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Practical synthesis of pinacolborane for one-pot synthesis of unsymmetrical biaryls via aromatic C–H borylation–cross-coupling sequence

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ABSTRACT

A method for practical preparation of pinacolborane from borane-diethylaniline and pinacol was newly developed. Aromatic C–H borylation of arenes with pinacolborane or bis(pinacolato)diboron catalyzed by 1/2[Ir(OMe)(COD)]$_2$-(4,4′-di-*tert*-butyl-2,2′-bipyridine) at 25 °C in hexane to give arylboronic esters was directly followed by cross-coupling with aromatic bromides at 60 °C in the presence of $PdCl_2$(dppf) (3.0 mol %) and K_3PO_4 in DMF. This one-pot, two-step procedure provided a variety of unsymmetrical biaryls in high yields.

1. Introduction

Unsymmetrical biaryls are an important class of compounds due to the frequent occurrence of these fragments in natural products, pharmaceuticals, agrochemicals, and functional organic materials.[1] Transition metal-catalyzed cross-coupling of arylmetal compounds with aryl halides or triflates has been proved to be a general method applicable for preparation of such unsymmetrical biaryls.[1d,f] Among them, much attention has been focused on the use of arylboronic acids or esters in laboratories and industries since they are nontoxic, thermally stable, and inert to water and oxygen. A traditional method for preparation of such arylboron compounds is alkylation of $B(OR)_3$ with aromatic lithium or magnesium reagents.[2] Alternative and milder variants displayed high functional group compatibility is palladium-catalyzed cross-couplings of aryl halides and triflates with bis(pinacolato)diboron (B_2pin_2, pin=$Me_4C_2O_2$)[3] or pinacolborane (HBpin).[4] Another economical and environmentally benign process is transition metal-catalyzed direct C–H borylation of arenes developed by Hartwig[5] and Smith.[6] Among the catalysts developed to date,[7] a combination of [Ir(OMe)(COD)]$_2$ and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) has been recognized to be the best catalyst, which allowed stoichiometric borylation of arenes with B_2pin_2 or HBpin at room temperature.[8]

Pinacolborane necessary for these coupling reactions is available from pinacol and borane–THF or borane–methyl sulfide complex (BMS).[9] However, the protocol using BH_3·THF and BH_3·SMe_2 is not suitable for large-scale preparation due to inconveniences such as the low concentration and instability of BH_3·THF, and the high volatility, flammability, and unpleasant odor of dimethyl sulfide from BH_3·SMe_2. Because of the growing importance of pinacolborane for the syntheses of boron compounds, a practical method for its large-scale preparation is desirable. Here, we describe a method for synthesizing pinacolborane from amine–borane complexes and its use for a sequence of the iridium-catalyzed aromatic C–H borylation and palladium-catalyzed cross-coupling with aryl bromides to create a convenient one-pot procedure for the synthesis of unsymmetrical biaryls.

2. Results and discussion

2.1. Synthesis of pinacolborane

The first synthesis of HBpin (**1**) in 63% yield reported by Knochel involves reaction between BH_3·SMe_2 (BMS) and pinacol (Eq. 1).[9] We used amine–borane complexes as a borane source due to their advantage in large-scale preparation because of high thermal stability, low vapor pressure, and inflammability.[10] Borane–amine complexes are accessible by a reaction between metal borohydride and HNR_3Cl[11] or by treatment of BH_3·THF or BH_3·SMe_2 with amines.[10] To investigate their reaction with pinacol to give HBpin,

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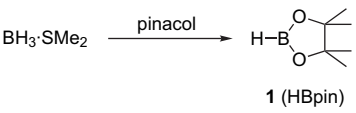
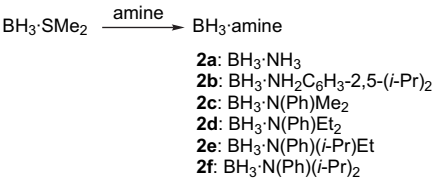
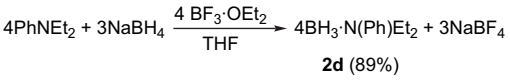
representative borane–amine complexes (**2**) were synthesized by treatment of BH_3·SMe with amines in THF.[10] Evaporation of the solvent and dimethyl sulfide in vacuo gave pure **2** in quantitative yields for NH_3, 2,6-diisopropylaniline, *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, *N*-ethyl-*N*-isopropylaniline, and diisopropylaniline (Eq. 2). Sodium borohydride is an economical borane source that has been utilized for the preparation of BH_3–THF or other borane-base adducts by treatment with BF_3·OEt_2.[12,13] Thus, we utilized this protocol for preparation of BH_3·N(Ph)Et_2 (**2d**) (Eq. 3). The reaction took place smoothly in the presence of *N*,*N*-diethylaniline in THF. Filtration of $NaBF_4$ through a Celite pad and evaporation of THF in vacuo afford **2d** in 89% yield. The preparation of **2d** suffered from some contamination of fluoroborane species. This byproduct was completely eliminated when $NaBH_4$ was used in slight excess (1.07 equiv) of the required stoichiometry for BF_3·OEt_2. By this method, 0.42 mol of pure **2d** was obtained from 0.5 mol of $NaBH_4$.



1 (HBpin) (1)



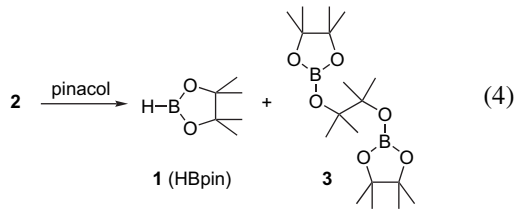
(2)



2d (89%) (3)

Reaction of pinacol with these borane–amines complexes in tetraglyme yielded HBpin (**1**) and B_2pin_3 (**3**)[14] with various molar ratios (Table 1). The conversions of borane–amine complexes (**2**, δ −21 to −6 ppm) and ratios of **1** (δ 28 ppm) and **3** (δ 20–22 ppm) were determined by ^{11}B NMR. The reaction was very slow for stable, small amine complexes such as NH_3 and dimethylaniline complexes (entries 1 and 3) and fast for sterically hindered 2,6-diisopropylaniline and diethylaniline complexes (entries 2 and 4).

Table 1
Synthesis of pinacolborane[a]



1 (HBpin) **3** (4)

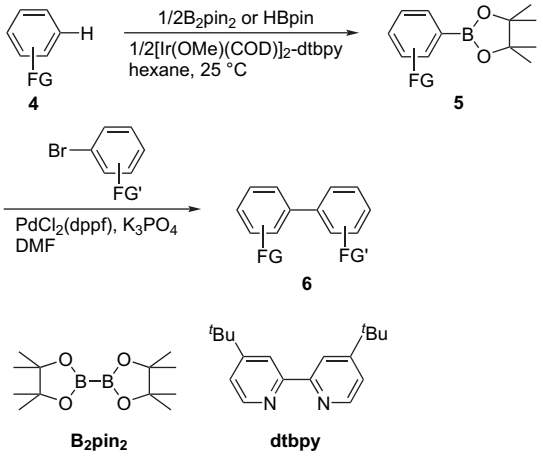
Entry	**2** (Amine=)	Conversion/%[b]	**1**/**3**	Isolated yield/%
1	NH_3 (**2a**)	12	42:58	
2	2,6-(*i*-Pr)$_2$C$_6$H$_3$NH$_2$ (**2b**)	82	85:15	
3	PhNMe_2 (**2c**)	43	60:40	
4	PhNEt_2 (**2d**)	100	100:0	(50)
5	PhNEt_2 (**2d**)[c]	100	100:0	(75)
6	PhN(*i*-Pr)Et (**2e**)	0		
7	PhN(*i*-Pr)$_2$ (**2f**)	0		

[a] A mixture of amine–borane complex (50 mmol) and pinacol (50 mmol) in tetraglyme (5 mL) was stirred for 1 h at 20 °C.
[b] Conversions and ratios determined by ^{11}B NMR.
[c] Compound **2d** (1.5 equiv) was used.

Further increase in steric hindrance by *N*-substituents resulted in no reaction (entries 6 and 7). Selectivities giving HBpin toward **3** were parallel to these reaction rates. Thus, 100% selectivity was achieved by diethylamine complex, which exhibited the fastest reaction rate among the six complexes examined (entry 4). However, isolation of HBpin suffered from low yields (ca. 50%) because of formation of nonvolatile **3** during distillation in vacuo. It was difficult to prevent this equilibration when stoichiometric amounts of **2d** and pinacol were used,[15] but the yield was improved to 75% in the presence of 50% excess of BH_3·N(Ph)Et_2 toward pinacol (entry 5).

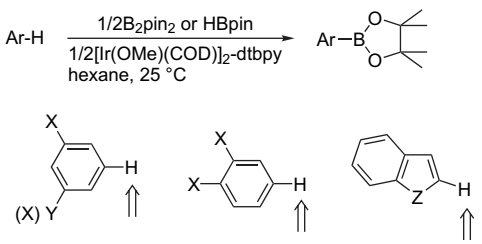
2.2. One-pot synthesis of biaryls

Aromatic C–H borylation with HBpin (**1**) or B_2pin_2 takes place at room temperature in the presence of an iridium(I)-dtbpy catalyst. The preparation of 1.1 equiv of arylboronate (**5**) was directly followed by cross-coupling with bromoarenes for one-pot synthesis of biaryls (**6**) (Scheme 1).



Scheme 1. One-pot synthesis of biaryls via aromatic C–H borylation–cross-coupling sequence.

Results of previous studies on aromatic C–H borylation of aromatic compounds reported by Smith's group[6] and by us[7,8] are summarized in Scheme 2. Functional group tolerance of the borylation is very high. The reaction selectively occurs at the C–H bond for substrates possessing Cl, Br, I, CF_3, OMe, CO_2Me, and CN groups. The reaction occurs only at aromatic C–H bonds even when the substrate has weaker benzylic C–H bonds.[16,17] The regiochemistry of the borylation of arenes is primarily controlled by the steric effects of substituents. The reaction occurs at C–H bonds located *meta* or *para* to a substituent in preference to those located *ortho*. Thus, 1,2-disubstituted arenes bearing identical substituents yield arylboronates as single isomers. The borylation of 1,3-disubstituted arenes proceeds at the common *meta* position; therefore,



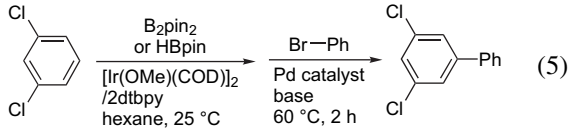
Scheme 2. Orientations of aromatic C–H borylation.

isomerically pure products are obtained even for two distinct substituents on the arenes.[7] In the case of five-membered heteroarenes such as furans, thiophenes, and pyrroles, the electronegative heteroatom causes the C–H bonds at the α-positions to be active so that borylation occurs at the α-positions.[18] Thus, the regioselective monoborylation of benzo-fused substrates is possible. In this study, we employed such arenes that produce a single arylboronic ester (**5**).

In one-pot, two-step reactions in which each step is catalyzed by different metal complexes, a catalyst used in the first step often inhibits second step. Thus, our initial efforts were focused on finding effective reaction conditions for the second cross-coupling step (Table 2). Pinacol 3,5-dichlorophenylborate (ca. 1.1 mmol) was prepared in situ by the C–H borylation of 1,3-dichlorobenzene (1.36 mmol) with pin_2B_2 **2** (0.65 mmol) in the presence of the 1/2[Ir(OMe)(COD)]$_2$-dtbpy catalyst (0.020 mmol) in hexane (2 mL) at 25 °C for 4 h. This solution was allowed to directly react with bromobenzene (1.0 mmol) at 60 °C for 2 h by using a variety of palladium catalysts (0.03 mmol), bases (3 mmol), and solvents (4 mL). Fortunately, it was found that a combination of $PdCl_2$(dppf), $K_3PO_4 \cdot nH_2O$, and DMF works well to form the desired 3,5-dichlorobiphenyl in 96% yield (entry 1). Use of $PdCl_2(PPh_3)_2$ (entry 2) or $Pd(dba)_2$ (entry 3) resulted in low yield due to formation of inactive palladium-black. As for bases, K_3PO_4 in DMF gave the best results among the four bases employed (entries 1 and 4–6). The reactions were faster in polar DMF (entry 7) than in less-polar dioxane and hexane (entries 7 and 8). The C–H borylation of 1,3-dichlorobenzene (1.30 mmol) with HBpin (1.43 mmol) at 25 °C for 8 h yielded pinacol 3,5-dichlorophenylboronate (ca. 1.1 mmol). Its cross-coupling with bromobenzene (1.0 mmol) with $PdCl_2$(dppf), $K_3PO_4 \cdot nH_2O$ in DMF was also effective for synthesis of 3,5-dichlorobiphenyl in 93% yield (entries 9).

Representative results of one-pot synthesis of unsymmetrical biaryls (**6**) via the sequential reactions involving aromatic C–H borylation of arenes with B_2pin_2 (method A) or that by HBpin (**1**) (method B) and the cross-coupling with bromoarenes under the optimal conditions shown in Table 2 are summarized in Table 3. The method provides a convenient and efficient route for preparing a variety of biaryls. Representative bromoarenes possessing an electron-withdrawing group, donating group, and an *ortho*-substituent afforded **6** in high yields (entries 1–7), while electron-rich (entry 3) or sterically hindered bromoarene (entry 4) required longer reaction times to complete the cross-coupling. The C–H borylation of 1,3-disubstituted arenes having two distinct substituents (entries 5 and 6) and 1,2-disubstituted arenes bearing identical substituents (entry 7) generated isomerically pure arylboronates and biaryls. Although α-heteroarylboronic acids such as 2-pyridineboronic acid and 2-pyrroleboronic acid are highly susceptible to hydrolytic protodeboration, the corresponding pinacol esters are sable for such B–C bond cleavage in the presence of a base. Thus, 2-indoleboronate generated from indole smoothly coupled with 2-bromothiophene (entry 8). There were no significant differences in the yields and reaction rates between method A and method B, but high stability of B_2pin_2 to air and water is convenient for handling and economical HBpin is suitable for large-scale preparation of arylboronates and biaryls.

Table 2
Reaction conditions for one-pot synthesis of biaryls[a]

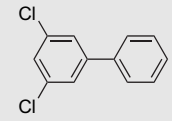
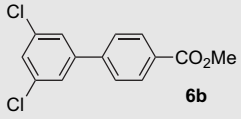
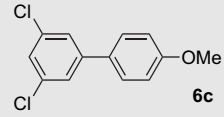
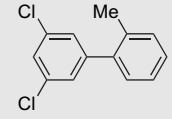
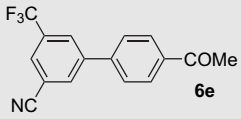
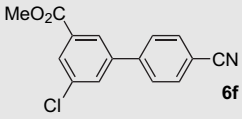
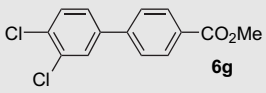
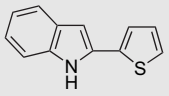


(5)

Entry	B_2pin_2 or HBpin	Pd catalyst	Base	Solvent	Yield/%[b]
1	B_2pin_2	$PdCl_2$(dppf)	K_3PO_4	DMF	96
2	B_2pin_2	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	55
3	B_2pin_2	$Pd(dba)_2$	K_3PO_4	DMF	1
4	B_2pin_2	$PdCl_2$(dppf)	Cs_2CO_3	DMF	88
5	B_2pin_2	$PdCl_2$(dppf)	K_2CO_3	DMF	80
6	B_2pin_2	$PdCl_2$(dppf)	KOAc	DMF	53
7	B_2pin_2	$PdCl_2$(dppf)	K_3PO_4	Dioxane	84
8	B_2pin_2	$PdCl_2$(dppf)	K_3PO_4	Hexane	9
9	HBpin	$PdCl_2$(dppf)	K_3PO_4	DMF	93

[a] C–H borylation of 1,3-dichlorobenzene (1.36 mmol) with B_2pin_2 (0.65 mmol) in hexane (2 mL) at 25 °C for 4 h in the presence of 1/2[Ir(OMe)(COD)]$_2$-dtbpy (3.0 mol %, 0.020 mmol) was followed by cross-coupling with bromobenzene (1.0 mmol) at 60 °C for 2 h by using Pd catalyst (0.030 mmol), base (3.0 mmol), and solvent (4 mL).
[b] GC yields based on bromobenzene.

Table 3
One-pot synthesis of biaryls via C–H borylation–cross-coupling sequence[a]

Entry	Product **6**[b]	Yield/%[c] (time/h)[d]	
		Method A[e]	Method B[f]
1	 **6a**	96[g] (2)	93[g] (2)
2	 **6b**	96 (2)	91[g] (2)
3	 **6c**	87 (4)	81 (4)
4	 **6d**	88 (4)	84 (8)
5	 **6e**	93 (2)	91 (2)
6	 **6f**	93 (2)	87 (2)
7	 **6g**	96 (2)	86 (2)
8	 **6h**	93 (2)	87 (2)

[a] The C–H borylation of arenes with B_2pin_2 (method A) or HBpin (method B) to give arylboronates (**5**, ca. 1.1 mmol) was followed by cross-coupling with aryl bromides (1.0 mmol) at 60 °C in the presence of $PdCl_2$(dppf) (0.03 mmol), K_3PO_4 (3 mmol) and DMF (4 mL).
[b] Left part of biaryls comes from arenes and right part from boromoarenes.
[c] Isolated yields.
[d] Reaction times at the cross-coupling stage.
[e] The C–H borylation of arene (1.30–1.43 mmol) with B_2pin_2 (0.63–0.69 mmol) was carried out for 0.5–8 h in the presence of 1/2[Ir(OMe)(COD)]$_2$-dtbpy (3.0 mol %, 0.020 mmol).
[f] Aromatic C–H borylation of arene (1.12–1.57 mmol) with HBpin (1.23–1.73 mmol) was carried out for 2–8 h in the presence of 1/2[Ir(OMe)(COD)]$_2$-dtbpy (3.0 mol %, 0.034–0.048 mmol).
[g] GC yields.

3. Experimental

3.1. Synthesis of borane–amine complexes (2)

Borane/amine complexes (**2**) were synthesized by the methods of Vaultier and Brown.[10] The synthesis of **2d** from $NaBH_4$, $BF_3{\cdot}OEt_2$, and $PhNEt_2$ was carried out as follows.

To a 500-mL flask charged with $NaBH_4$ (0.4 mol) and $PhNEt_2$ (0.5 mol) in THF (100 mL) was dropwise added $BF_3{\cdot}OEt_2$ (0.5 mol) at −78 °C. The mixture was allowed to warm slowly to room temperature and was stirred for 1–4 h. The complete disappearance of B–F species was checked by ^{11}B NMR. The mixture was diluted with pentane (100 mL) to precipitate $NaBF_4$. Filtration of solid residue through a Celite pad was followed by evaporation of the solvent and other volatiles. Further evaporation of trace amounts of volatiles in high vacuo (10^{-2} mmHg) for 16 h gave 72.5 g (89%) of **2d**. ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J=7.16 Hz, 6H), 1.84 (q, J=90.3 Hz, 3H, BH_3), 3.29–3.40 (m, 4H), 7.27 (t, J=7.34 Hz, 1H), 7.38 (t, J=7.94 Hz, 2H), 7.65 (d, J=8.48 Hz, 2H); ^{11}B NMR (128 MHz, $CDCl_3$) δ −12.0.

3.2. Synthesis of pinacolborane

A 100 mL-flask, equipped with a Claisen-head distillation apparatus, was charged with $BH_3{\cdot}N(Ph)Et_2$ (**2d**, 75 mmol) and tetraglyme (20 mL). A solution of pinacol (50 mmol) in tetraglyme (5 M solution, 10 mL) was dropwise added over 30 min to the flask cooled by a water bath (25 °C). The mixture was stirred for 30 min at room temperature. Distillation in vacuo gave pinacolborane (4.8 g, 75%). Bp 36 °C/42 mmHg. ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 12H), 4.10 (q, J=168 Hz, 1H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.1.

3.3. Procedure for one-pot biaryl cross-coupling using B_2pin_2 (method A)

A 25-mL flask equipped with a magnetic stirring bar, a septum inlet, and a condenser was charged with $[Ir(OMe)(COD)]_2$[19] (0.01 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy, 0.02 mmol), and bis(pinacolato)diboron (B_2pin_2, 0.65 mmol) and then flushed with nitrogen. Hexane (2 mL) and 1,3-dichlorobenzene (1.36 mmol) were added, and the mixture was then stirred at 25 °C for 4 h to give pinacol 3,5-dichlorophenylboronate (ca. 1.1 mmol). To this solution were added $PdCl_2$(dppf) (0.030 mmol), $K_3PO_4{\cdot}nH_2O$ (3 mmol), and DMF (4 mL), and the mixture was stirred at 60 °C for 2 h. The formation of methyl 4-(3,5-dichlorophenyl)benzoate (**2b**) in 96% yield was analyzed by GC and GC mass spectroscopy. The product was extracted with benzene, washed with brine, and dried over $MgSO_4$. Chromatography over silica gel (hexane/AcOEt) gave analytically pure **2b**.

3.4. Procedure for one-pot biaryl cross-coupling using HBpin (method B)

A 25-mL flask equipped with a magnetic stirring bar, a septum inlet, and a condenser was charged with $[Ir(OMe)(COD)]_2$[19] (0.02 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy, 0.04 mmol) and then flushed with nitrogen. Hexane (2 mL), pinacolborane (HBpin, 1.43 mmol), and 1,3-dichlorobenzene (1.3 mmol) were then added, and the mixture was stirred at 25 °C for 8 h to give pinacol 3,5-dichlorophenylboronate (ca. 1.1 mmol). The solution thus obtained was directly subjected to cross-coupling under the same conditions as those in the procedures described in Section 3.3.

3.5. Spectral data of biaryls

3.5.1. Compound ***6a***

^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J=1.8 Hz, 1H), 7.40 (tt, J=1.4 and 7.2 Hz, 1H), 7.43–7.48 (m, 2H), 7.46 (d, J=2.0 Hz, 2H), 7.54 (dt, J=1.5 and 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.64, 127.05, 127.11, 128.44, 129.01, 135.23, 138.52, 144.18; MS (EI): m/z (%) 152 (52), 186 (8), 222 ($[M]^+$, 100); HRMS (EI): calcd for $C_{12}H_8Cl_2$: 222.0003; found: 222.0018.

3.5.2. Compound ***6b***

^1H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 3H), 7.38 (t, J=1.8 Hz, 1H), 7.48 (d, J=1.7 Hz, 2H), 7.60 (d, J=8.0 Hz, 2H), 8.11 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.25, 125.75, 127.02, 127.94, 130.00, 130.28, 135.46, 142.74, 142.92, 166.60; MS (EI): m/z (%) 124 (6), 151 (8), 186 (41), 249 (100), 280 ($[M]^+$, 62); HRMS (EI): calcd for $C_{14}H_{10}Cl_2O_2$: 280.0058; found: 280.0043.

3.5.3. Compound ***6c***

^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 1H), 6.96 (dt, J=2.6 and 9.4 Hz, 2H), 7.26 (t, J=1.8 Hz, 1H), 7.40 (d, J=2.0 Hz, 2H), 7.45 (dt, J=2.6 and 9.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.34, 114.40, 125.08, 126.41, 128.12, 130.88, 135.14, 143.74, 159.95; MS (EI): m/z (%) 139 (12), 173 (6), 209 (22), 237 (28), 252 ($[M]^+$, 100); HRMS (EI): calcd for $C_{13}H_{10}Cl_2O_2$: 252.0109; found: 252.0098.

3.5.4. Compound ***6d***

^1H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 7.16–7.31 (m, 4H), 7.21 (d, J=1.7 Hz, 2H), 7.35 (t, J=1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.27, 125.98, 126.91, 127.69, 128.17, 129.41, 130.53, 134.55, 135.13, 139.12, 144.83; MS (EI): m/z (%) 165 (86), 166 (86), 201 (100), 236 ($[M]^+$, 83); HRMS (EI): calcd for $C_{13}H_{10}Cl_2$: 236.0160; found: 236.0153.

3.5.5. Compound ***6e***

^1H NMR (400 MHz, $CDCl_3$): δ 2.68 (s, 3H), 7.72 (dt, J=1.9 and 8.4 Hz, 2H), 7.95 (s, 1H), 8.10 (s, 2H), 8.12 (dt, J=1.5 and 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.64, 114.19, 117.06, 122.73 (q, J (CF)=1086 Hz), 127.35, 128.06, 128.06 (q, J (CF)=26.4 Hz), 129.26, 132.66 (q, J (CF)=135 Hz), 133.80, 137.27, 141.48, 142.31, 197.20; MS (EI): m/z (%) 177 (13), 226 (18), 246 (13), 274 (100), 289 ($[M]^+$, 24); HRMS (EI): calcd for $C_{16}H_{10}F_3NO$: 289.0714; found: 289.0737.

3.5.6. Compound ***6f***

^1H NMR (400 MHz, $CDCl_3$): δ 3.97 (s, 3H), 7.71 (d, J=8.1 Hz, 2H), 7.76 (t, J=2.0 Hz, 1H), 7.78 (d, H=8.6 Hz, 2H), 8.07 (t, J=1.6 Hz, 1H), 8.15 (t, J=1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.64, 112.10, 118.46, 126.50, 127.78, 129.43, 131.39, 132.81, 135.36, 141.07, 143.08, 165.43; MS (EI): m/z (%) 149 (23), 177 (70), 212 (13), 240 (100), 271 ($[M]^+$, 63); HRMS (EI): calcd for $C_{15}H_{10}ClNO_2$: 271.0400; found: 271.0394.

3.5.7. Compound ***6g***

^1H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 3H), 7.44 (dd, J=2.1 and 8.4 Hz, 1H), 7.53 (d, J=8.3 Hz, 1H), 7.61 (d, J=8.3 Hz, 2H), 7.70 (d, J=2.2 Hz, 1H), 8.11 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.22, 126.42, 126.87, 129.06, 129.68, 130.26, 130.84, 132.39, 133.08, 139.92, 142.99, 166.66; MS (EI): m/z (%) 124 (12), 151 (11), 186 (51), 249 (100), 280 ($[M]^+$, 70); HRMS (EI): calcd for $C_{14}H_{10}Cl_2O_2$: 280.0058; found: 280.0055.

3.5.8. Compound ***6h***

^1H NMR (400 MHz, $CDCl_3$): δ 6.73 (s, 1H), 7.09 (t, J=4.3 Hz, 1H), 7.11 (t, J=8.4 Hz, 1H), 7.19 (t, J=7.1 Hz, 1H), 7.26 (d, J=5.1 Hz, 1H), 7.28 (d, J=5.1 Hz, 1H), 7.37 (d, J=7.8 Hz, 1H), 7.59 (d, J=7.8 Hz, 1H), 8.22 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.37, 110.74, 120.41,

122.87, 124.56, 127.87, 129.04, 132.29, 135.58, 136.46; MS (EI): *m*/*z* (%) 100 (9), 127 (5), 154 (9), 171 (9), 199 ([M]$^+$, 100); HRMS (EI): calcd for $C_{12}H_9NS$: 199.0452; found: 199.0456.

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