

Supporting Information

for

Disubstituted Z-allylic esters by Wittig-Schlosser reaction using methylenetriphenylphosphorane

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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: CH₂Cl₂, Et₂O and toluene were distilled from CaH₂ under argon and stored over 3 Å MS. THF was distilled over sodium and benzophenone under an atmosphere of nitrogen. Petrol refers to the fraction that boils at 30-40 °C. PhLi (2.0 M in Bu₂O) was obtained from Acros Organics[®]. Chloromethyl pivalate was purchased from Sigma-Aldrich[®]. Other 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 F₂₅₄). The plates were visualised by irradiation with UV light (254 nm) and by immersion in phosphomolybdic acid or KMnO₄ solutions, followed by heating. Purification of reaction products was carried out by flash chromatography using silica gel (35-70 μM) or neutral alumina. Chiral HPLC was performed using Dionex ASI-100 plus auto sampler. Optical rotations were recorded on a Perkin-Elmer 241 Polarimeter, with a path length of 10 cm in CHCl₃. [α]_D values are given in 10⁻¹ deg cm²g⁻¹. Concentrations (*c*) are given in grams per 100 cm³. 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 ¹³C NMR spectra were recorded in CDCl₃ using Brücker AVC500 spectrometer. Chemical shifts are reported in ppm and referenced to the residual CHCl₃ at δ 7.27 for ¹H NMR spectra, and to the central line of CDCl₃ triplet at 77.0 for ¹³C NMR spectra. Coupling constants (*J*) are given in Hz. The ¹³C NMR peaks were assigned by standard methods using HSQC or 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.

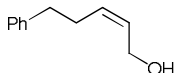
Gas Chromatography: The reported *E/Z* ratios were determined by GC/MS analysis of crude reaction mixtures, using an Agilent HP-5 column (dimethylsilicone capillary column, 30 m x 0.32 mm x 0.25 μm), He, 1 mL/min (initial temperature = 80 °C, max. temperature = 280 °C; rate = 20 °C/min unless otherwise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

2. General Procedure for disubstituted 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 (10 mL/mmol LiBr) was added to the anhydrous methyltriphenylphosphonium bromide (1.0 equiv) and stirred at rt for 10 min before cooling to $-78\text{ }^{\circ}\text{C}$. PhLi (2.0 M in Bu₂O, 1.0 equiv) was then added dropwise at $-78\text{ }^{\circ}\text{C}$, 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 $-78\text{ }^{\circ}\text{C}$ and a solution of the aldehyde (1.0 equiv) in THF (4 mL/mmol aldehyde) was added dropwise. After 10 min, when complete decolourisation had occurred, PhLi (2.0 M in Bu₂O, 1.05 equiv) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$, then allowed to reach rt over 15 min. After 30 min, the resulting β -lithiooxy ylide was re-cooled to $-78\text{ }^{\circ}\text{C}$ and to it was added dropwise a solution of halomethyl ester (1.05 equiv) in THF (4 mL/mmol of electrophile). After 30 min at $-78\text{ }^{\circ}\text{C}$, 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 Et₂O (3x15 mL), dried (MgSO₄) and evaporated under reduced pressure. Purification of the residue by column chromatography gave the disubstituted Z-allylic ester.

3. Characterization data for *Z*-allylic alcohols & esters **7a**, **8**, **9a–9m**, **9a-D**, **10**.

(*Z*)-5-Phenylpent-2-en-1-ol (**7a**)



A solution of anhydrous LiBr (868 mg, 10.0 mmol, 2.0 equiv, obtained by heating LiBr under argon until it melted, followed by cooling) in THF (50 mL) was added to anhydrous methyltriphenylphosphonium bromide (1786 mg, 5.0 mmol, 1.0 equiv) and stirred at rt for 10 min before cooling to $-78\text{ }^{\circ}\text{C}$. PhLi (2.5 mL, 2.0 M in Bu_2O , 5.0 mmol, 1.0 equiv) was then added dropwise at $-78\text{ }^{\circ}\text{C}$, 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 $-78\text{ }^{\circ}\text{C}$ and a solution of 3-phenylpropanal (671 mg, 5.0 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. After 10 min, when complete decolourisation had occurred, PhLi (2.6 mL, 2.0 M in Bu_2O , 5.25 mmol, 1.05 equiv) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$, then allowed to reach rt over 15 min. After 30 min the resulting β -lithiooxy ylide was re-cooled to $0\text{ }^{\circ}\text{C}$ and to it was added dropwise *via* cannula a solution of freshly distilled monomeric formaldehyde¹ (28 mL, $\sim 0.4\text{ M}$ in THF, 11 mmol, 1.1 equiv) at $0\text{ }^{\circ}\text{C}$. After 30 min at $0\text{ }^{\circ}\text{C}$, the temperature was slowly raised to rt and the reaction mixture stirred for further 2 h at rt. The reaction mixture was then poured into water (50 mL), extracted with Et_2O (3x25 mL), dried (MgSO_4) and evaporated under reduced pressure. Purification of the residue by column chromatography gave allylic alcohol **7a**² (147 mg, 18%) as a colourless oil; R_f 0.66 (20% EtOAc /petrol);

IR (film): 3333br, 3062s, 3025s, 2927s, 1603w, 1496s, 1453s, 1029s, 699s.

¹H NMR (500 MHz): 7.32-7.18 (5H, m, ArCH), 5.64-5.55 (2H, m, $\text{CH}=\text{CHCH}_2\text{OH}$), 4.02 (2H, t, J 5, CH_2OH), 2.70 (2H, t, J 7, CH_2Ph), 2.42 (2H, q, J 7, CH_2), 1.26 (1H, br. s, OH).

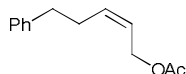
¹³C NMR (125 MHz): 141.5 (ArC), 131.6 ($\text{CH}=\text{CH}$), 129.3 (ArCH), 128.6 (ArCH), 128.3 ($\text{CH}=\text{CH}$), 126.0 (ArCH), 58.4 (CH_2OH), 35.7 (CH_2Ph), 29.3 (CH_2).

MS (Cl^+) 161(2), 180(100), 181(14), 182(2).

HRMS m/z ($\text{M}+\text{NH}_4^+$) found 180.1389, $\text{C}_{11}\text{H}_{18}\text{NO}$ requires 180.1388.

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

(*Z*)-5-Phenylpent-2-enyl acetate (**8**)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and bromomethyl acetate³ (168 mg, 1.1 mmol) to give (*Z*)-5-phenylpent-2-enyl acetate **8** (115mg, 57%) as a colourless oil; R_f 0.19 (5% Et_2O /petrol);

IR (film): 3085m, 3027s, 2931s, 2858s, 2360w, 1738s, 1603m, 1496m, 1372s, 1231s.

¹H NMR (500 MHz): 7.31-7.27 (2H, m, ArCH), 7.22-7.19 (3H, m, ArCH), 5.72-5.66 (1H, m, $\text{CH}=\text{CH}$), 5.58-5.53 (1H, m, $\text{CH}=\text{CH}$), 4.53 (2H, d, J 7, CH_2OAc), 2.70 (2H, t, J 7, CH_2Ar), 2.44 (2H, q, J 7, $\text{CH}_2\text{CH}=\text{CH}$), 2.05 (3H, s, $\text{CH}_3\text{C}=\text{O}$).

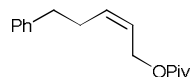
^{13}C NMR (500 MHz): 170.9 (C=O), 141.3 (ArC), 134.0 (CH=CH), 128.5 (ArCH), 128.4 (ArCH), 125.9 (ArCH), 124.1 (CH=CH), 60.2 (CH₂OAc), 35.6 (CH₂Ar), 29.4 (CH₂CH=CH), 21.0 (CH₃C=O).

MS (CI⁺): 204(45), 220(2), 222(100), 223(13).

HRMS m/z (M⁺) found 204.1150, C₁₃H₁₆O₂ requires 204.1150.

The isomeric ratio (*Z/E* 94:6) was determined by GC/MS, $t_{R(\text{minor})}$ = 8.41 min, $t_{R(\text{major})}$ = 8.34 min.

(*Z*)-5-Phenylpent-2-en-1-yl pivalate (**9a**)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (714 mg, 2.0 mmol) was reacted with 3-phenylpropanal (268 mg, 2.0 mmol) and chloromethyl pivalate (316 mg, 2.1 mmol) to give (*Z*)-5-phenylpent-2-en-1-yl pivalate **9a** (370 mg, 75%) as a colourless oil; *R*_f 0.14 (30% CH₂Cl₂/petrol);

IR (film): 3027s, 2969s, 1729s, 1479w, 1455w, 1282m, 1151s.

^1H NMR (500 MHz): 7.31 (2H, m, ArCH), 7.21-7.19 (3H, m, ArCH), 5.69-5.64 (1H, m, CH=CHCH₂OPiv), 5.57-5.52 (1H, m, CH=CHCH₂O), 4.52 (2H, d, *J* 7, CH₂O), 2.70 (2H, t, *J* 8, CH₂Ph), 2.45 (2H, q, *J* 8, PhCH₂CH₂), 1.20 (9H, s, C(CH₃)₃).

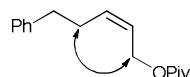
^{13}C NMR (125 MHz): 178.4 (C=O), 141.4 (ArC), 133.7 (CH=CHCH₂O), 128.5 (ArCH), 128.3 (ArCH), 126.0 (ArCH), 124.5 (CH=CHCH₂O), 60.2 (CH₂O), 38.7 (C(CH₃)₃), 35.6 (CH₂Ph), 29.4 (CH₂CH₂Ph), 27.2 (C(CH₃)₃).

MS (CI⁺): 264(100), 265(21), 266(2).

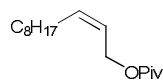
HRMS m/z (M+NH₄⁺) found 264.1963, C₁₆H₂₆NO₂ requires 264.1964.

Single isomer was observed (*Z:E* >99:1) by GC/MS. t_{R} = 8.66 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 4.52 (CH₂O) saw reciprocal signal enhancement at 2.45 (PhCH₂CH₂).



(*Z*)-Undec-2-en-1-yl pivalate (**9b**)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with nonanal (142 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (*Z*)-undec-2-en-1-yl pivalate **9b** (167 mg, 66%) as a colourless oil; *R*_f 0.26 (20% CH₂Cl₂/petrol);

IR (film): 3065s, 3027s, 2957s, 2856s, 1731s, 1151s.

^1H NMR (500 MHz): 5.66-5.61 (1H, m, CH=CHCH₂OPiv), 5.54-5.49 (1H, m, CH=CHCH₂OPiv), 4.61 (2H, d, *J* 7, CH₂OPiv), 2.10 (2H, q, *J* 7, CH₂CH=CH), 1.40-1.21 (12H, m, 6xCH₂), 1.20 (9H, s, C(CH₃)₃), 0.88 (3H, t, *J* 7, CH₃).

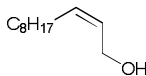
^{13}C NMR (125 MHz): 178.5 (C=O), 135.2 (CH=CHCH₂OPiv), 123.6 (CH=CHCH₂OPiv), 60.4 (CH₂OPiv), 38.7 (C(CH₃)₃), 31.9 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 27.6 (CH₂), 27.2 (C(CH₃)₃), 22.7 (CH₂), 14.1 (CH₃).

MS (CI⁺): 254(3), 272(100), 273(51), 274(1).

HRMS m/z (M^+) found 254.2238, $C_{16}H_{30}O_2$ requires 254.2246.

Single isomer was observed ($Z:E >99:1$) by GC/MS. $t_R = 8.06$ min.

(Z)-Undec-2-en-1-ol (7b)



A solution of anhydrous LiBr (174 mg, 2.0 mmol, 2.0 equiv, obtained by heating LiBr under argon until it melted, followed by cooling) in THF (10 mL) was added to anhydrous methyltriphenylphosphonium bromide (357 mg, 1.0 mmol, 1.0 equiv) and stirred at rt for 10 min before cooling to -78 °C. PhLi (0.5 mL, 2.0 M in Bu_2O , 1.0 mmol, 1.0 equiv) was then added dropwise at -78 °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 °C and a solution of nonanal (142 mg, 1.0 mmol, 1.0 equiv) in THF (10 mL) was added dropwise. After 10 min, when complete decolorization had occurred, PhLi (0.53 mL, 2.0 M in Bu_2O , 1.05 mmol, 1.05 equiv) was added dropwise to form a cherry-red solution. This solution was stirred for 30 min at -78 °C, then allowed to reach rt over 15 min. After 30 min, the resulting β -lithiooxy ylide was re-cooled to -78 °C and to it was added dropwise a solution of chloromethyl pivalate (158 mg, 1.05 mmol) in THF (2 mL) at -78 °C. After 30 min at -78 °C, the temperature was slowly raised to rt over 30 min and the reaction mixture stirred for further 2 h at rt. Petrol (50 mL) was then added, the mixture passed through a pad of silica (5 cm) and evaporated under reduced pressure. The crude ester was dissolved in Et_2O (10 mL), cooled to 0 °C (ice-bath) and to this was added portion-wise KO t -Bu (898 mg, 8 mmol, 8 equiv) and H_2O (0.4 mL) *via* syringe. The resulting slurry was stirred for 5 min at 0 °C, then the ice-bath was removed and the reaction was stirred at rt for 12 h. 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 (Z)-undec-2-en-1-ol **7b**⁴ (107 mg, 63%) as a colourless oil; R_f 0.23 (30% Et_2O /petrol);

IR (film): 3331br, 2925s, 2855s, 1465s, 1037s.

1H NMR (500 MHz): 5.63-5.53 (2H, m, $CH=CH$), 4.20 (2H, d, J 6, CH_2OH), 2.08 (2H, q, J 7, $CH_2CH=CH$), 1.40-1.22 (12H, m, $6 \times CH_2$), 0.89 (3H, t, J 7, CH_3).

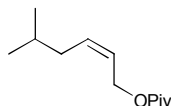
^{13}C NMR (125 MHz): 133.3 ($CH=CHCH_2OH$), 128.3 ($CH=CHCH_2OH$), 58.6 (CH_2OH), 31.9 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.4 ($CH_2CH=CH$), 22.7 (CH_2CH_3), 14.1 (CH_2CH_3).

MS (CI^+): 170(100), 171(13), 172(1).

HRMS m/z (M^+) found 170.1671, $C_{11}H_{22}O$ requires 170.1674.

A single isomer was observed ($Z:E >99:1$) by GC/MS. $t_R = 7.69$ min.

(Z)-5-Methylhex-2-en-1-yl pivalate (9c)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with 3-methylbutanal (86 mg, 1.0 mmol) and chloromethyl pivalate

(158 mg, 1.05 mmol) to give (*Z*)-5-methylhex-2-en-1-yl pivalate **9c** (142 mg, 72%) as a colourless oil; *R_f* 0.22 (20% Et₂O/petrol);

IR (film): 2959s, 1731s, 1480m, 1396m, 1282s, 1153s.

¹H NMR (500 MHz): 5.86-5.62 (1H, m, CH=CHCH₂OPiv), 5.60-5.55 (1H, m, CH=CHCH₂OPiv), 4.60 (2H, d, *J* 6, CH₂OPiv), 2.00 (2H, t, *J* 7, ⁱPrCH₂), 1.69-1.67 (1H, m, CH), 1.20 (9H, s, C(CH₃)₃), 0.91 (6H, d, *J* 7, (CH₃)₂CH).

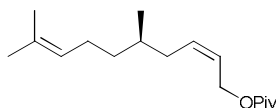
¹³C NMR (125 MHz): 178.5 (C=O), 133.8 (CH=CHCH₂OPiv), 124.3 (CH=CHCH₂OPiv), 60.4 (CH₂OPiv), 38.7 (C(CH₃)₃), 36.6 (ⁱPrCH₂), 28.4 ((CH₃)₂CH), 27.2 (C(CH₃)₃), 22.3 ((CH₃)₂CH).

MS (CI⁺): 199(51), 214(2), 215(1), 216(100), 217(12), 218(2).

HRMS *m/z* (M+H⁺) found 199.1700, C₁₂H₂₃O₂ requires 199.1698.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS. *t_R* = 5.13 min.

(*R,Z*)-5,9-Dimethyldeca-2,8-dien-1-yl pivalate (**9d**)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with (*R*)-3,7-dimethyloct-6-enal (154 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (*R,Z*)-5,9-dimethyldeca-2,8-dien-1-yl pivalate **9d** (266 mg, 78%) as a colourless oil; *R_f* 0.35 (20% CH₂Cl₂/petrol);

IR (film): 2965s, 2915s, 1731s, 1480s, 1459s, 1281m, 1150s, 963m.

[α]_D²⁵ = -8.1 (*c* 0.46, CHCl₃).

¹H NMR (500 MHz): 5.66-5.55 (2H, m, CH=CHCH₂OPiv), 5.10-5.07 (1H, m, C=CH), 4.60 (2H, d, *J* 6, CH₂OPiv), 2.13-1.91 (4H, m, 2xCH₂), 1.68 (3H, s, (CH₃)₂C=), 1.60 (3H, s, (CH₃)₂C=), 1.54-1.47 (1H, m, CHCH₃), 1.39-1.32 (1H, m, 1H of CH₂), 1.24-1.12 (10H, m, (CH₃)₃C, 1H of CH₂), 0.88 (3H, d, *J* 7, CHCH₃).

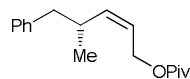
¹³C NMR (125 MHz): 178.5 (C=O), 133.7 (CH=CHCH₂OPiv), 131.2 (C=CH), 124.7 (C=CH), 124.4 (CH=CHCH₂OPiv), 60.4 (CH₂OPiv), 38.7 (C(CH₃)₃), 36.6 (CH₂), 34.8 (CH₂), 32.8 (CHCH₃), 27.2 (C(CH₃)₃), 25.7 (CH₃), 25.6 (CH₂), 19.4 (CH₃CH), 17.6 (CH₃).

MS (CI⁺): 266(2), 282(2), 284(100), 285(18), 286(2).

HRMS *m/z* (M⁺) found 266.2243, C₁₇H₃₀O₂ requires 266.2246.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS. *t_R* = 8.33 min.

(*R,Z*)-4-methyl-5-phenylpent-2-en-1-yl pivalate (9e**)**



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with freshly prepared (*R*)-2-methyl-3-phenylpropanal⁵ (148 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (*R,Z*)-4-methyl-5-phenylpent-2-en-1-yl pivalate **9e** as a colourless oil (185 mg, 71%, the *er* was determined by chiral HPLC on the deprotected alcohol, see below); *R*_f 0.30 (30% CH₂Cl₂/petrol);

IR (film): 2960s, 1728s, 1454m, 1281s, 1148s, 962m.

[α]_D²⁵ = +22.7 (*c* 0.50, CHCl₃).

¹H NMR (500 MHz): 7.28-7.25 (2H, m, ArCH), 7.20-7.13 (3H, m, ArCH), 5.47-5.40 (2H, m, CH=CH), 4.47-4.44 (1H, m, 1H of CH₂OPiv), 4.25-4.21 (1H, m, 1H of CH₂OPiv), 2.82-2.75 (1H, m, CHCH₃), 2.64-2.52 (2H, m, CH₂Ph), 1.17 (9H, s, C(CH₃)₃), 1.02 (3H, d, *J* 7, CHCH₃).

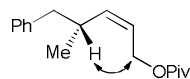
¹³C NMR (125 MHz): 178.4 (C=O), 140.2 (ArC), 139.8 (CH=CHCH₂OPiv), 129.2 (ArCH), 128.1 (ArCH), 125.9 (ArCH), 122.9 (CH=CHCH₂OPiv), 60.3 (CH₂OPiv), 43.6 (PhCH₂), 38.6 (C(CH₃)₃), 34.5 (CHCH₃), 27.2 (C(CH₃)₃), 20.8 (CHCH₃).

MS (CI⁺): 261(4), 278(100), 279(17), 280(2).

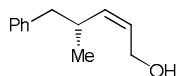
HRMS *m/z* (M+NH₄⁺) found 278.2113, C₁₇H₂₈NO₂ requires 278.2120.

Single isomer was observed (*Z:E* >99:1) by GC/MS. *t*_R = 8.22 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 4.47-4.44 (1H, m, 1H of CH₂OPiv) or 4.25-4.21 (1H, m, 1H of CH₂OPiv) saw reciprocal signal enhancement at 2.82-2.75 (1H, m, CHCH₃).



(*R,Z*)-4-methyl-5-phenylpent-2-en-1-ol



The (*R,Z*)-4-methyl-5-phenylpent-2-en-1-yl pivalate **9e** (65 mg, 0.25 mmol, 1 equiv) was dissolved in Et₂O (5 mL), cooled to 0 °C (ice-bath) and to this was added portion-wise *KOt*-Bu (225 mg, 2 mmol, 8 equiv) and H₂O (0.1 mL) *via* syringe. The resulting slurry was stirred for 5 min at 0 °C, then the ice-bath was removed and the reaction was stirred at rt for 16 h (monitored by TLC). The reaction mixture was then poured into saturated aqueous NH₄Cl (20 mL), extracted with Et₂O (3x15 mL), dried (MgSO₄) and evaporated under reduced pressure. Purification of the residue by column chromatography gave (*R,Z*)-4-methyl-5-phenylpent-2-en-1-ol (40 mg, 91%) as a colourless oil; *R*_f 0.21 (15% EtOAc/petrol);

IR (film): 3333br, 3026m, 2957s, 2925s, 2869m, 1654w, 1603w, 1494m, 1453s, 1372m, 1031s.

[α]_D²⁵ = -6.1 (*c* 0.89, CHCl₃).

¹H NMR (500 MHz): 7.31-7.28 (2H, m, ArCH), 7.22-7.14 (3H, m, ArCH), 5.49 (1H, dt, *J*₁ 10, *J*₂ 7, CH=CHCH₂OH), 5.32 (1H, t, *J* 10, CH=CHCH₂OH), 3.84-3.74 (2H, m, CH₂OH), 2.80-2.70 (2H, m, CHCH₃, 1H of CH₂Ph), 2.43 (1H, dd, *J*₁ 13, *J*₂ 9, 1H of CH₂Ph), 1.07 (3H, d, *J* 6, CHCH₃).

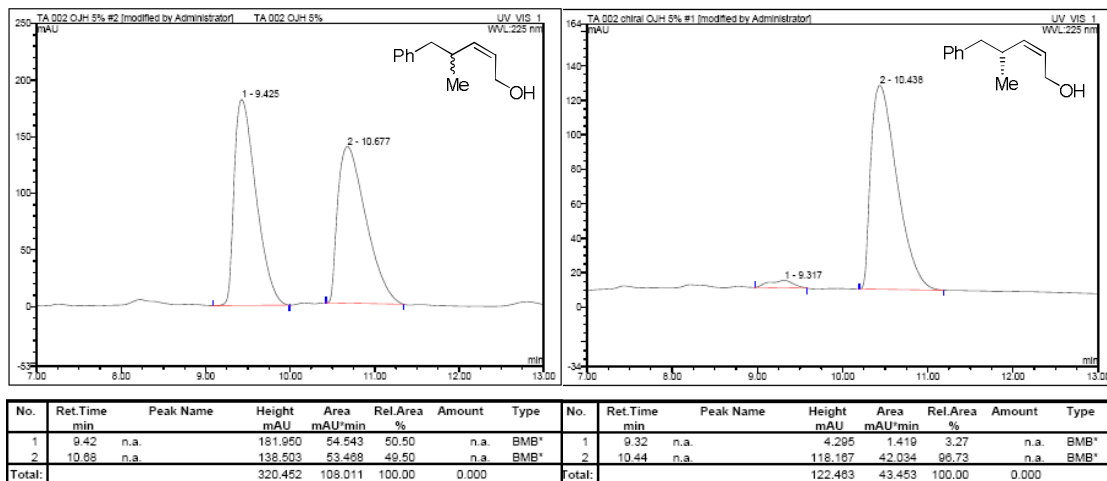
^{13}C NMR (125 MHz): 140.8 (ArC), 137.7 (CH=CHCH₂OH), 129.3 (ArCH), 128.2 (ArCH), 127.7 (CH=CHCH₂OH), 126.1 (ArCH), 58.5 (CH₂OH), 43.8 (CH₂Ph), 34.8 (CHCH₃), 21.3 (CHCH₃).

MS (CI⁺): 176(5), 177(1), 194(89), 195(10), 196(1).

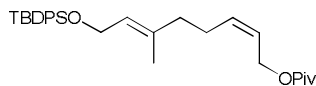
HRMS m/z (M+NH₄⁺) found 194.1551, C₁₂H₂₀NO requires 194.1545.

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

The enantiomeric ratio was determined to be 97:3 by chiral HPLC [DAICEL[®], Chiracel OJ-H column (4.6 mm x 250 mm), 95:5 hexane:*isopropanol*, 1 mL/min], with a UVD-170U UV/VIS detector at 225 nm, t_R 9.32 min (*minor*) and 10.44 min (*major*).



(2*Z*,6*E*)-8-((*tert*-Butyldiphenylsilyl)oxy)-6-methylocta-2,6-dien-1-yl pivalate (9f**)**



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with (*E*)-6-((*tert*-butyldiphenylsilyl)oxy)-4-methylhex-4-enal (366 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (2*Z*,6*E*)-8-((*tert*-butyldiphenylsilyl)oxy)-6-methylocta-2,6-dien-1-yl pivalate **9f** (327 mg, 68%) as a colourless oil; *Rf* 0.19 (30% CH₂Cl₂/petrol);

IR (film): 3071w, 2932s, 2857s, 1730s, 1478m, 1281m, 1149s.

^1H NMR (500 MHz): 7.71-7.69 (4H, m, ArCH), 7.44-7.37 (6H, m, ArCH), 5.63-5.50 (2H, m, CH=CHCH₂OPiv), 5.39 (1H, td, *J*₁ 6, *J*₂ 1, CH=C), 4.60 (2H, d, *J* 6, CH₂OPiv), 4.23 (2H, d, *J* 6, SiOCH₂), 2.21 (2H, q, *J* 7, CH₂), 2.06-2.03 (2H, m, CH₂), 1.45 (3H, s, CH₃), 1.21 (C(CH₃)₃), 1.05 (SiC(CH₃)₃).

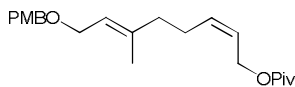
^{13}C NMR (125 MHz): 178.5 (C=O), 136.1 (CH=C), 135.6 (ArCH), 134.3 (ArC), 134.0 (CH=CHCH₂OPiv), 129.5 (ArCH), 127.6 (ArCH), 124.7 (CH=C), 123.9 (CH=CHCH₂OPiv), 61.1 (CH₂OPiv), 60.3 (CH₂OSi), 39.0 (CH₂), 38.7 ((CH₃)₃C-C=O), 27.2 ((CH₃)₃C-C=O), 26.8 ((CH₃)₃CSi), 25.8 (CH₂), 19.2 ((CH₃)₃CSi), 16.2 (CH₃).

MS (CI⁺): 479(2), 496(100), 497(25), 498(5).

HRMS m/z (M+H⁺) found 479.2972, C₃₀H₄₃O₃Si requires 479.2981.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS (initial temperature = 120 °C, max. temperature = 280 °C; rate = 20 °C/min). t_R = 9.59 min.

(2Z,6E)-8-((4-Methoxybenzyl)oxy)-6-methylocta-2,6-dien-1-yl pivalate (9g)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with (*E*)-6-((4-methoxybenzyl)oxy)-4-methylhex-4-enal (248 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (*2Z,6E*)-8-((4-methoxybenzyl)oxy)-6-methylocta-2,6-dien-1-yl pivalate **9g** (269 mg, 75%) as a colourless oil; *R*_f 0.23 (15% Et₂O/petrol);

IR (film): 2971s, 1727s, 1612m, 1513s, 1248s, 1153s, 821m.

¹H NMR (500 MHz): 7.27 (2H, d, *J* 9, *o*-ArCH), 6.88 (2H, d, *J* 9, *m*-ArCH), 5.64-5.59 (1H, m, CH=CHCH₂OPiv), 5.56-5.50 (1H, m, CH=CHCH₂OPiv), 5.41 (1H, td, *J*₁ 7, *J*₂ 1, PMBOCH₂CH=C), 4.60 (2H, d, *J* 7, CH₂OPiv), 4.44 (2H, s, CH₂PMP), 4.00 (2H, d, *J* 7, CH₂OPMB), 3.81 (3H, s, OCH₃), 2.26 (2H, q, *J* 7, CH₂), 2.12-2.09 (2H, m, CH₂), 1.65 (3H, s, CH₃), 1.20 (9H, s, C(CH₃)₃).

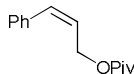
¹³C NMR (125 MHz): 178.4 (C=O), 159.1 (ArC), 139.2 (CH=C), 134.2 (CH=CHCH₂OPiv), 130.6 (ArC), 129.4 (*o*-ArCH), 124.1 (CH=CHCH₂OPiv), 121.6 (CH=C), 113.7 (*m*-ArCH), 71.7 (CH₂PMP), 66.2 (CH₂OPMB), 60.3 (CH₂OPiv), 55.3 (OCH₃), 39.2 (CH₂), 38.7 (C(CH₃)₃), 27.2 (C(CH₃)₃), 25.8 (CH₂), 16.4 (CH₃).

MS (CI⁺): 361(14), 378(100), 379(15), 380(4).

HRMS *m/z* (M+H⁺) found 361.2372, C₂₂H₃₃O₄ requires 361.2379.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS, (initial temperature = 120 °C, max. temperature = 280 °C; rate = 20 °C/min). *t*_R = 10.71 min.

(*Z*)-3-Phenylallyl pivalate (9h)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with freshly distilled benzaldehyde (106 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (*Z*)-3-phenylallyl pivalate **9h**⁶ (127 mg, 58%) as a colourless oil; *R*_f 0.30 (30% CH₂Cl₂/petrol);

IR (film): 2951s, 1763s, 1255s, 1150s.

¹H NMR (500 MHz): 7.38-7.35 (2H, m, ArCH), 7.30-7.24 (3H, m, ArCH), 6.67 (1H, d, *J* 12, PhCH=CH), 5.82 (1H, dt, *J*₁ 12, *J*₂ 7, PhCH=CH), 4.84 (2H, dd, *J*₁ 7, *J*₂ 2, CH₂OPiv), 1.23 (9H, s, C(CH₃)₃).

discernable data for *E*-isomer: 6.23 (1H, d, *J* 6, PhCH=CH), 6.00 (1H, ddd, *J*₁ 17, *J*₂ 10, *J*₃ 6, PhCH=CH), 1.24 (9H, s, C(CH₃)₃).

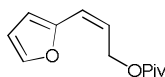
¹³C NMR (125 MHz): 178.4 (C=O), 136.1 (ArC), 132.8 (PhCH=CH), 128.7 (ArCH), 128.4 (ArCH), 127.5 (PhCH=CH), 126.2 (ArCH), 61.4 (CH₂OPiv), 38.7 (C(CH₃)₃), 27.2 (C(CH₃)₃).

MS (CI⁺): 219(2), 233(2), 236(100), 237(13).

HRMS *m/z* (M-H⁺) found 219.1383, C₁₄H₁₉O₂ requires 219.1385.

The isomeric ratio (*Z*:*E* 88:12) was determined by GC/MS. *t*_R(*major*) = 7.58 min, *t*_R(*minor*) = 7.93 min

(Z)-3-(Furan-2-yl)allyl pivalate (9i)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with freshly distilled furfural (96 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (Z)-3-(furan-2-yl)allyl pivalate **9i** (125 mg, 60%) as a light pink oil; *R*_f 0.20 (20% CH₂Cl₂/petrol);

IR (film): 2973s, 1730s, 1480m, 1282s, 1151s, 738s.

¹H NMR (500 MHz): 7.43 (1H, d, *J* 1, CH=CH-O), 6.41 (1H, dd, *J*₁ 3, *J*₂ 2, CH=CHCH₂OPiv), 6.32-6.30 (2H, m, 2xCH), 5.62 (1H, dt, *J*₁ 12, *J*₂ 6, CH=CHCH₂OPiv), 5.05 (2H, dd, *J*₁ 6, *J*₂ 2, CH₂OPiv), 1.23 (9H, s, C(CH₃)₃).

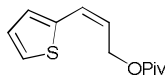
¹³C NMR (125 MHz): 178.4 (C=O), 152.1 (CH=C-O), 142.6 (CH=CH-O), 124.0 (CH=CHCH₂OPiv), 118.9 (CH=CHCH₂OPiv), 111.3 (CH=CH-O), 110.6 (CH-C-O), 62.4 (CH₂OPiv), 38.7 (C(CH₃)₃), 27.2 (C(CH₃)₃).

MS (CI⁺): 207(2), 208(100), 209(25), 210(5), 211(4).

HRMS *m/z* (M+H⁺) found 209.1176, C₁₂H₁₇O₃ requires 209.1178.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS, (initial temperature = 100 °C, max. temperature = 280 °C; rate = 20 °C/min). *t*_R = 4.03 min.

(Z)-3-(Thiophen-2-yl)allyl pivalate (9j)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with thiophene-2-carbaldehyde (112 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (Z)-3-(thiophen-2-yl)allyl pivalate **9j** (125 mg, 56%) as a light yellow oil; *R*_f 0.37 (5% Et₂O/petrol);

IR (film): 2973s, 1730s, 1479m, 1281s, 1150s, 699s.

¹H NMR (500 MHz): 7.34-7.33 (1H, m, CH=CH-S), 7.05-7.01 (2H, m, 12xCH₂), 6.69 (1H, d, *J* 12, CH=CHCH₂OPiv), 5.74-5.69 (1H, m, CH=CHCH₂OPiv), 4.94 (2H, dd, *J*₁ 6, *J*₂ 2, CH₂OPiv), 1.24 (9H, s, C(CH₃)₃).

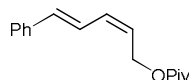
¹³C NMR (125 MHz): 178.4 (C=O), 139.1 (CH=C-S), 128.1 (CH=CHCH₂OPiv), 127.3 (CH=C-S), 126.5 (CH=CHCH₂OPiv), 124.5 (CH=CH-S), 124.3 (CH=CH-S), 61.6 (CH₂OPiv), 38.7 (C(CH₃)₃), 27.2 (C(CH₃)₃).

MS (CI⁺): 224(100), 225(15), 226(4), 227(1).

HRMS *m/z* (M⁺) found 224.0871, C₁₂H₁₆O₂S requires 224.0871.

The isomeric ratio (*Z*:*E* 95:5) was determined by GC/MS, *t*_{R(major)} = 7.83 min, *t*_{R(minor)} = 7.95 min.

(2Z,4E)-5-Phenylpenta-2,4-dien-1-yl pivalate (9k)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with cinnamaldehyde (132 mg, 1.0 mmol) and chloromethyl pivalate

(158 mg, 1.05 mmol) to give (2*Z*,4*E*)-5-phenylpenta-2,4-dien-1-yl pivalate **9k** (133 mg, 54%) as a colourless oil; *R*_f 0.14 (20% CH₂Cl₂/petrol);

IR (film): 2975s, 1730s, 1480w, 1282m, 1267m, 1158s, 738s.

¹H NMR (500 MHz): 7.44 (2H, d, *J* 7, ArCH), 7.34 (2H, t, *J* 7, ArCH), 7.27-7.24 (1H, m, ArCH), 7.07 (1H, dd, *J*₁ 15, *J*₂ 11, PhCH=CH), 6.63 (1H, d, *J* 15, PhCH), 6.34 (1H, t, *J* 11, CH=CHCH₂OPiv), 5.62 (1H, dt, *J*₁ 11, *J*₂ 7, CH=CHCH₂OPiv), 4.84 (2H, dd, *J*₁ 7, *J*₂ 1, CH₂OPiv), 1.23 (9H, s, C(CH₃)₃).

Discernable data for *E*-isomer: 4.73 (1H, dd, *J*₁ 6, *J*₂ 1, CH₂OPiv).

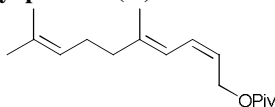
¹³C NMR (125 MHz): 178.5 (C=O), 136.9 (ArC), 134.9 (PhCH=CH), 132.6 (CH=CHCH₂OPiv), 128.7 (ArCH), 128.0 (ArCH), 126.6 (ArCH), 124.9 (CH=CHCH₂OPiv), 123.3 (PhCH=CH), 60.5 (CH₂OPiv), 38.8 (C(CH₃)₃), 27.2 (C(CH₃)₃).

MS (CI⁺): 241(10), 243(55), 244(100), 245(14), 262(17).

HRMS *m/z* (M+NH₄⁺) found 262.1814, C₁₆H₂₄NO₂ requires 262.1807.

The isomeric ratio (*Z*:*E* 92:8) was determined by GC/MS, (initial temperature = 100 °C, max. temperature = 280 °C; rate = 20 °C/min). *t*_{R(major)} = 8.30 min, *t*_{R(minor)} = 8.62 min.

(2*Z*,4*E*)-5,9-Dimethyldeca-2,4,8-trien-1-yl pivalate (**9l**)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with (*E*)-3,7-dimethylocta-2,6-dienal (152 mg, 1.0 mmol) and chloromethyl propionate (129 mg, 1.05 mmol) to give (2*Z*,4*E*)-5,9-dimethyldeca-2,4,8-trien-1-yl pivalate **9l** (138 mg, 53%) as a colourless oil; *R*_f 0.33 (5% Et₂O/petrol);

IR (film): 2974s, 2934m, 1728s, 1282m, 1157s, 738s.

¹H NMR (500 MHz): 6.39 (1H, t, *J* 11, CH=CHCH₂OPiv), 6.10 (1H, d, *J* 11, MeC=CH), 5.44 (1H, dt, *J*₁ 11, *J*₂ 7, CH=CHCH₂OPiv), 5.13-5.07 (1H, m, Me₂C=CH), 4.74 (2H, d, *J* 7, CH₂OPiv), 2.15-2.09 (4H, m, 2xCH₂), 1.78 (3H, s, CH₃), 1.69 (3H, s, CH₃), 1.62 (3H, s, CH₃), 1.21 (9H, s, C(CH₃)₃),

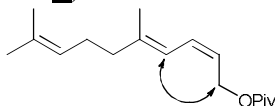
¹³C NMR (125 MHz): 178.5 (C=O), 142.0 (MeC=CH), 131.9 (Me₂C=CH), 128.5 (CH=CHCH₂OPiv), 123.8 (CH=CHCH₂OPiv), 122.1 (Me₂C=CH), 119.2 (MeC=CH), 60.6 (CH₂OPiv), 40.3 (CH₂), 38.7 (C(CH₃)₃), 27.2 (C(CH₃)₃), 27.1 (CH₂), 25.7 (CH₃), 17.7 (CH₃), 16.5 (CH₃).

MS (CI⁺): 262(8), 263(100), 264(13), 265(1).

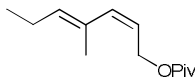
HRMS *m/z* (M⁺) found 264.2080, C₁₇H₂₈O₂ requires 264.2089.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS. *t*_R = 11.03 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 4.74 (CH₂OPiv) saw reciprocal signal enhancement at 6.10 (MeC=CH).



(2Z,4E)-4-Methylhepta-2,4-dien-1-yl pivalate (**9m**)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with freshly distilled (*E*)-2-methylpent-2-enal (98 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (2*Z*,4*E*)-4-methylhepta-2,4-dien-1-yl pivalate **9m** (210 mg, 52%) as a colourless oil; *R*_f 0.38 (20% CH₂Cl₂/petrol);

IR (film): 2974s, 1727s, 1267s, 1158s, 739s.

¹H NMR (500 MHz): 6.02 (1H, d, *J* 12, CH=CHCH₂OPiv), 5.42 (1H, dt, *J*₁ 12, *J*₂ 7, CH=CHCH₂OPiv), 5.33 (1H, t, *J* 7, CH=C), 4.77 (2H, dd, *J*₁ 7, *J*₂ 2, CH₂OPiv), 2.11 (2H, quin, *J* 7, CH₂CH=C), 1.76 (3H, s, CH=CCH₃), 1.21 (9H, s, (CH₃)₃C), 1.00 (3H, t, *J* 7, CH₃).

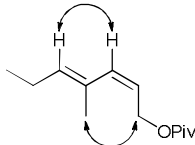
¹³C NMR (125 MHz): 178.4 (C=O), 136.8 (CH=CHCH₂OPiv), 134.4 (CH=C), 131.1 (CH=C), 122.8 (CH=CHCH₂OPiv), 61.6 (CH₂OPiv), 38.7 (C(CH₃)₃), 27.2 (C(CH₃)₃), 21.5 (CH₂CH=C), 16.2 (CH=CCH₃), 14.0 (CH₃CH₂).

MS (CI⁺): 210(100), 211(86), 212(14).

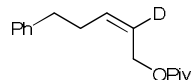
HRMS *m/z* (M⁺) found 210.1621, C₁₃H₂₂O₂ requires 210.1620.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS. *t*_R = 6.11 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 4.77 (CH₂OPiv) saw reciprocal signal enhancement at 1.76 (CH=CCH₃). Irradiation at 6.02 (CH=CHCH₂OPiv) saw reciprocal signal enhancement at 5.33 (C₂H₅CH=C).



(*Z*)-5-Phenylpent-(2*d*₁)-2-en-1-yl pivalate (**9a-D**)



Following the General Procedure for *Z*-allylic ester formation, methyl-(*d*₃)-triphenylphosphonium iodide (407 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and chloromethyl pivalate (158 mg, 1.05 mmol) to give (*Z*)-5-phenylpent-(2*d*₁)-2-en-1-yl pivalate **9a-D** (168 mg, 68%) as a colourless oil; *R*_f 0.37 (5% Et₂O/petrol);

IR (film): 2972s, 2934m, 2871w, 1729s, 1281m, 1151s, 965m.

¹H NMR (500 MHz): 7.31-7.28 (2H, m, ArCH), 7.21-7.18 (3H, m, ArCH), 5.66 (1H, t, *J* 7, CH=CD), 4.52 (2H, s, CH₂OPiv), 2.70 (2H, t, *J* 7, PhCH₂), 2.45 (2H, q, *J* 7, CH₂CH=CD), 1.19 (9H, s, C(CH₃)₃).

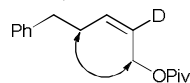
¹³C NMR (125 MHz): 178.4 (C=O), 141.4 (ArC), 133.6 (CH=CD), 128.5 (ArCH), 128.3 (ArCH), 125.9 (ArCH), 124.17 (CH=CD, T, ¹*J*_{CD} 24), 60.1 (CH₂OPiv), 38.7 (C(CH₃)₃), 35.6 (CH₂), 29.3 (CH₂), 27.2 (C(CH₃)₃).

MS (CI⁺): 247(6), 248(100), 249(18).

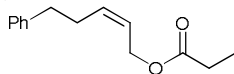
HRMS *m/z* (M⁺) found 247.1675, C₁₆H₂₁DO₂ requires 247.1677.

Single isomer was observed (*Z*:*E* >99:1) by GC/MS. *t*_R = 8.63 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 4.52 ($\underline{\text{CH}}_2\text{OPiv}$) saw reciprocal signal enhancement at 2.45 ($\underline{\text{CH}}_2\text{CH}=\text{CD}$).



(Z)-5-Phenylpent-2-en-1-yl propionate (10)



Following the General Procedure for disubstituted *Z*-allylic ester formation, methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) was reacted with 3-phenylpropanal (134 mg, 1.0 mmol) and chloromethyl propionate⁵ (129 mg, 1.05 mmol) to give (*Z*)-5-phenylpent-2-en-1-yl propionate **10** (118 mg, 54%) as a colourless oil; *R*_f 0.26 (5% Et₂O/petrol);

IR (film): 3063m, 3027m, 2981s, 1737s, 1454s, 1182s, 1080m.

¹H NMR (500 MHz): 7.31-7.27 (2H, m, ArCH), 7.21-7.18 (3H, m, ArCH), 5.71-5.65 (1H, m, CH=CHCH₂O), 5.58-5.53 (1H, m, CH=CHCH₂O), 4.54 (2H, d, *J* 7, CH₂O), 2.70 (2H, t, *J* 7, CH₂Ph), 2.45 (2H, q, *J* 7, CH₂), 2.32 (2H, q, *J* 7, CH₂CH₃), 1.14 (3H, t, *J* 7, CH₃).

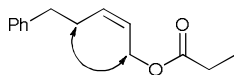
¹³C NMR (125 MHz): 174.3 (C=O), 141.3 (ArC), 133.9 (CH=CHCH₂O), 128.5 (ArCH), 128.3 (ArCH), 126.0 (ArCH), 124.3 (CH=CHCH₂O), 60.1 (CH₂O), 35.6 (CH₂Ph), 29.4 (CH₂), 27.6 (CH₂CH₃), 9.10 (CH₃).

MS (CI⁺): 236(100), 237(10).

HRMS *m/z* (M+NH₄⁺) found 237.1613, C₁₄H₂₂NO₂ requires 236.1651.

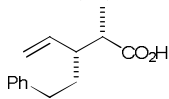
The isomeric ratio (*Z*:*E* 99:1) was determined by GC/MS, *t*_{R(major)} = 8.23 min, *t*_{R(minor)} = 8.29 min.

NOE Experiment: The stereochemistry was assigned as *Z* by NOE studies. Irradiation at 4.54 ($\underline{\text{CH}}_2\text{O}$) saw reciprocal signal enhancement at 2.45 ($\underline{\text{CH}}_2\text{CH}=\text{CHCH}_2\text{O}$).



4. Ireland-Claisen rearrangement of disubstituted *Z*-allylic propionate 10⁷

(±)-(2*R*,3*R*)-2-Methyl-3-phenethylpent-4-enoic acid (**12**)



n-BuLi (0.35 mL, 1.6 M in hexanes, 0.57 mmol, 1.15 equiv) was added dropwise to a solution of diisopropylamine (61 mg, 0.6 mmol, 1.2 equiv) in THF (1 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 **10** (109 mg, 0.5 mmol, 1.0 equiv) in THF (2.0 mL) was added dropwise. After 20 min at -78 °C, TBSOTf⁷ (159 mg, 0.6 mmol, 1.2 equiv) in THF (1.0 mL) was added followed by DMPU (0.96 mL), and the reaction mixture was stirred at -78 °C for a further 5 min. The reaction mixture was then allowed to warm to rt, then heated to reflux at 70 °C for 2 h. The reaction was then allowed to cool to rt, treated with 2 M aq. HCl (15 mL) and stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (4x25 mL). The combined organic extracts were dried (MgSO₄), evaporated under reduced pressure, then purified by column chromatography (30% Et₂O/petrol) to give the acid **12** as a colourless oil (74 mg, 67%, [75% yield based on recovered starting material], the dr was determined on the reduced alcohol, see below). *R*_f 0.31 (30% Et₂O/petrol);

IR (film): 2971s, 2870s, 1704s, 1445s, 1159m.

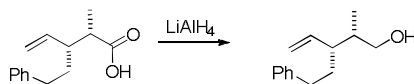
¹H NMR (500 MHz): 7.31-7.28 (2H, m, ArCH), 7.22-7.18 (3H, m, ArCH), 5.73 (1H, dt, *J*₁ 17, *J*₂ 10, CH₂=CH), 5.18 (1H, dd, *J*₁ 10, *J*₂ 2, 1H of CH₂=CH), 5.12 (1H, dd, *J*₁ 17, *J*₂ 1, 1H of CH₂=CH), 2.74-2.68 (1H, m, CHCH₃), 2.57-2.47 (2H, m, PhCH₂), 2.34-2.28 (1H, m, CH), 1.90-1.83 (1H, m, 1H of CH₂CH), 1.69-1.61 (1H, m, 1H of CH₂CH), 1.18 (3H, d, *J* 7, CHCH₃).

¹³C NMR (125 MHz): 181.8 (C=O), 142.2 (ArC), 138.9 (CH₂=CH), 128.40 (ArCH), 128.35 (ArCH), 125.8 (ArCH), 117.3 (CH₂=CH), 46.6 (CH), 43.8 (CHCH₃), 33.5 (CH₂), 33.2 (CH₂), 14.2 (CHCH₃).

MS (CI⁺): 216(5), 217(100), 218(51).

HRMS *m/z* (M+Na⁺) found 241.1200, C₁₄H₁₈NaO₂ requires 241.1199.

(±)-(2*R*,3*R*)-2-Methyl-3-phenethylpent-4-en-1-ol by reduction of acid (**12**)



A stirred suspension of LiAlH₄ (76 mg, 2.0 mmol) in THF (2 mL) at 0 °C was treated dropwise with a solution of the acid **12** (11 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 sat. aq. NH₄Cl (10 mL). The organic layer was separated, and aqueous layer was extracted with Et₂O (2 x 20 mL). The combined organic extracts were dried (MgSO₄), evaporated under reduced pressure, then purified by column chromatography (30% Et₂O/petrol) to give the title alcohol (9 mg, 90%). *R*_f 0.38 (30% Et₂O/petrol);

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

¹H NMR (500 MHz): 7.30-7.27 (2H, m, ArCH), 7.20-7.18 (3H, m, ArCH), 5.71 (1H, dt, *J*₁ 17, *J*₂ 10, CH₂=CH), 5.14 (1H, dd, *J*₁ 10, *J*₂ 2, 1H of CH₂=CH), 5.08 (1H, dd, *J*₁ 17, *J*₂ 2, 1H of CH₂=CH), 3.62 (1H, dd, *J*₁ 11, *J*₂ 6, 1H of CH₂OH), 3.46 (1H, dd, *J*₁ 11, *J*₂ 6, 1H of CH₂OH), 2.73-2.68 (1H, m, 1H of CH₂Ph), 2.50-2.43 (1H, m,

1H of CH_2Ph), 2.04-1.99 (1H, m, CH), 1.86-1.79 (1H, m, $CHCH_3$), 1.69-1.52 (2H, m, CH_2), 1.35 (1H, br. s., CH_2OH), 0.96 (3H, d, J 7, $CHCH_3$).

^{13}C NMR (125 MHz): 142.7 (ArC), 141.2 ($CH_2=CH$), 128.4 (ArCH), 128.3 (ArCH), 125.7 (ArCH), 116.1 ($CH_2=CH$), 66.4 (CH_2OH), 46.7 (CH), 39.8 ($CHCH_3$), 33.7 (CH_2), 33.1 (CH_2Ph), 14.9 ($CHCH_3$).

MS (Cl^+): 205(3), 220(24), 221(6), 222(100), 223(18), 224(3).

HRMS m/z ($M+H^+$) found 205.1587, $C_{14}H_{21}O$ requires 205.1587.

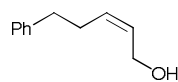
The dr >99:1 was determined by GC/MS, $t_R = 8.06$ min.

5. Reference

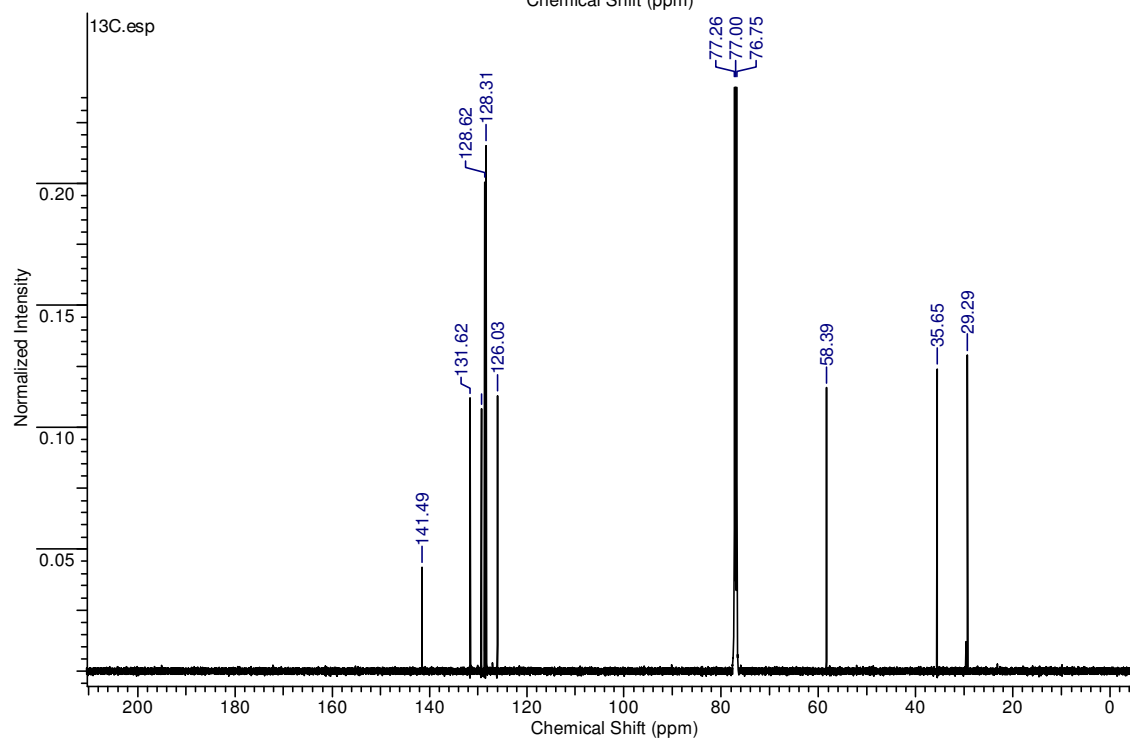
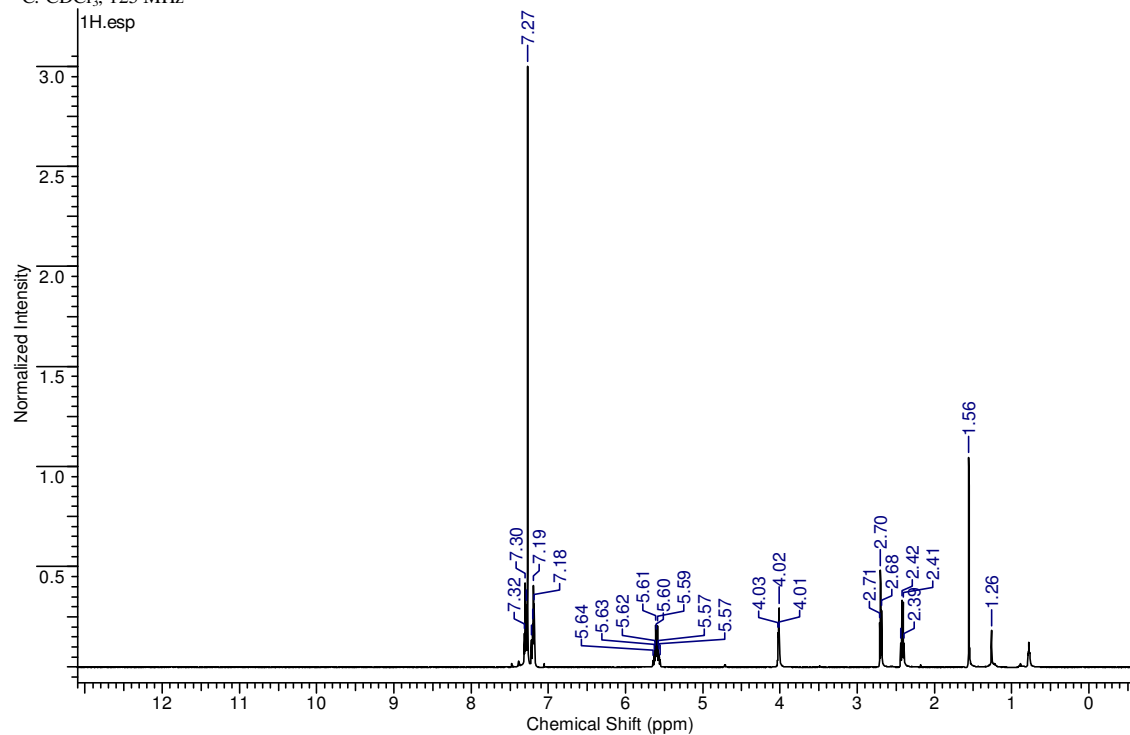
1. M. Schlosser, T. Jenny and Y. Guggisberg, *Synlett*, 1990, 704.
2. I. S. Kim, G. R. Dong and Y. H. Jung, *J. Org. Chem.*, 2007, **72**, 5424.
3. G. Sosnovsky, N. U. M. Rao, S. W. Li and H. M. Swartz, *J. Org. Chem.*, 1989, **54**, 3667.
4. R. Takeuchi and M. Kashio, *J. Am. Chem. Soc.*, 1998, **120**, 8647.
5. A. G. Myers, B. H. Yang and H. Chen, *Org. Synth.* 2000, **77**, 29.
6. T. L. Underiner, S. D. Paisley, J. Schmitter, L. Lesheski and H. L. Goering, *J. Org. Chem.* 1989, **54**, 2369.
7. Use of TMSCl (2 equiv) in this process (*cf* D. M. Hodgson and T. Arif, *Org. Lett.*, 2010, **13**, 4204.) gave acid **12** in higher yield (78%), but was less diastereoselective (85:15, determined on the reduced alcohol by GC/MS).

6. ^1H and ^{13}C NMR spectra of disubstituted *Z*-allylic alcohol & esters 7a, 8, 9a–9m, 9a-D, 10.

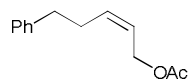
(*Z*)-5-Phenylpent-2-en-1-ol (7a)²



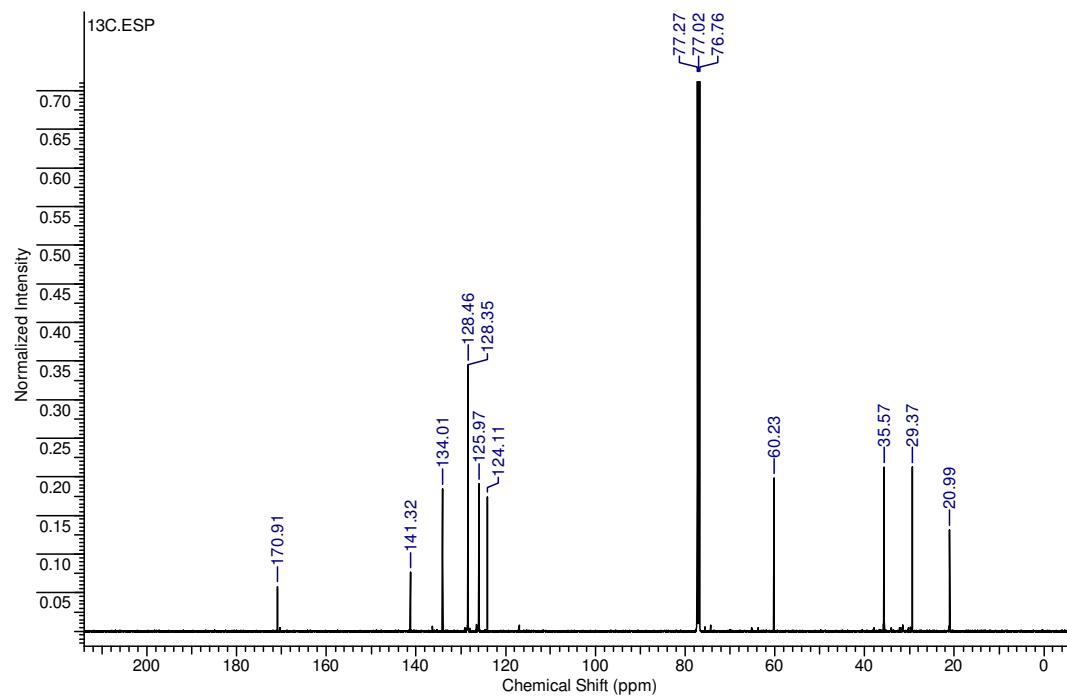
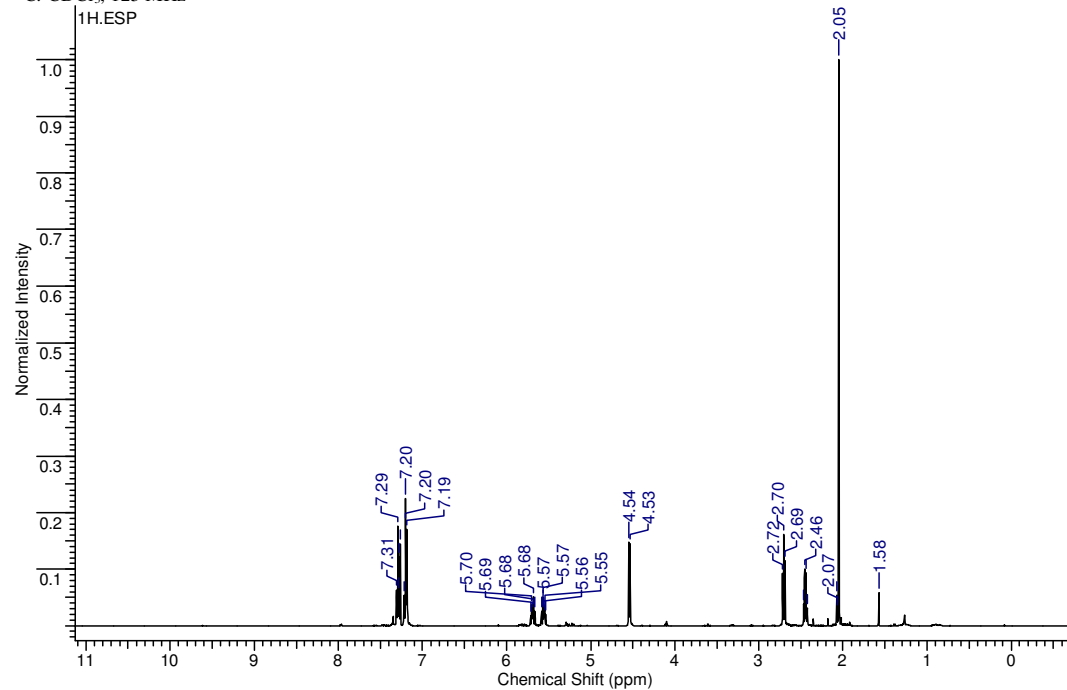
^1H : CDCl_3 , 500 MHz
 ^{13}C : CDCl_3 , 125 MHz



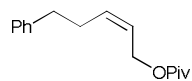
(Z)-5-Phenylpent-2-enyl acetate (8)



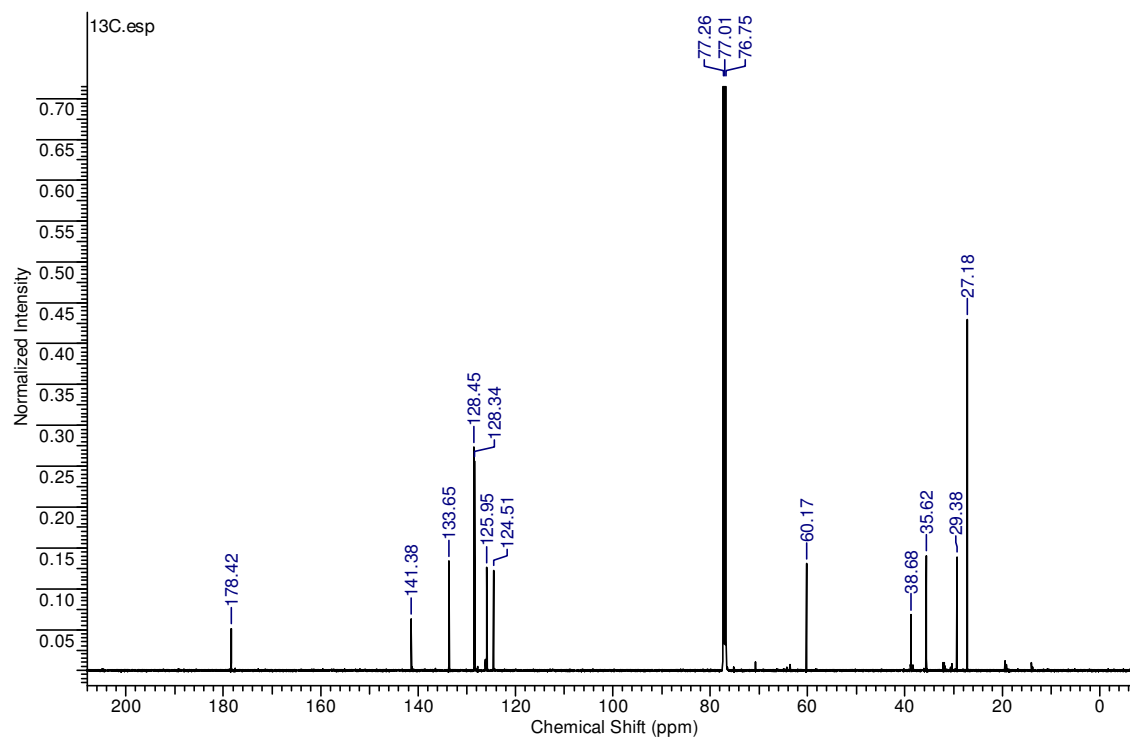
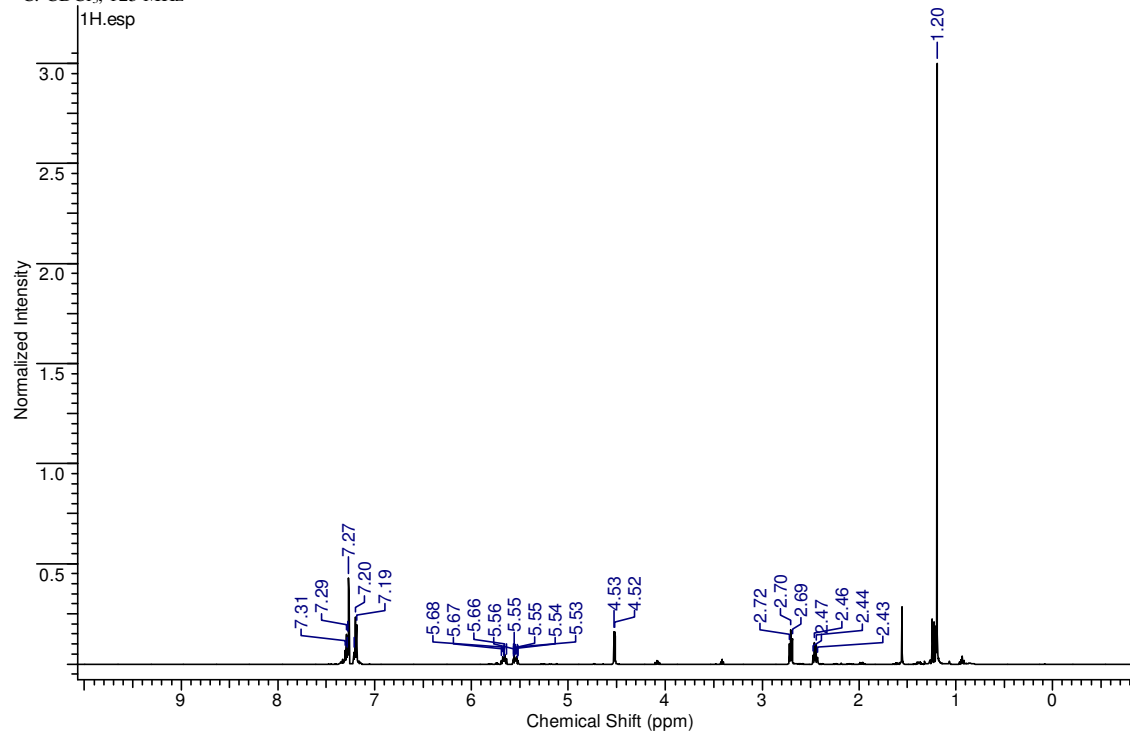
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



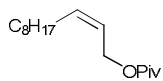
(Z)-5-Phenylpent-2-en-1-yl pivalate (9a)



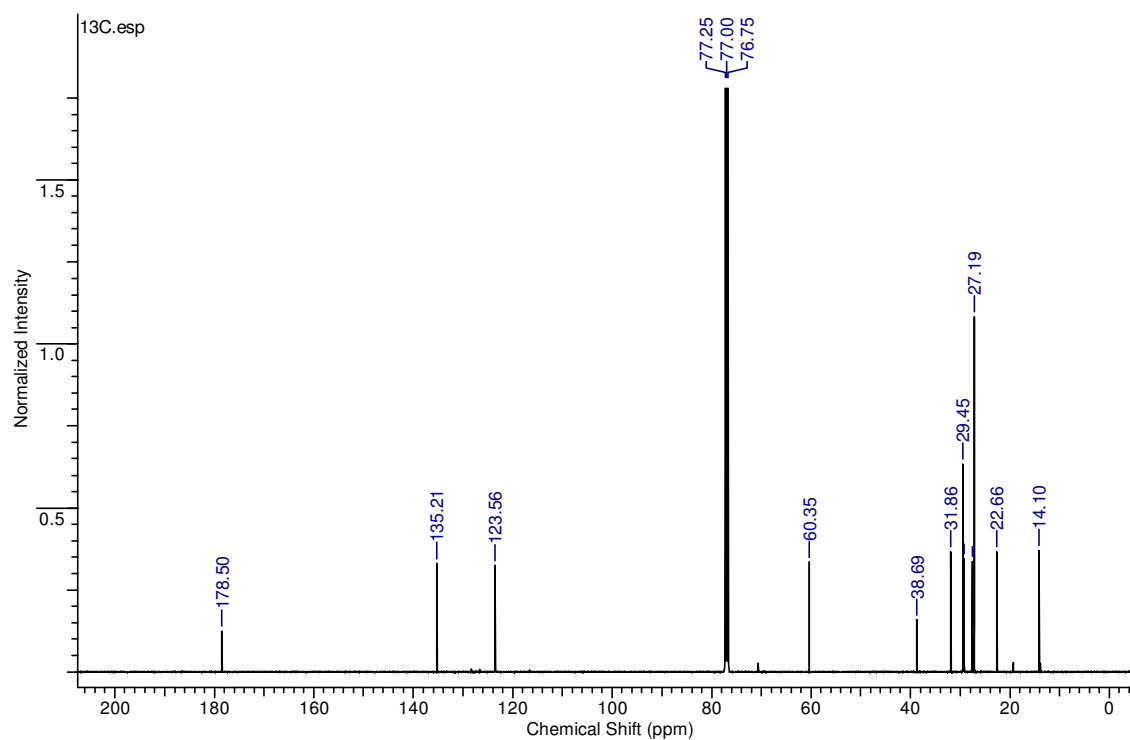
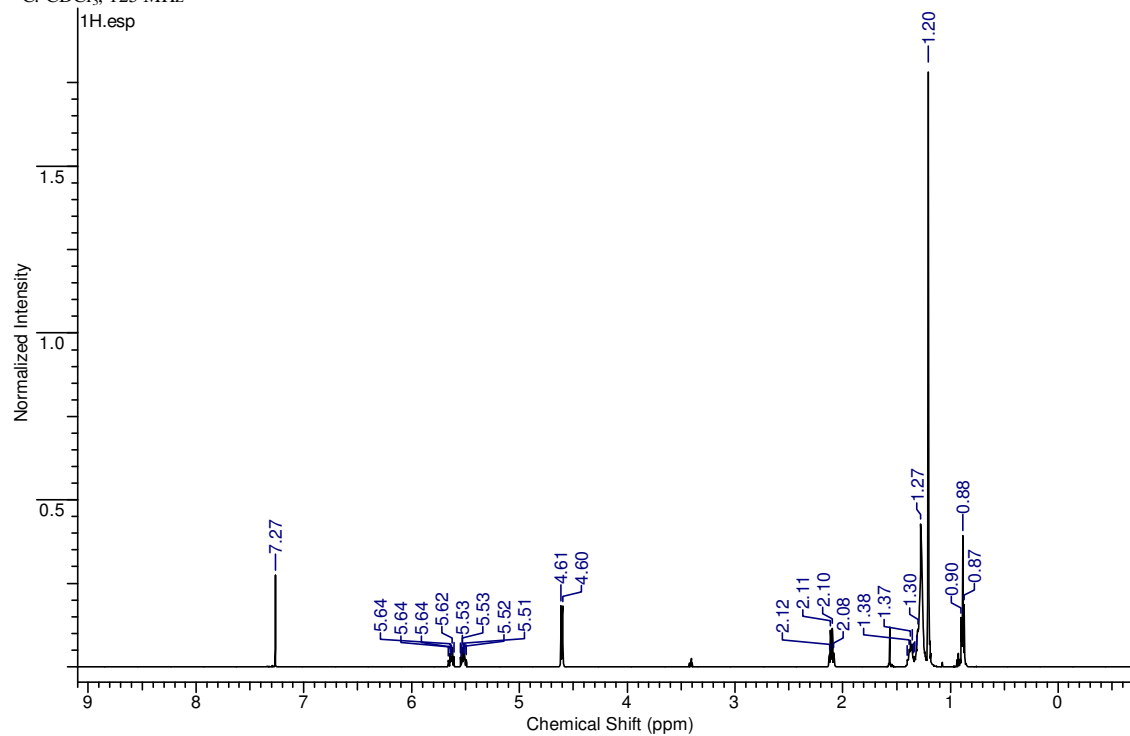
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



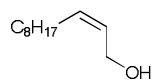
(Z)-Undec-2-en-1-yl pivalate (9b)



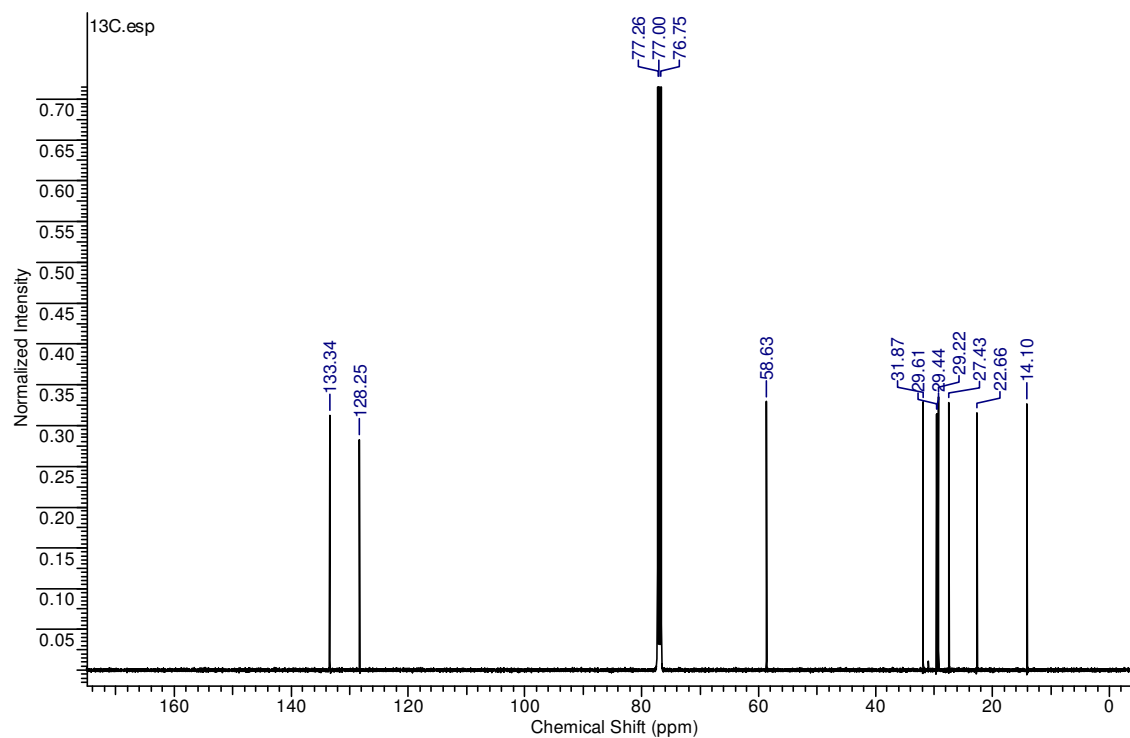
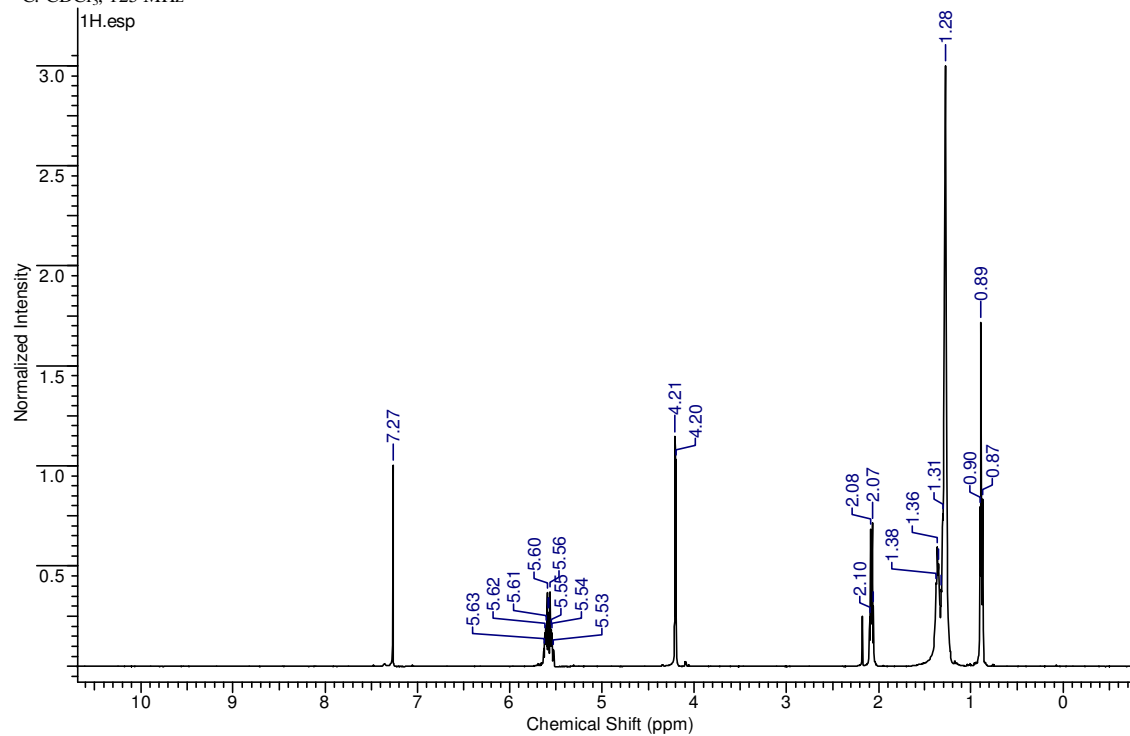
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



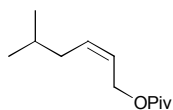
(Z)-Undec-2-en-1-ol (7b)⁴



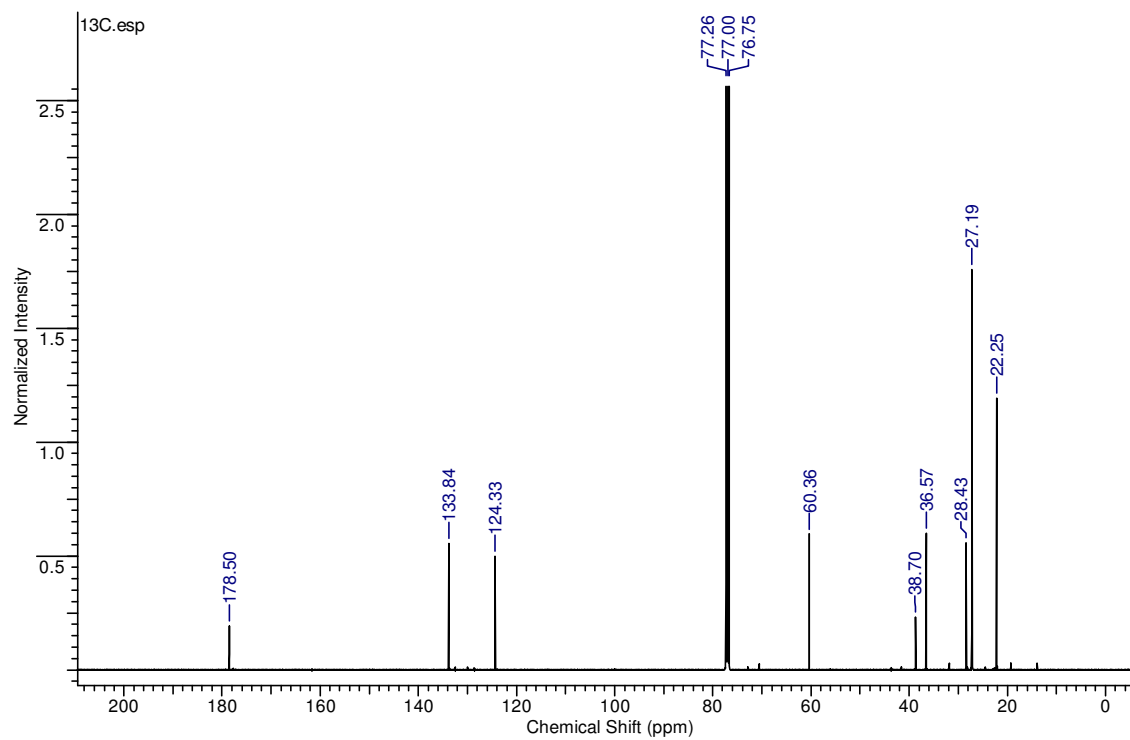
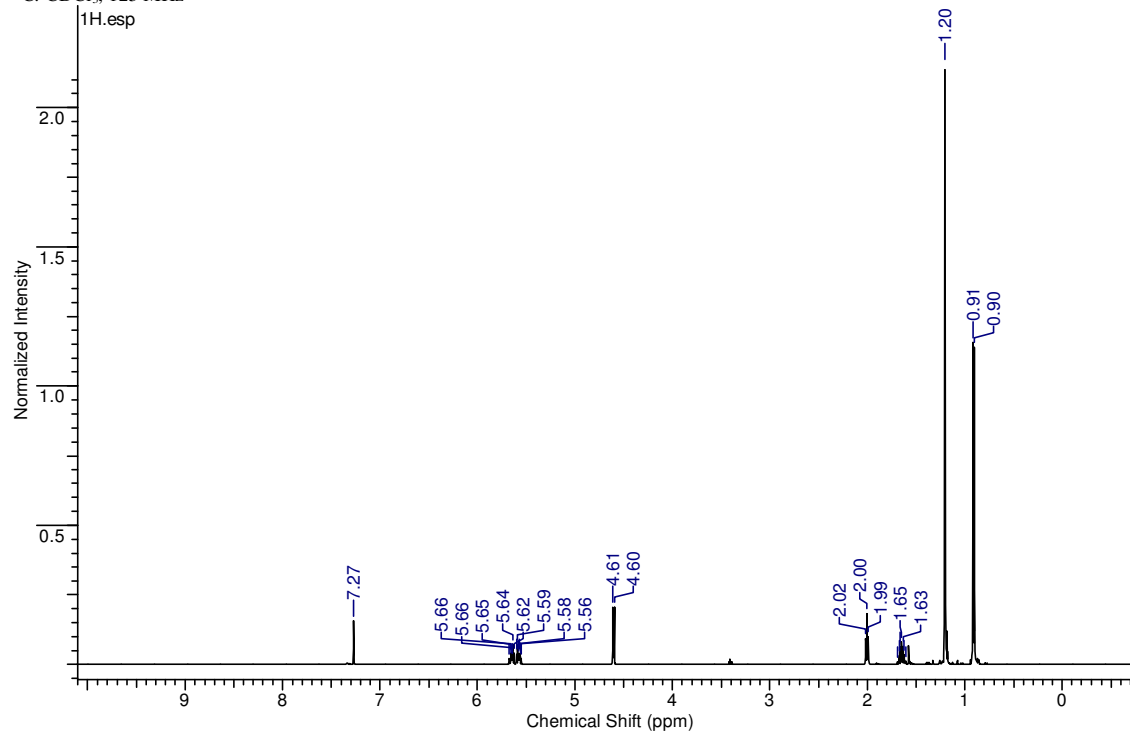
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



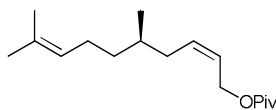
(Z)-5-Methylhex-2-en-1-yl pivalate (9c)



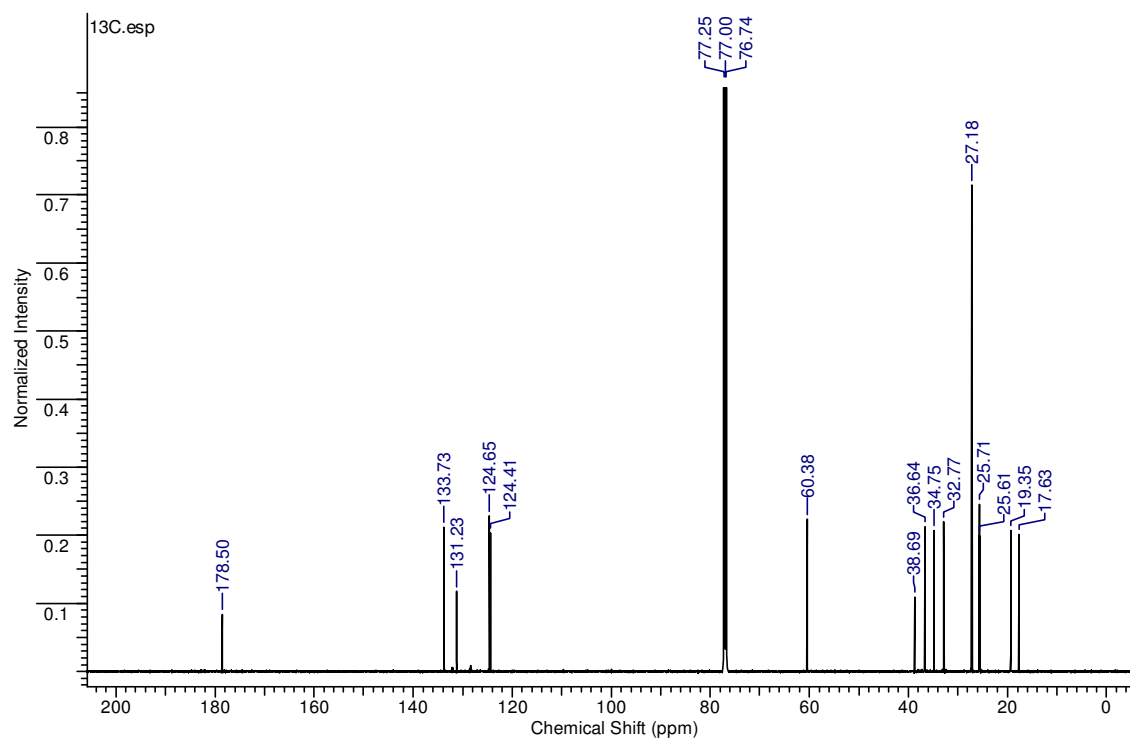
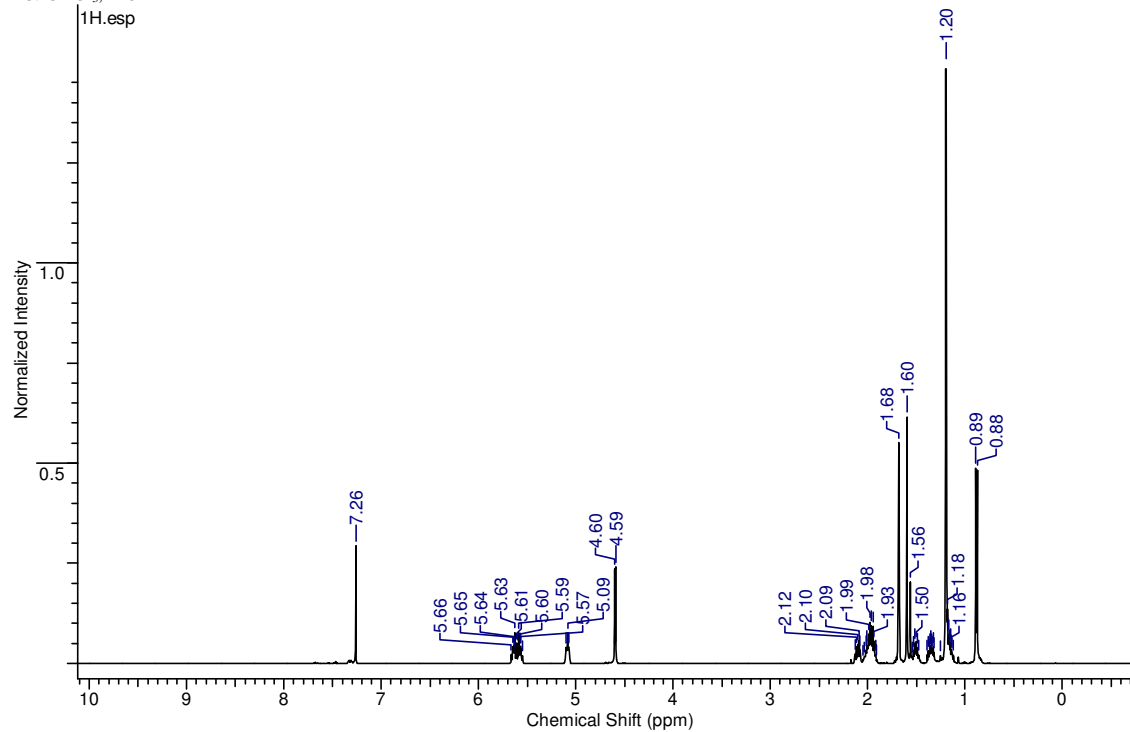
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



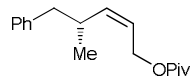
(*R,Z*)-5,9-Dimethyldeca-2,8-dien-1-yl pivalate (9d)



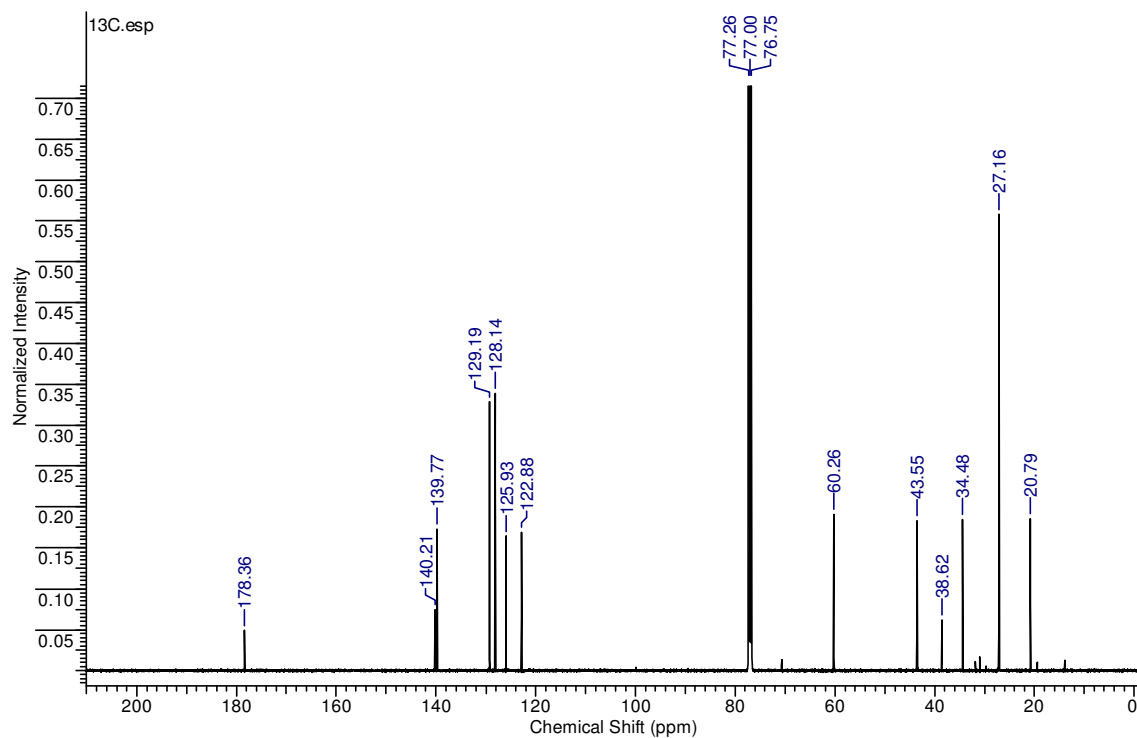
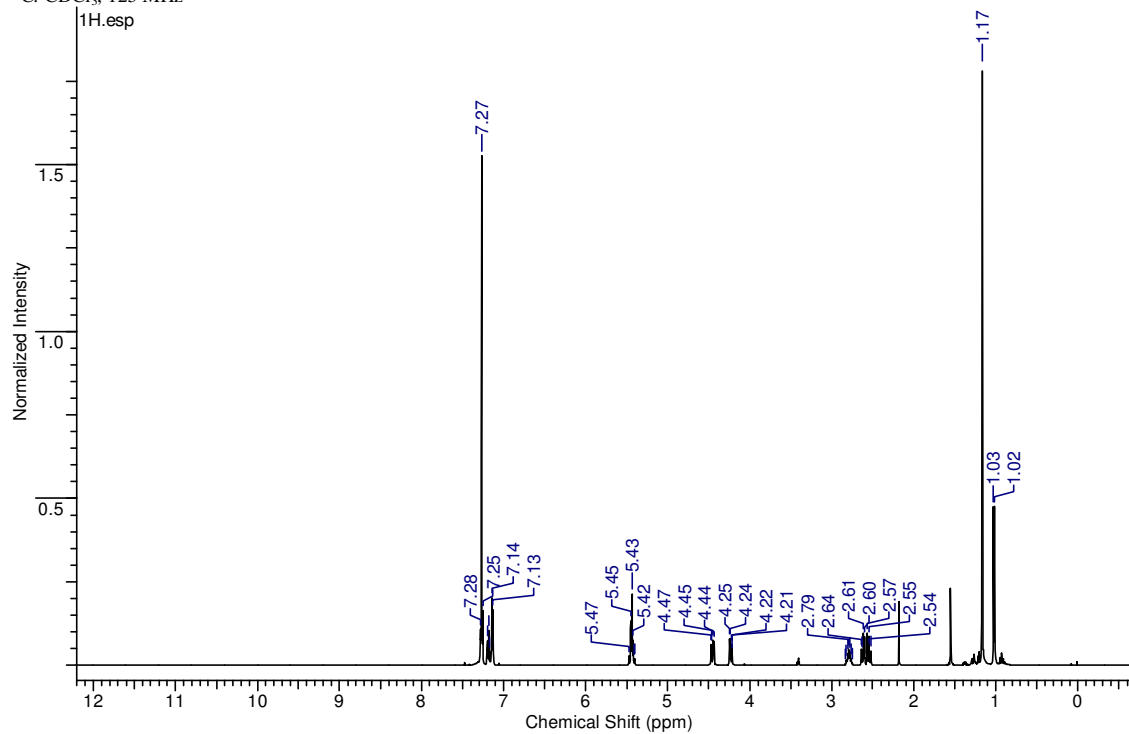
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



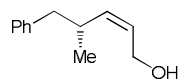
(*R,Z*)-4-methyl-5-phenylpent-2-en-1-yl pivalate (9e**)**



¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz

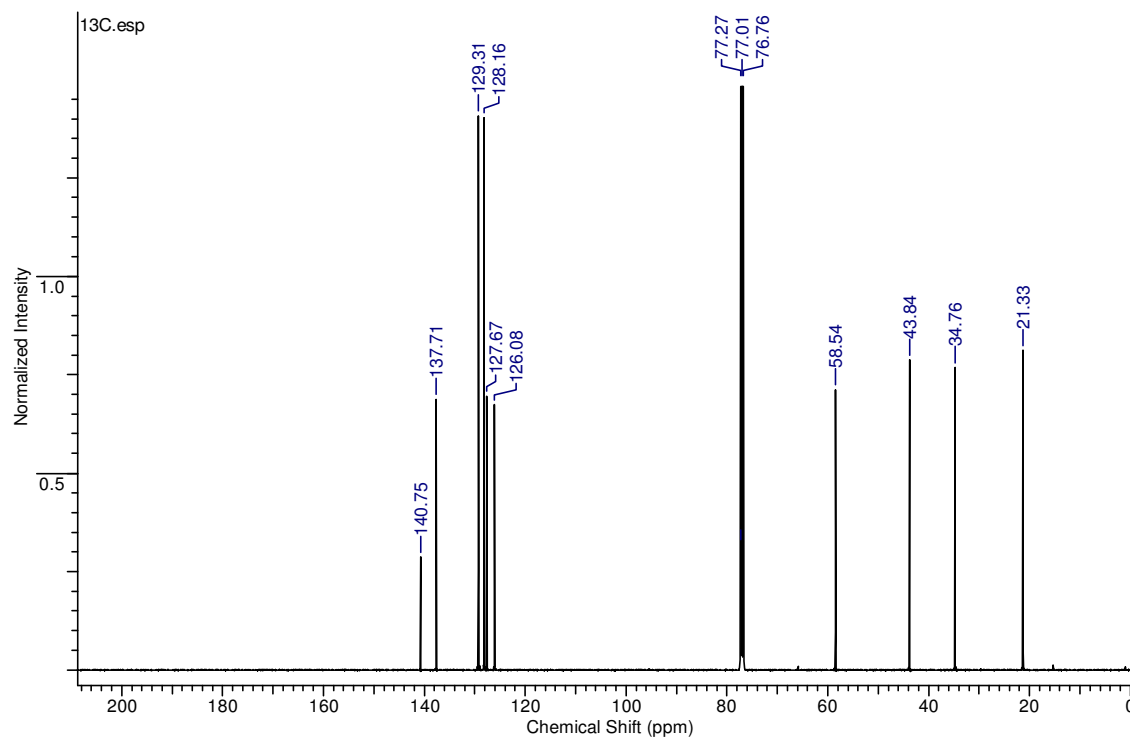
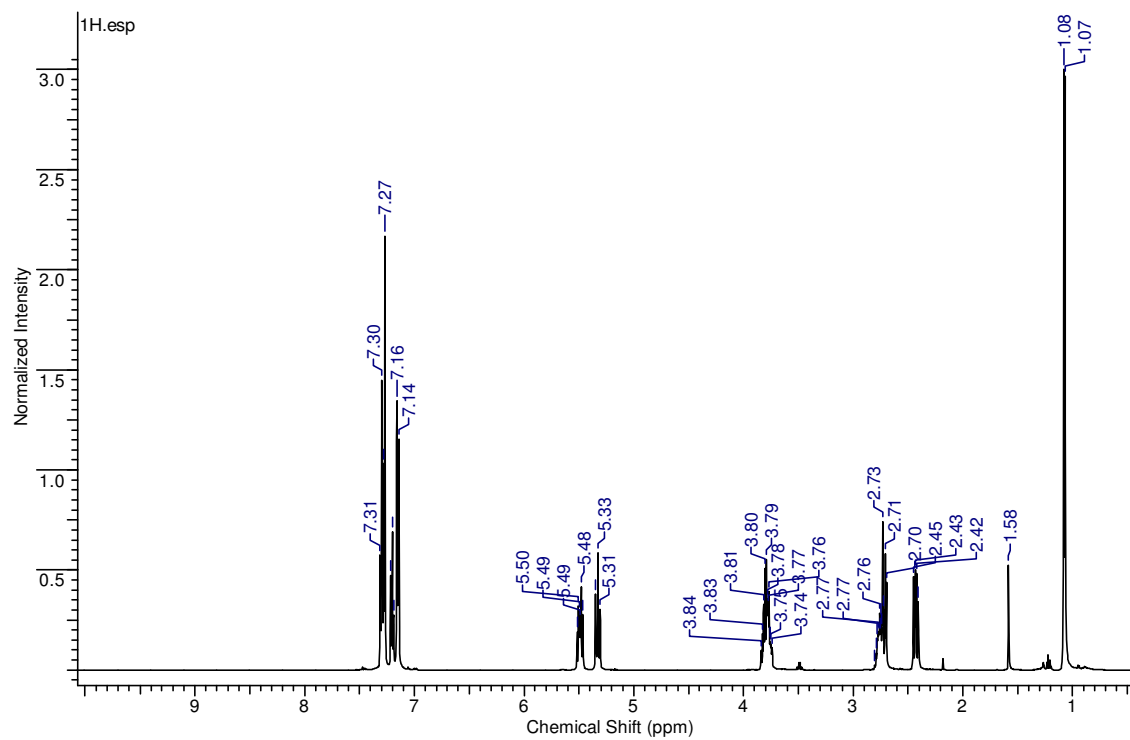


(R,Z)-4-methyl-5-phenylpent-2-en-1-ol

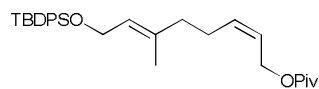


¹H: CDCl₃, 500 MHz

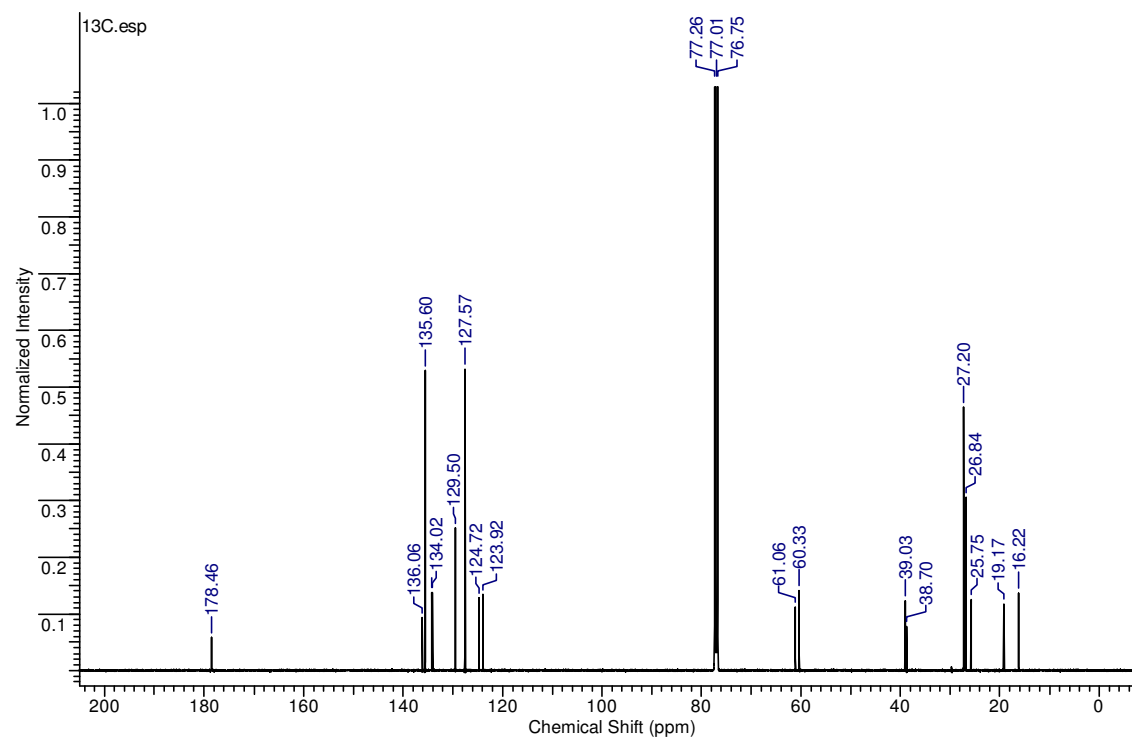
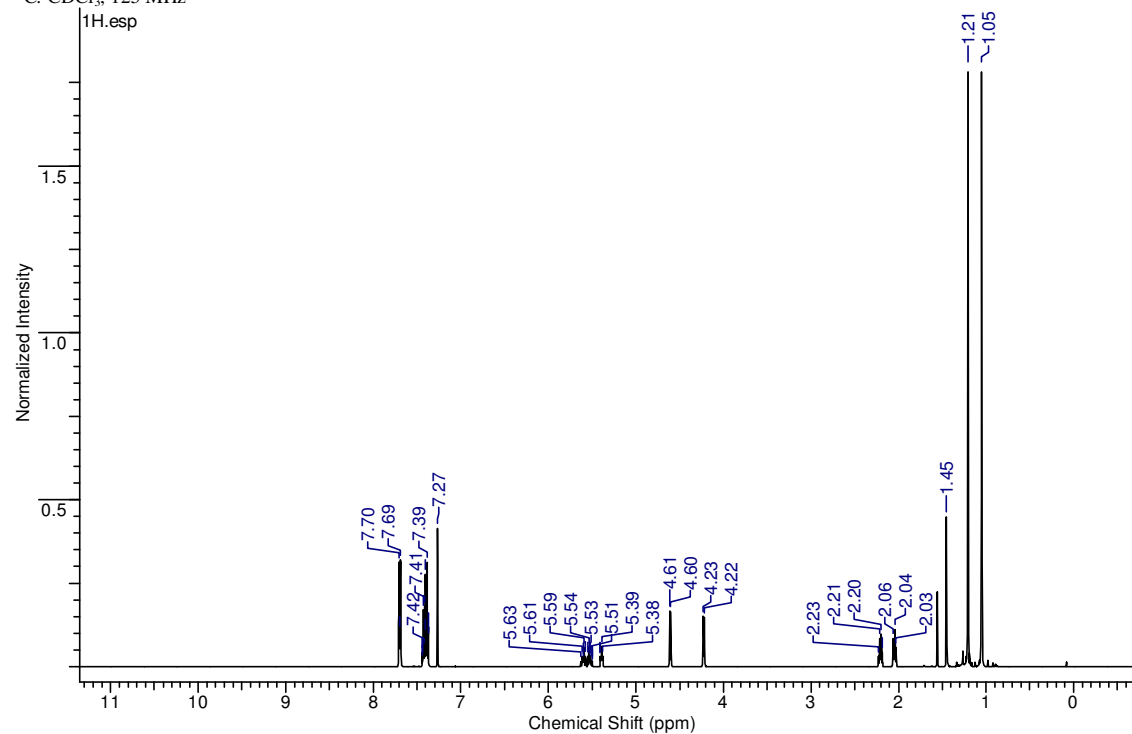
¹³C: CDCl₃, 125 MHz



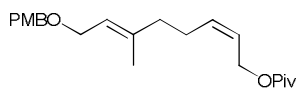
(2Z,6E)-8-((*tert*-Butyldiphenylsilyl)oxy)-6-methylocta-2,6-dien-1-yl pivalate (9f)



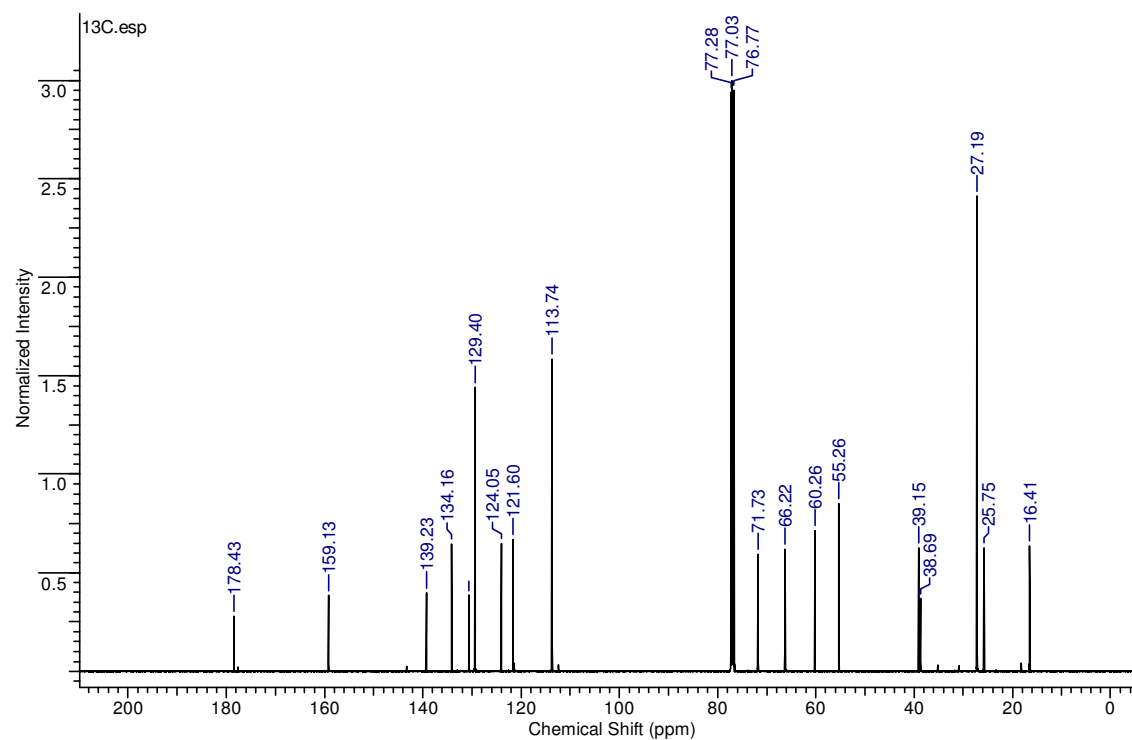
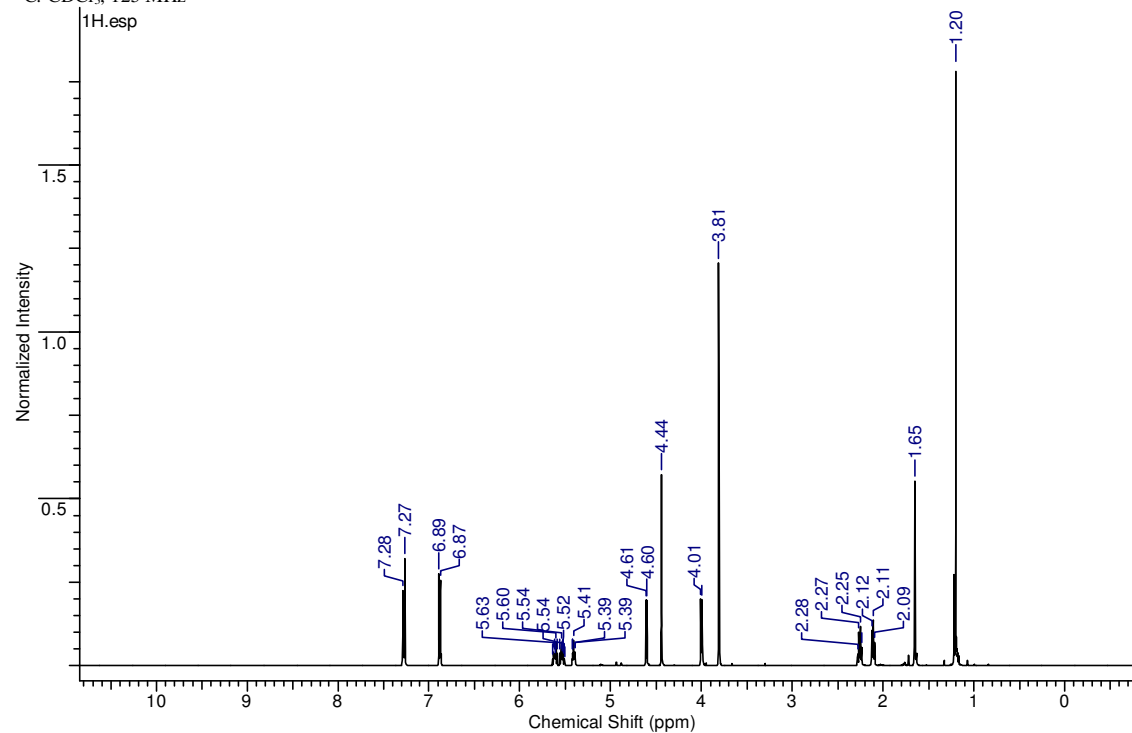
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



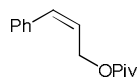
(2Z,6E)-8-((4-Methoxybenzyl)oxy)-6-methylocta-2,6-dien-1-yl pivalate (9g)



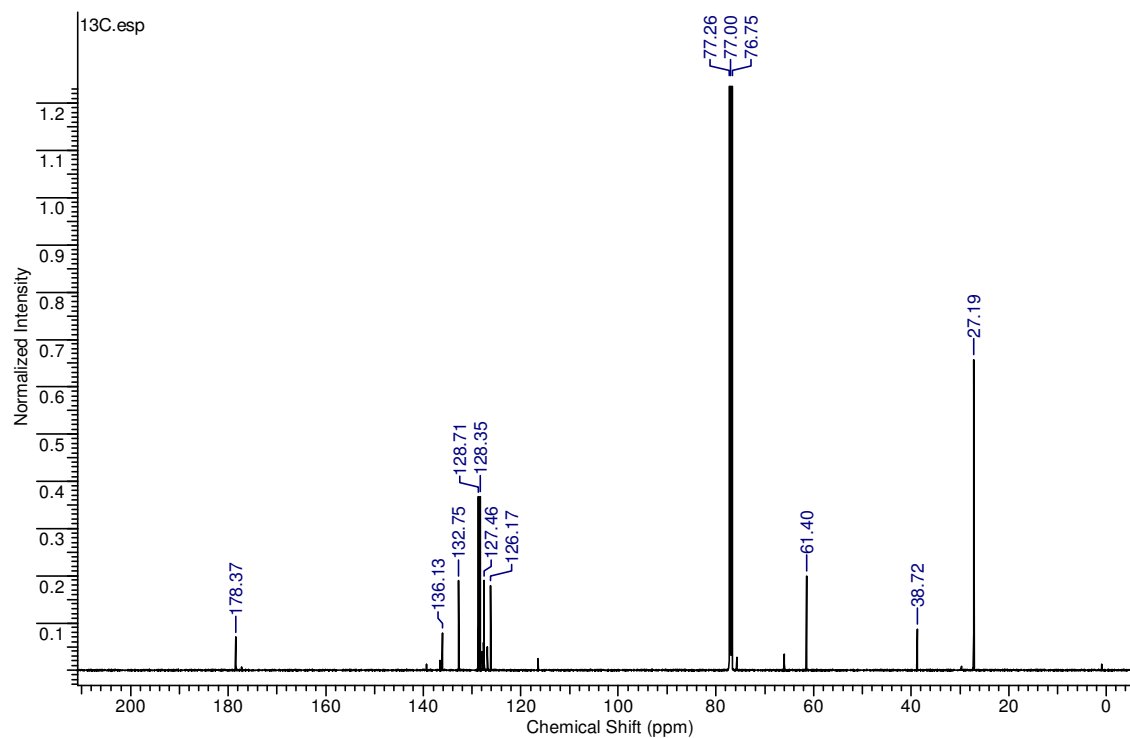
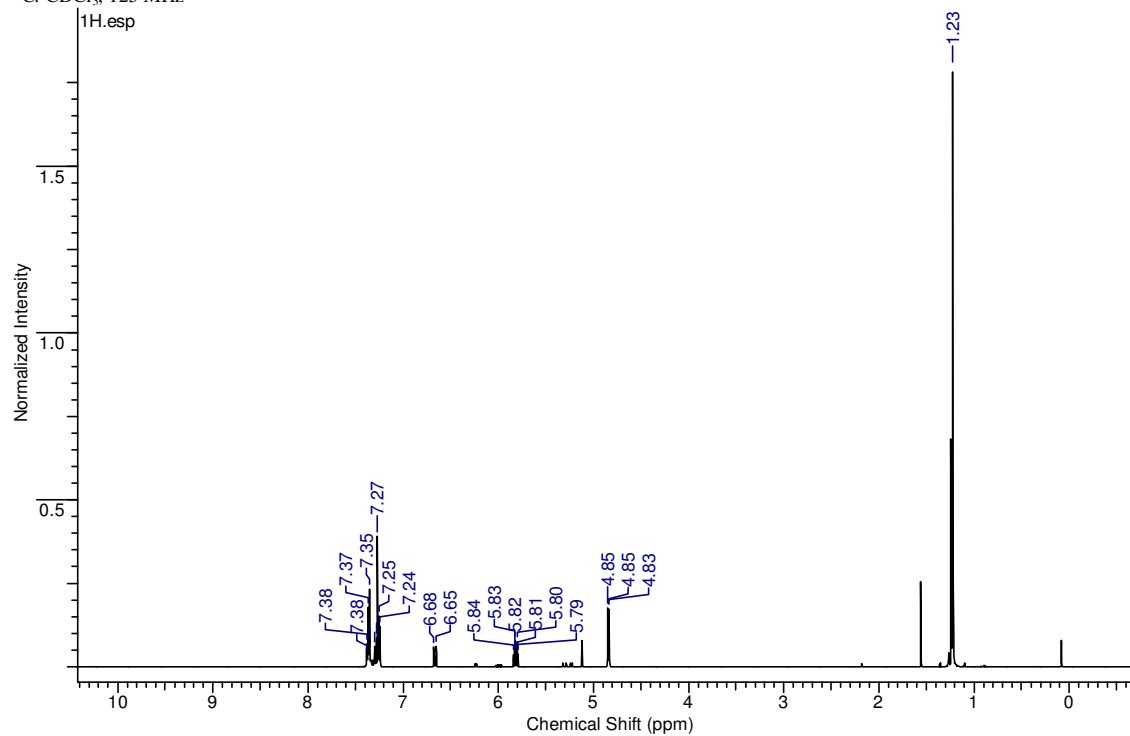
^1H : CDCl_3 , 500 MHz
 ^{13}C : CDCl_3 , 125 MHz



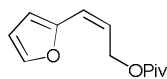
(Z)-3-Phenylallyl pivalate (9h)⁶



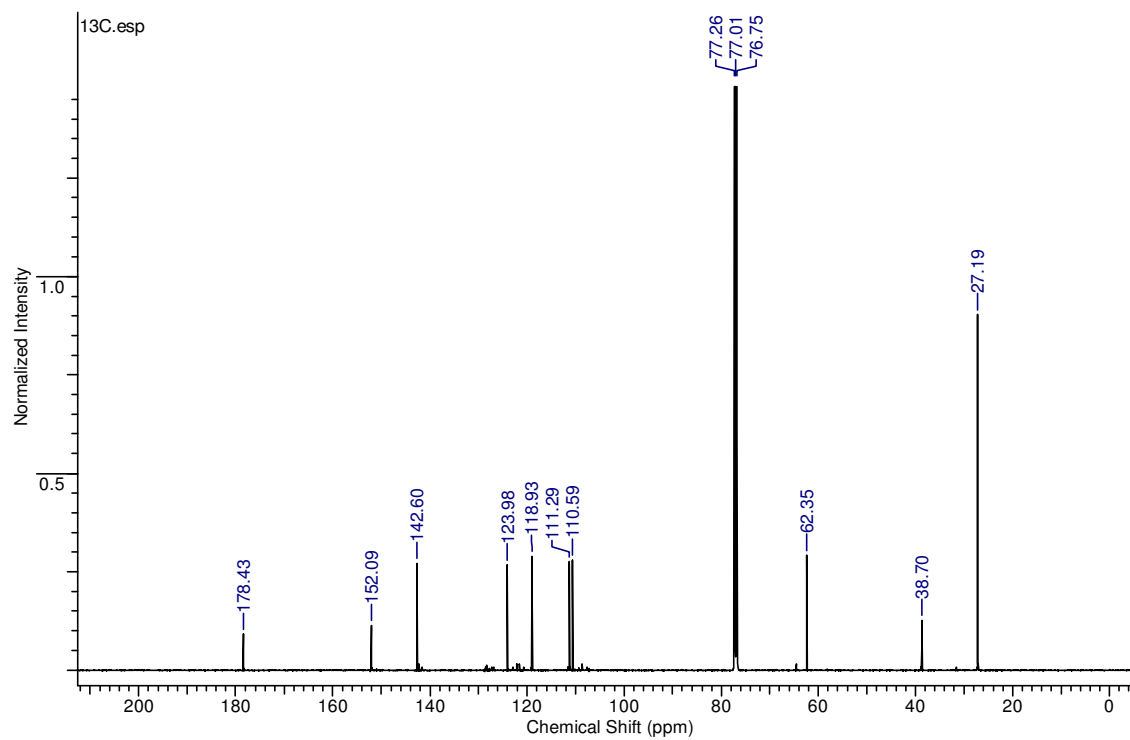
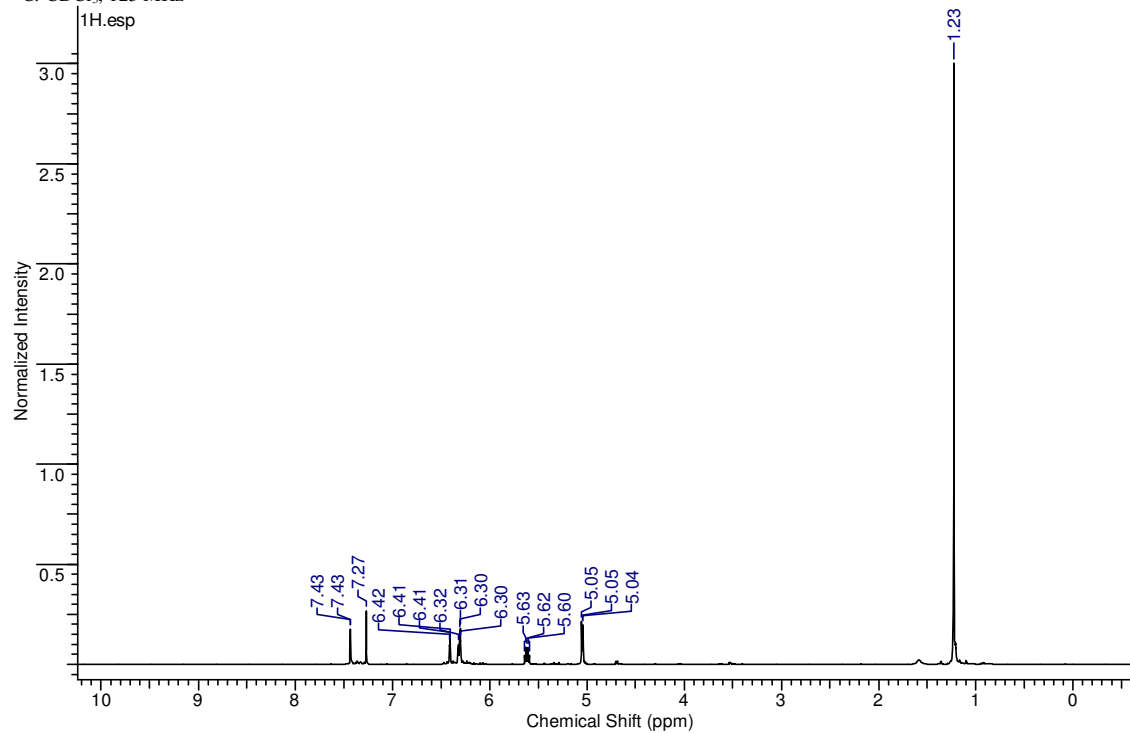
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



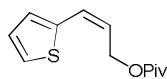
(Z)-3-(Furan-2-yl)allyl pivalate (9i)



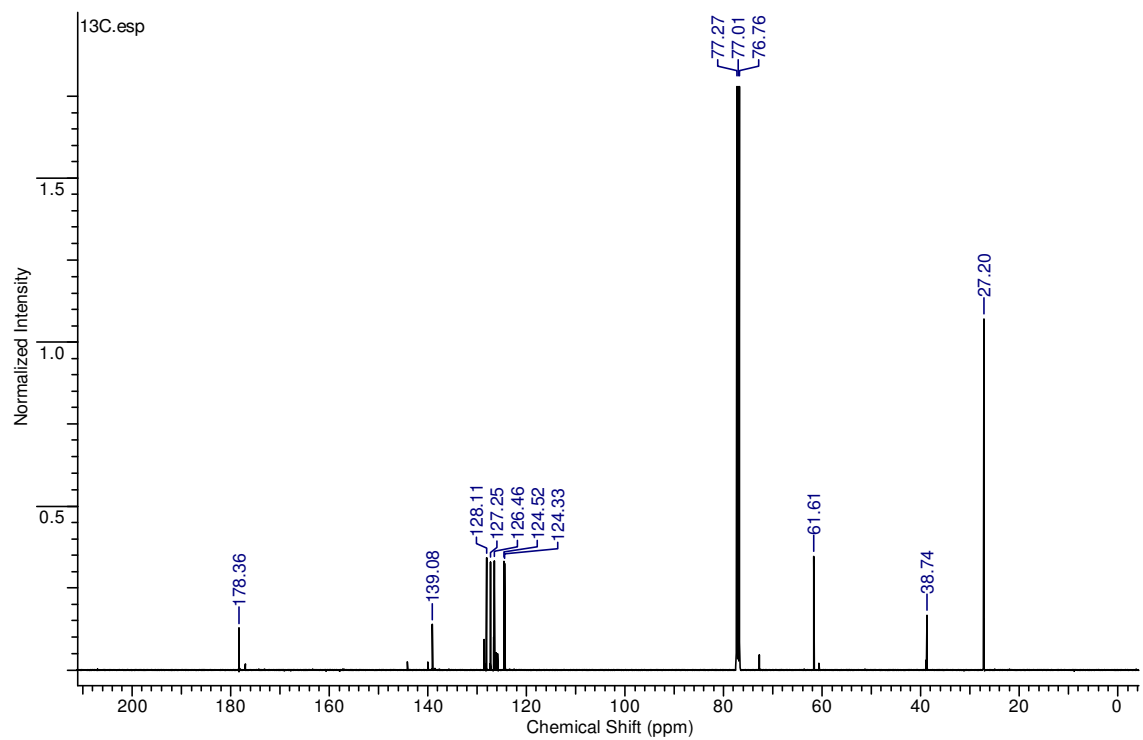
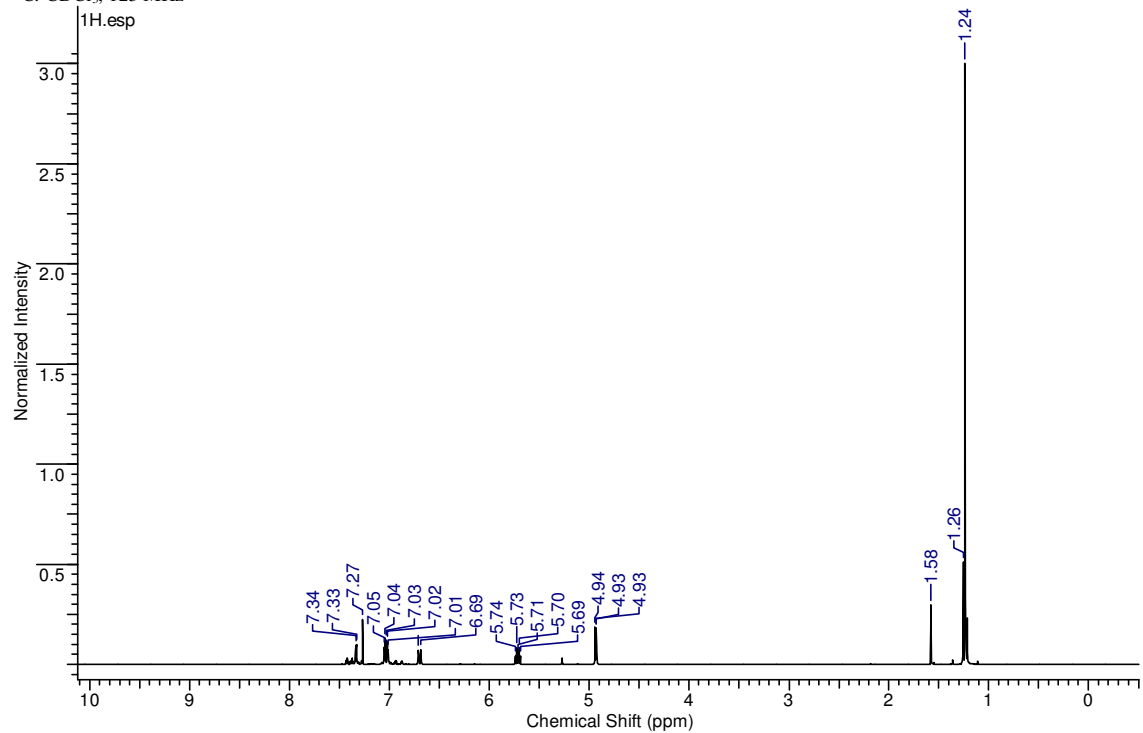
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



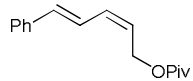
(Z)-3-(Thiophen-2-yl)allyl pivalate (9j)



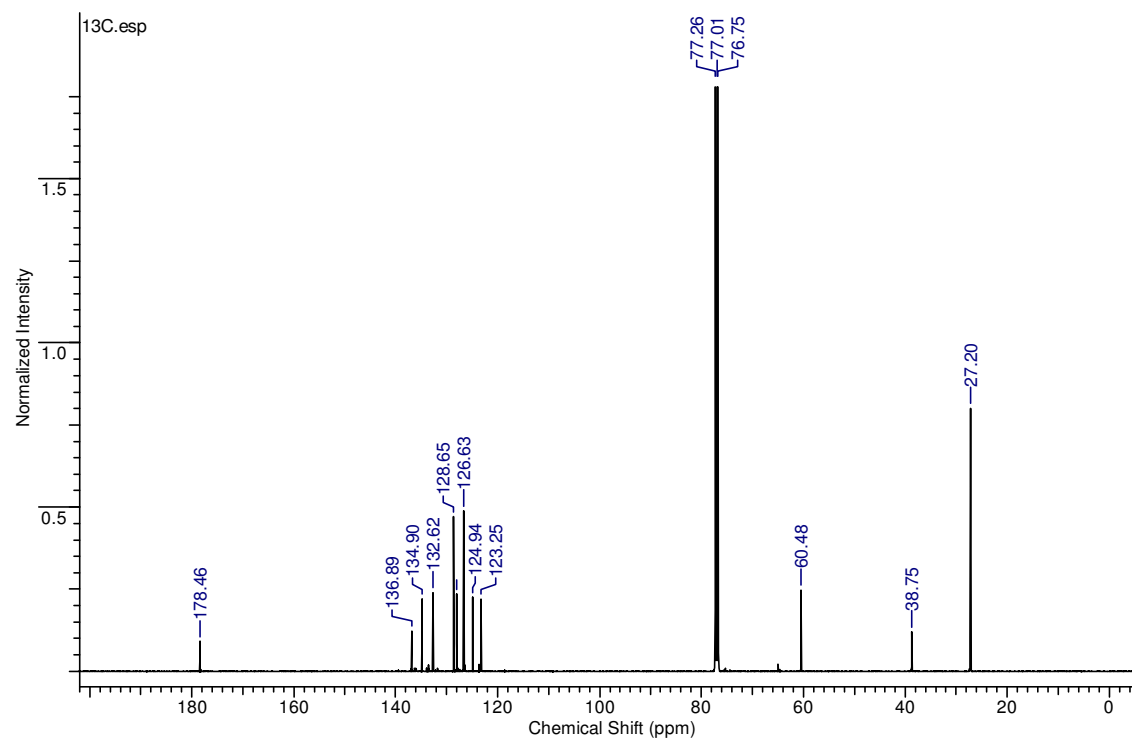
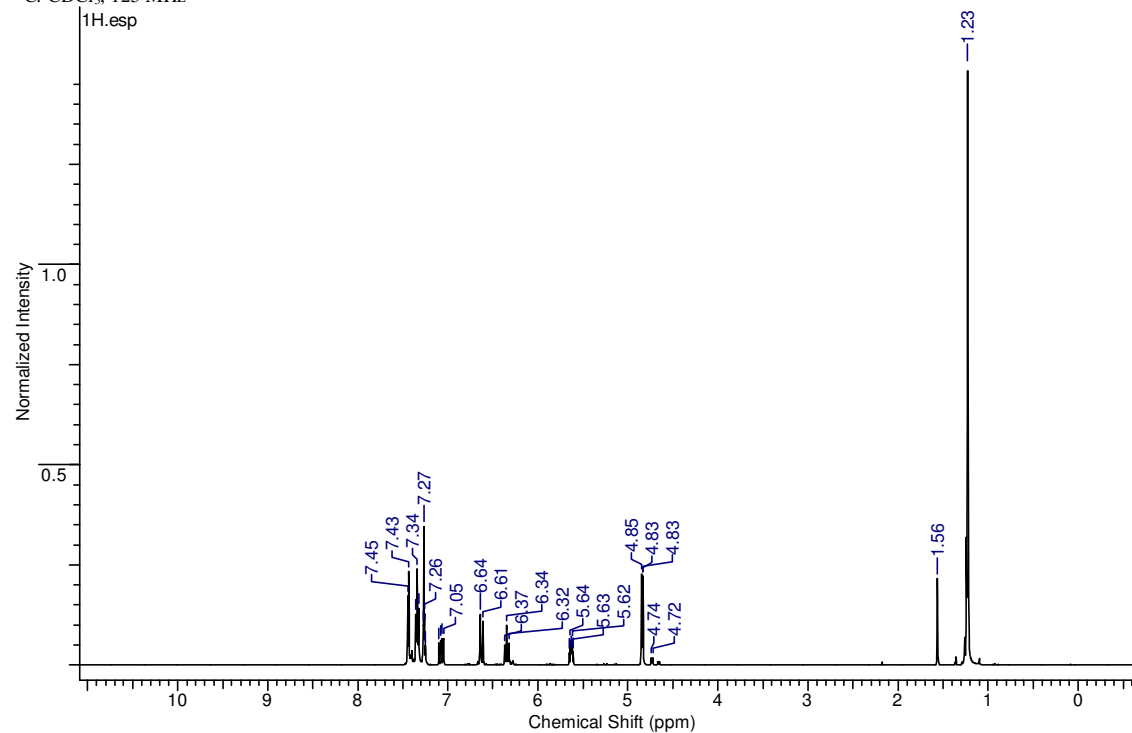
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



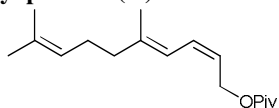
(2Z,4E)-5-Phenylpenta-2,4-dien-1-yl pivalate (9k)



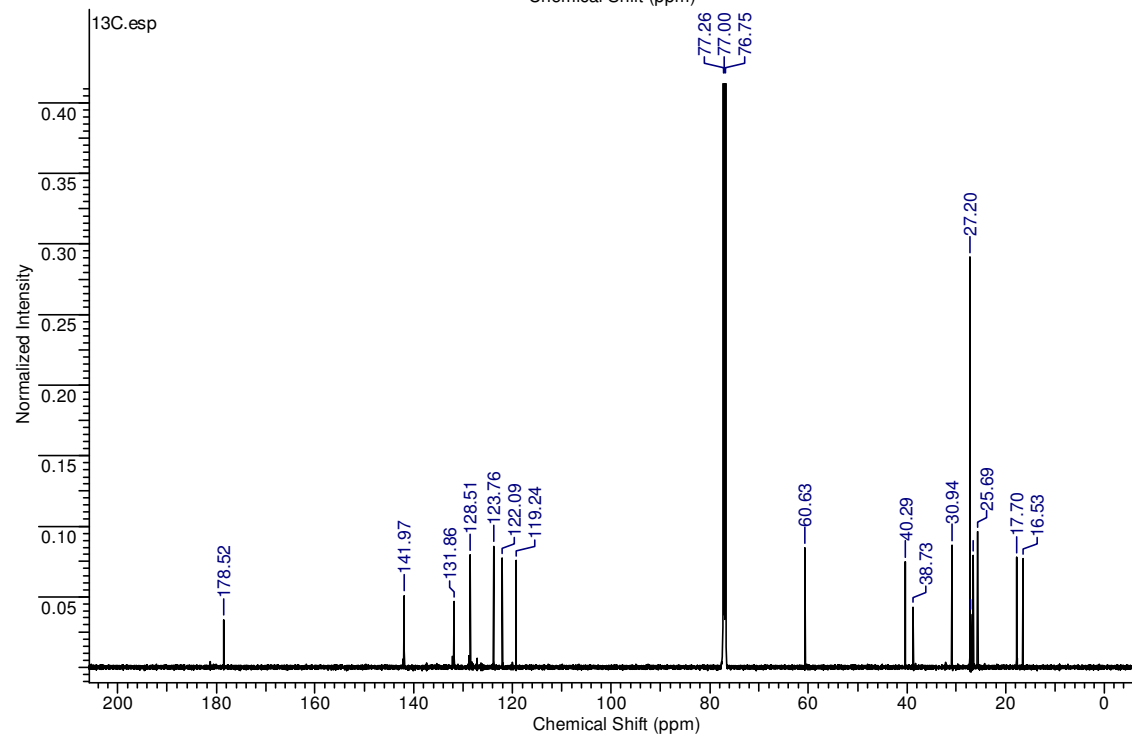
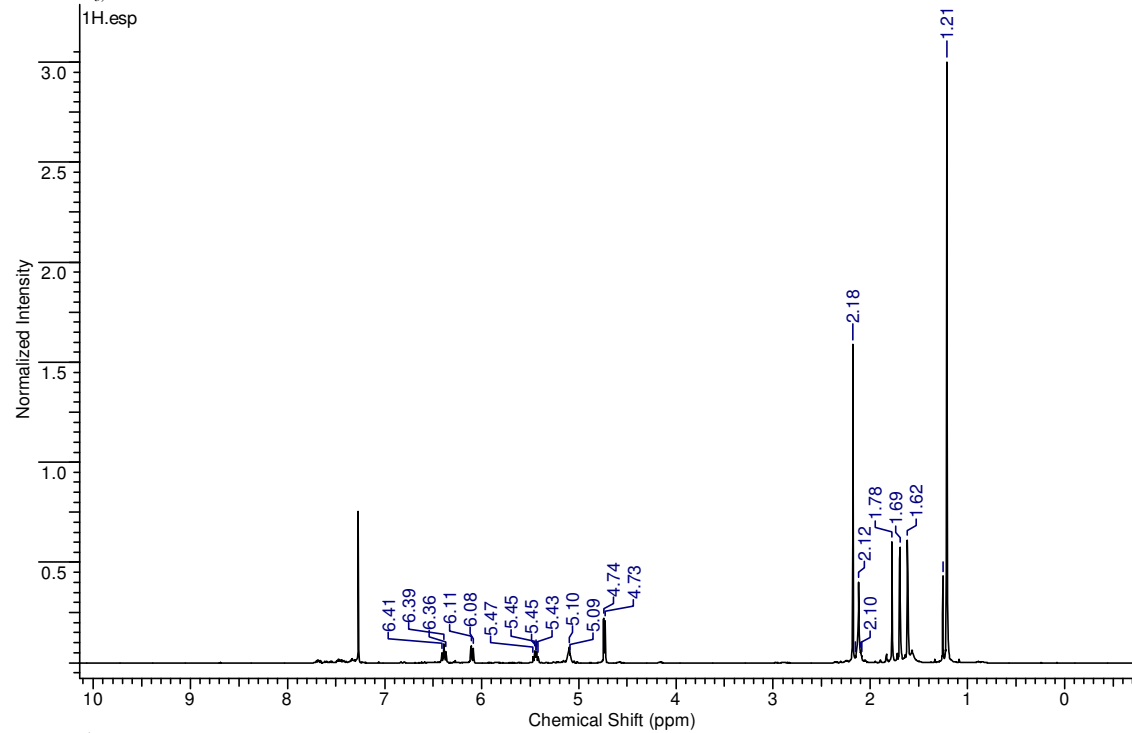
¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



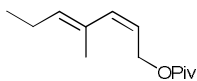
(2Z,4E)-5,9-Dimethyldeca-2,4,8-trien-1-yl pivalate (9I)



¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz

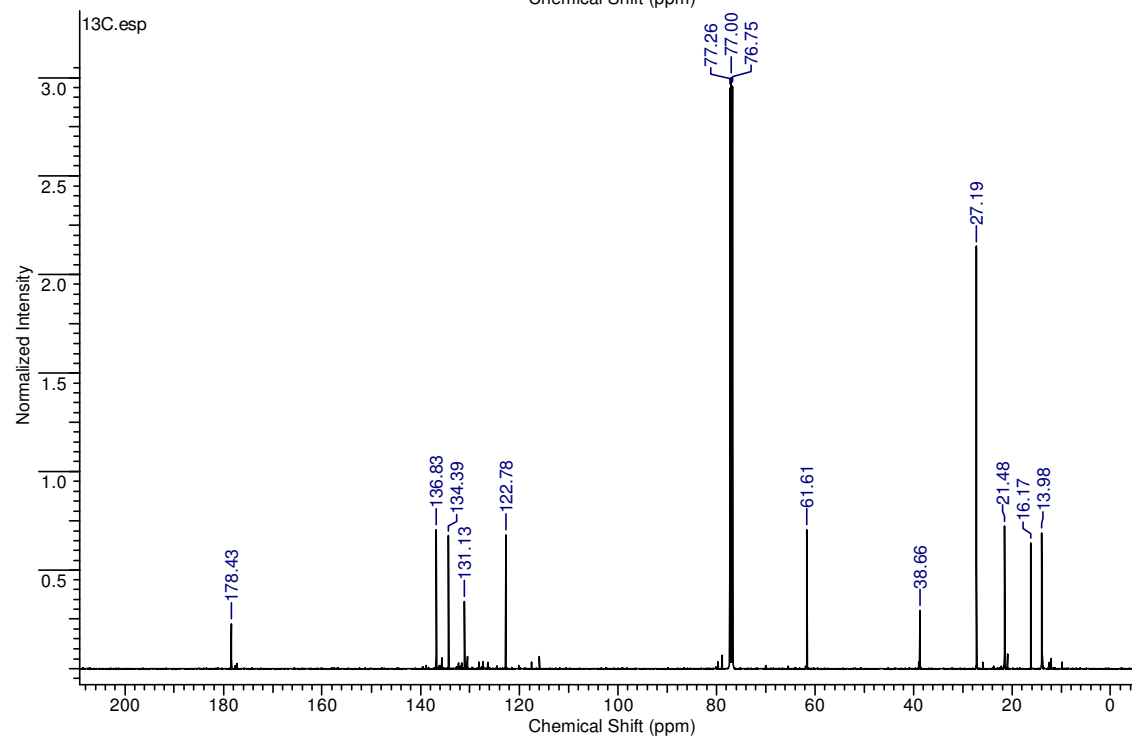
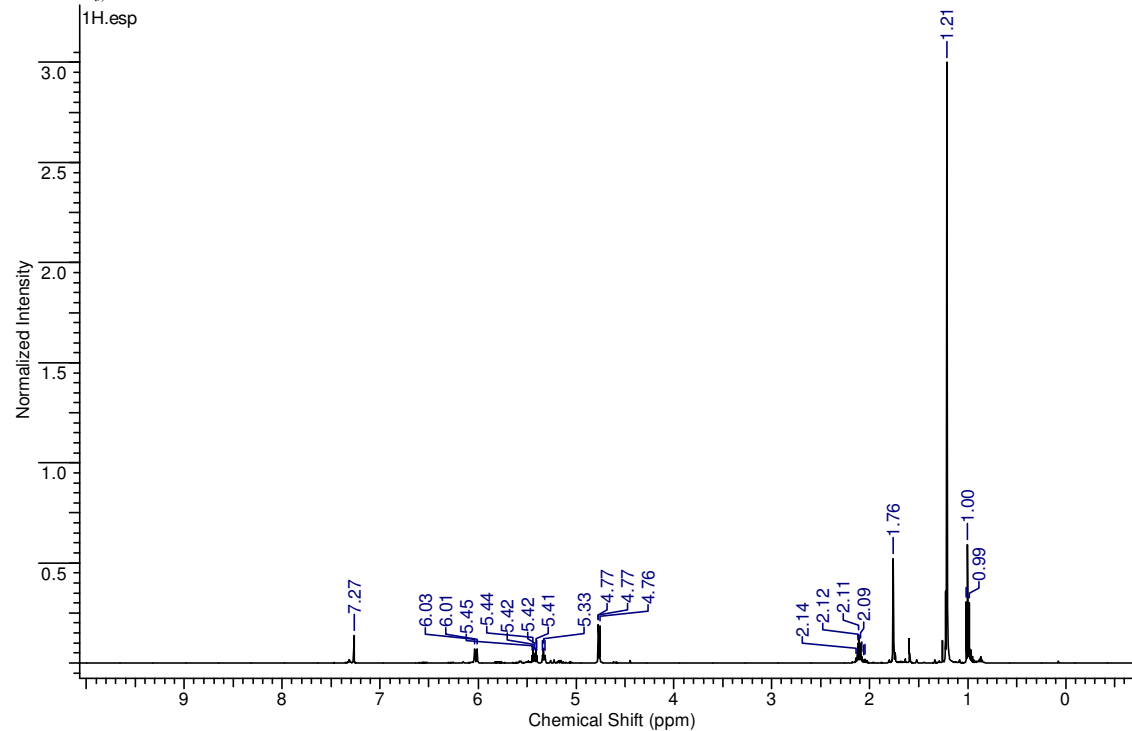


(2Z,4E)-4-Methylhepta-2,4-dien-1-yl pivalate (9m)

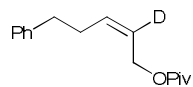


¹H: CDCl₃, 500 MHz

¹³C: CDCl₃, 125 MHz

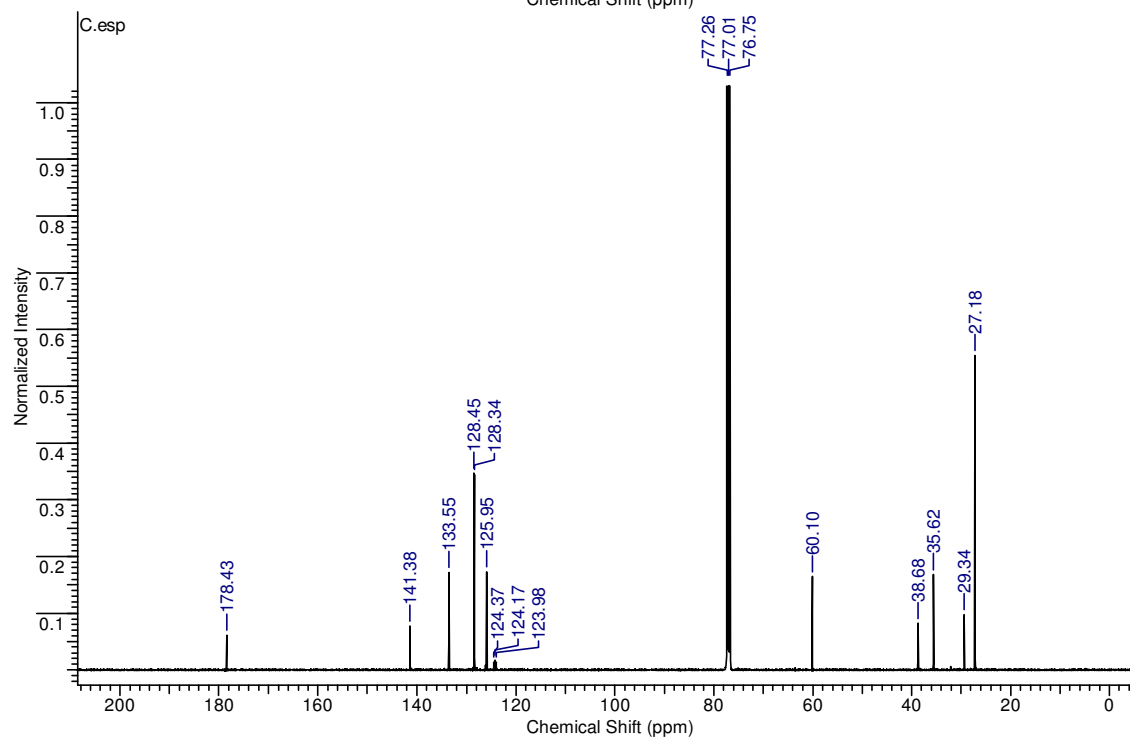
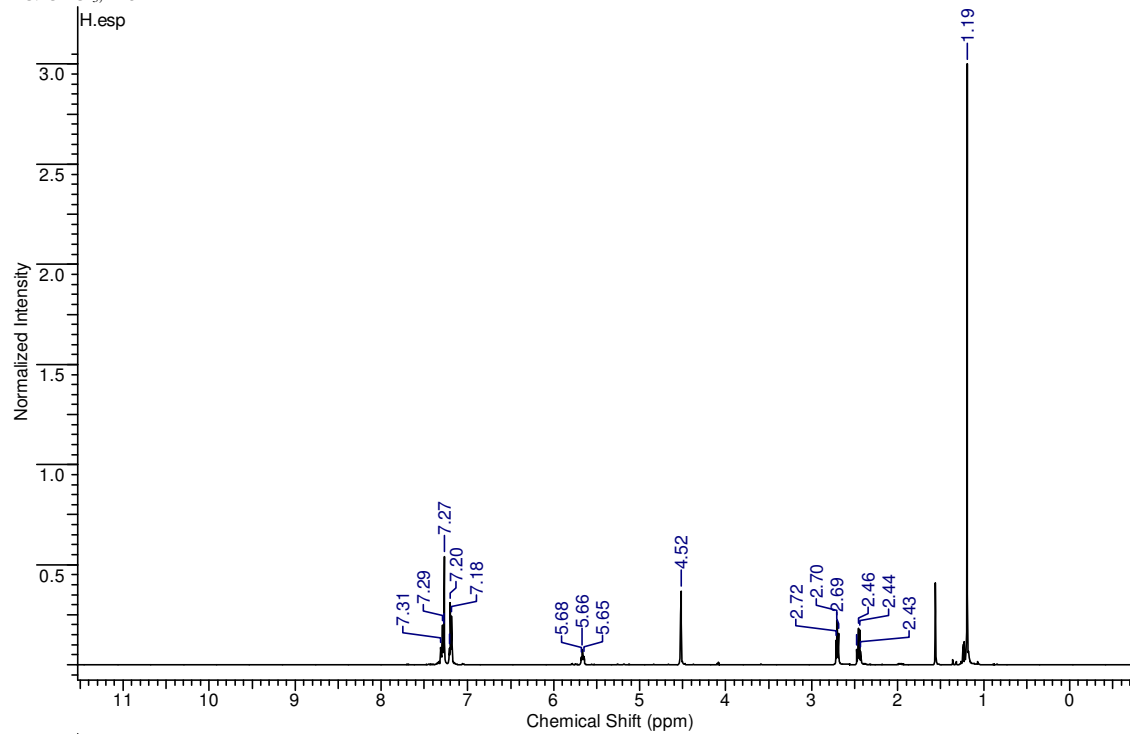


(Z)-5-Phenylpent-(2*d*)-2-en-1-yl pivalate (9a-D)

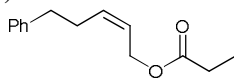


¹H: CDCl₃, 500 MHz

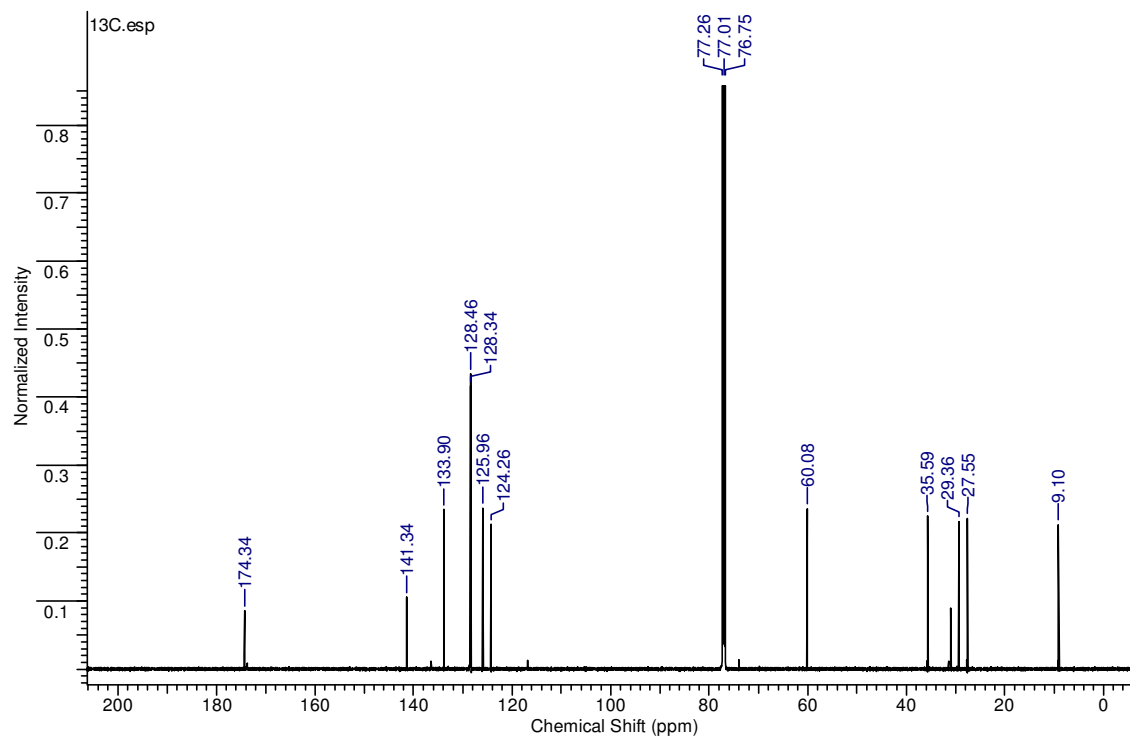
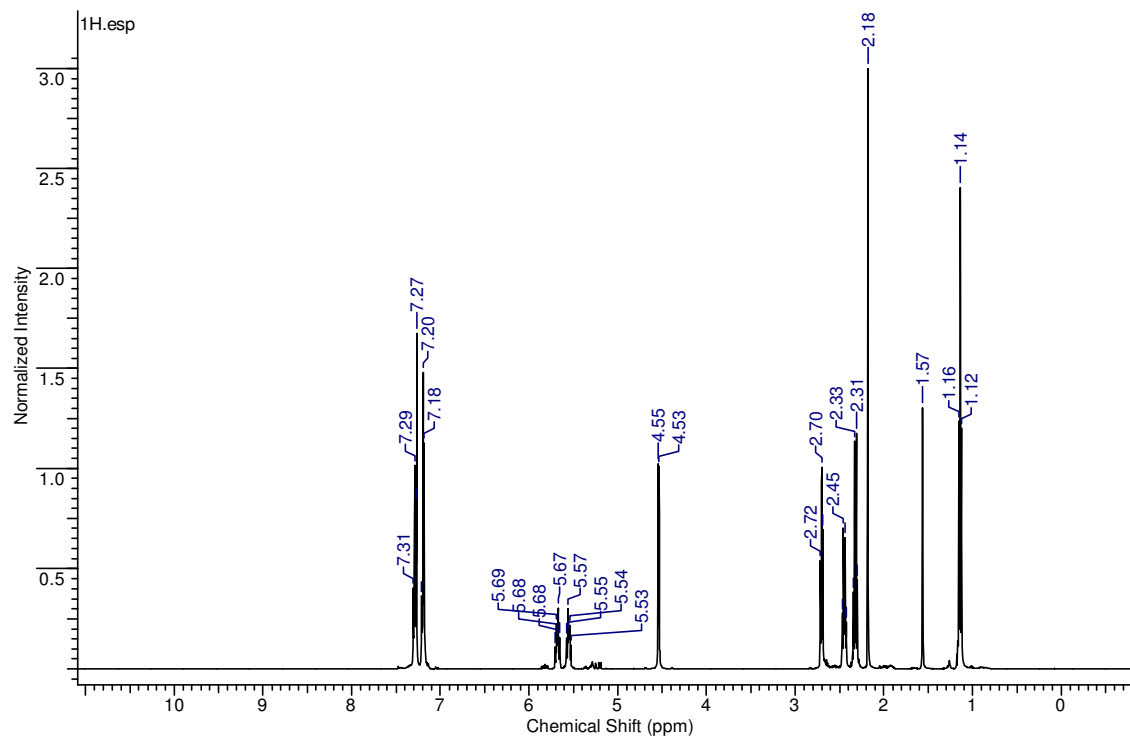
¹³C: CDCl₃, 125 MHz



(Z)-5-Phenylpent-2-en-1-yl propionate (10)

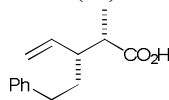


¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz



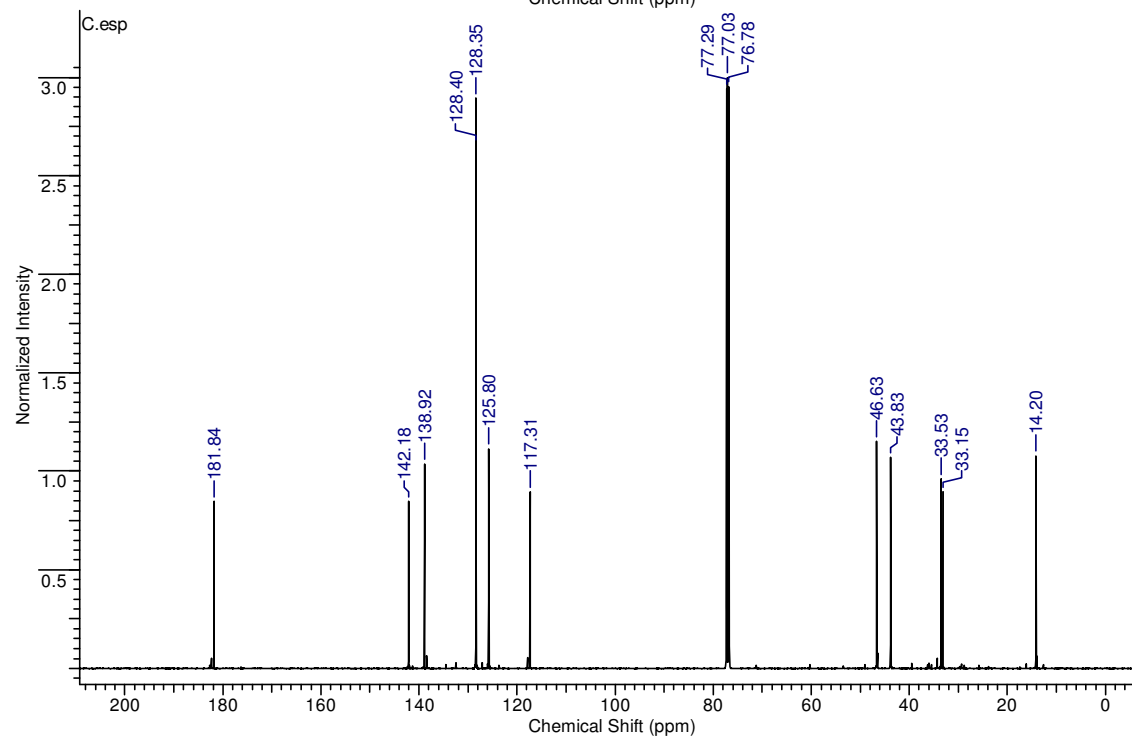
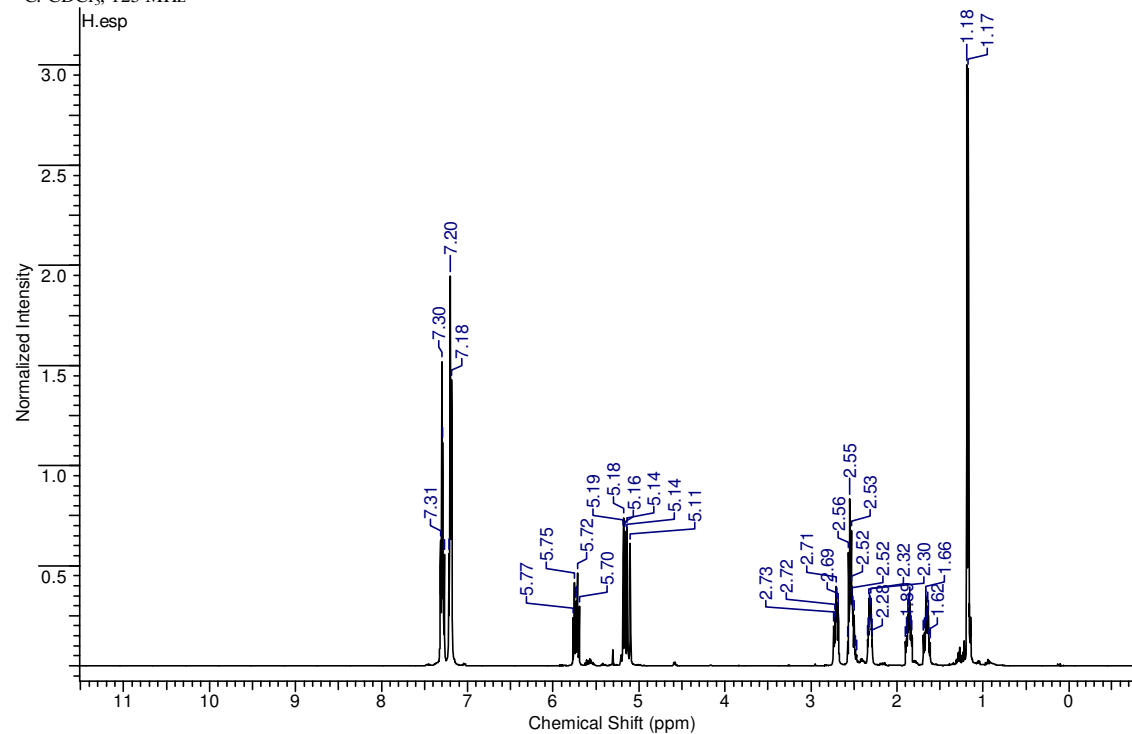
^1H and ^{13}C NMR spectra of acid 12

(±)-(2*R*,3*R*)-2-Methyl-3-phenethylpent-4-enoic acid (12)

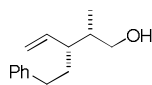


^1H : CDCl_3 , 500 MHz

^{13}C : CDCl_3 , 125 MHz



(±)-(2*R*,3*R*)-2-Methyl-3-phenethylpent-4-en-1-ol



¹H: CDCl₃, 500 MHz
¹³C: CDCl₃, 125 MHz

