

Supporting Information

Palladium-Catalyzed Intermolecular Heck-Type Reaction of Epoxides

Shenghan Teng, Malcolm E. Tessensohn, Richard D. Webster and Jianrong Steve Zhou*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

E-mail: jrzhou@ntu.edu.sg

Experimental procedures

Table of Contents

- I. General Information
- II. Reaction Optimization
- III. Heck-type reaction of cyclic epoxides
- IV. Heck-type reaction of acyclic epoxides
- V. Mechanistic Studies
- VI. Reference

I. General information

All NMR spectra were acquired on Bruker 500 MHz, 400 MHz or 300 MHz NMR spectrometers. ^1H NMR chemical shifts were recorded relative to tetramethylsilane (δ 0.00) or residual protiated solvents (CDCl_3 : δ 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. ^{13}C NMR spectra were obtained at 125 MHz on 500 MHz, 100 MHz on 400 MHz or 75 MHz on 300 MHz NMR instruments and chemical shifts were recorded relative to solvent resonance (CDCl_3 : δ 77.16). ^{19}F NMR spectra were recorded at 376 MHz on 400 MHz NMR spectrometers without any external standard. Proof of purity of new compounds was demonstrated with copies of ^1H , ^{13}C , and ^{19}F NMR spectra.

Glassware was dried at 120 °C for at least 3 hours before use. Anhydrous PhCF_3 and 1, 4-dioxane (Aldrich) was degassed by argon bubbling and then stored over activated 4 Å molecular sieve beads in an argon-filled glove box before use. Veratrole (1,2-dimethoxybenzene) were distilled from sodium under argon and stored over activated 4Å molecular sieve beads in an argon-filled glove box. All of anhydrous solvents were stored in Schlenk tubes in the glove box. Unless noted otherwise, commercially available chemicals were used as received without purification. GC internal standard $n\text{-C}_{12}\text{H}_{26}$ was degassed with argon and dried over activated 4Å molecular sieve beads before use.

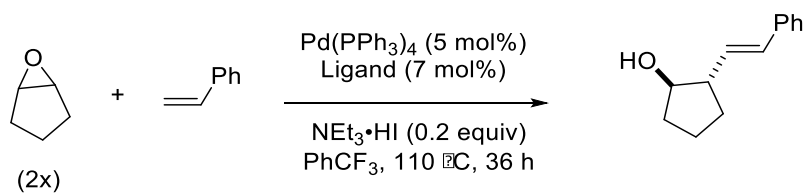
Flash chromatography was performed using Merck 40-63 D 60 Å silica gel. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J&W GC column DB-5MS-UI. GCMS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer. High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractometer. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiralcel columns at 25°C and a mixture of HPLC-grade hexanes and isopropanol were used as eluent. Optical rotation was measured using a JASCO P-1030 polarimeter equipped with a sodium vapor lamp at 589 nm and the concentration of samples was denoted as c .

II. Reaction optimization

A typical procedure for condition optimization. In an argon-filled glove box, Pd(PPh₃)₄ (5.8 mg, 0.005 mmol), Xantphos (4.1 mg, 0.007 mmol) and dry PhCF₃ (0.4 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, cyclopentene oxide (18 μL, 0.2 mmol), NEt₃·HI (4.6 mg, 0.02 mmol), styrene (11.6 μL, 0.1 mmol) and 10 μL of GC standard *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110 °C. After 24 h, the reaction mixture was cooled to room temperature and aliquots were passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC to determine calibrated yield of the product, ratio of trans and cis isomers and conversion of styrene.

Table S1. Effect of palladium source

Entry	Pd source	Conversion (%)	Yield (%) (<i>trans/cis</i>)
1	Pd(OAc) ₂	50	36 (8:1)
2	PdCl ₂	42	37 (6:1)
3	Pd(PPh ₃) ₂ Cl ₂	82	64 (8:1)
4	Pd(PPh ₃) ₄	87	80 (10:1)
5	Pd(dba) ₂	48	41 (8:1)
6	Pd ₂ (dba) ₃	38	36 (6:1)

Table S2. Effect of phosphine ligands

Entry	Ligand	Conversion (%)	Yield (%) (<i>trans/cis</i>)
1	none	96	30 (8:1)
2	PCy_3	57	2
3	Xphos	96	17 (5:1)
4	dppp	55	0
5	<i>rac</i> -BINAP	70	6
6	DPEphos	90	36 (7:1)
7	dppf	78	42 (8:1)
8	Xantphos	87	80 (10:1)

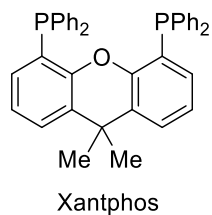
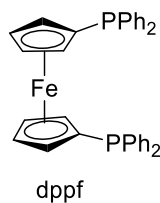
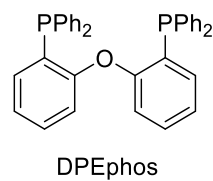
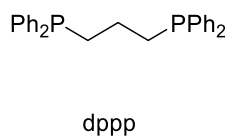
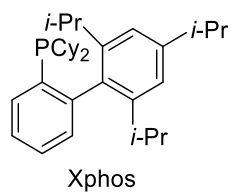
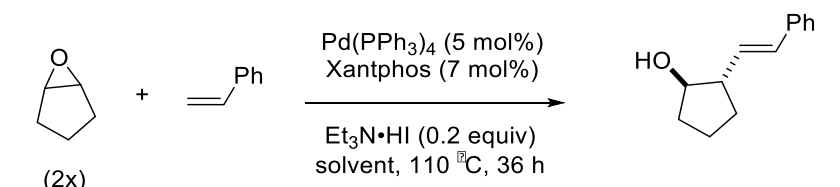
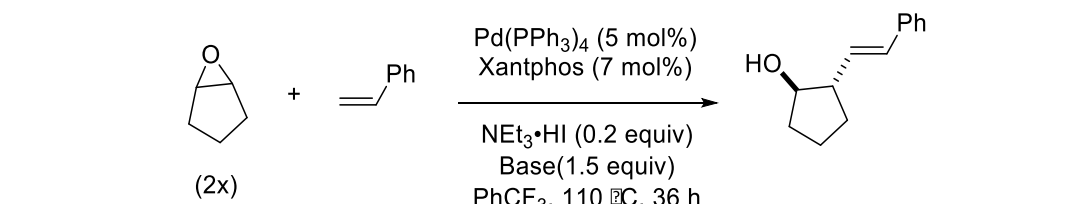


Table S3. Effect of solvents



Entry	Solvent	Conversion (%)	Yield (%) (<i>trans/cis</i>)
1	Toluene	80	55 (5:1)
2	<i>p</i> -Xylene	60	50 (8:1)
3	PhOMe	70	52 (8:1)
4	Veratrole	80	70 (10:1)
5	Dioxane	80	73 (10:1)
6	DME	64	56 (9:1)
7	DMA	70	51 (10:1)
8	DMF	63	53 (8:1)

Table S4. Effect of bases



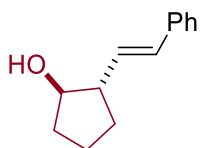
Entry	Base	Conversion (%)	Yield (%) (<i>trans/cis</i>)
1	none	87	80 (10:1)
2	K ₃ PO ₄	16	0
3	Cs ₂ CO ₃	18	0
4	KOAc	23	9
	Cy ₂ NMe	87	80 (10:1)
5	Et ₃ N	66	60 (10:1)
6	<i>i</i> -Pr ₂ NEt	64	57 (7:1)
7	DABCO	21	8
8	1,2,2,6,6-Pentamethylpiperidine	58	55 (10:1)
9	Proton sponge	59	54 (10:1)

Table S5. Effect of the ratio of reactants

Entry	x	Conversion (%)	Yield (%) (<i>trans/cis</i>)
1	1.5	87	75 (10:1)
2	1	77	55 (10:1)

III. Heck-type reaction of cyclic epoxides

A general procedure. In an argon-filled glove box, Pd(PPh₃)₄ (17.4 mg, 0.015 mmol), Xantphos (12.3 mg, 0.021 mmol) and dry PhCF₃ (1.2 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, cyclopentene oxide (54 μ L, 0.6 mmol), NEt₃·HI (13.8 mg, 0.06 mmol), styrene (1 equiv, 0.3 mmol) and 20 μ L of GC standard *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110 °C for 48 h. After cooled down to rt, the reaction mixture was subjected to flash chromatography with ethyl acetate/ hexanes as eluent. The structure of the desired product was confirmed by ¹H NMR spectroscopy of the purified sample, and ratio of isomers was determined by ¹H NMR spectroscopy of the reaction mixture after the reaction or GC and GCMS. 0.3 mmol of substituted styrene was used for isolation, unless stated otherwise. The reactions can also be conducted with standard Schlenk technique and a vacuum manifold.



(*E*)-*trans*-2-Styrylcyclopentanol (3a) [82537-31-3]¹

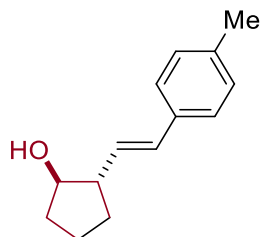
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as colorless oil. 43 mg, 77% yield.

The *trans/cis* ratio was determined to be 10:1 by crude ¹H NMR spectroscopy.

¹H NMR of the major isomer (400 MHz, CDCl₃): δ 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 8.3 Hz, 1H), 3.96 (ψq, *J* = 7.0 Hz, 1H), 2.53-2.45 (m, 1H), 2.09-1.96 (m, 2H), 1.82-1.50 (m, 5H).

¹³C NMR of the major isomer (100 MHz, CDCl₃): δ 137.4, 132.3, 130.5, 128.5, 127.2, 126.1, 78.7, 52.4, 33.6, 30.1, 21.3.

GC-MS (EI): Calcd for C₁₃H₁₆O M⁺: 188.1; found: 188.0.



(E)-trans-2-(4-Methylstyryl)cyclopentanol (3b)

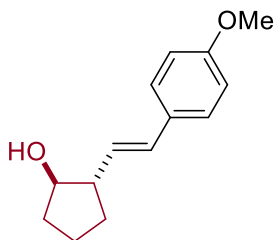
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:12) as white solid. 50 mg, 82% yield.

The *trans/cis* ratio was determined to be 7:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.43 (d, $J = 15.8$ Hz, 1H), 6.07 (dd, $J = 15.8, 8.3$ Hz, 1H), 3.94 (ψ q, $J = 7.0$ Hz, 1H), 2.50-2.42 (m, 1H), 2.32 (s, 3H), 2.06-1.94 (m, 2H), 1.82 (s, 1H), 1.81-1.48 (m, 4H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 136.9, 134.6, 131.2, 130.3, 129.2, 126.0, 78.7, 52.4, 33.6, 30.1, 21.3, 21.2.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ M^+ : 202.1; found: 202.1.

**(E)-trans-2-(4-Methoxystyryl)cyclopentanol (3c)**

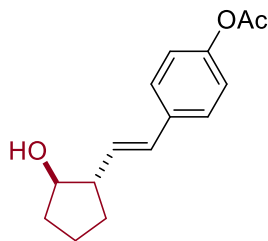
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as white solid. 48 mg, 73% yield.

The *trans/cis* ratio was determined to be 8:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.29-7.27 (m, 2H), 6.84-6.82 (m, 2H), 6.40 (d, $J = 15.8$ Hz, 1H), 5.98 (dd, $J = 15.8, 8.3$ Hz, 1H), 3.93 (ψ q, $J = 6.9$ Hz, 1H), 3.79 (s, 3H), 2.48-2.40 (m, 1H), 2.07-1.93 (m, 2H), 1.90 (s, 1H), 1.84-1.45 (m, 4H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 158.9, 130.2, 130.1, 129.8, 127.2, 114.0, 78.7, 55.3, 52.4, 33.6, 30.2, 21.2.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$ M^+ : 218.1; found: 218.0.



(*E*)-trans-2-(4-Acetoxyphenyl)cyclopentanol (3d)

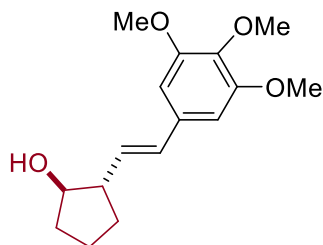
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as white solid. 48 mg, 65% yield.

The *trans/cis* ratio was determined to be 9:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.35 (d, $J = 6.7$ Hz, 2H), 7.02 (d, $J = 6.7$ Hz, 2H), 6.44 (d, $J = 15.8$ Hz, 1H), 6.09 (dd, $J = 15.8, 8.2$ Hz, 1H), 3.94 (ψ q, $J = 7.0$ Hz, 1H), 2.51-2.43 (m, 1H), 2.28 (s, 3H), 2.04-1.95 (m, 2H), 1.80-1.51 (m, 5H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 169.6, 149.8, 135.4, 132.7, 129.6, 127.1, 121.7, 78.8, 52.4, 33.8, 30.2, 21.4, 21.2.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ M^+ : 246.1; found: 246.1.



(*E*)-trans-2-(3,4,5-Trimethoxyphenyl)cyclopentanol (3e)

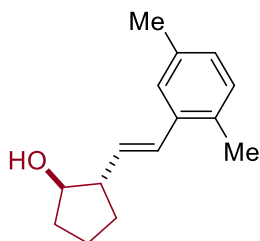
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:2) as white solid. 43 mg, 51% yield.

The *trans/cis* ratio was determined to be 7:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 6.58 (s, 2H), 6.39 (d, $J = 15.7$ Hz, 1H), 6.06 (dd, $J = 15.7, 8.2$ Hz, 1H), 3.97 (ψ q, $J = 7.1$ Hz, 1H), 3.87 (s, 6H), 3.84 (s, 3H), 2.52-2.44 (m, 1H), 2.06-1.96 (m, 2H), 1.83 (s, 1H), 1.82-1.62 (m, 3H), 1.56-1.50 (m, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 153.3, 137.5, 133.2, 131.8, 130.3, 103.1, 78.7, 60.9, 56.1, 52.2, 33.7, 30.1, 21.3.

MS (EI): Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$ M^+ : 278.2; found: 278.1.



(*E*)-trans-2-(2,5-dimethylstyryl)cyclopentanol (3f)

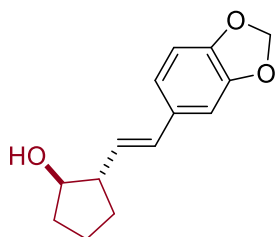
The product was isolated by flash chromatograph (ethyl acetate/hexanes 1:15) as colorless oil. 44 mg, 68% yield.

The *trans/cis* ratio was determined to be 8:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.26 (s, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 15.6$ Hz, 1H), 6.01 (dd, $J = 15.6, 8.4$ Hz, 1H), 3.97 (ψ q, $J = 6.8$ Hz, 1H), 2.55-2.47 (m, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.08-1.98 (m, 2H), 1.87-1.52 (m, 5H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 136.3, 135.5, 133.4, 132.1, 130.3, 128.5, 128.0, 126.2, 78.9, 52.8, 33.7, 30.3, 21.4, 21.2, 19.5.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$ M^+ : 216.2; found: 216.1.



(*E*)-trans-2-(3,4-Methylenedioxystyryl)cyclopentanol (3g)

Cy_2NMe (105 μL , 0.45 mmol) was added as a base to increase the yield of product.

The product was isolated by flash chromatograph (ethyl acetate/hexanes 1:6) as colorless oil. 48 mg, 70% yield.

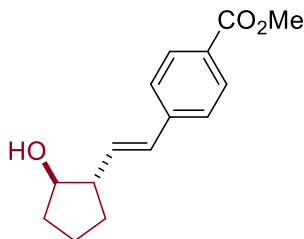
The *trans/cis* ratio was determined to be 9:1 by GC.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 6.88 (d, $J = 1.6$ Hz, 1H), 6.77-6.70 (m, 2H), 6.35 (d, $J = 15.8$ Hz, 1H), 5.93 (dd, $J = 15.8, 8.3$ Hz, 1H), 5.91 (s, 2H), 3.91 (ψ q, $J = 7.0$ Hz, 1H), 2.46-2.38 (m, 1H), 2.03-1.91 (m, 2H), 1.83 (s, 1H), 1.76-1.45 (m, 4H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 148.0, 146.8, 131.9, 130.5, 130.0, 120.5, 108.2, 105.5, 101.0,

78.7, 52.3, 33.6, 30.1, 21.2.

GC-MS (EI): Calcd for $C_{14}H_{16}O_3$ M^+ : 232.1; found: 232.0.



(E)-trans-2-(4-Methoxycarbonylstyryl)cyclopentanol (3h)

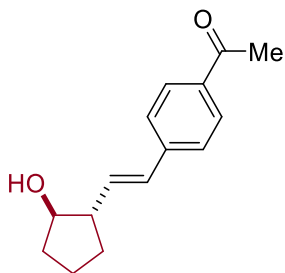
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as colorless oil. 46 mg, 62% yield.

The *trans/cis* ratio was determined to be 6:1 by crude 1H NMR spectroscopy.

1H NMR of the major isomer (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.28 (dd, J = 15.9, 8.2 Hz, 1H), 3.99 (ψ q, J = 7.0 Hz, 1H), 3.90 (s, 3H), 2.56-2.48 (m, 1H), 2.09-1.96 (m, 2H), 1.86 (s, 1H), 1.85-1.50 (m, 4H).

^{13}C NMR of the major isomer (100 MHz, $CDCl_3$): δ 167.0, 141.9, 135.3, 129.9, 129.6, 128.5, 125.9, 78.6, 52.4, 52.0, 33.8, 30.1, 21.4.

GC-MS (EI): Calcd for $C_{15}H_{18}O_3$ M^+ : 246.1; found: 246.0.



(E)-trans-2-(4-Acetylstyryl)cyclopentanol (3i)

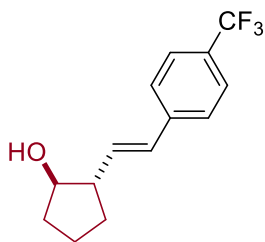
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as white solid. 42mg, 61% yield.

The *trans/cis* ratio was determined to be 10:1 by crude 1H NMR spectroscopy. Single crystals for X-ray diffraction were obtained by slow evaporation from a solution of 1:3 ethyl acetate/hexanes at room temperature. The relative configuration of the major isomer on cyclopentane was determined to be *trans* (CCDC: 1570943).

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.86 (d, $J = 8.3$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 2H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.30 (dd, $J = 15.9, 8.2$ Hz, 1H), 3.99 (ψ q, $J = 6.9$ Hz, 1H), 2.56 (s, 3H), 2.56-2.48 (m, 1H), 2.06-1.96 (m, 3H), 1.85-1.50 (m, 4H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 197.8, 142.3, 135.8, 129.6, 128.9, 126.2, 78.7, 52.5, 34.0, 30.2, 26.6, 21.5.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$ M^+ : 230.1; found: 230.0.



(*E*)-trans-2-(4-Trifluoromethylstyryl)cyclopentanol (3j)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:8) as colorless oil. 60 mg, 78% yield.

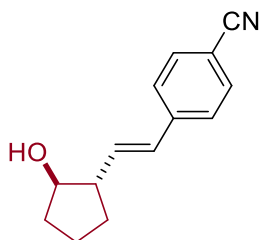
The *trans/cis* ratio was determined to be 7:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 6.50 (d, $J = 15.8$ Hz, 1H), 6.26 (dd, $J = 15.8, 8.2$ Hz, 1H), 4.00 (ψ q, $J = 7.0$ Hz, 1H), 2.57-2.49 (m, 1H), 2.08-1.98 (m, 2H), 1.87-1.77 (m, 1H), 1.74 (s, 1H), 1.73-1.61 (m, 2H), 1.57-1.52 (m, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 140.9, 135.1, 129.2, 128.9 (q, $J_{\text{CF}} = 32.4$ Hz), 126.2, 125.5 (q, $J_{\text{CF}} = 3.8$ Hz), 124.3 (q, $J_{\text{CF}} = 271.7$ Hz), 78.6, 52.3, 33.9, 30.0, 21.3.

^{19}F NMR (376.6 MHz, CDCl_3): δ -62.4.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}$ M^+ : 256.1; found: 256.0.



(*E*)-trans-2-(4-Cyanostyryl)cyclopentanol (3k)

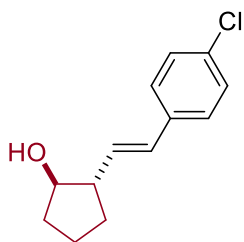
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as white solid. 44 mg, 69% yield.

The *trans/cis* ratio was determined to be 6:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 6.46 (d, $J = 15.9$ Hz, 1H), 6.29 (dd, $J = 15.9, 8.1$ Hz, 1H), 3.98 (ψ q, $J = 6.9$ Hz, 1H), 2.56-2.48 (m, 1H), 2.07-1.96 (m, 2H), 1.82-1.78 (m, 2H), 1.73-1.50 (m, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 142.1, 136.8, 132.5, 129.0, 126.6, 119.2, 110.3, 78.7, 52.4, 34.1, 30.1, 21.5.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}$ M^+ : 213.1; found: 213.1.



(*E*)-*trans*-2-(4-Chlorostyryl)cyclopentanol (3l)

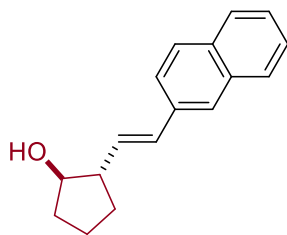
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:8) as colorless oil. 37 mg, 56% yield.

The *trans/cis* ratio was determined to be 5:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.29-7.22 (m, 4H), 6.40 (d, $J = 15.8$ Hz, 1H), 6.10 (dd, $J = 15.8, 8.2$ Hz, 1H), 3.94 (ψ q, $J = 7.0$ Hz, 1H), 2.50-2.42 (m, 1H), 2.07-1.93 (m, 2H), 1.81-1.74 (m, 2H), 1.72-1.56 (m, 2H), 1.52-1.45 (m, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 135.9, 133.0, 132.6, 129.2, 128.6, 127.3, 78.6, 52.3, 33.7, 30.1, 21.3.

GC-MS (EI): Calcd for $\text{C}_{13}\text{H}_{15}\text{ClO}$ M^+ : 222.1; found: 222.0.



(*E*)-trans-2-[(β -Naphthyl)vinyl]cyclopentanol (3m)

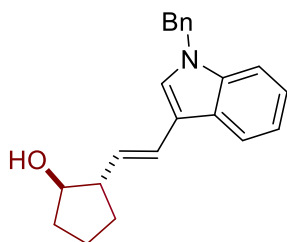
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:8) as white solid. 41 mg, 58% yield.

The *trans/cis* ratio was determined to be 6:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.80-7.76 (m, 3H), 7.70 (s, 1H), 7.59 (dd, J = 8.6, 1.7 Hz, 1H), 7.48-7.40 (m, 2H), 6.64 (d, J = 15.8 Hz, 1H), 6.27 (dd, J = 15.8, 8.3 Hz, 1H), 4.01 (ψ q, J = 7.0 Hz, 1H), 2.59-2.51 (m, 1H), 2.08-2.0 (m, 2H), 1.88-1.58 (m, 5H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 135.0, 133.8, 132.9, 132.8, 130.7, 128.2, 128.0, 127.8, 126.3, 125.8, 125.7, 123.7, 78.9, 52.6, 33.8, 30.3, 21.5.

GC-MS (EI): Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ M^+ : 238.1; found: 238.0.

**(*E*)-trans-2-[(*N*-benzylindol-3-yl)vinyl]cyclopentanol (3n)**

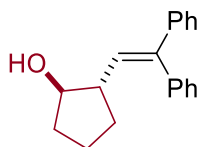
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:5) as white solid. 40 mg, 42% yield.

The *trans/cis* ratio was determined to be 5:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.86 (d, J = 6.5 Hz, 1H), 7.32-7.26 (m, 4H), 7.21-7.11 (m, 5H), 6.65 (d, J = 16.0 Hz, 1H), 6.08 (dd, J = 16.0, 8.4 Hz, 1H), 5.28 (s, 2H), 3.97 (ψ q, J = 6.9 Hz, 1H), 2.52-2.44 (m, 1H), 2.08-1.98 (m, 2H), 1.86-1.54 (m, 5H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.4, 137.3, 129.0, 128.9, 127.8, 127.0, 126.8, 126.5, 123.1, 122.4, 120.3, 120.1, 114.4, 110.0, 79.1, 53.4, 50.2, 33.5, 30.5, 21.3.

GC-MS (EI): Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}$ M^+ : 317.2; found: 317.2.

***trans*-2-(2,2-Diphenylvinyl)cyclopentanol (3o)**

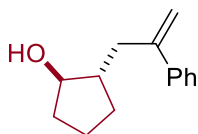
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as colorless oil. 72 mg, 90% yield.

The *trans/cis* ratio was determined to be 10:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.37-7.33 (m, 2H), 7.30-7.17 (m, 8H), 5.89 (d, J = 10.1 Hz, 1H), 3.98 (ψq, J = 6.6 Hz, 1H), 2.54-2.46 (m, 1H), 1.99-1.93 (m, 1H), 1.88-1.82 (m, 1H), 1.68-1.62 (m, 2H), 1.54-1.43 (m, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 142.8, 142.5, 140.1, 132.0, 130.0, 128.3, 128.1, 127.2, 127.1, 127.0, 79.8, 48.9, 34.0, 31.4, 21.6.

GC-MS (EI): Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ M^+ : 264.2; found: 264.0.



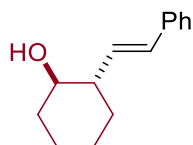
***trans*-2-(2-Phenallyl)cyclopentanol (3p)**

Dppf (11.7 mg, 0.021 mmol) was used instead of Xantphos, and dioxane (1.2 mL) instead of PhCF_3 to increase the yield of products from 37% to 52%. The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as colorless oil. 32 mg, 52% yield. Two isomers of terminal and internal alkenes were inseparable by silica and the ratio was determined to be 9:1 by GC.

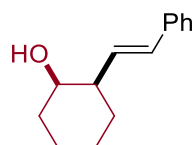
^1H NMR of the terminal alkene isomer (400 MHz, CDCl_3): δ 7.43-7.40 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.26 (m, 1H), 5.29 (d, J = 1.6 Hz, 1H), 5.10 (d, J = 1.6 Hz, 1H), 3.89 (ψq, J = 6.1 Hz, 1H), 2.69 (dd, J = 14.2, 5.4 Hz, 1H), 2.41 (dd, J = 14.2, 7.1 Hz, 1H), 1.95-1.80 (m, 3H), 1.72-1.40 (m, 5H).

^{13}C NMR of the terminal alkene isomer (100 MHz, CDCl_3): δ 148.0, 141.2, 128.5, 127.6, 126.4, 113.5, 79.2, 46.6, 40.0, 34.5, 30.0, 21.7.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ M^+ : 202.1; found: 202.0.



(major)



(minor)

(E)-2-Styrylcyclohexanol (4a and 4a') [865606-50-4 for *trans* isomer]¹

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as white solid. 52 mg, 85% yield.

The *trans/cis* ratio was determined to be 3:1 by GC. The two isomers were separated by silica.

¹H NMR of *trans* isomer (400 MHz, CDCl₃): δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (ψt, *J* = 7.5 Hz, 2H), 7.22 (ψt, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.35 (ψtd, *J* = 9.9, 4.0 Hz, 1H), 2.09-2.06 (m, 2H), 1.94 (s, 1H), 1.82-1.72 (m, 3H), 1.34-1.27 (m, 4H).

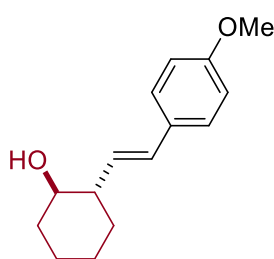
¹³C NMR of *trans* isomer (100 MHz, CDCl₃): δ 137.2, 132.3, 132.1, 128.7, 127.5, 126.3, 73.4, 50.7, 34.0, 31.6, 25.4, 25.0.

GC-MS (EI): Calcd for C₁₄H₁₈O M⁺: 202.1; found: 202.0.

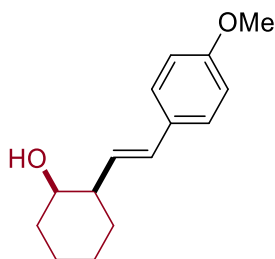
¹H NMR of *cis* isomer (400 MHz, CDCl₃): δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.31 (ψt, *J* = 7.4 Hz, 2H), 7.24-7.21 (m, 1H), 6.48 (d, *J* = 16.2 Hz, 1H), 6.35 (dd, *J* = 16.2, 7.0 Hz, 1H), 3.96-3.91 (m, 1H), 2.48-2.42 (m, 1H), 1.81-1.60 (m, 6H), 1.48-1.42 (m, 3H).

¹³C NMR of *cis* isomer (100 MHz, CDCl₃): δ 137.6, 131.6, 131.3, 128.7, 127.4, 126.3, 70.1, 45.1, 32.5, 26.6, 24.4, 21.2.

GC-MS (EI): Calcd for C₁₄H₁₈O M⁺: 202.1; found: 202.1.



(major)



(minor)

(E)-2-(4-Methoxystyryl)cyclohexanol (4b and 4b')

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:6) as white solid. 49 mg, 70% yield.

The *trans/cis* ratio was determined to be 2.7:1 by GC. The single crystals for X-ray diffraction were obtained by slow evaporation of a solution of 1:5 ethyl acetate/hexanes at rt. The configuration of the major isomer on cyclohexane was determined to be *trans* (CCDC: 1556727). The two isomers were separated by silica.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.30 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.46 (d, $J = 15.9$ Hz, 1H), 5.91 (dd, $J = 15.9, 8.8$ Hz, 1H), 3.80 (s, 3H), 3.30 (ψtd, $J = 9.9, 4.0$ Hz, 1H), 2.07-2.00 (m, 2H), 1.94 (s, 1H), 1.81-1.78 (m, 2H), 1.70-1.68 (m, 1H), 1.35-1.22 (m, 4H).

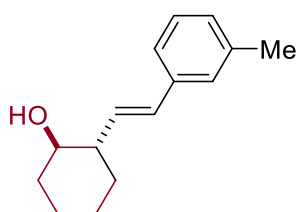
^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 159.1, 131.5, 129.9, 129.8, 127.3, 114.0, 73.3, 55.3, 50.6, 33.8, 31.6, 25.3, 24.8.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ M^+ : 232.2, found: 232.1.

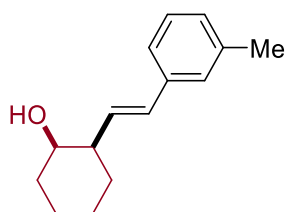
^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.31 (d, $J = 6.9$ Hz, 2H), 6.84 (d, $J = 6.9$ Hz, 2H), 6.42 (d, $J = 16.1$ Hz, 1H), 6.22 (dd, $J = 16.1, 7.1$ Hz, 1H), 3.95-3.88 (m, 1H), 3.80 (s, 3H), 2.45-2.40 (m, 1H), 1.78-1.58 (m, 7H), 1.50-1.42 (m, 2H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 159.2, 130.7, 130.4, 129.2, 127.4, 114.1, 70.1, 55.5, 45.0, 32.4, 26.7, 24.4, 21.2.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ M^+ : 232.2; found: 232.2.



(major)



(minor)

(*E*)-2-(3-Methylstyryl)cyclohexanol (4c and 4c')

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as foam. 52 mg, 80% yield. The *trans/cis* ratio was determined to be 3.2:1 by GC. The two isomers were separated by silica.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.22-7.16 (m, 3H), 7.04 (d, $J = 7.1$ Hz, 1H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.06 (dd, $J = 15.9, 8.8$ Hz, 1H), 3.34 (ψtd, $J = 9.8, 4.4$ Hz, 1H), 2.34 (s, 3H), 2.08-2.05 (m, 2H), 1.91 (s, 1H), 1.83-1.79 (m, 2H), 1.72-1.70 (m, 1H), 1.37-1.25 (m, 4H).

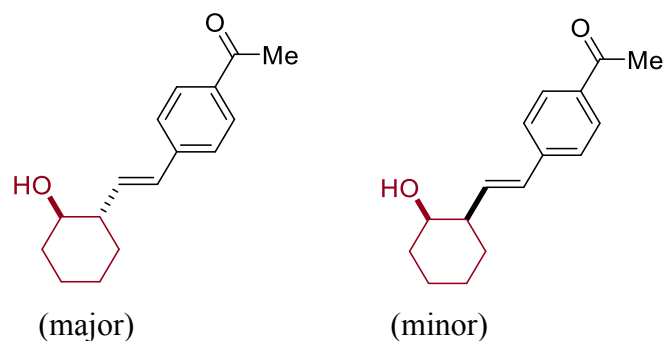
^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 138.3, 137.2, 132.2, 132.1, 128.6, 128.3, 127.0, 123.5, 73.4, 50.8, 34.0, 31.6, 25.4, 25.0, 21.5.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$ M^+ : 216.2; found: 216.0.

^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.22-7.17 (m, 3H), 7.04 (d, $J = 6.7$ Hz, 1H), 6.45 (d, $J = 16.1$ Hz, 1H), 6.33 (dd, $J = 16.1, 6.9$ Hz, 1H), 3.94-3.90 (m, 1H), 2.47-2.42 (m, 1H), 2.34 (s, 3H), 1.80-1.58 (m, 7H), 1.50-1.36 (m, 2H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 138.2, 137.5, 131.4, 131.3, 128.6, 128.2, 127.0, 123.5, 70.1, 45.1, 32.4, 26.6, 24.4, 21.5, 21.2.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$ M^+ : 216.2; found: 216.2.



(*E*)-2-(4-Acetylstyryl)cyclohexanol (4d and 4d')

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as white solid. 46 mg, 63% yield.

The *trans/cis* ratio was determined to be 2.7:1 by GC. The two isomers were separated by silica.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 6.54 (d, $J = 15.9$ Hz, 1H), 6.26 (dd, $J = 15.9, 8.6$ Hz, 1H), 3.40-3.36 (m, 1H), 2.57 (s, 3H), 2.13-2.02 (m, 2H), 1.89 (s, 1H), 1.82-1.78 (m, 2H), 1.72-1.68 (m, 1H), 1.36-1.23 (m, 4H).

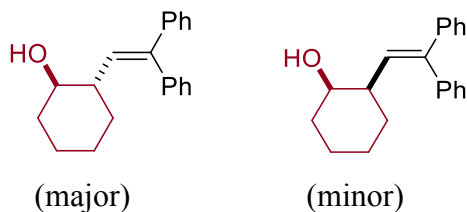
^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 197.7, 142.0, 135.9, 135.8, 130.8, 128.9, 126.3, 73.4, 50.6, 34.4, 31.4, 26.7, 25.2, 24.9.

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$ M^+ : 244.2; found: 244.1.

^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.88 (d, $J = 6.7$ Hz, 2H), 7.43 (d, $J = 6.7$ Hz, 2H), 6.51-6.49 (m, 2H), 3.97-3.94 (m, 1H), 2.58 (s, 3H), 2.48-2.42 (m, 1H), 1.81-1.58 (m, 6H), 1.54 (s, 1H), 1.49-1.32 (m, 2H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 197.7, 142.3, 135.8, 135.2, 130.0, 128.9, 126.3, 70.0, 45.3, 32.6, 26.7, 26.5, 24.4, 20.9.

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$ M^+ : 244.2; found: 244.1.



2-(2,2-Diphenylvinyl)cyclohexanol (4e and 4e')

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as foam. 68 mg, 81% yield. The *trans/cis* ratio was determined to be 2.7:1 by GC. The two isomers were separated by silica.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.40-7.22 (m, 10H), 5.91 (d, $J = 10.2$ Hz, 1H), 3.40 (ψtd, $J = 9.5$, 3.5 Hz, 1H), 2.22-2.12 (m, 1H), 2.02-1.95 (m, 1H), 1.71-1.60 (m, 4H), 1.31-1.08 (m, 4H).

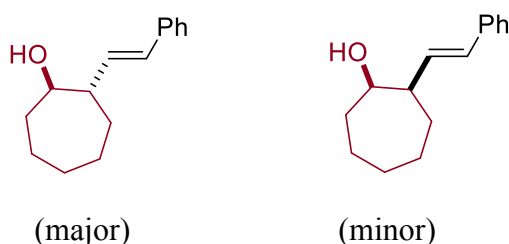
^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 144.4, 142.4, 139.9, 131.8, 129.9, 128.3, 128.2, 127.2, 127.1, 74.5, 46.8, 33.8, 31.8, 24.9, 24.8.

LC-MS (ESI): Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$ ($\text{M}+\text{H}$) $^+$: 279.2; found: 279.3.

^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.39-7.36 (m, 2H), 7.34-7.32 (m, 1H), 7.24-7.18 (m, 7H), 6.27 (d, $J = 10.4$ Hz, 1H), 3.84-3.79 (m, 1H), 2.47-2.41 (m, 1H), 1.77-1.62 (m, 4H), 1.50-1.34 (m, 4H), 1.28-1.23 (m, 1H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 142.8, 140.5, 130.4, 129.9, 128.4, 128.2, 127.4, 127.2, 127.1, 70.9, 41.9, 32.5, 28.2, 23.9, 21.1.

LC-MS (ESI): Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$ ($\text{M}+\text{H}$) $^+$: 279.2; found: 279.3.



(E)-2-Styrylcycloheptanol (4f and 4f') [865606-51-5 for *trans* isomer]¹

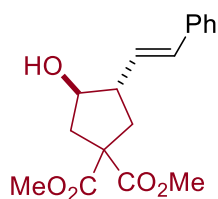
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as foam. 47 mg, 80% yield. The *trans/cis* ratio was determined to be 4.5:1 by GC. The two isomers cannot be separated by silica.

^1H NMR of a mixture of *trans* and *cis* isomers (400 MHz, CDCl_3): δ 7.39-7.36 (m, 2.4H), 7.33-7.29 (m, 2.4H), 7.25-7.22 (m, 1.2H), 6.51-6.46 (m, 1.2H), 6.34 (dd, $J = 16.0$, 8.0 Hz, 0.2H of *cis* isomer), 6.13 (dd, $J = 15.9$, 9.2 Hz,

¹H of *trans* isomer), 3.99-3.96 (m, 0.2H of *cis* isomer), 3.51 (ψtd, *J* = 8.6, 3.6 Hz, 1H of *trans* isomer), 2.62-2.57 (m, 0.2H of *cis* isomer), 2.21 (ψqd, *J* = 9.3, 3.1 Hz, 1H of *trans* isomer), 2.00-1.94 (m, 1.2H), 1.83 (d, *J* = 1.7 Hz, 1.2H), 1.78-1.47 (m, 10.8H).

¹³C NMR of a mixture of *trans* and *cis* isomers (100 MHz, CDCl₃): δ 137.5 and 137.2, 133.9 and 132.1, 131.2 and 131.3, 128.7, 127.5 and 127.4, 126.4 and 126.3, 75.9 and 73.7, 52.9 and 48.6, 35.1 and 34.9, 30.5 and 28.5, 27.8 and 28.3, 26.1 and 25.9, 22.4 and 22.7.

GC-MS (EI): Calcd for C₁₅H₂₀O M⁺: 216.2; found: 216.0.



Dimethyl (*E*)-*trans*-3-hydroxy-4-styrylcyclopentane-1,1-dicarboxylate (4g)

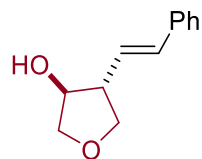
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as colorless oil. 67 mg, 74% yield.

The *trans/cis* ratio was determined to be 11:1 by crude ¹H NMR spectroscopy.

¹H NMR of the major isomer (400 MHz, CDCl₃): δ 7.36-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.09 (dd, *J* = 15.8, 7.6 Hz, 1H), 4.03 (ψq, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 2.71-2.64 (m, 3H), 2.30-2.22 (m, 2H), 2.13-2.06 (m, 1H).

¹³C NMR of the major isomer (100 MHz, CDCl₃): δ 173.1, 172.6, 137.1, 131.8, 129.9, 128.7, 127.5, 126.3, 77.1, 57.0, 53.2, 53.0, 51.4, 41.4, 37.7.

LC-MS (ESI): Calcd for C₁₇H₂₀O₅ (M+H)⁺: 305.1; found: 305.2.



(*E*)-*trans*-4-Styryltetrahydrofuran-3-ol (4h)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:2) as white solid. 45 mg, 79% yield.

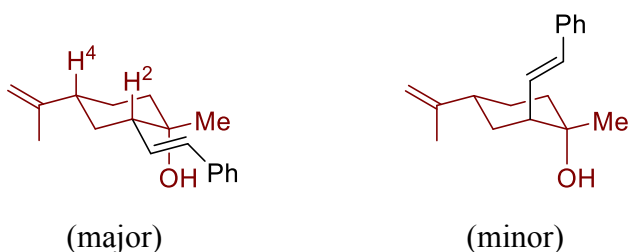
The *trans/cis* ratio was determined to be 15:1 by crude ¹H NMR spectroscopy. The two isomers cannot be

separated by silica.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.37-7.29 (m, 4H), 7.26-7.23 (m, 1H), 6.53 (d, $J = 15.8$ Hz, 1H), 6.10 (dd, $J = 15.8, 8.7$ Hz, 1H), 4.31-4.27 (m, 1H), 4.19 (dd, $J = 8.8, 7.0$ Hz, 1H), 4.01 (dd, $J = 9.7, 5.2$ Hz, 1H), 3.76 (dd, $J = 9.7, 3.4$ Hz, 1H), 3.72 (dd, $J = 8.8, 5.8$ Hz, 1H), 2.94-2.90 (m, 1H), 1.89 (s, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.0, 132.2, 128.8, 128.1, 127.7, 126.3, 77.9, 74.5, 72.1, 52.5.

GC-MS (EI): Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ M^+ : 190.1; found: 190.0.



The (+)-*trans*-limonene oxide **1c** [6909-30-4] was prepared by kinetic resolution of two (+)-limonene oxide isomers (from Aldrich) with pyrazole according to a reported process.² ^1H NMR of **1c** (400 MHz, CDCl_3): δ 4.66 (s, 2H), 2.99 (ψ d, $J = 4.1$ Hz, 1H), 2.05-2.02 (m, 2H), 1.92-1.86 (m, 1H), 1.75-1.72 (m, 2H), 1.71 (s, 3H), 1.40-1.36 (m, 2H), 1.32 (s, 3H). GC-MS (EI): Calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ M^+ : 152.1; found: 152.1.

The products were isolated by flash chromatography (ethyl acetate/hexanes 1:25) as colorless oil. 46 mg, 60% combined yield. The *cis/trans* ratio was determined to be 3:1 by GC. The two isomers were separated by silica. We detected a stronger cross-signal between hydrogens H^2 and H^4 in the major isomer and hence assigned it *cis* configuration with respect to the alcohol group.

Major *cis* isomer:

(1*S*,2*S*,4*R*)-1-Methyl-4-(2-propenyl)-(2*E*)-styrylcyclohexanol (4i)

^1H NMR (400 MHz, CDCl_3): δ 7.39 (d, $J = 7.3$ Hz, 2H), 7.31 (ψ t, $J = 7.3$ Hz, 2H), 7.26-7.20 (m, 1H), 6.44 (d, $J = 16.1$ Hz, 1H), 6.35 (dd, $J = 16.1, 8.2$ Hz, 1H), 4.74 (d, $J = 11.6$ Hz, 2H), 2.22-2.16 (m, 1H), 2.15-1.97 (m, 1H), 1.82 (ψ dt, $J = 13.2, 2.4$ Hz, 1H), 1.77 (s, 3H), 1.67-1.59 (m, 4H), 1.54-1.49 (m, 1H), 1.30 (s, 1H), 1.24 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 150.0, 137.7, 131.5, 131.2, 128.6, 127.2, 126.2, 108.8, 70.6, 50.4, 44.9, 40.0, 33.4, 29.6, 26.9, 21.1.

LC-MS (ESI): Calcd for $C_{18}H_{24}ONa$ ($M+Na$)⁺: 279.2; found: 279.2.

$[\alpha]^{23}_D = +17.5^\circ$ ($c = 1.80$, $CHCl_3$).

Minor *trans* isomer:

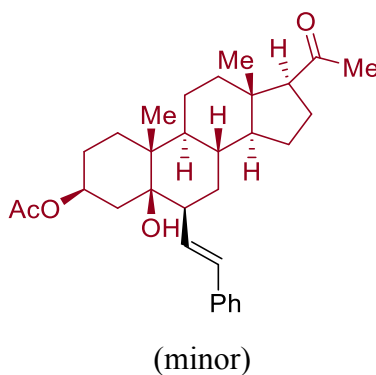
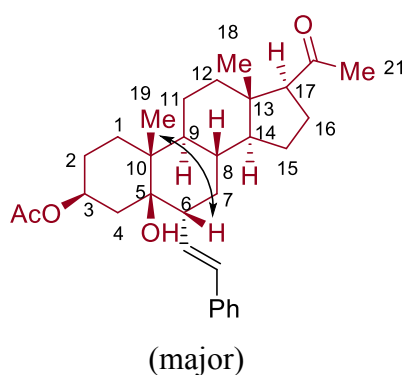
(1*R*,2*R*,4*R*)-1-Methyl-4-(2-propenyl)-(2*E*)-styrylcyclohexanol (4i')

¹H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, $J = 7.1$ Hz, 2H), 7.33 (ψ t, $J = 7.1$ Hz, 2H), 7.24-7.20 (m, 1H), 6.47 (d, $J = 15.7$ Hz, 1H), 6.32 (dd, $J = 15.7, 9.4$ Hz, 1H), 4.75 (s, 2H), 2.49-2.45 (m, 1H), 2.26-2.18 (m, 1H), 2.04 (ψ td, $J = 12.3, 4.3$ Hz, 1H), 1.74 (s, 3H), 1.72-1.59 (m, 5H), 1.40 (s, 1H), 1.19 (s, 3H).

¹³C NMR (100 MHz, $CDCl_3$): δ 149.6, 137.7, 131.6, 131.0, 128.7, 127.4, 126.3, 109.2, 71.5, 50.0, 38.8, 35.5, 33.2, 29.0, 26.8, 21.3.

LC-MS (ESI): Calcd for $C_{18}H_{24}ONa$ ($M+Na$)⁺: 279.2; found: 279.2.

$[\alpha]^{23}_D = +6.7^\circ$ ($c = 0.80$, $CHCl_3$).



A mixture of epoxide isomers (α : β 6:94) was prepared from pregnenolone acetate (Aldrich) with $KMnO_4$ and $CuSO_4(5H_2O)$.³ **3 β -Acetoxy-5 β ,6 β -epoxypregnan-20-one (1d) [6661-94-5]** ¹H NMR (400 MHz, $CDCl_3$): δ 4.80-4.74 (m, 1H), 3.08 (ψ d, $J = 2.1$ Hz, 1H), 2.48 (ψ t, $J = 8.9$ Hz, 1H), 2.17-2.11 (m, 2H), 2.10 (s, 3H), 2.03 (s, 3H), 2.01-1.95 (m, 2H), 1.85-1.82 (m, 1H), 1.70-1.62 (m, 2H), 1.49-1.18 (m, 10H), 1.07-1.03 (m, 1H), 1.00 (s, 3H), 0.71-0.64 (m, 1H), 0.59 (s, 3H). GC-MS (EI): Calcd for $C_{23}H_{34}O_4$ M^+ : 374.2; found: 374.2.

The reaction runs on 0.2 mmol scale. The two isomers of the Heck product were separated by flash chromatography (ethyl acetate/hexanes 1:4) as white solid. 50 mg, 53% combined yield. The ratio of α - and β -isomers in the crude mixture was determined to be 2.3:1 by ¹H NMR spectroscopy. The configuration of major

α -isomers in Ring B was assigned by detection of a strong NOE signal between H(6) and CH₃(19). The chemical shift of CH₃(19) was assigned by comparison with chemical shifts in pregnenolone acetate.⁴

Major isomer:

(3*S*,5*R*,6*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-5-hydroxy-10,13-dimethyl-6-((*E*)-styryl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (4j)

¹H NMR (400 MHz, CDCl₃): δ 7.38-7.35 (m, 2H), 7.29 (ψt, J = 7.6 Hz, 2H), 7.21-7.17 (m, 1H), 6.38-6.36 (m, 2H), 5.24-5.22 (m, 1H), 2.86 (s, 1H), 2.69-2.63 (m, 1H), 2.54 (ψt, J = 9.2 Hz, 1H), 2.25-2.15 (m, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.10-2.04 (m, 2H), 1.78-1.51 (m, 8H), 1.48-1.20 (m, 8H), 1.04 (s, 3H), 0.64 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 209.5, 169.7, 137.9, 131.3, 130.6, 128.6, 127.2, 126.3, 75.8, 71.0, 63.8, 56.9, 44.4, 44.3, 43.3, 41.2, 39.1, 34.5, 33.7, 31.6, 31.5, 26.0, 24.6, 24.4, 23.1, 21.8, 21.7, 17.2, 13.6.

HRMS (ESI): Calcd for C₃₁H₄₃O₄ (M+H)⁺: 479.3161; found: 479.3163.

$[\alpha]^{23}_{\text{D}} = +45.1^{\circ}$ (c = 0.30, CHCl₃).

Minor isomer:

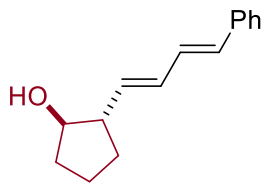
(3*S*,5*R*,6*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-5-hydroxy-10,13-dimethyl-6-((*E*)-styryl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (4j')

¹H NMR (400 MHz, CDCl₃): δ 7.39-7.37 (m, 2H), 7.34 (ψt, J = 7.4 Hz, 2H), 7.25-7.21 (m, 1H), 6.58-6.56 (m, 2H), 5.04-4.95 (m, 1H), 3.70 (s, 1H), 2.58-2.53 (ψt, J = 9.3 Hz, 1H), 2.26-2.17 (m, 2H), 2.13 (s, 3H), 2.09-2.04 (m, 2H), 2.01 (s, 3H), 1.85-1.82 (m, 2H), 1.66-1.58 (m, 5H), 1.52-1.47 (m, 5H), 1.30 (s, 3H), 1.28-1.20 (m, 4H), 0.66 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 209.6, 170.8, 138.0, 134.5, 130.0, 128.8, 127.5, 126.3, 77.8, 71.0, 63.9, 56.6, 47.6, 46.4, 44.6, 39.3, 37.8, 35.0, 34.6, 32.9, 31.7, 30.6, 29.9, 26.7, 24.5, 23.0, 21.6, 18.1, 13.9.

HRMS (ESI): Calcd for C₃₁H₄₃O₄ (M+H)⁺: 479.3161; found: 479.3159.

$[\alpha]^{23}_{\text{D}} = +19.9^{\circ}$ (c = 0.30, CHCl₃).



(1E,3E)-trans-2-[4-Phenylbuta-1,3-dien-1-yl]cyclopentanol (6a)

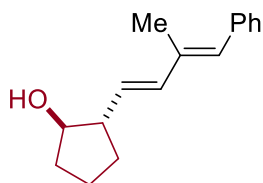
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as white solid. 34 mg, 53% yield.

The *trans/cis* ratio was determined to be 10:1 by GC.

^1H NMR of the all *trans* isomer (400 MHz, CDCl_3): δ 7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.23-7.19 (m, 1H), 6.76 (dd, $J = 15.6, 10.4$ Hz, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 6.30 (dd, $J = 15.2, 10.4$ Hz, 1H), 5.75 (dd, $J = 15.2, 8.3$ Hz, 1H), 3.92 (ψ q, $J = 6.9$ Hz, 1H), 2.47-2.39 (m, 1H), 2.06-1.94 (m, 2H), 1.82-1.58 (m, 4H), 1.50-1.45 (m, 1H).

^{13}C NMR of the all *trans* isomer (100 MHz, CDCl_3): δ 137.6, 137.0, 131.2, 131.1, 129.1, 128.7, 127.4, 126.4, 78.9, 52.3, 33.8, 30.2, 21.4.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ M^+ : 214.1; found: 214.1.



(1E,3E)-trans-2-[3-Methyl-4-phenylbuta-1,3-dien-1-yl]cyclopentanol (6b)

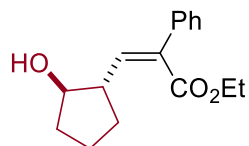
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as white solid. 41 mg, 60% yield.

The isomeric ratio was determined to be 10:1 by GC.

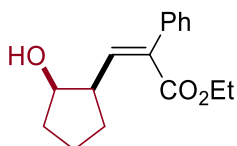
^1H NMR of the all *trans* isomer (400 MHz, CDCl_3): δ 7.36-7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.19 (m, 1H), 6.47 (s, 1H), 6.34 (d, $J = 15.6$ Hz, 1H), 5.69 (dd, $J = 15.6, 8.3$ Hz, 1H), 3.92 (ψ q, $J = 7.1$ Hz, 1H), 2.48-2.40 (m, 1H), 2.05-1.96 (m, 2H), 2.00 (s, 3H), 1.79-1.46 (m, 5H).

^{13}C NMR of the all *trans* isomer (100 MHz, CDCl_3): δ 138.1, 136.1, 135.6, 131.7, 130.3, 129.3, 128.2, 126.5, 79.0, 52.5, 33.8, 30.5, 21.4, 14.1.

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$ M^+ : 228.2; found: 228.1.



(major)



(minor)

(Z)-Ethyl 3-(2-hydroxycyclopentyl)-2-phenylacrylate (6c and 6c')

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:6) as colorless oil. 36 mg, 46% yield.

The *trans/cis* ratio was determined to be 2.6:1 by GC. The two isomers were separated on silica. The *Z* configuration of both isomers was established by NOE signals between the olefinic hydrogen and ortho hydrogens of phenyl group.

Major isomer:

^1H NMR (400 MHz, CDCl_3): δ 7.38-7.31 (m, 3H), 7.23-7.20 (m, 2H), 6.89 (d, $J = 10.6$ Hz, 1H), 4.20 (ψ q, $J = 7.1$ Hz, 2H), 4.10-4.03 (m, 1H), 2.54-2.45 (m, 1H), 2.03-1.96 (m, 1H), 1.89-1.81 (m, 1H), 1.73-1.65 (m, 2H), 1.58-1.47 (m, 2H), 1.39 (s, 1H), 1.25 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 167.3, 146.6, 135.5, 135.1, 130.0, 128.1, 127.6, 79.4, 61.1, 48.6, 34.5, 31.0, 21.9, 14.4.

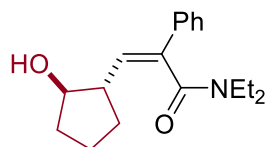
GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ M^+ : 260.1; found: 260.1.

Minor isomer:

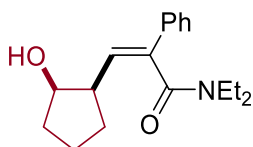
^1H NMR (400 MHz, CDCl_3): δ 7.35-7.29 (m, 5H), 6.06 (d, $J = 9.9$ Hz, 1H), 4.34-4.28 (m, 2H), 4.02-3.96 (m, 1H), 3.18 (d, $J = 3.0$ Hz, 1H), 2.98-2.89 (m, 1H), 2.12-2.02 (m, 2H), 1.82-1.63 (m, 3H), 1.52-1.46 (m, 1H), 1.31 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.1, 143.1, 137.6, 135.9, 128.5, 127.9, 127.4, 79.4, 61.5, 49.6, 34.5, 31.9, 22.4, 14.3.

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ M^+ : 260.1; found: 260.1.



(major)



(minor)

(Z)-N,N-Diethyl-3-(2-hydroxycyclopentyl)-2-phenylacrylamide (6d and 6d')

Cy₂NMe (105 μ L, 0.45 mmol) was added as a base to increase the yield of products.

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:2) as light yellow oil. 46 mg, 53% yield. The *trans/cis* ratio was determined to be 3:1 by crude ¹H NMR spectroscopy. The two isomers were separated by silica. The *Z* configuration of both isomers was established by NOE signals between the olefinic hydrogen and ortho hydrogens of phenyl group.

Major isomer:

¹H NMR (400 MHz, CDCl₃): δ 7.35-7.30 (m, 4H), 7.28-7.25 (m, 1H), 5.92 (d, *J* = 10.0 Hz, 1H), 4.34 (br s, OH), 3.89 (ψ q, *J* = 6.8 Hz, 1H), 3.69 (dq, *J* = 13.6, 7.1 Hz, 1H), 3.34 (dq, *J* = 13.6, 7.1 Hz, 1H), 3.21 (dq, *J* = 14.5, 7.1 Hz, 1H), 3.08 (dq, *J* = 14.5, 7.1 Hz, 1H), 2.50-2.42 (m, 1H), 2.07-1.95 (m, 2H), 1.80-1.52 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 170.6, 139.4, 136.4, 134.1, 129.0, 128.0, 125.5, 78.1, 49.9, 43.1, 39.4, 34.2, 31.6, 22.3, 14.0, 12.9.

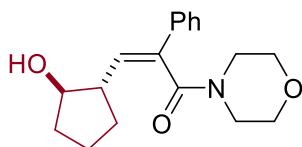
GC-MS (EI): Calcd for C₁₈H₂₅NO₂ M⁺: 287.2; found: 287.2.

Minor isomer (containing a small amount of the major isomer):

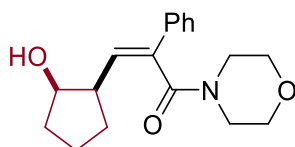
¹H NMR (400 MHz, CDCl₃): δ 7.37-7.25 (m, 5H), 6.06 (d, *J* = 9.4 Hz, 1H), 4.26 (ψ q, *J* = 5.8 Hz, 1H), 3.59 (dq, *J* = 13.6, 7.1 Hz, 1H), 3.44 (dq, *J* = 13.6, 7.1 Hz, 1H), 3.25-3.11 (m, 2H), 2.70-2.63 (m, 1H), 1.98-1.82 (m, 2H), 1.77-1.58 (m, 5H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 170.1, 139.4, 136.6, 128.9, 127.9, 125.6, 76.2, 45.9, 42.9, 39.0, 30.5, 22.3, 14.0, 12.9.

GC-MS (EI): Calcd for C₁₈H₂₅NO₂ M⁺: 287.2; found: 287.2.



(major)



(minor)

(Z)-3-(2-Hydroxycyclopentyl)-1-morpholino-2-phenylprop-2-en-1-one (6e and 6e')

Dioxane (1.2 mL) was used instead of PhCF₃. The product was isolated by flash chromatography (ethyl

acetate/hexanes 2:1) as colorless oil. 44 mg, 49% yield. The *trans/cis* ratio on the cyclopentane ring was determined to be 1.9:1 by GC. The *Z* configuration of both isomers was established by NOE signals between the olefinic hydrogen and ortho hydrogens of phenyl group.

Major isomer:

^1H NMR (400 MHz, CDCl_3): δ 7.35-7.28 (m, 5H), 6.00 (d, $J = 10.1$ Hz, 1H), 3.92 (ψ q, $J = 7.4$ Hz, 1H), 3.87-3.79 (m, 1H), 3.74-3.66 (m, 3H), 3.41 (ψ t, $J = 4.8$ Hz, 2H), 3.34-3.20 (m, 2H), 2.55-2.46 (m, 1H), 2.10-1.96 (m, 2H), 1.85-1.48 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 138.1, 136.0, 135.0, 129.1, 128.3, 125.6, 78.3, 67.0, 66.9, 49.9, 47.3, 42.2, 34.2, 31.5, 22.2.

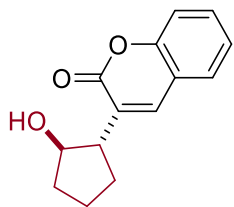
GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_3$ M^+ : 301.2; found: 301.2.

Minor isomer:

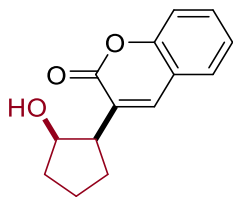
^1H NMR (400 MHz, CDCl_3): δ 7.38-7.31 (m, 4H), 7.29-7.26 (m, 1H), 6.19 (d, $J = 9.8$ Hz, 1H), 4.27 (ψ q, $J = 4.5$ Hz, 1H), 3.79-3.75 (m, 2H), 3.72-3.69 (m, 2H), 3.47-3.35 (m, 2H), 3.34-3.26 (m, 2H), 2.70-2.60 (m, 2H), 2.00-1.82 (m, 3H), 1.78-1.59 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.4, 137.9, 136.0, 131.7, 129.0, 128.2, 125.6, 76.3, 67.0, 47.1, 46.2, 42.0, 34.5, 30.5, 29.9, 22.4.

GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_3$ M^+ : 301.2; found: 301.2.



(major)



(minor)

3-(2-Hydroxycyclopentyl)coumarin (6f and 6f')

Cy_2NMe (105 μL , 0.45 mmol, 1.5 equiv) was added to the standard conditions. Without it, the combined yield was only 37%.

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:3) as white solid. 47 mg, 68% yield.

The *trans/cis* ratio was determined to be 3.5:1 by GC. The C3 alkylation of coumarin in both isomers was determined by X-ray diffraction of both isomers. The two isomers were separated on silica.

The relative configuration of the major isomer was determined to be *trans* on cyclopentane ring by X-ray diffraction (CCDC: 1816547). Single crystals suitable for X-ray diffraction were obtained by slow evaporation from a solution of 1:2 dichloromethane/ hexanes at room temperature.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.53 (s, 1H), 7.50-7.45 (m, 2H), 7.34-7.25 (m, 2H), 4.20-4.16 (m, 1H), 3.39 (s, 1H), 3.03-2.98 (m, 1H), 2.14-1.99 (m, 2H), 1.93-1.74 (m, 4H).

^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 163.2, 152.9, 137.4, 131.1, 131.0, 127.6, 124.7, 119.5, 116.6, 77.9, 50.9, 34.9, 29.6, 23.4.

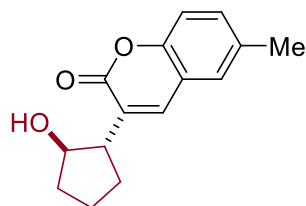
GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$ M^+ : 230.1; found: 230.1.

The relative configuration of the minor isomer on cyclopentane ring was determined to be *cis* (CCDC: 1815718). Single crystals suitable for X-ray diffraction were obtained by slow evaporation from a solution of 1:2 ethyl acetate/ hexanes at room temperature.

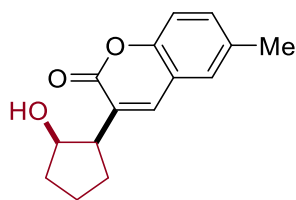
^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.64 (s, 1H), 7.49-7.46 (m, 2H), 7.32-7.24 (m, 2H), 4.62-4.57 (m, 1H), 3.19-3.12 (m, 1H), 2.16-1.86 (m, 4H), 1.82-1.65 (m, 2H), 1.54-1.51 (m, 1H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 162.4, 153.1, 139.8, 130.9, 128.3, 127.6, 124.5, 119.6, 116.5, 73.8, 46.6, 34.9, 27.0, 22.0.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$ M^+ : 230.1; found: 230.1.



(major)



(minor)

3-(2-Hydroxycyclopentyl)-6-methylcoumarin (6g and 6g')

Cy_2NMe (105 μL , 0.45 mmol) was added as a base to increase the yield of products.

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as white solid. 59 mg, 80% yield.

The *trans/cis* ratio was determined to be 2.8:1 by GC. The two isomers were separated on silica. The relative configuration of the major isomer on cyclopentane ring was determined to be *trans* (CCDC: 1816494). Single crystals suitable for X-ray diffraction were obtained by slow evaporation from a solution of 1:2 ethyl acetate/hexanes at room temperature.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.47 (s, 1H), 7.29-7.26 (m, 1H), 7.24-7.20 (m, 2H), 4.18-4.14 (m, 1H), 3.45 (s, 1H), 3.02-2.96 (m, 1H), 2.39 (s, 3H), 2.13-2.06 (m, 1H), 2.04-1.97 (m, 1H), 1.92-1.85 (m, 1H), 1.83-1.74 (m, 3H).

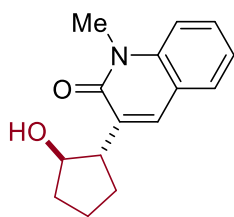
^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 163.5, 151.0, 137.4, 134.4, 132.1, 130.8, 127.4, 119.2, 116.2, 78.0, 50.9, 34.9, 29.6, 23.4, 20.9.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ M^+ : 244.1; found: 244.1.

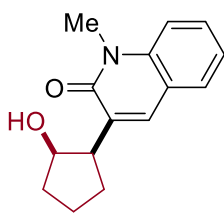
^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.58 (s, 1H), 7.28-7.25 (m, 2H), 7.21-7.18 (m, 1H), 4.59-4.55 (m, 1H), 3.17-3.11 (m, 1H), 2.39 (s, 3H), 2.15-1.85 (m, 4H), 1.81-1.61 (m, 2H), 1.57 (s, 1H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 162.7, 151.2, 139.8, 134.2, 131.9, 128.1, 127.5, 119.3, 116.2, 73.7, 46.6, 34.8, 27.0, 22.0, 20.9.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$ M^+ : 244.1; found: 244.1.



(major)



(minor)

3-(2-Hydroxycyclopentyl)-N-methyl-2-quinolinone (6h and 6h')

Cy_2NMe (105 μL , 0.45 mmol) was added as a base to increase the yield of products.

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:3) as light yellow oil. 38 mg, 52% yield. The *trans/cis* ratio was determined to be 2.5:1 by GC. The two isomers were separated on silica.

^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.57 (s, 1H), 7.55-7.52 (m, 2H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.28-7.24 (m, 1H), 5.01 (s, 1H), 4.04-3.99 (m, 1H), 3.78 (s, 3H), 3.19-3.14 (m, 1H), 2.07-1.80 (m, 5H), 1.70 (br s, OH).

^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 164.4, 138.7, 135.1, 133.3, 130.0, 128.6, 122.6, 120.9, 114.2, 78.8, 51.0, 35.0, 30.1, 29.6, 23.8.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$ M^+ : 243.1; found: 243.1.

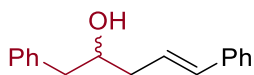
^1H NMR of *cis* isomer (400 MHz, CDCl_3): δ 7.65 (s, 1H), 7.57-7.52 (m, 2H), 7.36 (d, $J = 8.3$ Hz, 1H), 7.24-7.22 (m, 1H), 4.59-4.56 (m, 1H), 3.76 (s, 3H), 3.34-3.28 (m, 1H), 2.31 (br s, OH), 2.18-1.95 (m, 3H), 1.89-1.66 (m, 3H).

^{13}C NMR of *cis* isomer (100 MHz, CDCl_3): δ 163.4, 139.1, 136.7, 132.3, 130.0, 128.6, 122.4, 120.8, 114.1, 74.6, 47.6, 34.8, 30.1, 27.3, 22.2.

GC-MS (EI): Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$ M^+ : 243.1; found: 243.1.

IV. Heck-type reaction of acyclic epoxides

A general procedure. In an argon-filled glove box, $\text{Pd}(\text{PPh}_3)_4$ (17.4 mg, 0.015 mmol), dppf (11.7 mg, 0.021 mmol) and dry dioxane (1.2 mL) were charged into a dry 10 mL of Schlenk tube. After stirring at rt for 10 min, acyclic epoxide (0.6 mmol), $\text{NEt}_3 \cdot \text{HI}$ (13.8 mg, 0.06 mmol), styrene (35 μL , 0.3 mmol) and 20 μL of GC standard *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110 $^\circ\text{C}$ for 48 h. After cooled down to rt, the reaction mixture was subjected to flash chromatography with ethyl acetate/ hexanes as eluent. The structure of the desired product was confirmed by ^1H NMR spectroscopy of the purified sample, and the *trans/cis* ratio was determined by ^1H NMR spectroscopy of the crude reaction mixture or GC and GCMS. 0.3 mmol of styrene was used for all the isolation, unless stated otherwise. The reactions can also be conducted with standard Schlenk technique and a vacuum manifold.



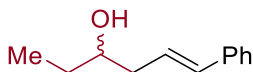
(*E*)-1,5-Diphenylpent-4-en-2-ol (5a)

A racemic epoxide was used. The product was isolated by flash chromatography (ethyl acetate/hexanes 1:25) as light yellow oil. 46 mg, 64% yield. The ratio of regioisomers was determined to be 11:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.35-7.25 (m, 6H), 7.23-7.17 (m, 4H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.24 (ψdt , $J = 15.9, 7.3$ Hz, 1H), 3.94 (m, 1H), 2.84 (dd, $J = 13.6, 4.9$ Hz, 1H), 2.74 (dd, $J = 13.6, 8.0$ Hz, 1H), 2.46-2.44 (m, 1H), 2.40-2.32 (m, 1H), 1.71 (s, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 138.5, 137.4, 133.3, 129.6, 128.7, 128.6, 127.4, 126.7, 126.3, 126.2, 72.3, 43.6, 40.6.

GC-MS (EI): Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ M^+ : 238.1; found: 238.0.



(E)-6-Phenylhex-5-en-3-ol (5b) [54985-35-2]⁵

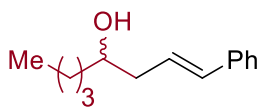
Veratrole (1.2 mL) was used instead of dioxane to increase the yield of product.

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:6) as light yellow oil. 40 mg, 76% yield. The ratio of regioisomers was determined to be 9:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38-7.36 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.22 (m, 1H), 6.49 (d, $J = 15.8$ Hz, 1H), 6.26 (ψ dt, $J = 15.8$, 6.9 Hz, 1H), 3.70-3.64 (m, 1H), 2.50-2.43 (m, 1H), 2.33-2.29 (m, 1H), 1.64 (s, 1H), 1.62-1.51 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.4, 133.2, 128.7, 127.4, 126.6, 126.2, 72.7, 40.8, 29.8, 10.1.

GC-MS (EI): Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ M^+ : 176.1; found: 176.1.



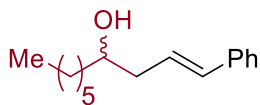
(E)-1-Phenyloct-1-en-4-ol (5c) [1488206-39-8]⁵

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as light yellow oil. 43 mg, 70% yield. The ratio of regioisomers was determined to be 12:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.49 (d, $J = 15.8$ Hz, 1H), 6.23 (ψ dt, $J = 15.8$, 6.9 Hz, 1H), 3.76-3.70 (m, 1H), 2.46-2.42 (m, 1H), 2.35-2.30 (m, 1H), 1.66 (s, 1H), 1.52-1.34 (m, 6H), 0.93 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.4, 133.2, 128.6, 127.4, 126.5, 126.2, 71.3, 41.3, 36.8, 28.0, 22.8, 14.2.

GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ M^+ : 204.2; found: 204.0.



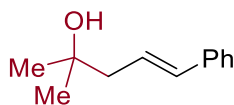
(*E*)-1-Phenyldec-1-en-4-ol (5d)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:15) as light yellow oil. 43 mg, 62% yield. The ratio of regioisomers was determined to be 8:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.20 (m, 1H), 6.49 (d, $J = 15.8$ Hz, 1H), 6.24 (ψdt, $J = 15.8, 7.2$ Hz, 1H), 3.76-3.70 (m, 1H), 2.48-2.42 (m, 1H), 2.35-2.28 (m, 1H), 1.55-1.50 (m, 4H), 1.36-1.27 (m, 7H), 0.89 (t, $J = 5.7$ Hz, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.5, 133.3, 128.7, 127.4, 126.6, 126.3, 71.4, 41.3, 37.1, 32.0, 29.5, 25.8, 22.8, 14.2.

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{24}\text{O}$ M^+ : 232.2; found: 231.9.



(4*E*)-2-Methyl-5-phenylpent-4-en-2-ol (5e)

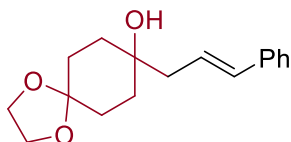
Cy_2NMe (105 μL , 0.45 mmol) was added as a base to increase the yield of product.

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as colorless oil. 27.5 mg, 52% yield. The ratio of regioisomers in the crude mixture was determined to be 12:1 by GC. The two isomers were separated by silica.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38 (d, $J = 7.8$ Hz, 2H), 7.33-7.29 (m, 2H), 7.24-7.22 (m, 1H), 6.47 (d, $J = 15.8$ Hz, 1H), 6.31 (dt, $J = 15.8, 7.5$ Hz, 1H), 2.39 (d, $J = 7.5$ Hz, 2H), 1.49 (s, 1H), 1.28 (s, 6H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.5, 133.9, 128.7, 127.4, 126.3, 125.9, 71.1, 47.5, 29.4.

GC-MS (EI): Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ M^+ : 176.1; found: 176.1.



8-Cinnamyl-1,4-dioxaspiro[4.5]decan-8-ol (5f)

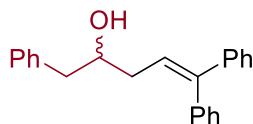
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:4) as colorless oil. 49 mg, 60% yield.

The ratio of regioisomers was determined to be 20:1 by GC.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38-7.28 (m, 4H), 7.25-7.21 (m, 1H), 6.47 (d, $J = 15.8$ Hz, 1H), 6.29 (dt, $J = 15.8, 7.4$ Hz, 1H), 3.96-3.94 (m, 4H), 2.39 (d, $J = 7.5$ Hz, 2H), 1.96-1.88 (m, 2H), 1.74-1.70 (m, 3H), 1.64-1.58 (m, 3H), 1.39 (br s, OH).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.3, 134.3, 128.7, 127.5, 126.3, 125.0, 108.9, 70.7, 64.4, 64.3, 46.2, 35.0, 30.7.

GC-MS (EI): Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$ M^+ : 274.2; found: 274.2.

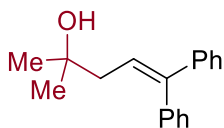
**1,5,5-Triphenylpent-4-en-2-ol (5g)**

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as light yellow oil. 71 mg, 75% yield. The ratio of regioisomers in the crude mixture was determined to be 20:1 by ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.36-7.13 (m, 15H), 6.19 (ψ t, $J = 7.4$ Hz, 1H), 3.93-3.87 (m, 1H), 2.78 (dd, $J = 13.6, 4.5$ Hz, 1H), 2.64 (dd, $J = 13.6, 8.3$ Hz, 1H), 2.38-2.34 (m, 2H), 1.69 (s, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 144.0, 142.4, 139.8, 138.3, 129.8, 129.3, 128.5, 128.2, 128.0, 127.2, 127.1, 127.0, 126.4, 125.2, 72.7, 43.4, 37.0.

GC-MS (EI): Calcd for $\text{C}_{23}\text{H}_{22}\text{O}$ M^+ : 314.2; found: 314.1.

**2-Methyl-5,5-diphenylpent-4-en-2-ol (5h)**

Veratrole (1.2 mL) was used instead of dioxane to increase the yield of product.

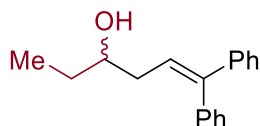
The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as light yellow oil. 48 mg, 64%

yield. The ratio of regioisomers was determined to be 12:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38-7.34 (m, 2H), 7.32-7.17 (m, 8H), 6.23 (t, $J = 7.6$ Hz, 1H), 2.31 (d, $J = 7.6$ Hz, 2H), 1.38 (s, 1H), 1.22 (s, 6H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 144.1, 142.7, 140.0, 130.0, 128.2, 128.1, 127.2, 127.1, 127.0, 125.0, 71.4, 43.6, 29.4.

GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ M^+ : 252.2; found: 252.0.



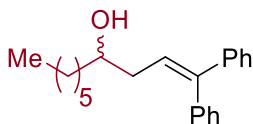
6,6-Diphenylhex-5-en-3-ol (5i)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:8) as light yellow oil. 53 mg, 70% yield. The ratio of regioisomers was determined to be 16:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38-7.34 (m, 2H), 7.31-7.29 (m, 1H), 7.25-7.17 (m, 7H), 6.17 (q, $J = 7.5$ Hz, 1H), 3.67-3.61 (m, 1H), 2.33-2.25 (m, 2H), 1.61 (s, 1H), 1.54-1.40 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 144.0, 142.6, 140.0, 130.0, 128.3, 128.2, 127.3, 127.2, 127.1, 125.6, 73.4, 37.3, 29.8, 10.0.

GC-MS (EI): Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ M^+ : 252.2; found: 252.0.



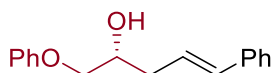
1,1-Diphenyldec-1-en-4-ol (5j)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:20) as light yellow oil. 61 mg, 66% yield. The ratio of regioisomers was determined to be 15:1 by crude ^1H NMR spectroscopy.

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.38-7.34 (m, 2H), 7.31-7.27 (m, 1H), 7.25-7.17 (m, 7H), 6.16 (ψt, $J = 7.6$ Hz, 1H), 3.72-3.68 (m, 1H), 2.36-2.22 (m, 2H), 1.54 (s, 1H), 1.46-1.25 (m, 10H), 0.87 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 144.0, 142.5, 139.9, 129.9, 128.2, 128.0, 127.2, 127.0, 126.9, 125.5, 71.9, 37.6, 37.0, 31.8, 29.2, 25.5, 22.6, 14.0.

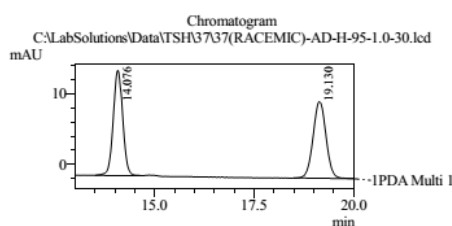
GC-MS (EI): Calcd for $\text{C}_{22}\text{H}_{28}\text{O}$ M^+ : 308.2; found: 307.9.



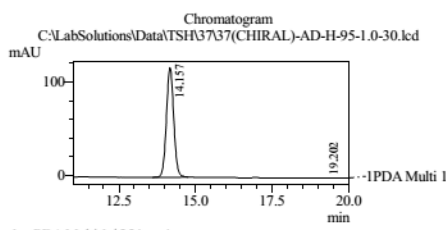
(2*R*,4*E*)-1-Phenoxy-5-phenyl-pent-4-en-2-ol (5k)

A sample of enantiopure epoxide (99.6% ee, TCI) was used. The product was isolated by flash chromatography (ethyl acetate/hexanes 1:8) as white solid. 47 mg, 62% yield in 99.7% ee. The ratio of regioisomers was determined to be 9:1 by crude ^1H NMR spectroscopy.

Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95:5, flow rate = 1.0 mL/min.



Peak#	Ret. Time	Area	Area %
1	14.076	246573	50.158
2	19.130	245018	49.842
Total		491591	100.000



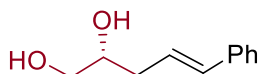
Peak#	Ret. Time	Area	Area %
1	14.157	1939370	99.856
2	19.202	2789	0.144
Total		1942158	100.000

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.37-7.34 (m, 2H), 7.31-7.26 (m, 4H), 7.23-7.19 (m, 1H), 6.98-6.91 (m, 3H), 6.51 (d, $J = 15.8$ Hz, 1H), 6.29 (ψdt, $J = 15.8, 7.2$ Hz, 1H), 4.17-4.11 (m, 1H), 4.01 (dd, $J = 9.4, 3.6$ Hz, 1H), 3.92 (dd, $J = 9.4, 7.0$ Hz, 1H), 2.57-2.52 (m, 2H), 2.39 (d, $J = 3.9$ Hz, 1H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 158.7, 137.3, 133.4, 129.7, 128.7, 127.5, 126.3, 125.4, 121.3, 114.8, 71.6, 69.9, 37.3.

GC-MS (EI): Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ M^+ : 254.1; found: 254.0.

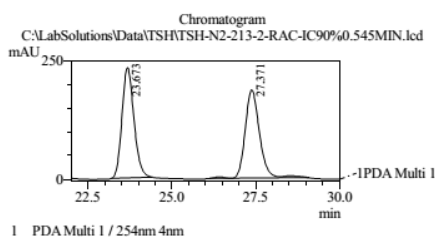
$[\alpha]_D^{23} = -15.3^\circ$ ($c = 1.40$, CHCl_3).



(2*R*,4*E*)-5-Phenyl-4-pent-4-ene-1,2-diol (5l)

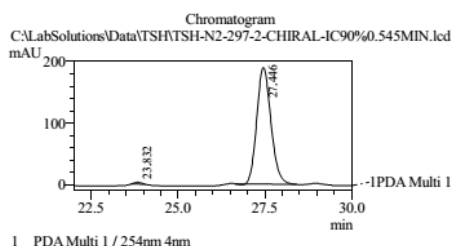
An epoxide of 99.6% ee (TCI) was used. The product was isolated by flash chromatography (ethyl acetate/ hexanes 1:1) as colorless oil. 26 mg, 48% yield. The ratio of regioisomers in the crude mixture was determined to be 8:1 by GC. The two isomers were separated by silica. The major isomer was in 98.5% ee.

Daicel Chiralcel IC, *n*-hexane/isopropanol 90:10, flow rate = 0.5 mL/min.



PeakTable

Peak#	Ret. Time	Area	Area %
1	23.673	5759727	50.740
2	27.371	5591797	49.260
Total		11351524	100.000



PeakTable

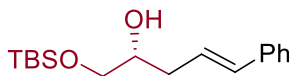
Peak#	Ret. Time	Area	Area %
1	23.832	41749	0.773
2	27.446	5361406	99.227
Total		5403154	100.000

¹H NMR of the major isomer (400 MHz, CDCl₃): δ 7.37-7.35 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.22 (ψdt, *J* = 15.8, 7.3 Hz, 1H), 3.88-3.82 (m, 1H), 3.73 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.54 (dd, *J* = 11.1, 7.1 Hz, 1H), 2.44-2.39 (m, 2H), 2.24 (s, 1H), 2.02 (s, 1H).

¹³C NMR of the major isomer (100 MHz, CDCl₃): δ 137.2, 133.5, 128.7, 127.6, 126.3, 125.5, 71.7, 66.5, 37.3.

GC-MS (EI): Calcd for C₁₁H₁₄O₂ M⁺: 178.1; found: 178.1.

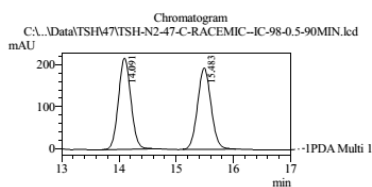
[α]_D²³ = +4.1° (*c* = 0.98, CHCl₃).



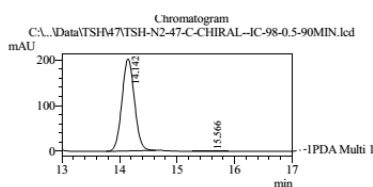
(2*R*,4*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5-phenyl-pent-4-en-2-ol (5m)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:25) as colorless oil. 60 mg, 68% yield. The ratio of regioisomers was determined to be 18:1 by crude ¹H NMR spectroscopy. The major isomer was in 99.6% ee.

Daicel Chiralcel IC, *n*-hexane/isopropanol 98:2, flow rate = 0.5 mL/min.



PeakTable			
Peak#	Ret. Time	Area	Area %
1	14.091	3284167	50.825
2	15.483	3177603	49.175
Total		6461770	100.000



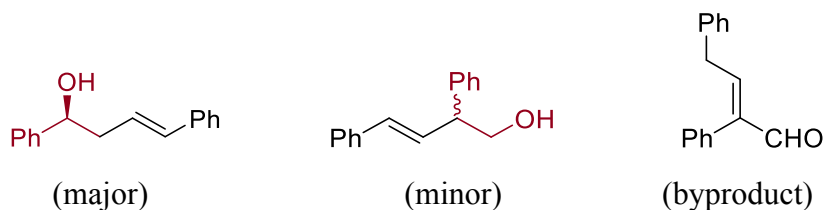
PeakTable			
Peak#	Ret. Time	Area	Area %
1	14.142	3035287	99.815
2	15.566	5640	0.185
Total		3040927	100.000

^1H NMR of the major isomer (400 MHz, CDCl_3): δ 7.37-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.25 (ψ dt, J = 15.8, 7.2 Hz, 1H), 3.82-3.75 (m, 1H), 3.67 (dd, J = 10.0, 3.7 Hz, 1H), 3.51 (dd, J = 10.0, 6.8 Hz, 1H), 2.45 (d, J = 4.0 Hz, 1H), 2.42-2.38 (m, 2H), 0.92 (s, 9H), 0.09 (s, 6H).

^{13}C NMR of the major isomer (100 MHz, CDCl_3): δ 137.6, 132.6, 128.6, 127.3, 126.2, 71.6, 66.7, 37.0, 26.0, 18.4, -5.1, -5.2.

LC-MS (ESI): Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$: 293.2; found: 293.2.

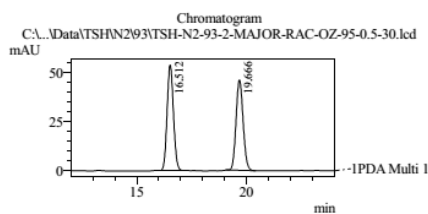
$[\alpha]_D^{23}$ = -3.4° (c = 0.60, CHCl_3).



An epoxide of 99.5% ee (Aldrich) was used. The product was isolated by flash chromatography (ethyl acetate/hexanes 1:12) as white solid. 28 mg, 42% combined yield of two regioisomers. The ratio of regioisomers in the crude mixture was determined to be 2:1 by GC. Epoxide isomerization to phenylacetaldehyde and subsequent aldol condensation produced two isomers of byproducts (34 mg, 52% yield with E/Z ratio of 7:1).

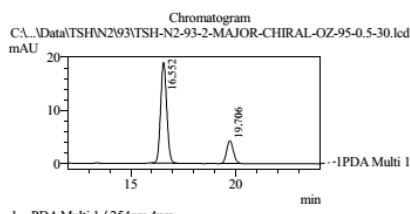
(E)-1,4-Diphenylbut-3-en-1-ol (5n) [84107-76-6]⁶

The major isomer was in 60% ee. Daicel Chiralcel OZ, *n*-hexane/isopropanol 95:5, flow rate = 0.5 mL/min.



PeakTable

Peak#	Ret. Time	Area	Area %
1	16.512	1071710	51.160
2	19.666	1023107	48.840
Total		2094818	100.000



PeakTable

Peak#	Ret. Time	Area	Area %
1	16.552	380978	80.701
2	19.706	91109	19.299
Total		472087	100.000

^1H NMR (400 MHz, CDCl_3): δ 7.39-7.34 (m, 6H), 7.32-7.28 (m, 3H), 7.24-7.22 (m, 1H), 6.51 (d, $J = 15.9$ Hz, 1H), 6.22 (ψdt , $J = 15.9, 7.4$ Hz, 1H), 4.84-4.80 (m, 1H), 2.70-2.66 (m, 2H), 2.06 (d, $J = 3.3$ Hz, OH).

^{13}C NMR (100 MHz, CDCl_3): δ 144.1, 137.4, 133.6, 128.7, 128.6, 127.8, 127.5, 126.3, 126.0, 125.9, 73.9, 43.2.

LC-MS (ESI): Calcd for $\text{C}_{16}\text{H}_{16}\text{ONa}$ ($\text{M}+\text{Na}$) $^+$: 247.1; found: 247.2.

$[\alpha]_D^{23} = -12.3^\circ$ ($c = 0.70$, CHCl_3).

(*E*)-2,4-Diphenylbut-3-en-1-ol (5n')

The minor isomer was in 0% ee. Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95:5, flow rate = 0.5 mL/min.

^1H NMR (400 MHz, CDCl_3): δ 7.39-7.34 (m, 4H), 7.32-7.29 (m, 5H), 7.26-7.20 (m, 1H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.39 (dd, $J = 16.0, 7.8$ Hz, 1H), 3.92 (ψt , $J = 6.0$ Hz, 2H), 3.71 (ψq , $J = 7.3$ Hz, 1H), 1.51 (t, $J = 6.3$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.0, 137.1, 132.4, 129.8, 129.0, 128.7, 128.2, 127.7, 127.2, 126.4, 66.6, 52.0.

LC-MS (ESI): Calcd for $\text{C}_{16}\text{H}_{16}\text{ONa}$ ($\text{M}+\text{Na}$) $^+$: 247.1; found: 247.2.

Byproduct: (*E*)-2,4-Diphenylbut-2-enal (5n'') [115872-75-8]⁷

The NMR spectroscopy of this compound was identified by comparison with reported NMR data.

^1H NMR (400 MHz, CDCl_3): δ 9.65 (s, 1H), 7.45-7.35 (m, 3H), 7.33-7.29 (m, 2H), 7.26-7.22 (m, 3H), 7.16-7.14 (m, 2H), 6.86 (t, $J = 7.6$ Hz, 1H), 3.68 (d, $J = 7.6$ Hz, 2H).

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{14}\text{O}$ M^+ : 222.1; found: 222.1.

V. Mechanistic studies

(a) Ring opening of epoxides with $\text{NEt}_3\cdot\text{HI}$

A typical procedure: Two 10 mL Schlenk tubes containing a magnetic stir bar were charged with cyclohexene oxide (10.4 μL , 0.1 mmol), $\text{NEt}_3\cdot\text{HI}$ (28 mg, 0.12 mmol), 10 μL of GC standard *n*-dodecane and dry PhCF_3 (0.3 mL). The experiments were conducted at 25 $^\circ\text{C}$ and 80 $^\circ\text{C}$, respectively. At intervals, aliquots of the reaction mixture were taken and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC analysis for determination of the yield of **1j**. Only the *trans* isomer of **1j** was detected by GC and GCMS.

Table S6. Ring opening of cyclohexene oxide in the presence of $\text{NEt}_3\cdot\text{HI}$

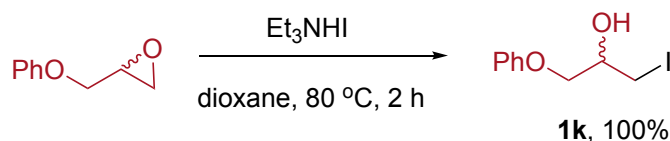
1j

Entry	Temp ($^\circ\text{C}$)	Time (min)	Yield (%)
1	25	120	0
2	80	40	42
3	80	60	65
4	80	120	100

trans-2-Iodocyclohexanol (**1j**) [10039-14-2]⁸

^1H NMR (400 MHz, CDCl_3): δ 4.07-4.00 (m, 1H), 3.65 (ψtd, $J = 9.9, 4.5$ Hz, 1H), 2.50-2.45 (m, 1H), 2.34 (br s, OH), 2.14-2.00 (m, 2H), 1.86-1.82 (m, 1H), 1.55-1.49 (m, 1H), 1.42-1.23 (m, 3H).

GC-MS (EI): Calcd for $\text{C}_6\text{H}_{11}\text{IO}$ M^+ : 226.0; found: 226.0.

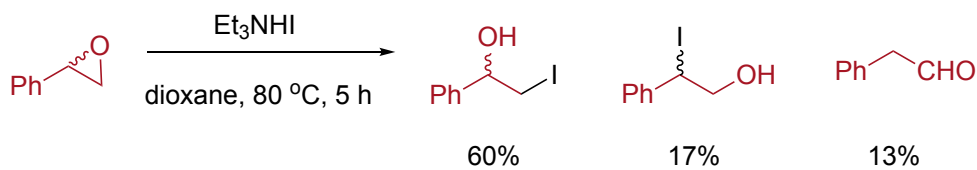


1-Iodo-3-phenoxypropan-2-ol (1k) [82430-40-8]⁹

Dioxane was used instead of PhCF₃, since dioxane was used in the catalytic reaction of terminal epoxides. The iodide was added selectively to the less hindered carbon of the epoxide by GCMS and NMR spectroscopy.¹⁰

¹H NMR (400 MHz, CDCl₃): δ 7.32-7.28 (m, 2H), 7.01-6.99 (m, 1H), 6.93-6.91 (m, 2H), 4.13-4.04 (m, 2H), 4.02-3.96 (m, 1H), 3.48 (dd, *J* = 10.3, 5.3 Hz, 1H), 3.40 (dd, *J* = 10.3, 5.8 Hz, 1H), 2.52 (br s, OH).

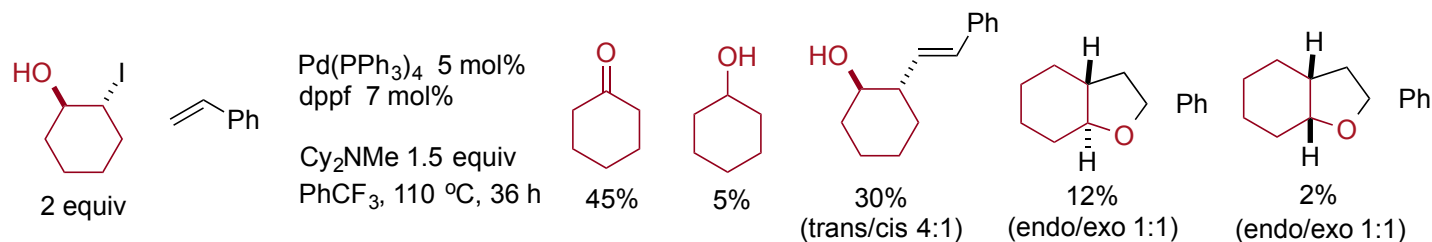
GC-MS (EI): Calcd for C₉H₁₁IO₂ M⁺: 278.0; found: 277.9.



For ring opening of styrene oxide, dioxane was used instead of PhCF₃. After 5 h, 90% conversion of epoxide was detected. The ratio of regioisomers generated from β- and α-attack was determined to be 3.5:1 by crude ¹H NMR spectroscopy. Phenylacetaldehyde was formed by epoxide isomerization in 13% NMR yield.

(b) Heck-type reaction of *trans*-2-iodocyclohexanol

A typical procedure: In an argon-filled glove box, Pd(PPh₃)₄ (29 mg, 0.025 mmol), dppf (19.5 mg, 0.035 mmol) and dry PhCF₃ (2 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, **1j** (226 mg, 1 mmol), styrene (58.5 μL, 0.5 mmol), Cy₂NMe (175 μL, 0.75 mmol) and 20 μL of GC standard *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110 °C for 24 h. After cooled down to rt, aliquots were taken from the reaction mixture and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC and GCMS to determine the distribution of products.



trans-2-Phenylcyclohexanol [2159069-08-4]¹¹ and *cis*-2-Phenylcyclohexanol [2159069-07-3]¹¹

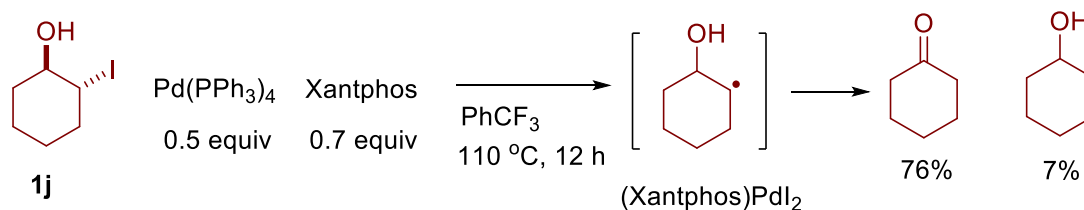
The four isomers were inseparable by silica gel and they were isolated by flash chromatography (hexanes) as colorless oil. 14 mg in total, containing 12% yield for the trans isomers and 2 mg of cis isomers. The endo/exo ratio of both trans and cis isomers was determined to be 1:1 by ^1H NMR spectroscopy. The structural assignment of the four isomers was assisted by comparison with reported NMR data.

^1H NMR of a mixture of four diastereomers (400 MHz, CDCl_3): δ 7.34-7.23 (m, 6H), 5.18 (ψt , $J = 7.3$ Hz, 0.1H), 5.09-5.05 (m, 1H), 4.96 (ψt , $J = 8.1$ Hz, 0.1H), 4.24 (ψq , $J = 3.4$ Hz, 0.1H), 4.02 (ψq , $J = 4.7$ Hz, 0.1H), 3.40 (ψtd , $J = 9.8, 3.6$ Hz, 0.5H), 3.24 (ψtd , $J = 10.3, 3.8$ Hz, 0.5H), 2.49-2.41 (m, 0.7H), 2.28-2.12 (m, 1.6H), 2.08-1.80 (m, 3.6H), 1.75-1.15 (m, 7.3H).

^{13}C NMR of a mixture of four diastereomers (100 MHz, CDCl_3): δ 145.1 and 145.0, 128.5 and 128.4, 127.1, 126.0 and 125.6, 84.5 and 84.2, 80.0 and 79.0, 46.9 and 44.2, 41.2 and 40.1, 31.8 and 31.6, 29.2 and 29.1, 26.0 and 25.9, 24.5.

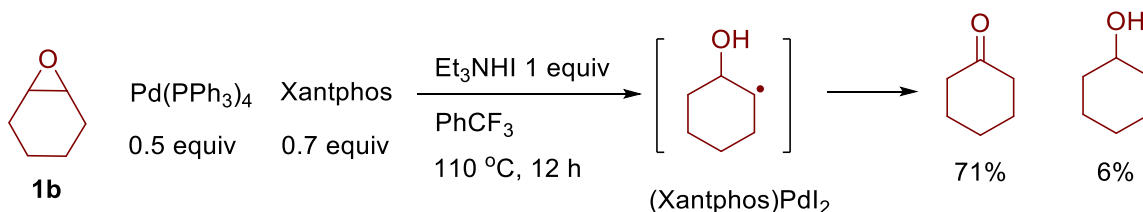
GC-MS (EI): Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ M^+ : 202.1; found: 202.1.

(c) A stoichiometric reaction of in situ formed palladium(0) complex of Xantphos and 1j



A typical procedure. In an argon-filled glove box, $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol), Xantphos (20 mg, 0.035 mmol) and dry PhCF_3 (0.4 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, **1j** (11.3 mg, 0.05 mmol) and 10 μL of GC standard, *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at $110\text{ }^\circ\text{C}$ for 12 h. After cooled down to rt, aliquots were taken from the reaction mixture and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC and GCMS to determine the distribution of products.

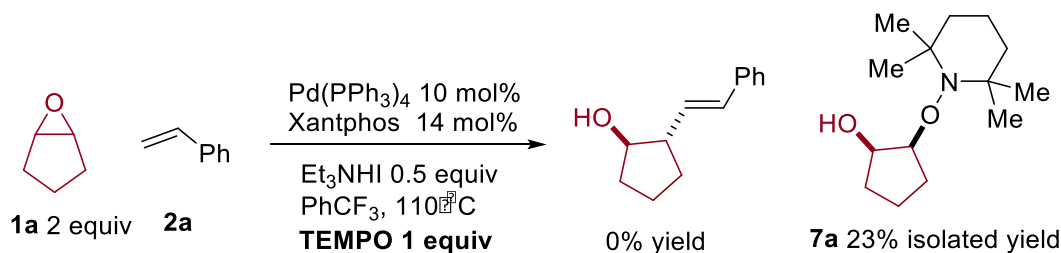
(d) A stoichiometric reaction with 1b in the presence of 1 equiv of Et_3NHI



A typical procedure. In an argon-filled glove box, $\text{Pd(PPh}_3)_4$ (29 mg, 0.025 mmol), Xantphos (20 mg, 0.035 mmol) and dry PhCF_3 (0.4 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, **1b** (5.2 μL , 0.05 mmol), $\text{NEt}_3\cdot\text{HI}$ (11.5 mg, 0.05 mmol), and 10 μL of GC standard, *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110°C for 12 h. After cooled down to rt, aliquots were taken from the reaction mixture and passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC and GCMS to determine the yields of products by comparing with authentic samples.

(e) TEMPO-trapping experiment

A typical procedure. In an argon-filled glove box, $\text{Pd(PPh}_3)_4$ (46.2 mg, 0.04 mmol), Xantphos (32.4 mg, 0.056 mmol) and dry PhCF_3 (0.8 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, cyclopentene oxide (71.2 μL , 0.8 mmol), $\text{NEt}_3\cdot\text{HI}$ (45.8 mg, 0.2 mmol), styrene (46.8 μL , 0.4 mmol), TEMPO (62.5 mg, 0.4 mmol) and 20 μL of GC standard, *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110°C for 24 h. After cooled down to rt, no Heck product was detected by GC and GCMS. The TEMPO-trapped byproduct was isolated and its *cis* configuration was assigned by comparison with reported NMR data.¹²



cis-2-[(2,2,6,6-Tetramethylpiperidin-1-yl)oxy]cyclopentanol (**7a**) [1826104-56-6]

The byproduct was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as light yellow oil. 22 mg, 23%

yield.

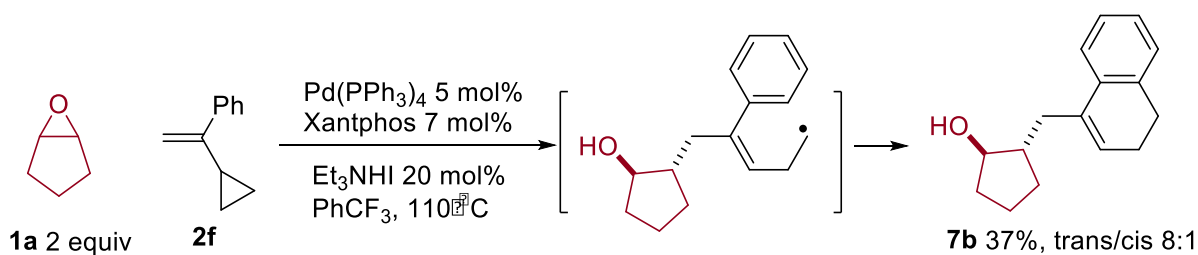
^1H NMR (400 MHz, CDCl_3): δ 4.20 (ψt , $J = 4.1$ Hz, 1H), 4.11 (ψtd , $J = 9.1, 4.2$ Hz, 1H), 2.44 (s, 1H), 2.09-2.01 (m, 1H), 1.81-1.62 (m, 4H), 1.55-1.36 (m, 7H), 1.22-1.08 (m, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 89.4, 71.6, 59.7, 40.4, 33.8, 30.8, 28.3, 20.7, 20.3, 19.5, 17.3.

HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{28}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 242.2120; found: 242.2120.

(f) Heck type reaction of α -cyclopropylstyrene

A typical procedure. In an argon-filled glove box, $\text{Pd}(\text{PPh}_3)_4$ (17.4 mg, 0.015 mmol), Xantphos (12.3 mg, 0.021 mmol) and dry PhCF_3 (1.2 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, cyclopentene oxide (54 μL , 0.6 mmol), $\text{NEt}_3\cdot\text{HI}$ (13.8 mg, 0.06 mmol), α -cyclopropylstyrene (43.3 mg, 0.3 mmol) and 20 μL of GC standard, *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110 $^\circ\text{C}$ for 48 h. After cooled down to rt, the reaction mixture was subjected to flash chromatography with ethyl acetate/ hexanes as eluent.



trans-2-[(3,4-Dihydro-1-naphthyl)methyl]cyclopentanol (**7b**)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:12) as colorless oil. 25 mg, 37% yield. The ratio of *trans* and *cis* isomers was determined to be 8:1 by GC and GCMS. No other isomer was detected by GCMS.

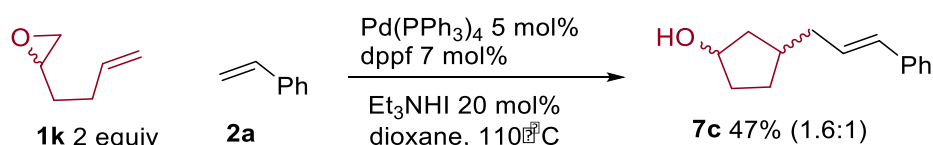
^1H NMR of *trans* isomer (400 MHz, CDCl_3): δ 7.30-7.14 (m, 4H), 5.90 (t, $J = 4.5$ Hz, 1H), 3.92 (ψq , $J = 5.8$ Hz, 1H), 2.74 (ψt , $J = 8.0$ Hz, 2H), 2.58 (dd, $J = 14.0, 7.0$ Hz, 1H), 2.36 (dd, $J = 14.0, 8.0$ Hz, 1H), 2.28-2.23 (m, 2H), 2.01-1.85 (m, 3H), 1.70-1.54 (m, 3H), 1.45 (s, 1H), 1.29-1.22 (m, 1H).

^{13}C NMR of *trans* isomer (100 MHz, CDCl_3): δ 136.9, 135.8, 134.7, 127.8, 126.9, 126.5, 126.1, 123.0, 79.4, 46.5, 37.3, 34.3, 30.3, 28.6, 23.3, 21.6.

GC-MS (EI): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$ M^+ : 228.2; found: 228.2.

(g) Heck-type reaction of 1,2-epoxy- 5-hexene

A typical procedure: In an argon-filled glove box, Pd(PPh₃)₄ (17.4 mg, 0.015 mmol), dppf (11.7 mg, 0.021 mmol) and dry dioxane (1.2 mL) were charged into a dry 10 mL Schlenk tube. After stirring at rt for 10 min, 1,2-epoxy-5-hexene (70 μL, 0.6 mmol), NEt₃·HI (13.8 mg, 0.06 mmol), styrene (35 μL, 0.3 mmol) and 20 μL of GC standard *n*-dodecane were added sequentially. The reaction mixture was capped tightly and vigorously stirred in a heating block maintained at 110 °C for 48 h. After cooled down to rt, the reaction mixture was subjected to flash chromatography with ethyl acetate/hexanes as eluent.



3-[(*E*)-Cinnamyl]cyclopentanol (**7c**)

The product was isolated by flash chromatography (ethyl acetate/hexanes 1:10) as colorless oil. 29 mg, 47% yield. The ratio of diastereomers was determined to be 1.6:1 by crude ¹H NMR spectroscopy.

¹H NMR of a mixture of two diastereomers (400 MHz, CDCl₃): δ 7.36-7.28 (m, 6.4H), 7.22-7.18 (m, 1.6H), 6.42-6.37 (m, 1.6H), 6.23 (major isomer, *ψ*td, *J* = 7.1, 1.7 Hz, 1H), 6.19 (minor isomer, *ψ*td, *J* = 6.8, 2.0 Hz, 0.6H), 4.39-4.29 (m, 1.6H), 2.34-2.14 (m, 4.8H), 2.04-1.95 (m, 1.6H), 1.84-1.42 (m, 8H), 1.30-1.24 (m, 1.6H).

¹³C NMR of a mixture of two diastereomers (100 MHz, CDCl₃): δ 137.9, 130.7, 129.9, 128.6 (and 128.9), 127.0, 126.1 (and 126.2), 73.8, 42.0 (and 42.3), 40.1 (and 39.4), 38.4 (and 37.4), 35.3 (and 35.6), 30.1 (and 30.0).

GC-MS (EI): Calcd for C₁₄H₁₈O M⁺: 202.1; found: 202.0.

(h) Synthesis of (bisphosphine)PdI₂ complexes

The complexes were prepared according to a reported procedure.¹³ A mixture of PdI₂ (108 mg, 0.3 mmol), bisphosphine (0.3 mmol) and dry toluene (0.3 mL) were added to a dry 10 mL Schlenk tube under argon. The reaction mixture was stirred at 120 °C for 3 h. After cooled down to rt, the crude product was filtered under vacuum in air, and then washed carefully with anhydrous Et₂O. The precipitate was collected and dried under vacuum. These complexes have poor solubility in d₆-DMSO.

Pd(Xantphos)I₂

¹H NMR (400 MHz, CD₂Cl₂): δ 7.73-7.71 (m, 8H), 7.47-7.09 (m, 18H), 1.82 (s, 6H).

¹³C NMR (100 MHz, CD₂Cl₂): δ 154.0, 135.2, 134.9, 132.7, 130.5, 130.3, 128.1, 127.9, 126.2, 124.0, 36.1, 29.0.

Broad peaks were recorded due to structural dynamics.

³¹P NMR (162 MHz, CD₂Cl₂): δ 16.3, 4.0 (due to partial ionization of the complex).

LC-MS (ESI): Calcd for C₃₉H₃₂OP₂I₂Pd (M-I)⁺: 811.0; found: 811.1.

Pd(dppf)I₂

¹H NMR (400 MHz, CD₂Cl₂): δ 7.95-7.90 (m, 8H), 7.55-7.47 (m, 12H), 4.40 (s, 4H), 4.20 (s, 4H).

¹³C NMR (100 MHz, CD₂Cl₂): δ 135.2, 135.2, 135.1, 134.4, 133.9, 131.0, 127.9, 127.9, 127.8, 127.7, 76.2, 76.1, 76.1, 75.8, 75.7, 75.3, 75.2, 73.7, 73.7, 73.6.

³¹P NMR (162 MHz, CD₂Cl₂): δ 24.5.

LC-MS (ESI): Calcd for C₃₄H₂₈FeP₂I₂Pd (M-I)⁺: 786.9; found: 786.4.

Pd(dppp)I₂

¹H NMR (400 MHz, CD₂Cl₂): δ 7.80-7.76 (m, 8H), 7.55-7.48 (m, 12H), 2.45-2.40 (m, 4H), 2.10-1.99 (m, 2H).

¹³C NMR (100 MHz, CD₂Cl₂): δ 133.8, 131.7, 131.3, 128.4, 25.3, 18.2.

³¹P NMR (162 MHz, CD₂Cl₂): δ 0.5.

LC-MS (ESI): Calcd for C₂₇H₂₆P₂I₂Pd (M-I)⁺: 645.0; found: 645.1.

(i) Cyclic voltammetry measurement

The cyclic voltammetry experiments were conducted with a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat in a three-electrode cell. All electrochemical measurements were carried out under an argon atmosphere and the samples were bubbled with argon before measurement. Cyclic voltammograms of 1.0 mM Pd complexes or alkyl iodides with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte were recorded respectively at a scan rate of 100 mV/s with a planar glassy carbon disc (1mm diameter) as working electrode, a platinum wire as counter electrode and an Ag wire (in 0.5 M *n*-Bu₄NPF₆ in CH₃CN) as a pseudo-reference electrode at 298±2 K.

Ferrocene (Fc) was added to the sample solution as an internal reference.

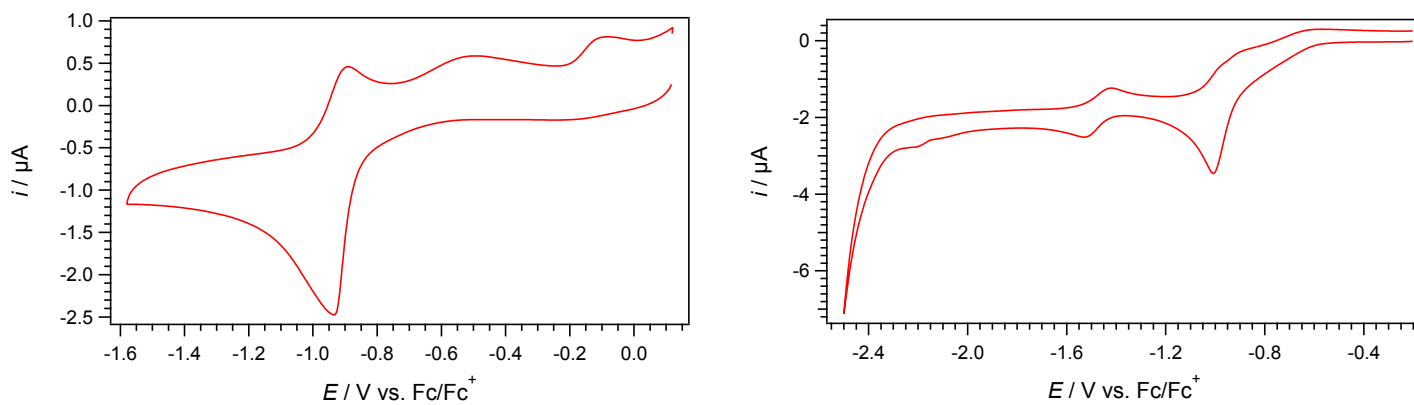


Figure S1. Cyclic voltammograms of 1.0 mM Pd(Xantphos)I₂ in PhCN (left) and DCM (right)

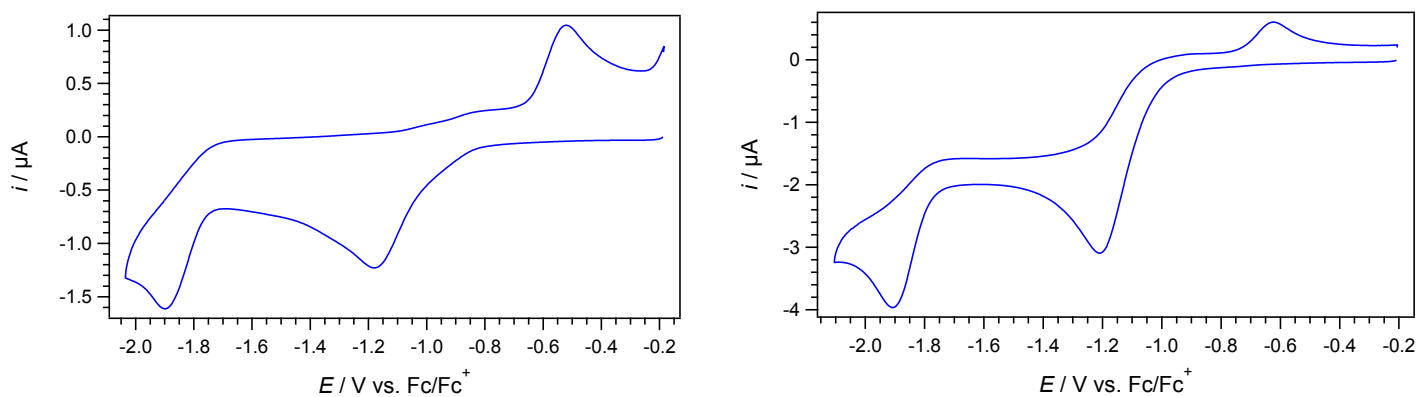


Figure S2. Cyclic voltammograms of 1.0 mM Pd(dppf)I₂ in PhCN (left) and DCM (right)

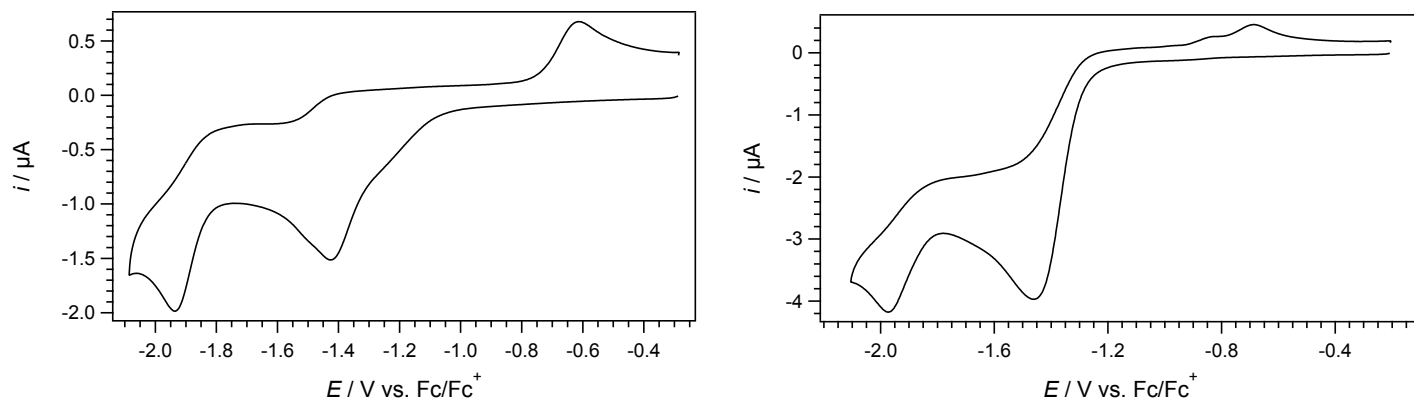


Figure S3. Cyclic voltammograms of 1.0 mM Pd(dppp)I₂ in PhCN (left) and DCM (right)

Table S7. Reduction potentials of Pd complexes ($E_{1/2}^{\text{red}}$). All potentials are reported as volts versus the ferrocene/ferrocenium couple

compound	solvent	$E_{1/2}$ (II/I)	$E_{1/2}$ (II/0)	$E_{1/2}$ (I/0)
Pd(Xantphos) I_2	DCM	-0.95		-1.48
	PhCN		-0.90	
Pd(dppf) I_2	DCM	-1.12		-1.84
	PhCN	-1.07		-1.82
Pd(dppp) I_2	DCM	-1.34		-1.90
	PhCN	-1.33		-1.88

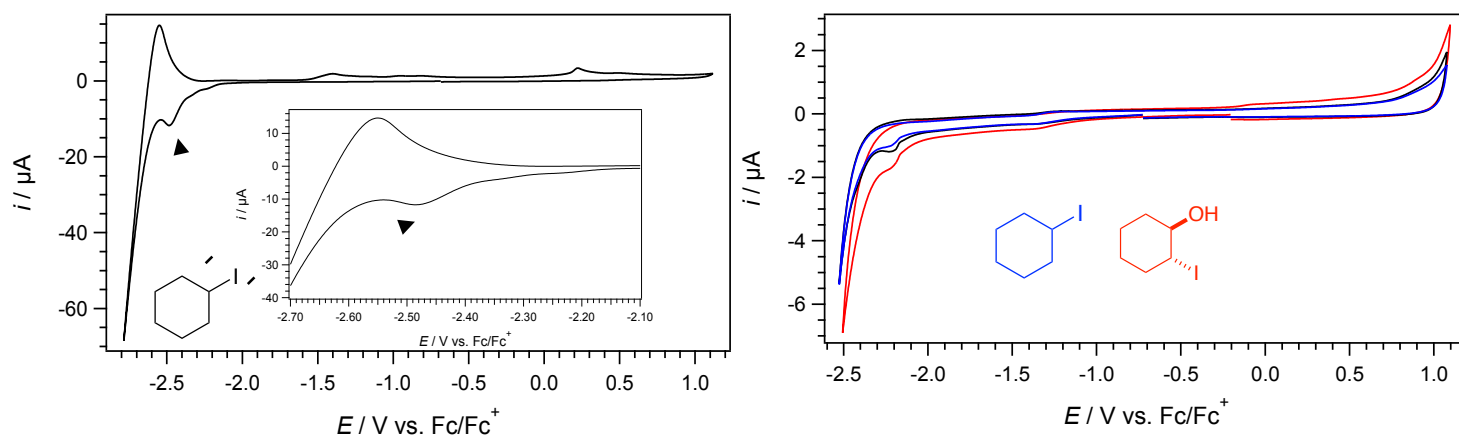


Figure S4. Cyclic voltammograms of 1.0 mM alkyl iodides in PhCN (left) and DCM (right). Reduction potential of CyI is -2.20 V in DCM and -2.47 V in PhCN and reduction potential of β -iodohydrin is -2.21 V in DCM.

VI. Reference

- (1) Ikeda, Y.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. Cobalt-Mediated Mizoroki–Heck-Type Reaction of Epoxide with Styrene. *Adv. Synth. Catal.* **2004**, *346*, 1631-1634.
- (2) Steiner, D.; Ivison, L.; Goralski, C. T.; Appell, R. B.; Gojkovic, J. R.; Singaram, B. A Facile and Efficient Method for the Kinetic Separation of Commercially Available *cis*- and *trans*-Limonene Epoxide. *Tetrahedron: Asymmetry* **2002**, *13*, 2359-2363.
- (3) Matovic, N. J.; Stuthe, J. M. U.; Challinor, V. L.; Bernhardt, P. V.; Lehmann, R. P.; Kitching, W.; De Voss, J. J. The Truth About False Unicorn (*Chamaelirium Luteum*): Total Synthesis of 23*R*,24*S*-Chiograsterol B Defines the Structure and Stereochemistry of the Major Saponins from this Medicinal Herb. *Chem.-Eur. J.* **2011**, *17*, 7578-7591.
- (4) Szendi, Z.; Forgó, P.; Sweet, F. Complete ¹H and ¹³C NMR Spectra of Pregnenolone. *Steroids* **1995**, *60*, 442-446.
- (5) Furlani, D.; Marton, D.; Tagliavini, G.; Zordan, M. Hydrated δ -Bonded Organometallic Cations in Organic Synthesis: I. Allyl-, Crotyl-, 1-Methylallyl-, Cyclohex-2-enyl-, and Cinnamyl-Stannation of Carbonyl Compounds in Water. *J. Organomet. Chem.* **1988**, *341*, 345-356.
- (6) (a) Nokami, J.; Anthony, L.; Sumida, S.-i. New Route to α -Adducts of Homoallylic Alcohols by an Acid-Catalyzed Stereospecific Allyl-Transfer Reaction from γ -Adducts. *Chem.-Eur. J.* **2000**, *6*, 2909-2913. (b) Lee, K. S.; Ready, J. M. Titanium-Mediated Oxidative Arylation of Homoallylic Alcohols. *Angew. Chem.* **2011**, *123*, 2159-2162.
- (7) Kim, J.-H.; Kulawiec, R. J. A Tandem Epoxide Isomerization–Aldol Condensation Process Catalyzed by Palladium Acetate–Tributylphosphine. *J. Org. Chem.* **1996**, *61*, 7656-7657.
- (8) (a) Durgaiiah, C.; Naresh, M.; Arun Kumar, M.; Swamy, P.; Reddy, M. M.; Srujana, K.; Narender, N. Regio- and Stereoselective Co-Iodination of Olefins Using NH₄I and Oxone. *Synth. Commun.* **2016**, *46*, 1133-1144. (b) Carrera, I.; Brovetto, M. C.; Seoane, G. A. Selenium-Catalyzed Iodohydrin Formation from Alkenes. *Tetrahedron Lett.* **2006**, *47*, 7849-7852.
- (9) (a) Sharghi, H.; Massah, A. R.; Eshghi, H.; Niknam, K. Crown Ethers as New Catalysts in the Highly Regioselective Halogenative Cleavage of Epoxides with Elemental Halogen. *J. Org. Chem.* **1998**, *63*, 1455-1461.

- (b) Ellwood, A. R.; Porter, M. J. Selective Conversion of Alcohols into Alkyl Iodides Using a Thioiminium Salt. *J. Org. Chem.* **2009**, *74*, 7982-7985.
- (10) (a) Iranpoor, N.; Firouzabadi, H.; Azadi, R.; Ebrahimzadeh, F. Regioselective Synthesis of *vic*-Halo Alcohols and Symmetrical or Unsymmetrical *vic*-Dihalides from Epoxides Using Triphenylphosphine *N*-Halo Imides. *Can. J. Chem.* **2006**, *84*, 69-75. (b) Kotsuki, H.; Shimanouchi, T.; Ohshima, R.; Fujiwara, S. Solvent-Free Organic Reactions on Silica Gel Supports. Facile Transformation of Epoxides to β -Halohydrins with Lithium Halides. *Tetrahedron* **1998**, *54*, 2709-2722. (c) Sabitha, G.; Satheesh Babu, R.; Rajkumar, M.; Reddy, C. S.; Yadav, J. S. Highly Regioselective Ring Opening of Epoxides and Aziridines Using Cerium(III) Chloride. *Tetrahedron Lett.* **2001**, *42*, 3955-3958.
- (11) Gharpure, S. J.; Vishwakarma, D. S.; Nanda, S. K. Lewis Acid Mediated “*endo-dig*” Hydroalkoxylation–Reduction on Internal Alkynols for the Stereoselective Synthesis of Cyclic Ethers and 1,4-Oxazepanes. *Org. Lett.* **2017**, *19*, 6534-6537.
- (12) Jahn, E.; Smrček, J.; Pohl, R.; Císařová, I.; Jones, P. G.; Jahn, U. Facile and Highly Diastereoselective Synthesis of *syn*- and *cis*-1,2-Diol Derivatives from Protected α -Hydroxy Ketones. *Eur. J. Org. Chem.* **2015**, *2015*, 7785-7798.
- (13) Yu, H.; Zhang, G.; Huang, H. Palladium - Catalyzed Dearomative Cyclocarbonylation by C-N Bond Activation. *Angew. Chem. Int. Ed.* **2015**, *54*, 10912-10916.