Supplementary Information

Au-catalyzed Cascade Addition/Cyclization/H-transfer Reactions of 3-(1-alkynyl)chromones to Construct 4*H*-Furo[3, 2-c]pyrans Scaffold[†]

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General information

Solvents were purified according to *Purification of Laboratory Chemicals* except as noted. Petroleum ether refers to the fraction with boiling point in the range 60–90 °C. All ¹H NMR and ¹³C NMR spectra were measured with TMS as the internal standard on a 500, 400 or 300 MHz NMR spectrometer. Chemical shift are expressed in ppm and *J* value are given in Hz. High resolution mass spectra were recorded on a mass spectrometer (EI). Column chromatography was performed with 300–400 mesh silica gel using flash column techniques.

A typical procedure for Table 2

To the solution of the substrates **1** (0.30 mmol) in dichloromethane (3 mL) was added (PPh₃)AuCl (0.003 mmol), AgOTf (0.003mmol) and hydrogen source **3** (0.36 mmol, 1.2 eq). The mixture was stirred at room temperature for the corresponding time and then evaporated. The crude product was directly purified by column chromatography to afford the corresponding product **2**.

Characterization of the products

2-phenyl-4H-furo[3,2-c]chromene (2a)

White solid; Yield: 90%; mp 91-92 °C; ¹H NMR (400MHz, CDCl₃): δ = 7.78 – 7.67 (m, 2H), 7.48 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.33 – 7.25 (m, 1H), 7.19 -7.07 (m, 1H), 7.02 – 6.94 (m, 1H), 6.93 – 6.86 (m, 1H), 6.54 (s, 1H), 5.41 (s, 2H); ¹³C NMR (100MHz, CDCl₃): δ = 154.3, 152.9, 145.3, 130.4, 128.7, 128.4, 127.5, 123.6, 121.5, 119.4, 116.7, 116.1, 115.6, 103.2, 65.8; HRMS calcd for C₁₇H₁₂O₂: 248.0837, found: 248.0841.

2-(4-(trifluoromethyl)phenyl)-4H-furo[3,2-c]chromene (**2b**)

Colorless oil; Yield: 87% ¹H NMR (500MHz, CDCl₃): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.08 (td, *J* = 7.8, 1.5 Hz, 1H), 6.92 (dt, *J* = 7.4, 3.7 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.57 (s, 1H), 5.33 (s, 2H); ¹³C NMR (125MHz, CDCl₃): δ = 153.2, 152.8, 146.6, 133.5, 129.1 (q, *J* = 25.6 Hz), 129.0, 125.8 (q, *J* = 2.8 Hz), 124.2 (q, *J* = 215.2 Hz), 123.6, 121.6, 119.7, 116.4, 115.8, 105.2, 65.7; HRMS calcd for C₁₈H₁₁F₃O₂: 316.0711, found: 316.0715.

2-(4-methoxyphenyl)-4H-furo[3,2-c]chromene (2c)

Colorless oil; Yield: 84%; ¹H NMR (500MHz, CDCl₃): δ = 7.62 – 7.55 (m, 2H), 7.38 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.03 (td, *J* = 7.9, 1.6 Hz, 1H), 6.93 – 6.86 (m, 3H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.34 (s, 1H), 5.34 (s, 2H), 3.78 (s, 3H); ¹³C NMR

(125MHz, CDCl₃): δ = 159.3, 154.6, 152.8, 144.7, 128.1, 125.2, 123.5, 121.5, 119.2, 116.9, 116.1, 115.7, 114.2, 101.7, 66.0, 55.4; HRMS calcd for C₁₈H₁₄O₃: 278.0943, found: 278.0944.

4-(4H-furo[3,2-c]chromen-2-yl)butanenitrile (2d)

Yellow oil; Yield: 81% ¹H NMR (500MHz, CDCl₃): δ = 7.31 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.98 (s, 1H), 5.33 (s, 2H), 2.90 – 2.80 (m, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.04 (p, *J* = 7.1 Hz, 2H); ¹³C NMR (125MHz, CDCl₃): δ = 154.1, 152.6, 144.9, 128.2, 121.4, 119.2, 119.1, 116.9, 116.1, 114.2, 105.0, 65.9, 26.9, 24.1, 16.4; HRMS calcd for C₁₅H₁₃NO₂: 239.0946, found: 239.0950.

2-(tert-butyl)-4H-furo[3,2-c]chromene (2e)

Colorless oil; Yield: 71%; ¹H NMR (300MHz, CDCl₃): δ = 7.35 (d, *J* = 8.0 Hz, 1H), 7.10 – 7.01 (m, 1H), 6.95 – 6.87 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.87 (s, 1H), 5.34 (s, 2H), 1.33 (s, 9H). ¹³C NMR (125MHz, CDCl₃): δ = 165.3, 152.5, 143.8, 127.7, 121.3, 119.0, 117.3, 115.9, 114.0, 100.6, 66.2, 33.0, 29.1; HRMS calcd for C₁₅H₁₆O₂: 228.1150, found: 228.1153.

8-chloro-2-phenyl-4H-furo[3,2-c]chromene (2f)

White solid; Yield: 72%; mp 121-123 °C; ¹H NMR (500MHz, CDCl₃): δ = 7.64 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.47 (s, 1H), 5.33 (s, 2H); ¹³C NMR (125MHz, CDCl₃): δ = 155.1, 151.3, 144.2, 130.1, 128.8, 127.9, 127.8, 126.5, 123.8, 119.2, 117.9, 117.4, 116.6, 103.2, 66.1; HRMS calcd for C₁₇H₁₁ClO₂: 282.0448, found: 282.0450.

8-methoxy-2-phenyl-4H-furo[3,2-c]chromene (**2g**)

White solid; Yield: 91%; mp 109-111 °C: ¹H NMR (500MHz, CDCl₃): δ = 7.67 – 7.63 (m, 2H), 7.37 – 7.32 (m, 2H), 7.25 – 7.21 (m, 1H), 6.96 (d, *J* = 3.0 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.61 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.48 (s, 1H), 5.26 (s, 2H), 3.77 (s, 3H); ¹³C NMR (125MHz, CDCl₃): δ = 154.5, 154.5, 146.9, 145.6, 130.4, 128.8, 127.7, 123.8, 117.3, 116.9, 116.6, 113.8, 104.5, 103.4, 65.6, 55.9; HRMS calcd for C₁₈H₁₄O₃: 278.0943, found: 278.0944.

4-methyl-2-phenyl-4H-furo[3,2-c]chromene (**2h**)

Colorless oil; Yield: 88%; ¹H NMR (300MHz, CDCl₃): δ = 7.77 – 7.69 (m, 2H), 7.48 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.45 - 7.37 (m, 2H), 7.33 – 7.24 (m, 1H), 7.16 – 7.09 (m, 1H), 7.00 – 6.93 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.54 (s, 1H), 5.65 (q,

J = 6.5 Hz, 1H), 1.67 (d, J = 6.5 Hz, 3H); ¹³C NMR (125MHz, CDCl₃): $\bar{\delta} = 154.3$, 152.7, 145.1, 130.5, 128.8, 128.4, 127.6, 123.7, 121.3, 120.6, 119.4, 116.5, 116.4, 103.1, 72.8, 22.0; HRMS calcd for C₁₈H₁₄O₂: 262.0994, found: 262.0997.

4-ethyl-2-phenyl-4H-furo[3,2-c]chromene (2i)

Colorless oil; Yield: 80%; ¹H NMR (400MHz, CDCl₃): δ = 7.76 – 7.70 (m, 2H), 7.49 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.31- 7.27 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.54 (s, 1H), 5.49 (t, *J* = 5.8 Hz, 1H), 2.02 – 1.92 (m, 2H), 1.10 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (125MHz, CDCl₃): δ = 154.2, 152.9, 145.4, 130.5, 128.8, 128.4, 127.6, 123.7, 121.1, 119.4, 119.2, 116.3, 116.3, 103.5, 77.6, 29.3, 9.1; HRMS calcd for C₁₉H₁₆O₂: 276.1150, found: 276.1156.

2,4-diphenyl-4H-furo[3,2-c]chromene (2j)

Colorless oil; Yield: 52%; ¹H NMR (500MHz, CDCl₃): δ = 7.74 – 7.68 (m, 2H), 7.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.47 - 7.37 (m, 5H), 7.33 – 7.27 (m, 1H), 7.20 – 7.12 (m, 1H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.54 (s, 1H), 6.40 (s, 1H); ¹³C NMR (125MHz, CDCl₃): δ = 154.4, 152.6, 145.4, 140.4, 130.4, 128.9, 128.8, 128.7, 127.7, 127.5, 123.7, 121.5, 119.6, 118.8, 116.5, 116.2, 104.2, 78.7; HRMS calcd for C₂₃H₁₆O₂: 324.1150, found: 324.1156.

2-phenyl-4-(4-(trifluoromethyl)phenyl)-4H-furo[3,2-c]chromene (2k)

Colorless oil; Yield: 61%; ¹H NMR (500MHz, CDCl₃): $\delta = 7.72 - 7.65$ (m, 4H), 7.61 (d, J = 8.1 Hz, 2H), 7.59 - 7.54 (m, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.19 - 7.14 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.57 (s, 1H), 6.39 (s, 1H). ¹³C NMR (125MHz, CDCl₃): $\delta = 154.7$, 152.2, 145.3, 144.17, 130.8 (q, J = 32.5), 130.1, 128.8, 128.8, 127.8, 127.6, 125.7 (d, J = 3.75), 124.0 (q, J = 270.0), 123.7, 121.8, 119.6, 117.9, 116.4, 116.0, 103.8, 77.7; HRMS calcd for C₂₄H₁₅F₃O₂: 392.1024, found: 392.1028.

4-(4-methoxyphenyl)-2-phenyl-4H-furo[3,2-c]chromene (2I)

Colorless oil; Yield: 50%; ¹H NMR (400MHz, CDCl₃): $\delta = 7.73 - 7.67$ (m, 2H), 7.55 (dd, J = 7.5, 1.5 Hz, 1H), 7.45 - 7.36 (m, 4H), 7.31 - 7.26 (m, 1H), 7.13 (td, J = 7.9, 1.6 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.96 - 6.87 (m, 3H), 6.49 (s, 1H), 6.39 (s, 1H), 3.82 (s, 3H). ¹³C NMR (100MHz, CDCl₃): $\delta = 160.1$, 154.4, 152.6, 145.6, 132.5, 130.4, 129.1, 128.8, 128.6, 127.6, 123.7, 121.4, 119.5, 118.8, 116.5, 116.2, 114.1, 104.3, 78.3, 55.4; HRMS calcd for C₂₃H₁₆O₂: 354.1256, found: 354.1261.

4-methyl-2-(p-tolyl)-4H-furo[3,2-c]chromene (2m)

Colorless oil; Yield: 83%; ¹H NMR (500MHz, CDCl₃): δ = 7.61 (d, *J* = 8.1 Hz, 2H), 7.46 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (td, *J* = 8.0, 1.5 Hz, 1H), 6.99 – 6.92 (m, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.48 (s, 1H), 5.64 (q, *J* = 6.5 Hz, 1H), 2.38 (s, 3H), 1.66 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125MHz, CDCl₃): δ = 154.6, 152.6, 144.6, 137.5, 129.5, 128.2, 127.8, 123.7, 121.3, 120.6, 119.3, 116.6, 116.3, 102.4, 72.8, 22.0, 21.3; HRMS calcd for C₁₉H₁₆O₂: 276.1150, found: 276.1156.

2-(4-methoxyphenyl)-4-methyl-4H-furo[3,2-c]chromene (2n)

Colorless oil; Yield: 86%; ¹H NMR (500MHz, CDCl₃): δ = 7.67 – 7.62 (m, 2H), 7.45 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.10 (td, *J* = 8.0, 1.6 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.40 (s, 1H), 5.63 (q, *J* = 6.5 Hz, 1H), 3.85 (s, 3H), 1.66 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125MHz, CDCl₃): δ = 159.3, 154.4, 152.6, 144.3, 128.1, 125.2, 123.6, 121.3, 120.7, 119.2, 116.6, 116.3, 114.2, 101.6, 72.8, 55.4, 22.0; HRMS calcd for C₁₉H₁₆O₃: 292.1099, found: 292.1103.

2-(*tert*-butyl)-4-methyl-4H-furo[3,2-c]chromene (**2o**)

Colorless oil; Yield: 68%; ¹H NMR (500MHz, CDCl₃): δ = 7.34 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.90 (td, *J* = 7.5, 1.1 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.85 (s, 1H), 5.56 (q, *J* = 6.5 Hz, 1H), 1.60 (d, *J* = 6.5 Hz, 3H), 1.32 (s, 9H); ¹³C NMR (125MHz, CDCl₃): δ = 165.2, 152.3, 143.4, 127.6, 121.1, 118.9, 118.9, 117.0, 116.1, 100.3, 73.0, 33.0, 29.1, 22.0; HRMS calcd for C₁₆H₁₈O₂: 242.1307, found: 242.1310.

8-methoxy-4-methyl-2-phenyl-4H-furo[3,2-c]chromene (**2p**)

Yellow oil; Yield: 83%; ¹H NMR (500MHz, CDCl₃): δ = 7.72 (dd, *J* = 5.1, 3.4 Hz, 2H), 7.41 (dd, *J* = 10.7, 4.9 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.67 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.54 (s, 1H), 5.55 (q, *J* = 6.5 Hz, 1H), 3.83 (s, 3H), 1.64 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125MHz, CDCl₃): δ = 154.4, 154.3, 146.6, 145.2, 130.4, 128.8, 127.6, 123.7, 121.5, 117.1, 117.0, 113.9, 104.5, 103.2, 72.4, 55.9, 21.6; HRMS calcd for C₁₉H₁₆O₃: 292.1099, found: 292.1101.

8-bromo-4-methyl-2-phenyl-4H-furo[3,2-c]chromene (**2q**)

Yellow oil; Yield: 77%; ¹H NMR (400MHz, CDCl₃): δ = 7.73 – 7.68 (m, 2H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.26 (m, 1H), 7.18 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 6.52 (s, 1H), 5.63 (q, *J* = 6.5 Hz, 1H), 1.65 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125MHz, CDCl₃): δ = 155.0, 151.6, 143.7,

130.8, 130.1, 128.8, 127.9, 123.8, 122.0, 121.5, 118.1, 113.5, 103.1, 73.1, 22.0; HRMS calcd for $C_{18}H_{13}BrO_2$: 340.0099, found: 340.0103.

8-chloro-4-methyl-2-(thiophen-3-yl)-4H-furo[3,2-c]chromene (2r)

White solid; Yield: 75%; mp 77-79 °C; ¹H NMR (400MHz, CDCl₃): δ = 7.55 (dd, J = 2.9, 1.2 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.03 (dd, J = 8.6, 2.5 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 6.35 (s, 1H), 5.61 (q, J = 6.5 Hz, 1H), 1.64 (d, J = 6.5 Hz, 3H); ¹³C NMR (100MHz, CDCl₃): δ = 151.9, 151.0, 143.2, 131.8, 127.7, 126.5, 126.3, 124.5, 121.2, 119.6, 119.0, 117.5, 102.8, 73.0, 21.9; HRMS calcd for C₁₆H₁₁ClO₂S: 302.0168, found: 302.0171.

Methyl 4-(4H-furo[3,2-c]chromen-2-yl)benzoate (2s)

Yellow solid; Yield: 81%; mp 130-131 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.47 (dd, J = 7.5, 1.6 Hz, 1H), 7.17 – 7.09 (m, 1H), 6.97 (td, J = 7.5, 1.1 Hz, 1H), 6.88 (dd, J = 8.1, 1.1 Hz, 1H), 6.64 (s, 1H), 5.39 (s, 2H), 3.92 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 166.83, 153.32, 146.69, 134.34, 130.27, 129.06, 128.69, 123.29, 121.72, 119.81, 116.42, 115.96, 105.59, 65.81, 52.26 ppm; HRMS calcd for C₁₉H₁₄O₄: 306.0892, found: 306.0888.

2-phenyl-4H-furo[3,2-c]chromen-7-ol (2t)

White solid; Yield: 87%; mp 143-144 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, J = 7.1 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.26 (t, J = 8.1 Hz, 1H), 6.51 (s, 1H), 6.48 – 6.41 (m, 2H), 5.38 (s, 2H), 5.03 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.19, 154.60, 153.67, 145.69, 130.65, 128.86, 127.44, 123.60, 120.61, 113.32, 110.50, 108.59, 104.07, 103.33, 66.35 ppm; HRMS calcd for C₁₇H₁₂O₃: 264.0786, found: 264.0788.

2-phenyl-4,5,6,7-tetrahydrobenzofuran (2u)

Colorless oil; Yield: 61%; ¹H NMR (400MHz, CDCl₃): δ = 7.65 – 7.59 (m, 2H), 7.38 – 7.32 (m, 2H), 7.23 – 7.17 (m, 1H), 6.48 (s, 1H), 2.70 – 2.63 (m, 2H), 2.47 (m, 2H), 1.92 – 1.82 (m, 2H), 1.80 – 1.72 (m, 2H); ¹³C NMR (125MHz, CDCl₃): δ = 151.6, 150.8, 131.5, 128.6, 126.6, 123.3, 119.0, 106.0, 23.3, 23.2, 23.1, 22.2; HRMS calcd for C₁₄H₁₄O: 198.1045, found: 198.1050.

2-isopropyl-4H-furo[3,2-c]chromene (**2v**)

Colorless oil; Yield: 82%; ¹H NMR (500MHz, CDCl₃): δ = 7.34 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.06 (td, *J* = 8.0, 1.5 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.86 – 6.82 (m, 1H), 5.88 (s, 1H), 5.35 (s, 2H), 3.04 – 2.97 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H); ¹³C

NMR (125MHz, CDCl₃): δ = 162.8, 152.5, 143.8, 127.7, 121.3, 118.9, 117.2, 115.9, 114.1, 101.3, 66.1, 28.1, 21.2; HRMS calcd for C₁₄H₁₄O₂: 214.0994, found: 214.0996.

2-(2-hydroxyphenyl)-5-phenylfuran-3-carbaldehyde (2w)

White solid; Yield: 72%; mp 131-133 °C; ¹H NMR (500MHz, DMSO- d_6): $\delta = 10.39$ (s, 1H), 9.97 (s, 1H), 7.84 – 7.81 (m, 2H), 7.62 (dd, J = 8.2, 1.6 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.33 (s, 1H), 7.08 – 7.05 (m, 1H), 7.01 (t, J = 7.6 Hz, 1H); ¹³C NMR (125MHz, DMSO- d_6): $\delta = 187.2$, 158.4, 155.5, 154.0, 132.3, 131.1, 129.6, 129.5, 128.9, 124.9, 124.4, 120.1, 117.0, 116.2, 104.1; HRMS calcd for C₁₇H₁₂O₃: 264.0786, found: 264.0790.



90 80 f1 (ppm)







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