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N-Heterocyclic Carbene-Palladium(II)-1-Methylimidazole Complex Catalyzed α-Arylation Reactions of Tetralones with Aryl Chlorides and Further Transformation of the Products

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NHC-Pd(II)-Im complex **1** have proven an efficient catalyst in the reaction between tetralones **2** and aryl chlorides **3**, giving the α-arylated tetralones **4** in good to high yields. In addition, if the above reaction mixture was exposed to air at room temperature for another 3 h, the normal α-arylated products **4** can be fully oxidized to 2-aryl-2'-hydroxytetralones **6** in good yields in a one-pot procedure. Furthermore, if the reaction mixture containing the oxidized products **6** was treated with TsOH/toluene solution under reflux for 19 h, the final aromatized products, 2-aryl-naphthalen-1-ols **5** can be achieved in acceptable to moderate yields. All reactions can tolerate various substituents on the tetralones **2** and aryl chlorides **3**, thus giving efficient method for the α-arylation of tetralones and further transformation of the products, and also enriching the applications of NHC-Pd(II) complexes in organic synthesis.

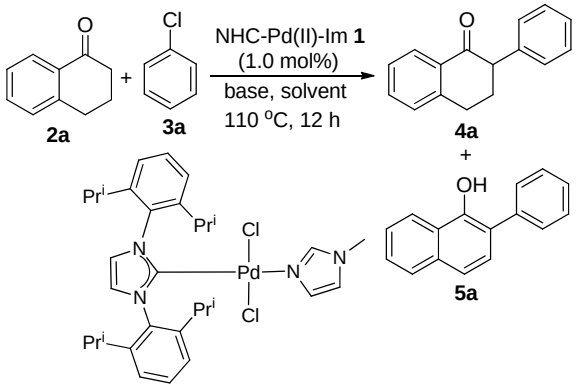
Introduction

During the past years, *N*-heterocyclic carbene (NHC)-metal complexes, which are usually air-, moisture- and thermal-stable, have proven efficient catalysts in the α-arylation of ketones and have become strong competitors to phosphine-metal complexes in such transformation.[1,2] In 2011, we developed a well-defined *N*-heterocyclic carbene-Pd(II)-1-methylimidazole [NHC-Pd(II)-Im] complex **1**,[3] and found it to be an efficient catalyst in the C-C and C-N coupling reactions using the inactive, while easily available and cost-superior aryl chlorides as the electrophiles.[4] For example, we recently reported a novel two-component, three-molecule reaction between 2,3-dihydroinden-1-ones and aryl chlorides in the presence of NHC-Pd(II)-Im complex **1**, and proposed the plausible reaction mechanism.[4k] Prompted by these results, we thus turned our interest to the reactions of their analogs, tetralones, with aryl chlorides catalyzed by NHC-Pd(II)-Im complex **1**, because 2-aryltetralones are also important precursors for the synthesis of benzophenanthridine bases and their derivatives.[5] However, to the best of our knowledge, compared to the abundant papers on the palladium-catalyzed α-aryaltion of other carbonyl containing compounds, very less attention was paid on the transition metal-catalyzed α-arylation of tetralones,[6] and only handful examples were reported on the palladium-catalyzed such reaction using aryl chlorides as the arylating agents with very lower yields,[6b,6d,6g] implying that great challenge still kept in such tranformation. Pleasantly, after careful investigations, we found that NHC-Pd(II)-Im complex **1** can efficiently catalyze the α-arylation of tetralones **2** with aryl chlorides **3**. In addition, successively treatment the above reaction mixture by air-oxidation, and acid-catalyzed aromatization, 2-aryl-naphthalen-1-ols **5** can be achieved in moderate to good yields. Furthermore, if the mixture of the α-arylation reaction was exposed to air at room temperature, the α-arylated products can be fully oxidized to 2-aryl-2'-hydroxytetralones **6** in a one-pot procedure. Herein, we report these results in detail.

Results and discussion

The optimization procedure was carried out using tetralone **2a** (1.0 mmol) and chlorobenzene **3a** (1.2 mmol) as the substrates, NHC-Pd(II)-Im complex **1** (1.0 mol%) as the catalyst at 110 °C for 12 h to evaluate various solvents (2.0 mL) and bases (2.0 equiv). Some representative results are shown in Table 1. Initially, toluene was chosen as the solvent to test bases. In the presence of KO^{t}Bu, the desired α-arylated **4a** was obtained in 68% yield, along with 2-phenylnaphtnalen-1-ol **5a** in 14% yield (Table 1, entry 1). In the presence of other bases such as NaO^{t}Bu and KOH, very low yields of products **4a** and **5a** were observed at the same time (Table 1, entries 2 and 3). In addition, using some other bases such as LiO^{t}Bu, K_2CO_3, Na_2CO_3, Cs_2CO_3, NaOH, $Na_3PO_4{\cdot}12H_2O$ and $K_3PO_4{\cdot}3H_2O$, no reaction occurred. Next, using KO^{t}Bu as the base, a variety of solvents was subsequently tested. Using dioxane as the solvent instead of toluene, **4a** was obtained in 76% yield along with **5a** in 18% yield (Table 1, entry 4). In other solvents such as CH_3CN, DMF and DMSO, no reaction occurred. Finally, the best result for the sole α-arylation reaction was achieved when the amount of KO^{t}Bu increased to 3.0 equiv (Table 1, entry 5).

Table 1. Representative results of NHC-Pd(II)-Im complex **1** catalyzed reaction of tetralone **2a** with chlorobenzene **3a**.



NHC-Pd(II)-Im **1**

Entry[a]	Base (equiv)	Solvent	Yield (%)[b]	
			4a	**5a**
1	KO^{t}Bu (2.0)	toluene	68	14
2	NaO^{t}Bu (2.0)	toluene	<5	7
3	KOH (2.0)	toluene	25	12
4	KO^{t}Bu (2.0)	dioxane	76	18
5	KO^{t}Bu (3.0)	dioxane	85	—

[a] All reactions were carried out using **1a** (1.0 mmol), **2a** (1.2 mmol), base, **1** (1.0 mol%) in solvent (2.0 mL) at 110 °C for 12 h. [b] Isolated yields.

With the optimal conditions for the α-arylation reaction established, the reactions between tetralone **2a** and a variety of aryl chlorides **3** were then first investigated (Table 2). As can be seen from Table 2, substituents on aryl chlorides **3** affected the reactions to some extent. For example, for the moderately electron-rich methyl substituted aryl chlorides **3b-d**, the reactions can be carried out at 110 °C to afford satisfactory yields (Table 2, entries 1-3). While for the reaction involving electron-rich 3-methoxyphenyl chloride **3e**, only moderate yields can be obtained even if the reaction temperature increased to 130 °C (Table 2, entries 4 and 5). For the reaction involving 4-methoxyphenyl chloride **3f**, high yield can still be achieved when the reaction temperature was elevated to 130 °C (Table 2, entries 6 and 7). For the reactions involving electron-poor fluorine substituted aryl chlorides **3g** and **3h**, moderate yields were obtained under identical conditions (Table 2, entries 8 and 9). Sterically hindered 2-methylphenyl chloride **3b** was the most suitable substrate to give product **4b** in the highest yield (Table 2, entry 1).

Table 2. NHC-Pd(II)-Im complex **1**-catalyzed α-arylation reaction between tetralone **2a** and aryl chlorides **3**.

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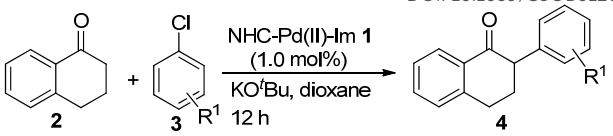
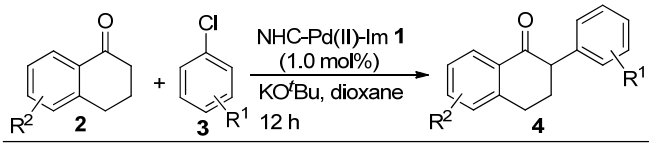


Entry[a]	**3** (R^2)	Temp. (°C)	Yield (%)[b]
1	**3b** (2-Me)	110	**4b**, 97
2	**3c** (3-Me)	110	**4c**, 80
3	**3d** (4-Me)	110	**4d**, 83
4	**3e** (3-OMe)	110	**4e**, 74
5	**3e**	130	**4e**, 72
6	**3f** (4-OMe)	110	**4f**, 77
7	**3f**	130	**4f**, 91
8	**3g** (3-F)	110	**4g**, 77
9	**3h** (4-F)	110	**4h**, 80

[a] All reactions were carried out using **2a** (0.5 mmol), **3** (0.6 mmol), KO^{t}Bu (3.0 equiv), **1** (1.0 mol%) in dioxane (1.0 mL) at the specified temperature for 12 h. [b] Isolated yields.

In addition, a variety of tetralones **2** and aryl chlorides **3** were further investigated under the optimal conditions to test the scope and limitations of this reaction. The results are illustrated in Table 3. As can be seen from Table 3, all reactions examined gave the desired α-arylated tetralones **4** in moderate to high yields. It seems that electron-rich, -poor, and sterically-hindered substituents on both substrates did not affect the reactions significantly. For example, electron-rich group such as 6-MeO and 7-MeO and electron-poor 7-F substituted tetralones **2b**, **2c** and **2d** worked well with various aryl chlorides **3** to give products **4i**-**4w** in moderate to high yields (Table 3). Sterically-hindered 2-methylphenyl chloride **3b** was also suitable substrate to give the corresponding products **4j**, **4q** and **4u** in good yields (Table 3, entries 3, 11, 15).

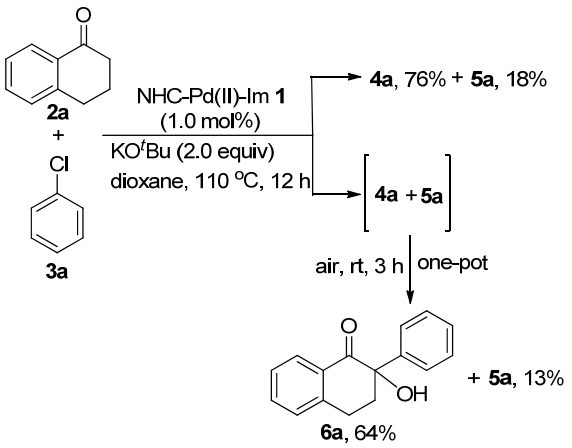
Table 3. NHC-Pd(II)-Im complex **1**-catalyzed α-arylation reaction between tetralones **2** and aryl chlorides **3**.



Entry[a]	2 (R^2)	3 (R^1)	Temp. (°C)	Yield (%)[b]
1	**2b** (6-OMe)	**3a** (H)	110	**4i**, 64
2	**2b**	**3a**	130	**4i**, 73
3	**2b**	**3b** (2-Me)	110	**4j**, 85
4	**2b**	**3c** (3-Me)	110	**4k**, 83
5	**2b**	**3d** (4-Me)	110	**4l**, 70
6	**2b**	**3e** (3-OMe)	110	**4m**, 82
7	**2b**	**3f** (4-OMe)	110	**4n**, 81
8	**2b**	**3h** (4-F)	110	**4o**, 77
9	**2c** (7-OMe)	**3a**	110	**4p**, 73
10	**2c**	**3a**	130	**4p**, 82
11	**2c**	**3b**	110	**4q**, 88
12	**2c**	**3d**	110	**4r**, 77
13	**2c**	**3f**	130	**4s**, 92
14	**2d** (7-F)	**3a**	110	**4t**, 73
15	**2d**	**3b**	110	**4u**, 78
16	**2d**	**3d**	110	**4v**, 81
17	**2d**	**3f**	110	**4w**, 84

[a] All reactions were carried out using **2** (0.5 mmol), **3** (0.6 mmol), KO^{t}Bu (3.0 equiv), **1** (1.0 mol%) in dioxane (1.0 mL) at the specified temperature for 12 h. [b] Isolated yields.

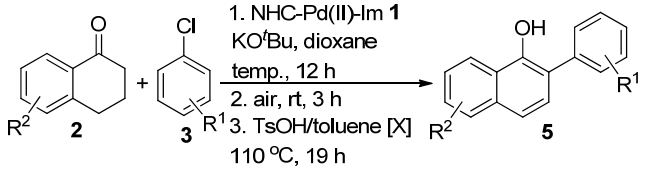
As can be seen from Table 1, entry 4, the normal α-arylated product **4a** and 2-phenyl-naphthalen-1-ol **5a** can be obtained in very high total yields at the same time in the presence of 2 equiv KO^{t}Bu in dioxane. In our initial assumption, 2-phenyl-naphthalen-1-ol **5a** can derive from the normal α-arylated product **4a** *via* aromatization under suitable conditions. As stated above, the NHC-Pd(II)-Im complex **1** catalyzed α-arylation reaction between a variety of tetralones **2** and aryl chlorides **3** can be successfully achieved to give the desired α-arylated products **4** in moderate to good yields under the optimal conditions (Tables 1-3). Encouraged by these successful results, we then turned our interest to the sole formation of products **5**. Considering that in our preliminary investigation on the NHC-Pd(II)-Im complex **1**-catalyzed α-arylation of oxindoles with aryl chlorides, the normal α-arylated products can be efficiently oxidized under air at room temperature in a one-pot procedure.[4j] Therefore, we hypothesized that the normal α-arylated products **4** would also be oxidized under air, and then the oxidized products would then aromatize to give the final 2-aryl-naphthalen-1-ols **5**. Control experiment showed that when the model reaction shown in Table 1, entry 4 was finished and then the mixture was stirred at room temperature under air for 3 h, the oxidized product **6a** can be obtained in 64% yield without any detection of product **4a**, implying that the normal α-arylated product **4a** can be actually fully oxidized by air in a one-pot procedure. However, comparable yield of product **5a** was observed in this case, implying that the aromatization of the oxidized product **6a** to product **5a** cannot easily take place under such conditions (Scheme 1).



Scheme 1. Control experiment on air-oxidation of product **4a**.

It was known that 2-aryl-2'-hydroxytetralone can aromatize to 2-aryl-naphthalen-1-ols in the presence of *p*-toluenesulfonic acid (TsOH).[7] Therefore, we then turned our interest to the cascade reaction involving three steps such as NHC-Pd(II)-Im complex **1** catalyzed α-arylation of tetralones **2** with aryl chlorides **3**, air-oxidation in a one-pot procedure and aromatization for the final formation of 2-aryl-naphthalen-1-ols **5**. The results are shown in Table 4. As can be seen from Table 4, after the normal α-arylation reaction under suitable conditions was finished, the reaction mixture was cooled to room temperature and exposed to air for another 3 h. Then the mixture was dropped to the solution of TsOH in toluene (the toluene solution was pre-refluxed for 2 h), and the mixture was then stirred at 110 °C for 19 h, finally giving the desired 2-aryl-naphthalen-1-ols **5** in acceptable to moderate yields. Similarly, for all reactions shown in Table 4, it seems that electron-rich, -neutral and -poor substituents on both substrates did not affect the reactions significantly.

Table 4. Cascade reactions for the formation of products **5**.

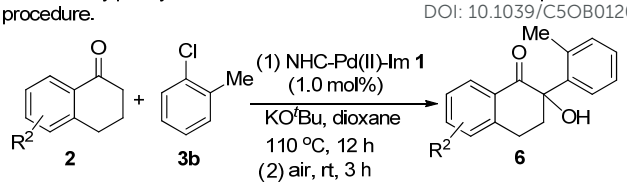


Entry[a]	2 (R^1)	3 (R^2)	Temp. (°C)	[X] (M)	Yield (%)[b]
1	**2a** (H)	**3a** (H)	110	0.3	**5a**, 71
2	**2a**	**3c** (3-Me)	110	0.4	**5b**, 60
3	**2a**	**3d** (4-Me)	110	0.3	**5c**, 58
4	**2a**	**3f** (4-OMe)	110	0.3	**5d**, 58
5	**2a**	**3h** (4-F)	130	0.4	**5e**, 57
6	**2b** (6-OMe)	**3c**	110	0.4	**5f**, 69
7	**2b**	**3d**	110	0.3	**5g**, 54
8	**2b**	**3e** (3-OMe)	130	0.4	**5h**, 58
9	**2b**	**3f**	110	0.3	**5i**, 54
10	**2b**	**3h**	130	0.4	**5j**, 58
11	**2c** (7-OMe)	**3d**	110	0.3	**5k**, 51
11	**2c**	**3f**	130	0.4	**5l**, 66
12	**2d** (7-F)	**3d**	110	0.3	**5m**, 53
13	**2d**	**3f**	110	0.3	**5n**, 58

[a] All reactions were carried out using **2** (0.5 mmol), **3** (0.6 mmol), KO^{t}Bu (2.0 equiv), **1** (1.0 mol%) in dioxane (1.0 mL) for 12 h, then the mixture was cooled to room temperature and stirred for another 3 h under air. Then the mixture was dropped to TsOH/toluene (10.0 mL, pre-refluxed for 2 h) and stirred at 110 °C for 19 h. [b] Isolated yields.

It was worthy of noting here that in the above cascade reaction, sterically-hindered substituents on the aryl chlorides affected the reactions significantly. For example, for the reactions between tetralones **2** and 2-methylphenyl chloride **3b**, the sequential α-arylation and air-oxidation reaction can take place smoothly to give the desired oxidized products **6** in good to high yields (Table 5). However, when the mixture was treated with TsOH/toluene solution, the reactions became disordered and no obvious product can be isolated by SiO_2 column chromatography.

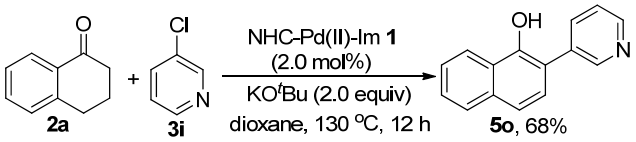
Table 5. NHC-Pd(II)-Im complex **1**-catalyzed reactions of tetralones **2** with 2-methylphenyl chloride **3b** and further oxidation in a one-pot procedure.



Entry[a]	2 (R^2)	Yield (%)[b]
1	**2a** (H)	**6b**, 87
2	**2b** (6-OMe)	**6c**, 82
3[c]	**2c** (7-OMe)	**6d**, 77
4	**2d** (7-F)	**6e**, 92

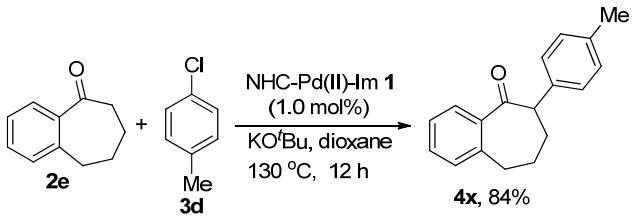
[a] Otherwise specified, all reactions were carried out using **2** (0.5 mmol), **3b** (0.6 mmol), **1** (1.0 mol%), KO^{t}Bu (2.0 equiv) in dioxane (1.0 mL) at 110 °C for 12 h, then the mixture was cooled to room temperature and stirred under air for another 3 h. [b] Isolated yields. [c] KO^{t}Bu (3.0 equiv) was added.

In addition, it was found that for the reaction between tetralone **2a** and heteroaryl chloride such as 3-chloropyridine **3i**, 2-(pyridine-3-yl)-naphthalen-1-ol **5o** can be obtained in 68% yield as the sole product under the normal α-arylation conditions after SiO_2-column chromatography, probably implying that the normal α-arylated product deriving from such reaction can be easily oxidized under air during the work-up process and the oxidized intermediate can proceed aromatization when SiO_2-column chromatography was carried out (Scheme 2).



Scheme 2. NHC-Pd(II)-Im complex **1**-catalyzed reaction between tetralone **2a** and 3-chloropyridine **3i**.

Finally, the reaction between 6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one **2e** with 4-methylphenyl chloride **3d** was also tested under identical conditions. As can be seen from Scheme 3, the reaction also worked well to give the desired α-arylated product **4x** in 84% yield.



Scheme 3. Reaction of **2e** with **3d** under the optimal conditions.

Conclusions

In conclusion, well-defined NHC-Pd(II)-Im complex **1** showed efficient catalytic activity toward the α-arylation of tetralones **2** with easily available and cheaper aryl chlorides **3**,

giving the desired α-arylated products **4** in good to high yields. After the α-arylation reaction was completed, the normal α-arylated products **4** can be further fully oxidized to the α-arylated-oxidized products, the 2-aryl-2'-hydroxytetralones **6**, in good yields in a one-pot procedure under air at room temperature. Furthermore, if the mixture of the above α-arylation-oxidation reaction was treated with TsOH/toluene solution under reflux, the final aromatized products, 2-aryl-naphthalen-1-ols **5**, can be achieved in acceptable to moderate yields. Various substituents on both substrates of tetralones **2** and aryl chlorides **3** are tolerated in all the above reactions, thus providing facile and versatile methodologies for the synthesis α-arylated tetralones, 2-aryl-2'-hydroxytetralones and 2-aryl-naphthalen-1-ols and also enriching the applications of NHC-Pd(II)-Im complex in organic synthesis.

Experimental

General Remarks. Melting points are uncorrected. NMR spectra were recorded at 500 (for ^{1}H NMR) or 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 is quadrupole. Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel.

General Procedure for the Formation of α-Arylated Products 4. Under N_2 atmosphere, NHC-Pd(II)-Im complex **1** (1.0 mol%), KO^{t}Bu (3.0 equiv), dioxane (1.0 mL), tetralones **2** (0.5 mmol) and aryl chlorides **3** (0.6 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at the specified temperature for 12 h. Then it was cooled to room temperature, diluted with ethyl acetate (10 mL) and acidified by saturated aqueous NH_4Cl to adjust the PH value to 7.0. Then the organic layer was separated and dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash column chromatography (eluent: petroleum/ethyl acetate = 150/1) to give pure products **4**.

General Procedure for the Formation of α-Arylated-Oxidized-Aromatized Products 5. Under N_2 atmosphere, NHC-Pd(II)-Im complex **1** (1.0 mol%), KO^{t}Bu (3.0 equiv), dioxane (1.0 mL), tetralones **2** (0.5 mmol) and aryl chlorides **3** (0.6 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at the specified temperature for 12 h. Then it was cooled to room temperature, exposed to air and stirred at room temperature for another 3 h. Then the mixture was dropped to a toluene solution of TsOH, which was pre-refluxed for 2 h, and the obtained mixture was refluxed for another 19 h. After the mixture was cooled to room temperature, it was diluted with ethyl acetate and washed by saturated aqueous $NaHCO_3$ (5 mL). The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash column chromatography (eluent: petroleum/ethyl acetate = 180/1) to give pure products **5**.

General Procedure for the Formation of α-Arylated-Oxidized Products 6. Under N_2 atmosphere, NHC-Pd(II)-Im complex **1** (1.0 mol%), KO^{t}Bu (3.0 equiv), dioxane (1.0 mL), tetralones **2** (0.5 mmol) and 2-methylphenyl chloride **3b** (0.6 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at the specified temperature for 12 h. Then it was cooled to room temperature, exposed to air and stirred at room temperature for another 3 h. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluent: petroleum/ethyl acetate = 50/1) to give pure products **6**.

Compound **4a**[2f]: white solid (188.7 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.40-2.48 (m, 2H), 3.00-3.13 (m, 2H), 3.81 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.25-7.37 (m, 5H), 7.51 (t, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 31.2, 54.3, 126.7, 126.9, 127.8, 128.4, 128.5, 128.7, 132.9, 133.4, 139.7, 144.0, 198.1.

Compound **4b**[2f]: yellow liquid (114.5 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.30 (s, 3H), 2.33 (dd, *J* = 8.5, 4.5 Hz, 1H), 2.42 (ddd, *J* = 23.5, 11.5, 4.5 Hz, 1H), 3.03 (dt, *J* = 10.2, 4.5 Hz, 1H), 3.12 (ddd, *J* = 16.0, 11.5, 4.5 Hz, 1H), 3.96 (dd, *J* = 11.5, 4.5 Hz, 1H), 7.03-7.05 (m, 1H), 7.12-7.20 (m, 3H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 29.3, 30.2, 51.4, 126.0, 126.6, 126.8, 127.5, 127.6, 128.7, 130.4, 132.9, 133.3, 136.4, 138.5, 144.0, 197.9.

Compound **4c**: white solid (94.4 mg, 80%); mp: 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H), 2.38-2.47 (m, 2H), 3.01-3.13 (m, 2H), 3.75 (dd, *J* = 10.0, 6.0 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.00 (s, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.20-7.24 (m, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.0 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 28.8, 31.2, 54.4, 125.4, 126.7, 127.7, 127.8, 128.4, 128.7, 129.2, 132.9, 133.3, 138.0, 139.7, 144.1, 198.2. MS (ESI): 259 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{16}NaO$ $[M+Na]^+$: 259.1099; found: 259.1085. IR (KBr) ν 3054, 2928, 2399, 1680, 1600, 1491, 1457, 1431, 1318, 1222, 1152, 906, 778, 740, 718, 700 cm^{-1}.

Compound **4d**[5d]: white solid (98.0 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H), 2.39-2.43 (m, 2H), 3.01-3.13 (m, 2H), 3.76 (dd, *J* = 9.5, 6.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 28.7, 31.1, 54.0, 126.7, 127.8, 128.2, 128.7, 129.2, 132.9, 133.3, 136.4, 136.6, 144.0, 198.3.

Compound **4e**: white solid (93.3 mg, 74%); mp: 85-87 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.41-2.45 (m, 2H), 3.02-3.14 (m, 2H), 3.76-3.79 (m, 4H), 6.74 (s, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 7.5, 2.5 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.0 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 31.1, 54.4, 55.2, 112.2, 114.5, 120.8, 126.8, 127.8, 128.7,

129.5, 132.9, 133.4, 141.2, 144.0, 159.7, 198.0. MS (ESI): 275 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{16}NaO_2$ $[M+Na]^+$: 275.1048; found: 275.1021. IR (KBr) ν 3067, 2935, 1680, 1600, 1491, 1461, 1424, 1355, 1322, 1295, 1033, 964, 920, 861, 821, 786, 750, 697 cm^{-1}.

Compound **4f**[8]: white solid (114.7 mg, 91%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.39-2.43 (m, 2H), 3.02-3.15 (m, 2H), 3.75 (t, *J* = 8.0 Hz,1H), 3.80 (s, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 31.2, 53.6, 55.3, 114.0, 126.7, 127.8, 128.7, 129.3, 131.8, 132.9, 133.4, 144.0, 158.5, 198.4.

Compound **4g**: white solid (92.4 mg, 77%); mp: 79-81 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.39-2.43 (m, 2H), 3.04 (dt, *J* = 16.5, 4.5 Hz, 1H), 3.12 (dt, *J* = 16.5, 7.5 Hz, 1H), 3.79 (t, *J* = 8.0 Hz, 1H), 6.90 (dt, *J* = 10.0, 2.0 Hz, 1H), 6.94-6.98 (m, 2H), 7.27-7.35 (m, 3H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 31.0, 54.1 (d, $J_{C\text{-}F}$ = 1.50 Hz), 113.8 (d, $J_{C\text{-}F}$ = 20.875 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.625 Hz), 124.2 (d, $J_{C\text{-}F}$ = 2.75 Hz), 126.8, 128.0, 128.8, 129.9 (d, $J_{C\text{-}F}$ = 8.25 Hz), 132.6, 133.6, 142.1 (d, $J_{C\text{-}F}$ = 7.25 Hz), 143.9, 162.9 (d, $J_{C\text{-}F}$ = 244.125 Hz), 197.4. MS (ESI): 263 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{16}H_{13}FNaO$ $[M+Na]^+$: 263.0848; found: 263.0839. IR (KBr) ν 3050, 2941, 2895, 1676, 1587, 1484, 1444, 1305, 1265, 1222, 1139, 1007, 962, 919, 884, 864, 823, 780, 741, 715, 685 cm^{-1}.

Compound **4h**[5d]: white solid (96.0 mg, 80%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.39-2.43 (m, 2H), 3.05 (dt, *J* = 16.5, 4.5 Hz, 1H), 3.14 (dt, *J* = 16.5, 7.5 Hz, 1H), 3.78 (t, *J* = 8.5 Hz, 1H), 7.03 (t, *J* = 8.5 Hz, 2H), 7.16 (dd, *J* = 8.5, 5.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.51 (td, *J* = 7.5, 1.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.9, 31.3, 53.7, 115.4 (d, $J_{C\text{-}F}$ = 21.25 Hz), 126.8, 127.8, 128.8, 129.9 (d, $J_{C\text{-}F}$ = 7.875 Hz), 132.7, 133.5, 135.4 (d, $J_{C\text{-}F}$ = 3.25 Hz), 143.9, 161.8 (d, $J_{C\text{-}F}$ = 241.375 Hz), 197.9.

Compound **4i**[5d]: white solid (92.0 mg, 73%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.38-2.42 (m, 2H), 2.96-3.09 (m, 2H), 3.76 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 31.3, 54.0, 55.4, 112.6, 113.3, 126.6, 126.8, 128.4, 128.5, 130.3, 140.0, 146.5, 163.6, 197.0.

Compound **4j**: yellow solid (113.1 mg, 85%); mp: 72-74 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.26-2.40 (m, 5H), 2.97 (dt, *J* = 16.5, 4.5 Hz, 1H), 3.03-3.10 (m, 1H), 3.83 (s, 3H), 3.92 (dd, *J* = 11.5, 5.0 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.02-7.04 (m, 1H), 7.10-7.20 (m, 3H), 8.06 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.7, 29.5, 30.3, 51.0, 55.3, 112.4, 113.1, 125.9, 126.59, 126.62, 127.5, 130.0, 130.4, 136.3, 138.8, 146.4, 163.5, 196.7. MS (ESI): 289 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_2$ $[M+Na]^+$: 289.1204; found: 289.1187. IR (KBr) ν 2935, 2822, 1680, 1603, 1491, 1454, 1355, 1249, 1152, 1096, 1020, 897, 852, 834, 799, 750, 731 cm^{-1}.

Compound **4k**: yellow solid (110.4 mg, 83%); mp: 84-86 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H), 2.37-2.41 (m, 2H), 2.95-3.07 (m, 2H), 3.71 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.85 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.97-7.00 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 29.0, 31.3, 54.0, 55.4, 112.5, 113.2, 125.4, 126.6, 127.6, 128.3, 129.1, 130.2, 138.0, 140.0, 146.5, 163.6, 197.1. MS (ESI): 289 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_2$ $[M+Na]^+$: 289.1204; found: 289.1175. IR (KBr) ν 2941, 1673, 1600, 1487, 1448, 1335, 1242, 1222, 1099, 1010, 920, 909, 901, 872, 851, 834, 786, 703 cm^{-1}.

Compound **4l**: yellow solid (93.1 mg, 70%); mp: 54-56 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.32 (s, 3H), 2.36 (dd, *J* = 12.5, 7.5 Hz, 2H), 2.94-3.06 (m, 2H), 3.70 (t, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 28.9, 31.2, 53.5, 55.3, 112.5, 113.2, 126.5, 128.2, 129.1, 130.2, 136.2, 136.9, 146.5, 163.5, 197.0. MS (ESI): 289 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_2$ $[M+Na]^+$: 289.1204; found: 289.1203. IR (KBr) ν 2935, 2849, 1686, 1597, 1514, 1494, 1451, 1341, 1245, 1103, 1030, 897, 816, 785, 753 cm^{-1}.

Compound **4m**: yellow solid (115.7 mg, 82%); mp: 77-79 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.35-2.40 (m, 2H), 2.94-3.05 (m, 2H), 3.72 (t, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.84 (s, 3H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.73 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.79 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.84 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 31.1, 53.9, 55.0, 55.3, 112.0, 112.5, 113.2, 114.4, 120.7,126.4, 129.3, 130.1, 141.5, 146.5, 159.6, 163.6, 196.7. MS (ESI): 305 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_3$ $[M+Na]^+$: 305.1154; found: 305.1143. IR (KBr) ν 2941, 2835, 1680, 1571, 1487, 1451, 1434, 1358, 1278, 1259, 1161, 1103, 1036, 1020, 917, 896, 877, 859, 826, 793, 775, 751, 695 cm^{-1}.

Compound **4n**[9]: white solid (114.3 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.34-2.39 (m, 2H), 2.95-3.08 (m, 2H), 3.71 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.79 (s, 3H), 3.86 (s, 3H), 6.71 (d, *J* = 2.5 Hz, 1H), 6.83-6.88 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 31.3, 53.1, 55.2, 55.4, 112.5, 113.2, 113.9, 126.5, 129.3, 130.2, 132.0, 146.5, 158.4, 163.5, 197.2.

Compound **4o**[10]: white solid (104.0 mg, 77%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.35-2.41 (m, 2H), 2.99 (dt, *J* = 17.0, 4.5 Hz, 1H), 3.05-3.11 (m, 1H), 3.74 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.87 (s, 3H), 6.73 (d, *J* = 2.5 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.02 (t, *J* = 9.0 Hz, 2H), 7.15 (dd, *J* = 8.5, 5.0 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.1, 31.4, 53.3, 55.5, 112.6, 113.3, 115.3 (d, $J_{C\text{-}F}$ = 21.25), 126.4, 129.9 (d, $J_{C\text{-}F}$ = 7.875), 130.3, 135.7 (d, $J_{C\text{-}F}$ = 3.625), 146.2, 161.8 (d, $J_{C\text{-}F}$ = 243.375), 163.7, 196.7.

Compound **4p**: yellow solid (92.0 mg, 73%); mp: 74-75 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.37-2.42 (m, 2H), 2.93-3.05 (m, 2H), 3.77 (t, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 7.08 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.17-7.19 (m, 3H), 7.24-7.27 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 31.4, 54.1, 55.4, 109.7, 121.7, 126.8, 128.4, 128.5, 129.9, 133.6, 136.6, 139.8, 158.4, 198.1. MS (ESI): 253 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223; found:

253.1223. IR (KBr) ν 2941, 2841, 1673, 1607, 1497, 1457, 1418, 1348, 1331, 1272, 1242, 1202, 1196, 1172, 1023, 881, 872, 844, 813, 775, 753, 730, 695 cm^{-1}.

Compound **4q**: yellow solid (117.1 mg, 88%); mp: 84-86 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.28-2.43 (m, 5H), 2.97 (dt, *J* = 16.5, 4.5 Hz, 1H), 3.02-3.08 (m, 1H), 3.82 (s, 3H), 3.94 (dd, *J* = 12.0, 4.5 Hz, 1H), 7.03-7.05 (m, 1H), 7.08 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.12-7.16 (m, 2H), 7.17-7.21 (m, 2H), 7.58 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 28.4, 30.5, 51.2, 55.4, 109.6, 121.6, 126.0, 126.8, 127.5, 129.9, 130.4, 133.8, 136.4, 136.6, 138.6, 158.4, 197.9. MS (ESI): 289 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_2$ $[M+Na]^+$: 289.1204; found: 289.1177. IR (KBr) ν 3021, 2935, 1912, 1683, 1610, 1570, 1497, 1348, 1331, 1242, 1166, 1033, 877, 833, 816, 798, 763, 750, 728, 713 cm^{-1}.

Compound **4r**: yellow liquid (102.5 mg, 77%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.33 (s, 3H), 2.35-2.39 (m, 2H), 2.92-3.04 (m, 2H), 3.73 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 7.06-7.08 (m, 3H), 7.13-7.18 (m, 3H), 7.57 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 27.8, 31.4, 53.7, 55.4, 109.7, 121.6, 128.2, 129.1, 129.9, 133.6, 136.4, 136.6, 136.7, 158.4, 198.2. MS (ESI): 289 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_2$ $[M+Na]^+$: 289.1204; found: 289.1174. IR (KBr) ν 3007, 2928, 2829, 2365, 2051, 1898, 1683, 1604, 1567, 1487, 1418, 1328, 1265, 1239, 1172, 1113, 1033, 960, 881, 816, 786, 755, 730, 705 cm^{-1}.

Compound **4s**[11]: yellow solid (129.8 mg, 92%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.33-2.38 (m, 2H), 2.92-3.04 (m, 2H), 3.71 (t, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.82 (s, 3H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.07 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.7, 31.3, 53.2, 55.1, 55.3, 109.7, 113.8, 121.5, 129.2, 129.8, 131.7, 133.5, 136.5, 158.3, 158.4, 198.2.

Compound **4t**: white solid (87.6 mg, 73%); mp: 88-90 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.41-2.45 (m, 2H), 2.99-3.11 (m, 2H), 3.78 (t, *J* = 7.5 Hz, 1H), 7.17-7.22 (m, 3H), 7.25-7.29 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.75 (dd, *J* = 9.0, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 31.1, 54.0, 113.5 (d, J_{C-F} = 21.75 Hz), 120.7 (d, J_{C-F} = 22.125 Hz), 127.0, 128.3, 128.6, 130.6 (d, J_{C-F} = 7.00 Hz), 134.4 (d, J_{C-F} = 6.00 Hz), 139.3, 139.7 (d, J_{C-F} = 2.875 Hz), 161.6 (d, J_{C-F} = 244.875 Hz), 197.1 (d, J_{C-F} = 1.5 Hz). MS (ESI): 263 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{16}H_{13}FNaO$ $[M+Na]^+$: 263.0848; found: 263.0835. IR (KBr) ν 3067, 2921, 2855, 1673, 1610, 1494, 1457, 1424, 1358, 1318, 1259, 1235, 1149, 1083, 962, 909, 886, 834, 811, 776, 750, 727 cm^{-1}.

Compound **4u**: colorless liquid (99.1 mg, 78%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.30 (s, 3H), 2.32-2.44 (m, 2H), 3.00-3.12 (m, 2H), 3.94 (dd, *J* = 12.0, 5.0 Hz, 1H), 7.02-7.04 (m, 1H), 7.13-7.20 (m, 4H), 7.26 (dd, *J* = 8.5, 5.0 Hz, 1H), 7.73 (dd, *J* = 9.0, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 28.6, 30.3, 51.1, 113.4 (d, J_{C-F} = 21.75 Hz), 120.6 (d, J_{C-F} = 22.125 Hz), 126.1, 126.9, 127.4, 130.5, 130.6, 134.5 (d, J_{C-F} = 6.00 Hz), 136.4, 138.2, 139.7, 161.5 (d, J_{C-F} = 244.75 Hz), 196.9. MS (ESI): 277 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{15}FNaO$ $[M+Na]^+$: 277.1005; found: 277.0977. IR (neat) ν 3054, 3014, 2935, 2868, 1690, 1610, 1494, 1418, 1355, 1312, 1259, 1232, 1149, 1106, 1053, 1027, 891, 834, 809, 796, 750, 733, 713 cm^{-1}.

Compound **4v**: yellow solid (102.9 mg, 81%); mp: 91-93 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.34 (s, 3H), 2.38-2.43 (m, 2H), 2.98-3.09 (m, 2H), 3.74 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.19 (td, *J* = 8.5, 3.0 Hz, 1H), 7.25 (dd, *J* = 8.5, 5.0 Hz, 1H), 7.74 (dd, *J* = 8.5, 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 28.0, 31.1, 53.6, 113.6 (d, J_{C-F} = 21.625 Hz), 120.7 (d, J_{C-F} = 22.125 Hz), 128.2, 129.3, 130.5 (d, J_{C-F} = 7.00 Hz), 134.4 (d, J_{C-F} = 6.00 Hz), 136.2, 136.6, 139.7 (d, J_{C-F} = 2.875 Hz), 161.6 (d, J_{C-F} = 244.875 Hz), 197.3 (d, J_{C-F} = 1.5 Hz). MS (ESI): 277 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{15}FNaO$ $[M+Na]^+$: 277.1005; found: 277.0981. IR (KBr) ν 2948, 2862, 1683, 1607, 1583, 1517, 1487, 1424, 1358, 1318, 1259, 1232, 1156, 902, 889, 848, 818, 786, 731, 705 cm^{-1}.

Compound **4w**: white solid (113.4 mg, 84%); mp: 102-104 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.37-2.42 (m, 2H), 2.99-3.10 (m, 2H), 3.73 (t, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 6.89 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 7.20 (td, *J* = 8.0, 3.0 Hz, 1H), 7.25-7.27 (m, 1H), 7.74 (dd, *J* = 9.0, 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 31.2, 53.2, 55.3, 113.6 (d, J_{C-F} = 21.75 Hz), 114.1, 120.7 (d, J_{C-F} = 22.125 Hz), 129.3, 130.6 (d, J_{C-F} = 7.00 Hz), 131.3, 134.4 (d, J_{C-F} = 6.00 Hz), 139.7 (d, J_{C-F} = 3.00 Hz), 158.6, 161.6 (d, J_{C-F} = 244.75 Hz), 197.4 (d, J_{C-F} = 1.625 Hz). MS (ESI): 293 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{15}FNaO_2$ $[M+Na]^+$: 293.0954; found: 293.0935. IR (KBr) ν 2921, 1686, 1607, 1517, 1491, 1421, 1355, 1315, 1255, 1176, 1149, 1106, 1027, 902, 882, 831, 788, 735, 703 cm^{-1}.

Compound **4x**: yellow liquid (105.1 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 1.79-1.87 (m, 1H), 2.06-2.19 (m, 3H), 2.33 (s, 3H), 2.96-3.00 (m, 1H), 3.06-3.11 (m, 1H), 4.02 (dd, *J* = 11.0, 5.0 Hz, 1H), 7.13-7.17 (m, 4H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 25.4, 31.2, 32.9, 55.4, 126.5, 128.4, 128.5, 129.0, 129.6, 131.4, 136.4, 137.2, 140.0, 141.1, 205.8. MS (ESI): 273 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO$ $[M+Na]^+$: 273.1251; found: 273.1250. IR (KBr) ν 3014, 2935, 2861, 1686, 1597, 1514, 1444, 1269, 1199, 1023, 980, 957, 813, 794, 761, 735 cm^{-1}.

Compound **5a**[12]: yellow solid (78.1 mg, 71%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 5.85 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.43 (td, *J* = 9.0, 4.5 Hz, 1H), 7.48-7.52 (m, 3H), 7.54 (d, *J* = 4.5 Hz, 4H), 7.81-7.83 (m, 1H), 8.29-8.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.2, 121.2, 122.4, 124.3, 125.5, 126.5, 127.5, 127.6, 127.9, 129.3, 129.6, 134.2, 137.4, 147.7.

Compound **5b**[13]: brown liquid (70.2 mg, 60%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 5.91 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.32-7.35 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.48-7.51 (m, 2H), 7.80-7.82 (m, 1H), 8.28-8.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 120.1, 121.3, 122.4, 124.2, 125.5, 126.2, 126.4, 127.4, 127.5, 128.6, 129.5, 130.0, 134.1, 137.3, 139.4, 147.7.

Compound **5c**: yellow solid (67.9 mg, 58%); mp: 74-76 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 5.86 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 3H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.49-7.52 (m, 2H), 7.80-7.82 (m, 1H), 8.27-8.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 120.1, 121.2, 122.4, 124.2, 125.4, 126.3, 127.4, 127.6, 129.2, 130.3, 134.0, 134.2, 137.7, 147.7. MS (ESI): 235 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{15}O$ $[M+H]^+$: 235.1123; found: 235.1109. IR (KBr) ν 3524, 3338, 1573, 1501, 1461, 1381, 1295, 1245, 1179, 1099, 1046, 1017, 879, 806, 746, 723 cm^{-1}.

Compound **5d**: brown solid (72.5 mg, 58%); mp: 103-105 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 3.88 (s, 3H), 5.81 (s, 1H), 7.07 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 8.5 Hz, 1H), 7.45-7.48 (m, 3H), 7.49-7.53 (m, 2H), 7.81-7.83 (m, 1H), 8.27-8.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 115.0, 120.0, 120.9, 122.3, 124.2, 125.5, 126.3, 127.4, 127.7, 129.4, 130.5, 134.0, 147.7, 159.3. MS (ESI): 273 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{14}NaO_2$ $[M+Na]^+$: 273.0891; found: 273.0867. IR (KBr) ν 3431, 1607, 1567, 1511, 1461, 1434, 1381, 1341, 1292, 1242, 1176, 1093, 1050, 1027, 879, 861, 834, 808, 781, 747, 713 cm^{-1}.

Compound **5e**: yellow solid (67.9 mg, 57%); mp: 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 5.67 (s, 1H), 7.19 (t, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 1H), 7.46-7.51(m, 5H), 7.80-7.82 (m, 1H), 8.26-8.28 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 116.5 (d, $J_{C\text{-}F}$ = 21.375 Hz), 120.29, 120.32, 122.3, 124.3, 125.6, 126.5, 127.5, 131.1 (d, $J_{C\text{-}F}$ = 8.00 Hz), 133.2 (d, $J_{C\text{-}F}$ = 3.25 Hz), 134.2, 147.7, 162.4 (d, $J_{C\text{-}F}$ = 246.375 Hz). MS (ESI): 239 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{12}FO$ $[M+H]^+$: 239.0867; found: 239.0864. IR (KBr) ν 3259, 1600, 1564, 1511, 1365, 1328, 1219, 1156, 1090, 1043, 881, 838, 816, 748 cm^{-1}.

Compound **5f**: yellow solid (91.0 mg, 69%); mp: 79-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.42 (s, 3H), 3.91 (s, 3H), 5.86 (s, 1H), 7.10 (d, J = 2.5 Hz, 1H), 7.15 (dd, J = 9.0, 2.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.34-7.29 (m, 4H), 7.40 (t, J = 7.5 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 55.3, 105.7, 117.9, 119.0, 119.5, 119.6, 124.2, 126.3, 128.3, 128.4, 129.5, 130.0, 135.6, 137.4, 139.4, 148.0, 158.2. MS (ESI): 265 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1229; found: 265.1217. IR (KBr) ν 3557, 3438, 1627, 1603, 1577, 1511, 1428, 1371, 1292, 1265, 1215, 1199, 1162, 1010, 942, 872, 856, 823, 798, 761, 713 cm^{-1}.

Compound **5g**: brown solid (71.3 mg, 54%); mp: 103-104 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 3.93 (s, 3H), 5.81 (s, 1H), 7.11 (d, J = 2.5 Hz, 1H), 7.15 (dd, J = 9.0, 2.5 Hz, 1H), 7.29-7.36 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 8.18 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 55.3, 105.7, 117.9, 119.0, 119.47, 119.51, 124.1, 128.4, 129.2, 130.3, 134.4, 135.6, 137.4, 148.0, 158.2. MS (ESI): 265 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1229; found: 265.1216. IR (KBr) ν 3557, 3424, 1627, 1600, 1577, 1514, 1428, 1371, 1295, 1265, 1219, 1196, 1162, 1020, 944, 876, 856, 823, 796 cm^{-1}.

Compound **5h**: yellow solid (81.2 mg, 58%); mp: 121-123 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 3.83 (s, 3H), 3.91 (s, 3H), 5.94 (s, 1H), 6.93 (dd, J = 8.5, 2.5 Hz, 1H), 7.03 (s, 1H), 7.08-7.10 (m, 2H), 7.15 (dd, J = 9.0, 2.5 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.2, 55.3, 105.7, 113.4, 114.7, 118.0, 119.0, 119.3, 119.5, 121.3, 124.2, 128.1, 130.6, 135.7, 138.9, 148.0, 158.3, 160.5. MS (ESI): 281 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172; found: 281.1169. IR (KBr) ν 3451, 1630, 1603, 1577, 1511, 1431, 1375, 1282, 1242, 1199, 1020, 942, 877, 852, 831, 766, 715 cm^{-1}.

Compound **5i**: white solid (75.6 mg, 54%); mp: 125-127 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 3.86 (s, 3H), 3.92 (s, 3H), 5.76 (s, 1H), 7.04 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 2.5 Hz, 1H), 7.15 (dd, J = 9.0, 2.5 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.26, 55.35, 105.7, 115.0, 117.9, 118.9, 119.2, 119.5, 124.1, 128.5, 129.5, 130.5, 135.5, 148.0, 158.1, 159.2. MS (ESI): 281 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172; found: 281.1169. IR (KBr) ν 3451, 2921, 2848, 1627, 1603, 1577, 1511, 1428, 1375, 1282, 1242, 1162, 1099, 1017, 940, 876, 853, 829, 765, 715 cm^{-1}.

Compound **5j**: brown solid (77.7 mg, 58%); mp: 95-97 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 3.92 (s, 3H), 5.62 (s, 1H), 7.11 (d, J = 2.5 Hz, 1H), 7.15-7.21 (m, 3H), 7.26 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 9.0, 5.5 Hz, 2H), 8.17 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 105.7, 116.4 (d, $J_{C\text{-}F}$ = 21.25 Hz), 118.1, 118.6, 119.2, 119.5, 124.1, 128.2, 131.1 (d, $J_{C\text{-}F}$ = 7.875 Hz), 133.4 (d, $J_{C\text{-}F}$ = 3.25 Hz), 135.7, 148.0, 158.3, 162.3 (d, $J_{C\text{-}F}$ = 246.00 Hz). MS (ESI): 291 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{13}FNaO_2$ $[M+Na]^+$: 291.0797; found: 291.0778. IR (KBr) ν 3497, 1630, 1597, 1573, 1507, 1424, 1375, 1288, 1262, 1219, 1023, 940, 877, 838, 765 cm^{-1}.

Compound **5k**: yellow solid (67.4 mg, 51%); mp: 100-101 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.41 (s, 3H), 3.93 (s, 3H), 5.81 (s, 1H), 7.15 (dd, J = 9.0, 2.5 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.38-7.41 (m, 3H), 7.55 (d, J = 2.5 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 55.3, 100.5, 119.1, 119.9, 121.8, 125.1, 125.2, 129.0, 129.1, 129.6, 130.2, 134.5, 137.6, 146.8, 157.6. MS (ESI): 287 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{16}NaO_2$ $[M+H]^+$: 287.1048; found: 287.1034. IR (KBr) ν 3543, 1627, 1603, 1573, 1504, 1461, 1424, 1371, 1269, 1215, 1146, 1023, 934, 879, 848, 823, 735, 722 cm^{-1}.

Compound **5l**: brown solid (92.4 mg, 66%); mp: 79-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 3.86 (s, 3H), 3.94 (s, 3H), 5.75 (s, 1H), 7.05 (d, J = 8.5 Hz, 2H), 7.15 (dd, J = 9.0, 2.5, Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 2.5 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 100.5, 115.0, 119.1, 119.9, 121.6, 125.1, 125.4, 129.1, 129.5, 129.6, 130.5, 146.8, 157.7, 159.3. MS (ESI): 303 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{16}NaO_3$ $[M+Na]^+$: 303.0997; found: 303.0975. IR (KBr) ν 3444, 1630, 1603, 1577, 1517, 1461, 1424, 1375, 1282, 1109, 1046, 1027, 932, 884, 851, 826, 738, 722 cm^{-1}.

Compound **5m**: yellow solid (66.8 mg, 53%); mp: 86-88 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 5.82 (s, 1H), 7.25 (td, J = 8.0, 2.5 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.78 (dd, J = 9.0, 5.5 Hz, 1H), 7.88 (dd, J = 10.5, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 106.3 (d, $J_{C\text{-}F}$ = 22.25 Hz), 116.6 (d, $J_{C\text{-}F}$ = 25.25 Hz), 120.0, 122.0, 125.1 (d, $J_{C\text{-}F}$ = 9.00 Hz), 126.9 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.1, 129.8 (d, $J_{C\text{-}F}$ = 8.75 Hz), 130.4, 131.1, 134.0, 138.0, 147.3 (d, $J_{C\text{-}F}$ = 5.375 Hz), 160.7 (d, $J_{C\text{-}F}$ = 243.375 Hz). MS (ESI): 275 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{13}FNaO$ $[M+Na]^+$: 275.0848; found: 275.0834. IR (KBr) ν

3523, 1636, 1603, 1511, 1448, 1368, 1209, 1149, 1040, 944, 879, 823, 788, 738, 718 cm^{-1}.

Compound **5n**: brown solid (77.7 mg, 58%); mp: 99-101 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 3.84 (s, 3H), 5.80 (s, 1H), 7.03 (d, J = 9.0 Hz, 2H), 7.23 (dd, J = 8.5, 2.5 Hz, 1H), 7.25 (d, J = 9.0 Hz, 1H), 7.40-7.43 (m, 3H), 7.76 (dd, J = 9.0, 5.5 Hz, 1H), 7.87 (dd, J = 10.5, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 106.2 (d, J_{C-F} = 22.25 Hz), 115.1, 116.5 (d, J_{C-F} = 25.375 Hz), 119.9, 121.8, 125.1 (d, J_{C-F} = 8.875 Hz), 127.0 (d, J_{C-F} = 1.875 Hz), 129.1, 129.8 (d, J_{C-F} = 8.75 Hz), 130.4, 131.0, 147.3 (d, J_{C-F} = 5.25 Hz), 159.5, 160.2 (d, J_{C-F} = 243.375 Hz). MS (ESI): 291 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{13}FNaO_2$ $[M+Na]^+$: 291.0797; found: 291.0781. IR (KBr) ν 3444, 1610, 1507, 1448, 1371, 1282, 1235, 1152, 1040, 944, 874, 824, 722 cm^{-1}.

Compound **5o:** white solid (75.2 mg, 68%); mp: 205-207 °C. ^1H NMR (500 MHz, DMSO-d_6, TMS) δ 7.46 (d, J = 8.5 Hz, 1H), 7.49 (ddd, J = 8.0, 5.0, 1.0 Hz, 1H), 7.53-7.56 (m, 3H), 7.90 (dd, J = 7.5, 2.5 Hz, 1H), 8.02 (dt, J = 8.0, 2.0 Hz, 1H), 8.30-8.32 (m, 1H), 8.54 (dd, J = 5.0, 2.0 Hz, 1H), 8.82 (d, J = 2.0 Hz, 1H), 9.53 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 120.0, 120.2, 122.4, 123.3, 125.4, 125.7, 126.4, 127.6, 128.0, 134.0, 134.6, 136.8, 147.4, 149.5, 150.1. MS (ESI): 222 $[M+H]^+$; HRMS (ESI) calcd. for $C_{15}H_{12}NO$ $[M+H]^+$: 222.0919; found: 222.0908. IR (KBr) ν 3054, 1567, 1504, 1481, 1385, 1312, 1189, 1106, 1040, 973, 952, 889, 864, 818, 800, 746, 710 cm^{-1}.

Compound **6a**: red liquid (76.2 mg, 64%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.44 (td, J = 12.5, 5.0 Hz, 1H), 2.66-2.74 (m, 2H), 2.87-2.92 (m, 1H), 4.24 (s, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.24-7.29 (m, 5H), 7.37 (t, J = 7.5 Hz, 1H), 7.50 (td, J = 7.5, 1.5 Hz, 1H), 8.17 (dd, J = 8.0, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 36.5, 77.7, 126.0, 126.9, 127.6, 128.0, 128.4, 129.0, 131.7, 134.1, 141.0, 144.3, 200.6. MS (ESI): 261 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{16}H_{14}NaO_2$ $[M+Na]^+$: 261.0891; found: 261.0874. IR (neat) ν 3477, 3054, 3021, 2928, 1686, 1600, 1491, 1451, 1361, 1288, 1225, 1159, 1076, 990, 939, 887, 848, 761, 738 cm^{-1}.

Compound **6b**: white solid (109.7 mg, 87%); mp: 107-109 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.24-2.31 (m, 1H), 2.58 (s, 3H), 2.60-2.66 (m, 1H), 2.88-2.95 (m, 2H), 4.12 (s, 1H), 6.80 (d, J = 7.5 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.5, 1.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.51 (td, J = 7.5, 1.5 Hz, 1H), 8.18 (dd, J = 8.5, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 26.6, 35.4, 79.3, 125.2, 126.8, 127.0, 127.7, 127.8, 128.9, 132.0, 132.8, 134.0, 137.5, 138.9, 144.4, 201.3. MS (ESI): 275 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{16}NaO_2$ $[M+Na]^+$: 275.1048; found: 275.1038. IR (KBr) ν 3431, 2365, 1680, 1597, 1487, 1461, 1371, 1308, 1275, 1222, 1156, 1066, 977, 947, 886, 848, 806, 768, 756, 705 cm^{-1}.

Compound **6c**: white solid (115.7 mg, 82%); mp: 147-149 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.23-2.29 (m, 1H), 2.55-2.61 (m, 4H), 2.83-2.88 (m, 2H), 3.85 (s, 3H), 4.16 (s, 1H), 6.64 (d, J = 2.5 Hz, 1H), 6.80 (d, J = 7.5 Hz,1H), 6.90-6.93 (m, 2H), 7.13 (td, J = 7.5, 1.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 8.15 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 27.0, 35.4, 55.5, 79.1, 112.6, 113.9, 125.1, 125.4, 126.9, 127.7, 130.3, 132.8, 137.6, 139.2, 147.1, 164.2, 199.7. MS (ESI): 305 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_3$ $[M+Na]^+$: 305.1154; found: 305.1141. IR (KBr) ν 3470, 3060, 2928, 1670, 1600, 1494, 1444, 1348, 1252, 1076, 1023, 995, 944, 915, 889, 861, 833, 791, 761, 753, 727 cm^{-1}.

Compound **6d**: yellow solid (108.6 mg, 77%); mp: 76-78 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.21-2.27 (m, 1H), 2.50-2.57 (m, 1H), 2.58 (s, 3H), 2.81-2.89 (m, 2H), 3.86 (s, 3H), 4.14 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 8.0 Hz,1H), 7.09 (d, J = 1.5 Hz, 2H), 7.12 (td, J = 8.0, 1.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 25.8, 35.6, 55.4, 79.2, 109.5, 122.4, 125.1, 126.8, 127.7, 130.0, 132.6, 132.7, 137.0, 137.5, 139.0, 158.6, 201.2. MS (ESI): 305 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{18}H_{18}NaO_3$ $[M+Na]^+$: 305.1154; found: 305.1121. IR (KBr) ν 3451, 3014, 2928, 2835, 1918, 1676, 1603, 1497, 1464, 1428, 1331, 1278, 1235, 1179, 1086, 1023, 964, 939, 899, 876, 829, 814, 793, 761, 746, 725 cm^{-1}.

Compound **6e**: brown solid (124.3 mg, 92%); mp: 81-83 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 2.23-2.29 (m, 1H), 2.54-2.61 (m, 4H), 2.86-2.94 (m, 2H), 4.02 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 7.13-7.24 (m, 4H), 7.82 (dd, J = 9.0, 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 25.9, 35.4, 79.1, 113.4 (d, J_{C-F} = 21.875 Hz), 121.4 (d, J_{C-F} = 22.125 Hz), 125.2, 126.6, 127.9, 130.7 (d, J_{C-F} = 7.125 Hz), 132.8, 133.4 (d, J_{C-F} = 6.25 Hz), 137.3, 138.7, 140.1 (d, J_{C-F} = 3.00 Hz), 161.6 (d, J_{C-F} = 245.5 Hz), 200.2. MS (ESI): 293 $[M+Na]^+$; HRMS (ESI) calcd. for $C_{17}H_{15}FNaO_2$ $[M+H]^+$: 293.0954; found: 293.0943. IR (KBr) ν 3431, 1680, 1610, 1590, 1494, 1421, 1371, 1345, 1318, 1272, 1239, 1159, 1083, 962, 945, 889, 829, 809, 785, 756, 730 cm^{-1}.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Copy of ^1H and ^{13}C NMR spectra of compounds **4-6**]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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