Electronic Supplementary Material (ESI) for Chemical Communications

Desymmetrization of Cyclic Olefins via Asymmetric Heck Reaction and Hydroarylation

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Supporting Information: procedures and characterization

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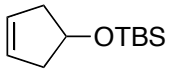
I. **General**

^{1}H NMR spectra were acquired at 400 MHz or 300 MHz and chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or residual protiated solvents ($CDCl_3$: δ 7.26; C_6D_6: δ 7.16; CD_2Cl_2: 5.30). 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 *n*H. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at 100 MHz on 400 MHz or 75 MHz on 300 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.25). Proof of purity of new compounds was demonstrated with copies of NMR spectra.

Dry diethyl ether, toluene, hexane and dichloromethane were collected from a solvent purification system containing a column of activated alumina (1 m x 2) under argon. DMSO, DMF and 1,4-dioxane (Aldrich) were used without further purification and were stored in the glove box. Dry THF was freshly distilled from sodium/benzophenone under argon before use. All of anhydrous solvents were stored over activated 4Å molecular sieve beads in Schlenk tubes in an argon-filled glove box. Unless noted otherwise, commercially available chemicals were used without further purification. The GC internal standard, *n*-dodecane was degassed and dried over activated 4 Å molecular sieve beads before use.

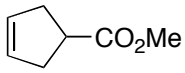
Glassware was dried at 120 ^{o}C for at least 3 hours before use. Flash chromatography was preformed using Merck 40-63D 60 Å silica gel. GC and GC/MS analysis were conducted with Agilent J&W GC column DB-5MS-UI. Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiracel columns at 25°C. 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*. X-ray crystallography analysis of single crystals was performed on a Bruker X8 APEX X-Ray diffractometer.

II. Substrate synthesis



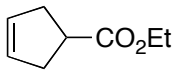
***4-(t*-Butyldimethylsiloxy)cyclopent-1-ene [68845-72-7].**[1] Under argon, to a dry 25-mL Schlenk tube was added cyclopent-3-enol (200 mg, 2.40 mmol), TBSCl (431 mg, 2.80 mmol), imidazole (194 mg, 2.80 mmol) and 5.0 mL dry DMF. After stirring at room temperature for 18 hours, diethyl ether (20 mL) was added. After extraction, the combined organic layers were dried over $MgSO_4$ and then evaporated to dryness under vacuum. The titled compound was obtained after flash chromatography (1:20 EA/hexanes) on silica gel as colorless oil (404 mg, 85% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.67 (s, 2H), 4.56-4.51 (m, 1H), 2.61-1.53 (m, 2H), 2.32-2.24 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H).



Methyl cyclopent-2-ene-1-carboxylate [58101-60-3]. Under argon, to a 100-mL Schlenk tube was added cyclopent-3-ene-1-carboxylic acid (3.36 g, 30 mmol), methyl iodide (8.50 g, 60 mmol), K_2CO_3 (10.0 g, 75 mmol) and dry DMF (25 mL). The resulting solution was stirred at room temperature for 16 hours until TLC indicated full conversion of carboxylic acid. Extractive workup with diethyl ether and water gave a pure product as light yellow oil (3.29 g, 87% yield). Some product may have been lost during concentration under reduced pressure.

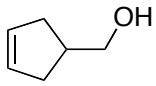
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.67 (s, 2H), 3.71 (s, 3H), 3.20-3.09 (m, 1H), 2.66 (ψd, J = 8.8 Hz, 4H).



Ethyl cyclopent-3-ene-1-carboxylate [21622-01-5].[2] Under argon, to a 25-mL Schlenk tube containing dry EtOH (5.0 mL) maintained in a -10 ^{o}C salt-ice bath, $SOCl_2$ (714 mg, 6.0 mmol) was added, followed by addition of cyclopent-3-ene-1-carboxylic acid (560 mg, 5.0 mmol) in one portion. The reaction mixture was stirred at room temperature for 3 hours and then refluxed for 1 hour until TLC showed full consumption of starting material. The titled compound was obtained after flash

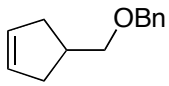
chromatography (1:20 EA/hexanes) as colorless oil (560 mg, 80% yield). Some product may be lost during concentration under reduced pressure.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.66 (s, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.14-3.06 (m, 1H), 2.65-2.63 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H).



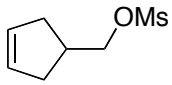
4-Hydroxymethylcyclopent-1-ene [25125-21-7].[3] Under argon, to dry THF (30 mL) in a dry 100-mL round bottom flask was added powder $LiAlH_4$ (3.14 g, 80 mmol). After the suspension was cooled to 0 ^{o}C in an ice bath, a solution of cyclopent-3-ene-1-carboxylic acid (2.24 g, 20 mmol) in THF (5.0 mL) was added over 10 min and an exothermic reaction was observed during addition. Then the reaction mixture was refluxed for 16 hours until TLC indicated full consumption of starting material. The reaction mixture was chilled to 0 ^{o}C and then was carefully quenched with 20 mL of saturated aq. NH_4Cl. After stirring for 30 minutes, the suspension was then passed through a pad of silica gel to remove aluminum salt with diethyl ether washing. The combined organic layers were dried over $MgSO_4$ and then evaporated to give the pure alcohol as colorless oil (1.69 g, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 (s, 2H), 3.57 (d, J = 5.9 Hz, 2H), 2.55-2.46 (m, 3H), 2.18-2.09 (m, 2H), 1.52 (br s, OH).



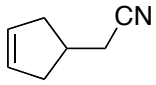
4-(Benzyloxymethyl)cyclopent-1-ene [260443-67-2].[4] 60% wt/wt NaH suspension in oil was washed with dry hexanes in the glove box and then dried under vacuum before use. Under argon, to a 25-mL Schlenk tube was added 4-hydroxymethylcyclopent-1-ene (490 mg, 5.0 mmol), NaH (240 mg, 10.0 mmol) and dry THF (5.0 mL). The suspension was stirred at room temperature for 1 hour and then benzyl bromide (1.28 g, 7.5 mmol) was added dropwise over 5 minutes. The reaction mixture was stirred at room temperature for 3 hours more until TLC show no more starting material remained. The reaction was quenched with 10 mL of saturated aq. NH_4Cl. After extraction from water, titled compound was obtained after flash chromatography (1:10 EA/hexanes) as colorless oil (714 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 5H), 5.66-5.64 (m, 2H), 4.52 (s, 2H), 3.37 (d, J = 7.2 Hz, 2H), 2.67-2.56 (m, 1H), 2.51-2.46 (m, 2H), 2.14-2.09 (m, 2H).



3-Cyclopentenylmethyl methanesulfonate [321386-75-8].[3] Under argon, to a 100-mL Schlenk flask was added hydroxymethylcyclopent-1-ene (490 mg, 5.0 mmol) and 25 mL of dry DCM. After the mixture was cooled to 0 ^{o}C in an ice bath, Et_3N (606 mg, 6.0 mmol) and MsCl (629 mg, 5.5 mmol) were added. The reaction mixture was stirred at 0 ^{o}C for 30 min, warmed to room temperature and kept stirred for 10 hours until TLC indicated full conversion of starting material. After the reaction was complete, the crude product was extracted with DCM from water. The organic layers were dried over Na_2SO_4 and then concentrated under reduced pressure. The titled compound was obtained after flash chromatography (1:5 EA/hexanes) as colorless oil (740 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (s, 2H), 4.13 (d, J = 7.3 Hz, 2H), 3.01 (s, 3H), 2.74-2.70 (m, 1H), 2.57-2.52 (m, 2H), 2.18-2.13 (m, 2H).



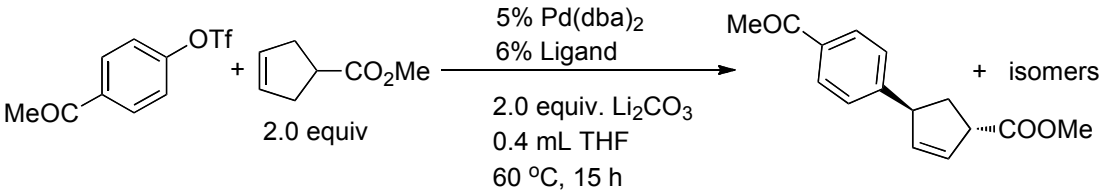
3-Cyclopentenylacetonitrile [21860-24-2]. Under argon, to a 100-mL Schlenk flask was added 3-cyclopentenylmethyl methanesulfonate (740 mg, 4.2 mmol), KCN (1.28 g, 19.70 mmol) and dry DMSO (30 mL). The reaction mixture was sealed and heated in a 50 ^{o}C oil bath for 3 days. After extraction using diethyl ether (100 mL x 2) from water, organic layers were dried over $MgSO_4$ and concentrated to give the pure product as colorless oil (337 mg, 75% yield).

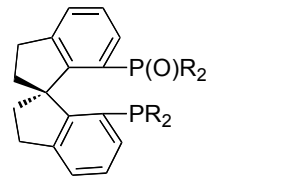
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (s, 2H), 2.66-2.64 (m, 3H), 2.40 (m, 2H), 2.20-2.16 (m, 2H).

IV. Condition optimization of asymmetric desymmetrization

Typical procedure: in an argon-filled glove box, a dry 10-mL reaction tube was charged with $Pd(dba)_2$ (5 mol%, 2.9 mg, 0.005 mmol), (*R*)-Xyl-DSP(O) (6 mol%, 4.2 mg, 0.006 mmol) and 0.2 mL of dry THF. After stirring at 25 °C for 15 minutes, Li_2CO_3 (14.8 mg, 0.20 mmol), *p*-acetylphenyl triflate (27 mg, 0.10 mmol), methyl cyclopent-2-ene-1-carboxylate (25 mg, 0.20 mmol) and GC standard, *n*-dodecane (10 μL) were added. The tube was capped tightly and stirred in a pre-warmed 60 °C oil bath until the aryl triflate was fully consumed (checked by GC). At intervals, an aliquot of the reaction mixture was taken in the glove box and quickly passed through a short plug of silica gel with diethyl ether washing. The filtrate was used in GC analysis to determine the conversion of ArOTf and GC yield and isomeric selectivity of the desired Heck product. For the determination of enantioselectivity of the main Heck product, the sample was dissolved in 1:10 *i*PrOH/hexanes and subjected to chiral HPLC analysis (Daicel CHIRALCEL OD-H; 2% *i*PrOH in hexanes; 0.5 mL/min).

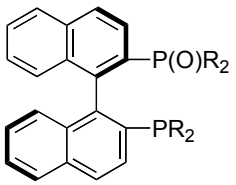
Table S1. Effect of chiral ligands





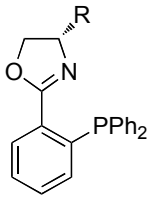
R = *m*-Xyl (*R*)-Xyl-SDP(O)

R = Ph (*R*)-Ph-SDP(O)



R = Ph (*R*)-BINAP(O)

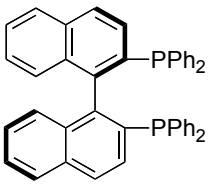
R = *m*-Xyl (*R*)-BINAP(O)



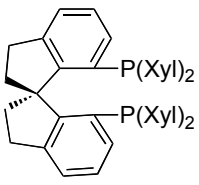
R = Ph (*R*)-Ph-PHOX

R = *i*Pr (*R*)-*i*Pr-PHOX

R = *t*Bu (*R*)-*t*Bu-PHOX



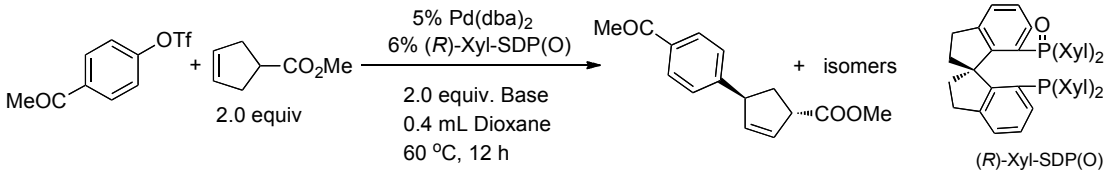
(*R*)-BINAP



(*R*)-Xyl-SDP

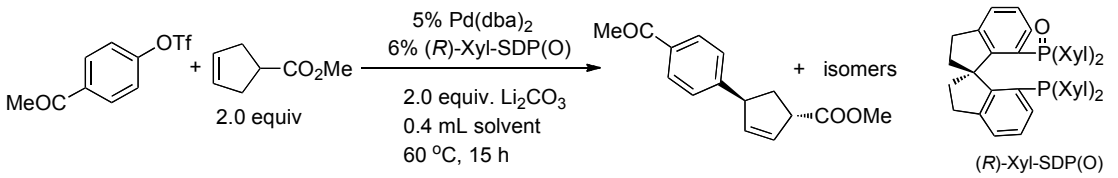
Entry	Ligand	Conv (%)	Yield (%)	Selectivity	Ee (%)
1	(*R*)-Xyl-SDP(O)	100	97	20:1	97
2	(*R*)-Ph-SDP(O)	62	40	26:1	90
4	(*R*)-BINAP(O)	94	70	4:1	-84
5	(*R*)-Xyl-BINAP(O)	100	94	7:1	-99
6	(*R*)-BINAP	86	54	1:3.6	-36
7	(*R*)-Xyl-SDP	61	44	1:3.5	-10
8	(*R*)-Ph-PHOX	36	<5	-	-
9	(*R*)-*i*Pr-PHOX	34	<5	-	-
10	(*R*)-*t*Bu-PHOX	57	39	1.2:1	-92

Table S2. Effect of bases



Entry	Base	Conv (%)	Yield (%)	Selectivity	Ee (%)
1	iPr$_2$NEt	100	90	26:1	97
2	Et$_3$N	87	71	16:1	97
3	2,6-Lutidine	93	83	20:1	97
4	Urotropine	32	<5	-	-
5	Proton sponge	86	78	10:1	97
6	Li$_2$CO$_3$	100	95	20:1	97
7	LiOAc	100	93	19:1	97

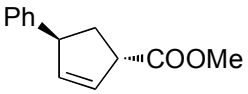
Table S3. Effect of solvents



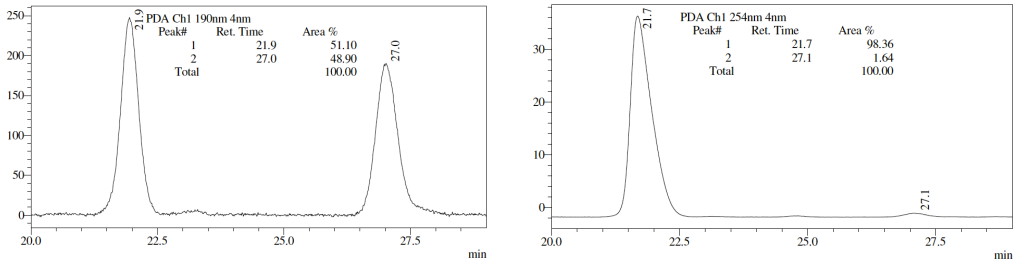
Entry	Solvent	Conv (%)	Yield (%)	Selectivity	Ee (%)
1	Toluene	100	83	26:1	98
2	TBME	100	83	14:1	98
3	*n*BuOH	74	66	10:1	98
4	THF	100	97	20:1	97
5	$PhCF_3$	100	78	12:1	98
6	1,4-Dioxane	100	95	20:1	97

IV. Asymmetric desymmetrization of substituted cyclopentenes

General procedure I using aryl triflates: In an argon-filled glove box, a dry 25-mL Schlenk tube was charged with $Pd(dba)_2$ (5 mol%, 14.4 mg, 0.025 mmol), (*R*)-Xyl-SDP(O) (6 mol%, 21.5 mg, 0.030 mmol) and 0.8 mL of dry THF. After stirring at room temperature for 15 minutes, Li_2CO_3 (74 mg, 1.0 mmol), aryl triflate (0.50 mmol), methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol) and GC standard *n*-dodecane (20 μL). The tube was capped tightly and stirred in an 80 ^oC oil bath until aryl triflate was fully consumed (monitored by GC). At the end of the reaction, the reaction mixture was directly filtered through a pad of silica gel with diethyl ether washings (20 mL) to remove the Pd catalyst and inorganic salts. The filtrate was concentrated on a rotary evaporator and the residue was directly subjected to flash chromatography. The enantioselectivity of the purified product was determined by chiral HPLC analysis. The general procedure was used unless stated otherwise. To facilitate chiral HPLC analysis, the racemic samples were prepared using racemic Xyl-SDP(O). Similar results were obtained by using standard Schlenk operations and a vacuum manifold instead of a glove box.



(1*S*,4*S*)-Methyl 4-phenylcyclopent-2-ene-1-carboxylate[90046-83-6]. The reaction was set up according to general procedure I by using phenyl triflate (0.50 mmol, 113 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 17 hours at 80 ^oC. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as light yellow oil (91 mg, 90% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 29:1 by GC. The ee of the purified products was determined to be 96% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 190 nm; flow rate = 0.5 mL/min). T_R = 27.1 min (minor) and 21.7 min (major).

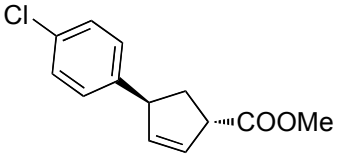


$[\alpha]^{22}_D$ = -1.1° (*c* = 1.2, $CHCl_3$) for a sample of 96% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 2H), 7.23-7.17 (m, 2H), 5.97-5.92 (m, 2H), 4.14-4.09 (m, 1H), 3.78-3.72 (m, 4H), 2.77-2.70 (m, 1H), 2.05-1.99 (m, 1H).

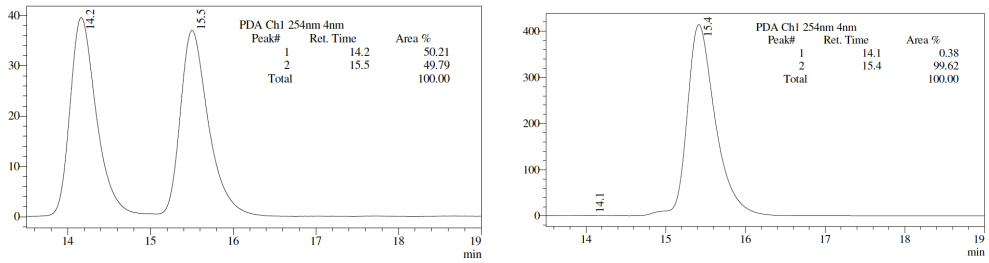
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 145.3, 137.7, 129.8, 128.8, 127.4, 126.6, 52.2, 51.1, 50.8, 37.3.

GCMS (EI): calcd for $C_{13}H_{14}O_2$ M: 202.10. Found: 202.04.



(1*S*,4*S*)-Methyl 4-(4-chlorophenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-chlorophenyl triflate (0.50 mmol, 130 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 20 hours at 80 °C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as light yellow oil (109 mg, 92% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 17:1 by GC.

The ee of the purified products was determined to be 99% by chiral HPLC analysis (Daicel CHIRALCEL AS-H; hexanes: *i*PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 14.1 min (minor) and 15.4 min (major).



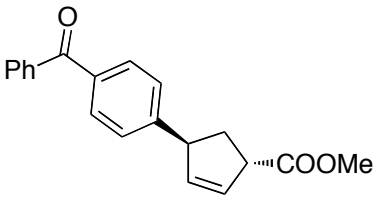
$[\alpha]^{22}_D$ = -0.18° (*c* = 2.5, $CHCl_3$) for a sample of 99% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 6.4 Hz, 2H), 7.11-7.08 (d, *J* = 6.4 Hz, 2H), 5.95-5.89 (m, 2H), 4.10-4.06 (m, 1H), 3.77-3.72 (m, 4H), 2.76-2.69 (m, 1H),

1.99-1.92 (m, 1H).

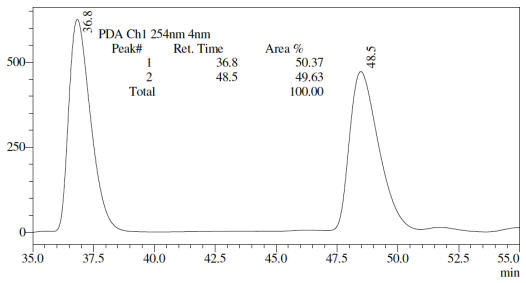
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 143.7, 137.2, 132.3, 130.3, 128.9, 128.7, 127.1, 52.6, 50.7, 50.4, 37.2.

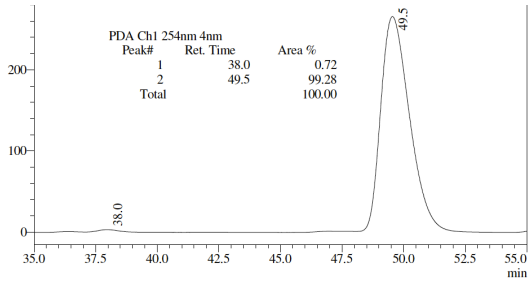
GCMS (EI): calcd for $C_{13}H_{13}ClO_2$ M: 236.06. Found: 236.0.



(1*R*,4*S*)-Methyl 4-(*p*-benzoylphenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-benzoylphenyl triflate (0.50 mmol, 165 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 15 hours at 60 °C. The titled compound was obtained after flash chromatography (1:20 EA/hexanes) as light yellow oil (145 mg, 95% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 15:1 by GC.

Ee of the purified products was determined to be 98% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; hexanes: *i*PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 38.0 min (minor) and 49.5 min (major).



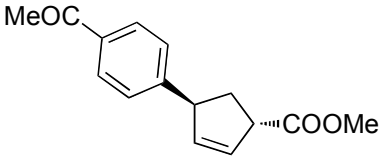


$[\alpha]^{22}_D$ = -0.7° (*c* = 3.2, $CHCl_3$) for a sample of 98% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81-7.74 (m, 4H), 7.61-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.29-7.27 (m, 2H), 6.00-5.96 (m, 2H), 4.22-4.17 (m, 1H), 3.80-3.73 (m, 4H), 2.83-2.74 (m, 1H), 2.08-1.99 (m, 1H).

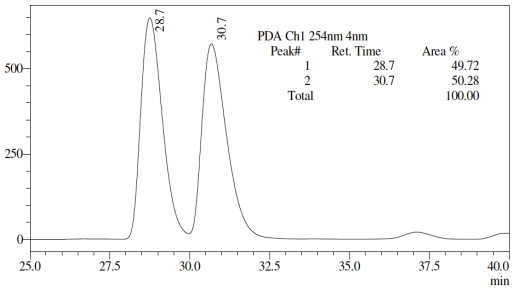
^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 174.5, 150.0, 137.8, 136.6, 135.8, 132.3, 130.6, 130.5, 130.0, 128.3, 127.2, 52.0, 50.8, 50.5, 36.8.

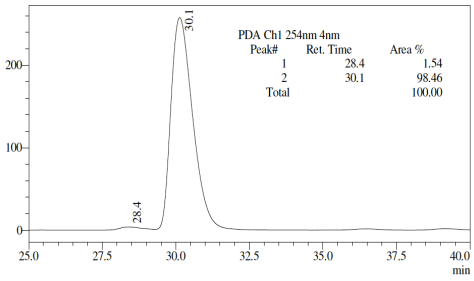
GCMS (EI): calcd for $C_{20}H_{18}O_3$ M: 306.13. Found: 306.10.



(1*S*,4*S*)-Methyl 4-(*p*-acetylphenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-acetylphenyl triflate (0.50 mmol, 134 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 15 hours at 60 ^{o}C. The titled compound was obtained after flash chromatography (1:20 EA/hexanes) as colorless oil (115 mg, 94% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 20:1 by GC.

The ee of the purified products was determined to be 97% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 28.4 min (minor) and 30.1 min (major).



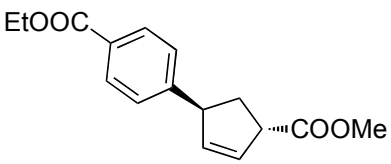


$[\alpha]^{22}_{D}$ = -0.56^{o} (*c* = 5.0, $CHCl_3$) for a sample of 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.99-5.92 (m, 2H), 4.20-4.15 (m, 1H), 3.79-3.73 (m, 4H), 2.82-2.73 (m, 1H), 2.59 (s, 3H), 2.05-1.95 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 174.5, 150.7, 136.6, 135.6, 130.5, 128.8, 127.4, 52.0, 50.8, 50.5, 36.8, 26.6.

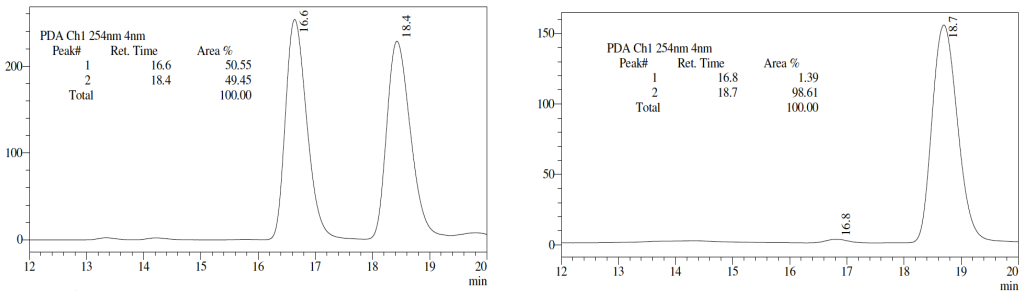
GCMS (EI): calcd for $C_{15}H_{16}O_3$ M: 244.11. Found: 244.02.



(1*S*,4*S*)-Methyl 4-(*p*-ethoxycarbonylphenyl)cyclopent-2-ene-1-carboxylate. The

reaction was set up according to general procedure I by using *p*-ethoxycarbonylphenyl triflate (0.50 mmol, 149 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 15 hours at 80 °C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as light yellow oil (120 mg, 88% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 15:1 by GC.

The ee of the purified products was determined to be 97% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 16.8 min (minor) and 18.7 min (major).

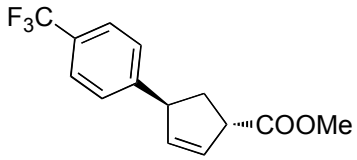


$[\alpha]^{22}_D$ = -0.27° (*c* = 2.6, $CHCl_3$) for a sample of 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.99-5.92 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.19-4.13 (m, 1H), 3.78-3.74 (m, 1H), 3.73 (s, 3H), 2.80-2.72 (m, 1H), 2.04-1.95 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 166.7, 150.5, 136.8, 130.5, 130.1, 128.6, 127.3, 61.0, 52.2, 51.0, 50.7, 37.0, 14.5.

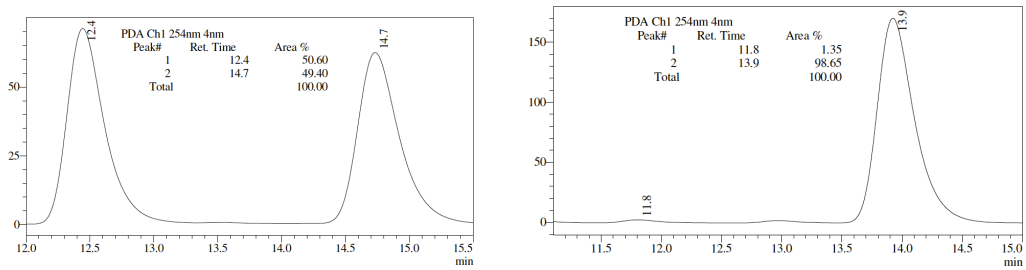
GCMS (EI): calcd for $C_{16}H_{18}O_4$ M: 274.12. Found: 274.0.



(1*S*,4*S*)-Methyl 4-(*p*-trifluoromethylphenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-trifluoromethylphenyl triflate (0.50 mmol, 147 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 6 hours at 80 °C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as colorless oil (116 mg, 86% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 21:1 by GC.

The ee of the purified products was determined to be 97% by chiral HPLC

analysis (Daicel CHIRALCEL AS-H; hexanes: *i*PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 11.8 min (minor) and 13.9 min (major).



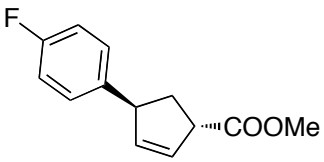
$[\alpha]^{22}_D$ = -1.2° (*c* = 2.3, $CHCl_3$) for a sample of 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.00-5.92 (m, 2H), 4.20-4.13 (m, 1H), 3.78-3.73 (m, 4H), 2.82-2.73 (m, 1H), 2.04-1.94 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 149.3, 136.8, 130.8, 129.0 (q, J_{C-F} = 32.4 Hz), 127.7, 125.7 (q, J_{C-F} = 3.8 Hz), 124.5 (q, J_{C-F} = 274.5 Hz), 52.3, 50.9, 50.7, 37.1.

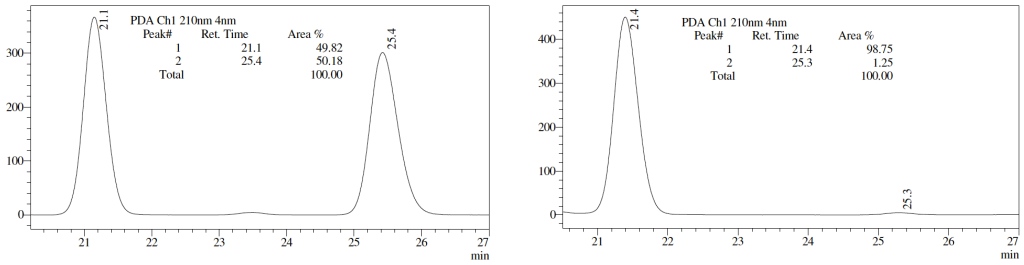
^{19}F NMR (282 MHz, $CDCl_3$): δ -62.4.

GCMS (EI): calcd for $C_{14}H_{13}F_3O_2$ M: 270.09. Found: 270.02.



(1*R*,4*S*)-Methyl 4-(*p*-fluorophenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-fluorophenyl triflate (0.50 mmol, 122 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 12 hours at 80 °C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as colorless oil (101 mg, 92% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 25:1 by GC.

The ee of the purified products was determined to be 98% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; hexanes: *i*-PrOH = 98:2; detection wavelengths = 210 nm; flow rate = 0.5 mL/min). T_R = 25.3 min (minor) and 21.4 min (major).



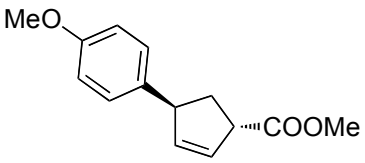
$[\alpha]^{22}_{D}$ = -0.9° (*c* = 2.3, $CHCl_3$) for a sample of 98% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13-7.10 (m, 2H), 6.99-6.95 (m, 2H), 5.93-5.92 (m, 2H), 4.11-4.07 (m, 1H), 3.76-3.69 (m, 4H), 2.75-2.67 (m, 1H), 2.04-1.91 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 161.8 (d, *J* = 244.3 Hz, *para*-C), 140.9 (d, *J* = 3.3 Hz, *ipso*-C) 137.5, 130.0, 128.7 (d, *J* = 7.8 Hz, *ortho*-C), 115.5 (d, *J* = 21.2 Hz, *meta*-C), 52.2, 50.7, 50.3, 37.4. The assignment was assisted by 2D ^{1}H-^{13}C HMQC.

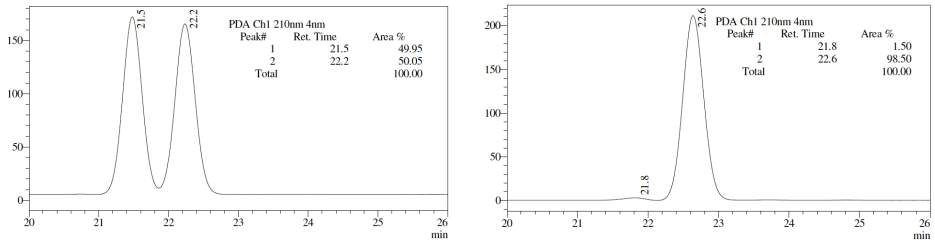
^{19}F NMR (282 MHz, $CDCl_3$): δ -116.9.

GCMS (EI): calcd for $C_{13}H_{13}FO_2$ M: 220.09. Found: 219.96.



(1*S*,4*S*)-Methyl 4-(4-methoxyphenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-methoxyphenyl triflate (0.50 mmol, 128 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 20 hours at 80 °C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as colorless oil (99 mg, 85% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 30:1 by GC.

The ee of the purified products was determined to be 97% by chiral HPLC analysis (Daicel CHIRALCEL IC-H; hexanes: *i*PrOH = 98:2; detection wavelengths = 210 nm; flow rate = 0.5 mL/min). T_R = 21.8 min (minor) and 22.6 min (major).

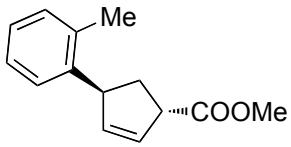


$[\alpha]^{22}_{D}$ = -2.7° (*c* = 2.7, $CHCl_3$) for a sample of 97% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 4.09-4.05 (m, 1H), 3.79 (s, 3H), 3.77-3.72 (m, 4H), 2.74-2.67 (m, 1H), 2.01-1.95 (m, 1H).

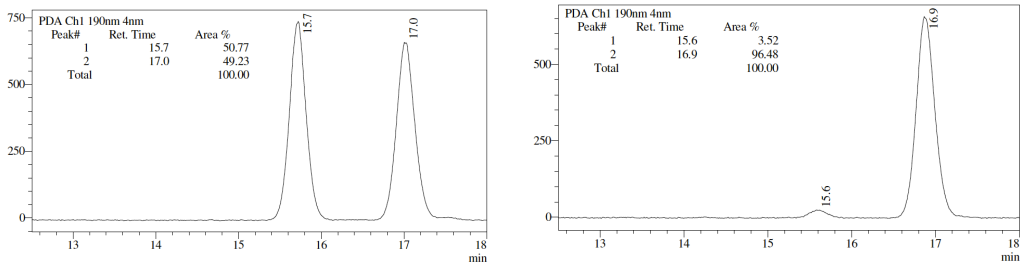
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 158.4, 138.0, 137.3, 129.4, 128.3, 114.2, 55.5, 52.1, 50.7, 50.2, 37.4.

GCMS (EI): calcd for $C_{14}H_{16}O_3$ M: 232.11. Found: 232.04.



(1*S*,4*S*)-Methyl 4-(*o*-tolyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *o*-tolyl triflate (0.50 mmol, 120 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 12 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as colorless oil (96 mg, 89% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 100:1 by GC.

The ee of the purified products was determined to be 93% by chiral HPLC analysis (Daicel CHIRALCEL IC-H; hexanes: *i*-PrOH = 99:1; detection wavelengths = 190 nm; flow rate = 0.5 mL/min). T_R = 15.6 min (minor) and 16.9 min (major).

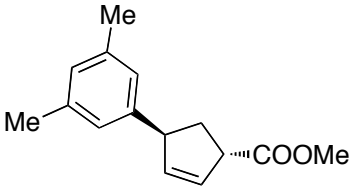


$[\alpha]^{22}_D$ = -0.48^o (c = 0.5, $CHCl_3$) for a sample of 93% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.07 (m, 4H), 5.98-5.92 (m, 2H), 4.33-4.22 (m, 1H), 3.78-3.71 (m, 4H), 2.80-2.73 (m, 1H), 2.37 (s, 3H), 1.94-1.87 (m, 1H).

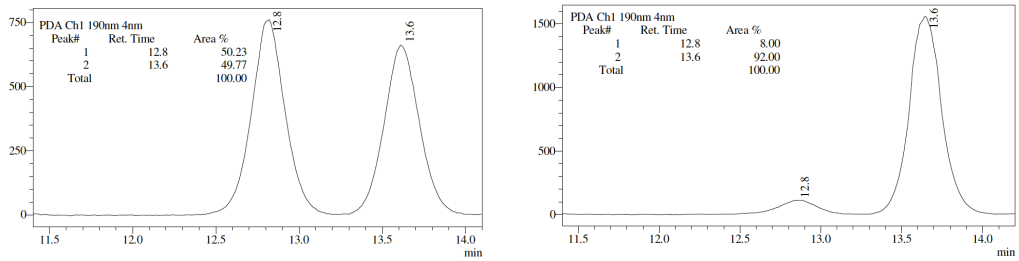
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 143.4, 137.3, 135.9, 130.5, 130.0, 126.5, 126.4, 126.1, 52.2, 50.6, 47.2, 35.9, 19.9.

GCMS (EI): calcd for $C_{14}H_{16}O_2$ M: 216.12. Found: 215.99.



(1*R*,4*S*)-Methyl 4-(*m*-xylyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *m*-xylyl triflate (0.50 mmol, 127 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 12 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as colorless oil (104 mg, 90% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 10:1 by GC.

The ee of the purified products was determined to be 84% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 190 nm; flow rate = 0.5 mL/min). T_R = 12.8 min (minor) and 13.6 min (major).

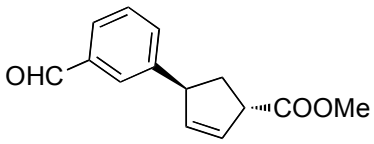


$[\alpha]^{22}_{D}$ = -0.76^{o} (*c* = 2.0, $CHCl_3$) for a sample of 84% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 1H), 6.79 (s, 2H), 5.95-5.89 (m, 2H), 4.06-4.01 (m, 1H), 3.77-3.72 (m, 4H), 2.73-2.66 (m, 1H), 2.29 (s, 6H), 2.04-1.97 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 145.2, 138.3, 138.0, 129.5, 128.3, 125.2, 52.2, 50.9, 50.8, 37.2, 21.5

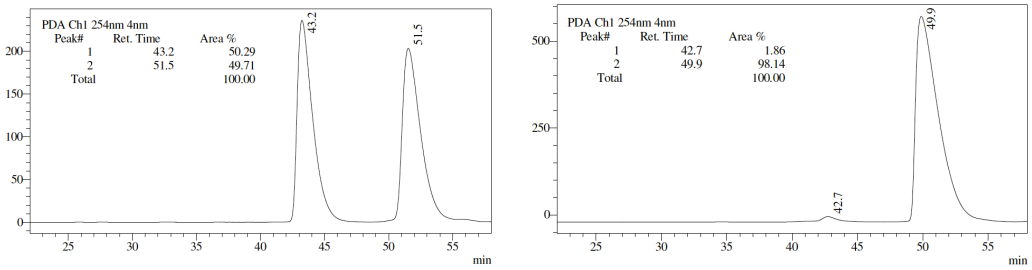
GCMS (EI): calcd for $C_{14}H_{18}O_2$ M: 230.13. Found: 230.10.



(1*S*,4*S*)-Methyl 4-(*m*-formylphenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *m*-formylphenyl triflate (0.50

mmol, 127 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 17 hours at 80 °C. The titled compound was obtained after flash chromatography (1:20 EA/hexanes) as colorless oil (95 mg, 83% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be >50:1 by GC.

The ee of the purified products was determined to be 96% by chiral HPLC analysis (Daicel CHIRALCEL AS-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 42.7 min (minor) and 49.9 min (major).

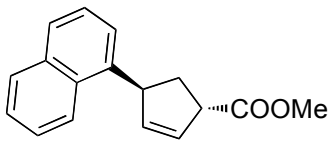


$[\alpha]^{22}_D$ = -0.22° (*c* = 4.3, $CHCl_3$) for a sample of 96% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.71-7.67 (m, 2H), 7.47-7.41 (m, 2H), 5.98-5.90 (m, 2H), 4.20-4.14 (m, 1H), 3.77-3.69 (m, 4H), 2.80-2.71 (m, 1H), 2.02-1.92 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 174.7, 146.4, 136.9, 136.7, 133.6, 130.7, 129.4, 128.4, 128.1, 52.2, 50.64, 50.62, 37.0.

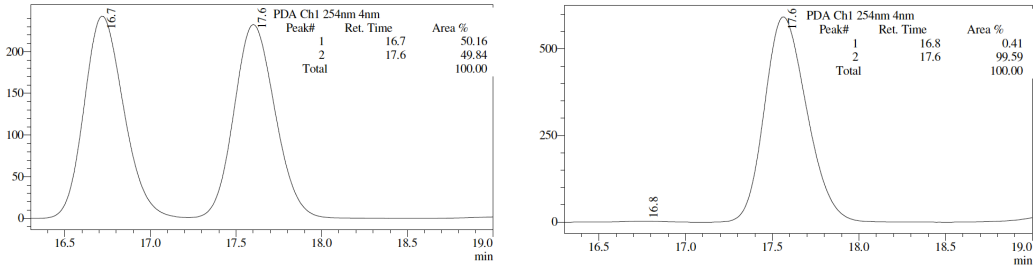
GCMS (EI): calcd for $C_{14}H_{14}O_3$ M: 230.09. Found: 230.02.



(1*S*,4*S*)-Methyl 4-(1-naphthyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using 1-naphthyl triflate (0.50 mmol, 138 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 17 hours at 80 °C. The titled compound was obtained after flash chromatography (1:25 EA/hexanes) as colorless oil (103 mg, 82% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 40:1 by GC.

The ee of the purified products was determined to be 99% by chiral HPLC analysis (Daicel CHIRALCEL IC-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths

= 254 nm; flow rate = 0.5 mL/min). T_R = 16.8 min (minor) and 17.6 min (major).

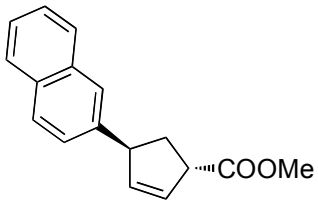


$[\alpha]^{22}_D$ = -0.36° (*c* = 2.0, $CHCl_3$) for a sample of 99% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 9.0, 1.6 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.54-7.45 (m, 2H), 7.37 (ψt, *J* = 7.4 Hz, 1H), 7.25 (d, J = 6.9 Hz, 1H), 6.12-6.03 (m, 2H), 4.85-4.84 (m, 1H), 3.75-3.70 (m, 4H), 2.98-2.89 (m, 1H), 2.09-2.00 (m, 1H).

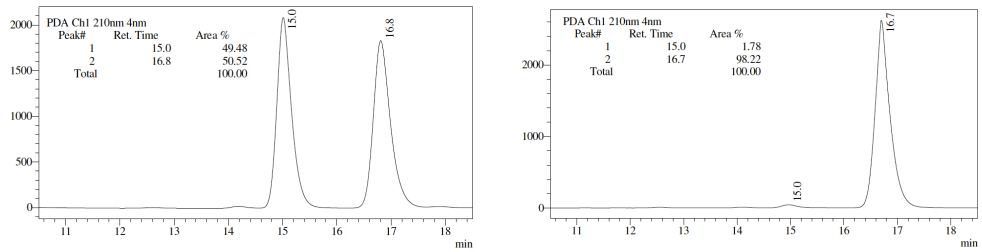
^{13}C NMR (75 MHz, $CDCl_3$): δ 175.1, 141.1, 136.8, 134.2, 131.9, 130.5, 128.9, 127.2, 126.2, 125.8, 125.7, 123.9, 123.0, 52.2, 50.6, 46.7, 36.4.

GCMS (EI): calcd for $C_{17}H_{16}O_2$ M: 252.12. Found: 252.06.



(1*S*,4*S*)-Methyl 4-(2-naphthyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to the general procedure I by using 2-naphthyl triflate (0.50 mmol, 138 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 20 hours at 80 °C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as colorless oil (116 mg, 92% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 15:1 by GC.

The ee of the purified products was determined to be 96% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; hexanes: *i*PrOH = 98:2; detection wavelengths = 210 nm; flow rate = 0.5 mL/min). T_R = 15.0 min (minor) and 16.7 min (major).

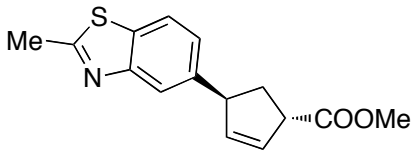


$[\alpha]^{22}_D$ = -0.25° (*c* = 1.9, $CHCl_3$) for a sample of 96% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.76 (m, 3H), 7.61 (s, 1H), 7.48-7.41 (m, 2H), 7.31 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.05-5.98 (m, 1H), 4.29-4.27 (m, 1H), 3.82-3.74 (m, 4H), 2.83-2.77 (m, 1H), 2.14-2.11 (m, 1H).

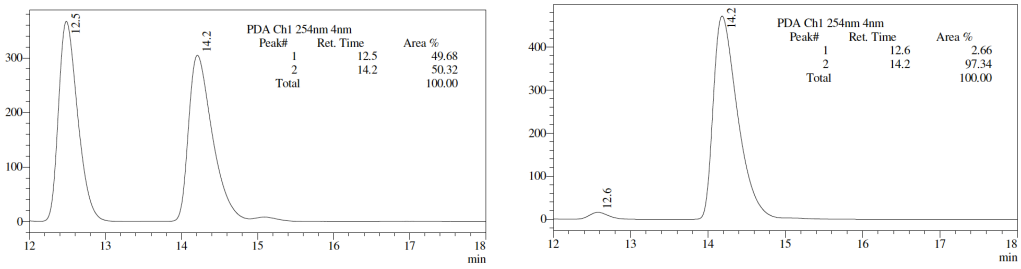
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 141.6, 137.6, 133.8, 132.6, 130.1, 128.5, 127.84, 127.81, 126.3, 126.1, 125.6, 125.5, 52.2, 51.2, 50.8, 37.1.

GCMS (EI): calcd for $C_{17}H_{16}O_2$ M: 252.12. Found: 252.08.



(1*S*,4*S*)-Methyl 4-(2-methylbenzothiazol-5-yl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to the general procedure I by using 2-methylbenzothiazol-5-yl triflate (0.50 mmol, 148 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 20 hours at 80 °C. The titled compound was obtained after flash chromatography (1:10 EA/hexanes) as colorless oil (115 mg, 84% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 12:1 by GC.

The ee of the purified products was determined to be 93% by chiral HPLC analysis (Daicel CHIRALCEL ID-H; Hexanes: *i*-PrOH = 80:20; detection wavelengths = 254 nm; flow rate = 1.0 mL/min). T_R = 12.6 min (minor) and 14.2 min (major).

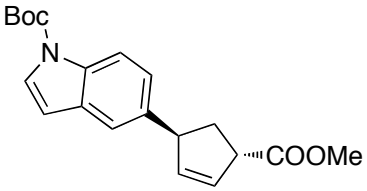


$[\alpha]^{22}_D$ = -1.9° (*c* = 1.0, $CHCl_3$) for a sample of 93% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 2H), 7.17 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.00-5.95 (m, 2H), 4.26-4.22 (m, 1H), 3.78-3.72 (m, 4H), 2.82 (s, 3H), 2.80-2.75 (m, 1H), 2.09-2.02 (m, 1H).

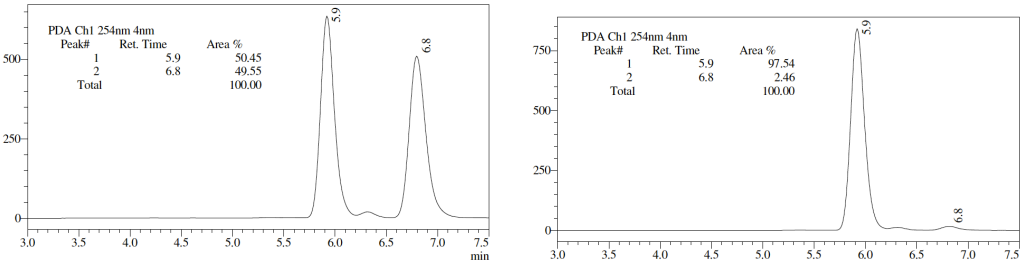
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 167.6, 154.1, 143.6, 137.5, 133.9, 130.2, 124.5, 121.6, 120.8, 52.2, 50.9, 50.7, 37.5, 20.4.

GCMS (EI): calcd for $C_{15}H_{15}NO_2S$ M: 273.08. Found: 273.01.



(1*S*,4*S*)-*N*-*Boc*-4-(5-indolyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to the general procedure I by using *N*-Boc-5-indolyl triflate (0.50 mmol, 183 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 20 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:40 EA/hexanes) as colorless oil (152 mg, 89% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 20:1 by GC.

The ee of the purified products was determined to be 95% by chiral HPLC analysis (Daicel CHIRALCEL ID-H; hexanes: *i*PrOH = 90:10; detection wavelengths = 254 nm; flow rate = 1.0 mL/min). T_R = 6.8 min (minor) and 5.9 min (major).

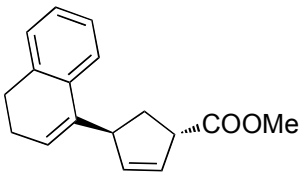


$[\alpha]^{22}_{D}$ = -2.2^{o} (*c* = 2.0, $CHCl_3$) for a sample of 95% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 3.6 Hz, 1H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.13 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.51 (d, *J* = 3.6 Hz, 1H), 6.01-5.93 (m, 2H), 4.22-4.19 (m, 1H), 3.80-3.77 (m, 1H), 3.72 (s, 3H), 2.80-2.73 (m, 1H), 2.08-2.04 (m, 1H), 1.67 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 150.0, 139.7, 138.1, 134.2, 131.1, 129.5, 126.4, 123.8, 119.3, 115.4, 107.4, 83.8, 52.1, 51.0, 50.8, 37.7, 28.4.

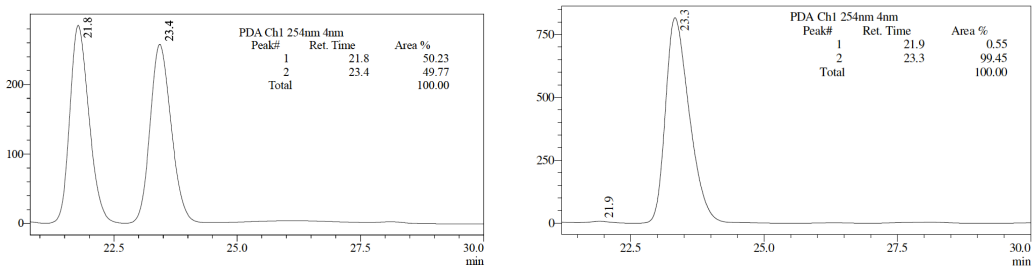
GCMS (EI): calcd for $C_{20}H_{23}NO_4$ M: 341.16. Found: [M-Boc]: 241.08.



(1*S*,4*S*)-Methyl 4-(3,4-dihydro-1-naphthyl)cyclopent-2-ene-1-carboxylate. The

reaction was set up according to the general procedure I by using 3,4-dihydro-1-naphyl triflate (0.50 mmol, 139 mg) and methyl cyclopent-2-ene-1-carboxylate (126 mg, 1.0 mmol). The reaction finished after 13 hours at 60 ^{o}C. The titled compound was obtained after flash chromatography (1:40 EA/hexanes) as colorless oil (117 mg, 92% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 10:1 by GC.

The ee of the purified products was determined to be 99% by chiral HPLC analysis (Daicel CHIRALCEL ID-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 21.9 min (minor) and 23.3 min (major).

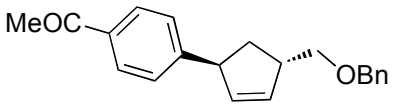


$[\alpha]^{22}_{D}$ = -0.8^{o} (*c* = 3.4, $CHCl_3$) for a sample of 99% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.15 (m, 4H), 5.99-5.93 (m, 2H), 5.82 (ψt, *J* = 4.2 Hz, 1H), 4.10-4.04 (m, 1H), 3.79-3.66 (m, 4H), 2.77-2.64 (m, 3H), 2.95-2.45 (m, 2H), 2.02-1.93 (m, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 175.2, 139.4, 137.0, 136.6, 135.0, 129.8, 127.8, 126.9, 126.6, 123.3, 123.1, 52.1, 50.3, 46.5, 34.9, 28.5, 23.3.

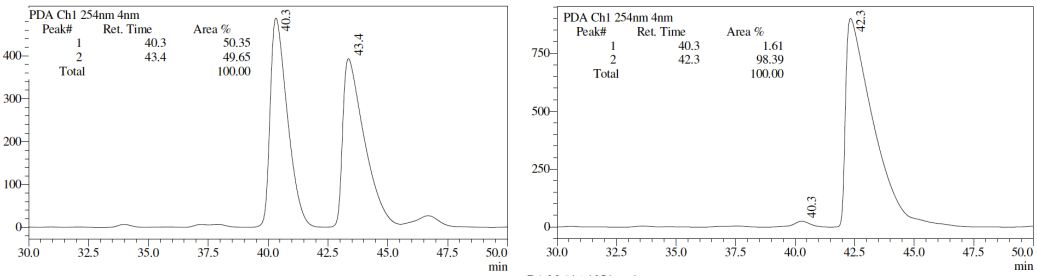
GCMS (EI): calcd for $C_{17}H_{18}O_2$ M: 254.1. Found: 254.0.



(1*S*,4*S*)-4-(*p*-acetylphenyl)-1-(benzyloxymethyl)cyclopent-2-ene. The reaction was set up according to general procedure I by using 4-acetylphenyl triflate (0.50 mmol, 134 mg) and 3-(benzyloxymethyl)cyclopent-1-ene (188 mg, 1.0 mmol). The reaction finished after 17 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:30 EA/hexanes) as light yellow oil (141 mg, 92% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 20:1 by GC.

The ee of the purified products was determined to be 97% by chiral HPLC

analysis (Daicel CHIRALCEL ID-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 40.3 min (minor) and 42.3 min (major).

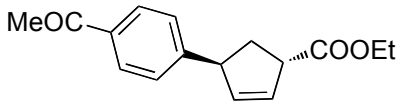


$[\alpha]^{22}_D$ = -0.27° (*c* = 2.2, $CHCl_3$) for a sample of 97% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.35-7.24 (m, 7H), 5.98-5.94 (m, 1H), 5.84-5.81 (m, 1H), 4.54 (s, 2H), 4.03-3.98 (m, 1H), 3.45-3.42 (m, 2H), 3.24-3.13 (m, 1H), 2.55 (s, 3H), 2.26-2.16 (m, 1H), 1.95-1.89 (m, 1H).

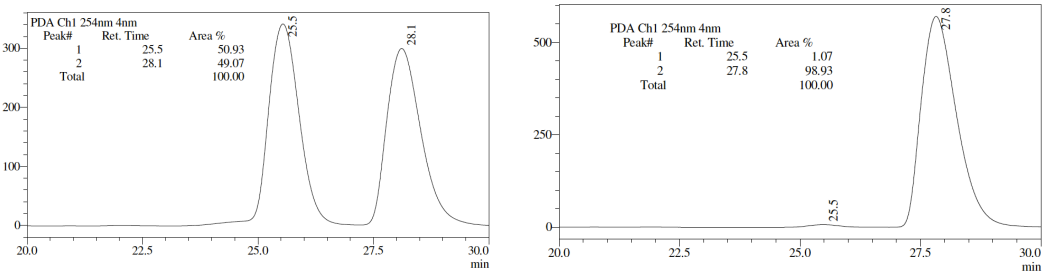
^{13}C NMR (75MHz, $CDCl_3$): δ 197.9, 151.9, 138.6, 135.5, 134.8, 134.2, 128.8, 128.5, 127.8, 127.7, 127.6, 127.5, 73.9, 73.3, 50.7, 46.3, 37.2, 26.7.

GCMS (ESI): calcd for $C_{21}H_{23}O_2$ [M+H]: 307.17. Found: 307.14



(1*S*,4*S*)-Ethyl 4-(*p*-acetylphenyl)cyclopent-2-ene-1-carboxylate. The reaction was set up according to general procedure I by using *p*-acetylphenyl triflate (0.50 mmol, 134 mg) and ethyl cyclopent-1-ene-3-carboxylate (140 mg, 1.0 mmol). The reaction finished after 17 hours at 80 °C. The titled compound was obtained after flash chromatography (1:20 EA/hexanes) as light yellow oil (110 mg, 85% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 20:1 by GC.

The ee of the purified products was determined to be 98% by chiral HPLC analysis (Daicel CHIRALCEL OD-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 25.5 min (minor) and 27.8 min (major).

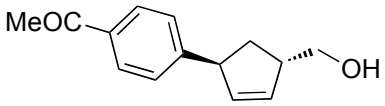


$[\alpha]^{22}_D$ = -0.53° (*c* = 3.2, $CHCl_3$) for a sample of 98% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.97-5.88 (m, 1H), 5.84-5.81 (m, 1H), 4.14 (q, *J* = 7.2 Hz, 3H), 3.73-3.69 (m, 1H), 2.77-2.56 (m, 1H), 2.55 (s, 3H), 1.97-1.93 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H).

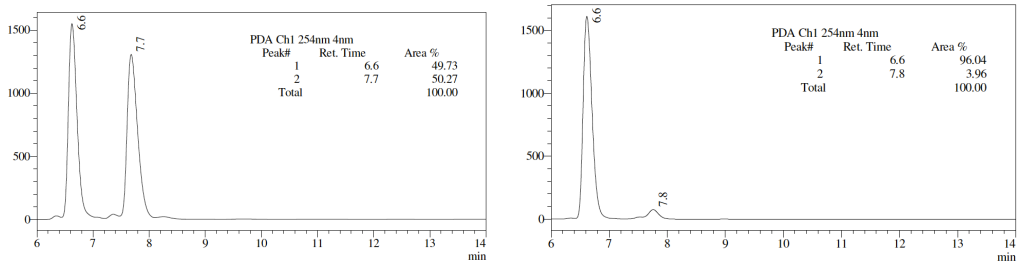
^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 174.2, 150.9, 136.6, 135.7, 130.8, 128.9, 127.5, 60.9, 50.9, 50.8, 36.9, 26.7, 14.4.

GCMS (EI): calcd for $C_{16}H_{18}O_3$ M: 258.13. Found: 258.1



(1*S*,4*S*)-4-(*p*-Acetylphenyl)-1-(hydroxymethyl)cyclopent-2-ene. The reaction was set up according to general procedure I by using 4-acetylphenyl triflate (0.50 mmol, 134 mg) and 3-(hydroxymethyl)cyclopent-1-ene (98 mg, 1.0 mmol). The reaction finished after 13 hours at 80 °C. The titled compound was obtained after flash chromatography (1:20 Et_2O/DCM) as light yellow oil (85 mg, 79% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 13:1 by GC.

The ee of the purified products was determined to be 92% by chiral HPLC analysis (Daicel CHIRALCEL ID-H; Hexanes: *i*-PrOH = 70:30; detection wavelengths = 254 nm; flow rate = 1.0 mL/min). T_R = 6.6 min (major) and 7.8 min (minor).

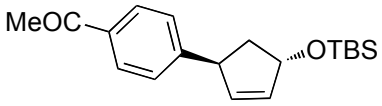


$[\alpha]^{22}_D$ = -1.0° (*c* = 2.9, $CHCl_3$) for a sample of 92% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.94-5.83 (m, 2H), 4.04-3.99 (m, 1H), 3.61 (d, *J* = 5.9 Hz, 2H), 3.10-3.07 (m, 1H), 2.55 (s, 3H), 2.29 (s, 1H), 2.27-2.21 (m, 2H including O*H*), 1.91-1.87 (m, 1H).

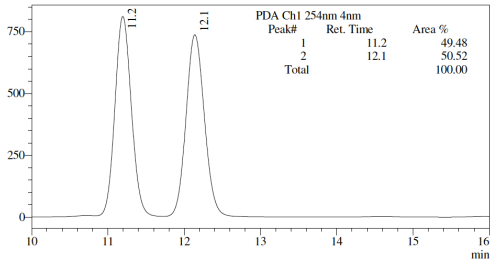
^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 152.0, 135.6, 135.4, 133.6, 128.8, 127.5, 66.1, 50.9, 48.6, 36.8, 26.7.

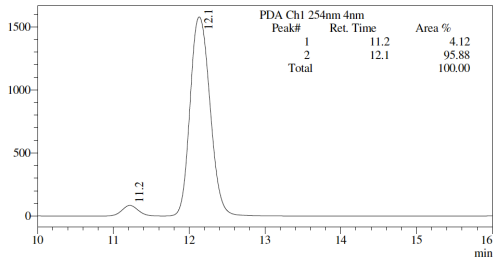
GCMS (EI): calcd for $C_{16}H_{18}O_3$ M: 216.12. Found: 216.10.



(1*S*,4*S*)-4-(*p*-Acetylphenyl)-1-(*t*-butyldimethylsiloxy)cyclopent-2-ene. The reaction was set up according to general procedure I by using 4-acetylphenyl triflate (0.50 mmol, 134 mg) and 3-(*t*-butyldimethylsiloxy)cyclopent-1-ene (198 mg, 1.0 mmol). The reaction finished after 15 hours at 80 °C. The titled compound was obtained after flash chromatography (1:40 EA/hexanes) as colorless oil (149 mg, 94% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 28:1 by GC.

The ee of the purified products was determined to be 92% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 12.1 min (major) and 11.2 min (minor).



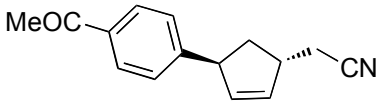


$[\alpha]^{22}_D$ = -1.6° (*c* = 1.1, $CHCl_3$) for a sample of 92% ee.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.96-5.93 (m, 2H), 5.08-5.07 (m, 1H), 4.19-4.16 (m, 1H), 2.56 (s, 3H), 2.29-2.23 (m, 1H), 2.07-2.01 (m, 1H), 0.91 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 151.3, 136.7, 135.6, 128.9, 127.5, 77.8, 50.3, 44.1, 26.7, 26.2, 18.5, -4.3, -4.4.

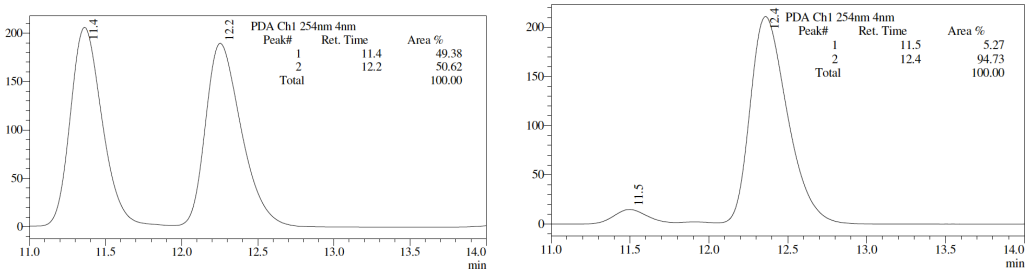
GCMS (ESI): calcd for $C_{19}H_{29}O_2Si$ (M+1): 317.19. Found: 317.11.



(1*S*,4*S*)-4-(*p*-Acetylphenyl)-1-(cynomethyl)cyclopent-2-eneThe reaction was set up according to the general procedure I except 8% $Pd(dba)_2$ (0.04 mmol, 23.0 mg) and 10% (*R*)-Xyl-SDP(O) (0.05 mmol, 35.8 mg) were used as catalyst together with 4-acetylphenyl triflate (0.50 mmol, 134 mg) and 3-(cyanomethyl)cyclopent-1-ene (107 mg, 1.0 mmol). The reaction finished after 16 hours at 80 °C. The titled

compound was obtained after flash chromatography (1:5 EA/hexanes) as colorless oil (103 mg, 92% yield). The ratio of the desired isomer versus all other isomers in the crude product was determined to be 20:1 by GC.

The ee of the purified products was determined to be 90% by chiral HPLC analysis (Daicel CHIRALCEL ID-H; Hexanes: *i*-PrOH = 70:30; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 11.5 min (minor) and 12.4 min (major).



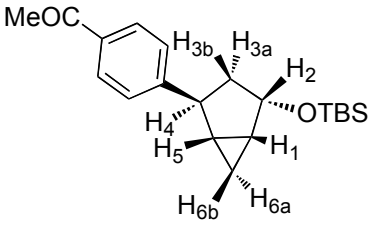
$[\alpha]^{22}_D = -0.02^o$ (c = 1.0, $CHCl_3$) for a sample of 90% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, J = 4.0, 2.0 Hz, 2H), 7.2 (d, J = 1.6 Hz, 2H), 5.95 (ψt, J = 2.0 Hz, 2H), 4.18-4.14 (m, 1H), 3.29-3.22 (m, 1H), 2.59 (s, 3H), 2.47 (d, J = 6.4 Hz, 2H), 2.65-2.17 (m, 1H), 2.13-2.06 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 150.6, 136.5, 135.8, 133.6, 129.0, 127.5, 118.9, 50.7, 42.3, 39.4, 26.8, 23.3.

GCMS (EI): calcd for $C_{15}H_{15}NO$ M: 225.12. Found: 225.04.

V. Derivatization of Heck products



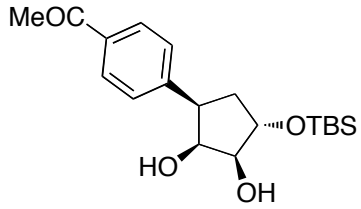
(1*R*,2*S*,4*S*,5*R*)-4-*p*-Acetylphenyl-2-(*t*-butyldimethylsilyloxy)bicyclo[3.1.0]hexane. The cyclopropanation was conducted by following a reported procedure.[5,6] Under argon, to a dry 10-mL Schlenk tube was added (1*S*,4*S*)-4-(*p*-acetylphenyl)-1-(*t*-butyldimethylsiloxy)cyclopent-2-ene (96% purity, 63 mg, 0.20 mmol) and dry DCM (0.5 mL), followed by Et_2Zn (492 mg, 95% pure, 10% wt in hexane, 0.4 mmol). After the reaction mixture was cooled to 0 ^oC in an ice bath, CH_2I_2 (107 mg, 0.4 mmol) was added dropwise over a period of 15 min. The reaction mixture was then stirred at 0 ^oC for 3 h and then at rt overnight. At the end of the reaction, the mixture was passed through a pad of silica with and DCM washing (50 mL). The filtrate was concentrated under reduced pressure and GC and ^1H NMR spectroscopy showed only a single isomer was obtained. Flash chromatography (1:40 EA/hexanes) gave the pure compound (63 mg, 96% yield) as colorless oil. ^1H NMR spectroscopy showed no second stereoisomer (*dr* >20:1). The relative configuration of the major isomer was determined by 2D ^1H-^1H NOESY, according to a key cross signal between H_1 and H_2 and lack of a cross signal between H_4 and H_5.

$[\alpha]^{20}_D = -0.028^o$ (*c* = 1.3, $CHCl_3$)

^1H NMR of the major isomer (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.77-4.72 (m, 1H), 3.31 (d, *J* = 8.0 Hz, 1H), 2.59 (s, 3H), 1.79-1.74 (m, 1H), 1.70-1.62 (m, 2H), 1.42-1.37 (m, 1H), 0.89 (s, 9H), 0.78-0.73 (m, 1H), 0.62-0.56 (m, 1H), 0.08 (s, 3H), 0.05 (s, 3H).

^{13}C NMR of the major isomer (100 MHz, $CDCl_3$): δ 198.0, 153.6, 135.4, 128.9, 127.4, 73.7, 44.9, 38.0, 26.8, 26.2, 23.7, 22.7, 18.5, 5.8, -4.2, -4.4.

GCMS (EI): calcd for $C_{20}H_{30}O_2Si$ [M-*t*Bu]: 273.13. Found: 273.12.



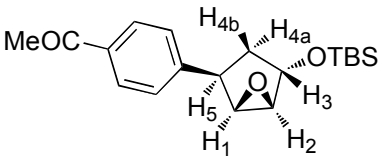
(1*S*,2*S*,3*S*,4*S*)-4-(*p*-Acetylphenyl)-1-(*t*-butyldimethylsilyloxy)-2,3-dihydroxy-cyclopentane. The *cis*-hydroxylation was conducted by following a reported procedure.[7] Under air, to 10-mL Schlenk tube was added (1*S*,4*S*)-4-(*p*-acetylphenyl)-1-(*t*-butyldimethylsiloxy)cyclopent-2-ene (96% purity, 63 mg, 0.2 mmol), analytical grade acetone (2.0 mL), and $KMnO_4$ (158 mg, 1.0 mmol) in 0.5 mL of deionized water. The tube was capped tightly and heated in a 50 ^oC oil bath for 24 h. After the reaction was finished, ^1H NMR spectroscopy of the crude product showed 9:1 facial selectivity. Flash chromatography (1:2 EA/hexanes) gave white solid in 90% yield (63 mg). The two isomers were not separated. Crystals suitable for X-ray diffractional analysis was obtained by vapor diffusion of hexanes into a solution in DCM at RT, which allowed the assignment of relative configuration of the major isomer of the diol.

$[\alpha]^{20}_D = -0.22^o$ (c = 1.8, $CHCl_3$).

^1H NMR of the major isomer (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 4.31-4.28 (m, 2H), 4.15-4.08 (m, 1H), 3.58-3.52 (m, 1H), 2.59 (s, 3H), 2.49-2.43 (m, 2H), 1.96-1.87 (m, 2H), 0.92 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H).

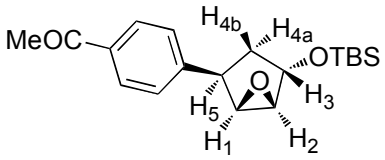
^{13}C NMR of the major isomer (100 MHz, $CDCl_3$): δ 198.2, 145.7, 136.1, 129.4, 128.8, 82.1, 78.3, 75.1, 46.1, 37.5, 26.9, 26.1, 18.4, 0.28, -4.3.

(ESI): calcd for $C_{19}H_{30}O_4SiNa$ [M+Na]: 373.18. Found: 373.18.



(1*S*,2*S*,3*S*,5*S*)-5-*p*-Acetylphenyl-3-(*t*-butyldimethylsilyloxy)-1,2-epoxycyclopentane. In air, to 10-mL Schlenk tube was added (1*S*,4*S*)-4-(*p*-acetylphenyl)-1-(*t*-butyldimethylsiloxy)cyclopent-2-ene (63 mg, 0.2 mmol) and analytical grade DCM (1.0 mL), followed by addition of *m*CPBA (50% purity, 138

mg, 0.4 mmol) in 5 portions in 15 min intervals. The reaction mixture was stirred at room temperature for 7 h until completion. The facial selectivity of epoxidation in the crude mixture was determined to be 6:1 by GC. The titled compound was obtained by silica gel flash chromatography by using 1:20 EA/hexanes to give a colorless oil in 76% yield (50 mg) and the two isomers were separated. The relative configuration of the major isomer was determined by 2D ^{1}H-^{1}H NOESY, based on a key cross signal between H_1 and H_5 and lack of a cross signal between H_3 and H_2.



$[\alpha]^{20}_{D} = -0.62^{o}$ (c = 1.0, $CHCl_3$).

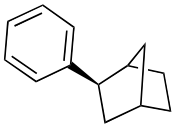
^{1}H NMR of the major isomer (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 4.45 (d, J = 4.8 Hz, 1H), 3.67 (d, J = 1.8 Hz, 1H), 3.55-3.41 (m, 2H), 2.59 (s, 3H), 1.95-1.88 (m, 1H), 1.72-1.55 (m, 1H), 0.93 (s, 9H), 0.12 (d, J = 1.8 Hz, 6H).

^{13}C NMR of the major isomer (75 MHz, $CDCl_3$): δ 198.1, 147.5, 136.0, 128.9, 128.3, 72.7, 59.8, 58.2, 53.7, 39.1, 26.8, 26.1, 18.4, -4.4, -4.5.

GCMS (ESI): calcd for $C_{19}H_{29}O_3Si$ (M+H): 333.19. Found: 333.11.

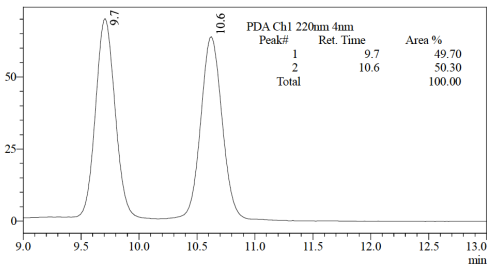
VI. Asymmetric hydroarylation of bicyclic olefins

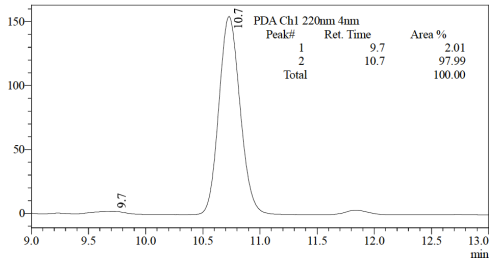
General procedure III using aryl triflates: In an argon-filled glove box, a dry 25-mL Schlenk tube was charged with $Pd(dba)_2$ (5 mol%, 14.4 mg, 0.025 mmol), (*R*)-Xyl-SDP(O) (6 mol%, 21.5 mg, 0.030 mmol) and 1.0 mL of dry DMF. After stirring at room temperature for 15 minutes, the mixture was treated with $NaCO_2H$ (68 mg, 1.0 mmol), aryl triflate (0.50 mmol), bicyclic olefin (1.0 mmol) and GC standard *n*-dodecane (20 μL). The tube was capped tightly and stirred in an 80 ^oC oil bath until aryl triflate was fully consumed (monitored by GC). At the end of the reaction, the reaction mixture was directly filtered through a pad of silica gel with diethyl ether washings (20 mL) to remove the Pd catalyst and inorganic salts. The filtrate was concentrated on a rotary evaporator and the residue was directly subjected to flash chromatography. The enantioselectivity of the purified product was determined by chiral HPLC analysis. The general procedure was used unless stated otherwise. To facilitate chiral HPLC analysis of Heck products, racemic samples were prepared by using racemic Xyl-SDP(O). Similar results were obtained by using standard Schlenk technique involving a vacuum manifold.



(2*R*)-*exo*-2-Phenylnorbornane [139152-86-6 for (2*R*) isomer]. The reaction was set up according to the general procedure III by using phenyl triflate (0.50 mmol, 113 mg) and norbornene (94 mg, 1.0 mmol). The reaction finished after 12 hours at 80 ^oC. The titled compound was obtained after flash chromatography (hexanes) as colorless oil (71 mg, 83% yield). The (*2R*) configuration of the major isomer was assigned by comparison with optical rotation.[8]

The ee of the purified products was determined to be 96% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 220 nm; flow rate = 0.5 mL/min). T_R = 9.7 min (minor) and 10.7 min (major).

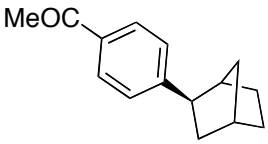




$[\alpha]^{20}_D$ = -0.06° (*c* = 0.6, $CHCl_3$).

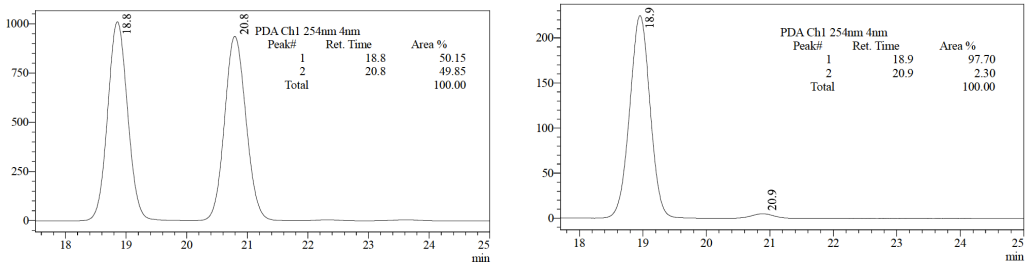
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.25 (m, 2H), 7.21-7.20 (m, 2H), 7.16-7.12 (m, 1H), 2.74 (dd, *J* = 8.8, 5.8 Hz, 1H), 2.37-2.34 (m, 2H), 1.79-1.74 (m, 1H), 1.69-1.63 (m, 1H), 1.61-1.51 (m, 3H), 1.38-1.31 (m, 1H), 1.29-1.24 (m, 1H), 1.19-1.16 (m, 1H).

GCMS (EI): calcd for $C_{13}H_{16}$ M: 172.13. Found: 172.10.



(2*R*)-*exo*-2-(*p*-Acetylphenyl)norbornane [54762-82-2 for racemates]. The reaction was set up according to the general procedure III by using *p*-acetyl phenyl triflate (0.50 mmol, 134 mg) and norbornene (94 mg, 1.0 mmol). The reaction finished after 20 hours at 80 °C. The titled compound was obtained after flash chromatography (1:50 ethyl acetate/hexanes) as colorless oil (100 mg, 93% yield).

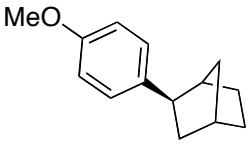
The ee of the purified products was determined to be 95% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 20.9 min (minor) and 18.9 min (major).



$[\alpha]^{20}_D$ = -0.4° (*c* = 1.1, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.82-2.77 (m, 1H), 2.58 (s, 3H), 2.39 (br s, 2H), 1.85-1.77 (m, 1H), 1.69-1.57 (m, 3H), 1.54-1.49 (m, 1H), 1.42-1.20 (m, 3H).

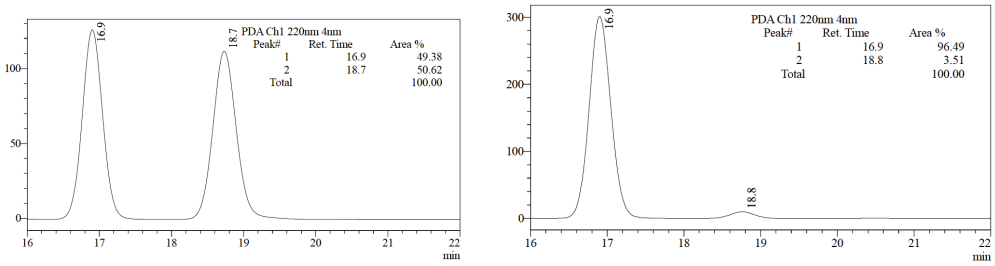
GCMS (EI): calcd for $C_{15}H_{18}O$ M: 214.14. Found: 214.04.



(2*R*)-*exo*-2-(*p*-Methoxylphenyl)norbornane [406946-53-0 for (2*R*) isomer]. The reaction was set up according to the general procedure III by using *p*-methoxylphenyl

triflate (0.50 mmol, 128 mg) and norbornene (94 mg, 1.0 mmol). The reaction finished after 16 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:50 Ethyl acetate/hexanes) as colorless oil (96 mg, 95% yield).

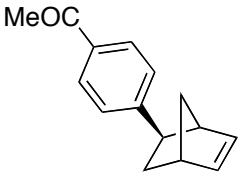
The ee of the purified products was determined to be 93% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 220 nm; flow rate = 0.5 mL/min). T_R = 18.8 min (minor) and 16.9 min (major).



$[\alpha]^{20}_{D}$ = -0.41^{o} (*c* = 2.0, $CHCl_3$).

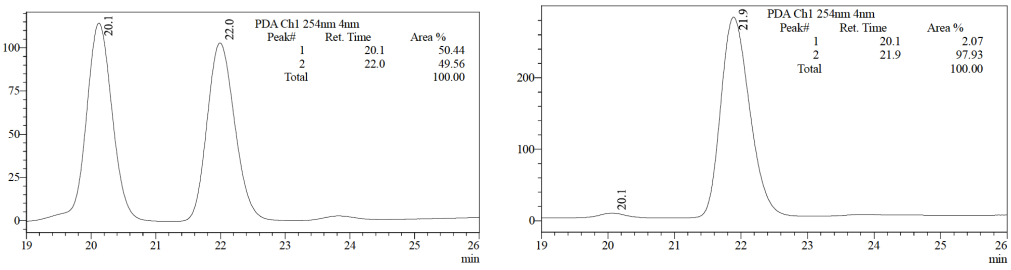
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.72-2.69 (m, 1H), 2.35-2.33 (m, 2H), 1.79-1.73 (m, 1H), 1.68-1.52 (m, 4H), 1.39-1.25 (m, 2H), 1.20-1.16 (m, 1H).

GCMS (EI): calcd for $C_{15}H_{18}O$ M: 202.14. Found: 202.09.



(5*R*)-*exo*-5-(*p*-Acetylphenyl)norborn-2-ene [for racemates 1092115-36-0]. The reaction was set up according to the general procedure III by using *p*-acetylphenyl triflate (0.50 mmol, 134 mg) and norbornadiene (92 mg, 1.0 mmol). The reaction finished after 12 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:50 ethyl acetate/hexanes) as colorless oil (85 mg, 80% yield).

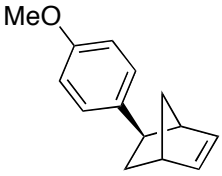
The ee of the purified products was determined to be 96% by chiral HPLC analysis (Daicel CHIRALCEL ID-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 20.1 min (minor) and 21.9 min (major).



$[\alpha]^{20}_{D} = -0.04^{o}$ (c = 1.0, $CHCl_3$).

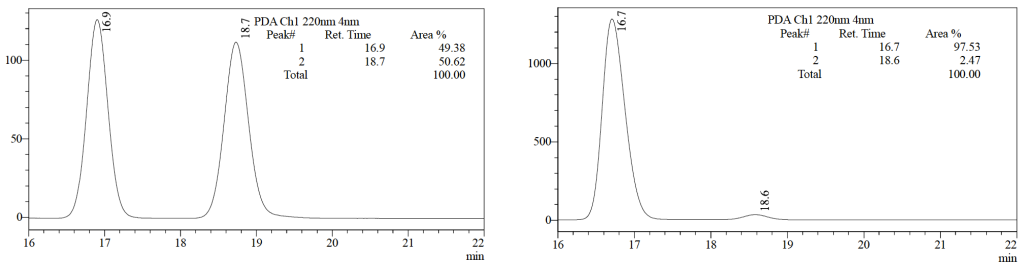
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 6.27-6.18 (m, 2H), 2.99 (s, 1H), 2.94 (s, 1H), 2.78-2.74 (m, 1H), 2.59 (s, 3H), 1.75-1.68 (m, 2H), 1.58-1.54 (m, 2H), 1.48-1.46 (m, 1H).

GCMS (EI): calcd for $C_{15}H_{16}O$ M: 212.12. Found: 212.09.



(5*R*)-*exo*-5-(*p*-Anisyl)norborn-2-ene [139152-93-5 for (5*R*) isomer]. The reaction was set up according to the general procedure III by using *p*-methoxyphenyl triflate (0.50 mmol, 128 mg) and norbornadiene (92 mg, 1.0 mmol). The reaction finished after 12 hours at 80 ^{o}C. The titled compound was obtained after flash chromatography (1:50 ethyl acetate/hexanes) as colorless oil (85 mg, 85% yield).

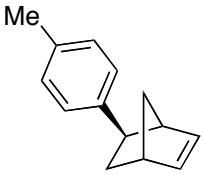
The ee of the purified products was determined after catalytic hydrogenation. The hydrogenation was carried out by using 10 mg of the product and 5% Pd/C (0.5 mg) in 0.2 mL of MeOH. The reaction finished after 7 hours under 100 psi of H_2. The ee after hydrogenation was determined to be 95% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 220 nm; flow rate = 0.5 mL/min). T_R = 18.6 min (minor) and 16.7 min (major).



$[\alpha]^{20}_{D} = -0.04^{o}$ (c = 0.8, $CHCl_3$).

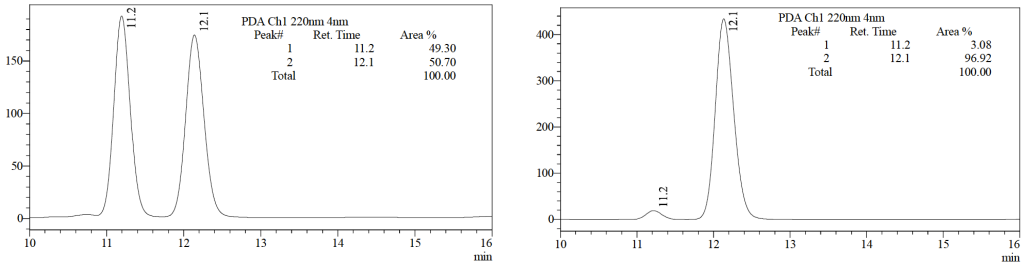
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.25-6.14 (m, 2H), 3.80 (s, 3H), 2.95 (s, 1H), 2.85-2.84 (m, 1H), 2.68-2.65 (m, 1H), 1.73-1.68 (m, 1H), 1.64-1.57 (m, 2H), 1.55-1.41 (m, 1H).

GCMS (EI): calcd for $C_{14}H_{16}O$ M: 200.12. Found: 200.09.



(5*R*)-*exo*-5-(*p*-Tolyl)norborn-2-ene [51690-57-4 for one stereoisomer]. The reaction was set up according to the general procedure III by using *p*-methylphenyl triflate (0.50 mmol, 120 mg) and norbornadiene (92 mg, 1.0 mmol). The reaction finished after 12 hours at 80 °C. The titled compound was obtained after flash chromatography (hexanes) as colorless oil (76 mg, 83% yield).

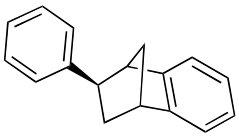
The ee of the purified products was determined to be 94% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*-PrOH = 98:2; detection wavelengths = 254 nm; flow rate = 0.5 mL/min). T_R = 11.2 min (minor) and 12.1 min (major).



$[\alpha]^{20}_D$ = -0.06° (c = 1.0, $CHCl_3$).

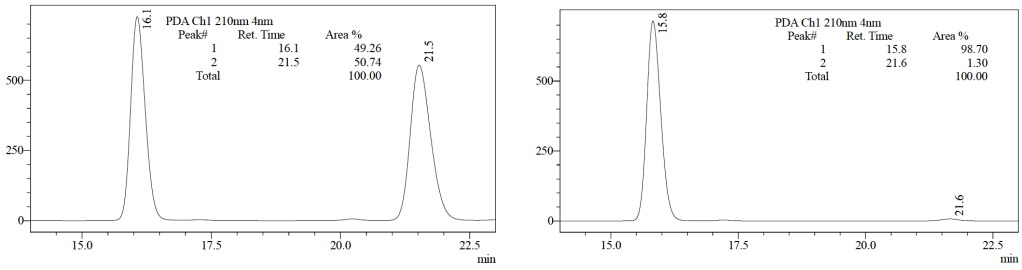
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.26-6.14 (m, 2H), 2.95 (s, 1H), 2.87 (s, 1H), 2.70-2.66 (m, 1H), 2.32 (s, 3H), 1.76-1.69 (m, 1H), 1.65-1.56 (m, 2H), 1.43-1.40 (m, 1H).

GCMS (EI): calcd for $C_{14}H_{16}$ M: 184.13. Found: 184.02.



(2*R*)-*exo*-2-Phenylbenzonorbornene [58653-72-8 for racemates]. The reaction was set up according to the general procedure III by using phenyl triflate (0.50 mmol, 113 mg) and benzonorbornadiene (142 mg, 1.0 mmol). The reaction finished after 12 hours at 80 °C. The titled compound was obtained after flash chromatography (hexanes) as colorless oil (95 mg, 86% yield).

The ee of the purified products was determined to be 97% by chiral HPLC analysis (Daicel CHIRALCEL OJ-H; Hexanes: *i*PrOH = 98:2; detection wavelengths = 210 nm; flow rate = 0.5 mL/min). T_R = 21.6 min (minor) and 15.8 min (major).



$[\alpha]^{20}_{D}$ = -0.74° (*c* = 1.3, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.33 (m, 4H), 7.26-7.20 (m, 3H), 7.13-7.10 (m, 2H), 3.46 (s, 2H), 2.89-2.84 (m, 1H), 2.08-1.98 (m, 2H), 1.97-1.82 (m, 2H).

GCMS (EI): calcd for $C_{17}H_{16}$ M: 220.13. Found: 220.00.

VII. Reference

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