Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Site-selective gold(I) catalyzed synthesis of 1,3-dioxin-3 ones via cascade reaction

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General Methods

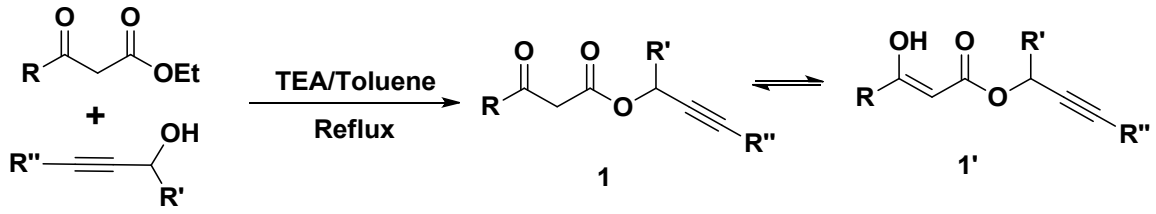
^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm).

LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Agilent Technologies LC/MSD Trap 1100 series (nebulizer: 15.0 PSI, dry Gas: 5.0 L/min, dry Temperature: 325 °C, capillary voltage positive scan: 4000 mA, capillary voltage negative scan: 3500 mA). Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification.

Compound **1m** was synthesized according to the literature.[1]

[1] Mhasni; O.; Erray, I.; Rezgui, F. *Synth. Commun.*, **2014**, *44*, 3320-3327.

General procedures for synthesis of 1a-u



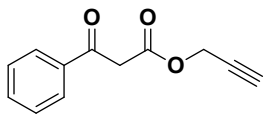
The procedure A and B are adapted from literature.[2]

Procedure A)

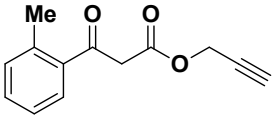
In a 2-neck flask, equipped with Dean-Stark condenser, the corresponding ethyl ester precursor is dissolved in toluene (0.1M). Then triethylamine (TEA, 2 eq) and propargyl alcohol (3 eq) are added. The reaction mixture is stirred and heated at 120 °C. After almost all solvent has been distilled the reaction is checked by thin layer chromatography (TLC), if starting materials persists, the same amount of toluene, TEA and propargyl alcohol were re-added. Upon completion, the solvent is evaporated and the crude is purified by flash chromatography using silica gel (*c*Hex:EtOAc 40/1).

Procedure B)

In a 2-neck flask, equipped with Dean-Stark condenser, the corresponding ethyl ester precursor is dissolved in toluene (0.1M). Then triethylamine (TEA, 2 eq) and functionalized propargyl alcohol (1.2 eq) are added. The reaction mixture is stirred and heated at 120 °C. After almost all solvent has been distilled the reaction is checked by thin layer chromatography (TLC), if starting materials persists, the same amount of toluene and TEA were re-added. When the reaction is over the solvent is evaporated and the crude is purified flash chromatography using silica gel (*c*Hex:EtOAc 40/1).



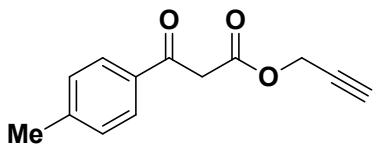
1a. Procedure A, 48h. Colorless oil, Y = 87%,**1a**:**1a'** = 84:16 by ^{1}H NMR. Signals of **1a**, ^{1}H NMR (400 MHz, $CDCl_3$, δ = 7.96 – 7.86 (m, 2H), 7.59 (ddt, *J* = 8.0, 6.8, 1.3 Hz, 1H), 7.51 – 7.44 (m, 2H), 4.75 (d, *J* = 2.5 Hz, 2H), 4.04 (s, 2H), 2.47 (t, *J* = 2.5, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.06, 166.92, 134.10, 129.06, 128.82, 128.72, 86.84, 75.53, 53.03, 45.76. Signals of **1a'**, ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 12.25 (s, 1H), 7.79 – 7.73 (m, 2H), 7.51 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 5.71 (s, 1H), 4.80 (d, *J* = 2.5 Hz, 2H), 2.52 – 2.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.62, 172.37, 136.05, 131.78, 128.99, 126.40, 77.43, 51.98. Anal. Calc. for ($C_{12}H_{10}O_3$: 202.06): C, 71.28; H, 4.98; found: C, 71.13; H, 4.71.



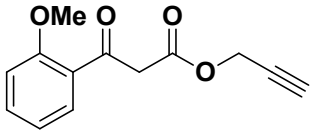
1b. Procedure A, 48h. Colorless oil, Y=82%, **1b:1b'** = 81:19 by ^{1}H NMR. Signals of **1b**, ^{1}H NMR (400 MHz, $CDCl_3$,) δ 7.65 – 7.61 (m, 1H), 7.40 (td, *J* = 7.4, 1.4 Hz, 1H), 7.30 – 7.24 (m, 2H), 4.73 (d, *J* = 2.4 Hz, 2H), 4.00 (s, 2H), 2.46 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =194.95, 166.95, 139.73, 132.50, 132.48, 129.37, 126.03, 125.96, 91.04, 75.49, 52.88, 47.93, 21.73. Signals of **1b'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.17 (s, 1H), 7.35 – 7.30 (m, 1H), 7.24 – 7.17 (m, 3H), 5.33 (s, 1H),

[2] a) Mottet, C.; Hamelin, O.; Garavel, G.; Depre´s, J.-P.; Greene, A. E. *J. Org. Chem.*; **1999**, *64*, 1380-1382.

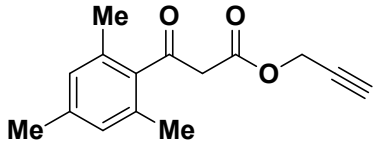
4.80 (d, *J* = 2.4 Hz, 2H), 2.51 (t, *J* = 2.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.06, 171.96, 136.78, 136.03, 131.26, 130.44, 128.60, 77.76, 77.27, 75.28, 51.87, 20.69. Anal. Calc. for ($C_{13}H_{12}O_3$: 216.24): C, 72.21; H, 5.59; found: C, 72.31; H, 5.41.



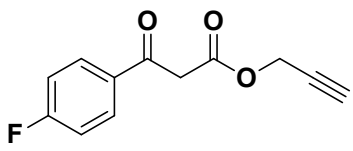
1c. Procedure A, 48h. Colorless oil, Y = 84%, **1c**:**1c'** = 82:18 by ^{1}H-NMR. Signals of **1a**, ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 7.79 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.71 (d, *J* = 2.4 Hz, 2H), 3.99 (s, 2H), 2.47 (t, *J* = 2.4 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.48, 166.84, 144.85, 133.35, 129.48, 128.60, 85.83, 75.33, 52.70, 45.41, 21.65. Signals of **1c'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.25 (s, 1H), 7.67 – 7.60 (m, 2H), 7.18 (dd, *J* = 9.3, 3.3 Hz, 2H), 5.65 (s, 1H), 4.76 (d, *J* = 2.4 Hz, 2H), 2.50 (t, *J* = 2.4 Hz, 1H), 2.35 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.50, 172.20, 142.12, 130.23, 129.29, 126.11, 77.69, 77.16, 75.07, 51.65, 21.46. Anal. Calc. for ($C_{13}H_{12}O_3$: 216.24): C, 72.21; H, 5.59; found: C, 72.08; H, 5.32.



1d. Procedure A, 48h Pale yellow oil, Y = 78%, **1d**:**1d'** = 75:25 by ^{1}H-NMR. Signals of **1d** ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.42 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.11 (m, 1H), 4.73 (d, *J* = 2.5 Hz, 2H), 4.01 (s, 2H), 3.81 (s, 3H), 2.47 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.69, 166.66, 159.93, 137.11, 129.78, 121.11, 120.45, 112.51, 86.84, 75.33, 55.42, 52.75, 45.59. Signals of **1d'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.23 (s, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.00 – 6.96 (m, 1H), 5.68 (d, *J* = 1.0 Hz, 1H), 4.78 (dd, *J* = 2.5, 1.0 Hz, 2H), 3.80 (s, 2H), 2.50 (td, *J* = 2.5, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.15, 172.08, 159.71, 134.46, 129.59, 118.54, 117.53, 111.26, 77.57, 77.25, 75.11, 55.32, 51.75. Anal. Calc. for ($C_{13}H_{12}O_4$: 232.24): C, 67.23; H, 5.21; found: C, 67.01; H, 5.12.

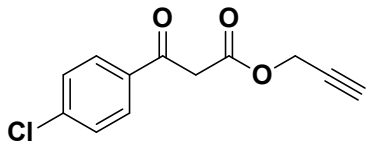


1e. Procedure A, 48h Pale yellow oil, Y = 74%, **1e**:**(*Z*)-1e'**:**(*E*)-1e'** = 33:53:14 by ^{1}H NMR. Signals of **(*Z*)-1e'**, ^{1}H NMR (400 MHz, $CDCl_3$,) δ = 12.02 (s, 1H), 6.86 (s, 2H), 5.15 (d, *J* = 1.3 Hz, 1H), 4.80 (d, *J* = 2.2 Hz, 2H, 2.53 – 2.50 (m, 1H), 2.27 (s, 6H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.46, 171.56, 138.97, 135.61, 133.02, 128.28, 92.45, 75.07, 60.20, 51.66, 19.53, 19.18. Signals of **1e**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83 (s, 2H), 4.74 – 4.70 (m, 2H), 3.77 (s, 2H), 2.47 (dt, *J* = 3.8, 1.8 Hz, 1H), 2.27 (s, 6H), 2.24 (s, 3H).Diagnostic signals ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.47, 165.87, 139.27, 137.90, 131.86, 128.68. Anal. Calc. for ($C_{15}H_{16}O_3$: 244.29): C, 73.75; H, 6.60; found: C, 73.51; H, 6.38.

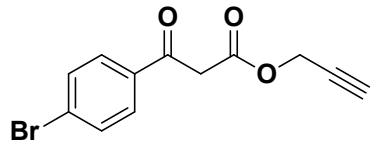


1f. Procedure A, 48h. Pale yellow oil, Y = 78%. **1f:1f'** = 83:17 by ^{1}H-NMR. Signals of **1f** ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 7.98 – 7.90 (m, 2H), 7.17 – 7.09 (m, 2H), , 4.73 (d, *J* = 2.4 Hz, 2H), 4.00 (s, 2H), 2.47 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.47, 166.70, 166.36 (d, *J* = 256.3 Hz), 131.46 (d, *J* = 9.6 Hz), 128.60 (d, *J* = 9.0 Hz), 116.22 (d, *J* = 22.1 Hz), 86.60, 75.59, 53.05, 45.66. ^{19}F-NMR (377 MHz, $CDCl_3$) δ = -103.61 (ddd, *J* = 13.7, 8.3, 5.3 Hz, 1F). Signals of **1f'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.27 (s, 1H), 7.79 – 7.70 (m,

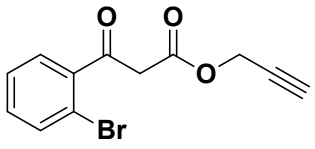
2H), 7.10 – 7.04 (m, 1H), 5.63 (s, 1H), 4.78 (d, *J* = 2.4 Hz, 2H), 2.50 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.27, 171.46, 164.96 (d, *J* = 252.2 Hz), 132.48 (d, *J* = 2.9 Hz), 115.93 (d, *J* = 21.8 Hz), 77.74, 77.19, 75.32, 52.00. ^{19}F-NMR (377 MHz, $CDCl_3$) δ = -107.88 (ddd, *J* = 13.7, 8.4, 5.2 Hz, 1F). Anal. Calc. for ($C_{12}H_9FO_3$: 220.05): C, 65.46; H, 4.12; found: C, 65.31; H, 4.00.



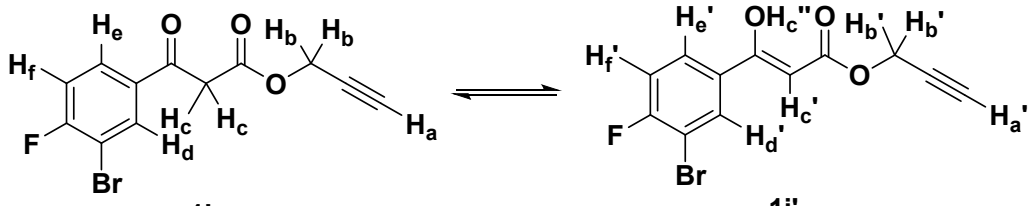
1g. Procedure A, 48h. Pale yellow solid, Y = 75%, **1g:1g'** = 74:26 by ^{1}H-NMR. Signals for **1g**, ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 7.88 – 7.82 (m, 2H), 7.47 – 7.40 (m, 2H), 4.74 (d, *J* = 2.5 Hz, 2H), 4.00 (s, 2H), 2.47 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.85, 166.60, 140.68, 134.34, 130.12, 129.39, 87.11, 75.63, 53.09, 45.68. Signals of **1g'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.24 (s, 1H), 7.72 – 7.65 (m, 2H), 7.40 – 7.35 (m, 2H), 5.67 (s, 1H), 4.79 (d, *J* = 2.5 Hz, 2H), 2.51 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.21, 171.25, 137.89, 131.75, 129.10, 127.69, 77.68, 77.16, 75.37, 52.07. Anal. Calc. for ($C_{10}H_7ClO_3$: 210.61): C, 57.03; H, 3.35; found: C, 56.81; H, 3.16.



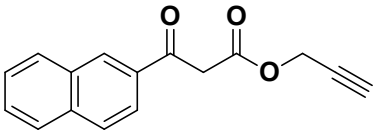
1h. Procedure A, 48h. Pale yellow oil, Y = 76%, **1h:1h'** = 74:26 by ^{1}H NMR. Signals of **1h** ^{1}H NMR (400 MHz, $CDCl_3$,) δ =, 7.79 – 7.75 (m, 2H), 7.63 – 7.58 (m, 2H), 4.73 (d, *J* = 2.5 Hz, 2H), 2.47 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.06, 166.57, 134.73, 132.38, 130.17, 129.44, 87.14, 75.64, 53.09, 45.65. Signals of **1h'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.22 (s, 1H), 7.63 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 5.67 (s, 1H), 4.79 (d, *J* = 2.5 Hz, 2H), 2.51 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.19, 171.30, 132.20, 132.07, 127.85, 126.34, 77.66, 77.14, 75.38, 52.08. Anal. Calc. for ($C_{12}H_9BrO_3$: 281.11): C, 51.27; H, 3.23; found: C, 51.03; H, 3.18.



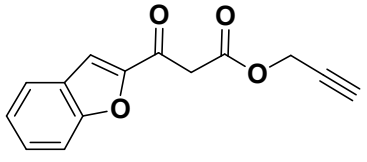
1i. Procedure A, 48h. Pale yellow oil, Y=74%, **1i:1i'** = 66:33 by ^{1}H-NMR. Signals of **1i** ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 7.61 (ddt, *J* = 7.9, 2.4, 1.2 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.37 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.32 (dt, *J* = 7.7, 1.6 Hz, 1H), 4.71 (d, *J* = 2.4 Hz, 2H), 4.06 (s, 1H), 2.47 (t, *J* = 2.5, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.07, 166.16, 139.92, 134.15, 132.70, 129.81, 127.78, 119.41, 92.66, 75.61, 53.00, 48.55. Signals of **1i'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.09 (d, *J* = 1.0 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.28 (dt, *J* = 8.7, 1.4 Hz, 1H), 7.26 – 7.22 (m, 2H), 5.50 (d, *J* = 1.0 Hz, 1H), 4.80 (dd, *J* = 2.5, 1.0 Hz, 3H), 2.51 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 173.01, 171.70, 135.65, 134.02, 131.57, 130.41, 127.56, 121.10, 77.61, 77.16, 75.44, 52.13. Anal. Calc. for ($C_{12}H_9BrO_3$: 281.11): C, 51.27; H, 3.23; found: C, 51.13; H, 3.11.



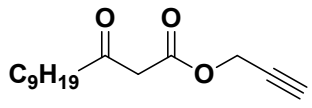
1j. Procedure A, 48h. Pale yellow oil Y = 71%, **1j:1j'** = 74:26 by ^{1}H-NMR. Signals of **1j**, ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 8.13 (dd, *J* = 6.5, 2.2 Hz, H_d), 7.85 (ddd, *J* = 8.6, 4.6, 2.2 Hz, H_e), 7.19 (dd, *J* = 8.6, 7.9 Hz, H_f), 4.73 (d, *J* = 2.4 Hz, $2H_b$), 3.98 (s, $2H_c$), 2.48 (t, *J* = 2.5 Hz, H_a). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.45, 166.32, 162.62 (d, *J* = 256.8 Hz), 134.63 (d, *J* = 1.9 Hz), 131.90 (d, *J* = 1.3 Hz), 129.99 (d, *J* = 8.7 Hz), 117.09 (d, *J* = 23.2 Hz), 110.27 (d, *J* = 22.1 Hz), 87.40, 75.71, 53.14, 45.53. Signals of **1j'**, ^{1}H NMR (401 MHz, cdcl$_3$) δ 12.22 (s, H_c''), 7.95 (dd, *J* = 6.6, 2.2 Hz, H_d'), 7.66 (ddd, *J* = 8.7, 4.6, 2.2 Hz, H_e'), 7.13 (dd, *J* = 8.7, 8.1 Hz, H_f'), 5.62 (s, H_c'), 4.78 (d, *J* = 2.5 Hz, $2H_b$'), 2.51 (t, *J* = 2.5 Hz, H_a'). ^{13}C NMR (101 MHz, cdcl$_3$) δ 170.93 (d, *J* = 222.6 Hz), 161.09 (d, *J* = 253.4 Hz), 133.50 (d, *J* = 3.6 Hz), 130.84 (d, *J* = 3.8 Hz), 128.78 (d, *J* = 81.5 Hz), 127.22 (d, *J* = 8.0 Hz), 116.74, 109.77 (d, *J* = 21.7 Hz), 77.07, 75.44, 52.14. Anal. Calc. for ($C_{12}H_8BrFO_3$: 299.10): C, 48.19; H, 2.70; found: C, 48.01; H, 2.31.



1k. Procedure A, 36h. Pale yellow solid, Y = 80%, **1k**:**1k'** = 71:29 by ^{1}H-NMR. Signals of **1k** ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 8.45 – 8.40 (m, 1H), 7.99 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.92 – 7.87 (m, 1H), 7.86 (s, 1H), 7.61 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.58 – 7.55 (m, 1H), 4.77 (d, *J* = 2.4 Hz, 2H), 4.17 (s, 2H), 2.46 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.00, 167.01, 136.11, 133.43, 132.64, 130.86, 129.92, 129.19, 129.01, 128.05, 127.24, 123.96, 87.29, 75.56, 53.07, 45.84. Signals of **1k'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.35 (s, 1H), 8.35 (t, *J* = 1.2 Hz, 1H), 7.90 (s, 2H), 7.83 (d, *J* = 3.9 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.54 – 7.48 (m, 2H), 5.85 (s, 1H), 4.83 (d, *J* = 2.4 Hz, 2H), 2.52 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.42, 172.40, 135.04, 133.02, 130.49, 129.33, 128.57, 127.96, 127.92, 127.22, 126.96, 122.75, 77.84, 77.31, 75.31, 52.03. Anal. Calc. for ($C_{16}H_{12}O_3$: 252.08): C, 76.18; H, 4.79; found: C, 76.00; H, 4.55.

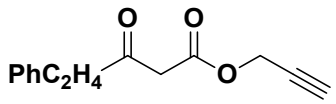


1l. Procedure A, 36h. White solid, Y = 74%, **1l**:**1l'** = 13:87 by ^{1}H-NMR. Signals of **1l'** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.78 (s, 1H), 7.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.48 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.30 (s, 1H), 7.29 – 7.25 (m, 1H), 5.90 (s, 1H), 4.81 (d, *J* = 2.4 Hz, 2H), 2.52 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.98, 162.70, 155.69, 149.56, 128.99, 127.94, 126.96, 123.80, 122.49, 111.86, 109.46, 88.01, 75.37, 52.13. Signals of **1l**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.25 – 7.22 (m, 3H), 4.76 (d, *J* = 2.4 Hz, 2H), 4.02 (s, 2H), 2.47 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 182.56, 166.27, 156.05, 151.76, 127.16, 124.38, 123.73, 114.34, 112.72, 77.68, 75.63, 53.12, 45.61. Anal. Calc. for ($C_{14}H_{10}O_4$: 242.06): C, 69.42; H, 4.16; found: C, 69.30; H, 4.00.

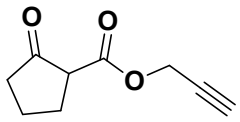


1n. Procedure A, 48h. Colorless oil, Y = 69%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.72 (d, *J* = 2.4 Hz, 2H), 3.47 (s, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J*

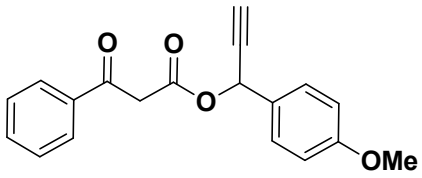
= 2.6 Hz, 1H), 1.56 (m, 4H), 1.33 –1.20 (m, 10H), 0.86 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 202.39, 166.60, 88.49, 75.50, 52.81, 49.02, 43.24, 32.02, 29.56, 29.51, 29.41, 29.16, 23.61, 22.82, 14.26. Anal. Calc. for ($C_{14}H_{22}O_3$: 238.16): C, 70.56; H, 9.30; found: C, 70.31; H, 9.21.



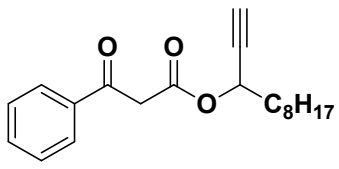
1o. Procedure A, 48h. Colorless oil, Y = 73%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.27 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.13 (m, 3H), 4.69 (d, *J* = 2.2 Hz, 2H), 3.45 (s, 2H), 2.95 – 2.81 (m, 4H), 2.48 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.31, 166.39, 140.56, 128.69, 128.46, 126.40, 89.05, 75.59, 52.83, 49.11, 44.61, 29.52. Anal. Calc. for ($C_{14}H_{14}O_3$: 230.26): C, 73.03; H, 6.13; found: C, 72.88; H, 5.92.



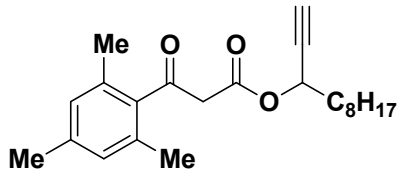
1p. Procedure A, 48h. Colorless oil, Y = 68%. ^{1}H-NMR (400 MHz, CDCl3) δ = 4.72 – 4.59 (m, 2H), 3.14 (t, *J* = 9.1 Hz, 1H), 2.45 (t, *J* = 2.5 Hz, 1H), 2.36-2.17 (m , 4H), 2.14 – 2.02 (m, 1H), 1.89 – 1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.50, 168.56, 77.19, 75.23, 54.40, 52.63, 37.92, 27.27, 20.85. Anal. Calc. for ($C_9H_{10}O_3$: 166.06): C, 65.05; H, 6.07; found: C, 64.88; H, 5.95.



1q. Procedure B, 12h. Yellow oil, Y = 82%, , **1q**:**1q'** = 88:22 by ^{1}H NMR. Signals of **1q** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.85 (m, 2H), 7.59 – 7.53 (m, 1H), 7.44 (d, *J* = 1.1 Hz, 2H), 7.42 (d, *J* = 1.9 Hz, 2H), 6.89 – 6.84 (m, 2H), 6.47 (d, *J* = 2.3 Hz, 1H), 4.01 (d, *J* = 1.1 Hz, 2H), 3.79 (s, 3H), 2.66 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.88, 166.39, 160.24, 133.72, 129.32, 128.74, 128.56, 128.45, 126.13, 113.99, 87.00, 75.76, 66.07, 55.30, 45.84. Signals of **1q'** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.32 (s, 1H), 7.77 – 7.72 (m, 2H), 7.53 – 7.49 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 3H), 6.95 – 6.90 (m, 2H), 6.54 (d, *J* = 2.3 Hz, 1H), 5.69 (s, 1H), 3.80 (s, 3H), 2.70 (d, *J* = 2.3 Hz, 1H). Diagnostic ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.31, 171.80, 135.86, 133.15, 131.49, 128.01, 114.09, 79.79, 75.54, 64.93. Anal. Calc. for ($C_{19}H_{16}O_4$: 308.33): C, 74.01; H, 5.23; found: C, 73.81; H, 5.06.

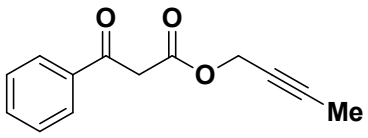


1r. Procedure B, 12h. Colorless oil, Y = 80%, **1r**:**1r' =** 68:32 by ^{1}H-NMR. Signals of **1r** ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.86 (m, 2H), 7.60 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.40 (td, *J* = 6.7, 2.2 Hz, 1H), 4.00 (s, 2H), 2.43 (d, *J* = 2.1 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.40 – 1.32 (m, 2H), 1.31 – 1.17 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.93, 166.42, 135.94, 133.72, 128.75, 128.47, 86.99, 73.85, 64.89, 45.87, 34.43, 31.78, 29.30, 29.11, 28.97, 24.70, 22.60, 14.05. Diagnostic signals for **1r'**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.36 (s, 1H), 7.79 – 7.73 (m, 2H), 7.49 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 5.68 (s, 1H), 5.47 (td, *J* = 6.7, 2.2 Hz, 1H), 2.48 (d, *J* = 2.1 Hz, 1H), 1.87 – 1.79 (m, 2H), 1.51 – 1.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.16, 172.05, 133.24, 131.41, 128.53, 126.11, 81.25, 80.72, 73.67, 63.70, 34.66, 29.30, 29.11, 29.06, 24.87. Anal. Calc. for ($C_{20}H_{26}O_3$: 314.43): C, 76.40; H, 8.34; found: C, 76.21; H, 8.15.



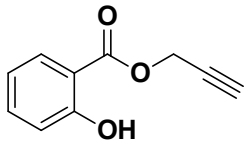
1s. Procedure B, 48h. Colorless oil, Y = 83%, **1s**:**1s'** = 33:66 by ^{1}H-NMR. Signals of **1s'** ^{1}H-NMR (400 MHz, $CDCl_3$,) δ = 12.14 (d, *J* =

1.7 Hz, 1H), 6.86 (s, 2H), 5.47 (tt, *J* = 6.7, 1.5 Hz, 1H), 5.12 (d, *J* = 0.8 Hz, 1H), 2.50 (d, *J* = 2.1 Hz, 1H), 2.28 (s, 6H), 2.25 (s, 3H), 1.84 (m, 2H), 1.48 (p, *J* = 7.5 Hz, 2H), 1.38 – 1.23 (m, 10H), 0.92 – 0.83 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.25, 171.54, 138.86, 135.62, 128.67, 128.26, 92.74, 81.27, 73.74, 63.70, 50.94, 34.62, 31.81, 29.37, 29.15, 29.07, 24.88, 22.63, 21.07, 19.58, 19.24, 14.07. Diagnostic signals for **1s**, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83 (s, 2H), 5.38 (tt, *J* = 6.6, 1.5 Hz, 1H), 5.13 (d, *J* = 0.9 Hz, 2H), 2.43 (d, *J* = 2.2 Hz, 1H), 1.73 (dt, *J* = 9.1, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.63, 165.66, 139.16, 138.01, 133.06, 131.98, 125.49, 80.74, 73.82, 64.80, 34.42, 30.30, 29.07, 24.73. Anal. Calc. for ($C_{23}H_{32}O_3$: 356.51): C, 77.49; H, 9.05; found: C, 77.31; H, 8.89.



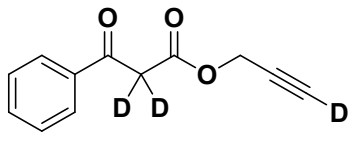
1t. Procedure A, 36h Colorless oil, Y = 76%, **1t**:**1t'** = 88:22 by ^{1}H-NMR. Signals of **1t** ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.81 (m, 2H), 7.54 (ddt, *J* = 8.6, 6.9, 1.3 Hz, 1H), 7.46 – 7.40 (m, 2H), 4.67 (d, *J* = 2.4 Hz, 1H), 3.99 (s, 1H), 1.78 (t, *J* = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.00, 166.87, 135.85, 133.74, 128.74, 128.46, 86.82, 83.64, 72.65, 53.65, 45.59. Signals of **1t'** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.32 (s, 1H), 7.75 – 7.70 (m, 2H), 7.47 – 7.39 (m, 1H), 7.39 – 7.34 (m, 2H), 5.67 (s, 1H), 4.73 (d, *J* = 2.3 Hz, 2H), 1.82 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.36, 172.01, 133.15, 131.42, 128.54, 126.08, 83.43, 73.06, 52.59. Anal. Calc. for ($C_{13}H_{12}O_3$: 216.24): C, 72.21; H, 5.59; found: C, 72.01; H, 5.29.

General procedure for the synthesis of compound 1u



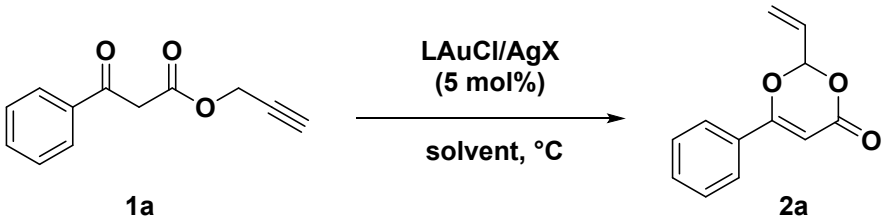
Compound **1u** was synthetized by refluxing salicylic acid (1 eq), DBU (1.1 eq) and propargyl alcohol (1.5 eq) in dry acetonitrile for 24 h. The solvent is then removed under vacuum and the crude purified by flash chromatography (cHex/AcOEt 10/1). Sticky colorless oil, unoptimized yield = 57%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 10.50 (s, 1H), 7.86 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.88 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 4.93 (d, *J* = 2.5 Hz, 2H), 2.54 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.55, 161.99, 136.39, 130.31, 119.55, 117.90, 112.04, 77.29, 75.84, 52.92. Anal. Calc. for ($C_{10}H_8O_3$: 176.05): C, 68.18; H, 4.58; found: C, 68.07; H, 4.35.

General procedure for the synthesis of compound 1a-D_3

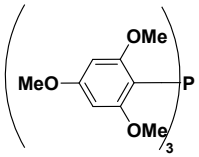
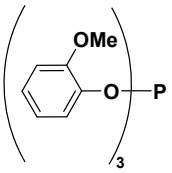
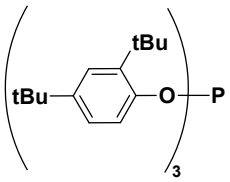


Compound **1a-D_3** was synthetized by refluxing under inert atmosphere **1a** (1 eq), TEA (1 eq) and D_2O (99.8% D, 20 eq) in dry THF for 24 h. The volatile compounds were then evaporated in vacuum and the product was used without further purification. , **1a-D_3**:**1a'-D_3** = 80:20 by ^{1}H NMR. Signals of **1a-D_3** ^{1}H NMR (400 MHz, $CDCl_3$, $-CD_2-$ = 91%, CD = 92%, O-CD_2 = 0%) δ = 7.95 – 7.88 (m, 2H), 7.58 (ddt, *J* = 8.6, 6.9, 1.3 Hz, 1H), 7.46 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 3H), 4.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.87, 166.67, 133.87, 131.54, 128.81, 128.48, 52.76. Signals of **1a'-D_3** ^{1}H NMR (400 MHz, $CDCl_3$, OD = 81, C_{sp2}D = 90%, O-CD_2 = 0%, CD = 94%) δ = 12.24 (s, 1H), 7.78 – 7.73 (m, 2H), 7.50 – 7.43 (m, 1H), 7.40 (ddt, *J* = 8.5, 6.9, 1.7 Hz, 2H), 5.70 (s, 1H), 4.79 (s, 2H), 2.51 (t, *J* = 2.5 Hz, 1H). Diagnostic ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.79, 128.58, 126.14, 51.71.

Table S1. Gold-catalyzed cascade reaction: conditions screening

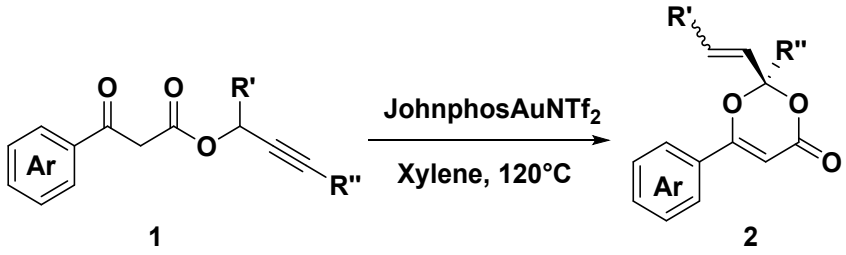


1a **2a**

Run	L	X$^-$	Solvent	Temp. (°C)	Yield (%)
1	JohnPhos	NTf_2^-	Toluene	60	35
2	JohnPhos	SbF_6^-	Toluene	60	37
3	JohnPhos	TFA^-	Toluene	60	N.R.
4	JohnPhos	OTf^-	Toluene	60	10
5	JohnPhos	NTf_2^-	Toluene	80	37
6	JohnPhos	NTf_2^-	Toluene	100	60
7	JohnPhos	NTf_2^-	Xylene	120	80
8	JohnPhos	NTf_2^-	Xylene	120	40[a]
9	JackiePhos	NTf_2^-	Toluene	60	43
10	CyJohnPhos	NTf_2^-	Toluene	60	40
11	XPhos	NTf_2^-	Toluene	60	40
12	Cy_3P	NTf_2^-	Toluene	60	N.R.
13		NTf_2^-	Toluene	60	N.R.
14		NTf_2^-	Toluene	60	N.R.
15		NTf_2^-	Toluene	60	Traces
16	Ph_3P	NTf_2^-	Toluene	60	22
17	Dppm[b]	NTf_2^-	Toluene	60	N.R.
18	Dppe[b]	NTf_2^-	Toluene	60	20
19	Biphep[b]	NTf_2^-	Toluene	60	13
20	XantaPhos[b]	NTf_2^-	Toluene	60	25 (**2a'**)
21	IPr	NTf_2^-	Toluene	60	20

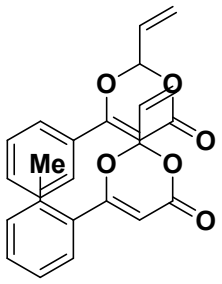
[a] KOAc (2 eq) were added; [b] For binuclear complexes the **L** loading was 2.5 mol%.

General procedure for gold-catalyzed cascade reaction of 2a-u



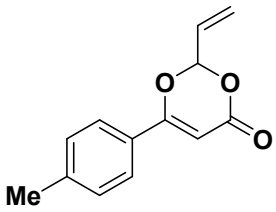
1 2

A 2-necked flask under inert atmosphere covered with an aluminium foil is charged with **1** (0.2 mmol), 1 mL of freshly distilled xylene and 7.7 mg (0.01 mmol) of JohnPhosAuNTf$_2$. The reaction is stirred for 1 h with a pre-heated oil bath at 120 °C. The product is purified by subjecting to flash chromatography (cHex:AcOEt 40:1) the reaction crude.

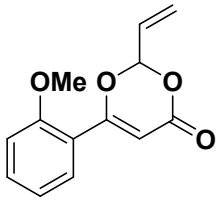


2a, Colorless oil. Yield = 80%. ^{1}H NMR (40 MHz, $CDCl_3$) δ = 7.73 – 7.71 (m, 1H), 7.55 – 7.51 (m, 1H), 7.47 – 7.43 (m, 3H), 6.18 – 6.11 (m, 1H), 6.02 (dt, *J* = 4.8, 1.2 Hz, 1H), 5.98 (s, 1H), 5.80 (dt, *J* = 16, 0.8 Hz, 1H), 5.62 (dt, *J* = 11.2, 0.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.96, 162.73, 132.45, 130.22, 130.11, 128.89(2C), 126.53(2C), 122.42, 99.42, 93.15. LC-ESI$^+$ (m/z) = 203.2 (M+H$^+$), 225.2 (M+Na$^+$). Anal. Calc. for ($C_{12}H_{10}O_3$: 202.21): C, 71.28; H, 4.98; found: C, 71.01; H, 4.65.

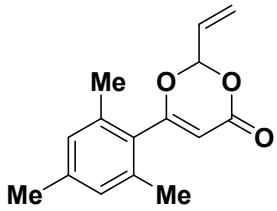
2b, Colorless oil. Yield = 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.42 (m, 1H), 7.39-7.35(m, 1H), 7.28 – 7.20 (m, 2H), 6.14-6.06 (m, 1H), 6.03 (dt, *J* = 4.8, 0.8 Hz, 1H), 5.76 (dt, *J* = 17.2, 0.8Hz, 1H), 5.66 (s, 1H), 5.58 (dt, *J* = 12, 0.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.91, 162.62, 137.46, 131.59, 131.55, 131.53, 130.34, 129.38, 126.31, 122.48, 99.44, 97.75, 25.23. LC-ESI$^+$ (m/z) = 217.2 (M+H$^+$), 239.2 (M+Na$^+$). Anal. Calc. for ($C_{13}H_{12}O_3$: 216.24): C, 72.21; H, 5.59; found: C, 72.11; H, 5.40.



2c, Colorless oil. Yield = 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.14 (ddd, *J* = 17.3, 10.7, 4.9 Hz, 1H), 6.02 – 5.98 (m, 1H), 5.92 (s, 1H), 5.79 (dt, *J* = 17.3, 1.0 Hz, 1H), 5.61 (dt, *J* = 10.7, 1.0 Hz, 1H), 2.40 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.13, 143.29, 130.32, 129.61, 127.31, 126.53, 122.30, 99.31, 92.33, 21.58. LC-ESI$^+$ (m/z) = 217.2 (M+H$^+$), 239.2 (M+Na$^+$). Anal. Calc. for ($C_{13}H_{12}O_3$: 216.24): C, 72.21; H, 5.59; found: C, 72.06; H, 5.31.

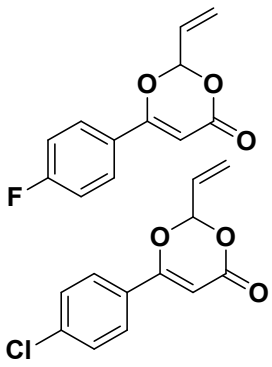


2d, Colorless oil. Yield = 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.30 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.21-7.20 (m, 1H), 7.07-7.04 (m, 1H), 6.18-6.10 (m, 1H), 6.01 (dt, *J* = 4.8, 1.2 Hz, 1H), 5.95 (s, 1H), 5.81– 5.76 (m, 1H), 5.62– 5.59 (m, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.80, 162.69, 159.87, 131.46, 130.19, 129.96, 122.44, 118.96, 118.14, 111.82, 99.44, 93.43, 55.43. LC-ESI$^+$ (m/z) = 233.2 (M+H$^+$), 487.2 (2 M+Na$^+$). Anal. Calc. for ($C_{13}H_{12}O_4$: 232.24): C, 67.23; H, 5.21; found: C, 67.04; H, 5.18.



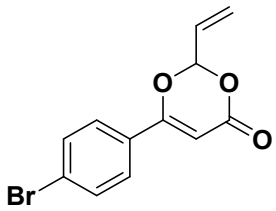
2e, Colorless oil. Yield = 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90 (s, 2H), 6.13 – 6.00 (m, 2H), 5.78 – 5.68 (m, 1H), 5.60 – 5.51 (m, 1H), 5.48 (s, 1H), 2.29 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.47, 140.37, 136.49, 130.17, 128.65, 122.24, 99.78, 99.25, 21.13, 19.84. LC-ESI$^+$ (m/z) =

245.2($M+H^+$), 267.2 ($M+Na^+$). Anal. Calc. for ($C_{15}H_{16}O_3$: 244.11): C, 73.75; H, 6.60; found: C, 73.56; H, 6.39.

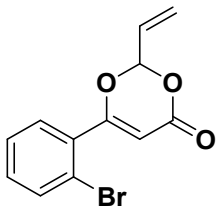


2f, Colorless oil. Yield = 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67– 7.63 (m, 2H), 7.44-7.41 (m, 2H), 6.17-6.09 (m, 1H), 6.00 (dt, *J* = 4.8, 0.8Hz, 1H), 5.90 (s, 1H), 5.78 (dt, *J* = 12.4, 0.8 Hz, 1H), 5.61 (dt, *J* = 10.8, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.91, 166.54, 164.01, 162.54, 130.10, 128.93, 128.84, 122.56, 116.31, 116.09, 99.47, 92.91, 92.89. LC-ESI$^+$ (m/z) = 221.2($M+H^+$), 463.2 ($2M+Na^+$). Anal. Calc. for ($C_{12}H_9FO_3$: 220.05): C, 65.46; H, 4.12; found: C, 65.31; H, 4.00.

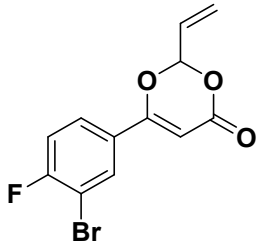
2g, Colorless oil. Yield = 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.55 (m, 1H), 7.51 – 7.35 (m, 1H), 6.17-6.09 (m,1H), 6.01 (dt, *J* = 4.8, 0.8 Hz, 1H), 5.94 (s, 1H), 5.78 (dt, *J* = 16.4, 0.8 Hz, 1H), 5.62 (dt, *J* = 10.0, 0.8Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.78, 162.40, 138.79, 130.04, 129.26, 128.56, 127.78, 122.64, 99.53, 93.43. LC-ESI$^+$ (m/z) = 237.2($M+H^+$), 239.2 ($M+H^+$). Anal. Calc. for ($C_{12}H_9ClO_3$: 236.65): C, 60.90; H, 3.83; found: C, 60.71; H, 3.55



2h, Colorless oil, Yield = 64%. ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.60-7.55 (m, 4H), 6.17-6.09 (m, 1H), 6.00 (dt, *J* = 9.2, 0.8 Hz, 1H), 5.95 (s, 1H), 5.78 (dt, *J* = 16.8, 1.2 Hz, 1H), 5.62 (dt, *J* = 10.8, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 162.40, 132.24, 130.02, 129.00, 127.91, 127.29, 122.68, 99.55, 93.47. LC-ESI$^+$ (m/z) = 281.2($M+H^+$), 283.2 ($M+H^+$). Anal. Calc. for ($C_{12}H_9BrO_3$: 279.97): C, 51.27; H, 3.23; found: C, 51.10; H, 3.01.

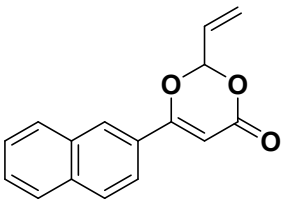


2i, Colorless oil. Yield = 64%.^{1}H NMR (401 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.40 – 7.31 (m, 2H), 6.14 – 6.06 (m, 2H), 5.80 (s, 1H), 5.81 – 5.75 (m, 1H), 5.60 – 5.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.82, 162.01, 133.97, 132.53, 132.51, 130.87, 129.99, 127.58, 122.52, 122.05, 99.86, 99.14. LC-ESI$^+$ (m/z) = 281.2($M+H^+$), 283.2 ($M+H^+$). Anal. Calc. for ($C_{12}H_9BrO_3$: 279.97): C, 51.27; H, 3.23; found: C, 51.16; H, 3.11.

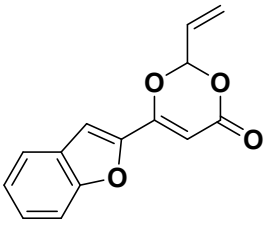


2j, Colorless oil. Yield = 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 6.4, 2.0Hz, 1H), 7.67-7.63 (m, 1H), 7.33 – 7.06 (m, 1H), 6.17 – 6.08 (m, 1H), 6.00 (dt, *J* = 5.2, 1.2 Hz, 1H), 5.91 (s, 1H), 5.79 (dt, *J* = 17.2, 0.8 Hz, 1H), 5.63 (dt, *J* = 10.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.49, 162.07, 161.49 (d, *J* = 255.4 Hz), 132.07 (d, *J* = 1.5 Hz), 129.87, 127.75 (d, *J* = 3.9 Hz), 127.48 (d, *J* = 8.2 Hz), 122.88, 117.11 (d, *J* = 23.3 Hz), 110.11 (d, *J* = 21.9 Hz), 99.68, 93.77 (d, *J* = 1.5 Hz). LC-ESI$^+$ (m/z) = 299.2($M+H^+$), 301.2 ($M+H^+$),

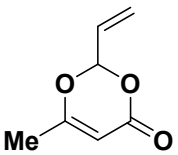
321.2 (M+Na$^+$). Anal. Calc. for ($C_{12}H_8BrFO_3$: 297.96): C, 48.19; H, 2.70; found: C, 48.01; H, 2.64.



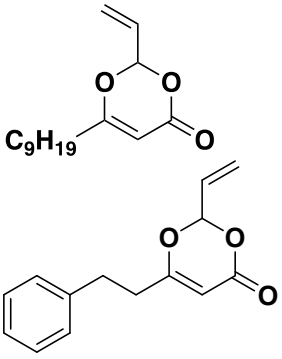
2k, Colorless stick oil. Yield = 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 1.6 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.70 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.60-7.52 (m, 2H), 6.25-6.17 (m, 1H), 6.09 (s, 1H), 6.08 – 6.07 (m, 1H), 5.84 (d, *J* = 17.2 Hz, 1H), 5.66 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.87, 162.79, 135.09, 132.65, 130.28, 129.14, 128.82, 128.33, 127.82, 127.58, 127.23, 127.11, 122.56, 122.37, 99.53, 93.51. LC-ESI$^+$ (m/z) = 253.2 (M+H$^+$) 527.2 (2M+Na$^+$). Anal. Calc. for ($C_{16}H_{12}O_3$: 252.08): C, 76.16; H, 4.79; found: C, 76.02; H, 4.65.



2l, Yellowish oil. Yield = 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 1H), 7.53-7.50 (m, 1H), 7.44 – 7.40 (m, 1H), 7.30 – 7.27 (m, 2H), 6.17 – 6.10 (m, 1H), 6.09 (s, 1H), 6.05 (dt, *J* = 4.8, 0.8 Hz, 1H), 5.79 (dt, *J* = 17.2, 0.8 Hz, 1H), 5.63 (dt, *J* = 10.4, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.90, 159.01, 156.01, 146.55, 130.03, 127.52, 127.36, 123.94, 122.70, 122.45, 111.86, 110.75, 99.81, 93.89. LC-ESI$^+$ (m/z) = 243.2 (M+H$^+$), 507.2 (2M+Na$^+$). Anal. Calc. for ($C_{14}H_{10}O_4$: 242.23): C, 69.42; H, 4.16; found: C, 69.28; H, 4.01.



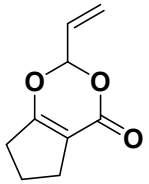
2m, Colorless oil. Yield = 75%.^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.01 (ddd, *J* = 17.1, 10.7, 4.9 Hz, 1H), 5.83 (d, *J* = 4.9 Hz, 1H), 5.69 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.54 (dd, *J* = 10.8, 1.0 Hz, 1H), 5.32 (d, *J* = 1.2 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.67, 161.91, 130.17, 122.16, 99.06, 96.31, 19.42. LC-ESI$^+$ (m/z) = 141.2 (M+H$^+$), 158.2 (M+NH$_4^+$), 303.2 (2M+Na$^+$). Anal. Calc. for ($C_7H_8O_3$: 140.05): C, 60.00; H, 5.75; found: C, 59.79; H, 5.55.



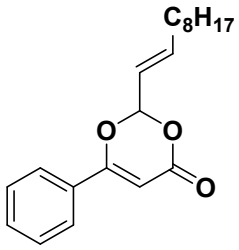
2n, Colorless oil. Yield = 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05-5.97 (m, 1H), 5.80(d, *J* = 4.8 Hz, 1H), 5.68 (d, *J* = 17.2 Hz, 1H), 5.53 (d, *J* = 10.4 Hz, 1H), 5.31 (s, 1H), 2.29 – 2.28 (m, 2H), 1.58-4.51 (m, 3H), 1.30-1.27 (m, 9H), 0.86 (t, *J* = 6.8 Hz, 5H). ^{13}C NMR (100MHz, $CDCl_3$) δ 175.28, 162.15, 130.26, 122.06, 99.03, 95.44, 33.16, 31.78, 29.32, 29.17, 29.14, 28.92, 25.78, 22.60, 14.04. LC-ESI$^+$ (m/z) = 239.2(M+H$^+$), 499.4 (2M+Na$^+$). Anal. Calc. for ($C_{14}H_{22}O_3$: 238.16): C, 70.56; H, 9.30; found: C, 70.25; H, 9.15.

2o, Colorless oil. Yield = 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.25 (m, 2H), 7.24 – 7.20 (m, 1H), 7.17 – 7.12 (m, 2H), 6.01 (ddd, *J* = 17.4, 10.7, 4.9 Hz, 1H), 5.74 (dt, *J* = 4.9, 1.1 Hz, 1H), 5.67 (dt, *J* = 17.3, 1.0 Hz, 1H), 5.54 (dt, *J* = 10.7, 1.0 Hz, 1H), 5.28 (d, *J* = 0.9 Hz, 1H), 2.92 – 2.85 (m, 2H), 2.65 – 2.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.80, 161.92, 139.41, 130.15, 128.64, 128.20, 126.61, 122.21, 99.14, 96.22, 34.85, 31.97. LC-

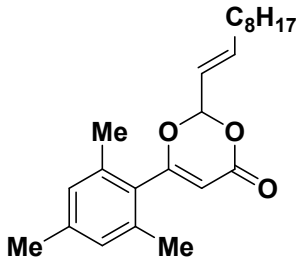
ESI$^+$ (m/z) = 231.2(M+H$^+$), 253.2 (M+Na$^+$). Anal. Calc. for ($C_{14}H_{14}O_3$: 230.09): C, 73.03; H, 6.13; found: C, 72.85; H, 6.05.



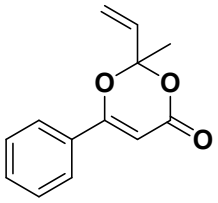
2p, Colorless oil. Yield = 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.04 (ddd, *J* = 17.3, 10.7, 4.8 Hz, 1H), 5.86 (dt, *J* = 4.8, 1.1 Hz, 1H), 5.70 (dt, *J* = 17.4, 1.0 Hz, 1H), 5.54 (dt, *J* = 10.8, 1.0 Hz, 1H), 2.65 – 2.50 (m, 4H), 2.10 – 1.92 (m, 2H). LC-ESI$^+$ (m/z) = 167.2(M+H$^+$). Anal. Calc. for ($C_9H_{10}O_3$: 166.06): C, 65.05; H, 6.07; found: C, 64.88; H, 6.01.



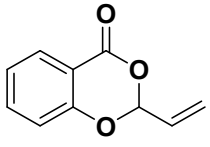
2r, Colorless oil. Yield = 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.56 – 7.49 (m, 1H), 7.44 (dd, *J* = 8.3, 6.8 Hz, 2H), 6.20 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.98 – 5.91 (m, 2H), 5.80 (ddt, *J* = 15.6, 5.8, 1.6 Hz, 1H), 2.21 – 2.13 (m, 2H), 1.51 – 1.38 (m, 2H), 1.36 – 1.20 (m, 10H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.15, 163.23, 140.37, 132.34, 130.27, 128.84, 126.54, 122.31, 100.33, 93.02, 32.06, 31.83, 29.36, 29.19, 29.10, 28.35, 22.63, 14.07. LC-ESI$^+$ (m/z) = 315.2(M+H$^+$), 651.2 (2M+Na$^+$). Anal. Calc. for ($C_{20}H_{26}O_3$: 314.19): C, 76.40; H, 8.34; found: C, 76.28; H, 8.09.



2s, Colorless oil. Yield = 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.89 (s, 2H), 6.16 (dtd, *J* = 15.6, 6.8, 0.9 Hz, 1H), 5.98 (dd, *J* = 5.7, 0.9 Hz, 1H), 5.73 (ddt, *J* = 15.6, 5.8, 1.6 Hz, 1H), 5.46 (s, 1H), 2.28 (s, 3H), 2.26 (s, 6H), 2.18 – 2.08 (m, 2H), 1.44 – 1.37 (m, 2H), 1.29 – 1.22 (m, 10H), 0.91 – 0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.62, 163.22, 140.24, 140.19, 136.45, 132.96, 128.61, 122.31, 100.16, 99.59, 31.99, 31.81, 29.33, 29.15, 29.06, 28.30, 22.61, 21.12, 19.83, 14.05. LC-ESI$^+$ (m/z) = 357.2(M+H$^+$), 735.4 (2M+Na$^+$). Anal. Calc. for ($C_{23}H_{32}O_3$: 356.24): C, 77.49; H, 9.05; found: C, 77.21; H, 8.81.



2t, Colorless oil. Yield = 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.51 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 5.94 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.88 (s, 1H), 5.57 (d, *J* = 17.3 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.96, 162.03, 135.38, 132.13, 128.84, 126.26, 124.86, 118.77, 105.38, 93.52, 92.62, 26.33. LC-ESI$^+$ (m/z) = 217.2(M+H$^+$), 239.2 (M+Na$^+$), 455.2 (2M+Na$^+$). Anal. Calc. for ($C_{13}H_{12}O_3$: 216.08): C, 72.21; H, 5.05; found: C, 77.21; H, 8.81.



2u, Pale yellow oil. Yield = 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.56 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.05 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.10 (ddd, *J* = 17.2, 10.7, 4.7 Hz, 1H), 5.99 (dt, *J* = 4.8, 1.1 Hz, 1H), 5.75 (dt, *J* = 17.3, 1.0 Hz, 1H), 5.58 (dt, *J* = 10.7, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.62, 157.91, 136.31, 130.65, 130.22, 123.49, 122.23, 116.79, 114.60, 99.57. LC-ESI$^+$ (m/z) =

177.2 ($M+H^+$) 194.2 ($M+NH_4^+$). Anal. Calc. for ($C_{10}H_8O_3$: 176.17): C, 68.18; H, 4.58; found: C, 68.01; H, 4.31.

Crystallographic data collection and structure determination for *2k*.

The X-ray intensity data were measured on a Bruker Apex III CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[3] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program,[3] and an empirical absorption correction was applied using SADABS.[4] The structures were solved by direct methods (SIR 2014)[5] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[6] using anisotropic thermal parameters for all non-hydrogen atoms. The aromatic vinylic and methine hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters *U(H)* = 1.2 *Ueq*(C) and allowed to ride on their carrier carbons. Two independent molecules are present in the asymmetric unit.

Crystal data and details of the data collection for compound ***2k*** are reported in **Table S1**. Molecular drawings were generated using Mercury [5].

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 1990308. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

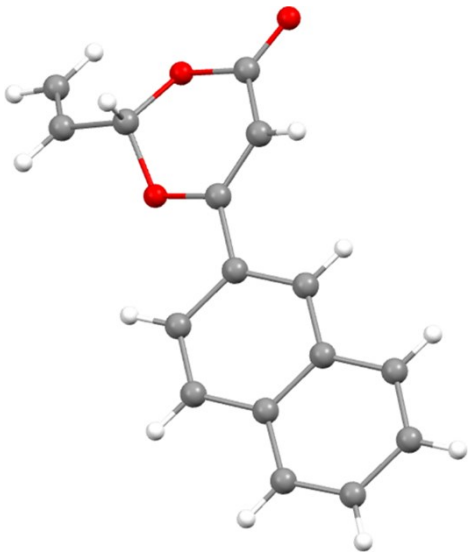


Figure S1. Crystal structure of one of the two independent molecules of **2k**

[3] *SMART & SAINT Software Reference Manuals*, version 5.051 (Windows NT Version), Bruker Analytical X-ray Instruments Inc.: Madison, Wi, **1998.**

[4] Sheldrick, G. M.; *SADABS-2008/1 - Bruker AXS Area Detector Scaling and Absorption Correction*, Bruker AXS: Madison, Wisconsin, USA, **2008**.

[5] Burla, M.C.; Caliandro, R.; Carrozzini, B.; Cascarano, G.L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; "Crystal structure determination and refinement via SIR2014" *J. Appl. Cryst.* **2015**, *48*, 306-309.

[6] Sheldrick, G. M.; *Acta Cryst C71*, **2015**, 3-8.

Table S2. Crystal data and structure refinement for compound ***2k***.

Compound	**2k**
Formula	$C_{16}H_{12}O_3$
Fw	252.26
T, K	100
λ, Å	1.54178
Crystal symmetry	Triclinic
Space group	*P-1*
a, Å	5.865(2)
b, Å	14.967(5)
c, Å	14.978(5)
α	72.081(10)
β	82.356(12)
γ	84.576(12)
Cell volume, Å^3	1237.8(7)
Z	4
D_c, Mg m^{-3}	1.354
μ(Mo-K_α), mm^{-1}	0.762
F(000)	528
Crystal size/ mm	0.20 x 0.03 x 0.03
θ limits, °	3.108 - 60.975
Reflections collected	3632
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	3632 [R(int) = 0.0723]
Goodness-of-fit-on F^2	1.240
R_1 (F)[a], wR_2 (F^2) [$I > 2\sigma(I)$]	0.1123, 0.2647
Largest diff. peak and hole, e. Å^{-3}	0.553 and -0.580

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.