals, biologically active compounds and materials.[1] Recently, the transition metal-catalyzed direct C−H bond arylation of (benz)imidazoles has been noticed as a potentially more efficient and convenient alternative for the straightforward synthesis of such compounds.[2] However, during the past years, the scope of the arylating reagents is limited to the more active aryl iodides and bromides.[3] To the best of our knowledge, only very few examples on the palladium-catalyzed direct C2-arylation of (benz)imidazoles using aryl chlorides in the presence of phosphine ligands were reported to date, despite their lower cost and more easy availability.[4] Therefore, despite that some progress has been made in the direct C2-arylation of (benz)imidazoles, the research for efficient methods using the more applicable, while less active, aryl chlorides as the arylating reagents is still in great demand.[5] Previously, we have reported that a well-defined *N*-heterocyclic carbene-Pd(II)-1-methylimidazole [NHC-Pd(II)-Im] complex **1** can easily activate aryl chlorides in traditional C−C couplings such as α-arylation of carbonyl compounds,[6] Suzuki−Miyaura coupling,[7] Mizoroki−Heck reaction,[8] Hiyama reaction[9] and C−N coupling.[10] Furthermore, in a very recent communication, we found that NHC-Pd(II)-Im complex **1** can also efficiently catalyze the direct C−H bond arylation of (benzo)oxazoles using aryl chlorides as the arylating reagents.[11] These results thus prompted us to further investigate its application in activating aryl chlorides toward the direct C2-arylation of (benz)imidazoles. Herein, we report these results in detail.

RESULTS AND DISCUSSION

Initially, 1-methylbenzimidazole **2a** (0.49 mmol) was chosen as the model substrate for the reaction with chlorobenzene **3a** (2.0 equiv) in the presence of NHC-Pd(II)-Im complex **1** (2.0 mol %) under various conditions. For example, in the first round, toluene/H_2O (2.0 mL/0.5 equiv) was chosen as the solvents to evaluate the effect of bases. The best result was achieved using KO^{t}Bu as the base to give the desired product **4a** in 89% yield (Table 1, entry 6), while in the presence of other bases such as K_2CO_3, KOH, $K_3PO_4{\cdot}3H_2O$, LiO^{t}Bu and NaO^{t}Bu, almost no product could be detected (Table 1, entries 1−5). The replacement of solvents from toluene/H_2O to THF/H_2O and dioxane/H_2O resulted in product **4a** only being isolated in 48 and 40% yields, respectively (Table 1, entries 7 and 8). In addition, in the presence of other solvents such as DMSO/H_2O, DMF/H_2O, CH_3CN/H_2O and DME/H_2O, no desired product could be detected (Table 1, entries 9−12). Furthermore, after careful investigations, it was found that the amount of H_2O dramatically affected the reaction. That is, the introduction of 0.5 equiv of H_2O was found to be necessary for such transformation. For instance, only 18% yield of product **4a** was obtained when dry toluene was used as the solvent (Table 1, entry 13). When 1.0 equiv of H_2O was added, a significantly higher yield (84%) was achieved (Table 1, entry 14). However, when the amount of H_2O was increased to 3.0 equiv, the yield of **4a** drastically decreased to 5% (Table 1, entry 15). These results thus encouraged us to further investigate the effect of H_2O.

It is known that KO^{t}Bu will be partially hydrolyzed to KOH and HO^{t}Bu under the above reaction conditions. Therefore, three more control experiments were carried out: (1) the combination of KO^{t}Bu (1.5 equiv), KOH (0.5 equiv) and HO^{t}Bu (0.5 equiv) was introduced instead of KO^{t}Bu (2.0

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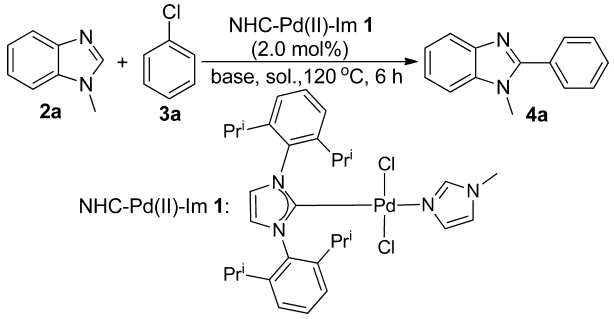
Table 1. Optimization for Complex 1 Catalyzed Direct C−H Bond Arylation of 1-Methylbenzimidazole 2a with Chlorobenzene 3a

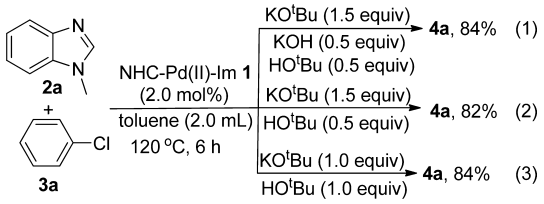


entry[a]	solvent	base	yield (%)
1	toluene/H_2O	K_2CO_3	ND
2	toluene/H_2O	KOH	ND
3	toluene/H_2O	$K_3PO_43H_2O$	ND
4	toluene/H_2O	LiO^{t}Bu	ND
5	toluene/H_2O	NaO^{t}Bu	<5
6	toluene/H_2O	KO^{t}Bu	89
7	THF/H_2O	KO^{t}Bu	48
8	dioxane/H_2O	KO^{t}Bu	40
9	DMSO/H_2O	KO^{t}Bu	ND
10	DMF/H_2O	KO^{t}Bu	ND
11	CH_3CN/H_2O	KO^{t}Bu	ND
12	DME/H_2O	KO^{t}Bu	ND
13	toluene	KO^{t}Bu	18
14[b]	toluene/H_2O	KO^{t}Bu	84
15[c]	toluene/H_2O	KO^{t}Bu	5

[a]If not otherwise specified, all reactions were carried out using **2a** (0.49 mmol), **3a** (2.0 equiv), base (2.0 equiv), **1** (2.0 mol %) in organic solvents (2.0 mL) and H_2O (0.5 equiv) at 120 °C for 6 h. [b]H_2O (1.0 equiv) was added. [c]H_2O (3.0 equiv) was added.

equiv) and H_2O (0.5 equiv), and product **4a** was obtained in a comparable yield (84%) (Table 1, entry 6 and Scheme 1, eq 1);

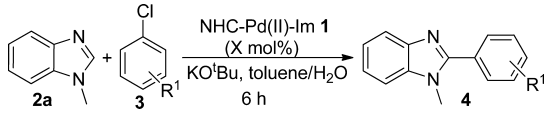
Scheme 1. Three Control Experiments



(2) the combination of KO^{t}Bu (1.5 equiv) and HO^{t}Bu (0.5 equiv) was introduced, and product **4a** was also formed in a comparable yield (82%) (Table 1, entry 6 and Scheme 1, eq 2); (3) the combination of KO^{t}Bu (1.0 equiv) and HO^{t}Bu (1.0 equiv) was introduced, and a similar yield of product **4a** was observed (84%) (Table 1, entry 14 and Scheme 1, eq 3). On the basis of these results, although the real function of H_2O was unclear at this stage, it could be inferred that when a combination of toluene and H_2O was used as the solvent, HO^{t}Bu derived from the hydrolysis of KO^{t}Bu might play an important role in such transformation.[12]

We next explored the scope of the C2-arylation of 1-methylbenzimidazole **2a** with a variety of aryl chlorides **3** under the identical optimal experimental conditions. Under the suitable conditions, the procedure proved to be general on all substrates tested (Table 2). It seems that the substituents on the aryl chlorides **3** affected the reactions to some extent. For

Table 2. NHC-Pd(II)-Im 1 Catalyzed Direct C−H Bond Arylation of 1-Methylbenzimidazole 2a with Aryl Chlorides 3



entry[a]	3 (R^1)	[X]	yield (%)
1	**3b** (4-Me)	2.0	**4b**, 85
2	**3c** (3-Me)	2.0	**4c**, 86
3	**3d** (2-Me)	2.0	**4d**, 52
4	**3d** (2-Me)	5.0	**4d**, 74
5	**3e** (4-OMe)	2.0	**4e**, 60
6	**3e** (4-OMe)	3.0	**4e**, 82
7	**3f** (3-OMe)	3.0	**4f**, 83
8[b]	**3g** (4-NMe_2)	3.0	**4g**, 42
9[b]	**3g** (4-NMe_2)	3.0	**4g**, 68
10[b]	**3h** (3-NMe_2)	3.0	**4h**, 87
11	**3i** (4-F)	2.0	**4i**, 82
12	**3j** (4-vinyl)	3.0	**4j**, 86
13	**3k** 	3.0	**4k**, 56
14	**3l** 	3.0	**4l**, 58

[a]If not otherwise specified, all reactions were carried out using **2a** (0.49 mmol), **3** (2.0 equiv), **1** (X mol %), KO^{t}Bu (2.0 equiv) in toluene/H_2O (2.0 mL/0.5 equiv) at 120 °C for 6 h. [b]The temperature was 130 °C.

example, for the reaction involving sterically hindered 2-methylphenyl chloride **3d**, good yields are obtained by simply increasing the catalyst loading, although only moderate yield can be obtained under the optimal reaction conditions (Table 2, entries 3 and 4). For electron-rich aryl chlorides such as 4-methoxyphenyl chloride **3e** and 4-dimethylaminophenyl chloride **3g**, slightly higher catalyst loading or elevated temperature is necessary for the achievement of higher yields (Table 2, entries 5 and 6; entries 8 and 9). In addition, heteroaryl chlorides such as 2-chloropyridine **3k** and 2-chlorothiophene **3l** could be used, giving rise to the desired products **4k** and **4l** in acceptable yields, respectively (Table 2, entries 13 and 14).

The reaction was further investigated using a variety of benzimidazoles **2** and aryl chlorides **3** as the substrates under the optimal conditions. As can be seen from Table 3, all 1-methylbenzimidazoles **2**, regardless of electron-rich substituents such as 5,6-Me_2 (**2b**), 5-Me (**2c**), 5-MeO (**2e**) or electron-poor substituents such as 5-F (**2d**) attaching on the phenyl groups, could react with aryl chlorides **3** smoothly to give the desired C2-arylated products **4** in good to high yields (Table 3, entries 1−17). In addition, it seems that for the reactions involving electron-poor 5-F-benzimidazole **2d**, better yields can be achieved under identical conditions (Table 3, entries 11−15). 1-Benzylbenzimidazole **2f** was also suitable for this reaction to give the corresponding products **4ad**−**4ag** in good yields (Table 3, entries 18−21).

Encouraged by the above results using benzimidazoles as the substrates, the optimal conditions were then expanded to the

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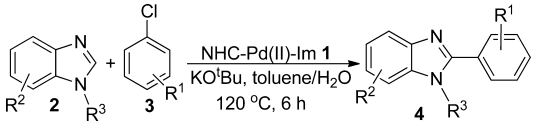
Table 3. NHC-Pd(II)-Im 1 Catalyzed Direct C−H Bond Arylation of Benzimidazoles 2 with Aryl Chlorides 3



entry[a]	2 (R^2/R^3)	3 (R^1)	yield (%)
1	**2b** (5,6-Me$_2$/Me)	**3a** (H)	**4m**, 87
2	**2b**	**3b** (4-Me)	**4n**, 84
3[b]	**2b**	**3e** (4-OMe)	**4o**, 82
4	**2b**	**3i** (4-F)	**4p**, 86
5[b]	**2b**	**3j** (4-vinyl)	**4q**, 84
6	**2c** (5-Me/Me)	**3a**	**4r**, 86
7	**2c**	**3b**	**4s**, 85
8[b]	**2c**	**3e**	**4t**, 84
9	**2c**	**3i**	**4u**, 88
10[b]	**2c**	**3j**	**4v**, 86
11	**2d** (5-F/Me)	**3a**	**4w**, 97
12	**2d**	**3b**	**4x**, 96
13	**2d**	**3e**	**4y**, 86
14	**2d**	**3i**	**4z**, 96
15	**2d**	**3j**	**4aa**, 88
16	**2e** (5-OMe/Me)	**3a**	**4ab**, 86
17	**2e**	**3b**	**4ac**, 84
18	**2f** (H/benzyl)	**3a**	**4ad**, 84
19	**2f**	**3b**	**4ae**, 85
20[b]	**2f**	**3e**	**4af**, 82
21	**2f**	**3j**	**4ag**, 84

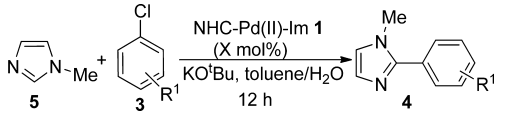
[a]If not otherwise specified, all reactions were carried out using **2a** (0.49 mmol), **3** (2.0 equiv), **1** (2.0 mol %), KO^{t}Bu (2.0 equiv) in toluene/H$_2$O (2.0 mL/0.5 equiv) at 120 °C for 6 h. [b]NHC-Pd(II)-Im **1** (3.0 mol %) was added.

reactions between 1-methylimidazole and aryl chlorides. It was found that the ratio between two substrates dramatically affected the reaction. For example, when the reaction between 1-methylimidazole (0.49 mmol) and chlorobenzene (2.0 equiv) was carried out under the optimal conditions shown in Table 1, entry 6, the desired C2-arylated product was obtained only in 29% yield, along with the 2,5-diarylated byproduct in 8% yield. To our pleasure, subtly changing the ratio of the substrates will result in exclusive C2-arylated selectivity. For instance, when excess 1-methylimidazole (2.0 equiv) was used as the substrate, the desired C2-arylated products could be achieved in good to high yields as the sole product under the optimal conditions. The results are shown in Table 4. It seems that substituents on the aryl chlorides have some effect on the reaction. For example, aryl chlorides having electron-rich groups such as 4-Me (**3b**) and 3-Me (**3c**) gave better yields than that having electron-neutral (**3a**) and electron-poor 4-F group (**3i**) (Table 4, entries 2 and 3 vs entries 1 and 5). In addition, 2-methylphenyl chloride **3d** gave inferior result (74%), maybe partially due to its steric hindrance (Table 4, entry 4).

CONCLUSIONS

In conclusion, NHC-Pd(II)-Im complex, as the nonphosphine complex, was first used as the catalyst in the direct C−H bond arylation of (benz)imidazoles using the less expensive, less active, and easily available aryl chlorides as the arylating reagents. Under the optimal conditions, various (benz)-imidazoles can react with kinds of activated, unactivated, and deactivated aryl chlorides smoothly to give the desired C2-arylated products in good to high yields.[13] For instance, both substrates bearing electron-rich, -neutral, and -poor substituents are tolerated in such transformation. The NHC-Pd(II) complex catalyzed direct C−H bond arylation between (benz)imidazoles and aryl chlorides reported in this paper will become a good, economical, and efficient supplement to the traditional methods for the formation of 2-aryl (benz)imidazoles.

Table 4. NHC-Pd(II)-Im 1 Catalyzed Direct C−H Bond Arylation of 1-Methylimidazole 5 with Aryl Chlorides 3



entry[a]	3 (R^1)	[X]	t (°C)	yield (%)
1	**3a** (H)	2	120	**4ah**, 86
2	**3b** (4-Me)	3	140	**4ai**, 99
3	**3c** (3-Me)	3	130	**4aj**, 97
4	**3d** (2-Me)	4	140	**4ak**, 74
5	**3i** (4-F)	4	140	**4al**, 84
6	**3j** (4-vinyl)	3	130	**4am**, 87

[a]All reactions were carried out using **5** (2.0 equiv), **3** (0.75 mmol), KO^{t}Bu (2.0 equiv), **1** (X mol %) in toluene/H$_2$O (2.0 mL/0.5 equiv) for 12 h.

EXPERIMENTAL SECTION

General Remarks. Melting points are uncorrected. NMR spectra were recorded at 300/500 (for ^{1}H NMR) or 75/125 MHz (for ^{13}C NMR), respectively. ^{1}H NMR and ^{13}C NMR spectra recorded in CDCl$_3$ 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 (HRMS, ESI) is 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 1 Catalyzed Reactions Between (Benz)imidazoles and Aryl Chlorides. Under N$_2$ atmosphere, KO^{t}Bu (0.98 mmol), NHC-Pd(II)-Im complex **1** (0.0098 mmol), toluene (2.0 mL), H$_2$O (0.245 mmol), benzimidazoles **2** (0.49 mmol) and aryl chlorides **3** (0.98 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at 120 °C for 6 h. Then the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 10:1 for benzimidazole derivatives and 3:1 for imidazole derivatives) to give the pure products **4**.

Compound **4a**:[3j] white solid (90.7 mg, 89%); ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 7.85−7.76 (m, 3H), 7.57−7.52 (m, 3H), 7.41−7.29 (m, 3H); ^{13}C{H} NMR (CDCl$_3$, 75 MHz) δ 153.7, 142.9, 136.5, 130.1, 129.7, 129.4, 128.6, 122.7, 122.4, 119.8, 109.6, 31.7.

Compound **4b**:[3j] white solid (92.6 mg, 85%); ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 7.85−7.80 (m, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.36−7.25 (m, 5H), 3.80 (s, 3H), 2.42 (s, 3H); ^{13}C{H} NMR (CDCl$_3$, 75 MHz) δ 153.8, 142.8, 139.7, 136.4, 129.24, 129.17, 127.1, 122.5, 122.2, 119.5, 109.5, 31.5, 21.3.

Compound **4c**:[3j] white solid (94.0 mg, 86%); ^{1}H NMR (CDCl$_3$, 500 MHz, TMS) δ 7.83−7.81 (m, 1H), 7.60 (s, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.34−7.28 (m, 4H), 3.79 (s, 3H), 2.42 (s, 3H); ^{13}C{H} NMR (CDCl$_3$, 75 MHz) δ 153.8, 142.7, 138.5, 136.4, 130.4, 130.1, 129.9, 128.3, 126.2, 122.6, 122.3, 119.6, 109.5, 31.5, 21.3.

Compound **4d**:[14] white solid (80.4 mg, 74%); ^{1}H NMR (CDCl$_3$, 500 MHz, TMS) δ 7.84−7.82 (m, 1H), 7.44−7.30 (m, 7H), 3.63 (s, 3H), 2.27 (s, 3H); ^{13}C{H} NMR (CDCl$_3$, 75 MHz) δ 153.7, 142.9,

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137.9, 135.5, 130.4, 130.2, 129.9, 129.8, 125.7, 122.5, 122.2, 119.8, 109.4, 30.5, 19.6.

Compound **4e**:[3j] white solid (96.2 mg, 82%); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.82−7.78 (m, 1H), 7.72 (d, J = 7.5 Hz, 2H), 7.40−7.29 (m, 3H), 7.05 (d, J = 7.5 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 160.6, 153.6, 142.8, 136.5, 130.7, 122.38, 122.37, 122.2, 119.4, 114.0, 109.4, 55.3, 31.6.

Compound **4f**:[15] white solid (96.8 mg, 83%); ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.84−7.82 (m, 1H), 7.46−7.40 (m, 2H), 7.34−7.30 (m, 4H), 7.07−7.05 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 159.7, 153.6, 142.8, 136.5, 131.3, 129.6, 122.8, 122.4, 121.6, 119.8, 115.9, 114.6, 109.6, 55.4, 31.7.

Compound **4g**:[16] white solid (83.8 mg, 68%); ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.80 (dd, J = 6.0, 2.5 Hz, 1H), 7.69 (d, J = 9.0 Hz, 2H), 7.35 (dd, J = 6.0, 2.5 Hz, 1H), 7.36−7.27 (m, 2H), 6.81 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.05 (s, 6H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 154.6, 151.0, 143.0, 136.6, 130.3, 121.94, 121.91, 119.1, 117.2, 111.6, 109.2, 40.1, 31.7.

Compound **4h**: yellow liquid (107.2 mg, 87%); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.86−7.80 (m, 1H), 7.39−7.28 (m, 4H), 7.12−7.11 (m, 1H), 7.01−6.97 (m, 1H), 6.87−6.83 (m, 1H), 3.84 (s, 3H), 3.01 (s, 6H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 154.7, 150.6, 142.8, 136.5, 130.7, 129.0, 122.5, 122.2, 119.6, 117.2, 113.6, 113.4, 109.5, 40.5, 31.6; MS (ESI) 252 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{18}N_3$ $[M + H]^+$ 252.1495, found 252.1506; IR (neat) ν 2363, 1607, 1483, 1436, 1348, 1284, 1242, 1126, 1062, 990, 956, 845, 776, 737, 695 cm^{-1}.

Compound **4i**:[17] white solid (90.8 mg, 82%); ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.82−7.80 (m, 1H), 7.74 (dd, J = 8.5, 5.0 Hz, 2H), 7.38−7.29 (m, 3H), 7.21 (t, J = 8.5 Hz, 2H), 3.82 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 125 MHz) δ 163.6 (d, J_{C-F} = 249.0 Hz), 152.7, 142.8, 136.5, 131.3 (d, J_{C-F} = 8.5 Hz), 130.2, 126.3 (d, J_{C-F} = 3.1 Hz), 123.8, 122.8, 122.5, 119.8, 115.8 (d, J_{C-F} = 21.6 Hz), 109.6, 31.6.

Compound **4j**: white solid (98.6 mg, 86%); mp 116−117 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.84−7.81 (m, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.35−7.27 (m, 3H), 6.75 (dd, J = 17.7, 10.8 Hz, 1H), 5.84 (d, J = 17.7 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H), 3.80 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 153.1, 142.3, 138.8, 136.3, 135.9, 129.5, 128.9, 126.3, 122.8, 122.5, 119.4, 115.4, 109.6, 31.6; MS (ESI) 235 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{15}N_2$ $[M + H]^+$ 235.1230, found 235.1228; IR (neat) ν 1630, 1464, 1402, 1377, 1322, 1250, 993, 909, 851, 821, 760, 745, 738, 702 cm^{-1}.

Compound **4k**:[18] white solid (57.5 mg, 56%); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 8.69−8.67 (m, 1H), 8.38 (d, J = 8.1 Hz, 1H), 7.85−7.80 (m, 2H), 7.44−7.28 (m, 4H), 4.25 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 150.5, 150.2, 148.5, 142.3, 137.2, 136.8, 124.7, 123.7, 123.3, 122.6, 119.9, 109.9, 32.6.

Compound **4l**:[16] white solid (61.0 mg, 58%); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.81−7.77 (m, 1H), 7.57−7.55 (m 1H), 7.51−7.49 (m, 1H), 7.35−7.26 (m, 3H), 7.19−7.16 (m, 1H), 3.94 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 147.7, 142.6, 136.4, 132.3, 128.5, 127.9, 127.8, 122.9, 122.6, 119.6, 109.3, 31.6.

Compound **4m**: white solid (100.6 mg, 87%); mp 171−172 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.76−7.73 (m, 2H), 7.57 (s, 1H), 7.54−7.47 (m, 3H), 7.15 (s, 1H), 3.81 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 152.9, 141.5, 135.2, 131.9, 131.2, 130.5, 129.4, 129.3, 128.6, 119.8, 109.8, 31.6, 20.6, 20.3; MS (ESI) 237 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{17}N_2$ $[M + H]^+$ 237.1386, found 237.1402; IR (neat) ν 1601, 1534, 1438, 1381, 1318, 1176, 1020, 1000, 924, 846, 818, 771, 690 cm^{-1}.

Compound **4n**: white solid (103.0 mg, 84%); mp 122−123 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.63 (d, J = 7.8 Hz, 2H), 7.57 (s, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.12 (s, 1H), 3.77 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 152.7, 140.6, 139.7, 134.8, 131.9, 131.3, 129.25, 129.18, 126.9, 119.3, 109.8, 31.6, 21.3, 20.5, 20.2; MS (ESI) 251 $[M + H]^+$; HRMS (ESI) calcd for $C_{17}H_{19}N_2$ $[M + H]^+$ 251.1543, found 251.1552; IR (neat) ν 1604, 1478, 1461, 1377, 1323, 1180, 1140, 1107, 1014, 871, 850, 819, 729, 681 cm^{-1}.

Compound **4o**: white solid (107.0 mg, 82%); mp 147−148 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.72 (d, J = 8.7 Hz, 2H), 7.56 (s, 1H), 7.13 (s, 1H), 7.01 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 160.6, 153.0, 141.5, 135.2, 131.6, 131.0, 130.7, 122.9, 119.6, 114.0, 109.7, 55.4, 31.6, 20.6, 20.3; HRMS (ESI) calcd for $C_{17}H_{19}N_2O$ $[M + H]^+$ 267.1492, found 267.1495; IR (neat) ν 1610, 1481, 1436, 1382, 1320, 1289, 1242, 1171, 1022, 875, 831, 792, 750, 717 cm^{-1}.

Compound **4p**: white solid (107.0 mg, 86%); mp 172−173 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.74−7.68 (m, 2H), 7.55 (s, 1H), 7.20−7.12 (m, 3H), 3.77 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 163.5 (d, J_{C-F} = 248.8 Hz), 151.6, 140.6, 134.8, 132.2, 131.6, 131.3 (d, J_{C-F} = 8.4 Hz), 130.2, 126.0, 123.5, 119.4, 115.7 (d, J_{C-F} = 21.7 Hz), 109.9, 31.6, 28.8, 20.5, 20.2; MS (ESI) 255 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{15}N_2F$ $[M + H]^+$ 255.1292, found 255.1294; IR (neat) ν 1607, 1525, 1436, 1377, 1318, 1219, 1157, 1003, 837, 809, 730, 706, 674 cm^{-1}.

Compound **4q**: white solid (107.9 mg, 84%); mp 142−143 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.74 (d, J = 8.4 Hz, 2H), 7.58 (s, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.15 (s, 1H), 6.75 (dd, J = 17.4, 11.1 Hz, 1H), 5.85 (d, J = 17.4 Hz, 1H), 5.36 (d, J = 11.1 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 152.2, 140.7, 138.7, 136.0, 134.9, 132.1, 131.5, 129.4, 129.0, 126.3, 119.4, 115.2, 109.8, 31.7, 20.5, 20.2; MS (ESI) 263 $[M + H]^+$; HRMS (ESI) calcd for $C_{18}H_{19}N_2$ $[M + H]^+$ 263.1543, found 263.1545; IR (neat) ν 1627, 1461, 1382, 1323, 1143, 1059, 1008, 990, 903, 841, 761, 716, 686 cm^{-1}.

Compound **4r**: white solid (93.6 mg, 86%); mp 122−123 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 7.73−7.71 (m, 2H), 7.61 (s, 1H), 7.50−7.46 (m, 3H), 7.22 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 3.77 (s, 3H), 2.49 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 125 MHz) δ 153.3, 142.6, 134.4, 132.0, 129.8, 129.5, 129.2, 128.5, 124.2, 119.2, 109.1, 31.5, 21.4; MS (ESI) 223 $[M + H]^+$; HRMS (ESI) calcd for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1232; IR (neat) ν 1494, 1461, 1372, 1322, 1013, 927, 862, 793, 768, 743, 701, 675 cm^{-1}.

Compound **4s**: white solid (98.4 mg, 85%); mp 118−119 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.75 (d, J = 8.1 Hz, 2H), 7.60 (s, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 3.81 (s, 3H), 2.49 (s, 3H), 2.42 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 153.3, 142.1, 140.0, 134.3, 132.3, 129.33, 129.26, 126.6, 124.3, 119.0, 109.1, 31.7, 21.5, 21.4; MS (ESI) 237 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{17}N_2$ $[M + H]^+$ 237.1386, found 237.1401; IR (neat) ν 1613, 1475, 1444, 1377, 1318, 1020, 878, 848, 821, 789, 747, 727 cm^{-1}.

Compound **4t**: white solid (103.7 mg, 84%); mp 105−106 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.66 (d, J = 8.7 Hz, 2H), 7.58 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.1 Hz, 1H), 6.98 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H), 2.48 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 160.6, 153.2, 142.5, 134.4, 131.9 130.6 123.8, 122.1, 118.9, 113.9, 108.9, 55.2, 31.5, 21.4; MS (ESI) 253 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{17}N_2O$ $[M + H]^+$ 253.1335, found 253.1344; IR (neat) ν 1607, 1481, 1464, 1448, 1385, 1328, 1179, 1245, 1109, 833, 781, 763, 738, 682 cm^{-1}.

Compound **4u**: white solid (103.4 mg, 88%); mp 129−130 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.77−7.68 (m, 2H), 7.58 (s, 1H), 7.27−7.11 (m, 4H), 3.81 (s, 3H), 2.49 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 163.6 (d, J_{C-F} = 249.1 Hz), 152.3, 142.2, 134.3, 132.5, 131.4 (d, J_{C-F} = 8.5 Hz), 125.8, 124.5, 123.5, 119.1, 115.8 (d, J_{C-F} = 21.7 Hz), 109.2, 31.6, 28.8, 21.5; MS (ESI) 241 $[M + H]^+$; HRMS (ESI) calcd for $C_{15}H_{14}N_2F$ $[M + H]^+$ 241.1136, found 241.1132; IR (neat) ν 1607, 1537, 1467, 1381, 1315, 1235, 1152, 838, 804, 791, 756, 733, 682 cm^{-1}.

Compound **4v**: white solid (104.5 mg, 86%); mp 121−122 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.68 (d, J = 8.1 Hz, 2H), 7.60 (s, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.73 (dd, J = 17.7, 10.8 Hz, 1H), 5.82 (d, J = 17.7 Hz, 1H), 5.32 (d, J = 10.8 Hz, 1H), 3.75 (s, 3H), 2.48 (s, 3H); ^{13}C{H} NMR ($CDCl_3$, 75 MHz) δ 152.9, 142.6, 138.6, 135.9, 134.5, 132.0, 129.4, 129.0, 126.2, 124.2, 119.1, 115.2, 109.0, 31.6, 21.4; MS (ESI) 249 $[M + H]^+$; HRMS (ESI) calcd for $C_{17}H_{17}N_2$ $[M + H]^+$ 249.1386, found

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249.1390; IR (neat) ν 1621, 1455, 1382, 1323, 1250, 1146, 1059, 1017, 985, 899, 843, 791, 739, 686 cm^{-1}.

Compound **4w**: white solid (107.5 mg, 97%); mp 102−103 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.73−7.70 (m, 2H), 7.50−7.45 (m, 4H), 7.25−7.22 (m, 1H), 7.02 (td, J = 9.0, 2.4 Hz, 1H), 3.80 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.4 (d, J_{C-F} = 236.0 Hz), 154.8, 142.7 (d, J_{C-F} = 12.6 Hz), 132.9, 129.9, 129.3 (d, J_{C-F} = 19.1 Hz), 128.6, 111.1, 110.7, 109.9 (d, J_{C-F} = 10.2 Hz), 105.1 (d, J_{C-F} = 24.1 Hz), 31.7; MS (ESI) 227 $[M + H]^+$; HRMS (ESI) calcd for $C_{14}H_{12}N_2F$ $[M + H]^+$ 227.0979, found 227.0976; IR (neat) ν 1621, 1593, 1489, 1472, 1424, 1374, 1326, 1143, 1020, 956, 900, 852, 791, 776, 751, 702 cm^{-1}.

Compound **4x**: a white solid (113.0 mg, 96%); mp 117−118 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.63 (d, J = 8.1 Hz, 2H), 7.47 (dd, J = 9.3, 2.4 Hz, 1H), 7.33−7.25 (m, 3H), 7.04 (td, J = 9.3, 2.4 Hz, 1H), 3.83 (s, 3H), 2.43 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.5 (d, J_{C-F} = 236.3 Hz), 154.9, 142.4, 142.3, 140.4, 132.8, 129.3 (d, J_{C-F} = 14.7 Hz), 126.3, 111.2, 110.8, 110.0 (d, J_{C-F} = 10.2 Hz), 105.0 (d, J_{C-F} = 24.2 Hz), 31.8, 21.4; MS (ESI) 241 $[M + H]^+$; HRMS (ESI) calcd for $C_{15}H_{14}N_2F$ $[M + H]^+$ 241.1136, found 241.1147; IR (neat) ν 1618, 1593, 1483, 1430, 1382, 1326, 1242, 1124, 1014, 955, 855, 828, 803, 775, 734, 716 cm^{-1}.

Compound **4y**: white solid (107.9 mg, 86%); mp 105−106 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.67 (d, J = 8.7 Hz, 2H), 7.44 (dd, J = 9.0, 2.4 Hz, 1H), 7.23 (dd, J = 9.0, 4.5 Hz, 1H), 7.04−6.98 (m, 3H), 3.85 (s, 3H), 3.80 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 160.9, 159.4 (d, J_{C-F} = 235.7 Hz), 154.8, 142.6 (d, J_{C-F} = 12.8 Hz), 132.8, 130.7, 121.6, 114.1, 110.8, 110.5, 109.8 (d, J_{C-F} = 10.2 Hz), 104.9 (d, J_{C-F} = 24.1 Hz), 55.3, 31.8; MS (ESI) 257 $[M + H]^+$; HRMS (ESI) calcd for $C_{15}H_{14}N_2FO$ $[M + H]^+$ 257.1085, found 257.1098; IR (neat) ν 1610, 1481, 1436, 1334, 1292, 1242, 1183, 1115, 1020, 955, 844, 826, 796, 778, 741, 716 cm^{-1}.

Compound **4z**: a white solid (114.8 mg, 96%); mp 124−125 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.73 (dd, J = 8.4, 5.4 Hz, 2H), 7.45 (dd, J = 9.3, 2.4 Hz, 1H), 7.29−7.18 (m, 3H), 7.04 (td, J = 9.3, 2.4 Hz, 1H), 3.82 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 163.7 (d, J_{C-F} = 249.6 Hz), 159.5 (d, J_{C-F} = 236.3 Hz), 153.9, 142.6 (d, J_{C-F} = 12.8 Hz), 132.8, 131.3 (d, J_{C-F} = 8.5 Hz), 130.2, 125.6 (d, J_{C-F} = 3.2 Hz), 115.9 (d, J_{C-F} = 21.8 Hz), 111.3, 111.0, 110.0 (d, J_{C-F} = 10.1 Hz), 105.1 (d, J_{C-F} = 24.1 Hz), 31.7; MS (ESI) 245 $[M + H]^+$; HRMS (ESI) calcd for $C_{14}H_{11}N_2F_2$ $[M + H]^+$ 245.0885, found 245.0895; IR (neat) ν 1587, 1483, 1430, 1388, 1326, 1233, 1155, 1121, 1090, 961, 850, 803, 733 cm^{-1}.

Compound **4aa**: white solid (108.8 mg, 88%); mp 144−145 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.74 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 9.0 Hz, 1H), 7.31 (dd, J = 9.0, 4.5 Hz, 1H), 7.08 (t, J = 9.0 Hz, 1H), 6.77 (dd, J = 17.4, 10.8 Hz, 1H), 5.87 (d, J = 17.7 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 3.88 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.4 (d, J_{C-F} = 236.2 Hz), 154.5, 142.7 (d, J_{C-F} = 12.8 Hz), 139.0, 135.8, 132.9, 129.4, 128.6, 126.4, 115.5, 111.0 (d, J_{C-F} = 26.0 Hz), 109.9 (d, J_{C-F} = 10.3 Hz), 105.1 (d, J_{C-F} = 24.1 Hz), 31.8; MS (ESI) 252 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{14}N_2F$ $[M + H]^+$ 253.1136, found 253.1150; IR (neat) ν 1624, 1481, 1438, 1405, 1326, 1273, 1143, 1000, 959, 909, 895, 851, 803, 738, 712 cm^{-1}.

Compound **4ab**:[19] white solid (100.4 mg, 86%); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.75−7.72 (m, 2H), 7.53−7.47 (m, 3H), 7.31 (d, J = 2.1 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 6.95 (dd, J = 9.0, 5.4 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 156.4, 153.5, 142.9, 130.9, 129.7, 129.6, 129.2, 128.6, 112.9, 110.0, 101.5, 55.7, 31.6.

Compound **4ac**: white solid (103.7 mg, 84%); mp 100−101 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.63 (d, J = 8.1 Hz, 2H), 7.32−7.30 (m, 3H), 7.23 (d, J = 8.7 Hz, 1H), 6.95 (dd, J = 8.7, 2.4 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.43 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 156.3, 153.9, 143.4, 139.7, 131.2, 129.3, 129.1, 127.2, 112.6, 109.8, 101.7, 55.8, 31.7, 21.3; MS (ESI) 253 $[M + H]^+$; HRMS (ESI) calcd for $C_{16}H_{17}N_2O$ $[M + H]^+$ 253.1335, found 253.1351; IR (neat) ν 1618, 1590, 1486, 1433, 1377, 1332, 1273, 1194, 1160, 1028, 948, 826, 798, 729, 713 cm^{-1}.

Compound **4ad**:[20] white solid (117.1 mg, 84%); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.88 (d, J = 8.1 Hz, 1H), 7.68−7.66 (m, 2H), 7.44−7.38 (m, 3H), 7.31−7.23 (m, 4H), 7.20−7.15 (m, 2H), 7.06 (d, J = 6.6 Hz, 2H), 5.40 (s, 2H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 154.0, 143.0, 136.2, 136.0, 129.9, 129.8, 129.1, 128.9, 128.6, 127.6, 125.8, 122.9, 122.5, 119.8, 110.4, 48.2.

Compound **4ae**:[20] white solid (124.2 mg, 85%); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.88 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.29−7.15 (m, 8H), 7.07 (d, J = 6.9 Hz, 2H), 5.41 (s, 2H), 2.38 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 154.0, 142.5, 140.1, 136.2, 135.8, 129.4, 129.0, 128.9, 127.6, 126.6, 125.8, 122.9, 122.6, 119.6, 110.4, 48.3, 21.3.

Compound **4af**:[20] white solid (126.2 mg, 82%); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.86 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.34−7.25 (m, 4H), 7.23−7.15 (m, 2H), 7.10−7.07 (m, 2H), 6.97−6.92 (m, 2H), 5.42 (s, 2H), 3.81 (s, 3H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 160.9, 153.8, 142.4, 136.2, 135.8, 130.6, 129.0, 127.7, 125.8, 122.8, 122.7, 121.7, 119.4, 114.1, 110.3, 55.2, 48.3.

Compound **4ag**: white solid (127.6 mg, 84%); mp 134−135 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 7.90 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.30−7.08 (m, 8H), 6.73 (dd, J = 17.4, 10.5 Hz, 1H), 5.82 (d, J = 17.4 Hz, 1H), 5.45 (s, 2H), 5.33 (d, J = 10.5 Hz, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$, 75 MHz) δ 153.5, 142.5, 138.9, 136.0, 135.81, 135.78, 129.2, 128.9, 128.7, 127.6, 126.4, 125.7, 123.0, 122.7, 119.6, 115.4, 110.4, 48.2; MS (ESI) 311 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{19}N_2$ $[M + H]^+$ 311.1543, found 311.1551; IR (neat) ν 1604, 1452, 1388, 1354, 1326, 1242, 1157, 1076, 980, 917, 854, 778, 761, 724, 716, 695 cm^{-1}.

Compound **4ah**:[21] colorless liquid (101.9 mg, 86%); ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.62 (d, J = 8.0 Hz, 2H), 7.45−7.38 (m, 3H), 7.11 (s, 1H), 6.95 (s, 1H), 3.72 (s, 3H); $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$) δ 147.7, 130.5, 128.5, 128.45, 128.36, 128.3, 122.2, 34.3.

Compound **4ai**:[22] colorless liquid (127.8 mg, 99%); ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.52 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 0.9 Hz, 1H), 6.95 (d, J = 0.9 Hz, 1H), 3.73 (s, 3H), 2.40 (s, 3H); $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$) δ 147.9, 138.4, 129.1, 128.4, 128.2, 127.7, 122.0, 34.6, 21.2.

Compound **4aj**:[23] colorless liquid (125.1 mg, 97%); ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.47 (s, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 1.5 Hz, 1H), 6.93 (d, J = 1.5 Hz, 1H), 3.71 (s, 3H), 2.39 (s, 3H); $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$) δ 147.8, 138.1, 130.3, 129.3, 129.2, 128.11, 128.10, 125.3, 122.1, 34.3, 21.2.

Compound **4ak**: colorless liquid (95.5 mg, 74%); ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.34−7.24 (m, 4H), 7.13 (s, 1H), 6.97 (s, 1H), 3.47 (s, 3H), 2.22 (s, 3H); $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$) δ 147.6, 138.2, 130.3, 130.22, 130.18, 129.1, 128.0, 125.4, 120.4, 33.2, 19.5; MS (ESI) 173 $[M + H]^+$; HRMS (ESI) calcd for $C_{11}H_{13}N_2$ $[M + H]^+$ 173.1073, found 173.1088; IR (neat) ν 1623, 1557, 1471, 1401, 1338, 1282, 1143, 1116, 1013, 987, 914, 906, 844, 791, 750, 717, 685 cm^{-1}.

Compound **4al**:[24] colorless liquid (110.8 mg, 84%); ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.60 (dd, J = 8.5, 5.5 Hz, 2H), 7.14 (t, J = 8.5 Hz, 2H), 7.10 (d, J = 1.0 Hz, 1H), 6.96 (d, J = 1.0 Hz, 1H), 3.72 (s, 3H); $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 247.1 Hz), 146.9, 130.5 (d, J_{C-F} = 8.3 Hz), 128.3, 126.8 (d, J_{C-F} = 3.3 Hz), 122.3, 115.5 (d, J_{C-F} = 21.6 Hz), 34.3.

Compound **4am**: colorless liquid (120.0 mg, 87%); ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.60 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 1.0 Hz, 1H), 6.94 (d, J = 1.0 Hz, 1H), 6.74 (dd, J = 18.0, 10.5 Hz, 1H), 5.81 (dd, J = 18.0, 0.5 Hz, 1H), 5.30 (dd, J = 10.5, 0.5 Hz, 1H), 3.72 (s, 3H); $^{13}C\{H\}$ NMR (125 MHz, $CDCl_3$) δ 147.4, 137.5, 136.1, 129.8, 128.5, 128.3, 126.1, 122.4, 114.6, 34.4; MS (ESI) 185 $[M + H]^+$; HRMS (ESI) calcd for $C_{12}H_{13}N_2$ $[M + H]^+$ 185.1073, found 185.1083; IR (neat) ν 1600, 1504, 1467, 1454, 1338, 1275, 1129, 1017, 949, 914, 846, 804, 778, 727, 692 cm^{-1}.

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■ ASSOCIATED CONTENT

Supporting Information

Copy of ^{1}H and ^{13}C NMR spectra of compounds **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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