Supporting Information

Stereospecific synthesis of alkylidenecyclopropanes via sequential cyclopropene carbomagnesation/1,3-carbon shift

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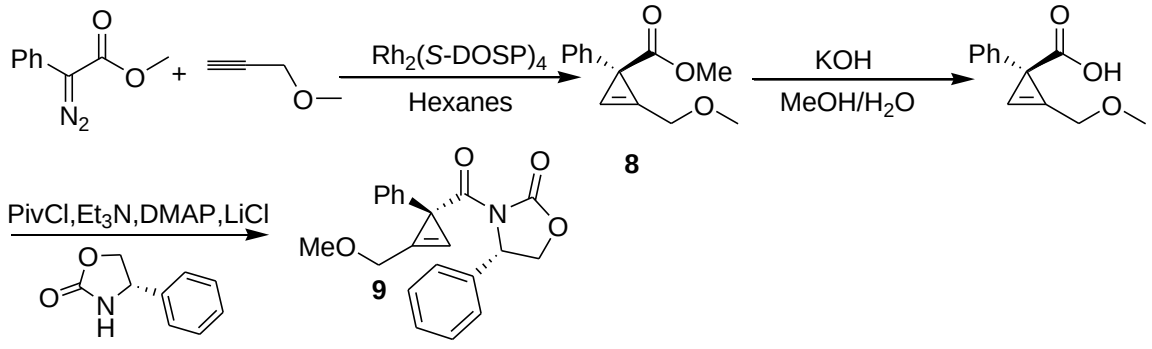
Experimental Procedures

General Considerations

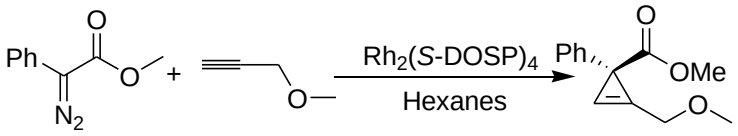
All reactions were carried out in glassware that was flame dried under vacuum, and cooled under nitrogen. Reactions were carried out in flasks with septum fitted inlet adapters (similar to CHEMGLASS CG1062-14) so that the flasks could be evacuated and refilled with nitrogen prior to the addition of liquids through the septum. All commercially available reagents were used as received without further purification. Hexanes, diethyl ether and CH_2Cl_2 were dried with columns prepacked with activated neutral alumina. THF was distilled from Na/benzophenone. Copper(I) iodide (98%) was stored under normal atmosphere. MeMgBr, EtMgBr, allylMgBr, *n*-$C_6H_{13}MgBr$ and (1,3-dioxan-2-ylethyl)magnesium bromide were purchased from Aldrich. *Cy*-$C_6H_{13}MgBr$ was purchased from TCI. Benzylmagnesium bromide was freshly prepared as a solution in diethyl ether (3.0 M). DIBAL-H was purchased from Aldrich as a neat material and diluted in a glove box to a concentration of 1.0 M in THF. Alternatively, DIBAL-H was purchased from Aldrich as a 1.0 M solution in THF. Rh_2(octanoate)$_4$ was purchased from Strem, and Rh_2(*S*-DOSP)$_4$ was purchased from Aldrich. Chromatography was performed on silica gel (ICN Silitech 32-62D, 60 Å). For ^{1}H-NMR, the abbreviation 'app' stands for apparent (e.g., 'app d'= apparent doublet). For ^{13}C-NMR, multiplicities were distinguished using an APT pulse sequence: Typical

methylene and quaternary carbons appear 'up'; methine and methyl carbons appear 'down'. Exceptions are methine carbons of alkynes and cyclopropenes, which usually have the same phase as 'normal' methylene and quaternary carbons. Enantiomeric excesses were determined by HPLC using isopropanol/hexane as the eluent and CHIRACEL OD ,OJ or AD columns. All reactions have been repeated, yields in the text below represent that observed in a single run. The yields in the tables represent the average of two or more runs, and therefore may differ slightly from those in the text below.

Scheme 1 Determination of Absolute Configuration of **8**



(*S*)-Methyl 2-methoxymethyl-1-phenylcycloprop-2-ene carboxylate (8):



8

A 50 mL round bottom flask was evacuated dried and purged with nitrogen three times. Hexanes (8 mL) were added via syringe, followed by the addition of methyl propagyl ether (421 mg, 6.0 mmol, 507 μL) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol). A solution of methyl α-phenyl-α-diazoacetate (352 mg, 2.0 mmol) in hexanes (2 mL) was slowly added at r.t. to the reaction mixture using a syringe pump at 1 mL/h. After the addition was completed, the mixture was allowed to stir for another 4 h. Then solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography (10% ethyl acetate in hexanes) to give 216 mg (0.99 mmol, 50% yield) of (*S*)-methyl-2-methoxymethyl-1-phenylcycloprop-2-ene carboxylate as a pale yellow oil.

HPLC analysis showed the material to be of 82% ee (using a chiral OJ column, flow rate of 1 mL/min, 3% slowing increased to 6% IPA in hexanes in 90 min, t_1 = 50.7 min, t_2 = 61.8 min).

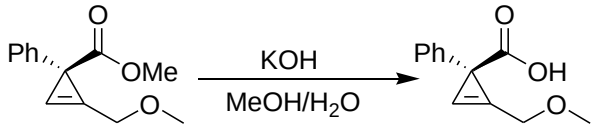
Small peaks attributable to impurities were observed in the ^{1}H NMR at 7.83, 7.09, 5.10, 3.83, 3.81, 3.77, 3.72, 3.35, 2.99 ppm and in the ^{13}C NMR at 194.1, 129.9, 128.9, 34.1 ppm.

$[\alpha]^{20}_D = -13^\circ$ (c. 1.38 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.30 (m, 4H), 7.21-7.24 (m, 1H), 6.99 (t, *J* = 1.6 Hz, 1H), 4.56 (dd, *J* = 15.8, 1.6 Hz, 1H), 4.48

(dd, J = 15.8, 1.6 Hz, 1H), 3.70 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4 (C), 140.8 (C), 134.9 (C), 128.3 (CH), 128.1 (CH), 126.6 (CH), 117.7 (CH), 100.8 (CH_2), 65.5 (C), 58.7 (CH_3), 52.2 (CH_3); IR (neat, cm^{-1}): 3134, 3059, 3026, 2994, 2950, 2827, 1717, 1602, 1495, 1435, 1359, 1230, 1108, 1039, 1022, 912, 893, 825, 791, 761, 701, 653, 546

HRMS-CI (CH_4)m/z: [M-OMe] Calculated for $C_{12}H_{11}O_2$, 187.0759, found 187.0754.

(*S*)- 2-Methoxymethyl-1-phenylcycloprop-2-ene carboxylic acid:



8

To a 100 mL round bottom flask was added (*S*)-methyl 2-(methoxymethyl)-1-phenylcycloprop-2-ene carboxylate (**8**) (445 mg, 2.04 mmol), followed by MeOH (9 mL) and H_2O (1 mL). KOH (571 mg, 10.2 mmol) was added to the reaction mixture. The reaction mixture was stoppered and allowed to stir at r.t. for 16 h. The volatile solvents were then removed on the rotary evaporator, and the remaining liquid was transferred to a separatory funnel filled with 4% KOH (10 mL). The aqueous layer was extracted three times with ethyl acetate (5 mL) and then acidified with 3 M HCl (10 mL). The aqueous layer was then extracted three times with ethyl acetate (5 mL), and

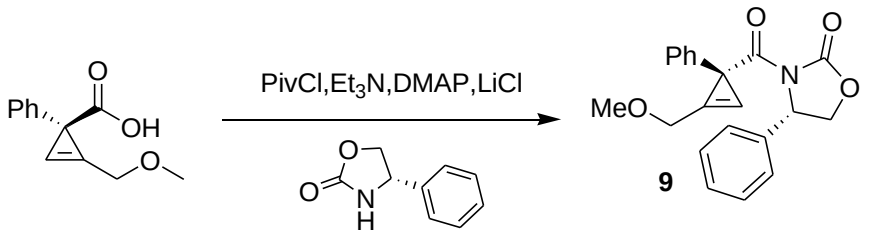
the combined organics were dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was chromatographed on a column of silica gel with 50% ethyl acetate in hexanes to provide 345 mg (1.69 mmol, 83% yield) of (*S*)-2-methoxymethyl-1-phenylcycloprop-2-ene carboxylic acid as a pale yellow oil.

HPLC analysis showed the material to be of 82% ee (Using a Chiracel OD column, flow rate of 1 mL/min, 1% IPA gradually increased to 5% IPA in hexanes in 60min, t_1 = 38.6 min, t_2 = 40.0 min)

$[\alpha]^{20}_D = -13^\circ$ (c. 0.98 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.27 (m, 5H), 6.99 (t, *J* = 1.6 Hz, 1H), 4.54 (dd, *J* = 15.8, 1.6 Hz, 1H), 4.49 (dd, J = 15.8, 1.6 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7 (C), 140.0 (C), 128.5 (CH), 128.2 (CH), 126.8 (CH), 117.2 (CH), 100.3 (CH_2), 65.4 (C), 58.8 (CH_3), 33.5 (C); IR (neat, cm^{-1}): 3138, 3026, 2934, 2828, 1686, 1495, 1447, 1413, 1227, 1193, 1109, 960, 911, 764, 701

HRMS-CI (CH_4)*m/z*: [M+H] Calculated for $C_{12}H_{13}O_3$, 205.0865, found 205.0863.

(4*S*)-3-[(1*S*)-2-Methoxymethyl-1-phenylcycloprop-2-enoyl]-4-phenyloxazolidin-2-one (9):

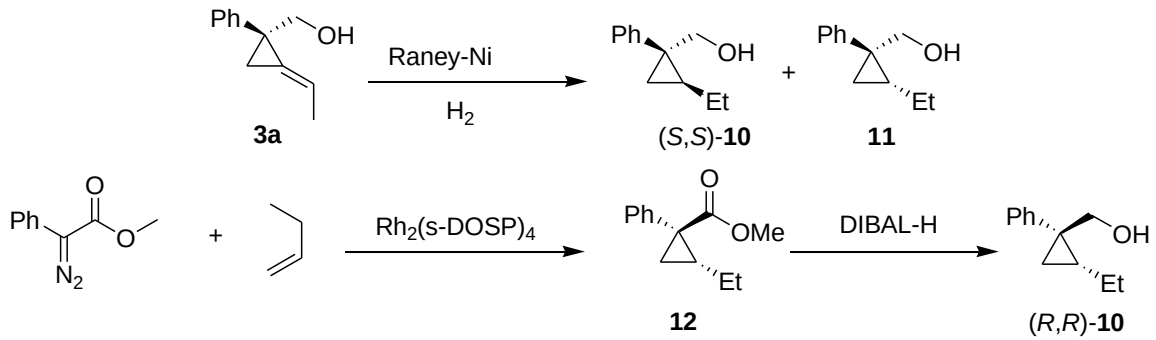


To a 100 mL round bottomed flask was added enantiomerically enriched (*S*)-2-methoxymethyl-1-phenylcycloprop-2-ene carboxylic acid (252 mg, 0.763 mmol, 82% ee).The flask was evacuated and refilled with nitrogen three times. THF (15 mL) was added to the flask, then the flask was cooled to −30 ˚C. Freshly distilled triethylamine (282 mg, 388 μL, 2.79 mmol) and pivaloyl chloride (140 mg, 143 μL, 1.17 mmol) were added sequentially, and stirring at −30 ˚C was continued for 2 h, during which time a large volume of white solid (Et_3N·HCl) precipitated. LiCl (145 mg, 3.41 mmol) was added and after 10 min, (*S*)-4-phenyloxazolidinone (224 mg, 1.39 mmol) and catalytic amount of 4-dimethylaminopyridine (9 mg, 0.07 mmol) were added. The reaction mixture was allowed to stir at −30 ˚C for 16 h and then slowly allowed to warm to r.t.. The mixture was then filtered on a Büchner funnel to remove the precipitate, and the precipitate was rinsed with additional THF (5 mL). The solvents were removed under reduced pressure at r.t., and the residue was partitioned between water (10 mL) and ethyl acetate (30 mL). The aqueous layer was extracted twice with ethyl acetate (5 mL), and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was chromatographed on a column of silica gel

with 10% ethyl acetate in hexanes. The yield of **9** was 186 mg (0.53 mmol, 70% yield). Compound **9** is a pale yellow oil. NMR analysis of the crude mixture showed a pair of diastereomers in a ratio of (11 : 1). Peaks in the ^{1}H NMR spectra at 5.45, 4.55, 4.48, 4.46 and 3.39 ppm were attributed to the minor diastereomer of **9**, which has the *R*-configuration at C-1. A peak attributable to an impurity was found in the ^{13}C NMR at 21.5 ppm. $[\alpha]^{20}_{D} = -115^{\circ}$ (c. 1.86 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.40 (m, 3H), 7.14-7.30 (m, 5H), 7.03 (t, *J* =1.7 Hz, 1H), 6.96-6.98 (m, 2H), 5.43 (dd, *J* = 5.0, 8.9 Hz, 1H), 4.61 (dd, *J* = 16.5, 1.8 Hz, 1H), 4.59 (app. t, *J* = 8.9 Hz, 1H), 4.39 (dd, *J* = 16.6, 1.6 Hz, 1H), 4.21 (dd, *J* = 5.0, 9.0 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 (C), 152.2 (C), 140.6 (C), 138.6 (C), 129.1 (CH), 128.9 (CH), 128.1 (CH), 126.7 (CH), 126.7 (CH), 126.6 (CH), 121.9 (C), 102.0 (C), 69.8 (CH_2), 66.2 (CH_2), 58.6 (CH), 57.7 (CH_3), 36.8 (C); IR (neat, cm^{-1}):3130, 3060, 3029, 2930, 2826, 1791, 1691, 1601, 1495, 1457, 1384, 1321, 1200, 1104, 1047, 913, 889, 822, 700, 636, 612, 585, 536 HRMS-CI (CH_4)*m/z*: [M+Na] calculated for $C_{21}H_{19}O_4NNa$, 372.1212, found 372.1199.

The X-ray crystal structure was determined for the minor diastereomer of **9**, which was described previously[1] and shown to have the *R*-configuration at C-1 of the cyclopropene.

Scheme 2 Assignment of Absolute Configuration of **2a**



The absolute configuration of **3a** was assigned by Raney-Ni reduction, which gave separable diastereomers (*S*,*S*)-**10** & **11**. (Scheme 2). The opposite enantiomer of **10** was produced upon reduction of the known compound **12**, which was prepared as described by Davies.[2] Davies had shown that **12** prepared from Rh_2(*S*-DOSP)$_4$ has the (1*R*,2*R*)-configuration.

Enantiomerically enriched compound (*S*,*S*)-**10** was compared with (*R*,*R*)-**10** by HPLC on a Chiracel OD column and the analysis confirmed that the absolute stereochemistry of compound **3a** is (*S*).

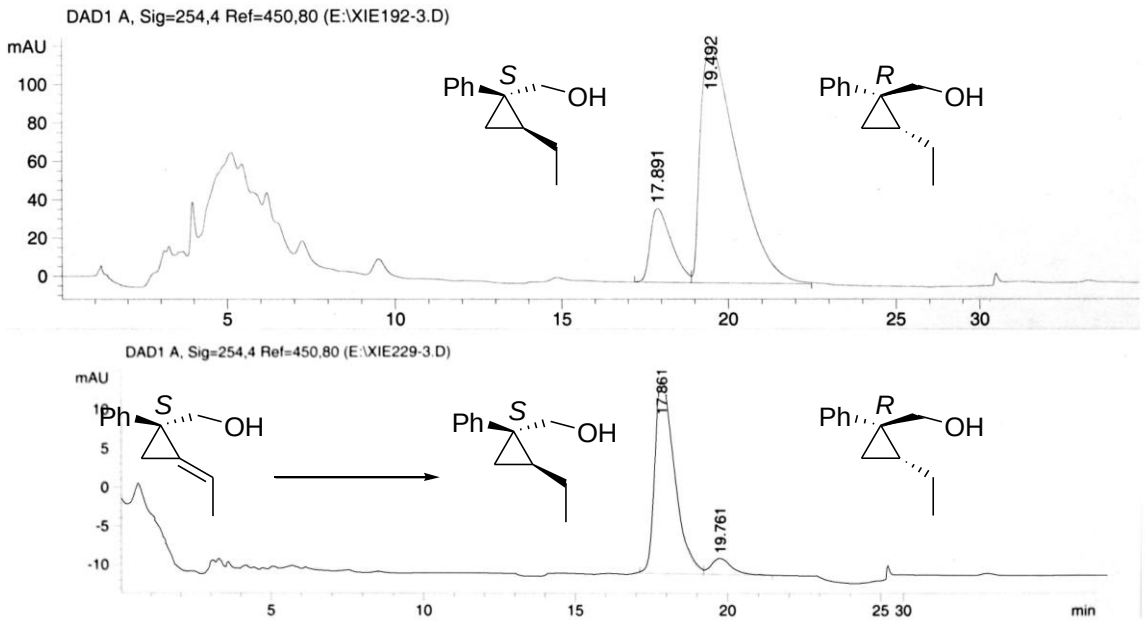
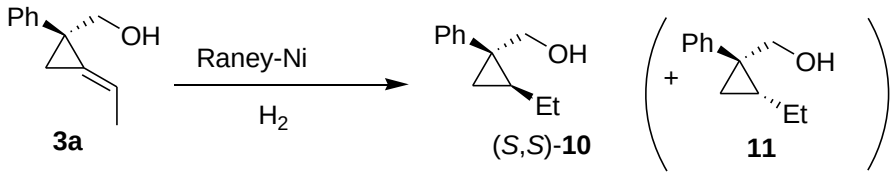


Figure 1 HPLC of enantiomerically enriched cyclopropane **10** prepared by the method described by Davies (top HPLC) and upon Raney-Ni reduction of methylenecyclopropane **3a** (bottom HPLC)

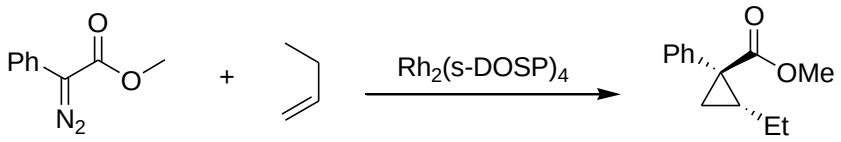
(1*S*,2*S*) 1-Phenyl-1-hydroxymethyl-2-ethyl cyclopropane[(*S*,*S*)-10]:



Enantiomerically enriched **3a** (53 mg, 0.31 mmol) was dissolved in ethanol and put into a 100mL round bottom flask. The flask was briefly evacuated and backfilled with hydrogen gas. Raney-Ni (about 10 mg) was added to the flask as a slurry in water. A balloon of hydrogen gas was put on top of the flask and the reaction was allowed to stir at r.t. for 3 h. The Raney-Ni

catalyst was removed by a magnetic stir bar. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography (10% ethyl acetate in hexanes) to give 53 mg (0.31 mmol, 100% yield) of (*S*,*S*)-**10** and **11** (55 : 45) as a colorless oil. Preparative HPLC (normal phase SiO_2, flow rate of 2 mL/min, 1% IPA in hexanes) was used to separate (*S*,*S*)-**10** from **11**. HPLC analysis showed (*S*,*S*)-**10** to be of 82% ee (Using a Chiracel OD column, flow rate of 1 mL/min, 1% IPA in hexanes, t_1 = 17.9 min, t_2 = 19.8 min). Spectral data are identical to that of (*R*,*R*)-**10**, which will be discussed below.

(1*S*,2*R*) Methyl 2-ethyl-1-phenylcyclopropanecarboxylate (12):

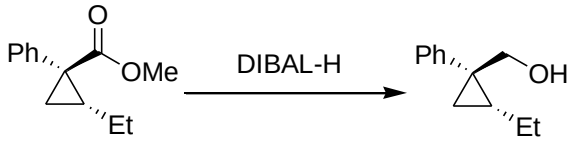


12

Compound **12** was prepared by a modified procedure of Davies.[1] A 100 mL three-neck flask was charged with Rh_2(*S*-DOSP)$_4$ (47 mg, 0.03 mmol). The flask was evacuated, filled with nitrogen and 20 mL of dry hexanes was added via syringe. The 3-neck flask was then cooled to 0 ˚C and fitted with a Dewar type condenser filled with dry ice / acetone. 1-Butene (approx. 1 mL) was condensed into the 3-neck flask under nitrogen atmosphere. A solution of methyl α-phenyl-α-diazoacetate (440 mg, 2.50 mmol) was dissolved in

hexanes (20 mL), and this solution was slowly added to the reaction mixture via syringe pump at a rate of 7 mL/h. After the addition was complete, the mixture was stirred at 0 ˚C for 8 h. Solvent and excess 1-butene were removed under reduced pressure, and the residue was purified by silica gel chromatography (5% diethyl ether in hexanes). The reaction yielded 220 mg (1.08 mmol, 43% yield) (1*R*,2*R*)-methyl 2-ethyl-1-phenylcyclopropane carboxylate (**12**) as a yellow oil. HPLC analysis showed the material to be of 70% ee (using a chiral OJ column, flow rate of 1 mL/min, 10% IPA in hexanes). Spectral and properties corresponded to those reported in the literature.[2]

(1*R*,2*R*) 1-Phenyl-1-hydroxymethyl-2-ethylcyclopropane [(*R*,*R*)-10]:



12 **(*R*,*R*)-10**

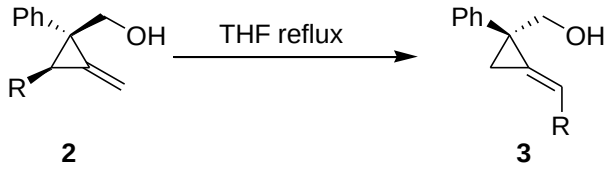
To a 50 mL round bottomed flask was added (1*S*,2*R*) methyl 2-ethyl-1-phenylcyclopropane carboxylate (**12**) (220 mg, 1.08 mmol) in THF (5 mL). The resulting solution was cooled in a bath of dry ice/acetone (−78 ˚C), and DIBAL-H (5.40 mmol, 5.4 mL of a 1.0 M solution in THF) was slowly added dropwise over the course of 10 min. The resulting mixture was allowed to stir

under nitrogen at −78 ˚C. When the reaction was judged complete by TLC analysis (approx. 1 h), the reaction mixture was quenched with saturated aqueous NH_4Cl at −78 ˚C. The reaction mixture was allowed to warm to r.t., and the aqueous layer was extracted with diethyl ether. The organic layers were combined, washed with brine and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel chromatography (20% ethyl acetate in hexanes) to give 87 mg (0.49 mmol, 46% yield) of (*R,R*)-**10** as a white solid, mp = 46-48 ˚C, HPLC analysis showed the material to be of 70% ee (using a chiral OD column, flow rate of 0.5 mL/min, 1% IPA in hexanes, t_1 = 17.9 min, t_2 = 19.5 min).

$[\alpha]^{20}_D$ = −40 ˚(c. 2.12 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.34 (m, 5H), 3.83 (dd, *J* = 11.2, 1.2 Hz, 1H), 3.34 (d, *J* = 11.2 Hz, 1H), 1.49 (s, 1H), 1.26-1.35 (m, 1H), 0.89-1.01 (m, 5H), 0.58-0.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7 (C), 130.5 (CH), 128.3 (CH), 126.7 (CH), 72.1 (CH_2), 33.9 (C), 24.3 (CH), 23.7 (CH_2), 15.3 (CH_2), 13.7 (CH_3). IR(neat,cm^{-1}): 3060, 3025, 2958, 2930, 2872, 1602, 1496, 1447, 1376, 1040, 763, 702

HRMS-CI (CH_4)*m/z*: [M-OH] calculated for $C_{12}H_{15}$, 159.1174, found, 159.1177.

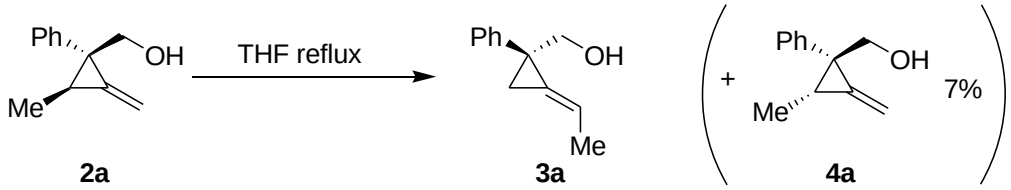
General procedure for [1,3] carbon shift reactions



Scheme 3 [1,3] carbon shift reaction

To a 100 mL round bottomed flask was added a solution of methylenecyclopropane **2** in THF. The reaction mixture was heated to reflux temperature for 16 h. THF was removed from the resulting mixture under reduced pressure and the crude product was purified by silica gel chromatography (10% ethyl acetate in hexane).

(*S*,*E*)-2-Hydroxymethyl-2-phenyl-ethylidenecyclopropane (3a):

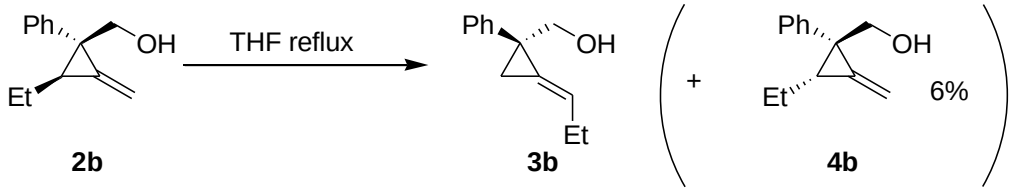


The general procedure for the [1,3] carbon shift reaction with **2a** (52 mg, 0.30 mmol) in THF (15 mL) gave 37 mg (0.21 mmol, 71% yield) of **3a** as a pale yellow oil. A similar experiment that began with 46 mg **2a** gave **3a** in 70% yield. Small peaks attributable to **4a** (7%) were detected in the ^{1}H NMR spectrum at 5.74, 5.57, 4.00, 3.58, 1.77 and 0.84 ppm and in the ^{13}C NMR at 129.9, 126.9 ppm. HPLC analysis showed the material to be of 82% ee (using a Chiral OD column, flow rate of 1 mL/min, 1% IPA in hexanes, t_1 = 22.0 min, t_2 = 31.8 min).

$[\alpha]^{20}_{D} = -76^{\circ}$ (c. 0.28 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.40 (m, 2H), 7.28-7.34 (m, 2H), 7.20-7.25 (m, 1H), 6.09-6.15 (m, 1H), 3.87 (dd, *J* = 11.3, 6.1 Hz, 1H), 3.72 (dd, *J* = 11.2, 6.6 Hz, 1H), 1.86 (dt, *J* = 6.5, 1.7 Hz, 3H), 1.51-1.55 (m, 1H), 1.41-1.45 (m, 1H), 1.37-1.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4 (C), 128.4 (CH), 128.2 (C), 128.0 (CH), 126.7 (CH), 114.7 (CH), 68.8 (CH_2), 31.0 (C), 16.9 (CH_3), 15.6 (CH_2); IR(neat, cm^{-1}):3351, 3083, 3059, 3028, 2957, 2924, 2855, 1602, 1495, 1464, 1416, 1378, 1303, 1222, 1176, 1029, 905, 760, 732, 699, 562, 542

HRMS-CI (NH_3) *m/z*: [M+NH_4] calculated for $C_{12}H_{18}NO$, 192.1388, found, 192.1380.

(*S*,*E*)-2-Hydroxymethyl-2-phenyl propylidenecyclopropane (3b):



2b **3b** **4b**

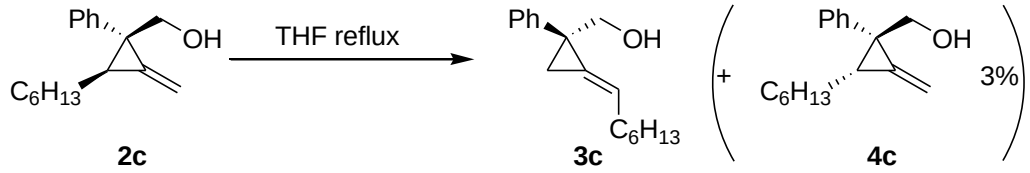
The general procedure for the [1,3] carbon shift reaction with **2b** (116 mg, 0.62 mmol) in THF (30 mL) gave 100 mg (0.53 mmol, 85% yield) of **3b** as a pale yellow oil. A similar experiment that began with 29 mg **2b** gave **3b** in 86% yield. Small peaks attributable to **4b** (6%) were detected in the ^1H NMR spectrum at 5.73, 5.61, 4.03, 3.58, 1.24 and 0.89 ppm and in the ^{13}C NMR at 129.7, 128.2, 126.7, 104.3, 70.0, 28.3, 22.0 ppm. HPLC analysis showed the

material to be of 82% ee (using a chiral OD column, flow rate of 1 mL/min, 1% IPA in hexanes, t_1 = 14.9 min, t_2 = 22.5 min).

$[\alpha]^{20}_D = -48^\circ$ (c. 0.50 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.40 (m, 2H), 7.29-7.33 (m, 2H), 7.20-7.25 (m, 1H), 6.10-6.15 (m, 1H), 3.87 (dd, *J* = 11.3, 6.1 Hz, 1H), 3.72 (dd, *J* = 11.3, 6.6 Hz, 1H), 2.21-2.28 (m, 2H), 1.55-1.58 (m, 1H), 1.41-1.45 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5 (C), 128.4 (CH), 128.0 (CH), 126.6 (CH), 126.5 (C), 121.4 (CH), 68.9 (CH_2), 30.0 (C), 25.0 (CH_2), 16.1 (CH_2), 13.6 (CH_3); IR(neat, cm^{-1}):3389, 2964, 2931, 2872, 1636, 1602, 1494, 1446, 1376, 1025, 698, 560

HRMS-CI (NH_3) *m/z*: [M+H] Calculated for $C_{13}H_{17}O$, 189.1279, found, 189.1271.

(*S*,*E*)-2-Hydroxymethyl-2-phenylheptylidenecyclopropane (3c):



2c **3c** **4c**

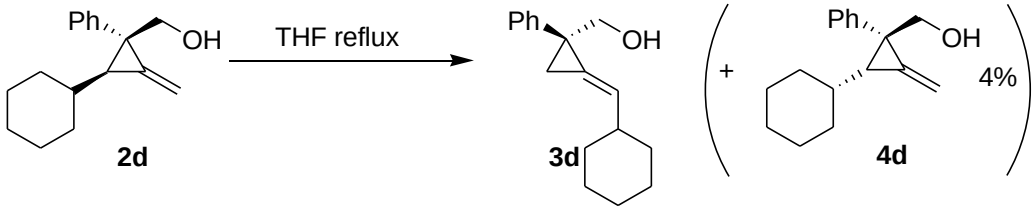
The general procedure for the [1,3] carbon shift reaction with **2c** (164 mg, 0.67 mmol) in THF (30 mL) gave 115 mg (0.47 mmol, 70% yield) of **3c** as a pale yellow oil. A similar experiment that began with 20 mg **2c** gave **3c** in 70% yield. Small peaks attributable to **4c** (3%) were detected in the ^{1}H NMR spectrum at 5.73, 5.57, 4.03 and 3.58 ppm. HPLC analysis showed the

material to be of 82% ee (using a chiral OD column, flow rate of 1 mL/min, 1% IPA in hexanes, t_1 = 16.4 min, t_2 = 24.3 min).

$[\alpha]^{20}_D = -47^\circ$ (c. 0.34 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.40 (m, 2H), 7.28-7.33(m, 2H), 7.20-7.24 (m, 1H), 6.07-6.12 (m, 1H), 3.88 (dd, *J* = 11.3, 6.1 Hz, 1H), 3.72 (dd, *J* = 11.3, 6.8 Hz, 1H), 2.19-2.25 (m, 2H), 1.24-1.56 (m, 11H), 0.88 (t, *J* = 7.0 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5 (C), 128.4 (CH), 127.9 (CH), 127.3 (C), 126.6 (CH), 120.2 (CH), 68.8 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 30.4 (C), 29.1 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 16.1 (CH_2), 14.1 (CH_3); IR(neat,cm^{-1}):2924, 2854, 2360, 2341, 1494, 1024, 764, 697, 502

HRMS-CI (NH_3) *m/z*: [M+NH_4] Calculated for $C_{17}H_{28}NO$, 262.2171, found, 262.2175.

(*S*,*E*)-2-Hydroxymethyl-2-phenyl-(cyclohexylmethylene)cyclopropane (3d):



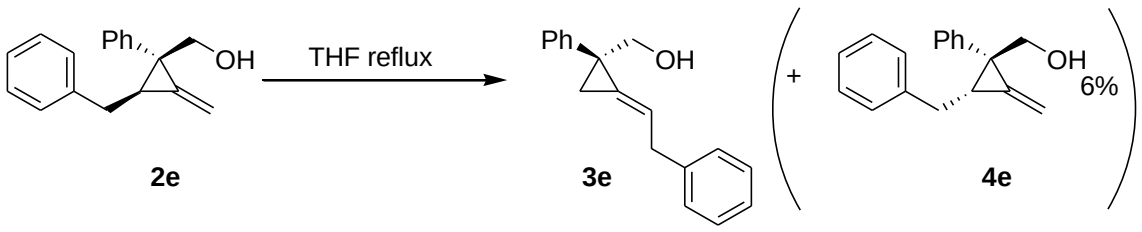
The general procedure for the [1,3] carbon shift reaction with **2d** (48 mg, 0.20 mmol) in THF (25 mL) gave 34 mg (0.14 mmol, 70% yield) of **3d** as a pale yellow oil. A similar experiment that began with 22 mg **2d** gave **3d** in 73% yield. Small peaks attributable to **4d** (4%) were detected in the ^{1}H NMR spectrum at 5.73, 5.63, 4.03 and 3.58 ppm. Small peaks attributable to **2d**

(3%) were also detected in the 1H NMR spectrum at 5.61 and 5.50 ppm. HPLC analysis showed the material to be of 82% ee (using a chiral OD column, flow rate of 1 mL/min, 1% IPA in hexanes, t_1 = 18.3 min, t_2 = 22.2 min).

$[\alpha]^{20}_D = -58^\circ$ (c. 0.26 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.39 (m, 2H), 7.28-7.32 (m, 2H), 7.20-7.24 (m, 1H), 6.01-6.04 (m, 1H), 3.88 (dd, *J* = 11.3, 5.6 Hz, 1H), 3.71 (dd, *J* = 11.3, 6.2 Hz, 1H), 2.17-2.25 (m, 1H), 1.81-1.84 (m, 2H), 1.71-1.75 (m, 2H), 1.64-1.67 (m, 1H), 1.58-1.59 (m, 1H), 1.39-1.46 (m, 2H), 1.17-1.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 (C), 128.4 (CH), 127.9 (CH), 126.5 (CH), 125.5 (CH), 125.5 (C), 68.8 (CH_2), 40.4 (CH), 32.8 (CH_2), 29.1 (C), 26.2 (CH_2), 26.1 (CH_2), 16.8 (CH_2); IR(neat,cm^{-1}):3058, 3026, 2923, 2850, 1601, 1495, 1446, 1176, 1026, 892, 760, 697

HRMS-CI (CH_4) *m/z*: [M−OH] Calculated for $C_{17}H_{21}$, 225.1643, found, 225.1641.

(*S*,*E*)-2-Hydroxymethyl-2-phenyl phenylethylidenecyclopropane (3e):

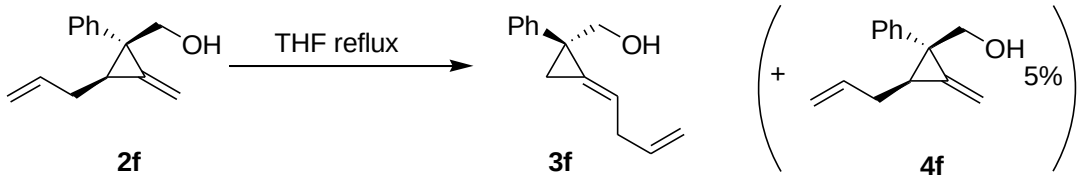


The general procedure for the [1,3] carbon shift reaction with **2e** (56 mg, 0.22 mmol) in THF (15mL) gave 44 mg (0.18 mmol, 82% yield) of **3e** as a pale yellow oil. A similar experiment that began with 16 mg **2e** gave **3e** in 85% yield. Small peaks attributable to **4e** (6%) were detected in the ^{1}H NMR spectrum at 5.80, 5.60, 4.05 and 3.65 ppm and in the ^{13}C NMR at 130.4, 129.7, 118.1, 105.2, 69.7, 35.5 and 26.9 ppm. HPLC analysis showed the material to be of 82% ee (using a chiral OD column, flow rate of 1 mL/min, 3% IPA in hexanes, t_1 = 17.5 min, t_2 = 21.3 min).

$[\alpha]^{20}_{D} = -91^{\circ}$ (c. 0.05 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.43 (m, 2H), 7.27-7.33 (m, 4H), 7.20-7.24 (m, 4H), 6.26-6.30 (m, 1H), 3.89 (dd, *J* = 11.4, 6.1 Hz, 1H), 3.74 (dd, *J* = 11.4, 6.8 Hz, 1H), 3.57 (d, *J* = 6.8 Hz, 2H), 1.55-1.58 (m, 2H), 1.40-1.41 (m, 1H); ^{13}C NMR (90 MHz, $CDCl_3$): δ 141.1 (C), 140.5 (C), 129.0 (C), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.0 (CH), 126.7 (CH), 126.0 (CH), 118.6 (CH), 68.8 (CH_2), 38.1 (CH_2), 30.9 (C), 15.9 (CH_2); IR(neat,cm^{-1}):3083, 3060, 3026, 2919, 1601, 1494, 1451, 1176, 1075, 1029, 904, 739, 698, 536

HRMS-CI (CH_4) *m/z*: [M−OH] Calculated for $C_{18}H_{17}$, 233.1330, found, 233.1339.

(*S*,*E*)-2-Hydroxymethyl-2-phenylbut-3-enylidenecyclopropane (3f):



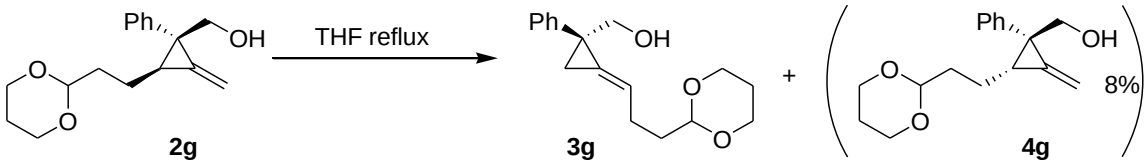
2f **3f** **4f**

The general procedure for the [1,3] carbon shift reaction with **2f** (12 mg, 0.06 mmol) in THF (15mL) gave 9 mg (0.05 mmol, 83% yield) of **3f** as a pale yellow oil. A similar experiment that began with 33 mg **2f** gave **3f** in 79% yield. Small peaks attributable to **4f** (5%) were detected in the ^{1}H NMR spectrum at 5.77, 5.62, 5.21, 5.17, 4.95, 4.91, 4.89, 4.03, 3.61, 1.96 and 1.81 ppm and in the ^{13}C NMR at 129.8 ppm. HPLC analysis showed the material to be of 82% ee (using a Chiral OD column, flow rate of 1 mL/min, 1% IPA in hexanes, t_1 = 22.7 min, t_2 = 34.7 min).

$[\alpha]^{20}_{D} = -47^{\circ}$ (c. 0.28 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.40 (m, 2H), 7.29-7.33(m, 2H), 7.21-7.25 (m, 1H), 6.09-6.13 (m, 1H), 5.87-5.97 (m, 1H), 5.00-5.11 (m, 2H), 3.88 (d, *J* = 11.3 Hz, 1H), 3.73 (d, *J* = 11.3 Hz, 1H), 2.96-3.01 (m, 2H), 1.41-1.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2 (C), 136.7 (CH), 128.9 (C), 128.4 (CH), 128.0 (CH), 126.7 (CH), 117.4 (CH), 115.1 (CH_2), 68.8 (CH_2), 35.9 (CH_2), 30.7 (C), 16.0 (CH_2); IR(neat, cm^{-1}): 3360, 3059, 3027, 2974, 2925, 1639, 1601, 1494, 1446, 1429, 1176, 1076, 1030, 994, 911, 760, 699, 538

HRMS-CI (NH_3) *m/z*: [M+NH_4] Calculated for $C_{14}H_{20}NO$, 218.1545, found, 218.1544.

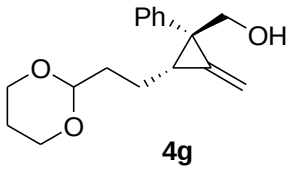
(*S*,*E*)-2-Hydroxymethyl-2-phenyl- 3-(1,3-dioxan-2-yl)propylidenecyclopropane (3g):



The general procedure for the [1,3] carbon shift reaction with **2g** (132 mg, 0.48 mmol) in THF (25 mL) gave 112 mg (0.41 mmol, 85% yield) of **3g** as a pale yellow oil. A similar experiment that began with 48 mg **2g** gave **3g** in 87% yield. $[\alpha]^{20}_{D} = -3^{\circ}$ (c. 0.80 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.39 (m, 2H), 7.28-7.33(m, 2H), 7.20-7.25 (m, 1H), 6.09-6.14 (m, 1H), 4.54 (t, *J*=5.1 Hz, 1H), 4.08-4.12 (m, 2H), 3.88 (dd, *J*=11.3, 5.9 Hz, 1H), 3.70-3.77 (m, 3H), 2.31-2.36 (m, 2H), 2.02-2.14 (m, 1H), 1.78-1.83 (m, 2H), 1.54-1.58 (m, 1H), 1.45-1.49 (m, 1H), 1.39-1.42 (m, 1H), 1.31-1.36 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3 (C), 128.4 (CH), 127.9 (CH), 127.8 (C), 126.6 (CH), 119.1 (CH), 102.0 (CH), 68.6 (CH_2), 67.0 (CH_2), 66.9 (CH_2), 34.4 (CH_2), 30.3 (C), 26.2 (CH_2), 25.8 (CH_2), 16.1 (CH_2); IR(neat, cm^{-1}):3324, 2961, 2892, 1721, 1637, 1441, 1368, 1323, 1192, 1122, 1068, 1037, 965, 926, 850, 565

HRMS-CI (CH_4) *m/z*: [M-OH] Calculated for $C_{17}H_{21}O_2$, 257.1542, found, 257.1543

(1*R*,2*S*)-2-Hydroxymethyl-2-phenyl 3-(2-(1,3-dioxan-2-yl)ethyl)methylenecyclopropane (4g):



4g

A small sample (0.5 mg) of **4g** was separated from **3g** by preparative HPLC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.40 (m, 2H), 7.28-7.33 (m, 2H), 7.23-7.24 (m, 1H), 5.72 (d, *J*=2.4 Hz, 1H), 5.59 (d, *J*=1.7 Hz, 1H), 4.42 (t, *J*=5.1 Hz, 1H), 4.03-4.06 (m, 2H), 3.94 (d, *J*=11.2 Hz, 1H), 3.64-3.72 (m, 3H), 0.83-2.10 (m, 8H)

Preparation of methylenecyclopropanes with functionalized phenyl groups

General procedures for cyclopropenation.

To a 100 mL dry round bottom flask was added hexanes followed by the addition of alkyne (5 equivalent, 2 mmol/mL) and a catalytic amount of Rh_2(octanoate)$_4$ (0.5 mol%). The appropriate diazo compound was dissolved in hexanes (1 equiv., 1 mmol/mL), and this solution was slowly added to the reaction mixture at r.t. using a syringe pump over a period of 8 h. After the addition was completed, the mixture was allowed to stir at r.t for another 4 h.

Solvent was removed and the crude product was purified by silica gel chromatography (20% ethyl acetate in hexanes).

General procedures for DIBAL-H reduction.

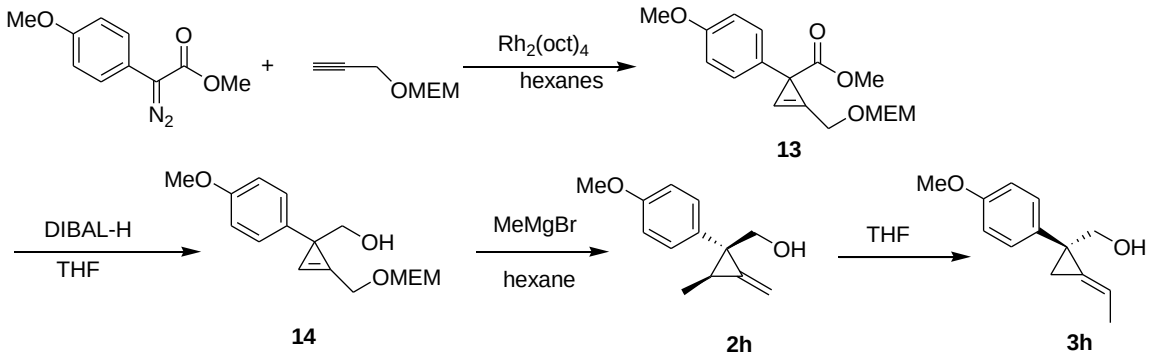
To a 50 mL round bottomed flask was added a solution of an alkyl cyclopropenoate in THF (0.2 mmol/mL). The resulting solution was cooled in a bath of dry ice/acetone (–78 ˚C), and DIBAL-H (5 equiv., 1.0 M in THF) was slowly added dropwise via syringe over the course of 10 min. The resulting mixture was allowed to stir under nitrogen at –78 ˚C. When the reaction was judged complete by TLC (usually about 1 h), the reaction mixture was quenched with saturated NH_4Cl at –78 ˚C. After the reaction mixture was warmed to r.t., the aqueous layer was extracted with diethyl ether. The organic layers were combined, washed with brine and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel chromatography (20% ethyl acetate in hexanes) to give the corresponding product as a colorless oil.

General procedures for Grignard reagent addition to 3-hydroxymethyl cyclopropenes.

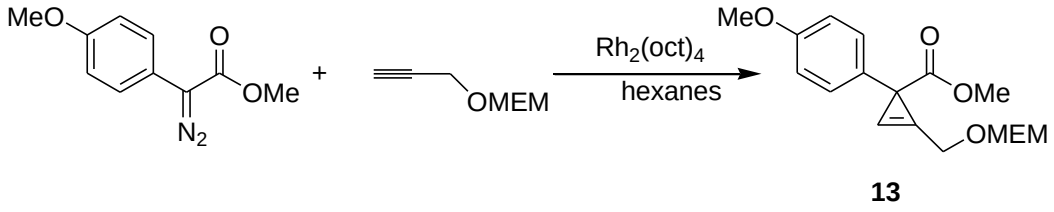
To a 25 mL round bottomed flask was added a solution of a 3-hydroxylmethyl cyclopropene in hexanes (0.1 mmol/mL). Grignard reagent (5.0 equiv) was slowly added via syringe with stirring. The resulting mixture was allowed to stir at r.t. for 16 h and quenched with saturated NH_4Cl

solution. The aqueous layer was extracted with ethyl acetate and the combined organics were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was purified by silica gel chromatography (10% ethyl acetate in hexanes) to give the corresponding methylenecyclopropane as a colorless oil.

Scheme 3 Preparation of 1h



Methyl 2-(2-methoxyethoxy-methoxymethyl)-1-(4-methoxyphenyl) cycloprop-2-ene carboxylate (13):



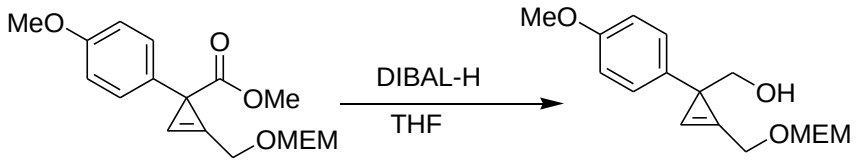
The general procedure for cyclopropenation using methyl α-(*p*-methoxyphenyl)-α-diazo acetate[3] (619 mg, 3.00 mmol), methoxyethoxymethyl propargyl ether (2.16 g, 15.0 mmol) and Rh_2(octanoate)$_4$ (23 mg, 0.03 mmol)

gave 420 mg (1.30 mmol, 39% yield) of **13** as a pale yellow oil. It was not possible to remove all of the ethyl acetate, even after prolonged exposure to vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.21 (m, 2H), 6.97-6.98 (m, 1H), 6.82-6.84 (m, 2H), 4.75 (d, *J* = 6.9 Hz, 1H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.69 (dd, *J* = 15.8, 1.6 Hz, 1H), 4.63 (dd, *J* = 15.8, 1.6 Hz, 1H), 3.77 (s, 3H), 3.69-3.71 (m, 2H), 3.67 (s, 3H), 3.52-3.54 (m, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3 (C), 158.3 (C), 133.0 (C), 129.7 (CH), 117.9 (C), 113.5 (CH), 101.0 (CH), 94.8 (CH_2), 71.7 (CH_2), 67.2 (CH_2), 60.1 (CH_2), 59.0 (CH_3), 55.2 (CH_3), 52.1 (CH_3), 33.3 (C); IR(neat,cm^{-1}): 3132, 2951, 2839, 1720, 1611, 1513, 1458, 1365, 1248, 1177, 1112, 1054, 842

HRMS-ESI *m/z*: [M+Na] Calculated for $C_{17}H_{22}O_6Na$, 345.1314, found, 345.1302.

[1-(4-Methoxyphenyl)-2-(2-methoxyethoxy-methoxymethyl) cycloprop-2-enyl)methanol (14):



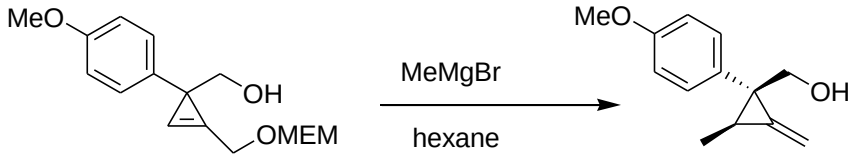
13 **14**

The general procedure for DIBAL-H reduction using **13** (387 mg, 1.20 mmol) and DIBAL-H (6.0 mmol, 6.0 mL of a 1.0 M solution in THF) gave 230 mg (0.78 mmol, 64% yield) of **14** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.19 (m, 2H), 7.08-7.09 (m, 1H), 6.83-6.85 (m, 2H), 4.80 (d, *J* = 6.9 Hz, 1H), 4.79 (d, *J* = 6.9 Hz, 1H), 4.68 (dd, *J* = 14.9, 0.8 Hz, 1H), 4.57 (dd, *J* = 14.9, 1.9 Hz, 1H), 4.25 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.77-3.81 (m, 4H), 3.68-3.71 (m, 2H), 3.50-3.53 (m, 2H), 3.36 (s, 3H), 1.90-1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5 (C), 137.4 (C), 127.8 (CH), 122.9 (C), 112.9 (CH), 106.7 (CH), 95.5 (CH_2), 72.1 (CH_2), 69.1 (CH_2), 67.6 (CH_2), 61.0 (CH_2), 59.4 (CH_3), 55.7 (CH_3), 32.9 (C); IR(neat,cm^{-1}): 3462, 3116, 2931, 1775, 1610, 1512, 1464, 1295, 1247, 1178, 1112, 1051, 838

HRMS-ESI *m/z*: [M+Na] Calculated for $C_{16}H_{22}O_5Na$, 317.1365, found, 317.1357

2α-Hydroxymethyl -2β-(*p*-methoxyphenyl)-3α-methyl-1-methylene cyclopropane (2h):



14 **2h**

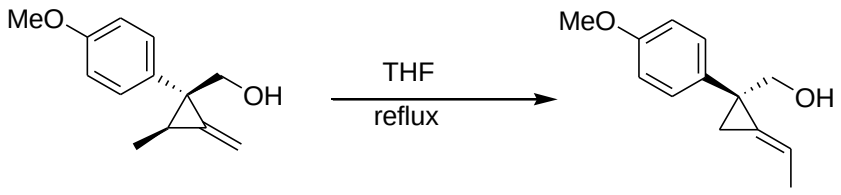
The general procedure for Grignard reagent addition using **14** (230 mg, 0.78 mmol) and methylmagnesium bromide (3.90 mmol, 1.30 mL of a 3.0M

solution in Et_2O) gave 46 mg (0.23 mmol, 35% yield) of **2h** as a colorless oil. The low yield of **2h** is due to the instability of the compound. Small peaks attributable to **3h** (20%) were detected in the ^1H NMR spectrum at 6.10 ppm and in the ^{13}C NMR at 129.1, 114.4, 29.7 and 15.3 ppm.

^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.34 (m, 2H), 6.84-6.87 (m, 2H), 5.60 (d, *J* = 2.4 Hz, 1H), 5.47 (d, *J* = 2.8 Hz, 1H), 3.83-3.89 (m, 2H), 3.79 (s, 3H), 1.85-1.87 (m, 1H), 1.73-1.75 (m, 1H), 1.34-1.37 (m, 3H); ^{13}C NMR (90 MHz, $CDCl_3$): δ 158.4 (C), 143.6 (C), 134.6 (C), 129.2 (CH), 113.8 (CH), 102.9 (CH_2), 65.2 (CH_2), 55.3 (CH_3), 33.2 (C), 23.7 (CH), 12.7 (CH_3); IR(neat,cm^{-1}): 3418, 3064, 3034, 2930, 2872, 2836, 2050, 1885, 1726, 1609, 1580, 1512, 1465, 1376, 1295, 1247, 1179, 1034, 891, 831, 805, 597, 540

HRMS-CI (CH_4) *m/z*: [M-OH] Calculated for $C_{13}H_{15}O$, 187.1123, found, 187.1124

(*E*)-2-Hydroxymethyl-2-(4-methoxyphenyl)-ethylidene cyclopropane (3h):



2h **3h**

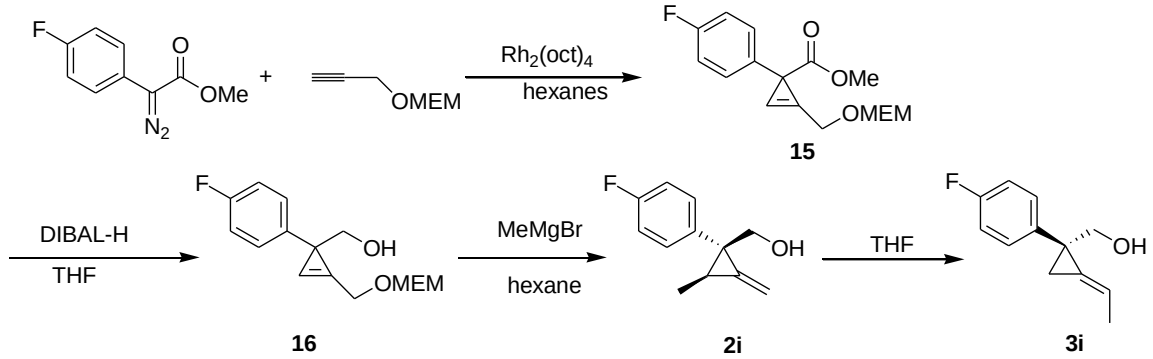
The general procedure for the [1,3] carbon shift reaction with **2h** (22 mg, 0.11 mmol) in THF (10 mL) gave 14 mg (0.07 mmol, 64% yield) of **3h** as a pale

yellow oil. Peaks attributable to inseparable impurities and decomposition (20%) were detected in the ^{1}H NMR spectrum at 5.59-5.67, 3.84-3.93 ppm and in the ^{13}C NMR spectrum at 30.4, 29.5 ppm.

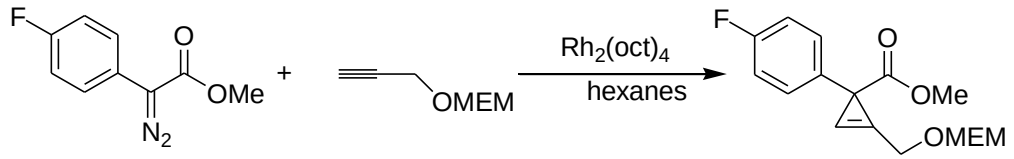
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.26 (m, 2H), 6.76-6.78 (m, 2H), 6.01-6.07 (m, 1H), 3.75 (d, J = 11.2 Hz, 1H), 3.72 (s, 3H), 3.60 (dd, J = 11.2, 0.6 Hz, 1H), 1.78 (dt, J = 6.5, 1.7 Hz, 3H), 1.48-1.49 (m, 1H), 1.39-1.43 (m, 1H), 1.25-1.29 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 (C), 133.4 (C), 129.3 (CH), 128.4 (C), 114.5 (CH), 113.8 (CH), 69.0 (CH_2), 55.3 (CH_3), 29.7 (C), 16.9 (CH_3), 15.3 (CH_2); IR (neat, cm^{-1}): 3414, 3036, 2926, 2856, 1729, 1677, 1610, 1579, 1513, 1463, 1413, 1377, 1293, 1247, 1179, 1108, 1073, 1034, 834, 802, 750, 682, 633, 546.

HRMS-CI (NH_3) *m/z*: [M+H] Calculated for $C_{13}H_{17}O_2$, 205.1229, found, 205.1231

Scheme 4



Methyl 1-(4-fluorophenyl)-2-(2-methoxyethoxy-methoxymethyl) cycloprop-2-ene carboxylate (15):



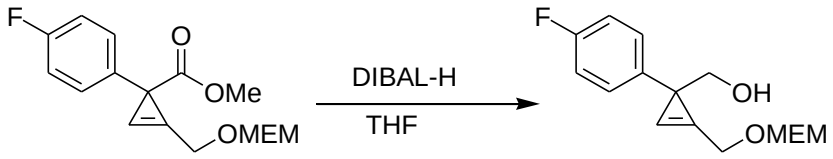
15

The general procedure for cyclopropenation using methyl α-(*p*-fluorophenyl)-α-diazo acetate[3] (582 mg, 3.00 mmol), methoxyethoxymethyl propagyl ether (2.16 g, 15.00 mmol) and Rh_2(octanoate)$_4$ (23 mg, 0.03 mmol) gave 584 mg (1.88 mmol, 56% yield) of **15** as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.29 (m, 2H), 6.94-7.00 (m, 3H), 4.76 (d, *J* = 6.9 Hz, 1H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.69 (dd, *J* = 15.9, 1.6 Hz, 1H), 4.63 (dd, *J* = 15.8, 1.6 Hz, 1H), 3.69-3.71 (m, 2H), 3.68 (s, 3H), 3.52-3.55 (m, 2H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9 (C), 161.6 (C) [d, ^{1}J(CF) = 244 Hz], 136.6 (C) [d, ^{4}J(CF) = 3 Hz], 130.0 (CH) [^{3}J(CF) = 8 Hz], 117.6 (C), 115.0 (CH) [^{2}J(CF) = 22 Hz], 100.8 (CH), 95.3 (CH_2), 71.7 (CH_2), 67.2 (CH_2), 59.9 (CH_2), 58.9 (CH_3), 52.2 (CH_3), 33.2 (C); IR(neat,cm^{-1}): 3132, 2892, 1720, 1510, 1436, 1222, 1161, 1112, 1055, 1028, 845

HRMS-ESI *m/z*: [M+Na] Calculated for $C_{16}H_{19}FO_5Na$, 333.1114, found, 333.1104

[1-(4-Fluorophenyl)-2-(2-methoxyethoxy-methoxymethyl) cycloprop-2-enyl]methanol (16):



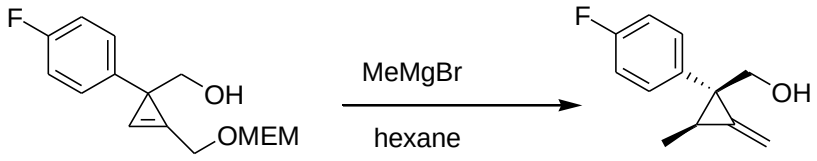
15 **16**

The general procedure for DIBAL-H reduction using **15 (**263 mg, 0.85 mmol) and DIBAL-H (4.20 mmol, 4.2 mL of a 1.0M solution in THF) gave 206 mg (0.73 mmol, 85% yield) of **16** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.24 (m, 2H), 7.08 (s, 1H), 6.95-6.99 (m, 2H), 4.80 (d, *J* = 6.9 Hz, 1H), 4.78 (d, *J* = 6.9 Hz, 1H), 4.67 (dd, *J* = 14.9, 0.9 Hz, 1H), 4.56 (dd, *J* = 14.9, 1.9 Hz, 1H), 4.25 (dd, *J* = 11.3, 7.3 Hz, 1H), 3.77 (dd, *J* = 11.3, 4.0 Hz, 1H), 3.67-3.70 (m, 2H), 3.49-3.52 (m, 2H), 3.35 (s, 3H), 1.96-1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (C) [d, $^{1}J(CF)$ = 242 Hz], 140.7 (C) [d, $^{4}J(CF)$ = 3 Hz], 127.8 (CH) [$^{3}J(CF)$ = 8 Hz], 122.3 (C), 114.9 (CH) [$^{2}J(CF)$ = 21 Hz], 106.0 (CH), 95.0 (CH_2), 71.7 (CH_2), 68.8 (CH_2), 67.2 (CH_2), 60.4 (CH_2), 59.0 (CH_3), 32.4 (C); IR(neat,cm^{-1}): 3440, 3118, 2928, 2888, 1777, 1603, 1509, 1223, 1161, 1112, 1053, 843, 817, 726

HRMS-ESI *m/z*: [M+Na] Calculated for $C_{15}H_{19}FO_4Na$, 305.1165, found, 305.1158

2α-Hydroxymethyl -2β-(*p*-fluorophenyl)-3α-methyl-1-methylene cyclopropane (2i):



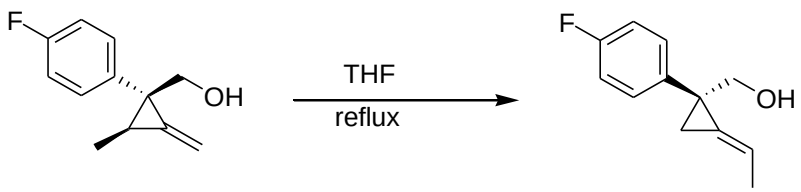
16 **2i**

The general procedure for Grignard reagent addition using **16** (206 mg, 0.73 mmol) and methylmagnesium bromide (3.60 mmol, 1.2 mL of a 3.0 M solution in Et_2O) gave 73 mg (0.38 mmol, 52% yield) of **2i** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.38 (m, 2H), 6.95-7.01 (m, 2H), 5.61 (d, *J*=2.6 Hz, 1H), 5.50 (d, *J*=2.0 Hz, 1H), 3.83-3.92 (m, 2H), 1.70-1.74 (m, 1H), 1.43-1.44 (m, 1H), 1.35 (d, *J*=6.5Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (C) [d, ^{1}J(CF) = 243 Hz], 143.2 (C), 138.5 (C) [d, ^{4}J(CF) = 3 Hz], 129.6 (CH) [^{3}J(CF) = 8 Hz], 115.2 (CH) [^{2}J(CF) = 21 Hz], 103.4 (C), 65.1 (CH_2), 33.2 (C), 24.1 (CH), 12.7 (CH_3); IR(neat,cm^{-1}): 3377, 3068, 2986, 2959, 2930, 2874, 1605, 1509, 1221, 1158, 1093, 1015, 894, 836, 817, 596, 532

HRMS-CI (CH_4) *m/z*: [M-OH] Calculated for $C_{12}H_{12}F$, 175.0923, found, 175.0920.

(*E*)-2-Hydroxymethyl-2-(4-fluorophenyl)-ethylidene cyclopropane (3i):



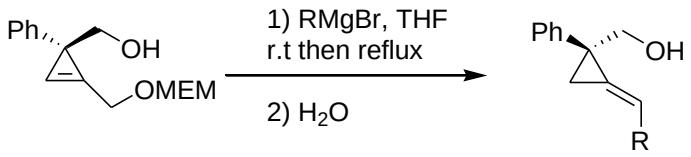
2i **3i**

The general procedure for the [1,3] carbon shift reaction with **2i** (50 mg, 0.26 mmol) in THF (25 mL) gave 40 mg (0.21 mmol, 80% yield) of **3i** as a pale yellow oil. Peaks attributable to **4i** (5%) were detected in the ^{1}H NMR spectrum at 5.69, 5.53, 3.92, 3.90, 3.56, 3.53 ppm and in the ^{13}C NMR spectrum at 131.4, 104.3, 70.0, 25.8, 20.7, 13.4 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.34 (m, 2H), 6.93-7.01 (m, 2H), 6.06-6.12 (m, 1H), 3.80 (d, *J* = 11.3 Hz, 1H), 3.65 (d, *J* = 11.3 Hz, 1H), 1.83 (dt, J = 6.5, 1.7 Hz, 3H), 1.54 (br, 1H), 1.47-1.51 (m, 1H), 1.29-1.32 (m, 1H);^{13}C NMR (100 MHz, CDCl3) δ 161.7 (C) [d, ^{1}J(CF) = 243 Hz], 137.1 (C) [d, ^{4}J(CF) = 3 Hz], 129.7 (CH) [^{3}J(CF) = 8 Hz], 128.0 (C), 115.1 (CH) [^{2}J(CF) = 21 Hz], 114.9 (CH), 68.9 (CH_2), 28.3 (C), 16.9 (CH_3), 15.6 (CH_2); IR (neat, cm^{-1}): 3368, 3041, 2968, 2920, 2860, 1602, 1510, 1440, 1406, 1377, 1296, 1221, 1179, 1158, 1028, 838, 816, 753, 722, 683, 634, 553, 537.

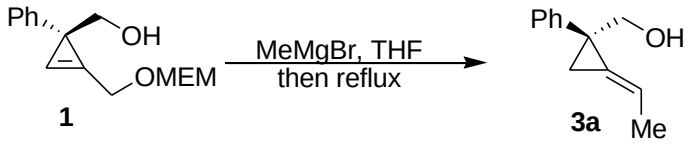
HRMS-CI (NH_3) *m/z*: [M-OH_2] Calculated for $C_{12}H_{11}F$, 174.0845, found, 174.0844

General procedure for the one pot reaction of cyclopropenes to give alkylidenecyclopropanes



To a 50 mL round bottomed flask was added a solution of (1-phenyl-2-methoxyethoxymethoxymethyl-cycloprop-2-ene)methanol in THF. The mixture was stirred with a magnetic stir bar and the appropriate Grignard reagent (5.0 equiv) was slowly added via syringe. The resulting mixture was allowed to stir at r.t. for 12 h and then heated to reflux for 5h. The reaction was quenched with saturated NH_4Cl. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was purified by silica gel chromatography (10% ethyl acetate / hexanes) to give the corresponding alkylidenecyclopropanes.

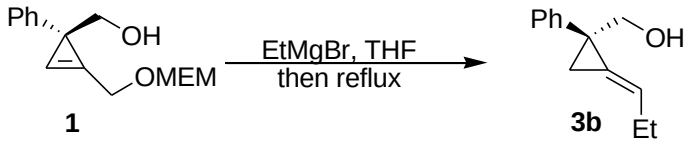
(*S*,*E*)-2-Hydroxymethyl-2-phenyl-ethylidenecyclopropane (3a):



1 **3a**

The general procedure for one pot alkylidenecyclopropane synthesis using (1-phenyl-2-methoxyethoxymethoxymethyl-cyclop-2-ene)methanol (**1**) (56 mg, 0.20 mmol), 3 mL THF and methylmagnesium bromide (1.00 mmol, 0.30 mL of a 3.0 M solution in Et_2O) gave 15 mg (0.086 mmol, 43% yield) of **3a** as a pale yellow oil.

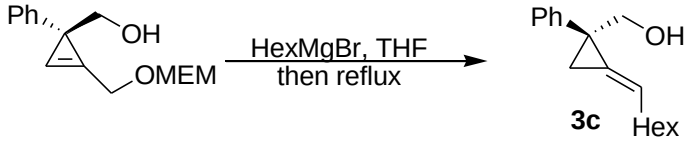
(*S*,*E*)-2-Hydroxymethyl-2-phenyl-propylidenecyclopropane (3b):



1 **3b**

The general procedure for one pot alkylidenecyclopropane synthesis using (1-phenyl-2-methoxyethoxymethoxymethyl-cyclop-2-ene)methanol (45 mg, 0.17 mmol), 3 mL THF and ethylmagnesium bromide (0.84 mmol, 0.28 mL of a 3.0 M solution in Et_2O) gave 18 mg (0.10 mmol, 59% yield) of **3b** as a pale yellow oil. A similar experiment that began with 123 mg of **1** gave **3b** in 64% yield.

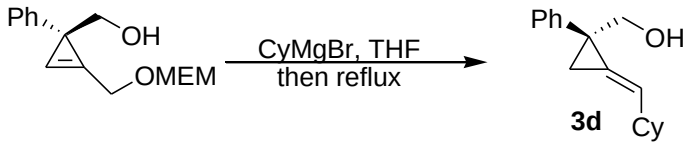
(*S*,*E*)-2-Hydroxymethyl-2-phenyl-heptylidenecyclopropane (3c):



3c

The general procedure for one pot alkylidenecyclopropane synthesis using (1-phenyl-2-methoxyethoxymethoxymethyl-cyclop-2-ene)methanol (63 mg, 0.24 mmol), 5 mL THF and hexylmagnesium bromide (2.4 mmol, 1.20 mL of a 2.0 M solution in Et_2O) gave 37 mg (0.15 mmol, 64% yield) of **3c** as a pale yellow oil. A similar experiment that began with 55 mg of **1** gave **3c** in 59% yield.

(*S*,*E*)-2-Hydroxymethyl-2-phenyl-(cyclohexylmethylene)cyclopropane (3d):



The general procedure for one pot alkylidenecyclopropane synthesis using (1-phenyl-2-methoxyethoxymethoxymethyl-cyclop-2-ene)methanol (160 mg, 0.61 mmol), 10 mL THF and CyMgBr (3.05 mmol, 3.1 mL of a 1.0 M solution in Et_2O) gave 72 mg (0.30 mmol, 49% yield) of **3d** as a pale yellow oil. A similar experiment that began with 133 mg of **1** gave **3d** in 43% yield.

References

(1) Liao, L.-A; Zhang, F; Dmintrenko, O.; Bach, R. D.; Fox, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 4490.

(2) Davies, H. M. L.; Bruzinski, P. R.; Fall, M. J. *Tetrahedron Letters* **1996**, *37*, 4133

(3) Rubina, M.; Woodward, E. W.; Rubin, M. *Org. Lett.* **2007**, *9*, 5501.