Electronic Supplementary Material (ESI) for Chemical Communications

Binuclear Fe-Complexes as Catalyst for the Ligand-free Regioselective Allylic Sulfenylation.

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General remarks

All the reactions and manipulations which are sensitive to air or moisture were performed under dry nitrogen by using standard Schlenk techniques. All solvents were purified prior to use. Thiols were purchased from Acros Organics, Sigma Aldrich or Alfa Aesar. NMR spectra were recorded on a Bruker AV 300 spectrometer at 300 MHz (^{1}H-NMR), 75 MHz (^{13}C-NMR), a Bruker AV 500 spectrometer at 500 MHz (^{1}H-NMR), 125.6 MHz (^{13}C-NMR) or a Bruker AV 250 spectrometer at 250 MHz (^{1}H-NMR), 62.5 MHz (^{13}C-NMR). Chemical shifts were reported in ppm down field using tetramethylsilane as an internal standard. IR spectra were measured on a Bruker Vector 22 FT-IR spectrometer in an ATR mode. Mass spectra were measured using electrospray ionization on a Bruker Micro-TOF-Q.

I. Preparation of iron complexes

***tetra-N*-Butylammonium *tris*-carbonylnitrosoferrate [TBAFe]/4**[1]. Sodium nitrite (8.4 g, 120 mmol) and *tetra*-butylammonium bromide (38.0 g, 120 mmol) were dissolved in degassed water (40 mL) under a nitrogen atmosphere at room temperature. A solution of iron pentacarbonyle (23.6 g, 120 mmol) in degassed dichloromethane (40 mL) was added to the solution at room temperature. The reaction mixture was stirred at room temperature for 3 h. The organic phase was separated, extracted with distilled water (2 x 20 mL), dried over Na_2SO_4, filtered and concentrated in vacuum. The resulting dark brown oily residue was diluted in a minimum amount of methanol and added dropwise to degassed water (500 mL) with vigorous stirring. After stirring for 30 min a yellow solid precipitated and was isolated as by filtration. The solid was again taken up in a small amount of methanol and filtered through a silica pad using a mixture of dichloromethane/methanol (3:1) as the eluent. After removal of the solvent TBAFe was obtained as a yellowish brown solid (111 mmol, 92 %). ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 3.18 (s, 8*H*), 1.65 (s, 8*H*), 1.46 (s, 8*H*), 1.03 (s, 12*H*) ppm; ^{13}C-NMR (125 MHz, CD_2Cl_2) δ 225.1, 59.3, 24.3, 20.1, 13.8

ppm; IR (Film) ν 2963 (w), 2876 (w), 1975 (m), 1851 (s), 1635 (s), 1470 (m), 1379 (w), 1035 (w), 883 (w), 737 (w), 621 (s), 524 (m) cm^{-1}; GC/MS (EI, 70 eV) m/z (%) = 170 (100), 142 (10), 114 (6), 88 (3); HRMS (ESI-HR) calc'd C_3FeNO_4: 169.9171, found: 169.9158.

Dibenzylthiolato dinitrosyl iron dimer 6[2] Iron(II)sulfate (5.0 g, 180 mmol) was dissolved in 4 M aqueous sulfuric acid solution (50 mL). Then sodium nitrite (2.0 g, 230 mmol) and benzyl mercaptan (5.0 mL, 420 mmol) were added simultaneously at room temperature. The resulting brown solution was stirred at room temperature for further 10 minutes. Then the pH value of the reaction mixture was set to 6 with a 6 M aqueous sodium hydroxide solution. The green precipitate was filtered and washed with water (25 mL), *iso*-propanol (10 mL) and petroleum ether (5 mL). After drying the black solid in vacuo it was extracted with benzene (3 x 50 mL) and evaporated to dryness. The crude product was purified by recrystallization from acetone/water. Iron complex **6** was obtained as a brown powder (2.7 g, 32 %). ^{1}H-NMR (300 MHz, CD_2Cl_2) δ7.57 – 7.26 (m, 10*H*), 4.44 (s, 2*H*), 4.39 (s, 2*H*) ppm; ^{13}C-NMR (63 MHz, CD_2Cl_2) δ 129.9, 129.8, 129.7, 129.6, 128.8, 49.7, 48.8 ppm; IR (Film) ν 1769 (s), 1720 (s), 1492 (m), 1452 (m), 1227 (w), 1068 (w), 1027 (w), 912 (w), 759 (m), 695 (s) cm^{-1}; GC/MS (EI, 70 eV) m/z (%) = 478 (5), 448 (100), 418 (63), 388 (36), 358 (55), 324 (4), 297 (6), 267 (55), 221 (1), 176 (12), 144 (5), 121 (1), 91 (80), 65 (6), 30 (2); HRMS (ESI-HR) calc'd $C_{14}H_{14}Fe_2N_4O_4S_2$: 477.9155, found: 477.9136; R_f 0.41 (petroleum ether).

***tetra-N*-Butylammonium *bis*-iodoso *bis*-nitroso ferrate**[3] TBAFe **4** (824 mg, 2 mmol) was dissolved in methylene chloride (25 mL) and iodine (900 mg, 3.5 mmol) was added slowly at 0 °C. After stirring for 2 h at room temperature the solution was evaporated to dryness and filtered through celite (eluent: methylene chloride). The solvent was removed in vacuum and the desired crude product was obtained as a

black solid. The formation of *tetra-N*-butylammonium *bis*-iodoso *bis*-nitroso ferrate was confirmed by IR and found sufficently pure for further conversion. IR (Film) ν 2958 (m), 2931 (m), 2872 (m), 1769 (s), 1711 (s), 1468 (s), 1379 (w), 1168 (w), 1031 (w), 879 (m), 735 (m) cm^{-1}; GC/MS (ESI, 70 eV) m/z (%) = 370 (1), 255 (1), 127 (100).

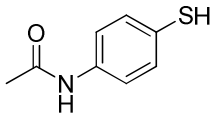
***tetra-N*-butylammonium *bis*-thiophenolato *bis*-nitroso ferrate 5**[4] Crude *tetra-N*-butylammonium *bis*-iodoso *bis*-nitroso ferrate (2.5 mmol) was dissolved in THF/MeOH (2:1, 30 mL) and sodium thiophenolate (1.3 g 10 mmol) was added. The reaction mixture was allowed to stir overnight at room temperature. After removal of the solvent the residue was taken up in methylene chloride and filtered through a plug of basic aluminium oxide. After addition of *n*-pentane product **5** was obtained at -18 °C as black crystals (28 %, 234 mg). ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 7.70 – 7.12 (m, 10 *H*), 3.12 (s, 8*H*), 1.59 (s, 8*H*), 1.39 (s, 8*H*), 0.96 (s, 12*H*) ppm; IR (Film) ν 2957 (m), 2872 (m), 1733 (s), 1686 (s), 157(m), 1471 (s), 1378 (m), 1166 (w), 1084 (w), 1067 (w), 1025 (w), 880 (m), 737 (s), 690 (s) cm^{-1}; GC/MS (ESI, 70 eV) m/z (%) = 334 (3), 304 (100), 274 (1), 225 (2), 157 (2), 109 (1); HRMS (ESI-HR) calc'd $C_{12}H_{10}FeN_2O_2S_2$: 478.7100, found: 478.7075.

[(SIPr)Fe(SBn)(NO)$_2$] 8. Ligand **2** (854 mg, 2 mmol) and sodium *tert*-butylat (192 mg, 2 mmol) were dissolved in THF (40 mL). The resulting solution was stirred at room temperature for 1 h. Then iron complex **6** (478 mg, 1 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The resulting deep red solution was filtered through celite and the solvent was removed in vacuo. The crude product was purified by column chromatography on neutral alumina oxide (*n*-pentane/methylene chloride 1/0 -> 0/1) and product **8** was obtained as a red-brown solid (200 mg, 32 %). Crystals which were suitable for x-ray analysis were obtained by slow evaporation from acetonitrile at -20 °C. IR (Film) ν 2963 (m), 1756 (s), 1700

(s), 1475 (m), 1452 (m), 1430 (m), 1284 (m), 1266 (m), 1242 (m), 804 (m), 758 (m), 732 (s), 700 (s) cm^{-1}; GC/MS (ESI, 70 eV) m/z (%) = 506 (11), 391 (100); HRMS (ESI-HR) calc'd $C_{27}H_{38}FeN_4O_2$: 506.2339, found: 506.2337.

II. Preparation of starting materials

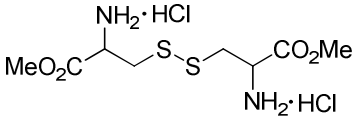
4-Acetamidothiophenol[5]



Experimental procedure: *p*-mercapto aniline (1.3g, 10 mmol) was dissolved in ethyl acetate (50 mL) and cooled to 0°C. Acetic anhydride (1.0 mL, 11 mmol) was added carefully and the reaction mixture was allowed to warm to room temperature within 1 h. The reaction mixture was diluted with ethyl acetate (50 mL) then washed with aqueous hydrochloric acid (1 N, 50 mL) and brine (50 mL). After drying over sodium sulfate the product was purified by flash chromatography on silica (petroleum ether/ethyl acetate 1:1).

Off-white solid, mp: 143°C, isolated yield: 78 % (1.01 g); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 2*H*), 7.31 – 7.06 (m, 4*H*), 3.42 (s, 1*H*), 2.17 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 168.2, 136.1, 130.7, 125.3, 120.6, 24.6 ppm; **IR** (Film) ν 3292 (w), 3179 (w), 3108 (w), 1658 (s), 1591 (s), 1521 (s), 1489 (s), 1392 (s), 1365 (s), 1314 (s), 1257 (m), 1100 (m), 1011 (m), 818 (s), 741 (m), 708 (m), 603 (m), 582 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 167 (56), 125 (100), 109 (7), 97 (22), 93 (24), 81 (21), 69 (18), 55 (15); **R_f** 0.40 (petroleum ether/ethyl acetate 1:2).

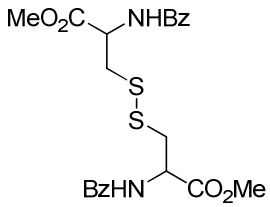
Cystin methylester hydrochloride[6]



Experimental procedure: Methanol (20 mL) was cooled to 0 °C and thionyl chloride (3.2 ml, 44 mmol) was added dropwise. Then L-cystine (2.4 g, 20 mmol) was added at room temperature and the reaction mixture was heated to reflux overnight. After removal of the solvent the residue was suspended in diethyl ether and cooled to 0 °C. The crude product was filtered off and recrystallized from hot methanol by addition of diethyl ether. The colourless crystals were filtered off and washed with a solution of diethyl ether/methanol (5:1) twice. After drying in vacuo the product was obtained as white crystals (12.3 g, 73%).

$[\alpha]^{20}_{D}$ -54.3° (c = 0.5, MeOH); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 4.66 – 4.54 (m, 2*H*), 3.87 (s, 6*H*), 3.48 – 3.34 (m, 4*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 172.1, 56.9, 54.4, 38.5 ppm; **IR** (Film) ν 2807 (b), 1742 (s), 1564 (w), 1539 (w), 1496 (m), 1430 (m), 1401 (w), 1381 (w), 1326 (w), 1242 (s), 1196 (s), 1060 (m), 991 (m), 926 (m), 881 (m), 842 (m), 821 (m), 774 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 323 (4), 301 (3), 291 (13), 269 (100), 242 (8), 166 (51), 134 (29), 101 (3), 88 (5); **HRMS** (ESI-HR) calc'd for $C_8H_{16}N_2O_4S_2$: 269.0624, found: 269.0613.

***N*-(Benzoyl)-*L*-cystine methyl ester[7]**

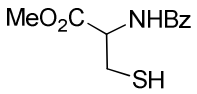


Experimental procedure: Cystin methylester hydrochloride (1.7 g, 5 mmol) was suspended in THF (30 mL) and cooled to 0 °C. Pyridine (7.2 mL, 50 mmol) and benzoyl chloride (1.4 mL, 12 mmol) were added and the reaction mixture was stirred overnight at room temperature. After addition of water (40 mL) the reaction mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with 2 N aqueous hydrochloric acid (2 x 25 mL), saturated sodium hydrogencarbonate solution (1 x 25 mL) and brine (1 x 25 mL). The organic phase was dried over sodium sulfate, filtered and evaporated to dryness to obtain the yellow

crude product which was recrystallized from methylene chloride/diethyl ether to yield the pure product in 55 % (1.3 g) as a white solid.

$[\alpha]^{20}_D$ -183.8° (c = 0.8, EtOH); mp: 181 °C; **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 7.89 – 7.75 (m, 2*H*), 7.59 – 7.35 (m, 3*H*), 7.12 (d, *J* = 7.3 Hz, 1*H*), 5.14 – 5.01 (m, 1*H*), 3.78 (s, 3*H*), 3.35 (d, *J* = 5.1 Hz, 2*H*) ppm; **^{13}C-NMR** (50 MHz, $CDCl_3$) δ 170.9, 167.1, 133.5, 132.0, 128.6, 127.2, 52.9, 52.3, 40.9 ppm; **IR** (Film) ν 3306 (w), 1735 (s), 1635 (s), 1602 (w), 1579 (w), 1522 (s), 1488 (m), 1434 (w), 1293 (m), 1267 (m), 1213 (s), 1160 (s), 1097 (w), 1024 (w), 1001 (w), 837 (w), 715 (m), 691 (s), 674 (m) cm^{-1}; **GC/MS** (ESI, 70 eV) m/z (%) = 477 (15), 445 (6), 417 (2), 272 (2), 238 (100), 222 (1), 135 (3), 105 (2); **R_f** 0.37 (petroleum ether/ethyl acetate 1:1).

N-(Benzoyl)-*L*-cysteine methyl ester[8]



Experimental procedure: *N*-(Benzoyl)-*L*-cysteine methyl ester was prepared according to an experimental procedure of *Corey* and coworkers[5]. *N*-(Benzoyl)-*L*-cystine methyl ester (1.2 g, 2.5 mmol) was placed in a flask and dimethoxyethan (35 mL), methanol (10 mL), water (5 mL) and triphenyl phoshine (2.0 g, 7.5 mmol) were added. The reaction mixture was heated to 90°C overnight. After cooling down to room temperature methylene chloride was added and the aqueous layer was extracted with methylene chloride (3 x 50 mL). The combined organic layers were dried over sodium sulfate. After filtration and removal of the solvents the crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to obtain the product as a white solid (686 mg, 57 %).

$[\alpha]^{20}_D$ -38.2° (c = 1, EtOH); mp: 62 °C; **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 2*H*), 7.62 – 7.39 (m, 3*H*), 7.07 (s, 1*H*), 5.15 – 5.03 (m, 1*H*), 3.84 (s, 3*H*), 3.15 (ddd, *J* = 9.0, 4.0, 1.3 Hz, 2*H*), 1.41 (t, *J* = 9.0 Hz, 1*H*) ppm; **^{13}C-NMR** (50 MHz, $CDCl_3$) δ 170.7, 133.6, 132.0, 128.7, 127.2, 53.9, 53.0, 27.0 ppm; **IR** (Film) ν 3274 (w), 2950 (w), 1732 (s), 1641 (s), 1529 (s), 1488 (m), 1434 (m), 1322 (s), 1293 (m), 1253 (m),

1218 (s), 1192 (m), 1174 (m), 1097 (m), 1065 (m), 999 (m), 911 (w), 801 (w), 695 (s), 637 (m), 616 (w) cm^{-1}; **GC/MS** (ESI, 70 eV) m/z (%) = 240 (14), 222 (8), 208 (10), 180 (13), 105 (100); $\mathbf{R_f}$ 0.61 (petroleum ether/ethyl acetate 1:1).

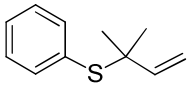
III. Iron-catalyzed allylic sulfenylation

General Procedure for $[Bu_4N]_2[((BnS)(NO)_2Fe)_2]$-catalyzed Allylic Sulfenylation (GP-I): Iron complex **6** (4.8 mg, 0.01 mmol) was dissolved in THF (0.5 mL) and potassium hydride (1 mg, 0.02 mmol) was added. After the reaction mixture was stirred for 3 h at room temperature a deep green solution of iron complex **7** was obtained. Then Bu_4NBr (6.4 mg, 0.02 mmol), carbonate (4 mmol) and benzyl mercaptan (4 mmol) were added successively. The Schlenk tube was closed and heated to 40 °C for 18 h. After evaporation of the solvent the product was isolated by column chromatography on silica. The product was obtained as a mixture of regioisomers, which were separated by column chromatography on silica.

a) Allylic Substitution with thiophenol

The product was obtained according to GP-I as a mixture of regioisomeres **9-A**/**9-B** 94:6. The product was isolated by column chromatography on silica (petroleum ether) in 93 % (165 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

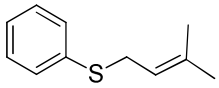
Major isomer: (1,1-Dimethyl-allylsulfanyl)-benzene 9-A[9]



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2*H*), 7.39 – 7.23 (m, 3*H*), 5.96 (dd, *J* = 17.3, 10.6 Hz, 1*H*), 4.91 (dd, *J* = 10.1, 0.5 Hz, 1*H*), 4.72 (dd, *J* = 16.9, 0.4 Hz, 1*H*), 1.36 (s, 6*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 144.7, 137.2, 132.4,

128.7, 128.3, 111.6, 50.0, 27.5 ppm; **IR** (Film) ν 2964 (m), 2923 (m), 2360 (m), 2341 (w), 1634 (w), 1473 (m), 1438 (m), 1377 (w), 1361 (w), 1121 (s), 1025 (w), 933 (w), 911 (m), 749 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 178 (18), 135 (1), 110 (100), 91 (1), 84 (2), 77 (5), 69 (84), 51 (9); $\mathbf{R_f}$ 0.30 (petroleum ether).

Minor isomer: 3-Methyl-but-2-enyl sulfanyl-benzene 9-B[10]

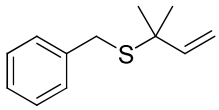


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.38 – 7.13 (m, 5*H*), 5.35 – 5.25 (m, 1*H*), 3.54 (d, *J* = 7.7 Hz, 2*H*), 1.71 (s, 3*H*), 1.59 (s, 3*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 136.9, 136.4, 129.7, 128.7, 126.0, 119.3, 32.2, 25.7, 17.7 ppm; **IR** (Film) ν 3059 (w), 2976 (w), 2929 (w), 1581 (m), 1478 (m), 1439 (m), 1376 (w), 1088 (w), 1024 (m), 737 (s), 689 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 178 (43), 161 (1), 147 (1), 135 (3), 110 (100), 99 (1), 91 (2), 77 (6), 69 (83), 65 (26), 51 (11); $\mathbf{R_f}$ 0.30 (petroleum ether).

b) Allylic Substitution with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **3-A**/**3-B** 93:7. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 80:1) in 84 % (161 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: (1,1-Dimethyl-allylsulfanylmethyl)-benzene 3-A[11]



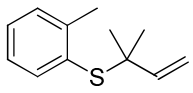
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 5*H*), 5.92 (dd, *J* = 17.3, 10.6 Hz, 1*H*), 5.13 – 4.95 (m, 2*H*), 3.60 (s, 2*H*), 1.39 (s, 6*H*) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 144.6, 138.4, 129.0, 128.4, 126.8, 111.6, 47.3, 34.1, 27.4 ppm; **IR** (Film) ν 3029 (w), 2964 (w), 1633 (w), 1494 (m), 1454 (m), 1362 (m), 1124 (s), 1029 (w), 995 (m), 912 (s), 764 (w), 695 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (66) [M^+],

177 (2), 124 (35), 101 (19), 91 (83), 77 (6), 69 (100), 65 (10), 45 (10), 41 (35); **R_f** 0.66 (petroleum ether/ethylacetate 20:1).

c) Allylic Substitution with 2-methyl-thiophenol

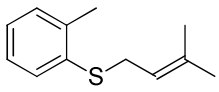
The product was obtained according to GP-I as a mixture of regio isomeres **12-A**/**12-B** 87:13. The product was isolated by column chromatography on silica (petroleum ether) in 78 % (150 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: 1-Methyl-2-(1,1-dimethyl-allylsulfanyl)-benzene 12-A



colouless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 1*H*), 7.25 – 7.20 (m, 2*H*), 7.16 – 7.06 (m, 1*H*), 5.98 (dd, *J* = 17.0, 10.5 Hz, 1*H*), 4.89 (dd, *J* = 10.4, 1.1 Hz, 1*H*), 4.73 (dd, *J* = 17.2, 0.8 Hz, 1*H*), 2.48 (s, 3*H*), 1.37 (s, 6*H*) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 144.9, 143.5, 138.5, 131.9, 130.3, 128.8, 125.6, 111.4, 51.0, 27.5, 26.9, 21.8 ppm; **IR** (Film) ν 2973 (w), 2927 (w), 1588 (w), 1466 (m), 1455 (m), 1378 (m), 1063 (m), 1043 (m), 742 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (55), 166 (1), 149 (2), 137 (2), 124 (100), 108 (1), 91 (24), 77 (10), 69 (95), 65 (5), 53 (5), 41 (43); **HRMS** (ESI-HR) calc'd for $C_{12}H_{16}S$: 192.0973, found: 192.0969; **R_f** 0.62 (petroleum ether).

Minor isomer: 1-Methyl-2-(3-methyl-but-2-enylsulfanyl)-benzene 12-B



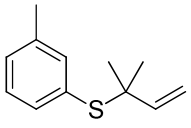
Colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1*H*), 7.19 – 7.04 (m, 3*H*), 5.36 – 5.27 (m, 1*H*), 3.51 (d, *J* = 7.9 Hz, 2*H*), 2.37 (s, 3*H*), 1.72 (s, 3*H*), 1.61 (s, 3*H*) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 145.9, 137.6, 136.7, 129.9, 128.4, 126.2, 125.6, 118.9, 31.4, 25.7, 20.4, 17.7 ppm; **IR** (Film) ν 2974 (w), 2920 (w), 1588 (w), 1466

(m), 1455 (m), 1378 (w), 1063 (w), 1042 (m), 742 (s), 709 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 246 (32), 192 (53), 180 (1), 149 (2), 124 (100), 84 (46), 77 (10), 69 (86), 49 (50), 41 (33); **HRMS** (ESI-HR) calc'd for $C_{12}H_{16}S$: 192.0973, found: 192.0969; $\mathbf{R_f}$ 0.60 (petroleum ether).

d) Allylic Substitution with 3-methyl-thiophenol

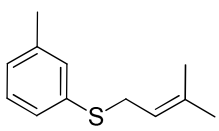
The product was obtained according to GP-I as a mixture of regio isomeres **11-A**/**11-B** 93:7. The product was isolated by column chromatography on silica (petroleum ether) in 93 % (178 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: 2-Methyl-2-(1,1-dimethyl-allylsulfanyl)-benzene 11-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 2*H*), 7.32 – 7.25 (m, 1*H*), 7.15 – 7.07 (m, 1*H*), 7.05 – 6.95 (m, 1*H*), 6.10 (dd, *J* = 17.4, 10.6 Hz, 1*H*), 4.92 (dd, *J* = 10.4, 0.8 Hz, 1*H*), 4.77 (dd, *J* = 17.1, 1.0 Hz, 1*H*), 2.15 (s, 3*H*), 1.41 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 145.4, 138.3, 138.1, 134.7, 133.1, 129.7, 127.9, 111.4, 49.8, 27.7, 21.0 ppm; **IR** (Film) ν 2966 (w), 1591 (m), 1474 (s), 1440 (m), 1376 (s),1327 (w), 1120 (s), 1045 (s), 994 (s), 910 (s), 856 (m), 779 (s), 693 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (38), 149 (1), 140 (4), 124 (100), 108 (2), 91 (16), 77 (4), 69 (60), 41 (25); **HRMS** (ESI-HR) calc'd for $C_{12}H_{16}S$: 192.0973, found: 192.0959; $\mathbf{R_f}$ 0.65 (petroleum ether).

Minor isomer: 2-Methyl-2-(3-methyl-but-2-enylsulfanyl)-benzene 11-B

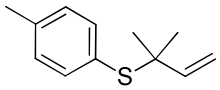


Colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 3*H*), 7.03 – 6.93 (m, 1*H*), 5.36 – 5.25 (m, 1*H*), 3.53 (d, *J* = 7.7 Hz, 2*H*), 2.32 (s, 3*H*), 1.71 (s, 3*H*), 1.60 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.5, 136.6, 136.3, 130.2, 128.6, 126.8, 126.5, 119.4, 32.2, 25.7, 21.3, 17.7 ppm; **IR** (Film) ν 2973 (w), 2917 (w), 1715 (w), 1592 (m), 1573 (w), 1474 (m), 1447 (m), 1376 (m), 1216 (w), 1101 (w), 1081 (w), 855 (m), 770 (s), 687 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (67), 149 (2), 124 (100), 108 (2), 91 (16), 77 (5), 69 (64), 41 (27); **HRMS** (EI) calc'd for $C_{12}H_{16}S$: 192.0973, found: 192.0975; **R_f** 0.63 (petroleum ether).

e) Allylic Substitution with 4-methyl-thiophenol

The product was obtained according to GP-I as a mixture of regio isomeres **10-A**/**10-B** 94:6. The product was isolated by column chromatography on silica (petroleum ether) in 76 % (146 mg) combined yield.

Major isomer: 3-Methyl-2-(1,1-dimethyl-allylsulfanyl)-benzene 10-A

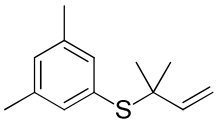


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.15 – 7.06 (m, 2H), 5.95 (dd, J = 17.4, 10.6 Hz, 1H), 4.90 (dd, J = 10.4, 0.9 Hz, 1H), 4.72 (dd, J = 17.2, 0.9 Hz, 1H), 2.34 (s, 3H), 1.34 (s, 6H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 144.8, 138.8, 137.2, 129.1, 128.9, 111.5, 49.8, 27.4, 21.2 ppm; **IR** (Film) ν 2974 (w), 2920 (w), 1491 (m), 1448 (m), 1377 (m), 1089 (m), 1040 (m), 1015 (m), 804 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (14), 124 (100), 108 (2), 91 (37), 77 (12), 69 (51), 53 (9); **HRMS** (EI) calc'd for $C_{12}H_{16}S$: 192.0973, found: 192.0961; **R_f** 0.61 (petroleum ether).

Allylic Substitution with 3,5-dimethyl-thiophenol

The product was obtained according to GP-I as a mixture of regio isomeres **20-A**/**20-B** 94:6. The product was isolated by column chromatography on silica (petroleum ether) in 72 % (149 mg) combined yield.

Major isomer: 2,4-Dimethyl-2-(1,1-dimethyl-allylsulfanyl)-benzene 20-A

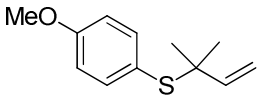


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ7.13 – 7.07 (m, 2*H*), 6.99 – 6.94 (m, 1*H*), 5.96 (dd, *J* = 17.1, 10.8 Hz, 1*H*), 4.92 (dd, *J* = 10.4, 0.8 Hz, 1*H*), 4.76 (dd, *J* = 17.4, 0.8 Hz, 1*H*), 2.29 (s, 6*H*), 1.35 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 144.9, 137.8, 134.7, 130.4, 127.0, 111.3, 49.7, 27.6, 21.1 ppm; **IR** (Film) ν 2964 (w), 2918 (w), 1599 (m), 1580 (m), 1454 (m), 1376 (w), 1360 (w), 1121 (s), 993 (m), 909 (s), 849 (s), 690 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 206 (20), 189 (1), 163 (2), 138 (100), 121 (4), 105 (33), 91 (12), 77 (12), 69 (50), 53 (11); **HRMS** (ESI-HR) calc'd for $C_{13}H_{18}S$: 206.1129, found: 206.1129; **R_f** 0.44 (petroleum ether).

f) Allylic Substitution with 4-methoxy-thiophenol

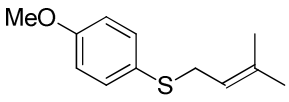
The product was obtained according to GP-I as a mixture of regio isomeres **13-A**/**13-B** 93:7. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 40:1) in 97 % (202 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether/ethyl acetate 20 : 1).

Major isomer: 1-(1,1-Dimethyl-allylsulfanyl)-4methoxy-benzene 13-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 2*H*), 6.87 – 6.78 (m, 2*H*), 5.94 (dd, *J* = 17.3, 10.5 Hz, 1*H*), 4.90 (dd, *J* = 10.4, 1.1 Hz, 1*H*), 4.70 (dd, *J* = 16.9, 0.5 Hz, 1*H*), 3.81 (s, 3*H*), 1.33 (s, 6) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 160.3, 144.7, 138.8, 123.3, 113.9, 111.5, 55.3, 49.7, 27.3 ppm; **IR** (Film) ν 2928 (w), 1591 (m), 1571 (w), 1491 (s), 1461 (m), 1440 (m), 1376 (w), 1284 (m), 1241 (s), 1171 (m), 1103 (m), 1030 (s), 823 (s), 798 (m), 638 (m), 625 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 208 (37), 140 (100), 125 (15), 96 (4), 69 (26), 41 (16); **HRMS** (ESI-HR) calc'd for $C_{12}H_{16}OS$: 208.0922, found: 208.0934; **R_f** 0.72 (petroleum ether/ethyl acetate 10:1).

Minor isomer: 1-Methoxy-4-(3-methyl-but-2-enylsulfanyl)-benzene 13-B[12]

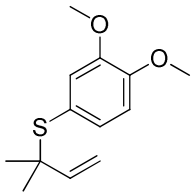


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 2*H*), 6.89 – 6.76 (m, 2*H*), 5.32 – 5.19 (m, 1*H*), 3.80 (s, 3*H*), 3.42 (d, *J* = 7.8 Hz, 2*H*), 1.69 (s, 3*H*), 1.46 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 159.0, 135.9, 134.0, 126.6, 119.8, 114.3, 55.3, 34.3, 25.7, 17.5 ppm; **IR** (Film) ν 2911 (w), 1591 (m), 1492 (s), 1461 (m), 1440 (m), 1284 (m), 1241 (s), 1172 (s), 1103 (m), 1031 (m), 824 (m), 798 (w), 638 (w), 626 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 208 (32), 140 (100), 125 (19), 108 (2), 96 (16), 69 (33), 53 (5), 41 (31); **R_f** 0.58 (petroleum ether/ethyl acetate 10:1).

g) Allylic Substitution with 3,4-dimethoxy-thiophenol

The product was obtained according to GP-I as a mixture of regio isomeres **14-A**/**14-B** 94:6. The product was isolated by column chromatography on silica (petroleum ether) in 83 % (199 mg) combined yield.

Major isomer: 1-(1,1-Dimethyl-allylsulfanyl)-3,4 dimethoxy-benzene 14-A

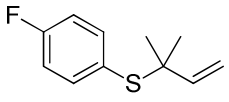


yellow oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.09 – 7.93 (m, 2*H*), 6.83 – 6.75 (m, 1*H*), 5.97 (dd, *J* = 17.4, 10.6 Hz, 1*H*), 4.92 (dd, *J* = 10.6, 0.9 Hz, 1*H*), 4.74 (dd, *J* = 17.3, 0.9 Hz, 1*H*), 3.87 (d, J = 4.7 Hz, 6H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 148.8, 147.2, 143.9, 129.2, 122.6, 119.1, 110.5, 109.7, 54.9, 54.8, 48.9, 28.7, 26.3 ppm; **IR** (Film) ν 2918 (w), 1742 (w), 1461 (m), 1371 (s), 1314 (m), 1229 (m), 1186 (m), 1140 (m), 1057 (w), 971 (w), 913 (w), 746 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 238 (41) [M], 170 (100), 155 (24), 127 (2), 109 (2), 96 (2), 69 (17), 41 (11); **HRMS** (ESI-HR) calc'd for $C_{13}H_{18}O_2S$: 261.0920, found: 261,0911; **R_f** 0.24 (petroleum ether/ethyl acetate 20:1).

h) Allylic Substitution with 4-fluor-thiophenol

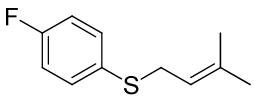
The product was obtained according to GP-I as a mixture of regio isomeres **18-A**/**18-B** 88:12. The product was isolated by column chromatography on silica (petroleum ether) in 50 % (98 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: 2-Fluor-(1,1-dimethyl-allylsulfanyl)-benzene 18-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 2*H*), 7.04 – 6.93 (m, 2*H*), 5.93 (dd, *J* = 17.4, 10.5 Hz, 1*H*), 4.91 (dd, *J* = 10.4, 1.0 Hz, 1*H*), 4.68 (dd, *J* = 17.7, 0.3 Hz, 1*H*), 1.34 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 163.4 (d, $J_{C\text{-}F}$ = 248.7 Hz), 144.4, 139.1 (d, $J_{C\text{-}F}$ = 9.0 Hz), 127.8, 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 111.8, 50.0, 27.2 ppm; **IR** (Film) ν 2966 (w), 1589 (m), 1488 (s), 1362 (w), 1220 (s), 1155 (m), 1121 (m), 1088 (w), 994 (w), 912 (m), 830 (s), 816 (m), 685 (m), 637 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 196 (41), 169 (1), 153 (1), 128 (75), 108 (4), 83 (16), 69 (100), 53 (3), 41 (43); **HRMS** (ESI-HR) calc'd for $C_{11}H_{13}FS$: 196.0722, found: 196.0699; **R_f** 0.44 (petroleum ether).

Minor isomer: 3-Fluor-(3-methyl-but-2-enylsulfanyl)-benzene 18-B



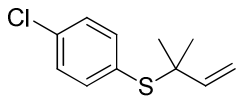
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 2*H*), 7.04 – 6.92 (m, 2*H*), 5.33 – 5.21 (m, 1*H*), 3.47 (d, *J* = 7.8 Hz, 2*H*), 1.70 (s, 3*H*), 1.50 (s, 3*H*) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 136.4, 133.3, 133.2, 119.4, 115.9, 115.6, 33.6, 25.6, 17.6 ppm; **IR** (Film) ν 2974 (w), 2916 (w), 1588 (m), 1489 (s), 1220 (s), 1153 (m), 1083 (m), 1042 (s), 1011 (m), 831 (s), 814 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 196 (49),

153 (1), 128 (60), 108 (3), 83 (24), 69 (100), 53 (6), 41 (51); **HRMS** (ESI-HR) calc'd for $C_{11}H_{13}FS$: 196.0722, found: 196.0696; $\mathbf{R_f}$ 0.45 (petroleum ether).

i) Allylic Substitution with 4-chlor-thiophenol

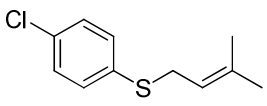
The product was obtained according to GP-I as a mixture of regio isomeres **17-A**/**17-B** 87:13. The product was isolated by column chromatography on silica (petroleum ether) in 68 % (145 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: 3-Chlor-(1,1-dimethyl-allylsulfanyl)-benzene 17-A[13]



yellow oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2*H*), 7.31 – 7.23 (m, 2*H*), 5.93 (dd, *J* = 17.1, 10.8 Hz, 1*H*), 4.92 (dd, *J* = 10.1, 0.4 Hz, 1*H*), 4.71 (dd, *J* = 16.9, 0.4 Hz, 1*H*), 1.35 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 144.4, 138.3, 135.1, 131.0, 130.8, 129.2, 128.5, 111.9, 50.3, 27.3 ppm; **IR** (Film) ν 2972 (w), 2913 (w), 1474 (s), 1447 (m), 1386 (m), 1218 (w), 1093 (s), 1010(s), 809 (s), 744(m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 212 (40), 188 (1), 144 (51), 108 (14), 69 (100), 53 (3), 41 (35); **HRMS** (ESI-HR) calc'd for $C_{11}H_{13}ClS$: 212.0426, found: 212.0430; $\mathbf{R_f}$ 0.43 (petroleum ether).

Minor isomer: 3-Chlor-(3-methyl-but-2-enylsulfanyl)-benzene 17-B[13]



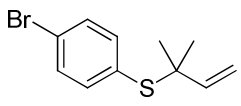
yellow oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 4*H*), 5.25 – 5.15 (m, 1*H*), 3.44 (d, *J* = 7.7 Hz, 2*H*), 1.63 (s, 3*H*), 1.51 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 135.72, 134.4, 131.1, 130.2, 127.8, 118.0, 31.5, 24.6, 16.7 ppm; **IR** (Film) ν 2968 (w), 2917 (w), 2360 (m), 2341 (m), 1315 (m), 1260 (m), 1151 (s), 1087 (s), 1014 (s), 798

(m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 212 (14), 157 (6), 144 (47), 108 (31), 99 (7), 69 (100), 53 (7); $\mathbf{R_f}$ 0.41 (petroleum ether).

j) Allylic Substitution with 4-brom-thiophenol

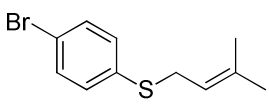
The product was obtained according to GP-I as a mixture of regio isomeres **16-A**/**16-B** 84:16. The product was isolated by column chromatography on silica (petroleum ether) in 81 % (207 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: 3-Brom-2-(1,1-dimethyl-allylsulfanyl)-benzene 16-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2*H*), 7.35 – 7.28 (m, 2*H*), 5.93 (dd, *J* = 17.4, 10.6 Hz, 1*H*), 4.93 (dd, *J* = 10.2, 0.4 Hz, 1*H*), 4.71 (dd, *J* = 17.0, 0.4 Hz, 1*H*), 1.35 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 144.4, 138.6, 131.7, 131.3, 123.4, 112.0, 50.3, 27.4 ppm; **IR** (Film) ν 2970 (w), 2913 (w), 1472 (s), 1448 (m), 1384 (m), 1218 (w), 1090 (s), 1068 (m), 1006 (s), 804 (s), 729 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 258 (25), 190 (33), 161 (1), 147 (1), 108 (16), 82 (2), 69 (100), 41 (27); **HRMS** (ESI-HR) calc'd for $C_{11}H_{13}BrS$: 255.9921, found: 255.9926; $\mathbf{R_f}$ 0.51 (petroleum ether).

Minor isomer: 4-Brom-(3-methyl-but-2-enylsulfanyl)-benzene 16-B



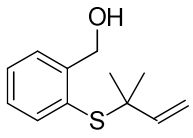
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 2*H*), 7.23 – 7.14 (m, 2*H*), 5.34 – 5.12 (m, 1*H*), 3.51 (d, *J* = 7.7 Hz, 2*H*), 1.71 (s, 3*H*), 1.59 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 136.8, 136.1, 131.7, 131.3, 119.9, 119.0, 32.3, 25.7, 17.8 ppm; **IR** (Film) ν 2972 (w), 2913 (w), 1472 (s), 1447 (m), 1384 (m), 1218 (w), 1090 (s), 1068 (m), 908 (w), 805 (s), 730 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 258 (22),

190 (31), 162 (1), 108 (19), 82 (2), 69 (100), 41(35); **HRMS** (ESI-HR) calc'd for $C_{11}H_{13}BrS$: 255.9921, found: 255.9920; $\mathbf{R_f}$ 0.50 (petroleum ether).

k) Allylic Substitution with 2-thio-benzylalcohol

The product was obtained according to GP-I as a mixture of regio isomeres **15-A**/**15-B** 91:9. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 10:1) in 65 % (135 mg) combined yield.

Major isomer: 2-(1,1-Dimethyl-propenylsulfanyl)-benzyl alcohol 15-A

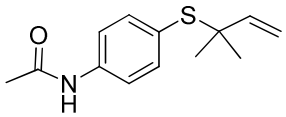


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2*H*), 7.43 – 7.29 (m, 1*H*), 7.28 – 7.19 (m, 1*H*), 5.97 (dd, *J* = 17.2, 10.6 Hz, 1*H*), 4.92 (dd, *J* = 10.1, 0.4 Hz, 1*H*), 4.84 (s, 2*H*), 4.79 – 4.69 (m, 1*H*), 2.02 (bs, 1*H*), 1.40 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 145.6, 144.7, 138.6, 130.9, 129.4, 128.7, 127.5, 111.8, 64.5, 51.2, 27.6 ppm; **IR** (Film) ν 3335 (br), 2964 (w), 1633 (w), 1439 (m), 1412 (m), 1377 (m), 1361 (m), 1193 (w), 1116 (s), 1065 (w), 1029 (s), 1002 (s), 912 (s), 753 (s), 685 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 208 (20), 190 (18), 175 (4), 139 (38), 121 (75), 69 (100), 41 (40); **HRMS** (ESI-HR) calc'd for $C_{12}H_{16}OS$: 208.0922, found: 208.0944; $\mathbf{R_f}$ 0.49 (petroleum ether/ethyl acetate 5:1).

l) Allylic Substitution with 4-thiophenyl acetamide

The product was obtained according to GP-I as a mixture of regio isomeres **19-A**/**19-B** 92:8. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 2:1) in 76 % (178 mg) combined yield.

Major isomer: *N*-(4-(1,1-dimethyl-but-2-enylsulfenyl)-phenyl)-acetamide 19-A

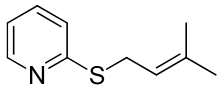


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 4*H*), 7.19 (bs, 1*H*), 5.94 (dd, *J* = 17.1, 10.6 Hz, 1*H*), 4.90 (dd, *J* = 10.3, 1.0 Hz, 1*H*), 4.70 (dd, *J* = 17.8, 0.5 Hz, 1*H*), 2.18 (s, 3*H*), 1.34 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 168.2, 144.6, 138.2, 131.7, 120.3, 119.2, 111.6, 50.2, 27.4 ppm; **IR** (Film) ν 3241(w), 3096 (w), 2964 (w), 1659 (s), 1587 (s), 1520 (s), 1489 (s), 1392 (s), 1367 (s), 1312 (s), 1255 (m), 1119 (m), 1016 (m), 994 (m), 901 (m), 824 (s), 753 (w), 685 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 236 (46), 180 (100), 166 (23), 138 (53), 124 (16), 101 (24); **HRMS** (ESI-HR) calc'd for $C_{13}H_{17}NOSNa$: 258.0923, found: 258.0910; **R_f** 0.22 (petroleum ether/ethyl acetate 2:1).

m) Allylic Substitution with pyridylthiol

The product was obtained according to GP-I as a mixture of regio isomeres **21-A**/**21-B** 52:48. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 30:1) in 77 % (137 mg) combined yield. Only the linear product **21-B** could be isolated due to isomerization of the branched product **21-A** within short time.

Minor isomer: 2-(3-Methyl-but-2-enylsulfanyl)-pyridine 21-B[14]

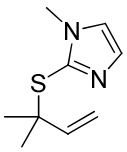


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.46 – 8.39 (m, 1*H*), 7.51 – 7.41 (m, 1*H*), 7.19 – 7.13 (m, 1*H*), 7.01 – 6.93 (m, 1*H*), 5.41 – 5.31 (m, 1*H*), 3.82 (d, *J* = 7.9 Hz, 2*H*), 1.73 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 159.6, 149.4, 136.5, 135.9, 122.2, 119.3, 119.1, 28.5, 25.8, 17.9 ppm; **IR** (Film) ν 2970 (w), 2914 (w), 2360 (w), 2341 (w), 1578 (s), 1556 (m), 1453 (s), 1414 (s), 1124 (s), 756 (s), 724 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 179 (22), 164 (4), 146 (100), 136 (14), 131 (22), 111 (75), 93 (16), 78 (22), 67 (52), 51 (19); **R_f** 0.43 (petroleum ether/ethyl acetate 20:1).

n) Allylic Substitution with *N*-methyl-2-mercapto imidazole

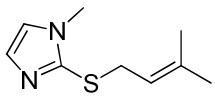
The product was obtained according to GP-I as a mixture of regio isomeres **22-A**/**22-B** 64:36. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 2:1) in 79 % (147 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether/ethyl acetate 3:1).

Major isomer: 2-(1,1-Dimethyl-propenylsulfanyl)-1-methyl-1*H*-imidazole 22-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 6.83 (d, *J* = 2.27 Hz, 1*H*), 6.65 (d, *J* = 2.64 Hz, 1*H*), 6.34 (dd, *J* = 17.4, 10.6 Hz, 1*H*), 5.28 – 5.15 (m, 2*H*), 3.58 (s, 3*H*), 1.89 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 161.5, 142.4, 116.9, 114.7, 113.8, 61.7, 35.0, 26.1 ppm; **IR** (Film) ν 2976 (w), 2929 (w), 1445 (m), 1404 (m), 1371 (s), 1286 (m), 1205 (s), 1182 (m), 1139 (m), 1088 (w), 927 (w), 709 (m), 670 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 182 (57), 167 (2), 149 (5), 136 (3), 114 (100), 81 (5), 69 (9), 41 (14); **HRMS** (ESI-HR) calc'd for $C_9H_{14}N_2S$: 205.0770, found: 205.0764; **R_f** 0.44 (petroleum ether/ethyl acetate 1:1).

Minor isomer: 2-(3-methyl-but-2-enylsulfanyl)-1-methyl-1*H*-imidazole 22-B



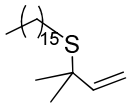
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 1.6 Hz, 1*H*), 6.93 (d, *J* = 1.3 Hz, 1*H*), 5.35 – 5.26 (m, 1*H*), 3.66 (d, *J* = 8.3 Hz, 2*H*), 3.62 (s, 3*H*), 1.69 (s, 3*H*), 1.52 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 141.6, 137.3, 129.1, 122.2, 118.8, 33.5, 33.3, 25.7, 17.4 ppm; **IR** (Film) ν 2969 (w), 2928 (w), 2358 (m), 2339 (m), 1454 (s), 1376 (m), 1280 (s), 1220 (w), 1123 (m), 914 (w), 844 (w), 745 (m), 688 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 182 (12), 167 (1), 149 (7), 136 (6), 114 (100), 99 (1), 81

(6), 72 (14), 53 (4); **HRMS** (ESI-HR) calc'd for $C_9H_{15}N_2S$: 183.0950, found: 183.0943; **R_f** 0.41 (petroleum ether/ethyl acetate 1:1).

o) Allylic Substitution with hexadecylthiol

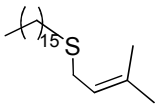
The product was obtained according to GP-I as a mixture of regio isomeres **23-A**/**23-B** 85:15. The product was isolated by column chromatography on silica (petroleum ether) in 88 % (278 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

Major isomer: 3-Hexadecyl-3-methyl-but-1-ene 23-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.85 (dd, *J* = 17.3, 10.5 Hz, 1*H*), 5.03 – 4.87 (m, 2*H*), 2.36 (t, *J* = 7.4 Hz, 2*H*), 1.60 – 1.45 (m, 2*H*), 1.36 (s, 6*H*), 1.25 (s, 28*H*), 0.87 (t, *J* = 6.7 Hz, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 145.0, 111.0, 46.2, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 27.5, 22.7, 14.1 ppm; **IR** (Film) ν 2921 (s), 2852 (s), 1465 (m), 1376 (w), 1362 (w), 1126 (m), 994 (w), 908 (m), 735 (m), 688 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 326 (20), 311 (3), 299 (2), 257 (47), 213 (2), 171 (1), 129 (1), 101 (6), 69 (100), 55 (8), 41 (13); **HRMS** (ESI-HR) calc'd for $C_{21}H_{42}S$: 326.3007, found: 326.2981; **R_f** 0.52 (petroleum ether).

Minor isomer: 1-Hexadecyl-3-methyl-but-2-ene 23-B



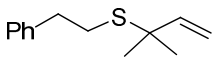
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.29 – 5.19 (m, 1*H*), 3.13 (d, *J* = 7.8 Hz, 2*H*), 2.45 (t, *J* = 7.4 Hz, 2*H*), 1.74 (s, 3*H*), 1.67 (s, 3*H*), 1.62 – 1.50 (m, 2*H*), 1.26 (m, 28*H*), 0.88 (t, *J* = 6.7 Hz, 3*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 134.9, 120.9, 31.9, 31.3, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.7, 22.7, 17.7, 14.1 ppm;

IR (Film) ν 2921 (s), 2852 (s), 2360 (w), 2341 (w), 1465 (m), 1376 (w), 844 (w), 806 (w), 720 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 326 (46), 311 (2), 257 (60), 213 (2), 171 (2), 129 (2), 101 (12), 83 (5), 69 (100), 55 (9), 41 (17); **HRMS** (ESI-HR) calc'd for $C_{21}H_{42}S$: 326.3007, found: 326.3040; $\mathbf{R_f}$ 0.50 (petroleum ether).

p) Allylic Substitution with 2-phenylethanethiol

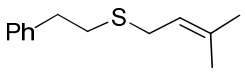
The product was obtained according to GP-I as a mixture of regio isomeres **24-A**/**24-B** 92:8. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 40:1) in 91 % (187 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether/ethyl acetate 40:1).

Major isomer: 2-(1-Methyl-but-2-enylsulfanyl-ethyl)-benzene 24-A



Colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 5*H*), 5.86 (dd, *J* = 17.3, 10.5 Hz, 1*H*), 5.04 – 4.89 (m, 2*H*), 2.87 – 2.77 (m, 2*H*), 2.66 – 2.58 (m, 2*H*), 1.38 (s, 6*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 144.8, 141.0, 128.4, 126.3, 111.3, 46.6, 36.2, 30.7, 27.5 ppm; **IR** (Film) ν 3028 (w), 2963 (m), 2923 (m), 2863 (w), 2360 (m), 2341 (m), 1633 (w), 1496 (m), 1454 (m), 1362 (m), 1125 (s), 995 (w), 911 (s), 734 (m), 697 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 206 (47), 191 (1), 138 (20), 115 (8), 104 (18), 91 (27), 77 (6), 69 (100), 53 (2), 41 (26) ; **HRMS** (ESI-HR) calc'd for $C_{13}H_{18}S$: 206.1129, found: 206.1126; $\mathbf{R_f}$ 0.48 (petroleum ether/ethyl acetate 20:1).

Minor isomer: 2-(3-Methyl-but-2-enylsulfanyl-ethyl)-benzene 24-B



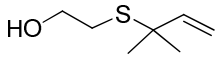
Colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 5*H*), 5.29 – 5.19 (m, 1*H*), 3.16 (d, *J* = 7.6 Hz, 2*H*); 2.92 – 2.83 (m, 2*H*), 2.77- 2.68 (m, 2*H*), 1.76 (s, 3*H*); 1.67 (s, 3*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 140.9, 135.4, 128.5, 126.3, 120.7, 36.5, 32.7, 29.7, 25.7, 17.8 ppm; **IR** (Film) ν 3022 (w), 2911 (w), 2360 (m), 2330 (m), 1508

(w), 1429 (w), 1377 (w), 835 (w), 733 (m), 699 (s), 669 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 206 (74), 191 (1), 138 (19), 115 (8), 104 (21), 91 (33), 77 (8), 69 (100), 51 (3), 41 (27); **HRMS** (ESI-HR) calc'd for $C_{13}H_{18}S$: 206.1129, found: 206.1142; $\mathbf{R_f}$ 0.46 (petroleum ether/ethyl acetate 20:1).

q) Allylic Substitution with 2-mercaptoethanol

The product was obtained according to GP-I as a mixture of regio isomeres **25-A**/**25-B** 92:8. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 3:1) in 69 % (101 mg) combined yield.

Major isomer: 2-(2-Methyl-But-2-enyl)-ethanol 25-A

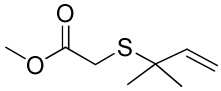


yellow oil; $\mathbf{R_f}$ 0.32 (petroleum ether/ethyl acetate 3:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.86 (dd, *J* = 17.3, 10.6 Hz, 1*H*), 5.09 – 4.90 (m, 2*H*), 3.69 (t, *J* = 6.2 Hz, 2*H*), 2.63 (t, *J* = 6.2 Hz, 2*H*), 1.39 (s, 6*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 144.7, 111.8, 61.4, 32.7, 27.7 ppm; **IR** (Film) ν 3351 (b), 2964 (m), 2924 (m), 2867 (w), 1633 (w), 1456 (m), 1413 (m), 1378 (m), 1363 (m), 1125 (s), 1043 (s), 1001 (s), 912 (s), 696 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 146 (33), 131 (1), 101 (8), 85 (1), 69 (100), 59 (3), 53 (6), 41 (47); **HRMS** (ESI-HR) calc'd for $C_7H_{14}OS$: 146.0765, found: 146.0756; $\mathbf{R_f}$ 0.32 (petroleum ether/ethyl acetate 3:1).

r) Allylic Substitution with 2-mercapto-glycolic acid methylester

The product was obtained according to GP-I as a mixture of regio isomeres **26-A**/**26-B** 91:9. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 10:1) in 62 % (108 mg) combined yield.

Major isomer: 1-Methyl-but-2-enylsulfanyl-acetic acid methyl ester 26-A

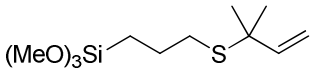


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.82 (dd, *J* = 17.3, 10.5 Hz, 1*H*), 5.11 – 4.94 (m, 2*H*), 3.71 (s, 3*H*), 3.17 (s, 2*H*), 1.39 (s, 6*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 171.4, 143.7, 112.5, 52.3, 47.4, 31.9, 27.1 ppm; **IR** (Film) ν 2966 (w), 1735 (s), 1435 (m), 1380 (w), 1364 (w), 1271 (s), 1121 (s), 1005 (m), 915 (m), 688 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 174 (45), 159 (1), 143 (8), 115 (3), 101 (46), 84 (10), 69 (100), 53 (5), 41 (37); **HRMS** (ESI-HR) calc'd for $C_8H_{14}O_2S$: 174.0715, found: 174.0699; **R_f** 0.39 (petroleum ether/ethyl acetate 10:1).

s) Allylic Substitution with 3-mercaptopropyl trimethoxysilan

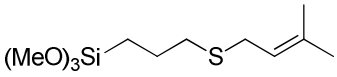
The product was obtained according to GP-I as a mixture of regioisomeres **27-A**/**27-B** 93:7. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 10:1) in 76 % (201 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether/ethyl acetate 10:1).

Major isomer: Trimethoxy-1-(3-(1,1-dimethyl-allylthio)propyl)silan 27-A



colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.85 (dd, *J* = 17.3, 10.6 Hz, 1*H*), 4.99 (dd, *J* = 10.5, 1.2 Hz, 1*H*), 4.93 (dd, *J* = 17.4, 1.2 Hz, 1*H*), 3.56 (s, 9*H*), 2.40 (t, *J* = 7.4 Hz, 2*H*), 1.76 – 1.55 (m, 2*H*), 1.36 (s, 6*H*), 0.80 – 0.68 (m, 2*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 145.0, 111.0, 50.5, 46.3, 32.1, 27.5, 23.2, 9.0 ppm; **IR** (Film) ν 2942 (m), 2840 (m), 2360 (m), 2342 (m), 1457 (w), 1191 (m), 1086 (s), 912 (w), 814 (m), 766 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 287 (100), 273 (5), 250 (13), 233 (11), 216 (14), 165 (18), 151 (16), 133 (8), 119 (2) ; **HRMS** (ESI-HR) calc'd for $C_{11}H_{24}O_3SSiNa$: 287.1100, found: 287.1100; **R_f** 0.19 (petroleum ether/ethyl acetate 10:1).

Minor isomer: Trimethoxy-1-(3-(3-methyl-but-2-enylthio)propyl)silan 27-B

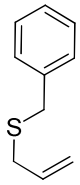


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.29 – 5.19 (m, 1*H*), 3.57 (s, 9*H*), 3.13 (d, *J* = 7.8 Hz, 2*H*), 2.49 (t, *J* = 7.4 Hz, 2*H*), 1.77 – 1.61 (m, 2*H*), 1.74 (s, 3*H*), 1.66 (s, 3*H*), 0.81 – 0.70 (m, 2*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 135.0, 120.8, 50.5, 34.2, 29.3, 25.7, 23.0, 17.7, 8.7 ppm; **IR** (Film) ν 2941 (m), 2839 (m), 2361 (m), 2342 (m), 1191 (m), 1086 (s), 811 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 287 (100), 273 (5), 165 (15), 151 (21), 133 (15) ; **HRMS** (ESI-HR) calc'd for $C_{11}H_{24}O_3SSiNa$: 287.1108, found: 287.1107; **R_f** 0.17 (petroleum ether/ethyl acetate 10:1).

t) Allylic Substitution of allyl methyl carbonate with benzyl mercaptan

The product was obtained according to GP-I. It was isolated by column chromatography on silica (petroleum ether) in 95 % (156 mg) yield.

Benzyl allyl sulfide 31[15]

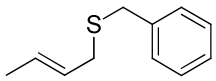


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 5*H*), 5.80 (ddt, *J* = 16.8, 12.1, 6.0 Hz, 1*H*), 5.17 – 5.04 (m, 2*H*), 3.66 (s, 2*H*), 3.04 (d, *J* = 7.2 Hz, 2*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.3, 134.2, 129.0, 128.5, 126.9, 117.3, 34.9, 34.1, 26.9 ppm; **IR** (Film) ν 3029 (w), 2912 (w), 1634 (w), 1494 (m), 1453 (m), 1227 (w), 1070 (m), 990 (m), 742 (m), 700 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 164 (26), 122 (20), 105 (3), 91 (100), 77 (5), 65 (8), 45 (8); **R_f** 0.39 (petroleum ether).

u) Allylic Substitution of 2-butenyl methyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **32-A**/**32-B** >99:<1. The product was isolated by column chromatography on silica (petroleum ether) in 94 % (168 mg) combined yield.

Major isomer: Benzyl crotyl sulphide 32-A[16]

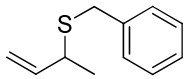


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.19, m, 5*H*), 5.61 – 5.37 (m, 2*H*), 3.66 (s, 3*H*), 3.04 – 2.95 (m, 2*H*), 1.76 – 1.68 (m, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.6, 129.0, 128.5, 128.4, 126.9, 126.8, 35.0, 33.3, 17.7 ppm; **IR** (Film) ν 3026 (w), 2915 (w), 1737 (m), 1494 (m), 1453 (m), 1417 (w), 1223 (w), 1069 (w), 963 (s), 931 (m), 764 (m), 696 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 178 (45), 124 (21), 91 (100), 77 (5), 65 (15), 55 (14), 45 (16); **HRMS** (ESI-HR) calc'd for $C_{11}H_{14}S$: 178.0816, found: 178.0802; **R_f** 0.32 (petroleum ether).

v) Allylic Substitution of 3-buten-2-yl methyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **32-B**/**32-A** 95:5. The product was isolated by column chromatography on silica gel (petroleum ether) in 88 % (157 mg) combined yield.

Major isomer: Benzyl-1-methylallyl sulfide 32-B[16]

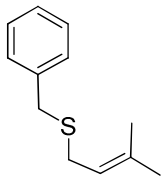


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.19 m, 5*H*), 5.78 – 5.63 (m, 1*H*), 5.11 – 4.96 (m, 2*H*), 3.72 – 3.58 (m, 2*H*), 3.21 (app. quint., *J* = 7.3 Hz, 1*H*), 1.31 (s, 3*H*), 1.28 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 140.5, 138:7, 128:9, 128:5, 126:8, 114.5, 42.5, 35.2, 20.0 ppm; **IR** (Film) ν 3029 (w), 2965 (w), 2925 (w), 1633 (w), 1494 (m), 1452 (m), 1414 (w), 1220 (w), 1071 (w), 1028 (m), 990 (m), 912 (s), 722 (s), 696 (s), 564 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 178 (17), 163 (1), 145 (1), 122 (19), 91 (100), 77 (11), 65 (21), 55 (20); **R_f** 0.31 (petroleum ether).

w) Allylic Substitution of 3-methyl-but-2-enyl methyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **3-B**/**3-A** 96:4. The product was isolated by column chromatography on silica (petroleum ether) in 80 % (154 mg) combined yield.

Major regioisomer: Benzyl 3-methylbut-2-enyl sulphide 3-B[17]

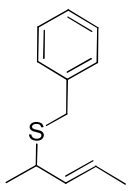


colourless oil; $\mathbf{R_f}$ 0.62(petroleum ether/ethyl acetate 20:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 5*H*), 5.28 – 5.17 (m, 1*H*), 3.68 (s, 2*H*), 3.05 (d, *J* = 7.8 Hz, 2*H*), 1.73 (s, 3*H*), 1.58 (s, 3*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 138.6, 135.5, 128.9, 128.4, 126.8, 120.4, 35.7, 29.1, 25.7, 17.8 ppm; **IR** (Film) ν 3028 (w), 2972 (w), 2913 (w), 1494 (m), 1452 (m), 1376 (m), 1333 (w), 1070 (w), 840 (m), 765 (m), 696 (s), 563 (w) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (32), 177 (2), 143 (1), 136 (4), 124 (25), 101 (19), 91 (100), 77 (10), 69 (85), 59 (12), 51 (11); $\mathbf{R_f}$ 0.62 (petroleum ether/ethyl acetate 20:1).

x) Allylic Substitution of 1-methyl-but-2-enyl methyl carbonate with benzyl mercaptan

The product was obtained according to GP-I. It was isolated by column chromatography on silica (petroleum ether) in 87 % (167 mg) yield.

Benzyl-4-pent-2enyl sulphide 33

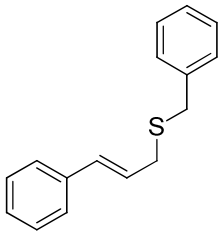


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.32 – 7.09 (m, 5*H*), 5.48 – 5.20 (m, 2*H*), 3.57 (d,*J* = 3.0 Hz, 2*H*), 3.19 – 3.07 (m, 1*H*), 1.65 (d, *J* = 6.1Hz, 3*H*), 1.20 (d, *J* = 6.9 Hz, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.9, 133.7, 128.9, 128.4, 126.8, 125.8, 41.8, 35.3, 20.6, 17.6 ppm; **IR** (Film) ν 2967 (w), 2918 (w), 1494 (m), 1451 (m), 1258 (m), 1018 (m), 963 (s), 695 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 192 (78), 177 (1), 124 (12), 101 (18), 91 (50), 69 (100), 41 (24); **HRMS** (ESI-HR) calc'd for $C_{12}H_{16}S$: 192.0973, found: 192.0968; **R_f** 0.54 (petroleum ether).

y) Allylic Substitution of cinnamyl *i*-butyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **34-A**/**34-B** >99:<1. The product was isolated by column chromatography on silica (petroleum ether) in 82 % (197 mg) combined yield.

Major isomer: Benzyl cinnamyl sulfide 34-A[13]

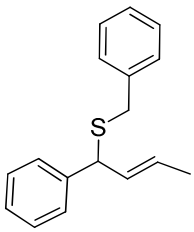


colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.45 – 7.17 (m, 10*H*), 6.40 (d, *J* = 15.7 Hz, 1*H*), 6.17 (dt, *J* = 15.1, 7.6 Hz, 1*H*), 3.70 (s, 2*H*), 7.16 (d, *J* = 7.2 Hz, 2*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 132.5, 129.0, 128.6, 128.5, 127.6, 127.0, 126.3, 125.8, 35.1, 33.7 ppm; **IR** (Film) ν 3026 (w), 1700 (w), 1676 (w), 1493 (m), 1452 (m), 1071 (m), 1027 (m), 963 (m), 748 (s), 694 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 240 (37), 214 (5), 181 (1), 149 (9), 117 (100), 91 (44), 77 (6), 65 (5), 45 (5); **R_f** 0.15 (petroleum ether).

z) Allylic Substitution of 1-phenyl-but-2-enyl *i*-butyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **35-A**/**35-B** 91:9. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 40:1) in 80 % (202 mg) combined yield.

Major isomer: Benzyl-(1-phenyl-but-2-enyl)-sulfide 35-A

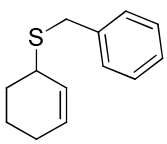


yellow oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.18 (m, 5*H*), 6.33 (d, *J* = 15.7 Hz, 1*H*), 6.08 (dd, *J* = 15.7, 9.0 Hz, 1*H*), 3.68 (s, 2*H*), 3.46 – 3.33 (m, 1*H*), 1.38 (d, *J* = 6.8 Hz, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.6, 136.7, 132.2, 129.9, 128.9, 128.6, 128.5, 127.5, 126.9, 126.3, 42.2, 35.4, 20.5 ppm; **IR** (Film) ν 2954 (m), 2922(m), 2853 (m), 1494 (w), 1453 (m), 963 (m), 748 (s), 694 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 254 (11), 246 (1), 163 (1), 131 (100), 115 (11), 103 (3), 91 (47), 77 (12), 57 (12), 43 (11); **HRMS** (ESI-HR) calc'd for $C_{17}H_{18}S$: 254.1129, found: 254.1135; **R_f** 0.38 (petroleum ether/ethyl acetate 40:1).

aa) Allylic Substitution of cyclohex-2-enyl *i*-butyl carbonate with benzyl mercaptan

The product was obtained according to GP-I. It was isolated by column chromatography on silica (petroleum ether) in 59 % (121 mg) yield.

(Cyclohex-2-enylsulfanylmethyl)-benzene 36[17]



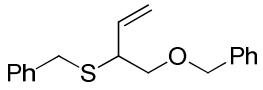
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 5*H*), 5.83 – 5.74 (m, 1*H*), 5.65 (ddt, *J* = 9.9, 3.8, 1.9 Hz, 1*H*), 3.76 (s, 2*H*), 3.32 – 3.23 (m, 1*H*), 2.05 – 1.96 (m,

2*H*), 1.96 – 1.69 (m, 3*H*), 1.64 – 1.55 (m, 1*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.7, 129.9, 128.9, 128.5, 127.5, 126.9, 40.0, 35.5, 29.0, 25.0 ppm; **IR** (Film) ν 3026 (w), 2929 (w), 1494 (m), 1453 (m), 1203 (w), 1069 (m), 1028 (m), 747 (s), 696 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 204 (14), 123 (4), 113 (5), 91 (50), 80 (100), 65 (11), 53 (8), 45 (15), 39 (9); **R_f** 0.36 (petroleum ether).

bb) Allylic Substitution of 1-benzyloxyprop-2-enyl *i*-butyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **37-A**/**37-B** 90:10. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 40:1) in 79 % (224 mg) combined yield.

Major isomer: 4-Benzyloxy-3-benzylsulfanyl-buten 37-A

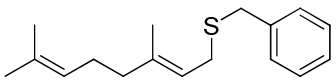


yellow oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 10*H*), 5.85 – 5.70 (m, 1*H*), 5.24 – 5.06 (m, 2*H*), 4.51 (s, 2*H*), 3.78 – 3.62 (m, 2*H*), 3.57 (dd, *J* = 6.3, 1.4 Hz, 2*H*), 3.39 (dt, *J* = 8.6, 6.5 Hz, 1*H*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 138.3, 138.0, 136.3, 129.0, 128.5, 128.4, 127.7, 127.6, 127.0, 117.1, 73.1, 72.0, 47.7, 34.9 ppm; **IR** (Film) ν 3029 (w), 2919 (w), 2852 (w), 1720 (w), 1495 (w), 1453 (m), 1102 (s), 1071 (m), 1027 (m), 969 (w), 737 (m), 697 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 284 (5), 193 (2), 176 (2), 160 (6), 123 (4), 105 (2), 91 (100), 65 (8), 45 (4); **HRMS** (ESI-HR) calc'd for $C_{18}H_{20}OSNa$: 307.1112, found: 307.1127; **R_f** 0.40 (petroleum ether/ethyl acetate 20:1).

cc) Allylic Substitution of geranyl *i*-butyl carbonate with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **29-B**/**29-A** 90:10. The product was isolated by column chromatography on silica (petroleum ether) in 76 % (199 mg) combined yield.

Major isomer: 3,7-Dimethyl-octa-2,6-dienyl-benzylsulfide 29-B[18]



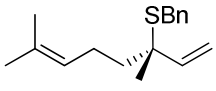
colourless oil; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.09 (m, 5*H*), 5.22 – 5.11 (m, 1*H*), 5.07 – 4.96 (m, 1*H*), 3.60 (s, 2*H*), 2.98 (d, *J* = 7.6 Hz, 2*H*), 2.08 -1.90 (m, 4*H*), 1.61 (s, 3*H*), 1.53 (s, 3*H*), 1.49 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 139.1, 138.7, 131.7, 128.9, 128.4, 126.8, 124.1, 120.4, 39.6, 65.5, 29.0, 26.5, 25.8, 17.8, 16.2 ppm; **IR** (Film) ν 2966 (w), 2915 (m), 2854 (w), 1494 (w), 1452 (m), 1377 (w), 1232 (w), 1070 (w), 839 (w), 767 (w), 697 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 260 (38), 214 (2), 191 (3), 169 (29), 136 (22), 123 (20), 91 (100), 81 (15), 69 (73) 41 (24); **HRMS** (ESI-HR) calc'd for $C_{17}H_{24}S$: 260.1599, found: 260.1616; **R_f** 0.42 (petroleum ether).

dd) Allylic Substitution of (*R*)-28 with benzyl mercaptan

The product was obtained according to GP-I as a mixture of regio isomeres **29-A**/**29-B** 88:12. The product was isolated by column chromatography on silica (petroleum ether) in 76 % (198 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether).

The enantiomeric ratio was determined by means of HPLC: DAICEL CHIRALCEL OJ, *n*-heptane/*iso*-propyl alcohol 99:1, flow rate: 1.0 mL/min, detector: 220 nm, R (t_R = 10.5 min), S (t_S = 12.7 min).

(*R*)-Linalyl-benzyl sulfide 29-A



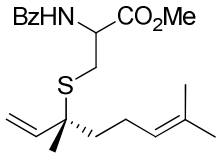
colourless oil; $[a]^{20}_D$ +11.7° (c = 0.4, $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 5*H*), 5.88 (dd, *J* = 17.3, 10.7 Hz, 1*H*), 5.14 (dd, *J* = 10.4, 0.8 Hz, 1*H*), 5.11 – 5.02 (m, 1*H*), 5.01 (dd, *J* = 17.7, 0.8 Hz, 1*H*), 3.57 (d, *J* = 2.3 Hz, 2*H*), 2.19 – 1.91 (m, 2*H*), 1.67 (s, 3*H*), 1.66 – 1.58 (m, 2*H*), 1.59 (s, 3*H*), 1.38 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz,

$CDCl_3$) δ 143.5, 138.4, 132.1, 129.1, 128.5, 126.7, 124.0, 112.5, 51.0, 40.2, 33.4, 25.7, 23.5, 23.2, 17.7 ppm; **IR** (Film) ν 2967 (m), 2923 (m), 1629 (w), 1495 (m), 1453(m), 1410 (w), 1374 (m), 1073 (w), 997 (w), 911 (m), 712 (s), 695 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 261 (27), 169 (3), 137 (100), 123 (1), 91 (13); **HRMS** (ESI-HR) calc'd for $C_{17}H_{24}SNa$: 283.1491, found: 283.1473; $\mathbf{R_f}$ 0.40 (petroleum ether).

ee) Allylic Substitution of (*R*)-28 with Bz-Cys-OMe

The product was obtained according to GP-I as a mixture of regio isomeres **30-A**/**30-B** 84:16 and a diastereomeric ratio of the branched product **30-A** 94:6. The product was isolated by column chromatography on silica (petroleum ether/ethyl acetate 5:1) in 65 % (242 mg) combined yield. The regioisomers were separated by means of semi-preparative HPLC (petroleum ether/ethyl acetate 10:1). The minor regioisomer **30-B** and the minor diastereomer were obtained as a mixture with the main diastereomer.

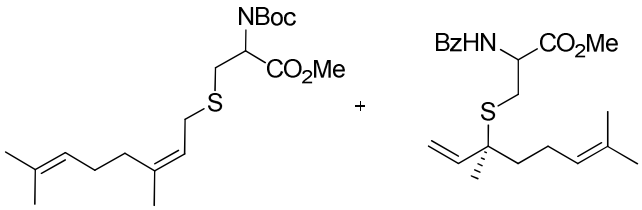
***Major isomer:* *N*-benzoyl-*R*-linalyl-*L*-cysteine methyl ester (*R*)-30-A**



colourless oil; $[\alpha]^{20}_D$ +6.2° (c = 1.2, $CHCl_3$); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7-87 – 7.78 (m, 2*H*), 7.57 – 7.41 (m, 3*H*), 6.88 (d, *J* = 7.4 Hz, 1*H*), 5.73 (dd, *J* = 17.3, 10.8 Hz, 1*H*), 5.07 (dd, *J* = 10.4, 0.7 Hz, 1*H*), 5.09 – 4.08 (m, 2*H*), 4.97 (dd, *J* = 17.2, 0.7 Hz, 1*H*), 3.79 (s, 3*H*), 2.99 (dd, *J* = 13.0, 4.9 Hz, 1*H*), 2.93 (dd, *J* =13.0, 5.1 Hz, 1*H*), 2.10 -1.89 (m, 2*H*), 1.67 (s, 3*H*), 1.63 – 1.55 (m, 2*H*), 1.58 (s, 3*H*), 1.33 (s, 3*H*) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 171.3, 166.9, 142.9, 133.8, 132.0, 131.9, 128.6, 127.1, 123.7, 113.1, 52.7, 52.0, 50.7, 40.2, 30.9, 25.7, 23.5, 23.2, 17.7 ppm; **IR** (Film) ν 2967 (w), 2926 (w), 2360 (w), 1743 (s), 1647 (s), 1519 (m), 1486 (m), 1437 (m), 1351 (m), 1266 (m), 1211 (s), 1177 (m), 1077 (w), 998 (w), 916 (w), 734 (s), 711 (s), 692 (s) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 398 (13), 260 (100), 242 (28), 228 (11), 215

(29), 202 (1), 144 (1), 110 (1); **HRMS** (ESI-HR) calc'd for $C_{21}H_{29}NO_3SNa$: 398.1760, found: 398.1759; $\mathbf{R_f}$ 0.26 (petroleum ether/ethyl acetate 5:1).

Mixture of *N-benzoyl* geranyl-*L*-cysteine methyl ester 47-B and *N*-benzoyl *S*-linalyl-*L*-cysteine methyl ester (*S*)-30-A



colourless oil; **^{1}H-NMR (minor diastereomer)** (300 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2*H*), 7.57 – 7.40 (m, 3*H*), 6.88 (d, *J* = 7.7 Hz, 1*H*), 5.72 (dd, *J* = 17.2, 10.6 Hz, 1*H*), 5.08 – 4.92 (m, 4 *H*), 3.79 (s, 3*H*), 2.99 (dd, *J* = 14.1, 6.0 Hz, 1*H*), 2.93 (dd, *J* = 13.0, 5.1 Hz, 1*H*) 2.15 – 1.87 (m, 2*H*), 1.69 – 1.54 (m, 8 *H*), 1.35 (s, 3*H*) ppm; **^{1}H-NMR (linear regioisomer)** (300 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2*H*), 7.57 – 7.40 (m, 3*H*), 6.95 (d, *J* = 7.3 Hz, 1 *H*), 5.24 – 5.15 (m, 1*H*), 5.07 – 4.98 (m, 2*H*), 3.81 (s, 3*H*), 3.28 – 2.99 (m, 4*H*), 2.13 – 1.89 (m, 2*H*), 1.71 – 1.54 (m, 10 *H*) ppm; **^{13}C-NMR** (mixture of isomeres) (63 MHz, $CDCl_3$) δ 171.5, 167.0, 140.2, 133.7, 131.9, 131.8, 128.6, 127.1, 123.8, 119.5, 52.7, 52.2, 39.6, 33.4, 30.1, 26.4, 25.7, 17.7, 16.1 ppm; **IR** (Film) ν 3329 (w), 2966 (w), 2922 (w), 1744 (s), 1645 (s), 1580 (w), 1529 (s), 1490 (m), 1439 (m), 1350 (m), 1212 (s), 1077 (w), 1027 (w), 999 (w), 916 (w), 802 (w), 712 (m), 692 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 398 (13), 355 (1), 260 (100), 242 (49), 228 (22), 215 (65), 202 (5), 180 (5), 144 (2), 110 (5); **HRMS** (ESI-HR) calc'd for $C_{21}H_{29}NO_3SNa$: 398.1760, found: 398.1757; $\mathbf{R_f}$ 0.26 (petroleum ether/ethyl acetate 5:1).

IV. References

[1] M. Holzwarth, A. Dieskau, M. Tabassam and B. Plietker, *Angew. Chem. Int. Ed.*, 2009, **48**, 7251.

[2] R. G. Bhattacharyya, M. Mallik and P. N. Ghosh, *Inorg. Chem. Acta*, 1990, **168**, 141.

[3] N. G. Connelly and C. Gardner, *J. Chem. Soc.* 1976, 1525.

[4] C.-Y. Chinag, M. L. Miller, J. H. Reibenspies and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2004, **126**, 10867.

[5] Y.-H. Ahn, J.-S. Lee and Y.-T. Chang, *J. Am. Chem. Soc.*, 2007, **129**, 4510.

[6] J. P. Casey and R. B. Martin, *J. Am. Chem. Soc.*, 1972, **94**, 6141.

[7] W. Voss, R. Guttmann and L. Klemm, *Biochem. Zeitschr.*, 1930, **327**, 340.

[8] S. Ranganathan and N. Jayaraman, *J. Chem. Soc., Chem. Commun.*, 1991, **14**, 934.

[9] E. J. Corey and M. M. Mehrotra, *Tetrahedron Lett.*, 1988, **29**, 57.

[10] H. Kwart and N. A. Johnson, *J. Am. Chem. Soc.*, 1977, **99**, 3441.

[11] J. F. Biellmann, J. B. Ducep and D. Schirlin, *Tetrahedron*, 1980, **36**, 1249.

[12] R. C. Cookson and P. R. Parsons, *J. Chem Soc., Chem. Commun.*, 1978, 822.

[13] A. B. Zaitsev, H. F. Caldwell, P. S. Pregosin and L. F. Veiros, *Chem. Eur. J.*, 2009, **15**, 6468.

[14] C. Goux, P. Lhotse and D. Sinou, *Tetrahedron Lett.*, 1992, **33**, 8099.

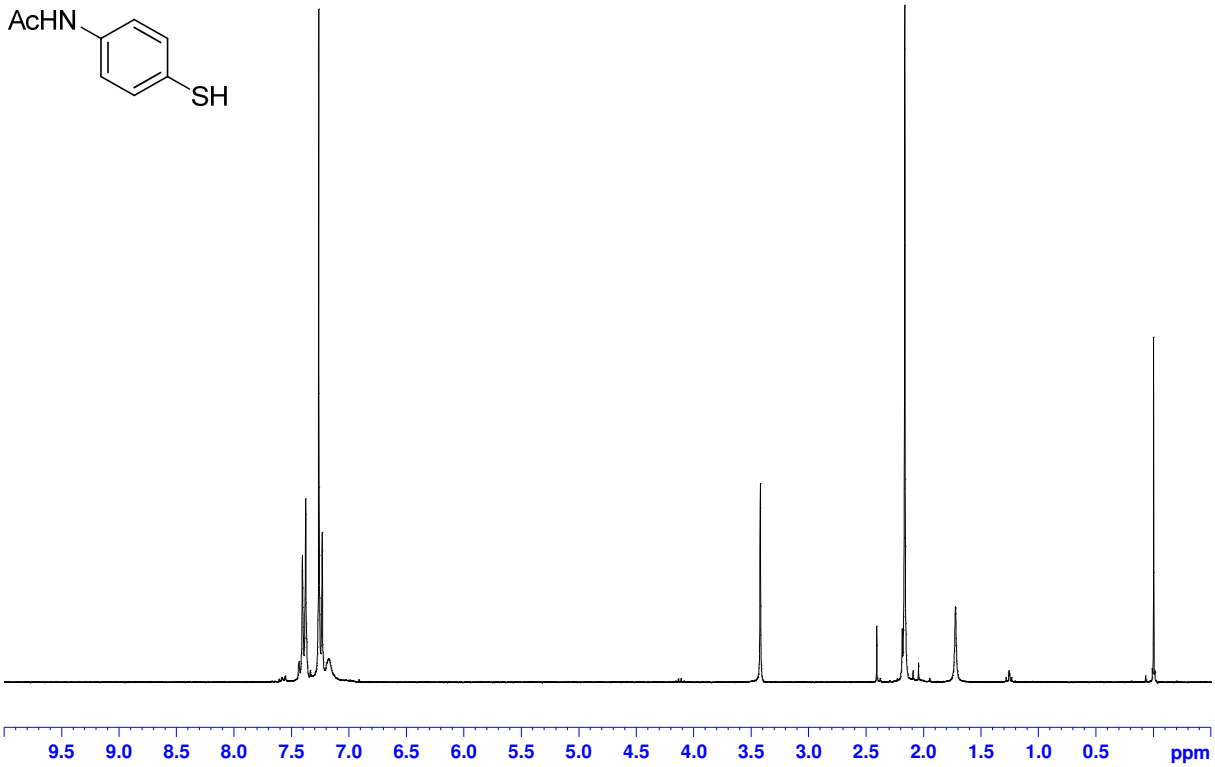
[15] G. A. Russell and L. L. Herold, *J. Org. Chem.*, 1985, **50**, 1037.

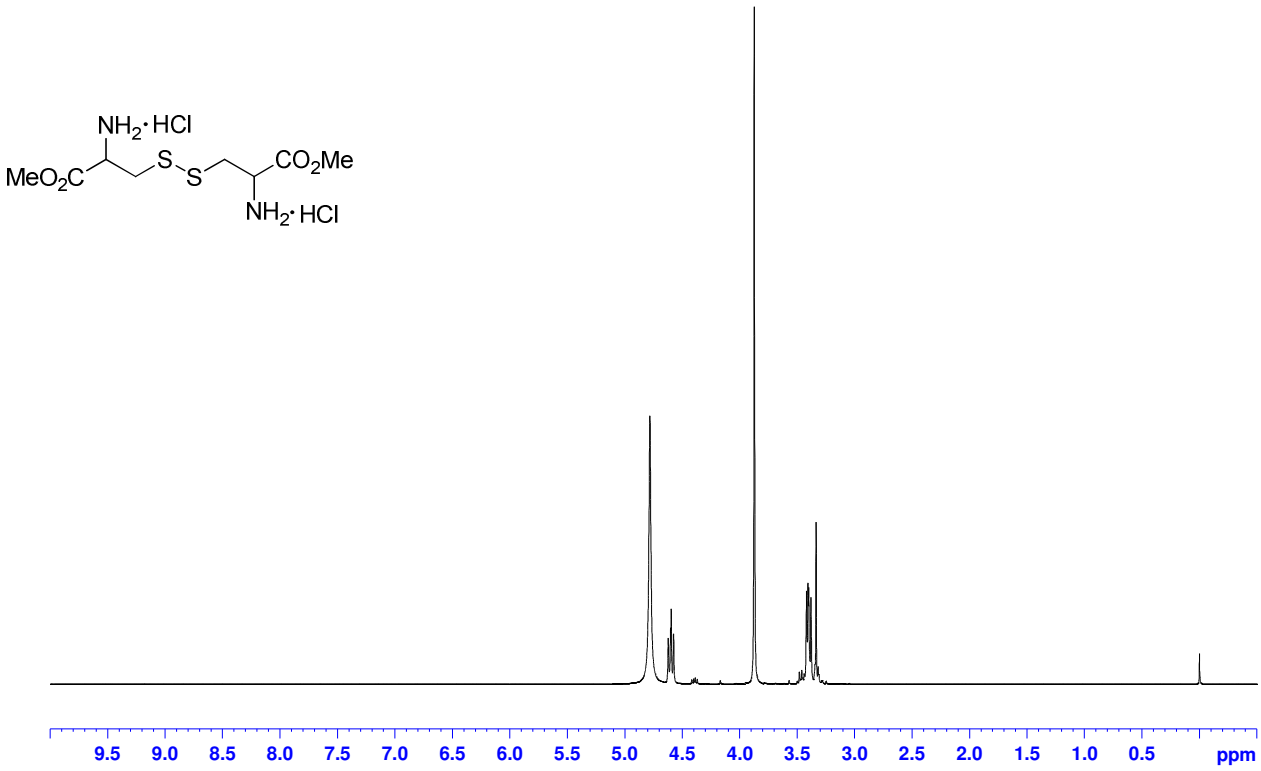
[16] J. B. Jones and D. W. Hysert, *Can. J. Chem.*, 1971, **49**, 325.

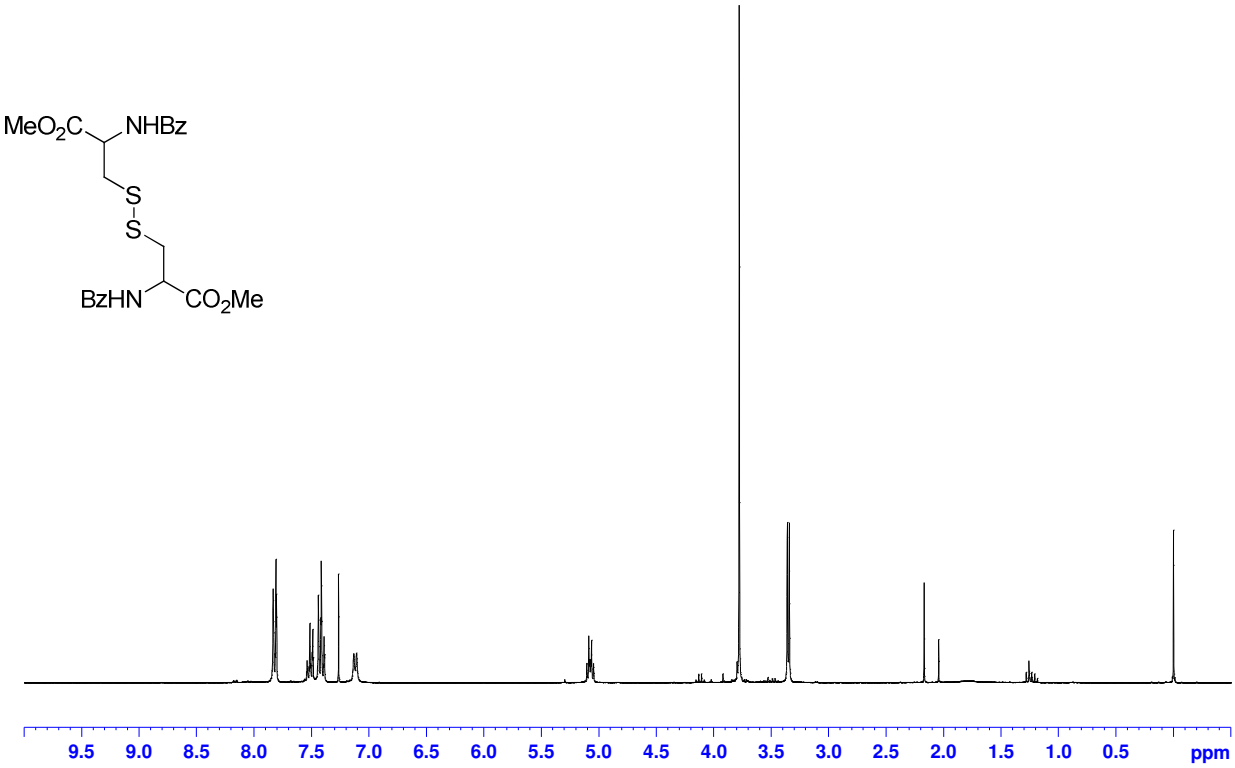
[17] K. L. Greenman, D. S. Carter and D. L. van Vranken, *Tetrahedron*, 2001, **57**, 5219.

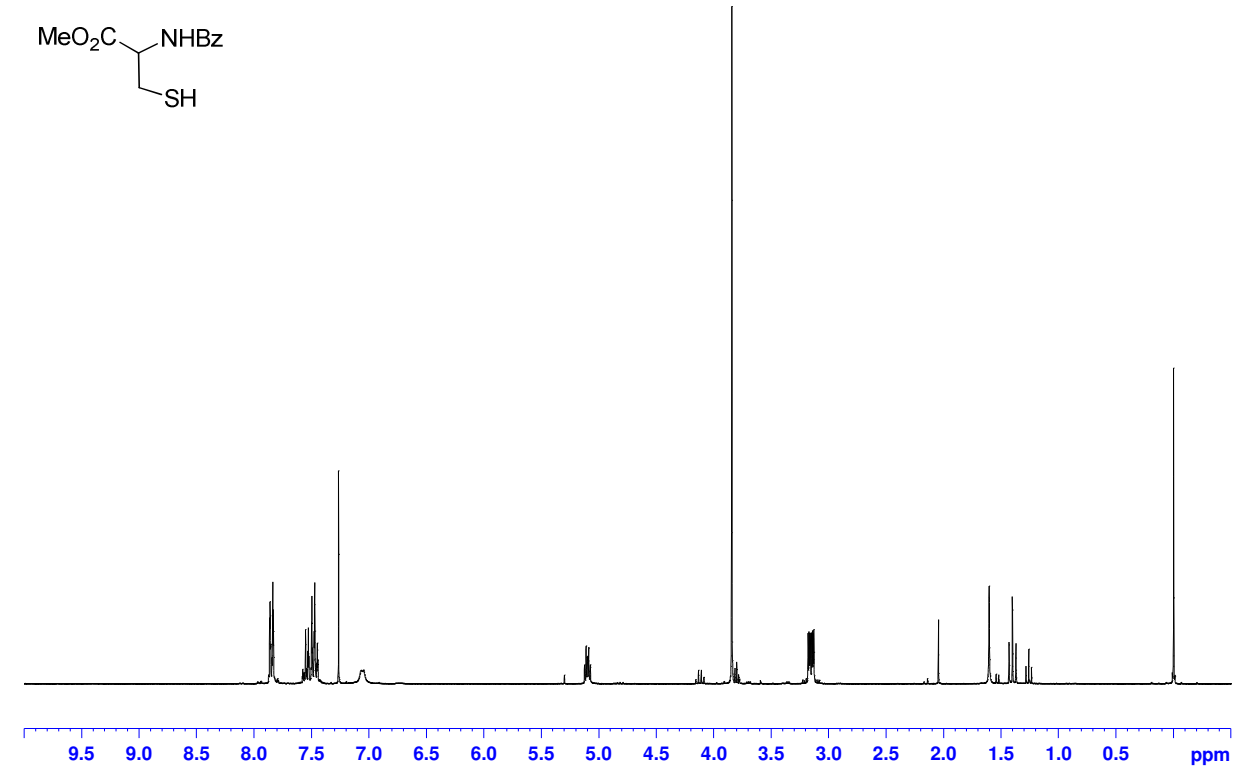
[18] T. Mukaiyama, T. Masui, T. and Izawa, *Chem. Lett.*, 1976, **5**, 1177.

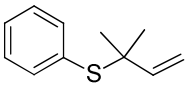
V. Spectra


AcHN
SH
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

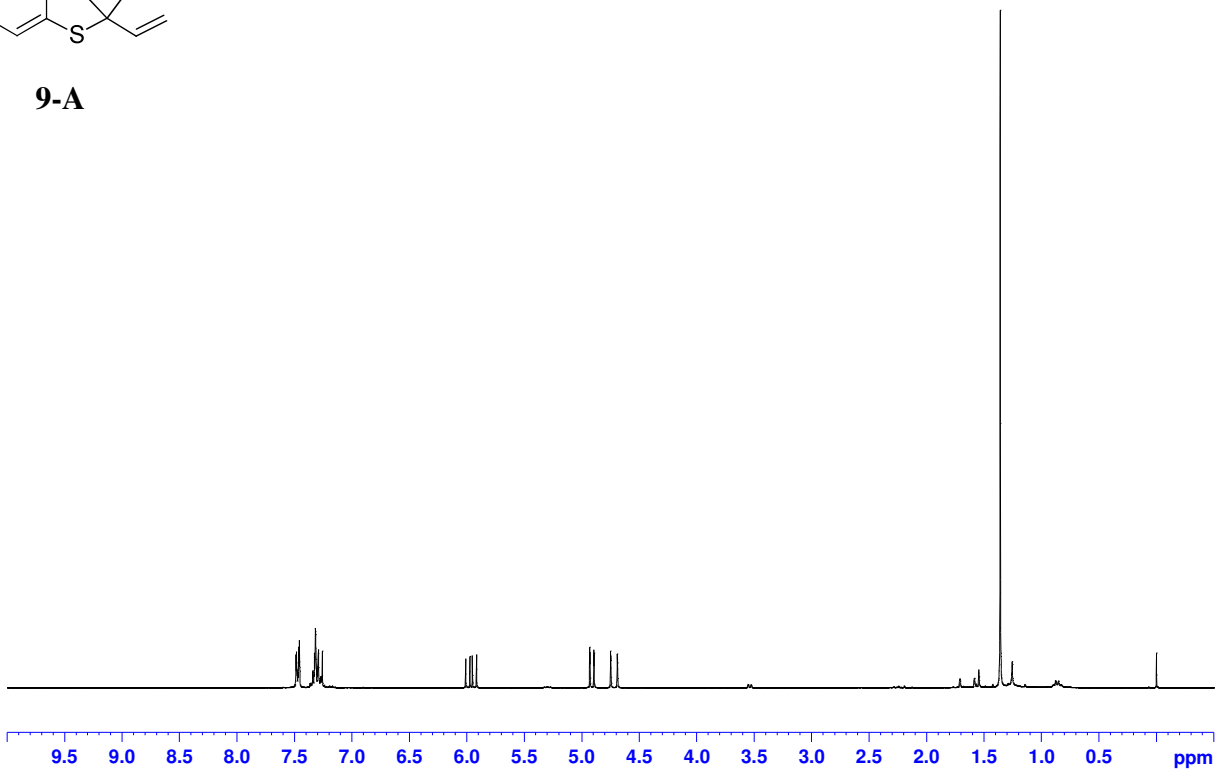

NH2· HCl
MeO2C
S
S
CO2Me
NH2· HCl
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

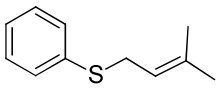






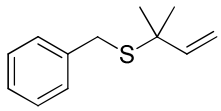
9-A


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



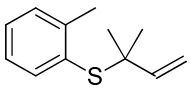
9-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



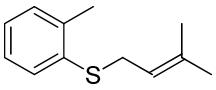
3-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



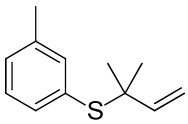
12-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



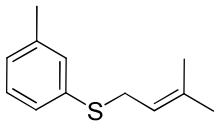
12-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



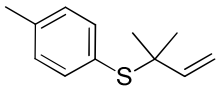
11-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



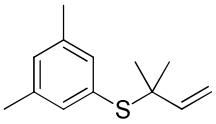
11-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



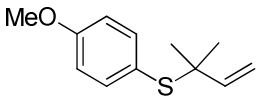
10-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



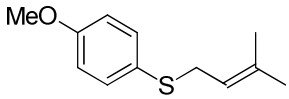
20-A

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


MeO

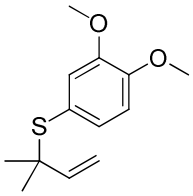
13-A

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


MeO
S

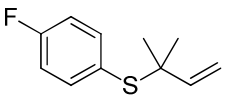
13-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

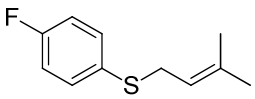

O
O
S

14-A

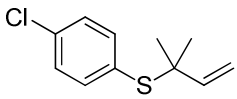
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



18-A

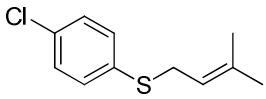


18-B


Cl
S

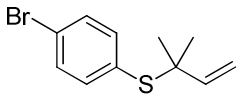
17-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

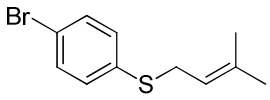

Cl
S

17-B

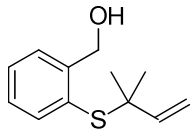
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



16-A

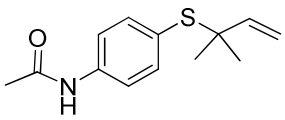


16-B


OH
S

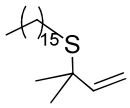
15-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


O
N
H
S

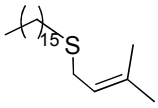
19-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



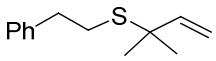
23-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

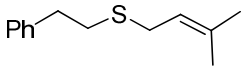


23-B

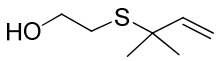
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



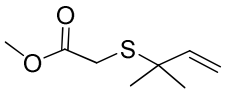
24-A



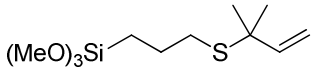
24-B



25-A

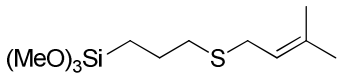


26-A


(MeO)3Si
S

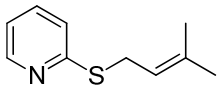
27-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


(MeO)3Si
S

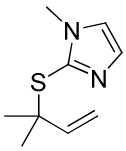
27-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


N
S

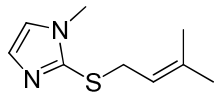
21-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


N
S
N

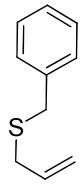
22-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



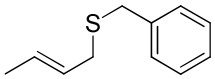
22-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



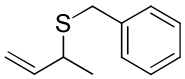
31

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



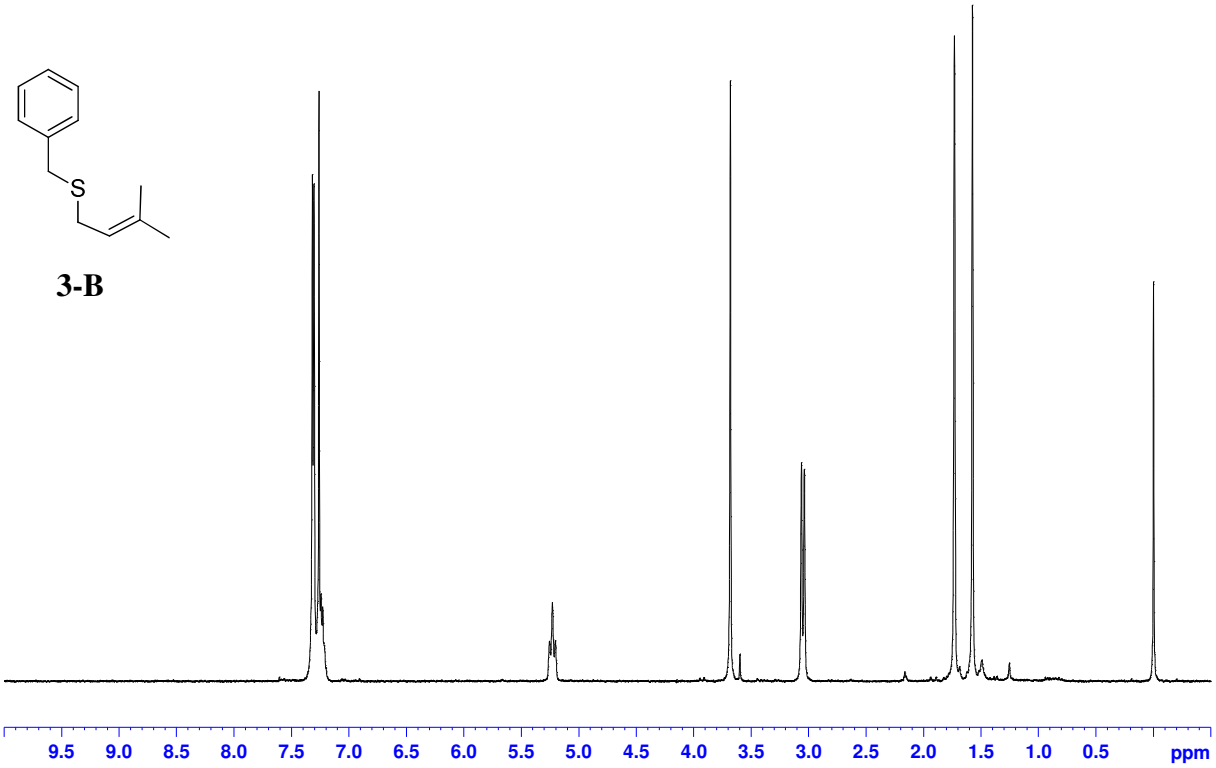
32-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

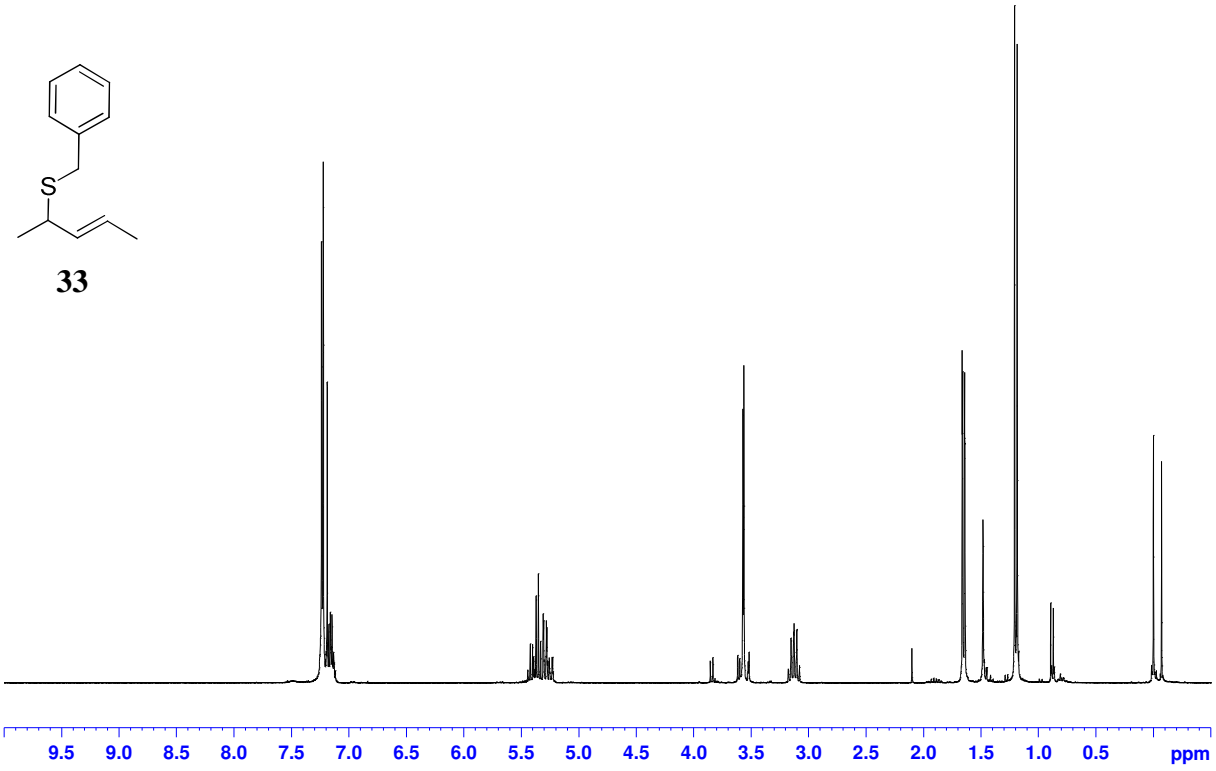


32-B

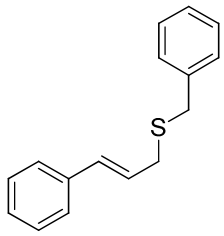
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



3-B

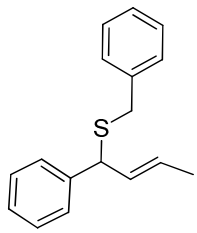


33


S

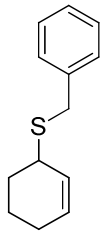
34-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


S

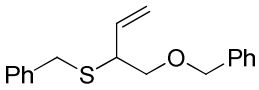
35-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



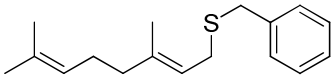
36

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



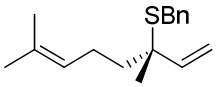
37-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


S

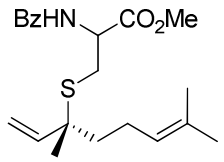
29-B

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


SBn

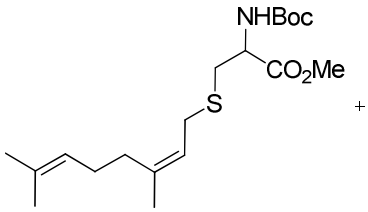
29-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

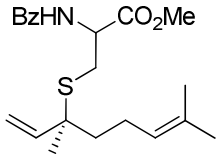

BzHN
CO2Me
S

30-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


NHBoc
CO2Me
S

30-B


BzHN
CO2Me
S

30-A

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

VI. X-Ray

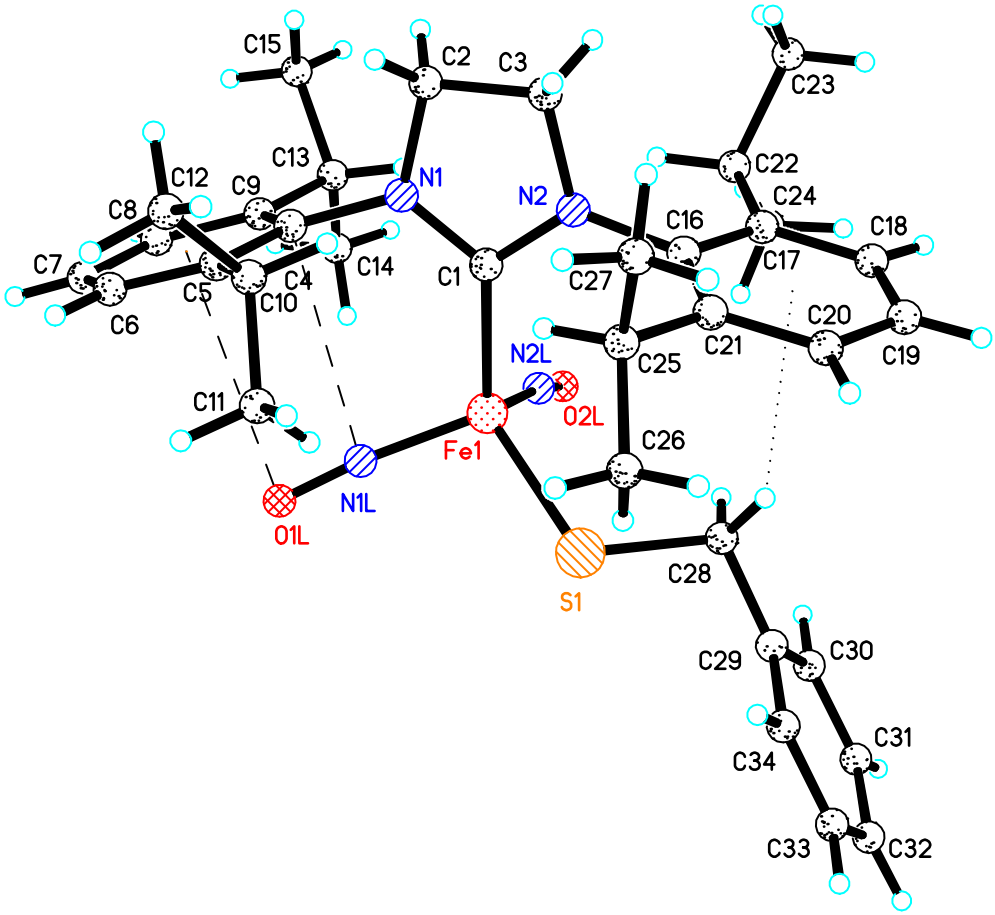


Table 1. Crystal data and structure refinement for s1756rm1.

Identification code	s1756rm1
Empirical formula	C34 H45 Fe N4 O2 S
Formula weight	629.65
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P2(1)/c
Unit cell dimensions	a = 16.974(4) A alpha = 90 deg. b = 12.877(3) A beta = 107.83(2) deg.

c = 16.927(5) A gamma = 90 deg.

Volume	3522.2(16) A^3
Z, Calculated density	4, 1.187 Mg/m^3
Absorption coefficient	0.521 mm^-1
F(000)	1340
Crystal size	0.3 x 0.3 x 0.2 mm
Theta range for data collection	2.02 to 25.00 deg.
Limiting indices	-20<=h<=19, -15<=k<=0, 0<=l<=20
Reflections collected / unique	6437 / 6204 [R(int) = 0.0370]
Completeness to theta = 25.00	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6204 / 0 / 387
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0842, wR2 = 0.1678
R indices (all data)	R1 = 0.1645, wR2 = 0.1950
Largest diff. peak and hole	0.478 and -0.342 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s1756rm1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	2776(1)	2626(1)	6686(1)	53(1)
N(1L)	3678(3)	3060(4)	7341(3)	68(2)
O(1L)	4227(3)	3365(5)	7867(3)	107(2)
N(2L)	1911(4)	3140(5)	6754(4)	87(2)
O(2L)	1368(4)	3522(7)	6956(5)	155(3)
N(1)	3184(3)	3752(3)	5287(3)	46(1)
C(1)	2799(3)	2952(4)	5499(3)	42(1)
C(2)	3000(4)	3908(5)	4391(3)	56(2)
N(2)	2361(3)	2487(4)	4785(2)	48(1)
C(3)	2472(4)	2987(5)	4044(3)	64(2)
C(4)	3817(3)	4369(4)	5864(3)	44(1)
C(5)	4644(3)	4054(4)	6052(4)	53(1)
C(6)	5231(4)	4680(5)	6590(4)	72(2)
C(7)	5029(5)	5548(6)	6928(5)	86(2)
C(8)	4218(4)	5859(6)	6731(4)	78(2)
C(9)	3589(4)	5272(5)	6193(3)	54(2)
C(10)	4891(4)	3097(5)	5686(4)	63(2)
C(11)	5191(6)	2260(7)	6337(6)	122(4)
C(12)	5533(6)	3302(6)	5250(6)	114(3)
C(13)	2700(4)	5629(6)	5991(4)	70(2)
C(14)	2459(5)	5807(7)	6766(6)	110(3)
C(15)	2574(6)	6639(7)	5495(7)	125(4)
C(16)	1878(4)	1560(5)	4695(3)	56(2)
C(17)	1019(4)	1677(6)	4514(4)	70(2)
C(18)	551(5)	761(7)	4354(5)	96(3)
C(19)	910(6)	-170(7)	4374(5)	103(3)
C(20)	1762(6)	-276(6)	4571(5)	92(3)
C(21)	2257(4)	607(5)	4722(4)	66(2)
C(22)	599(4)	2711(6)	4466(5)	86(2)
C(23)	86(6)	2936(8)	3556(6)	127(4)
C(24)	24(5)	2767(8)	5018(7)	120(3)
C(25)	3178(5)	471(6)	4894(6)	93(3)
C(26)	3566(6)	-368(8)	5509(7)	128(4)
C(27)	3367(8)	260(10)	4087(8)	174(6)
S(1)	2782(1)	983(1)	7082(1)	68(1)
C(28)	1717(4)	485(6)	6725(5)	89(3)
C(29)	1583(4)	-317(5)	7310(4)	62(2)
C(30)	970(5)	-186(6)	7657(5)	84(2)
C(31)	817(6)	-914(9)	8189(6)	108(3)
C(32)	1272(7)	-1773(9)	8363(6)	116(3)

C(33)	1897(7)	-1922(7)	8027(6)	105(3)
C(34)	2048(5)	-1198(6)	7493(5)	85(2)

Table 3. Bond lengths [A] and angles [deg] for s1756rm1.

Fe(1)-N(2L)	1.646(6)
Fe(1)-N(1L)	1.688(5)
Fe(1)-C(1)	2.065(5)
Fe(1)-S(1)	2.219(2)
N(1L)-O(1L)	1.144(6)
N(2L)-O(2L)	1.183(7)
N(1)-C(1)	1.327(6)
N(1)-C(4)	1.448(6)
N(1)-C(2)	1.466(6)
C(1)-N(2)	1.349(6)
C(2)-C(3)	1.493(7)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
N(2)-C(16)	1.430(7)
N(2)-C(3)	1.473(7)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(9)	1.394(8)
C(4)-C(5)	1.400(7)
C(5)-C(6)	1.385(8)
C(5)-C(10)	1.496(8)
C(6)-C(7)	1.348(9)
C(6)-H(6)	0.9300
C(7)-C(8)	1.372(9)
C(7)-H(7)	0.9300
C(8)-C(9)	1.395(8)
C(8)-H(8)	0.9300
C(9)-C(13)	1.512(8)
C(10)-C(12)	1.514(9)
C(10)-C(11)	1.515(9)
C(10)-H(10)	0.9800
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.505(10)
C(13)-C(15)	1.527(10)
C(13)-H(13)	0.9800
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(21)	1.380(9)

C(16)-C(17)	1.403(9)
C(17)-C(18)	1.401(9)
C(17)-C(22)	1.501(10)
C(18)-C(19)	1.341(11)
C(18)-H(18)	0.9300
C(19)-C(20)	1.388(12)
C(19)-H(19)	0.9300
C(20)-C(21)	1.391(9)
C(20)-H(20)	0.9300
C(21)-C(25)	1.510(10)
C(22)-C(24)	1.546(11)
C(22)-C(23)	1.547(11)
C(22)-H(22)	0.9800
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-C(26)	1.504(11)
C(25)-C(27)	1.521(13)
C(25)-H(25)	0.9800
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
S(1)-C(28)	1.837(7)
C(28)-C(29)	1.495(9)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-C(30)	1.354(10)
C(29)-C(34)	1.363(10)
C(30)-C(31)	1.377(11)
C(30)-H(30)	0.9300
C(31)-C(32)	1.329(12)
C(31)-H(31)	0.9300
C(32)-C(33)	1.361(13)
C(32)-H(32)	0.9300
C(33)-C(34)	1.377(11)
C(33)-H(33)	0.9300
C(34)-H(34)	0.9300

N(2L)-Fe(1)-N(1L)	118.1(3)
N(2L)-Fe(1)-C(1)	105.6(3)
N(1L)-Fe(1)-C(1)	106.8(2)
N(2L)-Fe(1)-S(1)	106.5(2)
N(1L)-Fe(1)-S(1)	101.4(2)
C(1)-Fe(1)-S(1)	119.19(16)
O(1L)-N(1L)-Fe(1)	170.0(6)

O(2L)-N(2L)-Fe(1)	167.7(7)
C(1)-N(1)-C(4)	124.6(4)
C(1)-N(1)-C(2)	114.8(4)
C(4)-N(1)-C(2)	120.2(4)
N(1)-C(1)-N(2)	106.5(4)
N(1)-C(1)-Fe(1)	125.4(4)
N(2)-C(1)-Fe(1)	127.7(4)
N(1)-C(2)-C(3)	102.1(4)
N(1)-C(2)-H(2A)	111.3
C(3)-C(2)-H(2A)	111.3
N(1)-C(2)-H(2B)	111.3
C(3)-C(2)-H(2B)	111.3
H(2A)-C(2)-H(2B)	109.2
C(1)-N(2)-C(16)	127.3(4)
C(1)-N(2)-C(3)	112.9(4)
C(16)-N(2)-C(3)	119.6(4)
N(2)-C(3)-C(2)	103.3(4)
N(2)-C(3)-H(3A)	111.1
C(2)-C(3)-H(3A)	111.1
N(2)-C(3)-H(3B)	111.1
C(2)-C(3)-H(3B)	111.1
H(3A)-C(3)-H(3B)	109.1
C(9)-C(4)-C(5)	122.2(5)
C(9)-C(4)-N(1)	119.2(5)
C(5)-C(4)-N(1)	118.6(5)
C(6)-C(5)-C(4)	116.8(6)
C(6)-C(5)-C(10)	121.0(6)
C(4)-C(5)-C(10)	122.2(5)
C(7)-C(6)-C(5)	122.4(6)
C(7)-C(6)-H(6)	118.8
C(5)-C(6)-H(6)	118.8
C(6)-C(7)-C(8)	120.4(6)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(7)-C(8)-C(9)	120.7(6)
C(7)-C(8)-H(8)	119.6
C(9)-C(8)-H(8)	119.6
C(4)-C(9)-C(8)	117.5(6)
C(4)-C(9)-C(13)	122.9(5)
C(8)-C(9)-C(13)	119.6(6)
C(5)-C(10)-C(12)	113.2(6)
C(5)-C(10)-C(11)	111.1(6)
C(12)-C(10)-C(11)	110.2(7)
C(5)-C(10)-H(10)	107.4
C(12)-C(10)-H(10)	107.4
C(11)-C(10)-H(10)	107.4
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5

H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(9)	111.5(6)
C(14)-C(13)-C(15)	108.7(7)
C(9)-C(13)-C(15)	110.3(6)
C(14)-C(13)-H(13)	108.8
C(9)-C(13)-H(13)	108.8
C(15)-C(13)-H(13)	108.8
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(21)-C(16)-C(17)	123.1(6)
C(21)-C(16)-N(2)	119.4(6)
C(17)-C(16)-N(2)	117.3(6)
C(18)-C(17)-C(16)	116.2(7)
C(18)-C(17)-C(22)	120.3(7)
C(16)-C(17)-C(22)	123.4(6)
C(19)-C(18)-C(17)	121.4(8)
C(19)-C(18)-H(18)	119.3
C(17)-C(18)-H(18)	119.3
C(18)-C(19)-C(20)	121.8(8)
C(18)-C(19)-H(19)	119.1
C(20)-C(19)-H(19)	119.1
C(19)-C(20)-C(21)	119.4(8)
C(19)-C(20)-H(20)	120.3
C(21)-C(20)-H(20)	120.3
C(16)-C(21)-C(20)	118.1(7)
C(16)-C(21)-C(25)	123.7(6)
C(20)-C(21)-C(25)	118.2(7)
C(17)-C(22)-C(24)	112.6(7)
C(17)-C(22)-C(23)	109.5(7)
C(24)-C(22)-C(23)	109.0(7)
C(17)-C(22)-H(22)	108.5
C(24)-C(22)-H(22)	108.5
C(23)-C(22)-H(22)	108.5
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5

H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-C(21)	115.1(7)
C(26)-C(25)-C(27)	109.1(8)
C(21)-C(25)-C(27)	109.7(8)
C(26)-C(25)-H(25)	107.6
C(21)-C(25)-H(25)	107.6
C(27)-C(25)-H(25)	107.6
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(28)-S(1)-Fe(1)	108.7(3)
C(29)-C(28)-S(1)	110.9(5)
C(29)-C(28)-H(28A)	109.5
S(1)-C(28)-H(28A)	109.5
C(29)-C(28)-H(28B)	109.5
S(1)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	108.1
C(30)-C(29)-C(34)	118.3(7)
C(30)-C(29)-C(28)	119.6(7)
C(34)-C(29)-C(28)	122.1(7)
C(29)-C(30)-C(31)	121.5(8)
C(29)-C(30)-H(30)	119.2
C(31)-C(30)-H(30)	119.2
C(32)-C(31)-C(30)	119.9(9)
C(32)-C(31)-H(31)	120.1
C(30)-C(31)-H(31)	120.1
C(31)-C(32)-C(33)	119.9(9)
C(31)-C(32)-H(32)	120.0
C(33)-C(32)-H(32)	120.0
C(32)-C(33)-C(34)	120.3(9)
C(32)-C(33)-H(33)	119.8
C(34)-C(33)-H(33)	119.8
C(29)-C(34)-C(33)	120.1(8)

C(29)-C(34)-H(34)	120.0
C(33)-C(34)-H(34)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s1756rm1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	46(1)	69(1)	45(1)	6(1)	13(1)	-2(1)
N(1L)	59(3)	87(4)	51(3)	-6(3)	5(3)	-14(3)
O(1L)	79(4)	150(5)	71(3)	-18(3)	-9(3)	-17(4)
N(2L)	66(4)	123(5)	81(4)	-3(4)	36(3)	10(4)
O(2L)	90(5)	213(8)	181(7)	-38(6)	67(5)	30(5)
N(1)	42(3)	50(3)	41(2)	3(2)	7(2)	-8(2)
C(1)	35(3)	50(3)	41(3)	-2(2)	9(2)	-2(2)
C(2)	61(4)	56(4)	45(3)	8(3)	4(3)	-16(3)
N(2)	51(2)	47(3)	41(2)	0(2)	9(2)	-15(2)
C(3)	75(4)	70(4)	41(3)	-7(3)	11(3)	-30(3)
C(4)	41(3)	43(3)	43(3)	-4(2)	8(2)	-11(2)
C(5)	41(3)	54(4)	58(3)	10(3)	7(3)	1(3)
C(6)	37(3)	71(5)	92(5)	-2(4)	-5(3)	-3(3)
C(7)	64(5)	89(6)	83(5)	-31(4)	-12(4)	-13(4)
C(8)	67(5)	73(5)	79(5)	-26(4)	-1(4)	-3(4)
C(9)	47(3)	58(4)	52(3)	-10(3)	6(3)	-4(3)
C(10)	49(3)	60(4)	79(4)	10(3)	18(3)	5(3)
C(11)	152(9)	92(6)	138(8)	52(6)	68(7)	55(6)
C(12)	141(8)	86(6)	151(9)	1(6)	98(7)	11(6)
C(13)	54(4)	72(5)	87(5)	-14(4)	25(4)	7(3)
C(14)	101(7)	113(7)	131(8)	-2(6)	55(6)	32(6)
C(15)	80(6)	126(8)	162(10)	46(7)	27(6)	32(6)
C(16)	66(4)	52(4)	49(3)	-10(3)	17(3)	-21(3)
C(17)	58(4)	84(5)	58(4)	3(3)	2(3)	-28(4)
C(18)	66(5)	108(7)	97(6)	-1(5)	2(4)	-47(5)
C(19)	109(8)	81(6)	108(7)	-7(5)	15(6)	-54(6)
C(20)	132(8)	53(4)	98(6)	-16(4)	44(6)	-22(5)
C(21)	81(5)	49(4)	70(4)	-13(3)	26(4)	-21(4)
C(22)	55(4)	91(6)	97(6)	8(5)	0(4)	-15(4)
C(23)	84(6)	151(9)	129(8)	47(7)	9(6)	-8(6)
C(24)	76(5)	144(9)	145(8)	10(7)	41(6)	11(6)
C(25)	95(6)	64(5)	133(8)	-9(5)	55(6)	0(4)
C(26)	117(8)	116(8)	153(9)	18(7)	42(7)	43(7)
C(27)	192(13)	180(12)	194(13)	73(10)	126(11)	59(10)
S(1)	49(1)	78(1)	70(1)	22(1)	6(1)	-6(1)
C(28)	57(4)	113(6)	80(5)	32(5)	-4(4)	-26(4)
C(29)	59(4)	71(4)	51(3)	-5(3)	10(3)	-17(3)
C(30)	84(5)	80(5)	87(5)	-7(4)	23(4)	-9(4)
C(31)	106(7)	134(9)	97(7)	2(6)	51(6)	-20(7)
C(32)	130(9)	114(8)	105(7)	28(6)	40(7)	-27(7)
C(33)	122(8)	80(6)	102(7)	18(5)	18(6)	-4(6)

C(34)	79(5)	84(6)	94(6)	2(5)	27(4)	-3(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s1756rm1.

	x	y	z	U(eq)
H(2A)	3501	3910	4229	67
H(2B)	2702	4552	4213	67
H(3A)	1945	3199	3660	76
H(3B)	2747	2525	3760	76
H(6)	5786	4494	6723	87
H(7)	5440	5939	7297	103
H(8)	4087	6469	6957	94
H(10)	4395	2831	5269	76
H(11A)	5689	2488	6747	183
H(11B)	5302	1636	6079	183
H(11C)	4773	2124	6598	183
H(12A)	5370	3894	4893	171
H(12B)	5578	2705	4926	171
H(12C)	6059	3435	5656	171
H(13)	2338	5094	5656	84
H(14A)	2630	5223	7131	166
H(14B)	1870	5886	6621	166
H(14C)	2725	6424	7039	166
H(15A)	2921	7171	5820	188
H(15B)	2005	6848	5358	188
H(15C)	2715	6532	4994	188
H(18)	-21	801	4231	115
H(19)	579	-760	4252	124
H(20)	1999	-932	4602	111
H(22)	1025	3249	4648	103
H(23A)	426	2838	3202	190
H(23B)	-111	3639	3509	190
H(23C)	-377	2469	3391	190
H(24A)	-430	2294	4811	180
H(24B)	-186	3461	5009	180
H(24C)	330	2581	5577	180
H(25)	3444	1129	5117	111
H(26A)	3410	-273	6004	193
H(26B)	4157	-331	5644	193
H(26C)	3377	-1034	5272	193
H(27A)	3220	-443	3915	261
H(27B)	3946	362	4169	261
H(27C)	3052	727	3666	261
H(28A)	1332	1055	6685	106
H(28B)	1608	183	6177	106
H(30)	644	408	7534	101
H(31)	397	-804	8426	130

H(32)	1164	-2271	8714	139
H(33)	2222	-2516	8159	126
H(34)	2469	-1311	7257	102

Table 6. Torsion angles [deg] for s1756rm1.

N(2L)-Fe(1)-N(1L)-O(1L)	36(4)
C(1)-Fe(1)-N(1L)-O(1L)	154(4)
S(1)-Fe(1)-N(1L)-O(1L)	-80(4)
N(1L)-Fe(1)-N(2L)-O(2L)	-33(4)
C(1)-Fe(1)-N(2L)-O(2L)	-153(3)
S(1)-Fe(1)-N(2L)-O(2L)	80(4)
C(4)-N(1)-C(1)-N(2)	-170.3(5)
C(2)-N(1)-C(1)-N(2)	2.5(6)
C(4)-N(1)-C(1)-Fe(1)	16.5(7)
C(2)-N(1)-C(1)-Fe(1)	-170.7(4)
N(2L)-Fe(1)-C(1)-N(1)	95.5(5)
N(1L)-Fe(1)-C(1)-N(1)	-31.0(5)
S(1)-Fe(1)-C(1)-N(1)	-144.9(4)
N(2L)-Fe(1)-C(1)-N(2)	-76.2(5)
N(1L)-Fe(1)-C(1)-N(2)	157.3(5)
S(1)-Fe(1)-C(1)-N(2)	43.4(5)
C(1)-N(1)-C(2)-C(3)	-5.1(7)
C(4)-N(1)-C(2)-C(3)	168.0(5)
N(1)-C(1)-N(2)-C(16)	176.6(5)
Fe(1)-C(1)-N(2)-C(16)	-10.4(8)
N(1)-C(1)-N(2)-C(3)	1.4(6)
Fe(1)-C(1)-N(2)-C(3)	174.4(4)
C(1)-N(2)-C(3)-C(2)	-4.5(7)
C(16)-N(2)-C(3)-C(2)	179.9(5)
N(1)-C(2)-C(3)-N(2)	5.3(6)
C(1)-N(1)-C(4)-C(9)	-93.3(7)
C(2)-N(1)-C(4)-C(9)	94.2(6)
C(1)-N(1)-C(4)-C(5)	88.9(7)
C(2)-N(1)-C(4)-C(5)	-83.6(7)
C(9)-C(4)-C(5)-C(6)	0.6(9)
N(1)-C(4)-C(5)-C(6)	178.4(5)
C(9)-C(4)-C(5)-C(10)	-178.7(5)
N(1)-C(4)-C(5)-C(10)	-1.0(8)
C(4)-C(5)-C(6)-C(7)	0.4(10)
C(10)-C(5)-C(6)-C(7)	179.8(7)
C(5)-C(6)-C(7)-C(8)	-1.5(13)
C(6)-C(7)-C(8)-C(9)	1.5(13)
C(5)-C(4)-C(9)-C(8)	-0.6(9)
N(1)-C(4)-C(9)-C(8)	-178.3(6)
C(5)-C(4)-C(9)-C(13)	179.4(6)
N(1)-C(4)-C(9)-C(13)	1.6(8)
C(7)-C(8)-C(9)-C(4)	-0.5(11)
C(7)-C(8)-C(9)-C(13)	179.6(7)
C(6)-C(5)-C(10)-C(12)	-53.9(9)
C(4)-C(5)-C(10)-C(12)	125.4(7)
C(6)-C(5)-C(10)-C(11)	70.7(8)
C(4)-C(5)-C(10)-C(11)	-110.0(7)

C(4)-C(9)-C(13)-C(14)	125.9(7)
C(8)-C(9)-C(13)-C(14)	-54.2(9)
C(4)-C(9)-C(13)-C(15)	-113.3(7)
C(8)-C(9)-C(13)-C(15)	66.6(9)
C(1)-N(2)-C(16)-C(21)	-85.3(7)
C(3)-N(2)-C(16)-C(21)	89.6(7)
C(1)-N(2)-C(16)-C(17)	99.8(7)
C(3)-N(2)-C(16)-C(17)	-85.3(7)
C(21)-C(16)-C(17)-C(18)	-0.3(10)
N(2)-C(16)-C(17)-C(18)	174.3(6)
C(21)-C(16)-C(17)-C(22)	-178.6(6)
N(2)-C(16)-C(17)-C(22)	-4.0(9)
C(16)-C(17)-C(18)-C(19)	0.0(12)
C(22)-C(17)-C(18)-C(19)	178.4(8)
C(17)-C(18)-C(19)-C(20)	1.4(14)
C(18)-C(19)-C(20)-C(21)	-2.5(14)
C(17)-C(16)-C(21)-C(20)	-0.7(10)
N(2)-C(16)-C(21)-C(20)	-175.3(6)
C(17)-C(16)-C(21)-C(25)	178.3(7)
N(2)-C(16)-C(21)-C(25)	3.8(10)
C(19)-C(20)-C(21)-C(16)	2.1(11)
C(19)-C(20)-C(21)-C(25)	-177.0(8)
C(18)-C(17)-C(22)-C(24)	54.4(10)
C(16)-C(17)-C(22)-C(24)	-127.3(7)
C(18)-C(17)-C(22)-C(23)	-67.1(9)
C(16)-C(17)-C(22)-C(23)	111.2(7)
C(16)-C(21)-C(25)-C(26)	134.3(8)
C(20)-C(21)-C(25)-C(26)	-46.6(10)
C(16)-C(21)-C(25)-C(27)	-102.2(9)
C(20)-C(21)-C(25)-C(27)	76.8(10)
N(2L)-Fe(1)-S(1)-C(28)	35.8(4)
N(1L)-Fe(1)-S(1)-C(28)	159.9(3)
C(1)-Fe(1)-S(1)-C(28)	-83.4(3)
Fe(1)-S(1)-C(28)-C(29)	-148.8(5)
S(1)-C(28)-C(29)-C(30)	123.5(6)
S(1)-C(28)-C(29)-C(34)	-58.2(9)
C(34)-C(29)-C(30)-C(31)	0.6(11)
C(28)-C(29)-C(30)-C(31)	178.9(7)
C(29)-C(30)-C(31)-C(32)	-0.7(14)
C(30)-C(31)-C(32)-C(33)	1.2(16)
C(31)-C(32)-C(33)-C(34)	-1.4(16)
C(30)-C(29)-C(34)-C(33)	-0.8(11)
C(28)-C(29)-C(34)-C(33)	-179.2(7)
C(32)-C(33)-C(34)-C(29)	1.3(14)

Symmetry transformations used to generate equivalent atoms:

VII. Chromatograms

Data File C:\HPCHEM\2\DATA\MH\MH111391.D

Sample Name: MH11-139H2a

Chiracel OJ, 1.0 ml/min, 99 : 1, 4 µl

Injection Date : 07.08.10 17:34:26
Sample Name : MH11-139H2a
Acq. Operator : Micha

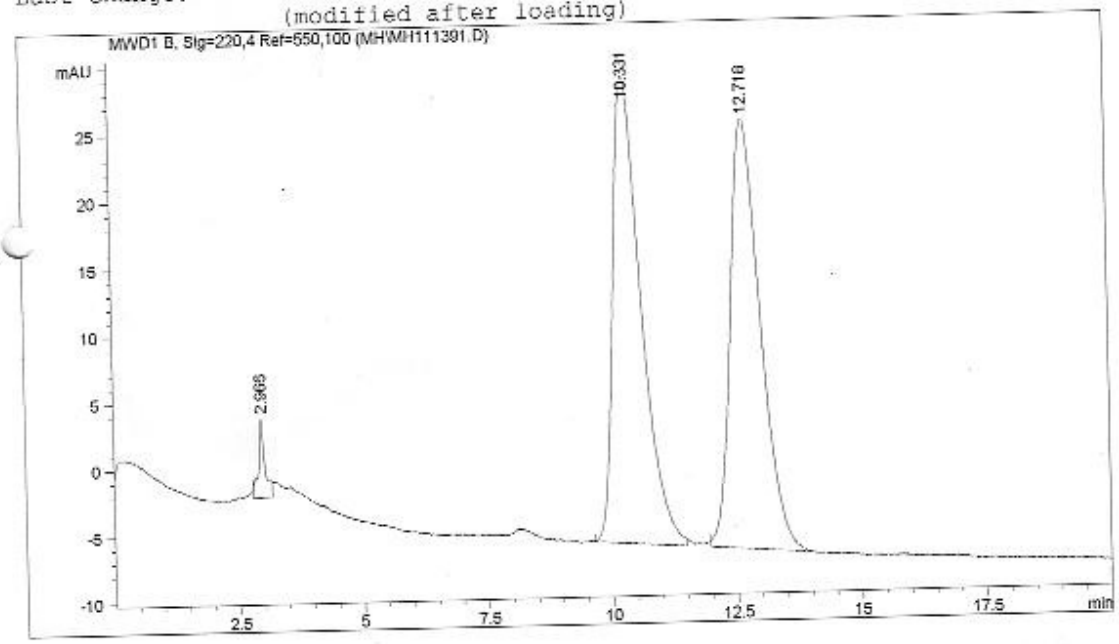
Vial : 8

Inj Volume : 4 µl

Acq. Method : C:\HPCHEM\2\METHODS\BP90_10.M
Last changed : 07.08.10 17:29:31 by Micha
(modified after loading)

Analysis Method : C:\HPCHEM\2\METHODS\BP90_10.M
Last changed : 07.08.10 17:57:43 by Micha
(modified after loading)

(rac)



Area Percent Report

1:1 (50:50)

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: MWD1 B, Sig=220,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.966	BB	0.1227	52.34853	5.94529	1.8918
2	10.331	BB	0.5954	1367.02332	35.01850	49.4012
3	12.718	BB	0.6568	1347.81641	32.16709	48.7071
Totals :				2767.18825	73.13088	

Instrument 2 07.08.10 17:57:54 Micha

Page 1 of 2

Data File C:\HPCHEM\2\DATA\MH\MH111450.D

Sample Name: MH11-145H

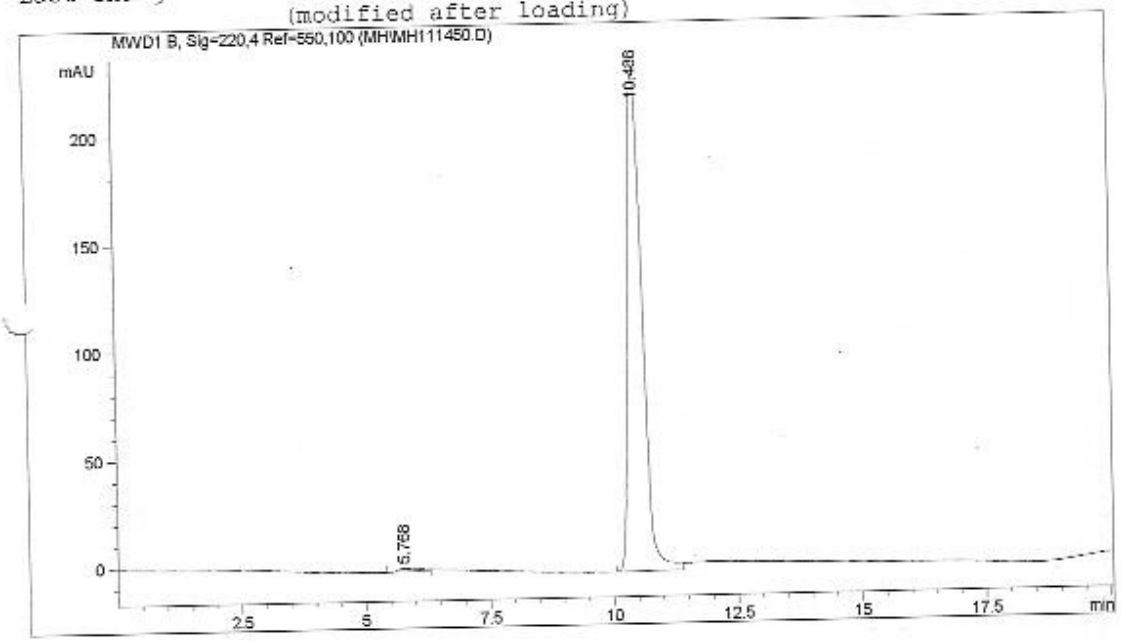
Chiracel OJ, 1.0 ml/min, 99 : 1, 2 µl

Injection Date : 08.08.10 15:22:44
Sample Name : MH11-145H
Acq. Operator : Micha

Vial : 9

Inj Volume : 2 µl

Method : C:\HPCHEM\2\METHODS\BP90_10.M
Last changed : 08.08.10 15:15:43 by Micha
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: MWD1 B, Sig=220,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.768	PB	0.3933	43.67129	1.42588	0.9063
2	10.488	PB	0.3496	4775.04980	230.58041	99.0937
Totals :				4818.72109	232.00630	

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 2 08.08.10 15:42:51 Micha

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