Supporting Information

Visible-light-enabled aerobic denitrative C3-alkenylation of indoles with β-nitrostyrenes

Ruchi Chawla, a Ritu Kapoor b and Lal Dhar S. Yadav* b

a Polymer Research Laboratory, Department of Chemistry, Motilal Nehru National Institute of Technology Allahabad, Prayagraj 211004, India
b Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211 002, India

E-mail: ldsyadav@hotmail.com (L.D.S. Yadav).

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**General Information:**

Reagents were obtained from commercial suppliers, and used without further purification unless otherwise specified by a reference. All reactions were performed under ambient air. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF<sub>254</sub> (Merck) plates. <sup>1</sup>H NMR spectra were recorded on a Bruker Advance II 400 NMR spectrometer in DMSO/CDCl<sub>3</sub> using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants (J) are reported in Hertz (Hz). <sup>13</sup>C NMR spectra were recorded on the same instrument at 100 MHz in DMSO/CDCl<sub>3</sub> and TMS was used as internal reference. The following abbreviations have been used to indicate the multiplicity: singlet (s), doublet (d), triplet (t) and multiplet (m). HRMS were recorded on a Waters Q-ToF Micro mass spectrometer.

**General procedure for the synthesis of 3-alkenylindoles 3:**

![Chemical structure](image)

A mixture of indole 1 (1.5 mmol) and β-nitrostyrenes 2 (1.0 mmol) in CH<sub>3</sub>CN (3 mL) was irradiated with visible light (white light emitting diodes (LED), 7.0 W, irradiation from side at a distance of 0.75 cm) in a 10 mL round bottom flask with stirring at r.t. for 18 h. Upon completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with EtOAc (3 x 15 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (EtOAc/n-hexane, 1:19) to afford an analytically pure sample of 3-alkenylindoles 3.
Characterization data for synthesized 3-alkenyldiones 3

(E)-3-styryl-1H-indole 3a\(^1,2\)

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.35 (s, 1H), 8.03 (d, \(J = 8.0\) Hz, 1H), 7.67 (d, \(J = 2.4\) Hz, 1H), 7.59 (d, \(J = 8.0\) Hz, 2H), 7.46 (d, \(J = 5.6\) Hz, 1H), 7.43 (d, \(J = 3.2\) Hz, 1H), 7.36 (t, \(J = 8.0\) Hz, 2H), 7.10 – 7.21 (m, 4H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 139.0, 137.5, 129.1, 126.7, 126.5, 125.9, 125.6, 123.7, 123.0, 122.2, 120.3, 120.1, 114.1, 112.4. HRMS (ESI): calculated for C\(_{16}\)H\(_{14}\)N [(M+H)\(^+\)] 220.1121; found 220.1137.

(E)-3-((4-methylstyryl)-1H-indole 3b\(^1,2\)

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.32 (s, 1H), 8.01 (d, \(J = 8.0\) Hz, 1H), 7.64 (d, \(J = 2.4\) Hz, 1H), 7.47 (d, \(J = 8.0\) Hz, 2H), 7.44 (d, \(J = 8.0\) Hz, 1H), 7.38 (d, \(J = 16.8\) Hz, 1H), 7.19 – 7.11 (m, 4H), 7.08 (d, \(J = 16.8\) Hz, 1H), 2.31 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 137.5, 136.2, 135.8, 129.7, 126.2, 125.8, 125.6, 123.8, 122.2, 122.0, 120.3, 120.0, 114.2, 112.3, 21.2. HRMS (ESI): calculated for C\(_{17}\)H\(_{16}\)N [(M+H)\(^+\)] 234.1277; found 234.1260.

(E)-3-((4-methoxystyryl)-1H-indole 3c\(^1,3\)

\(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.25 (s, 1H), 7.98 (d, \(J = 8.0\) Hz, 1H), 7.58 (d, \(J = 2.4\) Hz, 1H), 7.50 (d, \(J = 8.8\) Hz, 2H), 7.42 (d, \(J = 8.0\) Hz, 1H), 7.26 (d, \(J = 16.6\) Hz, 1H), 7.15 (t, \(J = 7.6\) Hz, 1H), 7.10 (t, \(J = 6.9\) Hz, 1H), 7.04 (d, \(J = 16.4\) Hz, 1H), 6.92 (d, \(J = 8.2\) Hz, 2H), 3.76 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 158.0, 137.0, 131.2, 126.6, 125.3, 125.2, 123.2, 121.7, 120.3, 119.8, 119.5, 114.1, 113.9, 111.9, 55.1. HRMS (ESI): calculated for C\(_{17}\)H\(_{16}\)NO [(M+H)\(^+\)] 250.1226; found 250.1196.
(E)-3-(4-fluorostyryl)-1H-indole 3d$^2$

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.34 (s, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.60 (m, 3H), 7.43 (t, $J = 8.4$ Hz, 1H), 7.39 (d, $J = 16.8$ Hz, 1H), 7.20 – 7.09 (m, 5H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 162.5, 160.1, 137.5, 135.6, 127.6, 127.5, 126.4, 125.6, 123.0, 122.9, 122.6, 122.2, 120.3, 120.1, 115.9, 115.7, 114.0, 112.4. HRMS (ESI): calculated for C$_{16}$H$_{13}$FN [(M+H)$^+$] 238.1027; found 238.1027.

(E)-3-(4-chlorostyryl)-1H-indole 3e$^{1,2}$

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.39 (s, 1H), 8.03 (d, $J = 7.2$ Hz, 1H), 7.67 (s, 1H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.49-7.43 (m, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.20 – 7.08 (m, 3H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 138.1, 137.5, 130.8, 129.0, 127.5, 126.9, 125.6, 124.0, 122.3, 120.4, 120.2, 114.0, 112.4. HRMS (ESI): calculated for C$_{16}$H$_{13}$ClN [(M+H)$^+$] 254.0731; found 254.0759.

(E)-3-(4-bromostyryl)-1H-indole 3f$^2$

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.41 (s, 1H), 8.04 (d, $J = 7.2$ Hz, 1H), 7.68 (s, 1H), 7.53-7.44 (m, 6H), 7.20 – 7.01 (m, 3H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 138.4, 137.5, 131.9, 127.8, 127.0, 125.5, 124.1, 122.3, 122.3, 120.4, 120.2, 119.2, 114.0, 112.4. HRMS (ESI): calculated for C$_{16}$H$_{13}$BrN [(M+H)$^+$] 298.0226; found 298.0271.
(E)-3-(2-chlorostyryl)-1H-indole 3g

1H NMR (400 MHz, DMSO) δ 11.47 (s, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.53 (d, J = 16.4 Hz, 1H), 7.50-7.46 (m, 2H), 7.39 (d, J = 12.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.24-7.17 (m, 3H). 13C NMR (100 MHz, DMSO) δ 137.6, 136.5, 131.7, 130.0, 128.0, 127.8, 127.7, 126.3, 126.0, 125.4, 122.4, 120.6, 120.0, 118.7, 114.0, 112.6. HRMS (ESI): calculated for C16H13ClN [(M+H)+] 254.0731; found 254.0723.

(E)-3-(2-(naphthalen-1-ylvinyl)-1H-indole 3h

1H NMR (400 MHz, DMSO) δ 11.42 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.88 (s, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 3.2 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.59 (t, J = 7.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.50 (d, J = 16.4 Hz, 1H), 7.47 (d, J = 7.4 Hz, 1H), 7.21-7.16 (m, 2H). 13C NMR (100 MHz, DMSO) δ 137.0, 135.6, 133.6, 130.6, 128.5, 126.6, 126.4, 126.0, 125.8, 125.3, 123.7, 121.9, 121.9, 119.9, 119.8, 119.5, 114.5, 112.0. HRMS (ESI): calculated for C20H16N [(M+H)+] 270.1277; found 270.1318.

3-((E)-2-(Thiophen-2-ylvinyl)-1H-indole 3i

1H NMR (400 MHz, DMSO) δ 11.34 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.32-7.31 (m, 2H), 7.17-7.10 (m, 4H), 7.01 (s, 1H). 13C NMR (100 MHz, DMSO) δ 144.1, 137.0, 127.8, 126.4, 124.9, 124.3, 123.0, 122.3, 121.8, 119.8, 119.7, 117.1, 113.2, 111.9. HRMS (ESI): calculated for C14H12NS [(M+H)+] 226.0685; found 226.0681.
(E)-5-methyl-3-styryl-1H-indole 3j

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.22 (s, 1H), 7.83 (s, 1H), 7.61 (d, $J = 2.3$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 16.8$ Hz, 1H), 7.37 – 7.32 (m, 3H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.10 (d, $J = 16.8$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 1H), 2.47 (s, 3H).

$^{13}$C NMR (100 MHz, DMSO) $\delta$ 139.1, 135.8, 129.0, 128.8, 126.6, 125.9, 123.8, 123.4, 123.2, 120.0, 113.6, 112.1, 21.9. HRMS (ESI): calculated for C$_{17}$H$_{16}$N [(M+H)$^+$] 234.1277; found 234.1260.

(E)-5-methoxy-3-styryl-1H-indole 3k

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.24 (s, 1H), 7.65 (s, 1H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.46 (d, $J = 17.2$ Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 3H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 16.4$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 3.86 (s, 3H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 154.4, 139.1, 132.4, 129.0, 126.6, 126.5, 126.2, 125.9, 123.2, 122.9, 114.0, 113.0, 112.1, 102.2, 56.0. HRMS (ESI): calculated for C$_{17}$H$_{16}$NO [(M+H)$^+$] 250.1226; found 250.1244.

(E)-5-fluoro-3-styryl-1H-indole 3l

$^1$H NMR (400 MHz, DMSO) $\delta$ 11.47 (s, 1H), 7.82 (d, $J = 10.0$ Hz, 1H), 7.75 (s, 1H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.45 – 7.41 (m, 2H), 7.35 (t, $J = 6.8$ Hz, 2H), 7.19 (t, $J = 6.6$ Hz, 1H), 7.10 (d, $J = 17.1$ Hz, 1H), 7.03 (t, $J = 8.4$ Hz, 1H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 159.0, 138.9, 134.0, 129.0, 128.1, 126.7, 126.0, 125.8, 123.9, 122.4, 114.4, 113.3, 110.4, 105.3. HRMS (ESI): calculated for C$_{16}$H$_{13}$FN [(M+H)$^+$] 238.1027; found 238.1007.
(E)-5-chloro-3-styryl-1H-indole 3m²

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 7.98 (s, 1H), 7.55 (d, \(J = 8.0\) Hz, 2H), 7.41 – 7.38 (m, 3H), 7.33 (d, \(J = 8.8\) Hz, 1H), 7.30 (d, \(J = 8.0\) Hz, 2H), 7.24 (dd, \(J = 8.6, 1.8\) Hz, 1H), 7.10 (d, \(J = 16.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl₃) δ 138.2, 135.1, 128.7, 126.9, 126.7, 126.2, 126.1, 125.9, 124.8, 123.0, 120.9, 119.7, 115.5, 112.4. HRMS (ESI): calculated for C\(_{16}\)H\(_{13}\)ClN [(M+H)+] 254.0731; found 254.0719.

(E)-5-bromo-3-styryl-1H-indole 3n²

\(^1\)H NMR (400 MHz, DMSO) δ 11.57 (s, 1H), 8.22 (s, 1H), 7.76 (s, 1H), 7.62 (d, \(J = 6.4\) Hz, 2H), 7.48 – 7.27 (m, 5H), 7.21 (d, \(J = 6.4\) Hz, 1H), 7.09 (d, \(J = 16.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO) δ 138.8, 136.0, 129.0, 127.5, 127.2, 126.8, 126.0, 124.7, 124.4, 122.3, 122.0, 114.3, 113.9, 112.9. HRMS (ESI): calculated for C\(_{16}\)H\(_{13}\)BrN [(M+H)+] 298.0226; found 298.0252.

(E)-3-styryl-1H-indole-5-carbonitrile 3o²

\(^1\)H NMR (400 MHz, DMSO) δ 11.88 (s, 1H), 8.63 (s, 1H), 7.88 (s, 1H), 7.65 (d, \(J = 7.6\) Hz, 2H), 7.61 (d, \(J = 8.4\) Hz, 1H), 7.53 – 7.48 (m, 2H), 7.36 (t, \(J = 7.2\) Hz, 2H), 7.22 (dd, \(J = 14.6, 6.8\) Hz, 2H). \(^{13}\)C NMR (100 MHz, DMSO) δ 139.0, 138.7, 129.0, 128.0, 127.1, 126.2, 125.9, 125.6, 125.5, 124.9, 121.4, 121.2, 115.2, 113.6, 102.2. HRMS (ESI): calculated for C\(_{17}\)H\(_{13}\)N\(_2\) [(M+H)+] 245.1073; found 245.1109.

(E)-2-methyl-3-styryl-1H-indole 3p¹³

\(^1\)H NMR (400 MHz, DMSO) δ 11.25 (s, 1H), 7.96 (d, \(J = 3.6\) Hz, 1H), 7.63 (d, \(J = 7.2\) Hz, 2H), 7.44-7.34 (m, 4H), 7.19 (t, \(J = 7.2\) Hz, 1H), 7.12 – 7.03 (m, 3H), 2.54 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO) δ 139.1, 135.6, 134.7, 128.8, 126.7, 126.6, 125.8, 125.3, 121.8, 121.8, 120.5,
119.8, 111.1, 110.7, 12.4. HRMS (ESI): calculated for C_{17}H_{16}N [(M+H)^+] 234.1277; found 234.1284.

(E)-3-(4-methoxystyryl)-2-methyl-1H-indole 3q^{3}

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.98-7.97 (m, 1H), 7.85 (s, 1H), 7.50-7.48 (m, 2H), 7.28-7.26 (m, 1H), 7.23- 7.16 (m, 3H), 7.09 (d, $J$ = 16.4 Hz, 1H), 6.95-6.93 (m, 2H), 3.85 (s, 3H), 2.50 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.6, 135.6, 134.1, 132.0, 126.9, 125.1, 121.8, 119.8, 119.8, 114.2, 111.2, 110.7, 55.5, 12.5. HRMS (ESI): calculated for C$_{18}$H$_{18}$NO [(M+H)^+] 264.1383; found 264.1370.

(E)-3-(4-chlorostyryl)-2-methyl-1H-indole 3r^{3}

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.95-7.94 (m, 1H), 7.82 (s, 1H), 7.43 (d, $J$ = 12.0 Hz, 2H), 7.30 (d, $J$ = 7.4 Hz, 2H), 7.26-7.23 (m, 2H), 7.22-7.19 (m, 2H), 7.04 (d, $J$ = 16.4 Hz, 1H), 2.47 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.6, 135.6, 135.0, 131.8, 128.8, 126.9, 126.6, 123.9, 122.4, 122.0, 120.6, 119.8, 110.9, 110.8, 12.5. HRMS (ESI): calculated for C$_{18}$H$_{15}$NCl [(M+H)^+] 268.0888; found 268.0919.

(E)-1-methyl-3-styryl-1H-indole 3s^{4}

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J$ = 8.0 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 2H), 7.29-7.13 (m, 8H), 7.02 (d, $J$ = 16.0 Hz, 1H), 3.72 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 33.0, 109.6, 114.1, 120.1, 120.3, 121.6, 122.3, 124.8, 125.8, 126.2, 126.5, 128.5, 128.7, 137.8, 138.7. HRMS (ESI): calculated for C$_{17}$H$_{16}$N [(M+H)^+] 234.1277; found 234.1290.
References

Copies of $^1$H NMR spectra of synthesized 3-alkenyldiones 3

$^1$H NMR spectrum of 3a

$^1$H NMR spectrum of 3b
$^1$H NMR spectrum of 3c

$^1$H NMR spectrum of 3d
$^1$H NMR spectrum of 3e

$^1$H NMR spectrum of 3f
\[^1\text{H} \text{NMR spectrum of } 3g\]

\[^1\text{H} \text{NMR spectrum of } 3h\]
The image shows the ⅜H NMR spectrum of compounds 3i and 3j. The spectra display the chemical shift values in parts per million (ppm) and show the positions and intensities of the peaks corresponding to the hydrogens in the molecules. The structures of 3i and 3j are depicted above the respective spectra, highlighting the hydrogen atoms whose resonances are observed in the NMR tests.
$^1$H NMR spectrum of 3k

$^1$H NMR spectrum of 3l
$^1$H NMR spectrum of 3m

$^1$H NMR spectrum of 3n
$^1$H NMR spectrum of 3o

$^1$H NMR spectrum of 3p
$^1$H NMR spectrum of 3q

$^1$H NMR spectrum of 3r
$^1$H NMR spectrum of 3s