Supporting Information

Syntheses of Nitromethyl-substituted Oxindole Derivatives via a Desulfonylation Cascade

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List of contents

General experimental Methods.................................................................1-2
General procedure for the syntheses of compounds 2a-j, 3a-3j............... 2-6
1H and 13C NMR spectra of compounds 3a-3j.........................................7-22

Experimental section

General: All reactions were carried out in a sealed tube; stirring was achieved with an oven-dried magnetic stirring bar. Solvents were purified by standard methods unless otherwise noted. Commercially available reagents were purchased from Aladdin Company in China and used throughout without further purification other than those detailed below. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis. Deuterated solvents were purchased from Cambridge Isotope laboratories. 1H and 13C NMR spectra were recorded on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz respectively. HRMS spectrometry (LC-HRMS) was recorded on a LXQ Spectrometer (Thermo Scientific) operating on ESI (MeOH as a solvent)
General procedure for the synthesis of compound 2

Primary amine (1.2 equiv) and Et$_3$N (2 equiv) were added to a dried flask, then benzenesulfonyl chloride (1 equiv) in dichloromethane was injected into it. The mixture was stirred at 0°C until TLC showed that benzenesulfonyl chloride was totally consumed. Water was added to the reaction mixture and extracted with dichloromethane. The combined organic layers were dried over Na$_2$SO$_4$, concentrated under reduced pressure. Without further purification, the residue was used for the next step. Methacryloyl chloride (2 equiv) in dichloromethane was added to the mixture of the above residue, triethylamine (2 equiv) and DMAP (0.1 equiv) in dichloromethane. The mixture was stirred overnight at room temperature. Then the reaction mixture was washed with saturated aqueous Na$_2$CO$_3$ (5 mL) and extracted with dichloromethane. The combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether : ethyl acetate =12:1) on silica gel to afford the corresponding product 2 in a total yield of 62~74%.

General procedure for the syntheses of compounds 3a-j

$N$-Methyl-$N$-(phenylsulfonyl)methacrylamide (2.0 mmol, 1.0 equiv) was added to a dried flask, followed by the addition of NaHCO$_3$ (2 mmol, 1.0 equiv), NaNO$_2$ (4.0 mmol, 2 equiv), K$_2$S$_2$O$_8$ (2.0 equiv) and anhydrous CH$_3$CN (2 mL). The reaction mixture was stirred at 120 °C for 18 h. After the reaction was completed, the reaction mixture was cooled down to room temperature and diluted with EtOAc, the combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum, and then purified by flash chromatography (Petroleum ether : EtOAc =25:1) to provide the title compound 3a as a sticky solid in a 88% yield. The same procedure for producing other compounds 3b-j.

1-iso-Propyl-3-methyl-3-(nitromethyl)indolin-2-one (3a)
IR: 2925, 2854, 2359, 1714, 1611, 1556, 1452, 1357, 1213, 754 cm⁻¹. ¹H-NMR (CDCl₃, 400MHz): δ (ppm) 7.33-7.04 (aromatic H, 4H), 4.96 (d, J=13.2 Hz, 1H), 4.77 (d, J=13.6 Hz, 1H), 4.68 (m, 1H), 1.56 (d, J=7.2 Hz, 6H), 1.40 (s, 3H); ¹³C-NMR (CDCl₃,100Hz): 19.3, 21.9, 44.3, 46.8, 79.1, 110.5, 122.3, 122.6, 129.0, 129.5, 142.4, 177.0; HRMS (ESI) m/z calculated for C₁₃H₁₇N₂O₃ 249.1239, [M+H]⁺, found 249.1249.

1-iso-Propyl-3,5-dimethyl-3-(nitromethyl)indolin-2-one (3b)

IR: 2974, 2855, 2359, 1713, 1619, 1557, 1382, 1294, 813 cm⁻¹. ¹H-NMR (CDCl₃, 400MHz):
δ (ppm) 7.11-6.86 (aromatic H, 3H), 4.93 (d, J=13.2 Hz, 1H), 4.75 (d, J=13.6 Hz, 1H), 4.64 (m, 1H), 2.38 (s, 3H), 1.55 (d, J=6.8 Hz, 6H), 1.37 (s, 3H); ¹³C-NMR (CDCl₃,100Hz): 19.1, 19.3, 22.0, 44.3, 46.6, 79.2, 111.4, 122.4, 122.9, 126.5, 139.1, 142.5, 177.3; HRMS (ESI) m/z calculated for C₁₄H₁₉N₂O₃ 263.1396 [M+H]⁺, found 263.1395.

5-(tert-Butyl)-1-isopropyl-3-methyl-3-(nitromethyl)indolin-2-one (3c)

IR: 3418, 2968, 2926, 2362, 1714, 1620, 1557, 1381, 1160, 658 cm⁻¹. ¹H-NMR (CDCl₃, 400MHz):
δ (ppm) 7.28-7.06 (aromatic H, 3H), 4.93 (d, J=13.6 Hz, 1H), 4.76 (d, J=13.2 Hz, 1H), 4.64 (m, 1H), 1.57 (d, J=6.8 Hz, 3H), 1.55 (d, J=6.8 Hz, 3H), 1.38 (s, 3H), 1.35 (s, 9H); ¹³C-NMR (CDCl₃,100Hz): 19.4, 22.7, 31.1, 35.1, 44.3, 46.6, 79.3, 107.8, 119.2, 122.1, 126.4,
3-Methyl-3-(nitromethyl)-1-propylindolin-2-one (3d)

IR: 3434, 2924, 2854, 1714, 1612, 1557, 1377, 1160, 753 cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400MHz): 
\(\delta\) (ppm) 7.35-6.92 (aromatic H, 4H), 4.98 (d, \(J=13.6\) Hz, 1H), 4.80 (d, \(J=13.2\) Hz, 1H), 3.82 (m, 1H), 3.69 (m, 1H), 1.77 (m, 2H), 1.42 (s, 3H), 1.02 (t, 3H); \(^{13}\)C-NMR (CDCl\(_3\), 100Hz): 14.1, 20.6, 22.0, 42.0, 47.0, 79.0, 109.2, 122.5, 127.0, 129.2, 143.1, 177.2; HRMS (ESI) m/z calculated for C\(_{17}\)H\(_{25}\)N\(_2\)O\(_3\) 305.1865 [M+H]\(^+\), found 305.1863.

3,5-Dimethyl-3-(nitromethyl)-1-propylindolin-2-one (3e)

IR: 2964, 2855, 2359, 1716, 1557, 1454, 1386, 1169, 813 cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400MHz): 
\(\delta\) (ppm) 7.28-6.74 (aromatic H, 3H), 4.95 (d, \(J=13.6\) Hz, 1H), 4.78 (d, \(J=13.6\) Hz, 1H), 3.78 (m, 1H), 3.67 (m, 1H), 2.39 (s, 3H), 1.78 (m, 2H), 1.40 (s, 3H), 1.00 (t, 3H); \(^{13}\)C-NMR (CDCl\(_3\), 100Hz): 11.4, 20.6, 22.0, 22.1, 41.9, 46.9, 79.1, 110.0, 122.3, 123.2, 126.3, 139.4, 143.1, 177.5; HRMS (ESI) m/z calculated for C\(_{14}\)H\(_{18}\)NaN\(_2\)O\(_3\) 285.1215 [M+Na]\(^+\), found 285.1214.

5-(tert-Butyl)-3-methyl-3-(nitromethyl)-1-propylindolin-2-one (3f)
1-Butyl-3-methyl-3-(nitromethyl)indolin-2-one (3g)

IR: 3418, 2925, 2855, 2362, 1718, 1557, 1451, 1384, 1171, 772 cm⁻¹; \(^1\)H-NMR (CDCl₃, 400MHz): \(\delta\) (ppm) 7.16-6.91 (aromatic H, 3H), 4.95 (d, \(J=13.2\) Hz, 1H), 4.78 (d, \(J=13.2\) Hz, 1H), 3.82 (m, 1H), 3.71 (m, 1H), 1.78 (m, 2H), 1.41 (s, 3H), 1.35 (s, 9H), 1.03 (t, 3H); \(^1\)C-NMR (CDCl₃, 100Hz): 19.7, 20.2, 22.7, 29.4, 31.6, 43.0, 47.0, 79.0, 109.1, 122.5, 127.0, 129.3, 143.0, 177.2; HRMS (ESI) m/z calculated for C₁₇H₂₅N₂O₃ 305.1865 [M+H]⁺, found 305.1863.

1-Butyl-3,5-dimethyl-3-(nitromethyl)indolin-2-one (3h)

IR: 2924, 2854, 2359, 1717, 1613, 1420, 1376, 1160, 754 cm⁻¹; \(^1\)H-NMR (CDCl₃, 400MHz): \(\delta\) (ppm) 7.35-6.92 (aromatic H, 4H), 4.98 (d, \(J=13.6\) Hz, 1H), 4.80 (d, \(J=13.6\) Hz, 1H), 3.84 (m, 1H), 3.72 (m, 1H), 1.75 (m, 2H), 1.46 (m, 2H), 1.44 (s, 3H), 1.00 (t, 3H); \(^1\)C-NMR (CDCl₃, 100Hz): 14.1, 20.7, 22.4, 22.7, 41.9, 46.8, 79.1, 106.5, 119.5, 122.1, 126.2, 142.9, 177.5; HRMS (ESI) m/z calculated for C₁₄H₁₉N₂O₃ 263.1396 [M+H]⁺, found 263.1395.
5-chloro-1-isopropyl-3-methyl-3-(nitromethyl)indolin-2-one (3i)

IR: 3928, 2974, 2460, 1786, 1658, 1576, 1450, 1397, 719 cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400MHz):
\[ \delta \text{ (ppm)} \ 7.15-7.04 \text{(aromatic H, 3H)}, \ 4.96 \text{ (d, } J=14.0 \text{ Hz, 1H)}, \ 4.75 \text{ (d, } J=13.6 \text{ Hz, 1H)}, \ 4.63 \text{(m, 1H)}, \ 1.55 \text{ (d, } J=7.2 \text{ Hz, 6H)}, \ 1.38 \text{(s, 3H)} \]; $^{13}$C-NMR (CDCl$_3$, 100Hz): 21.9, 23.8, 44.7, 46.3, 78.9, 111.1, 122.2, 123.4, 127.9, 129.4, 134.8, 143.6, 177.0; HRMS (ESI) m/z calculated for C$_{13}$H$_{16}$ClN$_2$O$_3$ 283.0849 [M+H]$^{+}$, found 283.0962.

5-bromo-1-isopropyl-3-methyl-3-(nitromethyl)indolin-2-one (3j)

IR: 3958, 2934, 2470, 1785, 1678, 1576, 1415, 1367, 719 cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400MHz):
\[ \delta \text{ (ppm)} \ 7.22-7.08 \text{(aromatic H, 3H)}, \ 4.96 \text{ (d, } J=13.6 \text{ Hz, 1H)}, \ 4.75 \text{ (d, } J=13.6 \text{ Hz, 1H)}, \ 4.60 \text{(m, 1H)}, \ 1.55 \text{ (d, } J=7.2 \text{ Hz, 6H)}, \ 1.38 \text{(s, 3H)} \]; $^{13}$C-NMR (CDCl$_3$, 100Hz): 21.8, 23.8, 44.7, 46.3, 78.8, 113.8, 122.7, 123.8, 125.1, 128.4, 128.6, 132.4, 143.8, 176.8; HRMS (ESI) m/z calculated for C$_{13}$H$_{16}$BrN$_2$O$_3$ 327.0344, [M+H]$^{+}$, found 327.0631.