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Supporting Information

Intramolecular Trapping of Ammonium Ylides with N-Benzoylbenzotriazoles in Aqueous Medium: Direct Access to Pseudoindoxyl Scaffold Lalita Devi,^{a,b} Rashmi Shukla,^a Namrata Rastogi^{*,a,b}

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1. Experimental Section

1.1 General experimental information

All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Melting points were recorded on a Precision melting point apparatus and are uncorrected. NMR spectra were recorded on a BruckerAvance spectrometer at 300, 400 or 500 MHz (¹H) and 75, 100 or 125 MHz (¹³C). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used. The ESI-HRMS spectra were recorded on Agilent 6520-Q-Tof LC/MS system. The NMR yields of products were calculated through ¹H NMR of crude reaction mixture using dibromo methane as internal standard and isolated yields were calculated after purification by column chromatography.

All the chemicals and catalysts were purchased from commercial sources and used as received. The o-amino benzoylbenzotriazoles **1a-1m** were prepared from corresponding *N*-alkyl anthranilic acids following the procedure reported by Çelic et al¹ and data for new compounds (**1b-1m**) is reported below. Further, all the aryldiazoacetates **2** are known compounds and were synthesized following the literature protocols.²

1.2 General procedure for the synthesis of 2,2-disubstituted indolin-3-ones 3

In a round bottom flask equipped with a magnetic stirring bar, the o-amino benzoylbenzotriazole **1** (0.5 mmol), aryldiazoacetate **2** (1.0 mmol, 2.0 equiv) and catalyst $Rh_2(OAc)_4$ (0.002 g, 0.005 mmol, 0.5 mol% w.r.t. **2**) were taken in distilled water (5 mL). The resulting reaction mixture was refluxed until completion of the reaction (1-2 h; TLC monitoring) and then cooled to the room temperature. After cooling, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried (Na₂SO₄) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the pure product **3**.

2. Spectroscopic Data

(1H-benzo[d][1,2,3]triazol-1-yl)(5-methyl-2-(methylamino)phenyl)methanone (1b)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 79-80 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.06-8.13 (m, 2H), 7.74 (d, J = 1.0 Hz, 1H), 7.55-7.60 (m, 1H), 7.40-7.46 (m, 2H), 7.27 (dd, J = 8.7 Hz, 2.0 Hz, 1H), 6.68 (d, J = 8.7 Hz, 1H), 2.92 (d, J = 5.1 Hz, 3H), 2.19 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.59, 151.91, 145.71, 137.54, 134.38, 132.85, 129.61, 125.69, 123.70, 120.06, 114.28, 111.40, 110.64, 29.90, 20.29; **HRMS** for C₁₅H₁₄N₄O: calcd. (M+H)⁺: 267.1240, found: 267.1242

(1H-benzo[d][1,2,3]triazol-1-yl)(4-fluoro-2-(methylamino)phenyl)methanone (1c)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 147-148 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.07-8.12 (m, 3H), 7.89 (br s, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 6.33-6.40 (m, 2H), 2.91 (d, J = 5.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.19 (d, J = 253.9 Hz), 166.68, 156.15 (d, J = 13.1 Hz), 145.66, 138.26 (d, J = 12.2 Hz),132.77, 129.77, 125.82, 120.13, 114.32, 107.53, 103.21 (d, J = 23.2 Hz), 97.40 (d, J = 25.6 Hz), 29.85; HRMS for C₁₄H₁₁FN₄O: calcd. (M+H)⁺: 271.0990, found: 271.0983

(1H-benzo[d][1,2,3]triazol-1-yl)(4-chloro-2-(methylamino)phenyl)methanone (1d)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 144-145 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.13-8.15 (m, 1H), 8.08-8.11 (m, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.58-7.62 (m, 1H), 7.44-7.48 (m, 1H), 6.74 (d, J = 2.0 Hz, 1H), 6.63 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 2.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.92, 154.14, 145.67, 142.89, 136.40, 132.68, 129.86, 125.90, 120.17, 115.32, 114.35, 111.03, 109.29, 29.82; HRMS for C₁₄H₁₁ClN₄O: calcd. (M+H)⁺: 287.0694, found: 287.0691

(1H-benzo[d][1,2,3]triazol-1-yl)(5-bromo-2-(methylamino)phenyl)methanone (1e)

Yellow solid; R_f 0.50 (20% EtOAc/hexane); Mp 133-134 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.10-8.17 (m, 3H), 7.59-7.64 (m, 2H), 7.45-7.53 (m, 2H), 6.66 (d, J = 9.1 Hz, 1H), 2.94 (d, J = 5.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.52, 152.33, 145.73, 138.65, 136.71, 132.67, 129.99, 126.03, 120.25, 114.38, 113.16, 112.12, 106.17, 29.91; HRMS for $C_{14}H_{11}BrN_4O$: calcd. (M+H)⁺: 331.0189, found: 331.0187

(1H-benzo[d][1,2,3]triazol-1-yl)(4-bromo-2-(methylamino)phenyl)methanone (1f)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 158-159 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H),7.69 (br s, 1H), 7.57-7.61 (m, 1H), 7.43-7.47 (m, 1H), 6.90 (d, J = 1.7 Hz, 1H), 6.77(dd, J = 8.7 Hz, 1.8 Hz, 1H), 2.92 (d, J = 5.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.09, 153.98, 145.68, 136.26, 132.67, 131.95, 129.90, 125.93, 120.19, 118.16, 114.37, 114.18, 109.66, 29.84; HRMS for C₁₄H₁₁BrN₄O: calcd. (M+H)⁺: 331.0189, found: 331.0190

(1H-benzo[d][1,2,3]triazol-1-yl)(5-iodo-2-(methylamino)phenyl)methanone (1g)

Yellow solid; R_f 0.50 (10% EtOAc/hexane); Mp 123-124 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 2.1 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.59-7.66 (m, 3H), 7.45-7.49 (m, 1H), 6.55 (d, J = 9.0 Hz, 1H), 2.93 (d, J = 4.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.37, 152.65, 145.72, 144.02, 142.60, 132.64, 129.96, 126.01, 120.24, 114.33, 113.62, 113.01, 74.35, 29.80; **HRMS** for $C_{14}H_{11}IN_4O$: calcd. (M+H)⁺: 379.0050, found: 379.0048

(1H-benzo[d][1,2,3]triazol-1-yl)(2-(methylamino)-5-trifluoromethoxy)phenyl)methanone (1h)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 94-95 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 2.5 Hz, 1H), 7.66 (br s, 1H), 7.58-7.64 (m, 1H), 7.44-7.49 (m, 1H), 7.33 (dd, J = 9.3 Hz, 2.2 Hz, 1H),6.73 (d, J = 9.3 Hz, 1H), 2.95 (d, J = 5.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.59, 152.25, 145.70, 137.59, 132.62, 130.02, 129.85, 127.67, 126.05, 122.44, 120.26, 114.43, 112.20, 110.29, 29.98; HRMS for C₁₅H₁₁F₃N₄O₂: calcd. (M+H)⁺: 337.0907, found: 337.0906

(1H-benzo[d][1,2,3]triazol-1-yl)(2-(ethylamino)phenyl)methanone (1i)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 103-104 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.12-8.15 (m, 1H), 8.06-8.10 (m, 1H), 7.96 (dd, J = 8.3 Hz, 1.5 Hz, 1H), 7.54-7.61 (m, 2H), 7.38-7.46 (m, 2H), 6.75 (d, J = 8.6 Hz, 1H), 6.60-6.65 (m, 1H), 3.23-3.31 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.55, 152.73, 145.71, 136.12, 135.09, 132.80, 129.65, 125.73, 120.10, 114.64, 114.31, 111.68, 110.51, 37.66, 14.50; **HRMS** for C₁₅H₁₄N₄O: calcd. (M+H)⁺: 267.1240, found: 267.1243

(1H-benzo[d][1,2,3]triazol-1-yl)(2-(benzylamino)phenyl)methanone (1j)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 116-117 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.15-8.17 (m, 1H), 8.09-8.11 (m, 1H), 7.99-8.02 (m, 2H), 7.58-7.62 (m, 1H), 7.44-7.48 (m, 1H), 7.29-7.40 (m, 5H), 7.22-7.26 (m, 1H), 6.74 (d, J = 8.3 Hz, 1H), 6.66-6.70 (m, 1H), 4.48 (d, J = 5.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 167.67, 152.48, 145.75, 138.15, 136.10, 135.13, 132.80, 129.77, 128.85, 127.48, 127.21, 125.83, 120.15, 115.28, 114.40, 112.19, 111.22,47.28; **HRMS** for C₂₀H₁₆N₄O: calcd. (M+H)⁺: 329.1397, found: 329.1397

(1H-benzo[d][1,2,3]triazol-1-yl)(2-(cyclopropylamino)phenyl)methanone (1k)

Yellow liquid; R_f 0.50 (10% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.10-8.13 (m, 1H), 8.04-8.08 (m, 1H), 7.94 (dd, J = 8.2 Hz, 1.4 Hz, 1H), 7.66 (br s, 1H), 7.54-7.59 (m, 1H), 7.39-7.46 (m, 2H), 7.18-7.21 (m, 1H), 6.65-6.70 (m, 1H), 2.46-2.53 (m, 1H), 0.75-0.82 (m, 2H), 0.52-0.57 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 167.48, 153.35, 145.69, 135.76, 134.73, 132.73, 129.72, 125.78, 120.09, 115.44, 114.33, 113.30, 111.03, 24.47, 7.72; HRMS for C₁₄H₁₆N₄O: calcd. (M+H)⁺: 279.1240, found: 279.1239

(1H-benzo[d][1,2,3]triazol-1-yl)(2-fluoro-6-(methylamino)phenyl)methanone (11)

Yellow solid; $R_f 0.50$ (20% EtOAc/hexane); Mp 126-127 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.58-7.62 (m, 1H), 7.42-7.46 (m, 1H), 7.31-7.37 (m, 1H), 6.47 (d, J = 8.6 Hz, 1H), 6.35-6.40 (m, 1H), 6.00 (br s, 1H), 2.84 (d, J = 5.0 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃) δ 165.37, 162.32 (d, J = 250.7 Hz), 151.58 (d, J = 4.8 Hz), 146.16, 135.58 (d, J = 11.8 Hz), 131.46, 130.08, 126.11, 120.32, 114.03, 106.86 (d, J = 2.7 Hz), 104.06 (d, J = 16.2 Hz), 102.92 (d, J = 22.6 Hz), 30.26; **HRMS** for C₁₄H₁₁FN₄O: calcd. (M+H)⁺: 271.0990, found: 271.0984

(1H-benzo[d][1,2,3]triazol-1-yl)(2-chloro-6-(methylamino)phenyl)methanone (1m)

Yellow solid; R_f 0.50 (15% EtOAc/hexane); Mp 133-134 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.27 (m, 1H), 8.07-8.09 (m, 1H), 7.62-7.66 (m, 1H), 7.46-7.50 (m, 1H), 7.28 (t, J = 8.3Hz, 1H), 6.74 (d, J = 8.6 Hz, 1H), 6.63 (d, J = 8.5 Hz, 1H), 4.71 (d, J = 4.4 Hz, 1H), 2.77 (d, J = 5.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.67, 149.28, 146.37, 133.43, 133.21, 131.15, 130.45, 126.45, 120.41, 117.79, 117.16, 114.20, 109.59, 30.39; HRMS for C₁₄H₁₁ClN₄O: calcd. (M+H)⁺: 287.0694, found: 287.0695

Ethyl 1-methyl-3-oxo-2-phenylindoline-2-carboxylate (3a)

Yellow liquid; yield 86% (127 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, J = 7.7 Hz, 1H), 7.43-7.49 (m, 1H), 7.27-7.32 (m, 5H), 6.80 (d, J = 8.3 Hz, 1H), 6.72 (t, J = 7.5 Hz, 1H), 4.15-4.26 (m, 2H), 2.97 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 194.35, 167.13, 161.31, 138.00, 133.83, 128.66, 128.53, 127.39, 125.87, 118.41, 118.16, 108.44, 79.96, 62.38, 30.10, 14.17; HRMS for C₁₈H₁₇NO₃: calcd. (M+H)⁺: 296.1281, found: 296.1272

Ethyl 1,5-dimethyl-3-oxo-2-phenylindoline-2-carboxylate (3b)

Yellow liquid; yield 65% (100 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.32 (m, 7H), 6.72-6.74 (m, 1H), 4.13-4.26 (m, 2H), 2.95 (s, 3H), 2.20 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 194.38, 167.28, 159.93, 139.36, 134.01, 128.59, 128.44, 127.63, 127.39, 125.25, 118.48, 108.36, 80.21, 62.28, 30.16, 20.36, 14.18; **HRMS** for C₁₉H₁₉NO₃: calcd. (M+H)⁺: 310.1438, found: 310.1437

Ethyl 6-fluoro-1-methyl-3-oxo-2-phenylindoline-2-carboxylate (3c)

Yellow solid; yield 35% (55 mg); R_f 0.50 (15% EtOAc/hexane); Mp 107-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.52 (m, 1H), 7.27-7.31 (m, 5H), 6.40-6.46 (m, 2H), 4.16-4.28 (m, 2H), 2.95 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 192.37, 170.13 (d, J = 255.0 Hz), 166.75, 162.92 (d, J = 14.0 Hz), 133.55, 128.75, 128.69, 128.20 (d, J = 12.6 Hz), 127.31, 114.95, 106.75 (d, J = 24.6 Hz), 95.30 (d, J = 26.6 Hz), 80.62, 62.54, 30.24, 14.15; HRMS for C₁₈H₁₆FNO₃: calcd. (M+H)⁺: 314.1187, found: 314.1178

Ethyl 6-chloro-1-methyl-3-oxo-2-phenylindoline-2-carboxylate (3d)

Yellow solid; yield 58% (95 mg); R_f 0.50 (15% EtOAc/hexane); Mp 94-95 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.2 Hz, 1H), 7.34-7.38 (m, 5H), 6.88 (d, J = 1.5 Hz, 1H), 6.76 (dd, J = 8.2 Hz, 1.6 Hz, 1H), 4.25-4.33 (m, 2H), 3.03 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 192.93, 166.69, 161.48, 144.72, 133.40, 128.77, 128.73, 127.28, 126.80, 118.95, 116.95, 108.60, 80.39, 62.65, 30.19, 14.15; HRMS for C₁₈H₁₆ClNO₃: calcd. (M+H)⁺: 330.0891, found: 330.0892

Ethyl 5-bromo-1-methyl-3-oxo-2-phenylindoline-2-carboxylate (3e)

Yellow solid; yield 67% (125 mg); R_f 0.50 (15% EtOAc/hexane); Mp 74-75 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.52 (dd, J = 8.7 Hz, 1.6 Hz, 1H), 7.26-7.31 (m, 5H), 6.72 (d, J = 8.7 Hz, 1H), 4.17-4.26 (m, 2H), 2.97 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 192.97, 166.66, 159.88, 140.40, 133.29, 128.77, 128.14, 127.28, 120.00, 110.23, 110.13, 80.33, 62.59, 30.20, 14.16; HRMS for C₁₈H₁₆BrNO₃: calcd. (M+H)⁺: 374.0386, found: 374.0384

Ethyl 6-bromo-1-methyl-3-oxo-2-phenylindoline-2-carboxylate (3f)

Yellow solid; yield 71% (132 mg); R_f 0.50 (15% EtOAc/hexane); Mp 113-114 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.1 Hz, 1H), 7.34-7.38 (m, 5H), 7.07 (s, 1H), 6.92 (dd, J = 8.2 Hz, 1.0 Hz, 1H), 4.25-4.33 (m, 2H), 3.03 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 193.15, 166.64, 161.44, 133.68, 133.34, 128.77, 128.74, 127.28, 126.81, 121.73, 117.32, 111.70, 80.27, 62.59, 30.18, 14.15; HRMS for C₁₈H₁₆BrNO₃: calcd. (M+H)⁺: 374.0386, found: 374.0388

Ethyl 5-iodo-1-methyl-3-oxo-2-phenylindoline-2-carboxylate (3g)

Yellow liquid; yield 56% (118 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 1.7 Hz, 1H), 7.67 (dd, J = 8.6 Hz, 1.9 Hz, 1H), 7.25-7.31 (m, 5H), 6.63 (d, J = 8.6 Hz, 1H), 4.16-4.28 (m, 2H), 2.95 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 192.67, 166.64, 160.27, 145.81, 134.28, 133.28, 128.78, 127.29, 120.79, 110.71, 80.06, 78.79, 62.60, 30.13, 14.17; HRMS for C₁₈H₁₆INO₃: calcd. (M+H)⁺: 422.0248, found: 422.0247

Ethyl 1-methyl-3-oxo-2-phenyl-5-(trifluoromethoxy)indoline-2-carboxylate (3h)

Yellow liquid; yield 66% (125 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.37 (br s, 1H), 7.26-7.34 (m, 6H), 6.80 (d, J = 8.8 Hz, 1H), 4.19-4.27 (m, 2H), 2.99 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 193.47, 166.64, 159.57, 141.06, 133.27, 131.71, 128.80, 127.29, 120.62 (q, J = 254.6 Hz), 118.54, 118.23, 109.20,

80.71, 62.65, 30.28, 14.14; **HRMS** for $C_{19}H_{16}F_3NO_4$: calcd. (M+H)⁺: 380.1104, found: 380.1104

Ethyl 1-ethyl-3-oxo-2-phenylindoline-2-carboxylate (3i)

Yellow liquid; yield 57% (88 mg); R_f 0.50 (15% EtOAc/hexane); ¹**H** NMR (300 MHz, CDCl₃) δ 7.52 (br d, J = 7.7 Hz, 1H), 7.42-7.48 (m, 1H), 7.21-7.29 (m, 5H), 6.81 (d, J = 8.3 Hz, 1H), 6.71 (t, J = 7.3 Hz, 1H), 4.16-4.27 (m, 2H), 3.40-3.53 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H); ¹³**C** NMR (100 MHz, CDCl₃) δ 194.90, 168.06, 160.40, 137.91, 134.52, 128.69, 128.53, 127.51, 126.05, 118.47, 117.93, 108.63, 79.69, 62.39, 39.07, 14.05, 13.05; **HRMS** for C₁₉H₁₉NO₃: calcd. (M+H)⁺: 310.1438, found: 310.1429

Ethyl 1-benzyl-3-oxo-2-phenylindoline-2-carboxylate (3j)

Yellow solid; yield 60% (111 mg); R_f 0.50 (15% EtOAc/hexane); Mp 129-130 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 7.7 Hz, 1H), 7.34-7.38 (m, 1H), 7.27-7.30 (m, 3H), 7.21-7.24 (m, 2H), 7.13-7.20 (m, 3H), 7.03-7.05 (m, 2H), 6.75 (t, J = 7.5 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 4.68, 4.59 (AB_q, J = 17.0 Hz, 2H), 3.90-4.05 (m, 2H), 1.05 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.51, 167.60, 160.90, 137.89, 137.11, 134.33, 128.89, 128.65, 128.54, 127.57, 127.18, 126.46, 125.89, 118.78, 118.67, 109.57, 80.24, 62.40, 48.45, 13.82; HRMS for C₂₄H₂₁NO₃: calcd. (M+H)⁺: 372.1594, found: 372.1594

Ethyl 1-cyclopropyl-3-oxo-2-phenylindoline-2-carboxylate (3k)

Yellow liquid; yield 24% (39 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.53 (m, 2H), 7.31-7.35 (m, 2H), 7.20-7.26 (m, 4H), 6.78-6.83 (m, 1H), 4.16-4.23 (m, 2H), 2.43-2.50 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H), 0.68-0.86 (m, 2H), 0.51-0.61 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 195.43, 167.44, 162.88, 137.65, 135.42, 128.41, 128.31, 127.84, 125.64, 119.57, 119.44, 11.32, 80.96, 62.22, 26.97, 14.17, 6.73, 5.15; HRMS for C₂₀H₁₉NO₃: calcd. (M+H)⁺: 322.1438, found: 322.1436

Ethyl 2-(3-methoxyphenyl)-1-methyl-3-oxoindoline-2-carboxylate (3l)

Yellow liquid; yield 63% (102 mg); R_f 0.50 (20% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 6.79-6.90 (m, 4H), 6.72 (t, J = 7.4 Hz, 1H), 4.15-4.27 (m, 2H), 3.72 (s, 3H), 2.98 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.13, 167.01, 161.25, 159.74, 138.00, 135.25, 129.65, 125.87, 119.64, 118.34, 118.16, 113.72, 113.57, 108.43, 79.82, 62.38, 55.31, 30.13, 14.17; HRMS for C₁₉H₁₉NO₄: calcd. (M+H)⁺: 326.1387, found: 326.1383

Ethyl 2-(4-methoxyphenyl)-1-methyl-3-oxoindoline-2-carboxylate (3m)

Yellow liquid; yield 65% (106 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.51 (br d, J = 7.7 Hz, 1H), 7.43-7.48 (m, 1H), 7.21-7.26 (m, 2H), 6.78-6.85 (m, 2H)

& br s, 1H merged), 6.68-6.74 (m, 1H), 4.14-4.25 (m, 2H), 3.72 (s, 3H), 2.96 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.77, 167.33, 161.24, 159.78, 137.95, 128.69, 125.84, 125.77, 118.38, 118.07, 114.13, 108.40, 79.57, 62.33, 55.31, 30.01, 14.17; HRMS for C₁₉H₁₉NO₄: calcd. (M+H)⁺: 326.1387, found: 326.1388

Ethyl 2-(4-fluorophenyl)-1-methyl-3-oxoindoline-2-carboxylate (3n)

Yellow liquid; yield 59% (92 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.52 (m, 2H), 7.32-7.36 (m, 2H), 6.99 (t, J = 8.3 Hz, 2H), 6.82 (d, J = 8.2 Hz, 1H), 6.73 (t, J = 7.2 Hz, 1H), 4.15-4.25 (m, 2H), 3.73 (s, 3H), 2.97 (s, 3H), 1.17 (t, J = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 194.24, 167.04, 162.91 (d, J = 246.1 Hz), 161.36, 138.11, 129.46 (d, J = 3.1 Hz), 129.30 (d, J = 8.2 Hz), 125.93, 118.45, 118.35, 115.57 (d, J = 21.5 Hz), 108.59, 79.39, 62.50, 30.19, 14.16; HRMS for C₁₈H₁₆FNO₃: calcd. (M+H)⁺: 314.1187, found: 314.1182

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-1-methyl-3-oxoindoline-2-carboxylate (30)

Yellow solid; yield 68% (115 mg); R_f 0.50 (15% EtOAc/hexane); Mp 87-88 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.52 (m, 2H), 6.70-6.83 (m, 5H), 5.88 (s, 2H), 4.14-4.25 (m, 2H), 2.96 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 194.45, 167.16, 161.17, 147.99, 147.93, 137.99, 127.31, 125.89, 120.84, 118.33, 118.22, 108.43, 108.29, 108.18 101.29, 79.59, 62.39, 30.04, 14.16; **HRMS** for C₁₉H₁₇NO₅: calcd. (M+H)⁺: 340.1179, found: 340.1175

Ethyl 2-(4-methoxyphenyl)-1,5-dimethyl-3-oxoindoline-2-carboxylate (3p)

Yellow liquid; yield 69% (117 mg); R_f 0.50 (20% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.30 (m, 2H), 7.22-7.25 (m, 2H), 6.80-6.83 (m, 2H), 6.72 (d, J = 8.2 Hz, 1H), 4.14-4.23 (m, 2H), 3.72 (s, 3H), 2.93 (s, 3H), 2.21 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.81, 167.47, 159.86, 159.72, 139.32, 128.68, 127.52, 125.94, 125.22, 118.45, 114.07, 108.31, 79.82, 62.24, 55.30, 30.08, 20.37, 14.19; **HRMS** for C₂₀H₂₁NO₄: calcd. (M+H)⁺: 340.1543, found: 340.1541

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-1,5-dimethyl-3-oxoindoline-2-carboxylate (3q)

Yellow liquid; yield 72% (127 mg); R_f 0.50 (20% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.30 (m, 2H), 6.83 (d, J = 1.8 Hz, 1H), 6.76-6.78 (m, 1H), 6.70-6.73 (m, 2H), 5.87 (s, 2H), 4.12-4.25 (m, 2H), 2.93 (s, 3H), 2.20 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.50, 167.31, 159.78, 147.94, 147.85, 139.37, 127.70, 127.48, 125.27, 120.81, 118.38, 108.36, 108.24, 108.20, 101.26, 79.83, 62.31, 30.10, 20.37, 14.18; HRMS for C₂₀H₁₉NO₅: calcd. (M+H)⁺: 354.1336, found: 354.1337

Ethyl 4-fluoro-2-(4-methoxyphenyl)-1-methyl-3-oxoindoline-2-carboxylate (3r)

Yellow solid; yield 42% (72 mg); R_f 0.50 (25% EtOAc/hexane); Mp 83-84 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.41 (m, 1H), 7.23 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 8.3 Hz, 1H), 6.32 (t, J = 8.6 Hz, 1H), 4.18-4.25 (m, 2H), 3.73 (s, 3H), 2.96 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 190.78, 166.90, 161.97 (d, J = 5.7 Hz), 160.28 (d, J = 261.9 Hz), 159.92, 139.50 (d, J = 10.2 Hz), 128.71, 125.31, 114.19, 107.03 (d, J = 17.4 Hz), 104.33 (d, J = 19.0 Hz), 104.15, 79.93, 62.54, 55.33, 30.38, 14.16; HRMS for C₁₉H₁₈FNO₄: calcd. (M+H)⁺: 344.1293, found: 344.1284

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-4-fluoro-1-methyl-3-oxoindoline-2-carboxylate (3s)

Yellow liquid; yield 42% (75 mg); R_f 0.50 (25% EtOAc/hexane); ¹**H** NMR (400 MHz, CDCl₃) δ 7.36-7.42 (m, 1H), 6.82 (s, 1H), 6.70-6.76 (m, 2H), 6.54 (d, J = 8.2 Hz, 1H), 6.32 (t, J = 8.5 Hz, 1H), 5.88 (s, 2H), 4.17-4.24 (m, 2H), 2.95 (s, 3H), 1.19 (t, J = 7.0 Hz, 3H); ¹³**C** NMR (100 MHz, CDCl₃) δ 190.48, 166.74, 161.90 (d, J = 6.0 Hz), 160.30 (d, J = 262.0 Hz), 148.08, 148.06, 139.57 (d, J = 10.4 Hz), 126.82, 120.85, 108.31, 108.18, 106.96 (d, J = 17.2 Hz), 104.49 (d, J = 18.8 Hz),104.18 (d, J = 3.6 Hz), 101.36, 79.93, 62.61, 30.40, 14.15; HRMS for C₁₉H₁₆FNO₅: calcd. (M+H)⁺: 358.1085, found: 358.1085

Ethyl 4-chloro-2-(4-methoxyphenyl)-1-methyl-3-oxoindoline-2-carboxylate (3t)

Yellow solid; yield 44% (79 mg); R_f 0.50 (25% EtOAc/hexane); Mp 109-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, J = 8.1 Hz, 1H), 7.23-7.26 (m, 2H), 6.81-6.85 (m, 2H), 6.67 (d, J = 8.3 Hz, 1H), 6.64 (d, J = 7.7 Hz, 1H), 4.14-4.27 (m, 2H), 3.73 (s, 3H), 2.96 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 191.72, 166.92, 162.31, 159.90, 137.83, 133.70, 128.68, 125.38, 119.26, 115.06, 114.15, 106.62, 79.85, 62.52, 55.33, 30.27, 14.17; HRMS for C₁₉H₁₈CINO₄: calcd. (M+H)⁺: 360.0997, found: 360.0988

Ethyl 6-chloro-2-(4-methoxyphenyl)-1-methyl-3-oxoindoline-2-carboxylate (3u)

Yellow solid; yield 50% (90 mg); R_f 0.50 (20% EtOAc/hexane); Mp 116-117 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 8.2 Hz, 1H), 6.18 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 6.76 (d, J = 1.2 Hz, 1H), 6.66 (dd, J = 8.2 Hz, 1.4 Hz, 1H), 4.12-4.24 (m, 2H), 3.70 (s, 3H), 2.91 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz,CDCl₃) δ 193.34, 166.88, 161.41, 159.92, 144.66, 128.61, 126.77, 125.33, 118.84, 116.93, 114.23, 108.55, 80.04, 62.52, 55.32, 30.09, 14.15; HRMS for C₁₉H₁₈ClNO₄: calcd. (M+H)⁺: 360.0997, found: 360.0988

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-6-bromo-1-methyl-3-oxoindoline-2-carboxylate (3v) Yellow solid; yield 48% (100 mg); R_f 0.50 (20% EtOAc/hexane); Mp 161-162 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.84 (d, J = 7.4 Hz, 1H), 6.79 (s, 1H), 6.71 (s, 2H), 5.88 (s, 2H), 4.20 (t, J = 6.6 Hz, 2H), 2.93 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz,CDCl₃) δ 193.25, 166.67, 161.30, 148.10, 133.68, 126.82, 126.78, 121.78, 120.76, 117.23, 111.70, 108.36, 108.05, 101.38, 79.91, 62.61, 30.11, 14.15; HRMS for C₁₉H₁₆BrNO₅: calcd. (M+H)⁺: 418.0285, found: 418.0291

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-1-methyl-3-oxo-5-(trifluoromethoxy)indoline-2carboxylate (3w)

Yellow liquid; yield 72% (152 mg); R_f 0.50 (20% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.36 (br s, 1H), 7.30-7.33 (m, 1H), 6.71-6.79 (m, 4H), 5.88 (s, 2H), 4.17-4.25 (m, 2H), 2.97 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz,CDCl₃) δ 193.58, 166.67, 159.43, 148.13, 141.07, 131.71, 126.67, 120.78, 120.61 (q, J = 255.2 Hz), 118.45, 118.25, 109.20,108.38, 108.03, 101.40, 80.34, 62.66, 30.21, 14.13; HRMS for C₂₀H₁₆F₃NO₆: calcd. (M+H)⁺: 424.1002, found: 424.1000

tert-Butyl 3-(2-(ethoxycarbonyl)-1-methyl-3-oxoindolin-2-yl)-1H-indole-1-carboxylate (3x)

Yellow liquid; yield 50% (108 mg); R_f 0.50 (20% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 1H), 7.92 (s, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.49-7.55 (m, 1H), 7.15-7.21 (m, 1H, merged with solvent peak), 6.91-7.00 (m, 2H), 6.81 (d, J = 8.3 Hz, 1H), 6.76 (t, J = 7.6 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.89 (s, 3H), 1.60 (s, 9H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz,CDCl₃) δ 193.94, 166.25, 161.20, 149.32, 138.47, 135.55, 127.90, 127.58, 125.75, 124.72, 122.98, 119.76, 118.44, 118.08, 115.35, 113.34, 108.54, 84.11, 62.63, 29.53, 28.17, 14.17; HRMS for C₂₅H₂₆N₂O₅: calcd. (M+H)⁺: 435.1914, found: 435.1912

Ethyl 1-ethyl-2-(3-methoxyphenyl)-3-oxoindoline-2-carboxylate (3y)

Yellow liquid; yield 68% (115 mg); R_f 0.50 (20% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.54 (m, 1H), 7.43-7.48 (m, 1H), 7.18-7.23 (m, 1H, merged with solvent peak), 6.78-6.84 (m, 4H), 6.69-6.74 (m, 1H), 4.16-4.26 (m, 2H), 3.72 (s, 3H), 3.43-3.52 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz,CDCl₃) δ 194.64, 167.92, 160.37, 159.74, 137.89, 135.93, 129.68, 126.05, 119.83, 118.46, 117.94, 113.69, 108.65, 79.56, 62.37, 55.30, 39.14, 14.05, 13.08; HRMS for C₂₀H₂₁NO₄: calcd. (M+H)⁺: 340.1543, found: 340.1549

Ethyl 1-benzyl-2-(4-methoxyphenyl)-3-oxoindoline-2-carboxylate (3z)

Yellow solid; yield 54% (108 mg); R_f 0.50 (20% EtOAc/hexane); Mp 141-142 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.14-7.18 (m, 4H), 7.05 (d, J = 6.9 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 6.74 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.2

Hz, 1H), 4.65, 4.57 (AB_q, J = 17.0 Hz, 2H), 3.89-4.05 (m, 2H), 3.72 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 194.94, 167.79, 160.86, 159.85, 137.84, 137.20, 128.93, 128.55, 127.18, 126.54, 126.23, 125.86, 118.79, 118.58, 114.39, 109.55, 79.90, 62.36, 55.34, 48.40, 13.85; **HRMS** for C₂₅H₂₃NO₄: calcd. (M+H)⁺: 402.1700, found: 402.1700

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-3-oxoindoline-2-carboxylate (3za)

Yellow solid; yield 53% (110 mg); R_f 0.50 (20% EtOAc/hexane); Mp 118-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.14-7.19 (m, 3H), 7.06 (d, J = 7.0 Hz, 2H), 6.77-6.70 (m, 4H), 6.60 (d, J = 8.2 Hz, 1H), 5.87 (d, J = 3.5 Hz, 2H), 4.66, 4.58 (AB_q, J = 17.1 Hz, 2H), 3.86-4.02 (m, 2H), 1.03 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.61, 167.60, 160.76, 148.12, 148.01, 137.92, 137.09, 128.56, 127.72, 127.20, 126.48, 125.92, 121.19, 118.69, 118.65, 109.53, 108.55, 108.22, 101.36, 79.82, 62.43, 48.29, 13.81; HRMS for C₂₅H₂₁NO₅: calcd. (M+H)⁺: 416.1492, found: 416.1502

Ethyl 1,2-dimethyl-3-oxoindoline-2-carboxylate (3zb)

Yellow liquid; yield 17% (20 mg); R_f 0.50 (15% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.53 (m, 1H), 7.40-7.45 (m, 1H), 6.66-6.74 (m, 2H), 4.04-4.15 (m, 2H), 2.90 (s, 3H), 1.50 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.55, 167.88, 161.11, 137.88, 125.47, 118.60, 117.72, 108.58, 74.01, 62.07, 28.80, 17.58, 14.14; HRMS for C₁₃H₁₅NO₃: calcd. (M+H)⁺: 234.1125, found: 234.1121

Diethyl 1-methyl-3-oxoindoline-2,2-dicarboxylate (3zc)

Yellow liquid; yield 15% (22 mg); R_f 0.50 (25% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.54 (m, 1H), 7.41-7.47 (m, 1H), 6.70-6.78 (m, 2H), 4.23 (q, J = 7.1 Hz, 4H), 3.08 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 188.38, 163.87, 161.40, 138.23, 125.77, 118.58, 118.48, 108.93, 79.43, 62.86, 39.48, 14.03; HRMS for C₁₅H₁₇NO₅: calcd. (M+H)⁺: 292.1179, found: 292.1180

3. References

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4. Copies of ¹H and ¹³C NMR Spectra





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Figure 54: ¹³C NMR spectrum of 3za



