Synthetic Test File

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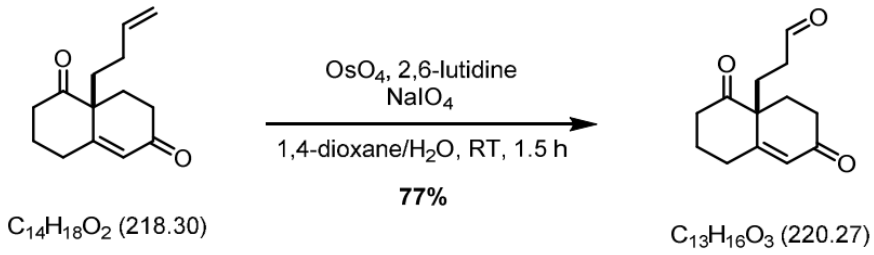
Examples 1 from

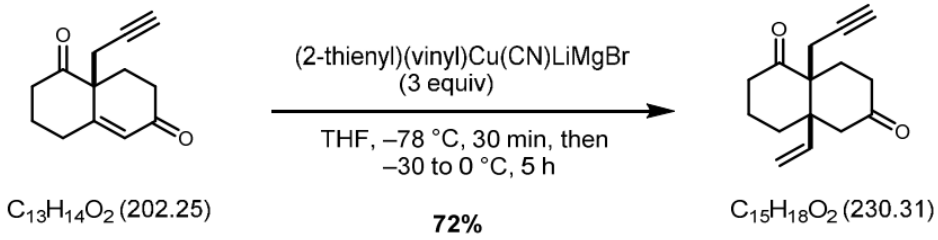
The reported molecular formulas and Calcd values should include any added atoms (usually H or Na). The ionization method and mass analyzer type (for example, Q-TOF, magnetic sector, or ion trap) should be reported. *The ACS Guide to Scholarly Communication* format for reporting accurate mass data is: HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{17}NO_3Na$ 258.1101; Found 258.1074.

Example 2 from Christmann et al. Org. Lett. 20XX,



To a solution of enone **14** (109 mg, 0.499 mmol, 1.0 equiv.) in 1,4-dioxane/water (3:1; 5 mL) 2,6-lutidine (116 µL, 0.999 mmol, 2.0 equiv.), NaIO4 (427 mg, 1.20 mmol, 4.0 equiv.) and aq. OsO4 (4 % w/w; 63 µL, 10 µmol, 2 mol%) were added. The mixture was stirred at room temperature for 1.5 h and quenched by the addition of water (4 mL). The mixture was extracted with dichloromethane (3x10 mL) and dried with Na2SO4. Purification of the residue by column chromatography (silica gel, pentane/ethyl acetate = 1:1) yielded the aldehyde (84.8 mg, 77%) as a colorless oil.

Rf = 0.3 (pentane/ethyl acetate 1:1, anysaldehyde); **[α]D21** = –57.6° (*c* = 1.40, CHCl3); **1H-NMR** (CDCl3, 500 MHz): δ = 9.71 (br s, 1H), 5.86 (br s, 1H), 2.79 (td, *J* = 15.0, 5.1 Hz, 1H), 2.65 (td, *J* = 13.9, 6.2 Hz, 1H), 2.53–2.27 (m, 7H), 2.17–2.06 (m, 2H), 2.04–1.94 (m, 2H), 1.66 (qt, J = 13.6, 4.1 Hz, 1H) ppm; **13C-NMR** (CDCl3, 126 MHz): δ = 210.2, 199.9, 197.7, 165.1, 126.7, 53.5, 38.6, 38.4, 33.3, 31.8, 26.1, 25.7, 23.2 ppm; **IR** (CDCl3): $\tilde{\nu}$ = 2954, 2874, 1707, 1665, 1616, 1449, 1348, 1219 cm-1; **HRMS** (ESI): m/z : calculated for C13H16O3+H+: [M+H+] 221.1172; found: 221.1165.



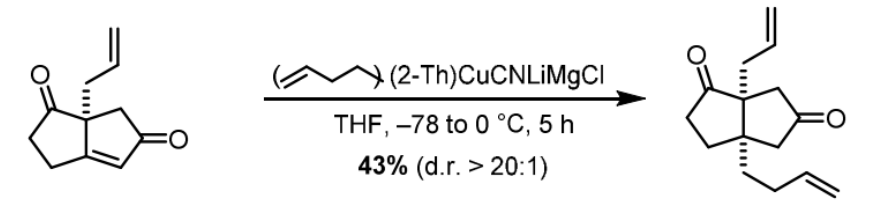
$C_{13}H_{14}O_2$ (202.25)

$C_{15}H_{18}O_2$ (230.31)

Using the enone (232 mg, 1.15 mmol, 1 equiv.) and vinyl cuprate (3 equiv). After purification by column chromatography (silica gel, pentane/ethyl acetate = 8:1) diene **25** was obtained as white solid (190 mg, 0.83 mmol, 72%).

Rf = 0.3 (pentane/ethyl acetate 8:1, anisaldehyde); **m.p.** = 117–119 °C; **[α]D20** = +45.1° (*c* = 1.04, CHCl3); **1HNMR** (CDCl3, 700 MHz): δ = 5.76 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.19 (d, *J* = 11.1 Hz, 1H), 5.12 (d, *J* = 17.4 Hz, 1H), 2.89 (dd, *J* = 17.1, 2.7 Hz, 1H), 2.72–2.59 (m, 3H), 2.47–2.43 (m, 2H), 2.33–2.29 (m, 1H), 2.22 (dd, *J* = 17.0, 2.7 Hz, 1H), 2.16–2.11 (m, 2H), 2.07–2.03 (m, 1H), 2.01 (t, *J* = 2.8 Hz, 1H), 1.94–1.86 (m, 1H), 1.62– 1.57 (m, 1H), 1.47 (dt, *J* = 14.7, 4.1 Hz, 1H) ppm; **13C-NMR** (CDCl3, 176 MHz): δ = 211.1, 210.7, 139.3, 116.8, 79.0, 72.3, 54.2, 50.0, 47.7, 38.4, 37.6, 30.9, 28.4, 25.1, 21.8 ppm; **IR** (CDCl3): $\tilde{\nu}$ = 2951, 2877, 1708, 1421, 1002, 930, 772, 736 cm-1; **HRMS** (ESI): m/z calculated for C15H18O2 [M+Na]+ 253.1199, found 253.1202.

An error was introduced for demonstration purposes



$C_{11}H_{12}O_2$ (176.21) $C_{15}H_{20}O_2$ (232.32)

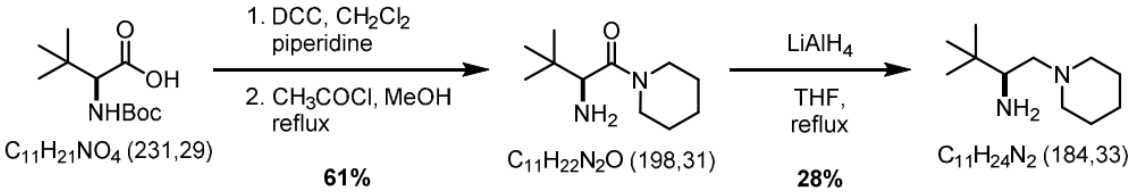
Compound **26** was prepared following the general procedure for the 1,4 cuprate addition (see page S39).

Using bicyclic enone **16** (25.0 mg, 142 µmol, 1 equiv.) and butenyl cuprate (10 equiv.). After purification by column chromatography (silica gel, pentane:ethyl acetate = 9:1) diene **26** was obtained as a colorless oil (14.3 mg, 43%).

R*f* = 0.3 (pentane:ethyl acetate = 9:1, KMnO4); [α]**D26** = +8.02° (c = 0.55, CHCl3); **1H NMR** (700 MHz, CDCl3) δ = 5.82 (ddt, *J*=16.8, 10.2, 6.5 Hz, 1H), 5.80 – 5.67 (m, 1H), 5.11 – 5.04 (m, 3H), 5.00 (dq, *J*=10.2, 1.4 Hz, 1H), 2.60 (d, *J*=19.4 Hz, 1H), 2.48 (ddd, *J*=20.1, 10.1, 5.4 Hz, 1H), 2.45 – 2.38 (m, 2H), 2.38 – 2.34 (m, 1H), 2.24 (ddt, *J*=14.2, 7.8, 1.2 Hz, 1H), 2.18 (dd, *J*=19.4, 1.9 Hz, 1H), 2.15 – 2.02 (m, 3H), 2.00 (ddd, *J*=13.7, 10.1, 7.4 Hz, 1H), 1.90 (ddd, *J*=14.1, 9.2, 5.4 Hz, 1H), 1.66 (td, *J*=12.6, 5.0 Hz, 1H), 1.56 (ddd, *J*=13.6, 11.8, 4.9 Hz, 1H) ppm; **13C NMR** (176 MHz, CDCl3) δ = 219.7, 214.9, 137.9, 132.8, 119.3, 115.4, 59.6, 50.0, 48.7, 44.7, 35.9, 34.6, 33.8, 29.0, 28.5 ppm; **IR** : $\tilde{\nu}$ = 3016, 2917, 2850, 1737, 1365, 1216, 1133, 996, 916, 753 cm- 1 ; HR**MS** (ESI): *m/z* calculated for C15H20NaO4 ([M + Na]+) 255.1356; found: 255.1372

An error was introduced form demonstration purposes

(*S*)-3,3-Dimethyl-1-(piperidin-1-yl)butan-2-amine (cat. 3)



Compound **cat. 3** was prepared following the general procedure for the catalyst preparation (see page 23).

Using *N*-Boc-(*S*)-*tert*-leucine (3.08 g, 13.3 mmol, 1 equiv.). After purification by column chromatography (methylene chloride/methanol=9:1, 0.2% NEt3) **cat. 3** was obtained as a colorless oil (419 mg, 2.27 mmol, 17% over three steps).

[α]D26 = +84.2° (*c* = 0.66, CHCl3); **1H NMR** (500 MHz, CDCl3): δ = 2.58 (dd, *J* = 11.0, 2.6 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.22 – 2.12 (m, 2H), 2.07 – 1.93 (m, 4H), 1.57 – 1.43 (m, 4H), 1.40 – 1.32 (m, 2H), 0.83 (s, 9H) ppm; **13C NMR** (126 MHz, CDCl3): δ = 61.1, 56.3 (2), 55.2, 33.0, 26.3 (2), 26.3 (3), 24.0 ppm; **IR** : $\tilde{\nu}$ = 2934, 2854, 2781, 2743, 2703, 1579, 1476, 1469, 1455, 1392, 1362, 1304, 1206, 1154, 1100, 1038, 1003, 986, 924, 908, 859, 793, 731 cm-1; HR**MS** (ESI): m/z calculated for C11H24N2H ([M+H]+) 185.2012, found 158.2013.

An error was introduced form demonstration purposes

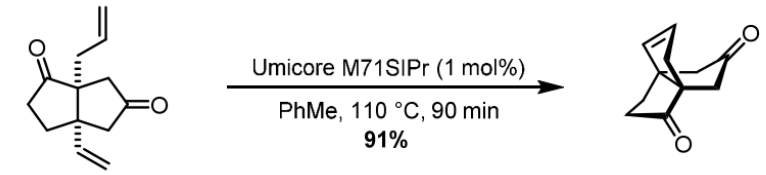
(*S*)-7a-(Pent-4-en-1-yl)-2,3,7,7a-tetrahydro-1H-indene-1,5(6H)-dione (12)

The enone was prepared following the general procedure for the Robinson annulation using (*S*)-proline (see page S26).

Using triketone (340 mg, 1.44 mmol, 1 equiv.). After purification by column chromatography (pentane:diethyl ether = 1:10) the enone was obtained as a colorless oil (226 mg, 1.02 mmol, 85%, 95% *ee*).

R*f* = 0.5 (pentane:diethyl ether = 1:10, PAN); **[α]D22** = +272.22° (*c* = 1.03, CHCl3); **1H NMR** (400 MHz, CDCl3): δ = 5.97 (d, *J* = 2.1 Hz, 1H), 5.71 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 – 4.92 (m, 2H), 2.96 (dddd, *J* = 17.4, 11.5, 9.2, 2.5 Hz, 1H), 2.84 – 2.64 (m, 2H), 2.54 – 2.35 (m, 3H), 2.24 (ddd, *J* = 13.7, 4.9, 2.3 Hz, 1H), 2.02 (qt, *J* = 7.0, 1.4 Hz, 2H), 1.80 – 1.59 (m, 3H), 1.51 – 1.39 (m, 2H) ppm; **13C NMR** (176 MHz, CDCl3): δ = 216.1, 198.3, 170.1, 137.6, 124.3, 115.7, 52.4, 36.0, 33.8, 33.6, 32.9, 27.1, 26.6, 23.7 ppm; **IR** : $\tilde{\nu}$ = 2942, 2867, 1740, 1666, 1643, 1439, 1416, 1356, 1206, 1101, 993, 912, 873, 854 cm-1; HR**MS** (ESI): m/z calculated for C14H18KO2 ([M+K]+) 257.0838, found 257.0930; **HPLC** Hydrodex-β-TBDAc; isotherm 170 °C; 1.1 mL/min He; Split 50:1; 3 µL, t1= 38.89 min. (*S*), t2= 40.17 min. (*R*).

(3a*S*,6a*R*)-2,3-Dihydro-3a,6a-propanopentalene-1,8(6*H*)-dione (31)



$C_{13}H_{16}O_2$ (204.26) $C_{11}H_{12}O_2$ (176.21)

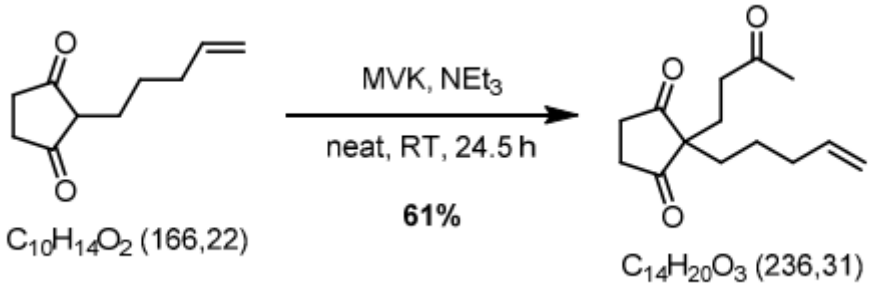
Compound **30** was prepared following the general procedure for the ring closing metathesis (see page S52).

Using diene **19** (2.5 g, 12.2 mmol, 1 equiv.). After purification by column chromatography (silica gel,

pentane:ethyl acetate = 6:1) propellane **31** was obtained as a colorless oil (1.96 g, 91%).

R*f* = 0.5 (pentane:ethyl acetate = 3:1, KMnO4); [α]**D27** = +43.28° (c = 0.95, CHCl3); **1H NMR** (700 MHz, CDCl3) δ = 5.76 (dt, *J*=4.8, 2.1 Hz, 1H), 5.73 (dt, *J*=4.8, 2.1 Hz, 1H), 2.90 (dt, *J*=17.5, 2.2 Hz, 1H), 2.57 – 2.50 (m, 3H), 2.46 (d, *J*=18.3 Hz, 2H), 2.44 – 2.41 (m, 2H), 2.28 (ddd, *J*=12.7, 8.1, 4.0 Hz, 1H), 1.81 (ddd, *J*=13.4, 10.6, 8.8 Hz, 1H) ppm; **13C NMR** (176 MHz, CDCl3) δ = 220.9, 216.4, 136.7, 130.8, 60.9, 60.3, 50.5, 45.8, 44.7, 38.1, 32.1 ppm; **IR** : $\tilde{\nu}$ = 2952, 2918, 2850, 1733, 1457, 1403, 1165, 753 cm-1; **HRMS** (EI): *m/z* calculated for C11H12O2 [M+H]+ 176.0837; found: 176.0829.

2-(3-Oxobutyl)-2-(pent-4-en-1-yl)cyclopentane-1,3-dione (6)

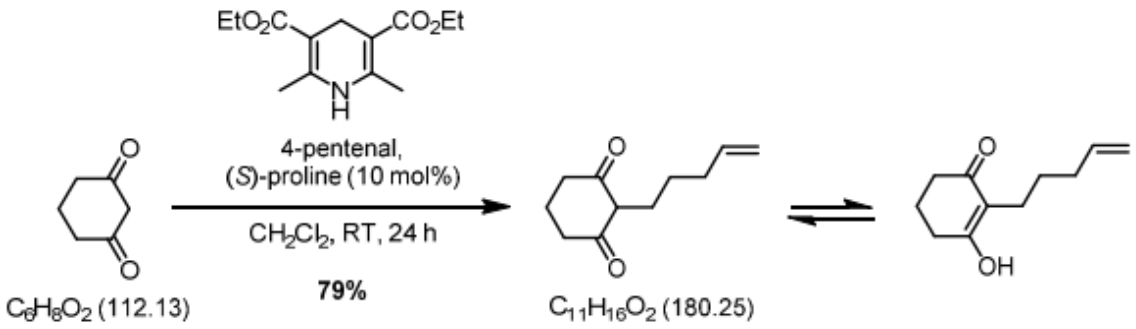


The triketone was prepared following the general procedure for the base mediated Michael addition (see page S10).

Using diketone (85 mg, 0.51 mmol, 1 equiv.). After purification by column chromatography (pentane:diethyl ether = 1:1 → 1:10) the triketone was obtained as a colorless oil (73 mg, 0.31 mmol, 61%).

R*f* = 0.4 (pentane:diethyl ether = 1:10, PAN); **1H NMR** (500 MHz, CDCl3): δ = 5.67 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 4.99 – 4.91 (m, 2H), 2.86 – 2.73 (m, 2H), 2.73 – 2.61 (m, 2H), 2.47 – 2.38 (m, 2H), 2.07 (s, 3H), 1.95 (m, 2H), 1.86 (t, *J* = 7.3 Hz, 2H), 1.64 – 1.53 (m, 2H), 1.25 – 1.16 (m, 2H) ppm; **13C NMR** (126 MHz, CDCl3): δ = 216.3 (2), 207.9, 137.6, 115.5, 59.4, 37.6, 35.7 (2), 34.3, 33.9, 30.1, 27.1, 23.7 ppm; **IR** : $\tilde{\nu}$ = 2922, 2880, 1760, 1715, 1640, 1419, 1365, 1167, 993, 914 cm-1; HR**MS** (ESI): m/z calculated for C14H20NaO3 ([M+Na]+) 259.1412, found 259.1307

2-(Pent-4-en-1-yl)cyclohexane-1,3-dione (SI12)



4-pentenal (587 µL, 5.95 mmol, 1 equiv.) was dissolved in anhydrous methylene chloride (60 mL). 1,3-cyclohexadione (2.0 g, 17.8 mmol, 3 equiv.), Hantzsch ester (3.01 g, 11.9 mmol, 2 equiv.) and (*S*)- proline (68.5 mg, 0.60 mmol, 10 mol%) were added successively. The mixture was stirred at room temperature for 24 hours. Water was added and the reaction mixture was extracted with methylene chloride (3 x 40 mL) and dried with anhydrous MgSO4. After filtration the mixture was concentrated under reduced pressure and subjected to column chromatography (pentane:diethyl ether = 1:10) which afforded the diketone as a colorless oil (845 mg, 4.69 mmol, 79%).

R*f* = 0.3 (pentane:diethyl ether = 1:10, PAN); **1H NMR** (500 MHz, CDCl3): δ = 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.02 – 4.90 (m, 2H), 2.46 (t, *J* = 6.5 Hz, 3H), 2.34 – 2.25 (m, 4H), 2.09 – 2.02 (m, 2H), 1.95 (p, *J* = 6.6 Hz, 2H), 1.45 (p, *J* = 7.7 Hz, 2H) ppm; **13C NMR** (126 MHz, CDCl3): δ = 205.4 (2), 139.3, 138.4*, 116.2, 114.9*, 114.5*, 67.6, 39.8, 33.9*, 33.8, 27.8, 26.8*, 23.1, 21.4*, 20.9, 18.3* ppm; **IR** : $\tilde{\nu}$ = 2934, 2872, 1710, 1692, 1599, 1382, 1256, 1235, 1173, 1108, 1028, 911, 774 cm-1; HR**MS** (ESI):, m/z calculated for C11H16NaO2 ([M+Na]+) 203.2368, found 203.2370.