Supplementary Information

Ruthenium(II)-catalyzed hydration of terminal alkynes in PEG-400
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1. General details

General information: Unless otherwise noted, all reagents were used as received from commercial suppliers. [Ru(p-cymene)Cl2]2 catalyst was obtained from Sigma-Aldrich and used without further purification. All reactions were performed in a screw-cap vial equipped with stirred bar. Reactions were monitored using thin-layer chromatography (SiO2). TLC plates were visualized with UV light (254 nm), iodine treatment or using p-anisaldehyde stain. Column chromatography was carried out using silica gel (60-120 mesh & 100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 101, 126 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl3 (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (J) are given in Hz. HRMS were recorded using ESI-TOF techniques.
2. Experimental procedures and analytical data:

**General procedure for hydration of terminal alkynes in PEG-400:** To a solution of alkyne (1.0 mmol) in PEG-400/H₂O (4:1) was added [Ru(p-cymene)Cl₂]₂ (0.01 mmol) and stirred at room temperature. After completion of the reaction, monitored by TLC, the reaction mixture was diluted with ether (10 mL), stirred for 10 min, and was allowed to stand in ice-salt bath to solidify PEG-400. The ether layer was decanted, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue obtained was purified by silica gel flash column chromatography using ethyl acetate in petroleum ether as eluent to give pure products.

**3-Acetyl-3-methylhexane-2, 5-dione (2b):**

![Structure of 3-Acetyl-3-methylhexane-2, 5-dione (2b)](image)

Prepared according to the general procedure as described above in 78% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford yellow oil; **¹H NMR** (300 MHz, CDCl₃) δ 3.05 (s, J = 6.6 Hz, 2H), 2.11 (s, 3H), 2.10 (s, 6H), 1.41 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 206.2, 205.8, 64.4, 49.2, 30.4, 26.5, 19.4; IR (neat) ν max 2937, 2310, 1704, 1419, 1359, 1132, 1077, 905, 758, 556; HRMS (ESI) [M + H]⁺ C₉H₁₅O₃ calcd 171.1016, found 171.1019.

**3-Oxobutyl benzoate (2c):**

![Structure of 3-Oxobutyl benzoate (2c)](image)

Prepared according to the general procedure as described above in 58% yield. It was purified by flash chromatography (20% EtOAc/hexanes) to afford a brownish liquid; **¹H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.98 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 – 7.40 (m, 2H), 4.61 – 4.57 (t, 2H), 2.91 (t, J = 6.3 Hz, 2H), 2.23 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 205.6, 166.4, 133.1, 129.6, 128.4, 59.9, 42.4, 30.3; IR (neat) ν max 2923, 2853, 1717, 1453, 1274, 1172, 1028, 712; HRMS (ESI) [M + H]⁺ C₁₁H₁₃O₃ calcd 193.0859, found 193.0860.
2-(2-Oxopropyl)isoindoline-1,3-dione (2d):

Prepared according to the general procedure as described above in 88% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a colour less liquid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.96 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 4.50 (s, 2H), 2.27 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.7, 167.8, 134.2, 132.1, 123.6, 47.1, 27.0; IR (neat) $\nu_{\text{max}}$ 3744, 1774, 1717, 1411, 1181, 1016, 889, 719; HRMS (ESI) [M + H]$^+$ C$_{11}$H$_{10}$NO$_3$ calcd 204.0655, found 204.0657.

4-(2, 5-Dimethoxyphenyl)-4-hydroxybutan-2-one (2e):

Prepared according to the general procedure as described above in 73% yield. It was purified by flash chromatography (15% EtOAc/hexanes) to afford a yellow liquid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.03 – 6.91 (m, 1H), 6.77 – 6.62 (m, 2H), 5.29 (dt, $J = 24.2, 12.1$ Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.38 (s, 1H), 2.85 (dd, $J = 17.3, 2.9$ Hz, 1H), 2.69 (dd, $J = 17.3, 9.4$ Hz, 1H), 2.12 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 209.5, 153.9, 149.9, 132.0, 112.9, 112.4, 111.3, 65.7, 55.8, 50.4, 30.7; IR (neat) $\nu_{\text{max}}$ 2932, 2858, 1710, 1607, 1510, 1259, 1168, 914, 838; HRMS (ESI) [M – H$_2$O]$^+$ C$_{12}$H$_{15}$O$_3$ calcd 207.1015, found 207.1008.

2-Methyl-2-(2-oxopropyl) cyclohexane-1, 3-dione (2f):

Prepared according to the general procedure as described above in 89% yield. It was purified by flash chromatography (10% EtOAc/hexanes) to afford a brown oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.25 (s, 2H), 2.79 – 2.57 (m, 4H), 2.31 – 2.12 (m, 2H), 2.09 (s, 3H), 2.08 – 2.03 (m,
1H), 1.23 (s, 3H); 13C NMR (126 MHz, CDCl₃) δ 210.5, 206.5, 59.9, 50.1, 37.5, 28.7, 22.9, 17.4; IR (neat) νmax 2927, 2309, 1711, 1425, 1309, 1117, 1069, 905; HRMS (ESI) [M + H]⁺ C₁₀H₁₅O₃ calcd 183.1016, found 183.1024.

5-Oxohexanoic acid (2h):

Prepared according to the general procedure as described above in 86% yield. It was purified by flash chromatography (50% EtOAc/hexanes) to afford a yellow oil; 1H NMR (500 MHz, CDCl₃) δ 2.54 (t, J = 7.2 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 2.16 (s, 3H), 1.95 – 1.86 (m, 2H). 13C NMR (75 MHz, CDCl₃) δ 208.25, 179.1, 42.3, 32.9, 29.9, 18.5; IR (neat) νmax 2927, 1707, 1367, 1068, 739; HRMS (ESI) [M + Na]⁺ C₆H₁₀NaO₃ calcd 153.0522, found 153.0533.

6-Oxoheptanoic acid (2i):

Prepared according to the general procedure as described above in 88% yield. It was purified by flash chromatography (50% EtOAc/hexanes) to afford a yellow oil; 1H NMR (400 MHz, CDCl₃) δ 2.43 – 2.37 (m, 2H), 2.33 – 2.27 (m, 2H), 2.08 (s, 3H), 1.60 – 1.52 (m, 4H). 13C NMR (126 MHz, CDCl₃) δ 208.8, 179.1, 43.2, 3.7, 29.9, 24.1, 23.1; IR (neat) νmax 3325, 2930, 2068, 1997, 1705, 1365, 1211, 966; HRMS (ESI) [M + Na]⁺ C₇H₁₂NaO₃ calcd 167.0679, found 167.0698.

2-Acetyl-2-(2-oxopropyl)cyclohexanone (2l):

Prepared according to the general procedure as described above in 80% yield. It was purified by flash chromatography (50% EtOAc/hexanes) to afford a colourless oil; 1H NMR (500 MHz, CDCl₃) δ 2.86 (s, 2H), 2.61 – 2.46 (m, 2H), 2.39 – 2.33 (m, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 2.02 (m, J = 15.2, 5.9, 3.1 Hz, 1H), 1.81 – 1.61 (m, 4H); 13C NMR (75 MHz, CDCl₃) δ 209.1, 206.3, 205.6, 66.0, 47.9, 41.0, 34.8, 30.4, 26.4, 26.1, 21.7; IR (neat) νmax 2937, 2310, 1704, 1419, 1359, 1132, 1077, 905, 758; HRMS (ESI) [M + Na]⁺ C₁₁H₁₆NaO₃ calcd 219.0991, found 219.0992.
Compound 2m:

Prepared according to the general procedure as described above in 58% yield. It was purified by flash chromatography (50% EtOAc/hexanes) to afford a white solid;\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 5.35 (t, J = 19.1 Hz, 1H), 4.61 (ddd, J = 11.4, 9.9, 4.3 Hz, 1H), 2.53 – 2.47 (t, 2H), 2.34 – 2.27 (m, 4H), 2.14 (s, 3H), 2.06 – 1.93 (m, 2H), 1.93 – 1.78 (m, 6H), 1.62 – 1.42 (m, 8H), 1.38 – 1.29 (m, 2H), 1.28 – 1.21 (m, 1H), 1.12 (m, 8H), 1.01 (s, 3H), 0.99 – 0.94 (m, 2H), 0.91 (t, J = 7.8 Hz, 3H), 0.86 (dd, J = 6.6, 2.3 Hz, 6H), 0.68 (s, 3H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ 208.1, 172.6, 139.6, 122.7, 74.0, 56.7, 56.2, 50.0, 42.5, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 33.6, 31.9, 29.9, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 19.0, 18.7, 11.9; IR (neat) ν\textsubscript{max} 2941, 2866, 1727, 1462, 1374, 1172, 1012, 751; HRMS (ESI) [M + H]\textsuperscript{+} C\textsubscript{33}H\textsubscript{56}O\textsubscript{3} calcd 499.4145, found 499.4151.

4-((4R,5S,6R)-4,5-Bis(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)butan-2-one (2n):

Prepared according to the general procedure as described above in 50% yield. It was purified by flash chromatography (50% EtOAc/hexanes) to afford a colour less oil;\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.33 – 7.06 (m, 13H), 4.88 (d, J = 2.8 Hz, 2H), 4.81 (dd, J = 10.8, 5.5 Hz, 1H), 4.61 – 4.52 (m, 4H), 4.46 (s, 2H), 4.43 (s, 2H), 3.89 – 3.76 (m, 2H), 3.74 – 3.49 (m, 6H), 2.92 – 2.54 (m, 2H), 2.16 (dd, J = 13.0, 5.1 Hz, 1H), 2.07 (s, 3H), 1.63 (ddd, J = 13.0, 11.6, 3.7 Hz, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 207.0, 138.7, 138.5, 138.2, 128.4, 128.4, 127.9, 127.9, 127.6, 127.6, 97.7, 78.2, 77.5, 75.0, 73.5, 71.8, 70.9, 68.9, 62.3, 43.3, 35.4, 30.5; IR (neat) ν\textsubscript{max} 2934, 1710, 1510, 1259, 914, 838; HRMS (ESI) [M + Na]\textsuperscript{+} C\textsubscript{33}H\textsubscript{36}NaO\textsubscript{6} calcd 527.2404, found 527.2432.
3. $^1$H & $^{13}$C NMR Spectra:

4-(Benzyloxy) butan-2-one (2a):

(1H NMR, 400 MHz, CDCl₃)

(13C NMR, 126 MHz, CDCl₃)
3-Acetyl-3-methylhexane-2, 5-dione (2b):

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\text{(H NMR 300 MHz, CDCl}_3) 
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3-Oxobutyl benzoate (2c):

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\text{(C NMR 101 MHz, CDCl}_3) 
\]
2-(2-Oxopropyl)isoindoline-1,3-dione (2d):
4-(2, 5-Dimethoxyphenyl)-4-hydroxybutan-2-one (2e):
2-Methyl-2-(2-oxopropyl) cyclohexane-1, 3-dione (2f):

(1H NMR 400 MHz, CDCl₃)

(13C NMR 125 MHz, CDCl₃)
4-Oxopentanoic acid (2g):

(3H NMR 300 MHz, CDCl₃)

(10C NMR 101 MHz, CDCl₃)
5-Oxohexanoic acid (2h):
6-Oxoheptanoic acid (2i):

\[ \text{\(\text{\textdegree} \text{H NMR 400 MHz, CDCl}_3\text{)}} \]

\[ \text{\(\text{\textdegree} \text{C NMR 126 MHz, CDCl}_3\text{)}} \]
4-Methyl-4-(3-oxobutoxy) cyclohexa-2, 5-dienone (2j):

(1H NMR 300 MHz, CDCl3)

(13C NMR 75 MHz, CDCl3)
2-Methyl-2-(2-oxopropyl) cyclopentane-1, 3-dione (2k):

2-acetyl-2-(2-oxopropyl)cyclohexanone (2l):
Compound 2m:
4-((4R,5S,6R)-4,5-Bis(benzyloxy)-6-(benzyloxymethyl)tetrahydro-2H-pyran-2-yloxy)butan-2-one (2n):