
Three-Component [3+2] Cycloaddition for Regio- and Diastereoselective Synthesis ofSpirooxindole-Pyrrolidines

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1. General information

All commercially available chemical reagents and solvents were purchased from Sigma-Aldrich, and Oakwood. \(^{1}\)H-NMR (400 MHz) and \(^{13}\)C-NMR spectra (101 MHz) were detected on Agilent NMR spectrometers. LC-MS were performed on an Agilent 2100 LC with 6130 quadrupole MS spectrometers. A linear gradient from 25:75 (v/v) MeOH/water to 100% MeOH over 7.0 min at a flow rate of 0.7 mL/min was used as a mobile phase. UV detections were conducted at 210 nm and 254 nm. Low resolution mass spectra were recorded in APCI (atmospheric pressure chemical ionization). A C18 column (5.0 \(\mu\)m, 6.0 x 50 mm) was used for the separation from Agela. The high-resolution mass spectra were obtained on a Waters Micromass GCT Premier. All products were purified on Agela Flash System with Venusil PrepG C18 column (10 \(\mu\)m, 120 Å, 21.2 mm x 250 mm).

2. General procedure for products

**General procedure I for one-pot synthesis of compound 1, 5 and 6.**

To a solution of cyclic amines 2 (1.3 mmol), aldehydes 3 (1.1 mmol), and olefinic oxindoles 4 (1.0 mmol) in 4 mL of EtOH was added BzOH (0.5 mmol). The reaction solution was stirred at 125 °C for 30 mins under microwave heating. Upon the completion of the reaction as monitored by LC-MS, the reaction mixture was evaporated to remove solvents, and the concentrated reaction solution was isolated by Agela Flash System to give product 1, 5 and 6.

**General procedure II for one-pot synthesis of compound 7a.**

To a solution of THIQ 2a (1.3 mmol), 2-azidobenzaldehyde or 2-nitrobenzaldehyde (1.1 mmol), and olefinic oxindoles 4a (1.0 mmol) in 4 mL of EtOH was added BzOH (0.5 mmol). The reaction solution was stirred at 125 °C for 30 mins under microwave heating. Upon the completion of the reaction as monitored by LC-MS, the reaction mixture was added to 1 mL of H\(_2\)O, Fe (2.5 mmol) and AcOH (3.0 mmol) *in situ*, then stirred at 85 °C for 6 h. the concentrated reaction solution was isolated by Agela Flash System to give product 7a.

3. Characterization of products

*Compound 1a*: white solid (63% yield). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 (d, \(J = 8.5\) Hz, 2H), 7.49 (d, \(J = 8.6\) Hz, 2H), 7.07 (td, \(J = 7.7, 1.2\) Hz, 1H), 6.90 (ddt, \(J = 14.3, 7.6, 4.5\) Hz, 3H), 6.76 – 6.68 (m, 3H), 6.39 (d, \(J = 7.8\) Hz, 1H), 5.29 (s, 1H), 4.90 (d, \(J = 9.1\) Hz, 1H), 3.77 (d, \(J = 9.1\) Hz, 1H), 3.54 (ddd, \(J = 14.3, 9.0, 3.6\) Hz, 2H), 3.35 (s, 3H), 3.00 – 2.91 (m, 2H), 2.76 (ddd, \(J = 12.7, 11.3, 3.2\) Hz, 1H), 2.56 – 2.49 (m, 1H), 0.62 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 175.2, 168.3, 143.1, 135.4, 135.1,
130.1, 129.3, 128.8, 126.2, 125.9, 122.1, 121.2, 107.8, 67.2, 65.9, 60.6, 56.5, 26.5, 13.5. HRMS (ESI-TOF, m/z): [M+H]\(^+\) calcd. for C\(_{29}\)H\(_{27}\)BrN\(_2\)O\(_3\) 531.1283, found: 531.1279.

**Compound Ib:** white solid (66% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68 – 7.63 (m, 2H), 7.40 – 7.27 (m, 5H), 7.12 – 7.01 (m, 3H), 6.93 – 6.88 (m, 1H), 6.86 – 6.79 (m, 1H), 6.13 (d, \(J = 7.7\) Hz, 1H), 4.28 – 4.22 (m, 2H), 3.62 (d, \(J = 9.6\) Hz, 1H), 3.58 – 3.48 (m, 2H), 3.24 – 3.14 (m, 4H), 3.06 (ddd, \(J = 10.9, 6.4, 1.9\) Hz, 1H), 2.68 (d, \(J = 16.2\) Hz, 1H), 2.38 (td, \(J = 11.0, 4.1\) Hz, 1H), 0.59 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.4, 169.9, 144.1, 139.5, 135.6, 134.8, 130.2, 129.3, 128.8, 128.6, 128.6, 127.9, 126.7, 125.5, 124.2, 122.7, 122.6, 107.9, 72.9, 69.7, 61.7, 60.2, 57.2, 46.2, 29.8, 26.4, 13.4. HRMS (ESI-TOF, m/z): [M+H]\(^+\) calcd. for C\(_{29}\)H\(_{28}\)N\(_2\)O\(_3\) 453.2178, found: 453.2181.

**Compound 1c:** white solid (72% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.1\) Hz, 2H), 7.64 (d, \(J = 8.0\) Hz, 2H), 7.09 (td, \(J = 7.7, 1.2\) Hz, 1H), 6.98 – 6.87 (m, 3H), 6.75 (ddd, \(J = 10.5, 8.5, 4.4\) Hz, 3H), 6.41 (d, \(J = 7.7\) Hz, 1H), 5.34 (s, 1H), 5.01 (d, \(J = 9.2\) Hz, 1H), 3.81 (d, \(J = 9.2\) Hz, 1H), 3.63 – 3.49 (m, 2H), 3.36 (s, 3H), 3.02 – 2.92 (m, 2H), 2.81 (ddd, \(J = 12.7, 11.2, 3.1\) Hz, 1H), 2.56 (ddd, \(J = 12.5, 3.3\) Hz, 1H), 0.64 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.4, 168.8, 145.8, 143.8, 135.5, 135.0, 128.8, 128.6, 128.2, 127.3, 126.1, 125.8, 125.4, 124.9, 122.2, 107.5, 67.9, 66.2, 61.0, 60.4, 60.1, 43.9, 27.1, 26.7, 26.7, 13.4. HRMS (ESI-TOF, m/z): [M+H]\(^+\) calcd. for C\(_{30}\)H\(_{27}\)F\(_3\)N\(_2\)O\(_3\) 521.2052, found: 521.2050.

**Compound Id:** white solid (60% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65 – 7.59 (m, 1H), 7.37 – 7.27 (m, 2H), 7.22 – 6.98 (m, 6H), 6.76 (dd, \(J = 10.5, 4.3\) Hz, 2H), 6.01 (d, \(J = 7.7\) Hz, 1H), 5.57 – 5.51 (m, 2H), 3.82 – 3.70 (m, 2H), 3.31 (dd, \(J = 6.4, 0.4\) Hz, 1H), 3.22 – 3.12 (m, 1H), 3.04 – 2.98 (m, 2H), 2.82 (d, \(J = 2.5\) Hz, 3H), 2.44 (d, \(J = 15.1\) Hz, 1H), 2.26 (d, \(J = 1.5\) Hz, 3H), 0.81 (t, \(J = 7.1\) Hz, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 176.47, 169.05, 144.3, 137.9, 134.9, 130.8, 129.0, 128.5, 127.2, 126.1, 125.6, 125.2, 124.3, 123.3, 122.9, 107.9, 67.9, 66.9, 60.9, 60.2, 57.0, 44.7, 26.2, 13.6. HRMS (ESI-TOF, m/z): [M+H]\(^+\) calcd. for C\(_{30}\)H\(_{29}\)BrF\(_2\)N\(_2\)O\(_3\) 485.2240, found: 485.2235.

**Compound 1e:** white solid (39% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (dd, \(J = 7.4, 0.8\) Hz, 1H), 7.38 (dd, \(J = 6.3, 2.6\) Hz, 1H), 7.31 (d, \(J = 7.2\) Hz, 1H), 7.22 – 7.09 (m, 5H), 7.02 (td, \(J = 7.6, 1.0\) Hz, 1H), 6.69 (dd, \(J = 9.7, 8.7\) Hz, 1H), 6.57 (d, \(J = 7.7\) Hz, 1H), 5.51 (d, \(J = 7.6\) Hz, 1H), 5.01 (s, 1H), 3.86 – 3.79 (m, 1H), 3.77 (d, \(J = 7.6\) Hz, 1H), 3.67 – 3.60 (m, 1H), 3.14 – 3.04 (m, 4H), 3.02 – 2.88 (m, 3H), 2.45 (d, \(J = 15.7\) Hz, 1H), 0.61 (t, \(J = 7.1\) Hz, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 175.2, 170.4, 143.7, 138.9, 134.5, 131.6, 128.7, 128.6, 126.9, 126.7, 126.3, 126.2, 126.1, 125.3, 121.9, 116.0, 107.3, 60.6, 60.4, 59.2, 59.0, 43.6, 26.4, 23.3, 13.4. HRMS (ESI-TOF, m/z): [M+H]\(^+\) calcd. for C\(_{29}\)H\(_{28}\)BrFN\(_2\)O\(_3\) 531.1283, found: 531.1279.
Compound 1f: white solid (77% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (dd, $J$ = 7.3, 1.2 Hz, 1H), 7.28 (d, $J$ = 7.4 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.13 – 7.01 (m, 7H), 6.94 – 6.88 (m, 1H), 5.47 (d, $J$ = 7.3 Hz, 1H), 4.68 (s, 1H), 3.90 (dd, $J$ = 10.7, 7.1 Hz, 1H), 3.70 (dt, $J$ = 6.8, 3.2 Hz, 2H), 3.42 (s, 3H), 3.06 (td, $J$ = 13.8, 4.7, 2.1 Hz, 2H), 2.99 – 2.90 (m, 1H), 2.37 (d, $J$ = 16.1 Hz, 1H), 0.71 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.4, 170.5, 139.4, 139.2, 134.9, 134.5, 130.4, 129.7, 128.8, 127.9, 127.7, 127.6, 126.9, 126.7, 126.1, 124.9, 122.7, 114.6, 71.4, 61.3, 60.7, 59.3, 58.9, 43.0, 29.7, 22.8, 13.4. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{29}$H$_{27}$ClN$_2$O$_3$ 487.1788, found: 487.1791.

Compound 1g: off-white solid (73% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 – 7.63 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 (dt, $J$ = 9.6, 4.3 Hz, 1H), 7.06 (t, $J$ = 4.3 Hz, 2H), 6.97 (d, $J$ = 2.5 Hz, 1H), 6.89 (dd, $J$ = 8.4, 2.5 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.15 (d, $J$ = 7.7 Hz, 1H), 4.27 – 4.18 (m, 2H), 3.81 (s, 3H), 3.61 (dd, $J$ = 15.4, 8.3 Hz, 3H), 3.24 – 3.16 (m, 1H), 3.15 (s, 3H), 3.05 (ddd, $J$ = 10.9, 6.3, 1.8 Hz, 1H), 2.67 (d, $J$ = 16.5 Hz, 1H), 2.37 (td, $J$ = 11.1, 4.1 Hz, 1H), 0.63 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.2, 169.9, 155.9, 139.5, 137.6, 135.5, 134.7, 131.4, 129.3, 128.6, 128.6, 127.9, 126.7, 125.5, 113.6, 111.3, 108.3, 73.1, 69.8, 61.6, 60.2, 57.6, 46.2, 29.8, 26.4, 13.4. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{30}$H$_{30}$N$_2$O$_4$ 483.2284, found: 483.2280.

Compound 1h: white solid (53% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (dd, $J$ = 1.2, 0.5 Hz, 1H), 7.31 (d, $J$ = 7.4 Hz, 1H), 7.18 (dt, $J$ = 16.2, 7.3, 1.2 Hz, 2H), 7.12 – 7.01 (m, 6H), 6.89 (ddd, $J$ = 7.9, 1.7, 0.8 Hz, 1H), 6.36 (d, $J$ = 7.9 Hz, 1H), 5.50 (d, $J$ = 7.4 Hz, 1H), 4.66 (s, 1H), 3.82 (dt, $J$ = 14.2, 7.1 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.13 – 3.03 (m, 2H), 3.02 – 2.92 (m, 4H), 2.35 (s, 3H), 0.62 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.9, 170.7, 141.2, 139.5, 135.5, 134.7, 131.2, 128.7, 128.3, 127.9, 127.5, 127.3, 127.0, 126.8, 126.9, 126.7, 125.9, 106.8, 71.2, 61.6, 60.5, 59.0, 43.2, 26.2, 22.9, 21.2, 13.4. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{30}$H$_{30}$N$_2$O$_3$ 467.2335, found: 467.2340.

Compound 1i: white solid (57% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 2.0 Hz, 1H), 7.30 (d, $J$ = 7.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.13 (m, 2H), 7.09 (d, $J$ = 19.8 Hz, 6H), 6.36 (d, $J$ = 8.3 Hz, 1H), 5.47 (d, $J$ = 7.2 Hz, 1H), 4.65 (s, 1H), 3.93 – 3.86 (m, 1H), 3.75 – 3.67 (m, 2H), 3.15 – 3.03 (m, 2H), 3.01 (s, 3H), 2.97 – 2.89 (m, 1H), 2.38 (d, $J$ = 16.2 Hz, 1H), 0.68 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.4, 170.3, 142.6, 139.2, 134.8, 134.4, 131.0, 129.1, 128.8, 127.9, 127.6, 126.9, 126.7, 126.1, 114.6, 108.4, 71.1, 61.7, 60.7, 58.9, 43.0, 26.3, 22.9, 13.5. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{29}$H$_{27}$BrN$_2$O$_3$ 531.1283, found: 531.1279.
**Compound 1j**: white solid (55% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 – 7.52 (m, 1H), 7.22 – 7.09 (m, 7H), 7.08 – 6.98 (m, 7H), 6.82 (dd, $J = 7.9$, 1.6 Hz, 2H), 6.41 – 6.36 (m, 1H), 5.64 (d, $J = 7.0$ Hz, 1H), 5.01 (d, $J = 15.8$ Hz, 1H), 4.73 (s, 1H), 4.58 (d, $J = 15.8$ Hz, 1H), 3.85 (d, $J = 6.9$ Hz, 1H), 3.10 – 2.90 (m, 3H), 2.36 (d, $J = 16.1$ Hz, 1H), 1.62 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 204.2, 176.2, 142.0, 139.7, 135.0, 134.8, 134.4, 128.8, 128.5, 128.4, 127.9, 127.7, 127.5, 127.4, 126.9, 126.5, 125.9, 125.8, 122.5, 108.7, 72.7, 67.5, 61.4, 57.7, 43.0, 28.9, 22.7. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{34}$H$_{30}$N$_2$O$_2$ 499.2386, found: 499.2390.

**Compound 1k**: white solid (68% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.53 (m, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 7.12 (d, $J = 7.5$ Hz, 1H), 7.05 (td, $J = 7.6$, 1.0 Hz, 1H), 6.70 (d, $J = 7.7$ Hz, 1H), 5.95 (d, $J = 3.3$ Hz, 1H), 5.79 (dd, $J = 3.3$, 0.6 Hz, 1H), 5.42 (d, $J = 7.5$ Hz, 1H), 4.70 (s, 1H), 3.86 – 3.78 (m, 1H), 3.68 – 3.59 (m, 2H), 3.17 (s, 3H), 3.12 – 3.00 (m, 3H), 2.49 – 2.42 (m, 1H), 0.65 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.3, 170.2, 152.7, 143.7, 138.7, 134.5, 128.8, 128.6, 126.9, 126.7, 126.1, 122.2, 120.8, 111.0, 107.3, 65.5, 60.6, 59.6, 58.7, 43.7, 26.5, 23.0, 13.4. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{27}$H$_{25}$Br$_2$N$_2$O$_4$ 521.1076, found: 521.1072.

**Compound 5a**: white solid (79% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 – 7.50 (m, 4H), 7.44 (dt, $J = 6.8$, 3.3 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.03 (dt, $J = 7.1$, 3.6, 1.2 Hz, 2H), 6.98 (ttdd, $J = 5.6$, 3.2, 1.5 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.75 – 6.64 (m, 3H), 5.26 (d, $J = 1.4$ Hz, 1H), 4.86 (d, $J = 10.0$ Hz, 1H), 3.73 (dd, $J = 10.0$, 1.1 Hz, 1H), 3.48 (ddd, $J = 7.2$, 3.1, 1.1 Hz, 2H), 3.39 (d, $J = 1.1$ Hz, 3H), 3.07 – 3.00 (m, 1H), 2.94 – 2.85 (m, 2H), 2.62 – 2.54 (m, 1H), 0.60 (td, $J = 7.1$, 1.1 Hz, 3H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.9, 168.5, 143.5, 139.5, 136.1, 131.7, 131.0, 130.3, 128.8, 126.8, 126.7, 125.8, 122.7, 121.8, 119.4, 118.2, 111.2, 110.6, 107.7, 64.8, 64.3, 61.3, 60.2, 58.4, 43.6, 27.0, 17.5, 13.4. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{31}$H$_{28}$BrN$_3$O$_3$ 570.1392, found: 570.1388.

**Compound 6a**: white solid (46% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 – 7.55 (m, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.16 – 7.01 (m, 3H), 6.91 – 6.83 (m, 1H), 6.82 – 6.67 (m, 1H), 6.58 (ddd, $J = 7.6$, 1.3, 0.5 Hz, 1H), 6.52 – 6.38 (m, 1H), 5.53 (d, $J = 3.0$ Hz, 1H), 4.73 (d, $J = 10.5$ Hz, 1H), 4.55 – 4.37 (m, 1H), 4.15 (dd, $J = 14.5$, 3.2 Hz, 1H), 3.88 (d, $J = 10.5$ Hz, 1H), 3.77 – 3.48 (m, 1H), 3.34 (s, 3H), 0.65 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.4, 169.5, 144.2, 141.2, 139.9, 137.7, 131.1, 129.1, 129.0, 128.2, 126.6, 125.9, 124.7, 123.0, 122.5, 120.7, 120.6, 108.1, 78.6, 71.9, 61.5, 60.5, 60.1, 60.0, 59.6, 25.8, 13.7. HRMS (ESI-TOF, m/z): [M+H]$^+$ calcd. for C$_{28}$H$_{25}$BrN$_2$O$_3$ 517.1127, found: 517.1131.
**Compound 7a**: white solid (NO₂ 32%, N₃ 51% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.84 (dt, J = 7.7, 1.4 Hz, 1H), 7.31 (dddd, J = 7.9, 7.4, 1.6, 0.9 Hz, 1H), 7.23 – 7.09 (m, 3H), 7.08 – 7.01 (m, 1H), 6.84 (td, J = 7.6, 1.0 Hz, 1H), 6.79 – 6.67 (m, 3H), 6.22 (ddd, J = 7.5, 1.2, 0.5 Hz, 1H), 5.85 – 5.79 (m, 1H), 4.81 (d, J = 8.0 Hz, 1H), 4.49 (s, 1H), 4.15 (d, J = 8.1 Hz, 1H), 3.99 (ddd, J = 12.3, 9.9, 3.4 Hz, 1H), 3.48 (s, 1H), 3.21 (ddd, J = 16.5, 11.8, 5.8 Hz, 1H), 3.14 – 3.08 (m, 1H), 2.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.5, 168.6, 144.2, 136.5, 134.5, 132.5, 129.6, 129.3, 128.7, 127.5, 127.1, 125.4, 124.3, 122.9, 122.6, 115.5, 108.0, 71.6, 71.6, 67.19, 65.9, 53.8, 46.0, 29.8, 26.3. HRMS (ESI-TOF, m/z): [M+H]⁺ calcd. for C₂₇H₂₃N₃O₂ 422.1869, found: 422.1873.
4. NMR Spectra of Products
5. X-Ray Report of 1a

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