Gold- and Brønsted Acid-Catalyzed Hydride Shift onto Allenes: Divergence in Product Selectivity

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General Information

All non-aqueous reactions, besides the catalysis, were performed under a positive pressure of N_2 using standard syringe-cannula/septa techniques. Commercially available reagents were used as received without further purification. Distilled solvents were dried over Na/benzophenone (THF) or CaH_2 (CH_2Cl_2) under N_2 gas. For chromatographic purification, technical-grade solvents were used. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using *Merck Silica Gel 60 F254* plates and visualized by fluorescence quenching at 254 nm. In addition, TLC plates were stained using anisaldehyde solution (338 mL ethanol, 9.2 mL anisaldehyde, 3.8 mL acetic acid, 12.5 mL *conc.* H_2SO_4). Chromatographic purification of products was performed on *silica gel 60, 230–400 mesh* using a forced flow of eluent at 0.1–0.5 bar pressure. Concentration under reduced pressure was performed by rotary evaporation at RT using a water jet pump. Purified compounds were further dried on high vacuum. NMR-spectra were measured in the given solvent at RT on *Bruker Avance 400* (400.2 MHz, ^1H; 100.6 MHz, ^{13}C) instrument operating at the denoted spectrometer frequency given in mega Hertz (MHz) for the specified nucleus. Chemical shifts δ are given in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ^1H- and ^{13}C-NMR spectra and calibrated against the solvent residual peak. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or as combination of them. Coupling constants *J* are given in Hertz (Hz). Infrared spectra were recorded on a *Perkin-Elmer 1600 Fourier Transform Spectrophotometer* as solution in CCl_4 and are reported as absorption maxima in cm^{-1}. Melting points were measured with a *Reichert microscope apparatus* in open capillaries and are uncorrected. Mass spectra were obtained on a *Hewlett-Packard HP 5989B* spectrometer *via* direct injection. Ionization was obtained by chemical ionization with ammonia (CI, NH_3). High-resolution mass spectrometry with electrospray ionization (ESI-MS) was performed on a *JEOL GCmate II* spectrometer. Fragment signals are given in mass per charge number (*m/z*).

Synthesis of allene substrates

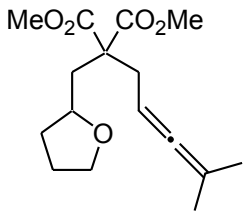
General procedure* A *for the preparation of allenyl malonates :

To a solution of monoalkylated malonate (1 eq.) in THF (0.25 M) was added portionwise NaH (1.2eq) at 0°C. Once, the H_2 evolution has ceased, the mesylated allenylmethanol (1.2 eq.) and tetrabutylammonium iodide (0.1 eq.) were added. The reaction was then stirred at room temperature for 2 hours, under nitrogen. The reaction mixture was quenched with saturated aqueous NH_4Cl, extracted with Et_2O (2x), dried over $MgSO_4$, concentrated under reduced pressure and the residue was subjected to purification to afford the corresponding allenyl malonate.

General procedure* B *for the preparation of other allenes :

To a solution of benzyl propargyl ether (1 eq.) in chloroform (0.2M) was added XphosAu(NCMe)SbF_6 (0.04 eq.) at room temperature. The solution was then refluxed under nitrogen gas. Upon completion of the reaction, triethylamine (0.1 eq.) was added. The solvent was removed under reduced pressure and the residue was subjected to purification to afford the corresponding allene.

***2-((tetrahydrofuran-2-yl)methyl)-2-(4-methylpenta-2,3-dienyl)-malonic acid dimethyl ester* (9)**



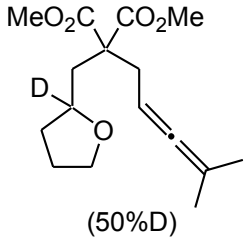
Following procedure A starting with dimethyl 2-((tetrahydrofuran-2-yl)methyl)malonate (1.54 mmol, 1 eq.) and 4-methylpenta-2,3-dienyl methanesulfonate (1.2 eq.).
Flash chromatography (SiO_2 PE/ AcOEt: 9/1).
Yield: 254 mg (56%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.78-4.72 (m, 1H), 3.95 (ddt, *J* = 6.7 Hz, *J* = 6.7 Hz, *J* = 6.2 Hz, 1H), 3.75-3.63 (m, 2H), 3.70 (s, 6H), 2.74 (dd, *J* = 14.4 Hz, *J* = 6.9 Hz, 1H), 2.64 (dd, *J* = 14.4 Hz, *J* = 8.4 Hz, 1H), 2.18 (dd, *J* = 14.5 Hz, *J* = 1.8 Hz, 1H), 2.15 (d, *J* = 9.0 Hz, 1H), 2.02-1.93 (m, 1H), 1.92-1.75 (m, 2H), 1.63 (t, *J* = 3.1 Hz, 6H), 1.54-1.45 (m, 1H).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.7, 171.8, 171.7, 95.0, 82.9, 74.7, 67.6, 56.4, 52.4, 52.3, 37.9, 32.7, 32.2, 25.5, 20.5, 20.4.
IR (CCl_4): ν (cm^{-1}) 2978, 2871, 1970, 1736, 1435, 1282, 1199, 1088.

MS (EI): m/z 296(M^+), 271, 253, 239.

MS (HRMS EI): m/z 296.1617 (Calcd. for $C_{16}H_{24}O_5$: 296.1624).

***2-((S)-(2-deutero)-tetrahydro-furan-2-ylmethyl)-2-(4-methyl-penta-2,3-dienyl)-malonic acid dimethyl ester* (9D)**



Following procedure **A** starting with dimethyl 2-((2-deutero-tetrahydrofuran-2-yl)methyl)malonate (0.26 mmol, 1 eq.) and 4-methylpenta-2,3-dienyl methanesulfonate (1.2 eq.).

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 72.6 mg (94%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.78-4.72 (m, 1H), 3.95 (ddt, *J* = 6.7 Hz, *J* = 6.7 Hz, *J* = 6.2 Hz, 0.5H), 3.75-3.63 (m, 2H), 3.70 (s, 6H), 2.74 (dd, *J* = 14.4 Hz, *J* = 6.9 Hz, 1H), 2.64 (dd, *J* = 14.4 Hz, *J* = 8.4 Hz, 1H), 2.18 (dd, *J* = 14.5 Hz, *J* = 1.8 Hz, 1H), 2.15 (d, *J* = 9.0 Hz, 1H), 2.02-1.93 (m, 1H), 1.92-1.75 (m, 2H), 1.63 (t, *J* = 3.1 Hz, 6H), 1.54-1.45 (m, 1H).

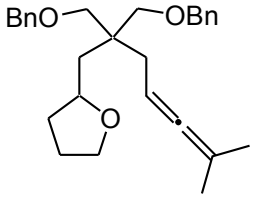
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.7, 171.8, 171.7, 95.0, 82.9, 74.7, 67.6, 56.4, 52.4, 52.3, 37.9, 32.7, 32.2, 25.5, 20.5, 20.4.

IR (CCl_4): ν (cm^{-1}) 2952, 2855, 1969, 1738, 1435, 1198, 1088.

MS (EI): m/z 297 (M^+), 272, 254, 240.

MS (HRMS EI): m/z 297.1677 (Calcd. for $C_{16}H_{23}O_5{}^2H$: 297.1686).

2-(2,2-bis((benzyloxy)methyl)-6-methylhepta-4,5-dienyl)-tetrahydrofuran (14a)



Following procedure **B** starting with 0.5 mmol of 2-(6-Benzyloxy-2,2-bis-benzyloxymethyl-6-methyl-hept-4-ynyl)-tetrahydro-furan

Flash chromatography (SiO_2 PE/ AcOEt: 95/5).

Yield: 69.3 mg (33%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.35-7.30 (m, 8H), 7.29-7.24 (m, 2H), 4.96-4.89 (m, 1H), 4.50 (s, 2H), 4.49 (s, 2H), 4.02-3.96 (m, 1H), 3.85 (dt, *J* = 7.3 Hz, *J* = 6.5 Hz, 1H), 3.66 (dt, *J* = 8.1 Hz, *J* = 6.0 Hz, 1H), 3.47 (dd, *J* = 17.1 Hz, 8.8 Hz, 2H), 3.45 (dd, *J* = 11.7 Hz, *J* = 9.0 Hz, 2H), 2.16 (qd, *J* = 13.6 Hz, *J* = 7.9 Hz, 2H), 2.01-1.93 (m, 1H), 1.90-1.75 (m, 2H), 1.71 (dd, *J* = 14.4 Hz, *J* = 8.3 Hz, 1H), 1.65 (s, 3H), 1.64 (s, 3H), 1.58 (dd, *J* = 14.4 Hz, *J* = 3.9 Hz, 1H), 1.49-1.40 (m, 1H).

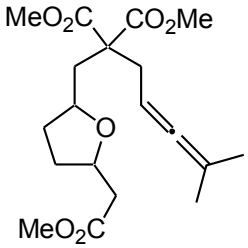
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.5, 139.1, 139.0, 128.2 (x4), 127.3 (x6), 93.4, 84.3, 75.9, 73.3, 73.1 (x3), 67.4, 41.8, 37.7, 33.1, 33.0, 25.5, 20.6 (x2).

IR (CCl_4): ν (cm^{-1}) 3066, 2985, 2859, 1951, 1496, 1454, 1361, 1087.

MS (EI): m/z 420 (M^+), 405, 312, 298, 221.

MS (HRMS EI): m/z 420.2654 (Calcd. for $C_{28}H_{36}O_3$: 420.2665).

2-((5-((methoxycarbonyl)methyl)-tetrahydrofuran-2-yl)methyl)-2-(4-methylpenta-2,3-dienyl)-malonic acid dimethyl ester **(14b)**



Following procedure **A** starting with dimethyl 2-((5-((methoxycarbonyl)methyl)-tetrahydrofuran-2-yl)methyl)malonate (1 mmol, 1 eq.) and 4-methylpenta-2,3-dienyl methanesulfonate (1.2 eq.).

Flash chromatography (SiO_2 PE/ AcOEt: 8/2).

Yield: 291 mg (79%) of colorless oil as a mixture of diastereoisomers (d.r. = 1.2:1).

^{1}H-NMR (400.2 MHz, $CDCl_3$): major diastereoisomer: δ 4.78-4.71 (m, 1H), 4.25 (quint, *J* = 6.8 Hz, 1H), 4.14-4.07 (m, 1H), 3.70 (s, 6H), 3.69 (s, 3H), 2.73 (dd, *J* = 14.4 Hz, *J* = 7.0 Hz, 1H), 2.65 (dd, *J* = 8.4 Hz, *J* = 3.1 Hz, 1H), 2.53 (dd, *J* = 11.8 Hz, *J* =6.9 Hz, 1H), 2.42 (t, *J* = 6.6 Hz, 1H), 2.17 (dd, *J* = 12.0 Hz, *J* = 3.1 Hz, 1H), 2.19-1.96 (m, 3H), 1.65 (s, 3H), 1.63 (s, 3H), 1.62-1.51 (m, 2H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): minor diastereoisomer: δ 4.78-4.71 (m, 1H), 4.19 (quint, *J* = 6.6 Hz, 1H), 3.94-3.86 (m, 1H), 3.70 (s, 3H), 3.68 (s, 6H), 2.72 (dd, *J* = 14.4 Hz, *J* = 6.9 Hz, 1H), 2.61 (dd, *J* = 8.4 Hz, *J* = 3.1 Hz, 1H), 2.57 (dd, *J* = 12.1 Hz, *J* = 6.8 Hz, 1H), 2.38 (t, *J* = 6.5 Hz, 1H), 2.25 (dd, *J* = 14.6 Hz, *J* = 3.2 Hz, 1H), 2.19-1.96 (m, 3H), 1.64 (s, 3H), 1.64 (s, 3H), 1.62-1.51 (m, 2H).

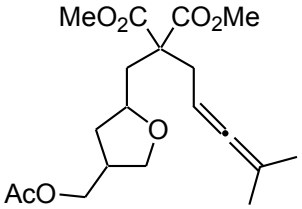
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.7, 171.6 (x2), 95.0, 82.9, 77.2, 74.7, 56.3, 52.3 (x2), 52.3, 51.5, 40.8, 38.5, 32.8, 32.5, 31.6, 21.0 (x2).

IR (CCl_4): ν (cm^{-1}) 2952, 1970, 1739, 1437, 1180, 1086.

MS (EI): m/z 368 (M^+), 306, 264, 256.

MS (HRMS EI): m/z 368.1829 (Calcd. for $C_{19}H_{28}O_7$: 368.1835).

2-((4-(acetoxymethyl)-tetrahydrofuran-2-yl)methyl)-2-(4-methylpenta-2,3-dienyl)-malonic acid dimethyl ester **(14c)**



Following procedure **A** starting with dimethyl 2-((4-(acetoxymethyl)-tetrahydrofuran-2-yl)methyl)malonate (1 mmol, 1 eq.) and 4-methylpenta-2,3-dienyl methanesulfonate (1.2 eq.).

Flash chromatography (SiO_2 PE/ AcOEt: 85/15).

Yield: 265 mg (72%) of colorless oil as a mixture of diastereoisomers (d.r. =2:1)

^{1}H-NMR (400.2 MHz, $CDCl_3$): major diastereoisomer: δ 4.79-4.72 (m, 1H), 4.07-4.01 (m, 1H), 3.98-3.89 (m,1H), 3.74 (dd, *J* = 8.7 Hz, *J* = 7.6 Hz, 1H), 3.70 (s, 6H), 3.56 (dd, *J* = 8.9 Hz, *J* = 6.1 Hz, 1H), 2.73 (dd, *J* = 14.6 Hz, *J* = 6.9 Hz, 1H), 2.63 (dd, *J* = 14.4 Hz, *J* = 8.2 Hz, 1H), 2.53 (quint, *J* = 7.5 Hz, 1H), 2.26 (dd, *J* = 14.9 Hz, *J* = 4.0 Hz, 1H), 2.21-2.12 (m, 2H), 2.06 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H), 1.34-1.15 (m, 2H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): minor diastereoisomer: δ 4.79-4.72 (m, 1H), 4.07-4.01 (m, 1H), 3.98-3.89 (m,1H), 3.85 (dd, *J* = 8.9 Hz, *J* = 7.0 Hz, 1H), 3.71 (s, 6H), 3.48 (dd, *J* = 8.9 Hz, *J* = 5.5 Hz, 1H), 2.75 (dd, *J* = 14.8 Hz, *J* = 6.7 Hz, 1H), 2.64 (dd, *J* = 14.3 Hz, *J* = 8.4 Hz, 1H), 2.53 (quint, *J* = 7.5 Hz, 1H), 2.21-2.12 (m, 2H), 2.05 (s, 3H), 1.85-1.75 (m, 2H), 1.65 (s, 3H), 1.64 (s, 3H), 0.87-0.95 (m, 1H).

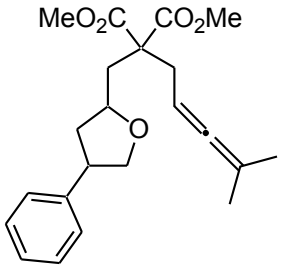
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.7, 171.7, 171.5, 171.0, 95.1, 82.8, 75.2, 70.1, 66.1, 56.4, 52.5, 52.3, 38.6, 38.0, 37.8, 35.9, 32.9, 20.5 (x2)

IR (CCl_4): ν (cm^{-1}) 2952, 1970, 1740, 1435, 1365, 1235, 1037.

MS (EI): m/z 368 (M^+), 304, 253, 213.

MS (HRMS EI): m/z 368.1838 (Calcd. for $C_{19}H_{28}O_7$: 368.1835).

***2-((tetrahydro-4-phenylfuran-2-yl)methyl)-2-(4-methylpenta-2,3-dienyl)-malonic acid dimethyl ester* (14d)**



Following procedure **A** starting with dimethyl 2-((tetrahydro-4-phenylfuran-2-yl)methyl)malonate (1 mmol, 1 eq.) and 4-methylpenta-2,3-dienyl methanesulfonate (1.2 eq.).

Flash chromatography (SiO_2 PE/ AcOEt: 95/5).

Yield: 312 mg (84%) of yellowish oil as a mixture of diastereoisomers (d.r. = 3:1)

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.24-7.20 (m, 3H), 4.83-4.75 (m, 1H), 4.17-4.10 (m, 1H), 4.06 (t, *J* = 8.1 Hz, 1H), 3.73 (s, 6H), 3.70 (t, *J* = 8.5 Hz, 1H), 3.39 (qd, *J* = 9.8 Hz, *J* = 8.1 Hz, 1H), 2.78 (dd, *J* = 14.5 Hz, *J* = 7.0 Hz, 1H), 2.68 (dd, *J* = 14.5 Hz, *J* = 8.3 Hz, 1H), 2.48 (ddd, *J* = 7.8 Hz, *J* = 6.2 Hz, *J* = 6.2 Hz, 1H), 2.37 (dd, *J* = 14.5 Hz, *J* = 8.4 Hz, 1H), 2.32 (dd, *J* = 14.1 Hz, *J* = 3.5 Hz, 1H), 1.74-1.66 (m, 1H), 1.66 (s, 3H), 1.65 (s, 3H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.24-7.20 (m, 3H), 4.83-4.75 (m, 1H), 4.34-4.27 (m, 1H), 4.06 (t, *J* = 8.1 Hz, 1H), 3.74 (s, 6H), 3.67 (t, *J* = 8.3 Hz, 1H), 3.46 (quint, *J* = 7.5 Hz, 1H), 2.80 (dd, *J* = 14.5 Hz *J* = 7.0 Hz, 1H), 2.70 (dd, *J* = 14.5 Hz, *J* = 8.3 Hz, 1H), 2.21 (dd, *J* = 14.6 Hz, *J* = 3.2 Hz, 1H), 2.15 (dd, *J* = 12.5 Hz, *J* = 7.5 Hz, 1H), 2.04 (ddd, *J* = 12.7 Hz, *J* = 8.4 Hz, *J* = 5.2 Hz, 1H), 1.74-1.66 (m, 1H), 1.66 (s, 3H), 1.65 (s, 3H).

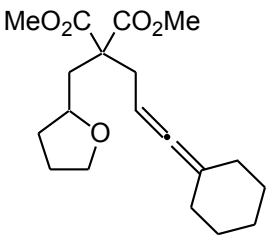
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.7, 171.6 (x2), 141.9, 128.5 (x2), 127.2 (x2), 126.5, 95.1, 82.9, 75.8, 73.9, 56.4, 52.5, 52.4, 45.5, 41.6, 38.1, 32.7, 20.5 (x2).

IR (CCl_4): ν (cm^{-1}) 3065, 2951, 2870, 1738, 1435, 1212, 1092.

MS (EI): m/z 372 (M^+), 258.

MS (HRMS EI): m/z 372.1908 (Calcd. for $C_{22}H_{28}O_5$: 372.1937).

***2-(3-cyclohexylideneallyl)-2-((tetrahydrofuran-2-yl)methyl)-malonic acid dimethyl ester* (14e)**



Following procedure **A** starting with dimethyl 2-((tetrahydrofuran-2-yl)methyl)malonate (1 mmol, 1 eq.) and 3-cyclohexylideneallyl methanesulfonate (1.2 eq.)

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 181 mg (54%) of yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.75 (ttt, *J* = 7.7 Hz, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 3.97 (quint, *J* = 6.6 Hz, 1H), 3.75-3.64 (m, 8H), 2.77 (dd, *J* = 14.4 Hz, *J* = 6.9 Hz, 1H), 2.67 (dd, *J* = 14.4 Hz, *J* = 8.5 Hz, 1H), 2.18 (d, *J* = 6.5 Hz, 2H), 2.09-1.93 (m, 5H), 1.92-1.75 (m, 2H), 1.59-1.46 (m, 7H).

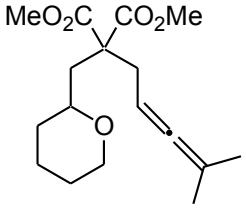
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 200.4, 171.8, 171.7, 102.2, 82.7, 74.7, 67.6, 56.4, 52.4, 52.3, 37.8, 33.0, 32.1, 31.5, 31.4, 27.2 (x2), 26.0, 25.5.

IR (CCl_4): ν (cm^{-1}) 2951, 2858, 1970, 1738, 1435, 1179.

MS (EI): m/z 336 (M^+), 257, 239, 216.

MS (HRMS EI): m/z 336.1938 (Calcd. for $C_{19}H_{28}O_5$: 336.1937).

2-((tetrahydro-2H-pyran-2-yl)methyl)-2-(4-methylpenta-2,3-dienyl)-malonic acid dimethyl ester **(14f)**



Following procedure **A** starting with dimethyl 2-((tetrahydro-2H-pyran-2-yl)methyl)malonate (1 mmol, 1 eq.) and 4-methylpenta-2,3-dienyl methanesulfonate (1.2 eq.).

Flash chromatography (SiO_2 PE/ AcOEt: 95/5).

Yield: 288 mg (93%) of yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.77-4.70 (m, 1H); 3.82 (d, *J* = 11.6 Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.36-3.25 (m, 2H), 2.68 (dd, *J* = 14.4 Hz, *J* = 6.9 Hz, 1H), 2.59 (dd, *J* = 14.4 Hz, *J* = 8.3 Hz, 1H), 2.10 (d, *J* = 10.3 Hz, 1H), 2.06 (dd, *J* = 13.4 Hz, *J* = 4.6 Hz, 1H), 1.84-1.77 (m, 1H), 1.65 (d, *J* = 3.4 Hz, 3H), 1.64 (d, *J* = 3.4 Hz, 3H), 1.55-1.42 (m, 4H), 1.327-1.26 (m, 1H).

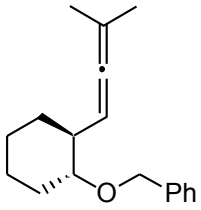
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 203.7, 171.9, 171.8, 95.0, 82.9, 73.9, 68.3, 55.7, 52.4, 52.2, 38.8, 33.5, 32.3, 25.6, 23.6, 20.5, 20.4.

IR (CCl_4): ν (cm^{-1}) 2939, 1970, 1737, 1436, 1203, 1092.

MS (EI): m/z 310 (M^+), 285, 271, 253.

MS (HRMS EI): m/z 310.1781 (Calcd. for $C_{17}H_{26}O_5$: 310.1780).

rac-1-(((1R,2S)-*2-(3-methylbuta-1,2-dienyl)cyclohexyloxy)methyl)benzene* (22)



Following procedure **B** starting with 0.5 mmol of *rac*-1-(((*1R,2S*)-2-(3-(benzyloxy)-3-methylbut-1-ynyl)cyclohexyloxy)methyl)benzene

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 108.8 mg (85%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 5.27 (dqq, *J* = 5.8 Hz, *J* = 2.9 Hz, *J* = 2.9 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 11.7 Hz, 1H), 3.14 (td, *J* = 9.5 Hz, *J* = 3.9 Hz, 1H), 2.17-2.10 (m, 2H), 1.89-1.76 (m, 2H), 1.72 (t, *J* = 2.9Hz, 6H), 1.70-1.65 (m, 1H), 1.39-1.14 (m, 4H).

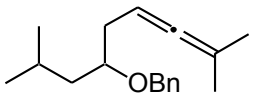
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 201.3, 139.2, 128.2 (x2), 127.6 (x2), 127.2, 95.6, 92.0, 81.9, 70.7, 43.1, 31.1, 30.9, 25.0, 24.4, 20.8, 20.6.

IR (CCl_4): ν (cm^{-1}) 3066, 2936, 1966, 1451, 1211, 1094.

MS (EI): m/z 256 (M^+), 241, 165, 150.

MS (HRMS EI): m/z 256.1840 (Calcd. for $C_{18}H_{24}O$: 256.1827).

***1-((2,8-dimethylnona-6,7-dien-4-yloxy)methyl)benzene* (28a)**



Following procedure **B** starting with 0.67 mmol of *rac*-1-(((*R*)-8-(benzyloxy)-2,8-dimethylnon-6-yn-4-yloxy)methyl)benzene

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 187.9 mg (92%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.37-7.29 (m, 4H), 7.23-7.18 (m, 1H), 5.02-4.94 (m, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.5 Hz, 1H), 3.57 (dddd, J = 8.9 Hz, J = 6.3 Hz, J = 4.6 Hz, J = 4.6 Hz, 1H), 2.27 (ddd, *J* = 14.3 Hz, *J* = 7.1 Hz, *J* = 4.6 Hz, 1H), 2.18 (ddd, *J* = 14.4 Hz, *J* =13.4 Hz, 7.0 Hz, 1H),

1.86-1.74 (m, 1H), 1.69 (s, 3H), 1.68 (s, 3H), 1.54 (ddd, *J* = 14.0 Hz, *J* = 8.4 Hz, *J* = 5.6 Hz, 1H), 1.34 (ddd, *J* = 13.9 Hz, *J* = 8.5 Hz, *J* = 4.5 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).

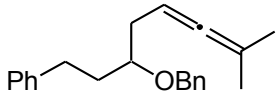
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 202.8, 138.9, 129.0, 128.2 (x2), 12.0 (x2), 127.3, 94.5, 84.8, 76.9, 70.7, 43.4, 33.8, 24.3, 23.4, 22.2, 20.6.

IR (CCl_4): ν (cm^{-1}) 3066, 2957, 1967, 1467, 1453, 1095.

MS (EI): m/z 258 (M^+), 256, 177, 157.

MS (HRMS EI): m/z 258.1974 (Calcd. for $C_{18}H_{26}O$: 258.1984).

1-((7-methyl-1-phenylocta-5,6-dien-3-yloxy)methyl)benzene **(28b)**



Following procedure **B** starting with 0.61 mmol of *rac*-1-(((*R*)-7-(benzyloxy)-7-methyl-1-phenyloct-5-yn-3-yloxy)methyl)benzene

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 145.7 mg (78%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.40-7.26 (m, 6H), 7.22-7.17 (m, 4H), 5.01-4.95 (m, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.49 (*J* = 11.6 Hz, 1H), 3.52-3.45 (m, 1H), 2.83-2.63 (m, 2H), 2.32 (ddd, *J* = 14.5 Hz, *J* = 7.1 Hz, *J* = 5.1 Hz, 1H), 2.25 (ddd, *J* = 14.3 Hz, *J* = 7.0 Hz, *J* = 6.9 Hz, 1H), 2.35-2.21 (m, 2H), 1.67 (d, *J* = 2.85 Hz, 6H).

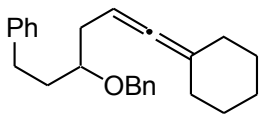
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 202.8, 142.4, 128.4 (x2), 128.3 (x2), 128.3 (x2), 127.9, 127.7 (x2), 127.4, 125.6, 94.7, 84.7, 78.1, 70.9, 35.5, 33.6, 21.7, 20.6 (x2).

IR (CCl_4): ν (cm^{-1}) 3029, 2957, 2858, 1496, 1454, 1069.

MS (EI): m/z 306 (M^+), 243, 217, 203.

MS (HRMS EI): m/z 306.1995 (Calcd. for $C_{22}H_{26}O$: 306.1984).

1-((6-cyclohexylidene-1-phenylhex-5-en-3-yloxy)methyl)benzene **(28c)**



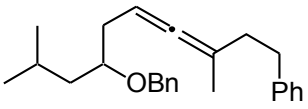
Following procedure **B** starting with 0.54 mmol of *rac*-1-(((*R*)-6-(1-(benzyloxy)cyclohexyl)-1-phenylhex-5-yn-3-yloxy)methyl)benzene

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 176.3 mg (93%) of yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.43-7.37 (m, 4H), 7.34-7.30 (m, 3H), 7.24-7.20 (m, 3H), 5.04 (ttt, *J* = 7.1 Hz, *J* = 2.1 Hz, *J* = 2.1 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 3.54 (tt, *J* = 6.0 Hz, *J* = 5.5 Hz, 1H), 2.88-2.80 (m, 1H), 2.74-2.67 (m, 1H), 2.37 (ddd, *J* = 14.4 Hz, *J* = 7.0 Hz, *J* = 4.9 Hz, 1H), 2.29 (dd, *J* = 14.3 Hz, *J* = 6.9 Hz, 1H), 2.17-2.11 (m, 4H), 1.98-1.93 (m, 2H), 1.65-1.52 (m, 6H).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 199.5, 142.4, 138.9, 128.4, 128.3 (x4), 127.7 (x2), 127.6, 127.4, 125.6, 102.1, 84.6, 78.1, 72.1, 35.5, 33.8, 31.6, 31.6, 31.5, 27.4 (x2), 26.1.
IR (CCl_4): ν (cm^{-1}) 3066, 1963, 1496, 1453, 1348, 1274, 1089.
MS (EI): m/z 346 (M^+), 255.
MS (HRMS EI): m/z 346.2297 (Calcd. for $C_{25}H_{30}O$: 346.2297).

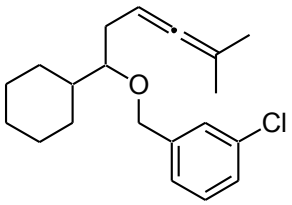
7-(benzyloxy)-3-methyl-1,9-diphenylnona-3,4-diene **(28d)**



Following procedure **B** starting with 1 mmol of *rac*-1-(((*4R*)-8-(benzyloxy)-2,8-dimethyl-10-phenyldec-6-yn-4-yloxy)methyl)benzene
Flash chromatography (SiO_2 PE/ AcOEt: 98/2).
Yield: 306 mg (88%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.37-7.27 (m, 8H), 7.23-7.17 (m, 2H), 5.11-5.05 (m, 1H), 4.61 (dd, *J* = 11.6 Hz, *J* = 2.4 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 3.54-3.47 (m, 1H), 2.74 (t, *J* = 7.9 Hz, 2H), 2.27-2.16 (m, 4H), 1.87-1.75(m, 1H), 1.72 (dd, *J* = 2.3 Hz, *J* = 1.1 Hz, 3H), 1.59-1.49 (m, 1H), 1.37-1.27 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 202.6, 142.3, 139.1, 128.5 (x2), 128.4 (x2), 128.3 (x2), 127.9 (x2), 127.5, 125.8, 98.7, 87.1, 77.1, 70.1, 43.6, 35.8, 34.2, 34.0, 24.6, 23.6, 22.5, 19.5.
IR (CCl_4): ν (cm^{-1}) 3066, 2957, 1963, 1496, 1454, 1368, 1095.
MS (EI): m/z 348 (M^+), 257, 244.
MS (HRMS EI): m/z 348.2452 (Calcd. for $C_{25}H_{32}O$: 348.2453).

***1-((7-methyl-1-phenylocta-5,6-dien-3-yloxy)methyl)-3-chlorobenzene* (28e)**



Following procedure **B** starting with 1 mmol of *rac*-1-((5-(benzyloxy)-1-cyclohexyl-5-methylhex-3-ynyloxy)methyl)-3-chlorobenzene

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 226 mg (71%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.27-7.23 (m, 3H), 5.07-4.95 (m, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.20 (td, *J* = 5.6 Hz, *J* = 5.6 Hz, 1H), 2.29 (ddd, *J* = 14.6 Hz, *J* = 7.0 Hz, *J* = 5.1 Hz, 1H), 2.20 (ddd, *J* = 14.6 Hz, *J* = 7.4 Hz, *J* = 5.7 Hz, 1H), 1.94-1.87 (m, 1H), 1.80-1.72 (m, 2H), 1.68 (s, 3H), 1.67 (s, 3H), 1.68-1.55 (m, 1H), 1.30-0.98 (m, 7H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 202.7, 141.3, 134.1, 129.5, 127.6, 127.4, 125.5, 95.6, 85.1, 83.8, 70.9, 41.0, 30.98, 29.2, 28.6, 26.6, 26.4, 26.3, 20.6, 20.6.

IR (CCl_4): ν (cm^{-1}) 2931, 2856, 1970, 1450, 1256, 1073.

MS (EI): m/z 318, 320 (M^+), 309, 307, 297, 295.

MS (HRMS EI): m/z 318.1758 (Calcd. for $C_{20}H_{27}ClO$: 318.1750).

Gold- and Brønsted Acid-Catalyzed Hydride Shift

General procedure* C1 *for the Brønsted acid catalysis:

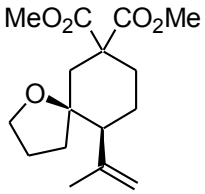
To a solution of the allene (1 eq.) in chloroform (0.2M) was added a solution (0.5M in DCM) of $HNTf_2$ (0.04 eq.) at room temperature and the reaction mixture was stirred under nitrogen. Upon completion of the reaction, triethylamine (0.1 eq.) was added. The solvent was next removed under reduced pressure and the residue was subjected to purification.

General procedure* C2 *for the gold(I) catalysis :

To a solution of the allene (1 eq.) in dichloromethane (0.2M) was added [(2,4-*t*-BuPhO)$_3$PAu(NCPh)]SbF_6 **13** (0.04 eq.) at room temperature and the reaction mixture was stirred under

nitrogen. Upon completion of the reaction, triethylamine (0.1 eq.) was added. The solvent was removed under reduced pressure and the residue was subjected to purification.

rac-*(*5S,10S*)-10-Isopropenyl-1-oxa-spiro[4.5]decane-7,7-dicarboxylic acid dimethyl ester* (10)



Following procedure **C1** starting with 0.1 mmol of **9**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 28.1 mg (95%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.82-4.80 (m, 1H), 4.75-4.73 (m, 1H), 3.73-3.69 (m, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.57 (dt, *J* = 15.3 Hz, *J* = 7.5 Hz, 1H), 2.54-2.49 (m, 2H), 2.36-2.25 (m, 1H), 2.05 (dd, *J* = 13.0 Hz, *J* = 3.2 Hz, 1H), 2.02-1.97 (m, 1H), 1.94-1.82 (m, 1H), 1.83 (d, *J* = 14.2 Hz, 1H), 1.79-1.68 (m, 1H), 1.70 (s, 3H), 1.56-1.44 (m, 3H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 173.0, 171.6, 147.0, 113.6, 82.8, 66.8, 53.4, 52.6, 52.2, 52.0, 41.6, 34.6, 31.2, 25.8, 25.3, 21.3.

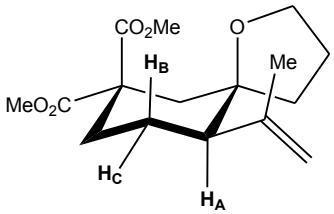
IR (CCl_4): ν (cm^{-1}) 3070, 2952, 2874, 1736, 1636, 1447, 1434, 1234, 1118, 1049.

MS (EI): m/z 296(M^+), 264, 252, 236, 212.

MS (HRMS EI): m/z 296.1633 (Calcd. for $C_{16}H_{24}O_5$: 296.1624).

Stereochemistry in 10:

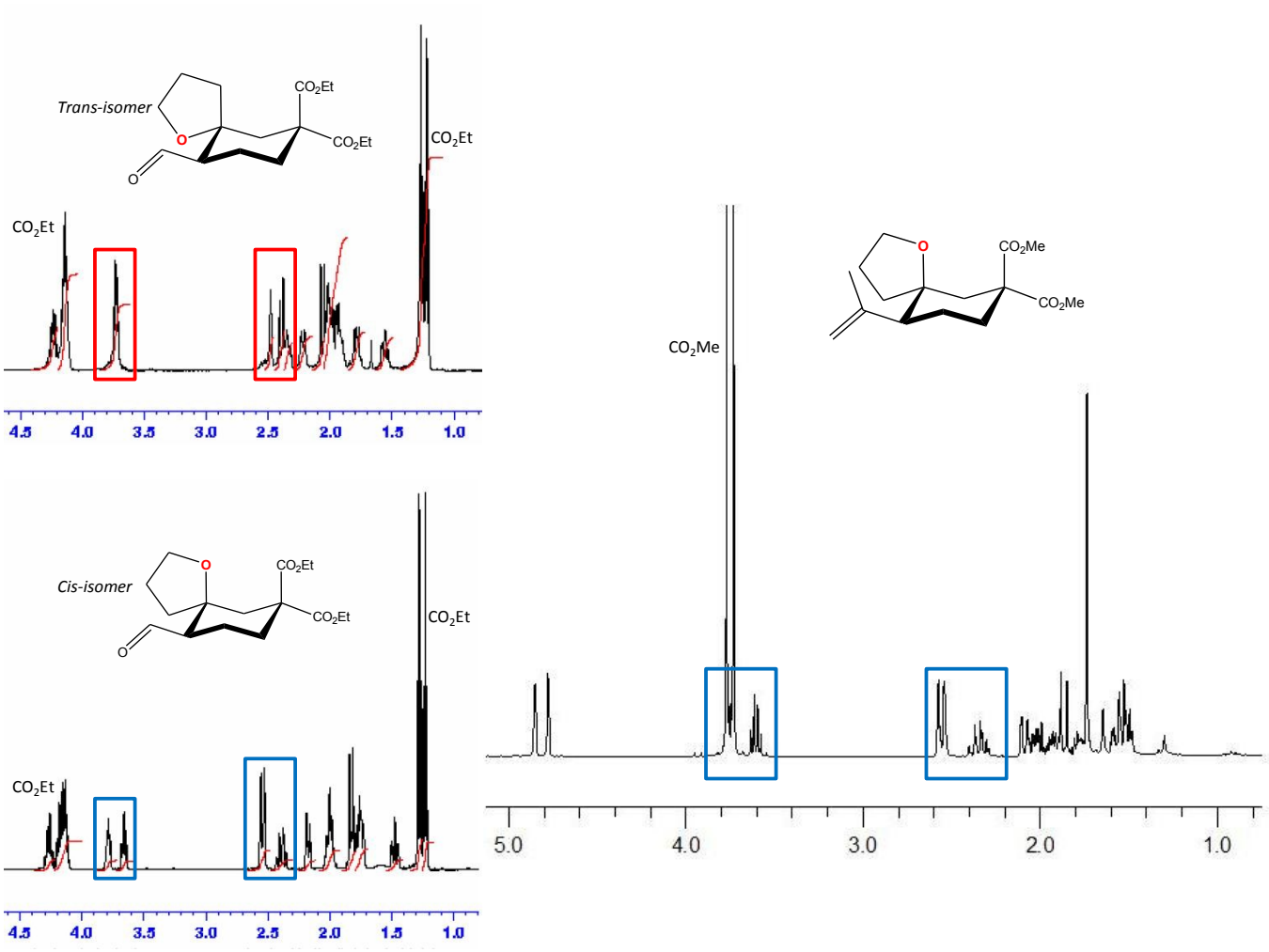
The isopropylidene moiety in spirocompound **10** was found to occupy an equatorial position on the basis of the values of the coupling constants of H_A, H_B and H_C:



δ (ppm) H_A: 2.05 (dd, J_{AB} = 13.0 Hz, J_{AC} = 3.2 Hz, 1H)

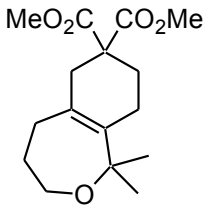
The relative configuration of the quaternary spiro center could not be proved using nOe experiments, due to overlapping in the methylene region. The structure assignement was made by comparison with structurally similar compounds described by Sames and coworkers, where the isopropylidene group is replaced by an aldehyde (*J. Am. Chem. Soc.*, **2005**, *127*, 12180 – compounds *cis*12 and *trans*12). The ^{1}H

NMR spectrum of compound **10** was indeed very similar to that of the *cis* spiro compound described by Sames and coworkers (see below).



The stereochemistry of compounds **15a-e** was assigned by analogy with that of compound **10**.

***Dimethyl 4,5,8,9-tetrahydro-1,1-dimethylbenzo[c]oxepine-7,7(*1H,3H,6H*)-dicarboxylate* (11)**



Following procedure **C2** starting with 0.2 mmol of **9**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 36.1 mg (61%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 3.73 (s,6H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.53 (bs, 2H), 2.22 (bt, 6.5 Hz, 2H), 2.08 (t, *J* = 6.4 Hz, 2H), 1.89 (bt, *J* = 6.2 Hz, 2H), 1.73 (t, *J* = 6.6 Hz, 2H), 1.23 (s, 6H).

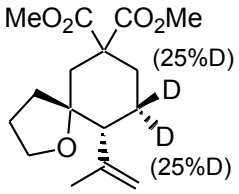
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 171.9 (x2), 132.6, 126.4, 81.2, 60.7, 53.5, 52.5 (x2), 37.8, 28.6, 28.0, 26.0(x2), 25.8, 24.4.

IR (CCl_4): ν (cm^{-1}) 2951, 1736, 1435, 1254.

MS (EI): m/z 296 (M^+), 282, 278, 265, 221.

MS (HRMS EI): m/z 296.1634 (Calcd. for $C_{16}H_{24}O_5$: 296.1624).

***rac-(5S,10S)*-9-deutero-10-isopropenyl-1-oxa-spiro[4.5]decane-7,7-dicarboxylic acid dimethyl ester (10D)**



Following procedure **C1** starting with 0.1 mmol of **9D**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 28.2 mg (95%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.82-4.80 (m, 1H), 4.75-4.73 (m, 1H), 3.73-3.69 (m, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.57 (dt, *J* = 15.3 Hz, *J* = 7.5 Hz, 1H), 2.54-2.49 (m, 2H), 2.36-2.25 (m, 0.75H), 2.05 (dd, *J* = 13.0 Hz, *J* = 3.2 Hz, 1H), 2.02-1.97 (m, 1H), 1.94-1.82 (m, 1H), 1.83 (d, *J* = 14.2 Hz, 1H), 1.79-1.68 (m, 1H), 1.70 (s, 3H), 1.56-1.44 (m, 2.75H).

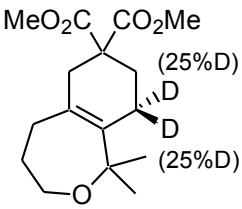
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 173.0, 171.6, 147.0, 113.6, 82.8, 66.8, 53.4, 52.6, 52.2, 52.0, 41.6, 34.6, 31.2(0.5C), 31.2(0.5C), 25.8, 25.3, 21.3.

IR (CCl_4): ν (cm^{-1}) 3071, 2954, 1728, 1448, 1435, 1270, 1109, 1047.

MS (EI): m/z 297 (M^+), 282, 254, 238, 214.

MS (HRMS EI): m/z 297.1671 (Calcd. for $C_{16}H_{23}O_5{}^2H$: 297.1686).

***9-deutero-1,1-dimethyl-1,4,5,6,8,9-hexahydro*-3H-*benzo[c]*oxepine-7,7-dicarboxylic acid dimethyl ester (11D)**



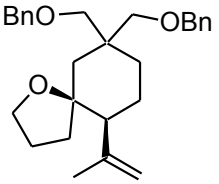
Following procedure **C2** starting with 0.1 mmol of **9D**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 16.0 mg (54%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 3.73 (s,6H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.53 (bs, 2H), 2.22 (bt, 6.5 Hz, 2H), 2.08 (t, *J* = 6.4 Hz, 2H), 1.89 (bt, *J* = 6.2 Hz, 1.5H), 1.73 (t, *J* = 6.6 Hz, 2H), 1.23 (s, 6H).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 171.9 (x2), 132.6, 126.4, 81.2, 60.7, 53.5, 52.5 (x2), 37.8, 28.6, 28.0, 26.0 (x2), 25.8, 24.4.
IR (CCl_4): ν (cm^{-1}) 2953, 1729, 1451, 1436, 1263, 1089.
MS (EI): m/z 297 (M^+), 282, 222.
MS (HRMS EI): m/z 297.1678 (Calcd. for $C_{16}H_{23}O_5{}^2H$: 297.1686).

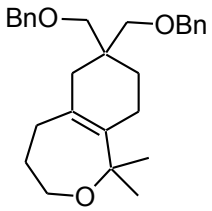
rac-(5S,6S)-*9,9-Bis-benzyloxymethyl-6-isopropenyl-1-oxa-spiro[4.5]decane* **(15a)**



Following procedure **C1** starting with 0.1 mmol of **14a**
Flash chromatography (SiO_2 PE/ AcOEt: 9/1).
Yield: 34.8 mg (83%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.34-7.30 (m, 8H), 7.30-7.25 (m, 2H), 4.81-4.79 (m, 1H), 4.73-4.71 (m, 1H), 4.57-4.50 (m, 4H), 3.80 (d, *J* = 9.0 Hz, 1H), 3.76 (ddd, *J* =7.8 Hz, *J* = 7.7 Hz, *J* = 4.8 Hz, 1H), 3.71-3.65 (m, 2H), 3.35 (d, *J* = 8.7 Hz, 1H), 3.22 (d, *J* = 8.7 Hz, 1H), 2.03-1.93 (m, 3H), 1.88 (dd, *J* = 14.2 Hz, *J* = 1.8 Hz, 1H), 1.82-1.65 (m, 3H), 1.74 (s, 3H), 1.46-1.30 (m, 3H), 1.22 (d, *J* =14.2 Hz, 1H).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 139.6, 139.1, 128.2 (x2), 128.1 (x2), 127.4 (x2), 127.2, 127.2 (x2), 127.0, 113.0, 83.9, 77.5, 77.2, 73.3, 73.0, 71.5, 67.2, 53.5, 41.3, 40.0, 36.4, 29.5, 25.6, 24.3, 21.2.
IR (CCl_4): ν (cm^{-1}) 3068, 2929, 2859, 1495, 1453, 1219, 1079.
MS (EI): m/z 420 (M^+), 329, 299, 215.
MS (HRMS EI): m/z 420.2646 (Calcd. for $C_{28}H_{36}O_3$: 420.665).

7,7-bis((benzyloxy)methyl)-1,3,4,5,6,7,8,9-octahydro-1,1-dimethylbenzo[c]oxepine **(16a)**



Following procedure **C2** starting with 0.1 mmol of **14a**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 38.2 mg (91%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.37-7.27 (m, 10H), 4.52 (dd, *J* = 14.7 Hz, *J* = 12.2 Hz, 4H), 3.59 (t, *J* = 6.7 Hz, 2H), 3.40 (d, *J* = 8.7 Hz, 2H), 3.34 (d, *J* = 8.7 Hz, 2H), 2.17 (t, *J* = 6.4 Hz, 2H), 1.95 (bs, 2H), 1.80 (bt, *J* = 5.9 Hz, 2H), 1.67 (tt, *J* = 6.5 hz, *J* = 6.5 Hz, 2H), 1.52 (t, *J* = 6.4 Hz, 2H), 1.22 (s, 6H).

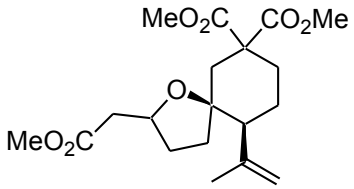
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 138.8 (x2), 132.7, 128.2 (x4), 127.4 (x4), 127.3 (x2), 127.1, 81.2, 73.2 (x2), 73.1 (x2), 60.8, 38.4, 37.6, 28.9, 26.5, 26.2, 26.1 (x2), 23.6.

IR (CCl_4): ν (cm^{-1}) 3066, 2941, 2791, 1496, 1454, 1361, 1085.

MS (EI): m/z 420 (M^+), 406, 312, 297, 216.

MS (HRMS EI): m/z 420.2653 (Calcd. for $C_{28}H_{36}O_3$: 420.2665).

rac-(5S,10S)-*10-Isopropenyl-2-methoxycarbonylmethyl-1-oxa-spiro[4.5]decane-7,7-dicarboxylic acid dimethyl ester* **(15b)**



Following procedure **C1** starting with 0.1 mmol of **14b**

Flash chromatography (SiO_2 PE/ AcOEt: 8/2).

Yield: 35.3 mg (96%) of colorless oil as a mixture of diasteroisomers (d.r. = 3.2:1)

^{1}H-NMR (400.2 MHz, $CDCl_3$): major diastereoisomer: δ 4.86 (dd, *J* = 2.5 Hz, *J* = 1.5 Hz, 1H), 4.76 (d, *J* = 1.9 Hz, 1H), 4.20-2.08 (m, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.88 (s, 3H), 2.61-1.94 (m, 7H), 1.95 (d, *J* = 13.7 Hz, 1H), 1.72 (s, 3H), 1.67-1.37 (m, 5H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): minor diastereoisomer: δ 4.85 (dd, *J* = 2.5 Hz, *J* = 1.5 Hz, 1H), 4.74 (d, *J* = 1.9 Hz, 1H), 4.20-2.08 (m, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 2.61-1.94 (m, 7H), 1.81 (d, *J* = 14.2 Hz, 1H), 1.72 (s, 3H), 1.67-1.37 (m, 5H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): major diastereoisomer: δ 173.1, 171.6 (x2), 146.6, 114.3, 83.4, 76.5, 53.1, 52.7, 51.9, 51.5, 44.2, 40.7, 34.8, 31.6, 31.2, 31.1, 25.4, 22.1.

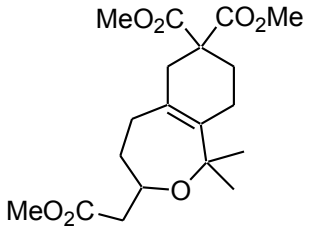
^{13}C-NMR (100.6 MHz, $CDCl_3$): minor diastereoisomer: δ 173.0, 171.6 (x2), 146.3, 113.9, 83.3, 74.1, 53.4, 52.2, 51.9, 51.5, 41.2, 40.6, 34.6, 31.2, 31.2, 29.7, 25.2, 21.4.

IR (CCl_4): ν (cm^{-1}) 2953, 1736, 1435, 1234.

MS (EI): m/z 368 (M^+), 353, 350, 337, 292.

MS (HRMS EI): m/z 368.1850 (Calcd. for $C_{19}H_{28}O_7$: 368.1835).

***Dimethyl 3-((methoxycarbonyl)methyl)-4,5,8,9-tetrahydro-1,1-dimethylbenzo[c]oxepine-7,7(*1H,3H,6H*)-dicarboxylate* (16b)**



Following procedure **C2** starting with 0.1 mmol of **14b**

Flash chromatography (SiO_2 PE/ AcOEt: 8/2).

Yield: 18.7 mg (51%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 3.99 (dddd, *J* = 9.8 Hz, *J* = 5.3 Hz, *J* = 5.3 Hz, *J* = 5.3 Hz, 1H), 3.96 (s, 3H), 3.72 (s, 3H), 3.66 (s, 3H), 2.84 (td, *J* = 13.0 Hz, *J* = 6.0 Hz, 1H), 2.65 (d, *J* = 17.3 Hz, 1H), 2.48 (dd, *J* = 14.4 Hz, *J* = 8.9 Hz, 1H), 2.40 (d, *J* = 17.2 Hz, 1H), 2.38 (dd, *J* = 14.4 Hz, *J* = 4.7 Hz, 1H), 2.27-2.21 (m, 1H), 1.95-1.80 (m, 4H), 1.55 (ddd, *J* = 13.1 Hz, *J* = 4.9 Hz, *J* = 1.8 Hz, 1H), 1.50-1.43 (m, 1H), 1.26 (s, 3H), 1.12 (s, 3H).

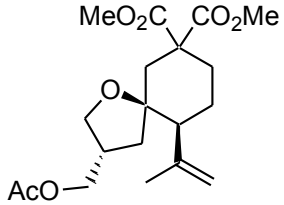
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 172.3, 172.0, 171.4, 132.6, 126.2, 81.2, 67.7, 53.4, 52.6, 52.5, 51.4, 42.0, 37.7, 29.7, 28.6, 28.0, 27.3, 24.7, 24.3.

IR (CCl_4): ν (cm^{-1}) 2933, 1737, 1711, 1641, 1436, 1255.

MS (EI): m/z 368 (M^+), 336, 325, 309, 295, 277.

MS (HRMS EI): m/z 368.1823 (Calcd. for $C_{19}H_{28}O_7$: 368.1835).

rac-(3S,5S,10S)-*3-Acetoxymethyl-10-isopropenyl-1-oxa-spiro[4.5]decane-7,7-dicarboxylic acid dimethyl ester* **(15c)**



Following procedure **C1** starting with 0.1 mmol of **14c**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 31.6 mg (86%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.84 (dd , *J* = 2.2 Hz, *J* = 1.4 Hz, 1H), 4.76 (d, *J* = 2.2 Hz, 1H), 4.11 (dd, *J* = 11.0 Hz, *J* = 7.8 Hz, 1H), 3.94 (dd, *J* = 11.0 Hz, *J* = 7.8 Hz, 1H), 3.87 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.28 (dd, *J* = 10.2 Hz, *J* = 8.8 Hz, 1H), 2.59 (dd, *J* = 14.2 Hz, *J* = 2.3 Hz, 1H), 2.50 (m, 1H), 2. 41 (m, 1H), 2.27 (dddd, *J* = 13.1 Hz, *J* = 3.7 Hz, *J* = 3.7 Hz, *J* = 3.6 Hz, 1H), 2.19 (dd, *J* = 12.6 Hz, *J* = 9.3 Hz, 1H), 2.05 (s, 3H), 2.00 (ddd, *J* = 10.8 Hz, 7.3 Hz, *J* = 3.5 Hz, 1H), 1.90 (d, *J* = 14.2 Hz, 1H), 1.71 (s, 3H), 1.56-1.44 (m, 2H), 1.24 (dd, *J* = 12.5 Hz, *J* = 9.3 Hz, 1H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 172.8, 171.5, 170.9, 146.6, 114.0, 83.3, 69.6, 65.5, 53.3, 52.7, 52.7, 52.0, 41.8, 39.4, 38.7, 31.0, 24.8, 21.4, 20.8.

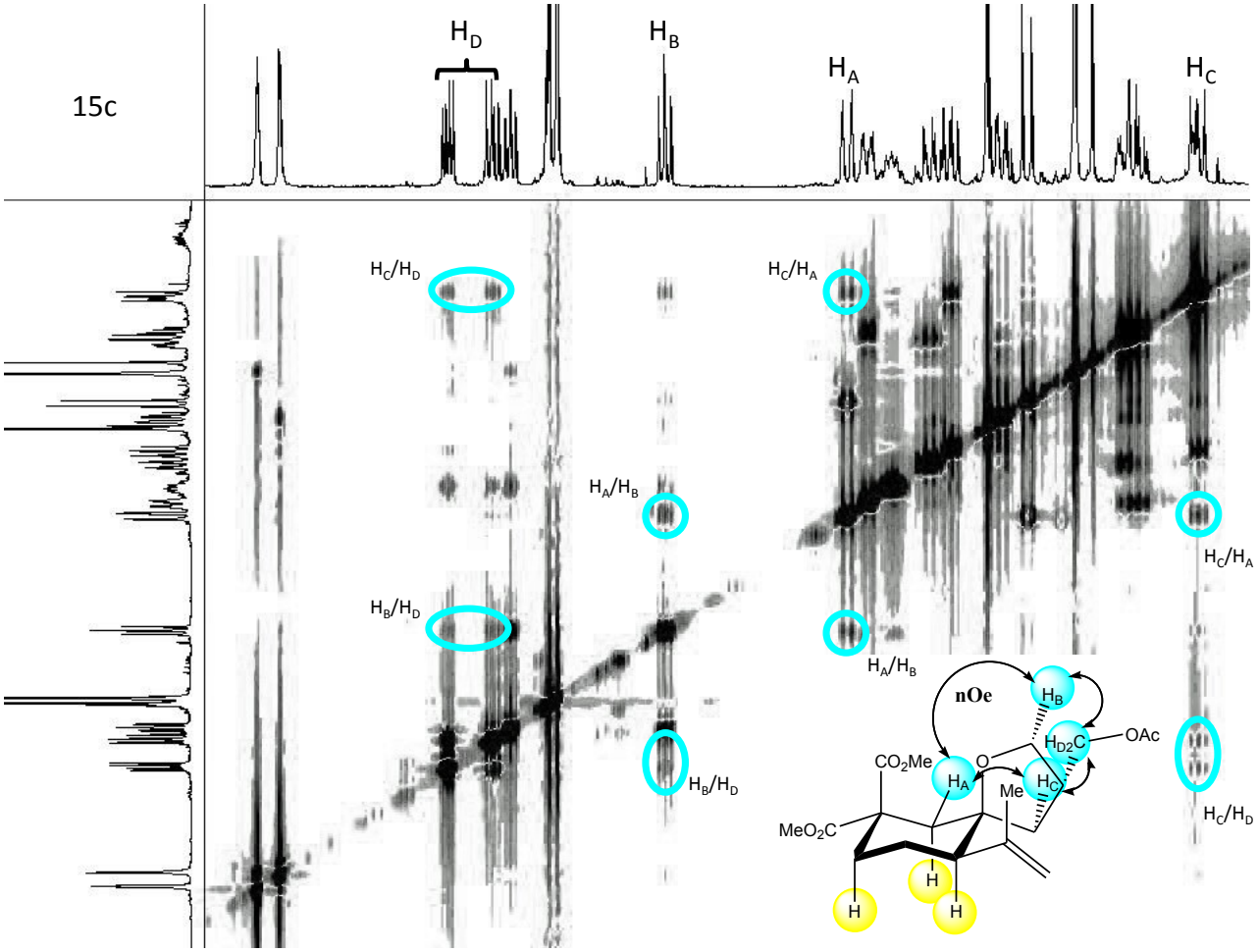
IR (CCl_4): ν (cm^{-1}) 2954, 1728, 1637, 1448, 1435, 1375, 1239, 1034.

MS (EI): m/z 368 (M^+), 336, 308, 295, 249, 195.

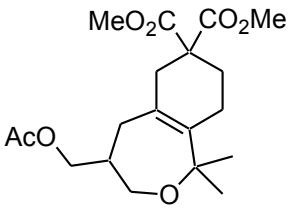
MS (HRMS EI): m/z 368.1823 (Calcd. for $C_{19}H_{28}O_7$: 368.1835).

Stereochemistry in 15c:

NOe experiments proved the relative configuration of the substituent on the THF ring (see below).



***Dimethyl 4-(acetoxymethyl)-4,5,8,9-tetrahydro-1,1-dimethylbenzo[c]oxepine-7,7(*1H,3H,6H*)-dicarboxylate* (16c)**



Following procedure **C2** starting with 0.1 mmol of **14c**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 25.0 mg (68%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 3.99 (dd, *J* = 7.2 Hz, 2.6 Hz, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 3.66 (dd, *J* = 12.5 Hz, *J* = 6.4 Hz, 1H), 3.38 (dd, *J* = 12.5 Hz, *J* = 6.4 Hz, 1H), 2.60-2.45 (m, 2H), 2.30-2.20 (m, 1H), 2.20-2.14 (m, 2H), 2.12-2.05 (m, 2H), 2.45 (s, 3H), 1.88 (t, *J* = 6.0 Hz, 2H), 1.23 (s, 3H), 1.22 (s, 3H).

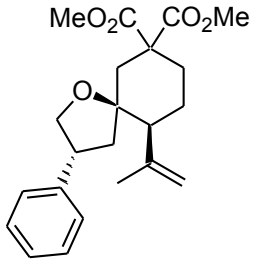
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 171.8, 171.7, 171.0, 133.4, 124.3, 81.6, 66.0, 62.4, 53.4, 52.6, 52.6, 38.3, 36.6, 31.0, 27.9, 25.9, 25.6, 24.3, 20.9.

IR (CCl_4): ν (cm^{-1}) 2953, 2855, 1973, 1435, 1365, 1244.

MS (EI): m/z 368 (M^+), 353, 338, 278.

MS (HRMS EI): m/z 368.1851 (Calcd. for $C_{19}H_{28}O_7$: 368.1835).

rac-(3R,5S,10S)-*10-Isopropenyl-3-phenyl-1-oxa-spiro[4.5]decane-7,7-dicarboxylic acid dimethyl ester* (15d)



Following procedure **C1** starting with 0.1 mmol of **14d**

Flash chromatography (SiO_2 PE/ AcOEt: 95/5).

Yield: 33.1 mg (89%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.24-7.20 (m, 3H), 4.90 (qd, *J* = 2.8 Hz, *J* = 1.3 Hz, 1H), 4.81 (d, *J* = 2.2 Hz, 1H), 4.03 (t, *J* = 7.9 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.53 (dd, *J* = 11.2 Hz, *J* = 8.5 Hz, 1H), 3.28-3.18 (m, 1H), 2.77 (dd, *J* = 14.2 Hz, *J* = 2.3 Hz, 1H), 2.59-2.48 (m, 2H), 2.40-2.28 (m, 1H), 2.06 (dd, *J* = 12.8 Hz, 1H), 2.02 (d, *J* = 14.2 Hz, 1H), 1.81 (s, 3H), 1.69 (dd, *J* = 12.6 Hz, *J* = 10.8 Hz, 1H), 1.60-1.48 (m, 2H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 172.9, 171.6, 146.7, 140.4, 128.5 (x2), 127.4 (x2), 126.6, 114.0, 83.6, 72.7, 53.6, 52.9, 52.2, 52.0, 45.8, 43.9, 42.1, 31.0, 24.7, 21.5.

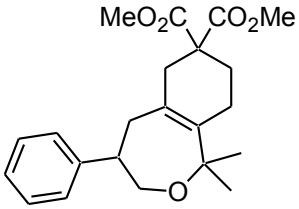
IR (CCl_4): ν (cm^{-1}) 3042, 2954, 1728, 1448, 1435, 1239, 1138, 1050.

MS (EI): m/z 372 (M^+), 340, 329, 313.

MS (HRMS EI): m/z 372.1920 (Calcd. for $C_{22}H_{28}O_5$: 372.1937).

Stereochemistry assigned by analogy with that of compound 15c.

***Dimethyl 4,5,8,9-tetrahydro-1,1-dimethyl-4-phenylbenzo[c]oxepine-7,7(*1H,3H,6H*)-dicarboxylate* (16d)**



Following procedure **C2** starting with 0.1 mmol of **14d**

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 23.4 mg (63%) of pale yellow oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.34-7.27 (m, 4H), 7.22-7.18 (m, 1H), 3.94 (dd, *J* = 12.4 Hz, *J* = 6.7 Hz, 1H), 3.75 (s, 3H), 3.75 (s, 3H), 3.72 (dd, *J* =12.3 Hz, *J* = 4.0 Hz, 1H), 3.08 (dddd, *J* = 9.3 Hz, *J* = 6.5 Hz, *J* = 6.5 Hz, *J* = 4.8 Hz, 1H), 2.85 (dd, *J* = 12.2 Hz, 11.1 Hz, 1H), 2.67 (dd, *J* = 17.6 Hz, *J* = 0.9 Hz, 1H), 2.47 (dt, *J* = 17.8 Hz, *J* = 2.1 Hz, 1H), 2.25-2.18 (m, 1H), 2.09-1.99 (m, 2H), 1.98-1.92 (m, 2H), 1.36 (s, 3H), 1.26 (s, 3H).

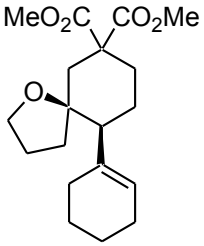
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 172.1, 171.6, 146.0, 133.4, 128.4 (x2), 127.4 (x2), 126.2, 125.8, 81.6, 67.0, 53.5, 52.6, 52.6, 43.7, 38.1, 37.5, 28.0, 26.9, 24.9, 24.4.

IR (CCl_4): ν (cm^{-1}) 3064, 2932, 2856, 1738, 1453, 1435, 1255, 1083.

MS (EI): m/z 372 (M^+), 357, 342, 327, 297.

MS (HRMS EI): m/z 372.1915 (Calcd. for $C_{22}H_{28}O_5$: 372.1937).

rac-(5S,10S)-*10-Cyclohex-1-enyl-1-oxa-spiro[4.5]decane-7,7-dicarboxylic acid dimethyl ester* (15e)



Following procedure **C1** starting with 0.1 mmol of **14e**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 27.2 mg (81%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 5.46 (s, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 3.71-3.66 (m, 1H), 3.54 (ddd, *J* = 15.3 Hz, *J* = 7.7 Hz, *J* = 7.7 Hz, 1H), 2.53-2.46 (m, 2H), 2.38-2.21 (m, 1H), 2.07-1.81 (m, 6H), 1.82 (d, *J* = 14.2 Hz, 1H), 1.75-1.67 (m, 1H), 1.58-1.37 (m, 8H).

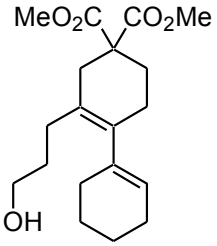
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 173.1, 171,7, 138.9, 124.7, 83.2, 66.9, 53.5, 52.8, 52.6, 52.0, 41.9, 34.7, 31.4, 27.2, 26.0, 25.5, 25.1, 23.3, 22.7.

IR (CCl_4): ν (cm^{-1}) 2952, 1737, 1447, 1434, 1235.

MS (EI): m/z 336 (M^+), 305, 294, 277, 259, 245, 233, 217.

MS (HRMS EI): m/z 336.1939 (Calcd. for $C_{19}H_{28}O_5$: 336.1937).

Dimethyl 4-cyclohexenyl-3-(3-hydroxypropyl)cyclohex-3-ene-1,1-dicarboxylate (16e)



Following procedure **C2** starting with 0.1 mmol of **14e**

Flash chromatography (SiO_2 PE/ AcOEt: 9/1).

Yield: 16.1 mg (48%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 5.29-5.34 (m, 1H), 3.72 (s, 6H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.50 (s, 2H), 2.14-1.99 (m, 7H), 1.95-1.89 (m, 2H), 1.70-1.53 (m, 8H).

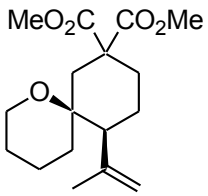
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 172.0 (x2), 139.4, 134.9, 126.6, 123.4, 62.7, 53.6, 52.5 (x2), 33.6, 30.8, 29.7, 28.1, 28.0, 27.0, 25.0, 22.9, 22.2.

IR (CCl_4): ν (cm^{-1}) 3632, 3475, 2934, 1736, 1448, 1253.

MS (EI): m/z 336 (M^+), 291, 276, 258, 245, 218.

MS (HRMS EI): m/z 336.1926 (Calcd. for $C_{19}H_{28}O_5$: 336.1937).

rac-(6S,11S)-*11-Isopropenyl-1-oxa-spiro[5.5]undecane-8,8-dicarboxylic acid dimethyl ester* **(15f)**



Following procedure **C2** starting with 0.1 mmol of **14f**

Flash chromatography (SiO_2 PE/ AcOEt: 95/5).

Yield: 24.8 mg (80%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 4.79 (s, 1H), 4.72 (d, *J* = 2.3 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.51 (m, 2H), 3.16 (dd, *J* = 14.8 Hz, *J* = 2.1 Hz, 1H), 2.50 (ddd, *J* = 12.8 Hz, *J* = 5.6 Hz, *J* = 2.8 Hz, 1H), 2.35 (qd, *J* = 13.1 Hz, *J* = 3.6 Hz, 1H), 1.90 (dd, *J* = 13.0 Hz, *J* = 3.3 Hz, 1H), 1.79 (td, *J* = 13.1 Hz, *J* = 6.4 Hz, 1H), 1.74 (s, 3H), 1.70-1.55 (m, 3H), 1.54 (d, *J* = 14.8 Hz, 1H), 1.47 (td, *J* = 13.1 Hz, *J* = 4.3 Hz, 1H), 1.44-1.34 (m, 2H), 1.20 (d, *J* = 13.5 Hz, 1H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): 173.2, 171.5, 147.8, 113.5, 72.5, 61.4, 55.2, 52.7, 52.6, 52.1, 35.1, 33.1, 31.7, 25.9, 24.0, 21.5, 19.1.

IR (CCl_4): ν (cm^{-1}) 3070, 2950, 2872, 1736, 1446, 1434, 1234, 1085.

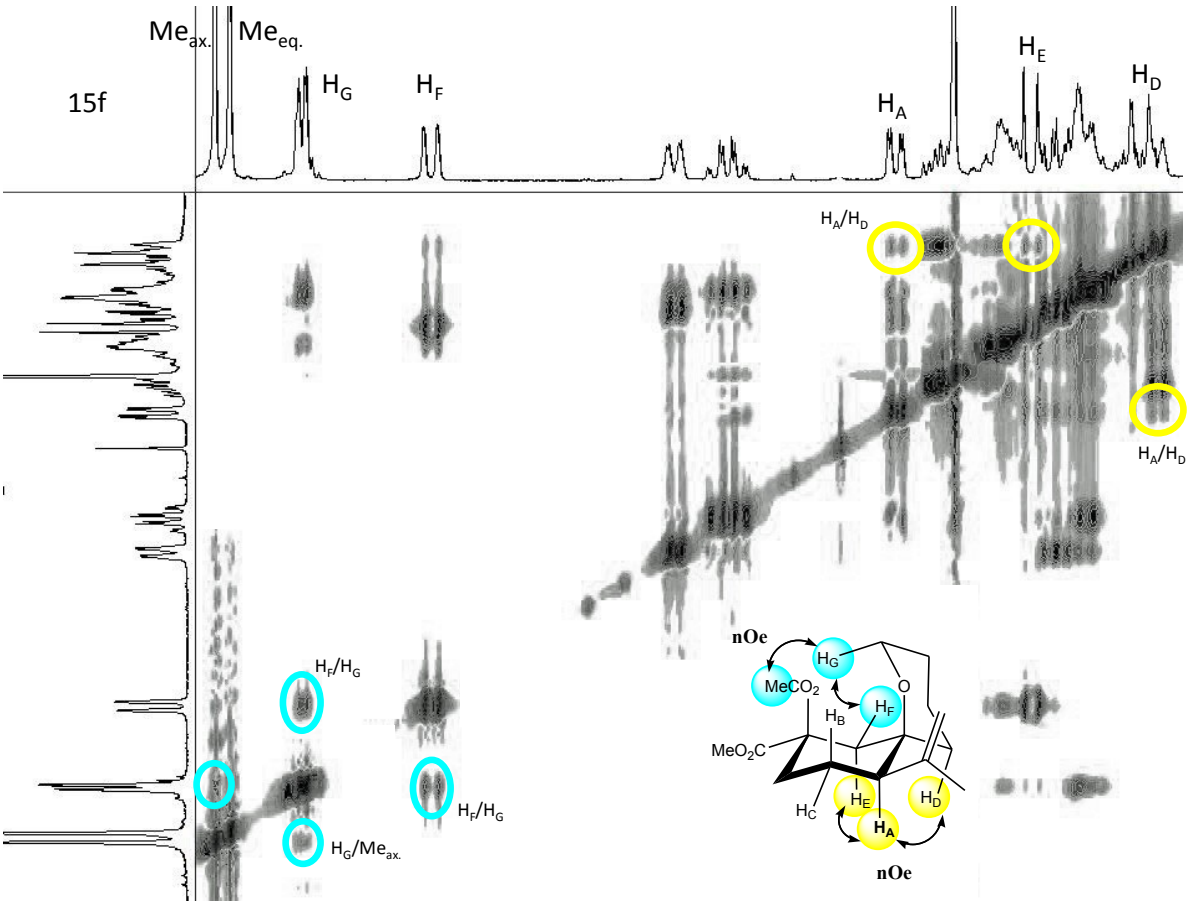
MS (EI): m/z 310 (M^+), 279, 278, 267, 251, 228

MS (HRMS EI): m/z 310.1773 (Calcd. for $C_{17}H_{26}O_5$: 310.1780).

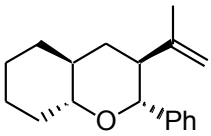
Stereochemistry in 15f:

The proposed relative stereochemistry is in agreement with the observed nOe effects. Moreover, as for compound **10**, the ^{1}H NMR spectrum of compound **15f** is similar to that of a compound described by Sames and coworkers, where the isopropylidene group is replaced by an aldehyde (*J. Am. Chem. Soc.*, **2005**, *127*, 12180).

δ (ppm) H_A: 1.90 (dd, J_{AB} = 13.0 Hz, J_{AC} = 3.3 Hz, 1H).



rac-(2R,3S,4aS,8aR)-*octahydro-2-phenyl-3-(prop-1-en-2-yl)*-2H-*chromene* (23)



Following procedure **C1** starting with 0.1 mmol of **22**

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 21.5 mg (84%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.40-7.23 (m, 5H), 4.64-4.63 (m, 1H), 4.60 (bs, 1H), 4.27 (d, *J* = 10.1 Hz, 1H), 3.18-3.12 (m, 1H), 2.45-2.39 (m, 1H), 2.01-1.95 (m, 1H), 1.85-1.79 (m, 2H), 1.73-1.67 (m, 2H), 1.45 (s, 3H), 1.50-1.25 (m, 5H), 1.13-1.03 (m, 1H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 146.1, 141.2, 128.0 (x2), 127.5, 127.4 (x2), 118.9, 84.3, 82.3, 51.2, 41.9, 37.5, 32.4, 31.6, 25.7, 25.1, 21.4.

IR (CCl_4): ν (cm^{-1}) 3075, 1999, 2858, 1643, 1497, 1451, 1100.

MS (EI): m/z 256 (M^+), 241, 150.

MS (HRMS EI): m/z 256.1859 (Calcd. for $C_{18}H_{24}O$: 256.1827).

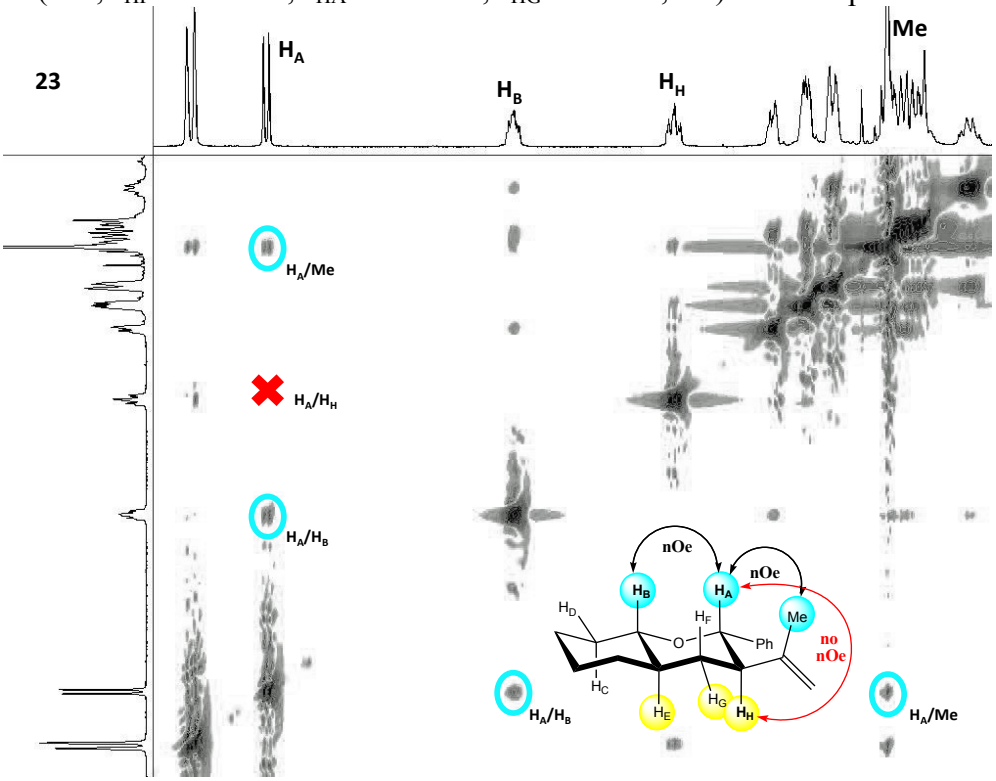
Stereochemistry in 23:

The relative stereochemistry was determined by coupling constants and nOe effects analysis.

δ (ppm) H_A: 4.27 (d, J_{AH} = 10.1 Hz, 1H) => axial position.

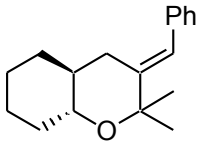
H_B: 3.14 (ddd, J_{BE} = 10.4 Hz, J_{BC} = 9.1 Hz, J_{BE} = 4.0 Hz, 1H) => axial position.

H_H: 2.40 (ddd, J_{HF} = 11.2 Hz, J_{HA} = 10.1 Hz, J_{HG} = 3.7 Hz, 1H) => axial position.



The stereochemistry of compounds **29a-e** was assigned by coupling constant analysis and by analogy with that of compound **23**.

rac-(E,4aS,8aR)-*3-benzylidene-octahydro-2,2-dimethyl*-2H-*chromene* (24)



Following procedure **C2** starting with 0.1 mmol of **22**

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 24.0 mg (94%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.40 (t, *J* = 7.5 Hz, 2H), 7.31-7.25 (m, 3H), 6.51 (d, *J* = 1.3 Hz, 1H), 3.49 (td, *J* = 10.0 Hz, *J* = 4.0 Hz, 1H), 2.82 (dd, *J* = 14.0 Hz, *J* = 4.0 Hz, 1H), 2.06 (ddd, *J* = 14.3 Hz, *J* = 12.6 Hz, *J* = 2.1 Hz, 1H), 1.96-1.83 (m, 2H), 1.79-1.61 (m, 2H), 1.60 (s, 3H), 1.53 (s, 3H), 1.46-1.19 (s, 4H), 1.11 (ddd, *J* = 16.1 Hz, *J* = 12.4 Hz, *J* = 3.2 Hz, 1H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 144.1, 137.8, 129.1 (x2), 128.0 (x2), 126.2, 121.1, 75.4, 74.4, 43.8, 32.8, 31.6, 31.0, 28.1, 25.5, 25.1, 25.0.

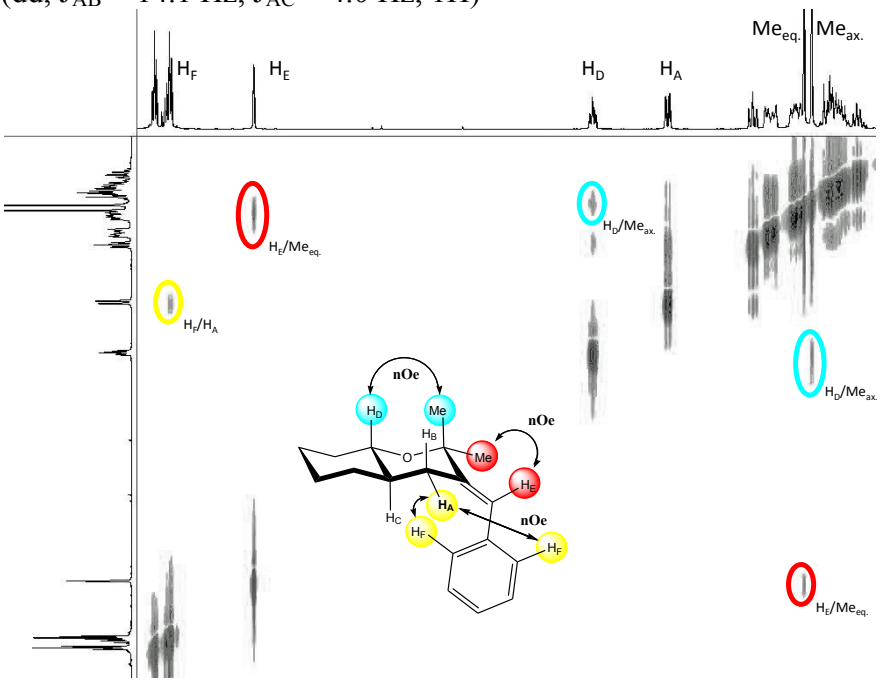
IR (CCl_4): ν (cm^{-1}) 3061, 2987, 2860, 1494, 1449, 1382, 1069.

MS (EI): m/z 256 (M^+), 241, 223, 197, 183.

MS (HRMS EI): m/z 256.1830 (Calcd. for $C_{18}H_{24}O$: 256.1827).

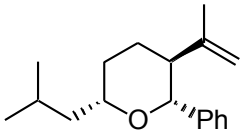
Stereochemistry in 24:

The relative stereochemistry was determined by coupling constants and nOe effects analysis.
δ (ppm) H_A: 2.75 (dd, J_{AB} = 14.1 Hz, J_{AC} = 4.0 Hz, 1H)



The stereochemistry of compounds **30a-e** was assigned by analogy with that of compound **24**.

rac-(2R,3S,6S)-*tetrahydro-6-isobutyl-2-phenyl-3-(prop-1-en-2-yl)*-2H-*pyran* (29a)



Following procedure **C1** starting with 0.1 mmol of **28a**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 22.4 mg (87%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.33-7.22 (m, 5H), 4.64 (quint, *J* = 1.5 Hz, 1H), 4.60 (s, 1H), 4.22 (d, *J* = 10.0 Hz, 1H), 3.55 (dddd, *J* = 11.1 Hz, *J* = 7.4 Hz, *J* = 5.8 Hz, *J* = 1.8 Hz, 1H), 2.26 (ddd, *J* = 11.9 Hz, *J* = 10.1 Hz, *J* = 3.8 Hz, 1H), 1.92 (ddd, *J* = 10.3 Hz, *J* = 6.5 Hz, *J* = 3.8 Hz, 1H), 1.83-1.71 (m, 2H), 1.76 (d, *J* = 11.8 Hz, 1H), 1.55 (ddd, *J* = 13.9 Hz, *J* = 7.1 Hz, *J* = 7.1 Hz, 1H), 1.37-1.48 (m, 1H), 1.45 (s, 3H), 1.29 (ddd, *J* = 13.4 Hz, *J* = 7.5 Hz, *J* = 5.6 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H).

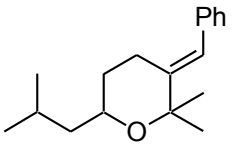
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 146.6, 141.7, 127.9 (x2), 127.5 (x2), 127.4, 111.9, 84.1, 76.5, 50.6, 45.5, 32.0, 30.6, 24.4, 23.1, 22.8, 21.6.

IR (CCl_4): ν (cm^{-1}) 3033, 2957, 1644, 1453, 1369, 1067.

MS (EI): m/z 258 (M^+), 244, 161.

MS (HRMS EI): m/z 258.1971 (Calcd. for $C_{18}H_{26}O$: 258.1984).

***(E)-3-benzylidene-tetrahydro-6-isobutyl-2,2-dimethyl*-2H-*pyran* (30a)**



Following procedure **C2** starting with 0.1 mmol of **28a**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 22.2 mg (86%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.37-7.32 (m, 2H), 7.25-7.20 (m, 3H), 6.45 (s, 1H), 3.86-3.80 (m, 1H), 2.78 (ddd, *J* = 14.3 Hz, *J* = 5.0 Hz, *J* = 4.1 Hz, 1H), 2.41 (tdd, *J* = 11.7 Hz, *J* = 5.6 Hz, *J* = 1.9 Hz, 1H), 1.89-1.79 (m, 1H), 1.73-1.66 (m, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.49-1.43 (m, 1H), 1.40-1.30 (m, 1H), 1.19 (ddd, *J* = 13.0 Hz, *J* = 8.3 Hz, *J* = 4.5 Hz, 1H), 0.94 (dd, *J* = 6.6 Hz, *J* = 2.4 Hz, 6H).

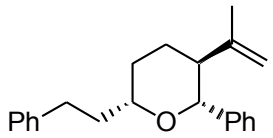
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 144.7, 137.9, 129.0 (x2), 128.0 (x2), 126.1, 121.3, 75.4, 67.8, 45.6, 33.6, 28.6, 24.8, 24.3, 23.4, 23.2, 22.2.

IR (CCl_4): ν (cm^{-1}) 3082, 2957, 1494, 1467, 1368, 1075.

MS (EI): m/z 258 (M^+), 244, 158.

MS (HRMS EI): m/z 258.2001 (Calcd. for $C_{18}H_{26}O$: 258.1984).

rac-(2R,3S,6S)-*tetrahydro-6-phenethyl-2-phenyl-3-(prop-1-en-2-yl)*-2H-*pyran* (29b)



Following procedure **C1** starting with 0.1 mmol of **28b**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 26.0 mg (85%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.36-7.27 (m, 7H), 7.21-7.17 (m, 3H), 4.64 (quint, *J* = 1.5 Hz, 1H), 4.60 (s, 1H), 4.22 (d, *J* = 10.0 Hz, 1H), 3.48 (dddd, *J* = 11.0 Hz, *J* = 6.8 Hz, *J* = 5.0 Hz, *J* = 1.9 Hz, 1H), 2.80-2.67 (m, 2H), 2.28 (ddd, *J* = 11.3 Hz, *J* = 10.3 Hz, *J* = 3.6 Hz, 1H), 2.00-1.89 (m, 2H), 1.85-1.68 (m, 3H), 1.56-1.49 (m, 1H), 1.44 (s, 3H).

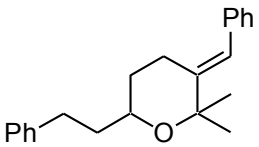
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 146.4, 142.4, 141.5, 128.5 (x2), 128.2 (x2), 128.0 (x2), 127.4(x3), 125.6, 111.9, 84.0, 77.0, 50.5, 37.7, 31.6, 31.5, 30.4, 21.5.

IR (CCl_4): ν (cm^{-1}) 3030, 2932, 2868, 1494, 1453, 1368, 1065.

MS (EI): m/z 306 (M^+), 291, 215, 202.

MS (HRMS EI): m/z 306.1960 (Calcd. for $C_{22}H_{26}O$: 306.1984).

***(E)-3-benzylidene-tetrahydro-2,2-dimethyl-6-phenethyl*-2H-*pyran* (30b)**



Following procedure **C2** starting with 0.1 mmol of **28b**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 26.6 mg (87%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.35-7.24 (m, 4H), 7.23-7.18 (m, 6H), 6.44 (s, 1H), 3.75-3.68 (m, 1H), 2.83-2.64 (m, 3H), 2.35 (dddd, *J* = 14.1 Hz, *J* = 12.0 Hz, *J* = 5.5 Hz, *J* = 1.9 Hz, 1H), 1.82 (dddd, *J* = 13.8 Hz, *J* = 8.8 Hz, *J* = 8.7 Hz, *J* = 5.4 Hz, 1H), 1.74-1.65 (m, 2H), 1.52 (s, 3H), 1.43 (s, 3H), 1.39 (ddd, *J* = 12.5 Hz, *J* = 12.0 Hz, *J* = 5.0 Hz, 1H)

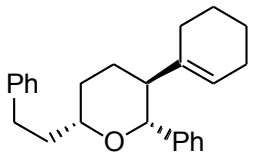
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 144.5, 142.4, 137.9, 129.0 (x2), 128.5 (x2), 128.2 (x2), 128.0 (x2), 126.2, 125.6, 121.4, 75.6, 68.8, 38.0, 33.3, 31.8, 28.5, 24.9, 23.3.

IR (CCl_4): ν (cm^{-1}) 3065, 2937, 1495, 1454, 1223, 1070.

MS (EI): m/z 306 (M^+), 291.

MS (HRMS EI): m/z 306.1994 (Calcd. for $C_{22}H_{26}O$: 306.1984).

rac-(2R,3S,6S)-*3-cyclohexenyl-tetrahydro-6-phenethyl-2-phenyl*-2H-*pyran* (29c)



Following procedure **C1** starting with 0.1 mmol of **28c**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 31.5 mg (91%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.31-7.23 (m, 7H), 7.30-7.16 (m, 3H), 5.30-5.26 (m, 1H), 4.19 (d, *J* = 9.9 Hz, 1H), 3.45 (dddd, *J* = 11.2 Hz, *J* = 6.9 Hz, *J* = 5.1 Hz, *J* = 1.6 Hz, 1H), 2.80-2.65 (m, 2H), 2.04-1.96 (m, 1H), 1.96-1.84 (m, 1H), 1.87-1.71 (m, 7H), 1.53-1.43 (m, 1H), 1.43-1.33 (m, 5H).

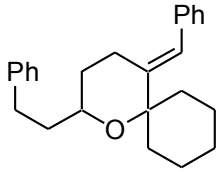
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 142.5, 142.1, 138.1, 128.5 (x2), 128.2 (x2), 127.7 (x2), 127.2 (x2), 127.1, 125.6, 123.2, 84.3, 76.9, 51.3, 37.8, 31.8, 31.6, 29.9, 27.8, 25.2, 22.9, 22.4.

IR (CCl_4): ν (cm^{-1}) 3065, 1495, 1454, 1203, 1065.

MS (EI): m/z 346 (M^+), 256, 244, 224.

MS (HRMS EI): m/z 346.2288 (Calcd. for $C_{25}H_{30}O$: 346.2297).

***2-Phenethyl-5-[1-phenyl-meth-(E)-ylidene]-1-oxa-spiro[5.5]undecane* (30c)**



Following procedure **C2** starting with 0.1 mmol of **28c**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 32.9 mg (95%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.42-7.39 (m, 4H), 7.35-7.30 (m, 3H), 7.25-7.19 (m, 3H), 6.45 (s, 1H), 3.79-3.72 (m, 1H), 3.01 (ddd, *J* = 13.9 Hz, *J* = 10.8 Hz, *J* = 5.4 Hz, 1H), 2.78 (ddd, *J* = 14.3 Hz, *J* = 4.9 Hz, *J* = 3.8 Hz, 1H), 2.68 (ddd, *J* = 13.9 Hz, *J* = 10.6 Hz, *J* = 5.9 Hz, 1H), 2.50-2.37 (m, 2H), 1.96-1.52 (m, 9H), 1.46-1.20 (m, 4H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 145.1, 142.7, 138.1, 129.0 (x2), 128.3 (x2), 128.0 (x2), 127.7 (x2), 127.6, 126.1, 121.3, 75.3, 68.2, 35.6, 36.2, 33.5, 32.6, 31.8, 26.2, 23.1, 21.8, 21.3.

IR (CCl_4): ν (cm^{-1}) 3065, 2935, 1495, 1453, 1211, 1095.

MS (EI): m/z 346 (M^+), 289, 157.

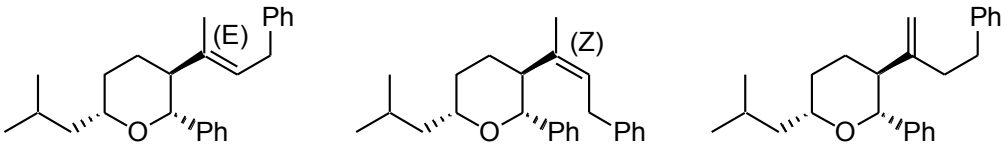
MS (HRMS EI): m/z 346.2295 (Calcd. for $C_{25}H_{30}O$: 346.2297).

rac-(2R,3S,6S)-*6-Isobutyl-3-((E)-1-methyl-3-phenyl-propenyl)-2-phenyl-tetrahydro-pyran*

rac-(2R,3S,6S)-*6-Isobutyl-3-((Z)-1-methyl-3-phenyl-propenyl)-2-phenyl-tetrahydro-pyran*

rac-(2R,3S,6S)-*tetrahydro-6-isobutyl-2-phenyl-3-(4-phenylbut-1-en-2-yl)*-2H-*pyran*

(29d)



Following procedure **C1** starting with 0.1 mmol of **28d**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 30.6 mg (88%) of colorless oil as an unseparable mixture of isomers in a ratio of 9.2:1:3.4.

^{1}H-NMR (400.2 MHz, $CDCl_3$): isomer E: δ 7.36-7.11 (m, 8H), 6.76 (d, *J* = 6.5 Hz, 2H), 5.21 (td, *J* = 7.8 Hz, *J* = 1.0 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 3.60-3.51 (m, 1H), 3.24 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H); 3.15 (dd, *J* = 15.9 Hz, *J* = 6.8 Hz, 1H), 2.31 (ddd, *J* = 11.4 Hz, *J* = 10.3 Hz, *J* = 4.1 Hz, 1H), 1.97-1.71 (m, 4H), 1.59-1.52 (m, 1H), 1.50 (s, 3H), 1.48-1.39 (m, 1H), 1.34-1.26 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): caracteristic peaks of the Z isomer: δ 6.87 (d, *J* = 7.1 Hz, 2H), 5.12 (td, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 4.39 (d, *J* = 10.0 Hz, 1H), 2.93-2.85 (m, 2H), 2.21-2.14 (m, 1H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): caracteristic peaks of the exomethylene isomer: δ 7.00 (d, *J* = 7.1 Hz, 2H), 4.84 (s, 1H), 4.80 (s, 1H), 2.53-2.39 (m, 1H).

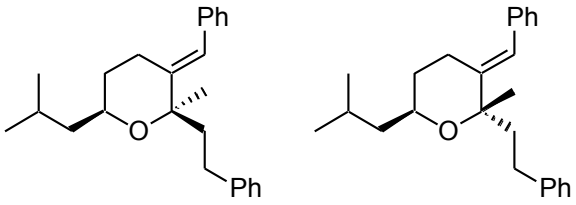
^{13}C-NMR (100.6 MHz, $CDCl_3$): isomer E: δ 141.8, 141.1, 137.0, 128.1 (x4), 128.0 (x2), 127.4 (x2), 127.3, 125.5, 125.2, 83.8, 76.5, 52.7, 45.5, 33.5, 32.0, 30.0, 24.3, 23.0, 22.8, 14.4.

IR (CCl_4): ν (cm^{-1}) 3025, 2957, 1467, 1378, 1130, 1075.

MS (EI): m/z 348 (M^+), 333, 257, 244.

MS (HRMS EI): m/z 348.2446 (Calcd. for $C_{25}H_{32}O$: 348.2453).

***(E)-3-benzylidene-tetrahydro-2-methyl-2,6-diphenethyl-*2H*-pyran* (30d)**



Following procedure **C2** starting with 1 mmol of **28d**

Flash chromatography (SiO_2 PE/ AcOEt: 98/2).

Yield: 29.6 mg (85%) of yellowish oil separated in a ratio of 2.3:1.

^{1}H-NMR (400.2 MHz, $CDCl_3$): major diastereoisomer δ 7.35-7.25 (m, 6H), 7.24-7.17 (m, 4H), 6.39 (s, 1H), 3.78 (tdd, *J* = 10.9 Hz, *J* = 8.7 Hz, *J* = 3.7 Hz, 1H), 2.87 (ddd, *J* = 13.4 Hz, *J* = 12.2 Hz, *J* = 5.0 Hz, 1H), 2.78 (ddd, *J* = 13.4 Hz, *J* = 12.1 Hz, *J* = 5.2 Hz, 1H), 2.70 (ddd, *J* = 14.1 Hz, *J* = 5.4 Hz, *J* = 5.4 Hz, 1H), 2.50 (dddd, *J* = 14.5 Hz, *J* = 10.0 Hz, *J* = 6.0 Hz, *J* = 1.6 Hz, 1H), 2.14 (ddd, *J* = 13.0 Hz, *J* = 12.1 Hz, *J* = 5.0 Hz, 1H), 2.02 (ddd, *J* = 13.5 Hz, *J* = 12.1 Hz, *J* = 5.2 Hz, 1H), 1.91-1.81 (m, 1H), 1.70-1.63 (m, 1H), 1.52-1.44 (m, 1H), 1.48 (s, 3H), 1.42-1.35 (m, 1H), 1.19 (ddd, *J* = 13.5 Hz, *J* = 8.5 Hz, *J* = 4.1 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H).

^{1}H-NMR (400.2 MHz, $CDCl_3$): minor diastereoisomer δ 7.39-7.35 (m, 4H), 7.27-7.17 (m, 6H), 6.50 (s, 1H), 3.94-3.86 (m, 1H), 2.84 (ddd, *J* = 14.5 Hz, *J* = 4.6 Hz, *J* = 3.5 Hz, 1H), 2.72 (ddd, *J* = 14.0 Hz, *J* = 13.4 Hz, *J* = 4.8 Hz, 1H), 2.65 (ddd, *J* = 14.0 Hz, *J* = 13.5 Hz, *J* = 5.2 Hz, 1H), 2.37 (dddd, *J* = 14.5 Hz, *J* = 12.8 Hz, *J* = 5.1 Hz, *J* = 1.8 Hz, 1H), 2.25 (ddd, *J* = 13.4 Hz, *J* = 12.4 Hz, *J* = 4.9 Hz, 1H), 2.01 (ddd, *J* = 13.6 Hz, *J* = 12.6 Hz, *J* = 5.4 Hz, 1H), 1.93-1.84 (m, 1H), 1.74-1.67 (m, 1H), 1.57 (s, 3H), 1.50 (ddd *J* = 13.8 Hz, *J* = 8.3 Hz, *J* = 5.9 Hz, 1H), 1.42-1.33 (m, 1H), 1.23 (ddd, *J* = 13.4 Hz, *J* = 8.1 Hz, *J* = 4.6 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): major diastereoisomer δ 144.1, 143.4, 137.9, 129.0 (x2), 128.5 (x2), 128.3 (x2), 128.0 (x2), 126.2, 125.5, 122.1, 77.2, 67.4, 45.6, 43.1, 32.9, 30.1, 24.4, 23.5, 23.5, 23.4, 22.2.

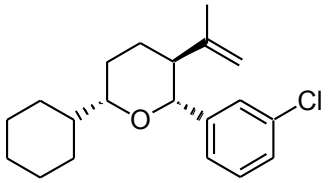
^{13}C-NMR (100.6 MHz, $CDCl_3$): minor diastereoisomer δ 143.7, 142.7, 137.8, 129.1 (x2), 128.4 (x2), 128.3 (x2), 128.0 (x2), 126.3, 125.7, 122.6, 77.2, 67.5, 46.0, 38.3, 33.4, 30.4, 25.2, 24.3, 23.6, 23.3, 22.7.

IR (CCl_4): ν (cm^{-1}) 3027, 2957, 1495, 1454, 1369, 1074.

MS (EI): m/z 348 (M^+), 333, 244.

MS (HRMS EI): m/z 348.2462 (Calcd. for $C_{25}H_{32}O$: 348.2453).

rac-(2R,3S,6S)-*2-(3-chlorophenyl)-tetrahydro-6-phenethyl-3-(prop-1-en-2-yl)*-2H-*pyran* (29e)



Following procedure **C1** starting with 0.1 mmol of **28e**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 23.9 mg (75%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.30 (s, 1H), 7.22-7.19 (m, 2H), 7.16 (ddd, *J* = 9.0 Hz, *J* = 4.4 Hz, *J* = 1.5 Hz, 1H), 4.66 (quint, *J* = 1.5 Hz, 1H), 4.58 (s, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.23 (ddd, *J* = 7.8 Hz, *J* = 5.9 Hz, *J* = 1.5 Hz, 1H), 2.13 (ddd, *J* = 11.7 Hz, *J* = 10.2 Hz, *J* = 3.6 Hz, 1H), 1.92 (ddd, *J* = 10.3 Hz, *J* = 5.8 Hz, *J* = 2.5 Hz, 1H), 1.88-1.80 (m, 1H), 1.78-1.55 (m, 6H), 1.52-1.38 (m, 2H), 1.45 (s, 3H), 1.35-0.93 (m, 5H).

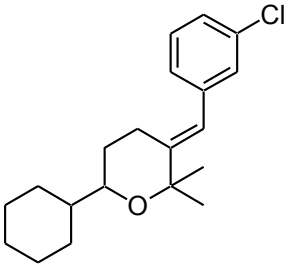
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 146.0, 144.0, 133.7, 129.0, 127.4, 127.3, 125.5, 112.2, 83.3, 82.4, 51.1, 42.9, 30.4, 29.1, 28.4, 27.8, 26.7, 26.3, 26.2, 21.6.

IR (CCl_4): ν (cm^{-1}) 3077, 2929, 2855, 1450, 1066.

MS (EI): m/z 318, 320 (M^+), 239, 237, 180, 178.

MS (HRMS EI): m/z 318.1754 (Calcd. for $C_{20}H_{27}ClO$: 318.1750).

***(E)-3-(3-chlorobenzylidene)-tetrahydro-2,2-dimethyl-6-phenethyl*-2H-*pyran* (30e)**



Following procedure **C2** starting with 0.1 mmol of **28e**

Preparatory thin layer chromatography (SiO_2 PE/ Et_2O: 98/2).

Yield: 22.0 mg (69%) of colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.21-7.16 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.22 (s, 1H), 3.38 (ddd, *J* = 108 Hz, *J* = 7.2 Hz, *J* = 2.9 Hz, 1H), 2.67 (ddd, *J* = 14.3 Hz, *J* = 5.0 Hz, *J* = 5.0 Hz, 1H), 2.37 (dddd, *J* = 14.32 Hz, *J* = 10.7 Hz, *J* = 5.8 Hz, *J* = 1.7 Hz, 1H), 2.03-1.95 (m, 1H), 1.75-1.60 (m, 5H), 1.44 (s, 3H), 1.40 (s, 3H), 1.40-1.10 (m, 5H), 1.01-0.87 (m, 2H).

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 146.9, 139.9, 133.9, 129.3, 129.0, 127.3, 126.3, 120.0, 75.5, 74.2, 43.0, 30.2, 29.5, 28.6, 28.6, 26.7, 26.3, 26.1, 24.8, 23.3.

IR (CCl_4): ν (cm^{-1}) 2980, 2854, 1593, 1450, 1378, 1156.

MS (EI): m/z 318, 320 (M^+), 305, 303, 287, 285, 237, 235, 223, 221.

MS (HRMS EI): m/z 318.1750 (Calcd. for $C_{20}H_{27}ClO$: 318.1750).