Supporting Information
for

The Beckmann Rearrangement Executed by Visible-light-Driven Generation of Vilsmeier-Haack Reagent

Vishnu P. Srivastava, Arvind K. Yadav and Lal Dhar S. Yadav*

Green Synthesis Lab, Department of Chemistry, University of Allahabad,
Allahabad-211002, India

E-mail: ldsyadav@hotmail.com

General Information: All commercially available reagents were obtained from commercial suppliers and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glass ware under a nitrogen atmosphere. 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 GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in CDCl$_3$/DMSO-$d_6$ using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants ($J$) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer.

Green LEDs (535 nm, 2.6 W) Rebel LED, mounted on a 25 mm Cool Base 161 lm@ 700mA was purchased from Commercial Supplier Luxeon Star LEDs Quadica Developments Inc. 47 6th Concession Rd. Brantford, Ontario N 32 5L7, Canada.

General procedure for the visible-light-driven Beckmann rearrangement

A mixture of ketoxime 1 (1.0 mmol), CBr$_4$ (2.0 equiv), eosin Y (2 mol%), DMF (20 mol%) and MeCN (3 mL) was taken in a hot oven dried round bottom flask and irradiated with green LEDs under a nitrogen atmosphere. After completion of the reaction as indicated by TLC, it was quenched with saturated aqueous sodium hydrogen carbonate (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc-hexane) to give the corresponding amide 2 in high yield. All the products are known compounds and were characterized by comparison of their mp, TLC, $^1$H NMR, $^{13}$C NMR and MS data with authentic samples obtained commercially or prepared by literature methods.$^{1-6}$
The characterization data of the synthesized compounds 2 are summarized below with relevant references.

**4-Methoxy-N-phenylacetamide (Table 3, entry 1)** \(^\text{1,2}\) : mp 128-130 °C [lit. mp 129-130 °C] \(^1\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 7.37 \text{ (d, } 2\text{H, } J = 9.0 \text{ Hz)}, 7.04 \text{ (br, } 1\text{H)}, 6.86 \text{ (d, } 2\text{H, } J = 9.0 \text{ Hz)}, 3.81 \text{ (s, } 3\text{H}), 2.13 \text{ (s, } 3\text{H})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 168.1, 156.6, 130.9, 122.0, 114.1, 55.4, 24.4\); HRMS (EI): calcd for C\(_9\)H\(_{11}\)NO\(_2\) 165.0790, found 165.0788.

**N-p-tolylacetamide (Table 3, entry 2)** \(^\text{1,2}\) : mp 149-150 °C [lit. mp 149-151 °C] \(^1\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 7.53 \text{ (br, } 1\text{H)}, 7.36 \text{ (d, } 2\text{H, } J = 8.2 \text{ Hz)}, 7.07 \text{ (d, } 2\text{H, } J = 8.2 \text{ Hz)}, 2.31 \text{ (s, } 3\text{H}), 2.15 \text{ (s, } 3\text{H})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 168.3, 135.4, 133.9, 129.4, 120.1, 24.4, 20.8\); HRMS (EI): calcd for C\(_9\)H\(_{11}\)NO 149.0841, found 149.0843.

**N-phenylacetamide (Table 3, entry 3)** \(^\text{1,2}\) : mp 115-116 °C [lit. mp 114-116 °C] \(^1\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 8.47 \text{ (br, } 1\text{H)}, 7.49 \text{ (d, } 2\text{H, } J = 8.5 \text{ Hz)}, 7.23 \text{ (t, } 2\text{H, } J = 7.8 \text{ Hz)}, 7.03 \text{ (t, } 1\text{H, } J = 7.3 \text{ Hz)}, 2.09 \text{ (s, } 3\text{H})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 168.9, 138.1, 129.0, 124.4, 120.2, 24.5\); HRMS (EI): calcd for C\(_8\)H\(_9\)NO 135.0684, found 135.0682.

**N-(4-hydroxyphenyl)acetamide (Table 3, entry 4)** \(^3\) : mp 167-169 °C [lit. mp 167-168 °C] \(^3\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 9.37 \text{ (br, } 1\text{H)}, 8.95 \text{ (s, } 1\text{H)}, 7.52 \text{ (d, } 2\text{H, } J = 8.0 \text{ Hz)}, 7.03 \text{ (d, } 2\text{H, } J = 8.0 \text{ Hz)}, 2.03 \text{ (s, } 3\text{H})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 167.7, 153.4, 130.2, 120.4, 115.4, 24.3\); HRMS (EI): calcd for C\(_8\)H\(_9\)NO\(_2\) 151.0633, found 151.0635.
**N-(3-methoxyphenyl)acetamide (Table 3, entry 5)**\(^{1,2}\): mp 87-89 °C [lit. mp 87-88 °C]\(^1\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 7.78\) (br, 1H), 7.27-7.16 (m, 2H), 6.96 (d, 1H, \(J = 8.1\) Hz), 6.62 (dd, 1H, \(J = 2.1\) Hz; 8.1 Hz), 3.78 (s, 3H), 2.19 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 168.0, 160.0, 139.2, 129.6, 110.0, 105.8, 155.2, 55.3, 24.5\); HRMS (EI): calcd for C\(_9\)H\(_{11}\)NO\(_2\) 165.0790, found 165.0783.

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\text{H} & \text{N} \\
\text{O} & \\
\text{O} & \\
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**N-(2-bromophenyl)acetamide (Table 3, entry 6)**\(^1\): mp 98-99 °C [lit. mp 97-99 °C]\(^1\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 8.33\) (d, 1H, \(J = 8.5\) Hz), 7.71 (br, 1H), 7.55 (dd, 1H, \(J = 8.1\) Hz; 1.5 Hz), 7.30 (dt, 1H, \(J = 1.3\) Hz; 8.1 Hz), 7.00 (t, 1H, \(J = 7.3\) Hz), 2.25 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 169.6, 139.5, 138.1, 132.4, 128.3, 122.1, 121.8, 24.8\); HRMS (EI): calcd for C\(_8\)H\(_8\)BrNO 212.9789, found 212.9792.

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\text{O} & \\
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**N-(4-bromophenyl)acetamide (Table 3, entry 7)**\(^{1,2}\): mp 165-166 °C [lit. mp 166-167 °C]\(^1\), \(^1\)H NMR (400 MHz, DMSO-\(d_6\)); 10.04 (br, 1H), 7.51 (d, 2H, \(J = 8.9\) Hz), 5.57 (d, 2H, \(J = 8.9\) Hz), 2.09 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)); \(\delta = 169.4, 139.6, 132.4, 128.2, 121.8, 24.8\); HRMS (EI): calcd for C\(_8\)H\(_8\)BrNO 212.9789, found 212.9788.

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\begin{align*}
\text{Br} & \text{N} \\
\text{O} & \\
\text{O} & \\
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**N-(4-nitrophenyl)acetamide (Table 3, entry 8)**\(^1\): mp 194-196 °C [lit. mp 195–197 °C]\(^4\), \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 10.10\) (br, 1H), 8.33 (d, 2H, \(J = 9.0\) Hz), 8.18 (d, 2H, \(J = 9.0\) Hz),

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2.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 169.5, 140.9, 138.4, 128.8, 124.1, 24.8; HRMS (EI): calcd for C$_8$H$_8$N$_2$O$_3$ 180.0535, found 180.0537.

![Structure](image)

$N$-(3-nitrophenyl)acetamide (Table 3, entry 9)$^{15}$: mp 154-155 °C [lit. mp 155-156 °C]$^3$, $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 8.80 (br, 1H), 8.38 (s, 1H), 8.06 (t, 1H, $J$ = 8.2 Hz), 7.81 (d, 1H, $J$ = 8.0 Hz), 7.49 (d, 1H, $J$ = 8.0 Hz), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.1, 150.5, 140.7, 132.5, 129.5, 124.6, 121.5, 20.3; HRMS (EI): calcd for C$_8$H$_8$N$_2$O$_3$ 180.0535, found 180.0536.

![Structure](image)

$N$-(2-nitrophenyl)acetamide (Table 3, entry 10)$^{15}$: mp 93-94 °C [lit. mp 93-94 °C]$^3$, $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 9.97 (br, 1H), 8.05 (d, 1H, $J$ = 8.6 Hz), 7.64 (d, 1H, $J$ = 8.1 Hz), 7.52 (t, 1H, $J$ = 8.0 Hz), 7.40 (t, 1H, $J$ = 7.2 Hz), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.2, 142.5, 134.7, 131.2, 130.1, 128.6, 124.2, 23.3; HRMS (EI): calcd for C$_8$H$_8$N$_2$O$_3$ 180.0535, found 180.0532.

![Structure](image)

$N$-phenylbenzamide (Table 3, entry 11)$^{2,6}$: mp 162-164 °C [lit. mp 162-163 °C]$^6$, $^1$H NMR$^6$ (400 MHz, CDCl$_3$); $\delta$ = 7.90 (bs, 1H), 7.87-7.82 (m, 2H), 7.62 (d, 2H, $J$ = 8.0 Hz), 7.55-7.48 (m, 1H), 7.45-7.44 (m, 2H), 7.36-7.30 (m, 2H), 7.15-7.12 (m, 1H); $^{13}$C NMR$^2$ (100 MHz, CDCl$_3$): $\delta$ = 165.8, 138.1, 132.0, 129.3, 128.9, 128.3, 127.2, 124.7, 120.4; HRMS (EI): calcd for C$_{13}$H$_{11}$NO 197.0841, found 197.0843.
**N-benzyl-2-phenylacetamide (Table 3, entry 12)**: mp 67-69 °C [lit. mp 68 °C], $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 7.36-7.25 (m, 8H), 7.20-7.16 (m, 2H), 5.79 (s, 1H), 4.38 (d, 2H, $J$ = 6 Hz), 3.64 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$ = 170.9, 138.1, 134.8, 129.3, 129.0, 128.6, 127.4, 127.2, 43.7, 43.5, 30.4; HRMS (EI): calcd for C$_{15}$H$_{15}$NO 225.1154, found 225.1155.

**e-Caprolactam (Table 3, entry 13)**: mp 71-72 °C [lit. mp 70-71 °C], $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 6.49 (br, 1H), 3.24-3.14 (m, 2H), 2.45-2.40 (m, 2H), 1.76-1.71 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$ = 179.3, 43.0, 36.8, 30.7, 29.9, 23.3; HRMS (EI): calcd for C$_6$H$_{11}$NO 113.0841, found 113.0839.

**ω-Laurolactam (Table 3, entry 14)**: mp 150-153 °C [lit. mp 149-153 °C], $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 7.05 (br, 1H), 2.42 (t, 2H, $J$ = 6 Hz), 2.24 (t, 2H, $J$ = 6 Hz), 1.66-1.62 (m, 4H), 1.35-1.30 (m, 14H); $^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$ = 173.4, 39.0, 36.8, 28.2, 26.6, 26.2, 26.0, 25.6, 25.1, 24.8, 24.5, 23.8; HRMS (EI): calcd for C$_{12}$H$_{23}$NO 197.1780, found 197.1782.

**N-isopropylisobutyramide (Table 3, entry 15)**: mp 101-103 °C [lit. mp 101-102 °C], $^1$H NMR (400 MHz, CDCl$_3$); $\delta$ = 6.20 (br, 1H). 4.13-4.00 (m, 1H), 2.30 (septet, 1H, $J$ = 6.9 Hz), 1.15 (d, 12H, $J$ = 6.9 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$); $\delta$ = 174.5, 41.6, 36.0, 23.5, 19.8; HRMS (EI): calcd for C$_7$H$_{15}$NO 129.1154, found 129.1153.
\textit{N-}(2-naphthyl)acetamide (Table 3, entry 16)\textsuperscript{5,6}: mp 132-133 °C [lit. mp 132-134 °C]\textsuperscript{6}, \textsuperscript{\textit{1}}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 8.60\) (s, 1H), 8.16 (s, 1H), 7.71-7.67 (m, 3H), 7.40-7.35 (m, 3H), 2.21 (s, 3H); \textsuperscript{\textit{13}}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 169.3, 135.5, 133.8, 130.5, 128.7, 127.7, 127.4, 126.3, 125.0, 120.2, 117.1, 24.5\); HRMS (EI): calcd for C\textsubscript{12}H\textsubscript{11}NO 185.0841, found 185.0843.

References: