Supporting Information

for

Cascade trifluoromethylthiolation and cyclization of N-[(3-aryl)propioloyl]indoles

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Experimental procedures, spectroscopic and X-ray data (CCDC 1968129 for compound 2a) and copies of NMR spectra
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1. **General information**

$^1$H and $^{19}$F NMR (CFCl$_3$ as external standard and low field is positive) spectra were recorded on a Bruker AM 400 spectrometer. $^{13}$C NMR spectra were recorded on a Bruker AM 400 or Bruker 600 spectrometers. Chemical shifts ($\delta$) were reported in ppm, and coupling constants ($J$) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by $^{19}$F NMR using (trifluoromethyl)benzene as an internal standard before working up the reaction. High resolution mass spectra (HRMS) were performed using a GC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system or as electron spray ionization (ESI/HRMS) using a Thermo Fischer Scientific LTQ FT Ultra instrument in DART-positive mode.

**Materials:** Unless otherwise noted, all reagents were obtained commercially and used without further purification. Reactions were performed under an atmosphere of N$_2$ using glassware that flame-dried under vacuum. AgSCF$_3$ was prepared following the literature.

2. **Preparation of substrates**

General procedure for the preparation of $N$-[(3-phenyl)propioloyl]indoles [1]

A solution of 3-phenylpropionic acid (1.46 g, 10.0 mmol, 1.0 equiv) and DMF (4 drops) in CH$_2$Cl$_2$ (25 mL) was prepared and cooled to 0 °C. A bubbler was attached to the vessel and (COCl)$_2$ (1.69 mL, 20.0 mmol, 2.0 equiv) was added dropwise. After 5 minutes, the reaction was allowed to warm to room temperature and stirred for 1 hour. The acyl chloride was concentrated in vacuo and redissolved in CH$_2$Cl$_2$. A solution of the indoles (10.0 mmol, 1.0 equiv), DMAP (61.1 mg, 0.5 mmol, 0.05 equiv) and NEt$_3$ (2.78 mL, 20.0 mmol, 2.0 equiv) in CH$_2$Cl$_2$ (20 mL) was prepared and cooled to 0 °C. The acyl chloride solution was added dropwise into the vessel containing indoles. After
5 minutes, the reaction was allowed to warm to room temperature and was stirred overnight. The reaction was quenched with a saturated NaHCO$_3$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The reaction was purified by a silica gel column chromatography to give product.

1-(1H-Indol-1-yl)-3-phenylprop-2-yn-1-one (1a)

![Chemical Structure](image)

Yield: 593.6 mg, 24%; Yellow solid; m.p. 88-90 °C (lit. [1]: 87–88 °C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 8.39 (d, $J = 8.1$ Hz, 1H), 7.74 (d, $J = 3.8$ Hz, 1H), 7.60-7.55 (m, 2H), 7.51-7.44 (m, 1H), 7.42-7.36 (m, 1H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.29-7.24 (m, 1H), 7.25-7.16 (m, 1H), 6.58 (d, $J = 3.8$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 149.6, 134.0, 131.8, 131.2, 129.9, 127.7, 125.4, 124.1, 123.3, 119.9, 118.3, 115.6, 108.8, 90.8, 80.7. HRMS (ESI-TOF): $m/z$ Calculated for C$_{17}$H$_{12}$NO [M+H]$^+$: 246.0913; Found: 246.0914. Note: the IR data are compatible with the data reported in ref. [1].

1-(5-Methoxy-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1b)

![Chemical Structure](image)

Yield: 605.2 mg, 22%; Yellow solid; m.p. 104-106 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 8.29 (d, $J = 8.9$ Hz, 1H), 7.73 (d, $J = 3.8$ Hz, 1H), 7.63-7.56 (m, 2H), 7.45-7.39 (m, 1H), 7.39-7.35 (m, 2H), 6.96 (d, $J = 2.5$ Hz, 1H), 6.89 (dd, $J = 9.0$, 2.5 Hz, 1H), 6.54 (d, $J = 3.8$ Hz, 1H), 3.79 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 156.0, 131.8, 131.2, 129.9, 128.8, 127.7, 126.1, 118.4, 116.4, 112.3, 108.7, 103.0, 90.9, 80.7, 54.6. IR (thin film) $\nu$ 3065, 2923, 2830, 2204, 1657, 1581, 1476, 1382, 1279, 1092 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{18}$H$_{14}$NO$_2$ [M+H]$^+$: 276.1019; Found: 276.1020.
1-(5-Nitro-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1c)

![Chemical structure of 1c]

Yield: 498.6 mg, 17%; Yellow solid; m.p. 120-122 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.51 (d, $J = 9.1$ Hz, 1H), 8.42 (d, $J = 2.2$ Hz, 1H), 8.18 (dd, $J = 9.1$, 2.3 Hz, 1H), 7.94 (d, $J = 3.8$ Hz, 1H), 7.69-7.56 (m, 2H), 7.52-7.44 (m, 1H), 7.42-7.32 (m, 2H), 6.76 (d, $J = 3.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 149.5, 143.6, 137.0, 132.0, 130.5, 130.0, 128.2, 127.8, 119.4, 117.7, 116.1, 115.5, 108.8, 92.5, 80.1. IR (thin film) ν 3123, 2951, 2261, 2207, 1971, 1675, 1518, 1445, 1324, 1194 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{17}$H$_{11}$N$_2$O$_3$ [M+H]$^+$: 291.0764; Found: 291.0766.

1-(3-Phenylpropioloyl)-1H-indole-5-carbonitrile (1d)

![Chemical structure of 1d]

Yield: 830.7 mg, 31%; Yellow solid; m.p. 112-114 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.47 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 3.8$ Hz, 1H), 7.81 (s, 1H), 7.63-7.57 (m, 2H), 7.52 (dd, $J = 8.6$, 1.6 Hz, 1H), 7.48-7.42 (m, 1H), 7.41-7.33 (m, 2H), 6.66 (d, $J = 3.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 149.5, 135.8, 131.9, 130.4, 130.1, 127.8, 127.5, 127.3, 124.6, 118.3, 117.8, 116.2, 108.0, 106.7, 92.2, 80.2. IR (thin film) ν 3135, 3144, 2243, 2231, 1663, 1612, 1488, 1463, 1364, 1191 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{18}$H$_{11}$N$_2$O [M+H]$^+$: 271.0866; Found: 271.0867.

Methyl 1-(3-phenylpropioloyl)-1H-indole-5-carboxylate (1e)

![Chemical structure of 1e]

Yield: 1.03 g, 34%; Yellow solid; m.p. 110-112 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.41 (d, $J = 8.7$ Hz, 1H), 8.21 (d, $J = 1.7$ Hz, 1H), 7.97 (dd, $J = 8.7$, 1.7 Hz, 1H), 7.81 (d, $J = 3.8$ Hz, 1H), 7.60 (d, $J = 6.9$ Hz, 2H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 2H), 6.66 (d, $J = 3.8$ Hz, 1H), 3.86 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.1,
149.6, 136.6, 131.9, 130.2, 129.9, 127.8, 126.6, 125.5, 125.2, 122.1, 118.0, 115.1, 109.0, 91.6, 80.5, 51.1. IR (thin film) ν 3150, 3072, 2948, 2207, 1778, 1714, 1672, 1436, 1291, 1197 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₉H₁₄NO₃ [M+H]⁺: 304.0968; Found: 304.0969.

1-(3-Phenylpropioloyl)-1H-indole-5-carbaldehyde (1f)

Yield: 818.4 mg, 30%; Yellow solid; m.p. 90-92 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 9.97 (s, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.00 (s, 1H), 7.84 (d, J = 3.8 Hz, 1H), 7.79 (dd, J = 8.6, 1.6 Hz, 1H), 7.61-7.56 (m, 2H), 7.46-7.40 (m, 1H), 7.38-7.32 (m, 2H), 6.70 (d, J = 3.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 190.8, 149.6, 137.4, 131.9, 130.3, 127.8, 127.1, 125.4, 122.6, 117.9, 115.8, 108.9, 91.9, 80.4. IR (thin film) ν 3395, 3371, 3147, 2745, 2216, 1702, 1669, 1436. HRMS (ESI-TOF): m/z Calculated for C₁₈H₁₂NO₂ [M+H]⁺: 274.0863; Found: 274.0863.

1-(5-Fluoro-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1g)

Yield: 1.05 g, 40%; Yellow solid; m.p. 95-97 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.30 (dd, J = 9.0, 4.7 Hz, 1H), 7.74 (d, J = 3.8 Hz, 1H), 7.62-7.47 (m, 2H), 7.42-7.34 (m, 1H), 7.34-7.24 (m, 2H), 7.10 (dd, J = 8.7, 2.5 Hz, 1H), 6.96 (td, J = 9.1, 2.6 Hz, 1H), 6.51 (d, J = 4.3 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ ppm -117.86 (s, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 158.9 (d, J = 242.4 Hz), 149.4, 131.8, 131.1 (d, J = 10.1 Hz), 130.3, 130.0, 127.6, 126.9, 118.1, 116.5, 111.7 (d, J = 24.9 Hz), 108.3 (d, J = 3.8 Hz), 105.7 (d, J = 24.1 Hz), 90.9, 80.3. IR (thin film) ν 3150, 3144, 3052, 2237, 1663, 1615, 1445, 1370, 1185 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₇H₁₁FNO [M+H]⁺: 264.0819; Found: 264.0820.
1-(5-Chloro-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1h)

![Chemical structure]

Yield: 390.9 mg, 14%; Yellow solid; m.p. 100-102 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.28 (d, $J = 8.7$ Hz, 1H), 7.74 (d, $J = 3.8$ Hz, 1H), 7.56 (d, $J = 6.9$ Hz, 2H), 7.44-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.20 (dd, $J = 8.8$, 2.1 Hz, 1H), 6.50 (d, $J = 3.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 149.4, 132.3, 131.8, 131.3, 130.1, 128.8, 127.7, 126.6, 124.2, 119.6, 118.1, 116.4, 107.9, 91.1, 80.4. IR (thin film) ν 3117, 3069, 2234, 2195, 1663, 1448, 1358, 1201, 1080, 726 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{17}$H$_{11}$ClNO [M+H]$^+$: 280.0524; Found: 280.0521.

1-(5-Bromo-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1i)

![Chemical structure]

Yield: 450.8 mg, 14%; Yellow solid; m.p. 116-118 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.27 (d, $J = 8.7$ Hz, 1H), 7.77 (d, $J = 3.8$ Hz, 1H), 7.65-7.57 (m, 3H), 7.48-7.41 (m, 1H), 7.41-7.33 (m, 3H), 6.55 (d, $J = 3.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 149.6, 134.3, 131.8, 130.6, 130.1, 127.7, 126.2, 125.9, 125.1, 118.0, 114.4, 113.6, 108.3, 91.4, 80.4. IR (thin film) ν 3102, 3059, 2207, 2165, 1666, 1530, 1436, 1185, 1080, 729 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{17}$H$_{11}$BrNO [M+H]$^+$: 324.0019; Found: 324.0019.

1-(4-Methyl-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1j)

![Chemical structure]

Yield: 414.2 mg, 16%; Yellow solid; m.p. 85-87 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.21 (d, $J = 8.2$ Hz, 1H), 7.70 (d, $J = 3.9$ Hz, 1H), 7.58-7.49 (m, 2H), 7.40-7.34 (m, 1H), 7.34-7.25 (m, 2H), 7.15 (t, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 7.3$ Hz, 1H), 6.59 (d, $J = 3.8$ Hz, 1H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 149.7, 133.8, 131.8, 129.9,
129.6, 129.4, 127.6, 124.8, 124.2, 123.8, 118.3, 113.0, 107.1, 90.6, 80.8, 17.3. IR (thin film) ν 3108, 3062, 2213, 1292, 1654, 1536, 1330, 1249, 1222, 1149 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₈H₁₄NO [M+H]⁺: 260.1070; Found: 260.1070.

1-(4-Methoxy-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1k)

Yield: 358.9 mg, 13%; Yellow solid; m.p. 98-100 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.00 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 3.8 Hz, 1H), 7.59 (d, J = 6.9 Hz, 2H), 7.44-7.38 (m, 1H), 7.38-7.29 (m, 2H), 7.22 (t, J = 8.2 Hz, 1H), 6.73 (d, J = 3.8 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 151.7, 149.8, 135.2, 131.8, 129.9, 127.7, 125.2, 123.8, 120.1, 118.4, 108.6, 105.8, 103.9, 90.7, 80.8, 54.4. IR (thin film) ν 3335, 3117, 3008, 2839, 2204, 1666, 1488, 1346, 1170, 1064 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₈H₁₄NO₂ [M+H]⁺: 276.1019; Found: 276.1019.

Ethyl 1-(3-phenylpropioyl)-1H-indole-4-carboxylate (1l)

Yield: 1.04 g, 33%; Yellow solid; m.p. 120-122 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.60 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 1.0 Hz, 1H), 7.85 (d, J = 3.8 Hz, 1H), 7.63-7.53 (m, 2H), 7.47-7.38 (m, 1H), 7.37-7.25 (m, 4H), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 165.4, 149.7, 134.7, 131.9, 130.2, 130.1, 127.7, 127.1, 125.8, 123.6, 121.4, 119.8, 118.1, 109.3, 91.2, 80.5, 59.8, 13.3. IR (thin film) ν 2981, 2908, 2207, 1720, 1693, 1596, 1518, 1433, 1337, 1182 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₂₀H₁₆NO₃ [M+H]⁺: 318.1125; Found: 318.1126.
1-(6-Methyl-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1m)

Yield: 316.9 mg, 12%; Yellow solid; m.p. 98-100 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 8.25 (s, 1H), 7.71 (d, $J = 3.8$ Hz, 1H), 7.64-7.59 (m, 2H), 7.47-7.40 (m, 1H), 7.37 (t, $J = 7.4$ Hz, 3H), 7.07 (d, $J = 7.9$ Hz, 1H), 6.56 (d, $J = 3.8$ Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 149.8, 134.5, 134.4, 131.8, 129.9, 127.8, 127.7, 124.8, 119.5, 118.4, 116.1, 108.8, 90.5, 80.9, 20.8. IR (thin film) $\nu$ 2972, 2920, 2216, 2023, 1965, 1711, 1663, 1300, 1197, 1110 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{18}$H$_{14}$NO [M+H]$^+$: 260.1070; Found: 260.1069.

1-(6-Methoxy-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1n)

Yield: 528.6 mg, 19%; Yellow solid; m.p. 102-104 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 8.00 (d, $J = 2.3$ Hz, 1H), 7.67 (d, $J = 3.8$ Hz, 1H), 7.61 (dt, $J = 7.0$, 1.4 Hz, 2H), 7.47-7.41 (m, 1H), 7.40-7.33 (m, 3H), 6.87 (dd, $J = 8.5$, 2.4 Hz, 1H), 6.54 (d, $J = 3.7$ Hz, 1H), 3.82 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 157.3, 149.9, 135.1, 131.8, 129.9, 127.7, 124.2, 123.6, 120.3, 118.4, 112.5, 108.6, 99.8, 90.5, 80.9, 54.7. IR (thin film) $\nu$ 3055, 2922, 2830, 2220, 1657, 1555, 1476, 1330, 1250, 1092 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{18}$H$_{14}$NO$_2$ [M+H]$^+$: 276.1019; Found: 276.1020.

1-(6-Chloro-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (1o)

Yield: 893.8 mg, 32%; Yellow solid; m.p. 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 8.46 (s, 1H), 7.77 (d, $J = 3.8$ Hz, 1H), 7.62 (d, $J = 7.1$ Hz, 2H), 7.50-7.31 (m, 4H), 7.22 (dd, $J = 8.4$, 1.9 Hz, 1H), 6.59 (d, $J = 3.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 149.6, 136.6, 134.4, 131.9, 130.2, 128.6, 127.8, 126.0, 123.9, 120.7, 118.2, 115.8, 108.3, 92.4, 80.1. IR (thin film) $\nu$ 3156, 3065, 2189, 2204, 1666, 1533, 1324, 1185, 1074, 759 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{17}$H$_{11}$ClNO [M+H]$^+$: 280.0524; Found: 280.0525.
1-(3-Methyl-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (3a)

Yield: 621.5 mg, 24%; Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.45 (d, $J = 6.8$ Hz, 1H), 7.68-7.63 (m, 2H), 7.56 (s, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.44-7.37 (m, 2H), 7.38-7.26 (m, 2H), 2.28 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 150.5, 135.5, 132.9, 132.3, 131.0, 128.8, 125.3, 124.3, 123.3, 119.6, 119.3, 119.1, 116.8, 91.3, 81.9, 9.8. IR (thin film) ν 2210, 2005, 1651, 1500, 1388, 1352, 1188, 1074, 898, 735 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{18}$H$_{14}$NO [M+H]$^+$: 260.1070; Found: 260.1071.

3-Phenyl-1-(3-phenyl-1H-indol-1-yl)prop-2-yn-1-one (3b)

Yield: 867.4 mg, 27%; Yellow solid; m.p. 110-112 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.49 (d, $J = 8.1$ Hz, 1H), 7.85 (s, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.60 (t, $J = 6.5$ Hz, 4H), 7.44-7.27 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 149.6, 134.8, 132.1, 131.8, 130.0, 128.8, 127.9, 127.7, 127.0, 126.6, 124.6, 123.7, 123.6, 122.0, 119.0, 118.3, 115.9, 90.9, 80.8. IR (thin film) ν 3075, 2216, 1726, 1678, 1609, 1494, 1460, 1396, 1276, 1210 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{23}$H$_{16}$NO [M+H]$^+$: 322.1226; Found: 322.1227.

1-(3-Phenylpropioyl)-1H-indole-3-carbonitrile (3c)

Yield: 643.3 mg, 24%; Yellow solid; m.p. 100-102 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.42 (d, $J = 8.3$ Hz, 1H), 8.31 (s, 1H), 7.72-7.61 (m, 3H), 7.54-7.45 (m, 1H), 7.45-7.36 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 150.4, 135.4, 132.8, 132.2, 130.9, 128.7, 125.3, 124.2, 123.2, 119.6, 119.2, 119.0, 116.8, 91.2, 81.9, 29.7. IR (thin film) ν
3150, 3062, 2249, 2198, 1687, 1606, 1442, 1361, 1182, 1040 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₈H₁₁N₂O [M+H]⁺: 271.0866; Found: 271.0867.

1-(3-Acetyl-1H-indol-1-yl)-3-phenylprop-2-yn-1-one (3d)

Yield: 918.1 mg, 32%; Yellow solid; m.p. 104-106 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.44-8.22 (m, 3H), 7.63 (d, J = 7.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.43-7.28 (m, 4H), 2.53 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 192.5, 149.6, 134.5, 131.9, 131.1, 130.5, 127.8, 126.8, 125.3, 124.7, 121.7, 121.3, 117.7, 115.0, 92.4, 80.1, 26.8. IR (thin film) ν 2954, 2225, 2138, 1720, 1684, 1503, 1435, 1197, 1083, 956 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₉H₁₄NO₂ [M+H]⁺: 288.1019; Found: 288.1020.

1-(1H-Indol-1-yl)-3-(p-tolyl)prop-2-yn-1-one (1p) [2]

To a solution of indole (292.8 mg, 2.5 mmol, 1.0 equiv) in CH₂Cl₂ (15 mL) was added 3-p-tolylpropionic acid (440.6 mg, 2.75 mmol, 1.1 equiv.) at 0 °C, then a mixture of DCC (773.6 mg, 3.75 mmol, 1.5 equiv) and DMAP (30.6 mg, 0.25 mmol, 0.1 equiv) in CH₂Cl₂ (10 mL) was added dropwise. The mixture was stirred at room temperature for 12 hours. Then, the crude was filtered and washed with CH₂Cl₂ and concentrated. The residue was purified by silica gel chromatography (hexane: EtOAc = 5:1) to give 1p (194.5 mg, 30%) as a yellow solid. m.p. 98-100 °C; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.52 (d, J = 8.2 Hz, 1H), 7.89 (s, 1H), 7.61 (d, J = 7.7 Hz, 3H), 7.41 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.31-7.24 (m, 3H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 150.9, 141.8, 135.1, 132.9, 131.1, 129.5, 126.6, 125.2, 124.3, 121.0, 116.7, 116.3, 109.7, 92.3, 81.5, 21.8. IR (thin film) ν 2917, 2204, 1748, 1669, 1590, 1497, 1442, 1346, 1089, 747 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₉H₁₄NO [M+H]⁺: 260.1070; Found: 260.1068.
3. General procedure for trifluoromethylthiolation and cyclization of N-[(3-aryl)propioloyl]indoles

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 1 or 3 (0.25 mmol, 1.0 equiv), AgSCF₃ (156.7 mg, 0.75 mmol, 3.0 equiv), (NH₄)₂S₂O₈ (171.2 mg, 0.75 mmol, 3.0 equiv) and NaHCO₃ (21.0 mg, 0.25 mmol, 1.0 equiv). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. Then DMSO (5.0 mL) was added by a syringe. The mixture was stirred at 80 °C for 12 h. A saturated ammonium chloride aqueous solution (5.0 mL) was added. The resulting mixture was filtered by Celite, eluted with ethyl acetate. The organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced vacuum. The residue purified with silica gel column chromatography to provide the pure product.

1-Phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2a)

Yield: 80.1 mg, 72%; Red solid; m.p. 118-120 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.79 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.52-7.46 (m, 5H), 7.39 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ ppm -39.99 (s, 3F), -40.88 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ ppm 160.1, 157.3, 142.1, 133.6, 133.2, 130.2, 128.7, 128.0, 127.4, 127.3 (q, J = 314 Hz), 127.2 (q, J = 313 Hz), 127.0, 123.8, 121.2, 118.6, 112.1, 105.3 (q, J = 2.6 Hz). IR (thin film) ν 2957, 2933, 2917, 2011, 1748, 1606, 1542, 1442, 1264, 1080 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₁₉H₁₀F₆NOS₂ [M+H]⁺: 446.0103; Found: 446.0130.
7-Methoxy-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2b)

Yield: 84.3 mg, 71%; Red solid; m.p. 110-112 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.70 (d, $J = 8.8$ Hz, 1H), 7.62-7.49 (m, 5H), 7.07 (s, 1H), 7.03 (d, $J = 8.8$ Hz, 1H), 3.84 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -40.11 (s, 3F), -40.94 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 161.0, 158.5, 157.4, 143.7, 135.8, 131.2, 129.1, 128.8, 128.4, 128.4 (q, $J = 313.1$ Hz), 128.1, 119.2, 118.4, 113.8, 105.8 (q, $J = 2.7$ Hz), 104.7, 55.7. IR (thin film) ν 3078, 2951, 2917, 2210, 2077, 2008, 1745, 1167, 1128, 1077 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{20}$H$_{12}$F$_6$NO$_2$S$_2$ [M+H]$^+$: 476.0208; Found: 476.0207.

7-Nitro-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2c)

Yield: 56.6 mg, 46%; Red solid; m.p. 116-118 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.51 (s, 1H), 8.32 (d, $J = 10.8$ Hz, 1H), 7.94 (d, $J = 8.9$ Hz, 1H), 7.59-7.47 (m, 5H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.39 (s, 3F), -40.69 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 159.5, 157.4, 144.4, 144.3, 135.7, 134.0, 130.7, 128.0, 127.6, 127.1 (q, $J = 314.1$ Hz), 127.0 (q, $J = 313.1$Hz), 126.3, 123.9, 120.3, 117.4, 112.3, 105.1 (q, $J = 2.6$ Hz). IR (thin film) ν 2929, 2144, 1736, 1612, 1533, 1334, 1167, 1140, 1089, 1007, 741 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{19}$H$_9$F$_6$NO$_3$S$_2$ [M+H]$^+$: 490.9953; Found: 490.9950.

3-Oxo-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indole-7-carbonitrile (2d)
Yield: 66.8 mg, 57%; Red solid; m.p. 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.97-7.87 (m, 2H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.58-7.42 (m, 5H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.47 (s, 3F), -40.70 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 159.6, 157.3, 143.8, 134.6, 133.9, 131.7, 130.7, 128.0, 127.6, 127.1 (q, $J = 313.1$ Hz), 127.0 (q, $J = 313.1$ Hz), 126.4, 125.7, 120.1 (d, $J = 2.4$ Hz), 117.3, 112.9, 107.7, 104.3 (q, $J = 2.7$ Hz). IR (thin film) ν 1078, 2963, 2869, 2192, 2014, 1736, 1615, 1346, 1077, 1019 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{20}$H$_9$F$_6$NOS$_2$ [M+H]$^+$: 471.0055; Found: 471.0054.

**Methyl 3-oxo-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indole-7-carboxylate (2e)**

Yield: 80.9 mg, 64%; Red solid; m.p. 128-130 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.29 (s, 1H), 8.10 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.55-7.44 (m, 5H), 3.87 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.73 (s, 3F), -40.83 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 165.2, 159.8, 157.4, 143.1, 135.4, 133.7, 130.4, 130.0, 128.0, 127.2 (q, $J = 314.1$ Hz), 127.1 (q, $J = 313.1$ Hz), 127.5, 126.7, 126.0, 123.1, 119.3, 111.8, 105.4 (q, $J = 2.6$ Hz), 51.3. IR (thin film) ν 2960, 2201, 2153, 1760, 1533, 1439, 1294, 1089 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{21}$H$_{12}$F$_6$NO$_3$S$_2$ [M+H]$^+$: 504.0157; Found: 504.0153.

**3-Oxo-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indole-7-carbaldehyde (2f)**

Yield: 42.7 mg, 36%; Red solid; m.p. 122-124 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 9.99 (s, 1H), 8.13 (s, 1H), 7.96 (s, 2H), 7.57-7.45 (m, 5H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.60 (s, 3F), -40.72 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 189.7, 159.8, 157.4, 143.4, 136.2, 134.2, 132.4, 130.5, 129.7, 128.0, 127.5, 127.2 (q, $J = 314.1$ Hz), 127.1 (q, $J = 313.1$ Hz), 126.6, 123.6, 119.7 (q, $J = 2.4$ Hz), 112.6, 105.4. IR (thin film)
ν 2842, 2796, 2159, 1754, 1203, 1086, 916 cm⁻¹. **HRMS (ESI-TOF):** \(m/z\) Calculated for \(\text{C}_{20}\text{H}_{10}\text{F}_{6}\text{NO}_{2}\text{S}_{2} [\text{M+H}^+]\): 474.0052; Found: 474.0048.

7-Fluoro-1-phenyl-2,9-bis(trifluoromethylthio)-3\textit{H}-pyrrolo[1,2-\textit{a}]indol-3-one (2g)

![Chemical structure](image)

Yield: 78.4 mg, 68%; Red solid; m.p. 120-122 °C. \(^1\)H NMR (400 MHz, CDCl₃) δ ppm 7.75 (dd, \(J = 8.8, 4.2\) Hz, 1H), 7.54-7.44 (m, 5H), 7.27 (d, \(J = 6.0\) Hz, 1H), 7.13 (td, \(J = 8.9, 2.5\) Hz, 1H). \(^1\)⁹F NMR (377 MHz, CDCl₃) δ ppm -39.84 (s, 3F), -40.90 (s, 3F), -116.24 to -116.29 (m, 1F). \(^{13}\)C NMR (101 MHz, CDCl₃) δ ppm 159.9, 159.2 (d, \(J = 243.4\) Hz), 157.4, 143.5, 135.0 (d, \(J = 10.1\) Hz), 130.4, 129.5, 128.0, 127.5, 127.2 (q, \(J = 313.1\) Hz), 127.1 (q, \(J = 313.1\) Hz), 126.8, 118.9, 116.5 (d, \(J = 25.7\) Hz), 113.0 (d, \(J = 9.1\) Hz), 107.3 (d, \(J = 25.6\) Hz), 104.6 (q, \(J = 2.6\) Hz). IR (thin film) ν 2969, 2290, 2356, 1739, 1442, 1258, 1092, 795 cm⁻¹. HRMS (ESI-TOF): \(m/z\) Calculated for \(\text{C}_{19}\text{H}_{9}\text{F}_{6}\text{NOS}_{2} [\text{M+H}^+]\): 464.0008; Found: 464.0006.

7-Chloro-1-phenyl-2,9-bis(trifluoromethylthio)-3\textit{H}-pyrrolo[1,2-\textit{a}]indol-3-one (2h)

![Chemical structure](image)

Yield: 83.5 mg, 70%; Red solid; m.p. 115-117 °C. \(^1\)H NMR (400 MHz, CDCl₃) δ ppm 7.72 (d, \(J = 8.5\) Hz, 1H), 7.56 (s, 1H), 7.53-7.44 (m, 5H), 7.36 (d, \(J = 8.5\) Hz, 1H). \(^1\)⁹F NMR (377 MHz, CDCl₃) δ -39.77 (s, 3F), -40.87 (s, 3F). \(^{13}\)C NMR (151 MHz, CDCl₃) δ ppm 160.9, 158.3, 144.2, 135.9, 132.4, 131.4, 130.7, 129.8, 129.0, 128.5, 128.2 (q, \(J = 314.0\) Hz), 128.1 (q, \(J = 312.5\) Hz), 127.7, 121.9, 120.2, 114.0, 105.2 (q, \(J = 2.7\) Hz). IR (thin film) ν 2969, 2815, 2358, 1739, 1442, 1258, 1092, 1001, 795 cm⁻¹. HRMS (ESI-TOF): \(m/z\) Calculated for \(\text{C}_{19}\text{H}_{9}\text{ClF}_{6}\text{NOS}_{2} [\text{M+H}^+]\): 479.9713; Found: 479.9710.
7-Bromo-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2i)

Yield: 95.6 mg, 73%; Red solid; m.p. 124-126 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.72 (s, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.51-7.47 (m, 6H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.75 (s, 3F), -40.86 (s, 3F). $^{13}$C NMR (151 MHz, CDCl$_3$) δ ppm 160.9, 158.3, 144.0, 136.3, 132.8, 132.5, 131.4, 129.0, 128.5, 128.2 (q, $J = 312.5$ Hz), 128.1 (q, $J = 312.5$ Hz), 127.7, 124.9, 120.5, 118.1, 114.4, 105.1 (q, $J = 2.6$ Hz). IR (thin film) ν 2954, 2908, 1739, 1606, 1554, 1439, 1352, 1167, 1089, 1001 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{19}$H$_9$BrF$_6$NOS$_2$ [M+H]$^+$: 523.9208; Found: 523.9206.

8-Methyl-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2j)

Yield: 54.3 mg, 47%; Red solid; m.p. 118-120 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.68 (d, $J = 8.1$ Hz, 1H), 7.52-7.35 (m, 5H), 7.24 (t, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 2.64 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -40.07 (s, 3F), -42.61 (s, 3F). $^{13}$C NMR (151 MHz, CDCl$_3$) δ ppm 161.1, 158.9, 143.8, 135.1, 134.7, 131.7, 130.8, 129.5, 129.0, 128.34, 128.33 (q, $J = 327.7$ Hz), 128.27, 128.0 (q, $J = 321.1$ Hz), 127.5, 119.9, 111.1, 106.1 (q, $J = 3.0$ Hz), 19.2. IR (thin film) ν 2966, 2923, 2017, 1742, 1524, 1479, 1355, 1122, 1019 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{20}$H$_{12}$F$_6$NOS$_2$ [M+H]$^+$: 460.0259; Found: 460.0258.

8-Methoxy-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2k)

Yield: 52.6 mg, 44%; Red solid; m.p. 130-132 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49-7.42 (m, 6H), 7.31 (d, $J = 2.3$ Hz, 1H), 6.79 (dd, $J = 8.8$, 2.3 Hz, 1H), 3.83 (s, 3H). $^{19}$F
NMR (377 MHz, CDCl₃) δ -40.24 (s, 3F), -41.96 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 160.4, 157.8, 155.3, 141.0, 134.7, 130.3, 129.9, 128.1, 127.4 (q, J = 313.1 Hz), 127.32 (q, J = 312.0 Hz), 127.27, 121.9, 118.0 (q, J = 2.2 Hz), 105.4, 105.1 (q, J = 2.6 Hz), 104.9, 54.5. HRMS (ESI-TOF): m/z Calculated for C₂₀H₁₂F₆NO₂S₂ [M+H]⁺: 476.0208; Found: 476.0207.

**Ethyl 3-oxo-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-α]indole-8-carboxylate (2l)**

Yield: 74.7 mg, 59%; Red solid; m.p. 92–94 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.96 (d, J = 5.7 Hz, 1H), 7.54–7.38 (m, 7H), 4.34 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ ppm -39.81 (s, 3F), -42.26 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ ppm 165.4, 160.0, 157.9, 143.8, 133.6, 130.2, 130.0, 128.0, 127.9, 127.7, 127.4, 127.2 (q, J = 314.1 Hz), 127.1 (q, J = 312.0 Hz), 126.9, 124.5, 119.5, 114.5, 104.3 (q, J = 2.5 Hz), 60.7, 13.0. IR (thin film) ν 3059, 2951, 2923, 1745, 1618, 1530, 1485, 1349, 1176, 1113 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₂₂H₁₄F₆NO₃S₂ [M+H]⁺: 518.0314; Found: 518.0315.

**6-Methyl-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-α]indol-3-one (2m)**

Yield: 52.0 mg, 45%; Red solid; m.p. 84-86 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.61 (s, 1H), 7.49–7.42 (m, 6H), 7.01 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ ppm -40.16 (s, 3F), -40.90 (s, 3F). ¹³C NMR (151 MHz, CDCl₃) δ ppm 161.3, 158.5, 142.4, 141.1, 134.6, 132.5, 131.1, 129.1, 128.42, 128.39 (q, J = 312.5 Hz), 128.35 (q, J = 312.5 Hz), 128.2, 126.2, 121.9, 118.9, 113.4, 106.6 (q, J = 2.5 Hz), 22.0. IR (thin film) ν 2972, 2923, 2881, 2023, 1729, 1612, 1445, 1346, 1167, 1104 cm⁻¹. HRMS (ESI-TOF): m/z Calculated for C₂₀H₁₂F₆NO₂S₂ [M+H]⁺: 460.0259; Found: 460.0258.
6-Methoxy-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2n)

Yield: 41.8 mg, 35%; Red solid; m.p. 98-100 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.50-7.45 (m, 5H), 7.43 (d, $J = 8.7$ Hz, 1H), 7.30 (d, $J = 2.3$ Hz, 1H), 6.78 (dd, $J = 8.8$, 2.3 Hz, 1H), 3.83 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -40.40 (s, 3F), -40.86 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 162.4, 161.7, 158.8, 141.5, 135.9, 131.2, 129.1, 128.5 (q, $J = 318.2$ Hz), 128.4, 128.33 (q, $J = 313.1$Hz), 128.3, 128.2, 123.2, 117.5, 114.1, 107.1 (q, $J = 2.6$ Hz), 97.0, 56.0. IR (thin film) ν 2936, 2367, 2017, 1757, 1615, 1491, 1349, 1270, 1092, 1034 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{20}$H$_{12}$F$_6$NO$_2$S$_2$ [M+H]$^+$: 476.0208; Found: 476.0210.

6-Chloro-1-phenyl-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2o)

Yield: 72.9 mg, 61%; Red solid; m.p. 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.82 (d, $J = 1.8$ Hz, 1H), 7.54-7.43 (m, 6H), 7.20 (d, $J = 1.9$ Hz, 1H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.89 (s, 3F), -40.84 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 159.9, 157.4, 142.3, 135.1, 133.3, 132.2, 130.3, 128.0, 127.5, 127.2 (q, $J = 314.1$ Hz), 127.1 (q, $J = 312.0$ Hz), 126.8, 124.5, 122.0, 118.7, 112.5, 104.9 (q, $J = 2.6$ Hz). IR (thin film) ν 3084, 2975, 2923, 2201, 2153, 1729, 1618, 1170, 1110, 1089 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{19}$H$_9$ClF$_6$NO$_2$S$_2$ [M+H]$^+$: 479.9713; Found: 479.9710.

1-(P-Tolyl)-2,9-bis(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (2p)

S17
Yield: 70.8 mg, 62%; Red solid; m.p. 106-108 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.90 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.51-7.48 (m, 3H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 7.8$ Hz, 1H), 2.51 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -40.09 (s, 3F), -40.80 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 161.4, 158.7, 143.2, 142.0, 134.8, 134.2, 129.7, 129.21, 129.18, 128.4 (q, $J = 313.1$ Hz), 126.9, 125.2, 124.8, 122.2, 118.8 (q, $J = 2.4$ Hz), 113.1, 106.2 (q, $J = 2.6$ Hz), 21.7. IR (thin film) ν 2159, 1998, 1766, 1603, 1488, 1442, 1131, 1074, 1013, 750 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{20}$H$_{12}$F$_6$NOS$_2$ [M+H]$^+$: 460.0259; Found: 460.0260.

9-Methyl-1-phenyl-2-(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (4a)

Yield: 42.5 mg, 47%; Red solid; $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.71 (d, $J = 8.0$ Hz, 1H), 7.48 (s, 5H), 7.38-7.24 (m, 2H), 7.08 (t, $J = 7.6$ Hz, 1H), 2.04 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -41.00 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 160.6, 157.6, 134.2, 134.1, 133.5, 129.7, 128.8, 128.2, 127.73, 127.66, 127.6 (q, $J = 313.1$), 123.6, 122.6, 120.5, 114.6, 111.9, 9.0. IR (thin film) ν 2966, 2917, 2364, 2186, 1953, 1726, 1587, 1536, 1137, 1092, 711 cm$^{-1}$. HRMS (ESI-TOF): m/z Calculated for C$_{19}$H$_{13}$F$_3$NOS $[M+H]^+$: 360.0664; Found: 360.0665.

1,9-Diphenyl-2-(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (4b)

Yield: 59.7 mg, 57%; Red solid; m.p. 132-134 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 7.9$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.25 (t, $J = 7.3$ Hz, 1H), 7.18 (s, 2H), 7.13 (s, 1H), 7.12-7.03 (m, 7H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ -40.75 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.8, 157.7, 134.1, 133.3, 132.0, 129.2, 128.7, 128.3, 128.2, 127.7, 127.5, 127.2, 127.2, 126.6 (q, $J = 313.1$Hz), 123.0, 121.8, 115.1, 112.1. HRMS (ESI-TOF): m/z Calculated for C$_{20}$H$_{15}$F$_3$NOS $[M+H]^+$: 422.0821; Found: 422.0821.
3-Oxo-1-phenyl-2-(trifluoromethylthio)-3H-pyrrolo[1,2-a]indole-9-carbonitrile (4c)

![Chemical Structure](image)

Yield: 33.1 mg, 36%; Red solid; m.p. 124-126 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.79 (d, $J$ = 8.1 Hz, 1H), 7.70 (d, $J$ = 7.1 Hz, 2H), 7.58-7.53 (m, 4H), 7.43 (t, $J$ = 7.8 Hz, 1H), 7.25 (t, $J$ = 7.7 Hz, 1H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ ppm -39.64 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 160.0, 155.1, 141.9, 132.4, 131.6, 130.5, 129.1, 128.0, 127.2 (q, $J$ = 314.1 Hz), 126.3, 124.3, 120.8, 117.2 (d, $J$ = 2.0 Hz), 112.3, 111.2, 92.8. IR (thin film) ν 2960, 2917, 2848, 2234, 2086, 1736, 1612, 1545, 1173, 1128, 1002 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{19}$H$_{10}$F$_3$N$_2$OS [M+H]$^+$: 371.0460; Found: 371.0461.

9-Acetyl-1-phenyl-2-(trifluoromethylthio)-3H-pyrrolo[1,2-a]indol-3-one (4d)

![Chemical Structure](image)

Yield: 36.9 mg, 38%; Red solid; m.p. 128-130 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, $J$ = 8.1 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.54-7.38 (m, 5H), 7.32 (t, $J$ = 7.8 Hz, 1H), 7.13 (t, $J$ = 7.7 Hz, 1H), 1.78 (s, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$) δ -40.04 (s, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.8, 160.2, 157.3, 136.8, 133.1, 130.2, 129.7, 129.3, 128.4, 128.1, 127.4, 127.3 (q, $J$ = 313.1Hz), 123.8, 122.7, 122.5, 118.3, 111.7, 30.4. IR (thin film) ν 3072, 2364, 2032, 1968, 1729, 1672, 1606, 1557, 1473, 1448, 1110, 904 cm$^{-1}$. HRMS (ESI-TOF): $m/z$ Calculated for C$_{20}$H$_{13}$F$_3$NO$_2$S [M+H]$^+$: 388.0614; Found: 388.0611.
4. Mechanistic experiments

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 1a (61.3 mg, 0.25 mmol, 1.0 equiv), AgSCF₃ (156.7 mg, 0.75 mmol, 3.0 equiv), (NH₄)₂S₂O₈ (171.2 mg, 0.75 mmol, 3.0 equiv), NaHCO₃ (21.0 mg, 0.25 mmol, 1.0 equiv), and TEMPO (195.3 mg, 1.25 mmol, 5.0 equiv). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. Then DMSO (5.0 mL) was added by a syringe. The mixture was stirred at 80 °C for 12 h. The internal standard PhCF₃ (61.4 μL, 0.5 mmol) was added, and the solution was then analyzed by ¹⁹F NMR spectroscopy. The desired product 2a was not formed.

¹⁹F NMR spectrum of the reaction mixture
A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 3b (80.4 mg, 0.25 mmol, 1.0 equiv), AgSCF₃ (156.7 mg, 0.75 mmol, 3.0 equiv), (NH₄)₂S₂O₈ (171.2 mg, 0.75 mmol, 3.0 equiv), NaHCO₃ (21.0 mg, 0.25 mmol, 1.0 equiv), and TEMPO (195.3 mg, 1.25 mmol, 5.0 equiv). The tube was sealed with a septum, evacuated and backfilled with nitrogen three times. Then DMSO (5.0 mL) was added by a syringe. The mixture was stirred at 80 °C for 12 h. The internal standard PhCF₃ (30.7 μL, 0.25 mmol) was added, and the solution was then analyzed by ¹⁹F NMR spectroscopy. Only trace of the desired product 4b was detected.

¹⁹F NMR spectrum of the reaction mixture
5. References
1. Yoon, H.; Rölz, M.; Landau, F.; Lautens, M. Angew. Chem. Int. Ed. 2017, 56, 10920-10923.
2. Wang, C.-S.; Roisnel, T.; Dixneuf, P. H.; Soulé, J.-F. Adv. Synth. Catal. 2019, 361, 445-405.

6. ORTEP Drawing of the X-Ray Crystallographic Structure of Compound 2a

The crystal structure has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 1968129. This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif
7. Copies of $^1$H and $^{13}$C NMR spectra for the products

$^1$H NMR spectrum of 1a in CDCl$_3$

$^{13}$C NMR spectrum of 1a in CDCl$_3$
$^1$H NMR spectrum of 1b in CDCl$_3$

$^{13}$C NMR spectrum of 1b in CDCl$_3$
$^{1}H$ NMR spectrum of 1c in CDCl$_3$

$^{13}C$ NMR spectrum of 1c in CDCl$_3$
$^1$H NMR spectrum of 1d in CDCl$_3$

$^{13}$C NMR spectrum of 1d in CDCl$_3$
$^1$H NMR spectrum of 1e in CDCl$_3$

$^{13}$C NMR spectrum of 1e in CDCl$_3$
$^1$H NMR spectrum of 1f in CDCl$_3$

![H NMR spectrum of 1f in CDCl$_3$](image1)

$^{13}$C NMR spectrum of 1f in CDCl$_3$

![C NMR spectrum of 1f in CDCl$_3$](image2)
$^1$H NMR spectrum of $1g$ in CDCl$_3$

$^{13}$C NMR spectrum of $1g$ in CDCl$_3$
$^1$H NMR spectrum of 1h in CDCl$_3$

$^{13}$C NMR spectrum of 1h in CDCl$_3$
$^1$H NMR spectrum of 1i in CDCl$_3$

$^{13}$C NMR spectrum of 1i in CDCl$_3$
$^1$H NMR spectrum of 1j in CDCl$_3$

![H NMR spectrum of 1j in CDCl$_3$]

$^{13}$C NMR spectrum of 1j in CDCl$_3$

![C NMR spectrum of 1j in CDCl$_3$]
$^1$H NMR spectrum of 1k in CDCl$_3$

$^{13}$C NMR spectrum of 1k in CDCl$_3$
$^{1}H$ NMR spectrum of 1i in CDCl$_3$

$^{13}C$ NMR spectrum of 1i in CDCl$_3$
$^1$H NMR spectrum of 1m in CDCl$_3$

$^{13}$C NMR spectrum of 1m in CDCl$_3$
$^1$H NMR spectrum of $1n$ in CDCl$_3$

$^{13}$C NMR spectrum of $1n$ in CDCl$_3$
$^1$H NMR spectrum of 1o in CDCl$_3$

$^{13}$C NMR spectrum of 1o in CDCl$_3$
$^1$H NMR spectrum of 1p in CDCl$_3$

$^{13}$C NMR spectrum of 1p in CDCl$_3$
$^1$H NMR spectrum of 3a in CDCl$_3$

$^{13}$C NMR spectrum of 3a in CDCl$_3$
$^{1}H$ NMR spectrum of 3b in CDCl$_3$

$^{13}$C NMR spectrum of 3b in CDCl$_3$
$^1$H NMR spectrum of 3c in CDCl$_3$

$^{13}$C NMR spectrum of 3c in CDCl$_3$
$^1$H NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
$^1$H NMR spectrum of 2a in CDCl$_3$

$^{19}$F NMR spectrum of 2a in CDCl$_3$
$^{13}$C NMR spectrum of 2a in CDCl$_3$

$^1$H NMR spectrum of 2b in CDCl$_3$
$^{19}$F NMR spectrum of 2b in CDCl$_3$

$^{13}$C NMR spectrum of 2b in CDCl$_3$
$^{1}$H NMR spectrum of 2c in CDCl$_3$

$^{19}$F NMR spectrum of 2c in CDCl$_3$
$^{13}$C NMR spectrum of 2c in CDCl$_3$

![13C NMR spectrum of 2c in CDCl$_3$](image)

$^1$H NMR spectrum of 2d in CDCl$_3$

![1H NMR spectrum of 2d in CDCl$_3$](image)
$^{19}\text{F NMR}$ spectrum of 2d in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of 2d in CDCl$_3$
$^1$H NMR spectrum of 2e in CDCl$_3$

$^{19}$F NMR spectrum of 2e in CDCl$_3$
$^{13}$C NMR spectrum of 2e in CDCl$_3$

$^1$H NMR spectrum of 2f in CDCl$_3$
$^{19}$F NMR spectrum of 2f in CDCl$_3$

![19F NMR spectrum of 2f in CDCl$_3$](image1)

$^{13}$C NMR spectrum of 2f in CDCl$_3$

![$^{13}$C NMR spectrum of 2f in CDCl$_3$](image2)
$^1$H NMR spectrum of 2g in CDCl$_3$

$^{19}$F NMR spectrum of 2g in CDCl$_3$
$^{13}$C NMR spectrum of 2g in CDCl$_3$

![13C NMR spectrum of 2g in CDCl$_3$](image)

$^1$H NMR spectrum of 2h in CDCl$_3$

![$^1$H NMR spectrum of 2h in CDCl$_3$](image)
$^{19}\text{F NMR}$ spectrum of $2h$ in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of $2h$ in CDCl$_3$
$^1$H NMR spectrum of $2i$ in CDCl$_3$

$^{19}$F NMR spectrum of $2i$ in CDCl$_3$
$^{13}\text{C NMR}$ spectrum of 2i in CDCl$_3$

$^1\text{H NMR}$ spectrum of 2j in CDCl$_3$
$^{19}$F NMR spectrum of 2j in CDCl$_3$

![Fluorine NMR spectrum of 2j in CDCl$_3$]

$^{13}$C NMR spectrum of 2j in CDCl$_3$

![Carbon NMR spectrum of 2j in CDCl$_3$]
$^{1}$H NMR spectrum of 2k in CDCl$_3$

$^{19}$F NMR spectrum of 2k in CDCl$_3$
$^{13}$C NMR spectrum of 2k in CDCl$_3$

$^1$H NMR spectrum of 2l in CDCl$_3$
$^{19}\text{F NMR}$ spectrum of 2l in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of 2l in CDCl$_3$
$^{1}H$ NMR spectrum of 2m in CDCl$_3$

$^{19}F$ NMR spectrum of 2m in CDCl$_3$
$^{13}$C NMR spectrum of 2m in CDCl$_3$

1H NMR spectrum of 2n in CDCl$_3$
$^{19}$F NMR spectrum of 2n in CDCl₃

$^{13}$C NMR spectrum of 2n in CDCl₃
$^1$H NMR spectrum of 2o in CDCl$_3$

$^{19}$F NMR spectrum of 2o in CDCl$_3$
$^{13}\text{C NMR}$ spectrum of $2o$ in CDCl$_3$

$^{1}\text{H NMR}$ spectrum of $2p$ in CDCl$_3$
$^{19}\text{F NMR}$ spectrum of $2\text{p}$ in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of $2\text{p}$ in CDCl$_3$
$^1$H NMR spectrum of 4a in CDCl$_3$

$^{19}$F NMR spectrum of 4a in CDCl$_3$
$^{13}$C NMR spectrum of 4a in CDCl$_3$
$^{19}$F NMR spectrum of $4b$ in CDCl$_3$

![$^{19}$F NMR spectrum of $4b$ in CDCl$_3$]

$^{13}$C NMR spectrum of $4b$ in CDCl$_3$

![$^{13}$C NMR spectrum of $4b$ in CDCl$_3$]
$^1$H NMR spectrum of 4c in CDCl$_3$

19$^F$ NMR spectrum of 4c in CDCl$_3$
$^{13}$C NMR spectrum of 4c in CDCl₃

$^1$H NMR spectrum of 4d in CDCl₃
$^{19}\text{F NMR}$ spectrum of $4\text{d}$ in CDCl$_3$

$^{13}\text{C NMR}$ spectrum of $4\text{d}$ in CDCl$_3$