

Supporting Information

For

Pd-Catalyzed Oxidative *ortho*-C–H Borylation of Arenes

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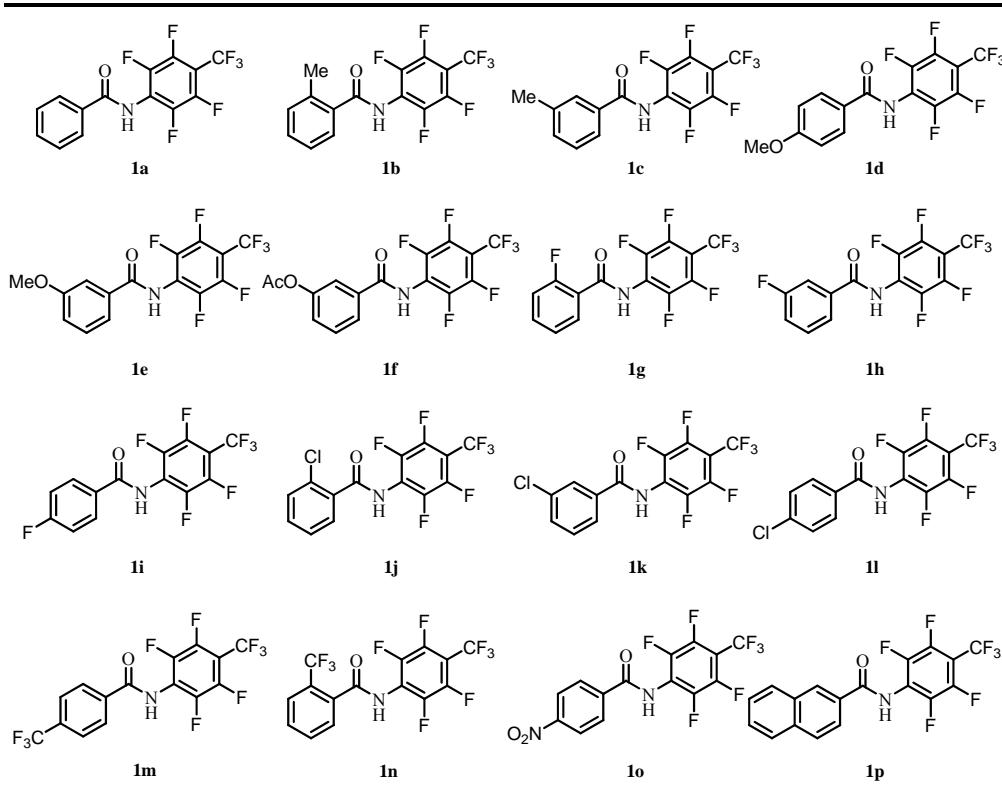
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1. General Information: All solvents were used as received from commercial sources without further purification. $B_2\text{pin}_2$ and $K_2\text{S}_2\text{O}_8$ were purchased from Oakwood and Acros respectively. Palladium acetate was purchased from Sigma-Aldrich and used without further purification. The dba-(**L1-L6**) ligands were prepared by literature methods.¹ ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 MHz and 100 MHz, respectively), Bruker DRX (500 MHz and 125 MHz, respectively), and Bruker-DRX (600 MHz and 150 MHz, respectively) instruments and are reported relative to the SiMe_4 or residual undeuterated solvent signals. High resolution mass spectra were recorded at the Center for Mass Spectrometry, The Scripps Research Institute.

2. Experimental Section

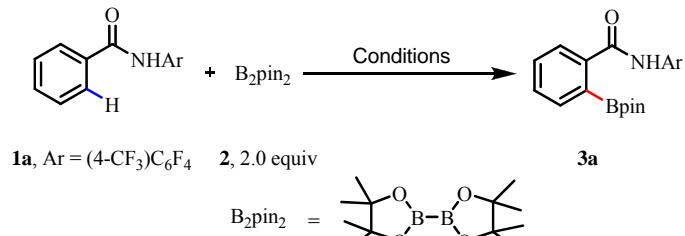
2.1 Preparation of Substrates.

All *N*-arylbenzamide substrates **1a-p** were prepared using our reported procedure.²



2.2 Reaction Optimization of C–H Borylation.

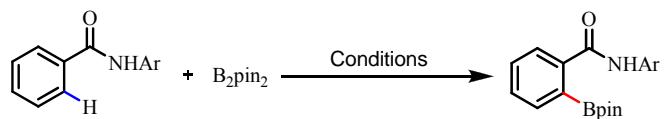
Table S1. Discovery of the C–H borylation^a.



Entry	Oxidant	Base	Additive	T(°C)	Yield (%)
1	Ag ₃ PO ₄	KH ₂ PO ₄	None	100	10
2	Ag ₃ PO ₄	None	None	100	16
3	Ag ₃ PO ₄	KH ₂ PO ₄	HOAc (0.5 eq)	100	23
4	None	KH ₂ PO ₄	HOAc (0.5 eq)	100	18
5	None	KH ₂ PO ₄	HOAc (1.0 eq)	100	3
6	None	KH ₂ PO ₄	HOAc (2.0 eq)	100	1
7	None	KH ₂ PO ₄	HOAc (5.0 eq)	100	trace
8	None	KH ₂ PO ₄	HOAc (0.5 eq)	120	NR
9	None	KH ₂ PO ₄	HOAc (0.5 eq)	80	18
10	None	KH ₂ PO ₄	HOAc (0.5 eq)	60	10
11	None	KH ₂ PO ₄	HOAc (0.5 eq)	40	6
12	None	KH ₂ PO ₄	HOAc (0.5 eq)	rt	NR
13	None	None	HOAc (0.5 eq)	80	20
14 ^b	None	None	HOAc (0.5 eq)	80	43

^a **1a** (0.1 mmol), B₂pin₂ (0.2 mmol), Pd(OAc)₂ (10 mol %), Base (1.0 equiv), oxidant (1.0 equiv), CH₃CN (1.0 mL), 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. ^b Pd(OAc)₂ (20 mol %).

Table S2. Screening of oxidants^a.



1a, Ar = (4-CF₃)C₆F₄ **2**, 2.0 equiv

3a

Entry	Oxidant	Yield (%)	Entry	Oxidant	Yield (%)
1	None	20	9	C	NR
2	Phl(OAc) ₂	trace	10	D	NR
3	Phl(CF ₃ CO ₂) ₂	NR	11	E	NR
4	Phl(OPiv) ₂	NR	12	AgOAc	NR
5	K₂S₂O₈	29	13	Ag ₃ PO ₄	trace
6	Ce(SO ₄) ₂	18	14	AgOAc + Tempo	NR
7	A	21 + 26(F) ^b	15	Ag ₂ CO ₃	NR
8	B	NR	16^c	None	59

^a **1a** (0.1 mmol), B₂pin₂ (0.2 mmol), Pd(OAc)₂ (10 mol %), oxidant (2.0 equiv), HOAc (0.5 equiv), CH₃CN (1.0 mL), 80 °C, 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. ^b Fluorinated product. ^c Pd(OAc)₂ (1.0 equiv).

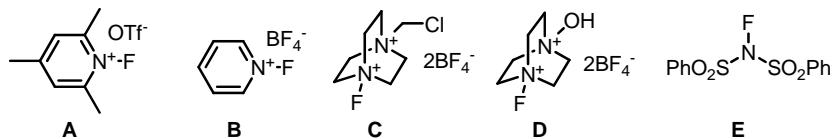
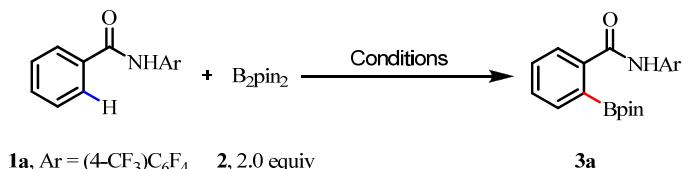


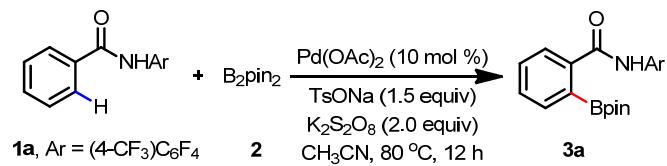
Table S3. Further optimization of C–H borylation^a.



Entry	Additive	Yield (%)
1	TsOH.H ₂ O (0.5 eq)	38
2	TsOH.H ₂ O (1.0 eq)	22
3	TsOH.H ₂ O + NaOAc (0.5 eq)	47 + 7(di)
4	TsOH.H ₂ O + TsONa (0.5 eq)	47 + 3(di)
5	TsOH.H ₂ O + TsONa (1.0 eq)	46
6	TsOH.H ₂ O + TsONa (1.5 eq)	45
7	TsOH.H ₂ O + TsONa (2.0 eq)	32
8	TsOH.H ₂ O + TsONa (3.0 eq)	35
9	TsONa (0.5 eq)	28
10	TsONa (1.0 eq)	50
11	TsONa (1.5 eq)	58
12	TsONa (2.0 eq)	55 + 5(di)

^a **1a** (0.1 mmol), B₂pin₂ (0.2 mmol), Pd(OAc)₂ (10 mol %), K₂S₂O₈ (2.0 equiv), additive (0.5 equiv), CH₃CN (1.0 mL), 80 °C, 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

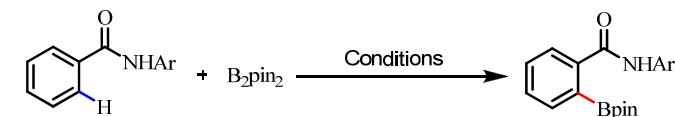
Table S4. Influence of the amount of boron regent **2**^a.



Entry	2 (equiv)	Yield (%)
1	1.0	31
2	1.5	35
3	2.0	53

^a **1a** (0.1 mmol), **2**, Pd(OAc)₂ (10 mol %), K₂S₂O₈ (0.2 mmol), TsONa (0.15 mmol), CH₃CN (1.0 mL), 80 °C, 12 h. ^b The yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

Table S5. Screening of solvents^a.



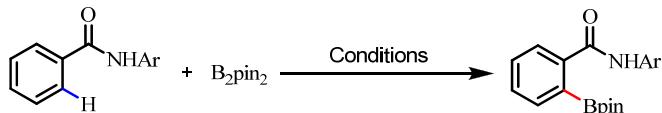
1a, Ar = (4-CF₃)C₆F₄ **2**, 2.0 equiv

3a

Entry	Solvent	Yield (%)	Entry	Solvent	Yield (%)
1	CH ₃ CN	58	7	DCM	trace
2	DMSO	NR	8	DCE	NR
3	DMF	trace	9	THF	9
4	dioxane	trace	10	t-AmylOH	5
5	toluene	trace	11	THF-4Me	trace
6	PhCF ₃	trace	12	EtOAc	NR

^a **1a** (0.1 mmol), B₂pin₂ (0.2 mmol), Pd(OAc)₂ (10 mol %), K₂S₂O₈ (2.0 equiv), TsONa (1.5 equiv), Solvent (1.0 mL), 80 °C, 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

Table S6. Screening of bases^a.



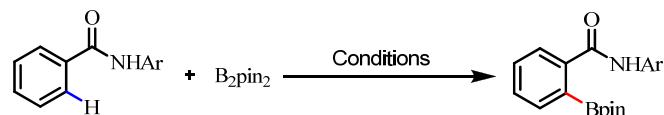
1a, Ar = (4-CF₃)C₆F₄ **2**, 2.0 equiv

3a

Entry	Base	Yield (%)	Entry	Base	Yield (%)
1	TsONa	58	8	Li ₂ CO ₃	NR
2	NaOAc	NR	9	K ₂ CO ₃	NR
3	LiOAc	NR	10	KHCO ₃	NR
4	KOAc	NR	11	CF ₃ CO ₂ Na	26
5	KH ₂ PO ₄	40	12	CF ₃ SO ₃ Na	18
6	K ₂ HPO ₄	32	13	LiCl	NR
7	K ₃ PO ₄	NR	14	None	24

^a **1a** (0.1 mmol), Bzpin₂ (0.2 mmol), Pd(OAc)₂ (10 mol %), K₂S₂O₈ (2.0 equiv), Base (1.5 equiv), CH₃CN (1.0 mL), 80 °C, 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

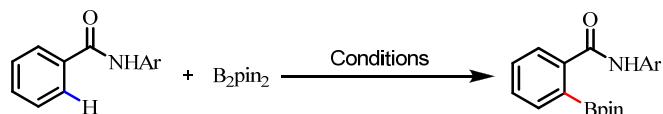
Table S7. Screening of oxidants^a.



1a, Ar = (4-CF ₃)C ₆ F ₄ 2, 2.0 equiv			3a		
Entry	Oxidant	Yield (%)	Entry	Oxidant	Yield (%)
1	K ₂ S ₂ O ₈	58	9	Oxone	NR
2	Na ₂ S ₂ O ₈	33	10	(t-BuO) ₂	5
3	Ag ₂ CO ₃	NR	11	PhI(OAc) ₂	trace
4	AgOAc	NR	12	PhI(CF ₃ CO ₂) ₂	trace
5	Ag ₂ O	NR	13	PhI(OPiv) ₂	trace
6	Ag ₃ PO ₄	3	14	Ce(SO ₄) ₂	11
7	AgOTs	9	15	Cu(OAc) ₂	NR
8	Ag ₂ O + BQ(0.5 eq)	NR	16	AgOAc + Tempo	NR

^a **1a** (0.1 mmol), Bzpin₂ (0.2 mmol), Pd(OAc)₂ (10 mol %), Oxidant (2.0 equiv), TsONa (1.5 equiv), CH₃CN (1.0 mL), 80 °C, 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

Table S8. Screening of Pd sources^a.



1a , Ar = (4-CF ₃)C ₆ F ₄	2 , 2.0 equiv	3a
Entry	Pd	Yield (%)
1	Pd(OAc) ₂	53
2	Pd(CH ₃ CN) ₂ (OTs) ₂	31
3	Pd(CH ₃ CN) ₄ (OTf) ₂	24
4	PdCl ₂ (CH ₃ CN) ₂	NR
5	Pd(CF ₃ CO ₂) ₂	54
6	Pd ₂ (dba) ₃	59

^a **1a** (0.1 mmol), B₂pin₂ (0.2 mmol), Pd (10 mol %), K₂S₂O₈ (2.0 equiv), TsONa (1.5 equiv), CH₃CN (1.0 mL), 80 °C, 12 h, the yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

Table S9. DBA-promoted C–H borylation^a.

1a, Ar = (4-CF₃)C₆F₄ **2** **Pd(OAc)₂ (10 mol %)**
Ligand **TsONa (1.5 equiv)**
K₂S₂O₈ (2.0 equiv)
CH₃CN, 80 °C, 12 h **3a**

Entry	Ligand	Yield (%) ^b	Entry	Ligand	Yield (%) ^b
1	-	53	7	L-3 (0.3 eq)	67 + 5(di)
2	L-1 (0.1 eq)	48 + 9(di)	8	L-4 (0.3 eq)	53 + 8(di)
3	L-1 (0.2 eq)	51 + 15(di)	9	L-5 (0.3 eq)	58 + 12(di)
4	L-1 (0.3 eq)	55 + 18(di)	10	L-6 (0.3 eq)	59 + 13(di)
5	L-1 (0.5 eq)	51 + 6(di)	11 ^c	L-3 (0.3 eq)	78 + 7(di)
6	L-2 (0.3 eq)	43 + 11(di)	12 ^d	L-3 (0.3 eq)	68 + 15(di)

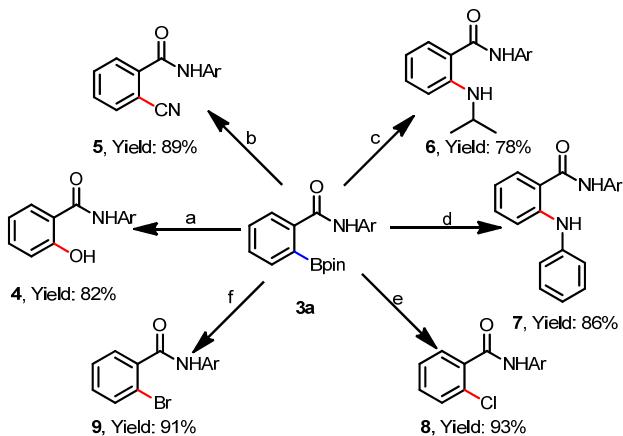
R = H (dba) **L-1**, 4, 4'-OMe **L-2**,
4,4'-CF₃ **L-3**, 4,4'-Cl **L-4**,
4,4'-F **L-5**, 3,3'-NO₂ **L-6**.

^a **1a** (0.1 mmol), **2** (0.2 mmol), Pd(OAc)₂ (10 mol %), K₂S₂O₈ (0.2 mmol), TsONa (0.15 mmol), CH₃CN (1.0 mL), 80 °C, 12 h. ^b The yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard. ^c 24 h. ^d **2** (0.3 mmol).

2.3 Typical Procedures for Pd(OAc)₂-Catalyzed C–H Borylation.

In a 20 mL sealed tube, *N*-arylbenzamide **1a** (34 mg, 0.10 mmol, 1.0 equiv.), B₂pin₂ (51 mg, 0.20 mmol, 2.0 equiv), Pd(OAc)₂ (2.3 mg, 0.01 mmol, 10 mol %), **L-3** (11.1 mg, 0.03 mmol, 30 mol %), K₂S₂O₈ (54 mg, 0.20 mmol, 2 equiv), TsONa (30 mg, 0.15 mmol, 1.5 equiv) were dissolved in CH₃CN (1 mL) under air. The reaction mixture was then tightly capped and stirred for 10 minutes at room temperature for proper mixing of the reactants, and then heated at 80 °C with vigorous stirring for 24 hours. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **3a** was obtained as a white amorphous solid (33 mg, 71% yield).

2.4 Transformations of **3a**^a.



^a Conditions: (a) **3a** (0.05 mmol), oxone (0.05 mmol) in H₂O (1.0 mL), acetone (1.0 mL), rt, 2 h. (b) **3a** (0.05 mmol), CuCN (0.05 mmol), K₂CO₃ (0.15 mmol), DMF (1.0 mL), 60 °C, 4 h. (c) **3a** (0.05 mmol), isopropylamine (0.06 mmol), Cu(OAc)₂ (10 mol %), 4Å MS, O₂ (1 atm), CH₂Cl₂ (1.0 mL), 40 °C, 12 h. (d) **3a** (0.05 mmol), aniline (0.06 mmol), Cu(OAc)₂ (10 mol %), 4Å MS, O₂ (1 atm), CH₂Cl₂ (1.0 mL), 40 °C, 12 h. (e) **3a** (0.05 mmol), CuCl₂ (0.15 mmol) in H₂O (1.0 mL), CH₃OH (1.0 mL), 90 °C, 24 h. (f) **3a** (0.05 mmol), CuBr₂ (0.15 mmol) in H₂O (1.0 mL), CH₃OH (1.0 mL), 80 °C, 24 h.

2.4.1 Synthesis of **4**³

To a solution of **3a** (23 mg, 0.05 mmol) in acetone (1 mL) at room temperature was added a solution of oxone (31 mg, 0.05 mmol) in H₂O (1 mL) dropwise. Upon complete addition, the reaction mixture was vigorously stirred for 2 hours. The reaction mixture was quenched with aqueous NaHSO₃, and then extracted three times with ethyl acetate. The combined organic phases were washed with brine followed by water, and concentrated *in vacuo*. The crude product was purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **4** was obtained as a white amorphous solid (14 mg, 82% yield).

2.4.2 Synthesis of **5**⁴

In a 20 mL sealed tube, **3a** (23 mg, 0.05 mmol), CuCN (4.5 mg, 0.05 mmol) and K₂CO₃ (21 mg, 0.15 mmol) were dissolved in DMF (1 mL) under air. The reaction mixture was then stirred at 60 °C for 4 hours. After cooled to room temperature, the reaction mixture was added a saturated solution NH₄Cl (4 mL), and the product was extracted with ethyl acetate (4 x 15 mL). The combined organic phases were washed with brine followed by water, dried with Na₂SO₄, filtered,

and concentrated *in vacuo*. The crude product was purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **5** was obtained as a pale yellow amorphous solid (16 mg, 89% yield).

2.4.3 Synthesis of $\mathbf{6}^5$

In 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm), **3a** (23 mg, 0.05 mmol), Cu(OAc)₂ (1.0 mg, 0.005 mmol), and powdered 4Å molecular sieves (40 mg) in CH₂Cl₂ (2 mL) was stirred for 5 minutes at room temperature. To this stirring suspension was added the isopropyl amine (5 µL, 0.06 mmol). The reaction tube was evacuated and back-filled with O₂ (5-times, balloon) and heated to 40 °C for 12 hours under vigorous stirring. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **6** was obtained as a yellow oil (15 mg, 78% yield).

2.4.4 Synthesis of $\mathbf{7}^5$

In 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm), **3a** (23 mg, 0.05 mmol), Cu(OAc)₂ (1.0 mg, 0.005 mmol), and powdered 4Å molecular sieves (40 mg) in CH₂Cl₂ (2 mL) was stirred for 5 minutes at room temperature. To this stirring suspension was added the aniline (5.5 µL, 0.06 mmol). The reaction tube was evacuated and back-filled with O₂ (5-times, balloon) and heated to 40 °C for 12 hours under vigorous stirring. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **7** was obtained as a white amorphous solid (18 mg, 86% yield).

2.4.5 Synthesis of $\mathbf{8}^6$

In a 20 mL sealed tube, **3a** (23 mg, 0.05 mmol), CuCl₂ (20 mg, 0.15 mmol) were dissolved in CH₃OH/H₂O (0.6 mL / 0.6 mL) under air. The reaction mixture was then stirred at 90 °C for 24 hours. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **8** was obtained as a white amorphous solid (17 mg, 93% yield).

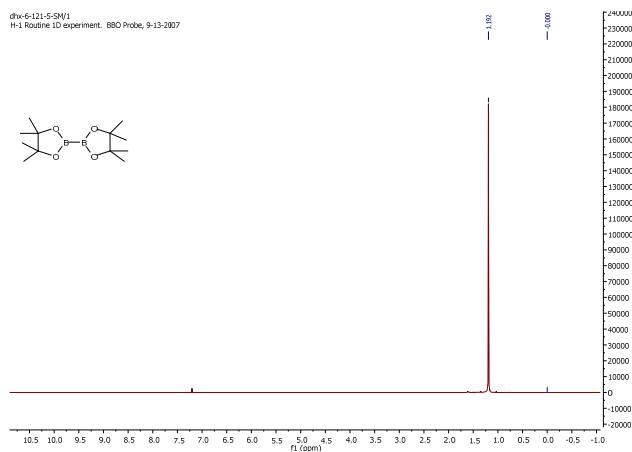
2.4.6 Synthesis of $\mathbf{9}^6$

In a 20 mL sealed tube, **3a** (23 mg, 0.05 mmol), CuBr₂ (34 mg, 0.15 mmol) were dissolved in CH₃OH/H₂O (0.6 mL / 0.6 mL) under air. The reaction mixture was stirred at 80 °C for 24 hours. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **9** was obtained as a white amorphous solid (19 mg, 91% yield).

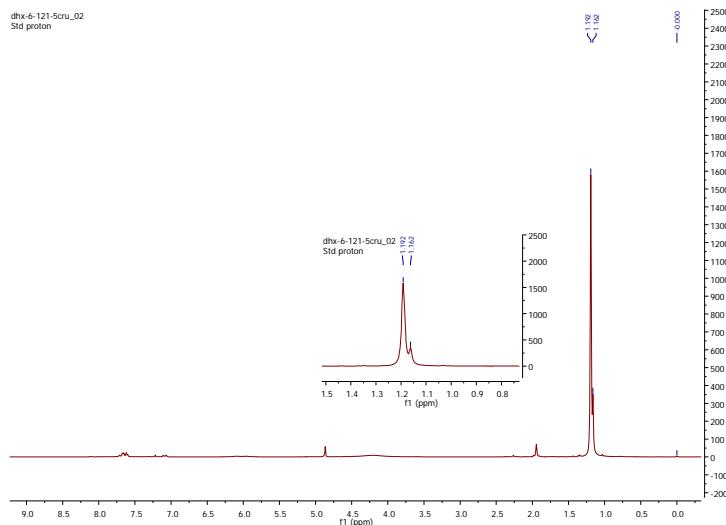
2.5 Control Experiment

(1) Stability of B_2pin_2 under standard reaction conditions^a.

The ^1H NMR spectrum of B_2pin_2



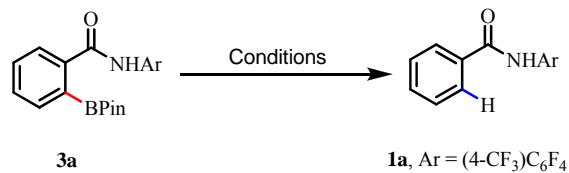
The ^1H NMR spectrum of B_2pin_2 under standard conditions



^a Standard reaction conditions: **2** (0.2 mmol), $\text{Pd}(\text{OAc})_2$ (5 mol %), **L-3** (15 mol %), $\text{K}_2\text{S}_2\text{O}_8$ (0.2 mmol), TsONa (0.15 mmol), CH_3CN (1 mL), 80 °C, 24 h.

Comparison of the above two ^1H NMR spectrum suggests that B_2pin_2 is quite stable under standard reaction conditions.

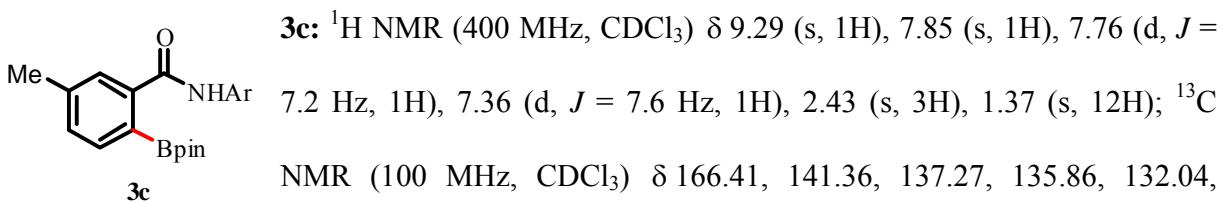
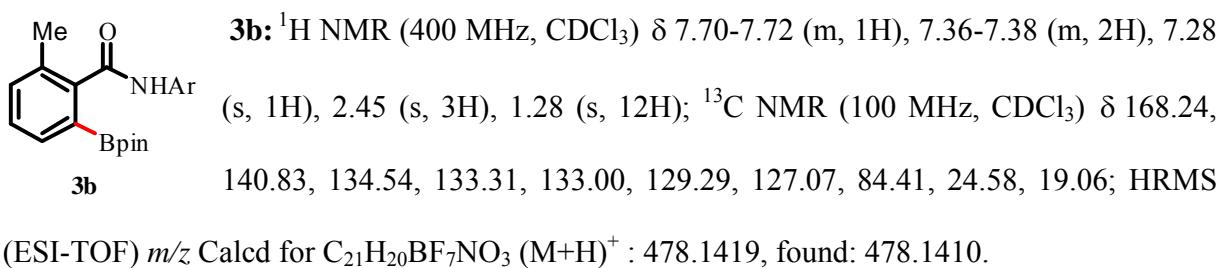
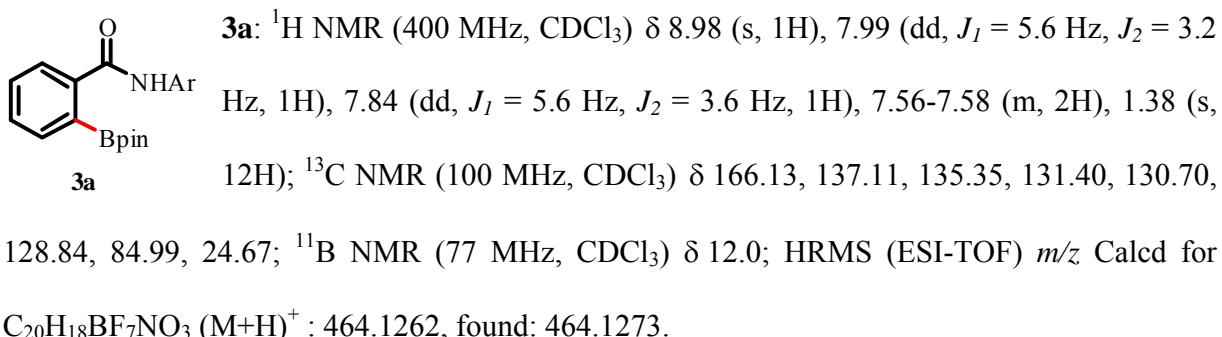
(2) Stability of product under standard reaction conditions^a.



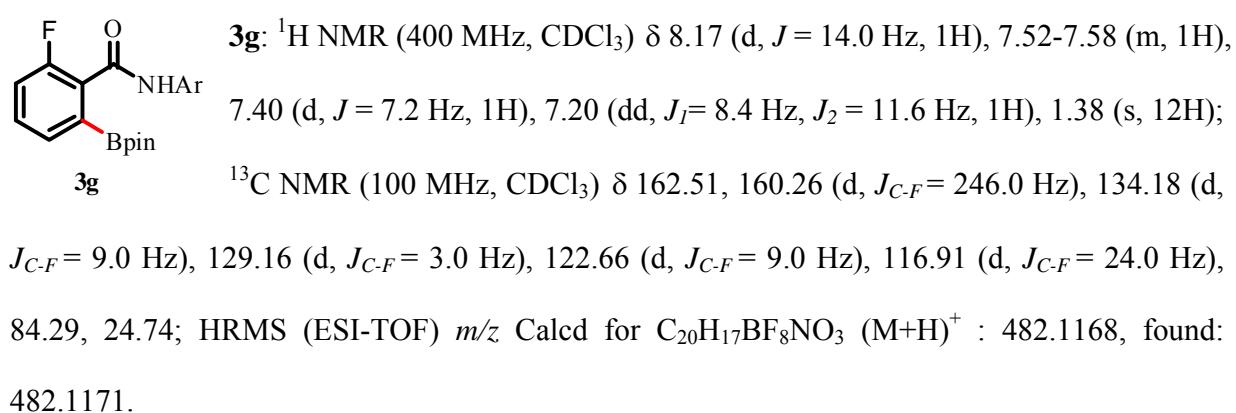
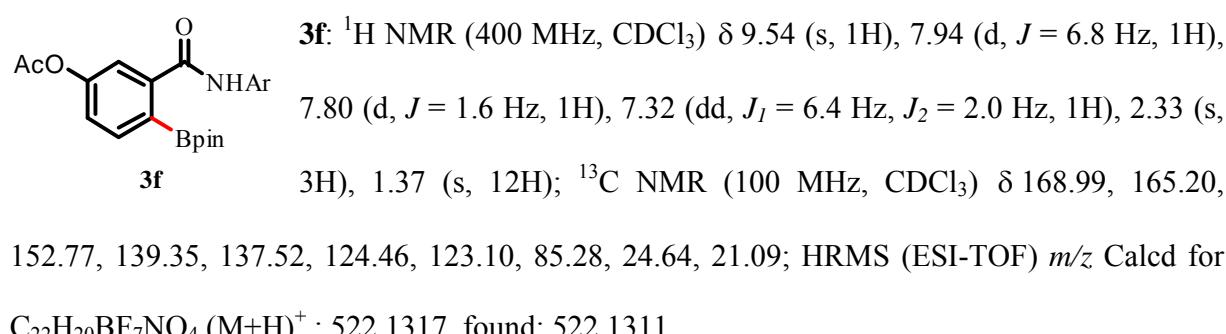
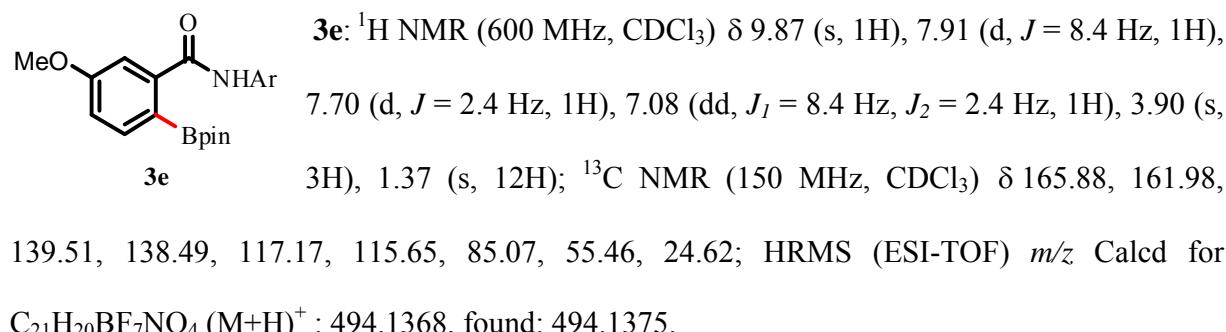
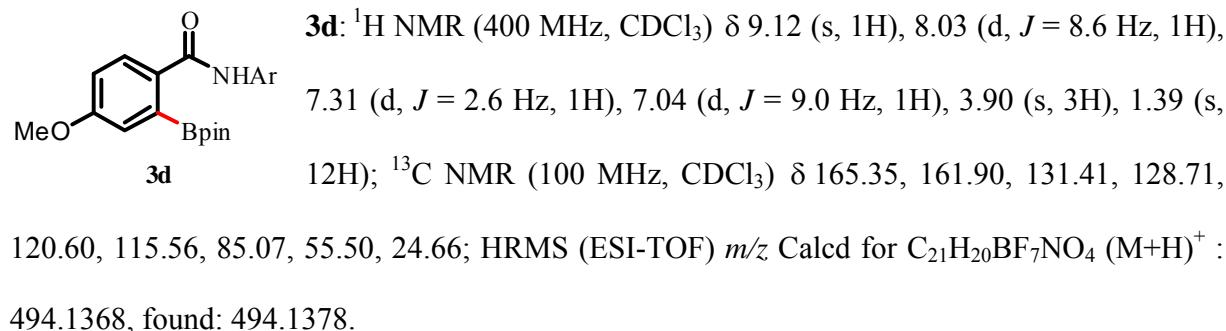
Base	3a (%)	1a (%)
TsONa	56	33
K ₃ PO ₄	0	87

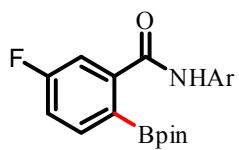
^a Conditions: **3a** (0.10 mmol, 1.0 equiv.), Pd(OAc)₂ (0.01 mmol, 10 mol %), **L-3** (0.03 mmol, 30 mol %), K₂S₂O₈ (0.20 mmol, 2 equiv), Base (0.15 mmol, 1.5 equiv), CH₃CN (1 mL), 80 °C, 8 h. The yield was determined by ¹H NMR analysis of the crude product using CH₂Br₂ as an internal standard.

3. Analytical Data

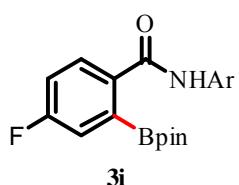


130.10, 84.95, 24.63, 21.43; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{20}BF_7NO_3$ ($M+H$)⁺: 478.1419, found: 478.1422.

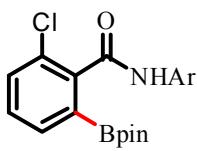




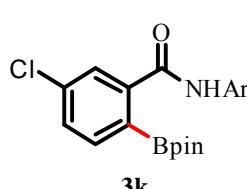
3h: ^1H NMR (600 MHz, CDCl_3) δ 9.59 (s, 1H), 7.93 (dd, $J_1 = 8.4$ Hz, $J_2 = 6.0$ Hz, 1H), 7.80 (dd, $J_1 = 10.2$ Hz, $J_2 = 2.4$ Hz, 1H), 7.24-7.27 (m, 1H), 1.38 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 164.90, 164.40 (d, $J_{\text{C}-\text{F}} = 250.5$ Hz), 140.18 (d, $J_{\text{C}-\text{F}} = 7.5$ Hz), 138.65 (d, $J_{\text{C}-\text{F}} = 7.5$ Hz), 118.34 (d, $J_{\text{C}-\text{F}} = 19.5$ Hz), 117.33 (d, $J_{\text{C}-\text{F}} = 22.5$ Hz), 85.38, 24.63; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{BF}_8\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 482.1168, found: 482.1179.



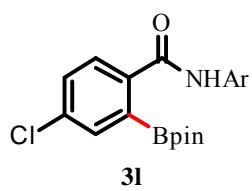
3i: ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 1H), 8.03-8.07 (m, 1H), 7.49-7.53 (m, 1H), 7.20-7.26 (m, 1H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.03, 164.43 (d, $J_{\text{C}-\text{F}} = 254.0$ Hz), 132.96 (d, $J_{\text{C}-\text{F}} = 3.0$ Hz), 131.81 (d, $J_{\text{C}-\text{F}} = 8.0$ Hz), 122.11 (d, $J_{\text{C}-\text{F}} = 21.0$ Hz), 117.55 (d, $J_{\text{C}-\text{F}} = 22.0$ Hz), 85.37, 24.66; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{BF}_8\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 482.1168, found: 482.1176.



3j: ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.2$ Hz, 1H), 7.57 (s, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.43 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.2$ Hz, 1H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.10, 138.77, 133.46, 132.09, 131.04, 130.88, 84.66, 24.60; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{BClF}_7\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 498.0873, found: 498.0890.

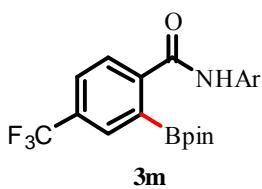


3k: ^1H NMR (400 MHz, CDCl_3) δ 9.31 (s, 1H), 8.03 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.94, 139.11, 137.57, 137.25, 131.28, 129.64, 85.37, 24.64; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{BClF}_7\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 498.0873, found: 498.0875.

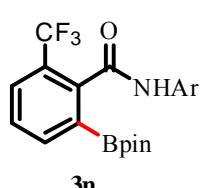


3l: ^1H NMR (400 MHz, CDCl_3) δ 9.12 (s, 1H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.80 (s, 1H), 7.52 (d, $J = 8.8$ Hz, 1H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.24, 138.23, 135.23, 135.20, 130.68, 130.56, 85.40, 24.65;

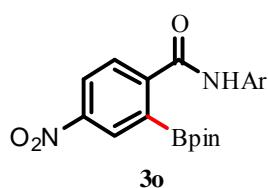
HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{BClF}_7\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 498.0873, found: 498.0885.



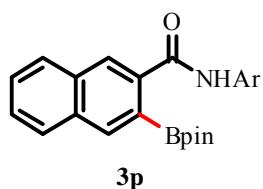
3m: ^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 1H), 8.11 (s, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.35, 140.83, 133.09 (q, $J_{C-F} = 33.7$ Hz), 132.36 (q, $J_{C-F} = 5.0$ Hz), 130.48, 129.35, 127.61, 123.50 (q, $J_{C-F} = 273.8$ Hz), 85.57, 24.66; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{21}\text{H}_{17}\text{BF}_{10}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 532.1136, found: 532.1151.



3n: ^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, $J = 7.4$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.35 (s, 1H), 1.28 (s, 12H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.24, 139.04, 138.64, 130.53, 128.60 (q, $J_{C-F} = 4.5$ Hz), 127.46 (q, $J_{C-F} = 31.5$ Hz), 123.45 (q, $J_{C-F} = 271.5$ Hz), 84.92, 24.54; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{21}\text{H}_{17}\text{BF}_{10}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$: 532.1136, found: 532.1130.

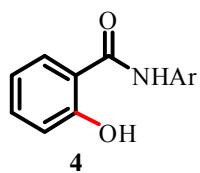


3o: ^1H NMR (400 MHz, CDCl_3) δ 9.05 (s, 1H), 8.70 (d, $J = 2.0$ Hz, 1H), 8.38 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.6$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 1.40 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.64, 149.01, 142.99, 130.45, 130.42, 125.55, 85.94, 24.67; HRMS (ESI-TOF) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{BF}_7\text{N}_2\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 509.1113, found: 509.1134.

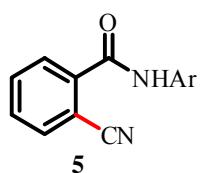


3p: ^1H NMR (400 MHz, CDCl_3) δ 9.37 (s, 1H), 8.59 (s, 1H), 8.39 (s, 1H), 7.92-7.97 (m, 2H), 7.61-7.63 (m, 2H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.19, 137.50, 133.93, 133.35, 133.26, 130.42, 128.89, 128.46,

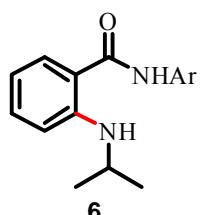
128.21, 128.12, 85.08, 24.71; HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{19}BF_7NO_3$ ($M+H$) $^+$: 514.1419, found: 514.1416.



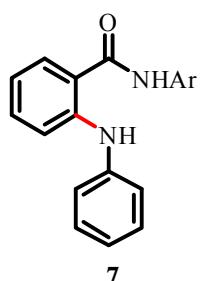
4: 1H NMR (400 MHz, acetone- d_6) δ 8.06 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.55 (dt, $J_1 = 7.2$ Hz, $J_2 = 1.6$ Hz, 1H), 7.06 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.8$ Hz, 1H), 7.02 (dt, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, acetone- d_6) δ 168.33, 161.25, 136.28, 129.91, 120.58, 118.78, 115.54; HRMS (ESI-TOF) m/z Calcd for $C_{14}H_7F_7NO_2$ ($M+H$) $^+$: 354.0365, found: 354.0367.



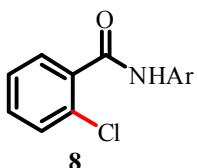
5: 1H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.02 (d, $J = 7.3$ Hz, 1H), 7.83-7.86 (m, 2H), 7.79-7.81 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.98, 158.65, 134.32, 133.23, 130.17, 124.67, 124.58, 121.66; HRMS (ESI-TOF) m/z Calcd for $C_{15}H_6F_7N_2O$ ($M+H$) $^+$: 363.0363, found: 363.0366.



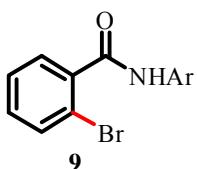
6: 1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.0$ Hz, 1H), 7.53 (s, 1H), 7.50 (s, 1H), 7.40 (t, $J = 7.8$ Hz, 1H), 6.78 (d, $J = 8.8$ Hz, 1H), 6.64 (t, $J = 7.5$ Hz, 1H), 3.70-3.74 (m, 1H), 1.26 (d, $J = 5.4$ Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.04, 150.14, 134.82, 128.80, 114.48, 112.86, 111.12, 43.53, 22.66; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{14}F_7N_2O$ ($M+H$) $^+$: 395.0989, found: 395.0983.



7: 1H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.73 (s, 1H), 7.70 (d, $J = 7.6$ Hz, 1H), 7.31-7.41 (m, 4H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.86 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.69, 147.27, 140.54, 134.29, 129.44, 128.66, 123.66, 121.91, 118.10, 115.91, 114.63; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{12}F_7N_2O$ ($M+H$) $^+$: 429.0832, found: 429.0838.



8²: ¹H NMR (400 MHz, acetone-*d*₆) δ 10.01 (s, 1H), 7.70 (dt, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.55-7.57 (m, 2H), 7.47-7.52 (m, 1H); ¹³C NMR (100 MHz, acetone-*d*₆) δ 165.44, 135.76, 133.02, 131.84, 131.13, 130.45, 128.22.



9: ¹H NMR (400 MHz, acetone-*d*₆) δ 10.00 (s, 1H), 7.74 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.66 (dd, *J*₁ = 7.6 Hz, *J*₂ = 2.0 Hz, 1H), 7.53 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.47 (td, *J*₁ = 7.6 Hz, *J*₂ = 2.0 Hz, 1H); ¹³C NMR (100 MHz, acetone-*d*₆) δ 166.23, 138.07, 134.32, 133.01, 130.30, 128.70, 120.14; HRMS (ESI-TOF) *m/z* Calcd for C₁₄H₆BrF₇NO (M+H)⁺: 415.9515, found: 415.9513.

4. References

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5. NMR Spectra for New Compounds

