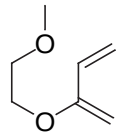


2-(2-Methoxyethoxy)-1,3-butadiene (**8**)

In a representative procedure, N-bromosuccinimide (100.25 g, 0.56 mol) was suspended in 2-methoxyethanol (560 mL) in a 2-neck round bottom flask under a nitrogen atmosphere. The reaction was cooled to -78 ˚C and purged with nitrogen. 1,3-Butadiene (60 mL, 0.75 mol) was condensed into the thick, slightly yellow reaction mixture. Maintaining positive nitrogen pressure the reaction was allowed to warm to rt with vigorous stirring. After 16 h to the now clear and colorless solution is added KOH (85%, 82 g, 1.24 mol) portionwise.

Caution. It is important to add the KOH slowly due to the exothermic nature of the reaction causing excess 1,3-butadiene to rapidly boil out of solution at approximately 40 ˚C.

The mixture turns a deep red color and reaches 90 ˚C due to the exothermic nature of the reaction. Upon cooling to rt the reaction is diluted with 400 mL of water. The product is extracted using pentane (4 x 250 mL). The combined pentane extract is washed with brine, dried ($MgSO_4$), filtered and condensed by rotoary evaporation. Distillation of the product (10 Torr, 60 ˚C) to afford 39.33 g (55.0%) of diene **8** as colorless oil.

Characterization:

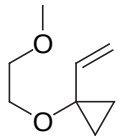
^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.71 (t, *J* = 4.75 Hz, 2H), 3.91 (t, *J* = 4.75, 2H), 4.14 (s, 2H), 5.10 (d, *J* = 10.7 Hz, 1H), 5.61 (d, *J* = 17.1 Hz, 1H), 6.15 (dd, *J* = 10.9, 17.3, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 59.15, 66.69, 70.76, 87.11, 114.44, 132.93, 158.12.

IR (film): 2928, 2880, 1648, 1583, 1457, 1357, 1309, 1199, 1134, 1095, 985, 920, 807.

HRMS (*m/z*): [M^+] calcd for $C_7H_{12}O_2$, 128.0837; found, 128.0834.

bp: 68-72 ˚C, 20 Torr



1-(2-Methoxy-ethoxy)-1-vinylcyclopropane (**9**)

A three-neck flask was equipped with a mechanical stirrer, double condenser and a constant rate addition funnel. Granular zinc (61.21 g, 936.4 mmol) and copper(I) chloride (9.32 g, 92 mmol) were suspended in diethyl ether (200 mL) using the mechanical stirrer. Diiodomethane (19 mL, 234 mmol) was added directly by syringe followed by acetyl chloride (1.5 mL, 21 mmol). A preheated oil bath (45-50 ˚C) was raised to heat the reaction mixture for 15 min, during which time the green-gray suspension became dark gray. Diene **8** was added dropwise over 1.5 h, during which time the dark gray suspension becomes nearly black. Additional diiodomethane (10 mL, 123 mmol) in diethyl ether (150 mL) was added dropwise over 1 h, during which time the black suspension became an orange solution. Heating continues (45-50 ˚C), during which time the reaction solution remained orange and a thick black precipitate was deposited. The reaction was monitored by GC and was complete 3 h after the addition of the final reagents.

The reaction was cooled to room temperature and the ethereal solution decanted away from the dark solids into an Erlenmeyer flask. The solids were rinsed with fresh ether (3 x 25 mL) and also transferred to the Erlenmeyer flask. The ethereal solution was chilled to 0 ˚C and sat. NH_4Cl (aq) (200 mL) was added. The aqueous layer was extracted with pentane (3 x 250 mL). The combined organic layers were washed with 1 M NaOH (3 x 100 mL), and then brine. The organic layer was dried over Na_2SO_4 concentrated by rotary evaporation and distilled from K_2CO_3 (10 Torr, 65 ˚C) to afford 17.6 g (53%) of **9**.

Characterization:

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.68-0.72 (m, 2H), 1.04-1.08 (m, 2H), 3.37 (s, 3H), 3.49-3.52 (m, 2H), 3.10-3.63 (m, 2H), 5.06 (d, *J* = 10.7 Hz, 1H), 5.20 (d, *J* = 17.3 Hz, 1H), 5.62 (dd, *J* = 10.5, 17.1 Hz, 1H).

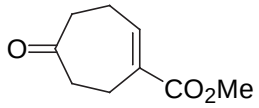
^{13}C NMR (75 MHz, $CDCl_3$, δ): 14.53, 59.04, 61.82, 66.78, 71.58, 112.17, 138.87.

IR (film): 2984.9, 2924.2, 2876.9, 1639.1, 1450.4, 1294.3, 1222.0, 1132.2, 1082.0, 913.6, 897.3 cm^{-1}.

HRMS (*m/z*): [M - H^+] calcd for $C_8H_{14}O_2$, 141.0916; found, 141.0919.

General procedure for the optimized [5 + 2] reaction

General Procedure: To an oven dried, argon-purged Schlenk flask was added $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol) and anhydrous 1,2-dichloroethane (2 mL) under an argon atmosphere. To this was added **9** (142.2 mg, 1 mmol), followed by addition of the alkyne (1.2 - 1.3 mmol). The flask was placed in an oil bath preheated to 80 ˚C. The reaction was monitored by TLC. Upon completion, the initially pale yellow solution turned dark red in color. The reaction mixture was treated with 1% HCl in MeOH (0.2 mL) and stirred open to the atmosphere until TLC indicated that the hydrolysis was complete, typically 10-15 min. For the larger scale reactions addition of water (1 equiv) accelerated the hydrolysis. The resultant mixture was filtered through a short pad of silica gel (Et_2O eluant) and concentrated in vacuo. The residue was purified by flash column chromatography.



5-Oxocyclohept-1-enecarboxylic acid methyl ester (**10**)

Characterization:

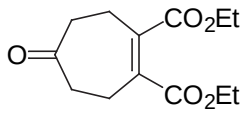
^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.51-2.58 (m, 2H), 2.62-2.76 (m, 6H), 3.76 (s, 3H), 7.15 (t, *J* = 5.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 22.5, 24.5, 40.9, 42.1, 52.1, 133.4, 140.9, 167.8, 211.8.

IR (neat): 2922, 2854, 1727, 1708, 1436, 1248, 1199, 1115, 1070, 735 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_9H_{12}O_3$, 168,0786; found, 168.0779.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19; Found: C, 64.53; H, 7.46.



5-Oxocyclohept-1-ene-1,2-dicarboxylic acid diethyl ester (**11**)

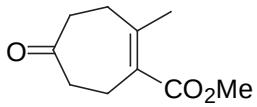
Characterization:

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.27 (t, 7.08 Hz, 6H), 2.64 (m, 8H), 4.19 (q, *J* = 7.08 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 13.89, 25.13, 41.50, 61.45, 138.17, 167.99, 209.82.

IR (neat): 2982, 2935, 1713, 1444, 1367, 1265, 1176, 1078, 1027 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_{13}H_{18}O_5$, 254.1154; found, 254.1159.



2-Methyl-5-oxocyclohept-1-enecarboxylic acid methyl ester (**12**)

Characterization:

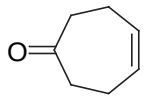
^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.09 (s, 3H), 2.38-2.42 (m, 2H), 2.48-2.52 (m, 4H), 2.57-2.59 (m, 2H), 3.72 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 23.63, 25.38, 32.82, 41.99, 43.76, 52.27, 129.41, 149.95, 169.90, 211.55.

IR (neat): 2951, 1710, 1636, 1434, 1280, 1213, 1106, 1051 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_{10}H_{14}O_3$, 182.0943; found, 182.0937.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.19; H, 7.74. Found: C, 65.75; H, 7.56.



Cyclohept-4-enone (**13**)

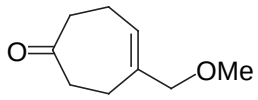
Characterization:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.33-2.35 (m, 4H), 2.61-2.65 (m, 4H), 5.77 (t, *J* = 3.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 23.9, 42.3, 129.5, 213.8.

IR (neat): 2925, 2852, 1706, 1438, 1350, 1257, 1201, 867 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_7H_{10}O$, 110.0732; found, 110.0734.



4-Methoxymethylcyclohept-4-enone (**14**)

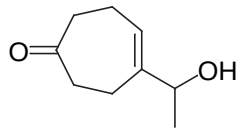
Characterization:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.33-2.39 (m, 4H), 2.60-2.64 (m, 4H), 3.29 (s, 3H), 3.79 (s, 2H), 5.82 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 23.53, 24.64, 41.91, 57.50, 76.58, 126.78, 137.96, 212.97.

IR (neat): 2923.7, 2819.4, 1704.6, 1449.5, 1349.3, 1213.2, 1192.1, 1082.1 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_9H_{14}O_2$, 154.0994; found, 154.0988.



4-(1-Hydroxyethyl)cyclohept-4-enone (**15**)

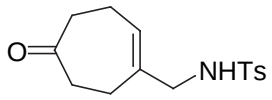
Characterization:

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.23 (d, *J* = 6.6 Hz, 3H), 1.86-1.90 (m, 1H), 2.55-2.58 (m, 4H), 4.20-4.22 (m, 1H), 5.79-5.80 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.67, 22.41, 23.64, 41.86, 42.78, 73.02, 123.73, 144.82, 213.30.

IR (neat): 3402.7 (s, br), 2970.3, 2897.5, 1694.1, 1442.2, 1367.4, 1318.0, 1214.0, 1069.5, 886.7 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_9H_{14}O_2$, 154.0994; found, 154.0993.



4-Methyl-*N*-(5-oxo-cyclohept-1-enylmethyl)benzenesulfonamide (**16**)

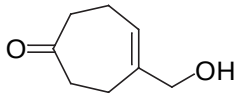
Characterization:

^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.19-2.23 (m, 4H), 2.38 (s, 3H), 2.43-2.48 (m, 4H), 3.42 (d, *J* = 6.3 Hz, 1H), 5.33 (t, *J* = 6.3 Hz, 1H), 5.64 (t, *J* = 4.4 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.36, 23.46, 25.07, 41.62, 41.71, 50.89, 126.95, 127.46, 129.52, 136.15, 136.93, 143.35, 212.95.

IR (neat): 3277.7, 2922.3, 1699.3, 1598.0, 1438.5, 1323.8, 1159.3, 1093.8, 1049.2, 816.2, 661.4 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_{15}H_{19}NO_3S$, 293.1086; found, 293.1080.



4-Hydroxymethylcyclohept-4-enone (**17**)

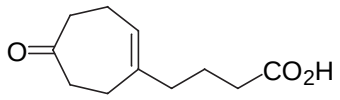
Characterization:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.28-2.31 (m, 4H), 2.54-2.57 (m, 4H), 2.81 (br s, 1H, –OH), 3.93 (s, 2H), 5.74 (t, *J* = 4.85, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 23.39, 24.49, 41.89, 41.95, 67.81, 124.36, 140.53, 213.70.

IR (neat): 3400.1 (br s), 2908.3, 2852.7, 1694.2, 1441.3, 1350.8, 1210.4, 1108.6, 1005.3, 884.5, 833.3 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_8H_{12}O_2$, 140.0837; found, 140.0842.



4-(5-Oxocyclohept-1-enyl)-butyric acid (**18**)

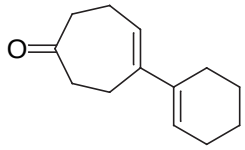
Characterization:

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.65-1.75 (m, 2H), 1.99-2.05 (m, 2H), 2.25-2.33 (m, 6H), 2.52-2.58 (m, 4H), 5.54(t, *J* = 5.37 Hz, 1H), 10.63 (s, 1H, COOH).

^{13}C NMR (75 MHz, $CDCl_3$, δ): 22.64, 23.48, 27.23, 33.22, 39.01, 41.96, 42.36, 124.37, 140.15, 179.35, 213.88.

IR (neat): 3164.8 (br), 2944.2, 1730.9, 1706.0, 1440.2, 1412.2, 1218.0, 1158.2, 899.3, 829.6 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_{11}H_{16}O_3$, 196.1099; found, 196.1100.



4-Cyclohex-1-enylcyclohept-4-enone (**19**)

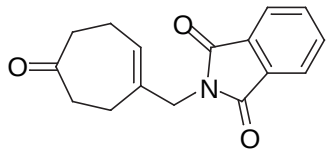
Characterization:

^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.53-1.61 (m, 2 H); 1.64-1.69 (m, 2H); 2.14-2.16 (m, 4H); 2.51-2.60 (m, 6H); 5.81 (br s, 1H); 5.90 (t, *J* = 6.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 22.0; 22.9; 23.5; 24.4; 25.7; 26.2; 42.4; 42.5; 122.9; 123.1; 137.4; 142.9; 213.4.

IR (neat): 2926, 2856, 1707, 1437, 1345, 1222, 796 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_{13}H_{18}O$, 190.1358; found, 190.1359.



2-(5-Oxocyclohept-1-enylmethyl)-isoindole-1,3-dione (**20**)

Characterization:

^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.35-2.42 (m, 4H), 2.56-2.63 (m, 4H), 4.21 (s, 2H), 5.75-5.84 (m, 1H), 7.71-7.74 (m, 2H), 7.84-7.86 (M, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ): 23.35, 25.87, 41.87, 42.07, 44.77, 123.35, 126.77, 136.88, 134.08, 135.21, 168.12, 212.69.

IR (neat): 2953.0, 2911.1, 2848.3, 1771.6, 1713.0, 1426.8, 1395.3, 1334.4, 1213.7, 1114.4, 957.6, 724.7 cm^{-1}.

HRMS (*m/z*): [M^+] calcd for $C_{16}H_{15}NO_3$, 269.1052; found, 269.1057.