Supporting Information

Cobalt-Catalyzed Diastereoselective Reductive [3+2] Cycloaddition of Allenenes and Enones

Hong-Tai Chang, Thiruvelllore Thatai Jayanth and Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

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Experimental Section

General: All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. Acetonitrile was dried with CaH_2 and distilled prior to use. $\text{Co}(\text{dppe})\text{I}_2$ ¹ was prepared by reported procedure. Compound **1a**, **1b**, **1c**, **1g**, **1h**, **1i** and **1j** were prepared using a procedure reported by our laboratories². Compounds **1d**,³ **1e**,³ **1f**³ and **1k**⁴ were prepared following literature procedures. Other reagents were commercially available and used as purchased.

General Procedure for the Synthesis of Cyclopentanols: A sealed tube containing $\text{CoI}_2(\text{dppe})$ (0.0500 mmol), zinc powder (2.75 mmol) and zinc iodide (0.0500 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled dry CH_3CN (2.0 mL), 1-phenylallene **1a** (1.00 mmol), methyl vinyl ketone **2a** (1.20 mmol), H_2O (2.00 mmol) were added to the sealed tube via syringes. The reaction mixture was heated with stirring at 80°C for 6 h and was then cooled, diluted with dichloromethane and stirred in the air for 10 min. The mixture was filtered through a Celite and silica gel pad and washed with dichloromethane. The filtrate was concentrated and the residue was purified on a silica gel column using hexane-ethyl acetate as eluent to afford the desired product **3a**.

References:

- [1] R. J. McKinney, *Inorg. Chem.* 21, **1982**, 2051 – 2056.
- [2] C. W. Huang, M. Shanmugasundaram, H. M. Chang, C.-H. Cheng, *Tetrahedron* **2003**, 59, 3635.
- [3] L. Brandsma and H. D. Verkruijsse, *Synthesis of acetylenes, allene and cumulenes – A laboratory manual*, Elsevier: Amsterdam, 1981.
- [4] R. A. Amos and J. A. Katzenellenbogen, *J. Org. Chem.*, **1978**, 43, 555

(1R*, 2R*)-1-Methyl-3-methylene-2-phenylcyclopentanol (3a)

¹H NMR (400 MHz, CDCl₃) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.29-7.24 (m, 3H), 5.06 (dd, *J* = 4.8 Hz, *J* = 2.4 Hz, 1H), 4.68 (d, *J* = 2.8 Hz, 1H), 3.49 (d, *J* = 2.8 Hz, 1H), 2.81-2.70 (m, 1H), 2.57-2.50 (m, 1H), 2.17-1.93 (m, 1H), 1.84-1.73 (m, 1H), 1.20 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 154.0, 138.3, 130.5, 128.3, 127.0, 108.5, 79.8, 61.9, 38.6, 30.4, 26.3. **HRMS calcd for C₁₃H₁₆O 188.1201; found 188.1203.**

(1R*, 2R*)-3-Methylene-2-phenyl-1-propylcyclopentanol (3b)

¹H NMR (400 MHz, CDCl₃) δ 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 3H), 5.07 (s, 1H), 4.68 (s, 1H), 3.54 (d, *J* = 2.4 Hz, 1H), 2.81-2.72 (m, 1H), 2.56 (dd, *J* = 16.4 Hz, *J* = 8.8 Hz, 1H), 1.96 (dd, *J* = 12.8 Hz, *J* = 8.0 Hz, 1H), 1.75 (dd, *J* = 16.8 Hz, *J* = 11.6 Hz, 1H), 1.43-1.36 (m, 4H), 0.89 (t, *J* = 6.4 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 154.2, 138.5, 130.6, 128.5, 126.9, 108.3, 82.2, 61.3, 42.1, 35.7, 30.3, 17.5, 14.6. **HRMS calcd for C₁₅H₂₀O 216.1514; found 216.1514.**

(1S*, 2R*)-1-Cyclohexyl-3-methylene-2-phenylcyclopentanol (3c)

¹H NMR (400 MHz, CDCl₃) δ 7.35-7.31 (m, 2H), 7.28-7.25 (m, 3H), 5.03 (d, *J* = 2.0 Hz, 1H), 4.61 (d, *J* = 2.0 Hz, 1H), 3.81 (d, *J* = 2.0 Hz, 1H), 2.75-2.68 (m, 1H), 2.54-2.48 (m, 1H), 1.93-1.87 (m, 2H), 1.80-1.69 (m, 5H), 1.27-1.02 (m, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 154.8, 139.0, 130.6, 128.3, 126.8, 108.2, 84.9, 56.9, 44.7, 31.8, 30.0, 28.7, 27.4, 26.5 (2C), 26.5. **HRMS** calcd for C₁₈H₂₄O 256.1827; found 256.1835.

1-(4-((1*R,2*R**)-2-Hydroxy-2-methyl-5-methylenecyclopentyl)phenyl)ethanone (3d)**

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.07 (dd, *J* = 2.4 Hz, *J* = 2.0 Hz, 1H), 4.63 (d, *J* = 2.4 Hz, 1H), 3.53 (d, *J* = 2.4 Hz, 1H), 2.80-2.72 (m, 1H), 2.58 (s, 3H), 2.58-2.52 (m, 1H), 1.99-1.93 (m, 1H), 1.86-1.77 (m, 1H), 1.21 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 197.9, 153.6, 144.4, 136.0, 130.8, 128.2, 109.0, 80.2, 61.9, 39.0, 30.3, 26.6, 26.3. **HRMS** calcd for C₁₅H₁₈O₂ 230.1307; found 230.1303.

(1*R,2*R**)-2-(4-methoxyphenyl)-1-methyl-3-methylenecyclopentanol (3e)**

¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.04 (dd, *J* = 1.2 Hz, *J* = 0.8 Hz, 1H), 4.67 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 3.44 (d, *J* = 2.0 Hz, 1H), 2.78-2.67 (m, 1H), 2.55-2.48 (m, 1H), 1.98-1.92 (m, 1H), 1.80-1.71 (m, 1H), 1.18 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 158.7, 154.3, 131.5, 130.1, 113.8, 108.4, 79.7, 61.1, 55.2, 38.4, 30.3, 26.3. **HRMS** calcd for C₁₄H₁₈O₂ 218.1307; found 218.1301.

(1R*, 2S*)-2-Butyl-1-methyl-3-methylenecyclopentanol (3f)

¹H NMR (400 MHz, CDCl₃) δ 4.91 (d, *J* = 2.4 Hz, 1H), 4.88 (d, *J* = 2.4 Hz, 1H), 2.45-2.34 (m, 2H), 2.02-2.00 (m, 1H), 1.80-1.64 (m, 2H), 1.58-1.33 (m, 6H), 1.30 (s, 3H), 0.90 (t, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 154.8, 106.5, 79.9, 54.0, 38.9, 31.2, 29.0, 26.8, 26.4, 23.2, 14.0. **HRMS calcd for C₁₁H₂₀O 168.1514; found 168.1521.**

(1R*, 2S*)-2-Decyl-1-ethyl-3-methylenecyclopentanol (3g)

¹H NMR (400 MHz, CDCl₃) δ 4.91 (d, *J* = 1.6 Hz, 1H), 4.87 (d, *J* = 1.6 Hz, 1H), 2.46-2.30 (m, 2H), 2.04 (s, 1H), 1.74-1.65 (m, 2H), 1.51-1.42 (m, 2H), 1.37-1.25 (m, 17H), 1.05-0.99 (m, 1H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 155.1, 106.2, 82.6, 52.4, 35.4, 31.9, 31.8, 30.2, 29.5, 29.3, 29.0, 29.1, 27.1, 22.7, 14.1, 8.5. **HRMS calcd for C₁₈H₃₄O 266.2610; found 266.2603.**

(1R*, 2S*)-2-Cyclohexyl-1-methyl-3-methylenecyclopentanol (3h)

¹H NMR (400 MHz, CDCl₃) δ 4.92 (dd, *J* = 1.6 Hz, *J* = 1.6 Hz, 1H), 4.82 (dd, *J* = 2.4 Hz, *J* = 1.2 Hz, 1H), 2.44-2.34 (m, 1H), 2.29-2.25 (m, 1H), 1.99 (s, 1H), 1.80-1.61 (m, 9H), 1.30 (s, 3H), 1.34-1.08 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 152.5, 108.1, 80.7, 59.6, 40.2, 37.7, 33.2, 30.6, 30.5, 29.5, 27.3, 26.9, 26.5. **HRMS calcd for C₁₃H₂₂O 194.1671; found 194.1677.**

(1R*, 2S*)-3-methylene-1-propyl-2-(thiophen-2-yl)cyclopentanol (3i)

¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 5.6 Hz, 1H), 7.03 (td, *J* = 5.2 Hz, *J* = 1.6 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 5.05 (d, *J* = 1.6 Hz, 1H), 4.81 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 1H), 2.72-2.65 (m, 1H), 2.55-2.48 (m, 1H), 1.94 (dd, *J* = 14.4 Hz, *J* = 8.4 Hz, 1H), 1.73 (dd, *J* = 22.4 Hz, *J* = 11.2 Hz, 1H), 1.57-1.31 (m, 4H), 0.88 (t, *J* = 6.4 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 153.8, 140.5, 127.2, 126.8, 125.0, 109.0, 81.7, 56.5, 41.6, 35.3, 29.4, 17.6, 14.6. **HRMS calcd for C₁₃H₁₈OS 222.1078; found 222.1081.**

(1R*, 2R*)-1-Methyl-3-methylene-2-(naphthalen-1-yl)cyclopentanol (3j)

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.88 (dd, *J* = 6.0 Hz, *J* = 2.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.52-7.45 (m, 3H), 5.07 (s, 1H), 4.66 (s, 1H), 4.54 (s, 1H), 2.88-2.81 (m, 1H), 2.67-2.59 (m, 1H), 2.11-2.03 (m, 1H), 1.98-1.89 (m, 1H), 1.23 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 155.2, 135.3, 134.0, 129.0, 127.9, 127.5, 126.0, 125.7, 125.5, 125.5, 123.4, 108.7, 80.2, 55.3, 39.0, 30.7, 27.1. **HRMS calcd for C₁₇H₁₈O 238.1358; found 238.1364.**

(1S*, 2R*)-1-Cyclohexyl-3-methylene-2-(naphthalen-1-yl)cyclopentanol (3k)

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.87 (dd, *J* = 6.8 Hz, *J* = 2.4 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.52-7.43 (m, 3H), 5.00 (d, *J* = 2.0 Hz, 1H), 4.62 (d, *J* = 2.0 Hz, 1H), 4.49 (d, *J* = 1.6 Hz, 1H), 2.86-2.76 (m, 1H), 2.63-2.57 (m, 1H), 2.06-1.82 (m, 3H), 1.71-1.69 (m, 2H), 1.61-1.55 (m, 1H), 1.26-1.24 (m, 2H), 1.17-1.03 (m, 3H), 0.95-0.90 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ 156.1, 136.5, 133.8, 133.7, 129.0, 128.2, 127.3, 125.9, 125.4 (2C), 123.1, 108.6, 85.1, 51.8, 44.8, 33.1, 30.3, 29.2, 27.6, 26.5, 26.4. **HRMS calcd for C₂₂H₂₆O 306.1984; found 306.1990.**

(1R*, 2R*)-1-Methyl-3-methylene-2-*o*-tolylcyclopentanol (3l)

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 6.8 Hz, 1H), 7.22-7.12 (m, 3H), 5.00 (d, *J* = 2.4 Hz, 1H), 4.57 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 1H), 2.78-2.71 (m, 1H), 2.58-2.51 (m, 1H), 2.36 (s, 3H), 2.01-1.94 (m, 1H), 1.86-1.78 (m, 1H), 1.22 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 155.0, 138.1, 137.2, 130.4, 129.9, 126.7, 125.9, 108.2, 80.44, 56.4, 38.8, 30.4, 26.8, 20.5. **HRMS calcd for C₁₄H₁₈O 202.1358; found 202.1358.**

(3aR*,9bR*)-3a-Methyl-1-methylene-1,2,3,3a-tetrahydrocyclopenta[*c*]isochromen-5(9bH)-one (3m)

¹H NMR (400 MHz, CDCl₃) δ 8.11 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.59 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.40 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.28 (dd, *J* = 7.6 Hz, *J* = 0.4 Hz, 1H), 5.00 (dd, *J* = 5.2 Hz, *J* = 2.4 Hz, 1H), 4.51 (dd, *J* = 5.2 Hz, *J* = 2.4 Hz, 1H), 3.44 (s, 1H), 2.67-2.61 (m, 2H), 2.34-2.28 (m, 1H), 1.97-1.89 (m, 1H), 1.43 (s, 3H). **¹³C NMR (125 MHz, CDCl₃)** δ 164.7, 152.1, 139.0, 133.7, 130.5, 129.1, 127.8, 123.2, 110.4, 90.6, 51.8, 37.9, 29.8, 23.4. **HRMS calcd for C₁₄H₁₄O₂ 214.0994; found 214.0993.**

(3aS*,6aR*)-6a-Methyl-4-methylene-hexahydrocyclopenta[b]furan-2-one (3n)

¹H NMR (400 MHz, CDCl₃) δ 5.02 (dd, *J* = 4.0 Hz, *J* = 2.0 Hz, 1H), 4.89 (d, *J* = 1.2 Hz, 1H), 2.97 (t, *J* = 8.0 Hz, 1H), 2.92-2.87 (m, 1H), 2.52-2.46 (m, 2H), 2.41-2.34 (m, 1H), 2.20-2.13 (m, 1H), 1.78-1.70 (m, 1H), 1.47 (s, 3H). **¹³C NMR (125 MHz, CDCl₃)** δ 176.4, 153.5, 109.3, 94.8, 48.9, 37.7, 37.2, 31.3, 24.3. **HRMS calcd for C₉H₁₂O₂ 152.0837; found 152.0835.**

Deuterium-labelling studies (eq. 3):

(1R*, 2R*)-1-Methyl-3-methylene-5-deutero-2-phenylcyclopentan(ol-*d*) (3a-d)

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.33 (m, 2H), 7.31-7.25 (m, 3H), 5.08 (dd, *J* = 4.4 Hz, *J* = 2.0 Hz, 1H), 4.71 (d, *J* = 2.4 Hz, 1H), 3.51 (s, 1H), 2.76-2.73 (m, 1H), 2.59-2.50 (m, 1H), 2.02-1.96 and 1.84-1.76 (m, 1H), 1.17 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 154.0, 138.3, 130.5, 128.3, 127.0, 108.5, 79.8, 61.9, 38.2 (triplet), 30.3, 26.3. **HRMS calcd for C₁₃H₁₄D₂O 190.1327; found 190.1322.**