Practical, Highly Stereoselective Allyl- and Crotylsilylation of Aldehydes Catalyzed by Readily Available Cinchona Alkaloid Amide

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Supplementary Information

Table of Contents page

1. General information S2

2. General procedure for one-pot preparation of the catalysts S2

3. Representative procedure for allylation reaction S5

4. Preliminary kinetic study of the allylation reaction S6

5. Analytical data of allylation and crotylation reaction products S7

6. NMR spectra of the products S26

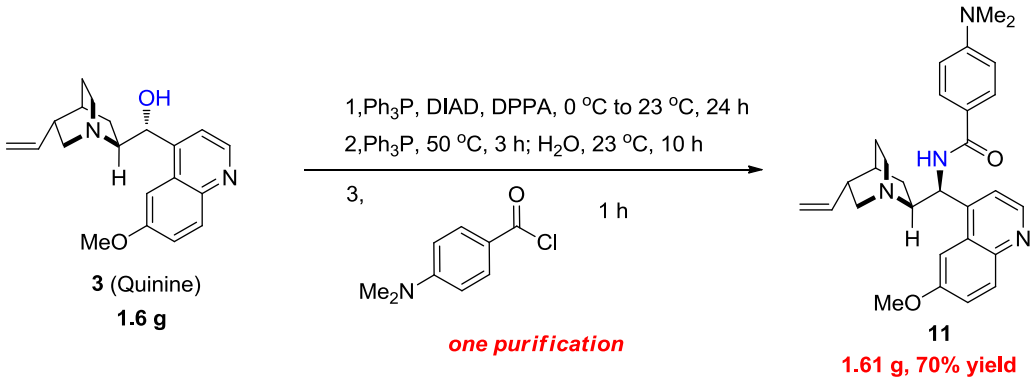
7. References S50

1. General Information

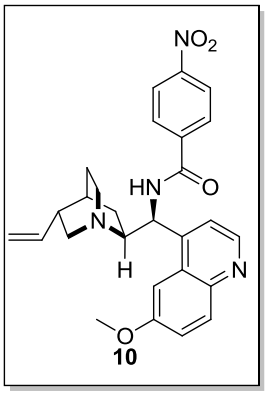
Melting point (**MP**) was obtained on Buchi B-540. Thin layer chromatography (**TLC**) was performed on Merck pre-coated TLC plates (Merck 60 F254), and compounds were visualized with a UV light at 254nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. **^{1}H** and **^{13}C NMR** spectra were recorded on a Bruker ACF300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (**HRMS**) were obtained on a Finnigan/MAT 95XL-T spectrometer. **Optical rotations** were recorded on an mrc AP81 automatic polarimeter. Enantiomeric excesses (**ee**) were determined by HPLC analysis on Agilent HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Chiralcel OD-H, Chiralpak AS-H, AD-H or IC.

All reactions were carried out under nitrogen atmosphere. Liquid reagents were handled with a micropipette. THF was dried on alumina columns using a solvent dispensing system. All commercially available aldehydes, allyltrichlorosilane and *N*, *N*-diisopropylethylamine were purchased for Aldrich and used as received for the reactions without any purification. Aldehyde **1d** and **1e** were prepared based on reported procedure[1-2]. (*E*)- and (*Z*)-crotyltrichlorosilanes were synthesized according to literature procedure[3].

2. General procedure for one-pot preparation of the catalysts.

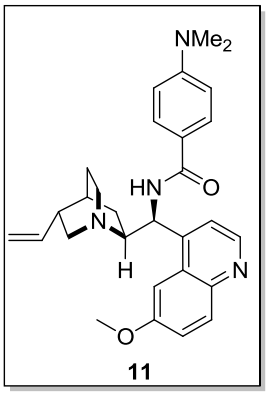


Quinine **3** (5 mmol) and triphenylphosphine (1.6 g, 6 mmol) were dissolved in anhydrous THF (25 mL), and the solution was cooled to 0 °C. Diethyl azodicarboxylate (1.0 g, 6 mmol) was subsequently added. To the resulting solution was added dropwise the solution of diphenyl phosphoryl azide (1.3 mL, 6 mmol) in anhydrous THF (10 mL) at 0 °C. The mixture was allowed to warm to ambient temperature. After 24 h, it was heated to 50°C when more triphenylphosphine (1.7 g, 6.5 mmol) was added, and the mixture was allowed to stir at 50 °C for additional 3 h. After that the solution was cooled to ambient temperature and H_2O (0.5 mL) was added[4]. After the reaction mixture was stirred for another 10 h, 4-(Dimethylamino) acid chloride (1.098 g, 6 mmol) was added in one portion, then the reaction mixture was kept stirring at room temperature for 1 h. Solvents were removed in vacuo, and the residue was dissolved in CH_2Cl_2/10% aqueous HCl (25 mL/25 mL). The aqueous phase was separated and washed with CH_2Cl_2 (25 mL × 4). It was subsequently basified with excess aqueous NH_3, and extracted with CH_2Cl_2 (25mL ×4). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. Purification by flash chromatography using silica gel with EtOAc/hexane (v/v = 1/1) then EtOAc/CH_3OH (v/v = 10/1) as an eluent yielded the corresponding amide containing product **11**.



10

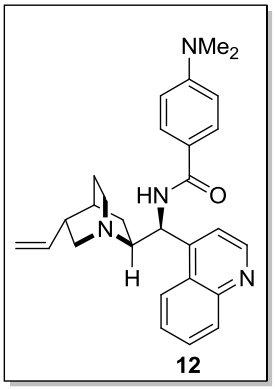
Pale yellow solid, 56% yield. **MP**: 78.9-79.7 °C. **TLC** (Methanol: Ethyl acetate, 10:1 v/v): R_f = 0.30. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.13 (s, 1H), 8.87 (s, 1H), 8.12 (ddd, *J* = 27.4, 17.0, 13.1 Hz, 4H), 7.87 (s, 1H), 7.69 (s, 1H), 7.47 (dd, *J* = 9.2, 2.6 Hz, 1H), 5.79 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.39 – 5.09 (m, 2H), 4.45 (s, 1H), 4.09 (s, 3H), 3.92 (d, *J* = 25.6 Hz, 1H), 3.61 (dd, *J* = 13.5, 10.4 Hz, 1H), 3.37 – 2.99 (m, 2H), 2.75 (s, 1H), 2.15 (dd, *J* = 20.5, 11.2 Hz, 3H), 1.91 (d, *J* = 13.3 Hz, 1H), 1.32-1.28 (d, *J* = 1.3 Hz, 2H), 0.89 (d, *J* = 6.2 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 165.08, 157.83, 147.64, 141.49, 132.76, 132.12, 131.82, 121.66, 121.53, 121.27, 114.51, 111.54, 56.33, 55.98, 55.56, 41.09, 39.74, 28.05, 27.50, 26.33. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{28}N_4O_4, M+H]^+$: 473.2183; Found: 473.2179. **Optical Rotation**: $[\alpha]_D^{23}$ = –55 (*c*1.0, CH_2Cl_2).



11

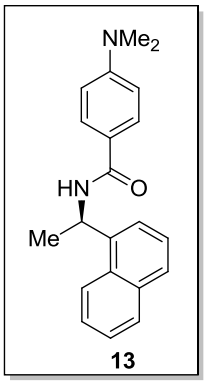
White solid 70% yield. **MP**: 119.1-120.1 °C. **TLC** (Methanol: Ethyl acetate, 10:1 v/v): R_f = 0.34. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.72 (dd, *J* = 9.6, 4.6 Hz, 1H), 8.02 (t, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 7.45 (dd, *J* = 8.8, 4.6 Hz, 1H), 7.42 – 7.32 (m, 1H), 6.65 (t, *J* = 9.3 Hz, 2H), 5.74 (td, *J* = 17.3, 9.0 Hz, 1H), 5.11 – 4.87 (m, 2H), 3.99 (d, *J* = 8.0 Hz, 3H), 3.37 – 3.26 (m, 1H), 3.19 (d, *J* = 8.5 Hz, 2H), 3.00 (d, *J* = 10.2 Hz, 6H), 2.84 – 2.66 (m, 2H), 2.33 (s, 2H), 2.21 (s, 1H), 1.79 – 1.57 (m, 3H), 1.47 (d, *J* = 8.0 Hz, 1H), 1.12 – 0.92 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.37, 157.70, 152.60, 147.57, 144.78, 141.29, 131.70, 128.69, 121.53, 120.72, 114.61, 111.01, 102.05, 56.06, 55.64, 40.93, 40.09, 39.60, 27.94, 27.41, 26.19. **HRMS**

(ESI) m/z Calcd for $[C_{29}H_{35}N_4O_2, M+H]^+$: 471.2776; Found: 471.2755. **Optical Rotation**: $[\alpha]_D^{23}$ = –50.3 (*c*1.0, CH_2Cl_2).



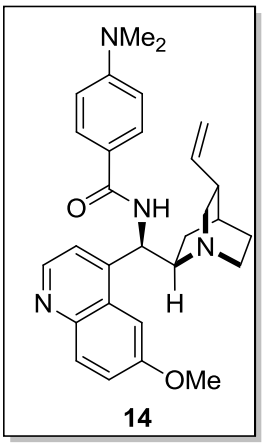
12

White solid. 68% Yield. **MP**: 145.5-146.4 °C. **TLC** (Methanol: Ethyl acetate, 10:1 v/v): R_f = 0.32. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.89 (d, *J* = 4.5 Hz, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 4.6 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.73 (ddd, *J* = 17.4, 10.2, 7.6 Hz, 1H), 5.45 (s, 1H), 4.98 (dd, *J* = 19.7, 13.7 Hz, 2H), 3.31 (dd, *J* = 13.8, 10.2 Hz, 1H), 3.23 – 3.10 (m, 2H), 3.03 (d, *J* = 13.2 Hz, 6H), 2.86 – 2.63 (m, 2H), 2.33 (s, 1H), 1.76 – 1.55 (m, 3H), 1.40 (dd, *J* = 13.2, 10.1 Hz, 1H), 1.07 (dd, *J* = 13.7, 6.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.52, 152.60, 150.08, 148.62, 141.29, 130.43, 128.97, 128.71, 126.57, 123.46, 120.78, 114.60, 111.02, 56.01, 40.84, 40.11, 39.65, 27.85, 27.38, 25.92. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{32}N_4O, M+H]^+$: 441.2649; Found: 441.2637. **Optical Rotation**: $[\alpha]_D^{23}$ = –52.5 (*c*1.0, CH_2Cl_2).



13

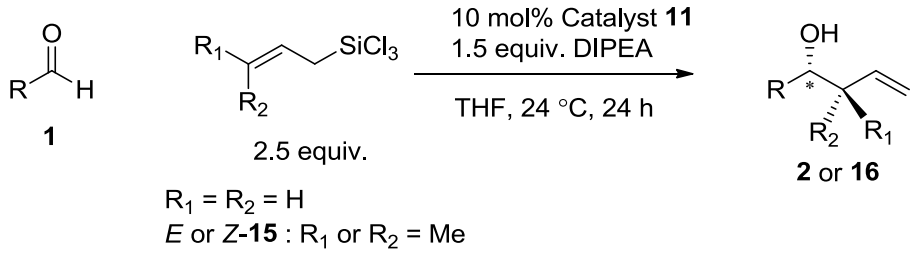
White solid. 50% yield. **MP**: 178.1-179.2 °C. **TLC** (Hexane: Ethyl acetate, 2:1 v/v): R_f = 0.4. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.43 – 8.18 (m, 1H), 8.03 – 7.80 (m, 2H), 7.78 – 7.45 (m, 6H), 6.64 (t, *J* = 10.6 Hz, 2H), 6.39 (d, *J* = 7.5 Hz, 1H), 6.16 (dd, *J* = 13.6, 6.8 Hz, 1H), 3.11 – 2.97 (m, 6H), 1.81 (dd, *J* = 13.2, 6.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 152.37, 138.75, 133.90, 131.27, 128.62, 128.39, 128.19, 126.47, 125.74, 125.15, 123.66, 122.60, 110.95, 44.87, 40.01, 20.78. **HRMS (ESI)** m/z Calcd for $[C_{21}H_{22}N_2O, M+Na]^+$: 341.1625; Found: 341.1635. **Optical Rotation**: $[\alpha]_D^{23}$ = -10 (*c*1.0, CH_2Cl_2).



14

White solid. 63% Yield. **MP**: 71.4-72.5 °C. **TLC** (Methanol: Ethyl acetate, 10:1 v/v): R_f = 0.38. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.6 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 2H), 7.93 – 7.66 (m, 3H), 7.54 (d, *J* = 4.6 Hz, 1H), 7.40 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.72 – 6.52 (m, 2H), 6.08 – 5.90 (m, 1H), 5.37 – 5.16 (m, 2H), 4.04 (s, 3H), 3.43 (d, *J* = 8.9 Hz, 1H), 3.14 (d, *J* = 15.7 Hz, 3H), 3.08 – 2.96 (m, 6H), 2.44 (s, 1H), 2.05 (d, *J* = 16.0 Hz, 2H), 1.84 – 1.60 (m, 3H), 1.54 – 1.41 (m, 1H), 1.19 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR** (75MHz, $CDCl_3$): δ 167.37, 157.70, 152.60, 147.57, 144.78, 141.29, 131.70, 128.68, 121.53, 120.72, 114.61, 111.06, 102.05, 56.09, 55.68, 40.93, 40.09, 39.64, 27.94, 27.41, 26.18. **HRMS (ESI)** m/z Calcd for $[C_{29}H_{35}N_4O_2, M+H]^+$: 471.2749; Found: 471.2771. **Optical Rotation**: $[\alpha]_D^{23}$ = +53.5 (*c*1.0, CH_2Cl_2).

3. Representative procedure for allylation reaction.



To a 4 mL vial equipped with a stir bar was added the catalyst (0.03 mmol, 10 mol%). The vial was taken into glovebox, where anhydrous THF (1 mL), DIPEA (0.45 mmol, 1.5 equiv.) and allyltrichlorosilane (0.75 mmol, 2.5 equiv.) were added. The reaction mixture was taken outside the glovebox and the aldehyde (0.3 mmol) was added using a micropipette (open to air). The reaction mixture changed to bright red in color upon addition of aldehyde. The vial was then sealed and the reaction mixture was allowed to stir at ambient temperature for 24 h. The crude reaction mixture was quenched by pouring into a mixture of dichloromethane (5 mL) and saturated $NaHCO_3$ solution (5 mL). The resulting mixture was vigorously stirred for 1 h, and then extracted with dichloromethane (3 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL), dried over anhydrous Na_2SO_4 and concentrated. Purification by silica gel chromatography yielded the recovered catalyst in quantitative yield and the desired product that was analyzed for purity by NMR and for enantioenrichment by chiral HPLC (Chiralcel OD-H, Chiralpark IC, AS-H or AD-H).

4. Preliminary kinetic studies of the allylation reaction.

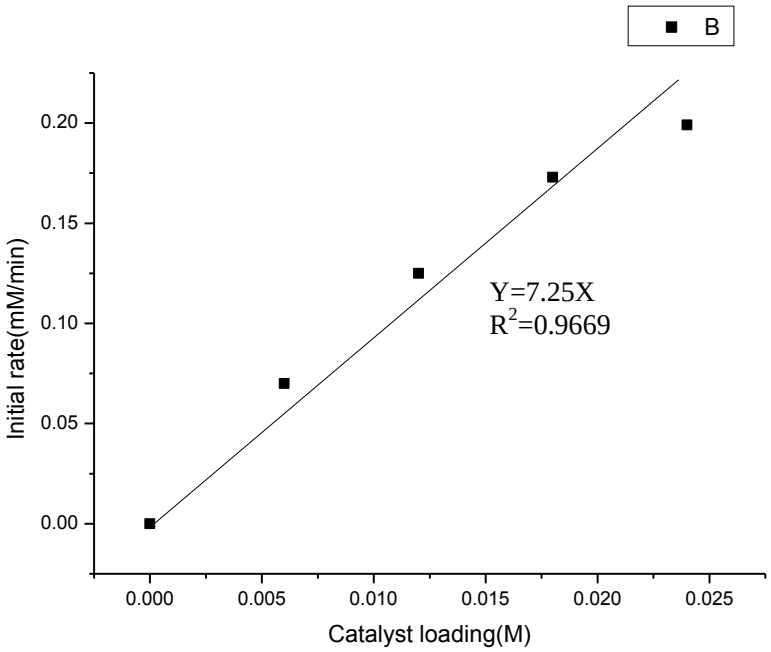
Determination of the dependence of the allylation reaction on catalyst:

To a 25 mL vial equipped with a stir bar was added the catalyst (0.036 mmol). The vial was taken into glovebox, where anhydrous THF (3 mL), DIPEA (0.45 mmol) and allyl trichlorosilane (2.5 mmol) were added. The reaction mixture was taken outside the glovebox, and the aldehyde (0.3 mmol) in 3 mL THF was added using a micropipette. The vial was then sealed and the reaction mixture was allowed to stir at ambient temperature. Real time conversion was determined by NMR (500MHz).

Table S1. Effect of initial catalyst concentration [**11**] on the rate of allylation reaction.

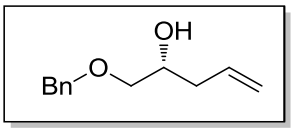
[Catalyst **11**]$_{initial}$ (M)	k_{obs} (mM/min)
0.006	0.07
0.0012	0.125
0.018	0.173
0.024	0.199

Figure S1. First order dependence on catalyst of allylation of aldehydes.



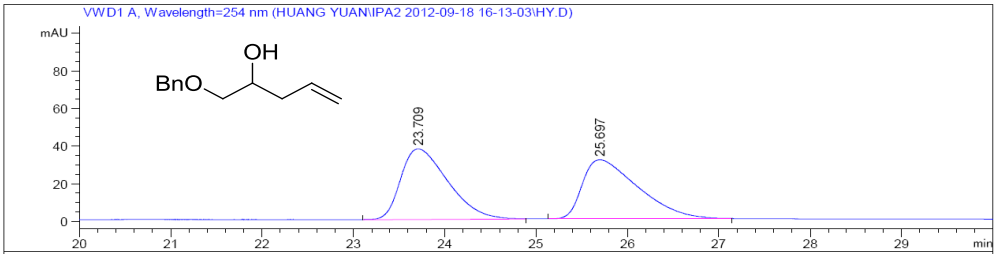
5. Analytical data of allylation and crotylation Reaction products.

(*R*)-1-(benzyloxy) pent-4-en-2-ol (2a, Entry 1, Table 2).



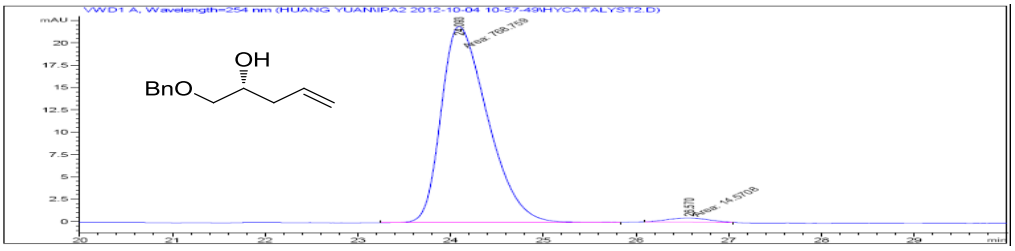
Colorless oil, 83% yield with catalyst **11**, 86% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f =0.63. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.44 – 7.32 (m, 5H), 5.87 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.22 – 5.05 (m, 2H), 4.60 (s, 2H), 3.99 – 3.85 (m, 1H), 3.56 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.42 (dd, *J* = 9.5, 7.4 Hz, 1H), 2.42 (d, *J* = 3.6 Hz, 1H), 2.36 – 2.24 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 137.89, 134.15, 128.39, 127.72, 127.66, 117.62, 73.82, 73.31, 69.65, 37.83.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -6.5 (0.24, $CHCl_3$). The absolute configuration of **2a** was assigned by comparing its specific rotation with that of the same compound reported in the literature.[5] 96% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1, flow rate = 1.0 ml/min, wavelength = 254nm, t_R = 24.09 min for major isomer, t_R = 26.57 min for minor isomer).



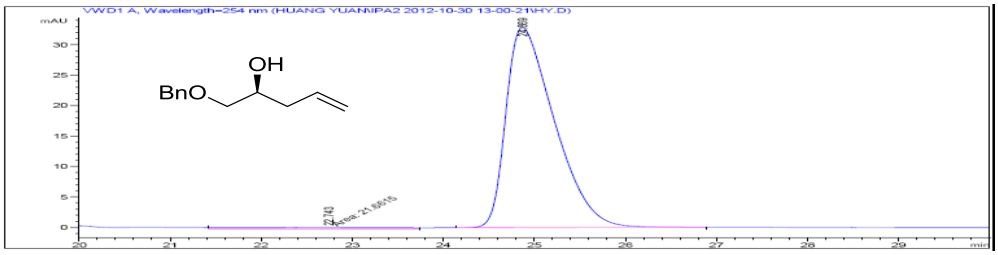
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	23.709	BB	0.5476	1339.75610	50.2753	?
2	25.697	BB	0.6046	1325.08594	49.7247	?

Catalyst 11



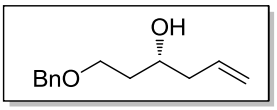
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.093	MM T	0.5834	768.75879	21.96027	98.1399
2	26.570	MM T	0.5240	14.57080	4.63433e-1	1.8601

Catalyst 14



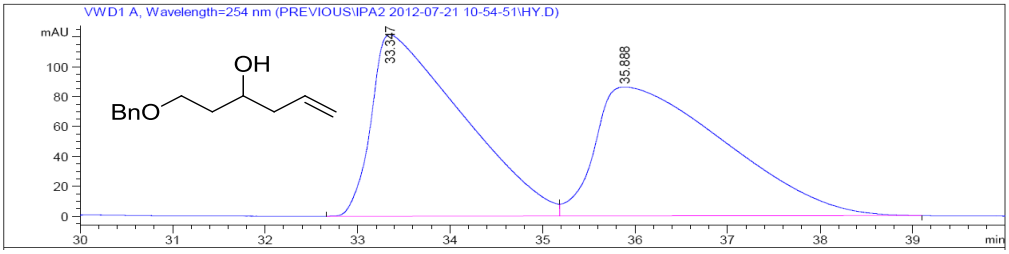
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.743	MM T	1.8050	21.66147	1.79953e-1	1.7558
2	24.869	BB	0.5637	1212.05530	32.83027	98.2442

(*R*)-1-(benzyloxy) hex-5-en-3-ol (2b, Entry 2, Table 2)



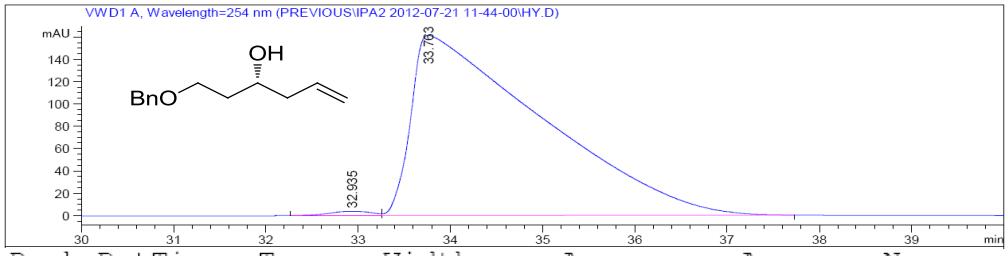
Colorless oil, 89% yield with catalyst **11**, 82% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.7. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.45 – 7.26 (m, 5H), 5.95 – 5.79 (m, 1H), 5.24 – 5.08 (m, 2H), 4.55 (s, 2H), 3.97 – 3.84 (m, 1H), 3.83 – 3.64 (m, 2H), 2.93 (s, 1H), 2.28 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.76 (m, 2H). **^{13}C NMR** (125 MHz, CDCl3): δ 137.99, 134.89, 128.47, 127.76, 127.69, 117.58, 73.32, 70.32, 68.91, 41.94, 35.90.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -10.75 (0.2, $CHCl_3$). The absolute configuration of **2b** was assigned by comparing its specific rotation with that of the same compound reported in the literature[6]. 99% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1, flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R\,=}$ 32.93 min for minor isomer, $t_{R\,=}$ 33.76 min for major isomer).



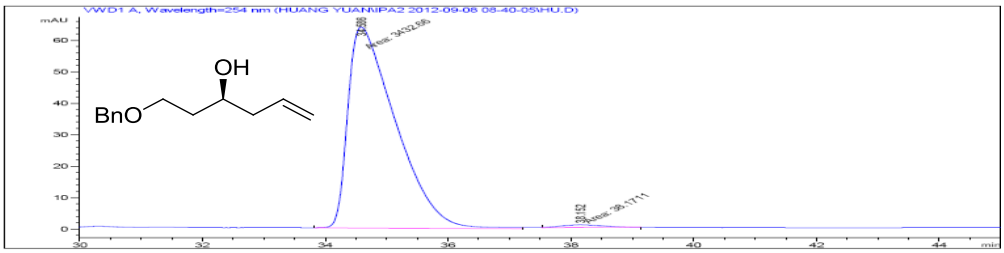
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	33.347	BV	0.8869	8338.98633	49.6179	?
2	35.888	VB	1.1540	8467.40430	50.3821	?

Catalyst 11



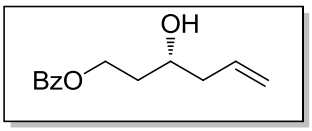
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	32.935	BV	0.3725	125.87055	0.7837	?
2	33.763	VB	1.2318	1.59353e4	99.2163	?

Catalyst 14



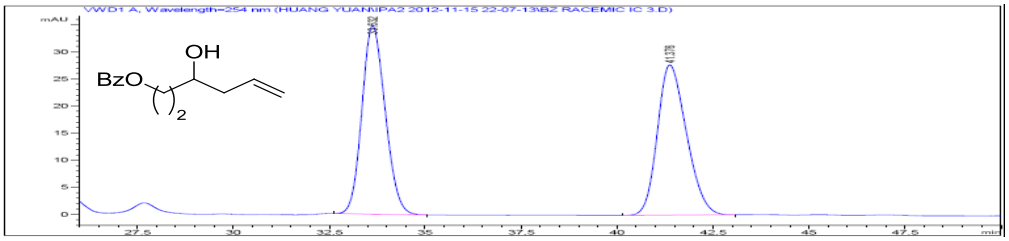
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.586	MM	0.8958	3432.65576	63.86703	98.9002
2	38.152	MM	0.7668	38.17105	8.29661e-1	1.0998

(*R*)-3-hydroxyhex-5-en-1-yl benzoate (2c, Entry 3, Table 2).



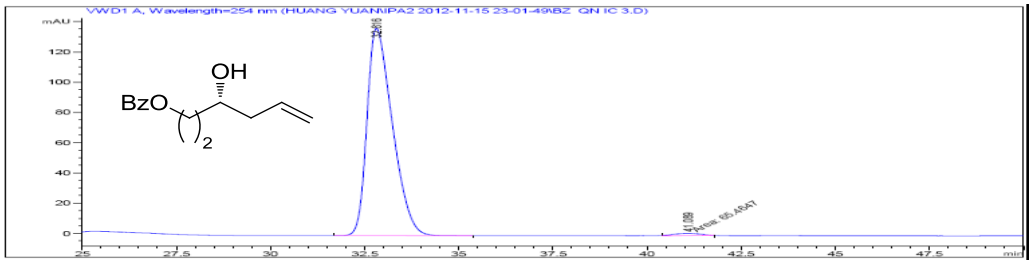
Colorless oil, 90% yield with catalyst **11**, 88% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.56. **^{1}H NMR** (300 MHz, $CHCl_3$): δ 8.17 – 8.01 (m, 2H), 7.70 – 7.44 (m, 3H), 6.01 – 5.78 (m, 1H), 5.32 – 5.11 (m, 2H), 4.62 (ddd, *J* = 11.2, 8.5, 5.3 Hz, 1H), 4.47 (dt, *J* = 11.2, 5.7 Hz, 1H), 3.89 (s, 1H), 2.50 – 2.19 (m, 3H), 2.13 – 1.74 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.71, 134.27, 132.93, 129.51, 128.31, 118.31, 67.51, 62.01, 41.89, 35.81. **HRMS (ESI)** m/z Calcd for $[C_{13}H_{16}O_3, M+H]^+$: 221.1123; Found:221.1218.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -8.333 (0.6, $CHCl_3$). The absolute configuration of **2c** was assigned by comparing its specific rotation with analogue. 98% ee. (HPLC condition: Chiralpark IC column, *n*-hexane/*i*-PrOH = 97:3, flow rate = 1.0 ml/min, wavelength = 254 nm, $t_{R\ =}$ 32.81 min for major isomer, $t_{R\ =}$ 41.08 min for minor isomer).



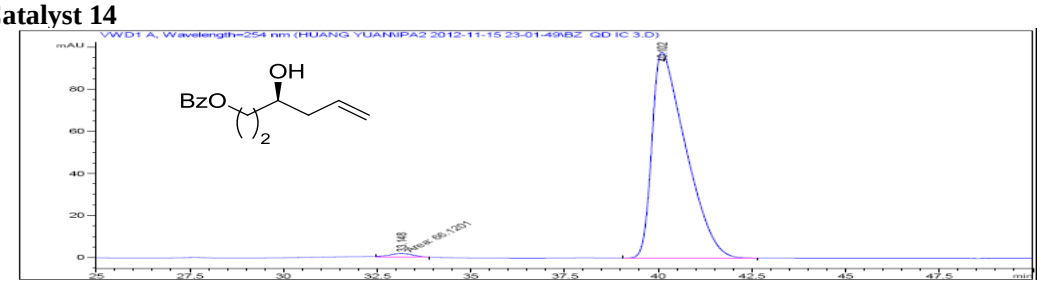
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.632	BB	0.6552	1467.33630	34.77836	50.0946
2	41.376	BB	0.8164	1461.79175	27.75877	49.9054

Catalyst 11



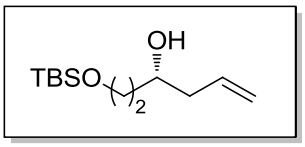
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.816	BB	0.7134	6411.59521	136.88773	98.9893
2	41.089	MM	0.7592	65.46473	1.43710	1.0107

Catalyst 14



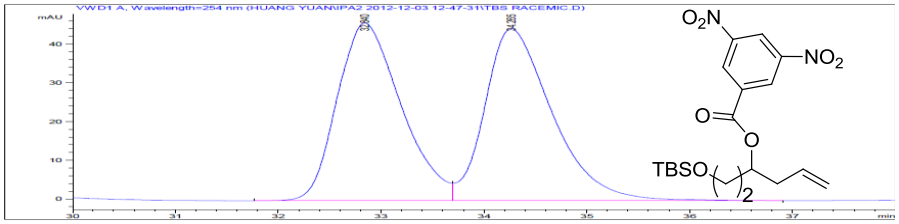
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.148	MM	0.6732	66.12014	1.63696	1.0698
2	40.102	BB	0.9104	6114.42871	97.66659	98.9302

(*R*)-1-((*tert*-butyldimethylsilyl)oxy) pent-4-en-2-ol (2d, Entry 4, Table 2).



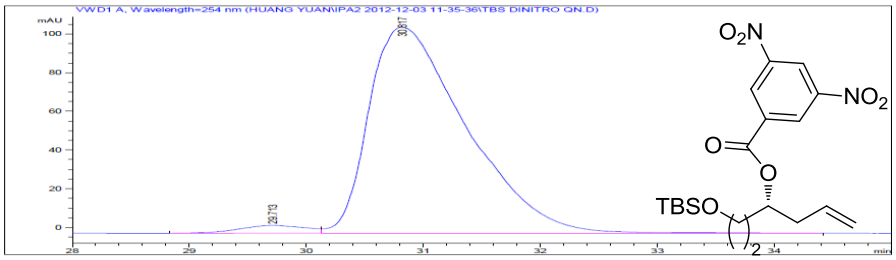
Colorless oil, 70% yield with catalyst **11**, 73% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.82. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.90 – 5.77 (m, 1H), 5.14 – 5.04 (m, 2H), 3.89 (dt, *J* = 9.9, 4.9 Hz, 2H), 3.84 – 3.76 (m, 2H), 3.37 (d, *J* = 2.0 Hz, 1H), 2.33 – 2.14 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 9H), 0.08 (d, *J* = 8.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 135.01, 117.29, 71.25, 62.58, 41.95, 37.76, 25.85, 25.64, -3.60, -5.58.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -6.76 (0.3, $CHCl_3$). The absolute configuration of **2d** was assigned by comparing its specific rotation with that of the same compound reported in the literature.[6] The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 95% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99.5:0.5, flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R=}$ 32.81 min for major isomer, $t_{R=}$ 41.08 min for minor isomer).



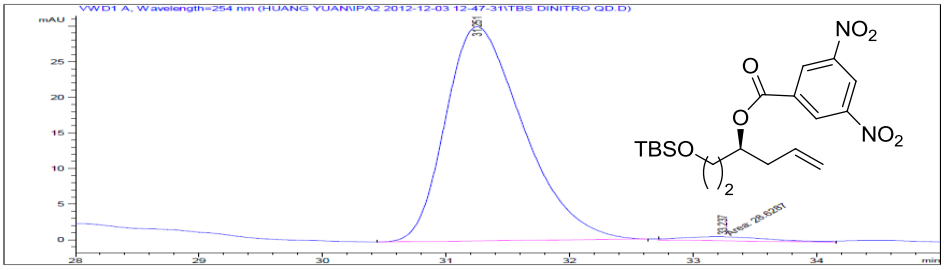
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.840	BV	0.6049	1979.97241	45.83814	49.5305
2	34.265	VB	0.6515	2017.50903	44.36768	50.4695

Catalyst 11



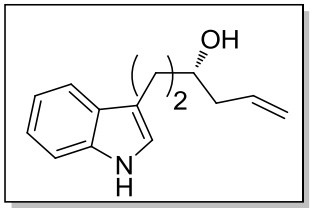
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.713	BV	0.5367	155.45979	3.96306	2.4720
2	30.817	VB	0.7723	6133.25781	106.27930	97.5280

Catalyst 14



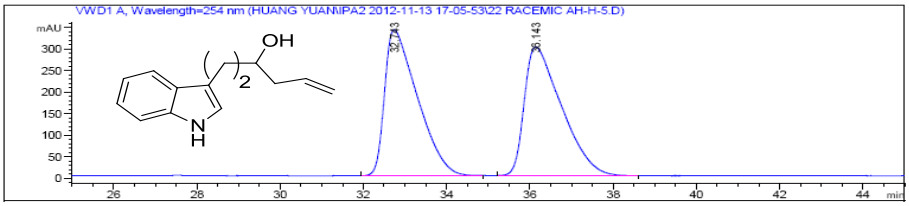
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.251	BB	0.6497	1315.46753	30.04878	97.8700
2	33.237	MM T	0.8480	28.62873	5.62688e-1	2.1300

(*R*)-1-(1H-indol-3-yl) pent-4-en-2-ol (2e, Entry 5, Table 2)



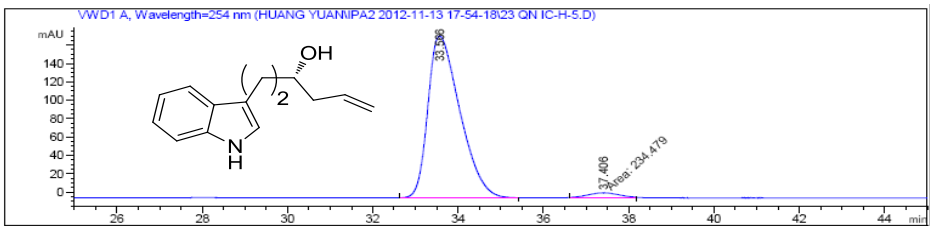
Colorless oil, 75% yield with catalyst **11**. 80% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.33. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.35 (m, 1H), 7.33 – 7.12 (m, 2H), 7.07 – 6.98 (m, 1H), 5.88 (dddd, *J* = 11.1, 9.3, 7.8, 6.5 Hz, 1H), 5.32 – 5.12 (m, 2H), 3.80 (ddd, *J* = 12.1, 7.7, 4.6 Hz, 1H), 3.10 – 2.82 (m, 2H), 2.50 – 2.33 (m, 1H), 2.33 – 2.16 (m, 1H), 2.00 – 1.88 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 136.40, 134.79, 127.49, 121.98, 121.20, 119.21, 118.94, 118.21, 116.21, 111.10, 70.31, 42.05, 37.10, 21.35. **HRMS (ESI)** m/z Calcd for $[C_{14}H_{16}NO, M]^+$: 215.1237; Found:215.1230.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -3.083(0.6, CH_2Cl_2). The absolute configuration of **2e** was assigned by comparing its specific rotation with analogue. 96% ee. (HPLC condition: Chiralpark IC column, *n*-hexane/*i*-PrOH = 95:5 flow rate = 1 ml/min, wavelength = 254 nm, $t_{R\ =}$ 33.56 min for major isomer, $t_{R\ =}$ 37.40 min for minor isomer).



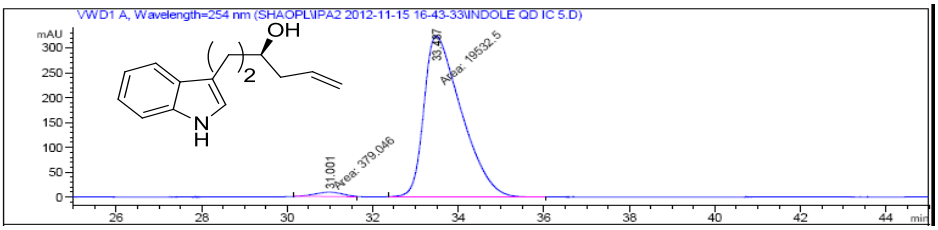
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	32.743	BB	0.7788	1.84917e4	49.9154	?
2	36.143	BB	0.8938	1.85544e4	50.0846	?

Catalyst 11



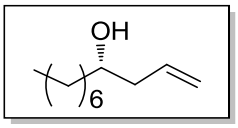
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	33.566	BB	0.7545	9156.17188	97.5031	?
2	37.406	MM T	0.7934	234.47859	2.4969	?

Catalyst 14



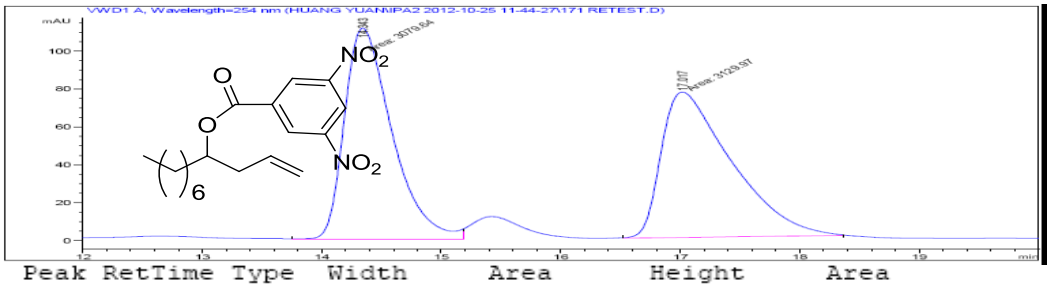
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	31.001	MM	0.7370	379.04581	1.9036	?
2	33.487	MM T	1.0082	1.95325e4	98.0964	?

(*S*)-hex-5-en-3-ol (2f, Entry 6, Table 2).



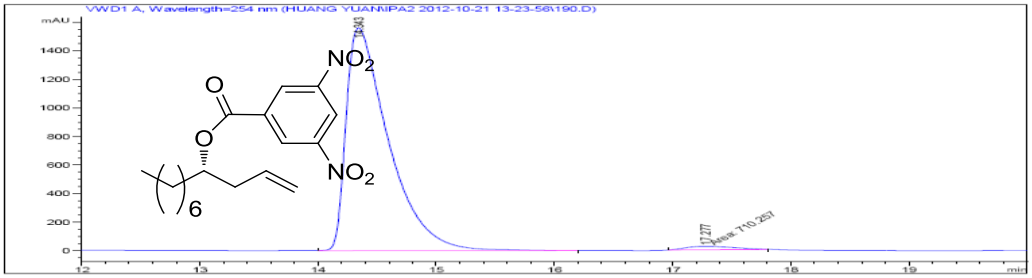
Colorless oil, 80% yield with catalyst **11**, 74% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.82. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.85 (dddd, *J* = 11.6, 9.4, 7.8, 6.5 Hz, 1H), 5.19 – 5.12 (m, 2H), 3.67 (s, 1H), 2.39 – 2.28 (m, 1H), 2.22 – 2.14 (m, 1H), 1.68 (s, 2H), 1.38 – 1.26 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 134.94, 118.03, 70.71, 41.94, 36.83, 31.82, 29.62, 29.27, 25.67, 22.65, 14.08.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -18 (0.5,CH_2Cl_2). The absolute configuration of **2f** was assigned by comparing its specific rotation with that of the same compound reported in the literature[6]. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 96% ee. (HPLC condition: Chiralpark AD-H column, *n*-hexane/*i*-PrOH = 99:1, flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R=}$ 14.34 min for major isomer, $t_{R=}$ 17.27 min for minor isomer).



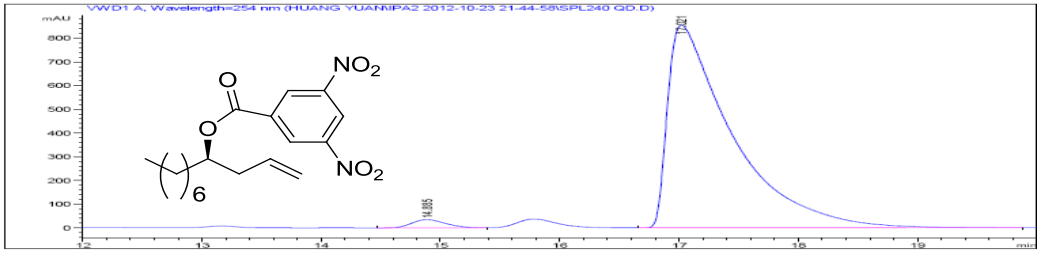
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.343	MM T	0.4611	3079.64185	111.32536	49.5948
2	17.017	MM T	0.6796	3129.96509	76.76212	50.4052

Catalyst 11



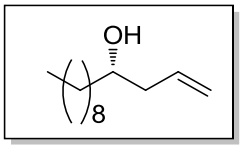
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.343	VB	0.3688	3.87400e4	1559.36267	98.1996
2	17.277	MM	0.4803	710.25714	24.64479	1.8004

Catalyst 14



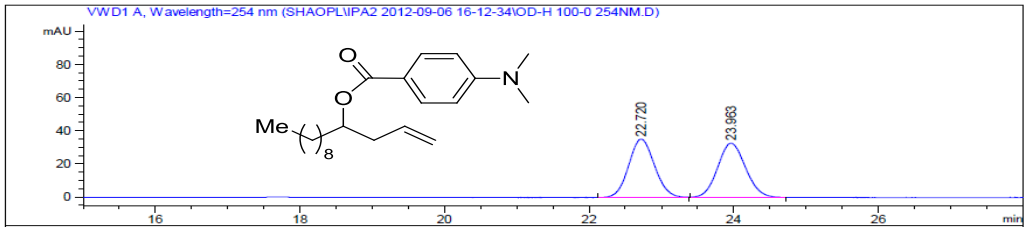
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.885	BV	0.3118	689.13580	34.38715	2.1064
2	17.021	BB	0.5274	3.20275e4	854.31805	97.8936

(*S*)-tridec-1-en-4-ol (2g, Entry 7, Table 2).



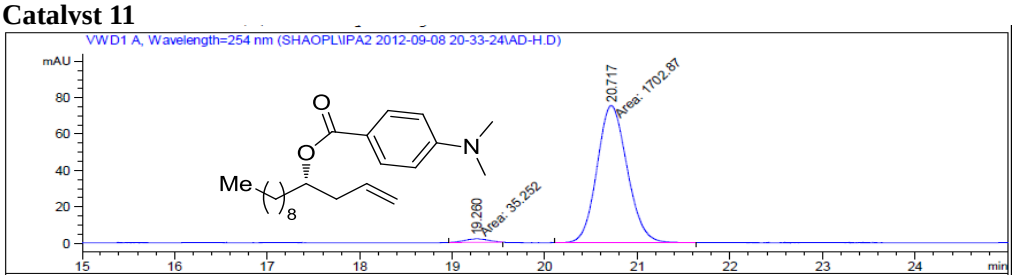
Colorless oil, 78% yield with catalyst **11**. 71% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.86. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.83 (dddd, *J* = 14.5, 9.5, 7.8, 6.6 Hz, 1H), 5.18 – 5.05 (m, 2H), 3.63 (s, 1H), 2.38 – 2.22 (m, 1H), 2.23 – 2.07 (m, 1H), 1.51 – 1.38 (m, 3H), 1.21 (d, *J* = 31.6 Hz, 14H), 0.88 (q, *J* = 6.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 134.85, 117.95, 70.62, 41.84, 36.74, 31.81, 29.61, 29.57, 29.48, 29.23, 25.58, 22.59, 14.02.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -20.3 (0.6, CH_2Cl_2). The absolute configuration of **2h** was assigned by comparing its specific rotation with that of the same compound reported in the literature[6]. The enantiomeric ratio of the compound was determined after converting to the corresponding para-dimethylaminobenzate. 96% ee. (HPLC condition: Chiralpark AD-H column, *n*-hexane/*i*-PrOH = 99:1, flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R=}$ 14.34 min for minor isomer, $t_{R=}$ 17.27 min for major isomer).



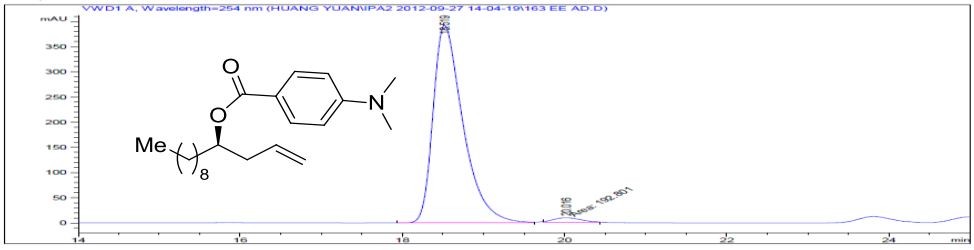
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	22.720	BB	0.3791	876.30060	49.8871	?
2	23.963	BB	0.3954	880.26752	50.1129	?

Catalyst 11



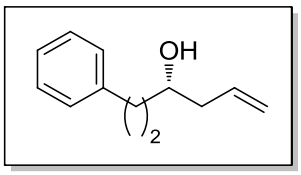
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	19.260	MM T	0.3020	35.25200	2.0282	?
2	20.717	MM T	0.3769	1702.86511	97.9718	?

Catalyst 14



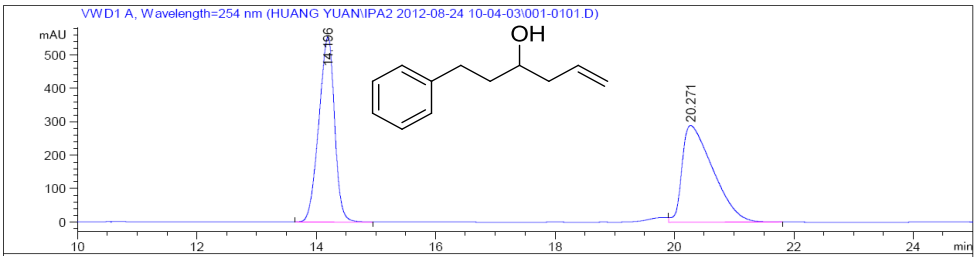
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.519	BV	0.3875	1.00688e4	392.25269	98.1211
2	20.016	MM T	0.3743	192.80145	8.58528	1.8789

(*R*)-1-phenylpent-4-en-2-ol (2h, Entry 8, Table 2)



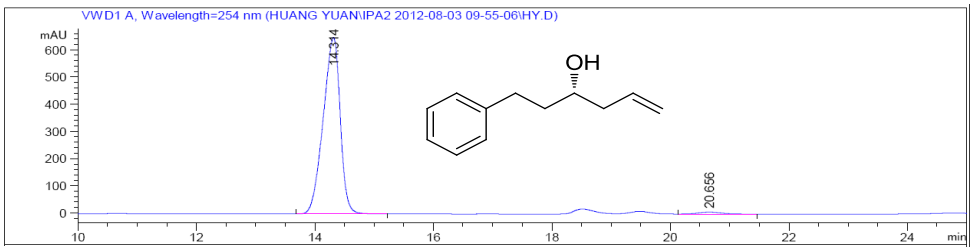
Colorless oil, 76% yield with catalyst **11**. 71% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.67. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.18 (m, 5H), 5.87 (dddd, *J* = 16.2, 9.5, 7.8, 6.6 Hz, 1H), 5.26 – 5.14 (m, 2H), 3.79 – 3.66 (m, 1H), 3.02 – 2.61 (m, 2H), 2.49 – 2.28 (m, 1H), 2.30 – 2.17 (m, 1H), 1.84 (ddd, *J* = 8.9, 7.2, 3.5 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 141.99, 134.54, 128.36, 128.33, 125.75, 118.22, 69.88, 41.98, 38.37, 31.97.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -3.2 (0.7, CH_2Cl_2). The absolute configuration of **2i** was assigned by comparing its specific rotation with that of the same compound reported in the literature[6]. 97% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95:5 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R\,=}$ 14.31 min for major isomer, $t_{R\,=}$ 20.65 min for minor isomer).



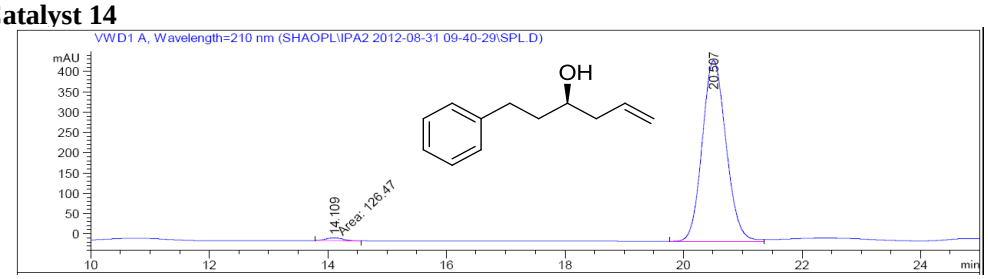
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.196	VB	0.2843	1.01754e4	49.5178	?
2	20.271	VB	0.5326	1.03736e4	50.4822	?

Catalyst 11



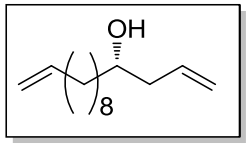
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.314	BB	0.3070	1.29713e4	98.5086	?
2	20.656	VB	0.3319	196.38721	1.4914	?

Catalyst 14



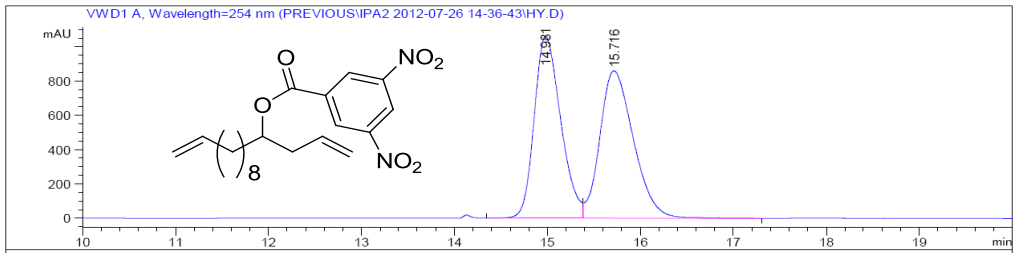
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.109	MM T	0.3210	126.46964	1.0075	?
2	20.507	BV	0.4355	1.24265e4	98.9925	?

(*S*)-tetradeca-1,13-dien-4-ol (2i, Entry 9, Table 2)



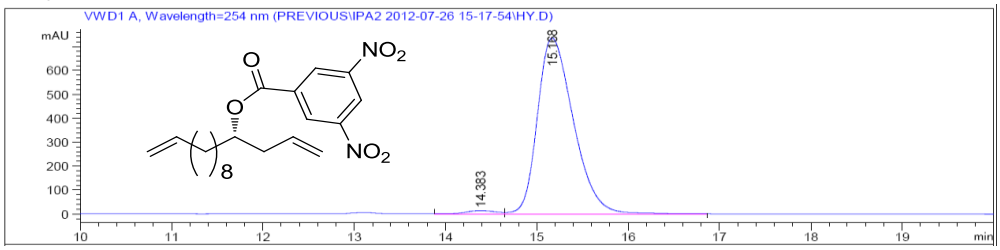
Colorless oil, 78% yield with catalyst **11**. 85% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.86. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.15 – 5.59 (m, 2H), 5.14 (dd, *J* = 10.2, 6.5 Hz, 2H), 5.05 – 4.82 (m, 2H), 3.63 (s, 1H), 2.37 – 2.23 (m, 1H), 2.19 – 2.08 (m, 1H), 2.03 (dd, *J* = 14.4, 6.9 Hz, 2H), 1.69 – 1.54 (m, 1H), 1.40 – 1.20 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$)**:** δ 139.22, 134.93, 118.03, 114.11, 70.70, 41.94, 36.82, 33.80, 29.63, 29.54, 29.42, 29.11, 28.92, 25.65. **HRMS (ESI)** m/z Calcd for $[C_{14}H_{26}O, M+H]^+$: 211.2043; Found:211.2010.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -14.2 (0.58, CH_2Cl_2). The absolute configuration of **2j** was assigned by comparing its specific rotation with analogue. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 97% ee. (HPLC condition: Chiralpark AS-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 0.4 ml/min, wavelength = 254 nm, $t_{R=}$ 14.38 min for minor isomer, $t_{R=}$ 15.16 min for major isomer).



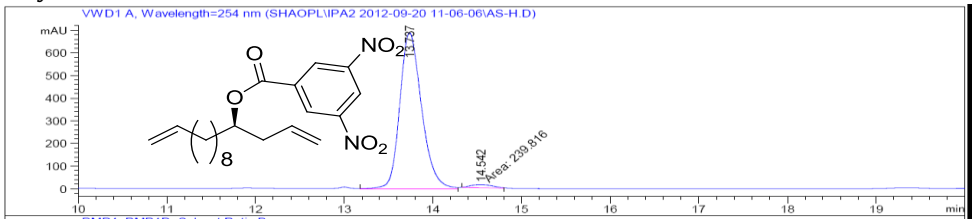
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.981	VV	0.3055	2.10622e4	49.3370	?
2	15.716	VB	0.3892	2.16283e4	50.6630	?

Catalyst 11



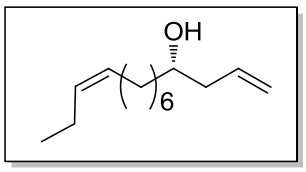
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	14.383	VV	0.3292	296.94052	1.4544	?
2	15.168	VB	0.4181	2.01201e4	98.5456	?

Catalyst 14



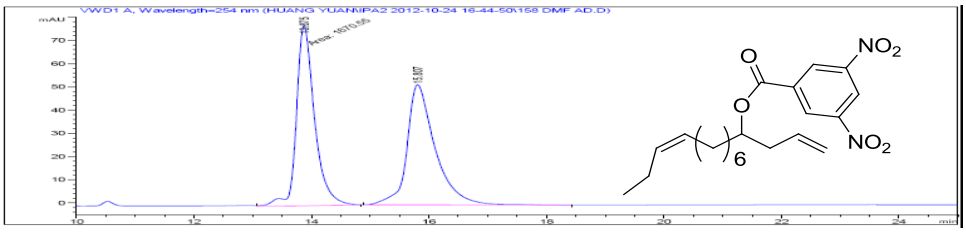
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	13.737	VV	0.2621	1.17392e4	97.9980	?
2	14.542	MM T	0.2751	239.81561	2.0020	?

(*S*, *Z*)- tetradeca- 1, 11-dien-4-ol (2j, Entry 10, Table 2)



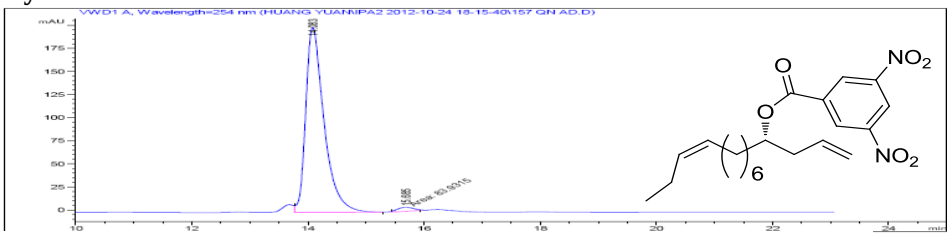
Colorless oil, 83% yield with catalyst **11**. 80% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.86. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.06 – 5.64 (m, 1H), 5.42 – 5.26 (m, 2H), 5.18 – 5.05 (m, 2H), 3.63 (s, 1H), 2.39 – 2.22 (m, 1H), 2.19 – 2.07 (m, 1H), 2.01 (dd, *J* = 13.5, 7.1 Hz, 3H), 1.32 (dd, *J* = 33.5, 27.4 Hz, 12H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 134.91, 134.59, 129.24, 118.08, 70.69, 41.94, 36.82, 33.80, 29.54, 29.42, 27.06, 25.65, 20.51, 14.39. **HRMS (ESI)** m/z Calcd for $[C_{14}H_{26}O, M+H]^+$: 211.2021; Found:211.2036.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = -11.24 (0.58, CH_2Cl_2). The absolute configuration of **2k** was assigned by comparing its specific rotation with analogue. The enantiomeric ratio of the compound was determined after converting to the corresponding 3,5-dinitrobenzate. 96% ee. (HPLC condition: Chiralpark AD-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R=}$ 14.38 min for minor isomer, $t_{R=}$ 15.16 min for major isomer).



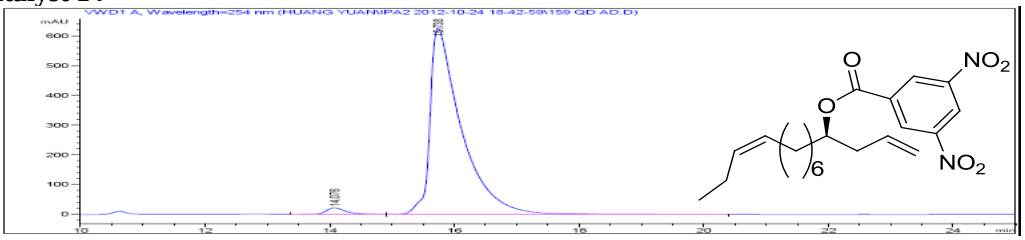
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.875	MM	0.3587	1670.54907	77.61031	49.2204
2	15.807	BB	0.4856	1723.46582	51.74753	50.7796

Catalyst 11



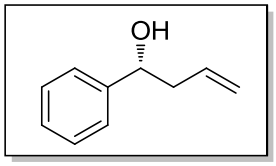
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.083	VB	0.3296	4376.14795	199.70766	98.1182
2	15.685	MM	0.3197	83.93155	4.37608	1.8818

Catalyst 14



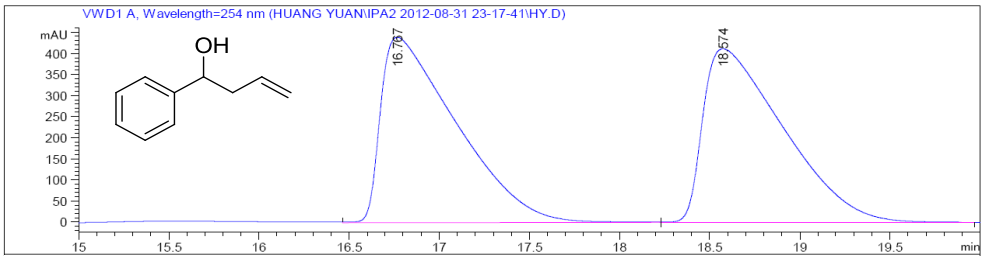
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.076	BB	0.3294	471.17883	21.52096	2.1129
2	15.738	BB	0.4903	2.18287e4	626.72638	97.8871

(*R*)-1-phenylbut-3-en-1-ol (2k, Entry 11, Table 2)



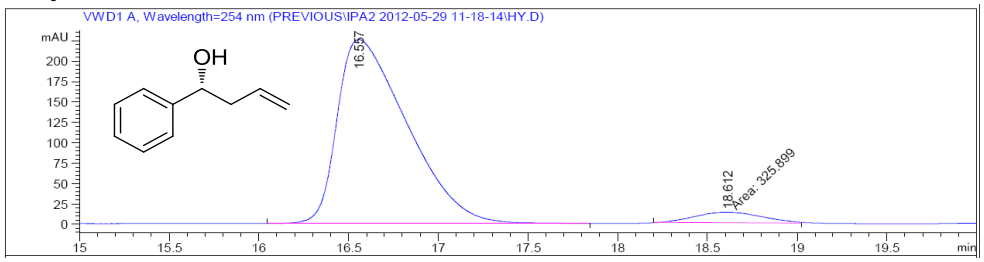
Pale yellow oil, 77% yield with catalyst **11**. 75% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.71. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H), 5.82 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.17 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.74 (dt, *J* = 6.4, 2.4 Hz, 1H), 2.58-2.6 (m, 2H), 2.06 (d, *J* = 2.8 Hz, 1H). **^{13}C NMR** (500 MHz, $CDCl_3$): δ 143.9, 134.5, 128.5, 127.6, 125.9, 118.5, 73.5, 44.1.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ +34.90 (c 0.7, $CHCl_3$). The absolute configuration of **2l** was assigned by comparing its specific rotation with that of the same compound reported in the literature[7]. 90% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95:5 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R\,=}$ 16.55 min for major isomer, $t_{R\,=}$ 18.61 min for minor isomer).



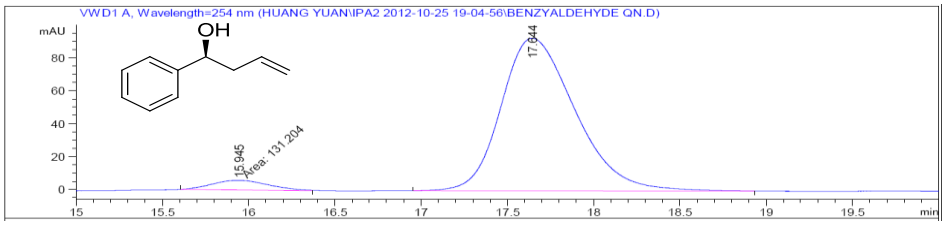
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	16.767	VV	0.4302	1.28100e4	50.1851	?
2	18.574	VB	0.4634	1.27155e4	49.8149	?

Catalyst 11



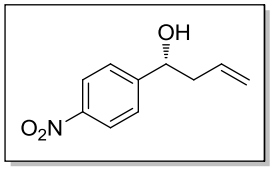
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	16.557	BB	0.4052	6091.40332	94.9216	?
2	18.612	MM	0.4265	325.89886	5.0784	?

Catalyst 14



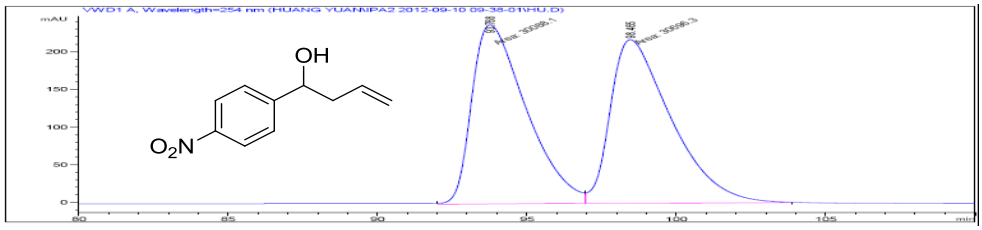
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	15.945	MM T	0.2625	131.20445	4.5226	?
2	17.644	BB	0.4545	2769.85913	95.4774	?

(*R*)-1-(4-nitrophenyl) but-3-en-1-ol (2l, Entry 12, Table 2)



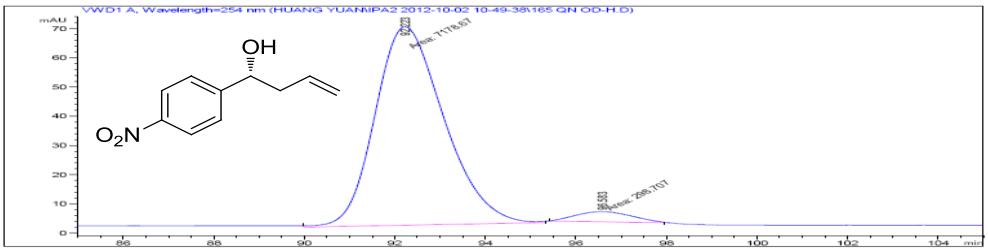
Yellow oil, 83% yield with catalyst **11**. 90% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.53. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.00 – 5.72 (m, 1H), 5.31 – 5.12 (m, 2H), 5.02 – 4.83 (m, 1H), 2.71 – 2.34 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 151.05, 133.13, 126.49, 123.54, 119.52, 72.10, 43.80.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ +56.25 (c 0.7, $CHCl_3$). The absolute configuration of **2m** was assigned by comparing its specific rotation with analogue. 92% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R\ =}$ 92.22 min for major isomer, $t_{R\ =}$ 96.58 min for minor isomer).



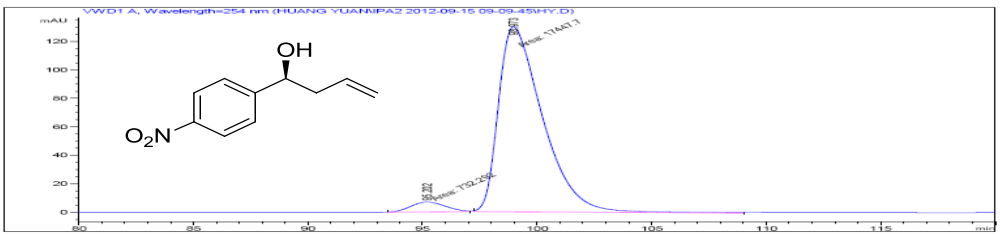
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	93.767	MF T	2.1273	3.03612e4	237.87502	49.1905
2	98.465	FM T	2.3972	3.13606e4	218.03786	50.8095

Catalyst 11



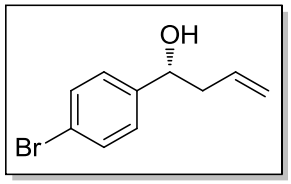
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	92.223	MM T	2.1002	7178.67383	67.87257	96.0052
2	96.583	MM T	1.4380	298.70679	3.46195	3.9948

Catalyst 14



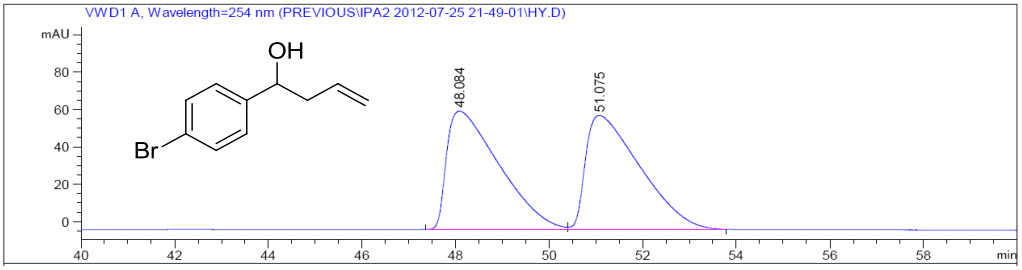
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	95.202	MM	1.7556	732.29230	6.95211	4.0280
2	98.973	MM	2.2382	1.74477e4	129.92540	95.9720

(*R*)-1-(4-bromophenyl) but-3-en-1-ol (2m, Entry 13, Table 2)



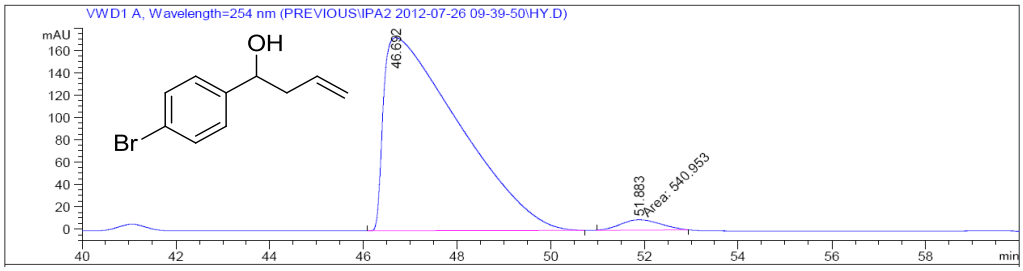
Yellow oil, 77% yield with catalyst **11**. 80% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.63. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.85 – 5.65 (m, 1H), 5.22 – 5.09 (m, 2H), 4.76 – 4.61 (m, 1H), 2.57 – 2.36 (m, 2H), 2.30 (d, *J* = 2.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 142.85, 133.96, 131.48, 127.59, 121.26, 118.82, 72.62, 43.78.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = +50.25 (c 0.5, $CHCl_3$). The absolute configuration of **2n** was assigned by comparing its specific rotation with that of the same compound reported in the literature[7]. 94% ee. (HPLC condition: Chiralpark AS-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 0.4 ml/min, wavelength = 254 nm, t_R = 92.22 min for major isomer, t_R = 96.58 min for minor isomer).



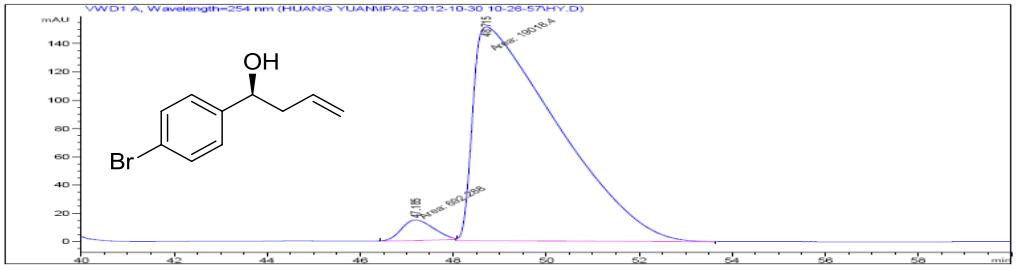
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	48.084	BV	1.0123	4931.82471	49.9894	?
2	51.075	VB	0.9647	4933.92334	50.0106	?

Catalyst 11



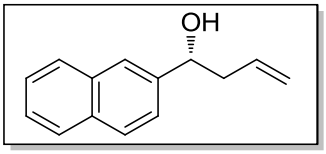
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	46.692	BB	1.3326	1.93625e4	97.2821	?
2	51.883	MM T	0.9849	540.95349	2.7179	?

Catalyst 14



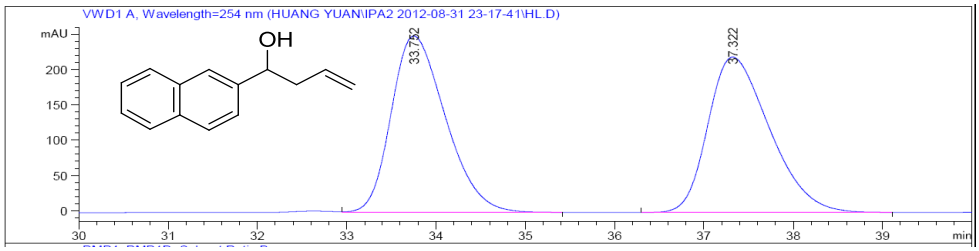
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.185	MM T	0.7979	692.28760	14.46010	3.5122
2	48.715	MM	2.1007	1.90184e4	150.88748	96.4878

(*R*)-1-(naphthalen-2-yl) but-3-en-1-ol (2n, Entry 14, Table 2)



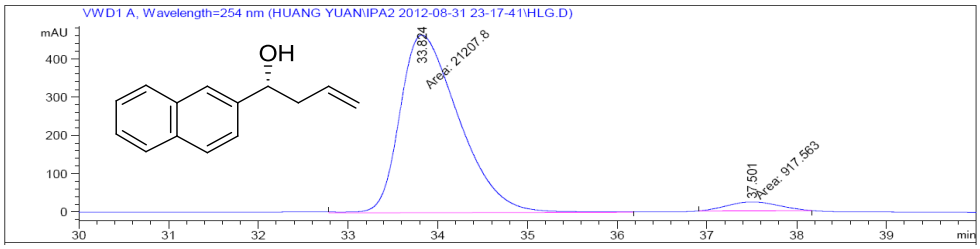
White solid, 80% yield with catalyst **11**. 89% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.71. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.1, 5.6 Hz, 4H), 7.52 (dd, *J* = 6.1, 1.9 Hz, 3H), 5.88 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.29 – 5.16 (m, 2H), 5.03 – 4.87 (m, 1H), 2.65 (dd, *J* = 9.0, 6.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 141.21, 134.31, 133.21, 132.89, 128.14, 127.89, 127.61, 126.06, 125.74, 124.44, 123.95, 118.44, 73.33, 43.67.

Optical Rotation (from reaction with catalyst **11**)**:** $[\alpha]^{25}_D$ = +11.33 (c = 0.3, $CHCl_3$). The absolute configuration of **2o** was assigned by comparing its specific rotation with that of the same compound reported in the literature[7]. 94% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95:5 flow rate = 0.5 ml/min, wavelength = 254 nm, t_R = 32.85 min for minor isomer, t_R = 35.98 min for major isomer).



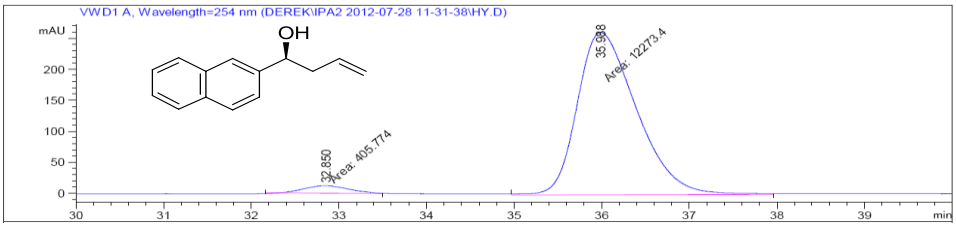
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	33.752	VB	0.6420	1.05991e4	50.0383	?
2	37.322	BB	0.7333	1.05829e4	49.9617	?

Catalyst 11



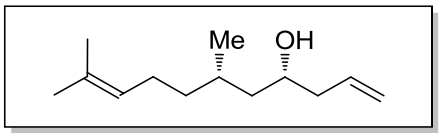
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	33.824	MM T	0.7615	2.12078e4	95.8529	?
2	37.501	MM T	0.6613	917.56256	4.1471	?

Catalyst 14



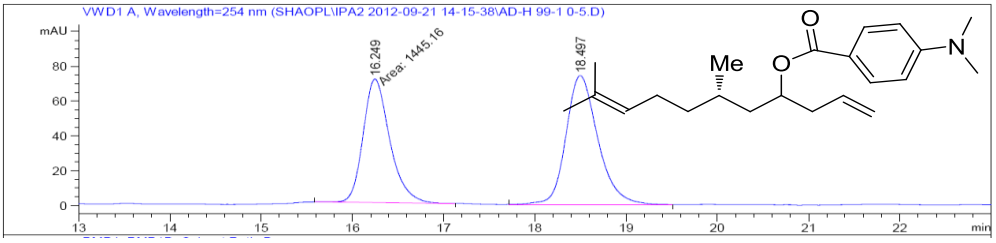
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	32.850	MM T	0.5748	405.77444	3.2003	?
2	35.988	MM T	0.7806	1.22734e4	96.7997	?

(4*R*, 6*S*)-6, 10-dimethylundeca-1, 9-dien-4-ol (2o and *epi*-2o, Scheme 2)



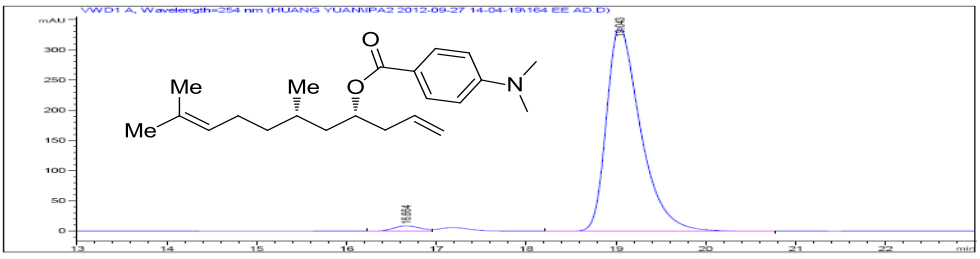
Colorless oil, 88% yield with catalyst 11. 80% yield with catalyst 14. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.86. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.92 – 5.72 (m, 1H), 5.22 – 5.02 (m, 3H), 3.81 – 3.65 (m, 1H), 2.37 – 2.22 (m, 1H), 2.11 (dd, *J* = 14.7, 7.0 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.68 (d, *J* = 0.8 Hz, 3H), 1.60 (s, 3H), 1.47 – 1.32 (m, 3H), 1.25 (s, 1H), 1.20 – 1.02 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 134.77, 131.17, 124.67, 118.10, 68.64, 44.23, 42.06, 36.63, 29.20, 25.63, 25.26, 20.14, 17.57. **HRMS (ESI)** m/z Calcd for $[C_{13}H_{24}O, M+H]^+$:197.1237; Found:197.1232.

The absolute configuration of **2n** was assigned by comparing its specific rotation with analogue. The enantiomeric ratio of the compound was determined after converting to the corresponding para-dimethylaminobenzate. 96% de. (HPLC condition: Chiralpark AD-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 1 ml/min, wavelength = 254 nm, $t_{R=}$ 16.66 min for minor isomer, $t_{R=}$ 19.043 min for major isomer).



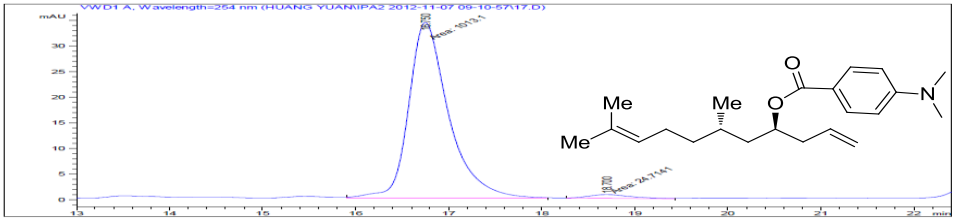
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	16.249	MM T	0.3393	1445.16003	44.5251	?
2	18.497	BB	0.3696	1800.56250	55.4749	?

Catalyst 11



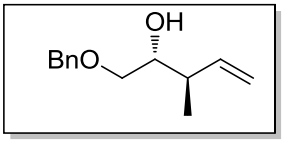
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.664	BV	0.3142	176.14960	8.62896	1.9520
2	19.043	BB	0.3961	8848.03125	337.19958	98.0480

Catalyst 14



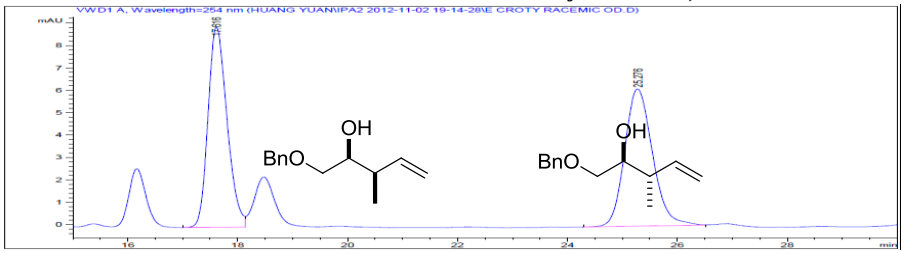
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.750	MM T	0.4938	1013.09784	34.19065	97.6186
2	18.700	MM T	0.5502	24.71406	7.48701e-1	2.3814

(2



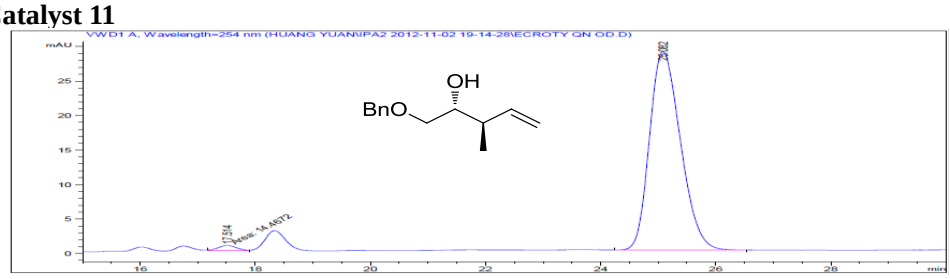
Colorless oil, 78% yield with catalyst **11**. 75% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.67. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 – 7.31 (m, 5H), 6.05 – 5.70 (m, 1H), 5.15 – 5.05 (m, 2H), 4.58 (s, 2H), 3.75 – 3.64 (m, 1H), 3.58 (dd, *J* = 9.8, 3.1 Hz, 2H), 3.45 (dd, *J* = 9.5, 7.6 Hz, 1H), 2.38 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.08, 138.4, 128.63, 128.46, 128.06, 115.59, 73.2, 72.8, 40.83, 16.19.

The absolute configuration of **16a** was assigned by comparing its specific rotation with that of the same compound reported in the literature[8]. 97% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 1 ml/min, wavelength = 254 nm, $t_{R\,=}$ 17.51 min for minor isomer, $t_{R\,=}$ 25.082 min for major isomer).



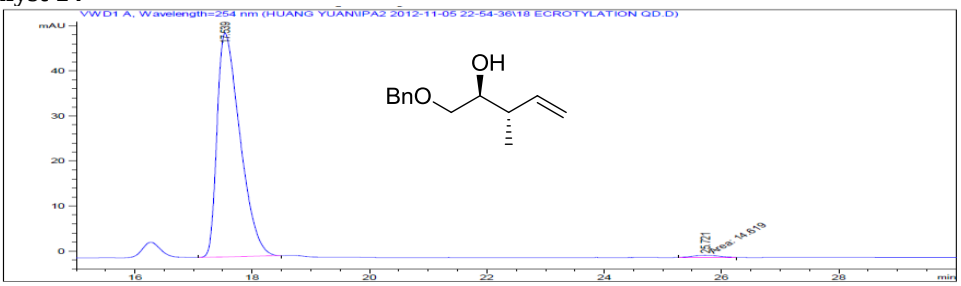
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.616	BV	0.3712	214.89020	8.94733	49.9462
2	25.276	BB	0.5476	215.35324	6.13437	50.0538

Catalyst 11



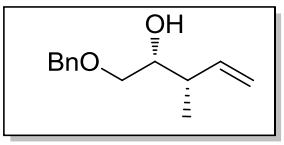
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.514	MM	0.3493	14.46722	6.90337e-1	1.3297
2	25.082	BB	0.5836	1073.56006	28.75398	98.6703

Catalyst 14



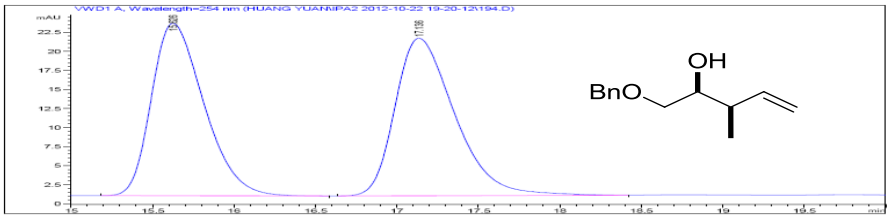
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.539	BB	0.4169	1350.21814	49.71557	98.9289
2	25.721	MM T	0.5040	14.61899	4.83451e-1	1.0711

(2*R*, 3*S*)-1-(benzyloxy)-3-methylpent-4-en-2-ol (16b, Entry 2, Table 3)



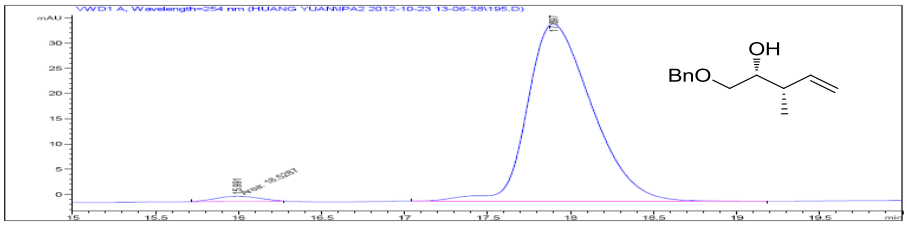
Colorless oil, 78% yield with catalyst **11**. 75% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.73. **^{1}H NMR** (300 MHz,$CDCl_3$): δ 7.44 – 7.32 (m, 5H), 5.79 (ddd, *J* = 17.4, 10.3, 7.9 Hz, 1H), 5.09 (ddd, *J* = 9.4, 5.2, 1.3 Hz, 2H), 4.59 (s, 2H), 3.69 (dt, *J* = 10.7, 3.6 Hz, 1H), 3.61 (dd, *J* = 9.5, 3.1 Hz, 1H), 3.44 (dd, *J* = 9.5, 7.7 Hz, 1H), 2.51 (d, *J* = 3.8 Hz, 1H), 2.38 (dd, *J* = 14.5, 6.9 Hz, 1H), 1.13 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 140.30, 137.95, 128.38, 127.69, 127.64, 115.01, 73.37, 73.29, 72.70, 41.03, 15.59.

The absolute configuration of **16b** was assigned by comparing its specific rotation with that of the same compound reported in the literature[8]. 96% ee. (HPLC condition: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 1 ml/min, wavelength = 254 nm, $t_{R\,=}$ 15.99 min for minor isomer, $t_{R\,=}$ 17.897 min for major isomer).



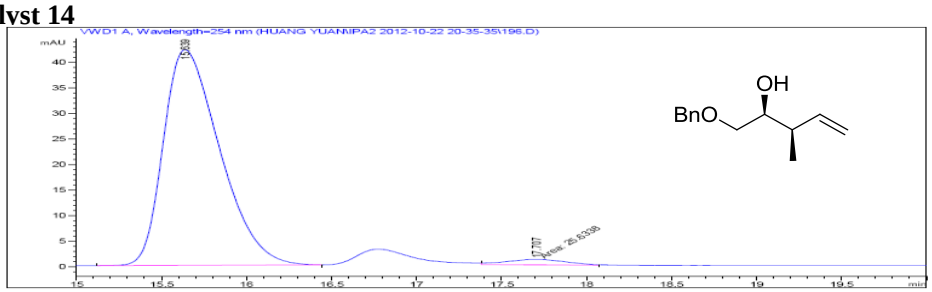
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.626	BB	0.3462	506.16656	22.61164	49.0324
2	17.136	BB	0.3912	526.14423	20.65609	50.9676

Ca



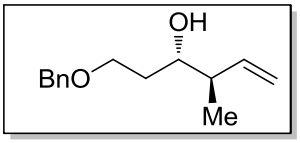
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.991	MM T	0.2991	18.52866	1.03261	1.9195
2	17.897	BB	0.4175	946.73584	35.12180	98.0805

Catalyst 14



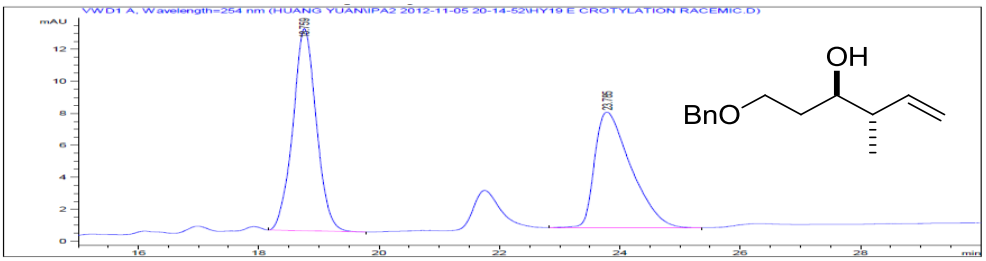
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.639	BB	0.3567	972.09192	42.20877	97.4308
2	17.707	MM T	0.4090	25.63383	1.04465	2.5692

(3*S*, 4*R*)-1-(benzyloxy)-4-methylhex-5-en-3-ol (16c, Entry 3, Table 3)



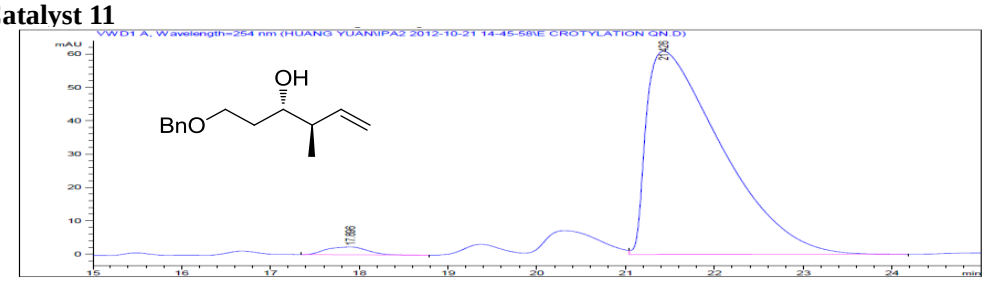
Colorless oil, 74% yield with catalyst **11**. 70% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.70. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 5.8, 2.1 Hz, 5H), 5.97 – 5.72 (m, 1H), 5.21 – 5.04 (m, 2H), 4.57 (d, *J* = 2.3 Hz, 2H), 3.73 (dt, *J* = 12.6, 5.7 Hz, 2H), 2.74 (td, *J* = 6.1, 1.8 Hz, 1H), 2.31 – 2.18 (m, 1H), 2.06 (s, 1H), 1.78 (dt, *J* = 7.6, 3.8 Hz, 2H), 1.12 – 1.03 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 140.39, 137.94, 128.35, 127.60, 115.42, 74.09, 73.25, 69.10, 43.94, 33.54, 15.75.

The absolute configuration of **16c** was assigned by comparing its specific rotation with that of the same compound reported in the literature[6]. 96% ee. (HPLC condition: Chiralpark AS-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R\,=}$ 17.89 min for minor isomer, $t_{R\,=}$ 21.42 min for major isomer).



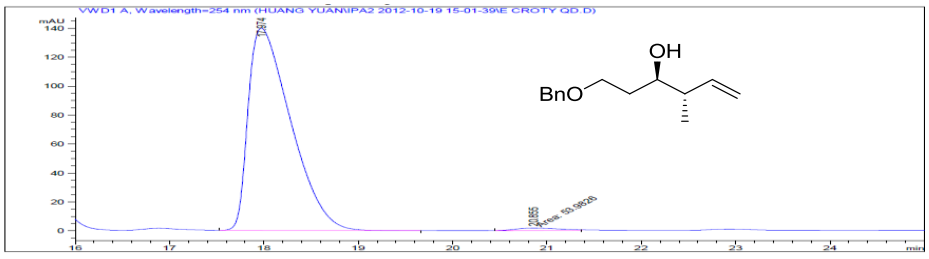
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.759	BB	0.4080	342.12155	12.63298	53.0776
2	23.785	BB	0.6235	302.44687	7.22332	46.9224

Catalyst 11



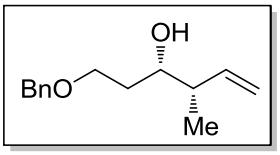
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.896	BB	0.4385	75.05269	2.38243	2.0413
2	21.426	VB	0.8754	3601.57568	60.94794	97.9587

Catalyst 14



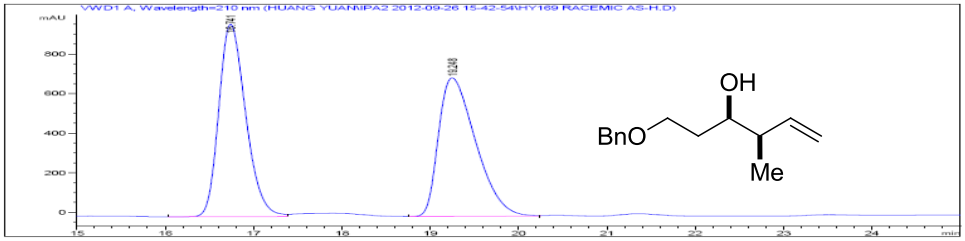
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.974	BB	0.4851	4375.88379	139.83545	98.7814
2	20.855	MM T	0.5361	53.98262	1.67838	1.2186

(3*S*, 4*S*)-1-(benzyloxy)-4-methylhex-5-en-3-ol (16d, Entry 4, Table 3)



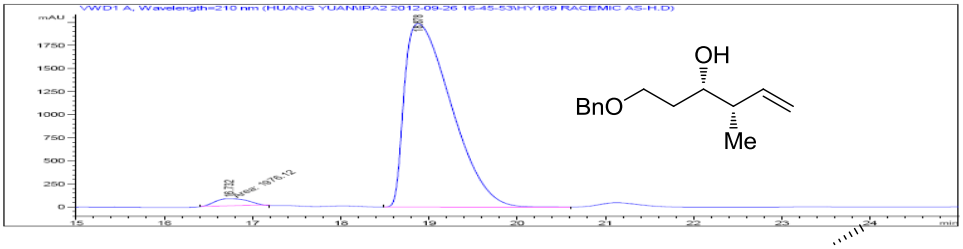
Colorless oil, 72% yield with catalyst **11**. 73% yield with catalyst **14**. **TLC** (Hexane: Ethyl acetate, 5:1 v/v): R_f = 0.73. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 5H), 5.86 – 5.71 (m, 1H), 5.12 – 4.99 (m, 2H), 4.53 (d, *J* = 6.3 Hz, 2H), 3.77 – 3.69 (m, 1H), 3.69 – 3.62 (m, 2H), 2.86 (d, *J* = 3.2 Hz, 1H), 2.26 (dd, *J* = 13.6, 6.8 Hz,1H), 1.87 – 1.76 (m, 1H), 1.75 – 1.65 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (**125 MHz, $CDCl_3$): δ 141.00, 137.94, 128.46, 127.75, 127.70, 114.99, 74.52, 73.37, 69.48, 43.87, 33.53, 15.03.

The absolute configuration of **16d** was assigned by comparing its specific rotation with that of the same compound reported in the literature[6]. 95% ee. (HPLC condition: Chiralpark AS-H column, *n*-hexane/*i*-PrOH = 99:1 flow rate = 0.5 ml/min, wavelength = 254 nm, $t_{R\,=}$ 17.89 min for minor isomer, $t_{R\,=}$ 21.42 min for major isomer).



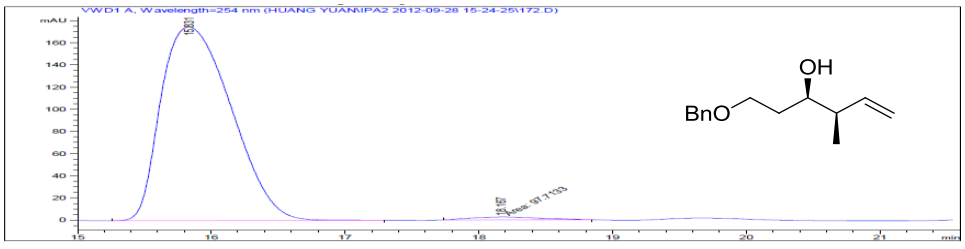
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.741	BV	0.3278	2.05592e4	971.79279	50.1059
2	19.248	BV	0.4563	2.04722e4	699.80621	49.8941

Catalyst 11



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.732	MM	0.4263	1976.11743	77.24966	2.6185
2	18.878	BV	0.5839	7.34904e4	1985.20959	97.3815

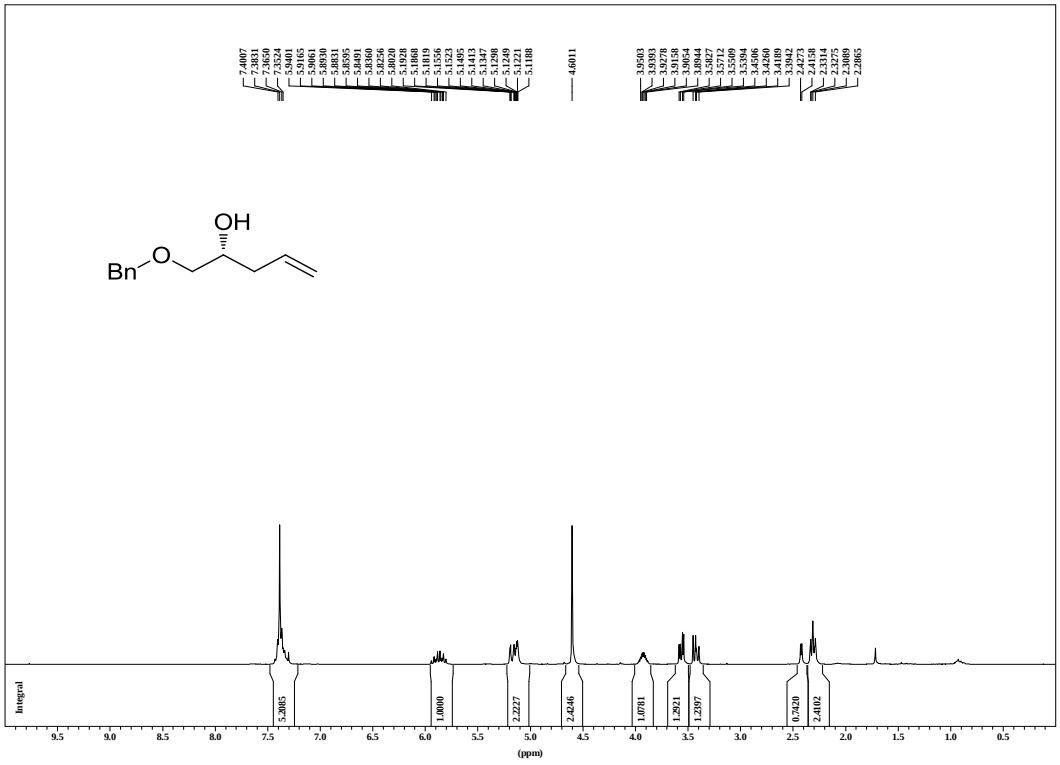
Catalyst 14

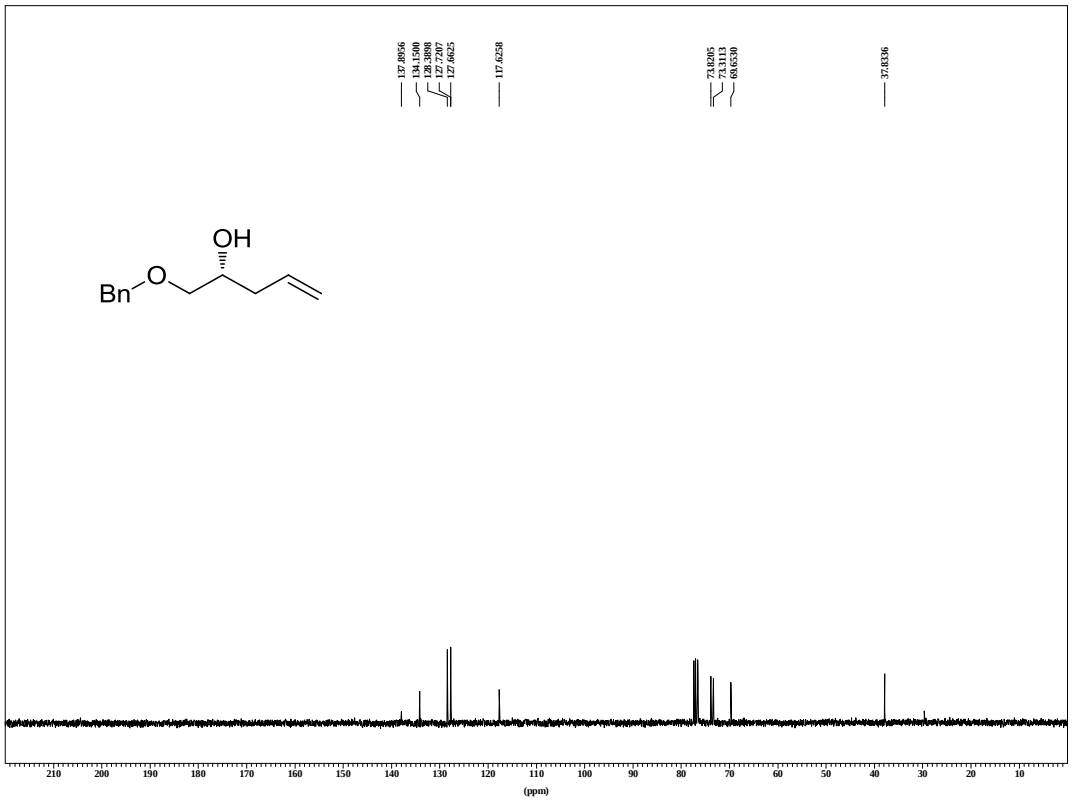


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.831	BB	0.6005	6382.69434	174.60312	98.4922
2	18.167	MM T	0.6207	97.71331	2.62356	1.5078

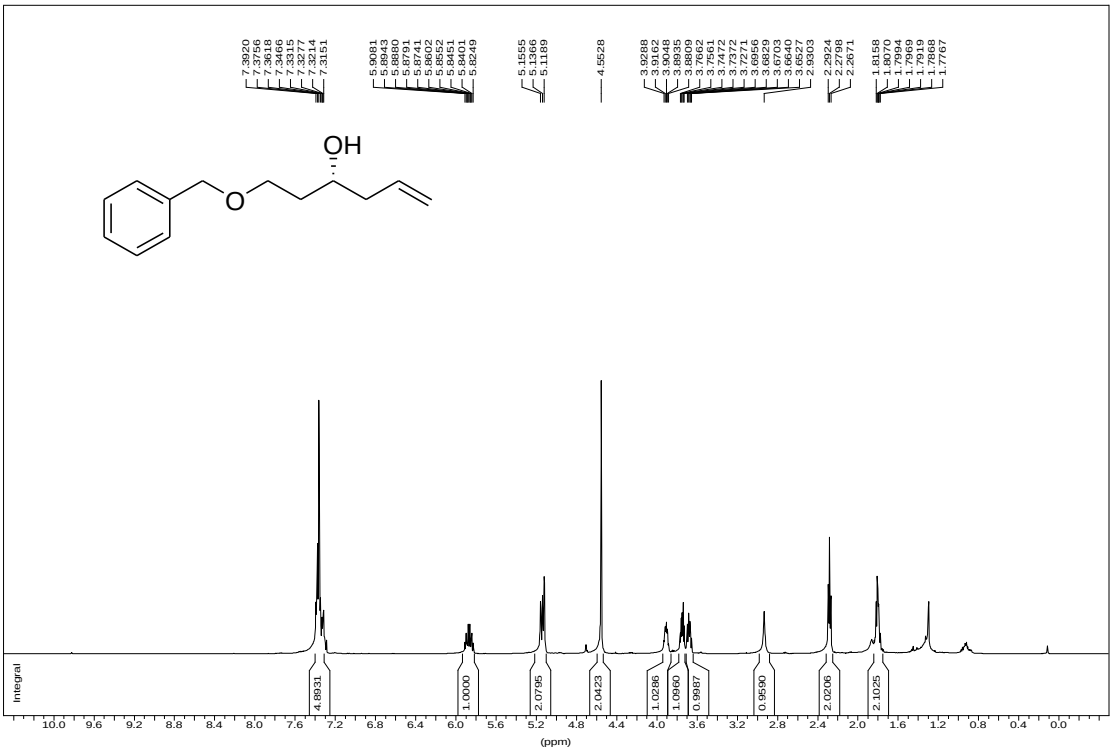
6. NMR Spectra of the Products

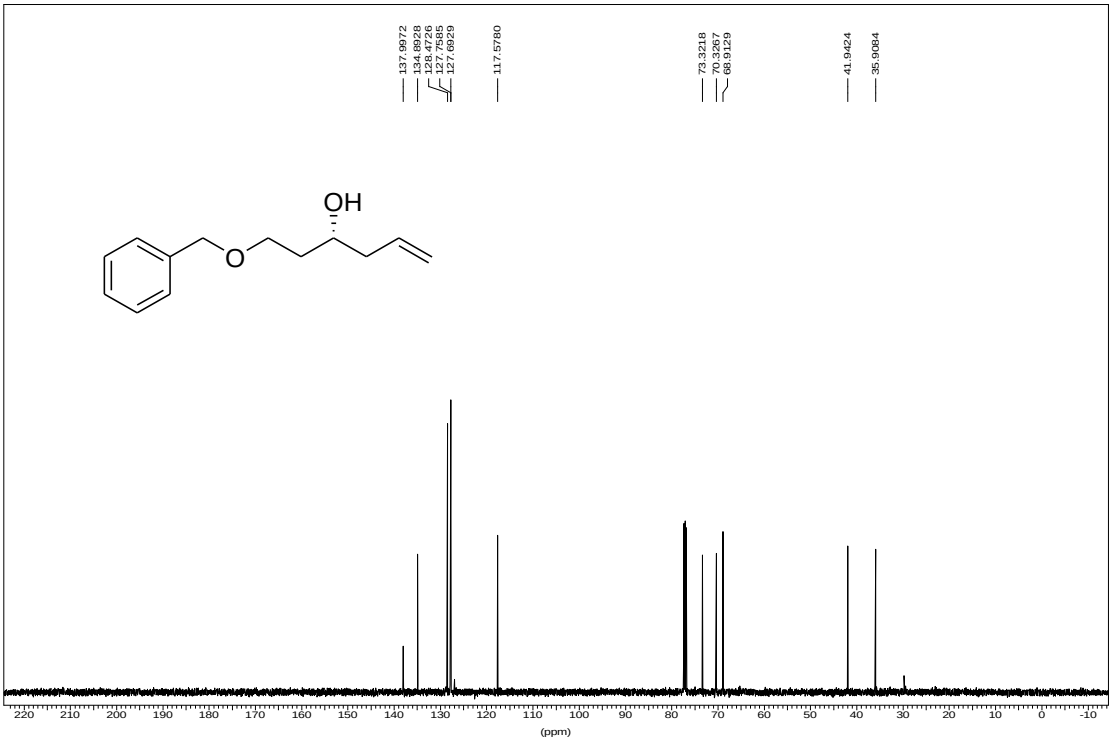
(*R*)-1-(benzyloxy) pent-4-en-2-ol (2a, Entry 1, Table 2)



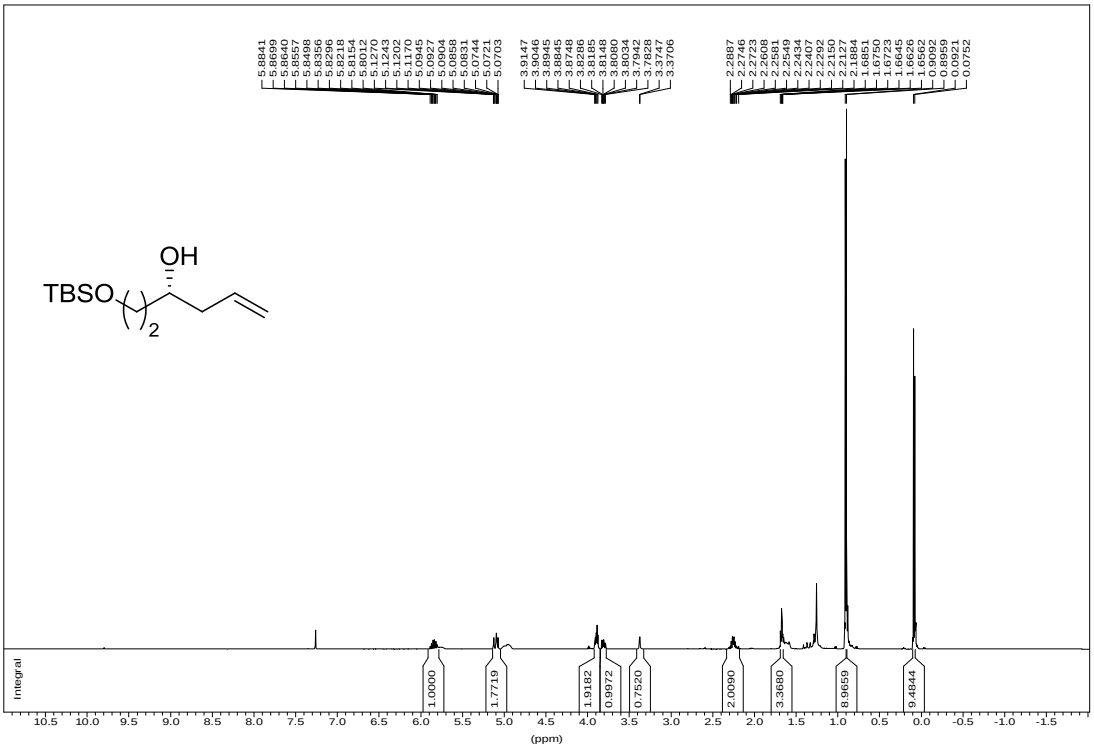


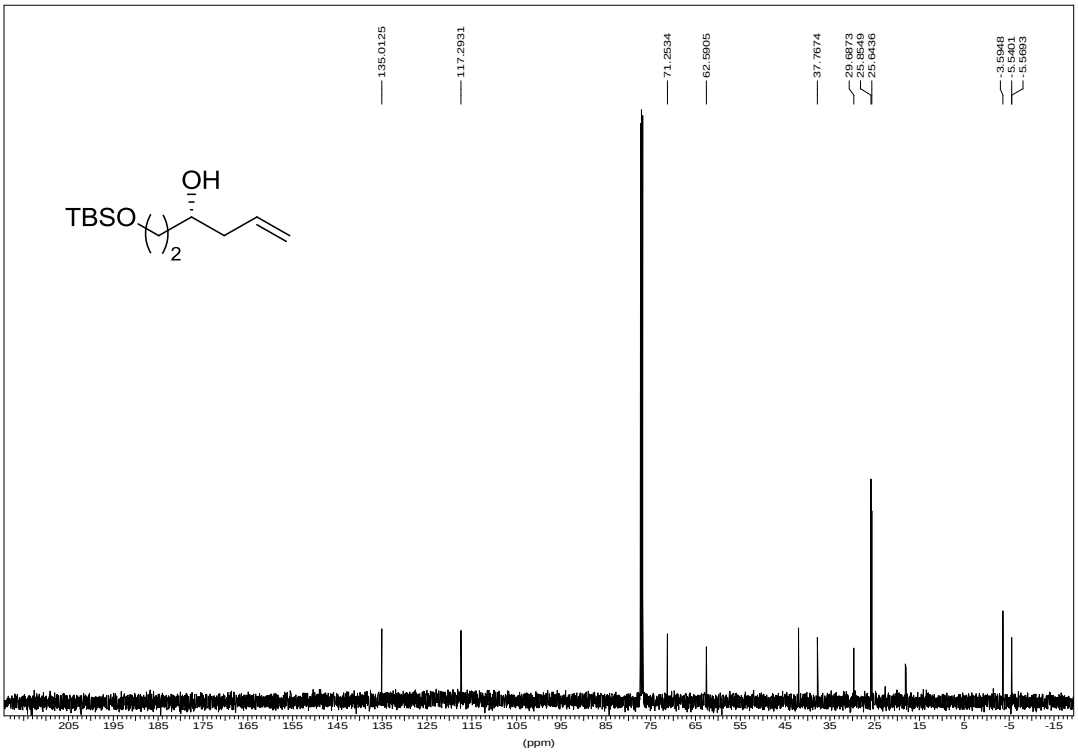
(*R*)-1-(benzyloxy)hex-5-en-3-ol (2b, Entry 2, Table 2)



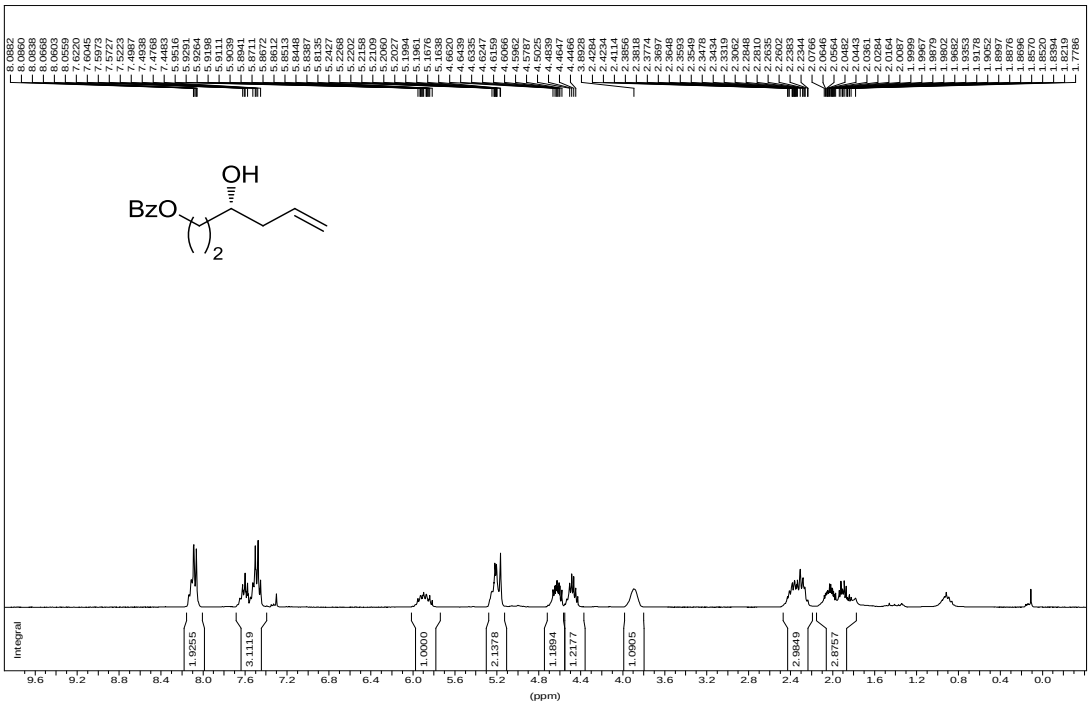


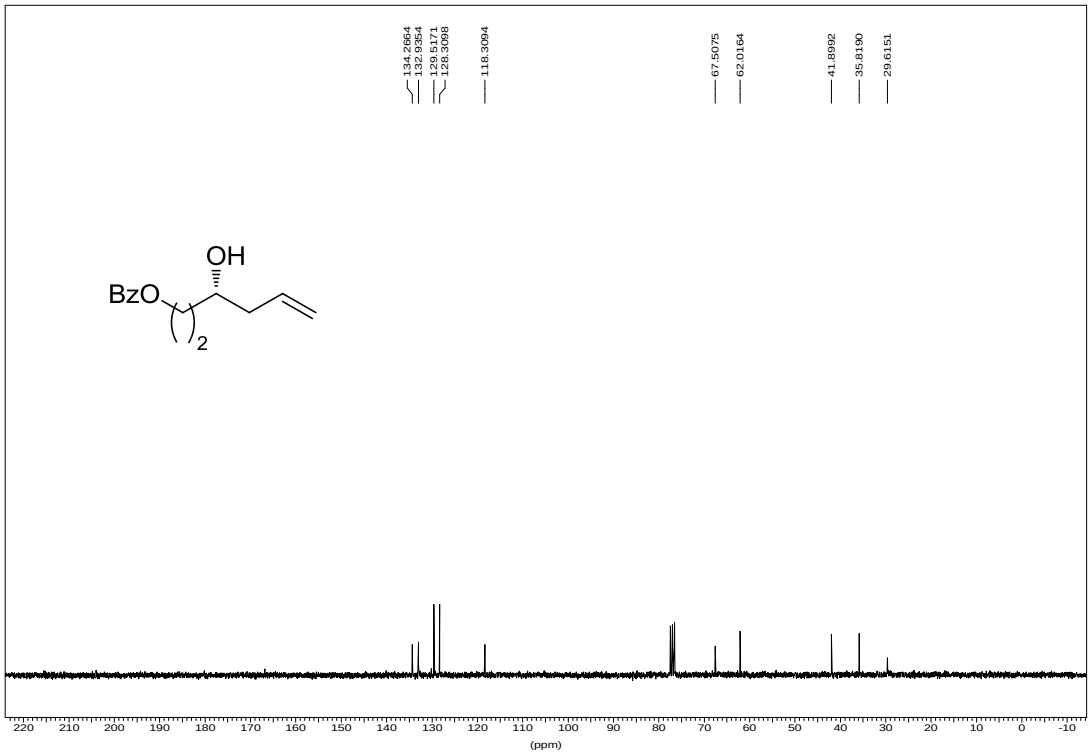
(*R*)-1-((tert-butyldimethylsilyl)oxy)pent-4-en-2-ol (2c, Entry 3, Table 2)



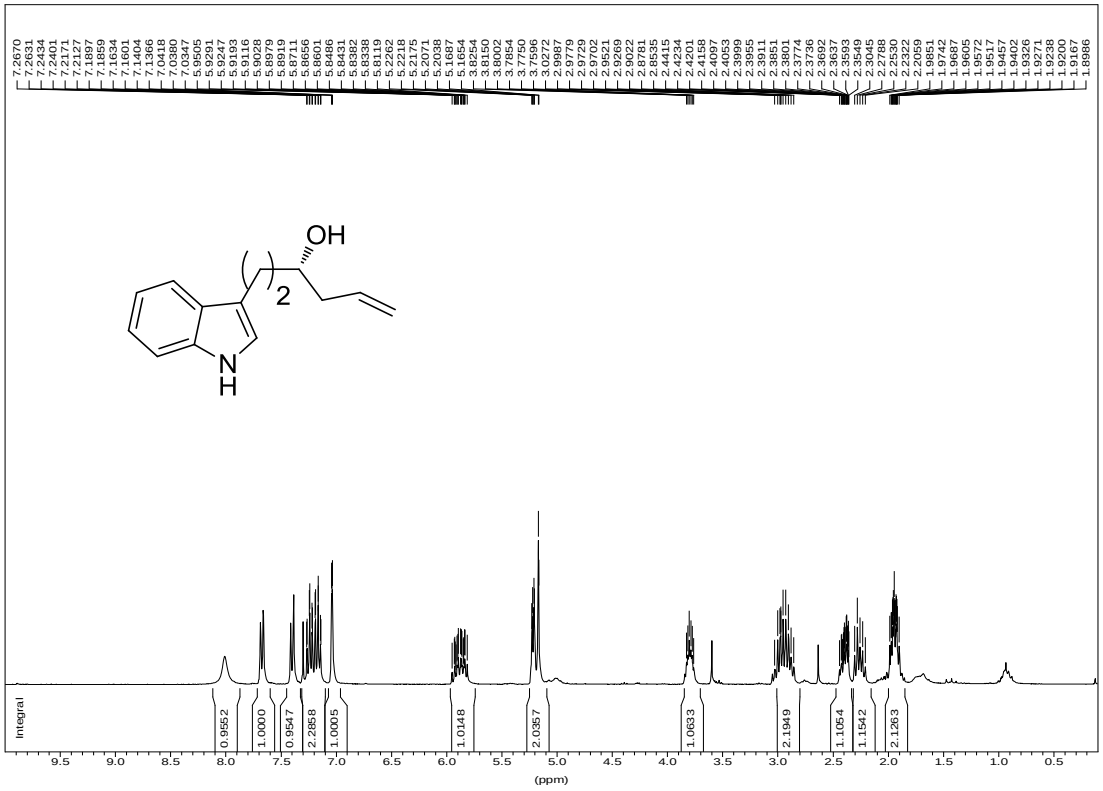


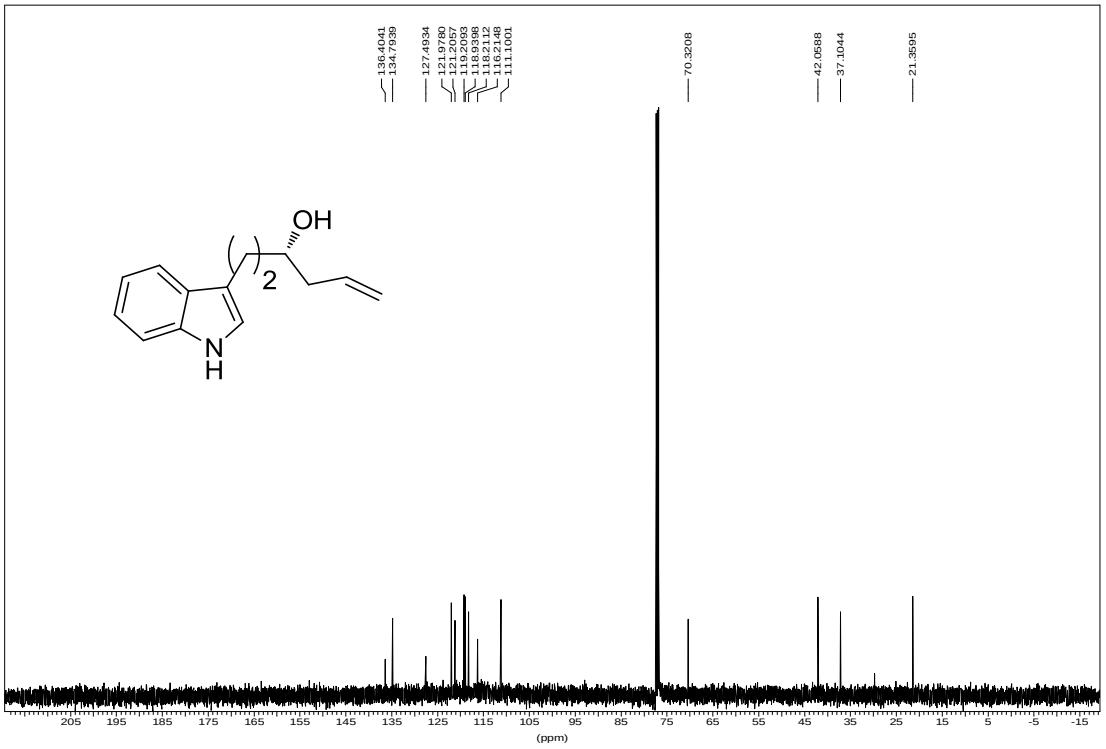
(*R*)-3-hydroxyhex-5-en-1-yl benzoate (2d, Entry 4, Table 2).



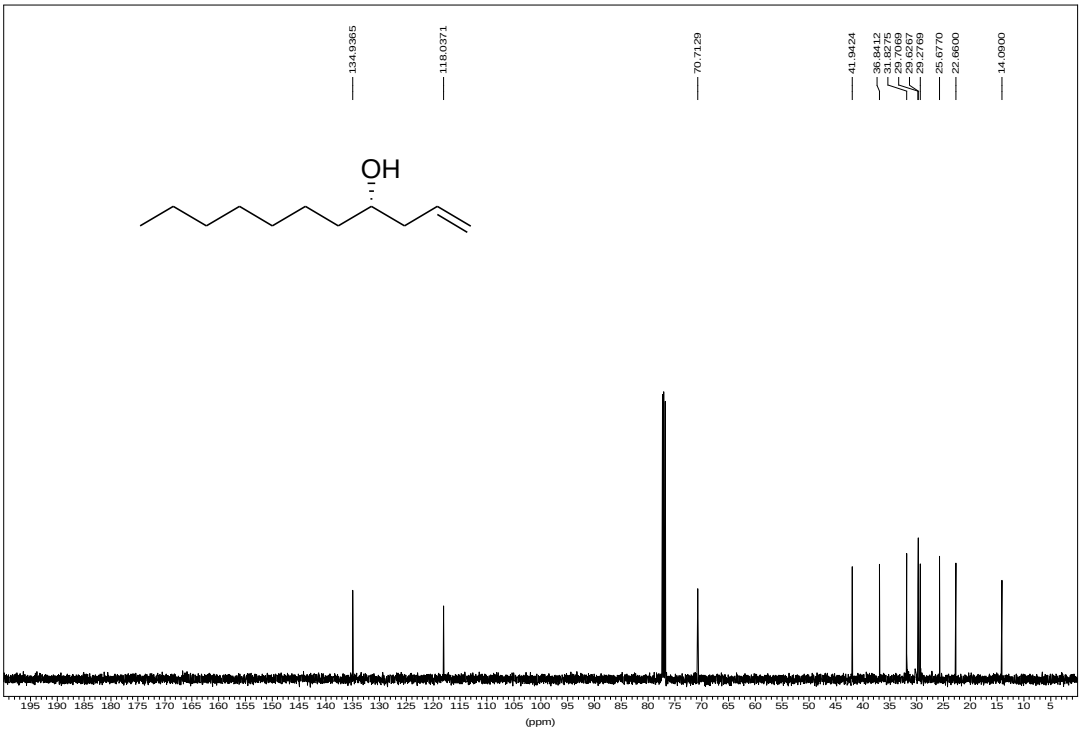


(*R*)-1-(1H-indol-3-yl) pent-4-en-2-ol (2e, Entry 5, Table 2)

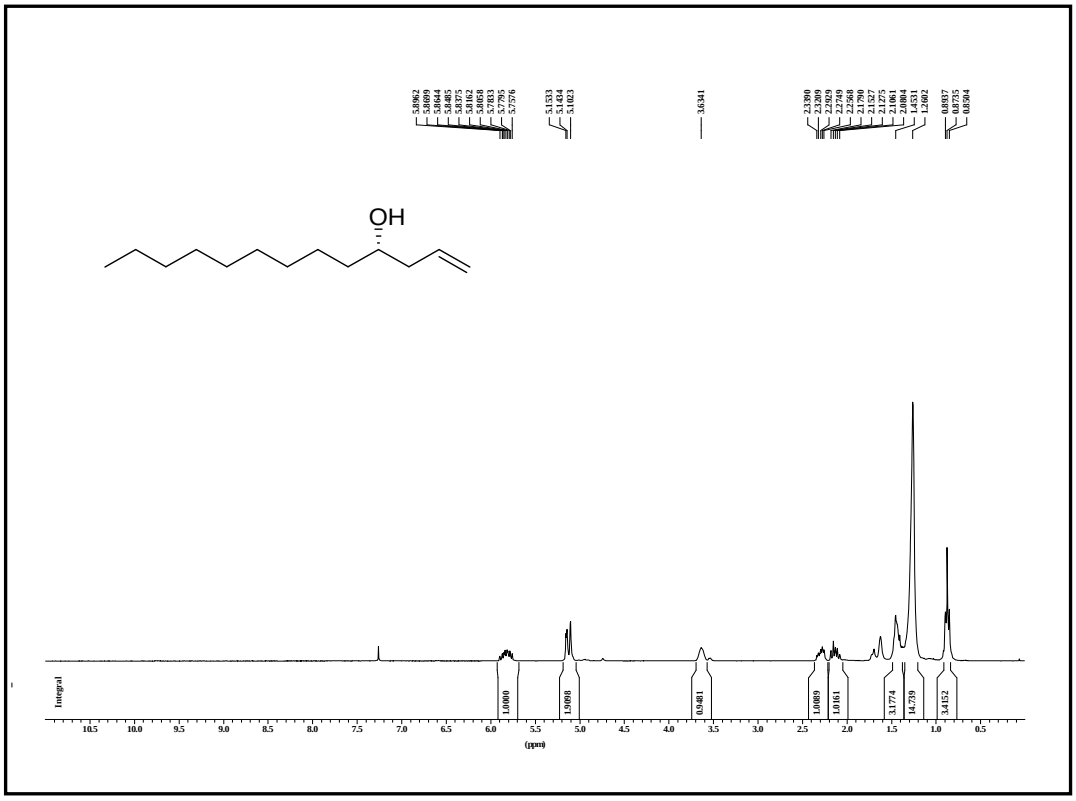


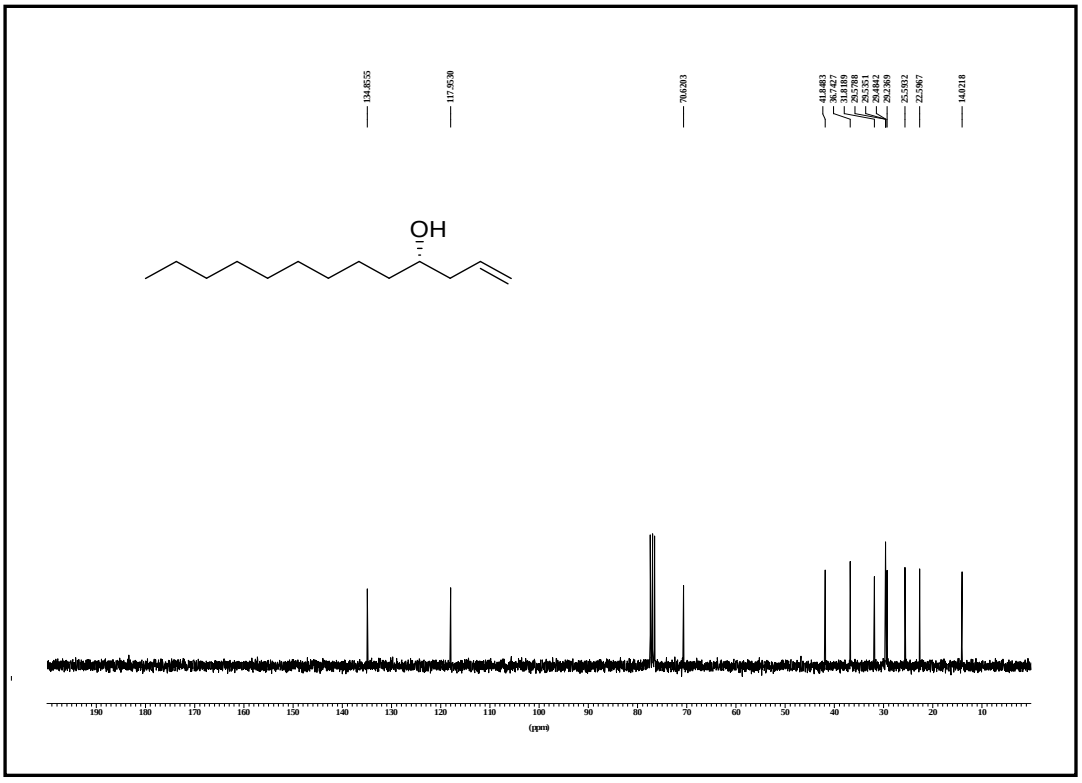


(*S*)-hex-5-en-3-ol (2f, Entry 6, Table 2).

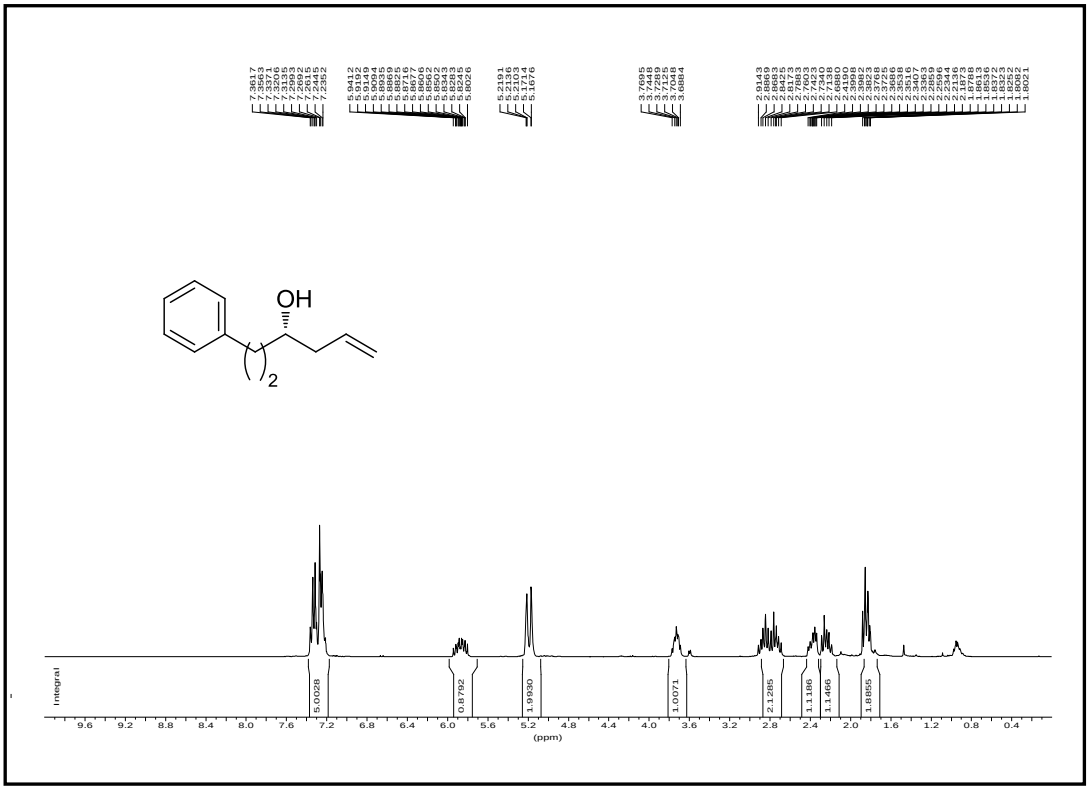


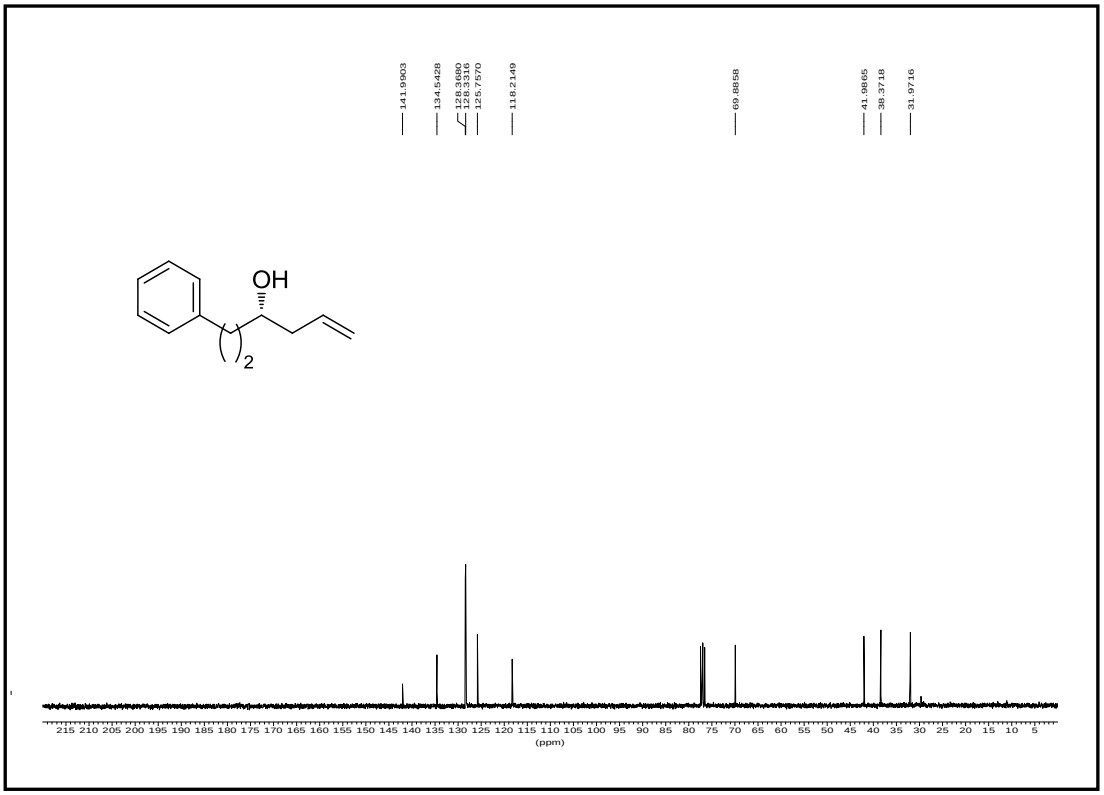
(*R*)-tridec-1-en-4-ol (2g, Entry 7, Table 2)



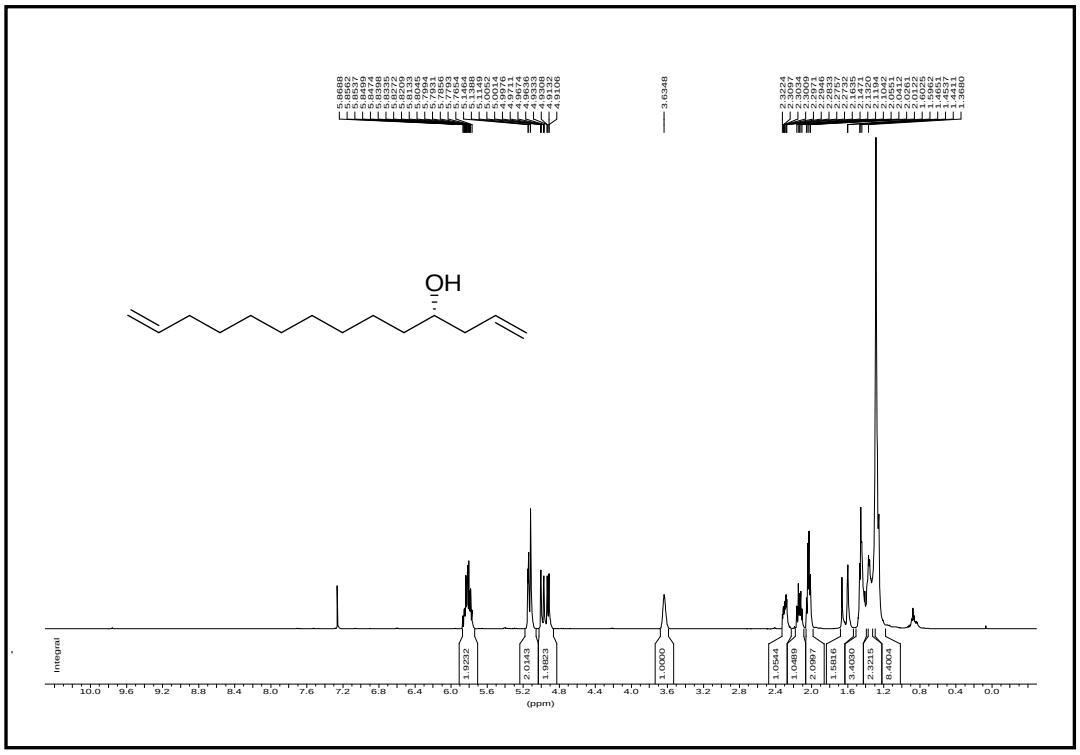


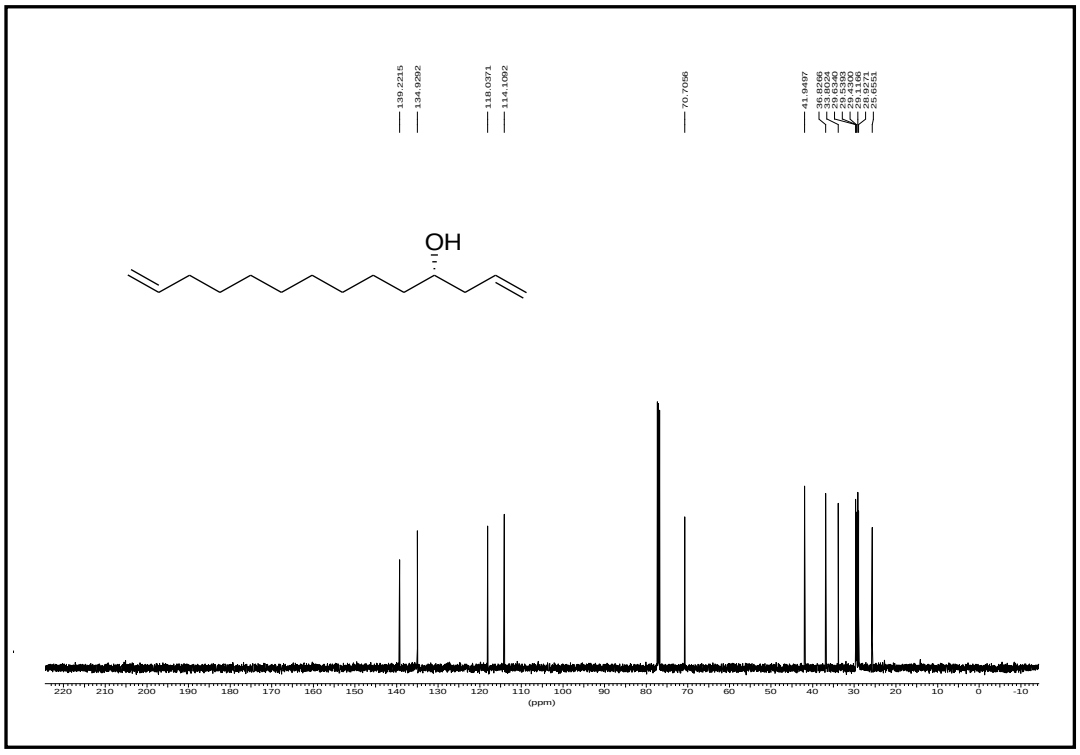
(*S*)-1-phenylhex-5-en-3-ol (2h, Entry 8, Table 2)



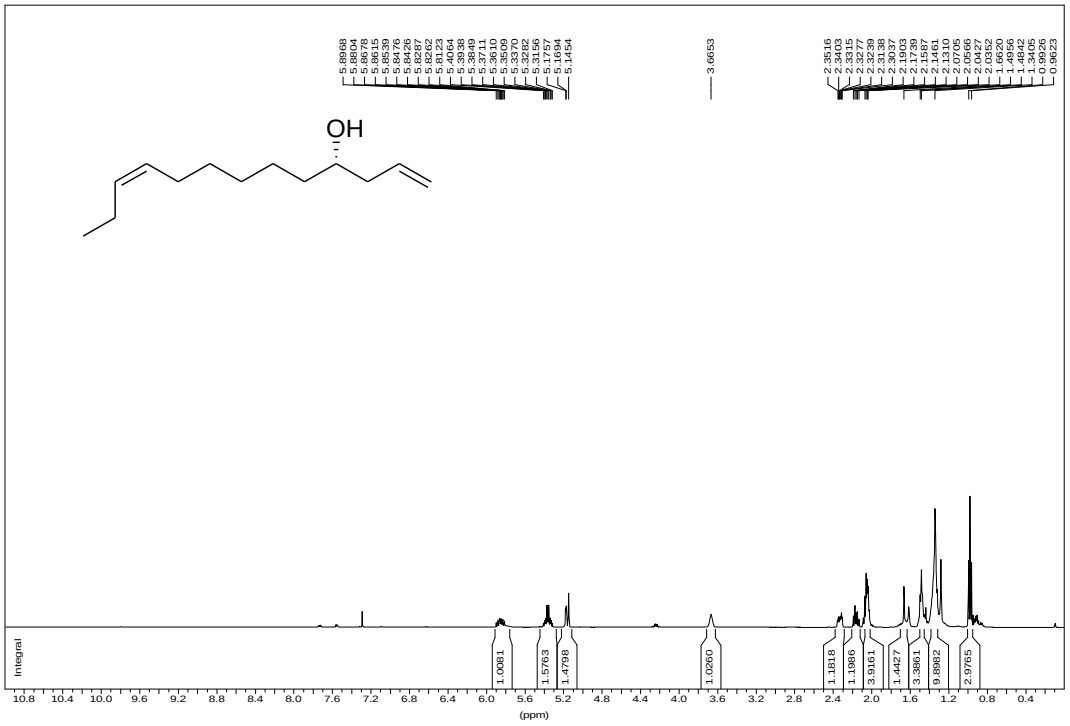


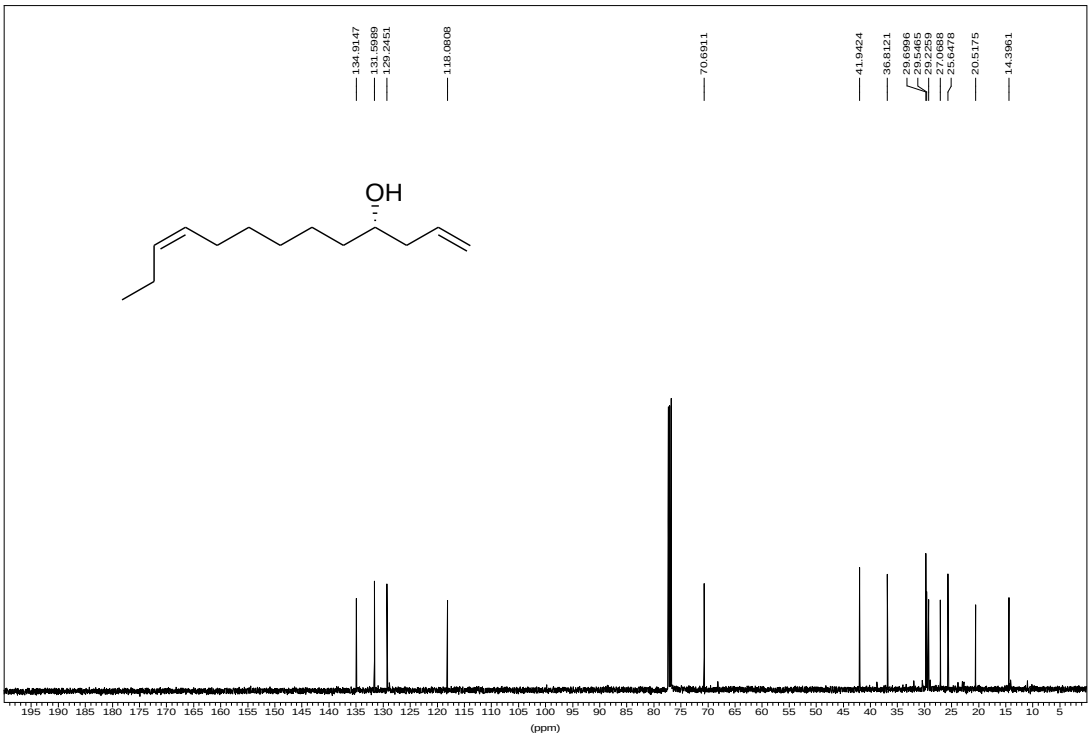
(*R*)-tetradeca-1,13-dien-4-ol (2i, Entry 9, Table 2)



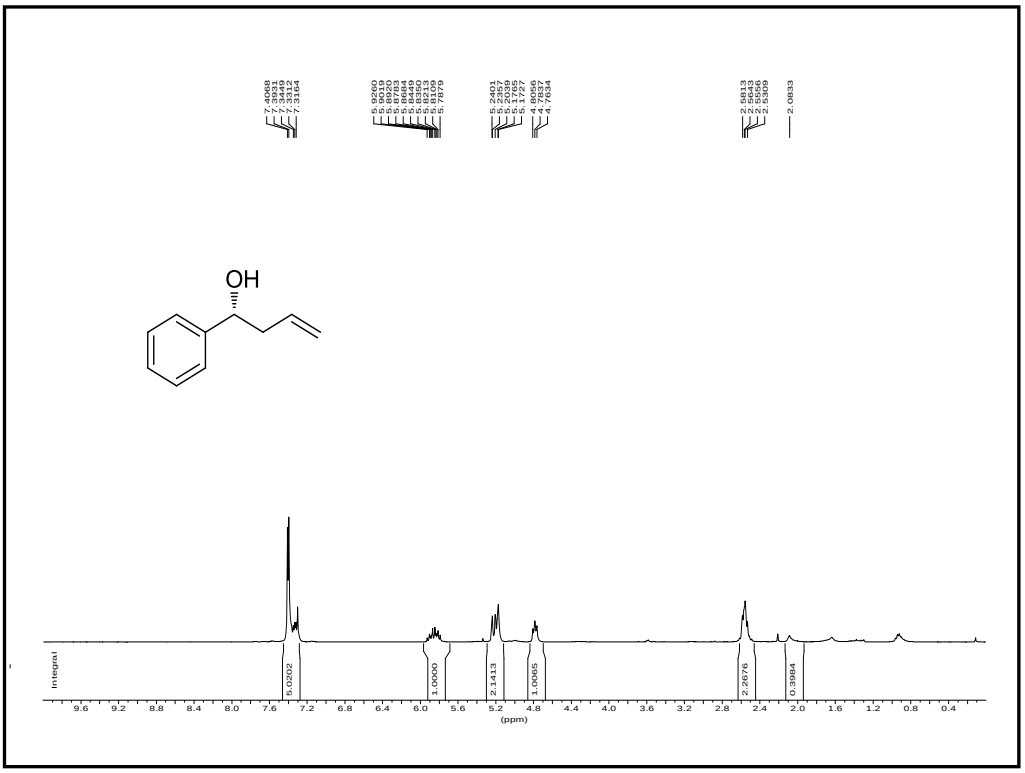


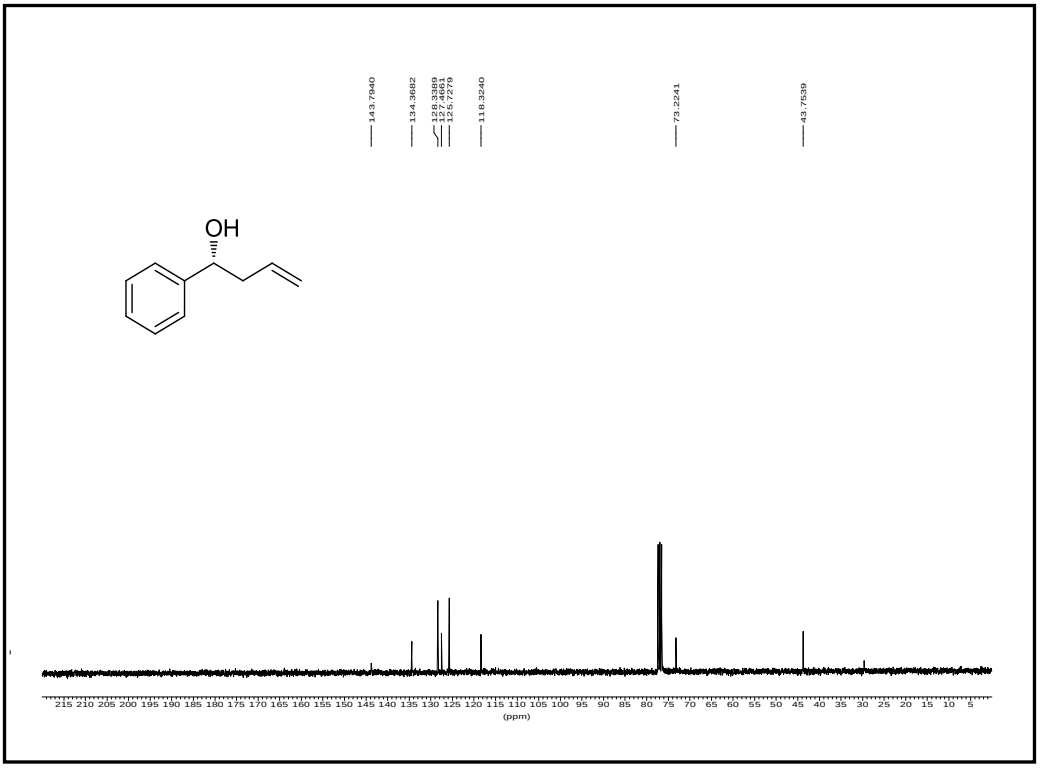
(*S*, *Z*)- tetradeca- 1, 11-dien-4-ol (2j, Entry 10, Table 2)



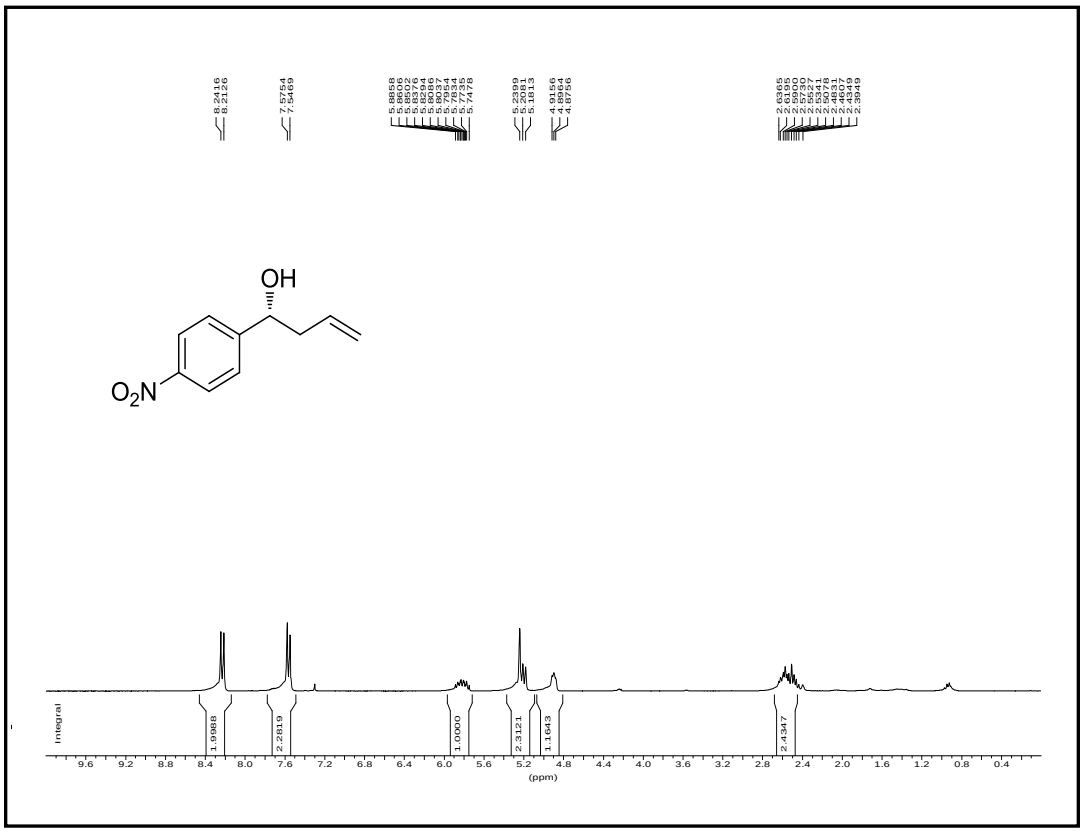


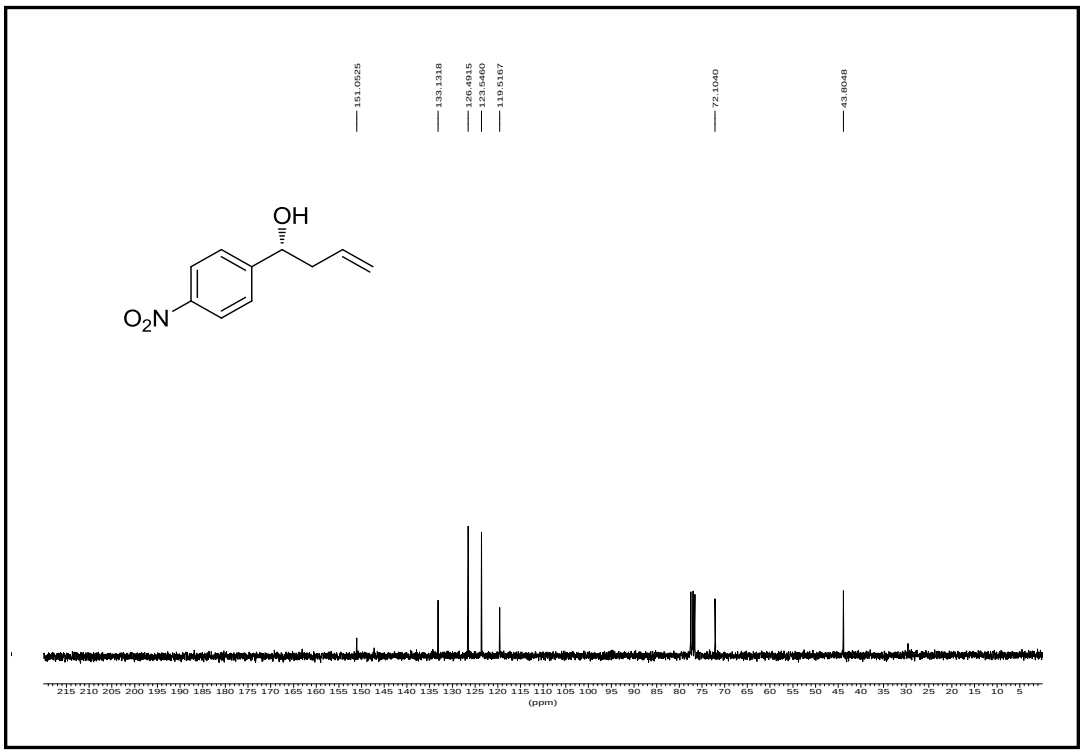
(*R*)-1-phenylbut-3-en-1-ol (2k, Entry 11, Table 2)



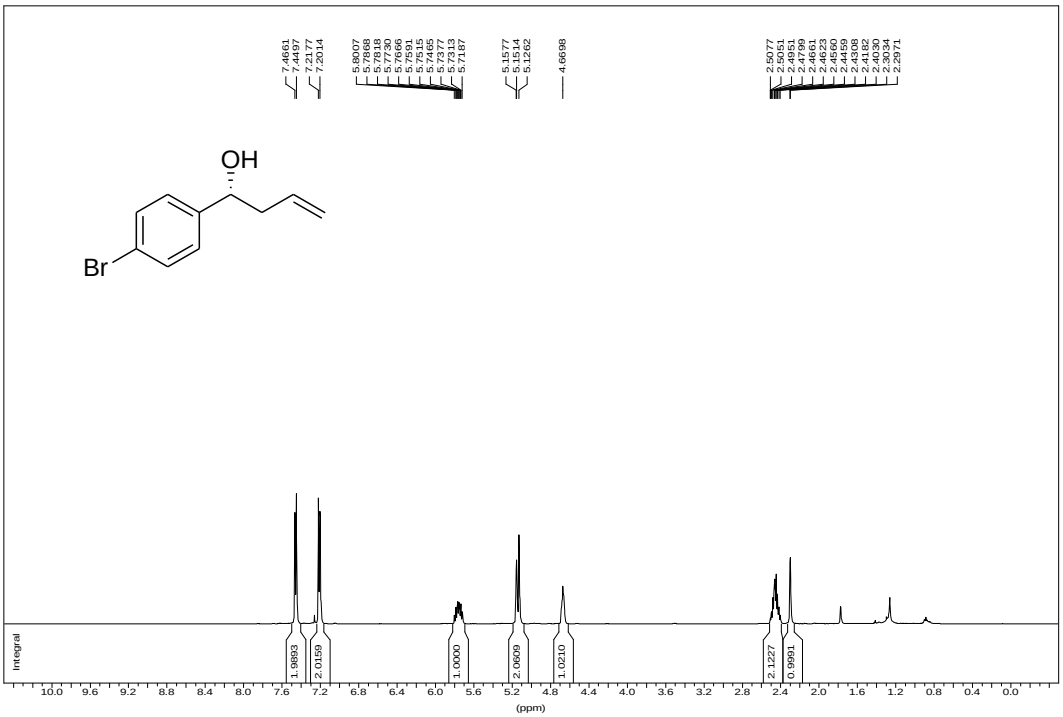


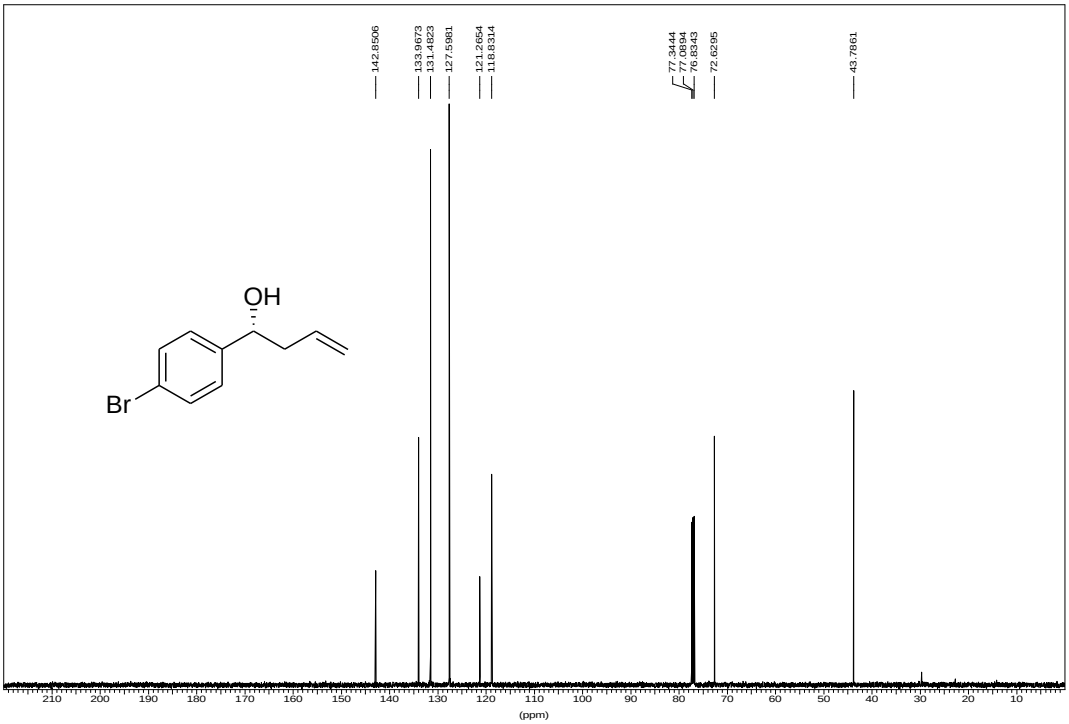
(*R*)-1-(4-nitrophenyl) but-3-en-1-ol (2l, Entry 12, Table 2)



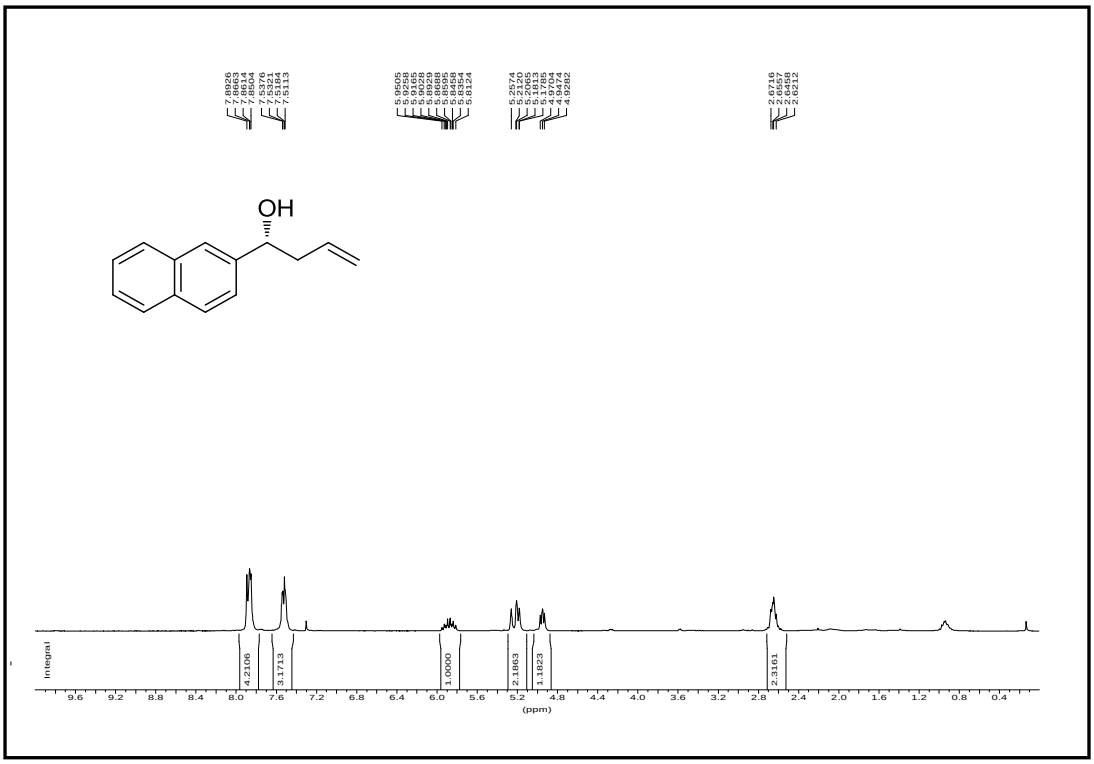


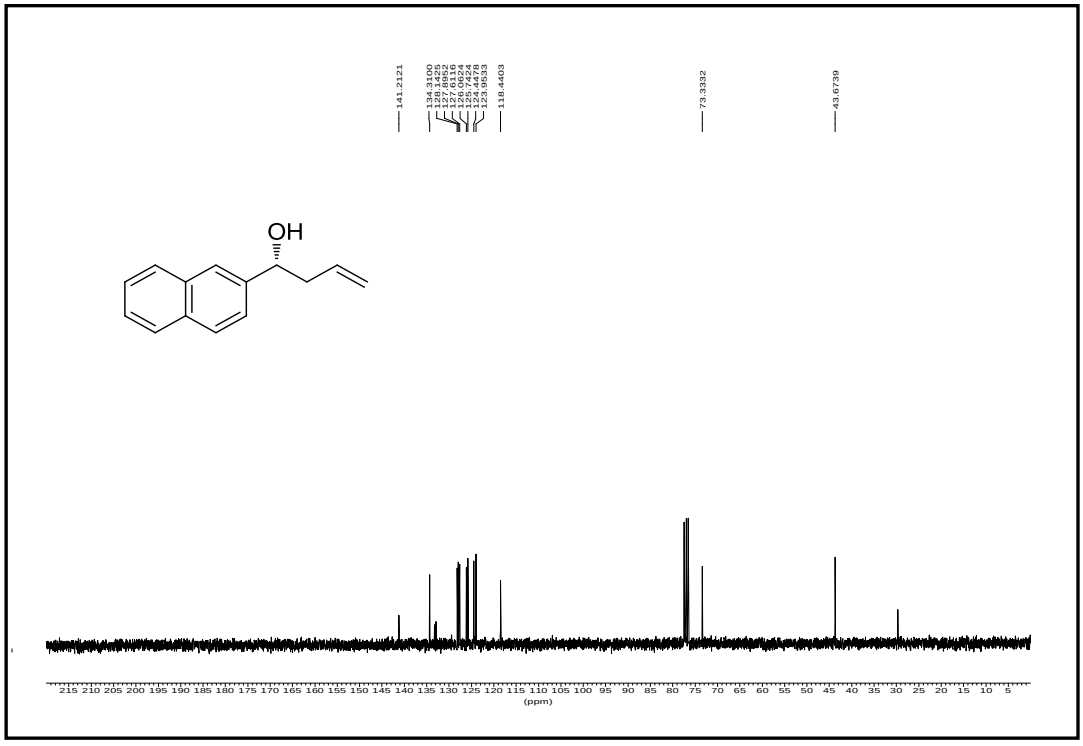
(*R*)-1-(4-bromophenyl)but-3-en-1-ol (2m, Entry 13, Table 2)



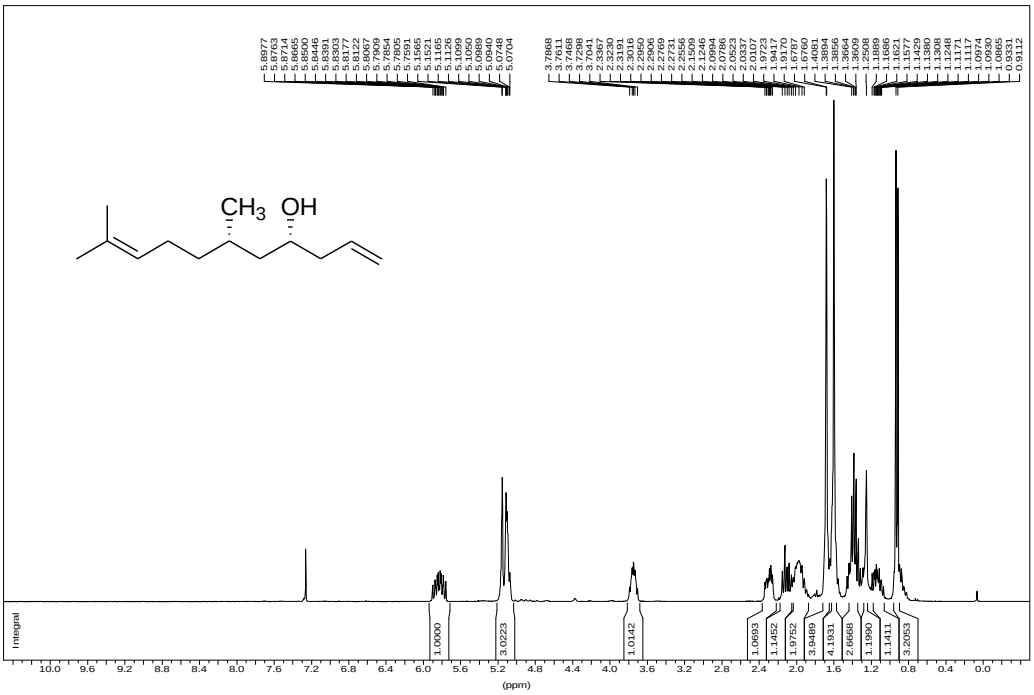


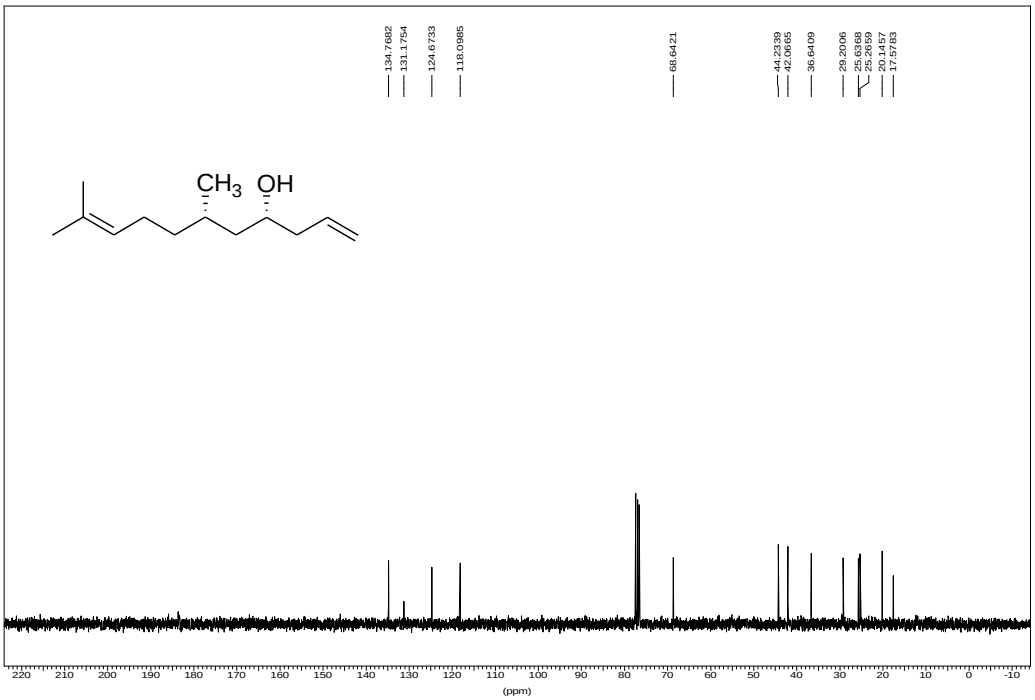
(*R*)-1-(naphthalen-2-yl) but-3-en-1-ol (2n, Entry 14, Table 2)



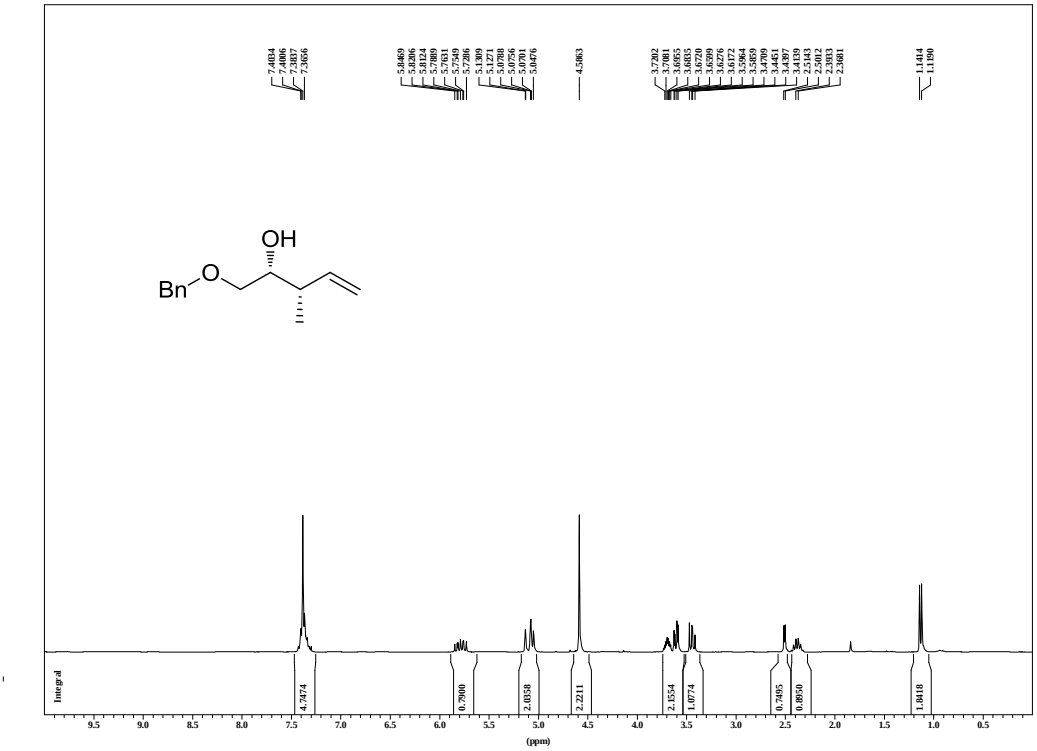


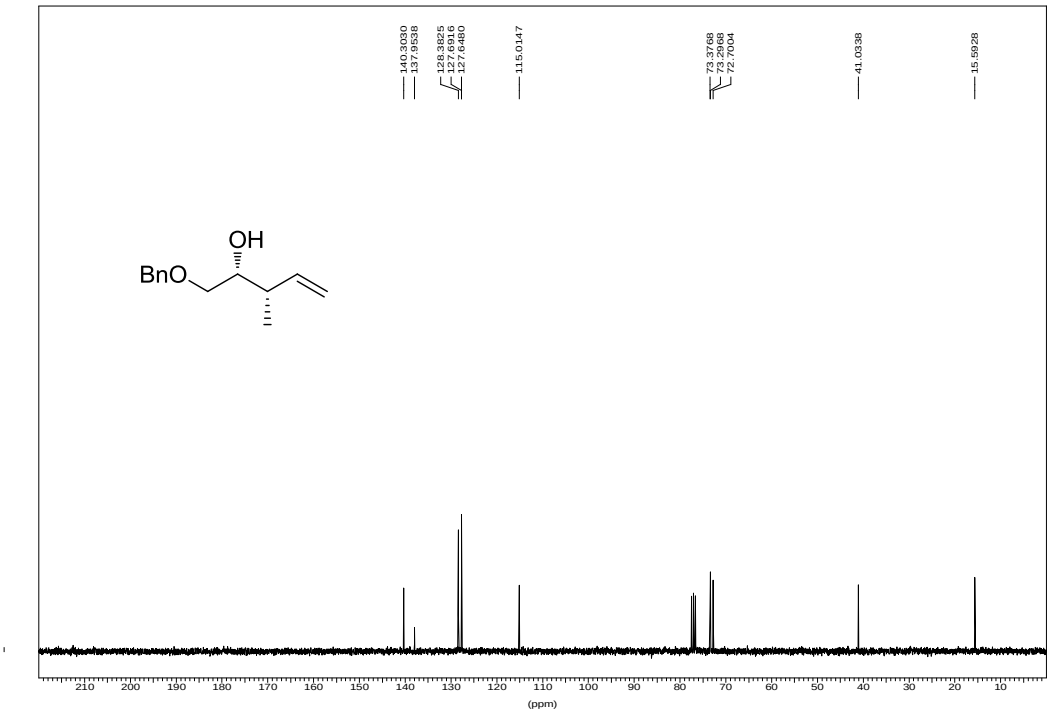
(4*R*, 6*S*)-6, 10-dimethylundeca-1, 9-dien-4-ol (2o, Scheme 2)



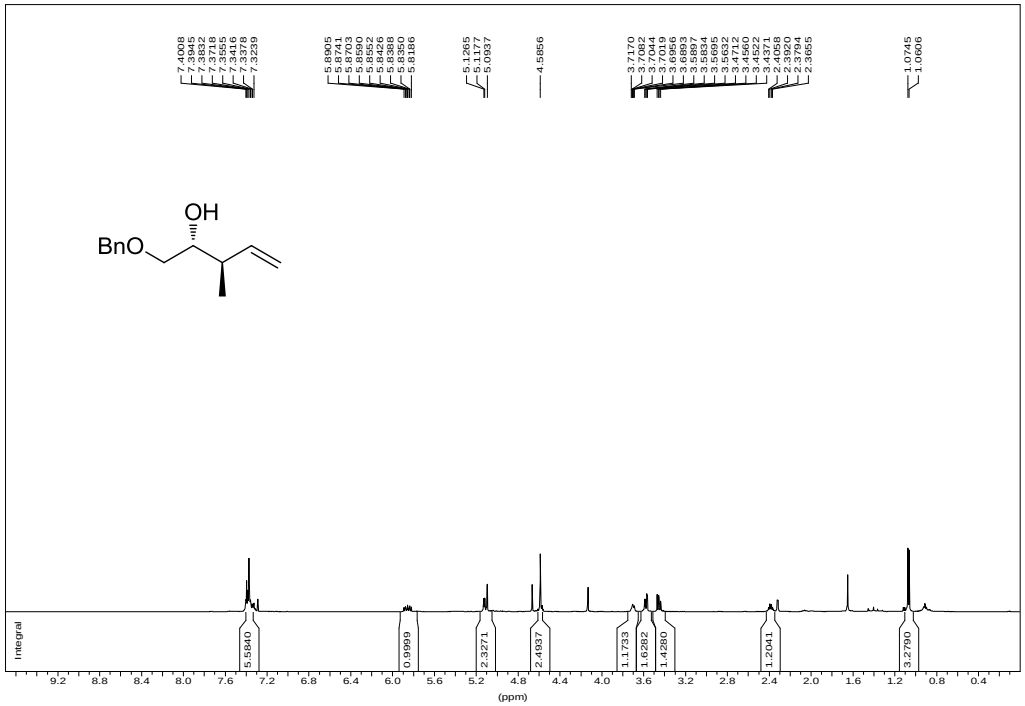


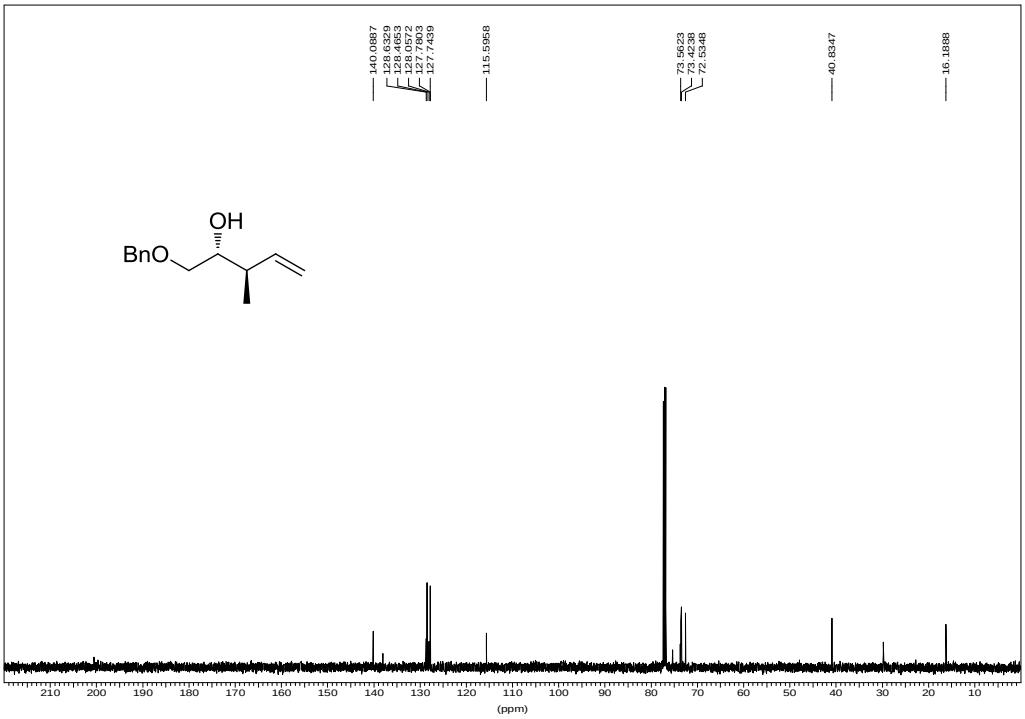
(2*R*, 3*R*)-1-(benzyloxy)-3-methylpent-4-en-2-ol (16a, Entry 1, Table 3)



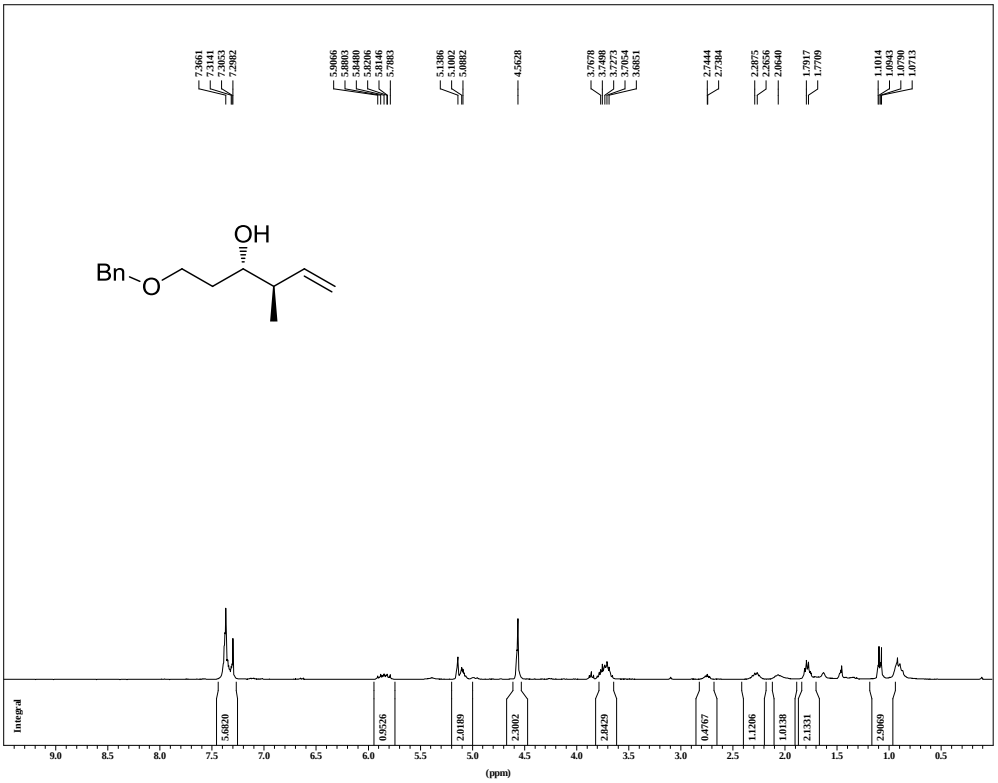


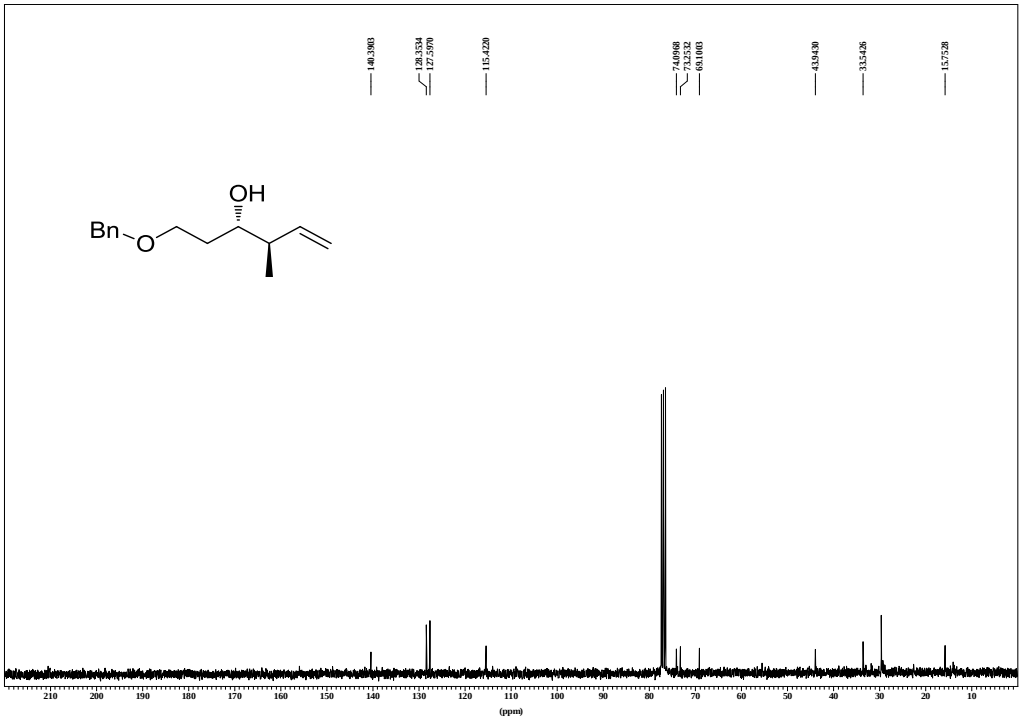
(2*R*, 3*S*)-1-(benzyloxy)-3-methylpent-4-en-2-ol (16b, Entry 2, Table 3)



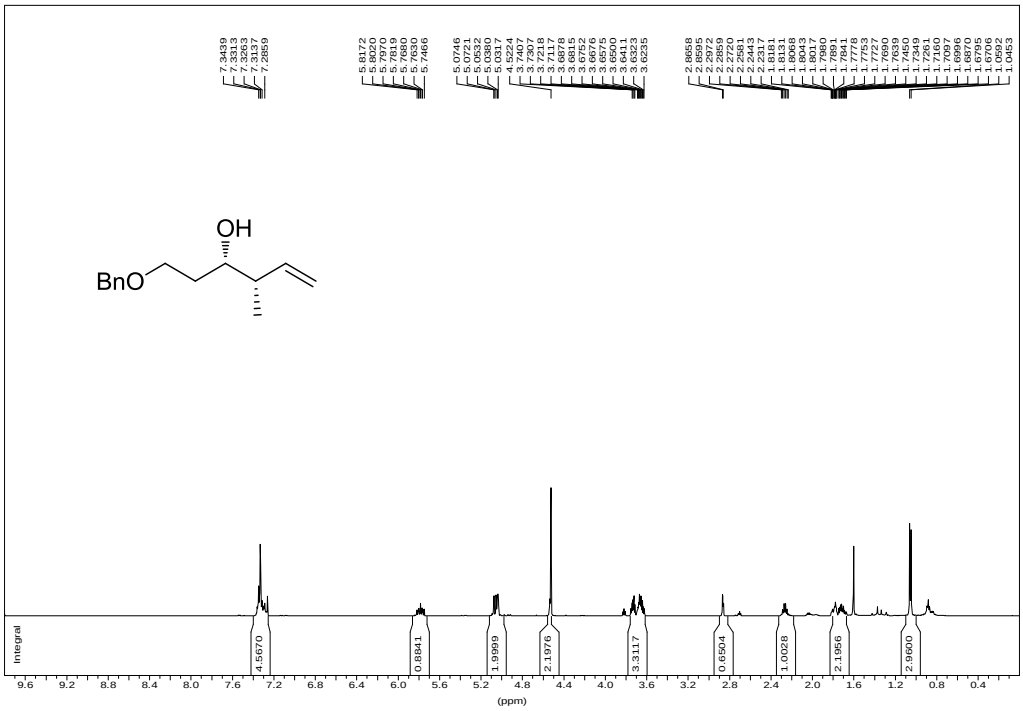


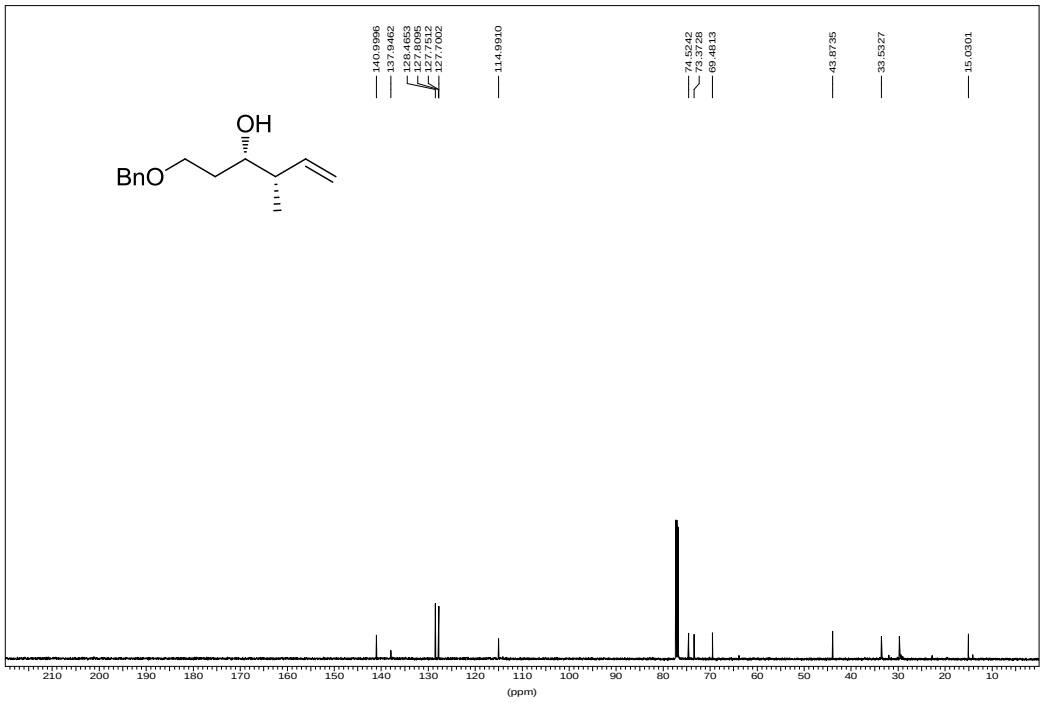
(3*S*, 4*R*)-1-(benzyloxy)-4-methylhex-5-en-3-ol (16c, Entry 3, Table 3)



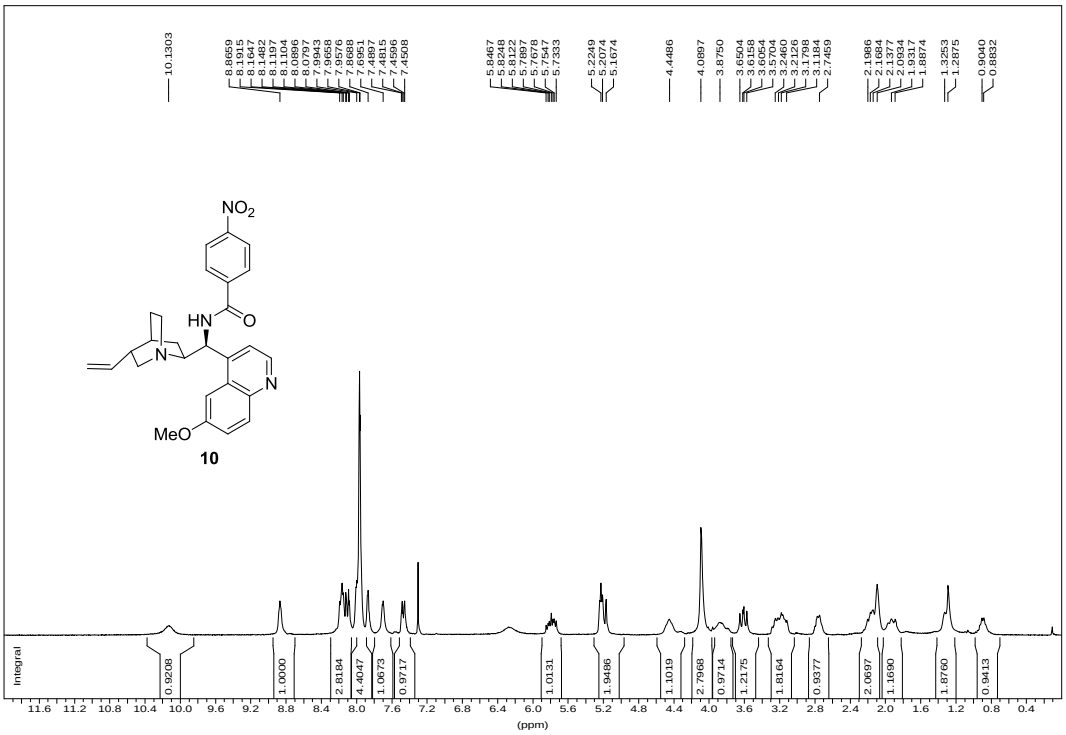


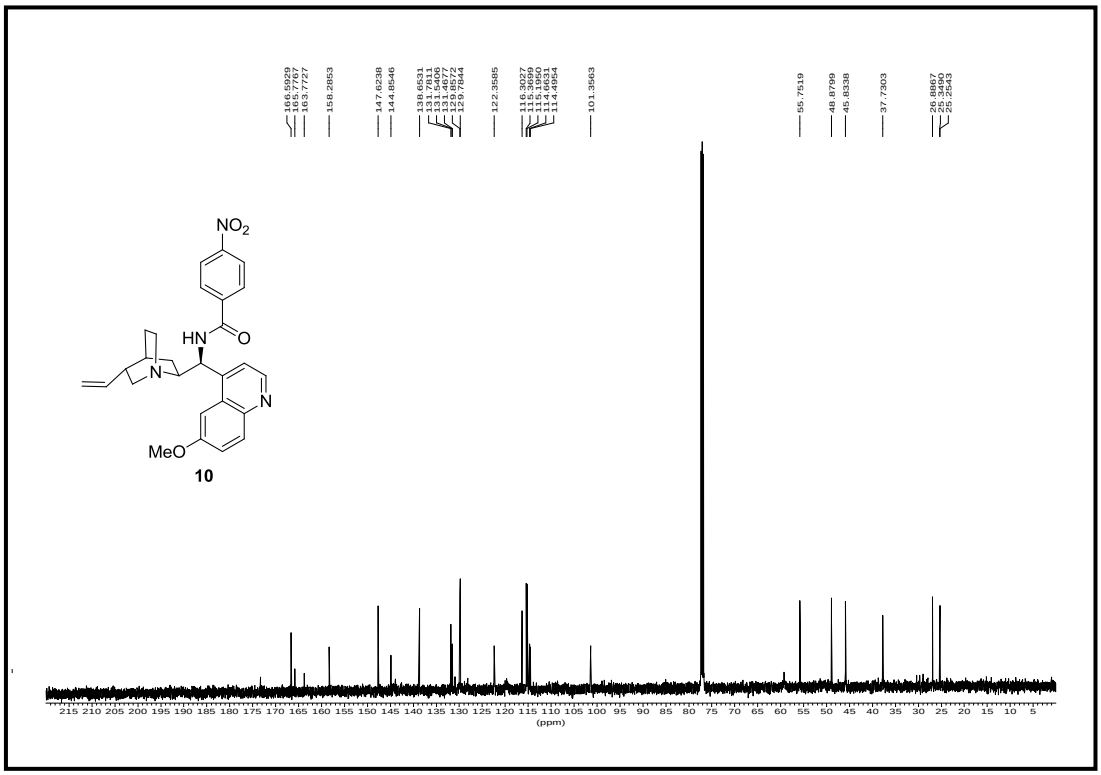
(3*S*, 4*S*)-1-(benzyloxy)-4-methylhex-5-en-3-ol (16d, Entry 4, Table 3)



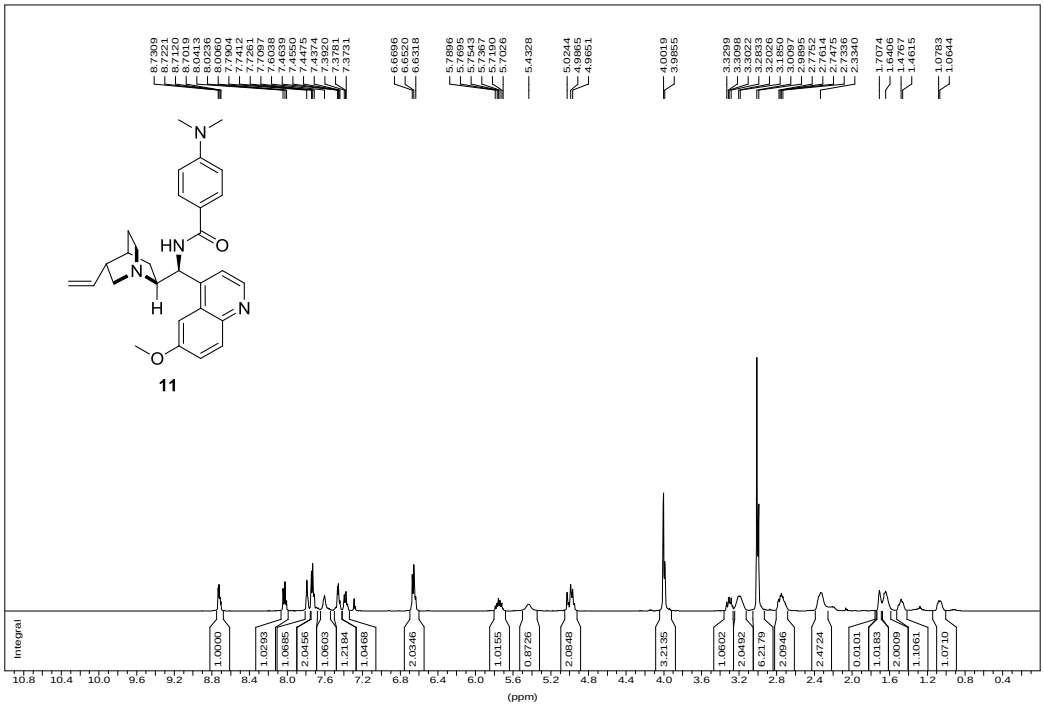


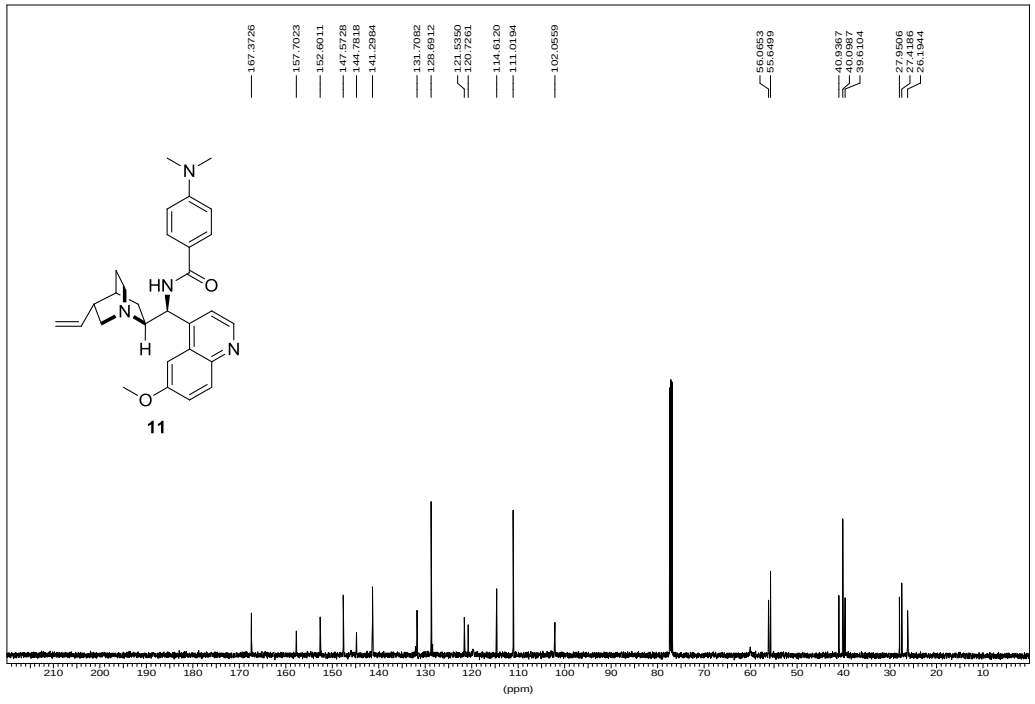
_N_-((_S_)-(6-methoxyquinolin-4-yl)((1_S_,2_S_,4_S_,5_R_)-5-vinylquinuclidin-2-yl)methyl)-4-nitrobenzamide



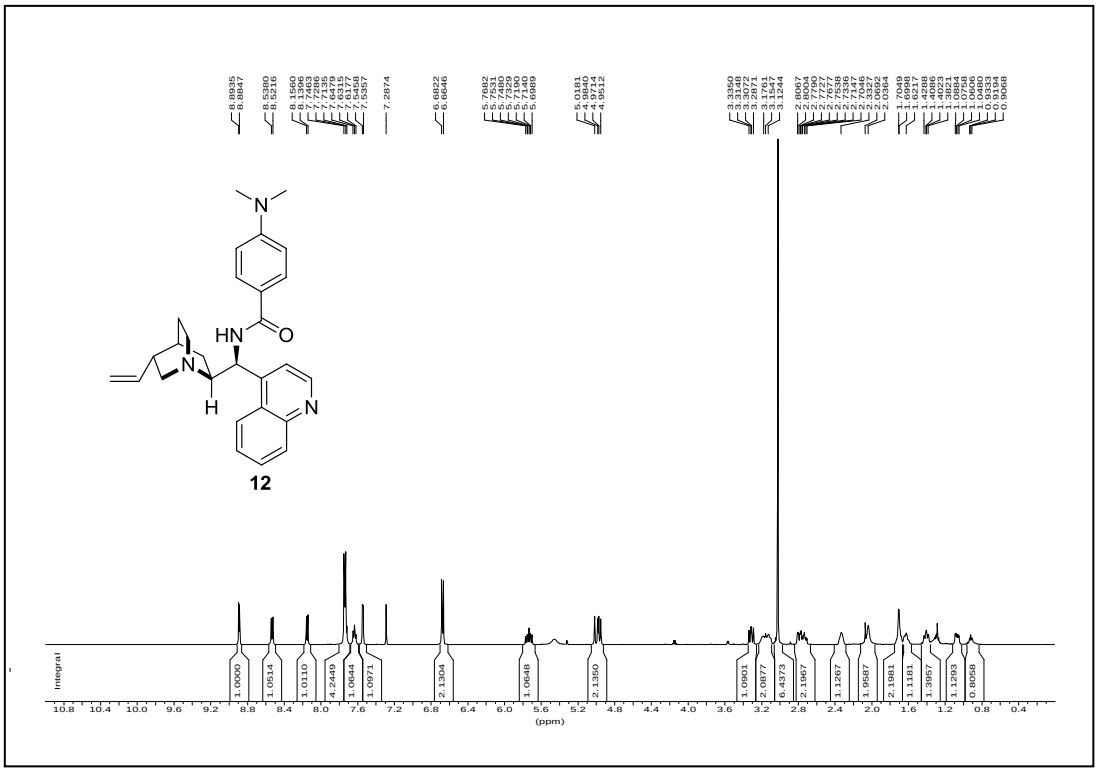


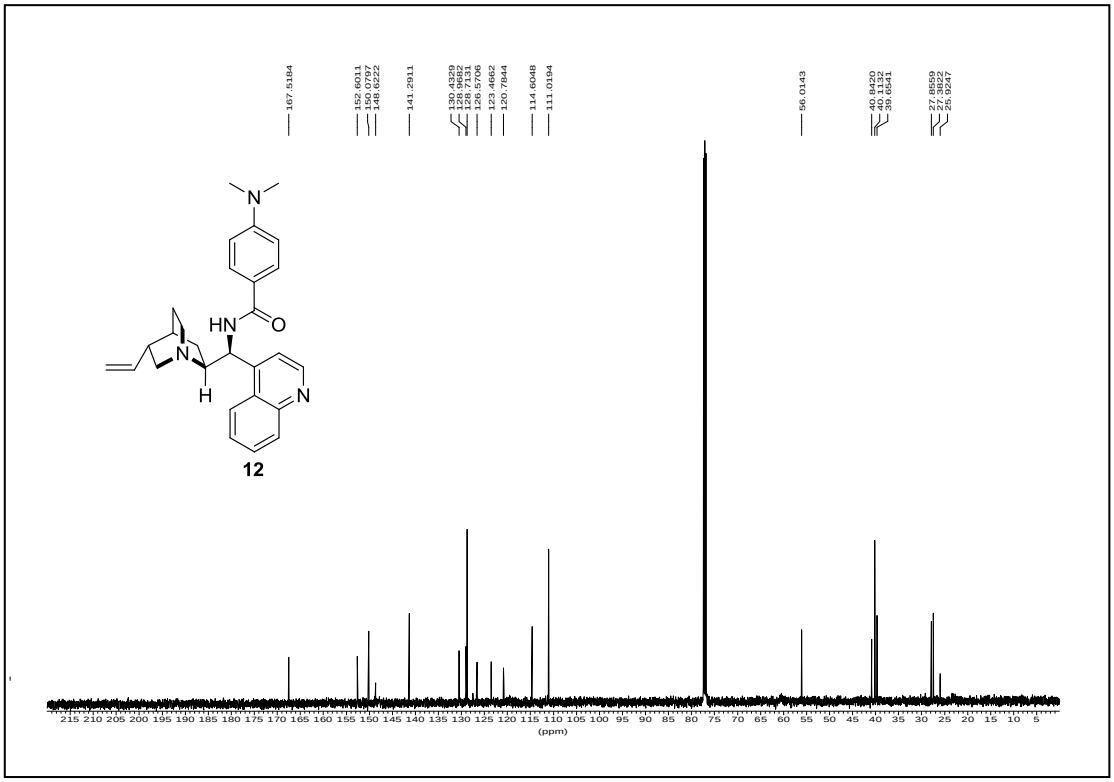
4-(dimethylamino)-*N*-((*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide



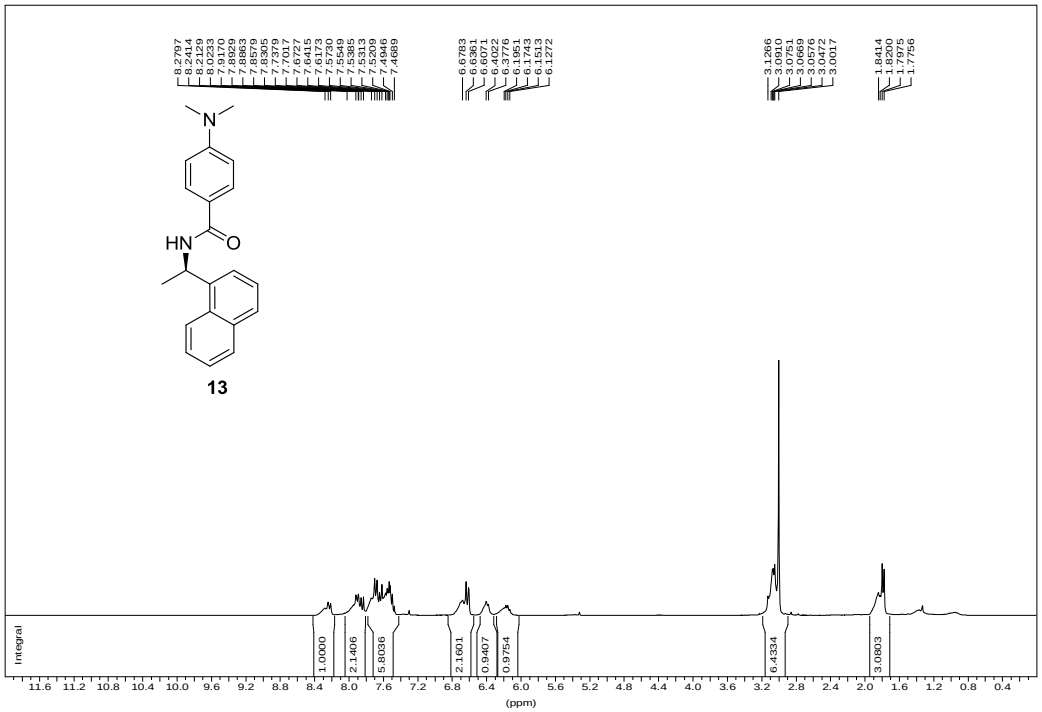


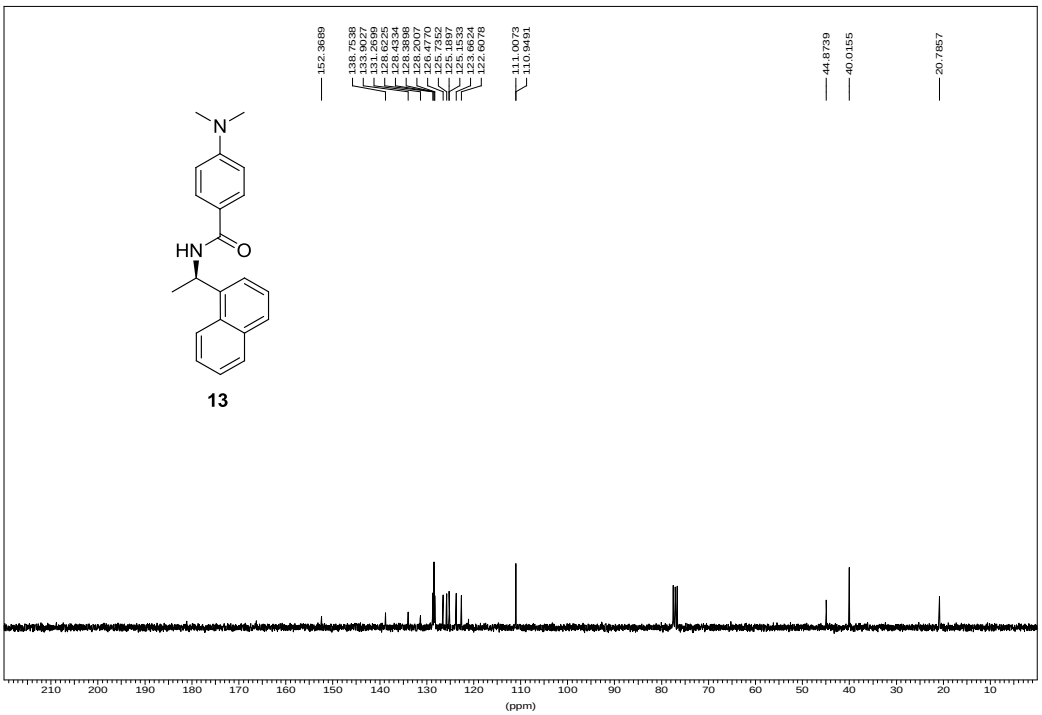
4-(dimethylamino)-*N*-((*S*)-quinolin-4-yl((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide



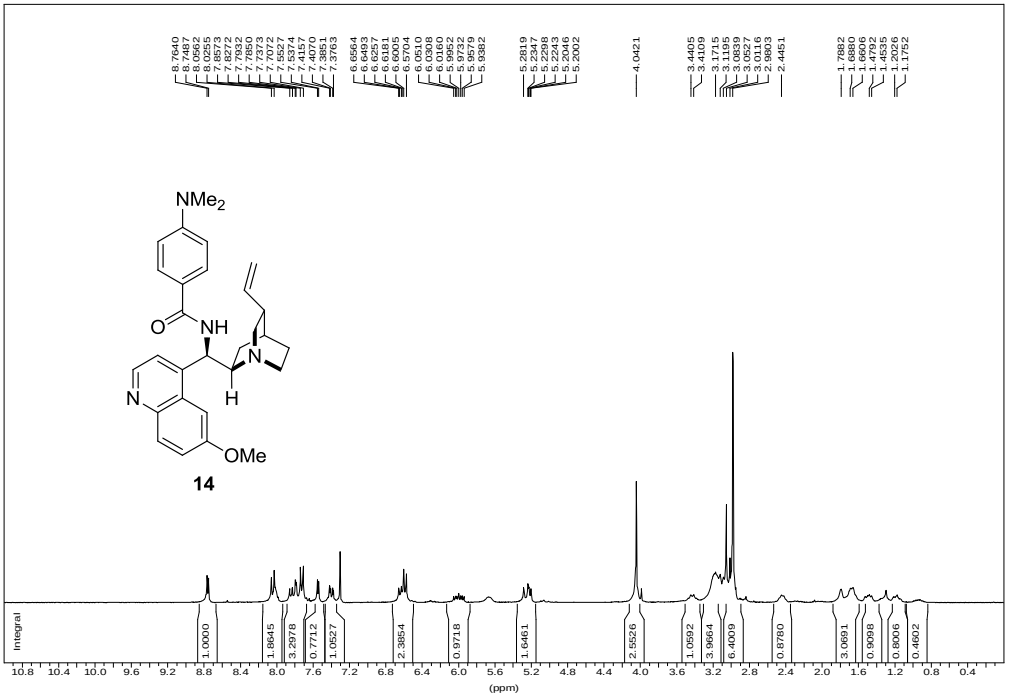


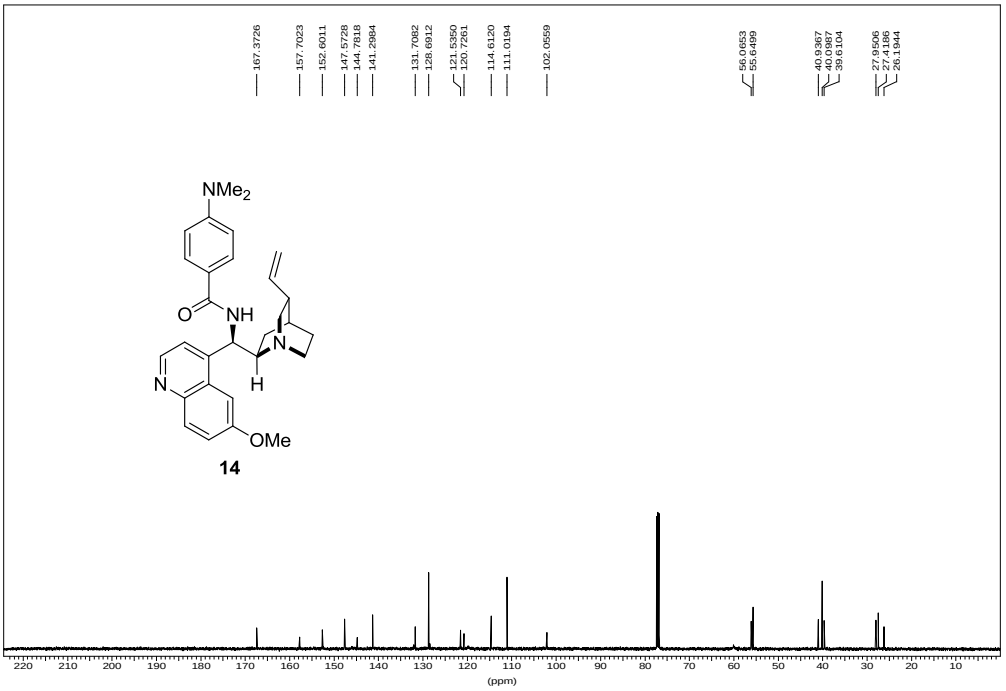
(*R*)-4-(dimethylamino)-*N*-(1-(naphthalen-1-yl)ethyl)benzamide





4-(dimethylamino)-*N*-((*R*)-(6-methoxyquinolin-4-yl)((1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)benzamide





7. References

1. F.-S. Maria, P. Nils, D. S. A. Krystle, D. Christine, F. Annika, G. Morten and L. Kristina, *J. Org. Chem*. 2009, **74**, 2755.
2. X. Li, D. Lantrip and P. L. Fuchs, *J. Am. Chem. Soc.* 2003, **125**, 14262.
3. K. Iseki, Y. Kuroki, M. Takahashi, S. Kishimoto and Y. Kobayashi, *Tetrahedron* 1997, **53**, 3513.
4. B. Vakulya, S. Varga, A. Csámpai and T. Soós, *Org. Lett.* 2005, **7**, 1967.
5. (*a*) H. Lachance, X. Lu, M. Gravel and D. G. Hall, *J. Am. Chem. Soc.* 2003, **125**, 10160. (*b*) K. Kubota and J. L. Leighton, *Angew. Chem. Int. Ed*. 2003, **42**, 946.
6. V. Rauniyar, H. Zhai and D. G. Hall, *J. Am. Chem. Soc.* 2008, **130**, 8481.
7. J. F. Traverse, Y. Zhao, A. H. Hoveyda and M. L. Snapper, *Org. Lett.* 2005, **7**, 3151.
8. B. M. Hackman, P. G. Lombardi and J. L. Leighton, *Org. Lett.* 2004, **6**, 4375.