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Synthesis of *N*-heterocyclic carbene-Pd(II)-5-phenyloxazole complexes and initial studies of their catalytic activity toward the Buchwald-Hartwig amination of aryl chlorides

Zhi-Mao Zhang, Yu-Ting Xu, Li-Xiong Shao*

College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Zhejiang Province 325035, People's Republic of China

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ABSTRACT

Three new *N*-heterocyclic carbene (NHC)-Pd(II) complexes using 5-phenyloxazole as the ancillary ligand have been obtained in moderate to good yields by a one-pot reaction of the corresponding imidazolium salts, palladium chloride and 5-phenyloxazole under mild conditions. Initial studies showed that one of the complexes is an efficient catalyst for the Buchwald-Hartwig amination of aryl chlorides with various secondary and primary amines under the varied catalyst loading of 0.01-0.05 mol%, thus it will enrich the chemistry of NHCs and give an alternative catalyst for the coupling of challenging while cost-low aryl chlorides.

1. Introduction

Traditionally, palladium-phosphine ligands system-catalyzed Buchwald-Hartwig amination is a popular methodology for the formation of *N*-containing compounds [1–4]. Compared to their tertiary phosphine counterparts, *N*-heterocyclic carbenes (NHCs) are usually more air-, thermal and moisture-stable. Consequently, during the past years, many NHC-palladium complexes have also been developed and applied in the Buchwald-Hartwig amination of aryl chlorides with various amines [5–24]. In these cases, development of highly efficient NHC-palladium complexes can be divided into two main different pathways: one is the modification of the NHC moieties usually using pyridines as the ancillary ligands [5–8,17–20,24]; the other is the changement of the ancillary ligands using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) as the NHC skeleton [12,13,16,21], and it seems that main interest was paid on the modification of NHC skeletons. However, besides some simple NHC moieties such as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene (IXy) and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), lengthy pathways were necessary for most other NHC skeletons. In addition, pyridines seemed to be the sole choice as the solvent and ancillary ligand in most cases. Through the hard research during the recent years, a new and convenient strategy for the synthesis of NHC-palladium complexes has been developed by our group. That is, the strategy that keeping the NHC skeleton as IPr and simply changing the ancillary ligands was performed. In the reactions, the ancillary ligands can be used only in equivalents amounts and all complexes can be achieved in good to high yields by a one-pot procedure from IPr·HCl, $PdCl_2$ and the ancillary ligands under mild conditions, providing an impressive method for the development of NHC-palladium complexes kept high catalytic activities *via* simple pathways [25–32]. Initial studies showed that they were also efficient catalysts for the cross-coupling reactions involving the challenging aryl chlorides and aryl sulfonates [33–52]. Encouraged by such successful results, we then continued this investigation by trying other easily available ancillary ligand to find out new NHC-palladium complexes. In this case, 5-phenyloxazole was chosen as the ancillary ligand, and some novel NHC-palladium complexes were then developed. Initial studies showed that they were also efficient catalysts for the Buchwald-Hartwig amination of aryl chlorides with various amines under very low catalyst loadings. In addition, comparison with some well-defined NHC-Pd(II) complexes were also performed under the same conditions and similar results were achieved, thus will give at least an alternative catalyst for the coupling of aryl chlorides. Herein, we report these results in detail.

* Corresponding author.
E-mail addresses: Shaolix@wzu.edu.cn, shaolix@163.com (L.-X. Shao).

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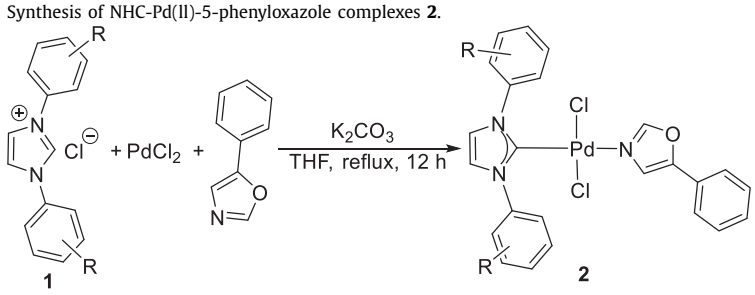
Table 1
Synthesis of NHC-Pd(II)-5-phenyloxazole complexes **2**.



Entry[a]	**1** (R) (equiv)	Yield (%)[b]
1	**1a** (2,6-^{i}Pr) (1.2)	**2a**, 74
2	**1b** (2,6-Me_2) (1.5)	**2b**, 85
3	**1c** (2,4,6-Me_3) (1.5)	**2c**, 80

[a] All reactions were carried out using **1**, $PdCl_2$ (0.15 mmol), 5-phenyloxazole (1.0 equiv) and K_2CO_3 (1.2 equiv) in THF (2.0 mL) under reflux for 12 h.
[b] Isolated yields.

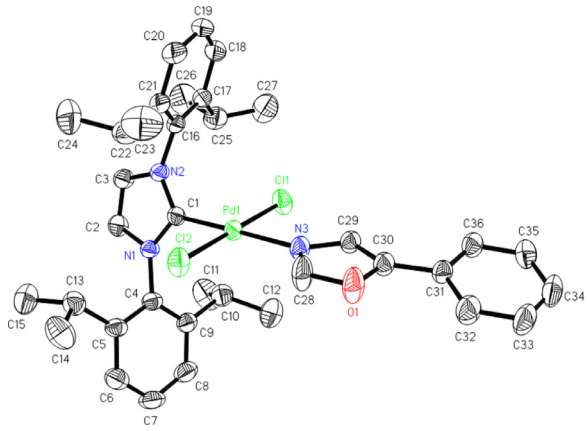
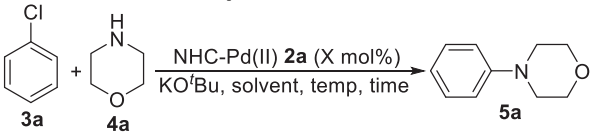


Fig. 1. The molecular structure of complex **2a** showing 30% probability ellipsoids; all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd(1)-C(1) = 1.963(3), Pd(1)-N(3) = 2.113(3), Pd(1)-Cl(1) = 2.2813(9), Pd(1)-Cl(2) = 2.3018(9); C(1)-Pd(1)-N(3) = 177.75(13), Cl(1)-Pd(1)-Cl(2) = 179.65(4), C(1)-Pd(1)-Cl(1) = 88.58(9), C(1)-Pd(1)-Cl(2) = 91.36(9), N(3)-Pd(1)-Cl(1) = 90.13(8), N(3)-Pd(1)-Cl(2) = 89.92(8).

Table 2
Repersentative results for the NHC-Pd(II) complex **2a** catalyzed reaction of chlorobenzene **3a** with morpholine **4a**.



Entry[a]	[X]	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	0.1	toluene	90	1	93
2	0.1	THF	90	1	60
3	0.1	dioxane	90	1	76
4	0.05	toluene	90	1	11
5	0.05	toluene	90	6	96
6	0.03	toluene	90	6	12
7	0.03	toluene	90	12	66
8	0.03	toluene	110	12	75
9	0.03	toluene	130	12	92

[a] Reaction conditions: **3a** (0.70 mmol), **4a** (0.84 mmol), KO^{t}Bu (0.91 mmol), **2a** (X mol%), solvent (1.0 mL)
[b] Isolated yields.

2. Results and discussion

2.1. Synthesis of NHC-Pd(II)-5-phenyloxazole complexes 2

First, the synthesis of NHC-Pd(II)-5-phenyloxazole complexes **2** was carried out using imidazolium salts **1**, $PdCl_2$ (0.15 mmol) and 5-phenyloxazole (1.0 equiv) in the presence of K_2CO_3 (1.2 equiv) in refluxing THF (2.0 mL) in a one-pot procedure for 12 h. All reactions performed well to give the desired complexes **2** in moderate to good yields (Table 1). The equivalents of the imidazolium salts have some effect on the reactions. For example, 1.2 equiv amounts of IPr·HCl are enough for the synthesis of complex **2a**, while 1.5 equiv amounts of IXy·HCl and IMes·HCl are necessary for the good yields of complexes **2b** and **2c**.

To confirm the structure of complexes **2**, besides normal methods such as ^{1}H and ^{13}C NMR, MS and elemental analysis, the single crystal of complex **2a** was also achieved and was fully analyzed by single crystal diffraction. As similar as those NHC-Pd(II) complexes using other *N*-containing ancillary ligands developed by our group [25–32], the central Pd atom in complex **2a** is also *C,N*-coordinated by the carbene carbon atom and the *N*-atom from 5-phenyloxazole, together with two chlorine atoms, showing a very slightly distorted square-planar geometry (Fig. 1). To further clarify the structure of complex **2a**, some representative bond distances and angles are also given in the Figure.

2.2. Buchwald-Hartwig amination of aryl chlorides

The evaluation of the catalytic activity of complexes **2** was investigated choosing the Buchwald-Hartwig amination of aryl chlorides. Initially, using complex **2a** (0.1 mol%) as the catalyst, the reaction between chlorobenzene **3a** (0.7 mmol) and morpholine **4a** (0.84 mmol) was carried out in toluene (1.0 mL) at 90 °C for 1 h to test various inorganic bases (0.91 mmol). In these cases, the best yield was achieved when potassium *tert*-butoxide was used, giving the desired product **5a** in 93% yield (Table 2, entry 1). In the presence of sodium *tert*-butoxide and potassium hydroxide, only 18 and 12% yields were observed, respectively. In addition, no reaction occurred once some other bases such as lithium *tert*-butoxide, lithium hydroxide, sodium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, cesium carbonate, sodium bicarbonate, potassium bicarbonate and potassium phosphate were added. Subsequently, using potassium *tert*-butoxide as the base, the reaction was then performed in various other solvents. For example, in non-polar solvents such as tetrahydrofuran and dioxane, 60 and 76% yields were found, respectively (Table 2, entries 2 and 3). In polar solvents such as dimethyl sulfox-

ide, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide, no reaction occurred. Based on the satisfactory result shown in Table 2, entry 1, the catalyst loading was then lowered to 0.05 mol%. Disappointingly, the yield drastically lowered from 93 to 11% within 1 h (Table 2, entry 1 *vs* 4). To our delight, 96% yield can be still given when the reaction time was prolonged to 6 h (Table 2, entry 5). Similarly, by adjusting the reaction temperature and time, high yield can be still achieved when only 0.03 mol% catalyst was added (Table 2, entry 9). Under such conditions, almost no desired product **5a** can be detected once complexes **2b** or **2c** were used as the catalyst. The comparison between some well-defined NHC-Pd(II) complexes with complex **2a** was also carried out under the identical conditions shown in Table 2, entry 9. As can be seen from Fig. 2, with NHC-Pd(II) complexes using different ancillary ligands such as 1-methylimidazole[25], 2-phenyl-4,5-dihydrooxazole[27], isoquinoline[28], 2-picolinic acid[30] and 3-chloropyridine[16] as the catalyst, similar comparable yields were observed, implying that complex **2a** using 5-phenyloxazole as the ancillary ligand can also be a potential catalyst in organic synthesis.

With the optimal conditions in hand, the reactions between various aryl chlorides **3** and secondary amines **4** were first investigated to test the scope and limitation of this methodology. The results are summarized in Table 3. It seems that all reactions performed well enough to give the desired coupling products **5** in good to high yields in the presence of 0.03 or 0.05 mol% com-

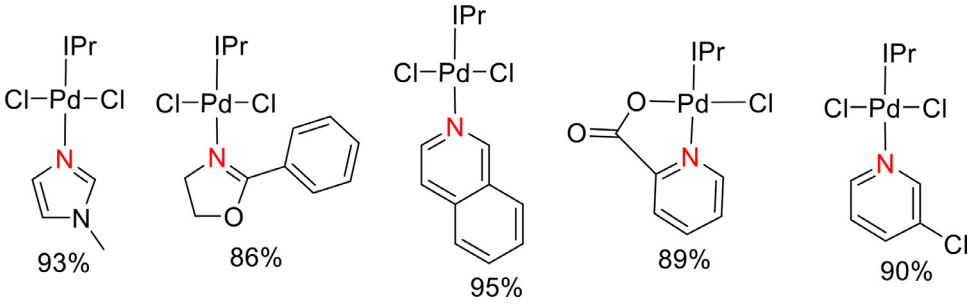
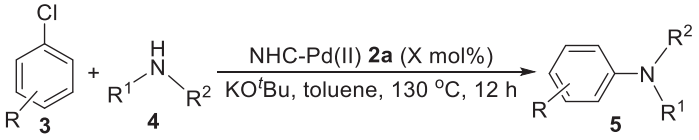
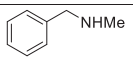
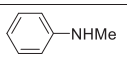


Fig. 2. Results using other well-defined NHC-pd(11) complexes as the catalyst.

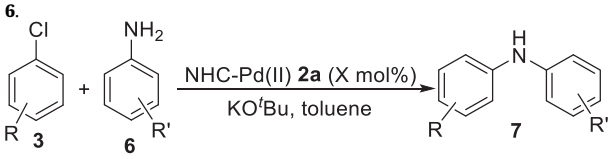
Table 3
NHC-Pd(II) complex **2a**-catalyzed reactions of aryl chlorides **3** with secondary amines **4**.[a,b]



Entry[a]	3 (R)	4	[X]	Yield (%)[b]
1	**3b** (2-Me)	**4a** 	0.03	**5b**, 91
2	**3c** (3-Me)		0.03	**5c**, 96
3	**3d** (4-Me)		0.03	**5d**, 89
4	**3e** (3-OMe)		0.03	**5e**, 90
6	**3f** (3-F)		0.03	**5f**, 92
7	**3g** (4-F)		0.03	**5g**, 82
8	**3h** 		0.03	**5h**, 71
9	**3b**	**4b** 	0.05	**5i**, 86
10	**3e**		0.03	**5j**, 89
11	**3a** (H)	**4c** 	0.05	**5k**, 85
12	**3b**		0.05	**5l**, 85
13	**3c**		0.05	**5m**, 98
14	**3e**		0.03	**5n**, 94
15	**3a**	**4d** 	0.03	**5o**, 84
16	**3b**		0.05	**5p**, 86
17	**3c**		0.05	**5q**, 97
18	**3d**		0.05	**5r**, 80
19	**3e**		0.03	**5s**, 92
20	**3f**		0.03	**5t**, 87
21	**3a**	**4e** 	0.03	**5u**, 84
22	**3c**		0.03	**5v**, 89
23	**3e**		0.03	**5w**, 96

[a] All reactions were carried out with **3** (0.70 mmol), **4** (0.84 mmol), KO^{t}Bu (0.91 mmol) and **2a** (X mol%) in toluene (1.0 mL) at 130 °C for 12 h.
[b] Isolated yields.

Table 4
NHC-Pd(II) complex **2a**-catalyzed reactions of aryl chlorides **3** with primary amines **6**.



Entry[a]	**3** (R)	**6** (R')	[X]	Temp (°C)	Time (h)	Yield (%)[b]
1	**3b** (2-Me)	**6a** (2-Me)	0.01	110	12	**7a**, 98
2	**3b**	**6b** (2,4-Me_2)	0.01	110	6	**7b**, 93
3	**3b**	**6c** (2,6-Me_2)	0.01	110	6	**7c**, 93
4	**3b**	**6d** (2,4,6-Me_3)	0.01	110	12	**7d**, 97
5	**3b**	**6e** (2-OMe)	0.03	130	24	**7e**, 90
6	**3i** (2,6-Me_2)	**6c**	0.01	110	12	**7f**, 99
7	**3j** (2,4,6-Me_3)	**6c**	0.01	110	24	**7g**, 99
8	**3k** (2,6-$^i Pr_2$)	**6c**	0.05	110	24	**7h**, 93

[a] Reaction conditions: **3** (0.70 mmol), **6** (0.84 mmol), KO^{t}Bu (0.91 mmol), **2a** (X mol%), toluene (1.0 mL)
[b] Isolated yields.

plex **2a**. For example, electron-rich, -poor and sterically-hindered groups substituted aryl chlorides **3** reacted with morpholine **4a** smoothly in the presence of 0.03 mol% complex **2a**, giving products **5b**-**g** in good to high yields (Table 3, entries 1-7). Heteroaryl chloride such as 2-chloropyridine **3h** is also suitable substrate to afford product **5h** in 71% yield (Table 3, entry 8). Other secondary amines such as pyrrolidine **4b**, piperidine **4c**, *N*-methyl-1-phenylmethanamine **4d** and *N*-methylaniline **4e** can be also converted to the corresponding *N*-arylated products **5i**-**w** in 80-98% yields smoothly (Table 3, entries 9-23).

To further test the compatibility of this methodology, the reactions between a variety of aryl chlorides **3** and anilines **6**, both having sterically-hindered substituents, were also investigated under the similar conditions (Table 4). For such challenging transformation, all reactions performed successfully to give the corresponding diarylamines **7** in 90-99% yields. Notably, for most reactions, the catalyst loading can be lowered to 0.01 mol%, giving the desired products **7** in 93-99% yields (Table 4, entries 1-4, 6 and 7). Compared to secondary amines, it seems that the reactions involving primary amines gave higher yields, affording products **7** in >90% yields in all cases checked, implying that such complex may be more efficient catalyst for the coupling of primary amines.

3. Conclusion

In conclusion, using 5-phenyloxazole as the ancillary ligand, a novel type of NHC-Pd(II) complexes can be obtained by the reaction of imidazolium salts, palladium chloride and 5-phenyloxazole in a one-pot procedure under mild conditions. All complexes are air- and thermal-stable, and can be kept under air for at least several months. Initial studies on the catalytic activities of such NHC-Pd(II) complexes were performed by the Buchwald-Hartwig reactions of aryl chlorides with a variety of secondary and primary amines. All amination reactions took place smoothly, giving the corresponding products in good to almost quantitative yields with the catalyst loadings varied from 0.01-0.05 mol%, thus new catalysts with efficient activity were developed and will give at least an alternative for the coupling reactions of challenging while cost-low aryl chlorides.

4. Experimental

4.1. General remarks

NMR spectra were recorded at 500 MHz (for ^{1}H NMR) or 125 MHz (for ^{13}C NMR), respectively. ^{1}H 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. All solvents were dried by standard methods. The mass analyzer type for the high resolution mass spectra (HRMS) is Q-TOF. All amines were distilled prior to using. Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel (300-400 mesh).

4.2. General procedure for the synthesis of NHC-Pd(II) complexes **2**

Under N_2 atmosphere, a mixture of imidazolium salts **1** (0.18 or 0.225 mmol), $PdCl_2$ (0.15 mmol), K_2CO_3 (0.18 mmol) and 5-phenyloxazole (0.15 mmol) was stirred in anhydrous THF (2.0 mL) under reflux for 12 h. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give complexes **2** as yellow solids.

Compound **2a**: yellow solid. m.p. 183.3-185.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.35 (s, 1H), 7.62 (s, 1H), 7.51-7.47 (m, 4H), 7.36-7.29 (m, 7H), 7.13 (s, 2H), 3.16 (hept, J = 6.5 Hz, 4H), 1.47 (d, J = 6.5 Hz, 12H), 1.12 (d, J = 6.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 152.7, 151.2, 146.7, 135.0, 130.3, 129.1, 128.8, 126.7, 125.1, 124.5, 124.0, 120.2, 28.7, 26.3, 23.2. IR (neat) ν 2964, 2862, 1739, 1593, 1465, 1411, 1382, 1349, 1328, 1235, 1206, 1162, 1108, 1045, 972, 944, 929, 843, 805, 765, 760 cm^{-1}. MS (ESI): 674 $[M\text{-}Cl]^+$. HRMS (ESI) calcd for $C_{36}H_{43}ClN_3OPd$ $[M\text{-}Cl]^+$: 674.2134; found: 674.2103. Anal. calcd for $C_{36}H_{43}Cl_2N_3OPd$·1/3toluene: C, 62.07%; H, 6.21%; N, 5.66%; found: C, 62.16%; H, 6.48%; N, 5.52%.

Compound **2b**: yellow solid. m.p. 231.0 °C (decomposed). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.37 (s, 1H), 7.64 (s, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.36-7.29 (m, 5H), 7.26-7.24 (m, 4H), 7.12 (s, 2H), 2.42 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 151.2, 151.1, 137.4, 136.6, 129.5, 129.1, 128.9, 128.6, 126.6, 124.4, 124.1, 120.1, 19.2. IR (neat) ν 3153, 3133, 2921, 2845, 1733, 1514, 1477, 1441, 1404, 1381, 1331, 1278, 1218, 1165, 1106, 1043, 967, 943, 926, 839, 821, 785, 761, 747 cm^{-1}. MS (ESI): 622 $[M+Na]^+$. HRMS (ESI) calcd for $C_{28}H_{27}Cl_2N_3OPdNa$ $[M+Na]^+$: 622.0460; found: 622.0455. Anal. calcd for $C_{28}H_{27}Cl_2N_3OPd$·1/4toluene: C, 57.46%; H, 4.70%; N, 6.76%; found: C, 57.19%; H, 4.99%; N, 6.40%.

Compound **2c**: yellow solid. m.p. 149.7-150.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.39 (s, 1H), 7.66 (s, 1H), 7.48 (d, J = 7.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 7.0 Hz, 1H), 7.07 (s, 2H), 7.05 (s, 4H), 2.36 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 151.1, 139.2, 136.2, 135.0, 129.3, 129.1, 128.93, 128.86, 126.7, 124.4, 124.3, 120.2, 21.2, 19.1. IR (neat) ν 3160, 2921, 1676, 1603, 1485, 1444, 1408, 1371, 1335, 1278, 1229, 1166, 1106, 1036, 965, 929, 852, 839, 764, 738 cm^{-1}. MS (ESI): 650 $[M+Na]^+$. HRMS (ESI) calcd for $C_{30}H_{31}Cl_2N_3OPdNa$ $[M+Na]^+$: 650.0774; found: 650.0783. Anal. calcd for $C_{30}H_{31}Cl_2N_3OPd$: C, 57.48%; H, 4.98%; N, 6.70%; found: C, 57.60%; H, 5.04%; N, 6.57%.

4.3. General procedure for the complex **2a**-catalyzed Buchwald-Hartwig amination of aryl chlorides

Under N_2 atmosphere, KO^{t}Bu (102.1 mg, 1.3 equiv) and a solution of complex **2a** (10-50 μL, 0.01-0.05 mol%, prepared from 5.0 mg of complex **2a** in 1.0 mL dichloromethane) were added into a Schlenk reaction tube. The tube was sealed and the solvent was removed under reduced pressure. Then toluene (1.0 mL),

amines (0.84 mmol) and aryl chlorides (0.70 mmol) were successively added. The mixture was stirred vigorously at the specified temperature for 6-24 h. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the corresponding products.

Compound **5a** [25]: white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.26 (t, J = 7.5 Hz, 2H), 6.90-6.85 (m, 3H), 3.82 (t, J = 4.5 Hz, 4H), 3.12 (t, J = 4.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 129.0, 119.9, 115.6, 66.8, 49.3.

Compound **5b** [25]: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.17 (t, J = 7.5 Hz, 2H), 7.02-6.97 (m, 2H), 3.83 (t, J = 4.5 Hz, 4H), 2.89 (t, J = 4.5 Hz, 4H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 132.6, 131.1, 126.6, 123.4, 119.0, 67.4, 52.3, 17.8.

Compound **5c** [25]: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.15 (t, J = 7.5 Hz, 1H), 6.71-6.69 (m, 3H), 3.82 (t, J = 4.5 Hz, 4H), 3.11 (t, J = 4.5 Hz, 4H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 138.7, 128.9, 120.8, 116.4, 112.8, 66.8, 49.4, 21.6.

Compound **5d** [25]: white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.07 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 3.83 (t, J = 4.5 Hz, 4H), 3.08 (t, J = 4.5 Hz, 4H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 129.6, 129.4, 116.0, 66.9, 49.9, 20.3.

Compound **5e** [25]: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.16 (t, J = 8.0 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 6.43-6.41 (m, 2H), 3.81 (t, J = 4.5 Hz, 4H), 3.76 (s, 3H), 3.11 (t, J = 4.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 152.6, 129.7, 108.3, 104.6, 102.1, 66.7, 55.0, 49.1.

Compound **5f** [29]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.18 (dd, J = 15.5, 8.0 Hz, 1H), 6.64 (dd, J = 8.0, 2.0 Hz, 1H), 6.57-6.52 (m, 2H), 3.82 (t, J = 5.0 Hz, 4H), 3.12 (t, J = 5.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8 (d, $J_{C\text{-}F}$ = 242.0 Hz), 152.9 (d, $J_{C\text{-}F}$ = 9.625 Hz), 130.1 (d, $J_{C\text{-}F}$ = 9.875 Hz), 110. 7 (d, $J_{C\text{-}F}$ = 2.375 Hz), 106.1 (d, $J_{C\text{-}F}$ = 21.375 Hz), 102.3 (d, $J_{C\text{-}F}$ = 25.0 Hz), 66.6, 48.7.

Compound **5g** [27]: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.96 (t, J = 8.5 Hz, 2H), 6.85 (dd, J = 8.5, 4.5 Hz, 2H), 3.84 (t, J = 4.5 Hz, 4H), 3.06 (t, J = 4.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3 (d, $J_{C\text{-}F}$ = 237.625 Hz), 147.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 117.4 (d, $J_{C\text{-}F}$ = 7.625 Hz), 115.5 (d, $J_{C\text{-}F}$ = 22.0 Hz), 66.8, 50.3.

Compound **5h** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.20 (d, J = 4.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 6.66-6.62 (m, 2H), 3.81 (t, J = 4.5 Hz, 4H), 3.49 (t, J = 4.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 147.9, 137.4, 113.7, 106.8, 66.7, 45.6.

Compound **5i** [28]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.10 (t, J = 7.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 3.17 (t, J = 6.5 Hz, 4H), 2.31 (s, 3H), 1.91 (quintet, J = 6.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 131.6, 128.7, 126.2, 120.2, 115.8, 51.0, 24.9, 20.4.

Compound **5j** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.11 (t, J = 8.0 Hz, 1H), 6.22 (dd, J = 8.0, 2.5 Hz, 1H), 6.18 (dd, J = 8.0, 2.0 Hz, 1H), 6.10 (t, J = 2.0 Hz, 1H), 3.77 (s, 3H), 3.25 (t, J = 7.0 Hz, 4H), 1.97-1.94 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 149.2, 129.7, 104.9, 100.5, 97.9, 55.0, 47.6, 25.3.

Compound **5k** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.25-7.21 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 7.5 Hz, 1H), 3.14 (t, J = 5.5 Hz, 4H), 1.69 (quintet, J = 5.5 Hz, 4H), 1.58-1.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 128.9, 119.1, 116.5, 50.6, 25.8, 24.3.

Compound **5l** [28]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.17-7.13 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 2.83 (t, J = 5.0 Hz, 4H), 2.30 (s, 3H), 1.70 (quintet, J = 5.5 Hz, 4H), 1.57 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 132.7, 130.9, 126.4, 122.6, 119.0, 53.4, 26.6, 24.4, 17.8.

Compound **5m** [28]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.12 (t, J = 7.5 Hz, 1H), 6.75-6.73 (m, 2H), 6.64 (d, J = 7.5 Hz, 1H), 3.12 (t, J = 5.5 Hz, 4H), 2.30 (s, 3H), 1.69 (quintet, J = 5.5 Hz, 4H), 1.58-1.53 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 138.5, 128.8, 120.1, 117.4, 113.6, 50.7, 25.9, 24.3, 21.7.

Compound **5n** [25]: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.14 (t, J = 8.0 Hz, 1H), 6.54 (dd, J = 8.0, 2.0 Hz, 1H), 6.47 (t, J = 2.5 Hz, 1H), 6.37 (dd, J = 8.0, 2.5 Hz, 1H), 3.77 (s, 3H), 3.14 (t, J = 5.5 Hz, 4H), 1.68 (quintet, J = 5.5 Hz, 4H), 1.58-1.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 153.5, 129.5, 109.2, 103.9, 102.7, 55.0, 50.5, 25.7, 24.3.

Compound **5o** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27 (t, J = 7.5 Hz, 2H), 7.21-7.17 (m, 5H), 6.72 (t, J = 8.5 Hz, 2H), 6.69 (t, J = 7.5 Hz, 1H), 4.49 (s, 2H), 2.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 139.0, 129.1, 128.5, 126.8, 126.7, 116.6, 112.4, 56.6, 38.4.

Compound **5p** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.36 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.18-7.12 (m, 2H), 7.06 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 4.01 (s, 2H), 2.56 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 139.1, 132.9, 131.1, 128.3, 128.2, 126.9, 126.4, 123.0, 120.1, 60.8, 40.9, 18.3.

Compound **5q** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27 (t, J = 7.5 Hz, 2H), 7.20 (d, J = 7.5 Hz, 3H), 7.08 (t, J = 8.0 Hz, 1H), 6.57-6.52 (m, 3H), 4.47 (s, 2H), 2.94 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 139.1, 138.7, 128.5, 126.77, 126.76, 117.6, 113.1, 109.7, 56.6, 38.3, 21.8.

Compound **5r** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27 (t, J = 7.5 Hz, 2H), 7.22-7.19 (m, 3H), 7.01 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 4.45 (s, 2H), 2.93 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 139.2, 129.7, 128.5, 126.9, 126.8, 125.8, 112.8, 57.0, 38.5, 20.2.

Compound **5s** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 7.5 Hz, 3H), 7.09 (t, J = 8.0 Hz, 1H), 6.35 (d, J = 8.0 Hz, 1H), 6.29-6.25 (m, 2H), 4.48 (s, 2H), 3.71 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 151.1, 138.9, 129.8, 128.5, 126.8, 126.7, 105.6, 101.4, 99.0, 56.5, 55.0, 38.4.

Compound **5t** [31]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.28 (t, J = 7.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.08 (dd, J = 16.0, 8.0 Hz, 1H), 6.45 (dd, J = 7.5, 2.0 Hz, 1H), 6.41-6.35 (m, 2H), 4.47 (s, 2H), 2.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2 (d, $J_{C\text{-}F}$ = 240.5 Hz), 151.4 (d, $J_{C\text{-}F}$ = 10.5 Hz), 138.4, 130.1 (d, $J_{C\text{-}F}$ = 10.25 Hz), 128.6, 127.0, 126.6, 107.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 102.9 (d, $J_{C\text{-}F}$ = 21.5 Hz), 99.2 (d, $J_{C\text{-}F}$ = 25.875 Hz), 56.4, 38.5.

Compound **5u** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.26-7.23 (m, 4H), 7.00 (d, J = 7.5 Hz, 4H), 6.93 (t, J = 7.0 Hz, 2H), 3.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 129.1, 121.2, 120.4, 40.2.

Compound **5v** [27]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.24 (dd, J = 8.0, 7.5 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.91 (t, J = 7.5 Hz, 1H), 6.84-6.82 (m, 2H), 6.77 (d, J = 7.0 Hz, 1H), 3.27 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 149.0, 138.9, 129.1, 129.0, 122.3, 121.4, 120.9, 120.1, 117.9, 40.2, 21.5.

Compound **5w** [25]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.57 (dd, J = 8.0, 1.5 Hz, 1H), 6.53 (t, J = 2.0 Hz, 1H), 6.47 (dd, J = 8.0, 2.0 Hz, 1H), 3.73 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 150.4, 148.8, 129.7, 129.2, 121.9, 121.5, 112.2, 105.9, 105.6, 55.1, 40.2.

Compound **7a** [28]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.16 (d, J = 7.5 Hz, 2H), 7.08 (td, J = 8.5, 1.0 Hz, 2H), 6.95 (d, J = 7.5 Hz, 2H), 6.87 (td, J = 7.5, 1.0 Hz, 2H), 5.09 (br, 1H), 2.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 130.7, 127.5, 126.7, 121.3, 118.3, 17.7.

Compound **7b** [28]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.13 (d, J = 7.0 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.00 (s, 1H), 6.92 (s, 2H), 6.82-6.79 (m, 2H), 5.01 (s, 1H), 2.27 (s, 3H), 2.22 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 138.9, 131.7, 131.5, 130.6, 129.1, 127.2, 126.7, 125.9, 120.5, 120.2, 116.4, 20.6, 17.7, 17.6.

Compound **7c** [35]: white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.11-7.09 (m, 3H), 7.05 (dd, J = 8.5, 6.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.14 (d, J = 8.0 Hz, 1H), 4.88 (s, 1H), 2.30 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 138.7, 135.5, 130.2, 128.5, 126.9, 125.5, 122.4, 118.1, 111.7, 18.1, 17.5.

Compound **7d** [28]: white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.08 (d, J = 7.5 Hz, 1H), 6.94-6.92 (m, 3H), 6.65 (t, J = 7.5 Hz, 1H), 6.12 (d, J = 8.0 Hz, 1H), 4.80 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 2.12 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 136.0, 135.5, 135.1, 130.1, 129.2, 126.9, 122.0, 117.7, 111.4, 20.8, 18.0, 17.5.

Compound **7e** [28]: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.31 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.89-6.80 (m, 3H), 5.87 (s, 1H), 3.88 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 140.8, 133.9, 130.8, 129.3, 126.6, 122.1, 120.8, 119.6, 119.3, 114.4, 110.4, 55.6, 17.8.

Compound **7f** [28]: white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.96 (d, J = 7.5 Hz, 4H), 6.83 (t, J = 7.5 Hz, 2H), 4.78 (s, 1H), 2.00 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 129.5, 128.7, 121.7, 19.0.

Compound **7g** [35]: white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.95 (d, J = 7.5 Hz, 2H), 6.80 (s, 3H), 4.70 (s, 1H), 2.25 (s, 3H), 1.98 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 139.0, 131.5, 130.5, 129.2, 128.8, 128.5, 121.0, 20.6, 19.1, 19.0.

Compound **7h** [35]: pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.14-7.09 (m, 3H), 6.92 (d, J = 7.5 Hz, 2H), 6.70 (t, J = 7.5 Hz, 1H), 4.78 (s, 1H), 3.15 (hept, J = 7.0 Hz, 2H), 1.97 (s, 6H), 1.11 (d, J = 7.0 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 143.1, 138.8, 129.5, 125.6, 124.8, 123.2, 119.6, 28.0, 23.4, 19.3.

Declaration of Competing Interest

None.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121683.

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