Supporting Information for

Synthesis of 3-Fluoroalkenyl-3-trifluoromethyl-2-oxindoles by the Reaction of Indoline-2,3-diones with Difluoromethylene Phosphetaine

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1. General Remarks

$^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a Bruker AM-400 spectrometer for solution in CDCl$_3$ with tetramethylsilane (TMS) as an internal standard; J-values are in Hz. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA+ mass spectrometer. 1,4-dioxane and toluene were distilled from sodium (Na) under argon (N$_2$) atmosphere. CH$_3$CN, DMF, DMSO, NMP were distilled from CaH$_2$ under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF 254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

2. Preparation of the known substrates 1a-1p.

Substrates 1a -1p were prepared according to the reported methods.$^{1-4}$

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3. General procedure for the synthesis of 3-fluoromethylenyl-3-trifluoromethyl substituted dioxindoles 3.

Into a 25 mL Schlenk tube with a magnetic stirrer, indoline-2,3-dione 1a (81 mg, 0.5 mmol) and difluoromethylene phosphabetaine (356 mg, 1.0 mmol) were added. The mixture was degassed and then NMP (1.0 mL) was added under N₂. The reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, ethyl acetate (EA) (10 mL) was added. The organic phases were washed with H₂O (5 mL × 3) and brine (5 mL × 1). After that, the organic phases were dried with Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product 3a.

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\text{3-[(fluoro(1-methyl-2-oxoindolin-3-ylidene)methyl)-1-methyl-3-(trifluoromethyl)indolin-2-one 3a. Column chromatography (petroleum ether : ethyl acetate = 3:1) on silica gel gave a pale yellow solid (72 %): mp 160–161 °C; }
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^1H\text{ NMR (400 MHz, CDCl}_3\text{) }\delta 7.77 (d, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 7.3 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 6.7 Hz, 2H), 6.99 (d, J = 7.7 Hz, 1H), 6.75 (d, J = 7.7 Hz, 1H), 3.40 (s, 3H), 3.05 (s, 3H). ^19F\text{ NMR (377 MHz, CDCl}_3\text{) }\delta -68.15 (s, 3F), -87.49 (td, J = 20.1, 12.5 Hz, 1F). ^13C\text{ NMR (101 MHz, CDCl}_3\text{) }\delta 167.7 (d, J = 6.1 Hz), 164.8 (d, J = 20.1 Hz), 161.4, 158.5, 146.6, 142.3, 130.9, 130.0 (d, J = 2.7 Hz), 125.3 (d, J = 13.4 Hz), 124.7, 123.0, 122.8 (qd, J = 283.7, 2.8 Hz), 122.6, 121.4, 119.9, 108.6, 107.9, 60.9 – 59.9 (m), 27.3, 26.0. IR (KBr)\text{ max } 3061, 2934, 1736, 1660, 1609, 1479, 1344, 1271, 1239, 1189, 1085, 747, 668 \text{ cm}^{-1}; \text{ MS (EI) m/z 390.0 [M]^{+}; HRMS (EI) m/z [M]^{+} calcd for C}_{29}H_{14}F_{4}N_{2}O_{2}, 390.0991; \text{ Found, 390.0996.}
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1-ethyl-3-((1-ethyl-2-oxoindolin-3-ylidene)fluoromethyl)-3-(trifluoromethyl)indolin-2-one 3b. Column chromatography (petroleum ether : ethyl acetate = 4:1) on silica gel gave a pale yellow solid (81 %): mp 138–139 °C; 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 1H), 7.38 (d, $J = 7.4$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 7.08 (t, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 7.9$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 4.04 (dq, $J = 14.4$, 7.3 Hz, 1H), 3.81 (dq, $J = 14.2$, 7.1 Hz, 1H), 3.67 – 3.51 (m, 2H), 1.41 (t, $J = 7.2$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H).

$^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -68.36 (s, 3F), -87.37 (q, $J = 20.7$ Hz, 1F).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.8 (d, $J = 5.4$ Hz), 164.2 (d, $J = 19.9$ Hz), 161.3, 158.4, 145.8, 141.5, 130.7, 129.9 (d, $J = 2.8$ Hz), 125.5 (d, $J = 13.5$ Hz), 124.8, 122.9 (qd, $J = 285.7$, 2.8 Hz), 122.7, 122.3, 121.6, 120.1, 108.6, 108.0, 61.0 – 60.0 (m), 36.0, 34.4, 12.6, 12.3. IR (KBr) $\text{max}^\text{ cm}$-1: 3059, 2980, 1732, 1608, 1476, 1360, 1261, 1224, 1182, 798, 678; MS (EI) m/z 418.0 [M]$^+$; HRMS (EI) m/z [M]$^+$ calcd for C$_{22}$H$_{18}$F$_4$N$_2$O$_2$, 418.1304; Found, 418.1312.

1-benzyl-3-((1-benzyl-2-oxoindolin-3-ylidene)fluoromethyl)-3-(trifluoromethyl)indolin-2-one 3c. Column chromatography (petroleum ether : ethyl acetate = 7:1) on silica gel gave a pale yellow solid (73 %): mp 178–179 °C; 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 7.5$ Hz, 1H), 7.47 – 7.42 (m, 3H), 7.30 (dt, $J = 17.2$, 8.4 Hz, 5H), 7.21 (t, $J = 7.8$ Hz, 1H), 7.16 (d, $J = 7.1$ Hz, 2H), 7.10 (dd, $J = 14.1$, 7.0 Hz, 2H), 6.83 (d, $J = 7.9$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 1H), 5.57 (d, $J = 16.0$ Hz, 1H), 4.86 (d, $J = 15.9$ Hz, 1H), 4.70 (t, $J = 16.1$ Hz, 2H). $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -67.84 (s, 3F), -86.71 (q, $J = 20.3$ Hz, 1F).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.8 (d, $J = 4.5$ Hz), 165.0 (d, $J = 20.1$ Hz), 161.8, 158.9, 146.2, 141.4, 135.5 (d, $J = 8.5$ Hz), 130.8, 130.0 (d, $J = 2.5$ Hz), 128.8, 128.7, 127.6 (d, $J = 4.1$ Hz), 127.2, 127.1, 125.5, 125.3, 124.8, 123.1, 123.0 (q, $J = 285.9$ Hz), 122.7, 121.4, 120.0, 113.8 (d, $J = 17.6$ Hz), 109.7, 109.1, 61.5 – 60.3 (m), 45.5, 43.5. IR (KBr)$_{\text{max}}$ 3060, 2925, 1740, 1660, 1607, 1480, 1353, 1252, 1179, 947, 743, 698; MS (EI) m/z 542.0 [M]$^+$; HRMS (EI) m/z [M]$^+$ calcd for C$_{32}$H$_{22}$F$_4$N$_2$O$_2$, 542.1617; Found, 542.1614.
3-(fluoro(2-oxo-1-phenylindolin-3-ylidene)methyl)-1-phenyl-3-(trifluoromethyl)indolin-2-one 3d. Column chromatography (petroleum ether : ethyl acetate = 8:1) on silica gel gave a pale yellow solid (61%): mp 220–221 °C; 1H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, $J = 7.4$ Hz, 1H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.56 – 7.51 (m, 2H), 7.48 (t, $J = 7.8$ Hz, 4H), 7.40 – 7.24 (m, 5H), 7.21 – 7.09 (m, 2H), 6.80 (dd, $J = 14.2$, 7.9 Hz, 2H). 19F NMR (377 MHz, CDCl$_3$) δ -68.22 (s, 3F), -86.03 (q, $J = 20.5$ Hz, 1F). 13C NMR (101 MHz, CDCl$_3$) δ 166.5, 164.2 (d, $J = 20.0$ Hz), 162.1, 159.2, 146.9, 142.39, 134.1 (d, $J = 29.7$ Hz), 130.7, 130.0 (d, $J = 2.6$ Hz), 129.7, 129.4, 128.7, 128.0, 127.4, 126.6, 125.6 (d, $J = 13.5$ Hz), 124.9, 123.0 (qd, $J = 282.7$, 2.9 Hz), 123.3, 123.2, 120.8, 119.9, 113.8 (d, $J = 17.7$ Hz), 109.8, 109.4, 61.2 – 60.1 (m). IR (KBr) max 3062, 2912, 1748, 1602, 1496, 1372, 1222, 1191, 745, 696 cm$^{-1}$; MS (EI) m/z 514.0 [M]$^+$; HRMS (EI) m/z [M]$^+$ calcd for C$_{30}$H$_{18}$F$_4$N$_2$O$_2$, 514.1304; Found, 514.1300.

1-allyl-3-((1-allyl-2-oxoindolin-3-ylidene)fluoromethyl)-3-(trifluoromethyl)indolin-2-one 3e. Column chromatography (petroleum ether : ethyl acetate = 5:1) on silica gel gave a pale yellow solid (54%): mp 147–149 °C; 1H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 6.3$ Hz, 2H), 7.28 (t, $J = 7.7$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 2H), 6.99 (d, $J = 7.9$ Hz, 1H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.03 (ddd, $J = 15.9$, 10.0, 4.9 Hz, 1H), 5.70 (ddd, $J = 16.2$, 10.3, 5.2 Hz, 1H), 5.40 (d, $J = 17.2$ Hz, 1H), 5.31 (d, $J = 10.3$ Hz, 1H), 5.18 (s, 1H), 5.14 (d, $J = 10.9$ Hz, 1H), 4.73 (dd, $J = 16.5$, 3.3 Hz, 1H), 4.31 (dd, $J = 16.6$, 4.8 Hz, 1H), 4.25 – 4.13 (m, 2H). 19F NMR (377 MHz, CDCl$_3$) δ -68.13 (s, 3F), -87.04 (q, $J = 20.5$ Hz, 1F). 13C NMR (101 MHz, CDCl$_3$) δ 167.1 (d, $J = 5.0$ Hz), 164.4 (d, $J = 20.0$ Hz), 161.5, 158.6, 146.0, 141.6, 131.6, 131.4, 130.8, 129.9 (d, $J = 2.7$ Hz), 125.4 (d, $J = 13.5$ Hz), 124.7, 123.0, 122.8 (qd, $J = 284.2$, 2.7Hz), 122.6, 121.4, 119.9, 117.7 (d, $J = 7.2$ Hz), 113.7 (d, $J = 17.6$ Hz), 109.6, 108.9, 61.55 – 59.89 (m), 43.9, 42.1. IR (KBr)$_{max}$ 3071, 2920, 1730, 1657, 1607, 1475, 1351, 1253, 1179, 941,747 cm$^{-1}$; MS (EI) m/z 442.0 [M]$^+$; HRMS (EI) m/z [M]$^+$ calcd for C$_{24}$H$_{18}$F$_4$N$_2$O$_2$, 442.1304; Found, 442.1309.
3-(fluoro(2-oxo-1-(prop-2-yn-1-yl)indolin-3-ylidene)methyl)-1-(prop-2-yn-1-yl)-3-(trifluoromethyl)indolin-2-one 3f. Column chromatography (petroleum ether : ethyl acetate = 6:1) on silica gel gave a pale yellow solid (72 %); mp 212–213 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J$ = 6.0 Hz, 1H), 7.49 (s, 1H), 7.42 (d, $J$ = 5.6 Hz, 1H), 7.36 (s, 1H), 7.27 (d, $J$ = 6.7 Hz, 1H), 7.16 (s, 2H), 7.02 (d, $J$ = 6.5 Hz, 1H), 4.99 (d, $J$ = 17.6 Hz, 1H), 4.34 (dd, $J$ = 23.1, 16.8 Hz, 3H), 2.38 (s, 1H), 2.21 (s, 1H). $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -68.11 (s, 3F), -86.43 (q, $J$ = 20.0 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.6, 163.8 (d, $J$ = 20.2 Hz), 161.6, 158.7, 145.0, 140.4, 131.0, 130.1 (d, $J$ = 2.6 Hz), 125.4 (d, $J$ = 13.5 Hz), 124.9, 123.5, 123.1, 122.7 (q, $J$ = 284.6 Hz), 121.0, 119.8, 109.7, 109.2, 76.5, 76.5, 72.9, 72.7, 61.3 - 60.5 (m), 30.8, 29.0. IR (KBr) $\text{max}$ 3299, 3039, 2922, 1741, 1660, 1609, 1477, 1351, 1181, 1108, 744, 672 cm$^{-1}$; MS (EI) m/z 438.0 [M]+; HRMS (EI) m/z [M]+ calcd for C$_{24}$H$_{14}$F$_{4}$N$_{2}$O$_{2}$, 438.0991; Found, 438.0995.

3-((1,5-dimethyl-2-oxoindolin-3-ylidene)fluoromethyl)-1,5-dimethyl-3-(trifluoromethyl)indolin-2-one 3g. Column chromatography (petroleum ether : ethyl acetate = 3:1) on silica gel gave a pale yellow solid (85 %): mp 158–159 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (s, 1H), 7.21 (d, $J$ = 8.0 Hz, 1H), 7.17 (s, 1H), 7.09 (d, $J$ = 7.8 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.61 (d, $J$ = 7.9 Hz, 1H), 3.34 (s, 3H), 3.00 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -68.16 (s, 3F), -87.76 (q, $J$ = 20.4 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.7 (d, $J$ = 5.8 Hz), 164.8 (d, $J$ = 20.2 Hz, 161.3, 158.4, 144.2, 140.1, 132.7, 132.0, 131.2, 130.3 (d, $J$ = 2.8 Hz), 126.0 (d, $J$ = 13.5 Hz), 125.5, 121.4, 122.9 (qd, $J$ = 285.2, 2.9 Hz), 119.9 (d, $J$ = 1.3 Hz), 108.3, 107.6. 60.8 – 60.2 (m), 27.3, 26.1, 21.1, 21.0. IR (KBr)$_{\text{max}}$ 3024, 2925, 2853, 1737, 1614, 1496, 1349, 1233, 1177, 1091, 972, 809, 649 cm$^{-1}$; MS (EI) m/z 418.4 [M]+; HRMS (EI) m/z [M]+ calcd for C$_{22}$H$_{18}$F$_{4}$N$_{2}$O$_{2}$, 418.1304; Found, 418.1307.
3-(fluoro(5-methyl-2-oxo-1-(prop-2-yn-1-yl)indolin-3-ylidene)methyl)-5-methyl-1-(prop-2-yn-1-yl)-3-(trifluoromethyl)indolin-2-one 3h. Column chromatography (petroleum ether : ethyl acetate = 6:1) on silica gel gave a pale yellow solid (74 %): mp 192–193 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.22 (s, 1H), 7.16 (t, J = 6.3 Hz, 2H), 6.91 (d, J = 7.9 Hz, 1H), 4.96 (d, J = 17.8 Hz, 1H), 4.39 – 4.24 (m, 3H), 2.40 (s, 3H), 2.35 (s, 4H), 2.19 (s, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -68.07 (s, 3F), -86.76 (q, J = 20.3 Hz, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 166.5 (d, J = 4.2 Hz), 163.86 (d, J = 20.4 Hz), 161.5, 158.6, 142.6, 138.2, 133.2, 132.6, 131.4, 130.4 (d, J = 2.7 Hz), 126.1 (d, J = 13.5 Hz), 125.6, 122.74 (qd, J = 283.0, 2.6 Hz), 121.1, 119.9 (d, J = 1.4 Hz), 113.7 (d, J = 17.9 Hz), 109.4, 108.9, 76.7, 72.8, 72.5, 60.89 – 60.10 (m), 30.8, 29.0, 21.2, 21.0. IR (KBr)max 3297, 2922, 1742, 1660, 1610, 1494, 1433, 1343, 1236, 1194, 966, 811, 667 cm⁻¹; MS (EI) m/z 466.0 [M⁺]; HRMS (EI) m/z [M⁺] calcd for C₂₆H₁₈F₄N₂O₂, 466.1304; Found, 466.1308.

1-benzyl-3-((1-benzyl-5-methoxy-2-oxoindolin-3-ylidene)fluoromethyl)-5-methoxy-3-(trifluoromethyl)indolin-2-one 3i. Column chromatography (petroleum ether : ethyl acetate = 7:1) on silica gel gave a pale yellow solid (73 %): mp 159–160 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (dd, J = 19.4, 7.8 Hz, 5H), 7.34 – 7.24 (m, 4H), 7.16 (d, J = 6.7 Hz, 2H), 7.05 (s, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 6.70 (d, J = 8.5 Hz, 1H), 6.51 (d, J = 8.5 Hz, 1H), 5.54 (d, J = 16.1 Hz, 1H), 4.77 (dd, J = 66.7, 16.1 Hz, 2H), 4.63 (d, J = 16.2 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -67.79 (s, 3F), -86.94 (q, J = 20.3 Hz, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 167.4 (d, J = 4.3 Hz), 164.8 (d, J = 19.8 Hz), 161.6, 158.8, 156.1, 155.8, 139.7, 135.6, 135.5, 135.3, 128.8, 128.7, 127.6 (d, J = 3.3 Hz), 127.2, 127.0, 123.0 (q, J = 285.6 Hz), 122.3, 120.7, 115.6 (d, J = 2.2 Hz), 115.3, 114.4 (d, J = 16.8 Hz), 112.1, 111.8 (d, J = 13.6 Hz), 110.2, 109.5, 61.3 – 60.6 (m), 55.9, 55.8, 45.5, 43.6. IR (KBr)max 3029, 2923, 2840, 1725, 1654, 1490, 1345, 1236, 1192, 1024, 806, 698 cm⁻¹; MS (EI) m/z 602.1 [M⁺]; HRMS (EI) m/z [M⁺] calcd for C₃₄H₃₆F₃N₂O₄, 602.1829; Found, 602.1816.
5-fluoro-3-(fluoro(5-fluoro-2-oxo-1-phenylindolin-3-ylidene)methyl)-1-phenyl-3-(trifluoromethyl)indolin-2-one 3j. Column chromatography (petroleum ether : ethyl acetate = 3:1) on silica gel gave a pale yellow solid (74 %): mp 166–167 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 1H), 7.16 (s, 2H), 7.06 (s, 1H), 6.93 (s, 1H), 6.70 (s, 1H), 3.38 (s, 3H), 3.06 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -68.14 (s, 3F), -85.08 – -87.66 (m, 1F), -119.24 (s, 1F), -120.29 (s, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 167.2 (d, J = 3.9 Hz), 164.5 (d, J = 19.3 Hz), 161.5, 160.2 (d, J = 10.1 Hz), 158.6, 157.8 (d, J = 7.5 Hz), 142.8, 138.4, 122.5 (q, J = 284.9 Hz), 122.1 (d, J = 9.4 Hz), 120.5 (d, J = 9.7 Hz), 117.4 (d, J = 23.3 Hz), 116.6 (d, J = 24.0 Hz), 113.2 (d, J = 26.4 Hz), 113.0 (d, J = 25.5), 109.3 (d, J = 8.0 Hz), 108.4 (d, J = 8.3 Hz), 61.0– 59.6 (m), 27.5, 26.2. IR (KBr) max 3080, 2929, 1741, 1661, 1615, 1491, 1345, 1270, 1201, 977, 869, 810 cm⁻¹; MS (EI) m/z 426.0 [M]⁺; HRMS (EI) m/z [M⁺] calcd for C₂₀H₁₂F₃N₂O₂, 426.0803; Found, 426.0798.

5-fluoro-3-(fluoro(5-fluoro-2-oxo-1-phenylindolin-3-ylidene)methyl)-1-phe-nyl-3-(trifluoromethyl)indolin-2-one 3k. Column chromatography (petroleum ether : ethyl acetate = 8:1) on silica gel gave a pale yellow solid (63 %): mp 248–249 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.2 Hz, 1H), 7.58 – 7.53 (m, 4H), 7.48 (dd, J = 14.3, 7.2 Hz, 3H), 7.39 (t, J = 7.3 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.24 (d, J = 7.0 Hz, 1H), 7.09 – 6.98 (m, 2H), 6.79 – 6.71 (m, 2H). ¹⁹F NMR (377 MHz, CDCl₃) δ -68.17 (s, 3F), -84.83 (q, J = 20.6 Hz, 1F), -118.64 – -119.01 (m, 1F), -119.28 – -119.75 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 166.0 (d, J = 4.5 Hz), 163.9 (d, J = 19.2 Hz), 162.1, 160.4 (d, J = 3.9 Hz), 159.2, 158.0, 143.1, 138.5, 133.9 (d, J = 30.4 Hz), 129.8, 129.6, 128.9, 128.2, 127.3, 126.4, 122.7 (qd, J = 284.5, 2.8 Hz), 120.6 (d, J = 9.6 Hz), 117.4 (d, J = 23.3 Hz), 116.7 (d, J = 24.0 Hz), 113.3 (d, J = 13.4 Hz), 113.1, 112.85, 112.96, 110.6 (d, J = 7.9 Hz), 110.1 (d, J = 8.1 Hz), 61.3 - 60.57 (m). IR (KBr) max 3063, 2924,1749, 1658, 1606, 1488, 1364, 1196, 817, 747, 695 cm⁻¹; MS (EI) m/z 550.1 [M]⁺; HRMS (EI) m/z [M⁺] calcd for C₃₀H₁₆F₆N₂O₂, 550.1116; Found, 550.1119.
1-benzyl-3-((1-benzyl-5-chloro-2-oxoindolin-3-ylidene)fluoromethyl)-5-chloro-3-(trifluoromethyl)indolin-2-one 3l. Column chromatography (petroleum ether : ethyl acetate = 7:1) on silica gel gave a pale yellow solid (57 %): mp 196–197 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 (s, 1H), 7.39 (d, \(J = 11.0 \text{ Hz}\), 5H), 7.19 (d, \(J = 8.1 \text{ Hz}\), 1H), 7.13 (d, \(J = 6.4 \text{ Hz}\), 2H), 6.73 (d, \(J = 8.2 \text{ Hz}\), 1H), 6.56 (d, \(J = 8.2 \text{ Hz}\), 1H), 5.53 (d, \(J = 16.0 \text{ Hz}\), 1H), 4.78 (dd, \(J = 54.9, 15.9 \text{ Hz}\), 2H), 4.62 (d, \(J = 16.0 \text{ Hz}\), 1H). \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -67.72 (s, 3F), -84.87 (q, \(J = 20.3 \text{ Hz}\), 1F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.1 (d, \(J = 5.2 \text{ Hz}\), 1H), 164.5 (d, \(J = 19.5 \text{ Hz}\), 161.8, 158.9, 144.8, 139.9, 134.9 (d, \(J = 7.1 \text{ Hz}\), 1H), 131.0, 130.0, 128.9, 128.9, 128.5, 128.3, 127.8, 127.1, 127.0, 125.7, 125.5, 125.1, 122.6 (q, \(J = 286.1 \text{ Hz}\), 122.4, 121.0, 113.6 (d, \(J = 18.3 \text{ Hz}\), 110.8, 110.1, 61.0 – 60.1 (m), 45.6, 43.6. IR (KBr) \(\text{max} 3067, 2924, 1745, 1661, 1607, 1482, 1342, 1250, 1180, 1116, 1077, 813, 738, 694 \text{ cm}^{-1}\); MS (EI) m/z 610.0 [M]\(^+\); HRMS (EI) m/z [M]\(^+\) calcd for C\(_{32}\)H\(_{20}\)Cl\(_2\)F\(_4\)N\(_2\)O\(_2\), 610.0838; Found, 610.0833.

1-ethyl-3-((1-ethyl-5-iodo-2-oxoindolin-3-ylidene)fluoromethyl)-5-iodo-3-(trifluoromethyl)indolin-2-one 3m. Column chromatography (petroleum ether : ethyl acetate = 2:1) on silica gel gave a pale yellow solid (49 %): mp 166–167 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (d, \(J = 1.7 \text{ Hz}\), 1H), 7.72 (dd, \(J = 8.3, 1.8 \text{ Hz}\), 2H), 6.75 (d, \(J = 8.3 \text{ Hz}\), 1H), 6.56 (d, \(J = 8.2 \text{ Hz}\), 1H), 3.94 (dt, \(J = 14.4, 7.1 \text{ Hz}\), 1H), 3.74 (dq, \(J = 14.5, 7.3 \text{ Hz}\), 1H), 3.59 – 3.51 (m, 2H), 1.35 (t, \(J = 7.3 \text{ Hz}\), 3H), 1.11 (t, \(J = 7.2 \text{ Hz}\), 3H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -68.28 (s, 3F), -85.49 (q, \(J = 20.6 \text{ Hz}\), 1F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.0 (d, \(J = 3.3 \text{ Hz}\), 1H), 163.6 (d, \(J = 19.5 \text{ Hz}\), 161.3, 158.4, 145.5, 141.0 (d, \(J = 12.5 \text{ Hz}\), 139.7, 138.6 (d, \(J = 2.7 \text{ Hz}\), 135.0, 134.0 (d, \(J = 14.2 \text{ Hz}\), 133.3, 123.3, 122.5 (qd, \(J = 286.5, 2.9 \text{ Hz}\), 121.9, 110.6, 110.1, 84.6 (d, \(J = 6.2 \text{ Hz}\), 61.3 – 59.8 (m), 36.2, 34.5, 12.5, 12.2. IR (KBr) \text{max} 3031, 2981, 2936, 1745, 1661, 1607, 1476, 1343, 1223, 1186, 1100, 810, 735 \text{ cm}^{-1}\); MS (EI) m/z 671.0 [M+H]\(^+\); HRMS (EI) m/z [M+H]\(^+\) calcd for C\(_{22}\)H\(_{17}\)F\(_4\)I\(_2\)N\(_2\)O\(_2\), 670.9310; Found, 670.9305.
4-bromo-3-((4-bromo-1-ethyl-2-oxoindolin-3-ylidene)fluoromethyl)-1-ethyl-3-(trifluoromethyl)indolin-2-one 3n. Column chromatography (petroleum ether : ethyl acetate = 2:1) on silica gel gave a pale yellow solid (53 %): mp 181–182 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (dd, $J = 15.6, 8.4$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 8.0$ Hz, 1H), 6.89 (d, $J = 7.7$ Hz, 1H), 6.68 (d, $J = 7.7$ Hz, 1H), 3.91 (dq, $J = 14.5, 7.3$ Hz, 1H), 3.76 (dq, $J = 14.3, 7.2$ Hz, 1H), 3.62 – 3.42 (m, 2H), 1.34 (t, $J = 7.3$ Hz, 3H), 1.07 (t, $J = 7.2$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -59.58 (q, $J = 21.4$ Hz, 1F), -66.20 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.7, 164.4 (d, $J = 19.0$ Hz), 159.4, 156.4, 147.8, 143.8, 131.6, 130.7 (d, $J = 1.6$ Hz), 128.6, 127.0, 123.0 (qd, $J = 288.6, 3.2$ Hz), 121.2, 120.6 (d, $J = 5.6$ Hz), 119.1, 118.9 (d, $J = 3.3$ Hz), 107.3, 106.8, 63.3 – 62.1 (m), 36.2, 34.6, 12.5, 12.1. IR (KBr) max 3048, 2982, 2938, 1736, 1644, 1598, 1453, 1340, 1263, 1195, 1109, 773, 671 cm$^{-1}$; MS (ESI) m/z 576.0 [M+H+2]$^+$; HRMS (ESI) m/z [M+H]$^+$ calcd for C$_{22}$H$_{17}$Br$_2$F$_4$N$_2$O$_2$, 574.9587; Found, 574.9577.

1-benzyl-3-((1-benzyl-7-methyl-2-oxoindolin-3-ylidene)fluoromethyl)-7-methyl-3-(trifluoromethyl)indolin-2-one 3o. Column chromatography (petroleum ether : ethyl acetate = 7:1) on silica gel gave a pale yellow solid (42 %): mp 192–194 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 – 7.66 (m, 1H), 7.34 – 7.15 (m, 9H), 7.07 (d, $J = 7.7$ Hz, 1H), 7.01 – 6.89 (m, 5H), 5.50 (d, $J = 17.4$ Hz, 1H), 5.10 (d, $J = 16.8$ Hz, 1H), 4.95 (d, $J = 13.3$ Hz, 1H), 4.91 (d, $J = 13.6$ Hz, 1H), 2.26 (s, 3H), 2.17 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -67.91 (s, 3F), -86.72 (q, $J = 20.5$ Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.9 (d, $J = 4.5$ Hz), 166.0 (d, $J = 20.2$ Hz), 161.9, 159.1, 144.5, 139.6, 137.9, 137.5, 134.8, 133.9 (d, $J = 2.8$ Hz), 128.8 (d, $J = 5.9$ Hz), 127.1 (d, $J = 6.5$ Hz), 125.9, 125.7, 123.5 (d, $J = 15.0$ Hz), 123.0 (qd, $J = 284.5, 3.6$ Hz), 122.9, 122.8, 122.7, 122.1, 120.7 (d, $J = 2.6$ Hz), 120.2, 119.7, 113.4 (d, $J = 16.9$ Hz), 60.3 (dd, $J = 26.9, 20.7$ Hz), 46.8, 44.8, 18.9, 18.7. IR (KBr)$_{max}$ 3063, 3030, 2929, 1738, 1658, 1599, 1446, 1352, 1228, 1190, 1074, 951, 911, 792, 728 cm$^{-1}$; MS (ESI) m/z 571.2 [M+H]$^+$; HRMS (ESI) m/z [M+H]$^+$ calcd for C$_{34}$H$_{27}$Br$_2$F$_4$N$_2$O$_2$, 571.2003; Found, 571.1995.
methyl 1-ethyl-3-((1-ethyl-7-(methoxycarbonyl)-2-oxoindolin-3-ylidene)fluoromethyl)-2-oxo-3-(trifluoromethyl)indoline-7-carboxylate 3p.

Column chromatography (petroleum ether : ethyl acetate = 4:1) on silica gel gave a pale yellow solid (39 %): mp 170–171 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J=6.8$ Hz, 1H), 7.67 (d, $J=7.0$ Hz, 1H), 7.53 (d, $J=7.3$ Hz, 1H), 7.40 (d, $J=7.1$ Hz, 1H), 7.06 (dt, $J=12.5$, 7.6 Hz, 2H), 4.04 (ddd, $J=19.4$, 16.4, 7.1 Hz, 2H), 3.96 (s, 3H), 3.88 (s, 3H), 3.73 (ddt, $J=21.2$, 14.1, 7.1 Hz, 2H), 1.29 (t, $J=7.2$ Hz, 3H), 0.93 (t, $J=7.1$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.30 (s, 3F), -86.15 (q, $J=21.1$ Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.0, 167.1, 167.0, 165.2 (d, $J=19.5$ Hz), 162.0, 159.1, 144.6, 139.8, 132.2, 131.1(d, $J=2.7$ Hz), 128.1, 128.0, 127.4, 123.5, 122.5 (qd, $J=286.3$, 3.4 Hz), 121.9, 121.7, 116.2, 115.9, 60.4, 52.6, 52.6, 39.0, 36.6, 12.6, 12.3. IR (KBr) $\nu_{\text{max}}$ 3052, 2947, 1729, 1663, 1596, 1446, 1352, 1317, 1271, 1203, 1116, 1072, 1010, 800, 746 cm$^{-1}$; MS (ESI) m/z 535.2 [M+H]$^+$; HRMS (ESI) m/z [M+H]$^+$ calcd for C$_{26}$H$_{23}$F$_4$N$_2$O$_6$, 535.1487; Found, 535.1471.


In 3 ml of methanol, the 3a (58.5 mg, 0.15 mmol) and Pd-black (32 mg, 10%) was hydrogenated for 36 h at room temperature. The mixture was filtered and the solvent was evaporated under reduced pressure. The residue was purified by Column chromatography on silica gel gave the 4a.

1-methyl-3-((1-methyl-2-oxoindolin-3-yl)methyl)-3-(trifluoromethyl)indolin-2-one 4a. Column chromatography (petroleum ether : ethyl acetate = 3:1) on silica gel gave a pale yellow solid (91 %): mp 155–156 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J=7.5$ Hz, 1H), 7.18 (dd, $J=7.0$, 5.0 Hz, 2H), 7.10 (t, $J=7.7$ Hz, 1H), 7.02 (t, $J=7.6$ Hz, 1H), 6.97 (t, $J=7.5$ Hz, 1H), 6.38 (s, 1H), 6.37 (s, 1H), 3.42 (t, $J=4.7$ Hz, 1H), 3.21 (d, $J=4.9$ Hz, 2H), 2.70 (s, 3H), 2.69 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.82 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.3, 171.8, 144.7, 144.3, 130.0, 128.2, 127.8, 125.9, 124.5 (q, $J=281.3$ Hz), 124.4, 122.0, 121.7, 120.9, 107.8, 107.5, 55.0 (q, $J=26.1$ Hz),
42.3, 28.1 (d, $J = 1.9$ Hz), 26.3, 25.9. IR (KBr) max 3060, 2928, 1724, 1611, 1482, 1349, 1290, 1171, 1090, 974, 762 cm$^{-1}$; MS (ESI) m/z 375.1 [M+H]$^+$; HRMS (ESI) m/z [M+H]$^+$ calcd for C$_{20}$H$_{18}$F$_3$N$_2$O$_2$, 375.1299; Found, 375.1307.

5. General procedure for the synthesis of 4b.

A solution of pyrazole (27.2 mg, 0.4 mmol) in DMF (0.3 mL) was added dropwise to a mixture of 3a (78.0 mg, 0.2 mmol) and K$_3$PO$_4$ (84.8 mg, 0.4 mmol) in DMF (0.3 mL) via syringe. The mixture was heated to 80 °C and stirred for 12 h (monitored by TLC). The reaction mixture was allowed to cool to room temperature and quenched with H$_2$O (10 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The organic layer was dried over MgSO$_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel gave the 4b.

3-((1H-imidazol-1-yl)(1-methyl-2-oxoindolin-3-ylidene)methyl)-1-methyl-3-(trifluoromethyl)indolin-2-one 4b. Column chromatography (petroleum ether : ethyl acetate = 3:1) on silica gel gave a pale yellow solid (84 %): mp 236–237 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 32.9$ Hz, 1H), 7.43 (dd, $J = 17.6, 9.4$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 8.7$ Hz, 1H), 7.18 (d, $J = 29.1$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 7.9$ Hz, 1H), 6.76 (t, $J = 7.7$ Hz, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 3.37 (s, 3H), 3.01 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -68.05 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.6, 163.7 (d, $J = 2.4$ Hz), 147.6 (d, $J = 2.0$ Hz), 143.9 (d, $J = 1.2$ Hz), 135.3 (d, $J = 10.0$ Hz), 133.1, 131.9, 130.6 (d, $J = 2.8$ Hz), 130.3, 124.3 (d, $J = 3.1$ Hz), 123.9, 123.8, 123.3 (q, $J = 285.6$ Hz), 123.2, 122.9, 122.7, 119.7 (d, $J = 3.2$ Hz), 118.5, 108.5, 108.0, 62.2(q, $J = 13.5$ Hz), 27.2, 26.1. IR (KBr)$_{\text{max}}$ 3120, 3070, 2926, 2854, 1740, 1604, 1491, 1374, 1082, 1044, 960, 751, 690, 669 cm$^{-1}$; MS (ESI) m/z 439.2 [M+H]$^+$; HRMS (ESI) m/z [M+H]$^+$ calcd for C$_{23}$H$_{18}$F$_3$N$_4$O$_2$, 439.1376; Found, 439.1369.

6. Copies of $^1$H NMR and $^{13}$C NMR spectra for the new product.
Figure S1: $^1$H NMR of 3a

Figure S2: $^{19}$F NMR of 3a
Figure S3: $^{13}$C NMR of 3a

Figure S4: $^1$H NMR of 3b
Figure S5: $^{19}$F NMR of 3b

Figure S6: $^{13}$C NMR of 3b
Figure S7: $^1$H NMR of 3c

Figure S8: $^{19}$F NMR of 3c
Figure S9: $^{13}$C NMR of 3c

Figure S10: $^1$H NMR of 3d
**Figure S11:** $^{19}$F NMR of 3d

**Figure S12:** $^{13}$C NMR of 3d
Figure S13: $^1$H NMR of 3e

Figure S14: $^{19}$F NMR of 3e
Figure S15: $^{13}$C NMR of $3e$

Figure S16: $^1$H NMR of $3f$
Figure S17: $^{19}$F NMR of 3f

Figure S18: $^{13}$C NMR of 3f
Figure S19: $^1$H NMR of $3g$

Figure S20: $^{19}$F NMR of $3g$
Figure S21: $^{13}$C NMR of 3g

Figure S22: $^1$H NMR of 3h
Figure S23: $^{19}$F NMR of 3h

Figure S24: $^{13}$C NMR of 3h
Figure S25: $^1$H NMR of 3i

Figure S26: $^{19}$F NMR of 3i
Figure S27: $^{13}$C NMR of 3i

Figure S28: $^1$H NMR of 3j
Figure S29: $^{19}$F NMR of 3j

Figure S30: $^{13}$C NMR of 3j
Figure S31: $^1$H NMR of 3k

Figure S32: $^{19}$F NMR of 3k
Figure S33: $^{13}$C NMR of 3k

Figure S34: $^1$H NMR of 3l
Figure S35: $^{19}$F NMR of 3l

Figure S36: $^{13}$C NMR of 3l
Figure S37: $^1$H NMR of 3m

Figure S38: $^{19}$F NMR of 3m
Figure S39: $^{13}$C NMR of $3m$

Figure S40: $^1$H NMR of $3n$
Figure S41: $^{19}$F NMR of $3n$

Figure S42: $^{13}$C NMR of $3n$
Figure S43: $^1$H NMR of 3o

Figure S44: $^1$H NMR of 3o
Figure S45: $^1$H NMR of $3o$

Figure S46: $^1$H NMR of $3p$
Figure S47: $^{19}$F NMR of 3p

Figure S48: $^{13}$C NMR of 3p
Figure S49: $^1$H NMR of 4a

Figure S50: $^{19}$F NMR of 4a
Figure S51: $^{13}$C NMR of 4a

Figure S52: $^1$H NMR of 4b
Figure S53: $^{19}$F NMR of 4b

Figure S54: $^{13}$C NMR of 4b
6. ORTEP drawing of the X-ray crystallographic structure of 4a

CCDC 1438186 contains the supplementary crystallographic data for the target compound 3a.

This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).