Supporting Information

for

Alkenes from β-lithiooxyphosphonium ylides generated by trapping α-lithiated terminal epoxides with triphenylphosphine

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Preparative details of 6, 7, 12 and 14 are reported, together with their spectroscopic data

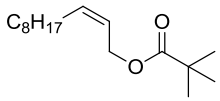
Contents

1. General details

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. THF and Et_2O were degassed and dried over activated alumina under nitrogen [1]. Petrol refers to the fraction of petroleum ether that boils at 30–40 °C. 2,2,6,6-Tetramethylpiperidine was distilled from CaH_2 under reduced pressure (60 °C, 43 mbar). LiBr was made anhydrous by being heated under nitrogen until it melted then cooled and dissolved in THF before being used. PPh_3 was dried overnight (~12 h) under high vacuum (~1 mbar). Benzaldehyde was distilled under reduced pressure (64 °C, 20 mbar) prior to use. Other starting materials were obtained commercially and were used without further purification. TLC analysis was carried out on aluminum-backed plates precoated with silica (60 F_{254}, Merck) and visualised by irradiation under UV light (λ = 254 nm) and by immersion in phosphomolybdic acid (PMA) solution followed by heating. IR spectra were recorded as thin films by using a 1750 Perkin-Elmer Paragon Fourier Transform spectrometer. The strength of absorbance is designated by the following abbreviations: br, s, m, and w, which refer to broad, strong, medium and weak, respectively. ^{1}H and ^{13}C NMR spectra were recorded by using Bruker AV400 and AVC500 spectrometers. Chemical shifts are reported in ppm and referenced to internal residual $CHCl_3$ at 7.27 ppm (^{1}H NMR spectra), and to the central line of the $CDCl_3$ triplet at 77.0 (^{13}C NMR spectra). Coupling constants, *J*, are given in Hz to the nearest 0.1 Hz. ^{13}C NMR data were assigned by standard methods using HSQC and DEPT experiments. *E*/*Z* ratios were determined by ^{1}H NMR analysis of crude products. Mass spectra were obtained by field ionisation (FI; Micromass GCT) or by electrospray ionisation (ESI; LCT Premier Reflectron TOF and Bruker MicroTOF) using tetraoctyl ammonium bromide or sodium dodecyl sulfate as lock mass; values are quoted as ratios of mass/charge (*m*/*z*) in Daltons, and relative intensities of assignable peaks observed are quoted as a percentage value.

2. **Synthesis of 6, 7, 12 and 14**

(*Z*)-Undec-2-en-1-yl pivalate (6)

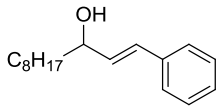


To a solution of 2,2,6,6-tetramethylpiperidine (168 µL, 1.0 mmol, 1.0 equiv) in THF (6 mL) at 0 ºC was added *n*-BuLi (0.40 mL, 2.5 M in hexanes, 1.0 mmol, 1.0 equiv) dropwise under stirring. The mixture was allowed to warm to room temperature over 30 min, during which time a pale yellow solution formed. This solution was then cooled to 0 °C and a solution of PPh_3 (262 mg, 1.0 mmol, 1.0 equiv) and anhydrous LiBr (87 mg, 1.0 mmol, 1.0 equiv) in THF (4 mL) was added dropwise followed immediately by a solution of 1,2-epoxydecane (156 mg, 1.0 mmol, 1.0 equiv) in THF (0.5 mL) slowly dropwise. This solution was then stirred at 0 ºC for 24 h during which time a red-orange colour developed. This mixture was then cooled to −78 ºC and a solution of chloromethyl pivalate (158 mg, 1.05 mmol, 1.05 equiv) in THF (0.5 mL/mmol) added slowly dropwise. The reaction mixture was stirred at −78 ºC for 2 h, then warmed to rt over 1 h and stirring was continued for a further 1 h. The mixture was quenched with saturated aq. NH_4Cl (20 mL), extracted with Et_2O (3 × 15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (20% CH_2Cl_2/petrol) gave allylic ester **6** [2] (66 mg, 26%) as a colourless oil; R_f 0.41, 20% CH_2Cl_2/petrol.

IR (neat) /cm^{-1}: 3066s, 3027s, 2957s, 2854m, 1732m, 1730m, 1151s; ^{1}H (500 MHz) δ = 5.66−5.61 (1 H, m, C**H**=CHCH$_2$), 5.55−5.50 (1 H, m, =C**H**CH$_2$), 4.61 (2 H, dt, *J* = 6.8, 0.60, CH$_2$OPiv), 2.10 (2 H, app q, *J* = 6.9, C**H**$_2$CH=), 1.39−1.23 (m, 12 H, 6 × CH$_2$), 1.19 (9 H, s, (CH$_3$)$_3$), 0.88 (3 H, t, *J* = 7.0, CH$_3$); ^{13}C (125 MHz) δ = 178.5 (C=O), 135.2 (CH$_2$**C**H=), 123.6 (=**C**HCH$_2$), 60.3 (CH$_2$O), 38.7 (C), 31.9 (CH$_2$), 29.4 (2 × CH$_2$), 29.3 (CH$_2$), 29.2 (CH$_2$) 27.6 (CH$_2$), 27.2 (3 × CH$_3$), 22.7 (CH$_2$), 14.1 (CH$_3$); LRMS (ESI+): 277.20 (75,

M+Na), 413.23 (75), 691.36 (70), 803.45 (100); HRMS (ESI+): 277.2138 calculated for $C_{16}H_{30}O_2Na$; found 277.2143.

(*E*)-1-Phenylundec-1-en-3-ol (7)



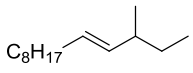
To a solution of 2,2,6,6-tetramethylpiperidine (168 µL, 1.0 mmol, 1.0 equiv) in THF (6 mL) at 0 ºC was added *n*-BuLi (0.40 mL, 2.5 M in hexanes, 1.0 mmol, 1.0 equiv) dropwise under stirring. The mixture was allowed to warm to room temperature over 30 min, during which time a pale yellow solution formed. This solution was then cooled to 0 ºC and a solution of PPh_3 (524 mg, 2.0 mmol, 2 equiv) and anhydrous LiBr (174 mg, 2.0 mmol, 2.0 equiv) in THF (8 mL) was added dropwise followed immediately by a solution of 1,2-epoxydecane (156 mg, 1.0 mmol, 1.0 equiv) in THF (0.5 mL) slowly dropwise. This solution was then stirred at 0 ºC for 24 h during which time a red-orange color developed. This mixture was then cooled to −78 ºC and a solution of benzaldehyde (112 mg, 1.05 mmol, 1.05 equiv) in THF (0.5 mL) added slowly dropwise. The reaction mixture was stirred at −78 ºC for 2 h, then warmed to rt over 1 h and stirring was continued for a further 1 h. The mixture was quenched with saturated aq. NH_4Cl (20 mL), extracted with Et_2O (3 × 15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (30% Et_2O/petrol) gave allylic alcohol **7** [3] (77 mg, 31%) as a pale yellow oil; R_f 0.41, 30% Et_2O/petrol; IR (neat) /cm^{-1}: 3351br w, 2924m, 2853m, 1494w, 1450w, 964m, 746s, 691s; ^1H (400 MHz) δ = 7.44−7.24 (5 H, m, Ph), 6.59 (1H, d, *J* = 15.8, CH(OH)CH=CH), 6.26 (1 H, dd, *J* = 15.8, 6.8, CH(OH)CH), 4.30 (1 H, app q, *J* = 6.6, CH(OH)), 1.80 (1 H, br. s, OH), 1.74−1.57 (2 H, m, CH_2CH(OH)), 1.55−1.23 (12 H, m, 6 × CH_2), 0.91 (3 H, t, *J* = 6.8, CH_3); ^{13}C (100 MHz) δ = 136.7 (ArC), 132.6 (CH(OH)CH=CH), 130.1 (CH(OH)CH), 128.5 (2 × ArCH), 127.5 (ArCH), 126.4 (2 × ArCH),

73.1 (CH(OH)), 37.3 (CH(OH)CH_2), 31.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.2 (CH_2), 25.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3); LRMS (ESI+): 269.19 (80, M+Na), 301.22 (55), 413.32 (55), 515.39 (100); HRMS (ESI+): (M+Na) 269.1876 calculated for $C_{17}H_{26}ONa$; found 269.1868.

_E_-allylic alcohol 7 and alkene 12 from epoxide 11 using _s_-BuLi.

To a solution of 1,2-epoxydecane (156 mg, 1.0 mmol, 1.0 equiv), PPh_3 (262 mg, 1.0 mmol, 1.0 equiv) and anhydrous LiBr (174 mg, 2.0 mmol, 2.0 equiv) in THF (14 mL) at −78 ºC was added *s*-BuLi (0.77 mL, 1.3 M in cyclohexane/hexane (92/8), 1.0 mmol, 1.0 equiv) very slowly dropwise over ~10 min. The reaction mixture was stirred at −78 ºC for 24 h, and then a solution of benzaldehyde (112 mg, 1.05 mmol, 1.05 equiv) in THF (0.5 mL/mmol) was added slowly dropwise. The reaction mixture was stirred at −78 ºC for 2 h, then warmed to rt over 1 h and stirring was continued for a further 1 h. The mixture was quenched with saturated aq. NH_4Cl (20 mL), extracted with Et_2O (3 × 15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (0−30% Et_2O/petrol) gave allylic alcohol **7** (45 mg, 18%) as a pale yellow oil; R_f 0.41, 30% Et_2O/petrol, and alkene **12** [4] (50 mg, 25%) as a colourless oil; R_f 0.87, 15% Et_2O/petrol.

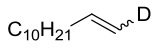
Data for (*E*)-3-methyltridec-4-ene (12)



IR (neat) /cm^{-1}: 2958w, 2923m, 2854w, 1457w, 1006w; ^1H (400 MHz) δ = 5.37 (1 H, dt, *J* = 15.2, 6.3, CH=CHCH_2), 5.27 (1 H, dd, *J* = 15.3, 7.3, CH=CHCH_2), 2.07−1.92 (3 H, m, $CHCH_3$, CH=CHCH_2), 1.41−1.23 (14 H, m, 7 × CH_2), 0.98 (3 H, d, *J* = 6.8, $CHCH_3$), 0.94−0.84 (6 H, m, 2 × CH_3); ^{13}C (100 MHz) δ = 136.1 (CH=), 128.7 (=CHCH_2), 38.5 (CH), 32.7 (CH_2), 32.0 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 22.8

(CH_2), 20.5 (CH_3), 14.1 (CH_3), 11.8 (CH_3); HRMS (FI+): 196.2191 calculated for $C_{14}H_{28}$; found 196.2194.

1-Deuterio-1-dodecene (14)

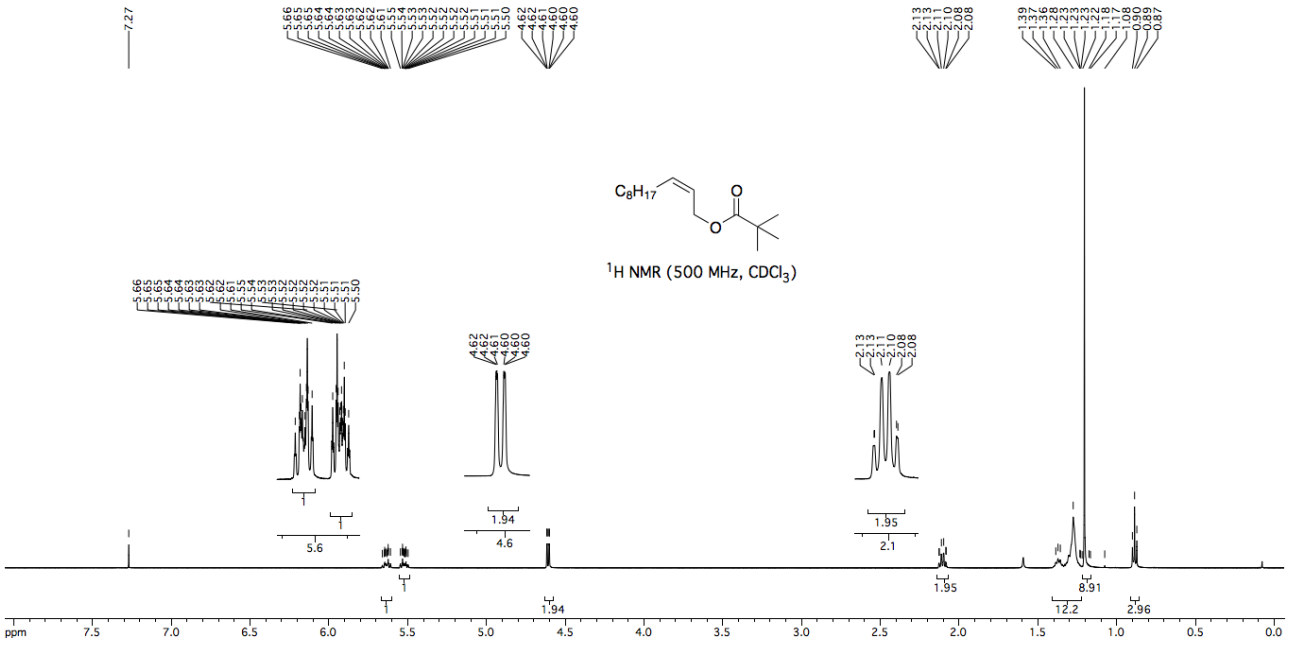


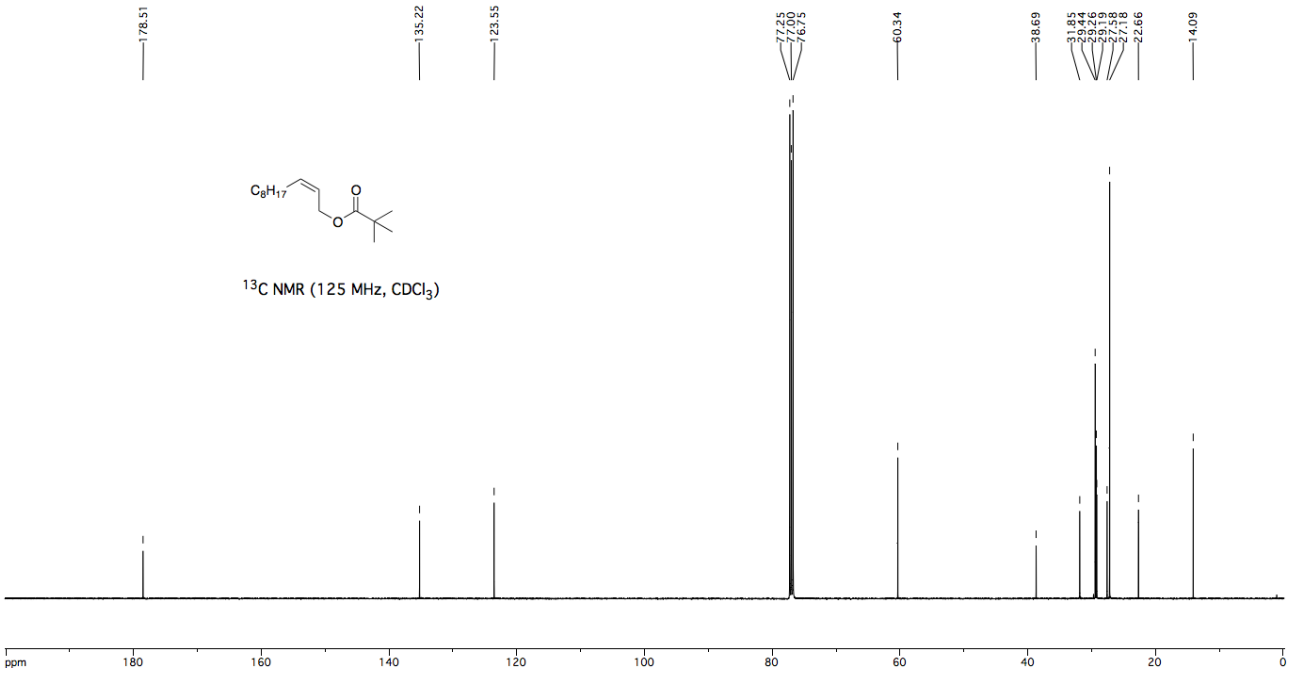
To a solution of 2,2,6,6-tetramethylpiperidine (168 µL, 1.0 mmol, 1.0 equiv) in THF (6 mL) at 0 ºC was added *n*-BuLi (0.40 mL, 2.5 M in hexanes, 1.0 mmol, 1.0 equiv) dropwise with stirring. The mixture was allowed to warm to room temperature over 30 min, during which time a pale yellow solution formed. This solution was then cooled to 0 ºC and a solution of PPh_3 (524 mg, 2.0 mmol, 2 equiv) and anhydrous LiBr (174 mg, 2.0 mmol, 2.0 equiv) in THF (8 mL) was added dropwise followed immediately by a solution of 1,2-epoxydodecane (184 mg, 1.0 mmol, 1.0 equiv) in THF (0.5 mL) slowly dropwise. This solution was then stirred at 0 ºC for 24 h during which time a red-orange color developed. This mixture was then cooled to −78 ºC and neat CD_3OD (162 µL, 4 mmol, 4 equiv) was added dropwise. The reaction mixture was stirred at −78 ºC for 2 h, then warmed to rt over 1 h and stirring was continued for a further 1 h. Saturated aq. NH_4Cl (10 mL) was then added to the mixture, then extracted with Et_2O (3 × 15 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (0−5% Et_2O/petrol) gave deuterated alkene **14** [5] (69 mg, 41%, 50% D) as a colourless oil; R_f 0.87, 5% Et_2O/petrol.

IR (neat) /cm^{-1}: 2957w, 2923m, 2853w, 1465w, 799w, 724w; ^1H (400 MHz) δ = 5.89–5.76 (1 H, m, CH=), 5.05–4.89 (0.99 H, m, =CHD), 2.09–2.00 (2 H, m, CH_2CH=), 1.43–1.18 (16 H, m, 8 × CH_2), 0.89 (3 H, t, J = 6.8, CH_3); ^{13}C (100 MHz) δ = 139.0 (=CH), 114.1 (=CH_2), 113.8 (T, $J_{C\text{-}D}$ = 23.6, CDH), 33.8 (CH_2CH=), 32.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3); HRMS (FI+): 169.1941 calculated for $C_{12}H_{23}D$; found 169.1942.

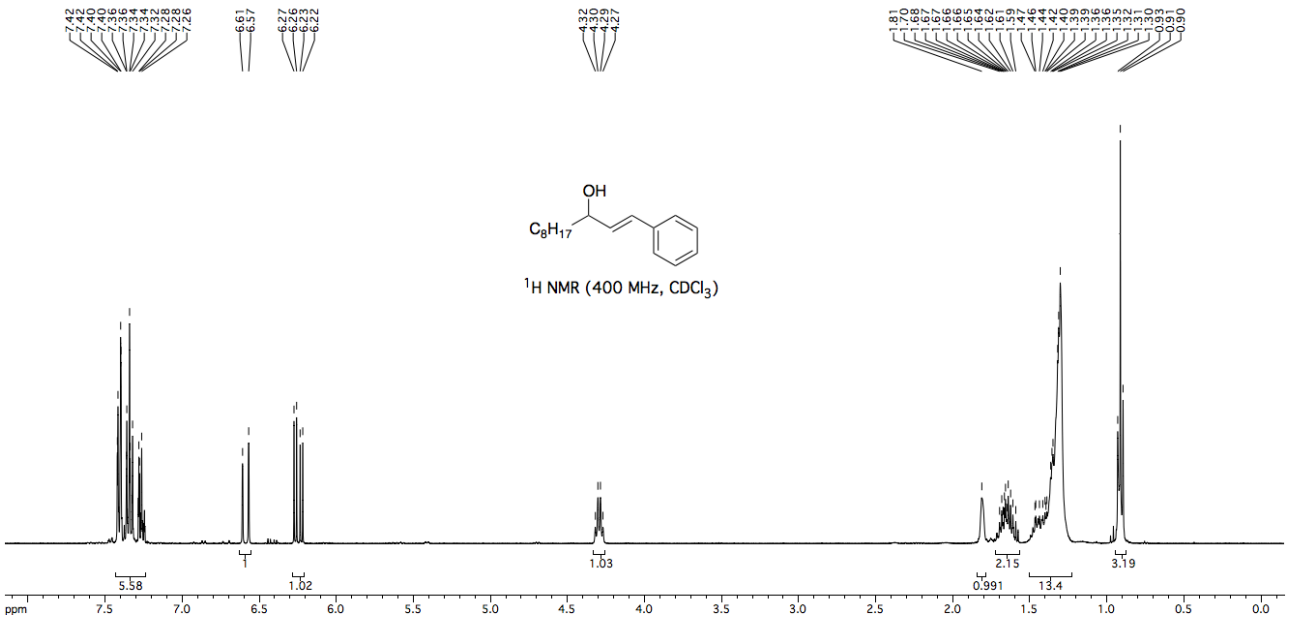
3. ^{1}H and ^{13}C spectra for 6, 7, 12 and 14

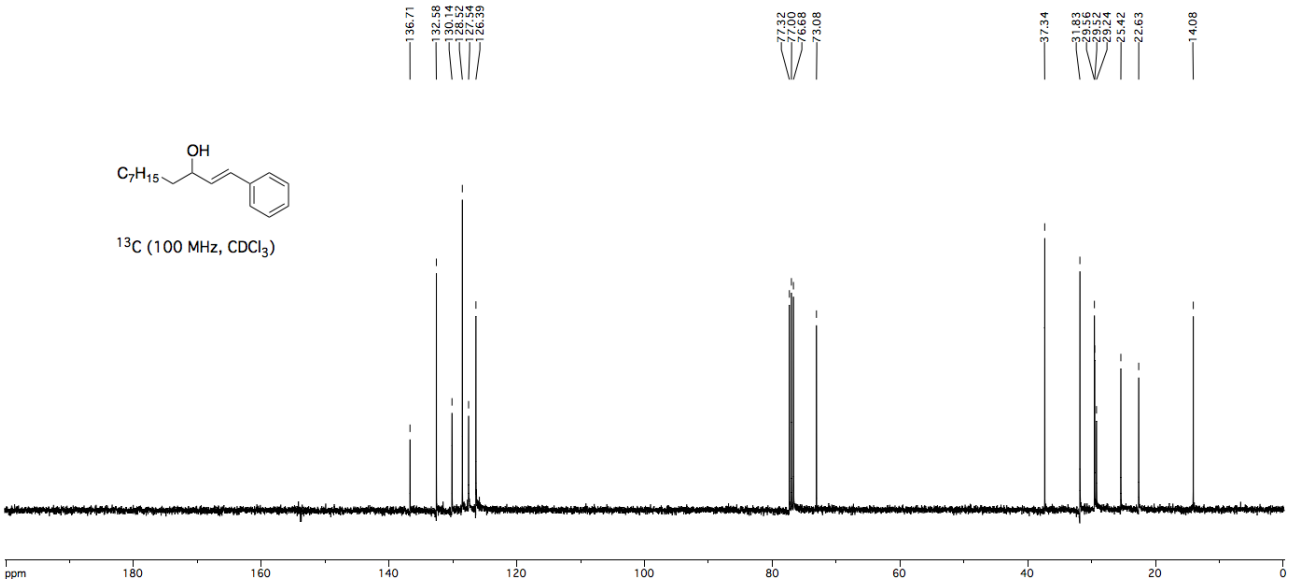
(*Z*)-Undec-2-en-1-yl pivalate (6)



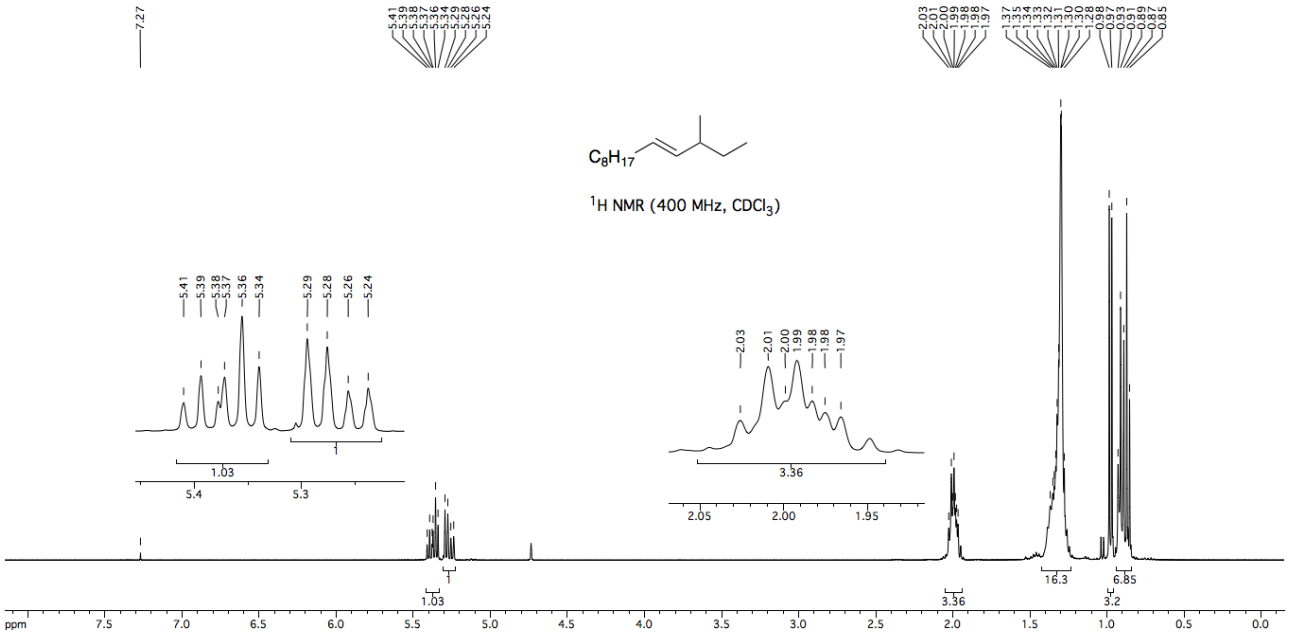


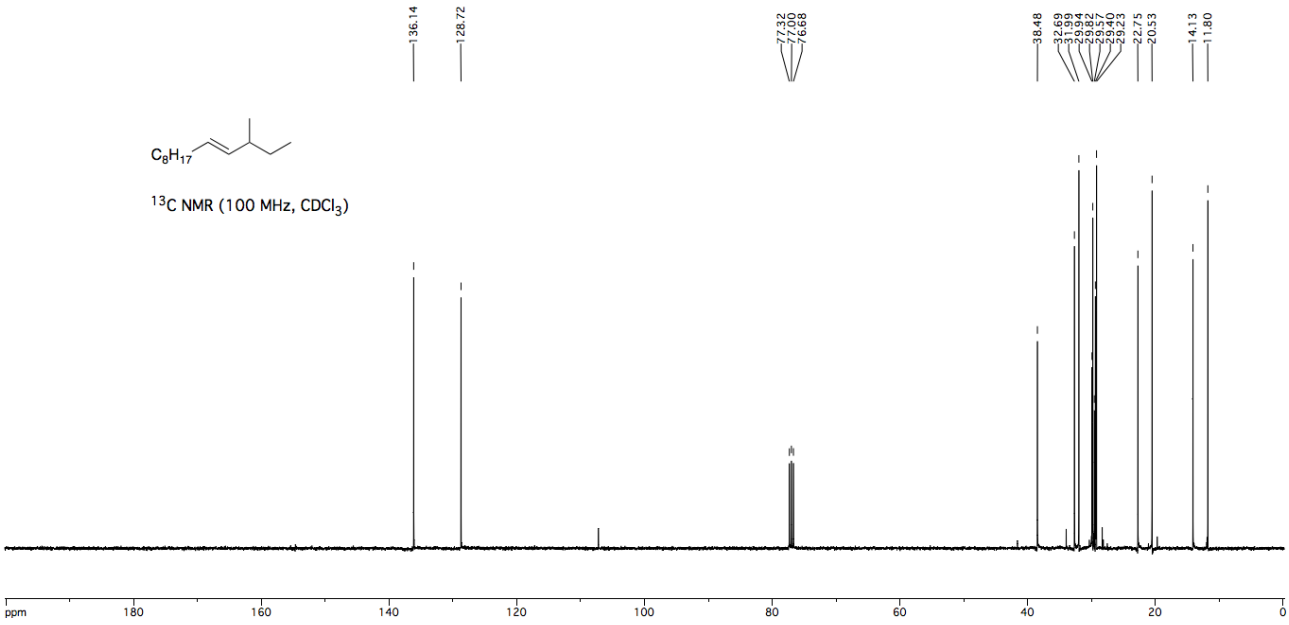
(*E*)-1-Phenylundec-1-en-3-ol (7)



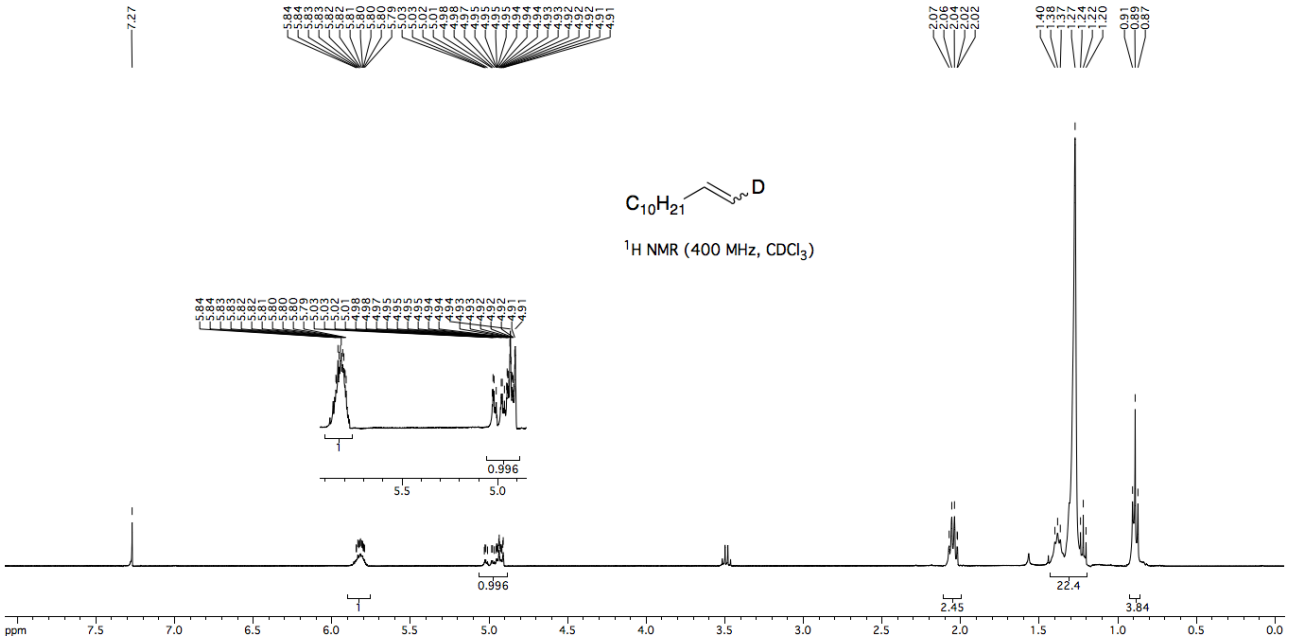


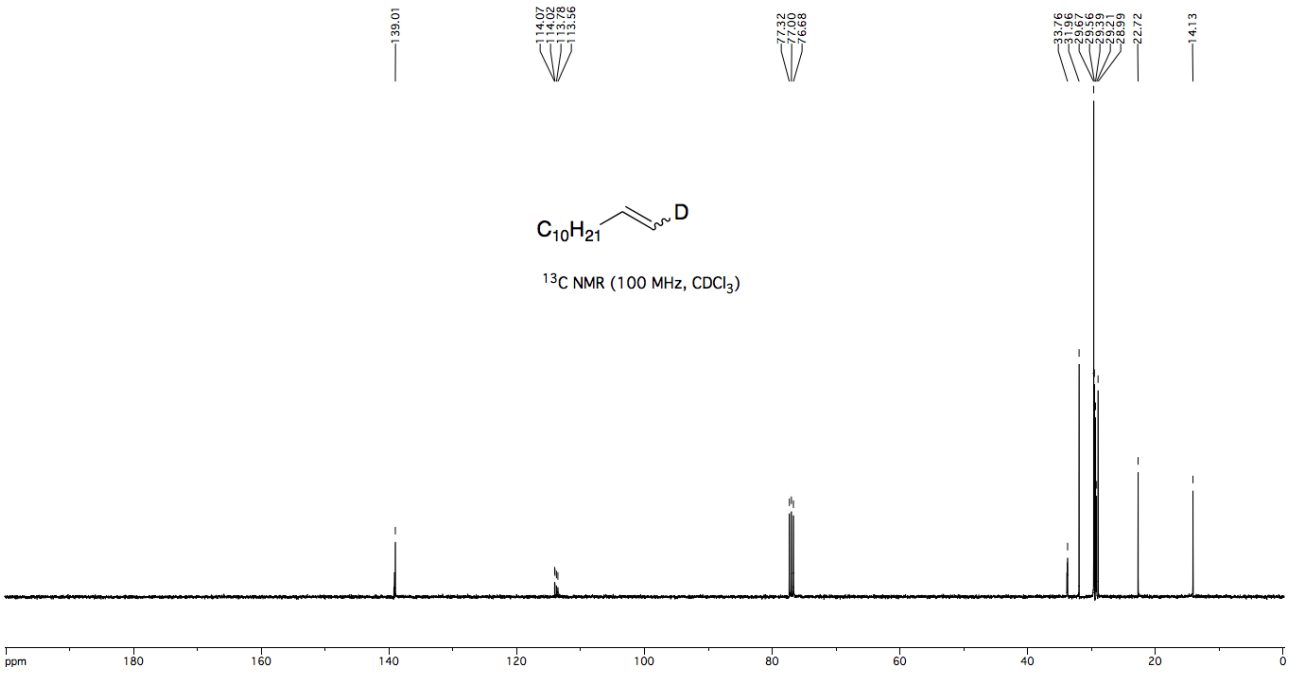
(*E*)-3-Methyltridec-4-ene (12)





1-Deuterio-decene (14)





4. References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. *J. Organometallics* **1996,** *15,* 1518−1520.
2. Hodgson, D. M.; Arif, T. *Chem. Commun.* **2011,** *47,* 2685−2687.
3. Hodgson, D. M.; Persaud, R. S. D. *Org. Biomol. Chem.,* **2012,** *10,* 7949–7951.
4. Kulinkovich, O. G.; Epstein, O. L.; Isakov, V. E.; Khmel'nitskaya, E. A. *Synlett* **2001,** 49–52.
5. Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983,** *24,* 2877–2880.