Supporting Information

Zn(OTf)₂ Catalyzed Ugi-type Reaction of 3-(2-Isocyanomethyl)indoles with Indole-Derived Ketimines: Rapid Access to Polycyclic Spiroindolines

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1) General Information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. $^1$H, $^{19}$F and $^{13}$C NMR spectra were obtained using a Bruker DPX-300 or DPX-500 spectrometer. Chemical shifts are reported in ppm from CDCl$_3$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, h=heptet, m=multiplet, br=broad.

Anhydrous solvents such as CH$_2$Cl$_2$, CICH$_2$CH$_2$Cl, CH$_3$CN, THF, toluene, EtOAc, acetone, EtOH as well as metal salts were purchased from Energy Chemical. Unless otherwise stated, all purchased reagents were used without further purification. All reactions involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere in dried Schlenk tube. The 3-(2-isocyanoethyl)indoles$^[1]$ 2-arylindoles$^[2]$, 2-aryl-3,3-difluoro-3H-indol3-ones$^[4]$ were prepared using the literature procedures.


2. General Procedure and Spectral Data of 3,3-difluoro-3H-indoles 2[3]

To a solution of indole (1 mmol) in CH$_3$CN (15 mL) were added Na$_2$CO$_3$ (1 g) and Selectfluor (2.2 mmol) at 0 °C. The mixture was stirred at this temperature for hours till the full consumption of indole. When the reaction was complete, CH$_2$Cl$_2$ (100 mL) was added and the mixture washed with H$_2$O (3×20mL) and brine (3×15mL). The organic extracts were dried over Na$_2$SO$_4$, and the solvent was concentrated in vacuo. The resulting residue was directly subjected to column chromatography using petroleum ether/EtOAc (from 10:1-3:1) as the eluent to afford the desired product 2. The spectral data of some new compounds are provided below.

Compound 2d was obtained in 86% yield as a yellow solid (m.p. 45-48 °C). $^1$H NMR (500 MHz, CDCl$_3$): δ 3.95 (s, 3H), 7.04-7.10 (m, 2H), 7.27 (t, $J$ = 5.0 Hz, 1H), 7.46-7.51 (m, 2H), 7.53 (d, $J$ = 5.0 Hz, 1H), 7.59 (d, $J$ = 5.0 Hz, 1H), 8.08 (d, $J$ = 5.0 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 167.99 (t, $J$ = 24 Hz), 159.66, 152.67 (t, $J$ = 10 Hz), 133.30, 132.94, 131.05 (t, $J$ = 3.8 Hz), 128.42 (t, $J$ = 25 Hz), 127.31, 123.34 (t, $J$ = 256 Hz), 122.60, 121.99, 120.47, 118.45 (t, $J$ = 2.5 Hz), 112.11, 55.98; $^{19}$F NMR (471 MHz, CDCl$_3$): δ -116.80 (m, 2F); IR: (KBr) $v_{\text{max}}$ 2940, 1599, 1579, 1461, 1271, 1078, 757; HRMS (EI): Exact mass calcd for C$_{15}$H$_{12}$F$_2$NO [M]$^+$: 260.0881, Found: 260.0879.

Compound 2f was obtained in 71% yield as a yellow solid (m.p. 85-87 °C). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.35 (t, $J$ = 10 Hz, 1H), 7.55-7.64 (m, 4H), 7.69-7.74 (m, 2H), 7.94 (d, $J$ = 10 Hz, 1H), 8.05 (d, $J$ = 10 Hz, 1H), 8.39 (d, $J$ = 10 Hz, 1H), 8.93 (d, $J$ = 10 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.46 (t, $J$ = 23 Hz), 152.78 (t, $J$ = 10 Hz), 134.21, 133.30, 133.23, 131.80, 130.53 (t, $J$ = 3.8 Hz), 128.86, 128.25, 128.12 (t, $J$ = 25 Hz), 127.59, 126.99, 126.45, 125.09 (t, $J$ = 2.5 Hz), 124.76, 124.04 (t, $J$ = 256 Hz), 122.90, 122.19; $^{19}$F NMR (471 MHz, CDCl$_3$): δ -112.72 (s, 2F); IR: (KBr) $v_{\text{max}}$ 2925, 1619, 1541, 1509, 1460, 1252, 1061, 765; HRMS (EI): Exact mass calcd for C$_{18}$H$_{12}$F$_2$N [M]$^+$: 280.0932, Found: 280.0939.
Compound 2m was obtained in 77% yield as a yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.86 (s, 3H), 6.98 (dd, $J = 10, 5.0$ Hz, 1H), 7.15 (d, $J = 5.0$ Hz, 1H), 7.46 (d, $J = 5.0$ Hz, 1H), 7.49-7.56 (m, 3H), 8.17 (d, $J = 5.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 167.52 (t, $J = 24$ Hz), 159.51, 145.60 (t, $J = 8.8$ Hz), 132.00, 130.41 (t, $J = 24$ Hz), 129.15 (t, $J = 2.5$ Hz), 128.83, 128.10, 122.92 (t, $J = 256$ Hz), 122.60, 116.98, 110.20, 55.87; $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -116.02 (s, 2F); IR: (KBr) $v_{\text{max}}$ 2967, 1606, 1551, 1478, 1364, 1265, 1066, 696; HRMS (EI): Exact mass calcd for C$_{15}$H$_{12}$F$_2$NO [M]$^+$: 260.0881, Found: 260.0875.

Compound 2r was obtained in 68% yield as a yellow solid (m.p. 55-56 °C). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32-7.36 (m, 1H), 7.40-7.43 (m, 2H), 7.45-7.49 (m, 1H), 7.50-7.54 (m, 3H), 7.66-7.68 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 157.34 (t, $J = 28$ Hz), 152.66 (t, $J = 8.8$ Hz), 133.39, 132.81, 130.68, 128.60, 128.46, 127.35 (t, $J = 24$ Hz), 123.40, 122.55, 120.50, 120.46 (t, $J = 255$ Hz), 103.34, 80.76 (t, $J = 2.5$ Hz); $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -122.40 (s, 2F); IR: (KBr) $v_{\text{max}}$ 2923, 2193, 1548, 1458, 1260, 1081, 1063, 756; HRMS (EI): Exact mass calcd for C$_{16}$H$_{10}$F$_2$N [M]$^+$: 254.0776, Found: 254.0775.
3. General Procedure and Spectral Data of Products 3 and 5

**General procedure for the synthesis of products 3:** To a 10.0 mL Schlenk tube were successively added Zn(OTf)$_2$ (8.1 mg, 0.0225 mmol), 3-(2-isocyanoethyl)indoles 1 (0.225 mmol), 2-aryl-3,3-difluoro-3H-indoles 2 (0.15 mmol), silica gel H (30 mg) and anhydrous ClICH$_2$CH$_2$Cl (1.0 mL). The reaction mixture was stirred vigorously at room temperature till almost full consumption of 2-aryl-3,3-difluoro-3H-indoles 2 as monitored by TLC (36-72 h). Then the reaction mixture was directly subjected to column chromatography using CH$_2$Cl$_2$/EtOAc (from 10:1-5:1) as the eluent to afford the desired product 3.

**General procedure for the synthesis of products 5:** To a 10.0 mL Schlenk tube were successively added Zn(OTf)$_2$ (8.1 mg, 0.0225 mmol), 3-(2-isocyanoethyl)indoles 1 (0.225 mmol), 2-aryl-3H-indol-3-ones 4 (0.15 mmol), anhydrous MgSO$_4$ (30 mg) and anhydrous ClICH$_2$CH$_2$Cl (1.0 mL). The reaction mixture was stirred vigorously at room temperature till almost full consumption of 2-aryl-3H-indol-3-ones 4 as monitored by TLC (36-48 h). Then the reaction mixture was directly subjected to column chromatography using CH$_2$Cl$_2$/EtOAc (from 10:1-5:1) as the eluent to afford the desired product 5.

The reaction was run at rt for 36 h, affording product 3a in 67% yield as a pale yellow solid (m.p. 153-158 °C). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.21-2.31 (m, 2H), 4.41-4.52 (m, 2H), 4.61 (brs, 1H), 4.96 (s, 1H), 6.36-6.41 (m, 2H), 6.63 (d, $J$ = 10 Hz, 1H), 6.79 (t, $J$ = 10 Hz, 1H), 7.01-7.07 (m, 5H), 7.41-7.44 (m, 2H), 7.46-7.50 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 179.77 (d, $J$ = 3.8 Hz), 151.30 (dd, $J$ = 7.6, 5.8 Hz), 148.18, 134.05 (d, $J$ = 6.3 Hz), 133.20, 130.15, 128.59, 127.88, 127.51, 126.32, 124.68, 123.62 (dd, $J$ = 259, 243 Hz), 122.66, 122.24 (dd, $J$ = 26, 25 Hz), 122.10, 119.49, 112.12, 109.24, 84.69, 74.46 (dd, $J$ = 30, 20 Hz), 71.31, 66.90, 39.15; $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -82.35 (d, $J$ = 254 Hz, 1F), -96.26 (d, $J$ = 254 Hz, 1F); IR: (KBr) $v_{max}$ 3422, 2930, 1665, 1608, 1469, 1258, 1089, 745; HRMS (EI): Exact mass calcd for C$_{25}$H$_9$F$_3$N$_3$ [M]$^+$: 399.1547, Found: 399.1550.
The reaction was run at rt for 36 h, affording product 3b in 61% yield as a yellow solid (m.p. 136-138 °C); 1H NMR (500 MHz, CDCl3): δ 2.20-2.31 (m, 2H), 4.40-4.52 (m, 2H), 4.61 (brs, 1H), 4.96 (s, 1H), 6.41-6.44 (m, 2H), 6.63 (d, J = 10 Hz, 1H), 6.68-6.72 (m, 2H), 6.83 (t, J = 10 Hz, 1H), 7.02-7.08 (m, 2H), 7.38-7.41 (m, 2H), 7.46-7.50 (m, 2H); 13C NMR (125 MHz, CDCl3): 179.68 (d, J = 2.5 Hz), 163.27, 161.31, 151.15 (dd, J = 7.5, 6.3 Hz), 148.04, 133.29, 130.06, 129.89 (dd, J = 5.0, 2.5 Hz), 128.76, 128.26 (d, J = 8.8 Hz), 124.71, 123.52 (dd, J = 258, 241 Hz), 122.60, 122.27, 122.11 (dd, J = 27, 26 Hz), 119.66, 114.45 (d, J = 23 Hz), 112.16, 109.27, 84.68, 76.89 (dd, J = 30, 20 Hz), 71.29, 66.96, 39.08; 19F NMR (471 MHz, CDCl3): δ -82.17 (d, J = 254 Hz, 1F), -96.69 (d, J = 254 Hz, 1F), -114.52 (s, 1F); IR: (KBr) νmax 3420, 2949, 1665, 1608, 1470, 1233, 1091, 823; HRMS (EI): Exact mass calcd for C25H18F3N3 [M]+: 417.1453, Found: 417.1457.

The reaction was run at rt for 36 h, affording product 3c in 52% yield as a yellow solid (m.p. 196-198 °C); 1H NMR (500 MHz, CDCl3): δ 2.21-2.31 (m, 2H), 4.41-4.52 (m, 2H), 4.62 (brs, 1H), 4.95 (s, 1H), 6.42-6.45 (m, 2H), 6.62 (d, J = 5 Hz, 1H), 6.86 (t, J = 5 Hz, 1H), 6.97-6.99 (m, 2H), 7.03 (d, J = 5 Hz, 1H), 7.06 (t, J = 5 Hz, 1H), 7.34-7.36 (m, 2H), 7.46-7.51 (m, 2H); 13C NMR (125 MHz, CDCl3): 179.54 (d, J = 2.5 Hz), 151.14 (dd, J = 7.5, 6.3 Hz), 148.03, 133.72, 133.34, 132.83 (d, J = 6.3 Hz), 129.89, 128.79, 127.81, 127.70, 124.71, 123.53 (dd, J = 259, 243 Hz), 122.63, 122.33, 122.08 (dd, J = 27, 25 Hz), 119.75, 112.20, 109.35, 84.69, 76.93 (dd, J = 30, 20 Hz), 71.33, 66.98, 38.95; 19F NMR (471 MHz, CDCl3): δ -82.29 (d, J = 254 Hz, 1F), -96.01 (d, J = 254 Hz, 1F); IR: (KBr) νmax 3433, 2989, 1621, 1588, 1455, 1188, 1012, 802; HRMS (EI): Exact mass calcd for C25H18ClF2N3 [M]+: 433.1157, Found: 433.1152.

The reaction was run at rt for 36 h, affording product 3d in 69% yield as a pale yellow solid (m.p. 115-117 °C). 1H NMR (500 MHz, CDCl3): δ 2.19-2.31 (m, 2H), 3.77 (s, 3H), 4.33-4.45 (m, 2H), 4.62 (s, 1H), 4.93 (s, 1H), 6.36 (d, J = 10 Hz, 1H), 6.40 (t, J = 10 Hz, 1H), 6.53 (td, J = 10, 5.0 Hz, 1H), 6.58 (d, J = 10 Hz, 1H), 6.68 (d, J = 10 Hz, 1H), 6.78 (td, J = 10, 5.0 Hz, 1H), 6.96-7.02 (m, 3H), 7.43-7.47 (m, 2H), 7.55 (d, J = 5.0 Hz, 1H); 13C NMR (125 MHz, CDCl3): δ 177.23, 157.82, 150.58 (t, 56
$J = 6.3$ Hz), 148.58, 132.92, 130.61, 129.52, 128.59, 128.28, 124.72, 123.62 (dd, $J = 260, 240$ Hz), 122.51 (dd, $J = 30, 28$ Hz), 121.94, 121.63, 119.61, 119.11, 111.42, 110.82, 108.94, 84.45, 76.36 (dd, $J = 31, 21$ Hz), 70.59, 66.02, 55.52, 39.51; $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -82.78 (d, $J = 254$ Hz, 1F), -97.37 (d, $J = 254$ Hz, 1F); IR: (KBr) $v_{\text{max}}$ 3421, 2931, 1661, 1607, 1483, 1256, 1086, 746; HRMS (EI): Exact mass calcd for C$_{26}$H$_{22}$F$_2$N$_3$O [M$^+$]: 430.1725, Found: 430.1734.

The reaction was run at rt for 36 h, affording product 3e in 70% yield as a yellow solid (m.p. 155-160 °C); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.23-2.32 (m, 2H), 4.44-4.56 (m, 2H), 4.67 (brs, 1H), 5.00 (s, 1H), 6.10 (t, $J = 5$ Hz, 1H), 6.31 (d, $J = 5$ Hz, 1H), 6.47 (t, $J = 5$ Hz, 1H), 6.56 (d, $J = 5$ Hz, 1H), 7.05-7.09 (m, 2H), 7.32-7.38 (m, 2H), 7.48-7.59 (m, 5H), 7.64-7.65 (m, 1H), 7.82 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 179.80 (d, $J = 3.8$ Hz), 151.34 (dd, $J = 7.5, 6.3$ Hz), 148.10, 133.27, 132.80, 132.47, 131.52 (d, $J = 5$ Hz), 130.13, 128.40, 127.83, 127.31, 127.26, 126.06, 125.83, 125.57, 124.74, 123.92, 123.77 (dd, $J = 259, 243$ Hz), 122.34, 122.29 (dd, $J = 27, 25$ Hz), 122.18, 119.34, 112.19, 109.04, 84.77, 77.63 (dd, $J = 30, 20$ Hz), 71.37, 66.96, 38.97; $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -82.02 (d, $J = 254$ Hz, 1F), -95.89 (d, $J = 254$ Hz, 1F); IR: (KBr) $v_{\text{max}}$ 3411, 2901, 1644, 1608, 1485, 1007, 802; HRMS (EI): Exact mass calcd for C$_{29}$H$_{21}$F$_2$N$_3$ [M$^+$]: 449.1704, Found: 449.1707.

The reaction was run at rt for 36 h, affording product 3g in 75% yield as a pale yellow solid (m.p. 198-200 °C). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.21-2.29 (m, 2H), 4.43-4.46 (m, 2H), 4.50 (brs, 1H), 4.96 (s, 1H), 6.31-6.34 (m, 2H), 6.50 (td, $J = 10, 5$ Hz, 1H), 7.02 (d, $J = 10$ Hz, 1H), 7.05-7.06 (m, 4H), 7.42-7.44 (m, 2H), 7.46-7.50 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 179.10 (d, $J = 2.5$ Hz), 157.93, 156.05, 151.16 (dd, $J = 7.5, 5$ Hz), 144.38 (d, $J = 1.3$ Hz), 133.90 (d, $J = 6.3$ Hz), 133.26, 131.49 (d, $J = 7.5$ Hz), 128.12, 127.66, 126.35, 124.71, 123.53 (d, $J = 258, 243$ Hz), 122.24, 122.19 (dd, $J = 28, 25$ Hz), 114.95 (d, $J = 24$ Hz), 112.09, 109.86 (d, $J = 6.3$ Hz), 109.73 (d, $J = 8.8$ Hz), 85.39, 77.41 (dd, $J = 30, 20$ Hz), 71.54, 66.88, 38.78; $^{19}$F NMR (471 MHz, CDCl$_3$): $\delta$ -82.47 (d, $J = 254$ Hz, 1F), -95.05 (d, $J = 254$ Hz, 1F), -125.11 (s, 1F); IR: (KBr) $v_{\text{max}}$ 3223, 2930, 1668, 1611, 1486, 1183, 1068, 747; HRMS (EI): Exact mass calcd for C$_{23}$H$_{18}$F$_3$N$_3$ [M$^+$]: 417.1453, Found: 417.1449.
The reaction was run at rt for 36 h, affording product 3h in 89% yield as a yellow solid (m.p. 200-202 °C). $^1$H NMR (300 MHz, CDCl₃): δ 2.18 (s, 3H), 2.24-2.27 (m, 2H), 4.41-4.46 (m, 2H), 4.48 (brs, 1H), 4.95 (s, 1H), 6.29-6.33 (m, 2H), 6.51 (td, $J = 9.0, 3.0$ Hz, 1H), 6.84-6.87 (m, 2H), 7.00-7.08 (m, 2H), 7.27-7.30 (m, 2H), 7.45-7.50 (m, 2H); $^{13}$C NMR (125 MHz, CDCl₃): 179.22 (d, $J = 3.8$ Hz), 157.98, 156.09, 151.20 (dd, $J = 7.5, 6.3$ Hz), 144.41, 137.77, 133.18, 131.62 (d, $J = 7.5$ Hz), 130.73 (d, $J = 5$ Hz), 128.33, 126.32, 124.69, 123.50 (dd, $J = 259, 243$ Hz), 122.30 (dd, $J = 26, 25$ Hz), 122.15, 114.66 (d, $J = 24$ Hz), 112.07, 109.85 (d, $J = 10$ Hz), 109.72 (d, $J = 6.3$ Hz), 85.37, 77.33 (dd, $J = 31, 21$ Hz), 71.51, 66.83, 38.80, 20.90; $^{19}$F NMR (282 MHz, CDCl₃): δ -82.60 (d, $J = 254$ Hz, 1F), -96.69 (d, $J = 254$ Hz, 1F), -125.29 (s, 1F); IR: (KBr) $\nu_{\text{max}}$ 3298, 2942, 1632, 1596, 1475, 1142, 1045, 842; HRMS (EI): Exact mass calcd for C$_{26}$H$_{20}$F$_3$N$_3$ [M]$^+$: 431.1609, Found: 431.1614.

The reaction was run at rt for 36 h, affording product 3i in 79% yield as a yellow solid (m.p. 207-210 °C). $^1$H NMR (500 MHz, CDCl₃): δ 2.15 (s, 3H), 2.20-2.30 (m, 2H), 4.43-4.46 (m, 2H), 4.49 (brs, 1H), 4.95 (s, 1H), 6.30-6.34 (m, 2H), 6.50 (td, $J = 10, 5.0$ Hz, 1H), 6.86 (d, $J = 10$ Hz, 1H), 6.97 (t, $J = 10$ Hz, 1H), 7.02 (d, $J = 5$ Hz, 1H), 7.06 (t, $J = 10$ Hz, 1H), 7.17 (s, 1H), 7.24-7.26 (m, 1H), 7.47-7.50 (m, 2H); $^{13}$C NMR (125 MHz, CDCl₃): 179.16 (d, $J = 3.8$ Hz), 157.96, 156.08, 151.19 (dd, $J = 7.5, 6$ Hz), 144.53, 133.70 (d, $J = 6.3$ Hz), 133.23, 131.67 (d, $J = 7.5$ Hz), 128.79, 127.62, 127.02, 124.72, 123.54, 123.40 (dd, $J = 260, 243$ Hz), 122.18, 122.16 (dd, $J = 26, 25$ Hz), 114.88 (d, $J = 24$ Hz), 112.06, 109.76 (d, $J = 24$ Hz), 109.53 (d, $J = 8.8$ Hz), 85.46, 77.50 (dd, $J = 30, 20$ Hz), 71.47, 66.86, 38.68, 21.14; $^{19}$F NMR (471 MHz, CDCl₃): δ -81.75 (d, $J = 254$ Hz, 1F), -96.80 (d, $J = 254$ Hz, 1F), -125.28 (s, 1F); IR: (KBr) $\nu_{\text{max}}$ 3402, 2914, 1654, 1605, 1563, 1461, 1081, 762; HRMS (EI): Exact mass calcd for C$_{26}$H$_{20}$F$_3$N$_3$ [M]$^+$: 431.1609, Found: 431.1604.

The reaction was run at rt for 72 h, affording product 3j in 30% yield as a yellow oil; $^1$H NMR (300 MHz, CDCl₃): δ 2.18-2.35 (m, 2H), 4.44-4.49 (m, 2H), 4.55 (brs, 1H), 4.94 (s, 1H), 6.37-6.41 (m, 1H), 6.47 (dd, $J = 9, 3$ Hz, 1H), 6.60 (td, $J = 9, 3$ Hz, 1H), 6.70-7.73 (m, 1H), 6.94-7.02 (m, 3H), 7.09 (t, $J = 9$ Hz, 1H), 7.48-7.52 (m, 2H); $^{13}$C NMR (125 MHz, CDCl₃): 178.68, 158.07, 156.19, 150.80 (dd, $J = 7.4, 5.2$ Hz),
144.53, 138.36, 133.35, 131.82 (d, J = 10 Hz), 127.09, 126.77, 125.96, 124.82, 123.08 (dd, J = 273, 245 Hz), 122.73, 122.27 (dd, J = 27, 24 Hz), 115.10 (d, J = 24 Hz), 112.37, 110.20 (d, J = 8.8 Hz), 109.77 (d, J = 24 Hz), 85.63, 71.73, 66.92, 39.08; \(^{19}\text{F NMR (282 MHz, CDCl}_3\)): \(\delta\) -85.09 (d, J = 251 Hz, 1F), -97.77 (d, J = 251 Hz, 1F), -124.91 (s, 1F); \(\text{IR: (KBr) } v_{\text{max}} 3415, 2952, 1670, 1596, 1552, 1431, 1087, 753; \) HRMS (EI): Exact mass calcd for C\(_{23}\)H\(_{16}\)F\(_3\)N\(_3\)S [M]+: 423.1017, Found: 423.1021.

The reaction was run at rt for 48 h, affording product \(3k\) in 50% yield as a yellow solid (m.p. 194-197 °C); \(^1\text{H NMR (500 MHz, CDCl}_3\)): \(\delta\) 2.22-2.30 (m, 2H), 2.39 (s, 3H), 4.42-4.53 (m, 2H), 4.60 (brs, 1H), 4.94 (s, 1H), 6.37 (t, J = 10 Hz, 1H), 6.41 (d, J = 10 Hz, 1H), 6.62 (d, J = 5 Hz, 1H), 6.77-6.84 (m, 3H), 7.00-7.03 (m, 3H), 7.35 (t, J = 10 Hz, 1H), 7.40-7.43 (m, 2H); \(^{13}\text{C NMR (125 MHz, CDCl}_3\)): 180.01 (d, J = 3.8 Hz), 151.70 (dd, J = 7.5, 5 Hz), 148.22, 137.64, 134.37 (d, J = 6.3 Hz), 132.98, 130.02, 128.55, 127.79, 127.49, 126.24, 124.86 (dd, J = 259, 243 Hz), 123.86, 122.70, 120.02 (dd, J = 25, 24 Hz), 119.47, 109.44, 109.27, 84.64, 77.10 (dd, J = 30, 20 Hz), 71.29, 66.93, 39.07, 16.98; \(^{19}\text{F NMR (471 MHz, CDCl}_3\)): \(\delta\) -84.39 (d, J = 254 Hz, 1F), -95.05 (d, J = 254 Hz, 1F); \(\text{IR: (KBr) } v_{\text{max}} 3425, 2933, 1660, 1601, 1484, 1262, 1101, 735; \) HRMS (EI): Exact mass calcd for C\(_{26}\)H\(_{21}\)F\(_3\)N\(_3\) [M]+: 413.1704, Found: 413.1708.

The reaction was run at rt for 36 h, affording product \(3l\) in 69% yield as a yellow solid (m.p. 176-179 °C); \(^1\text{H NMR (500 MHz, CDCl}_3\)): \(\delta\) 2.17-2.30 (m, 2H), 2.33 (s, 3H), 4.40-4.52 (m, 2H), 4.59 (brs, 1H), 4.92 (s, 1H), 6.36-6.40 (m, 2H), 6.63 (d, J = 5 Hz, 1H), 6.78 (td, J = 10, 5 Hz, 1H), 6.94 (d, J = 5 Hz, 1H), 7.00-7.03 (m, 3H), 7.27-7.30 (m, 2H), 7.41-7.43 (m, 2H); \(^{13}\text{C NMR (125 MHz, CDCl}_3\)): 180.02 (d, J = 2.5 Hz), 149.18 (dd, J = 7.5, 6.3 Hz), 148.25, 134.14 (d, J = 6 Hz), 133.98, 131.90, 130.20, 128.56, 127.83, 127.48, 126.37, 124.68, 123.69 (dd, J = 259, 243 Hz), 122.65, 122.20 (dd, J = 26, 24 Hz), 119.44, 112.06, 109.23, 84.86, 77.72 (dd, J = 30, 20 Hz), 71.24, 66.90, 39.19, 20.72; \(^{19}\text{F NMR (471 MHz, CDCl}_3\)): \(\delta\) -81.93 (d, J = 254 Hz, 1F), -97.38 (d, J = 254 Hz, 1F); \(\text{IR: (KBr) } v_{\text{max}} 3422, 2928, 1679, 1608, 1496, 1072, 740; \) HRMS (EI): Exact mass calcd for C\(_{26}\)H\(_{21}\)F\(_3\)N\(_3\) [M]+: 413.1704, Found: 413.1700.
The reaction was run at rt for 36 h, affording product 3m in 49% yield as a pale yellow solid (m.p. 180-182 °C). 1H NMR (500 MHz, CDCl3): δ 2.19-2.30 (m, 2H), 3.79 (s, 3H), 4.40-4.52 (m, 2H), 4.61 (brs, 1H), 4.89 (s, 1H), 6.36-6.40 (m, 2H), 6.63 (d, J = 10 Hz, 1H), 6.78 (td, J = 10, 5.0 Hz, 1H), 6.95-6.99 (m, 2H), 7.01-7.03 (m, 3H), 7.06-7.08 (m, 1H), 7.43-7.44 (m, 2H); 13C NMR (125 MHz, CDCl3): δ 180.13 (d, J = 2.5 Hz), 155.54, 148.26, 145.16 (dd, J = 8.8, 6.3 Hz), 134.09 (d, J = 6.3 Hz), 130.25, 128.59, 127.88, 127.50, 126.45, 123.67 (dd, J = 259, 244 Hz), 122.74 (dd, J = 26, 24 Hz), 122.65, 121.00, 119.48, 113.46, 109.28, 107.95, 85.11 (d, J = 1.3 Hz), 78.02 (dd, J = 31, 20 Hz), 71.28 (d, J = 1.3 Hz), 66.96, 55.90, 39.24; 19F NMR (471 MHz, CDCl3): δ -82.24 (d, J = 254 Hz, 1F), -97.80 (d, J = 254 Hz, 1F); IR: (KBr) νmax 3396, 2893, 1645, 1614, 1468, 1307, 1070, 788; HRMS (EI): Exact mass calcd for C26H22F2N3O [M]+: 430.1725, Found: 430.1734.

The reaction was run at rt for 36 h, affording product 3n in 54% yield as a yellow solid (m.p. 149-154 °C); 1H NMR (500 MHz, CDCl3): δ 2.21-2.32 (m, 2H), 4.42-4.53 (m, 2H), 4.60 (brs, 1H), 4.91 (s, 1H), 6.37-6.40 (m, 2H), 6.63 (d, J = 5 Hz, 1H), 6.79 (td, J = 10, 5 Hz, 1H), 6.97-7.00 (m, 1H), 7.01-7.04 (m, 3H), 7.15-7.22 (m, 2H), 7.40-7.42 (m, 2H); 13C NMR (125 MHz, CDCl3): 179.64 (d, J = 2.5 Hz), 158.29 (d, J = 240 Hz), 148.08, 147.43 (dd, J = 7.5, 6.3 Hz), 133.62 (d, J = 6 Hz), 130.03, 128.66, 128.04, 127.57, 126.32, 123.23 (dd, J = 32, 25 Hz), 122.98 (dd, J = 259, 241 Hz), 122.63, 120.46 (d, J = 24 Hz), 119.58, 113.27 (d, J = 7.5 Hz), 111.39 (d, J = 24 Hz), 109.28, 85.05, 78.01 (dd, J = 30, 20 Hz), 71.32, 66.92, 39.24; 19F NMR (471 MHz, CDCl3): δ -82.68 (d, J = 254 Hz, 1F), -97.34 (d, J = 254 Hz, 1F), -120.82 (s, 1F); IR: (KBr) νmax 3256, 2950, 1678, 1608, 1491, 1271, 1182, 1070, 743; HRMS (EI): Exact mass calcd for C25H18F3N3 [M]+: 417.1453, Found: 417.1456.

The reaction was run at rt for 36 h, affording product 3o in 64% yield as a yellow solid (m.p. 105-107 °C); 1H NMR (500 MHz, CDCl3): δ 2.20-2.32 (m, 2H), 4.41-4.53 (m, 2H), 4.60 (brs, 1H), 4.93 (s, 1H), 6.37-6.40 (m, 2H), 6.63 (d, J = 10 Hz, 1H), 6.79 (td, J = 10, 1 Hz, 1H), 6.97 (d, J = 10 Hz, 1H), 7.01-7.04 (m, 3H), 7.39-7.40 (m, 2H), 7.43-7.45 (m, 2H); 13C NMR (125 MHz, CDCl3): 179.37 (d, J = 3.8 Hz), 149.82 (dd, J = 7.5, 6.3 Hz), 148.02, 133.46 (d, J = 5 Hz), 133.30, 129.98, 128.70, 128.10, 127.61, 127.06, 126.31, 124.75, 123.77 (dd, J = 27, 25 Hz), 122.81 (dd, J = 259, 243

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Hz), 122.65, 119.63, 113.33, 109.27, 84.79, 77.87 (dd, J = 30, 20 Hz), 71.37, 66.90, 39.28; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)): \(\delta\) -82.84 (d, J = 254 Hz, 1F), -97.15 (d, J = 254 Hz, 1F); IR: (KBr) \(v_{\text{max}}\) 3382, 2945, 1658, 1597, 1475, 1296, 743; HRMS (EI): Exact mass calcd for \(\text{C}_{25}\text{H}_{18}\text{ClF}_{2}\text{N}_3\) [M]: 433.1157, Found: 433.1155.

The reaction was run at rt for 36 h, affording product 3p in 63% yield as a yellow solid (m.p. 102-103 °C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 2.21-2.30 (m, 2H), 2.43 (s, 3H), 4.41-4.52 (m, 2H), 4.60 (brs, 1H), 4.94 (s, 1H), 6.37 (t, J = 10 Hz, 1H), 6.41 (d, J = 5 Hz, 1H), 6.62 (d, J = 10 Hz, 1H), 6.79 (t, J = 10 Hz, 1H), 6.84-6.87 (m, 2H), 7.00-7.02 (m, 3H), 7.34 (d, J = 5 Hz, 1H), 7.39-7.43 (m, 2H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 179.85 (d, J = 3.8 Hz), 151.59 (dd, J = 7.5, 6.3 Hz), 148.21, 143.91, 134.29 (d, J = 6.2 Hz), 130.22, 128.56, 127.80, 127.48, 126.30, 124.34, 123.68 (dd, J = 258 , 243 Hz), 123.18, 122.68, 119.55 (dd, J = 28, 25 Hz), 119.48, 112.64, 109.28, 84.55, 77.64 (dd, J = 30, 20 Hz), 71.33, 66.90, 39.09, 22.04; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)): \(\delta\) -82.12 (d, J = 254 Hz, 1F), -95.45 (d, J = 254 Hz, 1F); IR: (KBr) \(v_{\text{max}}\) 3293, 2912, 1667, 1601, 1432, 1297, 1040, 751; HRMS (EI): Exact mass calcd for \(\text{C}_{26}\text{H}_{21}\text{F}_{2}\text{N}_3\) [M]: 413.1704, Found: 413.1706.

The reaction was run at rt for 48 h, affording product 3q in 44% yield as a yellow solid (m.p. 126-128 °C); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 2.24-2.27 (m, 2H), 2.58 (s, 3H), 4.44-4.53 (m, 2H), 4.75 (brs, 1H), 4.98 (s, 1H), 6.37 (t, J = 10 Hz, 1H), 6.49 (d, J = 10 Hz, 1H), 6.59 (d, J = 5 Hz, 1H), 6.82 (t, J = 10 Hz, 1H), 6.99-7.03 (m, 4H), 7.30-7.33 (m, 2H), 7.44-7.46 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 180.02 (d, J = 3.8 Hz), 149.94 (dd, J = 7.5, 6.3 Hz), 147.93, 135.50, 134.61 (d, J = 5 Hz), 130.36, 128.58, 127.73, 127.54, 126.10, 123.44 (dd, J = 259 , 240 Hz), 123.02, 122.85 (dd, J = 27, 24 Hz), 122.77, 122.64, 122.20, 119.65, 109.33, 83.18, 77.12 (dd, J = 30, 20 Hz), 70.93, 66.90, 39.20, 19.26; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)): \(\delta\) -80.75 (d, J = 254 Hz, 1F), -94.91 (d, J = 254 Hz, 1F); IR: (KBr) \(v_{\text{max}}\) 3409, 2927, 1668, 1609, 1482, 1259, 1461, 1089, 738; HRMS (EI): Exact mass calcd for \(\text{C}_{26}\text{H}_{21}\text{F}_{2}\text{N}_3\) [M]: 413.1704, Found: 413.1691.
The reaction was run at rt for 36 h, affording product 3r in 64% yield as a yellow solid (m.p. 124-126 °C); "H NMR (500 MHz, CDCl3): δ 1.76 (s, 3H), 2.14-2.19 (m, 1H), 2.26-2.32 (m, 1H), 4.44-4.50 (m, 1H), 4.56-4.63 (m, 1H), 4.72 (brs, 1H), 4.79 (s, 1H), 5.74 (d, J = 10 Hz, 1H), 6.35 (d, J = 5 Hz, 1H), 6.43 (t, J = 10 Hz, 1H), 7.06-7.09 (m, 2H), 7.32-7.38 (m, 2H), 7.49-7.53 (m, 4H), 7.57-7.58 (m, 1H), 7.64-7.66 (m, 1H), 7.84 (s, 1H); 13C NMR (125 MHz, CDCl3): 175.36 (d, J = 3.8 Hz), 151.67 (dd, J = 7.5, 6.3 Hz), 148.83, 133.29, 133.23, 132.87, 132.58, 131.70 (d, J = 6.3 Hz), 128.76, 128.64, 127.81, 127.36, 127.29, 125.72, 125.58, 124.87, 124.66, 123.98 (dd, J = 259, 241 Hz), 123.30, 122.45 (dd, J = 27, 25 Hz), 122.27, 121.58, 112.50, 107.19, 87.08, 77.69 (dd, J = 30, 20 Hz), 70.93, 66.72, 35.11, 17.63; 19F NMR (471 MHz, CDCl3): δ -79.72 (d, J = 254 Hz, 1F), -95.79 (d, J = 254 Hz, 1F); IR: (KBr) vmax 3300, 2925, 1671, 1608, 1480, 1265, 1090, 808; HRMS (EI): Exact mass calecd for C30H23F2N3 [M]+: 463.1860, Found: 463.1858.

The reaction was run at rt for 36 h, affording product 3s in 68% yield as a yellow solid (m.p. 142-146 °C); "H NMR (500 MHz, CDCl3): δ 1.60 (s, 3H), 2.25-2.27 (m, 2H), 4.44-4.55 (m, 3H), 4.94 (s, 1H), 6.20-6.21 (m, 2H), 6.26 (s, 1H), 7.05-7.08 (m, 2H), 7.32-7.38 (m, 2H), 7.48-7.56 (m, 4H), 7.58 (d, J = 10 Hz, 1H), 7.65 (d, J = 10 Hz, 1H), 7.76 (s, 1H); 13C NMR (125 MHz, CDCl3): 179.76 (d, J = 3.8 Hz), 151.51 (dd, J = 7.6, 5.8 Hz), 145.93, 133.29, 132.76, 132.43, 131.80 (d, J = 6.3 Hz), 130.48, 129.05, 128.83, 127.29, 127.20, 127.14, 126.24, 125.83, 125.49, 124.75, 123.96, 123.78 (dd, J = 260, 243 Hz), 123.14, 122.30 (dd, J = 27, 25 Hz), 122.15, 112.17, 109.25, 85.40, 77.69 (dd, J = 31, 21 Hz), 71.57, 67.03, 38.29, 20.03; 19F NMR (471 MHz, CDCl3): δ -81.92 (d, J = 254 Hz, 1F), -95.22 (d, J = 254 Hz, 1F); IR: (KBr) vmax 3421, 2930, 1665, 1610, 1487, 1255, 1073, 766; HRMS (EI): Exact mass calecd for C30H23F2N3 [M]+: 463.1860, Found: 463.1866.

The reaction was run at rt for 36 h, affording product 3t in 71% yield as a yellow solid (m.p. 159-164 °C); "H NMR (500 MHz, CDCl3): δ 2.26-2.28 (m, 2H), 3.11 (s, 3H), 4.47-4.50 (m, 3H), 4.95 (s, 1H), 6.03 (dd, J = 10, 5 Hz, 1H), 6.06 (d, J = 5 Hz, 1H), 6.28 (d, J = 10 Hz, 1H), 7.06-7.09 (m, 2H), 7.33-7.38 (m, 2H), 7.48-7.53 (m, 2H), 7.56-7.61 (m, 3H), 7.65-7.68 (m, 1H), 7.80 (s, 1H); 13C NMR (125 MHz, CDCl3): 179.47 (d, J = 2.5 Hz), 153.69, 151.45 (dd, J = 7.5, 5
Hz), 142.35, 133.32, 132.79, 132.46, 131.83 (d, J = 5 Hz), 131.72, 127.85, 127.33, 127.24, 126.10, 125.89, 125.58, 124.72, 123.96, 123.79 (dd, J = 260, 244 Hz), 122.29 (dd, J = 27, 25 Hz), 122.19, 114.29, 112.20, 110.14, 109.56, 85.77, 77.62 (dd, J = 31, 21 Hz), 71.93, 67.03, 55.96, 38.14; $^{19}$F NMR (471 MHz, CDCl$_3$): δ -82.40 (d, J = 254 Hz, 1F), -94.46 (d, J = 254 Hz, 1F); IR: (KBr) $v_{\text{max}}$ 3385, 2927, 1669, 1611, 1492, 1208, 811, 751; HRMS (EI): Exact mass calcd for C$_{30}$H$_{25}$F$_2$N$_3$O [$M^+$]: 479.1809, Found: 479.1808.

The reaction was run at rt for 36 h, affording product 3u in 86% yield as a yellow solid (m.p. 223-225 °C); $^1$H NMR (500 MHz, CDCl$_3$): δ 2.23-2.32 (m, 2H), 4.47-4.50 (m, 2H), 4.54 (s, 1H), 5.01 (s, 1H), 6.15 (td, J = 10, 5 Hz, 1H), 6.19 (dd, J = 10, 5 Hz, 1H), 6.28 (dd, J = 10, 5 Hz, 1H), 7.07-7.10 (m, 2H), 7.35-7.41 (m, 2H), 7.48-7.53 (m, 2H), 7.58-7.61 (m, 3H), 7.68 (d, J = 5 Hz, 1H), 7.83 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 179.12 (d, J = 2.5 Hz), 157.72, 155.84, 151.18 (dd, J = 7.5, 6.3 Hz), 144.31, 133.32, 132.85, 132.44, 131.35 (dd, J = 29, 7.5 Hz), 127.71, 127.50, 127.35, 126.21, 126.08, 125.81, 124.77, 123.88, 123.66 (dd, J = 260, 244 Hz), 122.31, 122.22 (dd, J = 27, 25 Hz), 114.71 (d, J = 24 Hz), 112.15, 109.57, 109.43 (d, J = 15 Hz), 85.37, 77.64 (dd, J = 31, 21 Hz), 71.54, 66.94, 38.72; $^{19}$F NMR (471 MHz, CDCl$_3$): δ -81.93 (d, J = 254 Hz, 1F), -96.32 (d, J = 250 Hz, 1F), -125.20 (s, 1F); IR: (KBr) $v_{\text{max}}$ 3416, 2912, 1684, 1607, 1466, 1108, 782; HRMS (EI): Exact mass calcd for C$_{20}$H$_{20}$F$_2$N$_3$ [M$^+$]: 467.1609, Found: 467.1603.

The reaction was run at rt for 36 h, affording product 3v in 78% yield as a yellow solid (m.p. 244-247 °C); $^1$H NMR (500 MHz, CDCl$_3$): δ 2.21-2.32 (m, 2H), 4.44-4.55 (m, 2H), 4.62 (s, 1H), 5.01 (s, 1H), 6.13 (d, J = 10 Hz, 1H), 6.34 (dd, J = 10, 5 Hz, 1H), 6.51 (d, J = 5 Hz, 1H), 7.05-7.10 (m, 2H), 7.36-7.42 (m, 2H), 7.50-7.56 (m, 3H), 7.59-7.62 (m, 2H), 7.69 (d, J = 5 Hz, 1H), 7.79 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 178.99 (d, J = 3.8 Hz), 151.08 (dd, J = 7.5, 6.3 Hz), 146.86, 133.31, 132.90, 132.41, 131.78, 131.03 (d, J = 5 Hz), 128.09, 127.76, 127.47, 127.35, 126.50, 126.15, 125.83, 124.83, 123.93, 123.80, 123.52 (dd, J = 260, 243 Hz), 122.56, 122.35, 122.19 (dd, J = 27, 25 Hz), 112.08, 109.66, 84.96, 77.76 (dd, J = 31, 21 Hz), 71.12, 67.00, 38.68; $^{19}$F NMR (471 MHz, CDCl$_3$): δ -80.93 (d, J = 259 Hz, 1F), -97.90 (d, J = 259 Hz, 1F); IR: (KBr) $v_{\text{max}}$ 3482, 2935, 1667, 1598, 1432, 1204, 741; HRMS (EI): Exact mass calcd for C$_{20}$H$_{20}$ClF$_2$N$_3$ [M$^+$]: 483.1314, Found: 483.1310.
The reaction was run at rt for 36 h, affording product 3w in 52% yield as a yellow solid (m.p. 125-128 °C); 1H NMR (500 MHz, CDCl3): δ 2.21-2.32 (m, 2H), 4.44-4.54 (m, 2H), 4.62 (brs, 1H), 5.00 (s, 1H), 6.09 (d, J = 5 Hz, 1H), 6.47 (dd, J = 10, 5 Hz, 1H), 6.63 (d, J = 5 Hz, 1H), 7.05-7.10 (m, 2H), 7.36-7.43 (m, 2H), 7.50-7.56 (m, 3H), 7.59-7.62 (m, 2H), 7.69 (d, J = 10 Hz, 1H), 7.78 (s, 1H); 13C NMR (125 MHz, CDCl3): 178.96 (d, J = 3.8 Hz), 151.07 (dd, J = 7.5, 6.3 Hz), 147.31, 133.31, 132.92, 132.41, 132.23, 131.02 (d, J = 5 Hz), 130.92, 127.81, 127.47, 127.38, 126.55, 126.16, 125.84, 125.47, 124.85, 123.92, 123.49 (dd, J = 260, 243 Hz), 122.36, 122.19 (dd, J = 27, 25 Hz), 112.07, 110.79, 110.14, 84.88, 77.79 (dd, J = 31, 21 Hz), 71.03, 67.02, 38.61; 19F NMR (471 MHz, CDCl3): δ -80.78 (d, J = 259 Hz, 1F), -98.11 (d, J = 259 Hz, 1F); IR: (KBr) νmax 3223, 2930, 1668, 1469, 1308, 1091, 747; HRMS (EI): Exact mass calced for C20H20BrF2N3 [M]+: 527.0809, Found: 527.0804.

The reaction was run at rt for 36 h, affording product 3x in 53% yield as a yellow solid (m.p. 130-133 °C); 1H NMR (500 MHz, CDCl3): δ 1.69 (s, 3H), 2.21-2.28 (m, 2H), 4.41-4.52 (m, 2H), 4.58 (brs, 1H), 4.98 (s, 1H), 5.85 (d, J = 10 Hz, 1H), 6.10 (s, 1H), 6.38 (d, J = 5 Hz, 1H), 7.05-7.08 (m, 2H), 7.34-7.37 (m, 2H), 7.48-7.52 (m, 2H), 7.55-7.58 (m, 3H), 7.65-7.67 (m, 1H), 7.77 (s, 1H); 13C NMR (125 MHz, CDCl3): 179.98 (d, J = 3.8 Hz), 151.35 (dd, J = 7.5, 6.3 Hz), 148.47, 138.77, 133.25, 132.74, 132.44, 131.64 (d, J = 5 Hz), 127.78, 127.44, 127.25, 127.24, 126.11, 125.75, 125.50, 124.73, 123.97, 123.74 (dd, J = 260, 244 Hz), 122.28 (dd, J = 27, 25 Hz), 122.13, 122.04, 120.22, 112.18, 109.81, 85.04, 77.74 (dd, J = 31, 20 Hz), 71.06, 66.92, 38.64, 20.82; 19F NMR (471 MHz, CDCl3): δ -81.53 (d, J = 254 Hz, 1F), -96.34 (d, J = 250 Hz, 1F); IR: (KBr) νmax 3289, 2971, 1665, 1608, 1508, 1470, 1063, 742; HRMS (EI): Exact mass calced for C20H20BrF2N3 [M]+: 463.1860, Found: 463.1856.

The reaction was run at rt for 36 h, affording product 3y in 51% yield as a yellow solid (m.p. 141-142 °C); 1H NMR (500 MHz, CDCl3): δ 1.92 (s, 3H), 2.20-2.26 (m, 1H), 2.30-2.34 (m, 1H), 4.41-4.55 (m, 3H), 5.06 (s, 1H), 6.05 (t, J = 10 Hz, 1H), 6.24 (d, J = 5 Hz, 1H), 6.45 (d, J = 10 Hz, 1H), 7.07 (t, J = 10 Hz, 1H), 7.12 (d, J = 5 Hz, 1H), 7.32-7.38 (m, 2H), 7.49-7.57 (m, 4H), 7.64 (d, J = 10 Hz, 2H), 7.82 (s, 1H); 13C NMR (125 MHz, CDCl3): 179.91 (d, J = 2.5 Hz), 151.21 (dd, J = 7.5, 5 Hz), 146.79, 133.22, 132.85, 132.50, 131.26 (d, J = 5 Hz), 129.55,
129.05, 127.70, 127.25, 127.03, 125.96, 125.85, 125.57, 124.74, 123.95, 123.57 (dd, J = 260, 244 Hz), 122.13, 122.09 (dd, J = 27, 25 Hz), 119.66, 119.55, 118.27, 112.16, 84.41, 77.78 (dd, J = 31, 20 Hz), 71.49, 66.90, 39.07, 16.42. $^{19}$F NMR (471 MHz, CDCl$_3$): δ -79.93 (d, J = 254 Hz, 1F), -99.45 (d, J = 254 Hz, 1F); IR: (KBr) $\nu$ max 3415, 2927, 1665, 1609, 1495, 1468, 1259, 1091, 752; HRMS (EI): Exact mass calcd for C$_{30}$H$_{25}$F$_{2}$N$_{3}$ [M]$^+$: 463.1860, Found: 463.1857.

The reaction was run at rt for 48 h, affording product 5a in 65% yield as a yellow foamy solid (m.p. 138-141 °C); $^1$H NMR (500 MHz, CDCl$_3$): δ 2.29-2.38 (m, 2H), 4.34-4.39 (m, 1H), 4.43-4.49 (m, 1H), 4.73 (brs, 1H), 4.98 (s, 1H), 6.44 (t, J = 10 Hz, 1H), 6.52 (d, J = 10 Hz, 1H), 6.69 (d, J = 5 Hz, 1H), 6.86 (t, J = 10 Hz, 1H), 6.99-7.07 (m, 4H), 7.19 (d, J = 10 Hz, 1H), 7.43-7.45 (m, 2H), 7.61-7.65 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 194.95, 178.36, 162.08, 148.14, 137.43, 135.15, 129.50, 128.84, 127.85, 127.55, 125.97, 125.12, 122.69, 122.15, 121.19, 119.82, 113.35, 109.50, 84.75, 77.31, 73.32, 66.12, 38.99; IR: (KBr) $\nu$ max 3365, 2931, 1711, 1663, 1605, 1472, 1320, 1153, 739; HRMS (EI): Exact mass calcd for C$_{25}$H$_{19}$N$_{3}$O [M]$^+$: 377.1528, Found: 377.1525.

The reaction was run at rt for 48 h, affording product 5b in 54% yield as a yellow foamy solid (m.p. 155-157 °C); $^1$H NMR (500 MHz, CDCl$_3$): δ 2.31-2.40 (m, 2H), 4.38-4.43 (m, 1H), 4.47-4.54 (m, 1H), 4.82 (brs, 1H), 5.03 (s, 1H), 6.24 (td, J = 10, 5 Hz, 1H), 6.47 (d, J = 5 Hz, 1H), 6.62-6.67 (m, 2H), 7.06 (t, J = 10 Hz, 1H), 7.24 (d, J = 10 Hz, 1H), 7.31-7.35 (m, 2H), 7.54 (d, J = 5 Hz, 1H), 7.59-7.68 (m, 5H), 7.85 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 195.07, 178.36, 162.15, 148.09, 137.49, 132.76, 132.69, 132.68, 129.45, 128.83, 127.85, 127.76, 127.31, 126.00, 125.64, 125.55, 124.56, 122.93, 122.47, 122.23, 121.28, 119.75, 113.45, 109.38, 84.86, 77.44, 73.41, 66.17, 38.97; IR: (KBr) $\nu$ max 3367, 2926, 1714, 1666, 1604, 1473, 1321, 1156, 744; HRMS (EI): Exact mass calcd for C$_{29}$H$_{21}$N$_{3}$O [M]$^+$: 427.1685, Found: 427.1677.

The reaction was run at rt for 36 h, affording product 5c in 56% yield as a yellow oil; $^1$H NMR (500 MHz, CDCl$_3$): δ 2.28-2.37 (m, 2H), 2.52 (s, 3H), 4.35-4.40 (m, 1H), 4.43-4.49 (m, 1H), 4.71 (brs, 1H), 4.96 (s, 1H), 6.42 (t, J = 5 Hz, 1H), 6.52 (d, J = 5 Hz, 1H), 6.68 (d, J = 5 Hz, 1H), 6.79 (d, J = 5 Hz, 1H), 6.85 (t, J = 5 Hz, 1H), 6.98-7.05 (m, 4H), 7.43-7.49 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 195.60, 178.65, 162.71, 148.19, 141.56, 136.73, 135.53, 129.59, 128.80, 127.82, 127.48, 125.08, 123.84,
122.72, 119.80, 118.94, 110.54, 109.50, 84.86, 76.95, 73.10, 66.14, 38.93, 18.10; IR: (KBr) ν<sub>max</sub> 3391, 2928, 1704, 1665, 1596, 1485, 1314, 1029, 746; HRMS (EI): Exact mass calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O [M]<sup>+</sup>: 391.1685, Found: 391.1682.

The reaction was run at rt for 36 h, affording product 5d in 61% yield as a yellow oil; ¹H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.28-2.32 (m, 2H), 2.33 (s, 3H), 4.33-4.38 (m, 1H), 4.42-4.49 (m, 1H), 4.71 (brs, 1H), 4.93 (s, 1H), 6.43 (t, J = 5 Hz, 1H), 6.52 (d, J = 5 Hz, 1H), 6.68 (d, J = 10 Hz, 1H), 6.85 (td, J = 10, 5 Hz, 1H), 6.98-7.05 (m, 3H), 7.10 (d, J = 10 Hz, 1H), 7.41-7.47 (m, 4H); ¹³C NMR (125 MHz, CDCl<sub>3</sub>): 194.99, 178.53, 160.43, 148.20, 138.64, 135.33, 131.95, 129.57, 128.80, 127.80, 127.46, 125.42, 125.15, 122.69, 121.20, 119.77, 113.23, 109.50, 84.89, 77.68, 73.28, 66.15, 39.01, 20.56; IR: (KBr) ν<sub>max</sub> 3390, 2925, 1714, 1667, 1620, 1487, 1340, 1045, 745; HRMS (EI): Exact mass calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O [M]<sup>+</sup>: 391.1685, Found: 391.1686.

The reaction was run at rt for 36 h, affording product 5e in 37% yield as a yellow oil; ¹H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.27-2.37 (m, 2H), 2.65 (s, 3H), 4.36-4.40 (m, 1H), 4.43-4.49 (m, 1H), 4.83 (brs, 1H), 5.04 (s, 1H), 6.44 (t, J = 10 Hz, 1H), 6.57 (d, J = 10 Hz, 1H), 6.68 (d, J = 10 Hz, 1H), 6.88 (td, J = 10, 5 Hz, 1H), 6.98-7.05 (m, 4H), 7.45-7.50 (m, 4H); ¹³C NMR (125 MHz, CDCl<sub>3</sub>): 195.13, 178.48, 161.16, 147.93, 139.30, 135.35, 129.71, 128.84, 127.80, 127.46, 125.08, 124.41, 123.55, 122.74, 122.66, 121.92, 119.91, 109.52, 83.12, 77.36, 72.79, 66.07, 39.24, 18.95; IR: (KBr) ν<sub>max</sub> 3413, 2929, 1713, 1667, 1602, 1486, 1317, 1052, 739; HRMS (EI): Exact mass calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O [M]<sup>+</sup>: 391.1685, Found: 391.1682.

The reaction was run at rt for 48 h, affording product 5f in 40% yield as a yellow oil; ¹H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.84 (s, 3H), 2.17-2.22 (m, 1H), 2.33-2.39 (m, 1H), 4.35-4.41 (m, 1H), 4.48-4.53 (m, 1H), 4.75 (brs, 1H), 4.78 (s, 1H), 6.16 (d, J = 5 Hz, 1H), 6.49 (d, J = 5 Hz, 1H), 6.79 (t, J = 5 Hz, 1H), 7.00-7.07 (m, 4H), 7.18 (d, J = 10 Hz, 1H), 7.43-7.47 (m, 2H), 7.62-7.65 (m, 2H); ¹³C NMR (125 MHz, CDCl<sub>3</sub>): 195.36, 174.68, 162.27, 148.79, 137.41, 134.80, 133.70, 129.00, 128.08, 127.76, 127.48, 125.92, 124.71, 122.26, 121.94, 121.73, 113.61, 107.59, 86.57, 77.21, 72.79, 65.94, 35.04, 17.52; IR: (KBr) ν<sub>max</sub> 3375, 2923, 1715, 1668, 1606, 1473, 1322, 1051, 744; HRMS (EI): Exact mass calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O [M]<sup>+</sup>: 391.1685, Found: 391.1682.
The reaction was run at rt for 48 h, affording product 5g in 44% yield as a yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 2.27-2.37 (m, 2H), 3.52 (s, 3H), 4.34-4.47 (m, 2H), 4.52 (brs, 1H), 4.94 (s, 1H), 6.22 (d, \(J = 2.5\) Hz, 1H), 6.44-6.49 (m, 2H), 7.00-7.06 (m, 4H), 7.19 (d, \(J = 5\) Hz, 1H), 7.43-7.45 (m, 2H), 7.61-7.65 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 194.91, 178.10, 162.19, 154.21, 142.29, 137.44, 135.30, 131.04, 127.86, 127.54, 125.95, 125.14, 122.19, 121.28, 115.00, 113.39, 110.66, 109.08, 85.74, 77.31, 73.84, 66.17, 56.21, 38.35; IR: (KBr) \(\nu_{\max}\) 3382, 2929, 1715, 1665, 1605, 1492, 1321, 1042, 754; HRMS (EI): Exact mass calcd for C\(_{26}\)H\(_{21}\)N\(_3\)O\(_2\) \([M]^+\): 407.1634, Found: 407.1636.

The reaction was run at rt for 48 h, affording product 5h in 60% yield as a yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 2.28-2.38 (m, 2H), 4.34-4.46 (m, 2H), 4.66 (brs, 1H), 4.99 (s, 1H), 6.38 (dd, \(J = 10, 5\) Hz, 1H), 6.44 (dd, \(J = 10, 5\) Hz, 1H), 6.56 (td, \(J = 10, 5\) Hz, 1H), 7.02-7.08 (m, 4H), 7.18 (d, \(J = 10\) Hz, 1H), 7.44-7.46 (m, 2H), 7.61-7.65 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 194.67, 177.72, 161.93, 158.15, 156.26, 144.35, 137.48, 134.96, 130.89 (d, \(J = 7.5\) Hz), 128.00, 127.80, 126.01, 125.13, 122.30, 121.17, 115.25 (d, \(J = 24\) Hz), 113.33, 110.08 (d, \(J = 7.5\) Hz), 109.81 (d, \(J = 25\) Hz), 85.43, 77.20, 73.49, 66.12, 38.69; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)): δ -124.63 (s, 1F); IR: (KBr) \(\nu_{\max}\) 3398, 2925, 1712, 1665, 1622, 1482, 1260, 740; HRMS (EI): Exact mass calcd for C\(_{25}\)H\(_{18}\)F\(_3\)N\(_3\)O \([M]^+\): 395.1434, Found: 395.1440.

4. Transformation of compound 3b
To a dried 10.0 mL Schlenk tube were successively added compound 3b (41.7 mg, 0.1 mmol), m-CPBA (51.6 mg, 0.3 mmol), CH₂Cl₂ (2.0 mL) and potassium hydroxide (28 mg, 0.5 mmol) at -10 °C. The resulting reaction mixture was then stirred at 25 °C for 3 h till full consumption of compound 3b as monitored by TLC. The crude reaction mixture was directly purified by column chromatography using CH₂Cl₂/EtOAc (from 10:1) as the eluent to provide the corresponding product 6 in 27% yield as a yellow oil (12.1 mg).

**Data of compound 6**: ¹H NMR (300 MHz, CDCl₃): δ 2.69-2.75 (m, 1H), 2.91-3.02 (m, 1H), 4.12-4.23 (m, 1H), 4.42-4.50 (m, 1H), 5.70 (dd, J = 9, 1.5 Hz, 1H), 6.62-6.68 (m, 2H), 7.05-7.10 (m, 3H), 7.31 (t, J = 9 Hz, 1H), 7.44 (td, J = 9, 3 Hz, 1H), 7.51 (d, J = 9 Hz, 1H), 7.60-7.65 (m, 2H), 7.89 (d, J = 9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): 170.86, 170.18, 163.55, 161.57, 161.54, 141.62, 139.18 (dd, J = 6.5, 5.1 Hz), 135.52, 133.17 (d, J = 2.5 Hz), 128.77, 128.49, 127.85, 127.12, 127.11, 126.66 (dd, J = 28, 25 Hz), 126.55 (d, J = 1.3 Hz), 124.61, 122.34 (dd, J = 260, 253 Hz), 117.68 (d, J = 1.3 Hz), 115.13 (d, J = 23 Hz), 104.97, 77.16 (dd, J = 23, 20 Hz), 70.13, 64.09, 37.53; ¹⁹F NMR (282 MHz, CDCl₃): δ -79.87 (d, J = 240 Hz, 1F), -111.33 (d, J = 240 Hz, 1F), -112.41 (s, 1F); IR: (KBr) ν<sub>max</sub> 2943, 1690, 1645, 1594, 1432, 1002, 744; HRMS (ESI): Exact mass calcd for C₂₅H₁₆F₃N₃O₂ [M+H]<sup>+</sup>: 448.1267, Found: 448.1265.

5. X-Ray crystallographic data for compounds 3p, 5a and 6

Compound 3p
Data intensity of 3p was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 100(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F² with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number: 1830099 (3p).

Crystal data

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X-ray structure of product 3p
Compound 5a

Data intensity of 5a was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 100(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number: 1830098 (5a).

Crystal data.

Identification code exp_234
Empirical formula C$_{25}$H$_{19}$N$_3$O
Formula weight 377.43
Temperature/K 100.01(10)
Crystal system triclinic
Space group P-1

$\alpha$/Å 8.2339(2)
$\beta$/Å 14.7918(4)
$\gamma$/Å 17.1794(5)
$\alpha$/ 101.330(2)
$\beta$/ 95.203(2)
$\gamma$/ 106.126(2)
Volume/Å$^3$ 1947.28(9)
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F(000) 792.0
Crystal size/mm$^3$ 0.45 × 0.38 × 0.34
Radiation CuKα ($\lambda = 1.54184$)

2θ range for data collection/° 9.216 to 134.14
Index ranges $-9 \leq h \leq 5$, $-17 \leq k \leq 17$, $-19 \leq l \leq 20$
Reflections collected 19522
Independent reflections 6920 [$R_{\text{int}} = 0.0399$, $R_{\text{sigma}} = 0.0407$]
Data/restraints/parameters 6920/0/527

Goodness-of-fit on $F^2$ 1.030
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Final R indexes [all data] $R_1 = 0.0445$, $wR_2 = 0.1005$
Largest diff. peak/hole / e Å$^{-3}$ 0.38/-0.31
Compound 6

Data intensity of 6 was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 100(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on \( F^2 \) with anisotropic displacement parameters for non-H atoms using SHELX-97. CCDC deposition number: 1830573 (6).
6. Copies of $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR Spectra
S50