Supplementary Material

Copper-catalyzed Intramolecular Domino Synthesis of 6H-Chromeno[4,3-b]quinolines in Green Condition

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General information

All chemicals were purchased from Merck and Fluka companies. All yields refer to isolated products. $^1$H and $^{13}$C NMR spectra were recorded on a Brucker, Rheinstetten, Germany (at 500 and 400 MHz) NMR spectrometer using tetramethylsilane (TMS) as internal standard. Melting points were determined in a capillary tube and are not corrected. The progress of reaction was followed with TLC using silica gel SILG/UV 254 and 365 plates. All products are known compounds and their structures were deduced by $^1$H and $^{13}$C NMR spectroscopy.

General procedure for the preparation of compounds 3aa–3bf, exemplified with 3aa:

A mixture of 3,4-dimethoxyaniline (1.0 mmol), 2-propargyl salicylaldehyde (1.0 mmol), CuI (0.2 mmol), in 3 mL H$_2$O-EtOH (50:50) was stirred in a sealed vessel for 6 hours at 100 °C. After reaction completion (TLC), the reaction mixture was cooled to room temperature, then, the aqueous phase was separated by suction and the semisolid residue was purified by column chromatography on silica gel (eluent: hexane–EtOAc) afforded 3aa.

Characterization data for 6H-chromeno[4,3-b]quinolines (3aa-3bf):

$^{9,10}$-dimethoxy-6H-chromeno[4,3-b]quinoline (3aa): mp 138–140 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 4.02 (s, 3H), 4.08 (s, 3H), 5.26 (s, 2H), 7.03 (s, 1H), 7.21 (d, $J = 9.0$ Hz, 1H), 7.45 (t, $J = 7.0$ , 1.5 Hz, 1H), 7.68 (t, $J = 7.0$ , 1.5 Hz, 1H), 7.77 (s, 1H), 7.82 (d, $J = 9.0$ Hz, 1H), 9.90 (d, $J = 9.0$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 56.0, 56.2, 66.8, 104.9, 108.5, 118.2, 122.2, 124.3, 127.1, 127.6, 128.3, 129.2, 132.3, 144.9, 148.7, 149.8, 152.4, 157.1 ppm.

$^{4,9,10}$-trimethoxy-6H-chromeno[4,3-b]quinoline (3ab): mp 151–153 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 3.94 (s, 3H), 4.01 (s, 3H), 4.06 (s, 3H), 5.39 (s, 2H), 6.96 (d, $J = 8.0$ Hz, 1H), 7.01 (s, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 7.46 (s, 1H), 7.72 (s, 1H), 8.02 (d, $J = 7.5$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 56.0, 56.1, 56.2, 68.8, 105.0, 108.3, 113.2, 116.9, 121.9, 123.2, 124.4, 127.8, 129.3, 145.5, 148.9, 149.9, 152.7, 152.8, 157.2 ppm.
**2-bromo-9,10-dimethoxy-6H-chromeno[4,3-b]quinoline (3ac):** mp 144–146 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta = 2.64$ (s, 3H), 2.68 (s, 3H), 4.09 (s, 2H), 5.75-5.88 (m, 3H), 6.01-6.12 (m, 2H), 6.70 (s, 1H), 7.03 (s, 1H), ppm; $^{13}$C NMR (DMSO-$d_6$, 125 MHz): $\delta = 55.6, 55.7, 67.5, 105.5, 107.5, 117.0, 122.0, 122.8, 123.1, 124.4, 129.6, 131.1, 144.4, 145.5, 149.4, 152.2, 156.5$ ppm.

**9,10-dimethoxy-2-nitro-6H-chromeno[4,3-b]quinoline (3ad):** mp 160–162 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 4.01$ (s, 3H), 4.06 (s, 3H), 5.30 (s, 2H), 6.87 (d, $J = 8.5$ Hz, 1H), 6.99 (s, 1H), 7.40 (dd, $J = 9.0, 2.0$ Hz, 1H), 7.44 (s, 1H), 7.68 (s, 1H), 8.51 (d, $J = 2.5$ Hz, 1H), ppm; $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 56.0, 56.1, 68.4, 105.0, 108.1, 115.0, 119.0, 122.8, 123.4, 125.3, 127.6, 129.3, 133.7, 145.3, 145.4, 150.1, 152.7, 155.8$ ppm.

**6H-chromeno[4,3-b][1,3]dioxolo[4,5-g]quinoline (3ba):** mp 139–141 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 5.29$ (s, 2H), 6.11 (s, 2H), 6.87 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.01 (s, 1H), 7.40 (m, 3H), 7.67 (s, 1H), 8.50 (s, 1H), ppm; $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 68.3, 101.2, 102.5, 106.3, 119.3, 123.8, 124.7, 126.1, 127.7, 130.0, 133.7, 142.8, 148.1, 148.6, 149.0, 156.8$ ppm.

**4-methoxy-6H-chromeno[4,3-b][1,3]dioxolo[4,5-g]quinoline (3bb):** mp 175–177 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 3.92$ (s, 3H), 5.35 (s, 2H), 6.08 (s, 2H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.98 (s, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 7.39 (s, 1H), 7.65 (s, 1H), 8.0 (d, $J = 8.0$ Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 56.1, 68.6, 101.6, 102.6, 106.0, 113.2, 116.9, 121.8, 123.1, 124.2, 124.5, 129.8, 146.3, 146.5, 146.7, 147.7, 148.7, 150.6$ ppm.

**2-bromo-6H-chromeno[4,3-b][1,3]dioxolo[4,5-g]quinoline (3bc):** mp 160–162 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 5.27$ (s, 2H), 6.09 (s, 2H), 6.85 (d, $J = 8.5$ Hz, 1H), 6.98 (s, 1H), 7.37-7.39 (m, 2H), 7.62 (s, 1H), 8.48 (s, 1H), ppm; $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta = 68.3, 101.7, 102.5, 106.0, 115.0, 119.0, 122.8, 124.8, 125.1, 127.6, 129.6, 133.7, 145.4, 146.6, 148.0, 150.9, 155.8$ ppm.

**2-nitro-6H-chromeno[4,3-b][1,3]dioxolo[4,5-g]quinoline (3bd):** mp 153–155 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 5.30$ (s, 2H), 6.10 (s, 2H), 6.85 (d, $J = 8.0$ Hz, 1H), 7.14 (t, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 8.0$ Hz, 1H),
7.44 (s, 1H), 7.67 (s, 1H), 8.48 (d, \( J = 8.0 \) Hz, 1H), ppm; \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta = 68.2, 101.6, 102.7, 106.7, 108.8, 115.6, 117.1, 119.9, 122.6, 126.3, 130.2, 133.5, 145.6, 146.0, 149.0, 152.7, 160.2 \) ppm.

8H-benzo[5,6]chremeno[4,3-b][1,3]dioxolo[4,5-g]quinoline (3be): mp 166–168 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta = 5.23 \) (s, 2H), 6.09 (s, 2H), 7.03 (s, 1H), 7.20 (d, \( J = 8.5 \) Hz, 1H), 7.44 (t, \( J = 7.5 \) Hz, 1H), 7.51 (s, 1H), 7.64 (t, \( J = 7.5 \) Hz, 1H), 7.73 (s, 1H), 7.80-7.82 (m, 2H), 9.88 (d, \( J = 7.5 \) Hz, 1H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta = 68.7, 101.6, 102.5, 106.2, 116.3, 118.2, 123.5, 124.3, 124.8, 127.1, 127.6, 128.3, 129.8, 130.7, 131.2, 132.3, 146.1, 147.8, 148.7, 150.6, 157.1 \) ppm.

3-methoxy-6H-chromeno[4,3-b][1,3]dioxolo[4,5-g]quinoline (3bf): mp 170–172 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta = 3.84 \) (s, 3H), 5.27 (s, 2H), 6.08 (s, 2H), 6.52 (d, \( J = 2.5 \) Hz, 1H), 6.70 (dd, \( J = 8.0, 2.5 \) Hz, 1H), 6.99 (s, 1H), 7.38 (s, 1H), 7.62 (s, 1H), 8.29 (d, \( J = 9.0 \) Hz, 1H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta = 55.4, 68.6, 101.6, 101.8, 102.7, 105.9, 109.4, 113.5, 117.8, 121.4, 122.4, 123.8, 126.2, 129.7, 147.1, 148.7, 149.4, 157.7 \) ppm.