Synthesis of Fluorinated Amphoteric Organoborons via Iodofluorination of Alkynyl and Alkenyl MIDA Boronates

Wen-Xin Fan,a Ji-Lin Li,a Wen-Xin Lv,a Ling Yang,a Qingjiang Li,a and Honggen Wang* a,b

a Guangdong Provincial Key Laboratory of Chiral Molecule and Drug Discovery, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China. E-mail: wanghg3@mail.sysu.edu.cn
b State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, China

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I. General Information

Unless otherwise noted, all commercially available materials were used without further purification.

NMR–spectra were recorded on Bruker AvanceIII–400M and AscendTM 500M in solvents as indicate. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (δ = 0). The residual solvent signals were used as references. The following abbreviations were used to describe peak splitting patterns: s (singlet), d (doublet), t (triplet), q (quartet), septet (sept), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), triplet of doublets (td). Coupling constants (J) were reported in hertz unit (Hz).

High–resolution mass spectra (HRMS) were recorded on a Bruker VPEXII spectrometer with EI and ESI mode unless otherwise stated.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm⁻¹).

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished by UV light (254 nm), or KMnO₄ staining solutions followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS) on Agilent Technologies 5977A MSD. Flash column chromatography was performed using silica gel (200–300 mesh).

No attempts were made to optimize yields for substrate synthesis or products derivatizations.

All the starting materials¹⁴ were prepared according to literature procedures.

II. Synthesis and Characterization of Compounds

i. General Procedure for Iodofluorination Reaction (general procedure A)
To a 15-mL screw cap vial equipped with a stirring bar, were added alkynyl (alkenyl) MIDA boronates (0.2 mmol, 1.0 equiv), 1,3-diodo-5,5-dimethylhydantoin/DIH (0.2 mmol, 1.0 equiv), CH$_2$Cl$_2$ (0.1-1.0 mL) and Et$_3$N·3HF (280 μL, 9.0 equiv). The solution was stirred at room temperature or 0 °C for 5-60 min (for alkynyl MIDA boronates) or 1-5 min (for alkenyl MIDA boronates). The resulting mixture was quenched with 0.2 M Na$_2$S$_2$O$_3$ solution and then extracted with EtOAc. The organic phase was washed with 0.2 M HCl and saturated NaCl. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. After removing the EtOAc under vacuum, the crude product was obtained. If necessary, recrystallization (acetone/diethyl ether) was conducted to get pure product.

ii. Gram-scale reactions

\[
\begin{align*}
\text{To a 100-mL round-bottom flask equipped with a stirring bar, were added 4-methylphenyl ethynyl MIDA boronates (4 mmol, 1.0 equiv), DIH (1.0 equiv), CH}_2\text{Cl}_2 (20 mL) and Et}_3\text{N·3HF (9.0 equiv). The solution was stirred at room temperature for 15 min. The resulting mixture was quenched with 0.2 M Na}_2\text{S}_2\text{O}_3 \text{ solution and then extracted with EtOAc. The organic phase was washed with 0.2 M HCl and saturated NaCl. The combined organic layer was dried over anhydrous Na}_2\text{SO}_4 \text{ and concentrated under reduced pressure. After removing the EtOAc under vacuum, the product was obtained as light yellow solid (1.53 g, 92%).}
\end{align*}
\]

\[
\begin{align*}
\text{To a 100-mL round-bottom flask equipped with a stirring bar, were added phenylvinyl MIDA boronates (3 mmol, 1.0 equiv), DIH (1.0 equiv), CH}_2\text{Cl}_2 (15 mL) and Et}_3\text{N·3HF (9.0 equiv). The solution was stirred at room temperature for 5 min. The resulting mixture was quenched with 0.2 M Na}_2\text{S}_2\text{O}_3 \text{ solution and then extracted with EtOAc. The organic phase was washed with 0.2 M HCl and saturated NaCl. The combined organic layer was dried over anhydrous Na}_2\text{SO}_4 \text{ and concentrated under reduced pressure. After removing the EtOAc under vacuum, the product was obtained as white to light yellow solid (1.19 g, 99%).}
\end{align*}
\]
iii. Preparation of Starting Materials

a) Preparation of alkynyl MIDA boronates

Figure S1 General procedure for the preparation of alkynyl MIDA boronates

Preparation of 1-Ethynylboronate ester. According to the synthetic procedure in the literature, to an oven-dried 100-mL round-bottomed flask equipped with a magnetic stir bar, were added THF (15 mL) and trimethylborate (2.45 mL, 22 mmol, 1.1 equiv) via a syringe. The resulting solution was cooled to -78 °C. The addition funnel was charged with the first portion of ethynyl magnesium bromide solution (20 mL, 20 mmol, 1 M in THF) which was then added dropwise over 30 min. The reaction mixture was stirred at -78 °C for 1 h and warmed up to ambient temperature over 3 h to result in a thick white slurry. A 100 mL of 3-neck round-bottomed flask equipped with a stirring bar, a thermometer, and a distillation train was charged with N-methyliminodiacetic acid/MIDA (44 mmol, 2.2 equiv) and DMSO (20 mL). The solution was heated to 130 °C. 20 mL of hexanes was added dropwise to the MIDA solution, resulting in a homogeneous light-orange solution. The previously prepared suspension was added over the course of 30 min via a syringe. After the addition was completed the reaction vessel was washed with THF (2*10 mL) and the washes were transferred to the reaction vessel containing the MIDA solution. The volatiles (THF and MeOH) were allowed to distill off (~15 min). The reaction vessel was allowed to cool to ambient temperature. The reaction mixture was then transferred to a 1 L separatory funnel. To this was added 150 mL water, 150 mL of brine, 210 mL of ethyl acetate, and 140 mL of acetone. The organic layer was separated, and the aqueous layer was extracted twice with 300 mL of a 3:2 ethyl acetate: acetone solution. The combined organic fractions were then washed with 100 mL of brine (five times) and dried over Na2SO4. The organic fractions were then concentrated to form a light brown solid. The solid was dissolved in 10 mL of
dichloromethane and then was precipitated by 500 mL of diethyl ether, then stirred for 30 min. The resulting solid was collected via filtration and washed with diethyl ether (2*50 mL). The resulting solid was ethynyl MIDA boronate (around 60% yield).

Preparation of arylethynyl MIDA boronates 1a-1o. According to the synthetic procedure in the literature, a 25-mL round-bottom flask equipped with a magnetic stir bar was charged with an aryl iodide (2 mmol, 1.0 equiv), ethynyl MIDA boronate (380 mg, 2 mmol, 1.0 equiv), CuI (38.1 mg, 10 mol %), PdCl₂(PPh₃)₂ (70.2 mg, 5 mol %), and placed under nitrogen atmosphere. Then, anhydrous DMF (10 mL) and Et₃N (0.84 mL) were introduced via a syringe, and the reaction mixture was allowed to stir at room temperature until ethynyl B(MIDA) boronate was consumed completely, after which the mixture was poured into a separatory funnel containing water. Extraction with ethyl acetate (3*25 mL) was carried out, and the combined organic extracts were washed with brine (3*20 mL), dried over Na₂SO₄ and concentrated in vacuo to give a crude residue. The crude product was subsequently subjected to flash column chromatography on silica gel to afford the desired compound.

Preparation of alkylethynyl MIDA boronates.

According to the synthetic procedure in the literature, to a THF (10 mL) solution of alkyl acetylene (20 mmol, 1.0 equiv) in a 50 mL of Schlenk tube equipped with a magnetic stir bar under an argon atmosphere, ethyl magnesium bromide solution (20 mL, 20 mmol, 1.0 M in THF) was added dropwise over 30 min at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. Then the reaction mixture was added dropwise to a solution of trimethylborate (2.45 mL, 22 mmol, 1.1 equiv) in THF (10 mL) at -78 °C over 30 min. The reaction mixture was stirred at -78 °C for 1 h and warmed up to ambient temperature over 3 h to result in a white slurry. A 100 mL of 3-neck round-bottomed flask equipped with a stirring bar, a thermometer, and a distillation train was charged with N-methyliminodiacetic acid (MIDA, 44 mmol, 2.2 equiv) and DMSO (20 mL). The solution was heated to 130 °C. 20 mL of hexanes was added dropwise to the MIDA solution, resulting in a homogeneous light orange solution. The previously prepared suspension was added over a course of 30 min via a syringe. After the addition
was completed, the reaction vessel was washed with THF (2*10 mL) and the washes were transferred to the reaction vessel containing the MIDA solution. The volatiles (THF and MeOH) were allowed to distill off (~15 min). The reaction vessel was allowed to cool to ambient temperature. The reaction mixture was then transferred to a 1 L separatory funnel. To this was added 150 mL of de-ionized water, 150 mL of brine, 210 mL of ethyl acetate, and 140 mL of acetone. The organic layer was separated, and the aqueous layer was extracted twice with 300 mL of a 3:2 ethyl acetate: acetone solution. The combined organic fractions were then washed with 100 mL of brine (at least five times) and dried over Na$_2$SO$_4$. The organic fractions were then concentrated to form a light brown solid. The solid was dissolved in 10 mL of dichloromethane and then was precipitated by 500 mL of diethyl ether. The resulting solid was collected via filtration and washed with diethyl ether (2*50 mL). The resulting white solid was product (around 50% yield).

b) Preparation of alkenyl MIDA boronates

All the alkenyl MIDA boronates were prepared according to literature procedures.$^3$

iv. Derivatizations of Products

Conversion of MIDA Boronate to Trifluoroborate

According to the synthetic procedure in the literature,$^4$ to a stirred solution of 2b (0.2 mmol) in methanol (40 mL/mmol) was added aq KHF$_2$ solution (3 equiv, 4.5 M solution) and the mixture was stirred at 70 °C for 0.5 h. The solvent was removed under reduced pressure and the crude residue was thoroughly dried under high vacuum. The solid was extracted with hot acetone and filtered and the solvent evaporated. The crude product was recrystallized (acetone/hexanes) to yield the corresponding potassium trifluoroborate derivative.

Synthesis of compound 6
According to the synthetic procedure in the literature, to a mixture of 2a (0.3 mmol, 1.0 equiv), Zn(CN)$_2$ (0.9 mmol, 3.0 equiv), Cu(NO$_3$)$_2$·3H$_2$O (0.6 mmol, 2.0 equiv) and CsF (0.3 mmol, 1.0 equiv) was added MeOH/H$_2$O (5:1, 3.6 mL). The mixture was stirred at 70 °C overnight. After cooled to the room temperature, the solution was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel with a mixture of petroleum ether and EtOAc as eluent to afford the product as colorless oil.

**Synthesis of compound 7**

![Synthesis of compound 7](image)

The product 7 was synthesized according to the procedure in the literature.

**Synthesis of compound 8**

![Synthesis of compound 8](image)

To a 15 mL Schlenk tube equipped with a stirring bar, were added 2b (0.1 mmol, 42 mg, 1.0 equiv), CuI (0.17 mmol, 32.5 mg, 1.7 equiv) and KF (0.15 mmol, 9 mg, 1.5 equiv) in glovebox. The reaction vessel was taken out, and 0.375 mL dry DMPU were added under N$_2$ protection. The reaction mixture was stirred at 80 °C until 2b was consumed (about 24 h). The resulting mixture was quenched with saturated NH$_4$Cl and extracted with EtOAc. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with petroleum ether as eluent.
Synthesis of compound 9

To a 15 mL Schlenk tube equipped with a stirring bar, were added 2b (0.1 mmol, 42 mg, 1.0 equiv), CuCN (0.17 mmol, 15.2 mg, 1.7 equiv) and KF (0.15 mmol, 9 mg, 1.5 equiv) in glovebox. The reaction vessel was taken out, and 0.375 mL dry DMPU were added under N₂ protection. The reaction mixture was stirred at 80 °C until 2b was consumed (about 12 h). The resulting mixture was quenched with saturated NH₄Cl and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography (petroleum ether: EtOAc = 10:1).

Synthesis of compound 10

To a 15 mL Schlenk tube equipped with a stirring bar were added 2b (0.2 mmol, 84 mg, 1.0 equiv), CuCl (0.34 mmol, 33.6 mg, 1.7 equiv) and KF (0.85 mmol, 50 mg, 4.3 equiv) in glovebox. The reaction vessel was taken out, and 4-methoxybenzenethiol (0.3 mmol, 42 mg, 1.5 equiv) in 0.8 mL dry DMPU were added via syringe under N₂ protection. The reaction mixture was stirred at 80 °C until 2b was consumed (about 18 h). The resulting mixture was quenched with saturated NH₄Cl and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography (petroleum ether).

Synthesis of compound 11
To a 15 mL Schlenk tube equipped with a stirring bar were added 2b (0.15 mmol, 63 mg, 1.0 equiv), CuCl (0.225 mmol, 25.5 mg, 1.7 equiv) and KF (0.66 mmol, 37.5 mg, 4.3 equiv) in glovebox. The reaction vessel was taken out, and ethynylbenzene (0.225 mmol, 23 mg, 1.5 equiv) in 0.6 mL dry DMPU were added via syringe under N₂ protection. The reaction mixture was stirred at 80 °C until 2b was consumed (about 24 h). The resulting mixture was quenched with saturated NH₄Cl and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography (petroleum ether).

v. Characterization of compounds

Following general procedure A (the reaction was stirred at room temperature for 30 min), 2a was obtained in 87% yield (70 mg) as a white to light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.35. ¹H NMR (500 MHz, Acetone-d₆) δ 7.70 – 7.68 (m, 2H), 7.48 – 7.46 (m, 3H), 4.41 (d, J = 17.1 Hz, 2H), 4.22 (d, J = 17.1 Hz, 2H), 3.24(s, 3H). ¹³C NMR (126 MHz, Acetone-d₆) δ 168.4 , 163.8 (d, J = 258.8 Hz), 135.4 (d, J = 31.7 Hz), 131.0 (d, J = 2.6 Hz), 130.3 (d, J = 3.6 Hz), 129.0 , 63.88, 63.86, 47.7. ¹⁹F NMR (376 MHz, Acetone-d₆) δ -59.60. ¹¹B NMR (128 MHz, Acetone-d₆) δ 9.88. HRMS (EI) m/z calcd for C₁₃H₁₂BFINO₄Na [M+Na]+: 425.9783, found: 425.9780. ATR-FTIR (cm⁻¹): 2960, 2921, 2850, 1761, 1635, 1617, 1444, 1335, 1282, 1225, 1124, 1036, 1012, 1047, 768, 692, 603, 540.

Following general procedure A (the reaction was stirred at room temperature for 20 min), 2b was obtained in 82% yield (68 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.35. ¹H NMR (400 MHz, Acetone-d₆) δ 7.59 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 4.40 (d, J = 17.1 Hz, 2H), 4.21 (d, J = 17.1 Hz, 2H), 3.22 (s, 3H), 2.38 (s, 3H). ¹³C NMR (101 MHz, Acetone-d₆) δ 168.4 , 163.9 (d, J = 258.2 Hz), 141.2 , 132.5 (d, J = 31.6 Hz), 130.2 (d, J = 3.7 Hz), 129.5 , 63.90, 63.87, 47.7 , 21.4. ¹⁹F NMR (376 MHz, Acetone-d₆) δ -59.74. ¹¹B NMR (128 MHz, Acetone-d₆) δ 9.84.
Following general procedure A (the reaction was stirred at room temperature for 20 min), 2c was obtained in 77% yield (74 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.38. 1H NMR (400 MHz, Acetone-d6) δ 7.91 – 7.66 (m, 6H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 4.42 (d, J = 17.2 Hz, 2H), 4.23 (d, J = 17.1 Hz, 2H), 3.26 (s, 3H). 13C NMR (126 MHz, Acetone-d6) δ 168.4, δ 163.5 (d, J = 257.8 Hz), 143.5, 140.7, 134.2 (d, J = 31.9 Hz), 130.9 (d, J = 3.6 Hz), 129.9, 128.8, 127.9, 127.4, 63.9, 47.8. 19F NMR (376 MHz, Acetone-d6) δ -60.43. 11B NMR (128 MHz, Acetone-d6) δ 9.64. HRMS (EI) m/z calcd for C19H14BFINO4Na [M+Na]+: 502.0097, found: 502.0099.

Following general procedure A (the reaction was stirred at 0 °C for 20 min), 2d was obtained in 87% yield (75 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.35. 1H NMR (400 MHz, Acetone-d6) δ 7.67 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.39 (d, J = 17.0 Hz, 2H), 4.20 (d, J = 17.1 Hz, 2H), 3.86 (s, 3H), 3.21 (s, 3H). 13C NMR (101 MHz, Acetone-d6) δ 168.4, 163.5 (d, J = 257.3 Hz), 162.5, 132.0 (d, J = 3.9 Hz), 127.4 (d, J = 32.7 Hz), 114.1, 63.89, 63.87, 55.7, 47.7. 19F NMR (376 MHz, Acetone-d6) δ -59.82. 11B NMR (128 MHz, Acetone-d6) δ 9.93. HRMS (EI) m/z calcd for C14H12BFINO5Na [M+Na]+: 455.9889, found: 455.9888.
FTIR (cm⁻¹): 3013, 2921, 2849, 1775, 1757, 1632, 1508, 1454, 1285, 1252, 1128, 1040, 1024, 952, 828, 790.

Following general procedure A (the reaction was stirred at room temperature for 60 min), 2e was obtained in 92% yield (90 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.34. ¹H NMR (400 MHz, Acetone-d₆) δ 7.86 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 4.42 (d, J = 17.0 Hz, 2H), 4.22 (d, J = 17.1 Hz, 2H), 3.24 (s, 3H). ¹³C NMR (126 MHz, Acetone-d₆) δ 162.3 (d, J = 258.3 Hz), 134.4 (d, J = 32.6 Hz), 121.3 (q, J = 258.3 Hz). ¹⁹F NMR (376 MHz, Acetone-d₆) δ -57.69 – 58.70 (m), -59.60 – -61.34 (m). ¹¹B NMR (128 MHz, Acetone-d₆) δ 9.89. HRMS (EI) m/z calcd for C₁₄H₁₁BF₄INO₅Na [M+Na]⁺: 509.9606, found: 509.9604.

Following general procedure A (the reaction was stirred at room temperature for 45 min), 2f was obtained in 89% yield (82 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.31. ¹H NMR (400 MHz, Acetone-d₆) δ 7.76 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 4.40 (d, J = 17.0 Hz, 2H), 4.21 (d, J = 17.1 Hz, 2H), 3.23 (s, 3H), 2.28 (s, 3H). ¹³C NMR (101 MHz, Acetone-d₆) δ 169.4, 168.4, 163.0 (d, J = 258.1 Hz), 153.0 (d, J = 2.6 Hz), 132.7 (d, J = 32.2 Hz), 131.7 (d, J = 3.6 Hz), 122.4, 47.7, 21.0. ¹⁹F NMR (376 MHz, Acetone-d₆) δ -59.90. ¹¹B NMR (128 MHz, Acetone-d₆) δ 9.94. HRMS (EI) m/z calcd for C₁₅H₁₄BF₄INO₆Na [M+Na]⁺: 483.9838, found: 483.9836. ATR-FTIR (cm⁻¹): 3012, 2920, 2849, 1771, 1758, 1633, 1502, 1450, 1335, 1285, 1127, 1043, 1022, 951, 871, 829, 635, 570.
Following general procedure A (the reaction was stirred at room temperature for 30 min), 2g was obtained in 91% yield (76 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.32. \(^{1}\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 7.77 (ddd, \(J = 8.9, 5.4, 1.0\) Hz, 2H), 7.25 (td, \(J = 8.9, 0.8\) Hz, 2H), 4.42 (dd, \(J = 17.0, 1.1\) Hz, 2H), 4.21 (d, \(J = 17.1\) Hz, 2H), 3.23 (s, 3H). \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 168.5, 162.9 (d, \(J = 248.8\) Hz), 161.1 (d, \(J = 258.7\) Hz), 132.0 (d, \(J = 8.8\) Hz), 130.6 (d, \(J = 32.7\) Hz), 115.3 (d, \(J = 21.9\) Hz), 62.7, 47.0. \(^{19}\)F NMR (376 MHz, Acetone-\(d_6\)) \(\delta\) -59.59, -111.06 (td, \(J = 9.7, 9.2, 4.6\) Hz). \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 9.82.

**HRMS (EI) m/z** calcd for C\(_{13}\)H\(_{11}\)BF\(_2\)INO\(_4\)Na [M+Na\(^+\)]: 443.9689, found: 443.9690. **ATR-FTIR (cm\(^{-1}\))**: 3012, 2960, 2921, 2850, 1760, 1631, 1503, 1334, 1282, 1124, 1047, 955, 839, 804, 700, 566, 514.

Following general procedure A (the reaction was stirred at room temperature for 45 min), 2h was obtained in 78% yield (68 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.33. \(^{1}\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 7.73 (d, \(J = 7.6\) Hz, 2H), 7.52 (d, \(J = 8.4\) Hz, 2H), 4.41 (d, \(J = 17.1\) Hz, 2H), 4.21 (d, \(J = 17.1\) Hz, 2H), 3.23 (s, 3H). \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta\) 168.4, 162.5 (d, \(J = 258.2\) Hz), 136.3 (d, \(J = 2.3\) Hz), 134.1 (d, \(J = 32.7\) Hz), 132.1 (d, \(J = 3.4\) Hz), 129.2, 63.9, 47.7. \(^{19}\)F NMR (376 MHz, Acetone-\(d_6\)) \(\delta\) -60.56. \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 9.77. **HRMS (EI) m/z** calcd for C\(_{13}\)H\(_{11}\)BCIFINO\(_4\)Na [M+Na\(^+\)]: 459.9393, found: 459.9390. **ATR-FTIR (cm\(^{-1}\))**: 3009, 2959, 2921, 2850, 1760, 1631, 1503, 1334, 1282, 1225, 1124, 1047, 955, 839, 804, 700, 566, 514.

Following general procedure A (the reaction was stirred at room temperature for 50 min), 2i was obtained in 84% yield (81 mg) as a light yellow solid after removing the solvent. Rf
Following general procedure A (the reaction was stirred at room temperature for 20 min), 2j was obtained in 96% yield (80 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.35. $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 7.40 – 7.26 (m, 4H), 4.42 (d, $J$ = 17.0 Hz, 2H), 4.22 (d, $J$ = 17.0 Hz, 2H), 3.29 (s, 3H), 2.37 (d, $J$ = 2.2 Hz, 3H). $^{13}$C NMR (126 MHz, Acetone-$d_6$) $\delta$ 167.3, 164.1 (d, $J$ = 265.1 Hz), 141.8, 140.6, 134.5 (d, $J$ = 28.4 Hz), 130.5, 130.2 (d, $J$ = 2.5 Hz), 129.9, 128.8 (d, $J$ = 1.4 Hz), 128.3, 127.7, 127.6 (d, $J$ = 2.0 Hz), 62.6, 59.7.  $^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -56.82. $^{11}$B NMR (128 MHz, Acetone-$d_6$) $\delta$ 9.72. HRMS (EI) m/z calc[d for C$_{14}$H$_{14}$BFNO$_2$Na [M+Na]$^+$: 439.9939, found: 439.9940. ATR-FTIR (cm$^{-1}$): 3019, 3009, 2962, 2921, 2850, 1737, 1648, 1449, 1289, 1121, 1057, 992, 869, 838, 793, 767, 608.

Following general procedure A (the reaction was stirred at room temperature for 60 min), 2k was obtained in 58% yield (56 mg) as a light yellow solid after recrystallization. Rf (dichloromethane/EtOAc 1:1): 0.37. $^1$H NMR (500 MHz, Acetone-$d_6$) $\delta$ 7.59 – 7.50 (m, 3H), 7.50 – 7.42 (m, 5H), 7.42 – 7.37 (m, 1H), 4.26 (d, $J$ = 17.0 Hz, 2H), 3.93 (d, $J$ = 17.0 Hz, 2H), 2.61 (s, 3H). $^{13}$C NMR (126 MHz, Acetone-$d_6$) $\delta$ 167.3, 164.1 (d, $J$ = 265.1 Hz), 141.8, 140.6, 134.5 (d, $J$ = 28.4 Hz), 130.5, 130.2 (d, $J$ = 2.5 Hz), 129.9, 128.8 (d, $J$ = 1.4 Hz), 128.3, 127.7, 127.6 (d, $J$ = 2.0 Hz), 62.6, 59.7.  $^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -60.78. $^{11}$B NMR (128 MHz, Acetone-$d_6$) $\delta$ 9.75. HRMS (EI) m/z calc[d for C$_{13}$H$_{11}$BBrFINO$_4$Na [M+Na]$^+$: 503.8888, found: 503.8888. ATR-FTIR (cm$^{-1}$): 2961, 2921, 2850, 1760, 1645, 1632, 1484, 1334, 1280, 1045, 1015, 954, 828, 751, 700, 539.
Following general procedure A (the reaction was stirred at room temperature for 30 min), 2l was obtained in 91% yield (80 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.32. \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta 7.74–7.72\) (m, 1H), \(7.70–7.63\) (m, 1H), \(7.55–7.44\) (m, 2H), \(4.40\) (d, \(J = 17.0\) Hz, 2H), \(4.21\) (d, \(J = 17.1\) Hz, 2H), \(3.25\) (s, 3H). \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta 168.4, 162.1\) (d, \(J = 259.1\) Hz), \(137.3\) (d, \(J = 32.3\) Hz), \(134.3, 131.0, 131.0\) (d, \(J = 1.9\) Hz), \(130.2\) (d, \(J = 3.1\) Hz), \(129.0\) (d, \(J = 3.1\) Hz), \(63.9\), \(63.8\), \(47.8\). \(^{19}\)F NMR (376 MHz, Acetone-\(d_6\)) \(\delta -60.46\). \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta 9.72\). HRMS (EI) m/z calced for \(\text{C}_{19}\text{H}_{16}\text{BFINO}_4\text{Na} [\text{M}+\text{Na}]^+: 502.0097\), found: 502.0104.

Following general procedure A (the reaction was stirred at room temperature for 15 min), 2m was obtained in 86% yield (79 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.35. \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta 7.20–7.18\) (m, 2H), \(6.89\) (d, \(J = 9.2\) Hz, 1H), \(4.38\) (d, \(J = 17.0\) Hz, 2H), \(4.34–4.29\) (m, 4H), \(4.19\) (d, \(J = 17.1\) Hz, 2H), \(3.20\) (s, 3H). \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta 168.4, 163.3\) (d, \(J = 257.5\) Hz), \(146.2, 143.9, 128.2\) (d, \(J = 32.4\) Hz), \(123.8\) (d, \(J = 4.3\) Hz), \(119.3\) (d, \(J = 3.7\) Hz), \(117.5, 65.4, 65.1, 63.91, 63.88, 47.7\). \(^{19}\)F NMR (376 MHz, Acetone-\(d_6\)) \(\delta -59.65\). \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta 9.82\). HRMS (EI) m/z calced for \(\text{C}_{15}\text{H}_{14}\text{BFINO}_6\text{Na} [\text{M}+\text{Na}]^+: 483.9393\), found: 483.9392. ATR-FTIR (cm\(^{-1}\)): 3111, 3071, 3008, 2960, 2922, 2850, 1745, 1590, 1469, 1338, 1299, 1113, 1078, 1055, 1008, 951, 877, 851, 791, 682, 606, 447.
Following general procedure A (the reaction was stirred at room temperature for 15 min), 2n was obtained in 61% yield (50 mg) as a light yellow solid after recrystallization. Rf (dichloromethane/EtOAc 1:1): 0.40. 1H NMR (400 MHz, Acetone-d6) δ 8.20 (d, J = 2.4 Hz, 1H), 7.64 (dd, J = 5.1, 1.3 Hz, 1H), 7.63 (ddd, J = 5.0, 3.0, 1.3 Hz, 1H), 4.39 (d, J = 17.0 Hz, 2H), 4.20 (d, J = 17.1 Hz, 2H), 3.18 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 168.6, 158.7 (d, J = 251.4 Hz), 134.0 (d, J = 35.4 Hz), 129.8 (d, J = 6.5 Hz), 127.8 (d, J = 4.4 Hz), 128.2, 62.8, 47.1. 19F NMR (376 MHz, Acetone-d6) δ -62.58. 11B NMR (128 MHz, Acetone-d6) δ 9.96. HRMS (EI) m/z calcd for C11H10BFINO4SNa [M+Na]+: 431.9347, found: 431.9350. ATR-FTIR (cm⁻¹): 3115, 3012, 2933, 1761, 1615, 1338, 1287, 1123, 1052, 1023, 955, 872, 791, 681.

Following general procedure A (the reaction was stirred at room temperature for 15 min), 2o was obtained in 65% yield (75 mg) as a light yellow solid after recrystallization. Rf (dichloromethane/EtOAc 1:1): 0.38. 1H NMR (500 MHz, DMSO-d6) δ 7.41 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.35 (s, 1H), 4.37 (d, J = 17.3 Hz, 2H), 4.12 (d, J = 17.3 Hz, 2H), 2.93 (s, 3H), 2.88 (dd, J = 8.6, 3.9 Hz, 2H), 2.48 – 2.38 (m, 2H), 2.31 (d, J = 9.4 Hz, 1H), 2.08 (dt, J = 18.5, 8.7 Hz, 1H), 1.97 (dd, J = 8.6, 4.5 Hz, 2H), 1.81 – 1.76 (m, 1H), 1.57 (dd, J = 16.4, 7.1 Hz, 2H), 1.49 – 1.37 (m, 3H), 0.84 (s, 3H). 13C NMR (126 MHz, DMSO-d6) δ 220.6, 169.1, 162.7 (d, J = 257.7 Hz), 142.5, 136.8, 131.7 (d, J = 31.8 Hz), 129.8, 127.1, 125.6, 63.2, 50.1, 47.8, 47.4, 44.3, 37.8, 35.8, 31.7, 29.2, 26.2, 25.5, 21.6, 13.9. 19F NMR (376 MHz, DMSO-d6) δ -59.17. 11B NMR (128 MHz, Acetone-d6) δ 9.74. HRMS (EI) m/z calcd for C25H28BFINO3Na [M+Na]+: 602.0986, found: 602.0936. ATR-FTIR (cm⁻¹): 2964, 2931, 2865, 1776, 1761, 1730, 1627, 1451, 1284, 1123, 1043, 1025, 1011, 873, 801, 703, 541.
Following general procedure A (the reaction was stirred at room temperature for 20 min), 2p was obtained in 88% yield (65 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.43. \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 4.32 (d, \(J = 17.0\) Hz, 2H), 4.10 (d, \(J = 17.1\) Hz, 2H), 3.09 (s, 3H), 2.74 (dt, \(J = 23.6, 7.5\) Hz, 2H), 1.61 (h, \(J = 7.4\) Hz, 2H), 0.98 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta\) 168.3 (d, \(J = 264.0\) Hz), 168.3, 63.6, 47.5, 37.7 (d, \(J = 29.9\) Hz), 20.1, 13.7. \(^{19}\)F NMR (376 MHz, Acetone-\(d_6\)) \(\delta\) -71.21 (t, \(J = 23.5\) Hz). \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 9.62. HRMS (EI) m/z calcd for C\(_{10}\)H\(_{13}\)BF\(_2\)INO\(_4\)Na [M+Na\(^+\)]: 391.9939, found: 391.9937. ATR-FTIR (cm\(^{-1}\)): 3010, 2963, 2921, 2851, 1760, 1749, 1642, 1456, 1337, 1282, 1042, 1016, 870, 829, 751, 700.

Following general procedure A (the reaction was stirred at room temperature for 10 min), 2q was obtained in 86% yield (63 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.39. \(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta\) 4.00 (d, \(J = 17.0\) Hz, 2H), 3.85 (d, \(J = 17.4\) Hz, 2H), 2.85 (s, 3H), 2.48 – 2.38 (m, 1H), 0.86 – 0.84 (m, 4H). \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta\) 168.4, 166.5 (d, \(J = 258.2\) Hz), 63.6, 47.5, 16.4 (d, \(J = 29.2\) Hz), 6.7 (d, \(J = 3.4\) Hz). \(^{19}\)F NMR (376 MHz, Acetone-\(d_6\)) \(\delta\) -91.26 (d, \(J = 27.7\) Hz). \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 9.57. HRMS (EI) m/z calcd for C\(_{10}\)H\(_{13}\)BF\(_2\)INO\(_4\)Na [M+Na\(^+\)]: 389.9782, found: 389.9780. ATR-FTIR (cm\(^{-1}\)): 3006, 2959, 2932, 2871, 1759, 1745, 1637, 1450, 1337, 1285, 1042, 1016, 967, 897, 866, 700, 599.

Following general procedure A (the reaction was stirred at room temperature for 20 min), 2r was obtained in 96% yield (74 mg) as a white solid after removing the solvent. Rf
Following general procedure A (the reaction was stirred at room temperature for 15 min), 2s was obtained in 91% yield (73 mg) as a white solid after removing the solvent. $R_f$ (dichloromethane/EtOAc 1:1): 0.38. $^1$H NMR (500 MHz, Acetone-$d_6$) $\delta$ 4.31 (d, $J = 16.9$ Hz, 2H), 4.10 (d, $J = 17.0$ Hz, 2H), 3.67 (t, $J = 6.5$ Hz, 2H), 3.08 (s, 3H), 2.93 (dt, 2H), 2.07 – 2.03 (m, 2H). $^{13}$C NMR (126 MHz, Acetone-$d_6$) $\delta$ 168.3, 167.1 (d, $J = 263.7$ Hz), 63.62, 63.61, 47.6, 44.8, 33.6 (d, $J = 30.2$ Hz), 29.8. $^{19}$F NMR (376 MHz, Acetone-$d_6$) $\delta$ -71.69 (t, $J = 22.5$ Hz). $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 14.63. HRMS (EI) m/z calcd for C$_{11}$H$_{16}$BFINO$_4$Na [M+Na]$^+$: 425.9549, found: 425.9551. ATR-FTIR (cm$^{-1}$): 3009, 2969, 2920, 2850, 1763, 1640, 1338, 1300, 1291, 1040, 955, 875, 829, 754, 700, 638, 536, 401.

Following general procedure A (the reaction was stirred at room temperature for 15 min), 2t was obtained in 94% yield (72 mg) as a white solid after removing the solvent. $R_f$ (dichloromethane/EtOAc 1:1): 0.41. $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 4.32 (d, $J = 17.2$ Hz, 2H), 4.12 (d, $J = 17.0$ Hz, 2H), 4.03 (dt, $J = 26.9$, 8.8 Hz, 1H), 3.06 (s, 3H), 2.22 – 2.15 (m, 4H), 2.02 – 1.92 (m, 1H), 1.84 – 1.71 (m, 1H). $^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 168.4, 168.2 (d, $J = 263.3$
$^{18}$Hz), 63.6 , 47.5 , 40.4 (d, $J = 33.4$ Hz), 26.0 , 18.3. $^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -81.13 (d, $J = 26.9$ Hz). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 9.55. HRMS (EI) m/z calcd for C$_{11}$H$_{14}$BFINO$_4$Na [M+Na]$^+$: 403.9939, found: 403.9938. ATR-FTIR (cm$^{-1}$): 2988, 2939, 2859, 1758, 1631, 1455, 1333, 1278, 1114, 1027, 956, 906, 873, 804, 408.

Following general procedure A (the reaction was stirred at room temperature for 20 min), 2u was obtained in 90% yield (75 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.41. $^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.38 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 4.32 (d, $J = 17.2$ Hz, 2H), 4.15 (d, $J = 24.7$ Hz, 2H), 4.10 (d, $J = 17.2$ Hz, 2H), 3.04 (s, 3H). $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 167.5, 165.7 (d, $J = 263.4$ Hz), 135.8 (d, $J = 1.9$ Hz), 128.7, 128.5, 127.0, 62.9, 46.7, 41.0 (d, $J = 30.8$ Hz). $^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -70.18 (t, $J = 24.2$ Hz). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 9.65. HRMS (EI) m/z calcd for C$_{14}$H$_{14}$BFINO$_4$Na [M+Na]$^+$: 439.9939, found: 439.9940. ATR-FTIR (cm$^{-1}$): 2965, 2901, 1772, 1759, 1638, 1334, 1287, 1221, 1126, 1106, 1039, 870, 776, 701, 520.

Following general procedure A (the reaction was stirred at room temperature for 3 min), 4a was obtained in 71% yield (58 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.40. $^1$H NMR (500 MHz, Acetone-$d_6$) δ 7.52 (d, $J = 7.0$ Hz, 2H), 7.46 – 7.32 (m, 3H), 5.59 (dd, $J = 46.1$, 8.6 Hz, 1H), 4.42 (d, $J = 17.2$ Hz, 1H), 4.31 (d, $J = 17.1$ Hz, 1H), 4.23 (d, $J = 17.2$ Hz, 1H), 4.13 (dd, $J = 8.92$, 7.55 Hz, 2H), 3.38 (s, 3H). $^{13}$C NMR (126 MHz, Acetone-$d_6$) δ 168.1, 168.0, 139.4 (d, $J = 20.7$ Hz), 129.7 (d, $J = 2.2$ Hz), 128.8, 128.3 (d, $J = 5.9$ Hz), 96.7 (d, $J = 170.3$ Hz), 65.2, 63.6, 63.5, 47.2 (d, $J = 4.5$ Hz). $^{19}$F NMR (376 MHz, Acetone-$d_6$) δ -146.04 (d, $J = 45.9$ Hz). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 11.02. HRMS (EI) m/z calcd for C$_{13}$H$_{14}$BFINO$_4$Na [M+Na]$^+$: 427.9939, found: 427.9943. ATR-FTIR (cm$^{-1}$):
Following general procedure A (the reaction was stirred at room temperature for 2 min), 4b was obtained in 93% yield (78 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.41. 

\[ \delta \text{H NMR (400 MHz, DMSO-d}_6\] \( \delta \) 7.57 – 7.48 (m, 1H), 7.32 – 7.19 (m, 3H), 5.80 (dd, \( J \) = 46.6, 11.1 Hz, 1H), 4.52 (d, \( J \) = 17.5 Hz, 1H), 4.29 – 4.23 (m, 1H), 4.20 (d, \( J \) = 17.6 Hz, 1H), 4.15 (dd, \( J \) = 11.1, 4.4 Hz, 1H), 3.94 (dd, \( J \) = 17.3, 1.2 Hz, 1H), 3.13 (s, 3H), 2.39 (s, 3H), 1.3 C NMR (101 MHz, DMSO-d6) \( \delta \) 168.3, 136.4 (d, \( J \) = 4.3 Hz), 136.3 (d, \( J \) = 19.3 Hz), 130.3, 129.1 (d, \( J \) = 3.1 Hz), 126.4 (d, \( J \) = 4.1 Hz), 126.2 (d, \( J \) = 1.9 Hz), 92.4 (d, \( J \) = 166.2 Hz), 64.3, 62.5, 62.4, 46.9 (d, \( J \) = 6.4 Hz), 19.1. 

\[ \delta \text{F NMR (376 MHz, DMSO-d}_6\] \( \delta \) -139.63 (d, \( J \) = 46.5 Hz). 

\[ \delta \text{B NMR (128 MHz, DMSO-d}_6\] \( \delta \) 11.09. 

\[ \delta \text{HRMS (EI) m/z calcd for C}_{14}H_{16}BFNO_4Na [M+Na]^+: 442.0096, found: 442.0093. ATR-FTIR (cm\(^{-1}\)): 3022, 2995, 2973, 2921, 1756, 1339, 1287, 1048, 1029, 1006, 905, 859, 759, 720, 585, 455. 

Following general procedure A (the reaction was stirred at room temperature for 2 min), 4c was obtained in 92% yield (78 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.38. 

\[ \delta \text{H NMR (400 MHz, Acetone-d}_6\] \( \delta \) 7.44 (dd, \( J \) = 13.9, 7.9 Hz, 1H), 7.35 (d, \( J \) = 7.7 Hz, 1H), 7.30 (d, \( J \) = 10.0 Hz, 1H), 7.18 – 7.10 (m, 1H), 5.60 (dd, \( J \) = 45.9, 7.8 Hz, 1H), 4.41 (d, \( J \) = 17.1 Hz, 1H), 4.34 (dd, \( J \) = 17.1, 2.5 Hz, 1H), 4.21 (d, \( J \) = 17.1 Hz, 1H), 4.15 (m, 2H), 3.39 (s, 3H), 1.3 C NMR (101 MHz, Acetone-d6) \( \delta \) 168.0, 167.9, 163.2 (d, \( J \) = 243.6 Hz), 142.3 (dd, \( J \) = 21.2, 7.3 Hz), 130.6 (d, \( J \) = 8.3 Hz), 124.4 (dd, \( J \) = 6.4, 2.8 Hz), 116.3 (dd, \( J \) = 21.2, 2.0 Hz), 114.9 (dd, \( J \) = 22.7, 6.5 Hz), 95.4 (d, \( J \) = 174.8 Hz), 65.1, 63.63, 63.59, 47.2 (d, \( J \) = 3.8 Hz). 

\[ \delta \text{F NMR (376 MHz, Acetone-d}_6\] \( \delta \) -114.84 (td, \( J \) = 9.5, 5.9 Hz), -149.79 (d, \( J \) = 45.9 Hz). 

\[ \delta \text{B NMR (128 MHz, Acetone-d}_6\] \( \delta \) 10.79. 

\[ \delta \text{HRMS (EI) m/z calcd for C}_{14}H_{16}BFNO_4Na [M+Na]^+: 442.0096, found: 442.0093. ATR-FTIR (cm\(^{-1}\)): 3022, 2995, 2973, 2921, 1756, 1339, 1287, 1048, 1029, 1006, 905, 859, 759, 720, 585, 455. 

\[ \delta \]
Following general procedure A (the reaction was stirred at room temperature for 1 min), 4d was obtained in 75% yield (67 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.30. 1H NMR (400 MHz, DMSO-d6) δ 7.49 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 5.54 (dd, J = 16.0, 8.2 Hz, 1H), 4.41 (d, J = 17.4 Hz, 1H), 4.29 (dd, J = 17.2, 2.4 Hz, 1H), 4.18 – 4.05 (m, 4H), 4.00 (d, J = 17.7 Hz, 1H), 3.11 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 168.2, 168.20, 137.8 (d, J = 20.9 Hz), 131.9, 127.9 (d, J = 5.8 Hz), 127.7, 119.2, 94.8 (d, J = 171.0 Hz), 63.9, 62.5, 62.50, 46.7, 22.2. 19F NMR (376 MHz, DMSO-d6) δ -146.06 (d, J = 44.9 Hz). 11B NMR (128 MHz, DMSO-d6) δ 11.02. HRMS (EI) m/z calcd for C15H15BF2INO2Na [M+Na]+: 467.0049, found: 467.0053. ATR-FTIR (cm⁻¹): 3003, 2961, 1773, 1747, 1343, 1309, 1079, 1038, 866, 692, 574, 555, 451.

Following general procedure A (the reaction was stirred at room temperature for 7 min), 4e was obtained in 96% yield (91 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.30. 1H NMR (400 MHz, Acetone-d6) δ 7.69 – 7.55 (m, 2H), 7.43 – 7.33 (m, 3H), 5.89 (d, J = 43.7 Hz, 1H), 4.61 (d, J = 12.3 Hz, 1H), 4.48 (d, J = 12.3 Hz, 1H), 4.36 (d, J = 17.1 Hz, 1H), 4.31 (dd, J = 17.0, 1.3 Hz, 1H), 4.22 (d, J = 16.9 Hz, 1H), 4.21 (d, J = 17.1 Hz, 1H), 3.29 (s, 3H), 1.98 (s, 3H). 13C NMR (101 MHz, Acetone-d6) δ 170.2, 167.8, 167.7, 137.1 (d, J = 22.2 Hz), 129.7, 129.5 (d, J = 7.3 Hz), 128.4, 97.1 (d, J = 177.6 Hz), 67.8, 65.1, 64.4, 64.3, 47.7 (d, J = 5.6 Hz), 20.8. 19F NMR (376 MHz, Acetone-d6) δ -160.20. 11B NMR (128 MHz, Acetone-d6) δ 11.03. HRMS (EI) m/z calcd for C16H18BFINO4Na [M+Na]+: 500.0151,
found: 500.0148. ATR-FTIR (cm⁻¹): 3006, 2960, 2922, 1765, 1732, 1738, 1453, 1340, 1283, 1225, 1036, 964, 860, 761, 701, 588, 450.

Following general procedure A (the reaction was stirred at room temperature for 1 min), 4f was obtained in 91% yield (67 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.36.

\[ \text{1H NMR (400 MHz, Acetone-}d_6) \delta 4.35 (dd, J = 17.1, 4.6 Hz, 2H), 4.29 – 4.09 (m, 3H), 3.92 (dd, J = 11.1, 4.1 Hz, 1H), 3.33 (s, 3H), 1.91 – 1.62 (m, 2H), 1.61 – 1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). \]

\[ \text{13C NMR (101 MHz, Acetone-}d_6) \delta 168.0, 167.9, 94.4 (d, J = 175.8 Hz), 64.6, 63.7, 46.6, 38.1 (d, J = 20.7 Hz), 19.2 (d, J = 2.5 Hz), 14.2. \]

\[ \text{19F NMR (376 MHz, Acetone-}d_6) \delta -165.85 (t, J = 42.5 Hz). \]

\[ \text{11B NMR (128 MHz, Acetone-}d_6) \delta 10.39. \]

HRMS (EI) m/z calcd for C₁₀H₁₆BFINO₄Na \[ [M+Na]^+ \]: 394.0095, found: 394.0081. ATR-FTIR (cm⁻¹): 2996, 2959, 2933, 2876, 1759, 1449, 1339, 1295, 1099, 1029, 1007, 946, 856.

Following general procedure A (the reaction was stirred at room temperature for 1 min), 4g was obtained in 62% yield (46 mg) as a white solid after recrystallization. Rf (dichloromethane/EtOAc 1:1): 0.35. 1H NMR (500 MHz, Acetone-\textit{d}₆) \delta 4.35 (d, J = 17.2 Hz, 2H), 4.33 (d, J = 16.9 Hz, 1H), 4.21 (d, J = 16.8 Hz, 1H), 4.14 (d, J = 17.2 Hz, 1H), 3.94 (dd, J = 10.3, 3.3 Hz, 1H), 3.53 (ddd, J = 47.2, 8.3, 3.8 Hz, 1H), 3.33 (s, 3H), 1.35 – 1.21 (m, 1H), 0.66 – 0.56 (m, 2H), 0.57 – 0.44 (m, 2H). 13C NMR (126 MHz, Acetone-\textit{d}₆) \delta 168.1, 168.0, 98.4 (d, J = 220.6 Hz), 64.5, 63.7, 46.5, 16.7 (d, J = 25.5 Hz), 4.9 (d, J = 9.7 Hz), 3.5 (d, J = 3.2 Hz). 19F NMR (376 MHz, Acetone-\textit{d}₆) \delta -153.74 (d, J = 47.2 Hz). 11B NMR (128 MHz, Acetone-\textit{d}₆) \delta 10.36. HRMS (EI) m/z calcd for C₁₀H₁₄BFINO₄Na [M+Na]⁺: 391.9939, found: 391.9943. ATR-FTIR (cm⁻¹): 3010, 2920, 1771, 1756, 1331, 1277, 1234, 1070, 1015, 1003, 955, 852, 721, 658, 542, 483.
Following general procedure A (the reaction was stirred at room temperature for 2 min), 4h was obtained in 93% yield (81 mg) as a white solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.39. ¹H NMR (400 MHz, Acetone-d₆) δ 7.31 (dd, J = 8.8, 7.3 Hz, 2H), 6.97 (t, J = 8.5 Hz, 3H), 4.91 – 4.64 (m, 1H), 4.41 (ddd, J = 15.1, 10.3, 3.4 Hz, 4H), 4.26 (d, J = 17.1 Hz, 1H), 4.17 (d, J = 17.2 Hz, 1H), 4.02 (dd, J = 10.3, 5.6 Hz, 1H), 3.37 (s, 3H). ¹³C NMR (101 MHz, Acetone-d₆) δ 167.8, 159.6, 130.4, 122.0, 115.5, 93.5 (d, J = 179.9 Hz), 72.0 (d, J = 20.9 Hz), 64.9, 63.90, 63.88, 46.9. ¹⁹F NMR (376 MHz, Acetone-d₆) δ -159.44 – -181.89 (m). ¹¹B NMR (128 MHz, Acetone-d₆) δ 10.57. HRMS (EI) m/z calcd for C₁₄H₁₆BFINO₅Na [M+Na]^+: 458.0045, found: 458.0045. ATR-FTIR (cm⁻¹): 3023, 2949, 1761, 1485, 1281, 1241, 1047, 1034, 1024, 948, 819, 506.

Following general procedure A (the reaction was stirred at room temperature for 2 min), 4i was obtained in 95% yield (77 mg) as a light yellow solid after removing the solvent. Rf (dichloromethane/EtOAc 1:1): 0.40. ¹H NMR (400 MHz, DMSO-d₆) δ 7.43 – 7.36 (m, 2H), 7.32 (m, 3H), 5.47 (d, J = 45.9 Hz, 1H), 4.44 (d, J = 17.3 Hz, 1H), 4.30 (d, J = 17.1 Hz, 1H), 4.13 (d, J = 17.4 Hz, 1H), 4.03 (d, J = 17.1 Hz, 1H), 3.91 (dd, J = 43.6, 1.7 Hz, 1H), 3.09 (s, 3H). ¹³C NMR (126 MHz, DMSO-d₆) δ 168.4, 168.2, 141.3 (d, J = 20.9 Hz), 127.9, 127.6, 124.7 (d, J = 8.6 Hz), 92.0 (d, J = 177.6 Hz), 63.1, 62.8, 46.1. ¹⁹F NMR (376 MHz, Acetone-d₆) δ -181.02 – -181.60 (m). ¹¹B NMR (128 MHz, Acetone-d₆) δ 10.66. HRMS (EI) m/z calcd for C₁₃H₁₄BFINO₄Na [M+Na]^+: 427.9939, found: 427.9940.
The product 5 was obtained in 99% yield (73 mg) as a white solid after recrystallization. Rf (dichloromethane/EtOAc 1:1): 0.08. $^1$H NMR (400 MHz, Acetone-d$_6$) $\delta$ 7.45 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 7.9 Hz, 2H), 2.33 (s, 3H). $^{13}$C NMR (126 MHz, Acetone-d$_6$) $\delta$ 157.32 (d, $J$ = 244.1 Hz), 139.06, 134.64 (d, $J$ = 35.0 Hz), 130.24 (d, $J$ = 3.2 Hz), 128.98, 21.27. $^{19}$F NMR (376 MHz, Acetone-d$_6$) $\delta$ -61.54 – -94.73 (m), -138.90 (q, $J$ = 43.9 Hz). $^{11}$B NMR (128 MHz, Acetone-d$_6$) $\delta$ 1.36 (q, $J$ = 42.3 Hz). HRMS (EI) m/z calcd for C$_9$H$_7$BF$_4$I [M-K]: 328.9629, found: 328.9625.

The product 6 was obtained in 65% NMR yield (45% isolated yield, 37 mg) as a light yellow oil. Rf (petroleum ether): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 – 7.80 (m, 2H), 7.56 (t, $J$ = 7.4 Hz, 1H), 7.49 (t, $J$ = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.61 (d, $J$ = 281.3 Hz), 132.79, 129.31 (d, $J$ = 5.7 Hz), 128.91 (d, $J$ = 25.3 Hz), 128.68, 115.20 (d, $J$ = 4.1 Hz), 34.88 (d, $J$ = 30.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -55.27.

The product 7 was obtained in 70% yield (18 mg) as a colorless oil. Rf (petroleum ether/EtOAc 20:1): 0.22. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (t, $J$ = 7.3 Hz, 1H), 7.27 (d, $J$ = 7.4 Hz, 2H), 7.21 (t, $J$ = 7.7 Hz, 2H), 7.14 (d, $J$ = 8.8 Hz, 2H), 6.77 (d, $J$ = 8.8 Hz, 2H), 7.73 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.4 (d, $J$ = 270.3 Hz), 160.4, 131.7, 130.8 (d, $J$ = 2.9 Hz), 129.2 (d, $J$ = 25.6 Hz), 128.7, 128.7, 122.0 (d, $J$ = 3.8 Hz), 115.9 (d, $J$ = 3.2 Hz), 114.8, 96.3 (d, $J$ = 21.2 Hz), 55.5. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -80.15. HRMS (EI) m/z calcd for C$_{16}$H$_{12}$FNONa [M+Na]$^+$: 276.0795, found: 276.0790.
The product 8 was obtained in 50% yield (13 mg) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.2$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 5.99 (d, $J = 34.6$ Hz, 1H), 2.36 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -89.79 (d, $J = 34.6$ Hz).

The product 9 was obtained in 45% yield (8 mg) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 5.35 (d, $J = 32.8$ Hz, 1H), 2.42 (s, 3H).

The product 10 was obtained in 65% yield (36 mg, E:Z = 1:1) as a colorless oil. Rf (petroleum ether): 0.30. For E-isomer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.12 (d, $J = 20.1$ Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H). For Z-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 7.0$ Hz, 2H), 7.37 (d, $J = 7.0$ Hz, 2H), 7.16 (d, $J = 7.7$ Hz, 2H), 6.89 (d, $J = 7.0$ Hz, 2H), 6.06 (dd, $J = 34.7$, 1.6 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H).

For E-isomer: $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.3, 156.8 (d, $J = 247.2$ Hz), 139.7, 131.6, 129.0, 128.3 (d, $J = 28.5$ Hz), 127.1 (d, $J = 6.6$ Hz), 126.5, 115.0, 104.3 (d, $J = 38.3$ Hz), 55.6, 21.6. For Z-isomer: $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.5, 156.2 (d, $J = 247.3$ Hz), 139.0, 132.7, 129.4, 128.9 (d, $J = 27.6$ Hz), 125.7, 123.7 (d, $J = 6.6$ Hz), 115.0, 102.4 (d, $J = 19.6$ Hz), 55.6, 21.4. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -99.22 (d, $J = 20.1$ Hz), -110.92 (d, $J = 34.7$ Hz). HRMS (EI) m/z calcd for C$_{18}$H$_{13}$FOSK [M+K]$^+$: 313.0459, found: 313.0479.
The product 11 was obtained in 46% yield (18 mg) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 7.9$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 5.73 (d, $J = 33.2$ Hz, 1H), 2.39 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -102.14 (d, $J = 33.2$ Hz).

vi. X-ray Crystal Structure Data

Crystal structure data for 2a:

Experimental

Single crystals of C$_{13}$H$_{12}$NO$_4$IBF 2a were colorless crystal. A suitable crystal was selected on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 99.99(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.


Crystal structure determination of 2a

Crystal Data for C$_{13}$H$_{12}$NO$_4$IBF ($M = 402.95$ g/mol): monoclinic, space group I2/a (no. 15), $a = 27.8895(3)$ Å, $b = 6.86390(10)$ Å, $c = 34.3921(3)$ Å, $β = 105.2960(10)^\circ$, $V = 6350.48(13)$ Å$^3$, $Z = 16$, $T = 99.99(10)$ K, $μ$ (CuKα) = 16.076 mm$^{-1}$, $Dcalc$ = 1.686 g/cm$^3$, 31719 reflections measured (5.328° ≤ 2θ ≤ 154.028°), 6495 unique ($R_{int} = 0.0332$, $R_{sigma} = 0.0232$) which were used in all calculations. The final $R_1$ was 0.0310 (I > 2σ(I)) and $wR_2$ was 0.0844 (all data).
Fig. S2. Absolute configuration of 2a (CCDC 1942792).

Table 1 Crystal data and structure refinement for 2a.

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Data/restraints/parameters & 6495/0/381 \\
Goodness-of-fit on F^2 & 1.048 \\
Final R indexes [I>=2\sigma (I)] & R_1 = 0.0310, wR_2 = 0.0820 \\
Final R indexes [all data] & R_1 = 0.0324, wR_2 = 0.0844 \\
Largest diff. peak/hole / e Å^-3 & 0.85/-1.26 \\

Crystal structure data for 4b:

Experimental

Single crystals of C_{14}H_{16}INO_{4}BF 4b were colorless crystal. A suitable crystal was selected on a 
**XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 100.00(10) K during 
data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program 
using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares 
minimisation.

   Cryst. 42, 339-341.

Crystal structure determination of 4b

**Crystal Data** for C_{14}H_{16}INO_{4}BF (M =418.99 g/mol): monoclinic, space group P2_1/c (no. 14), a = 
12.7883(2) Å, b = 11.1705(2) Å, c = 10.9261(2) Å, \( \beta = 102.020(2)^{\circ} \), \( V = 1526.59(5) \AA^3 \), 
Z = 4, \( T = 100.00(10) \) K, \( \mu(\text{CuK}\alpha) = 16.743 \text{ mm}^{-1} \), \( D_{cal} = 1.823 \text{ g/cm}^3 \), 29253 reflections measured (7.068^\circ \leq \Theta 
\leq 154.102^\circ), 3120 unique \( (R_{int} = 0.0461, R_{sigma} = 0.0205) \) which were used in all calculations. The final 
\( R_1 \) was 0.0309 (I > 2\sigma(I)) and \( wR_2 \) was 0.0870 (all data).
Fig. S3. Absolute configuration of 4b (CCDC 1953148).

Table 1 Crystal data and structure refinement for 4b.

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Goodness-of-fit on F^2 1.137
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Final R indexes [all data] R1 = 0.0322, wR2 = 0.0870
Largest diff. peak/hole / e Å^-3 1.17/-1.02

**Crystal structure data for 4j:**

**Experimental**

Single crystals of C_{13}H_{14}NO_{4}IBF 4j were colorless crystal. A suitable crystal was selected on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.


**Crystal structure determination of 4j**

Crystal Data for C_{13}H_{14}NO_{4}IBF (M =404.96 g/mol): orthorhombic, space group Pbca (no. 61), a = 12.6367(3) Å, b = 14.4997(3) Å, c = 15.6349(4) Å, V = 2864.76(12) Å^3, Z = 8, T = 100.00(10) K, μ(CuKα) = 17.818 mm^-1, Dcalc = 1.878 g/cm^3, 9854 reflections measured (10.876° ≤ 2θ ≤ 152.32°), 2867 unique (Rint = 0.0739, Rsigma = 0.0577) which were used in all calculations. The final R1 was 0.0631 (1 > 2σ(I)) and wR2 was 0.1931 (all data).
Fig. S4. Absolute configuration of 4j (CCDC 1956650).

Table 1 Crystal data and structure refinement for fanwx_190923.

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III. References


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S75
S99