SUPPORTING INFORMATION

Structure-Odor Activity Studies on Monoterpenoid Mercaptans Synthesized by Changing the Structural Motifs of the Key Food Odorant 1-*p*-Menthene-8-thiol

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Syntheses and substance characterization

If the respective alcohols for the OH/SH-exchange reaction were commercially not available, these were either obtained by hydrogenation of unsaturated analogues or by a reduction of the corresponding ketones or carboxylic acids.

Hydrogenation of unsaturated monoterpenoids

The respective monoterpenoid (10 mmol) was dissolved in methanol (50 mL) and platinum(IV) oxide (a spatula tip full) was added. Hydrogenation was performed in an autoclave by means of hydrogen for 2 h at a pressure of 5 bar. The solution was filtered and the solvent was removed under reduced pressure.

Reduction of ketones and carboxylic acids

Carboxylic acids or ketones (10 mmol) were dissolved in anhydrous diethyl ether (30 mL) and cooled to 0 °C. A solution of lithium aluminium hydride (0.78 g; 20 mmol) in anhydrous diethyl ether (30 mL) was slowly added and then stirred at RT for 2 h. Anhydrous diethyl ether (50 mL), saturated ammonium chloride solution (30 mL), and HCl (2 mol/L; 30 mL) were carefully added at 0 °C. The aqueous layer was washed twice with diethyl ether (50 mL), the combined organic layers were washed twice with saturated sodium hydrogen carbonate solution (30 mL) and finally dried over sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel using pentane as the eluent.

Synthetic route used in the preparation of 1-*p*-menthene-8-thiol and its enantiomers, respectively

1-*p*-Menthene-8-thiol and its enantiomers were synthesized using Lawesson's reagent (**Figure S1**).

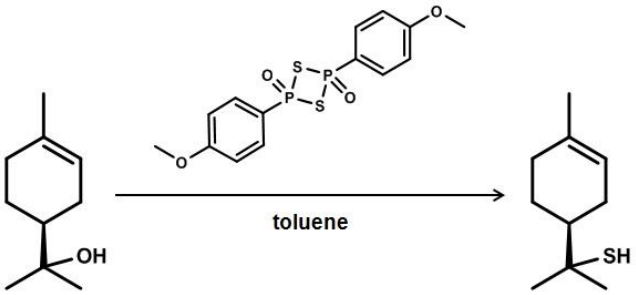


Figure S1. Synthetic route used for the enantioselective preparation of 1-*p*-menthene-8-thiol.

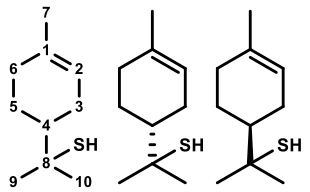
Lawesson's reagent (4.05 g; 10 mmol) was dissolved in toluene (150 mL). Then racemic *α*-terpineol or the (*R*)- and (*S*)-enantiomer (10 mmol) was added, and the mixture was stirred for 2 h at 120 °C. After cooling, the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The remaining salt was removed by SAFE-distillation. The distillate was dried over anhydrous sodium sulfate and after removal of the solvent, the product was purified by means of column chromatography on silica gel (silica 60, 0.040 - 0.063 mm) (Merck, Darmstadt, Germany) using pentane as the eluent.

Compounds **1a, 1b** and **1c**

1-*p*-menthene-8-thiol, yield: 4 %

(*R*)-1-*p*-menthene-8-thiol, yield: 6 %

(*S*)-1-*p*-menthene-8-thiol, yield: 3 %



educts: *α*-terpineol, (*R*)-(+)-*α*-terpineol, (*S*)-(-)-*α*-terpineol

RI (FFAP): 1577

RI (DB-5): 1285

MS-EI: *m/z* (intensity in %) 121 (100), 136 (82), 93 (80), 41 (35), 75 (35), 81 (33), 67 (25), 79 (25), 95 (25), 69 (22), 77 (22), 91 (21), 53 (15), 68 (15), 55 (13), 92 (12), 107 (12), 137 (12), 43 (11), 94 (11), 170 (10, M^+), 65 (8), 105 (8), 122 (8), 59 (7), 108 (6), 155 (5)

MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 136 (18), 138 (12), 171 (12, $[M+H]^+$), 93 (7), 95 (5)

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.36 (s, 3H, H-C9), 1.33 – 1.37 (m, 1H, H-C5), 1.42 (s, 3H, H-C10), 1.45 (s, SH), 1.54 – 1.59 (m, 1H, H-C4), 1.67 (s, 3H, H-C7), 1.91 – 1.93 (m, 1H, H-C3), 1.96 – 1.97 (m, 1H, H-C5), 1.99 - 2.03 (m, 2H, H-C6), 2.11 – 2.17 (m, 1H, H-C3), 5.38 – 5.41 (m, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 23.27 (C7), 24.86 (C5), 27.39 (C3), 30.17 (C9), 31.14 (C6), 31.46 (C10), 45.95 (C4), 47.91 (C8), 120.48 (C2), 133.88 (C1)

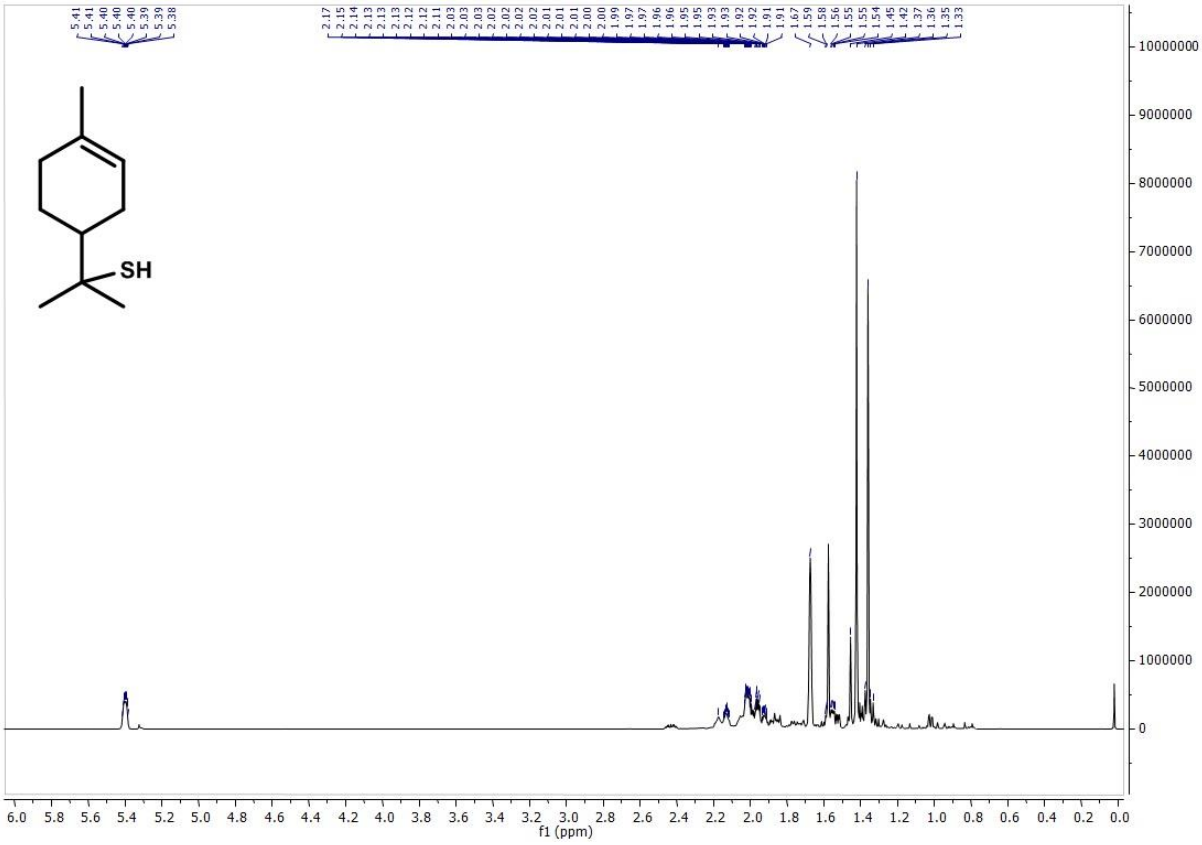


Figure S2. ^{1}H NMR spectrum of 1-*p*-menthene-8-thiol.

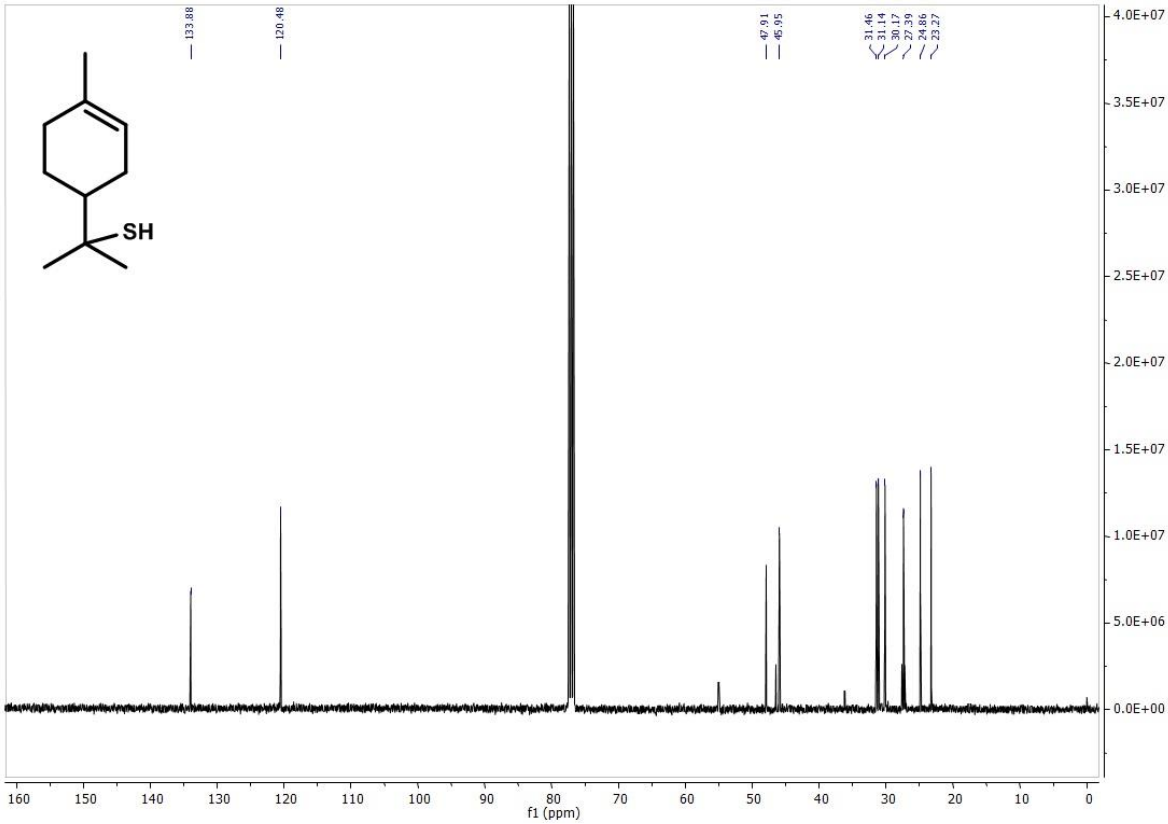


Figure S3. ^{13}C NMR spectrum of 1-*p*-menthene-8-thiol.

Synthetic route A for mercaptan preparation

Seventeen compounds were obtained by using the strategy consisting of tosylation, thioacetylation, and reduction as shown in **Figure S4**.

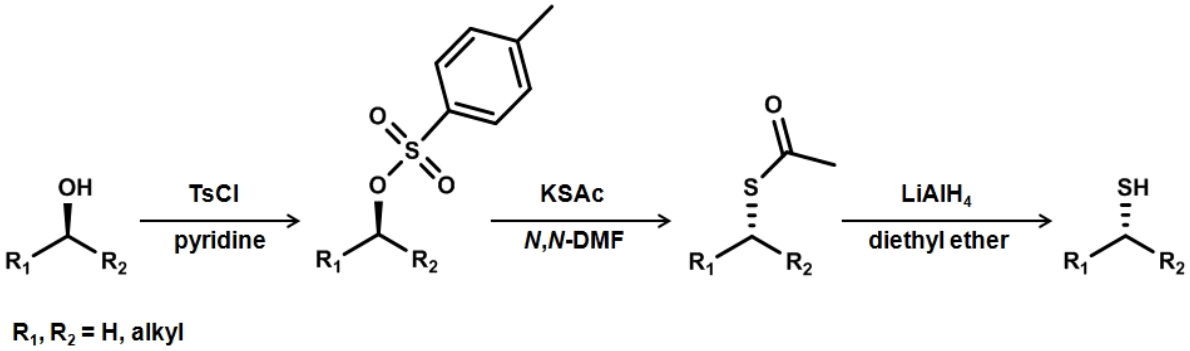


Figure S4. Route assigned as “synthetic route A”.

a) Tosylation. The respective alcohol (10 mmol) was dissolved in pyridine (20 mL) and cooled to 0 °C. *p*-Toluene sulfonyl chloride (2.10 g; 11 mmol) was added, and the solution was stirred overnight at RT. Hexane (30 mL) was added, the reaction mixture was filtered, and the residue was washed with hexane (30 mL). The organic layer was carefully extracted with HCl (5 mol/L; 30 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure.

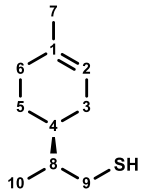
b) Thioacetylation. The tosylate (7 mmol) was dissolved in *N*,*N*-dimethylformamide (20 mL) and potassium thioacetate (2.39 g; 21 mmol) was added. The solution was stirred at 85 °C for 2 h and then diluted with diethyl ether (30 mL). The organic layer was washed twice with brine (20 mL), dried over sodium sulfate and concentrated under reduced pressure. The thioacetate was purified by means of column chromatography on silica gel using pentane/diethyl ether (98+2; by vol.) as the eluent.

c) Reduction. The thioacetate (4 mmol) was dissolved in anhydrous diethyl ether (15 mL) and cooled to 0 °C. A solution of lithium aluminium hydride (0.31 g; 8 mmol) in anhydrous diethyl ether (15 mL) was slowly added and then stirred at RT for 2 h. Anhydrous diethyl ether (30 mL), saturated ammonium chloride solution (20 mL), and

HCl (2 mol/L; 20 mL) were added at 0 °C. The aqueous layer was washed twice with diethyl ether (30 mL), the combined organic layers were washed twice with saturated sodium hydrogen carbonate solution (20 mL) and dried over sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silca gel using pentane as the eluent.

Compound **2**

(*4S,8R*)-1-*p*-menthene-9-thiol



educt: (*4S,8R*)-1-*p*-menthene-9-ol

a) 1st intermediate:
(R)-2-((S)-4-methylcyclohex-3-en-1-yl)propyl 4-methylbenzenesulfonate,
yield: 73 %

b) 2nd intermediate:
S-((R)-2-((S)-4-methylcyclohex-3-en-1-yl)propyl) ethanethioate,
yield: 84 %,
MS-EI: *m/z* (intensity in %) 169 (100), 43 (52), 93 (38), 95 (36), 79 (25), 81 (24), 135 (24), 94 (20), 41 (18), 67 (18), 55 (16), 107 (15), 121 (15), 170 (15), 77 (12), 75 (10), 91 (10), 136 (8), 113 (6), 53 (5), 171 (5), 212 (3, M^+)

c) analyte:
yield: 83 %
RI (FFAP): 1710
RI (DB-5): 1364

MS-EI: *m/z* (intensity in %) 94 (100), 95 (94), 93 (80), 79 (77), 67 (65), 81 (63), 41 (60), 170 (59, M^+), 68 (53), 91 (44), 55 (43), 136 (43), 77 (40), 121 (32), 107 (30), 53 (28), 123 (28), 75 (26), 92 (22), 69 (18), 113 (18), 168 (18), 47 (16), 65 (15), 80 (15), 137 (15), 168 (15), 153 (14), 78 (11), 96 (10), 105 (10), 108 (10), 155 (10), 171 (9)
MS-CI (isobutane): *m/z* (intensity in %) 171 (100, $[M+H]^+$), 137 (34), 93 (14), 95 (12), 123 (12) 170 (11), 91 (7), 172 (5)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.98 (d, *J* = 6.6 Hz, 3H, H-C10), 1.25 - 1.34 (m, 1H, H-C5), 1.28 (t, *J* = 8.0 Hz, SH), 1.51 - 1.64 (m, 2H, H-C4, H-C8), 1.66 (s, 3H, H-C7), 1.68 - 1.80 (m, 2H, H-C3, H-C5), 1.91 – 2.06 (m, 3H, H-C3, H-C6), 2.42 - 2.49 (m, 1H, H-C9), 2.62 - 2.69 (m, 1H, H-C9), 5.37 - 5.41 (m, 1H, H-C2)
^{13}C NMR (101 MHz, $CDCl_3$): δ 15.10 (C10), 23.44 (C7), 27.12 (C5), 27.45 (C3), 29.52 (C9), 30.69 (C6), 36.75 (C4), 40.63 (C8), 120.54 (C2), 134.04 (C1)

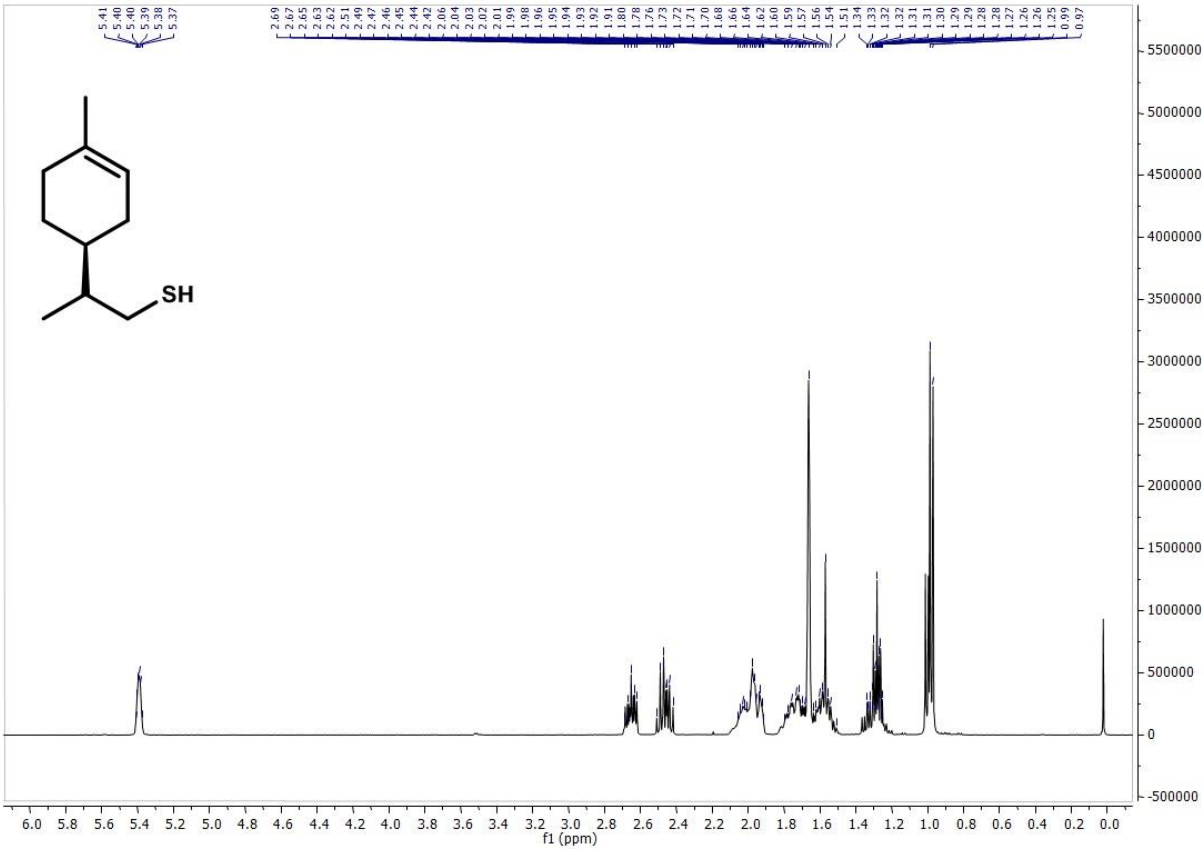


Figure S5. ^{1}H NMR spectrum of (*4S,8R*)-1-*p*-menthene-9-thiol.

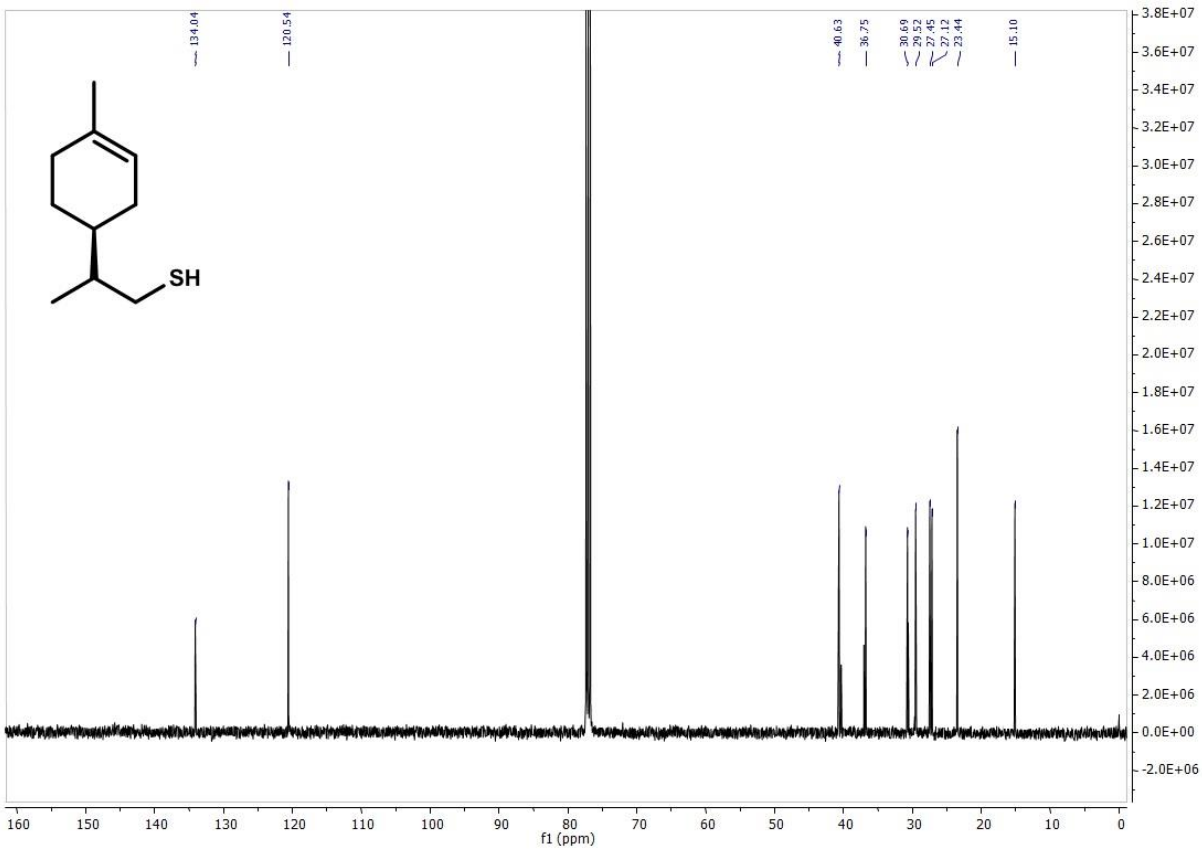
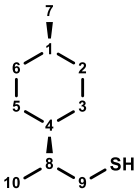


Figure S6. ^{13}C NMR spectrum of (*4S,8R*)-1-*p*-menthene-9-thiol.

Compound **6a**

p*-menthane-9-thiol, *diastereomer 1:

(*R*)-2-((*1s,4S*)-4-methylcyclohexyl)propane-1-thiol



educt: (*4S*,*8R*)-*p*-menthene-9-ol

a) 1st intermediate (obtained by hydrogenation):

p-menthane-9-ol, diastereomer 1:

(R)-2-((1s,4S)-4-methylcyclohexyl)propane-1-thiol, yield: 50 %,

MS-EI: *m/z* (intensity in %) 55 (100), 69 (67), 81 (51), 96 (45), 95 (38), 41 (29), 97 (27), 83 (24), 67 (18), 68 (12), 138 (12), 82 (11), 123 (11), 109 (9), 125 (9), 57 (8), 43 (6), 42 (5), 53 (5), 54 (5), 56 (5), 58 (5), M^+ absent

b) 2nd intermediate:

(R)-2-((1s,4S)-4-methylcyclohexyl)propyl 4-methylbenzenesulfonate,

crude yield: 65 % (*sum of diastereomers, see also compound 6b*)

c) 3rd intermediate:

S-((R)-2-((1s,4S)-4-methylcyclohexyl)propyl) ethanethioate,

yield: 45 %,

MS-EI: *m/z* (intensity in %) 43 (100), 138 (79), 55 (57), 81 (54), 95 (53), 139 (50), 171 (50), 140 (42), 41 (35), 137 (31), 69 (30), 96 (25), 83 (20), 67 (18), 163 (17), 123 (15), 82 (13), 180 (13), 97 (11), 79 (10), 109 (10), 77 (9), 170 (8), 42 (7), 53 (7), 165 (7), 169 (7), 54 (6), 68 (6), 162 (6), 172 (6), 214 (6, M^+), 47 (5), 57 (5), 91 (5), 181 (5), 196 (5)

d) analyte:

yield: 36 %

RI (FFAP): 1548

R (FFAP): 1307

MS-EI: *m/z* (intensity in %) 55 (100), 138 (61), 69 (57), 96 (52), 81 (51), 41 (50), 95 (36), 172 (35, M^+), 47 (24), 138 (23), 82 (22), 75 (20), 67 (19), 83 (19), 109 (17), 43 (16), 53 (15), 79 (14), 97 (11), 94 (10), 139 (10), 57 (9), 68 (9), 77 (9), 123 (8), 74 (7), 84 (7), 93 (7), 54 (6), 68 (6), 173 (6), 171 (5)

MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 173 (35, $[M+H]^+$), 128 (32), 97 (15), 140 (8), 171 (8), 174 (6)

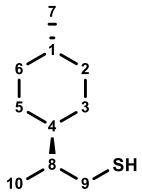
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.87 (d, *J* = 6.5 Hz, 3H, H-C7), 0.88 – 0.96 (m, 2H, H-C3, H-C5), 0.94 (d, *J* = 6.8 Hz, 3H, H-C10), 0.92 – 1.10 (m, 2H, H-C2, H-C6), 1.24 (t, *J* = 8.0 Hz, SH), 1.23 – 1.31 (m, 1H, H-C1), 1.26 – 1.33 (m, 1H, H-C8), 1.42 – 1.49 (m, 1H, H-C4), 1.57 – 1.66 (m, 1H, H-C2), 1.58 – 1.65 (m, 1H, H-C6), 1.66 – 1.75 (m, 2H, H-C3, H-C5), 2.37 – 2.43 (m, 1H, H-C9), 2.57 – 2.63 (m, 1H, H-C9)

^{13}C NMR (101 MHz, $CDCl_3$): δ 15.41 (C10), 22.66 (C7), 28.40 (C6), 29.57 (C9), 30.66 (C2), 32.85 (C1), 35.32 (C5), 35.44 (C3), 40.79 (C8), 41.34 (C4)

Compound **6b**

p*-menthane-9-thiol, *diastereomer 2:

(*R*)-2-((*1r,4R*)-4-methylcyclohexyl)propane-1-thiol



educt: (*4S*,*8R*)-*p*-menthene-9-ol

a) 1st intermediate (obtained by hydrogenation):

p-menthane-9-ol, *diastereomer 2*:

(R)-2-((1r,4R)-4-methylcyclohexyl)propane-1-thiol, yield: 35 %,

MS-EI: *m/z* (intensity in %) 55 (100), 69 (51), 81 (51), 96 (42), 95 (37), 41 (30), 97 (24), 83 (19), 67 (17), 68 (13), 82 (12), 123 (11), 138 (10), 109 (9), 43 (7), 57 (7), 42 (6), 53 (6), 54 (6), 56 (6), 58 (6), 125 (6), M^+ absent

b) 2nd intermediate:

(R)-2-((1r,4R)-4-methylcyclohexyl)propyl 4-methylbenzenesulfonate,

crude yield: 65 % % (*sum of diastereomers, see also compound 6a*)

c) 3rd intermediate:

S-((R)-2-((1r,4R)-4-methylcyclohexyl)propyl) ethanethioate,

yield: 30 %,

MS-EI: *m/z* (intensity in %) 43 (100), 138 (69), 81 (54), 95 (52), 55 (50), 171 (46), 140 (43), 139 (40), 41 (37), 69 (28), 83 (22), 96 (22), 137 (21), 67 (17), 123 (16), 82 (14), 97 (14), 42 (9), 53 (9), 75 (9), 68 (8), 79 (8), 109 (8), 162 (7), 163 (7), 170 (7), 196 (7), 54 (6), 77 (6), 93 (6), 94 (6), 110 (5), 214 (5, M^+)

d) analyte:

yield: 23 %

RI (FFAP): 1577

R (FFAP): 1324

MS-EI: *m/z* (intensity in %) 138 (100), 55 (76), 69 (57), 96 (56), 81 (53), 95 (49), 41 (41), 67 (32), 47 (30), 172 (30, M^+), 83 (24), 68 (18), 57 (17), 123 (17), 79 (15), 82 (15), 53 (14), 109 (14), 54 (13), 139 (12), 53 (11), 52 (11), 74 (10), 97 (9), 93 (6), 110 (6)

MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 173 (62, $[M+H]^+$), 138 (34), 97 (17), 140 (9), 171 (9), 174 (8)

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.85 – 0.90 (m, 1H, H-C6), 0.91 (d, *J* = 7.0 Hz, 3H, H-C7), 0.96 (d, *J* = 6.8 Hz, 3H, H-C10), 1.23 (t, *J* = 8.0 Hz, SH), 1.30 – 1.38 (m, 2H, H-C3, H-C5), 1.35 – 1.42 (m, 5H, H-C2, H-C4, H-C6), 1.44 – 1.53 (m, 2H, H-C3, H-C5), 1.56 – 1.62 (m, 1H, H-C8), 1.71 – 1.79 (m, 1H, H-C1), 2.37 – 2.46 (m, 1H, H-C10), 2.60 – 2.68 (m, 1H, H-C10)

^{13}C NMR (101 MHz, $CDCl_3$): δ 15.71 (C10), 19.09 (C7), 24.26 (C6), 25.69 (C2), 28.91 (C1), 29.65 (C9), 31.29 (C3), 31.40 (C5), 38.69 (C8), 39.79 (C4)

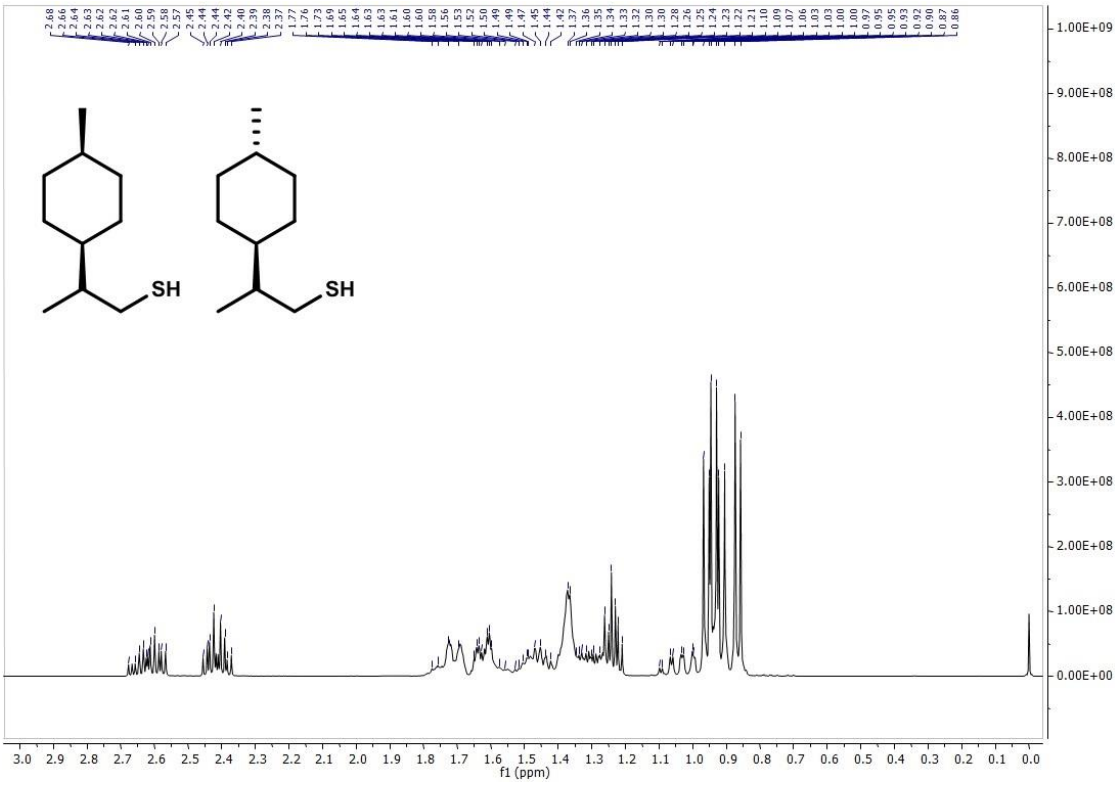


Figure S7. ^{1}H NMR spectrum of *p*-menthane-9-thiol (mixture of 2 diastereomers).

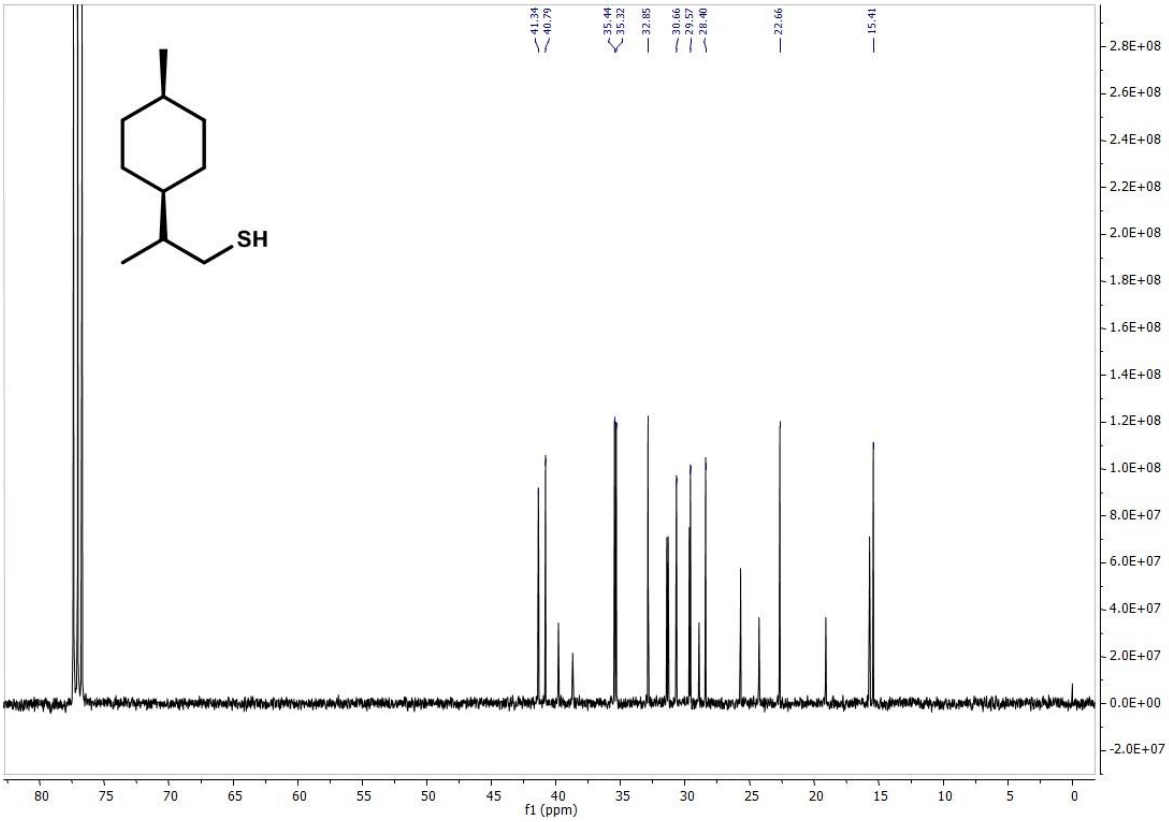


Figure S8. ^{13}C NMR spectrum of *p*-menthane-9-thiol (mixture of 2 diastereomers); signals of diastereomer 1.

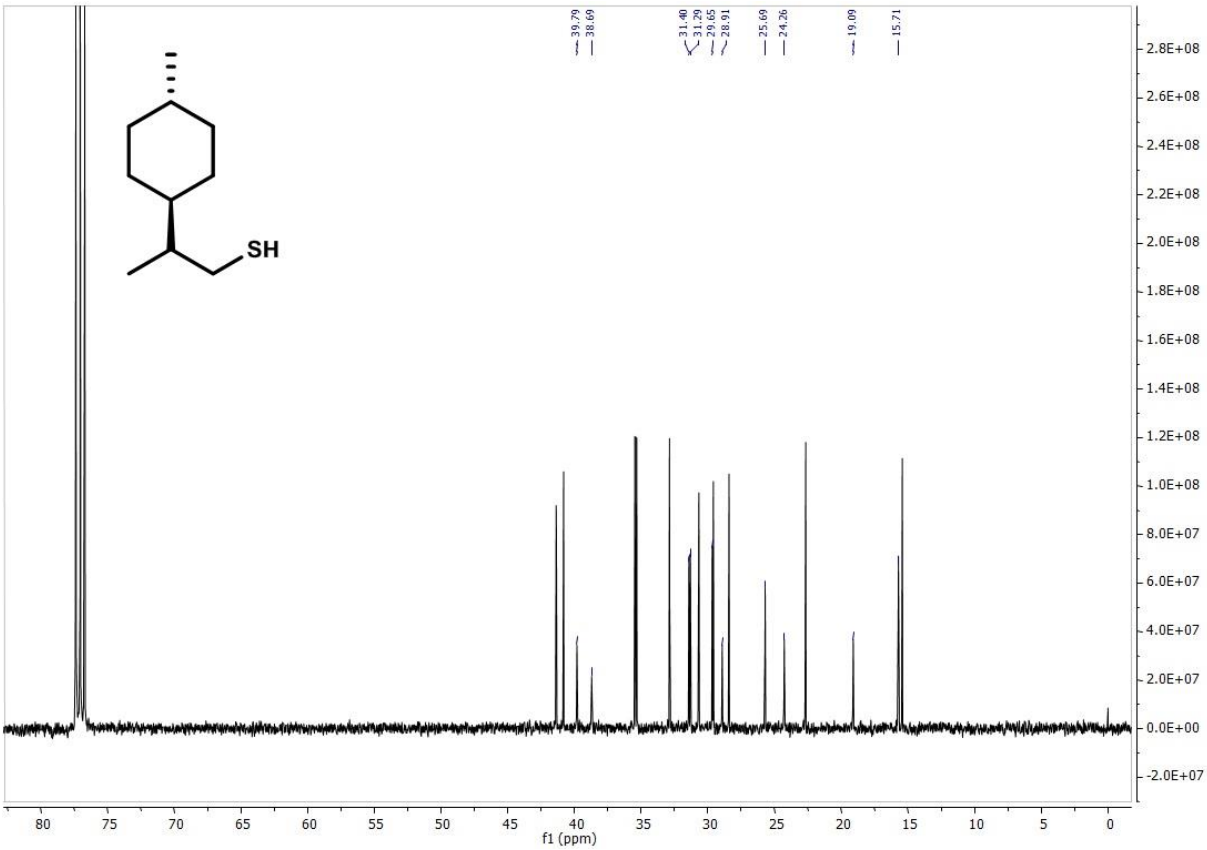
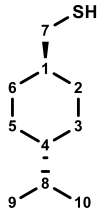


Figure S9. ^{13}C NMR spectrum of *p*-menthane-9-thiol (mixture of 2 diastereomers); signals of diastereomer 2.

Compound **7**

(*1R,4R*)-*p*-menthane-7-thiol



educt: (*1R,4R*)-4-isopropylcyclohexane-1-carboxylic acid

a) 1st intermediate (obtained by reduction):
(1R,4R)-p-menthane-7-thiol, yield: 83 %,
MS-EI: *m/z* (intensity in %) 95 (100), 69 (24), 41 (18), 67 (18), 55 (16), 81 (14), 96 (10), 83 (9), 109 (9), 79 (8), 94 (7), 43 (7), 82 (6),57 (6), 123 (5), 138 (5), M^+ absent

b) 2nd intermediate:
(1R,4R)-4-(1-methylethyl)cyclohexyl)methyl 4-methylbenzenesulfonate,
crude yield: 64 %

c) 3rd intermediate:
S-((1R,4R)-4-(1-methylethyl)cyclohexylmethyl) ethanethioate,
yield: 21 %,
MS-EI: *m/z* (intensity in %) 138 (100), 43 (85), 95 (54), 139 (38), 171 (38), 81 (37), 167 (35), 69 (38), 41 (23), 83 (22), 67 (20), 55 (17), 137 (16), 123 (15), 79 (14), 109 (14), 82 (12), 196 (11), 77 (8), 93 (8), 96 (8), 169 (8), 57 (7), 94 (7), 127 (6), 129 (6), 156 (5), 168 (5), 172 (5), 181 (5), 214 (5, M^+)

d) analyte:

yield: 69 %

RI (FFAP): 1601

RI (DB-5): 1330

MS-EI: *m/z* (intensity in %) 95 (100), 69 (47), 138 (37), 109 (31), 172 (31, M^+), 67 (30), 81 (28), 83 (24), 55 (21), 41 (17), 82 (14), 94 (14), 96 (14), 123 (14), 79 (12), 110 (12), 57 (10), 93 (8), 43 (7), 128 (7), 53 (6), 68 (5), 80 (5), 139 (5), 173 (5)

MS-CI (isobutane): *m/z* (intensity in %) 173 (100, $[M+H]^+$), 139 (94), 138 (41), 95 (21), 97 (17), 171 (12), 140 (9), 172 (8), 174 (8)

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.85 (d, *J* = 6.8 Hz, 6H, H-C9, H-C10), 0.89 – 1.02 (m, 5H, H-C2, H-C3, H-C4, H-C5, H-C6), 1.29 (t, *J* = 8.1 Hz, 1H, H-C1), 1.38 – 1.44 (m, 1H, H-C8), 1.71 – 1.76 (m, 3H, H-C2, H-C6, SH), 1.87 – 1.93 (m, 2H, H-C3, H-C5), 2.41 (dd, *J* = 8.2 Hz, 6.5 Hz, 2H, H-C7)

^{13}C NMR (101 MHz, $CDCl_3$): δ 19.85 (C9, C10), 29.38 (C3, C5), 31.61 (C7), 32.23 (C2, C6), 32.80 (C8), 41.27 (C1), 44.00 (C4)

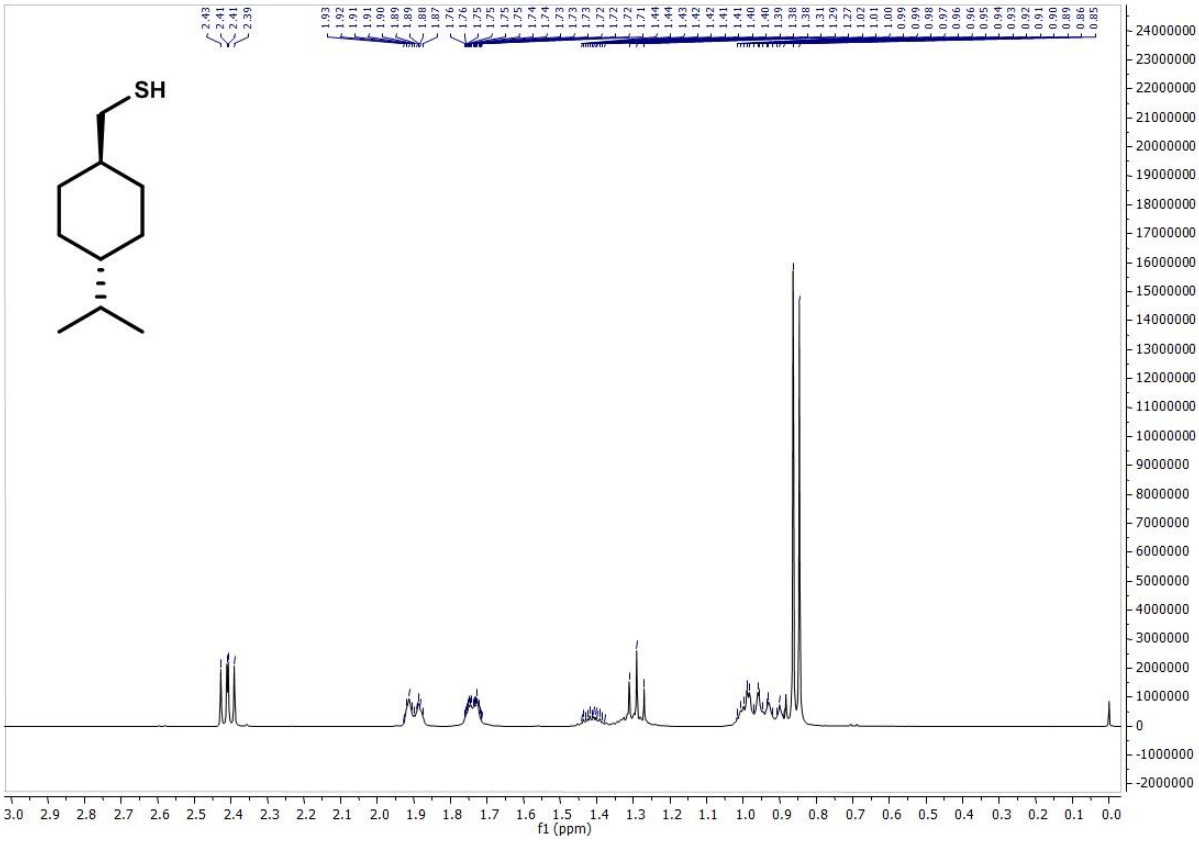


Figure S10. ^{1}H NMR spectrum of (*1R,4R*)-*p*-menthane-7-thiol.

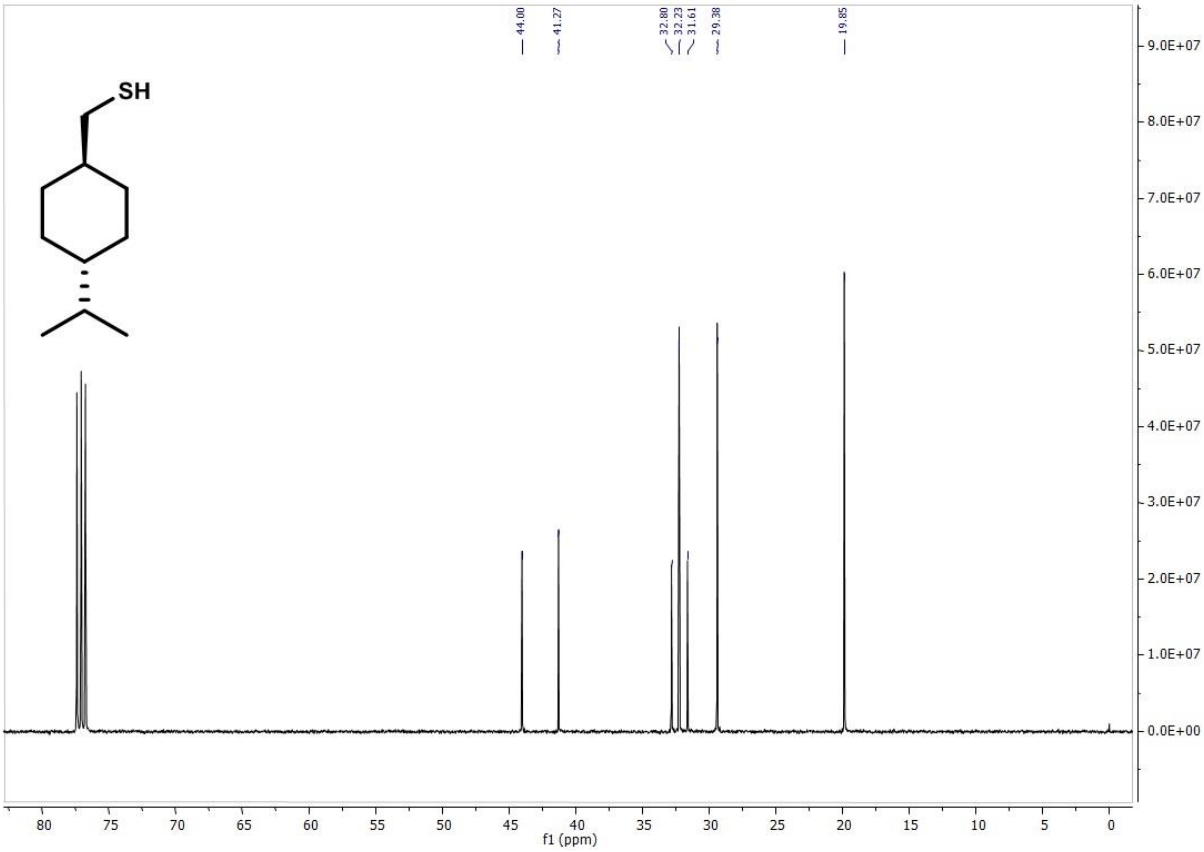
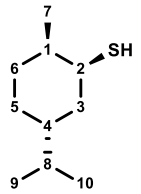


Figure S11. ^{13}C NMR spectrum of (*1R,4R*)-*p*-menthane-7-thiol.

Compound **8a**

(*1R,2S,4R*)-*p*-menthane-2-thiol



educt: (-)-dihydrocarveol

a) 1st intermediate (obtained by hydrogenation):
(-)-tetrahydrocarveol, yield: 90 %,
MS-EI: *m/z* (intensity in %) 95 (100), 57 (41), 55 (34), 113 (33), 43 (27), 81 (27), 41 (24), 82 (23), 69 (21), 67 (18), 83 (18), 138 (18), 96 (17), 123 (14), 109 (10), 70 (9), 71 (9), 68 (8), 56 (7), 79 (7), 45 (6), 53 (6), 110 (6), M^+ absent

b) 2nd intermediate:
((1R,3R,6R)-6-methyl-3-(propan-2-yl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 22 %

c) 3rd intermediate:
S-((1S,3R,6R)-6-methyl-3-(propan-2-yl)cyclohexyl) ethanethioate,
yield: 74 %,
MS-EI: *m/z* (intensity in %) 138 (100), 95 (66), 83 (41), 81 (35), 43 (27), 55 (24), 69 (21), 67 (12), 82 (12), 96 (12), 123 (12), 139 (12), 41 (11), 57 (10), 137 (9), 94 (8), 97 (8), 79 (6), 109 (5), 171 (4), 214 (3, M^+)

d) analyte:

yield: 74 %

RI (FFAP): 1491

RI (DB-5): 1272

MS-EI: *m/z* (intensity in %) 95 (100), 138 (48), 81 (37), 83 (28), 55 (26), 67 (22), 69 (19), 82 (17), 96 (17), 123 (17), 172 (17, M^+), 94 (13), 41 (12), 57 (8), 68 (8), 139 (8), 43 (7), 79 (7), 97 (6), 109 (5), 173 (3)

MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 140 (11), 95 (10), 91 (9), 138 (7), 173 (4, $[M+H]^+$)

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.86 (d, *J* = 6.6 Hz, 3H, H-C10), 0.86 (d, *J* = 6.6 Hz, 3H, H-C9), 0.93 (d, *J* = 6.7 Hz, 3H, H-C7), 0.94 – 1.01 (m, 1H, H-C5), 1.23 (d, J = 7.1 Hz, SH), 1.37 – 1.55 (m, 5H, H-C3, H-C4, H-C6, H-C8), 1.63 – 1.72 (m, 2H, H-C1, H-C5), 1.90 (dq, *J* = 12.7, 2.5 Hz, 1H, H-C6), 3.32 (dq, *J* = 6.9, 3.4 Hz, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 19.64 (C9), 19.86 (C10), 20.53 (C7), 28.18 (C3), 29.40 (C5), 32.37 (C8), 36.25 (C1), 36.59 (C4), 38.56 (C6), 44.12 (C2)

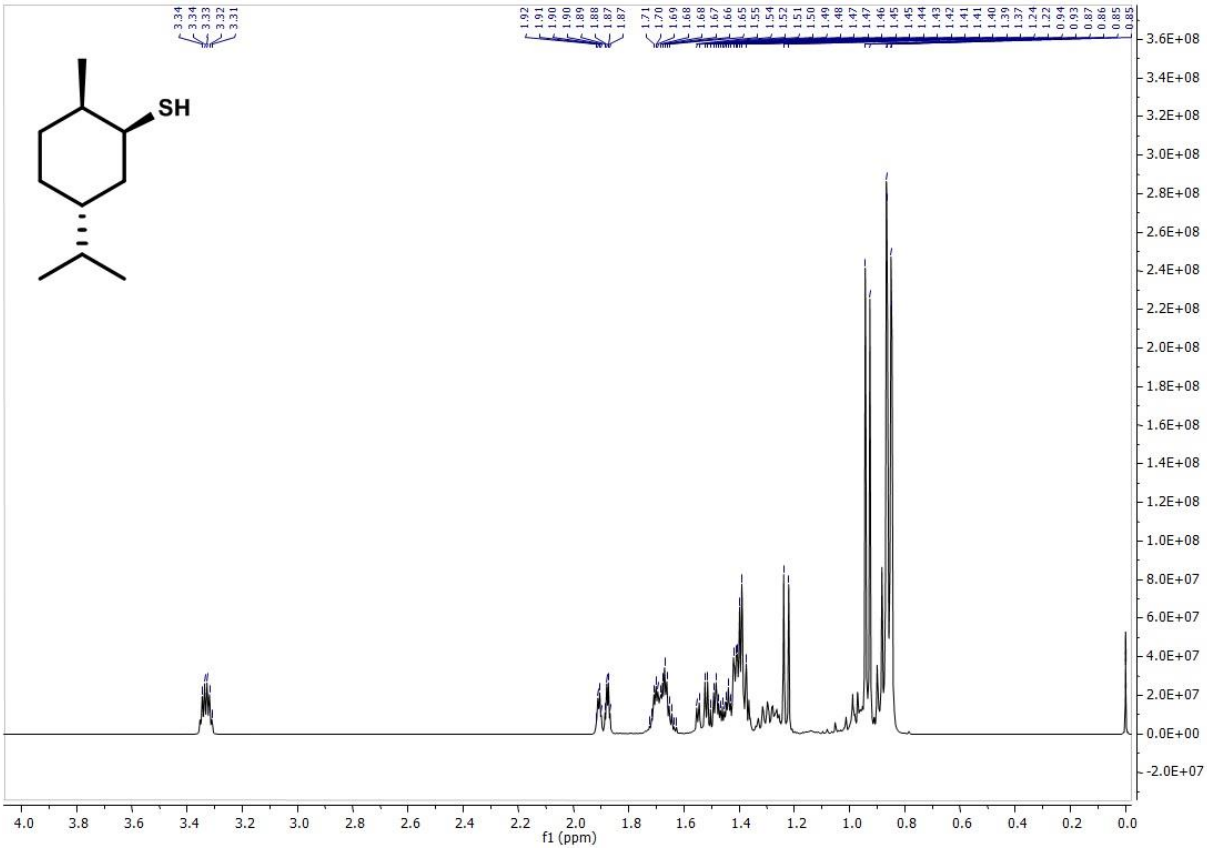


Figure S12. ^{1}H NMR spectrum of (*1R,2S,4R*)-*p*-menthane-2-thiol.

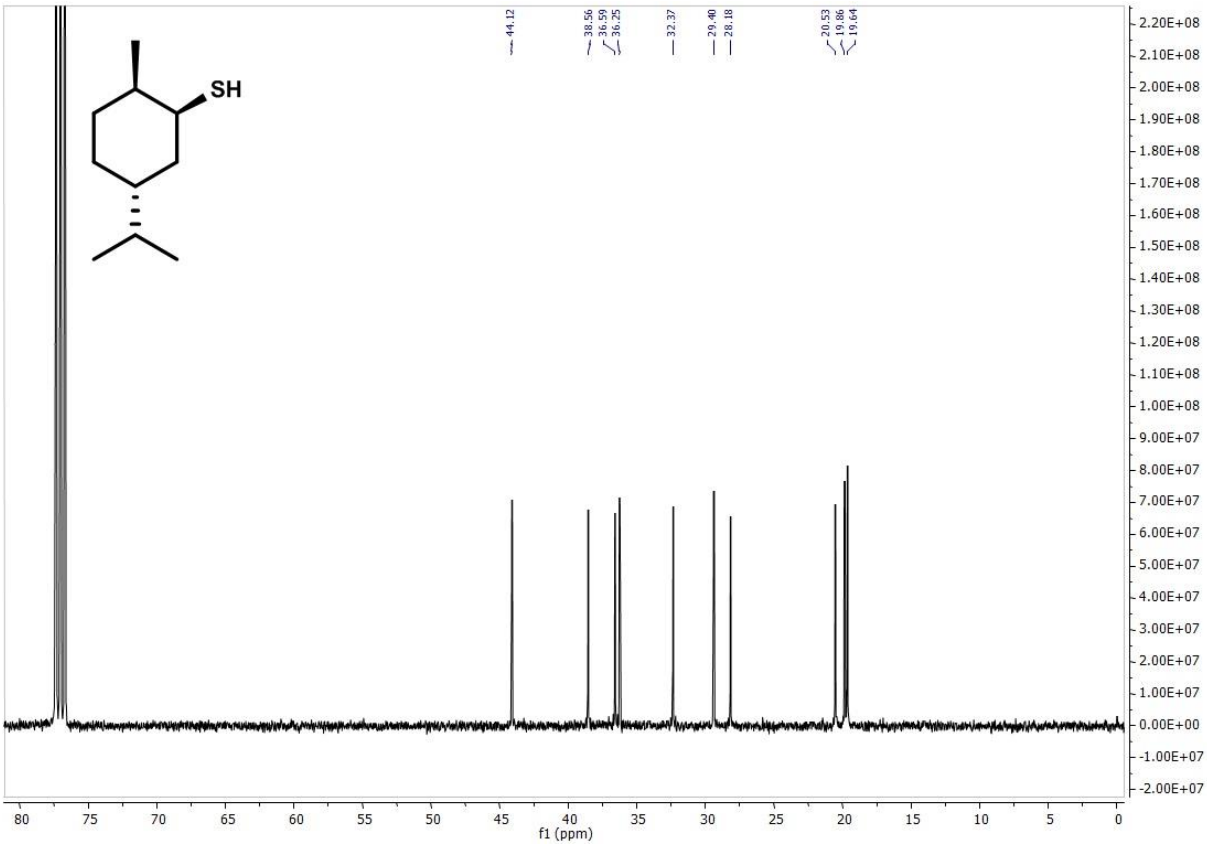
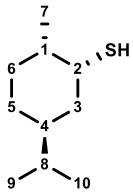


Figure S13. ^{13}C NMR spectrum of (*1R,2S,4R*)-*p*-menthane-2-thiol.

Compound **8b**

(*1S,2R,4S*)-*p*-menthane-2-thiol



educt: (+)-dihydrocarveol

a) 1st intermediate (obtained by hydrogenation):
(+)-tetrahydrocarveol, yield: 86 %,
MS-EI: *m/z* (intensity in %) 95 (100), 57 (36), 55 (35), 113 (34), 81 (25), 82 (24), 43 (23), 69 (23), 67 (22), 41 (20), 96 (19), 138 (18), 83 (16), 71 (11), 123 (11), 80 (9), 70 (8), 109 (8), 45 (6), 59 (6), 68 (6), 94 (6), 83 (5), 110 (5), 156 (1, M^+)

b)2nd intermediate:
((1S,3S,6S)-6-methyl-3-(propan-2-yl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 45 %

c) 3rd intermediate:
S-((1R,3S,6S)-6-methyl-3-(propan-2-yl)cyclohexyl) ethanethioate,
yield: 81 %,
MS-EI: *m/z* (intensity in %) 138 (100), 95 (72), 83 (46), 81 (41), 43 (32), 55 (28), 69 (23), 41 (16), 67 (15), 96 (14), 123 (14), 139 (13), 57 (12), 82 (12), 94 (10), 97 (8), 79 (7), 68 (5), 80 (5), 109 (5), 171 (4), 214 (2, M^+)

d) analyte:

yield: 54 %

RI (FFAP): 1485

RI (DB-5): 1271

MS-EI: *m/z* (intensity in %) 95 (100), 138 (46), 81 (40), 83 (31), 55 (30), 67 (23), 69 (19), 82 (18), 96 (18), 41 (17), 96 (17), 123 (16), 172 (15, M^+), 94 (14), 57 (9), 68 (9), 43 (8), 79 (8), 139 (7), 53 (6), 97 (6), 109 (6), 80 (5), 93 (5)

MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 138 (10), 140 (10), 91 (6), 95 (5), 173 (2, $[M+H]^+$)

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.86 (d, *J* = 6.6 Hz, 3H, H-C10), 0.86 (d, *J* = 6.6 Hz, 3H, H-C9), 0.93 (d, *J* = 6.7 Hz, 3H, H-C7), 0.94 – 1.01 (m, 1H, H-C5), 1.23 (d, J = 7.1 Hz, SH), 1.37 – 1.55 (m, 5H, H-C3, H-C4, H-C6, H-C8), 1.63 – 1.72 (m, 2H, H-C1, H-C5), 1.90 (dq, *J* = 12.7, 2.5 Hz, 1H, H-C6), 3.33 (dq, *J* = 6.9, 3.4 Hz, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 19.64 (C9), 19.86 (C10), 20.53 (C7), 28.18 (C3), 29.40 (C5), 32.37 (C8), 36.25 (C1), 36.59 (C4), 38.56 (C6), 44.12 (C2)

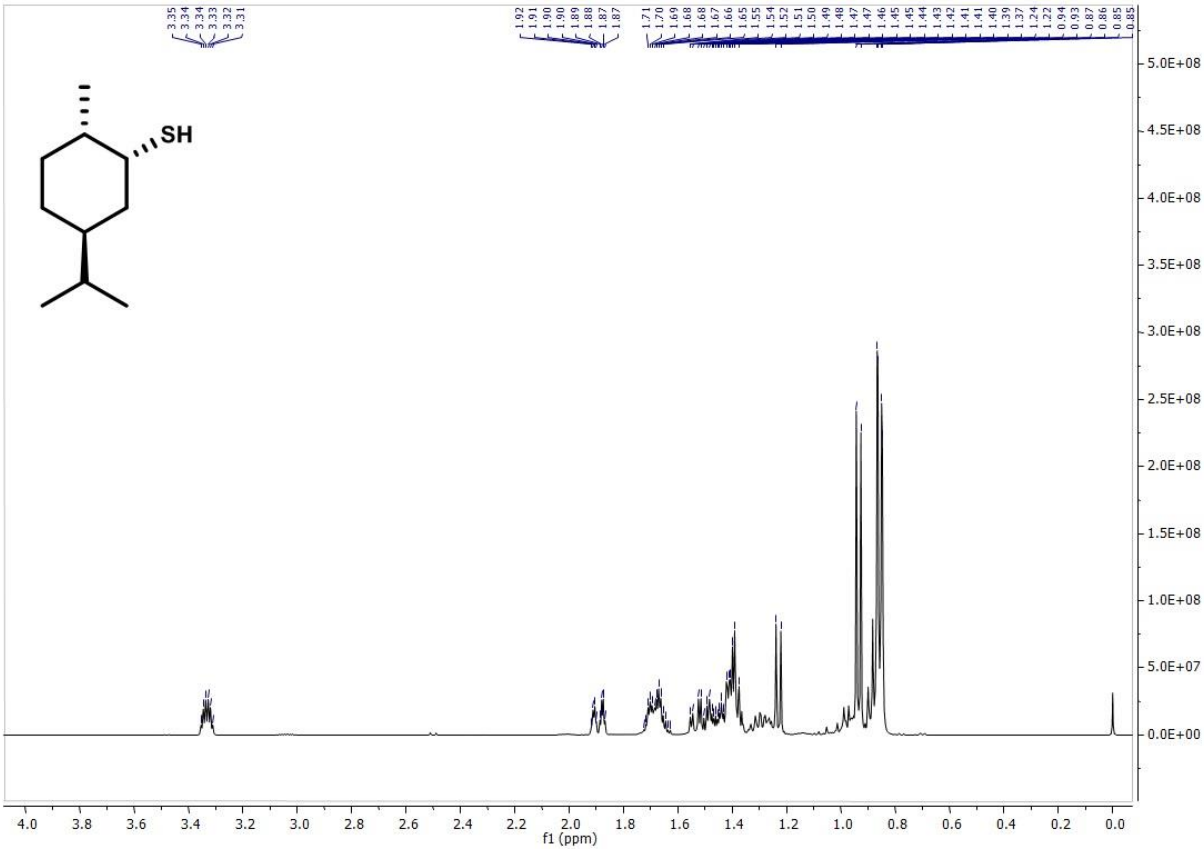


Figure S14. ^{1}H NMR spectrum of (*1S,2R,4S*)-*p*-menthane-2-thiol.

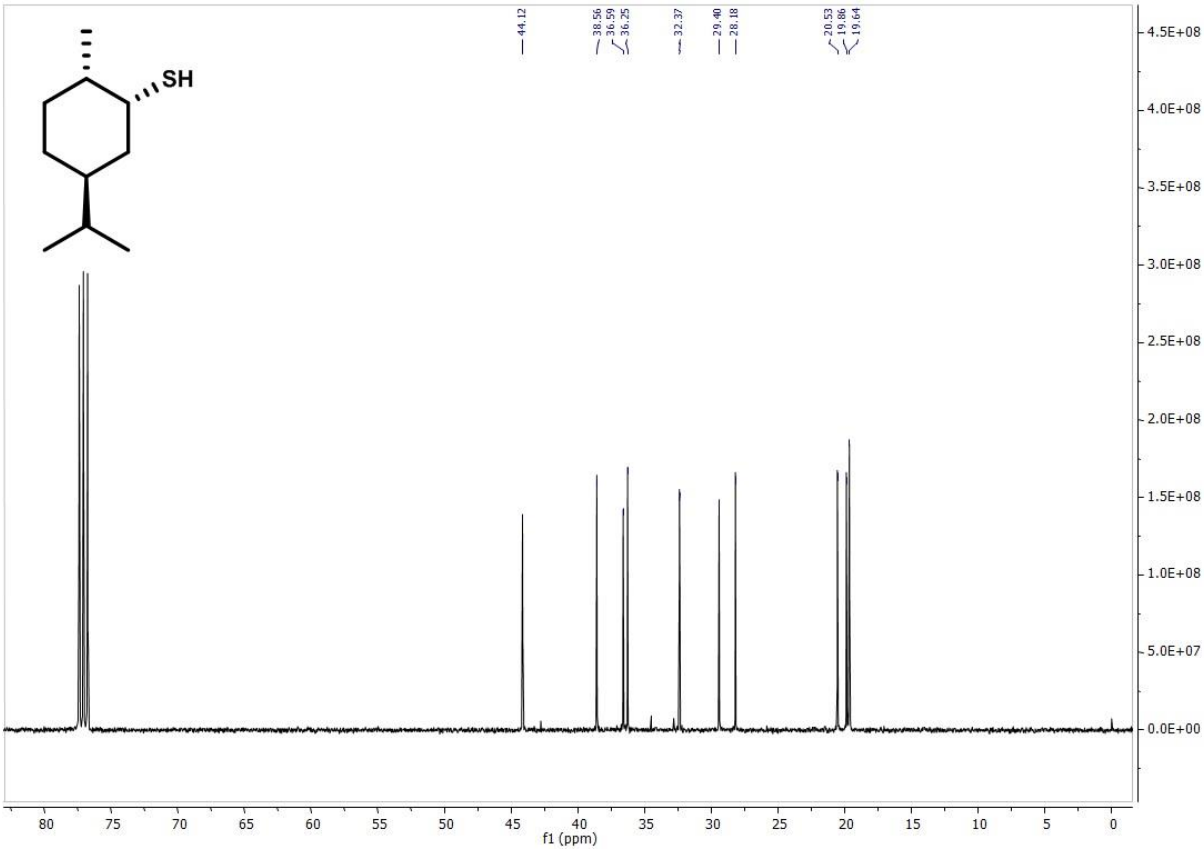
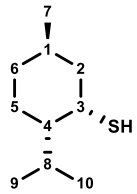


Figure S15. ^{13}C NMR spectrum of (*1S,2R,4S*)-*p*-menthane-2-thiol.

Compound **9a**

(*1R,3S,4S*)-*p*-menthane-3-thiol



educt: (-)-menthol

a) 1st intermediate:

((1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl) 4-methylbenzenesulfonate,

crude yield: 33 %

b) 2nd intermediate:

S-((1S,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl) ethanethioate,

yield: 76 %,

MS-EI: *m/z* (intensity in %) 138 (100), 95 (85), 81 (59), 83 (50), 86 (38), 55 (31), 69 (25), 67 (20), 123 (16), 96 (16), 82 (16), 139 (15), 134 (14), 57 (12), 97 (11), 94 (10), 79 (9), 128 (7), 171 (6), 214 (1, M^+)

c) analyte:

yield: 77 %

RI (FFAP): 1461

RI (DB-5): 1241

MS-EI: *m/z* (intensity in %) 95 (100), 81 (38), 138 (36), 123 (23), 55 (22), 83 (22), 67 (19), 96 (19), 69 (15), 82 (14), 172 (14, M^+), 94 (8), 68 (7), 139 (6), 79 (5), 119 (5)

MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 140 (9), 138 (6), 173 (1, $[M+H]^+$)

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.80 – 0.86 (m, 1H, H-C6), 0.86 (d, *J* = 6.3 Hz, 3H, H-C7), 0.90 (d, *J* = 3.3 Hz, 3H, H-C10), 0.91 (d, *J* = 3.3 Hz, 3H, H-C10), 1.03 (ddt, *J* = 12.4, 9.6, 3.3 Hz, 1H, H-C4), 1.22 (d, *J* = 6.9 Hz, SH), 1.25 – 1.33 (m, 1H, H-C5), 1.39 (ddd, J = 13.0, 11.7, 3.8 Hz, 1H, H-C2), 1.44 – 1.53 (m, 1H, H-C8) , 1.65 – 1.89 (m, 4H, H-C1, H-C2, H-C5, H-C6), 3.48 – 3.51 (m, 1H, H-C3)

^{13}C NMR (101 MHz, $CDCl_3$): δ 20.41 (C9), 20.90 (C10), 22.19 (C7), 24.22 (C5), 25.98 (C1), 30.35 (C8), 35.33 (C6), 40.22 (C3), 44.07 (C2), 48.29 (C4)

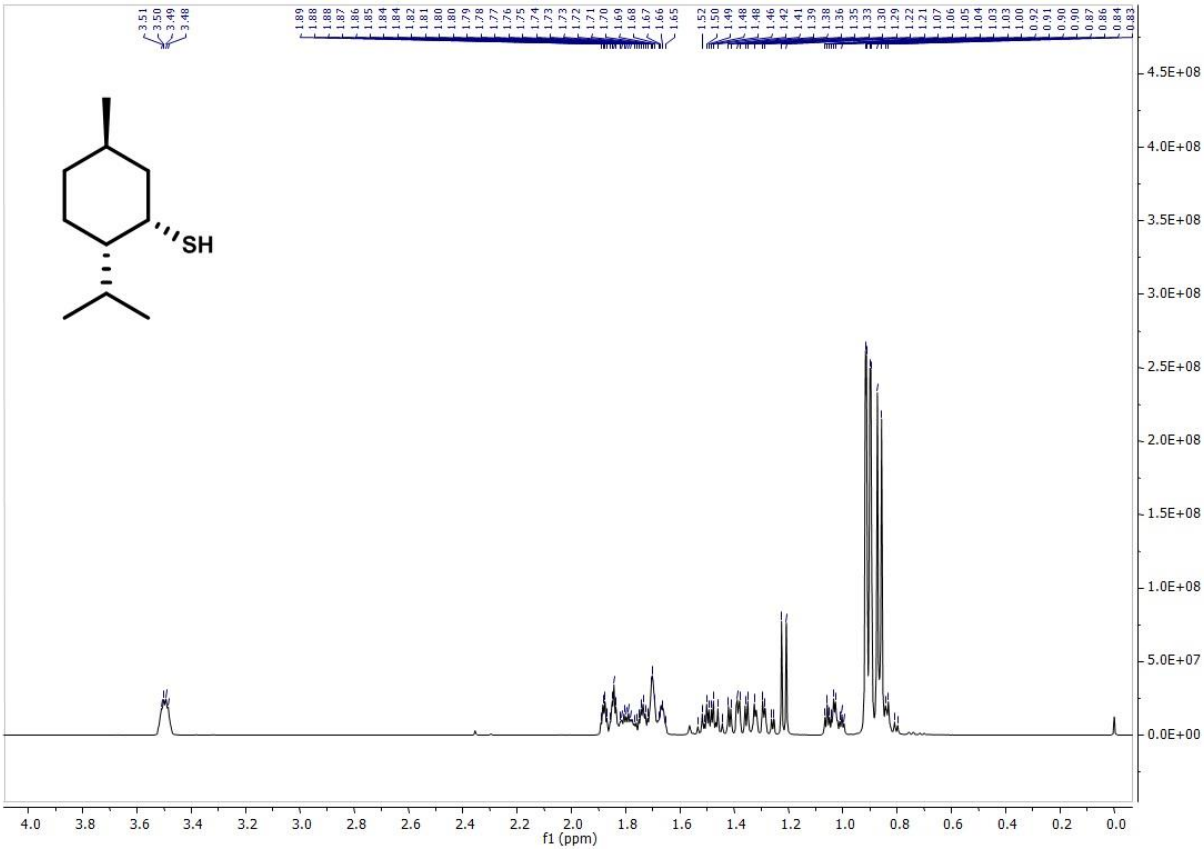


Figure S16. ^{1}H NMR spectrum of (*1R,3S,4S*)-*p*-menthane-3-thiol.

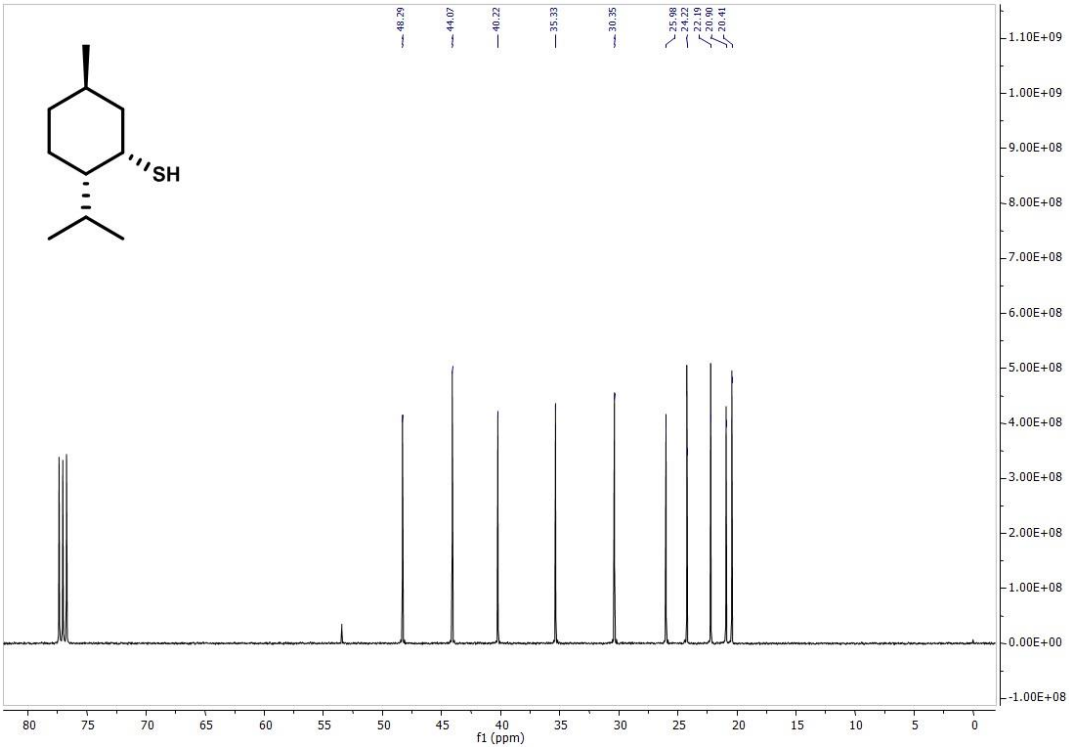
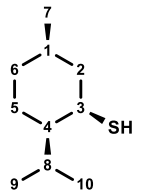


Figure S17. ^{13}C NMR spectrum of (*1R,3S,4S*)-*p*-menthane-3-thiol.

Compound **9b**

(*1R,3R,4R*)-*p*-menthane-3-thiol



educt: (+)-isomenthol

a) 1st intermediate:
((1S,2R,5R)-5-methyl-2-(propan-2-yl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 38 %

b) 2nd intermediate:
S-((1R,2R,5R)-5-methyl-2-(propan-2-yl)cyclohexyl) ethanethioate,
yield: 64 %,
MS-EI: *m/z* (intensity in %) 138 (100), 95 (91), 81 (64), 83 (57), 86 (41), 55 (34), 69 (28), 67 (23), 123 (19), 96 (18), 139 (18), 82 (17), 134 (13), 57 (13), 97 (13), 79 (12), 94 (11), 128 (8), 171 (7), 214 (3, M^+)

c) analyte:
yield: 59 %
RI (FFAP): 1520
RI (DB-5): 1274

MS-EI: *m/z* (intensity in %) 95 (100), 81 (62), 55 (43), 83 (39), 123 (32), 67 (31), 69 (28), 138 (28), 172 (27, M^+), 96 (22), 82 (19), 139 (12), 57 (11), 79 (11), 53 (9), 94 (9), 93 (8), 109 (7), 77 (6), 87 (5), 91 (5)
MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 140 (13), 138 (5), 173 (1, $[M+H]^+$)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.94 (d, *J* = 3.3 Hz, 3H, H-C9), 0.96 (d, *J* = 3.3 Hz, 3H, H-C10), 1.08 (d, *J* = 7.1 Hz, 3H, H-C7), 1.20 – 1.26 (m, 1H, H-C4), 1.33 – 1.41 (m, 1H, H-C6), 1.43 (d, *J* = 6.4 Hz, SH), 1.45 – 1.55 (m, 2H, H-C5, H-C6), 1.59 – 1.83 (m, 4H, H-C1, H-C2, H-C5, H-C8), 1.91 – 1.97 (m, 1H, H-C2), 3.40 – 3.45 (m, 1H, H-C3)
^{13}C NMR (101 MHz, $CDCl_3$): δ 21.17 (C9), 21.81 (C10), 21.88 (C7), 22.33 (C5), 28.96 (C8), 29.31 (C1), 31.52 (C6), 39.95 (C3), 40.94 (C2), 47.32 (C4)

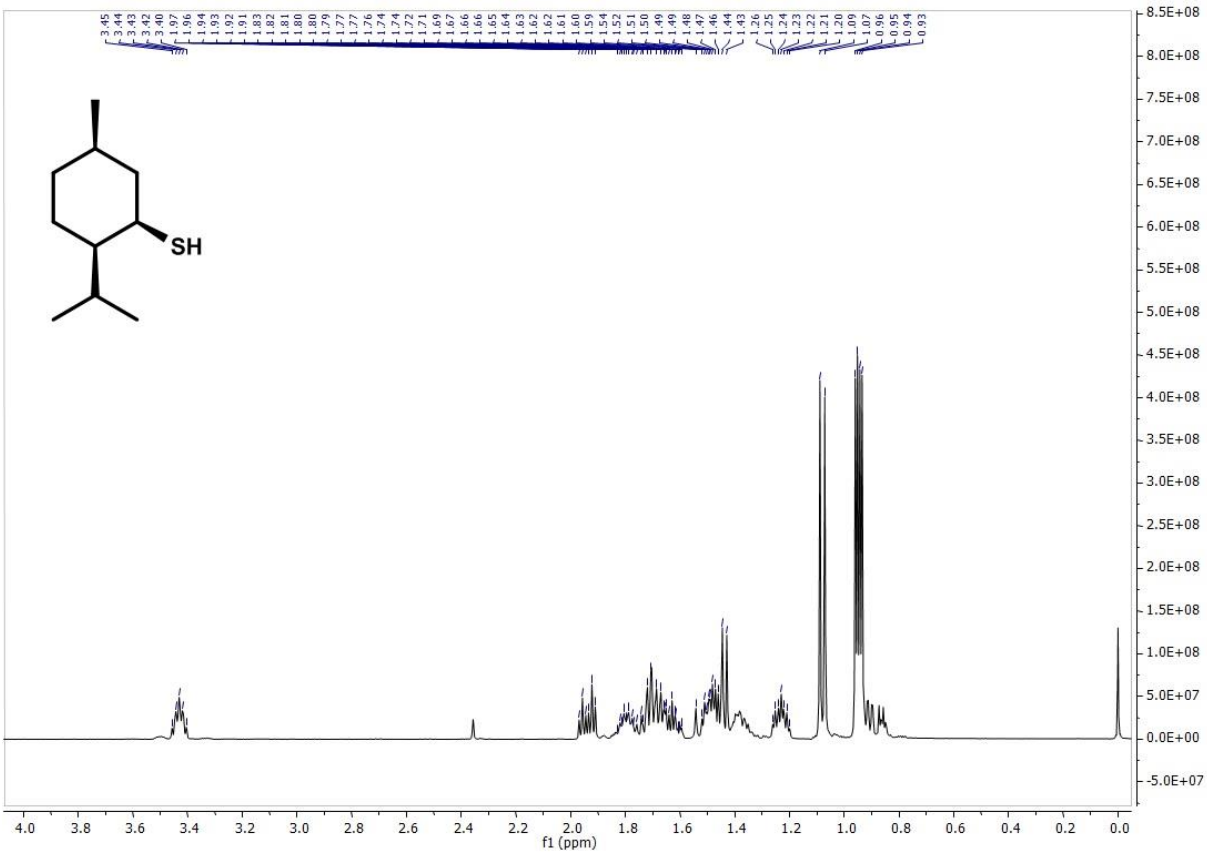


Figure S18. ^{1}H NMR spectrum of (*1R,3R,4R*)-*p*-menthane-3-thiol.

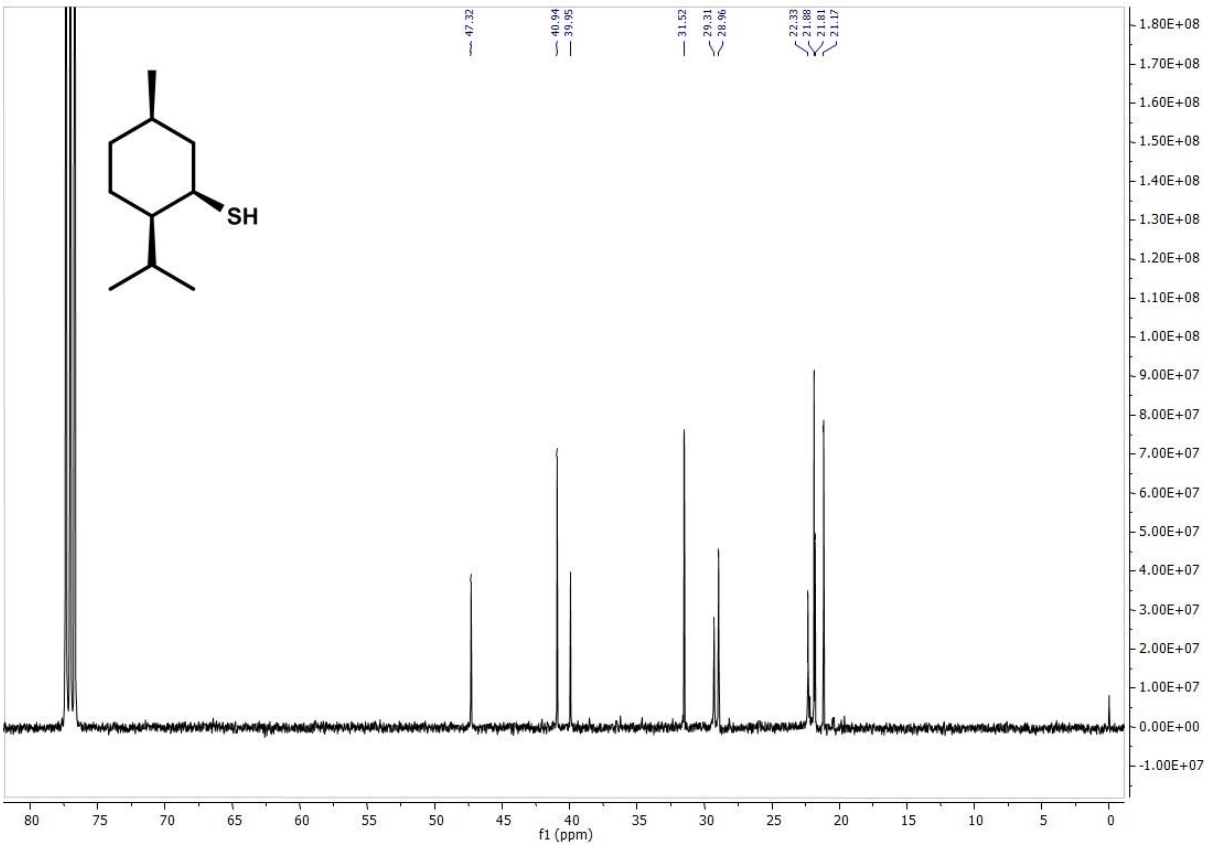
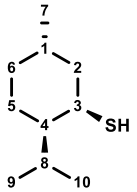


Figure S19. ^{13}C NMR spectrum of (*1R,3R,4R*)-*p*-menthane-3-thiol.

Compound **9c**

(*1S,3R,4R*)-*p*-menthane-3-thiol



educt: (+)-menthol

a) 1st intermediate:
((1S,2R,5S)-5-methyl-2-(propan-2-yl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 30 %

b) 2nd intermediate:
S-((1R,2R,5S)-5-methyl-2-(propan-2-yl)cyclohexyl) ethanethioate,
yield: 68 %,
MS-EI: *m/z* (intensity in %) 95 (100), 138 (100), 81 (75), 83 (65), 86 (62), 69 (32), 55 (31), 67 (27), 123 (20), 84 (20), 82 (19), 96 (18), 49 (18), 139 (15), 137 (14), 97 (13), 57 (13), 94 (13), 109 (8), 171 (5), 214 (2, M^+)

c) analyte:
yield: 74 %
RI (FFAP): 1461
RI (DB-5): 1241

MS-EI: *m/z* (intensity in %) 95 (100), 138 (61), 81 (60), 67 (34), 172 (32, M^+), 83 (30), 55 (29), 123 (29), 96 (21), 82 (21), 69 (18), 94 (17), 79 (12), 68 (11), 139 (9), 57 (9), 80 (8), 109 (8), 53 (7), 97 (7), 93 (6)
MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 140 (10), 138 (7), 173 (4, $[M+H]^+$)
^{1}H NMR (400 MHz; $CDCl_3$): δ 83 – 0.91 (m, 1H, H-C6), 0.86 (d, *J* = 6.4 Hz, 3H, H-C7), 0.90 (d, *J* = 3.3 Hz, 3H, H-C9), 0.91 (d, 3.3 Hz, 3H, H-C10), 1.03 (ddt, *J* = 12.5, 9.6, 3.3 Hz, 1H, H-C4), 1.22 (d, *J* = 7.0 Hz, SH), 1.25 – 1.33 (m, 1H, H-C5), 1.39 (ddd, *J* = 13.1, 11.7, 3.8 Hz, 1H, H-C2), 1.44 – 1.53 (m, 1H, H-C8) , 1.65 - 1.89 (m, 4H, H-C1, H-C2, H-C3, H-C5, H-C6), 3.48 – 3.52 (m, 1H, H-C3)
^{13}C NMR (101 MHz, $CDCl_3$): δ 20.41 (C9), 20.90 (C10), 22.18 (C7), 24.21 (C5), 25.98 (C1), 30.36 (C8), 35.33 (C6), 40.22 (C3), 44.07 (C2), 48.29 (C4)

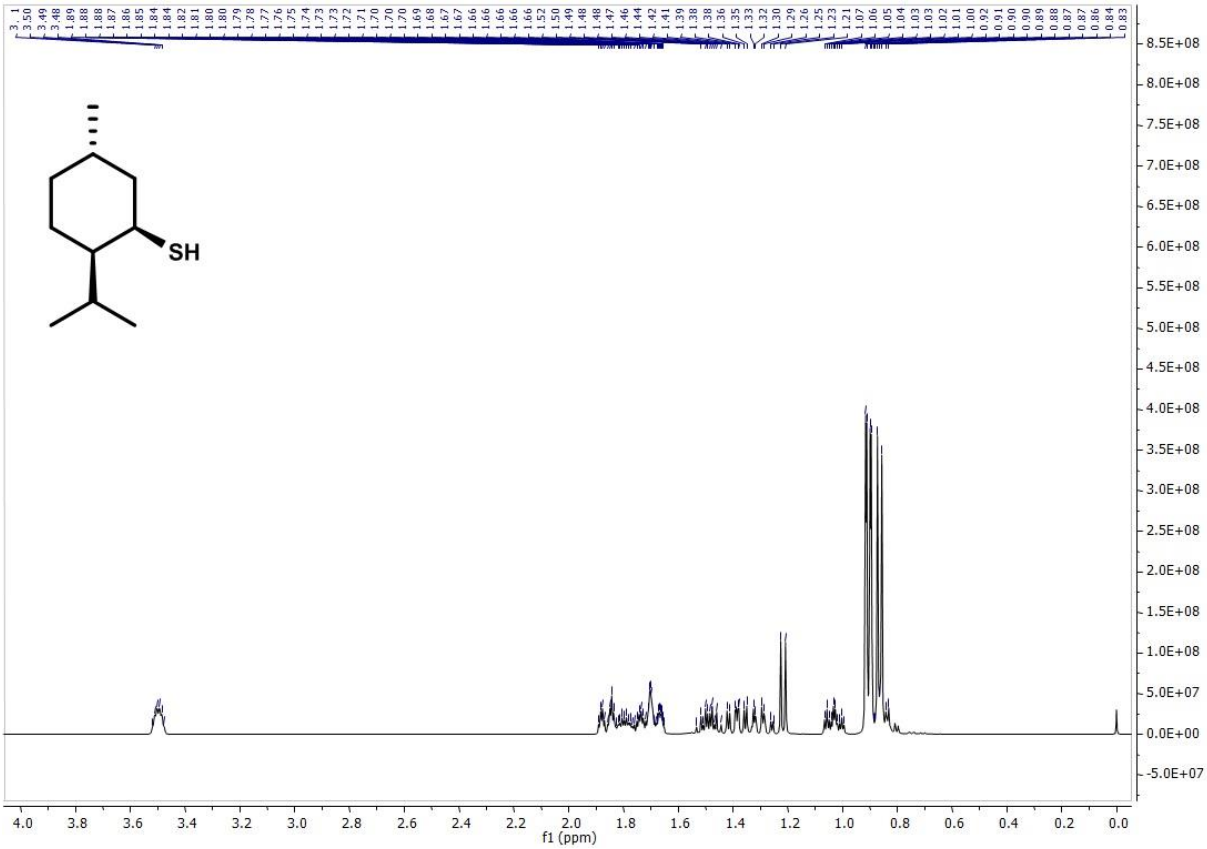


Figure S20. ^{1}H NMR spectrum of (*1S,3R,4R*)-*p*-menthane-3-thiol.

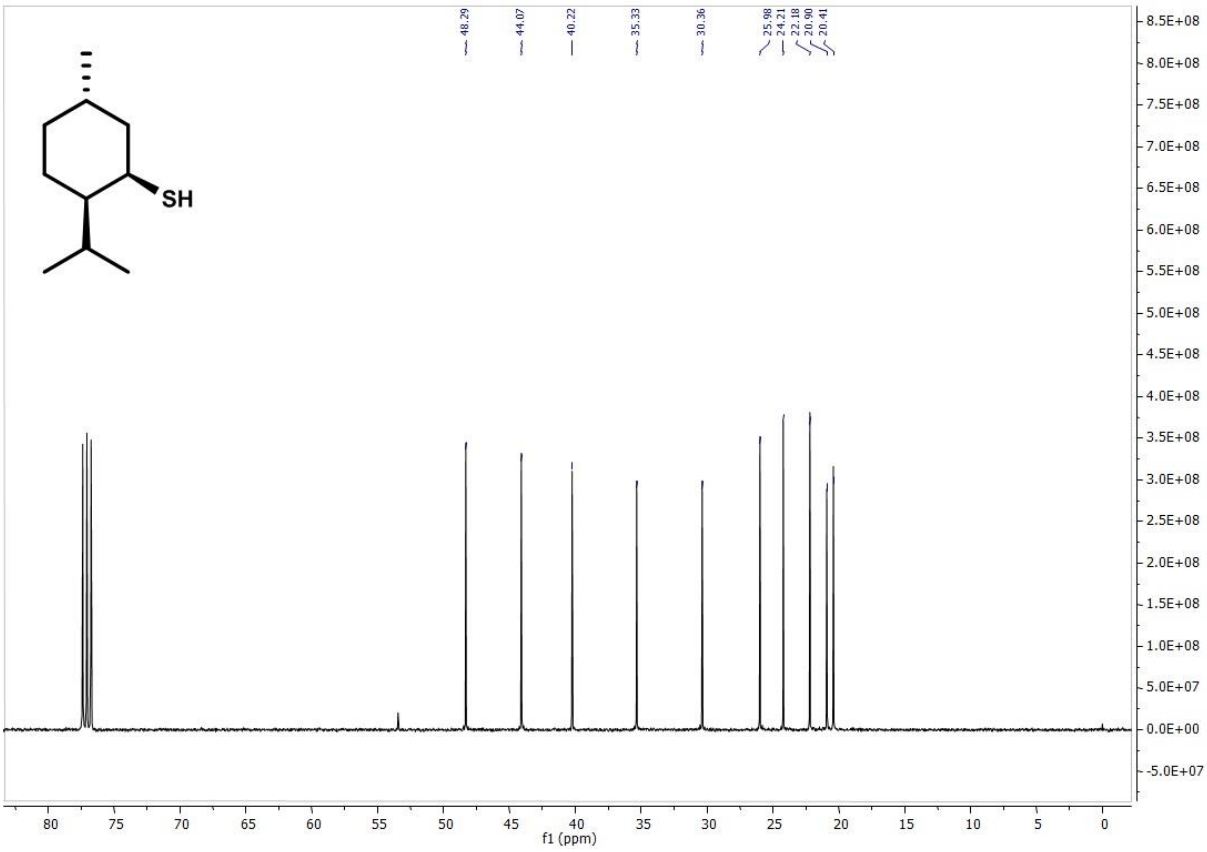
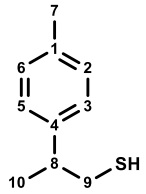


Figure S21. ^{13}C NMR spectrum of (*1S,3R,4R*)-*p*-menthane-3-thiol.

Compound **12**

***p*-cymene-9-thiol**



educt: *p*-cymene-9-ol

a) 1st intermediate:
2-(p-tolyl)propyl 4-methylbenzenesulfonate,
crude yield: 52 %

b) 2nd intermediate:
S-(2-p-tolylpropyl) ethanethioate,
yield: 78 %,
MS-EI: *m/z* (intensity in %) 119 (100), 132 (89), 117 (32), 91 (26), 115 (15), 133 (10), 120 (9), 77 (8), 43 (7), 65 (7), 118 (6), 103 (5), 105 (5), 116 (5), 208 (2, M^+)

c) analyte:
yield: 95 %
RI (FFAP): 1813
RI (DB-5): 1324

MS-EI: *m/z* (intensity in %) 119 (100), 91 (27), 117 (20), 166 (17, M^+), 120 (12), 115 (8), 77 (6), 65 (5), 103 (5)
MS-CI (isobutane): *m/z* (intensity in %) 133 (100), 134 (12), 119 (11), 166 (4), 167 (3, $[M+H]^+$)
^{1}H NMR (400 MHz; $CDCl_3$): δ 1.22 (dd, *J* = 7.2, 9.0 Hz, SH), 1.33 (d, *J* = 6.9 Hz, 3H, H-C10), 2.33 (s, 3H, H-C7), 2.63 – 2.70 (m, 1H, H-C9), 2.74 – 2.81 (m, 1H, H-C9), 2.86 (h, *J* = 6.8 Hz, 1H, H-C8), 7.09 (d, *J* = 8.2 Hz, 2H, H-C3, H-C5), 7.13 (d, *J* = 8.6 Hz, 2H, H-C2, H-C6)
^{13}C NMR (101 MHz, $CDCl_3$): δ 20.80 (C10), 21.04 (C7), 32.66 (C9), 42.93 (C8), 127.04 (C3, C5), 129.22 (C2, C6), 136.13 (C1), 141.84 (C4)

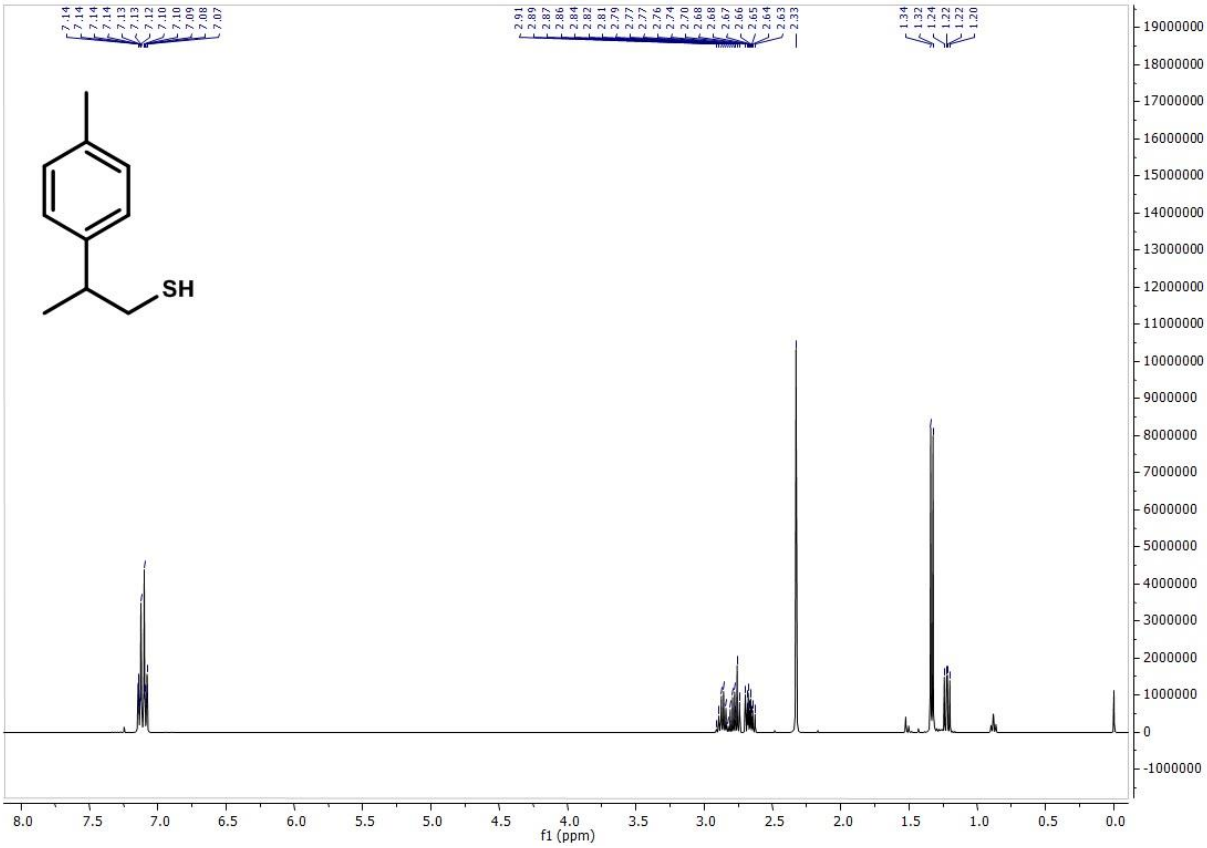


Figure S22. ^{1}H NMR spectrum of *p*-cymene-9-thiol.

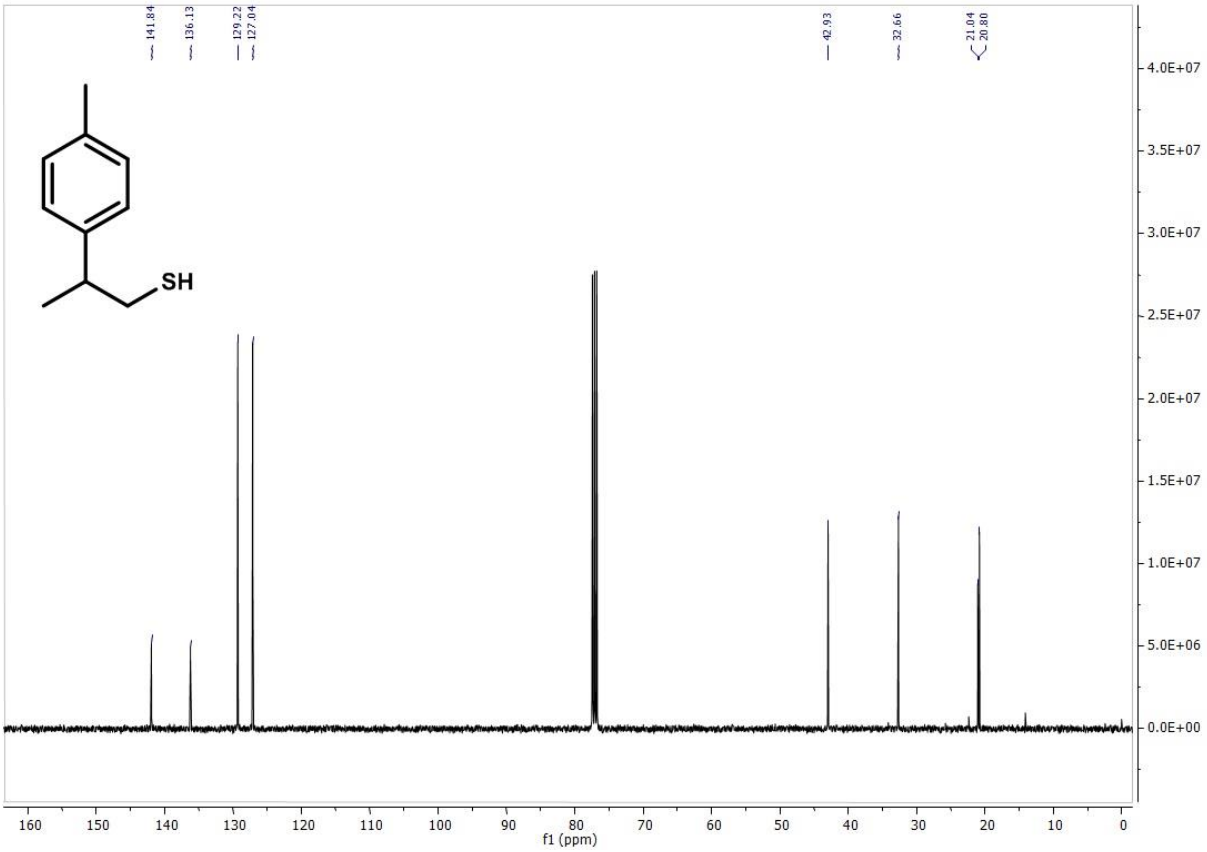
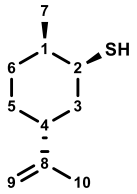


Figure S23. ^{13}C NMR spectrum of *p*-cymene-9-thiol.

Compound **15a**

(*1R,2S,4R*)-8-*p*-menthene-2-thiol



educt: (-)-dihydrocarveol

a) 1st intermediate:
((1R,3R,6R)-6-methyl-3-(1-methylethenyl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 96 %

b) 2nd intermediate:
S-((1S,3R,6R)-6-methyl-3-(1-methylethenyl)cyclohexyl) ethanethioate,
yield: 49 %,
MS-EI: *m/z* (intensity in %) 93 (100), 107 (98), 79 (91), 121 (74), 136 (65), 81 (37), 67 (34), 108 (27), 94 (25), 91 (24), 170 (22), 77 (20), 55 (19), 68 (17), 53 (16), 80 (15), 105 (12), 137 (11) 122 (9), 65 (8), 69 (8), 82 (7), 101 (5), 127 (5), 212 (1, M^+)

c) analyte:
yield: 93 %
RI (FFAP): 1592
RI (DB-5): 1282

MS-EI: *m/z* (intensity in %) 79 (100), 121 (98), 107 (97), 93 (94), 136 (92), 41 (48), 81 (46), 67 (44), 68 (37), 55 (35), 91 (29), 95 (28), 53 (27), 94 (27), 77 (25), 108 (25), 170 (25, M^+), 44 (16), 80 (15), 92 (15), 69 (12), 105 (12), 122 (12), 137 (12), 82 (11), 65 (10), 119 (8), 155 (7)
MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 171 (28, $[M+H]^+$), 138 (21), 136 (13), 95 (11), 170 (6)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.96 (d, *J* = 6.7 Hz, 3H, H-C7), 1.14 – 1.21 (m, 1H, H-C5), 1.26 (d, *J* = 6.9 Hz, SH), 1.43 – 1.49 (m, 2H, H-C6), 1.71 (s, 3H, H-C10), 1.69 – 1.79 (m, 3H, H-C1, H-C3, H-C5), 1.92 – 1.98 (m, 1H, H-C3), 2.30 (tt, *J* = 12.4, 3.3 Hz, 1H, H-C4), 3.35 – 3.40 (m, 1H, H-C2), 4.68 (d, *J* = 1.0 Hz, 1H, H-C9), 4.70 (d, *J* = 1.0 Hz, 1H, H-C9)
^{13}C NMR (101 MHz, $CDCl_3$): δ 20.52 (C7), 21.10 (C10), 28.14 (C6), 31.54 (C5), 35.97 (C1), 37.87 (C4), 40.17 (C3), 43.82 (C2), 108.61 (C9), 149.81 (C8)

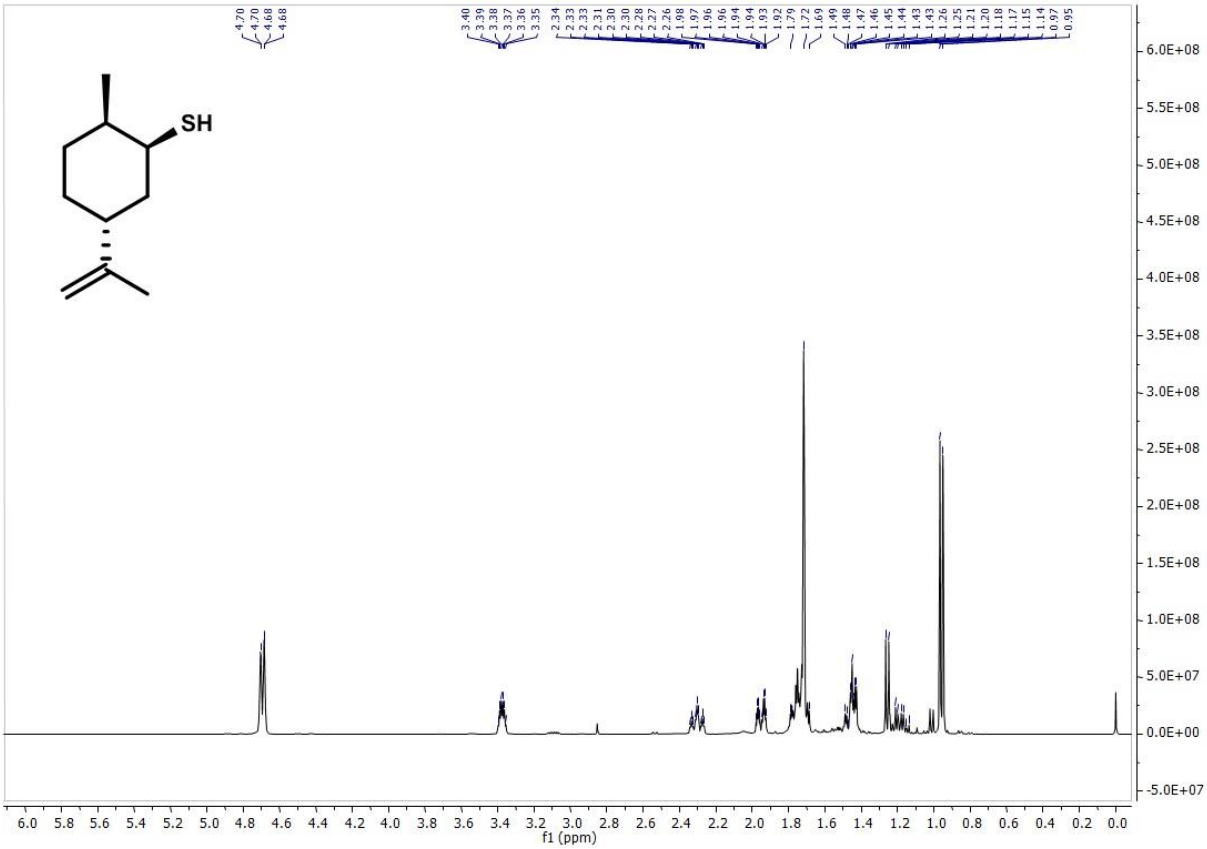


Figure S24. ^{1}H NMR spectrum of (*1R,2S,4R*)-8-*p*-menthene-2-thiol.

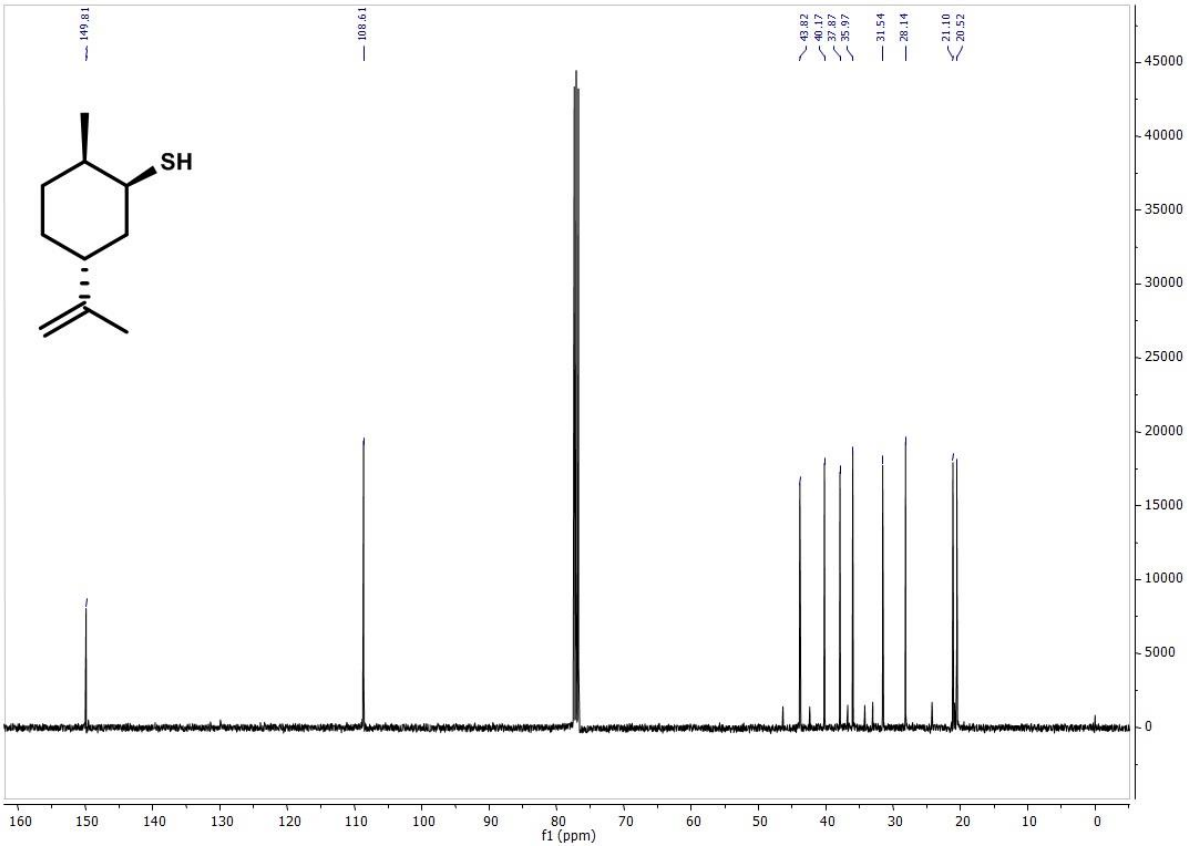
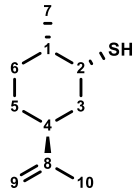


Figure S25. ^{13}C NMR spectrum of (*1R,2S,4R*)-8-*p*-menthene-2-thiol.

Compound **15b**

(*1S,2R,4S*)-8-*p*-menthene-2-thiol



educt: (+)-dihydrocarveol

a) 1st intermediate:
((1S,3S,6S)-6-methyl-3-(1-methylethenyl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 92 %

b) 2nd intermediate:
S-((1R,3S,6S)-6-methyl-3-(1-methylethenyl)cyclohexyl) ethanethioate,
yield: 65 %,
MS-EI: *m/z* (intensity in %) 93 (100), 107 (92), 79 (89), 121 (88), 136 (77), 67 (33), 81 (33), 108 (29), 91 (27), 170 (26), 94 (24), 55 (41), 95 (20), 77 (19), 92 (17), 68 (16), 53 (15), 155 (13), 105 (11), 137 (11), 122 (9), 69 (8), 82 (7), 101 (5), 212 (1, M^+)

c) analyte:
yield: 75 %
RI (FFAP): 1591
RI (DB-5): 1282

MS-EI: *m/z* (intensity in %) 121 (100), 107 (98), 93 (95), 136 (94), 79 (93), 44 (52), 41 (48), 81 (42), 67 (38), 68 (34), 95 (30), 91 (29), 94 (27), 45 (25), 53 (25), 77 (25), 94 (25), 108 (22), 170 (22, M^+), 137 (15), 69 (13), 65 (12), 80 (12), 105 (11), 122 (10), 155 (9), 73 (8)
MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 171 (11, $[M+H]^+$), 138 (9), 136 (6), 95 (6)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.96 (d, *J* = 6.6 Hz, 3H, H-C7), 1.15 – 1.23 (m, 1H, H-C5), 1.26 (d, *J* = 6.9 Hz, SH), 1.43 – 1.49 (m, 2H, H-C6), 1.69 – 1.79 (m, 3H, H-C1, H-C3, H-C5), 1.72 (s, 3H, H-C10), 1.92 – 1.98 (m, 1H, H-C3), 2.30 (tt, *J* = 12.4, 3.3 Hz, 1H, H-C4), 3.35 – 3.40 (m, 1H, H-C2), 4.68 (d, *J* = 1.1 Hz, 1H, H-C9), 4.70 (d, *J* = 1.1 Hz, 1H, H-C9)
^{13}C NMR (101 MHz, $CDCl_3$): δ 20.52 (C7), 21.10 (C10), 28.14 (C6), 31.54 (C5), 35.97 (C1), 37.87 (C4), 40.17 (C3), 43.82 (C2), 108.61 (C9), 149.81 (C8)

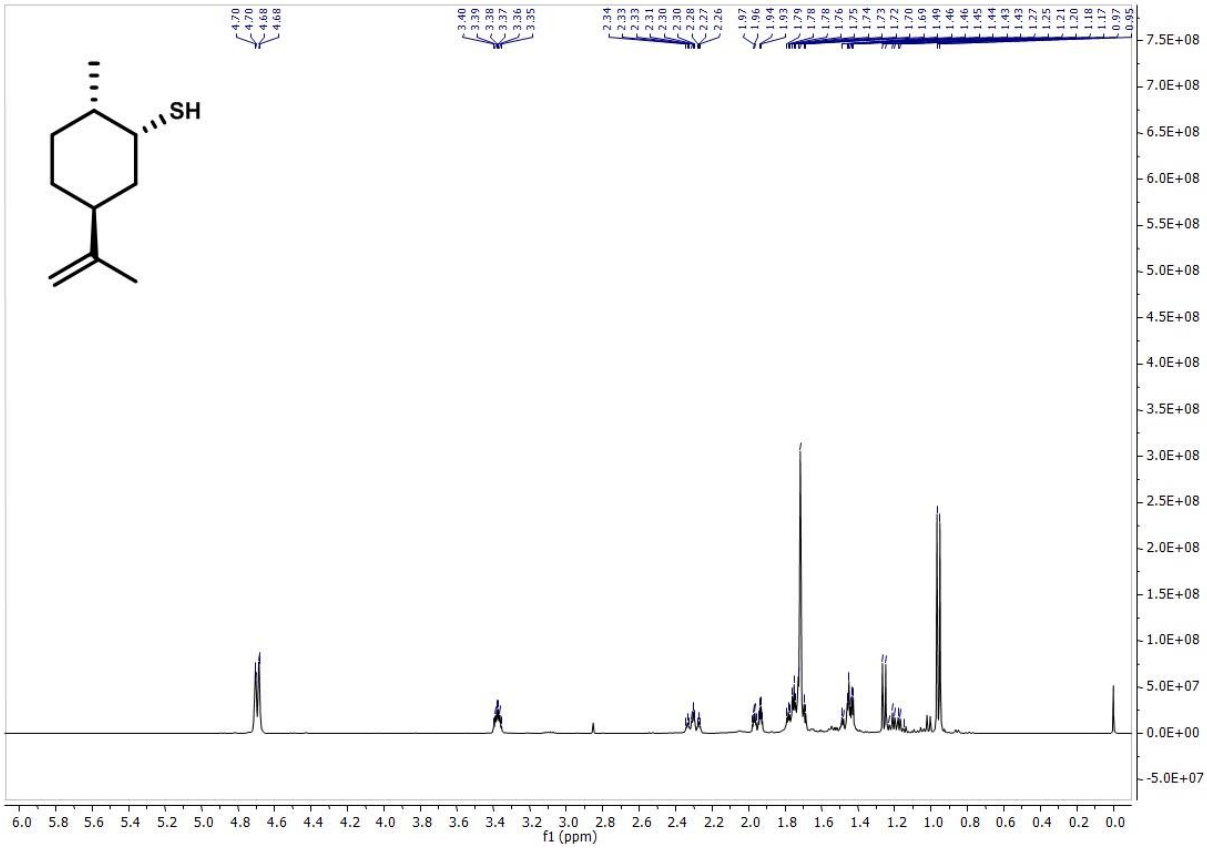


Figure S26. ^{1}H NMR spectrum of (*1S,2R,4S*)-8-*p*-menthene-2-thiol.

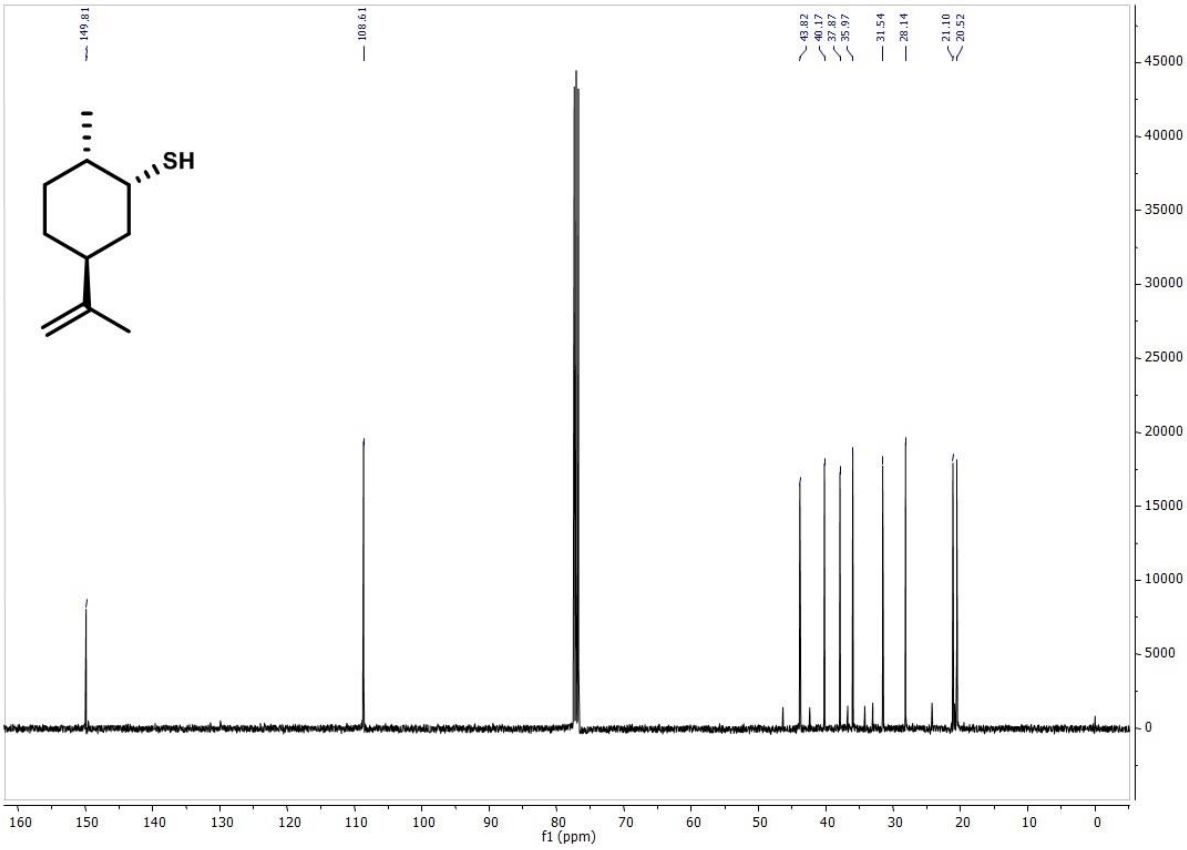
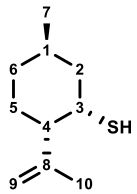


Figure S27. ^{13}C NMR spectrum of (*1S,2R,4S*)-8-*p*-menthene-2-thiol.

Compound **16a**

(*1R,3S,4S*)-8-*p*-menthene-3-thiol



educt: (-)-isopulegol

a) 1st intermediate:
((1R,2S,5R)-5-methyl-2-(1-methylethenyl)cyclohexyl) 4-methylbenzenesulfonate,
crude yield: 86 %

b) 2nd intermediate:
S-((1S,2S,5R)-5-methyl-2-(1-methylethenyl)cyclohexyl) ethanethioate,
yield: 65 %,
MS-EI: *m/z* (intensity in %) 81 (100), 155 (98), 95 (57), 94 (52), 79 (49), 67 (46), 121 (29), 55 (28), 107 (23), 123 (22), 170 (22), 99 (21), 75 (19), 68 (19), 69 (17), 53 (16), 97 (16), 85 (13), 78 (11), 109 (10), 113 (8), 212 (1, M^+)

c) analyte:
yield: 67 %
RI (FFAP): 1558
RI (DB-5): 1266

MS-EI: *m/z* (intensity in %) 155 (100), 81 (52), 95 (36), 170 (35, M^+), 121 (31), 93 (28), 79 (25), 137 (24), 136 (22), 123 (21), 67 (19), 107 (19), 111 (19), 55 (15), 87 (14), 91 (14), 99 (13), 156 (12), 168 (12), 68 (11), 77 (10), 101 (10), 69 (8), 109 (7), 113 (7), 127 (7), 153 (5), 171 (5)
MS-CI (isobutane): *m/z* (intensity in %) 171 (100, $[M+H]^+$), 137 (31), 172 (11), 173 (7)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.89 – 1.02 (m, 2H, H-C2, H-C6), 0.95 (d, *J* = 6.6 Hz, 3H, H-C7), 1.27 – 1.38 (m, 1H, H-C5), 1.45 – 1.54 (m, 1H, H-C1), 1.64 – 1.70 (m, 2H, H-C5, H-C6), 1.71 (s, 3H, H-C10), 1.85 – 1.92 (m, 2H, H-C4, SH), 2.01 – 2.07 (m, 1H, H-C2), 3.46 (ddd, *J* = 10.8, 10.0, 4.3 Hz, 1H, H-C3), 4.85 – 4.86 (m, 1H, H-C9), 4.89 – 4.91 (m, 1H, H-C9)
^{13}C NMR (101 MHz, $CDCl_3$): δ 19.20 (C10), 22.23 (C7), 29.66 (C5), 31.45 (C1), 34.33 (C6), 42.68 (C2), 54.14 (C4), 70.36 (C3), 112.83 (C9), 146.65 (C8)

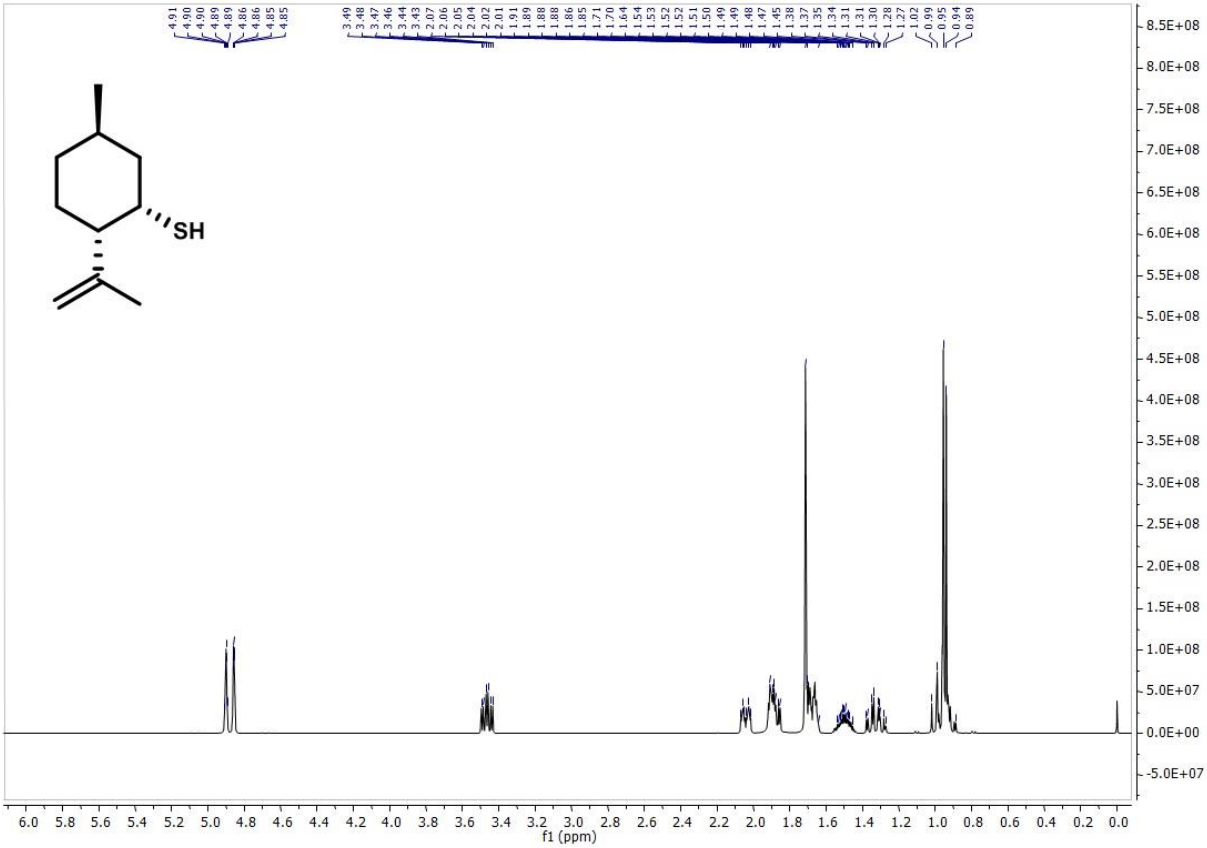


Figure S28. ^{1}H NMR spectrum of (*1R,3S,4S*)-8-*p*-menthene-3-thiol.

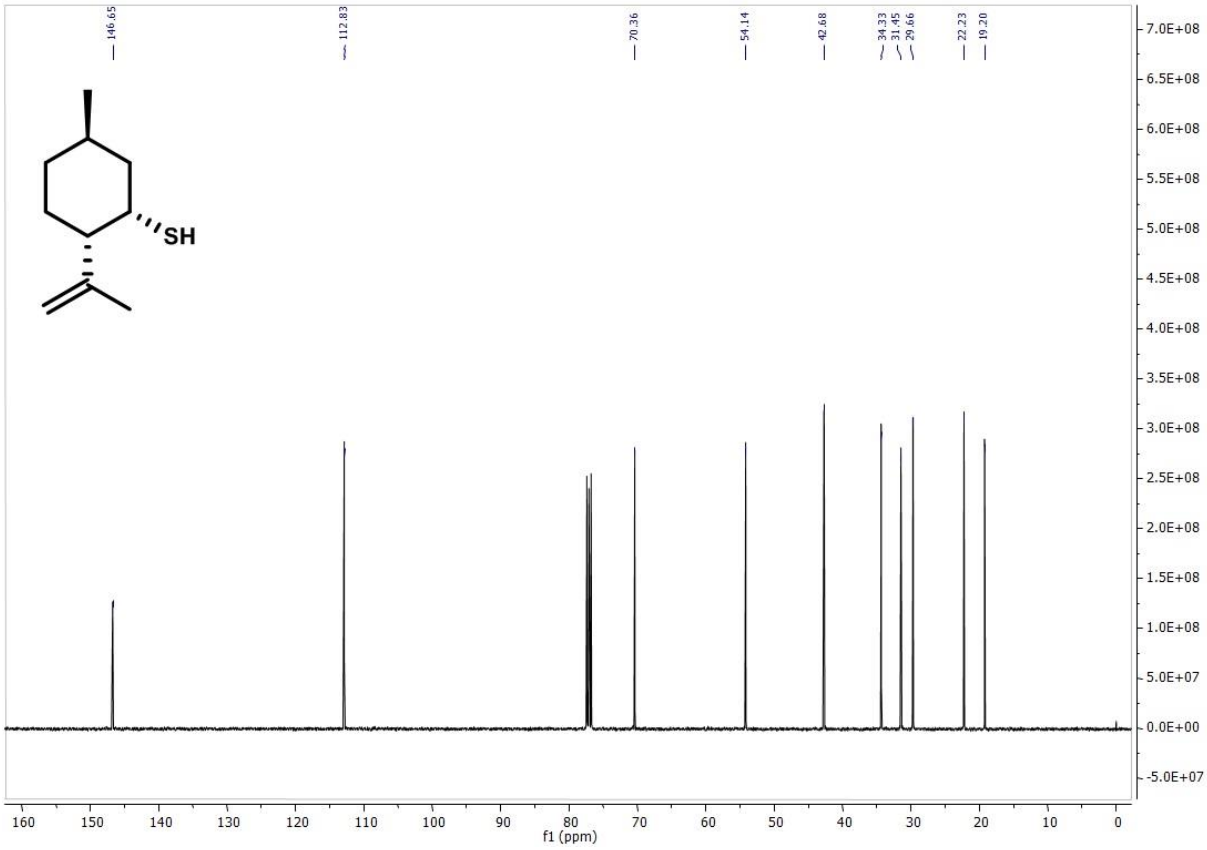
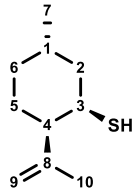


Figure S29. ^{13}C NMR spectrum of (*1R,3S,4S*)-8-*p*-menthene-3-thiol.

Compound **16b**

(*1S,3R,4R*)-8-*p*-menthene-3-thiol



educt: (+)-isopulegol

a) 1st intermediate:

((1S,2R,5S)-5-methyl-2-(1-methylethenyl)cyclohexyl) 4-methylbenzenesulfonate,

crude yield: 79 %

b) 2nd intermediate:

S-((1R,2R,5S)-5-methyl-2-(1-methylethenyl)cyclohexyl) ethanethioate,

yield: 84 %,

MS-EI: *m/z* (intensity in %) 128 (100), 169 (48), 95 (46), 93 (45), 81 (42), 107 (28), 43 (27), 79 (27), 135 (25), 136 (22), 67 (20), 121 (17), 55 (16), 113 (15), 41 (13), 94 (13), 155 (13), 79 (12), 91 (12), 108 (9), 170 (9), 53 (8), 69 (8), 85 (8), 99 (8), 129 (8), 164 (7), 212 (3, M^+)

c) analyte:

yield: 62 %

RI (FFAP): 1558

RI (DB-5): 1267

MS-EI: *m/z* (intensity in %) 81 (100), 155 (75), 95 (58), 41 (51), 93 (48), 79 (47), 67 (46), 55 (44), 121 (38), 68 (29), 123 (27), 107 (26), 53 (25), 170 (25, M^+), 77 (23), 137 (23), 69 (22), 91 (21), 99 (21), 87 (20), 111 (20), 136 (20), 101 (16), 75 (15), 94 (15), 109 (15), 77 (14), 85 (14), 82 (12), 80 (12), 127 (11), 113 (10), 156 (9), 168 (9), 92 (8), 105 (8), 171 (3)

MS-CI (isobutane): *m/z* (intensity in %) 171 (100, $[M+H]^+$), 137 (29), 95 (14), 91 (10), 172 (9), 155 (5)

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.89 – 1.02 (m, 2H, H-C2, H-C6), 0.95 (d, *J* = 6.6 Hz, 3H, H-C7), 1.28 – 1.38 (m, 1H, H-C5), 1.45 – 1.54 (m, 1H, H-C1), 1.65 – 1.70 (m, 2H, H-C5, H-C6), 1.71 (s, 3H, H-C10), 1.85 – 1.92 (m, 2H, H-C4, SH), 2.01 – 2.07 (m, 1H, H-C2), 3.46 (ddd, *J* = 10.8, 10.0, 4.3 Hz, 1H, H-C3), 4.85 – 4.86 (m, 1H, H-C9), 4.89 – 4.91 (m, 1H, H-C9)

^{13}C NMR (101 MHz, $CDCl_3$): δ 19.20 (C10), 22.23 (C7), 29.66 (C5), 31.45 (C1), 34.33 (C6), 42.68 (C2), 54.14 (C4), 70.36 (C3), 112.83 (C9), 146.65 (C8)

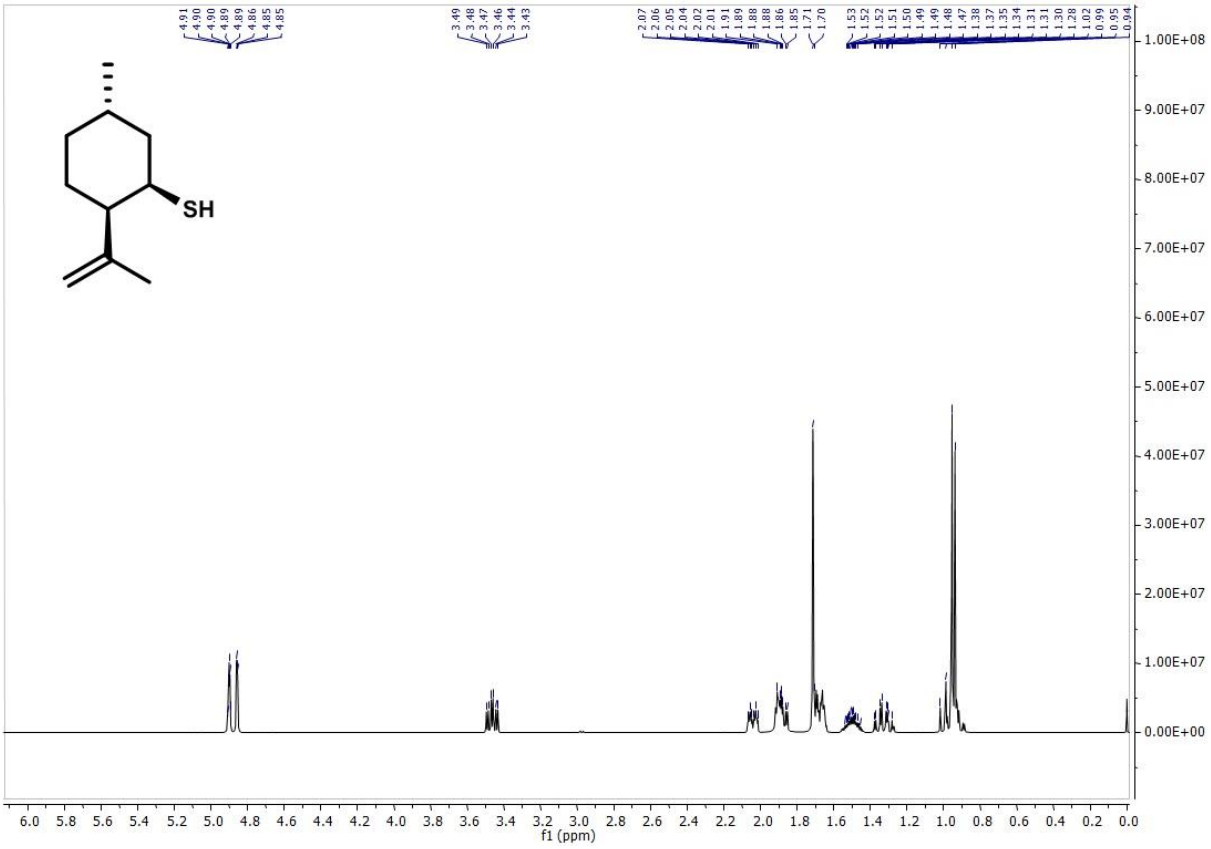


Figure S30. ^{1}H NMR spectrum of (*1S,3R,4R*)-8-*p*-menthene-3-thiol.

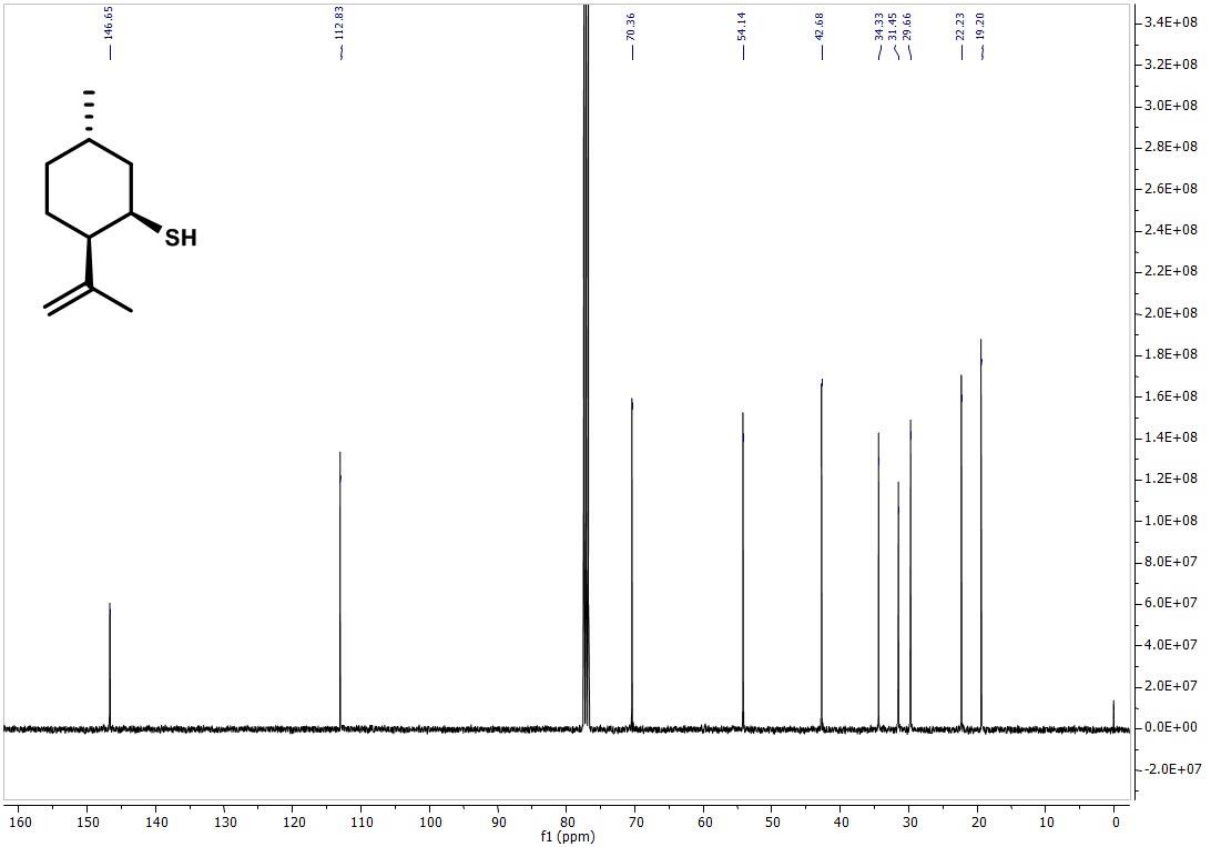
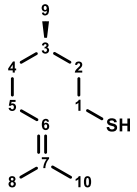


Figure S31. ^{13}C NMR spectrum of (*1S,3R,4R*)-8-*p*-menthene-3-thiol.

Compound **18a**

(*3R*)-*β*-thio citronellol



educt: (*R*)-(+)-*β*-citronellol

a) 1st intermediate:
(3R)-3,7-dimethyloct-6-en-1-yl 4-methylbenzenesulfonate,
crude yield: 62 %

b) 2nd intermediate:
(3R)-S-(3,7-dimethyloct-6-en-1-yl) ethanethioate,
yield: 93 %,
MS-EI: *m/z* (intensity in %) 69 (100), 171 (58), 115 (49), 55 (31), 81 (28), 95 (22), 101 (20), 67 (19), 82 (14), 68 (9), 123 (8), 83 (8), 138 (7), 53 (6), 103 (6), 47 (6), 137 (6), 172 (6), 214 (2, M^+)

c) analyte:
yield: 76 %
RI (FFAP): 1541
RI (DB-5): 1278

MS-EI: *m/z* (intensity in %) 69 (100), 55 (51), 115 (45), 67 (33), 81 (31), 101 (29), 95 (29), 129 (27), 82 (20), 47 (16), 68 (15), 83 (14), 56 (12), 61 (12), 123 (12), 70 (11), 53 (10), 171 (10), 172 (8, M^+)
MS-CI (isobutane): *m/z* (intensity in %) 173 (100, $[M+H]^+$), 174 (14), 139 (8)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.91 (d, *J* = 6.5 Hz, 3H, H-C9), 1.13 – 1.22 (m, 1H, H-C4), 1.30 – 1.39 (m, 1H, H-C4), 1.33 (t, *J* = 7.6 Hz, SH), 1.43 – 1.52 (m, 1H, H-C2), 1.53 – 1.69 (m, 2H, H-C2, H-C3), 1.63 (s, 3H, H-C10), 1.71 (s, 3H, H-C8), 1.92 – 2.08 (m, 2H, H-C5), 2.48 – 2.64 (m, 2H, H-C1), 5.09 – 5.14 (m, 1H, H-C6)
^{13}C NMR (101 MHz, $CDCl_3$): δ 17.66 (C3), 19.12 (C9), 22.48 (C1), 25.41 (C5), 25.72 (C10), 31.49 (C8), 36.72 (C4), 41.44 (C2), 124.63 (C6), 131.34 (C7)

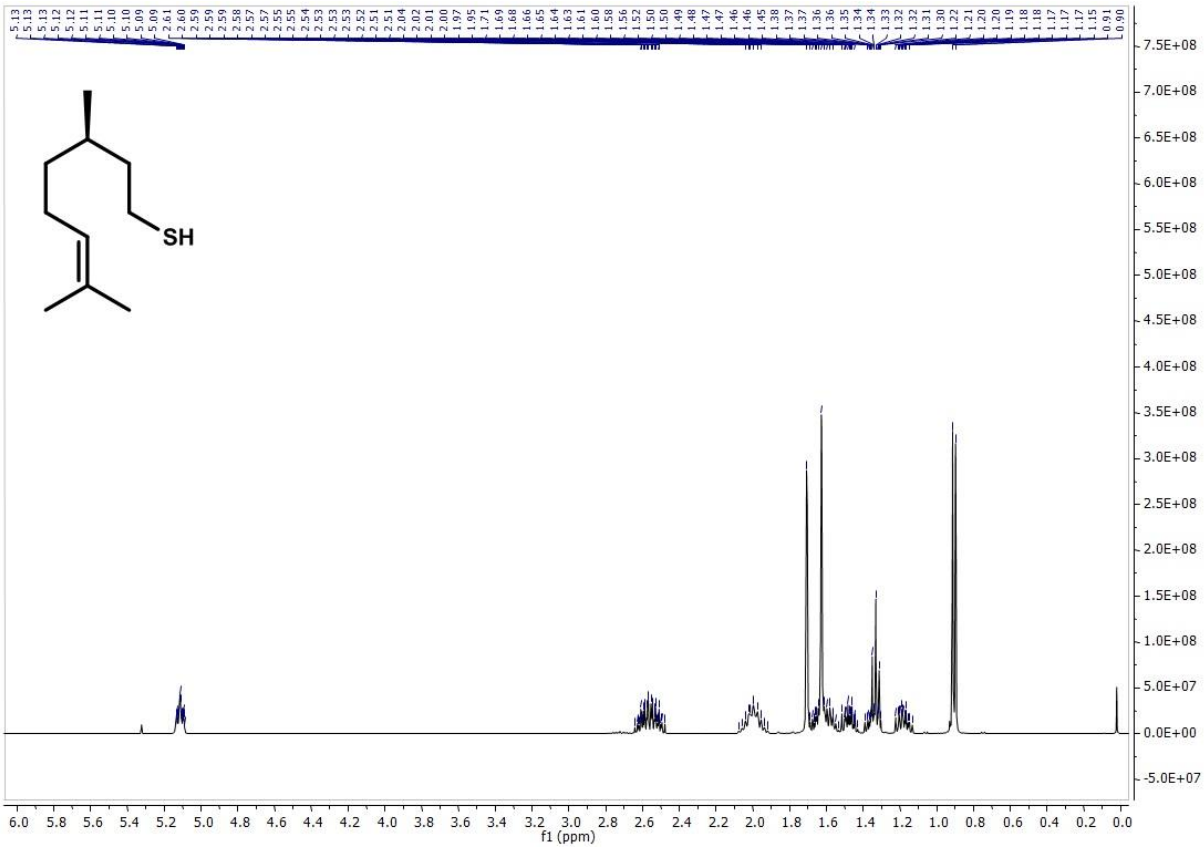


Figure S32. ^{1}H NMR spectrum of (*3R*)-*β*-thio citronellol.

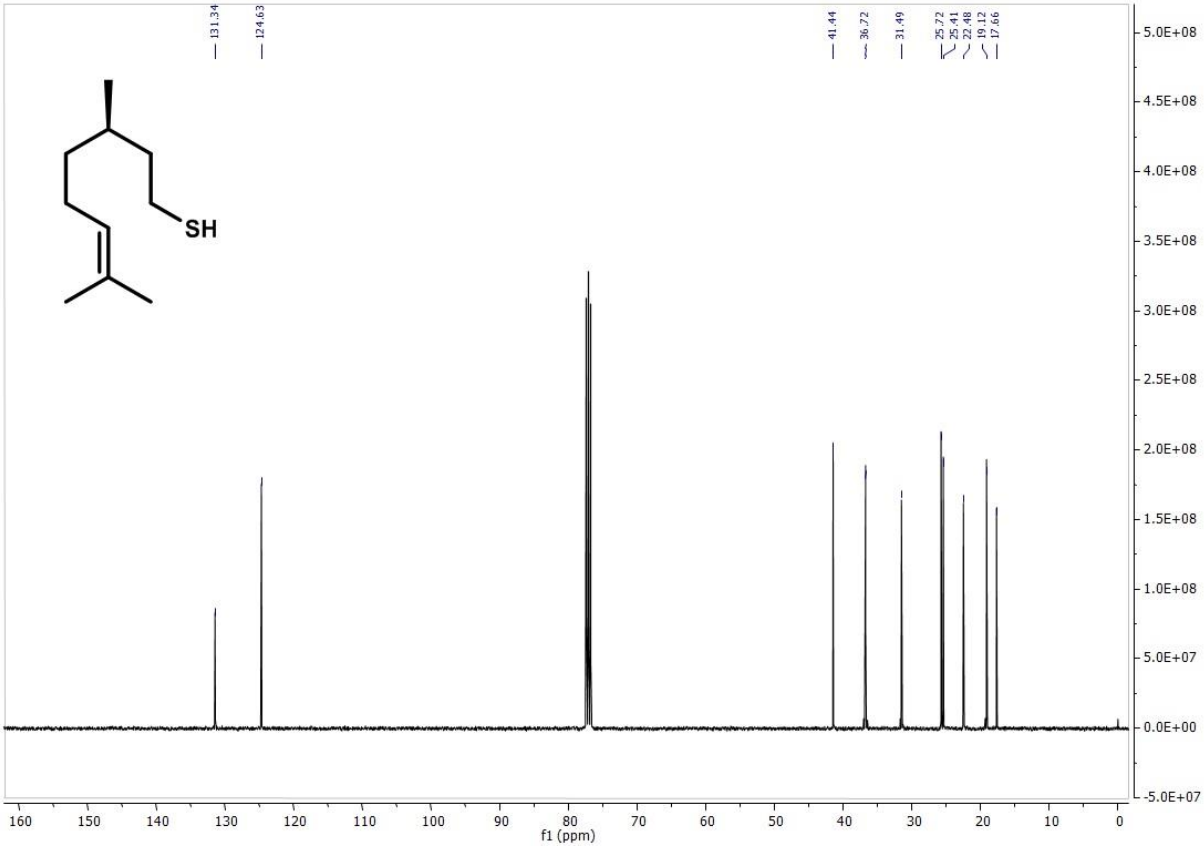
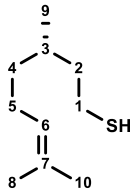


Figure S33. ^{13}C NMR spectrum of (*3R*)-*β*-thio citronellol.

Compound **18b**

(*3S*)-*β*-thio citronellol



educt: (*S*)-(-)-*β*-citronellol

a) 1st intermediate:
(3S)-3,7-dimethyloct-6-en-1-yl 4-methylbenzenesulfonate,
crude yield: 51 %

b) 2nd intermediate:
(3S)-S-(3,7-dimethyloct-6-en-1-yl) ethanethioate,
yield: 87 %,
MS-EI: *m/z* (intensity in %) 69 (100), 171 (69), 115 (56), 81 (30), 55 (28), 95 (24), 101 (23), 68 (18), 82 (15), 172 (11), 123 (10), 138 (9), 83 (8), 137 (8), 172 (5), 214 (3, M^+)

c) analyte:
yield: 84 %
RI (FFAP): 1541
RI (DB-5): 1278

MS-EI: *m/z* (intensity in %) 69 (100), 55 (68), 115 (58), 67 (36), 81 (34), 101 (34), 129 (30), 95 (27), 47 (20), 82 (20), 68 (14), 83 (14), 56 (13), 61 (13), 123 (12), 53 (11), 70 (11), 87 (10), 171 (10), 57 (8), 172 (8, M^+)
MS-CI (isobutane): *m/z* (intensity in %) 173 (100, $[M+H]^+$), 174 (12)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.88 (d, 3H, H-C9), 1.14 – 1.20 (m, 1 H, H-C4), 1.28 – 1.35 (m, 1H, H-C4), 1.31 (t, *J* = 7.6 Hz, SH), 1.42 – 1.49 (m, 1H, H-C2), 1.52 – 1.65 (m, 1H, H-C3), 1.60 (s, 3H, H-C10), 1.53 – 1.65 (m, 1H, H-C2), 1.69 (s, 3H, H-C8), 1.90 – 2.05 (m, 2H, H-C5), 2.45 – 2.62 (m, 2H, H-C1), 5.07 – 5.11 (m, 1H, H-C6)
^{13}C NMR (101 MHz, $CDCl_3$): δ 17.66 (C3), 19.12 (C9), 22.48 (C1), 25.41 (C5), 25.72 (C10), 31.49 (C8), 36.72 (C4), 41.44 (C2), 124.63 (C6), 131.34 (C7)

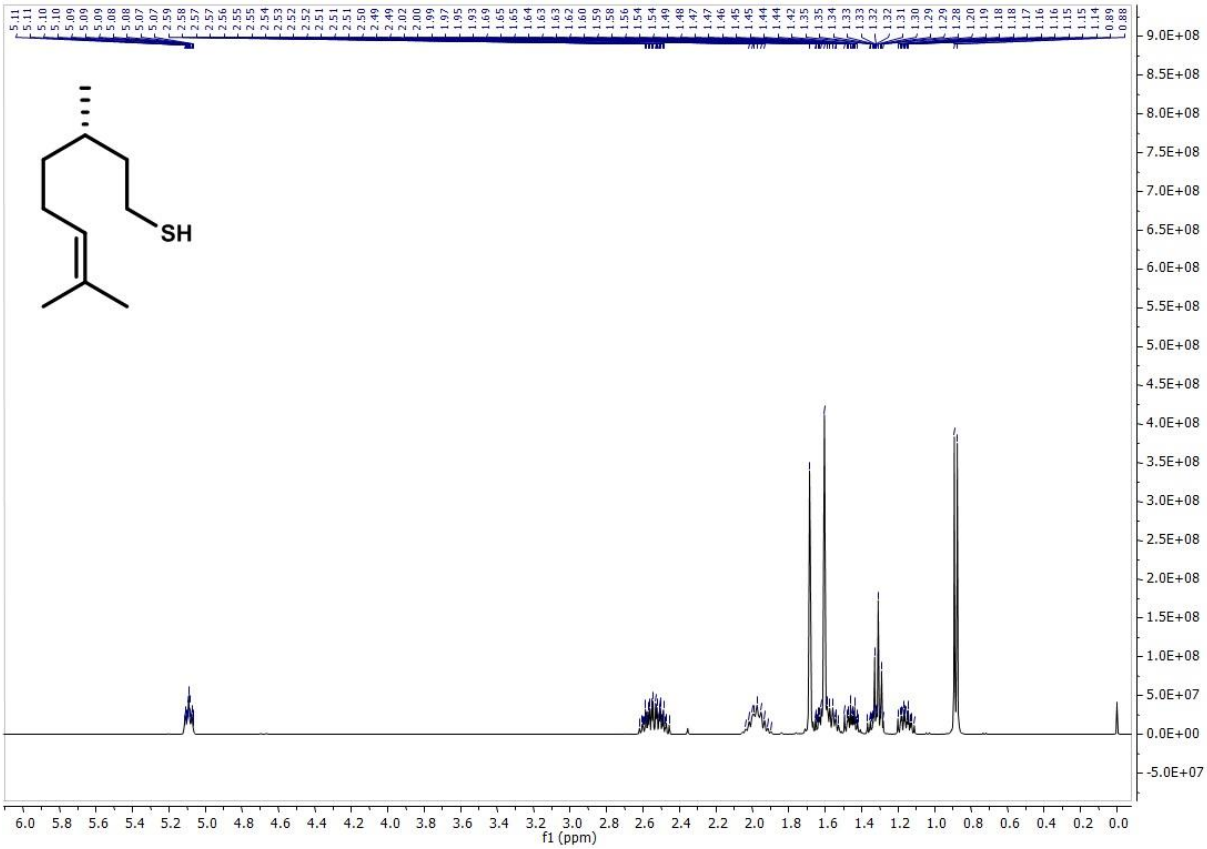


Figure S34. ^{1}H NMR spectrum of (*3S*)-*β*-thio citronellol.

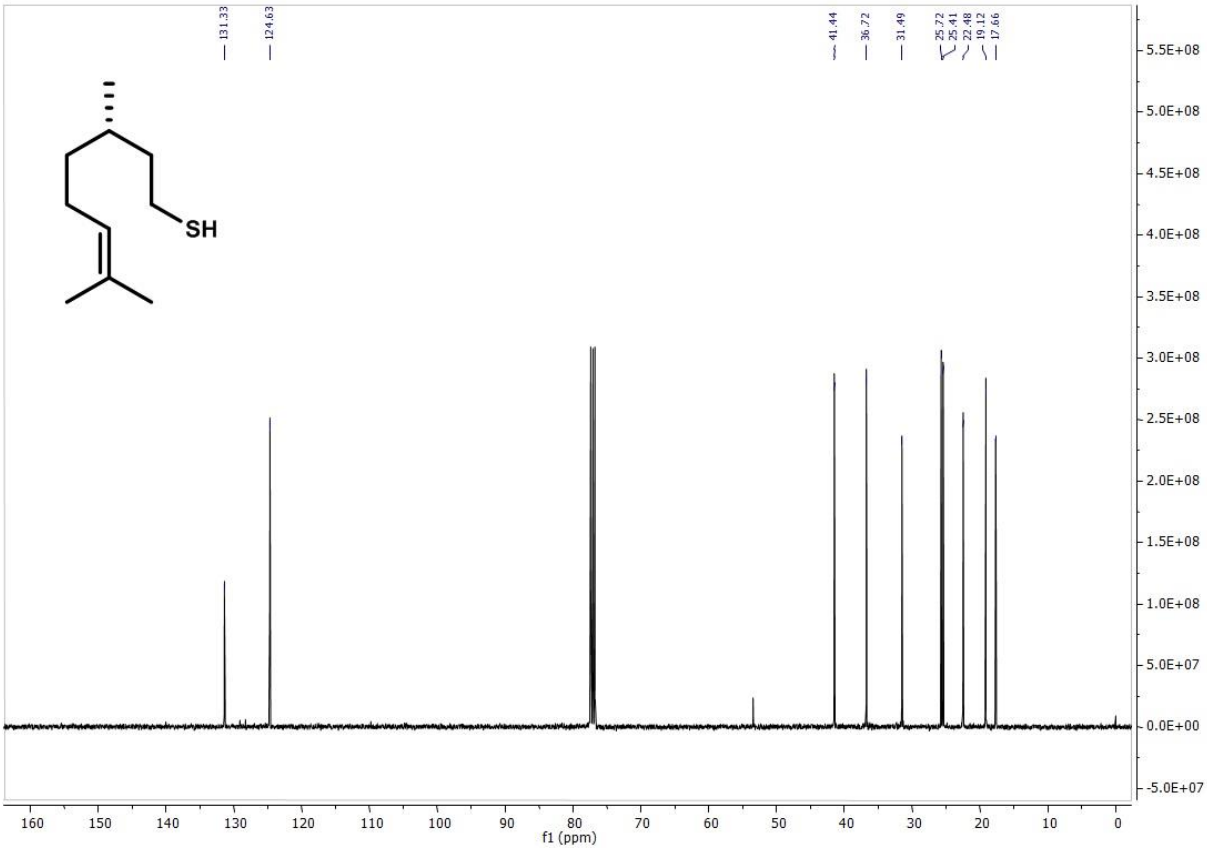
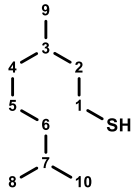


Figure S35. ^{13}C NMR spectrum of (*3S*)-*β*-thio citronellol.

Compound **22**

dihydro thio citronellol



educt: dihydro citronellol

a) 1st intermediate:
3,7-dimethyloctyl 4-methylbenzenesulfonate,
crude yield: 72 %

b) 2nd intermediate:
S-(3,7-dimethyloctyl) ethanethioate,
yield: 79 %,
MS-EI: *m/z* (intensity in %) 43 (100), 156 (49), 70 (48), 83 (43), 173 (40), 69 (38), 55 (32), 57 (24), 56 (21), 111 (18), 71 (17), 84 (14), 97 (12), 140 (12), 85 (11), 112 (7), 125 (6), 132 (5), 216 (1, M^+)

c) analyte:
yield: 87 %
RI (FFAP): 1440
RI (DB-5): 1242

MS-EI: *m/z* (intensity in %) 70 (100), 56 (58), 69 (53), 55 (47), 57 (26), 84 (26), 72 (25), 140 (25), 111 (22), 83 (19), 51 (12), 47 (11), 97 (9), 112 (9), 85 (7), 125 (6), 67 (5), 141 (4), 174 (2, M^+)
MS-CI (isobutane): *m/z* (intensity in %) 175 (100, $[M+H]^+$), 141 (19), 140 (17), 176 (13), 173 (11)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.87 (d, *J* = 6.7 Hz, 9H, H-C8, H-C9, H-C10), 1.09 – 1.17 (m, 3H, H-C4, H-C5), 1.22 – 1.28 (m, 3H, H-C4, H-C6), 1.31 (t, *J* = 7.5 Hz, SH), 1.41 – 1.63 (m, 4H, H-C2, H-C3, H-C7), 2.49 – 2.58 (m, 2H, H-C1)
^{13}C NMR (101 MHz, $CDCl_3$): δ 19.22 (C9), 22.53 (C1), 22.60 (C8), 22.70 (C10), 24.64 (C6), 27.96 (C7), 31.84 (C3), 36.90 (C4), 39.24 (C5), 41.52 (C2)

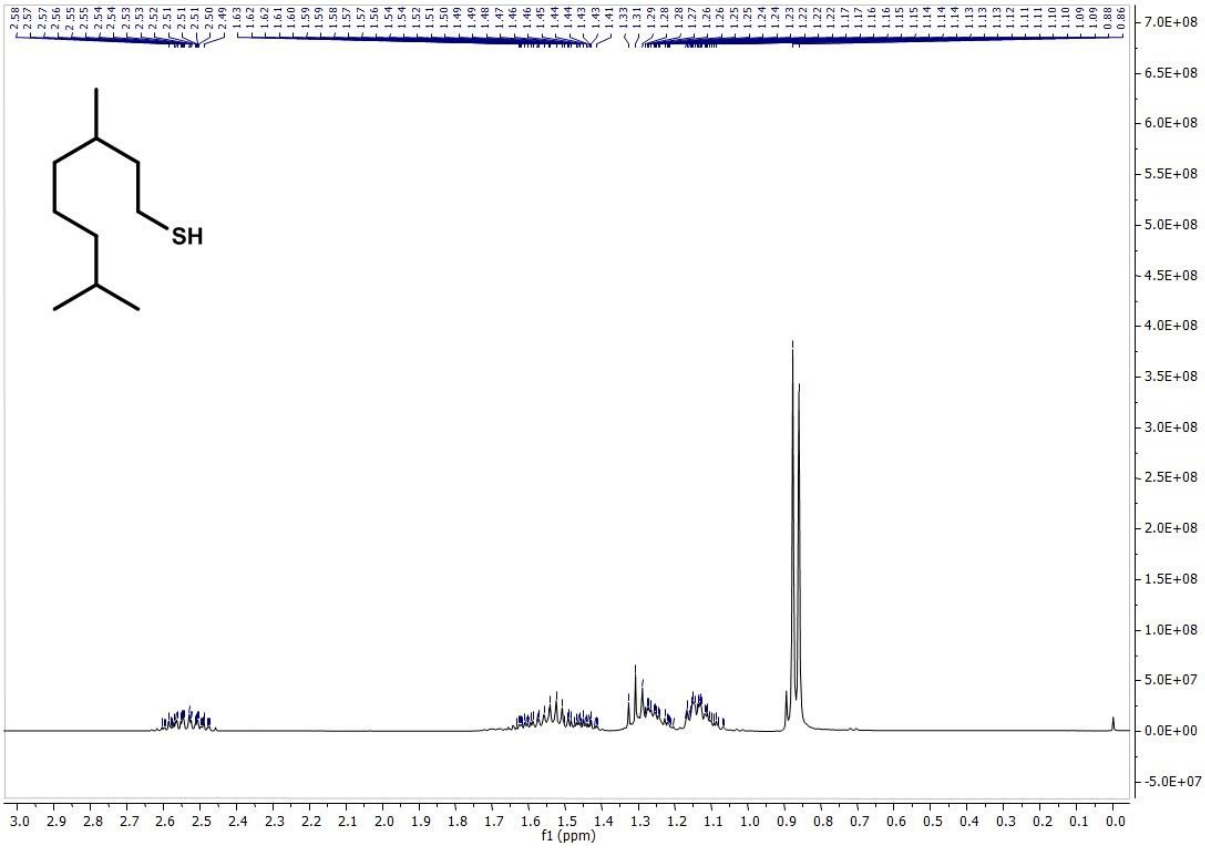


Figure S36. ^{1}H NMR spectrum of dihydro thio citronellol.

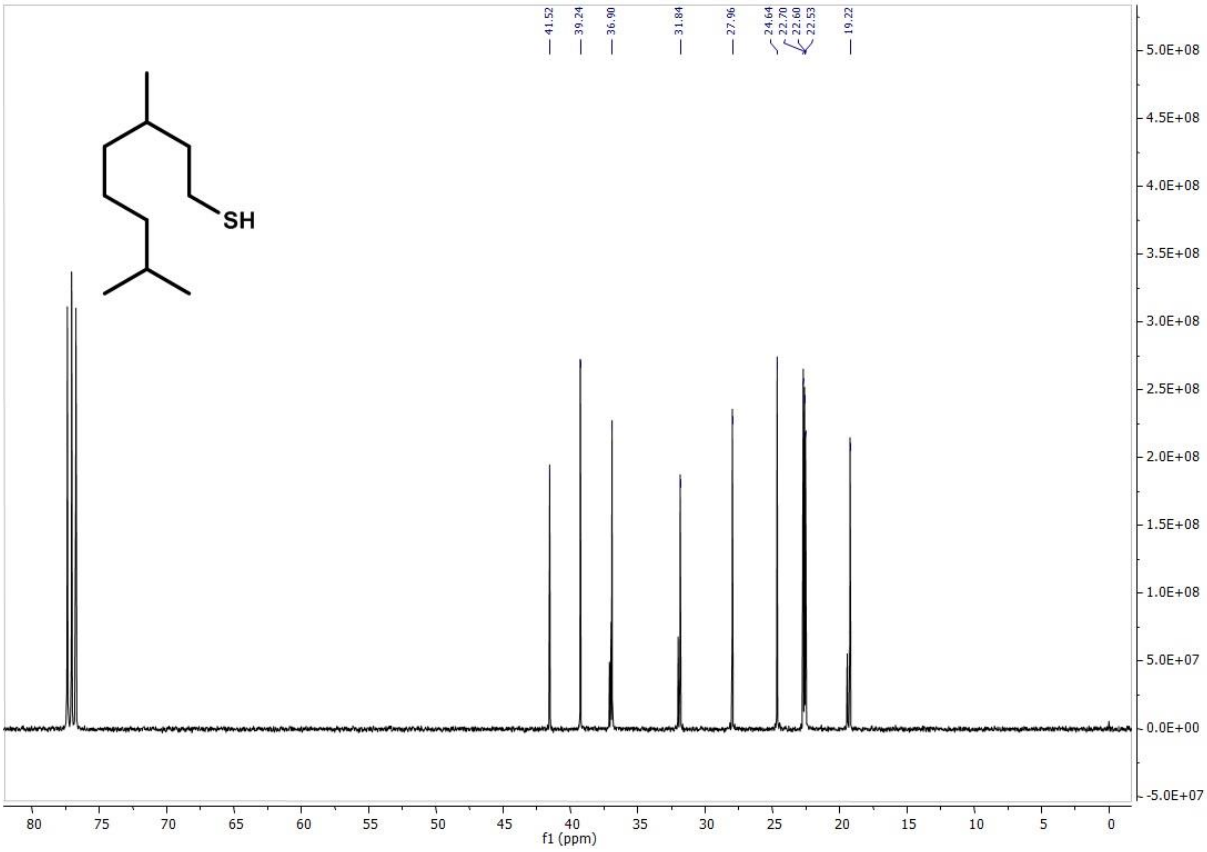


Figure S37. ^{13}C NMR spectrum of dihydro thio citronellol.

Synthetic route B for mercaptan preparation

Eight compounds were obtained by using a strategy consisting of direct tosylation and reduction as shown in **Figure S38**.

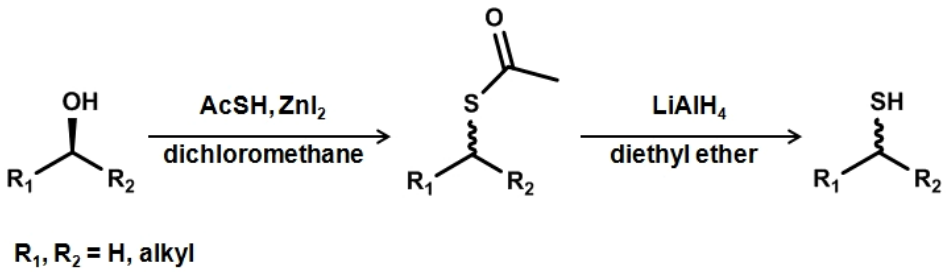


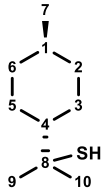
Figure S38. Route assigned as “synthetic route B”.

a) Direct thioacetylation. The alcohol (10 mmol) was dissolved in dichloromethane (20 mL) and a mixture of thioacetic acid (0.92 g; 12 mmol) and zinc iodide (1.60 g; 5 mmol) was added. The reaction mixture was stirred at RT for 5 h, then diluted with water (20 mL) and filtered. The residue was washed with dichloromethane (15 mL) and the aqueous layer was also washed twice with dichloromethane (20 mL). The combined organic layers were washed with saturated sodium hydrogen carbonate solution (20 mL) and brine (20 mL) and were dried over sodium sulfate. The solvent was removed under reduced pressure and the thioacetate was purified by column chromatography on silica gel with pentane/diethyl ether (98+2; by vol.) as the eluent.

b) Reduction to the thiol. The thioacetate (4 mmol) was dissolved in anhydrous diethyl ether (15 mL) and cooled to 0 °C. A solution of lithium aluminium hydride (0.31 g; 8 mmol) in anhydrous diethyl ether (15 mL) was slowly added and then stirred at RT for 2 h. Anhydrous diethyl ether (30 mL), saturated ammonium chloride solution (20 mL), and HCl (2 mol/L; 20 mL) were added at 0 °C. The aqueous layer was washed twice with diethyl ether (30 mL) and the combined organic layers were washed twice with saturated sodium hydrogen carbonate solution (20 mL) and dried over sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silca gel using pentane as the eluent.

Compound **5**

(*1R,4R*)-*p*-menthane-8-thiol



educt: (*1R,4R*)-*p*-menthane-8-ol

a) intermediate:

S-(2-((1R,4R)-4-methylcyclohexyl)propan-2-yl) ethanethioate,

yield: 63 %,

MS-EI: *m/z* (intensity in %) 83 (100), 139 (56), 138 (47), 55 (29), 69 (27), 81 (21), 97 (20), 75 (19), 57 (17), 95 (14), 67 (8), 84 (6), 123 (5), 140 (5), 171 (2), M^+ absent

b) analyte:

yield: 87 %

RI (FFAP): 1436

RI (DB-5): 1232

MS-EI: *m/z* (intensity in %) 55 (100), 75 (94), 83 (64), 74 (62), 69 (38), 81 (37), 139 (36), 95 (30), 67 (26), 57 (20), 97 (15), 53 (12), 68 (12), 59 (10), 82 (9), 123 (7), 109 (6), 138 (5), 140 (4), 172 (2, M^+)

MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 140 (11), $[M+H]^+$ absent

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.87 (d, *J* = 6.5 Hz, 3H, H-C7), 0.88 – 0.96 (m, 2H, H-C2, H-C6), 1.11 – 1.16 (m, 2H, H-C3, H-C5), 1.19 – 1.33 (m, 2H, H-C1, H-C4), 1.35 (s, 6H, H-C9, H-C10), 1.55 (s, SH), 1.72 – 1.78 (m, 2H, H-C2, H-C6), 1.86 – 1.92 (m, 2H, H-C3, H-C5)

^{13}C NMR (101 MHz, $CDCl_3$): δ 22.51 (C7), 27.94 (C3, C5), 31.09 (C9, C10), 32.53 (C1), 35.36 (C2 ,C6), 48.24 (C8), 49.65 (C4)

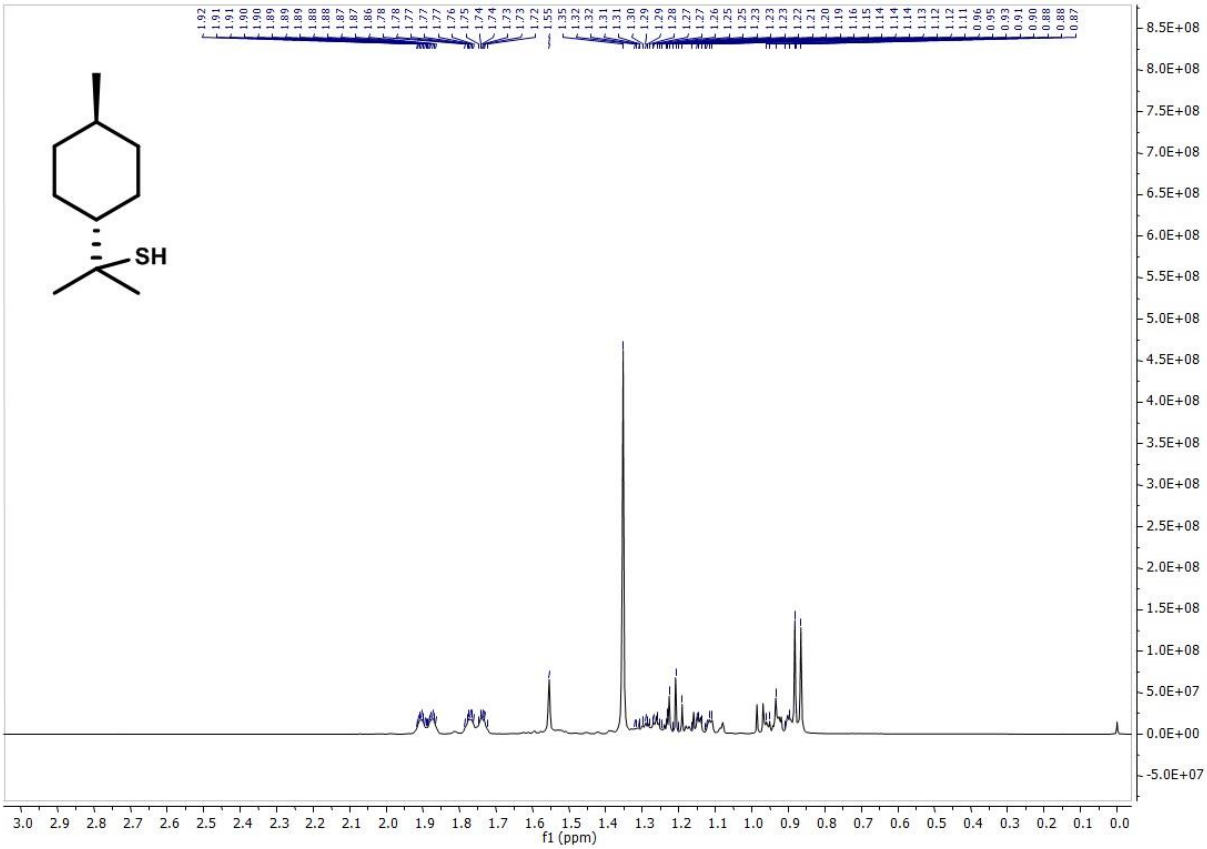


Figure S38. ^{1}H NMR spectrum of (*1R,4R*)-*p*-menthane-8-thiol.

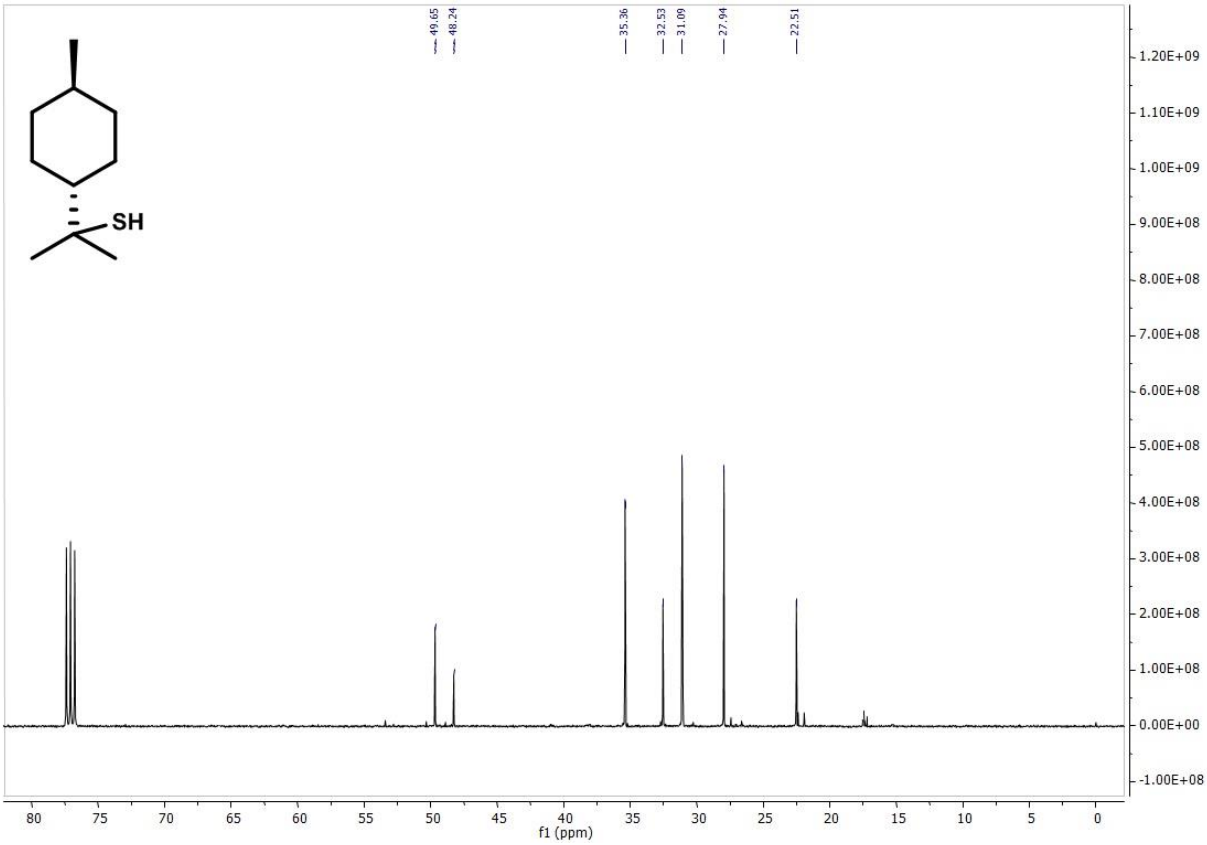
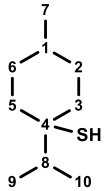


Figure S39. ^{13}C NMR spectrum of (*1R,4R*)-*p*-menthane-8-thiol.

Compound **10**

***p*-menthane-4-thiol**



educt: terpinen-4-ol

a)1st intermediate (obtained by hydrogenation):
dihydroterpinen-4-ol, yield: 69 %,
MS-EI: *m/z* (intensity in %) 113 (100), 95 (75), 43 (41), 99 (20), 41 (12), 67 (11), 55 (9), 114 (8), 111 (7), 57 (6), 69 (6), 96 (6), 70 (5), 81 (5), 156 (1, M^+)

b) 2nd intermediate:
S-(4-methyl-1-(propan-2-yl)cyclohexan-1-yl) ethanethioate,
yield: 27 %,
MS-EI: *m/z* (intensity in %) 83 (100), 139 (45), 138 (40), 55 (38), 69 (31), 57 (22), 43 (20), 54 (19), 81 (19), 97 (19), 41 (16), 95 (12), 67 (8), 84 (6), 171 (2), M^+ absent

b) analyte:
yield: 73 %
RI (FFAP): 1438
RI (DB-5): 1237

MS-EI: *m/z* (intensity in %) 83 (100), 75 (94), 139 (70), 74 (68), 55 (64), 81 (37), 69 (36), 41 (30), 95 (23), 97 (23), 57 (22), 67 (18), 172 (12, M^+), 43 (10), 59 (9), 77 (8), 82 (8), 53 (7), 76 (7), 123 (7), 79 (6), 84 (6), 96 (6), 173 (3)
MS-CI (isobutane): *m/z* (intensity in %) 139 (100), 140 (11), 173 (2, $[M+H]^+$)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.87 (d, *J* = 6.6 Hz, 3H, H-C7), 0.88 – 0.97 (m, 2H, H-C3, H-C2), 1.08 – 1.18 (m, 2H, H-C2, H-C3), 1.22 – 1.33 (m, 2H, H-C1, H-C8), 1.35 (d, *J* = 0.6 Hz, 6H, H-C9, H-C10), 1.56 (s, SH), 1.72 – 1.79 (m, 2H, H-C2, H-C6), 1.86 – 1.92 (m, 2H, H-C3, H-C5)
^{13}C NMR (101 MHz, $CDCl_3$): δ 22.51 (C7), 27.95 (C3, C5), 31.09 (C9, C10), 32.54 (C1), 35.37 (C2, C6), 48.26 (C4), 49.65 (C8)

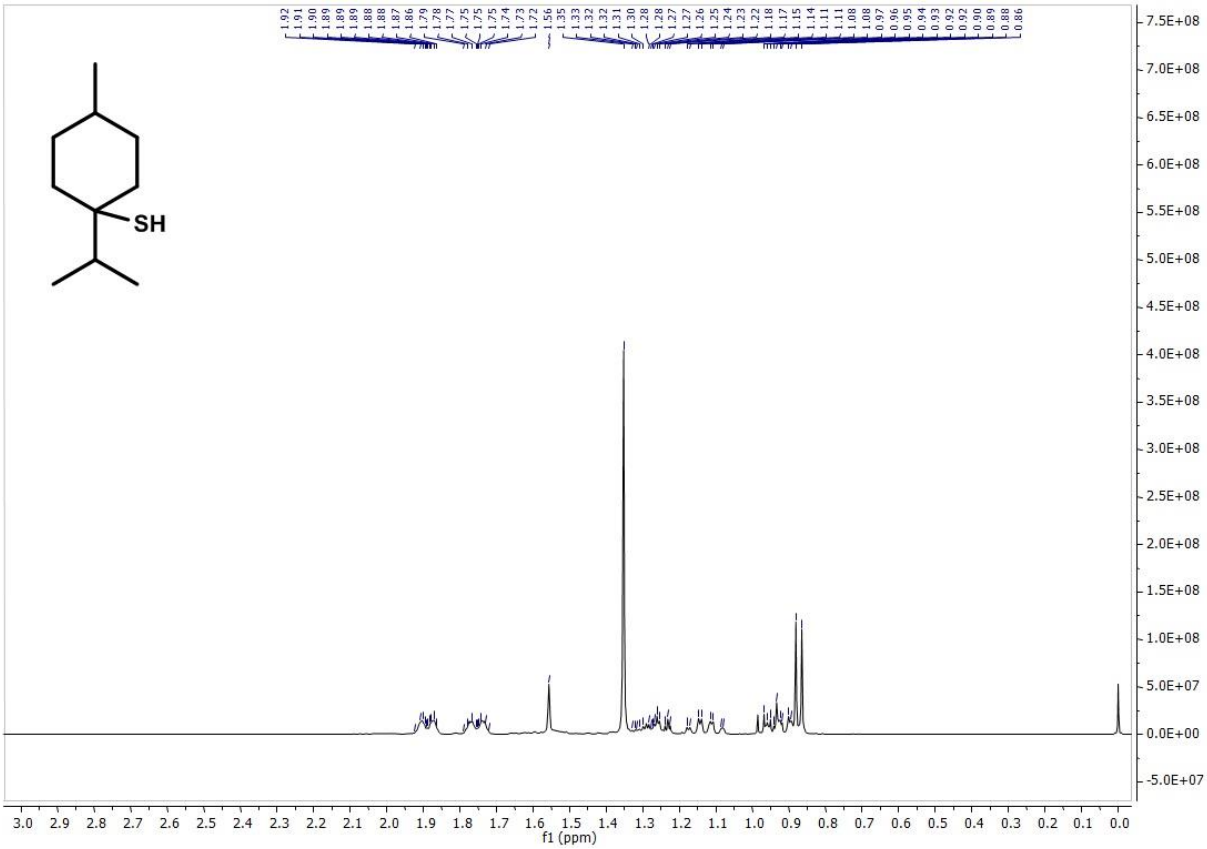


Figure S40. ^{1}H NMR spectrum of *p*-menthane-4-thiol.

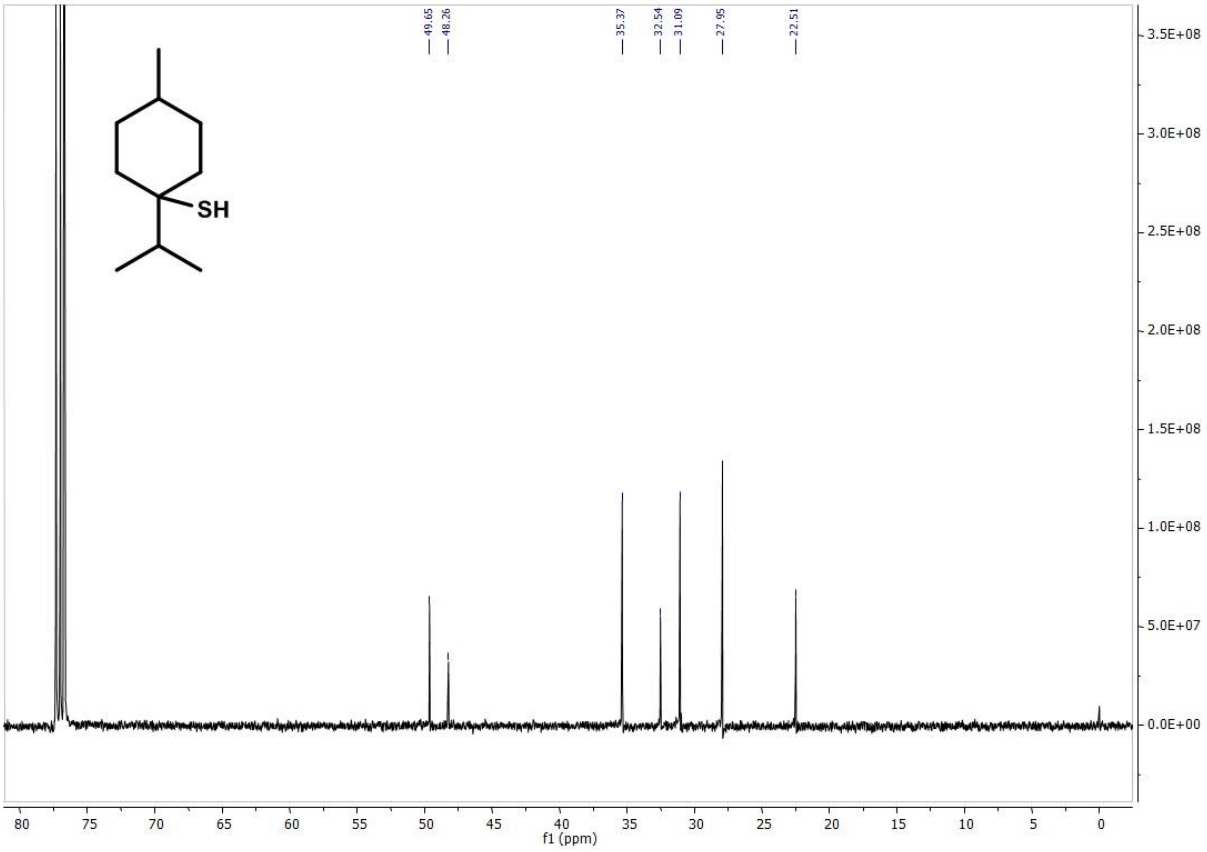
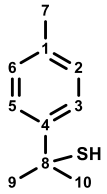


Figure S41. ^{13}C NMR spectrum of *p*-menthane-4-thiol.

Compound **11**

_p_-cymene-8-thiol



educt: *p*-cymene-8-ol

a) intermediate:

S-(2-(p-tolyl)propan-2-yl) ethanethioate

yield: 72 %,

MS-EI: *m/z* (intensity in %) 133 (100), 105 (40), 134 (13), 91 (12), 93 (11), 117 (8), 115 (6), 77 (5), 208 (3, M^+)

b) analyte:

yield: 79 %

RI (FFAP): 1722

RI (DB-5): 1280

MS-EI: *m/z* (intensity in %) 133 (100), 105 (37), 117 (28), 91 (22), 132 (22), 115 (18), 93 (15), 134 (12), 41 (11), 65 (10), 77 (8), 59 (6), 131 (5), 166 (2, M^+)

MS-CI (isobutane): *m/z* (intensity in %) 133 (100), 134 (13), $[M+H]^+$ absent

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.81 (s, 6H, H-C9, H-C10), 2.21 (s, SH), 2.32 (s, 3H, H-C7), 7.12 (d, *J* = 8.0 Hz, 2H, H-C2, H-C6), 7.45 (d, *J* = 8.3 Hz, 2H, H-C3, H-C5)

^{13}C NMR (101 MHz, $CDCl_3$): δ 20.96 (C7), 34.56 (C9, C10), 45.70 (C8), 125.33 (C3, C5), 128.93 (C2, C6), 136.26 (C1), 145.59 (C4)

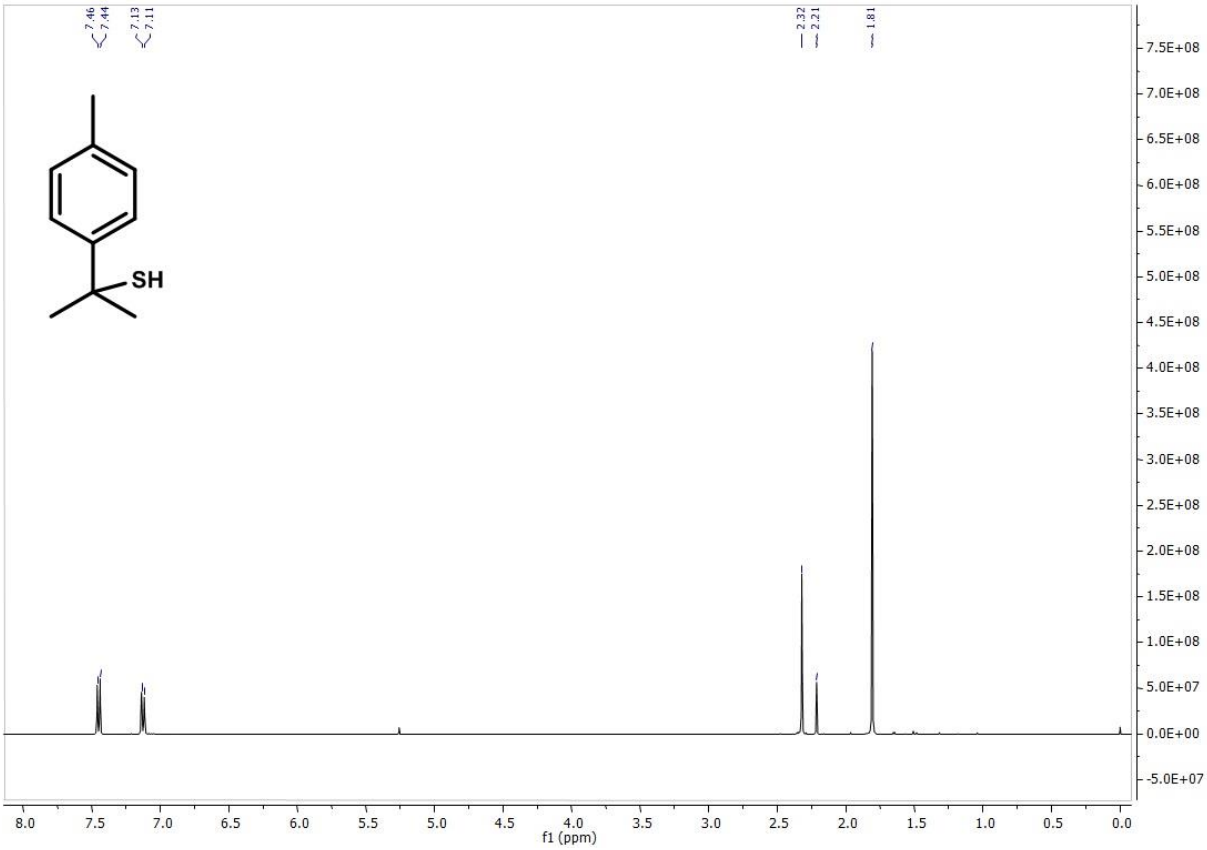


Figure S42. ^{1}H NMR spectrum of *p*-cymene-8-thiol.

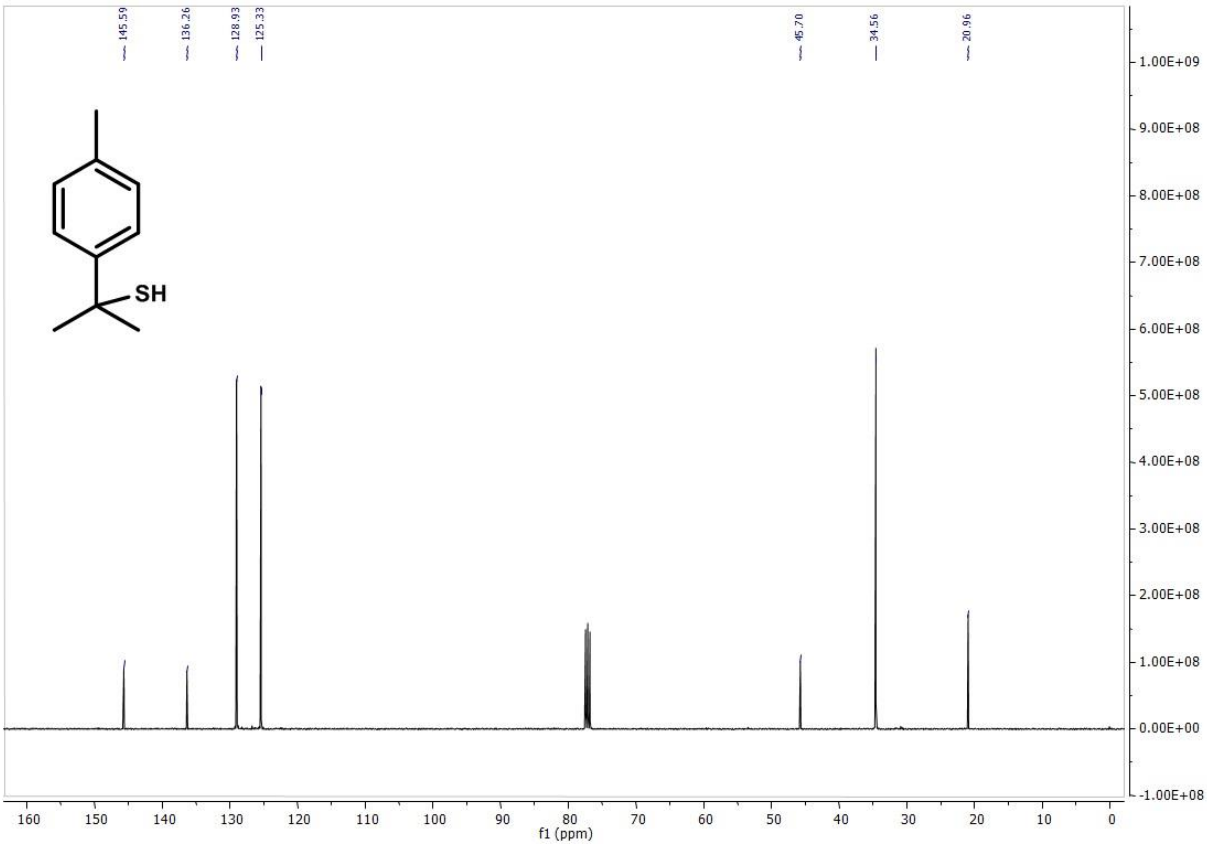
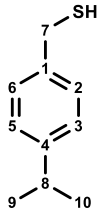


Figure S43. ^{13}C NMR spectrum of *p*-cymene-8-thiol.

Compound **13**

***p*-cymene-7-thiol**



educt: *p*-cymene-7-ol

a) intermediate:

S-(4-(propan-2-yl)benzyl) ethanethioate,

yield: 29 %,

MS-EI: *m/z* (intensity in %) 133 (100), 105 (28), 165 (17), 117 (16), 91 (14), 208 (14, M^+), 134 (12), 164 (8), 118 (7), 115 (6), 123 (5)

b) analyte:

yield: 19 %

RI (FFAP): 1857

RI (DB-5): 1346

MS-EI: *m/z* (intensity in %) 133 (100), 105 (44), 117 (25), 166 (24, M^+), 91 (21), 118 (16), 134 (14), 115 (13), 77 (13), 92 (10), 65 (8), 79 (7), 151 (5)

MS-CI (isobutane): *m/z* (intensity in %) 133 (100), 134 (12), 167 (6, $[M+H]^+$)

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.23 (d, *J* = 6.9 Hz, 6H, H-C9, H-C10), 2.28 – 2.34 (m, SH), 2.84 – 2.94 (m, 1H, H-C8), 4.57 (s, 2H, H-C7), 7.19 (d, *J* = 8.2 Hz, 2H, H-C3, H-C5), 7.25 (d, *J* = 8.2 Hz, 2H, H-C2, H-C6)

^{13}C NMR (101 MHz, $CDCl_3$): δ 24.07 (C9, C10), 33.91 (C8), 65.10 (C7), 126.62 (C3, C5), 127.23 (C2, C6), 138.40 (C1), 148.40 (C4)

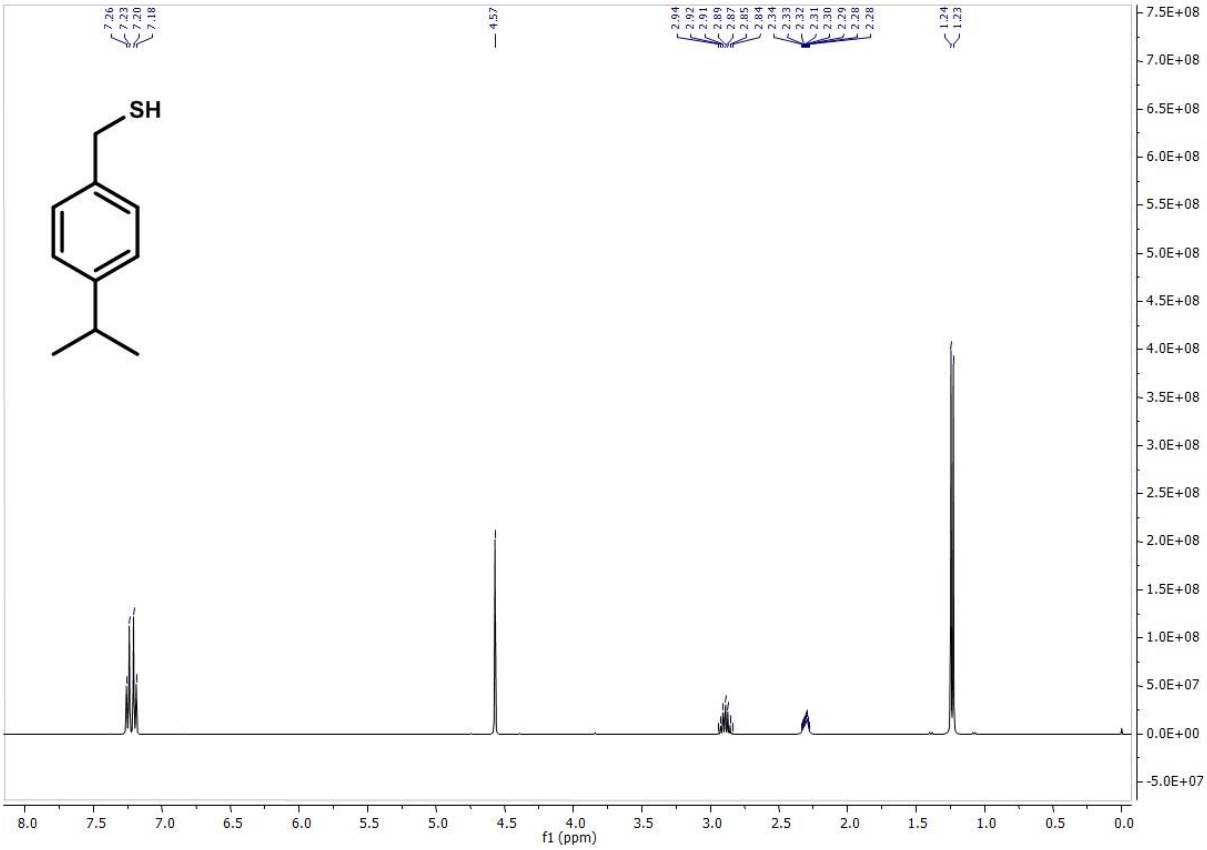


Figure S44. ^{1}H NMR spectrum of *p*-cymene-7-thiol.

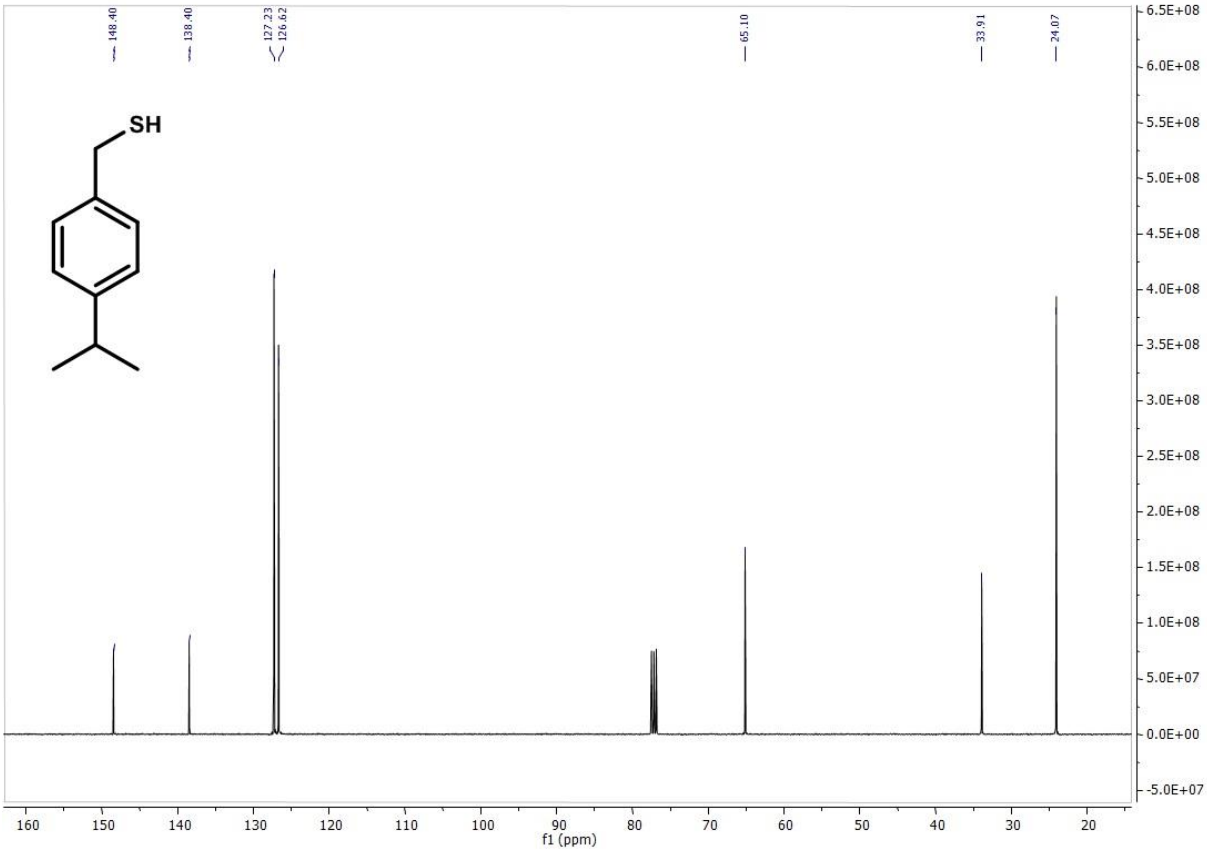
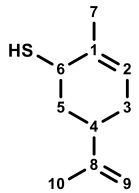


Figure S45. ^{13}C NMR spectrum of *p*-cymene-7-thiol.

Compound **17**

(*4R*)-1,8-*p*-menthadiene-6-thiol



educt: (-)-carveol

a) intermediate:

S-(2-methyl-5-(1-methylethenyl)cyclohex-2-en-1-yl) ethanethioate,

yield: 35 %,

MS-EI: *m/z* (intensity in %) 93 (100), 91 (58), 119 (44), 107 (40), 77 (38), 55 (37), 79 (32), 134 (31), 167 (29), 105 (25), 92 (22), 125 (21), 53 (19), 135 (18), 168 (16), 65 (16), 69 (15), 99 (14), 67 (10), 78 (9), M^+ absent

b) analyte:

yield: 83 %

RI (FFAP): 1650

RI (DB-5): 1279

MS-EI: *m/z* (intensity in %) 91 (100), 93 (78), 119 (78), 134 (66), 77 (53), 125 (45), 79 (41), 105 (41), 107 (39), 92 (36), 65 (28), 85 (25), 124 (24), 78 (17), 106 (16), 55 (15), 53 (14), 99 (13), 67 (12), 97 (10), 51 (9), 135 (7), 168 (6, M^+)

MS-CI (isobutane): *m/z* (intensity in %) 135 (100), 93 (23), 107 (22), 136 (12), 134 (7), $[M+H]^+$ absent

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.74 (d, *J* = 7.0 Hz, SH), 1.76 (s, 3H, H-C10), 1.81 (s, 3H, H-C7), 1.91 – 1.92 (m, 1H, H-C3), 1.93 – 1.95 (m, 2H, H-C5), 2.12 – 2.20 (m, 1H, H-C3), 2.50 – 2.57 (m, 1H, H-C4), 3.43 – 3.45 (m, 1H, H-C6), 4.73 (d, *J* = 1.0 Hz, 1H, H-C9), 4.76 (d, *J* = 1.0 Hz, 1H, H-C9), 5.42 – 5.44 (m, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 20.97 (C10), 21.90 (C7), 30.73 (C3), 34.93 (C4), 37.83 (C5), 40.11 (C6), 109.00 (C9), 123.44 (C2), 135.21 (C1), 149.10 (C8)

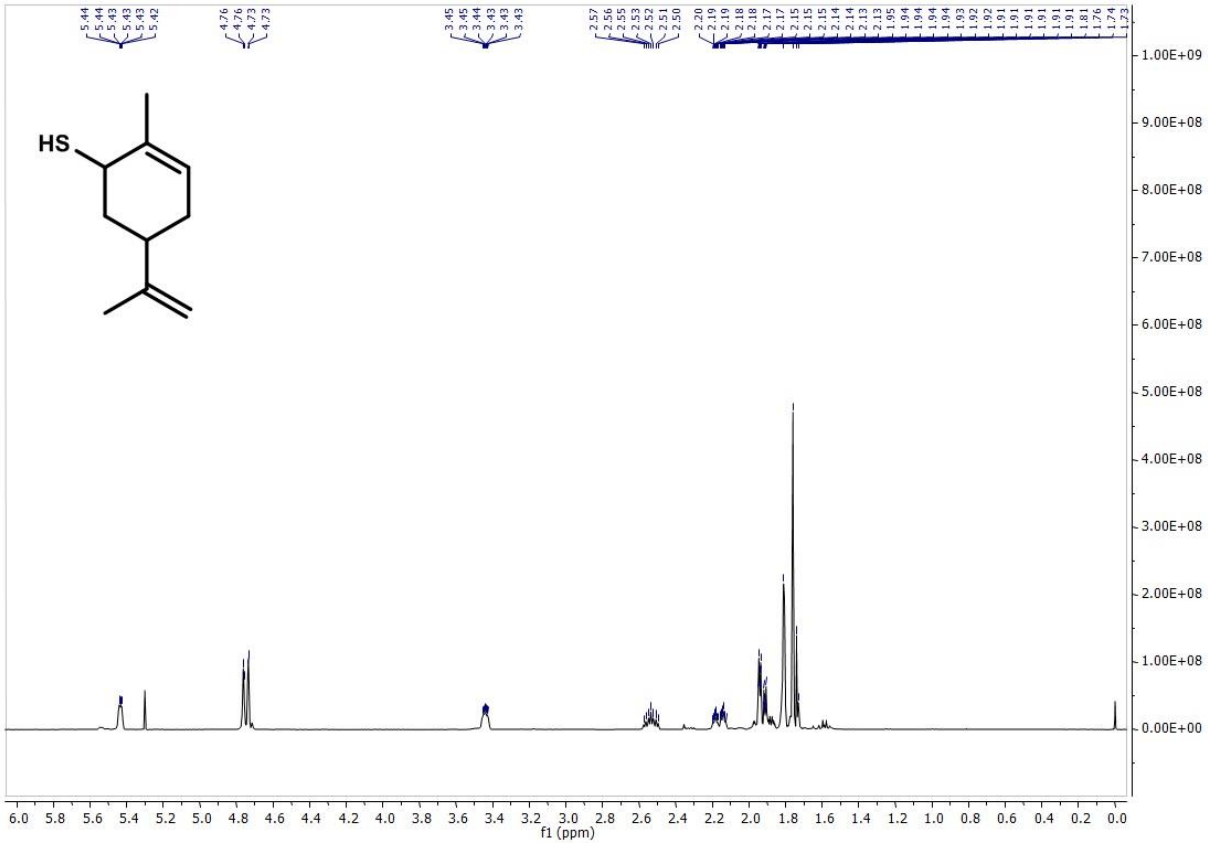


Figure S46. ^{1}H NMR spectrum of (*4R*)-1,8-*p*-menthadiene-6-thiol.

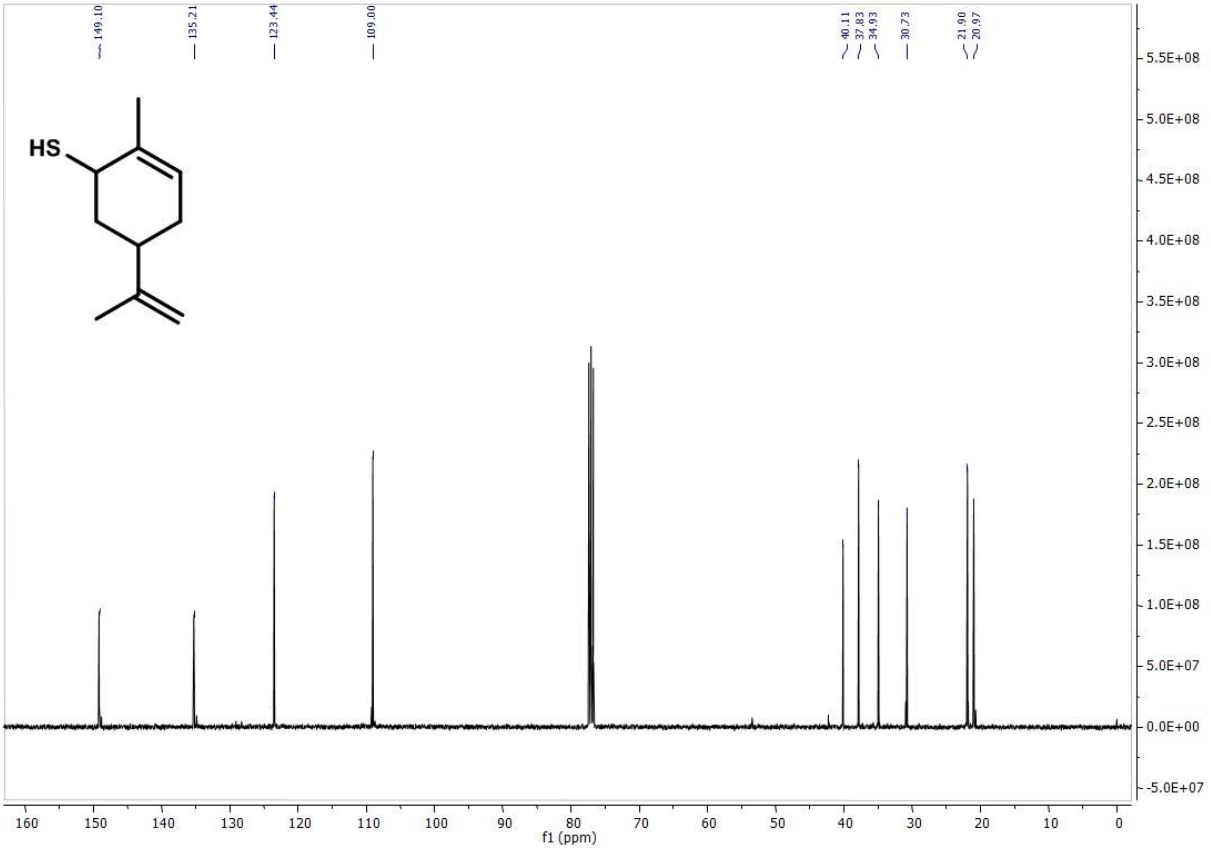
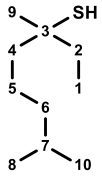


Figure S47. ^{13}C NMR spectrum of (*4R*)-1,8-*p*-menthadiene-6-thiol.

Compound **23**

tetrahydro thio linalool



educt: linalool

a) 1st intermediate (obtained by hydrogenation):

tetrahydro linalool, yield: 79 %,

MS-EI: *m/z* (intensity in %) 73 (100), 69 (59), 55 (25), 43 (21), 111 (17), 129 (11), 41 (9), 57 (8), 45 (6), 70 (6), 74 (5), 83 (5), 125 (3), 143 (3), M^+ absent

b) 2nd intermediate:

S-(3,7-dimethyloctan-3-yl) ethanethioate

yield: 52 %,

MS-EI: *m/z* (intensity in %) 71 (100), 57 (98), 85 (98), 43 (79), 140 (53), 55 (40), 141 (35), 69 (30), 41 (27), 99 (24), 70 (22), 89 (12), 83 (11), 111 (8), 56 (7), 86 (7), 59 (6), 72 (6), 125 (4), 142 (4), 145 (5), 159 (2), 173 (1), M^+ absent

c) analyte:

yield: 81 %

RI (FFAP): 1320

RI (DB-5): 1181

MS-EI: *m/z* (intensity in %) 55 (100), 43 (78), 57 (77), 69 (76), 71 (63), 41 (60), 85 (56), 70 (55), 141 (48), 89 (39), 56 (22), 83 (19), 140 (15), 42 (12), 99 (12), 111 (12), 49 (11), 84 (10), 145 (8), 53 (7), 59 (7), 61 (7), 67 (7), 88 (6), 174 (6, M^+)

MS-CI (isobutane): *m/z* (intensity in %) 141 (100), 99 (14), 91 (9), 95 (9), 142 (9), 93 (6), 97 (5), $[M+H]^+$ absent

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.88 (d, *J* = 6.6 Hz, 6H, H-C8, H-C10), 0.95 (t, *J* = 7.4 Hz, 3H, H-C1), 1.14 – 1.19 (m, 2H, H-C6), 1.33 (s, 3H, H-C9), 1.34 – 1.42 (m, 2H, H-C5), 1.51 (s, SH), 1.52 – 1.64 (m, 5H, H-C2, H-C4, H-C7)

^{13}C NMR (101 MHz, $CDCl_3$): δ 9.21 (C1), 22.51 (C5), 22.63 (C8, C10), 27.89 (C7), 29.71 (C9), 36.86 (C2), 39.35 (C6), 44.02 (C4), 48.77 (C3)

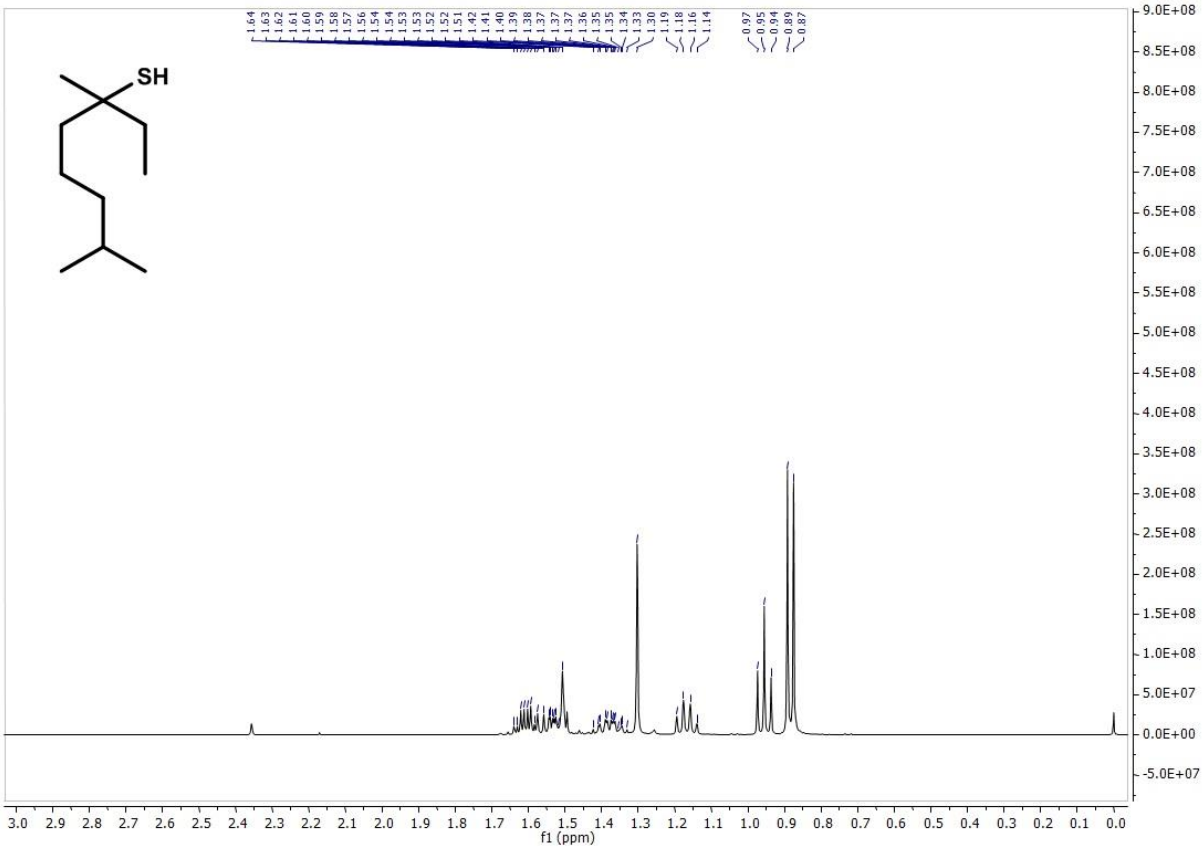


Figure S48. ^{1}H NMR spectrum of tetrahydro thio linalool.

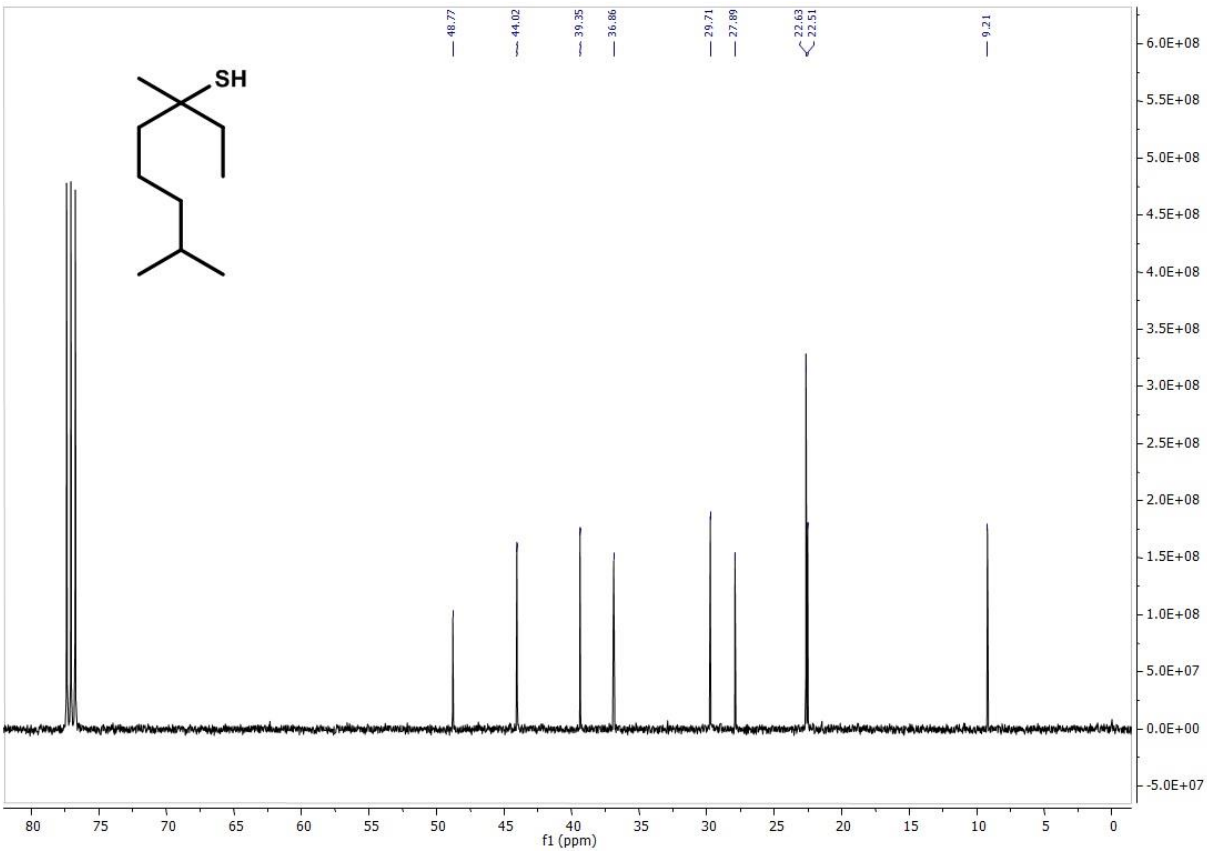
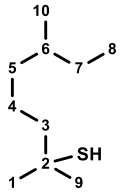


Figure S49. ^{13}C NMR spectrum of tetrahydro thio linalool.

Compound **24**

tetrahydro thio myrcenol



educt: tetrahydro myrcenol

a) intermediate:

S-(2,6-dimethyloctan-2-yl) ethanethioate

yield: 20 %,

MS-EI: *m/z* (intensity in %) 57 (100), 71 (71), 43 (68), 85 (68), 41 (42), 55 (36), 69 (36), 140 (29), 141 (28), 56 (26), 70 (16), 75 (14), 99 (13), 83 (12), 84 (9), 111 (7), 142 (6), M^+ absent

b) product:

yield: 93 %

RI (FFAP): 1310

RI (DB-5): 1177

MS-EI: *m/z* (intensity in %) 57 (100), 41 (83), 43 (80), 69 (77), 55 (76), 71 (66), 85 (61), 56 (59), 75 (76), 79 (48), 141 (41), 83 (22), 140 (20), 84 (15), 99 (12), 111 (12), 42 (10), 67 (10), 74 (10), 53 (9), 59 (8), 142 (5), 174 (5, M^+)

MS-CI (isobutane): *m/z* (intensity in %) 141 (100), 99 (14), 142 (12), $[M+H]^+$ absent

^{1}H NMR (400 MHz; $CDCl_3$): δ 0.85 – 0.88 (m, 6H, H-C8, H-C10), 1.06 – 1.18 (m, 1H, H-C5, H-C7), 1.27 – 1.39 (m, 4H, H-C4, H-C5, H-C6, H-C7), 1.37 (s, 6H, H-C1, H-C9), 1.40 – 1.46 (m, 1H, H-C4), 1.51 – 1.56 (m, 2H, H-C3), 1.68 (s, SH)

^{13}C NMR (101 MHz, $CDCl_3$): δ 11.41 (C8), 19.20 (C10), 22.84 (C4), 29.50 (C7), 32.86 (C1, C9), 34.33 (C6), 36.91 (C5), 44.84 (C2), 46.86 (C3)

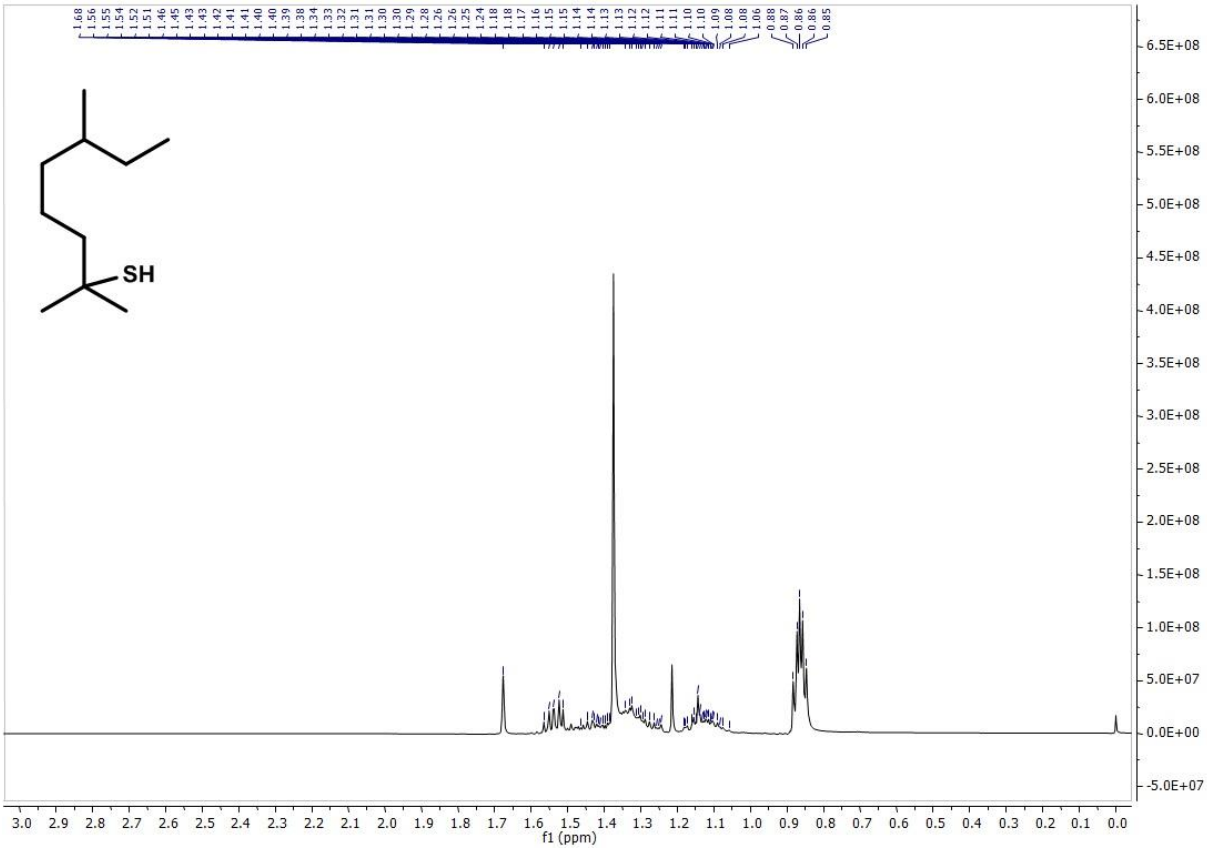


Figure S50. ^{1}H NMR spectrum of tetrahydro thio myrcenol.

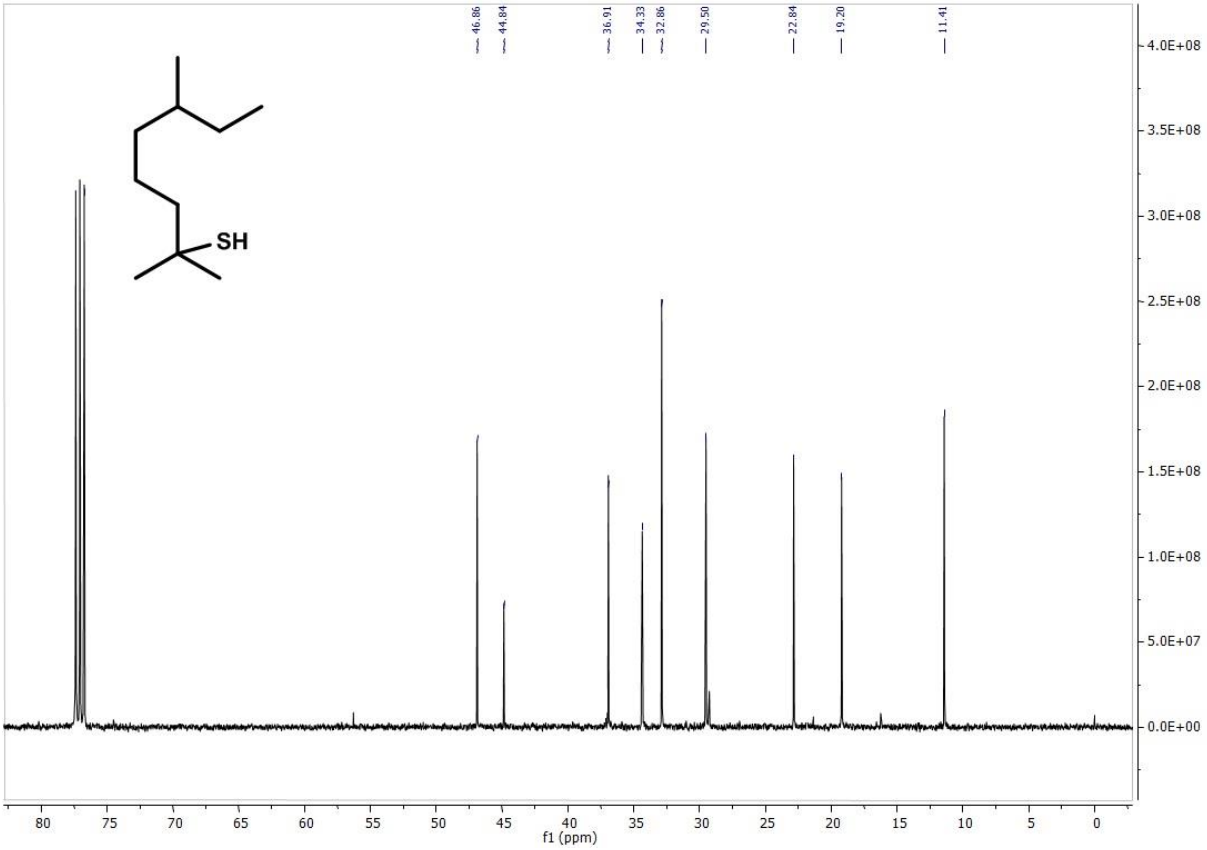


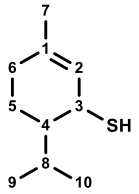
Figure S51. ^{13}C NMR spectrum of tetrahydro thio myrcenol.

Synthetic route used in the preparation of two diastereomers of 1-*p*-menthene-3-thiol (compounds 4a and 4b) from linalool using synthetic route B

The two diastereomers of 1-*p*-menthene-3-thiol were synthesized using synthetic route B.

Compound **4a**

1-*p*-menthene-3-thiol, *diastereomer 1*



educt: linalool

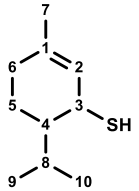
a) intermediate:
S-(3-methyl-6-(propan-2-yl)cyclohex-2-en-1-yl) ethanethioate, diastereomer 2
yield: 22 %,
MS-EI: *m/z* (intensity in %) 81 (100), 93 (74), 137 (54), 91 (32), 77 (30), 95 (22), 43 (20), 69 (20), 79 (20), 136 (16), 41 (15), 121 (11), 92 (10), 94 (9), 55 (6), 67 (6), 82 (5), 105 (5), 138 (5), 170 (1), 212 (1, M^+)

b) analyte:
yield: 22 %
RI (FFAP): 1533
RI (DB-5): 1268

MS-EI: *m/z* (intensity in %) 81 (100), 137 (82), 93 (79), 91 (38), 77 (36), 95 (32), 69 (30), 79 (24), 41 (22), 43 (15), 121 (14), 136 (13), 92 (12), 67 (11), 94 (10), 55 (9), 82 (8), 53 (7), 65 (7), 85 (7), 138 (7), 119 (6), 170 (2, M^+)
MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 138 (11), 171 (2, $[M+H]^+$)^{1}H NMR (400 MHz; $CDCl_3$): δ0.91 (d, *J* = 6.6 Hz, 3H, H-C9), 0.97 (d, *J* = 6.7 Hz, 3H, H-C10), 1.18 – 1.24 (m, 1H, H-C4), 1.22 (d, *J* = 7.2 Hz, SH), 1.30 – 1.35 (m, 1H, H-C5), 1.59 – 1.66 (m, 1H, H-C8), 1.65 (s, 3H, H-C7), 1.73 – 1.77 (m, 1H, H-C5), 1.95 – 2.00 (m, 1H, H-C6), 3.58 – 3.62 (m, 1H, H-C3), 5.58 – 5.61 (m, 1H, H-C2)
^{13}C NMR (101 MHz, $CDCl_3$): δ 20.63 (C9), 20.69 (C10), 20.71 (C5), 23.17 (C7), 29.58 (C4), 31.29 (C6), 39.29 (C3), 45.51 (C4), 125.16 (C2), 135.05 (C1)

Compound **4b**

1-*p*-menthene-3-thiol, *diastereomer 2*



educt: linalool

a) intermediate:
S-(3-methyl-6-(propan-2-yl)cyclohex-2-en-1-yl) ethanethioate, diastereomer 1
yield: 43 %,
MS-EI: *m/z* (intensity in %) 81 (100), 93 (86), 137 (76), 91 (34), 77 (27), 95 (22), 136 (19), 69 (17), 79 (19), 43 (14), 121 (12), 41 (11), 92 (9), 138 (8), 119 (7), 55 (5), 67 (5), 94 (5), 105 (5), 170 (1), 212 (1, M^+)

b) analyte:
yield: 59 %
RI (FFAP): 1544
RI (DB-5): 1280

MS-EI: *m/z* (intensity in %) 81 (100), 137 (88), 93 (63), 91 (27), 95 (27), 77 (25), 69 (22), 79 (18), 136 (12), 41 (12), 121 (10), 43 (9), 67 (8), 92 (8), 94 (7), 55 (6), 138 (6), 82 (5), 119 (5), 170 (3, M^+)
MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 138 (12), 171 (1, $[M+H]^+$)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.82 (d, *J* = 6.9 Hz, 3H, H-C9), 0.96 (d, *J* = 6.8 Hz, 3H, H-C10), 1.30 – 1.45 (m, 2H, H-C4, H-C5), 1.55 (d, *J* = 7.8 Hz, SH), 1.66 (s, 3H, H-C7), 1.78 – 1.84 (m, 1H, H-C5), 1.91 – 1.96 (m, 2H, H-C6), 2.01 – 2.06 (m, 1H, H-C8), 3.36 – 3.41 (m, 1H, H-C3), 5.39 – 5.42 (m, 1H, H-C2)
^{13}C NMR (101 MHz, $CDCl_3$): δ 17.47 (C9), 21.17 (C5), 21.58 (C10), 23.39 (C7), 27.46 (C8), 29.07 (C6), 39.67 (C3), 49.06 (C4), 123.38 (C2), 135.47 (C1)

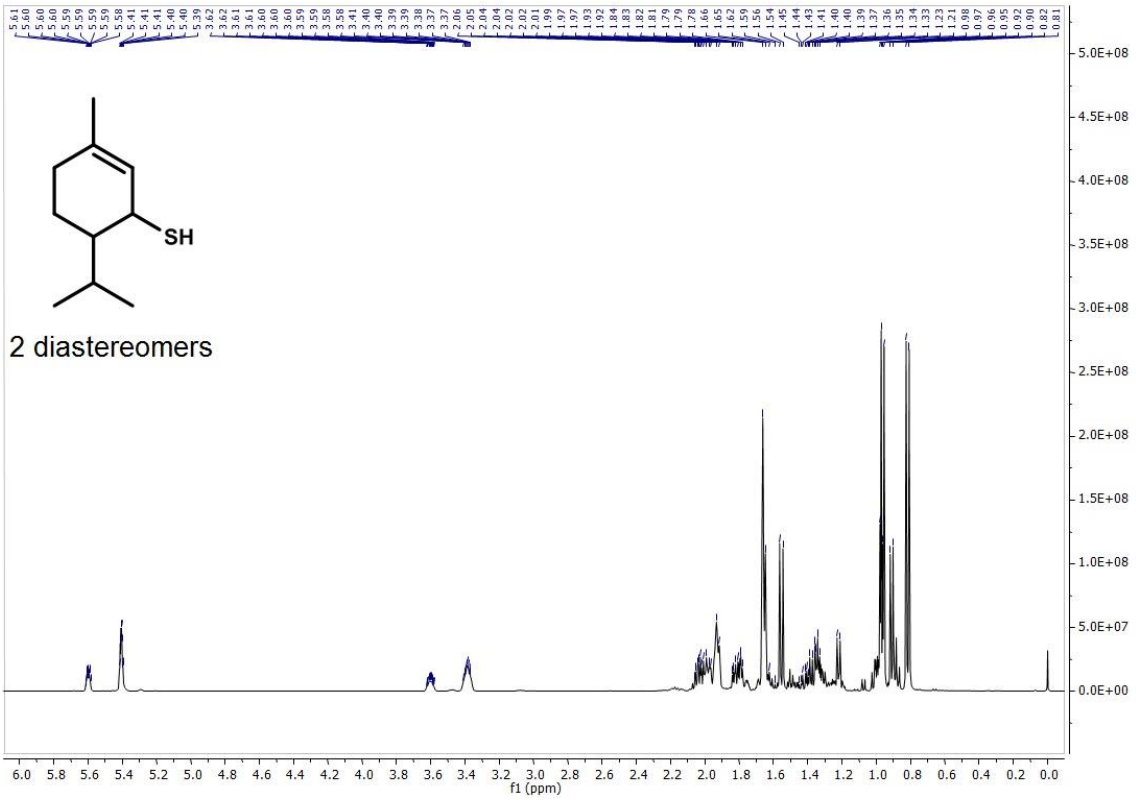


Figure S52. ^{1}H NMR spectrum of 1-*p*-menthene-3-thiol (mixture of 2 diastereomers).

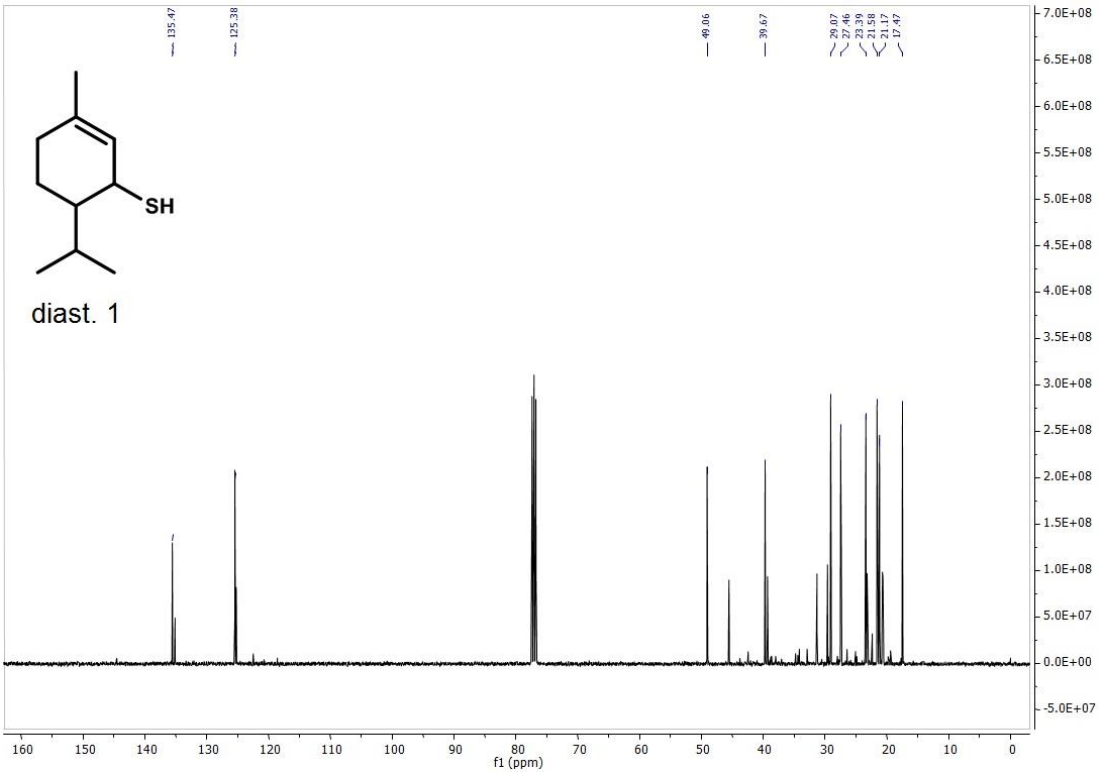


Figure S53. ^{13}C NMR spectrum of 1-*p*-menthene-3-thiol (mixture of 2 diastereomers); signals of diastereomer 1.

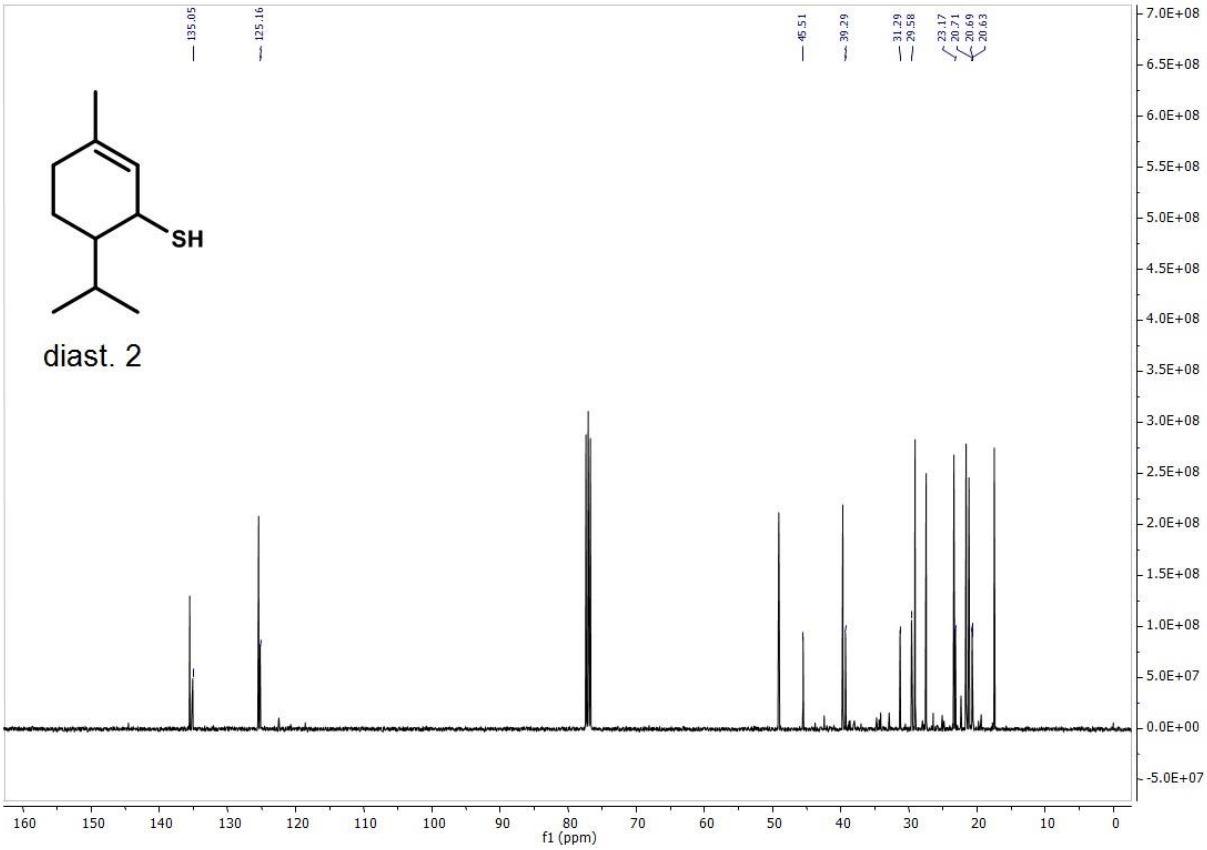


Figure S54. ^{13}C NMR spectrum of 1-*p*-menthene-3-thiol (mixture of 2 diastereomers); signals of diastereomer 2.

Synthesis of 1-*p*-menthene-4-thiol (3)

1-*p*-Menthene-4-thiol was synthesized by epoxidation of terpinolene, reaction to the episulfide, and reduction, as shown in **Figure S55**.

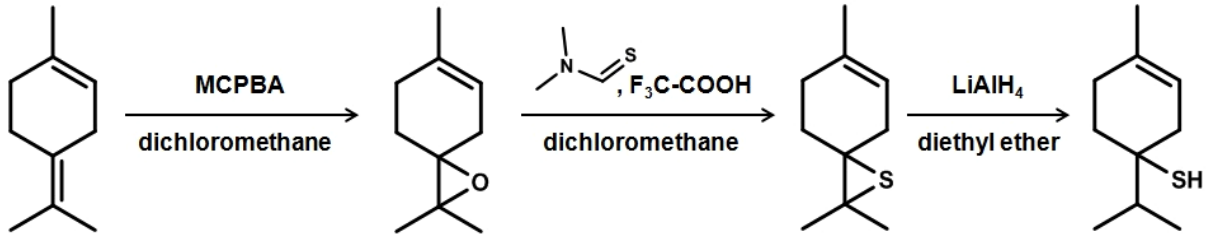


Figure S55. Synthetic strategy used for the preparation of 1-*p*-menthene-4-thiol.

a) Epoxidation of terpinolene. Terpinolene (1.36 g; 10 mmol) was dissolved in anhydrous dichloromethane (20 mL) and 3-chloroperoxybenzoic acid (77 %) (2.36 g; 10 mmol) in anhydrous dichloromethane (30 mL) was dropwise added. The solution was stirred for 30 min at 0 °C and for further 30 min at RT. After the addition of an aqueous sodium carbonate solution (10 %; 20 mL), the reaction mixture was stirred for 30 min. The organic layer was separated and washed twice with water (50 mL) before dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by means of column chromatography on silica gel with pentane as the eluent.

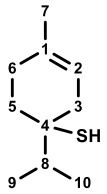
b) Reaction to the episulfide. The epoxide (1.18 g; 7 mmol) was dissolved in anhydrous dichloromethane (20 mL) and *N*,*N*-dimethyl thioformamide (1.25 g; 14 mmol) was added. After addition of trifluoroacetic acid (0.08 g; 0.7 mmol) the reaction mixture was stirred for 3 h at 60 °C. The solvent was removed under reduced pressure, the residue was dissolved in pentane (30 mL) and the solution was washed twice with water (20 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The episulfide was cleaned up by means of column chromatography on silica gel with pentane as the eluent.

c) Reduction. The episulfide (4 mmol) was dissolved in anhydrous diethyl ether (15 mL) and cooled to 0 °C. A solution of lithium aluminium hydride (0.31 g; 8 mmol)

in anhydrous diethyl ether (15 mL) was slowly added and then stirred at RT for 2 h. Anhydrous diethyl ether (30 mL), saturated ammonium chloride solution (20 mL), and HCl (2 mol/L; 20 mL) were added at 0 °C. The aqueous layer was washed twice with diethyl ether (30 mL) and the combined organic layers were washed twice with saturated sodium hydrogen carbonate solution (20 mL) and dried over sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silca gel using pentane as the eluent.

Compound **3**

1-*p*-menthene-4-thiol



educt: terpinolene

a) 1st intermediate:
2,2,6-trimethyl-1-oxaspiro[2.5]oct-5-ene,
yield: 89 %,
MS-EI: *m/z* (intensity in %) 79 (100), 110 (62), 95 (35), 77 (20), 91 (16), 93 (16), 94 (15), 67 (14), 41 (8), 43 (7), 68 (7), 80 (7), 53 (6), 65 (5), 78 (5), 81 (5), 109 (5), 111 (5), 152 (2, M^+)

b) 2nd intermediate:
2,2,6-trimethyl-1-thiaspiro[2.5]oct-5-ene,
yield: 41 %,
MS-EI: *m/z* (intensity in %) 135 (100), 79 (46), 93 (34), 91 (28), 107 (23), 77 (17), 119 (14), 136 (12), 94 (10), 41 (9), 105 (8), 65 (7), 43 (6), 53 (6), 59 (6), 67 (6), 85 (6), 92 (6), 75 (5), 168 (5, M^+)

c) analyte:
yield: 23 %
RI (FFAP): 1535
RI (DB-5): 1260

MS-EI: *m/z* (intensity in %) 93 (100), 81 (41), 92 (40), 69 (33), 136 (32), 91 (22), 77 (19), 102 (15), 79 (14), 41 (13), 67 (11), 95 (11), 170 (11, M^+), 121 (9), 137 (9), 94 (8), 53 (7), 65 (6), 43 (5)
MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 171 (11, $[M+H]^+$), 138 (10), 136 (5)
^{1}H NMR (400 MHz; $CDCl_3$): δ 0.99 (d, *J* = 1.8 Hz, 3H, H-C10), 1.01 (d, *J* = 1.8 Hz, 3H, H-C9), 1.39 (s, SH), 1.54 – 1.62 (m, 1H, H-C6), 1.67 – 1.74 (m, 1H, H-C8), 1.69 (s, 3H, H-C7), 1.80 – 1.86 (m, 1H, H-C6), 1.93 – 2.00 (m, 1H, H-C5), 2.19 – 2.32 (m, 3H, H-C3, H-C5), 5.27 – 5.31 (m, 1H, H-C2)
^{13}C NMR (101 MHz, $CDCl_3$): δ 17.40 (C10), 17.73 (C9), 23.23 (C7), 27.99 (C6), 34.38 (C5), 37.99 (C8), 38.63 (C3), 50.71 (C4), 118.53 (C2), 133.27 (C1)

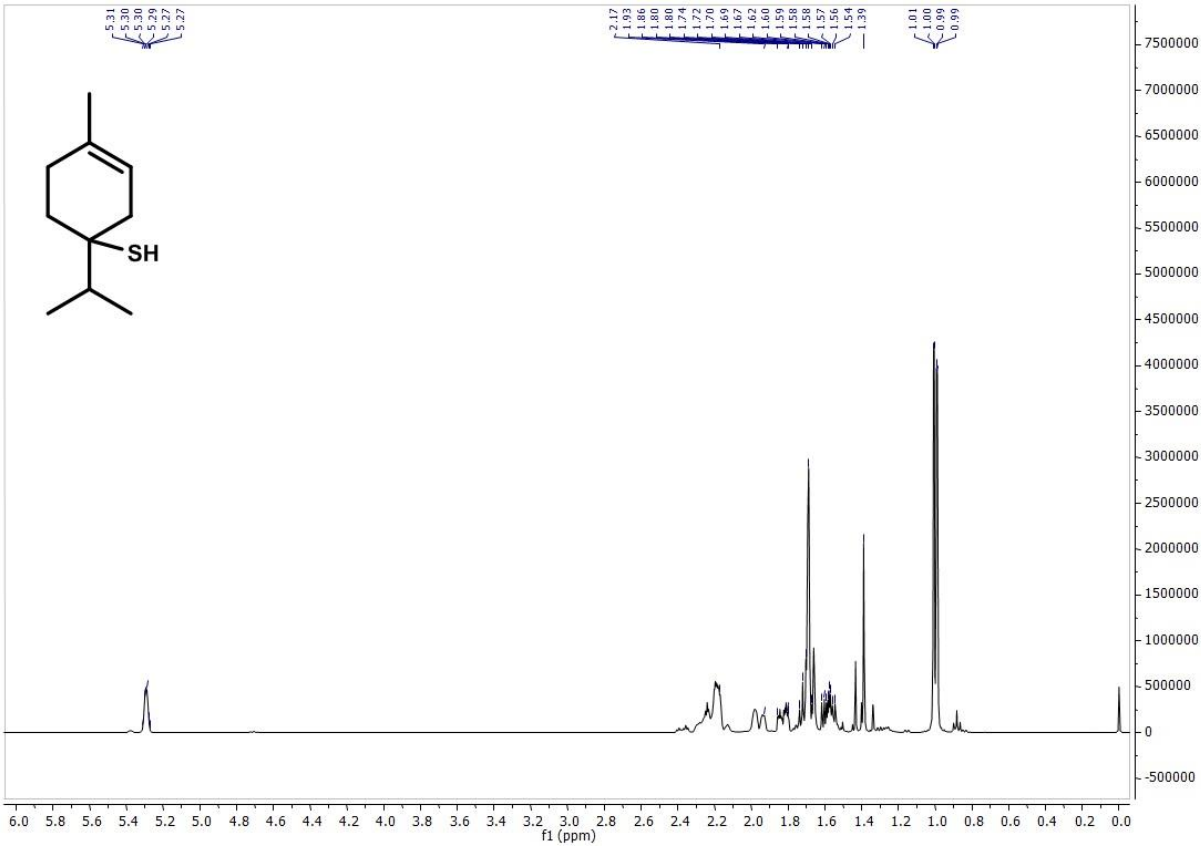


Figure S56. ^{1}H NMR spectrum of 1-*p*-menthene-4-thiol.

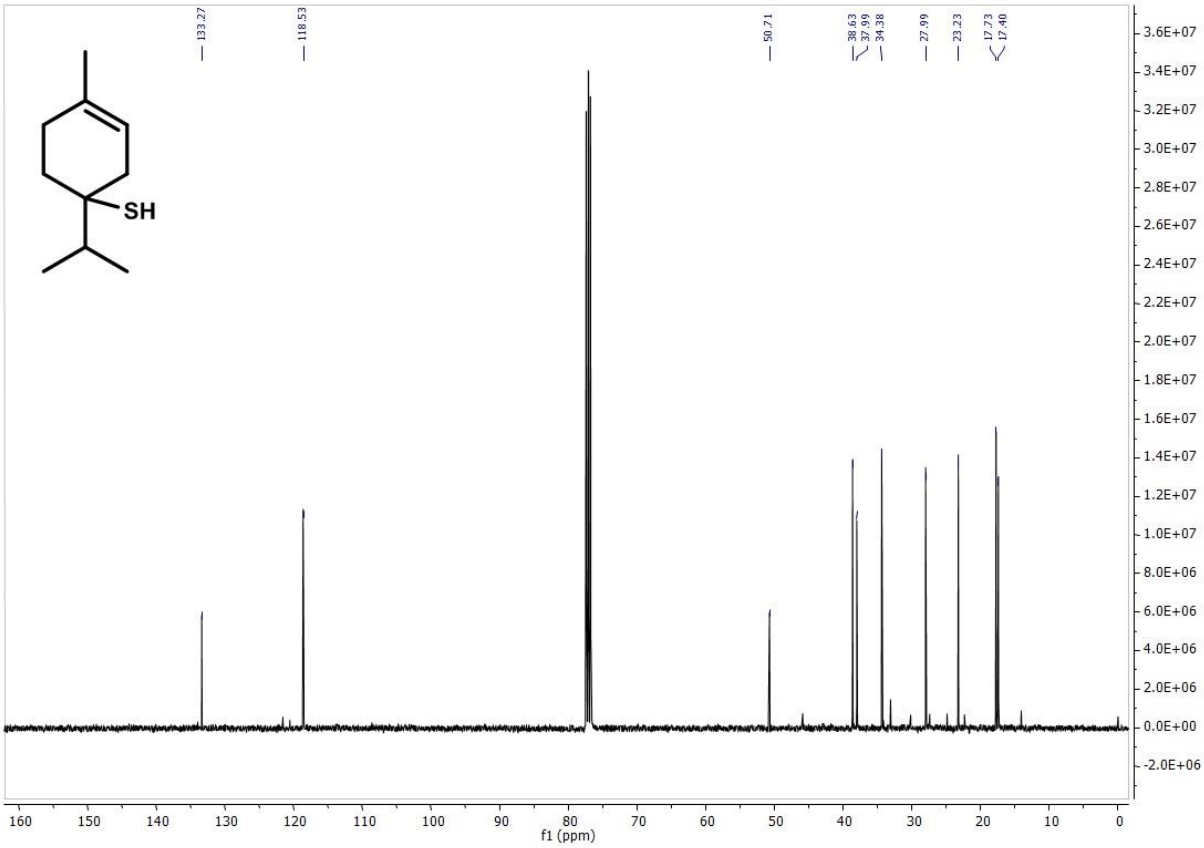


Figure S57. ^{13}C NMR spectrum of 1-*p*-menthene-4-thiol.

Synthesis of thio geraniol (compound 19) and thio nerol (21)

A mixture of thio geraniol and thio nerol was synthesized from linalool as shown in **Figure S58**.

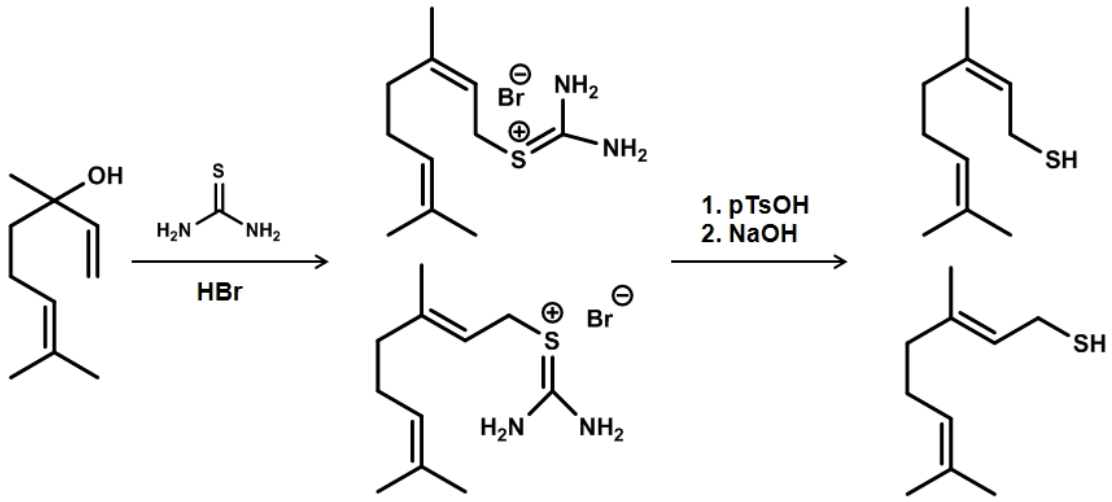
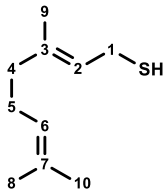


Figure S58. Synthetic route used for the preparation of thio geraniol and thio nerol.

Linalool (1.54 g; 10 mmol) was placed in a round bottom flask and thi ourea (0.84 g; 11 mmol) and hydrogen bromide solution (48 %; 1.5 mL) were added. The solution was stirred at RT for 24 h and *p*-toluene sulfonic acid (2.06 g; 12 mmol) in water (10 mL) was added. After 10 min the precipitate was filtered off and diethyl ether (30 mL) was added. The solution was washed twice with water (10 mL), dried over sodium sulfate and the solvent was removed under reduced pressure. The obtained powder was added to a sodium hydroxide solution (20 %; 15 mL) and stirred at RT for 2 h. Diethyl ether (20 mL) was added and the organic layer was washed for three times with brine (15 mL). The aqueous layer was extracted twice with diethyl ether (20 mL) and the combined organic layers were dried over sodium sulfate. After evaporation of the solvent the compounds were purified by means of column chromatorgraphy on silica gel with pentane as the eluent.

Compound **19**

thio geraniol, yield: 41 %



educt: linalool

RI (FFAP): 1599

RI (DB-5): 1287

MS-EI: *m/z* (intensity in %) 41 (51), 155 (18), 67 (16), 93 (12), 123 (9), 53 (8), 59 (8), 101 (8), 137 (6), 81 (5), M^+ absent

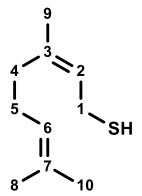
MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 95 (14), 138 (11), 169 (6), 171 (5, $[M+H]^+$)

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.39 (t, *J* = 7.1 Hz, SH), 1.60 (s, 3H, H-C10), 1.65 (s, 3H, H-C9), 1.68 (s, 3H, H-C8), 1.98 – 2.12 (m, 4H, H-C4, H-C5), 3.14 – 3.18 (m, 2H, H-C1), 5.06 – 5.10 (m, 1H, H-C6), 5.32 – 5.37 (m, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 15.77 (C9), 17.70 (C10), 22.11 (C1), 25.68 (C8), 26.40 (C5), 39.40 (C4), 123.31 (C2), 123.91 (C6), 131.68 (C7), 137.50 (C3)

Compound **21**

thio nerol, yield: 14 %



educt: linalool

RI (FFAP): 1573

RI (DB-5): 1271

MS-EI: *m/z* (intensity in %) 69 (100), 41 (55), 93 (25), 67 (20), 137 (16), 68 (14), 155 (14), 53 (13), 81 (10), 59 (9), 101 (8), 91 (7), 121 (7), 79 (6), 89 (6), 123 (5), 136 (5), 170 (3, M^+)

MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 95 (19), 171 (16, $[M+H]^+$), 91 (14), 93 (11), 138 (11), 109 (5)

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.40 (s, *J* = 7.1 Hz, SH), 1.62 (s, 3H, H-C10), 1.68 (s, 3H, H-C8), 1.69 (s, 3H, H-C9), 1.98 – 2.12 (m, 4H, H-C4, H-C5), 3.12 – 3.16 (m, 2H, H-C1), 5.09 – 5.12 (m, 1H, H-C6), 5.32 – 5.37 (m, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 17.68 (C9), 22.00 (C10), 23.25 (C1), 25.71 (C8), 26.49 (C5), 31.68 (C4), 123.88 (C2), 124.17 (C6), 132.09 (C7), 137.42 (C3)

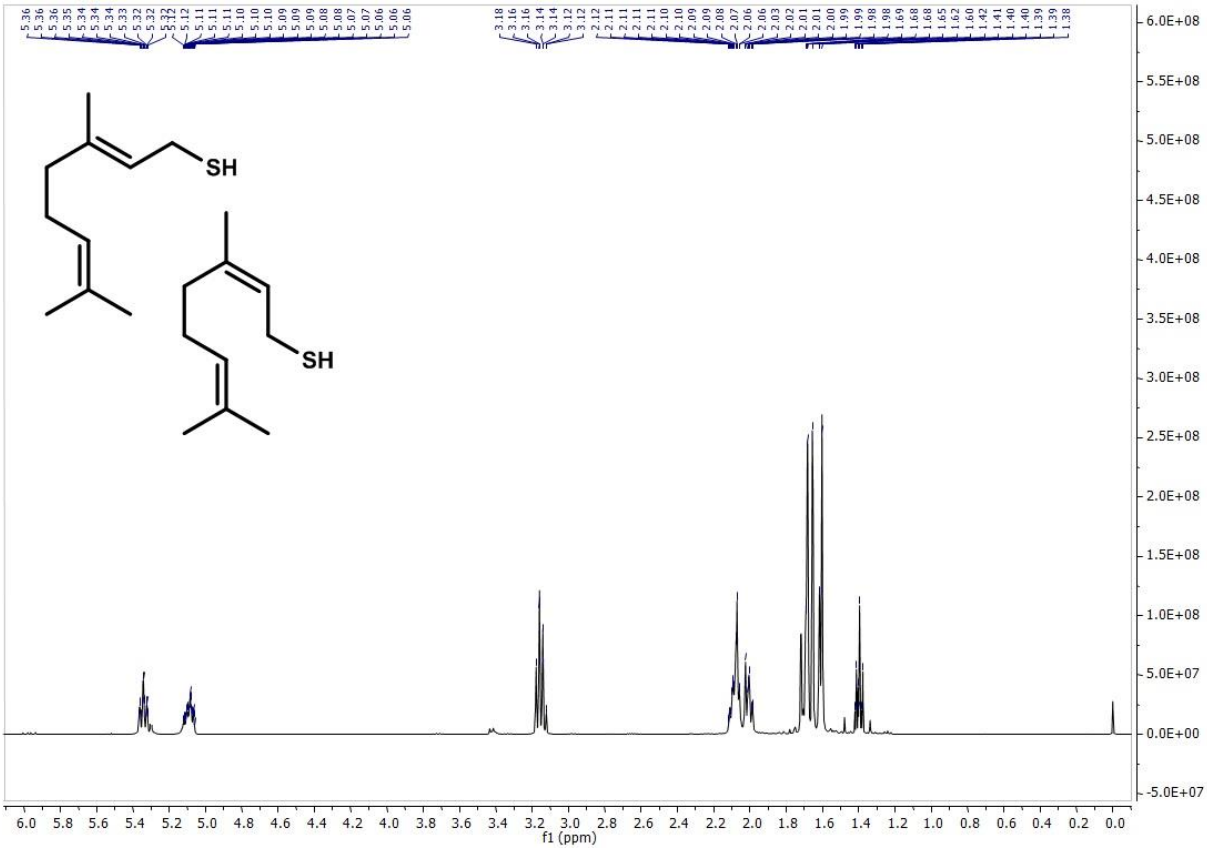


Figure S59. ^{1}H NMR spectrum of a mixture of thio geraniol and thio nerol.

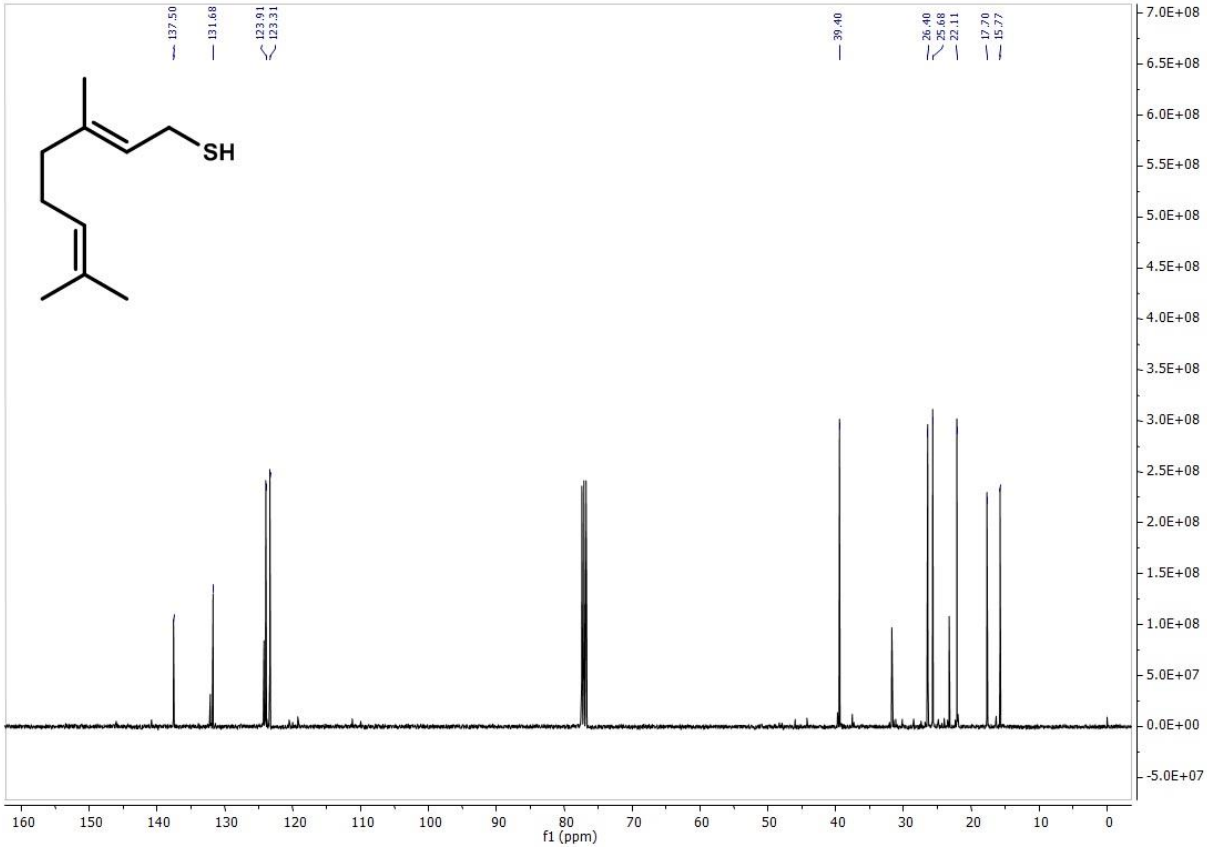
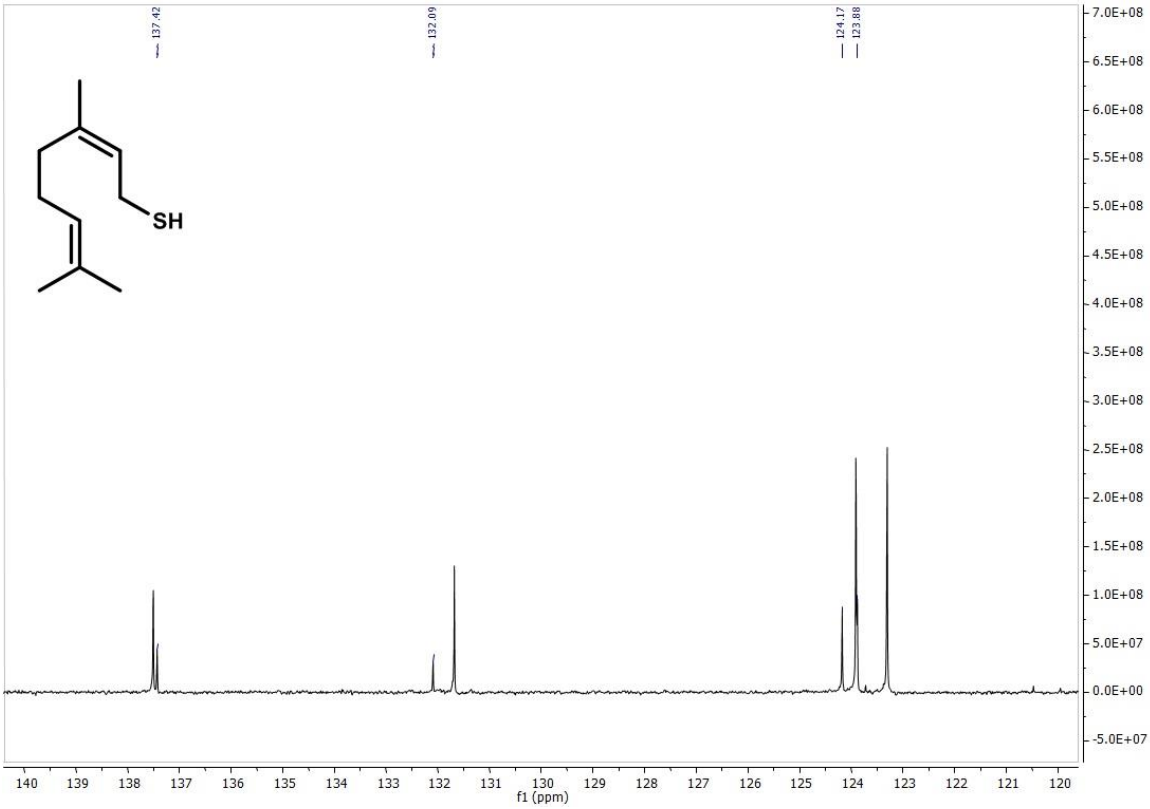
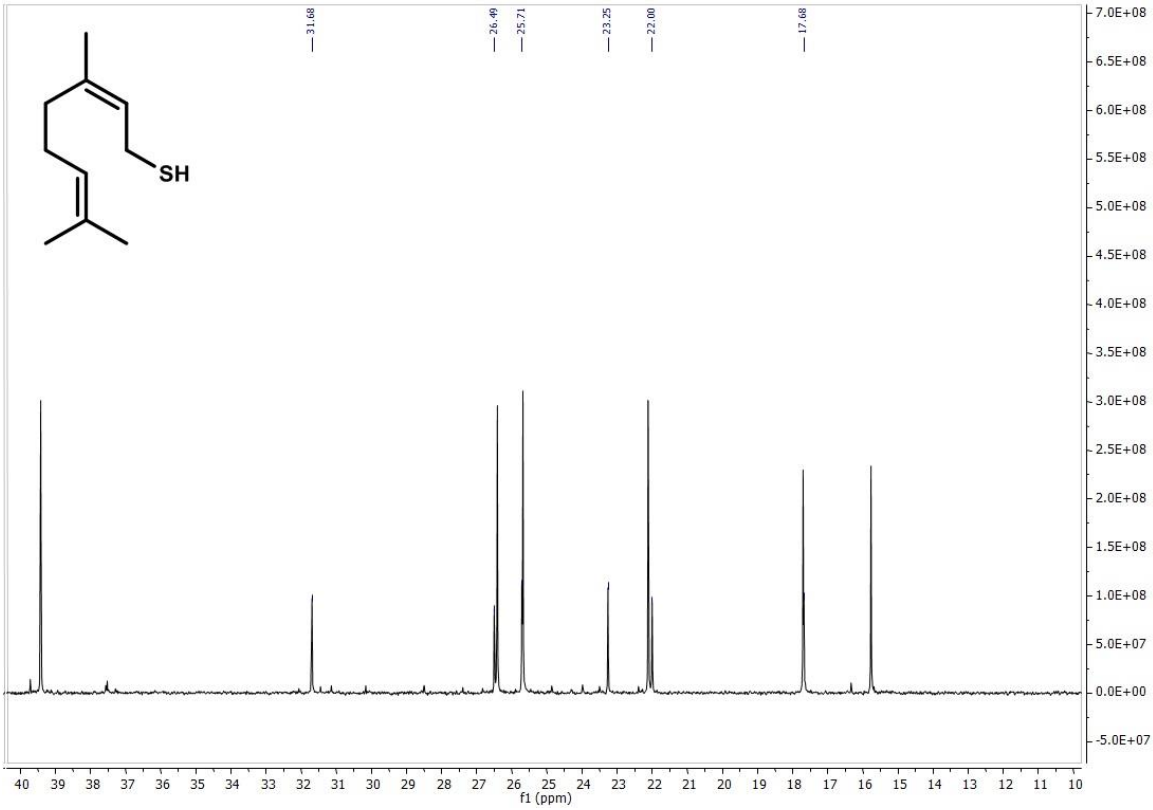


Figure S60. ^{13}C NMR spectrum of a mixture of thio geraniol and thio nerol; signals of thio geraniol.



Figures S61. ^{13}C NMR spectrum of a mixture of thio geraniol and thio nerol; signal of thio nerol I.



Figures S62. ^{13}C NMR spectrum of a mixture of thio geraniol and thio nerol; signals of thio nerol II.

Synthesis of thio linalool (20)

Synthesis of thio linalool was done from geraniol, as shown in **Figure S63**.

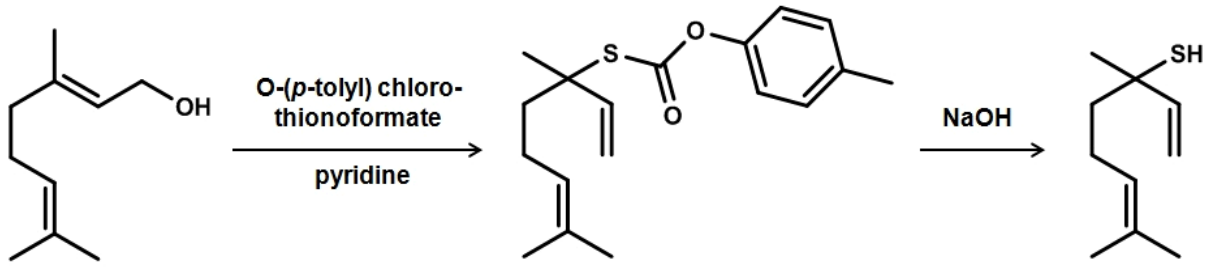
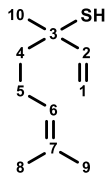


Figure S63. Synthetic route used for the preparation of thio linalool.

Geraniol (1.54 g; 10 mmol) was dissolved in pyridine (15 mL) and cooled to 0 °C. *O*-(*p*-tolyl) chloro thionoformate (1.87 g; 10 mmol) was carefully added and the solution was stirred at RT for 2 h. Diethyl ether (30 mL) was added and the reaction mixture was washed twice with 2 N sodium hydroxide solution (20 mL), 2 N hydrogen chloride solution (20 mL) and brine (20 mL). The solvent was removed under reduced pressure. The intermediate was reduced with lithium aluminium hydride and purified by column chromatography on silica gel with pentane as the eluent.

Compound **20**

thio linalool, yield: 14 %



educt: geraniol

RI (FFAP): 1439

RI (DB-5): 1194

MS-EI: *m/z* (intensity in %) 41 (100), 69 (95), 93 (77), 55 (38), 67 (33), 53 (30), 80 (30), 81 (29), 43 (26), 45 (22), 121 (19), 79 (18), 136 (18, M^+), 87 (16), 68 (15), 44 (14), 91 (14), 92 (14), 95 (14), 59 (12), 94 (8), 107 (8), 127 (6)

MS-CI (isobutane): *m/z* (intensity in %) 137 (100), 91 (45), 95 (43), 171 (11, $[M+H]^+$), 107 (9), 136 (9), 138 (7), 123 (6), 172 (5)

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.48 (s, 3H, H-C9), 1.60 (s, 3H, H-C10), 1.65 – 1.69 (m, 2H, H-C4), 1.68 (s, 3H, H-C8), 1.78 (s, SH), 1.98 – 2.09 (m, 2H, H-C5), 4.96 – 4.99 (m, 1H, H-C1), 5.06 – 5.12 (m, 2H, H-C1, H-C6), 5.97 (dd, *J* = 17.2 Hz, 10.6 Hz, 1H, H-C2)

^{13}C NMR (101 MHz, $CDCl_3$): δ 17.64 (C10), 23.98 (C5), 25.66 (C8), 28.51 (C9), 44.20 (C4), 48.29 (C3), 111.15 (C1), 123.72 (C6), 131.94 (C7), 145.95 (C2)

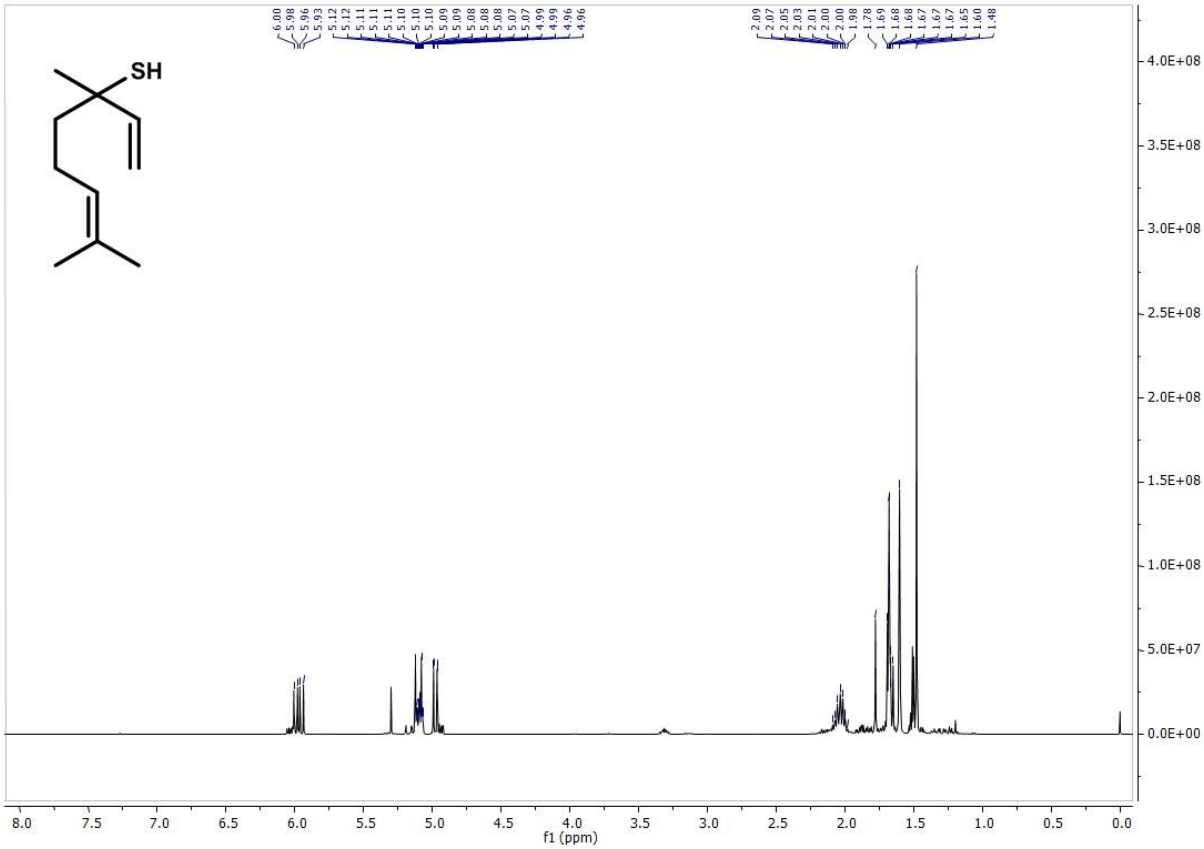


Figure S64. ^{1}H NMR spectrum of thio linalool.

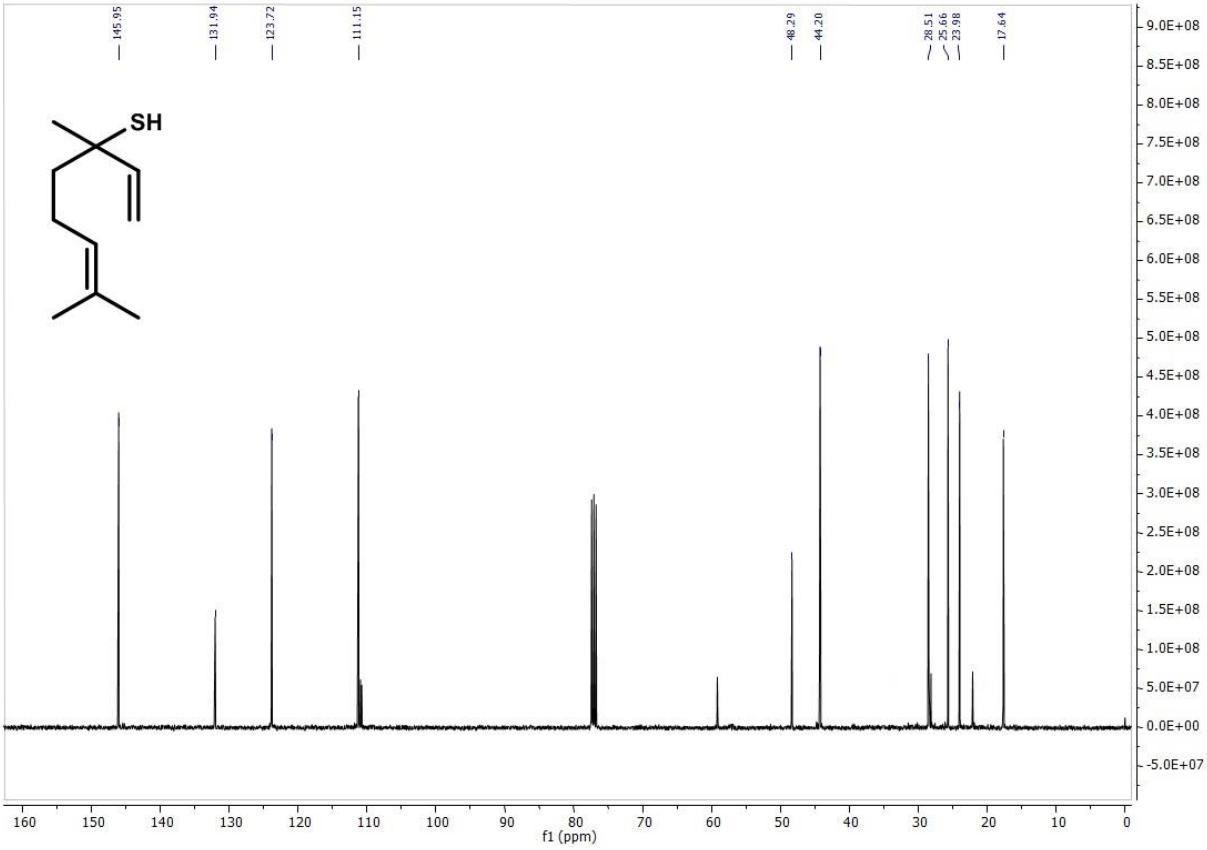
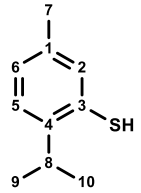


Figure S65. ^{13}C NMR spectrum of thio linalool.

Further spectroscopic data

Compound **14**

***p*-cymene-3-thiol**



RI (FFAP): 1867

RI (DB-5): 1315

MS-EI: *m/z* (intensity in %) 151 (100), 166 (44, M^+), 91 (33), 149 (31), 115 (28), 136 (22), 162 (21), 117 (20), 161 (20), 118 (15), 39 (14), 45 (14), 65 (14), 77 (14), 105 (14), 124 (14), 134 (14), 147 (14), 41 (12), 116 (9), 119 (9), 51 (8), 59 (8), 152 (7), 89 (5), 92 (5), 167 (5)

MS-CI (isobutane): *m/z* (intensity in %) 167 (100, $[M+H]^+$), 166 (16), 168 (15), 125 (9), 165 (7)

^{1}H NMR (400 MHz; $CDCl_3$): δ 1.23 (d, *J* = 6.8 Hz, 6H, H-C9, H-C10), 2.26 (s, 3H, H-C7), 3.14 – 3.21 (m, 1H, H-C8), 3.24 (s, SH), 6.96 (d, *J* = 7.9 Hz, 1H, H-C6), 7.09 (s, 1H, H-C2), 7.12 (d, *J* = 7.9 Hz, 1H, H-C5)

^{13}C NMR (101 MHz, $CDCl_3$): δ 20.70 (C7), 22.91 (C9, C10), 30.93 (C8), 125.52 (C5), 127.16 (C6), 129.39 (C3), 131.27 (C2), 135.89 (C1), 143.43 (C4)

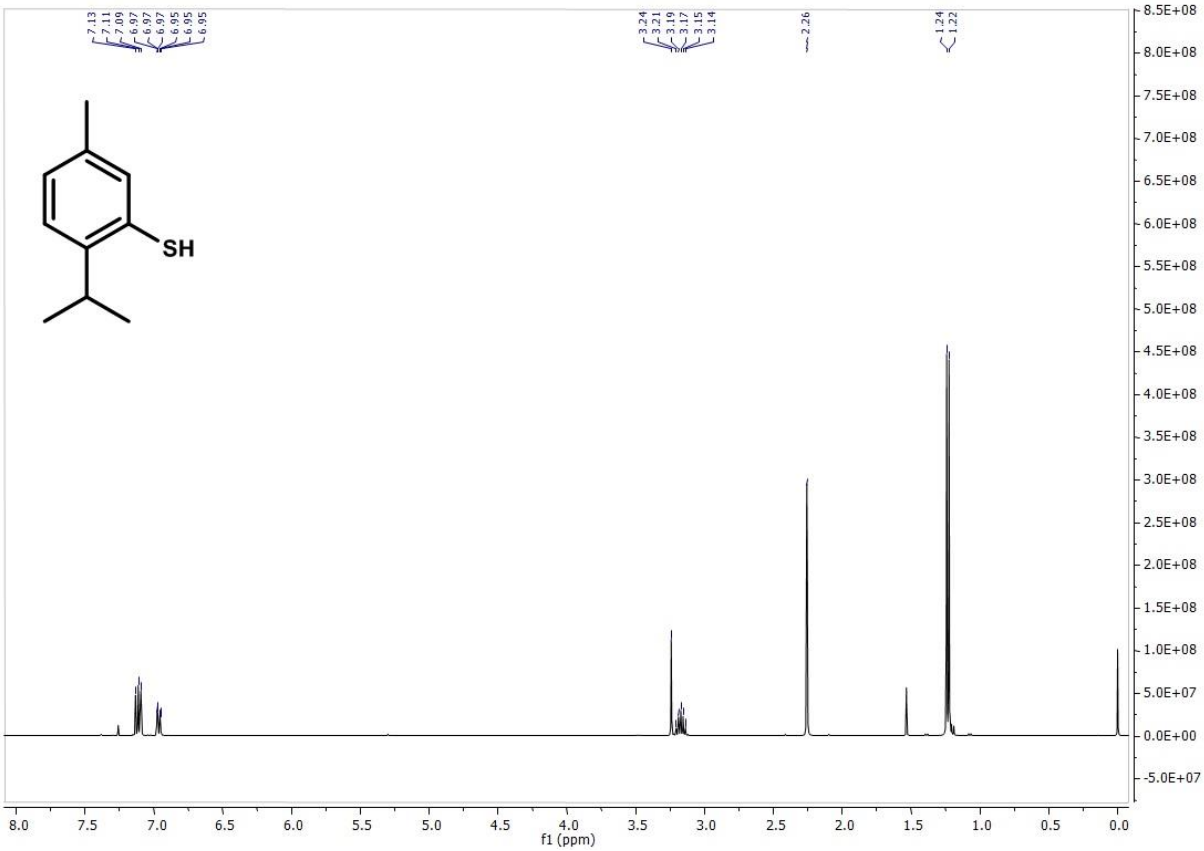


Figure S66. ^{1}H NMR spectrum of *p*-cymene-3-thiol.

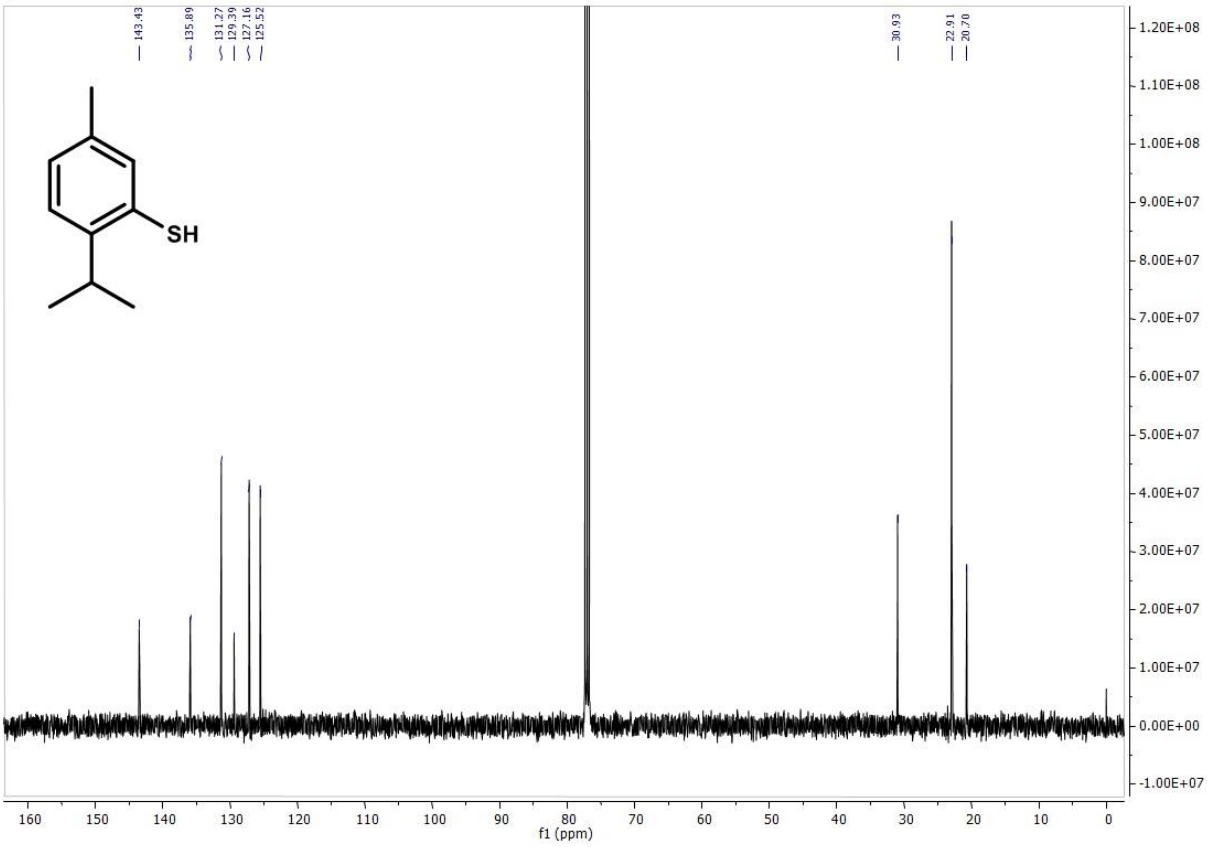


Figure S67. ^{13}C NMR spectrum of *p*-cymene-3-thiol.