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Palladium-catalyzed Suzuki–Miyaura coupling of aryl sulfamates with arylboronic acids†

Zhan-Yong Wang,[a] Qin-Na Ma,[a] Ren-Hao Li[a] and Li-Xiong Shao*[a,b]

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Readily available NHC–Pd(II)–Mp complexes **2** showed efficient catalytic activity toward the Suzuki–Miyaura coupling of aryl sulfamates with arylboronic acids or potassium phenyltrifluoroborate, giving the expected coupling products in good to high yields. It should be noted that this is the first example so far of the phosphine-free, NHC–Pd(II) complexes catalyzed Suzuki–Miyaura coupling of aryl sulfamates with arylboronic acids.

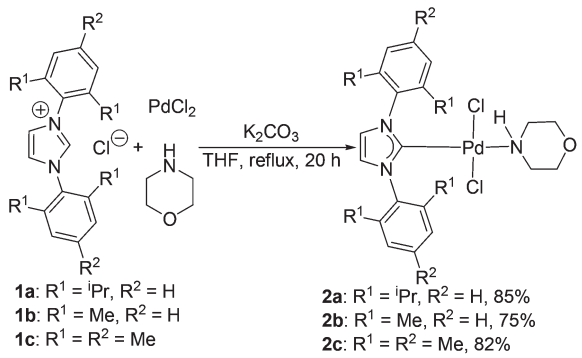
Introduction

Transition metal catalyzed Suzuki–Miyaura coupling is one of the most versatile methods for the formation of carbon–carbon bonds.[1] Traditionally, aryl (pseudo)halides have been used as electrophiles. During the past few years, electrophiles have been extended to more challenging substrates such as C–O-based electrophiles.[2] Recently, we have reported that the N-heterocyclic carbene–palladium(II)-1-methylimidazole [NHC–Pd(II)–Im] complex is an efficient catalyst for the Suzuki–Miyaura coupling of aryl sulfonates with arylboronic acids using morpholine as the sole solvent. Further control experiments showed that in the reported procedure, the imidazole moiety in the NHC–Pd(II)–Im complex can be displaced by morpholine, thus resulting in the N-heterocyclic carbene–palladium(II)–morpholine [NHC–Pd(II)–Mp] complex as a real precatalyst, which can also display a similar catalytic activity to that of the NHC–Pd(II)–Im complex.[3] These results thus motivated us to further investigate these complexes in the Suzuki–Miyaura coupling using other less active, challenging C–O-based electrophiles.

Sulfamates, which can also be easily prepared from cheap and commercially available phenols with dimethylsulfamoyl chloride, are also attractive electrophiles. Compared to the transition metal complexes catalyzed coupling reactions using aryl sulfonates as electrophiles,[3] less attention has been paid to the field of aryl sulfamates, which are more unreactive in coupling reactions.[4,5] In addition, although significant progress has been achieved, reported methods are mainly limited to Ni catalysts, which still have some drawbacks such as relatively high catalyst loading, along with phosphine-based ligands. Furthermore, to the best of our knowledge, at present, no Pd-catalyzed reactions of aryl sulfamates with arylboronic acids are known. Thus, we turned our attention to the NHC–Pd(II) complexes catalyzed Suzuki–Miyaura coupling of aryl sulfamates. In our further investigations, it was found that N-heterocyclic carbene–palladium(II)–morpholine [NHC–Pd(II)–Mp] complexes are efficient catalysts in the Suzuki–Miyaura coupling of aryl sulfamates with arylboronic acids or potassium phenyltrifluoroborate. Herein, we report these results in detail.

Results and discussion

First, using our previously reported procedure,[6] NHC–Pd(II)–Mp complexes **2** were easily obtained in 75–85% yield from commercially available imidazolium salts **1**, $PdCl_2$ and morpholine in a one-step process (Scheme 1). The complexes are air-, moisture- and thermal-stable and can be kept under air at least for several weeks.

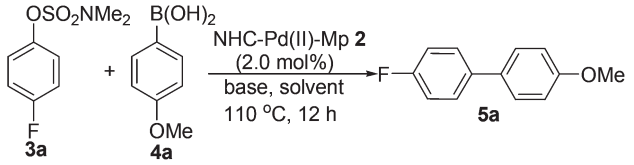


Scheme 1 Synthesis of the NHC–Pd(II)–Mp complexes **2**.

[a]*College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Wenzhou, Zhejiang Province 325035, People's Republic of China. E-mail: Shaolix@wzu.edu.cn; Fax: +86 57786689300; Tel: +86 57786689300*
[b]*College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang Province 321004, People's Republic of China*

†Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of compounds **2** and **5**. See DOI: 10.1039/c3ob41382a

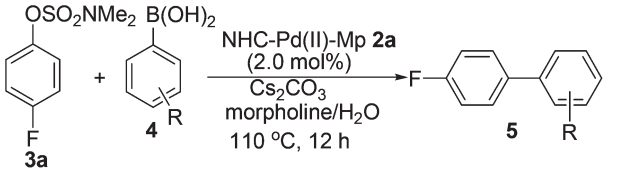
Table 1 Optimization of the NHC–Pd(II)–Mp complexes **2** catalyzed coupling of sulfamate **3a** with 4-methoxyphenylboronic acid **4a**

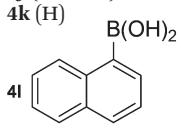
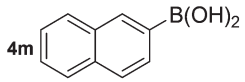


Entry[a]	2	Base	Solvent	Yield[b] (%)
1	**2a**	$KF{\cdot}2H_2O$	Morpholine–H_2O	6
2	**2a**	$K_3PO_4{\cdot}3H_2O$	Morpholine–H_2O	84
3	**2a**	K_2CO_4	Morpholine–H_2O	51
4	**2a**	$Na_3PO_4{\cdot}12H_2O$	Morpholine–H_2O	57
5	**2a**	$KHCO_3$	Morpholine–H_2O	5
6	**2a**	KAOc	Morpholine–H_2O	26
7	**2a**	Cs_2CO_3	Morpholine–H_2O	94
8	**2a**	KO^tBu	Morpholine–H_2O	48
9	**2a**	NaO^tBu	Morpholine–H_2O	24
10	**2a**	Cs_2CO_3	Toluene–H_2O	7
11	**2a**	Cs_2CO_3	DMF–H_2O	20
12	**2a**	Cs_2CO_3	Dioxane–H_2O	5
13	**2b**	Cs_2CO_3	Morpholine–H_2O	72
14	**2c**	Cs_2CO_3	Morpholine–H_2O	81
15	**2a**	Cs_2CO_3	Morpholine	60
16	**2a**	Cs_2CO_3	Morpholine–H_2O[c]	89
17	**2a**	Cs_2CO_3	Morpholine–H_2O[d]	83
18	**2a**	Cs_2CO_3	Morpholine–H_2O[e]	38
19	**2a**	No base	Morpholine–H_2O	ND

[a] Unless otherwise specified, all reactions were carried out using **3a** (0.7 mmol), **4a** (1.2 mol%), and base (3.0 equiv.) in the mixture of organic solvent (1.0 mL) and H_2O (0.1 mL) at 110 °C for 12 h. [b] Isolated yields. [c] Morpholine–H_2O = 1.0/0.2 mL. [d] Morpholine–H_2O = 1.0/0.3 mL. [e] Morpholine–H_2O = 1.0/0.5 mL.

Table 2 NHC–Pd(II)–Mp complex **2a** catalyzed coupling of sulfamate **3a** with arylboronic acid **4** under optimal conditions



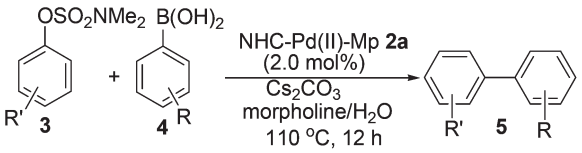
Entry[a]	4 (R)	Yield[b] (%)
1	**4a** (4-MeO)	**5a**, 94
2	**4b** (3-MeO)	**5b**, 80
3	**4c** (2-MeO)	**5c**, 30
4	**4d** (4-Me)	**5d**, 93
5	**4e** (3-Me)	**5e**, 88
6	**4f** (2-Me)	**5f**, 74
7	**4g** (4-F)	**5g**, 84
8	**4h** (3-F)	**5h**, 57
9	**4i** (2-F)	**5i**, <5
10	**4j** (3,5-Me_2)	**5j**, 89
11	**4k** (H)	**5k**, 85
12	 **4l**	**5l**, 80
13	 **4m**	**5m**, 92

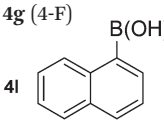
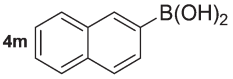
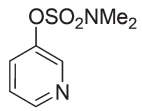
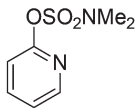
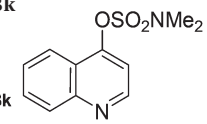
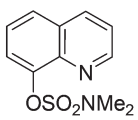
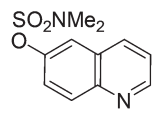
[a] All reactions were carried out using **3a** (0.7 mmol), **4** (1.2 equiv.), **2a** (2.0 mol%), and Cs_2CO_3 (3.0 equiv.) in the mixture of morpholine (1.0 mL) and H_2O (0.1 mL) at 110 °C for 12 h. [b] Isolated yields.

Subsequently, using sulfamate **3a** (0.7 mmol) and 4-methoxyphenylboronic acid **4a** (1.2 equiv.) as the model coupling partners, a mixture of morpholine and H_2O (1.0 mL/0.1 mL) as the solvent, and the NHC–Pd(II)–Mp complex **2a** (2.0 mol%) as the catalyst, initial investigations were carried out at 110 °C for 12 h to find the most efficient base (Table 1, entries 1–9). It was found that Cs_2CO_3 was the best base to give the expected coupling product **5a** in 94% yield (Table 1, entry 7). The solvent effect was also investigated and the mixture of morpholine and water was shown to be the best (Table 1, entry 7 *vs.* entries 10–12). Further studies showed that the NHC–Pd(II)–Mp complex **2a** showed the best catalytic activity over complexes **2b** (72%) and **2c** (81%) (Table 1, entry 7 *vs.* entries 13 and 14). In addition, it was found that the water added as the co-solvent had some effect on this reaction. For example, when morpholine alone was used as the solvent, product **5a** can only be obtained in 60% yield (Table 1, entry 15). Furthermore, the yield of **5a** decreased when the amount of the water added was increased (Table 1, entries 16–18). Therefore, it can be concluded that the mixture solvent of morpholine and water (1.0/0.1 mL) was the most suitable (Table 1, entry 7). Introduction of an additional base such as Cs_2CO_3 was also essential for this reaction, which suggests that morpholine in this case cannot play the role of a suitable base (Table 1, entry 19).

Under optimal conditions, the reactions between sulfamate **3a** and a range of arylboronic acids **4** were first investigated (Table 2). As can be seen from Table 2, most reactions proceeded well to give the corresponding coupling products **5** in good to high yields under optimal conditions. It seems that substituents on the different positions of phenyl groups of arylboronic acids **4** affected the reactions to some extent. For instance, both electron-rich (MeO- and Me-) and electron-poor (F-) substituents on the *para*-position of arylboronic acids **4** gave the best yields, and those on the *meta*-position gave moderate yields, while those on the *ortho*-position gave the worst yields (Table 2, entries 1–3, 4–6 and 7–9). It may be attributed to the steric hindrance of the corresponding substituents. In addition, only 30% yield of product **5c** was obtained for the reaction involving 2-methoxyphenylboronic acid **4c**, probably due also to the coordination of the *ortho*-oxygen atom to the metal center (Table 2, entry 3). Furthermore, almost no product was detected when 2-fluorophenylboronic acid was used (Table 2, entry 9), which may also be attributed to its lower reactivity in the transmetallation process.[7] In these cases, lower yields for fluorophenylboronic acids were found when compared to the previous nickel-catalyzed reactions of this type, maybe due mainly to the inferior catalytic activity of the NHC–Pd(II)–Mp complex in such reactions.[4h] The reactions involving 1-naphthylboronic acid **4l** and its analogue, 2-naphthylboronic acid **4m**, performed well to give products **5l**

Table 3 NHC–Pd(II)–Mp complex **2a** catalyzed coupling of sulfamates **3a** with arylboronic acid **4** under optimal conditions



Entry[a]	3 (R′)	4 (R)	Yield[b] (%)
1	**3b** (H)	**4b** (3-MeO)	**5n**, 81
2	**3b**	**4a** (4-MeO)	**5o**, 92
3	**3c** (3-Me)	**4j** (3,5-Me_2)	**5p**, 81
4	**3c**	**4a**	**5q**, 85
5	**3d** (4-MeO)	**4a**	**5r**, 81
6	**3d**	**4k** (H)	**5o**, 83
7	**3e** (3-F)	**4a**	**5s**, 95
8	**3e**	**4b**	**5t**, 93
9	**3e**	**4h** (3-F)	**5u**, 85
10	**3e**	**4n** (4-CF_3)	**5v**, 90
11	**3f** (4-Ac)	**4k**	**5w**, 81
12	**3f**	**4a**	**5x**, 85
13	**3f**	**4d** (4-Me)	**5y**, 83
14	**3f**	**4b**	**5z**, 87
15	**3g** (4-CF_3)	**4k**	**5aa**, 99
16[c]	**3h** (3-CHO)	**4k**	**5ab**, 60
17[c]	**3h** (3-CHO)	**4g** (4-F)	**5ac**, 50
18	**3f**	 **4l**	**5ad**, 80
19	**3f**	 **4m**	**5ae**, 87
20	**3b**	**4m**	**5af**, 83
21	**3i**	**4a**	**5ag**, 98
22	 **3i**	**4d**	**5ah**, 95
23	**3i**	**4b**	**5ai**, 97
24	 **3j**	**4a**	**5aj**, 82
25	**3k**	**4a**	**5ak**, 86
26	 **3k**	**4d**	**5al**, 94
27	 **3l**	**4a**	**5am**, 92
28	**3l**	**4d**	**5an**, 94
29	**3m**	**4a**	**5ao**, 87
30	 **3m**	**4d**	**5ap**, 94

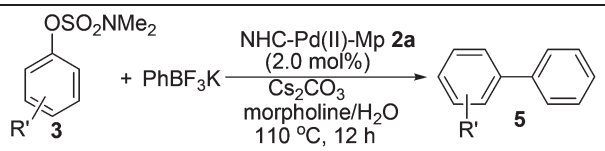
[a] All reactions were carried out using **3** (0.7 mmol), **4** (1.2 equiv.), **2a** (2.0 mol%), and Cs_2CO_3 (3.0 equiv.) in the morpholine (1.0 mL) and H_2O (0.1 mL) at 110 °C for 12 h. [b] Isolated yields. [c] The temperature was 130 °C.

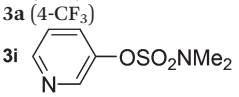
and **5m** in 80% and 92% yields, respectively (Table 2, entries 12 and 13).

Furthermore, the scope of this reaction was next examined with regard to functional group tolerance both on the substrates **2** and on boronic acids **3** (Table 3). As can be seen from Table 3, most reactions proceeded smoothly to give the desired coupling products **5** in good to high yields under identical conditions. It seems that with the combination of sulfamates **3** and arylboronic acids **4** shown in Table 3, substituents on both substrates have almost no effect on the reactions in these cases. Furthermore, the formyl group on the sulfamate is also tolerated to give the corresponding coupling products **5ab** and **5ac** in acceptable yields, respectively (Table 3, entries 16 and 17). Moreover, heteroaryl sulfamates **3i–3m** were also found to be good partners under identical conditions to give the desired products **5ag–5ap** in good to high yields (Table 3, entries 21–30).

During the past few years, organotrifluoroborate alkali metal salts, which generally possess the advantages of greater stability to air/water, easy isolation and avoidance of trimer formation than normal arylboronic acids, have been extensively used in the Suzuki–Miyaura coupling.[8] Therefore, the reactions between a variety of sulfamates **3** and potassium phenyltrifluoroborate were also tested under identical conditions. To our delight, all reactions proceeded smoothly to give the desired coupling products **5** in moderate to high yields. It seems that electron-neutral and -rich substituents on the phenyl ring of sulfamates gave products **5aq** and **5ar** in low yields, respectively (Table 4, entries 2 and 3). Heteroaryl sulfamate **3i** worked well to give product **5at** in 84% yield (Table 4, entry 7). It should also be noted that similar yields can be achieved for the reactions of substrates **3a** and **3f** with phenylboronic acid or potassium phenyltrifluoroborate, respectively (Table 4, entry 1 *vs.* Table 2, entry 11; Table 4, entry 5 *vs.* Table 3, entry 11).

Table 4 NHC–Pd(II)–Mp complex **2a** catalyzed coupling of sulfamates **3** with potassium phenyltrifluoroborate under optimal conditions



Entry[a]	3 (R′)	Yield[b] (%)
1	**3a** (4-F)	**5k**, 84
2	**3a** (H)	**5aq**, 66
3	**3a** (3-Me)	**5ar**, 72
4	**3a** (3-F)	**5as**, 82
5	**3a** (4-Ac)	**5w**, 80
6	**3a** (4-CF_3)	**5aa**, 81
7	 **3i**	**5at**, 84

[a] All reactions were carried out using **3** (0.7 mmol), $PhBF_3K$ (1.2 equiv.), **2a** (2.0 mol%), and Cs_2CO_3 (3.0 equiv.) in morpholine (1.0 mL) and H_2O (0.1 mL) at 110 °C for 12 h. [b] Isolated yields.

Conclusions

In conclusion, we have reported the first example so far of the phosphine-free, NHC–Pd(II)–Mp complexes catalyzed Suzuki–Miyaura coupling of aryl sulfamates with arylboronic acids or potassium phenyltrifluoroborate in this paper. The Suzuki–Miyaura coupling can tolerate a variety of substrates. Under optimal conditions, most reactions proceeded smoothly to give the desired coupling products in moderate to high yields. The NHC–Pd(II)–Mp complexes **2**, which are air-, thermal- and moisture-stable, can be easily prepared from commercially available imidazolium salts, $PdCl_2$ and morpholine in a one-pot procedure in high yields, thus making the procedure more practical in organic synthesis.

Experimental

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 given in Hz. Organic solvents used were dried by standard methods. The mass analyzer type for the high resolution mass spectra (HRMS) is quadrupole (for ESI†). Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel (300–400 mesh) using CH_2Cl_2 (for complexes **2**) and petroleum ether (for compounds **5**) as the eluents, respectively.

General procedure for the synthesis of NHC–Pd(II)–Mp complexes 2

Under a N_2 atmosphere, a mixture of imidazolium salts **1** (0.6 mmol), $PdCl_2$ (0.57 mmol), K_2CO_3 (0.6 mmol) and morpholine (2.4 mmol) was stirred in anhydrous THF (2.0 mL) under reflux for 20 h. Then the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give the pure NHC–Pd(II)–Mp complexes **2** as yellow solids.

General procedure for the NHC–Pd(II)–Mp complex 2a-catalyzed Suzuki–Miyaura coupling of aryl sulfamates with arylboronic acids

Under a N_2 atmosphere, sulfamates **3** (0.7 mmol), arylboronic acids or potassium phenyltrifluoroborate **4** (0.84 mmol), the NHC–Pd(II)–Mp complex **2a** (2.0 mol%), Cs_2CO_3 (3.0 equiv.), morpholine (1.0 mL) and H_2O (0.1 mL) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at 110 °C for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2) to give the pure products.

Compound **2a**:[3] a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.50 (t, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 4H), 7.09 (s, 2H), 3.60 (dd, J = 12.0, 3.0 Hz, 2H), 3.26–3.21 (m, 2H), 3.07–3.02 (m, 6H), 2.50–2.41 (m, 3H), 1.45 (d, J = 6.5 Hz, 12H), 1.10 (d, J = 6.5 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 146.5, 135.0, 130.1, 124.8, 123.8, 67.6, 46.9, 28.6, 26.2, 23.1.

Compound **2b**: a yellow solid. Mp: 274 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.34 (dd, J = 8.4, 6.6 Hz, 2H), 7.25–7.22 (m, 4H), 7.08 (s, 2H), 3.60 (dd, J = 12.0, 3.3 Hz, 2H), 3.24 (td, J = 12.0, 2.1 Hz, 2H), 3.06–2.93 (m, 2H), 2.48–2.44 (m, 2H), 2.35 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 137.4, 136.6, 129.4, 128.3, 123.8, 67.6, 46.9, 19.0. IR (ν): 1474, 1437, 1255, 1092, 1049, 892, 874, 769, 748, 708 cm^{-1}. MS (ESI) 540 $[M + H]^+$; HRMS (ESI) calcd for $C_{23}H_{30}Cl_2N_3OPd$ $[M + H]^+$: 540.0798, found: 540.0826. Anal. calcd for $C_{25}H_{34}Cl_2N_3OPd$: requires C, 52.69%; H, 6.01%, N, 7.37%; found: C, 53.22%; H, 5.90%, N, 7.08%.

Compound **2c**: a yellow solid. Mp: 278 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.04 (s, 4H), 7.02 (s, 2H), 3.62 (dd, J = 12.1, 3.0 Hz, 2H), 3.25 (td, J = 12.0, 2.1 Hz, 2H), 3.08–3.00 (m, 2H), 2.52–2.47 (m, 2H), 2.37 (s, 6H), 2.30 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 139.0, 136.2, 135.0, 129.0, 123.9, 67.6, 46.9, 21.1, 18.9. IR (ν): 1480, 1437, 1255, 1109, 1092, 1049, 892, 880, 744, 733, 695 cm^{-1}. MS (ESI) 568 $[M + H]^+$; HRMS (ESI) calcd for $C_{25}H_{34}Cl_2N_3OPd$ $[M + H]^+$: 568.1112, found: 568.1133. Anal. calcd for $C_{23}H_{30}Cl_2N_3OPd$: requires C, 50.98%; H, 5.58%, N, 7.76%; found: C, 50.89%; H, 5.42%, N, 7.58%.

Compound **5a**:[3] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.35–7.30 (m, 4H), 7.07 (t, J = 5.1 Hz, 2H), 6.94 (d, J = 5.1 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 244.0 Hz), 159.1, 136.9 (d, J_{C-F} = 3.3 Hz), 132.7, 128.1 (d, J_{C-F} = 7.9 Hz), 128.0, 115.5 (d, J_{C-F} = 21.3 Hz), 114.2, 55.2.

Compound **5b**:[3] a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.53 (dd, J = 8.5, 5.0 Hz, 2H), 7.34 (t, J = 7.0 Hz, 1H), 7.13–7.06 (m, 4H), 6.89 (dd, J = 8.0, 2.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 244.9 Hz), 159.9, 141.7, 137.1 (d, J_{C-F} = 3.3 Hz), 129.8, 128.7 (d, J_{C-F} = 8.0 Hz), 119.5, 115.6 (d, J_{C-F} = 21.4 Hz), 112.8, 112.5, 55.3.

Compound **5c**:[3] a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.40–7.35 (m, 2H), 7.22–7.16 (m, 2H), 7.00–6.84 (m, 4H), 3.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 244.3 Hz), 156.3, 134.4 (d, J_{C-F} = 3.0 Hz), 131.1 (d, J_{C-F} = 7.8 Hz), 130.7, 129.6, 128.7, 120.8, 114.8 (d, J_{C-F} = 21.1 Hz), 111.2, 55.4.

Compound **5d**:[3] a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.52–7.44 (m, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.11–7.03 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, J_{C-F} = 244.4 Hz), 137.3, 137.2 (d, J_{C-F} = 2.9 Hz), 136.9, 129.5, 128.4 (d, J_{C-F} = 7.8 Hz), 126.8, 115.5 (d, J_{C-F} = 21.3 Hz), 21.0.

Compound **5e**:[3] a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.51–7.46 (m, 2H), 7.31–7.28 (m, 3H), 7.13–7.03 (m, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 244.6 Hz), 140.2, 138.4, 137.4 (d, J_{C-F} = 3.0 Hz), 128.7, 128.6 (d, J_{C-F} = 8.0 Hz), 128.0, 115.5 (d, J_{C-F} = 21.3 Hz), 21.5.

Compound **5f**:[3] a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.26–7.18 (m, 6H), 7.06 (t, J = 8.5 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 244.1 Hz), 140.9,

137.8 (d, J_{C-F} = 3.4 Hz), 135.3, 130.7 (d, J = 7.9 Hz), 130.3, 129.8, 127.4, 125.8, 114.9 (d, J_{C-F} = 21.1 Hz), 20.4.

Compound **5g**:[9] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.48–7.41 (m, 4H), 7.12–7.04 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 245.0 Hz), 136.4 (d, J_{C-F} = 3.3 Hz), 128.5 (d, J_{C-F} = 8.0 Hz), 115.6 (d, J_{C-F} = 21.3 Hz).

Compound **5h**:[3] a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.49–7.46 (m, 2H), 7.35–7.31 (m, 1H), 7.27–7.25 (m, 1H), 7.20–7.17 (m, 1H), 7.10–7.06 (m, 2H), 7.01–6.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 244.4 Hz), 162.7 (d, J_{C-F} = 245.9 Hz), 142.5 (d, J_{C-F} = 7.6 Hz), 136.0 (dd, J_{C-F} = 2.8, 2.8 Hz), 130.3 (d, J_{C-F} = 8.4 Hz), 128.7 (d, J_{C-F} = 8.0 Hz), 122.6 (d, J_{C-F} = 2.6 Hz), 115.7 (d, J_{C-F} = 21.4 Hz), 114.0 (d, J_{C-F} = 21 Hz), 113.9 (d, J_{C-F} = 21.9 Hz).

Compound **5j**:[3] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.50 (dd, J = 8.5, 5.5 Hz, 2H), 7.14 (s, 2H), 7.08 (t, J = 8.5 Hz, 2H), 6.98 (s, 1H), 2.36 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 244.4 Hz), 140.3, 138.3, 137.5 (d, J_{C-F} = 3.3 Hz), 128.9, 128.6 (d, J_{C-F} = 8.0 Hz), 124.9, 115.4 (d, J_{C-F} = 21.3 Hz), 21.3.

Compound **5k**:[10] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.53–7.49 (m, 4H), 7.40 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.09 (t, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 244.7 Hz), 140.2, 137.3 (d, J_{C-F} = 3.4 Hz), 128.8, 128.6 (d, J_{C-F} = 8.0 Hz), 127.2, 127.0, 115.6 (d, J_{C-F} = 21.2 Hz).

Compound **5l**:[3] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.91–7.83 (m, 3H), 7.53–7.38 (m, 6H), 7.19–7.16 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, J_{C-F} = 244.6 Hz), 139.1, 136.6 (d, J_{C-F} = 3.3 Hz), 133.8, 131.6, 131.5 (d, J_{C-F} = 8.0 Hz), 128.3, 127.9, 127.8, 127.0, 126.1, 125.83, 125.80, 125.7, 125.3, 115.2 (d, J_{C-F} = 21.1 Hz).

Compound **5m**:[3] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.91 (s, 1H), 7.83–7.79 (m, 3H), 7.61–7.56 (m, 3H), 7.46–7.42 (m, 2H), 7.10 (t, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 245.1 Hz), 137.5, 137.1 (d, J_{C-F} = 3.1 Hz), 133.6, 132.5, 128.9 (d, J_{C-F} = 8.0 Hz), 128.5, 128.1, 127.6, 126.3, 125.9, 125.6, 125.3, 115.6 (d, J_{C-F} = 21.3 Hz).

Compound **5n**:[3] a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.58–7.54 (m, 2H), 7.42–7.28 (m, 4H), 7.17–7.11 (m, 2H), 6.86 (ddd, J = 8.1, 2.4, 0.9 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 142.7, 141.1, 129.7, 128.7, 127.4, 127.1, 119.6, 112.8, 112.6, 55.2.

Compound **5o**:[3] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.45–7.41 (m, 4H), 7.30 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 140.7, 133.7, 128.7, 128.1, 127.7, 126.7, 114.1, 55.2.

Compound **5p**:[3] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.38–7.35 (m, 2H), 7.28 (t, J = 7.5 Hz, 1H), 7.18 (s, 2H), 7.11 (d, J = 7.5 Hz, 1H), 6.96 (s, 1H), 2.38 (s, 3H), 2.35 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 141.3, 138.1, 128.8, 128.5, 127.9, 127.8, 125.1, 124.3, 21.5, 21.4.

Compound **5q**:[3] a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.39 (d, J = 8.7 Hz, 2H), 7.24–7.14 (m, 3H), 6.99 (d, J = 7.2 Hz, 1H), 6.83 (d, J = 8.7 Hz, 2H), 3.67 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 140.7, 138.1, 133.7, 128.6, 128.0, 127.4, 127.3, 123.8, 114.0, 55.1, 21.5.

Compound **5r**:[11] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.47 (d, J = 9.0 Hz, 4H), 6.95 (d, J = 9.0 Hz, 4H), 3.84 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 133.5, 127.7, 114.2, 55.3.

Compound **5s**:[12] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.34 (d, J = 8.7 Hz, 2H), 7.23–7.08 (m, 4H), 6.81 (d, J = 8.7 Hz, 2H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 243.7 Hz), 159.5, 143.0 (d, J_{C-F} = 7.7 Hz), 132.3 (d, J_{C-F} = 2.3 Hz), 130.1 (d, J_{C-F} = 8.3 Hz), 128.0, 122.2 (d, J_{C-F} = 2.8 Hz), 114.2, 113.4 (d, J_{C-F} = 21.8 Hz), 113.3 (d, J_{C-F} = 21.0 Hz), 55.2.

Compound **5t**:[13] a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.39–7.28 (m, 4H), 7.26–7.00 (m, 3H), 6.91 (ddd, J = 8.1, 2.4, 0.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (d, J_{C-F} = 244.0 Hz), 160.0, 143.4 (d, J_{C-F} = 7.6 Hz), 141.4 (d, J_{C-F} = 2.1 Hz), 130.1 (d, J_{C-F} = 8.4 Hz), 129.9, 122.8 (d, J_{C-F} = 2.6 Hz), 119.6, 114.1 (d, J_{C-F} = 21.0 Hz), 114.0 (d, J_{C-F} = 21.9 Hz), 113.2, 112.9, 55.3.

Compound **5u**:[14] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.39–7.24 (m, 6H), 7.06–7.03 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 244.5 Hz), 142.2 (d, J_{C-F} = 7.6 Hz), 130.4 (d, J_{C-F} = 8.4 Hz), 122.7, 114.6 (d, J_{C-F} = 21 Hz), 114.0 (d, J_{C-F} = 22.1 Hz).

Compound **5v**:[14] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.67 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.42–7.38 (m, 1H), 7.34 (dt, J = 7.5, 1.5 Hz, 1H), 7.25 (dt, J = 9.5, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (d, J_{C-F} = 244.9 Hz), 143.4, 142.0 (d, J_{C-F} = 7.6 Hz), 130.5 (d, J_{C-F} = 8.0 Hz), 130.0 (q, J_{C-F} = 32.4 Hz), 127.4, 125.8 (q, J_{C-F} = 3.6 Hz), 124.2 (q, J_{C-F} = 270.4 Hz), 122.9 (d, J_{C-F} = 2.9 Hz), 115.0 (d, J_{C-F} = 21.1 Hz), 114.2 (d, J_{C-F} = 22.1 Hz).

Compound **5w**:[10] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.02 (d, J = 8.7 Hz, 2H), 7.68–7.60 (m, 4H), 7.46–7.36 (m, 3H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 145.7, 139.8, 135.8, 128.90, 128.86, 128.2, 127.20, 127.15, 26.6.

Compound **5x**:[15] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.00 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 159.8, 145.2, 135.2, 132.1, 128.9, 128.3, 126.5, 114.3, 55.3, 26.5.

Compound **5y**:[15] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.00 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 2.61 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 145.6, 138.2, 136.9, 135.5, 129.6, 128.8, 127.0, 126.9, 26.6, 21.1.

Compound **5z**:[16] a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.99 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.13 (t, J = 2.1 Hz, 1H), 6.92 (dd, J = 8.1, 2.1 Hz, 1H), 3.84 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 159.9, 145.3, 141.1, 135.7, 129.8, 128.7, 127.0, 119.5, 113.3, 112.9, 55.1, 26.4.

Compound **5aa**:[17] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.69 (s, 4H), 7.60–7.58 (m, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7,

139.8, 129.4 (q, J_{C-F} = 32.3 Hz), 129.0, 128.2, 127.4, 127.3, 125.7 (q, J_{C-F} = 3.8 Hz), 124.3 (q, J_{C-F} = 270.3 Hz).

Compound **5ab**:[18] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 10.07 (s, 1H), 8.08 (s, 1H), 7.84 (dd, J = 7.5, 1.5 Hz, 2H), 7.62–7.57 (m, 3H), 7.46 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 142.1, 139.6, 136.9, 133.0, 129.4, 128.9, 128.5, 128.1, 127.9, 127.1.

Compound **5ac**:[19] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 10.07 (s, 1H), 8.04 (s, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.60–7.56 (m, 3H), 7.15 (t, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 162.8 (d, J_{C-F} = 246.1 Hz), 141.1, 136.9, 135.8 (d, J_{C-F} = 3.25 Hz), 132.8, 129.5, 128.71 (d, J_{C-F} = 8.25 Hz), 128.68, 127.7, 115.9 (d, J_{C-F} = 21.5 Hz).

Compound **5ad**:[20] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.09 (d, J = 8.4 Hz, 2H), 7.91 (t, J = 7.8 Hz, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.57–7.41 (m, 4H), 2.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 145.7, 139.0, 136.0, 133.8, 131.2, 130.3, 128.4, 128.3, 126.9, 126.3, 125.9, 125.5, 125.3, 26.6.

Compound **5ae**:[21] a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.02 (d, J = 8.4 Hz, 3H), 7.90–7.68 (m, 6H), 7.50–7.22 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 145.7, 137.1, 135.8, 133.5, 133.0, 129.0, 128.7, 128.3, 127.7, 127.5, 126.6, 126.5, 126.4, 125.2, 26.7.

Compound **5af**:[3] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.00 (s, 1H), 7.86–7.80 (m, 3H). 7.71–7.67 (m, 3H), 7.47–7.42 (m, 4H), 7.33 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.2, 125.9, 125.7, 125.5.

Compound **5ag**:[3] a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.70 (d, J = 1.5 Hz, 1H), 8.42 (d, J = 4.5 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.19 (dd, J = 8.0, 5.0 Hz, 1H), 6.88 (d, J = 9.0 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 147.6, 147.5, 136.0, 133.7, 129.9, 128.0, 123.3, 114.3, 55.1.

Compound **5ah**:[12] a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.82 (d, J = 2.4 Hz, 1H), 8.54 (dd, J = 4.8, 1.5 Hz, 1H), 7.80 (dt, J = 8.1, 1.5 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.30–7.23 (m, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 137.7, 136.3, 134.6, 133.8, 129.6, 126.7, 123.2, 20.9.

Compound **5ai**:[12] a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.84 (d, J = 2.1 Hz, 1H), 8.57 (dd, J = 4.8, 1.5 Hz, 1H), 7.83 (dt, J = 7.8, 1.8 Hz, 1H), 7.39–7.30 (m, 2H), 7.15–7.08 (m, 2H), 7.09 (t, J = 1.8 Hz, 1H), 6.93 (ddd, J = 8.1, 2.4, 0.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 148.3, 148.1, 139.1, 136.3, 134.2, 129.9, 123.3, 119.4, 113.2, 112.8, 55.1.

Compound **5aj**:[22] a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.64–8.61 (m, 1H), 7.94 (dt, J = 3.0, 9.6 Hz, 2H), 7.67–7.59 (m, 2H), 7.11 (ddd, J = 2.1, 4.8, 7.2 Hz, 1H), 6.97 (dt, J = 2.7, 9.6 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 156.9, 149.3, 136.4, 131.8, 128.0, 121.2, 119.6, 113.9, 55.1.

Compound **5ak**:[23] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.91 (d, J = 4.5 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 4.5 Hz, 1H), 7.05 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 149.6, 148.4, 148.3, 130.7, 130.0, 129.5, 129.3, 126.8, 126.5, 125.8, 121.2, 114.0, 55.3.

Compound **5al**:[24] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.81 (d, J = 4.5 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.84 (dd, J = 8.5, 1.0 Hz, 1H), 7.60 (t, J = 8.5 Hz, 1H), 7.38–7.35 (m, 1H), 7.28 (d, J = 8.5 Hz, 2H), 7.22–7.00 (m, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 148.6, 148.4, 138.3, 134.9, 129.5, 129.3, 129.24, 129.18, 126.7, 126.5, 125.8, 121.2, 21.2.

Compound **5am**:[22] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.95 (d, J = 4.0 Hz, 1H), 8.15 (dd, J = 8.5, 1.5 Hz, 1H), 7.75 (dd, J = 8.5, 1.5 Hz, 1H), 7.69 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.36 (dd, J = 8.5, 4.0 Hz, 1H), 7.04 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 150.0, 145.9, 140.3, 136.2, 131.7, 131.6, 129.9, 128.7, 127.0, 126.2, 120.8, 113.5, 55.2.

Compound **5an**:[25] a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.79 (dd, J = 4.0, 1.5 Hz, 1H), 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.59–7.54 (m, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.18–7.15 (m, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 145.9, 140.7, 136.8, 136.4, 136.0, 130.3, 129.9, 128.6, 128.5, 127.1, 126.1, 120.7, 21.1.

Compound **5ao**:[26] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.73 (dd, J = 4.5, 1.5 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.78 (dd, J = 8.5, 2.0 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.20 (dd, J = 8.5, 4.5 Hz, 1H), 6.85 (d, J = 8.5 Hz, 2H), 3.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 149.7, 147.0, 138.6, 136.0, 132.4, 129.5, 128.8, 128.3, 128.2, 124.4, 121.2, 114.2, 55.1.

Compound **5ap**:[26] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.73 (dd, J = 4.0, 1.5 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.80 (dd, J = 9.0, 2.0 Hz, 1H), 7.77 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.20 (dd, J = 8.5, 3.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 147.2, 139.0, 137.4, 137.1, 136.1, 129.5, 129.0, 128.3, 127.0, 124.8, 121.2, 21.0.

Compound **5aq**:[15] a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.58–7.56 (m, 4H), 7.41 (t, J = 7.5 Hz, 4H), 7.31 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 128.7, 127.2, 127.1.

Compound **5ar**:[3] a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.59–7.56 (m, 2H), 7.43–7.37 (m, 4H), 7.31 (t, J = 7.2 Hz, 2H), 7.14 (d, J = 7.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 141.2, 138.3, 128.7, 128.6, 127.97, 127.95, 127.15, 127.13, 124.3, 21.5.

Compound **5as**:[13] a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.56–7.52 (m, 2H), 7.44–7.24 (m, 6H), 7.04–6.98 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 244.0 Hz), 143.5 (d, J_{C-F} = 7.6 Hz), 139.9 (d, J_{C-F} = 2.1 Hz), 130.2 (d, J_{C-F} = 8.4 Hz), 128.9, 127.8, 127.1, 122.7 (d, J_{C-F} = 2.8 Hz), 114.0 (d, J_{C-F} = 20.6 Hz), 113.9.

Compound **5at**:[15] a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.84 (d, J = 2.1 Hz, 1H), 8.58 (dd, J = 4.8, 1.5 Hz, 1H), 7.84 (dt, J = 8.1, 1.8 Hz, 1H), 7.57–7.31 (m, 6H). ^{13}C NMR

(125 MHz, $CDCl_3$) δ 148.3, 148.2, 137.7, 136.5, 134.2, 128.9, 127.9, 127.0, 123.4.

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