

Electronic Supplementary Information

Substrate-controlled product divergence in the reaction of α -fluoro- β -ketoamides with arynes

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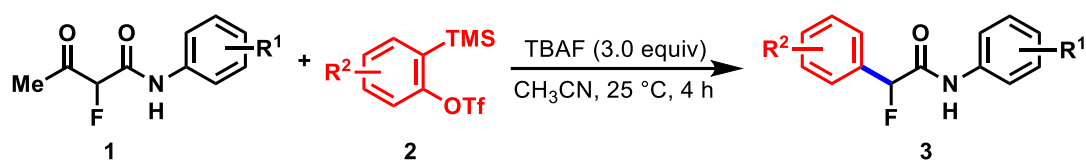
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General experimental information

All reactions were performed under an air atmosphere in oven-dried round-bottom flasks. The reactions were monitored by TLC visualized by UV (254 nm) and/or with iodine. Column chromatography was performed on 100-200 mesh silica gel using ethyl acetate-hexane gradient system. NMR data were recorded at Bruker AV 400 MHz in CDCl₃ using as internal standards the residual CHCl₃ signal for ¹H NMR (δ = 7.26 ppm) and the deuterated solvent signal for ¹³C NMR (δ = 77.16 ppm). Coupling constants are given in Hertz (Hz), and the classical abbreviations are used to describe the signal multiplicities. Melting points were measured with a Büchi B-540 apparatus and were uncorrected. High-resolution mass spectra were obtained using Q-TOF mass spectrometer. All commercially available reagents were used as received. The primary and secondary α -fluoro- β -ketoamides (**1a-1v** & **5a-5h**) were synthesized from the corresponding primary and secondary amines¹ following the literature procedure.² 2-(Trimethylsilyl)phenyltrifluoromethanesulfonate (**2a**) and other aryne precursors were synthesized following the literature procedure (**2b-2i**).³

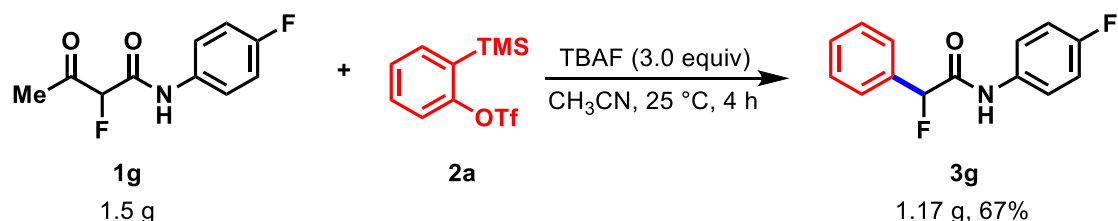
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 2. (a) B. Miriyala and J. S. Williamson, An efficient and rapid synthesis of β -carboxamide derivatives using 2,2-dimethyl-2H,4H-1,3-dioxin-4-ones by microwave irradiation. *Tetrahedron Lett.*, 2003, **44**, 7957–7959. (b) J. Bi, Z. Zhang, Q. Liu and G. Zhang, Catalyst-Free and Highly Selective Electrophilic Mono-Fluorination of Acetoacetamides: Facile and Efficient Preparation of 2-Fluoroacetoacetamides in PEG-400. *Green Chem.*, 2012, **14**, 1159-1162.
 3. (a) X. Yang and G. C. Tsui, Copper-mediated trifluoromethylation–allylation of arynes. *Org. Lett.* 2018, **20**, 1179–1182. (b) K. Nogi, T. Fujihara, J. Terao and Y. Tsuji, Y. Cobalt- and Nickel-catalyzed carboxylation of alkenyl and sterically hindered aryl triflates utilizing CO₂. *J. Org. Chem.* **2015**, **80**, 11618–11623.

General procedure for the synthesis of α -Fluoro- α -arylacetomides **3**



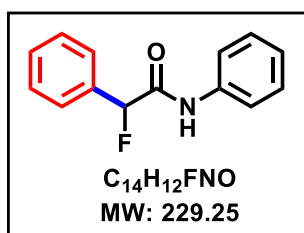
An oven-dried round bottom flask charged with 2-fluoro-3-oxo-*N*-phenylbutanamide **1** (0.20 mmol) was sealed, evacuated, and backfilled with nitrogen. Subsequently, freshly distilled CH₃CN (2.0 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2** (0.30 mmol), and TBAF (0.60 mmol) were added, and the reaction mixture was stirred at 25 °C for 4 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated, and the crude reaction mixture was extracted using ethyl acetate (15 × 3 mL) and water (15 mL). The organic layer was washed with brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent to afford product **3**.

Gram scale synthesis of α -Fluoro- α -arylacetamide **3g**



An oven-dried round bottom flask charged with 2-fluoro-3-oxo-*N*-phenylbutanamide **1g** (1.5 g, 7.05 mmol) was sealed, evacuated, and backfilled with nitrogen. Subsequently, freshly distilled CH₃CN (10.0 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (3.2 g, 10.6 mmol), and TBAF (21.1 mmol) were added, and the reaction mixture was stirred at 25 °C for 4 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated, and the crude reaction mixture was extracted using ethyl acetate (150 × 3 mL) and water (150 mL). The organic layer was washed with brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent to afford the product **3g** as white solid (1.17 g, 67%).

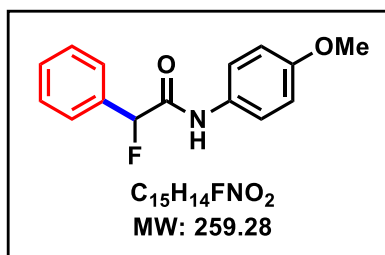
Compound **3a**: 2-Fluoro-*N*,2-diphenylacetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3a** as white solid (33 mg, 72%). R_f (Ethyl acetate/Hexane: 10/90) = 0.35.

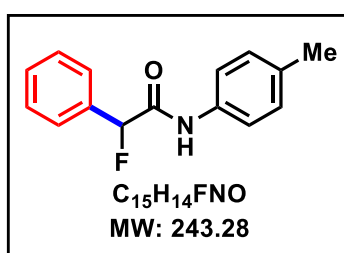
Mp 104-106 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.5 (d, *J*_{C-F} = 20.5 Hz, C), 136.7 (C), 134.5 (d, *J*_{C-F} = 19.0 Hz, C), 129.7 (d, *J*_{C-F} = 2.4 Hz, CH), 129.2 (CH), 129.2 (CH), 128.9 (CH), 128.9 (CH), 126.8 (d, *J*_{C-F} = 6.5 Hz, CH), 126.8 (d, *J*_{C-F} = 6.5 Hz, CH), 125.2 (CH), 120.2 (CH), 120.2 (CH), 92.0 (d, *J*_{C-F} = 188.3 Hz, CH). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.16 (s, 1H), 7.62-7.60 (m, 1H), 7.59-7.58 (m, 1H), 7.55-7.50 (m, 2H), 7.46-7.40 (m, 3H), 7.38-7.33 (m, 2H), 7.19-7.14 (m, 1H), 5.90 (d, *J* = 48.4 Hz, 1H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -175.2 (s). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₄H₁₃FNO 230.0976; found 230.0980.

Compound 3b: 2-Fluoro-*N*-(4-methoxyphenyl)-2-phenylacetamide



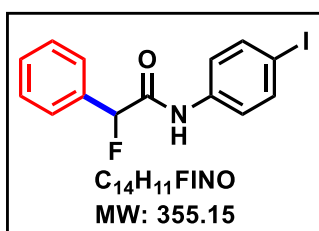
Following the general procedure, treatment of 2-fluoro-*N*-(4-methoxyphenyl)-3-oxobutanamide **1b** (45 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3b** as white solid (36 mg, 70%). *R_f* (Ethyl acetate/Hexane: 20/80) = 0.37. **Mp** 104-106 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 167.2 (d, *J*_{C-F} = 16.7 Hz, C), 157.9 (C), 135.3 (d, *J*_{C-F} = 15.3 Hz, C), 130.4 (C), 130.2 (d, *J*_{C-F} = 2.2 Hz, CH), 129.4 (CH), 129.4 (CH), 127.3 (d, *J*_{C-F} = 5.5 Hz, CH), 127.3 (d, *J*_{C-F} = 5.5 Hz, CH), 122.4 (CH), 122.4 (CH), 114.8 (CH), 114.8 (CH), 92.0 (d, *J*_{C-F} = 151.9 Hz, CH), 55.4 (CH₃). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.10 (s, 1H), 7.53-7.47 (m, 4H), 7.50-7.40 (m, 3H), 6.90-6.86 (m, 2H), 5.88 (d, *J* = 48.4 Hz, 1H), 3.80 (s, 3H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -175.3 (s). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₅FNO₂ 260.1081; found 260.1078.

Compound 3c: 2-Fluoro-2-phenyl-*N*-(*p*-tolyl)acetamide



Following the general procedure, treatment of 2-fluoro-3-oxo-*N*-(*p*-tolyl)butanamide **1c** (42 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3c** as brown solid (33 mg, 68%). *R_f* (Ethyl acetate/Hexane: 10/90) = 0.37. **Mp** 126-128 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.4 (d, *J*_{C-F} = 20.6 Hz, C), 134.9 (C), 134.7 (d, *J*_{C-F} = 19.1 Hz, C), 134.2 (C), 129.7 (CH), 129.7 (CH), 129.7 (d, *J*_{C-F} = 2.7 Hz, CH), 128.9 (CH), 128.9 (CH), 126.8 (d, *J*_{C-F} = 6.5 Hz, CH), 126.8 (d, *J*_{C-F} = 6.5 Hz, CH), 120.2 (CH), 120.2 (CH), 92.0 (d, *J*_{C-F} = 188.2 Hz, CH), 21.0 (CH₃). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.16 (s, 1H), 7.54-7.51 (m, 2H), 7.50-7.45 (m, 2H), 7.45-7.40 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.86 (d, *J* = 48.4 Hz, 1H), 2.33 (s, 3H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -175.2 (s). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₅FNO 244.1132; found 244.1128.

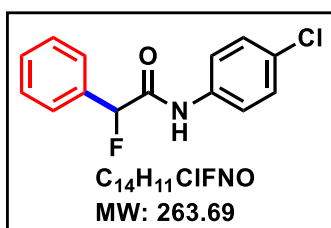
Compound 3d: 2-Fluoro-*N*-(4-iodophenyl)-2-phenylacetamide



Following the general procedure, treatment of 2-fluoro-*N*-(4-iodophenyl)-3-oxobutanamide **1d** (64 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3d** as white solid (49 mg, 69%). *R_f* (Ethyl acetate/Hexane:

10/90) = 0.37. **Mp** 144-146 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.6 (d, *J*_{C-F} = 16.7 Hz, C), 138.2 (CH), 138.2 (CH), 136.6 (C), 134.3 (d, *J*_{C-F} = 15.4 Hz, C), 129.8 (d, *J*_{C-F} = 1.0 Hz, CH), 129.0 (CH), 129.0 (CH), 126.7 (d, *J*_{C-F} = 5.2 Hz, CH), 126.7 (d, *J*_{C-F} = 5.2 Hz, CH), 122.0 (CH), 122.0 (CH), 92.0 (d, *J*_{C-F} = 150.6 Hz, CH), 88.6 (C). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.17 (s, 1H), 7.66-7.63 (m, 2H), 7.52-7.47 (m, 2H), 7.44-7.40 (m, 3H), 7.40-7.36 (m, 2H), 5.88 (d, *J* = 48.4 Hz, 1H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -175.8 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₄H₁₂FINO 355.9942; found 355.9943.

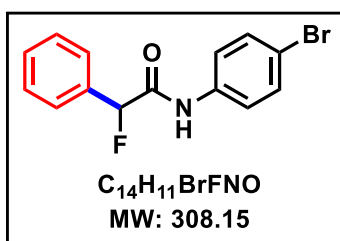
Compound 3e: *N*-(4-chlorophenyl)-2-fluoro-2-phenylacetamide



Following the general procedure, treatment of *N*-(4-chlorophenyl)-2-fluoro-3-oxobutanamide **1e** (46 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded

the product **3e** as white solid (32 mg, 61%). *R_f* (Ethyl acetate/Hexane: 20/80) = 0.50. **Mp** 133-135 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.6 (d, *J*_{C-F} = 20.8 Hz, C), 135.3 (C), 134.4 (d, *J*_{C-F} = 19.1 Hz, C), 130.3 (C), 129.8 (CH), 129.3 (CH), 129.3 (CH), 129.0 (CH), 129.0 (CH), 126.7 (d, *J*_{C-F} = 6.4 Hz, CH), 126.7 (d, *J*_{C-F} = 6.4 Hz, CH), 121.4 (CH), 121.4 (CH), 92.0 (d, *J*_{C-F} = 188.4 Hz, CH). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.16 (s, 1H), 7.57-7.53 (m, 2H), 7.52-7.48 (m, 2H), 7.45-7.40 (m, 3H), 7.33-7.29 (m, 2H), 5.90 (d, *J* = 48.8 Hz, 1H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -175.9 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₄H₁₂ClFNO 264.0586; found 264.0588.

Compound 3f: *N*-(4-bromophenyl)-2-fluoro-2-phenylacetamide

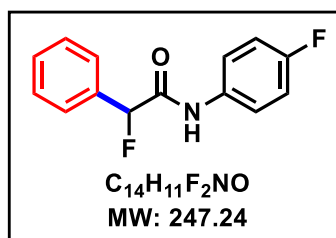


Following the general procedure, the treatment of *N*-(4-bromophenyl)-2-fluoro-3-oxobutanamide **1f** (55 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3f** as white solid (37 mg, 60%). *R_f*

(Ethyl acetate/Hexane: 20/80) = 0.50. **Mp** 160-162 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.6 (d, *J*_{C-F} = 20.8 Hz, C), 135.8 (C), 134.3 (d, *J*_{C-F} = 19.1 Hz, C), 132.3 (CH), 132.3 (CH), 129.8 (CH), 129.0 (CH), 129.0 (CH), 126.7 (d, *J*_{C-F} = 6.4 Hz, CH), 126.7 (d, *J*_{C-F} = 6.4 Hz, CH), 121.7 (CH), 121.7 (CH), 118.0 (C), 92.0 (d, *J*_{C-F} = 188.4 Hz, CH). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.19 (s,

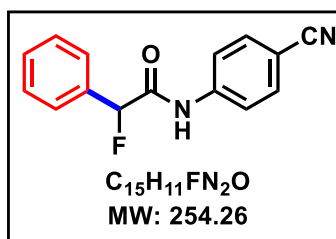
1H), 7.54-7.48 (m, 4H), 7.47-7.46 (m, 2H), 7.45-7.40 (m, 3H), 5.89 (d, $J = 48.4$ Hz, 1H). ^{19}F NMR (376 MHz, δ ppm/ CDCl_3): -175.8 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{12}\text{BrFNO}$ 308.0081; found 308.0084.

Compound 3g: 2-Fluoro-*N*-(4-fluorophenyl)-2-phenylacetamide



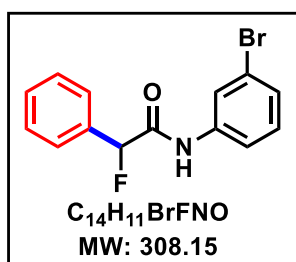
Following the general procedure, the treatment of 2-fluoro-*N*-(4-fluorophenyl)-3-oxobutanamide **1g** (43 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3g** as white solid (39 mg, 79%). R_f (Ethyl acetate/Hexane: 20/80) = 0.47. **Mp** 134-136 °C. ^{13}C NMR (100 MHz, δ ppm/ CDCl_3): 166.6 (d, $J_{\text{C-F}} = 16.5$ Hz, C), 160.0 (d, $J_{\text{C-F}} = 194.3$ Hz, C), 134.5 (d, $J_{\text{C-F}} = 14.9$ Hz, C), 132.8 (C), 129.8 (CH), 129.0 (CH), 129.0 (CH), 126.7 (d, $J_{\text{C-F}} = 5.2$ Hz, CH), 126.7 (d, $J_{\text{C-F}} = 5.2$ Hz, CH), 122.0 (d, $J_{\text{C-F}} = 6.4$ Hz, CH), 122.0 (d, $J_{\text{C-F}} = 6.4$ Hz, CH), 116.0 (d, $J_{\text{C-F}} = 18.0$ Hz, CH), 116.0 (d, $J_{\text{C-F}} = 18.0$ Hz, CH), 92.0 (d, $J_{\text{C-F}} = 150.4$ Hz, CH). ^1H NMR (400 MHz, δ ppm/ CDCl_3): 8.18 (s, 1H), 7.58-7.53 (m, 2H), 7.53-7.48 (m, 2H), 7.45-7.40 (m, 3H), 7.06-7.0 (m, 2H), 5.89 (d, $J = 48.4$ Hz, 1H). ^{19}F NMR (376 MHz, δ ppm/ CDCl_3): -116.9 (s), -175.8 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{12}\text{F}_2\text{NO}$ 248.0881; found 248.0883.

Compound 3h: *N*-(4-cyanophenyl)-2-fluoro-2-phenylacetamide



Following the general procedure, the treatment of *N*-(4-cyanophenyl)-2-fluoro-3-oxobutanamide **1h** (44 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3h** as white solid (34 mg, 67%). R_f (Ethyl acetate/Hexane: 20/80) = 0.50. **Mp** 175-177 °C. ^{13}C NMR (100 MHz, δ ppm/ CDCl_3): 169.0 (d, $J_{\text{C-F}} = 21.2$ Hz, C), 140.7 (C), 134.0 (d, $J_{\text{C-F}} = 19.2$ Hz, C), 133.5 (CH), 133.5 (CH), 130.0 (d, $J_{\text{C-F}} = 2.2$ Hz, CH), 129.0 (CH), 129.0 (CH), 126.6 (d, $J_{\text{C-F}} = 6.6$ Hz, CH), 126.6 (d, $J_{\text{C-F}} = 6.6$ Hz, CH), 120.1 (CH), 120.1 (CH), 118.7 (C), 108.3 (C), 92.0 (d, $J_{\text{C-F}} = 188.6$ Hz, CH). ^1H NMR (400 MHz, δ ppm/ CDCl_3): 8.38 (s, 1H), 7.76-7.72 (m, 2H), 7.65-7.61 (m, 2H), 7.51-7.48 (m, 2H), 7.45-7.41 (m, 3H), 5.92 (d, $J = 48.4$ Hz, 1H). ^{19}F NMR (376 MHz, δ ppm/ CDCl_3): -176.3 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{FN}_2\text{O}$ 255.0928; found 255.0936.

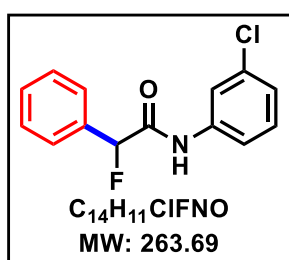
Compound 3i: *N*-(3-bromophenyl)-2-fluoro-2-phenylacetamide



Following the general procedure, the treatment of *N*-(3-bromophenyl)-2-fluoro-3-oxobutanamide **1i** (55 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3i** as white solid (45 mg, 73%). *R_f*(Ethyl acetate/Hexane:

10/90) = 0.40. **Mp** 77-79 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.7 (d, *J*_{C-F} = 20.8 Hz, C), 138.0 (C), 134.3 (d, *J*_{C-F} = 19.1 Hz, C), 130.5 (CH), 129.9 (CH), 129.0 (CH), 129.0 (CH), 128.3 (CH), 126.7 (d, *J*_{C-F} = 6.5 Hz, CH), 126.7 (d, *J*_{C-F} = 6.5 Hz, CH), 123.1 (CH), 123.0 (C), 118.6 (CH), 92.0 (d, *J*_{C-F} = 188.4 Hz, CH). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.10 (s, 1H), 7.87 (t, *J* = 2.0 Hz, 1H), 7.53-7.47 (m, 3H), 7.46-7.41 (m, 3H), 7.31-7.28 (m, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 5.90 (d, *J* = 48.4 Hz, 1H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -176.2 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₄H₁₂BrFNO 308.0081; found 308.0084.

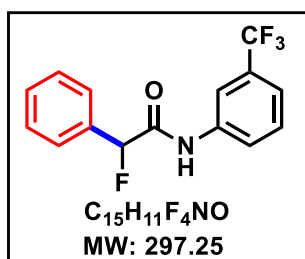
Compound 3j: *N*-(3-chlorophenyl)-2-fluoro-2-phenylacetamide



Following the general procedure, the treatment of *N*-(3-chlorophenyl)-2-fluoro-3-oxobutanamide **1j** (46 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded product **3j** as white solid (34 mg, 65%). *R_f*(Ethyl acetate/Hexane: 10/90) =

0.37. **Mp** 74-76 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.7 (d, *J*_{C-F} = 20.9 Hz, C), 137.9 (C), 135.0 (C), 134.3 (d, *J*_{C-F} = 19.2 Hz, C), 130.2 (CH), 129.8 (d, *J*_{C-F} = 2.3 Hz, CH), 129.0 (CH), 129.0 (CH), 126.7 (d, *J*_{C-F} = 6.6 Hz, CH), 126.7 (d, *J*_{C-F} = 6.6 Hz, CH), 125.3 (CH), 120.3 (CH), 118.1 (CH), 92.0 (d, *J*_{C-F} = 188.4 Hz, CH). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.21 (s, 1H), 7.73 (t, *J* = 2.0 Hz, 1H), 7.51-7.48 (m, 2H), 7.45-7.40 (m, 4H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.15-7.12 (m, 1H), 5.89 (d, *J* = 48.4 Hz, 1H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -175.9 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₄H₁₂ClFNO 264.0586; found 264.0586.

Compound 3k: 2-Fluoro-2-phenyl-*N*-(3-(trifluoromethyl)phenyl)acetamide

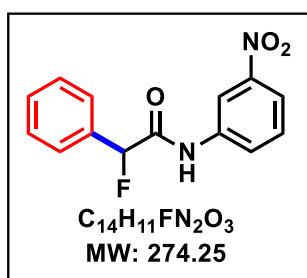


Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-(3-(trifluoromethyl)phenyl)butanamide **1k** (53 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3k** as yellow liquid (36 mg, 60%). *R_f* (Ethyl

acetate/Hexane: 10/90) = 0.45. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 167.0 (d, *J*_{C-F} = 16.8 Hz, C), 137.3 (C), 134.2 (d, *J*_{C-F} = 15.2 Hz, C), 131.7 (q, *J*_{C-F} = 25.7 Hz, C), 129.9 (CH), 129.8 (CH), 129.0 (CH), 129.0 (CH), 126.7 (d, *J*_{C-F} = 5.2 Hz, CH), 126.7 (d, *J*_{C-F} = 5.2 Hz, CH), 123.8 (q, *J*_{C-F} = 216.8

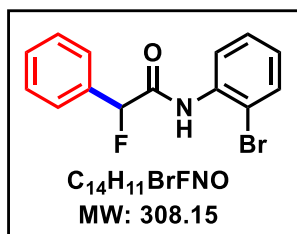
Hz, C), 123.2 (CH), 121.8 (q, J_{C-F} = 2.9 Hz, CH), 117.0 (d, J_{C-F} = 2.8 Hz, CH), 92.0 (d, J_{C-F} = 150.5 Hz, CH). $^1\text{H NMR}$ (400 MHz, δ ppm/ CDCl_3): 8.27 (s, 1H), 7.90 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.49-7.40 (m, 5H), 5.92 (d, J = 48.0 Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/ CDCl_3): -62.8 (s), -176.6 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{F}_4\text{NO}$ 298.0850; found 298.0851.

Compound 3l: 2-Fluoro-*N*-(3-nitrophenyl)-2-phenylacetamide



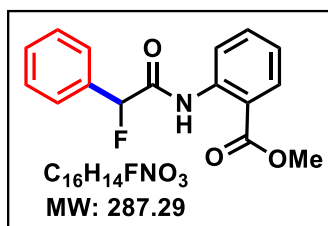
Following the general procedure, the treatment of 2-fluoro-*N*-(3-nitrophenyl)-3-oxobutanamide **1l** (48 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3l** as white solid (35 mg, 63%). R_f (Ethyl acetate/Hexane: 20/80) = 0.32. **Mp** 117-119 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/ CDCl_3): 167.1 (d, J_{C-F} = 21.3 Hz, C), 148.7 (C), 137.9 (C), 134.0 (d, J_{C-F} = 19.2 Hz, C), 130.1 (CH), 130.0 (d, J_{C-F} = 2.3 Hz, CH), 129.0 (CH), 129.0 (CH), 126.6 (d, J_{C-F} = 6.6 Hz, CH), 126.6 (d, J_{C-F} = 6.6 Hz, CH), 125.8 (CH), 119.8 (CH), 115.1 (CH), 92.0 (d, J_{C-F} = 188.5 Hz, CH). $^1\text{H NMR}$ (400 MHz, δ ppm/ CDCl_3): 8.50 (s, 1H), 8.38 (s, 1H), 8.14-7.95 (m, 2H), 7.67-7.40 (m, 6H), 5.94 (d, J = 48.4 Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/ CDCl_3): -176.8 (s). **HRMS** (ESI) m/z : $[\text{M}-\text{H}]^-$ Calcd for $\text{C}_{14}\text{H}_{10}\text{FN}_2\text{O}_3$ 273.0681; found 273.0675

Compound 3m: *N*-(2-bromophenyl)-2-fluoro-2-phenylacetamide



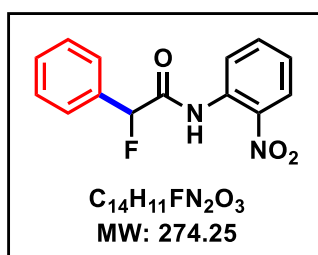
Following the general procedure, the treatment of *N*-(2-bromophenyl)-2-fluoro-3-oxobutanamide **1m** (55 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3m** as yellow solid (36 mg, 58%). R_f (Ethyl acetate/Hexane: 5/95) = 0.37. **Mp** 66-68 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/ CDCl_3): 166.7 (d, J_{C-F} = 21.1 Hz, C), 134.8 (C), 134.5 (d, J_{C-F} = 19.3 Hz, C), 132.6 (CH), 129.8 (CH), 129.0 (CH), 129.0 (CH), 128.6 (CH), 126.8 (d, J_{C-F} = 6.5 Hz, CH), 126.8 (d, J_{C-F} = 6.5 Hz, CH), 126.1 (CH), 122.0 (CH), 114.0 (C), 92.1 (d, J_{C-F} = 189.0 Hz, CH). $^1\text{H NMR}$ (400 MHz, δ ppm/ CDCl_3): 8.78 (s, 1H), 8.36 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.59-7.53 (m, 3H), 7.46-7.40 (m, 3H), 7.32 (t, J = 7.2 Hz, 1H), 7.03 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 5.92 (d, J = 48.0 Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/ CDCl_3): -176.3 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{12}\text{BrFNO}$ 308.0081; found 308.0070.

Compound 3n: Methyl 2-(2-fluoro-2-phenylacetamido)benzoate



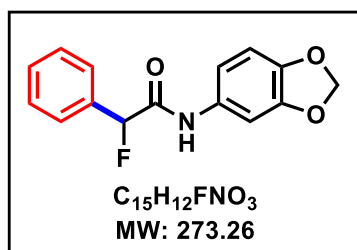
Following the general procedure, the treatment of methyl 2-(2-fluoro-3-oxobutanamido)benzoate **1n** (51 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3n** as brown solid (38 mg, 67%). R_f (Ethyl acetate/Hexane: 10/90) = 0.40. **Mp** 83-85 °C. ^{13}C NMR (100 MHz, δ ppm/ $CDCl_3$): 168.5 (C), 167.6 (d, J_{C-F} = 21.3 Hz, C), 140.4 (C), 134.9 (d, J_{C-F} = 19.6 Hz, C), 134.8 (CH), 131.1 (CH), 129.5 (d, J_{C-F} = 2.1 Hz, CH), 128.8 (CH), 128.8 (CH), 126.6 (d, J_{C-F} = 6.7 Hz, CH), 126.6 (d, J_{C-F} = 6.7 Hz, CH), 123.5 (CH), 120.6 (CH), 116.0 (C), 92.0 (d, J_{C-F} = 190.2 Hz, CH), 52.7 (CH_3). 1H NMR (400 MHz, δ ppm/ $CDCl_3$): 12.05 (s, 1H), 8.72 (dd, J = 8.4 Hz, 0.8 Hz, 1H), 8.07 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.58-7.52 (m, 3H), 7.44-7.37 (m, 3H), 7.16-7.12 (m, 1H), 5.90 (d, J = 48.0 Hz, 1H), 3.98 (s, 3H). ^{19}F NMR (376 MHz, δ ppm/ $CDCl_3$): -178.1 (s). HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{16}H_{15}FNO_3$ 288.1030; found 288.1022.

Compound 3o: 2-Fluoro-N-(2-nitrophenyl)-2-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-N-(2-nitrophenyl)-3-oxobutanamide **1o** (48 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3o** as white solid (40 mg, 71%). R_f (Ethyl acetate/Hexane: 10/90) = 0.35. **Mp** 93-95 °C. ^{13}C NMR (100 MHz, δ ppm/ $CDCl_3$): 167.8 (d, J_{C-F} = 21.7 Hz, C), 137.0 (C), 136.1 (CH), 134.3 (d, J_{C-F} = 19.7 Hz, C), 133.8 (C), 129.9 (d, J_{C-F} = 2.0 Hz, CH), 129.0 (CH), 129.0 (CH), 126.5 (d, J_{C-F} = 6.8 Hz, CH), 126.5 (d, J_{C-F} = 6.8 Hz, CH), 126.1 (CH), 124.3 (CH), 122.3 (CH), 91.9 (d, J_{C-F} = 190.4 Hz, CH). 1H NMR (400 MHz, δ ppm/ $CDCl_3$): 11.34 (s, 1H), 8.78 (dd, J = 8.8 Hz, 1.2 Hz, 1H), 8.27 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.69-7.64 (m, 1H), 7.56-7.53 (m, 2H), 7.46-7.41 (m, 3H), 7.27-7.23 (m, 1H), 5.93 (d, J = 48.0 Hz, 1H). ^{19}F NMR (376 MHz, δ ppm/ $CDCl_3$): -178.8 (s). HRMS (ESI) m/z : $[M-H]^-$ Calcd for $C_{14}H_{10}FN_2O_3$ 273.0681; found 273.0677.

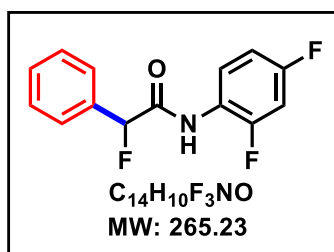
Compound 3p: N-(benzo[d][1,3]dioxol-5-yl)-2-fluoro-2-phenylacetamide



Following the general procedure, the treatment of N-(benzo[d][1,3]dioxol-5-yl)-2-fluoro-3-oxobutanamide **1p** (48 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3p** as grey solid (35 mg, 64%). R_f (Ethyl acetate/Hexane: 20/80) = 0.40. **Mp** 104-106 °C. ^{13}C NMR

(100 MHz, δ ppm/ CDCl_3): 166.4 (d, $J_{\text{C-F}} = 20.8$ Hz, C), 148.0 (C), 144.9 (C), 134.6 (d, $J_{\text{C-F}} = 19.1$ Hz, C), 130.9 (C), 129.7 (CH), 128.9 (CH), 128.9 (CH), 126.8 (d, $J_{\text{C-F}} = 6.4$ Hz, CH), 126.8 (d, $J_{\text{C-F}} = 6.4$ Hz, CH), 113.5 (CH), 108.3 (CH), 102.9 (CH), 101.5 (CH_2), 91.9 (d, $J_{\text{C-F}} = 188.2$ Hz, CH). **^1H NMR** (400 MHz, δ ppm/ CDCl_3): 8.10 (s, 1H), 7.52-7.48 (m, 2H), 7.45-7.41 (m, 3H), 7.29 (d, $J = 2.0$ Hz, 1H), 6.88 (dd, $J = 8.4$ Hz, 2.0 Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 5.95 (s, 2H), 5.87 (d, $J = 48.8$ Hz, 1H). **^{19}F NMR** (376 MHz, δ ppm/ CDCl_3): -175.5 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{FNO}_3$ 274.0874; found 274.0868.

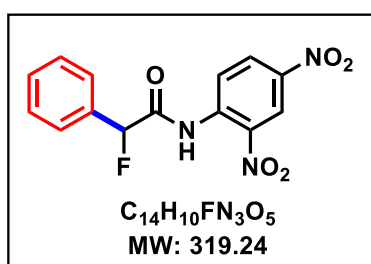
Compound 3q: *N*-(2,4-difluorophenyl)-2-fluoro-2-phenylacetamide



Following the general procedure, the treatment of *N*-(2,4-difluorophenyl)-2-fluoro-3-oxobutanamide **1q** (46 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3q** as yellow solid (33 mg, 63%).

R_f (Ethyl acetate/Hexane: 15/85) = 0.50. **Mp** 77-79 °C. **^{13}C NMR** (100 MHz, δ ppm/ CDCl_3): 166.7 (d, $J_{\text{C-F}} = 17.0$ Hz, C), 159.2 (dd, $J_{\text{C-F}} = 196.4$ Hz, 9.1 Hz, C), 153.0 (dd, $J_{\text{C-F}} = 196.4$ Hz, 9.4 Hz, C), 134.3 (d, $J_{\text{C-F}} = 15.3$ Hz, C), 129.8 (d, $J_{\text{C-F}} = 1.7$ Hz, CH), 129.0 (CH), 129.0 (CH), 126.7 (d, $J_{\text{C-F}} = 5.3$ Hz, CH), 126.7 (d, $J_{\text{C-F}} = 5.3$ Hz, CH), 123.1 (dd, $J_{\text{C-F}} = 7.2$ Hz, 1.0 Hz, CH), 121.6 (dd, $J_{\text{C-F}} = 7.9$ Hz, 2.9 Hz, C), 111.5 (dd, $J_{\text{C-F}} = 17.4$ Hz, 3.0 Hz, CH), 103.9 (dd, $J_{\text{C-F}} = 21.3$ Hz, 18.4 Hz, CH), 92.0 (d, $J_{\text{C-F}} = 150.6$ Hz, CH). **^1H NMR** (400 MHz, δ ppm/ CDCl_3): 8.32 (s, 1H), 8.29-8.23 (m, 1H), 7.54-7.50 (m, 2H), 7.47-7.41 (m, 3H), 6.94-6.85 (m, 2H), 5.92 (d, $J = 48.4$ Hz, 1H). **^{19}F NMR** (376 MHz, δ ppm/ CDCl_3): -113.7 (d, $J_{\text{F-F}} = 4.9$ Hz), -125.6 (d, $J_{\text{F-F}} = 5.3$ Hz), -176.5 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NO}$ 266.0787; found 266.0777.

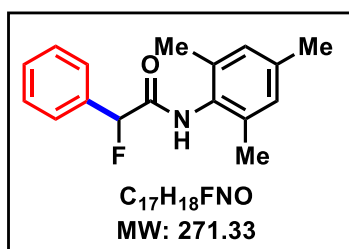
Compound 3r: *N*-(2,4-dinitrophenyl)-2-fluoro-2-phenylacetamide



Following the general procedure, the treatment of *N*-(2,4-dinitrophenyl)-2-fluoro-3-oxobutanamide **1r** (57 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3r** as yellow

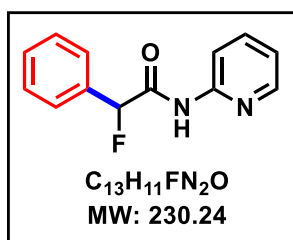
solid (31 mg, 49%). R_f (Ethyl acetate/Hexane: 15/85) = 0.47. **Mp** 111-113 °C. **^{13}C NMR** (100 MHz, δ ppm/ CDCl_3): 168.3 (d, $J_{\text{C-F}} = 22.1$ Hz, C), 142.6 (C), 138.7 (C), 135.9 (C), 133.5 (d, $J_{\text{C-F}} = 19.8$ Hz, C), 130.3 (CH), 130.2 (d, $J_{\text{C-F}} = 1.9$ Hz, CH), 129.2 (CH), 129.2 (CH), 126.3 (d, $J_{\text{C-F}} = 7.0$ Hz, CH), 126.3 (d, $J_{\text{C-F}} = 7.0$ Hz, CH), 122.6 (CH), 122.2 (CH), 91.8 (d, $J_{\text{C-F}} = 190.6$ Hz, CH). **^1H NMR** (400 MHz, δ ppm/ CDCl_3): 11.62 (s, 1H), 9.17 (d, $J = 2.8$ Hz, 1H), 9.09 (d, $J = 9.6$ Hz, 1H), 8.49 (dd, $J = 9.6$ Hz, 2.8 Hz, 1H), 7.54-7.52 (m, 2H), 7.49-7.44 (m, 3H), 5.99 (d, $J = 48.0$ Hz, 1H). **^{19}F NMR** (376 MHz, δ ppm/ CDCl_3): -179.9 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{FN}_3\text{O}_5$ 320.0677; found 320.0679.

Compound 3s: 2-Fluoro-*N*-mesityl-2-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-*N*-mesityl-3-oxobutanamide **1s** (47 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3s** as white solid (36 mg, 66%). R_f (Ethyl acetate/Hexane: 20/80) = 0.45. **Mp** 128-130 °C. ^{13}C NMR (100 MHz, δ ppm/ $CDCl_3$): 167.1 (d, J_{C-F} = 21.4 Hz, C), 137.4 (C), 135.2 (C), 135.2 (C), 135.0 (d, J_{C-F} = 19.2 Hz, C), 129.7 (C), 129.5 (d, J_{C-F} = 2.2 Hz, CH), 129.1 (CH), 129.1 (CH), 128.8 (CH), 128.8 (CH), 126.5 (d, J_{C-F} = 6.6 Hz, CH), 126.5 (d, J_{C-F} = 6.6 Hz, CH), 93.5 (d, J_{C-F} = 187.0 Hz, CH), 21.0 (CH₃), 18.3 (CH₃), 18.3 (CH₃). 1H NMR (400 MHz, δ ppm/ $CDCl_3$): 7.71 (s, 1H), 7.58-7.55 (m, 2H), 7.46-7.41 (m, 3H), 6.90 (s, 2H), 5.96 (d, J = 48.4 Hz, 1H), 2.28 (s, 3H), 2.14 (s, 6H). ^{19}F NMR (376 MHz, δ ppm/ $CDCl_3$): -176.8 (s). **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for $C_{17}H_{19}FNO$ 272.1445; found: 272.1440.

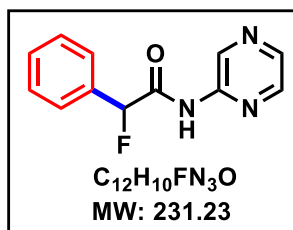
Compound 3t: 2-Fluoro-2-phenyl-*N*-(pyridin-2-yl)acetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-(pyridin-2-yl)butanamide **1t** (39 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3t** as brown solid (25 mg, 54%). R_f (Ethyl acetate/Hexane: 10/90) = 0.22.

Mp 104-106 °C. ^{13}C NMR (100 MHz, δ ppm/ $CDCl_3$): 167.2 (d, J_{C-F} = 21.8 Hz, C), 150.4 (C), 148.1 (CH), 138.6 (CH), 134.4 (d, J_{C-F} = 19.4 Hz, C), 129.7 (d, J_{C-F} = 2.2 Hz, CH), 128.9 (CH), 128.9 (CH), 126.6 (d, J_{C-F} = 6.6 Hz, CH), 126.6 (d, J_{C-F} = 6.6 Hz, CH), 120.7 (CH), 114.3 (CH), 91.7 (d, J_{C-F} = 189.3 Hz, CH). 1H NMR (400 MHz, δ ppm/ $CDCl_3$): 8.9 (s, 1H), 8.32 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.73-7.68 (m, 1H), 7.53-7.50 (m, 2H), 7.40-7.39 (m, 3H), 7.10-7.06 (m, 1H), 5.90 (d, J = 48.0 Hz, 1H). ^{19}F NMR (376 MHz, δ ppm/ $CDCl_3$): -177.4 (s). **HRMS** (ESI) m/z : $[M+H]^+$ Calcd for $C_{13}H_{12}FN_2O$ 231.0928; found 231.0925.

Compound 3u: 2-Fluoro-2-phenyl-*N*-(pyrazin-2-yl)acetamide

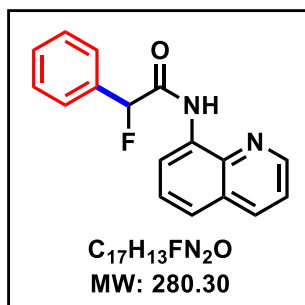


Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-(pyrazin-2-yl)butanamide **1u** (39 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3u** as yellow solid (21 mg, 46%). R_f (Ethyl acetate/Hexane: 30/70) =

0.32. **Mp** 116-118 °C. ^{13}C NMR (100 MHz, δ ppm/ $CDCl_3$): 167.2 (d, J_{C-F} = 22.2 Hz, C), 147.2 (C), 142.4 (CH), 141.2 (CH), 137.2 (CH), 134.0 (d, J_{C-F} = 19.4 Hz, C), 130.0 (d, J_{C-F} = 2.1 Hz, CH), 129.0 (CH), 129.0 (CH), 126.6 (d, J_{C-F} = 6.7 Hz, CH), 126.6 (d, J_{C-F} = 6.7 Hz, CH), 91.7 (d, J_{C-F} = 189.3 Hz,

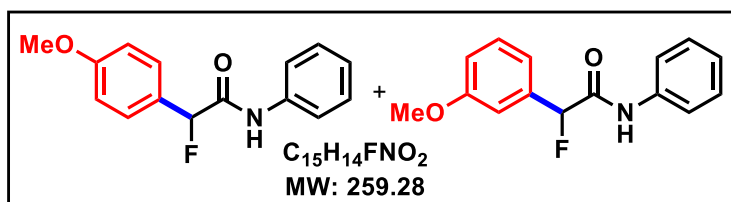
CH). $^1\text{H NMR}$ (400 MHz, δ ppm/ CDCl_3): 9.55 (s, 1H), 8.84 (s, 1H), 8.40 (d, $J = 2.0$ Hz, 1H), 8.30 (s, 1H), 7.52-7.49 (m, 2H), 7.45-7.41 (m, 3H), 5.95 (d, $J = 48.0$ Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/ CDCl_3): -177.5 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{11}\text{FN}_3\text{O}$ 232.0881; found 232.0881.

Compound 3v: 2-Fluoro-2-phenyl-*N*-(quinolin-8-yl)acetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-(quinolin-8-yl)butanamide **1v** (49 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (90 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3v** as white solid (32 mg, 58%). R_f (Ethyl acetate/Hexane: 10/90) = 0.35. **Mp** 91-33 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/ CDCl_3): 167.0 (d, $J_{\text{C-F}} = 17.0$ Hz, C), 148.8 (CH), 138.9 (C), 136.4 (CH), 135.1 (d, $J_{\text{C-F}} = 15.5$ Hz, C), 133.6 (C), 129.6 (CH), 128.9 (CH), 128.9 (CH), 128.1 (C), 127.2 (CH), 126.8 (d, $J_{\text{C-F}} = 5.1$ Hz, CH), 126.8 (d, $J_{\text{C-F}} = 5.1$ Hz, CH), 122.6 (CH), 122.0 (CH), 117.0 (CH), 92.2 (d, $J_{\text{C-F}} = 151.3$ Hz, CH). $^1\text{H NMR}$ (400 MHz, δ ppm/ CDCl_3): 10.88 (s, 1H), 8.88 (dd, $J = 4.4$ Hz, 1.6 Hz, 1H), 8.80 (dd, $J = 6.8$ Hz, 2.4 Hz, 1H), 8.16 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.65-7.60 (m, 2H), 7.57-7.51 (m, 2H), 7.49-7.46 (m, 1H), 7.45-7.38 (m, 3H), 6.01 (d, $J = 48.4$ Hz, 1H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/ CDCl_3): -176.4 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{14}\text{FN}_2\text{O}$ 281.1085; found 281.1080.

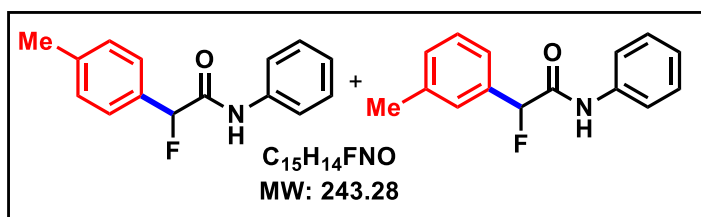
Compound 3w and 3w': 2-Fluoro-2-(4-methoxyphenyl)-*N*-phenylacetamide and 2-fluoro-2-(3-methoxyphenyl)-*N*-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2b** (98 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3w** and **3w'** as a 1:1 mixture of regioisomers as white solid (32 mg, 61%). Compound **3w**: R_f (Ethyl acetate/Hexane: 20/80) = 0.40. **Mp** 75-77 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/ CDCl_3): 166.4 (d, $J_{\text{C-F}} = 20.4$ Hz, C), 160.0 (C), 136.7 (C), 136.0 (d, $J_{\text{C-F}} = 19.2$ Hz, C), 130.0 (CH), 129.3 (CH), 129.3 (CH), 125.2 (CH), 120.2 (CH), 120.2 (CH), 118.9 (d, $J_{\text{C-F}} = 6.8$ Hz, CH), 115.4 (d, $J_{\text{C-F}} = 1.8$ Hz, CH), 112.3 (d, $J_{\text{C-F}} = 7.0$ Hz, CH), 91.9 (d, $J_{\text{C-F}} = 189.1$ Hz, CH), 55.5 (CH_3). $^1\text{H NMR}$ (400 MHz, δ ppm/ CDCl_3): 8.14 (s, 1H), 7.61-7.59 (m, 1H), 7.58-7.56 (m, 1H), 7.37-7.31 (m, 3H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.05 (s, 1H), 6.95-6.93 (m, 1H), 5.86 (d, $J = 48.4$ Hz, 1H), 3.82 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/ CDCl_3): -176.2 (s). **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{FNO}_2$ 260.1081; found 260.1085. Compound **3w'**: R_f (Ethyl acetate/Hexane: 20/80) = 0.37. **Mp** 94-96 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/ CDCl_3): 166.8 (d, $J_{\text{C-F}} = 21.3$ Hz, C), 160.8 (d, $J_{\text{C-F}} = 2.6$ Hz, C), 136.8 (C), 129.3 (CH), 129.3 (CH), 128.8 (d, $J_{\text{C-F}} = 5.4$ Hz, CH), 128.8 (d, $J_{\text{C-F}} = 5.4$

Hz, CH), 126.7 (d, J_{C-F} = 19.6 Hz, C), 125.2 (CH), 120.1 (CH), 120.1 (CH), 114.4 (CH), 114.4 (CH), 92.0 (d, J_{C-F} = 187.0 Hz, CH), 55.5 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 8.19 (s, 1H), 7.62-7.59 (m, 2H), 7.45-7.41 (m, 2H), 7.38-7.34 (m, 2H), 7.19-7.14 (m, 1H), 6.95-6.91 (m, 2H), 5.84 (d, J = 49.2 Hz, 1H), 3.82 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -169.4 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₅H₁₅FNO₂ 260.1081; found 260.1086.

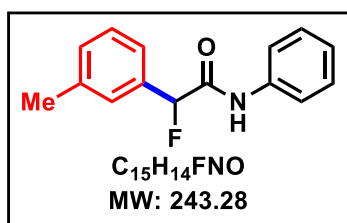
Compound 3x and 3x': 2-Fluoro-*N*-phenyl-2-(*p*-tolyl)acetamide and 2-fluoro-*N*-phenyl-2-(*m*-tolyl)acetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesul-

fonate **2c** (94 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3x** and **3x'** as a 1:1 mixture of regioisomers as white solid (33 mg, 68%). Compound **3x**: R_f (Ethyl acetate/Hexane: 20/80) = 0.50. **Mp** 74-76 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 166.7 (d, J_{C-F} = 20.4 Hz, C), 139.8 (C), 136.8 (C), 134.5 (d, J_{C-F} = 19.1 Hz, C), 129.6 (CH), 129.6 (CH), 129.2 (CH), 129.2 (CH), 128.8 (CH), 128.8 (CH), 125.1 (CH), 120.1 (CH), 120.1 (CH), 92.1 (d, J_{C-F} = 188.2 Hz, CH), 21.5 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 8.20 (s, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 7.41-7.30 (m, 5H), 7.23 (d, 6.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 5.86 (d, J = 48.8 Hz, 1H), 2.38 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -174.5 (s). Compound **3x'**: **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 166.6 (d, J_{C-F} = 20.6 Hz, C), 138.7 (C), 136.8 (C), 134.5 (d, J_{C-F} = 19.1 Hz, C), 130.5 (CH), 129.2 (CH), 129.2 (CH), 127.5 (d, 6.2 Hz, CH), 127.0 (d, 6.0 Hz, CH), 125.1 (CH), 123.9 (d, 6.4 Hz, CH), 120.1 (CH), 120.1 (CH), 92.0 (d, J_{C-F} = 187.8 Hz, CH), 21.4 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 8.2 (s, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 7.41-7.30 (m, 5H), 7.23 (d, 6.8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 5.86 (d, J = 48.8 Hz, 1H), 2.38 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -172.9 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₅H₁₅FNO 244.1132; found 244.1134

Compound 3y: 2-Fluoro-*N*-phenyl-2-(*m*-tolyl)acetamide

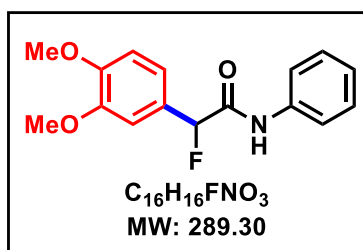


Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 3-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d** (94 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3y** as white solid (34 mg, 70%). R_f

(Ethyl acetate/Hexane: 20/80) = 0.50. **Mp** 102-104 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 166.6 (d, J_{C-F} = 20.7 Hz, C), 138.7 (C), 136.8 (C), 134.5 (d, J_{C-F} = 18.8 Hz, C), 130.5 (d, J_{C-F} = 2.4 Hz, CH), 129.4 (CH), 129.4 (CH), 128.8 (CH), 127.5 (d, J_{C-F} = 6.3 Hz, CH), 125.1 (CH), 123.9 (d, J_{C-F} = 6.5 Hz, CH), 120.1 (CH), 120.1 (CH), 92.1 (d, J_{C-F} = 188.0 Hz, CH), 21.5 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 8.21 (s, 1H), 7.62 (s, 1H), 7.60 (s, 1H), 7.38-7.31 (m, 5H), 7.24-7.21 (m,

1H), 7.17 (t, $J = 7.6$ Hz, 1H), 5.86 (d, $J = 48.4$ Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, δ ppm/ CDCl_3): -174.5 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{FNO}$ 244.1132; found 244.1135.

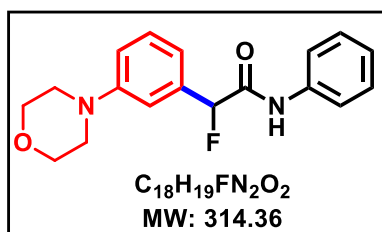
Compound 3z: 2-(3,4-Dimethoxyphenyl)-2-fluoro-*N*-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2e** (107 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3z** as white solid (35 mg, 61%).

R_f (Ethyl acetate/Hexane: 20/80) = 0.22. **Mp** 115-117 °C. ^{13}C NMR (100 MHz, δ ppm/ CDCl_3): 166.7 (d, $J_{\text{C-F}} = 21.4$ Hz, C), 150.3 (d, $J_{\text{C-F}} = 2.6$ Hz, C), 149.3 (C), 136.8 (C), 129.2 (CH), 129.2 (CH), 127.0 (d, $J_{\text{C-F}} = 19.6$ Hz, C), 125.1 (CH), 120.1 (CH), 120.1 (CH), 120.0 (d, $J_{\text{C-F}} = 6.8$ Hz, CH), 111.3 (CH), 110.1 (d, $J_{\text{C-F}} = 5.5$ Hz, CH), 92.0 (d, $J_{\text{C-F}} = 187.7$ Hz, CH), 56.0 (CH_3), 56.0 (CH_3). ^1H NMR (400 MHz, δ ppm/ CDCl_3): 8.20 (s, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 7.35 (t, $J = 8.0$ Hz, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 7.0 (s, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 5.83 (d, $J = 48.4$ Hz, 1H), 3.88 (s, 6H). ^{19}F NMR (376 MHz, δ ppm/ CDCl_3): -171.0 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{FNO}_3$ 290.1187; found 290.1180.

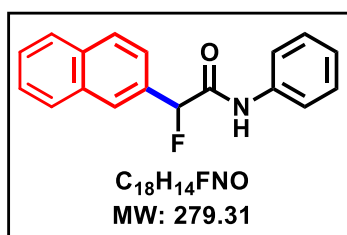
Compound 3aa: 2-fluoro-2-(3-morpholinophenyl)-*N*-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 3-morpholino-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2f** (115 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH_3CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3aa** as white solid (34 mg, 54%).

R_f (Ethyl acetate/Hexane: 20/80) = 0.20. **Mp** 138-140 °C. ^{13}C NMR (100 MHz, δ ppm/ CDCl_3): 166.6 (d, $J_{\text{C-F}} = 20.6$ Hz, C), 151.7 (C), 136.8 (C), 135.6 (d, $J_{\text{C-F}} = 19.1$ Hz, C), 129.8 (CH), 129.3 (CH), 129.3 (CH), 125.2 (CH), 120.1 (CH), 120.1 (CH), 117.8 (d, $J_{\text{C-F}} = 7.0$ Hz, CH), 116.8 (d, $J_{\text{C-F}} = 2.2$ Hz, C), 113.8 (d, $J_{\text{C-F}} = 6.9$ Hz, CH), 92.2 (d, $J_{\text{C-F}} = 188.8$ Hz, CH), 67.0 (CH_2), 67.0 (CH_2), 49.2 (CH_2), 49.2 (CH_2). ^1H NMR (400 MHz, δ ppm/ CDCl_3): 8.13 (s, 1H), 7.60 (d, $J = 7.6$ Hz, 2H), 7.40-7.30 (m, 3H), 7.16 (t, $J = 7.2$ Hz, 1H), 7.05-7.0 (m, 2H), 6.96-6.91 (m, 1H), 5.85 (d, $J = 48.4$ Hz, 1H), 3.85 (t, $J = 4.4$ Hz, 4H), 3.18 (t, $J = 3.6$ Hz, 4H). ^{19}F NMR (376 MHz, δ ppm/ CDCl_3): -176.2 (s). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{FN}_2\text{O}_2$ 315.1503; found 315.1501.

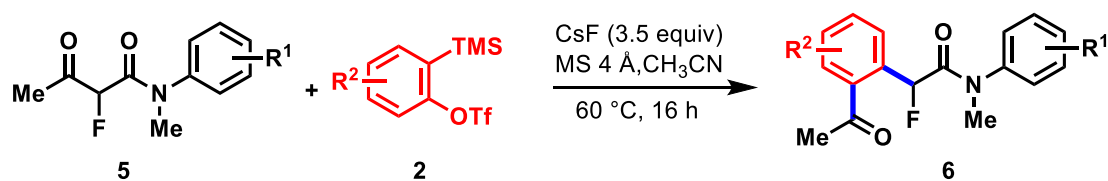
Compound 3ab: 2-fluoro-2-(naphthalen-2-yl)-*N*-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-3-oxo-*N*-phenylbutanamide **1a** (39 mg, 0.20 mmol) with 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **2g** (104 mg, 0.30 mmol) in the presence of TBAF (0.60 mL, 0.60 mmol) in CH₃CN (2 mL) at 25 °C for 4 h followed by column chromatography afforded the product **3ab** as white solid (37 mg, 67% yield). *R_f*(Ethyl acetate/Hexane: 20/80) = 0.40.

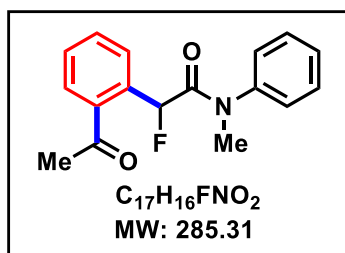
Mp 143-145 °C. ¹³C NMR (100 MHz, δ ppm/CDCl₃): 166.5 (d, *J*_{C-F} = 20.7 Hz, C), 136.8 (C), 133.8 (d, *J*_{C-F} = 1.8 Hz, C), 133.1 (C), 131.8 (d, *J*_{C-F} = 18.9 Hz, C), 129.3 (CH), 129.3 (CH), 128.9 (CH), 128.5 (CH), 127.9 (CH), 127.1 (CH), 126.8 (d, *J*_{C-F} = 8.0 Hz, CH), 126.8 (CH), 125.2 (CH), 123.6 (d, *J*_{C-F} = 5.4 Hz, CH), 120.2 (CH), 120.2 (CH), 92.2 (d, *J*_{C-F} = 188.5 Hz, CH). ¹H NMR (400 MHz, δ ppm/CDCl₃): 8.26 (s, 1H), 8.0 (s, 1H), 7.91-7.83 (m, 3H), 7.65 (m, 3H), 7.55-7.50 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.07 (d, *J* = 48.4 Hz, 1H). ¹⁹F NMR (376 MHz, δ ppm/CDCl₃): -174.9 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₈H₁₅FNO 280.1132; found 280.1142.

General procedure for the insertion reaction of *N*-methyl- α -fluoro- β -ketoamides **5**



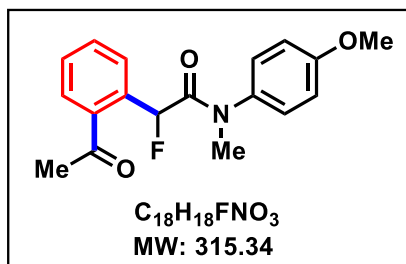
An oven-dried round bottom flask charged with 2-fluoro-*N*-methyl-3-oxo-*N*-phenylbutanamide **5** (0.20 mmol) and MS 4 Å (100 mg) was sealed, evacuated, and backfilled with nitrogen. Subsequently, freshly distilled CH₃CN (2.0 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2** (0.50 mmol), and CsF (0.70 mmol) were added, and the reaction mixture was stirred at 60 °C for 16 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated, and the crude reaction mixture was extracted using ethyl acetate (3 × 15 mL) and water (15 mL). The organic layer was washed with brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent to afford the product **6**.

Compound 6a: 2-(2-Acetylphenyl)-2-fluoro-N-methyl-N-phenylacetamide



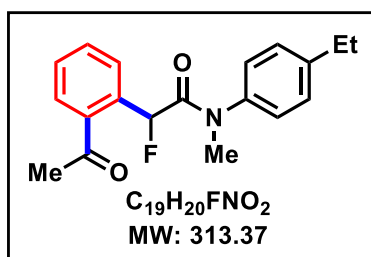
Following the general procedure, the treatment of 2-fluoro-N-methyl-3-oxo-N-phenylbutanamide **5a** (42 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6a** as white solid (41 mg, 72%). **R_f** (Ethyl acetate/Hexane: 30/70) = 0.27. **Mp** 117-119 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 200.0 (C), 167.0 (d, *J*_{C-F} = 21.6 Hz, C), 143.1 (C), 137.3 (d, *J*_{C-F} = 19.0 Hz, C), 134.5 (C), 133.0 (CH), 130.3 (CH), 129.5 (CH), 129.5 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 126.8 (d, *J*_{C-F} = 18.1 Hz, CH), 87.5 (d, *J*_{C-F} = 173.1 Hz, CH), 37.8 (CH₃), 28.0 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.85 (d, *J* = 7.6 Hz, 1H), 7.76 (d, 7.6 Hz, 1H), 7.62-7.57 (m, 3H), 7.48-7.42 (m, 3H), 7.39-7.35 (m, 1H), 6.33 (d, *J* = 47.6 Hz, 1H), 3.34 (s, 3H), 2.55 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -179.9 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₇H₁₇FNO₂ 286.1238; found 286.1239.

Compound 6b: 2-(2-Acetylphenyl)-2-fluoro-N-(4-methoxyphenyl)-N-methylacetamide



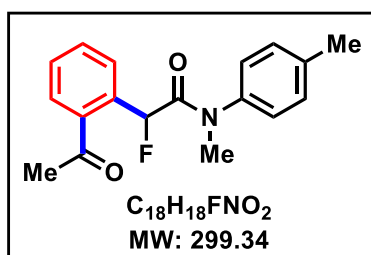
Following the general procedure, the treatment of 2-fluoro-N-(4-methoxyphenyl)-N-methyl-3-oxobutanamide **5b** (48 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6b** as white solid (38 mg, 60%). **R_f**(Ethyl acetate/Hexane: 30/70) = 0.22. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 200.0 (C), 167.3 (d, *J*_{C-F} = 21.4 Hz, C), 159.2 (C), 137.4 (d, *J*_{C-F} = 19.0 Hz, C), 135.8 (C), 134.6 (d, *J*_{C-F} = 2.9 Hz, C), 132.9 (d, *J*_{C-F} = 2.1 Hz, CH), 130.2 (CH), 129.4 (CH), 129.4 (CH), 128.0 (CH), 126.8 (d, *J*_{C-F} = 18.0 Hz, CH), 114.6 (CH), 114.6 (CH), 87.6 (d, *J*_{C-F} = 172.9 Hz, CH), 55.5 (CH₃), 38.0 (CH₃), 28.1 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.83 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 6.32 (d, *J* = 47.6 Hz, 1H), 3.82 (s, 3H), 3.29 (d, *J* = 2.0 Hz, 3H), 2.53 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -180.0 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₈H₁₉FNO₃ 316.1343; found 316.1346.

Compound 6c: 2-(2-Acetylphenyl)-*N*-(4-ethylphenyl)-2-fluoro-*N*-methylacetamide



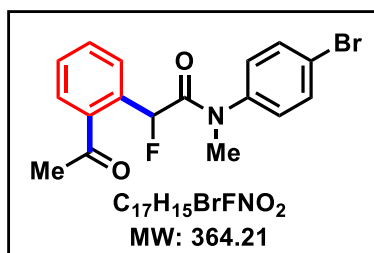
Following the general procedure, the treatment of *N*-(4-ethylphenyl)-2-fluoro-*N*-methyl-3-oxobutanamide **5c** (47 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6c** as yellow liquid (40 mg, 63%). R_f (Ethyl acetate/Hexane: 30/70) = 0.27. ^{13}C NMR (100 MHz, δ ppm/CDCl₃): 200.0 (C), 167.1 (d, J_{C-F} = 21.5 Hz, C), 144.2 (C), 140.6 (C), 137.4 (d, J_{C-F} = 18.9 Hz, C), 134.6 (d, J_{C-F} = 2.9 Hz, C), 132.9 (d, J_{C-F} = 2.1 Hz, CH), 130.2 (CH), 128.9 (CH), 128.9 (CH), 128.1 (CH), 128.0 (CH), 128.0 (CH), 126.8 (d, J_{C-F} = 18.2 Hz, CH), 87.5 (d, J_{C-F} = 173.0 Hz, CH), 37.8 (CH₃), 28.5 (CH₃), 28.1 (CH₂), 15.4 (CH₃). 1H NMR (400 MHz, δ ppm/CDCl₃): 7.84 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.34 (d, J = 47.6 Hz, 1H), 3.32 (d, J = 1.6 Hz, 3H), 2.7 (q, J = 7.6 Hz, 2H), 2.54 (s, 3H), 1.27 (t, J = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, δ ppm/CDCl₃): -179.8 (s). HRMS (ESI) m/z : [M+H]⁺ Calcd for C₁₉H₂₁FNO₂ 314.1551; found 314.1551.

Compound 6d: 2-(2-Acetylphenyl)-2-fluoro-*N*-methyl-*N*-(*p*-tolyl)acetamide



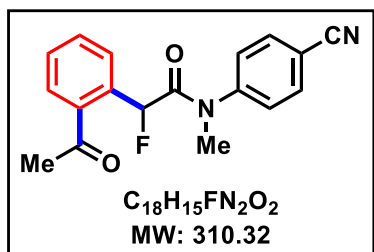
Following the general procedure, the treatment of 2-fluoro-*N*-methyl-3-oxo-*N*-(*p*-tolyl)butanamide **5d** (45 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6d** as white solid (41 mg, 69%). R_f (Ethyl acetate/Hexane: 30/70) = 0.27. Mp 111-113 °C. ^{13}C NMR (100 MHz, δ ppm/CDCl₃): 200.0 (C), 167.1 (d, J_{C-F} = 21.5 Hz, C), 140.5 (C), 138.0 (C), 137.4 (d, J_{C-F} = 19.1 Hz, C), 134.6 (d, J_{C-F} = 2.9 Hz, C), 133.0 (d, J_{C-F} = 2.1 Hz, CH), 130.2 (CH), 130.1 (CH), 130.1 (CH), 128.1 (CH), 128.0 (CH), 128.0 (CH), 126.8 (d, J_{C-F} = 18.1 Hz, CH), 87.8 (d, J_{C-F} = 173.0 Hz, CH), 38.0 (CH₃), 28.1 (CH₃), 21.2 (CH₃). 1H NMR (400 MHz, δ ppm/CDCl₃): 7.84 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.47-7.41 (m, 3H), 7.25 (d, J = 7.6 Hz, 2H), 6.34 (d, J = 47.2 Hz, 1H), 3.31 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, δ ppm/CDCl₃): -180.0 (s). HRMS (ESI) m/z : [M+H]⁺ Calcd for C₁₈H₁₉FNO₂ 300.1394; found 300.1395.

Compound 6e: 2-(2-Acetylphenyl)-*N*-(4-bromophenyl)-2-fluoro-*N*-methylacetamide



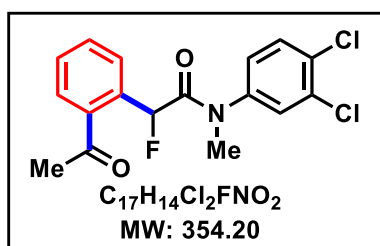
Following the general procedure, the treatment of *N*-(4-bromophenyl)-2-fluoro-*N*-methyl-3-oxobutanamide **5e** (58 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6e** as white solid (44 mg, 61%). **R_f** (Ethyl acetate/Hexane: 30/70) = 0.27. **Mp** 120-122 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 200.1 (C), 166.9 (d, *J*_{C-F} = 21.1 Hz, C), 142.2 (C), 137.3 (d, *J*_{C-F} = 18.7 Hz, C), 134.3 (d, *J*_{C-F} = 2.9 Hz, C), 133.1 (d, *J*_{C-F} = 2.2 Hz, CH), 132.8 (CH), 132.8 (CH), 130.5 (CH), 130.1 (CH), 130.1 (CH), 128.3 (CH), 126.7 (d, *J*_{C-F} = 18.8 Hz, CH), 122.1 (C), 88.7 (d, *J*_{C-F} = 172.9 Hz, CH), 37.8 (CH₃), 28.0 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.88 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.64-7.58 (m, 3H), 7.50-7.43 (m, 3H), 6.28 (d, *J* = 47.2 Hz, 1H), 3.30 (s, 3H), 2.58 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -180.3 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₇H₁₆BrFNO₂ 364.0343; found 364.0347.

Compound 6f: 2-(2-Acetylphenyl)-*N*-(4-cyanophenyl)-2-fluoro-*N*-methylacetamide



Following the general procedure, the treatment of *N*-(4-cyanophenyl)-2-fluoro-*N*-methyl-3-oxobutanamide **5f** (47 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6f** as white solid (37 mg, 59%). **R_f** (Ethyl acetate/Hexane: 30/70) = 0.20. **Mp** 145-147 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 200.3 (C), 166.6 (d, *J*_{C-F} = 23.1 Hz, C), 147.4 (C), 137.1 (d, *J*_{C-F} = 18.8 Hz, C), 134.0 (d, *J*_{C-F} = 2.7 Hz, C), 133.5 (CH), 133.5 (CH), 133.3 (d, *J*_{C-F} = 2.4 Hz, CH), 130.7 (CH), 129.1 (CH), 128.7 (CH), 128.4 (CH), 126.5 (d, *J*_{C-F} = 19.1 Hz, CH), 118.3 (C), 111.8 (C), 87.8 (d, *J*_{C-F} = 174.4 Hz, CH), 38.7 (CH₃), 28.0 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.91 (d, *J* = 7.6 Hz, 1H), 7.80-7.72 (m, 5H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 41.6 Hz, 1H), 3.39 (s, 3H), 2.57 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -180.3 (s). **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₁₈H₁₆FN₂O₂ 311.1190; found 311.1193.

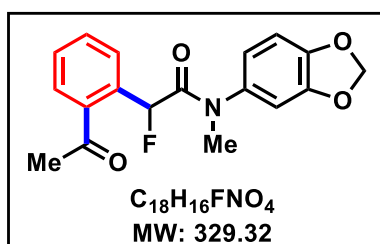
Compound 6g: 2-(2-Acetylphenyl)-*N*-(3,4-dichlorophenyl)-2-fluoro-*N*-methylacetamide



Following the general procedure, the treatment of *N*-(3,4-dichlorophenyl)-2-fluoro-*N*-methyl-3-oxobutanamide **5g** (56 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography af-

forded the product **6g** as white solid (45 mg, 64%). R_f (Ethyl acetate/Hexane: 30/70) = 0.32. **Mp** 126-128 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/CDCl₃): 200.0 (C), 166.7 (d, $J_{\text{C-F}}$ = 20.3 Hz, C), 142.6 (C), 137.0 (d, $J_{\text{C-F}}$ = 19.0 Hz, C), 134.2 (d, $J_{\text{C-F}}$ = 2.6 Hz, C), 133.3 (C), 133.2 (d, $J_{\text{C-F}}$ = 2.2 Hz, CH), 132.5 (C), 131.2 (CH), 130.5 (CH), 130.5 (CH), 128.4 (CH), 127.9 (CH), 126.6 (d, $J_{\text{C-F}}$ = 18.8 Hz, CH), 87.7 (d, $J_{\text{C-F}}$ = 173.0 Hz, CH), 37.8 (CH₃), 27.9 (CH₃). $^1\text{H NMR}$ (400 MHz, δ ppm/CDCl₃): 7.90 (d, J = 7.2 Hz, 1H), 7.77-7.71 (m, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.55-7.44 (m, 3H), 6.29 (d, J = 47.6 Hz, 1H), 3.30 (s, 3H), 2.56 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/CDCl₃): -180.6 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₇H₁₅Cl₂FNO₂ 354.0458; found 354.0461.

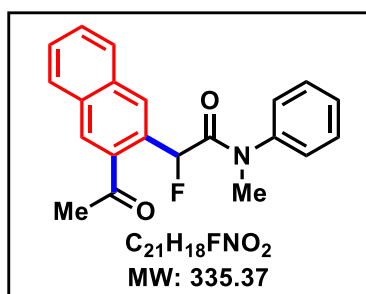
Compound 6h: 2-(2-Acetylphenyl)-*N*-(benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-*N*-methylacetamide



Following the general procedure, the treatment of *N*-(benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-*N*-methyl-3-oxobutanamide **5h** (51 mg, 0.20 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (149 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chroma-

tography afforded the product **6h** as white solid (43 mg, 65%). R_f (Ethyl acetate/Hexane: 30/70) = 0.22. **Mp** 110-112 °C. $^{13}\text{C NMR}$ (100 MHz, δ ppm/CDCl₃): 201.0 (C), 168.3 (d, $J_{\text{C-F}}$ = 21.3 Hz, C), 149.1 (C), 148.4 (C), 138.4 (d, $J_{\text{C-F}}$ = 19.0 Hz, C), 137.9 (C), 135.5 (d, $J_{\text{C-F}}$ = 2.8 Hz, C), 134.0 (CH), 131.3 (CH), 129.1 (CH), 127.8 (d, $J_{\text{C-F}}$ = 16.5 Hz, CH), 123.0 (CH), 110.3 (CH), 109.4 (CH), 102.8 (CH₂), 88.6 (d, $J_{\text{C-F}}$ = 173.0 Hz, CH), 39.0 (CH₃), 29.0 (CH₃). $^1\text{H NMR}$ (400 MHz, δ ppm/CDCl₃): 7.86 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.07 (m, 2H), 6.84 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 47.2 Hz, 1H), 6.01 (s, 2H), 3.28 (s, 3H), 2.55 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, δ ppm/CDCl₃): -180.2 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₈H₁₇FNO₄ 330.1136; found 330.1139.

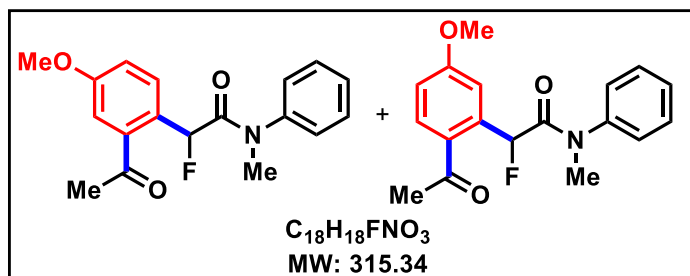
Compound 6i: 2-(3-Acetylnaphthalen-2-yl)-2-fluoro-N-methyl-N-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-N-methyl-3-oxo-N-phenylbutanamide **5a** (42 mg, 0.20 mmol) with 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **2h** (174 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6i** as brown solid (39 mg, 58%). R_f (Ethyl acetate/Hexane:

30/70) = 0.32. **Mp** 149-152 °C. ^{13}C NMR (100 MHz, δ ppm/CDCl₃): 199.9 (C), 167.4 (d, J_{C-F} = 21.4 Hz, C), 143.2 (C), 134.9 (d, J_{C-F} = 2.1 Hz, C), 132.9 (d, J_{C-F} = 18.3 Hz, C), 132.7 (d, J_{C-F} = 2.7 Hz, C), 132.5 (CH), 131.9 (C), 129.5 (CH), 129.5 (CH), 129.0 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 127.3 (CH), 126.4 (d, J_{C-F} = 18.5 Hz, CH), 87.7 (d, J_{C-F} = 173.7 Hz, CH), 37.9 (CH₃), 27.9 (CH₃). 1H NMR (400 MHz, δ ppm/CDCl₃): 8.38 (s, 1H), 8.16 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.64-7.58 (m, 3H), 7.55 (t, J = 8.4 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 6.49 (d, J = 47.2 Hz, 1H), 3.36 (s, 3H), 2.67 (s, 3H). ^{19}F NMR (376 MHz, δ ppm/CDCl₃): -179.3 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₂₁H₁₉FNO₂ 336.1394; found 336.1389.

Compound 6j and 6j': 2-(2-Acetyl-4-methoxyphenyl)-2-fluoro-N-methyl-N-phenylacetamide and 2-(2-acetyl-5-methoxyphenyl)-2-fluoro-N-methyl-N-phenylacetamide

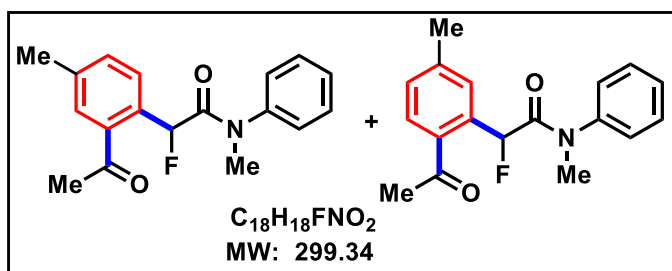


Following the general procedure, the treatment of 2-fluoro-N-methyl-3-oxo-N-phenylbutanamide **5a** (42 mg, 0.20 mmol) with 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2b** (164 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol)

and MS 4 Å (100 mg) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6j** and **6j'** as a separable 1:1 mixture of regioisomers as white solid (39 mg, 61%). R_f (Ethyl acetate/Hexane: 30/70) = 0.25. Compound **6j**: **Mp** 102-104 °C. ^{13}C NMR (100 MHz, δ ppm/CDCl₃): 199.8 (C), 167.4 (d, J_{C-F} = 17.4 Hz, C), 159.3 (C), 143.0 (C), 136.2 (C), 129.5 (CH), 129.5 (CH), 128.7 (CH), 128.6 (C), 128.2 (CH), 128.2 (CH), 128.1 (CH), 117.0 (CH), 116.8 (CH), 87.0 (d, J_{C-F} = 137.8 Hz, CH), 55.7 (CH₃), 37.9 (CH₃), 28.2 (CH₃). 1H NMR (400 MHz, δ ppm/CDCl₃): 7.67 (d, 8.8 Hz, 1H), 7.49-7.47 (m, 2H), 7.43 (t, 7.6 Hz, 2H), 7.37-7.33 (m, 1H), 7.30 (s, 1H), 7.12-7.10 (m, 1H), 6.26 (d, J = 48.4 Hz, 1H), 3.85 (s, 3H), 3.32 (s, 3H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, δ ppm/CDCl₃): -177.7 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₈H₁₉FNO₃ 316.1343; found 316.1338. Compound **6j'**: R_f (Ethyl acetate/Hexane: 30/70) = 0.22. **Mp** 110-112 °C. ^{13}C NMR (100 MHz, δ ppm/CDCl₃): 198.2 (C), 166.8 (d, J_{C-F} = 21.3 Hz, C), 163.3 (d, J_{C-F} = 2.6 Hz, C), 143.3 (C), 140.6 (d, J_{C-F} = 18.1 Hz, C), 133.1 (CH), 129.5 (CH), 129.5 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 127.3 (d, J_{C-F} = 2.3 Hz, C), 113.1 (CH), 112.1 (d, J_{C-F} = 20.8 Hz, CH),

87.9 (d, $J_{C-F} = 174.0$ Hz, CH), 55.6 (CH₃), 37.8 (CH₃), 27.7 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.83 (d, 8.8 Hz, 1H), 7.64-7.62 (m, 2H), 7.48-7.44 (m, 2H), 7.39-7.35 (m, 1H), 7.27 (s, 1H), 6.90-6.86 (m, 1H), 6.33 (d, $J = 47.6$ Hz, 1H), 3.90 (s, 3H), 3.33 (s, 3H), 2.50 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -179.7 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₈H₁₉FNO₃ 316.1343; found 316.1338.

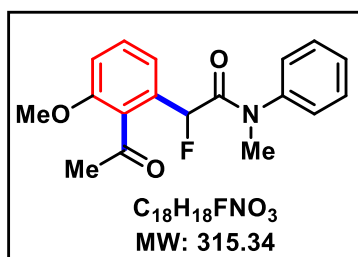
Compound 6k and 6k': 2-(2-acetyl-4-methylphenyl)-2-fluoro-N-methyl-N-phenylacetamide and 2-(2-acetyl-5-methylphenyl)-2-fluoro-N-methyl-N-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-*N*-methyl-3-oxo-*N*-phenylbutanamide **5a** (42 mg, 0.20 mmol) with 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2c** (156 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) in

CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6k** and **6k'** as an inseparable mixture of regioisomers in 1:1 ratio as white solid (39 mg, 65%). R_f (Ethyl acetate/Hexane: 30/70) = 0.34. M_p 117-119 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃, representative peaks of **6k**): 200.1 (C), 167.2 (d, $J_{C-F} = 21.8$ Hz, C), 143.9 (C), 143.1 (C), 137.4 (d, $J_{C-F} = 18.5$ Hz, C), 134.6 (d, $J_{C-F} = 2.9$ Hz, C), 133.6 (CH), 130.7 (CH), 129.5 (CH), 129.5 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 127.5 (d, $J_{C-F} = 18.0$ Hz, CH), 87.7 (d, $J_{C-F} = 172.8$ Hz, CH), 37.8 (CH₃), 28.1 (CH₃), 21.9 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.75 (d, $J = 8.0$ Hz, 1H), 7.65-7.60 (m, 3H), 7.59-7.53 (m, 4H), 6.32 (d, 47.6 Hz, 1H), 3.33 (s, 3H), 2.52 (s, 3H), 2.42 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -179.6 (s). **¹³C NMR** (100 MHz, δ ppm/CDCl₃, representative peaks of **6k'**): 199.5 (C), 167.1 (d, $J_{C-F} = 21.5$ Hz, C), 143.2 (C), 138.0 (C), 134.7 (d, $J_{C-F} = 19.4$ Hz, C), 131.9 (d, $J_{C-F} = 2.5$ Hz, C), 131.0 (CH), 128.7 (CH), 129.4 (CH), 129.4 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 126.9 (d, $J_{C-F} = 17.2$ Hz, CH), 87.5 (d, $J_{C-F} = 172.4$ Hz, CH), 37.8 (CH₃), 27.9 (CH₃), 21.2 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.48-7.42 (m, 4H), 7.41-7.34 (m, 3H), 7.22 (d, $J = 8.0$ Hz, 1H), 6.29 (d, 47.2 Hz, 1H), 3.33 (s, 3H), 2.51 (s, 3H), 2.41 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -179.9 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₈H₁₉FNO₂ 300.1394; found 300.1399.

Compound 6l: 2-(2-acetyl-3-methoxyphenyl)-2-fluoro-N-methyl-N-phenylacetamide

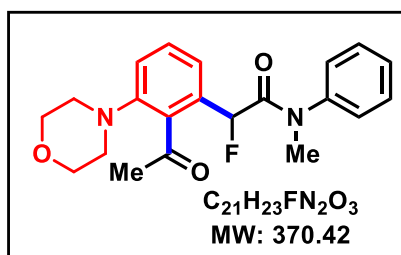


Following the general procedure, the treatment of 2-fluoro-*N*-methyl-3-oxo-*N*-phenylbutanamide **5a** (42 mg, 0.20 mmol) with 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2i** (164 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product **6l** as colourless liquid (35

mg, 56%). R_f (Ethyl acetate/Hexane: 40/60) = 0.37. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 203.6 (C), 167.1 (d, $J_{C-F} = 22.3$ Hz, C), 157.3 (C), 142.5 (C), 134.9 (d, $J_{C-F} = 20.0$ Hz, C), 131.4 (CH), 129.8

(CH), 129.8 (CH), 129.0 (C), 128.4 (CH), 128.0 (CH), 128.0 (CH), 119.5 (d, J_{C-F} = 11.9 Hz, CH), 111.9 (CH), 86.2 (d, J_{C-F} = 174.7 Hz, CH), 55.9 (CH₃), 38.1 (CH₃), 32.3 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.42-7.33 (m, 4H), 7.29-7.27 (m, 2H), 7.18 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.91 (d, J = 47.2 Hz, 1H), 3.80 (s, 3H), 3.32 (s, 3H), 2.38 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -175.2 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₈H₁₉FNO₃ 316.1343; found 316.1346.

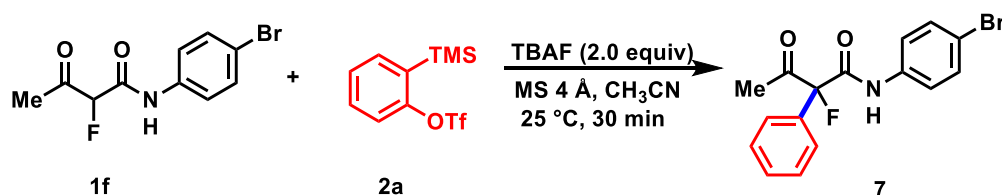
Compound 6m: 2-(2-acetyl-3-morpholinophenyl)-2-fluoro-*N*-methyl-*N*-phenylacetamide



Following the general procedure, the treatment of 2-fluoro-*N*-methyl-3-oxo-*N*-phenylbutanamide **5a** (42 mg, 0.20 mmol) with 3-morpholino-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2f** (192 mg, 0.50 mmol) in the presence of CsF (106 mg, 0.70 mmol) in CH₃CN (2 mL) at 60 °C for 16 h followed by column chromatography afforded the product

6m as white solid (39 mg, 52%). R_f (Ethyl acetate/Hexane: 30/70) = 0.20. **Mp** 178-180 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 206.3 (C), 167.1 (d, J_{C-F} = 22.8 Hz, C), 150.1 (C), 142.1 (C), 137.0 (C), 132.8 (d, J_{C-F} = 21.2 Hz, C), 130.5 (CH), 129.8 (CH), 129.8 (CH), 128.5 (CH), 127.8 (CH), 123.1 (d, J_{C-F} = 9.0 Hz, CH), 123.1 (d, J_{C-F} = 9.0 Hz, CH), 120.7 (CH), 85.6 (d, J_{C-F} = 175.4 Hz, CH), 67.2 (CH₂), 67.2 (CH₂), 55.5 (CH₂), 55.5 (CH₂), 38.1 (CH₃), 31.7 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 7.42-7.29 (m, 5H), 7.17-7.10 (m, 3H), 5.82 (d, J = 47.6 Hz, 1H), 3.74 (t, J = 4.0 Hz, 4H), 3.31 (s, 3H), 2.87 (t, J = 4.0 Hz, 4H), 2.40 (s, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -173.8 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₂₁H₂₄FN₂O₃ 371.1765; found 371.1783.

Procedure for the synthesis of 2-fluoro-3-oxo-*N*,2-diphenylbutanamide **7**



An oven-dried round bottom flask charged with *N*-(4-bromophenyl)-2-fluoro-3-oxobutanamide **1f** (0.20 mmol) and MS 4 Å (100 mg) was sealed, evacuated, and backfilled with nitrogen. Subsequently, Freshly distilled CH₃CN (2.0 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.30 mmol), and TBAF (0.40 mmol) were added, and the reaction mixture was stirred at 25 °C for 30 min. After the completion of the reaction, as indicated by TLC, the solvent was evaporated off, and the crude reaction mixture was purified using flash column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent to afford the product **7** as white solid. R_f (Ethyl acetate/Hexane: 20/80) = 0.37. **Mp** 126-128 °C. **¹³C NMR** (100 MHz, δ ppm/CDCl₃): 200.4 (d, J_{C-F} = 21.4 Hz, C), 163.0 (d, J_{C-F} = 17.4 Hz, C), 135.7 (C), 133.2 (d, J_{C-F} = 17.2 Hz, C), 132.3 (CH), 132.3 (CH), 130.0 (d, J_{C-F} = 1.4 Hz, CH), 129.1 (CH), 129.1 (CH), 125.5 (d, J_{C-F} = 6.5 Hz, CH), 125.5 (d, J_{C-F} = 6.5 Hz, CH), 121.8 (CH), 121.8 (CH), 118.2

(C), 99.8 (d, $J_{C-F} = 158.8$ Hz, C), 26.4 (CH₃). **¹H NMR** (400 MHz, δ ppm/CDCl₃): 8.14 (s, 1H), 7.65-7.61 (m, 2H), 7.50-7.45 (m, 4H), 7.45-7.39 (m, 3H), 2.39 (d, $J = 3.6$ Hz, 3H). **¹⁹F NMR** (376 MHz, δ ppm/CDCl₃): -115.9 (s). **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₁₆H₁₄BrFNO₂ 350.0186; found 350.0188.

X-Ray Data Collection and Structure Refinement Details for compound **6f**:

A good quality single crystal of size 0.26 x 0.17 x 0.11 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **6f** were collected on the Bruker APEX-II CCD area-detector at 272(2) K. Data collection was performed using ω -scans of at 272(2) K by Bruker APEX2. Cell determination, and data reduction was performed using the Bruker SAINT software. Structure solution and refinement were performed by using SHELX-97. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

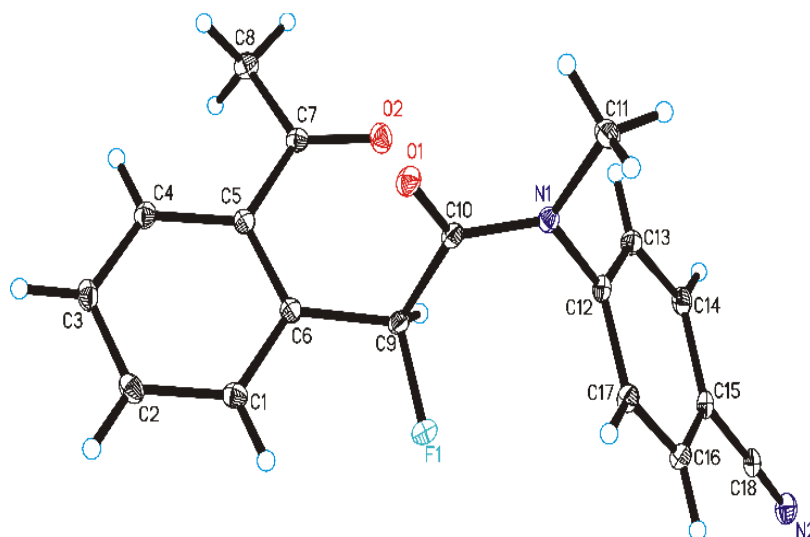


Figure 1 ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **6f** determined at 273K.

Crystallization: The compound **6f** (5mg) was dissolved in a 1 mL mixture of *n*-hexane/DCM (1:1) and placed in a cabinet to evaporate slowly. After two days, **6f** was obtained as white crystals.

Table 1 Crystal data and structure refinement details for **6f**.

Compound	6f
Empirical formula	C ₁₈ H ₁₅ F N ₂ O ₂
Formula weight	310.32
Crystal System	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.912(2)
<i>b</i> (Å)	13.614(3)
<i>c</i> (Å)	14.075(4)
α (°)	90.00
β (°)	101.443(8)
γ (°)	90.00
<i>V</i> (Å ³)	1485.9(7)
<i>Z</i>	4
<i>D</i> _c (g/cm ³)	1.387
<i>F</i> ₀₀₀	648
μ (mm ⁻¹)	0.100
θ_{\max} (°)	28.32
Total reflections	22134
Unique reflections	3677
Reflections [<i>I</i> > 2σ(<i>I</i>)]	3093
Parameters	210
<i>R</i> _{int}	0.0504
Goodness-of-fit	1.059
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0441
<i>wR</i> (<i>F</i> ² , all data)	0.1033
CCDC No.	2024815

