

Highly Diastereoselective Preparation of (*E*)- Alkenylsilanes bearing an α -Chiral Center

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Supporting information

Experimental procedures, analytical and spectroscopy data for starting materials and final products (69 pages).

General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under argon. Syringes used to transfer reagents and solvent were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). The enantiomeric purity was determined by chiral HPLC- or capillary GC-analysis. In all cases, the HPLC- or GC-analysis was calibrated with a sample of the racemate. All NMR spectra were run in CDCl₃ and referenced to the solvent peak (CDCl₃: ¹³C NMR, δ 77.0; ¹H NMR, δ 7.26). The concentrations of diorganozinc reagent solutions were determined by reaction with iodine and back titration with aqueous sodium thiosulfate.

TP1: Typical procedure for S_N2' substitutions of fluorobenzoates with dialkylzincs^{1,2}

A flame-dried flask equipped with a magnetic stirring bar, an argon inlet, and a septum was charged with CuCN·2LiCl solution (1.0 M in THF, 1.2 equiv), NMP (sufficient to give an overall ratio of solvents THF: NMP = 2:1), and then the mixture was cooled at –30 °C. To this solution was added dropwise the dialkylzinc reagent (2.4 equiv). The resulting mixture was stirred at –30 °C for 45 min, and then the pentafluorobenzoate (1.0 equiv) was added dropwise as a solution in THF. The reaction mixture was stirred at the required temperature until the conversion was complete (15-25 h) and saturated aqueous NH₄Cl solution (5 mL) was added. The quenched reaction mixture was poured into 25 % aq. ammonia (2 mL), aq. sat. NH₄Cl (100 mL) and Et₂O (100 mL) and stirred at 25 °C until the copper salts had dissolved then extracted with Et₂O (3 x 100 mL). The combined extracts were washed with water, brine and dried over MgSO₄. Evaporation of the solvents and purification by column chromatography afforded the desired alkenylsilanes of type **1**.

TP2: Typical procedure for S_N2' substitutions of fluorobenzoates with diarylzincs³

Preparation of the diarylzinc reagent (1mmol of R₂Zn):

The aryl iodide (1.0 equiv.) and Li(acac) (0.1 equiv.) were dissolved in dry NMP (1.5 mL) and *i*Pr₂Zn (0.55 equiv.) was added at 0 °C. The reaction mixture was stirred at room temperature and the completion of the iodine-zinc exchange was checked by GC-analysis using tetradecane as internal standard.

¹ Harrington-Frost, N.; Leuser, H.; Calaza, M. I.; Kneisel, F. F.; Knochel, P. *Org. Lett.* **2003**, 5, 2111.

² Leuser, H.; Perrone, S.; Liron, F.; Kneisel, F. F.; Knochel, P. *Angew. Chem. Int. Ed.* **2005**, 44, 4627.

³ (a) Kneisel, F. F.; Dochnahl, M.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, 43, 1017. (b) Kneisel, F. F.; Leuser, H.; Knochel, P. *Synthesis* **2005**, 2625.

S_N2' substitution:

The freshly prepared diarylzinc reagent (2.4 equiv) was cooled at $-30\text{ }^{\circ}\text{C}$ and $\text{CuCN}\cdot 2\text{LiCl}$ solution (1 M in THF, 1.2 equiv) was added. The resulting mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 45 min, and then the pentafluorobenzoate (1.0 equiv) was added dropwise as a solution in THF. The reaction mixture was stirred at the required temperature until the conversion was complete (15-25 h) and saturated aqueous NH_4Cl solution (5 mL) was added. The quenched reaction mixture was poured into 25 % aq. ammonia (2 mL), aq. sat. NH_4Cl (100 mL) and Et_2O (100 mL) and stirred at $25\text{ }^{\circ}\text{C}$ until the copper salts had dissolved, then extracted with Et_2O (3 x 100 mL). The combined extracts were washed with water, brine and dried over Mg_2SO_4 . Evaporation of the solvents and purification by column chromatography afforded the desired alkenylsilanes **1e** and **1f**.

TP3: Typical procedure for Friedel-Crafts acylations⁴

In flame-dried flask equipped with a magnetic stirring bar, an argon inlet, and a septum was placed dry CH_2Cl_2 (2 mL) and anhydrous AlCl_3 (1.1 equiv). This suspension was cooled to $-78\text{ }^{\circ}\text{C}$ and the appropriate acyl chloride (1.1 equiv) was added followed by the alkenylsilane (1.0 equiv) as a solution in CH_2Cl_2 (2 mL). The reaction mixture was stirred at room temperature or at $-40\text{ }^{\circ}\text{C}$ until completion (2-5 h) and then poured into diluted HCl (20 mL) and Et_2O . The aqueous phase is extracted with Et_2O (3 x 20 mL) and the combined extracts were washed with Na_2CO_3 saturated solution, brine and dried over Mg_2SO_4 . Evaporation of the solvents and purification by column chromatography afforded the desired α,β -unsaturated ketone of type **6**.

TP4: Typical procedure for the ozonolysis (derivatization to the corresponding carboxylic acid for determination of the *ee*)²

Ozone was led through a solution of the alkenylsilane (1.0 equiv) in acetone (10 mL) at $-78\text{ }^{\circ}\text{C}$ until the solution turned blue (3 –10 min); the excess of O_3 was removed by a nitrogen current. At $0\text{ }^{\circ}\text{C}$ Jones reagent (2.67 M, ca. 3 equiv.) was added dropwise until the orange colour persisted. The mixture was stirred for an additional 15 minutes and *i*-PrOH (8 mL) was added until the mixture turned green. It is allowed to warm up to room temperature and the solvents were evaporated. The residue was taken up in water and ether (1/4) and after acido/basic workup the desired carboxylic acid was obtained.

⁴ Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Baily, T. R. *J. Org. Chem.* **1980**, *45*, 3017.

Starting materials:**1-(tert-Butyl-dimethyl-silanyl)-but-2-yn-1-ol (*rac*-3a):**

This compound was prepared starting from 2-butyne-1-ol (700 mg, 10.0 mmol) according to the literature procedure.⁵ After purification by chromatography (silica gel, pentane/Et₂O, 20:1) **1a** (1.36 g, 7.42 mmol, 74%) was obtained as a pale yellow oil.

¹H-NMR (CDCl₃, 300MHz): δ = 4.18 (q, *J* = 2.66 Hz, 1H), 1.89 (s, *J* = 2.66 Hz, 3H), 0.97 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H).

¹³C-NMR (CDCl₃, 75MHz): δ = 84.4, 80.5, 55.5, 27.2, 17.3, 4.2, -7.6, -8.2.

MS (EI, 70 eV), *m/z* (%): 184 (0.75, M⁺), 141 (5), 115 (6), 99 (20), 73 (100), 59 (7).

IR (neat, v/cm⁻¹): 3448, 2960, 2900, 2864, 2310, 1696, 1590, 1466, 1250, 976, 838, 782.

HRMS (EI): calcd. for C₁₀H₂₀OSi [M]⁺: 184.1283, found: 184.1263.

1-(Dimethyl-phenyl-silanyl)-oct-2-yn-1-ol (*rac*-3b):⁶

To a solution of PhMe₂SiCl (1.84 mL, 11.0 mmol, 1.1 equiv) in anhydrous THF (30 mL) was added lithium wire (560 mg, 80 mmol, 8.0 equiv). The dark purple suspension was stirred at 24 °C for 18 h. The resultant PhMe₂SiLi⁷ solution was transferred by canula to a clean flask and cooled to -78 °C. 2-Octynal (1.42 mL, 10 mmol) in 5 mL THF was then added dropwise. The solution was stirred for 30 min at -78 °C before being poured into aqueous NH₄Cl (50 mL). The resultant layers were separated and the aqueous phase was extracted with Et₂O (3 x 50 mL). The combined organic phases were washed with brine, dried over MgSO₄ and the solvent was evaporated under vacuo. Purification by chromatography (silica gel, pentane/Et₂O, 9:1) afforded *rac*-**1b** (1.91 g, 7.35 mmol, 73%) as a pale yellow oil.

¹H-NMR (CDCl₃, 300 MHz): δ = 7.61-7.65 (m, 2H), 7.43-7.34 (m, 3H), 4.25 (t, *J* = 2.42 Hz, 1H), 2.26-2.21 (td, *J* = 2.42 Hz, *J* = 7.04 Hz, 2H) 1.54-1.27 (m, 7H), 0.92-0.87 (t, *J* = 7.0 Hz, 3H), 0.43 (s, 3H), 0.42 (s, 3H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 135.5, 134.3, 129.6, 127.8, 89.0, 80.0, 56.2, 31.0, 28.5, 22.1, 19.0, 13.9, -5.5, -5.8.

MS (EI, 70 eV), *m/z* (%): 260.16 (5, M⁺), 245 (30), 215 (100), 189 (82), 135 (30), 75 (16)

IR (neat, v/cm⁻¹): 3421, 3070, 2956, 2930, 2859, 1696, 1457, 1427, 1378, 1329, 1247, 1112, 972, 830, 783, 732, 696 cm⁻¹.

HRMS (EI): calcd. for C₁₆H₂₄OSi [M]⁺: 260.1596, found: 260.1602.

⁵ Sakaguchi, K.; Higashino, M.; Ohfuné, Y. *Tetrahedron* **2003**, 59, 6647.

⁶ Romero, A.; Woerpel, K. A. *Org. Lett.* **2006**, 8, 2127.

⁷ Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520.

1-(tert-Butyl-dimethyl-silanyl)-but-2-yn-1-one (4a):

This compound was prepared starting from **1a** (720 mg, 3.9 mmol) according to the literature procedure⁵. Purification by chromatography (silica gel, pentane/ Et₂O, 40:1) afforded **2a** (634 mg, 3.39 mmol, 87%) as yellow oil.

¹H-NMR (CDCl₃, 300 MHz): δ = 1.87 (s, 3H), 0.75 (s, 9H), 0.00 (s, 6H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 98.7, 89.2, 85.4, 26.7, 17.2, 4.8, -7.1.

MS (EI, 70 eV), m/z (%): 181 (0.10, M⁺), 167 (4), 126 (17), 97 (54), 73 (100), 59 (9).

IR (neat, ν/cm^{-1}): 2957, 2936, 2892, 2280, 2192, 1594, 1466, 1252, 1142, 840, 820, 804, 780.

HRMS (EI): calcd. for C₁₀H₁₇OSi [M-H]⁺: 181.1049, found: 181.1023.

1-(Dimethyl-phenyl-silanyl)-oct-2-yn-1-one (4b):⁸

DMSO (1.45 mL, 20.4 mmol, 1.7 equiv) was added to a solution of oxalyl chloride (1.55 mL, 18 mmol, 1.5 equiv) in CH₂Cl₂ (40 mL) at -78 °C. After 10 min **1b** (3.0 g, 11.5 mmol) was added dropwise as a solution in CH₂Cl₂ (10 mL) followed by Et₃N (6.24 mL, 44.4 mmol, 3.7 equiv) after 15 min. Extraction with Et₂O and purification by chromatography (silica gel, pentane/ Et₂O, 95:5) afforded **2b** (2.18 g, 8.48 mmol, 74%) as a yellow oil.

¹H-NMR (CDCl₃, 300 MHz): δ = 7.60-7.57 (m, 2H), 7.42-7.36 (m, 3H), 2.38 (t, J = 7.2 Hz, 2H), 1.57-1.48 (m, 2H), 1.35-1.30 (m, 4H), 0.91-0.86 (t, J = 7.2 Hz, 3H), 0.54 (s, 6H)

¹³C-NMR (CDCl₃, 75 MHz): δ = 134.1, 133.5, 129.9, 127.9, 104.7, 84.8, 30.9, 27.4, 22.0, 19.3, 13.8, -5.0.

MS (EI, 70 eV), m/z (%): 258 (2, M⁺), 257 (7), 243 (8), 215 (71), 202 (50), 135 (100), 105 (8).

IR (neat, ν/cm^{-1}): 2932, 2957, 2181, 1591, 1428, 1249, 1112, 782, 696.

HRMS (EI): calcd. for C₁₆H₂₂OSi [M⁺]: 258.1440, found: 258.1444.

(+)-(1R)-1-(tert-Butyl-dimethyl-silanyl)-but-2-yn-1-ol ((+)-(R)-3a):⁸

Ketone **2a** (1.49 g, 8.18 mmol) in THF (40 mL) was cooled to -30 °C and (R)-2-methyl-CBS-oxazaborolidine (1.0 M in toluene, 8.2 mL, 8.2 mmol) was added, followed by dropwise addition of BH₃·Me₂S (0.46 mL, 4.9 mmol) as a solution in THF (5 mL). The mixture was stirred at -30 °C for 30 min and quenched with MeOH (20 mL). The organic phase was extracted with Et₂O (3 x 50 mL), dried over MgSO₄ and the solvent was evaporated under vacuo. Purification by chromatography (silica gel, pentane/Et₂O, 20:1) afforded (+)-(R)-**1a** (1.39 g, 7.55 mmol, 92%, 92% ee) as a pale yellow oil.

⁸ Guitchin, B. K. ; Bienz, S. *Organometallics* **2004**, 23, 4944.

$[\alpha]_D^{20} = + 62.8$ ($c = 1.32$, CH_2Cl_2).

For spectral data see *rac*-**1a**.

(+)-(1*R*)-1-(Dimethyl-phenyl-silanyl)-oct-2-yn-1-ol ((+)-(R)-3b):

Prepared following the same procedure as for (+)-(R)-**1a**, with the ketone **2b** (2.14 g, 8.29 mmol), (*R*)-2-methyl-CBS-oxazaborolidine (1.0 M in toluene, 8.3 mL, 8.3 mmol) and $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (0.47 mL, 4.97 mmol) as a solution in THF (5 mL). Purification by chromatography (silica gel, pentane/Et₂O, 9:1) afforded (+)-(R)-**1b** (1.96 g, 7.54 mmol, 91%, 90% *ee*) as a yellow oil.

$[\alpha]_D^{20} = + 57.6$ ($c = 1.45$, CHCl_3).

For spectral data see *rac*-**1b**.

(+)-(1*R*,2*Z*)-1-(tert-Butyl-dimethyl-silanyl)-but-2-en-1-ol ((+)-(R)-5a):

This compound was prepared starting from (+)-(R)-**1a** (368 mg, 2.0 mmol) according to the literature procedure.⁵ Purification by chromatography (silica gel, pentane/Et₂O, 40:1) afforded (+)-(R)-**3a** (297 mg, 1.60 mmol, 80%, 92% *ee*) as a colorless oil.

$[\alpha]_D^{20} = + 82.3$ ($c = 0.87$, CH_2Cl_2).

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 100 °C; $t_R(\text{min}) = 20.09$ (*R*, major), 21.41 (*S*, minor).

¹H-NMR (CDCl_3 , 300 MHz): $\delta = 5.51\text{--}5.43$ (m, 2H), 4.46 (d, $J = 10.41$ Hz, 1H), 1.60 (d, $J = 6.55$ Hz, 3H), 0.92 (s, 9H), 0.00 (s, 3H), -0.09 (s, 3H).

¹³C-NMR (CDCl_3 , 75 MHz): $\delta = 132.2, 123.0, 61.9, 26.9, 17.4, 13.9, -7.4, -8.4$.

MS (EI, 70 eV), m/z (%): 186.1423 (0.04, M^+), 129 (17), 115 (3), 75 (13), 73 (100), 59 (5).

IR (neat, v/cm^{-1}): 3370, 2930, 2859, 1722, 1523, 1464, 1351, 1251, 1168, 959, 841.

HRMS (EI): calcd. for $\text{C}_{10}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 186.1440, found: 186.1423.

(+)-(1*R*,2*Z*)-1-(Dimethyl-phenyl-silanyl)-oct-2-en-1-ol ((+)-R-5b):

Prepared following the same procedure as for (+)-(R)-**3a**, starting from (+)-(R)-**1b** (3.38 g, 13 mmol). Purification by chromatography (silica gel, pentane/Et₂O, 95:5) afforded (+)-(R)-**3b** (2.77 g, 10.57 mmol, 82%, 90% *ee*) as a colorless oil.

$[\alpha]_D^{20} = + 86.2$ ($c = 1.54$, CHCl_3).

GC (Chirasil-Dex CB), 140 °C constant; $t_R(\text{min}) = 38.15$ (*R*, major), 40.78 (*S*, minor).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.60-7.57 (m, 2H), 7.39-7.26 (m, 3H), 5.49-5.32 (m, 2H), 4.45 (d, J = 9.6 Hz, 1H), 2.04-1.92 (m, 1H), 1.83-1.72 (m, 1H), 1.28-1.21 (m, 6H), 0.87 (t, J = 7.26 Hz, 3H), 0.36 (s, 3H, CH_3), 0.33 (s, 3H, CH_3).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 136.2, 134.2, 130.0, 129.8, 129.3, 127.7, 63.5, 31.5, 29.3, 27.8, 22.5, 14.0, -5.48, -5.97.

MS (EI, 70 eV), m/z (%): 262.1761 (0.15, M^+), 247 (4), 219 (1), 135 (100), 75 (3).

IR (neat, v/cm^{-1}): 3419, 2925, 2956, 2855, 1427, 1246, 1112, 962, 812, 697.

HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{26}\text{OSi}$ [M^+]: 262.1753, found: 262.1761.

(-)-(1*R*,2*Z*)-1-(tert-Butyl-dimethyl-silanyl)-but-2-enyl pentafluorobenzoate ((-)-*R*-2a):

This compound was prepared starting from (+)-(*R*)-**3a** (226 mg, 1.2 mmol) according to the literature procedure^{1,2}, with pentafluorobenzoylchloride (0.23 mL, 1.68 mmol), DMAP (20.5 mg, 0.17 mmol) and pyridine (0.14 mL, 1.68 mmol). Purification by chromatography (silica gel, pentane/ Et_2O , 98:2 + 1% Et_3N) afforded (-)-(*R*)-**4a** (433 mg, 1.14 mmol, 95%, 92% *ee*) as a colorless oil.

$[\alpha]_{\text{D}}^{20}$ = - 17.1 (c = 1.59, CH_2Cl_2).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 5.90 (d, J = 10.33 Hz, 1H), 5.67-5.47 (m, 2H), 1.77 (dd, J = 6.69 Hz, J = 1.44 Hz, 3H), 0.90 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 159.4, 147.3, 143.9, 139.7, 136.4, 127.3, 109.1, 68.1, 27.1, 17.3, 14.0, -7.7, -11.0.

MS (EI, 70 eV), m/z (%): 380 (0.09, M^+), 323 (17), 269 (25), 194 (24), 185 (9), 73 (100), 59 (9).

IR (neat, v/cm^{-1}): 2932, 2860, 1737, 1651, 1524, 1503, 1471, 1422, 1333, 1251, 1225, 1149, 1104, 1005, 946, 806, 768.

HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{21}\text{F}_5\text{O}_2\text{Si}$ [M^+]: 380.1231, found: 380.1242.

(-)-(1*R*,2*Z*)-1-(dimethyl-phenyl-silanyl)-oct-2-enyl pentafluorobenzoate ((-)-*R*-2b):

Prepared following the same procedure as for (-)-(*R*)-**4a**, starting from (+)-(*R*)-**3b** (1.52 g, 5.8 mmol) with pentafluorobenzoylchloride (1.12 mL, 8.12 mmol), DMAP (100 mg, 0.81 mmol) and pyridine (0.66 mL, 8.12 mmol). Purification by chromatography (silica gel, pentane/ Et_2O , 99:1 + 1% Et_3N) afforded (-)-(*R*)-**4b** (2.51 g, 5.51 mmol, 95%, 90% *ee*) as a colorless oil.

$[\alpha]_{\text{D}}^{20}$ = - 7.94 (c = 1.36, CHCl_3)

^1H -NMR (CDCl_3 , 600 MHz): δ = 7.55-7.54 (m, 2H), 7.40-7.34 (m, 3H), 5.92 (d, 1H, J = 10.24 Hz), 5.49-5.45 (m, 1H), 5.39 (t, J = 10.38 Hz, 1H), 2.10-2.04 (m, 1H), 1.82-1.78 (m, 1H), 1.29-1.17 (m, 6H), 0.87 (t, J = 7.26 Hz, 3H), 0.41 (s, 3H), 0.40 (s, 3H).

^{13}C -NMR (CDCl_3 , 150 MHz): 159.02, 146.10, 144.39, 143.87, 142.07, 138.46, 136.8, 134.6, 134.1, 133.2, 129.7, 127.8, 124.2, 108.85, 69.5, 31.4, 28.9, 27.9, 22.4, 13.9, -5.5, -5.6.

MS (EI, 70 eV), m/z (%): 456.15 (8, M^+), 441 (14), 427 (78), 378 (22), 331 (25), 269 (100), 194 (22), 135 (54), 121 (7).

IR (neat, v/cm^{-1}): 2958, 2929, 2858, 1733, 1651, 1522, 1495, 1427, 1330, 1250, 1219, 1113, 996, 942, 808, 771, 733, 698.

HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{25}\text{F}_5\text{O}_2\text{Si}$ [M^+]: 456.1544, found: 456.1517.

Products:

(-)-(3*R*,1*E*)-tert-Butyl-dimethyl-(3-methyl-oct-1-enyl)-silane ((-)-(R)-1a):

Prepared according to **TP1** using (1*R*,2*Z*)-1-(tert-butyl-dimethyl-silanyl)-but-2-enyl 2,3,4,5,6-pentafluorobenzoate (-)-(R)-**2a** (380 mg, 1.0 mmol, 92% *ee*), THF (1.0 mL), dipentylzinc solution (4.8 M in THF, 0.5 mL, 2.4 mmol, 2.4 equiv), $\text{CuCN}\cdot 2\text{LiCl}$ (1.0 M in THF, 1.2 mL, 1.2 mmol, 1.2 equiv) and NMP (1.3 mL). The resulting mixture was stirred at -78 °C to -50 °C for 24 h. After purification by column chromatography (silica gel, 100% pentane), (-)-(R)-**1a** was obtained as a colorless oil (194 mg, 0.81 mmol, 81%, 90% *ee*).

$[\alpha]_{\text{D}}^{20} = -21.9$ (c = 1.29, CH_2Cl_2)

^1H -NMR (CDCl_3 , 300 MHz): δ = 5.88 (*dd*, J = 7.16 Hz, J = 18.65 Hz, 1H), 5.35 (*dd*, J = 1.09 Hz, J = 18.65 Hz, 1H), 2.10-2.15 (m, 1H), 1.26 (m, 8H), 0.97 (*d*, J = 6.72 Hz, 3H), 0.86 (s, 9H), 0.003 (s, 6H).

^{13}C -NMR (CDCl_3 , 75 MHz): δ = 154.5, 124.1, 40.6, 36.5, 31.9, 26.9, 26.4, 22.6, 20.2, 16.5, 14.1, -5.9, -6.1.

MS (EI, 70 eV), m/z (%): 240.23 (0.23, M^+), 225 (3), 183 (100), 141 (2), 127 (4), 113 (10), 99 (7), 59 (13).

IR (neat, v/cm^{-1}): 2954, 2927, 2856, 1614, 1247, 991, 829.

HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{32}\text{Si}$ [M^+]: 240.2273, found: 240.2287.

The *ee* of (-)-(R)-**1a** was determined by GC analysis (see appendix) after transformation into (2*R*)-2-methylheptanoic acid¹ according to **TP4**:

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C; $t_R(\text{min}) = 28.05$ (*S*, minor), 28.97 (*R*, major).

$[\alpha]_D = -15.6$ ($c = 0.55$, EtOH).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 2.46$ (qt, $J = 7.2$ Hz, 6.9 Hz, 1H), 1.20-1.50 (m, 7H), 1.62-1.75 (m, 1H), 1.18 (d, $J = 7.2$ Hz, 3H), 0.84-0.93 (m, 3H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): 183.0, 39.3, 33.5, 31.7, 26.8, 22.5, 16.8, 14.0.

IR (neat, v/cm^{-1}): 3600-2200, 1710.

(–)-(3*R*,1*E*)-tert-Butyl-(3,4-dimethyl-pent-1-enyl)-dimethyl silane ((–)-(*R*)-1*b*):

Prepared according to **TP1** using (–)-(*R*)-**2a** (353 mg, 0.93 mmol, 92% *ee*), THF (1.0 mL), diisopropylzinc solution (5.9 M in Et_2O , 0.42 mL, 2.16 mmol, 2.4 equiv), $\text{CuCN} \cdot 2\text{LiCl}$ (1.0 M in THF, 1.1 mL, 1.11 mmol, 1.2 equiv) and NMP (1.0 mL). The resulting mixture was stirred at –78 °C to –50 °C for 24 h. After purification by column chromatography (silica gel, 100% pentane), (–)-(*R*)-**1b** was obtained as a colorless oil (177 mg, 0.84 mmol, 90%, 90% *ee*).

$[\alpha]_D^{20} = -29.2$ ($c = 1.185$, CH_2Cl_2)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 5.92$ (dd, $J = 7.39$ Hz, $J = 18.68$ Hz, 1H), 5.54 (dd, $J = 1.11$ Hz, $J = 18.68$ Hz, 1H), 2.01-1.94 (m, 1H), 1.57-1.51 (m, 1H), 0.95 (d, $J = 6.81$ Hz, 3H), 0.86 (s, 9H), 0.86-0.83 (m, 6H), 0.004 (s, 6H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 153.2$, 125.7, 47.3, 33.1, 26.8, 20.2, 20.1, 17.2, 16.9, –5.56, –5.64.

MS (EI, 70 eV), m/z (%): 212.20 (0.69, M^+), 197 (3), 156 (15), 155 (100), 127 (5), 113 (13), 99 (14), 85 (12), 73 (25), 59 (16).

IR (neat, v/cm^{-1}): 2956, 2928, 2856, 1614, 1248, 993, 830.

HRMS (EI): calcd. for $\text{C}_{13}\text{H}_{28}\text{Si}$ [M^+]: 212.1960, found: 212.1964.

The *ee* of (–)-(*R*)-**1b** was determined by GC analysis (see appendix) after transformation into (2*R*)-2,3-dimethylbutanoic acid⁹ according to **TP4**:

GC (Chirasil-Dex CB), 50 °C (1 min), ramp of 2 °C/ min to 140 °C; $t_R(\text{min}) = 27.80$ (*S*, minor), 28.59 (*R*, major).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): 10.3 (s, broad, 1H), 2.14-2.05 (m, 2H), 1.14 (d, $J = 6.9$ Hz, 3H), 1.10 (d, $J = 6.3$ Hz, 3H), 0.99 (d, $J = 6.3$ Hz, 3H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 184.0$, 46.7, 31.7, 21.5, 19.5, 14.0.

IR (neat, v/cm^{-1}): 2986, 2928, 2896, 1654, 1448, 773.

⁹ Registry N°: [27855-05-06] for (+)-(*R*)-2,3 dimethylbutanoic acid, Levene, P. A. ; Marker, R. E. ; *J. Biol. Chem.* **1935**, 111, 299.

(-)-(3*R*,1*E*)-tert-Butyl-dimethyl-(3-methyl-pent-1-enyl)-silane ((-)-(R)-1*c*):

Prepared according to **TP1** using (1*R*,2*Z*)-1-(tert-butyl-dimethyl-silanyl)-but-2-enyl 2,3,4,5,6-pentafluorobenzoate (-)-(R)-**2a** (380 mg, 1 mmol, 92% *ee*), THF (1.0 mL), diethylzinc solution (0.24 mL, 2.4 mmol, 2.4 equiv), CuCN·2LiCl (1.0 M in THF, 1.2 mL, 1.2 mmol, 1.2 equiv) and NMP (1.0 mL). The resulting mixture was stirred at -78 °C to -50 °C for 24 h. After purification by column chromatography (silica gel, 100% pentane), (-)-(R)-**1c** was obtained as a colorless oil (176 mg, 0.89 mmol, 89%, 88% *ee*).

$[\alpha]_D^{20} = -26.3$ ($c = 1.10$, CH₂Cl₂)

¹H-NMR (CDCl₃, 300 MHz): $\delta = 5.88$ (dd, $J = 7.06$ Hz, $J = 18.66$ Hz, 1H), 5.54 (dd, $J = 1.13$ Hz, $J = 18.66$ Hz, 1H), 2.07-2.03 (m, 1H), 1.34-1.27 (m, 1H), 0.97 (d, $J = 6.73$ Hz, 3H), 0.86 (s, 9H), 0.004 (s, 6H).

¹³C-NMR (CDCl₃, 75 MHz): 154.2, 124.4, 42.2, 29.3, 26.4, 19.7, 16.5, 11.7, -5.9, -6.0.

MS (EI, 70 eV), m/z (%): 198.17 (1.21, M⁺), 183 (3), 141 (100), 127 (3), 113 (12), 99 (14), 85 (21), 73 (25), 59 (19).

IR (neat, ν/cm^{-1}): 2955, 2928, 2856, 1615, 1248, 991, 829.

HRMS (EI): calcd. for C₁₂H₂₆Si [M⁺]: 198.1804, found: 198.1781.

The *ee* of (-)-(R)-**1c** was determined by GC analysis (see appendix) after transformation into (2*R*)-2-methylbutanoic acid¹⁰ according to **TP4**:

GC (Chirasil-Dex CB), 50 °C (1 min), ramp of 2 °C/ min to 140 °C; $t_R(\text{min}) = 22.58$ (*S*, minor), 23.14 (*R*, major).

¹H-NMR (CDCl₃, 300 MHz): 11.5 (s, broad, 1H), 2.47-2.38 (m, 1H), 1.78-1.49 (m, 2H), 1.21 (d, $J = 7.0$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz): 183.5, 41.2, 26.7, 16.5, 13.9.

IR (neat, ν/cm^{-1}): 2980, 2945, 2880, 1652, 1468, 1100, 829, 785.

(-)-(3*S*,1*E*)-tert-Butyl-dimethyl-(3-phenyl-but-1-enyl)-silane ((-)-(S)-1*d*):

Prepared according to **TP1** using (1*R*,2*Z*)-1-(tert-butyl-dimethyl-silanyl)-but-2-enyl 2,3,4,5,6-pentafluorobenzoate (-)-(R)-**2a** (328 mg, 0.86 mmol, 92% *ee*), THF (1.0 mL), diphenylzinc solution (1.0 M in toluene, 2.61 mL, 2.59 mmol, 3.0 equiv). The toluene of the diphenylzinc solution was evaporated under vacuo at 25 °C and replaced by NMP (1.2 mL) and then CuCN·2LiCl (1.0 M in THF, 1.29 mL, 1.2 mmol, 1.5 equiv) was added to this solution at -30 °C. It is stirred for 45 min before the benzoate **2a** was added. The resulting mixture was

¹⁰ Registry N°: [1730-91-2] for (+)-(S)-2-methylbutanoic acid (Aldrich catalogue).

stirred at $-30\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ for 24 h. After purification by column chromatography (silica gel, 100% pentane), (–)-(S)-**1d** was obtained as a colorless oil (182 mg, 0.74 mmol, 86%, 89% *ee*).

$[\alpha]_{\text{D}}^{20} = -4.0$ ($c = 1.15$, CH_2Cl_2)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.34\text{--}7.29$ (m, 2H), 7.22–7.18 (m, 3H), 6.21 (dd, $J = 5.95$ Hz, $J = 18.67$ Hz, 1H), 5.54 (dd, $J = 1.53$ Hz, $J = 18.67$ Hz, 1H), 3.05 (m, 1H), 1.37 (d, $J = 6.02$ Hz, 3H), 0.88 (s, 9H), 0.02 (s, 6H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 152.1$, 145.7, 128.4, 127.4, 125.9, 125.0, 45.6, 26.5, 20.8, 16.6, -6.04 , -6.09 .

MS (EI, 70 eV), m/z (%): 246.18 (0.74, M^+), 231 (1), 189 (100), 145 (4), 135 (23), 105 (5), 73 (35), 59 (32).

IR (neat, v/cm^{-1}): 2953, 2931, 2853, 1674, 1602, 1471, 1245, 1006, 828, 700.

HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{26}\text{Si}$ [M^+]: 246.1804, found: 246.1810.

The *ee* of (–)-(S)-**1d** was determined by GC analysis (see appendix) after transformation into (2*R*)-2-phenylpropanoic acid¹¹ according to **TP4**:

GC (Chirasil-Dex CB), $70\text{ }^{\circ}\text{C}$ (1 min), ramp of $2\text{ }^{\circ}\text{C}/\text{min}$ to $140\text{ }^{\circ}\text{C}$; $t_{\text{R}}(\text{min}) = 42.37$ (S, minor), 43.61 (R, major).

$[\alpha]_{\text{D}} = -62.1$ ($c = 0.45$, CHCl_3)¹¹

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): $\delta = 7.24\text{--}7.40$ (m, 5H), 3.74 (q, $J = 7.0$ Hz, 1H), 1.52 (d, $J = 7.0$ Hz, 3H).

$^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): 180.3, 139.8, 128.7, 127.6, 127.4, 45.3, 18.1.

IR (neat, v/cm^{-1}): 3690–2210, 1950, 1710, 1600, 1590.

(+)-4-[(1*S*,2*E*)-3-(tert-Butyl-dimethyl-silanyl)-1-methyl-allyl]-methylbenzoate ((+)-(S)-1e**):**

Prepared according to **TP2** using (–)-(R)-**2a** (266 mg, 0.7 mmol, 92% *ee*), THF (1.0 mL), Ar_2Zn (prepared from 4-iodomethylbenzoate (880 mg, 3.36 mmol, 4.8 equiv), $i\text{Pr}_2\text{Zn}$ (0.31 mL, 1.84 mmol, 2.4 equiv) and $\text{Li}(\text{acac})$ (35 mg, 0.33 mmol, 0.48 equiv)), $\text{CuCN}\cdot 2\text{LiCl}$ (1.0 M in THF, 0.84 mL, 0.84 mmol, 1.2 equiv) and NMP (2.0 mL). The resulting mixture was stirred at $-30\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$ for 24 h. After purification by column chromatography (silica gel, 100% pentane), (+)-(S)-**1e** was obtained as a colorless oil (138 mg, 0.45 mmol, 65%, 89% *ee*).

¹¹ Aldrich catalogue: (R)-(-)-2-phenylpropanoic acid (98 % *ee*): $[\alpha]_{\text{D}}^{20} = -72$ ($c = 1.6$, CHCl_3).

$[\alpha]_D^{20} = +1.5$ ($c = 1.37$, acetone)

HPLC (column: OD-H; *n*-heptane 100%, 0.5 mL/min): t_R (min) = 26.27 (*R*, minor), 33.04 (*S*, major).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.97$ (d, $J = 8.42$, 2H), 7.25 (d, $J = 8.17$, 2H), 6.15 (dd, $J = 5.95$ Hz, $J = 18.66$ Hz, 1H), 5.67 (dd, $J = 1.51$ Hz, $J = 18.66$ Hz, 1H), 3.90 (s, 3H), 3.55 (m, 1H), 1.37 (d, $J = 7.02$ Hz, 3H), 0.85 (s, 9H), 0.006 (s, 6H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 167.1$, 151.1, 129.8, 128.0, 127.4, 126.1, 51.9, 45.6, 26.4, 20.5, 16.5, -6.11 .

MS (EI, 70 eV), m/z (%): 304.18 (0.36, M^+), 273 (3), 247 (100), 193 (4), 157 (9), 89 (2), 73 (7), 59 (5).

IR (neat, v/cm^{-1}): 2950, 2922, 2856, 1722, 1607, 1459, 1434, 1275, 1110, 828.

HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$ [M^+]: 304.1859, found: 304.1840.

(+)-(3*S*,1*E*)-tert-Butyl-[3-(3-methoxy-phenyl)-but-1-enyl]-dimethyl silane ((+)-(S)-1f):

Prepared according to **TP2** using (–)-(*R*)-**2a** (285 mg, 0.75 mmol, 92% *ee*), THF (1.0 mL), Ar_2Zn (prepared from 3-iodoanisole (842 mg, 3.60 mmol, 4.8 equiv), $i\text{Pr}_2\text{Zn}$ (0.33 mL, 1.98 mmol, 2.4 equiv) and $\text{Li}(\text{acac})$ (38 mg, 0.36 mmol, 0.48 equiv)), $\text{CuCN}\cdot 2\text{LiCl}$ (1.0 M in THF, 0.90 mL, 0.90 mmol, 1.2 equiv) and NMP (2.0 mL). The resulting mixture was stirred at -30°C to 25°C for 24 h. After purification by column chromatography (silica gel, 100% pentane), (+)-(S)-**1f** was obtained as a colorless oil (124 mg, 0.45 mmol, 60%, 90% *ee*).

$[\alpha]_D^{20} = +4.0$ ($c = 0.3$, acetone)

HPLC (column: OD-H; *n*-heptane 100%, 0.5 mL/min): t_R (min) = 12.95 (*R*, minor), 15.08 (*S*, major).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.24$ -7.18 (m, 2H), 6.80-6.71 (m, 2H), 6.17 (dd, $J = 5.96$ Hz, $J = 18.66$ Hz, 1H), 5.67 (dd, $J = 1.48$ Hz, $J = 18.66$ Hz, 1H), 3.78 (s, 3H), 3.45 (m, 1H), 1.34 (d, $J = 7.02$ Hz, 3H), 0.86 (s, 9H), 0.00 (s, 6H).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 159.6$, 151.9, 147.4, 129.2, 125.1, 119.8, 113.1, 111.3, 55.1, 45.6, 26.5, 20.7, 16.6, -6.04 , -6.11 .

MS (EI, 70 eV), m/z (%): 276.19 (4, M^+), 220 (15), 219 (100), 204 (15), 189 (6), 165 (12), 159 (3), 135 (3), 89 (2), 73 (11), 59 (7).

IR (neat, v/cm^{-1}): 2950, 2928, 2851, 1596, 1462, 1248, 1152, 1045, 828, 778, 699.

HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{28}\text{OSi}$ [M^+]: 276.1909, found: 276.1906.

(-)-(3*R*,1*E*)-tert-Butyl-dimethyl-(3-methyl-5-phenyl-pent-1-enyl)-silane ((-)-(R)-1*g*):

Prepared according to **TP1** using (-)-(R)-**2a** (380 mg, 1.0 mmol, 92% *ee*), THF (1.0 mL), [Ph(CH₂)₂]₂Zn (1.5 M in THF, 1.6 mL, 2.4 mmol, 2.4 equiv), CuCN·2LiCl (1.0 M in THF, 1.2 mL, 1.2 mmol, 1.2 equiv) and NMP (2.0 mL). The resulting mixture was stirred at -30 °C to 25 °C for 6 days. After purification by column chromatography (silica gel, 100% pentane), (-)-(R)-**1g** was obtained as a colorless oil (164 mg, 60%, 84% *ee*).

$[\alpha]_{\text{D}}^{20} = -17.4$ (*c* = 1.14, CHCl₃)

¹H-NMR (CDCl₃, 300 MHz): δ = 7.30-7.14 (m, 5H), 5.93 (dd, *J* = 7.20 Hz, *J* = 18.66 Hz, 1H), 5.62 (dd, *J* = 1.04 Hz, *J* = 18.6 Hz, 1H), 2.65-2.51 (m, 2H), 2.25-2.10 (m, 1H), 1.67-1.59 (m, 2H), 1.04 (d, *J* = 6,7 Hz, 3H), 0.89 (s, 9H), 0.056 (s, 3H), 0.049 (s, 3H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 154.1, 142.8, 128.4, 128.2, 125.6, 125.1, 40.2, 38.4, 33.7, 26.4, 20.2, 16.5, -5.9, -6.0.

MS (EI, 70 eV), *m/z* (%): 259.19 (24, M⁺), 217 (100), 173 (1), 157 (5), 135 (3), 91 (12), 73 (10), 59 (13).

IR (neat, ν/cm⁻¹): 2951, 2926, 2854, 1613, 1454, 1246, 827, 696.

HRMS (EI): calcd. for C₁₇H₂₇Si [M-CH₃]⁺: 259.1882, found: 259.1897.

The *ee* of **1g** was determined by GC analysis (see appendix) after transformation into (2*R*)-2-methyl-4-phenylbutanoic acid¹² according to **TP4**:

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C; *t_R*(min) = 57.03 (*S*, minor), 59.56 (*R*, major).

¹H-NMR (CDCl₃, 200 MHz): δ = 1.20 (dd, *J* = 7.5 Hz, *J* = 6.0 Hz, 3H), 1.5-2.3 (m, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.46 (q, *J* = 7.5 Hz, 1H), 7.2 (m, 5H).

(+)-(3*S*,1*E*)-Dimethyl-(3-methyl-oct-1-enyl)-phenyl silane ((+)-(S)-1*h*):

Prepared according to **TP1** using (1*R*,2*Z*)-1-(dimethyl-phenyl-silanyl)-oct-2-enyl-pentafluorobenzoate (-)-(R)-**2b** (2.35 g, 5.15 mmol, 90% *ee*), THF (3.0 mL), dimethylzinc solution (2.0 M in toluene, 6.2 mL, 12.36 mmol, 2.4 equiv), CuCN·2LiCl (1.0 M in THF, 6.2 mL, 6.2 mmol, 1.2 equiv) and NMP (8.0 mL). The resulting mixture was stirred at -30 °C for 16 h and warmed up at 0 °C (5 h). After purification by column chromatography (silica gel, 100% pentane), (+)-(S)-**1h** was obtained as a colorless oil (1.27 g, 4.89 mmol, 95%, 89% *ee*).

$[\alpha]_{\text{D}}^{20} = +20.6$ (*c* = 1.37, CHCl₃)

¹² Anastasis, P.; Freer, I.; Overton, K. H.; Picken, D.; Rycroft, D. S.; Singh, S. B. *J. Chem. Soc. Perkin Trans. I* **1987**, 2427.

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz): δ = 7.55-7.53 (m, 2H), 7.37-7.35 (m, 3H), 6.02 (dd, J = 7.07 Hz, J = 18.63 Hz, 1H), 5.71 (dd, J = 1.08 Hz, J = 18.63 Hz, 1H), 2.21-2.17 (m, 1H), 1.33-1.28 (s, 6H), 1.00 (d, 3J = 6.73 Hz, 3H), 0.90 (t, J = 7.10 Hz, 3H), 0.33 (s, 3H).

$^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz): δ = 155.2, 139.5, 133.8, 128.7, 127.6, 124.7, 40.3, 36.4, 31.9, 26.9, 22.6, 19.9, 14.1, -2.33, -2.35.

MS (EI, 70 eV), m/z (%): 260.19 (7.05, M^+), 246 (9), 245 (45), 201 (12), 189 (7), 161 (37), 147 (11), 135 (100), 121 (46), 73 (7), 59 (7)

IR (neat, v/cm^{-1}): 2956, 2925, 2856, 1614, 1427, 1246, 1112, 990, 821, 727, 696.

HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{28}\text{Si}$ [M^+]: 260.1960, found: 260.1953.

The *ee* of **1h** was determined by GC analysis (see appendix) after transformation into (2*S*)-2-methylheptanoic acid according to **TP4**:

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/min to 140 °C; $t_R(\text{min})$ = 27.54 (*S*, major), 28.71 (*R*, minor).

For analytical data see derivatization of compound **1a**.

(+)-(3*S*,1*E*)- (3-Ethyl-oct-1-enyl)-dimethylphenyl silane ((+)-(S)-1i**):**

Prepared according to **TP1** using (1*R*,2*Z*)-1-(dimethyl-phenyl-silanyl)-oct-2-enyl 2,3,4,5,6-pentafluorobenzoate (–)-(*R*)-**2b** (534 mg, 1.17 mmol, 90% *ee*), THF (1.0 mL), diethylzinc solution (0.3 mL, 2.8 mmol, 2.4 equiv.), $\text{CuCN}\cdot 2\text{LiCl}$ (1.0 M in THF, 1.4 mL, 1.4 mmol, 1.2 equiv.) and NMP (1.4 mL). The resulting mixture was stirred at –30 °C for 16 h. After purification by column chromatography (silica gel, 100% pentane), (+)-(*S*)-**1i** was obtained as a colorless oil (275 mg, 1.00 mmol, 86%, 89% *ee*).

$[\alpha]_D^{20} = +3.6$ (c = 1.15, CHCl_3)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 7.57-7.53 (m, 2H), 7.37-7.36 (m, 3H), 5.88 (dd, J = 7.85 Hz, J = 18.58 Hz, 1H), 5.73 (d, J = 18.58 Hz, 1H), 1.96-1.94 (m, 1H), 1.44-1.24 (m, 10H), 0.92-0.79 (m, 6H), 0.34 (s, 6H)

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 153.7, 139.6, 133.8, 128.7, 127.6, 127.1, 48.6, 34.4, 31.9, 27.5, 26.9, 22.6, 14.1, 11.7, -2.3.

MS (EI, 70 eV), m/z (%): 274.21 (6.41, M^+), 259 (26), 215 (9), 203 (2), 161 (22), 148 (9), 135 (100), 121 (36), 105 (4), 59 (6).

IR (neat, v/cm^{-1}): 2956, 2919, 2852, 1612, 1462, 1245, 1111, 992, 819, 729, 698.

HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{30}\text{Si}$ [M^+]: 274.2117, found: 274.2130.

The *ee* of **1i** was determined by GC analysis (see appendix) after transformation into (2*S*)-2-Ethylheptanoic acid¹³ according to **TP4**:

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/min to 140 °C; *t_R*(min) = 31.49 (*S*, major), 32.24 (*R*, minor).

¹H-NMR (CDCl₃, 400 MHz): δ = 11.77 (s, 1H), 2.29 (m, 1H), 1.58 (m, 2H), 1.50 (m, 2H), 1.41 (m, 2H), 1.24-1.30 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H).

¹³C-NMR (CDCl₃, 100 MHz): 183.4, 47.2, 31.7, 27.0, 25.2, 22.5, 13.9, 11.7.

MS (EI, 70 eV), *m/z* (%): 158 (3, *M*⁺), 130 (11), 101 (26), 88 (100), 73 (54), 55 (11), 43 (14), 41 (15).

(+)-(3*R*,1*E*)-(3-Isopropyl-oct-1-enyl)-dimethylphenyl silane ((+)-(R)-1j):

Prepared according to TP1 using (1*R*,2*Z*)-1-(dimethyl-phenyl-silanyl)-oct-2-enyl 2,3,4,5,6-pentafluorobenzoate (–)-(R)-**2b** (455 mg, 1.0 mmol, 90% *ee*), THF (1.0 mL), diisopropylzinc solution (5.9 M in Et₂O, 0.4 mL, 2.4 mmol, 2.4 equiv), CuCN·2LiCl (1.0 M in THF, 1.2 mL, 1.2 mmol, 1.2 equiv) and NMP (1.3 mL). The resulting mixture was stirred at –50 °C to –30 °C for 16 h. After purification by column chromatography (silica gel, 100% pentane), (+)-(R)-**6c** was obtained as a colorless oil (258 mg, 0.89 mmol, 89%, 87% *ee*).

[α]_D²⁰ = + 4.7 (*c* = 1.10, CHCl₃)

¹H-NMR (CDCl₃, 300 MHz): δ = 7.56-7.53 (m, 2H), 7.37-7.35 (m, 3H), 5.89 (dd, *J* = 8.48 Hz, *J* = 18.65 Hz, 1H), 5.70 (d, *J* = 18.65 Hz, 1H), 1.87-1.80 (m, 1H), 1.68-1.52 (m, 1H), 1.31-1.22 (m, 8H), 0.91-0.83 (m, 6H), 0.34 (s, 6H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 151.9, 139.6, 133.8, 128.7, 128.3, 127.6, 53.6, 31.9, 31.6, 27.3, 22.7, 20.7, 19.2, 14.1, –2.2.

MS (EI, 70 eV), *m/z* (%): 288.22 (5,54, *M*⁺), 273 (21), 245 (8), 229 (5), 211 (4), 161 (15), 135 (100), 121 (26), 73 (4), 59 (7).

IR (neat, ν/cm^{–1}): 2955, 2926, 2871, 1613, 1465, 1427, 1246, 1112, 995, 817, 727, 697.

HRMS (EI): calcd. for C₁₉H₃₂Si [*M*⁺]: 288.2273, found: 288.2267.

The *ee* of **1j** was determined by GC analysis (see appendix) after transformation into (4*R*,2*E*)-4-Isopropyl-1-phenyl-non-2-en-1-one (**6h**) according to **TP3**:

HPLC (column: OD-H; *n*-heptane 100%, 0.5 mL/min): *t_R*(min) = 46.93 (*S*, minor), 50.70 (*R*, major).

For analytical data see compound **6h**.

¹³ Behr, A.; Brehme, V. A. *Adv. Synth. Catal.* **2002**, *344*, 525.

(+)-(3*S*,1*E*)- Dimethyl-phenyl-(3-phenyl-oct-1-enyl)-silane ((+)-(S)-1*k*):

Prepared according to **TP1** using (1*R*,2*Z*)-1-(dimethyl-phenyl-silanyl)-oct-2-enyl 2,3,4,5,6-pentafluorobenzoate (–)-(R)-**2b** (677 mg, 1.48 mmol, 90% *ee*), THF (1.0 mL), diphenylzinc solution (1.0 M in toluene, 3.6 mL, 3.6 mmol, 2.4 equiv). The toluene of the diphenylzinc solution was evaporated under vacuo at 25 °C and replaced by NMP (1.5 mL) and then the solution of CuCN·2LiCl (1.0 M in THF, 1.8 mL, 1.8 mmol, 1.2 equiv) was added to this solution at –30 °C. It is stirred for 45 min before the benzoate **2b** was added. The resulting mixture was stirred at –30 °C for 16 h and warmed up to 0 °C (5 h). After purification by column chromatography (silica gel, 100% pentane), (+)-(S)-**1k** was obtained as a colorless oil (410 mg, 1.27 mmol, 86%, 89% *ee*).

$[\alpha]_D^{20} = +15.1$ (*c* = 1.35, CHCl₃)

¹H-NMR (CDCl₃, 600 MHz): δ = 7.52-7.50 (m, 2H), 7.36-7.30 (m, 5H), 7.22-7.18 (m, 3H), 6.24 (dd, *J* = 7.04 Hz, *J* = 18.56 Hz, 1H), 5.78 (dd, *J* = 1.17 Hz, *J* = 18.56 Hz, 1H), 3.33-3.30 (m, 1H), 1.76-1.68 (m, 2H), 1.29-1.28 (m, 6H), 0.87 (t, *J* = 6.72 Hz, 3H) 0.32 (s, 6H).

¹³C-NMR (CDCl₃, 150 MHz): δ = 152.1, 144.5, 139.2, 133.8, 128.8, 128.3, 127.7, 127.6, 126.6, 126.0, 52.5, 35.4, 31.8, 27.2, 22.5, 14.0, –2.40, –2.44.

MS (EI, 70 eV), *m/z* (%): 322.21 (6, M⁺), 307 (25), 251 (11), 244 (11), 229 (4), 197 (8), 173 (28), 161 (73), 136 (14), 135 (100), 121 (18), 105 (3), 91 (4), 59 (3).

IR (neat, ν/cm^{–1}): 2955, 2927, 2856, 1600, 1452, 1427, 1246, 1113, 989, 820, 728, 698,.

HRMS (EI): calcd. for C₂₂H₃₀Si [M⁺]: 322.2117, found: 322.2132.

The *ee* of **1k** was determined by GC analysis (see appendix) after transformation into (4*S*,2*E*)-1,4-Diphenyl-non-2-en-1-one (**6i**) according to **TP3**:

HPLC (column: OD-H; *n*-heptane/*i*PrOH 98:2, 0.5 mL/min): *t_R*(min) = 13.18 (*R*, minor), 14.96 (*S*, major).

For analytical data see compound **6i**.

α,β -Unsaturated ketones from the Friedel-Crafts acylation:**(+)-(4*R*,2*E*)- 4-Methyl-1-phenyl-non-2-en-1-one ((+)-(R)-6a):**

Prepared according to **TP3** using (3*R*,1*E*)-tert-butyl-dimethyl-(3-methyl-oct-1-enyl)-silane **1a** (146 mg, 0.60 mmol, 90% *ee*), AlCl₃ (100 mg, 0.73 mmol, 1.2 equiv.), benzoylchloride (0.085 mL, 0.73 mmol, 1.2 equiv.) and CH₂Cl₂ (4.0 mL). The resulting mixture was stirred at -78 °C to rt for 3 h. After purification by column chromatography (silica gel, pentane/Et₂O, 98:2), (+)-(R)-**6a** was obtained as a colorless oil (90 mg, 0.40 mmol, 65%, 90% *ee*).

$[\alpha]_D^{20} = + 6.97$ (c = 0.97, CHCl₃)

¹H-NMR (CDCl₃, 300 MHz): δ = 7.94-7.90 (m, 2H), 7.58-7.43 (m, 3H), 6.96 (dd, *J* = 7.65 Hz, *J* = 15.47 Hz, 1H), 6.82 (dd, *J* = 0.78 Hz, *J* = 15.47 Hz, 1H), 2.45-2.36 (m, 1H), 1.27-1.44 (m, 8H), 1.11 (d, *J* = 6.71 Hz, 3H), 0.88 (t, *J* = 6.90 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 191.1, 155.4, 138.1, 132.5, 128.5, 128.4, 124.1, 37.1, 36.1, 31.8, 26.9, 22.5, 19.5, 14.0.

MS (EI, 70 eV), *m/z* (%): 230.16 (20, M⁺), 201 (6), 173 (38), 159 (13), 133 (9), 120 (22), 105 (100), 91 (10), 77 (31), 55 (5).

IR (neat, v/cm⁻¹): 2956, 2925, 2855, 1669, 1619, 1447, 1277, 1217, 1013, 982, 694.

HRMS (EI): calcd. for C₁₆H₂₂O [M⁺]: 230.1671, found: 230.1651.

(-)-(6*R*,4*E*)- 2,2,6,7-Tetramethyl-oct-4-en-3-one ((-)-(R)-6b):

Prepared according to **TP3** using (3*R*,1*E*)-tert-Butyl-(3,4-dimethyl-pent-1-enyl)-dimethyl-silane **1b** (201 mg, 0.95 mmol, 90% *ee*), AlCl₃ (160 mg, 1.14 mmol, 1.2 equiv.), pivaloylchloride (144 mg, 1.14 mmol, 1.2 equiv.) and CH₂Cl₂ (4.0 mL). The resulting mixture was stirred at -78 °C to rt for 3 h. After purification by column chromatography (silica gel, pentane/Et₂O, 98:2), (-)-(R)-**6b** was obtained as a colorless oil (107 mg, 0.59 mmol, 62%, 90% *ee*).

$[\alpha]_D^{20} = - 32.4$ (c = 1.23, CHCl₃)

¹H-NMR (CDCl₃, 300 MHz): δ = 6.85 (dd, *J* = 8.34 Hz, *J* = 15.30 Hz, 1H), 6.43 (dd, *J* = 1.09 Hz, *J* = 15.30 Hz, 1H), 2.16-2.08 (m, 1H), 1.68-1.58 (m, 1H), 1.15 (s, 9H), 1.01 (d, *J* = 6.82 Hz, 3H), 0.88 (t, *J* = 6.90 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz): 204.4, 151.5, 123.3, 137, 43.1, 42.8, 32.6, 26.2, 19.8, 19.7, 16.4.

MS (EI, 70 eV), *m/z* (%): 182. 16 (7, M⁺), 125 (166), 113 (3), 97 (12), 83 (20), 69 (18), 55 (100), 41 (10).

IR (neat, v/cm⁻¹): 2961, 2873, 1687, 1625, 1475, 1462, 1367, 1075, 987, 863.

HRMS (EI): calcd. for $C_{12}H_{22}O$ [M^+]: 182.1671, found: 182.1668.

(-)-(5*R*,3*E*)- 5,6-Dimethyl-hept-3-en-2-one ((-)-(R)-6c):

Prepared according to **TP3** using (3*R*,1*E*)-tert-Butyl-(3,4-dimethyl-pent-1-enyl)-dimethylsilane **1b** (127 mg, 0.6 mmol, 90% *ee*), $AlCl_3$ (97 mg, 0.73 mmol, 1.2 equiv.), acetylchloride (57 mg, 0.73 mmol, 1.2 equiv.) and CH_2Cl_2 (3.0 mL). The resulting mixture was stirred at $-78^\circ C$ to $-30^\circ C$ for 3 h. After purification by column chromatography (silica gel, pentane/ Et_2O , 9:1), (-)-(R)-**6c** was obtained as a colorless oil (56 mg, 0.40 mmol, 68%, 90% *ee*).

$[\alpha]_D^{20} = -26.3$ ($c = 1.05$, $CHCl_3$)

1H -NMR ($CDCl_3$, 400 MHz): $\delta = 6.72$ (dd, $J = 8.16$ Hz, $J = 15.99$ Hz, 1H), 6.03 (dd, $J = 1.09$ Hz, $J = 15.99$ Hz, 1H), 2.25 (s, 3H), 2.17-2.10 (m, 1H), 1.69-1.62 (m, 1H), 1.03 (d, $J = 6.80$ Hz, 3H), 0.88 (t, $J = 6.73$ Hz, 3H).

^{13}C -NMR ($CDCl_3$, 100 MHz): $\delta = 198.8, 152.6, 130.4, 43.0, 32.6, 26.9, 19.9, 19.7, 16.3$.

MS (EI, 70 eV), m/z (%): 140.12 (11, M^+), 125 (25), 107 (9), 98 (100), 97 (58), 83 (76), 70 (18), 55 (22), 42 (70).

IR (neat, v/cm^{-1}): 2960, 2930, 2874, 1674, 1624, 1459, 1359, 1253, 982.

HRMS (EI): calcd. for $C_9H_{16}O$ [M^+]: 140.1201, found: 140.1200.

(-)-(4*R*,2*E*)- 1-Furan-2-yl-4,5-dimethyl-hex-2-en-1-one ((-)-(R)-6d):

Prepared according to **TP3** using (3*R*,1*E*)-tert-Butyl-(3,4-dimethyl-pent-1-enyl)-dimethylsilane **1b** (127 mg, 0.6 mmol, 90% *ee*), $AlCl_3$ (97 mg, 0.73 mmol, 1.2 equiv.), furoylchloride (95 mg, 0.73 mmol, 1.2 equiv.) and CH_2Cl_2 (3.0 mL). The resulting mixture was stirred at $-78^\circ C$ to rt for 10 h. After purification by column chromatography (silica gel, pentane/ Et_2O , 98:2), (-)-(R)-**6d** was obtained as a colorless oil (76 mg, 0.40 mmol, 66%, 90% *ee*).

$[\alpha]_D^{20} = -28.2$ ($c = 0.95$, $CHCl_3$)

1H -NMR ($CDCl_3$, 400 MHz): $\delta = 7.61$ (dd, $J = 1.69$ Hz, $J = 0.75$ Hz, 1H), 7.23 (dd, $J = 3.58$ Hz, $J = 0.75$ Hz, 1H), 7.10 (dd, $J = 8.30$ Hz, $J = 15.49$ Hz, 1H), 6.75 (dd, $J = 1.13$ Hz, $J = 15.49$ Hz, 1H), 6.55 (dd, $J = 1.71$ Hz, $J = 3.55$ Hz, 1H), 2.25-2.20 (m, 1H), 1.72-1.65 (m, 1H), 1.07 (d, $J = 6.79$ Hz, 3H), 0.91 (t, $J = 6.75$ Hz, 3H), 0.89 (t, $J = 6.75$ Hz, 3H).

^{13}C -NMR ($CDCl_3$, 100 MHz): 178.2, 153.4, 146.4, 123.9, 117.4, 112.2, 43.3, 32.7, 19.9, 19.7, 16.3.

MS (EI, 70 eV), m/z (%): 192.11 (57, M^+), 177 (55), 150 (43), 134 (14), 121 (100), 110 (63), 95 (85), 79 (19), 55 (11), 43 (14).

IR (neat, v/cm^{-1}): 2960, 2928, 2873, 1665, 1618, 1568, 1465, 1394, 1009, 756.

HRMS (EI): calcd. for $C_{12}H_{16}O_2$ [M^+]: 192.1150, found: 192.1161.

(-)-(6*R*,4*E*)- 2,2,6-Trimethyl-oct-4-en-3-one ((-)-(R)-6e):

Prepared according to **TP3** using (3*R*,1*E*)-tert-butyl-dimethyl-(3-methyl-pent-1-enyl)-silane **1c** (168 mg, 0.85 mmol, 88% *ee*), $AlCl_3$ (125 mg, 0.93 mmol, 1.2 equiv.), pivaloylchloride (112 mg, 0.93 mmol, 1.2 equiv.) and CH_2Cl_2 (4.0 mL). The resulting mixture was stirred at $-78\text{ }^{\circ}C$ to rt for 3 h. After purification by column chromatography (silica gel, pentane/ Et_2O , 98:2), (-)-(R)-**6e** was obtained as a colorless oil (111 mg, 0.60 mmol, 78%, 88% *ee*).

$[\alpha]_D^{20} = -18.4$ ($c = 1.25$, $CHCl_3$)

1H -NMR ($CDCl_3$, 400 MHz): $\delta = 6.81$ (dd, $J = 7.98$ Hz, $J = 15.30$ Hz, 1H), 6.44 (dd, $J = 1.10$ Hz, $J = 15.30$ Hz, 1H), 2.41-2.16 (m, 1H), 1.41-1.36 (m, 2H), 1.15 (s, 9H), 1.04 (d, $J = 6.73$ Hz, 3H), 0.86 (t, $J = 7.42$ Hz, 3H).

^{13}C -NMR ($CDCl_3$, 100 MHz): 204.6, 152.6, 122.5, 42.9, 38.4, 28.8, 26.2, 19.2, 11.6.

MS (EI, 70 eV), m/z (%): 168.15 (4, M^+), 111 (100), 83 (1), 69 (5), 55 (5), 41 (5).

IR (neat, v/cm^{-1}): 2963, 2930, 2873, 1689, 1623, 1477, 1457, 1351, 1076, 985.

HRMS (EI): calcd. for $C_{11}H_{20}O$ [M^+]: 168.1514, found: 168.1528.

(-)-(4*S*,2*E*)- 1,4-Diphenyl-pent-2-en-1-one ((-)-(S)-6f):

Prepared according to **TP3** using (3*R*,1*E*)-tert-butyl-dimethyl-(3-methyl-pent-1-enyl)-silane **1d** (90 mg, 0.36 mmol, 89% *ee*), $AlCl_3$ (53 mg, 0.43 mmol, 1.2 equiv.), benzoylchloride (0.046 mL, 0.43 mmol, 1.2 equiv.) and CH_2Cl_2 (3.0 mL). The resulting mixture was stirred at $-78\text{ }^{\circ}C$ to rt for 3 h. After purification by column chromatography (silica gel, pentane/ Et_2O , 9:1), (-)-(S)-**6f** was obtained as a colorless oil (60 mg, 0.26 mmol, 71%, 89% *ee*).

$[\alpha]_D^{20} = -5.6$ ($c = 1.06$, $CHCl_3$)

1H -NMR ($CDCl_3$, 400 MHz): $\delta = 7.91$ -7.88 (m, 2H), 7.57-7.52 (m, 1H), 7.47-7.43 (m, 2H), 7.36-7.33 (m, 2H), 7.27-7.24 (m, 3H), 7.21 (dd, $J = 6.77$ Hz, $J = 15.48$ Hz, 1H), 6.84 (dd, $J = 1.48$ Hz, $J = 15.48$ Hz, 1H), 3.77-3.70 (m, 1H), 1.51 (d, $J = 7.05$ Hz, 3H).

^{13}C -NMR ($CDCl_3$, 100 MHz): 191.1, 153.1, 143.4, 137.9, 132.6, 128.7, 128.5, 128.4, 127.4, 126.7, 124.4, 42.5, 20.5.

MS (EI, 70 eV), m/z (%): 236. 11 (9, M^+), 221 (5), 207 (2), 157 (2), 131 (19), 115 (12), 105 (100), 91 (14), 77 (39), 50 (3).

IR (neat, v/cm^{-1}): 3060, 3027, 2967, 2929, 2872, 1667, 1616, 1447, 1286, 1252, 1212, 1006, 759.

HRMS (EI): calcd. for $C_{17}H_{16}O$ [M^+]: 236.1201, found: 236. 1178.

(+)-(4S,2E)- 4-Ethyl-1-phenyl-non-2-en-1-one ((+)-(S)-6g):

Prepared according to **TP3** using (3*S*,1*E*)- (3-Ethyl-oct-1-enyl)-dimethyl-phenyl-silane **1i** (200 mg, 0.72 mmol, 89% *ee*), AlCl₃ (115 mg, 0.86 mmol, 1.2 equiv.), benzoylchloride (0.10 mL, 0.86 mmol, 1.2 equiv.) and CH₂Cl₂ (5.0 mL). The resulting mixture was stirred at –78 °C to 0 °C for 6 h. After purification by column chromatography (silica gel, pentane/Et₂O, 95:5), (+)-(S)-**6g** was obtained as a colorless oil (140 mg, 0.58 mmol, 80%, 89% *ee*).

$[\alpha]_D^{20} = + 8.4$ (*c* = 1.055, CHCl₃)

¹H-NMR (CDCl₃, 300 MHz): δ = 7.94-7.91 (m, 2H), 7.55-7.44 (m, 3H), 6.84-6.82 (m, 2H), 2.21-2.13 (m, 1H), 1.55-1.27 (m, 10H), 0.92-0.85 (m, 6H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 190.9, 154.3, 138.1, 132.5, 128.5, 128.4, 125.8, 45.0, 34.1, 31.9, 27.3, 27.0, 22.5, 14.1, 11.8.

MS (EI, 70 eV), *m/z* (%): 244.18 (48, M⁺), 215 (27), 187 (45), 173 (23), 159 (14), 124 (14), 120 (22), 105 (100), 91 (10), 77 (21).

IR (neat, v/cm⁻¹): 2958, 2927, 2856, 1669, 1618, 1447, 1361, 1284, 1248, 1213, 983, 769, 694, 658.

HRMS (EI): calcd. for C₁₇H₂₄O [M⁺]: 244.1827, found: 244.1838.

(+)-(4R,2E)- 4-Isopropyl-1-phenyl-non-2-en-1-one ((+)-(R)-6h):

Prepared according to **TP3** using (3*R*,1*E*)-(3-Isopropyl-oct-1-enyl)-dimethyl-phenyl-silane **1j** (269 mg, 0.93 mmol, 87% *ee*), AlCl₃ (150 mg, 1.12 mmol, 1.2 equiv.), benzoylchloride (0.13 mL, 0.86 mmol, 1.2 equiv.) and CH₂Cl₂ (5.0 mL). The resulting mixture was stirred at –78 °C to –30 °C for 3 h. After purification by column chromatography (silica gel, pentane/Et₂O, 98:2), (+)-(R)-**6h** was obtained as a colorless oil (206 mg, 0.80 mmol, 86%, 87% *ee*).

$[\alpha]_D^{20} = + 12.1$ (*c* = 1.22, CHCl₃)

HPLC (column: OD-H; *n*-heptane 100%, 0.5 mL/min): *t_R*(min) = 46.93 (*S*, minor), 50.70 (*R*, major).

¹H-NMR (CDCl₃, 300 MHz): δ = 7.94-7.91 (m, 2H), 7.58-7.44 (m, 3H), 6.92-6.77 (m, 2H), 2.11-2.00 (m, 1H), 1.81-1.64 (m, 1H), 1.58-1.27 (m, 8H), 0.94 (d, *J* = 6.76 Hz, 3H), 0.92 (m, 6H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 190.7, 152.8, 138.2, 132.5, 128.5, 128.4, 126.7, 49.9, 31.9, 31.8, 31.6, 27.4, 22.5, 20.7, 19.3, 14.1.

MS (EI, 70 eV), *m/z* (%): 258.19 (36, M⁺), 215 (59), 187 (37), 159 (61), 145 (23), 133 (20), 120 (45), 105 (100), 91 (14), 77 (30), 43 (13).

IR (neat, ν/cm^{-1}): 2955, 2927, 2871, 2856, 1668, 1620, 1465, 1447, 1369, 1255, 1214, 1009, 986, 771, 694, 661.

HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{26}\text{O}$ [M^+]: 258.1984, found: 258.1992.

(+)-(4*S*,2*E*)- 1,4-Diphenyl-non-2-en-1-one ((+)-(S)-6i):

Prepared according to **TP3** using (3*R*,1*E*)-Dimethyl-phenyl-(3-phenyl-oct-1-enyl)-silane **1k** (300 mg, 0.93 mmol), AlCl_3 (149 mg, 1.11 mmol, 1.2 equiv.), benzoylchloride (0.13 mL, 1.11 mmol, 1.2 equiv.) and CH_2Cl_2 (8.0 mL). The resulting mixture was stirred at -78°C to rt for 3 h. After purification by column chromatography (silica gel, pentane/ Et_2O , 95:5), (+)-(S)-**6i** was obtained as a colorless oil (203 mg, 0.70 mmol, 75%, 89% *ee*).

$[\alpha]_{\text{D}}^{20} = +18.3$ ($c = 1.22$, CHCl_3)

HPLC (column: OD-H; *n*-heptane/*i*PrOH 98:2, 0.5 mL/min): $t_R(\text{min}) = 13.18$ (*R*, minor), 14.96 (*S*, major).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.92\text{--}7.89$ (m, 2H), 7.59–7.54 (m, 1H), 7.49–7.44 (m, 2H), 7.38–7.33 (m, 2H), 7.28–7.24 (m, 3H), 7.20 (dd, $J = 7.88$ Hz, $J = 15.43$ Hz, 1H), 6.85 (d, $J = 15.43$ Hz, 1H), 3.53 (q, $J = 7.58$ Hz, 1H), 1.87–1.84 (m, 2H), 1.32–1.31 (m, 6H), 0.89 (t, $J = 6.52$ Hz, 3H)

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 190.9$, 152.4, 142.5, 137.9, 132.6, 128.7, 128.5, 128.4, 127.7, 126.7, 125.1, 49.1, 35.2, 31.7, 27.2, 22.5, 14.0.

MS (EI, 70 eV), m/z (%): 292.18 (8), 274 (3), 235 (7), 187 (8), 172 (15), 117 (24), 105 (100), 77 (18).

IR (neat, ν/cm^{-1}): 2954, 2927, 2856, 1667, 1615, 1447, 1282, 1250, 1010, 982, 757, 694.

HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{24}\text{O}$ [M^+]: 292.1827, found: 292.186.

(+)-(4*S*,2*E*)- 1-(2-Fluoro-phenyl)-4-methyl-non-2-en-1-one ((+)-(S)-6j):

Prepared according to **TP3** using (3*S*,1*E*)-Dimethyl-(3-methyl-oct-1-enyl)-phenyl silane **1h** (340 mg, 1.3 mmol, 89% *ee*), AlCl_3 (208 mg, 1.56 mmol, 1.2 equiv.), 2-fluorobenzoylchloride (0.18 mL, 1.56 mmol, 1.2 equiv.) and CH_2Cl_2 (5.0 mL). The resulting mixture was stirred at -78°C to -40°C for 4 h. After purification by column chromatography (silica gel, pentane/ Et_2O , 98:2), (+)-(S)-**6j** was obtained as a colorless oil (220 mg, 0.88 mmol, 68%, 89% *ee*).

$[\alpha]_{\text{D}}^{20} = +17.7$ ($c = 1.08$, CHCl_3)

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.69$ (dt, $J = 1.82$ Hz, $J = 7.50$ Hz, 1H), 7.54–7.47 (m, 1H), 7.24 (t, $J = 7.53$ Hz, 1H), 7.18–7.11 (m, 1H), 6.87 (dd, $J = 1.89$ Hz, $J = 15.56$ Hz, 1H), 6.66

(dd, $J = 2.67$ Hz, $J = 15.56$ Hz, 1H), 2.45-2.37 (m, 1H), 1.47-1.30 (m, 8H), 1.08 (d, $J = 6.72$ Hz, 3H), 0.88 (t, $J = 6.90$ Hz, 3H).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 190.0, 162.6, 159.2, 155.8, 133.5, 130.8, 127.8, 124.3, 116.5, 116.2, 36.9, 36.0, 31.8, 26.8, 22.5, 19.4, 14.0$.

MS (EI, 70 eV), m/z (%): 248.15 (15, M^+), 191 (29), 177 (12), 163 (5), 151 (8), 138 (12), 123 (100), 109 (17), 95 (17), 55 (8), 43 (10).

IR (neat, v/cm^{-1}): 2958, 2926, 2856, 1670, 1616, 1451, 1285, 1209, 763.

HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{21}\text{FO}$ [M^+]: 248.1576, found: 248.1564.

Procedure for the *ipso*-borodesilylation: formation of the boronic ester derivative **7**:¹⁴

(+)-(3*S*,1*E*)-4,4,5,5-Tetramethyl-2-(3-methyl-oct-1-enyl)-[1,3,2]dioxaborolane ((+)-(*S*)-**7**):

In flame-dried flask equipped with a magnetic stirring bar, an argon inlet, and a septum was placed (3*S*,1*E*)-Dimethyl-(3-methyl-oct-1-enyl)-phenyl silane **1h** (780 mg, 3.0 mmol, 89% *ee*) and dry dichloromethane (2 mL). This solution was cooled to -30 °C and BCl_3 (1.0 M solution in CH_2Cl_2 , 12.0 mL, 12.0 mmol, 4.0 equiv.) was added dropwise. The resulting mixture was stirred at -30 °C for 5 h before a solution of pinacol (1.06 g, 9.0 mmol, 3.0 equiv.) and Et_3N (2.54 mL, 18.0 mmol, 6.0 equiv.) in dichloromethane (5 mL) was added. After stirring the mixture at 24 °C for 16 h, saturated aqueous Na_2CO_3 (ca. 8 mL) was added. The aqueous phase was extracted with Et_2O (3 x 20 mL) and the combined extracts were washed with brine and dried over Mg_2SO_4 . Evaporation of the solvents and purification by column chromatography (silica gel, pentane/ Et_2O , 98:2) afforded (+)-(*S*)-**7** (544 mg, 2.16 mmol, 72% yield) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = +14.6$ ($c = 1.12$, CHCl_3).

^1H -NMR (CDCl_3 , 400 MHz): $\delta = 6.52$ (dd, $J = 7.18$ Hz, $J = 18.03$ Hz, 1H), 5.37 (d, $J = 18.03$ Hz, 1H), 2.19-2.16 (m, 8H), 1.25 (m, 12H), 0.98 (d, $J = 6.74$, 3H), 0.88 (t, $J = 6.90$, 3H).

^{13}C -NMR (CDCl_3 , 100 MHz): $\delta = 160.2, 82.9, 39.4, 36.1, 31.9, 26.9, 24.8, 22.6, 19.5, 14.0$.

MS (EI, 70 eV), m/z (%): 252.23 (10, M^+), 237 (19), 195 (32), 153 (26), 139 (27), 124 (34), 109 (10), 101 (33), 84 (100), 69 (15), 40 (15).

IR (neat, v/cm^{-1}): 2958, 2926, 2857, 1636, 1461, 1359, 1318, 1144, 998, 970, 849, 656.

HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{29}\text{BO}_2$ [M^+]: 252.2261, found: 252.2267.

¹⁴ Itami, K. ; Kamei, T. ; Yoshida, J.-I., *J. Am. Chem. Soc.* **2003**, *125*, 14670.

Procedure for the Suzuki-Miyaura Cross-coupling Reaction:¹⁴**(+)-(3*S*,1*E*)- 4-(3-Methyl-oct-1-enyl)-ethyl benzoate ((+)-(S)-8):**

To a solution of Pd(PPh₃)₄ (60 mg, 0.05 mmol, 5 mol %), in dry dioxane (5.0 mL) were added 4-ethyl-iodobenzoate (276 mg, 1.0 mmol, 1.0 equiv.), (+)-(S)-**7** (252 mg, 1 mmol) and NaOH (2.0 M in water, 1 mL, 2.0 mmol, 2.0 equiv.) at 25 °C. The resulting mixture was stirred at 100 °C for 3 h. After cooling the reaction mixture to room temperature water (ca. 4.0 mL) was added. The aqueous phase was extracted with Et₂O (3 x 20 mL) and the combined organic phases were dried over Mg₂SO₄. Evaporation of the solvents and purification by column chromatography (silica gel, pentane/Et₂O, 98:2) afforded (+)-(S)-**8** (233 mg, 0.85 mmol, 85%, 89% *ee*) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = +40.2$ (*c* = 1.06, CHCl₃).

¹H-NMR (CDCl₃, 300 MHz): δ = 7.96 (d, *J* = 8.40 Hz, 2H), 7.38 (d, *J* = 8.40 Hz, 2H), 6.37 (d, *J* = 15.94 Hz, 1H), 6.22 (dd, *J* = 7.71 Hz, *J* = 15.88 Hz, 1H), 4.36 (q, *J* = 7.11 Hz, 2H), 2.37-2.19 (m, 1H), 1.39 (t, *J* = 7.13 Hz, 3H), 1.31-1.28 (m, 8H), 1.08 (d, *J* = 6.75 Hz, 3H), 0.88 (t, *J* = 6.85 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 166.5, 142.4, 139.8, 129.8, 128.5, 127.2, 125.7, 60.7, 37.3, 36.9, 31.9, 27.0, 22.6, 20.4, 14.3, 14.0.

MS (EI, 70 eV), *m/z* (%): 274.19 (30, M⁺), 229 (23), 203 (44), 176 (31), 159 (29), 148 (15), 131 (100), 129 (28), 115 (21), 91 (9).

IR (neat, v/cm⁻¹): 2956, 2925, 2855, 1714, 1606, 1458, 1269, 1176, 1098, 1019, 969, 763.

HRMS (EI): calcd. for C₁₈H₂₆O₂ [M⁺]: 274.1933, found: 274.1925.

(+)-(3*S*,1*E*)- (3-Methyl-oct-1-enyl)-benzene ((+)-(S)-9):

To a solution of Pd(PPh₃)₄ (55 mg, 0.047 mmol, 5 mol %), in dry dioxane (5.0 mL) were added iodobenzene (194 mg, 0.95 mmol, 1.0 equiv.), (+)-(S)-**7** (240 mg, 0.95 mmol) and NaOH (2.0 M in water, 0.95 mL, 1.9 mmol, 2.0 equiv.) at 25 °C. The resulting mixture was stirred at 100 °C for 3 h. After cooling the reaction mixture to room temperature water (ca. 4.0 mL) was added. The aqueous phase was extracted with Et₂O (3 x 20 mL) and the combined organic phases were dried over Mg₂SO₄. Evaporation of the solvents and purification by column chromatography (silica gel, 100% pentane) afforded (+)-(S)-**9** (160 mg, 0.79 mmol, 83%, 89% *ee*) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = +42.6$ (*c* = 1.65, CHCl₃)

¹H-NMR (CDCl₃, 300 MHz): δ = 7.40-7.19 (m, 5H), 6.37 (d, J = 15.88 Hz, 1H), 6.13 (dd, J = 7.90 Hz, J = 15.88 Hz, 1H), 2.36-2.25 (m, 1H), 1.39-1.32 (m, 8H), 1.11 (d, J = 6.76 Hz, 3H), 0.92 (t, J = 6.89 Hz, 3H).

¹³C-NMR (CDCl₃, 75 MHz): δ = 138.0, 137.1, 128.4, 127.9, 126.7, 125.9, 37.3, 37.1, 32.0, 27.1, 22.6, 20.7, 14.1.

MS (EI, 70 eV), m/z (%): 202.17 (21), 145 (2), 131 (100), 104 (26), 91 (26), 77 (2), 41 (2).

IR (neat, ν/cm^{-1}): 2955, 2924, 2855, 1493, 1449, 963, 744, 690.

HRMS (EI): calcd. for C₁₅H₂₂BO₂ [M⁺]: 202.1721, found: 202.1729.

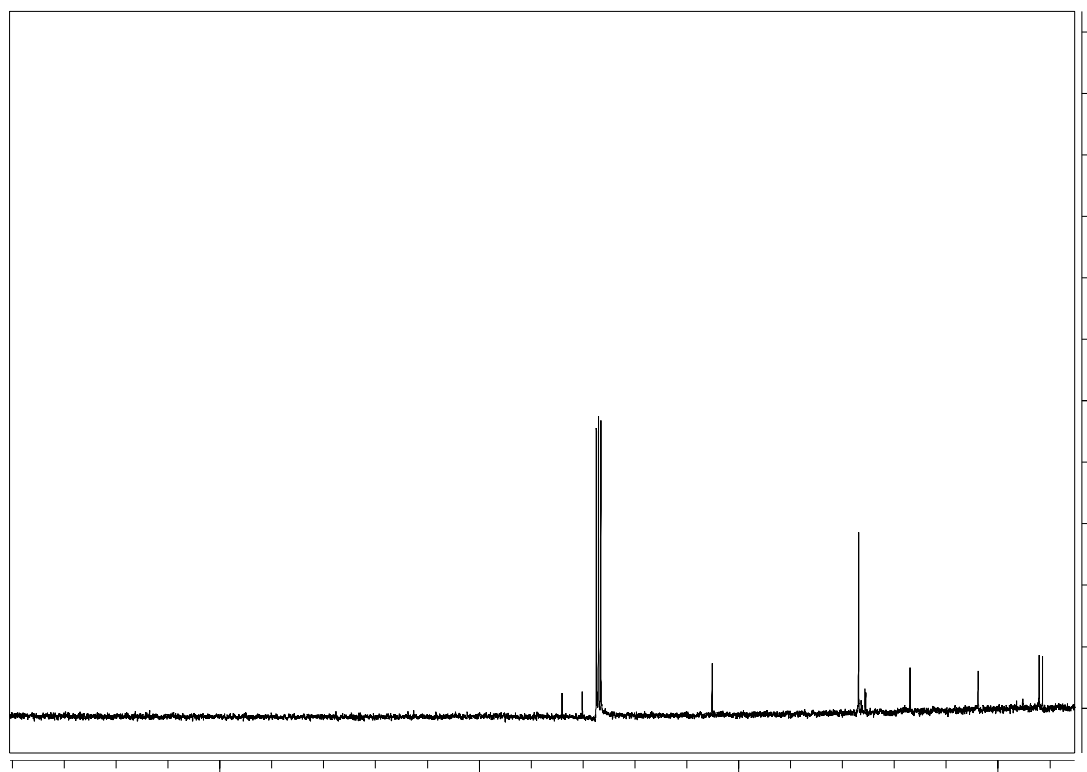
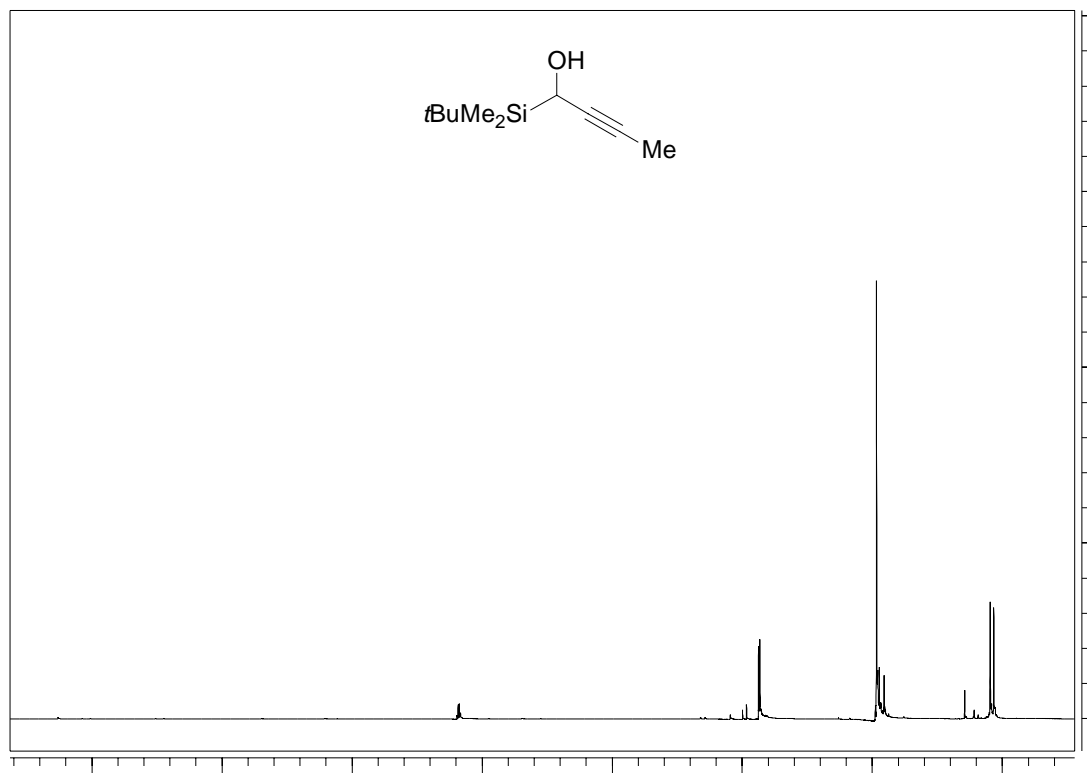
One-pot *ipso*-borodesilylation – Cross-coupling procedure: Synthesis of (+)-(3*S*,1*E*)- (3-Methyl-oct-1-enyl)-benzene ((+)-(S)-9):¹⁵

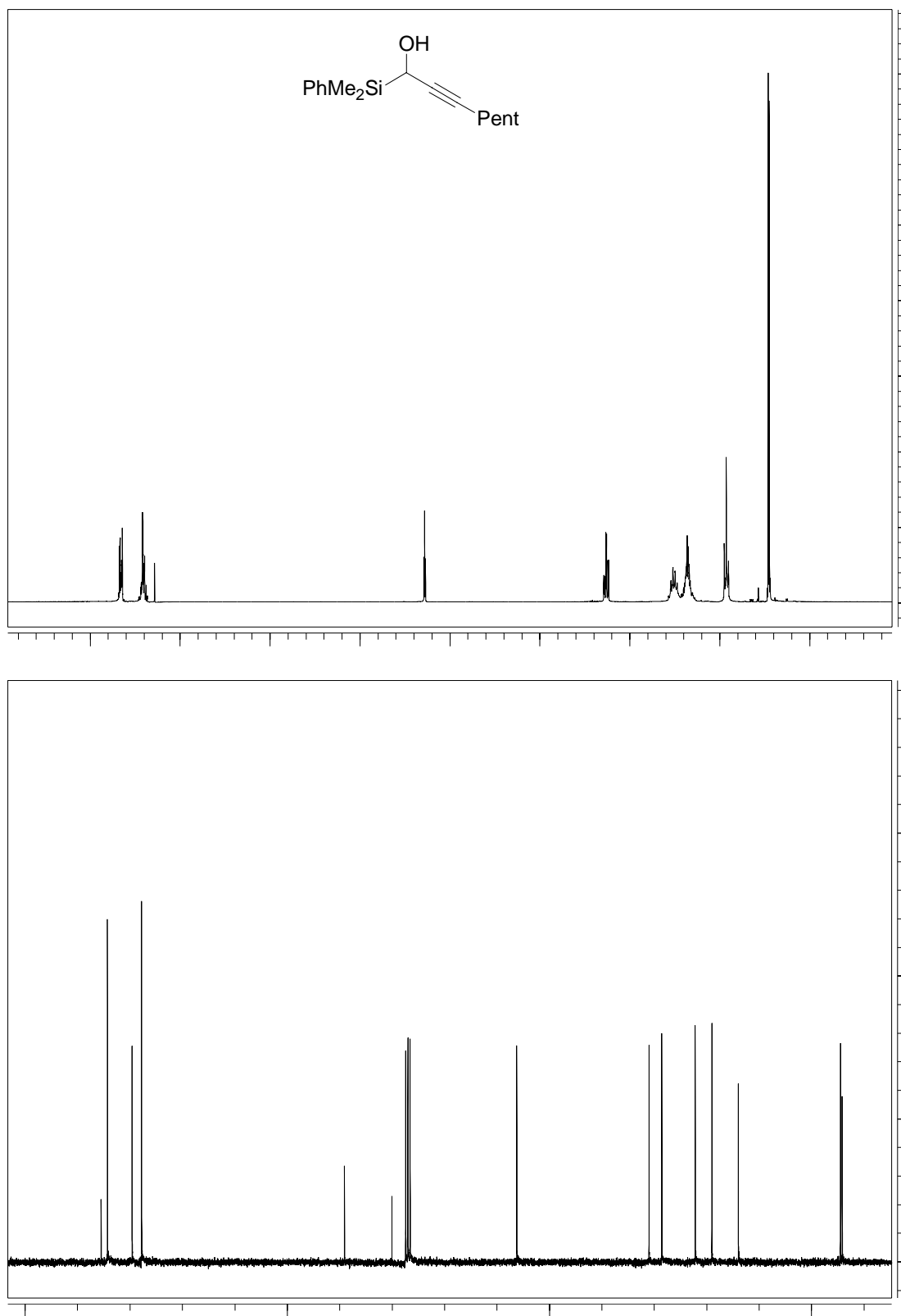
In flame-dried flask equipped with a magnetic stirring bar, an argon inlet, and a septum was placed (3*S*,1*E*)-Dimethyl-(3-methyl-oct-1-enyl)-phenyl silane **1h** (120 mg, 0.5 mmol, 89% *ee*) and dry dichloromethane (0.5 mL). This solution was cooled to –30 °C and BCl₃ (1.0 M solution in CH₂Cl₂, 2.0 mL, 2.0 mmol, 4.0 equiv.) was added dropwise and the resulting mixture was stirred at –30 °C for 5 h. The solvent was evaporated at reduced pressure and the residue was dissolved in toluene (5 mL). Then a solution of iodobenzene (102 mg, 0.5 mmol, 1.0 equiv.) and Pd(PPh₃)₄ (28 mg, 0.025 mmol, 5 mol %) in toluene (3 mL) was added at 25 °C followed by Na₂CO₃ (2.0 M solution in water, 0.5 mL, 1.0 mmol, 2.0 equiv.). The resulting mixture was stirred at 90 °C for 5 h. After cooling the reaction mixture to room temperature water (ca. 4.0 mL) was added. The aqueous phase was extracted with Et₂O (3 x 10 mL) and the combined organic phases were dried over Mg₂SO₄. Evaporation of the solvents and purification by column chromatography (silica gel, 100% pentane) afforded (+)-(S)-**9** (60 mg, 0.30 mmol, 60 %, 89% *ee*) as a colorless oil.

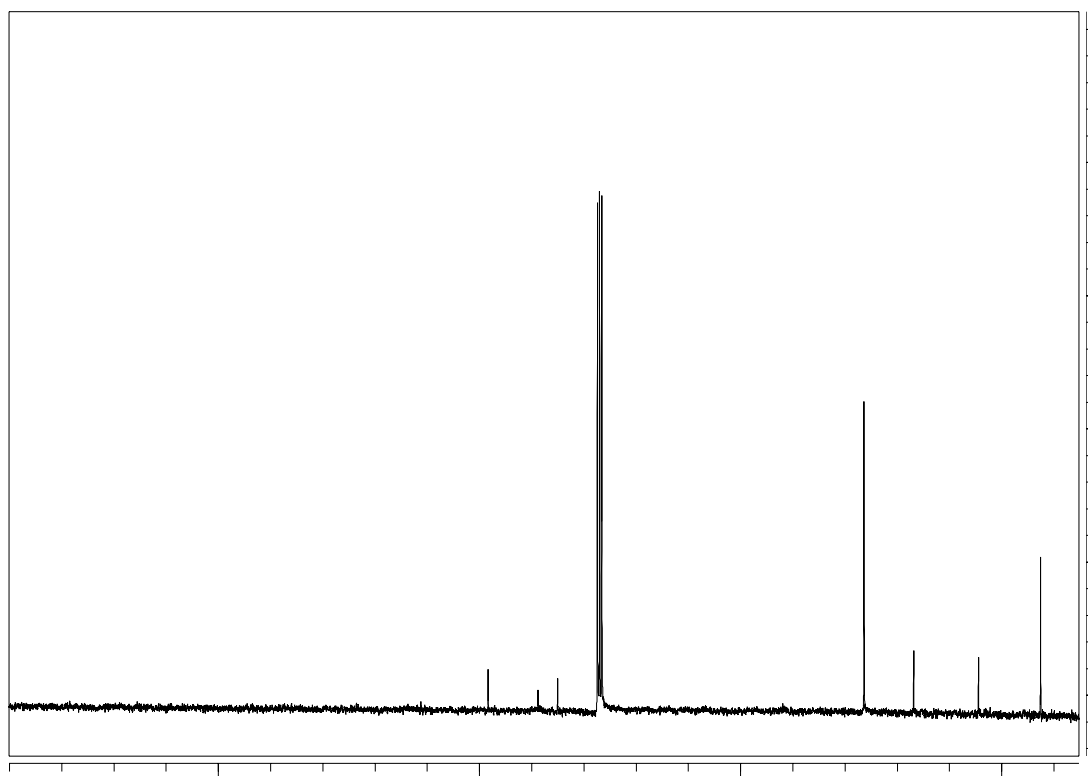
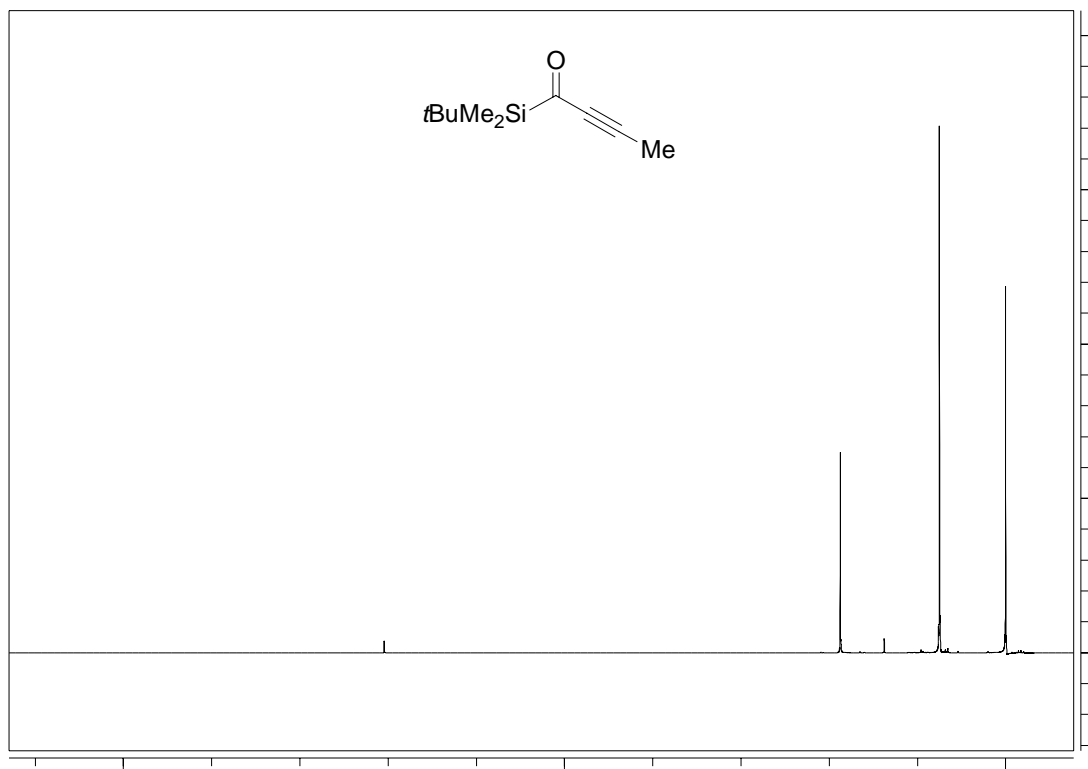
For compound **8** and **9** the *ee* is checked by transformation into (2*S*)-2-methylheptanoic acid by ozonolysis (**TP4**) reaction and showed no lost of the enantiomeric excess.

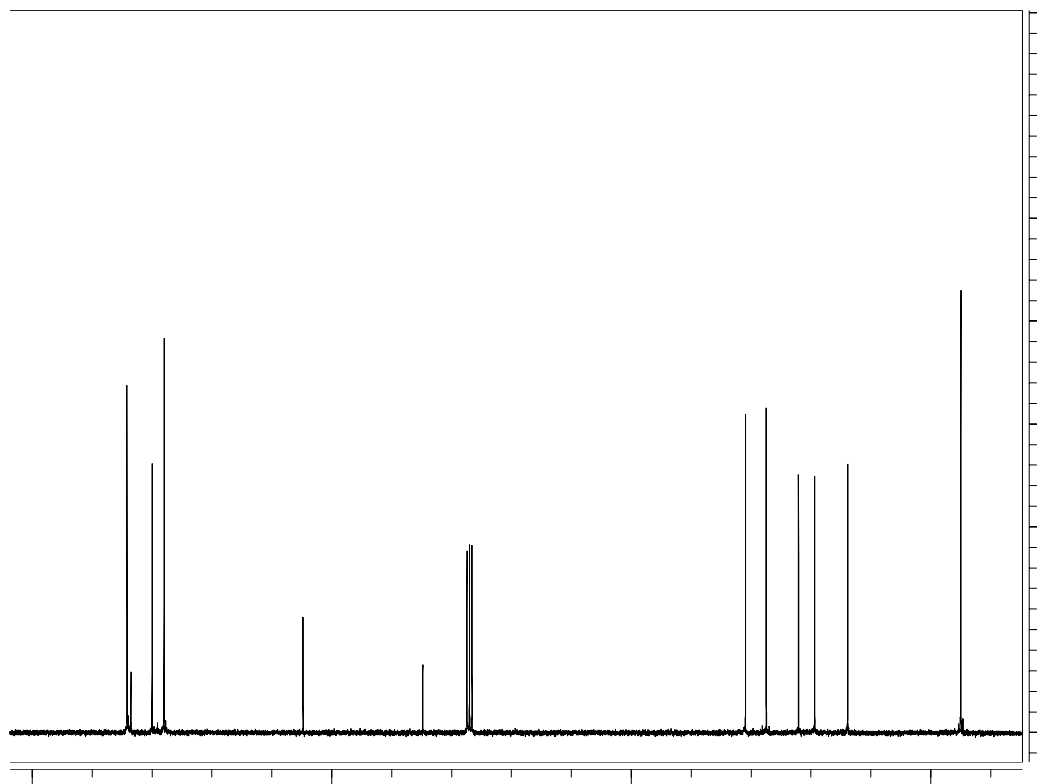
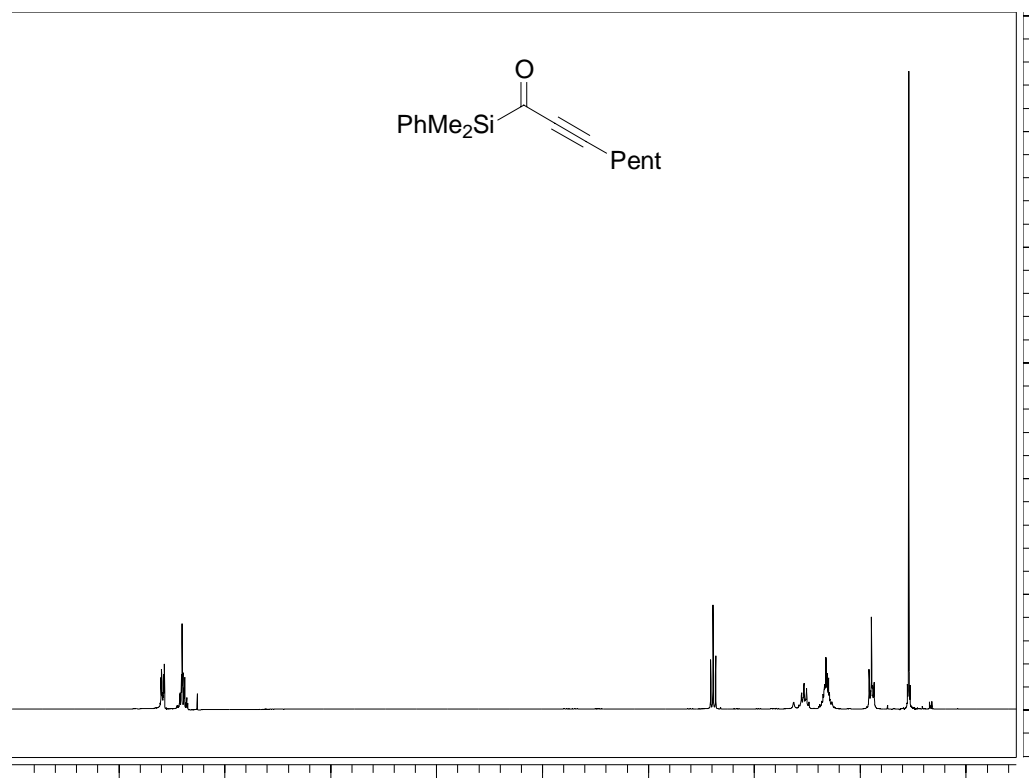
¹⁵ Babudri, F.; Farinola, G. M.; Fiandanese, V.; Mazzone L.; Naso, F. *Tetrahedron* **1998**, *54*, 1085. Zhao, Z.; Snieckus, V. *Org. Lett.* **2005**, *7*, 2523.

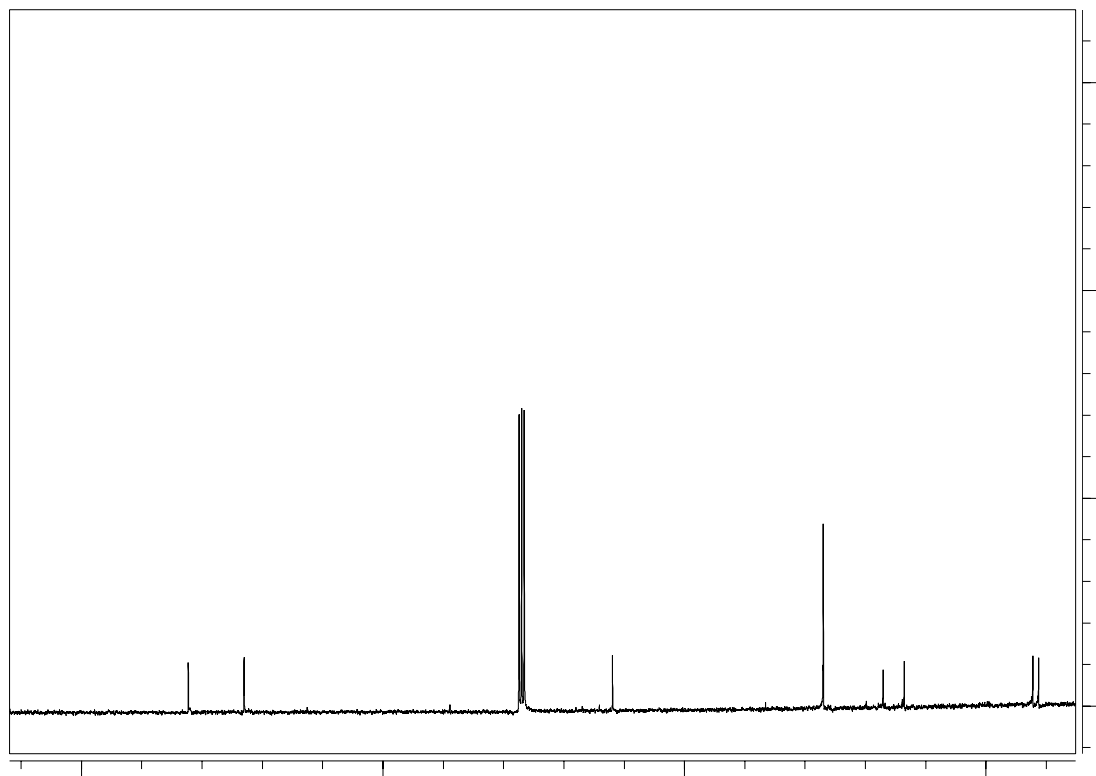
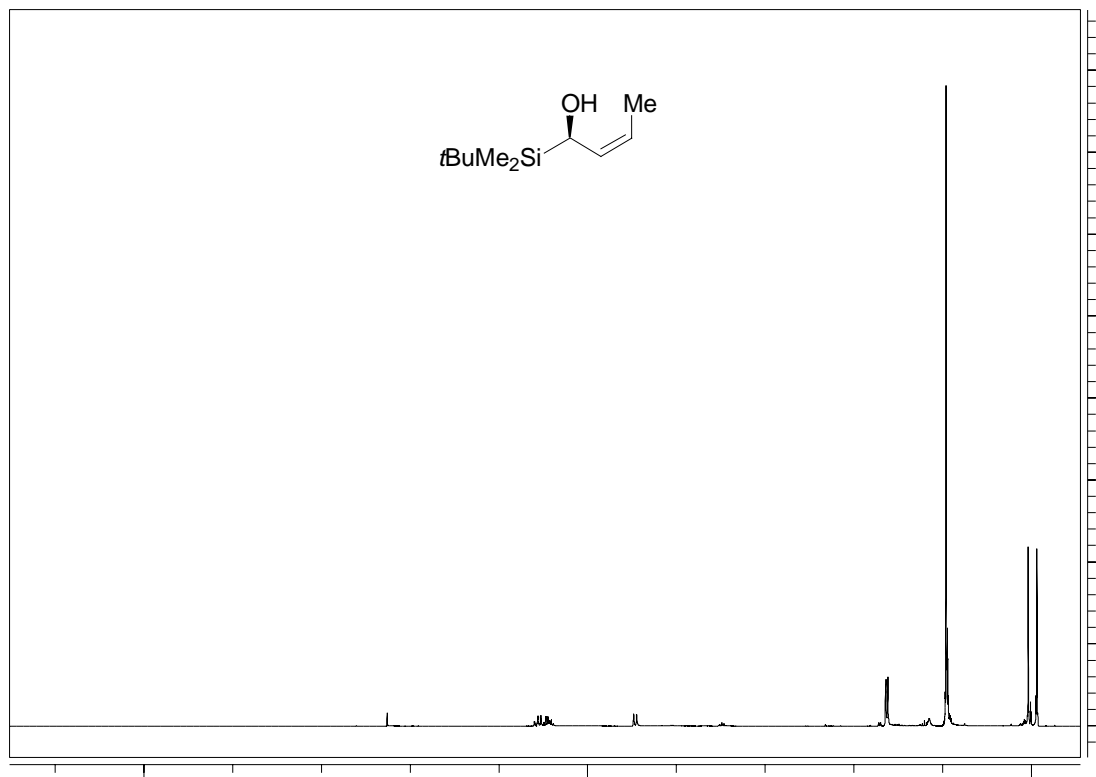
Spectrums:

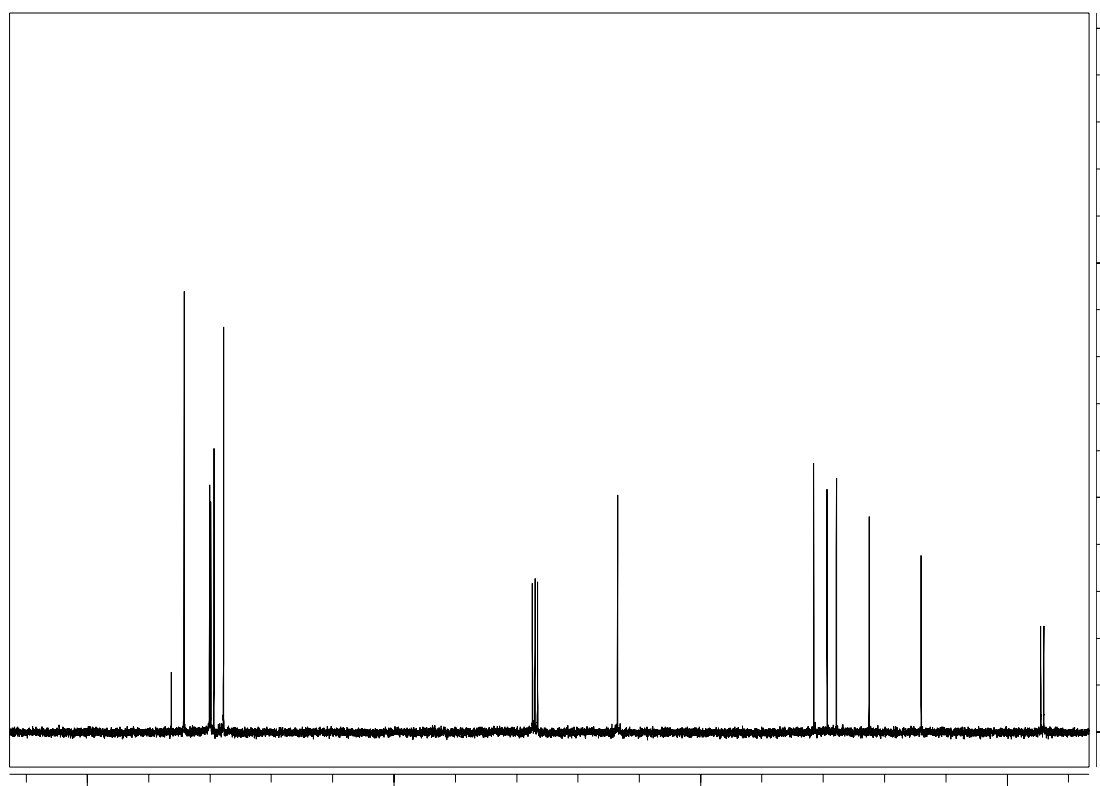
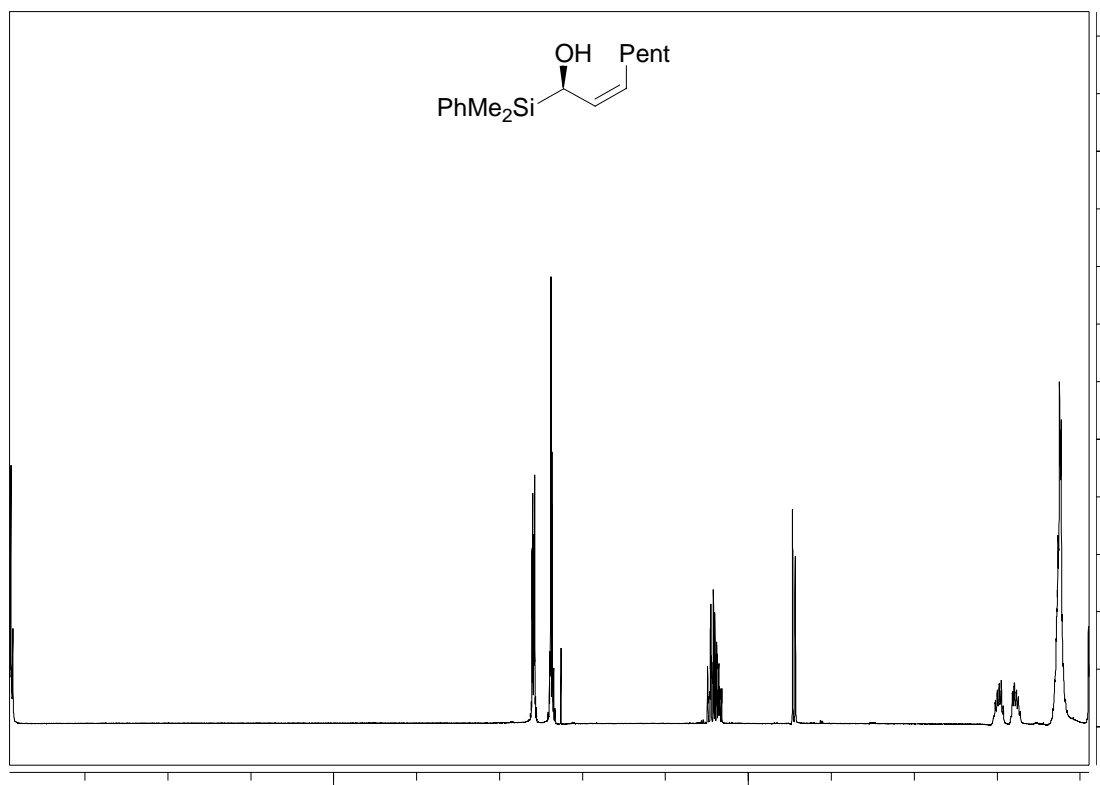
1-(*tert*-Butyl-dimethyl-silanyl)-but-2-yn-1-ol (*rac*-3a):

1-(Dimethyl-phenyl-silanyl)-oct-2-yn-1-ol (*rac*-3b):

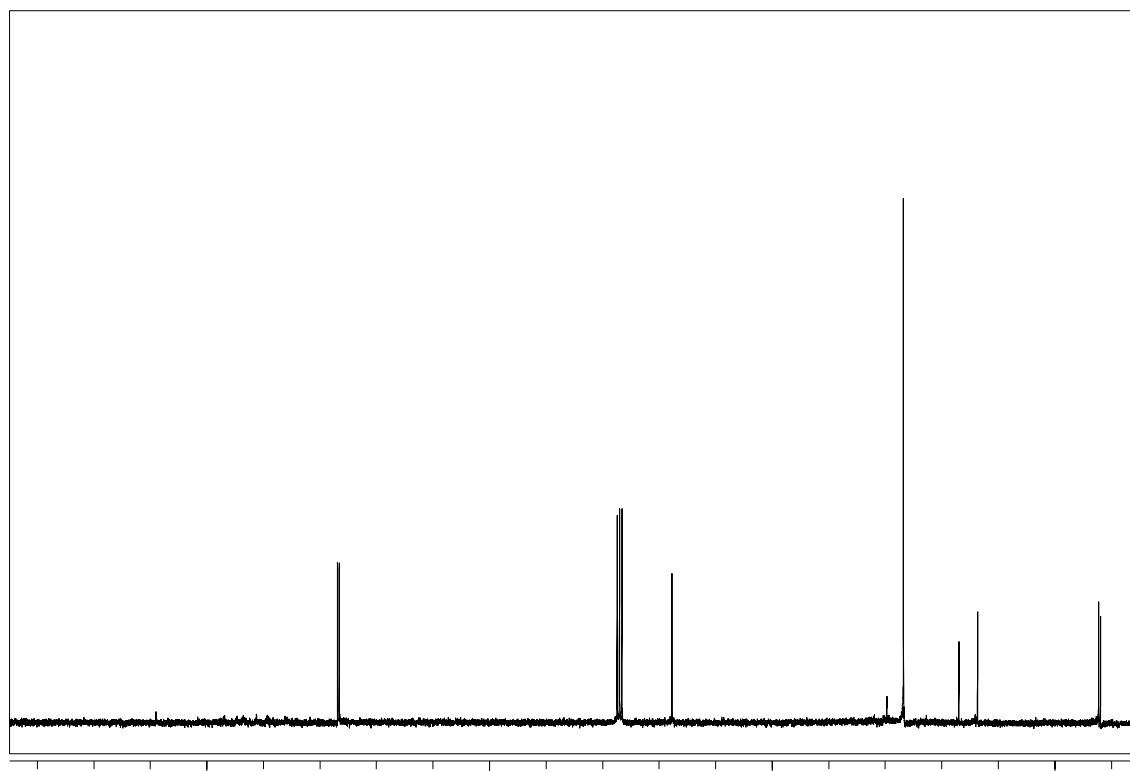
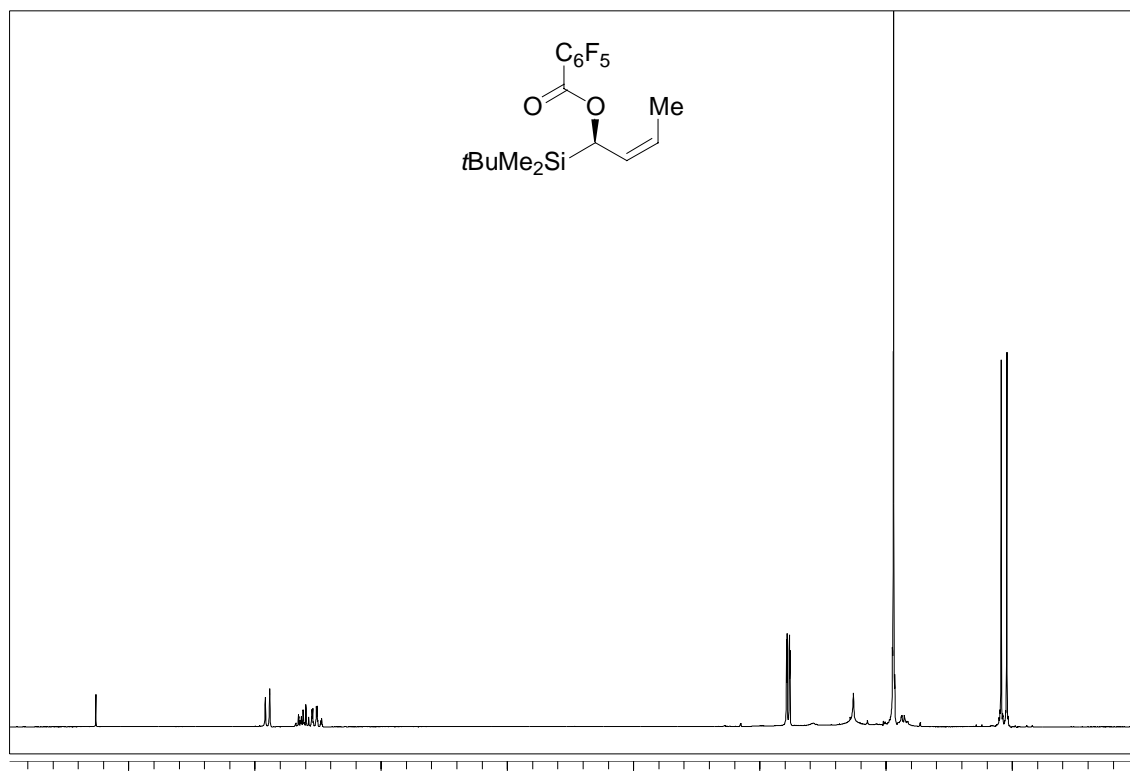
1-(tert-Butyl-dimethyl-silanyl)-but-2-yn-1-one (4a):

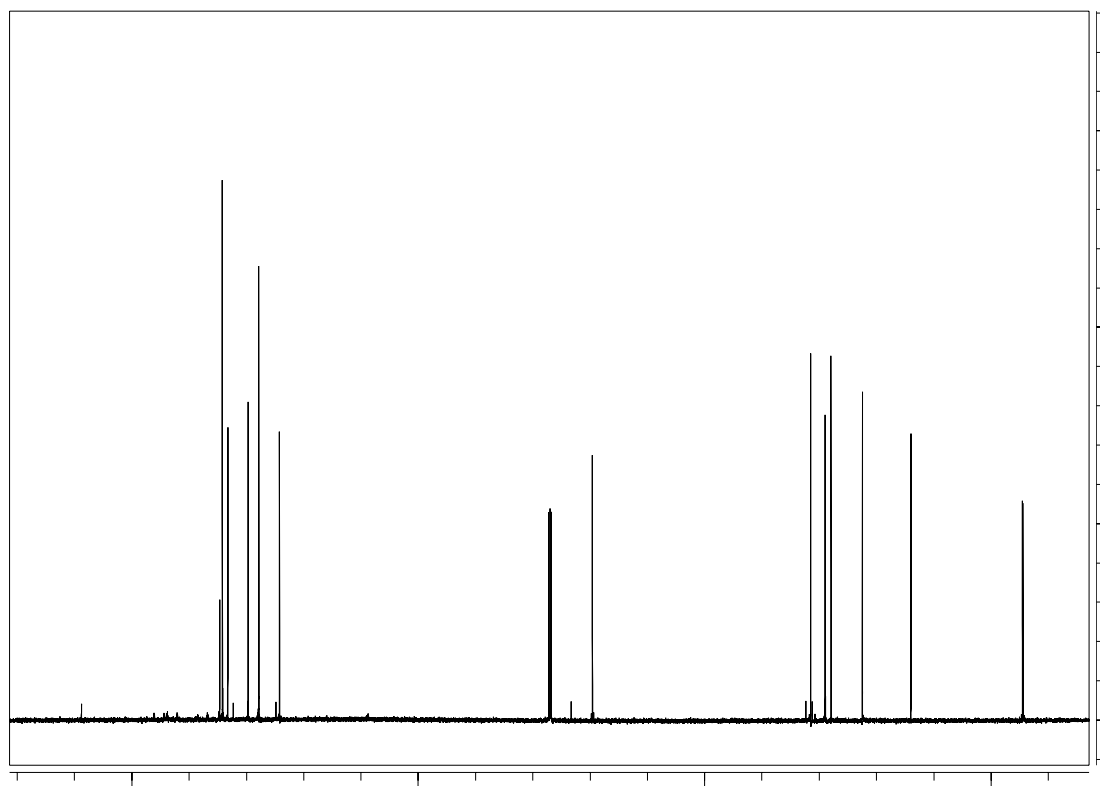
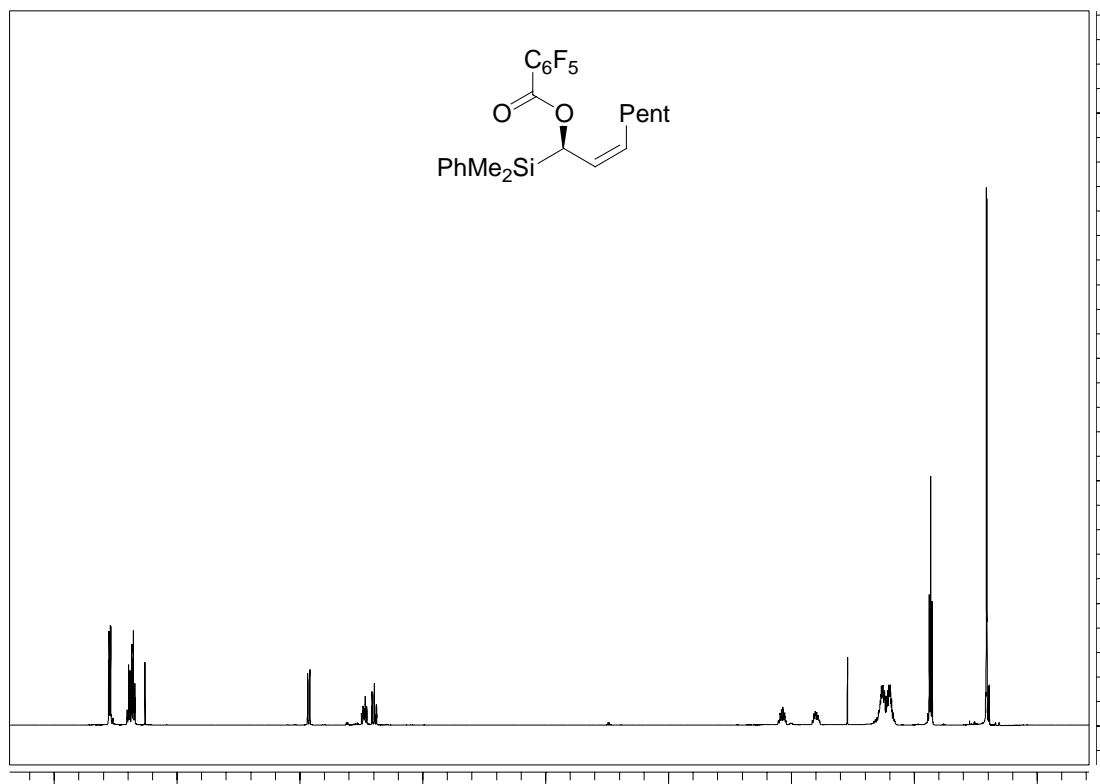
1-(Dimethyl-phenyl-silanyl)-oct-2-yn-1-one (4b) :

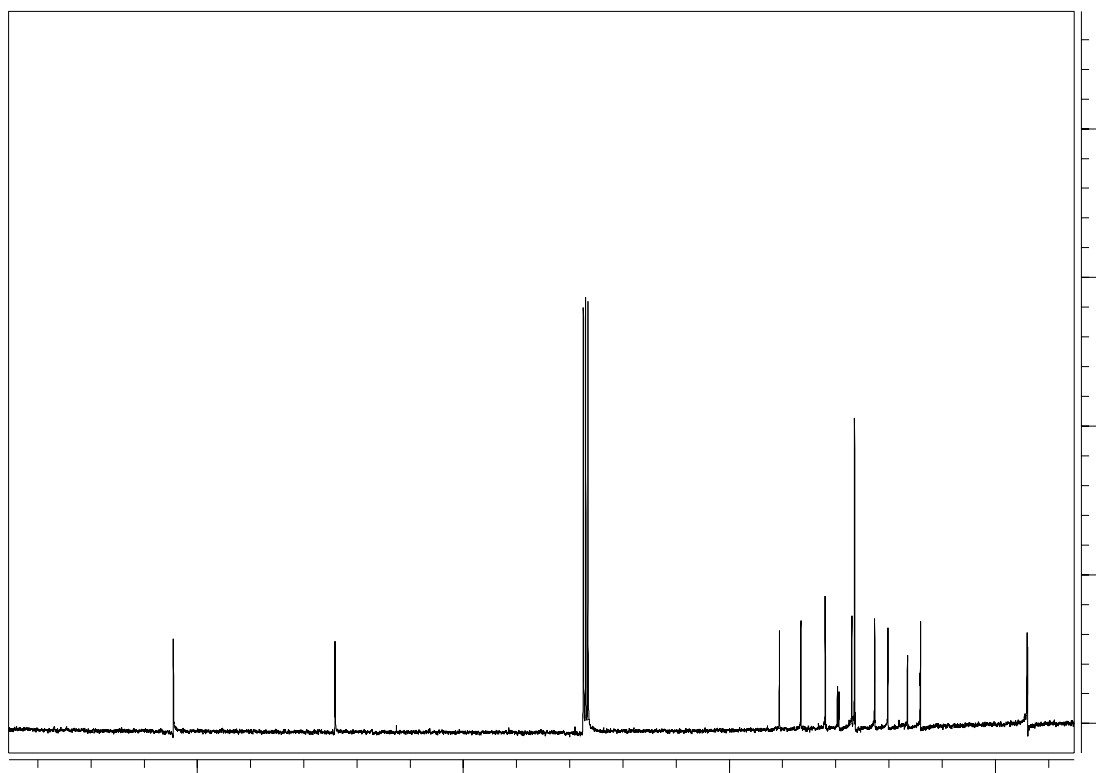
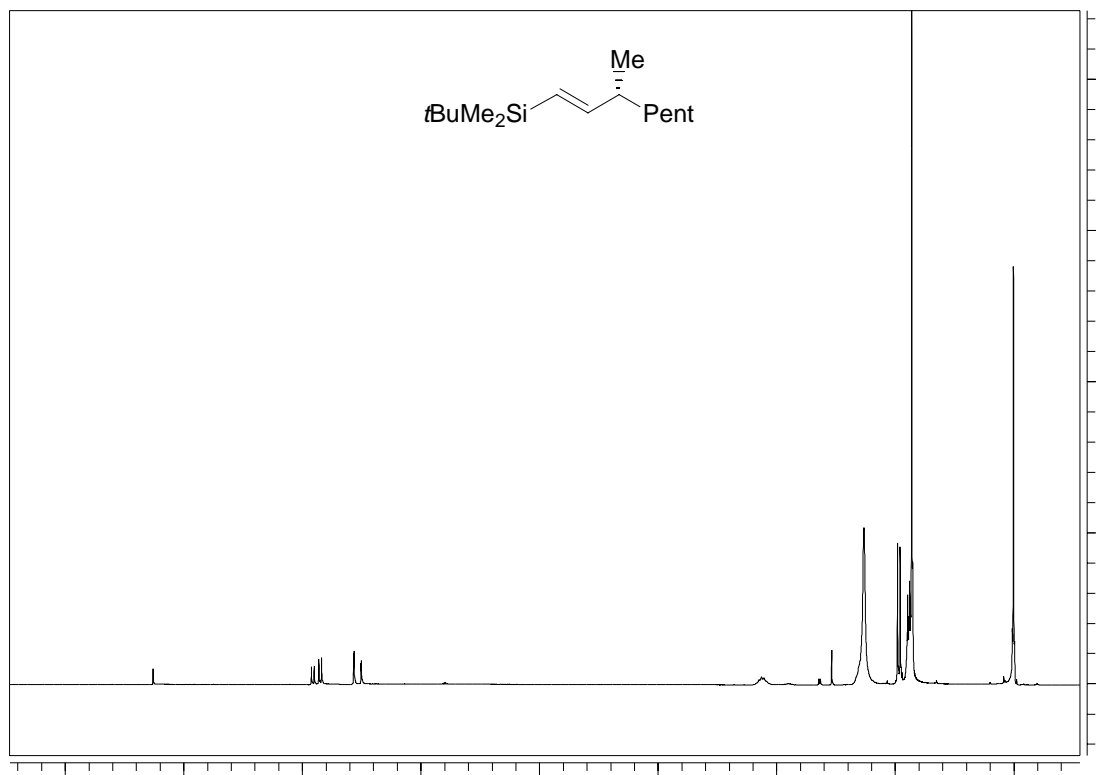
(1*R*,2*Z*)-1-(tert-Butyl-dimethyl-silanyl)-but-2-en-1-ol ((*R*)-5a):

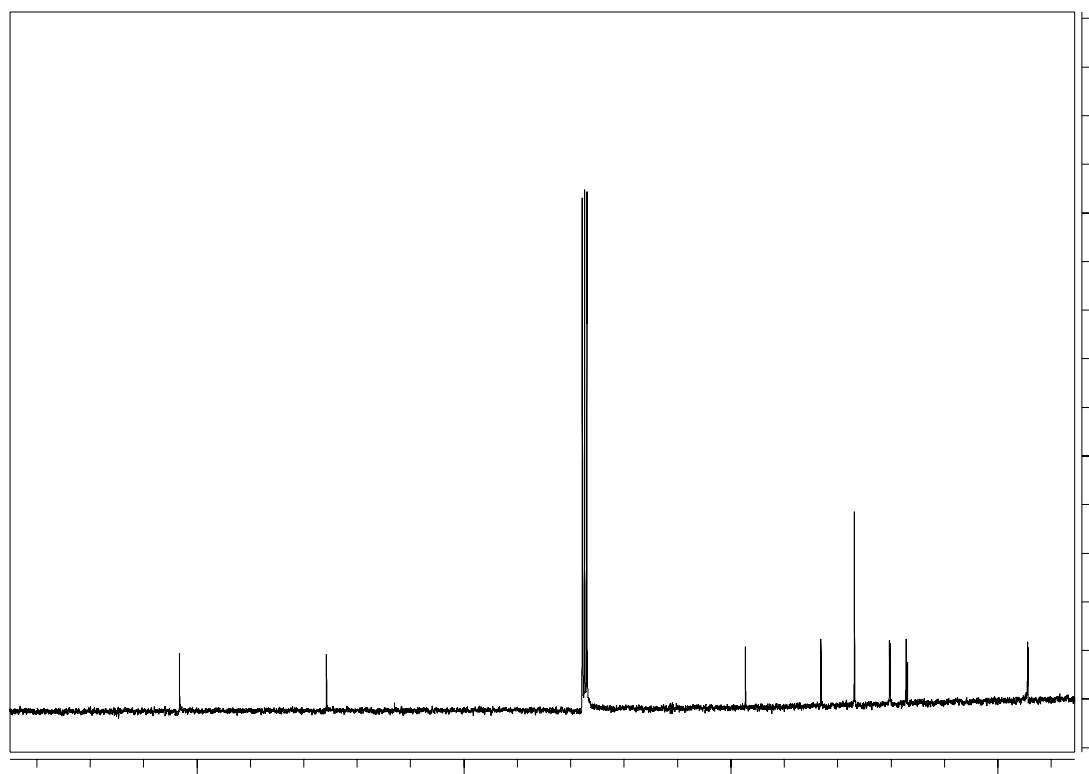
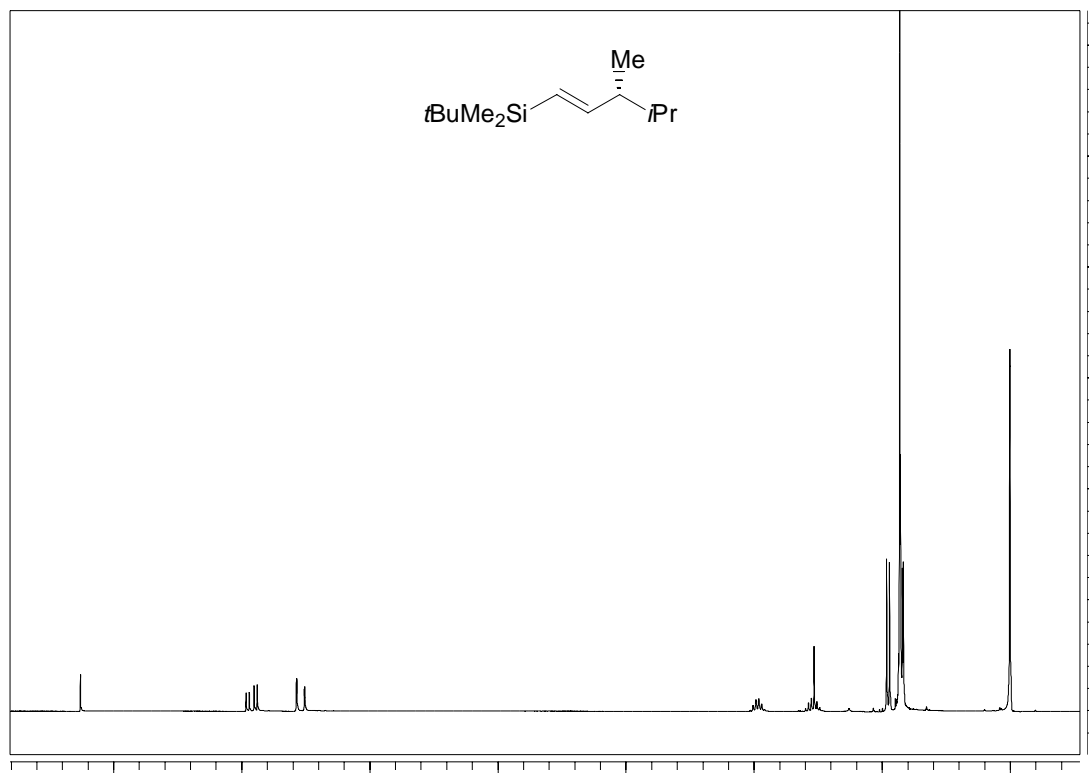
(1*R*,2*Z*)-1-(Dimethyl-phenyl-silanyl)-oct-2-en-1-ol ((*R*)-5b):

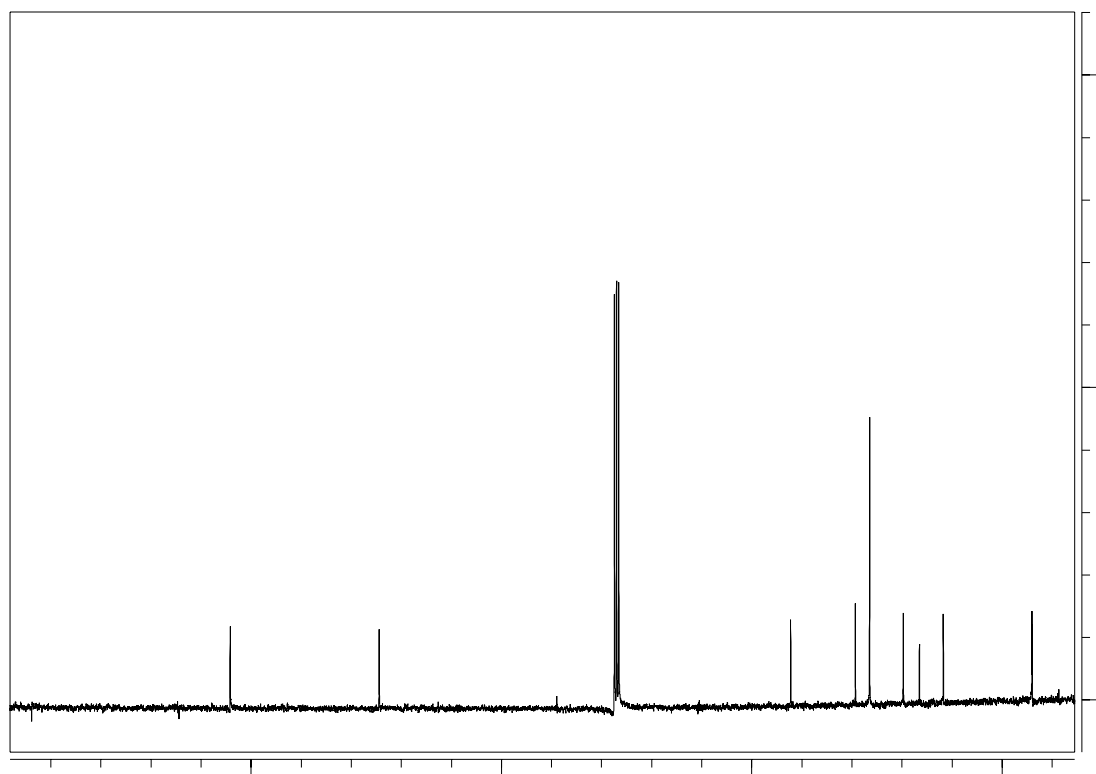
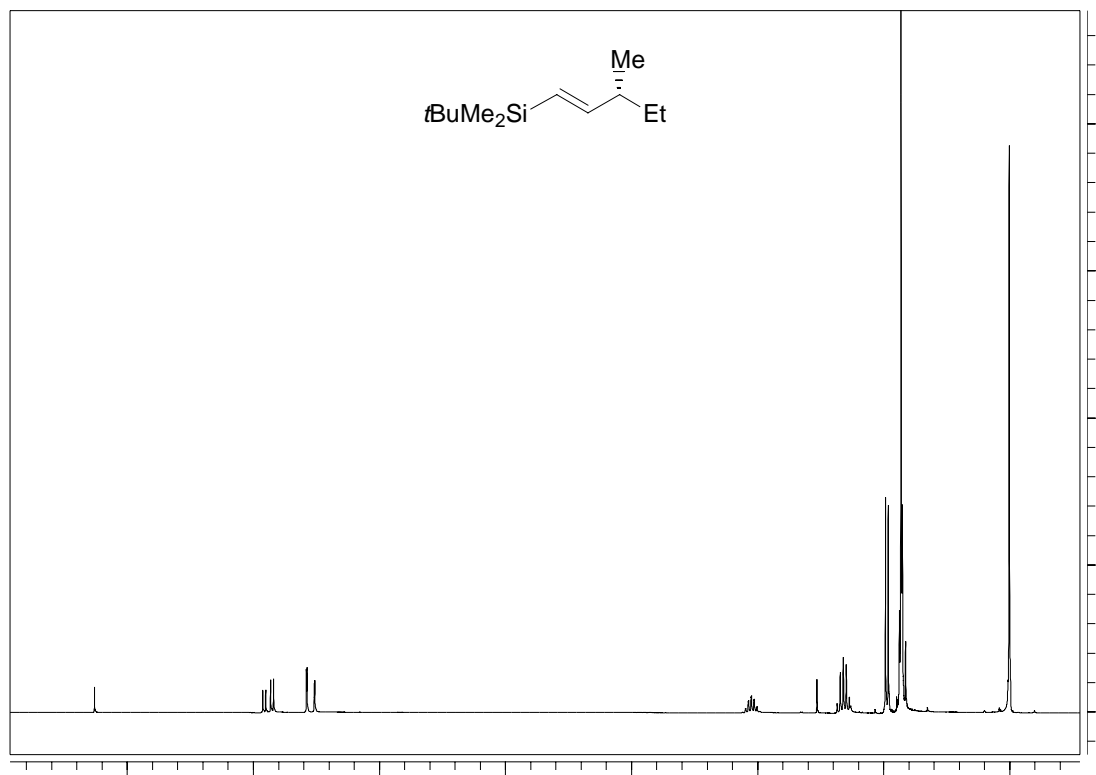
(1*R*,2*Z*)-1-(tert-butyl-dimethyl-silanyl)-but-2-enyl pentafluorobenzoate ((*R*)-2a):

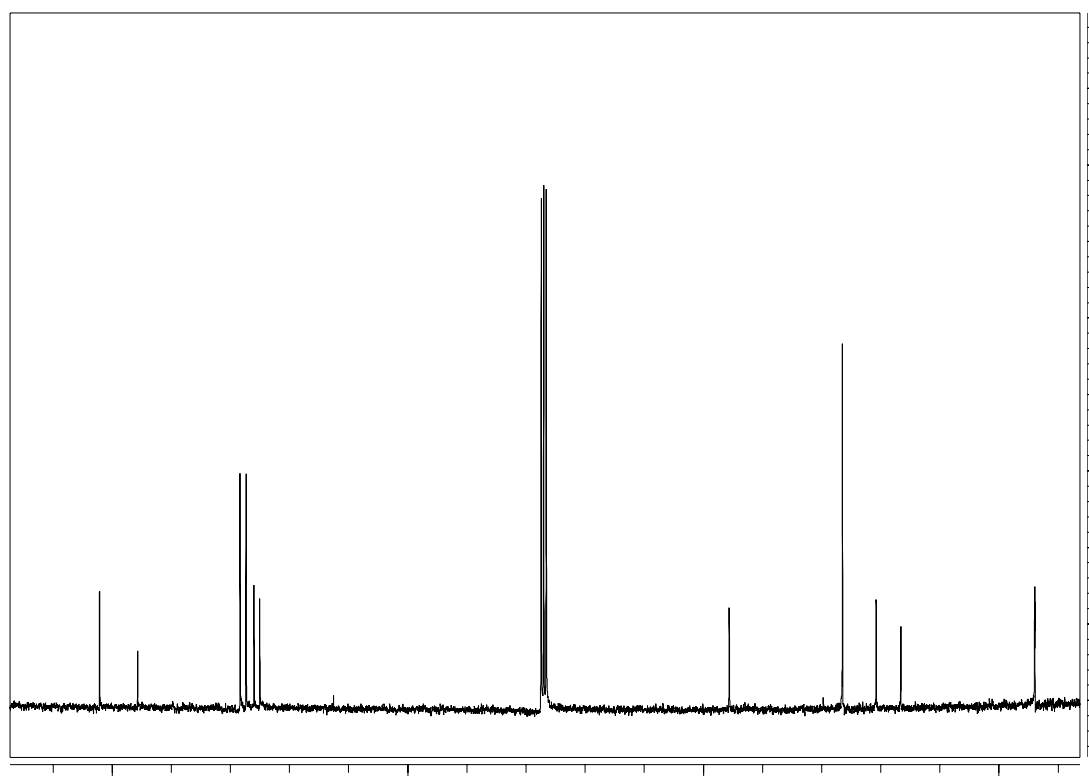
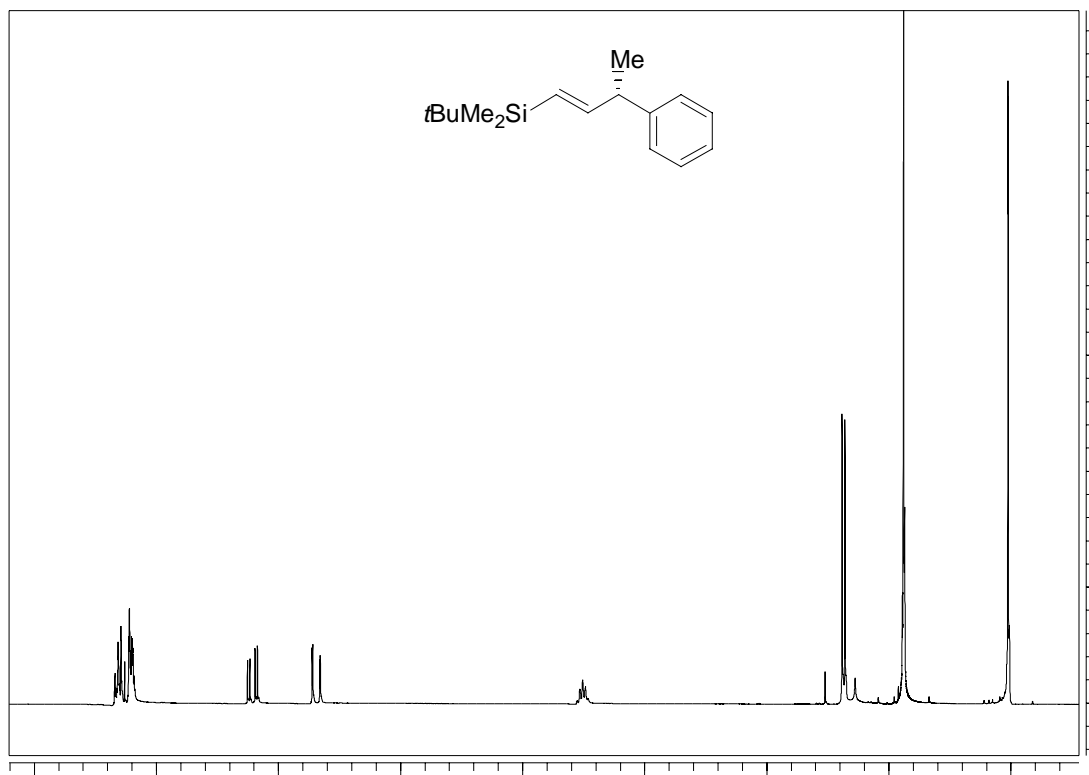


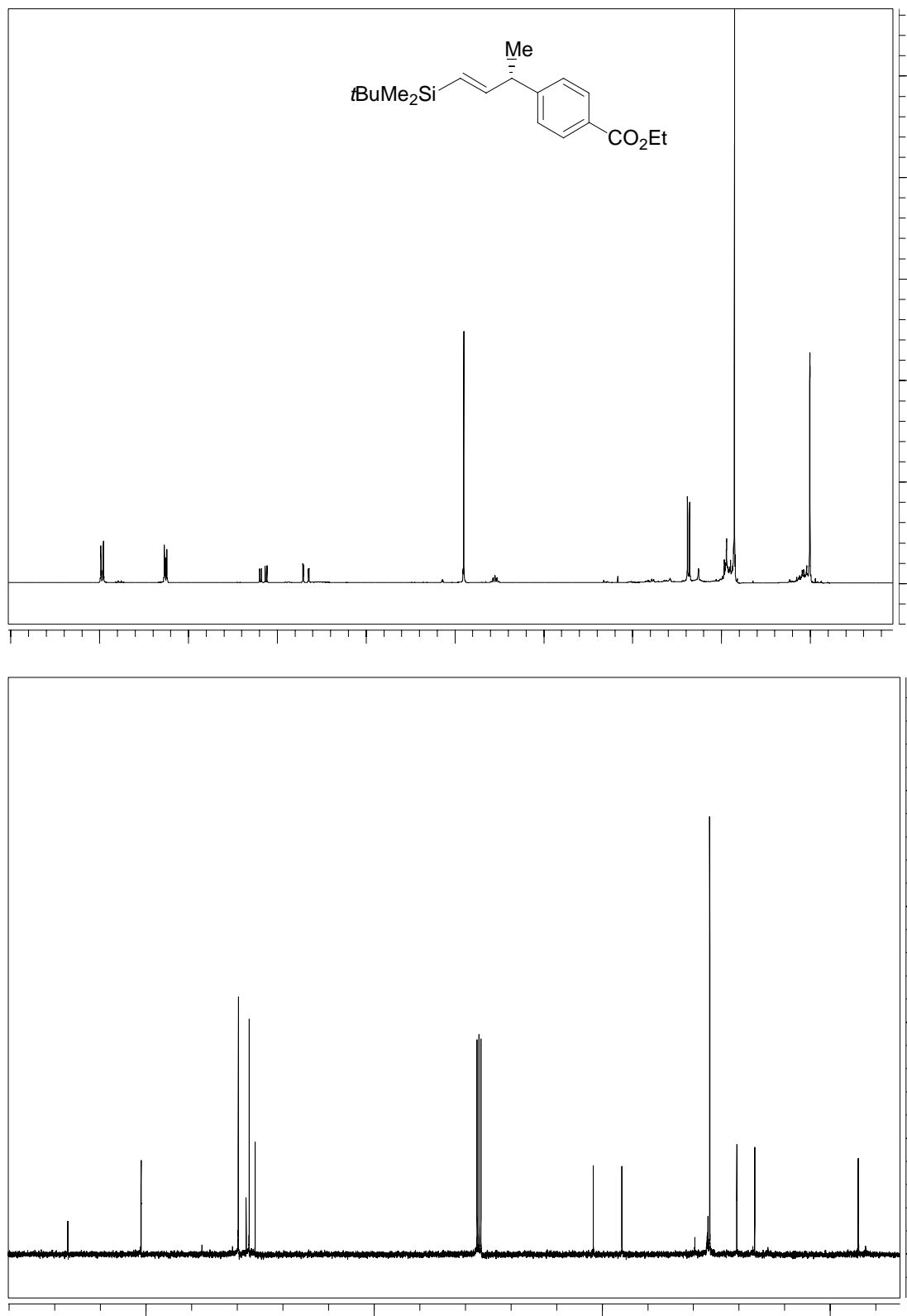
(1*R*,2*Z*)- 1-(dimethyl-phenyl-silanyl)-oct-2-enyl pentafluorobenzoate ((*R*)-2b):

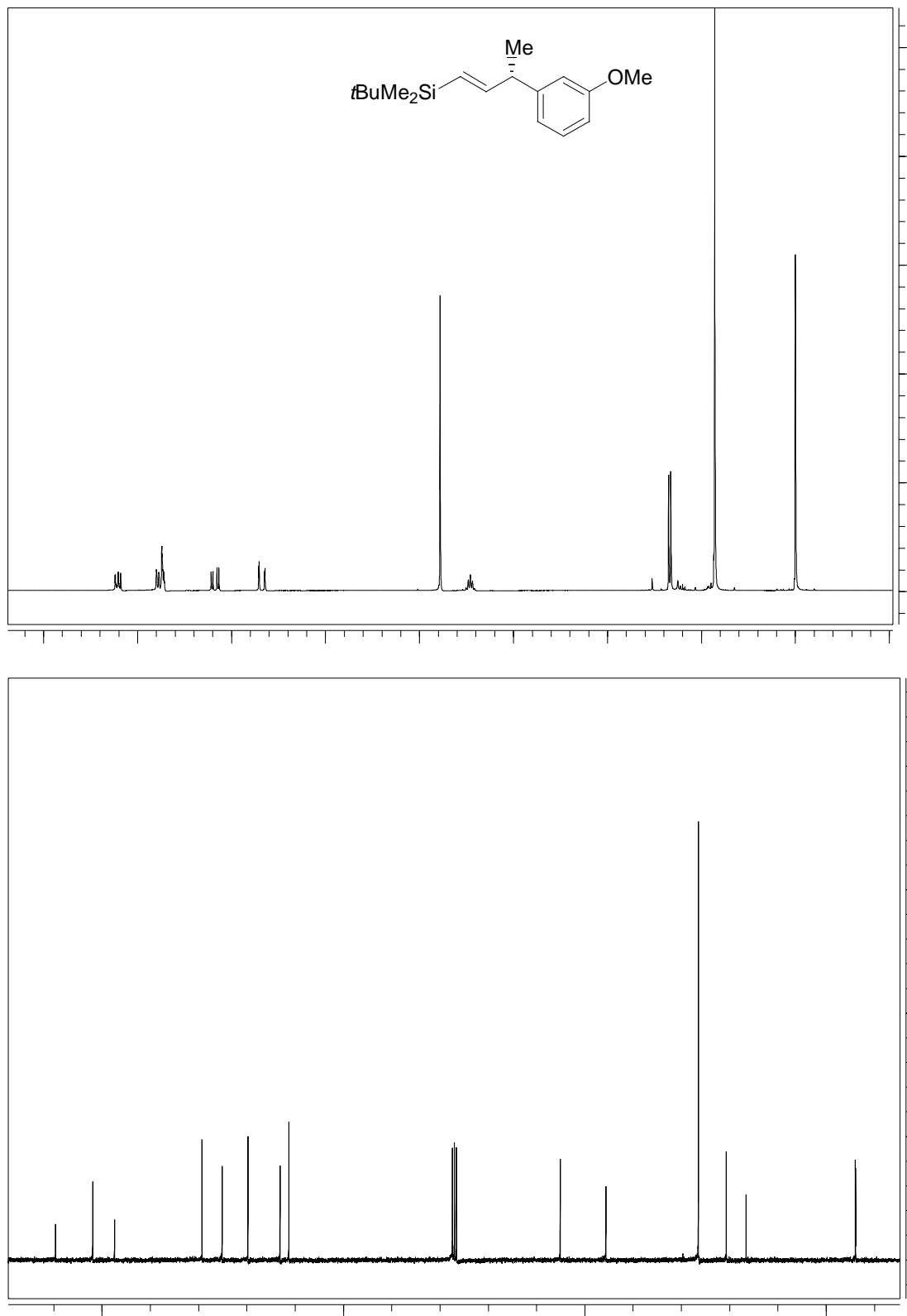
(3*R*,1*E*)-tert-Butyl-dimethyl-(3-methyl-oct-1-enyl)-silane ((*R*)-1a):

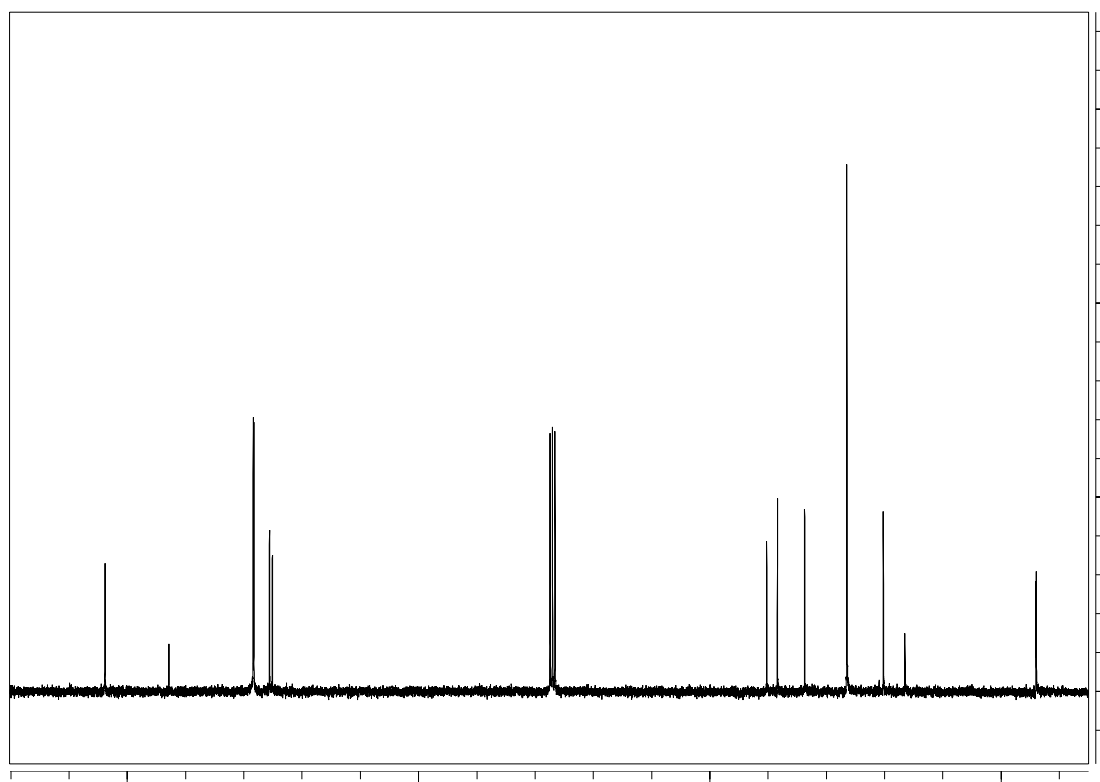
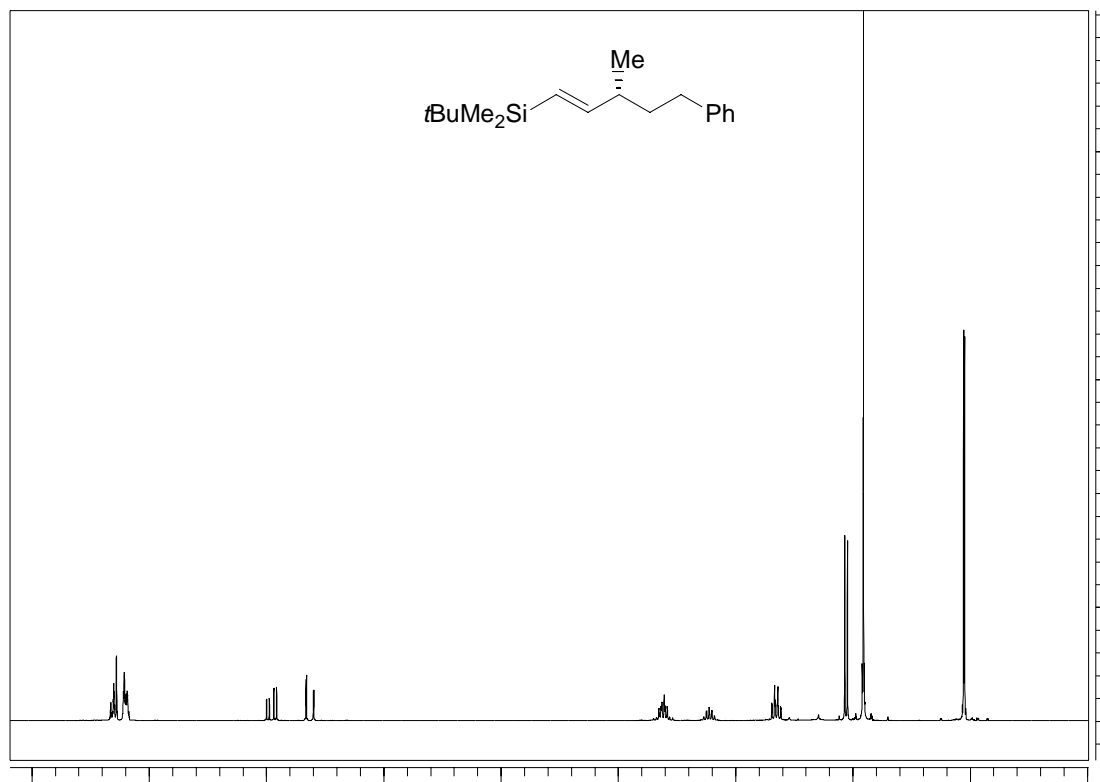
(3*R*,1*E*)-tert-Butyl-(3,4-dimethyl-pent-1-enyl)-dimethylsilane ((*R*)-1b):

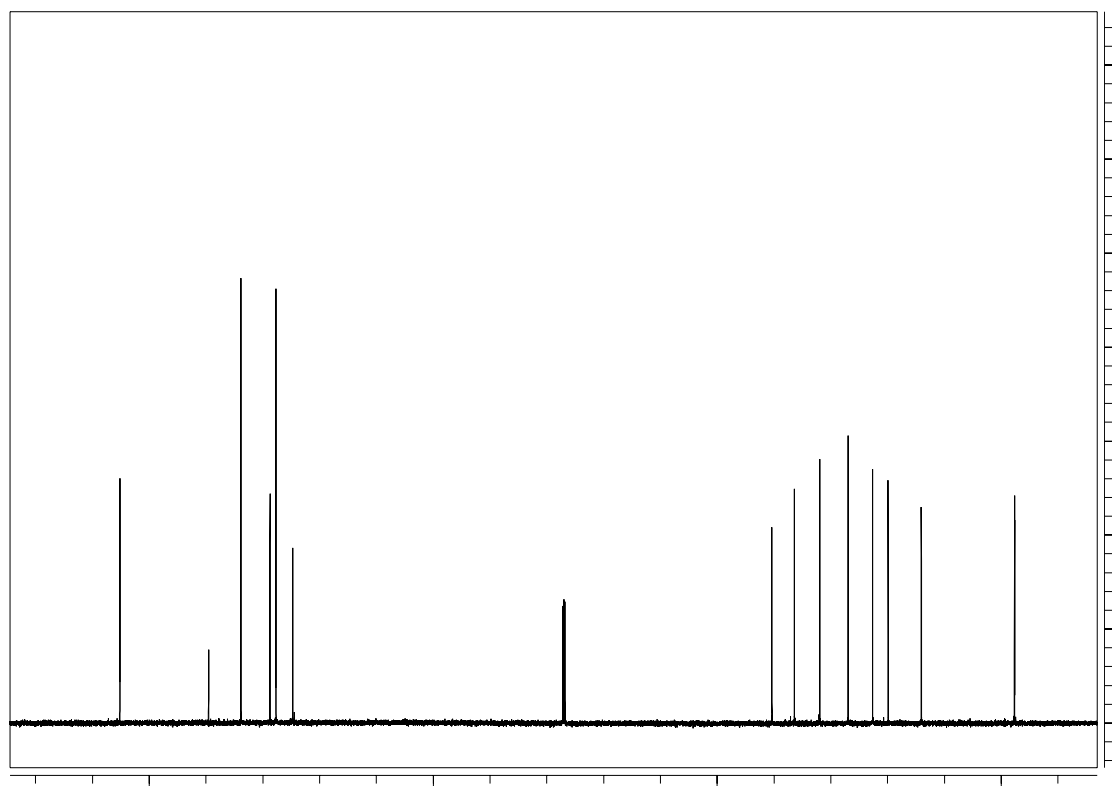
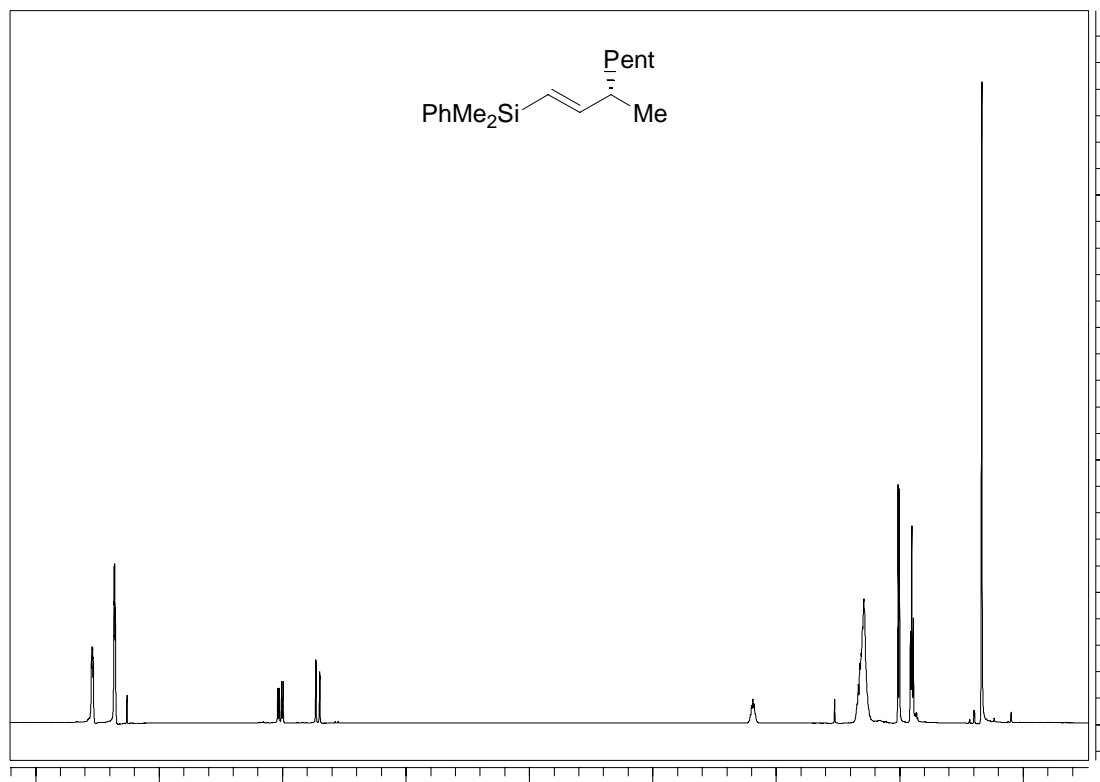
(3*R*,1*E*)-tert-Butyl-dimethyl-(3-methyl-pent-1-enyl)-silane ((*R*)-1c):

(3*S*,1*E*)-tert-Butyl-dimethyl-(3-phenyl-but-1-enyl)-silane ((*S*)-1d):

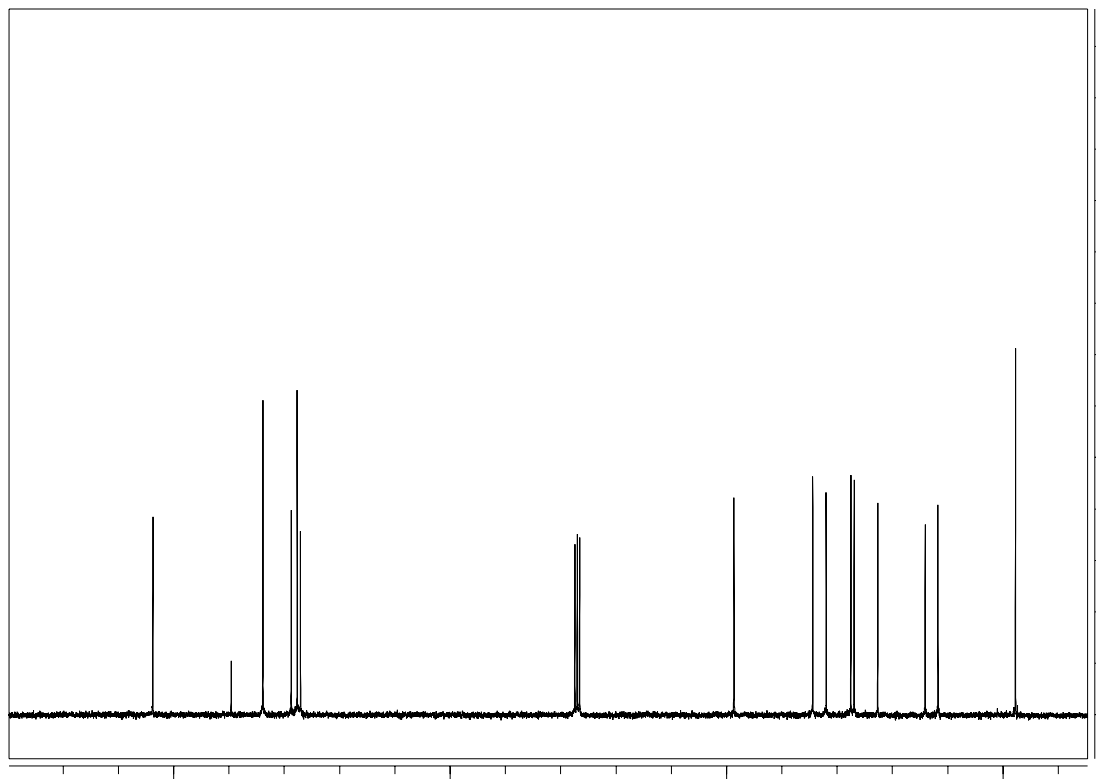
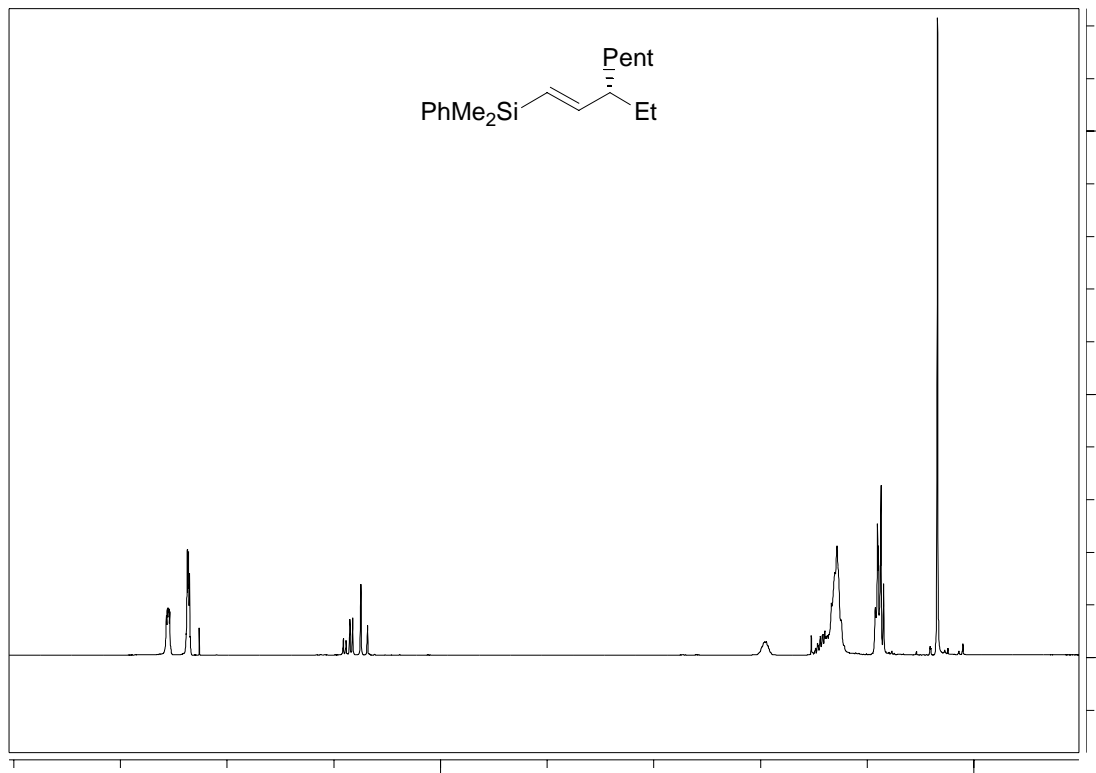
4-(1*S*,2*E*)-3-(tert-Butyl-dimethyl-silanyl)-1-methyl-allyl-methylbenzoate ((*S*)-1e):

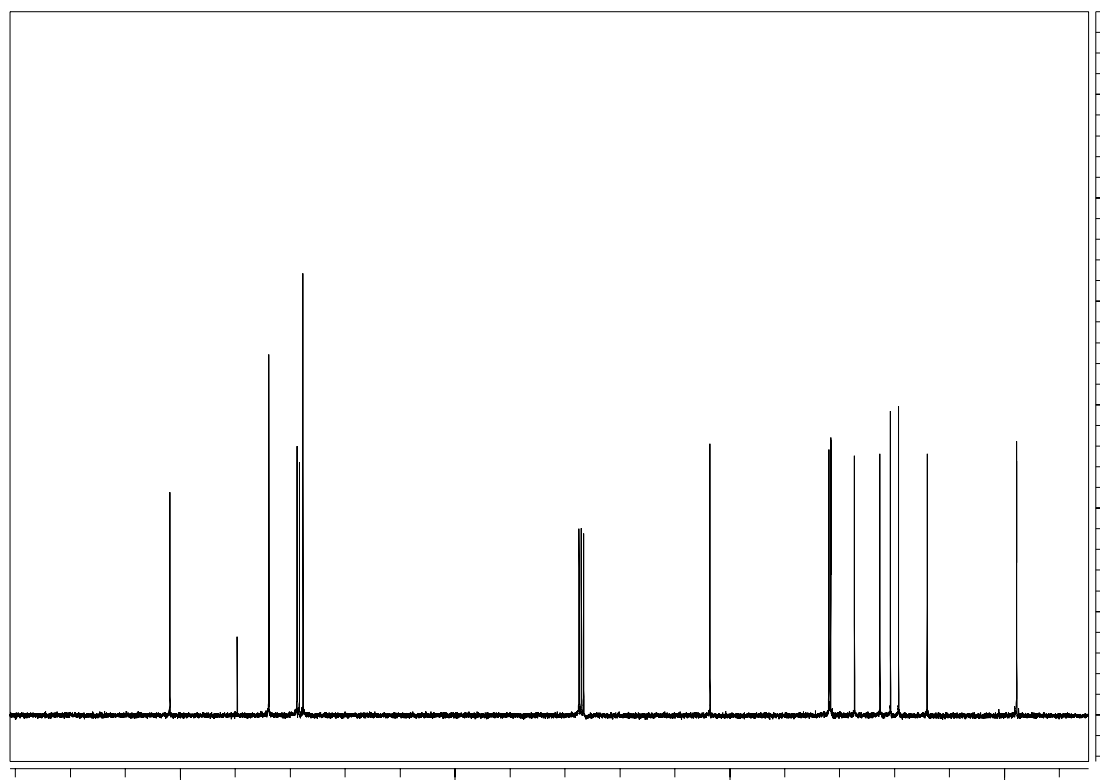
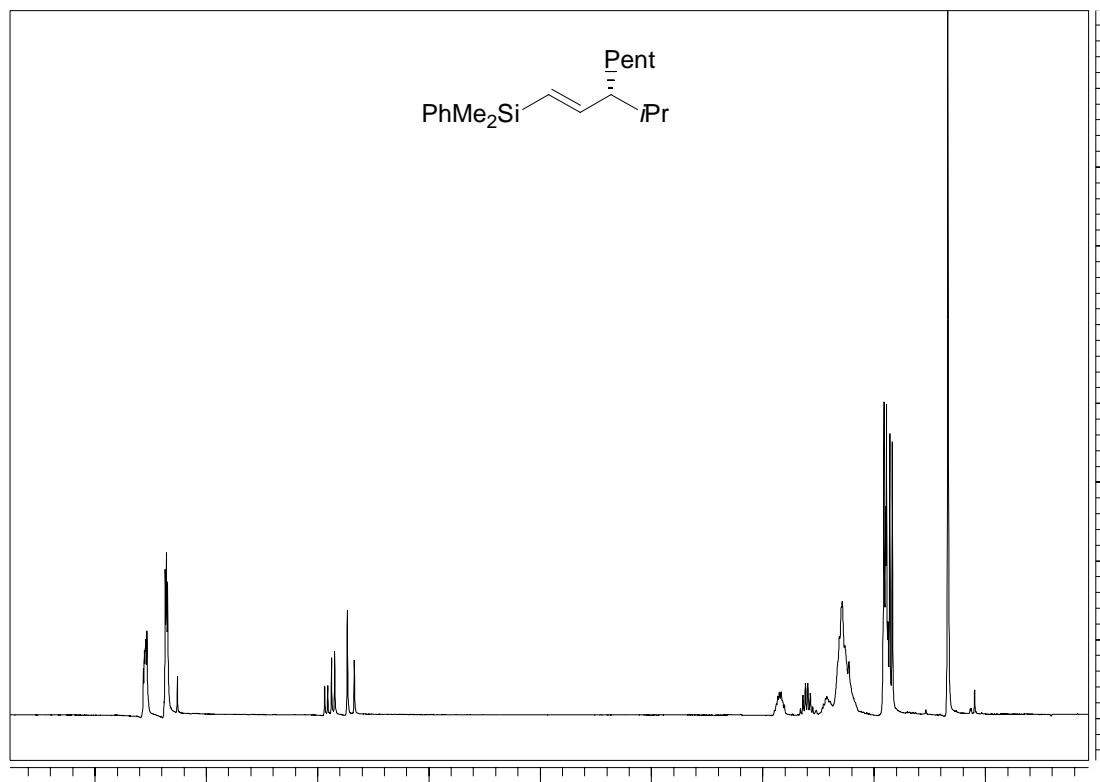
(3*S*,1*E*)-tert-Butyl-[3-(3-methoxy-phenyl)-but-1-enyl]-dimethylsilane ((*S*)-1f):

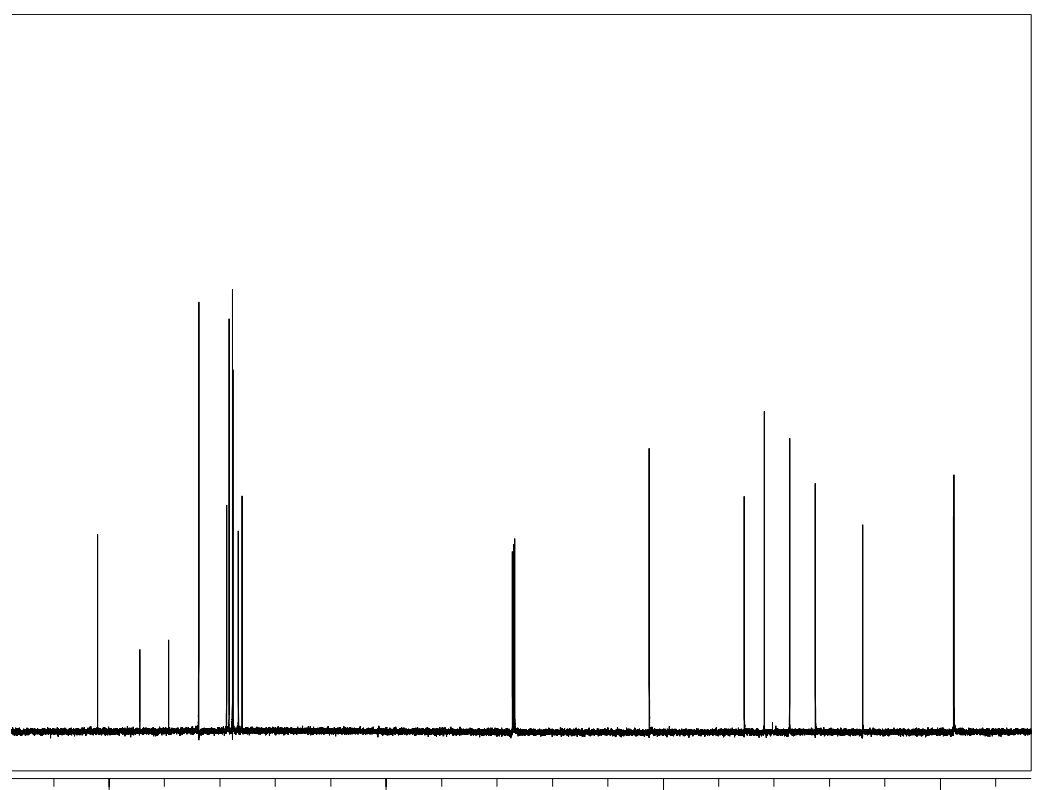
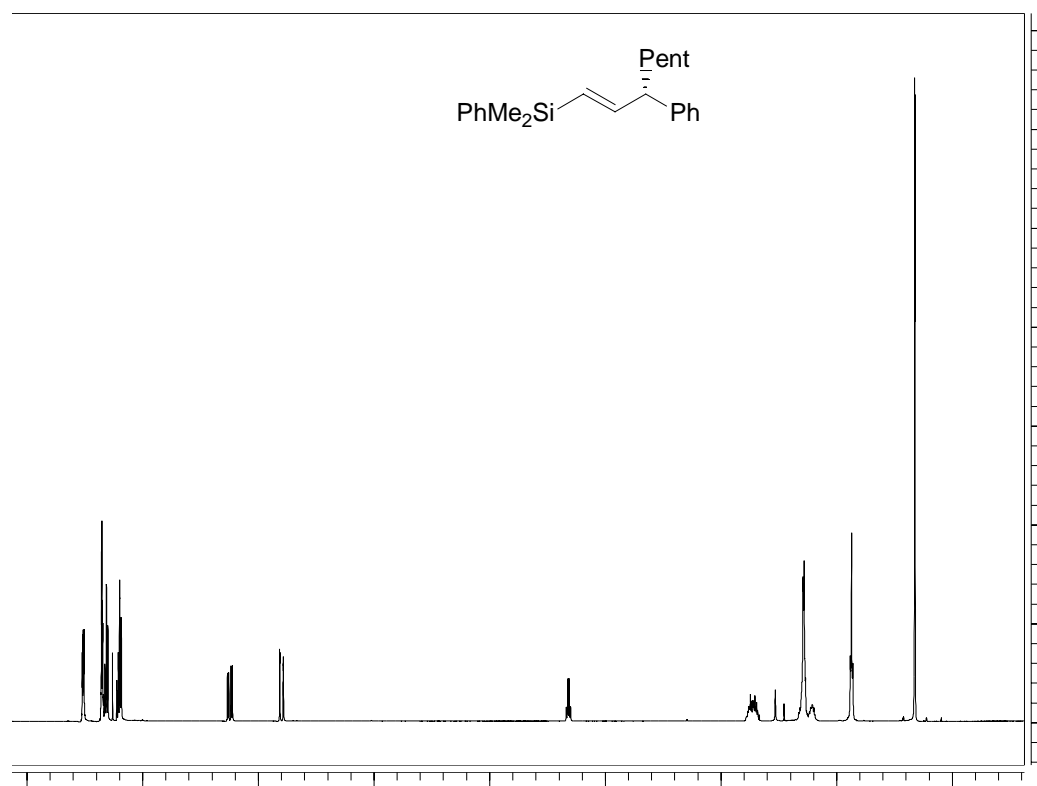
(3*R*,1*E*)-tert-Butyl-dimethyl-(3-methyl-5-phenyl-pent-1-enyl)-silane ((*R*)-1g):

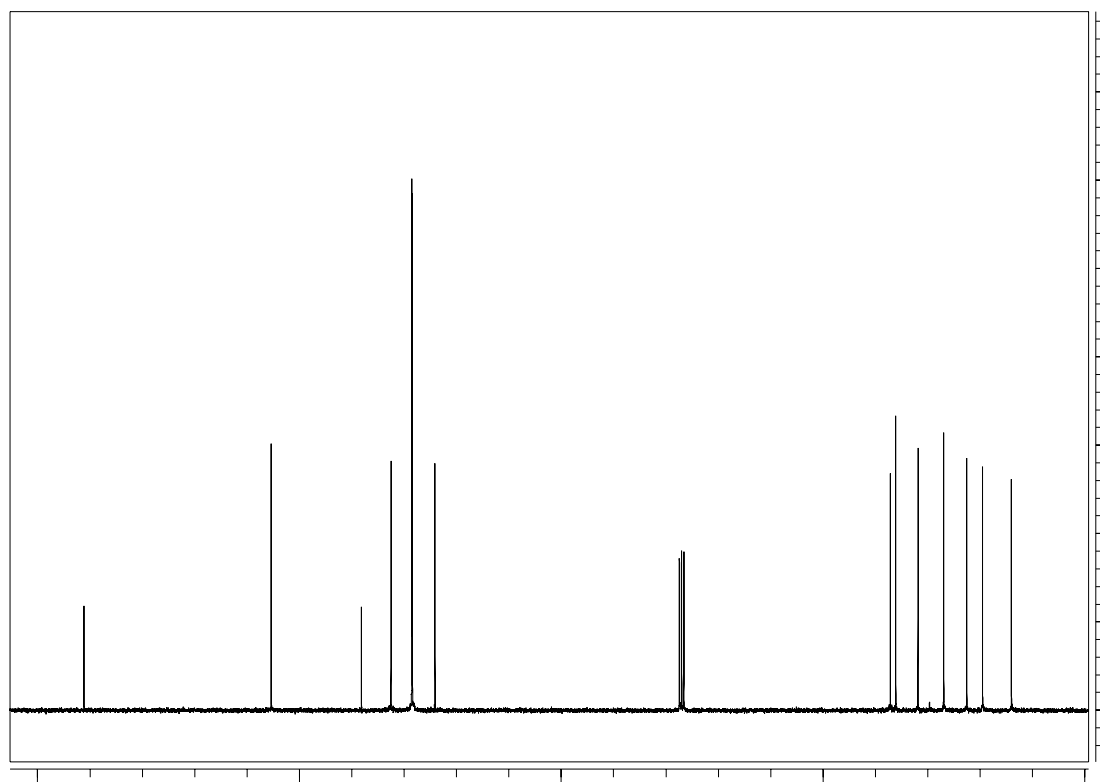
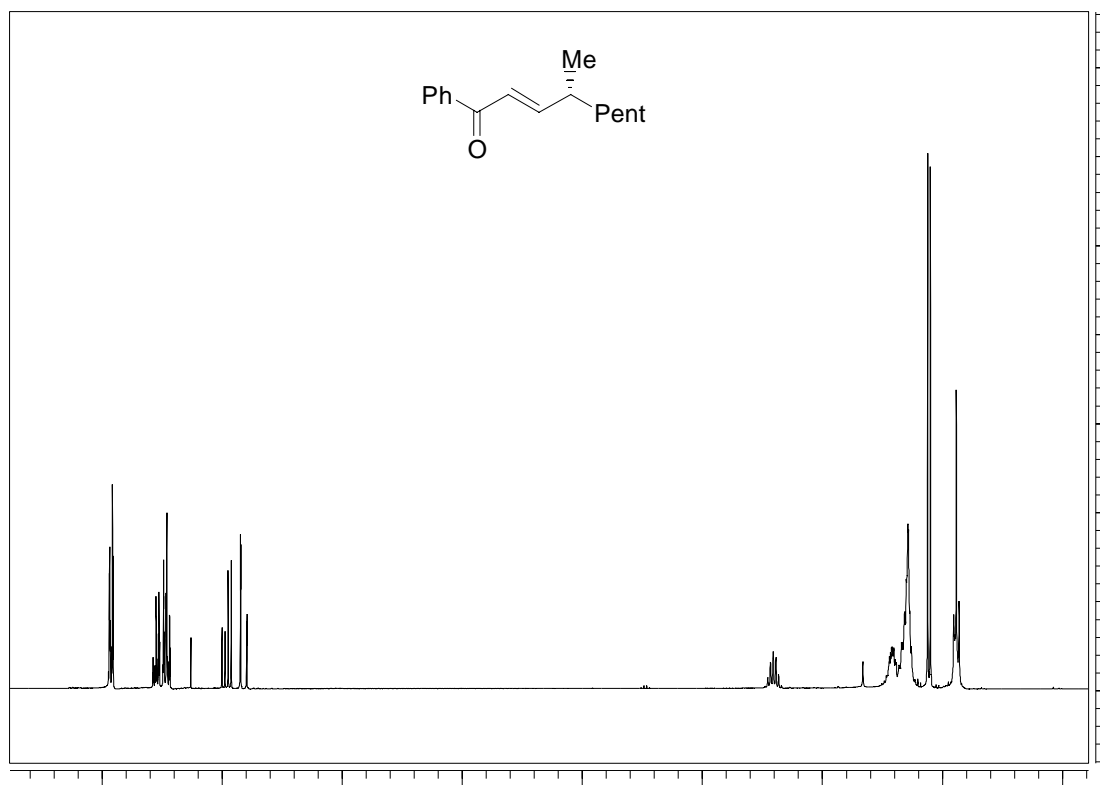
(3*S*,1*E*)-Dimethyl-(3-methyl-oct-1-enyl)-phenyl silane ((*S*)-1h):

(3*S*,1*E*)- (3-Ethyl-oct-1-enyl)-dimethyl-phenyl-silane ((*S*)-1i):

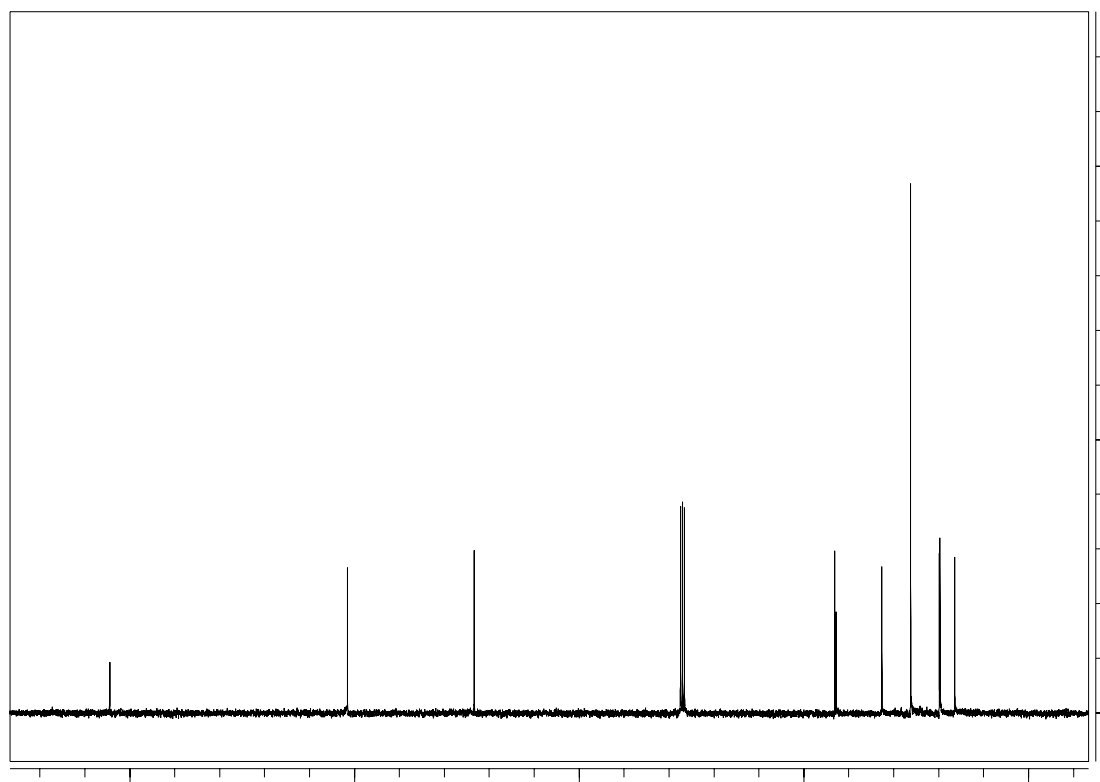
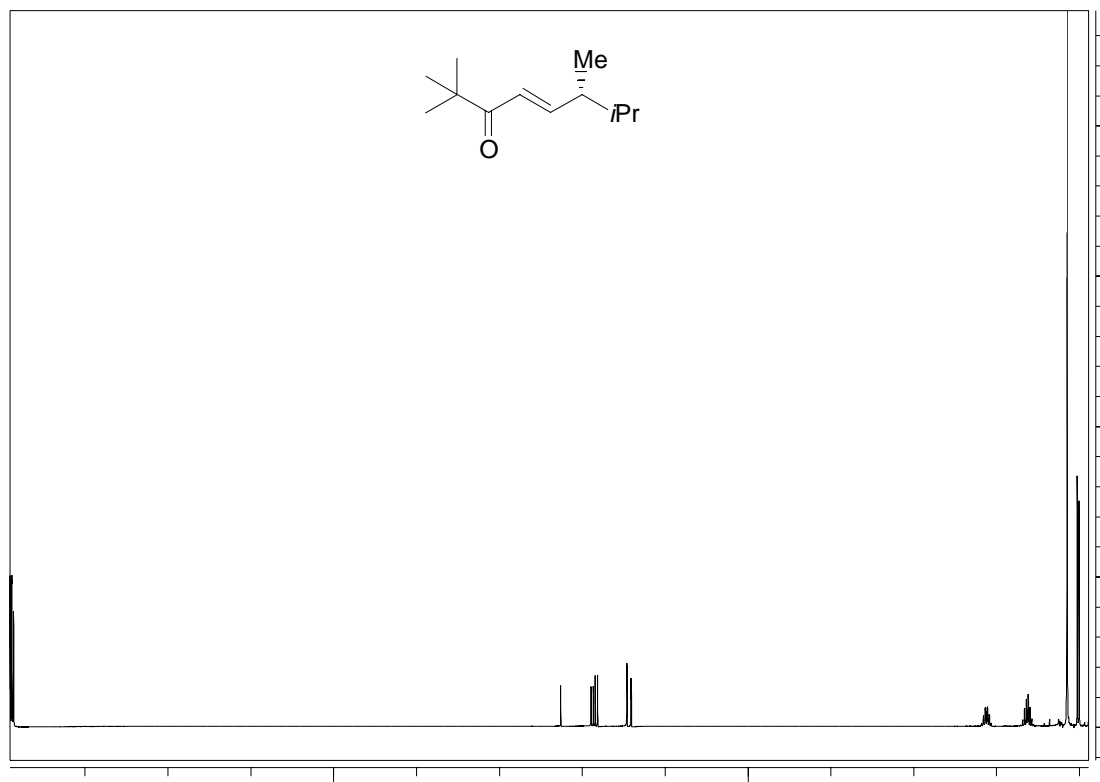


(3*R*,1*E*)- (3-Isopropyl-oct-1-enyl)-dimethyl-phenyl-silane ((*R*)-1j):

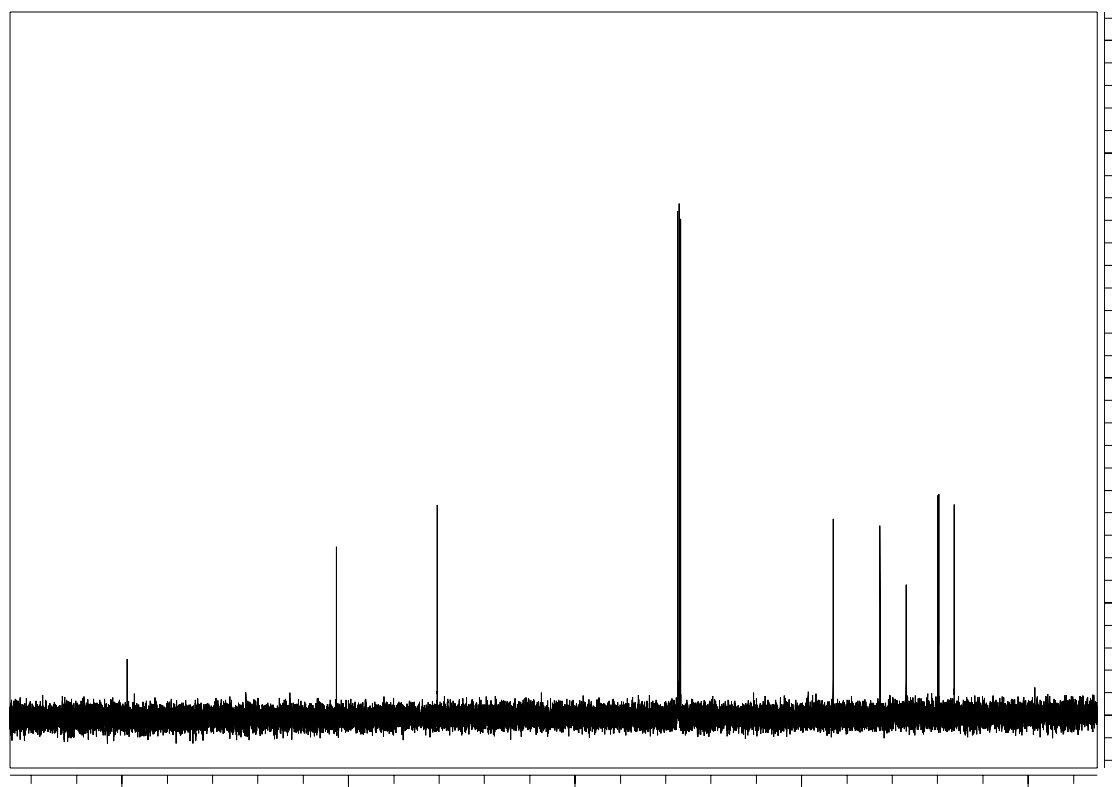
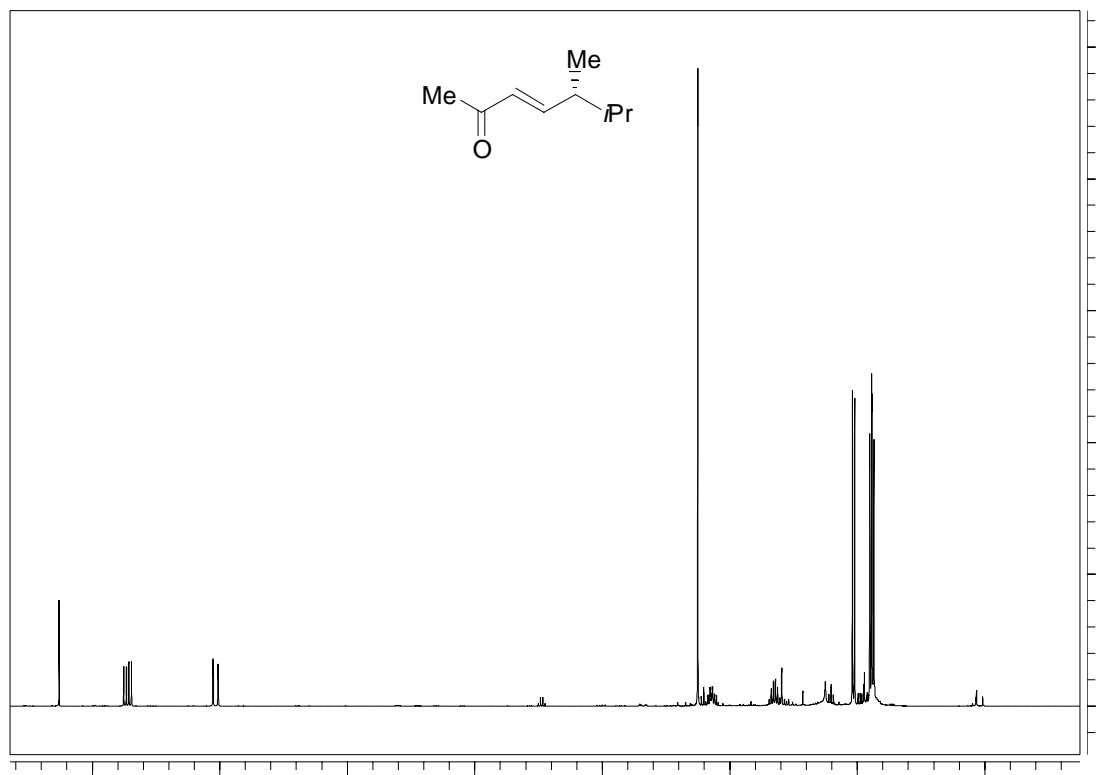
(3*S*,1*E*)- Dimethyl-phenyl-(3-phenyl-oct-1-enyl)-silane ((*S*)-1k):

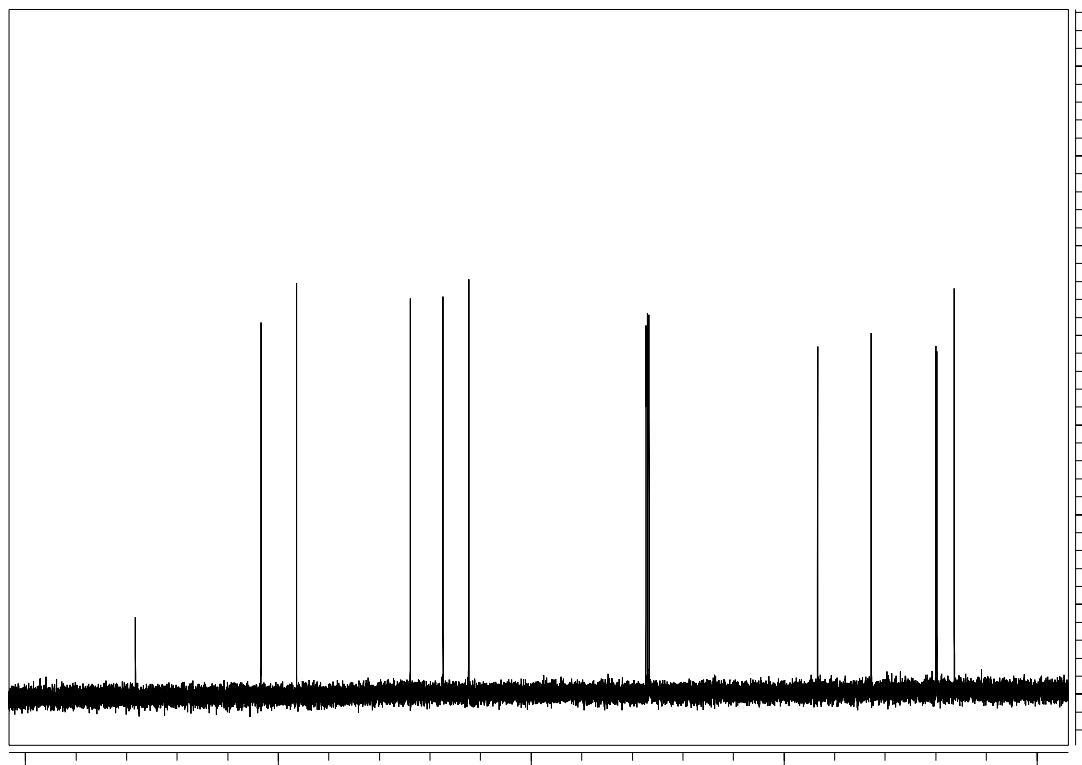
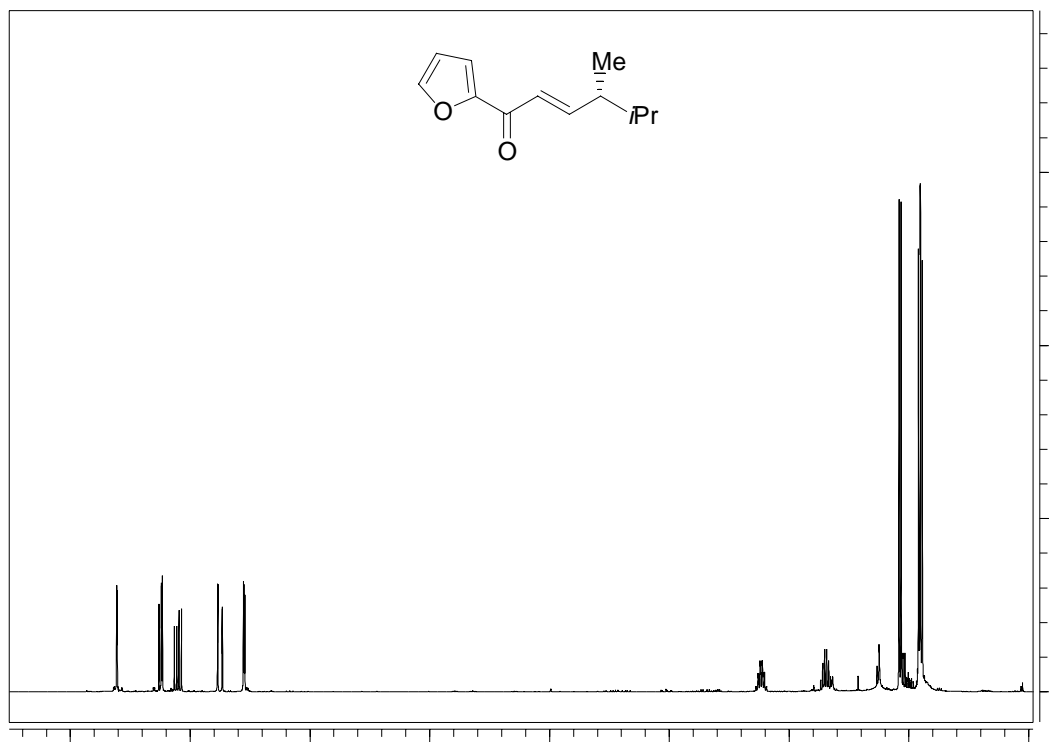
(4*R*,2*E*)- 4-Methyl-1-phenyl-non-2-en-1-one ((*R*)-6a):

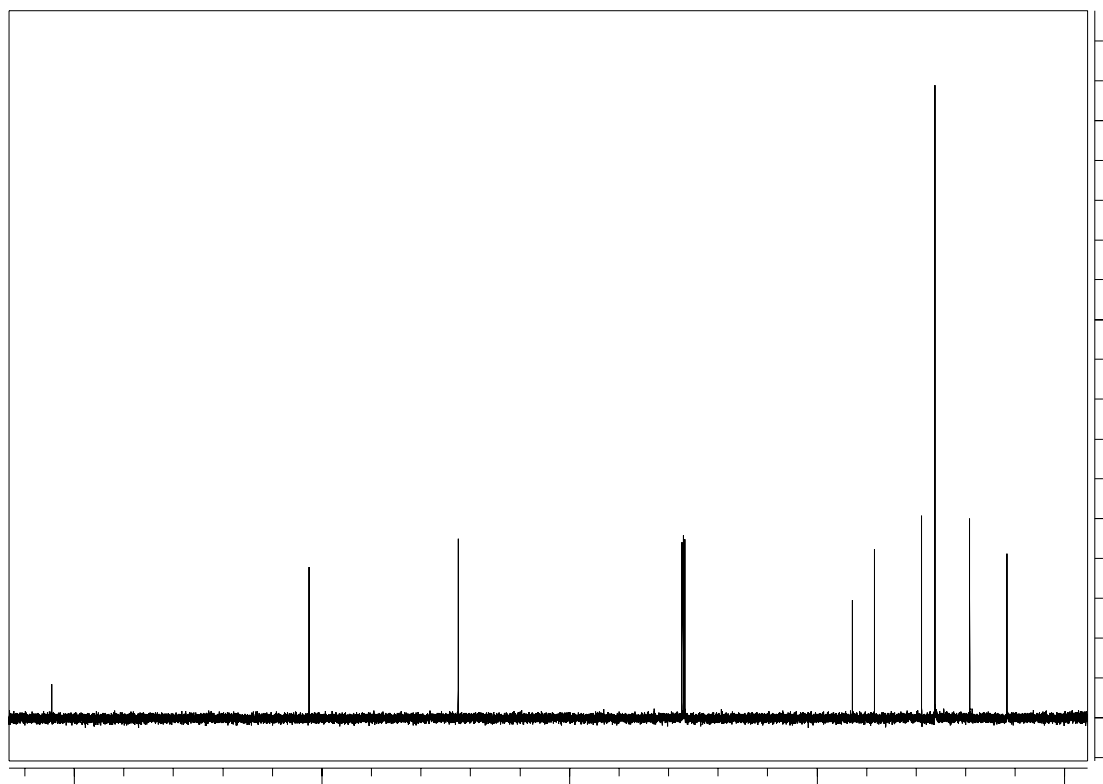
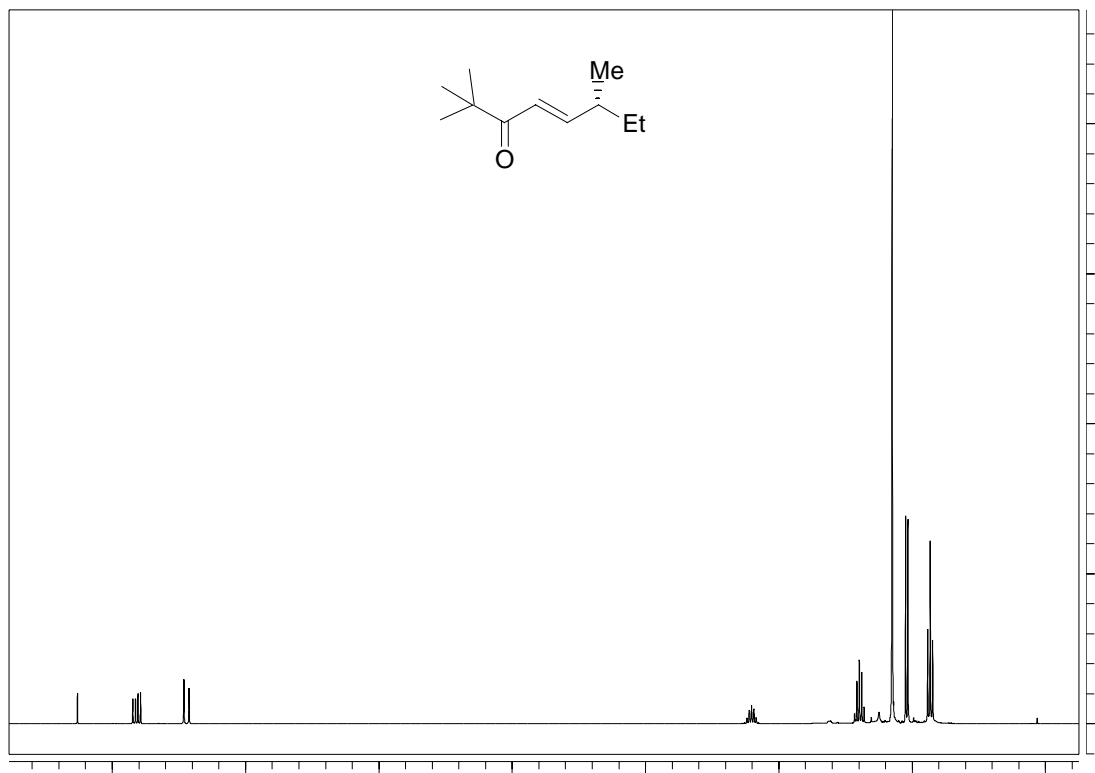
(6*R*,4*E*)- 2,2,6,7-Tetramethyl-oct-4-en-3-one ((*R*)-6b):

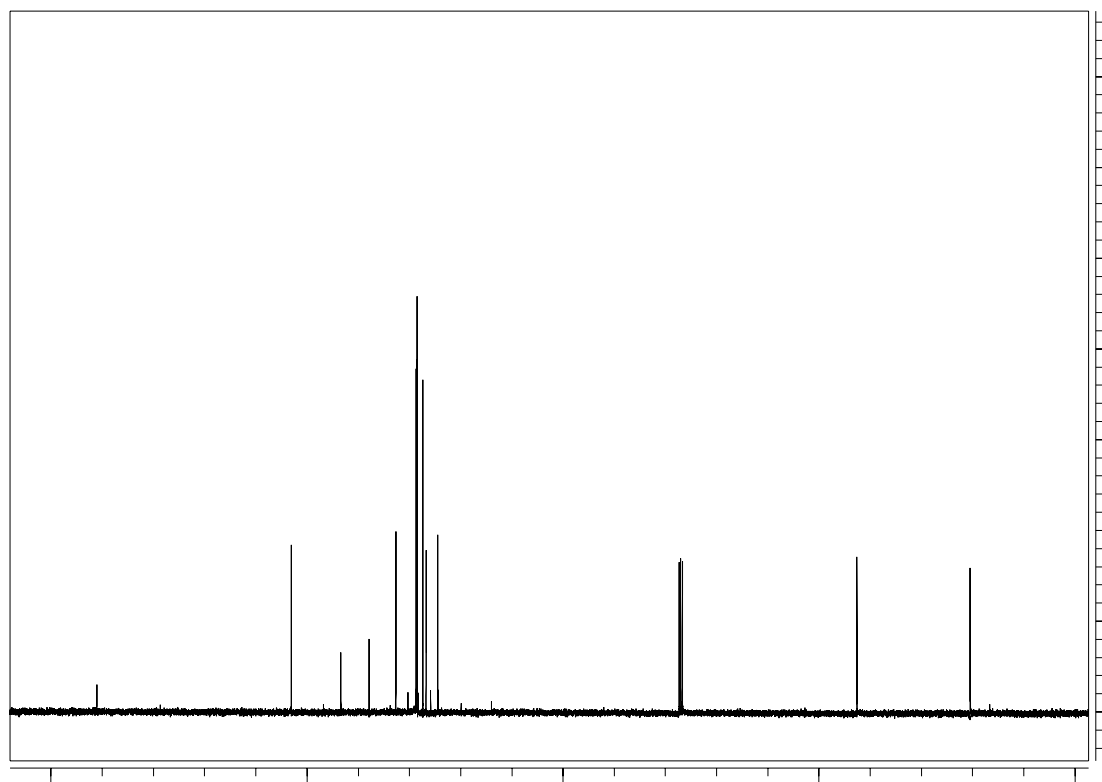
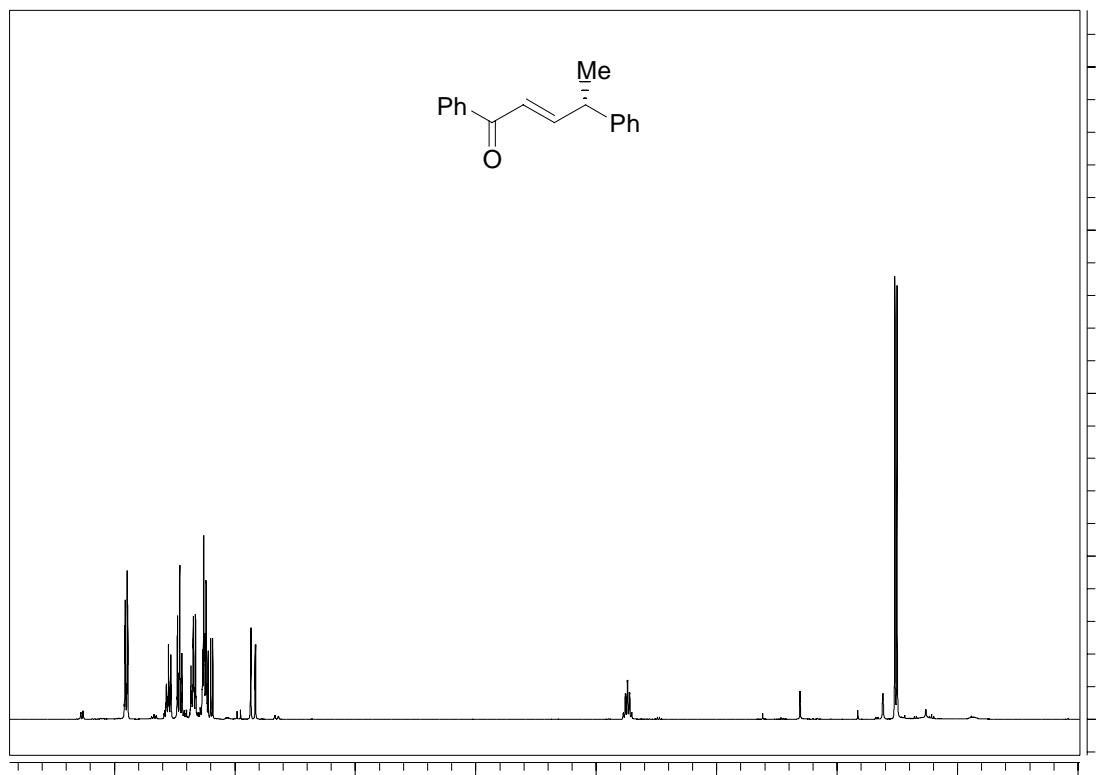


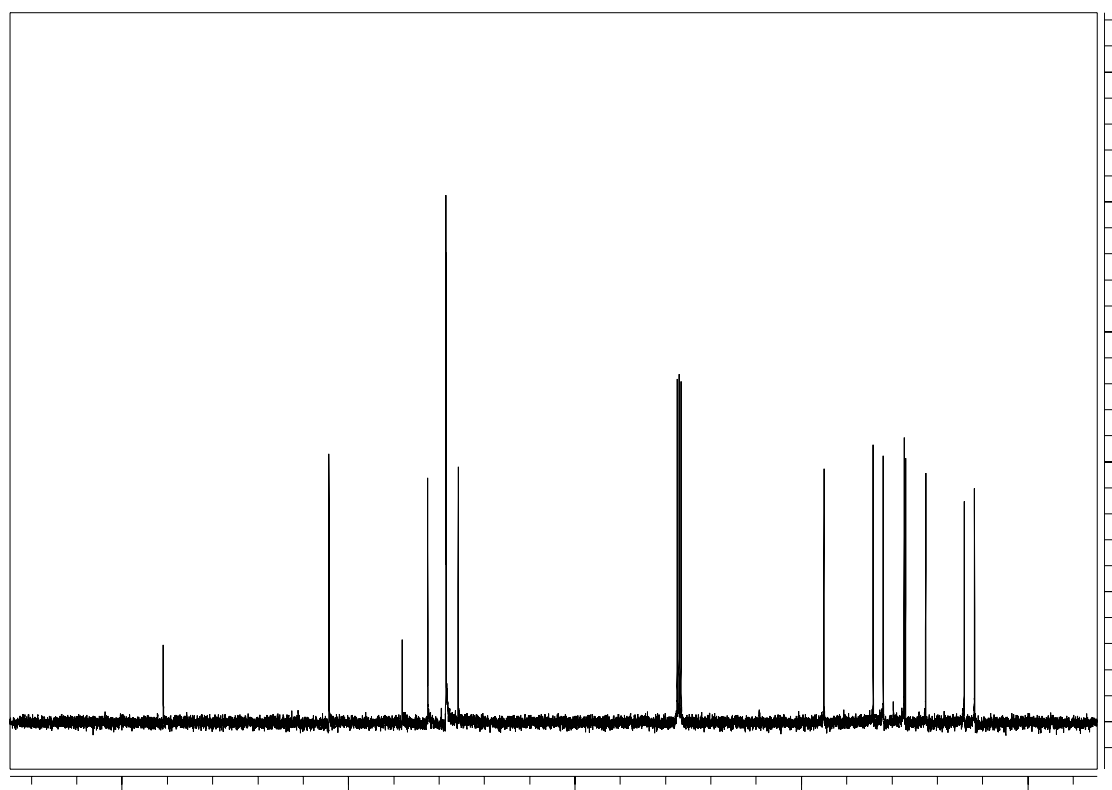
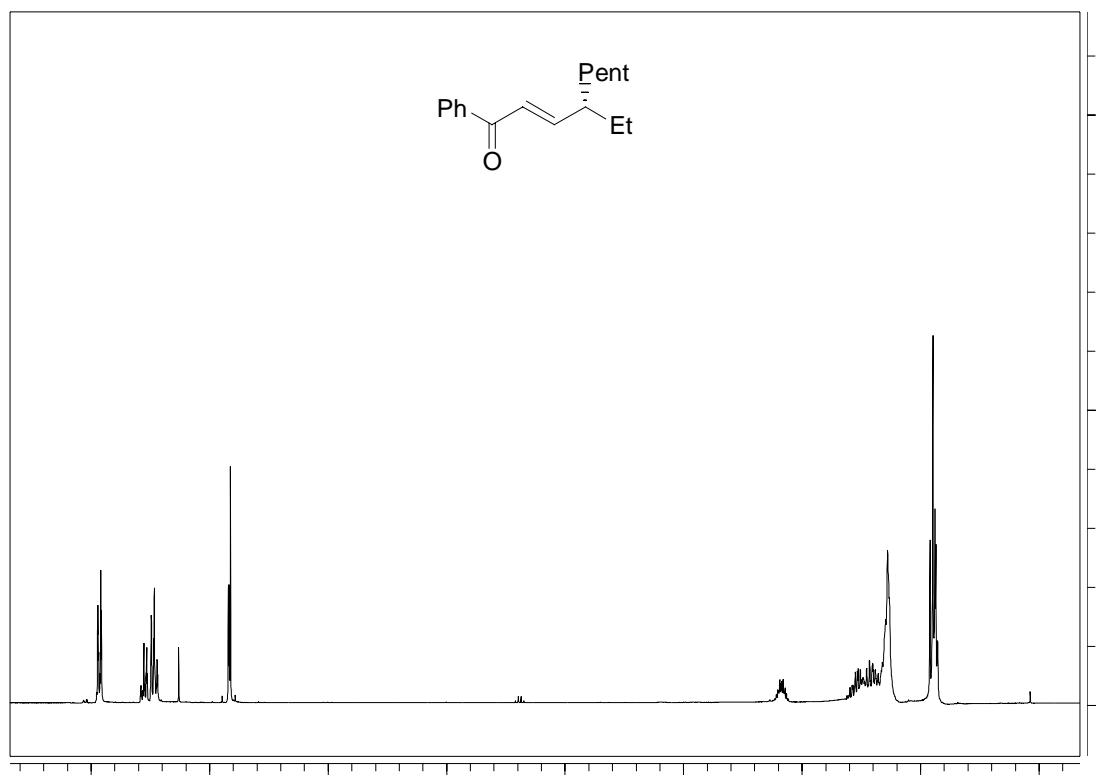
(5*R*,3*E*)- 5,6-Dimethyl-hept-3-en-2-one ((*R*)-6c):

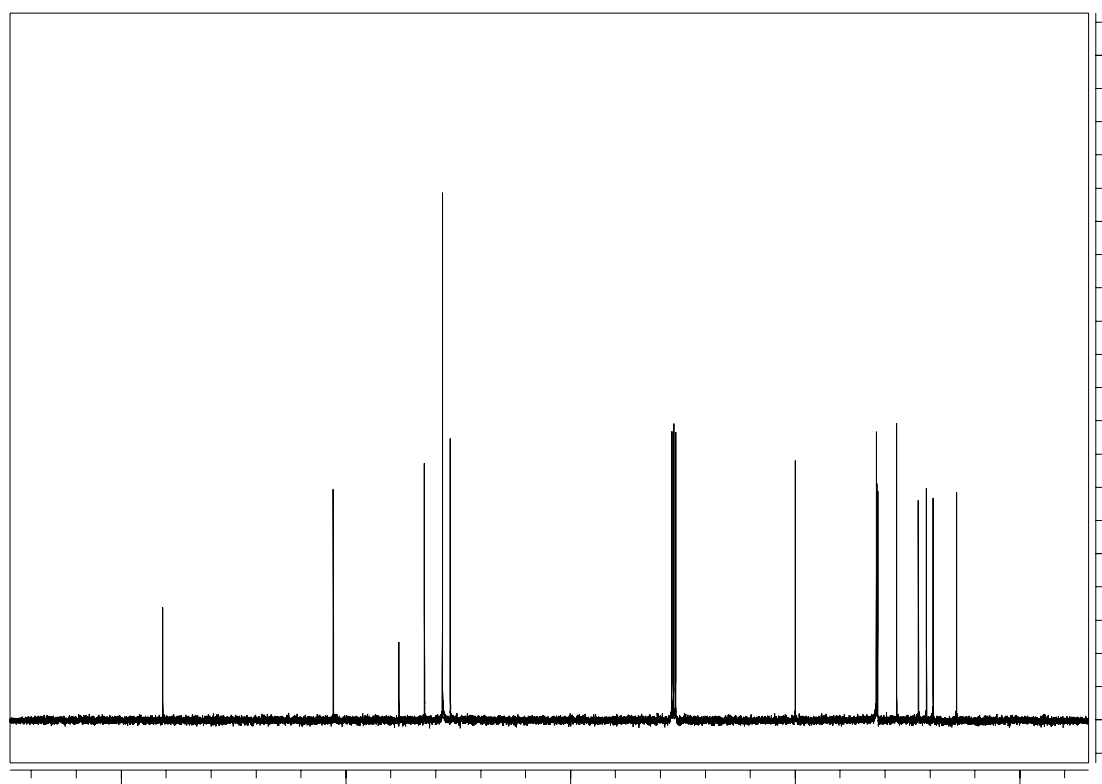
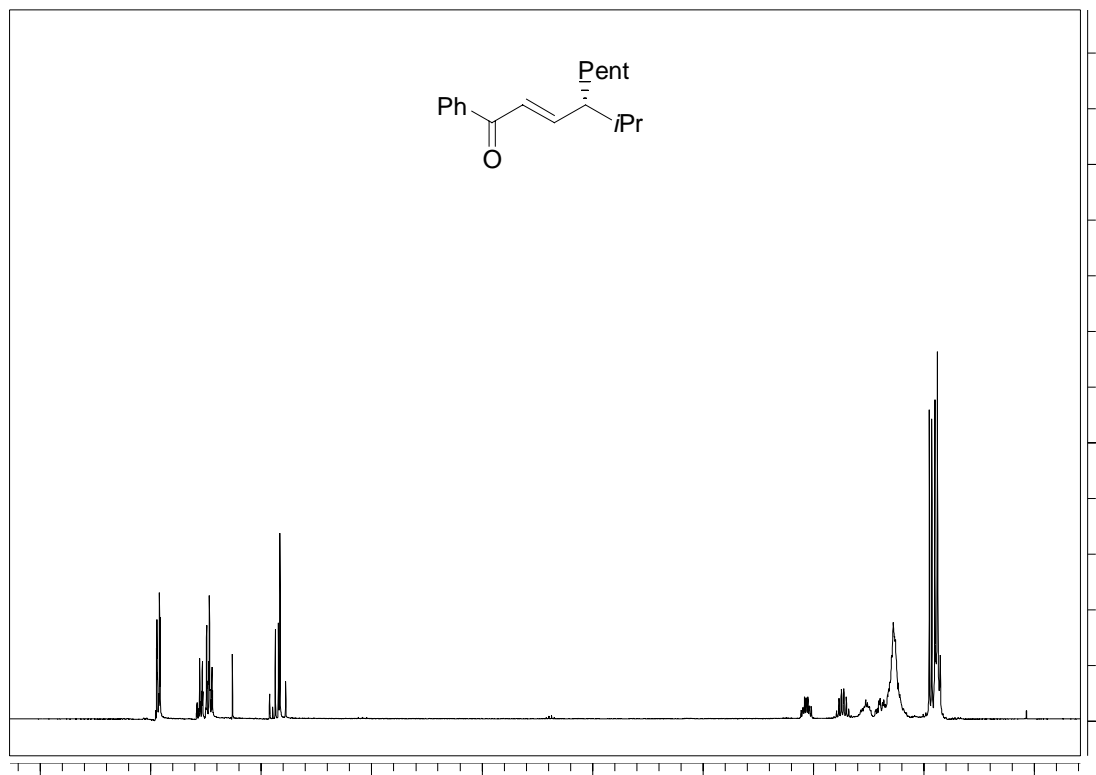


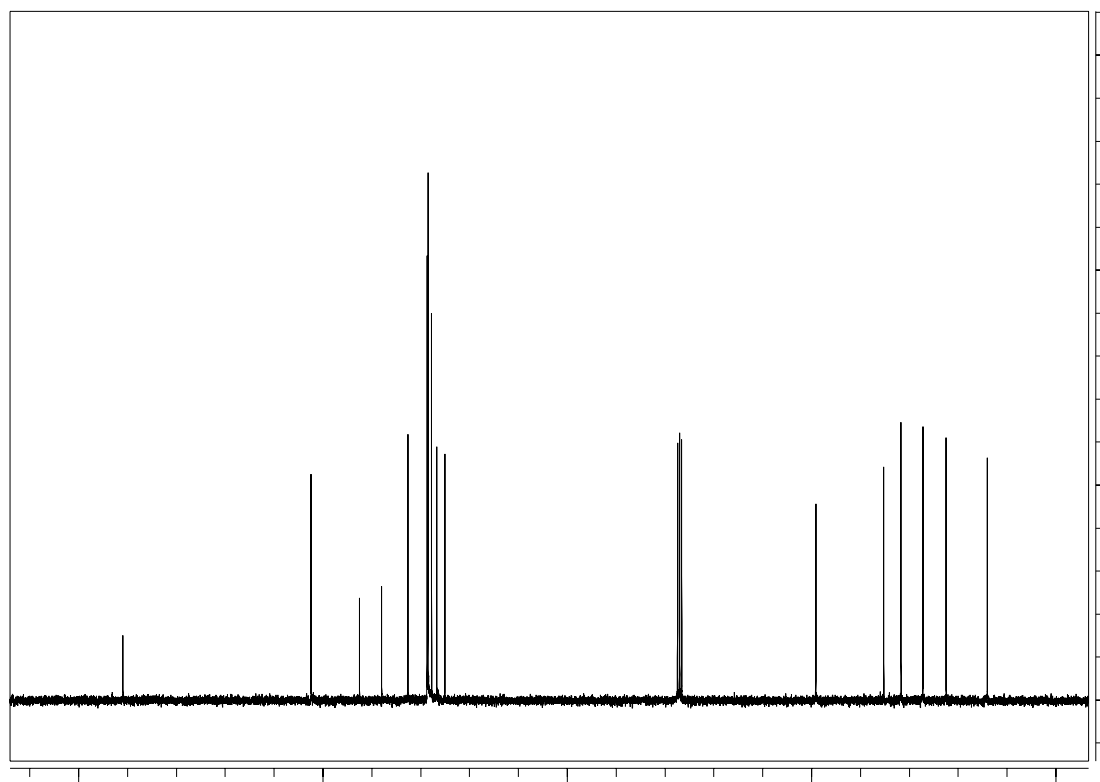
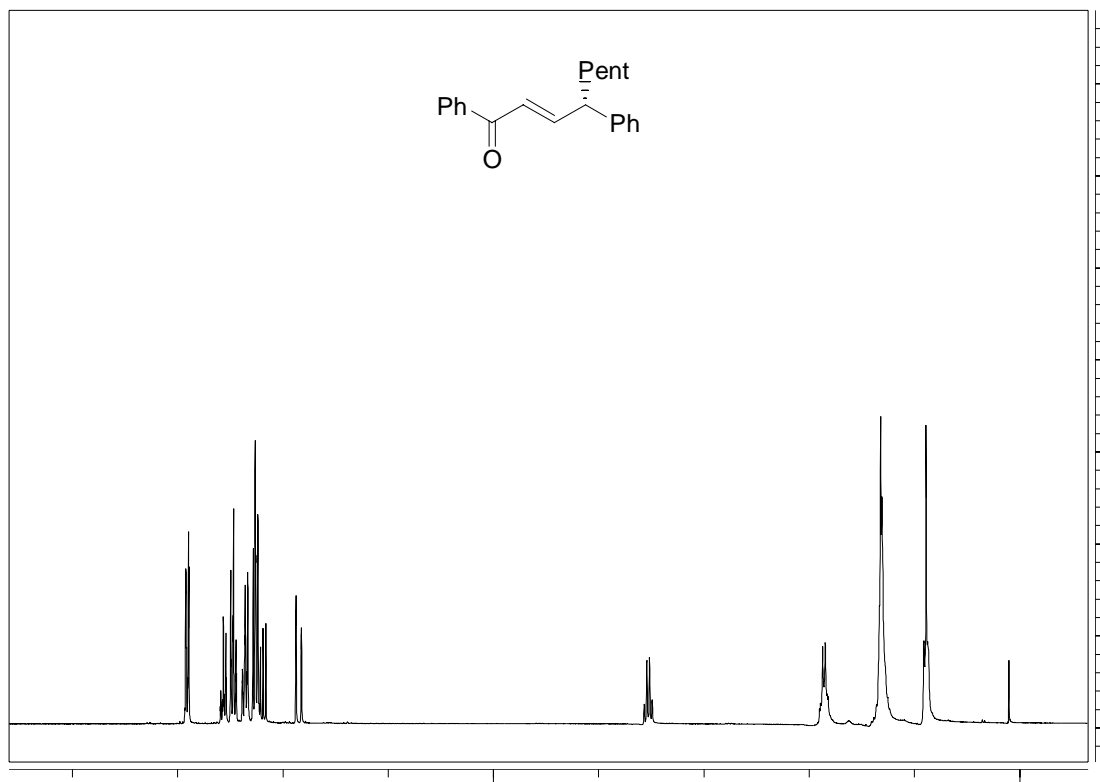
(4*R*,2*E*)- 1-Furan-2-yl-4,5-dimethyl-hex-2-en-1-one ((*R*)-6d):

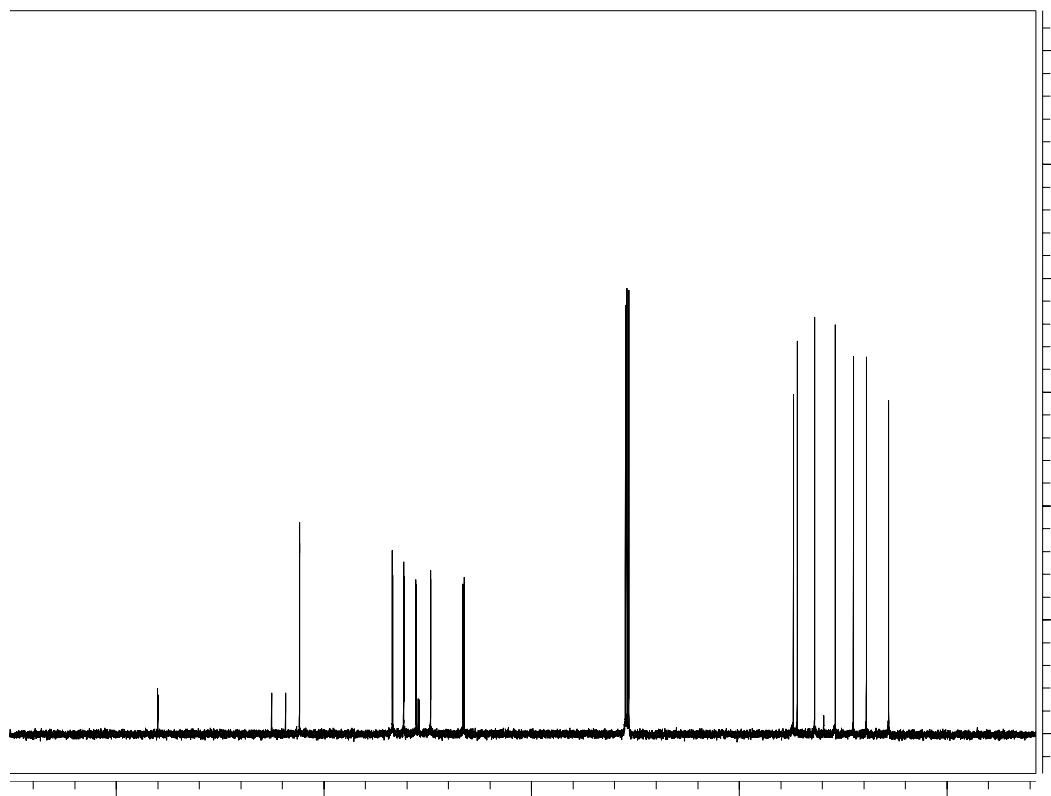
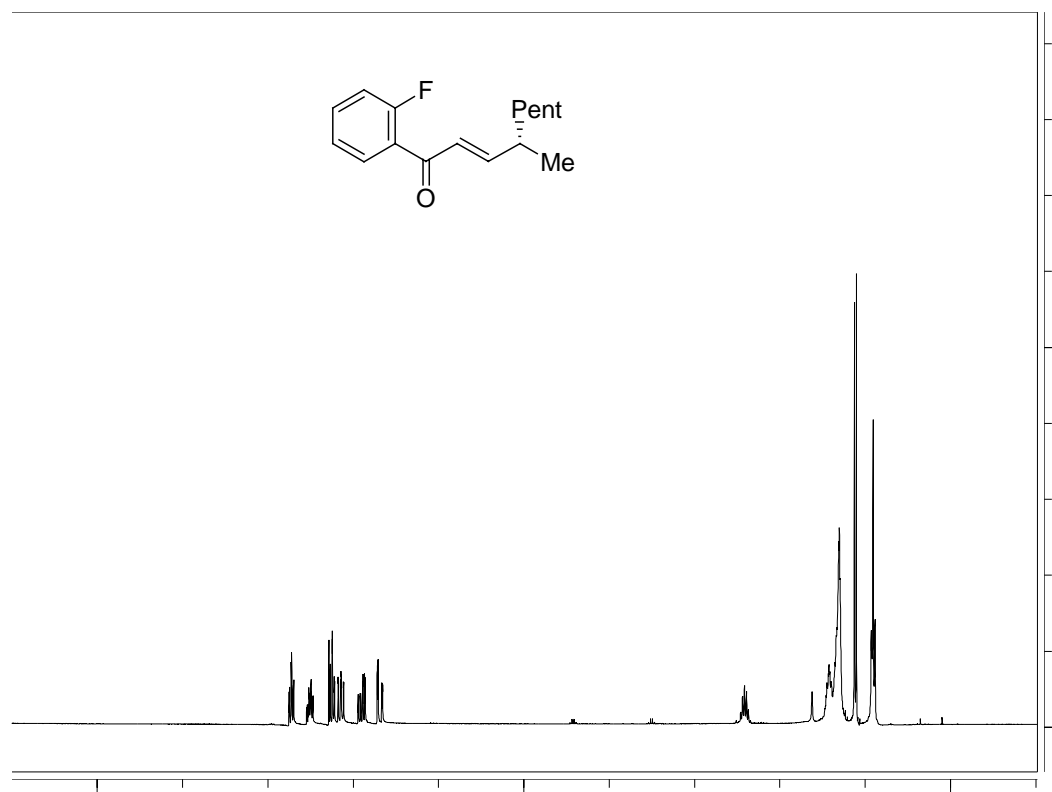
(6*R*,4*E*)- 2,2,6-Trimethyl-oct-4-en-3-one ((*R*)-6e):

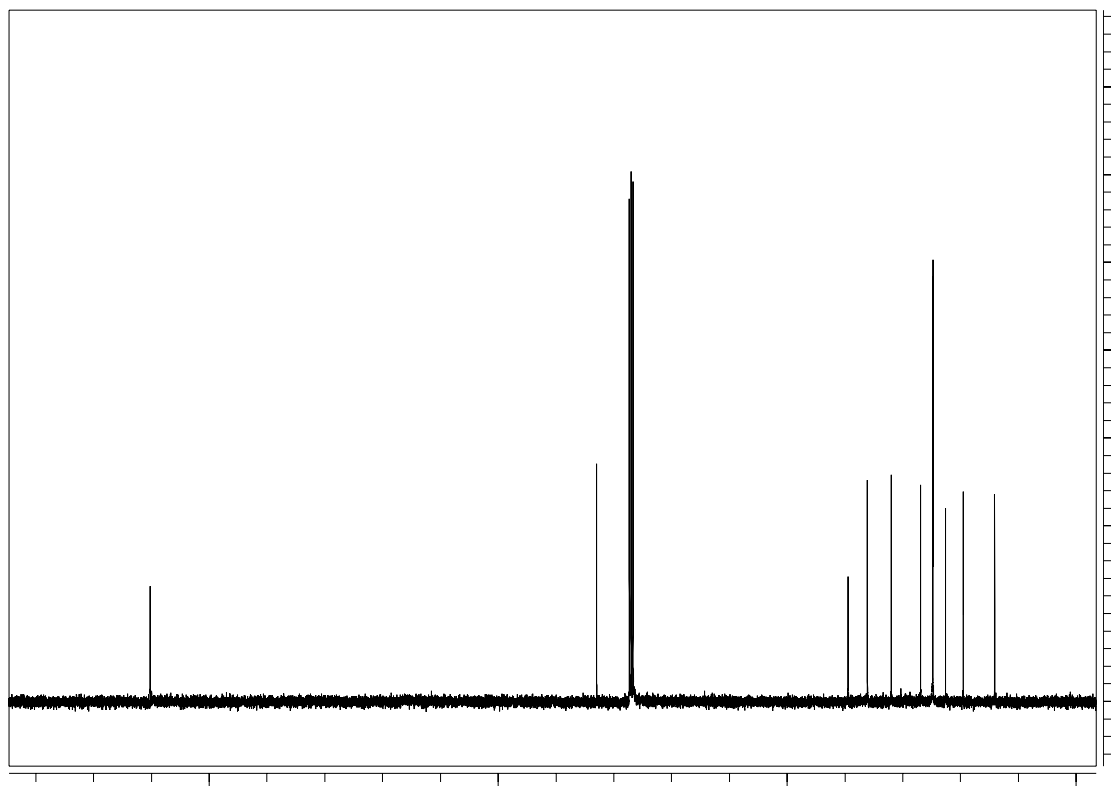
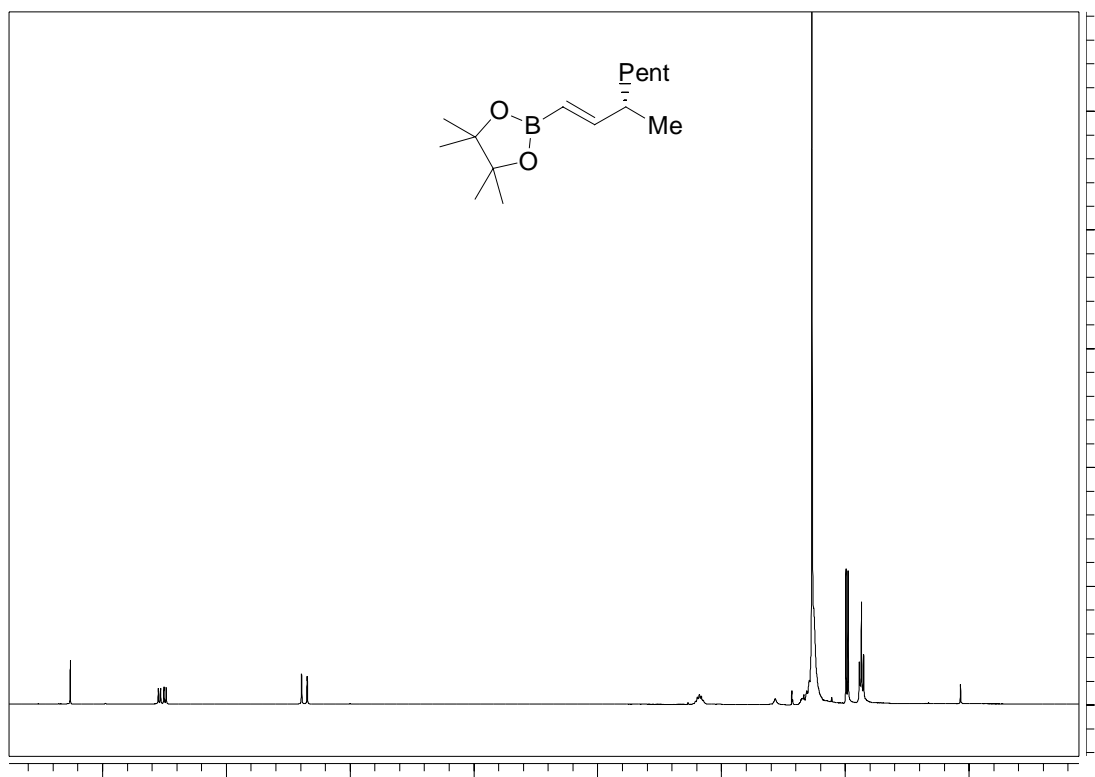
(4*S*,2*E*)- 1,4-Diphenyl-pent-2-en-1-one ((*S*)-6f):

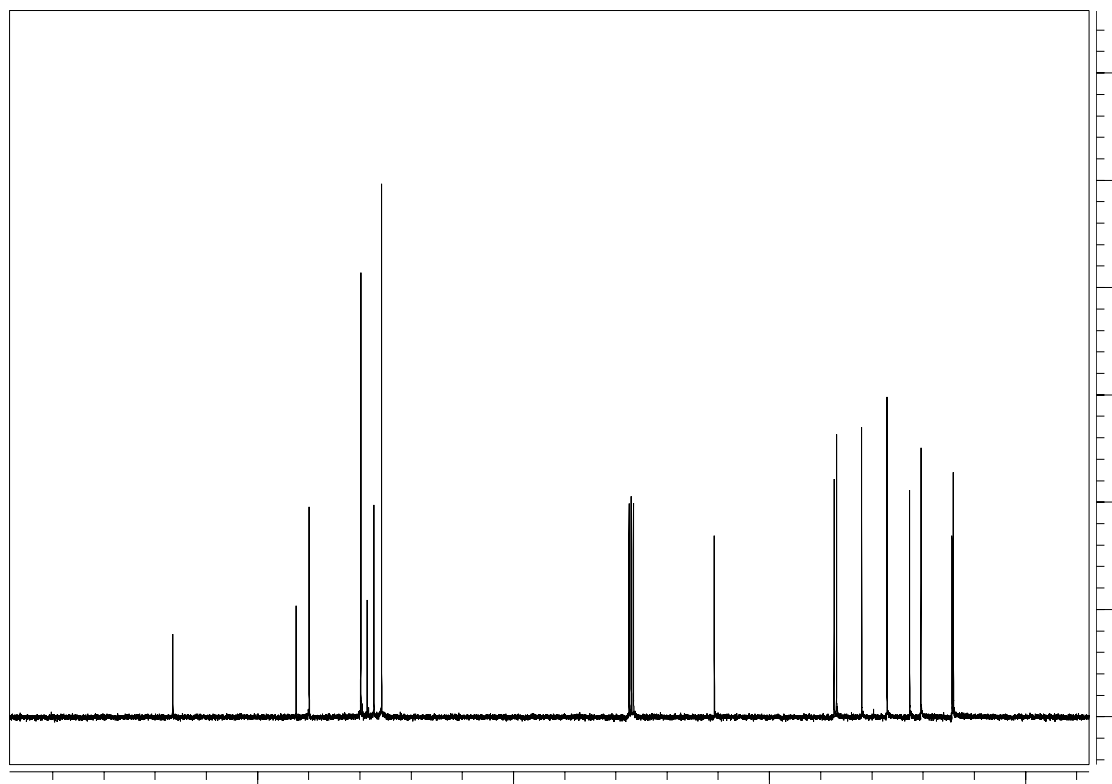
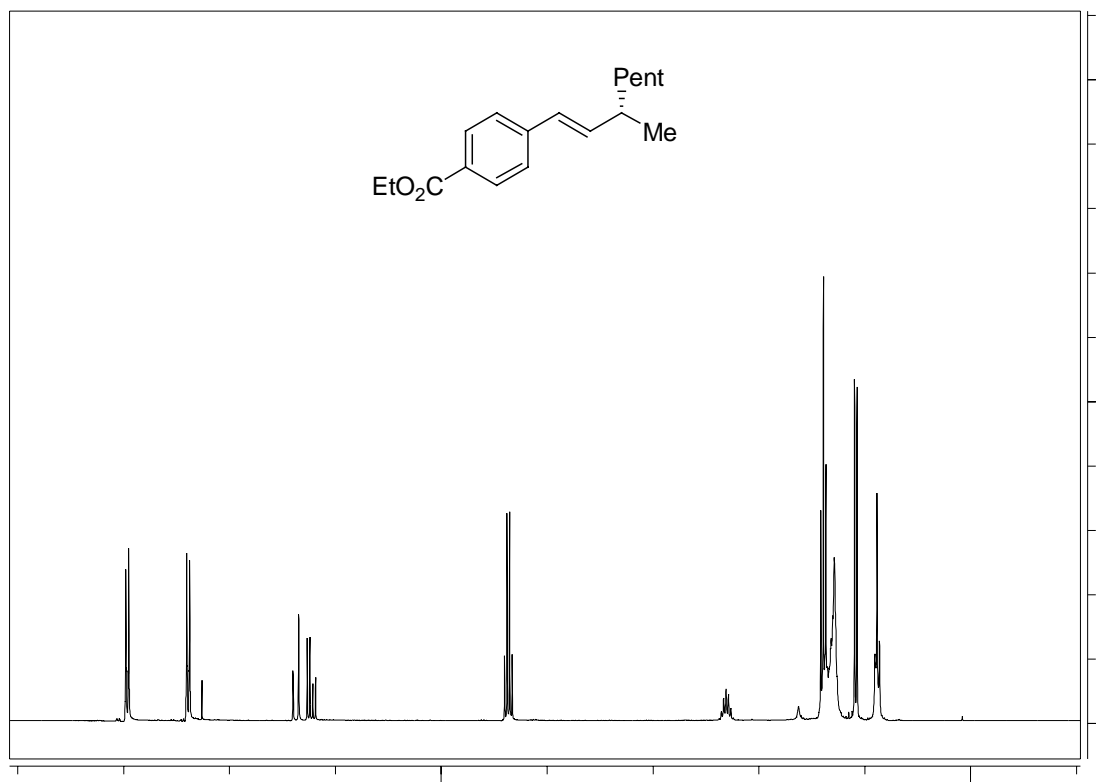
(4*S*,2*E*)- 4-Ethyl-1-phenyl-non-2-en-1-one ((*S*)-6g):

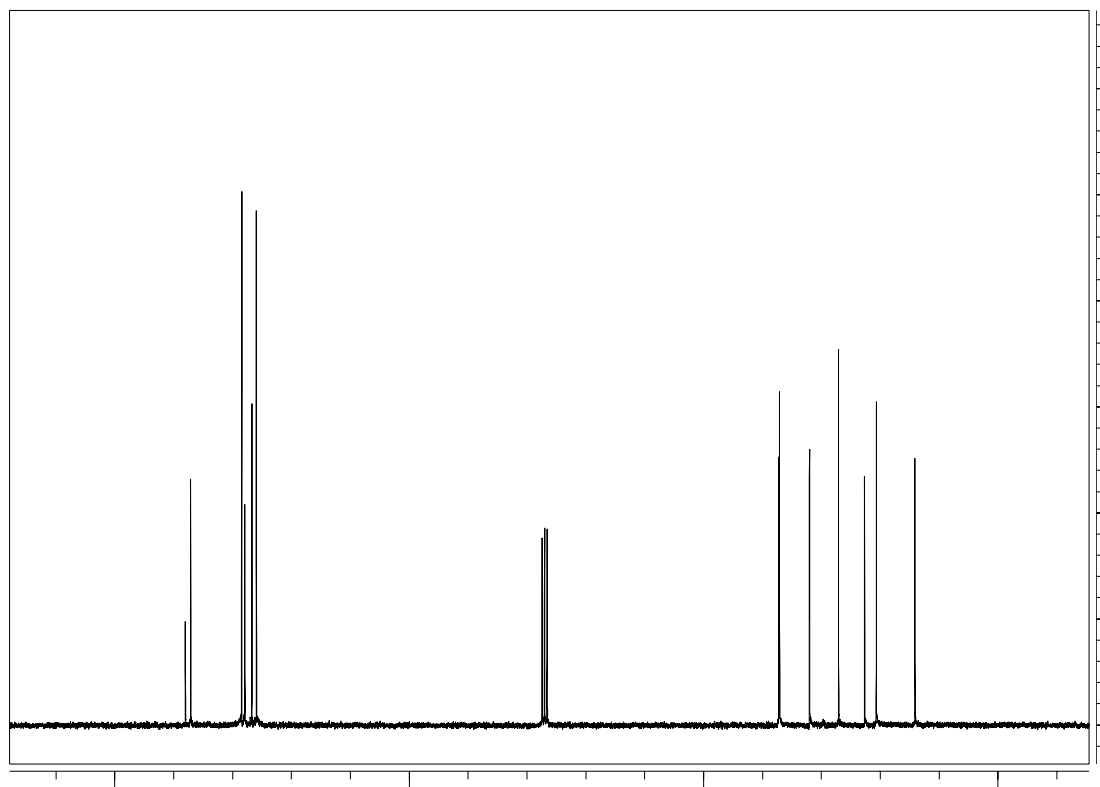
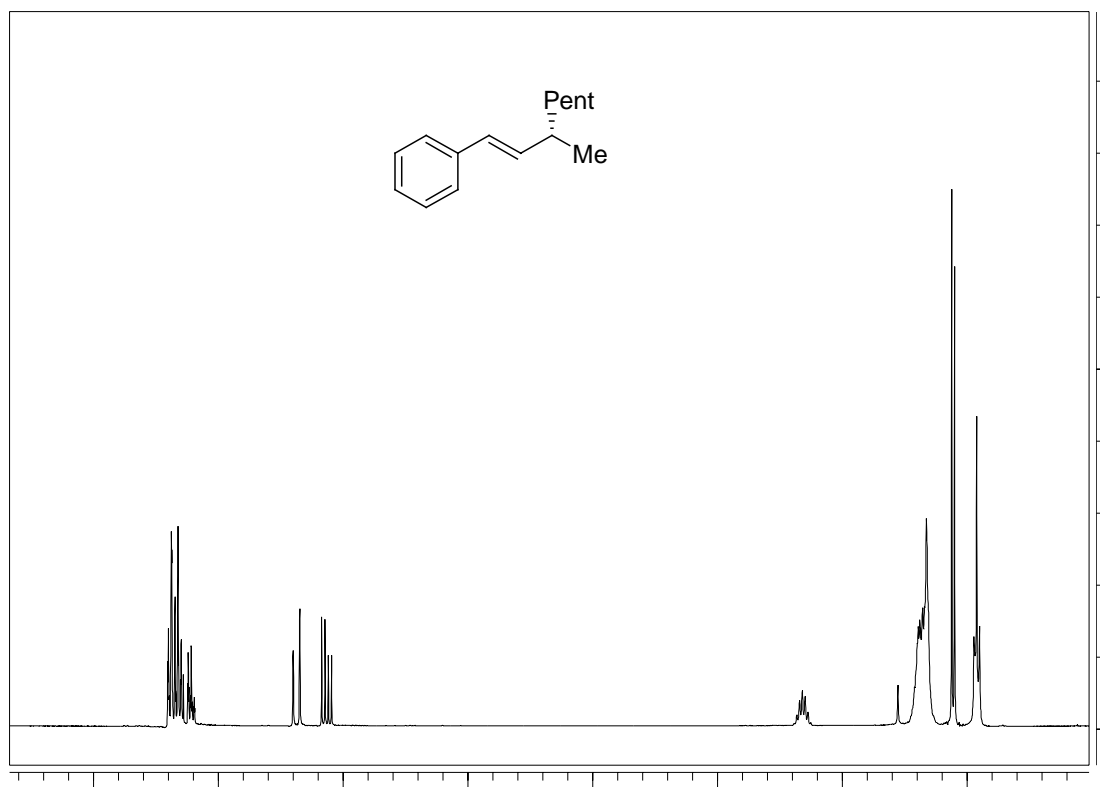
(4*R*,2*E*)- 4-Isopropyl-1-phenyl-non-2-en-1-one ((*R*)-6h):

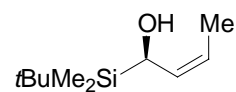
(4*S*,2*E*)-1,4-Diphenyl-non-2-en-1-one ((*S*)-6i):

(4*S*,2*E*)- 1-(2-Fluoro-phenyl)-4-methyl-non-2-en-1-one ((*S*)-6j):

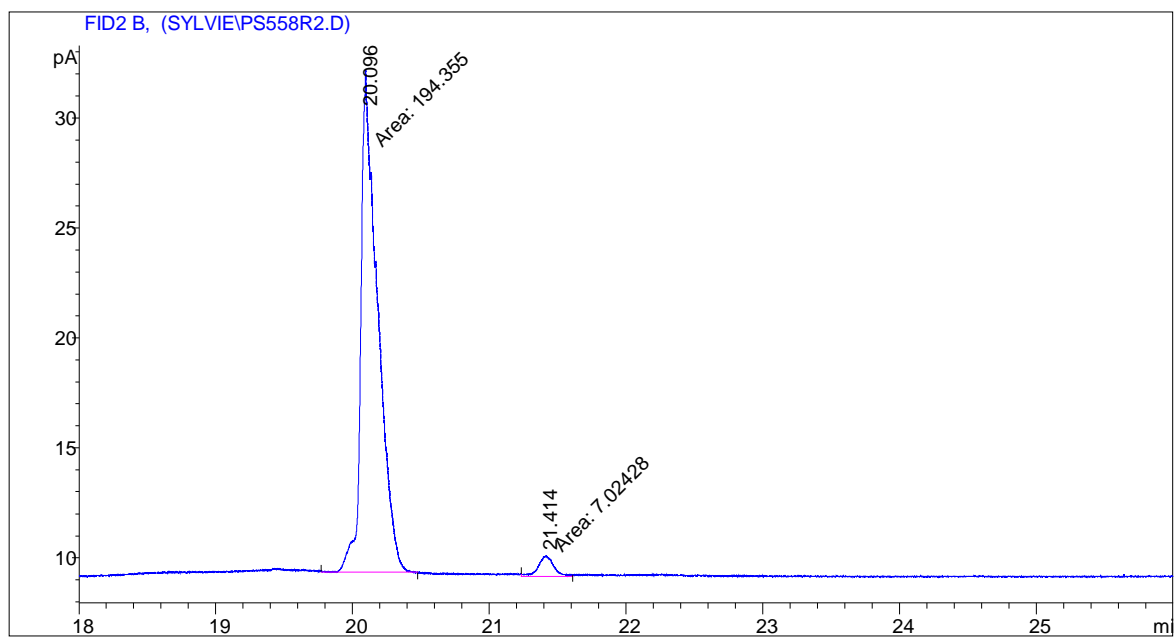
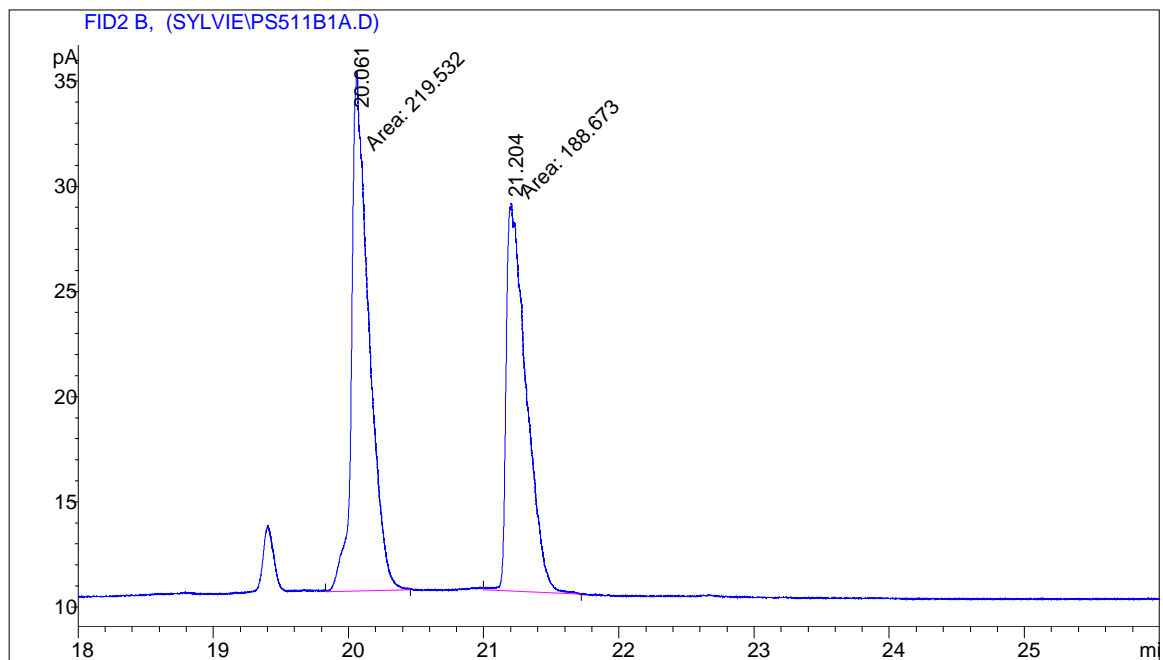
(3*S*,1*E*)- 4,4,5,5-Tetramethyl-2-(3-methyl-oct-1-enyl)-[1,3,2]dioxaborolane ((*S*)-7):

(3*S*,1*E*)- 4-(3-Methyl-oct-1-enyl)-ethyl benzoate ((*S*)-8):

(3*S*,1*E*)- (3-Methyl-oct-1-enyl)-benzene ((*S*)-9):

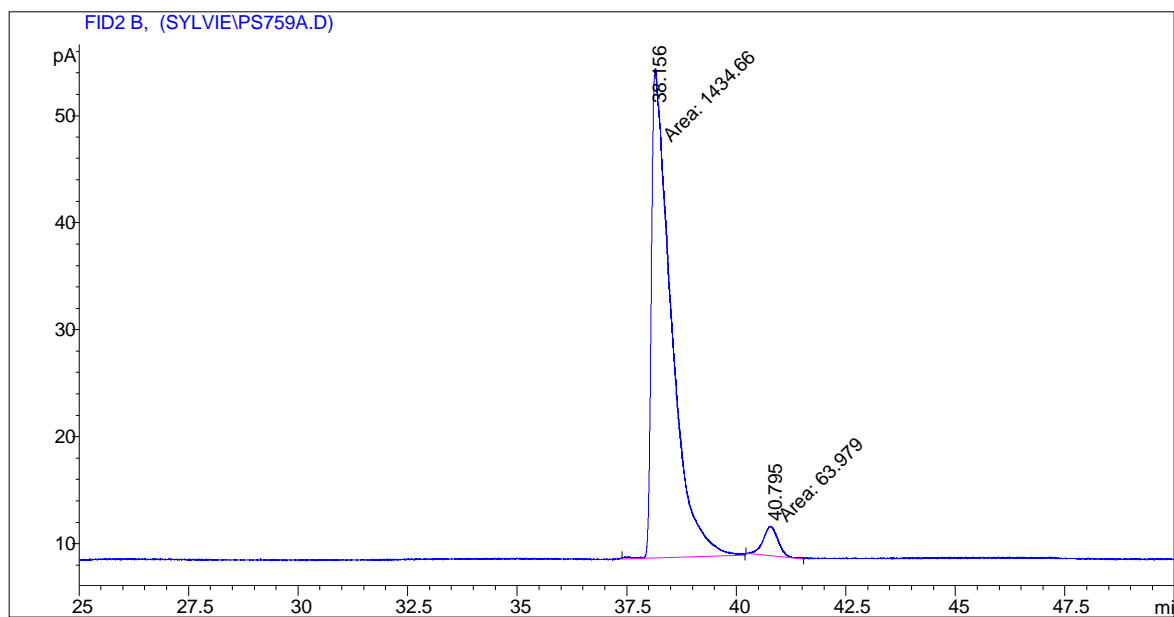
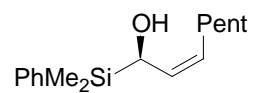
Appendix: Chromatograms for determination of the *ee***(1*R*,2*Z*)-1-(tert-Butyl-dimethyl-silanyl)-but-2-en-1-ol ((*R*)-5a):**

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 100 °C



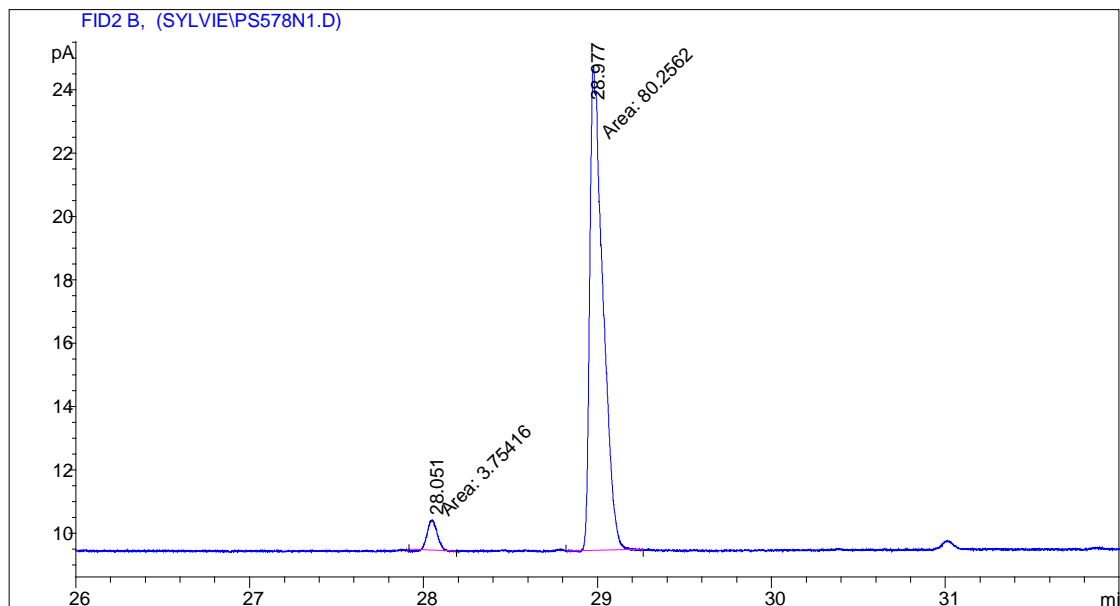
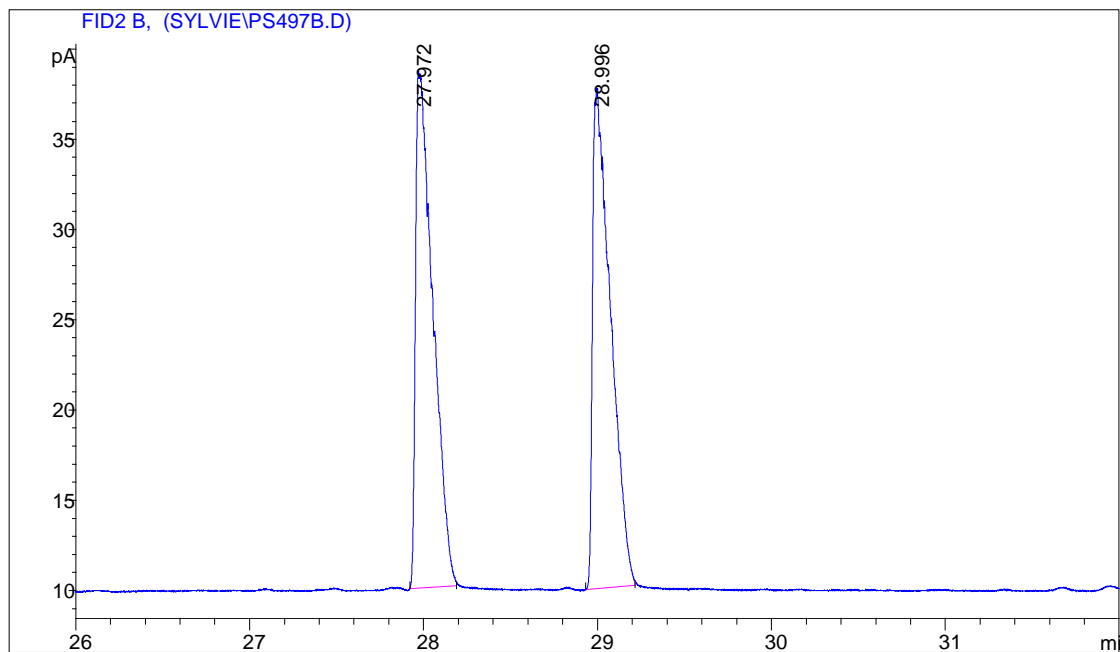
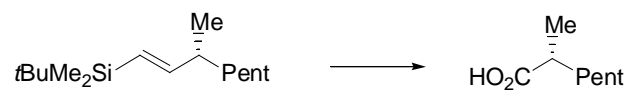
(1*R*,2*Z*)-1-(Dimethyl-phenyl-silanyl)-oct-2-en-1-ol ((*R*)-5b):

GC: Chirasil-Dex CB, 140 °C constant.



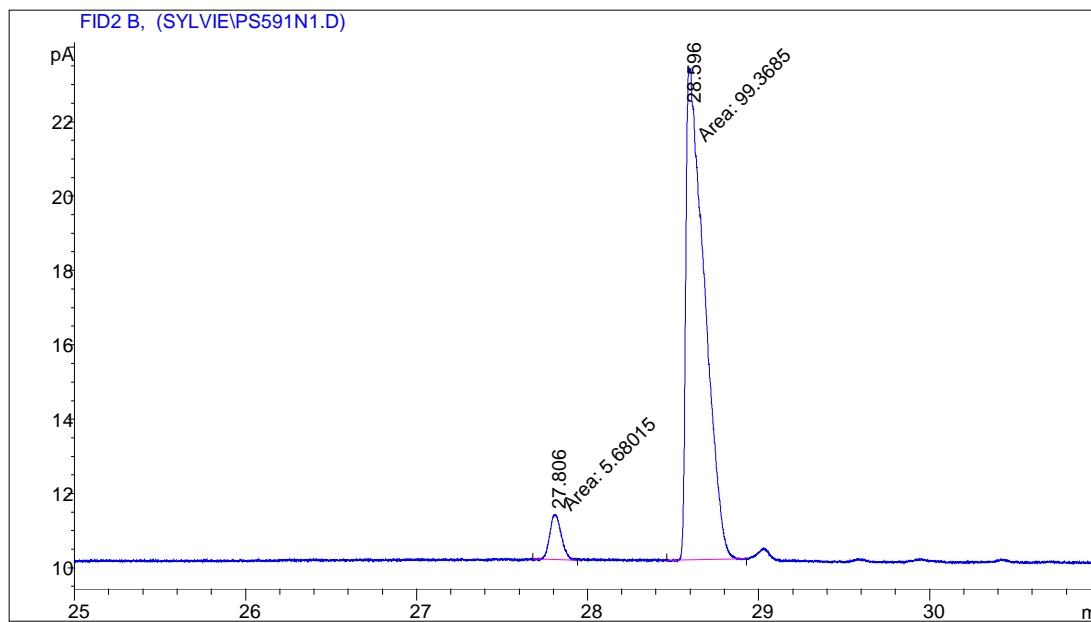
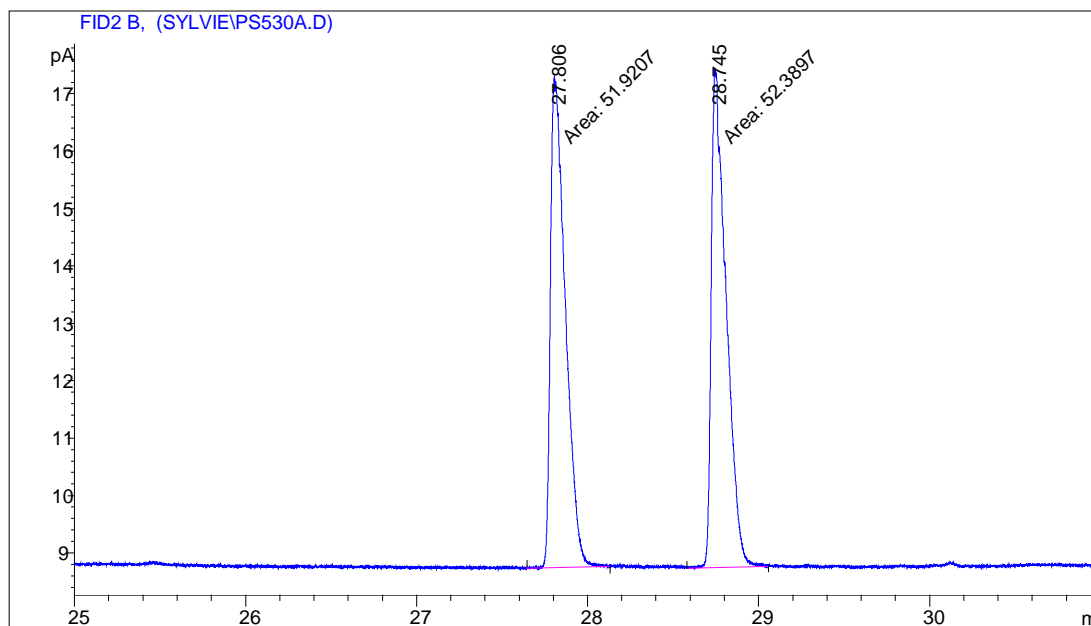
(2*R*)-2-methylheptanoic acid: determination of the *ee* for **1a**

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C



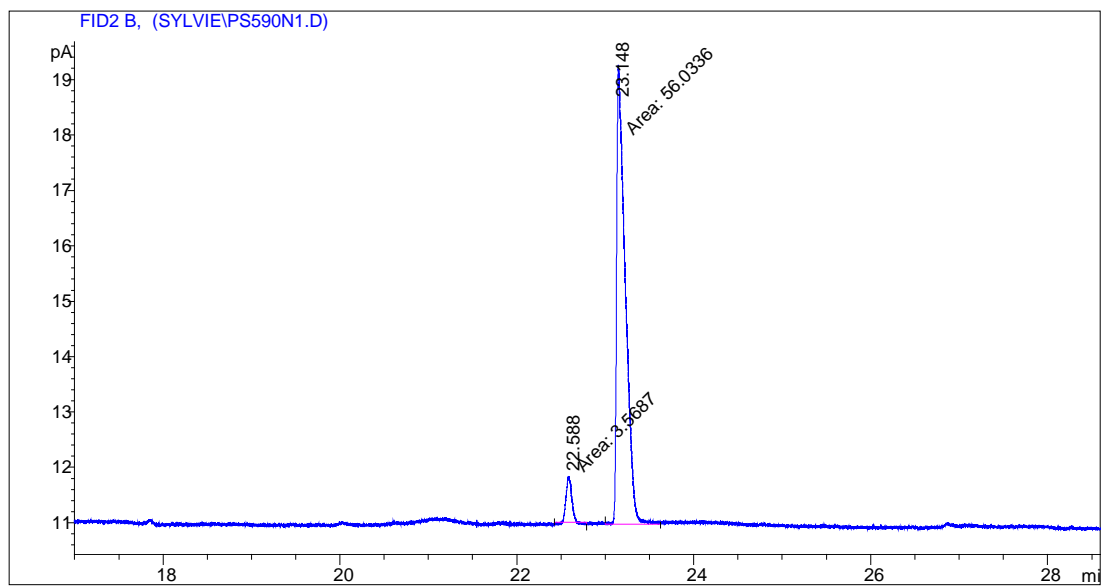
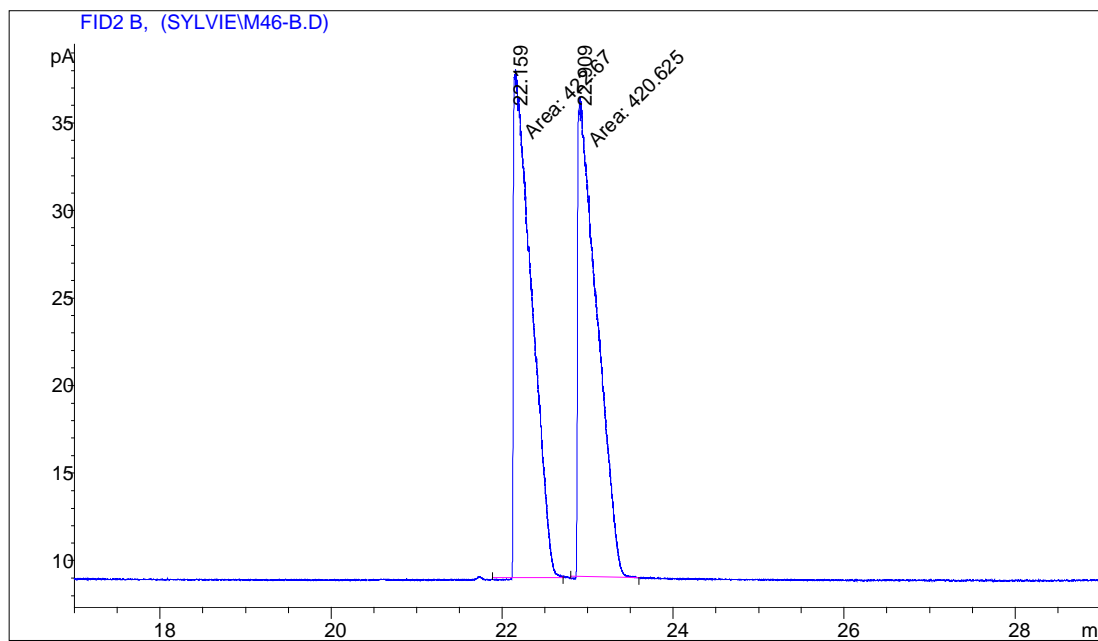
(2R)-2-3-dimethylbutanoic acid: determination of the *ee* for **1b**.

GC (Chirasil-Dex CB), 50 °C (1 min), ramp of 2 °C/ min to 140 °C



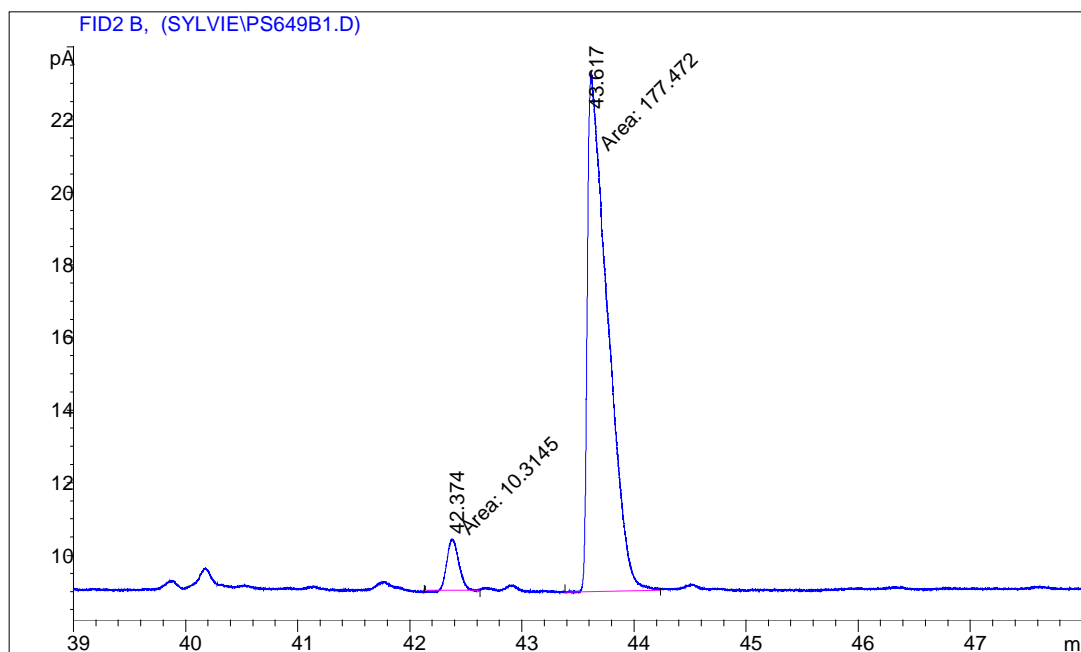
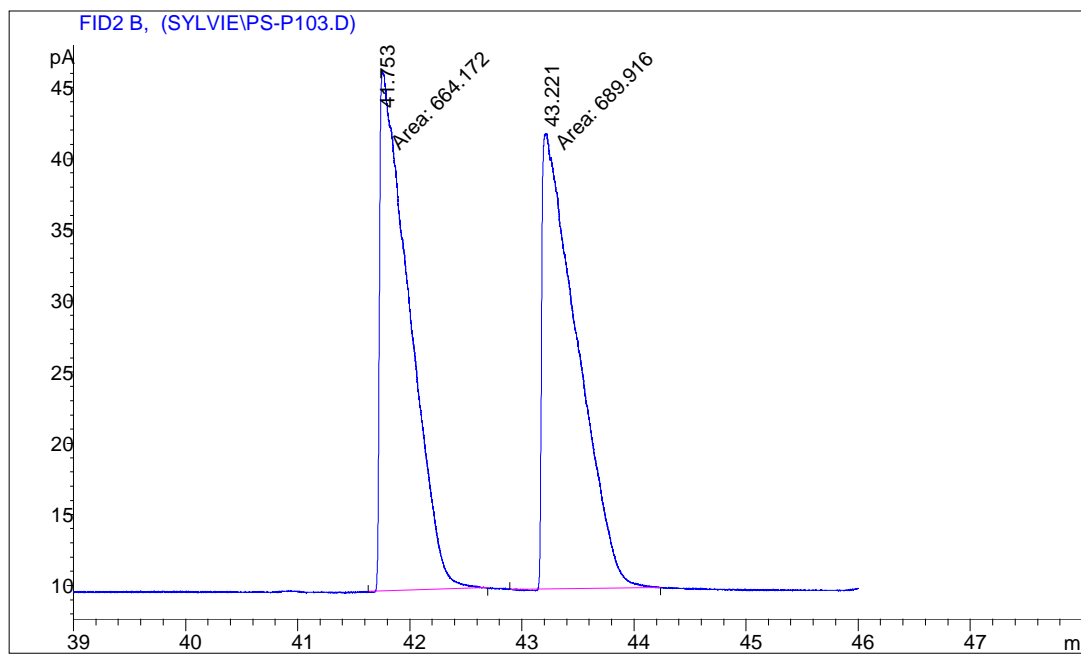
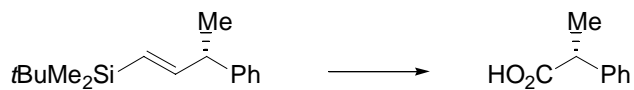
(2*R*)-2-methylbutanoic acid: determination of the *ee* for **1c**

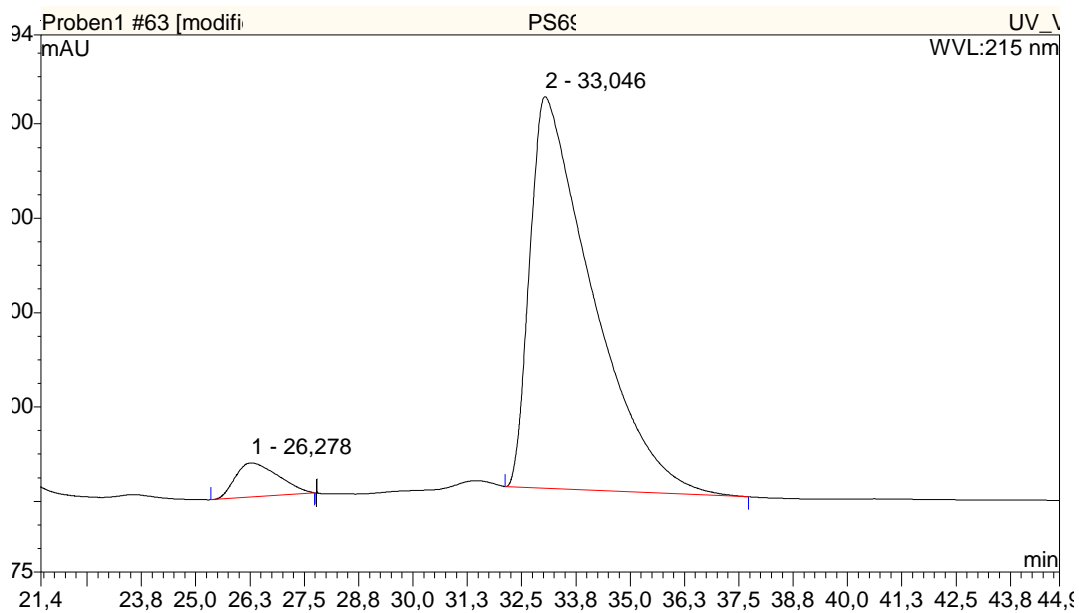
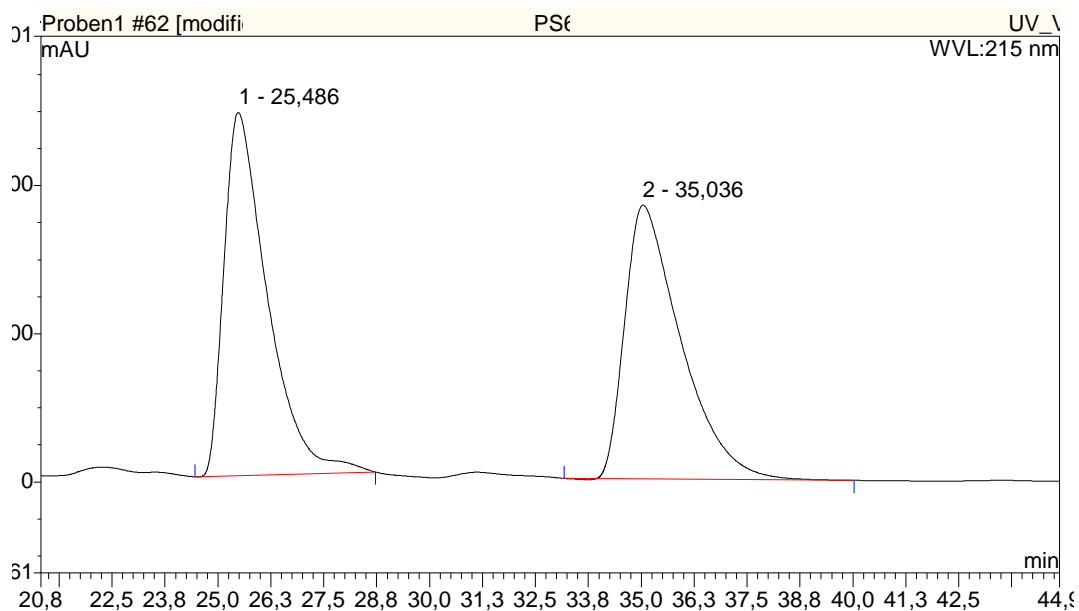
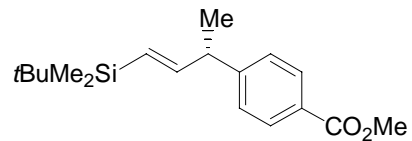
GC (Chirasil-Dex CB), 50 °C (1 min), ramp of 2 °C/ min to 140 °C

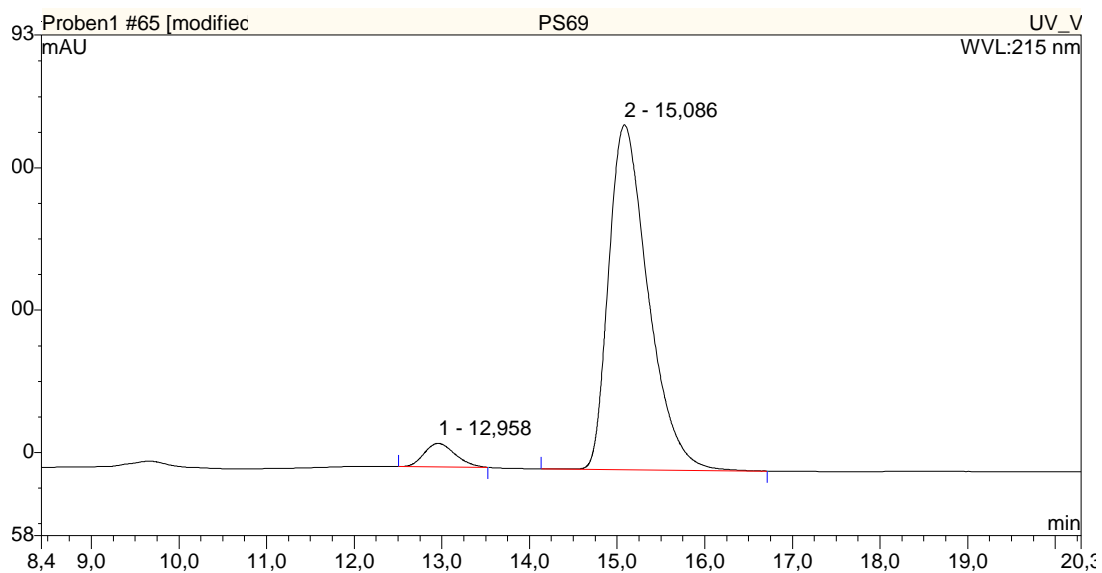
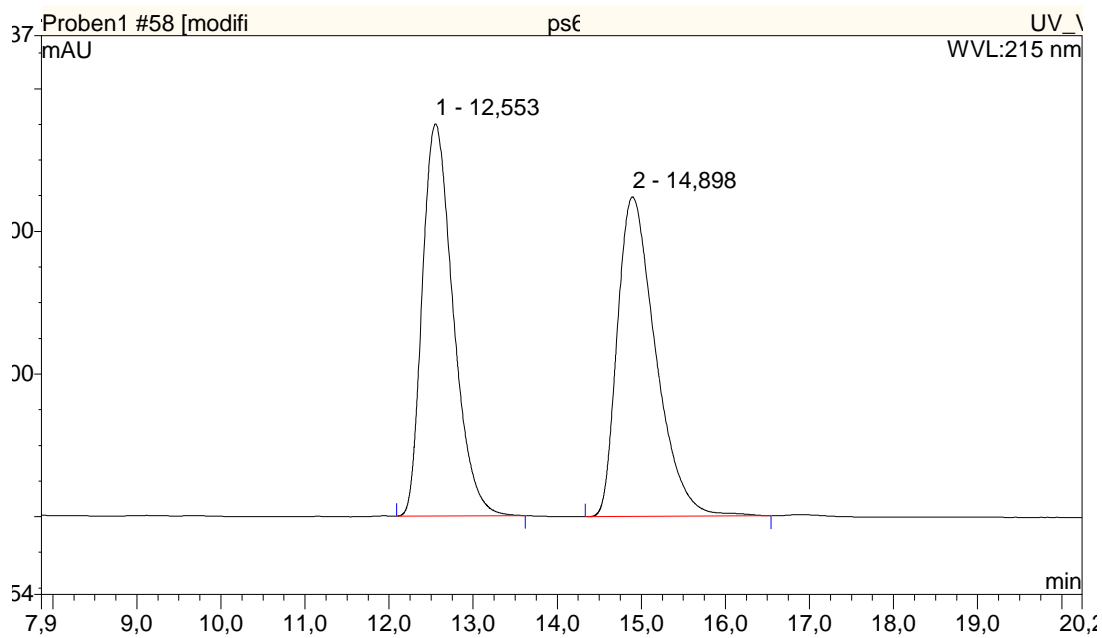
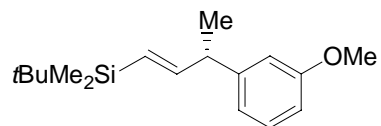


(2R)-2-phenylpropanoic acid: determination of the *ee* for **1d**

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C

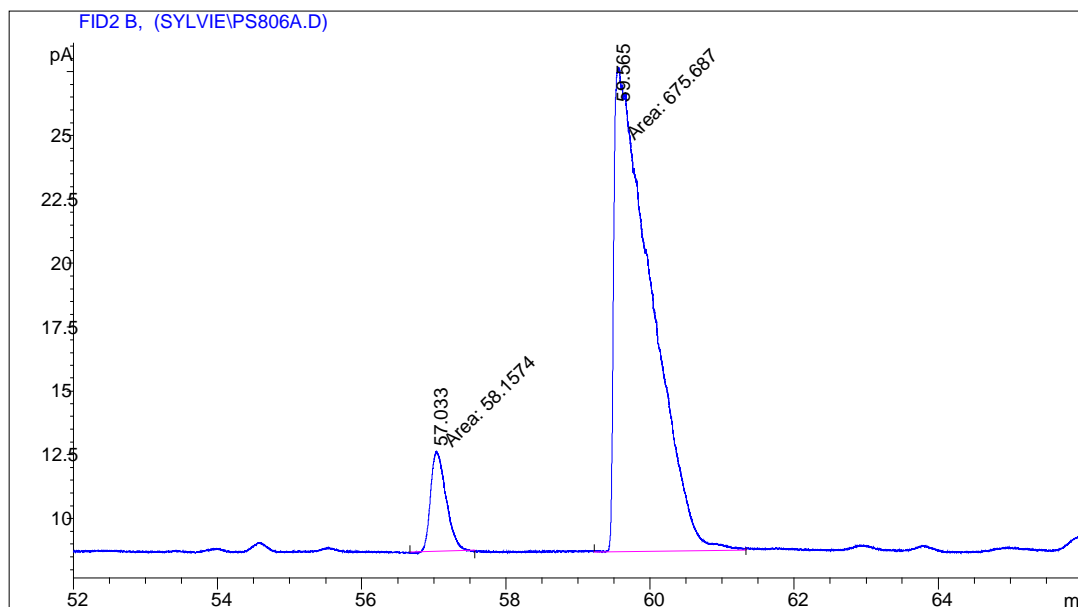
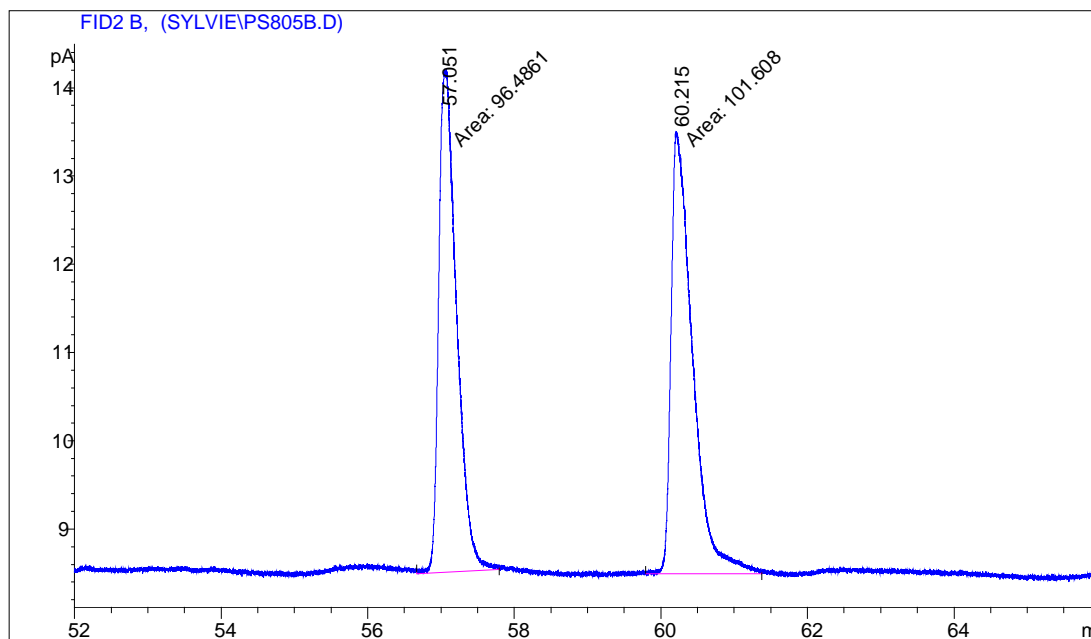
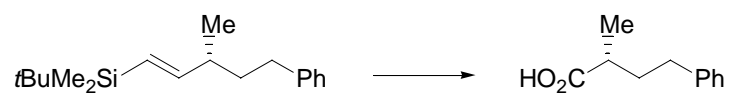


4-[(1S,2E)-3-(tert-Butyl-dimethyl-silanyl)-1-methyl-allyl]- methylbenzoate (1e).HPLC: column: OD-H; *n*-heptane 100%, 0.5 mL/min.

(3*S*,1*E*)-tert-Butyl-[3-(3-methoxy-phenyl)-but-1-enyl]-dimethyl-silane (1f).HPLC: column: OD-H; *n*-heptane 100%, 0.5 mL/min.

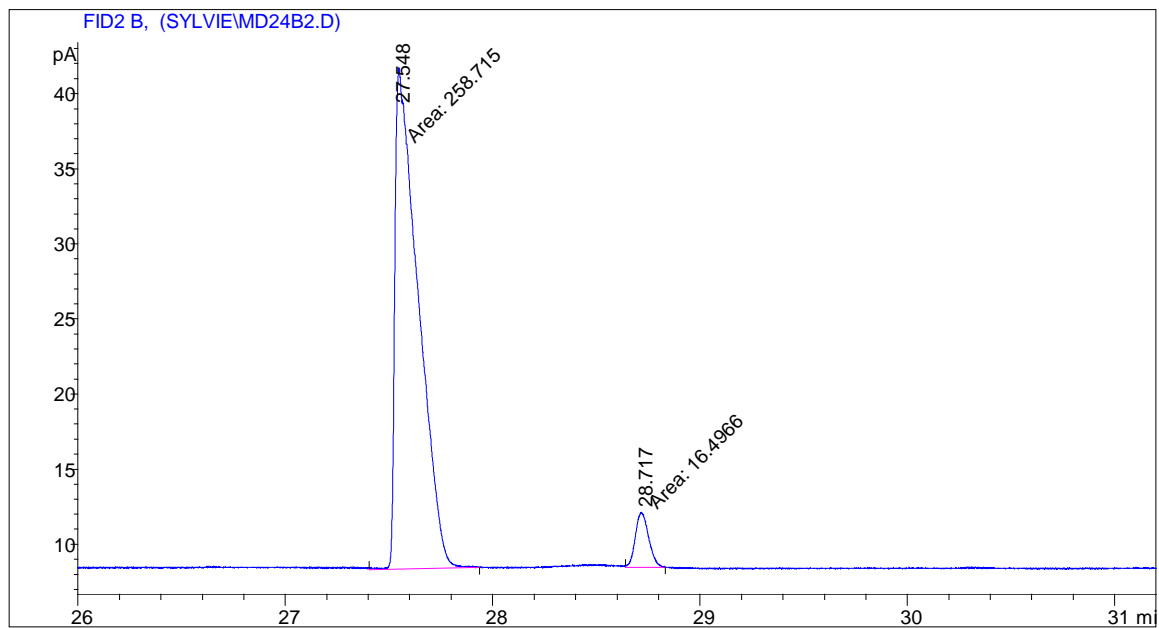
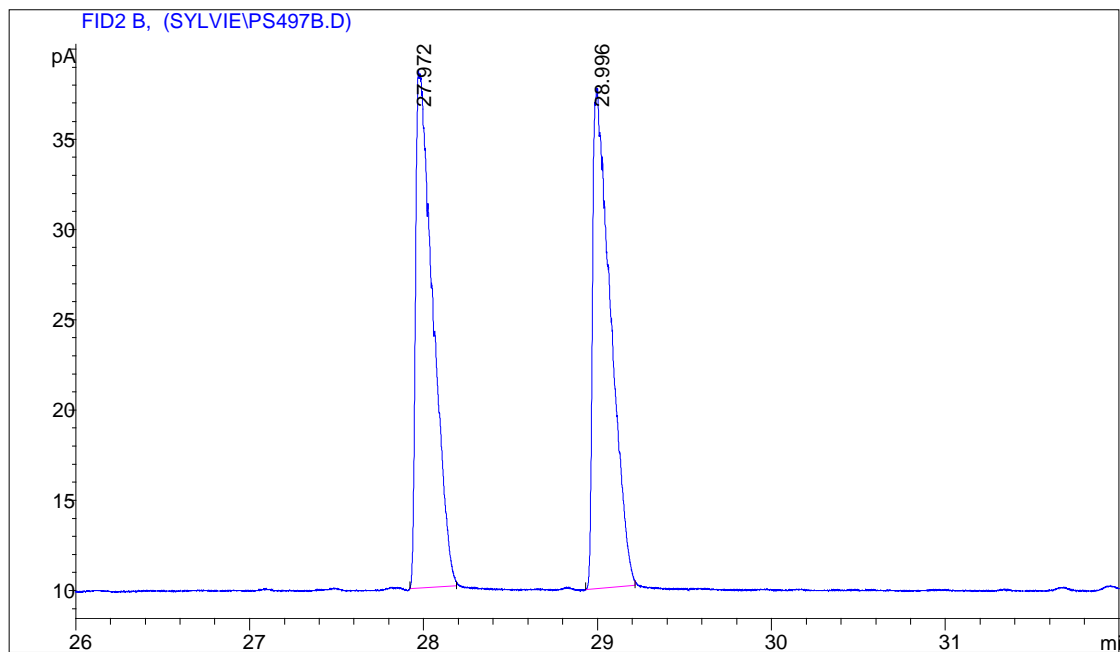
(2R)-2-methyl-4-phenylbutanoic acid: determination of the *ee* for **1g**

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C



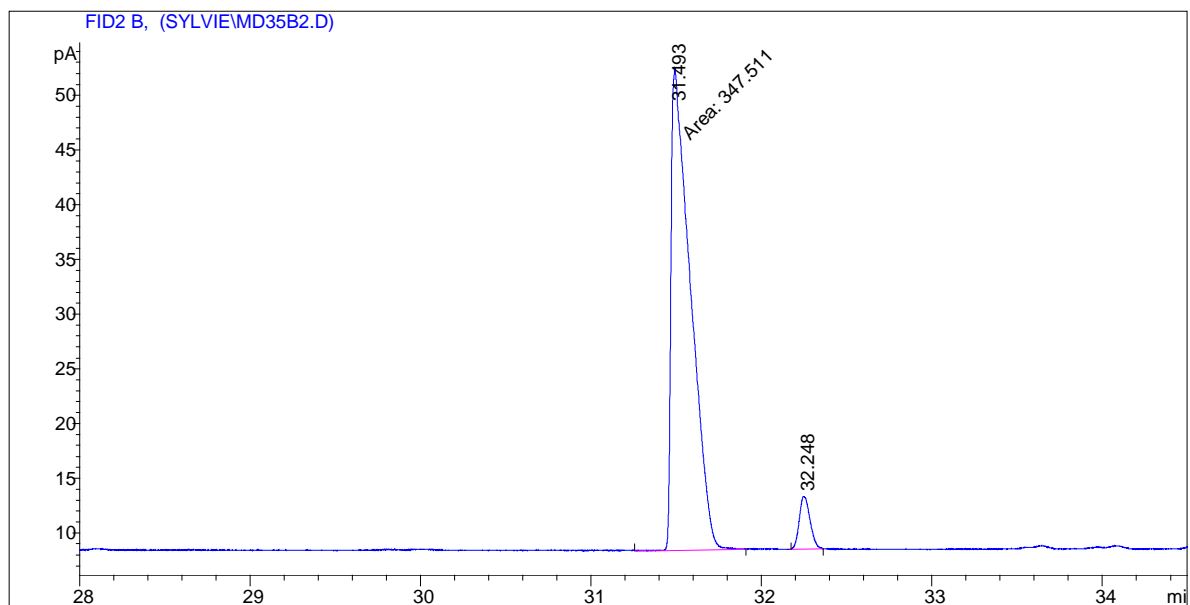
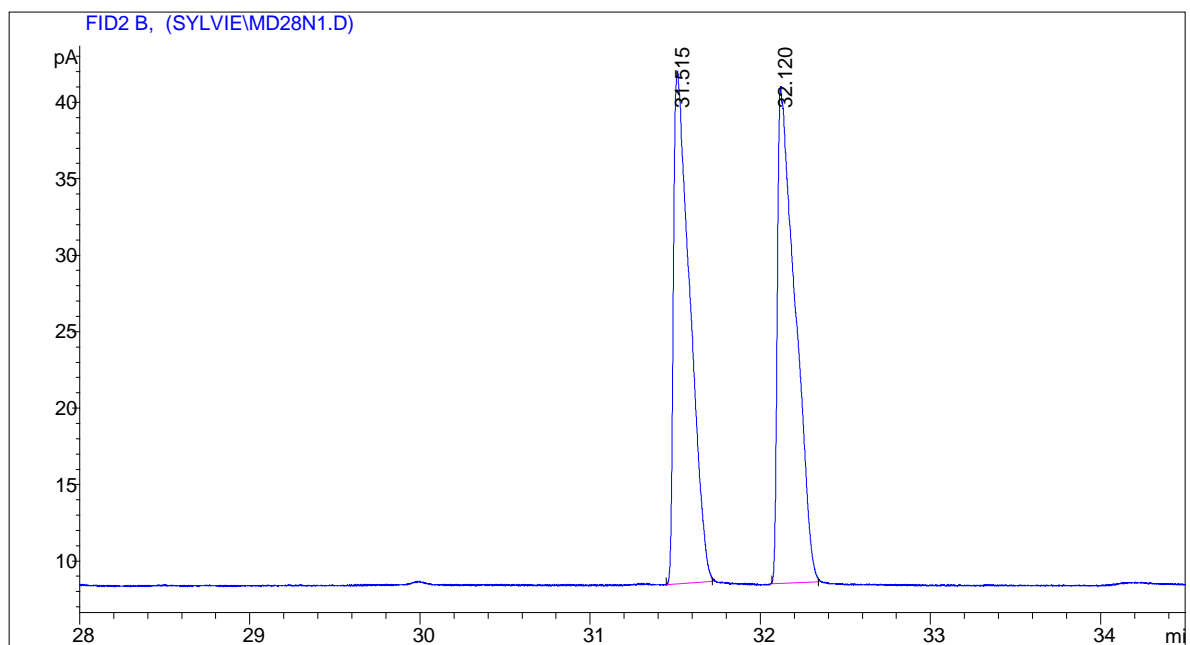
(2S)-2-methylheptanoic acid: determination of the *ee* for **1h**

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C



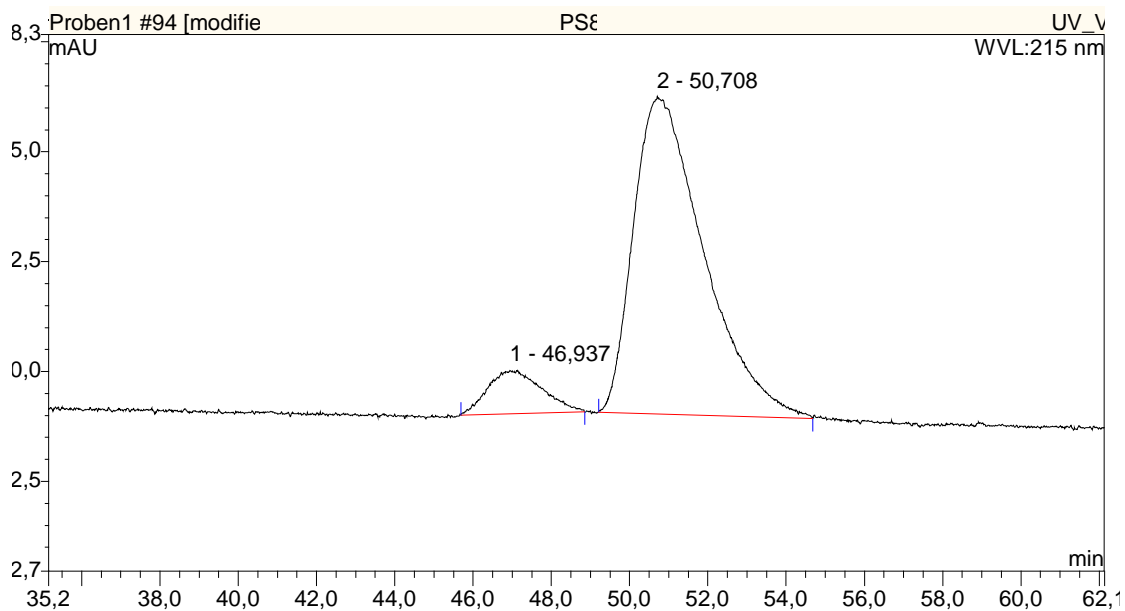
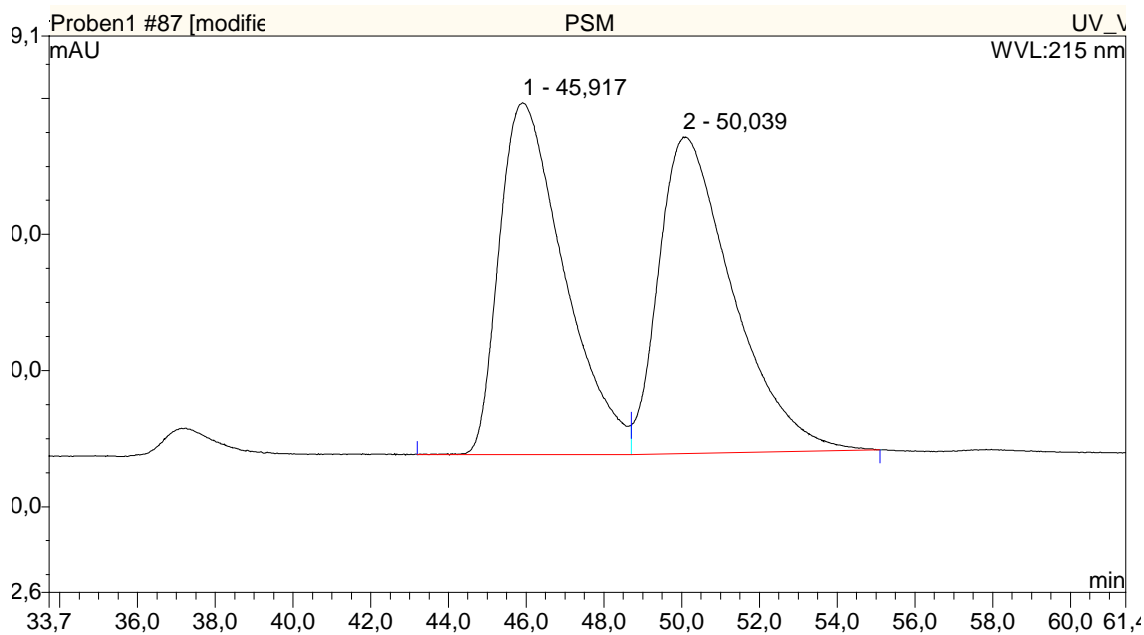
(2S)-2-Ethylheptanoic acid: determination of the *ee* for **1i**

GC (Chirasil-Dex CB), 70 °C (1 min), ramp of 2 °C/ min to 140 °C



(4*R*,2*E*)- 4-Isopropyl-1-phenyl-non-2-en-1-one (6h): determination of the *ee* for **1j**

HPLC : column: OD-H; *n*-heptane 100%, 0.5 mL/min.



(4*S*,2*E*)-1,4-Diphenyl-non-2-en-1-one (6i): determination of the *ee* for **1k**

HPLC: column: OD-H; *n*-heptane / *i*PrOH 98:2, 0.5 mL/min.

