Supporting Information
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A Practical Synthesis of (S)-Cyclopent-2-enol.

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Supporting Information
Reactions were performed under N$_2$ and glassware was dried using a heatgun and under vacuum. A dry ice/isopropanol bath was used to obtain a temperature at –78 °C. Silica gel 60 (40-63 µm, SdS) was used for flash chromatography. Thin-layer chromatography was performed on Merck silica gel 60 F254 plates. Visualisation of TLC plates was accomplished with one or more of the following methods: 254 nm UV light; dipping in the different staining solution: KMnO$_4$ (5 g), Na$_2$CO$_3$ (30 g) in H$_2$O (500 mL); phosphomolybdic acid (25 g), cerium sulphate (10 g) and H$_2$SO$_4$ conc (940 mL); vaniline (3 g) and H$_2$SO$_4$ conc (4 mL) in EtOH (250 mL) and subsequent heating. Commercial reagents were used as received unless otherwise stated. Solvents for reactions (THF, Et$_2$O and CH$_2$Cl$_2$) were filtered over columns of activated alumina under a positive pressure of argon. Solvents for extraction and flash column chromatography were of technical grade and distilled before use. $^1$H and $^{13}$C-NMR spectra were recorded on a Bruker AVANCE-300 spectrometer operating at 300 MHz for $^1$H and 75 MHz for $^{13}$C at 22 °C unless otherwise noted. Chemical shift are reported in units of δ (ppm) using as the internal standard either residual CDCl$_3$ (δ = 7.26 for $^1$H NMR spectra and δ = 77.0 for $^{13}$C NMR spectra) or Si(CH$_3$)$_4$ (δ = 0 for $^1$H NMR and $^{13}$C NMR spectra). Multiplicities are given as s (singulet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad) for $^1$H spectra. Coupling constant, $J$, are reported in Hz. Infrared spectra were recorded on a Jasco FT-IR-460 Plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR System and are reported in wave numbers (cm$^{-1}$). LRMS & HRMS: Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV. Gas chromatographic mass spectra (GC-MS) analyses were performed on a Finnigan Trace GC 2000 gas chromatograph equipped with an autosampler and a Trace MS mass selective
detector. Microanalyses were obtained from Ilse Beetz, Mikroanalytisches Laboratorium, 96317 Kronach, Germany.

**Pent-4-enoic acid N-methoxy-N-methylamide (3).** To a solution of 4-pentenoic acid 2 (20.0 g, 200 mmol) in CH$_2$Cl$_2$ (1 L) at 0 °C was added Et$_3$N (55 mL, 400 mmol), isobutyl chloroformate (30 mL, 220 mmol) and $N,O$-dimethylhydroxylamine (13.0 g, 210 mmol) followed by Et$_3$N (55 mL, 400 mmol). The reaction mixture was stirred overnight at room temperature. It was then treated with saturated NaHCO$_3$ and washed with brine. The aqueous layer was extracted with Et$_2$O, the combined organic layers were dried over Na$_2$SO$_4$ and concentrated. The crude product was purified by FC (pentane/Et$_2$O 60:40) to give 3 (28.0 g, 98%). Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.87-5.76 (m, 1H), 5.07-4.93 (m, 2H), 3.65 (s, 3H), 3.14 (s, 3H), 2.49 (t, $J$ = 7.5 Hz, 2H), 2.38-2.31 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 173.7 (1CO), 137.4 (1HC=CH$_2$), 115.0 (1HC=CH$_2$), 61.1 (1OCH$_3$), 32.1 (1NCH$_3$), 31.1 (1CH$_2$=CH$_2$), 28.5 (1CH$_2$), 30.8 (1CH$_2$CO). IR (neat): 2977, 2939, 1737, 1660, 1463, 1415, 1383, 1177, 994. MS (EI, 70ev) m/z (%) 143 (M$^+$, 57), 83 (79), 61 (91), 55 (100), 53 (46), 46 (51), 41 (57), 39 (71).

**1-Trimethylsilylhept-6-en-1-yne-3-one (4).** n-BuLi (2.5 M in hexane, 48 mL, 120 mmol) was added dropwise to a solution of (trimethylsilyl)acetylene (21 mL, 150 mmol) in THF (75 mL) at −78 °C. The mixture was stirred for 30 min. The lithium (trimethylsilyl)acetylide reagent was transferred via cannula to the Weinreb amide 3 (10 g, 70 mmol) in THF (70 mL) at −78 °C, stirred for 1 h and let warm up to room temperature. Then, 1 M HCl was added dropwise until disappearance of the white precipitate. The reaction mixture was extracted with Et$_2$O and the combined organic
layers were washed with brine. The organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by FC (pentane to pentane/Et$_2$O 97:3) to afford 4 (11.95 g, 95%). Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 5.84$-5.75 (m, 1H), 5.07-4.97 (m, 2H), 2.65 (t, $J = 7.5$ Hz, 2H), 2.43-2.38 (m, 2H), 0.23 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 186.8$ (1CO), 136.2 (1HC=CH$_2$), 115.7 (1HC=CH$_2$), 101.9 (1C=CSi(CH$_3$)$_3$), 98.0 (1C=CSi(CH$_3$)$_3$), 44.3 (1CH$_2$C=C), 27.8 (1CH$_2$), -0.8 (3Si(CH$_3$)$_3$). IR (neat): 2153, 1675, 1643, 1252, 841. MS (EI, 70ev) m/z (%) 180 (M$^+$, 3%), 179 (4), 165 (47), 125 (100), 97 (62), 75 (55), 73 (74), 59 (26), 43 (22). ESI-HRMS (C$_{10}$H$_{17}$OSi): 181.1049 (calculated); 181.1045 (found).

1-Trimethylsilylhept-6-en-1-yn-3-ol (5). A mixture of 4 (9.0 g, 50 mmol) and (S,S)-Noyori's catalyst (600 mg, 1.00 mmol), prepared from (1S,2S)-1,2-diphenyl-N-(p-tolylsulfonyl)ethylenediamine (830 mg, 2.3 mmol) and dichloro($\eta^6$-p-cymene)-ruthenium(II) dimer (700 mg, 1.14 mmol), in 2-propanol (500 mL) was stirred at room temperature for 24 h. The reaction mixture was then concentrated under reduced pressure. The crude product was purified by FC (pentane) to afford 5 (7.85 g, 95%). Optical purity: 99% ee, determined by GC analysis on a chiral phase 35% heptakies-(2,3-O-dimethyl-6-O-tert-butyldimethylsilyl)-β-cyclodextrin in 5% phenyl polymer, 110 °C, (R)-5: 19.53 min, (S)-5 20.57 min. Colorless liquid. $[\alpha]_{D}^{22} = +8.7^\circ$ (c = 1.0, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 5.89$-5.79 (m, 1H), 5.10-5.00 (m, 2H), 4.98-4.97 (m, OH), 2.26-2.19 (m, 2H), 1.86-1.75 (m, 2H), 0.17 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 137.6$ (HC=CH$_2$), 115.3 (HC=CH$_2$), 106.5 (C=CSi(CH$_3$)$_3$), 89.7 (C=CSi(CH$_3$)$_3$), 62.4 (CHOH), 36.7 (CH$_2$), 29.4 (CH$_2$C=C), -0.2 (Si(CH$_3$)$_3$). IR (neat): 3330, 2361, 2169, 1249, 1012, 837. MS
(TOF, 70 ev) m/z (intensity) 183.1208 (M⁺, 430), 167.0936 (620), 149.0788 (650), 147.0735 (370). ESI⁺-TOF-HRMS (C₁₀H₁₉OSi): 183.1205 (calculated); 183.1208 (found).

5-(tert-Butyldimethylsilyloxy)-7-trimethylsilylhept-1-en-6-yne (6). Alcohol 5 (2.00 g, 11 mmol) was added to a solution of tert-butyldimethylsilyl chloride (2.48 g, 16.5 mmol) and imidazole (1.12 g, 1.65 mmol) in dry dimethylformamide (10 mL). The solution was stirred at room temperature under N₂ over night. Then, dichloromethane and water were added to the mixture. The organic phase was washed with saturated aqueous NaHCO₃ and extracted with cyclohexane. The organic phase was washed with water then dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by FC (pentane to pentane/Et₂O 9:1) to give the silyl ether 6 (3.15 g, 97%).

Colorless oil. [α]D²² = −34.4° (c = 1.0, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ = 5.88-5.75 (m, 1H), 5.07-4.94 (m, 2H), 4.35 (t, J = 6.25 Hz, 1H), 2.20-2.16 (m, 2H), 1.79-1.72 (m, 2H), 0.90 (s, 9H), 0.15 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ = 138.0 (1HC=CH₂), 114.8 (1HC=CH₂), 107.6 (1C=CSi(CH₃)₃), 88.6 (1C=CSi(CH₃)₃), 62.7 (1CHOTBDMS), 37.7 (1CH₂), 29.5 (1CH₂C=C), 25.8 (SiC(CH₃)₃), 18.3 (SiC(CH₃)₃), -0.2 (3Si(CH₃)₃), -4.4 (1SiCH₃), -4.9 (1SiCH₃). IR (neat): 2361, 2173, 1338, 1249, 1090, 837, 776. MS (TOF, 70 ev) m/z (intensity) 319.1884 ([M+Na]. ESI⁺-TOF-MS 319.1889 (calculated), 319.1889 (found).

5-(tert-Butyldimethylsilyloxy)hept-1-en-6-yne (7). To a stirred solution of 6 (2.00 g, 6.75 mmol) in THF (22.5 mL) and MeOH (22.5 mL) was added K₂CO₃ (1.60 g, 11.5 mmol). The reaction mixture was stirred at room temperature for 2 h. Then, a 1 M
HCl solution was added and the mixture was extracted with pentane. The organic layer was washed with water, saturated aqueous NaHCO$_3$, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by FC (pentane to pentane/Et$_2$O 90:10) to afford 7 (1.44 g, 95%).

Colorless oil. $[\alpha]_D^{22} = -33.4^\circ$ (c = 1.0, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) δ = 5.87-5.75 (m, 1H), 5.08-4.94 (m, 2H), 4.39-4.34 (dt, $J = 2.1, 6.4$ Hz, 1H), 2.38 (s, 1H), 2.22-2.16 (m, 2H), 1.81-1.73 (m, 2H), 0.90 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 137.8 (HC$\equiv$CH$_2$), 114.9 (HC$\equiv$CH$_2$), 85.4 (C=CH), 72.1 (C=CH), 62.1 (CHOSi), 37.7 (CH$_2$), 29.3 (CH$_2$C=C), 25.8 (SiC(CH$_3$)$_3$), 18.2 (SiC(CH$_3$)$_3$), −4.5 (SiCH$_3$), −5.1 (SiCH$_3$). IR (neat): 3311, 1251, 834, 776, 653. ESI$^+$-TOF-HRMS (C$_{13}$H$_{25}$OSi): 225.1675 (calculated); 225.1676 (found).

3-$(\text{tert-Butyldimethylsilyloxy})$-1,6-heptadiene (8). A solution of 7 (1.00 g, 4.46 mmol) in 1,4-dioxane (45 mL) and pyridine (4.6 mL) was treated with Lindlar’s catalyst (100 mg). The mixture was hydrogenated under pressure (10 bars) for 2 h. The reaction mixture was filtered through a pad of Celite, and rinsed with Et$_2$O. The solvent was evaporated under reduce pressure. The crude product was purified by FC (pentane/Et$_2$O 95:5) to afford 8 (918 mg, 91%).

Colorless oil. $[\alpha]_D^{22} = +3.4^\circ$ (c = 1.0, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) δ = 5.82-5.77 (m, 2H), 5.18-4.92 (m, 4H), 4.12-4.08 (m, 1H), 2.38 (s, 1H), 2.14-2.05 (m, 2H), 1.60-1.55 (m, 2H), 0.90 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 141.6 (HC$\equiv$CH$_2$), 138.7 (HC$\equiv$CH$_2$), 114.4 (HC$\equiv$CH$_2$), 113.7 (HC=CH$_2$), 73.3 (CHOSi), 37.2 (CH$_2$), 29.4 (1CH$_2$C=C), 25.9 (SiC(CH$_3$)$_3$), 18.2 (1SiC(CH$_3$)$_3$), −4.3 (SiCH$_3$), −4.8 (SiCH$_3$). IR (neat): 1251, 833, 774.
(2-Cyclopenten-1-yl) dimethyl(tert-butyl)silyl ether (9).  

**Procedure A.** To a solution of diene 8 (350 mg, 1.54 mmol) in CH$_2$Cl$_2$ (35 mL) was added Hoveyda-Grubbs 1$^{st}$ generation (= dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium(II)) catalyst (46 mg, 0.077 mmol). The reaction was stirred at room temperature overnight, filtered through a pad of Celite, and rinsed with Et$_2$O. The solvent was evaporated under reduce pressure. The crude product was purified by FC (pentane) to afford 9 (254 mg, 83%).  

**Procedure B.** To a solution of diene 8 (350 mg, 1.54 mmol) in CH$_2$Cl$_2$ (35 mL) was added Grubbs 1$^{st}$ generation catalyst (= bis(tricyclohexylphosphine) benzyldiene ruthenium(IV) chloride (63 mg, 0.077 mmol). The reaction was stirred at room temperature overnight, filtered through a pad of Celite, and rinsed with ether. The solvent was evaporated under reduce pressure. The crude product was purified by FC (pentane) to afford 9 (151 mg, 48%).  

**Procedure C.** To a solution of diene 8 (350 mg, 1.54 mmol) in CH$_2$Cl$_2$ (35 mL) was added Grubbs 1$^{st}$ generation catalyst (127 mg, 0.154 mmol). The reaction was stirred at room temperature overnight, filtered through a pad of Celite, and rinsed with ether. The solvent was evaporated under reduce pressure. The crude product was purified by FC (pentane) to afford 9 (305 mg, 97%).  

Colorless oil. [α]$^2_\text{D}$ = $-61.7^\circ$ (c = 1.0, CHCl$_3$); lit.: [α]$^2_\text{D}$ = $-84.9^\circ$ (c = 0.8, CHCl$_3$).  

$^1$H NMR (300 MHz, CDCl$_3$) δ = 5.91-5.88 (m, 1H), 5.73-5.70 (m, 1H), 4.93-4.90 (m, 1H), 2.52-2.44 (m, 1H), 2.24-2.16 (m, 2H), 1.69-1.60, (m, 1H), 0.90 (s, 9H), 0.08 (s, 6H).  

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 133.9 (C=CHCO), 133.5 (C=CHCO), 78.1 (CH–O), 33.5 (CH$_2$CHO), 31.0 (1CH$_2$C=C), 26.0 (SiC(CH$_3$)$_3$), 18.3 (SiC(CH$_3$)$_3$), −4.5 (SiCH$_3$), −4.6 (SiCH$_3$). IR 2956, 2928, 1159, 832, 772 cm$^{-1}$. MS (EI, 70 ev) m/z (%) 198 (M$^+$, 6%), 167 (9%), 141 (66%), 125 (20%), 78 (34%), 75 (100%) 73 (44%),
(–)-(S)-Cyclopent-2-enol (1). To a solution of 9 (198 mg, 1.00 mmol) in THF (2.30 mL) was added Bu₄NF (1.0 M in THF, 1.2 mL) dropwise at 0 °C. After stirring at room temperature for 2 h, the mixture was extracted with Et₂O. The extract was washed with brine and dried over Na₂SO₄ then concentrated under reduced pressure. The crude product was purified by FC (pentane/Et₂O 60:40) to give the alcohol 1 (70 mg, 83%). Optical purity: 96% ee, determined by GC analysis on a chiral phase 50% DIGLYB in PSO86, 60-200 °C, (S)-1: 15.14 min, (R)-1 16.77 min.

Colorless liquid. [α]D²² = –114° (c = 1, CH₂Cl₂); lit.: [α]D²² = –118.7° (c = 1, CH₂Cl₂).¹ ¹H NMR (300 MHz, CDCl₃) δ 5.90 (m, C=CH), 5.75 (m, CH=CH), 4.80 (m, 1H), 2.80 (br., OH), 2.4 (m, 2H), 2.20 (m, 2H), 1.60 (m, 2H).¹³C NMR (75 MHz, CDCl₃) δ 134.65, 13319, 77.14, 32.95, 30.80. All physical and spectral data were in accordance with literature data.²,³

Optical purity: 96% ee, determined by GC analysis on a chiral phase 50% Diglycidyl in PSO86, 60-200 °C, (S)-5: 15.14 min, (R)-5: 16.77 min.

Optical purity: 99% ee, determined by GC analysis on a chiral phase 35% heptakis-(2,3-O-dimethyl-6-O-tert-butyldimethylsilyl)-β-cyclodextrin in 5% phenyl polymer, 110 °C, (R)-5: 19.53 min, (S)-5: 20.57 min.
C<sub>7</sub>H<sub>13</sub>NO<sub>2</sub> 143.09
C_{10}H_{18}OSi

182, 11

/ppm/
OTBDMS

C_{11}H_{22}OSi
198.14