Contents

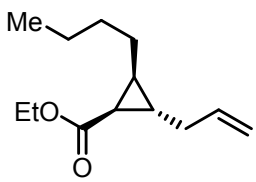
1. General experimental detail

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of argon. Et2O and THF were dried from Pure-Solv® Purification System (Innovative Technology©). DCM was distilled from CaH2. Toluene, 2-MeTHF and MTBE were distilled from sodium and benzophenone. All other commercially obtained eagents were used as received. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, phosphomolybdic acid, or potassium permanganate. Column chromatography was performed using Fluka silica gel 60 Å (40- 63 μm, 230-400 mesh). 1H NMR spectra were recorded on Bruker spectrometers (AVIII 400 and AVIII 300) and are reported relative to deuterated solvent signals. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (1H NMR: δ = 7.26; 13C NMR: δ = 77.00). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility at the Technion. Reactions were monitored by gas chromatography spectrometry (GC) using an Agilent Technologies 7820A GC with an Agilent Technologies 19091J-413 (30 m × 0.3 mm) column or (GC-MS) Thermo Scientific TM Ion Trap GC/MS: ITQTM 900 with a Varian Factor Four Capilary colum (VF-5 ms, 30 m × 0.25 mm). HPLC chromatograms were recorded using Agilent© 1100 Series line. Following chiral columns were tested: CHIRAL PAK® AD-H (0.46 cm Ø × 25 cm), CHIRALCEL® OD (0.46 cm Ø × 25 cm) and CHIRALCEL® IA column (0.46 cm Ø × 25 cm). Enantiomeric excesses were determined by chiral-GC: Bruker Daltonics- SCION GC-456 with the column of Hydrodex β-6TBDM (25 m × 0.25 mm). Temperature programs for chiral GC are described as follows: initial temperature (°C)- initial time (min)–temperature gradient (°C/min)–final temperature (°C). All 1,1-disubstituted cyclopropenes were prepared according to literature procedures.[1-3]

2. Representative procedure for the copper catalyzed hydroallylation of 1,2-disubstituted cyclopropenes (RP-1)

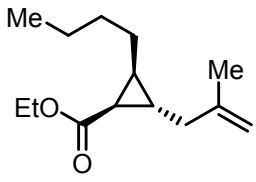
LiO*t*Bu (60.0 mg, 0.76 mmol, 1.5 equiv.) was flame-dried under vacuo in a Schlenk tube. Upon cooling, the tube was flushed with argon and CuI (4.76 mg, 0.025 mmol, 5.0 mol%) and DPEPhos (16.2 mg, 0.03 mmol, 6.0 mol%) were added followed by dry THF (1.5 mL), and stirring was continued for 5 minutes at room temperature. Dimethoxymethylsilane (250µL, 2.0 mmol, 4.0 equiv.) was added slowly (CAUTION: vigorous foaming in the beginning) and stirring was continued for 5 minutes before the cyclopropene (1.0 equiv.) and allyl phosphate (2.0 equiv.) in THF (0.5 mL) were added. Stirring was continued at room temperature until complete consumption of cyclopropene was judged by TLC (hexanes/ethyl acetate, 20:1, usually between 15 to 60 minutes). Upon completion, saturated ammonium chloride solution (2.0 mL) was slowly added followed by a few drops of 1M HCl. The mixture was stirred until complete discoloration which takes about 30 minutes. The resulting cloudy mixture was diluted with saturated ammonium chloride solution, extracted two times with Et_2O, the combined extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 50:1) yielded the product as colorless oils.

Ethyl 2-allyl-3-butylcyclopropane-1-carboxylate (**3a**)



88% yield (920 mg, 4.4 mmol on 5.0 mmol scale). **Diastereomeric ratio:** 95:5. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.87 – 5.72 (m, 1H), 5.05 (dt, J = 8.3, 3.9 Hz, 1H), 4.99 (dd, J = 10.2, 1.2 Hz, 1H), 4.22 – 4.02 (m, 2H), 2.11 (dt, J = 13.2, 6.5 Hz, 1H), 2.07 – 1.96 (m, 1H), 1.64 – 1.49 (m, 1H), 1.45 (td, J = 8.8, 3.4 Hz, 1H), 1.38 (dt, J = 11.2, 6.5 Hz, 1H), 1.34 – 1.28 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H), 1.07 (tt, J = 13.0, 6.5 Hz, 1H), 0.95 – 0.79 (m, 4H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.9, 136.6, 115.6, 60.3, 36.9, 31.9, 29.3, 26.7, 26.5, 25.0, 22.5, 14.5, 14.2 ppm. **HRMS** (APCI): m/z calculated for $C_{13}H_{23}O_2$ $[M+H]^+$: 211.169, found 211.170.

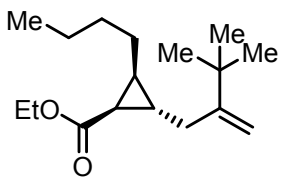
Ethyl 2-butyl-3-(2-methylallyl)cyclopropane-1-carboxylate (**3b**)



76% yield (85 mg, 0.38 mmol). **Diastereomeric ratio:** 95:5. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 4.72 (s, 2H), 4.22 – 4.01 (m, 2H), 2.05 (dd, J = 15.3, 6.2 Hz, 1H), 1.93 (dd, J = 15.3, 6.6 Hz, 1H), 1.74 (s, 3H), 1.67 – 1.48 (m, 2H), 1.43 (dq, J = 6.7, 4.9 Hz, 2H), 1.40 – 1.29 (m, 4H), 1.29 – 1.21 (m, 3H), 1.13 – 1.01 (m, 1H), 0.96 – 0.82 (m, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.9, 144.8, 110.6, 60.3, 41.3,

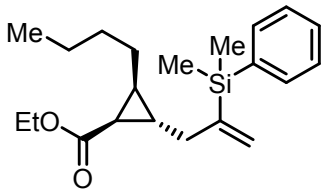
31.9, 29.8, 26.7, 26.4, 25.5, 22.8, 22.5, 14.5, 14.2 ppm. **HRMS** (APCI): m/z calculated for $C_{14}H_{25}O_2$ $[M+H]^+$: 225.185, found 225.189.

Ethyl 2-butyl-3-(3,3-dimethyl-2-methylenebutyl)cyclopropane-1-carboxylate (**3c**)



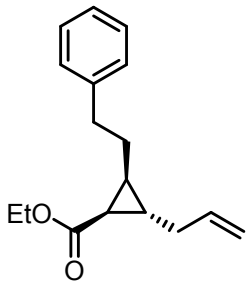
68% yield (90 mg, 0.34 mmol). **Diastereomeric ratio:** 91:9. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 4.88 (s, 1H), 4.84 (d, J = 1.1 Hz, 1H), 4.13 (qd, J = 7.1, 0.9 Hz, 2H), 2.09 (dd, J = 17.2, 5.6 Hz, 1H), 1.99 (dd, J = 17.4, 5.8 Hz, 1H), 1.74 – 1.60 (m, 1H), 1.56 – 1.47 (m, 1H), 1.47 – 1.39 (m, 2H), 1.38 – 1.28 (m, 4H), 1.28 – 1.22 (m, 3H), 1.14 – 1.05 (m, 1H), 1.03 (s, 9H), 0.94 – 0.82 (m, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 173.0, 156.6, 106.9, 60.3, 35.9, 35.0, 31.9, 30.4, 29.4, 27.0, 26.8, 25.8, 22.5, 14.5, 14.2 ppm. **HRMS** (APCI): m/z calculated for $C_{17}H_{31}O_2$ $[M+H]^+$: 267.232, found 267.222.

Ethyl 2-butyl-3-(2-(dimethyl(phenyl)silyl)allyl)cyclopropane-1-carboxylate (**3d**)



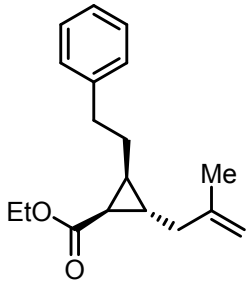
82% yield (141 mg, 0.41 mmol). **Diastereomeric ratio:** 91:9.**^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.52 – 7.46 (m, 2H), 7.40 – 7.30 (m, 3H), 5.83 – 5.73 (m, 1H), 5.50 – 5.39 (m, 1H), 4.18 – 3.98 (m, 2H), 2.13 – 2.00 (m, 2H), 1.62 – 1.51 (m, 1H), 1.48 – 1.40 (m, 1H), 1.40 – 1.31 (m, 2H), 1.31 – 1.26 (m, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.06 – 0.92 (m, 1H), 0.92 – 0.84 (m, 3H), 0.84 – 0.75 (m, 1H), 0.43 – 0.31 (m, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 173.0, 156.6, 106.9, 60.3, 35.9, 35.0, 31.9, 30.4, 29.4, 27.0, 26.8, 25.8, 22.5, 14.5, 14.2 ppm. **HRMS** (APCI): m/z calculated for $C_{21}H_{33}O_2Si$ $[M+H]^+$: 345.224, found 345.232.

Ethyl 2-allyl-3-phenethylcyclopropane-1-carboxylate (**3e**)



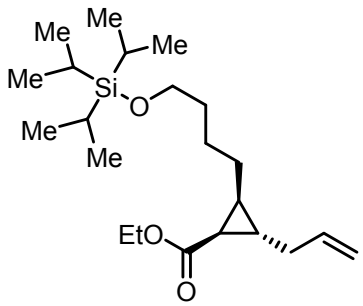
79% yield (102 mg, 0.40 mmol). **Diastereomeric ratio:** 92:8. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31 – 7.22 (m, 2H), 7.17 (m, 3H), 5.87 – 5.65 (m, 1H), 5.08 – 4.94 (m, 2H), 4.16 – 4.07 (m, 2H), 2.71 – 2.57 (m, 2H), 2.14 – 1.97 (m, 2H), 1.97 – 1.89 (m, 1H), 1.90 – 1.79 (m, 1H), 1.49 (dd, J = 8.9, 4.9 Hz, 1H), 1.46 – 1.34 (m, 1H), 1.31 – 1.20 (m, 3H), 1.11 (dt, J = 14.3, 7.0 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.8, 142.0, 136.4, 128.7, 128.4, 125.9, 115.7, 60.4, 36.7, 35.9, 28.8, 28.6, 26.9, 24.9, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{17}H_{23}O_2$ [M+]: 259.169, found 259.168.

Ethyl 2-(2-methylallyl)-3-phenethylcyclopropane-1-carboxylate (**3f**)



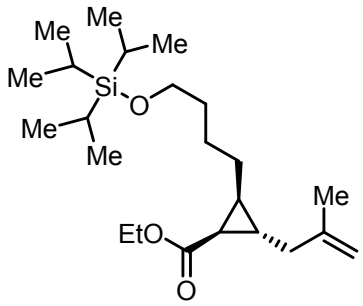
76% yield (104 mg, 0.38 mmol). **Diastereomeric ratio:** 92:8. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32 – 7.21 (m, 2H), 7.21 – 7.10 (m, 3H), 4.78 – 4.64 (m, 2H), 4.18 – 4.05 (m, 2H), 2.68 – 2.55 (m, 2H), 1.99 (ddd, J = 20.0, 13.2, 6.0 Hz, 2H), 1.93 – 1.79 (m, 2H), 1.73 (s, 3H), 1.53 – 1.38 (m, 2H), 1.35 – 1.19 (m, 3H), 1.18 – 1.04 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.8, 144.6, 142.0, 128.7, 128.4, 125.9, 110.7, 60.4, 41.1, 35.9, 29.2, 28.9, 26.5, 25.4, 22.8, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{18}H_{25}O_2$ $[M+H]^+$: 273.185, found 273.185.

Ethyl 2-allyl-3-(4-((triisopropylsilyl)oxy)butyl)cyclopropane-1-carboxylate (**3g**)



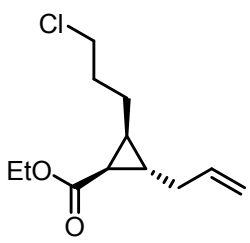
84% yield (161 mg, 0.42 mmol). **Diastereomeric ratio:** 92:8. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.79 (dqd, J = 20.4, 10.2, 6.8 Hz, 1H), 5.05 (ddd, J = 8.1, 5.6, 3.9 Hz, 1H), 4.99 (dd, J = 10.2, 1.7 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.66 (t, J = 6.5 Hz, 2H), 2.12 (dt, J = 13.1, 5.7 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.69 – 1.43 (m, 5H), 1.39 (ddd, J = 13.3, 9.9, 4.3 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.15 – 0.97 (m, 23H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.8, 136.5, 115.6, 63.6, 60.3, 36.9, 32.9, 29.3, 26.7, 26.7, 26.0, 25.0, 18.2, 14.5, 12.2 ppm. **HRMS** (APCI): m/z calculated for $C_{22}H_{43}O_3Si$ $[M+H]^+$: 383.298, found 383.299.

Ethyl 2-(2-methylallyl)-3-(4-((triisopropylsilyl)oxy)butyl)cyclopropane-1-carboxylate (**3h**)



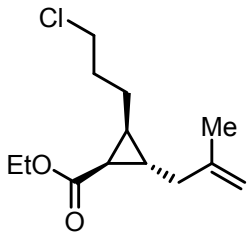
93% yield (185 mg, 0.47 mmol). **Diastereomeric ratio:** 93:7. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 4.71 (s, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.65 (t, J = 6.4 Hz, 2H), 2.05 (dd, J = 15.3, 6.3 Hz, 1H), 1.92 (dd, J = 15.3, 6.7 Hz, 1H), 1.73 (s, 3H), 1.59 – 1.48 (m, 2H), 1.48 – 1.29 (m, 5H), 1.25 (t, J = 7.1 Hz, 3H), 1.21 – 0.92 (m, 23H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.8, 144.7, 110.7, 63.6, 60.3, 41.3, 32.9, 29.8, 26.8, 26.4, 26.0, 25.5, 22.8, 18.2, 14.5, 12.2 ppm. **HRMS** (APCI): m/z calculated for $C_{23}H_{45}O_3Si$ [M+]: 397.313, found 397.311.

Ethyl 2-allyl-3-(3-chloropropyl)cyclopropane-1-carboxylate (**3i**)



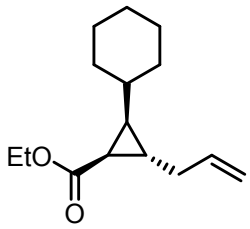
87% yield (100 mg, 0.43 mmol). **Diastereomeric ratio:** 92:8. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.88 – 5.68 (m, 1H), 5.08 – 4.96 (m, 2H), 4.18 – 4.05 (m, 2H), 3.57 – 3.49 (m, 2H), 2.14 (dt, J = 13.0, 6.4 Hz, 1H), 2.01 (dt, J = 15.0, 6.7 Hz, 1H), 1.93 – 1.61 (m, 4H), 1.50 (dd, J = 8.8, 4.9 Hz, 1H), 1.41 (tt, J = 11.6, 5.7 Hz, 1H), 1.30 – 1.21 (m, 3H), 1.14 – 1.04 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.6, 136.2, 115.9, 60.5, 44.7, 36.7, 32.7, 28.1, 26.7, 24.9, 24.2, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{12}H_{20}ClO_2$ $[M+H]^+$: 231.114, found 231.115.

Ethyl 2-(3-chloropropyl)-3-(2-methylallyl)cyclopropane-1-carboxylate (**3j**)



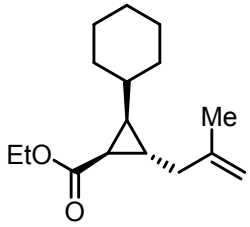
83% yield (102 mg, 0.42 mmol). **Diastereomeric ratio:** 93:7. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 4.72 (d, J = 8.1 Hz, 2H), 4.11 (dq, J = 11.4, 7.2 Hz, 2H), 3.56 – 3.48 (m, 2H), 2.06 (dd, J = 15.5, 6.6 Hz, 1H), 1.93 (dd, J = 15.2, 6.8 Hz, 1H), 1.87 – 1.75 (m, 3H), 1.73 (d, J = 5.2 Hz, 3H), 1.72 – 1.62 (m, 1H), 1.52 – 1.39 (m, 2H), 1.25 (q, J = 7.4 Hz, 3H), 1.14 – 1.03 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.6, 144.5, 110.8, 60.5, 44.7, 41.2, 32.7, 28.6, 26.4, 25.3, 24.3, 22.8, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{13}H_{22}ClO_2$ $[M+H]^+$: 245.130, found 245.134.

Ethyl 2-allyl-3-cyclohexylcyclopropane-1-carboxylate (**3k**)



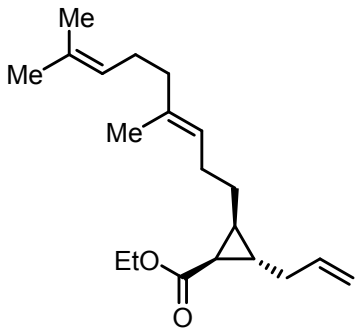
89% yield (1.05 g, 4.44 mmol, on 5.0 mmol scale). **Diastereomeric ratio:** 95:5. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.78 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (ddd, J = 17.1, 3.3, 1.6 Hz, 1H), 5.00 – 4.95 (m, 1H), 4.12 (qd, J = 7.1, 1.1 Hz, 2H), 2.14 (dt, J = 14.5, 6.5 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.83 – 1.74 (m, 1H), 1.71 (dd, J = 9.7, 6.2 Hz, 1H), 1.67 – 1.59 (m, 2H), 1.52 – 1.44 (m, 2H), 1.44 – 1.35 (m, 1H), 1.32 (ddd, J = 10.6, 7.2, 3.8 Hz, 1H), 1.29 – 1.21 (m, 4H), 1.21 – 0.95 (m, 4H), 0.87 (ddd, J = 16.3, 10.6, 5.8 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 173.0, 136.7, 115.6, 60.3, 37.2, 36.0, 35.5, 33.3, 33.2, 26.6, 26.2, 26.2, 26.0, 24.8, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{15}H_{25}O_2$ $[M+H]^+$: 237.185, found 237.189.

Ethyl 2-cyclohexyl-3-(2-methylallyl)cyclopropane-1-carboxylate (**3l**)



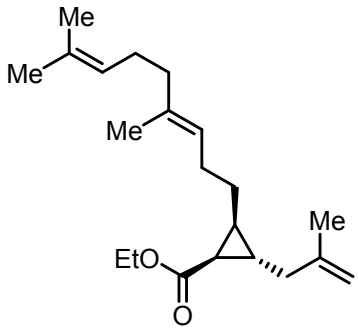
92% yield (115 mg, 0.46 mmol). **Diastereomeric ratio:** 91:9.**^{1}H NMR (400 MHz, $CDCl_3$) δ** 4.75 – 4.66 (m, 2H), 4.13 (qd, J = 7.1, 0.8 Hz, 2H), 2.02 (dd, J = 15.0, 6.2 Hz, 1H), 1.92 (dd, J = 15.0, 6.3 Hz, 1H), 1.82 – 1.66 (m, 6H), 1.52 – 1.40 (m, 3H), 1.40 – 1.28 (m, 1H), 1.28 – 1.22 (m, 3H), 1.22 – 0.92 (m, 6H), 0.92 – 0.80 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 173.0, 144.7, 110.8, 60.3, 41.6, 36.4, 35.6, 33.3, 33.3, 26.5, 26.2, 26.1, 25.8, 25.3, 22.8, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{16}H_{27}O_2$ $[M+H]^+$: 251.201, found 251.191.

Ethyl 2-allyl-3-((E)-4,8-dimethylnona-3,7-dien-1-yl)cyclopropane-1-carboxylate (**3m**)



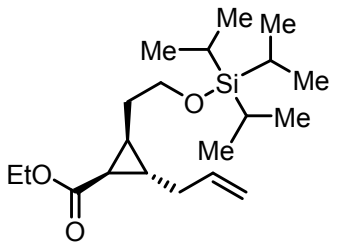
73% yield (111 mg, 0.37 mmol). **Diastereomeric ratio:** 96:4. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.87 – 5.71 (m, 1H), 5.21 – 5.05 (m, 2H), 5.05 – 4.95 (m, J = 12.0, 6.8, 1.7 Hz, 2H), 4.20 – 4.05 (m, 2H), 2.12 – 1.93 (m, 8H), 1.72 – 1.65 (m, 3H), 1.60 (s, 6H), 1.65 – 1.51 (m, 2H), 1.51 – 1.44 (m, 1H), 1.40 (ddd, J = 11.5, 7.6, 3.4 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.17 – 1.06 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.8, 136.5, 135.5, 131.5, 124.5, 124.0, 115.6, 60.3, 39.9, 36.8, 28.9, 28.0, 27.1, 26.8, 26.8, 25.9, 25.0, 17.8, 16.1, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{20}H_{33}O_2$ $[M+H]^+$: 305.248, found 305.248.

Ethyl 2-((E)-4,8-dimethylnona-3,7-dien-1-yl)-3-(2-methylallyl)cyclopropane-1-carboxylate (**3n**)



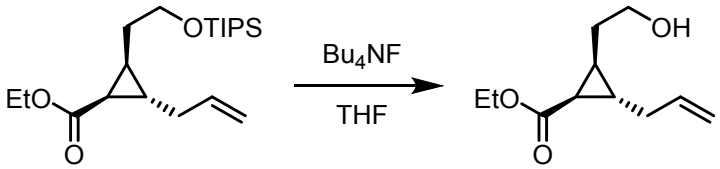
69% yield (110 mg, 0.35 mmol). **Diastereomeric ratio:** 94:6. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.17 – 5.02 (m, 2H), 4.72 (s, J = 24.5 Hz, 2H), 4.17 – 4.08 (m, 2H), 2.12 – 1.87 (m, J = 15.2, 8.4 Hz, 8H), 1.79 – 1.70 (m, 3H), 1.70 – 1.63 (m, 4H), 1.63 – 1.50 (m, 7H), 1.50 – 1.40 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.17 – 1.05 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.9, 144.7, 135.5, 131.5, 124.5, 124.0, 110.6, 60.3, 41.3, 39.9, 29.5, 28.0, 27.2, 26.8, 26.5, 25.9, 25.5, 22.8, 17.8, 16.1, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{21}H_{35}O_2$ $[M+H]^+$: 319.263, found 319.265.

Ethyl 2-allyl-3-(2-((triisopropylsilyl)oxy)ethyl)cyclopropane-1-carboxylate (**SI-1**)



73% yield (257 mg, 0.73 mmol). **Diastereomeric ratio:** 91:9.**^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.81 (ddt, J = 16.7, 10.2, 6.4 Hz, 1H), 5.05 (ddd, J = 17.2, 3.4, 1.6 Hz, 1H), 4.99 (dd, J = 10.2, 1.8 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.77 – 3.60 (m, 2H), 2.08 (t, J = 6.5 Hz, 2H), 1.84 (dq, J = 13.0, 6.7 Hz, 1H), 1.75 (td, J = 13.5, 6.2 Hz, 1H), 1.49 (dd, J = 8.8, 4.9 Hz, 1H), 1.41 (qd, J = 6.6, 3.9 Hz, 1H), 1.36 – 1.28 (m, J = 10.7, 4.4 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.16 – 0.95 (m, 21H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.9, 136.5, 115.7, 63.2, 60.4, 36.8, 30.4, 26.7, 26.0, 24.6, 18.2, 14.5, 12.1 ppm. **HRMS** (APCI): m/z calculated for $C_{20}H_{39}O_3Si$ $[M+H]^+$: 355.266, found 355.265.

Ethyl allyl-3-(2-hydroxyethyl)cyclopropane-1-carboxylate (**SI-2**)[4]

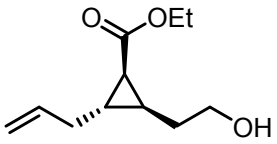


Ethyl 2-allyl-3-(2-((triisopropylsilyl)oxy)ethyl)cyclopropane-1-carboxylate (177 mg, 0.5 mmol, 1.0 equiv.) was dissolved in THF (1 mL) and the mixture stirred in a flame-dried Schlenk tube under an argon atmosphere on an ice bath. Tetra n-butylammonium fluoride solution (1.0 mL, 1M in THF, 1.0 mmol, 2.0 equiv.) was slowly added and stirring continued at room temperature until completion was judged by TLC (hexanes/ethyl acetate, 20:1). The reaction was quenched with the addition of saturated ammonium chloride solution, the mixture extracted two times with ethyl acetate, the combined extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 4:1) yielded the product as a colorless oil.

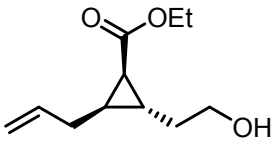
81% yield (81 mg, 0.40 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.81 (ddt, J = 16.7, 10.2, 6.4 Hz, 1H), 5.05 (ddd, J = 17.2, 3.4, 1.6 Hz, 1H), 4.99 (dd, J = 10.2, 1.8 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.77 – 3.60 (m, 2H), 2.08 (t, J = 6.5 Hz, 2H), 1.84 (dq, J = 13.0, 6.7 Hz, 1H), 1.75 (td, J = 13.5, 6.2 Hz, 1H), 1.49 (dd, J = 8.8, 4.9 Hz, 1H), 1.41 (qd, J = 6.6, 3.9 Hz, 1H), 1.36 – 1.28 (m, J = 10.7, 4.4 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.16 – 0.95 (m, 21H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 172.9, 136.5, 115.7, 63.2, 60.4, 36.8, 30.4, 26.7, 26.0, 24.6, 18.2, 14.5, 12.1 ppm. **HRMS** (APCI): m/z calculated for $C_{11}H_{19}O_3$ $[M+H]^+$: 199.133, found 199.133.

To determine relative configuration of the minor diastereomer, the synthesis of SI-2 with low diastereoselectivity was accomplished by following representative procedure 1 (**RP-1**) in the absence of ligand followed by TBAF deprotection as described for SI-2. The 13C-NMR of the minor diastereomer of SI-2 is given below including a comparison with literature precedent.[4]

3. Identification of major diastereomer from copper mediated hydroallylation



4



5

Comparison ^{1}H-NMR spectra:

4	**SI-2**	**5**
5.93 - 5.73	5.81	5.83
5.16 - 4.99	5.13 – 5.03 5.03 – 4.96	5.06 4.98
4.13	4.11	4.12
3.68	3.64	3.71
2.41 - 1.98	2.16 2.00	2.41 - 2.18
1.97 - 1.74 1.71 1.55	1.94 – 1.72 1.68 – 1.55 1.53	1.72 - 1.50
1.49 - 1.38	1.45 – 1.37	1.41
1.27	1.25	1.26
1.36 - 1.17	1.19	1.21

Comparison ^{13}C-NMR spectra (major diastereomer):

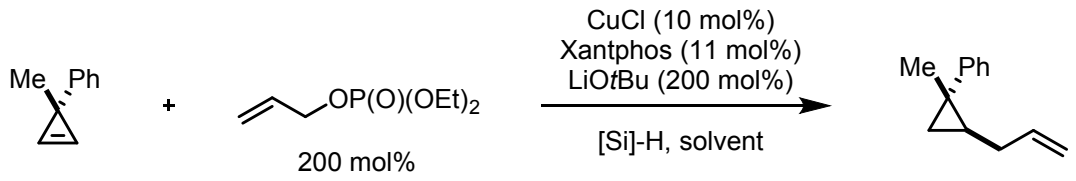
Δppm	**4**	**SI-2**	**5**	**Δppm**
-0,1	172,8	172,9	172,4	-0,5
-0,3	136,1	136,4	137,3	0,9
-0,3	115,6	115,9	115,1	-0,8
-0,2	62,6	62,8	62,3	-0,5
-0,1	60,4	60,5	60,3	-0,2
-0,2	36,5	36,7	35,9	-0,8
-0,4	29,6	30,0	30,8	0,8
-0,1	26,3	26,4	27,8	1,4
-0,3	25,4	25,7	24,8	-0,9
-0,2	24,4	24,6	24,2	-0,4
-0,3	14,2	14,5	14,3	-0,2

Comparison ^{13}C-NMR spectra (minor diastereomer):

Δppm	**4**	**SI-2**	**5**	**Δppm**
0,2	172,8	172,6	172,4	-0,2
-1,3	136,1	137,4	137,3	-0,1
0,4	115,6	115,2	115,1	-0,1
0,2	62,6	62,4	62,3	-0,1
-0,1	60,4	60,5	60,3	-0,2
0,5	36,5	36,0	35,9	-0,1
-1,4	29,6	31,0	30,8	-0,2
-1,6	26,3	27,9	27,8	-0,1
0,5	25,4	24,9	24,8	-0,1
0,1	24,4	24,3	24,2	-0,1
-0,2	14,2	14,4	14,3	-0,1

4. Optimization for diastereoselective hydroallylation of 3,3-disubstituted cyclopropenes

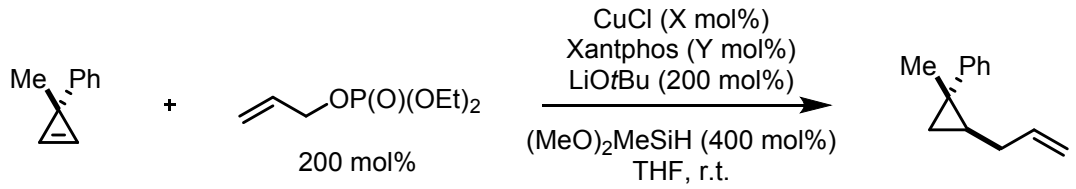
4.1. Screening of silane source and solvent[a]



[Si]-H [mol%]	Solvent	T [°C]	Conversion [%]	GC yield [%]	d.r.
$(MeO)_2MeSiH$ (400)	THF (0.33M)	25	100	62	17:1
$(EtO)_2MeSiH$ (400)	THF (0.33M)	25	100	63	14:1
PMHS (400)	THF (0.33M)	25	100	6	12:1
$(TMSO)_2MeSiH$ (400)	THF (0.33M)	25	100	47	18:1
TMS_3SiH (400)	THF (0.33M)	25	100	7	7:1
Me_2PhSiH (400)	THF (0.33M)	25	100	26	20:1
$PhSiH_3$ (400)	THF (0.33M)	25	100	59	10:1
$(MeO)_2MeSiH$ (200)	THF (0.33M)	0	100	22	17:1
$(TMSO)_2MeSiH$ (200)	THF (0.33M)	0	100	< 5	n.d.
$(MeO)_2MeSiH$ (400)	Et_2O (0.33M)	25	100	< 5	n.d.
$(TMSO)_2MeSiH$ (400)	Et_2O (0.33M)	25	0	-	-

[a] all reactions performed on 0.2 mmol scale. Analysis performed after addition of Celite® to the reaction mixture and filtration through a plug of silica. Tetradecane as internal standard.

4.2. Screening of optimal copper source and catalyst concentration[a]



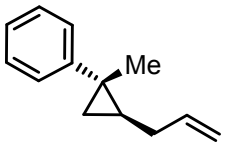
CuX [mol%]	Ligand [mol%]	Silane [mol%]	Solvent [conc.]	GC yield [%]	d.r.
CuBr (10)	Xantphos (11)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	84	21:1
CuI (10)	Xantphos (11)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	87	24:1
$Cu(OAc)_2$ (10)	Xantphos (11)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	41	10:1
CuOAc (10)	Xantphos (11)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	74	12:1
CuTC (10)	Xantphos (11)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	58	13:1
$[Cu(MeCN)_4]PF_6$ (10)	Xantphos (11)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	40	6:1
CuI (5)	Xantphos (6)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	83	> 50:1
CuI (10)	Xantphos (11)	$(MeO)_2MeSiH$ (200)	THF (0.25M)	74	> 50:1
CuI (5)	Xantphos (6)	$(MeO)_2MeSiH$ (200)	THF (0.25M)	68	21:1
CuI (5)	Xantphos (6)	$(MeO)_2MeSiH$ (400)	THF (0.25M)	80 (isolated)	n.d.

[a] all reactions performed on 0.2 mmol scale. Analysis performed after addition of Celite® to the reaction mixture and filtration through a plug of silica. Tetradecane as internal standard.

5. Representative procedure for the copper catalyzed hydroallylation of 3,3-disubstituted cyclopropenes (RP-2):

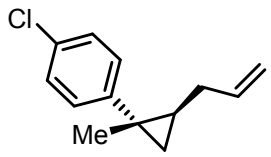
LiO*t*Bu (80.1 mg, 1.0 mmol, 2.0 equiv.) was flame-dried under vacuo in a Schlenk tube. Upon cooling, the tube was flushed with argon and CuI (4.76 mg, 0.025 mmol, 5.0 mol%) and Xantphos (18.28mg, 0.03 mmol, 6.0 mol%) were added followed by dry THF (1.5 mL), and stirring was continued for 5 minutes at room temperature. Dimethoxymethylsilane (250µL, 2.0 mmol, 4.0 equiv.) was added slowly (CAUTION: vigorous foaming in the beginning) and stirring was continued for 5 minutes before the cyclopropene (1.0 equiv.) and allyl phosphate (2.0 equiv.) in THF (0.5 mL) were added. Stirring was continued at room temperature until complete consumption of cyclopropene was judged by TLC (hexanes, usually between 30 to 120 minutes). Upon completion, the mixture was directly loaded onto a silica gel column. Flash chromatography (hexanes) yielded the product as colorless oils.

2-Allyl-1-methylcyclopropyl)benzene (**5a**)



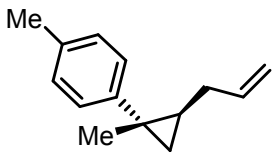
80% yield (690 mg, 4.0 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32 – 7.22 (m, 4H), 7.19 – 7.13 (m, 1H), 5.98 (ddt, J = 16.6, 10.2, 6.3 Hz, 1H), 5.12 (dq, J = 17.2, 1.7 Hz, 1H), 5.02 (ddd, J = 10.2, 3.1, 1.5 Hz, 1H), 2.39 – 2.16 (m, 2H), 1.41 (s, J = 9.8 Hz, 3H), 1.16 – 1.03 (m, 2H), 0.48 – 0.37 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 148.6, 138.5, 128.3, 127.0, 125.6, 114.7, 33.9, 25.5, 24.1, 20.5, 20.4 ppm. **HRMS** (APCI): m/z calculated for $C_{13}H_{16}Na$ $[M+Na]^+$: 195.115, found 195.115.

2-Allyl-1-methylcyclopropyl)-4-chlorobenzene (**5b**)



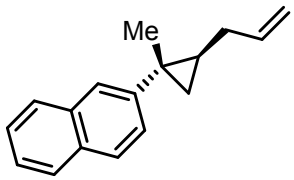
73% yield (75 mg, 0.36 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.25 – 7.20 (m, 2H), 7.20 – 7.13 (m, 2H), 5.96 (ddt, J = 16.5, 10.2, 6.3 Hz, 1H), 5.11 (ddd, J = 17.2, 3.5, 1.7 Hz, 1H), 5.02 (ddd, J = 10.2, 3.2, 1.4 Hz, 1H), 2.37 – 2.09 (m, 2H), 1.38 (s, J = 8.4 Hz, 3H), 1.13 – 0.99 (m, 2H), 0.52 – 0.41 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 147.2, 138.2, 131.2, 128.4, 128.4, 114.8, 33.8, 25.6, 23.7, 20.6, 20.3 ppm. **HRMS** (APCI): m/z calculated for $C_{13}H_{16}Cl$ $[M+H]^+$: 207.094, found 207.090.

2-Allyl-1-methylcyclopropyl)-4-methylbenzene (**5c**)



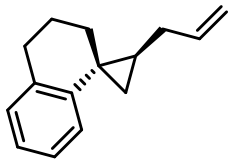
72% yield (67 mg, 0.36 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.15 (m, 2H), 7.10 (m, 2H), 5.98 (ddt, J = 16.5, 10.2, 6.3 Hz, 1H), 5.12 (ddd, J = 17.2, 3.5, 1.6 Hz, 1H), 5.02 (ddd, J = 10.2, 3.1, 1.2 Hz, 1H), 2.32 (s, J = 8.8 Hz, 3H), 2.31 – 2.12 (m, 2H), 1.39 (s, J = 9.6 Hz, 3H), 1.15 – 1.00 (m, 2H), 0.47 – 0.35 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 145.7, 138.5, 135.1, 129.0, 127.0, 114.6, 33.9, 25.3, 23.87, 21.1, 20.6, 20.4 ppm. **HRMS** (APCI): m/z calculated for $C_{14}H_{19}$ $[M+H]^+$: 187.148, found 187.145.

2-Allyl-1-methylcyclopropyl)naphthalene (**5d**)



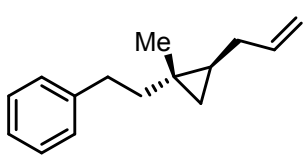
60% yield (72 mg, 0.30 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.83 – 7.73 (m, 3H), 7.73 – 7.64 (m, 1H), 7.50 – 7.35 (m, 3H), 6.03 (ddt, J = 16.6, 10.2, 6.3 Hz, 1H), 5.16 (dd, J = 17.2, 1.4 Hz, 1H), 5.05 (dd, J = 10.2, 1.3 Hz, 1H), 2.45 – 2.18 (m, 2H), 1.50 (s, 3H), 1.28 – 1.16 (m, 2H), 0.53 (t, J = 4.3 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 146.0, 138.4, 133.6, 131.9, 128.0, 127.7, 127.6, 126.0 (2C), 125.3, 125.1, 114.87, 33.9, 25.3, 24.4, 20.4 ppm. **HRMS** (APCI): m/z calculated for $C_{18}H_{23}$ $[M+OH]^+$: 239.143, found 239.141.

2-Allyl-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene] (**5e**)



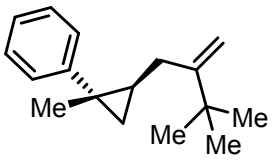
63% yield (67 mg, 0.31 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.22 – 6.94 (m, 3H), 6.68 (m, 1H), 5.94 (ddt, J = 16.7, 10.2, 6.3 Hz, 1H), 5.08 (ddd, J = 17.1, 3.5, 1.7 Hz, 1H), 4.99 (ddd, J = 10.2, 2.9, 1.6 Hz, 1H), 2.93 – 2.75 (m, 2H), 2.42 – 2.26 (m, 1H), 2.26 – 2.11 (m, 1H), 2.01 – 1.82 (m, 2H), 1.79 (dd, J = 13.8, 8.0 Hz, 1H), 1.76 – 1.64 (m, 1H), 1.34 – 1.07 (m, 2H), 0.55 (dd, J = 5.7, 4.6 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 142.8, 138.2, 137.3, 128.8, 126.2, 124.6, 121.9, 114.8, 33.6, 31.0, 29.5, 29.3, 24.5, 22.7 (2C) ppm. **HRMS** (APCI): m/z calculated for $C_{15}H_{21}O$ $[M+H_3O]^+$: 217.159, found 217.157.

2-Allyl-1-methylcyclopropyl)ethyl)benzene (**5f**)



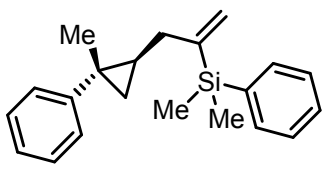
65% yield (65 mg, 0.32 mmol, obtained as a 67:33 mixture of diastereomers). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.33 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 5.90 (dddt, J = 16.5, 10.1, 9.2, 6.2 Hz, 1H), 5.07 (dtd, J = 17.2, 3.6, 1.8 Hz, 1H), 4.97 (dtd, J = 10.2, 3.4, 1.4 Hz, 1H), 2.83 – 2.59 (m, 2H), 2.22 – 1.97 (m, 2H), 1.71 – 1.41 (m, 2H), 1.11 (t, J = 6.0 Hz, 3H), 0.71 – 0.55 (m, 1H), 0.46 (dt, J = 8.3, 4.1 Hz, 1H), 0.03 – -0.07 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$, both diastereomers are reported) δ** 143.3, 143.1, 138.95, 138.89, 128.48, 128.45, 128.44, 128.40, 125.74, 125.69, 114.23, 114.16, 43.93, 36.74, 33.90, 33.84, 33.55, 33.44, 24.74, 24.35, 23.19, 19.79, 19.69, 19.14, 19.05, 17.4 ppm. **HRMS** (APCI): m/z calculated for $[M-H_2+NH_4]^+$: 216.175, found 216.174.

2-(3,3-Dimethyl-2-methylenebutyl)-1-methylcyclopropyl)benzene (**5g**)



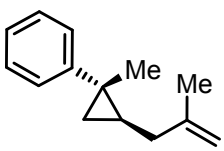
51% yield (58 mg, 0.25 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30 – 7.22 (m, 4H), 7.13 (dtd, J = 9.2, 6.0, 3.1 Hz, 1H), 4.94 – 4.85 (m, 2H), 2.37 – 2.26 (m, 1H), 2.24 – 2.12 (m, 1H), 1.37 (s, 3H), 1.32 – 1.12 (m, 2H), 1.08 (s, 9H), 0.50 – 0.39 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 157.9, 148.7, 128.3, 126.5, 125.4, 106.6, 36.1, 31.5, 29.5, 26.1, 23.7, 21.4, 19.8 ppm. **HRMS** (APCI): m/z calculated for $C_{17}H_{25}$ $[M+H]^+$: 229.196, found 229.194.

Dimethyl(2-methyl-2-phenylcyclopropyl)prop-1-en-2-yl)(phenyl)silane (**5h**)



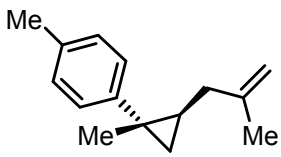
78% yield (120 mg, 0.39 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.60 – 7.44 (m, 2H), 7.36 (m, 3H), 7.31 – 7.22 (m, 2H), 7.16 m, 3H), 5.95 – 5.77 (m, 1H), 5.47 (dd, J = 13.8, 12.5 Hz, 1H), 2.30 (d, J = 1.4 Hz, 2H), 1.40 – 1.28 (s, 3H), 1.19 – 1.04 (m, 2H), 0.39 (d, J = 7.6 Hz, 6H), 0.08 (dd, J = 3.0, 1.4 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 150.1, 148.6, 138.4, 134.1, 129.1, 128.3, 127.9, 126.4, 125.9, 125.4, 35.5, 25.7, 23.8, 21.4, 19.9, -2.90, -2.93 ppm. **HRMS** (APCI): m/z calculated for $C_{21}H_{27}Si$ $[M+H]^+$: 307.188, found 307.185.

1-Methyl-2-(2-methylallyl)cyclopropyl)benzene (**5j**)



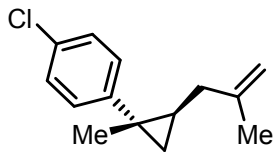
62% yield (58 mg, 0.31 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.33 – 7.23 (m, 4H), 7.20 – 7.13 (m, 1H), 4.81 (s, 1H), 4.76 (d, J = 0.9 Hz, 1H), 2.31 – 2.11 (m, 2H), 1.81 (s, 3H), 1.40 (s, J = 3.0 Hz, 3H), 1.22 – 1.10 (m, 2H), 0.49 – 0.37 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 148.6, 146.1, 128.3, 126.7, 125.5, 110.1, 37.9, 25.2, 23.9, 23.0, 20.9, 20.2 ppm. **HRMS** (APCI): m/z calculated for $C_{14}H_{19}$ $[M+H]^+$: 187.148, found 187.146.

1-Methyl-4-(1-methyl-2-(2-methylallyl)cyclopropyl)benzene (**5l**)



71% yield (71 mg, 0.35 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.15 (m, 2H), 7.09 (m, 2H), 4.81 (s, 1H), 4.76 (s, 1H), 2.36 – 2.29 (m, 3H), 2.20 (qd, J = 16.3, 6.3 Hz, 2H), 1.81 (s, 3H), 1.38 (s, 3H), 1.16 – 1.05 (m, 2H), 0.46 – 0.35 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 146.2, 145.7, 135.0, 129.0, 126.7, 110.1, 37.8, 25.0, 23.6, 23.0, 21.1, 20.7, 20.4 ppm. **HRMS** (APCI): m/z calculated for $C_{15}H_{21}$ $[M+H]^+$: 201.164, found 201.162.

1-Methyl-4-(1-methyl-2-(2-methylallyl)cyclopropyl)benzene (**5m**)



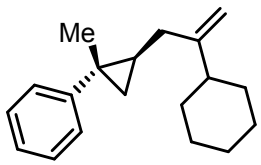
71% yield (71 mg, 0.35 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.26 – 7.19 (m, 2H), 7.19 – 7.13 (m, 2H), 4.78 (s, 1H), 4.76 (s, 1H), 2.35 – 2.09 (m, 3H), 1.80 (s, 4H), 1.37 (s, 4H), 1.19 – 1.02 (m, 3H), 0.53 – 0.38 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 147.2, 145.9, 131.1, 128.4, 128.1, 110.2, 37.7, 25.4, 23.5, 23.0, 21.0, 20.1 ppm. **HRMS** (APCI): m/z calculated for $C_{14}H_{18}Cl$ $[M+H]^+$: 221.110, found 221.109.

6. Representative procedure for the copper catalyzed hydroallylation of 1,1-disubstituted cyclopropenes with bis(trichloroethyl) phosphates

LiO*t*Bu (32 mg, 0.4 mmol, 2.0 equiv.) was flame-dried under vacuo in a Schlenk tube. Upon cooling, the tube was flushed with argon and $Cu(OAc)_2$ (1.82 mg, 0.01 mmol, 5.0 mol%) and Xantphos (7.71mg, 0.012 mmol, 6.0 mol%) were added followed by dry THF (600 µL), and stirring was continued for 5 minutes at room temperature. Dimethoxymethylsilane (100 µL, 0.8 mmol, 4.0 equiv.) was added slowly (CAUTION: vigorous foaming in the beginning) and stirring was continued for 5 minutes before the cyclopropene (3.0 equiv.) and bis(trichloroethyl) allyl phosphate (1.0 equiv.) in THF (200 µL) were added. Stirring was continued at room temperature

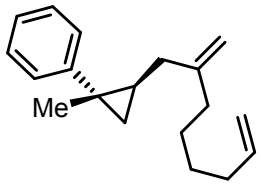
until complete consumption of cyclopropene was judged by TLC (hexanes, usually between 30 to 120 minutes). Upon completion, the mixture was directly loaded onto a silica gel column. Flash chromatography (hexanes) yielded the product as colorless oils.

2-(2-Cyclohexylallyl)-1-methylcyclopropyl)benzene (**5i**)



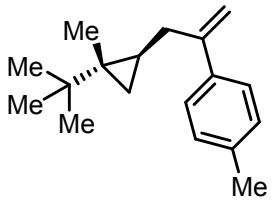
77% yield (39 mg, 0.15 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32 – 7.23 (m, 4H), 7.18 – 7.12 (m, 1H), 4.85 (dd, J = 3.1, 1.5 Hz, 1H), 4.78 (dd, J = 1.4, 0.9 Hz, 1H), 2.23 (d, J = 6.4 Hz, 2H), 1.98 – 1.62 (m, 6H), 1.39 (s, 3H), 1.33 – 1.08 (m, 7H), 0.48 – 0.39 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 155.4, 148.7, 128.3, 126.7, 125.4, 107.2, 44.7, 34.8, 32.7, 32.7, 27.0, 27.0, 26.6, 25.4, 23.8, 21.1, 20.1 ppm. **HRMS** (APCI): m/z calculated for $C_{19}H_{27}$ $[M+H]^+$: 255.211, found 255.209.

1-Methyl-2-(2-methyleneoct-7-en-1-yl)cyclopropyl)benzene (**5k**)



65% yield (33 mg, 0.13 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31 – 7.22 (m, 4H), 7.18 – 7.12 (m, 1H), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.01 (ddd, J = 17.1, 3.6, 1.6 Hz, 1H), 4.94 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 4.86 (d, J = 0.9 Hz, 1H), 4.79 – 4.74 (m, 1H), 2.26 – 2.15 (m, 2H), 2.15 – 2.02 (m, 4H), 1.53 – 1.40 (m, 4H), 1.40 (s, 4H), 1.20 – 1.09 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.9, 148.6, 139.1, 128.3, 126.7, 125.5, 114.5, 109.2, 36.5, 36.1, 33.8, 28.8, 27.5, 25.3, 23.8, 21.0, 20.2 ppm. **HRMS** (APCI): m/z calculated for $C_{19}H_{27}$ $[M+H]^+$: 255.211, found 255.209.

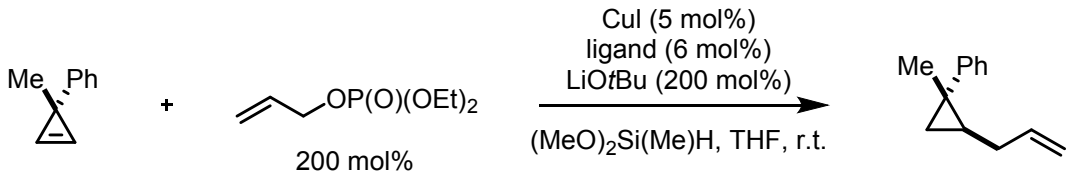
2-Allyl-1-methylcyclopropyl)ethyl)benzene (**5n**)



62% yield (30 mg, 0.12 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.35 (m, 2H), 7.13 (m, 2H), 5.28 (d, J = 0.7 Hz, 1H), 5.16 (dd, J = 2.9, 1.4 Hz, 1H), 2.50 (d, J = 6.9 Hz, 2H), 2.35 (s, 3H), 1.05 – 0.99 (m, 3H), 0.99 – 0.91 (m, 1H), 0.88 – 0.73 (m, 9H), 0.64 (dd, J = 9.1, 4.5 Hz, 1H), -0.17 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.0, 139.1, 137.1, 129.0, 126.1, 111.2, 35.2, 32.8, 27.2, 26.7, 21.2, 18.6, 16.5, 16.0 ppm. **HRMS** (APCI): m/z calculated for $C_{18}H_{27}$ $[M+H]^+$: 243.211, found 243.209.

7. Optimization for enantioselective hydroallylation of 3,3-disubstituted cyclopropenes

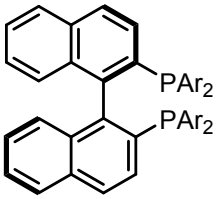
7.1. Screening of chiral phosphine ligands under standard conditions[a]



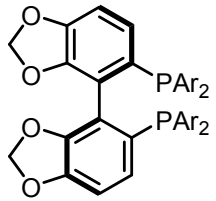
Exp No	Ligand [mol%]	Time	GC yield [%]	e.r.
1	(R)-BINAP (6)	1 h	93	55:45
2	(R)-H8-BINAP (6)	1 h	90	55:45
3	(R)-tol-BINAP (6)	1 h	97	58:42
4	(R)-DM-BINAP (6)	1 h	76	63:37
5	(R)-SEGPHOS (6)	2 h	99	60:40
6	(R)-DM-SEGPHOS (6)	1 h	76	64:36
7	(R)-DTBM-SEGPHOS (6)	2 h	91	75:25
8	(S)-Ph-BPE (6)	2 h	66	56:44
9	(R)-JOSIPHOS (6)	2 h	76	60:40
10	(R)-Walphos (6)	1 h	n.d.	51:49
11	(R)-MeO-DM-BIPHEP (6)	1 h	70	61:39
12	(-)-Ph-SKP (6)	1 h	64	44:56
13	(S)-DIFLUORPHOS (6)	1 h	56	51:49
14	(R)-Trost-DACH (6)	1 h	48	55:45
15	(R)-Ph-SDP (6)	1 h	82	53:47
16	(S)-DTBM-BINAP (6)	1 h	81	47:53
17	(R)-DTBM-BIPHEP (6)	1 h	76	67:33
18	(-)-DM-SKP (6)	1 h	72	43:57
19	(R)-DM-SDP (6)	1 h	84	53:47
20	(+)-catASium T3	1 h	85	36:64

[a] all reactions performed on 0.2 mmol scale. Analysis performed after addition of Celite® to the reaction mixture and filtration through a plug of silica. Tetradecane as internal standard.

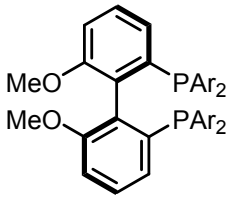
7.2. Structures of screened ligands



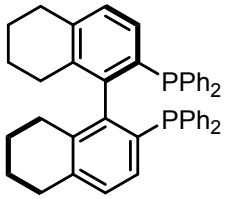
BINAP (Ar = Ph)
tol-BINAP (Ar = 4-MeC_6H_4)
DM-BINAP (Ar = 3,5-$Me_2C_6H_3$)
DTBM-BINAP (Ar = 3,5-$(MeO)_2$-4-*t*Bu-C_6H_2)



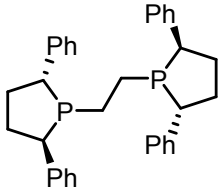
SEGPHOS (Ar = Ph)
DM-SEGPHOS (Ar = 3,5-$Me_2C_6H_3$)
DTBM-SEGPHOS (Ar = 3,5-$(MeO)_2$-4-*t*Bu-C_6H_2)



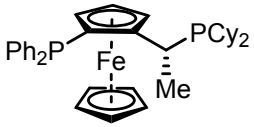
DM-MeO-BIPHEP (Ar = 3,5-$Me_2C_6H_3$)
DTBM-MeO-BIPHEP (Ar = 3,5-$(MeO)_2$-4-*t*Bu-C_6H_2)



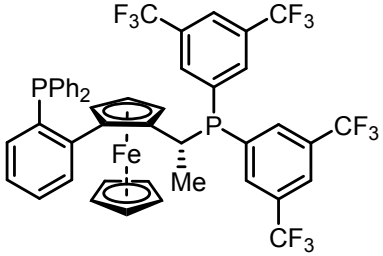
H_8-BINAP



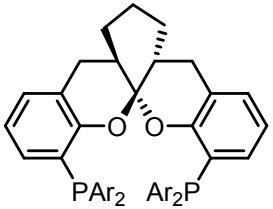
Ph-BPE



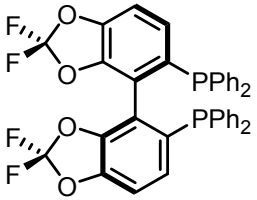
JOSIPHOS
SL-J001-01



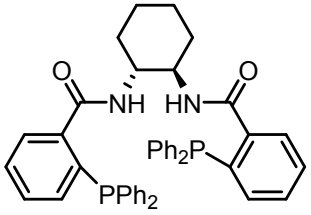
WALPHOS



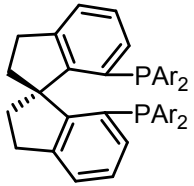
Ph-SKP (Ar = Ph)
DM-SKP (Ar = 3,5-$Me_2C_6H_3$)



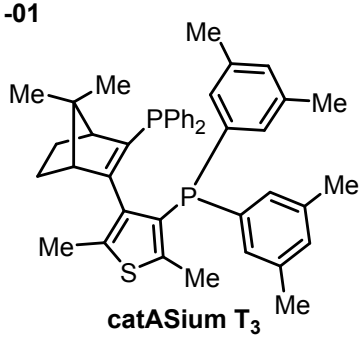
DIFLUORPHOS



Trost DACH

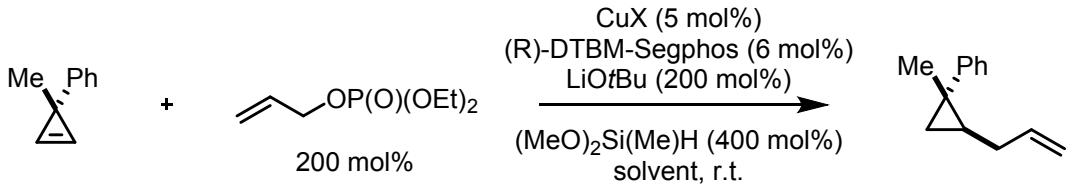


Ph-SDP (Ar = Ph)
DM-SDP (Ar = 3,5-$Me_2C_6H_3$)



catASium T_3

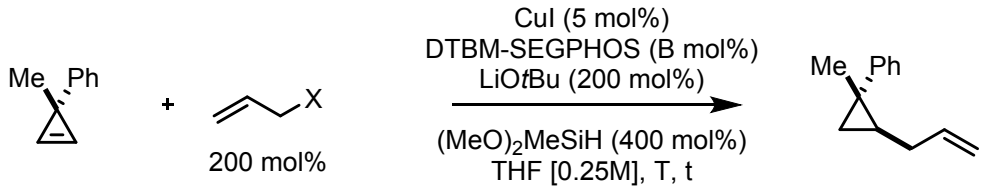
7.3. Screening optimal copper source and solvent[a]



Exp No	Copper salt [mol%]	Solvent [M]	GC yield [%]	e.r.
1	CuCl (5)	THF (0.25M)	53	69:31
2	$[Cu(MeCN)_4]PF_6$ (5)	THF (0.25M)	52	62:38
3	Cu(OAc) (5)	THF (0.25M)	51	65:35
4	CuCl (5)	THF (0.33M)	60	63:37
5	$[Cu(MeCN)_4]PF_6$ (5)	THF (0.33M)	49	56:44
6	Cu(OAc) (5)	THF (0.33M)	56	63:37
7	CuI (5)	Et_2O (0.25M)	68	74:26
8	CuI (5)	CH_2Cl_2 (0.25M)	< 5	n.d.
9	CuI (5)	PhMe (0.25M)	49	81:19
10	CuI (5)	MeCN (0.25M)	58	66:34
11	CuTC (5)	THF (0.25M)	73	65:35
12	CuOAc (5)	THF (0.25M)	26	76:24

[a] all reactions performed on 0.2 mmol scale. Analysis performed after addition of Celite® to the reaction mixture and filtration through a plug of silica. Tetradecane as internal standard.

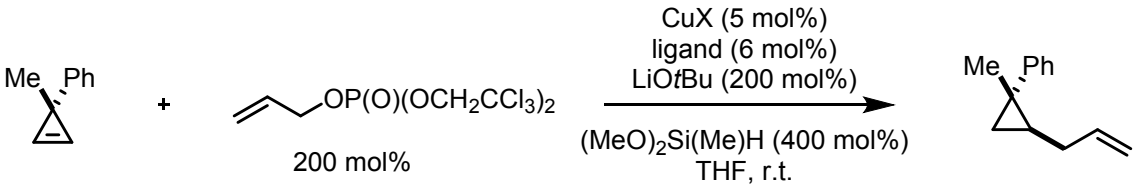
7.4. Influence Catalyst Loading and Allylating Reagent[a]



Exp No	Ligand [mol%]	X =	Comment	GC yield [%]	e.r.
1	(R)-DTBM-SEGPHOS (6)	OTs	-	69	67:33
2	(R)-DTBM-SEGPHOS (6)	$OC(O)C_6F_5$	-	16	86:14
3	(R)-DTBM-SEGPHOS (6)	Cl	-	< 5	n.d.
4	(R)-DTBM-SEGPHOS (6)	OP(O)pin	-	41	86:14
5	(R)-DTBM-SEGPHOS (6)	OP(O)neo	-	78	77:23
6	(R)-DTBM-SEGPHOS (6)	$OP(O)(OCH_2CCl_3)_2$	-	42	88:12
7	(R)-DTBM-SEGPHOS (6)	$OP(O)(OEt)_2$	3.0 eq allylX	76	75:25
8	(R)-DTBM-SEGPHOS (6)	$OP(O)(OEt)_2$	4.0 eq allylX	79	75:25
9	(R)-DTBM-SEGPHOS (10)	$OP(O)(OEt)_2$	1 h	66	75:25
10	(R)-DTBM-SEGPHOS (15)	$OP(O)(OEt)_2$	1 h	59	70:30
11	(R)-DM-SEGPHOS (6)	Cl, 18 h	-70 to -20	14	94:06
12	(R)-DM-SEGPHOS (6)	Br, 18 h	-70 to -20	25	76:24
13	(R)-DM-SEGPHOS (6)	I, 18 h	-70 to -20	18	63:37

[a] all reactions performed on 0.2 mmol scale. Analysis performed after addition of Celite® to the reaction mixture and filtration through a plug of silica. Tetradecane as internal standard.

7.5. Performance of Bis(trichloroethyl) Phosphate Allylating Reagent[a]



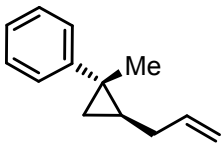
Exp No	Copper salt [mol%]	Ligand [mol%]	T [°C]	GC yield [%]	e.r.
1	CuI (5)	(R)-DTBM-SEGPHOS (6)	25	42	88:12
2	CuTC (5)	(R)-DTBM-SEGPHOS (6)	25	48	86:14
3	$Cu(OAc)_2$ (5)	(R)-DTBM-SEGPHOS (6)	25	50	86:14
4	$Cu(OAc)_2$ (5)	(R)-DM-SEGPHOS (6)	25	49	79:21
5	$Cu(OAc)_2$ (5)	(R)-DM-BINAP (6)	25	71	74:26
6	$Cu(OAc)_2$ (5)	(R)-DTBM-BIPHEP (6)	25	55	79:21
7	$Cu(OAc)_2$ (5)	(+)-catASium T3	25	57	52:48
8	CuI (5)	(R)-DM-SEGPHOS (6)	25	62	78:22
9	CuI (5)	(R)-DM-BINAP (6)	25	66	75:25
10	CuI (5)	(+)-catASium T3	25	58	54:46
11	$Cu(OAc)_2$ (5)	(R)-DiPr-BINAP (6)	25	67	68:32
12	$Cu(OAc)_2$ (10)	(R)-DTBM-SEGPHOS (12)	25	21	n.d.
13	$Cu(OAc)_2$ (5)	(R)-DiPr-TADDOL (6)	25	83	54:46
14	$Cu(OAc)_2$ (5)	(R)-C3-TUNEPHOS (6)	25	38	80:20
15	CuI (5)	(R)-DM-SEGPHOS (6)	25	62	78:22
16	CuI (5)	(R)-DM-BINAP (6)	25	66	75:25
17	Cu(OAc)2 (5)	(R)-DM-BINAP (6)	0	50	80:20
18	CuI (5)	(R)-DM-BINAP (6)	0	62	78:22
19	CuI (5)	(R)-DM-SEGPHOS (6)	-20	19	94:06
20	CuI (5)	(R)-DM-BINAP (6)	-20	45	82:18
21	Cu(OAc)2 (5)	(R)-DM-SEGPHOS (6)	-20	15	93:07
22	Cu(OAc)2 (5)	(R)-DM-BINAP (6)	-20	34	86:14

[a] all reactions performed on 0.2 mmol scale. Analysis performed after addition of Celite® to the reaction mixture and filtration through a plug of silica. Tetradecane as internal standard.

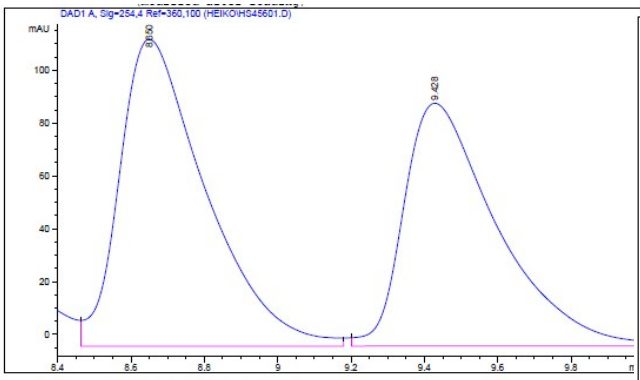
8. Representative procedure for the enantioselective copper catalyzed hydroallylation of 3,3-disubstituted cyclopropenes with bis(trichloroethyl) phosphates

LiO*t*Bu (32 mg, 0.4 mmol, 2.0 equiv.) was flame-dried under vacuo in a Schlenk tube. Upon cooling, the tube was flushed with argon and $Cu(OAc)_2$ (1.82 mg, 0.01 mmol, 5.0 mol%) and **L13** (8.72mg, 0.012 mmol, 6.0 mol%) were added followed by dry THF (600 µL), and stirring was continued for 5 minutes at room temperature. Dimethoxymethylsilane (100 µL, 0.8 mmol, 4.0 equiv.) was added slowly (CAUTION: vigorous foaming in the beginning) followed by tetradecane (50 µL as internal standard) and stirring was continued for 5 minutes before the mixture was cooled to –20°C. After 10 minutes, the cyclopropene (3.0 equiv.) and bis(trichloroethyl) allyl phosphate (1.0 equiv.) in THF (200 µL) were added. Stirring was continued for 18 h at the same temperature. Upon completion, the mixture was directly loaded onto a silica gel column or analyzed by GC and chiral HPLC. Flash chromatography (hexanes) yielded the product as colorless oils.

2-Allyl-1-methylcyclopropyl)benzene (**5a**)



71% yield, determined by GC using tetradecane as internal standard. HPLC analysis (CHIRALCEL OD, 100% hexanes, 0.6 mL/min, 254 nm, tR1 = 8.5 min, tR2 = 9.4 min) indicated 92:08 enantiomeric ratio.

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Use Multiplier & Dilution Factor with ISTDs


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   2   9.428 BP    0.2623 1626.73950   91.98537  46.1235

Totals :                  3526.92407  208.32208
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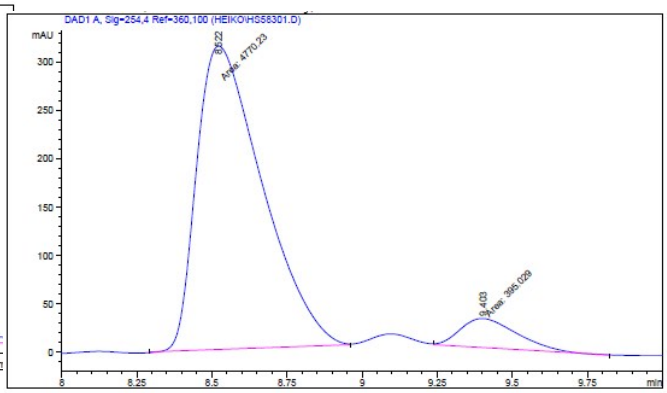


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Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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   2   9.403 MM T  0.2188  395.02921   30.09607   7.6478

Totals :                  5165.26016  344.20413
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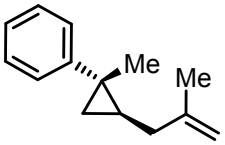
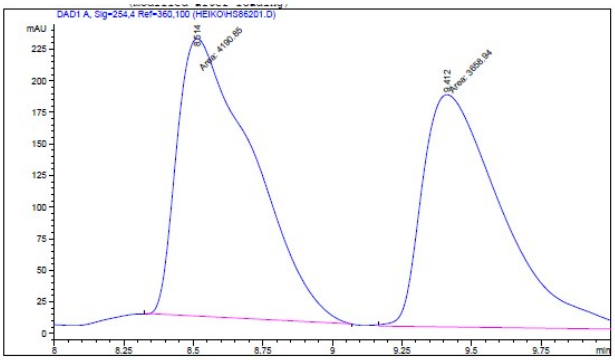
1-Methyl-2-(2-methylallyl)cyclopropyl)benzene (**5j**)



70% yield, determined by GC using tetradecane as internal standard. HPLC analysis (CHIRALCEL OD, 100% hexanes, 0.6 mL/min, 254 nm, tR1 = 8.5 min, tR2 = 9.3 min) indicated 93:07 enantiomeric ratio.

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Dilution              :      1.0000
Sample Amount         :      5.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
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   1   8.514 MM T  0.3180 4190.85352  219.66322  53.3880
   2   9.412 MM T  0.3916 9658.94385  183.88760  46.6120

Totals :                  7849.79736  403.55083
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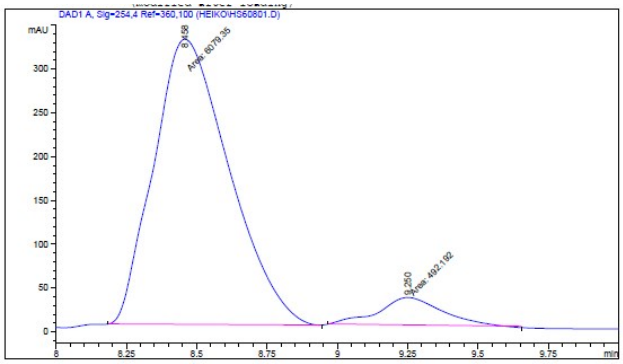


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Dilution              :      1.0000
Sample Amount         :      5.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
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   1   8.458 MM    0.3111 6079.35205  325.68515  92.5103
   2   9.250 MM    0.2620  492.19199   31.30944   7.4897

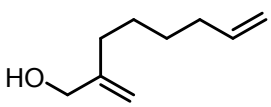
Totals :                  6571.54404  356.99459
```

9. Substrate syntheses

9.1. Representative procedure for the synthesis of 2-substituted allylic alcohols[5]:

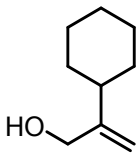
Mg turnings (730 mg, 30.0 mmol, 3.0 equiv.) were placed in a flame-dried flask equipped with a reflux condenser under an argon atmosphere. Et_2O (10 mL) was added followed by DIBAL-H (1M in hexane, 200 µL) and a crystal of iodine. 6-Bromo-1-hexene (3.61 mL, 27.0 mmol, 2.7 equiv.) in Et_2O (20 mL) was slowly added and the mixture refluxed for 1 h. After being cooled to room temperature, CuI (286 mg, 1.5 mmol, 0.15 equiv.) followed by freshly distilled propargyl alcohol (577 µL, 10.0 mmol, 1.0 equiv.) were added. The mixture was then refluxed for 18 h before it was poured onto saturated ammonium chloride solution after being cooled to room temperature. The mixture was extracted two times with Et_2O, the combined extracts were washed with brine, dried over sodium sufalte and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 9:1) yielded the product as a colorless oil.

2-Methyleneoct-7-en-1-ol (**SI-3**)



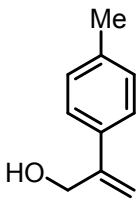
66% yield (910 mg, 6.56 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.02 (dd, J = 3.4, 1.7 Hz, 2H), 5.00 – 4.90 (m, 2H), 4.86 (d, J = 1.1 Hz, 1H), 4.08 (d, J = 8.1 Hz, 2H), 2.11 – 1.94 (m, 4H), 1.58 – 1.30 (m, 4H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 149.2, 139.0, 114.6, 109.3, 66.0, 33.7, 32.9, 28.8, 27.3 ppm. **HRMS** (APCI): m/z calculated for C_9H_{15} $[M\text{-}OH]^+$: 123.117, found 123.117.

2-Cyclohexylprop-2-en-1-ol (**SI-4**)[6]



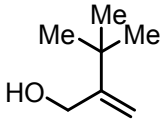
Prepared following described procedure. Analytical data in accordance with literature**. 86% yield** (1.2 g, 8.6 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.00 (d, J = 1.3 Hz, 1H), 4.87 (s, 1H), 4.11 (s, 2H), 1.94 (t, J = 11.5 Hz, 1H), 1.78 (dd, J = 7.1, 5.7 Hz, 4H), 1.67 (dd, J = 19.8, 12.2 Hz, 1H), 1.61 – 1.38 (m, 1H), 1.38 – 1.08 (m, 5H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 154.7, 107.6, 65.4, 41.4, 32.6, 26.9, 26.4 ppm.

2-(*p*-Tolyl)prop-2-en-1-ol (**SI-5**)[7]



Prepared followed described procedure. Analytical data in accordance with literature. **68% yield** (1.0 g, 6.76 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 5.44 (s, 1H), 5.31 (d, J = 1.2 Hz, 1H), 4.53 (d, J = 4.4 Hz, 2H), 2.36 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 147.2, 137.9, 135.7, 129.4, 126.1, 111.9, 65.2, 21.3 ppm.

3,3-Dimethyl-2-methylenebutan-1-ol (**SI-6**)[5]

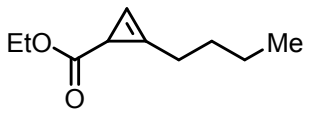


Prepared followed described procedure. Analytical data in accordance with literature. **37 % yield** (419 mg, 3.67 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 1H NMR (400 MHz, CDCl3) δ 5.06 (d, J = 1.1 Hz, 1H), 4.99 (d, J = 0.8 Hz, 1H), 4.20 (s, 2H), 1.57 – 1.31 (m, 1H), 1.09 (s, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 157.5, 107.0, 63.1, 35.0, 29.6 ppm.

9.2. Representative procedure for the synthesis of cyclopropenes via rhodium catalyzed diazo decomposition following representative procedure[8]

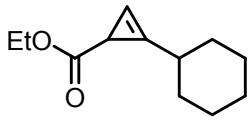
(Hex-5-yn-1-yloxy)triisopropylsilane (1.13 g, 5.0 mmol, 1.0 equiv.) and $Rh_2(OAc)_4$ (11 mg, 0.025 mmol, 0.5 mol%) were dissolved in CH_2Cl_2 (50 mL) and stirred at room temperature in a single-necked flask. Ethyl diazoacetate (1.19 mL, 48 wt% in CH_2Cl_2, 5.0 mmol, 1.0 equiv.) was added with a syringe pump over 18 h. The volatiles were then removed under reduced pressure and the residue purified by flash chromatography (hexanes/Et_2O, 9:1) to give the product as a pale yellow liquid.

Ethyl 2-butylcycloprop-2-ene-1-carboxylate[9] (**SI-7**)



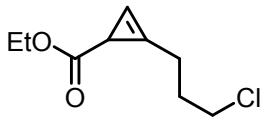
Prepared followed described procedure. Analytical data in accordance with literature. **58% yield** (9.67 g, 57,5 mmol, on 100 mmol scale with 3.0 equiv. of alkyne). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 6.28 (d, J = 1.2 Hz, 1H), 4.14 – 4.02 (m, 2H), 2.45 (t, J = 7.3 Hz, 2H), 2.07 (d, J = 1.4 Hz, 1H), 1.62 – 1.48 (m, 2H), 1.41 – 1.30 (m, 2H), 1.23 – 1.16 (m, 3H), 0.86 (q, J = 7.2 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 176.6, 115.6, 94.0, 60.1, 28.8, 24.7, 22.2, 19.7, 14.4, 13.7 ppm.

Ethyl 2-cyclohexylcycloprop-2-ene-1-carboxylate (**SI-8**)[9]



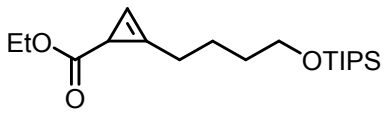
Prepared followed described procedure. Analytical data in accordance with literature **. 69% yield** (2.69 g, 13.8 mmol, on 20 mmol scale with 3.0 equiv. of alkyne). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 6.28 (t, J = 1.4 Hz, 1H), 4.18 – 4.06 (m, 2H), 2.56 (td, J = 9.3, 4.1 Hz, 1H), 2.13 (d, J = 1.4 Hz, 1H), 1.92 – 1.79 (m, 2H), 1.72 (dd, J = 15.2, 12.3 Hz, 2H), 1.60 (d, J = 9.4 Hz, 2H), 1.49 – 1.27 (m, 4H), 1.27 – 1.22 (m, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 177.0, 119.3, 92.9, 60.3, 34.39, 30.4 (d), 26.1, 25.3 (d), 19.3, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_{12}H_{19}O_2$ $[M+H]^+$: 195.138, found 195.141.

Ethyl 2-(3-chloropropyl)cycloprop-2-ene-1-carboxylate (**SI-9**)[10]



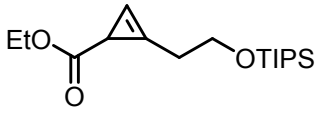
Prepared followed described procedure. Analytical data in accordance with literature **. 51% yield** (1.91 g, 10.1 mmol, on 20 mmol scale with 2.0 equiv. of alkyne). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 6.43 (d, J = 0.7 Hz, 1H), 4.19 – 4.02 (m, 2H), 3.68 – 3.52 (m, 2H), 2.86 – 2.56 (m, 2H), 2.15 (d, J = 0.5 Hz, 1H), 2.13 – 2.01 (m, 2H), 1.30 – 1.21 (m, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 176.4, 114.3, 95.7, 60.5, 44.0, 29.8, 22.5, 19.8, 14.5 ppm. **HRMS** (APCI): m/z calculated for $C_9H_{14}ClO_2$ $[M+H]^+$: 189.068, found 189.072.

Ethyl 2-(4-((triisopropylsilyl)oxy)butyl)cycloprop-2-ene-1-carboxylate (**SI-10**)



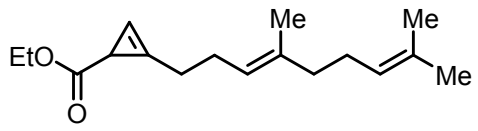
21% yield (1.40 g, 4.11 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 6.33 (q, J = 1.4 Hz, 1H), 4.21 – 4.03 (m, 2H), 3.75 – 3.63 (m, 2H), 2.58 – 2.45 (m, 2H), 2.13 (d, J = 1.5 Hz, 1H), 1.73 – 1.54 (m, 4H), 1.30 – 1.20 (m, 3H), 1.18 – 0.95 (m, 21H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 176.8, 115.7, 94.3, 63.1, 60.3, 32.5, 25.0, 23.3, 19.9, 18.2, 14.5, 12.1 ppm. **HRMS** (APCI): m/z calculated for $C_{19}H_{37}O_3Si$ $[M+H]^+$: 341.251, found 341.259.

Ethyl 2-(4-((triisopropylsilyl)oxy)ethyl)cycloprop-2-ene-1-carboxylate (**SI-11**)



34% yield (528 mg, 1.69 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ**) δ 6.40 (dd, J = 2.7, 1.3 Hz, 1H), 4.19 – 4.02 (m, 2H), 3.90 (t, J = 6.8 Hz, 2H), 2.90 – 2.61 (m, 2H), 2.19 – 2.11 (m, 1H), 1.28 – 1.21 (m, 3H), 1.13 – 0.98 (m, 21H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 176.6, 113.2, 95.6, 60.7, 60.3, 29.1, 19.6, 18.1, 14.5, 12.1 ppm. **HRMS** (APCI): m/z calculated for $C_{17}H_{33}O_3Si$ $[M+H]^+$: 313.219, found 313.219.

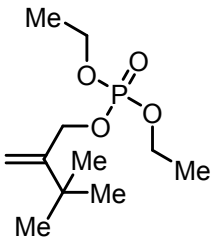
Ethyl (E)-2-(4,8-dimethylnona-3,7-dien-1-yl)cycloprop-2-ene-1-carboxylate (**SI-12**)



35% yield (577 mg, 2.21 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ**) 6.33 (d, J = 1.4 Hz, 1H), 5.14 (t, J = 7.1 Hz, 1H), 5.08 (t, J = 6.8 Hz, 1H), 4.18 – 4.05 (m, 2H), 2.57 – 2.48 (m, 2H), 2.28 (q, J = 7.3 Hz, 2H), 2.13 (d, J = 1.5 Hz, 1H), 2.10 – 2.02 (m, 2H), 2.02 – 1.93 (m, 2H), 1.67 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 176.7, 136.6, 131.6, 124.3, 122.9, 115.5, 94.4, 60.3, 39.8, 26.7, 25.8, 25.4, 25.4, 19.9, 17.8, 16.2, 14.5 ppm. **HRMS** (APCI): m/z calculated for for $C_{17}H_{27}O_2$ $[M+H]^+$: 263.201, found 263.200.

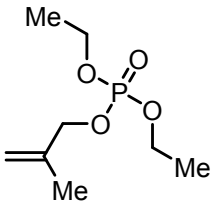
9.3. Representative procedure for the synthesis of allyl phosphates following representative procedure[11]

3,3-Dimethyl-2-methylenebutyl diethyl phosphate (**SI-13**)



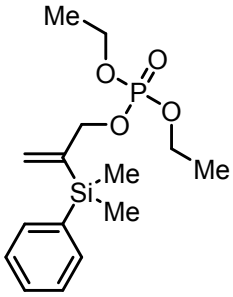
34% yield (1.7 g, 6.79 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.14 (s, 1H), 5.06 (s, 1H), 4.57 (d, J = 6.2 Hz, 2H), 4.17 – 4.05 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H), 1.10 (s, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 151.96 (d, J = 7.2 Hz), 110.15 (s), 67.32 (d, J = 5.4 Hz), 63.88 (d, J = 5.9 Hz), 34.93 (s), 29.45 (s), 16.27 (d, J = 6.7 Hz) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -0.91 ppm. **HRMS** (APCI): m/z calculated for $C_{11}H_{24}O_4P$ $[M+H]^+$: 251.141, found 251.139.

Diethyl (2-methylallyl) phosphate (**SI-14**)



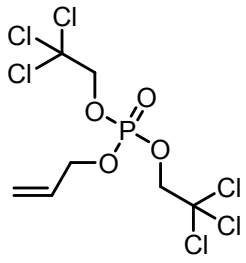
70% yield (2.91 g, 14.0 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.04 (s, 1H), 4.93 (s, 1H), 4.42 (d, J = 7.0 Hz, 2H), 4.21 – 4.02 (m, 4H), 1.78 (d, J = 8.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 140.3 (d, J = 7.3 Hz), 113.3 (s), 70.85 (d, J = 5.6 Hz), 63.9 (d, J = 5.8 Hz), 19.1 (s), 16.3 (d, J = 6.7 Hz) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -0.88. **HRMS** (APCI): m/z calculated for $C_8H_{18}O_4P$ $[M+H]^+$: 209.094, found 209.095.

2-(Dimethyl(phenyl)silyl)allyl diethyl phosphate (**SI-15**)[12]



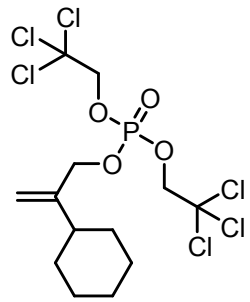
Propargyl alcohol (577 µL, 10.0 mmol, 1.0 equiv.) was dissolved in freshly distilled CH_2Cl_2 (20 mL) and the mixture stirred in a flame-dried flask under an argon atmosphere on an ice bath. $[Cp^*Ru(MeCN)^3)]PF_6$ (50.4 mg, 0.1 mmo, 1 mol%) was added followed by dropwise addition of dimethylphenylsilane (1.69 mL, 11.0 mmol, 1.1 equiv.). The cooling bath was removed and stirring continued until completion was judged by TLC (hexanes/ethyl acetate, 10:1). Then distilled Et_3N (2.79 mL, 20.0 mmol, 2.0 equiv.), a few crystals of DMAP and diethyl chlorophosphate (1.88 mL, 13.0 mmol, 1.3 equiv.) were added and stirring continued for 18 h. The reaction was quenched with the addition of saturated ammonium chloride solution, the mixture extracted two times with CH_2Cl_2, the combined extracts were washed with water, dried over sodium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 20:1) yielded the product as a colorless oil.**67% yield** (2.20 g, 6.7 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.56 – 7.47 (m, 2H), 7.40 – 7.30 (m, 3H), 5.98 (dd, J = 4.1, 2.0 Hz, 1H), 5.56 – 5.48 (m, 1H), 4.60 (dt, J = 5.8, 1.5 Hz, 2H), 4.09 – 3.98 (m, 4H), 1.38 – 1.20 (m, 6H), 0.48 – 0.34 (m, J = 3.3 Hz, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 145.0 (d, J = 7.4 Hz), 137.0 (s), 134.0 (s), 133.8 (s), 128.0 (s), 126.9 (s), 70.4 (d, J = 5.8 Hz), 63.8 (d, J = 5.8 Hz), 16.2 (d, J = 6.8 Hz), -3.0 (s) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -1.09. **HRMS** (APCI): m/z calculated for $C_{15}H_{26}O_4PSi$ $[M+H]^+$: 329.134, found 329.135.

Allyl bis(2,2,2-trichloroethyl) phosphate (**SI-16**)



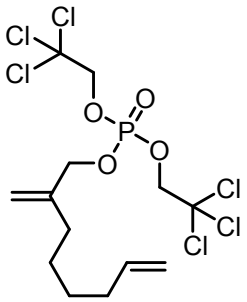
74% yield (2.98 g, 7.43 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.99 (ddd, J = 22.6, 10.9, 5.8 Hz, 1H), 5.43 (dd, J = 17.1, 1.2 Hz, 1H), 5.34 (dd, J = 10.4, 0.9 Hz, 1H), 4.77 – 4.67 (m, 2H), 4.67 – 4.54 (m, 4H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 131.6 (d, J = 6.7 Hz), 119.8 (s), 94.7 (d, J = 11.3 Hz), 77.3 (d, J = 4.3 Hz), 69.8 (d, J = 5.9 Hz) ppm. **HRMS** (APCI): m/z calculated for $C_7H_{10}Cl_6O_4P$ $[M+H]^+$: 398.845, found 398.844.

2-Cyclohexylallyl bis(2,2,2-trichloroethyl) phosphate (**SI-17**)



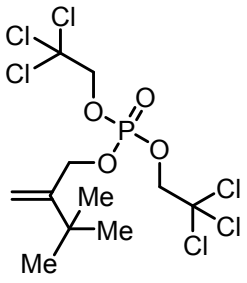
75% yield (723 mg, 1.50 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.12 (d, J = 11.0 Hz, 1H), 5.01 (d, J = 14.9 Hz, 1H), 4.68 (d, J = 7.5 Hz, 2H), 4.63 (d, J = 6.6 Hz, 4H), 2.02 (dd, J = 18.2, 6.6 Hz, 1H), 1.79 (t, J = 12.4 Hz, 4H), 1.69 (dd, J = 12.3 Hz, 1H), 1.37 – 1.05 (m, 5H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 148.5 (d, J = 6.8 Hz), 112.6 (s), 94.8 (d, J = 11.4 Hz), 77.3 (d, J = 4.3 Hz), 71.1 (d, J = 6.1 Hz), 40.8 (s), 32.2 (s), 26.7 (s), 26.3 (s) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -4.3 ppm. **HRMS** (APCI): m/z calculated for $C_{13}H_{20}Cl_6O_4P$ $[M+H]^+$: 480.923, found 480.929.

2-Methyleneoct-7-en-1-yl bis(2,2,2-trichloroethyl) phosphate (**SI-18**)



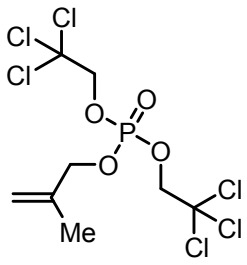
73% yield (703 mg, 1.46 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.89 – 5.71 (m, 1H), 5.14 (s, 1H), 5.02 (s, 2H), 4.95 (dd, J = 10.2, 1.0 Hz, 1H), 4.70 – 4.57 (m, 6H), 2.11 (dd, J = 13.6, 5.8 Hz, 2H), 2.04 (dd, J = 17.1, 10.2 Hz, 2H), 1.56 – 1.34 (m, 4H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 143.2 (d, J = 6.9 Hz), 138.8 (s), 114.8 (s), 114.2 (s), 94.8 (d, J = 11.4 Hz), 77.3 (d, J = 4.3 Hz), 71.7 (d, J = 6.1 Hz), 33.7 (s), 32.5 (s), 28.6 (s), 26.9 (s) ppm**. ^{31}P NMR (162 MHz, $CDCl_3$) δ** -4.2 ppm. **HRMS** (APCI): m/z calculated for $C_{13}H_{20}Cl_6O_4P$ $[M+H]^+$: 480.923, found 480.928.

3,3-Dimethyl-2-methylenebutyl bis(2,2,2-trichloroethyl) phosphate (**SI-19**)



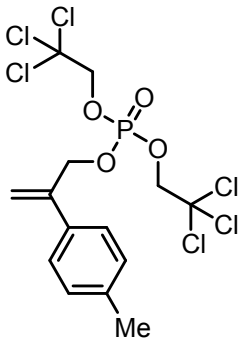
74% yield (673 mg, 1.47 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.19 (s, 1H), 5.15 (s, J = 6.4 Hz, 1H), 4.77 (dd, J = 7.0, 0.8 Hz, 2H), 4.63 (d, J = 6.5 Hz, 4H), 1.12 (s, J = 4.7 Hz, 9H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 151.0 (d, J = 6.8 Hz), 112.1 (s), 94.8 (d, J = 11.4 Hz), 77.3 (d, J = 4.3 Hz), 69.4 (d, J = 6.0 Hz), 35.0 (s), 29.5 (s) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -4.4 ppm. **HRMS** (APCI): m/z calculated for $C_{11}H_{18}Cl_6O_4P$ $[M+H]^+$: 454.907, found 454.905.

2-Methylallyl bis(2,2,2-trichloroethyl) phosphate (**SI-20**)



85% yield (932 mg, 2.25 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.10 (s, 1H), 5.02 (s, 1H), 4.63 (d, J = 6.5 Hz, 4H), 4.61 (d, J = 7.8 Hz, 2H), 1.81 (s, 3H) ppm**.** **^{13}C NMR (101 MHz, $CDCl_3$) δ** 139.3 (d, J = 6.8 Hz), 115.0 (s), 94.8 (d, J = 11.3 Hz), 77.3 (d, J = 4.3 Hz), 72.7 (d, J = 6.0 Hz), 19.1 (s) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ** -4.2 ppm. **HRMS** (APCI): m/z calculated for $C_8H_{12}Cl_6O_4P$ $[M+H]^+$: 412.860, found 412.864.

2-(p-Tolyl)allyl bis(2,2,2-trichloroethyl) phosphate (**SI-21**)



58% yield (750 mg, 1.53 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.35 (m, 2H), 7.18 (m, 2H), 5.58 (s, J = 60.2 Hz, 1H), 5.43 (s, 1H), 5.09 (d, J = 8.0 Hz, 2H), 4.56 – 4.44 (m, 4H), 2.35 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 142.2 (d, J = 6.8 Hz), 138.3 (s), 134.3 (s), 129.5 (s), 126.2 (s), 116.1 (s), 94.7 (d, J = 11.4 Hz), 77.2 (s), 70.7 (d, J = 6.0 Hz), 21.3 (s) ppm. **HRMS** (APCI): m/z calculated for $C_{32}H_{39}Cl_{12}O_{12}P_2$ $[2M+2AcOH]^+/2$: 551.500, found 551.497.

10. References

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