Supporting Information-I

Direct Organocatalytic Transfer Hydrogenation and C-H Oxidation: High-Yielding Synthesis of 3-Hydroxy-3-alkyloxindoles

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General Experimental Procedures

A. **General Methods:** The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400/500 MHz and 100/125 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra (HRMS) were recorded on ESI-TOF maXis. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Mass spectra were recorded on either

VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromate, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or and/or by treatment with a solution of 1.5 g $KMnO_4$, 10 g K_2CO_3, and 1.25 mL 10% NaOH in 200 mL water.

B. **Materials:** All solvents and commercially available chemicals were used as received without further purification unless otherwise stated.

C. **Procedure A: General procedure for the Hantzsch ester mediated reduction of N-protected-3-substituted-eneindolin-2-ones 1:** A washed and dry 25 mL RB flask equipped with a magnetic bar was charged with dry DCM (10 mL). To this, 0.3 mmol (1.0 equiv.) of N-protected-3-substituted-eneindolin-2-one **1** was added followed by 0.36 mmol (1.2 equiv.) of Hantzsch ester. The reaction mixture was stirred for 8-12 h. The progress of the reaction was monitored by TLC analysis. Pure N-protected-3-substitued-oxindole products **2** were obtained by column chromatography (silica gel, mixture of hexanes/ethyl acetate). We performed the reduction of 3-alkylidene-2-oxindoles **1** using Hantzsch ester mediated transfer hydrogenation reduction method (Method-1) and Pd/C-catalyzed hydrogenation with hydrogen gas reduction method (Method-2, as similar to procedure mentioned in ref. 1). The ^{1}H NMR of compound **2** was matched with previously reported data (ref. 2-11). Full spectral information of new compounds **2n**, **2o**, **2r** and **2v** are given as there is no report of these compounds.

D. **Procedure B: General procedure for the TMG-catalyzed oxidation of N-protected-3-substituted-oxindoles:** An ordinary glass vial equipped with a magnetic stirring bar was charged with dry THF (1.0 mL). To this, 0.2 mmol of 3-substitued-oxindole **2** was added followed by the addition of TMG **3h** (10 mol%, 2.3 mg) were added. The reaction mixture was stirred at 25 °C for 2-6 h. The progress of the reaction was monitored by TLC analysis. Pure 3-hydroxy-3-substitued-oxindole products **4** were obtained by column chromatography (silica gel, mixture of hexanes/ethyl acetate).

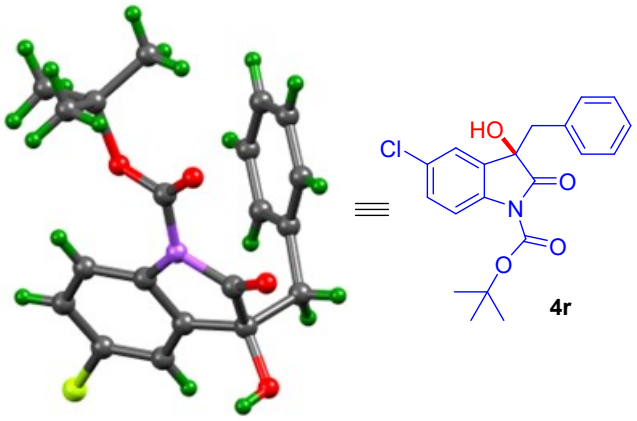
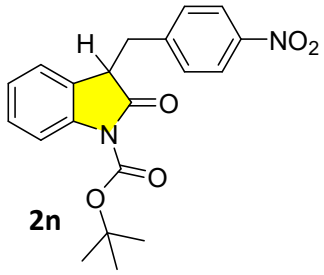
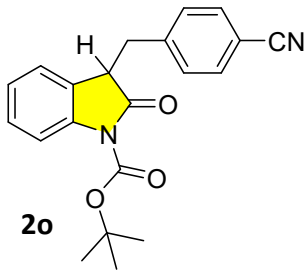


Figure S1: Crystal structure of *tert*-butyl 3-benzyl-5-chloro-3-hydroxy-2-oxoindoline-1-carboxylate (**4r**).

***tert*-Butyl 3-(4-nitrobenzyl)-2-oxoindoline-1-carboxylate (2n):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1.5 : 8.5 to 2.0 : 8.0) and was isolated as a white solid. Mp.: 146-148 ˚C. Yield: 80% (88 mg). IR (Neat): 2958, 2922, 2852, 1785, 1733, 1710, 1606, 1523, 1464, 1347, 1288, 1254, 1151, 1109, 856, 770, 721 and 698 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.09 (2H, dd, *J* = 6.8, 2.0 Hz), 7.86 (1H, dd, *J* = 8.8, 3.6 Hz), 7.72 (1H, d, *J* = 8.4 Hz), 7.29 (2H, d, *J* = 8.8 Hz), 7.07 (1H, dt, *J* = 0.8, 3.8 Hz), 6.92 (1H, d, *J* = 7.6 Hz), 3.91-3.88 (1H, m), 3.50 (1H, dd, *J* = 13.6, 4.8 Hz), 3.25 (1H, dd, *J* = 13.6, 7.6 Hz), 1.62 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 174.7 (C, *C*=O), 148.9 (C, *C*=O), 147.1 (C), 144.8 (C), 140.1 (C), 130.4 (2 x CH), 128.7 (CH), 126.1 (C), 124.2 (CH), 123.9 (CH), 123.6 (2 x CH), 115.2 (CH), 84.6 (C, O-*C*Me_3), 47.0 (CH), 37.0 (CH_2), 28.1 (3 x CH_3). HRMS (ESI-TOF) *m*/*z*: 369.1450 $[M + H]^+$, calcd for $C_{20}H_{21}N_2O_5$ 369.1450.

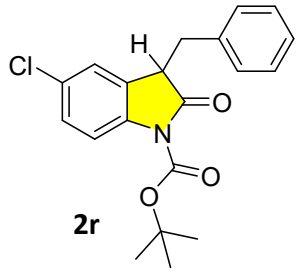


***tert*-Butyl 3-(4-cyanobenzyl)-2-oxoindoline-1-carboxylate (2o):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1.5 : 8.5 to 2.0 : 8.0) and was isolated as a white solid. Mp.: 137-139 ˚C. Yield: 92% (96 mg). IR (Neat): 3019, 2984, 2931, 2231, 1789, 1760, 1732, 1607, 1464, 1370, 1350, 1294, 1251, 1216, 1146, 1093, 1059, 997, 837, 747, 665, 625, 575 and 548 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.72 (1H, d, *J* = 8.5 Hz), 7.53 (2H, d, *J* = 8.5 Hz), 7.29-7.26 (1H, m), 7.24 (2H, d, *J* = 8.5 Hz), 7.08 (1H, dt, *J* = 0.5, 7.5 Hz), 6.89 (1H, d, *J* =



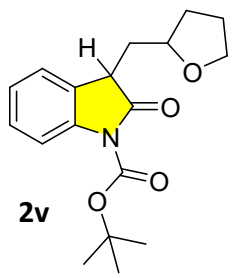
7.5 Hz), 3.87 (1H, dd, *J* = 8.0, 5.0 Hz), 3.47 (1H, dd, *J* = 14.0, 5.0 Hz), 3.18 (1H, dd, *J* = 13.5, 8.0 Hz), 1.63 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 174.8 (C, *C*=O), 148.8 (C, *C*=O), 142.6 (C), 140.0 (C), 132.1 (2 x CH), 130.2 (2 x CH), 128.6 (CH), 126.2 (C), 124.1 (CH), 123.9 (CH), 118.6 (C), 115.0 (CH), 110.8 (C), 84.5 (C, O-*C*Me_3), 46.9 (CH), 37.2 (CH_2), 28.0 (3 x CH_3). HRMS (ESI-TOF) *m*/*z*: 371.1372 [M + Na] $^+$, calcd for $C_{21}H_{20}N_2O_3Na$ 371.1372.

***tert*-Butyl 3-benzyl-5-chloro-2-oxoindoline-1-carboxylate (2r):** Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1.8 : 8.2 to 2.2 : 7.8) and was isolated as a white solid. Mp.: 164-166 °C. Yield: 91% (98 mg). IR (Neat): 3401, 3030, 2981, 2931, 1768, 1730, 1604, 1474, 1607, 1370, 1337, 1295, 1252, 1151, 1108, 1079, 1000, 822, 751, 700, 601 and 545 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (1H, d, *J* = 8.5 Hz), 7.30-7.24 (3H, m), 7.21 (1H, dd, *J* = 8.5, 2.5 Hz), 7.14 (2H, d, *J* = 8.0 Hz), 6.71 (1H, s), 3.79 (1H, dd, *J* = 9.0, 4.5 Hz), 3.47 (1H, dd, *J* = 14.0, 5.0 Hz), 2.97 (1H, dd, *J* = 14.0, 9.0 Hz), 1.62 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 174.5 (C, *C*=O), 149.0 (C, *C*=O), 138.6 (C), 136.8 (C), 129.39 (C), 129.35 (2 x CH), 128.9 (C), 128.6 (2 x CH), 128.2 (CH), 127.1 (CH), 124.6 (CH), 116.1 (CH), 84.6 (C, O-*C*Me_3), 47.5 (CH), 37.5 (CH_2), 28.1 (3 x CH_3). HRMS (ESI-TOF) *m*/*z*: 380.1029 [M + Na] $^+$, calcd for $C_{20}H_{20}ClNO_3Na$ 380.1029.



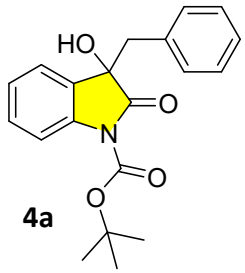
2r

***tert*-Butyl 2-oxo-3-((tetrahydrofuran-2-yl)methyl)indoline-1-carboxylate) (2v):** Prepared following the Pd/C reduction procedure and purified by column chromatography using EtOAc/hexane (2.0 : 8.0 to 2.5 : 7.5) and was isolated as a white solid. Mp.: 138-140 °C. Yield: 87% (83 mg). IR (Neat): 3433, 2959, 2854, 1776, 1730, 1613, 1463, 1371, 1345, 1291, 1251, 1153, 1038, 917, 846 and 771 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, *dr* = 1.2:1, major isomer): δ 7.82 (2H, dd, *J* = 6.4, 2.4 Hz), 7.14 (2H, t, *J* = 6.0 Hz), 4.10-4.05 (1H, m), 3.84-3.80 (1H, m), 3.68-3.63 (2H, m), 1.97-1.90 (4H, m), 1.639 (9H, s, O-C(CH_3)$_3$), 1.54-1.47 (2H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz, *dr* = 1.2:1, major isomer): δ 176.3 (C, *C*=O), 149.5 (C, *C*=O), 140.3 (C), 128.0 (CH), 127.7 (C), 124.0 (CH), 123.8 (CH), 115.0 (CH), 83.9 (C, O-*C*Me_3), 75.8 (CH), 67.3 (CH_2), 44.0 (CH), 37.0 (CH_2), 31.50 (CH_2), 28.13 (3 x CH_3), 25.5 (CH_2). ^{1}H NMR ($CDCl_3$, 400 MHz, *dr* = 1.2:1, minor isomer): δ 7.38 (1H, d, *J* = 6.0 Hz), 7.31-7.27 (3H,



2v

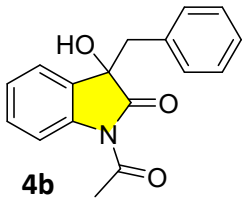
m), 4.19-4.14 (1H, m), 3.91 (1H, q, J = 6.4 Hz), 3.78-3.74 (2H, m), 2.31-2.26 (1H, m), 2.21-2.08 (3H, m), 1.89-1.82 (2H, m), 1.643 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz, *dr* = 1.2:1, minor isomer): δ 176.5 (C, *C*=O), 149.3 (C, *C*=O), 139.9 (C), 128.03 (C), 128.0 (CH), 124.6 (CH), 124.1 (CH), 114.9 (CH), 84.2 (C, O-*C*Me$_3$), 75.4 (CH), 67.8 (CH_2), 43.5 (CH), 37.4 (CH_2), 31.46 (CH_2), 28.11 (3 x CH_3), 25.7 (CH_2). HRMS (ESI-TOF) *m*/*z*: 318.1701 $[M + H]^+$, calcd for $C_{18}H_{24}NO_4$ 318.1705.



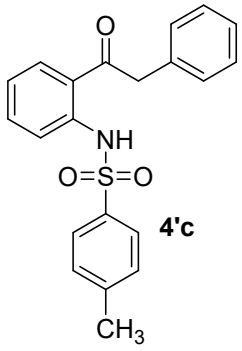
4a

***tert*-Butyl 3-benzyl-3-hydroxy-2-oxoindoline-1-carboxylate (4a):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 78-79 °C. Yield: 96% (65 mg). IR (Neat): 3447, 3085, 3059, 2982, 2930, 2249, 1779, 1732, 1608, 1463, 1350, 1293, 1247, 1154, 1112, 1050, 1004, 942, 849 and 751 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (1H, d, J = 8.5 Hz), 7.26 (1H, dt, J = 7.8, 1.0 Hz), 7.18 (1H, dd, J = 7.5, 1.5 Hz), 7.16-7.10 (4H, m), 6.88 (2H, d, J = 7.5 Hz), 3.49 (1H, br s, O*H*), 3.27 (1H, d, J = 13.0 Hz), 3.15(1H, d, J = 12.5 Hz), 1.56 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.9 (C, *C*=O), 148.5 (C, *C*=O), 139.1 (C), 133.3 (C), 130.2 (2 x CH), 129.7 (CH), 128.2 (C), 127.8 (2 x CH), 127.0 (CH), 124.5 (CH), 124.3 (CH), 114.9 (CH), 84.3 (C, O-*C*(CH$_3$)$_3$), 77.1 (C, *C*-OH), 45.9 (CH_2), 27.9 (3 x CH_3). HRMS (ESI-TOF) *m*/*z*: 362.1368 $[M + Na]^+$, calcd for $C_{20}H_{21}NO_4Na$ 362.1368.

1-Acetyl-3-benzyl-3-hydroxyindolin-2-one (4b): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.0 : 8.0 to 2.5 : 7.5) and was isolated as a white colour gummy liquid. Yield: 91% (51 mg). IR (Neat): 3413, 3088, 3059, 3033, 2917, 1763, 1713, 1610, 1465, 1372, 1339, 1273, 1190, 1164, 1113, 1080, 1016, 989, 913, 783, 757, 701, 608, 566 and 485 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (1H, d, J = 8.0 Hz), 7.32-7.29 (2H, m), 7.23-7.20 (1H, m), 7.16-7.09 (3H, m), 6.83 (2H, d, J = 7.0 Hz), 3.55-3.51 (1H, br s, O*H*), 3.29 (1H, d, J = 13.0 Hz), 3.18 (1H, d, J = 13.0 Hz), 2.46 (3H, s, COCH_3). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 178.8 (C, *C*=O), 170.2 (C, *C*=O), 139.5 (C), 132.9 (C), 130.1 (CH), 130.0 (2 x CH), 128.4 (C), 128.0 (2 x CH), 127.4 (CH), 125.4 (CH), 124.0 (CH), 116.4 (CH), 77.4 (C, *C*-OH), 45.9 (CH_2), 26.1 (CH_3). HRMS (ESI-TOF) *m*/*z*: 282.1131 $[M + H]^+$, calcd for $C_{17}H_{16}NO_3$ 282.1130.

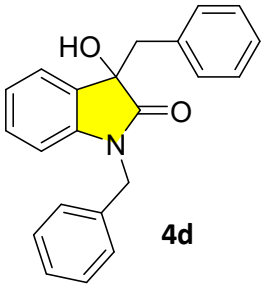


4b



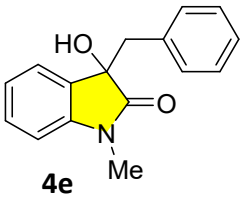
4'c

4-Methyl-N-(2-(2-phenylacetyl)phenyl)benzenesulfonamide (4'c): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (3.0 : 7.0 to 3.5 : 6.5) and was isolated as a white colour gummy liquid. Yield: 56% (45 mg). IR (Neat): 3058, 2925, 1650, 1601, 1576, 1493, 1451, 1339, 1288, 1255, 1159, 1090, 990, 918, 814, 757, 700, 661, 630, 565, 546 and 509 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 11.36 (1H, s, N*H*), 7.91 (1H, dd, *J* = 8.25, 1.0 Hz), 7.71 (1H, dd, *J* = 8.25, 1.0 Hz), 7.70 (2H, d, *J* = 8.5 Hz), 7.45 (1H, dt, *J* = 8.0, 1.5 Hz), 7.35-7.27 (3H, m), 7.20 (2H, d, *J* = 8.0 Hz), 7.14 (2H, d, *J* = 7.0 Hz), 7.05 (1H, dt, *J* = 8.0, 1.0 Hz), 4.22 (2H, s), 2.36 (3H, s). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 201.8 (C, *C*=O), 143.8 (C), 140.6 (C), 136.7 (C), 134.9 (CH), 133.9 (C), 131.5 (CH), 129.6 (2 x CH), 129.3 (2 x CH), 128.7 (2 x CH), 127.25 (2 x CH), 127.18 (CH), 122.6 (CH), 121.8 (C), 119.4 (CH), 46.4 (CH_2), 21.5 (CH_3). HRMS (ESI-TOF) *m/z*: 366.1162 $[M + H]^+$, calcd for $C_{21}H_{20}SNO_3$ 366.1164.



4d

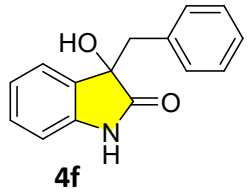
1,3-Dibenzyl-3-hydroxyindolin-2-one (4d): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 8.5 to 3.0 : 7.0) and was isolated as a white colour gummy liquid. Yield: 59% (39 mg). IR (Neat): 3373, 3085, 3062, 3033, 2922, 2851, 1703, 1614, 1493, 1468, 1436, 1353, 1298, 1285, 1199, 1170, 1112, 1079, 996, 933, 821, 781, 751, 698, 638, 584, 547, 484 and 455 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.37 (1H, m), 7.22-7.05 (8H, m), 6.94 (2H, d, *J* = 7.2 Hz), 6.71 (2H, dd, *J* = 7.6, 1.2 Hz), 6.44 (1H, d, *J* = 8.0 Hz), 5.00 (1H, d, *J* = 16.0 Hz), 4.45 (1H, d, *J* = 16.0 Hz), 3.43 (1H, d, *J* = 12.8 Hz), 3.30 (1H, d, *J* = 12.8 Hz), 3.20 (1H, s, O*H*). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 177.6 (C, *C*=O), 142.7 (C), 134.9 (C), 133.8 (C), 130.4 (2 x CH), 129.8 (CH), 129.1 (C), 128.6 (2 x CH), 128.1 (2 x CH), 127.3 (CH), 126.9 (CH), 126.6 (2 x CH), 124.4 (CH), 122.9 (CH), 109.6 (CH), 77.5 (C, *C*-OH), 44.8 (CH_2), 43.7 (CH_2). HRMS (ESI-TOF) *m/z*: 352.1316 $[M + Na]^+$, calcd for $C_{22}H_{19}NO_2Na$ 352.1313.



4e

3-Benzyl-3-hydroxy-1-methylindolin-2-one (4e): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 8.5 to 3.0 : 7.0) and was isolated as a white colour gummy liquid. Yield: 56% (28 mg). IR (Neat): 3327, 3065, 3031, 2961, 2849, 1693, 1615, 1494, 1468, 1439, 1369, 1300, 1212, 1172, 1112, 1029, 1079, 752, 696, 583

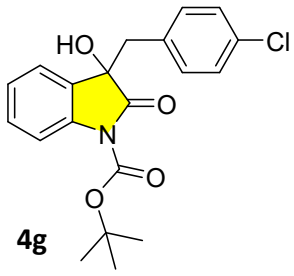
and 546 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24 (1H, d, *J* = 9.2 Hz), 7.20 (1H, d, *J* = 8.0 Hz), 7.12-7.07 (3H, m), 7.04 (1H, dt, *J* = 7.2, 0.8 Hz), 6.93 (2H, dd, *J* = 7.2, 1.6 Hz), 6.61 (1H, d, *J* = 8.0 Hz), 3.33 (1H, d, *J* = 12.8 Hz), 3.18 (1H, d, *J* = 13.2 Hz), 2.96 (3H, s). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 177.9 (C, *C*=O), 143.1 (C), 134.0 (C), 130.2 (2 x CH), 129.6 (CH), 129.3 (C), 127.7 (2 x CH), 126.8 (CH), 124.4 (CH), 122.8 (CH), 108.1 (CH), 77.4 (C, *C*-OH), 44.9 (CH_2), 25.9 (CH_3). HRMS (ESI-TOF) *m/z*: 254.1176 $[M + H]^+$, calcd for $C_{16}H_{16}NO_2$ 254.1181.



4f

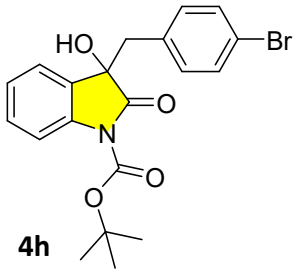
3-Benzyl-3-hydroxyindolin-2-one (4f): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (3.0 : 7.0 to 3.5 : 6.5) and was isolated as a white colour gummy liquid. Yield: 59% (28 mg). IR (Neat): 3345, 3147, 3090, 2921, 2850, 1706, 1626, 1474, 1358, 1291, 1219, 1181, 1113, 1083, 985, 836, 789, 756, 700, 654, 575, 542 and 497 cm^{-1}. ^1H NMR ($CDCl_3$ + 3 drops of CD_3OD, 400 MHz): δ 6.96-6.92 (2H, m), 6.89-6.84 (3H, m), 6.78 (1H, dt, *J* = 7.6, 0.8 Hz), 6.72 (2H, dd, *J* = 7.6, 1.6 Hz), 6.45 (1H, d, *J* = 8.4 Hz), 3.85 (1H, br s, O*H*), 3.05 (1H, d, *J* = 12.8 Hz), 2.91 (1H, d, *J* = 12.8 Hz). ^{13}C NMR ($CDCl_3$ + 3 drops of CD_3OD, DEPT-135, 100 MHz): δ 180.1 (C, *C*=O), 140.6 (C), 133.9 (2 x C), 129.9 (2 x CH), 129.0 (CH), 127.2 (2 x CH), 126.2 (CH), 124.2 (CH), 121.9 (CH), 109.6 (CH), 77.2 (C, *C*-OH), 43.6 (CH_2). HRMS (ESI-TOF) *m/z*: 262.0844 $[M + Na]^+$, calcd for $C_{15}H_{13}NO_2Na$ 262.0844.

***tert*-Butyl 3-(4-chlorobenzyl)-3-hydroxy-2-oxoindoline-1-carboxylate (4g):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.7 : 7.3 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 110-112 °C. Yield: 85% (64 mg). IR (Neat): 3452, 2956, 2922, 2850, 1791, 1736, 1611, 1482, 1465, 1371, 1343, 1288, 1250, 1117, 1084, 844, 774, 755, 669, 576 and 545 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.63 (1H, d, *J* = 8.0 Hz), 7.30 (1H, dt, *J* = 7.5, 2.0 Hz), 7.20-7.14 (2H, m), 7.09 (2H, d, *J* = 8.5 Hz), 6.83 (2H, d, *J* = 8.5 Hz), 3.30 (1H, s, O*H*), 3.23 (1H, d, *J* = 13.0 Hz), 3.11 (1H, d, *J* = 13.0 Hz), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.8 (C, *C*=O), 148.4 (C, *C*=O), 139.2 (C), 133.1 (C), 131.9 (C), 131.6 (2 x CH), 130.1 (CH), 128.1 (2 x CH), 127.9 (C), 124.7 (CH), 124.3 (CH), 115.1 (CH), 84.7 (C, O-*C*Me$_3$), 76.9 (C, *C*-OH), 45.2 (CH_2), 28.0 (3 x CH_3). LCMS *m/z*: 374.35 $[M + H]^+$, calcd for $C_{20}H_{21}ClNO_4$



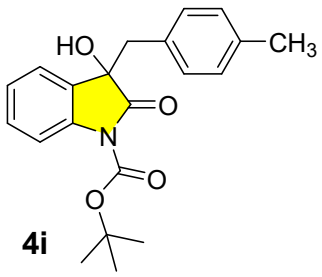
4g

374.1154; Anal. calcd for $C_{20}H_{20}ClNO_4$ (373.1081): C, 64.26; H, 5.39; N, 3.74%; Found: C, 64.32; H, 5.43; N, 3.65%.



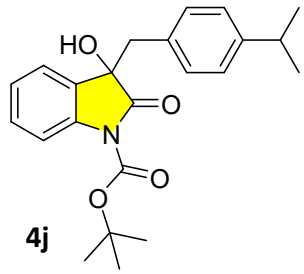
4h

***tert*-Butyl 3-(4-bromobenzyl)-3-hydroxy-2-oxoindoline-1-carboxylate (4h):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 125-127 °C. Yield: 95% (79 mg). IR (Neat): 3444, 3031, 2976, 2919, 2852, 1776, 1731, 1611, 1478, 1466, 1371, 1345, 1288, 1250, 1147, 1112, 1047, 1004, 937, 842, 782, 748, 699, 611, 576 and 541 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.63 (1H, d, *J* = 8.0 Hz), 7.30 (1H, dt, *J* = 7.5, 2.0 Hz), 7.26-7.24 (2H, m), 7.19-7.14 (2H, m), 6.77 (2H, d, *J* = 8.5 Hz), 3.30 (1H, s, O*H*), 3.22 (1H, d, *J* = 13.0 Hz), 3.09 (1H, d, *J* = 13.0 Hz), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.7 (C, *C*=O), 148.3 (C, *C*=O), 139.1 (C), 132.3 (C), 131.9 (2 x CH), 131.0 (2 x CH), 130.0 (CH), 127.8 (C), 124.6 (CH), 124.2 (CH), 121.3 (C), 115.1 (CH), 84.7(C, O-*C*Me$_3$), 76.8 (C, *C*-OH), 45.2 (CH_2), 28.0 (3 x CH_3). HRMS (ESI-TOF) *m*/*z*: 440.0473 $[M + Na]^+$, calcd for $C_{20}H_{20}BrNO_4Na$ 440.0473.



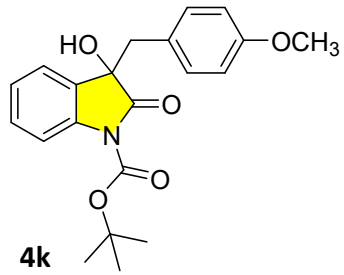
4i

***tert*-Butyl 3-hydroxy-3-(4-methylbenzyl)-2-oxoindoline-1-carboxylate (4i):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.2 : 7.8 to 2.8 : 7.2) and was isolated as a white solid. Mp.: 112-114 °C. Yield: 85% (60 mg). IR (Neat): 3447, 2978, 2922, 2852, 1776, 1731, 1680, 1512, 1479, 1468, 1371,1343, 1288, 1250, 1147, 1106, 1043, 1003, 936, 840, 814, 751, 668, 581 and 536 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 (1H, d, *J* = 8.0 Hz), 7.28 (1H, dt, *J* = 7.8, 1.6 Hz), 7.20 (1H, dd, *J* = 7.6, 1.6 Hz), 7.14 (1H, dt, *J* = 7.2, 0.8 Hz), 6.93 (2H, d, *J* = 7.6 Hz), 6.79 (2H, d, *J* = 8.0 Hz), 3.23 (1H, d, *J* = 12.8 Hz), 3.22 (1H, br s, O*H*), 3.11 (1H, d, *J* = 12.8 Hz), 2.24 (3H, s, Ar-CH_3), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 176.9 (C, *C*=O), 148.5 (C, *C*=O), 139.2 (C), 136.6 (C), 130.1 (2 x CH), 130.0 (CH), 129.7 (C), 128.6 (2 x CH), 128.2 (C), 124.5 (CH), 124.3 (CH), 114.9 (CH), 84.3 (C, O-*C*Me$_3$), 77.0 (C, *C*-OH), 45.5 (CH_2), 27.9 (3 x CH_3), 21.0 (CH_3). LCMS *m*/*z*: 354.15 ($M + H^+$), calcd for $C_{21}H_{24}NO_4$ 354.1750; Anal. calcd for $C_{21}H_{23}NO_4$ (353.1627): C, 71.17; H, 6.83; N, 3.95%; Found: C, 71.26; H, 6.68; N, 3.92%.



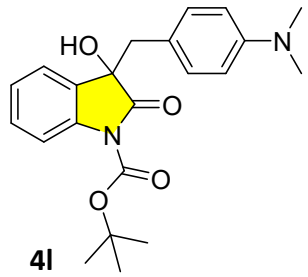
4j

***tert*-Butyl 3-hydroxy-3-(4-isopropylbenzyl)-2-oxoindoline-1-carboxylate (4j):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.2 : 7.8 to 2.8 : 7.2) and was isolated as a white solid. Mp.: 100-104 ˚C. Yield: 84% (64 mg). IR (Neat): 3457, 3009, 2964, 2926, 2827, 1777, 1731, 1608, 1511, 1497, 1466, 1371, 1343, 1289, 1248, 1146, 1110, 1054, 1006, 936, 841, 749, 666, 585 and 552 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (1H, d, *J* = 8.0 Hz), 7.30-7.26 (1H, m), 7.19-7.13 (2H, m), 6.99 (2H, d, *J* = 7.5 Hz), 6.83 (2H, d, *J* = 8.0 Hz), 3.24 (1H, d, *J* = 13.0 Hz), 3.17 (1H, br s, O*H*), 3.10 (1H, d, *J* = 13.0 Hz), 2.80 (1H, sep, *J* = 7.0 Hz), 1.57 (9H, s, O-C(CH_3)$_3$), 1.17 (6H, d, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.9 (C, *C*=O), 148.5 (C, *C*=O), 147.6 (C), 139.1 (C), 130.4 (C), 130.2 (2 x CH), 129.8 (CH), 128.2 (C), 125.9 (2 x CH), 124.5 (CH), 124.3 (CH), 114.9 (CH), 84.3 (C, O-*C*Me_3), 76.9 (C, *C*-OH), 45.6 (CH_2), 33.6 (CH), 27.9 (3 x CH_3), 23.9 (CH_3), 23.8 (CH_3). LCMS *m*/*z*: 381.60 [M], calcd for $C_{23}H_{27}NO_4$ 381.4648; Anal. calcd for $C_{23}H_{27}NO_4$ (381.1940): C, 72.42; H, 7.13; N, 3.67%; Found: C, 72.53; H, 7.16; N, 3.61%.



4k

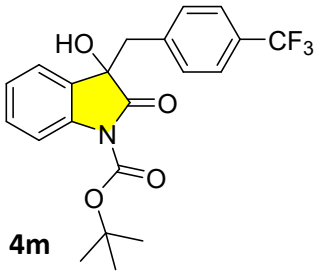
***tert*-Butyl 3-hydroxy-3-(4-methoxybenzyl)-2-oxoindoline-1-carboxylate (4k):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 2.8 : 7.2) and was isolated as a white solid. Mp.: 94-95 ˚C. Yield: 65% (48 mg). IR (Neat): 3450, 2978, 2933, 2839, 1779, 1730, 1611, 1512, 1466, 1395, 1369, 1346, 1290, 1249, 1177, 1149, 1113, 1035, 1003, 940, 839, 756, 675, 606, 580, 564 and 542 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (1H, d, *J* = 8.4 Hz), 7.28 (1H, dt, *J* = 7.6, 1.2 Hz), 7.20-7.12 (2H, m), 6.81 (2H, d, *J* = 8.8 Hz), 6.65 (2H, d, *J* = 8.4 Hz), 3.71 (3H, s, OCH_3), 3.37 (1H, br s, O*H*), 3.21 (1H, d, *J* = 13.2 Hz), 3.09 (1H, d, *J* = 12.8 Hz), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 177.1 (C, *C*=O), 158.6 (C, *C*=O), 148.5 (C), 139.1 (C), 131.2 (2 x CH), 129.7 (CH), 128.2 (C), 125.2 (C), 124.5 (CH), 124.3 (CH), 114.9 (CH), 113.3 (2 x CH), 84.3 (C, O-*C*Me_3), 77.1 (C, *C*-OH), 55.0 (CH_3, OCH_3), 45.0 (CH_2), 27.9 (3 x CH_3). LCMS *m*/*z*: 368.20 [M – H], calcd for $C_{21}H_{22}NO_5$ 368.4035; Anal. calcd for $C_{21}H_{23}NO_5$ (369.1576): C, 68.28; H, 6.28; N, 3.79%; Found: C, 68.45; H, 6.25; N, 3.86%.



4l

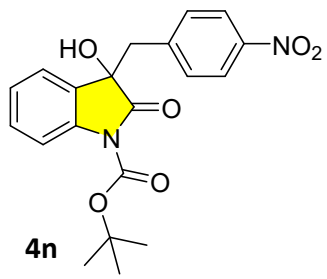
***tert*-Butyl 3-(4-(dimethylamino)benzyl)-3-hydroxy-2-oxoindoline-1-carboxylate (4l):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.8 : 7.2 to 3.2 : 6.8) and was isolated as a colourless gummy liquid. Yield: 61% (47 mg). IR (Neat): 3447, 2984, 2921, 2846, 2796, 1783, 1728, 1611, 1521, 1464, 1365, 1341, 1285, 1245, 1143, 1107, 1056, 1003, 937, 842, 811, 751, 664, 576 and 539 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.66 (1H, d, *J* = 8.0 Hz), 7.30-7.26 (1H, m), 7.19-7.12 (2H, m), 6.79 (2H, d, *J* = 8.8 Hz), 6.51 (2H, d, *J* = 8.8 Hz), 3.17 (1H, d, *J* = 13.2 Hz), 3.11 (1H, br s, O*H*), 3.03 (1H, d, *J* = 13.2 Hz), 2.86 (6H, s, NMe_2), 1.58 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 177.1 (C, *C*=O), 149.6 (C, *C*=O), 148.6 (C), 139.2 (C), 130.9 (2 x CH), 129.6 (CH), 128.5 (C), 124.4 (CH), 124.3 (CH), 120.8 (C), 114.9 (CH), 112.1 (2 x CH), 84.2 (C), 77.0 (C, *C*-OH), 45.0 (CH_2), 40.5 (2 x CH_3, N(CH_3)$_2$), 28.0 (3 x CH_3). LCMS *m*/*z*: 383.40 $[M + H]^+$, calcd for $C_{22}H_{27}N_2O_4$ 383.4608; Anal. calcd for $C_{22}H_{27}N_2O_4$ (382.1893): C, 69.09; H, 6.85; N, 7.32%; Found: C, 69.21; H, 7.05; N, 7.27%.

***tert*-Butyl 3-hydroxy-2-oxo-3-(4-(trifluoromethyl)benzyl)indoline-1-carboxylate (4m):**



4m

Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 94-96 °C. Yield: 91% (74 mg). IR (Neat): 3446, 2981, 2925, 2859, 1793, 1737, 1610, 1479, 1469, 1369, 1343, 1290, 1249, 1147, 1124, 1067, 1019, 938, 842, 755 and 599 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (1H, d, *J* = 8.0 Hz), 7.40 (2H, d, *J* = 8.4 Hz), 7.35-7.30 (1H, m), 7.22-7.16 (2H, m), 7.03 (2H, d, *J* = 8.0 Hz), 3.38 (1H, d, *J* = 12.8 Hz), 3.21 (1H, d, *J* = 12.8 Hz), 3.12 (1H, br s, O*H*), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 176.7 (C, *C*=O), 148.3 (C, *C*=O), 139.0 (C), 137.5 (C), 130.6 (3 x CH), 130.2 (CH), 129.4 (C, q, *J* = 32.0 Hz), 127.7 (C), 125.1 (C, q, *J* = 270.0 Hz, *C*F_3), 124.7 (2 x CH, q, *J* = 4.0 Hz), 124.2 (CH), 115.1 (CH), 84.7 (C, O-*C*Me_3), 76.9 (C, *C*-OH), 45.6 (CH_2), 27.9 (3 x CH_3). LCMS *m*/*z*: 406.25 [M – H], calcd. for $C_{21}H_{19}F_3NO_4$ 406.3751; Anal. calcd. for $C_{21}H_{20}F_3NO_4$ (407.1344): C, 64.81; H, 4.95; N, 3.44%; Found: C, 64.72; H, 4.92; N, 3.48%.

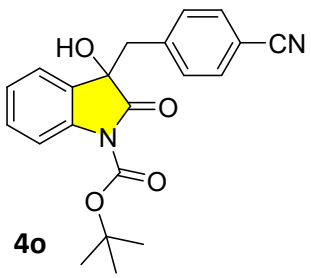


4n

***tert*-Butyl 3-hydroxy-3-(4-nitrobenzyl)-2-oxoindoline-1-carboxylate (4n):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 :

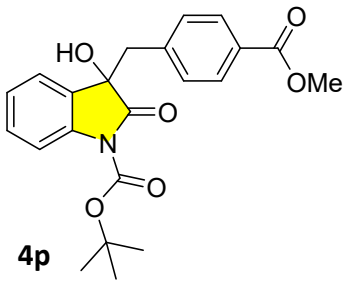
7.0) and was isolated as a white solid. Mp.: 98-100 ˚C. Yield: 90% (69 mg). IR (Neat): ν_{max} 3356, 2961, 2921, 2852, 1786, 1716, 1607, 1519, 1465, 1347, 1291, 1251, 1151, 1115, 856, 757 and 698 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.01 (2H, d, *J* = 8.5 Hz), 7.66 (1H, d, *J* = 8.5 Hz), 7.33 (1H, dt, *J* = 7.5, 2.0 Hz), 7.19-7.15 (2H, m), 7.12 (2H, d, *J* = 9.0 Hz), 3.37 (1H, d, *J* = 13.0 Hz), 3.24 (1H, d, *J* = 13.0 Hz), 3.09 (1H, br s, O*H*), 1.58 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.2 (C, *C*=O), 148.3 (C, *C*=O), 147.2 (C), 141.2 (C), 139.1 (C), 131.2 (2 x CH), 130.4 (CH), 127.3 (C), 124.8 (CH), 124.2 (CH), 123.0 (2 x CH), 115.2 (CH), 85.0 (C, O-*C*(CH$_3$)$_3$), 76.6 (C, *C*-OH), 45.4 (CH_2), 28.0 (3 x CH_3). LCMS *m*/*z*: 385.25 $[M + H]^+$, calcd for $C_{20}H_{21}N_2O_6$ 385.1400; Anal. calcd for $C_{20}H_{20}N_2O_6$ (384.1321): C, 62.49; H, 5.24; N, 7.29%. Found: C, 62.51; H, 5.26, N, 8.07%.

***tert*-Butyl 3-(4-cyanobenzyl)-3-hydroxy-2-oxoindoline-1-carboxylate (4o):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 62-64 ˚C. Yield: 88% (64 mg). IR (Neat): 3434, 2975, 2923, 2850, 2232, 1777, 1727, 1607, 1509, 1479, 1465, 1371, 1342, 1285, 1248, 1116, 1043, 1003, 936, 840, 745, 668, 579 and 555 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.63 (1H, d, *J* = 10.5 Hz), 7.43 (2H, d, *J* = 10.0 Hz), 7.31 (1H, dt, *J* = 9.5, 2.5 Hz), 7.18-7.12 (2H, m), 7.04 (2H, d, *J* = 10.0 Hz), 3.51 (1H, br s, O*H*), 3.32 (1H, d, *J* = 16.0 Hz), 3.18 (1H, d, *J* = 16.0 Hz), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.4 (C, *C*=O), 148.2 (C, *C*=O), 139.1 (C), 138.9 (C), 131.6 (2 x CH), 131.1 (2 x CH), 130.2 (CH), 127.5 (C), 124.7 (CH), 124.2 (CH), 118.6 (C), 115.1 (CH), 111.0 (C), 84.9 (C, O-*C*Me$_3$), 76.7 (C, *C*-OH), 45.6 (CH_2), 27.9 (3 x CH_3). LCMS *m*/*z*: 363.30 [M-H], calcd for $C_{21}H_{19}N_2O_4$ 363.3866; Anal. calcd for $C_{21}H_{20}N_2O_4$ (364.1423): C, 69.22; H, 5.53; N, 7.69%; Found: C, 69.15; H, 5.58; N, 7.61%.



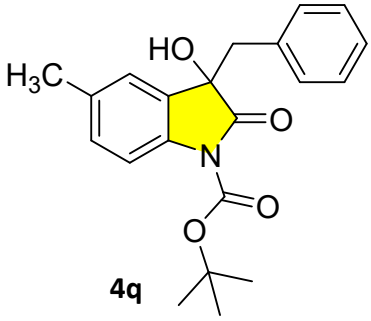
4o

***tert*-Butyl 3-hydroxy-3-(4-(methoxycarbonyl)benzyl)-2-oxoindoline-1-carboxylate (4p):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.6 : 7.4 to 3.0 : 7.0) and was isolated as a colourless gummy liquid. Yield: 87% (69 mg). IR (Neat): 3452, 2981, 2953, 2931, 1778, 1722, 1610, 1467, 1437, 1281, 1251, 1149, 1111, 1049, 939, 863, 842 and 753 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78 (2H, d, *J* = 8.0 Hz), 7.60 (1H, d, *J* = 8.4 Hz), 7.29-



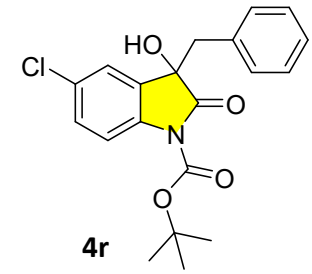
4p

7.25 (1H, m), 7.17-7.11 (2H, m), 6.98 (2H, d, J = 8.0 Hz), 3.86 (3H, s, OCH_3), 3.63 (1H, br s, OH), 3.33 (1H, d, J = 12.8 Hz), 3.20 (1H, d, J = 12.8 Hz), 1.55 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 176.6 (C, *C*=O), 166.9 (C, O-*C*=O), 148.4 (C, *C*=O), 139.0 (C), 138.8 (C), 130.3 (2 x CH), 130.0 (CH), 129.1 (2 x CH), 128.8 (C), 127.8 (C), 124.6 (CH), 124.2 (CH), 115.0 (CH), 84.5 (C, O-*C*Me$_3$), 76.9 (C, *C*-OH), 52.0 (CH_3, OCH_3), 45.7 (CH_2), 27.9 (3 x CH_3). HRMS (ESI-TOF) *m*/*z*: 420.1420 $[M + Na]^+$, calcd for $C_{22}H_{23}NO_6Na$ 420.1423.



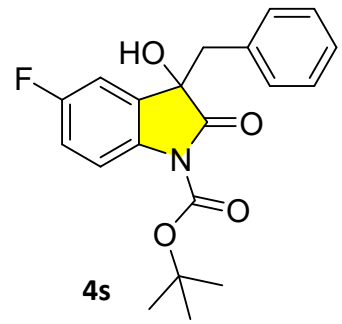
4q

***tert*-Butyl 3-benzyl-3-hydroxy-5-methyl-2-oxoindoline-1-carboxylate (4q):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 98-100 ˚C. Yield: 87% (62 mg). IR (Neat): 3451, 3033, 2980, 2925, 2855, 1777, 1732, 1600, 1490, 1454, 1370, 1337, 1281, 1249, 1153, 1125, 937, 820, 767, 700 and 551 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (1H, d, J = 8.0 Hz), 7.19-7.13 (3H, m), 7.09 (1H, dd, J = 8.0, 1.0 Hz), 6.99 (1H, s), 6.92 (2H, dd, J = 8.0, 1.5 Hz), 3.25 (1H, d, J = 13.0 Hz), 3.13 (1H, d, J = 13.0 Hz), 2.79 (1H, br s, OH), 2.32 (3H, s, Ar-CH_3), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.8 (C, *C*=O), 148.6 (C, *C*=O), 136.9 (C), 134.3 (2 x C), 133.3 (C), 130.4 (CH), 130.3 (2 x CH), 127.9 (2 x CH), 127.1 (CH), 124.8 (CH), 114.8 (CH), 84.2 (C, O-*C*Me$_3$), 76.7 (C, *C*-OH), 46.1 (CH_2), 28.0 (3 x CH_3), 21.0 (CH_3). HRMS (ESI-TOF) *m*/*z*: 376.1524 $[M + Na]^+$, calcd for $C_{21}H_{23}NO_4Na$ 376.1525.



4r

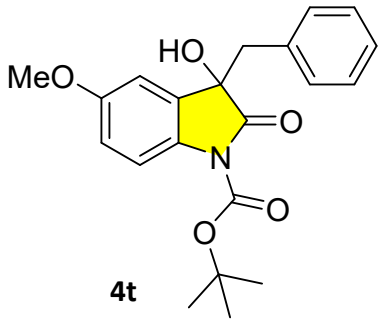
***tert*-Butyl 3-benzyl-5-chloro-3-hydroxy-2-oxoindoline-1-carboxylate (4r):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 143-145 ˚C. Yield: 92% (69 mg). IR (Neat): 3453, 3031, 2981, 2930, 1779, 1732, 1610, 1480, 1467, 1348, 1290, 1252, 1149, 1049, 939, 842, 784, 751, 700, 575, 541 and 508 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (1H, d, J = 9.0 Hz), 7.26 (1H, dd, J = 8.5, 2.5 Hz), 7.21-7.14 (4H, m), 6.92 (2H, dd, J = 8.0, 1.5 Hz), 3.24 (1H, d, J = 13.0 Hz), 3.14 (1H, d, J = 13.0 Hz), 2.82 (1H, s, OH), 1.57 (9H, s, O-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 176.1 (C, *C*=O), 148.3 (C, *C*=O), 137.7 (C), 132.7 (C), 130.2 (2 x CH), 130.1 (C), 129.9 (CH), 129.8 (C), 128.1



4s

(2 x CH), 127.4 (CH), 124.6 (CH), 116.3 (CH), 84.8 (C, O-*C*Me$_3$), 76.96 (C, *C*-OH), 46.2 (CH$_2$), 28.0 (3 x CH$_3$). HRMS (ESI-TOF) *m*/*z*: 396.0995 [M + Na]$^+$, calcd for $C_{20}H_{20}ClNO_4Na$ 396.0979.

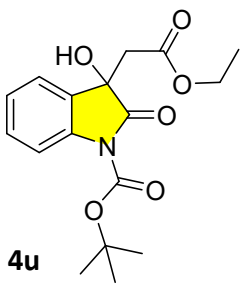
***tert*-Butyl 3-benzyl-5-fluoro-3-hydroxy-2-oxoindoline-1-carboxylate (4s):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.7 : 7.3 to 3.2 : 6.8) and was isolated as a white solid. Mp.: 125-128 °C. Yield: 85% (61 mg). IR (Neat): 3445, 2978, 2955, 2924, 2851, 1779, 1733, 1484, 1371, 1344, 1297, 1267, 1148, 776, 740 and 701 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.63 (1H, dd, *J* = 9.0, 2.5 Hz), 7.19-7.14 (3H, m), 6.98 (1H, dt, *J* = 9.0, 2.5 Hz), 6.93 (2H, dd, *J* = 8.0, 1.5 Hz), 6.90 (1H, dd, *J* = 7.5, 2.5 Hz), 3.25 (1H, d, *J* = 13.0 Hz), 3.15 (1H, d, *J* = 13.0 Hz), 3.05 (1H, br s, O*H*), 1.57 (9H, s, O-C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, DEPT-135, 125 Hz): δ 176.5 (C, *C*=O), 159.8 (C, d, *J* = 243.75 Hz, *C*-F), 148.4 (C, *C*=O), 135.1 (C, d, *J* = 2.5 Hz), 132.8 (C), 130.2 (2 x CH), 129.9 (C, d, *J* = 8.75 Hz), 128.0 (2 x CH), 127.3 (CH), 116.4 (CH, d, *J* = 3.75 Hz), 116.3 (CH, d, *J* = 11.25 Hz), 111.8 (CH, d, *J* = 25.0 Hz), 84.6 (C, O-*C*Me$_3$), 77.1 (C, *C*-OH), 46.1 (CH$_2$), 28.0 (3 x CH$_3$). HRMS (ESI-TOF) *m*/*z*: 380.1276 [M + Na]$^+$, calcd for $C_{20}H_{20}FNO_4Na$ 380.1274.



4t

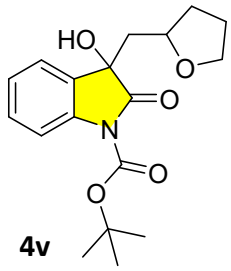
***tert*-Butyl 3-benzyl-3-hydroxy-5-methoxy-2-oxoindoline-1-carboxylate (4t):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.6 : 7.4 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 102-104 °C. Yield: 92% (68 mg). IR (Neat): 3445, 2980, 2937, 2837, 1776, 1730, 1601, 1487, 1370, 1337, 1277, 1248, 1152, 1123, 1040, 1013, 936, 846, 774, 740, 701, 617 and 557 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.57 (1H, d, *J* = 8.8 Hz), 7.19-7.14 (3H, m), 6.96 (2H, dd, *J* = 7.6, 1.6 Hz), 6.81 (1H, dd, *J* = 8.8, 2.8 Hz), 6.66 (1H, d, *J* = 2.8 Hz), 3.73 (3H, s, OC*H*$_3$), 3.27 (1H, d, *J* = 13.2 Hz), 3.10 (1H, d, *J* = 12.8 Hz), 2.85 (1H, br s, O*H*), 1.58 (9H, s, O-C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, DEPT-135, 125 MHz): δ 176.8 (C, *C*=O), 156.8 (C), 148.6 (C, *C*=O), 133.3 (C), 132.4 (C), 130.4 (2 x CH), 129.1 (C), 128.0 (2 x CH), 127.2 (CH), 116.1 (CH), 115.5 (CH), 109.9 (CH), 84.2 (C, O-*C*Me$_3$), 77.1 (C, *C*-OH), 55.6 (CH$_3$, O*C*H$_3$), 46.0 (CH$_2$), 28.0 (3 x CH$_3$). HRMS (ESI-TOF) *m*/*z*: 392.1476 [M + Na]$^+$, calcd for $C_{21}H_{23}NO_5Na$ 392.1474.

***tert*-Butyl 3-(2-ethoxy-2-oxoethyl)-3-hydroxy-2-oxoindoline-1-carboxylate (4u):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.2 : 7.8 to 2.5 : 7.5) and was isolated as a white



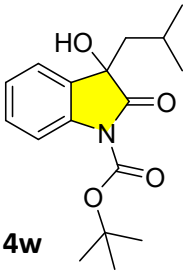
4u

colour gummy liquid. Yield: 80% (54 mg). IR (Neat): 3443, 2977, 2925, 2854, 1776, 1727, 1643, 1609, 1530,1469, 1370, 1345, 1290, 1249, 1148, 1090, 1027, 1004, 942, 842, 753 and 683 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.87 (1H, d, *J* = 8.0 Hz), 7.42 (1H, dd, *J* = 7.5, 1.0 Hz), 7.38 (1H, dt, *J* = 8.0, 1.5 Hz), 7.20 (1H, dt, *J* = 7.5, 1.0 Hz), 4.24 (1H, s, O*H*), 4.11 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.04 (1H, d, *J* = 16.0 Hz), 2.91 (1H, d, *J* = 15.5 Hz), 1.64 (9H, s, O-C(CH_3)$_3$), 1.18 (3H, t, *J* = 7.5 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 174.8 (C, *C*=O), 169.9 (C, *C*=O), 149.0 (C, *C*=O), 139.8 (C), 130.5 (CH), 128.0 (C), 125.0 (CH), 123.7 (CH), 115.5 (CH), 84.7 (C, O-*C*Me$_3$), 77.3 (C, *C*-OH), 61.3 (CH_2, OCH_2CH_3), 41.8 (CH_2), 28.1 (3 x CH_3), 13.9 (CH_3, OCH_2CH_3). HRMS (ESI-TOF) *m*/*z*: 358.1267 [M + Na]$^+$, calcd for $C_{17}H_{21}NO_6Na$ 358.1267.



4v

***tert*-Butyl 3-hydroxy-2-oxo-3-((tetrahydrofuran-2-yl)methyl)indoline-1-carboxylate (4v):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.1 : 7.9 to 2.5 : 7.5) and was isolated as a white colour gummy liquid. Yield: 86% (57 mg). IR (Neat): 3322, 2955, 2920, 2852, 1778, 1727, 1613, 1460, 1440, 1370, 1348, 1297, 1252, 1190, 1152, 1065, 1036, 965, 926, 844, 771 and 562 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, *dr* = 4.3:1, major isomer): δ 7.83 (1H, d, *J* = 8.5 Hz), 7.40 (1H, dd, *J* = 2.5, 1.0 Hz), 7.34 (1H, dt, *J* = 8.0, 1.0 Hz), 7.19 (1H, dt, *J* = 7.5, 0.5 Hz), 5.28 (1H, s), 4.46-4.41 (1H, m), 3.98-3.92 (1H, m), 3.86-3.82 (1H, m), 2.15 (1H, dd, *J* = 14.5, 11.0 Hz), 1.96-1.83 (3H, m), (1H, br s, O*H*), 1.63 (9H, s, O-C(CH_3)$_3$), 1.58-1.43 (1H, m). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz, *dr* = 4.3:1, major isomer): δ 176.3 (C, *C*=O), 149.3 (C, *C*=O), 139.0 (C), 130.0 (C), 129.7 (CH), 124.7 (CH), 123.5 (CH), 115.2 (CH), 84.2 (C, O-*C*Me$_3$), 75.5 (C, *C*-OH), 74.7 (CH), 68.2 (CH_2), 43.4 (CH_2), 32.2 (CH_2), 28.1 (3 x CH_3), 25.0 (CH_2). LCMS *m*/*z*: 332.20 [M – H], calcd for $C_{18}H_{22}NO_5$ 332.3710; Anal. calcd for $C_{18}H_{23}NO_5$ (333.1576): C, 64.85; H, 6.95; N, 4.20%; Found: C, 64.92; H, 7.06; N, 4.28%.

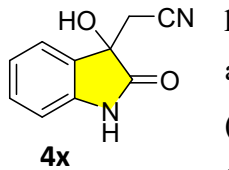


4w

***tert*-Butyl 3-hydroxy-3-isobutyl-2-oxoindoline-1-carboxylate (4w):** Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.5 : 7.5 to 2.8 : 7.2) and was isolated as a white colour gummy liquid. Yield: 65% (40 mg). IR (Neat): 3480, 2964, 2932, 2870, 1761, 1734, 1608, 1522, 1481, 1468, 1368, 1349, 1289, 1249, 1152, 1099, 840, 772, 752 and 588 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.85 (1H, d, *J* = 8.0 Hz), 7.40 (1H, dd,

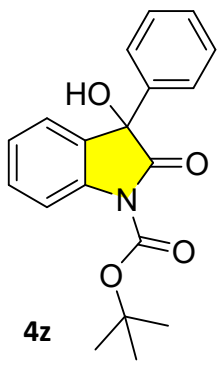
J = 5.0, 1.0 Hz), 7.37 (1H, dt, *J* = 8.0, 1.0 Hz), 7.21 (1H, dt, *J* = 7.5, 1.0 Hz), 2.80 (1H, d, *J* = 4.0 Hz), 1.95 (2H, d, *J* = 6.0 Hz), 1.64 (9H, s, O-C(C*H*$_3$)$_3$), 1.44 (1H, hep, *J* = 6.5 Hz), 0.80 (3H, d, *J* = 6.5 Hz), 0.74 (3H, d, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 177.1 (C, *C*=O), 149.0 (C, *C*=O), 139.5 (C), 129.9 (CH), 128.9 (C), 124.8 (CH), 124.2 (CH), 115.3 (CH), 84.6 (C, O-*C*(CH$_3$)$_3$), 76.2 (C, *C*-OH), 47.8 (CH_2), 28.1 (3 x CH_3), 24.1(CH), 23.8 (CH_3), 23.5 (CH_3). LCMS *m*/*z*: 306.20 [M + H]$^+$, calcd for $C_{17}H_{24}NO_4$ 306.3768; Anal. calcd for $C_{17}H_{23}NO_4$ (305.1627): C, 66.86; H, 7.59; N, 4.59 %; Found: C, 66.98; H, 7.65; N, 4.52%.

2-(3-hydroxy-2-oxoindolin-3-yl)acetonitrile (4x): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.6 : 7.4 to 3.0 : 7.0) and was isolated as a white solid. Mp.: 108-110 °C. Yield: 91% (34 mg). IR (Neat): 3305, 2921, 2852, 1727, 1610, 1514, 1463, 1370, 1288, 1251, 1156, 980, 836, 771 and 508 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 10.54 (1H, s, N*H*), 7.46 (1H, d, *J* = 7.0 Hz), 7.29 (1H, dt, *J* = 7.75, 1.0 Hz), 7.04 (1H, t, *J* = 7.5 Hz), 6.87 (1H, d, *J* = 8.0 Hz), 6.59 (1H, s, O*H*), 3.04 (1H, d, *J* = 16.5 Hz), 2.95 (1H, d, *J* = 16.5 Hz). ^{13}C NMR (DMSO-d$_6$, DEPT-135, 125 MHz): δ 176.7 (C, *C*=O), 141.6 (C), 130.0 (CH), 129.8 (C), 124.1 (CH), 122.0 (CH), 117.1 (C, *C*N), 110.0 (CH), 72.0 (C, *C*-OH), 26.1 (CH_2). HRMS (ESI-TOF) *m*/*z*: 211.0484 [M + Na]$^+$, calcd for $C_{10}H_8N_2O_2Na$ 211.0483.



4x

3-hydroxy-3-methylindolin-2-one (4y): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (2.8 : 7.2 to 3.0 : 7.0) and was isolated as a white colour gummy liquid. Yield: 85% (28 mg). IR (Neat): 3445, 2978, 2930, 2851, 2228, 1786, 1763, 1730, 1607, 1480, 1465, 1370, 1347, 1288, 1251, 1146, 1093, 1056, 1002, 935, 840, 754, 678 and 578 cm^{-1}. ^{1}H NMR ($CDCl_3$ + 3 drops of DMSO-d$_6$, 400 MHz): δ 9.41 (1H, s, N*H*), 7.19 (1H, d, *J* = 7.2 Hz), 7.03 (1H, dt, *J* = 7.6, 1.2 Hz), 6.84 (1H, dt, *J* = 7.6, 0.8 Hz), 6.70 (1H, d, *J* = 7.6 Hz), 4.99 (1H, s, O*H*), 1.39 (3H, s). ^{13}C NMR ($CDCl_3$ + 3 drops of DMSO-d$_6$, DEPT-135, 100 MHz): δ 180.5 (C, *C*=O), 140.4 (C), 132.7 (C), 128.6 (CH), 123.1 (CH), 121.9 (CH), 109.8 (CH), 73.1 (C, *C*-OH), 24.3 (CH_3). HRMS (ESI-TOF) *m*/*z*: 186.0532 [M + Na]$^+$, calcd for $C_9H_9NO_2Na$ 186.0531.

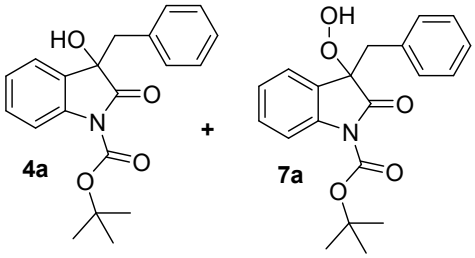


4z

***tert*-Butyl 3-hydroxy-2-oxo-3-phenylindoline-1-carboxylate (4z):** Prepared following the procedure **B** and purified by column chromatography

using EtOAc/hexane (2.2 : 7.8 to 2.8 : 7.2) and was isolated as a white solid. Mp.: 109-110 ˚C. Yield: 71% (46 mg). IR (Neat): 3352, 2957, 2924, 2852, 1786, 1727, 1606, 1584, 1480, 1467, 1450, 1341, 1310, 1284, 1252, 1149, 1113, 1013, 837, 773 and 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (1H, d, *J* = 8.5 Hz), 7.40 (1H, dt, *J* = 7.75, 1.5 Hz), 7.37-7.30 (6H, m), 7.20 (1H, dt, *J* = 7.5, 1.0 Hz), 3.45 (1H, br s, O*H*), 1.63 (9H, s, O-C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 175.8 (C, *C*=O), 149.0 (C, *C*=O), 139.8 (C), 139.7 (C), 130.18 (CH), 130.16 (C), 128.64 (2 x CH), 128.56 (CH), 125.5 (2 x CH), 125.3 (CH), 125.0 (CH), 115.4 (CH), 84.9 (C, O-*C*Me$_3$), 77.7 (C, *C*-OH), 28.0 (3 x CH_3). LCMS *m/z*: 326.20 $[M + H]^+$, calcd. for $C_{19}H_{20}NO_4$ 326.3664; Anal. calcd for $C_{19}H_{19}NO_4$ (325.1314): C, 70.14; H, 5.89; N, 4.31 %. Found: C, 70.21; H, 5.87, N, 4.34 %; HRMS (ESI-TOF) *m/z*: 348.1213 $[M + Na]^+$, calcd for $C_{19}H_{19}NO_4Na$ 348.1213.

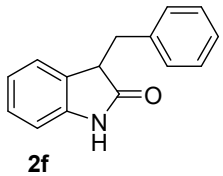
***tert*-Butyl 3-benzyl-3-hydroxy-2-oxoindoline-1-carboxylate (4a) and *tert*-butyl 3-benzyl-3-hydroperoxy-2-oxoindoline-1-carboxylate (7a):**



Prepared following the Wei's procedure and purified by column chromatography using EtOAc/hexane (2.5: 7.5 to 3.0: 7.0) and was isolated as a white solid of 1:1 mixture of **4a** and **7a** in 26 mg. Mp.: 78-79 ˚C. Yield: 26% (26 mg). For **4a**, see: IR (Neat): 3376, 2981, 1788, 1733, 1609, 1466, 1369, 1346, 1286, 1250, 1147, 907 and 729 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (1H, d, *J* = 8.0 Hz), 7.30 (1H, dd, *J* = 8.0,1.5 Hz), 7.20-7.10 (5H, m), 6.92-6.90 (2H, m), 3.28 (1H, d, *J* = 13.0 Hz), 3.16 (1H, d, *J* = 13.0 Hz), 1.57 (9H, s). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 177.0 (C, *C*=O), 148.5 (C, *C*=O), 139.2 (C), 133.3 (C), 130.4 (2 x CH), 129.9 (CH), 128.1 (C), 127.9 (2 x CH), 127.1 (CH), 124.6 (CH), 124.3 (CH), 115.0 (CH), 84.4 (C), 77.1 (C, *C*-OH), 46.0 (CH_2), 28.0 (3 x CH_3). HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{20}H_{25}N_2O_4$ 357.1814; Found: 357.1814. For **7a**, see. IR (Neat): 3376, 2981, 1788, 1733, 1609, 1466, 1369, 1346, 1286, 1250, 1147, 907 and 729 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.0 (1H, br s), 7.67 (1H, d, *J* = 8.0 Hz), 7.30 (1H, dd, *J* = 8.0,1.5 Hz), 7.20-7.10 (5H, m), 6.92-6.90 (2H, m), 3.28 (1H, d, *J* = 13.0 Hz), 3.14 (1H, d, *J* = 13.0 Hz), 1.57 (9H, s). ^{13}C NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 173.8 (C, *C*=O), 148.5 (C, *C*=O), 140.3 (C), 132.3 (C), 130.5 (2 x CH), 130.3 (CH), 128.0 (2 x CH), 127.3 (CH), 125.1 (C), 124.5 (CH), 124.5 (CH), 115.1 (CH), 88.1 (C), 84.6 (C, *C*-OOH), 41.0

(CH_2), 28.0 (3 x CH_3). HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{20}H_{25}N_2O_5$ 373.1763; Found : 373.1761.

3-benzylindolin-2-one (2f): Prepared following the Wei's procedure and purified by column chromatography using EtOAc/hexane (3.0: 7.0) and was isolated as a pale-yellow solid. Mp.: 128-130°C. Yield: 32% (14 mg). IR (Neat): 3254, 2923, 1706, 1619, 1469, 1371, 1237, 1044 and 751 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10 (1H, br s, N-*H*), 7.27-7.14 (6H, m), 6.90 (1H, dt, *J* = 7.5 Hz, 1.0 Hz), 6.81 (1H, d, *J* = 7.5 Hz), 6.75 (1H, d, *J* = 7.5 Hz), 3.74 (1H, dd, *J* = 5.0, 4.5 Hz), 3.49 (1H, dd, *J* = 9.0, 4.5 Hz), 2.95 (1H, dd, *J* = 9.0, 4.5 Hz). ^{13}C NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 179.0 (C, *C*=O), 141.2 (C), 137.8 (C), 129.4 (2 x CH), 128.9 (C), 128.3 (2 x CH), 127.9 (CH), 126.7 (CH), 124.9 (CH), 122.0 (CH), 109.5 (CH), 47.4 (CH), 36.6 (CH_2). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}NO$ 224.1075; Found: 224.1070.



2f

On-Line ESI-HRMS (Positive Mode) Spectrums of the Hydroxylation Reaction of 3-Alkyloxindole 2h Catalyzed by TMG 3h in THF at 25 °C During the 0.5 to 2 h Time.

1st Inject.

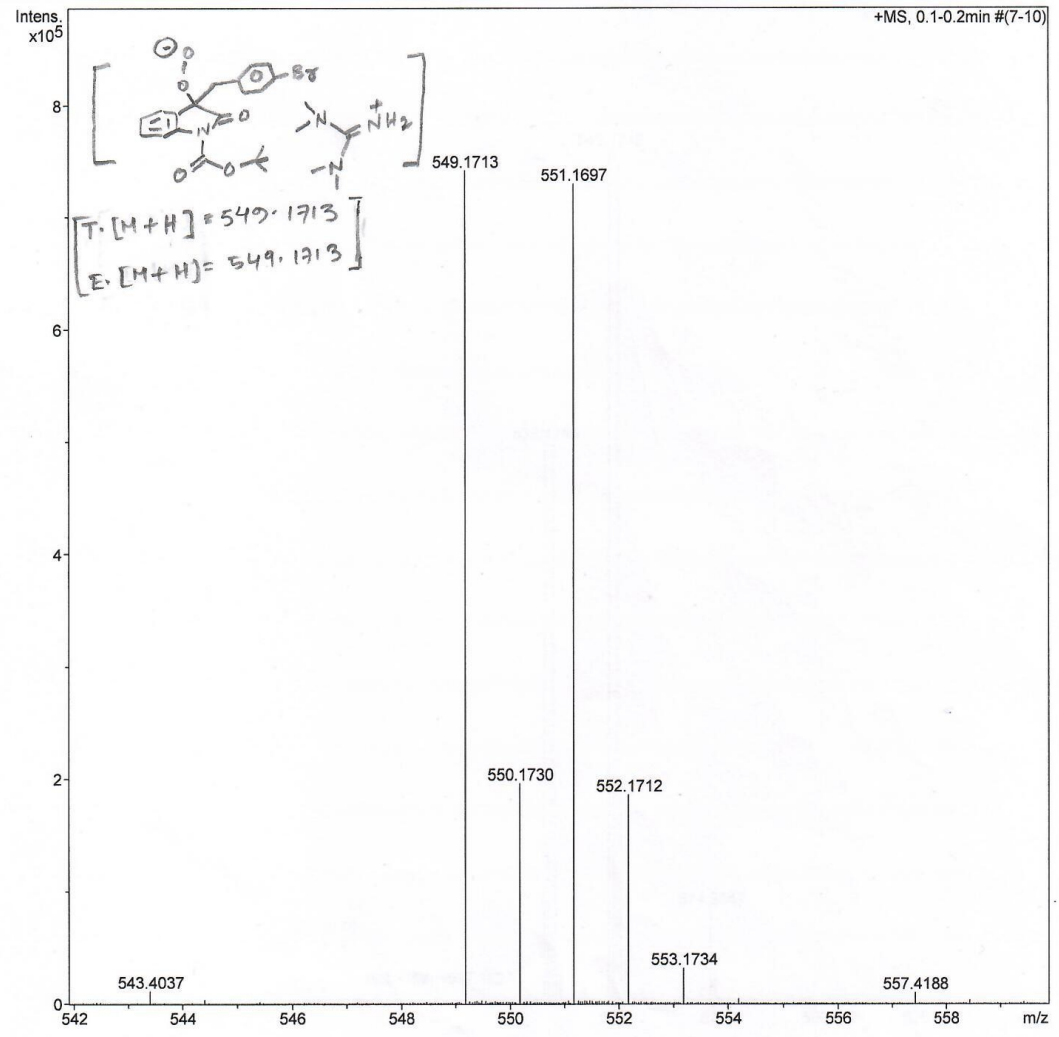
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF DBR\MAR\pr-01-time-2.45-1.d	Acquisition Date	2/24/2018 3:03:57 AM
Method	tune_low_Pos-R2.m	Operator	Rajesh Vashisth
Sample Name	pr-01-time-2.45	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



2nd Inject

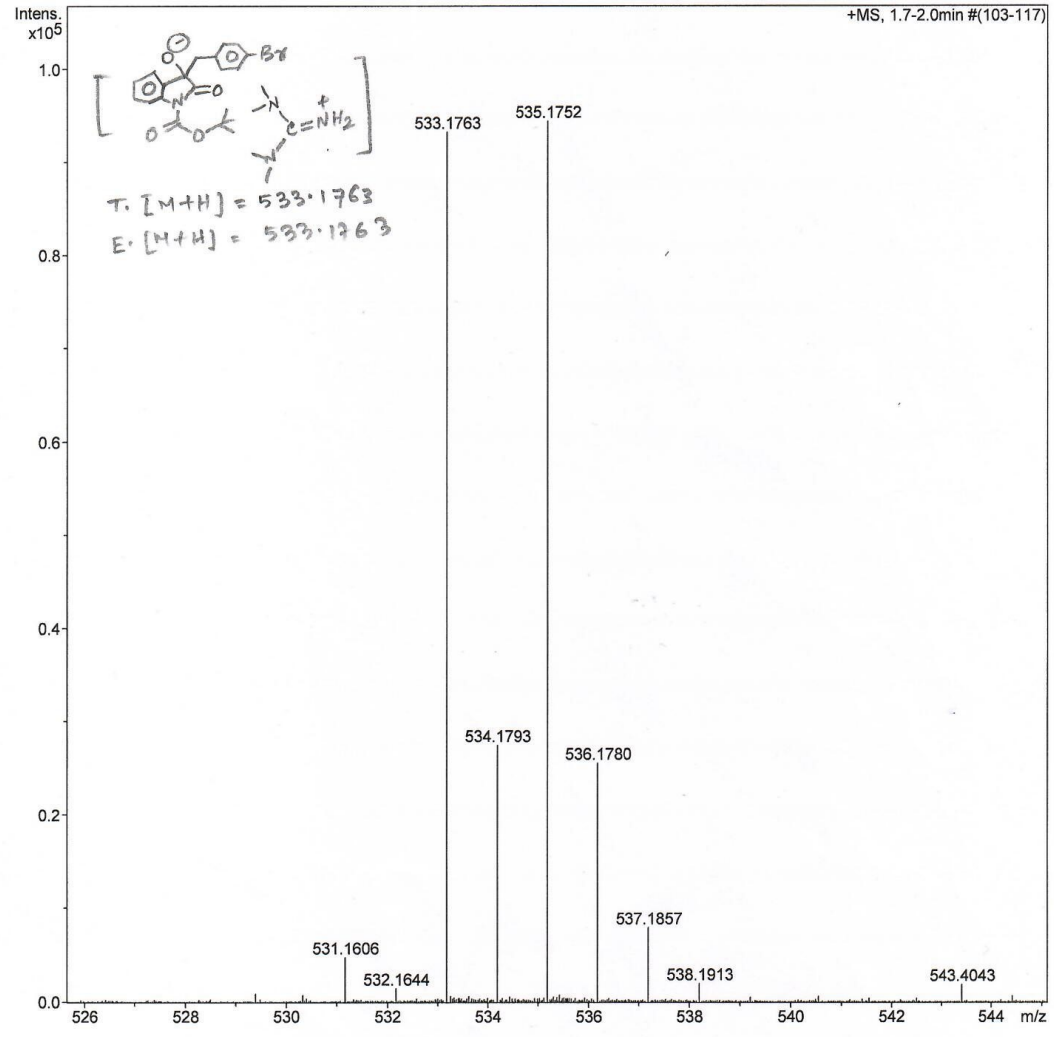
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF DBR\MAR\pr-01-time-3.15-1.d	Acquisition Date	2/24/2018 3:20:23 AM
Method	tune_low.m	Operator	Rajesh Vashisth
Sample Name	pr-01-time-3.15	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



3rd Inject

UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

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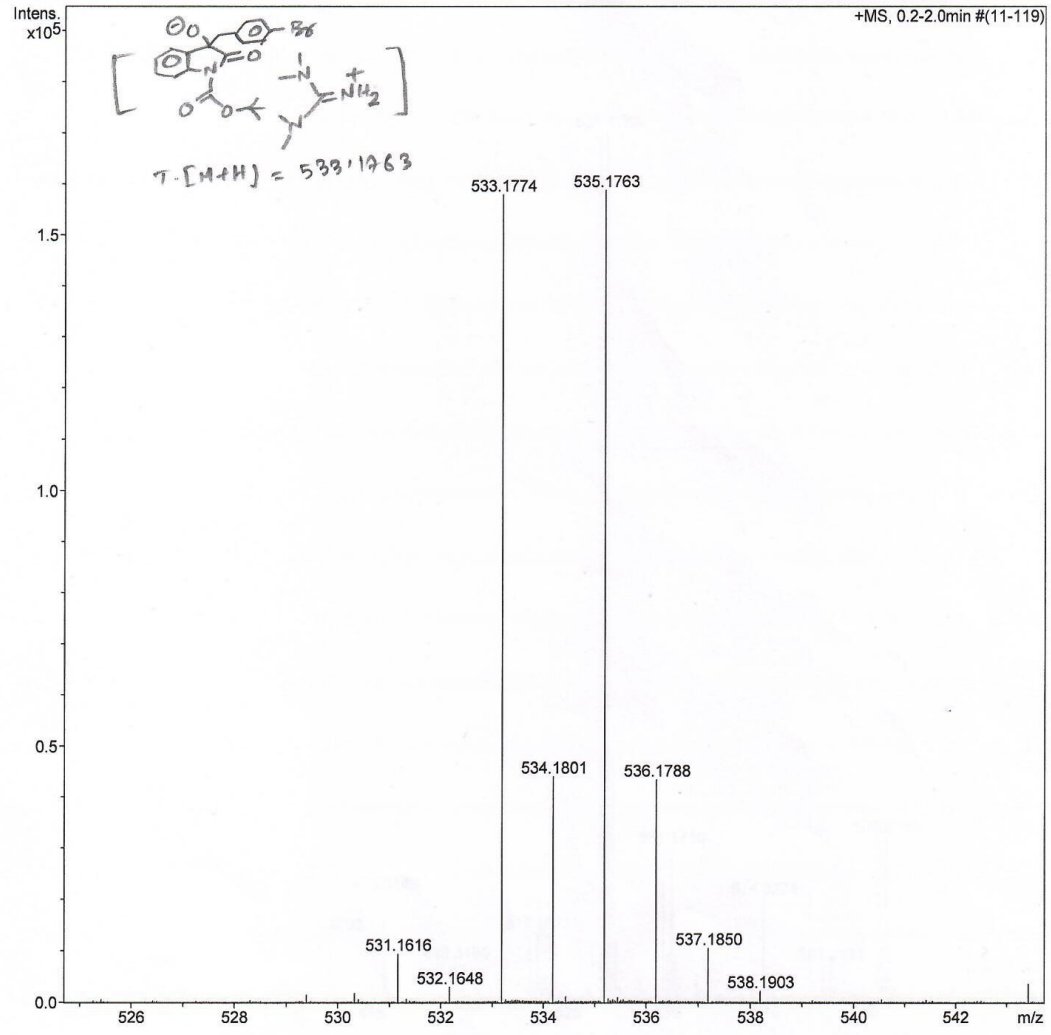
Method	tune_low.m	Operator	Rajesh Vashisth
Sample Name	PR-01-time-3.45pm	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



4th inject

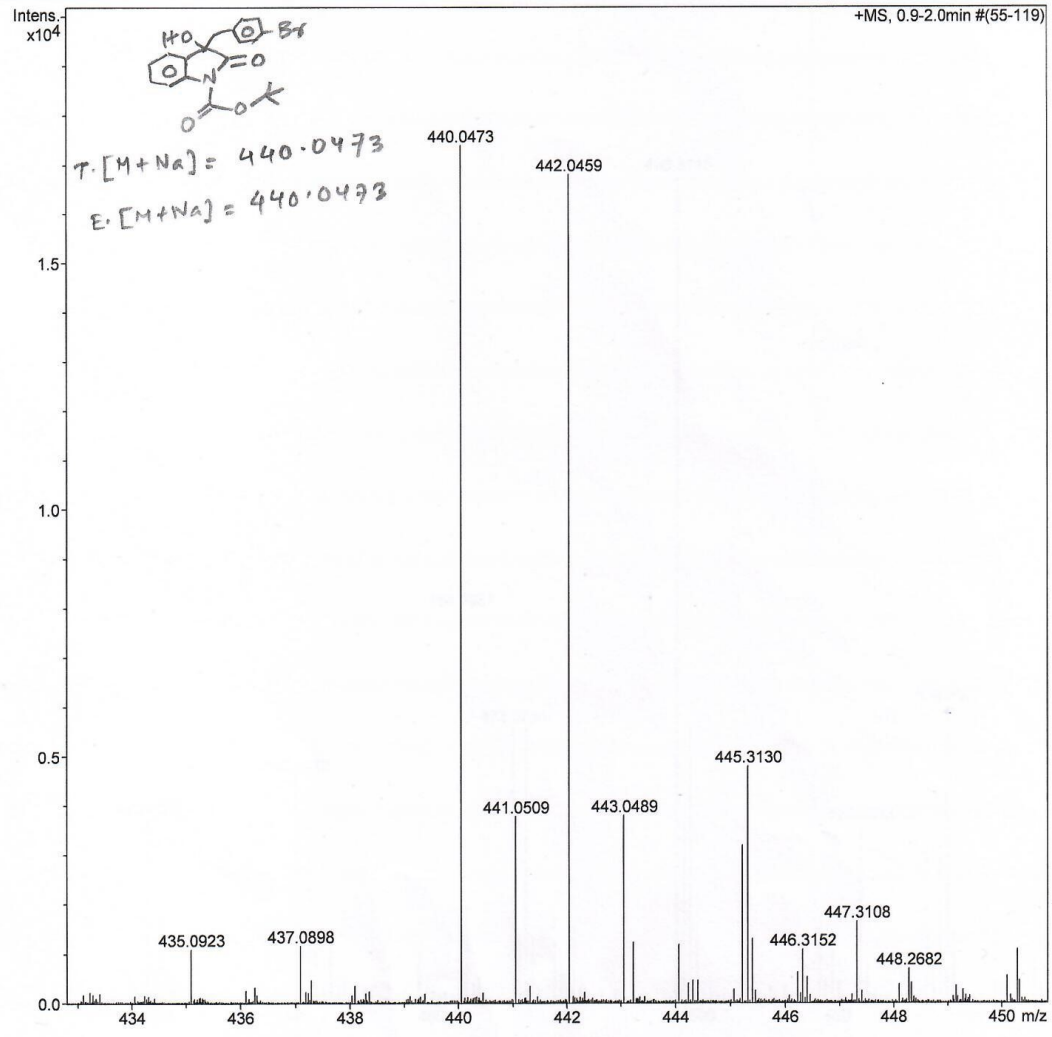
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF DBR\MAR\PR-01-time-4.15pm-2.d	Acquisition Date	2/24/2018 4:29:44 AM
Method	tune_low_Pos.m	Operator	Rajesh Vashisth
Sample Name	PR-01-time-4.15pm	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



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5th Entry

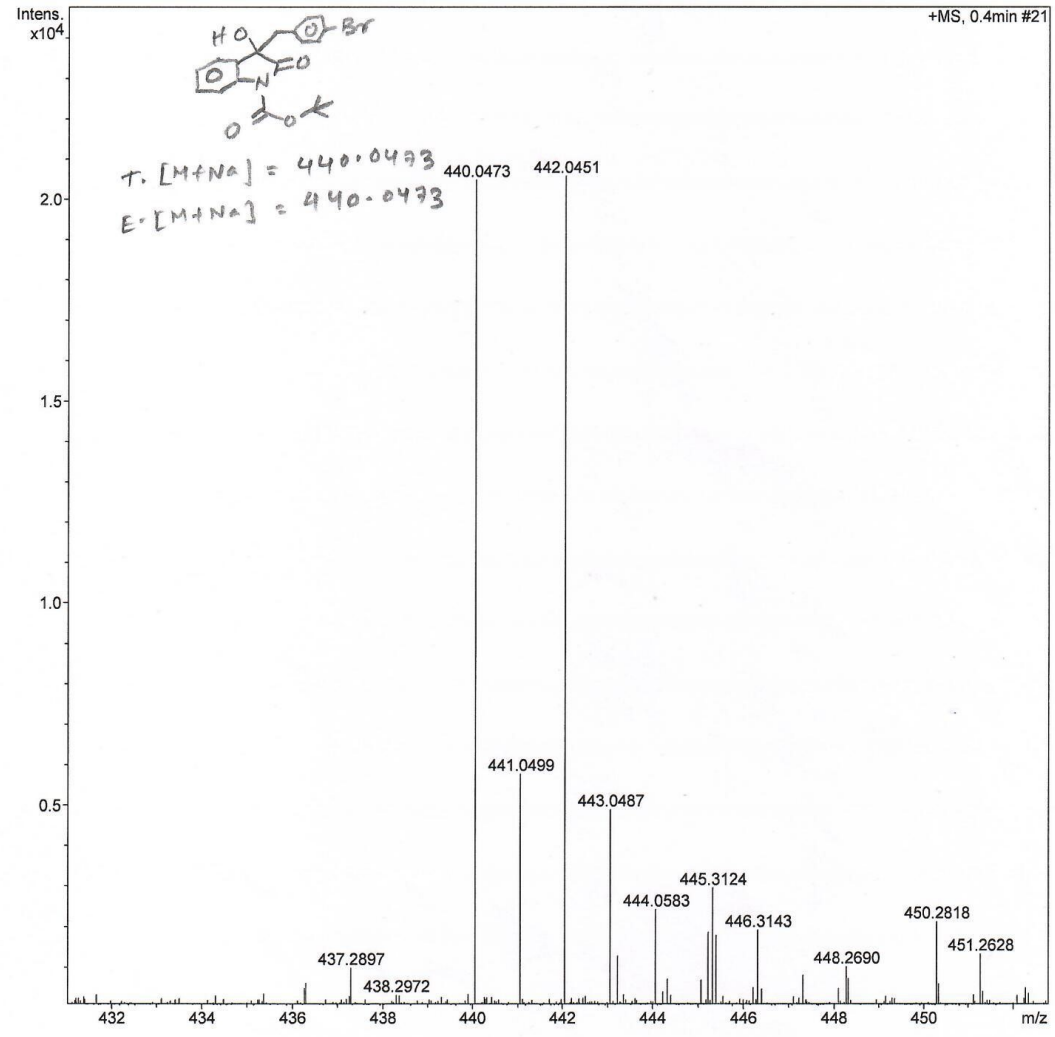
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF DBR\MAR\PR-01-time-4.45pm-3.d	Acquisition Date	2/24/2018 4:57:40 AM
Method	tune_low_Pos.m	Operator	Rajesh Vashisth
Sample Name	PR-01-time-4.45pm	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



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