Supplementary Material for Organic & Biomolecular Chemistry
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Efficient and flexible Synthesis of Chiral γ- and δ-Lactones

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Supporting Information

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1. General

Infrared spectra were recorded on a Bruker Equinox 55 FTIR spectrometer and ^{1}H NMR spectra were run on a Bruker Avance DRX 500. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are presented as follows: chemical shift, multiplicity, coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 NMR spectrometer (125 MHz) with complete proton decoupling. Chemical shifts are given in ppm from tetramethylsilane with the solvent as the internal standard ($CHCl_3$: δ 77.0 ppm). High resolution mass spectra (HRMS) were run on a Micromass MasSpec in direct insertion mode. HRMS data provide accurate masses for the molecular ion (M^+) or suitable fragments. Analytical thin layer chromatography was performed on pre-coated Merck silica gel 60-F254 plates. Merck silica gel (Kieselgel 60, 230-400 mesh) was used for flash chromatography. Solvents for extraction and chromatography were of technical grade quality and distilled before use. Reactions were conducted in flame-dried glassware with magnetic stirring under an inert atmosphere of dry argon. Commercially available reagents were used without further purification.

2. Determination of Enantiomeric Purity

Enantiomeric excesses (ee's) were determined either directly by capillary GC analysis using a chiral stationary phases (FS-Hydrodex β-3P, FS-Hydrodex β-6TBDM) or after derivatization with (*R*)- or (*S*)-1-phenylethyl isocyanate ((*R*)- or (*S*)-1-PEIC) or (*S*)-(+)- or (*R*)-(−)-α-1-methoxy−1-trifluoromethyl-phenylacetyl chloride (MTPA chloride). (*R*)- and (*S*)-1-PEIC and (*R*)- and (*S*)-MTPA chloride were purchased from Fluka in the highest commercially available optical purity, (Fluka Chiraselect ≥ 99.5% ee). Derivatization procedures for *Mosher esters*[1, 2] and carbamates (1-PEC)[3-5] followed established protocols.

Capillary gas chromatography was performed with a Hewlett Packard 5890 Series II Gas Chromatograph, Fision GC 8000 Gas Chromatograph or Thermo Scientific Trace GC 2000 connected to a Trace MS detector (Thermo Scientific) with He as a carrier gas. Colums: FS-Hydrodex β-3P (25m x 0.25mm id x 0.25µm film; Macherey-Nagel) set at a column head pressure of 7 psi; FS-Hydrodex β-6TBDM (20m x 0.25mm id x 0.25µm film; Macherey-Nagel) set at a column head pressure of 5 psi; EC-5 (5% phenyl, 95% methylpolysiloxane, 15m x 0.25mm id x 0.25µm film; Alltech) operated with constant flow of 1.2 cm^3 min^{-1} helium.

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2. J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, 1973, **95**, 512-519.
3. K. H. Engel, W. Albrecht and J. Heidlas, *J. Agric. Food Chem.*, 1990, **38**, 244-247.
4. K. H. Engel, R. A. Flath, W. Albrecht and R. Tressl, *J. Chromatogr.*, 1989, **479**, 176-180.
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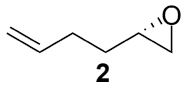
3. Synthesis of Substrates

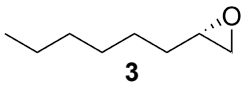
Chiral terminal epoxides were obtained by hydrolytic kinetic resolution (HKR), using (*S,S*)-(+)- or (*R,R*)-(–)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) **1** as catalyst, according to published procedures.[6, 7] The enantiomeric excess (ee) of the chiral epoxides was generally > 99%.



2

(*S*)-1,2-Epoxy-5-hexene [2]

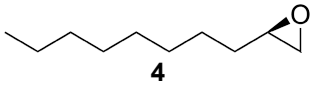
Prepared from (±)-1,2-epoxy-5-hexene (9.81 g, 100 mmol), AcOH (120 mm^3, 2.1 mmol), THF (1 cm^3) and H_2O (1 g, 55 mmol) in the presence of (*S,S*)-**1** (302 mg, 0.5 mmol) to yield **2** (4.3 g, 44%). Ee: > 99%, determined as the 1-cyano-2-trimethylsiloxy-5-hexene[8] on Hydrodex β-6TBDM. Separation was achieved under programmed conditions: 50 °C (2 min isotherm) at 2 °C min^{-1} to 130 °C, t_R (minor) = 30.4 min, t_R (major) = 31.5 min), R = 4.47.



3

(*S*)-1,2-Epoxy-octane [3]

Prepared from (±)-1,2-epoxy-octane (8.0 g, 62 mmol), AcOH (120 mm^3, 2.1 mmol), THF (1 cm^3) and H_2O (618 mg, 34.1 mmol) in the presence of (*S,S*)-**1·OTs**[7] (26 mg, 0.32 μmol) to yield **3** (3.4 g, 43%). Ee: > 99%, determined by gas chromatography on Hydrodex β-3P. Separation was achieved under programmed conditions: 40 °C (2 min isotherm) at 1 °C min^{-1} to 75 °C, t_R (minor) = 29.7 min, t_R (major) = 30.4 min), R = 1.84.



4

(*R*)-1,2-Epoxy-decane [4]

Prepared from (±)-1,2-epoxy-decane (3.0 g, 19.2 mmol) and H_2O (242 mg, 13.4 mmol) in the presence of (*S,S*)-**1·OTs**[7] (7.8 mg, 10.1 μmol) to yield **4** (1.2 g, 40%). Ee: > 99%, determined by gas chromatography on Hydrodex β-3P. Separation was achieved under programmed conditions: 50 °C (2 min isotherm) at 2 °C min^{-1} to 120 °C, t_R (major) = 26.1 min, t_R (minor) = 26.9 min), R = 1.86.

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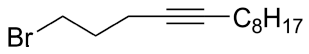
7. L. P. C. Nielsen, C. P. Stevenson, D. G. Blackmond and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2004, **126**, 1360-1362.
8. B. Mirmashhori, N. Azizi and M. R. Saidi, *Journal of Molecular Catalysis A: Chemical*, 2006, **247**, 159-161.



5

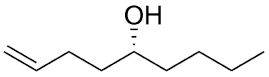
1-Bromotridec-4-yne [5] [9]

1-Decyne (2.5 g, 18.1 mmol) in THF (20 cm^3) was treated over 10 min with stirring with a solution of *n*-BuLi in hexane (1.58 M, 9.5 cm^3, 15.1 mmol) at -78 °C and stirring was continued for 30 min. After addition of DMPU (1.8 cm^3), the mixture was transferred to a solution of 1,3-dibromopropane (3.0 g, 15.1 mmol) in THF (15 cm^3) and allowed to warm to room temperature over 1h. After stirring for 14 h saturated aqueous solution of NH_4Cl (30 cm^3, saturated aqueous solution) was added and the alkyne was extracted with ether (3 x 40 cm^3). The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. Purification was achieved by column chromatography (SiO_2) using petroleum ether for elution to yield **5** (2.9 g, 73%) as a colorless oil.

δ_H(500 MHz; $CDCl_3$) 3.51-3.53 (t, *J* = 6.6 Hz, 2H), 2.32-2.36 (m, 2H), 2.11-2.15 (m, 2H), 2.01 (dt, *J*= 6.7, 6.8 Hz, 2H), 1.43-1.50 (m, 2H), 1.22-1.40 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 81.6, 77.9, 32.5, 32.0, 31.8, 29.2, 29.1, 29.0, 28.9, 22.7, 18.7, 17.5, 14.1; ν_{max}(film)/cm^{-1} 2927, 2855, 1465, 1433, 1378, 1350, 1331, 1272, 1247, 1206, 1169, 961, 854, 765, 723, 652; Accurate mass (EI) calcd for $C_{13}H_{23}Br$ (M^+) 258.099213. Found 258.098312.

Alkylation of terminal epoxides by Grignard reagents: general procedure

A solution of the alkenylmagnesium bromide, prepared from alk-1-enyl bromide (8 mmol) and Mg turnings (12 mmol) in Et_2O (10 cm^3), was transferred via cannula, into a well stirred suspension (at -40 °C) of cuprous iodide (0.56 mmol, 7 mol%) in THF (15 cm^3). After 10 minutes a solution of the epoxide (6 mmol) in THF (10 cm^3) was added dropwise and the stirring was continued for 4 h at this temperature. The mixture was allowed to come to room temperature and hydrolyzed with NH_4Cl (25 cm^3, saturated aqueous solution). The products were extracted with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and evaporated. The crude product was resuspended in pentane and placed in a fridge for crystallisation (-20 °C). Pure alk-1-enols were obtained as colorless crystals (70-90% yield). Alk-1-enols (< C_{12}) were purified by flash chromatography (SiO_2, hexane:Et_2O = 2:1, v:v).



6

(*R*)-Non-1-en-5-ol [6]

Prepared from 1-propyl bromide (2.13 g, 17.3 mmol), Mg (0.5 g, 20.4 mmol) in Et_2O (15 cm^3), CuI (0.27 g, 1.43 mmol), and epoxide **2** (1 g, 10.2 mmol) in THF (35 cm^3) as described to yield **6** (1.1 g, 74%) as a colorless oil. Ee: > 97% according to ^{1}H-NMR of the corresponding *Mosher* ester.[1, 2]

δ_H(500 MHz; $CDCl_3$) 5.84 (tdd, *J* = 16.9, 10.2, 6.7, 1H), 5.02-5.07 (m, 1H), 4.95-4.99 (m, 1H), 3.59-3.65 (m, 1H), 2.09-2.25 (m, 2H), 1.24-1.61 (m, 9H), 0.91 (t, *J* = 7.1 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 138.6, 114.7, 71.5, 37.2, 36.5, 30.1, 27.8, 22.7, 14.1; ν_{max}(film)/cm^{-1} 3346, 3078, 2931, 2860, 1822, 1641, 1415, 1379, 1340, 1210, 11263, 1039, 996, 909, 788, 732, 644; Accurate mass (EI) calcd for $C_9H_{18}O$ (M^+) 142.136242. Found 142.135765

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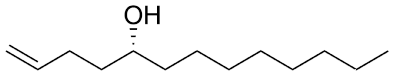
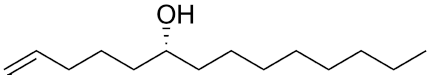


7

(*R*)-Tridec-1-en-5-ol [7]

Prepared from allylmagnesium bromide (1M sol. THF, 5.5 cm^3, 5.5 mmol), CuI (93 mg, 0.49 mmol), and epoxide **4** (0.5 g, 3.21 mmol) in THF (10 cm^3) as described to yield **7** (0.49 g, 77%) as colorless crystals. Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 120 °C (2 min isotherm) at 4 °C min^{-1} to 250 °C; t_R (major) = 24.6 min, t_R (minor) = 24.8 min; R = 1.82.

δ_H(500 MHz; $CDCl_3$) 5.80-5.84 (m, 1H), 4.95-5.07 (m, 2H), 3.59-3.64 (m, 1H), 2.09-2.27 (m, 2H), 1.37-1.61 (m, 6H), 1.20-1.36 (m, 11H), 0.88 (t, J = 7.0 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 138.7, 114.7, 71.5, 37.5, 36.5, 31.9, 30.1, 29.7, 29.6, 29.3, 25.6, 22.7, 14.1; ν_{max}(solid)/cm^{-1} 3344, 3077, 2926, 2855, 1822, 1641, 1466, 1377, 1261, 1127, 994, 910, 804, 722, 658; Accurate mass (EI) calcd for $C_{13}H_{24}$ ($M-H_2O^+$) 180.188228. Found 180.187801.

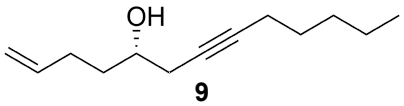


8

(*R*)-Tetradec-1-en-6-ol [8]

Prepared from 4-bomo-but-1-ene (0.74 g, 5.5 mmol), Mg (0.2 g, 8 mmol) in Et_2O (6 cm^3), CuI (93 mg, 0.49 mmol), and epoxide **4** (0.5 g, 3.21 mmol) as described to yield **8** (0.56 g, 82%) as colorless crystals. Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 120 °C (2 min isotherm) at 4 °C min^{-1} to 180 °C, and at 1.5 °C min^{-1} to 210 °C; t_R (major) = 32.5 min, t_R (minor) = 32.8 min; R = 1.42.

δ_H(500 MHz; $CDCl_3$) 5.75-5.90 (m, 1H), 4.99-5.04 (m, 1H), 4.93-4.97 (m, 1H), 3.63-3.56 (m, 1H), 2.14-2.01 (m, 2H), 1.35-1.21 (m, 12H), 1.61-1.37 (m, 7H), 0.88 (t, J = 7.0 Hz, 1H); δ_C(125 MHz; $CDCl_3$) 138.7, 114.5, 71.8, 37.5, 36.9, 33.7, 31.9, 29.7, 29.6, 29.3, 25.6, 24.9, 22.7, 14.1; ν_{max}(solid)/cm^{-1} 3330, 3078, 2924, 2853, 1642, 1468, 1378, 1344, 1133, 1090, 1024, 992, 910, 829, 721, 639 cm^{-1}; Accurate mass (EI) calcd for $C_{14}H_{28}O$ (M^+) 212.213646. Found 212.214016.



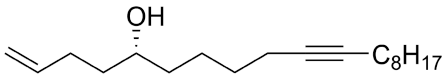
9

(5*S*)-Tridec-1-en-7-yn-5-ol [9] [10, 11]

A stirred solution of 1-heptyne (1.3 g, 13.2 mmol) in THF (20 cm^3) at -78 °C was treated with n-BuLi (7.7 cm^3, 12.2 mmol of an 1.58 M solution in hexane). The mixture was cooled (0 °C) and maintained at this temperature for 15 min. Then, the epoxide **2** (1.0 g, 10.2 mmol) in THF (5 cm^3) was added with stirring at -78 °C followed by $BF_3 \cdot Et_2O$ (1.5 cm^3, 12.2 mmol). After 2h the reaction was hydrolyzed with NH_4Cl (30 cm^3 of a saturated aqueous solution). After warming to room temperature the product was extracted with Et_2O. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Purification was achieved by chromatography on silica gel (petroleum ether: Et_2O, 3:1) to yield **9** (1.8 g, 91%) as a colorless oil.

Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 120 °C (2 min isotherm) at 4 °C min^{-1} to 180 °C, and at 1.5 °C min^{-1} to 210 °C; t_R (major) = 28.2 min, t_R (minor) = 28.4 min; R = 1.29.

δ_H(500 MHz; $CDCl_3$) 5.78-5.88 (m, 1H), 5.02-5.08 (m, 1H), 3.75-3.67 (m, 1H), 2.37-2.43 (m, 1H), 2.25-2.32 (m, 1H), 2.24-2.09 (m, 4H), 1.95-2.00 (m, 2H), 1.59-1.64 (m, 2H), 1.53-1.45 (m, 2H), 1.39-1.27 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 138.2, 114.8, 83.4, 75.8, 69.6, 35.2, 31.1, 29.9, 28.7, 27.8, 22.2, 18.7, 14.0; ν_{max}(film)/cm^{-1} 3375, 3078, 2932, 2860, 1826, 1641, 1434, 1379, 1330, 1079, 1024, 994, 911, 848, 725, 657; Accurate mass (EI) calcd for $C_{13}H_{22}O$ (M^+) 194.166912. Found 194.167066.

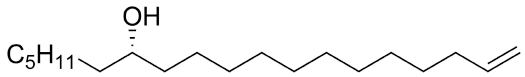


10

(*R*)-Nonadec-1-en-10-yn-5-ol [10]

Prepared from 1-bromotridec-4-yne (2.5 g, 9.7 mmol), Mg (0.35 g, 14.5 mmol) in THF (15 cm^3), CuI (263 mg, 1.39 mmol), and epoxide **2** (0.73 g, 7.42 mmol) in THF (30 cm^3) as described to yield **10** (1.73 g, 84%). Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 120 °C (2 min isotherm) at 4 °C min^{-1} to 180 °C, and at 1 °C min^{-1} to 250 °C; t_R (major) = 64.5 min, t_R (minor) = 65.2 min; R = 2.03.

δ_H(500 MHz; $CDCl_3$) 5.80-5.89 (m, 1H), 5.02-5.08 (m, 1H), 4.95-4.99 (m, 1H), 3.66-3.60 (m, 1H), 2.26-2.09 (m, 6H), 1.62-1.40 (m, 10H), 1.40-1.33 (m, 3H), 1.32-1.23 (m, 7H), 0.88 (t, J = 7.00 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 138.6, 114.8, 80.5, 79.9, 71.4, 37.0, 36.4, 31.9, 30.1, 29.22, 29.16, 29.13, 29.10, 28.9, 24.8, 22.7, 18.8, 18.7, 14.1; ν_{max}(film)/cm^{-1} 3356, 3078, 2931, 2858, 1642, 1463, 1379, 1334, 1098, 995, 911, 724; Accurate mass (EI) calcd for $C_{19}H_{34}O$ (M^+) 278.261444. Found 278.260966.



11

(*S*)-Nonadec-18-en-7-ol [11]

Prepared from 11-bromoundec-1-ene (1g, 4.31 mmol), Mg (0.16 g, 6.5 mmol) in THF (5 cm^3), CuI (57 mg, 0.3 mmol), and epoxide **3** (0.37 g, 2.87 mmol) in THF (15 cm^3) as described to yield **11** (0.57 g, 70%) as colorless crystals. Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 120 °C (2 min isotherm) at 4 °C min^{-1} to 180 °C, and at 1°C min^{-1} to 250 °C; t_R (major) = 63.3 min, t_R (minor) = 63.8 min, R = 1.36.

δ_H(500 MHz; $CDCl_3$) 5.77-5.86 (m, 1H), 4.96-5.02 (m, 1H), 4.90-4.95 (m, 1H), 3.61-3.55 (m, 1H), 2.07-2.01 (m, 2H), 1.49-1.21 (m, 28H), 0.88 (t, J = 7.0 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 139.2, 114.1, 72.0, 37.50, 37.50, 33.8, 31.8, 29.70, 29.68, 29.61, 29.58, 29.48, 29.38, 29.14, 28.94, 25.65, 25.61, 22.6, 14.1; ν_{max}(solid)/cm^{-1} 3316, 3222, 3082, 2956, 2920, 2849, 1641, 1466, 1345, 1133, 1076, 1025, 991, 914, 859, 832, 722, 670, 643; Accurate mass (EI) calcd for $C_{19}H_{38}O$ (M^+) 282.290939. Found 282.292266.

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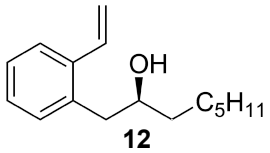
10. M. Yamaguchi and I. Hirao, *Tetrahedron Lett.*, 1983, **24**, 391-394.
11. A. Rodriguez, M. Nomen, B. W. Spur, J. J. Godfroid and T. H. Lee, *Tetrahedron*, 2001, **57**, 25-37.



12

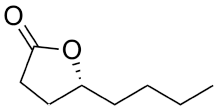
(*S*)-1-(2-Vinylphenyl)octan-2-ol [12]

Prepared from 2-bromostyrene (1g, 5.5 mmol), Mg (0.2 g, 8.2 mmol) in Et_2O (6 cm^3), CuI (83 mg, 0.44 mmol), an epoxide **3** (0.53 g, 4.1 mmol) in THF (15 cm^3) as described to yield **12** (0.87 g, 91%). Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 120 °C (2 min isotherm) at 4 °C min^{-1} to 200 °C, and at 1.5 °C min^{-1} to 225 °C; t_R (major) = 35.8 min, t_R (minor) = 36.0 min, R = 1.50.

δ_H(500 MHz; $CDCl_3$) 7.54-7.50 (m, 1H), 7.26-7.21 (m, 2H), 7.20-7.16 (m, 1H), 6.98-7.05 (m, 1H), 5.62-5.68 (m, 1H), 5.29-5.33 (m, 1H), 3.83-3.76 (m, 1H), 2.90-2.95 (m, 1H), 2.70-2.76 (m, 1H), 1.58-1.25 (m, 11H), 0.89 (t, J = 7.0 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 137.1, 136.1, 134.6, 130.7, 127.8, 126.8, 126.0, 115.8, 72.2, 41.2, 37.0, 31.8, 29.3, 25.7, 22.6, 14.0; ν_{max}(film)/cm^{-1} 3361, 3086, 3062, 3018, 2928, 2856, 1917, 1823, 1626, 1603, 1483, 1454, 1415, 1377, 1124, 1038, 989, 911, 879, 851, 773, 737, 659; Accurate mass (EI) calcd for $C_{16}H_{24}O$ (M^+) 232.181738. Found 232.182716.

General procedure for oxidative cleavage of the terminal double bond by OsO_4 [12, 13]

The alk-1-enol (2 mmol) was dissolved in DMF (0.2 M), and OsO_4 (250 mm^3, 0.01 eq, 2.5% in *t*BuOH) was added and stirred for 5 min while the color changed. Oxone (DuPont, 8 mmol) was added in one portion and the reaction was stirred at RT until TLC ensured complete reaction, usually 2h. Na_2SO_3 (12 mmol) was added and stirred for 1h. The product was extracted with EtOAc and 1N HCl was added to dissolve the salts. The organic extracts were washed with 1N HCl (3x) and brine, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The product was purified by flash column chromatography using mixtures of Et_2O/hexane.

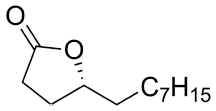


13

(4*R*)-Octan-4-olide [13]

Oxidative cleavage of **6** (0.4 g, 2.8 mmol) with OsO_4 (353 mm^3) and Oxone (8.6 g, 14.1 mmol) in DMF (14 cm^3) afforded lactone **13** (0.38 g, 95%) as a colorless oil. Ee: >99%, as determined by gas chromatography on Hydrodex β-3P under programmed conditions, from 50 °C (2 min isotherm) at 2 °C min^{-1} to 200 °C (2 min isotherm), t_R (major) = 25.2 min, t_R (minor) = 25.4 min, R = 1.93.

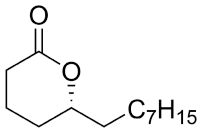
12. B. R. Travis, R. S. Narayan and B. Borhan, *J. Am. Chem. Soc.*, 2002, **124**, 3824-3825.
13. J. M. Schomaker, B. R. Travis and B. Borhan, *Org. Lett.*, 2003, **5**, 3089-3092.



14

(4*R*)-Dodecan-4-olide [14]

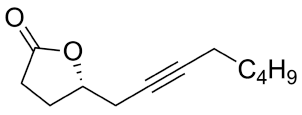
Oxidative cleavage of **7** (0.25 g, 1.26 mmol) with OsO_4 (158 mm^3, 12.6 μmol) and Oxone (3.1g, 5.04 mmol) in DMF (6.3 cm^3) afforded lactone **14** (0.24 g, 97%) as a colorless oil. Ee: >99%, as determined by gas chromatography on Hydrodex β-3P under programmed conditions, from 50 °C (2 min isotherm) at 2 °C min^{-1} to 200 °C (2 min isotherm), t_R (major) = 64.6 min, t_R (minor) = 65.5 min, R = 1.35.



15

(5*R*)-Tridecan-5-olide [15]

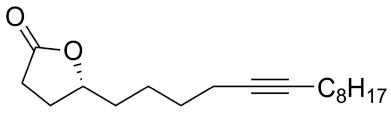
Oxidative cleavage of **8** (0.25 g, 1.18 mmol) with OsO_4 (148 mm^3, 11.8 μmol) and Oxone (2.9g, 4.72 mmol) in DMF (5.9 cm^3) afforded lactone **15** (0.22 g, 87%) as a colorless oil.



16

(4*S*)-Dodec-6-yn-4-olide [16]

Oxidative cleavage of **9** (0.3 g, 1.54 mmol) with OsO_4 (194 mm^3) and Oxone (4.7 g) in DMF (7.7 cm^3) afforded lactone **16** (0.28 g, 92%) as a colorless oil. The ee of the lactone **16** was determined after hydrogenation to the saturated (4*S*)-dodecan-4-olide using Pt/C and H_2. Ee: >99%, as determined by gas chromatography on Hydrodex β-3P under programmed conditions, from 50 °C (2 min isotherm) at 2 °C min^{-1} to 200 °C (2 min isotherm), t_R (major) = 64.6 min, t_R (minor) = 65.5 min, R = 1.35. Spectroscopic data were in agreement with published data.[14]

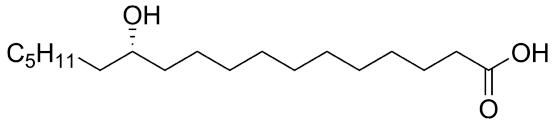


17

(4*R*)-Octadec-9-yn-4-olide [17]

Oxidative cleavage of **10** (0.3 g, 1.1 mmol) with OsO_4 (135 mm^3) and Oxone (3.3 g, 5.4 mmol) in DMF (5.4 cm^3) afforded lactone **17** (0.25 g, 84%) as a colorless oil. Spectroscopic data were in agreement with published data.[15]

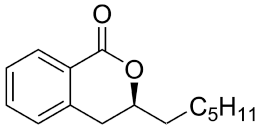
14. W. Sucrow and U. Klein, *Chemische Berichte*, 1975, **108**, 3518-3521.
15. K. Mori, *Eur. J. Org. Chem.*, 2005, 2040-2044.



18

(12*S*)-12-Hydroxyoctadecanoic acid [18]

Oxidative cleavage of **11** (0.25 g, 0.9 mmol) with OsO_4 (250 mm^3) and Oxone (2.7 g, 4.4 mmol) in DMF (4.4 cm^3) afforded hydroxy acid **18** (0.21 g, 81%) as a colorless oil. Ee: > 99%, as determined by gas chromatography of the corresponding (*R*)- and (*S*)-PEC derivatives on an EC-5 column,[5] programmed from 50 °C (1 min isotherm) at 20 °C min^{-1} to 120 °C, and at 1 °C min^{-1} to 280 °C (2 min isotherm); t_R (major) = 121.1 min, t_R (minor) = 121.6 min, R = 1.84.

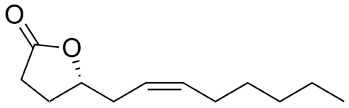


19

(S)-3-Hexylisochroman-1-one [19]

Oxidative cleavage of **12** (0.4 g, 1.7 mmol) with OsO_4 (216 mm^3) and Oxone (5.3 g, 8.6 mmol) in DMF (8.6 cm^3) afforded lactone **19** (0.38 g, 96%) as a colorless liquid. Ee: > 99% ee, as determined, after lactone ring opening to the N-butylcarboxamide followed by formation of the corresponding (*R*)- and (*S*)-PEC derivatives,[3] by gas chromatography on an EC-5 column, programmed from 200 °C (2 min isotherm) at 4 °C min^{-1} to 250 °C; t_R (major) = 18.7 min, t_R (minor) = 19.1 min; R = 2.58.

δ_H(500 MHz; $CDCl_3$) 8.11-8.07 (m, 1H), 7.50-7.54 (m, 1H), 7.36-7.40 (m, 1H), 7.22-7.25 (m, 1H), 4.48-4.55 (m, 1H), 3.01-2.87 (m, 2H), 1.92-1.84 (m, 1H), 1.67-1.76 (m, 1H), 1.67-1.52 (m, 1H), 1.51-1.40 (m, 1H), 1.40-1.24 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); δ_C(125 MHz; $CDCl_3$) 165.7, 139.2, 133.6, 130.2, 127.6, 127.3, 125.3, 78.7, 35.0, 33.2, 31.7, 29.0, 24.9, 22.5, 14.0; ν_{max}(film)/cm^{-1} 3429, 2930, 2858, 2250, 1723, 1608, 1460, 1360, 1282, 1238, 1115, 1086, 1031, 912, 802, 744, 694, 648; Accurate mass (EI) calcd for $C_{15}H_{20}O_2$ (M^+) 232.145447. Found 232.146330.



20

(4*S*,6*Z*)-6-Dodecen-4-olide [20]

Hydrogenation of lactone **16** was performed according to published procedure,[15] using lactone **16** (150 mg, 0.77 mmol) and Lindlar's catalyst (22 mg). After removal of catalyst **20** (142 mg, 93%) was isolated as colorless oil. The ee of the received lactone **20** was determined as described for lactone **16**, >99% ee. Spectroscopic data were in agreement with published data.[14]

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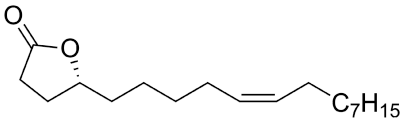


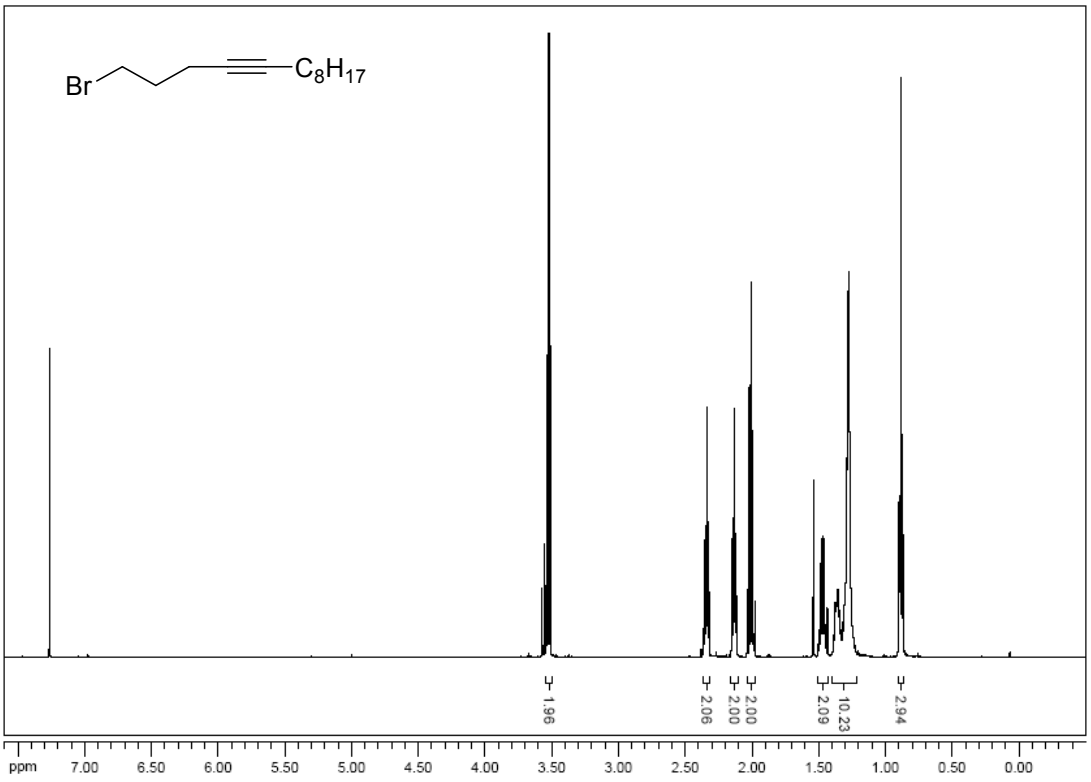
21

(4*R*,9*Z*)-9-Octadecen-4-olide [21]

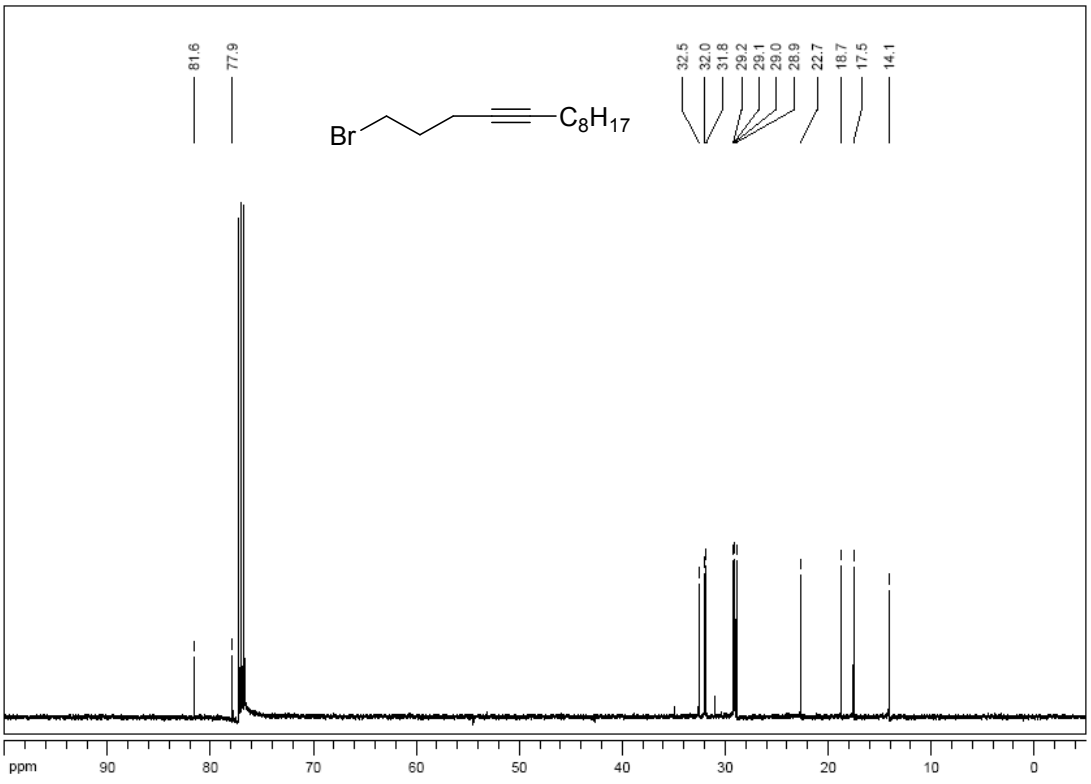
Hydrogenation of the acetylenic lactone **17** (150 mg, 0.54 mmol) was achieved according to a published procedure[15] with Lindlar's catalyst (15 mg). After removal of catalyst **21** (135 mg, 90%) was isolated as colorless oil.

Spectroscopic data were in agreement with published data.[15]

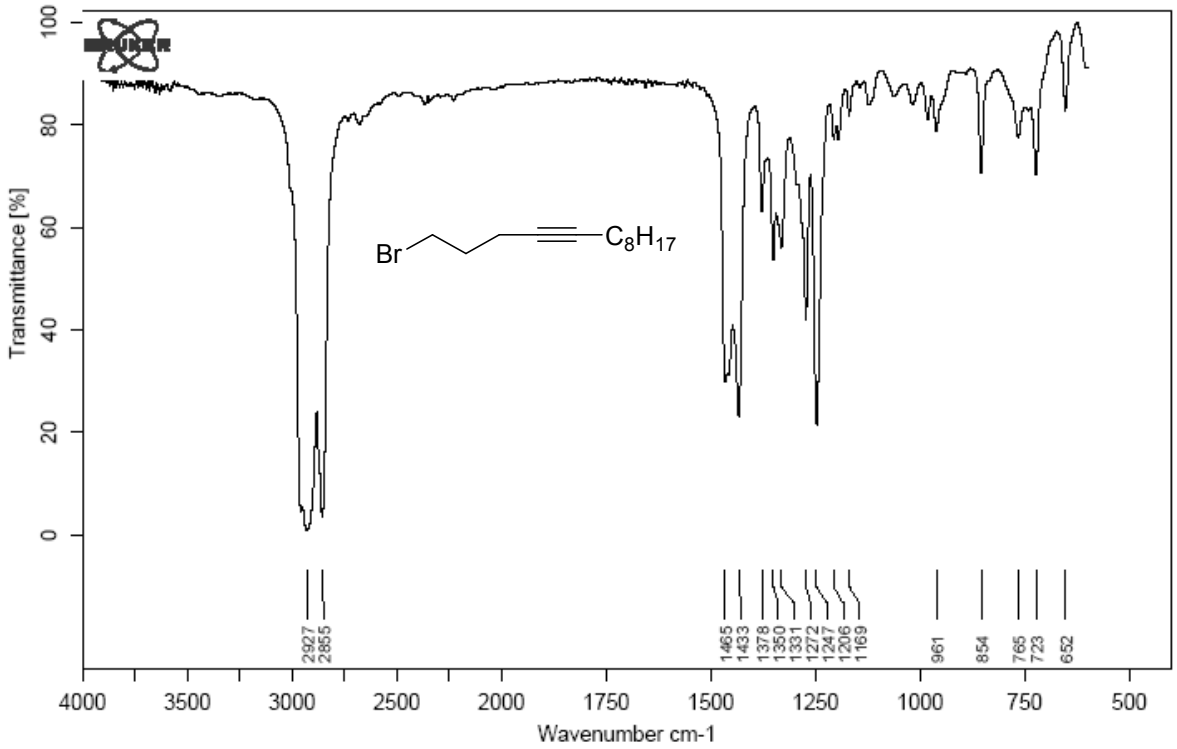
^{1}H-NMR (500 MHz) 1-bromotridec-4-yne [5] ($CDCl_3$)



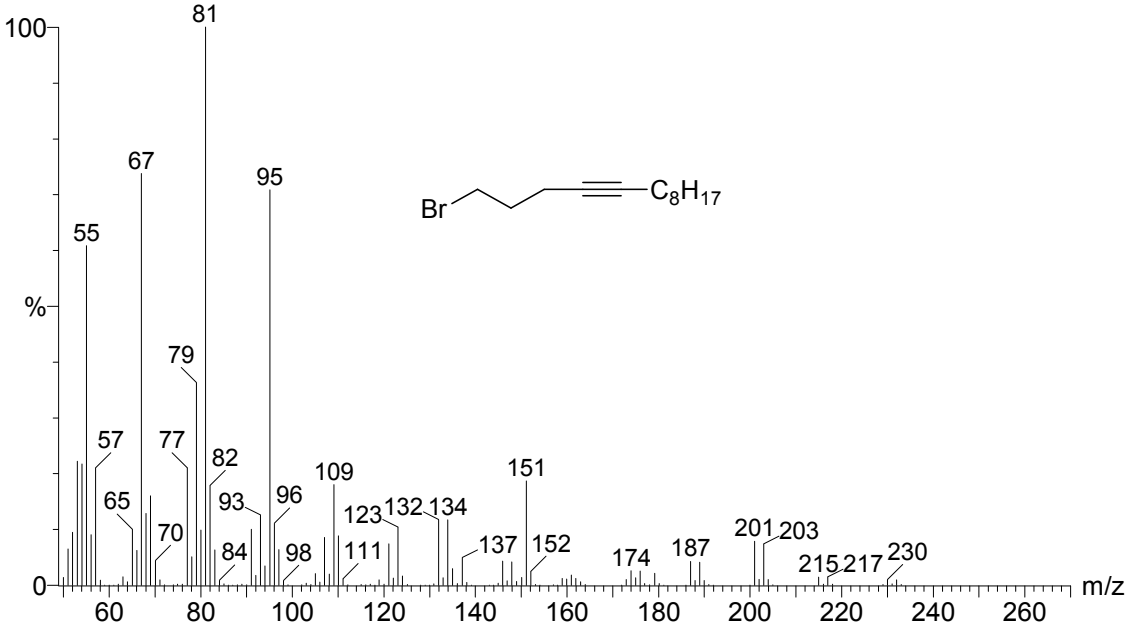
^{13}C-NMR (125 MHz) 1-bromotridec-4-yne [5] ($CDCl_3$)



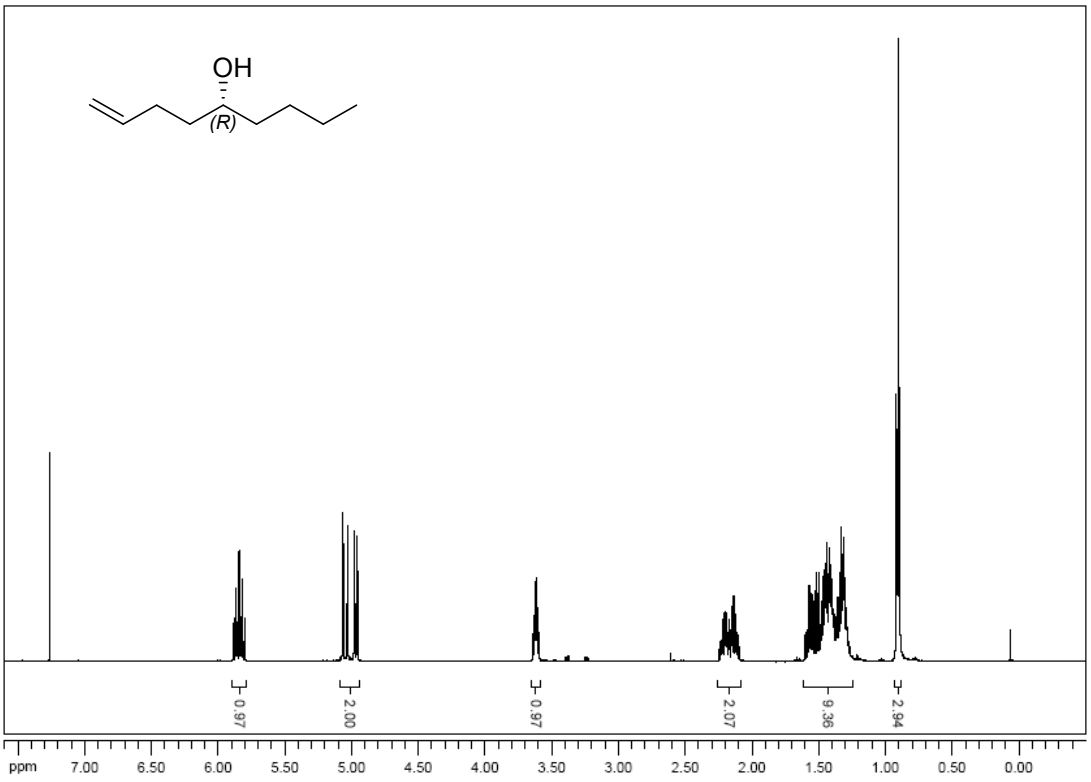
IR-Spectrum **1-bromotridec-4-yne [5]**



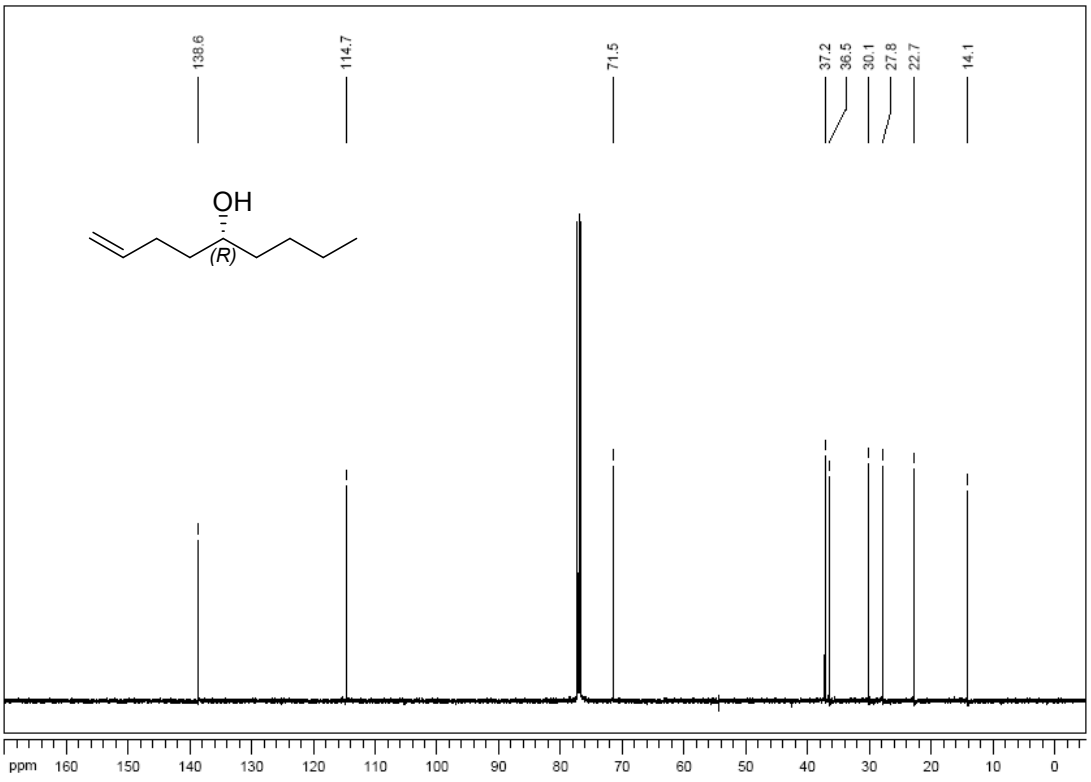
MS-Spectrum **1-bromotridec-4-yne [5]**



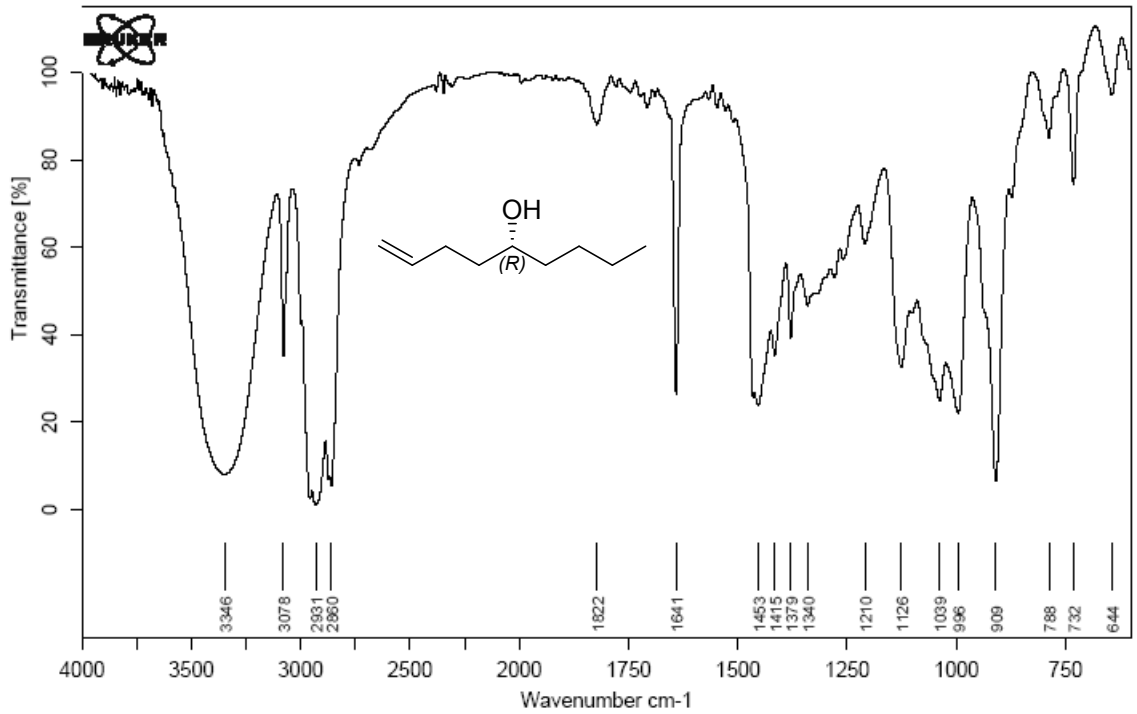
^{1}H-NMR (500 MHz) (*R*)-non-1-en-5-ol [6] ($CDCl_3$)



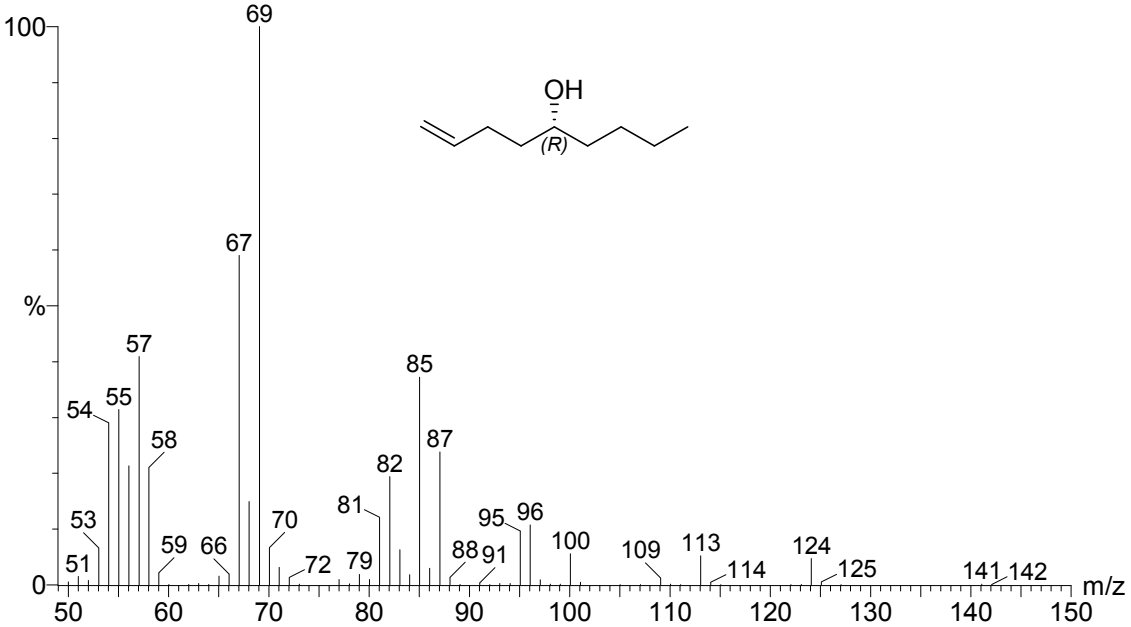
^{13}C-NMR (125 MHz) (*R*)-non-1-en-5-ol [6] ($CDCl_3$)



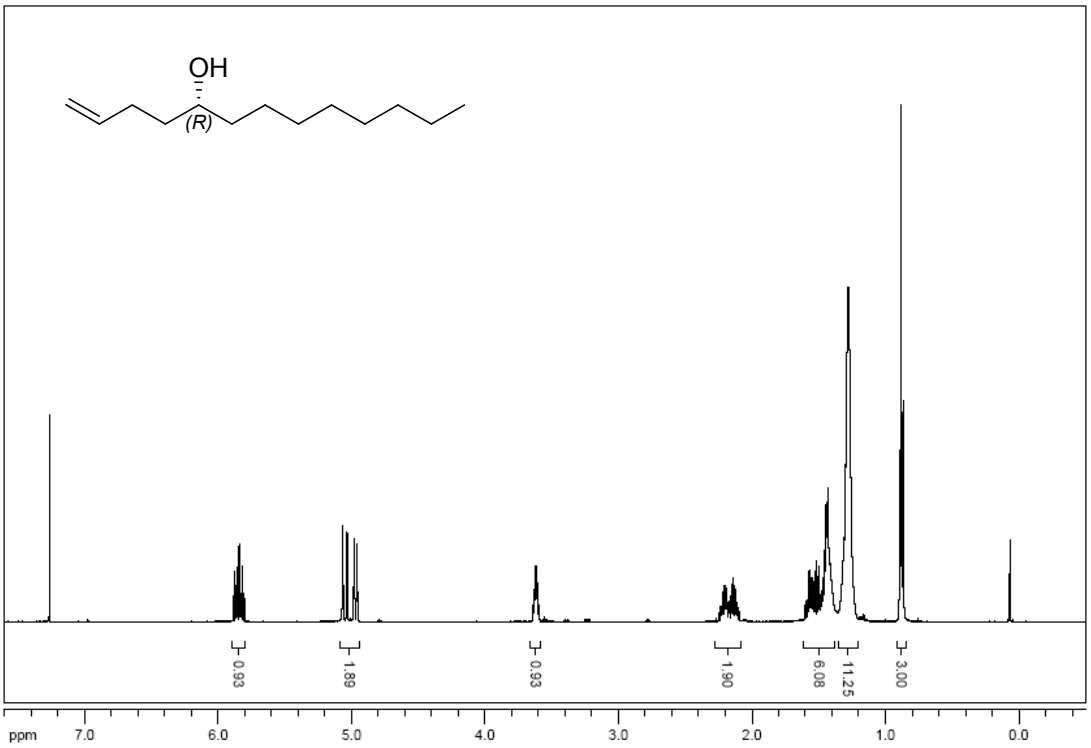
IR-Spectrum (*R*)-non-1-en-5-ol [6]



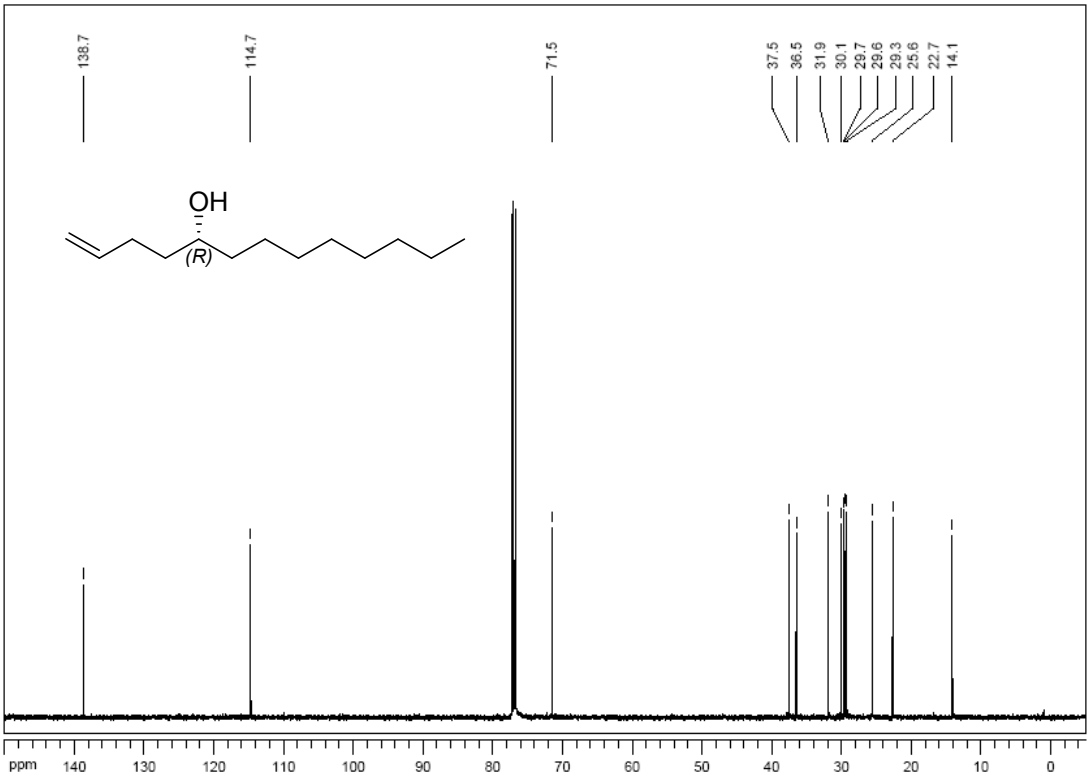
MS-Spectrum (*R*)-non-1-en-5-ol [6]



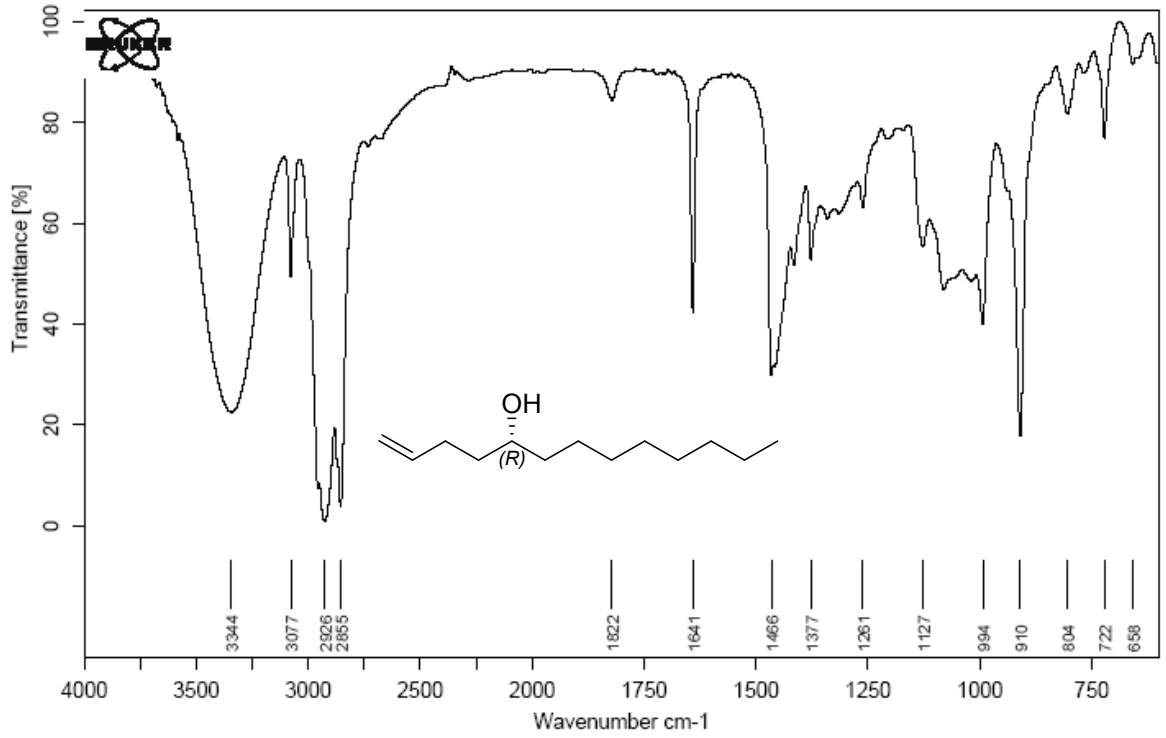
^{1}H-NMR (500 MHz) (*R*)-tridec-1-en-5-ol [7] ($CDCl_3$)



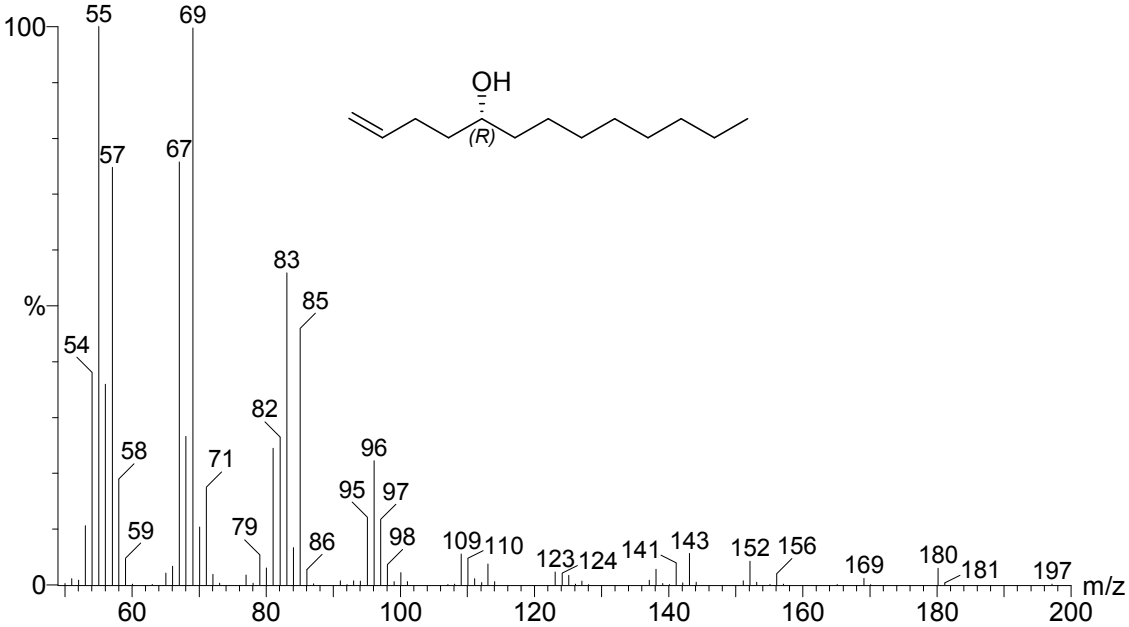
^{13}C-NMR (125 MHz) (*R*)-tridec-1-en-5-ol [7] ($CDCl_3$)



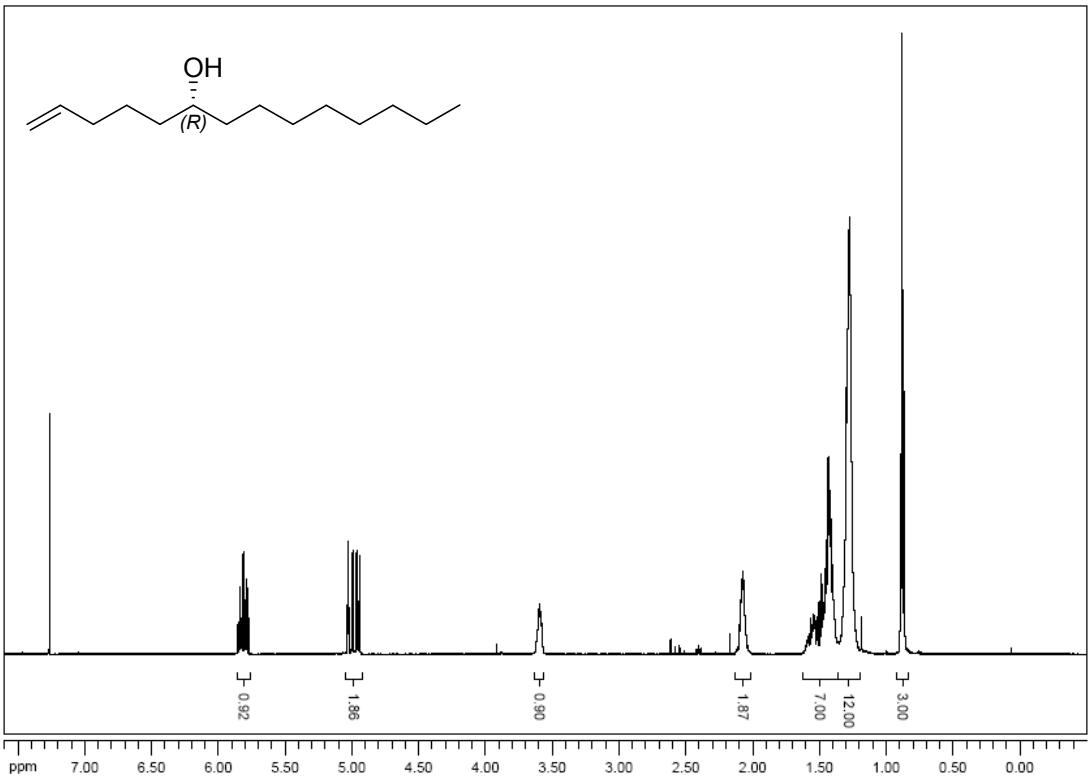
IR-Spectrum **(*R*)-tridec-1-en-5-ol [7]**



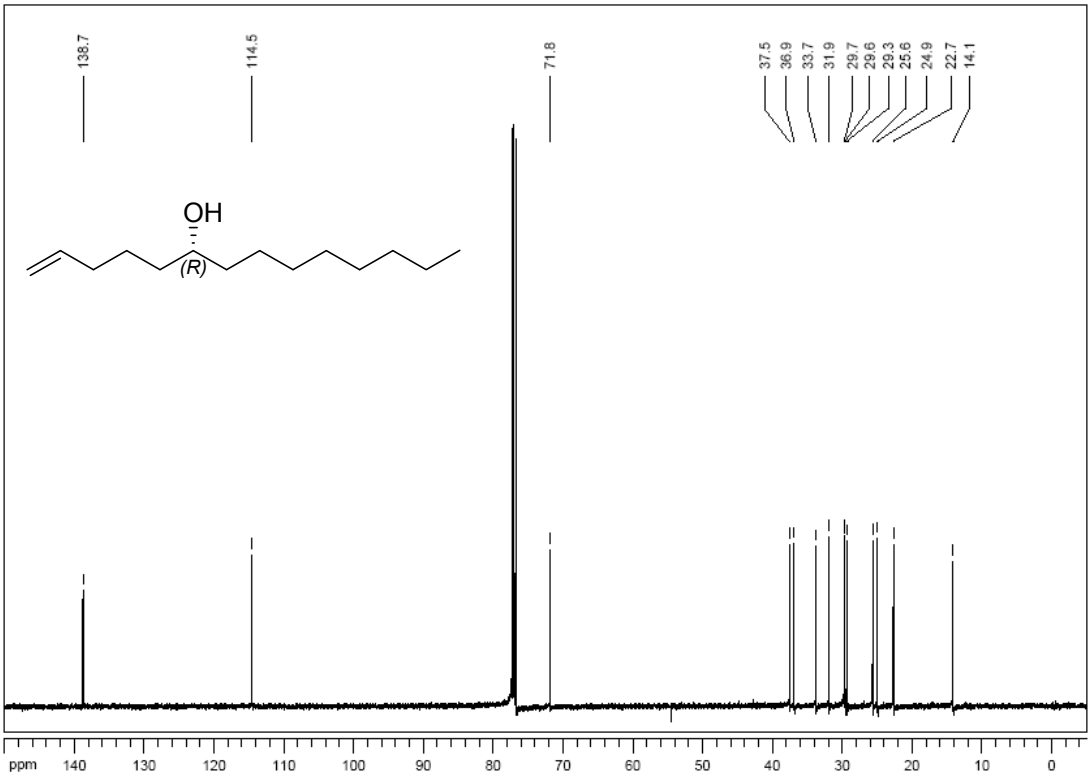
MS-Spectrum **(*R*)-tridec-1-en-5-ol [7]**



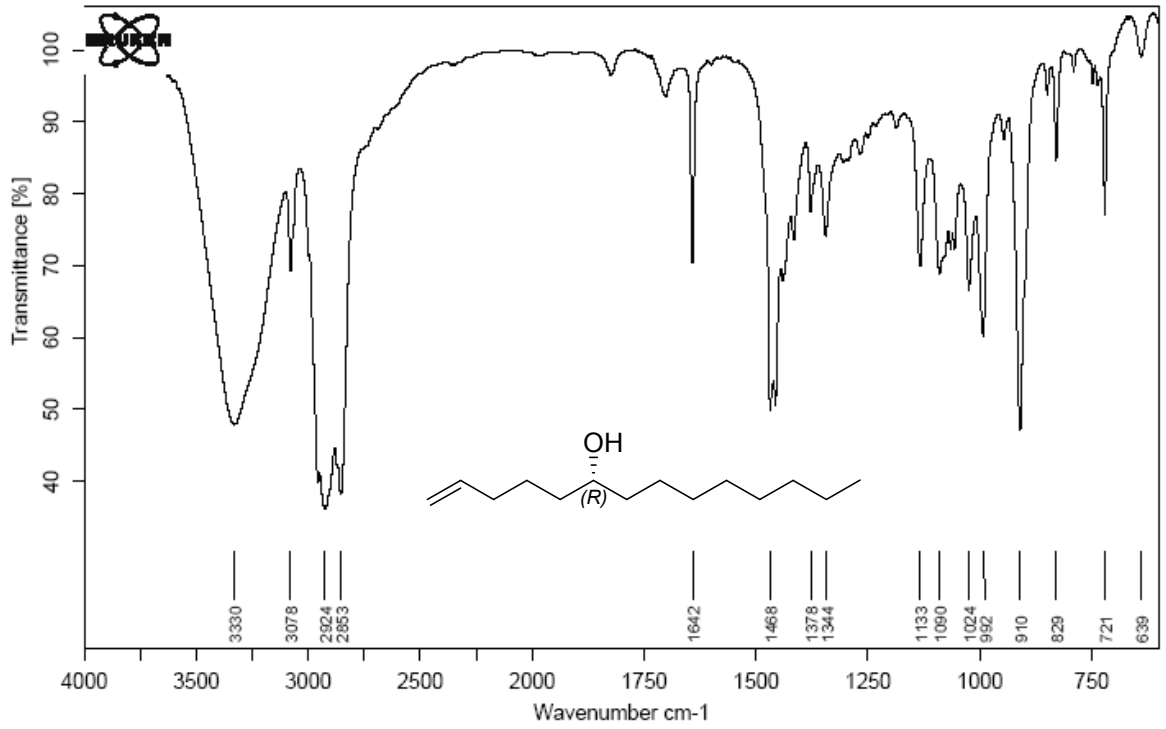
^{1}H-NMR (500 MHz) (*R*)-tetradec-1-en-6-ol [8] ($CDCl_3$)



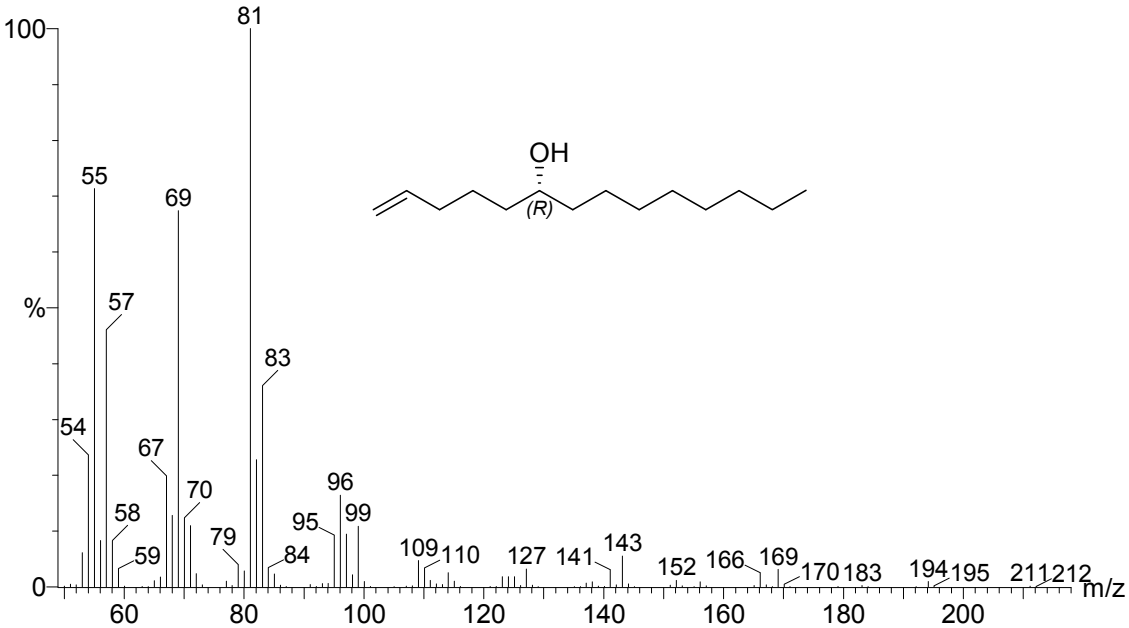
^{13}C-NMR (125 MHz) (*R*)-tetradec-1-en-6-ol [8] ($CDCl_3$)



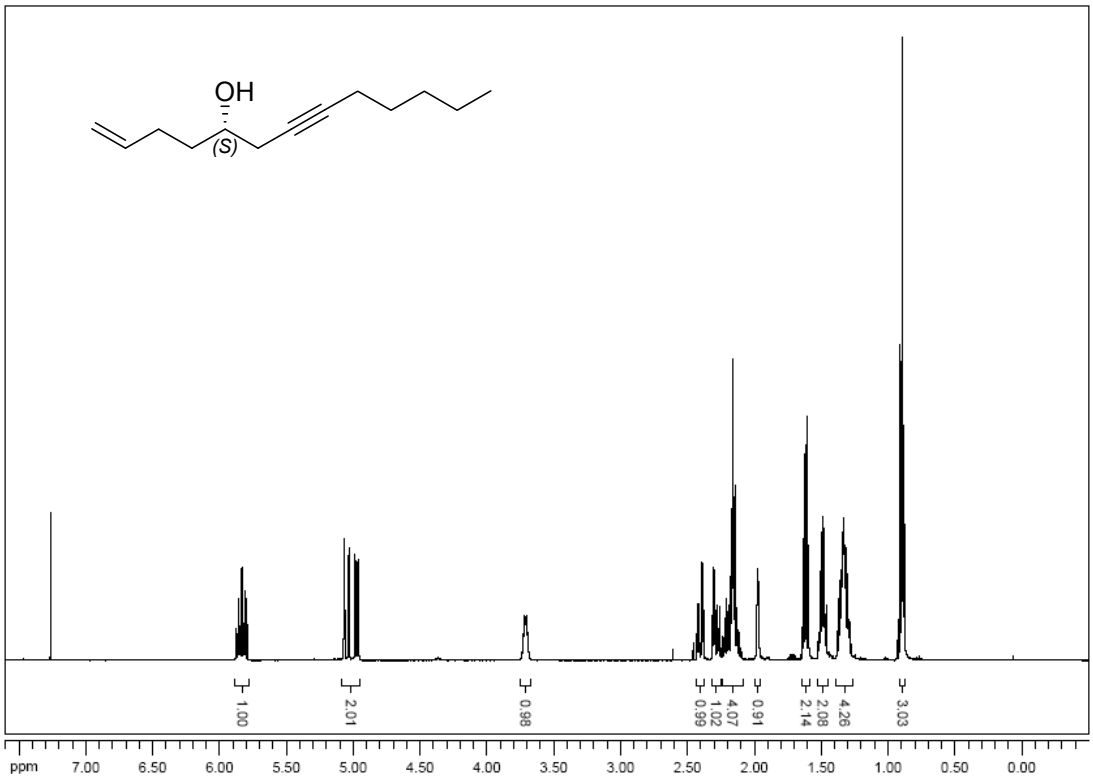
IR-Spectrum (*R*)-tetradec-1-en-6-ol [8]



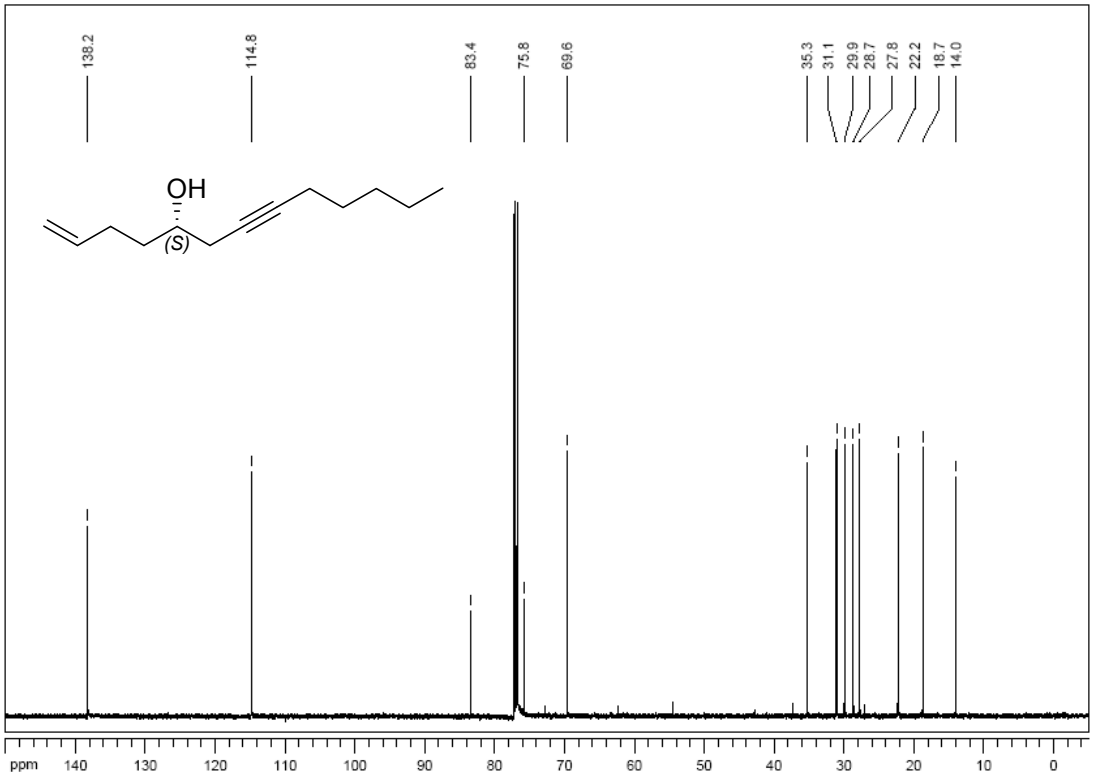
MS-Spectrum (*R*)-tetradec-1-en-6-ol [8]



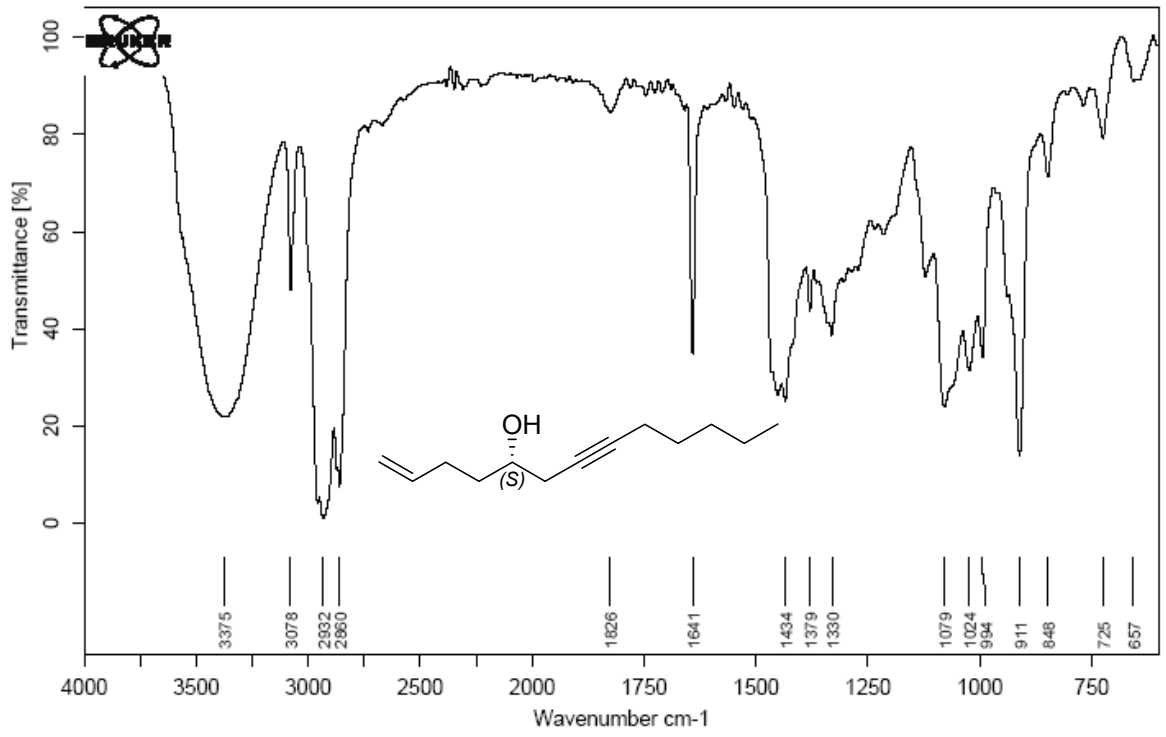
^{1}H-NMR (500 MHz) **(5*S*)-tridec-1-en-7-yn-5-ol [9] ($CDCl_3$)**



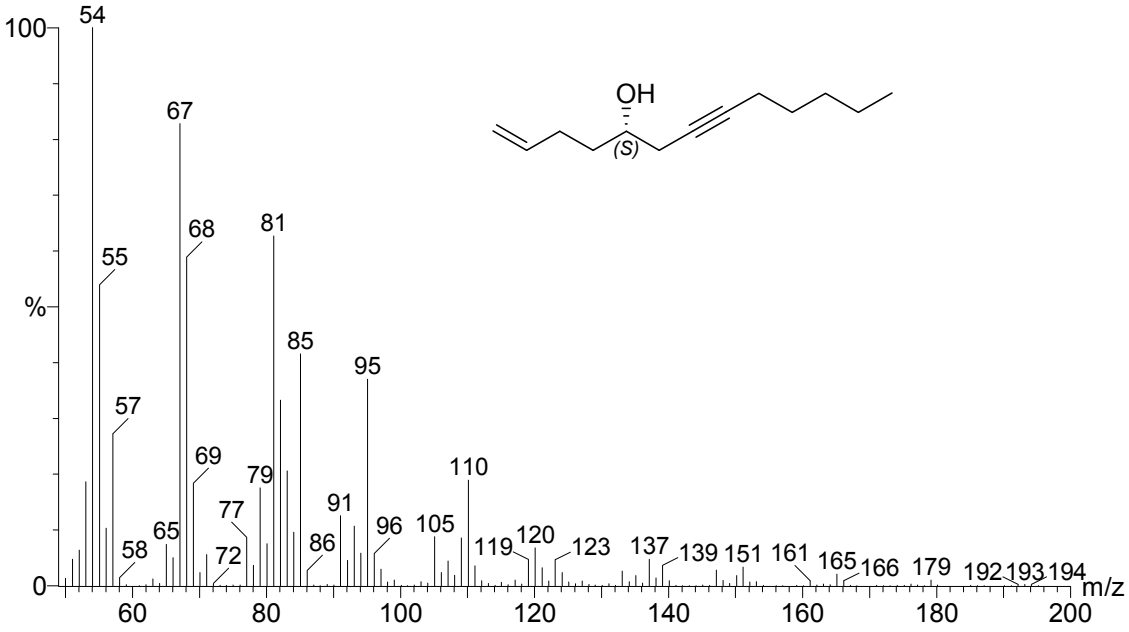
^{13}C-NMR (125 MHz) **(5*S*)-tridec-1-en-7-yn-5-ol [9] ($CDCl_3$)**



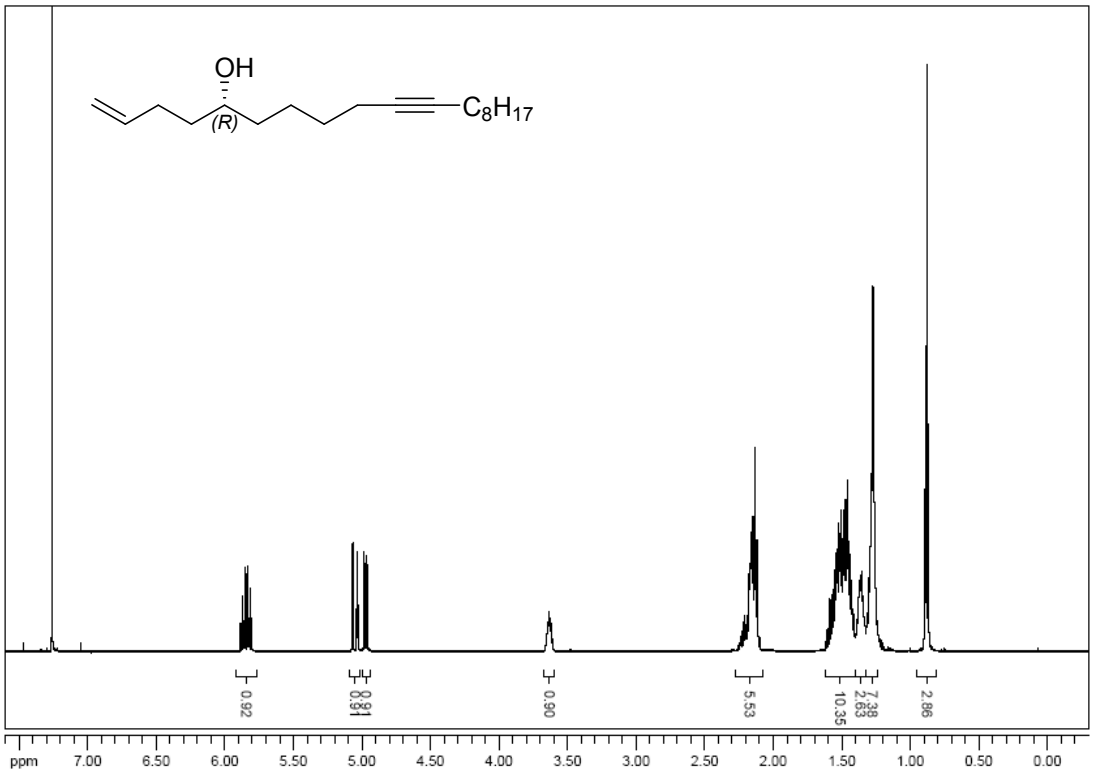
IR-Spectrum (5*S*)-tridec-1-en-7-yn-5-ol [9]



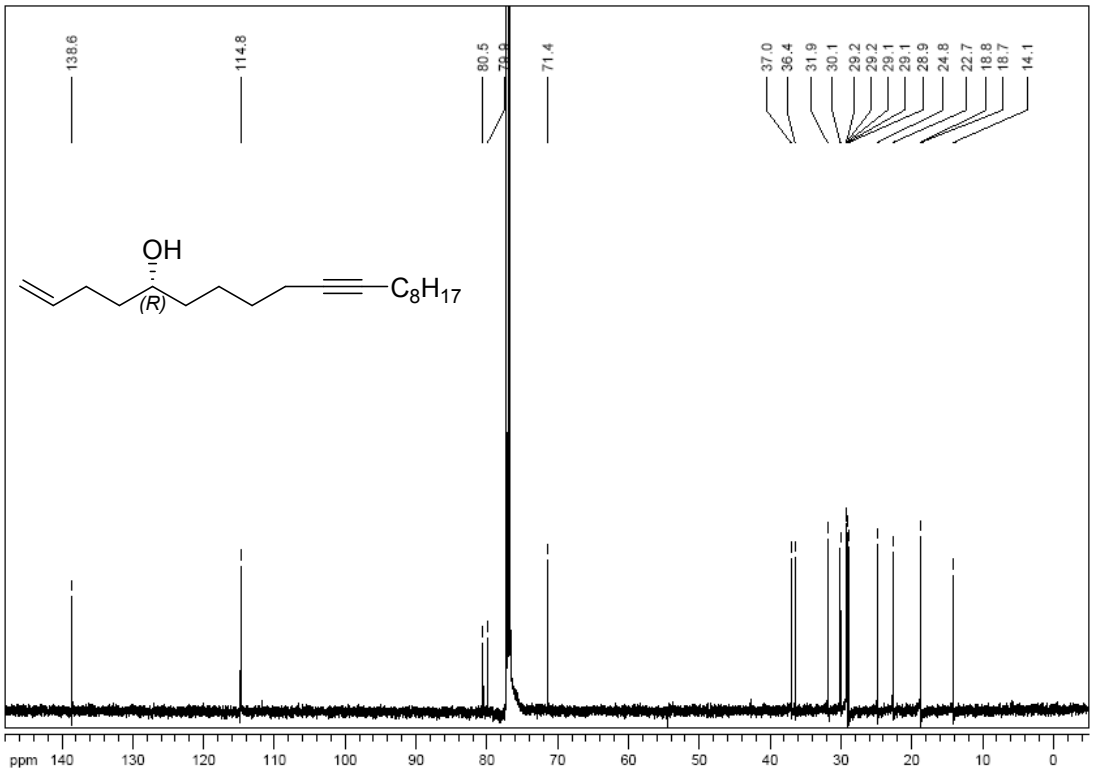
MS-Spectrum (5*S*)-tridec-1-en-7-yn-5-ol [9]



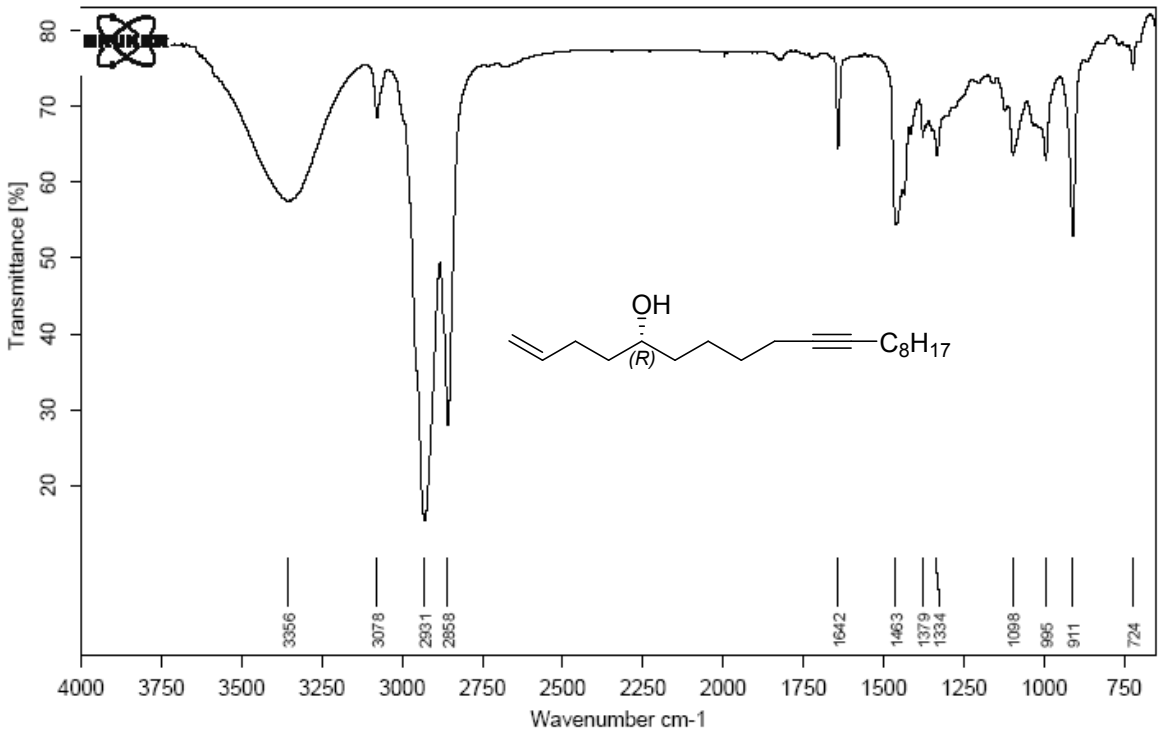
^{1}H-NMR (500 MHz) (*R*)-nonadec-1-en-10-yn-5-ol [10] ($CDCl_3$)



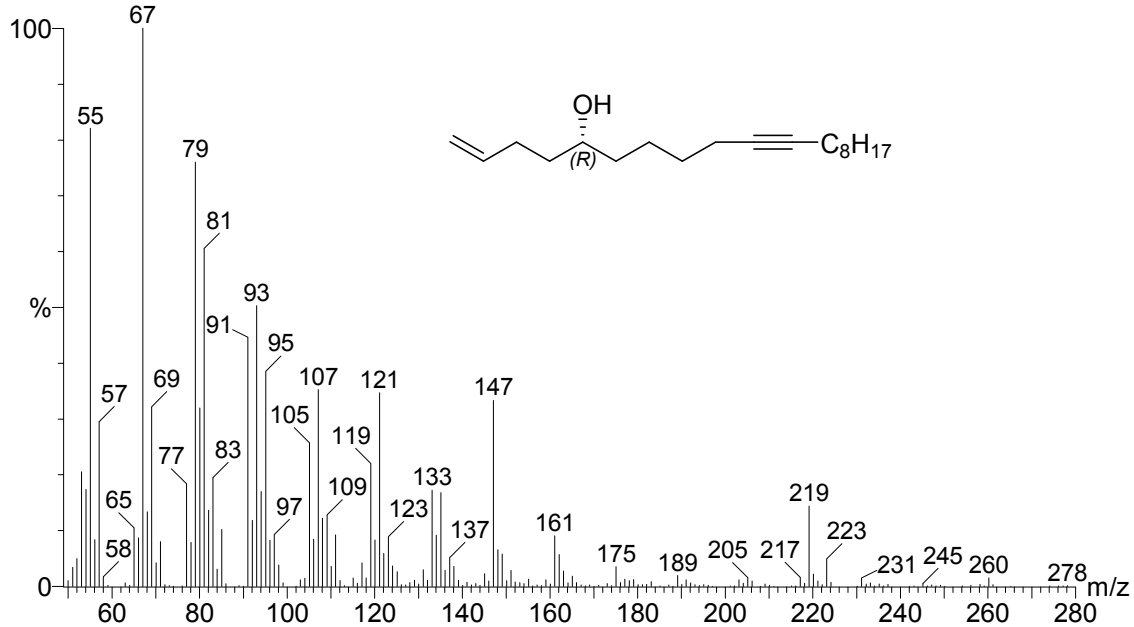
^{13}C-NMR (125 MHz) (*R*)-nonadec-1-en-10-yn-5-ol [10] ($CDCl_3$)



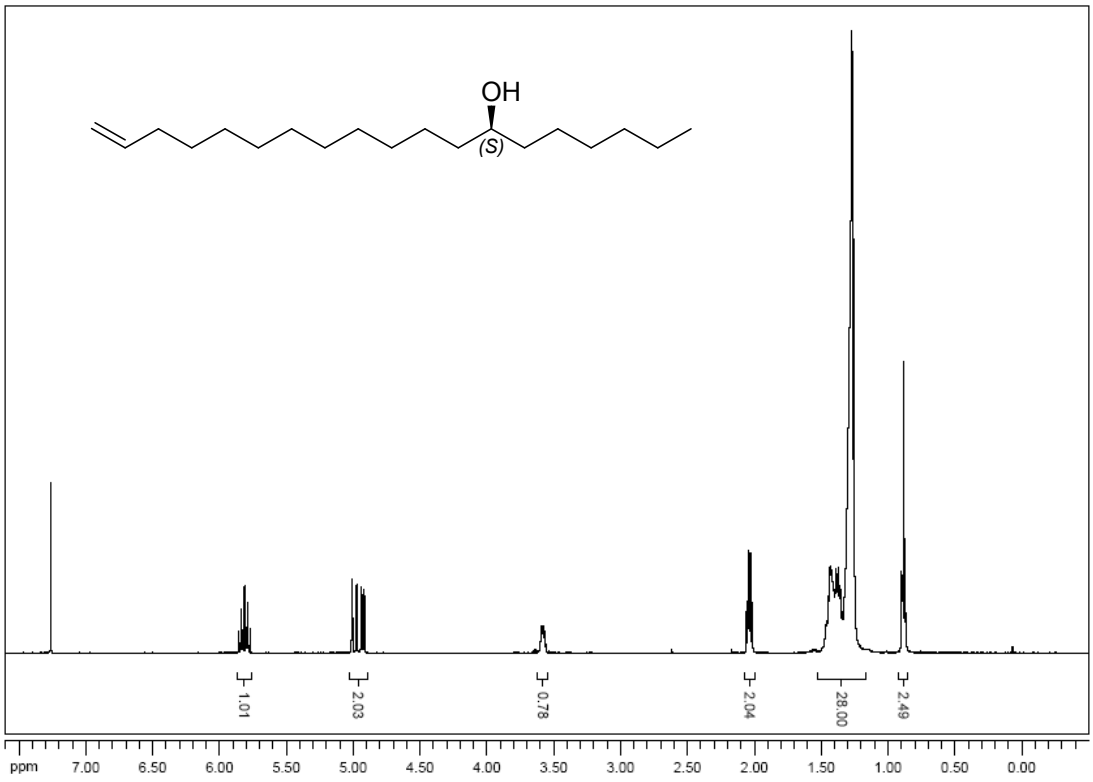
IR-Spectrum (*R*)-nonadec-1-en-10-yn-5-ol [10]



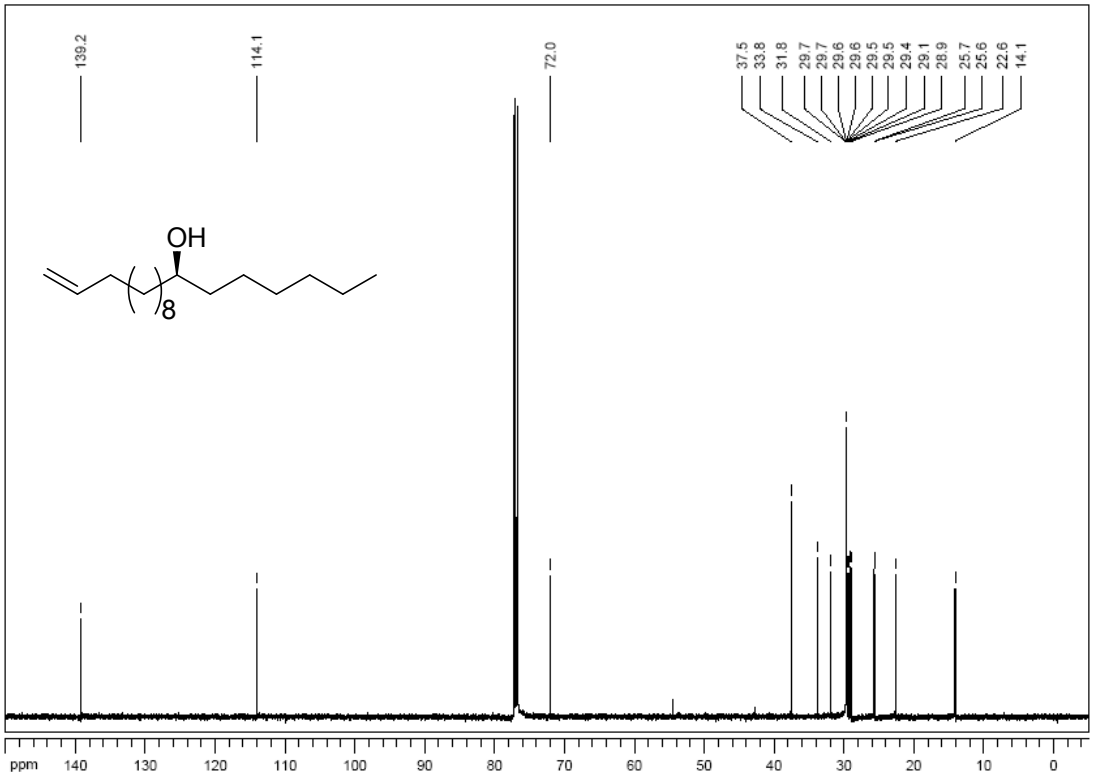
MS-Spectrum (*R*)-nonadec-1-en-10-yn-5-ol [10]



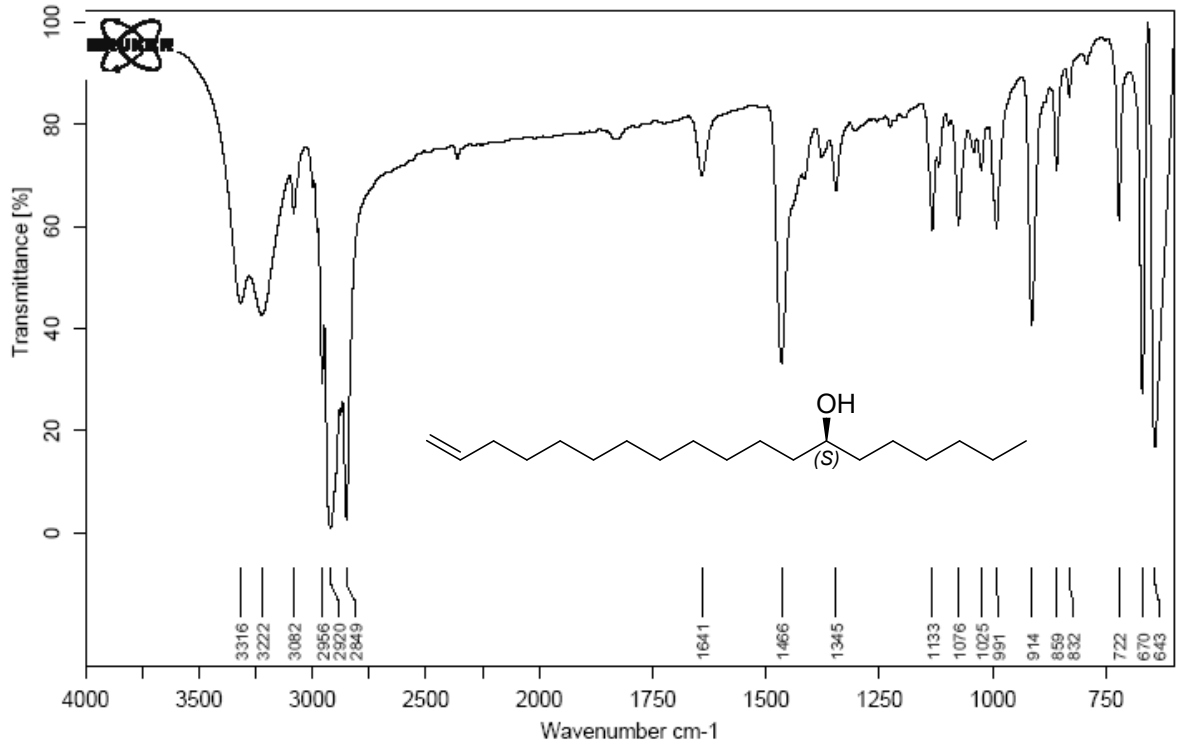
^{1}H-NMR (500 MHz) **(*S*)-nonadec-18-en-7-ol [11] ($CDCl_3$)**



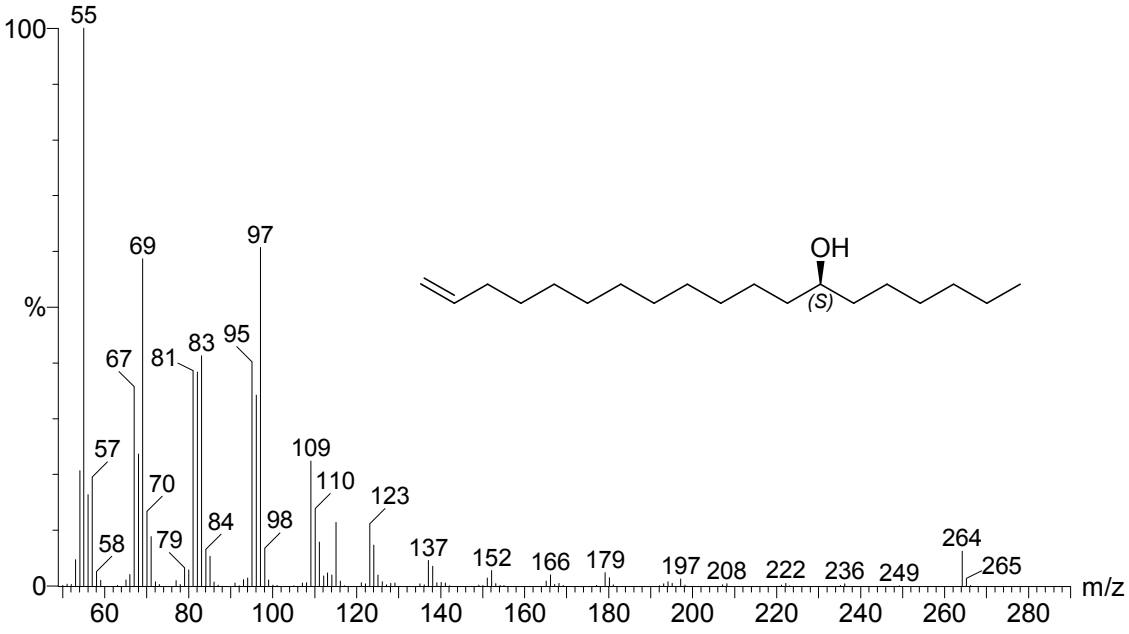
^{13}C-NMR (125 MHz) **(*S*)-nonadec-18-en-7-ol [11] ($CDCl_3$)**



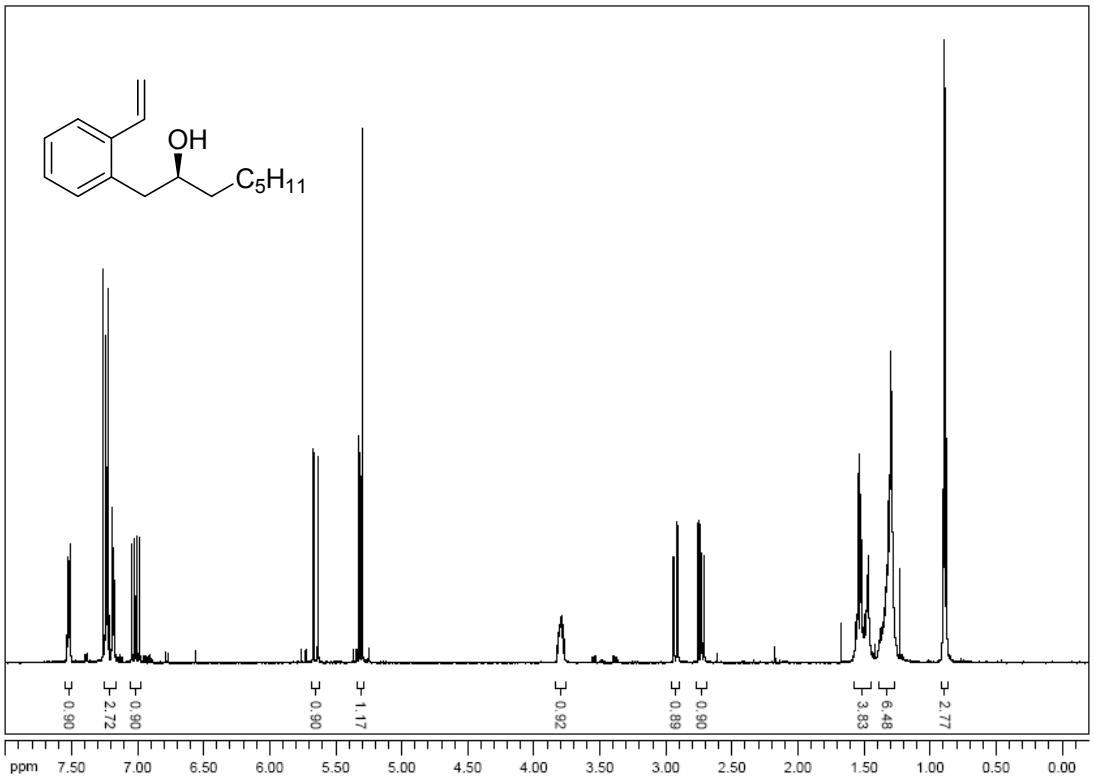
IR-Spectrum **(*S*)-nonadec-18-en-7-ol [11]**



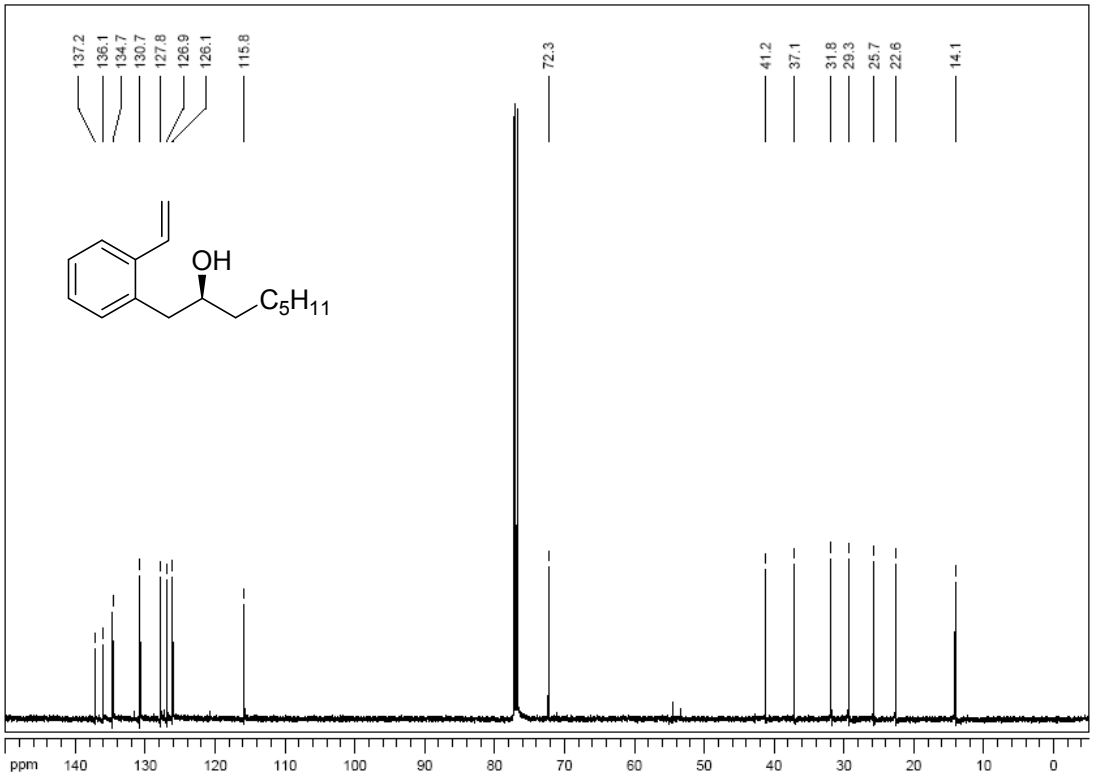
MS-Spectrum **(*S*)-nonadec-18-en-7-ol [11]**



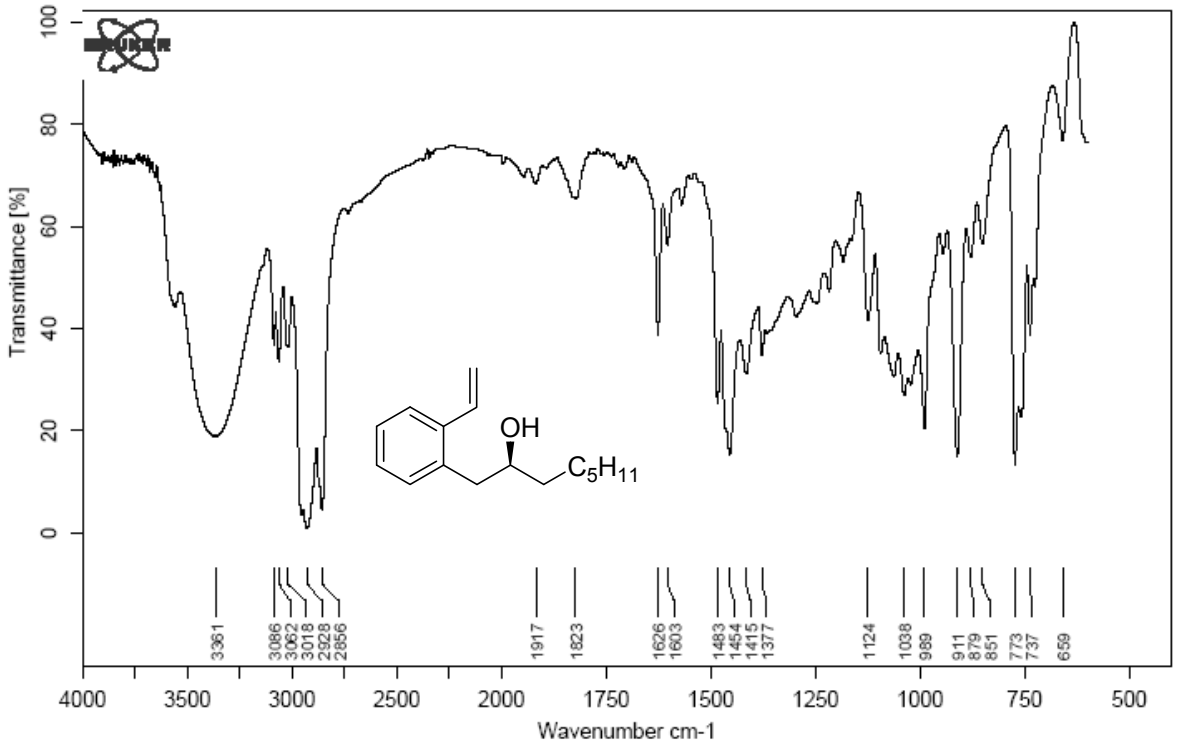
^{1}H-NMR (500 MHz) **(*S*)-1-(2-vinylphenyl)octan-2-ol [12] ($CDCl_3$)**



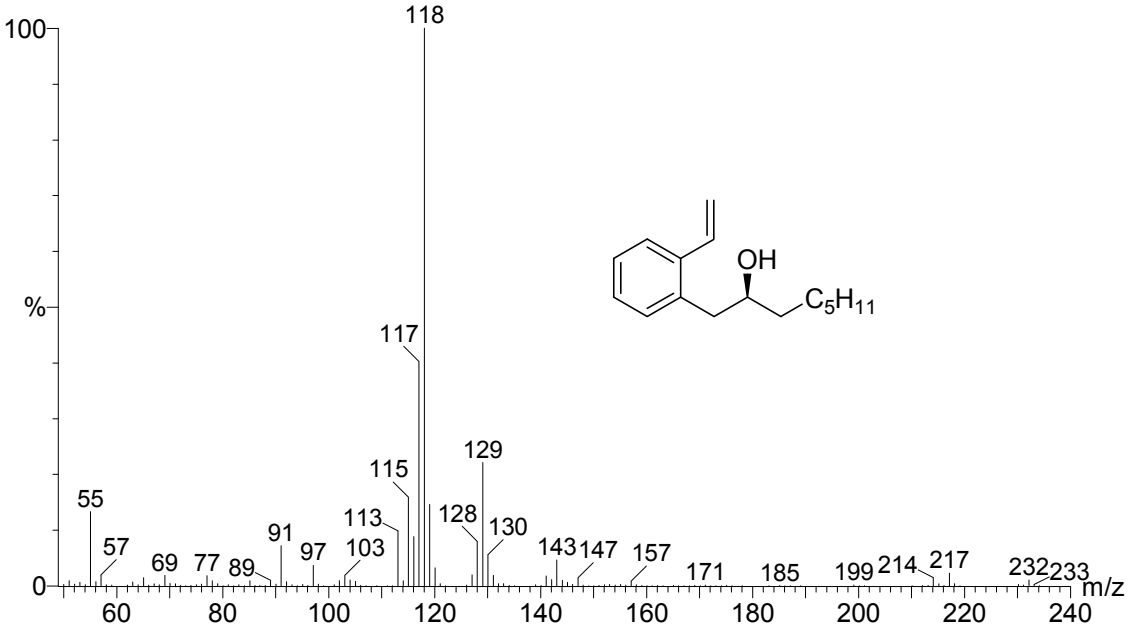
^{13}C-NMR (125 MHz) **(*S*)-1-(2-vinylphenyl)octan-2-ol [12] ($CDCl_3$)**



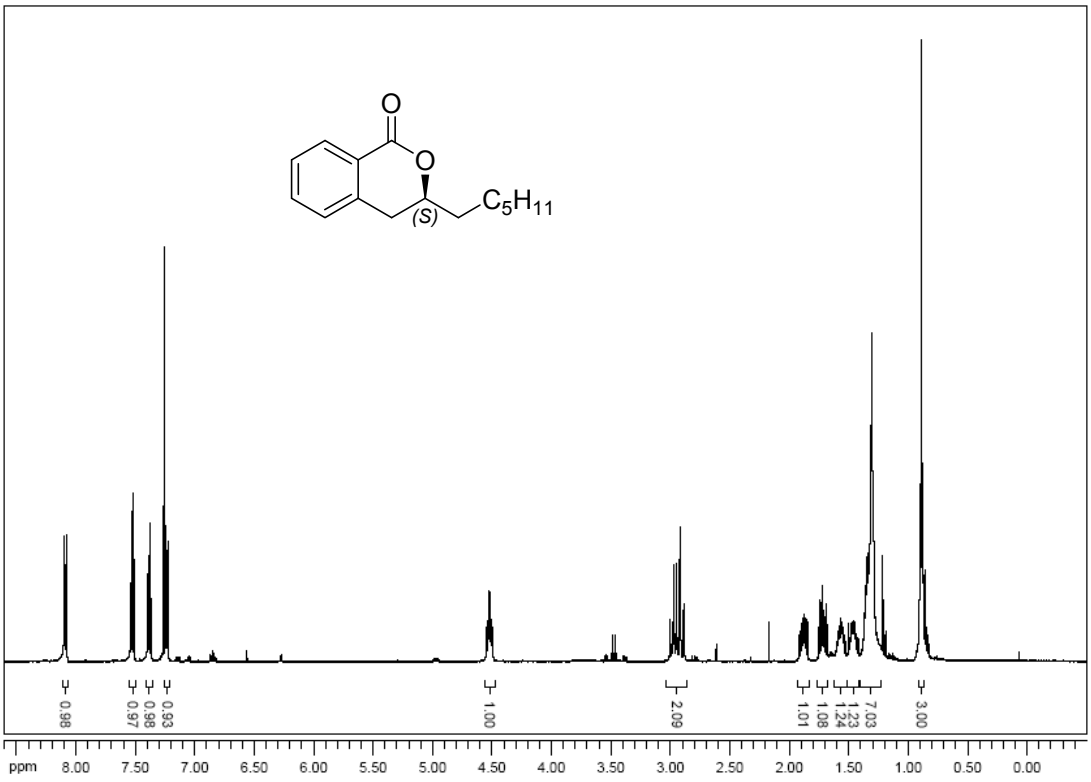
IR-Spectrum **(*S*)-1-(2-vinylphenyl)octan-2-ol [12]**



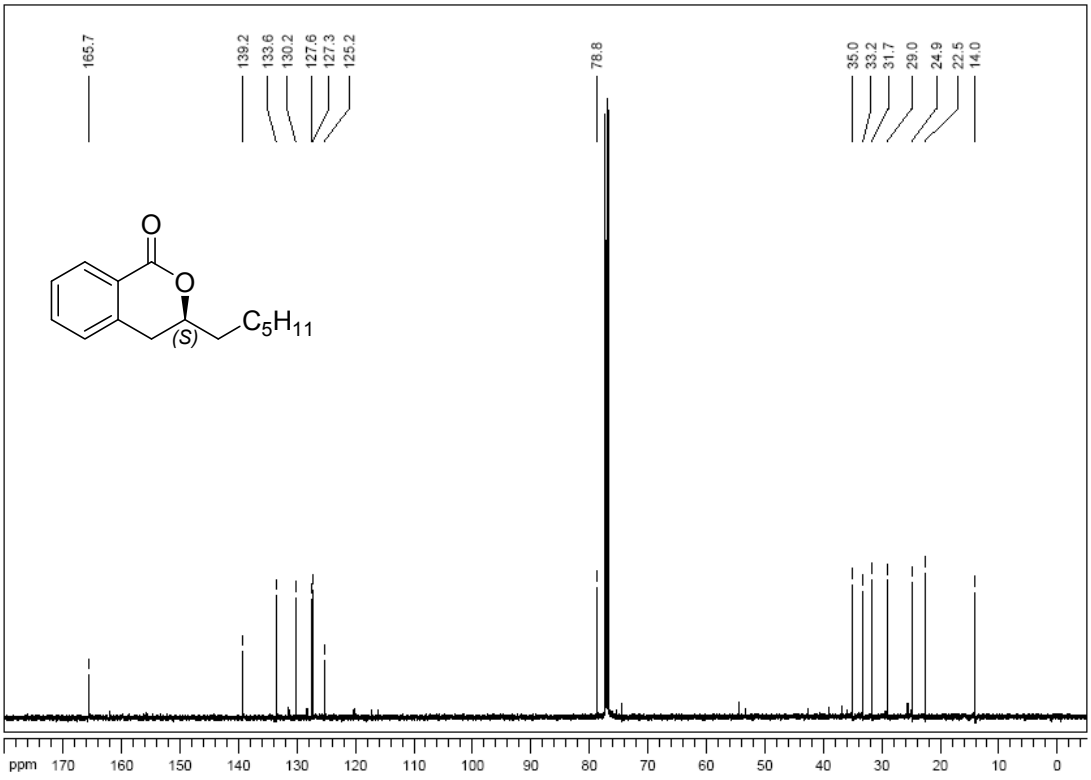
MS-Spectrum **(*S*)-1-(2-vinylphenyl)octan-2-ol [12]**



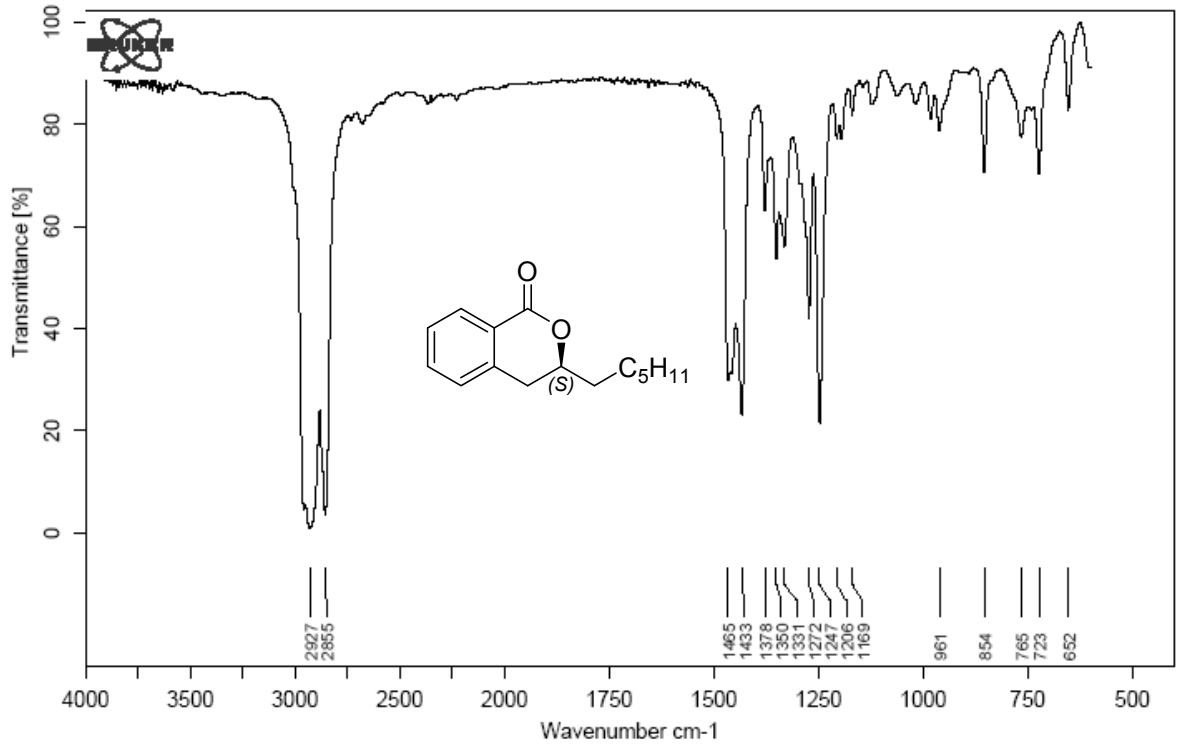
^{1}H-NMR (500 MHz) (S)-3-hexylisochroman-1-one [19] ($CDCl_3$)



^{13}C-NMR (125 MHz) (S)-3-hexylisochroman-1-one [19] ($CDCl_3$)



IR-Spectrum (S)-3-hexylisochroman-1-one [19]



MS-Spectrum (S)-3-hexylisochroman-1-one [19]