Electronic Supplementary Material (ESI) for ChemComm.

Index

General synthetic and analytical methods

Chemicals were purchased from Sigma Aldrich Chemie GmbH (Steinheim, Germany), TCI (Zwijndrecht, Belgium) or Thermo Fisher (Karlsruhe, Germany) and used without purification. Solvents for reactions were dried using a MB SPS-800 system (MBraun (Garching, Germany)). Solvents for column chromatography were purified by distillation. Thin-layer chromatography was performed with 0.2 mm precoated plastic sheets Polygram® Sil G/UV254 (Machery-Nagel (Düren, Germany)). Column chromatography was carried out using Merck (Darmstadt, Germany) silica gel 60 (70-200 mesh) or Florisil (60-100 mesh, Sigma-Aldrich). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker (Billerica, USA) AV I (400 MHz) and AV III HD Prodigy (500 MHz) spectrometers, and were referenced against $CDCl_3$ (δ = 7.26 ppm) and C_6D_6 (δ = 7.16 ppm) for ^{1}H-NMR and $CDCl_3$ (δ = 77.16 ppm) and C_6D_6 (δ = 128.06 ppm) for ^{13}C-NMR. Standard GC-MS analyses were carried out with an Agilent (Santa Clara, USA) HP 7890B gas chromatograph fitted with a HP5-MS silica capillary column (30m, 0.25mm i. d., 0.50 μm film) connected to a HP 5977A inert mass detector. Used MS parameters were 1) transfer line: 250 °C, and 2) electron energy: 70 eV. The GC parameters were 1) inlet pressure: 77.1 kPa, He 23.3 mL min^{-1}, 2) temperature programme: 5 min at 50 °C increasing at 10 °C min^{-1} to 320 °C, 3) injection volume: 1 μL, 4) split ratio50:1, 60 s valve time and 5) carrier gas: He at 1 mL min^{-1}. Retention indices (*I*) were determined from a homologous series of *n*-alkanes (C_8-C_{40}). GC/MS-QTOF analyses for HREI-MS measurements were performed on a 7890B GC equipped with a HP5-MS fused silica capillary column (30 m, 0.25 mm i. d., 0.50 μm film) connected to a 7200 accurate-mass Q-TOF detector (Agilent). MS parameters were 1) transfer line: 250 °C and 2) electron energy: 70 eV. GC parameters were 1) inlet pressure: 83.2 kPa, He at 24.6 mL min^{-1}, 2) temperature program: 5 min at 50 °C increasing at 10 °C min^{-1} to 320 °C, 3) injection volume: 1 μL, 4) split ratio: 50:1, 60 s valve time, and 5) carrier gas: He at 1 mL min^{-1}. Optical rotary powers were recorded on a P8000 Polarimeter (Krüss). IR Spectra were measured with a Bruker Alpha FT-IR spectrometer. The intensities of the peaks were described as s (strong), m (medium), and w (weak). UV/Vis spectra were recorded on a Cary 100 UV/Vis spectrometer (Agilent).

Culture conditions and sampling

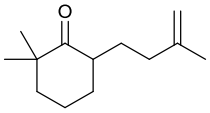
For analysis of the volatile terpenes, agar plate cultures of *Fusarium sporotrichioides* DSM 62425 on solid CM medium and of *Penicillium decumbens* DSM 845 on solid PDA medium were inoculated with one piece of a pre-culture grown on the same medium. Cultures were grown for 5 days at 28°C in the dark. The emitted volatile compounds were trapped on a charcoal filter using the CLSA technique.[1,2] The collected material was extracted with dichloromethane (50 μL), and the extract was directly subjected to GC-MS analysis.

CM medium: Salt solution (50 mL L^{-1}), micronutrient solution (1 mL L^{-1}), vitamin solution (1 mL L^{-1}), yeast extract (1 g L^{-1}), peptone (2 g L^{-1}), casamino acids (1 g L^{-1}), glucose (10 g L^{-1}), agar (15 g L^{-1}).
Salt solution: KCl (10.4 g L^{-1}), $MgSO_4 \cdot 7H_2O$ (10.4 g L^{-1}), KH_2PO_4 (30.4 g L^{-1}).
Micronutrient solution: $FeSO_4 \cdot 7\ H_2O$ (10 g L^{-1}), $MgSO_4 \cdot 7\ H_2O$ (50 g L^{-1}).
Vitamin solution: Biotin (0.5 g L^{-1}), nicotinic acid (50 g L^{-1}), 4-aminobenzoic acid (16 g L^{-1}) and pyridoxal hydrochloride (20 g L^{-1}).

PDA medium: Potato infusion (1 L), glucose (20 g L^{-1}) and agar (15 g L^{-1}).
Potato infusion: Potatoes (200 g), were sliced, scrubbed and boiled in water (1 L) for 1 h. The resulting infusion was passed through a cotton cloth to remove solid material.

Synthetic procedures

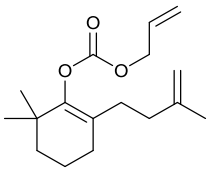
2,2-Dimethyl-6-(3-methylbut-3-en-1-yl)cyclohexan-1-one (8)



n-Butyllithium (1.6 M in hexane, 5.20 mL, 8.32 mmol, 1.05 eq) was added dropwise to a solution of diisopropylamine (842 mg, 8.32 mmol, 1.05 eq) in THF (40 mL) at 0 °C under argon atmosphere. The resulting mixture was stirred for 30 min at 0 °C and subsequently cooled to –78 °C. 2,2-Dimethylcyclohexanone (**7**, 1.00 g, 7.92 mmol, 1.00 eq) dissolved in HMPA (2.84 g, 15.85 mmol, 2.0 eq) was added dropwise and the pale blue mixture was warmed to –40 °C over 2 h. After cooling to –78 °C, 4-iodo-2-methylbut-1-ene (**12**) (2.33 g, 11.89 mmol, 1.50 eq) was added dropwise, the reaction mixture was stirred at a temperature of –78 °C for 30 min and subsequently warmed to room temperature over 18 h. NH_4Cl solution (sat., 40 mL) was added and the biphasic mixture was diluted with water (100 mL) and Et_2O (40 mL). The aqueous layer was extracted with Et_2O (40 mL) and the combined organic layers were washed with HCl (1 M, 2x 100 mL), dried with $MgSO_4$, filtrated and concentrated *in vacuo*. Column chromatography (silica gel, petroleum ether/Et_2O 60:1) yielded **8** (458 mg, 2.36 mmol, 30%) as a colourless oil.

TLC (petroleum ether/Et_2O 60:1): R_f = 0.40. **GC** (HP-5): I = 1381. **^{1}H-NMR** (400 MHz, C_6D_6): δ = 4.81 (m, 2H, CH_2), 2.33-2.24 (m, 1H, CH), 2.18-2.08 (m, 1H, CH_2), 2.07-1.94 (m, 2H, CH_2), 1.76-1.68 (m, 1H, CH_2), 1.67 (br s, 3H, CH_3), 1.54-1.38 (m, 2H, CH_2), 1.31-1.21 (m, 3H, CH_2), 1.10 (s, 3H, CH_3), 1.08-0.95 (m, 1H, CH_2), 0.92 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100 MHz, C_6D_6): δ = 214.3 (C_q), 146.0 (C_q), 110.4 (CH_2), 45.36 (CH), 45.35 (C_q), 42.0 (CH_2), 35.9 (CH_2), 34.9 (CH_2), 28.1 (CH_2), 26.1 (CH_3), 24.9 (CH_3), 22.5 (CH_3), 21.9 (CH_2) ppm. **IR** (ATR): $\tilde{\nu}$ = 3072 (w), 2966 (w), 2929 (m), 2866 (w), 1703 (s), 1648 (w), 1451 (m), 1384 (w), 1372 (w), 1036 (w), 884 (m), 860 (w), 431 (w) cm^{-1}. **UV/Vis** (MeOH): λ_{max} (lg ε): 204 (1.537) nm. **EI-MS** (70 eV): *m/z* (%) = 194 (17), 170 (7), 126 (74), 111 (100), 95 (29), 82 (25), 81 (26), 70 (72), 69 (40), 67 (33), 55 (57), 43 (34), 41 (63), 29 (22) cm^{-1}. **HREI-MS** calcd. for $C_{13}H_{22}O^{\bullet+}$: 194.1671, found: 194.1669.

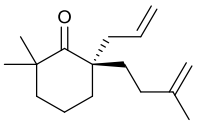
Allyl (6,6-dimethyl-2-(3-methylbut-3-en-1-yl)cyclohex-1-en-1-yl) carbonate (9)



Compound **8** (786 mg, 4.05 mmol, 1.0 eq), dissolved in THF (7 mL), was added dropwise to a solution of NaHMDS (4.85 mmol, 1.2 eq) in THF (25 mL) at 0 °C under argon atmosphere. The mixture was stirred for 10 min and cooled to –78 °C. Allyl chloroformate (634 mg, 5.26 mmol, 1.3 eq), dissolved in THF (15 mL), was added dropwise. The solution turned to deep red and was slowly warmed to room temperature overnight. The resulting yellow suspension was quenched by the addition of water (10 mL), NH_4Cl solution (sat. 10 mL) and hexane (10 mL). The biphasic mixture was stirred for 30 min before the layers were separated. The aqueous layer was extracted with Et_2O (3x 20 mL) and the combined organic layers were washed with brine (60 mL), dried with $MgSO_4$, filtrated and concentrated *in vacuo*. Column chromatography (silica gel, petroleum ether/Et_2O 100:1) produced **9** (779 mg, 2.93 mmol, 72%) as a colourless oil.

TLC (petroleum ether/Et_2O 40:1): R_f = 0.45. **GC** (HP-5): I = 1721. **^{1}H-NMR** (500 MHz, C_6D_6): δ = 5.70 (ddt, $^3J_{H,H}$ = 5.6 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 17.2 Hz, 1H, CH), 5.14 (ddt, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 17.2 Hz, $^2J_{H,H}$ = 1.5 Hz, 1H, CH_2), 4.95 (ddt, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 10.5 Hz, $^2J_{H,H}$ = 1.3 Hz, 1H, CH_2), 4.82-4.80 (m, 1H, CH_2), 4.79-4.77 (m, 1H, CH_2), 4.44 (dt, $^4J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 5.6 Hz, 2H, CH_2), 2.21-2.11 (m, 4H, 2x CH_2), 1.90-1.86 (m, 2H, CH_2), 1.67 (s, 3H, CH_3), 1.49-1.39 (m, 4H, 2x CH_2), 1.16 (s, 6H, 2x CH_3) ppm. **^{13}C-NMR** (125 MHz, C_6D_6): δ = 154.2 (C_q), 148.6 (C_q), 145.7 (C_q), 132.3 (CH), 124.5 (C_q), 118.2 (CH_2), 110.4 (CH_2), 68.4 (CH_2), 39.6 (CH_2), 35.5 (C_q), 35.4 (CH_2), 29.6 (CH_2), 29.0 (CH_2), 27.3 (2x CH_3), 22.5 (CH_3), 19.5 (CH_2) ppm. **IR** (ATR): $\tilde{\nu}$ = 2965 (w), 2932 (w), 2867 (w), 1754 (s), 1683 (w), 1649 (w), 1454 (w), 1362 (w), 1291 (m), 1230 (s), 1152 (m), 1128 (w), 1985 (w), 1058 (w), 1022 (m), 992 (m), 936 (w), 886 (m), 849 (w), 782 (m), 554 (w), 519 (w), 435 (w) cm^{-1}. **UV/Vis** (MeCN): λ_{max} (lg ε): No absorption > 200 nm. **EI-MS** (70 eV): *m*/*z* (%) = 193 (5), 179 (9), 178 (7), 177 (7), 176 (25), 135 (11), 125 (5), 123 (9), 121 (15), 119 (9), 110 (7), 109 (69), 107 (13), 105 (11), 97 (8), 96 (8), 95 (76), 85 (13), 83 (35), 80 (12), 69 (50), 67 (46), 55 (37), 53 (7), 44 (11), 43 (30), 41 (100), 39 (13). **HRESI-MS** calcd. for $C_{17}H_{26}O_3Na^+$: 301.1774, found: 301.1774.

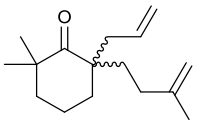
(*R*)-2-Allyl-6,6-dimethyl-2-(3-methylbut-3-en-1-yl)cyclohexan-1-one (10)



Bis(3,5,3′,5′-dimethoxydibenzylideneacetone)palladium(0) (Pd(dmdba)$_2$, 188 mg, 0.23 mmol, 0.1 eq) and (*S*)-4-*tert*-Butyl-2-[2-(diphenylphosphino)phenyl]-2-oxazoline ((*S*)-*t*-Bu-PHOX, **13**, 112 mg, 0.29 mmol, 0.13 eq) were dissolved in benzene (60 mL, degassed by an argon stream for 1.5 h) under argon atmosphere at room temperature. After stirring the brown-yellow suspension for 30 min at room temperature and cooling to 10 °C, **9** (644 mg, 2.31 mmol, 1.0 eq), dissolved in degassed benzene (5 mL), was added dropwise. The resulting mixture was stirred for 15 h, maintaining 10 °C, concentrated under reduced pressure and subjected to column chromatography (silica gel, petroleum ether/Et_2O 100:1), yielding **10** (415 mg, 1.77 mmol, 76%) as a colourless oil. GC analysis on a homochiral stationary phase showed an *ee* of 82% (Fig. S1).

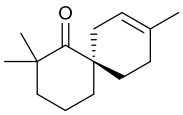
Optical rotary power: $[\alpha]_D^{21.0}$ = +2.7 (*c* 0.11, CH_2Cl_2). **TLC** (petroleum ether/Et_2O 20:1): R_f = 0.78. **GC** (HP-5): *I* = 1592. **^{1}H-NMR** (400 MHz, C_6D_6): δ = 5.71 (dddd, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 16.9 Hz, 1H, CH), 5.04-4.99 (m, 1H, CH_2), 5.02-4.95 (m, 1H, CH_2), 4.79-4.75 (m, 2H, CH_2), 2.38 (dddd, $^4J_{H,H}$ = 1.3 Hz, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 6.6 Hz, $^2J_{H,H}$ = 13.9 Hz, 1H, CH_2), 2.19 (dddd, $^4J_{H,H}$ = 0.9 Hz, $^4J_{H,H}$ = 0.9 Hz, $^3J_{H,H}$ = 8.0 Hz, $^2J_{H,H}$ = 13.9 Hz, 1H, CH_2), 2.05-1.94 (m, 1H, CH_2), 1.86-1.76 (m, 1H, CH_2), 1.74-1.64 (m, 2H, CH_2), 1.64 (br s, 3H, CH_3), 1.59-1.40 (m, 3H, CH_2), 1.40-1.31 (m, 3H, CH_2), 1.05 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100 MHz, C_6D_6): δ = 216.5 (C_q), 146.0 (C_q), 135.1 (CH), 118.0 (CH_2), 110.3 (CH_2), 50.9 (C_q), 44.4 (C_q), 42.1 (CH_2), 39.8 (CH_2), 36.1 (CH_2), 35.1 (CH_2), 32.8 (CH_2), 27.8 (CH_3), 27.1 (CH_3), 22.7 (CH_3), 17.9 (CH_2) ppm. **IR** (ATR): $\tilde{\nu}$ = 2932 (m), 2867 (w), 1692 (m), 1649 (w), 1454 (m), 1381 (w), 1360 (w), 1291 (w), 1265 (w), 1115 (w), 993 (m), 914 (m), 885 (m) cm^{-1}. **UV/Vis** (MeCN): λ_{max} (lg ε): No absorption > 200 nm. **EI-MS** (70 eV): *m*/*z* (%) = 234 (5), 193 (40), 178 (6), 177 (5), 167 (10), 166 (100), 165 (6), 151 (36), 138 (5), 137 (5), 135 (9), 133 (8), 125 (11), 123 (16), 121 (9), 110 (20), 109 (22), 108 (8), 107 (18), 105 (7), 98 (11), 97 (12), 95 (35), 94 (23), 93 (19), 91 (10), 82 (16), 81 (25), 80 (9), 79 (27), 77 (8), 70 (8), 69 (56), 67 (29), 55 (27), 53 (11), 43 (32), 41 (51), 39 (12). **HREI-MS** calcd. for $C_{16}H_{26}O^{\bullet+}$: 234.1978, found: 234.1970.

(*rac*)-2-Allyl-6,6-dimethyl-2-(3-methylbut-3-en-1-yl)cyclohexan-1-one ((*rac*)-10)



Compound (*rac*)-**10** (239 mg, 1.02 mmol, 35%) was obtained by the same procedure as (*R*)-**10** starting from **9** (795 mg, 2.88 mmol, 1.0 eq), only the ligand **13** (0.13 eq) was substituted by triphenylphosphine (0.25 eq). NMR spectra showed the same signals as for (*R*)-**10**.

(*R*)-2,2,9-Trimethylspiro[5.5]undec-8-en-1-one (11)

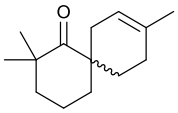


Grubbs-Hoveyda-II catalyst (42 mg, 0.07 mmol, 0.05 eq), was added to a solution of **10** (314 mg, 1.34 mmol, 1.0 eq) in benzene (15 mL, degassed by a stream of argon for 1.5 h) under argon atmosphere. The resulting green suspension was warmed to 60 °C, stirred for 7.5 h, cooled to room temperature and concentrated *in vacuo*. The residue was purified via column chromatography (silica gel, petroleum ether/Et_2O 40:1), yielding **11** (262 mg, 1.27 mmol, 95%) as a colourless oil.

Optical rotary power: $[\alpha]_D^{21.0}$ = +56.9 (*c* 0.12, CH_2Cl_2). **TLC** (petroleum ether/Et_2O 40:1): R_f = 0.28. **GC** (HP-5): *I* = 1556. **^{1}H-NMR** (400 MHz, C_6D_6): δ = 5.24-5.21 (m, 1H, CH), 2.38-2.28 (m, 1H, CH_2), 2.20-2.09 (m, 1H, CH_2), 1.91-1.83 (m, 1H, CH_2), 1.76-1.70 (2H, CH_2), 1.66-1.55 (m, 1H, CH_2), 1.57 (s, 3H, CH_3), 1.52-1.44 (m, 1H, CH_2), 1.44-1.37 (m, 4H, 2x CH_2), 1.36-1.26 (m, 1H, CH_2), 1.10 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm. **^{13}C-NMR** (100 MHz, C_6D_6): δ = 217.9 (C_q), 132.3 (C_q), 119.3 (CH), 46.0 (C_q), 44.6 (C_q), 40.1 (CH_2), 34.6 (CH_2), 33.7 (CH_2), 31.2 (CH_2), 28.0 (CH_3), 27.4 (CH_3), 26.9 (CH_2), 23.4 (CH_3), 18.0 (CH_2) ppm. **IR** (ATR): $\tilde{\nu}$ = 2960 (m), 2927 (m), 2868 (m), 2853 (m), 1767 (w), 1693 (s), 1449 (m), 1381 (w), 1361 (w), 1268 (w),1214 (w), 1121 (m), 1065 (w), 1045 (w), 990 (m), 943 (w), 861 (w), 803 (w), 548 (w), 435 (w) cm^{-1}. **UV/Vis** (MeCN): λ_{max} (lg ε): No absorption > 200 nm. **EI-MS** (70 eV): *m*/*z* (%) = 207 (11), 206 (100), 191 (19), 164 (11), 163 (25), 150 (13), 149 (33), 137 (13), 136 (49), 135 (29), 134 (45), 131 (16), 123 (18), 122 (14), 121 (46), 120 (11), 119 (18), 118 (21), 111 (9), 109 (17), 108 (44), 107 (62), 106 (9), 105 (23), 95 (36), 94 (32), 93 (75), 92 (15), 91 (39), 82 (11), 81 (25), 80

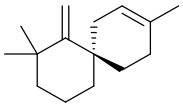
(12), 79 (53), 77 (28), 69 (33), 68 (16), 67 (19), 65 (9), 55 (25), 53 (13), 43 (19), 41 (36), 39 (11). **HREI-MS** calcd. for $C_{14}H_{22}O^{\bullet+}$: 206.1665, found: 206.1660.

(*rac*)-2,2,9-Trimethylspiro[5.5]undec-8-en-1-one ((*rac*)-11)



Compound (*rac*)-**11** (150 mg, 0.73 mmol, 77%) was obtained by the same procedure as (*R*)-**11**, starting from (*rac*)-**10** (219 mg, 0.94 mmol, 1.0 eq). NMR spectra showed the same signals as for (*R*)-**11**.

(+)-(*R*)-Isochamigrene ((*R*)-5)

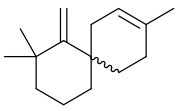


n-Butyllithium (1.6 M in hexane, 1.19 mL, 1.91 mmol, 3.9 eq) was added to a suspension of dimethyldiphenylphosphonium iodide (**14**, 252 mg, 0.75 mmol, 1.5 eq) in THF (5 mL) under argon atmosphere at –10 °C. The resulting mixture was stirred for 30 min maintaining –10 °C and subsequently for 1.5 h at room temperature. The mixture was cooled to 0 °C, **11** (100 mg in 1 mL THF, 0.49 mmol, 1.0 eq) was added dropwise and stirring was continued for 20 min at 0 °C and for 2 h at room temperature. *t*-BuOH (182 mg, 2.45 mmol, 5.0 eq) was added dropwise, leading to formation of a colourless precipitate and the resulting suspension was diluted with water (20 mL). The mixture was extracted with pentane (3x 10 mL) and the combined organic layers were washed with brine (40 mL), dried with $MgSO_4$, filtrated and concentrated under reduced pressure. Column chromatography (silica gel, pentane) yielded (*R*)-**5** (86 mg, 0.42 mmol, 86%) as a colourless oil.

Optical rotary power: $[\alpha]_D^{21.0}$ = +24.9 (*c* 0.20, CH_2Cl_2). **TLC** (pentane): R_f = 0.80. **GC** (HP-5): *I* = 1494. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 5.31-5.27 (m, 1H, CH), 5.00 (s, 1H, CH_2), 4.91 (s, 1H, CH_2), 2.13-2.02 (m, 2H, CH_2), 2.00-1.93 (m, 1H, CH_2), 1.93-1.77 (m, 2H, CH_2), 1.70-1.64 (m, 1H, CH_2), 1.64-1.61 (m, 3H, CH_3), 1.60-1.52 (m, 2H, CH_2), 1.44-1.32 (m, 3H, CH_2), 1.27-1.20 (m, 1H, CH_2), 1.14 (s, 3H, CH_3), 1.12 (s, 3H, CH_3) ppm.

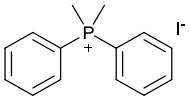
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 161.3 (C_q), 133.2 (C_q), 120.4 (CH), 107.3 (CH_2), 41.6 (CH_2), 39.5 (CH_2), 37.9 (C_q), 37.5 (CH_2), 36.8 (C_q), 33.7 (CH_2), 31.8 (CH_3), 31.2 (CH_3), 28.0 (CH_2), 23.3 (CH_3), 18.6 (CH_2) ppm. **IR** (ATR): $\tilde{\nu}$ = 2960 (m), 2922 (m), 2909 (m), 2868 (m), 2843 (m), 1621 (w), 1447 (m), 1377 (w), 1359 (w), 1192 (w), 1147 (w), 1091 (w), 1060 (w), 1015 (w), 994 (w), 856 (m), 766 (w), 663 (w) cm^{-1}. **UV/Vis** (MeCN): λ_{max} (lg ε): No absorption > 200 nm. **EI-MS** (70 eV): *m*/*z* (%) = 204 (19), 190 (15), 189 (100), 175 (9), 162 (7), 163 (15), 148 (10), 147 (13), 136 (7), 133 (25), 121 (36), 106 (8), 105 (24), 95 (8), 94 (9), 93 (22), 91 (14), 81 (7), 79 (11), 77 (6). **HREI-MS** calcd. for $C_{15}H_{24}^{\bullet+}$: 204.1873, found: 204.1874.

(*rac*)-Isochamigrene ((*rac*)-5)



Racemic isochamigrene ((*rac*)-**5**, 49 mg, 0.24 mmol, quant.) was obtained by the same procedure as (*R*)-**5**, starting from (*rac*)-**11** (50 mg, 0.24 mmol, 1.0 eq). NMR spectra showed the same signals as for (*R*)-**5**.

Dimethyldiphenylphosphonium iodide (14)



MeI (3.79 g, 26.9 mmol, 5.0 eq) was added to a suspension of diphenylphosphine (1.00 g, 5.37 mmol, 1.0 eq) and K_2CO_3 (1.48 g, 10.7 mmol, 2 eq) in THF (20 mL) under argon atmosphere and stirred at room temperature for 4 d. The produced colourless precipitate was collected and washed with Et_2O. The obtained solid material was dissolved in chloroform, the remaining solid was filtered off and the clear solution was concentrated *in vacuo*, producing **14** (1.12 g, 3.27 mmol, 61%) as a colourless solid.

^{1}H-NMR (500 MHz, DMSO-d_6): δ = 7.96-7.90 (m, 4H, 4x CH), 7.84-7.79 (m, 2H, 2x CH), 7.74-7.69 (m, 4H, 4x CH), 2.67 (s, 3H, CH_3), 2.64 (s, 3H, CH_3) ppm. **^{13}C-NMR** (125 MHz, DMSO-d_6): δ = 134.18 (CH), 134.16 (CH), 131.9 (2x CH), 131.8 (2x CH), 129.7 (2x CH),

129.6 (2x CH), 122.3 (C_q), 121.6 (C_q), 7.9 (CH_3), 7.4 (CH_3) ppm. **^{31}P-NMR** (202 MHz, DMSO-d_6): $\delta = 21.9$ ppm.

GC analyses on a homochiral stationary phase

The separation of the enantiomers of **10** was conducted on an Agilent 7820A gas chromatograph with a fused Cyclosil-B column (Agilent, 30 m length, 0.25 mm diameter, 0.25 mm film) with settings 1) inlet pressure: 89.1 kPa, 2) N_2: 23.3 mL/min, 3) injection volume: 1 μL, 4) temperature programme: Starting temperature 60 °C, increasing at a rate of 0.25 °C min^{-1} to 123 °C, then increasing at a rate of 20 °C min^{-1} to 245 °C, holding the temperature for 5 min, 5) split ratio: 10:1, valve time 60 s.

The determined *ee* of (*R*)-**10** was 82%.

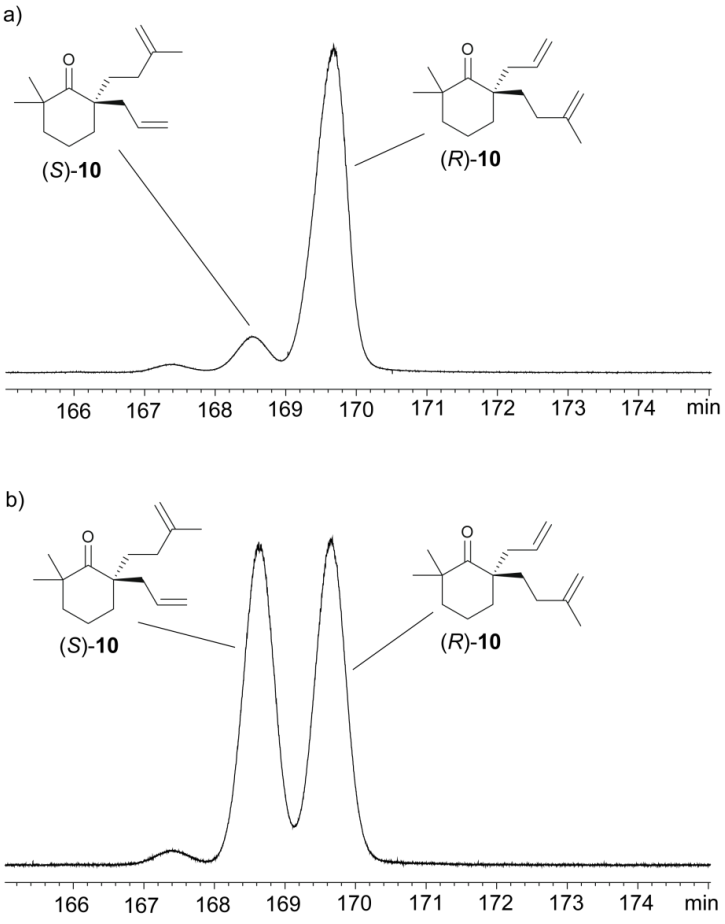


Figure S1. Separation of the enantiomers of **10** via GC on a homochiral stationary phase. a) Synthetic (*R*)-**10** (82% *ee*); b) synthetic (*rac*)-**10**.

GC-MS analyses on a homochiral stationary phase

Chiral GC-MS analyses of terpene mixtures and headspace extracts were carried out with a HP 7890B gas chromatograph with a fused Cyclosil-B column (Agilent, 30 m length, 0.25 mm diameter, 0.25 mm film) connected to a HP 5977A inert mass detector. MS parameters were 1) 250 °C at the transfer line and 2) 70 eV electron ionisation energy. GC parameters were 1) 77.1 kPa inlet pressure, 2) He: 23.3 mL/min, 3) injection volume: 1 μL, 4) temperature programme: Starting temperature 50 °C, increasing at a rate of 5 °C min^{-1} to 200 °C holding the temperature for 5 min, 5) splitless mode, valve time 60 s.

For comparison of retention, commercial standards of (–)-(*R*)-**15** and (–)-**20** were used, as well as the headspace extract from *Penicillium decumbens* DSM 845, which contains (+)-**20** as the major constituent.[3]

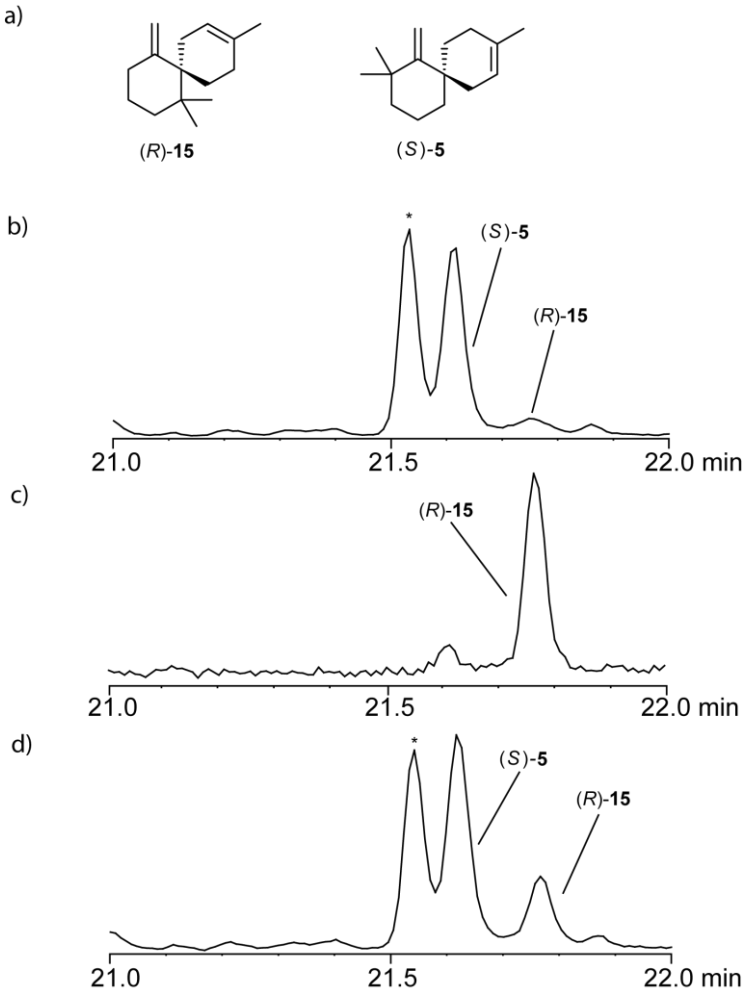


Figure S2. Analysis of **15** by GC-MS on a homochiral stationary phase. a) structures of identified signals; b) headspace extract of *F. sporotrichioides*; c) commercial standard of (*R*)-**15**; d) coinjection of b + c. The marked signal corresponds to (*E*)-β-farnesene.

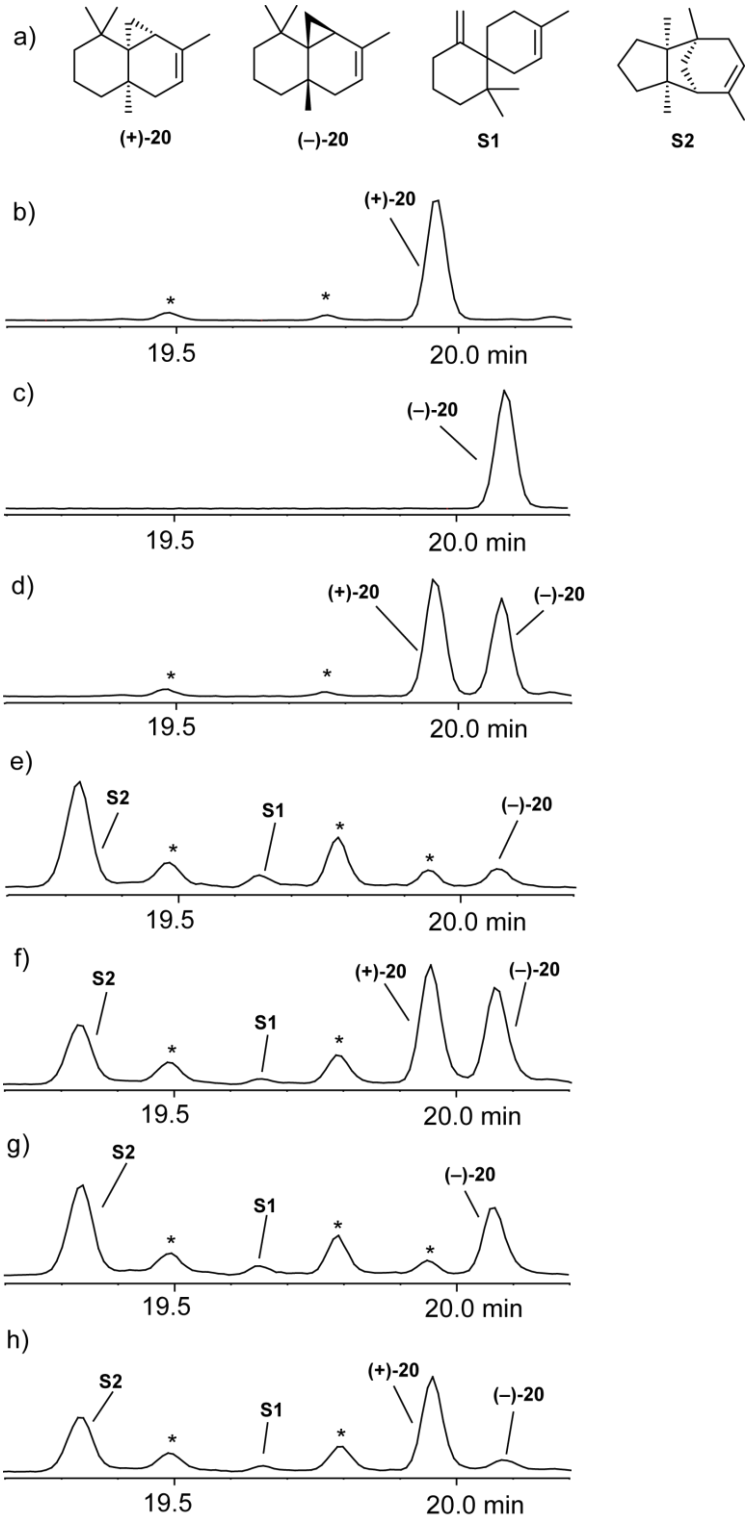


Figure S3. Analysis of the composition of (+)- and (–)-**20** by GC-MS on a homochiral stationary phase. a) Compound structures for identified signals; b) headspace extract from *P. decumbens*; c) commercial standard of (–)-**20**; d) coinjection b + c; e) headspace extract from *F. sporotrichioides*; f) coinjection d + e; g) coinjection c + e; h) b + e. Unidentified signals are marked with asterisks.

NMR spectra

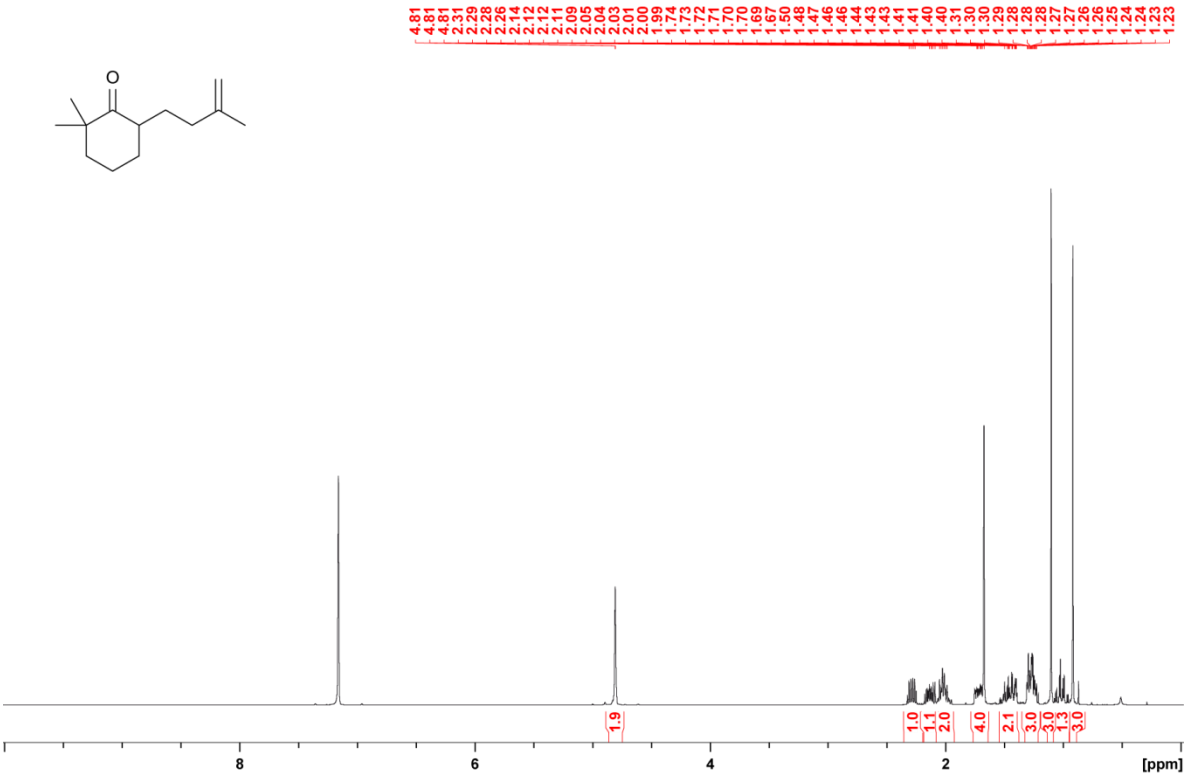


Figure S4. ^{1}H-NMR spectrum of **8** (400 MHz, C_6D_6).

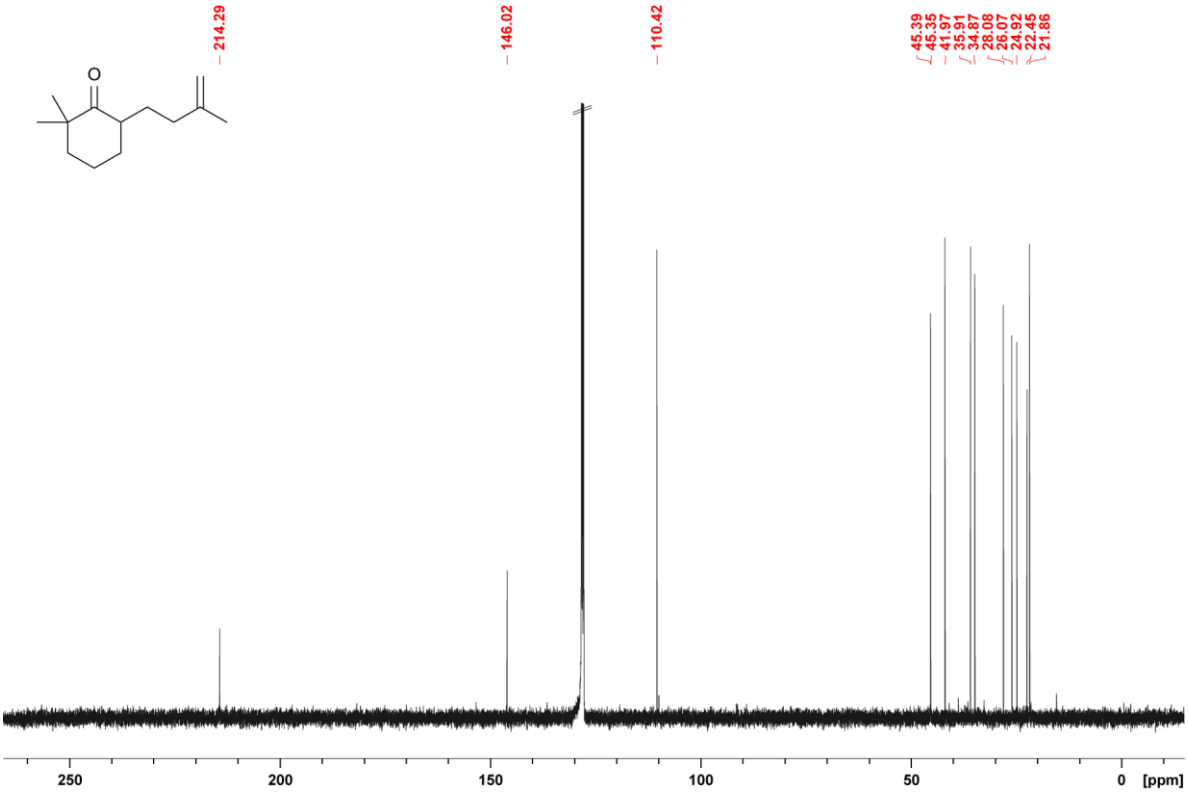


Figure S5. ^{13}C-NMR spectrum of **8** (100 MHz, C_6D_6).

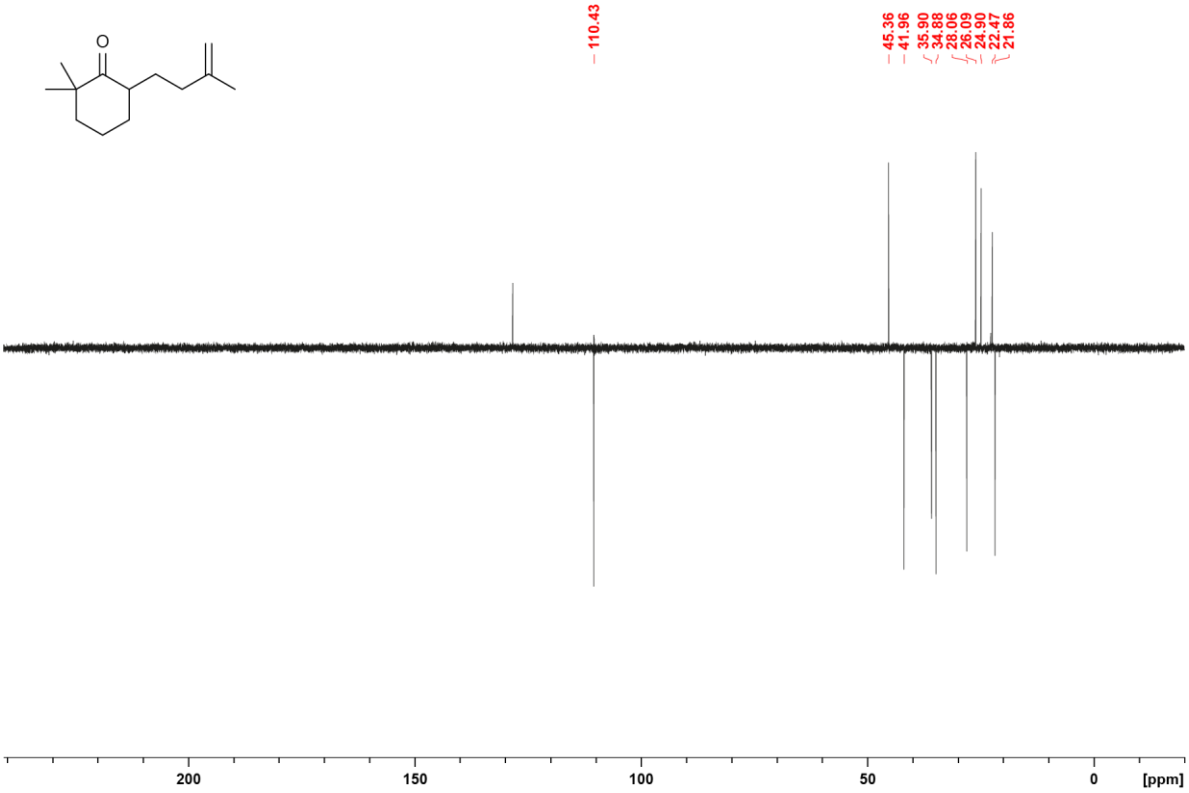


Figure S6. DEPT spectrum of **8** (100 MHz, C_6D_6).

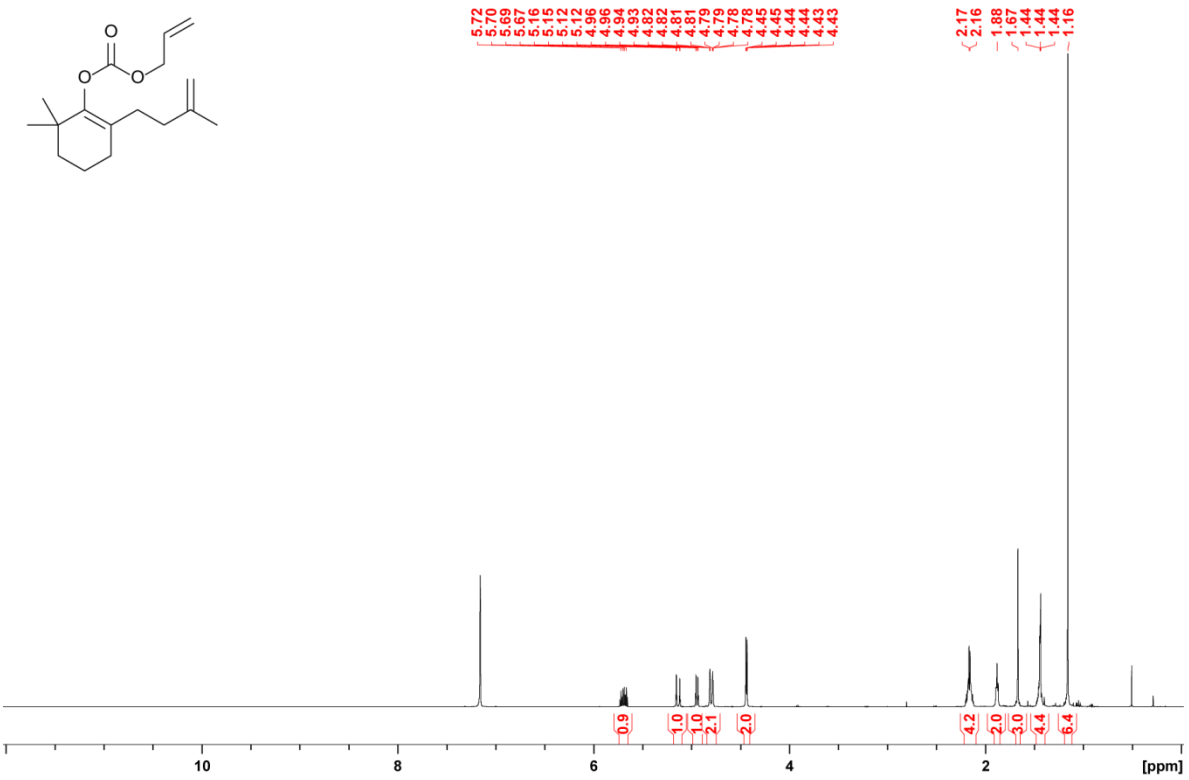


Figure S7. ^{1}H-NMR spectrum of **9** (500 MHz, C_6D_6).

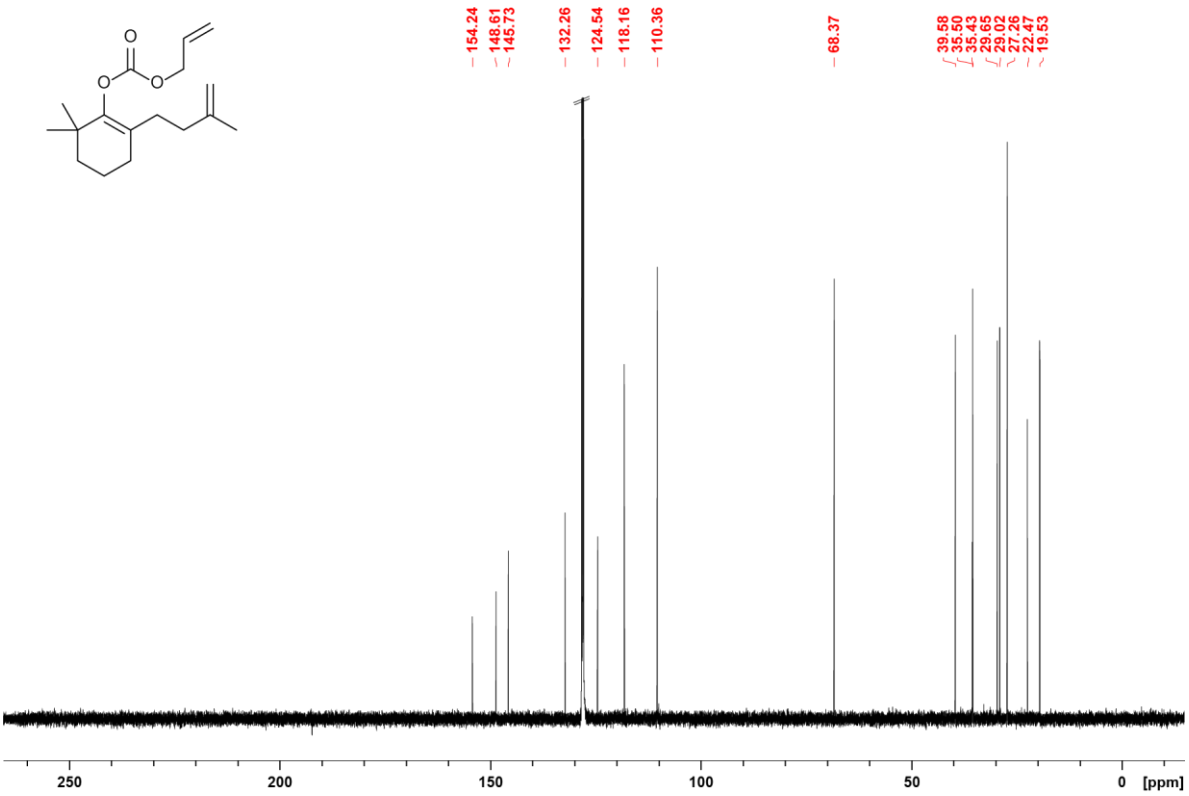


Figure S8. ^{13}C-NMR spectrum of **9** (125 MHz, C_6D_6).

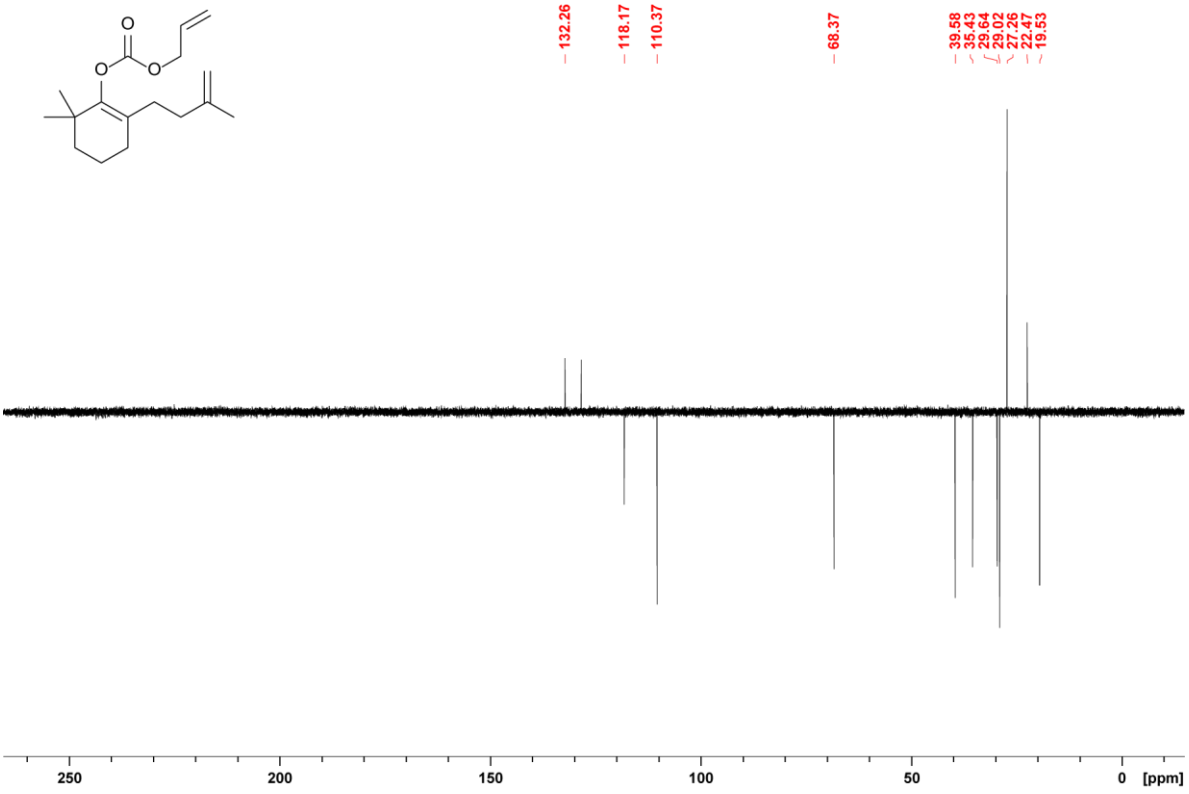


Figure S9. DEPT spectrum of **9** (125 MHz, C_6D_6).

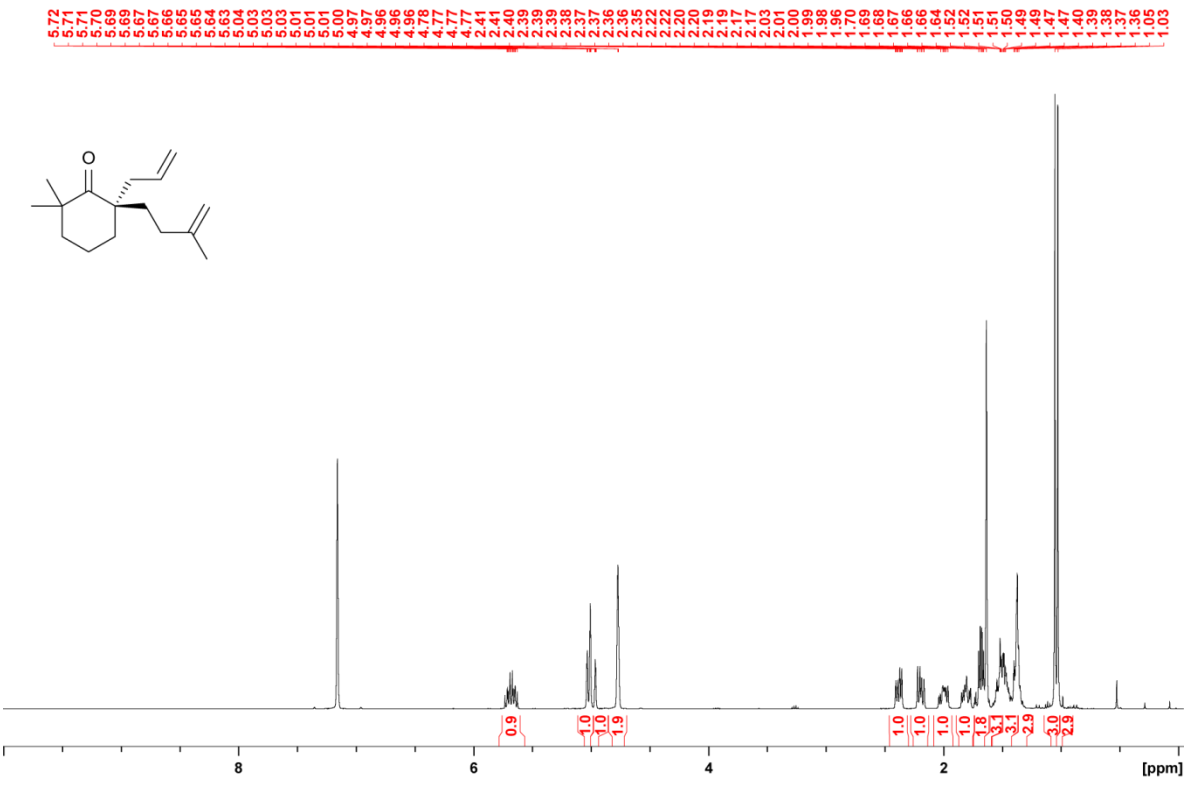


Figure S10. ^{1}H-NMR spectrum of **10** (400 MHz, C_6D_6).

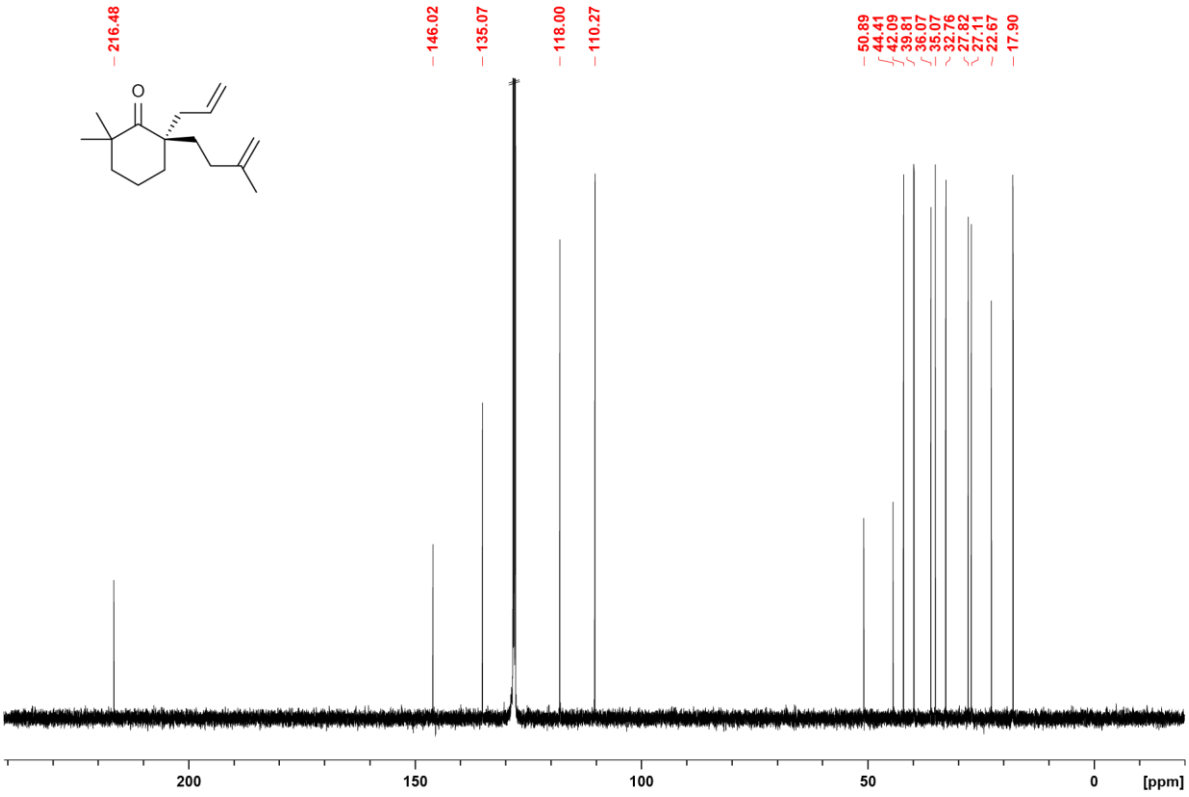


Figure S11. ^{13}C-NMR spectrum of **10** (100 MHz, C_6D_6).

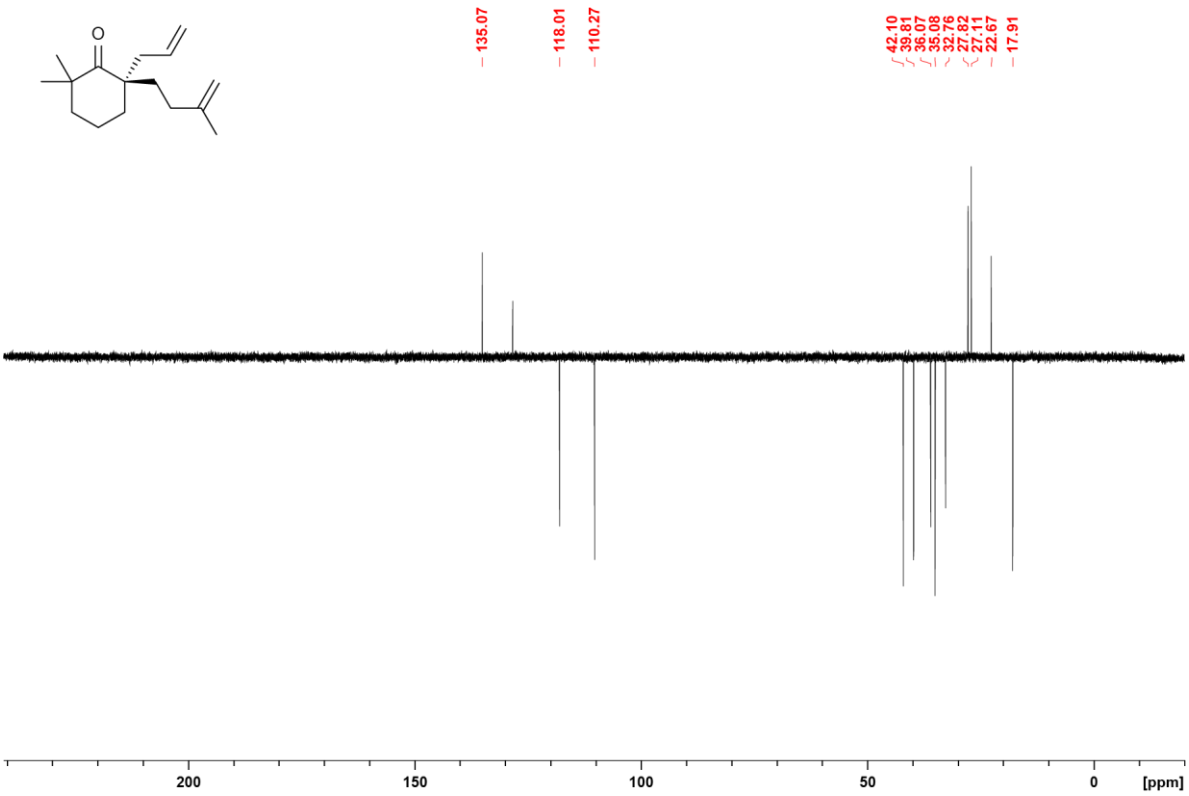


Figure S12. DEPT spectrum of **10** (100 MHz, C_6D_6).

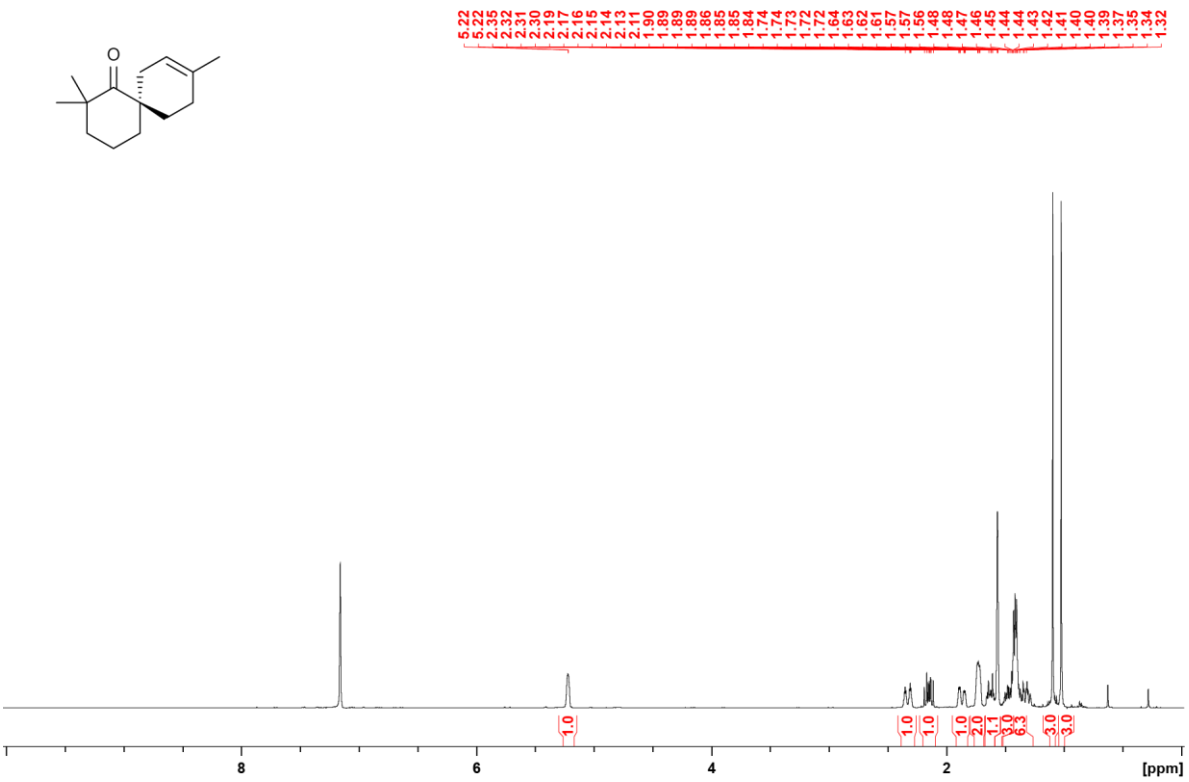


Figure S13. ^{1}H-NMR spectrum of **11** (400 MHz, C_6D_6).

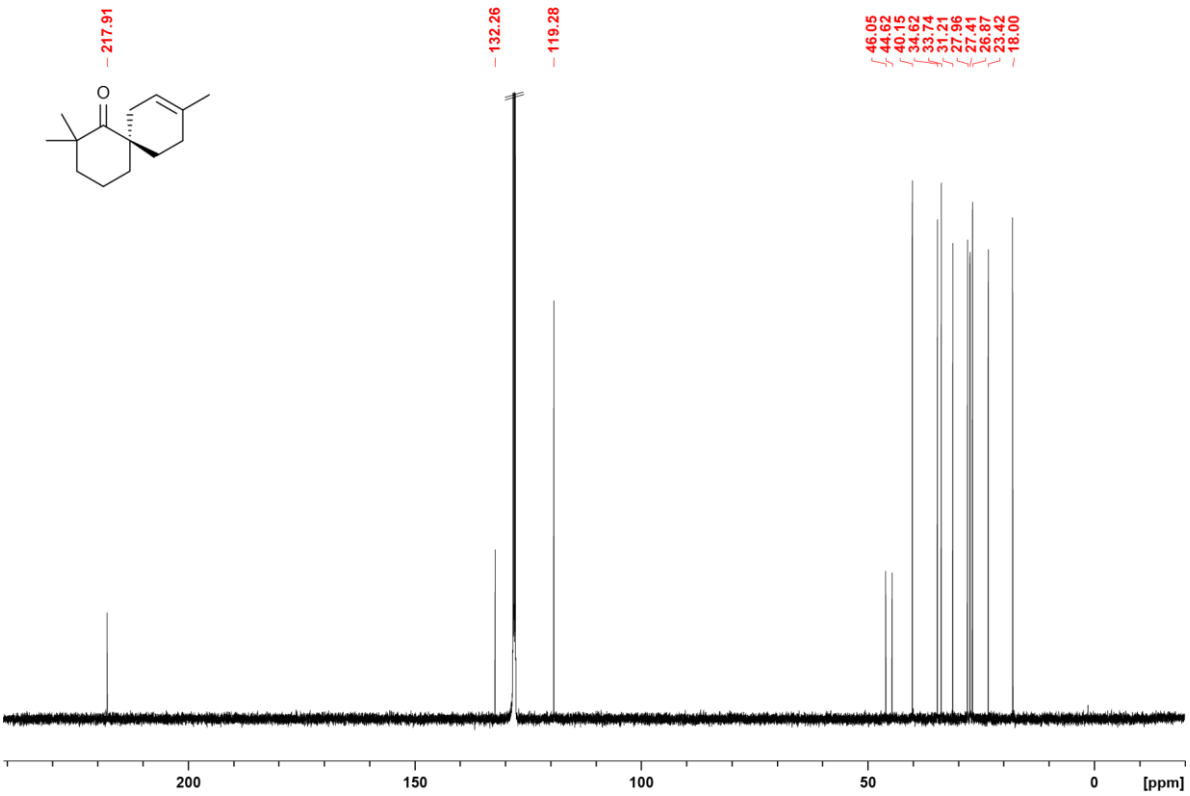


Figure S14. ^{13}C-NMR spectrum of **11** (100 MHz, C_6D_6).

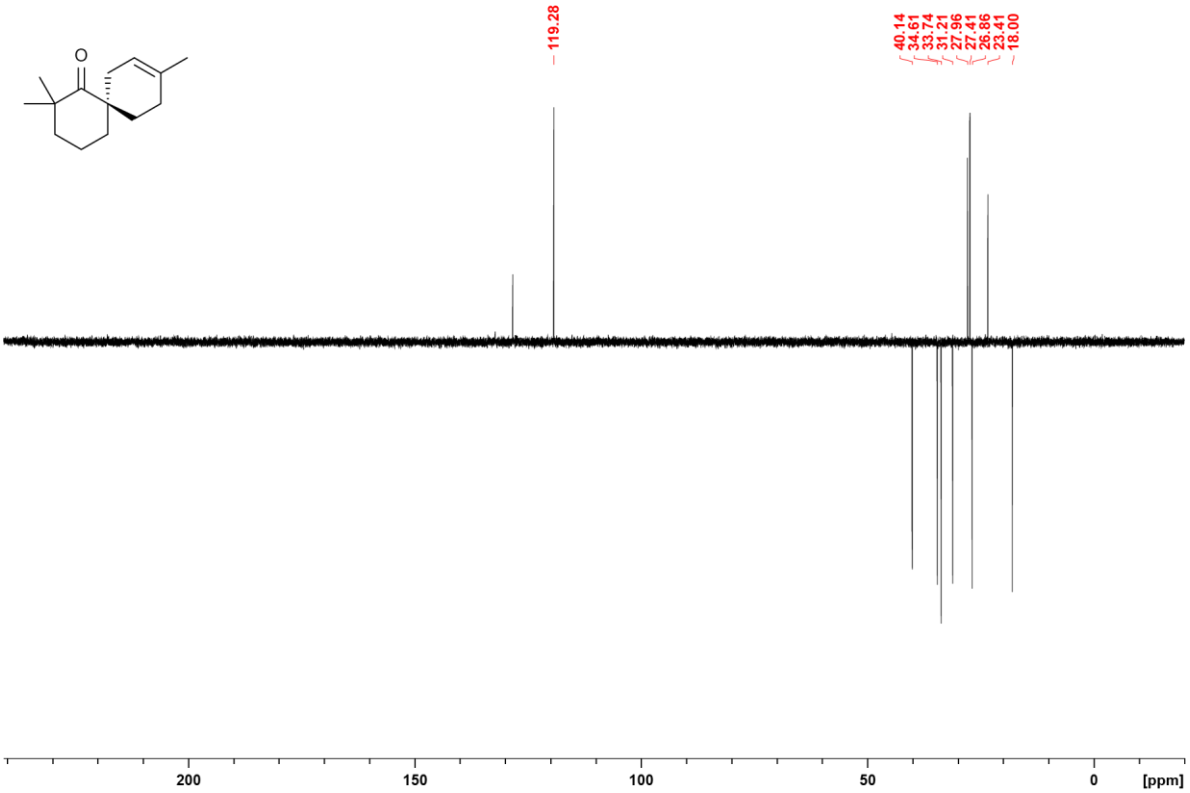


Figure S15. DEPT spectrum of **11** (100 MHz, C_6D_6).

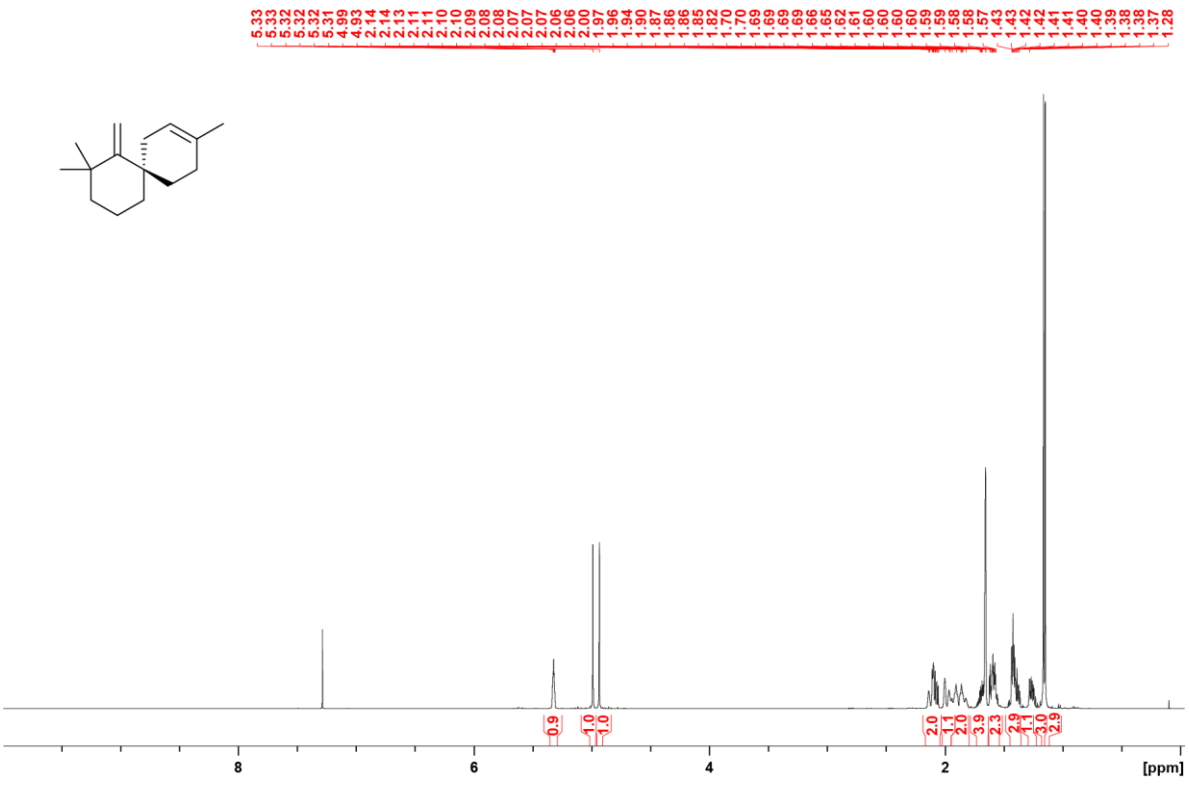


Figure S16. ^{1}H-NMR spectrum of (*R*)-**5** (500 MHz, $CDCl_3$).

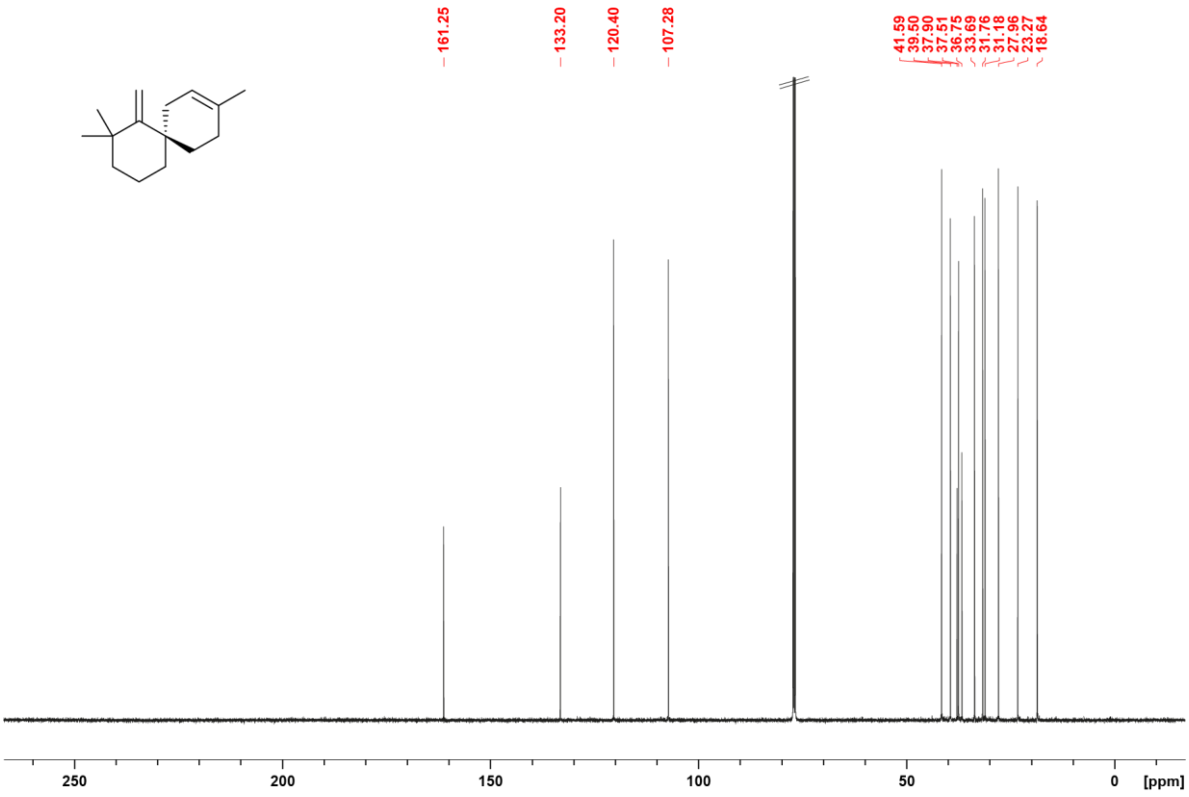


Figure S17. ^{13}C-NMR spectrum of (*R*)-**5** (125 MHz, $CDCl_3$).

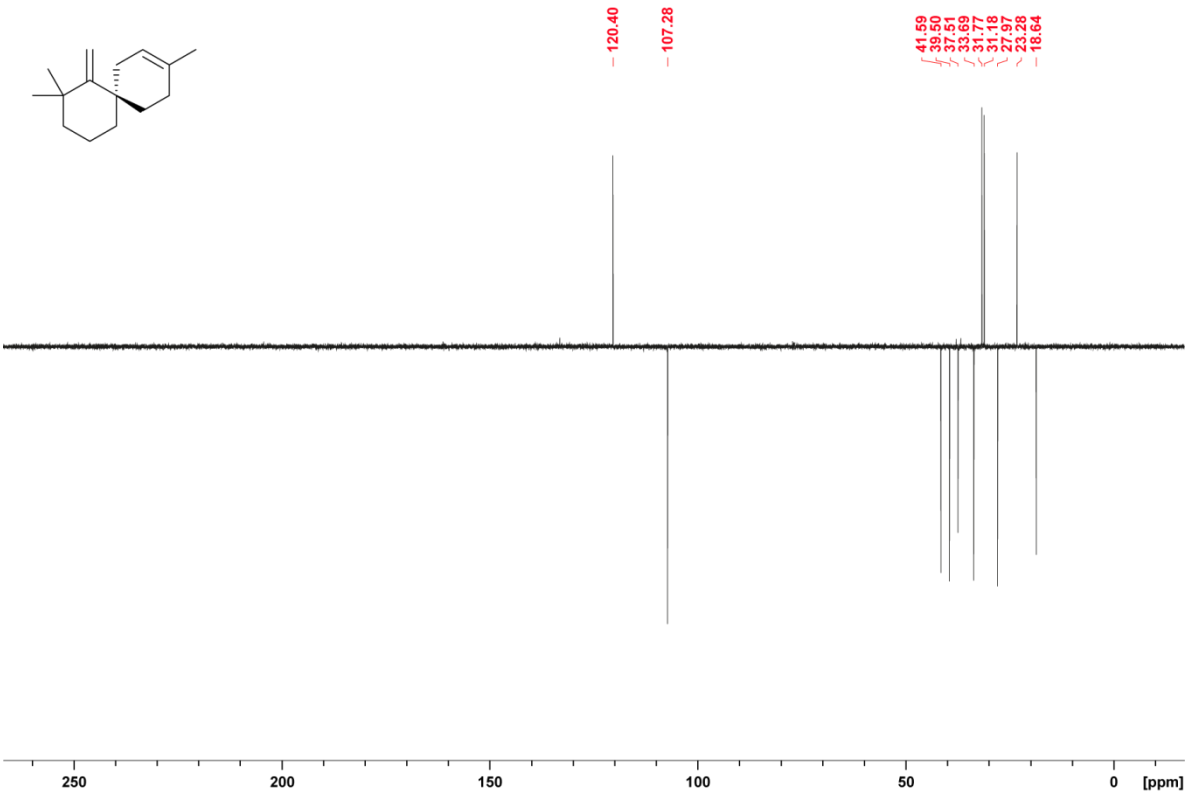


Figure S18. DEPT spectrum of (*R*)-**5** (125 MHz, $CDCl_3$).

References

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