Supporting Information

Functionalized Cyclobutanes Via Heck Cyclization

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Part I

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General

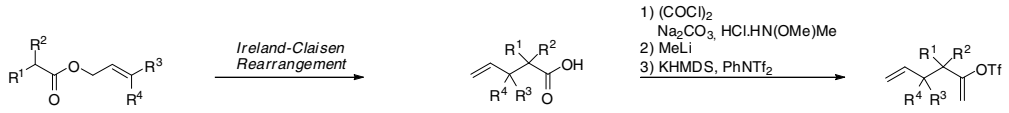
All reactions were carried out in flame-dried glassware under argon atmosphere. Solvents were purified by distillation over the agents indicated: DCM (P_4O_{10}), Et_2O (Na), THF (Na), DMF (P_4O_{10}), MeOH (Mg). NEt_3, diisopropylamine and TMSCl were distilled over CaH_2 prior to use. All commercially available compounds (Aldrich, FLUKA, Acros) were used without further purification.
Monitoring of the reactions was carried out by thin layer chromatography (TLC) with E. Merck silica gel 60-F^{254} plates. Flash column chromatography was performed with Merck silica gel (0.04-0.63 µm, 240-400 mesh). NMR spectra were recorded either on a Bruker Avance DRX 400 or on a DRX 600 spectrometer.
Unless otherwise stated, all NMR spectra were measured in $CDCl_3$ solution and are referenced to the residual $CHCl_3$ signal (1H, δ = 7.26; 13C, δ = 77.16). All ^1H and ^{13}C shifts are given in ppm (s = singlet; d = doublet; t = triplet; q = quadruplet; hept = heptet; m = multiplet; br s = broad signal). Coupling constants *J* are given in Hz. Proton and carbon assignment was confirmed, when possible, by correlated spectroscopy (COSY, HSQC, HMBC). Stereochemical assignment was confirmed by NOESY experiments. IR spectra were recorded as thin films on a silicon disc on a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra were measured either on a Micromass, trio 200 Fisions Instrument or a Kratos Profile HV-4 Instrument. High resolution mass spectra (HRMS) were performed with a Finnigan MAT 8230 with a resolution of 10000. Melting points (mp) were determined on a *Leica* Galen III apparatus and are uncorrected.

Starting Materials

(*E*)-Pent-2-en-1-ol,[1] (*E*)-4-methyl-pent-2-en-1-ol,[1] (*E*)-3-methoxy-prop-3-en-1-ol,[2] isobutyric acid but-2-enyl ester (**17a**),[3] propionic acid 3-methyl-but-2-enyl ester (**17e**)[4] were prepared according to literature procedures. The yields and the analytical data were in accordance with the literature references.

[1] Mulzer, J.; Lammer, O. *Chem. Ber.* **1986**, *119*, 2178.
[2] Glorius, F.; Neuhurger, M.; Pfaltz, A. *Helv. Chim. Acta* **2001**, *84*, 3178.
[3] Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
[4] Yadav, J. S.; Reddy, G. S.; Srinivas, D.; Himabindu, K.; *Synth. Commun.* **1998**, *28*, 2337.

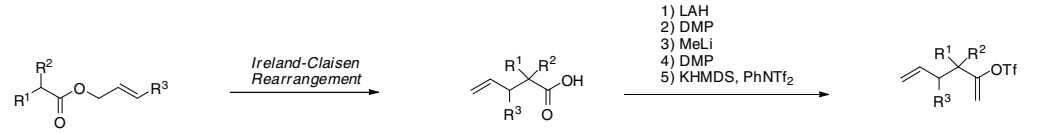
Strategies for Preparation of Enol Triflates (1a – 1i)



17a R^1, R^2, R^3 = Me, R^4 = H
17b R^1, R^2 = Me, R^3 = Et, R^4 = H
17c R^1,R^2 = Me, R^3 = *i*-Pr, R^4 = H
17d R^1 = OBn, R^2 = H, R^3, R^4 = Me
17e R^1, R^3, R^4 = Me, R^2 = H
17f R^1, R^3 = Me, R^2 = OPMB, R^4 = H
17g R^1, R^2 = Me, R^3= OMe, R^4 = H

18a R^1, R^2, R^3 = Me, R^4 = H
18b R^1, R^2 = Me, R^3 = Et, R^4 = H
18c R^1,R^2 = Me, R^3 = *i*-Pr, R^4 = H
18d R^1 = OBn, R^2 = H, R^3, R^4 = Me
18e R^1, R^3, R^4 = Me, R^2 = H
18f R^1, R^3 = Me, R^2 = OPMB, R^4 = H
18g R^1, R^2 = Me, R^3= OMe, R^4 = H

1a R^1, R^2, R^3 = Me, R^4 = H
1b R^1, R^2 = Me, R^3 = Et, R^4 = H
1c R^1,R^2 = Me, R^3 = *i*-Pr, R^4 = H
1d R^1 = OBn, R^2 = H, R^3, R^4 = Me
1e R^1, R^3, R^4 = Me, R^2 = H
1f R^1, R^3 = Me, R^2 = OPMB, R^4 = H
1g R^1, R^2 = Me, R^3= OMe, R^4 = H



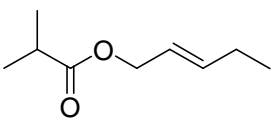
17h R^1, R^2= Ph, R^3 = Me
17i R^1, R^2 = Ph R^3 = *i*-Pr

18h R^1, R^2 = Ph, R^3 = Me
18i R^1, R^2 = Ph, R^3 = *i*-Pr

1h R^1, R^2 = Ph, R^3 = Me
1i R^1, R^2 = Ph, R^3 = *i*-Pr

General Procedure for Esters obtained from Acid Chlorides

To a solution of acid chloride (1.0 eq.) in DCM (0.7 M) was added pyridine (1.1 eq.) at 0 °C. After 10 min, allylic alcohol (1.0 eq.) was added slowly. The resulting suspension was stirred at room temperature until completion (TLC). 1 N HCl was added, the layers were separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed successively with sat. $NaHCO_3$ solution and brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo.* Purification was carried out either by column chromatography (pentane/Et_2O) to yield the products in analytically pure forms.



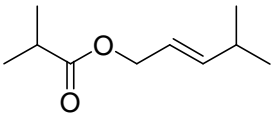
Isobutyric acid (*E*)-pent-2-enyl ester (17b)

(1.5 g, 94%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (m, 1H), 5.55 (m, 1H), 4.51 (dd, 2H, *J* = 6.4, 1.1 Hz,), 2.55 (hept, 1H, *J* = 7.0 Hz), 2.07 (m, 2H), 1.17 (d, 6H, *J* = 7.0 Hz), 1.00 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.1, 137.8, 123.2, 65.1, 34.2, 25.3, 19.2 (2C), 13.3.

IR ν_{max} = 2930, 2860, 1735, 1474, 1381, 1153 cm^{-1}.



Isobutyric acid (*E*)-4-methyl-pent-2-enyl ester (17c)

(3.2 g, 94%, colorless oil)

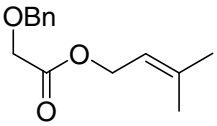
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73 (m, 1H), 5.51 (m, 1H), 4.51 (m, 2H), 2.56 (hept, 1H, *J* = 7.0 Hz), 2.31 (m, 1H), 1.17 (d, 6H, *J* = 7.0 Hz), 1.01 (d, 6H, *J* = 6.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.1, 143.0, 121.3, 65.2, 34.2, 30.1, 22.2 (2C), 19.1 (2C).

MS (EI, 70 eV, 30 °C): *m/z*: 170, 82, 71, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{10}H_{18}O_2$: 170.1304, found: 170.1307.

IR ν_{max} = 2925, 2854, 1740, 1459, 1377, 1155 cm^{-1}.



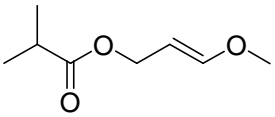
2-Benzyloxy-acetic acid 3-methyl-but-2-enyl ester (17d)

(2.3 g, 98%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (m, 5H), 5.35 (m, 1H), 4.67 (d, 2H, *J* = 7.3 Hz), 4.63 (s, 2H), 4.09 (s, 2H), 1.76 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5, 140.1, 137.6, 128.6 (2C), 128.2 (2C), 128.1, 118.4, 73.8, 67.7, 62.0, 25.8 (2C).

IR ν_{max} = 2975, 2854, 1731, 1497, 1453, 1380, 1202, 1121, 747, 700 cm^{-1}.



Isobutyric acid (*E*)-3-methoxy-allyl ester (17g)

(1.6 g, 85 %, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (d, 1H, *J* = 12.6 Hz), 4.92 (dt, 1H, *J* = 12.6, 7.7 Hz), 4.48 (dd, 2H, *J* = 7.7, 0.7 Hz), 3.56 (s, 3H), 2.54 (hept, 1H, *J* = 7.0 Hz), 1.15 (d, 6H, *J* = 7.0 Hz).

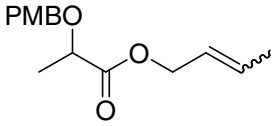
^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.3, 153.2, 97.3, 62.5, 56.2, 34.2, 19.1, 18.9.

MS (EI, 70 eV, 30 °C): *m/z*: 158, 87, 71, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_8H_{14}O_3$: 158.0943, found: 158.0943.

General Procedure for Esters obtained from Carboxylic Acids

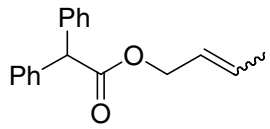
To a solution of carboxylic acid (1.3 eq), allylic alcohol (1.0 eq) and DMAP (cat.) in DCM (0.3 M) was added DIC (1.2 eq.) at 0 °C. The resulting suspension was stirred for 2 h at 0 °C and then at room temperature until completion (TLC). After filtration and removal of DCM *in vacuo*, the residue was taken up in Et_2O and filtered again. Concentration of the solvent *in vacuo* and column chromatography yielded the products in analytically pure forms.



2-(4-Methoxy-benzyloxy)-propionic acid but-2-enyl ester (17f)
(1.9 g, quant., colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, 2H, *J* = 8.9 Hz), 6.86 (d, 2H, *J* = 8.4 Hz), 5.80 (m, 1H), 5.59 (m, 1H), 4.60 (d, 1H, *J* = 11.2 Hz), 4.56 (d, 2H, *J* = 6.5 Hz), 4.37 (d, 1H, *J* = 11.2 Hz), 4.02 (q, 1H, *J* = 6.8 Hz), 3.79 (s, 3H), 1.72 (m, 3H), 1.40 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.3, 159.5, 131.9, 129.9, 129.8 (2C), 124.9, 114.0 (2C), 73.9, 71.8, 65.6, 55.4, 18.8, 17.9.



Diphenyl-acetic acid but-2-enyl ester (17h)

(2.7 g, quant., colorless oil)

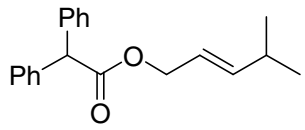
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (m, 10H), 6.03 (m, 1H), 5.86 (m, 1H), 5.31 (s, 1H), 4.87 (dd, 2H, *J* = 6.5, 1.1 Hz), 1.98 (dd, 3H, *J* = 6.4, 1.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ =172.4, 138.9 (2C), 131.8, 128.7 (6C), 127.7 (4C), 124.9, 66.0, 57.2, 17.8.

MS (EI, 70 eV, 30 °C): *m/z*: 266, 167, 152, 55.

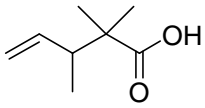
HRMS (70 eV, 30 °C): *m/z* calcd for $C_{18}H_{18}O_2$: 266.1307, found: 266.1312.

IR ν_{max} = 3029, 2942, 1732, 1600, 1495, 1453, 1376, 1148, 700, 637 cm^{-1}.



Diphenyl-acetic acid (*E*)- 4-methyl-pent-2-enyl ester (17i)
(1.6 g, 90%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (m, 10H), 5.70 (dd, 1H, *J* = 15.4, 6.4 Hz), 5.50 (m, 1H), 5.04 (s, 1H), 4.60 (d, 2H, *J* = 6.4 Hz), 2.29 (m, 1H), 0.98 (d, 6H, *J* = 6.8 Hz).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 143.7, 138.9 (2C), 131.8, 128.8 (4C), 128.7 (3C), 127.4 (2C), 120.8 , 66.1, 57.2, 30.9, 22.1 (2C).
MS (EI, 70 eV, 50 °C): *m/z*: 294, 226, 167, 152.
HRMS (70 eV, 30 °C): *m/z* calcd for $C_{20}H_{22}O_2$: 294.1620, found: 294.1625.
IR ν_{max} = 3062, 3029, 2959, 1737, 1600, 1496, 1453, 1305, 1147, 700, 638 cm^{-1}.



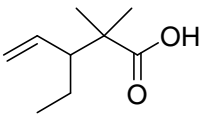
2,2,3-Trimethyl-pent-4-enoic acid (18a)

To a stirred solution of isobutyric acid but-2-enyl ester (5.7 g, 40 mmol) in Et_2O (400 mL) was added KHMDS (0.5 M in toluene, 50 mmol, 100 mL) at -78 °C. After being stirred for 5 min at -78 °C, the reaction mixture was allowed to reach room temperature. 1 N HCl was added at 0 °C, the layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by Kugelrohr distillation (50 mbar, 120 °C) to yield 5.2 g (93%) pure acid as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.50 (br s, 1H), 5.73 (m, 1H), 5.06 (m, 2H), 2.52 (m, 1H), 1.15 (s, 3H), 1.13 (s, 3H), 1.01 (d, 3H, *J* = 6.9 Hz).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.4, 139.6, 116.2, 45.6, 45.3, 23.1, 20.9, 15.4.
MS (EI, 70 eV, 30 °C): *m/z*: 142, 127, 88, 73, 59, 55.
HRMS (70 eV, 30 °C): *m/z* calcd for $C_8H_{14}O_2$: 142.0994, found: 142.0998.
IR ν_{max} = 2961, 2919, 1702, 1462, 1378 cm^{-1}.

General Procedure for Ireland-Claisen Rearrangement using LDA/TMSCl

To a solution of diisopropylamine (2.06 eq.) in THF (0.5 M) was added *n*-BuLi (2 eq., 2.5 M in hexanes) at -78 °C and stirring was continued for 30 min at 0 °C. The solution was added to allylic ester (1 eq.) in THF (0.1 M) at -78 °C. After stirring for 1 h, trimethylchlorosilane (2.1 eq.) was added and the resulting mixture was kept at -78

°C for an additional hour. The reaction mixture was allowed to warm to room temperature and further stirred until completion (TLC). The reaction was quenched at 0 °C using 1 M HCl solution and stirring was continued for 30 min. After dilution with Et_2O, the layers were separated and the organic layer was washed successively with 1 M HCl solution and brine. The solvent was removed *in vacuo* and the residue dissolved in hexanes. 2 N NaOH solution was added and the mixture stirred for 30 min at 0 °C. After separation of the layers, the organic layer was washed two times with 2 N NaOH solution. The combined aqueous layers were acidified with 1 N HCl solution at 0 °C and extracted four times with DCM. After drying over Mg_2SO_4, filtration and removal of the solvent *in vacuo* the carboxylic acids were obtained in analytically pure forms.



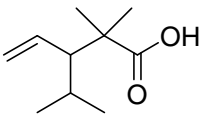
3-Ethyl-2,2-dimethyl- pent-4-enoic acid (18b)

(630 mg, 65%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.51 (ddd, 1H, *J* = 16.9, 10.0, 7.0 Hz), 5.06 (dd, 1H, *J* = 10.0, 2.3, Hz), 5.01 (dd, 1H, *J* = 16.9, 2.3 Hz), 2.13 (m, 1H), 1.21 (m, 2H), 1.14 (s, 3H), 1.12 (s, 3H), 0.84 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.8, 137.7, 118.4, 53.8, 45.7, 24.1, 22.6, 20.8, 12.7.

IR ν_{max} = 2965, 2921, 1710, 1465, 1379 cm^{-1}.



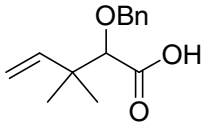
3-Isopropyl-2,2-dimethyl-pent-4-enoic acid (18c)

(250 mg, 70%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65 (ddd, 1H, J = 16.9, 10.2, 6.6 Hz), 5.14 (dd, 1H, *J* = 10.1, 2.4 Hz), 5.03 (dd, 1H, *J* = 16.9, 2.4 Hz), 2.18 (m, 1H, CH), 1.78 (m, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 0.89 (d, 3H, *J* = 6.8 Hz), 0.85 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.7, 135.5, 118.8, 57.4, 45.3, 28.7, 26.1, 23.3, 21.0, 19.7.

IR ν_{max} = 2967, 2925, 1699, 1460, 1375 cm^{-1}.



2-Benzyloxy-3,3-dimethyl-pent-4-enoic acid (18d)

(730 mg, 73%, colorless oil)

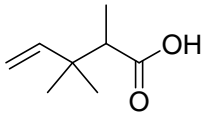
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 5H), 5.94 (dd, 1H, *J* = 17.6, 10.5 Hz), 5.05 (m, 2H), 4.68 (d, 1H, *J* = 11.6 Hz), 4.42 (d, 1H, *J* = 11.6 Hz), 3.70 (s, 1H), 1.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.3, 143.7, 137.0, 128.6 (2C), 128.2 (3C), 113.2, 85.5, 73.4, 40.7, 23.5, 23.4.

MS (ESI): *m/z*: 257, 211, 189, 102, 91.

HRMS (ESI): *m/z* calcd for $C_{14}H_{18}O_3Na$: 257.1154, found: 257.1148.

IR ν_{max} = 2970, 1717, 1455, 1239, 1114, 738, 699 cm^{-1}.



2,3,3-Trimethyl-pent-4-enoic acid (18e)

(400 mg, 40%, colorless oil)

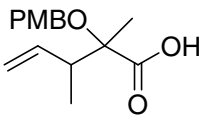
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (dd, 1H, *J* = 17.3, 10.8 Hz), 5.00 (m, 2H), 2.39 (q, 1H, *J* = 7.1 Hz), 1.12 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.2, 145.9, 112.5, 48.9, 38.6, 25.2, 23.8, 12.9.

MS (EI, 70 eV, 30 °C): *m/z*: 142, 127, 97, 85, 69, 57.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_8H_{14}O_2$: 142.0994, found: 142.0997.

IR ν_{max} = 2971, 1704, 1462, 1417, 1378, 1287 cm^{-1}.



2-(4-Methoxy-benzyloxy)-2,3-dimethyl-pent-4-enoic acid (18f)

(250 mg, 63%, colorless oil, d.r. = 3:1)

major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 2H), 6.89 (m, 2H), 5.81 (m, 1H), 5.13 (m, 2H), 4.48 (m, 2H), 3.81 (s, 3H), 2.66 (m, 1H), 1.52 (s, 3H), 1.12 (d, 3H, *J* = 6.9 Hz).

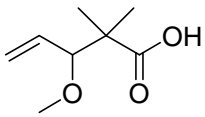
^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.0, 159.5, 138.3, 130.1, 129.4 (2C), 117.2, 114.1 (2C), 83.0, 66.7, 55.5, 46.0, 18.7, 15.0.

minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 2H), 6.89 (m, 2H), 5.96 (m, 1H), 5.07 (m, 2H), 4.48 (m, 2H), 3.80 (s, 3H), 2.66 (m, 1H), 1.51 (s, 3H), 1.10 (d, 3H, *J* = 6.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.0, 159.5, 138.3, 130.1, 129.4 (2C), 116.5, 114.1 (2C), 83.0, 66.2, 55.5, 45.6, 18.7, 15.0.

IR ν_{max} = 2935, 1718, 1611, 1459, 1382, 1172 cm^{-1}.



3-Methoxy-2,2-dimethyl-pent-4-enoic acid (18g)

(350 mg, 70%, colorless oil)

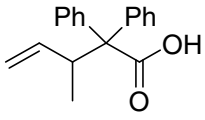
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.67 (ddd, 1H, *J* = 17.2, 10.4, 8.2 Hz), 5.38 (dd, 1H, *J* = 17.2, 1.7 Hz), 5.31 (dd, 1H, *J* = 10.4, 1.7 Hz), 3.69 (d, 1H, *J* = 8.2 Hz), 3.31 (s, 3H), 1.18 (s, 3H), 1.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 133.5, 121.2, 87.8, 57.1, 46.5, 22.9, 19.7.

MS (EI, 70 eV, 30 °C): *m/z*: 158, 99, 82, 71, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_8H_{14}O_3$: 158.0943, found: 158.0943.

IR ν_{max} = 2938, 2824, 1704, 1450, 1388, 1182 cm^{-1}.



3-Methyl-2,2-diphenyl-pent-4-enoic acid (18h)

(1.4 g, 94 %, white solid)
Mp = 155 °C

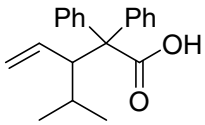
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (m, 10H), 5.63 (ddd, 1H, *J* = 17.4, 10.1, 7.2 Hz), 5.02 (m, 2H), 3.88 (m, 1H), 0.91 (d, 3H, *J* = 7.7 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.6, 139.7, 139.4 (2C), 130.9 (2C), 130.5 (2C), 127.6 (2C), 127.3 (2C), 127.2 (2C), 116.6, 64.8, 40.3, 16.6.

MS (EI, 70 eV, 30 °C): *m/z*: 266, 221, 211, 194, 183, 165, 152, 133, 115, 105, 91, 77.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{18}H_{18}O_2$: 266.1307, found: 266.1306.

IR ν_{max} = 3025, 2940, 1699, 1600, 1497, 1370, 1260, 709 cm^{-1}.



3-Isopropyl-2,2-diphenyl-pent-4-enoic acid (18i)

(760 mg, 76 %, white solid)
Mp = 162 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (m, 10H), 5.57 (ddd, 1H, *J* = 17.0, 10.1, 6.8 Hz), 5.21 (dd, 1H, *J* = 17.0, 2.2 Hz), 5.16 (dd, 1H, *J* = 10.1, 2.2 Hz), 3.49 (m, 1H), 1.96 (m, 1H), 1.01 (d, 3H, *J* = 6.7 Hz), -0.16 (d, 3H, *J* = 6.7 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.8, 140.7, 140.4, 134.5, 131.2 (2C), 130.3 (2C), 127.9 (2C), 127.4 (2C), 127.3 (2C), 119.6, 64.9, 52.0, 28.6, 23.8, 17.4.

MS (EI, 70 eV, 100 °C): *m/z*: 294, 212, 194, 165, 128, 105, 91, 77.

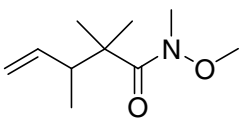
HRMS (70 eV, 100 °C): *m/z* calcd for $C_{20}H_{22}O_2$: 294.1620, found: 294.1628.

IR ν_{max} = 2959, 1700, 1699, 1498, 1444, 1386, 1261, 715 cm^{-1}.

General procedure for Weinreb Amides obtained from Carboxylic Acids

To a solution of carboxylic acid (1.0 eq.) in DCM (0.5 M) was added oxalyl chloride (2 eq.) and DMF (cat.) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C and for one additional hour at room temperature. After evaporation of the solvent, the crude acid chloride was dissolved in Et_2O (0.5 M). This was added to an ice cooled suspension of *N,O*-dimethylhydroxylamine hydrochloride (2.0 eq.), anhydrous Na_2CO_3 (4.0 eq.) and pyridine (cat.) in Et_2O (0.5 M). The resulting reaction mixture was stirred overnight at room temperature.

After addition of water, the organic layer was separated, dried over Mg_2SO_4 and concentrated *in vacuo* to afford the products as coloured oils. Purification was carried out by column chromatography (pentanes/Et_2O).



2,2,3-Trimethyl-pent-4-enoic acid methoxy-methyl-amide (19a)
(6.0 g, 93%, yellow oil)

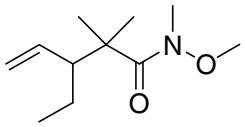
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.72 (m, 1H), 5.01 (m, 2H), 3.67 (s, 3H), 3.16 (s, 3H), 2.86 (m, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 0.93 (d, 3H, *J* = 6.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.2, 140.5, 115.9, 60.9, 46.9, 42.9, 34.5, 22.9, 21.6, 15.3.

MS (EI, 70 eV, 30 °C): *m/z*: 185, 125, 97, 83, 69, 61.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{10}H_{19}NO_2$: 185.1416, found: 185.1413.

IR ν_{max} = 2972, 1654, 1474, 1389 cm^{-1}.



3-Ethyl-2,2,-dimethyl-pent-4-enoic acid methoxy-methyl-amide (19b)
(310 mg, 95%, yellow oil)

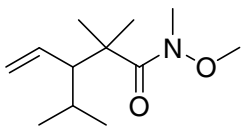
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 (m, 1H), 5.09 (dd, 1H, *J* = 10.2, 2.3 Hz), 5.01 (dd, 1H, *J* = 16.9, 2.3 Hz), 3.67 (s, 3H), 3.16 (s, 3H), 2.49 (m, 1H), 1.28 (m, 2H), 1.16 (s, 3H), 1.15 (s, 3H), 0.82 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.2, 138.9, 118.2, 60.6, 51.5, 46.9, 34.1, 23.2, 22.3, 21.8, 12.7.

MS (EI, 70 eV, 30 °C): *m/z*: 199, 139, 111, 69, 57.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{11}H_{21}NO_2$: 199.1572, found: 199.1575.

IR ν_{max} = 2960, 1664, 1469, 1382 cm^{-1}.



3-Isopropyl-2,2-dimethyl-pent-4-enoic acid methoxy-methyl-amide (19c)
(640 mg, 85%, yellow oil)

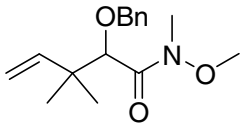
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (m, 1H), 5.09 (dd, 1H, *J* = 10.1, 2.5 Hz), 4.97 (dd, 1H, *J* = 16.9, 2.5 Hz), 3.67 (s, 3H), 3.15 (s, 3H), 2.51 (dd, 1H, *J* = 10.3, 3.8 Hz), 1.71 (m, 1H), 1.22 (s, 3H), 1.16 (s, 3H), 0.85 (d, 3H, *J* = 3.9 Hz), 0.84 (d, 3H, *J* = 4.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.5, 136.4, 117.8, 60.5, 55.1, 46.6, 34.2, 28.4, 25.1, 23.6, 22.5, 20.0.

MS (EI, 70 eV, 30 °C): *m/z*: 213, 153, 125, 83, 69, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{12}H_{23}NO_2$: 213.1729, found: 213.1726

IR ν_{max} = 2955, 1658, 1463, 1380 cm^{-1}.



2-Benzyloxy-3,3-dimethyl-pent-4-enoic acid methoxy-methyl-amide (19d)
(448 mg, 76%, colorless oil)

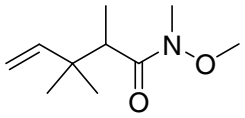
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 5H), 6.03 (dd, 1H, *J* = 17.3, 10.9 Hz), 5.01 (m, 2H), 4.67 (d, 1H, *J* = 12.3 Hz), 4.36 (d, 1H, *J* = 12.3 Hz), 4.22 (bs, 1H), 3.48 (s, 3H), 3.17 (s, 3H), 1.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.5, 144.7, 137.0, 128.4 (2C), 127.7 (3C), 112.1, 79.9, 71.9, 60.9, 41.6, 32.3, 24.1, 23.9.

MS (ESI): *m/z*: 300, 278, 260, 232, 189, 171.

HRMS (ESI): *m/z* calcd for $C_{16}H_{23}O_3NNa$: 300.1576, found: 300.1568.

IR ν_{max} = 2965, 1635, 1453, 1117, 730, 698 cm^{-1}.



2,3,3-Trimethyl-pent-4-enoic acid methoxy-methyl-amide (19e)
(400 mg, 91%, colorless oil)

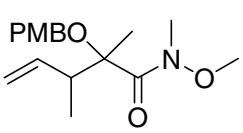
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.94 (dd, 1H, *J* = 17.3, 10.9 Hz), 4.95 (m, 2H), 3.66 (s, 3H), 3.16 (s, 3H), 2.88 (bs, 1H), 1.08 (s, 3H), 1.06 (s, 3H), 1.05 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.0, 146.7, 111.5, 61.4, 42.3, 39.4, 32.1, 24.9, 24.0, 13.4.

MS (EI, 70 eV, 30 °C): *m/z*: 185, 125, 97, 83, 69, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{10}H_{19}O_2N$: 185.1416, found: 185.1411.

IR ν_{max} = 2967, 1650, 1473, 1387 cm^{-1}.



2-(4-Methoxy-benzyloxy)-2,3-dimethyl-pent-4-enoic acid methoxy-methyl-amide (19f)
(200 mg, 93%, colorless oil)

major diastereomer:

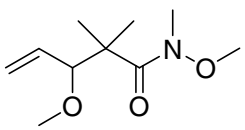
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (m, 2H), 6.87 (m, 2H), 5.72 (m, 1H), 5.07 (m, 2H), 4.41 (m, 2H), 3.80 (s, 3H), 3.64 (s, 3H), 3.33 (s, 3H), 2.98 (m, 1H), 1.43 (s, 3H), 1.11 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 159.1, 139.2, 130.9, 128.8 (2C), 116.2, 113.9 (2C), 84.1, 66.0, 60.5, 55.4, 44.1, 33.6, 16.9, 14.4.

minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (m, 2H), 6.87 (m, 2H), 6.04 (m, 1H), 5.07 (m, 2H), 4.41 (m, 2H), 3.81 (s, 3H), 3.66 (s, 3H), 3.33 (s, 3H), 2.98 (m, 1H), 1.41 (s, 3H), 0.99 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 159.1, 139.2, 130.9, 128.8 (2C), 116.2, 113.9 (2C), 84.1, 65.9, 60.5, 55.4, 44.1, 33.6, 16.9, 14.1.



3-Methoxy-2,2-dimethyl-pent-4-enoic acid methyl methoxy amide (19g)
(1.1 g, 95%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.69 (ddd, 1H, *J* = 17.2, 10.4, 7.7 Hz), 5.26 (m, 2H), 4.08 (d, 1H, *J* = 7.7 Hz), 3.69 (s, 3H), 3.26 (s, 3H), 3.17 (s, 3H), 1.24 (s, 3H), 1.14 (s, 3H).

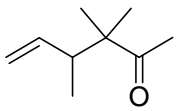
^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.5, 133.1, 119.3, 86.2, 60.7, 56.9, 47.8, 34.3, 20.9, 19.3.

MS (EI, 70 eV, 30 °C): *m/z*: 201, 141, 113, 100, 81, 71.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{10}H_{19}O_3N$: 201.1365, found: 201.1368.

General Procedure for Methyl Ketones obtained from Weinreb Amides

1.6 M MeLi (1.8 eq.) was added to Weinreb amide (1 eq.) in Et_2O (0.05 M) at 0 °C. The reaction mixture was stirred until completion (TLC). Sat. NH_4Cl solution was added, the layers were separated, and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo*. After purification by column chromatography the product was obtained as colorless oil.



3,3,4-Trimethyl-hex-5-en-2-one (20a)

(2.0 g, 88%, colorless liquid)

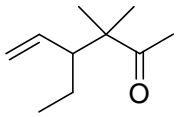
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (m, 1H), 5.02 (m, 2H), 2.49 (m, 1H), 2.11 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H), 0.91 (d, 3H, *J* = 6.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.8, 139.7, 115.5, 50.8, 44.3, 25.6, 22.3, 20.1, 15.2.

MS (EI, 70 eV, 30 °C): *m/z*: 140, 122, 107, 97, 86, 71.

HRMS (70 eV, 30 °C): *m/z* calcd. for $C_9H_{16}O$: 140.1201, found: 140.1221

IR ν_{max} = 2927, 2849, 1712, 1456, 1380 cm^{-1}.



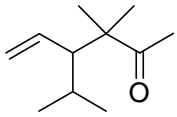
4-Ethyl-3,3-dimethyl-hex-5-en-2-one (20b)

(207 mg, 95%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.47 (m, 1H), 5.12 (dd, 1H, *J* = 10.2, 2.1 Hz), 5.03 (dd, 1H, *J* = 16.8, 2.1 Hz), 2.12 (m, 4H), 1.21 (m, 2H), 1.04 (s, 3H), 1.03 (s, 3H), 0.83 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.0, 137.8, 118.1, 53.3, 51.1, 25.7, 23.1, 22.5, 20.0, 12.7.

IR ν_{max} = 2933, 2857, 1718, 1464, 1385 cm^{-1}.



4-Isopropyl-3,3-dimethyl-hex-5-en-2-one (20c)

(460 mg, 88%, colorless oil)

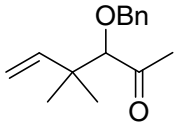
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.61 (ddd, 1H, *J* = 16.9, 10.2, 6.7 Hz), 5.13 (dd, 1H, *J* = 10.2, 2.4 Hz), 5.02 (dd, 1H, *J* = 16.9, 2.4 Hz), 2.19 (dd, 1H, *J* = 10.2, 6.7 Hz), 2.13 (s, 3H), 1.65 (m, 1H), 1.12 (s, 3H), 1.01 (s, 3H), 0.85 (d, 3H, *J* = 6.9 Hz), 0.83 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.2, 135.4, 118.9, 56.3, 51.3, 28.6, 25.7, 24.9, 23.7, 20.3, 19.8.

MS (EI, 70 eV, 30 °C): *m/z*: 168, 149, 125, 97, 83, 71.

No HRMS determined due to fast fragmentation *in vacuo*.

IR ν_{max} = 2923, 2851, 1710, 1459, 1382 cm^{-1}.



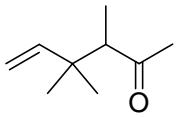
3-Benzyloxy-4,4-dimethyl-hex-5-en-2-one (20d)

(270 mg, 72%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 5H), 6.00 (dd, 1H, *J* = 17.5, 10.8 Hz), 5.01 (m, 2H), 4.55 (d, 1H, *J* = 11.7 Hz), 4.39 (d, 1H, *J* = 11.7 Hz), 3.47 (s, 1H), 2.12 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.7, 143.9, 137.6, 128.6 (2C), 128.0 (3C), 112.7, 92.7, 73.4, 40.6, 27.9, 24.5, 23.4.

HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_2Na$: 255.1361, found: 255.1353.



3,4,4-Trimethyl-hex-5-en-2-one (20e)

(400 mg, 91%, colorless oil)

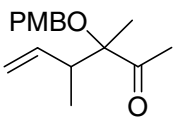
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (dd, 1H, *J* = 17.4, 10.8 Hz), 4.97 (m, 2H), 2.53 (q, 1H, *J* = 7.1 Hz), 2.13 (s, 3H), 1.05 (s, 3H), 1.04 (s, 3H), 1.02 (d, 3H, *J* = 7.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.9, 146.2, 112.1, 39.1, 32.1, 24.7 (2C), 24.5, 12.5.

MS (EI, 70 eV, 30 °C): *m/z*: 140, 125, 97, 69, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_9H_{16}O$: 140.1201, found: 140.1197.

IR ν_{max} = 2925, 2847, 1714, 1458, 1379 cm^{-1}.



3-(4-Methoxy-benzyloxy)-3,4-dimethyl-hex-5-en-2-one (20f)

(105 mg, 67%, colorless oil)

major diastereomer:

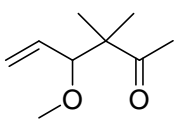
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (m, 2H), 6.89 (m, 2H), 5.66 (m, 1H), 5.05 (m, 2H), 4.31 (m, 2H), 3.81 (s, 3H), 2.64 (m, 1H), 2.21 (s, 3H), 1.29 (s, 3H), 1.09 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.8, 159.3, 138.6, 130.8, 128.8 (2C), 116.4, 114.0 (2C), 86.6, 66.2, 55.5, 44.9, 25.5, 15.2, 14.4.

minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (m, 2H), 6.89 (m, 2H), 5.99 (m, 1H), 5.05 (m, 2H), 4.31 (m, 2H), 3.81 (s, 3H), 2.64 (m, 1H), 2.22 (s, 3H), 1.28 (s, 3H), 0.95 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.8, 159.3, 139.0, 130.9, 128.7 (2C), 115.6, 114.0 (2C), 86.6, 66.0, 55.5, 43.9, 25.5, 15.7, 14.2.



4-Methoxy-3,3-dimethyl-hex-5-en-2-one (20g)

(235 mg, 82%, colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.63 (m, 1H), 5.34 (dd, 1H, *J* = 10.4, 1.6 Hz), 5.26 (dd, 1H, *J* = 17.2, 1.6 Hz), 4.71 (d, 1H, *J* = 8.0 Hz), 3.22 (s, 3H), 2.16 (s, 3H), 1.12 (s, 3H), 1.01 (s, 3H).

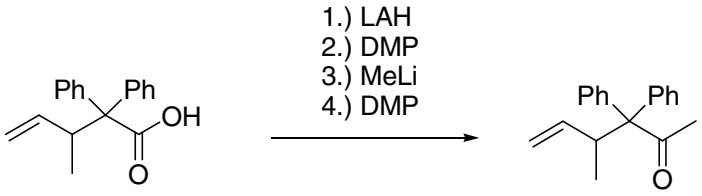
^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.0, 134.2, 120.2, 88.0, 56.9, 51.5, 26.5, 22.3, 18.8.

MS (EI, 70 eV, 30 °C): *m/z*: 156, 82, 71, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_9H_{16}O_2$: 156.1150, found: 156.1153.

IR ν_{max} = 2927, 2857, 1730, 1465, 1379, 1124 cm^{-1}.

4-Methyl-3,3-diphenyl-hex-5-en-2-one (20h)



To $LiAlH_4$ (1 M in THF, 6 mmol, 2.5 eq.) in THF (6 mL) was added a solution of 3-methyl -2,2-diphenyl-pent-4-enoic acid (0.65 g, 2.4 mmol, 1 eq.) in THF (18 mL) at 0 °C. The reaction mixture was stirred at room temperature for 15 h (TLC). The resulting suspension was diluted with Et_2O and treated with sat. K,Na-tartrate solution and stirred for additional 24 h. After separation of the layers, the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield 0.49 g (80%) 3-methyl-2,2-diphenyl-pent-4-en-1-ol as colorless oil.

3-Methyl-2,2-diphenyl-pent-4-en-1-ol (0.30 g, 1.19 mmol, 1 eq.) in DCM (9 mL) was added to a solution of Dess-Martin periodinane (0.61 g, 1.43 mmol, 1.2 eq.) in DCM (6 mL) at 0 °C. The reaction was allowed to warm to room temperature for 3.5 h (TLC), after which a white precipitate had formed. Et_2O was added and the mixture was cooled to 0 °C. After addition of sodium thiosulfate (2.4 g) and sat. $NaHCO_3$ solution (10 mL), the mixture was allowed to reach room temperature and was stirred for additional 20 min, after which the precipitate had dissolved. The layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with sat. $NaHCO_3$ solution and brine, dried over Mg_2SO4, filtered and concentrated *in vacuo* to yield 3-methyl-2,2-diphenyl-pent-4-enal (298 mg, quant.) as colorless oil which was used immediately without purification.

To a solution of 3-methyl-2,2-diphenyl-pent-4-enal (298 mg, 1.19 mmol, 1 eq.) in Et_2O (20 mL) was added MeLi (1.6 M in Et_2O, 1.55 mmol, 1.3 eq.) at 0 °C. After being stirred for 30 min (TLC), the reaction was quenched with sat. NH_4Cl solution.

The layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield 4-methyl-3,3-diphenyl-hex-5-en-2-ol (317 mg, quant.) as colorless oil which was used immediately without further purification.

4-Methyl-3,3-diphenyl-hex-5-en-2-ol (308 mg, 1.16 mmol, 1 eq.) in DCM (9 mL) was added to a solution of Dess-Martin periodinane (590 mg, 1.39 mmol, 1.2 eq.) in DCM (6 mL) at 0 °C. The reaction was allowed to warm to room temperature for 4 h (TLC), after which a white precipitate had formed. Et_2O was added and the mixture was cooled to 0 °C. After addition of sodium thiosulfate (2.3 g) and sat. $NaHCO_3$ solution (10 mL), the mixture was allowed to reach room temperature and was stirred for additional 15 min, after which the precipitate had dissolved. The layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with sat. $NaHCO_3$ solution and brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (pentanes/Et_2O) to yield 4-methyl-3,3-diphenyl-hex-5-en-2-one (**21h**) (299 mg, 97%) as white solid.

Mp = 108 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 10H), 5.61 (m, 1H), 4.95 (m, 2H), 3.87 (m, 1H), 1.97 (s, 3H), 0.81 (d, 3H, J = 6.8 Hz).

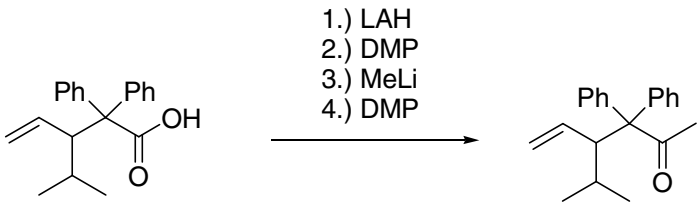
^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.0, 140.3, 139.0, 138.5, 130.9 (2C), 130.7 (2C), 128.4 (2C), 127.9 (2C), 127.3 (2C), 116.0, 71.0, 39.8, 27.3, 16.5.

MS (EI, 70 eV, 40 °C): *m/z*: 264, 221, 209, 192, 181, 165.

HRMS (70 eV, 40 °C): *m/z* calcd for $C_{19}H_{20}O$: 264.1514, found: 264.1522.

IR ν_{max} = 2935, 1709, 1602, 1425, 1381, 730, 699 cm^{-1}.

4-Isopropyl-3,3-diphenyl-hex-5-en-2-one (20i)



(470 mg, 70% (4 steps), white solid)

Mp = 112 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 10H), 5.64 (m, 1H), 5.18 (m, 2H), 3.48 (d, 1H, *J* = 10.5 Hz), 1.96 (s, 3H), 1.92 (m, 1H), 1.07 (d, 3H, *J* = 6.7 Hz), -0.25 (d, 3H, *J* = 6.7 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 206.7, 139.7, 139.6, 134.9, 131.5 (2C), 130.5 (2C), 128.4 (2C), 127.7 (2C), 127.4, 126.9, 119.0, 70.9, 51.8, 28.6, 27.1, 23.8, 16.5.

MS (EI, 70 eV, 60 °C): *m/z*: 292, 249, 210, 193, 167, 129, 81, 77, 64.

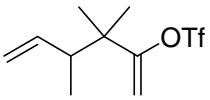
HRMS (70 eV, 60 °C): *m/z* calcd for $C_{21}H_{24}O$: 292.1827, found: 292.1819.

IR ν_{max} = 2929, 1705, 1600, 1420, 1385, 726, 702 cm^{-1}.

General Procedure for Enol Triflates Obtained from Methyl Ketones

To a solution of 0.5 M KHMDS (1.3 eq.) in THF (0.5 M) was added methylketone (1 eq.) in THF (0.5 M) at -78 °C. After being stirred for 45 min at 0 °C, the solution was cooled to -78 °C and *N*-phenyl(bistrifluorosulfonimide) (1.3 eq.) in THF (1 M) was added. The reaction mixture was allowed to warm to room temperature over night. The solvent was removed *in vacuo* and the residue purified by column chromatography (pentanes/Et_2O, 5% NEt_3) to afford the product as colorless oil.

Enoltriflates **1c**, **1g**, **1h** and **1i** were directly used as crude products due to their instability when subjected to column chromatography.



Trifluoro-methanesulfonic acid 2,2,3-trimethyl-1-methylene-pent-4-enyl ester (1a)
(2.2 g, 75%) colorless oil

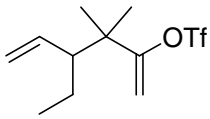
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.70 (m, 1H), 5.15 (d, 1H, *J* = 4.4 Hz), 5.05 (m, 2H), 4.93 (d, 1H, *J* = 4.4 Hz), 2.33 (m, 1H), 1.10 (s, 3H), 1.08 (s, 3H), 0.97 (d, 3H, *J* = 6.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.9, 139.1, 118.6, 116.2, 101.3, 43.3, 42.6, 23.8, 21.7, 14.8.

MS (EI, 70 eV, 30 °C): *m/z*: 272, 257, 218, 122, 107, 97, 81, 67.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{10}H_{15}O_3SF_3$: 272.0694, found: 272.0700.

IR ν_{max} = 3081, 2981, 2886, 1653, 1461, 1338, 1102 cm^{-1}.



Trifluoro-methanesulfonic acid 3-ethyl-2,2-dimethyl-1-methylene-pent-4-enyl ester (1b)
(191 mg, 65%, colorless oil)

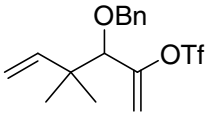
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46 (m, 1H), 5.15 (m, 2H), 5.04 (dd, 1H, *J* = 16.7, 2.3 Hz), 4.92 (d, 1H, *J* = 4.5 Hz), 1.92 (m, 1H), 1.51 (m, 2H), 1.09 (s, 3H), 1.08 (s, 3H), 0.83 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.2, 137.3, 118.7, 118.2, 101.4, 52.3, 42.7, 24.5, 21.9, 21.6, 12.7.

MS (EI, 70 eV, 30 °C): *m/z*: 286, 218, 136, 84, 69.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{11}H_{17}O_3SF_3$: 286.0851, found: 286.0855.

IR ν_{max} = 3085, 2975, 2885, 1650, 1457, 1335, 1105 cm^{-1}.



Trifluoro-methanesulfonic acid 2-benzyloxy-3,3-dimethyl-1-methylene-pent-4-enyl ester (1d)
(290 mg, 81%, colorless oil)

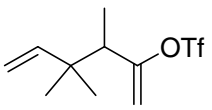
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 5H), 5.88 (dd, 1H, *J* = 17.3, 10.9 Hz), 5.39 (d, 1H, J = 3.4 Hz), 5.25 (d, 1H, *J* = 3.4 Hz), 5.01 (m, 2H), 4.72 (d, 1H, *J* = 11.7 Hz), 4.36 (d, 1H, *J* = 11.7 Hz), 3.61(s, 1H), 1.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.4, 143.5, 137.6, 128.5 (2C), 128.1 (2C), 127.9, 118.5, 113.1, 107.5, 85.4, 71.9, 41.3, 23.2 (2C).

MS (EI, 70 eV, 30 °C): *m/z*: 364, 273, 196, 160, 107, 91, 69.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{16}H_{19}O_4SF_3$: 364.0956, found: 364.0951.

IR ν_{max} = 3079, 2878, 1637, 1455, 1333, 1112, 729, 702 cm^{-1}.



Trifluoro-methanesulfonic acid 2,3,3-trimethyl-1-methylene-pent-4-enyl ester (1e)
(400 mg, 91%, colorless oil)

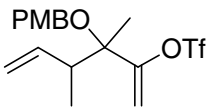
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78 (dd, 1H, *J* = 17.4, 10.8 Hz), 5.18 (d, 1H, *J* = 3.8 Hz), 5.00 (m, 2H), 4.89 (d, 1H, *J* = 3.8 Hz), 2.29 (q, 1H, *J* = 7.2 Hz), 1.10 (d, 3H, *J* = 7.2 Hz), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.1, 145.2, 118.6, 112.7, 104.8, 48.4, 39.3, 25.6, 23.8, 14.2.

MS (EI, 70 eV, 30 °C): *m/z*: 272, 229, 160, 139, 123, 107, 91, 81, 69, 53.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{10}H_{15}O_3SF_3$: 272.0694, found: 272.0699.

IR ν_{max} = 3080, 2979, 2884, 1650, 1464, 1336, 1105 cm^{-1}.



Trifluoro-methanesulfonic acid 2-(4-methoxy-benzyloxy)-2,3-dimethyl-1-methylene-pent-4-enyl ester (1f)
(150 mg, 95%, colorless oil)

major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (m, 2H), 6.88 (m, 2H), 5.74 (m, 1H), 5.39 (m, 1H), 5.23 (m, 1H), 5.09 (m, 2H), 4.38 (s, 2H), 3.80 (s, 3H), 2.59 (m, 1H), 1.34 (s, 3H), 1.09 (d, 3H, *J* = 6.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.3, 156.3, 138.4, 130.7, 128.8 (2C), 121.1, 116.7, 113.9 (2C), 104.9, 80.2, 64.9, 55.4, 45.9, 16.9, 14.1.

MS (EI, 70 eV, 30 °C): *m/z*: 394, 261, 219, 164, 136, 121.

HRMS (70 eV, 30°C): *m/z* calcd for $C_{17}H_{21}O_5SF_3$: 394.1062, found: 394.1079.

IR ν_{max} = 3075, 2942, 1610, 1461, 1372, 1170, 1029 cm^{-1}.

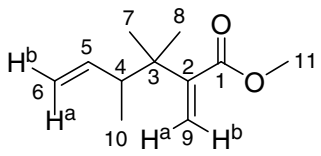
minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (m, 2H), 6.88 (m, 2H), 5.97 (m, 1H), 5.39 (m, 1H), 5.23 (m, 1H), 5.09 (m, 2H), 4.38 (s, 2H), 3.81 (s, 3H), 2.59 (m, 1H), 1.33 (s, 3H), 1.03 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.3, 156.3, 138.8, 130.7, 128.8 (2C), 121.1, 116.7, 113.9 (2C), 104.9, 80.2, 64.8, 55.4, 45.2, 16.9, 13.8.

General Procedure for Pd(0) Catalyzed Tandem Cyclization Carbonylation Reaction

To a solution of enol triflate (1 eq.) in MeOH/DMF (2:1, 0.06 M) is added NEt_3 (3.2 eq.) and $Pd(PPh_3)_4$ (0.1 eq.). The resulting mixture was stirred under CO atmosphere at 50 °C until completion (TLC). 1 N HCl and Et_2O were added, the layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed successively with sat. $NaHCO_3$, H_2O and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (pentanes/Et_2O) of the residue afforded the product as colorless oil.



3,3,4-Trimethyl-2-methylene-hex-5-enoic acid methyl ester (9a)
(3%, colorless oil)

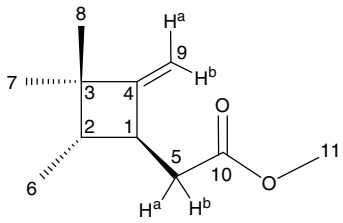
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.99 (d, 1H, *J* = 0.7 Hz, H-9b), 5.92 (m, 1H, H-5), 5.48 (d, 1H, *J* = 0.7 Hz, H-9a), 4.98 (m, 2H, H-6ab), 3.73 (s, H-11), 2.83 (m, 1H, H-4), 1.11 (s, 3H, H-7), 1.09 (s, 3H, H-8), 0.89 (d, 3H, *J* = 6.8 Hz, H-10).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.5 (C-1), 149.1 (C-2), 141.2 (C-5), 122.9 (C-9), 115.0 (C-6), 51.7 (C-11), 43.2 (C-4), 41.0 (C-3), 24.8 (C-7), 23.2 (C-8), 15.2 (C-10).

MS (EI, 70 eV, 30 °C): *m/z*: 182, 167, 150, 139, 121, 99, 81, 67, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{11}H_{18}O_2$: 182.1307 found: 182.1309.

IR ν_{max} = 3080, 2971, 1721, 1624, 1439, 1372, 1268, 1172 cm^{-1}.



(2,3,3-Trimethyl-4-methylene-cyclobutyl)-acetic acid methyl ester (7a)

d.e. > 98%
(mixture of enantiomers, 65%, colorless oil)

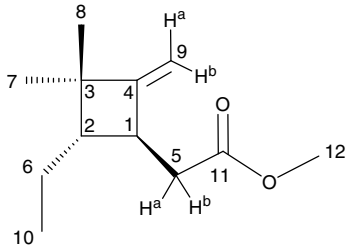
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.70 (d, 1H, *J* = 2.8 Hz, H-9b), 4.63 (d, 1H, *J* = 2.5 Hz, H-9a), 3.65 (s, 3H, H-11), 2.83 (ddddd, 1H, *J* = 8.4, 7.0, 6.4, 2.8, 2.5 Hz, H-1), 2.54 (dd, 1H, *J* = 15.1, 6.4 Hz, H-5a), 2.38 (dd, 1H, *J* = 15.1, 8.1 Hz, H-5b), 1.68 (dq, 1H, *J* = 7.0, 8.4 Hz, H-2), 1.05 (s, 3H, H-8), 1.02 (s, 3H, H-7), 0.98 (d, 3H, *J* = 7.0 Hz, H-6).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2 (C-10), 161.4 (C-4), 100.3 (C-9), 51.5 (C-11), 44.2 (C-3), 44.0 (C-2), 43.9 (C-1), 37.9 (C-5), 27.2 (C-8), 22.0 (C-7), 13.7 (C-6).

MS (EI, 70 eV, 30 °C): *m/z*: 182, 167, 150, 139, 123, 107, 93, 81, 67, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{11}H_{18}O_2$: 182.1307 found: 182.1311.

IR ν_{max} = 2920, 2854, 1648, 1460, 1372 cm^{-1}.



(2-Ethyl-3,3-dimethyl-4-methylene-cyclobutyl)-acetic acid methyl ester (7b)

d.e. > 98%
(mixture of enantiomers, 60%, colorless oil)

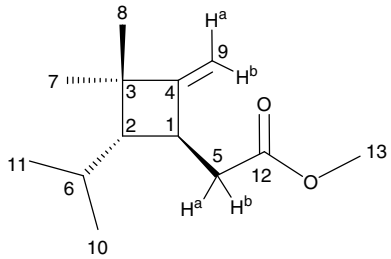
^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.69 (d, 1H, *J* = 2.7 Hz, H-9b), 4.63 (d, *J* = 2.7 Hz, 1H, H-9a), 3.65 (s, 3H, H-12), 2.87 (m, 1H, H-1), 2.52 (dd, 1H, *J* = 15.1, 7.1 Hz, H-5a), 2.42 (dd, 1H, *J* = 15.1, 7.2 Hz, H-5b), 1.55 (m, 1H, H-2), 1.48 (ddq, 1H, *J* = 13.0, 7.4, 7.0, Hz, H-6a), 1.42 (ddq, 1H, *J* = 13.0, 7.4, 7.0 Hz, H-6b), 1.10 (s, 3H, H-8), 1.06 (s, 3H, H-7), 0.84 (t, 3H, *J* = 7.4 Hz, H-10).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 173.3 (C-11), 161.3 (C-4), 100.3 (C-9), 51.5 (C-12), 51.2 (C-2), 44.2 (C-3), 42.2 (C-1), 38.6 (C-5), 28.2 (C-8), 23.2 (C-6), 21.2 (C-7), 12.9 (C-10)

MS (EI, 70 eV, 30 °C): *m/z*: 196, 181, 121, 107, 93, 81, 67, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{12}H_{20}O_2$: 196.1463, found: 196.1462.

IR ν_{max} = 2923, 2852, 1646, 1463, 1370 cm^{-1}.



(2-Isopropyl -3,3-dimethyl-4-methylene-cyclobutyl)-acetic acid methyl ester (7c)

d.e. > 98%
(mixture of enantiomers, 70%, colorless oil)

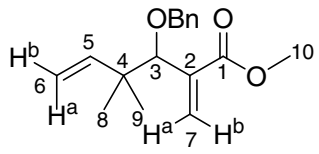
^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.69 (d, 1H, *J* = 2.8 Hz, H-9b), 4.65 (d, *J* = 2.6 Hz, 1H, H-9a), 3.66 (s, 3H, H-13), 2.96 (m, 1H, H-1), 2.54 (dd, 1H, *J* = 15.5, 4.5 Hz, H-5a), 2.44 (dd, 1H, *J* = 15.5, 8.6 Hz, H-5b), 1.75 (dhept, 1H, *J* = 10.6, 6.6 Hz, H-6), 1.28 (dd, 1H, *J* = 10.6, 8.9 Hz, H-2), 1.12 (s, 3H, H-8), 1.09 (s, 3H, H-7), 0.84 (d, 3H, *J* = 6.6 Hz, H-10), 0.82 (d, 3H, *J* = 6.6 Hz, H-11).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 173.2 (C-12), 161.3 (C-4), 100.1 (C-9), 56.6 (C-2), 51.5 (C-13), 44.0 (C-3), 41.3 (C-1), 39.1 (C-5), 29.9 (C-6), 28.3 (C-8), 22.2 (C-7), 22.2 (C-10), 20.7 (C-11).

MS (EI, 70 eV, 30 °C): *m/z*: 210, 195, 163, 154, 135, 123, 107, 95, 83, 67, 55.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{13}H_{22}O_2$: 210.1619, found: 210.1620.

IR ν_{max} = 2926, 2855, 1651, 1467, 1373 cm^{-1}.



3-Benzyloxy-4,4-dimethyl-2-methylene-hex-5-enoic acid methyl ester (9d)

(70%, colorless oil)

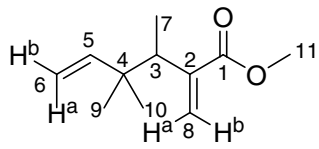
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 5H, Ar), 6.36 (d, 1H, *J* = 1.7 Hz, H-7b), 5.90 (dd, 1H, *J* = 17.5, 10.8 Hz, H-5), 5.82 (br s, 1H, H-7a), 4.95 (dd, 1H, *J* = 10.8, 1.4 Hz, H-6b), 4.92 (dd, 1H, *J* = 17.5, 1.4 Hz, H-6a), 4.48 (d, 1H, *J* = 11.7 Hz, OCH_2), 4.32 (br s, 1H, H-3), 4.29 (d, 1H, *J* = 11.7 Hz, OCH_2), 3.75 (s, 3H, H-10), 1.01 (s, 3H, H-8), 1.00 (s, 3H, H-9).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.1 (C-1), 144.5 (C-5), 139.0 (C-2), 138.7 (C, Ar), 128.3 (2CH, Ar), 127.7 (2CH, Ar), 127.5 (CH, Ar), 126.6 (C-7), 112.4 (C-6), 82.5 (C-3), 71.2 (OCH_2), 52.0 (C-10), 42.1 (C-4), 23.4 (C-8), 22.3 (C-9).

MS (EI, 70 eV, 30 °C): *m/z*: 274, 242, 205, 183, 168, 147, 115, 105, 91, 77, 69.

HRMS (70 eV, 30°C): *m/z* calcd for $C_{17}H_{22}O_3$: 274.1569, found: 274.1573.

IR ν_{max} = 2975, 2854, 1661, 1464, 1375, 1118, 735, 698 cm^{-1}.



3,4,4-Trimethyl-2-methylene-hex-5-enoic acid methyl ester (9e)

(70%, colorless oil)

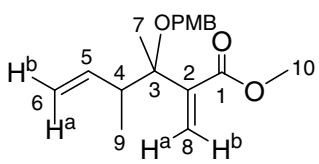
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.23 (s, 1H, H-8b), 5.81 (dd, 1H, *J* = 17.5, 10.9 Hz, H-5), 5.47 (s, 1H, H-8a), 4.93 (dd, 1H, *J* = 10.9, 1.5 Hz, H-6b), 4.88 (dd, 1H, *J* = 17.5, 1.5 Hz, H-6a), 3.73 (s, 3H, H-11), 2.92 (q, 1H, *J* = 7.3 Hz, H-3), 1.03 (d, 3H, *J* = 7.3 Hz, H-7), 0.95 (s, 3H, H-9), 0.94 (s, 3H, H-10).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.2 (C-1), 146.5 (C-5), 144.0 (C-2), 124.8 (C-8), 111.6 (C-6), 52.0 (C-11), 41.5 (C-3), 40.0 (C-4), 24.6 (C-9), 23.8 (C-10), 15.7 (C-7).

MS (EI, 70 eV, 30 °C): *m/z*: 182, 150, 114, 91, 69, 53.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{11}H_{18}O_2$: 182.1307, found: 182.1304.

IR ν_{max} = 3083, 2969, 1723, 1625, 1436, 1415, 1376, 1273, 1170 cm^{-1}.



3-(4-Methoxy-benzyloxy)-3,4-dimethyl-2-methylene-hex-5-enoic acid methyl ester (9f)
(22%, colorless oil)

major diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 (m, 2H, Ar), 6.88 (m, 2H, Ar), 6.17 (d, 1H, *J* = 1.2 Hz, H-8b), 5.85 (ddd, 1H, *J* = 18.7, 10.3, 8.3 Hz, H-5), 5.69 (d, 1H, *J* = 1.2 Hz, H-8a), 5.02 (m, 2H, H-6ab), 4.33 (m, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.74 (s, 3H, H-10), 2.92 (m, 1H, H-4), 1.43 (s, 3H, H-7), 1.04 (d, 3H, *J* = 6.9 Hz, H-9).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.8 (C-1), 158.8 (C, Ar), 143.6 (C-5), 140.4 (C-2), 131.6 (C, Ar), 128.4 (2CH, Ar), 125.4 (C-8), 115.5 (C-6), 113.8 (2CH, Ar), 80.6 (C-3), 64.3 (OCH_2), 55.4 (OCH_3), 51.8 (C-10), 46.0 (C-4), 19.5 (C-7), 14.7 (C-9).

MS (EI, 70 eV, 30 °C): *m/z*: 304, 168, 153, 137, 121.

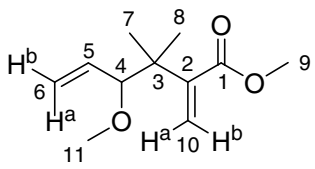
HRMS (70 eV, 30 °C): *m/z* calcd for $C_{18}H_{24}O_4$: 304.1675, found: 304.1668.

IR ν_{max} = 2982, 2875, 1659, 1460, 1368, 1120 cm^{-1}.

minor diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 (m, 2H, Ar), 6.88 (m, 2H, Ar), 6.12 (d, 1H, *J* = 1.1 Hz, H-8b), 6.01 (ddd, 1H, *J* = 18.0, 10.9, 8.3 Hz, H-5), 5.65 (d, 1H, *J* = 1.1 Hz, H-8a), 5.02 (m, 2H, H-6ab), 4.33 (m, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.72 (s, 3H, H-10), 2.92 (m, 1H, H-4), 1.43 (s, 3H, H-7), 1.04 (d, 3H, *J* = 6.9 Hz, H-9).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.9 (C-1), 158.9 (C, Ar), 143.9 (C-5), 140.7 (C-2), 131.7 (C, Ar), 128.4 (2CH, Ar), 125.1 (C-8), 114.4 (C-6), 113.8 (2CH, Ar), 81.3 (C-3), 64.3 (OCH_2), 55.4 (OCH_3), 51.8 (C-10), 45.3 (C-4), 18.9 (C-7), 14.2 (C-9).



4-Methoxy-3,3-dimethyl-2-methylene-hex-5-enoic acid methyl ester (9g)

(22%, colorless oil)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.99 (d, 1H, *J* = 0.5 Hz, H-10b), 5.63 (ddd, 1H, *J* = 18.3, 10.5, 7.8 Hz, H-5), 5.55 (d, 1H, *J* = 0.5 Hz, H-10a), 5.23 (ddd, 1H, *J* = 10.5, 2.0, 1.0 Hz, H-6b), 5.17 (ddd, 1H, *J* = 18.3, 2.0, 1.0 Hz, H-6a), 4.02 (ddd, 1H, *J* = 7.8, 1.0, 1.0 Hz, H-4), 3.72 (s, 3H, H-9), 3.20 (s, 3H, H-11), 1.17 (s, 3H, H-7), 1.10 (s, 3H, H-8).

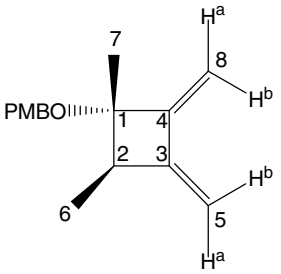
^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.1 (C-1), 146.9 (C-2), 134.9 (C-5), 123.1 (C-10), 118.6 (C-6), 86.4 (C-4), 56.9 (C-11), 51.2 (C-9), 42.1 (C-3), 23.0 (C-7), 22.5 (C-8).

No HRMS determined due to fast fragmentation *in vacuo*.

IR ν_{max} = 2970, 2889, 1754, 1462, 1131 cm^{-1}.

General Procedure for Pd(0) Catalyzed Cyclization Reaction

To a solution of enol triflate (1 eq.) in MeOH/DMF (2:1, 0.06 M) is added NEt_3 (3.2 eq.) and $Pd(PPh_3)_4$ (0.1 eq.). The resulting mixture was stirred at 50 °C until completion (TLC). 1 N HCl and Et_2O were added, the layers were separated and the aqueous phase was extracted three times with Et_2O. The combined organic layers were washed successively with sat. $NaHCO_3$, H_2O and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (pentanes/Et_2O) of the residue afforded the product as colorless oil.



1,2-Dimethyl-3,4-dimethylene-cyclobutoxymethyl)-4-methoxy-benzene (8f)

(mixture of enantiomers, 25%, d.r.: 1:1)

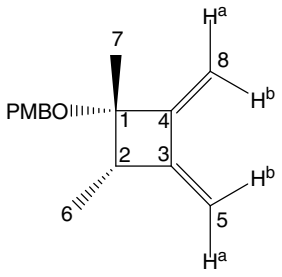
diastereomer I:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (br s, 2H, Ar), 6.81 (br s, 2H, Ar), 5.26 (s, 1H, H-8b), 5.25 (d, 1H, J = 2.4 Hz, H-5a), 4.99 (s, 1H, H-8a), 4.83 (d, 1H, *J* = 2.4 Hz, H-5b), 4.45 (s, 2H, OCH_2), 3.76 (s, 3H, OCH_3), 3.16 (m, 1H, H-2), 1.33 (s, 3H, H-7), 1.11 (d, 3H, *J* = 6.8 Hz, H-6).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.4 (C, Ar), 153.3 (C-4), 149.1 (C-3), 130.4 (C, Ar), 129.0 (2CH, Ar), 113.7 (2CH, Ar), 103.7 (C-8), 103.2 (C-5), 82.1 (C-1), 65.2 (OCH_2), 55.2 (OCH_3), 45.4 (C-2), 19.4 (C-7), 13.2 (C-6).

MS (EI, 70 eV, 30 °C): *m/z*: 244, 229, 215, 135, 121, 110, 91, 77.

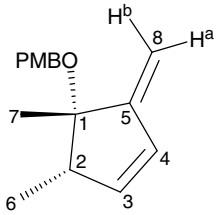
HRMS (70 eV, 30 °C): *m/z* calcd for $C_{16}H_{20}O_2$: 244.1463, found: 244.1448.



diastereomer II:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (br s, 2H, Ar), 6.84 (br s, 2H, Ar), 5.18 (d, 1H, *J* = 2.0 Hz, H-5a), 5.13 (s, 1H, H-8b), 4.98 (s, 1H, H-8a), 4.84 (d, 1H, *J* = 2.0 Hz, H-5b), 4.32 (s, 2H, OCH_2), 3.77 (s, 3H, OCH_3), 2.73 (m, 1H, H-2), 1.40 (s, 3H, H-7), 1.13 (d, 3H, *J* = 6.8 Hz, H-6).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.4 (C, Ar), 155.3 (C-4), 147.7 (C-3), 130.0 (C, Ar), 129.0 (2CH, Ar), 113.7 (2CH, Ar), 106.7 (C-5), 106.3 (C-8), 82.4 (C-1), 65.1 (OCH_2), 55.2 (OCH_3), 51.0 (C-2), 23.7 (C-7), 21.7 (C-6).



1,2-Dimethyl-5-methylene-cyclopent-3-enyloxymethyl)-4-methoxy-benzene (6f)
(mixture of enantiomers, 35%, d.r.: 1:1)

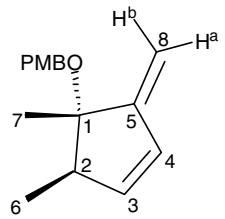
diastereomer I:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (m , 2H, Ar), 6.84 (m, 2H, Ar), 6.14 (m, 1H, H-4), 5.98 (m, 1H, H-3), 5.28 (s, 1H, H-8a), 4.99 (s, 1H, H-8b), 4.50 (d, 1H, *J* = 10.0 Hz, OCH_2), 4.44 (d, 1H, *J* = 10.0 Hz, OCH_2), 3.75 (s, 3H, OCH_3), 2.89 (m, 1H, H-2), 1.42 (s, 3H, H-7), 1.19 (d, 3H, *J* = 6.8 Hz, H-6).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.4 (C, Ar), 156.5 (C-5), 142.1 (C-3), 130.5 (C-4), 130.2 (C, Ar), 129.0 (2CH, Ar), 113.7 (2CH, Ar), 81.6 (C-1), 66.0 (OCH_2), 55.2 (OCH_3), 41.6 (C-2), 23.2 (C-7), 15.1 (C-6).

MS (EI, 70 eV, 30 °C): *m/z*: 244, 226, 211, 196, 179, 165, 149, 134, 123, 121.

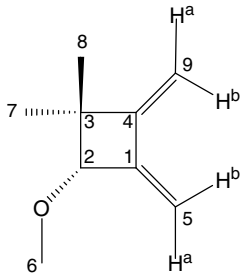
HRMS (70 eV, 30 °C): *m/z* calcd for $C_{16}H_{20}O_2$: 244.1463, found: 244.1453.



diastereomer II:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (m , 2H, Ar), 6.81 (m, 2H, Ar), 6.17 (m, 1H, H-4), 5.94 (m, 1H, H-3), 5.12 (s, 1H, H-8a), 4.94 (s, 1H, H-8b), 4.24 (d, 1H, *J* = 10.7 Hz, OCH_2), 4.18 (d, 1H, *J* = 10.7 Hz, OCH_2), 3.77 (s, 3H, OCH_3), 3.02 (m, 1H, H-2), 1.28 (s, 3H, H-7), 1.05 (d, 3H, *J* = 6.8 Hz, H-6).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.4 (C, Ar), 155.9 (C-5), 142.2 (C-3), 130.9 (C-4), 130.2 (C, Ar), 129.0 (2CH, Ar), 113.7 (2CH, Ar), 84.9 (C-1), 64.4 (OCH_2), 55.2 (OCH_3), 46.0 (C-2), 23.2 (C-7), 14.9 (C-6).



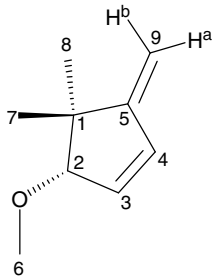
2-Methoxy-1,1-dimethyl-3,4-dimethylene-cyclobutane (8g)

(mixture of enantiomers, 30%, colorless oil)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.28 (d, 1H, *J* = 2.5 Hz, H-5a), 5.14 (s, 1H, H-9a), 4.76 (s, 1H, H-9b), 5.08 (d, 1H, *J* = 2.5 Hz, H-5b), 3.94 (dd, 1H, *J* = 2.5, 2.5 Hz, H-2), 3.41 (s, 3H, H-6), 1.25 (s, 3H, H-7), 1.14 (s, 3H, H-8).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.9 (C-4), 148.9 (C-1), 105.9 (C-5), 101.6 (C-9), 85.6 (C-2), 58.1 (C-6), 47.1 (C-3), 26.1 (C-7), 20.7 (C-8).

No HRMS determined due to fast fragmentation *in vacuo*.



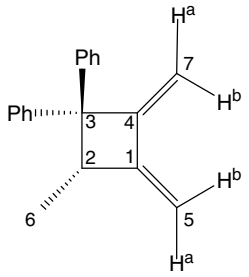
3-Methoxy-4,4-dimethyl-5-methylene-cyclopentene (6g)

(mixture of enantiomers, 30 %, colorless oil)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.26 (d, 1H, *J* = 5.8 Hz, H-2), 6.06 (ddd, 1H, *J* = 5.8, 0.5, 0.5 Hz, H-1), 4.89 (s, 1H, H-9a), 4.70 (s, H-9b), 3.96 (s, H-3), 3.41 (s, 3H, H-6), 1.18 (s, 3H, H-7), 1.09 (s, 3H, H-8).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.1 (C-5), 134.9 (C-1), 133.9 (C-2), 103.3 (C-9), 93.2 (C-3), 58.0 (C-6), 47.1 (C-4), 22.9 (C-8), 22.5 (C-7).

No HRMS determined due to fast fragmentation *in vacuo*.



2-Methyl-1,4-dimethylene-3,3-diphenyl-cyclobutane (8h)

(mixture of enantiomers, 87%, colorless oil)

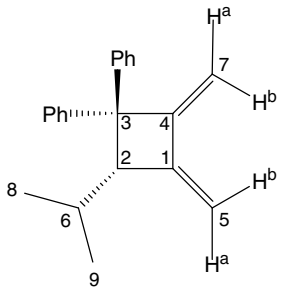
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 (m, 2H, Ar), 7.26 (m, 4H, Ar), 7.22 (m, 2H, Ar), 7.19 (m, 2H, Ar), 5.55 (s, 1H, H-7a), 5.33 (d, 1H, *J* = 2.9 Hz, H-5b), 5.11 (s, 1H, H-7b), 4.84 (d, 1H, *J* = 2.9 Hz, H-5a), 3.92 (ddq, 1H, *J* = 7.1, 2.9, 2.9 Hz, H-2), 0.85 (d, 3H, *J* = 7.1 Hz, H-6).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.5 (C-4), 152.5 (C-1), 147.4 (C, Ar), 143.5 (C, Ar), 129.4 (2CH, Ar), 128.7 (2CH, Ar), 128.0 (4CH, Ar), 126.6 (CH, Ar), 125.6 (CH, Ar), 106.3 (C-7), 103.3 (C-5), 61.8 (C-3), 46.5 (C-2), 16.2 (C-6).

MS (EI, 70 eV, 30 °C): *m/z*: 246, 231, 217, 202, 191, 165, 155, 115, 101, 91, 74.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{19}H_{18}$: 246.1409, found: 246.1413.

IR ν_{max} = 3058, 3028, 2956, 2922, 1600, 1492, 1445, 1386, 765, 699 cm^{-1}.



2-Isopropyl-1,4-dimethylene-3,3-diphenyl-cyclobutane (8i)

(mixture of enantiomers, 75%, colorless oil)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37 (m, 2H, Ar), 7.28 (m, 2H, Ar), 7.26 (m, 1H, Ar), 7.18 (m, 2H, Ar), 7.17 (m, 1H, Ar), 7.11 (m, 2H, Ar), 5.45 (s, 1H, H-7a), 5.33 (d, 1H, *J* = 2.5 Hz, H-5b), 4.97 (s, 1H, H-7b), 4.88 (d, 1H, *J* = 2.5 Hz, H-5a), 3.42 (ddd, 1H, *J* = 9.7, 2.5, 2.5 Hz, H-2), 1.55 (dqq, 1H, *J* = 9.7, 6.7, 6.7 Hz, H-6), 0.85 (d, 3H, *J* = 6.7 Hz, H-8), 0.61 (d, 3H, *J* = 6.7 Hz, H-9).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.1 (C-4), 149.9 (C-1), 146.6 (C, Ar), 144.4 (C, Ar), 129.6 (2CH, Ar), 128.3 (2CH, Ar), 128.1 (2CH, Ar), 127.3 (2CH, Ar), 126.1 (2CH, Ar), 104.9 (C-7), 104.8 (C-5), 61.9 (C-3), 59.6 (C-2), 28.8 (C-6), 22.2 (C-8), 20.6 (C-9).

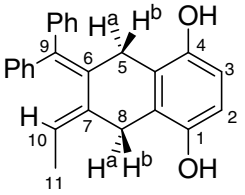
MS (EI, 70 eV, 30 °C): *m/z*: 274, 259, 231, 217, 202, 180, 165, 152, 115, 103, 91, 77.

HRMS (70 eV, 30 °C): *m/z* calcd for $C_{21}H_{22}$: 274.1722, found: 274.1727.

IR ν_{max} = 3062, 3032, 2965, 2925, 1600, 1493, 1449, 745, 702 cm^{-1}.

Procedure for Diels Alder Reaction

2-Methyl-1,4-dimethylene-3,3-diphenyl-cyclobutane (1 eq.) was dissolved in benzene (0.03 M), BHT (cat.) and benzoquinone (2 eq.) were added and the resulting reaction mixture was stirred at 110 °C until completion (TLC). After concentration of the solvent *in vacuo,* the residue was purified by column chromatography to yield the product in analytically pure form.



6-Benzhydrylidene-7-eth-(*E*)-ylidene-5,6,7,8-tetrahydro-naphthalene-1,4-diol (16)
(60%, orange solid)
Mp = 135 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (m, 10H, Ar), 6.72 (d, 1H, *J* = 10.4 Hz, H-3), 6.66 (d, 1H, *J* = 10.4 Hz, H-2), 5.26 (q, 1H, *J* = 7.0 Hz, H-10), 3.38 (m, 4H, H-5ab, H-8ab), 1.45 (d, 3H, *J* = 7.0 Hz, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.3, 186.8, 143.7, 142.1, 141.6, 140.7, 139.6, 136.6, 136.3, 133.6, 132.2, 130.1, 129.9, 128.3 (2C), 127.8 (2C), 127.6 (2C), 127.2 (2C), 126.4, 30.8, 27.5, 13.9.

MS (EI, 70 eV, 30 °C): *m/z*: 352, 337, 309, 289, 275, 252, 218, 165.

HRMS (70 eV, 30°C): *m/z* calcd for $C_{25}H_{22}O_2$ - 2H: 352.1463, found: 352.1452.

IR ν_{max} = 3600, 3074, 3029, 2959, 1605, 1475, 845 cm^{-1}.