Supporting Information

for

Convergent Synthesis of Trisubstituted *Z*-Allylic Esters by Wittig-Schlosser Reaction

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1. General Details

All reactions requiring anhydrous conditions were carried out under an atmosphere of argon in flame-dried glassware. Syringes, needles and cannula were oven-dried.

Materials: CH_2Cl_2, Et_2O and toluene were distilled from CaH_2 under argon and stored over 3 Å molecular sieves. THF was distilled over sodium and benzophenone under an atmosphere of nitrogen. Petrol refers to the fraction that boils at 30-40 ^oC. PhLi (2.0 M in Bu_2O) was obtained from Acros Organics. Starting materials were obtained commercially and used without further purification, unless stated otherwise.

Chromatography: Thin layer chromatography (TLC) was performed on aluminium-backed plates pre-coated with silica (Merck 60 F_{254}). The plates were visualized by irradiation with UV light (254 nm) and by immersion in phosphomolybdic acid or $KMnO_4$ solutions, followed by heating. Purification of reaction products was carried out by flash chromatography using silica gel (35-70 µM) or neutral alumina.

Melting points were determined using Gallenkamp apparatus and are uncorrected. IR spectra were recorded as thin films on NaCl plates using a Perkin-Elmer Paragon Fourier Transform spectrometer; abbreviations br, s, m, and w refer to broad, strong, medium and weak, respectively.

NMR : ^1H NMR and ^{13}C NMR spectra were recorded using Brücker DQX400, DPX250 or AVB500 spectrometers. Chemical shifts are reported in ppm and referenced to the internal residual $CHCl_3$ lock: at 7.27 for ^1H NMR spectra and to the central line of $CDCl_3$ triplet at 77.0 for ^{13}C NMR spectra. Coupling constants (*J*) are given in Hz. The ^{13}C NMR peaks were assigned by standard methods using HMQC and DEPT experiments. *E/Z* Assignments were based on NOE studies.

Mass Spectra: Low and high resolution mass spectra [MS(TOF Cl^+)] were recorded on a Micromass GCT equipped with a reflectron TOF mass spectrometer operating at 60 *eV* (Flow rate (He) = 1 mL/min) and Brücker MicrOTOF II.

Gas Chromatography: The reported *E/Z* ratios were determined by GC/MS analysis of crude reaction mixtures, using an Agilent HP-5 column (dimethylsilicone capillary column, 30 m x 0.32 mm x 0.25 µm), He, 1 mL/min (initial temperature = 80 ^oC, max. temperature = 280 ^oC; rate = 20 ^oC/min).

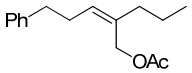
Optical rotations were recorded on a Perkin-Elmer 241 Polarimeter, with a path length of 10 cm in $CHCl_3$. $[\alpha]_D$ values are given in 10^{-1} deg cm^2g^{-1}. Concentrations (*c*) are given in grams per 100 cm^3.

2. General Procedure for *Z*-allylic esters

A solution of anhydrous LiBr (2.0 equiv, obtained by heating LiBr under argon until it melted, followed by cooling) in THF (2.5 mL/mmol LiBr) was added to the anhydrous alkyltriphenylphosphonium bromide (1.0 equiv) and stirred at rt for 10 min before cooling to –78 ^{o}C. PhLi (2.0 M in Bu_2O, 1.0 equiv) was then added dropwise at –78 ^{o}C, the cooling bath was removed and the reaction mixture was warmed to rt over 15 min, during which time it became homogenous. After 30 min at rt, the reaction mixture was re-cooled to –78 ^{o}C and a solution of the aldehyde (1.0 equiv) in THF (1 mL/mmol aldehyde) was added dropwise. After 10 min, when complete decolorization had occurred, PhLi (2.0 M in Bu_2O, 1.1 equiv) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at –78 ^{o}C, then allowed to reach rt over 15 min. After 30 min the resulting β-lithiooxy ylide was re-cooled to –78 ^{o}C and to it was added dropwise a solution of halomethyl ester (1.1 equiv) in THF (1 mL/mmol of electrophile) at –78 ^{o}C. After 30 min at –78 ^{o}C, the temperature was slowly raised to rt over 30 min and the reaction mixture stirred for a further 2 h at rt. The reaction mixture was then poured into water (20 mL), extracted with Et_2O (3x15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography gave the *Z*-allylic ester.

3. Characterization data for *Z*- allylic esters (entries 6a-6i, 7a-7e, 8a-8d, 9a-9c)

(*Z*)-5-Phenyl-2-propylpent-2-enyl acetate (6a)



Following the General Procedure for *Z*-allylic ester formation, n-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-5-phenyl-2-propylpent-2-enyl acetate **6a** (197 mg, 80%) as a colorless oil; *Rf* 0.30 (5% Et_2O/petrol);

IR (film): 3062w, 3027m, 2959s, 2871s, 1739s, 1496m, 1454s, 1232s.

^{1}H NMR (500 MHz): 7.30-7.27 (2H, m, ArC*H*), 7.21-7.17 (3H, m, ArC*H*), 5.46 (1H, t, *J* 7, C*H*=C), 4.51 (2H, s, CH_2O), 2.68 (2H, t, *J* 7, CH_2Ar), 2.42 (2H, q, *J* 7, CH_2CH=), 2.05 (3H, s, CH_3C=O), 2.03-1.99 (2H, m, CH_2C=), 1.41 (2H, sxt, *J* 7, CH_2CH$_3$), 0.88 (3H, t, *J* 7, CH$_3$).

^{13}C NMR (125 MHz): 171.1 (*C*=O), 141.6 (Ar*C*), 134.4 (CH=*C*), 129.9 (*C*H=C), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 125.9 (Ar*C*H), 61.8 (*C*H$_2$O), 37.4 (*C*H$_2$C=), 36.1 (*C*H$_2$Ar), 29.7 (*C*H$_2$CH=), 21.2 (*C*H$_2$CH$_3$), 21.0 (*C*H$_3$C=O), 13.7 (CH$_3$).

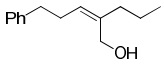
MS (CI$^+$) 246(1), 247(2), 264(100), 265(20), 266(2).

HRMS *m/z* (M+NH$_4^+$) found 264.1964, $C_{16}H_{22}NO_2$ requires 264.1964.

The isomeric ratio (*Z:E* >99:1) was determined by GC/MS, t_R = 9.55 min.

Z-Allylic alcohol from *Z*-Allylic acetates:

(*Z*)-5-Phenyl-2-propylpent-2-en-1-ol



A solution of anhydrous LiBr (2 equiv, obtained by heating LiBr under argon until it melted, followed by cooling) in THF (5 mL) was added to anhydrous butyltriphenylphosphonium bromide (399 mg, 1.0 mmol, 1.0 equiv) and stirred at rt for 10 min before cooling to –78 ^{o}C. PhLi (0.5 mL, 2.0 M in Bu_2O, 1.0 mmol, 1.0 equiv) was then added dropwise at –78 ^{o}C, the cooling bath was removed and the reaction mixture was warmed to rt over 15 min, during which time it became homogenous. After 30 min at rt, the reaction mixture was re-cooled to –78 ^{o}C and a solution of 3-phenylpropanal (134mg, 1.0 mmol, 1.0 equiv) in THF (1 mL) was added dropwise. After 10 min, when complete decolorization had occurred, PhLi (0.55 mL, 2.0 M in Bu_2O, 1.1 mmol, 1.1 equiv) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at –78 ^{o}C, then allowed to reach rt over 15 min. After 30 min the resulting β-lithiooxy ylide was re-cooled to –78 ^{o}C and to it was added dropwise a solution of bromomethyl acetate (168 mg, 1.1 mmol) in THF (2 mL) at –78 ^{o}C. After 30 min at –78 ^{o}C, the temperature was slowly raised to rt over 30 min and the reaction mixture stirred for further 2 h at rt. Then the solvent was removed under reduced pressure, the crude product was dissolved in MeOH (10 mL) and NaOMe (54 mg, 1.0 mmol) was added and stirred for 1 h at RT (monitored by TLC). The reaction mixture was then poured into water (20 mL), extracted with Et_2O (3x15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography gave the *Z*-allylic alcohol (157 mg, 77%) as a colorless oil;

IR (film) 3430br, 3027m, 2958s, 2929s, 2871s, 1725s, 1603w, 1496m, 1454m, 1165s, 904s.

^{1}H NMR (500 MHz) 8.05 (1H, s, O*H*), 7.30-7.27 (2H, m, ArC*H*), 7.21-7.17 (3H, m, ArC*H*), 5.49 (1H, t, *J* 7, CH=C), 4.59 (2H, s, CH_2OH), 2.68 (2H, t, *J* 8, CH_2Ar), 2.43 (2H, q, *J* 8, CH_2CH=C), 2.05 (2H, t, *J* 8, CH_2C=CH), 1.45-1.40 (2H, m, CH_2CH$_3$), 0.89 (3H, t, *J* 7, CH$_3$).

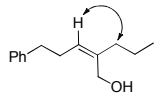
^{13}C NMR (125 MHz) 161.0 (*C*H=C), 141.5 (Ar*C*), 133.8 (CH=*C*), 130.5 (Ar*C*), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 125.9 (Ar*C*H), 61.1 (*C*H$_2$OH), 37.3 (*C*H$_2$C=CH), 36.0 (*C*H$_2$Ar), 29.7 (*C*H$_2$CH=C), 21.1 (*C*H$_2$CH$_3$), 13.7 (CH$_3$).

MS (CI$^+$) 222(100), 221(30).

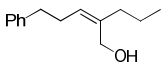
HRMS *m/z* (M+NH$_4^+$) found 221.1767, $C_{14}H_{23}NO$ requires 221.1780.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 9.30 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 5.49 ppm (C***H***=C) saw reciprocal signal enhancement at 2.05 ppm (C***H***$_2$C=CH).



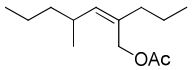
(*Z*)-5-Phenyl-2-propylpent-2-en-1-ol



A solution of anhydrous LiBr (2 equiv, obtained by heating LiBr under argon until it melted, followed by cooling) in THF (5 mL) was added to anhydrous butyltriphenylphosphonium bromide (399 mg, 1.0 mmol, 1.0 equiv) and stirred at rt for 10 min before cooling to –78 ^{o}C. PhLi (0.5 mL, 1.0 mmol, 1.0 equiv, 2.0 M in Bu$_2$O) was then added dropwise at –78 ^{o}C, the cooling bath was removed and the reaction mixture was warmed to rt over 15 min, during which time it became homogenous. After 30 min at rt, the reaction mixture was re-cooled to –78 ^{o}C and a solution of 3-phenylpropanal (134mg, 1.0 mmol, 1.0 equiv) in THF (1 mL) was added dropwise. After 10 min, when complete decolorization had occurred, PhLi (0.55 mL, 1.1 mmol, 1.1 equiv, 2.0 M in Bu$_2$O) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at –78 ^{o}C, then allowed to reach rt over 15 min. After 30 min the resulting β-oxido ylide was re-cooled to –78 ^{o}C and added dropwise *via* cannula to a solution of anhydrous paraformaldehyde (40 mg, 1.2 mmol) in THF (10 mL) at –78 ^{o}C. After 30 min at –78 ^{o}C, the temperature was slowly raised to rt over 30 min. and the reaction mixture stirred for further 2 h at rt. The reaction mixture was then poured into water (20 mL), extracted with Et$_2$O (3x15 mL), dried (MgSO$_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography gave allylic alcohol (107 mg, 52%) as a colorless oil;

Data as above.

(*Z*)-4-Methyl-2-propylhept-2-enyl acetate (6b)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with freshly distilled 2-methylpentanal (100 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-4-methyl-2-propylhept-2-enyl acetate **6b** (155 mg, 73%) as a colorless oil; *Rf* 0.59 (5% Et$_2$O/petrol);

IR (film): 2958s, 2928s, 2871s, 1742s, 1457m, 1371m, 1230s.

^{1}H NMR (500 MHz): 5.17 (1H, d, *J* 10, C*H*=C), 4.61-4.54 (2H, m, CH_2O), 2.48-2.40 (1H, m, C*H*CH_3), 2.07-2.00 (5H, m, CH_3C=O, CH_2C=), 1.43 (2H, sxt, *J* 7, CH_2CH_3), 1.30-1.15 (4H, m, CH_2), 0.93 (3H, d, *J* 7, CH_3CH), 0.90-0.85 (6H, m, CH_3).

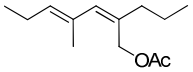
^{13}C NMR (125 MHz): 171.2 (*C*=O), 137.9 (*C*H=C), 131.9 (CH=*C*), 62.2 (*C*H_2O), 39.9 (*C*H_2), 37.4 (*C*H_2C=), 32.1 (*C*HCH=C), 21.5 (*C*H_3C=O), 21.2 (*C*H_3CH), 21.0 (*C*H_2), 20.6 (*C*H_2CH$_3$), 14.2 (*C*H_3), 13.6 (CH_3).

MS (CI$^+$) 213(42), 228(2), 230(100), 231(15), 232(2).

HRMS *m/z* (M+H$^+$) found 213.1847, $C_{13}H_{25}O_2$ requires 213.1855.

The isomeric ratio (*Z:E* >99:1) was determined by GC/MS, t_R = 6.54 min.

(2*Z*,4*E*)-4-Methyl-2-propylhepta-2,4-dienyl acetate (6c)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with freshly distilled (*E*)-2-methylpent-2-enal (98 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (2*Z*,4*E*)-4-methyl-2-propylhepta-2,4-dienyl acetate **6c** (159 mg, 76%) as a colorless oil; *Rf* 0.29 (30% CH_2Cl_2 /petrol);

IR (film): 2962s, 2934m, 2873m, 1742s, 1458m, 1370m, 1232s.

^{1}H NMR (500 MHz): 5.90 (1H, s, C*H*=C), 5.22 (1H, t, *J* 7, CH$_2$C*H*=C), 4.70 (2H, s, CH_2OAc), 2.11-2.05 (7H, m, CH_2CH=C, =CCH_2, CH_3C=O), 1.69 (3H, s, CH=CCH_3), 1.48-1.45 (2H, m, CH_2CH$_3$), 0.98 (3H, t, *J* 7, CH_3CH$_2$CH=C), 0.91 (3H, t, *J* 7, CH_3CH$_2$CH$_2$).

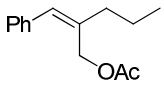
^{13}C NMR (125 MHz): 171.1 (*C*=O), 134.7 (*C*H=C), 133.3 (CH=*C*), 132.3 (CH$_2$*C*H=C), 131.1 (CH$_2$CH=*C*), 62.9 (*C*H$_2$OAc), 37.4 (CH=C*C*H$_2$), 21.5 (*C*H$_2$CH=C), 21.2 (CH$_2$*C*H$_2$CH$_3$), 21.1 (*C*H$_3$C=O), 16.6 (CH=C*C*H$_3$), 14.1 (*C*H$_3$CH$_2$CH=C), 13.8 (CH$_2$*C*H$_3$).

MS (CI$^+$): 228(100), 229(20).

HRMS *m/z* (M+NH$_4^+$) found 228.1958, $C_{13}H_{26}NO_2$ requires 228.1964.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 6.81 min.

(*Z*)-2-Benzylidenepentyl acetate (6d)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with freshly distilled benzaldehyde (106 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-2-benzylidenepentyl acetate **6d** (155 mg, 71%) as a colorless oil; *Rf* 0.31 (5% Et$_2$O/petrol);

IR (film): 3025m, 2960s, 2872s, 1739s, 1599w, 1493s, 1446s, 1369s, 1231s, 1025s.

^{1}H NMR (500 MHz): 7.35-7.19 (5H, m, ArC*H*), 6.57 (1H, s, C*H*=C), 4.73 (2H, s, CH_2O), 2.24 (2H, td, J_1 7, J_2 1, CH_2C=), 2.09 (3H, s, CH_3C=O), 1.61-1.54 (2H, m, CH_2CH$_3$), 0.98 (3H, t, *J* 7, CH$_3$).

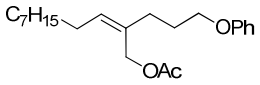
^{13}C NMR (125 MHz): 171.1 (*C*=O), 136.9 (CH=*C*), 136.7 (Ar*C*), 130.5 (*C*H=C), 128.7 (2xAr*C*H), 128.2 (2xAr*C*H), 126.9 (Ar*C*H), 62.7 (*C*H$_2$O), 37.6 (*C*H$_2$C=CH), 21.2 (*C*H$_2$CH$_3$), 21.0 (*C*H$_3$C=O), 13.8 (CH$_3$).

MS (CI^+) 218(76), 235(3), 236(100), 237(21), 238(2).

HRMS *m/z* (M^+) found 218.1309, $C_{14}H_{18}O_2$ requires 218.1307.

The isomeric ratio (*Z:E* 92:8) was determined by GC/MS, $t_{R\ (major)}$ = 8.56 min, $t_{R\ (minor)}$ = 8.74 min.

(*Z*)-2-(3-Phenoxypropyl)undec-2-enyl acetate (6e)



Following the General Procedure for *Z*-allylic ester formation, (4-phenoxybutyl)triphenylphosphonium bromide (491 mg, 1.0 mmol) was reacted with nonanal (142 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-2-(3-phenoxypropyl)undec-2-enyl acetate **6e** (237 mg, 68%) as a colorless oil; *Rf* 0.24 (5% Et_2O/petrol);

IR (film): 2925s, 2854s, 1740s, 1600s, 1587m, 1497s, 1369m.

^{1}H NMR (500 MHz): 7.31-7.26 (2H, m, ArC*H*), 6.95-6.89 (3H, m, ArC*H*), 5.48 (1H, t, *J* 7, C*H*=C), 4.64 (2H, s, CH_2O), 3.96 (2H, t, *J* 7, CH_2OPh), 2.26 (2H, t, *J* 7, CH_2C=), 2.10-2.06 (5H, m, CH_3C=O, CH_2CH=), 1.95-1.89 (2H, m, CH_2CH_2OPh), 1.34-1.26 (12H, m, CH_2x6), 0.89 (3H, t, *J* 7, CH_3).

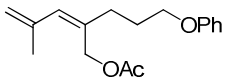
^{13}C NMR (125 MHz): 171.2 (*C*=O), 159.0 (OAr*C*), 132.5 (CH=*C*), 132.0 (*C*H=C), 129.4 (Ar*C*H), 120.5 (Ar*C*H), 114.5 (Ar*C*H), 67.1 (*C*H_2OPh), 62.0 (*C*H_2OAc), 31.9 (*C*H_2), 31.6 (*C*H_2C=), 29.8 (*C*H_2), 29.3 (*C*H_2), 29.2 (*C*H_2), 27.8 (*C*H_2CH=C), 27.7 (*C*H_2CH_2OPh), 22.7 (*C*H_2), 21.0 (*C*H_3C=O), 14.1 (CH_3).

MS (CI^+) 364(100), 365(2), 366(2).

HRMS *m/z* ($M+NH_4^+$) found 364.2852, $C_{22}H_{38}NO_3$ requires 364.2852.

The isomeric ratio (*Z:E* >99:1) was determined by GC/MS, t_R = 13.21 min.

(*Z*)-4-Methyl-2-(3-phenoxypropyl)penta-2,4-dienyl acetate (6f)



Following the General Procedure for *Z*-allylic ester formation, (4-phenoxybutyl)triphenylphosphonium bromide (491 mg, 1.0 mmol) was reacted with freshly distilled methacrolein (70 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-4-methyl-2-(3-phenoxypropyl)penta-2,4-dienyl acetate **6f** (189 mg, 69%) as a colorless oil; *Rf* 0. 37 (10% Et_2O /petrol);

IR (film): 3063w, 3040s, 2944m, 1739s, 1600s, 1587m, 1497m, 1244s.

^{1}H NMR (500 MHz): 7.31-7.27 (2H, m, ArC*H*), 6.96-6.90 (3H, m, ArC*H*), 5.95 (1H, s, C*H*=C), 5.00 (1H, s, 1H of CH_2=C), 4.78 (2H, s, CH_2OAc), 4.76 (IH, s, 1H of CH_2=C), 3.98 (2H, t, *J* 6, CH_2OAr), 2.33 (2H, t, *J* 7, CH_2C=CH), 2.07 (3H, s, CH_3C=O), 1.99-1.93 (2H, m, CH_2), 1.81 (3H, s, CH_2=CHCH_3).

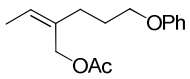
^{13}C NMR (125 MHz): 171.0 (*C*=O), 159.0 (OAr*C*), 140.8 (CH2=*C*), 134.4 (CH=*C*), 132.9 (*C*H=C), 129.4 (Ar*C*H), 120.6 (Ar*C*H), 115.6 (*C*H_2=C), 114.5 (Ar*C*H), 67.0 (*C*H_2OAr), 62.7 (*C*H_2OAc), 31.7 (*C*H_2C=CH), 27.7 (*C*H_2), 23.2 (CH_2=C*C*H_3), 21.0 (*C*H_3C=O).

MS (CI^+): 274(21), 275(60), 276(11), 292(100), 293(19), 294(3).

HRMS *m/z* (M^+) found 274.1568, $C_{17}H_{22}O_3$ requires 274.1569.

Single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 9.66 min.

(*Z*)-2-Ethylidene-5-phenoxypentyl acetate (6g)



Following the General Procedure for *Z*-allylic ester formation, (4-phenoxybutyl)triphenylphosphonium bromide (491 mg, 1.0 mmol) was reacted with freshly distilled acetaldehyde (44 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-2-ethylidene-5-phenoxypentyl acetate **6g** (158 mg, 64%) as a colorless oil; *Rf* 0.16 (5% Et_2O/petrol);

IR (film): 2941s, 1737s, 1600s, 1497s, 1367s, 1242s, 1172m, 1097m.

^{1}H NMR (500 MHz): 7.31-7.26 (2H, m, ArC*H*), 6.96-6.89 (3H, m, ArC*H*), 5.57 (1H, q, *J* 7, C*H*=C), 4.66 (2H, s, CH_2OAc), 3.96 (2H, t, *J* 7, CH_2OPh), 2.26 (2H, t, *J* 7, CH_2C=), 2.07 (3H, s, CH_3C=O), 1.94-1.89 (2H, m, CH_2CH$_2$OPh), 1.69 (3H, d, *J* 7, CH_3CH=C).

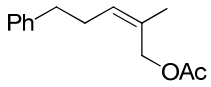
^{13}C NMR (125 MHz): 171.2 (*C*=O), 159.0 (OAr*C*), 133.5 (CH=*C*), 129.4 (Ar*C*H), 125.8 (*C*H=C), 120.5 (Ar*C*H), 114.5 (Ar*C*H), 67.1 (*C*H_2OAr), 61.7 (*C*H_2OAc), 31.7 (*C*H_2C=CH), 27.7 (*C*H_2), 20.9 (*C*H_3C=O), 13.3 (*C*H_3CH=C).

MS (CI$^+$) 248(100), 249(21), 250(3).

HRMS *m/z* (M$^+$) found 248.1453, $C_{15}H_{20}O_3$ requires 248.1412.

The isomeric ratio (*Z:E* >99:1) was determined by GC/MS, t_R = 9.99 min.

(*Z*)-2-Methyl-5-phenylpent-2-enyl acetate (6h)



Following the General Procedure for *Z*-allylic ester formation, ethyltriphenylphosphonium bromide (371 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and bromomethyl acetate (168 mg, 1.1 mmol) to give (*Z*)-2-methyl-5-phenylpent-2-enyl acetate **6h** (170 mg, 78%) as a colorless oil; *Rf* 0.22 (5% Et_2O/petrol);

IR (film): 3062w, 3027m, 2926s, 2857s, 1738s, 1603w, 1496m, 1454s.

^{1}H NMR (500 MHz): 7.31-7.27 (2H, m, ArC*H*), 7.21-7.18 (3H, m, ArC*H*), 5.46 (1H, t, *J* 7, C*H*=C), 4.51 (2H, s, CH_2O), 2.67 (2H, t, *J* 7, CH_2Ar), 2.40 (2H, q, *J* 7, CH_2CH=), 2.06 (3H, s, CH_3C=O), 1.75 (3H, d, *J* 1, CH_3C=).

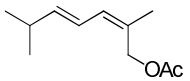
^{13}C NMR (125 MHz): 171.1 (*C*=O), 141.6 (Ar*C*), 130.5 (CH=*C*), 129.7 (*C*H=C), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 125.9 (Ar*C*H), 63.1 (*C*H_2OAc), 36.0 (Ar*C*H_2), 29.7 (ArCH$_2$*C*H$_2$), 21.43 (CH=C*Me*), 20.96 (*C*H_3C=O).

MS (CI$^+$) 236(100), 237(14), 238(1).

HRMS *m/z* (M+NH_4^+) found 236.1655, $C_{14}H_{22}NO_2$ requires 236.1651.

The isomeric ratio (*Z:E* 87:13) was determined by GC/MS, $t_{R\ (major)}$ = 3.31 min, $t_{R\ (minor)}$ = 3.51 min (initial temperature = 180 ^{o}C, max. temperature = 280 ^{o}C; rate = 20 ^{o}C/min).

(2*Z*,4*E*)-2,6-Dimethylhepta-2,4-dien-1-yl acetate (6i)



Following the General Procedure for *Z*-allylic ester formation, ethyltriphenylphosphonium bromide (724 mg, 2.0 mmol) was reacted with (*E*)-4-methylpent-2-enal[1] (196 mg, 2.0 mmol) and bromomethyl acetate (337 mg, 2.2 mmol) to give (2*Z*,4*E*)-2,6-dimethylhepta-2,4-dien-1-yl acetate **6i** (185 mg, 51%) as a colorless oil; *Rf* 0.36 (5% Et_2O/petrol);

IR (film): 3057s, 2966s, 1739s, 1371s, 1240s.

^{1}H NMR (500 MHz): 1.01 (3H, s, CH_3), 1.02 (3H, s, CH_3), 1.82 (3H, s, CH_3C=CH), 2.08 (3H, s, CH_3C=O), 2.39-2.33 (1H, m, C*H*), 4.70 (2H, s, CH_2OAc), 5.66 (1H, dd, J_1 15, J_2 7, C*H*=CH), 5.98 (1H, d, *J* 11, C*H*=C), 6.24 (1H, dd, J_1 15, J_2 11, CH=C*H*).

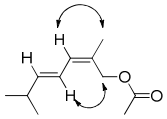
^{13}C NMR (125 MHz): 20.9 (*C*H_3), 21.6 (*C*H_3C=O), 22.3 (*C*H_3), 31.3 (*C*H), 63.3 (*C*H_2O), 122.1 (CH=*C*H), 129.4 (CH=*C*), 130.4 (*C*H=C), 142.8 (*C*H=CH), 171.2 (*C*=O).

Single isomer was observed (*Z:E* >99:1) by GC/MS. $t_{R\ (major)}$ = 5.68 min.

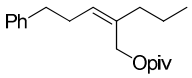
MS (CI$^+$) 179(4), 181(24), 182(100), 183(33), 184(7), 199(9).

HRMS *m/z* (M+NH_4^+) found 199.1568, $C_{11}H_{21}NO_2$ requires 199.1572.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 5.66 ppm (C***H***=C) saw reciprocal signal enhancement at 1.82 ppm (C***H***$_3$C=CH); and irradiation at 4.70 ppm (C***H***$_2$O) saw reciprocal signal enhancement at 6.24 ppm (Me_2CHCH=C***H***).



(*Z*)-5-Phenyl-2-propylpent-2-enyl pivalate (7a)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and chloromethyl pivalate (166 mg, 1.1 mmol, Aldrich) to give (*Z*)-5-phenyl-2-propylpent-2-enyl pivalate **7a** (214 mg, 74%) as a colorless oil; *Rf* 0.31 (5% Et_2O/petrol);

IR (film): 3085w, 3063m, 2959s, 2931s, 2871m, 2360w, 2341w, 1942w, 1867w, 1729s, 1604m, 1496m, 1454s, 1281m, 1151s.

^{1}H NMR (500 MHz): 7.30-7.27 (2H, m, ArC*H*), 7.20-7.18 (3H, m, ArC*H*), 5.44 (1H, t, *J* 7, C*H*=C), 4.50 (2H, s, CH_2O), 2.67 (2H, t, *J* 7, CH_2Ar), 2.42 (2H, q, *J* 7, CH_2CH=C), 2.03 (2H, t, *J* 7, CH_2C=CH), 1.41 (2H, apparant dq, J_1 15, J_2 7, CH_2CH_3), 1.20 (9H, s, *t*-Bu), 0.88 (3H, t, *J* 7, CH_3).

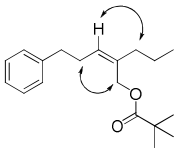
^{13}C NMR (125 MHz): 178.5 (*C*=O), 14.7 (Ar*C*), 134.7 (CH=*C*), 129.5 (*C*H=C), 128.5 (2xAr*C*H), 128.3 (2xAr*C*H), 125.8 (Ar*C*H), 61.8 (*C*H_2O), 38.8 ((CH_3)$_3$*C*), 37.5 (*C*H_2C), 36.1 (*C*H_2Ar), 29.6 (*C*H_2CH=C), 27.2 ((*C*H_3)$_3$C), 21.1 (*C*H_2CH_3), 13.7 (CH_3).

MS (CI$^+$) 286(18), 287(75), 288(100), 289(94), 290(2).

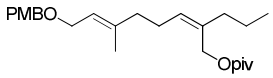
HRMS *m/z* (M+H^+) found 290.2227, $C_{19}H_{30}O_2$ requires 290.2246.

The isomeric ratio (*Z:E* >99:1) was determined by GC/MS, t_R =10.38 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 5.44 ppm (C***H***=C) saw reciprocal signal enhancement at 2.03 ppm (C***H***$_2$C=CH); and irradiation at 4.50 (C***H***$_2$O) saw reciprocal signal enhancement at 2.42(C***H***$_2$CH=CH).



(2*Z*,6*E*)-8-((4-Methoxybenzyl)oxy)-6-methyl-2-propylocta-2,6-dien-1-yl pivalate (7b)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with (*E*)-6-((4-methoxybenzyl)oxy)-4-methylhex-4-enal **13** (248 mg, 1.0 mmol) and chloromethyl pivalate (166 mg, 1.1 mmol, Aldrich) to give (2*Z*,6*E*)-8-((4-methoxybenzyl)oxy)-6-methyl-2-propylocta-2,6-dien-1-yl pivalate **7b** (402 mg, 71%) as a colorless oil; *Rf* 0.29 (10% Et_2O/petrol);

IR (film): 2960s, 2933s, 2871s, 2062w, 1881w, 1727s, 1612m, 1513s.

^{1}H NMR (500 MHz): 7.27 (2H, d, *J* 9, ArC*H*), 6.88 (2H, d, *J* 9, ArC*H*), 5.38 (2H, m, C*H*=CMe, C*H*=CH_2OPv), 4.57 (2H, s, CH_2OPv), 4.43 (2H, s, CH_2Ar), 3.99 (2H, d, *J* 7, CH_2OAr), 3.81 (OCH_3), 2.25-2.01 (6H, m, CH_2 x 3), 1.64 (3H, s, CH=CCH_3), 1.44-1.40 (2H, m, CH_2CH$_3$), 1.20 (9H, s, C(CH_3)$_3$), 0.87 (3H, t, *J* 7, CH_2CH_3).

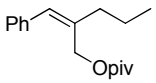
^{13}C NMR (125 MHz): 178.5 (*C*=O), 159.1 (CH_3OAr*C*), 139.5 (CH=*C*Me), 134.2 (CH=*C*CH_2OPv), 130.6 (Ar*C*), 129.9 (*C*H=CCH_2OPv), 129.4 (Ar*C*H), 121.4 (*C*H=CMe), 113.7 (Ar*C*H), 71.7 (*C*H_2Ar), 66.2 (*C*H_2OAr), 61.9 (*C*H_2OPv), 55.3 (O*C*H_3), 39.7 (*C*H_2), 38.8 (*C*(CH_3)$_3$), 37.5 (*C*H_2), 27.2 (C(*C*H_3)$_3$), 25.9 (*C*H_2), 21.1 (*C*H_2CH$_3$), 16.4 (CH=C*C*H_3), 13.7 (CH_2*C*H_3).

MS (CI^+): 420(100), 421(26), 422(6).

HRMS *m/z* (M+NH_4^+) found 421.3202, $C_{25}H_{43}NO_4$ requires 421.3192.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 14.57 min.

(*Z*)-2-Benzylidenepentyl pivalate (7c)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with benzaldehyde (106 mg, 1.0 mmol) and chloromethyl pivalate (166 mg, 1.1 mmol, Aldrich) to give (*Z*)-2-benzylidenepentyl pivalate **7c** (172 mg, 66%) as a colorless oil; *Rf* 0.42 (5% Et_2O/petrol);

IR (film): 3026w, 2961s, 2872s, 1730s, 1599w, 1479s, 1365m, 1280s, 1149s, 1031m.

^{1}H NMR (500 MHz): 7.36-7.20 (5H, m, ArC*H*), 6.57 (1H, s, C*H*=C), 4.72 (2H, s, C$H_2$0), 2.26-2.23 (2H, m, CH_2C), 1.61-1.54 (2H, m, CH_2CH$_3$), 1.24 (9H, s, *t*-Bu), 0.98 (3H, t, *J* 7, CH_3).

Discernable data for (*E*): 6.17(1H, s, C*H*=C)

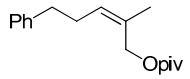
^{13}C NMR (125 MHz): 178.4 (*C*=O), 137.0 (CH=*C*), 136.9 (Ar*C*), 130.2 (*C*H=C), 128.7 (2xAr*C*H), 128.2 (2xAr*C*H), 126.8 (Ar*C*H), 62.8 (*C*H_2O), 38.9 (*C*$(CH_3)_3$), 37.9 (*C*H_2C=CH), 27.2 (C(*C*$H_3)_3$), 21.2 (*C*H_2CH_3), 13.8 (*C*H_3).

MS (CI^+) 276(2), 278(100), 279(19), 280(4).

HRMS *m/z* (M+NH_4^+) found 278.2130, $C_{17}H_{28}NO_2$ requires 278.2120.

The isomeric ratio (*Z:E* 88:12) was determined by GC/MS, $t_{R\ (major)}$ = 9.42 min, $t_{R\ (minor)}$ = 9.48 min.

(*Z*)-2-Methyl-5-phenylpent-2-enyl pivalate (7d)



Following the General Procedure for *Z*-allylic ester formation, ethyltriphenylphosphonium bromide (371 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and chloromethyl pivalate (166 mg, 1.1 mmol, Aldrich) to give (*Z*)-2-methyl-5-phenylpent-2-enyl pivalate **7d** (212 mg, 82%) as a colorless oil; *Rf* 0.33 (5% Et_2O/petrol);

IR (film): 3084m, 2972s, 2871s, 1728s, 1496s, 1479m, 1281s, 1151s, 699s.

^{1}H NMR (500 MHz): 7.30-7.27 (2H, m, ArC*H*), 7.21-7.18 (3H, m, ArC*H*), 5.42 (1H, t, *J* 7, C*H*=C), 4.51 (2H, m, CH_2O), 2.67 (2H, t, *J* 7, CH_2Ar), 2.41 (2H, q, *J* 7, CH_2CH=C), 1.73 (3H, d, *J* 1, CH_3C=CH), 1.21 (9H, s, (C$H_3)_3$C).

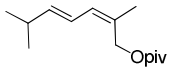
^{13}C NMR (125 MHz): 178.5 (*C*=O), 141.7 (Ar*C*), 130.9 (CH=*C*), 129.1 (*C*H=C), 128.5 (2xAr*C*H), 128.3 (2xAr*C*H), 125.9 (Ar*C*H), 63.0 (*C*H_2O), 38.8 ((CH$_3)_3$*C*), 36.0 (*C*H_2Ar), 29.6 (*C*H_2CH=C), 27.2 ((*C*$H_3)_3$C), 21.2 (*C*H_3C=).

MS (CI^+) 260(9), 276(1), 278(100), 279(40), 280(4).

HRMS *m/z* (M^+) found 260.1783, $C_{17}H_{24}O_2$ requires 260.1776.

The isomeric ratio (*Z:E* >99:1) was determined by GC/MS, t_R = 9.54 min.

(2*Z*,4*E*)-2,6-Dimethylhepta-2,4-dien-1-yl pivalate (7e)



Following the General Procedure for *Z*-allylic ester formation, ethyltriphenylphosphonium bromide (742 mg, 2.0 mmol) was reacted with (*E*)-4-methylpent-2-enal[1] (196 mg, 2.0 mmol) and chloromethyl pivalate (332 mg, 2.2 mmol, Aldrich) to give (2*Z*,4*E*)-2,6-dimethylhepta-2,4-dien-1-yl pivalate **7e** (283 mg, 63%) as a colorless oil; *Rf* 0.26 (2% Et_2O/petrol);

IR (film): 2962s, 2935m, 2872m, 1728s, 1282m, 1155s.

^{1}H NMR (500 MHz): 1.00 (3H, s, CH_3), 1.03 (3H, s, CH_3), 1.22 (9H, s, (C$H_3)_3$C), 1.80 (3H, s, CH_3), 2.44-2.27 (1H, m, C*H*), 4.70 (2H, s, CH_2OPiv), 5.69-5.59 (1H, dd, J_1 15, J_2 7, CH=C*H*), 5.96 (1H, d, *J* 11, C*H*=C), 6.26 (1H, dd, J_1 15, J_2 11, C*H*=CH).

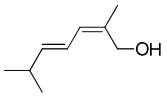
^{13}C NMR (125 MHz): 21.4 (*C*H_3C=CH), 22.4 ((*C*$H_3)_2$C), 27.2 ((*C*$H_3)_3$C), 31.3 ((CH$_3)_2$*C*), 38.9 (((CH$_3)_3$*C*), 63.3 (*C*H_2OPiv), 122.3 (CH=*C*H), 129.7 (*C*H=C), 130.0 (CH=*C*), 142.4 (*C*H=CH), 178.5 (*C*=O).

MS (CI^+) 222(5), 223(32), 224(100), 225(35), 227(2), 242(19).

HRMS *m/z* (M+NH_4^+) found 242.2118, $C_{14}H_{28}NO_2$ requires 242.2120

Single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 6.70 min.

(2*Z*,4*E*)-2,6-Dimethylhepta-2,4-dien-1-ol



To a stirred solution of KOt-Bu (1.18 g, 10.53 mmol) in Et_2O (10 mL), cooled to 0 ^oC, was added H_2O (0.5 mL) *via* a syringe. To this reaction mixture was added (2*Z*,4*E*)-2,6-dimethylhepta-2,4-dien-1-yl pivalate **(7e)** (262 mg, 1.17 mmol). The reaction mixture was stirred at rt and monitored by TLC. Then after 16 h the reaction was quenched with sat. aq. NH_4Cl (5 mL), extracted with Et_2O (3x15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography gave the (2*Z*,4*E*)-2,6-dimethylhepta-2,4-dien-1-ol[1] as a colorless oil. (151 mg, 92%); *Rf* 0.22 (20% Et_2O/petrol);

IR (film): 3418br, 2975s, 2934s, 2873s, 1723s, 1465m, 1383m.

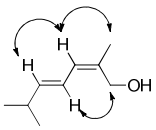
^{1}H NMR (500 MHz): 6.27 (1H, ddd, J_1 15, J_2 11, J_3 1, *i*-PrCH=C*H*), 5.91 (1H, d, *J* 11, C*H*=CMe), 5.63 (1H, dd , J_1 15, J_2 7, *i*-PrC*H*=CH), 4.26 (2H, s, CH_2OH), 2.40-2.31 (1H, m, C*H*(Me)$_2$), 1.87 (3H, s, CH=C*Me*), 1.01 (6H, d, *J* 7, CH(*Me*)$_2$).

^{13}C NMR (125 MHz): 141.9 (*i*-Pr*C*H=CH), 134.4 (CH=*C*Me), 128.4 (*i*-PrCH=*C*H), 122.2 (*C*H=CMe), 61.9 (*C*H_2OH), 31.3 (*C*H(Me)$_2$), 22.37 (CH(*Me*)$_2$), 21.41 (CH=C*Me*).

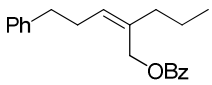
MS (Cl^+): 139(2), 146(10), 148(100), 149(9), 158(3), 160(19).

HRMS *m/z* (M^-H^+) found 139.1131, $C_9H_{15}O$ requires 139.1123.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 1.87 ppm (CH=C***Me***) saw reciprocal signal enhancement at 5.91 ppm (C***H***=CMe), irradiation at 4.26 ppm (C***H***$_2$O) saw reciprocal signal enhancement at 6.27 ppm (*i*-PrCH=C***H***); also irradiation at 5.91 ppm (C***H***=CMe) saw reciprocal signal enhancement at 5.63 (*i*-PrC***H***=CH).



(*Z*)-5-Phenyl-2-propylpent-2-enyl benzoate (8a)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and chloromethyl benzoate (188 mg, 1.1 mmol) to give (*Z*)-5-phenyl-2-propylpent-2-enyl benzoate **8a** (219 mg, 71%) as a colorless oil; *Rf* 0.45 (30% CH_2Cl_2/petrol);

IR (film): 3062w, 3027w, 2959s, 2871s, 1719s, 1452s, 1269s, 1110s.

^{1}H NMR (500 MHz): 8.03 (2H, d, *J* 8, ArC*H*), 7.58-7.54 (1H, m, ArC*H*), 7.46-7.43 (2H, m, ArC*H*), 7.29-7.26 (2H, m, ArC*H*), 7.20-7.16 (3H, m, ArC*H*), 5.52 (1H, t, *J* 7, C*H*=C), 4.76 (2H, s, CH_2OBz), 2.73-2.70 (2H, m, CH_2Ar), 2.52-2.46 (2H, m, CH_2CH=C), 2.13 (2H, t, *J* 7, CH_2C=CH), 1.50-1.46 (2H, m, CH_2CH$_3$), 0.90 (3H, t, *J* 7, CH$_3$).

Discernable data for *E*-isomer: 4.34 (1H, t, *J* 7, C*H*=C), 1.58-1.52 (2H, m, CH_2CH$_3$), 0.99 (3H, t, *J* 7, CH_3).

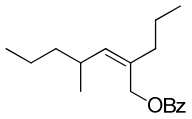
^{13}C NMR (125 MHz): 166.6 (*C*=O), 141.6 (CH$_2$Ar*C*), 134.4 (CH=*C*), 132.9 (Ar*C*H), 130.4 (Ar*C*C=O), 130.1 (*C*H=C), 129.6 (Ar*C*H), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 128.3 (Ar*C*H), 125.9 (Ar*C*H), 62.3 (*C*H$_2$OBz), 72.6 (*C*H$_2$C=), 36.1 (*C*H$_2$Ar), 29.7 (*C*H$_2$CH=C), 21.2 (CH$_2$*C*H$_3$), 13.8 (CH$_3$).

MS (CI$^+$): 326(100), 327(28), 328(4).

HRMS *m/z* (M+NH$_4^+$) found 326.2112, $C_{21}H_{28}NO_2$ requires 326.2120.

The isomeric ratio (*Z:E* 98:2) was determined by GC/MS analysis of crude. $t_{R\ (major)}$ = 12.40 min, $t_{R\ (minor)}$ = 11.93 min.

(*Z*)-4-Methyl-2-propylhept-2-en-1-yl benzoate (8b)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (798 mg, 2.0 mmol) was reacted with freshly distilled 2-methylpentanal (200 mg, 2.0 mmol) and chloromethyl benzoate (341 mg, 2.1 mmol) to give (*Z*)-4-methyl-2-propylhept-2-en-1-yl benzoate **8b** (362 mg, 66%) as a colorless oil; *Rf* 0.33 (20% CH$_2$Cl$_2$/petrol);

IR (film): 2958s, 2871s, 1721s, 1453m, 1268s.

^{1}H NMR (500 MHz): 8.05 (2H, d, *J* 8, ArC*H*), 7.58-7.55 (1H, m, ArC*H*), 7.47-7.44 (2H, m, ArC*H*), 5.24 (1H, d, *J* 10, C*H*=C), 4.88-4.80 (2H, m, CH_2OBz), 2.56-2.49 (1H, m, C*H*CH$_3$), 2.18-2.09 (2H, m, CH=CCH_2), 1.51 (2H, sxt, *J* 7, CH_2CH$_3$), 1.34-1.19 (4H, m, 2xCH_2), 0.98 (3H, d, *J* 7, CHCH_3), 0.92 (3H, t, *J* 7, CH_3), 0.87 (3H, t, *J* 7, CHCH_3).

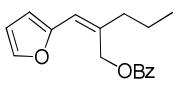
^{13}C NMR (125 MHz): 166.7 (*C*=O), 138.2 (*C*H=C), 132.8 (Ar*C*H), 131.9 (CH=*C*), 130.5 (Ar*C*), 129.6 (Ar*C*H), 128.3 (Ar*C*H), 62.8 (*C*H$_2$OBz), 39.9 (*C*H$_2$), 37.7 (*C*H$_2$), 32.2 (*C*HCH$_3$), 21.6 (*C*H$_2$), 21.3 (*C*H$_2$), 20.7 (*C*H$_3$CH), 14.2 (*C*H$_3$), 13.7 (*C*H$_3$).

MS (CI$^+$) 273(4), 274(40), 275(100), 276(13), 277(2).

HRMS *m/z* (M$^+$) found 274.1937, $C_{18}H_{26}O_2$ requires 274.1933.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 8.43 min.

(*Z*)-2-(Furan-2-ylmethylene)pentyl benzoate (8c)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (798 mg, 2.0 mmol) was reacted with freshly distilled furfural (192 mg, 2.0 mmol) and chloromethyl benzoate (341 mg, 2.1 mmol) to give (*Z*)-2-(furan-2-ylmethylene)pentyl benzoate **8c** (399 mg, 74%) as a light yellow oil; *Rf* 0.35 (20% CH$_2$Cl$_2$/petrol);

IR (film): 2959s, 2871s, 1721s, 1452s, 1269br, 1111s.

^{1}H NMR (500 MHz): 8.08 (2H, d, *J* 8, ArC*H*), 7.60-7.57 (1H, m, ArC*H*), 7.48-7.45 (2H, m, ArC*H*), 7.41 (1H, s, O-C*H*=CH), 6.41 (1H, br. s., C*H*=C-O), 6.32 (1H, s, O-CH=C*H*), 6.31 (1H, s, C*H*=C), 5.28 (2H, s, CH_2OBz), 2.34 (2H, t, *J* 8, CH=CCH_2), 1.62 (2H, sxt, *J* 8, CH_2CH$_3$), 0.99 (3H, t, *J* 7, CH_3).

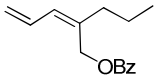
^{13}C NMR (125 MHz): 166.6 (*C*=O), 152.0 (O-*C*=CH), 142.0 (O-*C*H=CH), 135.3 (CH=*C*CH$_2$), 132.9 (Ar*C*H), 130.3 (Ar*C*), 129.6 (Ar*C*H), 18.4 (Ar*C*H), 117.9 (*C*H=CCH$_2$), 111.2 (*C*H=C-O), 109.7 (*C*H=CH-O), 63.8 (*C*H$_2$OBz), 38.0 (*C*H$_2$CH$_2$CH$_3$), 21.4 (*C*H$_2$CH$_3$), 13.8 (*C*H$_3$).

MS (CI$^+$) 270(81), 271(100), 272(15), 273(3), 288(10).

HRMS *m/z* (M+NH$_4^+$) found 288.1583, $C_{17}H_{22}NO_3$ requires 288.1600.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 8.42 min.

(*Z*)-2-Propylpenta-2,4-dienyl benzoate (8d)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with freshly distilled acrolein (56 mg, 1.0 mmol) and chloromethyl benzoate (188 mg, 1.1 mmol) to give (*Z*)-2-propylpenta-2,4-dienyl benzoate **8d** (173 mg, 75%) as a colorless oil; *Rf* 0.34 (20% CH_2Cl_2 /petrol);

IR (film): 3057m, 2962s, 2874m, 1720s, 1602w, 1452m, 1267s, 1113s.

^{1}H NMR (500 MHz): 8.06-8.04 (2H, m, ArC*H*), 7.58-7.55 (1H, m, ArC*H*), 7.46-7.43 (2H, m, ArC*H*), 6.75 (1H, dt, J_1 17, J_2 10, CH$_2$=C*H*), 6.11 (1H, d, *J* 11, C*H*=C), 5.25 (1H, dd, J_1 17, J_2 2, 1H of CH_2=CH), 5.16 (1H, dd, J_1 10, J_2 2, 1H of CH_2=CH), 4.97 (2H, s, CH_2OBz), 2.22 (2H, t, *J* 7, =CCH_2), 1.57-1.53 (2H, m, CH_2CH$_3$), 0.94 (3H, t, *J* 7, CH$_3$).

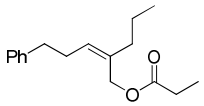
^{13}C NMR (125 MHz): 166.5 (*C*=O), 136.3 (CH=*C*), 132.9 (Ar*C*H), 132.0 (CH$_2$=*C*H), 130.7 (*C*H=C), 130.2 (Ar*C*), 129.6 (Ar*C*H), 128.4 (Ar*C*H), 118.1 (*C*H$_2$=CH), 62.3 (*C*H$_2$OBz), 37.7 (*C*H$_2$CH$_2$CH$_3$), 21.2 (*C*H$_2$CH$_3$), 13.8 (CH$_3$).

MS (CI$^+$): 230(2), 231(100), 232(15), 248(42).

HRMS *m/z* (M+NH$_4^+$) found 248.1651, $C_{15}H_{22}NO_2$ requires 248.1651.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 9.13 min.

(*Z*)-5-Phenyl-2-propylpent-2-enyl propionate (9a)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and chloromethyl propionate (135 mg, 1.1 mmol) to give (*Z*)- 5-phenyl-2-propylpent-2-enyl propionate **9a** (149 mg, 57%) as a colorless oil; *Rf* 0.20 (5% Et_2O/petrol);

IR (film): 3027s, 2959s, 2871m, 1737s, 1454m, 1178s.

^{1}H NMR (500 MHz): 7.30-7.28 (2H, m, ArC*H*), 7.20-7.17 (3H, m, ArC*H*), 5.45 (1H, t, *J* 7, C*H*=C), 4.52 (2H, s, CH_2O), 2.67 (2H, t, *J* 7, CH_2CH=C), 2.42 (2H, q, *J* 7, CH_2Ar), 2.33 (2H, q, *J* 7, CH_2C=O), 2.03

(2H, t, *J* 7, C*H*$_2$C=CH), 1.41 (2H, sxt, *J* 7, C*H*$_2$CH$_3$), 1.14 (3H, t, *J* 7, C*H*$_3$CH$_2$C=O), 0.88 (3H, t, *J* 7, CH$_2$C*H*$_3$).

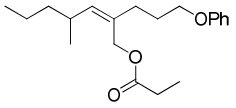
^{13}C NMR (125 MHz): 174.5 (*C*=O), 141.6 (Ar*C*), 134.5 (CH=*C*), 129.8 (*C*H=C), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 125.8 (Ar*C*H), 61.6 (*C*H$_2$O), 37.4 (*C*H$_2$C=CH), 36.1 (*C*H$_2$CH=C), 29.6 (*C*H$_2$Ar), 27.6 (*C*H$_2$C=O), 21.2 (*C*H$_2$CH$_3$), 13.7 (*C*H$_3$CH$_2$), 9.1 (*C*H$_3$CH$_2$C=O).

MS (CI$^+$): 278(100), 279(18).

HRMS *m/z* (M+NH$_4^+$) found 278.2108, $C_{17}H_{28}NO_2$ requires 278.2120.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 10.00 min.

(*Z*)-4-Methyl-2-(3-phenoxypropyl)hept-2-enyl propionate (9b)



Following the General Procedure for *Z*-allylic ester formation, (4-phenoxybutyl)triphenylphosphonium bromide (491 mg, 1.0 mmol) was reacted with 2-methylpentanal (100 mg, 1.0 mmol) and chloromethyl propionate (135 mg, 1.1 mmol) to give (*Z*)-4-methyl-2-(3-phenoxypropyl)hept-2-enyl propionate **9b** (163 mg, 51%) as a colorless oil; *Rf* 0.52 (10% Et$_2$O/petrol);

IR (film): 2956s, 2871s, 1600m, 1466m, 1245s, 1174s.

^{1}H NMR (500 MHz): 7.30-7.26 (2H, m, ArC*H*), 6.95-6.89 (3H, m, ArC*H*), 5.22 (1H, d, *J* 10, C*H*=C), 4.67-4.61 (2H, m, C*H*$_2$OC=O), 3.96 (2H, t, *J* 7, C*H*$_2$OAr), 2.47-2.43 (1H, m, CHMe), 2.34 (2H, q, *J* 7, C*H*$_2$C=O), 2.25 (2H, t, *J* 7, C*H*$_2$C=CH), 1.95-1.89 (2H, m, C*H*$_2$CH$_2$OAr), 1.29-1.18 (4H, m, C*H*$_2$), 1.15 (3H, t, *J* 7, C*H*$_3$CH$_2$C=O), 0.92 (3H, d, *J* 7, C*H*$_3$CH), 0.85 (3H, t, *J* 7, C*H*$_3$CH$_2$).

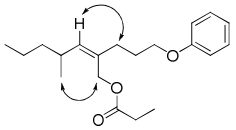
^{13}C NMR (125 MHz): 174.5 (*C*=O), 159.0 (OAr*C*), 138.4 (*C*H=C), 131.2 (CH=*C*), 129.4 (Ar*C*H), 120.5 (Ar*C*H), 114.5 (Ar*C*H), 67.1 (*C*H$_2$OAr), 62.1 (*C*H$_2$OC=O), 39.8 (*C*H$_2$), 32.2 (*C*HMe), 31.7 (*C*H$_2$C=CH), 27.7 (*C*H$_2$C=O), 27.6 (*C*H$_2$CH$_2$OAr), 21.5 (CH*C*H$_3$), 20.6 (CH$_2$*C*H$_3$), 14.2 (CH$_2$*C*H$_3$), 9.17 (*C*H$_3$CH$_2$C=O).

MS (CI$^+$): 318(100), 319(27).

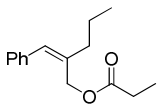
HRMS *m/z* (M$^+$) found 318.2207, $C_{20}H_{30}O_3$ requires 318.2195.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 11.58 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 5.22 ppm (C***H***=C) saw reciprocal signal enhancement at 2.25 ppm (C***H***$_2$C=CH); and irradiation at 4.67-4.61 (C***H***$_2$O) saw reciprocal signal enhancement at 0.92 (C***H***$_3$CH).



(*Z*)-2-Benzylidenepentyl propionate (9c)



Following the General Procedure for *Z*-allylic ester formation, *n*-butyltriphenylphosphonium bromide (399 mg, 1.0 mmol) was reacted with freshly distilled benzaldehyde (106 mg, 1.0 mmol) and

chloromethyl propionate (135 mg, 1.1 mmol) to give (*Z*)-2-benzylidenepentyl propionate **9c** (153 mg, 66%) as a colorless oil; *Rf* 0.32 (10% Et_2O/petrol);

IR (film): 2959s, 1737s, 1462m, 1361m, 1176s.

^{1}H NMR (500 MHz): 7.35-7.32 (2H, m, ArC*H*), 7.26-7.20 (3H, m, ArC*H*), 6.57 (1H, s, C*H*=C), 4.74 (2H, s, CH_2OC=O), 2.37 (2H, q, *J* 7, CH_2C=O), 2.24 (2H, td, J_1 7, J_2 1, CH_2C=CH), 1.61-1.54 (2H, m, CH_2CH$_3$), 1.17 (3H, t, *J* 7,CH_3CH$_2$C=O), 0.98 (3H, t, *J* 7, CH_3CH$_2$).

^{13}C NMR (125 MHz): 174.4 (*C*=O), 136.9 (Ar*C*), 136.8 (CH=*C*), 130.4 (*C*H=C), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 126.8 (Ar*C*H), 62.6 (*C*H$_2$OC=O), 37.7 (*C*H$_2$C=CH), 27.7 (*C*H$_2$C=O), 21.2 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$), 9.2 (*C*H$_3$CH$_2$C=O).

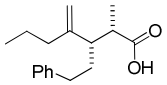
MS (CI$^+$): 232(30), 250(100).

HRMS *m/z* (M+NH$_4^+$) found 250.1805, $C_{15}H_{24}NO_2$ requires 250.1807.

A single isomer was observed (*Z:E* >99:1) by GC/MS. t_R = 9.03 min.

4. Ireland-Claisen rearrangement of *Z*-allylic propionate 9a

(±)-(2*R*,3*R*)-2-Methyl-4-methylene-3-(phenethyl)-heptanoic acid (11)



n-BuLi (0.65 mL, 1 mmol, 2 equiv, 1.54 M in hexanes) was added dropwise to a solution of diisopropylamine (101 mg, 1 mmol, 2 equiv) in THF (1.25 mL) at −78 °C. After 5 min, the flask was removed from the ice bath and stirring was continued at rt for 20 min before being cooled to −78 °C, at which point a solution of propionate ester **9a** (130 mg, 0.5 mmol, 1 equiv) in THF (2.5 mL) was added dropwise to the reaction vessel. After 1.5 h at −78 °C, TMSCl (108 mg, 1 mmol, 2 equiv) was added, the reaction mixture was stirred at −78 °C for 20 min, then at 0 °C for 10 min. The reaction mixture was allowed to warm to rt and then refluxed at 70 °C for 6 h. The reaction was then allowed to cool to RT, treated with 2 M aqueous HCl (15 mL) and stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (4 x 25 mL). The combined organic extracts were dried ($MgSO_4$), evaporated under reduced pressure, then purified by column chromatography (30% Et_2O/petrol) to furnish the acid **11** as a colorless oil (104 mg, 80%, the dr was determined on the reduced alcohol, see below). *Rf* 0.30 (30% Et_2O/petrol);

IR (film): 2959s, 2872s, 1707s, 1455s, 1251m, 1152m.

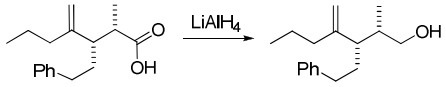
^{1}H NMR (500 MHz): 7.30-7.25 (3H, m, ArC*H*), 7.20-7.14 (2H, m, ArC*H*), 4.96 (1H, s, 1H of CH_2=C), 4.89 (1H, s, 1H of CH_2=C), 2.65-2.58 (2H, m, CH_2Ph), 2.48-2.40 (2H, m, CH_2C=CH_2), 2.06-1.92 (2H, m, CH_2CH), 1.84-1.78 (1H, m, C*H*COOH), 1.74-1.66 (1H, m, C*H*CH_2), 1.58-1.42 (2H, m, CH_2CH_3), 1.16 (3H, d, *J* 7, CH_3CH), 0.96 (3H, t, *J* 7, CH$_2$CH_3).

^{13}C NMR (125 MHz): 181.3 (*C*=O), 149.0 (*C*=CH$_2$), 142.4 (Ar*C*), 128.3 (Ar*C*H), 125.8 (Ar*C*H), 111.3 (C=*C*H$_2$), 48.2 (*C*HCH$_2$), 42.6 (*C*HCH$_3$), 36.1 (*C*H$_2$C=CH$_2$), 33.3 (*C*H$_2$Ph), 31.0 (*C*H$_2$CH), 20.7 (*C*H$_2$CH$_3$), 14.0 (*C*H$_3$CH), 13.7 (*C*H$_3$).

MS (CI$^+$) 283(100), 284(18).

HRMS *m/z* (M+Na$^+$) found 283.1669, $C_{17}H_{24}NaO_2$ requires 283.1669.

(±)-(2*R*,3*R*)-2-Methyl-4-methylene-3-(phenethyl)-heptan-1-ol by reduction of acid (11)



A stirred suspension of $LiAlH_4$ (76 mg, 2 mmol) in THF (2 mL) at 0 °C was treated dropwise with a solution of the acid **11** (13 mg, 0.05 mmol) in THF (5 mL). A vigorous reaction ensued and after stirring for 10 min, the reaction mixture was quenched by the careful addition of NH_4Cl (10 mL). The organic layer was separated, and aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic extracts were dried ($MgSO_4$), evaporated under reduced pressure, then purified by column chromatography (30% Et_2O/petrol) to furnish the title alcohol (12 mg, quant). *Rf* 0.30 (30% Et_2O/petrol);

IR (film): 3617br, 3054s, 2960s, 2873s, 2305w, 1808br, 1595w, 1954m, 1265s.

^{1}H NMR (500 MHz): 7.30-7.28 (2H, m, ArC*H*), 7.20-7.17 (3H, m, ArC*H*), 4.95 (1H, s, 1H of CH_2=C), 4.88 (1H, s, 1H of CH_2=C), 3.55 (1H, dd, J_1 11, J_2 5, CH_2OH), 3.42 (1H, dd, J_1 11, J_2 6, CH_2OH), 2.66-

2.60 (1H, m, 1H of C*H*$_2$Ph), 2.42-2.36 (1H, m, 1H of C*H*$_2$Ph), 2.07-1.92 (2H, m, C*H*$_2$), 1.85-1.78 (1H, m, C*H*), 1.73-1.51 (4H, m, 2xC*H*$_2$), 1.45-1.33 (1H, m, C*H*), 0.99 (3H, t, *J* 7, C*H*$_3$CH$_2$), 0.94 (3H, d, *J* 7, C*H*$_3$CH).

^{13}C NMR (125 MHz): 150.8 (CH$_2$=*C*), 142.9 (Ar*C*), 128.3 (Ar*C*H), 125.7 (Ar*C*H), 110.5 (*C*H$_2$=C), 67.1 (*C*H$_2$OH), 49.0 (*C*H), 38.1 (CH$_3$*C*H), 35.3 (*C*H$_2$), 33.8 (*C*H$_2$Ph), 31.4 (*C*H$_2$), 20.8 (*C*H$_2$), 14.5 (*C*H$_3$CH), 14.2 (*C*H$_3$).

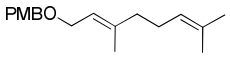
MS (CI$^+$) 268(6), 269(100), 270(18), 271(5).

HRMS *m/z* (M+Na$^+$) found 269.1877, C$_{17}$H$_{26}$NaO requires 269.1876.

The dr (= 95:5) was determined by GC/MS, $t_{R\,(major)}$ = 9.43 min. $t_{R\,(minor)}$ = 9.47 min.

Synthesis of diterpene (6*S*,7*R*,*Z*)-7-hydroxy-2-((*E*)-6-hydroxy-4-methylhex-4-enylidene)-6,10-dimethylundec-9-enyl acetate (12)

(*E*)-1-(((3,7-Dimethylocta-2,6-dien-1-yl)oxy)methyl)-4-methoxybenzene



To a suspension of NaH (2.4 g, 60.0 mmol, 60%) in THF (100 mL) at 0 °C was added geraniol (4.63 g, 30.0 mmol) dropwise over 10 min. The mixture was stirred at this temperature for a further 30 min, then PMBCl (4.93 g, 31.5 mmol) and $Bu_4N^+I^-$ (554 mg, 1.5 mmol) was added. The reaction was allowed to warm to rt overnight. The reaction was quenched with MeOH (10 mL), diluted with water (100 mL), extracted with Et_2O (2x50 mL), washed with brine (100 mL), dried ($MgSO_4$), filtered, evaporated under reduced pressure and purified by chromatography (10% Et_2O/petrol) to give the protected alcohol[2] (7.33 g, 89%) as a colorless oil; R*f* 0.37 (10% Et_2O/petrol).

IR(film): 3340br, 2915s, 2856s, 2060w, 1882w, 1716m, 1612m, 1513s, 1249s.

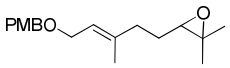
^{1}H NMR (400 MHz): 7.29 (2H, d, *J* 9, ArC*H*), 6.89 (2H, d, *J* 9, ArC*H*), 5.40 (1H, t, *J* 7, C=C*H*), 5.11 (1H, t, *J* 7, C=C*H*), 4.45 (2H, s, CH_2Ar), 4.01 (2H, d, *J* 7, CH_2OPMB), 3.81 (3H, s, CH_3O), 2.14-2.03 (4H, m, 2 x CH_2), 1.69 (CH_3), 1.65 (CH_3), 1.61 (CH_3).

^{13}C NMR (100 MHz): 159.1 (CH_3OAr*C*), 140.3 (*C*=CH), 131.7 (C=*C*H), 130.7 (Ar*C*), 129.5 (Ar*C*H), 124.0 (C=*C*H), 120.9 (C=*C*H), 113.7 (Ar*C*H), 71.6 (*C*H_2Ar), 66.3 (*C*H_2OPMB), 55.3 (O*C*H_3), 39.6 (*C*H_2), 26.4 (*C*H_2), 25.7 (*C*H_3), 17.7 (*C*H_3), 16.5 (CH_3).

MS (CI^+) 275(57), 290(7), 291(2), 292(100), 293(27), 294(3).

HRMS *m/z* ($M+H^+$) found 275.2007, $C_{18}H_{27}O_2$ requires 275.2011.

(*E*)-3-(5-((4-Methoxybenzyl)oxy)-3-methylpent-3-en-1-yl)-2,2-dimethyloxirane



To a solution of (*E*)-1-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methyl)-4-methoxybenzene (7.00 g, 25.5 mmol) in CH_2Cl_2 (150 mL) at 0 °C was added *m*-CPBA (5.8 g, 25.9 mmol,~77%) in four portions once every 30 min. The mixture was further stirred at 0 °C for 30 min and then diluted with sat. aq. $NaHCO_3$ (100 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (100 mL), brine (100 mL), dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (20% Et_2O/petrol) to give epoxide (5.57 g, 75%) as a colorless oil; R*f* 0.24 (20% Et_2O/petrol).

IR(film): 2960s, 2855s, 1613s, 1513s, 1462s, 1248s.

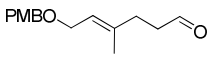
^{1}H NMR (400 MHz): 7.27 (2H, d, *J* 9, ArC*H*), 6.88 (2H, d, *J* 9, ArC*H*), 6.44 (1H, t, *J* 7, C=C*H*), 4.44 (2H, s, CH_2Ar), 4.00 (2H, d, *J* 7, CH_2OPMB), 3.81 (3H, s, OCH_3), 2.71 (1H, t, *J* 6, C*H*O), 2.26-2.11 (2H, m, CH_2), 1.70-1.64 (5H, m, CH_2, CH_3), 1.31 (CH_3C), 1.26 (CH_3C).

^{13}C NMR (100 MHz): 159.1 (CH_3OAr*C*), 139.3 (*C*=CH), 130.6 (Ar*C*), 129.4 (Ar*C*H), 121.5 (C=*C*H), 113.8 (Ar*C*H), 71.8 (*C*H_2Ar), 66.3 (*C*H_2OPMB), 64.0 (*C*H-C), 58.4 (*C*(CH_3)$_2$), 55.3 (O*C*H_3), 36.2 (*C*H_2), 27.2 (*C*H_2), 24.9 (*C*H_3C), 18.8 (*C*H_3C), 16.6 (CH_3).

MS (CI^+) 289(13), 302(5), 306(8), 308(100), 309(13).

HRMS *m/z* (M^-H^+) found 289.1805, $C_{18}H_{25}O_3$ requires 289.1804.

(*E*)-6-((4-Methoxybenzyl)oxy)-4-methylhex-4-enal (13)



(*E*)-3-(5-((4-Methoxybenzyl)oxy)-3-methylpent-3-en-1-yl)-2,2-dimethyloxirane (5.0 g, 17.2 mmol) in Et_2O (20 mL) was added to a solution of $HIO_4.2H_2O$ (2.76 g, 13.0 mmol) in THF (150 mL) at 0 ^oC. After stirring for 30 min, sat. $NaHCO_3$ (20 mL) was added slowly, and stirring was continued for 15 min at 0 ^oC. The resulting mixture was filtered through celite and the filter cake washed with Et_2O (30 ml). The combined filtrate was extracted with Et_2O (2 x 100 mL) and the combined organic layers were dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (30% Et_2O/petrol) to give aldehyde **13** (3.09 g, 72%) as a colorless oil; R*f* 0.21 (30% Et_2O/petrol).

IR(film): 2911s, 2837s, 2723s, 1723s, 1612m, 1513s, 1248s.

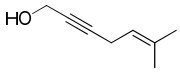
^1H NMR (400 MHz): 9.75 (1H, brs, C*H*O), 7.26 (2H, d, *J* 9, ArC*H*), 6.87 (2H, d, *J* 9, ArC*H*), 5.42-5.38 (1H, m, C=C*H*), 4.42 (2H, s, C*H*Ar), 3.98 (2H, d, *J* 7, CH_2OPMB), 3.78 (3H, s, OCH_3), 2.57-2.53 (2H, m, CH_2), 2.37-2.33 (2H, m, CH_2), 1.65 (3H, s, CH_3).

^{13}C NMR (400 MHz): 202.0 (*C*HO), 159.2 (CH_3OAr*C*), 138.0 (*C*=CH), 130.5 (Ar*C*), 129.4 (Ar*C*H), 121.9 (C=*C*H), 113.8 (Ar*C*H), 71.9 (*C*H_2Ar), 66.1 (*C*H_2OPMB), 55.3 (O*C*H_3), 41.8 (*C*H_2CHO), 31.5 (CH_2), 16.7 (CH_3).

MS (CI^+) 248(6), 266(100), 267(32), 268(2).

HRMS *m/z* (M^+) found 248.1408, $C_{15}H_{20}O_3$ requires 248.1407.

6-Methylhept-5-en-2-yn-1-ol (17)



To a solution of propargyl alcohol (2.13 g, 38 mmol) in THF (100 mL) was added *n*-BuLi (47 mL, 1.6 M in hexanes, 75 mmol) dropwise at 0 ^oC over 1 h. After 30 min, CuI (714 mg, 3.75 mmol) was added in one portion at 0 ^oC. After a further 30 min, a solution of prenyl bromide (5.51 g, 37 mmol) in THF (120 mL) was added dropwise at 0 ^oC. The reaction mixture was allowed to warm to rt overnight, quenched with sat. aq. NH_4Cl (60 mL), extracted with ether (3x50 mL), dried ($MgSO_4$) and concentrated. The residue was chromatographed (SiO_2, 20% Et_2O/petrol) to give 6-methylhept-5-en-2-yn-1-ol **17**[3] as light yellow oil (4.35 g, 95%), *Rf* 0.22 (20% Et_2O/petrol);

IR (film): 3384br, 2978s, 2933m, 2217w, 2183m, 1720s, 1364s, 1232m, 1140s.

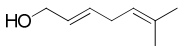
^1H NMR (500 MHz): 5.18-5.16 (1H, m, C=C*H*), 4.24 (2H, br.s., CH_2OH), 2.92 (2H, d, *J* 7, CH_2CH=C), 1.70 (3H, s, CH_3C=CH), 1.62 (3H, s, CH_3C=CH).

^{13}C NMR (125 MHz): 134.1 (*C*=CH), 118.6 (C=*C*H), 85.1 (*C*≡CCH$_2$OH), 77.8 (C≡*C*CH$_2$OH), 51.4 (*C*H_2OH), 25.5 (CH_3), 17.9 (CH_3), 17.7 (C=CHCH_2).

MS (CI^+) 122(3), 123(48), 124(100), 125(10), 126(1).

HRMS *m/z* (M^+) found 124.0893, $C_8H_{12}O$ requires 124.0888.

(*E*)-6-Methylhepta-2,5-dien-1-ol (18)



A solution of enyne **17** (5.87 g, 47.3 mmol) in THF (10 mL) was added dropwise to a suspension of $LiAlH_4$ (2.70 g, 71 mmol) in THF (75 mL) at 0 °C. the reaction mixture was heated at reflux for 8 h, then cooled , quenched with 1 M HCl (aq), and extracted with ether (3 x 50 mL). The combined organic layers were washed with brine (50 mL x 2), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was chromatographed (SiO_2, 20% Et_2O/petrol) to give allylic alcohol **18**[3] (5.56 g, 93%) as a colorless oil; *Rf* 0.19 (20% Et_2O/petrol);

IR (film): 3322s, 2968s, 2918s, 1669m, 1443s, 1377s.

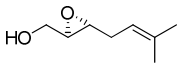
^{1}H NMR (400 MHz): 5.68-5.65 (2H, m, C*H*=C*H*), 5.14 (1H, tt, J_1 7, J_2 1, C*H*=C), 4.09 (2H, t, *J* 5, CH_2OH), 2.74 (2H, t, *J* 5, CH_2CH=CH), 1.72 (3H, s, CH_3), 1.62 (3H, s, CH_3).

^{13}C NMR (100 MHz): 132.9 (*C*=CH), 131.9 (*C*H=CH), 128.8 (CH=*C*H), 121.5 (C=*C*H), 63.8 (*C*H_2OH), 30.9 (*C*H_2CH=C), 25.7 (*C*H_3), 17.7 (*C*H_3).

MS (CI^+): 124(1), 125(1), 126(100), 127(12), 128(1), 144(74).

HRMS *m/z* ($M+NH_4^+$) found 144.1381, $C_8H_{18}NO$ requires 144.1383.

((2*R*,3*R*)-3-(3-Methylbut-2-enyl)oxiran-2-yl)methanol (19)



To a cooled (⁻30 °C) suspension of activated, powdered 4 A° MS (5.21 g) in CH_2Cl_2 (100 mL) were added (⁻)-diisopropyltartrate (0.26 mL, 1.23 mmol), $Ti(OPr^i)_4$ (0.33 mL, 1.11 mmol), and TBHP (2.18 mL, ~5.5 M in decane, 12 mmol). After 20 min, a solution of allylic alcohol **18** (1.55 g, 12.3 mmol) in CH_2Cl_2 (90 mL) was added at ⁻30 °C over 20 min. The resulting mixture was stirred at that temperature for 5 h, then quenched with a cooled solution of $FeSO_4.7H_2O$ (3.34 g, 12.0 mmol) and tartaric acid (1.80 g, 12.0 mmol) in de-ionized water (100 mL), stirred vigorously for 30 min, and extracted with ether (3x50 mL). The combined organic layers were treated with a pre-cooled (0 °C) solution of 30% (w/v) NaOH (20 mL) in brine and stirred for 1 h at rt. The two layers were separated and the aqueous layer was extracted with ether (3x30 mL). The combined organic layers were washed with brine (2 x 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was chromatographed (SiO_2, 50% Et_2O/petrol) to give epoxyalcohol **19**[3] (1.25 g, 71%) as a colorless oil; *Rf* 0.22 (50% Et_2O/petrol);

$[\alpha]_D^{23}$ = +18.8 (*c* 1.1, $CHCl_3$) {lit.[3] $[\alpha]_D^{27}$ = +19.15 (*c* 2.25, $CHCl_3$)}

IR (film): 3423 br, 2977s, 2917s, 1742m, 1673w, 1451s, 1377s, 1226m.

^{1}H NMR (500 MHz): 5.17-5.13 (1H, m, C*H*=C), 3.93-3.89 (1H, m, 1H of CH_2OH), 3.64-3.59 (1H, m, 1H of CH_2OH), 2.99-2.94 (2H, m, C*H*C*H*CH_2OH), 2.39-2.34 (1H, m, 1H of CH_2CH=C), 2.28-2.23 (1H, m, 1H of CH_2CH=C), 1.92-1.89 (1H, m, O*H*), 1.72 (3H, s, CH_3), 1.63 (3H, s, CH_3).

^{13}C NMR (125 MHz): 135.1 (*C*=CH), 117.9 (C=*C*H), 61.7 (*C*H_2OH), 58.0 (*C*HCH_2OH), 55.5 (*C*HCHCH_2OH), 30.1 (*C*H_2CH=C), 25.7 (CH_3), 17.9 (CH_3).

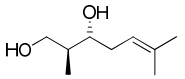
MS (CI^+): 140(11), 141(14), 142(39), 143(100), 144(13).

HRMS *m/z* ($M-H^+$) found 141.0914, $C_8H_{13}O_2$ requires 141.0916.

The *ee* value of epoxyalcohol **19** was assumed to be the same as that of its benzoate derivative. The later was determined to be 96% by chiral GC analysis: Chiral GC (β-cyclodextrin column (0.22 mm x 30 m,

thickness 0.25 mm), using He as a carrier gas (flow rate = 0.7 mL/min, injector T = 220 °C; detector: FID, T = 250 °C); 70–120 °C (0.5 °C/min) $t_{R(major)}$ = 43.46 min, $t_{R\ (minor)}$ = 44.32 min).

(2*S*,3*R*)-2,6-Dimethylhept-5-ene-1,3-diol (20)[3]



To a suspension of purified[4] CuBr.Me_2S (62 mg, 0.30 mmol) in THF (10 mL) at -20 °C was added MeMgBr (3 M in Et_2O, 3 mL, 9 mmol) dropwise. After 30 min, the reaction mixture was cooled to −40 °C then a solution of epoxy alcohol **19** (427 mg, 3 mmol, Et_2O (10 mL)) was added dropwise. The reaction mixture then allowed to warm to −20 °C during 1 h, stirred for further 6 h, slowly warmed to rt (over 3 h) and stirred at this temperature for 1 h. The reaction was then quenched with sat. aq. NH_4Cl (20 mL) at 0 °C. and extracted with EtOAc (20 mL x 4) and evaporated under reduced pressure. The residue was dissolved in 1:1 acetone:water (6 mL), $NaIO_4$ (641 mg, 3 mmol, 0.5 equiv) was added at 0 °C and the reaction was stirred at rt for 30 min, washed with sat. aq $NaHSO_3$ (20 mL), extracted with EtOAc (4 x 20 mL), concentrated under reduced pressure and purified by chromatography to give diol **20**[3] (395 mg, 83%) as a colorless oil; *Rf* 0.35 (50% EtOAc/petrol);

$[\alpha]_D^{23}$ = +18.5 (*c* 0.62, $CHCl_3$) {lit.[3] $[\alpha]_D^{20}$ = +20.6 (*c* 1.2, EtOH)}

IR (film): 3356br, 2917s, 1453s, 1377s, 1030s, 910s.

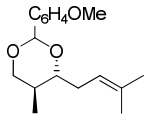
^{1}H NMR (500 MHz): 5.17 (1H, td, J_1 7, J_2 1, C=C*H*), 3.75-3.62 (2H, m, CH_2OH), 3.56-3.52 (1H, m, C*H*OH), 3.07 (1H, br. s., CH_2O*H*), 2.45 (1H, br. s, CHO*H*), 2.30-2.18 (2H, m, CH_2CHOH), 1.79-1.73 (4H, m, C*H*CH_3, CH_3), 1.66 (3H, s, CH_3), 0.90 (3H, d, *J* 7, CH_3CH).

^{13}C NMR (125 MHz): 136.2 (*C*=CH), 119.5 (C=*C*H), 77.1 (*C*HOH), 67.8 (*C*H_2OH), 39.7 (*C*HCH$_3$), 34.3 (*C*H_2CHOH), 26.0 (*C*H_3), 18.0 (*C*H_3), 13.9 (*C*H_3CH).

MS (CI^+): 157(5), 159(100), 160(18), 161(3).

HRMS *m/z* ($M+H^+$) found 159.1379, $C_9H_{19}O_2$ requires 159.1380.

(4*R*,5*S*)-2-(4-Methoxyphenyl)-5-methyl-4-(3-methylbut-2-en-1-yl)-1,3-dioxane (21).



To a solution of diol **20** (1.58 g, 10 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added *p*-anisaldehyde dimethylacetal (2.00 g, 11 mmol) followed by camphorsulfonic acid (116 mg, 0.05 mmol). The resulting solution was warmed to rt and stirred for 5 h, then diluted with Et_2O (100 mL) and washed with sat. aq NH_4Cl (50 mL). The aquous phase was extracted with Et_2O (2 x 30 mL), the combined organic layers were dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (10% Et_2O/petrol) to give acetal **21** (2.63 g, 95%) as a colorless oil; R*f* 0.33 (10% Et_2O/petrol).

$[\alpha]_D^{23}$ = +17.2 (*c* 0.7, $CHCl_3$)

IR(film): 2957s, 2836s, 2032w, 1896w, 1698m, 1614s, 1517s.

^{1}H NMR (400 MHz): 7.43 (2H, d, *J* 9, *o*-ArC*H*), 6.90 (2H, d, *J* 9, *m*-ArC*H*), 5.45 (1H, s, C*H*Ar), 5.39-5.30 (1H, m, C=C*H*), 4.09 (1H, dd, J_1 11, J_2 5, CH_2O), 3.82 (3H, s, OCH_3), 3.46 (3H, m, CH_2O, C*H*O),

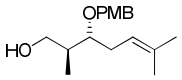
2.57-2.20 (2H, m, CH_2CH=C), 1.91 (1H, m, CHCH$_3$), 1.74 (3H, s, CH_3), 1.65 (3H, s, CH_3), 0.80 (3H, d, *J* 7, CH_3CH).

^{13}C NMR (100 MHz): 160.3 (*p*-Ar*C*), 133.5 (*C*=CH), 131.9 (Ar*C*), 127.8 (*o*-*C*HAr), 120.6 (C=*C*H), 114.0 (m-Ar*C*H), 101.5 (*C*HAr), 83.7 (*C*HO), 73.5 (*C*H$_2$O), 55.8 (O*C*H$_3$), 33.9 (*C*HCH$_3$), 32.0 (*C*H$_2$CH=C), 26.3 (*C*H$_3$), 18.4 (*C*H$_3$), 13.0 (*C*H$_3$CH).

MS (CI$^+$) 275(6), 276(2), 277(100), 278(19), 279(4).

HRMS *m/z* (M–H$^+$) found 275.1647, $C_{17}H_{23}O_3$ requires 275.1647.

(2*S*,3*R*)-3-((4-Methoxybenzyl)oxy)-2,6-dimethylhept-5-en-1-ol (22)



To a solution of acetal **21** (2.21 g, 8 mmol) in CH_2Cl_2 was added DIBALH (20 mL, 1 M in hexanes, 20 mmol,) at -78 ^{o}C. After stirring for 12 h at 0 ^{o}C, the reaction mixture was allowed to reach rt, then quenched with MeOH (10 mL) at 0 ^{o}C and sat. aq solution of potassium sodium tartarate (10 mL) and Et_2O (30 mL) was added. The mixture was warmed to rt and stirred vigorously until the white slurry completely dissolved. The aqueous layer was then extracted with Et_2O (2 x 30 mL), the combined organic layers dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (40% Et_2O/petrol) to give alcohol **22** (1.97 g, 88%) as a colorless oil; R*f* 0.41 (40% Et_2O/petrol).

$[\alpha]_D^{23}$ = -50.5 (*c* 2.5, $CHCl_3$)

IR(film): 3435br, 2963s, 2915s, 2060w, 1883w, 1672m, 1513s, 1248s.

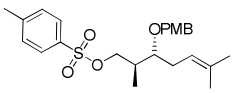
^{1}H NMR (500 MHz): 7.26 (2H, d, *J* 9, *o*-ArC*H*), 6.88 (2H, d, *J* 9, *m*-ArC*H*), 5.21 (1H, t, *J* 7, C=C*H*), 4.60 (1H, d, *J* 11, CH_2Ar), 4.37 (1H, d, *J* 11, CH_2Ar), 3.81 (3H, s, OCH_3), 3.68 (1H, ddd, J_1 11, J_2 7, J_3 3, 1H of CH_2OH), 3.55 (1H, ddd, J_1 11, J_2 6, J_3, 5, 1H of CH_2OH), 3.41 (1H, m, C*H*O), 2.88 (1H, dd, J_1 7, J_2 5, O*H*), 2.44-2.29 (2H, m, CH_2CH=C), 1.86 (1H, qd, J_1 7, J_2 3, CHCH$_3$), 1.73 (3H, s, CH_3), 1.65 (3H, s, CH_3), 0.92 (3H, d, *J* 7, CHCH_3).

^{13}C NMR (125 MHz): 133.5 (*p*-Ar*C*), 133.5 (*C*=CH), 130.3 (Ar*C*), 129.5 (*o*-Ar*C*H), 119.6 (C=*C*H), 113.9 (*m*-Ar*C*H), 84.1 (*C*HO), 71.4 (*C*H$_2$Ar), 66.7 (*C*H$_2$OH), 55.3 (*C*H$_3$O), 37.9 (*C*HCH$_3$), 29.7 (*C*H$_2$CH=C), 25.9 (*C*H$_3$), 18.0 (*C*H$_3$), 14.4 (CH*C*H$_3$).

MS (CI$^+$) 277(21), 278(6), 279(100), 280(19), 281(3), 296(3).

HRMS *m/z* (M+NH$_4^+$) found 296.2224, $C_{17}H_{30}NO_3$ requires 296.2226.

(2*S*,3*R*)-3-((4-Methoxybenzyl)oxy)-2,6-dimethylhept-5-en-1-yl 4-methylbenzenesulfonate



To a solution of TsCl (1.95 g, 10.23 mmol), DMAP (59 mg, 0.07 mmol) and Et_3N (1.72 g, 17.00 mmol) in CH_2Cl_2 (30 mL) at 0 ^{o}C was added a solution of alcohol **22** (1.90 g, 6.82 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was warmed to rt, stirred for 3 h, diluted with brine (30 mL), extracted with CH_2Cl_2 (2 x 30 mL), dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (20% Et_2O/petrol) to give (2*S*,3*R*)-3-((4-methoxybenzyl)oxy)-2,6-dimethylhept-5-en-1-yl 4-methylbenzenesulfonate (2.72 g, 92%) as a colorless oil; R*f* 0.31 (20% Et_2O/petrol).

$[\alpha]_D^{23}$ = -21.0 (*c* 4.4, $CHCl_3$)

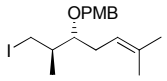
IR(film): 3033s, 2968s, 2932s, 1612s, 1598s, 1513s, 1359s, 1211s.

^{1}H NMR (500 MHz): 7.78 (2H, d, *J* 8, *o*-ArC*H*), 7.31 (2H, d, *J* 8, *m*-ArC*H*), 7.15 (2H, d, *J* 9, *o*-ArC*H*), 6.85 (2H, d, *J* 9, *m*-ArC*H*), 5.14 (1H, t, *J* 7, C*H*=C), 4.46 (1H, d, *J* 11, CH_2Ar), 4.25 (1H, d, *J* 11, CH_2Ar), 4.08 (2H, d, *J* 5, CH_2OSO$_2$), 3.79 (3H, s, OCH_3), 3.34-3.30 (1H, m, C*H*OPMB), 2.42 (3H, s, CH_3Ar), 2.31-2.15 (2H, m, CH_2CH=C), 2.01-1.96 (1H, m, C*H*CH$_3$), 1.70 (3H, s, CH_3), 1.60 (3H, s, CH_3), 0.93 (3H, d, *J* 7, CHCH_3).

^{13}C NMR (125 MHz): 159.1 (Ar*C*), 144.6 (CH$_3$Ar*C*), 133.6 (*C*=CH), 133.1 (Ar*C*), 130.6 (Ar*C*), 129.8 (*m*-Ar*C*H), 129.4 (*o*-Ar*C*H), 127.9 (*o*-Ar*C*H), 119.4 (C=*C*H), 113.7 (*m*-Ar*C*H), 79.2 (*C*HOPMB), 72.8 (*C*H$_2$OSO$_2$), 71.4 (*C*H$_2$Ar), 55.2 (*C*H$_3$O), 36.4 (*C*HCH$_3$), 29.1 (*C*H$_2$CH=C), 25.9 (*C*H$_3$), 21.6 (*C*H$_3$Ar), 18.0 (*C*H$_3$), 13.7 (CH*C*H$_3$).

HRMS *m/z* (M$^-$H$^+$) found 432.1973, $C_{24}H_{32}SO_5$ requires 432.1970.

1-((((2*R*,3*R*)-1-Iodo-2,6-dimethylhept-5-en-3-yl)oxy)methyl)-4-methoxybenzene (23)



To a solution of (2*S*,3*R*)-3-((4-methoxybenzyl)oxy)-2,6-dimethylhept-5-en-1-yl-4-methyl benzenesulfonate (2.10 g, 4.85 mmol) in anhydrous acetone (50 mL) was added anhydrous NaI (2.18 g, 14.55 mmol). The resulting mixture was refluxed for 5 h in the dark. The reaction mixture was allowed to cool to rt and then petrol (100 mL) was added. The precipitates were filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and purified by chromatography (10% Et$_2$O/petrol) to give iodide **23** (1.79 g, 95%) as a colorless oil; R*f* 0.25 (10% Et$_2$O/petrol).

$[\alpha]_D^{23}$ = -43.0 (*c* 4.8, CHCl$_3$)

IR(film): 2964s, 2931s, 2911s, 2872s, 2062w, 1881w, 1586m, 1506s, 1248s.

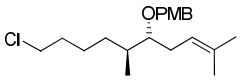
^{1}H NMR (500 MHz): 7.28 (2H, d, *J* 9, ArC*H*), 6.89 (2H, d, *J* 9, ArC*H*), 5.24-5.21 (1H, m, C*H*=C), 4.56 (1H, d, *J* 11, CH_2Ar), 4.42 (1H, d, *J* 11, CH_2Ar), 3.81 (3H, s, OCH_3), 3.45 (1H, dd, J_1 9, J_2 6, CH_2I), 3.34 (1H, dd, J_1 9, J_2 3, C*H*2I), 3.30 (1H, dt, J_1 7, J_2 5, C*H*OPMB), 2.41-2.21 (2H, m, CH_2CH=C), 1.73 (3H, s, CH_3), 1.65 (3H, s, CH_3), 1.64-1.58 (1H, m, C*H*CH$_3$), 0.97 (3H, d, J 7, CHCH_3).

^{13}C NMR (125 MHz): 159.2 (MeOAr*C*), 133.5 (*C*=CH), 130.7 (Ar*C*), 129.6 (Ar*C*H), 119.7 (C=*C*H), 113.8 (Ar*C*H), 81.6 (*C*HOPMB), 71.7 (*C*H$_2$Ar), 55.3 (O*C*H$_3$), 37.8 (*C*HCH$_3$), 28.7 (*C*H$_2$CH=C), 25.9 (*C*H$_3$), 18.0 (*C*H$_3$), 17.4 (CH*C*H$_3$), 15.9 (*C*H$_2$I).

MS (CI$^+$) 386(38), 388(100), 389(50), 390(63), 391(50).

HRMS *m/z* (M+NH$_4^+$) found 389.1218, $C_{17}H_{28}NOI$ requires 389.1216.

1-((((5*R*,6*S*)-10-Chloro-2,6-dimethyldec-2-en-5-yl)oxy)methyl)-4-methoxybenzene (24)



To a solution of iodide **23** (194 mg, 0.5 mmol) in Et$_2$O (5 mL) at -78 ^{o}C was added dropwise *t*-BuLi (0.65 mL, 1.6 M in hexanes, 1 mmol). After 10 min, the reaction mixture was warmed to rt and left to stand for 30 min. The mixture was cooled to -35 ^{o}C and transferred to a suspension of CuI (50 mg, 0.26 mmol) in THF (5 mL) at -35 ^{o}C. The reaction mixture was allowed to warm to -10 ^{o}C over 30 min and then cooled to -35 ^{o}C. 1-Chloro-3-iodopropane (153 mg, 0.75 mmol) was added dropwise and the reaction stirred for

1.5 h, then allowed to warm to rt over 2 h, then stirred overnight. The reaction was quenched with sat. aq NH_4Cl (10 mL). The aqueous phase was extracted with Et_2O (2 x 30 mL), and the combined organic layers were dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (5% Et_2O/petrol) to give chloride **24** (125 mg, 74%) as a colorless oil; R*f* 0.37 (5% Et_2O/petrol).

$[\alpha]_D^{23} = -4.5$ (*c* 0.8, $CHCl_3$)

IR(film): 2932 s, 1612m, 1513s, 1463m, 1247s.

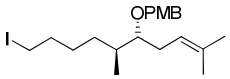
^{1}H NMR (500 MHz): 7.26 (2H, d, *J* 9, ArC*H*), 6.88 (2H, d, *J* 9, ArC*H*), 5.19 (1H, t, *J* 7, C*H*=C), 4.50-4.40 (2H, m, CH_2Ar), 3.81 (3H, s, OCH_3), 3.53 (2H, t, *J* 7, CH_2Cl), 3.21 (1H, q, *J* 5, C*H*OPMB), 2.23-2.20 (2H, m, CH_2CH=C),1.79-1.68 (4H, m, CH_3, C*H*CH_3), 1.63 (3H, s, CH_3), 1.54-1.47 (2H, m, CH_2), 1.37-1.13 (4H, m, 2xCH_2), 0.90 (3H, d, *J* 7, CHCH_3).

^{13}C NMR (125 MHz): 159.0 (CH_3OAr*C*), 132.6 (*C*=CH), 131.2 (Ar*C*), 129.3 (Ar*C*H), 121.1 (C=*C*H), 113.7 (Ar*C*H), 82.9 (*C*HOPMB), 71.3 (*C*H_2Ar), 55.3 (O*C*H_3), 45.1 (*C*H_2Cl), 35.7 (*C*HCH_3), 32.9 (*C*H_2CH=C), 31.5 (*C*H_2), 29.0 (*C*H_2CH_2Cl), 25.9 (*C*H_2), 24.6 (*C*H_3), 18.0 (*C*H_3), 15.4 (CH*C*H_3).

MS (CI^+) 337(3), 338(31), 339(100), 340(29), 341(33), 342(6), 357(2).

HRMS *m/z* ($M+NH_4^+$) found 357.2432, $C_{20}H_{36}NO_2Cl$ requires 357.2435.

1-((((5*R*,6*S*)-10-Iodo-2,6-dimethyldec-2-en-5-yl)oxy)methyl)-4-methoxybenzene



To stirred solution of chloride **24** (1.30 g, 3.84 mmol) in 3-pentanone (50 mL) was added NaI (2.31 g, 15.40 mmol). The reaction mixture was heated at reflux for 24 h in the dark. The mixture was allowed to cool to rt then partitioned between water (100 mL) and Et_2O (100 mL). The ether layer was washed with brine (50 mL), dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (5% Et_2O/petrol) to give the title iodide (1.65 g, 98%) as a colorless oil; Rf 0.39 (5% Et_2O/petrol).

$[\alpha]_D^{25} = -11.9$ (*c* 3.4, $CHCl_3$)

IR(film): 2957s, 2932s, 2859s, 1612m, 1513s, 1301s.

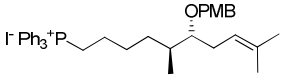
^{1}H NMR (500 MHz): 7.26 (2H, d, *J* 9, ArC*H*), 6.88 (2H, d, *J* 9, ArC*H*), 5.19 (1H, t, *J* 7, C=C*H*), 4.50-4.40 (2H, m, CH_2Ar), 3.81 (3H, s, OCH_3), 3.22-3.17 (3H, m, C*H*OPMB, CH_2I), 2.22-2.20 (2H, m, CH_2CH=C), 1.84-1.77 (2H, m, CH_2), 1.72-1.67 (4H, m, CH_3, C*H*CH_3), 1.63 (3H, s, CH_3), 1.51-1.44 (2H, m, CH_2), 1.34-1.12 (2H, m, CH_2), 0.89 (3H, d, *J* 7, CHCH_3).

^{13}C NMR (125 MHz): 159.0 (CH_3OAr*C*), 132.7 (*C*=CH), 131.2 (Ar*C*), 129.3 (Ar*C*H), 121.0 (C=*C*H), 113.7 (Ar*C*H), 82.9 (*C*HOPMB), 71.3 (*C*H_2Ar). 55.3 (O*C*H_3), 35.6 (*C*HCH_3), 33.8 (*C*H_2CH=C), 31.1 (*C*H_2), 29.0 (*C*H_2), 28.3 (*C*H_3), 18.0 (*C*H_3), 15.5 (CH*C*H_3), 7.3 (*C*H_2I).

MS (CI^+) 430(100), 431(21), 432(4).

HRMS *m/z* ($M+H^+$) found 431.1433, $C_{20}H_{32}IO_2$ requires 431.1447.

((5*S*,6*R*)-6-((4-Methoxybenzyl)oxy)-5,9-dimethyldec-8-en-1-yl)triphenylphosphonium iodide (14)



A stirred solution of 1-((((5*R*,6*S*)-10-iodo-2,6-dimethyldec-2-en-5-yl)oxy)methyl)-4-methoxybenzene

(1.28 g, 2.97 mmol) and PPh_3 (858 mg, 3.27 mmol) in toluene (20 mL) was refluxed for 14 h in the dark. The mixture was then cooled to rt and petrol (100 mL) was added. The solvent was decanted and the glassy solid was washed with petrol and Et_2O. The residue was dried under reduced pressure overnight to give phosphonium salt **14** (2.01 g, 97%) as a colorless glassy solid,

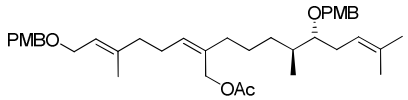
IR(film): 2965s, 2935s, 2875s, 2210s, 1613s.

^{1}H NMR (500 MHz): 7.80-7.67 (15H, m, ArC*H*), 7.19 (2H, d, *J* 8, ArC*H*), 6.78 (2H, d, *J* 8, ArC*H*), 5.13 (1H, t, *J* 7, C=C*H*), 4.44-4.32 (2H, m, CH_2Ar), 3.74 (3H, s, OCH_3), 3.57 (2H, m, CH_2P^+), 3.13 (1H, q, *J* 5, C*H*OPMB), 2.15 (1H, brs, 1H of CH_2CH=C), 1.79-1.44 (12H, m, CH_2x2, CH_3x2, C*H*CH_3, 1H of CH_2), 1.13-1.07 (1H, m, 1H of CH_2), 0.82 (3H, d, *J* 7, CHCH_3).

^{13}C NMR (125 MHz): 158.9 (CH_3OAr*C*), 135.1 (Ar*C*H), 133.6 (Ar*C*H), 132.7 (*C*=CH), 131.2 (Ar*C*), 130.6 (Ar*C*H), 129.4 (Ar*C*H), 120.8 (C=*C*H), 118.4 (Ar*C*), 117.7 (Ar*C*), 113.6 (Ar*C*H), 83.0 (*C*HOPMB), 71.3 (*C*H_2Ar), 55.3 (O*C*H_3), 35.5 (*C*HCH_3), 31.6 (*C*H_2CH=C), 29.0 (*C*H_2), 28.1 (*C*H_2P+), 25.9 (*C*H_3), 23.0 (*C*$H_2CH_2P^+$), 22.8 (*C*H_2), 18.0 (*C*H_3), 15.6 (CH*C*H_3).

HRMS *m/z* ($M+Na^+$) found 588.3133, $C_{38}H_{46}NaO_2P$ requires 588.3128.

(6*S*,7*R*,*Z*)-7-((4-Methoxybenzyl)oxy)-2-((*E*)-6-((4-methoxybenzyl)oxy)-4-methylhex-4-en-1-ylidene)-6,10-dimethylundec-9-en-1-yl acetate (25)



A solution of anhydrous LiBr (44 mg, 0.5 mmol, 2 equiv, obtained by heating LiBr under argon until it melted, followed by cooling) in THF (5 mL) was added to anhydrous phosphonium salt **14** (173 mg, 0.25 mmol) and stirred at rt for 10 min before cooling to –78 ^{o}C. PhLi (0.12 ml, 0.25 mmol, 2.0 M in Bu_2O) was then added dropwise at –78 ^{o}C, The reaction mixture was stirred for 30 min at –78 ^{o}C and a solution of aldehyde **13** (62 mg, 0.25 mmol) in THF (1 mL) was added dropwise. After 10 min, when complete decolorization had occurred, PhLi (0.14 mL, 0.27 mmol, 2.0 M in Bu_2O) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at –78 ^{o}C, then allowed to reach rt over 15 min, then the resulting β-lithiooxy ylide was re-cooled to –78 ^{o}C and to it was added dropwise a solution of bromomethyl acetate (42 mg, 0.27 mmol) in THF (1 mL) at –78 ^{o}C. After 30 min at –78 ^{o}C, the temperature was slowly raised to rt over 30 min and the reaction mixture stirred for a further 2 h at rt. The reaction mixture was then poured into water (10 mL), extracted with Et_2O (3 x 15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (30% Et_2O/petrol) gave *Z*-allylic ester **25** (95 mg, 63%) as a colorless oil; *Rf* 0.37 (30% Et_2O/petrol);

$[\alpha]_D^{18} = -3.2$ (*c* 0.9, $CHCl_3$)

IR (film): 3155w, 2935m, 2859m, 2253s, 1730m, 1612w, 1513s, 1247s.

^{1}H NMR (500 MHz): 7.28-7.25 (4H, m, ArC*H* x 4), 6.89-6.86 (4H, m, ArC*H* x 4), 5.41-5.39 (2H, m, C*H*=CCH_2OAc, PMBOCH_2C*H*=C), 5.19 (1H, t, *J* 7, C=C*H*), 4.58 (2H, s, CH_2OAc), 4.48-4.41 (4H, m, CH_2OAr x 2), 3.99 (2H, d, *J* 7, CH_2OPMB), 3.81-3.80 (6H, m, OCH_3 x 2), 3.20 (1H, q, *J* 6, C*H*OPMB), 2.25-2.01 (11H, m, CH_2 x 4, CH_3C=O), 1.81-1.68 (4H, m, C*H*CH_3, CH_3), 1.65 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.50-1.42 (2H, m, CH_2), 1.34-1.10 (2H, m, CH_2CHMe), 0.89 (3H, d, *J* 7, CHCH_3).

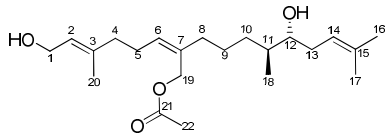
^{13}C NMR (125 MHz): 171.1 (CH_3*C*=O), 159.1 (CH_3OAr*C*), 159.0 (CH_3OAr*C*), 139.5 (*C*=CHCH_2OPMB), 134.1 (Me_2*C*=CH), 132.5 (AcOCH_2*C*=CH), 131.3 (Ar*C*), 130.6 (Ar*C*), 130.2

(AcOCH$_2$*C*=CH), 129.4 (Ar*C*H), 129.3 (Ar*C*H), 121.4 (Me$_2$C=*C*H), 121.3 (C=*C*H), 113.7 (Ar*C*H), 113.6 (Ar*C*H), 83.1 (*C*HOPMB), 71.7 (*C*H$_2$OAr), 71.2 (*C*H$_2$OAr), 66.2 (*C*H$_2$OPMB), 61.9 (*C*H$_2$OAc), 55.3 (O*C*H$_3$ x 2), 39.6 (*C*H$_2$), 35.7 (*C*HCH$_3$), 35.6 (*C*H$_2$), 32.1 (*C*H$_2$), 28.9 (*C*H$_2$), 26.0 (*C*H$_2$), 25.9 (*C*H$_3$), 25.8 (*C*H$_2$), 21.0 (*C*H$_3$C=O), 17.9 (*C*H$_3$), 16.5 (*C*H$_3$), 15.3 (CH*C*H$_3$).

MS (CI$^+$) 629(100), 630(39), 631(8).

HRMS *m/z* (M+Na$^+$) found 629.3787, $C_{38}H_{54}NaO_6$ requires 629.3813.

(6*S*,7*R*,*Z*)-7-Hydroxy-2-((*E*)-6-hydroxy-4-methylhex-4-enylidene)-6,10-dimethylundec-9-enyl acetate (12)



To a stirred solution of PMB ether **25** (231 mg, 0.38 mmol) in CH_2Cl_2 (3.8 mL) and H_2O (0.23 mL) at rt was added DDQ (179 mg, 0.79 mmol). After the reaction was complete (TLC monitoring, 45-60 min), sat. aq $NaHCO_3$ (10 mL) was added and mixture was extracted with CH_2Cl_2 (3 x 15 mL), dried ($MgSO_4$), evaporated under reduced pressure and purified by chromatography (30% Et_2O/petrol) to afford diterpene **12**[5] (102 mg, 73%) *Rf* 0.15 (30% Et_2O/petrol);

IR (film): 3395br, 2926s, 1738m, 1659m, 1444s, 1377m.

$[\alpha]_D^{25} = -2.62$ (*c* 1.18, $CHCl_3$), {lit.[5] $[\alpha]_D^{20} = -2.3$ (*c* 0.15, $CHCl_3$)}

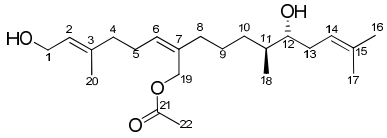
^{1}H NMR (500 MHz): 5.43-5.39 (2H, m, C-2, C-6), 5.18 (1H, t, *J* 7, C-14), 4.59 (2H, brs, C-19), 4.15 (2H, d, *J* 7, C-1), 3.42-3.39 (1H, m, C-12), 2.25 (2H, q, *J* 7, C-5), 2.18-2.01 (8H, m, C-4, C-8, C-9, C-13), 2.07 (3H, s, C-22), 1.75 (3H, s, C-16), 1.68 (3H, s, C-17), 1.66 (3H, s, C-20), 1.53-1.48 (1H, m, C-11), 1.18-1.10 (2H, m, C-10).

^{13}C NMR (125 MHz): 171.2 (C-21), 138.7 (C-3), 135.4 (C-15), 134.0 (C-7), 130.3 (C-6), 124.1 (C-2), 120.5 (C-14), 75.5 (C-12), 61.9 (C-19), 59.4 (C-1), 39.4 (C-4), 38.1 (C-11), 35.5 (C-8), 32.6 (C-13), 31.6 (C-10), 25.98 (C-5), 25.87 (C-16), 25.47 (C-9), 21.0 (C-22), 18.0 (C-17), 16.2 (C-20), 15.4 (C-18).

MS (CI$^+$) 389(100), 390(25), 391(5).

HRMS *m/z* (M+Na$^+$) found 389.2658, $C_{22}H_{38}NaO_4$ requires 389.2662.

6. Comparison of NMR data between Natural and Synthetic diterpene (12)



Comparison of NMR data of Natural[5] and synthetic diterpene (12)				
Atom #	**^{1}H NMR of Natural diterpene[5]** ($CDCl_3$)	**^{1}H NMR of synthetic diterpene** ($CDCl_3$)	**^{13}C NMR of Natural diterpene[5]** ($CDCl_3$)	**^{13}C NMR of synthetic diterpene** ($CDCl_3$)
1	4.13, d, *J* 7.2	4.15, d, *J* 7	58.5	59.4
2	5.40, brt, *J* 7.2	5.43-5.39, m	124.2	124.1
3	-	-	137.0	138.7
4	2.08, m	2.18-2.01, m	39.0	39.4
5	2.22, m	2.25, q, *J* 7	25.6	25.98
6	5.38, brt	5.43-5.39, m	129.9	130.3
7	-	-	133.6	134.0
8	2.00, m	2.18-2.01, m	35.1	35.5
9	1.30, m	2.18-2.01, m	25.2	25.47
10	1.13, m	1.18-1.10, m	31.0	31.6
11	1.55, m	1.53-1.48, m	37.6	38.1
12	3.40, dt, J_1 7.6, J_2 5.2	3.42-3.39, m	75.1	75.5
13	2.12, m	2.18-2.01, m	32.1	32.6
14	5.17, brt, *J* 7.2	5.18, t, *J* 7	120.6	120.5
15	-	-	135.6	135.4
16	1.74, brs	1.75, s	25.5	25.87
17	1.65, brs	1.68, s	17.5	18.0
18	0.90, d, *J* 6.8	0.91, d, *J* 7	15.1	15.4
19	4.57, brs	4.59, brs	61.5	61.9
20	1.64, brs	1.66, s	15.7	16.2
21	-	-	170.8	171.2
22	2.05, s	2.07, s	20.5	21.0

7. References

1 Borch, R. F.; Evans, A. J.; Wade, J. J. *J. Am. Chem. Soc*. **1977**, *99*, 1612−1619.

2 Shindo, T.; Fukuyama, Y.; Sugai, T. *Synthesis* **2004**, 692−700.

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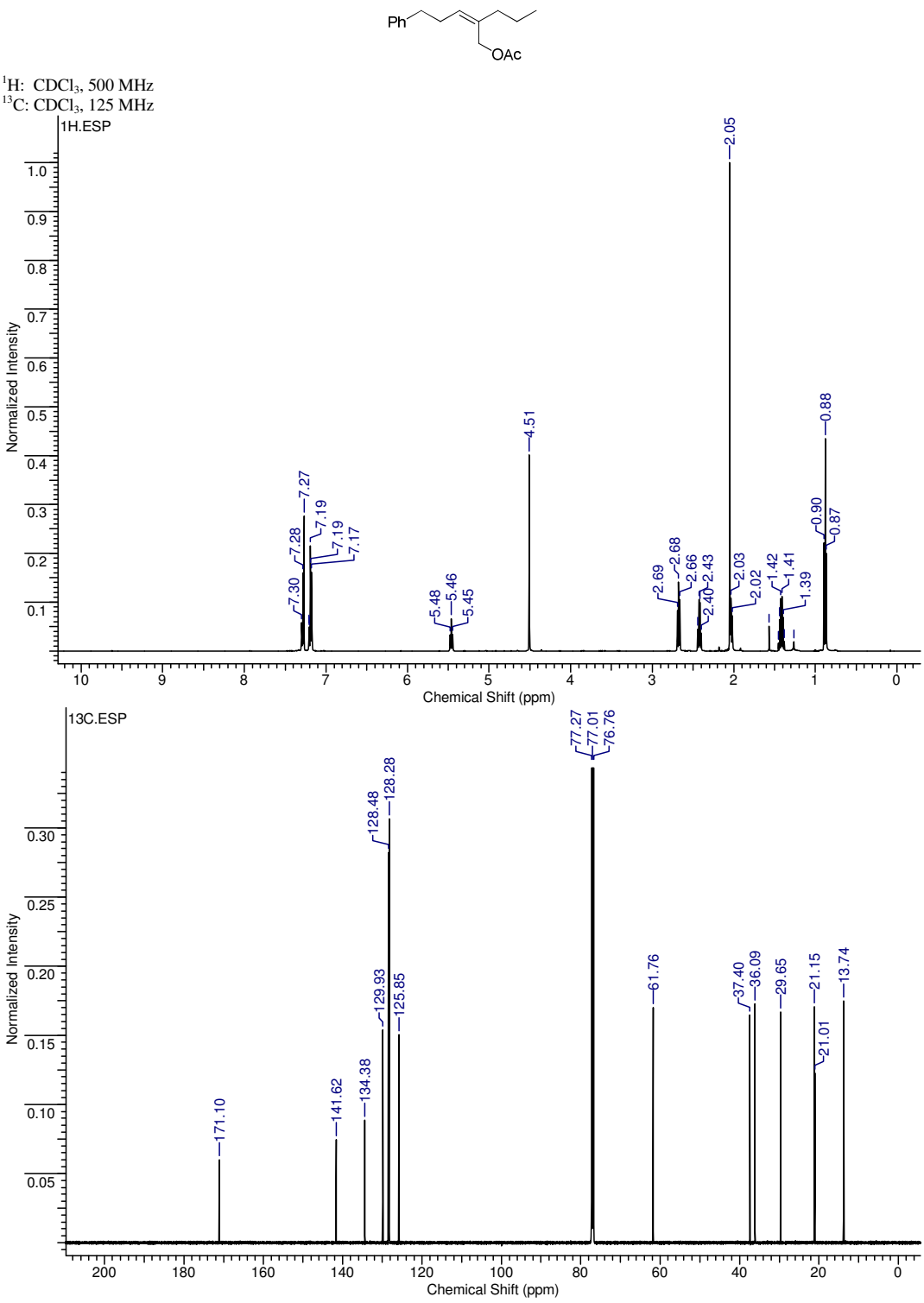
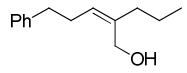
8. ^{1}H and ^{13}C NMR spectras of *Z*- allylic esters (entries 6a-6i, 7a-7e, 8a-8d, 9a-9c)

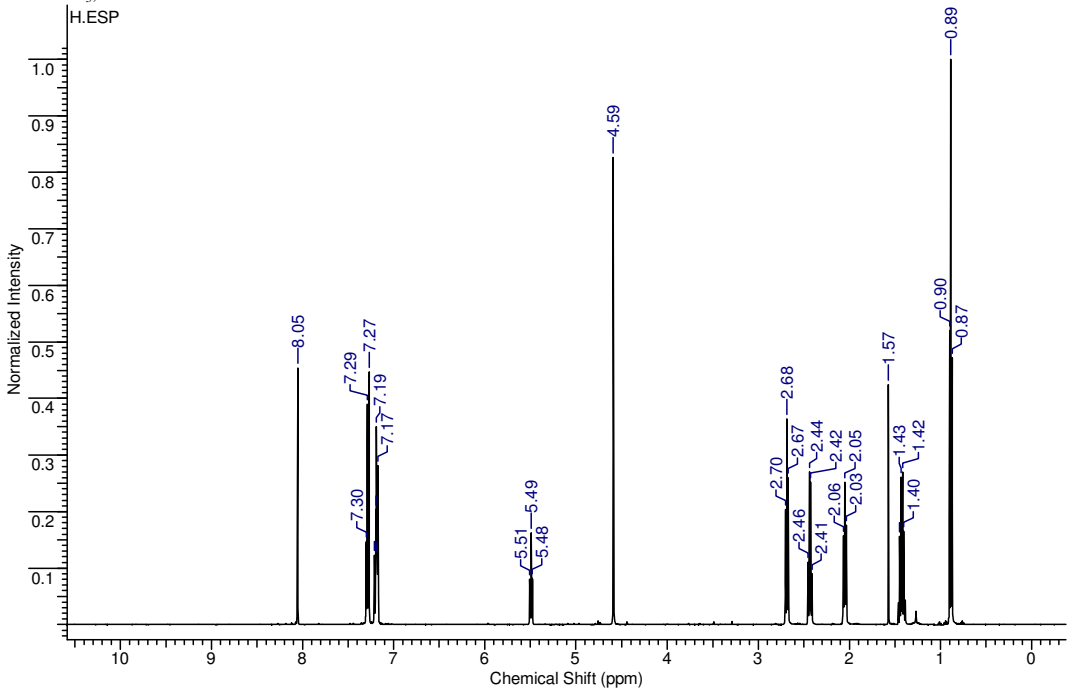
(*Z*)-5-Phenyl-2-propylpent-2-enyl acetate (6a)

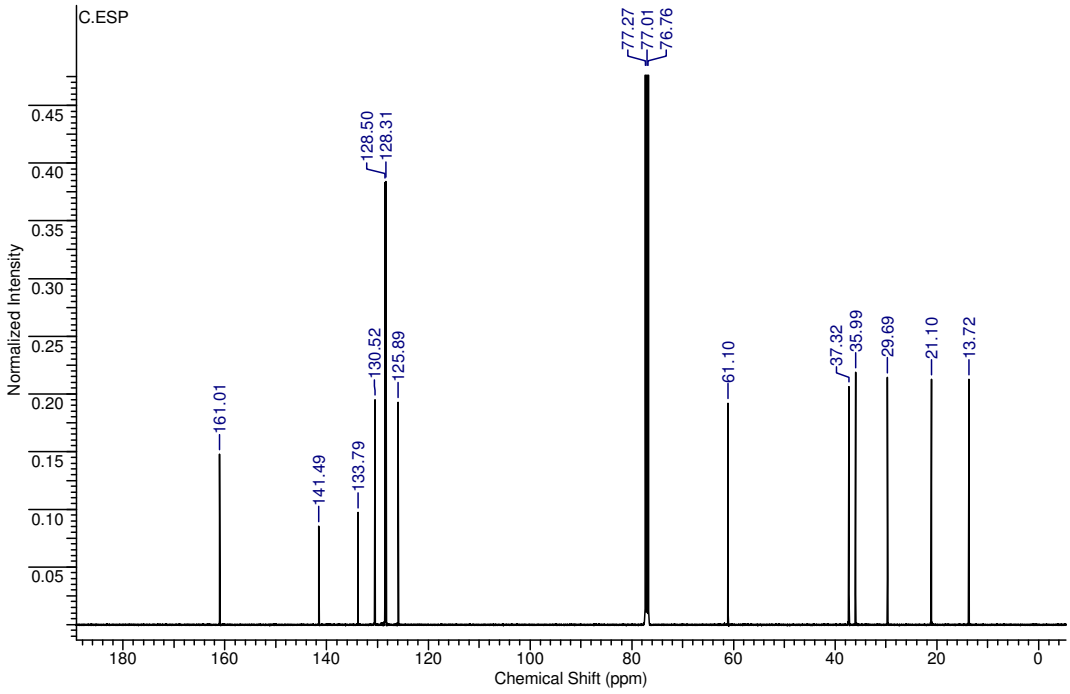


(*Z*)-5-Phenyl-2-propylpent-2-en-1-ol

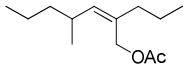


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz





(*Z*)-4-Methyl-2-propylhept-2-enyl acetate (6b)



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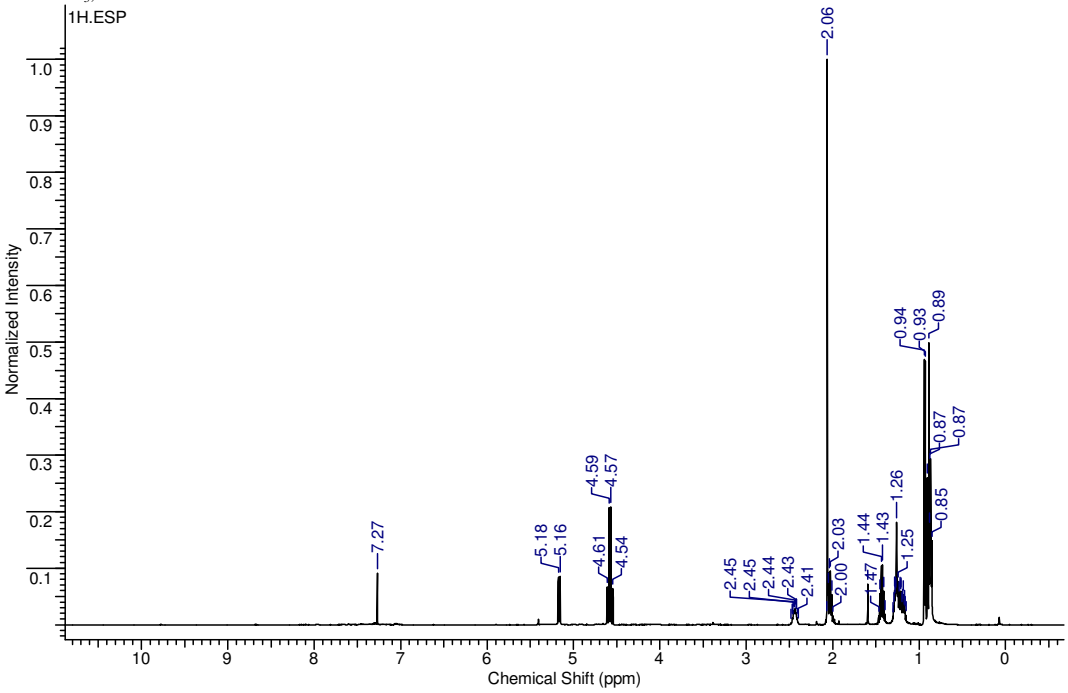
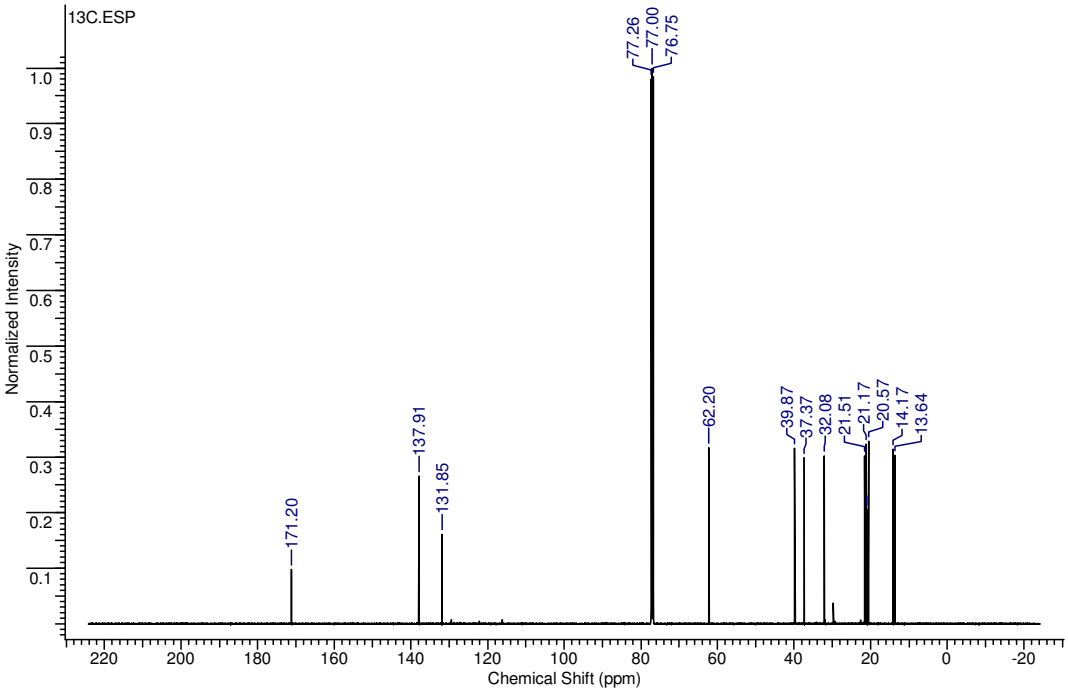
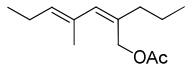
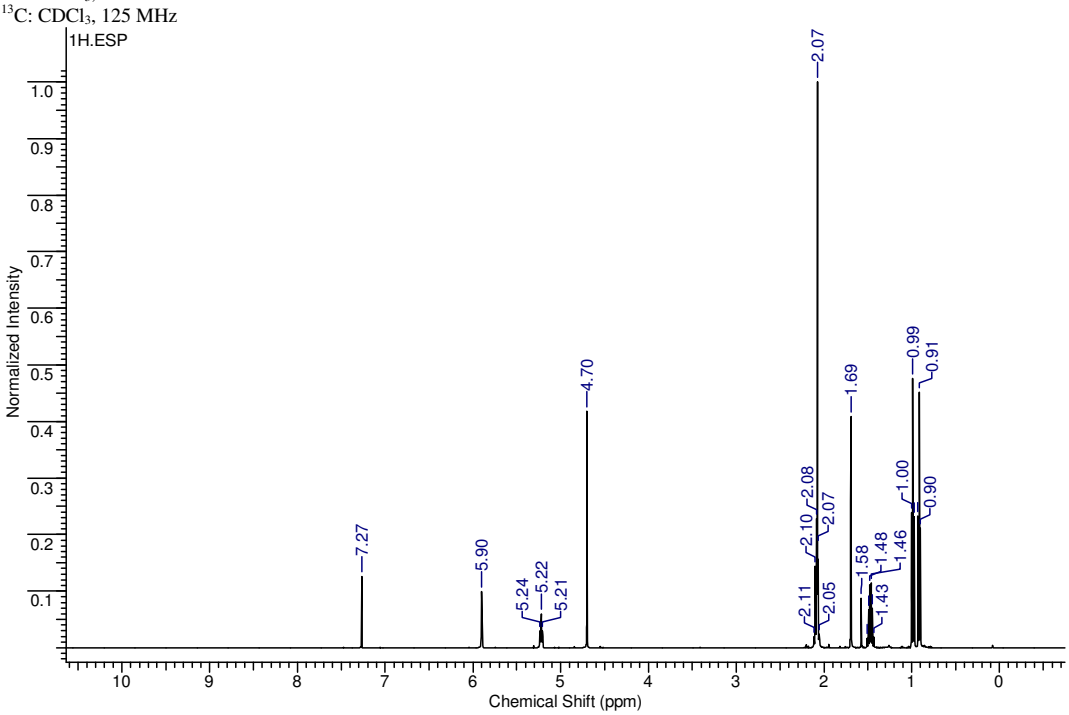


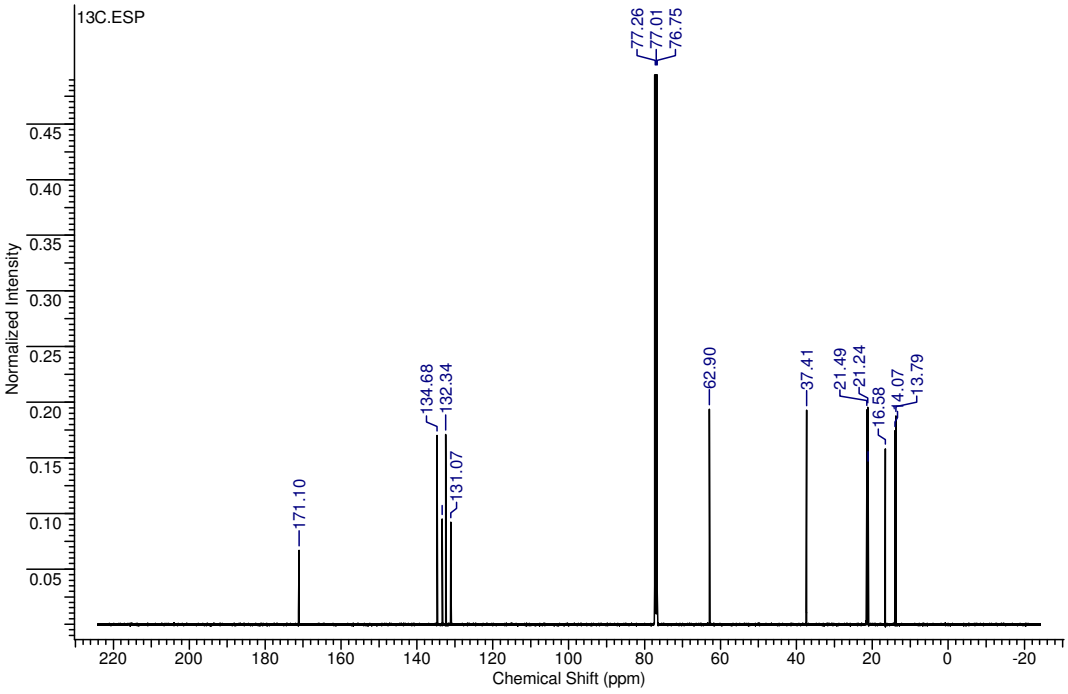


(2*Z*,4*E*)-4-Methyl-2-propylhepta-2,4-dienyl acetate (6c)

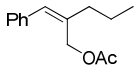


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

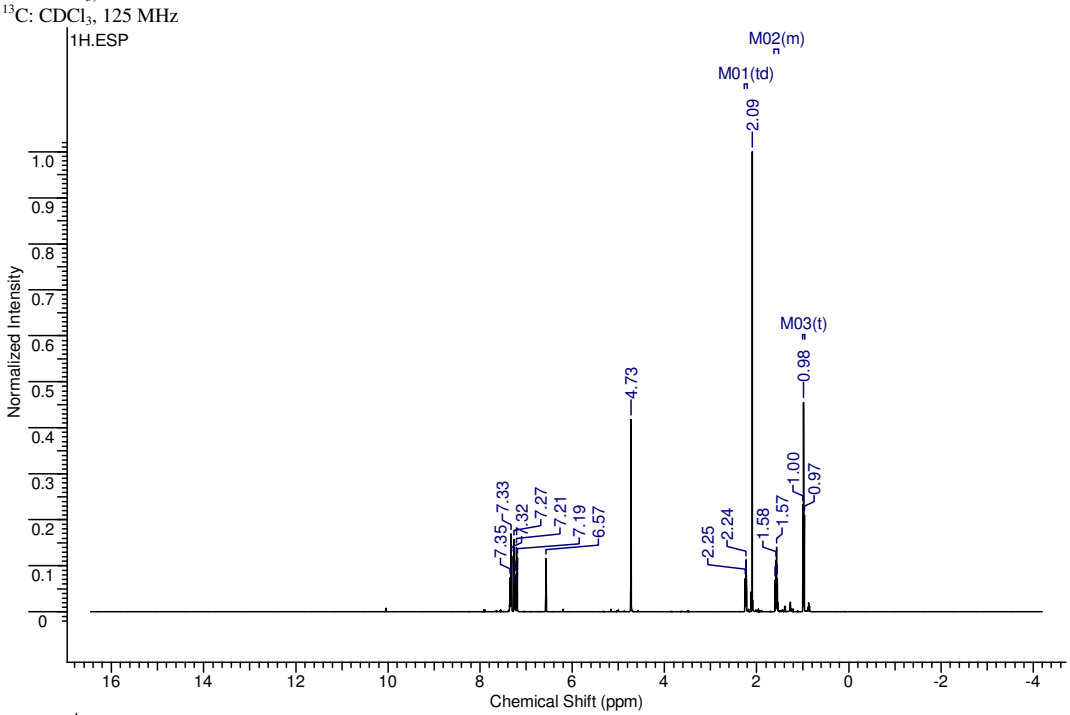


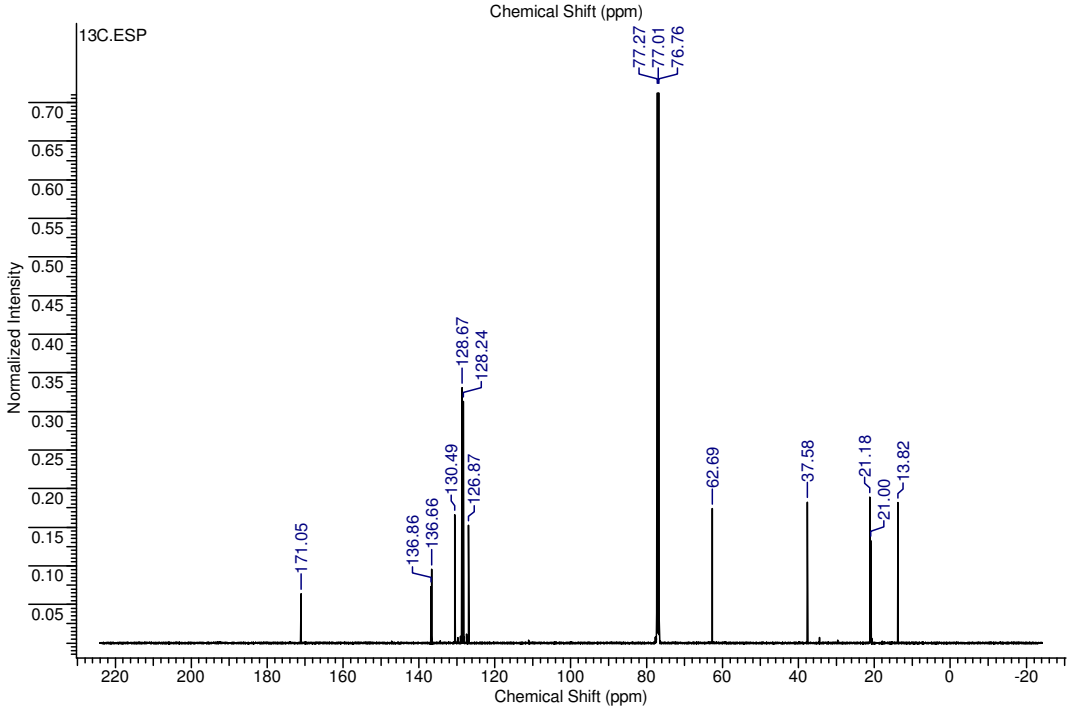


(*Z*)-2-Benzylidenepentyl acetate (6d)

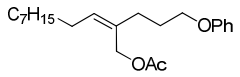


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz





(*Z*)-2-(3-Phenoxypropyl)undec-2-enyl acetate (6e)



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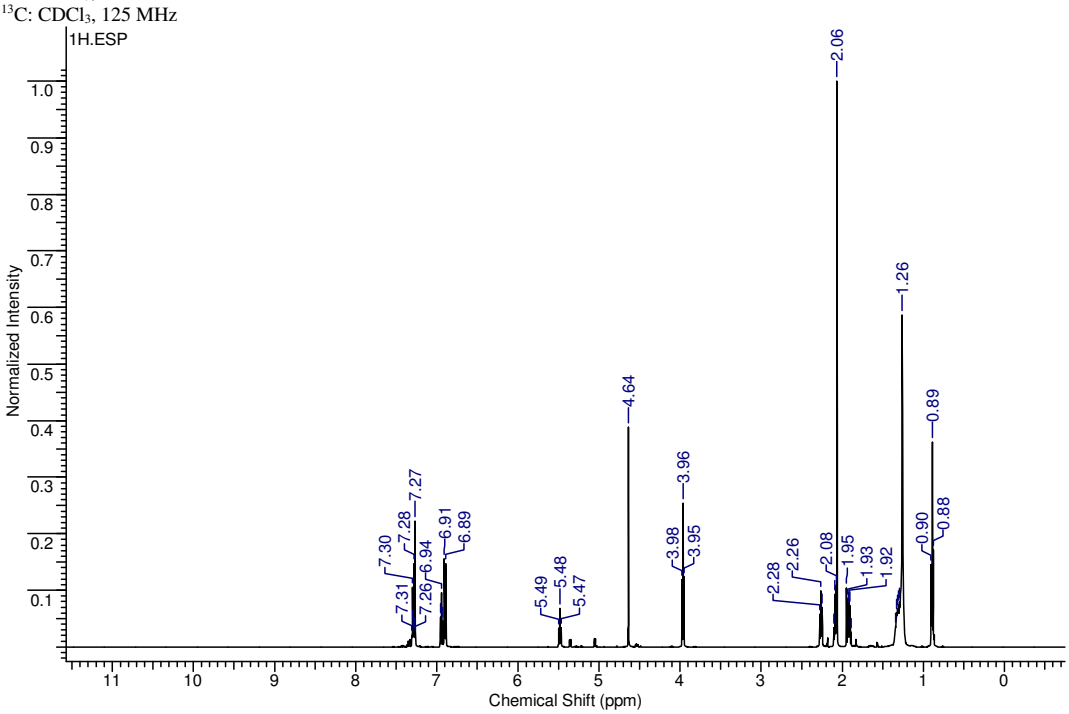
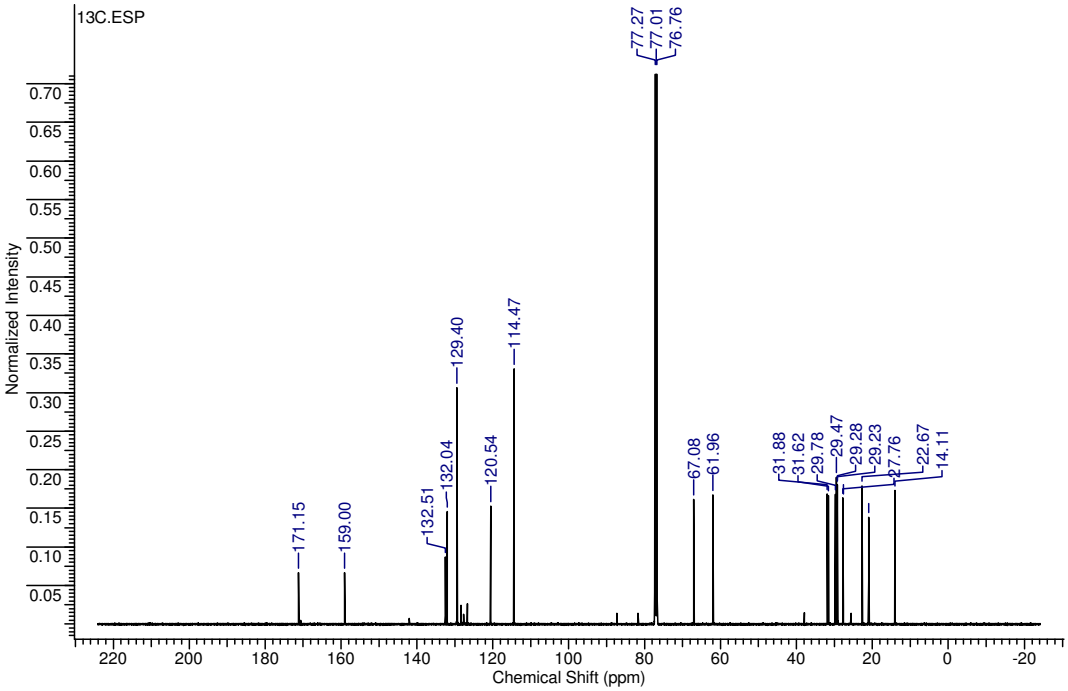
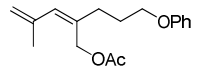
^{13}C: $CDCl_3$, 125 MHz





(*Z*)-4-Methyl-2-(3-phenoxypropyl)penta-2,4-dienyl acetate (6f)



^{1}H: $CDCl_3$, 500 MHz
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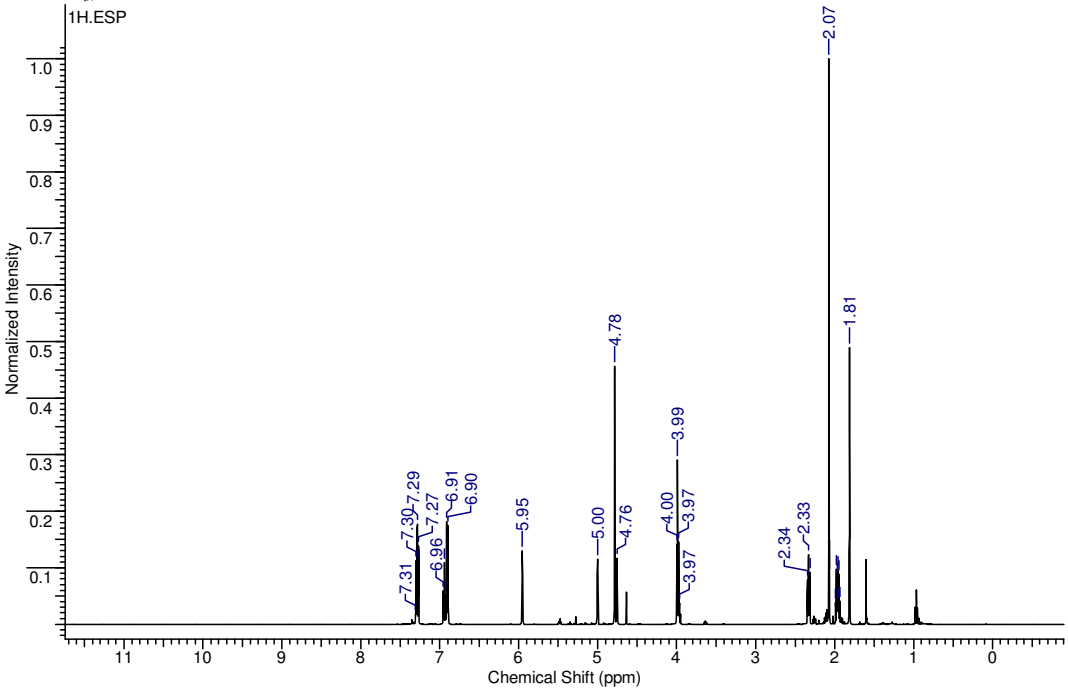
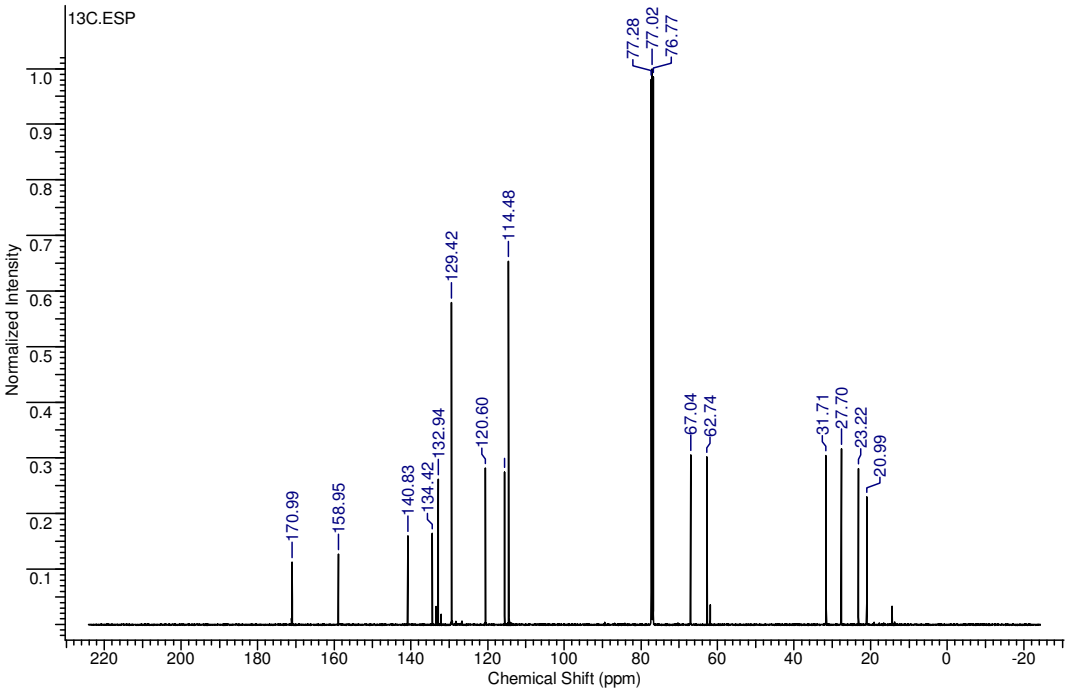
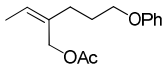
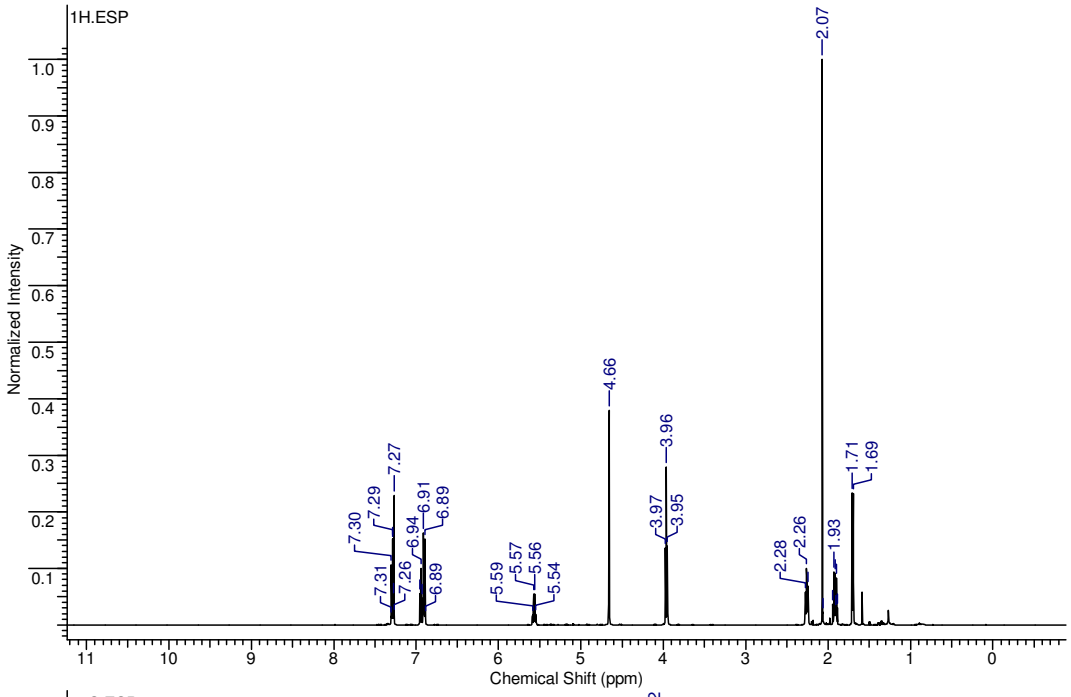


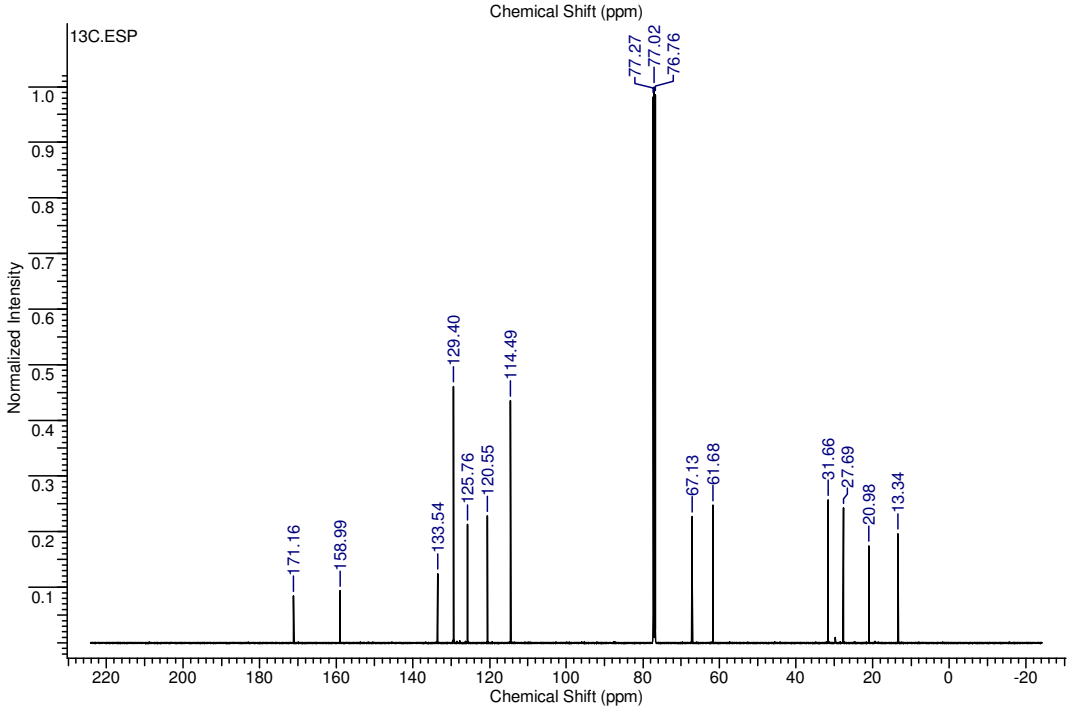


((Z)-2-Ethylidene-5-phenoxypentyl acetate (6g)

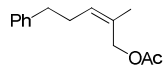


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

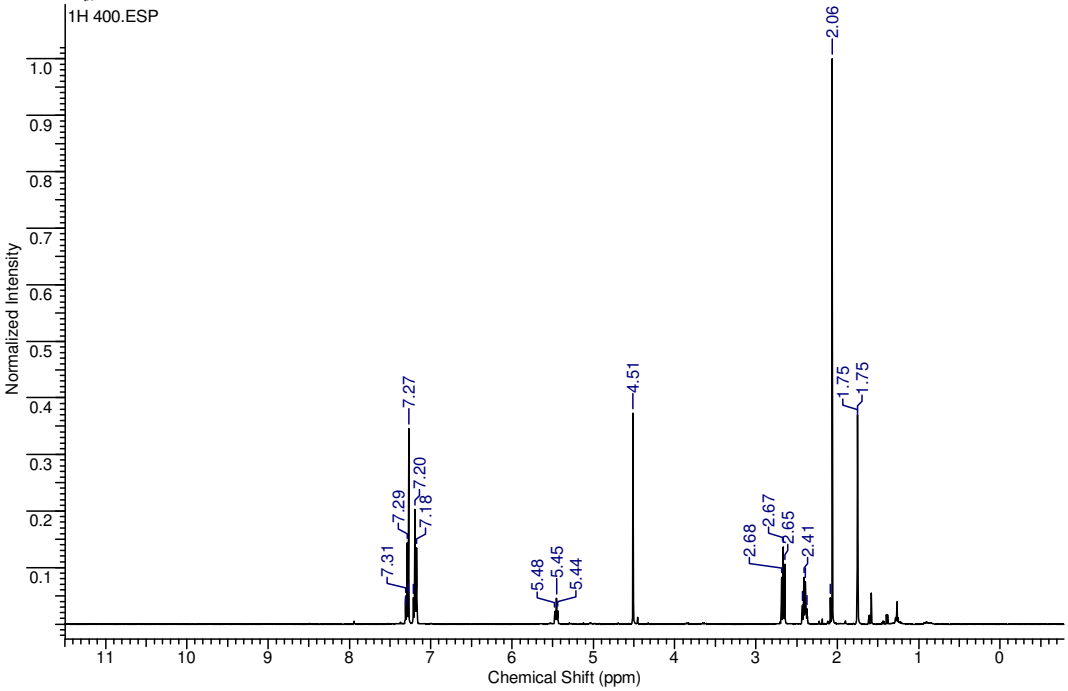


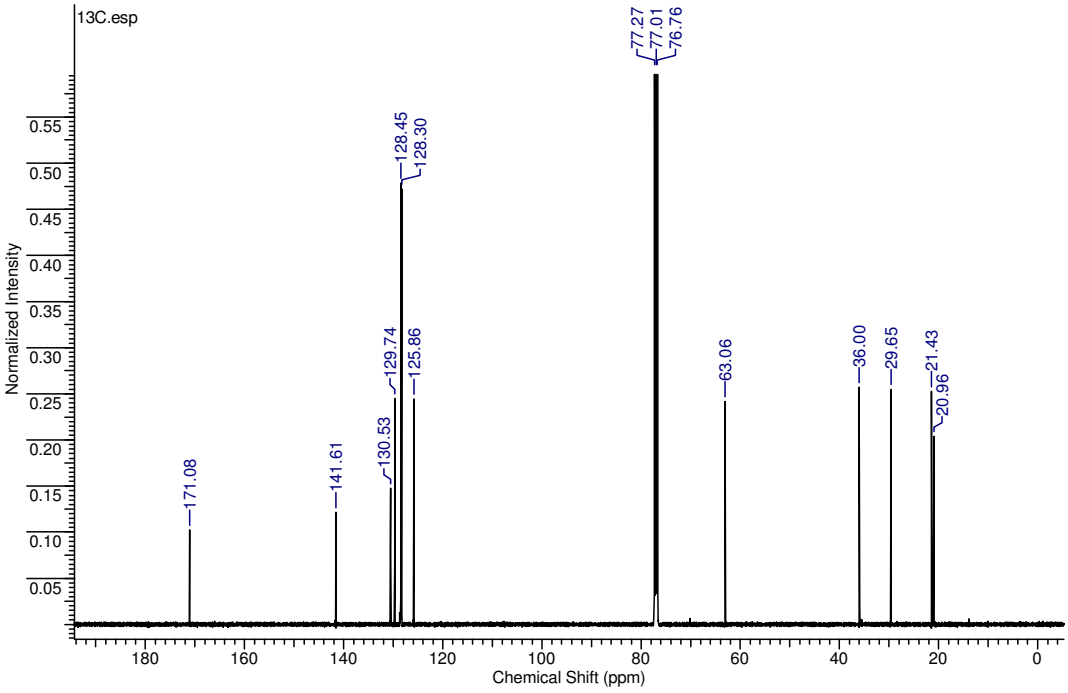


(*Z*)-2-Methyl-5-phenylpent-2-enyl acetate (6h)

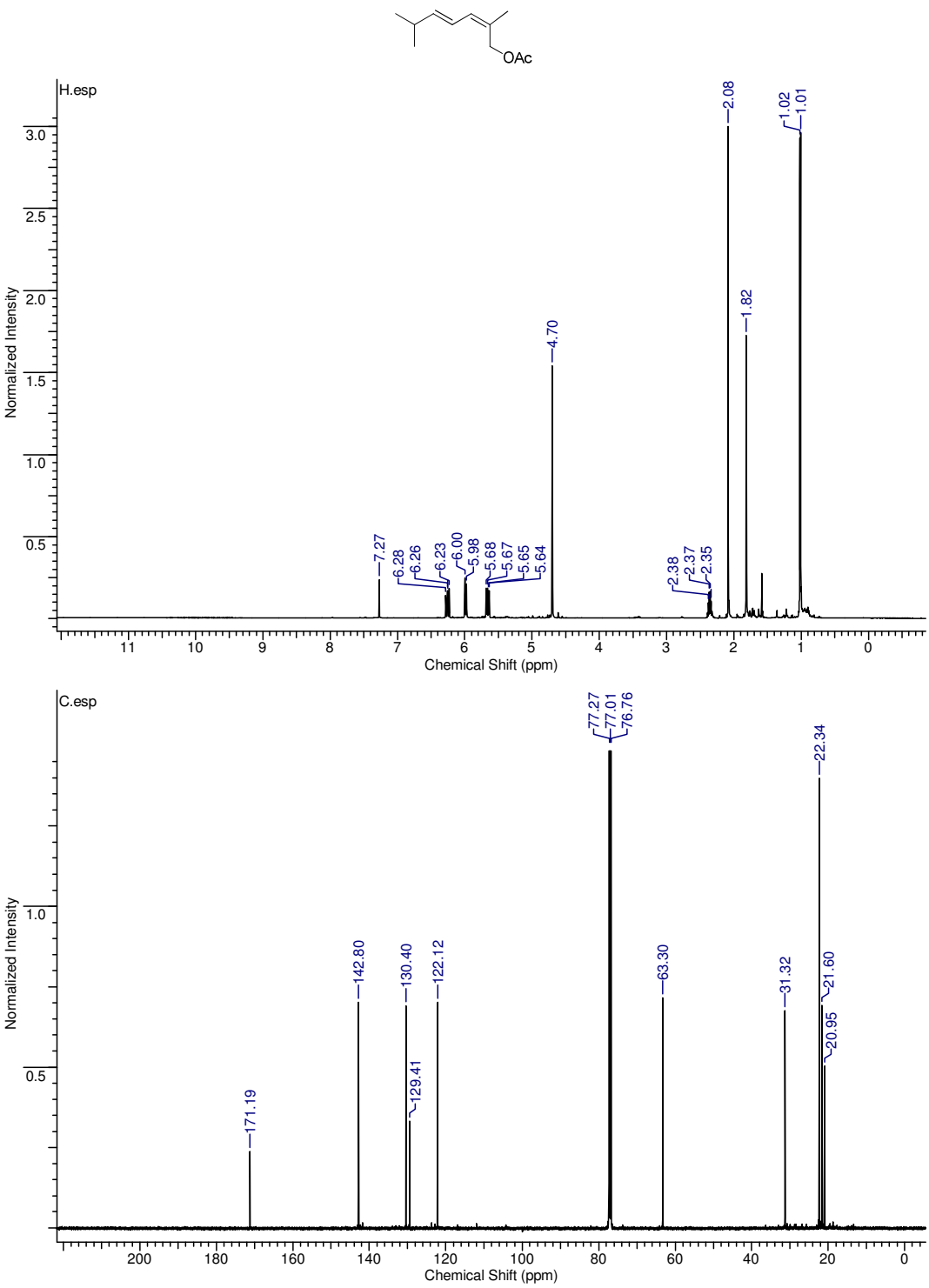


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz





(2*Z*,4*E*)-2,6-dimethylhepta-2,4-dien-1-yl acetate (6i)



(*Z*)-5-Phenyl-2-propylpent-2-enyl pivalate (7a)

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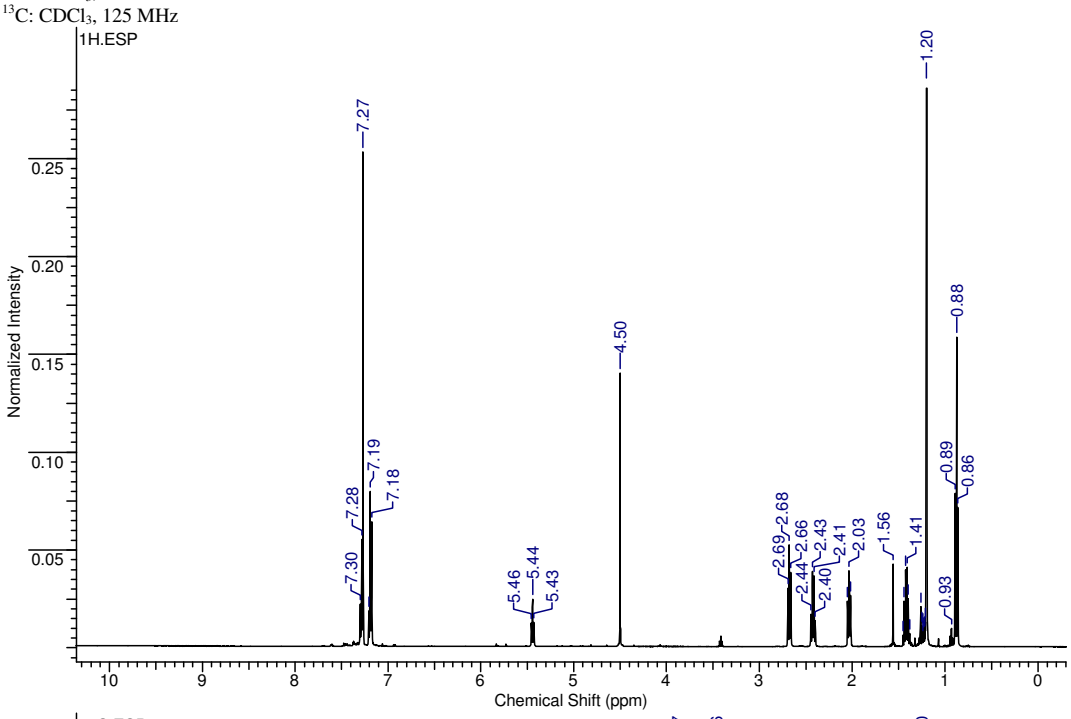
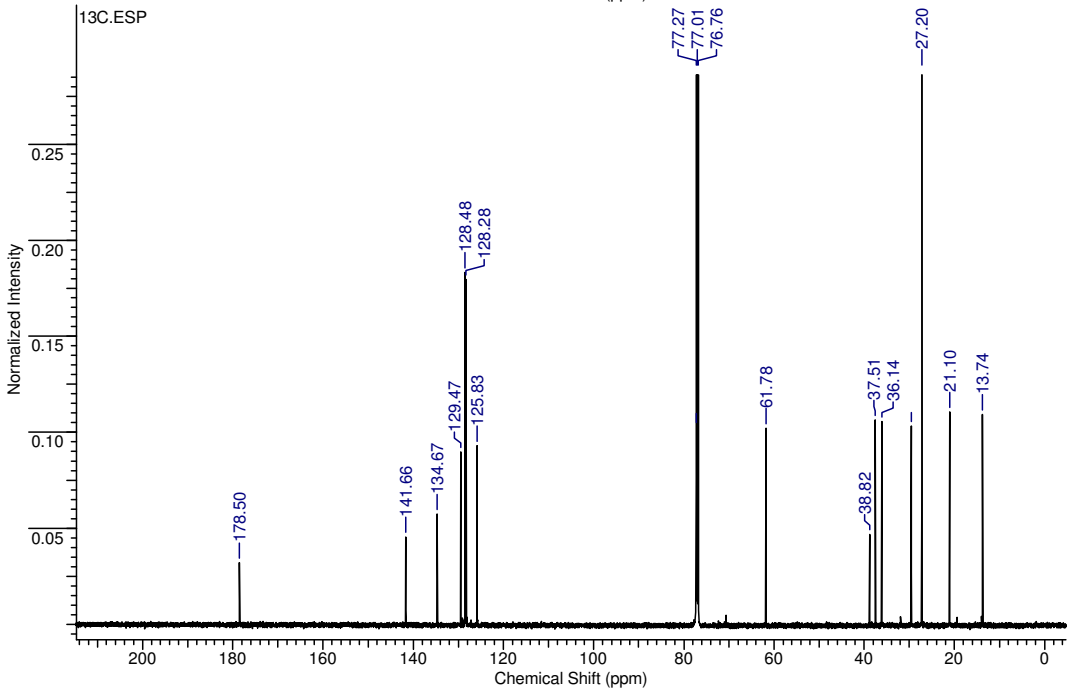
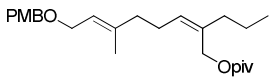
^{13}C: $CDCl_3$, 125 MHz

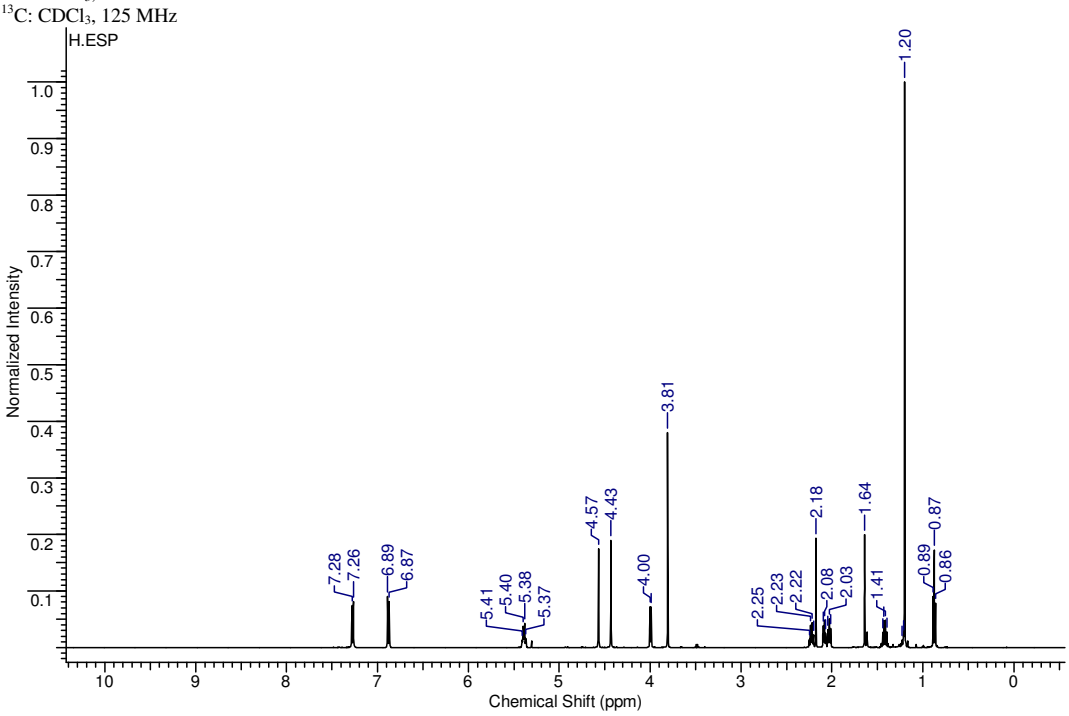


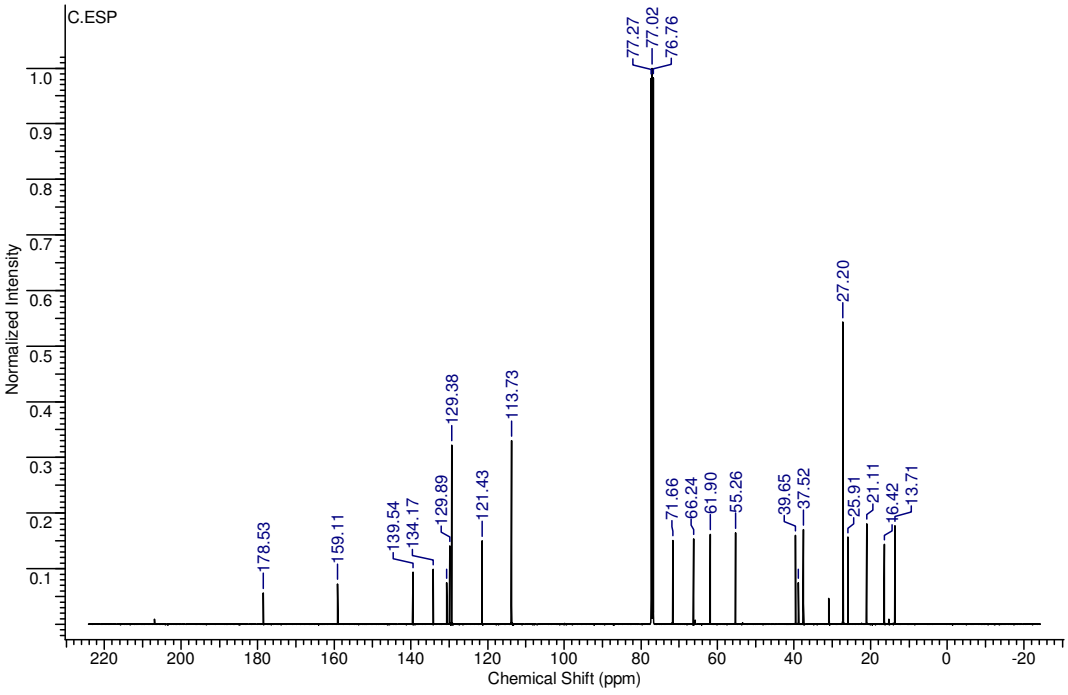


(2*Z*,6*E*)-8-((4-methoxybenzyl)oxy)-6-methyl-2-propylocta-2,6-dien-1-yl pivalate (7b)

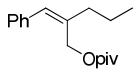


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz





(*Z*)-2-Benzylidenepentyl pivalate (7c)



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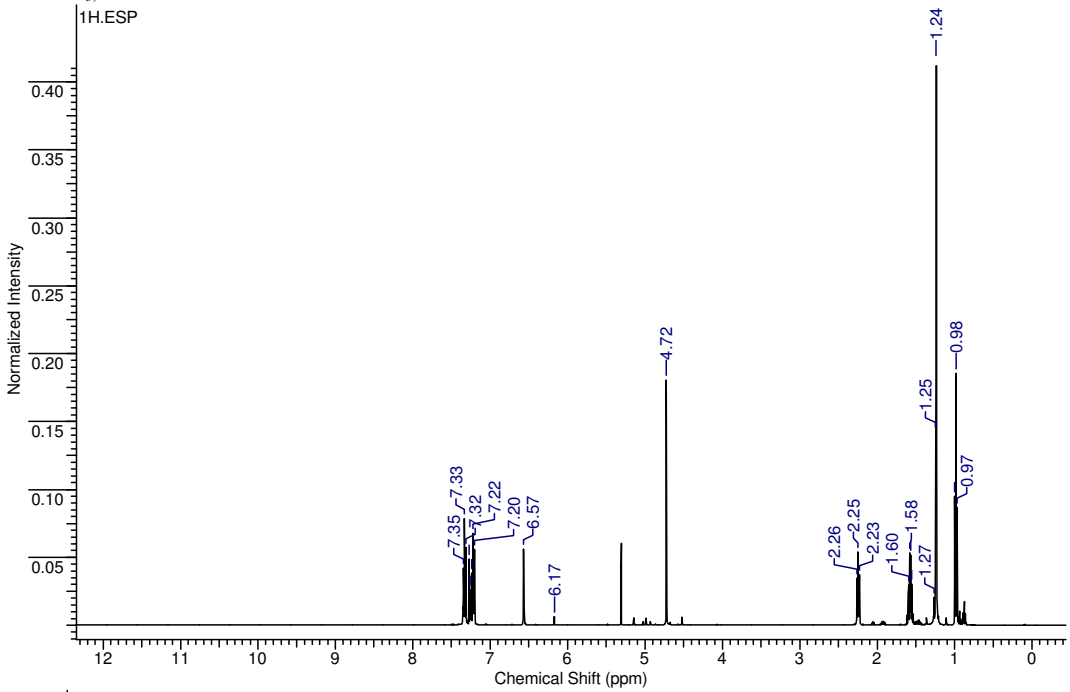
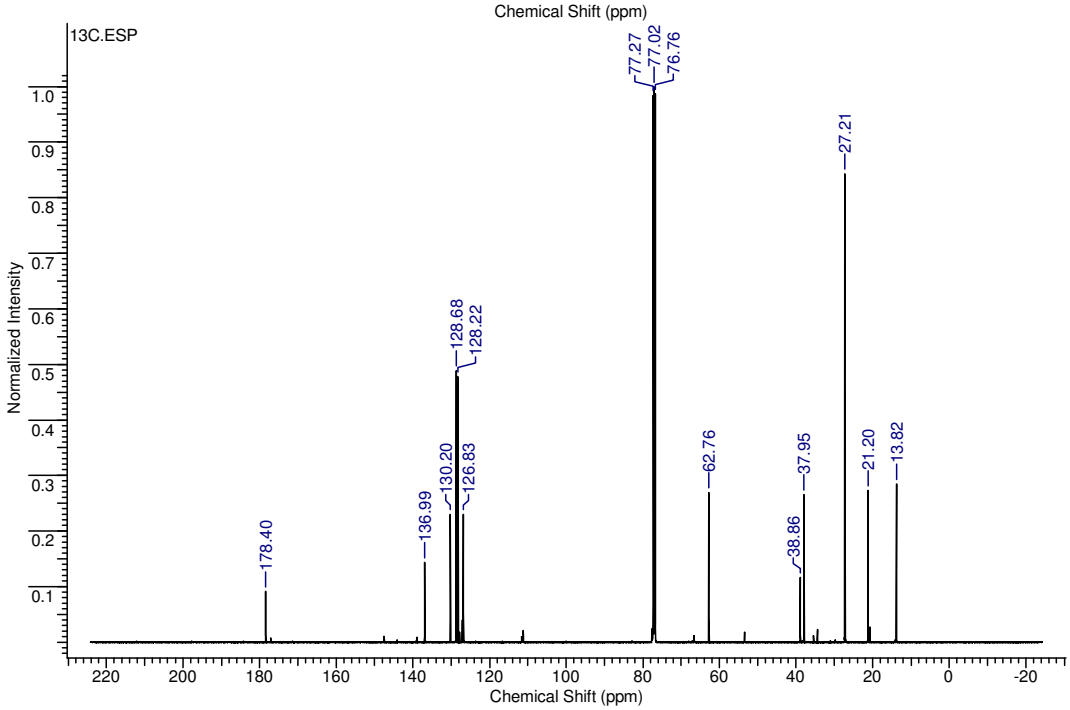
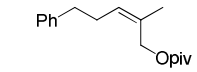




(*Z*)-2-Methyl-5-phenylpent-2-enyl pivalate (7d)



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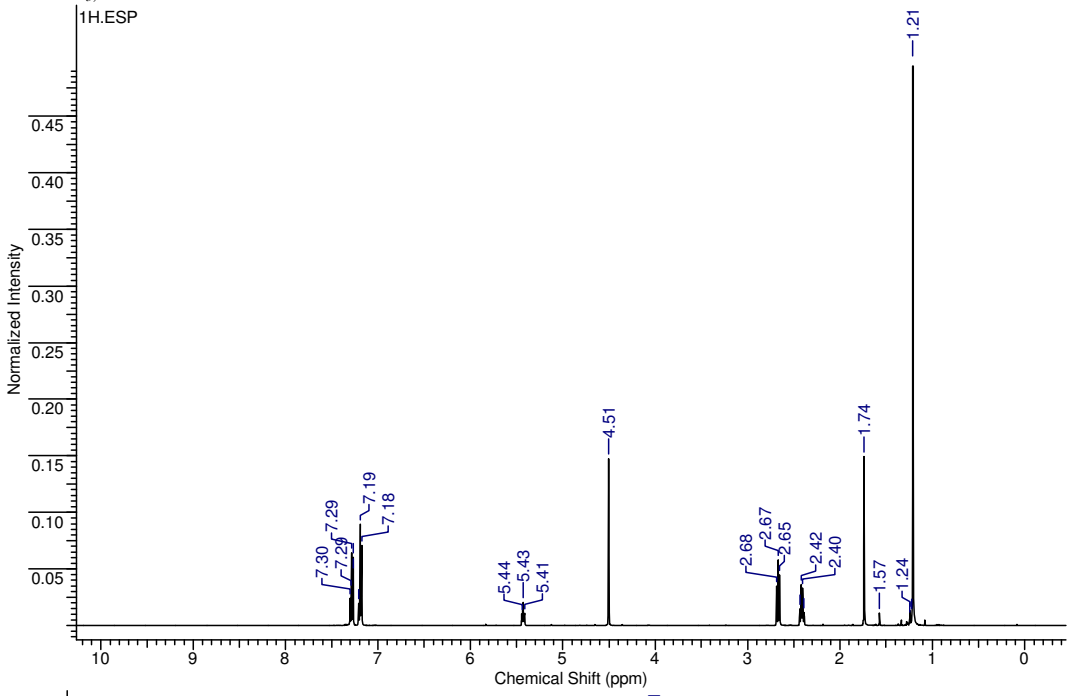
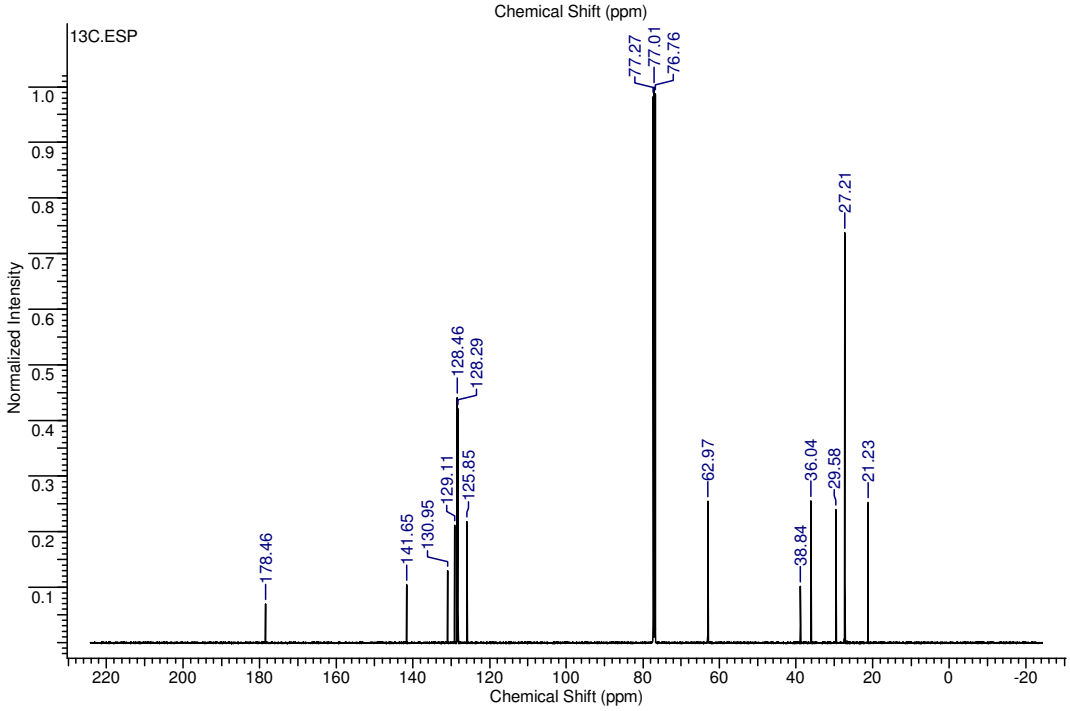
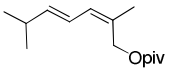
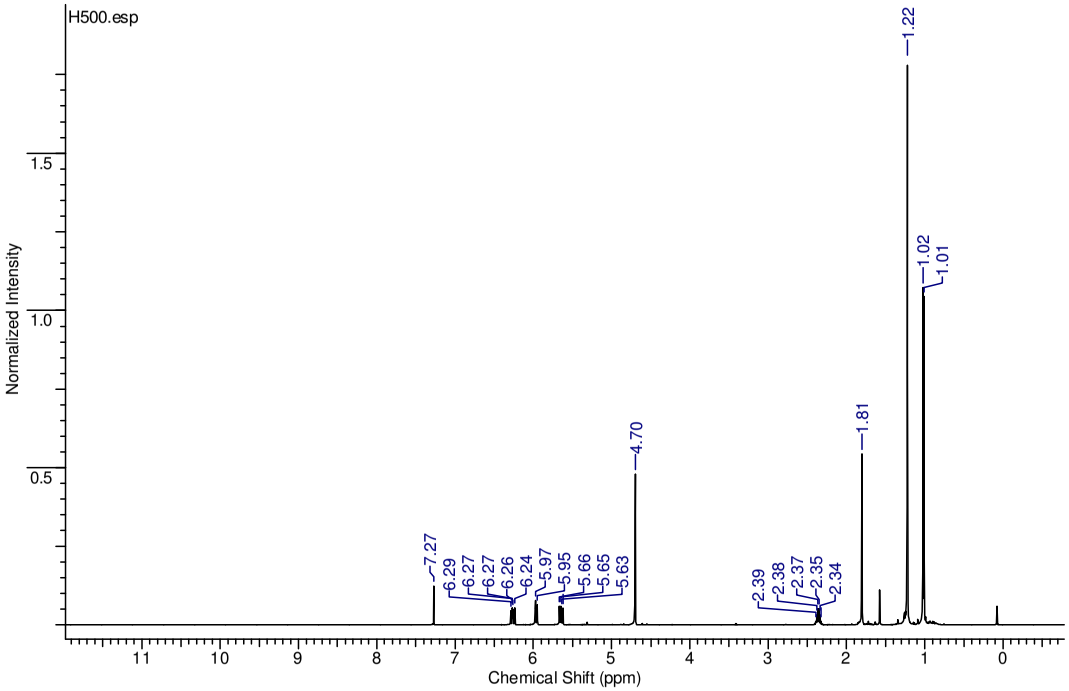
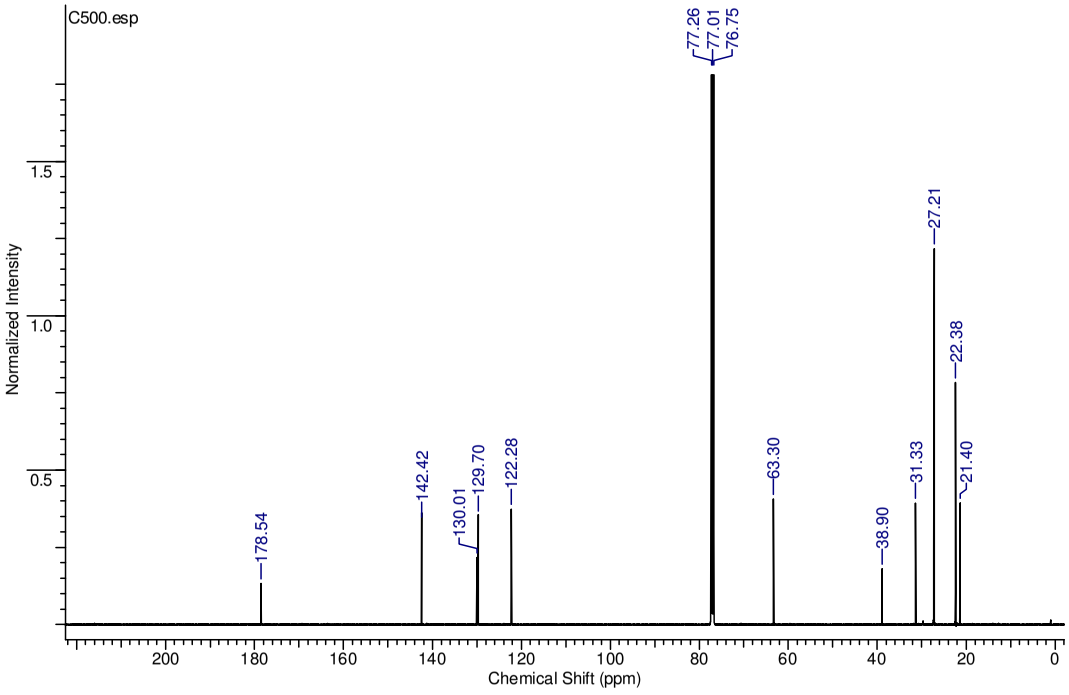




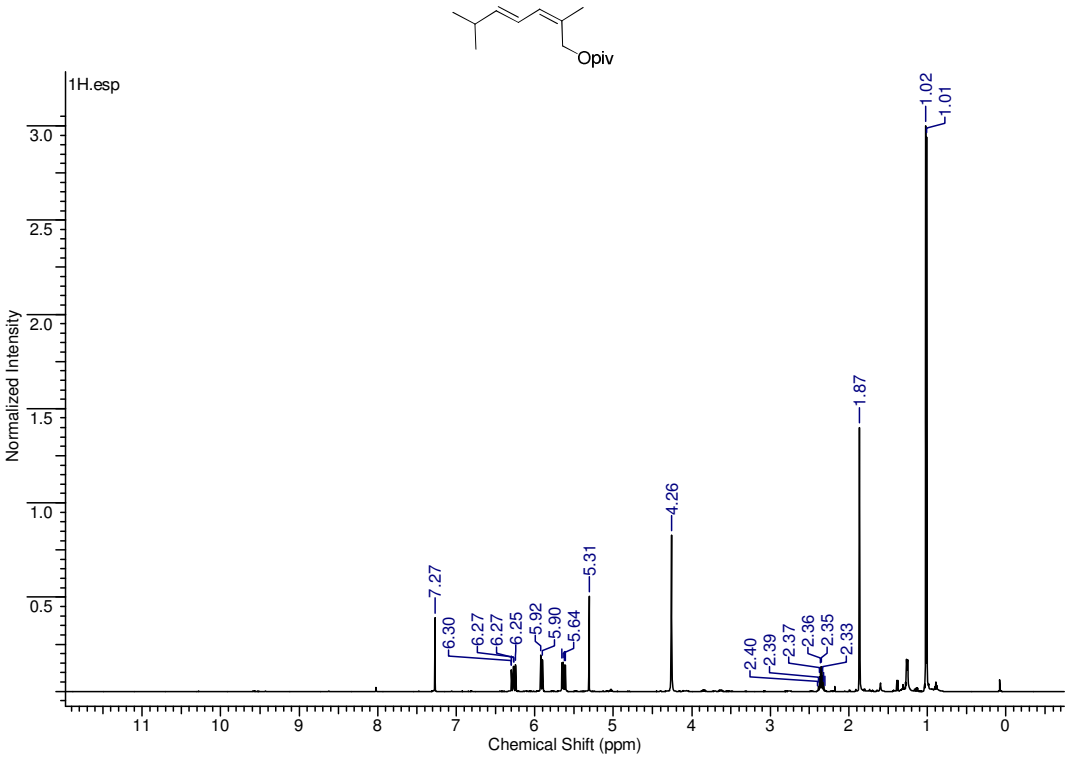
(2*Z*,4*E*)-2,6-Dimethylhepta-2,4-dien-1-yl pivalate (7e)

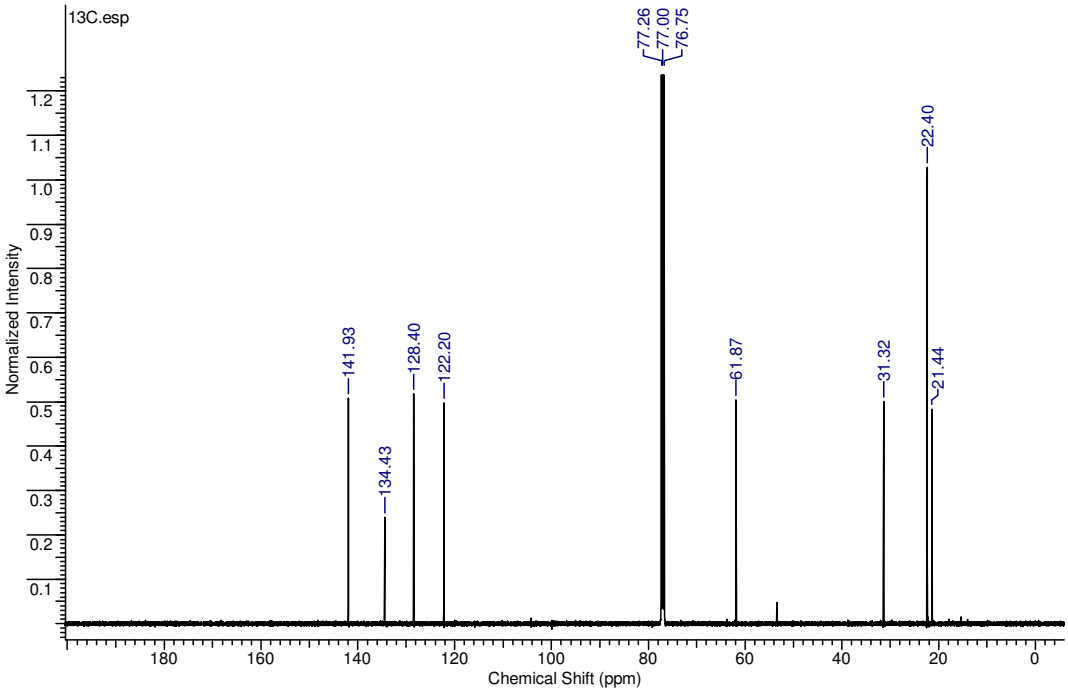




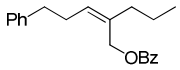


(2*Z*,4*E*)-2,6-Dimethylhepta-2,4-dien-1-ol





(*Z*)-5-Phenyl-2-propylpent-2-enyl benzoate (8a)



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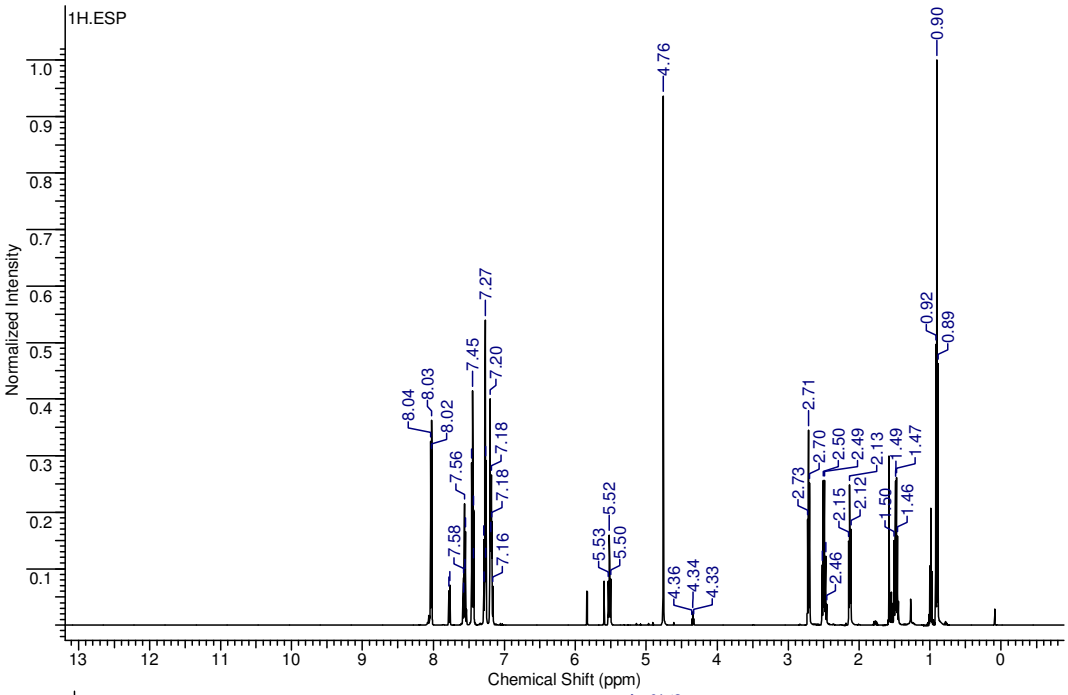
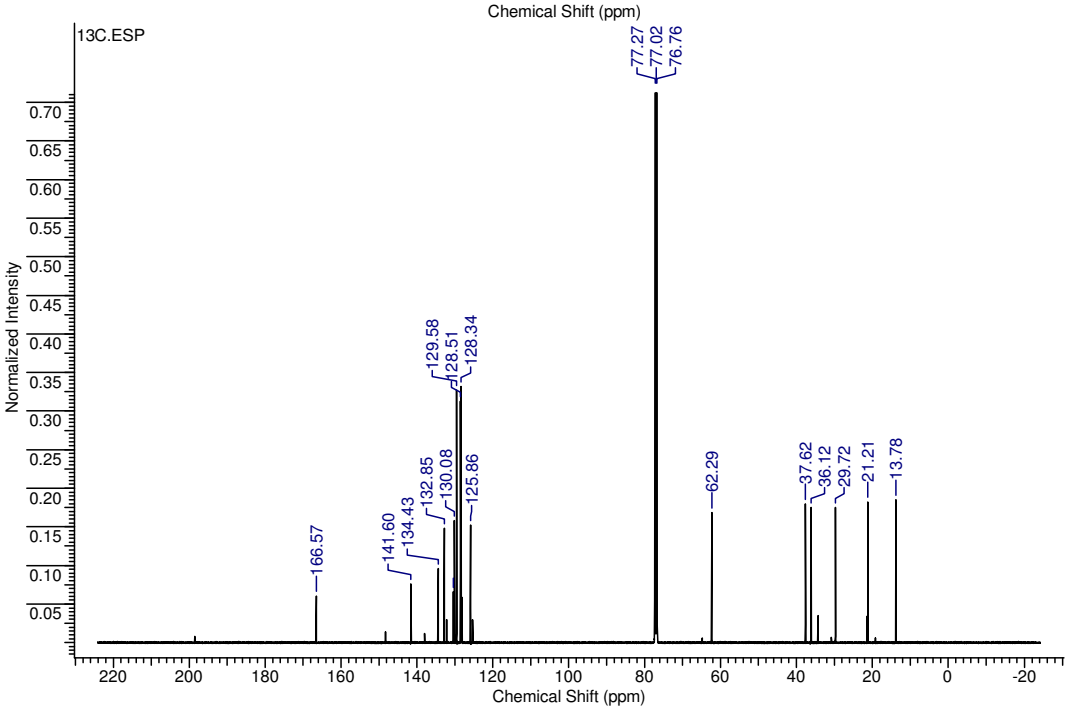
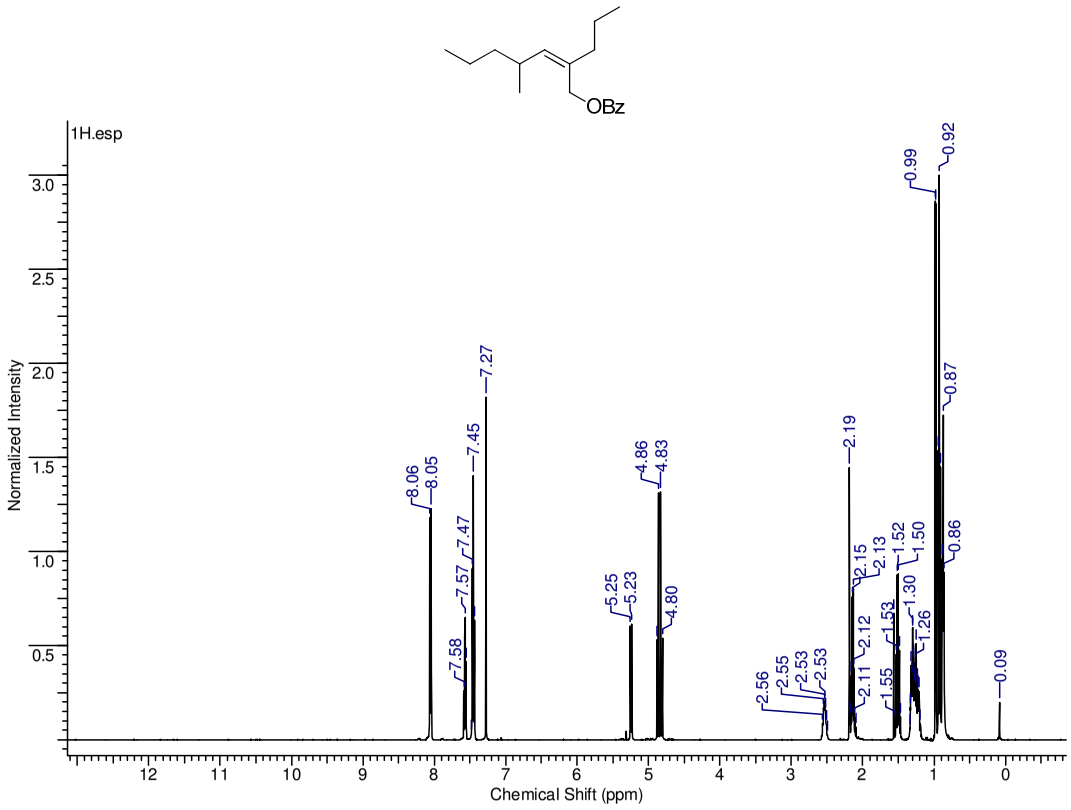
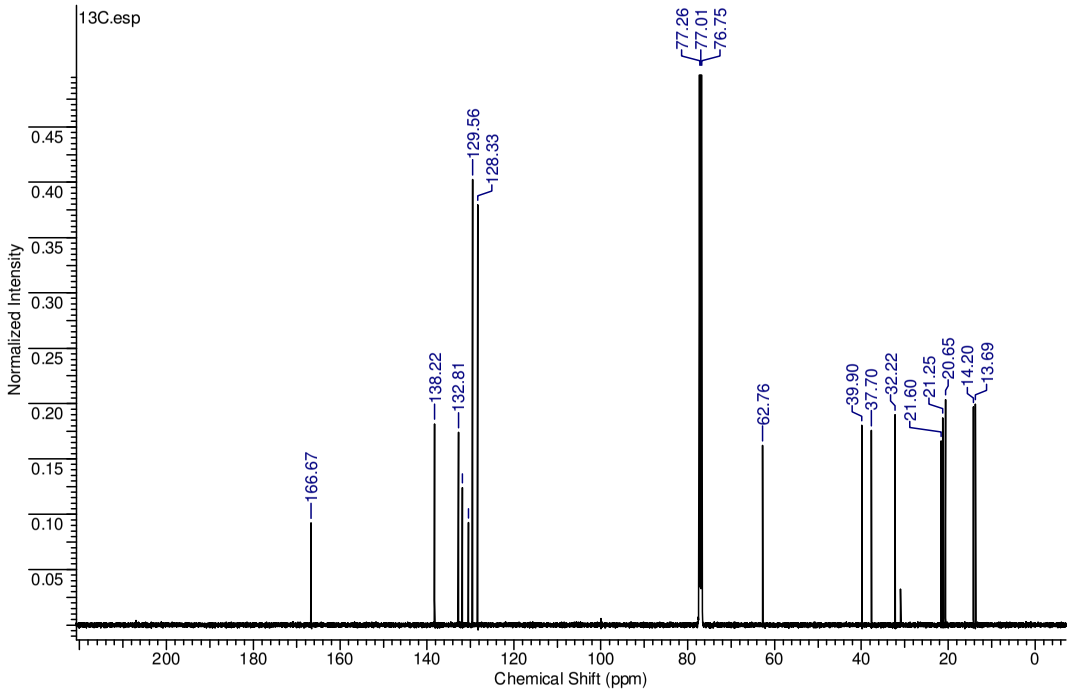


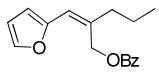


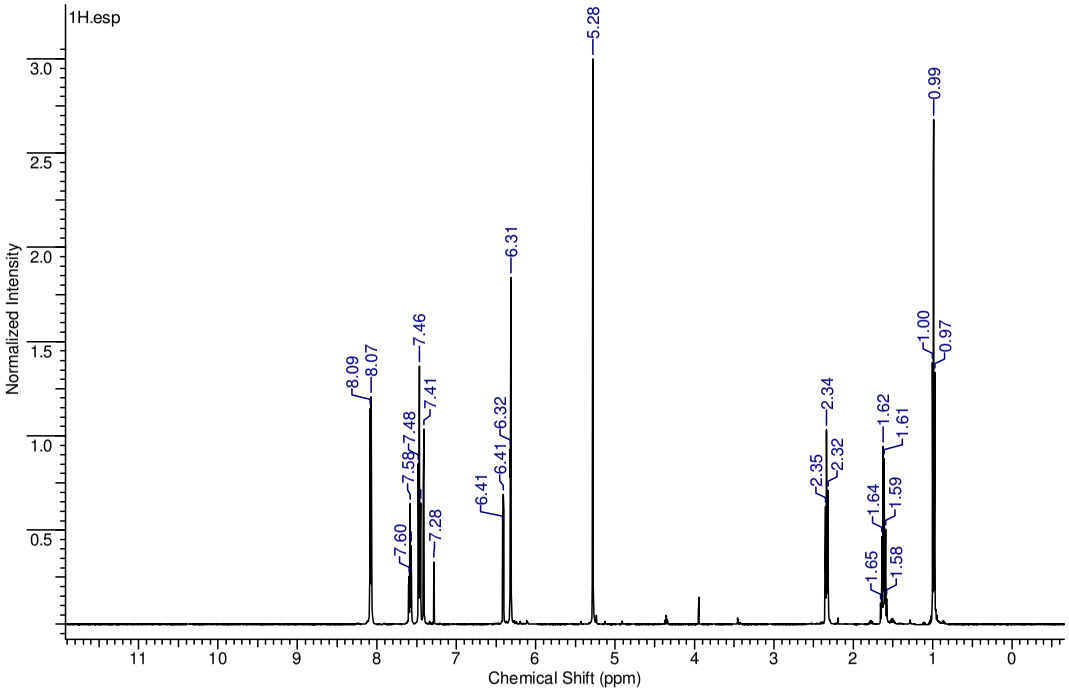
(*Z*)-4-Methyl-2-propylhept-2-en-1-yl benzoate (8b)

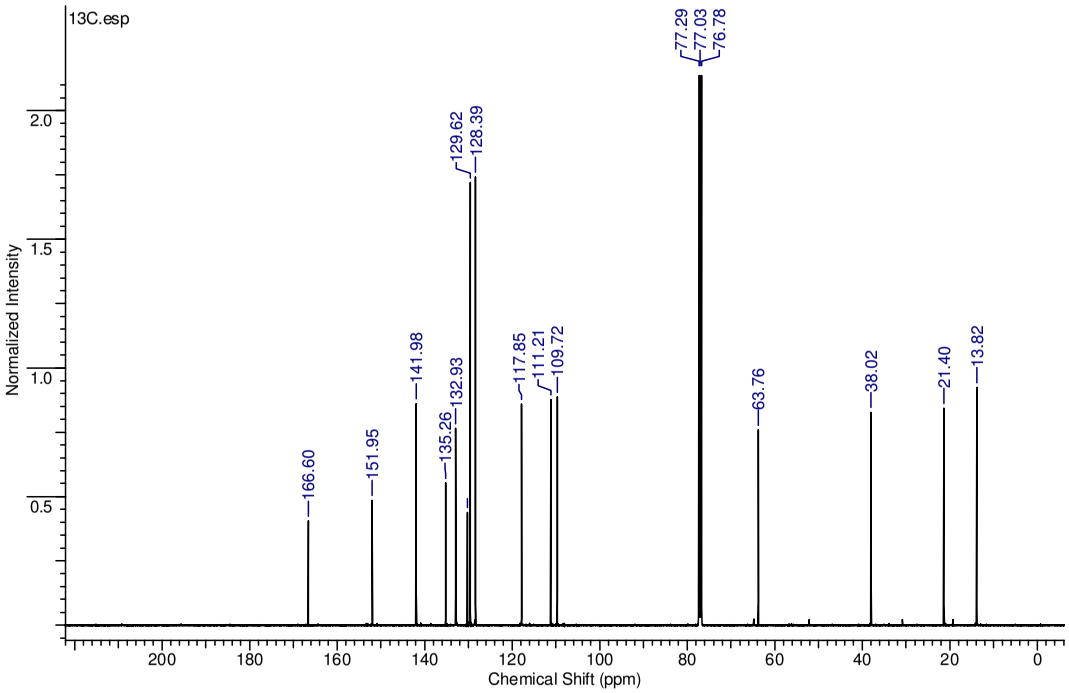




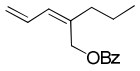
(*Z*)-2-(Furan-2-ylmethylene)pentyl benzoate (8c)



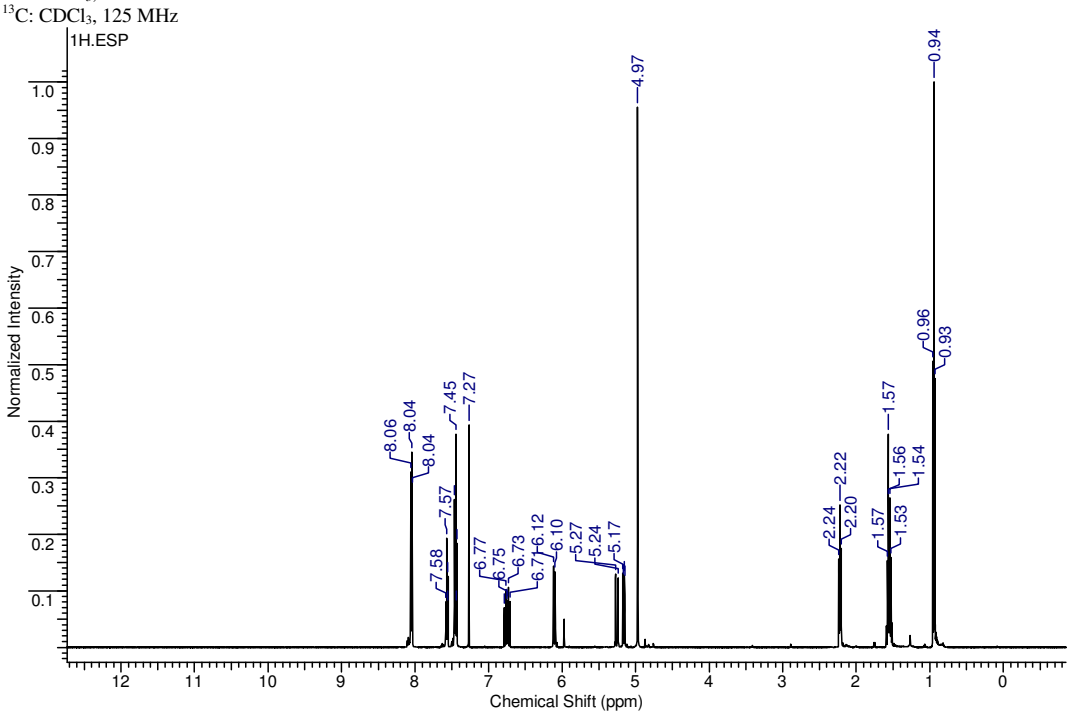


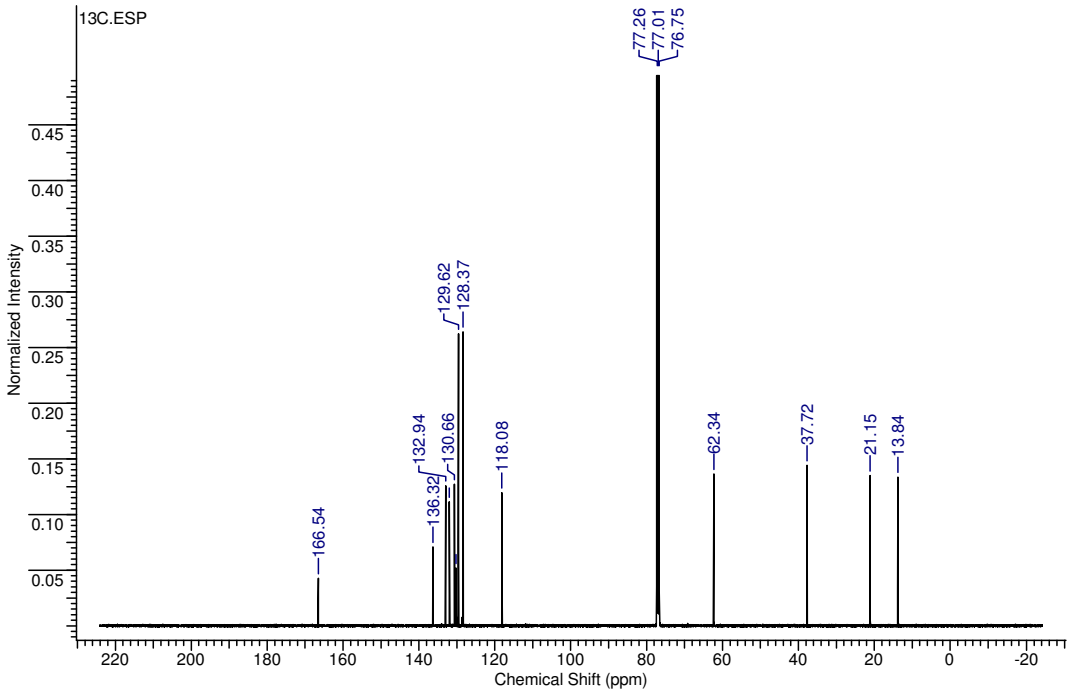


(*Z*)-2-Propylpenta-2,4-dienyl benzoate (8d).

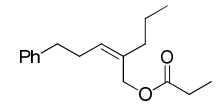


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

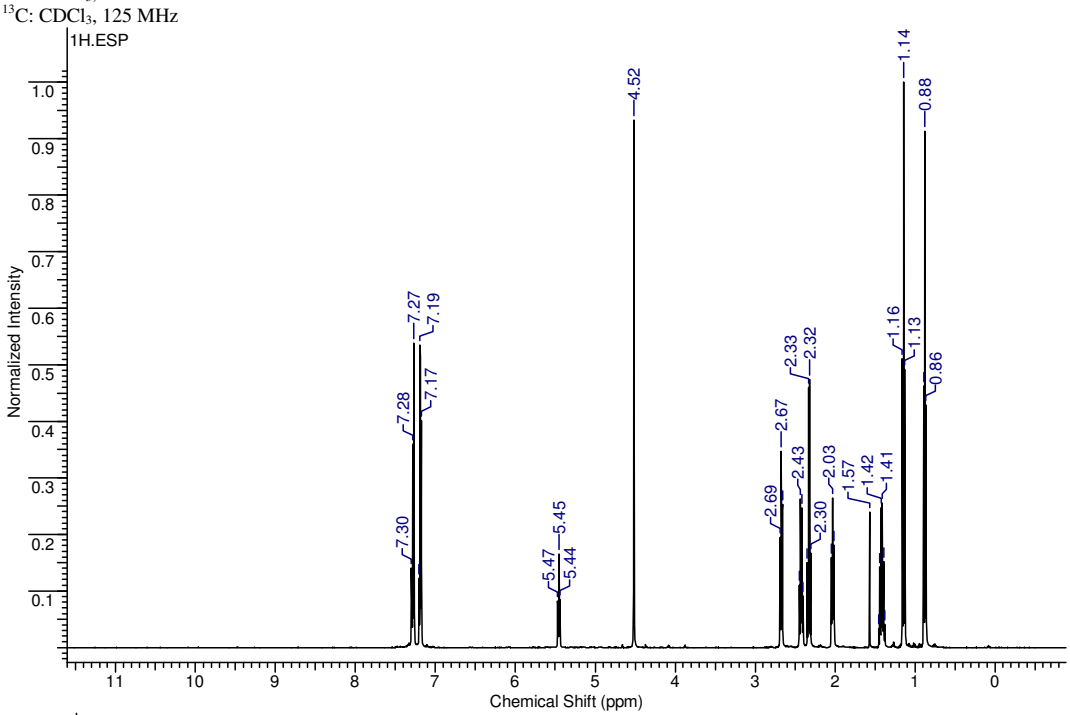


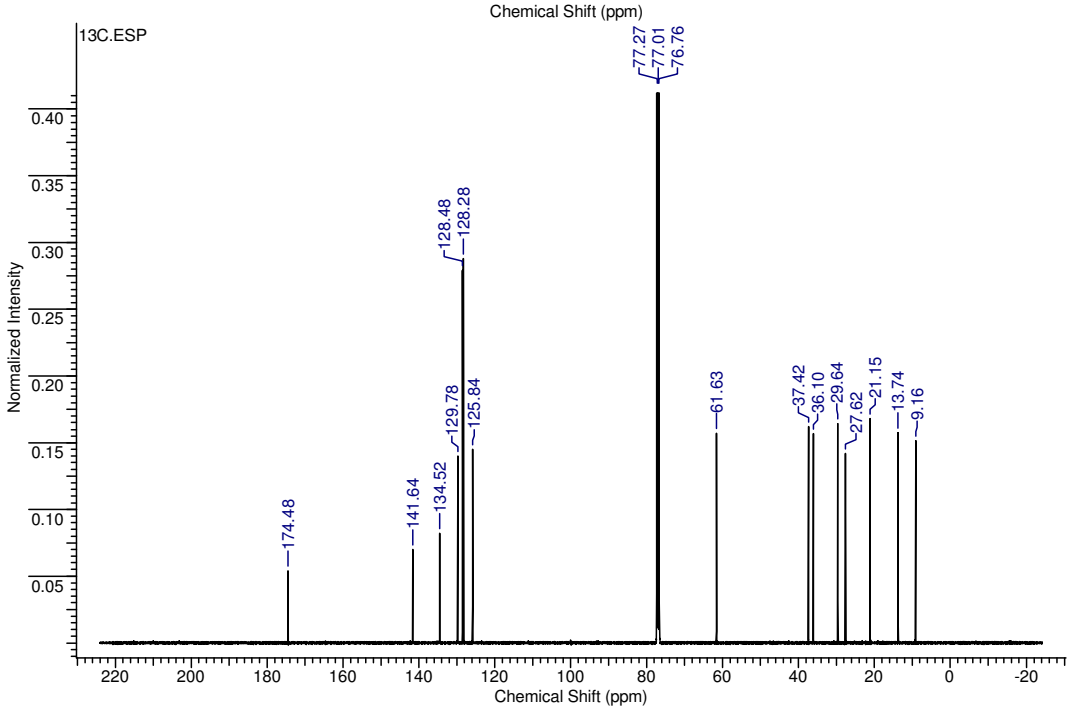


(*Z*)-5-Phenyl-2-propylpent-2-enyl propionate (9a)

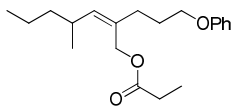


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

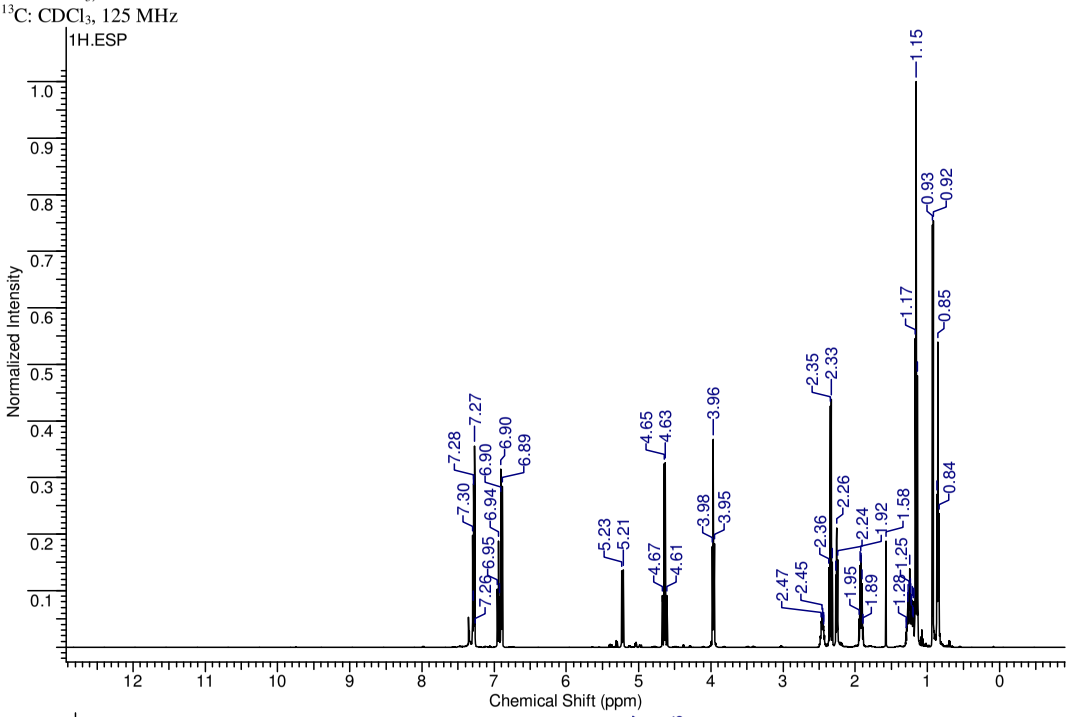


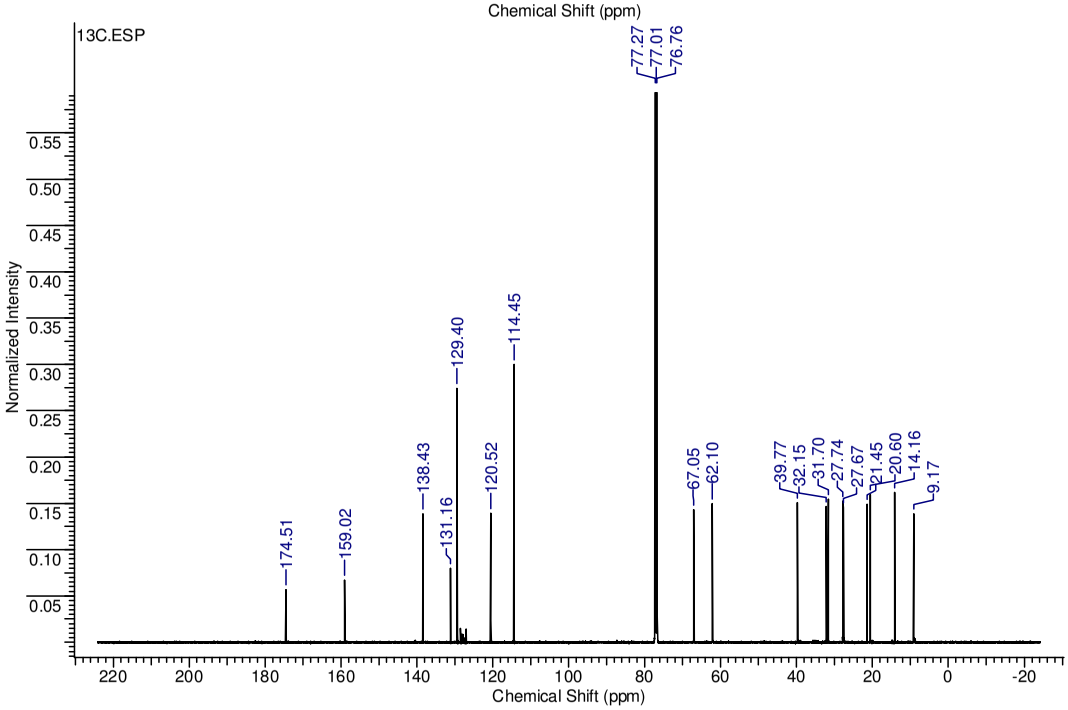


(*Z*)-4-Methyl-2-(3-phenoxypropyl)hept-2-enyl propionate (9b)

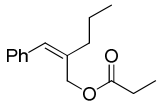


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

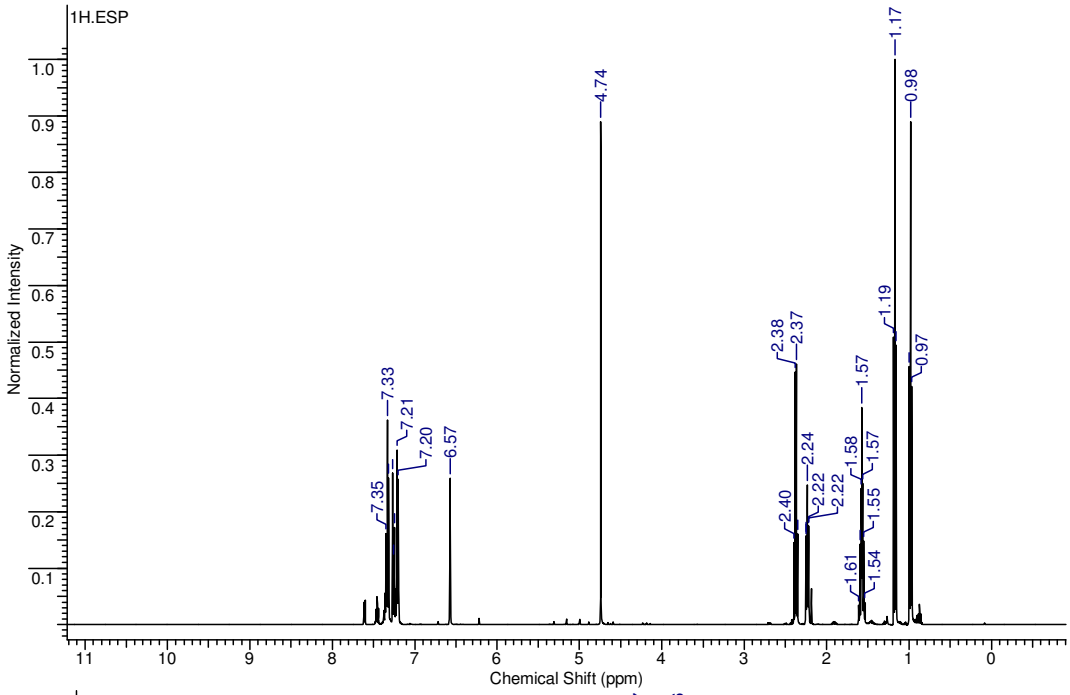


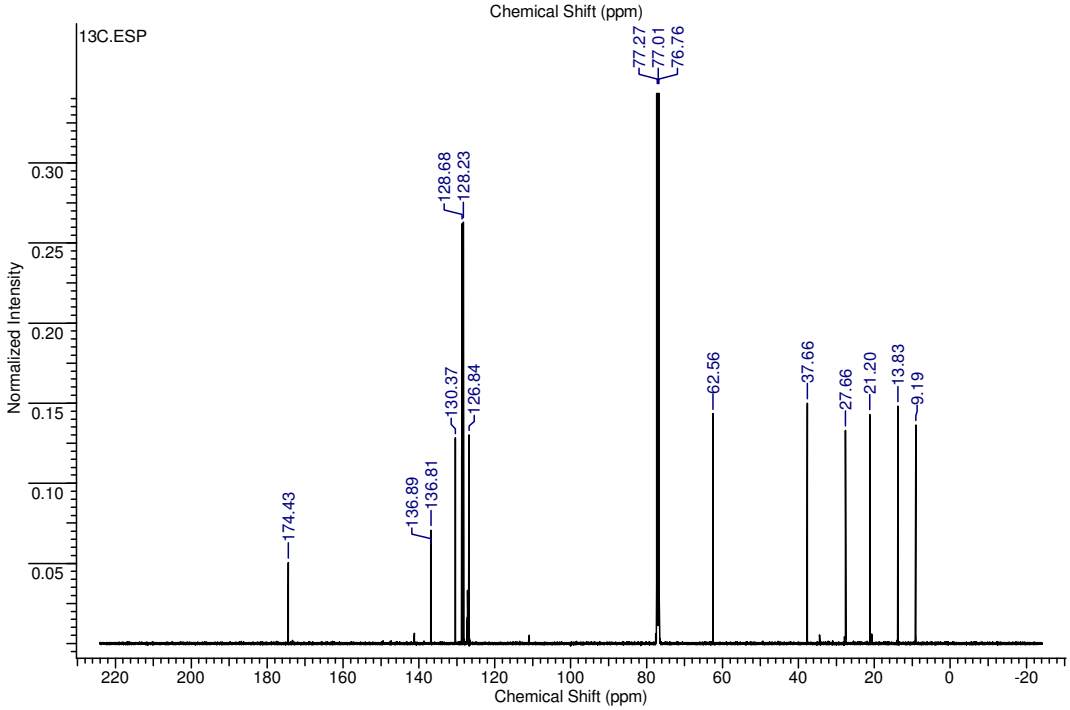


(*Z*)-2-Benzylidenepentyl propionate (9c)



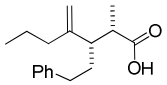
^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz



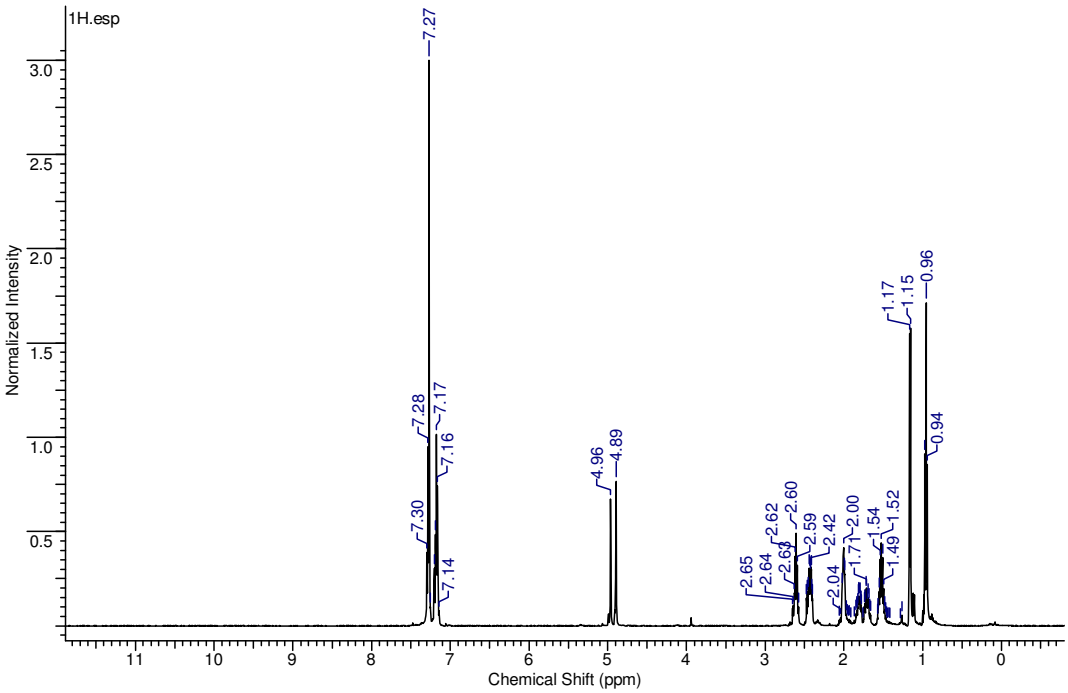


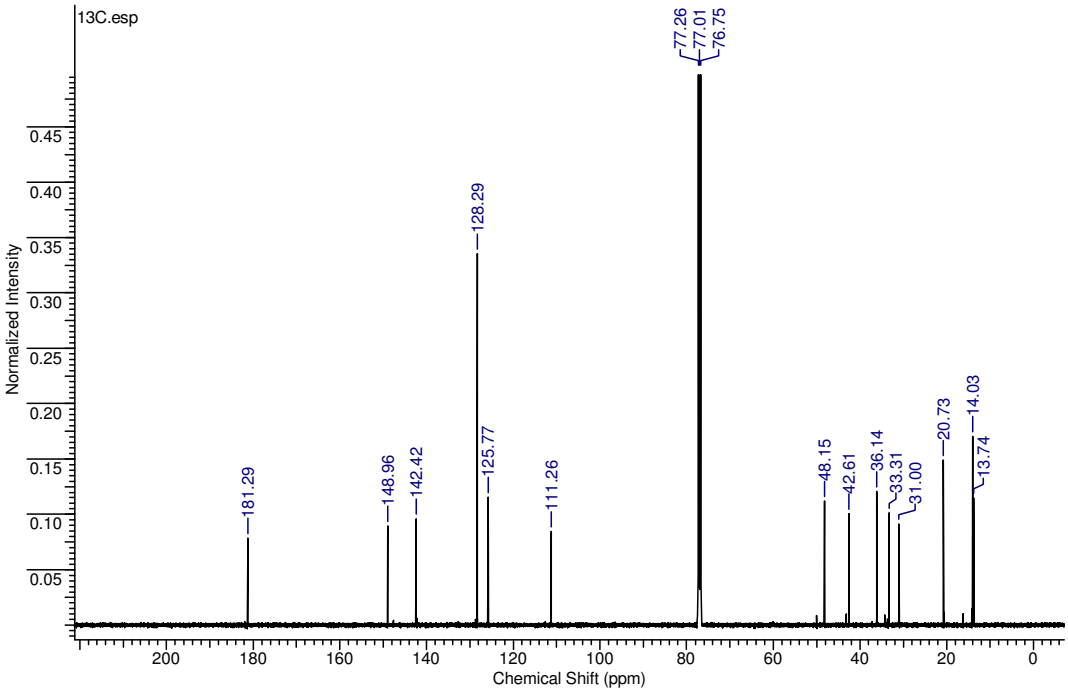
9. ^{1}H and ^{13}C NMR spectra of acid 11

(±)-(2*R*,3*R*)-2-Methyl-4-methylene-3-(phenethyl)-heptanoic acid (11)

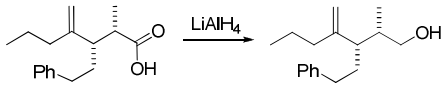


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

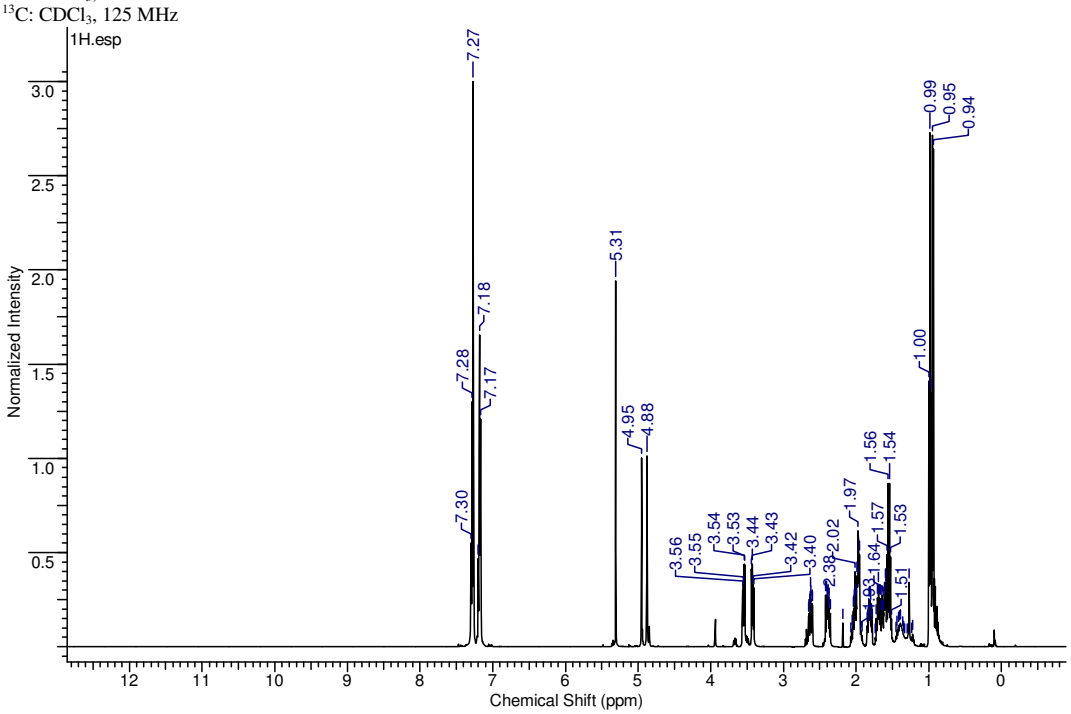


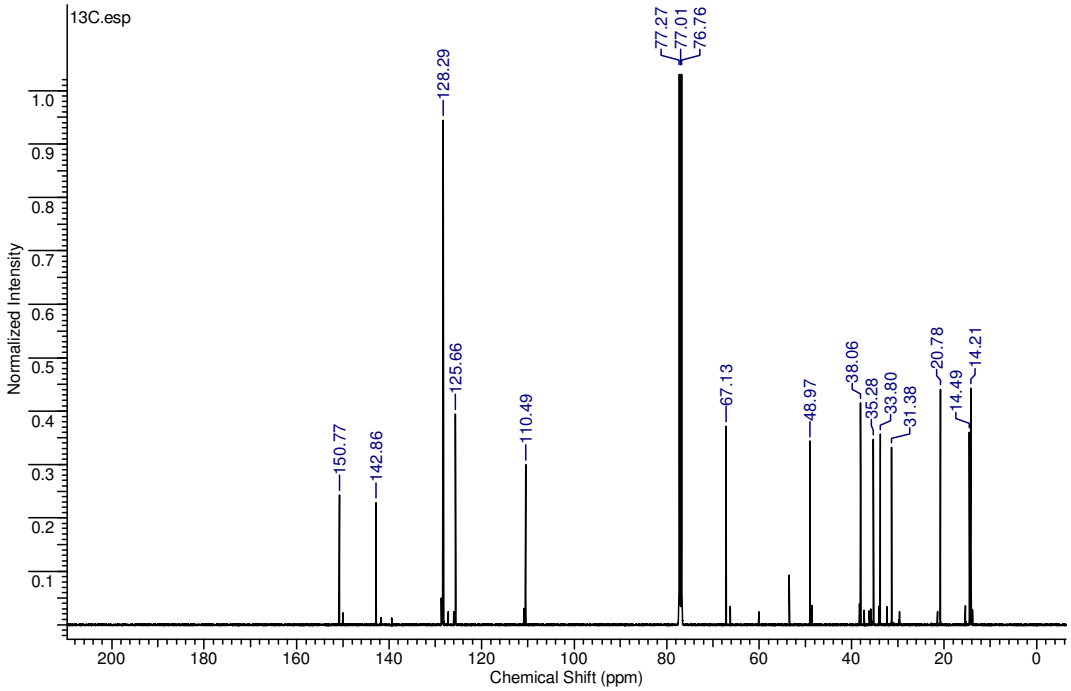


(±)-(2*R*,3*R*)-2-Methyl-4-methylene-3-(phenethyl)-heptan-1-ol by reduction of (11)



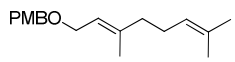
^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz



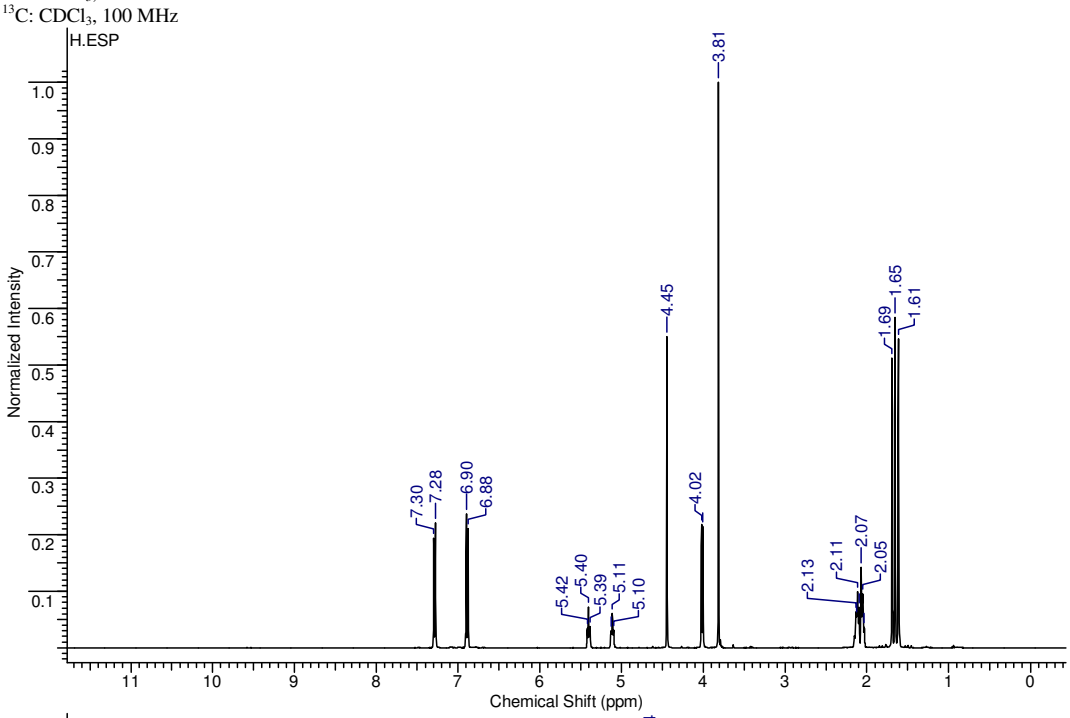


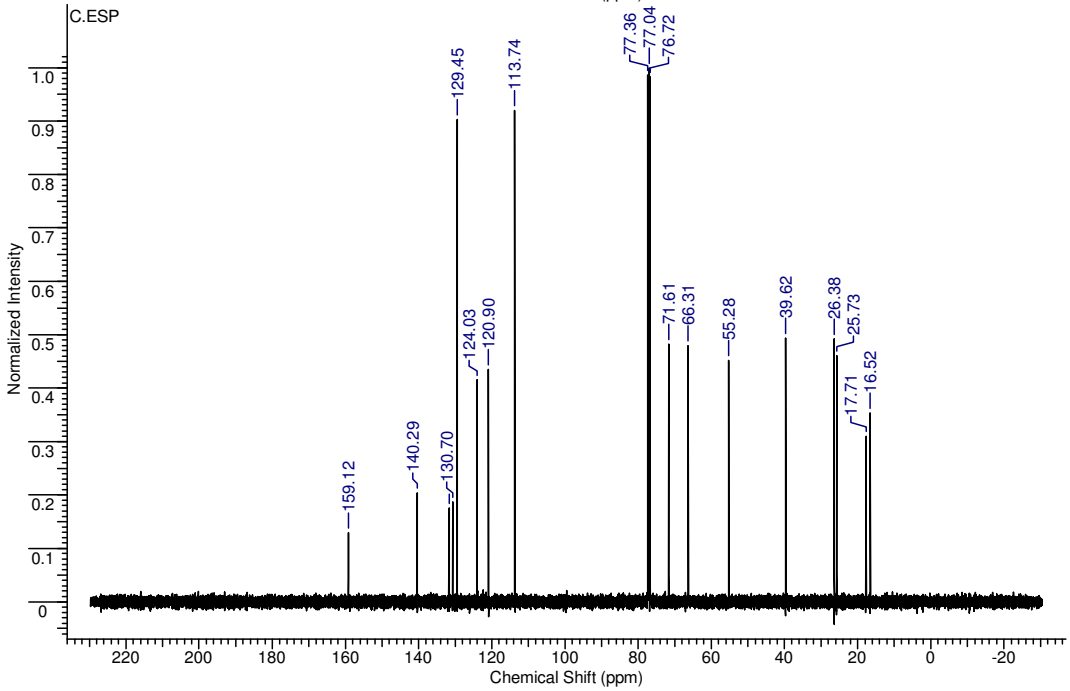
10. ^{1}H and ^{13}C NMR spectra for the synthesis of (*Z*)-7-hydroxy-2-((*E*)-6-hydroxy-4-methylhex-4-enylidene)-6,10-dimethylundec-9-enyl acetate (12)

(*E*)-1-(((3,7-Dimethylocta-2,6-dien-1-yl)oxy)methyl)-4-methoxybenzene

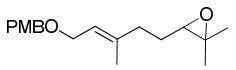


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

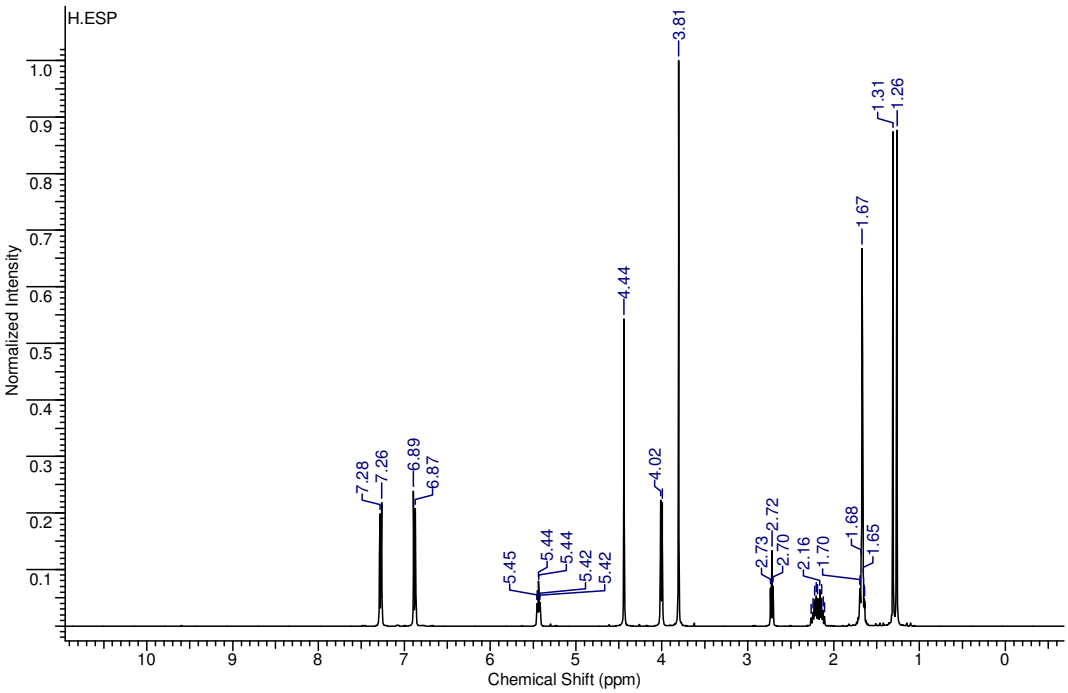


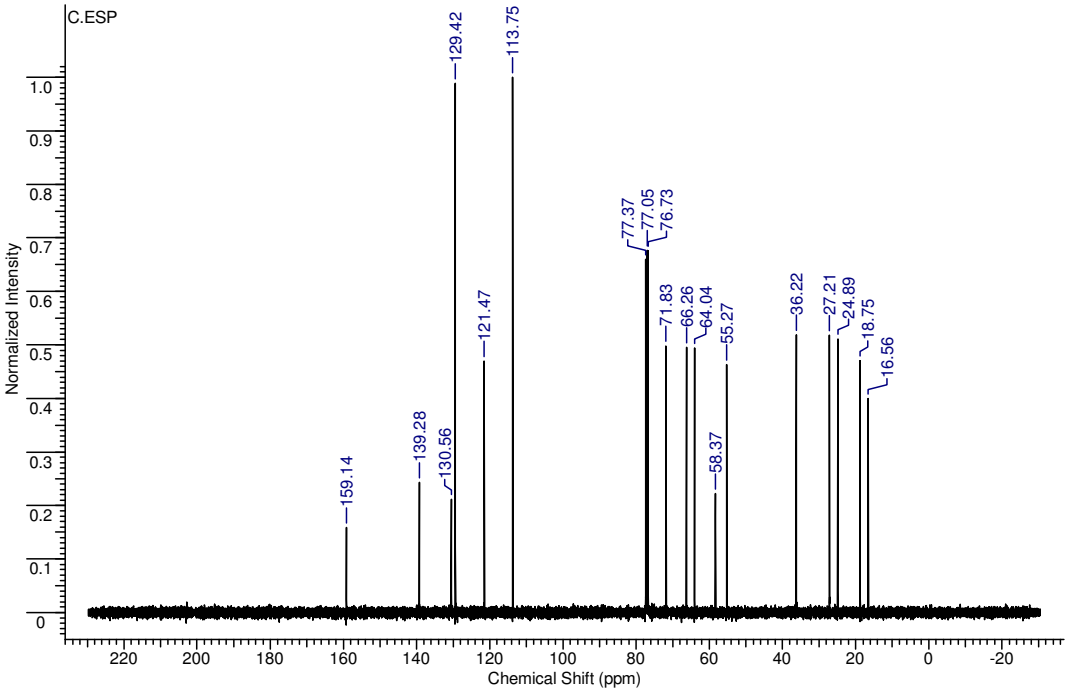


(*E*)-3-(5-((4-Methoxybenzyl)oxy)-3-methylpent-3-en-1-yl)-2,2-dimethyloxirane

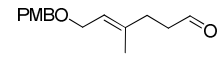


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

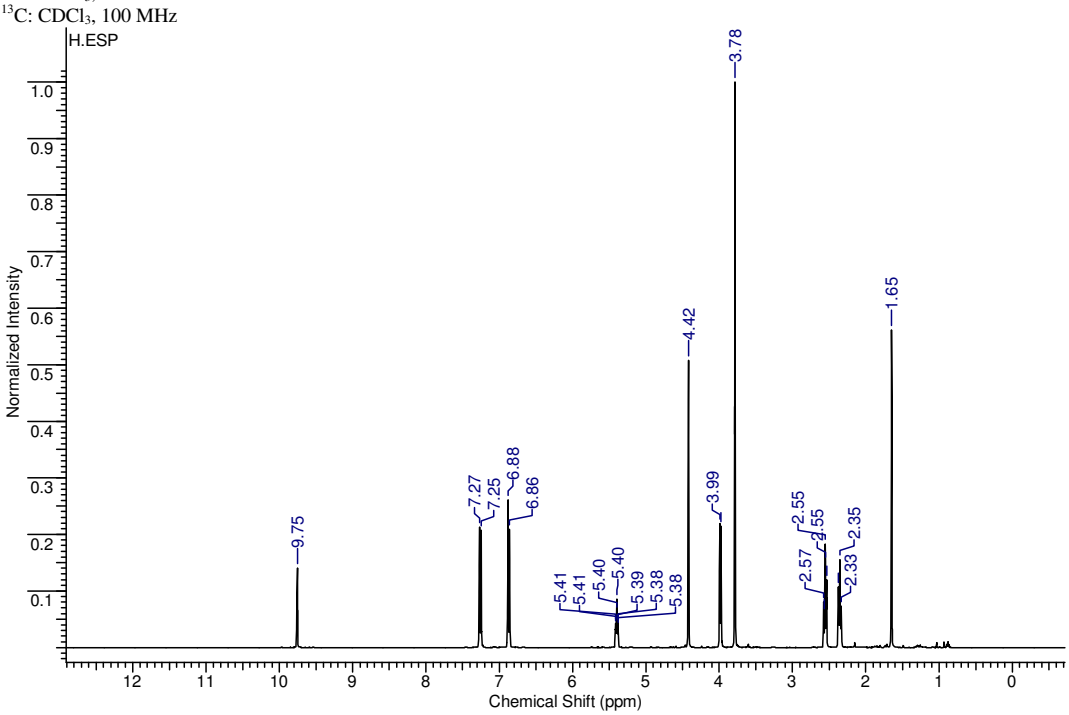


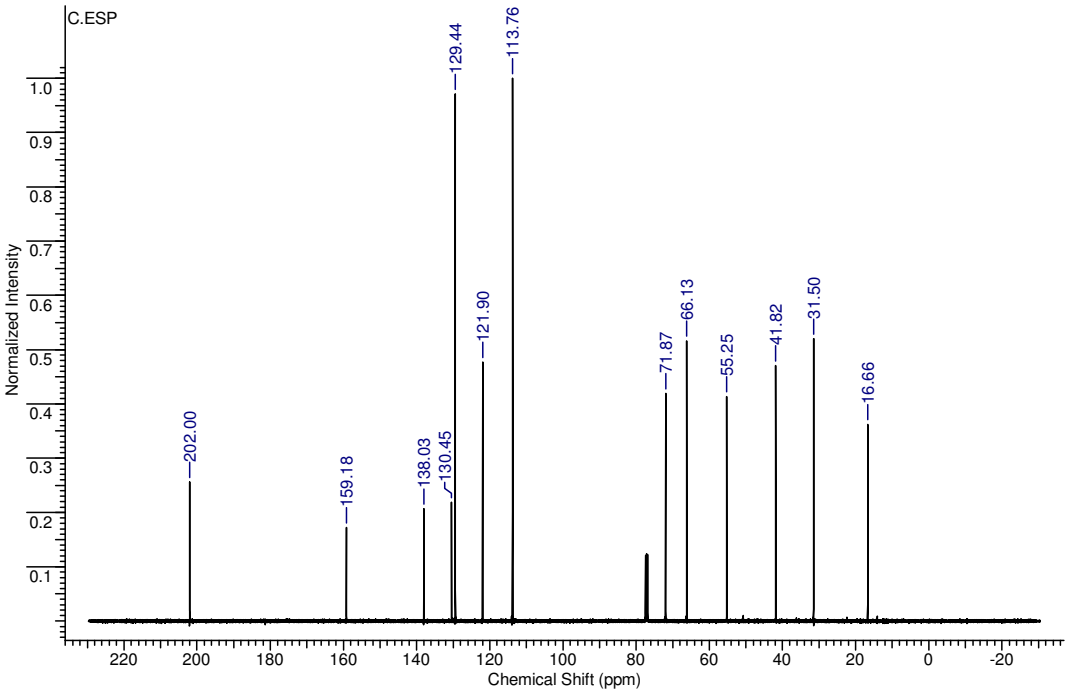


(*E*)-6-((4-Methoxybenzyl)oxy)-4-methylhex-4-enal (13)

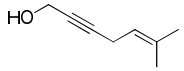


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

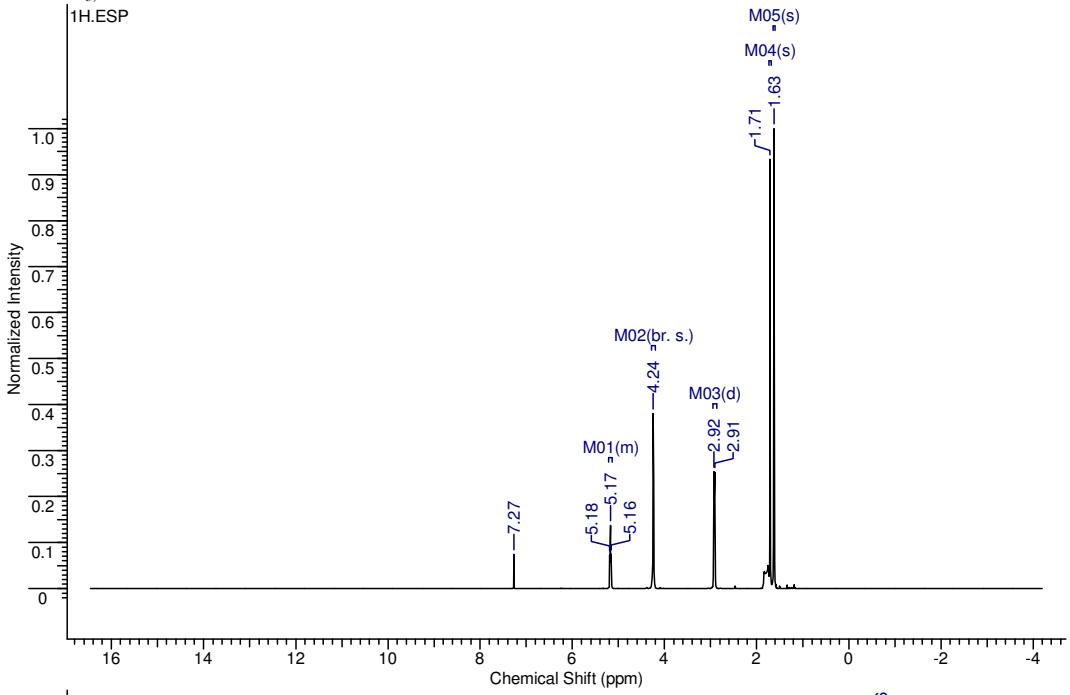


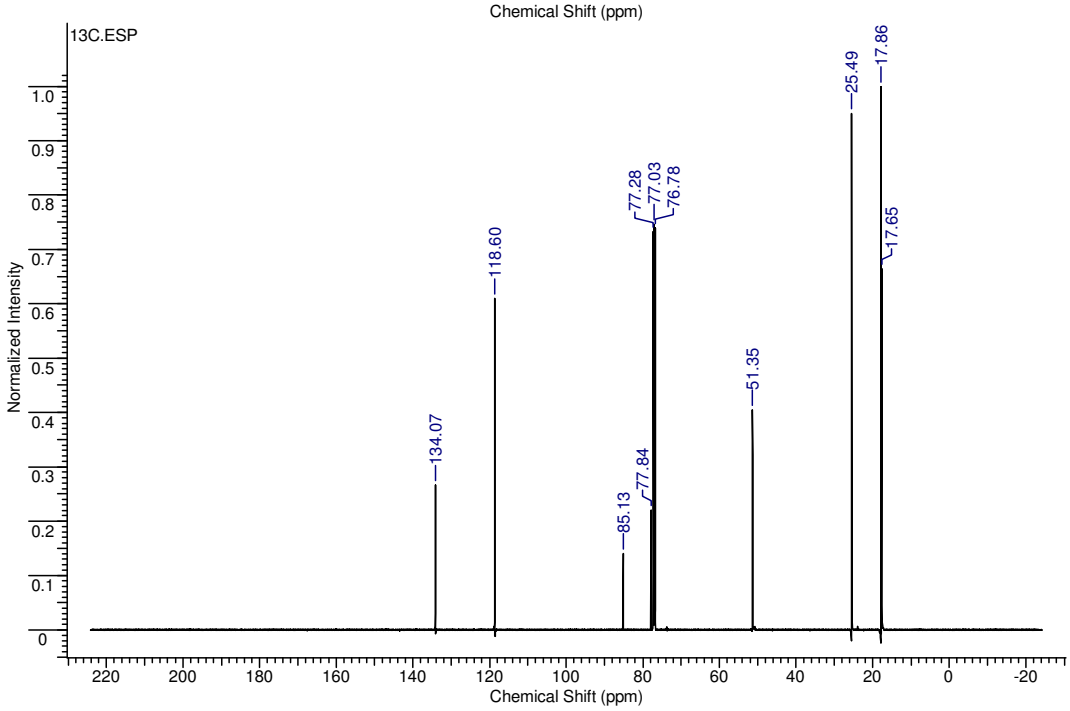


6-Methylhept-5-en-2-yn-1-ol (17)

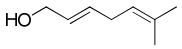


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

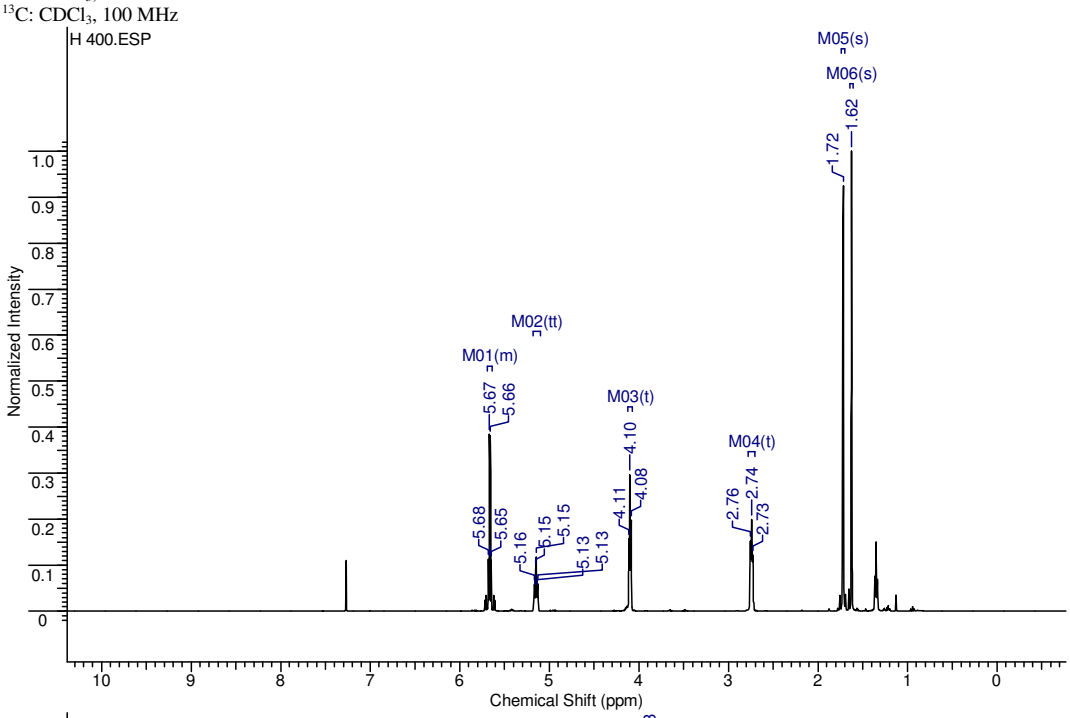


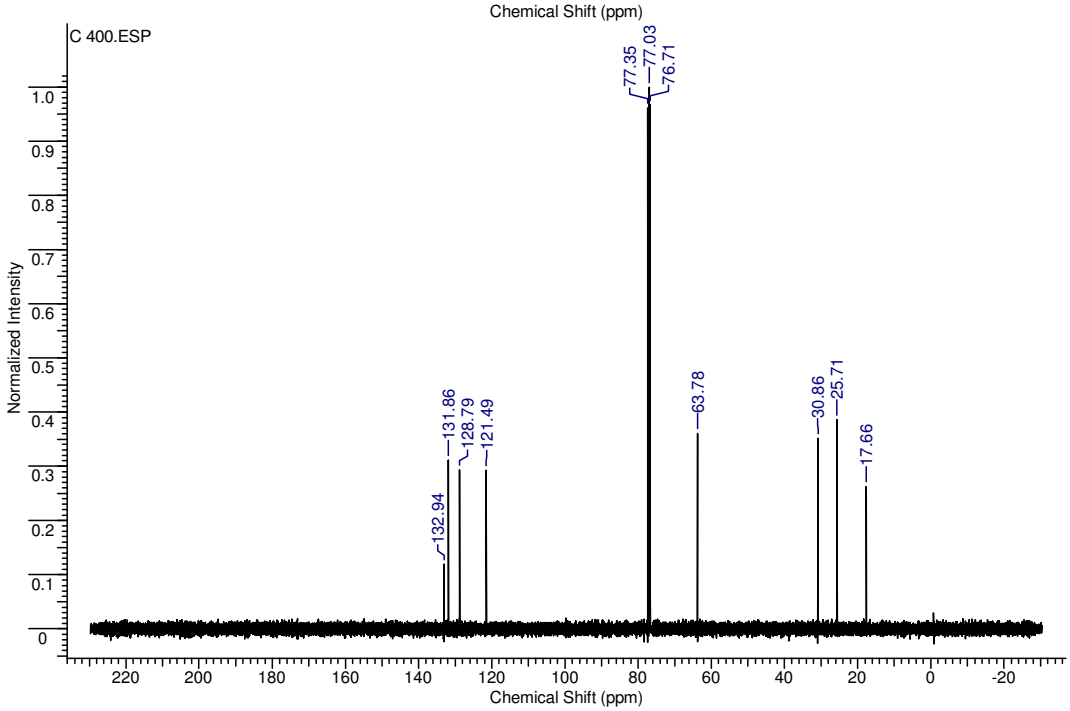


(*E*)-6-Methylhepta-2,5-dien-1-ol (18)

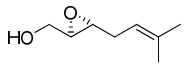


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

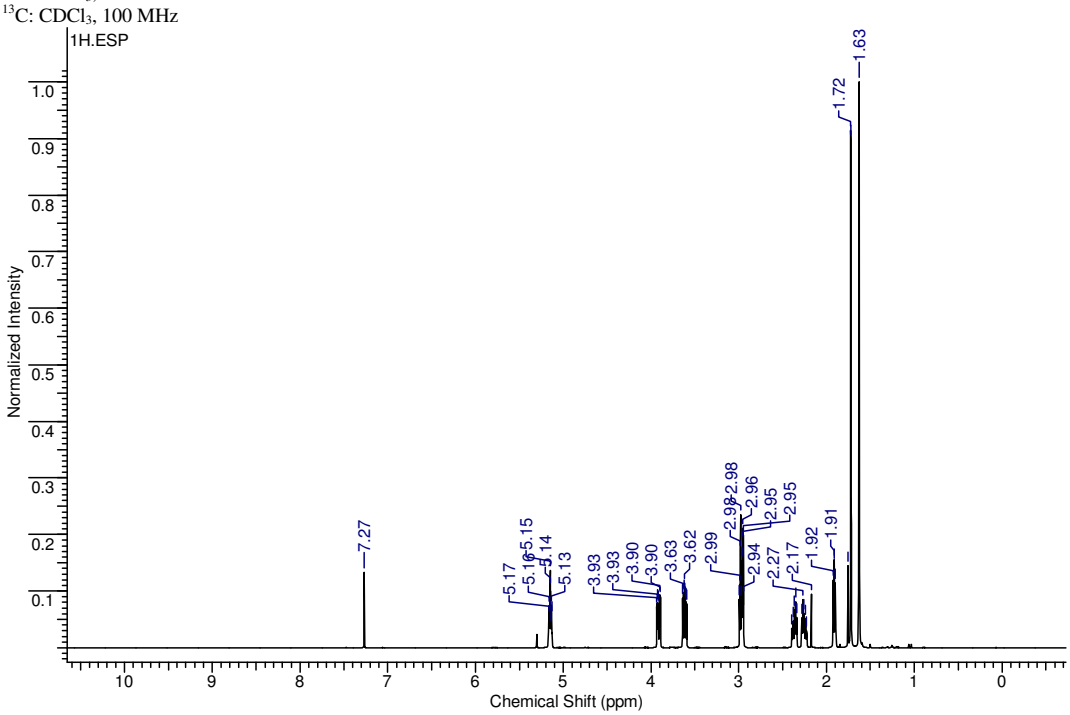


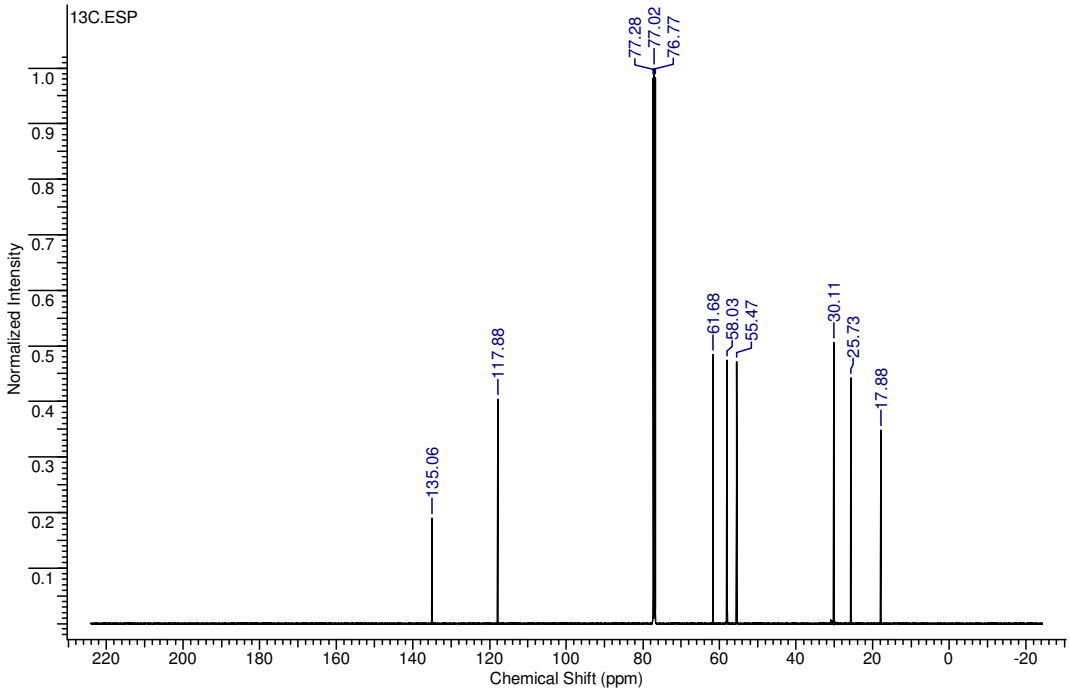


((2*S*,3*S*)-3-(3-Methylbut-2-enyl)oxiran-2-yl)methanol (19)

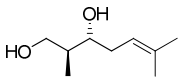


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

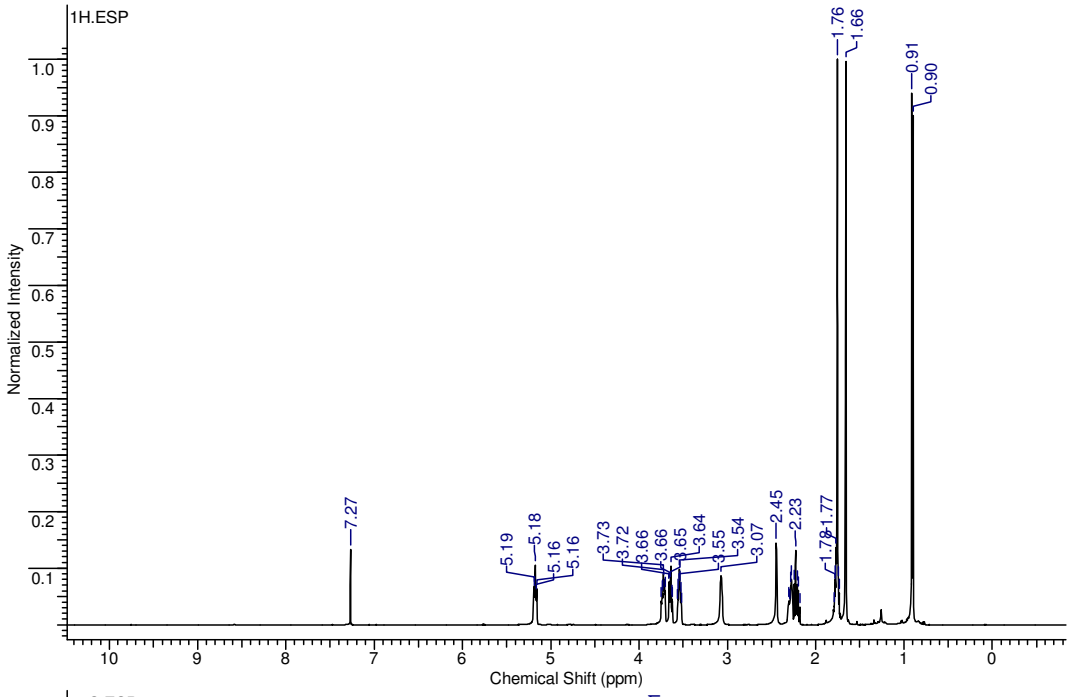


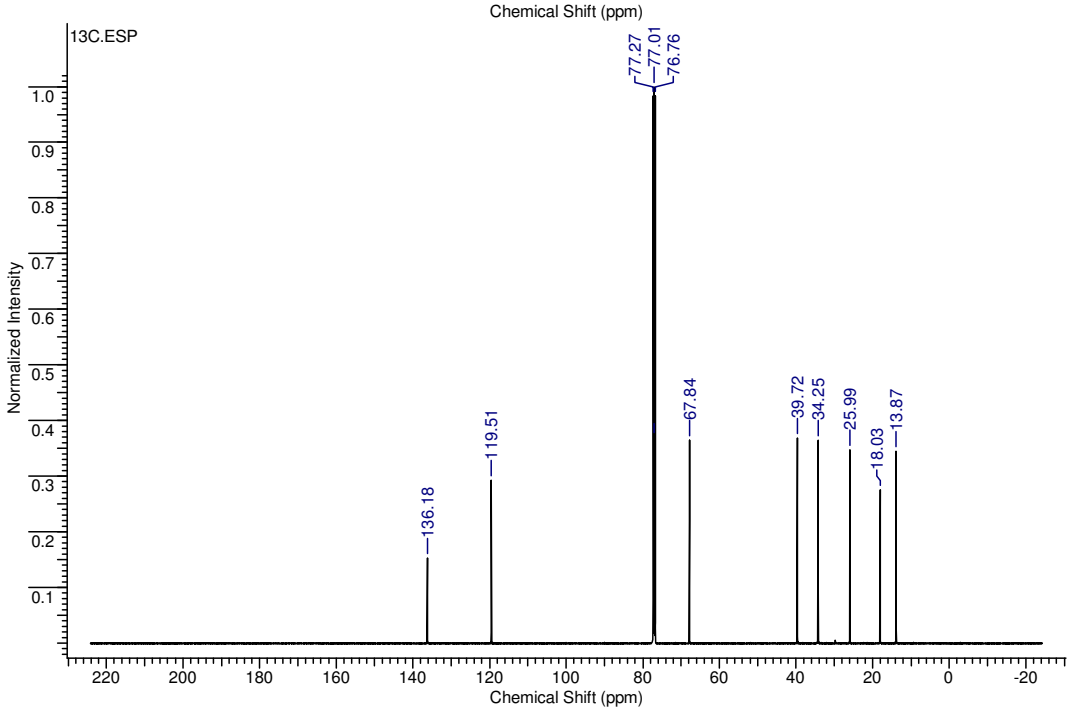


(2*S*,3*R*)-2,6-Dimethylhept-5-ene-1,3-diol (20)

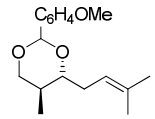


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

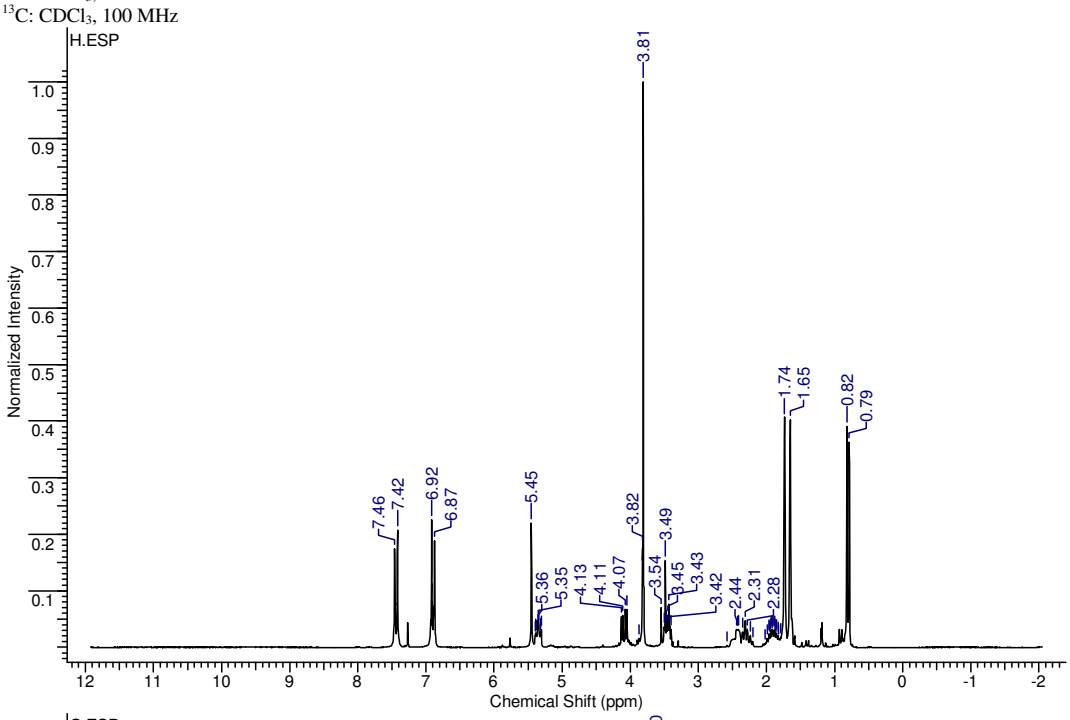


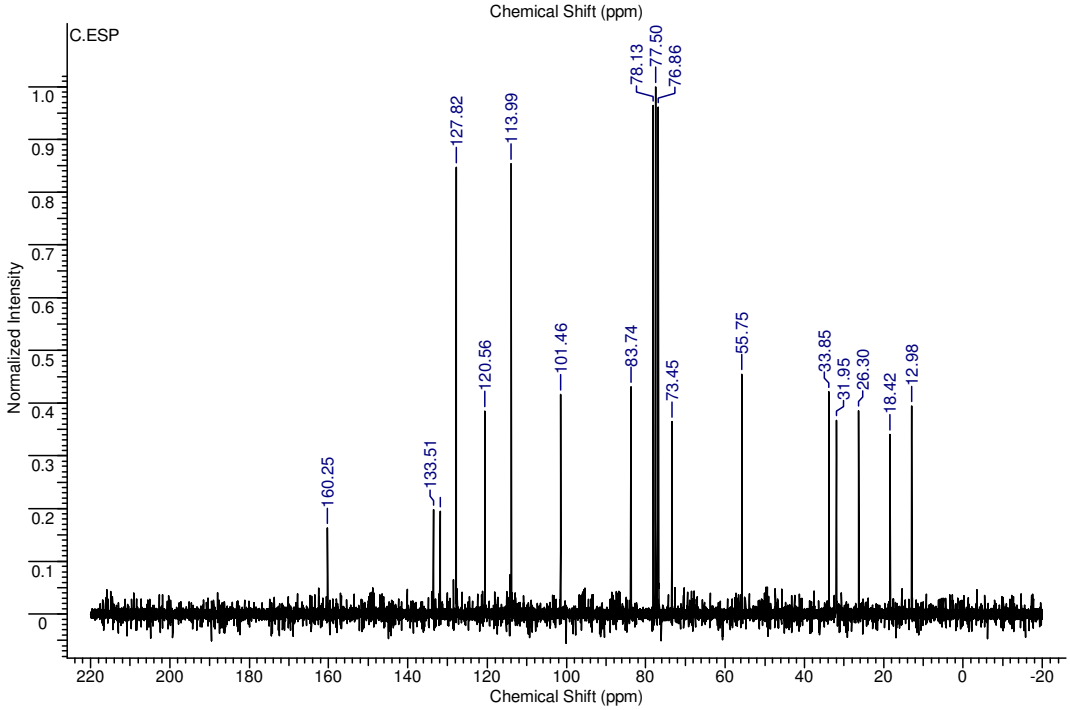


(4*R*,5*S*)-2-(4-methoxyphenyl)-5-methyl-4-(3-methylbut-2-en-1-yl)-1,3-dioxane (21)

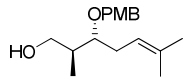


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

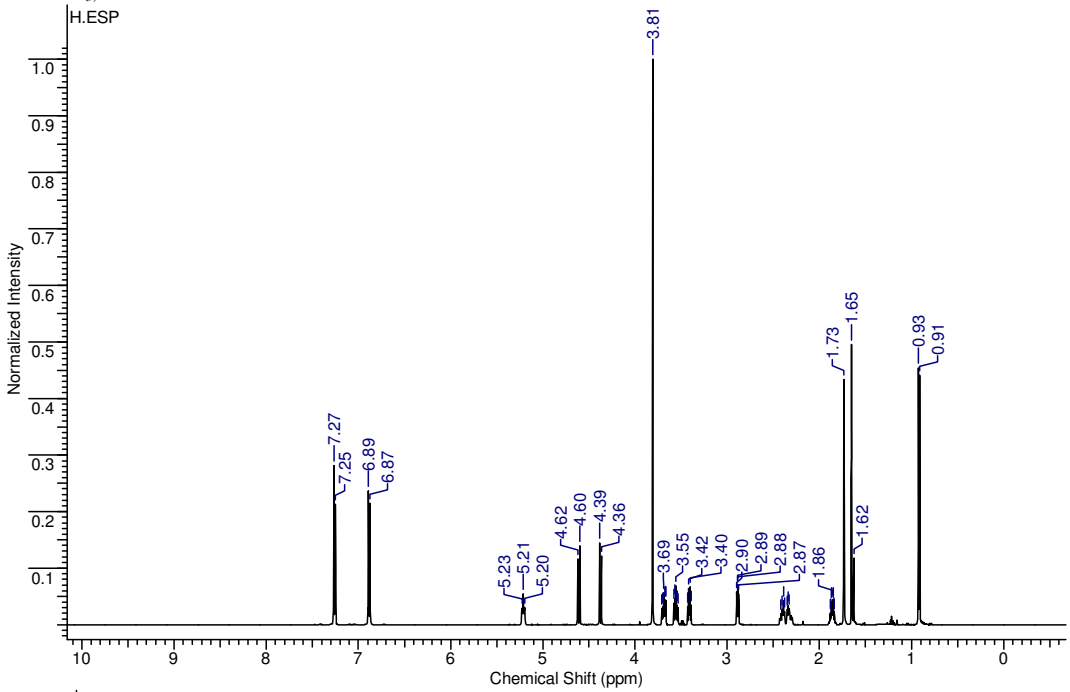


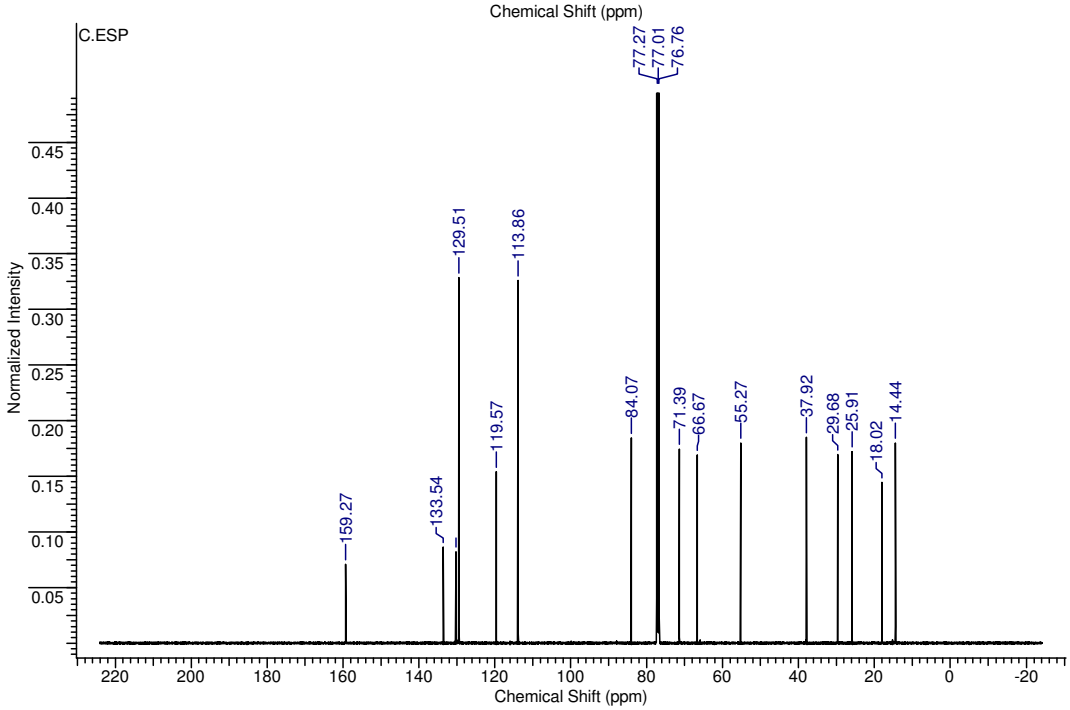


(2*S*,3*R*)-3-((4-methoxybenzyl)oxy)-2,6-dimethylhept-5-en-1-ol (22)

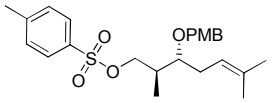


^{1}H: $CDCl_3$, 400 MHz
^{13}C: $CDCl_3$, 100 MHz

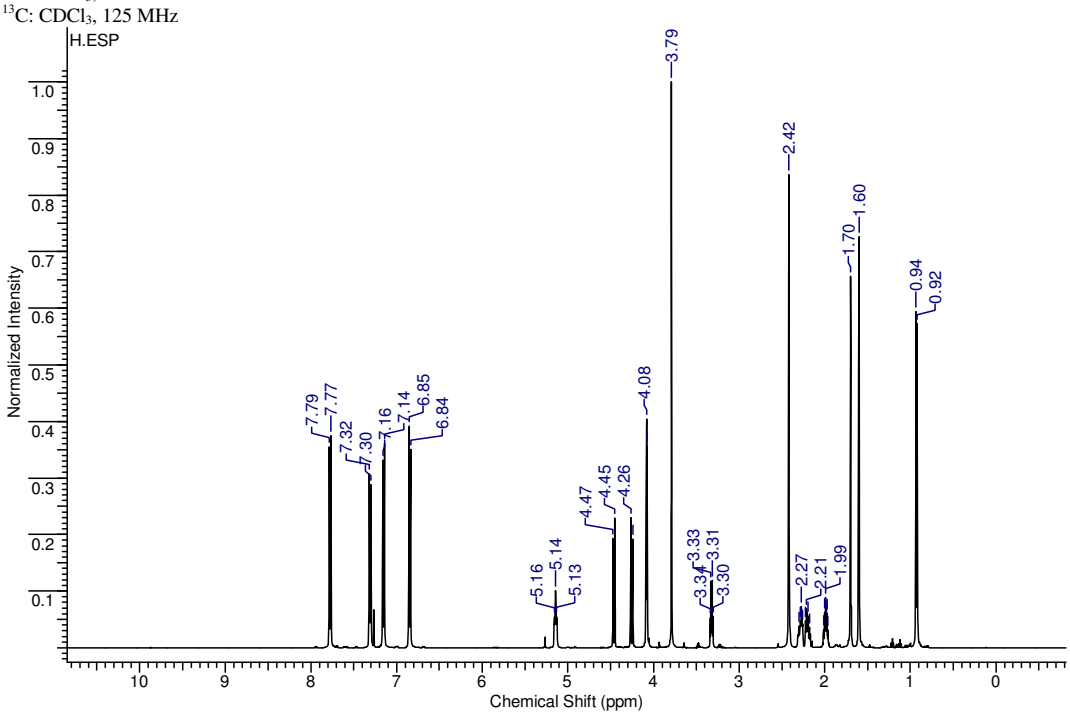


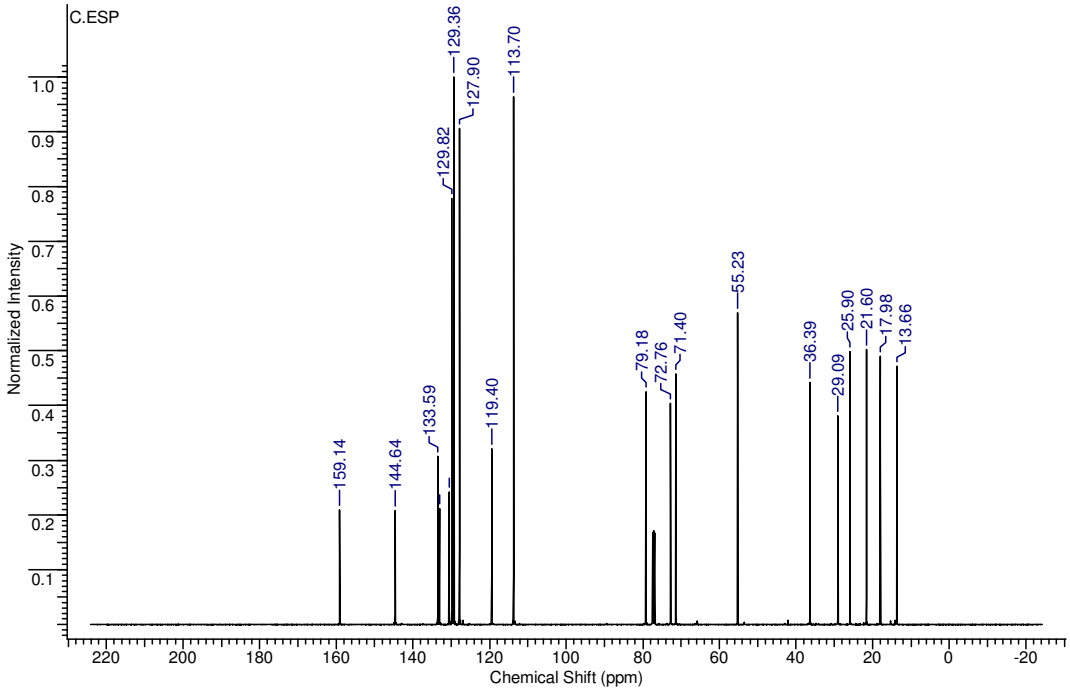


(2*S*,3*R*)-3-((4-methoxybenzyl)oxy)-2,6-dimethylhept-5-en-1-yl 4-methylbenzenesulfonate

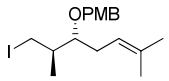


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

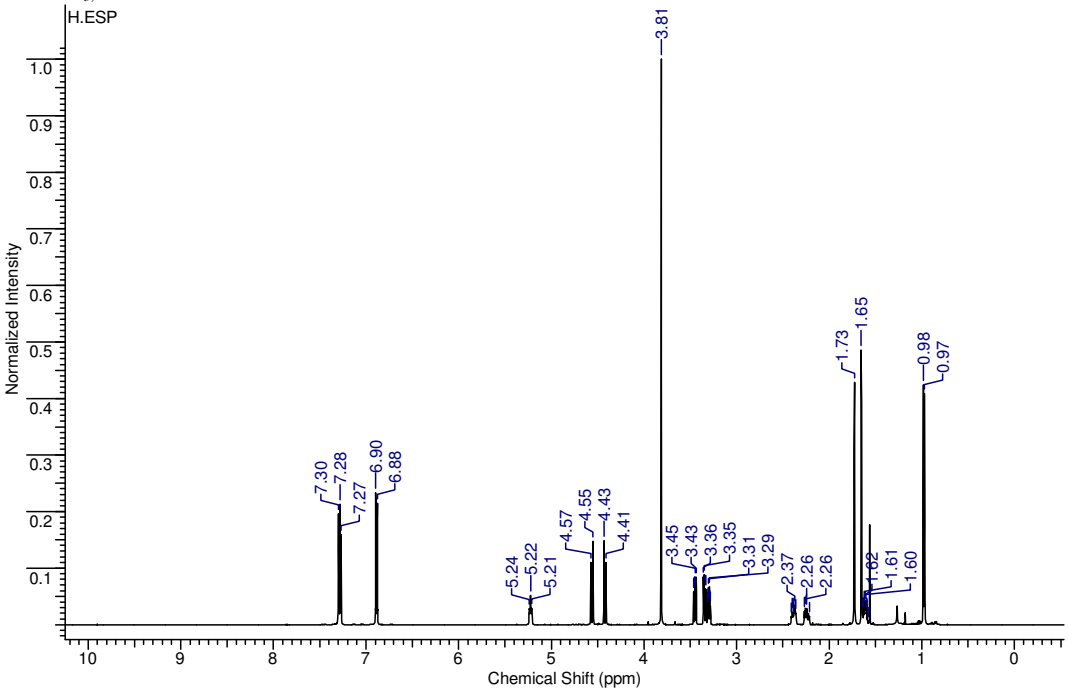


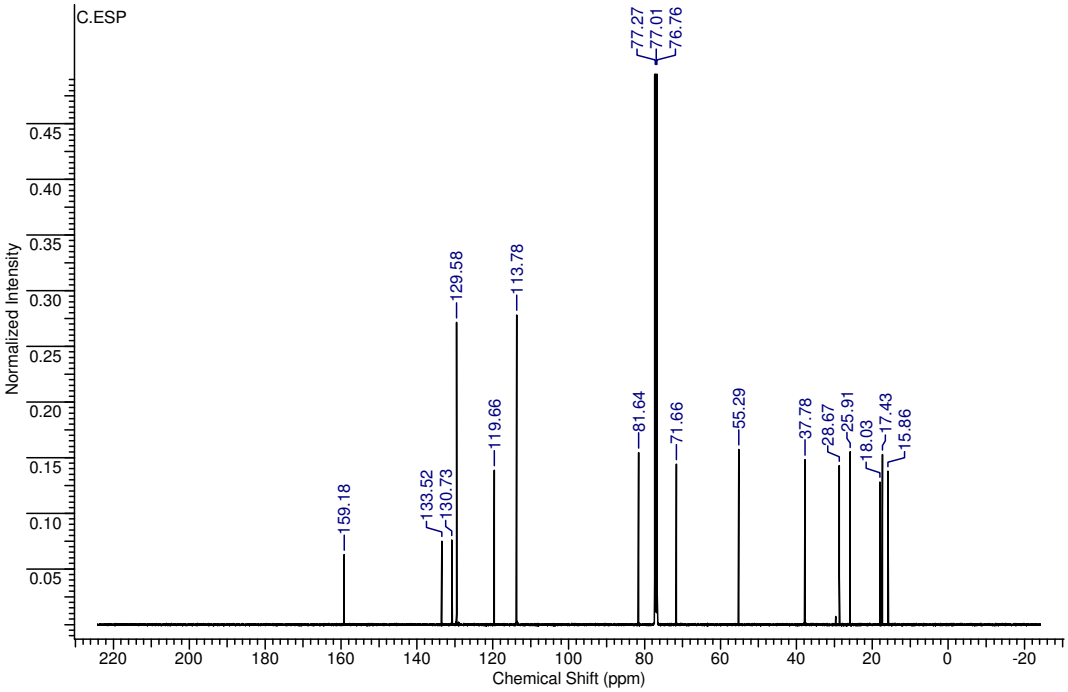


1-((((2*R*,3*R*)-1-iodo-2,6-dimethylhept-5-en-3-yl)oxy)methyl)-4-methoxybenzene (23)

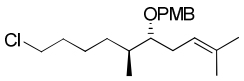


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

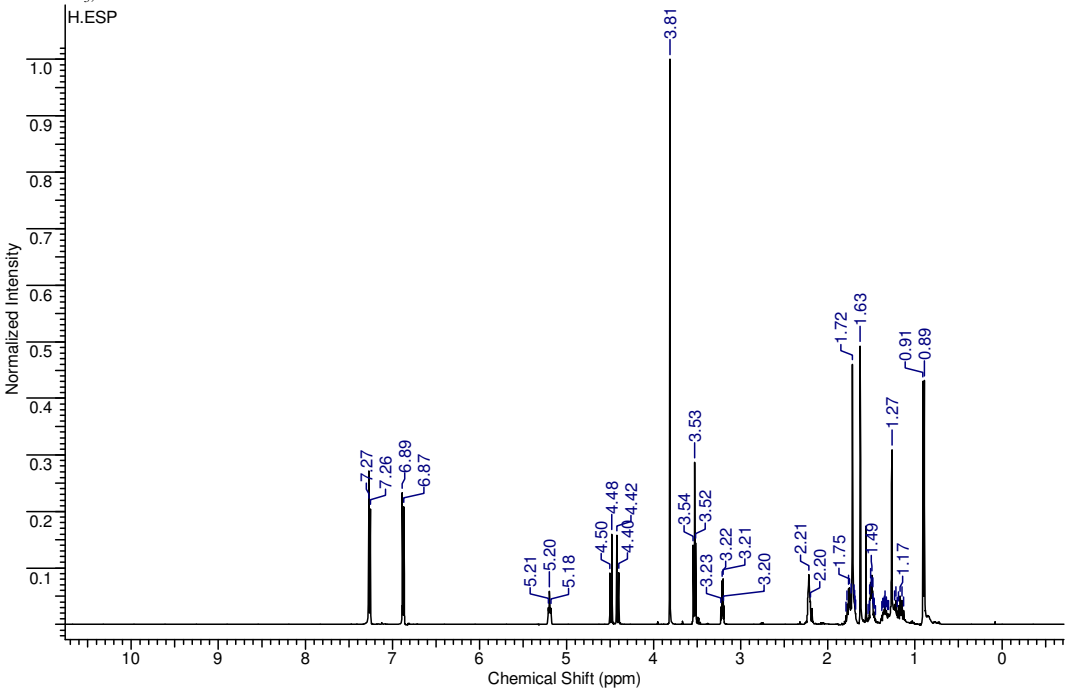


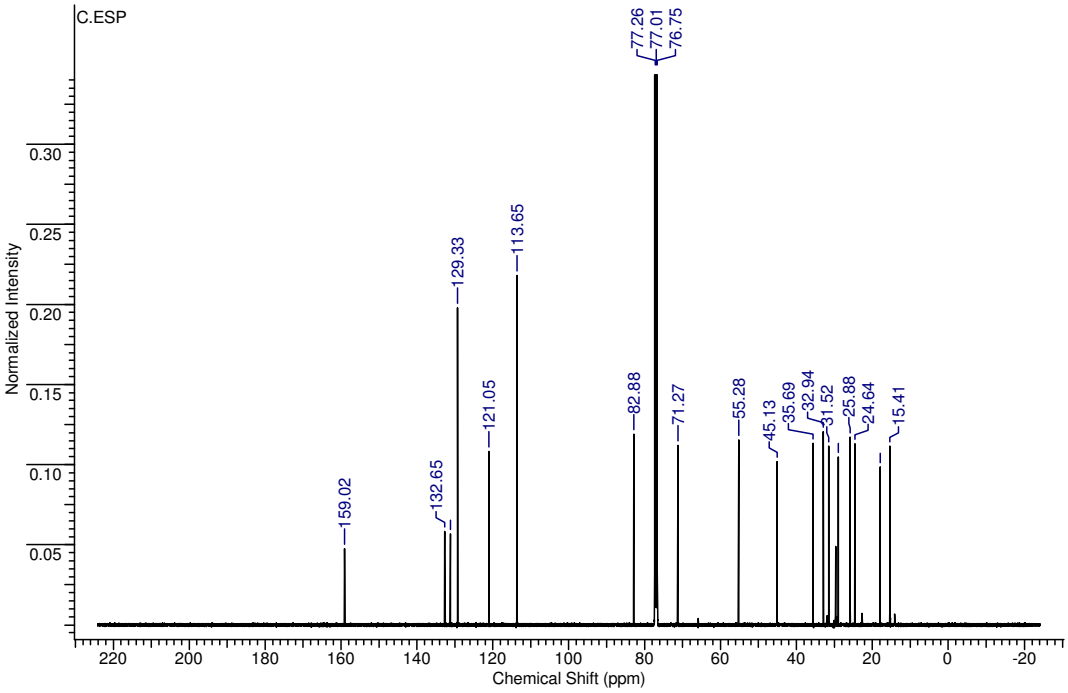


1-((((5*R*,6*S*)-10-chloro-2,6-dimethyldec-2-en-5-yl)oxy)methyl)-4-methoxybenzene (24)

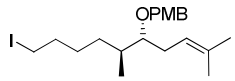


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

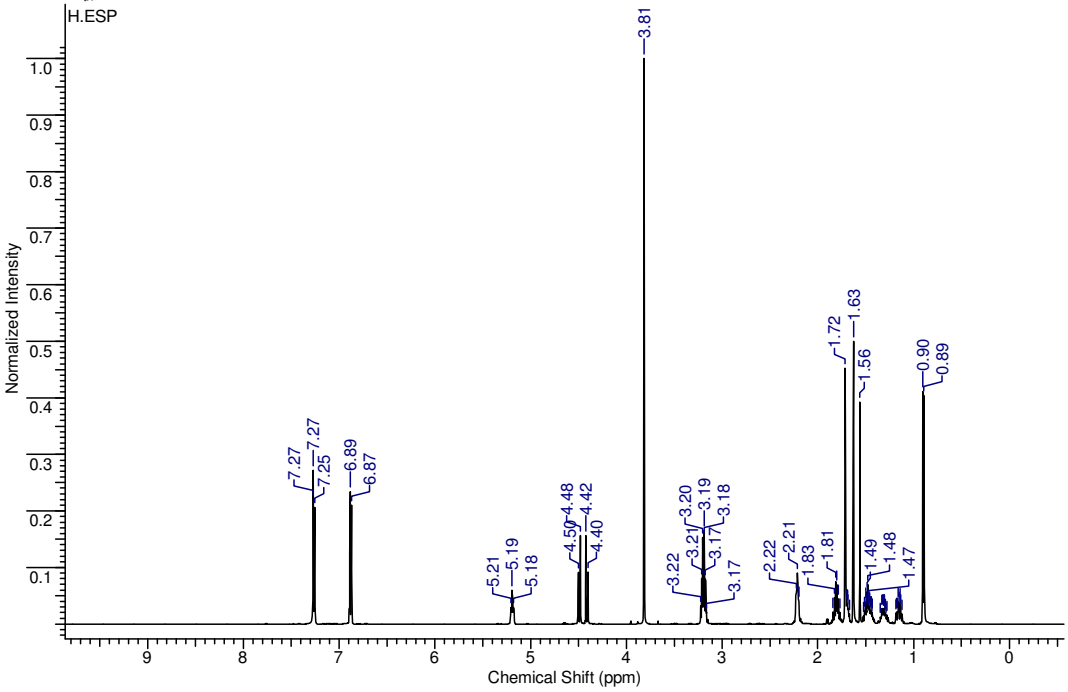


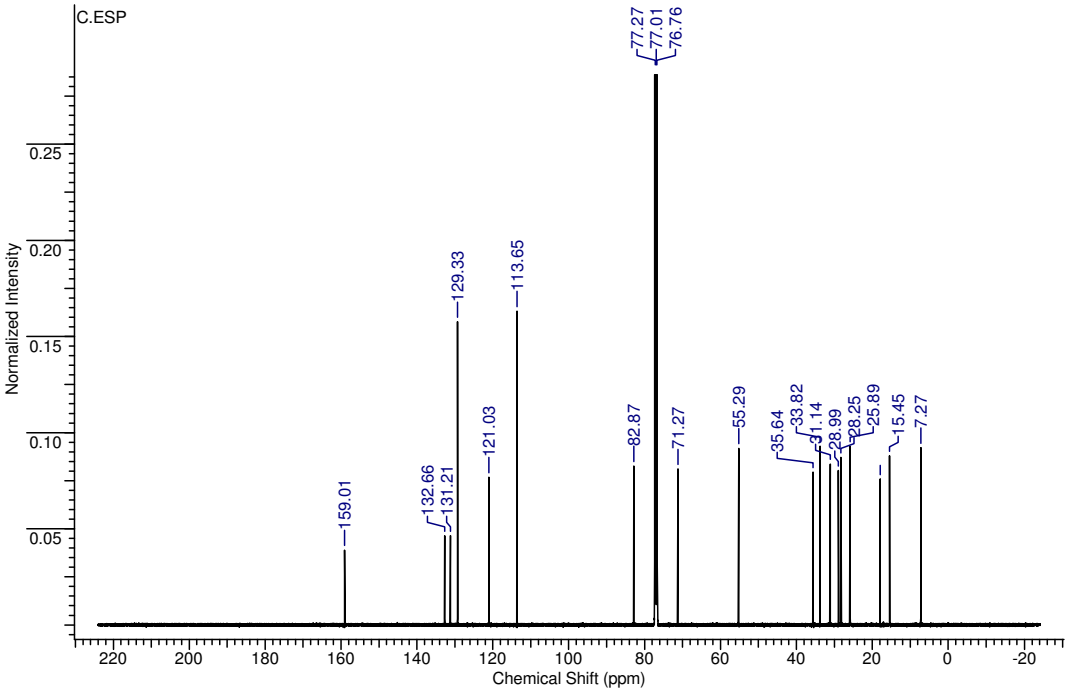


1-((((5*R*,6*S*)-10-iodo-2,6-dimethyldec-2-en-5-yl)oxy)methyl)-4-methoxybenzene

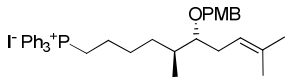


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

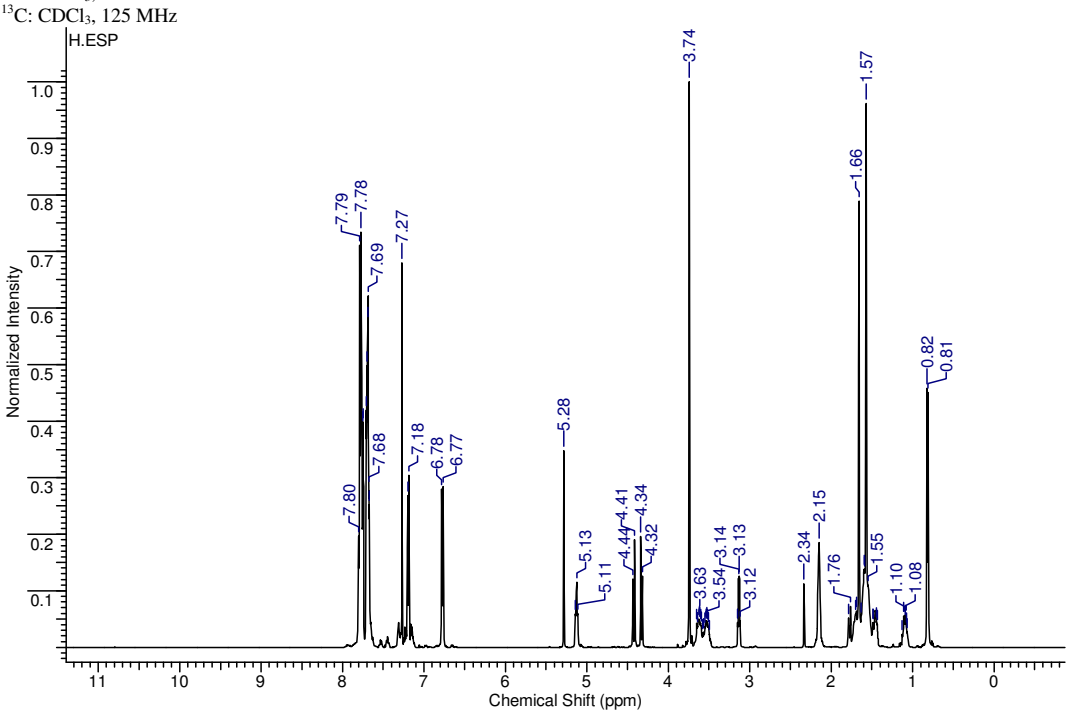


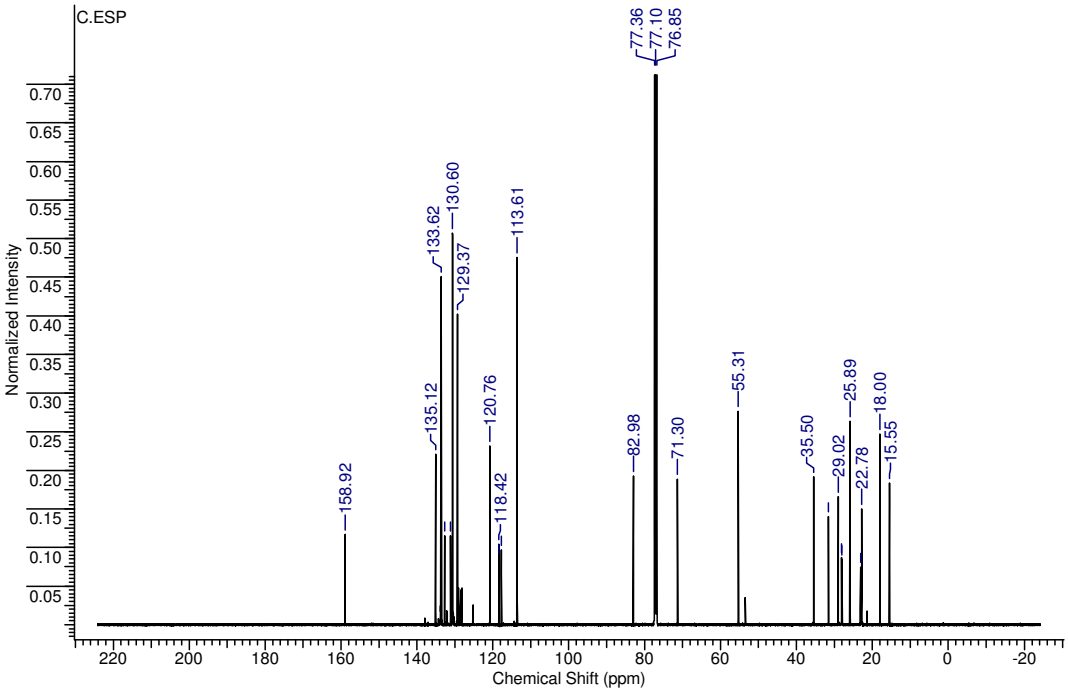


((5*S*,6*R*)-6-((4-methoxybenzyl)oxy)-5,9-dimethyldec-8-en-1-yl)triphenylphosphonium iodide (14)

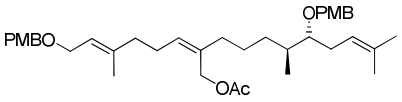


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz

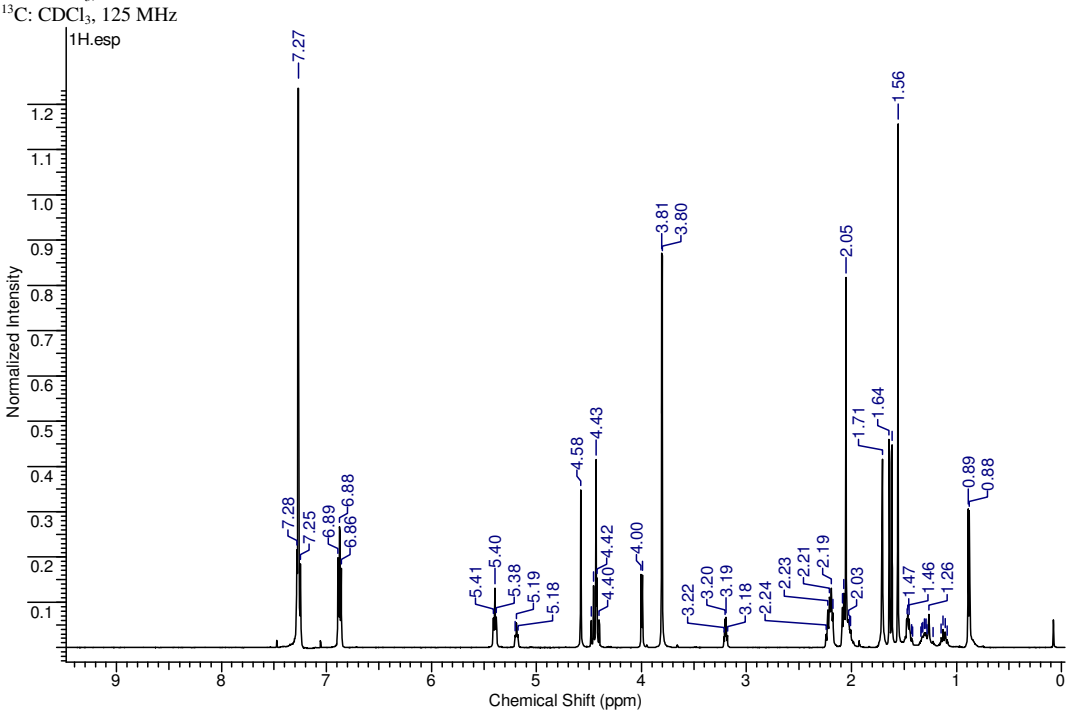


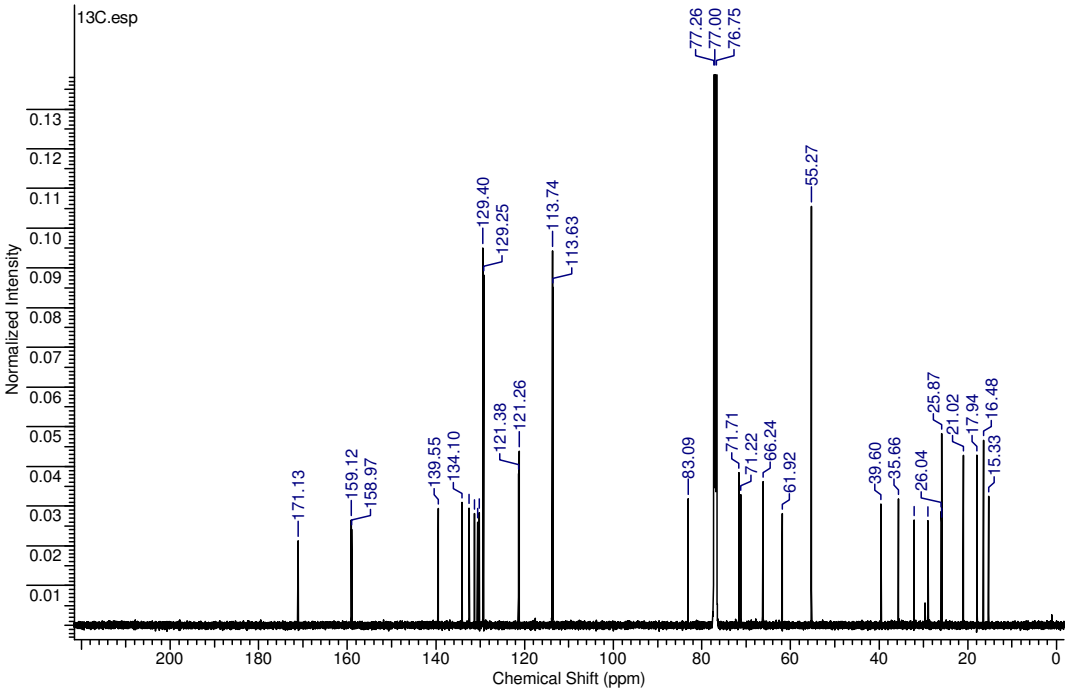


(6*S*,7*R*,*Z*)-7-((4-methoxybenzyl)oxy)-2-((*E*)-6-((4-methoxybenzyl)oxy)-4-methylhex-4-en-1-ylidene)-6,10-dimethylundec-9-en-1-yl acetate (25)

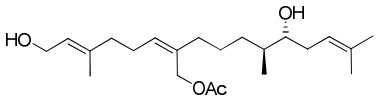


^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz





(6*S*,7*R*,*Z*)-7-hydroxy-2-((*E*)-6-hydroxy-4-methylhex-4-enylidene)-6,10-dimethylundec-9-enyl acetate (12)



^{1}H: $CDCl_3$, 500 MHz
^{13}C: $CDCl_3$, 125 MHz