Supporting information for:

# Highly Enantioselective Palladium-Catalyzed Umpolung Allylation of Aldehydes

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## CONTENTS:

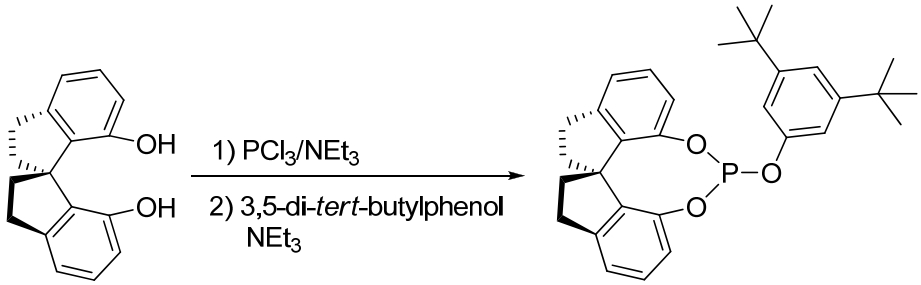


**General.** All reactions and manipulations were performed using standard Schlenk techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen atmosphere. $Et_3N$ was distilled over $CaH_2$ under nitrogen atmosphere. $PCl_3$ was fresh distilled before use. Commercially available aldehydes and allylic alcohols were purified by recrystallization or distillation before use. $Pd(OAc)_2$, *n*-BuLi (2.15 M solution in hexane), $Et_3B$ (1.0 M in hexane), $Et_2Zn$ (2.8 M in hexane), 3,5-ditertbutylphenol, and 2,6-ditertbutyl-4-methylphenol were purchased from Acros and Alderich Co. Ltd. and used as received. $Pd(dba)_2$ was prepared according to the literature procedure.[1] Ligands **2b**, **2d**, **3a** are commercially available from Aldrich, Strem and Jiuzhou Pharma Co. Ltd. and other ligands were prepared according to the literature procedures.[2] Melting points were measured on a RY-I apparatus and uncorrected. NMR spectra were recorded with a Bruker AV 300 spectrometer at 300 MHz ($^1$H NMR), 75 MHz ($^{13}$C NMR) and 121.5 MHz ($^{31}$P NMR) or a Varian Mercury Plus 400 spectrometer at 400 MHz ($^1$H NMR), 100 MHz ($^{13}$C NMR) and 162 MHz ($^{31}$P NMR). Chemical shifts (δ values) were reported in ppm down field from internal $Me_4Si$ ($^1$H and $^{13}$C NMR) and external 85% $H_3PO_4$ ($^{31}$P NMR), respectively. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. Elemental analyses were performed on Yanaca CDRDER MT-3 instrument. Mass spectra were recorded on a VG-7070E spectrometer. HPLC analyses were performed on a Hewlett Packard Model HP 1100 Series. SFC analyses were performed using a Mettler-Toledo Model Analytix SFC.

[1] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet and J. A. Ibers, *J. Organometal. Chem.*, 1974, **65**, 253–266.
[2] (*a*) P. H. Dussault and K. R. Woller, *J. Org. Chem.*, 1997, **62**, 1556–1559; (*b*) H. Zhou, W.-H. Wang, Y. Fu, J.-H. Xie, W.-J. Shi, L.-X. Wang, Q.-L. Zhou, *J. Org. Chem.*, 2003, **68**, 1582–1584; (*c*) W.-J. Shi, L.-X. Wang, Y. Fu, S.-F. Zhu and Q.-L. Zhou, *Tetrahedron: Asymmetry*, 2003, **14**, 3867–3872; (*d*) W.-J. Shi, J.-H. Xie and Q.-L. Zhou, *Tetrahedron: Asymmetry*, 2005, **16**, 705–710; (*e*) S.-F. Zhu, Y. Yang, L.-X. Wang, B. Liu and Q.-L. Zhou, *Org. Lett.*, 2005, **7**, 2333–2335; (*f*) H.-F. Duan, J.-H. Xie, W.-J. Shi, Q. Zhang and Q.-L. Zhou, *Org. Lett.*, 2006, **8**, 1479–1481; (*g*) W. Zhang, S.-F. Zhu, X.-C. Qiao and Q.-L. Zhou, *Chem. Aisan J.*, 2008, **3**, 2105–2111.

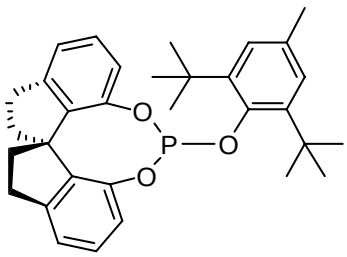
## 1 Preparation of New Chiral Phosphite Ligands

**Synthesis of (*S*)-3,5-di-tert-butylphenyl-(1,1′-spirobiindane-7,7′-diyl)phosphite ((*S*)-3d)**




A solution of (*S*)-1,1′-spirobiindane-7,7′-diol (500 mg, 1.98 mmol) and $Et_3N$ (445 mg, 4.4 mmol) in THF (20 mL) was cooled to −78 °C and fresh distilled $PCl_3$ (288 mg, 2.10 mmol) was added with stirring. After the addition of $PCl_3$, the reaction mixture was stirred for 1 h at −78 °C, warmed to room temperature and continuously stirred overnight. The resulting suspension was filtered under nitrogen and the filtrate was concentrated in vacuum. The residue was re-dissolved with THF (10 mL) and the solution was cooled to −78 °C and treated with lithium 3,5-di-*tert*-butylphenolate prepared from 3,5-di-*tert*-butylphenol (2.0 mmol) and butyllithium (2.15 M solution in hexane, 1.0 mL, 2.2 mmol) in 10 mL THF at −78 °C. The resulting solution was warmed to room temperature and stirred for 2 days. The solvent was removed in vacuum and the residue was filtered through a silica gel plug eluting with ethyl acetate/petroleum ether (1:40, v/v) to afford pure product in 72% yield as a white solid, mp 88–90 °C. $[\alpha]_D^{20}$ = –366 (*c* 0.5, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.19–6.97 (m, 6H, Ar-H), 6.72 (d, *J* = 10.4 Hz 1H, Ar-H), 3.14–3.03 (m, 2H, $CH_2$), 2.88–2.79 (m, 2H, $CH_2$), 2.30–2.22 (m, 2H, $CH_2$), 2.05–1.92 (m, 2H, $CH_2$), 1.29 (s, 18H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.5, 146.1, 145.8, 145.0, 144.9, 143.5, 140.3, 128.6, 128.1, 127.5, 123.3, 122.7, 121.9, 121.5, 59.6, 39.1, 38.1, 36.3, 33.0, 31.1, 30.8; $^{31}$P NMR (161 MHz, $CDCl_3$) δ 124.7 (s); MS (EI) m/z 486 ($M^+$); Anal. Calcd for $C_{31}H_{35}O_3P$: C 76.52, H 7.25; Found: C 76.36; H 7.38.

**Synthesis of (*S*)-2,6-di-tert-butyl-4-methylphenyl-(1,1′-spirobiindane-7,7′-diyl)phosphite ((*S*)-3e)**




Ligand (*S*)-**3e** was synthesized from (*S*)-1,1′-spirobiindane-7,7′-diol and lithium 2,6-di-tert-butyl-4-methylphenolate by the same procedure as that for (*S*)-**3d**. 53% yield; white solid, mp 125–127 °C. $[\alpha]_D^{20}$ = –272 (*c* 0.5, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.23–6.97 (m, 7H, Ar-H), 6.73 (d, *J* = 7.8 Hz , 1H, Ar-H), 3.13–3.02 (m, 2H, $CH_2$), 2.87–2.78 (m, 2H, $CH_2$), 2.29–2.21 (m, 5H), 2.03–1.91 (m, 2H, $CH_2$), 1.28 (s, 18H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.1, 145.8, 145.3, 145.0, 144.9, 143.3, 140.3, 136.0, 132.0, 128.6, 128.1, 125.8, 122.8, 121.9, 121.4, 59.5, 39.1, 38.1, 36.1, 34.5, 33.1, 32.4, 31.2, 30.8, 21.4; $^{31}$P NMR (161 MHz, $CDCl_3$) δ 124.8 (s); MS (EI) m/z 500 ($M^+$); Anal. Calcd for $C_{32}H_{37}O_3P$: C 76.78, H 7.45; Found: C 76.91, H 7.62.

## 2 Typical Palladium-Catalyzed Allylation Procedures

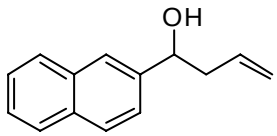
**2.1 Typical procedure for palladium-catalyzed allylation of aromatic aldehydes with allylic alcohols:** A oven-dried Schlenk tube was charged with $Pd(dba)_2$ (8.0 mg, 0.014 mmol ) and (*S*)-**3e** (14.0 mg, 0.028 mmol) in an argon-filled glove-box. Diethyl ether (0.8 mL) was added to the Schlenk tube with a syringe, and the resulting mixture was stirred at 25 °C for 1 h. 2-Naphthaldehyde (44 mg, 0.28 mmol), propan-2-en-1-ol (65 mg, 1.12 mmol) and $Et_3B$ (1.4 mL, 1.0 M in hexane, 1.4 mmol) were added sequentially. The Schlenk tube was then sealed with a glass stopple and the mixture was stirred at 25 °C for 3 days. The reaction mixture was concentrated under reduced pressure, and the residue was chromatographied on silica gel column with ethyl acetate/petroleum ether (1:5, v/v) to afford (*S*)-1-(2-naphthyl)but-3-en-1-ol (**7aa**) in 93 % yield as colorless oil. Enantiomeric excess (96%) was determined by chiral HPLC analyses using a Chiralcel OJ column.

**2.2 Typical procedure for palladium-catalyzed allylation of aliphatic aldehydes with allylic alcohols:** A oven-dried Schlenk tube was charged with $Pd(dba)_2$ (8.0 mg, 0.014 mmol ) and (*S*)-**3e** (14.0 mg, 0.028 mmol) in an argon-filled glove-box. Diethyl ether (0.8 mL) was added to the Schlenk tube with a syringe, and the resulting mixture was stirred at 25 °C for 1 h. 3-Phenylpropanal (38 mg, 0.28 mmol), propan-2-en-1-ol (65 mg, 1.12 mmol), oven-dried silical gel (80 mg) and $Et_3B$ (1.4 mL, 1.0 M in hexane, 1.4 mmol) were added sequentially. The Schlenk tube was then sealed with a glass stopple and the mixture was stirred at 25 °C for 4 days. The reaction mixture was concentrated under reduced pressure, and the residue was chromatographied on silica gel column with ethyl acetate/petroleum ether (1:5, v/v) to afford (*R*)-1-phenyl-hexa-5-en-3-ol (**7qa**) in 83 % yield as colorless oil. Enantiomeric excess (93%) was determined by chiral HPLC analyses using a Chiralcel OD column.

**2.3 Typical procedure for palladium-catalyzed allylation of aromatic aldehydes with various allylic donors:** A oven-dried Schlenk tube was charged with $Pd(dba)_2$ (8.0 mg, 0.014 mmol ) and (*R*)-**3e** (14.0 mg, 0.028 mmol) in an argon-filled glove-box. THF (2.0 mL) was added to the Schlenk tube with a syringe, and the resulting mixture was stirred at 25 °C for 1 h. 2-Naphthaldehyde (44 mg, 0.28 mmol), allyl acetate (42 mg, 0.42 mmol) and $Et_2Zn$ (0.1 mL, 2.8 M in hexane, 0.28 mmol) were added sequentially at 10 °C. The Schlenk tube was then sealed with a glass stopple and the mixture was stirred at 10 °C for 5 days. The reaction mixture was concentrated under reduced pressure, and the residue was chromatographied on silica gel column with ethyl acetate/petroleum ether (1:5, v/v) to afford (*R*)-1-(2-naphthyl)but-3-en-1-ol (**7aa**) in 97 % yield as colorless oil. Enantiomeric excess (95%) was determined by chiral HPLC analyses using a Chiralcel OJ column.

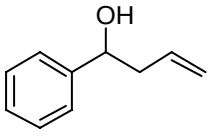
## 3 Analytical Data for Homoallylic Alcohols

**(*S*)-1-(2-Naphtyl)but-3-en-1-ol (7aa)**[3]




Colorless oil; 93% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.74–7.69 (m, 4H, Ar-H), 7.39–7.35 (m, 3H, Ar-H), 5.80–5.65 (m, 1H, CH), 5.11–5.02 (m, 2H, $CH_2$), 4.80 (t, $J$ = 6.3 Hz, 1H, CH), 2.52–2.44 (m, 2H, $CH_2$), 2.19 (s, 1H, OH); 96% ee [HPLC condition: Chiralcel OJ column, *n*-hexane/propan-2-ol = 90:10, flow rate = 1.0 mL/min, wavelength = 220 nm, $t_R$ = 12.9 min for (*S*)-enantiomer, $t_R$ = 18.5 min for (*R*)-enantiomer], $[\alpha]_D^{27}$ = –66.9 (*c* 1.20, $CHCl_3$) [lit: $[\alpha]_D$ = –55.0 (*c* 1.16, $CHCl_3$) for 90% ee, (*S*)].

**(*S*)-1-Phenylbut-3-en-1-ol (7ba)**[4]




Colorless oil; 65% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H, Ar-H), 5.88–5.73 (m, 1H, CH), 5.19–5.12 (m, 2H, $CH_2$), 4.75–4.71 (m, 1H, CH), 2.56–2.43 (m, 2H, $CH_2$), 2.08 (d, $J$ = 2.1 Hz, 1H, OH); 95% ee [HPLC condition: Chiralcel OD column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 19.2 min for (*R*)-enantiomer and $t_R$ =23.8 min for (*S*)-enantiomer]; $[\alpha]_D^{20}$ = –48.2 (*c* 0.50, benzene) [lit: $[\alpha]_D$ = +43.7 (*c* 6.7, benzene) for 90% ee, (*R*)].

**(*S*)-1-(2-Methylphenyl)but-3-en-1-ol (7ca)**[5]

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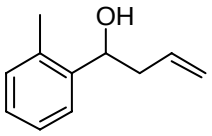
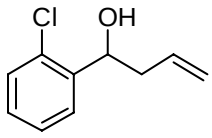
[3] A. V. Malkov, M. Bell, M. Orsini, D. Pernazza, A. Massa, P. Herrmann, P. Meghani and P. Kočovský, *J. Org. Chem.*, 2003, **68**, 9659–9668.
[4] M. Riediker and R. O. Duthaler, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 494–495.
[5] A. Kina, T. Shimada and T. Hayashi, *Adv. Synth. Catal.*, 2004, **346**, 1169–1174.



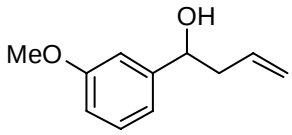
Colorless oil; 70% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, $J$ = 7.2 Hz, 1H, Ar-H), δ 7.18–7.04 (m, 3H, Ar-H), 5.85–5.71 (m, 1H, CH), 5.14–5.06 (m, 2H, $CH_2$), 4.91–4.87 (m, 1H, CH), 2.46–2.32 (m, 2H, $CH_2$), 2.26 (s, 3H, $CH_3$), 1.94 (d, $J$ = 2.7 Hz, 1H, OH); 91% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 17.4 min for (*R*)-enantiomer and $t_R$ = 21.3 min for (*S*)-enantiomer]; $[\alpha]_D^{29}$ = –42.1 (*c* 0.47, EtOH) [lit: $[\alpha]_D^{20}$ = –46.8 (*c* 1.26, EtOH) for 90% ee, (*S*)].

**(-)-1-(2-Chlorophenyl)but-3-en-1-ol (7da)**[6]



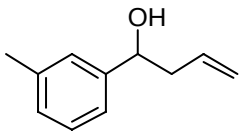
Colorless oil; 90% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.50–7.46 (m, 1H, Ar-H), 7.26–7.08 (m, 3H, Ar-H), 5.85–5.71 (m, 1H, CH), 5.13–5.04 (m, 3H, CH and $CH_2$), 2.59–2.50 (m, 1H, $CH_2$), 2.35–2.24 (m, 1H, $CH_2$), 2.21 (d, $J$ = 3.3 Hz, 1H, OH); 89% ee [HPLC condition: Chiralcel OB column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 8.3 min (major) and $t_R$ = 9.9 min (minor)]; $[\alpha]_D^{20}$ = –72.6 (*c* 1.07, benzene).

**(–)-1-(3-Methoxyphenyl)but-3-en-1-ol (7ea)**[7]



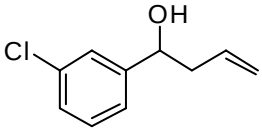
Colorless oil; 87% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.28–7.22 (m, 1H, Ar-H), 6.93–6.91 (m, 2H, Ar-H), 6.83–6.78 (m, 1H, Ar-H), 5.87–5.73 (m, 1H, CH), 5.19–5.11 (m, 2H, $CH_2$), 4.72–4.67 (m, 1H, CH), 3.80 (s, 3H, $CH_3$), 2.52–2.44 (m, 2H, $CH_2$), 2.14 (br, 1H, OH); 96% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 51.6 min (minor) and $t_R$ = 54.1 min (major)]; $[\alpha]^{23}_D$ = –25.4 (*c* 1.25, benzene).

**(–)-1-(3-Methylphenyl)but-3-en-1-ol (7fa)**[8]



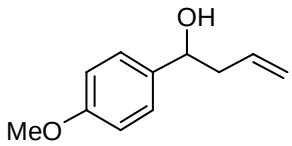
Colorless oil; 72% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.17–6.98 (m, 4H, Ar-H), 5.79–5.64 (m, 1H, CH), 5.10–5.02 (m, 2H, $CH_2$), 4.59 (t, $J$ = 6.5 Hz, 1H, CH), 2.43–2.38 (m, 2H, $CH_2$), 2.27 (s, 3H, $CH_3$), 2.09 (s, 1H, OH); 96% ee [HPLC condition: Chiralcel OD column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 16.5 min (minor) and $t_R$ = 22.1 min (major)]; $[\alpha]_D^{23}$ = –35.3 (*c* 0.15, benzene).

**(–)-1-(3-Chlorophenyl)but-3-en-1-ol (7ga)**[8]



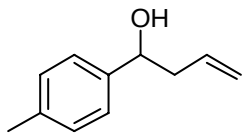
Colorless oil; 82% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 1H, Ar-H), 7.20–7.12 (m, 3H, Ar-H), 5.78–5.63 (m, 1H, CH), 5.12–5.06 (m, 2H, $CH_2$), 4.63–4.60 (m, 1H, CH), 2.44–2.34 (m, 2H, $CH_2$), 2.13 (s, 1H, OH); 93% ee [HPLC condition: Chiralcel OB column, *n*-hexane/propan-2-ol = 98:2, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 9.7 min (major) and $t_R$ = 11.9 min (minor)]; $[\alpha]_D^{23}$ = –28.6 (*c* 0.90, benzene).

**(*S*)-1-(4-Methoxyphenyl)but-3-en-1-ol (7ha)**[9]



Colorless oil; 63% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, $J$ = 8.7 Hz, 2H, Ar-H), 6.80 (d, $J$ = 8.7 Hz, 2H, Ar-H), 5.78–5.63 (m, 1H, CH), 5.08–5.01 (m, 2H, $CH_2$), 4.61–4.55 (m, 1H, CH), 3.71 (s, 3H, $CH_3$), 2.43–2.38 (m, 2H, $CH_2$), 2.10 (s, 1H, OH); 94% ee [HPLC condition: Chiralcel OD column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 28.7 min for (*R*)-enantiomer and $t_R$ = 34.0 min for (*S*)-enantiomer]; $[\alpha]_D^{20}$ = –33.7 (*c* 0.73, benzene) [lit: $[\alpha]_D^{23}$ = +30.5 (*c* 1.0, benzene) for 95% ee, (*R*)].

**(*S*)-1-(4-Methylphenyl)but-3-en-1-ol (7ia)**[3]

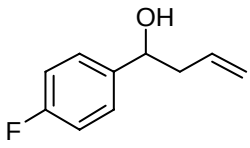


Colorless oil; 69% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, $J$ =7.8 Hz, 2H, Ar-H), 7.16 (d, $J$ = 7.8 Hz, 2H, Ar-H), 5.86–5.72 (m, 1H, CH), 5.17–5.10 (m, 2H, $CH_2$), 4.70–4.66 (m, 1H, CH), 2.51–2.47 (m, 2H, $CH_2$), 2.34 (s, 3H, $CH_3$), 2.08 (d, $J$ = 2.4 Hz, 1H, OH); 95% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 22.2 min for (*R*)-enantiomer and $t_R$ = 24.8 min for (*S*)-enantiomer]; $[\alpha]^{23}_D$ = –47.2 (*c* 0.38, $CHCl_3$) [lit: $[\alpha]_D$

[6] Z. Zha, A. Hui, Y. Zhou, Q. Miao, Z. Wang and H. Zhang, *Org. Lett.*, 2005, **7**, 1903–1905.
[7] G-L. Li and G. Zhao, *J. Org. Chem.*, 2005, **70**, 4272–4278.
[8] H. Yamataka, K. Nishikawa and T. Hanafusa, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2145–2150.
[9] M. Wadamoto, N. Ozasa, A. Yanagisawa and H. Yamamoto, *J. Org. Chem.*, 2003, **68**, 5593–5601.

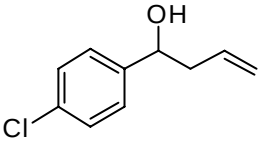
= –31.1 (*c* 0.9, $CHCl_3$) for 87% ee, (*S*)].

**(–)-1-(4-Fluorophenyl)but-3-en-1-ol (7ja)**[8]



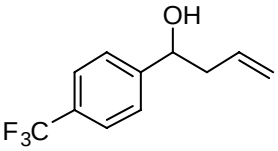
Colorless oil; 77% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.4 and 5.4 Hz, 2H, Ar-H), 6.95 (t, *J* = 8.7 Hz, 2H, Ar-H), 5.78–5.63 (m, 1H, CH), 5.11–5.04 (m, 2H, $CH_2$), 4.67–4.60 (m, 1H, CH), 2.43–2.37 (m, 2H, $CH_2$), 2.11 (d, *J* = 3.0 Hz, 1H, OH); 96% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 22.0 min (minor) and $t_R$ = 22.9 min (major)]; $[\alpha]_D^{23}$ = –32.1 (*c* 1.0, benzene).

**(*S*)-1-(4-Chlorophenyl)but-3-en-1-ol (7ka)**[10]



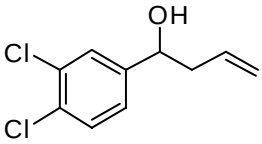
Colorless oil; 81% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25–7.18 (m, 4H, Ar-H), 5.76–5.62 (m, 1H, CH), 5.09–5.04 (m, 2H, $CH_2$), 4.62–4.59 (m, 1H, CH), 2.44–2.33 (m, 2H, $CH_2$), 2.14 (d, *J* = 3.0 Hz, 1H, OH); 95% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 25.0 min for (*R*)-enantiomer and $t_R$ = 26.3 min for (*S*)-enantiomer]; $[\alpha]_D^{20}$ = –28.5 (*c* 1.15, benzene) [lit: $[\alpha]_D^{28}$ = +26.4 (*c* 0.38, benzene) for 98% ee, (*R*)].

**(*S*)-1-(4-Trifluoromethylphenyl)but-3-en-1-ol (7la)**[3]



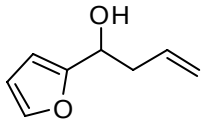
Colorless oil; 83% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.39 (d, *J* = 8.1 Hz, 2H, Ar-H), 5.78–5.63 (m, 1H, CH), 5.12–5.07 (m, 2H, $CH_2$), 4.75–4.68 (m, 1H, CH), 2.51–2.32 (m, 2H, $CH_2$), 2.17 (d, *J* = 3.3 Hz, 1H, OH); 92% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 19.8 min for (*R*)-enantiomer and $t_R$ =20.9 min for (*S*)-enantiomer]; $[\alpha]_D^{23}$ = –35.7 (c 0.78, $CH_2Cl_2$) [lit: $[\alpha]_D$ = –33.6 (*c* 0.25, $CH_2Cl_2$) for 91% ee, (*S*)].

**(–)-1-(3,4-Dichlorophenyl)but-3-en-1-ol (7ma)**[11]



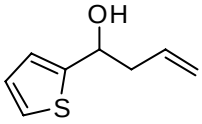
Colorless oil; 86% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.38–7.31 (m, 2H, Ar-H), 7.11–7.08 (m, 1H, Ar-H), 5.76–5.62 (m, 1H, CH), 5.12–5.06 (m, 2H, $CH_2$), 4.65–4.59 (m, 1H, CH), 2.48–2.29 (m, 2H, $CH_2$), 2.15 (d, *J* = 3.3 Hz, 1H, OH); 92% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 25.8 min (minor) and $t_R$ = 29.2 min (major)]; $[\alpha]_D^{23}$ = –23.2 (*c* 1.30, benzene).

**(*S*)-1-(2-Furyl)but-3-en-1-ol (7na)**[9]



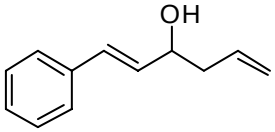
Colorless oil; 52% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H, CH), 6.33–6.24 (m, 2H, CH), 5.88–5.73 (m, 1H, CH), 5.21–5.12 (m, 2H, $CH_2$), 4.77–4.72 (m, 1H, CH), 2.66–2.60 (m, 2H, $CH_2$), 2.11 (s, 1H, OH); 97% ee [HPLC condition: Chiralcel OD column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 21.0 min for (*R*)-enantiomer and $t_R$ =23.2 min for (*S*)-enantiomer]; $[\alpha]_D^{20}$ = –28.4 (*c* 0.28, $Et_2O$) [lit: $[\alpha]_D^{26}$ = +29.9 (*c* 1.0, $Et_2O$) for 95% ee, (*R*)].

**(*S*)-1-(2-Thienyl)but-3-en-1-ol (7oa)**[12]



Colorless oil; 60% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25–7.22 (m, 1H, CH), 6.97–6.94 (m, 2H, CH), 5.89–5.75 (m, 1H, CH), 5.21–5.13 (m, 2H, $CH_2$), 4.99–4.94 (m, 1H, CH), 2.63–2.58 (m, 2H, $CH_2$), 2.32 (s, 1H, OH); 96% ee [HPLC condition: Chiralcel OD column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 22.5 min for (*R*)-enantiomer and $t_R$ =24.3 min for (*S*)-enantiomer]; $[\alpha]_D^{23}$ = –20.0 (*c* 0.53, $CH_2Cl_2$) [lit: $[\alpha]_D^{27}$ = –8.2 (*c* 1.20, $CH_2Cl_2$) for 80% ee, (*S*)].

**(*S*)-1-Phenyl-hexa-1,5-dien-3-ol (7pa)**[13]

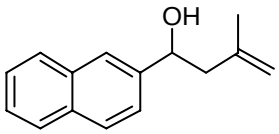


Colorless oil; 88% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.39–7.20 (m, 5H, Ar-H), 6.60 (d, *J* = 15.9 Hz, 1H, CH), 6.27–6.19 (m, 1H, CH), 5.93–5.78 (m, 1H, CH), 5.20–5.13 (m, 2H, $CH_2$), 4.38–4.31 (m, 1H, CH), 2.49–2.32 (m, 2H,

[10] K. Sugimoto, S. Aoyagi, C. Kibayashi, *J. Org. Chem.*, 1997, **62**, 2322–2323.
[11] R. A. Batey, A. N. Thadani, D. V. Smil and A. J. Lough, *Synthesis*, 2000, 990–998.
[12] S. Singh, S. Kumar and S. S. Chimni, *Tetrahedron: Asymmetry*, 2002, **13**, 2679–2687.
[13] Â. de Fátima, L. K. Kohn, J. E. de Carvalho and R. A. Pilli, *Bioorg. Med. Chem.*, 2006, **14**, 622–631.

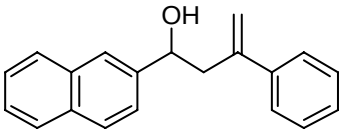
$CH_2$), 1.90 (s, 1H, OH); 94% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 99:1, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 36.2 min for (*R*)-enantiomer and $t_R$ = 38.5 min for (*S*)-enantiomer]; $[\alpha]_D^{23}$ = –23.2 (*c* 0.38, $CHCl_3$) [lit: $[\alpha]_D^{25}$ = –22.4 (*c* 2.0, $CHCl_3$) for 96% ee, (*S*)].

**(–)-1-(2-Naphtyl)-3-methylbut-3-en-1-ol (7ab)**[14]



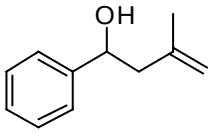

Colorless oil, 72% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.83–7.79 (m, 4H, Ar-H), 7.50–7.43 (m, 3H, Ar-H), 4.98–4.87 (m, 3H, CH and $CH_2$), 2.51–2.48 (m, 2H, $CH_2$), 2.29 (s, 1H, OH), 1.81 (s, 3H, $CH_3$); 93% ee [HPLC condition: Chiralcel OJ column, *n*-hexane/propan-2-ol = 90:10, flow rate = 1.0 mL/min, wavelength = 225 nm, $t_R$ = 12.4 min (major), $t_R$ = 16.2 min (minor)]; $[\alpha]_D^{26}$ = –70.7 (*c* 1.05, $CHCl_3$) [lit: $[\alpha]_D$ = +56.7 (*c* 0.51, $CHCl_3$) for 62% ee].

**(–)-1-(Naphthalen-2-yl)-3-phenylbut-3-en-1-ol (7ac)**



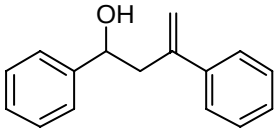

Colorless oil, 74% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H, Ar-H), 7.69 (s, 1H, Ar-H), 7.44–7.41 (m, 5H, Ar-H), 7.36–7.28 (m, 3H, Ar-H), 5.36 (d, *J* = 1.2 Hz, 1H, CH), 5.12 (d, *J* = 0.9 Hz, 1H, CH), 4.83 (q, *J* = 4.5 Hz, 1H, CH), 3.06–3.00 (m, 1H, $CH_2$), 2.94–2.86 (m, 1H, $CH_2$), 2.28 (s, 1H, OH); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 145.1, 141.4, 140.5, 133.4, 133.1, 128.6, 128.2, 128.0, 127.8, 127.7, 126.4, 126.1, 125.8, 124.6, 124.1, 115.9, 72.3, 45.9; EI-HRMS Calcd for $C_{20}H_{18}O$: 274.1357. Found: 274.1371; 95% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 90:10, flow rate = 1.0 mL/min, wavelength = 225 nm, $t_R$ = 12.3 min (major) , $t_R$ = 14.4 min (minor)]; $[\alpha]_D^{23}$ = –48.6 (*c* 1.35, $CHCl_3$).

**(*S*)-1-Phenyl-3-methylbut-3-en-1-ol (7bb)**[14]



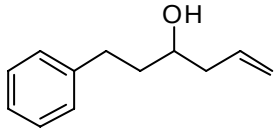

Colorless oil, 68% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.39–7.24 (m, 5H, Ar-H), 4.92–4.77 (m, 3H, CH and $CH_2$), 2.44–2.41 (m, 2H, $CH_2$), 2.18 (s, 1H, OH), 1.79 (s, 3H, $CH_3$); 93% ee [HPLC condition: Chiralpak AD-H column, *n*-hexane/propan-2-ol = 95:5, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 8.5 min for (*S*)-enantiomer, $t_R$ = 9.1 min for (*R*)-enantiomer]; $[\alpha]_D^{23}$ = –81.5 (*c* 0.8, benzene) [lit: $[\alpha]_D$ = +40.0 (*c* 0.58, benzene) for 66% ee, (*R*)].

**(–)-1,3-Diphenylbut-3-en-1-ol (7bc)**[14]



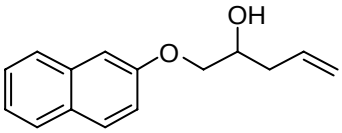

Colorless oil, 92% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.37–7.33 (m, 2H, Ar-H), 7.25–7.12 (m, 8H, Ar-H), 5.31 (d, *J* = 1.2 Hz, 1H, CH), 5.05 (s, 1H, CH), 4.62 (q, *J* = 4.2 Hz, 1H, CH), 2.93–2.86 (m, 1H, $CH_2$), 2.80–2.71 (m, 1H, $CH_2$), 2.05 (s, 1H, OH); 96% ee [SFC condition: Chiralpak AD-H column, *sc* $CO_2$/propan-2-ol = 90:10, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 210 nm, $t_R$ = 8.9 min (major), $t_R$ = 10.4 min (minor)]; $[\alpha]_D^{30}$ = –21.2 (*c* 1.45, $CHCl_3$) [lit: $[\alpha]_D^{22}$ = –16.7 (*c* 1.72, $CHCl_3$) for 59% ee].

**(*R*)-1-Phenyl-hexa-5-en-3-ol (7qa)**[3]




Colorless oil, 83% yield; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.24–7.08 (m, 5H, Ar-H), 5.82–5.67 (m, 1H, CH), 5.10–5.04 (m, 2H, $CH_2$), 3.65–3.55 (m, 1H, CH), 2.79–2.55 (m, 2H, $CH_2$), 2.30–2.05 (m, 2H, $CH_2$), 1.75–1.65 (m, 3H, $CH_2$ and OH); 93% ee [HPLC condition: Chiralcel OD column, *n*-hexane/propan-2-ol = 95:5, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 9.3 min for (*S*)-enantiomer and $t_R$ = 13.7 min for (*R*)-enantiomer]; $[\alpha]_D^{23}$ = +15.2 (*c* 0.63, $CHCl_3$) [lit: $[\alpha]_D$ = +1.8 (*c* 0.9, $CHCl_3$) for 49% ee, (*R*)].

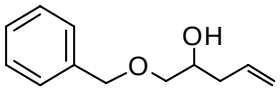
**(–)-1-(Naphthalen-2-yloxy)pent-4-en-2-ol (7ra)**




White solid, 91% yield. Mp: 57 °C. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.69–7.62 (m, 3H, Ar-H), 7.37–7.23 (m, 2H, Ar-H), 7.10–7.04 (m, 2H, Ar-H), 5.89–5.75 (m, 1H, CH), 5.15–5.06 (m, 2H, $CH_2$), 4.02–3.87 (m, 3H, $CH_2$ and CH), 2.36 (br, 3H, OH and $CH_2$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 155.5, 133.5, 132.8, 128.5, 128.2, 126.6, 125.8, 125.4, 122.8, 117.7, 117.2, 106.0, 70.5, 68.34, 36.9; EI-HRMS Calcd for $C_{15}H_{16}O_2$: 228.1150, Found: 228.1152; 87% ee [HPLC condition: Chiralpak OD-H column, *n*-hexane/propan-2-ol = 95:5, flow rate = 1.0 mL/min, wavelength = 227 nm, $t_R$ = 18.9 min (major) and $t_R$ = 25.0 min (minor)]; $[\alpha]_D^{20}$ = –3.6 (c 0.73, EtOH).

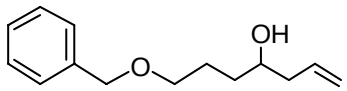
[14] M. Nakajima, S. Kotani, T. Ishizuka and S. Hashimoto, *Tetrohedron Lett.*, 2005, **46**, 157–159.

**(*R*)-1-(Benzyloxy)-2-hydroxypent-4-ene (7sa)**[15]



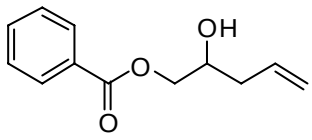
Colorless oil, 65% yield, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H, Ar-H), 5.88–5.77 (m, 1H, CH), 5.15–5.08 (m, 2H, $CH_2$), 4.56 (s, 2H, $CH_2$), 3.92–3.85 (m, 1H, CH), 3.52 (dd, *J* = 9.6, 3.2 Hz, 1H, $CH_2$), 3.37 (dd, *J* = 9.6, 7.6 Hz, 1H, $CH_2$), 2.37 (d, *J* = 3.6 Hz, 1H, OH), 2.28 (t, *J* = 6.4 Hz, 2H, $CH_2$); 88% ee [HPLC condition: Chiralpak AS column, *n*-hexane/propan-2-ol = 98:2, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 8.4 min for (*S*)-enantiomer and $t_R$ = 9.8 min for (*R*)-enantiomer]; $[\alpha]_D^{26}$ = –2.83 (c 1.88, $CHCl_3$) [lit: $[\alpha]_D^{29}$ = –3.1 (c 2.07, $CHCl_3$), (*R*)].

**(*S*)-1-(Benzyloxy)-4-hydroxypent-6-ene (7ta)**[16]



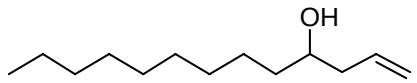
Colorless oil, 67% yield, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H, Ar-H), 5.89–5.78 (m, 1H, CH), 5.14–5.09 (m, 2H, $CH_2$), 4.52 (s, 2H, $CH_2$), 3.69–3.62 (m, 1H, CH), 3.51 (t, *J* = 6.0 Hz, 2H, $CH_2$), 2.44 (br s, 1H, OH), 2.31–2.14 (m, 2H, $CH_2$), 1.81–1.61 (m, 3H, $CH_2$), 1.50–1.45 (m, 1H, $CH_2$); 93% ee [HPLC condition: Chiralpak AS column, *n*-hexane/propan-2-ol = 95:5, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 6.0 min (*R*) and $t_R$ = 7.9 min (*S*)]; $[\alpha]_D^{24}$ = –4.3 (c 1.25, $CH_2Cl_2$) [lit: $[\alpha]_D$ = –7.2 (c 1.24, $CH_2Cl_2$) for 91% ee, (*S*)].

**(–)-2-Hydroxypent-4-enyl benzoate (7ua)**[17]



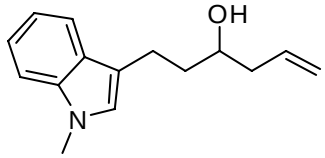
Colorless oil, 88% yield, $^1$H NMR (300 MHz, $CDCl_3$) δ 8.00–7.95 (m, 2H, Ar-H), 7.51–7.46 (m, 1H, Ar-H), 7.38–7.33 (m, 2H, Ar-H), 5.86–5.72 (m, 1H, CH), 5.14–5.07 (m, 2H, $CH_2$), 4.31 (dd, *J* = 11.4 and 3.6 Hz, 1H, $CH_2$), 4.20 (dd, *J* = 11.4 and 6.6 Hz, 1H, $CH_2$), 3.99 (br, 1H, CH) 2.37 (br, 1H, OH), 2.33–2.21 (m, 2H, $CH_2$); 83% ee [HPLC condition: Chiralpak AS column, *n*-hexane/propan-2-ol = 98:2, flow rate = 1.0 mL/min, wavelength = 230 nm, $t_R$ = 13.6 min for (minor) and $t_R$ = 16.5 min for (major)]; $[\alpha]_D^{30}$ = –4.5 (c 1.1, $CHCl_3$).

**(+)-Tridec-1-en-4-ol (7va)**[18]



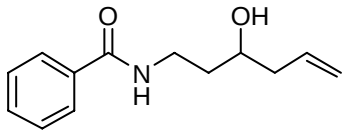
Colorless oil, 70% yield, $^1$H NMR (400 MHz, $CDCl_3$) δ 5.91–5.76 (m, 1H, CH), 5.16–5.11 (m, 2H, $CH_2$), 3.61–3.67 (m, 1H, CH), 2.35–2.26 (m, 1H, $CH_2$), 2.19–2.08 (m, 1H, $CH_2$), 1.62 (br s, 1H, OH), 1.47–1.40 (br m, 3H, $CH_2$), 1.35–1.20 (br, 13H, $CH_2$), 0.87 (t, *J* = 6.4 Hz, 3H, $CH_3$); 92% ee [enantioselevtivity was determined by SFC analysis of the corresponding benzoate using a Chiralpak AD-H column, sc $CO_2$/propan-2-ol = 97:3, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 215 nm, $t_R$ = 6.0 min (major) and $t_R$ = 7.1 min (minor)]; $[\alpha]_D^{30}$ = +11.2 (c 1.3, $CHCl_3$).

**(–)-1-(1-Methyl-1H-indol-3-yl)hex-5-en-3-ol (7wa)**



Colorless oil, 62% yield, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.37–7.28 (m, 2H, Ar-H), 7.19 (t, *J* = 7.2 Hz, 1H, Ar-H), 6.91 (s, 1H, Ar-H), 5.96–5.85 (m, 1H, CH), 5.24–5.19 (m, 2H, $CH_2$), 3.84–3.77 (m, 4H, $CH_3$ and CH), 3.05–2.87 (m, 2H, $CH_2$), 2.43–2.37 (m, 1H, $CH_2$), 2.31–2.22 (m, 1H, $CH_2$), 1.98–1.91 (m, 3H, OH and $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.4, 135.2, 128.1, 126.5, 121.8, 119.3, 118.9, 118.4, 114.9, 109.5, 70.6, 42.4, 37.6, 32.8, 21.6; EI-HRMS Calcd for $C_{15}H_{19}NO$: 229.1467. Found: 229.1462; 93% ee [HPLC condition: Chiralpak AS column, *n*-hexane/propan-2-ol = 97:3, flow rate = 1.0 mL/min, wavelength = 210 nm, $t_R$ = 22.6 min (major) and $t_R$ = 26.1 min (minor)]; $[\alpha]_D^{25}$ = –14.2 (c 0.88, $CH_2Cl_2$).

**(–)-N-(3-Hydroxyhex-5-enyl)benzamide (7xa)**

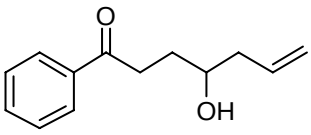


Colorless oil, 80% yield, $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* =7.2 Hz, 2H, Ar-H), 7.68 (t, *J* =5.6 Hz, 1H, NH), 7.41 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.31 (t, *J* = 8.0 Hz, 1H, Ar-H), 5.81–5.71 (m, 1H, CH), 5.06–5.01 (m, 2H, $CH_2$), 4.11 (br, 1H, OH), 3.77–3.68 (m, 2H, $CH_2$), 3.38–3.30 (m, 1H, CH), 2.25–2.15 (m, 2H, $CH_2$), 1.77–1.69 (m, 1H, $CH_2$), 1.59–1.50 (m, 1H,

[15] W. R. Roush, L. K. Hoong, M. A. J. Palmer, J. A. Straub and A. D. Palkowitz, *J. Org. Chem.*, 1990, **55**, 4117–4126.
[16] J. Lu, S.-J. Ji, Y.-C.Teo, T.-P. Loh, *Org. Lett.*, 2005, **7**, 159–161.
[17] J. Cossy, S. Bouzbouz and J. C. Caille, *Tetrahedron: Asymmetry*, 1999, **10**, 3859–3862.
[18] H. Kakiya, S. Nishimae, H. Shinokubo and K. Oshima, *Tetrahedron*, 2001, **57**, 8807–8815.

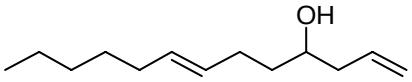
$CH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.5, 134.9, 134.4, 131.7, 128.7, 127.2, 118.0, 69.3, 42.2, 37.7, 36.1; EI-HRMS Calcd for $C_{13}H_{17}NO_2$: 219.1259. Found: 219.1257; 93% ee [SFC condition: Chiralpak AD-H column, *sc* $CO_2$/propan-2-ol = 95:5, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 230 nm, $t_R$ = 22.4 min (major) and $t_R$ = 24.1 min (minor)]; $[\alpha]_D^{25}$ = –6.2 (c 1.08, $CH_2Cl_2$).

**(–)-4-Hydroxy-1-phenylhept-6-en-1-one (7ya)**



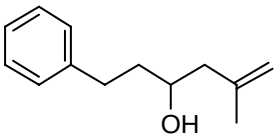

Colorless oil, 91% yield, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2H, Ar-H), 7.56–7.51 (m, 1H, Ar-H), 7.43 (t, *J* = 7.6 Hz, 1H, Ar-H), 5.89–5.78 (m, 1H, CH), 5.15–5.11 (m, 2H, $CH_2$), 3.76–3.70 (m, 1H, CH), 3.22–3.08 (m, 2H, $CH_2$), 2.36–2.18 (m, 3H, OH and $CH_2$), 2.03–1.95 (m, 1H, $CH_2$), 1.86–1.77 (m, 1H, $CH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 200.9, 137.1, 134.8, 133.3, 128.8, 128.3, 118.4, 70.4, 42.5, 35.1, 31.0; EI-HRMS Calcd for $C_{13}H_{16}O_2$: 204.1150. Found: 204.1151; 94% ee [SFC condition: Chiralpak AD-H column, *sc* $CO_2$/propan-2-ol = 90:10, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 240 nm, $t_R$ = 10.6 min (major) and $t_R$ = 11.5 min (minor)]; $[\alpha]_D^{27}$ = –7.8 (c 0.4, $CH_2Cl_2$).

**(+)-(*E*)-Trideca-1,7-dien-4-ol (7za)**



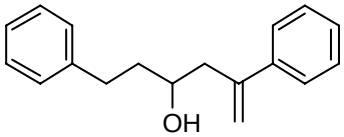

Colorless oil, 77% yield, $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.87–5.76 (m, 1H, CH), 5.48–5.36 (m, 2H, CH), 5.14–5.10 (m, 2H, $CH_2$), 3.69–3.62 (m, 1H, OH), 2.31 (m, 1H, $CH_2$), 2.18–2.11 (m, 3H, $CH_2$), 1.98–1.94 (m, 2H, $CH_2$), 1.75 (br, 1H, OH), 1.55–1.49 (m, 2H, $CH_2$), 1.36–1.20 (m, 6H, $CH_2$), 0.87 (t, *J* = 6.4 Hz, 3H, $CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 135.1, 131.3, 129.7, 118.1, 70.5, 66.1, 42.1, 36.7, 32.8, 31.6, 29.5, 29.1, 22.8; EI-HRMS Calcd for $C_{13}H_{24}O$: 196.1827. Found: 196.1821; 91% ee [enantioselevtivity was determined by SFC analysis of the corresponding 3,5-dinitrobenzoate using a Chiralpak AD-H column, *sc* $CO_2$/propan-2-ol = 92:8, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 230 nm, $t_R$ = 4.9 min (major) and $t_R$ = 5.6 min (minor)]; $[\alpha]_D^{25}$ = + 9.9 (c 0.95, $CH_2Cl_2$).

**(*S*)-5-Methyl-1-phenyl-5-hexen-3-ol (7qb)[19]**



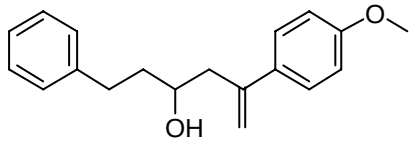

Colorless oil, 83% yield, $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.31–7.15 (m, 5H, Ar-H), 4.88 (s, 1H, CH), 4.80 (s, 1H, CH), 3.80–3.70 (m, 1H, CH), 2.88–2.77 (m, 1H, $CH_2$), 2.75–2.64 (m, 1H, $CH_2$), 2.26–2.09 (m, 2H, $CH_2$), 1.82–1.70 (m, 6H, $CH_3$ and OH and $CH_2$); 85% ee [SFC condition: Chiralcel OD-H column, *Sc* *sc* $CO_2$/propan-2-ol = 90:10, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 210 nm, $t_R$ = 4.3 min for (*S*)-enantiomer and $t_R$ = 5.7 min for (*R*)-enantiomer]; $[\alpha]_D^{26}$ = –15.3 (c 0.95, $CHCl_3$) [lit: $[\alpha]_D^{25}$ = –18.12 (*c* 0.63, $CHCl_3$) for (*S*)].

**(–)-1,5-Diphenylhex-5-en3-ol (7qc)[20]**




Colorless oil, 62% yield, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.47–7.22 (m, 10H, Ar-H), 5.47 (d, *J* = 1.2 Hz, 1H, CH), 5.23 (s, 1H, CH), 3.76 (br, 1H, CH), 2.91–2.83 (m, 2H, $CH_2$), 2.74–2.61 (m, 2H, $CH_2$), 1.91–1.81 (m, 3H, OH and $CH_2$); 83% ee [SFC condition: Chiralcel OD-H column, *sc* $CO_2$/propan-2-ol = 80:20, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 210 nm, $t_R$ = 5.3 min (major) and $t_R$ = 6.8 min (minor)]; $[\alpha]_D^{26}$ = –7.0 (c 1.2, $CHCl_3$).

**(–)-5-(4-Methoxyphenyl)-1-phenylhex-5-en-3-ol (7qd)**



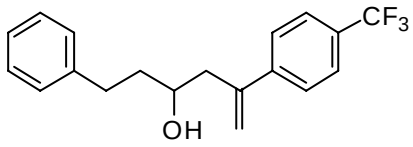

Colorless oil, 57% yield, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.37–7.19 (m, 7H, Ar-H), 6.89–6.87 (m, 2H, Ar-H), 5.37 (d, *J* = 1.2 Hz, 1H, CH), 5.10 (s, 1H, CH), 3.83 (s, 3H, $CH_3$), 3.77 (m, 1H, CH), 2.87–2.79 (m, 2H, $CH_2$), 2.71–2.65 (m, 1H, $CH_2$), 2.59–2.52 (m, 1H, $CH_2$), 1.87–1.80 (m, 2H, $CH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.5, 144.7, 142.3, 132.9, 128.6, 127.6, 126.0, 114.1, 69.3, 55.5, 44.0, 38.8, 32.3; EI-HRMS Calcd for $C_{19}H_{22}O_2$: 282.1620. Found: 282.1612; 86% ee [SFC condition: Chiralpak AD-H column, *sc* $CO_2$/propan-2-ol = 80:20, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 210 nm, $t_R$ = 7.8 min (major) and $t_R$ = 9.5 min (minor)]; $[\alpha]_D^{26}$ = –26.6 (c 0.9, $CHCl_3$).

**(–)-1-Phenyl-5-(4-(trifluoromethyl)phenyl)hex-5-en-3-ol (7qe)**

Colorless oil, 69% yield, $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.51 (d, *J* = 8.0 Hz,

[19] (*a*) H. Hanawa, D. Uraguchi, S. Konishi, T. Hashimoto and K. Maruoka, *Chem. Eur. J.*, 2003, **9**, 4405–4413; (*b*) V. Rauniyar, H. Zhai and D. G. Hall, *J. Am. Chem. Soc.*, 2008, **130**, 8481–8490.

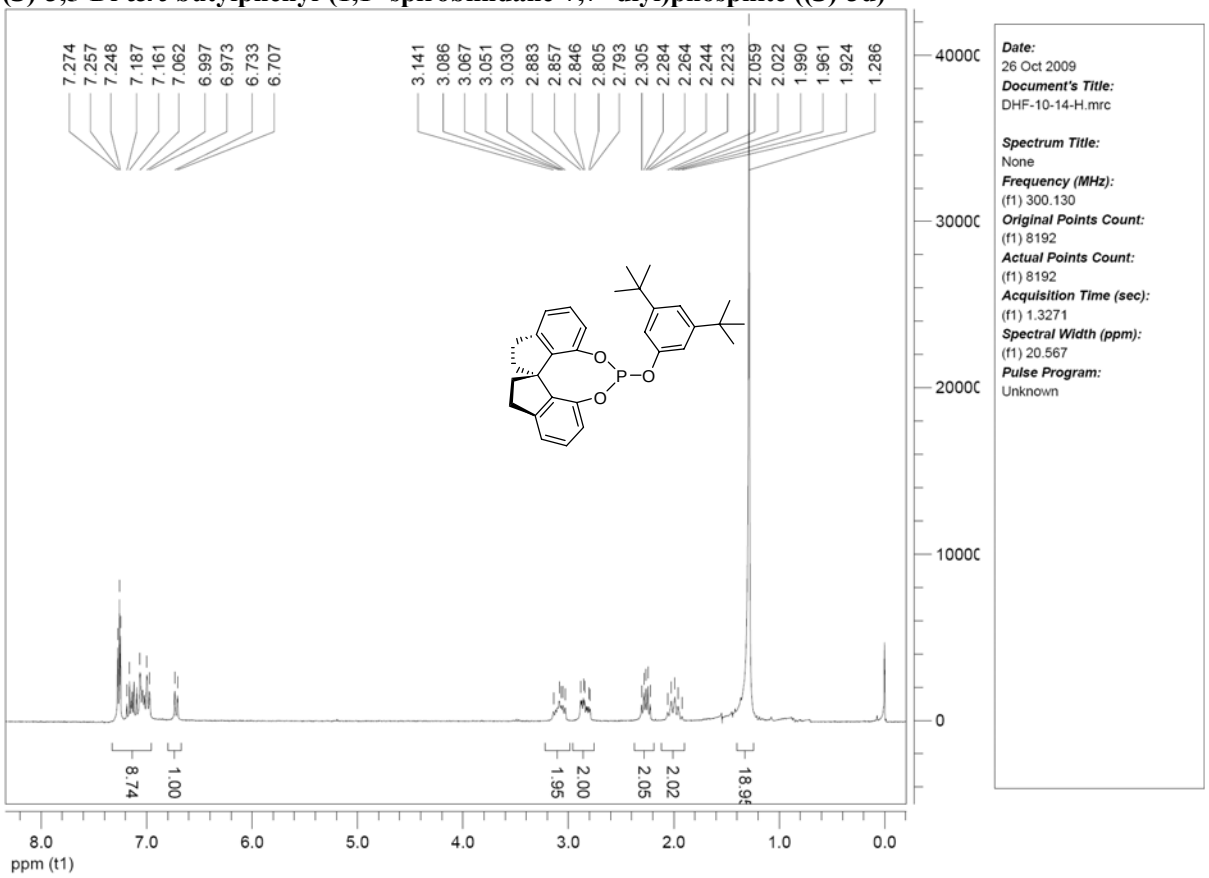
[20] Y. Hanzawa, N. Kowase, S.-i. Momose and T. Taguchi, *Tetrahedron*, 1998, **54**, 11387–11398.

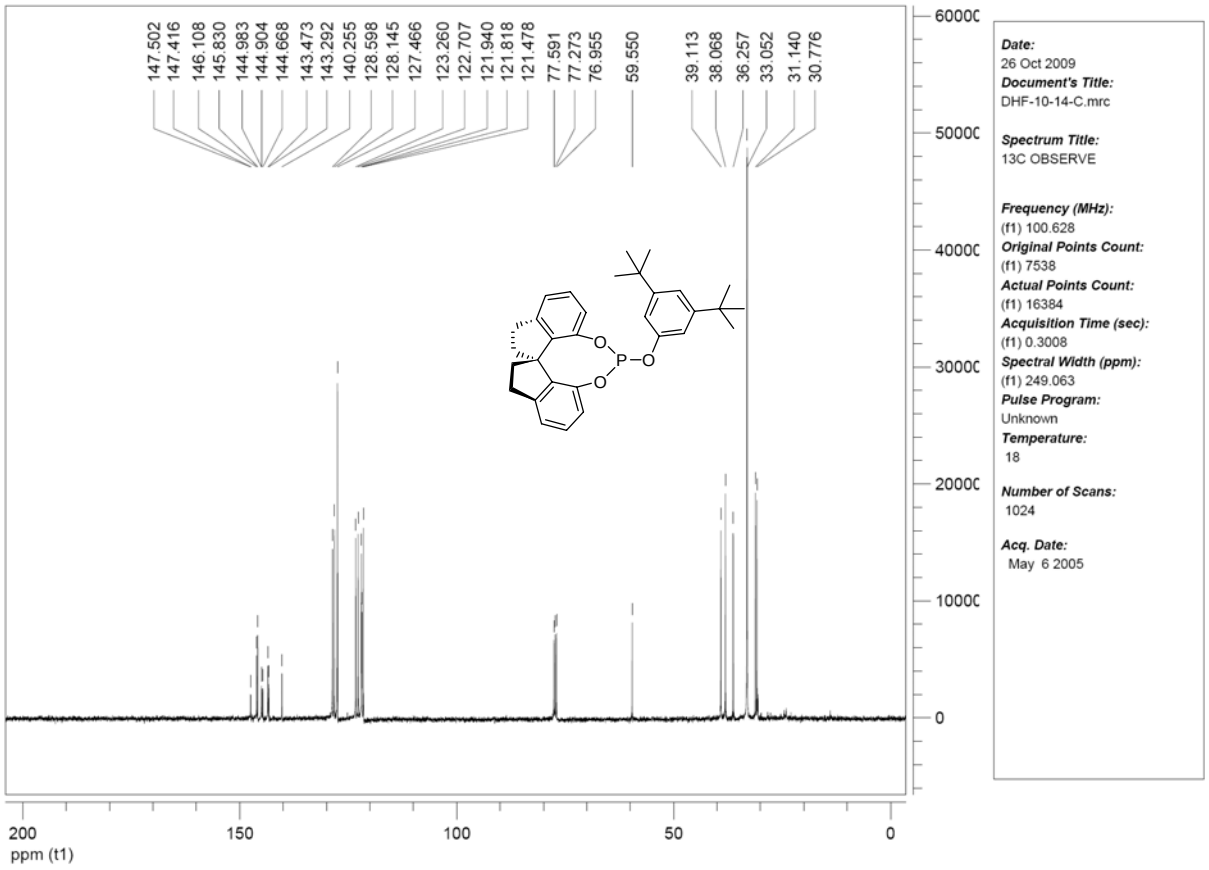



2H, Ar-H), 7.32 (t, $J$ = 7.6 Hz, 2H, Ar-H), 7.26–7.21 (m, 3H, Ar-H), 5.51 (s, 1H, CH), 5.32 (s, 1H, CH), 3.77–3.71 (m, 1H, CH), 2.90–2.81 (m, 2H, $CH_2$), 2.74–2.65 (m, 2H, $CH_2$), 2.36 (br, 1H, OH), 1.94–1.81 (m, 2H, $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.6, 144.5, 142.1, 128.7, 128.6, 126.8, 126.2, 125.7, 117.5, 69.3, 43.8, 38.9, 32.2; EI-HRMS Calcd for $C_{19}H_{19}F_3O$: 320.1388. Found: 320.1377; 86% ee [SFC condition: Chiralcel OD-H column, *sc* $CO_2$/propan-2-ol = 90:10, $P_{CO2}$ = 100 bar, flow rate = 2.0 mL/min, wavelength = 210 nm, $t_R$ = 8.7 min (major) and $t_R$ = 12.5 min (minor)]; $[\alpha]_D^{26}$ = –6.5 (c 1.53, $CHCl_3$).

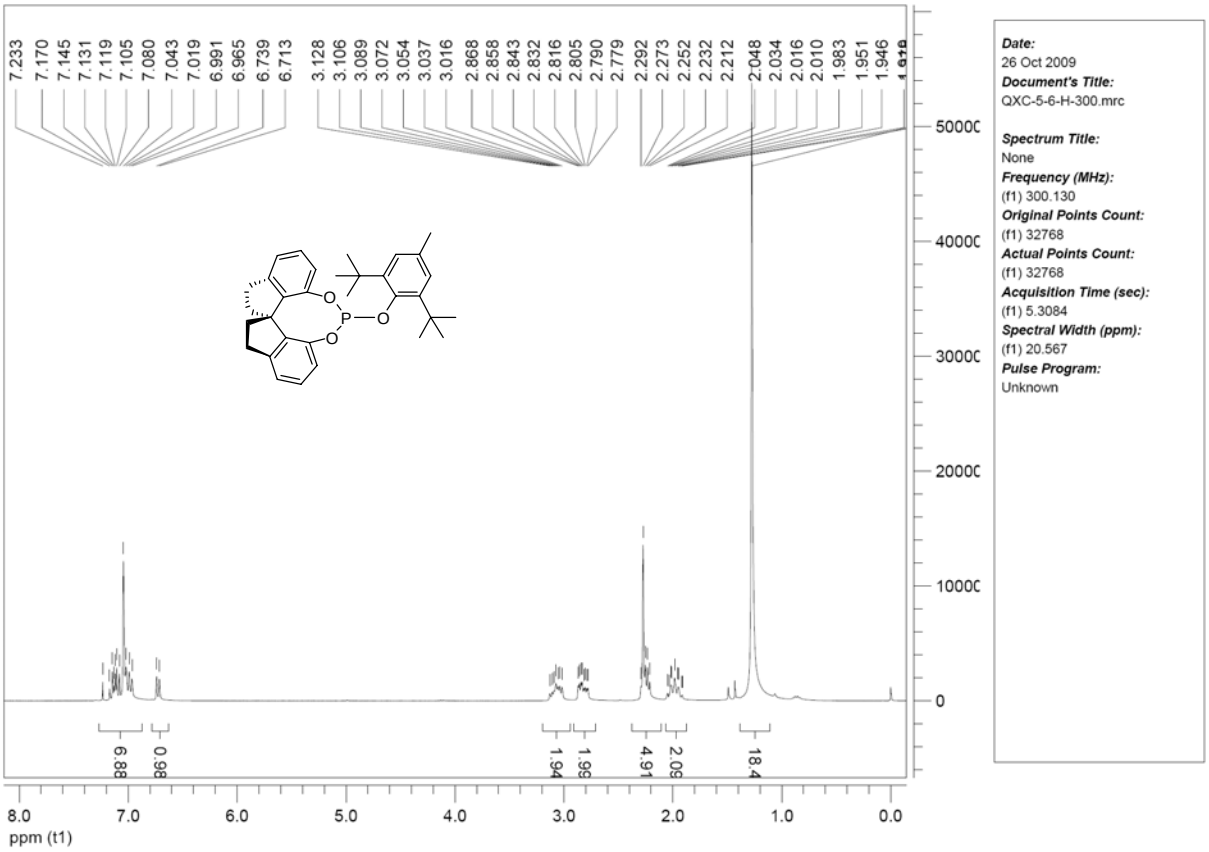
## 4 NMR Spectra for New Compounds

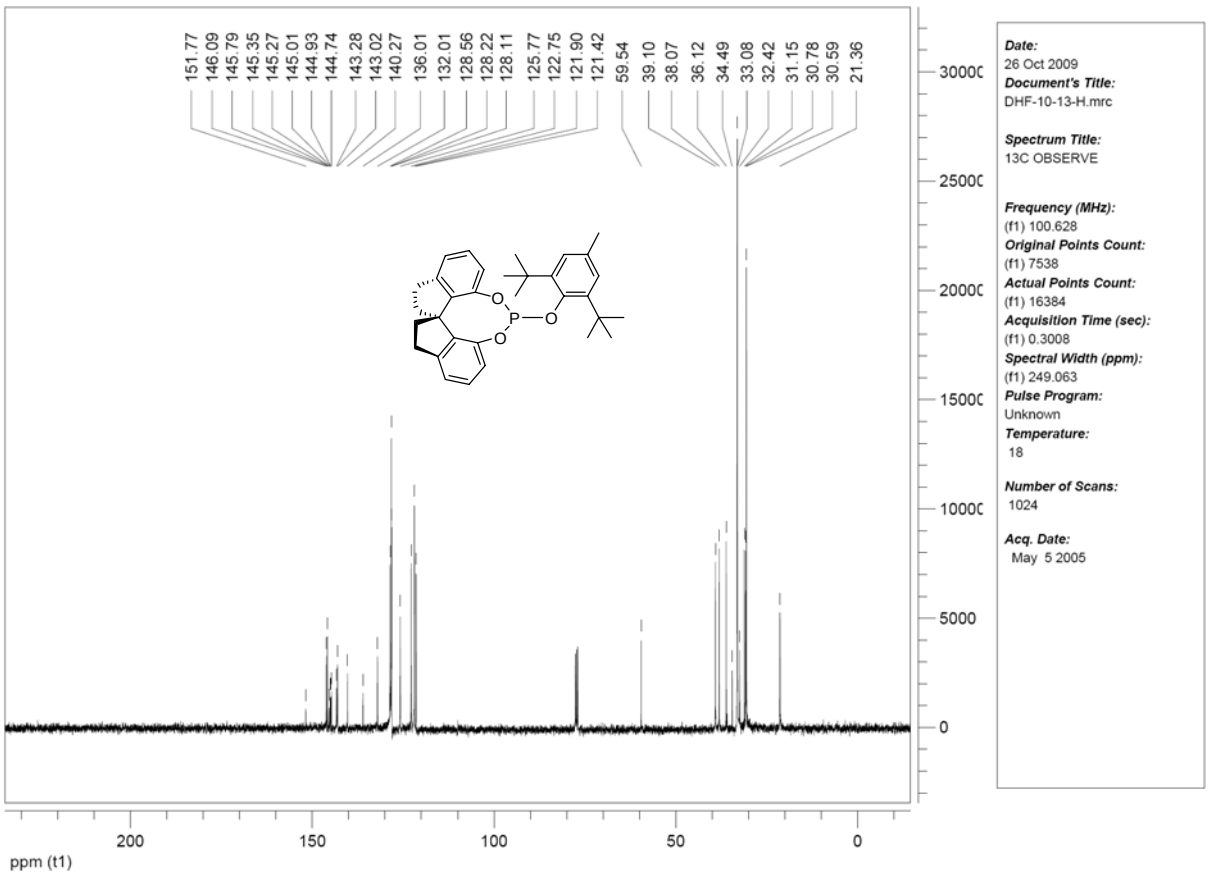
### (*S*)-3,5-Di-*tert*-butylphenyl-(1,1′-spirobiindane-7,7′-diyl)phosphite ((*S*)-3d)



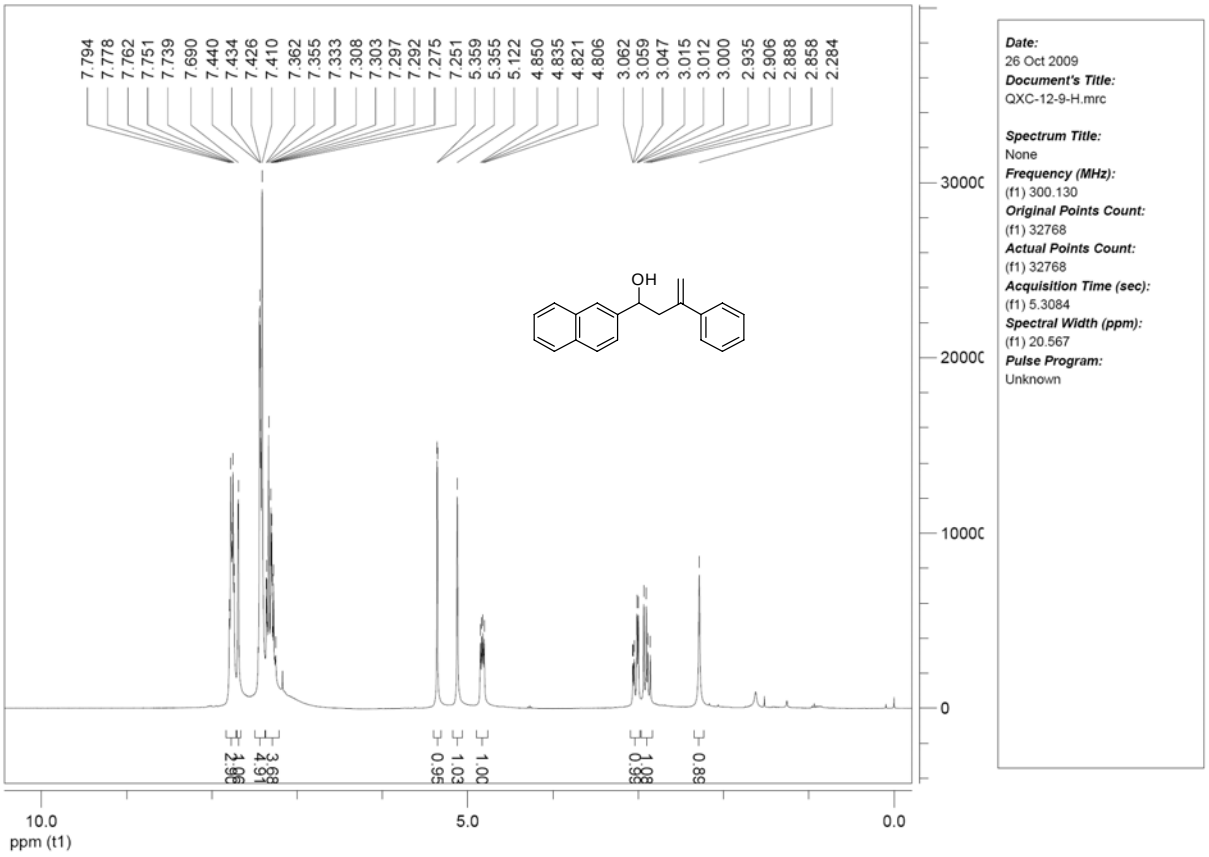



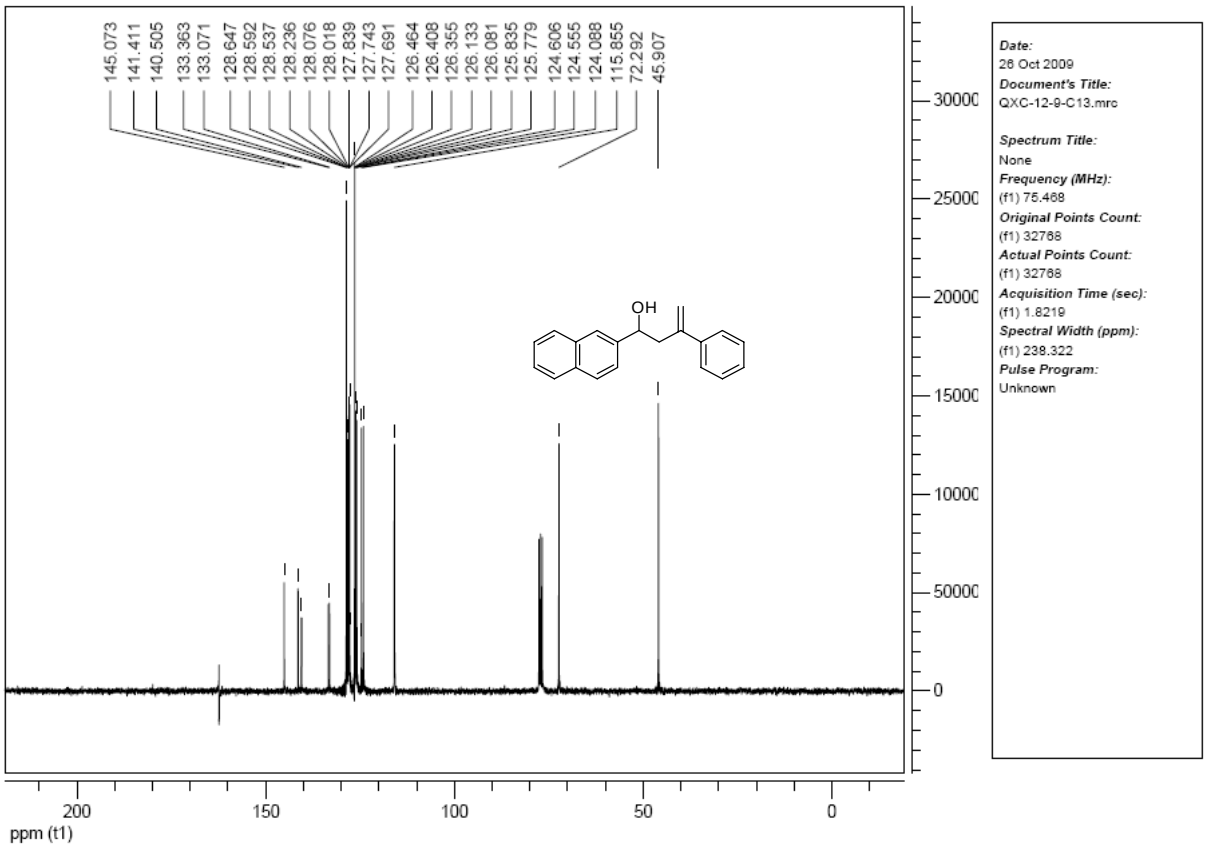
**(*S*)-2,6-Di-*tert*-butyl-4-methylphenyl-(1,1′-spirobiindane-7,7′-diyl)phosphite ((*S*)-3e)**



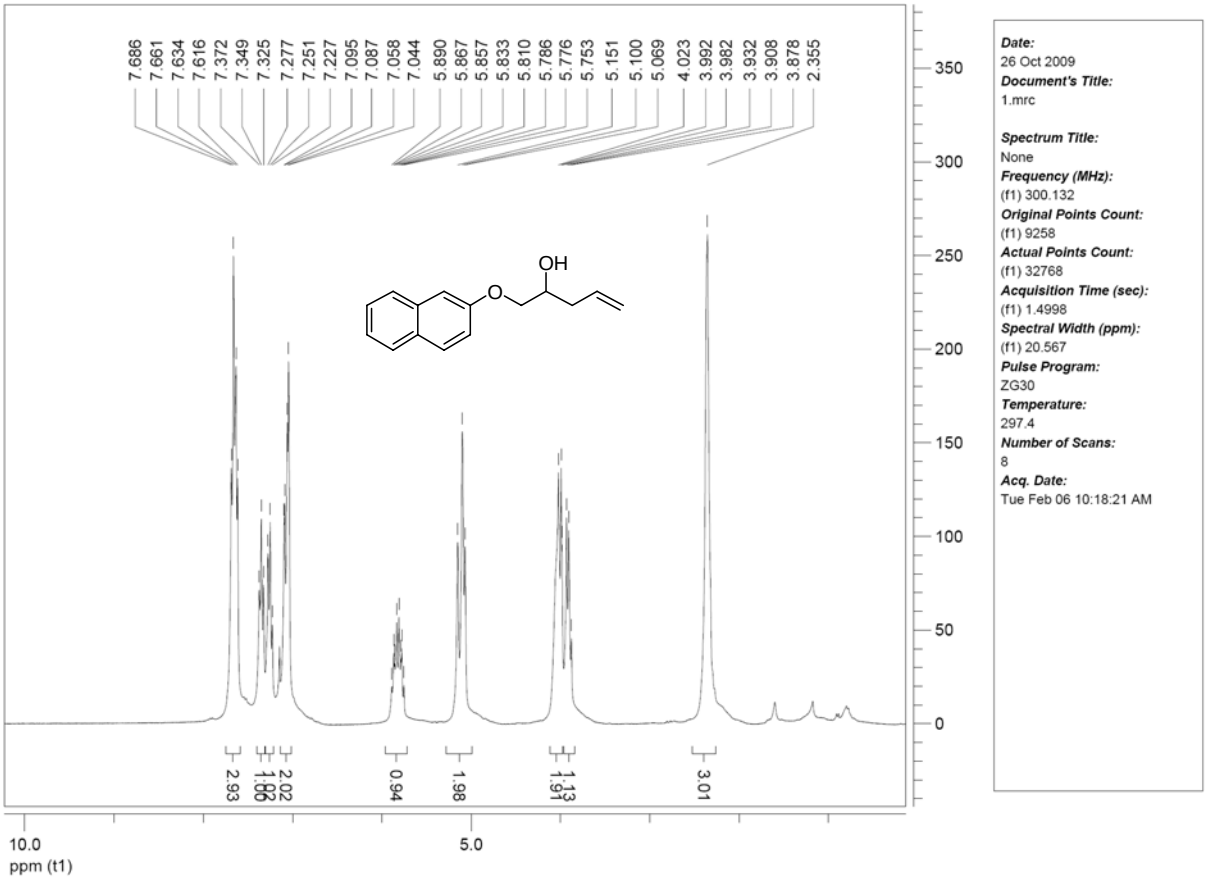



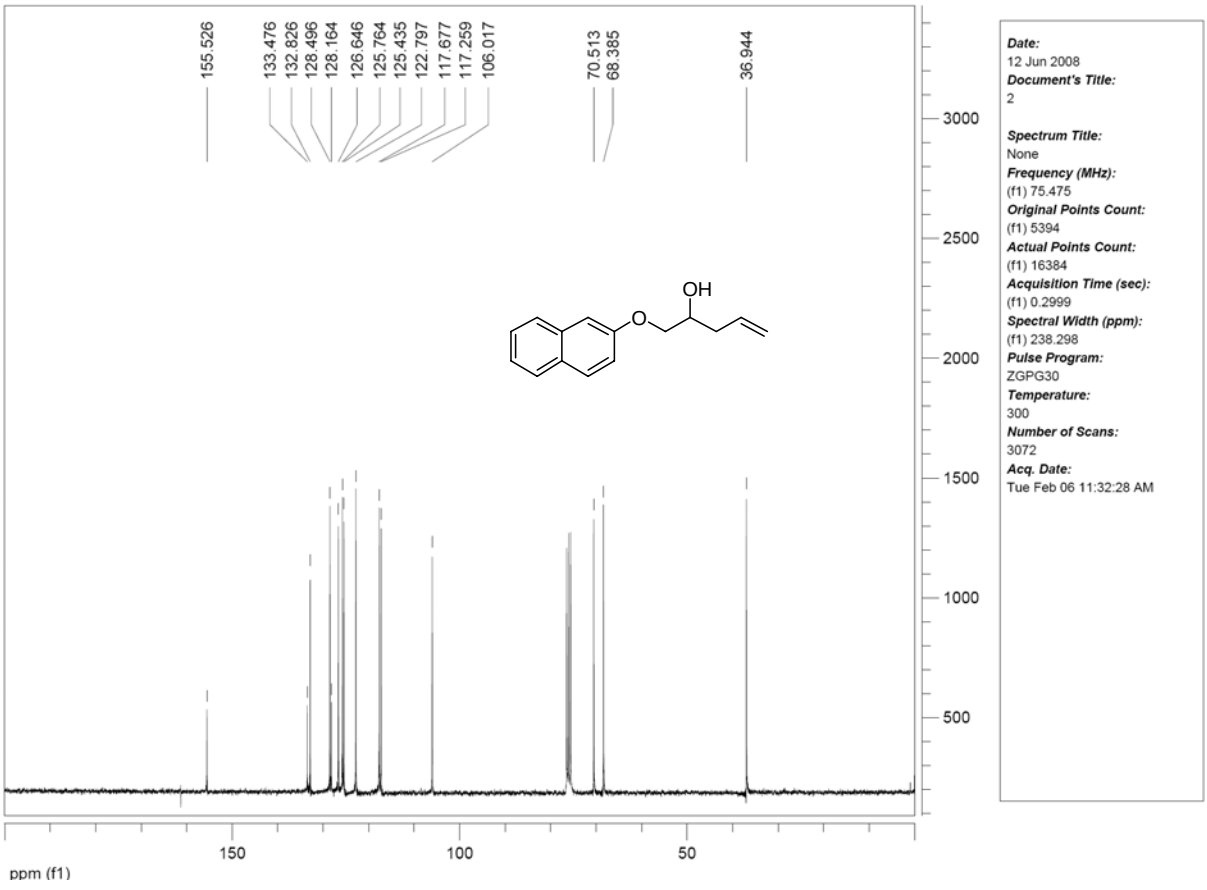
**1-(Naphthalen-2-yl)-3-phenylbut-3-en-1-ol (7ab)**



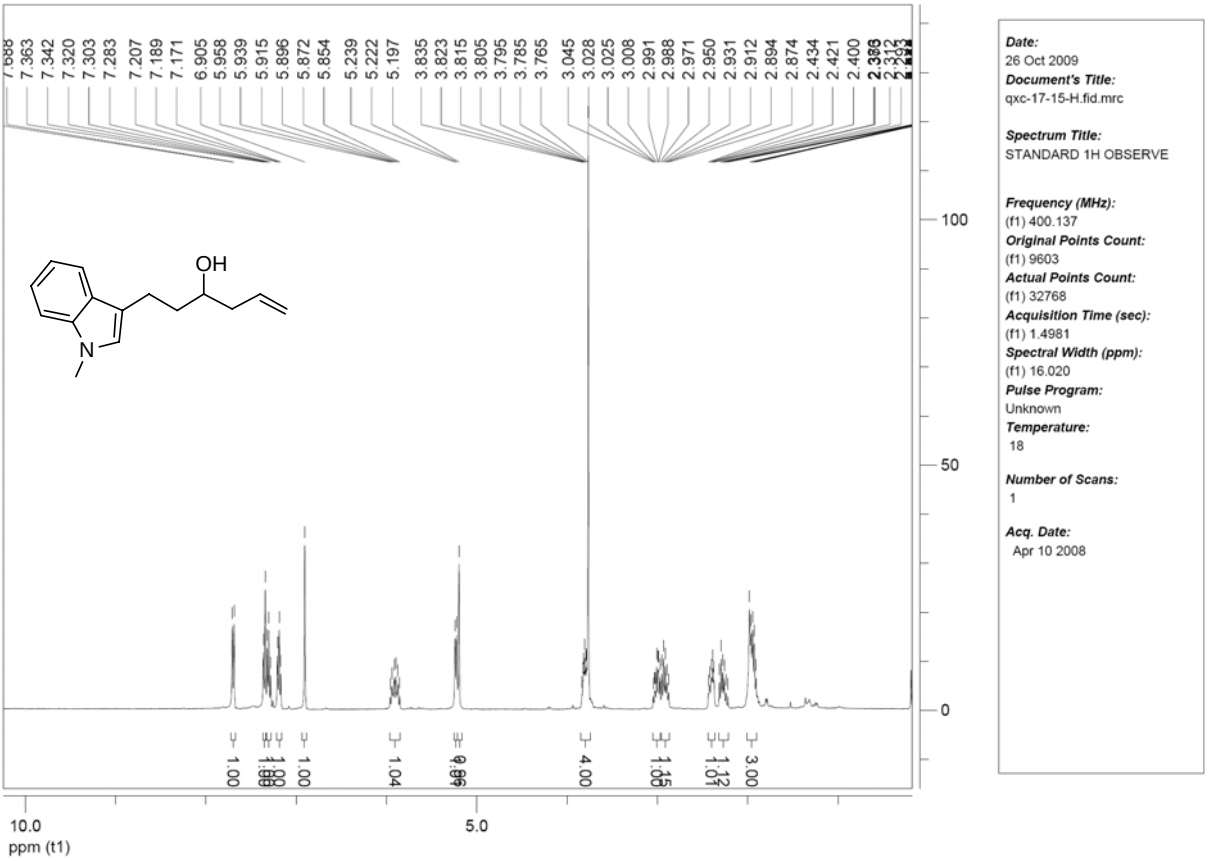



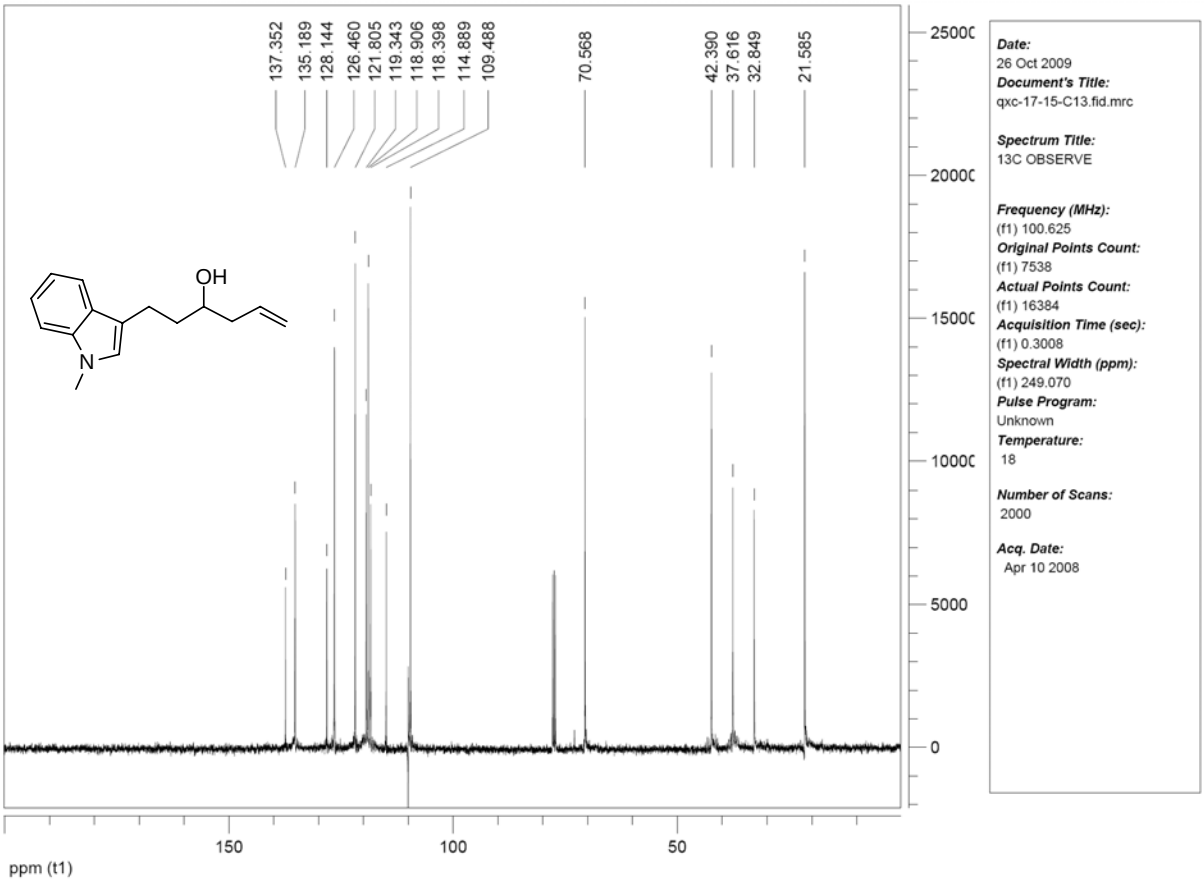
**1-(Naphthalen-2-yloxy)pent-4-en-2-ol (7ra)**



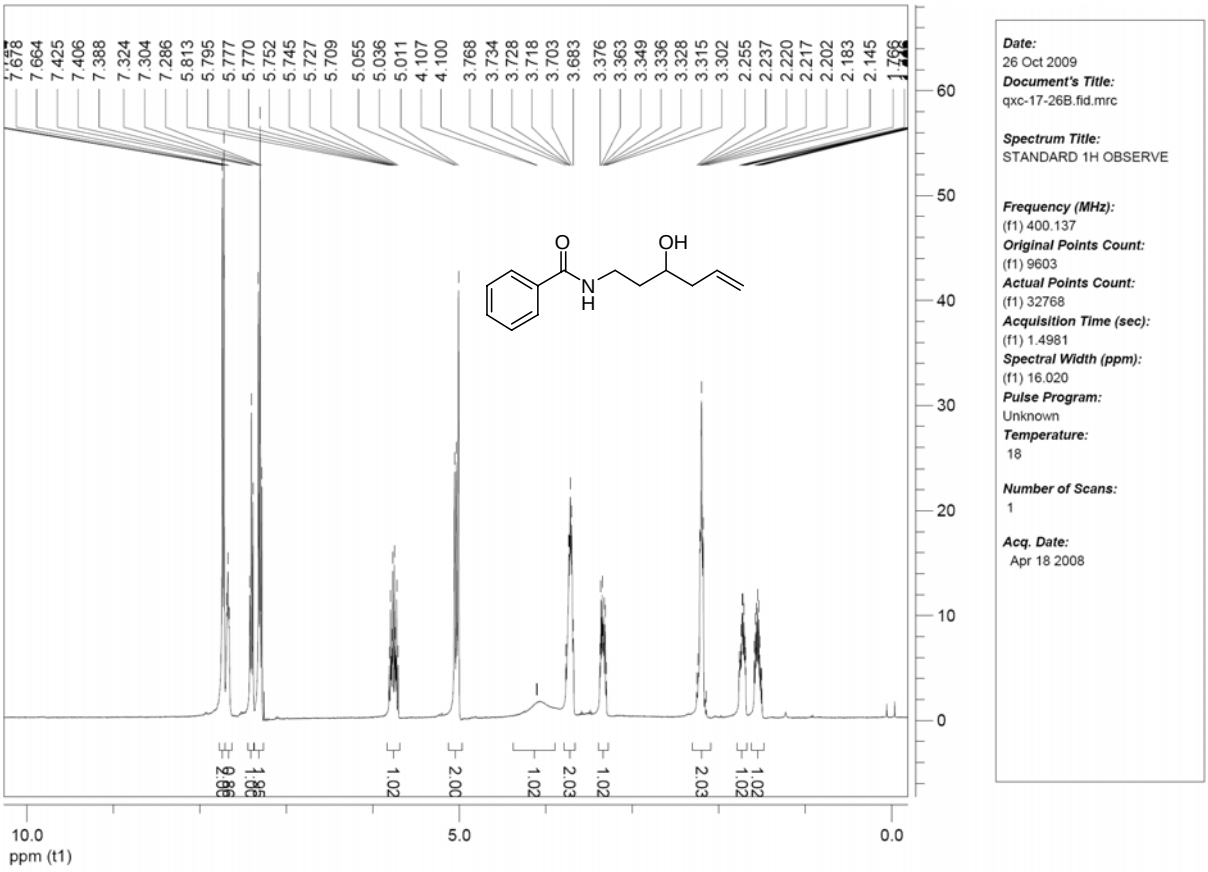



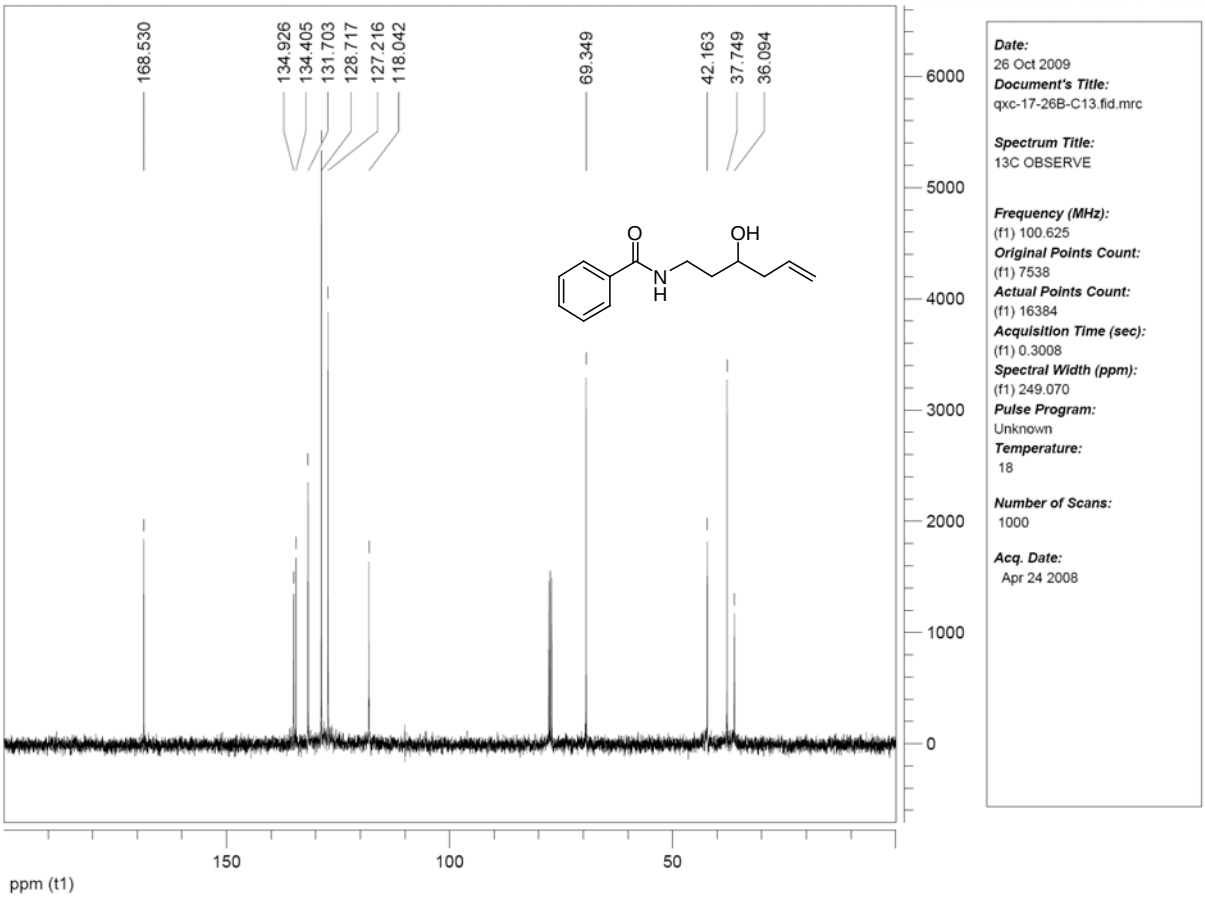
**1-(1-Methyl-1H-indol-3-yl)hex-5-en-3-ol (7wa)**



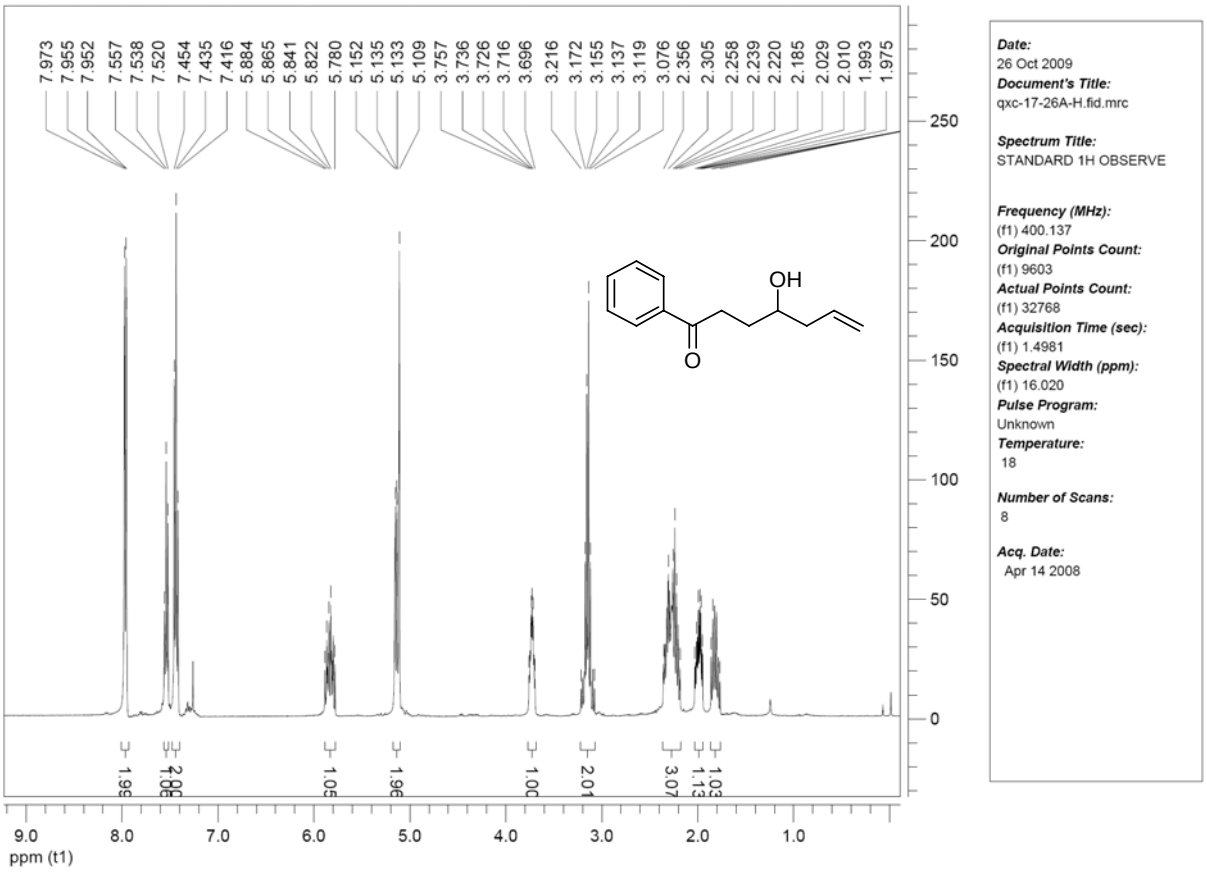



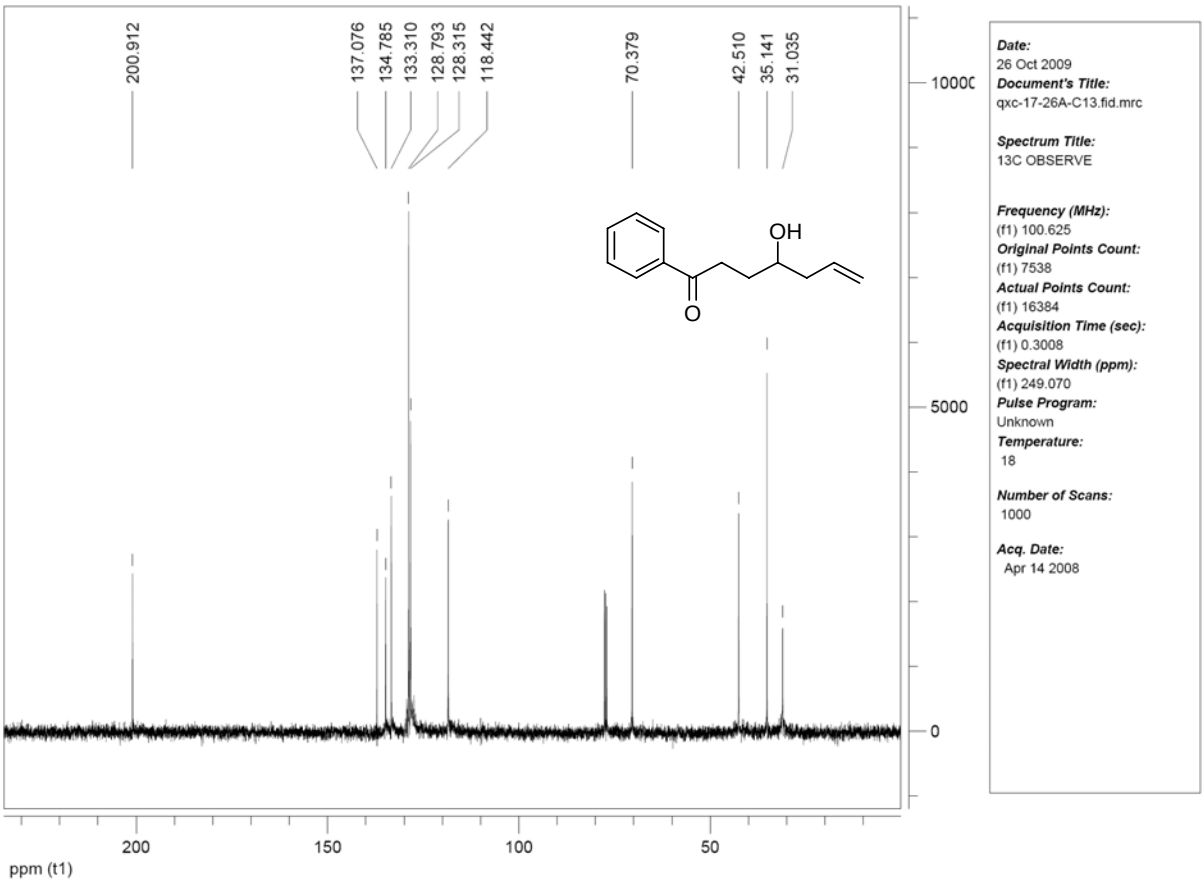
**_N_-(3-Hydroxyhex-5-enyl)benzamide (7xa)**



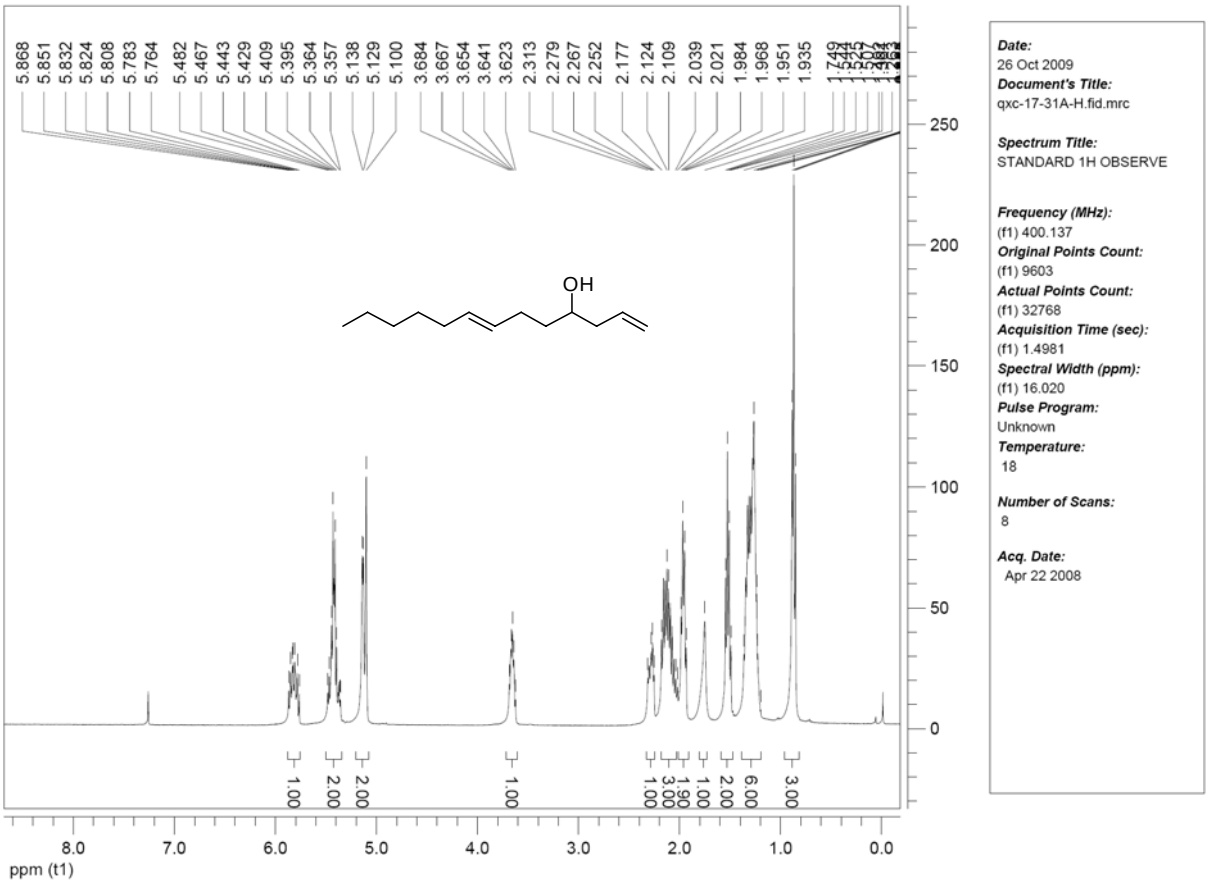



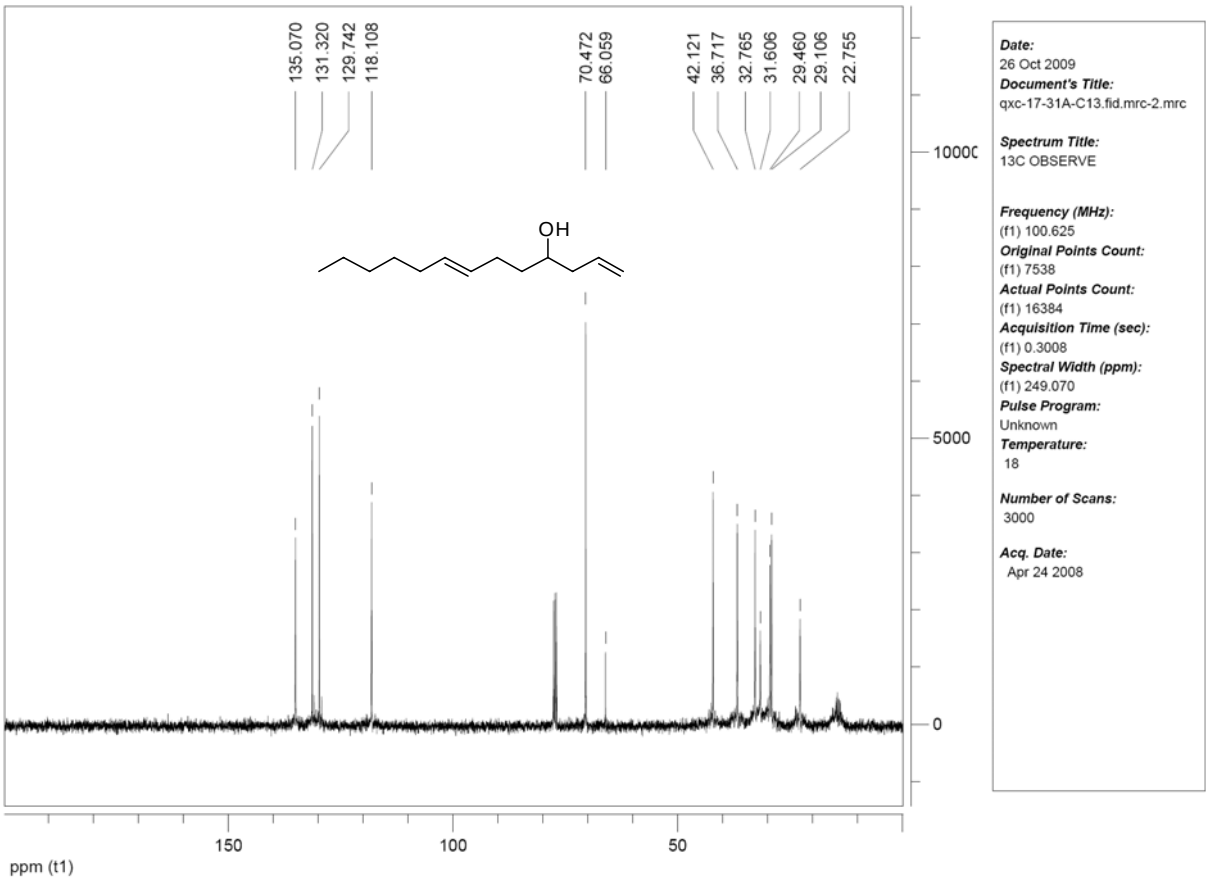
**4-Hydroxy-1-phenylhept-6-en-1-one (7ya)**



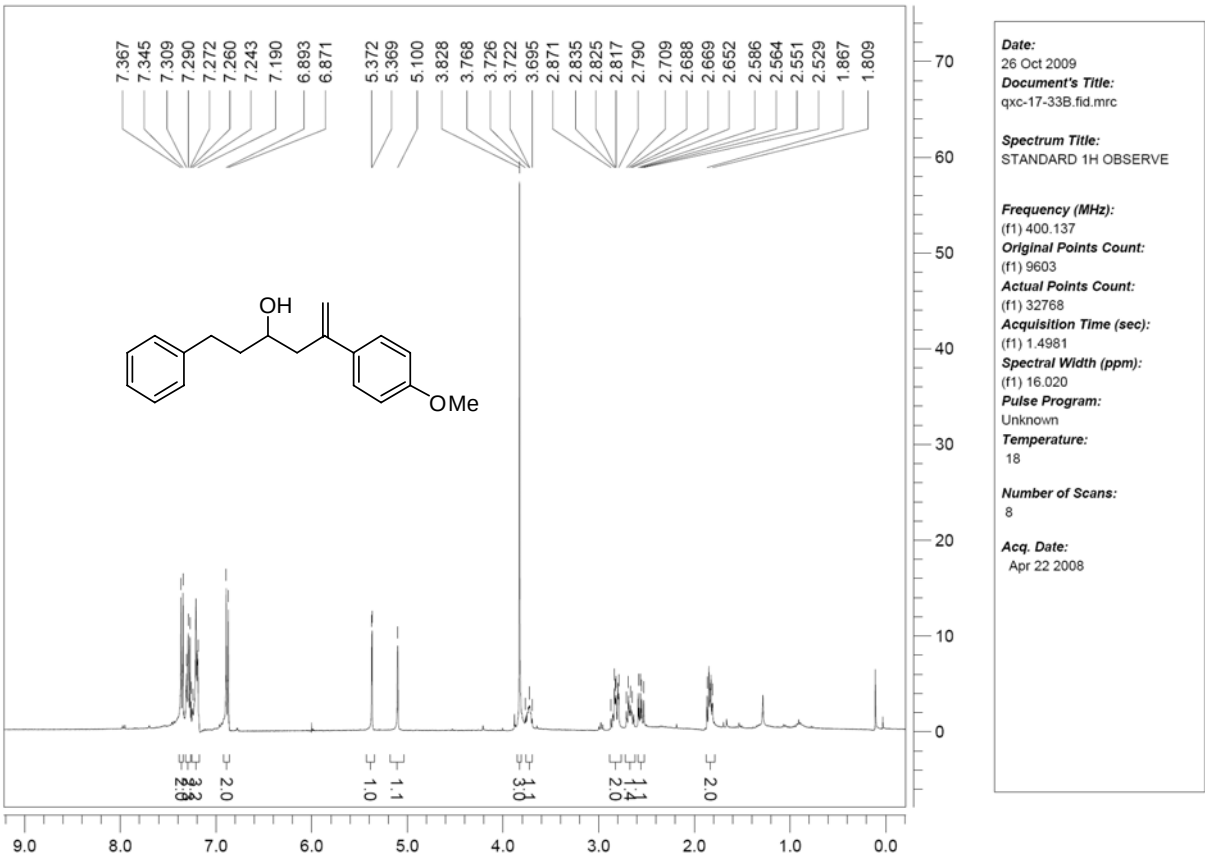



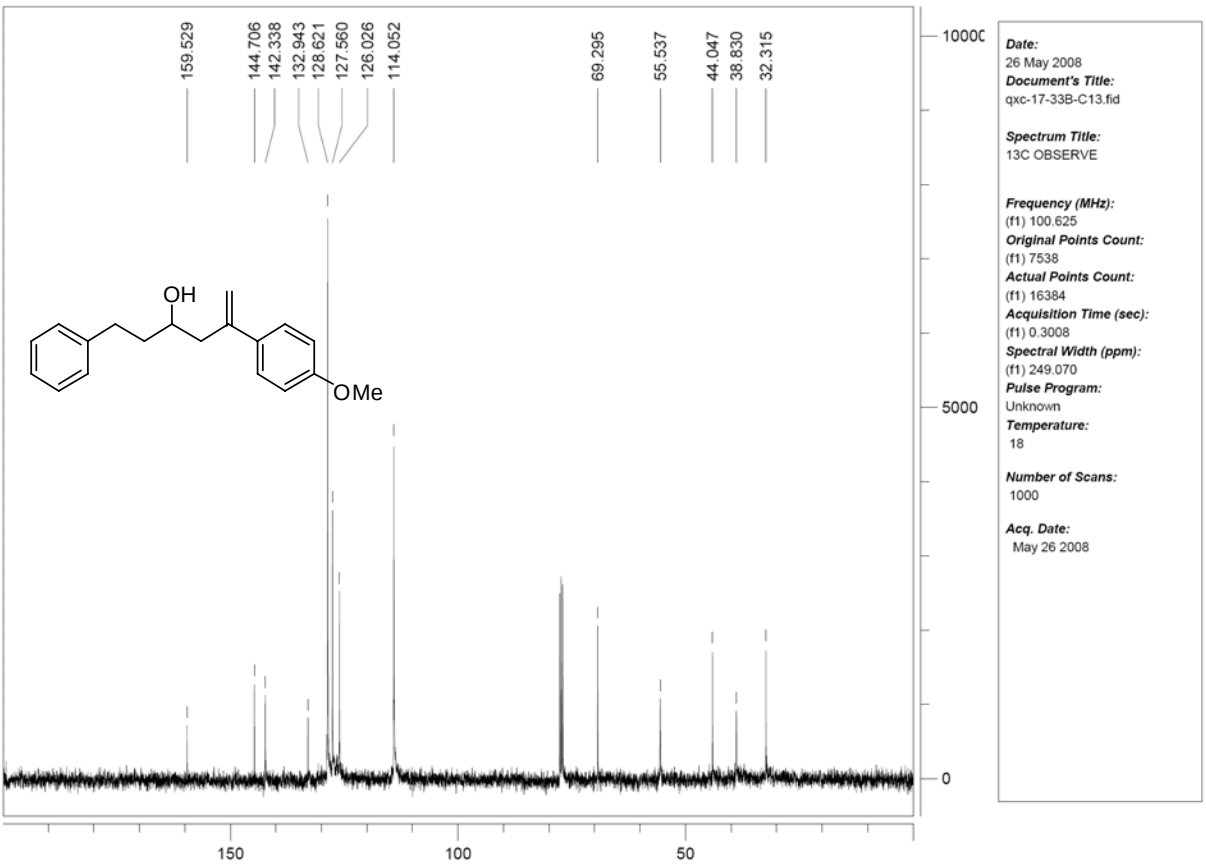
**(*E*)-Trideca-1,7-dien-4-ol (7za)**



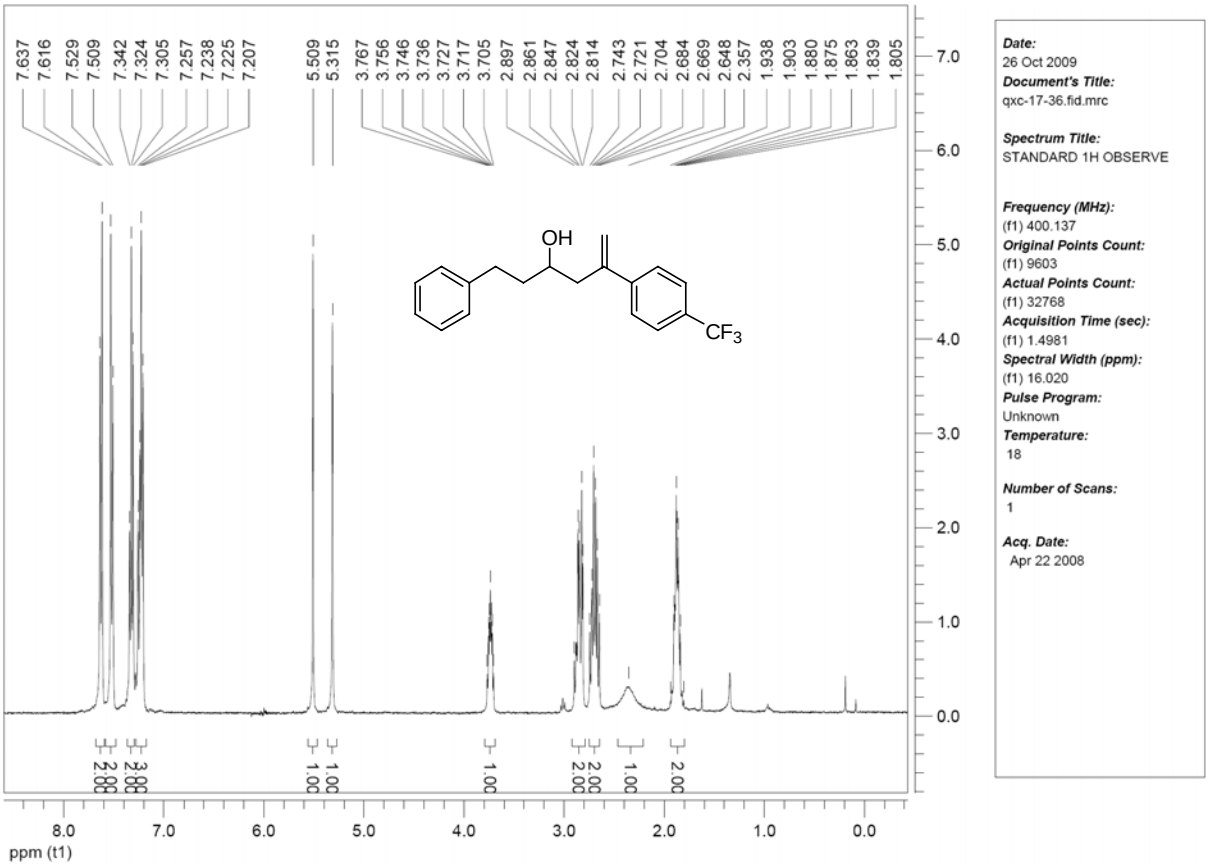



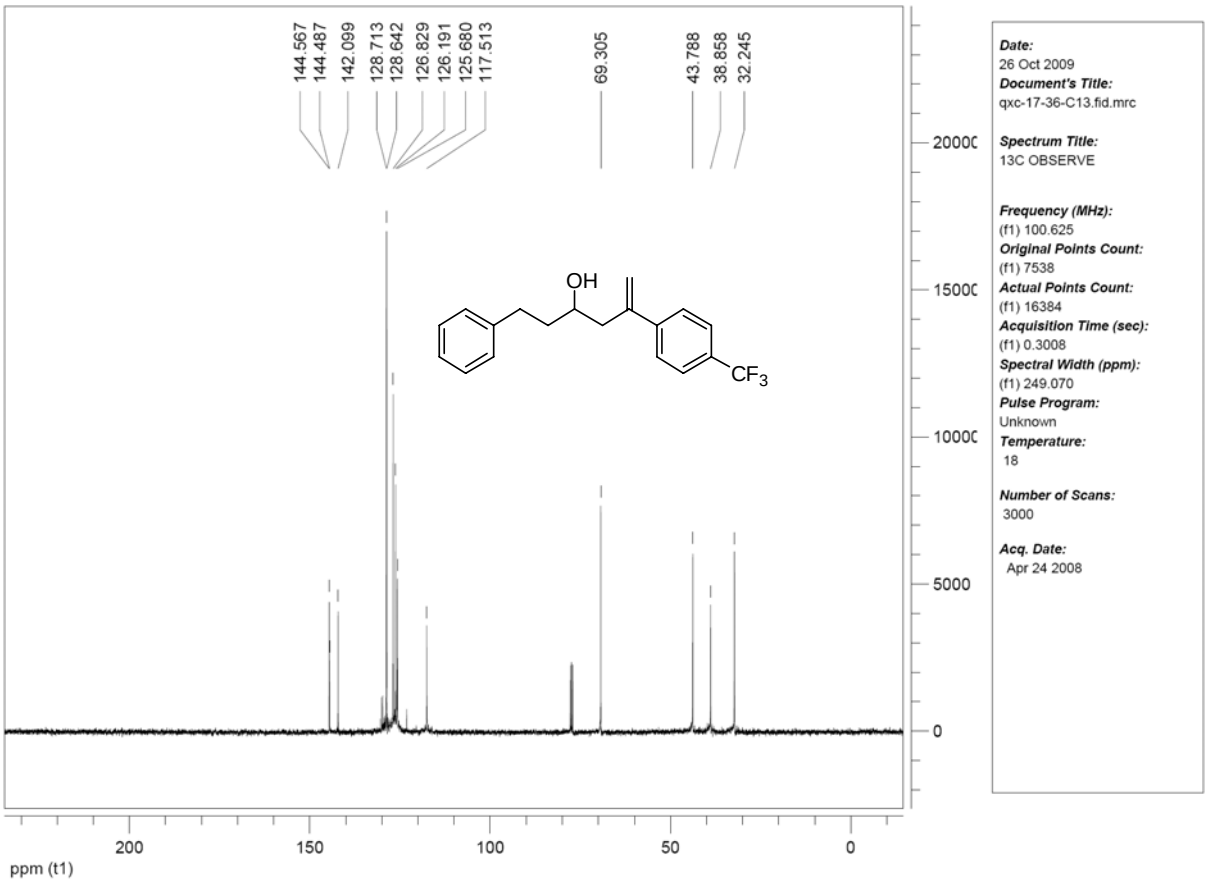
**5-(4-Methoxyphenyl)-1-phenylhex-5-en-3-ol (7qd)**



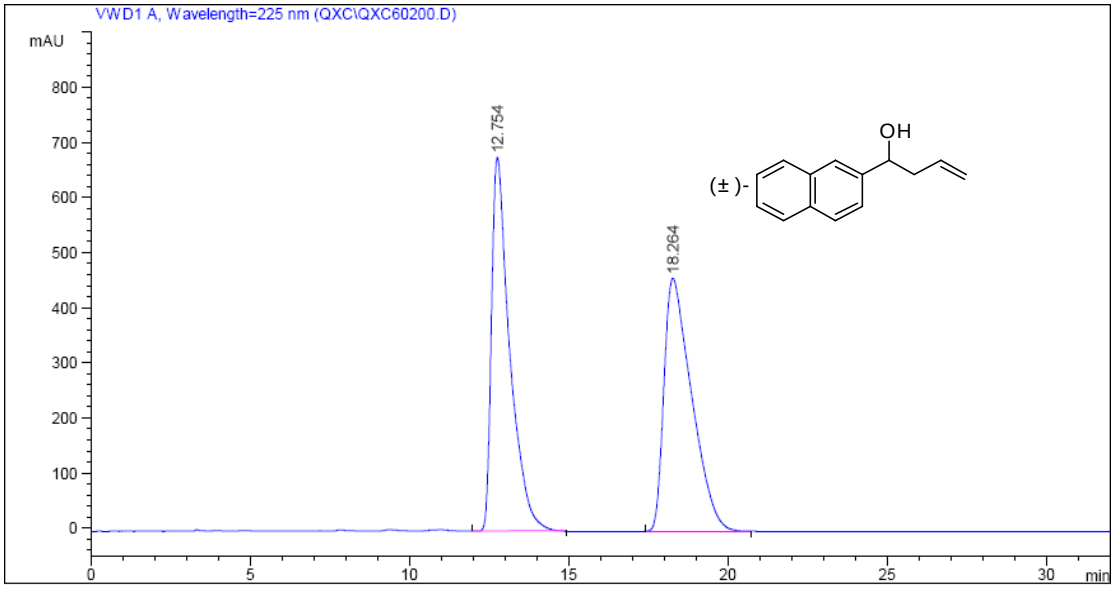
**1-Phenyl-5-(4-(trifluoromethyl)phenyl)hex-5-en-3-ol (7qe)**

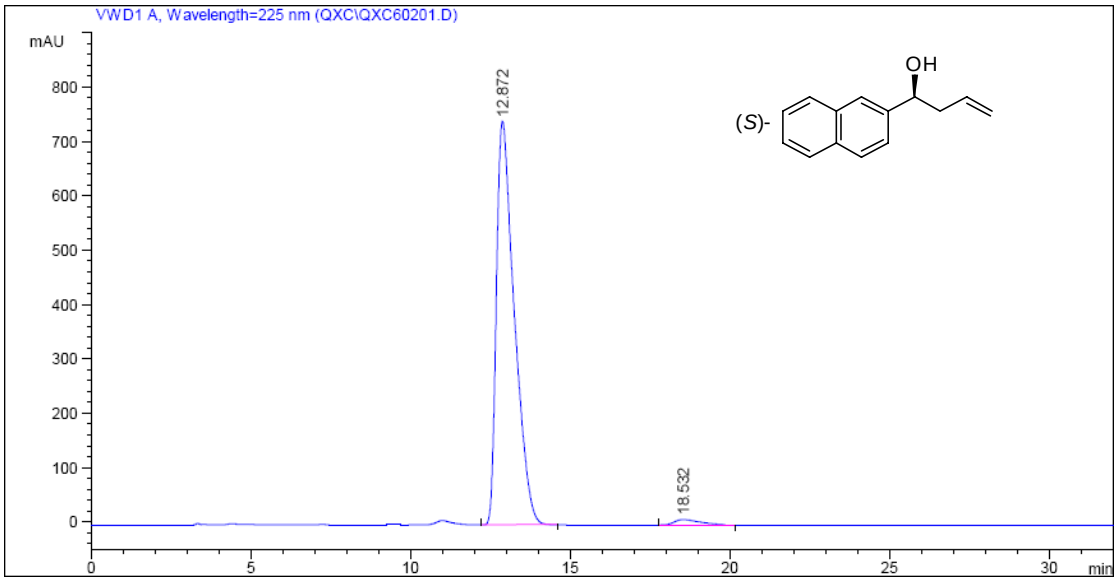


## 5 HPLC and SFC Charts for Homoallylic Alcohols

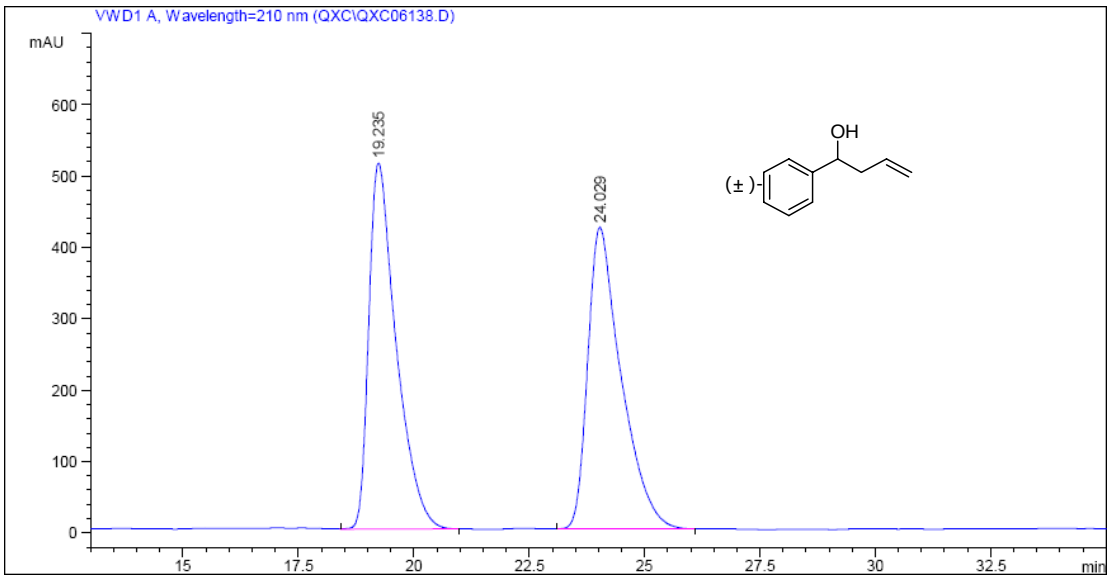
### 2-Naphtylbut-3-en-1-ol (7aa)

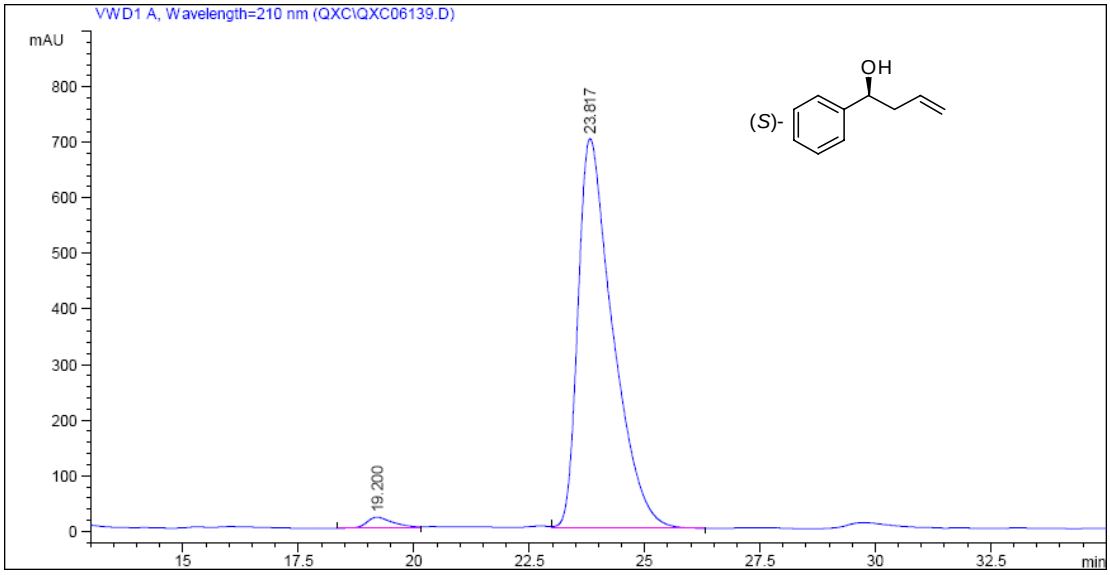



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.872 | VB | 0.5669 | 2.88274e4 | 741.85315 | 97.9943 |
| 2 | 18.532 | BB | 0.8242 | 590.03552 | 10.25416 | 2.0057 |

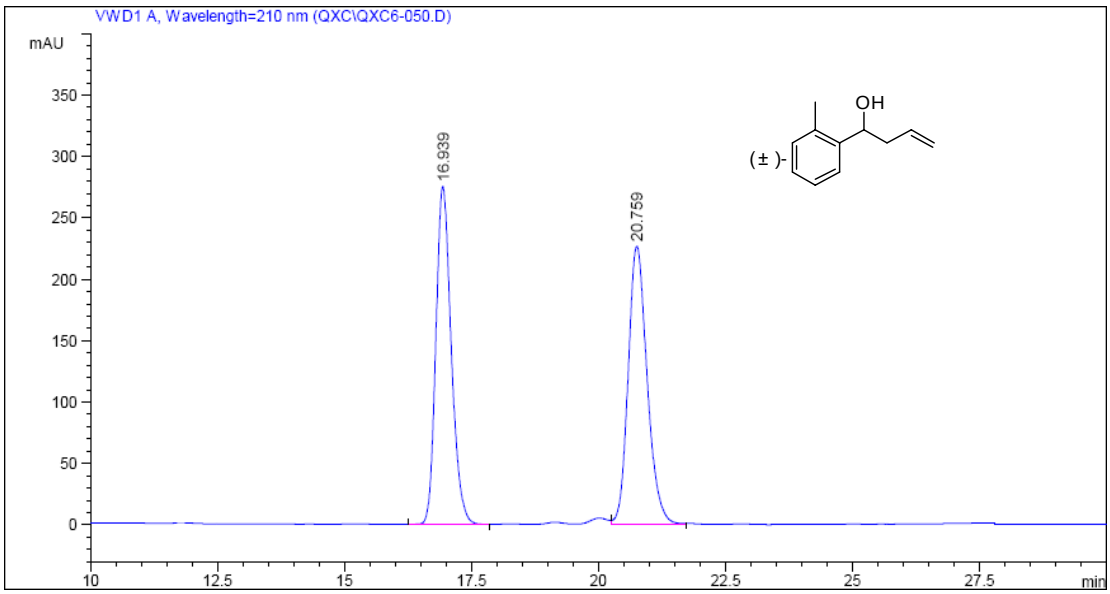
**1-Phenylbut-3-en-1-ol (7ba)**

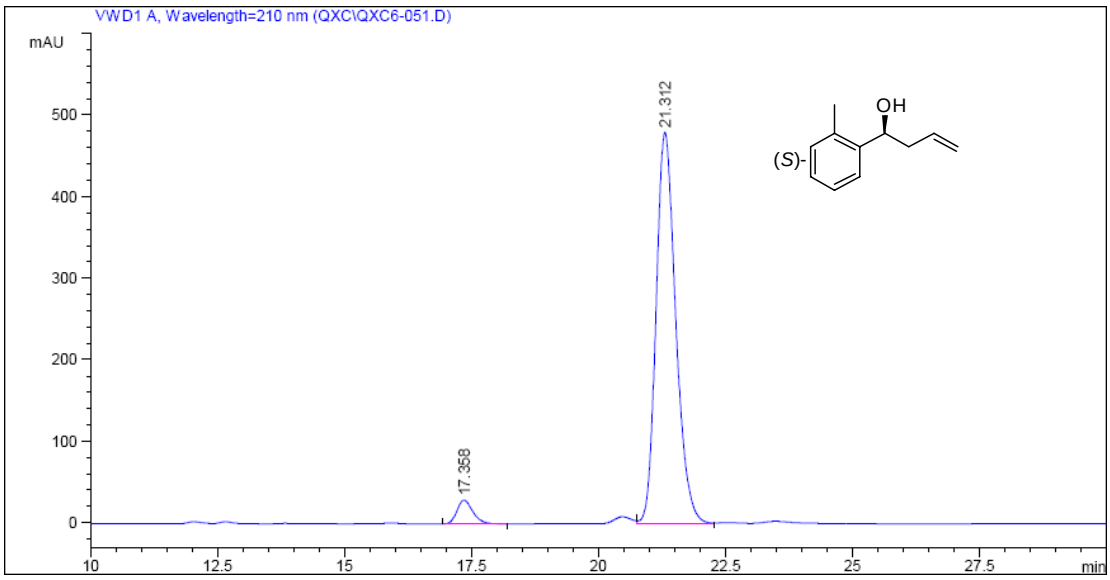



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.200 | VV | 0.6336 | 913.84613 | 20.73353 | 2.4182 |
| 2 | 23.817 | VV | 0.7641 | 3.68758e4 | 702.25085 | 97.5818 |

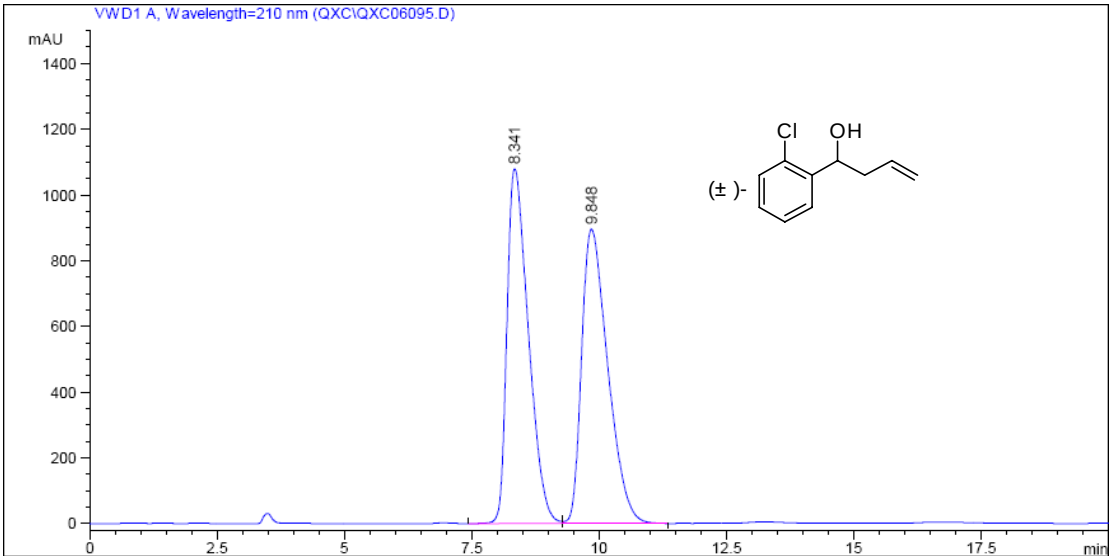
**1-(2-Methylphenyl)but-3-en-1-ol (7ca)**

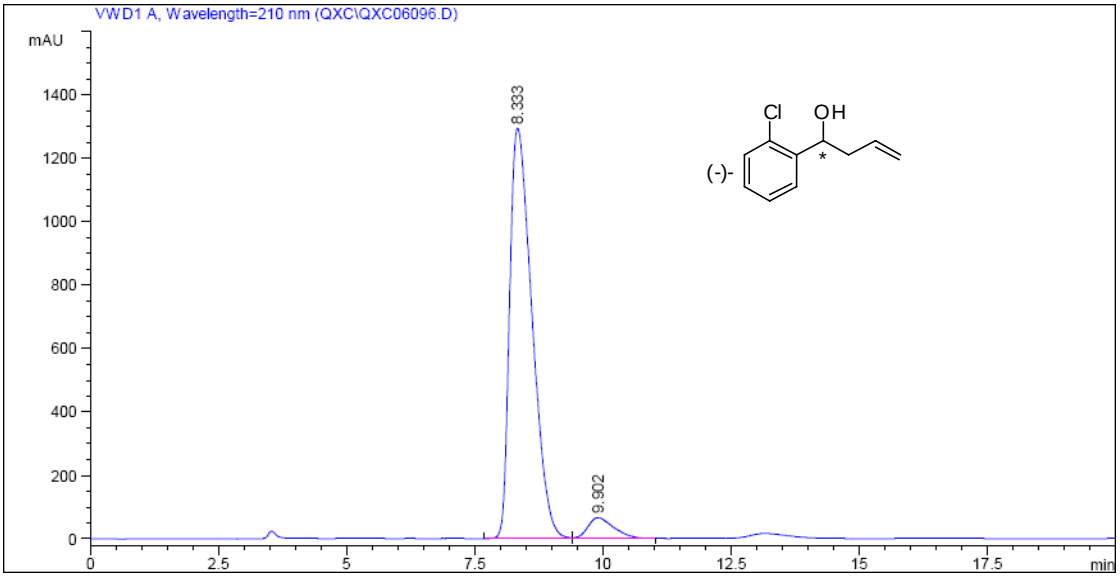



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.358 | PP | 0.3338 | 638.10925 | 29.18002 | 4.7055 |
| 2 | 21.312 | VV | 0.4133 | 1.29229e4 | 479.76920 | 95.2945 |

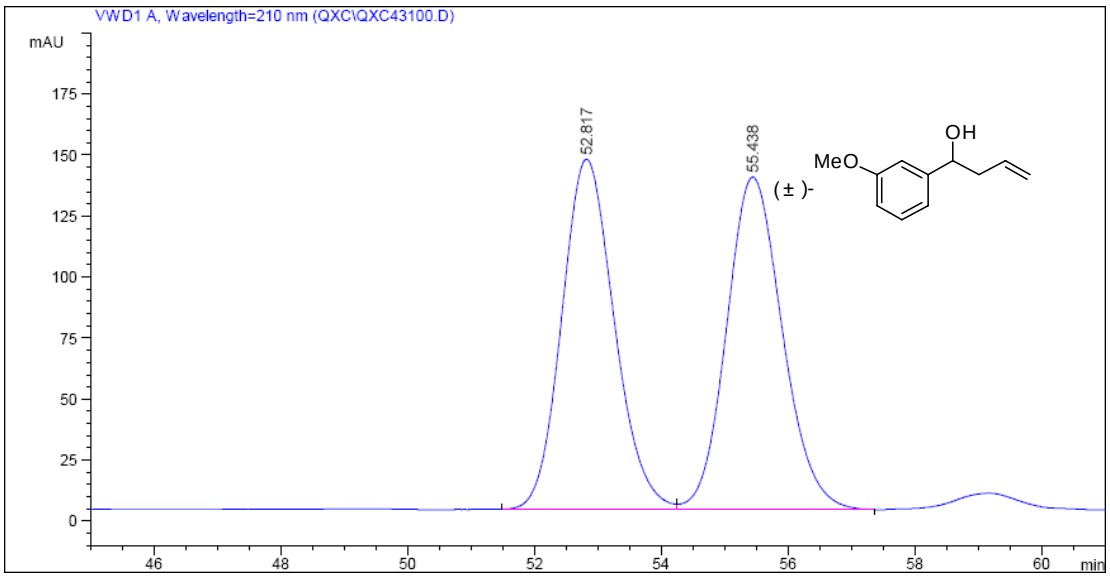
**1-(2-Chlorophenyl)but-3-en-1-ol (7da)**

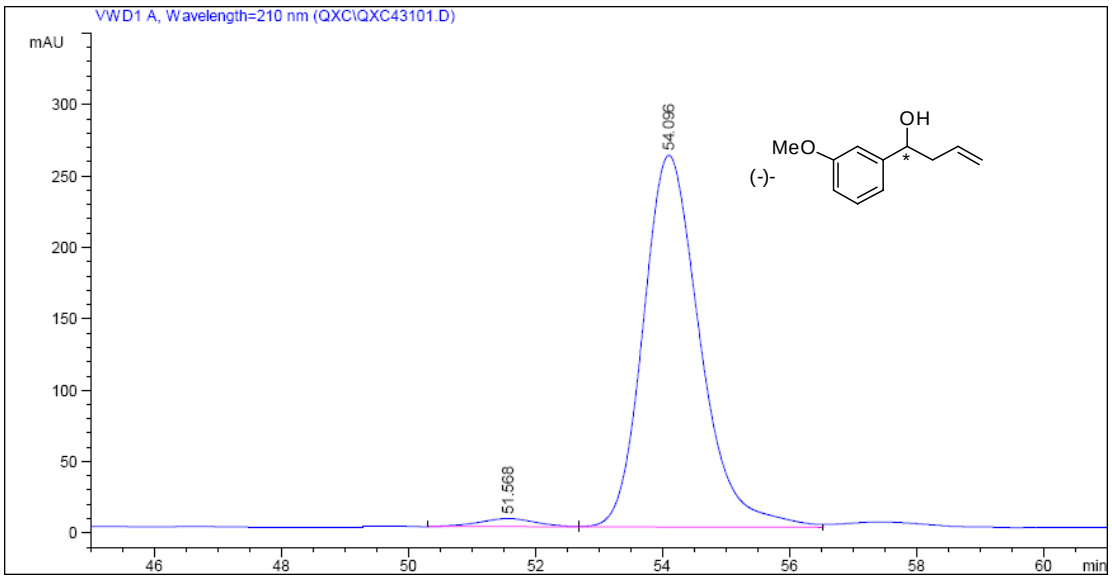



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.333 | BV | 0.4672 | 3.90378e4 | 1293.30054 | 94.4093 |
| 2 | 9.902 | VB | 0.5224 | 2311.74780 | 65.97372 | 5.5907 |

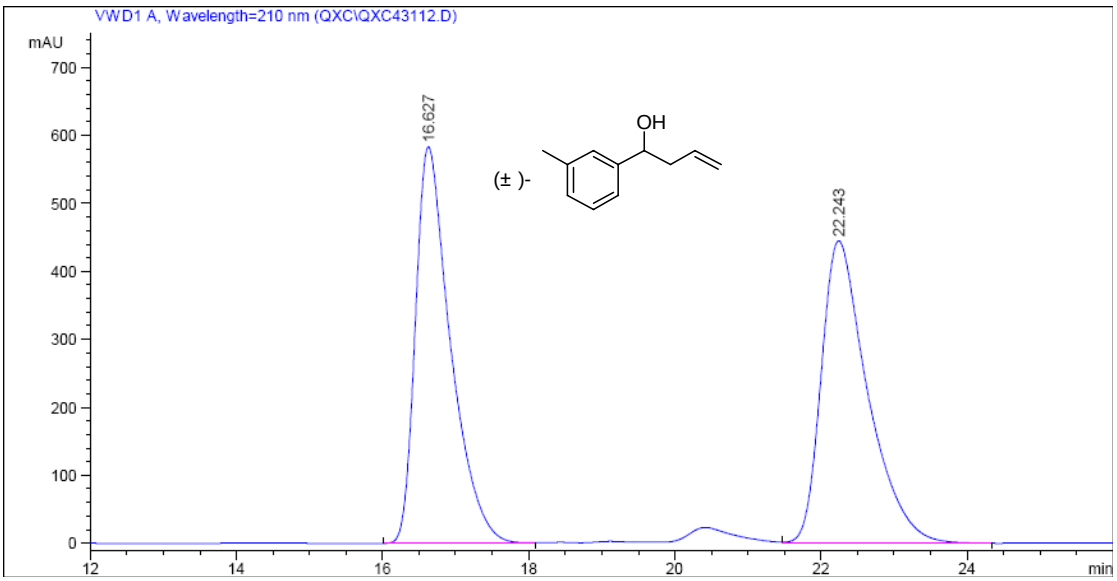
**(–)-1-(3-Methoxyphenyl)but-3-en-1-ol (7ea)**

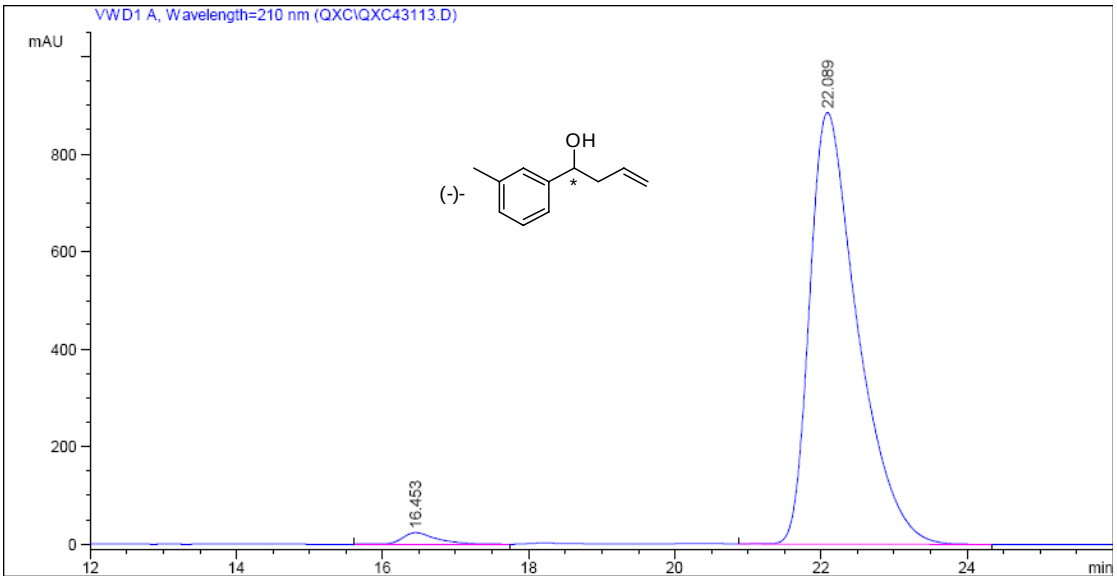



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 51.568 | PV | 0.8408 | 356.68362 | 5.79130 | 2.1648 |
| 2 | 54.096 | VB | 0.9536 | 1.61198e4 | 260.44543 | 97.8352 |

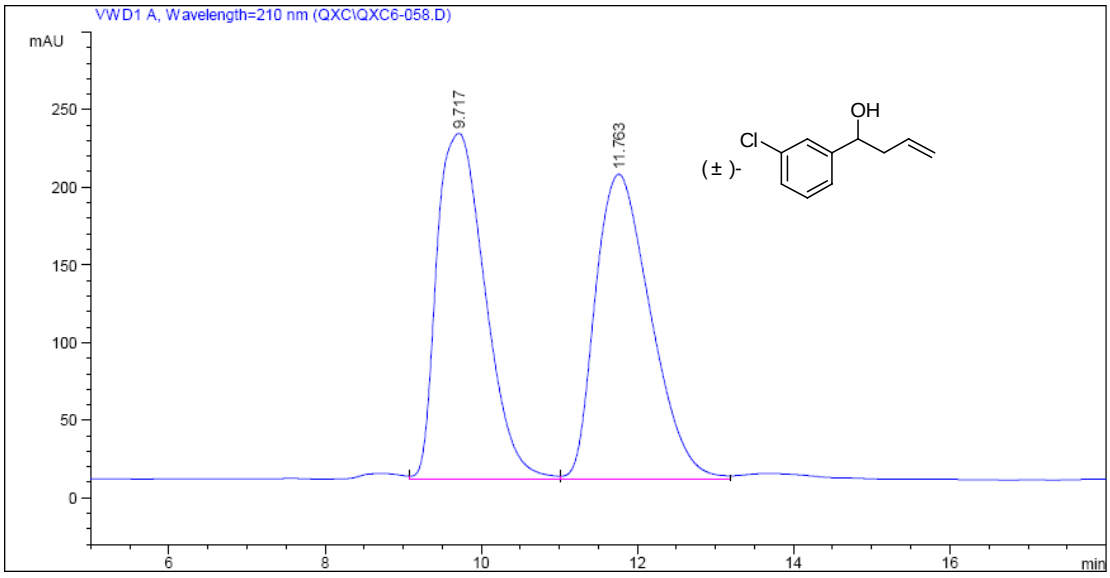
**1-(3-Methylphenyl)but-3-en-1-ol (7fa)**

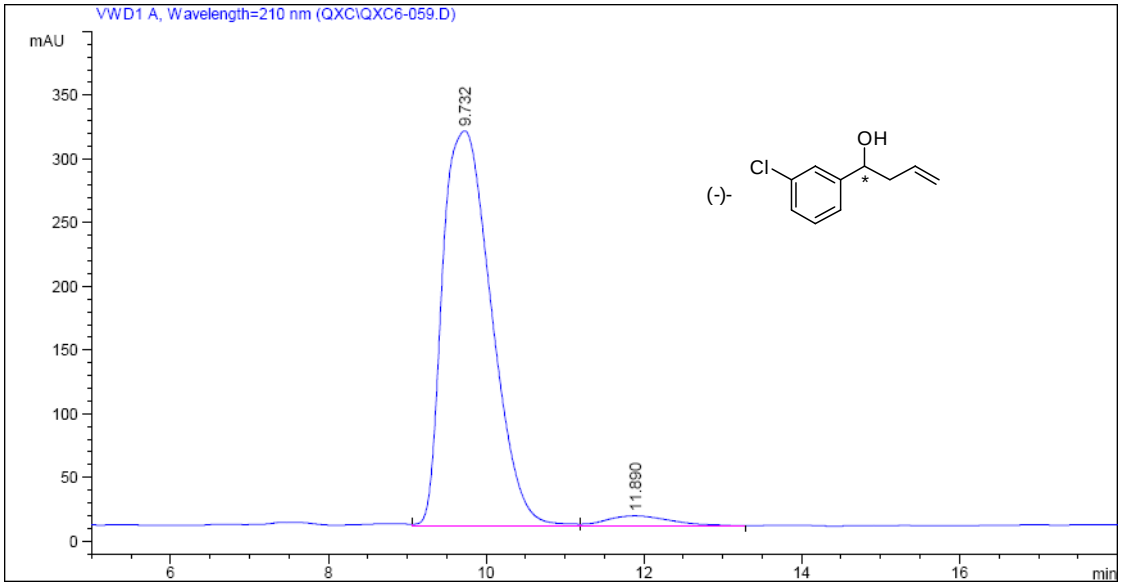



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.453 | BB | 0.4822 | 792.20239 | 24.02969 | 1.9157 |
| 2 | 22.089 | VP | 0.6824 | 4.05613e4 | 886.35663 | 98.0843 |

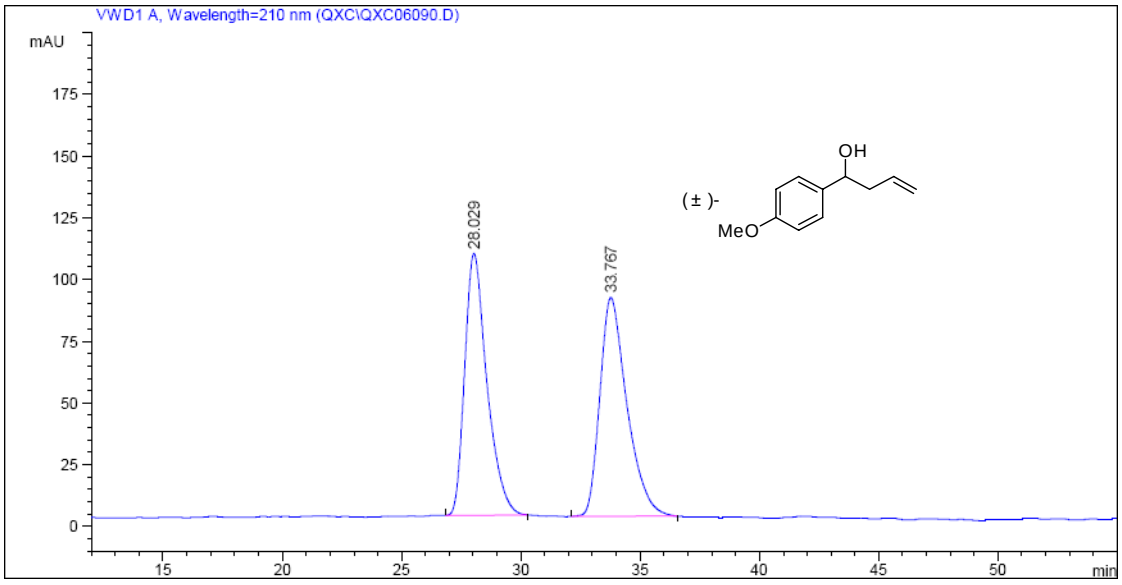
**1-(3-Chlorophenyl)but-3-en-1-ol (7ga)**

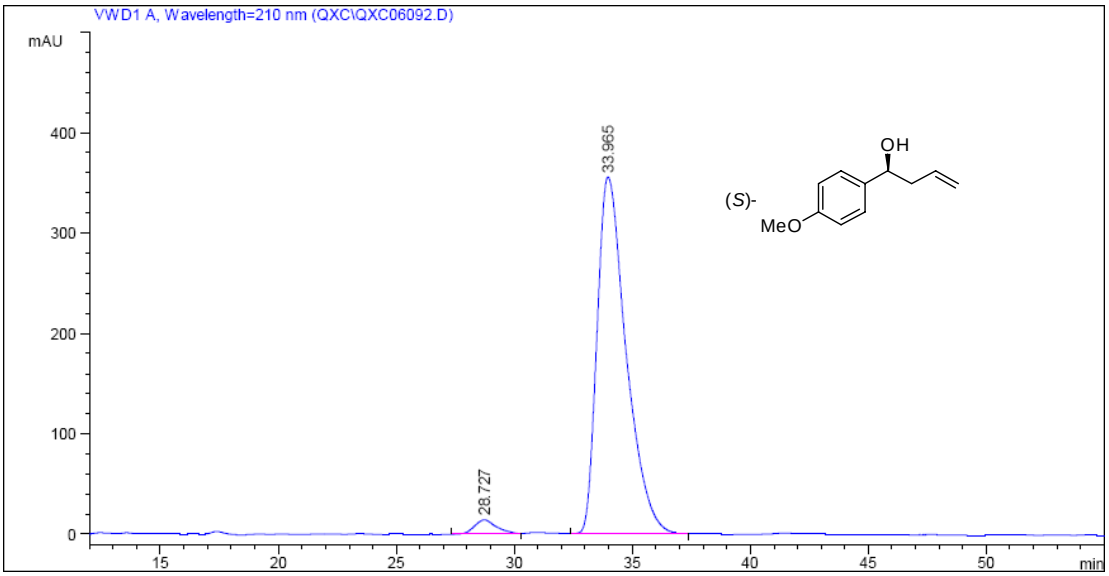



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.732 | VV | 0.6749 | 1.33100e4 | 310.47159 | 96.5036 |
| 2 | 11.890 | VV | 0.8637 | 482.23096 | 8.18245 | 3.4964 |

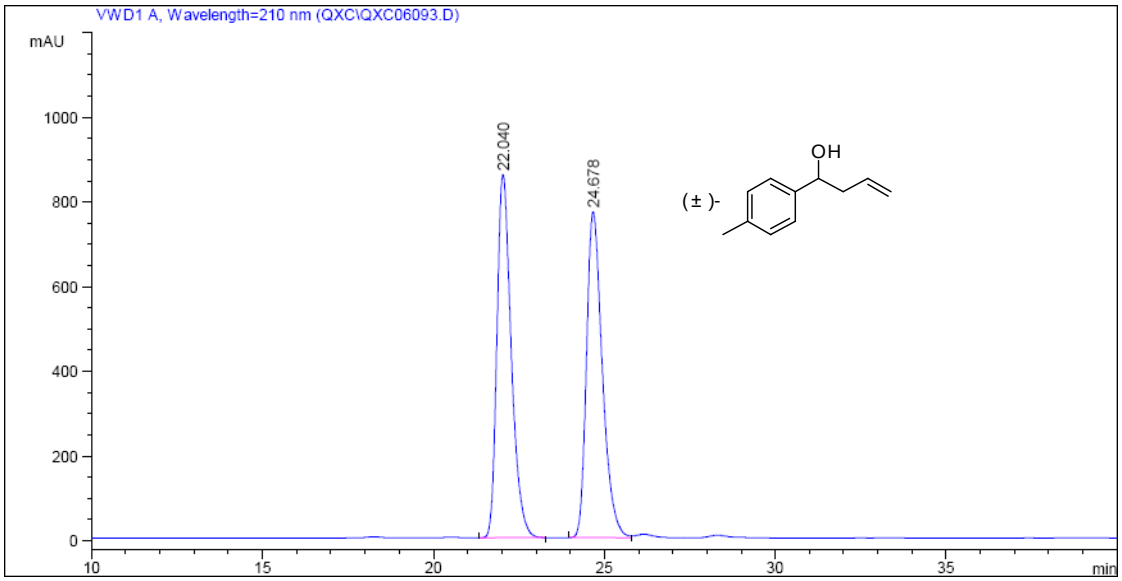
**1-(4-Methoxyphenyl)but-3-en-1-ol (7ha)**

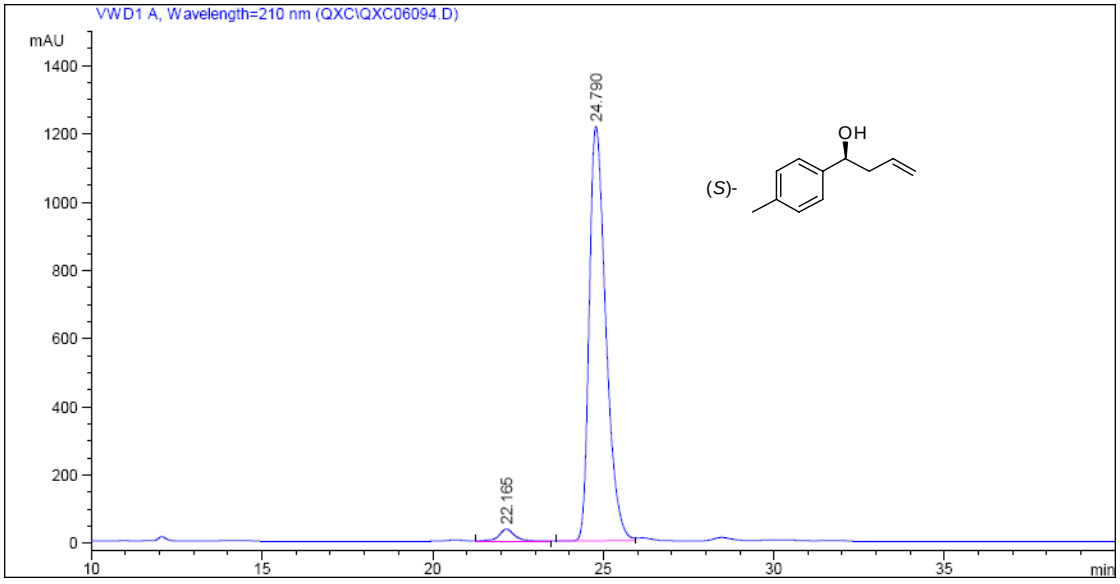



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 28.727 | BV | 0.9831 | 998.80981 | 14.62654 | 3.1695 |
| 2 | 33.965 | VP | 1.2826 | 3.05145e4 | 355.94009 | 96.8305 |

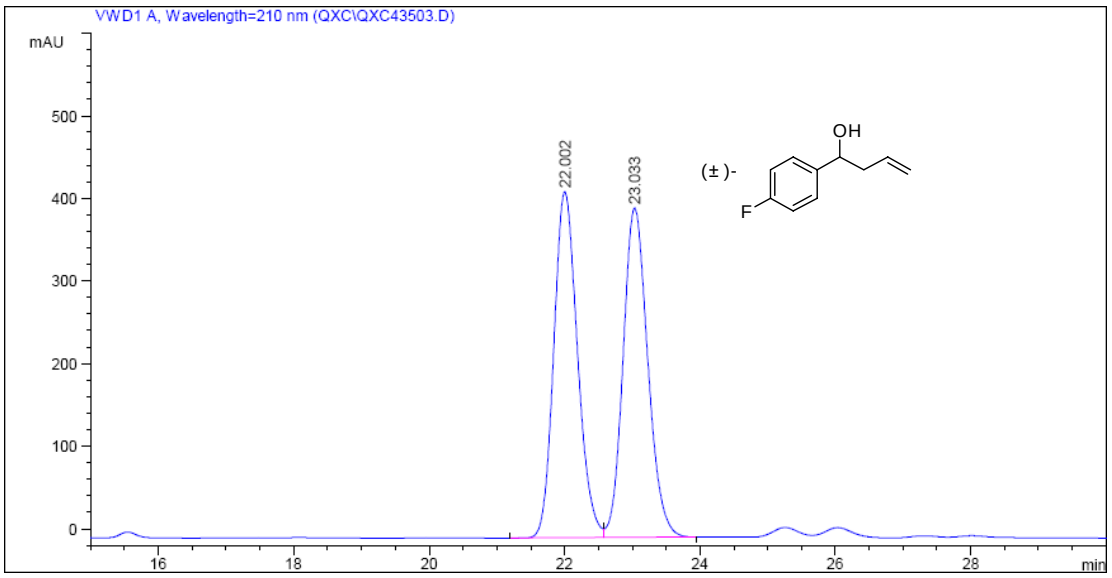
**1-(4-Methylphenyl)but-3-en-1-ol (7ia)**

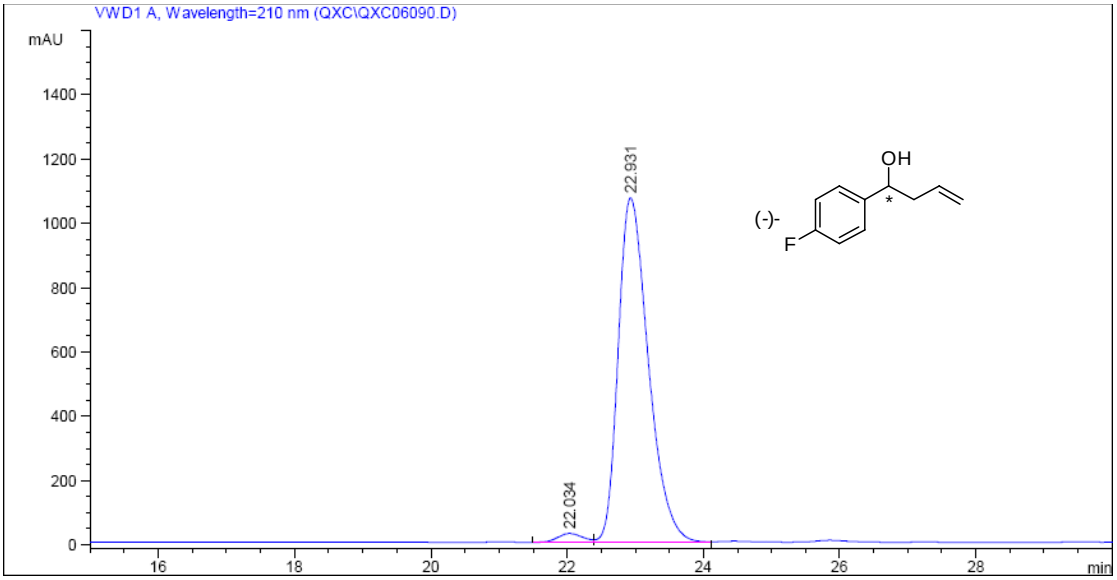



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.165 | VB | 0.4668 | 1125.70715 | 35.28979 | 2.6679 |
| 2 | 24.790 | BV | 0.5192 | 4.10683e4 | 1216.06665 | 97.3321 |

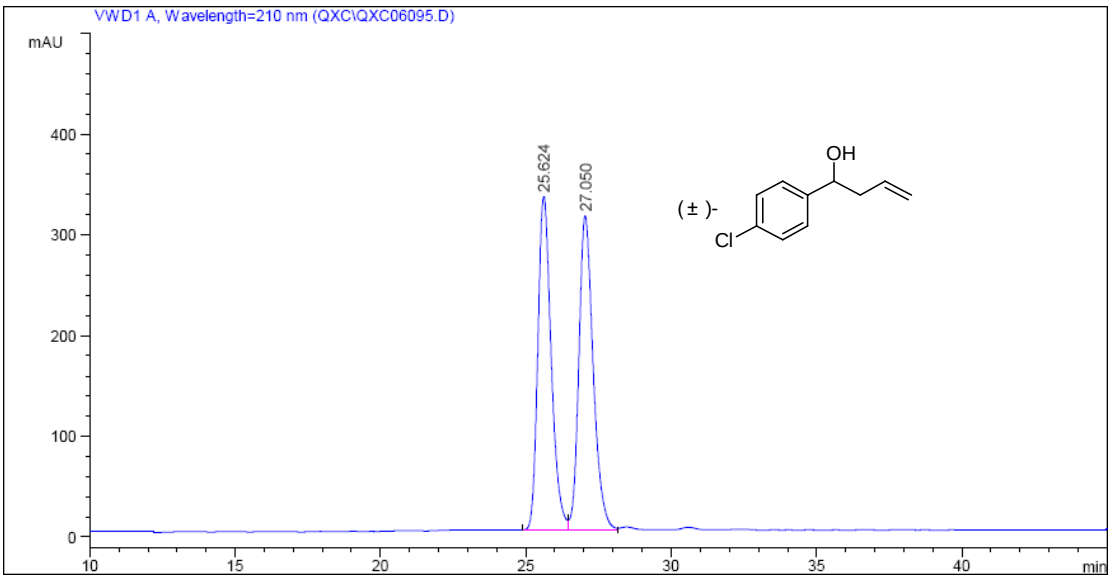
**1-(4-Fluorophenyl)but-3-en-1-ol (7ja)**

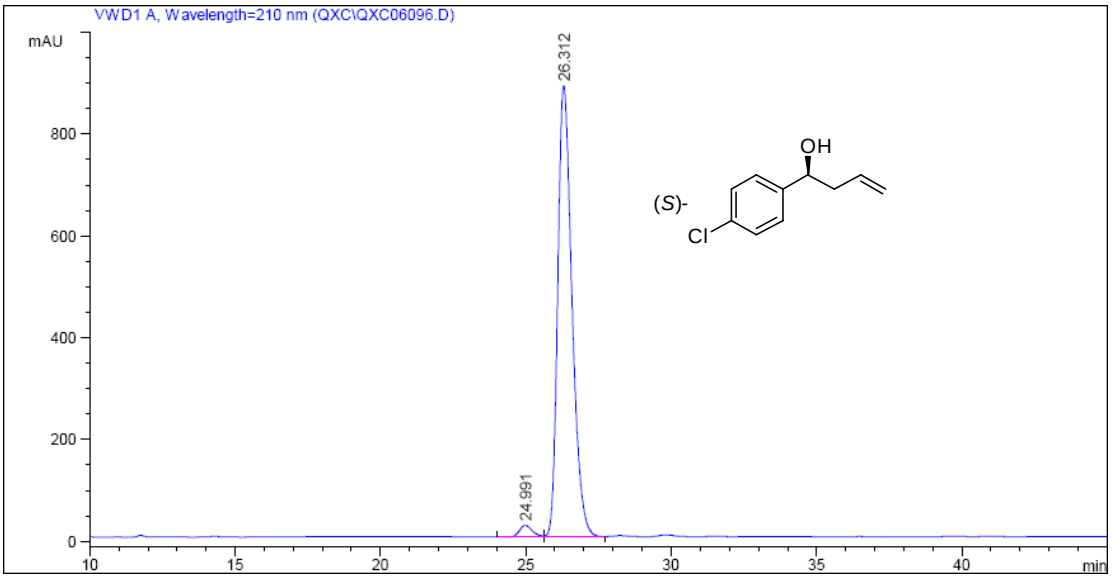



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.034 | VV | 0.3912 | 697.10730 | 27.55626 | 2.0722 |
| 2 | 22.931 | VV | 0.4751 | 3.29446e4 | 1071.65112 | 97.9278 |

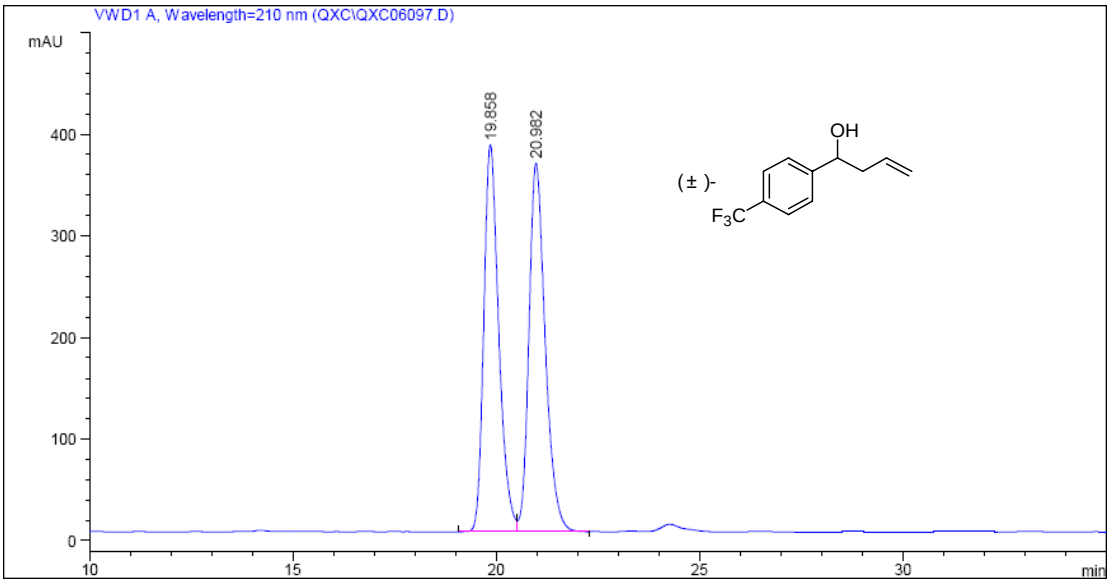
**1-(4-Chlorophenyl)but-3-en-1-ol (7ka)**

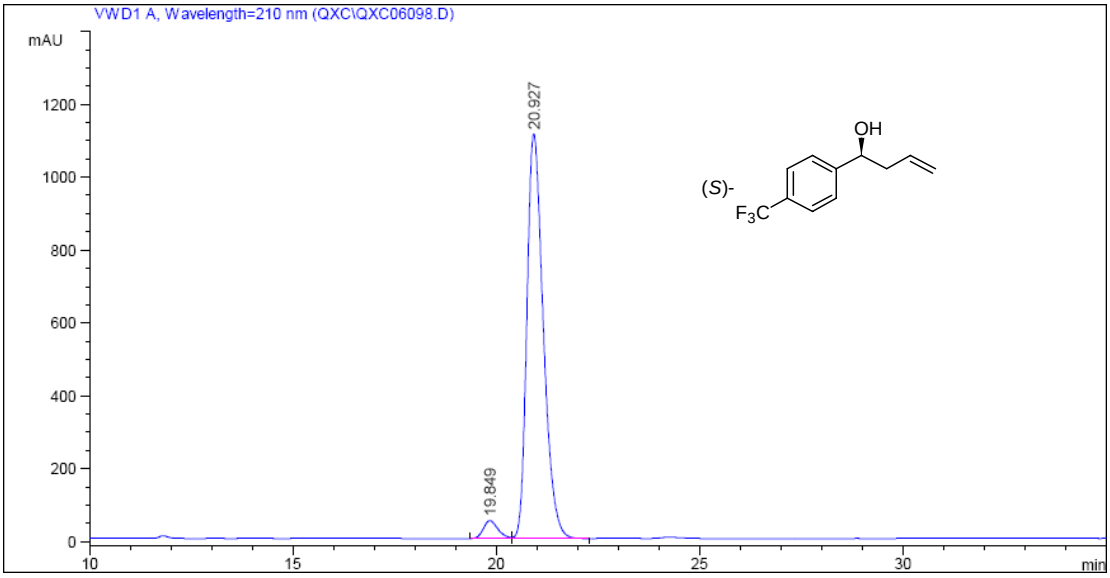



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 24.991 | VV | 0.4728 | 718.45959 | 23.14384 | 2.3313 |
| 2 | 26.312 | VB | 0.5210 | 3.00997e4 | 887.29016 | 97.6687 |

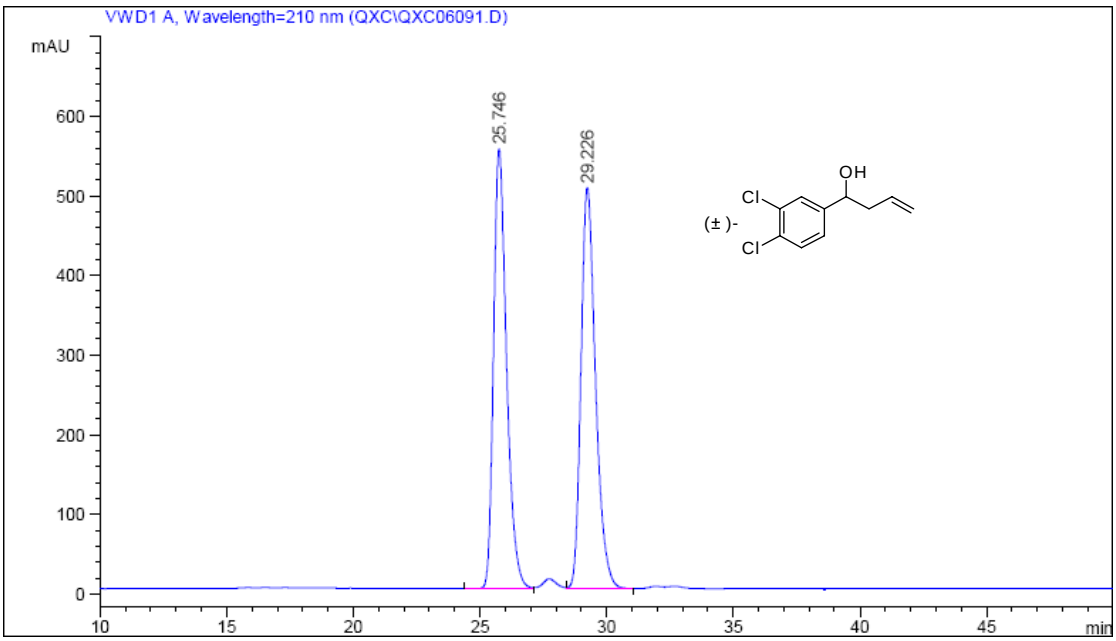
**1-(4-Trifluoromethylphenyl)but-3-en-1-ol (7la)**

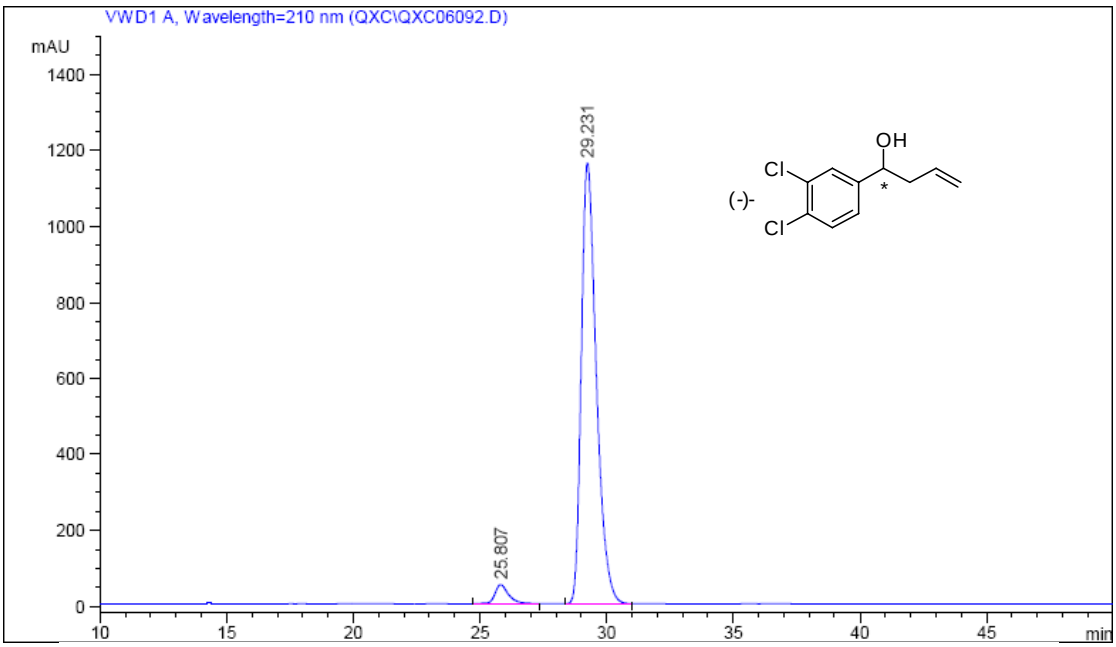



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.849 | BV | 0.3820 | 1243.27222 | 49.71237 | 3.8440 |
| 2 | 20.927 | VB | 0.4315 | 3.10998e4 | 1110.63440 | 96.1560 |

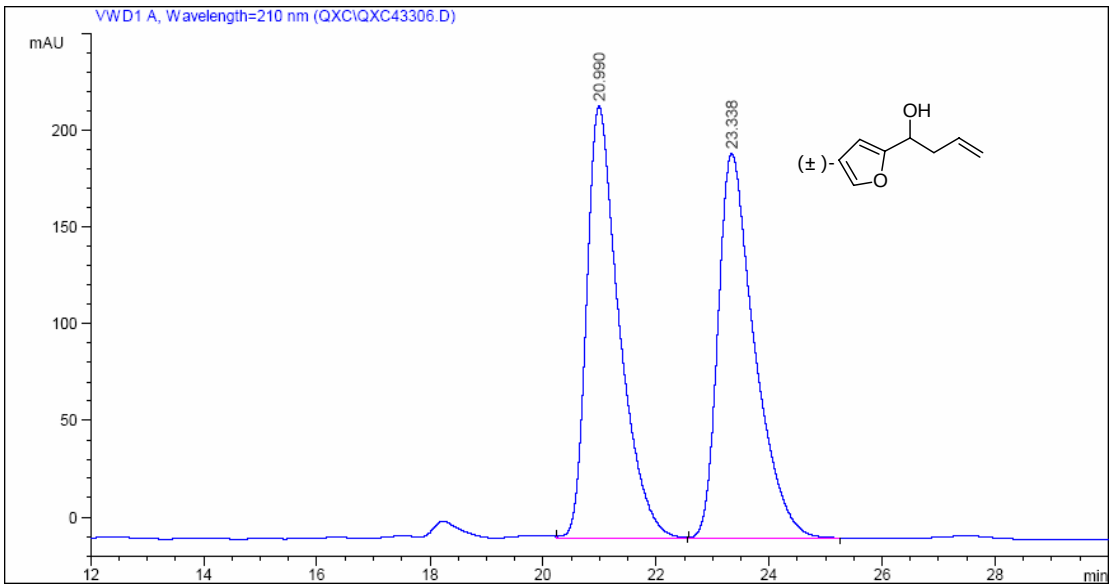
**1-(3,4-Dichlorophenyl)but-3-en-1-ol (7ma)**

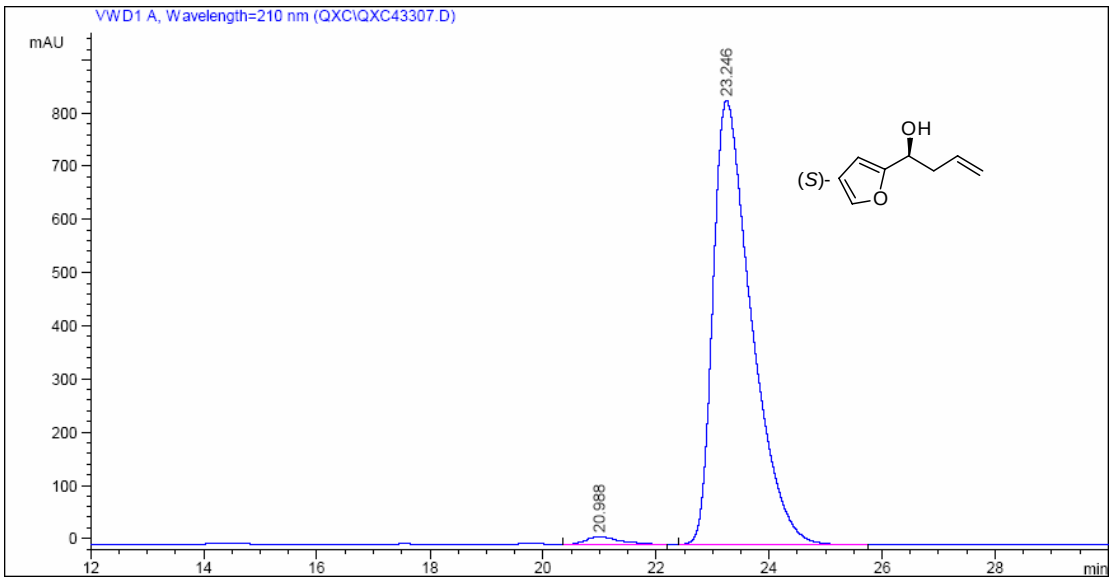



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 25.807 | BB | 0.5576 | 1904.49890 | 50.53869 | 3.8341 |
| 2 | 29.231 | PB | 0.6275 | 4.77680e4 | 1159.84619 | 96.1659 |

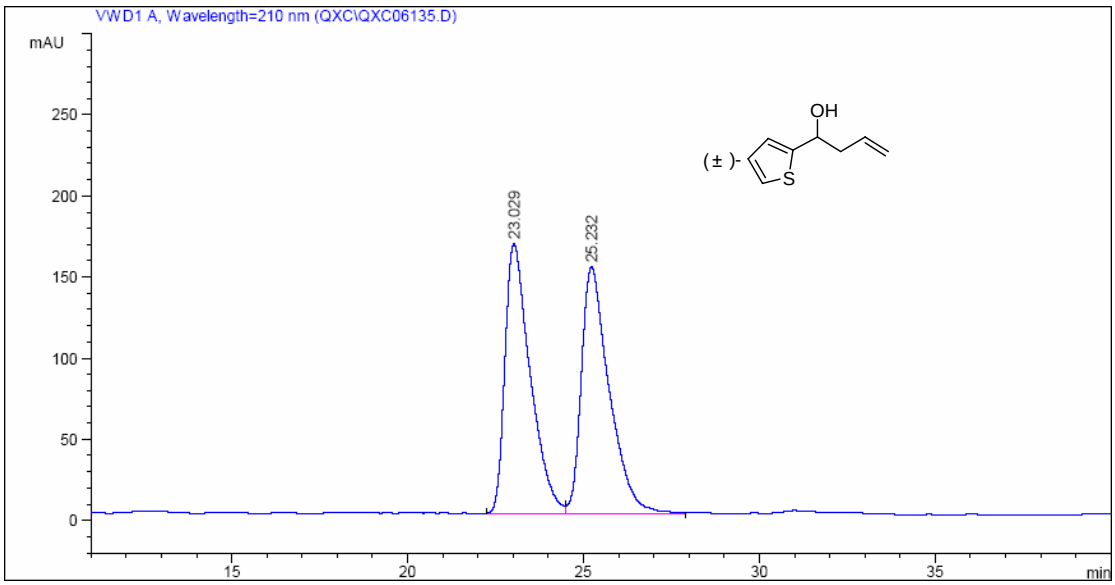
**1-(2-Furyl)but-3-en-1-ol (7na)**

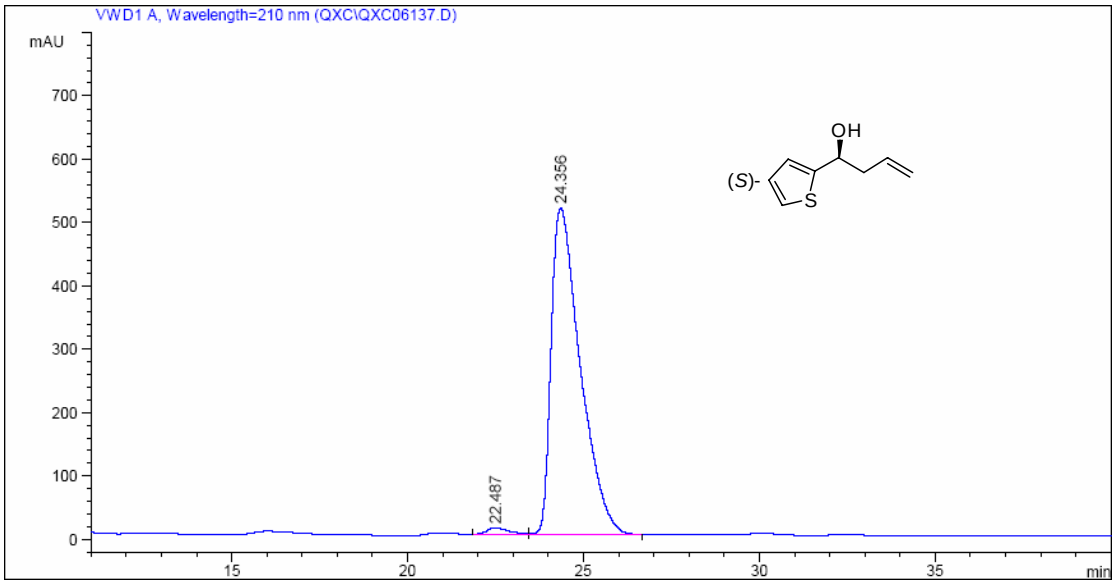



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.988 | VB | 0.6252 | 604.36084 | 14.31089 | 1.5132 |
| 2 | 23.246 | BP | 0.6952 | 3.93339e4 | 834.91901 | 98.4868 |

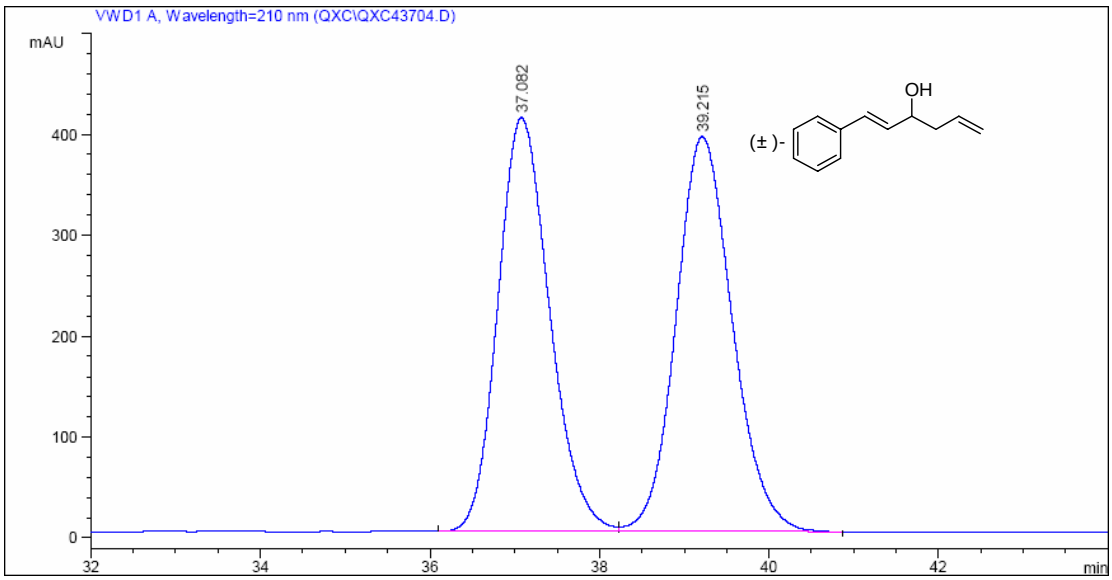
**1-(2-Thienyl)but-3-en-1-ol (7oa)**

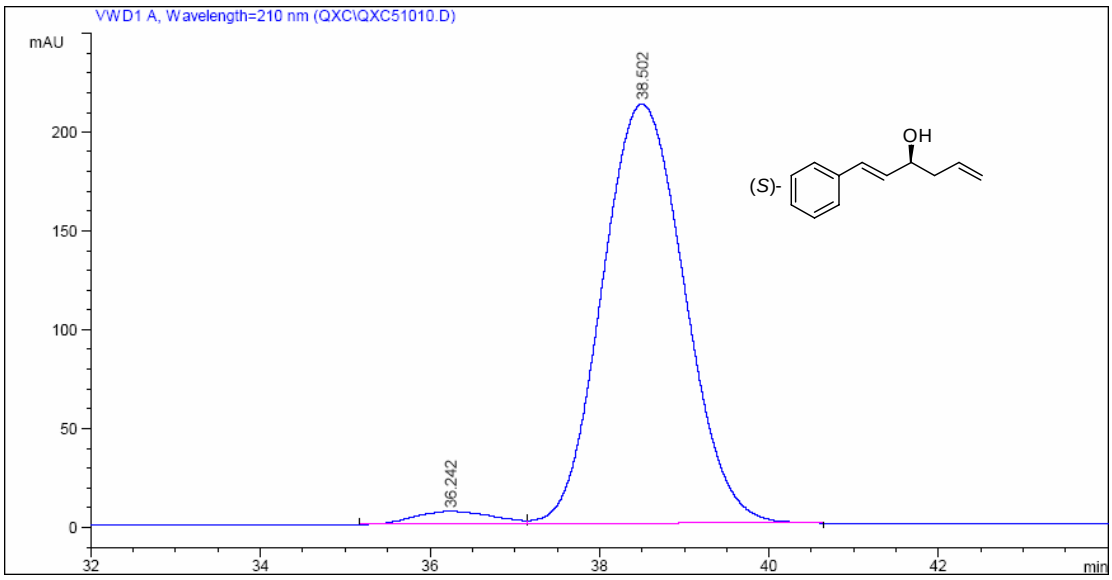



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.487 | VV | 0.6883 | 554.43054 | 11.48785 | 1.8291 |
| 2 | 24.356 | VP | 0.8647 | 2.97573e4 | 516.24829 | 98.1709 |

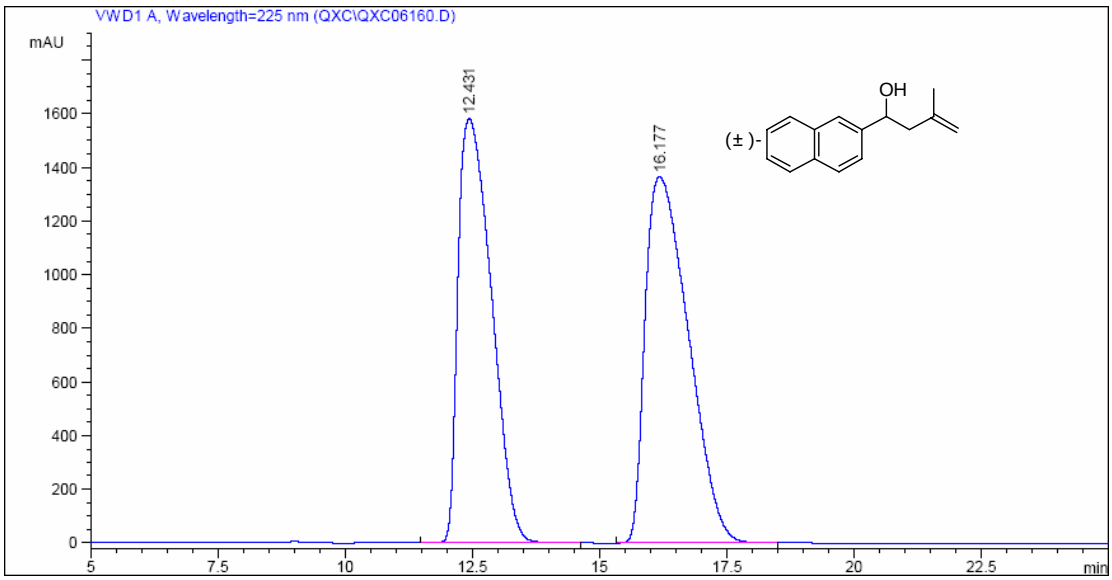
**1-Phenyl-hexa-1,5-dien-3-ol (7pa)**

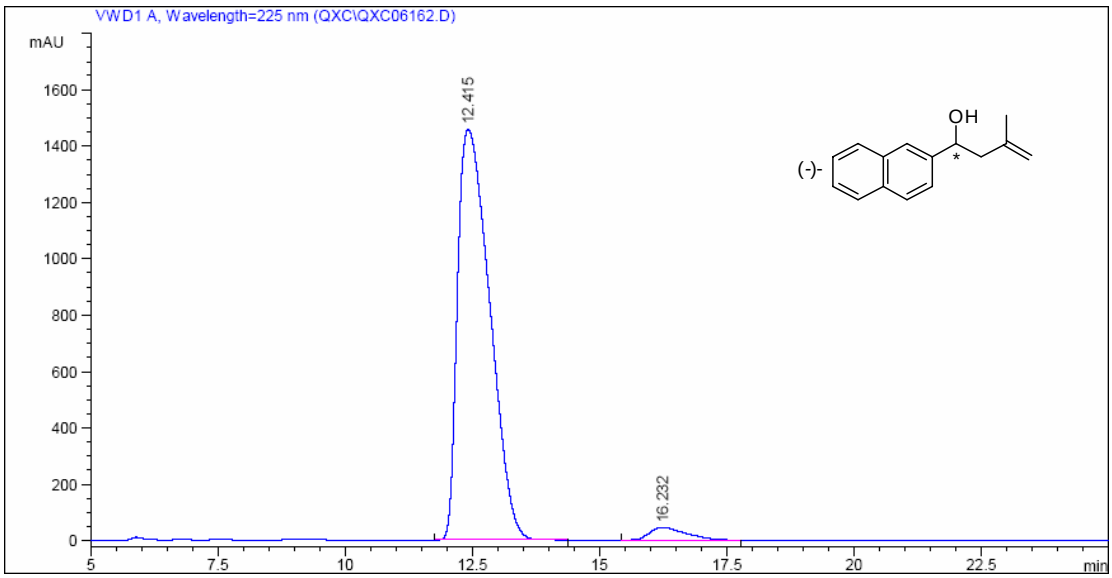



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 36.242 | PV | 0.7794 | 411.15222 | 6.31957 | 2.7980 |
| 2 | 38.502 | VB | 1.0721 | 1.42835e4 | 212.21214 | 97.2020 |

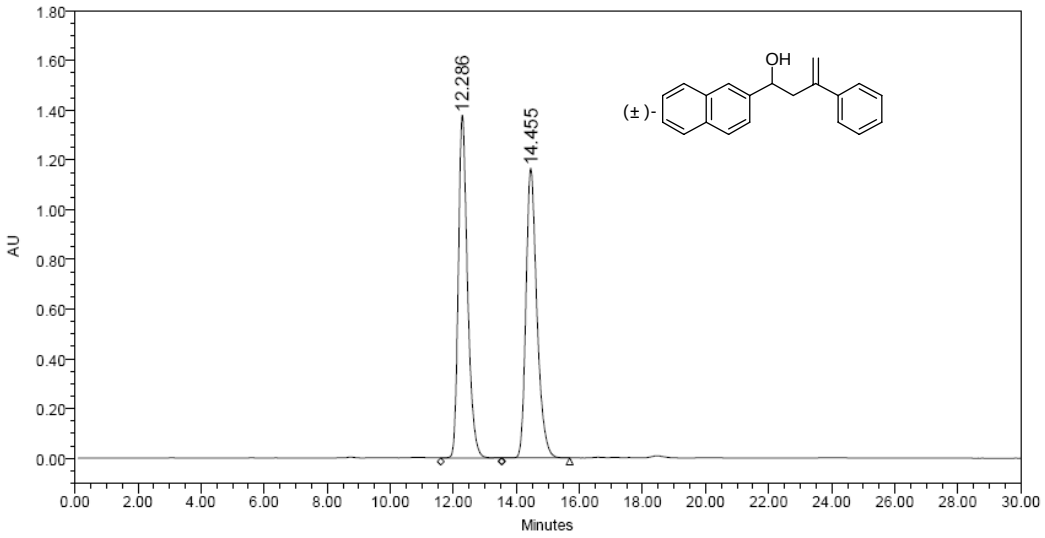
**1-(2-Naphtyl)-3-methylbut-3-en-1-ol (7ab)**

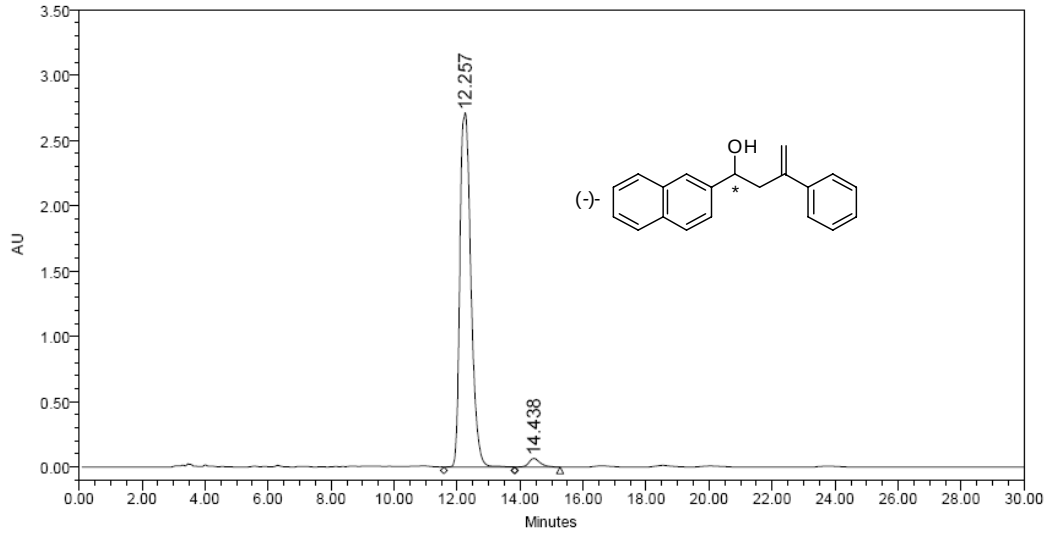



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.415 | VB | 0.7257 | 6.39852e4 | 1459.03687 | 96.5463 |
| 2 | 16.232 | BB | 0.7206 | 2288.94067 | 46.32555 | 3.4537 |

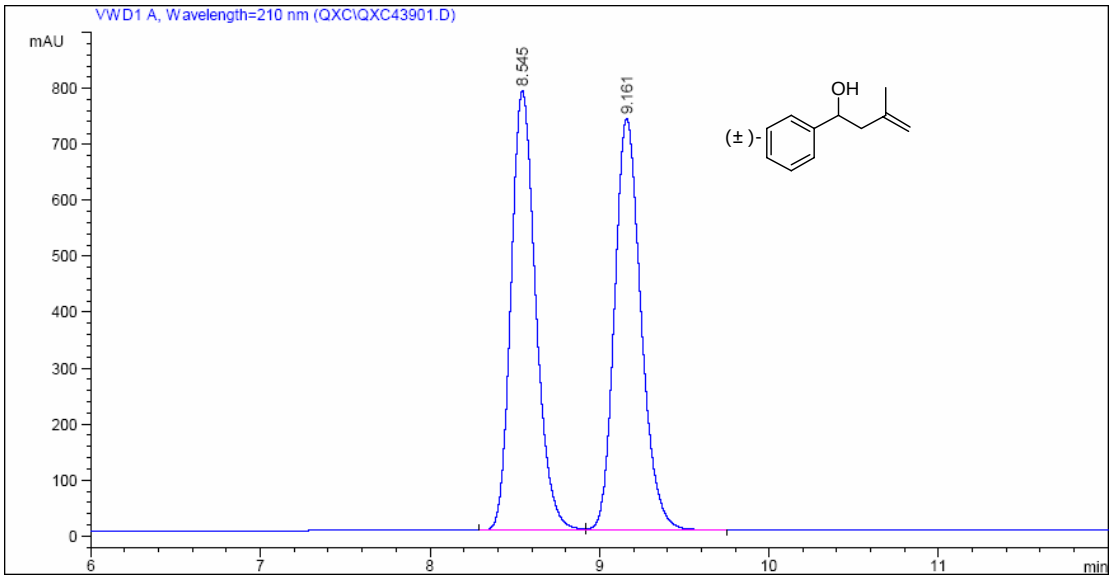
**1-(Naphthalen-2-yl)-3-phenylbut-3-en-1-ol (7ac)**

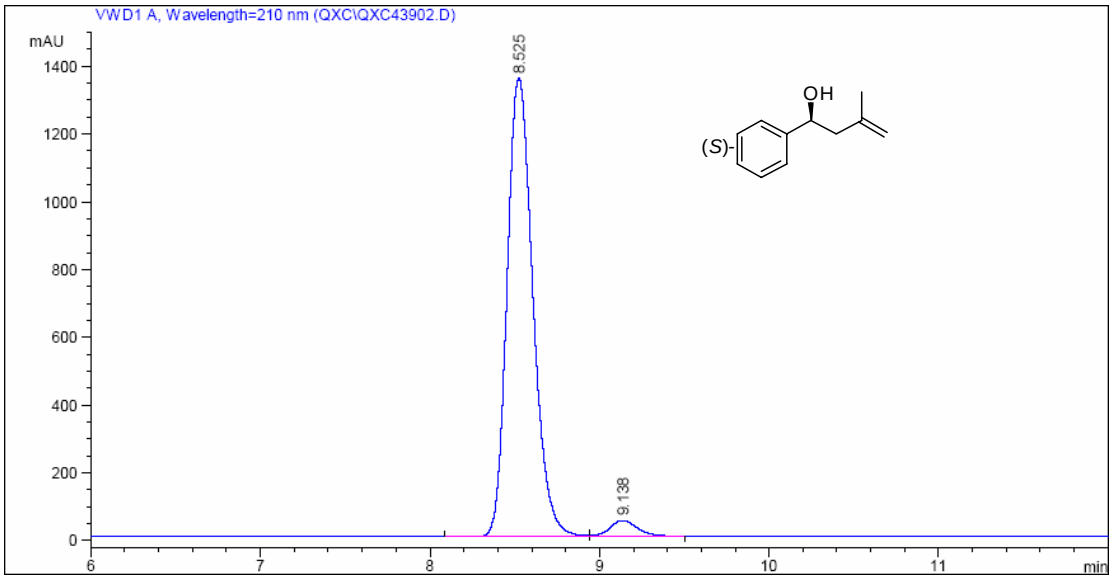



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 12.257 | 65934584 | 97.68 | 2715054 |
| 2 | 14.438 | 1569159 | 2.32 | 65018 |

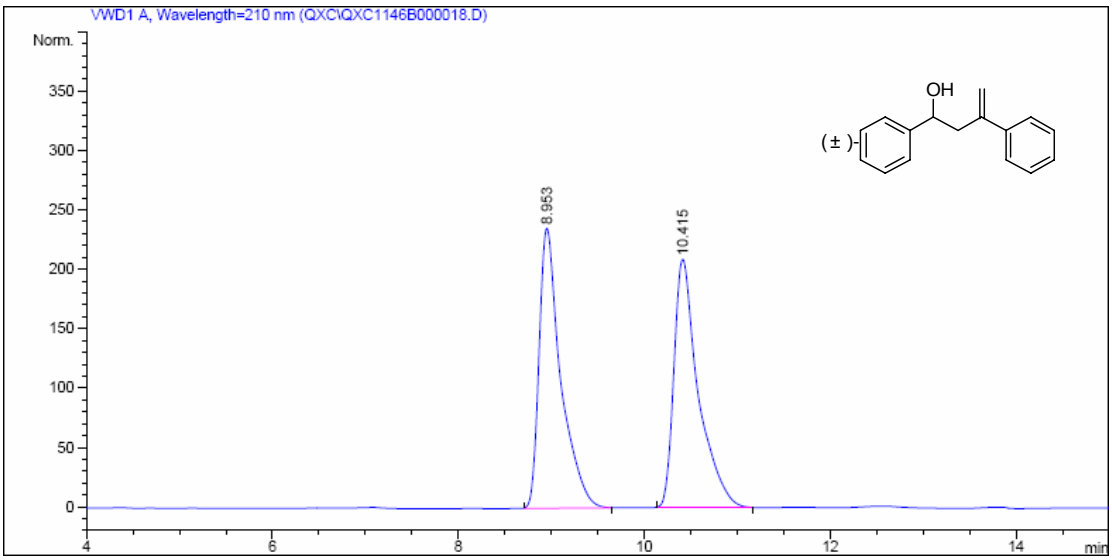
**1-Phenyl-3-methylbut-3-en-1-ol (7bb)**

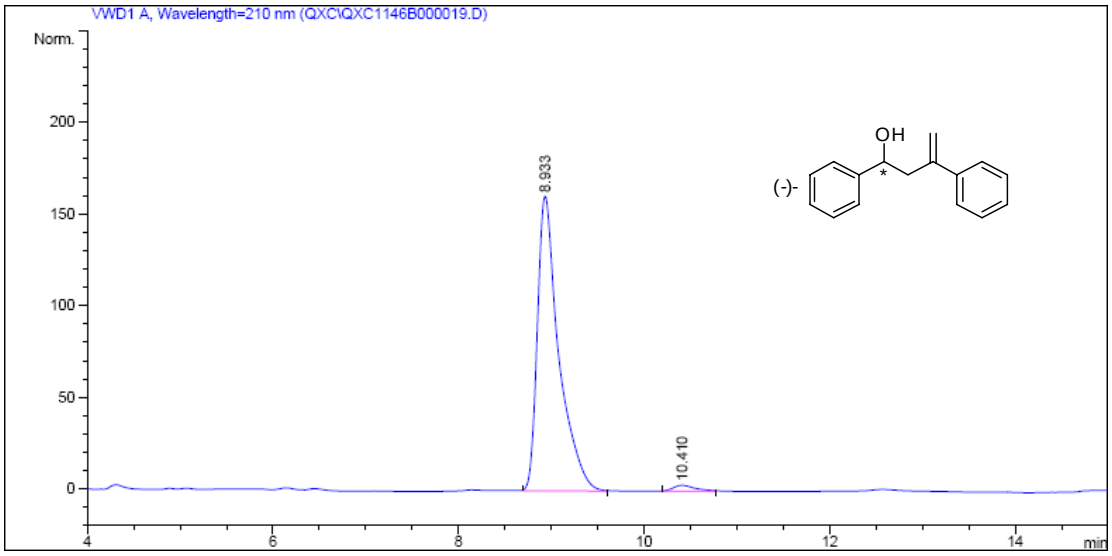



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.525 | VV | 0.1638 | 1.42839e4 | 1354.46619 | 96.2222 |
| 2 | 9.138 | VV | 0.1755 | 560.80896 | 48.05576 | 3.7778 |

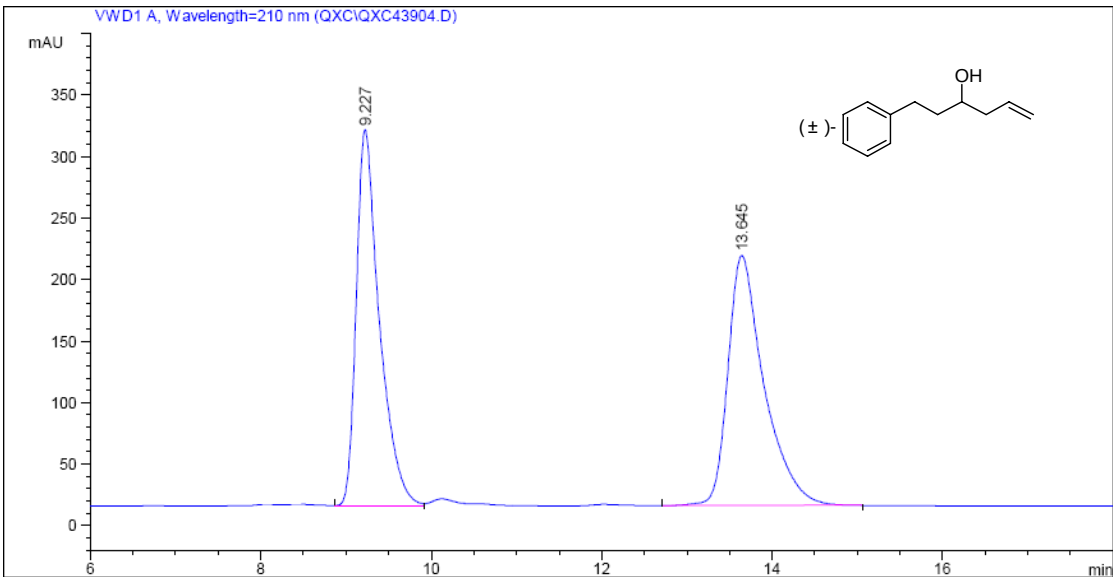
**1,3-Diphenylbut-3-en-1-ol (7bc)**

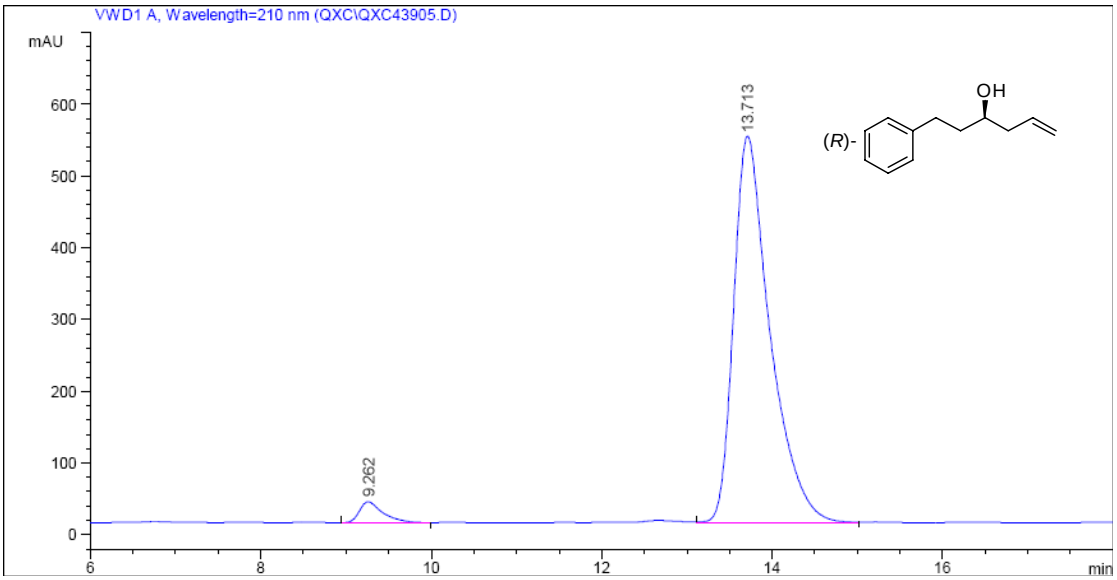



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 8.933 | BB | 0.2336 | 2573.29395 | 97.9572 |
| 2 | 10.410 | BB | 0.2366 | 53.66257 | 2.0428 |

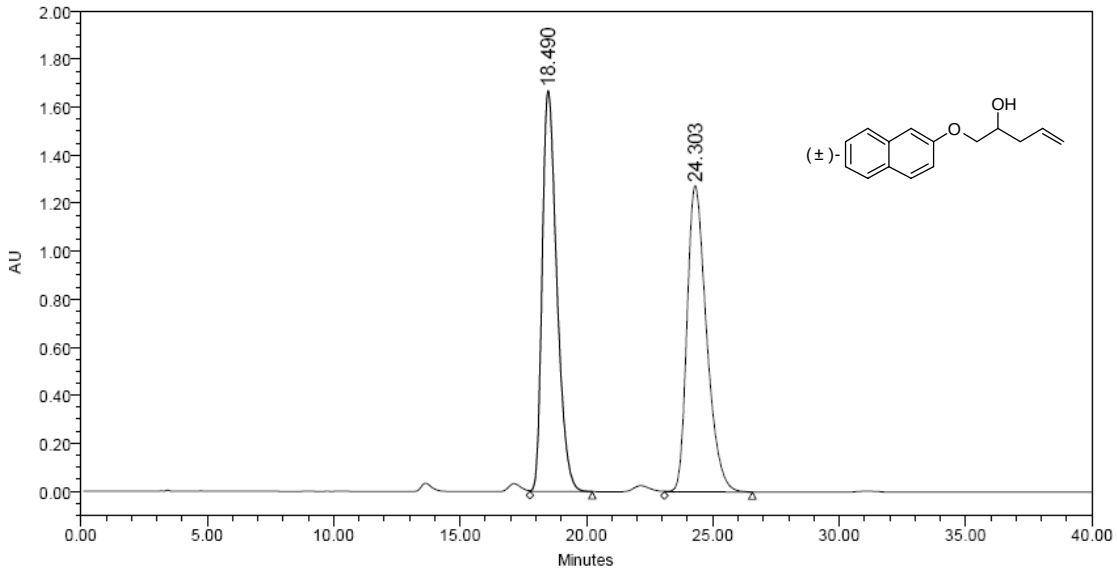
**1-Phenyl-hexa-5-en-3-ol (7qa)**

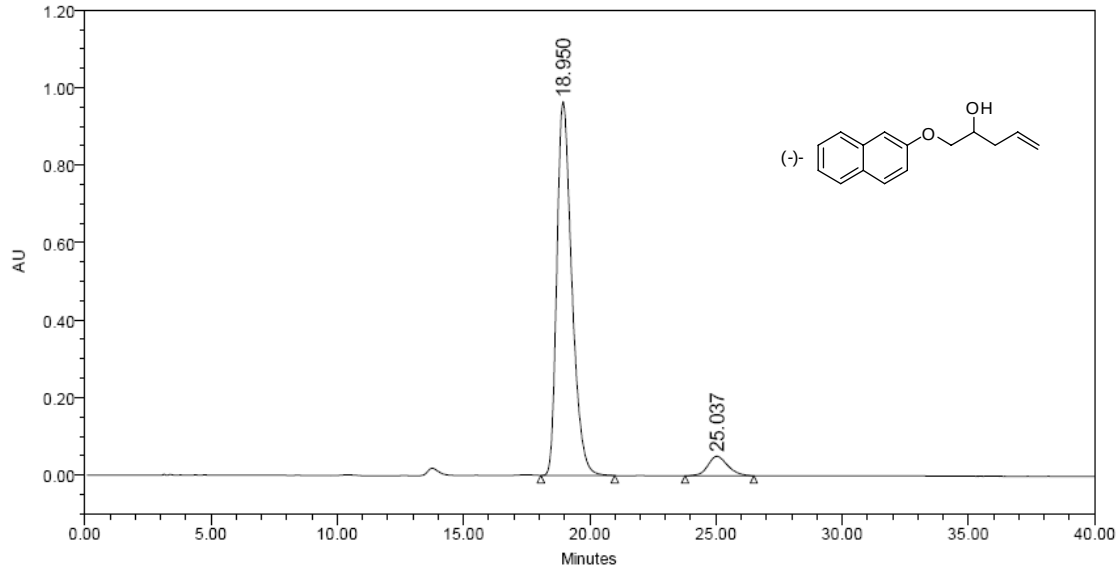



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.262 | VB | 0.2783 | 562.63861 | 29.44474 | 3.3904 |
| 2 | 13.713 | VB | 0.4360 | 1.60325e4 | 538.74188 | 96.6096 |

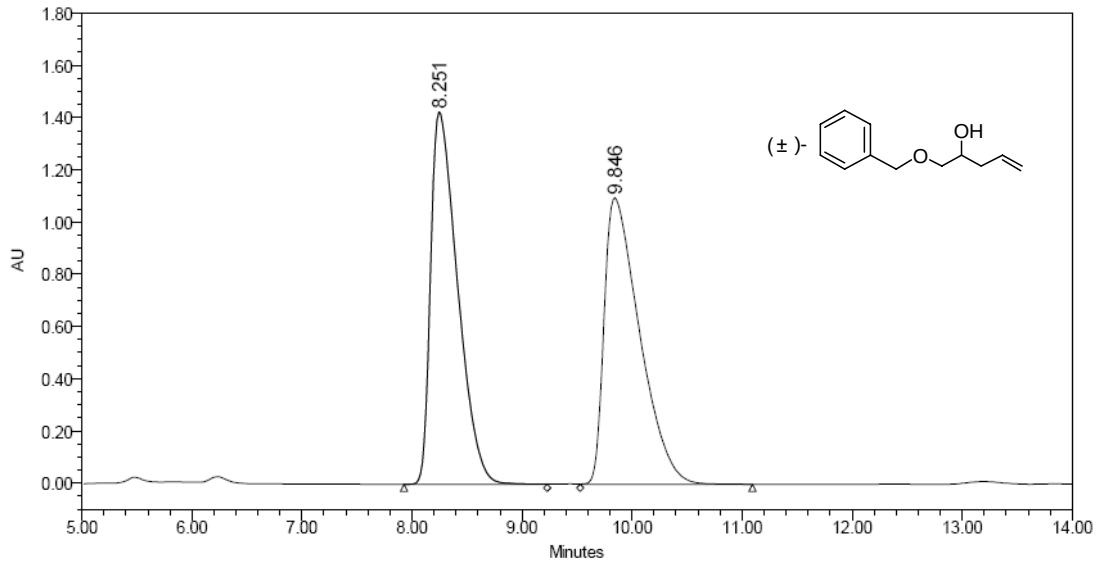
**1-(Naphthalen-2-yloxy)pent-4-en-2-ol (7ra)**

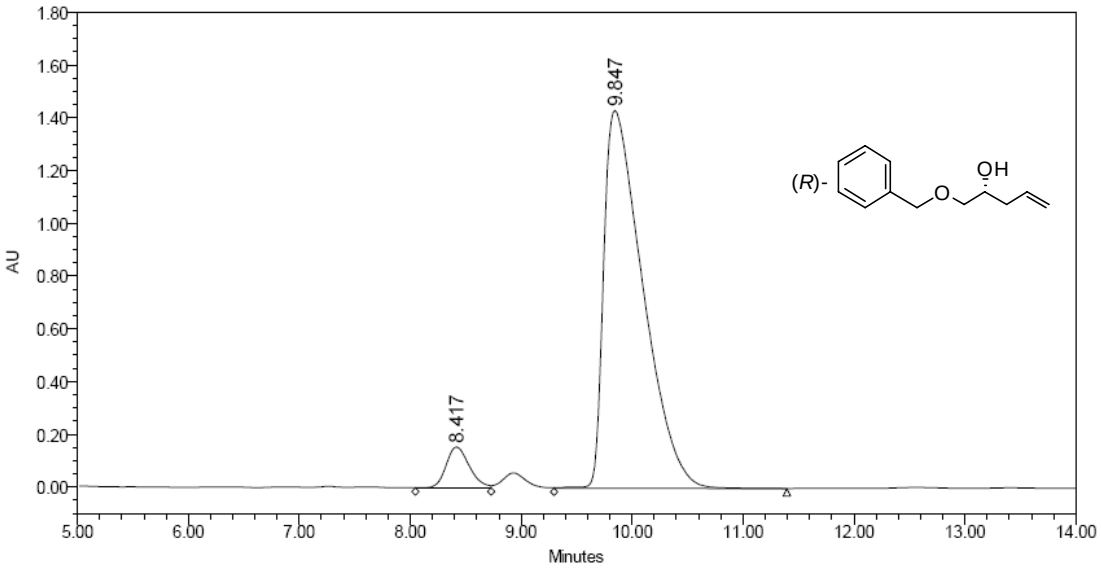



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 18.950 | 39646166 | 93.58 | 964391 |
| 2 | 25.037 | 2720729 | 6.42 | 50062 |

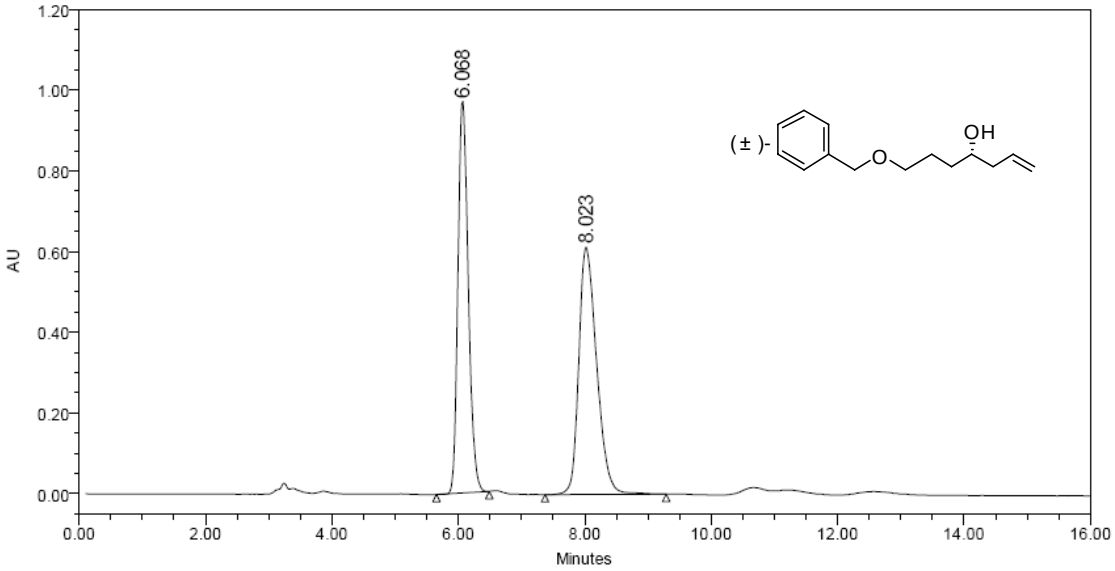
**1-(Benzyloxy)-2-hydroxypent-4-ene (7sa)**

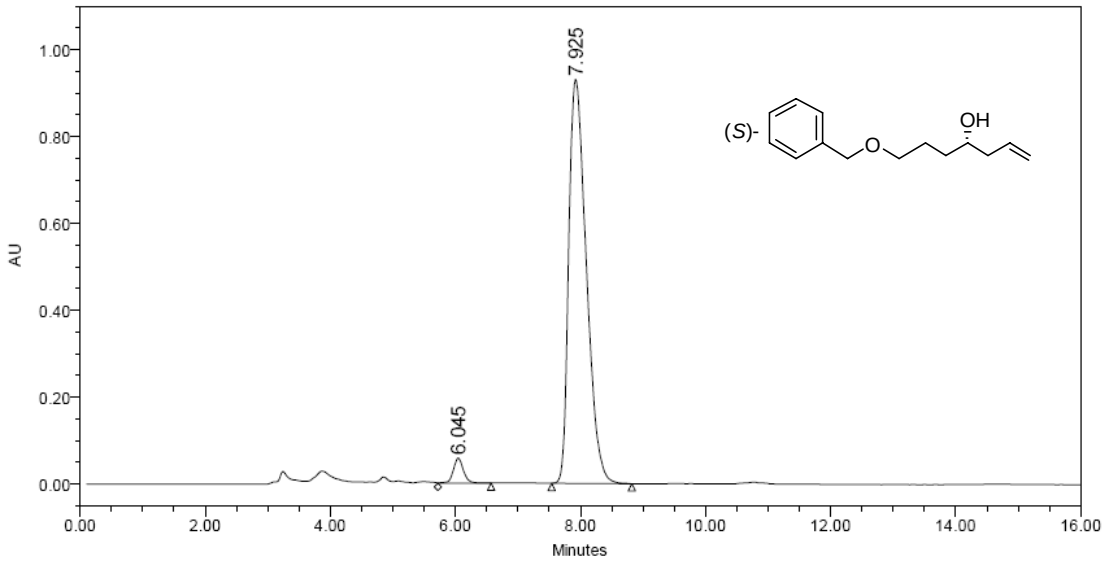



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 8.417 | 2256927 | 6.04 | 155562 |
| 2 | 9.847 | 35100852 | 93.96 | 1433594 |

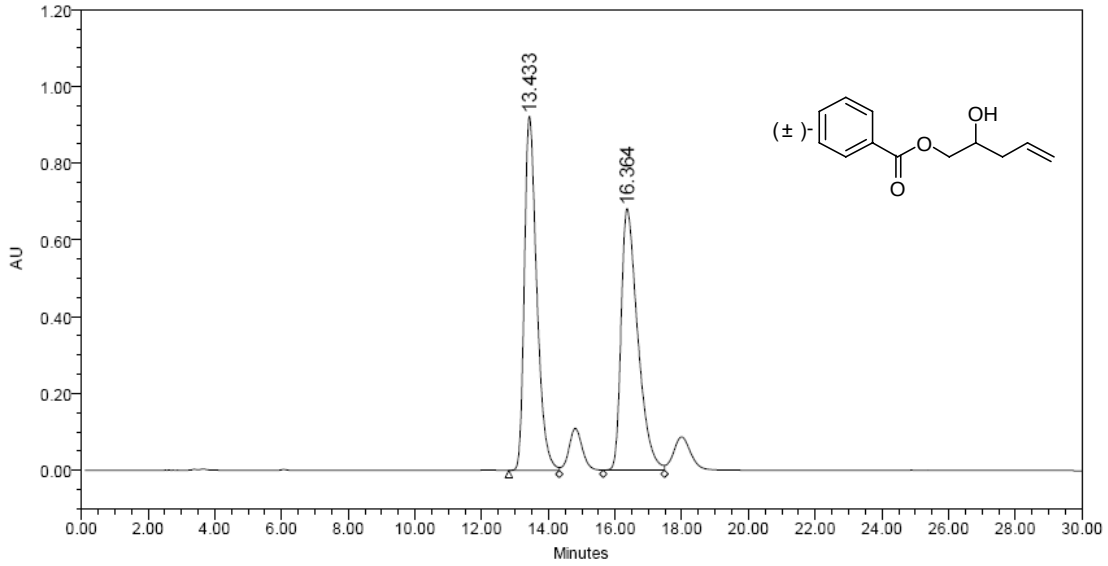
**1-(Benzyloxy)-4-hydroxypent-6-ene (7ta)**

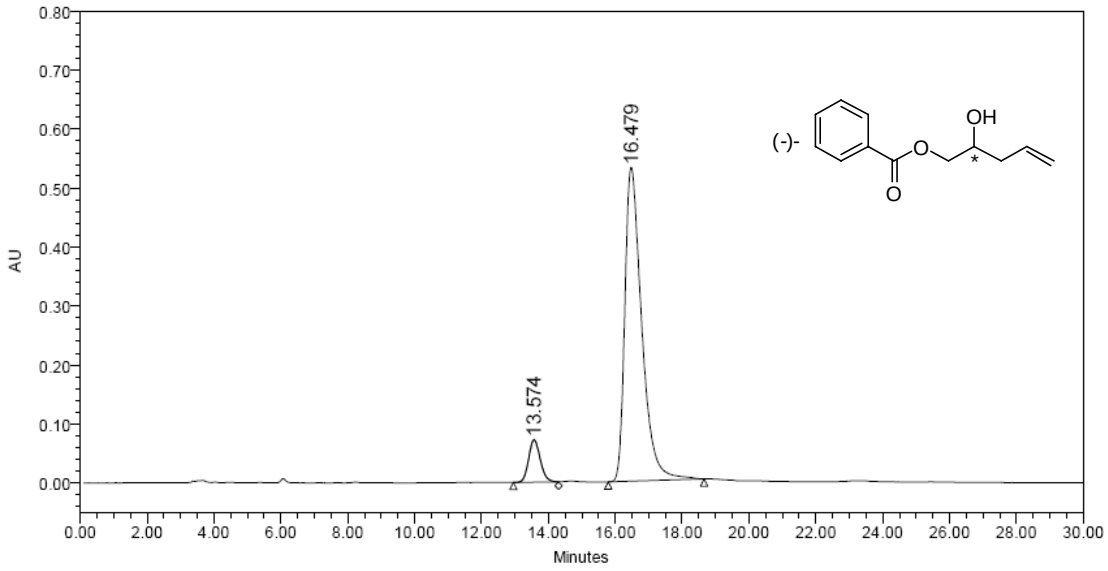



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 6.045 | 656775 | 3.50 | 57951 |
| 2 | 7.925 | 18096825 | 96.50 | 930855 |

**2-Hydroxypent-4-enyl benzoate (7ua)**

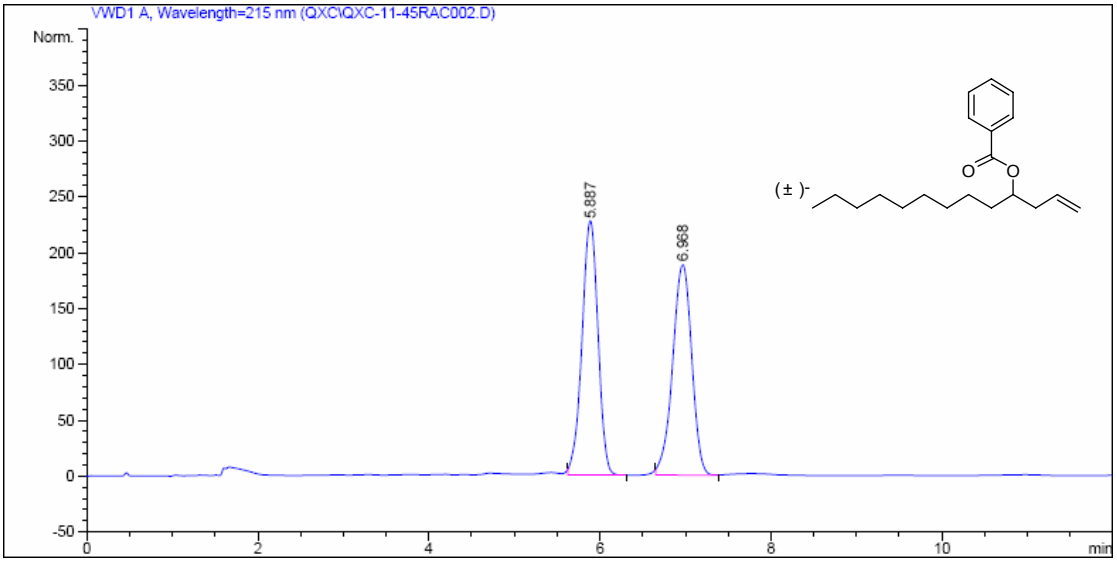


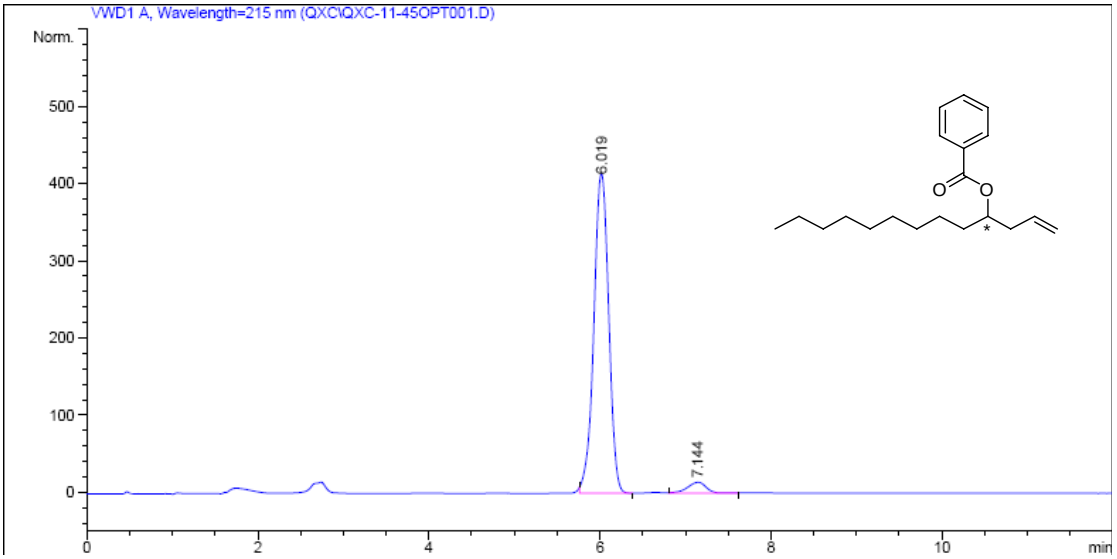




| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 13.574 | 1748290 | 8.58 | 72115 |
| 2 | 16.479 | 18633800 | 91.42 | 532363 |

**Tridec-1-en-4-ol (7va)**

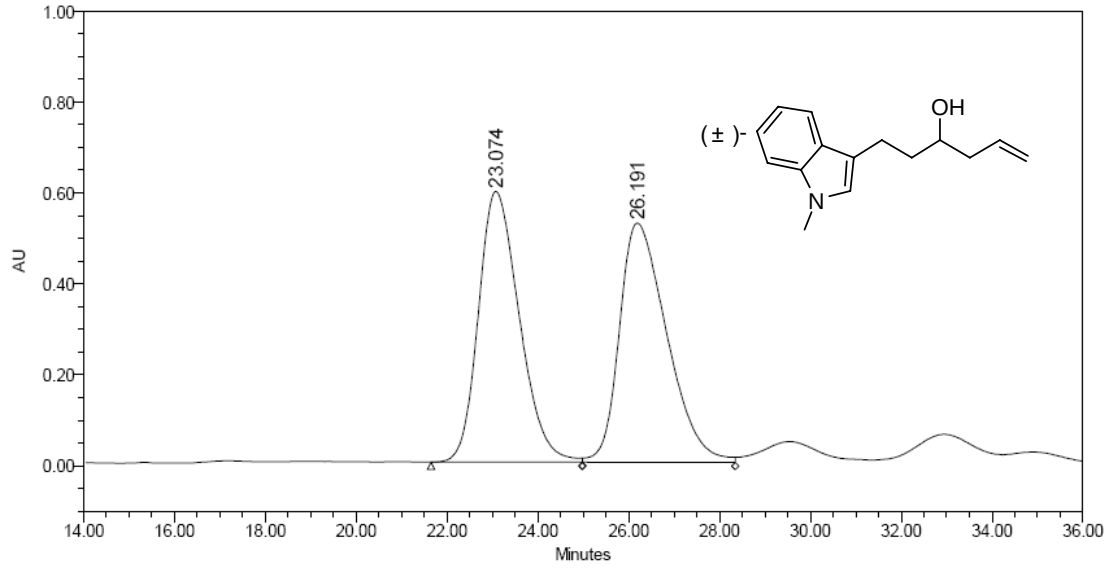
The ee was determined by SFC analysis of the corresponding benzoate.

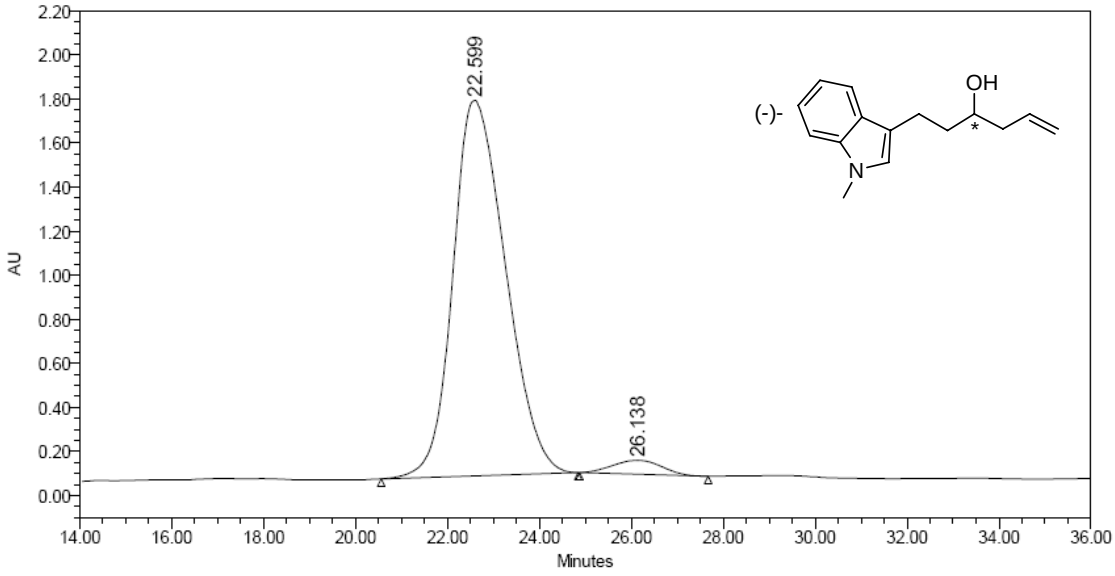



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 6.019 | BB | 0.1892 | 5000.97510 | 95.7697 |
| 2 | 7.144 | BB | 0.2527 | 220.90178 | 4.2303 |

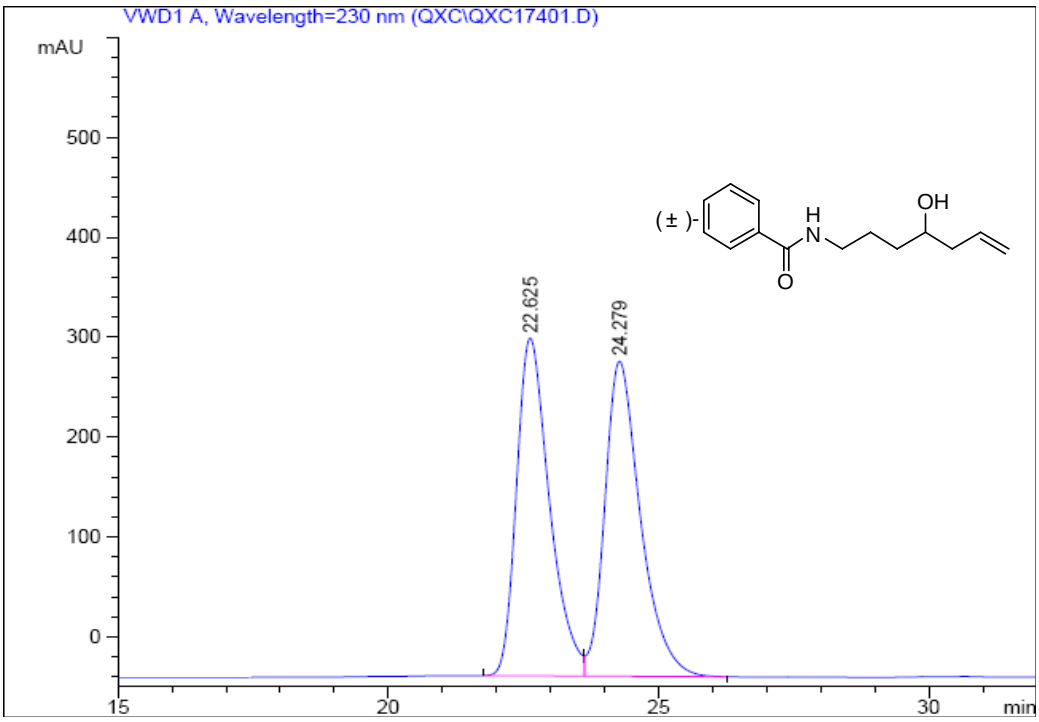
**1-(1-Methyl-1H-indol-3-yl)hex-5-en-3-ol (7wa)**

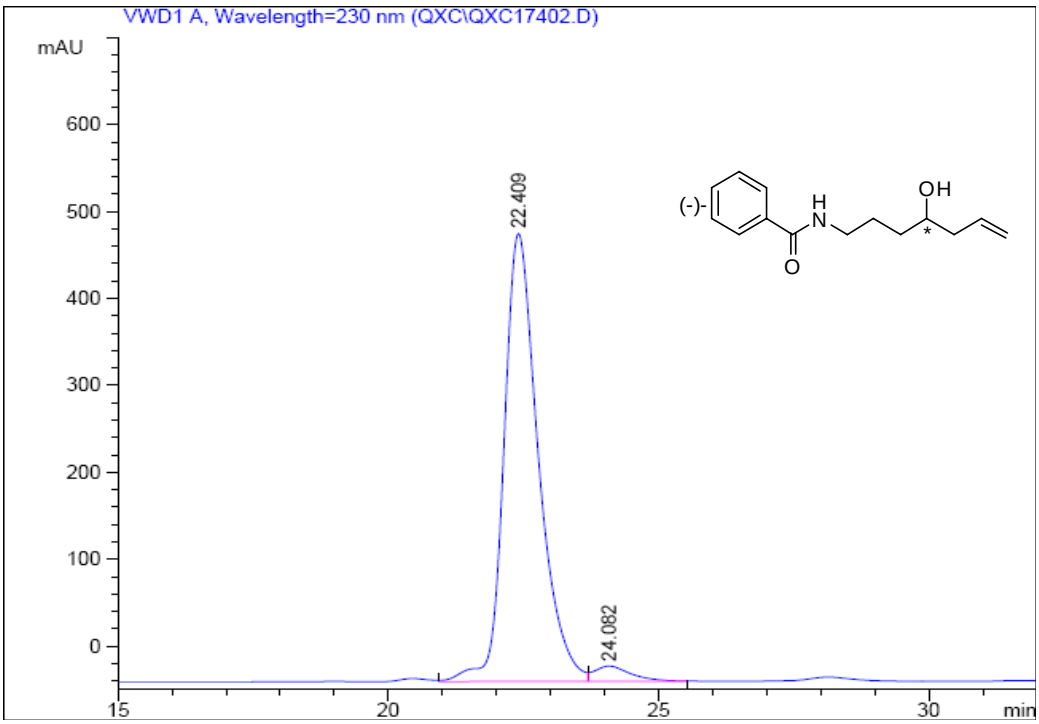



| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 22.599 | 135621348 | 96.66 | 1704793 |
| 2 | 26.138 | 4681644 | 3.34 | 63433 |

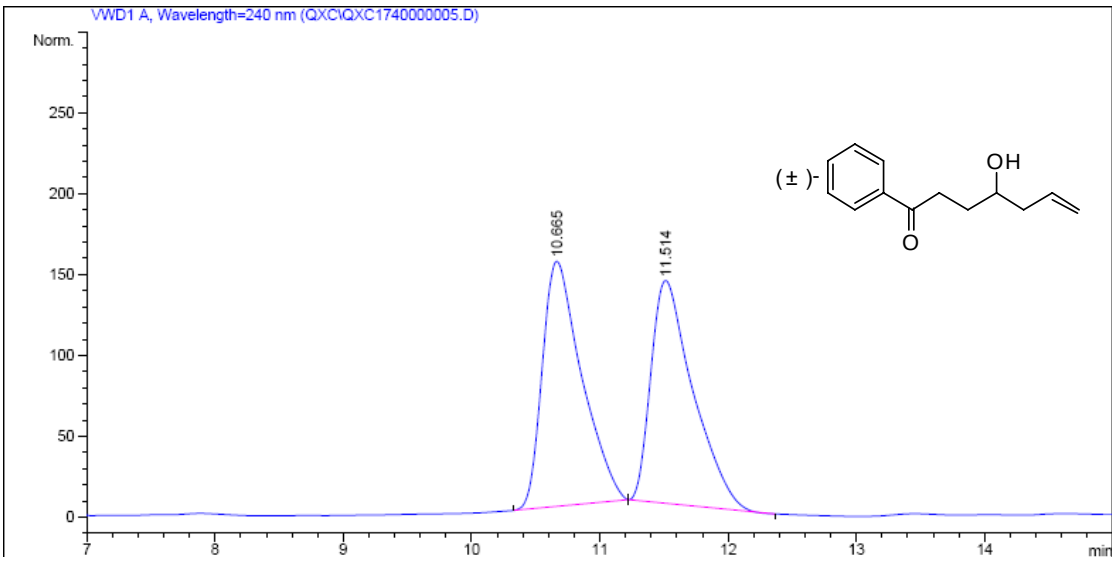
***N*-(3-Hydroxyhex-5-enyl)benzamide (7xa)**

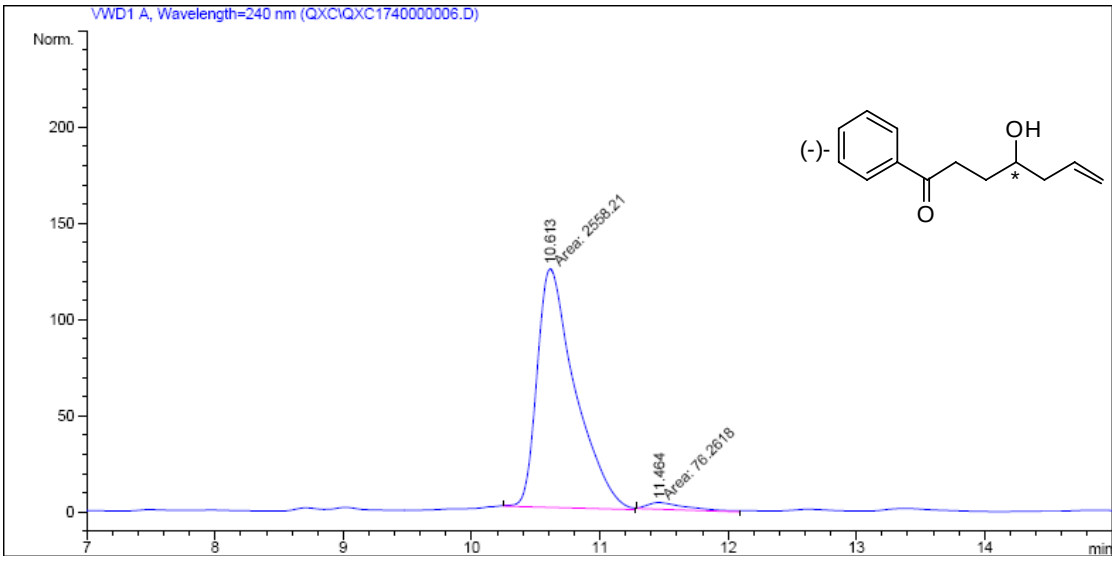



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.409 | VV | 0.6681 | 2.28135e4 | 515.12451 | 96.5228 |
| 2 | 24.082 | VB | 0.6786 | 821.85913 | 17.55812 | 3.4772 |

**4-Hydroxy-1-phenylhept-6-en-1-one (7ya)**

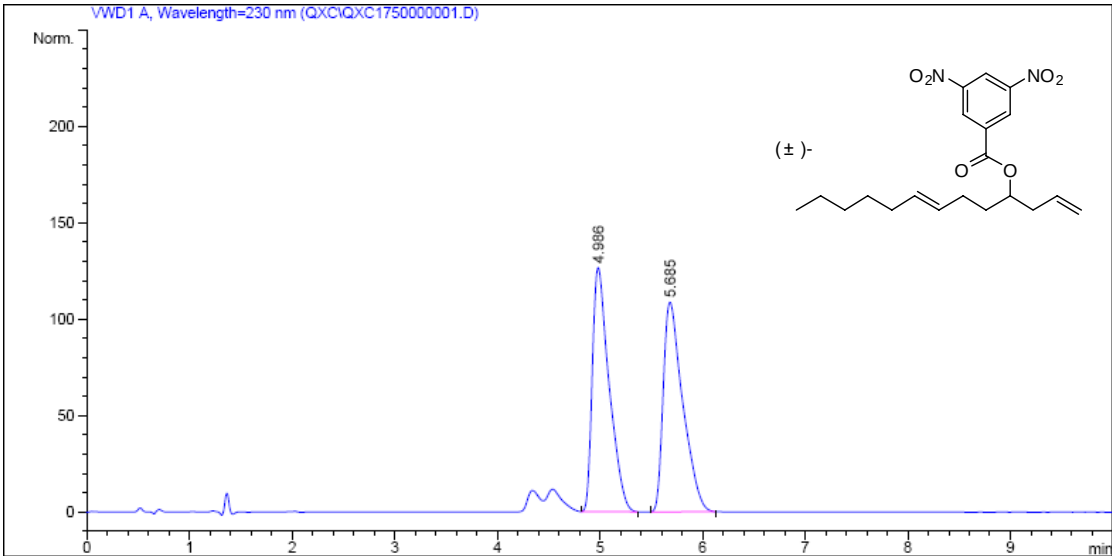


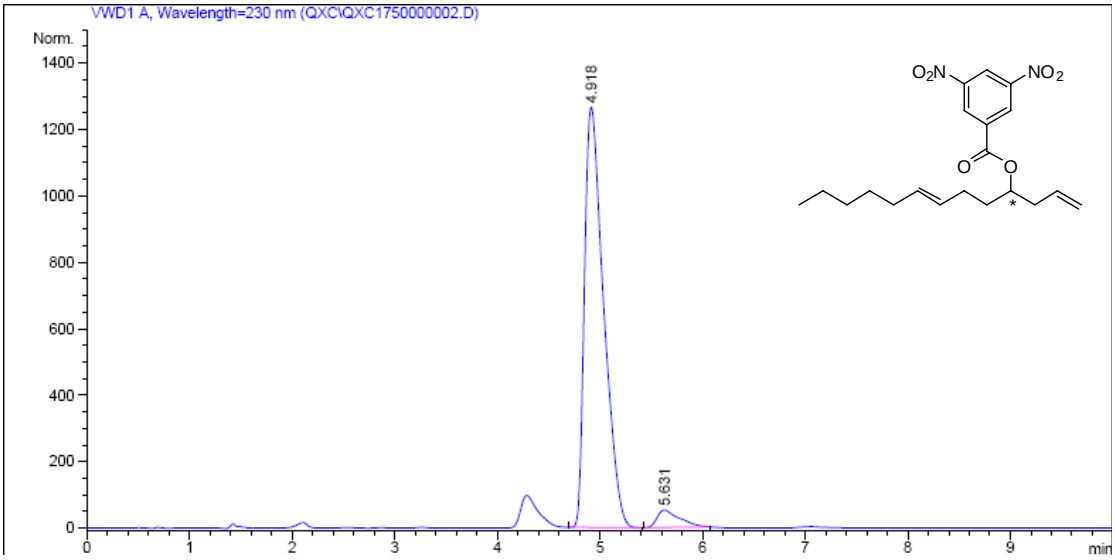




| Peak # | RetTime [min] | Type | Width [min] | Area mAU | Area *s | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.613 | MM | 0.3437 | 2558.20557 | | 97.1052 |
| 2 | 11.464 | MM | 0.3628 | 76.26183 | | 2.8948 |

**(*E*)-Trideca-1,7-dien-4-ol (7za)**

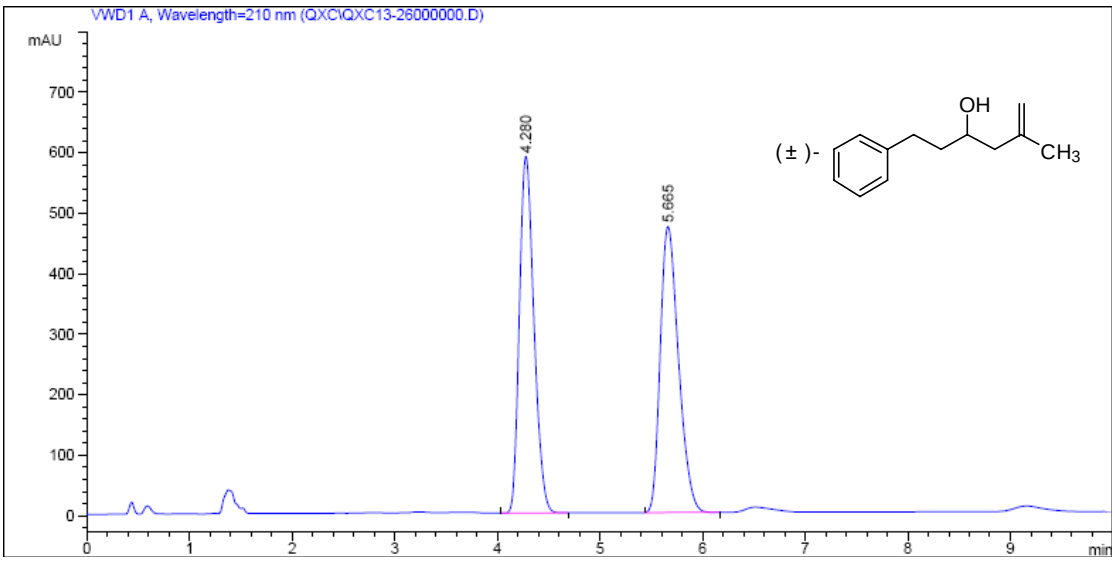
The ee was determined by SFC analysis of the corresponding 3,5-dinitrobenzoate.

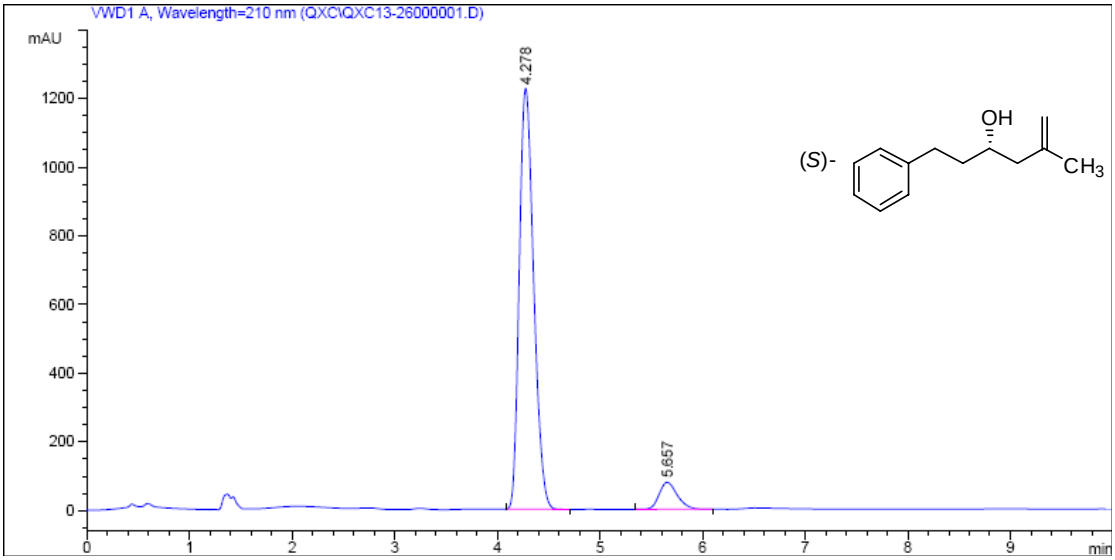



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 4.918 | BB | 0.1939 | 1.63008e4 | 95.3728 |
| 2 | 5.631 | BB | 0.2208 | 790.86682 | 4.6272 |

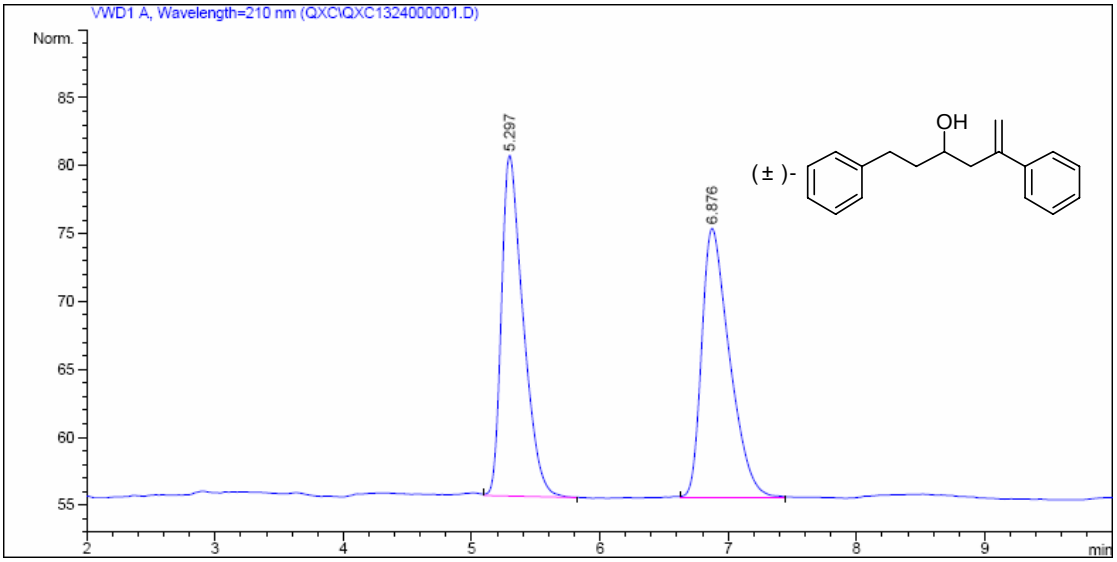
**5-Methyl-1-phenyl-5-hexen-3-ol (7qb)**

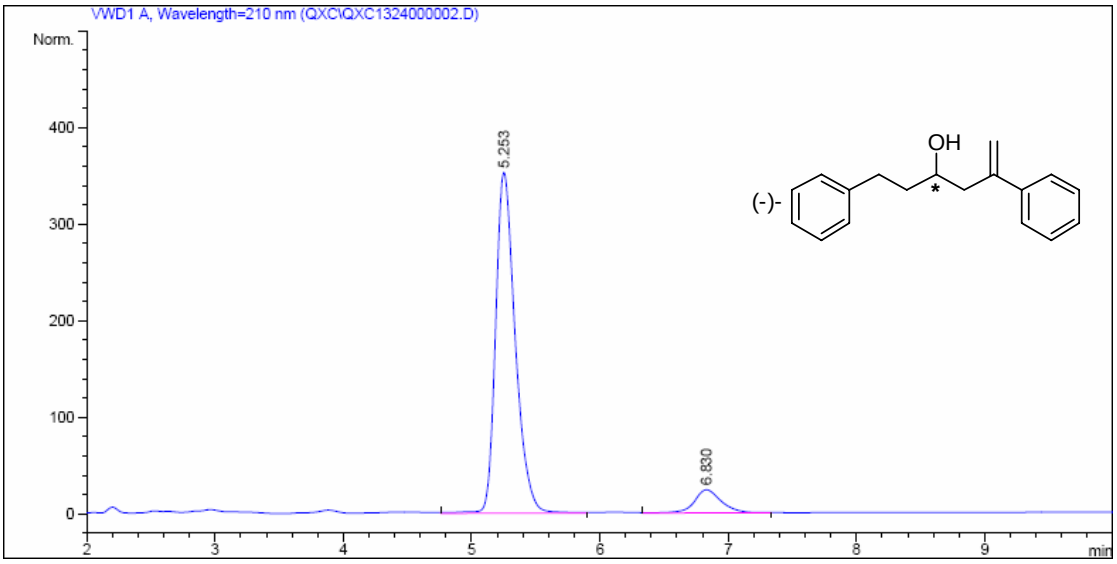



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 4.278 | BB | 0.1546 | 1.19602e4 | 92.5308 |
| 2 | 5.657 | BB | 0.1900 | 965.44751 | 7.4692 |

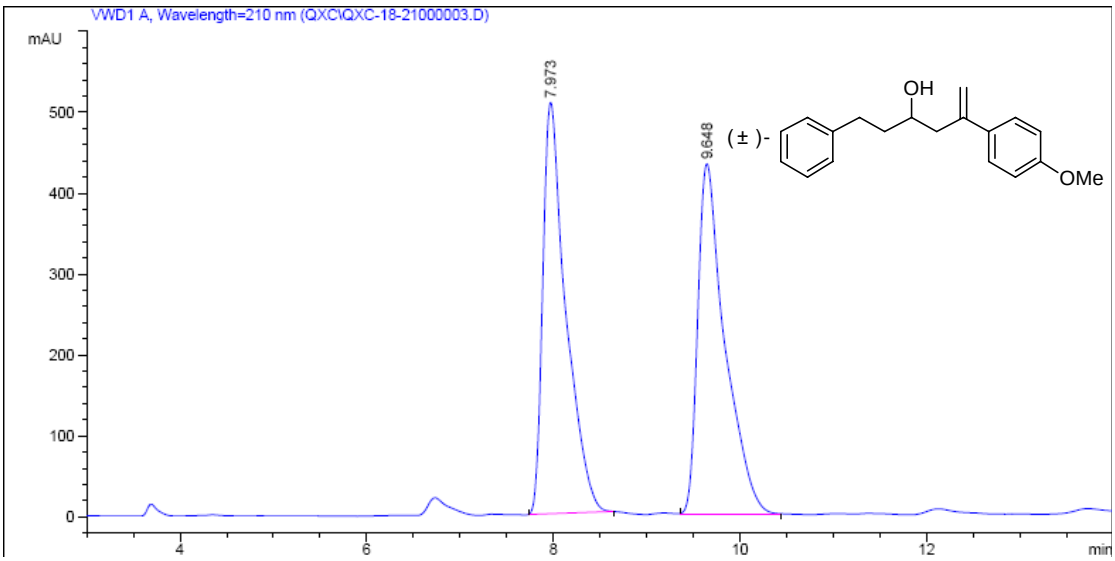
**1,5-Diphenylhex-5-en3-ol (7qc)**

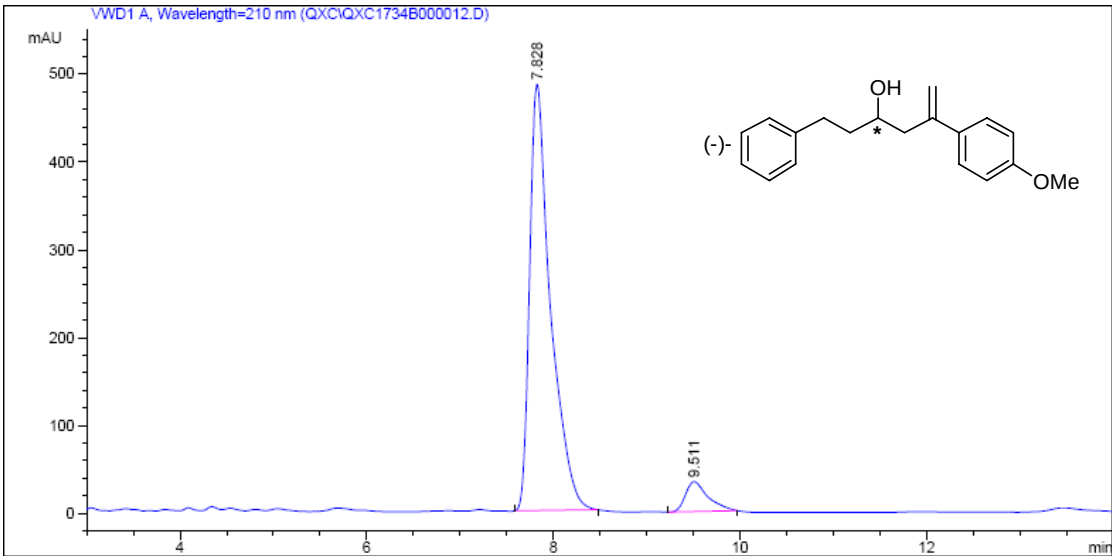



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 5.253 | VV | 0.1622 | 3758.80713 | 91.4037 |
| 2 | 6.830 | VB | 0.2189 | 353.50784 | 8.5963 |

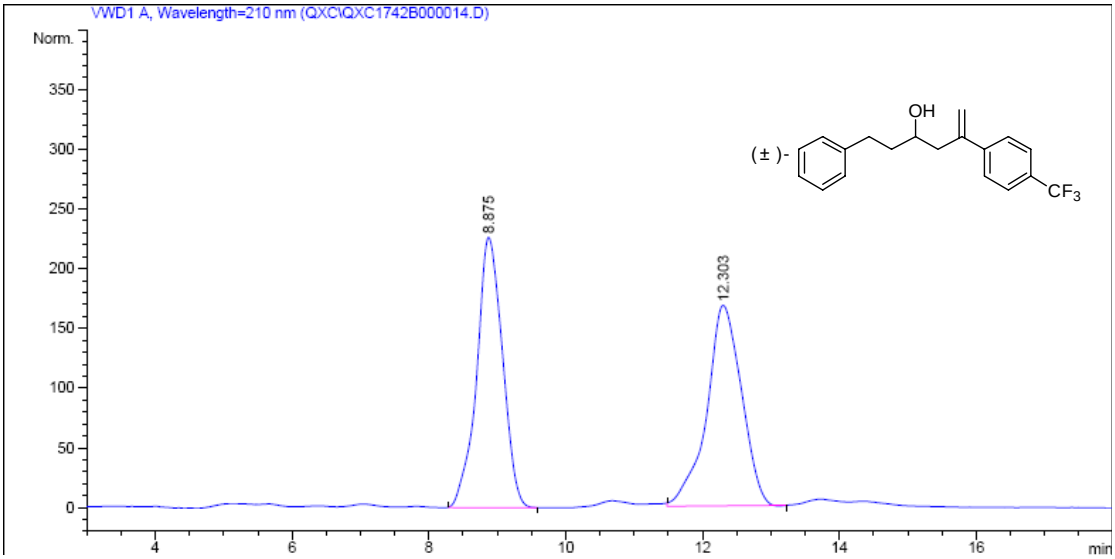
**5-(4-Methoxyphenyl)-1-phenylhex-5-en-3-ol (7qd)**

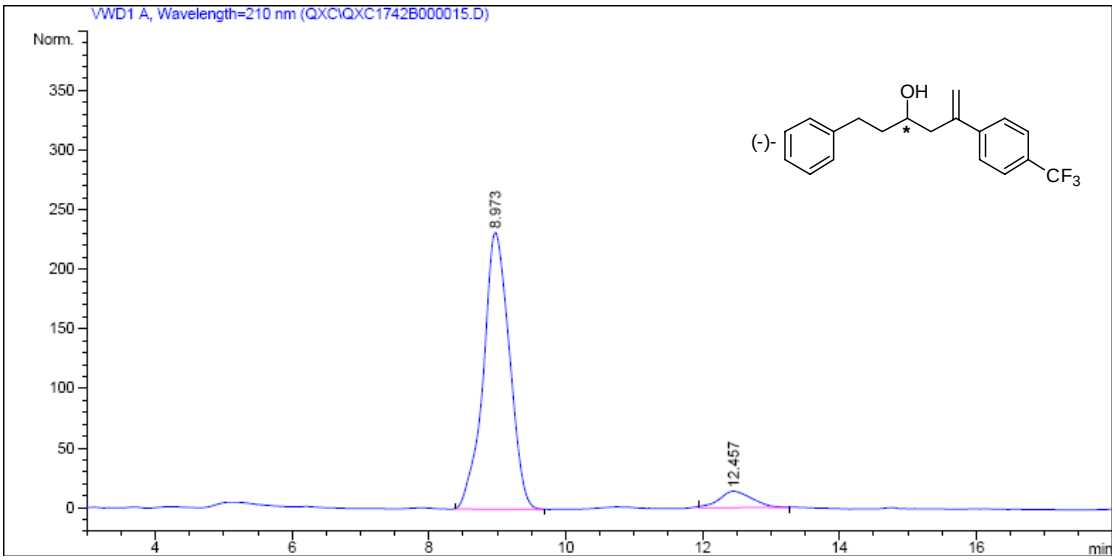



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 7.828 | BB | 0.2278 | 7536.00732 | 92.9717 |
| 2 | 9.511 | BB | 0.2482 | 569.69128 | 7.0283 |

**1-Phenyl-5-(4-(trifluoromethyl)phenyl)hex-5-en-3-ol (7qe)**




| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Area % |
|---|---|---|---|---|---|
| 1 | 8.973 | BB | 0.4155 | 6150.49609 | 93.0220 |
| 2 | 12.457 | BB | 0.4780 | 461.37439 | 6.9780 |