Supporting Information

Catalytic Asymmetric Aldehyde Prenylation and Application in the Total Synthesis of (–)-Rosiridol and (–)-Bifurcadiol

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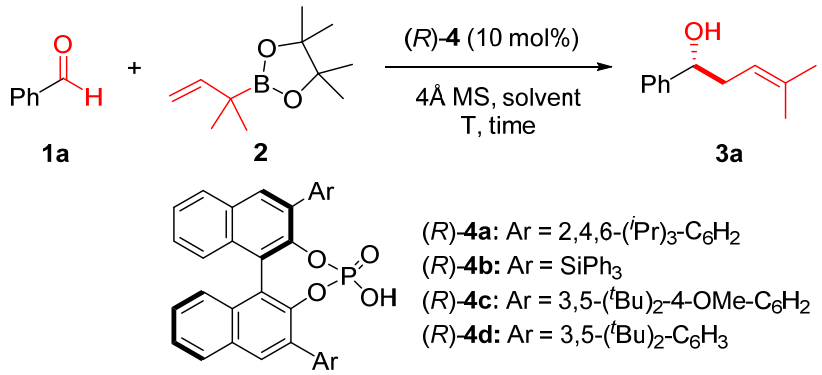
General information

All reactions involving air-sensitive compounds were performed in oven-dried glassware by using standard Schlenk techniques. All reactions were monitored by TLC, TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). ^{13}C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.2 ppm). ^{19}F NMR (471 MHz) spectra were recorded on a Bruker Avance 500 instrument. Optical rotations were measured on a Hanon Automatic Polarimeter P850. Infrared spectra were recorded on a NICOLET FT/IR-200 spectrometer. High resolution MS (ESI-orbitrap) were obtained on Thermo Fisher Q Exactive Mass Spectrometer. Melting points were recorded on an X-4 series microscope melting point apparatus at ambient pressure.

Table S1 Optimization of the reaction conditions[a]



entry	catalyst	solvent	T / °C	time/h	yield/%[b]	*ee*/%[c]
1	–	toluene	rt	5	82	0
2	**4a**	toluene	0	12	86	73
3	**4b**	toluene	0	18	92	26
4	**4c**	toluene	0	10	85	56
5	**4d**	toluene	0	13	92	64
6	**4a**	THF	0	12	89	60
7	**4a**	DCM	0	10	93	48
8	**4a**	toluene	–20	20	90	95
9	**4a**	toluene	–30	24	94	95
10	**4a**	toluene	–40	28	92	96
11	**4a**	toluene	–50	30	89	97
12	**4a**	toluene	–60	32	93	98
13[d]	**4a**	toluene	–60	36	89	76
14[e]	**4a**	toluene	–60	38	90	83
15[f]	**4a**	toluene	–60	26	92	98

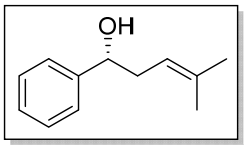
[a] Reaction conditions (unless otherwise specified): **1a** (0.10 mmol), **2** (0.15 mmol), (*R*)-**4** (10 mol%), 4 Å MS (25 mg), solvent (0.3 mL). [b] Isolated yield. [c] The enantiomeric excess (ee) was determined by chiral HPLC analysis. [d] In the absence of 4 Å MS. [e] 5 mol% of (*R*)-**4a**. [f] 15 mol% of (*R*)-**4a**.

General procedure for asymmetric isoprenylboration of aldehydes

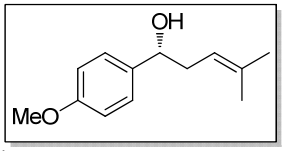
To an oven dried 2 mL test tube with a stir bar was added catalyst **(*R*)-4** (10 mol%) and 4 Å MS (25.0 mg). In nitrogen atmosphere, aldehyde **1** (1.0 equiv, 0.10 mmol) and anhydrous solvent (0.2 mL) were added at rt. The reaction mixture was then cooled to the temperature indicated in the main text followed by the addition of a solution of dimethyl allylboration pinacol ester **2**[1] (1.5 equiv, 0.15 mmol) (0.1 mL of solvent) over 20 minutes. The mixture was stirred for the time indicated in the main text at the same temperature, then subjected to the preparative thin layer chromatography.

Characterization data of chiral homoprenyl alcohols

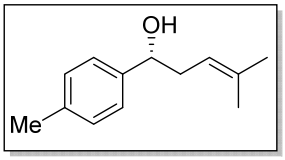
(*R*)-4-methyl-1-phenylpent-3-en-1-ol (3a): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 93% yield (16.3 mg) as a colorless oil. R_f = 0.53 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel OD-H column, *n*-hexane:*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 7.10 min, t_{major} = 8.07 min), *ee* = 98%, $[\alpha]_D^{25}$ = +27.0 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.33 (m, 4H), 7.28−7.27 (m, 1H), 5.18 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.69 (dd, *J* = 7.7, 5.3 Hz, 1H), 2.62−2.30 (m, 2H), 2.00 (brs, 1H), 1.73 (s, 3H), 1.62 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.30, 135.68, 128.33, 127.38, 125.82, 119.77, 74.06, 38.30, 25.89, 17.97 ppm. IR (neat): ν = 3373, 2917, 2348, 1493, 1451, 1108, 1050, 753, 700 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{17}O^+$, 177.1201, found: 177.1270.



(*R*)-1-(4-methoxyphenyl)-4-methylpent-3-en-1-ol (3b): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 92% yield (19.0 mg) as a yellow oil. R_f = 0.34 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel OD-H column, *n*-hexane:*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 9.11 min, t_{major} = 10.07 min), *ee* = 96%, $[\alpha]_D^{25}$ = +45.6 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.15 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H), 4.62 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.80 (s, 3H), 2.51−2.45 (m, 1H), 2.39−2.35 (m, 1H), 2.02 (brs, 1H), 1.72 (s, 3H), 1.61 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.94, 136.51, 135.39, 127.06, 119.92, 113.73, 73.70, 55.29, 38.19, 25.88, 17.98 ppm. IR (neat): ν = 3409, 2965, 2348, 1612, 1512, 1443, 1246, 1175, 830 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{19}O_2^+$, 207.2808, found: 207.1379.

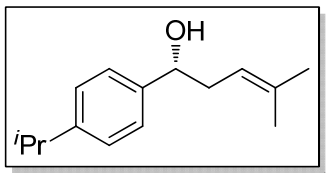


(*R*)-4-methyl-1-(p-tolyl)pent-3-en-1-ol (3c): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 95% yield (18.1 mg) as a colorless oil. R_f = 0.62 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 28.08 min, t_{major} = 29.41 min), *ee* = 98%, $[\alpha]_D^{25}$ = +62.9 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.16 (dd, *J* =

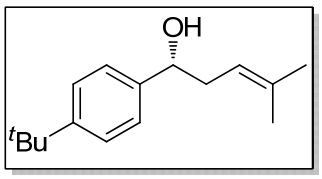


7.2, 7.0 Hz, 1H), 4.64 (dd, *J* = 7.8, 5.3 Hz, 1H), 2.50−2.46 (m, 1H), 2.44−2.41 (m, 1H), 2.34 (s, 3H), 2.00 (brs, 1H), 1.72 (s, 3H), 1.61 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.36, 137.01, 135.46, 129.02, 125.78, 119.93, 73.93, 38.23, 25.89, 21.11, 17.99 ppm. IR (neat): ν = 3379, 2918, 2348, 1900, 1514, 1447, 1050, 816, 555 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{19}O^+$, 191.1358, found: 191.1038.

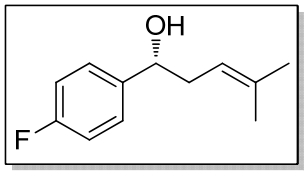
(*R*)-1-(4-isopropylphenyl)-4-methylpent-3-en-1-ol (3d): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 92% yield (20.0 mg) as a brown oil. R_f = 0.52 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 12.67 min, t_{major} = 14.18 min), *ee* = 98%, $[\alpha]_D^{25}$ = +51.8 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.20 (dd, *J* = 7.5, 7.2 Hz, 1H), 4.65 (dd, *J* = 8.2, 5.0 Hz, 1H), 2.91 (m, 1H), 2.51−2.46 (m, 1H), 2.41−2.38 (m, 2H), 1.74 (s, 3H), 1.62 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.08, 141.72, 135.46, 126.39, 125.82, 120.02, 73.96, 38.17, 33.83, 25.90, 24.03, 17.98 ppm. IR (neat): ν = 3380, 2961, 1904, 1671, 1452, 1102, 885, 828, 577 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{15}H_{23}O^+$, 219.1671, found: 219.1620.



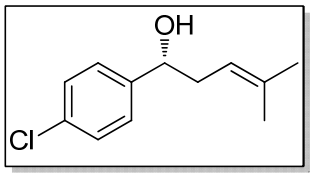
(*R*)-1-(4-(tert-butyl)phenyl)-4-methylpent-3-en-1-ol (3e): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 94% yield (21.8 mg) as a colorless oil. R_f = 0.47 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 11.00 min, t_{major} = 12.47 min), *ee* = 98%, $[\alpha]_D^{25}$ = +52.5 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.20 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H), 4.66 (dd, *J* = 8.2, 4.9 Hz, 1H), 2.50−2.46 (m, 1H), 2.43−2.38 (m, 1H), 1.74 (s, 3H), 1.63 (s, 3H), 1.33 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.33, 141.32, 135.46, 125.55, 125.25, 120.07, 73.88, 38.13, 34.51, 31.39, 25.91, 17.99 ppm. IR (neat): ν = 3374, 2963, 1510, 1450, 1363, 1053, 829, 801, 581 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{16}H_{25}O^+$, 233.1827, found: 233.1872.



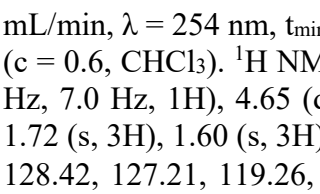
(*R*)-1-(4-fluorophenyl)-4-methylpent-3-en-1-ol (3f): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 92% yield (17.8 mg) as a brown oil. R_f = 0.59 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 99:1, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 30.44 min, t_{major} = 37.85 min), *ee* = 97%, $[\alpha]_D^{25}$ = +21.5 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.30 (m, 2H), 7.03−7.00 (m, 2H), 5.14 (dd, *J* = 7.3, 7.0 Hz, 1H), 4.65 (dd, *J* = 7.7, 5.4 Hz, 1H), 2.49−2.42 (m, 1H), 2.40−2.35 (m, 1H), 1.72 (s, 3H), 1.60 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.07 (d, 245.4 Hz), 139.95, 135.95, 127.40 (d, 7.9 Hz), 119.44, 115.08 (d, 21.3 Hz), 73.40, 38.38, 25.88, 17.94 ppm. IR (neat): ν = 3382, 2915, 1604, 1510, 1223, 1052, 833, 786, 555 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{16}FO^+$, 195.1107, found: 195.0871.



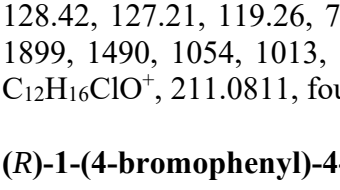
(*R*)-1-(4-chlorophenyl)-4-methylpent-3-en-1-ol (3g): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 90% yield (18.9 mg) as a colorless oil. R_f = 0.63 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 99:1, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 26.34 min, t_{major} = 28.25 min), *ee* = 95%, $[\alpha]_D^{25}$ = +41.23 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.27 (m, 4H), 5.13 (dd, *J* = 7.5 Hz, 7.0 Hz, 1H), 4.65 (dd, *J* = 7.6, 5.4 Hz, 1H), 2.50−2.33 (m, 2H), 2.08 (brs, 1H), 1.72 (s, 3H), 1.60 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.71, 136.17, 132.97, 128.42, 127.21, 119.26, 73.33, 38.31, 25.89, 17.97 ppm. IR (neat): ν = 3374, 2914, 1899, 1490, 1054, 1013, 825, 720, 548 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{16}ClO^+$, 211.0811, found: 211.0727.



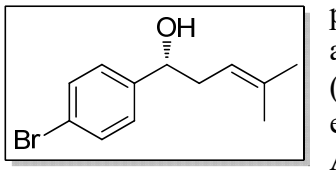
(*R*)-1-(4-bromophenyl)-4-methylpent-3-en-1-ol (3h): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 91% yield (23.1 mg) as a colorless oil. R_f = 0.60 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 20.70 min, t_{major} = 22.19 min), *ee* = 94%, $[\alpha]_D^{25}$ = +53.9 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.13 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.64 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.55−2.27 (m, 2H), 1.72 (s, 3H), 1.60 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.24, 136.20, 131.37, 127.57, 121.07, 119.23, 73.36, 38.27, 25.89, 17.98 ppm. IR (neat): ν = 3374, 2913, 1899, 1486, 1069, 1009, 883, 821, 546 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{16}BrO^+$, 255.0306, found: 255.2473.



(*R*)-1-([1,1'-biphenyl]-4-yl)-4-methylpent-3-en-1-ol (3i): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 98% yield (24.6 mg) as a colorless oil. R_f = 0.48 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 22.03 min, t_{major} = 27.03 min), *ee* = 98%, $[\alpha]_D^{25}$ = +52.4 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61−7.58 (m, 4H), 7.49−7.41 (m, 4H), 7.36 (d, *J* = 7.3 Hz, 1H), 5.22 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.74 (dd, *J* = 8.0, 5.1 Hz, 1H), 2.62−2.41 (m, 2H), 1.76 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.34, 140.94, 140.33, 135.84, 128.76, 127.09, 126.28, 119.72, 73.81, 38.29, 25.93, 18.03 ppm. IR (neat): ν = 3393, 2924, 2304, 1486, 1378, 1048, 1005, 884, 573 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{18}H_{21}O^+$, 253.1514, found: 253.0743.

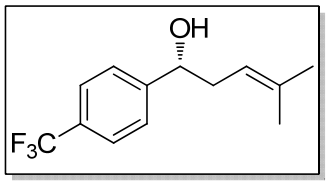


(*R*)-4-methyl-1-(4-nitrophenyl)pent-3-en-1-ol (3j): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 93% yield (20.5 mg) as a brown oil. R_f = 0.32 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 37.72 min, t_{major} = 39.57 min), *ee* = 95%, $[\alpha]_D^{25}$ = +44.23

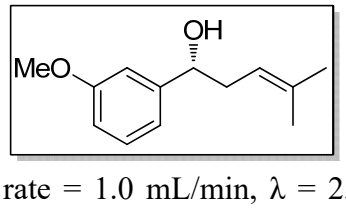


(c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 5.13 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 4.79 (dd, *J* = 6.5 Hz, 6.5 Hz, 1H), 2.45−2.43 (m, 2H), 2.25 (brs, 1H), 1.73 (s, 3H), 1.59 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.58, 147.18, 137.12, 126.55, 123.53, 118.49, 73.00, 38.37, 25.90, 17.98 ppm. IR (neat): ν = 3417, 2915, 2451, 1602, 1519, 1058, 854, 710, 542 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{16}NO_3^+$, 222.1052, found: 222.0894.

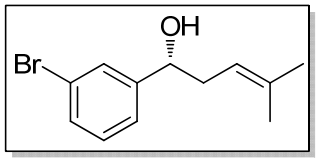
(*R*)-4-methyl-1-(4-(trifluoromethyl)phenyl)pent-3-en-1-ol (3k): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 96% yield (21.5 mg) as a chocolate oil. R_f = 0.59 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 31.91 min, t_{major} = 41.39 min), *ee* = 98%, $[\alpha]_D^{25}$ = +4.5 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.15 (dd, *J* = 8.0, 7.0 Hz, 1H), 4.74 (dd, *J* = 6.5 Hz, 6.5 Hz, 1H), 2.46−2.42 (m, 2H), 2.16 (brs, 1H), 1.74 (s, 3H), 1.60 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.18, 136.59, 129.53 (q, *J* = 32.4 Hz), 126.07, 125.23 (q, *J* = 3.8 Hz), 124.21 (q, *J* = 272.4 Hz), 118.97, 73.33, 38.35, 25.88, 17.94 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.43 ppm. IR (neat): ν = 3384, 2917, 1620, 1418, 1326, 1165, 1126, 842, 607 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{16}F_3O^+$, 245.1075, found: 245.1358.



(*R*)-1-(3-methoxyphenyl)-4-methylpent-3-en-1-ol (3l): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 93% yield (19.1 mg) as a slightly yellow oil. R_f = 0.63 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel IC-3 column, *n*-hexane:*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 14.17 min, t_{major} = 15.14 min), *ee* = 95%, $[\alpha]_D^{25}$ = +44.2 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 4.7 Hz, 2H), 6.86−6.76 (m, 1H), 5.17 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.65 (dd, *J* = 7.8, 5.2 Hz, 1H), 3.81 (s, 3H), 2.48−2.41 (m, 2H), 1.72 (s, 3H), 1.61 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.69, 146.06, 135.64, 129.34, 119.76, 118.18, 112.87, 111.34, 73.96, 55.24, 38.23, 25.89, 17.98 ppm. IR (neat): ν = 3317, 2914, 1927, 1600, 1487, 1260, 1044, 877, 699 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{19}O_2^+$, 207.1307, found: 207.1482.

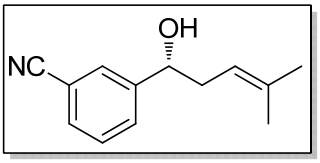


(*R*)-1-(3-bromophenyl)-4-methylpent-3-en-1-ol (3m): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 94% yield (23.9 mg) as a colorless oil. R_f = 0.35 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel OD-H column, *n*-hexane:*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 7.67 min, t_{major} = 8.75 min), *ee* = 97%, $[\alpha]_D^{25}$ = +52.66 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.44−7.42 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 5.19 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.68 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.56−2.38 (m, 2H), 2.13 (brs, 1H), 1.78 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.59, 136.38, 130.38, 129.89, 128.95, 124.44,

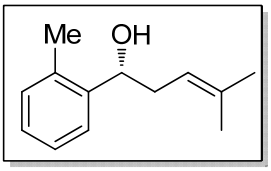


122.49, 119.18, 73.29, 38.30, 25.91, 18.00 ppm. IR (neat): ν = 3374, 2914, 1939, 1594, 1569, 1193, 1053, 783, 696 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{16}BrO^+$, 255.0306, found: 255.1043.

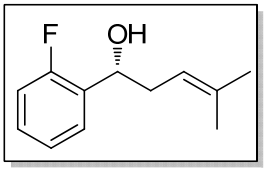
(*R*)-3-(1-hydroxy-4-methylpent-3-en-1-yl)benzonitrile (3n): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 92% yield (18.4 mg) as a colorless oil. R_f = 0.72 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel OD-H column, *n*-hexane:*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 13.93 min, t_{major} = 15.22 min), *ee* = 95%, $[\alpha]_D^{25}$ = +48.5 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.61–7.51 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 5.16–5.08 (m, 1H), 4.70 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.42−2.30 (m, 2H), 1.73 (s, 3H), 1.58 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.71, 136.87, 130.93, 130.31, 129.53, 129.04, 118.92, 118.65, 112.27, 72.89, 38.35, 25.90, 17.96 ppm. IR (neat): ν = 3355, 2915, 2230, 1443, 1058, 902, 801, 694, 607 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{16}NO^+$, 202.1154, found: 202.1038.



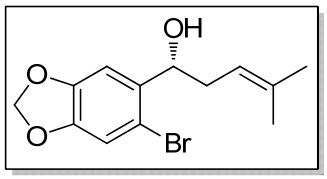
(*R*)-4-methyl-1-(o-tolyl)pent-3-en-1-ol (3o): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 99% yield (18.8 mg) as a slightly yellow oil. R_f = 0.58 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 11.43 min, t_{major} = 13.89 min), *ee* = 96%, $[\alpha]_D^{25}$ = +36.2 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.24 (dd, *J* = 13.2, 5.8 Hz, 1H), 7.20−7.07 (m, 2H), 5.22 (dd, *J* = 7.5 Hz, 7.0 Hz, 1H), 4.92 (dd, *J* = 8.0, 4.9 Hz, 1H), 2.49−2.37 (m, 2H), 2.33 (s, 3H), 1.93 (brs, 1H), 1.74 (s, 3H), 1.63 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.37, 135.61, 134.41, 130.28, 127.10, 126.22, 125.20, 120.06, 70.45, 37.12, 25.91, 19.07, 17.95 ppm. IR (neat): ν = 3379, 2917, 2230, 1450, 1047, 882, 756, 726, 452 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{19}O^+$, 191.1358, found: 191.1322.



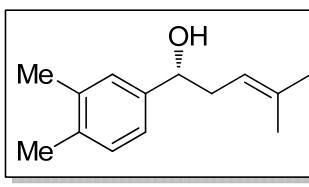
(*R*)-1-(2-fluorophenyl)-4-methylpent-3-en-1-ol (3p): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 95% yield (18.4 mg) as a colorless oil. R_f = 0.35 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel IF-3 column, *n*-hexane:*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 21.76 min, t_{major} = 23.94 min), *ee* = 90%, $[\alpha]_D^{25}$ = +18.36 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.46 (m, 1H), 7.23 (dd, *J* = 14.2, 7.0 Hz, 1H), 7.15−7.12 (m, 1H), 7.07−6.94 (m, 1H), 5.19 (dd, *J* = 7.5, 7.0 Hz, 1H), 5.00 (dd, *J* = 6.5 Hz, 6.0 Hz, 1H), 2.49−2.42 (m, 2H), 2.08 (brs, 1H), 1.73 (s, 3H), 1.61 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.73 (d, 245.7 Hz), 136.04, 131.21 (d, 13.1Hz), 128.64 (d, 8.3 Hz), 127.23 (d, 4.7 Hz), 124.13 (d, 3.4 Hz), 119.35, 115.15 (d, 21.9Hz), 68.08, 37.00, 25.89, 17.91 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ −119.65 ppm. IR (neat): ν = 3380, 2916, 1586, 1454, 1222, 1055, 886, 823, 757, 519 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{16}FO^+$, 195.1107, found: 195.0835.



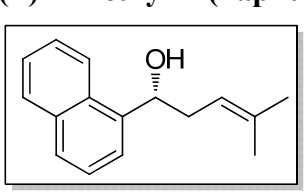
(*R*)-1-(6-bromobenzo[d][1,3]dioxol-5-yl)-4-methylpent-3-en-1-ol (3q): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 94% yield (28.0 mg) as a white solid, R_f = 0.38 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 25.09 min, t_{major} = 39.37 min), *ee* = 90%, $[\alpha]_D^{25}$ = +48.5 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.95 (s, 1H), 5.96 (d, *J* = 2.0 Hz, 3H), 5.22 (dd, *J* = 7.3 Hz, *J* = 7.0 Hz, 1H), 4.97 (dd, *J* = 8.5, 4.1 Hz, 1H), 2.53−2.38 (m, 1H), 2.31−2.65 (m, 1H), 1.75 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.62, 147.36, 136.64, 136.09, 119.46, 112.36, 111.97, 107.25, 101.68, 72.64, 36.68, 25.95, 18.03 ppm. IR (neat): ν = 3348, 2687, 2105, 1354, 1157, 982, 746, 716, 500 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{16}BrO_3^+$, 299.1304, found: 299.0205.



(*R*)-1-(3,4-dimethylphenyl)-4-methylpent-3-en-1-ol (3r): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 93% yield (18.7 mg) as a colorless oil. TLC: R_f = 0.66 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 13.30 min, t_{major} = 14.39 min), *ee* = 99%, $[\alpha]_D^{25}$ = +16.56 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.12−7.08 (m, 2H), 5.19 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H), 4.62 (dd, *J* = 8.1, 5.0 Hz, 1H), 2.50−2.46 (m, 1H), 2.44−2.36 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.95 (brs, 1H), 1.74 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.41, 129.59, 127.11, 123.25, 120.09, 73.96, 38.22, 25.90, 19.83, 19.45, 18.02 ppm. IR (neat): ν = 3384, 2920, 1672, 1470, 1054, 880, 820, 786, 718, 589 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{14}H_{21}O^+$, 205.1514, found: 205.1456.



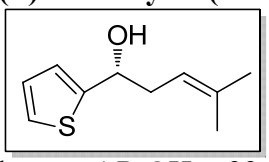
(*R*)-4-methyl-1-(naphthalen-1-yl)pent-3-en-1-ol (3s): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 98% yield (22.1 mg) as a slightly yellow oil. R_f = 0.50 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 21.83 min, t_{major} = 26.31 min), *ee* = 98%, $[\alpha]_D^{25}$ = +53.06 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.57−7.43 (m, 4H), 5.48 (dd, *J* = 8.3, 4.4 Hz, 1H), 5.32 (dd, *J* = 7.5, 7.0 Hz, 1H), 2.73−2.64 (m, 1H), 2.61−2.57 (m, 1H), 2.17 (brs, 1H), 1.76 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.84, 135.74, 133.80, 130.42, 128.91, 127.84, 125.91, 125.47, 123.13, 122.81, 120.18, 70.86, 37.40, 25.94, 18.06 ppm. IR (neat): ν = 3387, 2914, 1596, 1510, 1376, 1069, 884, 778, 733, 437 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{16}H_{19}O^+$, 227.1358, found: 227.1035.



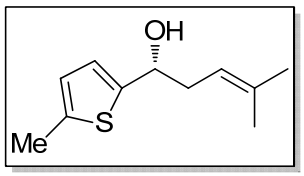
(*R*)-4-methyl-1-(naphthalen-2-yl)pent-3-en-1-ol (3t): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 96% yield (21.7 mg) as a colorless oil. R_f = 0.55 (PE/EA= 10:1). The

enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 30.04 min, t_{major} = 32.22 min), *ee* = 99%, $[\alpha]_D^{25}$ = +23.0 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89−7.78 (m, 4H), 7.55−7.41 (m, 3H), 5.21 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.86 (dd, *J* = 7.7, 5.4 Hz, 1H), 2.61−2.49 (m, 2H), 1.74 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.69, 135.84, 133.32, 132.93, 128.10, 127.96, 127.68, 126.06, 125.72, 124.46, 124.13, 119.69, 74.15, 38.21, 25.92, 18.04 ppm. IR (neat): ν = 3378, 2912, 1601, 1510, 1445, 1052, 895, 818, 747 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{16}H_{19}O^+$, 227.1358, found: 227.0879.

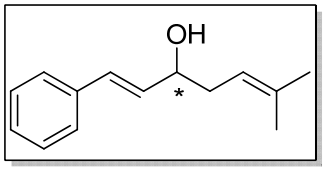
(*R*)-4-methyl-1-(thiophen-2-yl)pent-3-en-1-ol (3u): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 94% yield (17.1 mg) as a slightly yellow oil. R_f = 0.43 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel IC-3 column, *n*-hexane:*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 29.49 min, t_{major} = 32.86 min), *ee* = 99%, $[\alpha]_D^{25}$ = +23.6 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25−7.22 (m, 1H), 6.97 (d, *J* = 4.6 Hz, 2H), 5.19 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.93 (dd, *J* = 7.0 Hz, 6.0 Hz, 1H), 2.62−2.52 (m, 2H), 2.14 (brs, 1H), 1.74 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.24, 136.09, 126.57, 124.42, 123.55, 119.18, 70.09, 38.27, 25.92, 18.06 ppm. IR (neat): ν = 3384, 2914, 1671, 1441, 1231, 1038, 878, 852, 698 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{10}H_{15}OS^+$, 183.0675, found: 183.1035.



(*R*)-4-methyl-1-(5-methylthiophen-2-yl)pent-3-en-1-ol (3v): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 97% yield (19.0 mg) as a slightly yellow oil. R_f = 0.57 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel OD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 12.79 min, t_{major} = 14.73 min), *ee* = 96%, $[\alpha]_D^{25}$ = +28.3 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, *J* = 3.3 Hz, 1H), 6.60 (d, *J* = 2.6 Hz, 1H), 5.18 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.82 (dd, *J* = 6.5 Hz, 6.5 Hz, 1H), 2.61−2.48 (m, 2H), 2.46 (s, 3H), 2.07 (brs, 1H), 1.73 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.74, 139.07, 135.76, 124.54, 123.58, 119.38, 70.20, 38.03, 25.90, 18.07, 15.37 ppm. IR (neat): ν = 3460, 2918, 2734, 1674, 1377, 1160, 1066, 797, 542 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{11}H_{17}OS^+$, 197.0922, found: 197.1038.

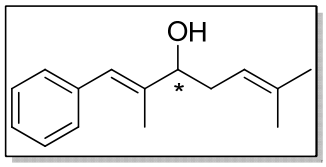


(–)-(*E*)-6-methyl-1-phenylhepta-1,5-dien-3-ol (3w): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 93% yield (18.8 mg) as a slightly yellow oil. R_f = 0.69 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 20.30 min, t_{major} = 22.99 min), *ee* = 93%, $[\alpha]_D^{25}$ = −11.8 (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26−7.20 (m, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.20 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.30 (dd, *J* = 6.5, 6.0 Hz, 1H), 2.37−2.34 (m, 2H), 1.74 (s, 3H), 1.66 (s, 3H) ppm. ^{13}C NMR (126

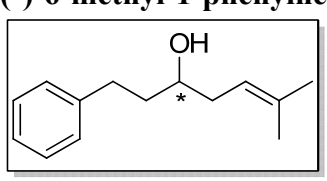


MHz, $CDCl_3$) δ 136.86, 135.63, 132.03, 130.05, 128.56, 127.55, 126.47, 119.28, 72.51, 36.40, 25.95, 18.09 ppm. IR (neat): ν = 3362, 2913, 1596, 1377, 1093, 966, 838, 747, 536 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{14}H_{19}O^+$, 203.1358, found: 203.1034.

(–)-(*E*)-2,6-dimethyl-1-phenylhepta-1,5-dien-3-ol (3x): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 94% yield (20.3 mg) as a slightly yellow oil. R_f = 0.52 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel IC-3 column, *n*-hexane:*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 23.88 min, t_{major} = 27.62 min), *ee* = 98%, $[\alpha]_D^{25}$ = −25.76 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35−7.35 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 5.18 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.18 (dd, *J* = 6.5, 6.0 Hz, 1H), 2.39−2.36 (m, 2H), 1.89 (s, 3H), 1.75 (s, 3H), 1.68 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.91, 137.73, 135.22, 128.99, 128.08, 126.34, 125.48, 119.84, 67.97, 34.45, 25.94, 25.62, 18.05, 13.71 ppm. IR (neat): ν = 3375, 2915, 1599, 1492, 1046, 917, 863, 745, 514 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{15}H_{21}O^+$, 217.1514, found: 217.0957.

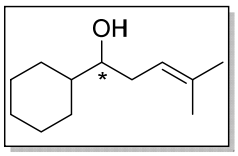


(–)-6-methyl-1-phenylhept-5-en-3-ol (3y): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 96% yield (19.6 mg) as a colorless oil. R_f = 0.33 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 31.30 min, t_{major} = 33.02 min), *ee* = 84%, $[\alpha]_D^{25}$ = −14.96 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.30−7.27 (m, 2H), 7.20 (dd, *J* = 17.4, 7.4 Hz, 3H), 5.17 (dd, *J* = 7.5, 7.0 Hz, 1H), 3.64 (dd, *J* = 6.5, 6.0 Hz, 1H), 2.88−2.77 (m, 1H), 2.77−2.63 (m, 1H), 2.20 (t, *J* = 6.8 Hz, 2H), 1.86−1.76 (m, 2H), 1.74 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.24, 135.42, 128.45, 125.77, 119.92, 71.02, 38.46, 36.35, 32.18, 25.96, 18.03 ppm. (neat): ν = 3384, 2925, 1943, 1665, 1452, 1053, 873, 699, 541 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{14}H_{21}O^+$, 205.1514, found: 205.1359.



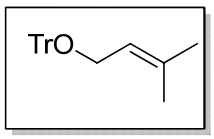
(–)-5-methyl-1-phenylhex-4-en-2-ol (3z): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 96% yield (18.2mg) as a slightly yellow oil. R_f = 0.57 (PE/EA= 10:1). The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1.0 mL/min, λ = 254 nm, t_{minor} = 10.45 min, t_{major} = 11.87 min), *ee* = 89%, $[\alpha]_D^{25}$ = −35.74 (c = 0.6, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35−7.28 (m, 2H), 7.23−7.22 (m, 3H), 5.21 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H), 3.86−3.81 (m, 1H), 2.83 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.72 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.23 (t, *J* = 6.7 Hz, 2H), 1.75 (s, 3H), 1.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.72, 135.14, 129.40, 128.49, 126.38, 119.96, 72.68, 43.30, 35.54, 25.95, 18.04 ppm. IR (neat): ν = 3401, 2916, 1947, 1601, 1495, 1451, 1049, 856, 699 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{13}H_{19}O^+$, 191.1358, found:191.1278.

(–)-1-cyclohexyl-4-methylpent-3-en-1-ol (3aa): According to the general procedure for the asymmetric isoprenylboration of aldehydes, the title compound was obtained in 94% yield (17.1 mg) as a colorless oil. R_f = 0.50 (PE/EA= 10:1). Enantiomeric excess was determined with the 2,4-dinitrobenzoate ester of compound **3aa** by HPLC (Chiralcel AD-H column, *n*-hexane:*i*-PrOH = 98:2, flow rate = 1 mL/min, λ = 254 nm, t_{minor} = 11.57 min, t_{major} = 13.80 min), *ee* = 84%, $[\alpha]_D^{25} = -28.0$ (c = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26−5.13 (m, 1H), 3.43−3.30 (m, 1H), 2.23−2.12 (m, 2H), 1.76 (s, 3H), 1.66 (m, 3H), 1.95−1.50 (m, 5H), 1.44−0.98 (m, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.10, 120.66, 75.78, 43.09, 32.98, 29.21, 28.19, 26.58, 26.34, 26.20, 25.96, 17.98 ppm. (neat): ν = 3383, 2923, 2234, 1785, 1451, 1208, 1107, 753, 720 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{12}H_{23}O^+$, 183.1317, found: 183.1671.

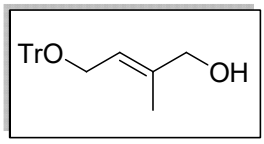


Synthetic applications

(((3-methylbut-2-en-1-yl)oxy)methanetriyl)tribenzene (6)[2]: Under argon, 3-methyl-2-buten-1-ol **5** (1.2 equiv, 5 g, 58.0 mmol) and trityl chloride (1.0 equiv, 13.75 g, 50 mmol) were dissolved into CH_2Cl_2 (160 mL) producing a clear olive green solution. After cooling to 0 °C, Et_3N (2.0 equiv, 16 mL, 160 mmol) and DMAP (10 mol%, 100 mg, catalytic) were added causing the solution to turn yellow and form a white precipitate. The reaction was allowed to warm to 23 °C and stir overnight. The reaction was diluted with Et_2O (150 mL) and washed with 1% HCl (3 x 10 mL). The organic layer was dried over brine and Na_2SO_4, and condensed. The crude material was purified by silica chromatography (PE/EA = 10:1) to give 18.3 g (quantitative) of the desired trityl ether **6** as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.4, 1.2 Hz, 8H), 7.34 (t, *J* = 7.6 Hz, 5H), 7.27 (t, *J* = 7.0 Hz, 3H), 5.50 (t, *J* = 6.5, 1.3 Hz, 1H), 3.64 (d, *J* = 6.6 Hz, 2H), 1.79 (s, 3H), 1.53 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.90, 140.56, 128.61, 127.92, 127.11, 126.16, 87.23, 66.48, 60.09, 59.70 ppm. IR (neat): ν = 3338, 3085, 3058, 3032, 2917, 2861, 1596, 1490, 1448, 1381, 1319, 1266, 1221, 1154, 1054, 899, 950, 763, 746, 706, 649, 633 cm^{-1}. HRMS (ESI; m/z): $[M+Na]^+$ calcd for $C_{24}H_{24}NaO^+$, 351.1287, found: 351.1276.

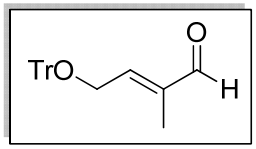


(*E*)-2-methyl-4-(trityloxy)but-2-en-1-ol (7)[3]**:** Under argon, SeO_2 (0.02 equiv, 57 mg, 0.52 mmol) and salicylic acid (0.12 equiv, 0.36 g, 2.6 mmol) were dissolved in CH_2Cl_2 (20 mL). Then $^tBuO_2H$ (5 N in benzene, 2.1 equiv, 10.3 mL, 50.7 mmol) was added. After stirring for 15 min, ether **6** (1.0 equiv, 8 g, 24 mmol) in CH_2Cl_2 (20 mL) was added dropwise and the reaction was allowed to stir for 48 h. The reaction was diluted with Et_2O (100 mL) and washed with 1.0 N NaOH (3 x 25 mL). The organic layer was dried with brine and Na_2SO_4, and condensed. The crude material was purified by silica chromatography (PE/EA = 5:1) to provide 3.2 g (40% yield) of alcohol **7** as a viscous clear oil. 3.4 g (45%) of starting material **6** was recovered along with 0.23 g of crude aldehyde **8**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 6H), 7.30 (t, *J* = 7.7 Hz, 6H), 7.24 (t, *J* = 7.3 Hz, 3H), 5.69 (t, *J* = 6.2 Hz, 1H), 4.02 (s, 2H), 3.69 (d, *J* = 6.2 Hz, 2H), 1.51 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.25, 137.53, 128.72, 127.83, 126.96, 122.32, 86.83, 68.20, 60.90

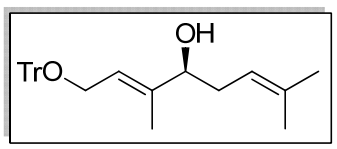


ppm. IR (neat): ν = 3338, 3085, 3058, 3032, 2917, 2861, 1596, 1490, 1448, 1381, 1319, 1266, 1221, 1154, 1054, 899, 950, 763, 746, 706, 649, 633 cm^{-1}. HRMS (ESI; m/z): $[M+Na]^+$ calcd for $C_{24}H_{24}NaO_2^+$, 367.4462, found: 367.3273.

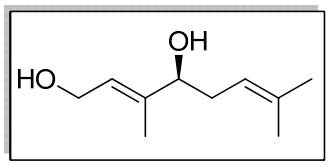
(*E*)-2-methyl-4-(trityloxy)but-2-enal (8)[4]: Allylic alcohol **7** (1.0 equiv, 3.2 g, 9.3 mmol) was dissolved into CH_2Cl_2 (175 mL). MnO_2 (31.2 equiv, 25 g, 0.29 mol) was added portionwise until the starting material was consumed as indicated by TLC. The mixture was filtered over celite, rinsing with CH_2Cl_2. Solvents were removed under reduced pressure to provide 2.7 g (85% yield) of the desired aldehyde **8** as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.55–7.45 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 6H), 7.32–7.22 (m, 4H), 6.61 (t, *J* = 1.5 Hz, 1H), 4.06 (d, *J* = 5.5 Hz, 2H), 1.59 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.53, 150.45, 143.64, 138.57, 128.62, 128.01, 127.29, 87.40, 61.57, 9.49 ppm. IR (KBr): ν = 3082, 3068, 3022, 2897, 2861, 1596, 1490, 1448, 1319, 1221, 1159, 1024, 920, 905, 763, 758, 673 cm^{-1}. HRMS (ESI; m/z): $[M+Na]^+$ calcd for $C_{24}H_{22}NaO_2^+$, 365.4303, found: 365.3721.



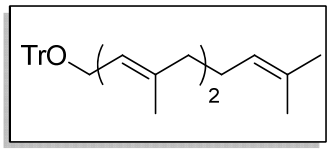
(*S*,*E*)-3,7-dimethyl-1-(trityloxy)octa-2,6-dien-4-ol (9): To an oven-dried 2 mL test tube with a stir bar was added catalyst (*R*)-**4a** (7.2 mg, 10 mol%) and aldehyde **8** (1.0 equiv, 34.2 mg, 0.1 mmol). In a nitrogen atmosphere, anhydrous toluene (0.2 mL) was added, and the reaction mixture was cooled to −60 °C, followed by the addition of a solution of dimethyl allylboration pinacol ester (1.5 equiv, 0.15 mmol) in anhydrous toluene (0.1 mL) over 10 min. The mixture was stirred for 32 h until consuming aldehyde **8**. Finally, the reaction mixture was subjected to the preparative thin-layer chromatography (PE/EA =10:1). The title compound was obtained in 89% yield (37.9 mg) as a slightly yellow oil. The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, n-hexane/i-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, tminor = 16.33 min, tmajor = 23.06 min), *ee* = 99 %, $[\alpha]_D^{25}$ = −53.2 (c = 0.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.56–7.48 (m, 5H), 7.34 (t, *J* = 7.6 Hz, 5H), 7.30–7.24 (m, 4H), 5.87–5.63 (m, 1H), 5.35–4.98 (m, 1H), 4.15–4.00 (m, 1H), 3.74 (d, *J* = 6.1 Hz, 2H), 2.34–2.25 (m, 2H), 1.78 (s, 3H), 1.69 (s, 3H), 1.52 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.28, 139.35, 134.94, 128.70, 127.78, 126.90, 122.95, 119.92, 86.76, 76.56, 61.01, 34.07, 25.93, 18.03, 12.31 ppm. IR (neat): ν = 3384, 3103, 3042, 2787, 2294, 1594, 1483, 1443, 1373, 1191, 1156, 1100, 876, 836, 763, 758, 673 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{29}H_{33}O_2^+$, 427.5898, found: 427.8794.



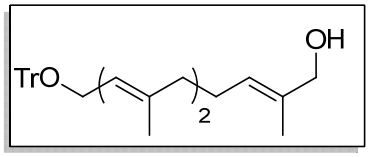
(–)-rosiridol: To an oven-dried 2 mL test tube with a stir bar was added trifluoromethanesulfonic acid (10 mol%) and compound **9** (37.9 mg). Then anhydrous CH_3OH (0.2 mL) was added, and the reaction mixture was cooled to 0 °C. Finally the reaction mixture was directly subjected to the preparative thin-layer chromatography (PE/EA =10:1). The title compound was obtained in 85% yield (13.9 mg) as a slightly yellow oil. $[\alpha]_D^{25}$ = −4.73 (c = 0.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.77−5.54 (m, 1H), 5.21−4.97 (m, 1H), 4.20 (dd, *J* = 6.6, 3.7 Hz, 2H), 4.10−3.92 (m, 1H), 2.27−2.23 (m, 2H), 1.72 (s, 3H), 1.68 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.36, 135.26, 124.51, 119.73, 76.37, 59.09, 34.15, 25.90, 18.01, 12.19 ppm. IR (neat): ν = 3354,



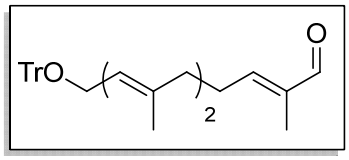
3075, 3009, 2830 2405, 1654, 1534, 1478, 1357, 1201, 1111, 978, 856, 775, 654, 573 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{10}H_{19}O_2^+$, 171.1307, found: 171.1207.

((((2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)oxy)methanetriyl)tribenzene (11)[5]**:** 

Under argon, *trans trans* Farnesol **10** (1.0 equiv, 5 g, 23 mmol) and trityl chloride (1.2 equiv, 6.3 g, 27 mmol) were dissolved into CH_2Cl_2 (120 mL) producing a clear olive green solution. After cooling to 0 °C, Et_3N (2.0 equiv, 8.3 mL, 43 mmol) and DMAP (10 mol%, 50 mg, catalytic) were added causing the solution to turn yellow and form a white precipitate. The reaction was allowed to warm to 23 °C and stir overnight. The reaction was diluted with Et_2O (120 mL) and washed with 1% HCl (2 x 10 mL). The organic layer was dried over brine and Na_2SO_4 and condensed. The crude material was purified by silica chromatography (PE/EA = 5:1) to give 9.3 g (quantitative) of the desired trityl ether **11** as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.4 Hz, 7H), 7.28 (t, *J* = 7.6 Hz, 6H), 7.20−7.18 (m, 2H), 5.45 (t, *J* = 6.3 Hz, 1H), 5.11−5.14 (m, 2H), 3.60 (d, *J* = 6.4 Hz, 2H), 2.19−1.90 (m, 10H), 1.67 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H), 1.46 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.48, 138.55, 135.21, 131.30, 128.77, 127.77, 126.86, 124.44, 124.02, 121.44, 86.67, 61.36, 39.79, 39.66, 26.83, 26.42, 25.76, 17.75, 16.60, 16.11 ppm. IR (neat): ν = 3057, 3022, 2921, 2854, 1954, 1664, 1597, 1447, 1379, 1220, 1153, 1051, 897, 761, 745, 704, 632 cm^{-1}. HRMS (ESI; m/z): $[M+Na]^+$ calcd for $C_{34}H_{40}NaO^+$, 487.3079, found: 487.2938.

(2*E*,6*E*,10*E*)-2,6,10-trimethyl-12-(trityloxy)dodeca-2,6,10-trien-1-ol (12)[6]: 

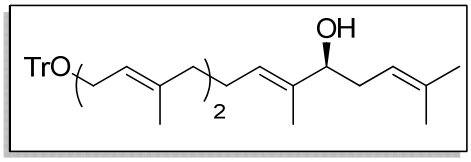
Under argon, SeO_2 (0.03 equiv, 23.0 mg, 0.32 mmol) and salicylic acid (0.2 equiv, 220.8 mg, 2.1 mmol) were dissolved into CH_2Cl_2 (20 mL). Then $^tBuO_2H$ (5 N in benzene, 2.0 equiv, 6.4 mL, 21.0 mmol) was added. After stirring for 15 min, ether **11** (1.0 equiv, 5 g, 10.7 mmol) in CH_2Cl_2 (20 mL) was added dropwise and the reaction was allowed to stir for 48 h. The reaction was diluted with Et_2O (50 mL) and washed with 1 N NaOH (3 x 25 mL). The organic layer was dried with brine and Na_2SO_4, and condensed. The crude material was purified by silica chromatography (PE/EA = 5:1) to provide 2.3 g (45%) of alcohol **12** as a viscous clear oil. 2.2 g (45%) of starting material **11** was recovered along with 0.15 g of crude aldehyde **13**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 5H), 7.30 (t, *J* = 7.6 Hz, 7H), 7.23 (t, *J* = 7.3 Hz, 3H), 5.46 (t, *J* = 6.0 Hz, 1H), 5.42−5.37 (m, 1H), 5.15 (t, *J* = 6.3 Hz, 1H), 3.98 (s, 2H), 3.61 (d, *J* = 6.4 Hz, 2H), 2.26−1.97 (m, 9H), 1.66 (s, 3H), 1.63 (s, 3H), 1.48 (s, 3H), 1.27 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.41, 138.43, 134.81, 134.70, 128.72, 127.74, 126.84, 126.09, 124.28, 121.43, 86.66, 69.01, 61.33, 39.58, 39.31, 26.33, 26.23, 25.78, 16.56, 16.05, 13.70 ppm. IR (neat): ν = 3348, 3157, 3103, 2872, 2543, 1876, 1754, 1697, 1545, 1400, 1367, 1209, 1052, 920, 761, 720, 698, 612 cm^{-1}. HRMS (ESI; m/z): $[M+Na]^+$ calcd for $C_{34}H_{40}NaO_2^+$, 503.3028, found: 503.3721.

(2*E*,6*E*,10*E*)-2,6,10-trimethyl-12-(trityloxy)dodeca-2,6,10-trienal (13)[7]: 

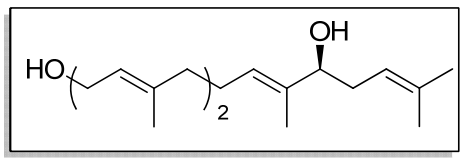
Allylic alcohol **13** (1.0 equiv, 2.3 g, 4.8 mmol) was dissolved into CH_2Cl_2 (50 mL). MnO_2 (30.0 equiv, 12.5 g, 0.14 mol) was added portionwise until the starting material was consumed as indicated by TLC. The mixture was filtered over celite, rinsing with CH_2Cl_2. Solvents were

removed under reduced pressure to provide 1.9 g (85% yield) of the desired aldehyde **13** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.48 (d, *J* = 7.3 Hz, 6H), 7.30 (t, *J* = 7.5 Hz, 7H), 7.23 (td, *J* = 6.2, 5.3, 3.2 Hz, 5H), 6.47 (t, *J* = 7.8 Hz, 1H), 5.51−5.39 (m, 1H), 5.19 (t, *J* = 7.3 Hz, 1H), 3.62 (d, *J* = 6.4 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.23−2.10 (m, 4H), 2.09−1.97 (m, 2H), 1.74 (s, 3H), 1.66 (s, 3H), 1.48 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.28, 154.43, 144.40, 139.37, 138.23, 133.62, 128.71, 127.75, 126.86, 125.33, 121.58, 86.65, 61.27, 39.44, 38.00, 27.48, 26.29, 16.56, 15.99, 9.24 ppm. IR (neat): ν = 3264, 3150, 2670, 2423, 1976, 1740, 1624, 1454, 1397, 1321, 1275, 1020, 950, 834, 734, 640, 623 cm^{-1}. HRMS (ESI; m/z): $[M+Na]^+$ calcd for $C_{34}H_{38}NaO_2^+$, 501.2872, found: 501.2047.

(*S*,6*E*,10*E*,14*E*)-2,6,10,14-tetramethyl-16-(trityloxy)hexadeca-2,6,10,14-tetraen-5-ol (14): To an oven-dried 2 mL test tube with a stir bar was added catalyst **(*R*)-4a** (10 mol%) and aldehyde **13** (47.8 mg, 0.1mmol). In a nitrogen atmosphere, anhydrous toluene (0.2 mL) was added, and the reaction mixture was then cooled to –60 °C, followed by the addition of a solution of dimethyl allylboration pinacol ester (0.15 mmol) in anhydrous toluene (0.1 mL) over 10 min. The mixture was stirred for 32 h until consuming aldehyde **13**. Finally, the reaction mixture was directly subjected to the preparative thin-layer chromatography (PE/EA =10:1). The title compound was obtained in 89% yield (51.0 mg) as a slightly yellow oil. The enantiomeric purity was determined by HPLC (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, tminor = 16.33 min, tmajor = 23.06 min), *ee* = 99 %, $[\alpha]_D^{25}$ = −53.2 (c = 0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.45 (m, 6H), 7.31 (t, *J* = 7.6 Hz, 6H), 7.24 (t, *J* = 7.3 Hz, 3H), 5.46 (t, *J* = 6.4 Hz, 1H), 5.41 (t, *J* = 6.9 Hz, 1H), 5.16 (t, *J* = 6.4 Hz, 1H), 5.14−5.08 (m, 1H), 3.99 (dd, *J* = 7.6, 5.7 Hz, 1H), 3.62 (d, *J* = 6.4 Hz, 2H), 2.34−2.26 (m, 1H), 2.26−2.18 (m, 1H), 2.14 (dt, *J* = 15.9, 7.1 Hz, 5H), 2.05 (d, *J* = 5.3 Hz, 5H), 1.74 (s, 3H), 1.66 (s, 3H), 1.64 (s, 3H), 1.63 (s, 3H), 1.49 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.44, 138.47, 136.77, 134.94, 134.55, 128.74, 127.75, 126.84, 126.10, 124.23, 121.42, 120.31, 86.65, 77.26，61.33, 39.62, 39.37, 34.26, 26.40, 26.26, 25.93, 18.04, 16.59, 16.08, 11.71 ppm. IR (neat): ν = 3348, 3224, 2720, 2543, 2130, 1987, 1823, 1723, 1547, 1374, 1298, 1235, 1054, 921, 893, 810, 732, 639 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{39}H_{49}O_2^+$, 549.3657, found: 549.3349.

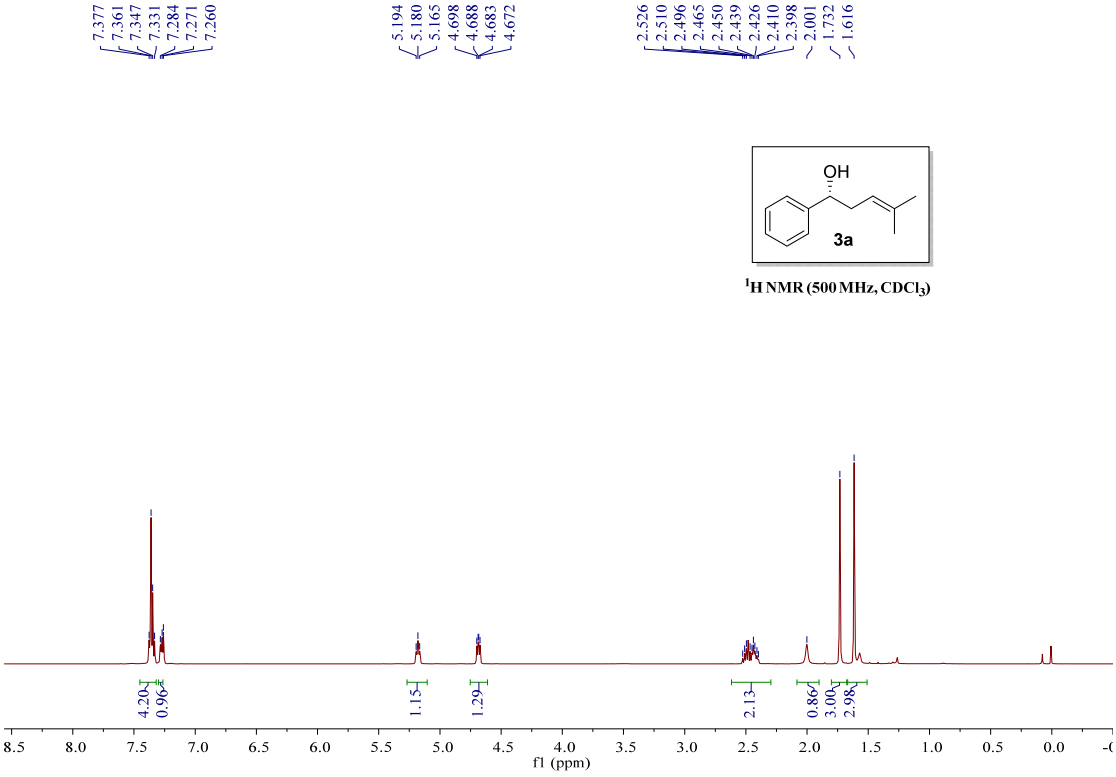


(–)-bifurcadiol: To an oven-dried 2 mL test tube with a stir bar was added trifluoromethanesulfonic acid (10 mol%) and compound **14** (51.0 mg). Then anhydrous CH_3OH (0.2 mL) was added, and the reaction mixture was then cooled to 0 °C. Finally the reaction mixture was directly subjected to the preparative thin-layer chromatography (PE/EA =10:1). The title compound was obtained in 80% yield (22.8 mg) as a slightly yellow oil. $[\alpha]_D^{25}$ = −4.73 (c = 0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45−5.41(m, 1H), 5.34−5.29 (m, 1H), 5.15−5. 12 (m, 1H), 5.07−5. 04 (m, 1H), 4.18 (d, *J* = 6.9 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 1H), 3.18 (s, 2H), 2.24–1.99 (m, 8H), 1.77–1.47 (m, 15H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.65, 135.03, 133.84, 132.72, 128.71, 124.04, 123.37, 120.65, 87.49, 59.37, 55.65, 39.52, 39.38, 32.52, 26.30, 26.13, 25.77, 17.94, 16.28, 15.95 ppm. IR

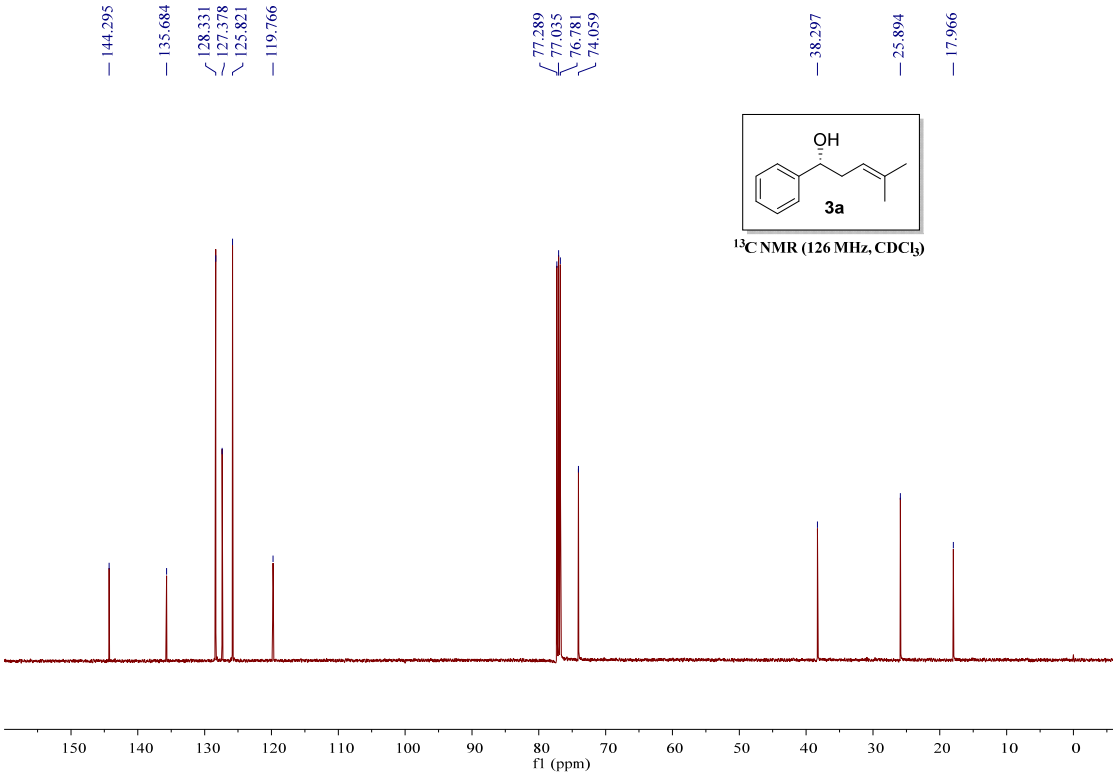


(neat): ν = 3438, 3154, 2642, 2421, 2334, 2032, 1923, 1832, 1622, 1347, 1319, 1234, 1020, 910, 824, 798, 712, 593 cm^{-1}. HRMS (ESI; m/z): $[M+H]^+$ calcd for $C_{20}H_{35}O_2^+$, 307.2559, found: 307.2498.

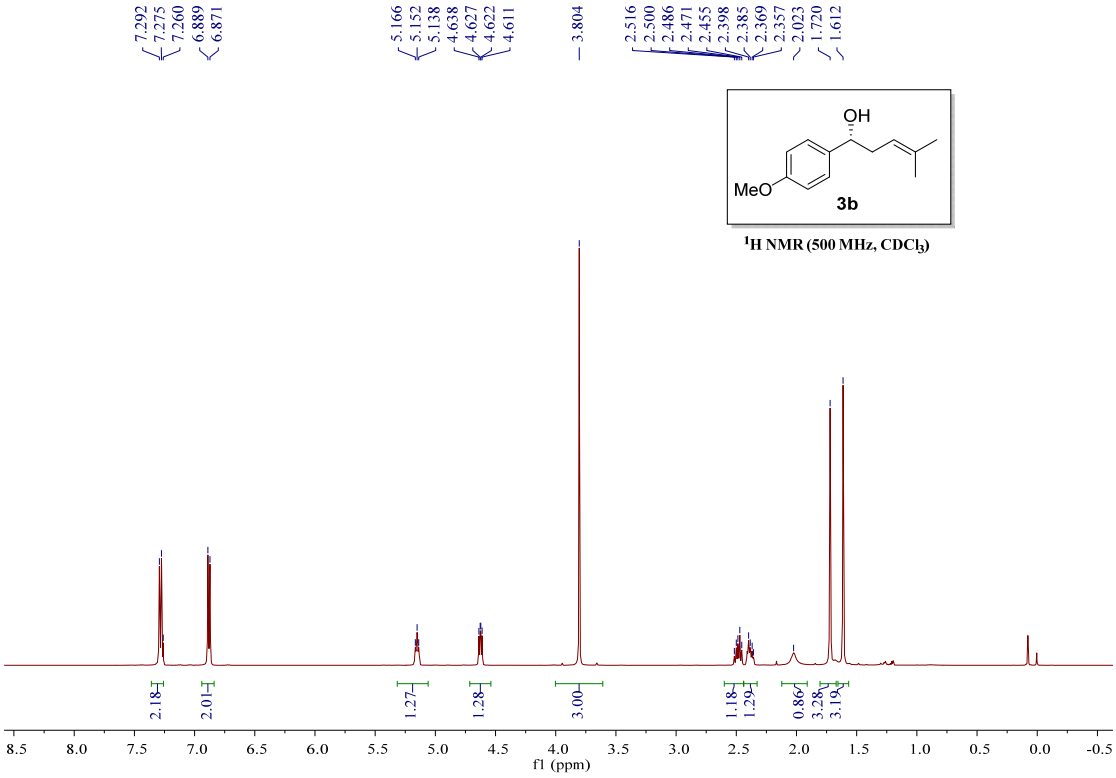
Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra



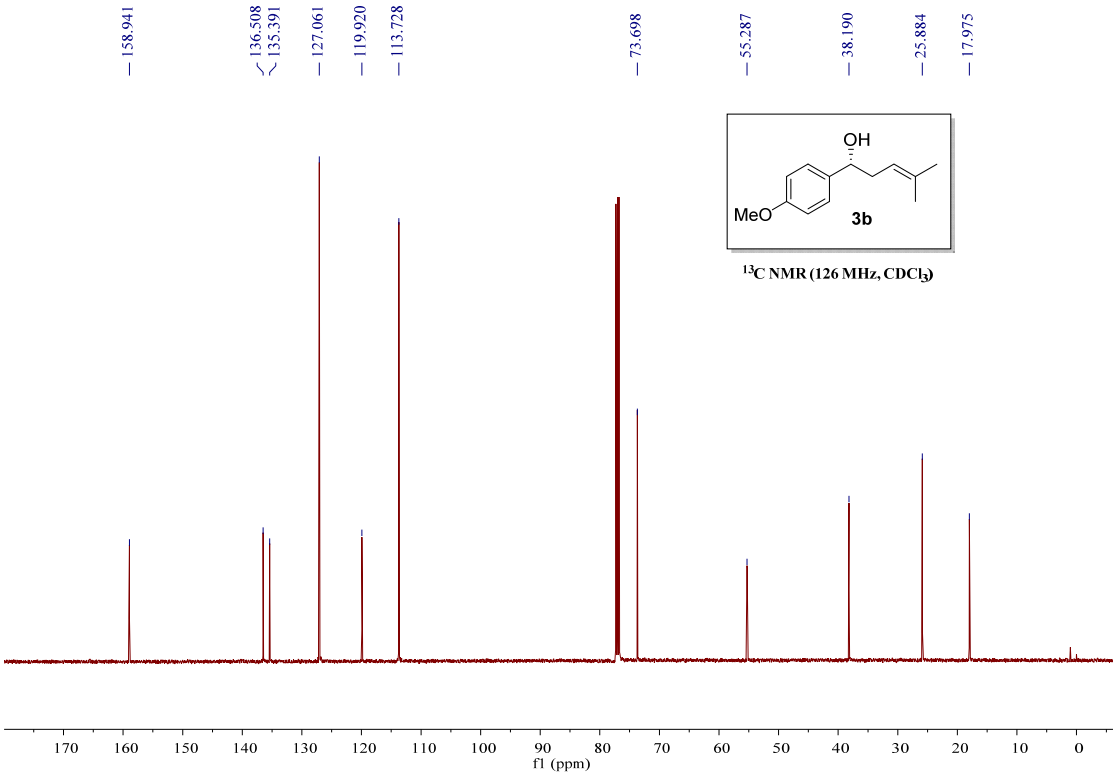
^{1}H NMR (500 MHz, $CDCl_3$)



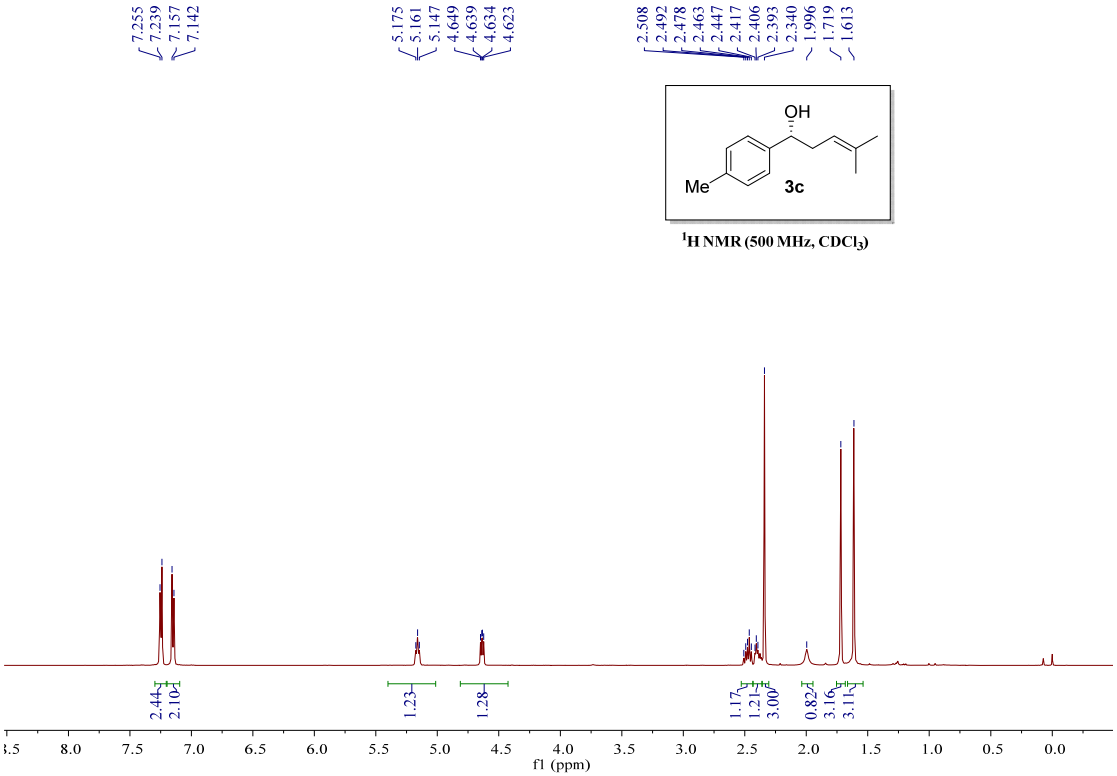
^{13}C NMR (126 MHz, $CDCl_3$)



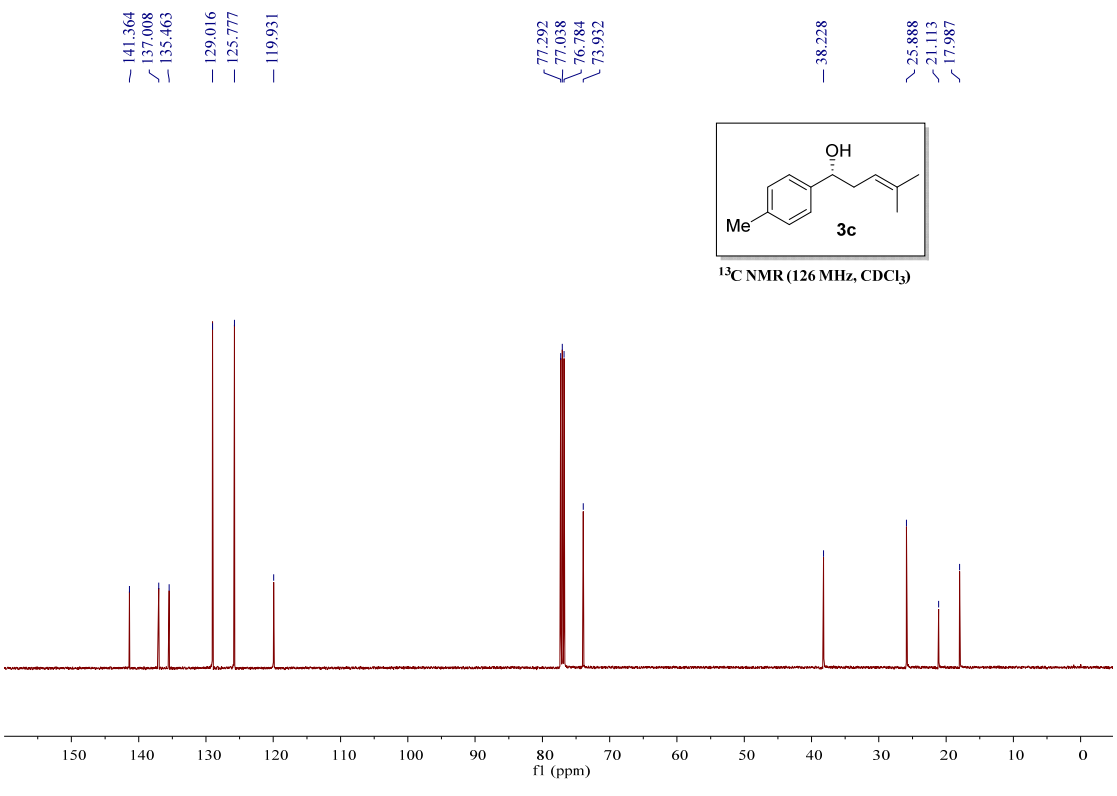
^{1}H NMR (500 MHz, $CDCl_3$)



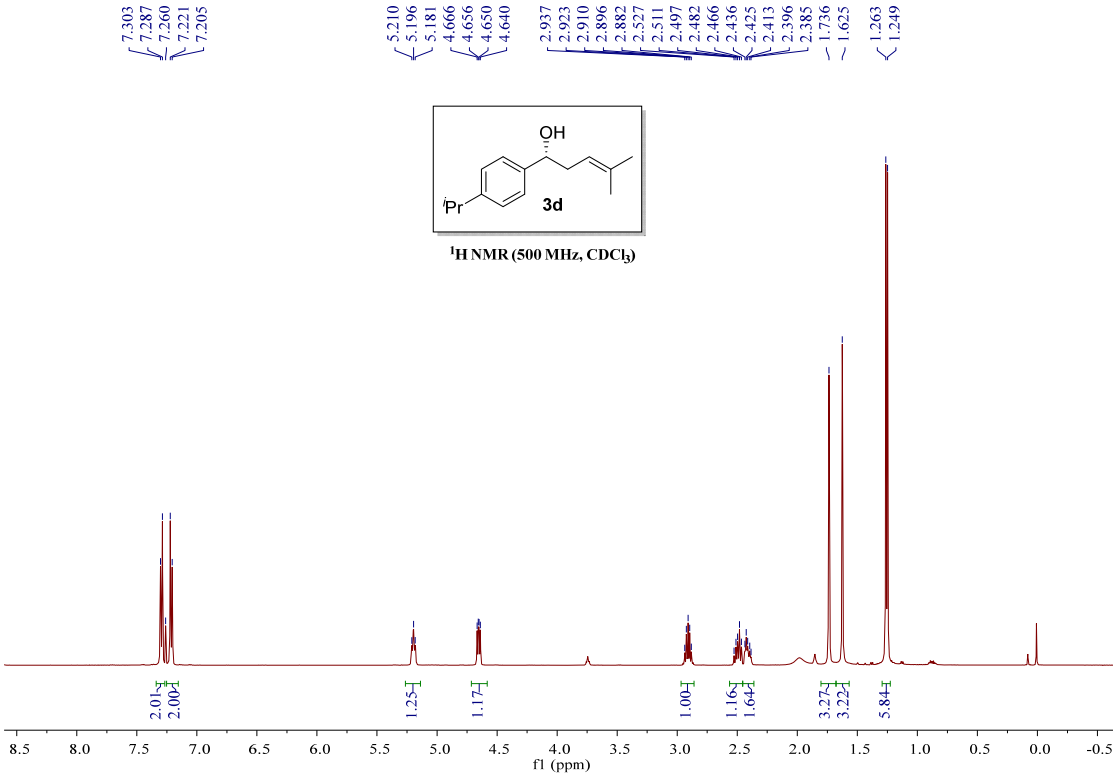
^{13}C NMR (126 MHz, $CDCl_3$)



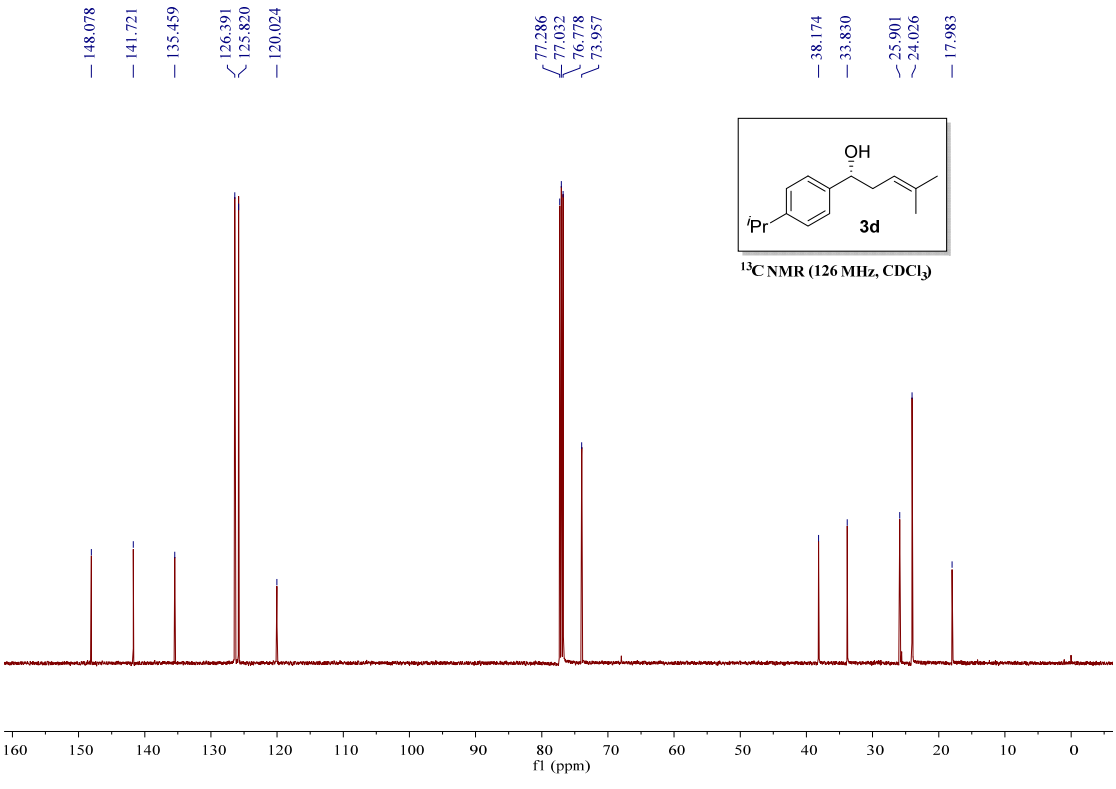
^{1}H NMR (500 MHz, $CDCl_3$)



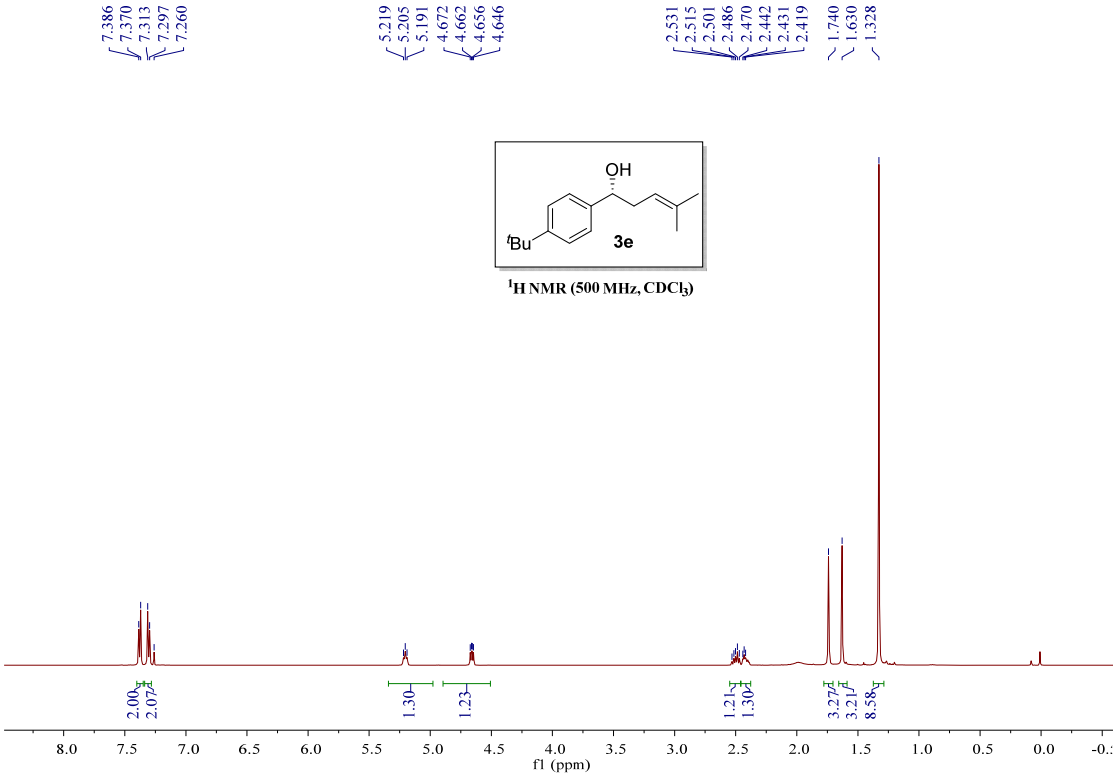
^{13}C NMR (126 MHz, $CDCl_3$)



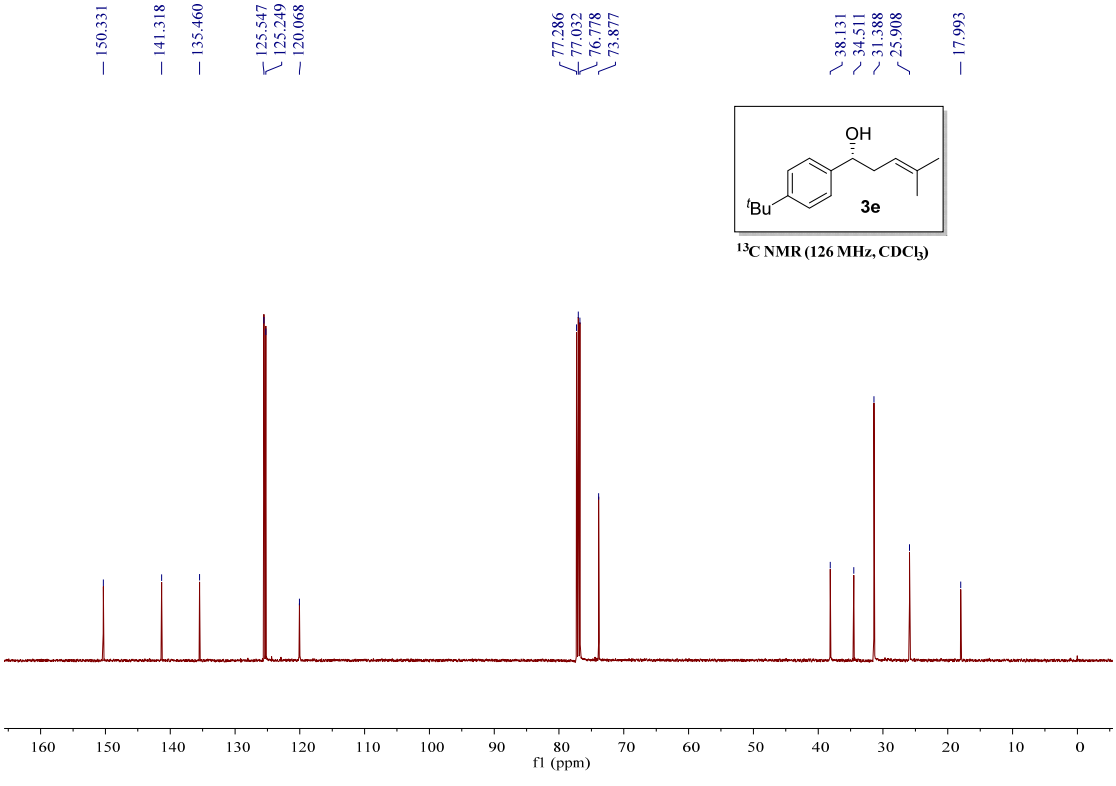
^{1}H NMR (500 MHz, $CDCl_3$)



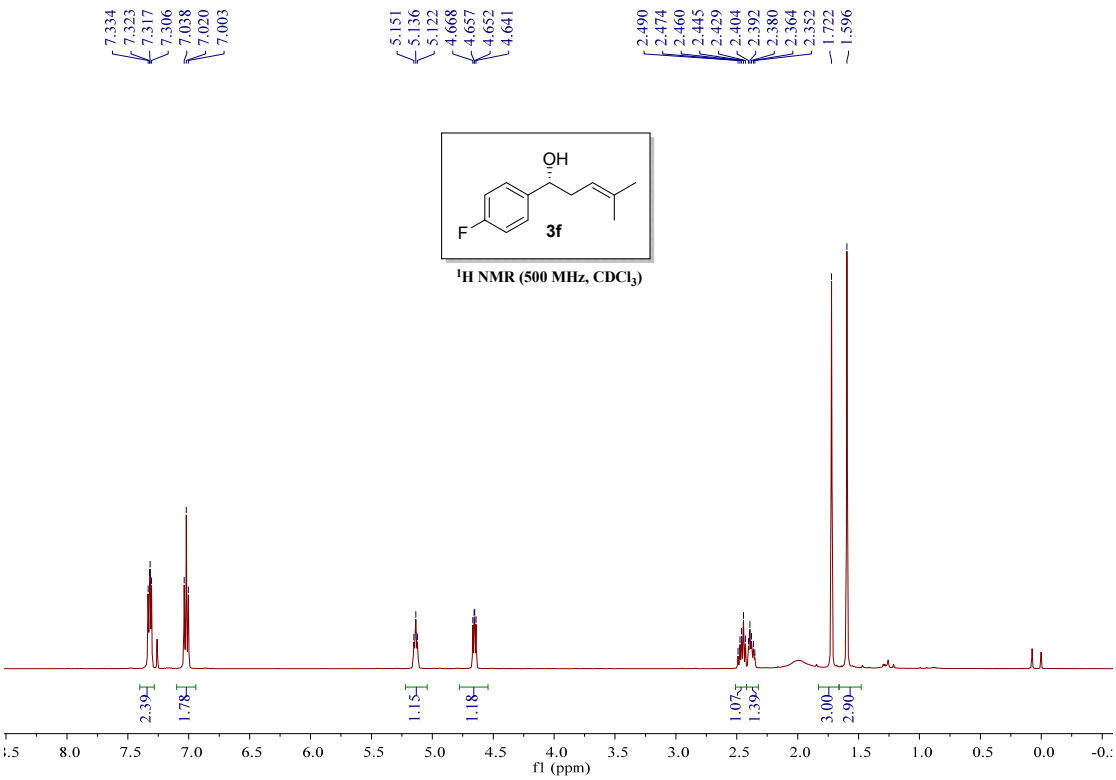
^{13}C NMR (126 MHz, $CDCl_3$)



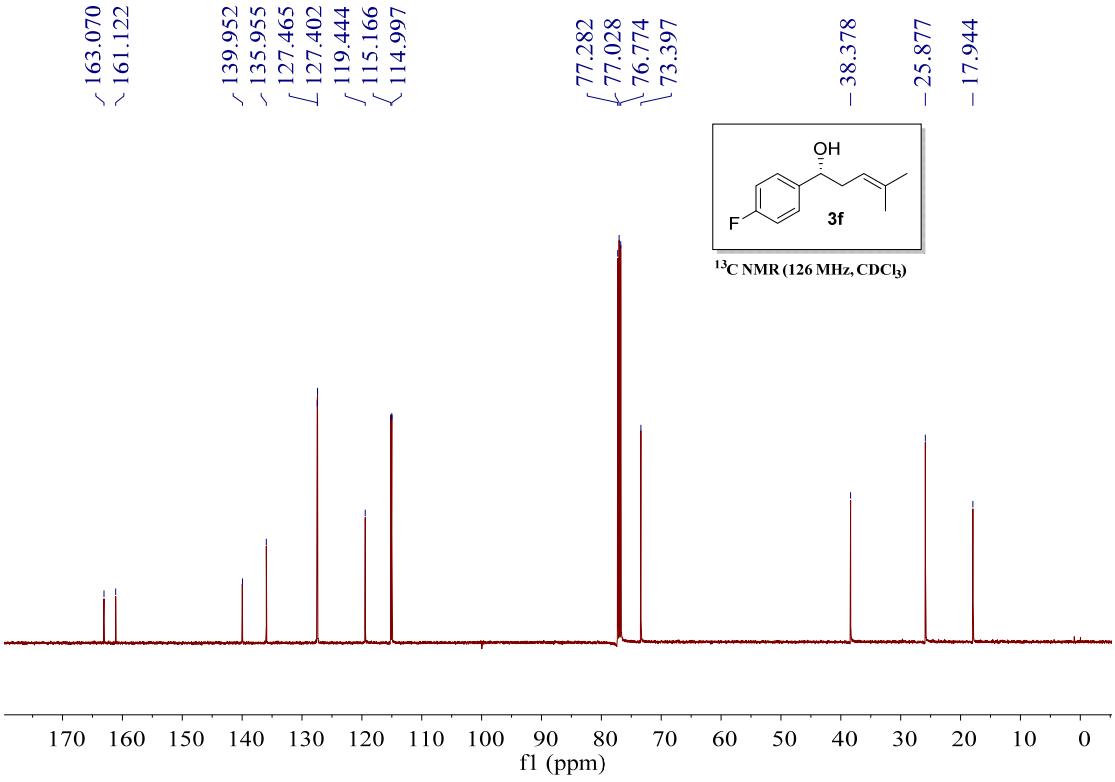
^{1}H NMR (500 MHz, $CDCl_3$)



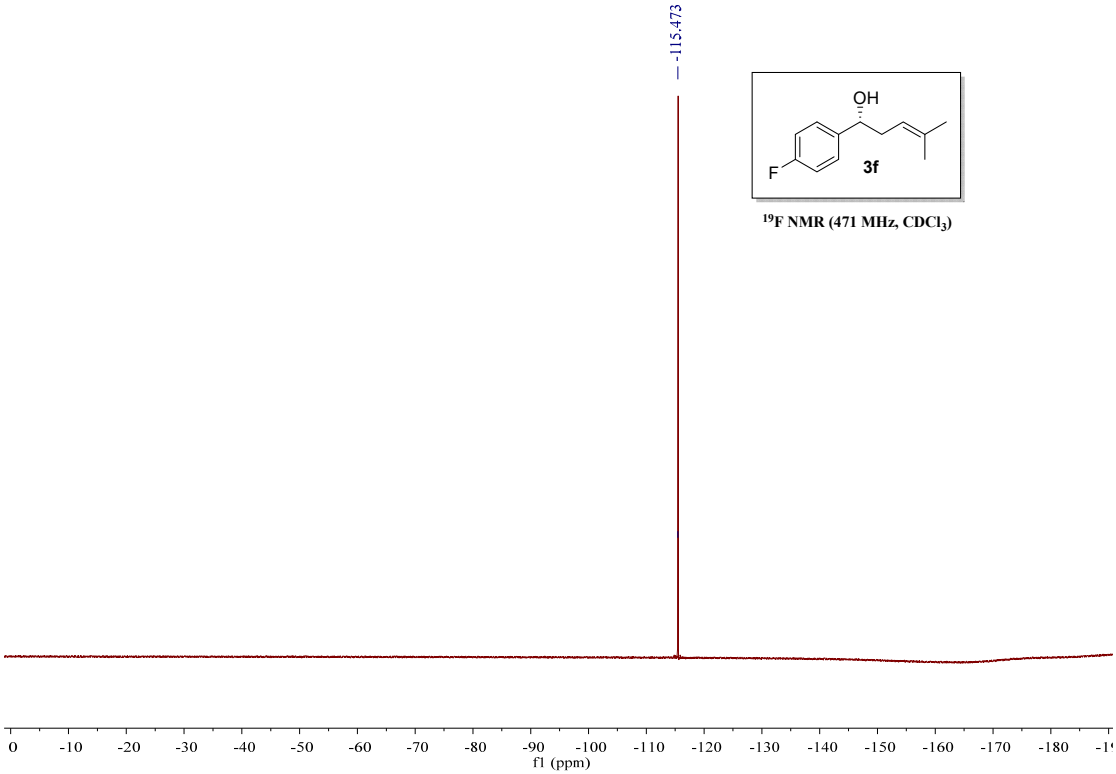
^{13}C NMR (126 MHz, $CDCl_3$)



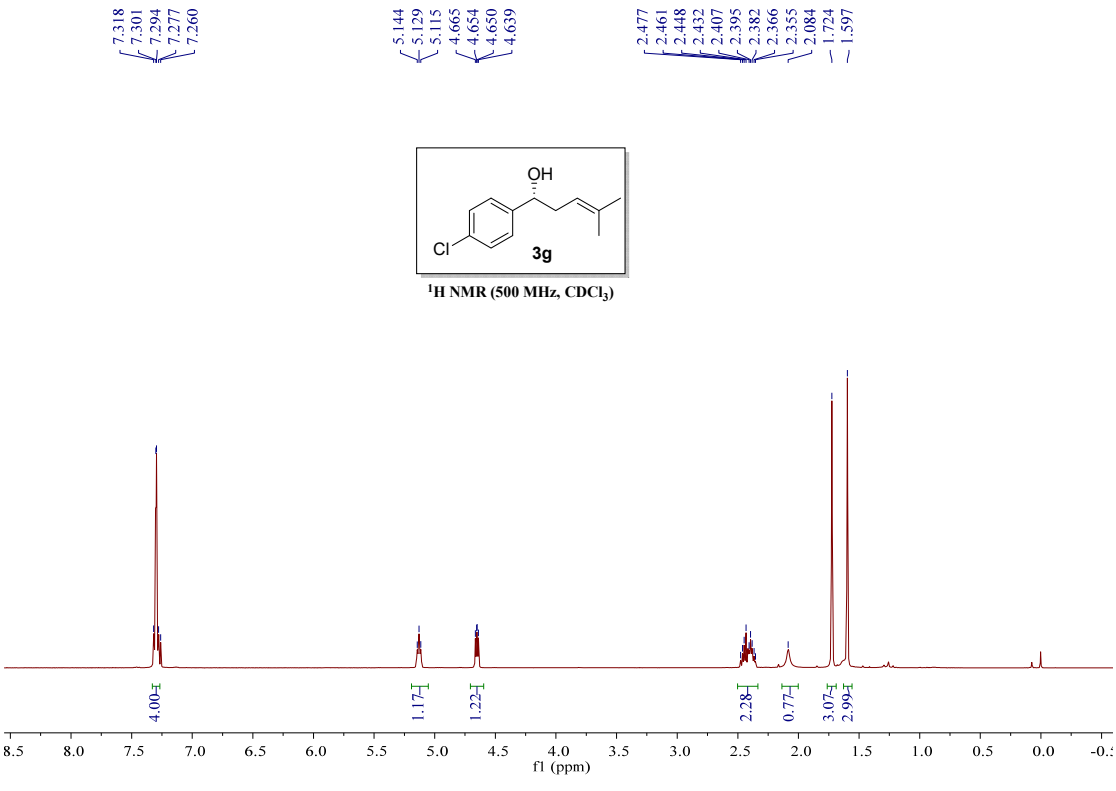
^{1}H NMR (500 MHz, $CDCl_3$)



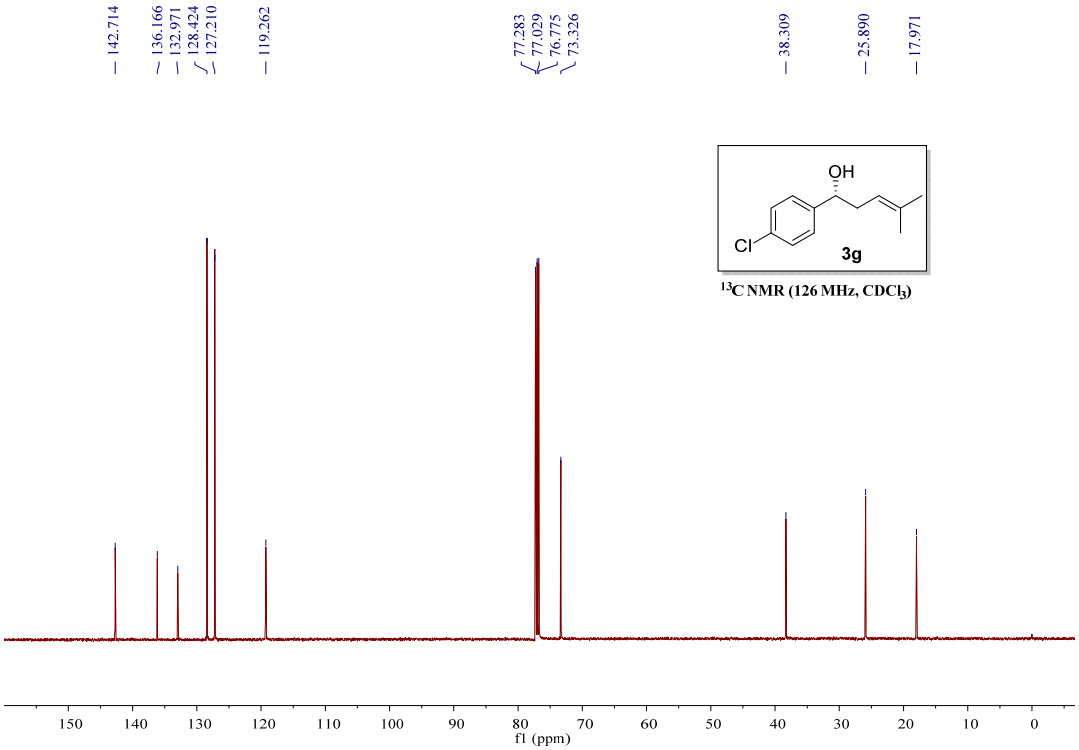
^{13}C NMR (126 MHz, $CDCl_3$)



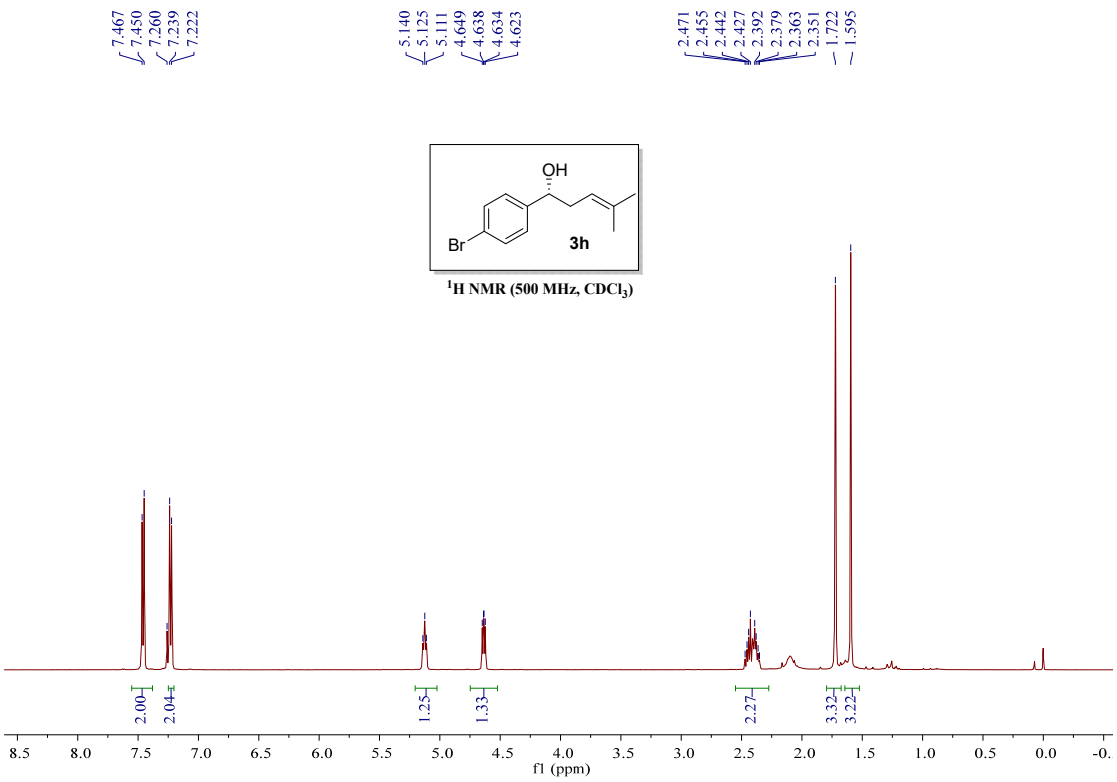
^{19}F NMR (471 MHz, $CDCl_3$)



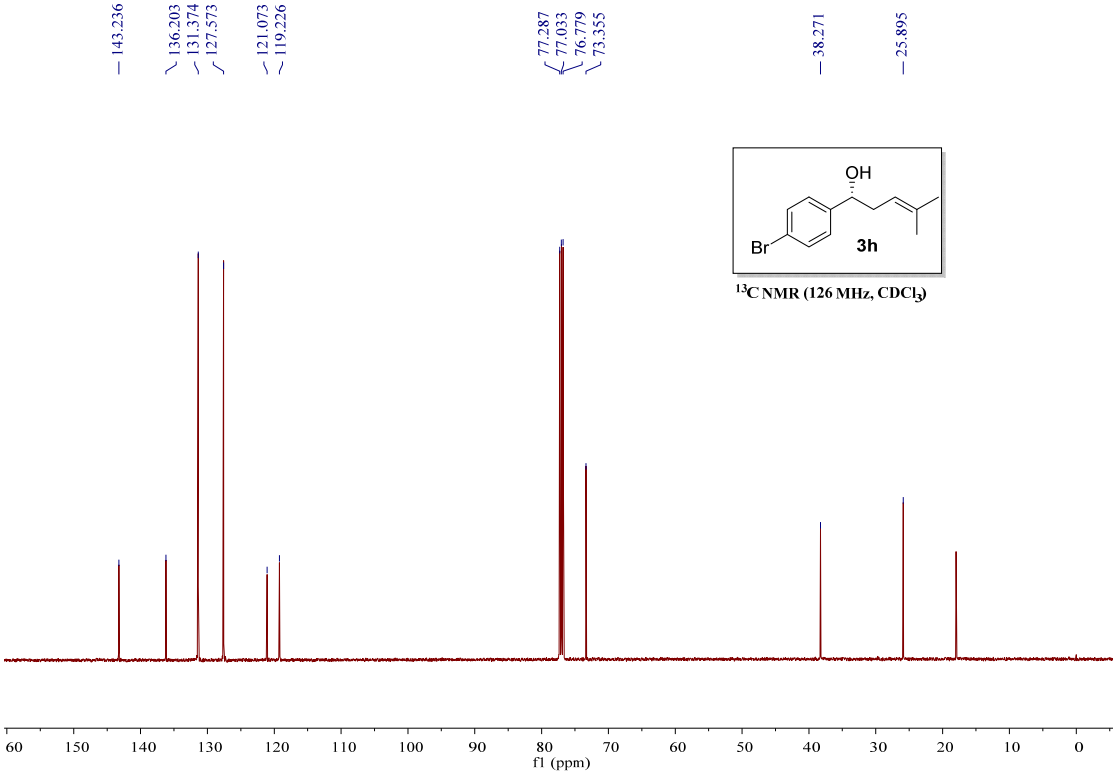
^{1}H NMR (500 MHz, $CDCl_3$)



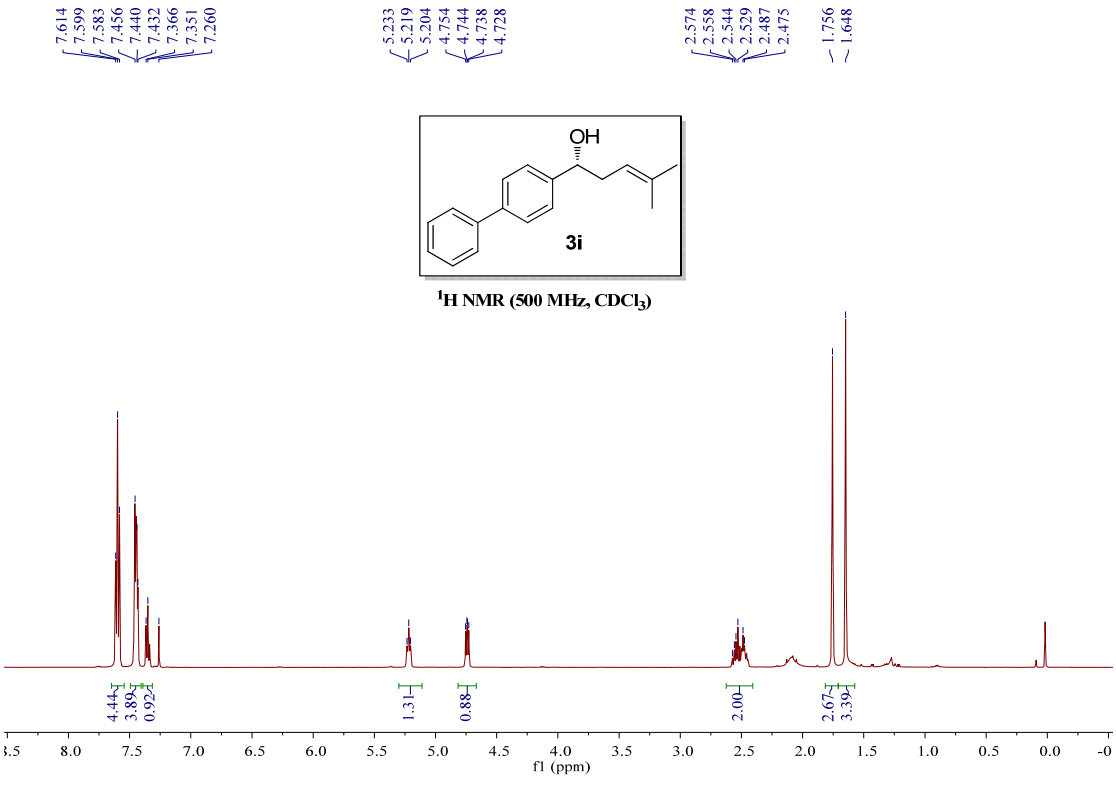
^{13}C NMR (126 MHz, $CDCl_3$)



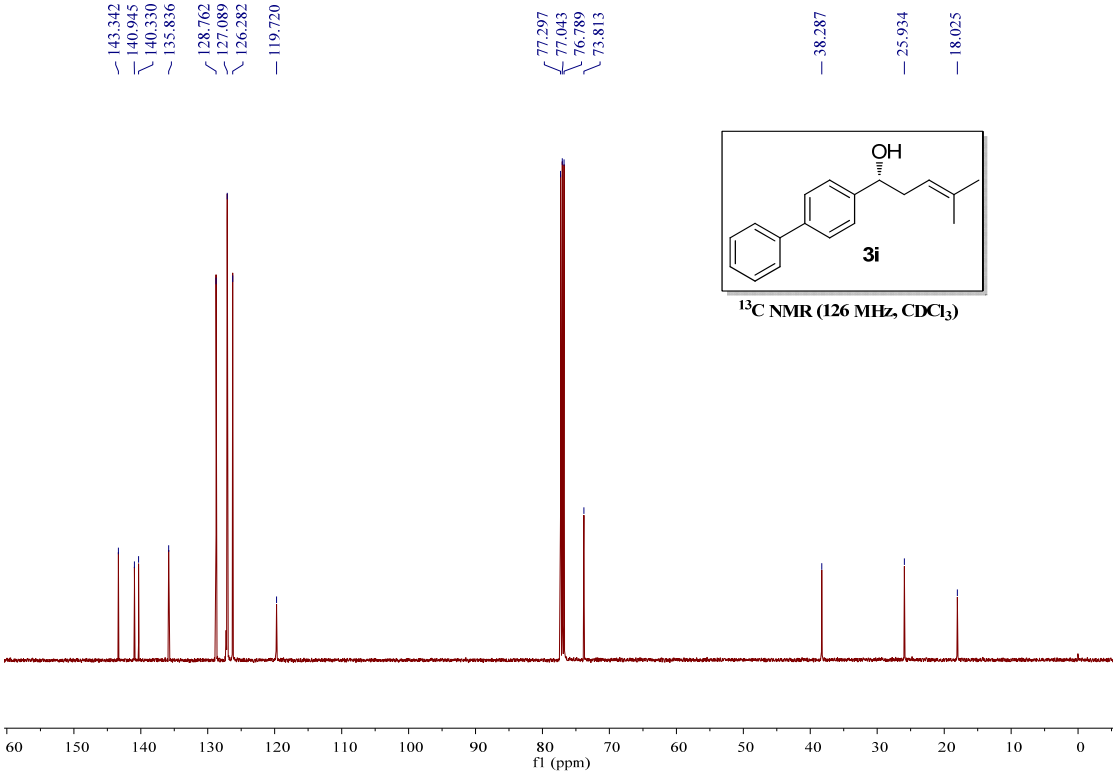
^{1}H NMR (500 MHz, $CDCl_3$)



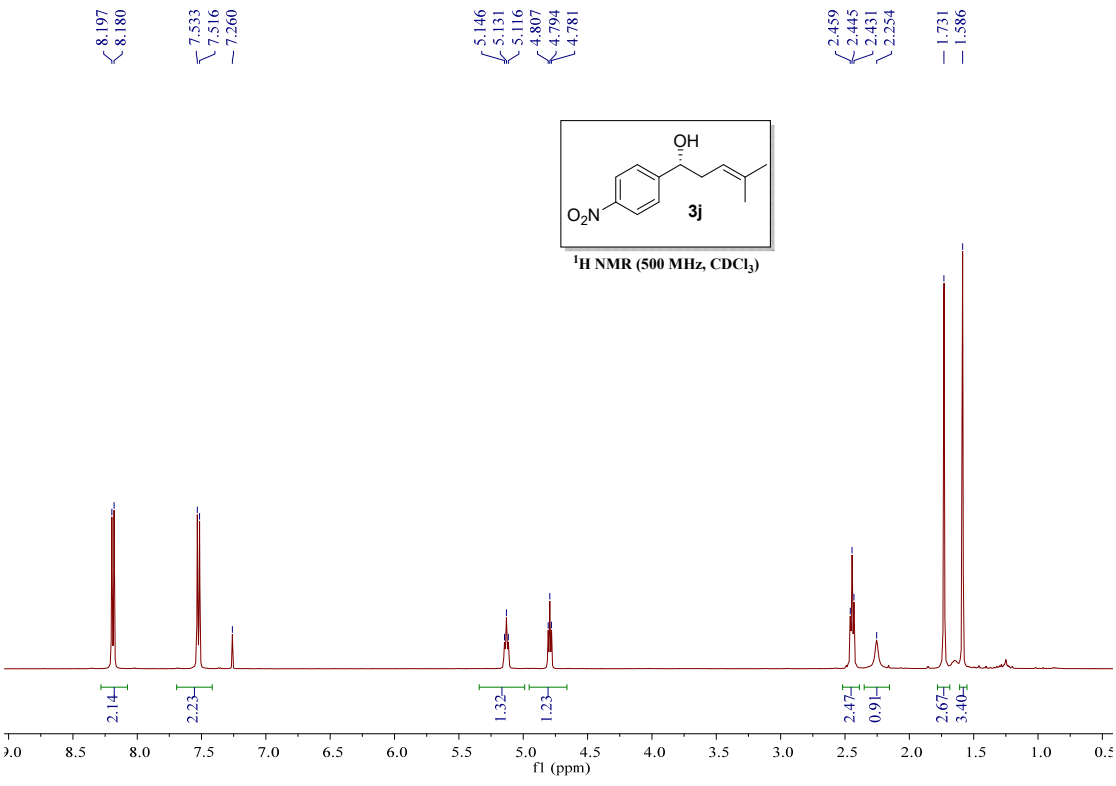
^{13}C NMR (126 MHz, $CDCl_3$)



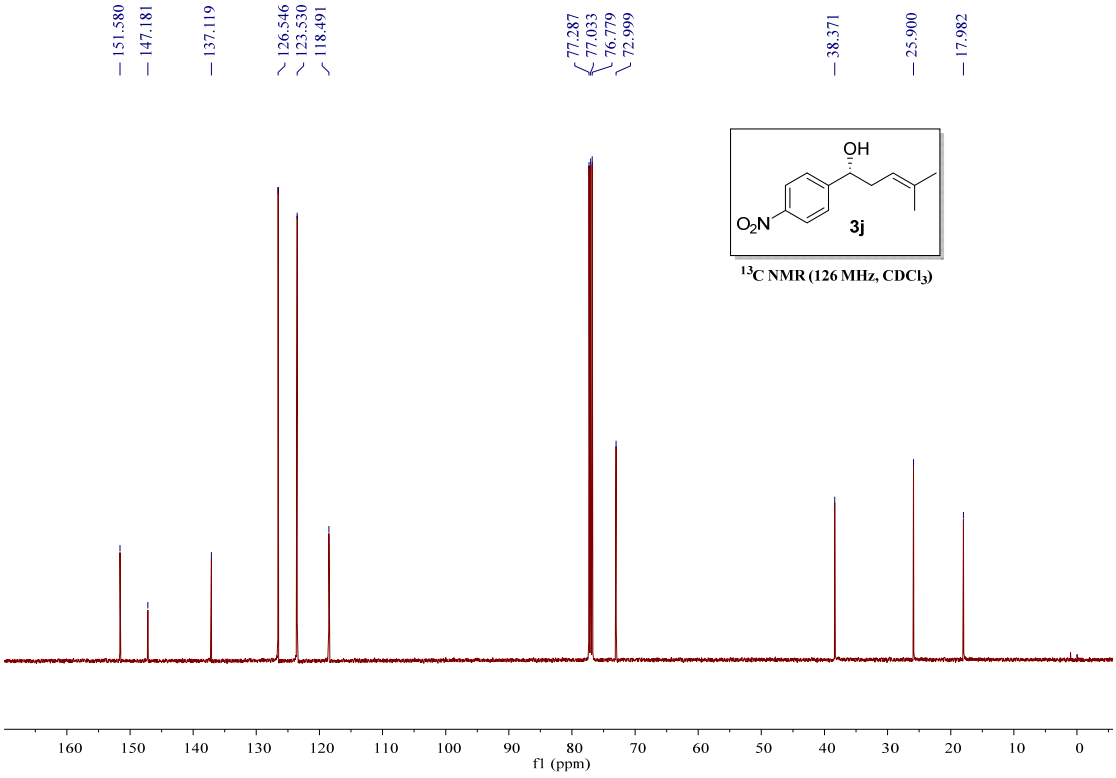
^{1}H NMR (500 MHz, $CDCl_3$)



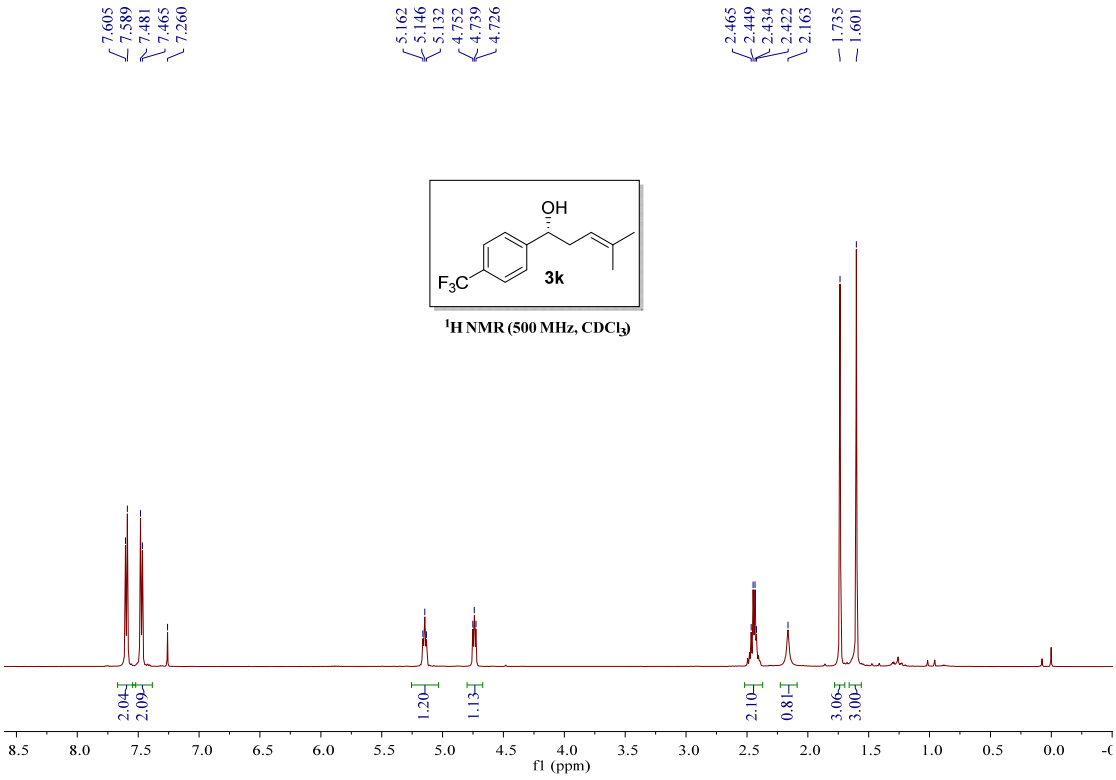
^{13}C NMR (126 MHz, $CDCl_3$)



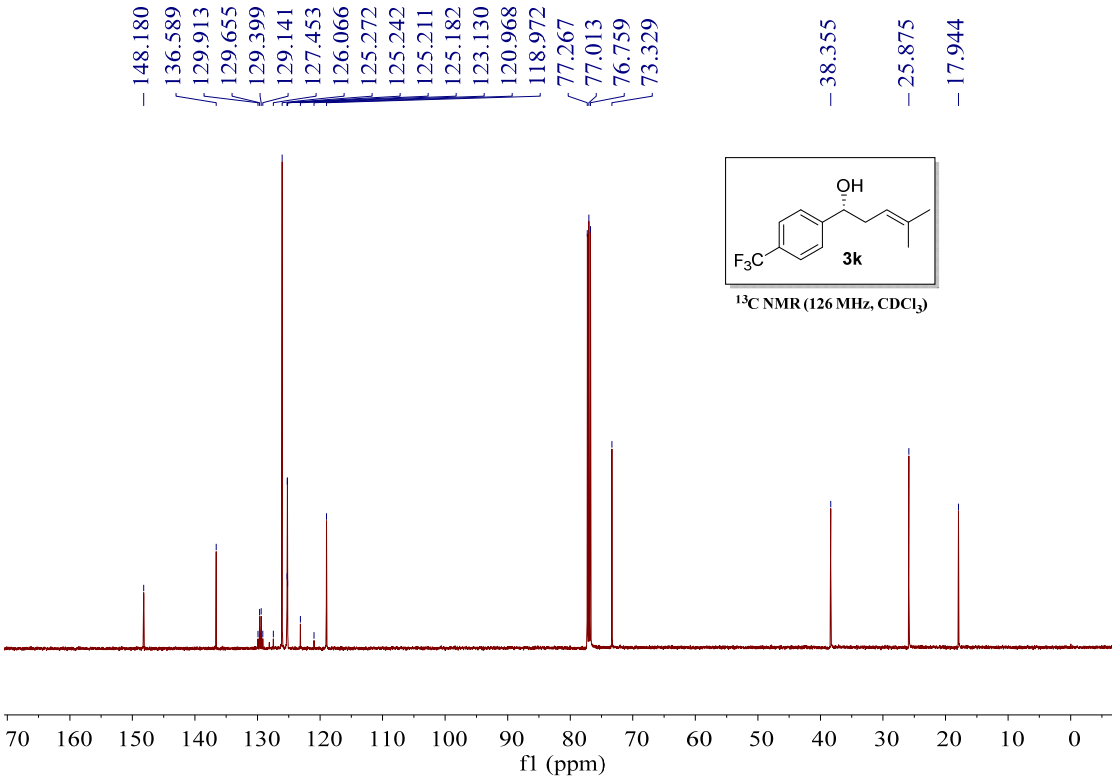
^{1}H NMR (500 MHz, $CDCl_3$)



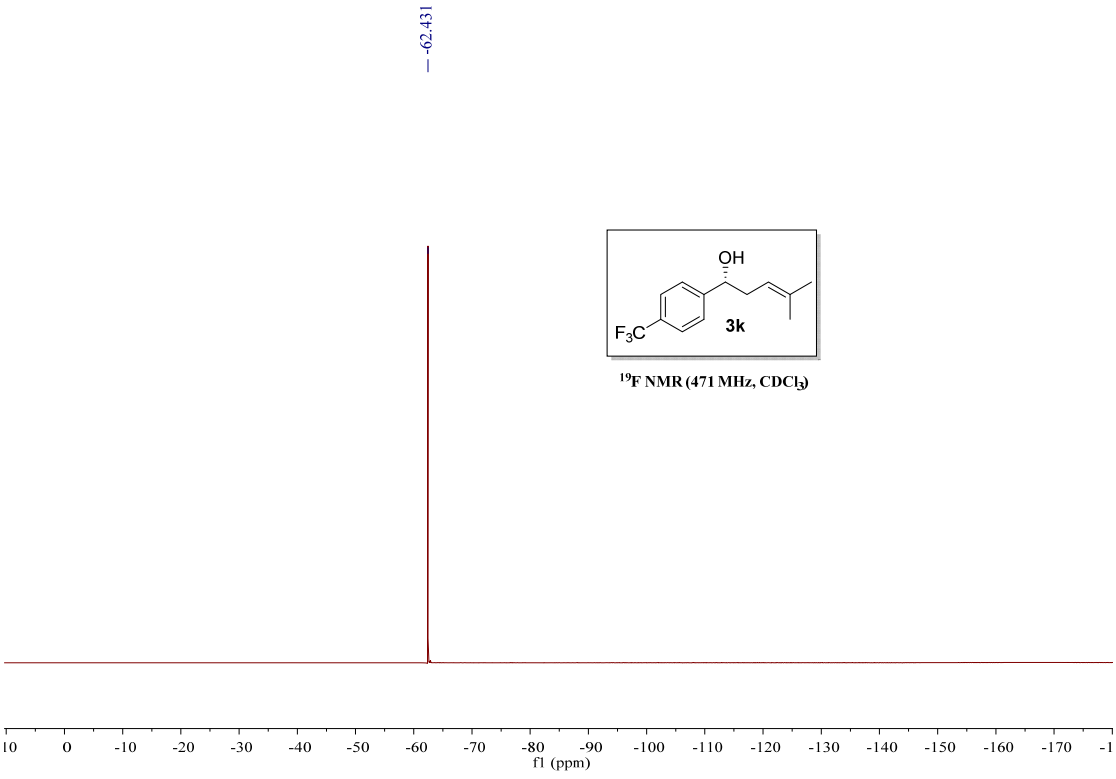
^{13}C NMR (126 MHz, $CDCl_3$)



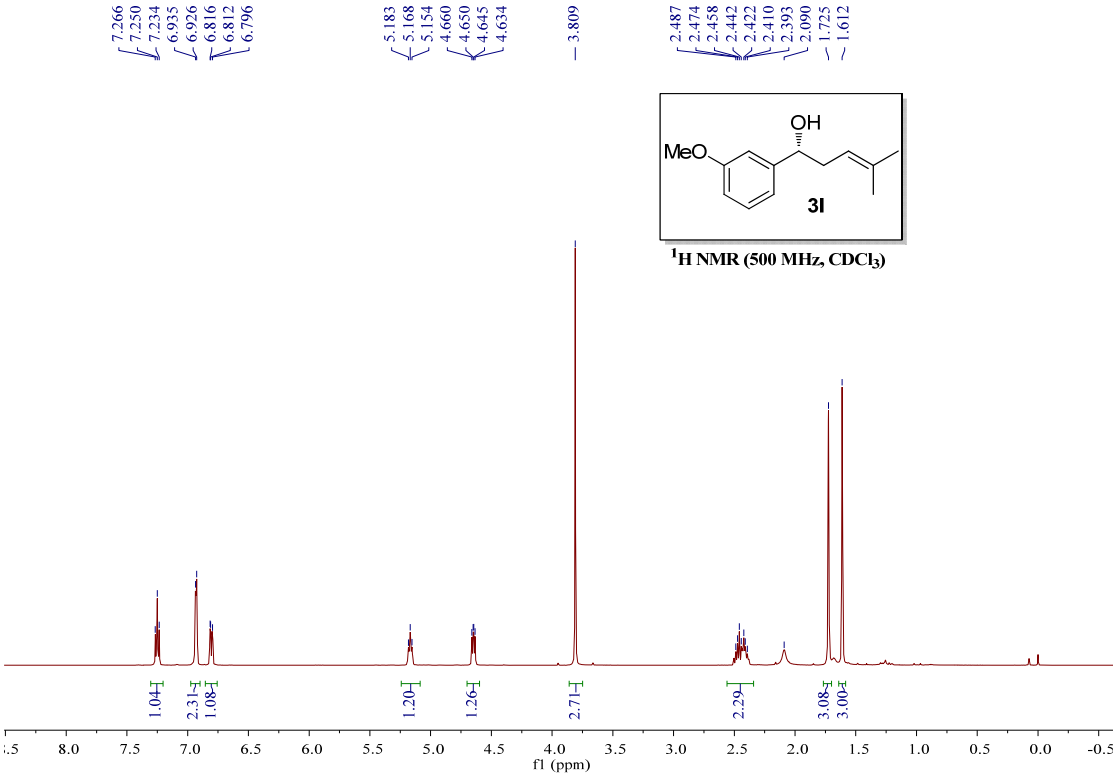
^{1}H NMR (500 MHz, $CDCl_3$)



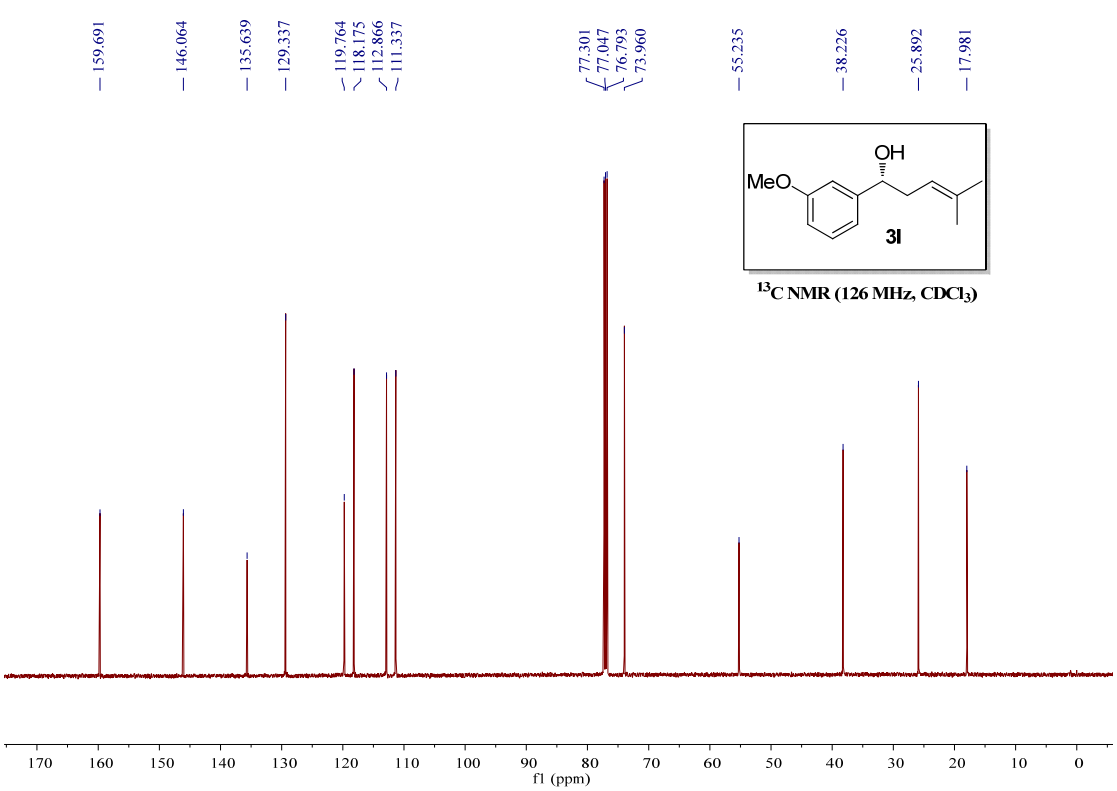
^{13}C NMR (126 MHz, $CDCl_3$)



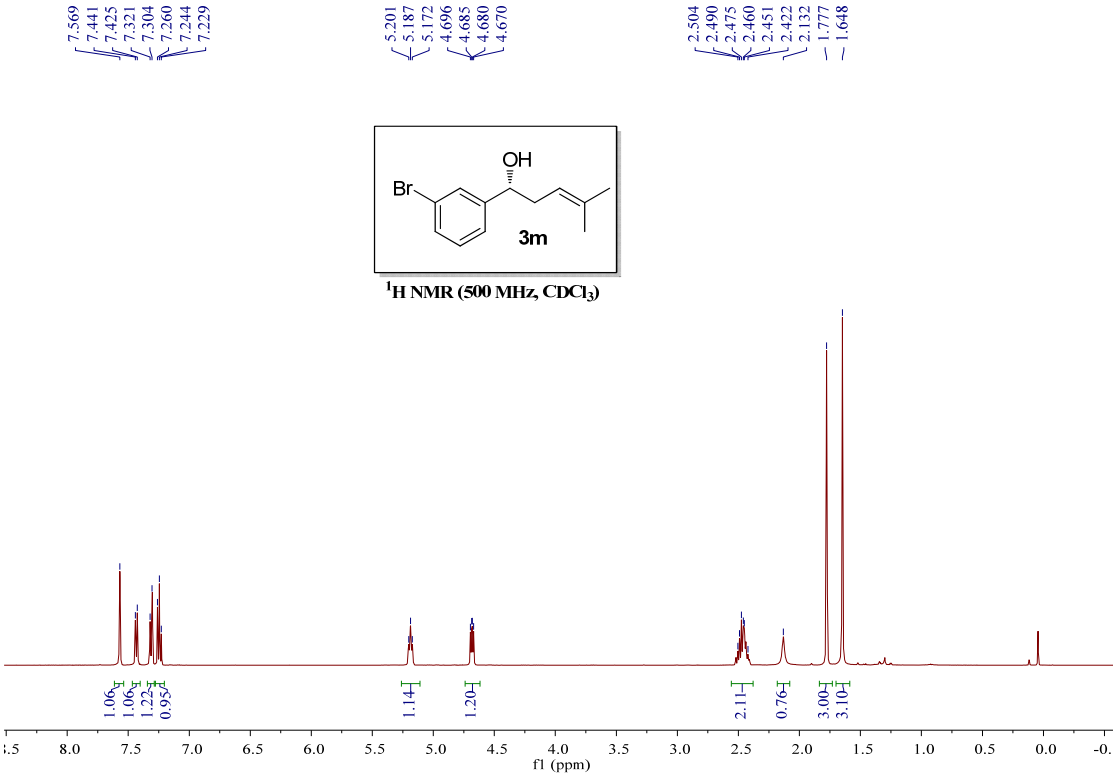
^{19}F NMR (471 MHz, $CDCl_3$)



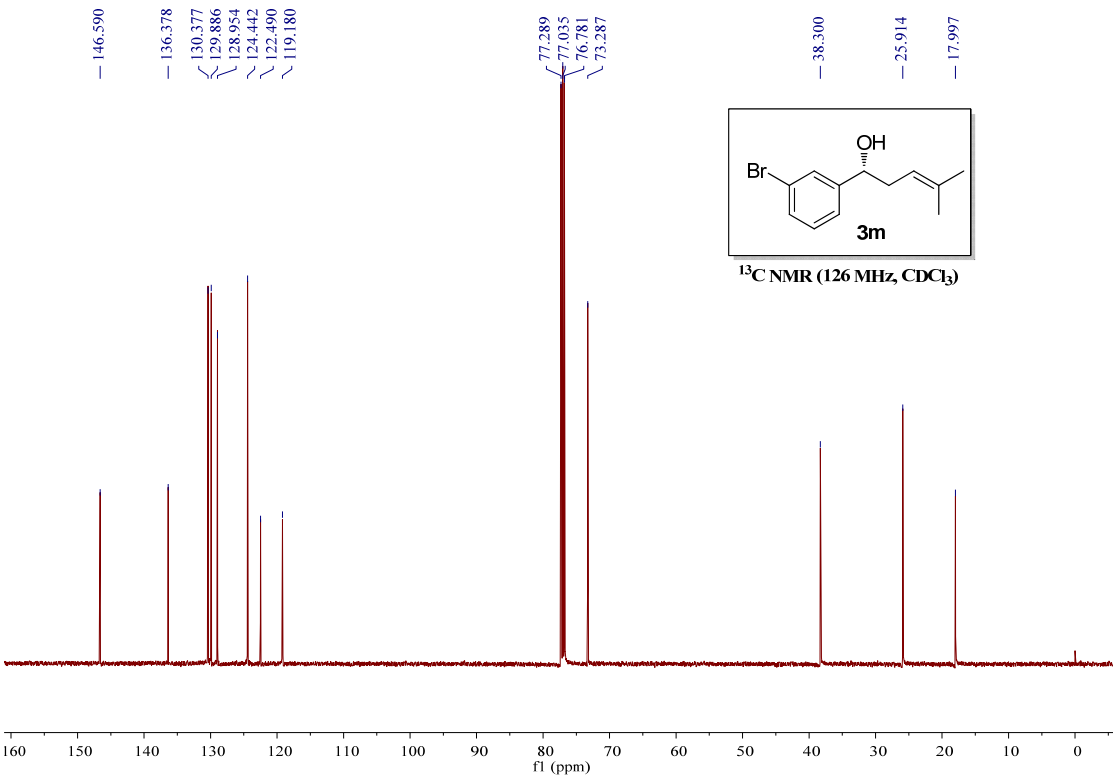
^{1}H NMR (500 MHz, $CDCl_3$)



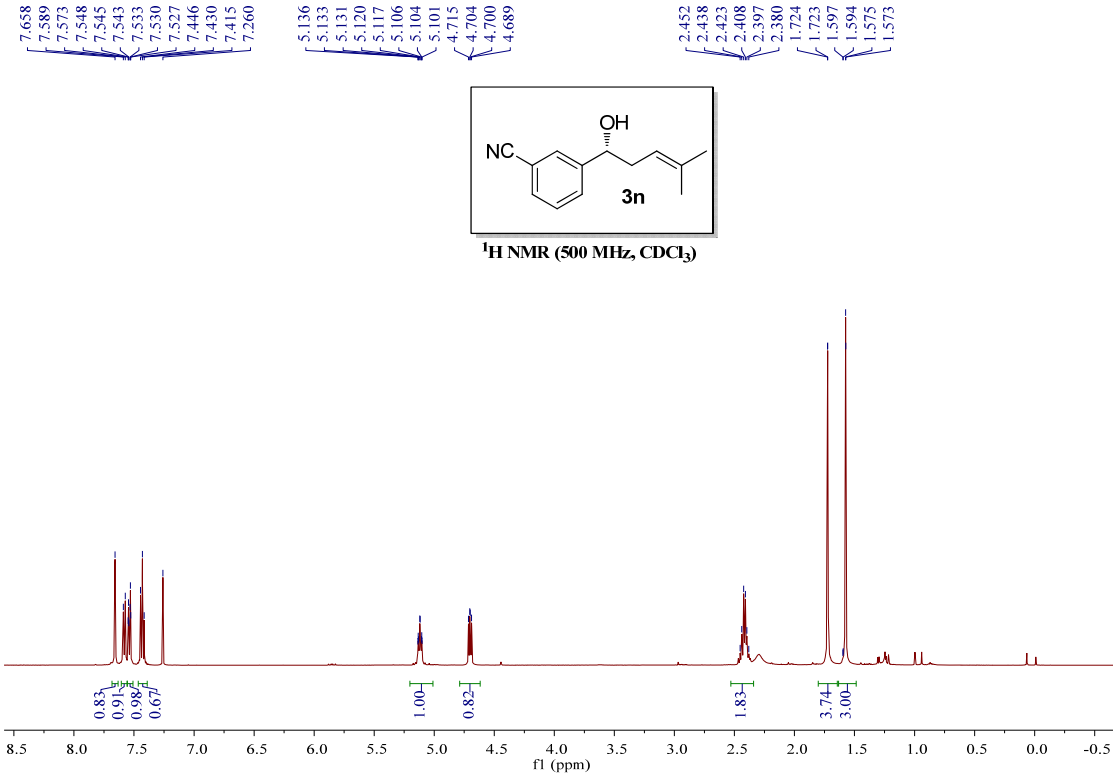
^{13}C NMR (126 MHz, $CDCl_3$)



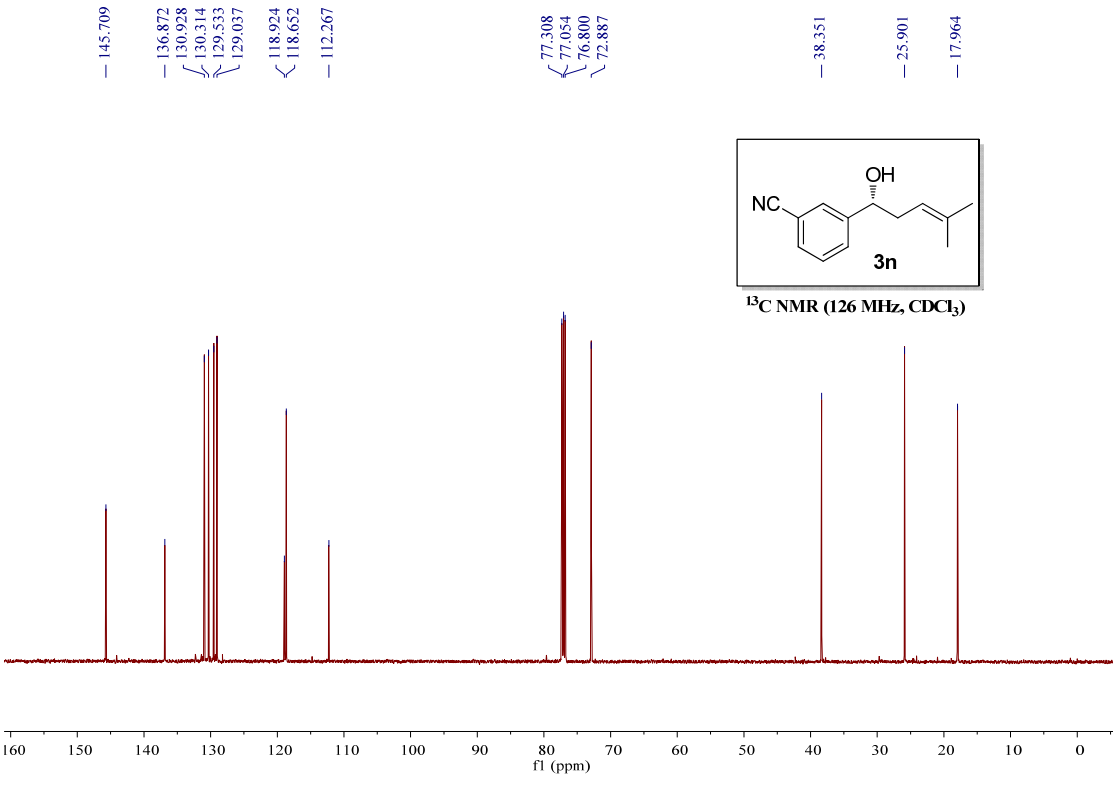
^{1}H NMR (500 MHz, $CDCl_3$)



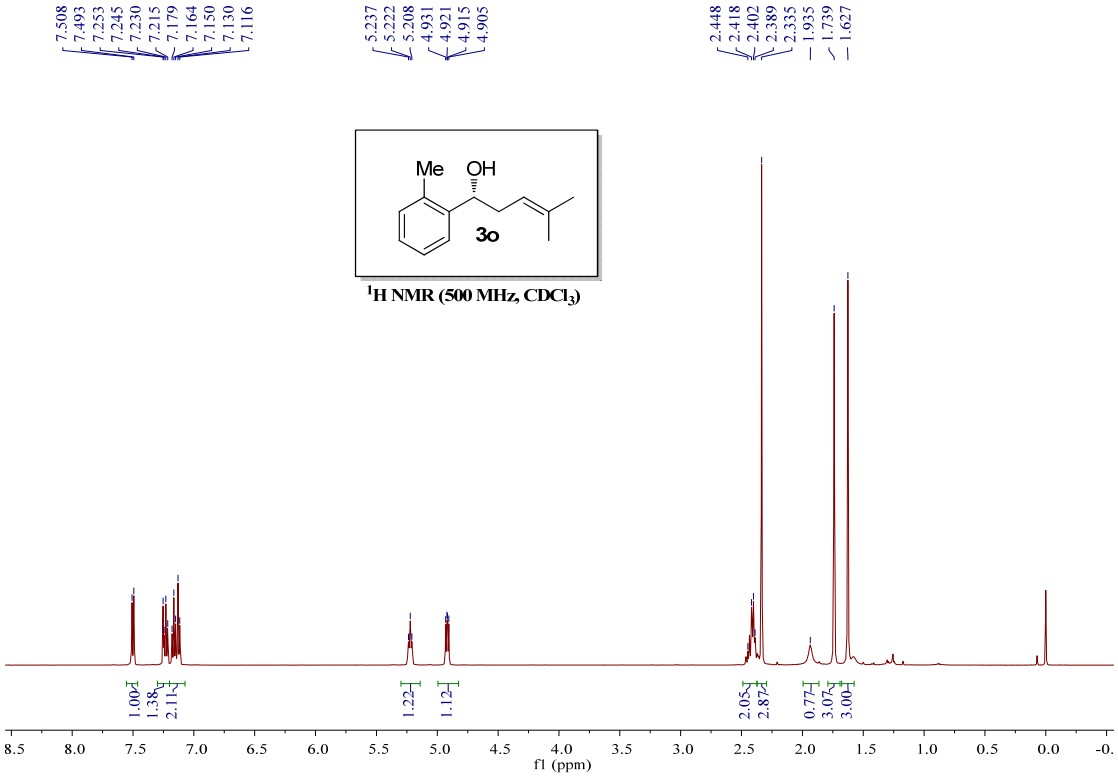
^{13}C NMR (126 MHz, $CDCl_3$)



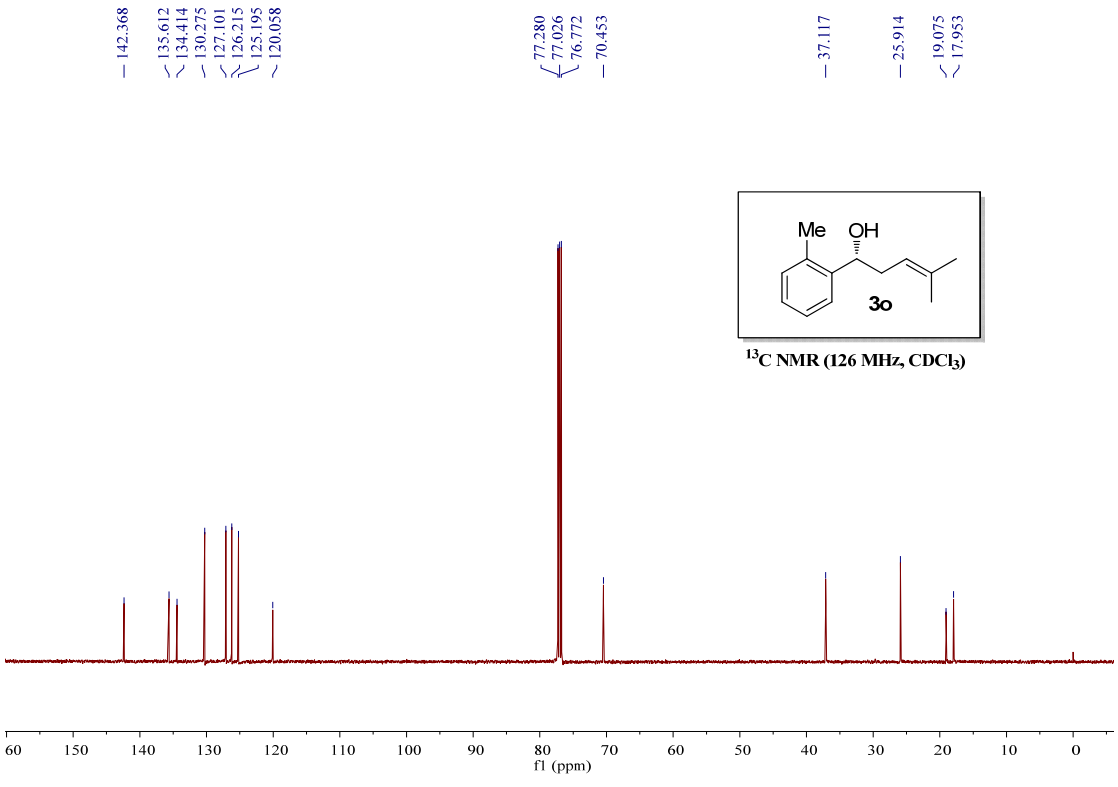
^{1}H NMR (500 MHz, $CDCl_3$)



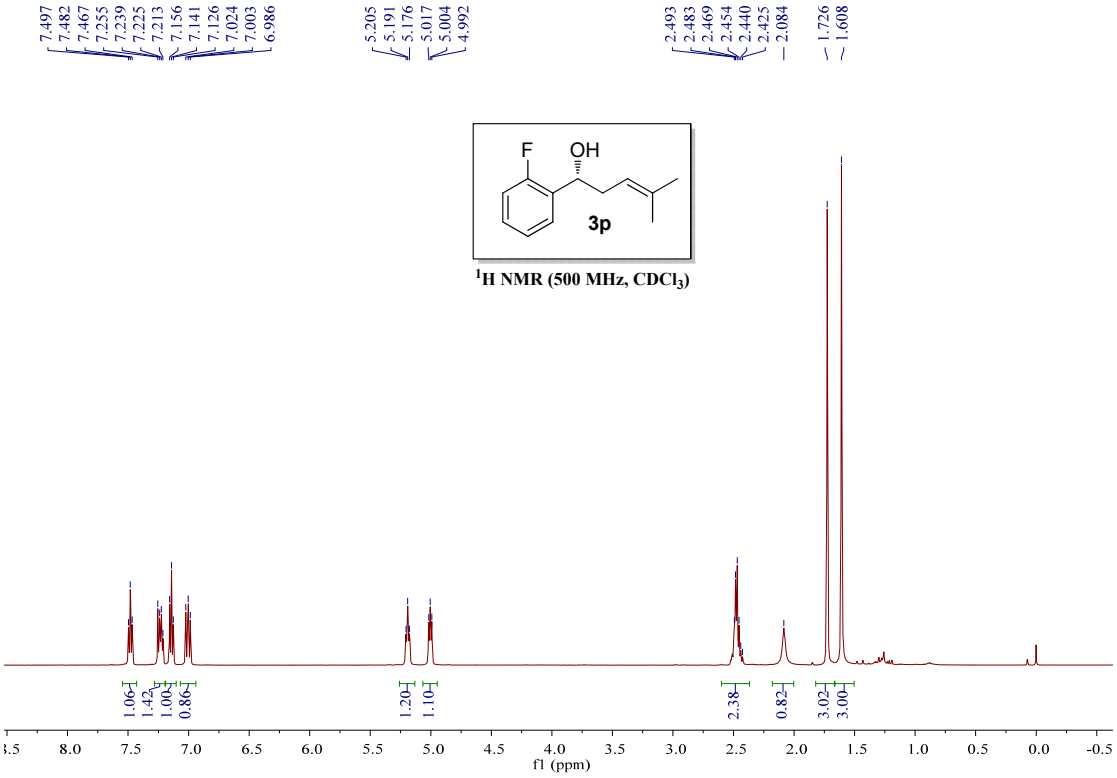
^{13}C NMR (126 MHz, $CDCl_3$)



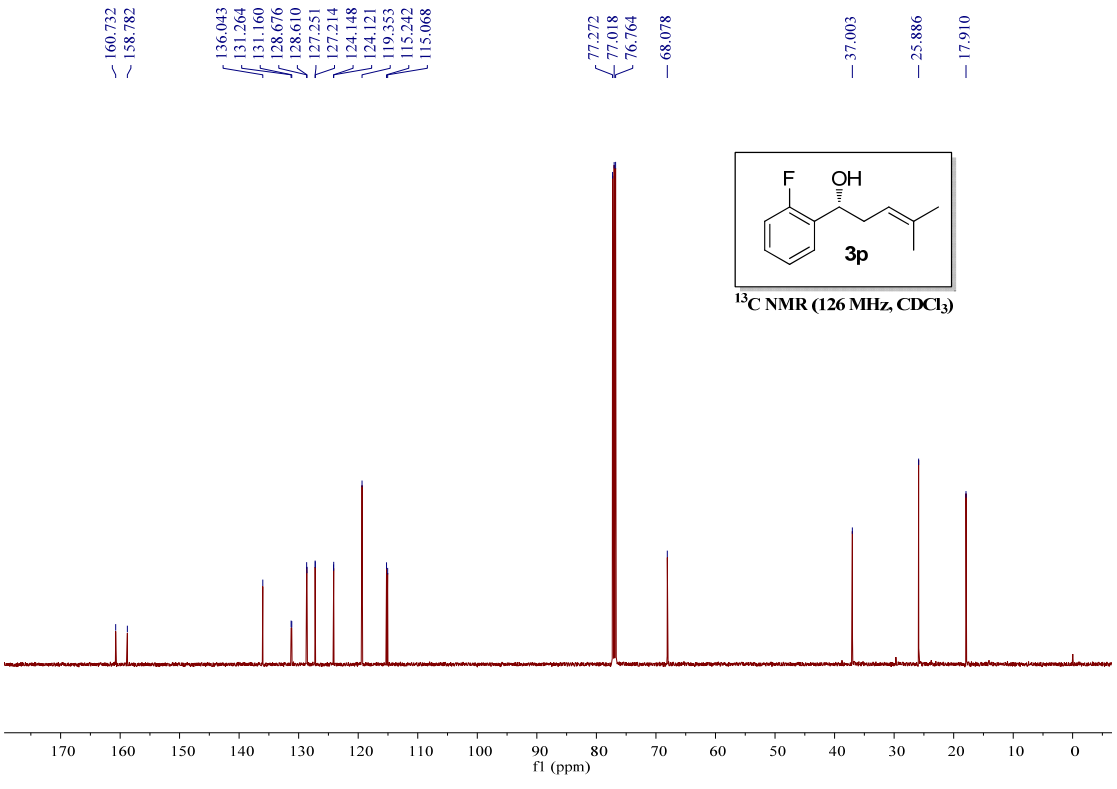
^{1}H NMR (500 MHz, $CDCl_3$)



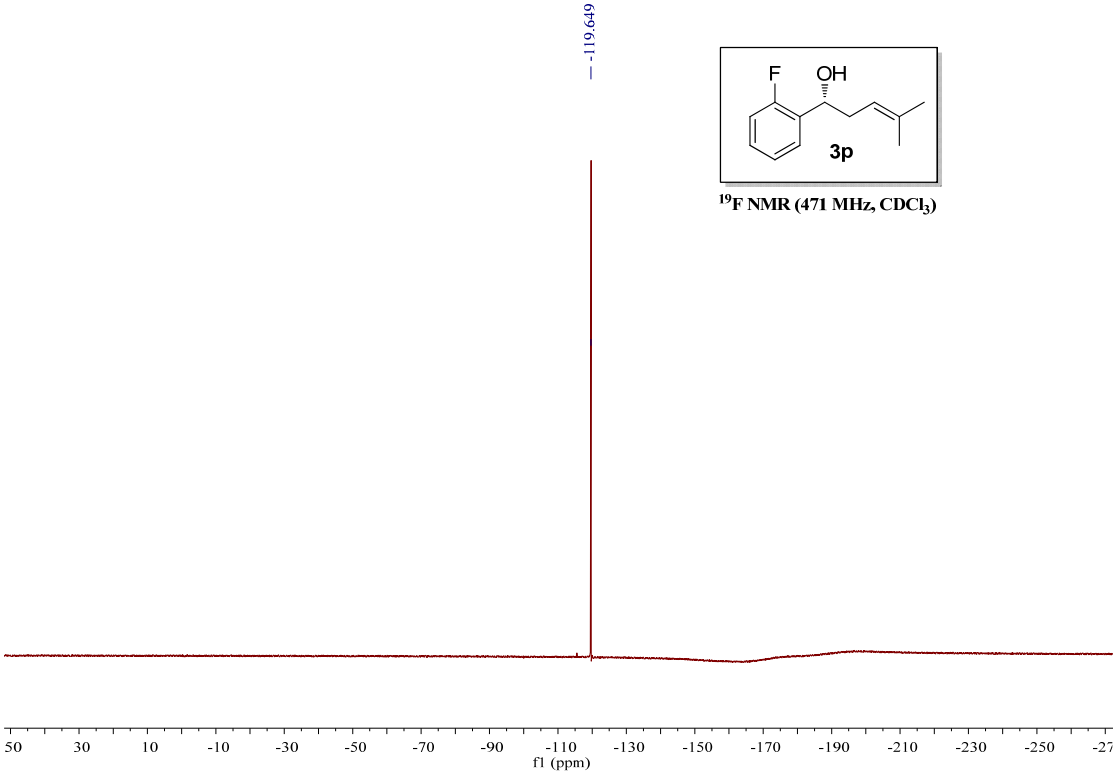
^{13}C NMR (126 MHz, $CDCl_3$)



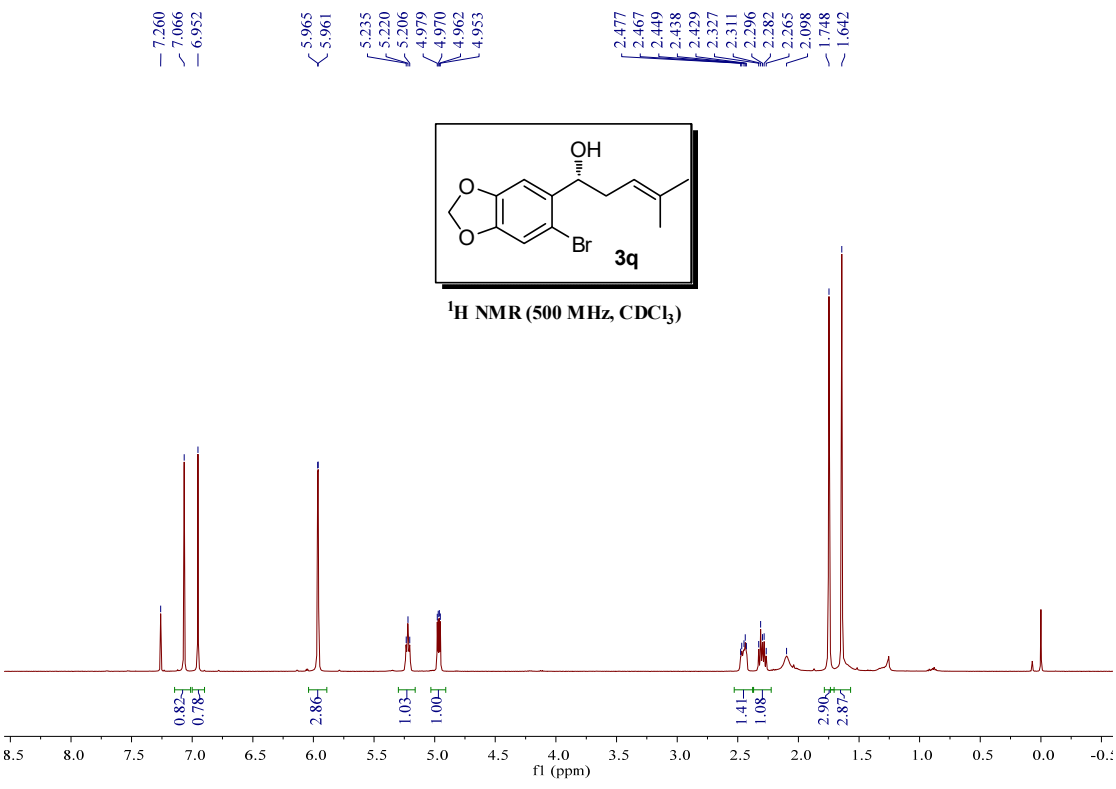
^{1}H NMR (500 MHz, $CDCl_3$)



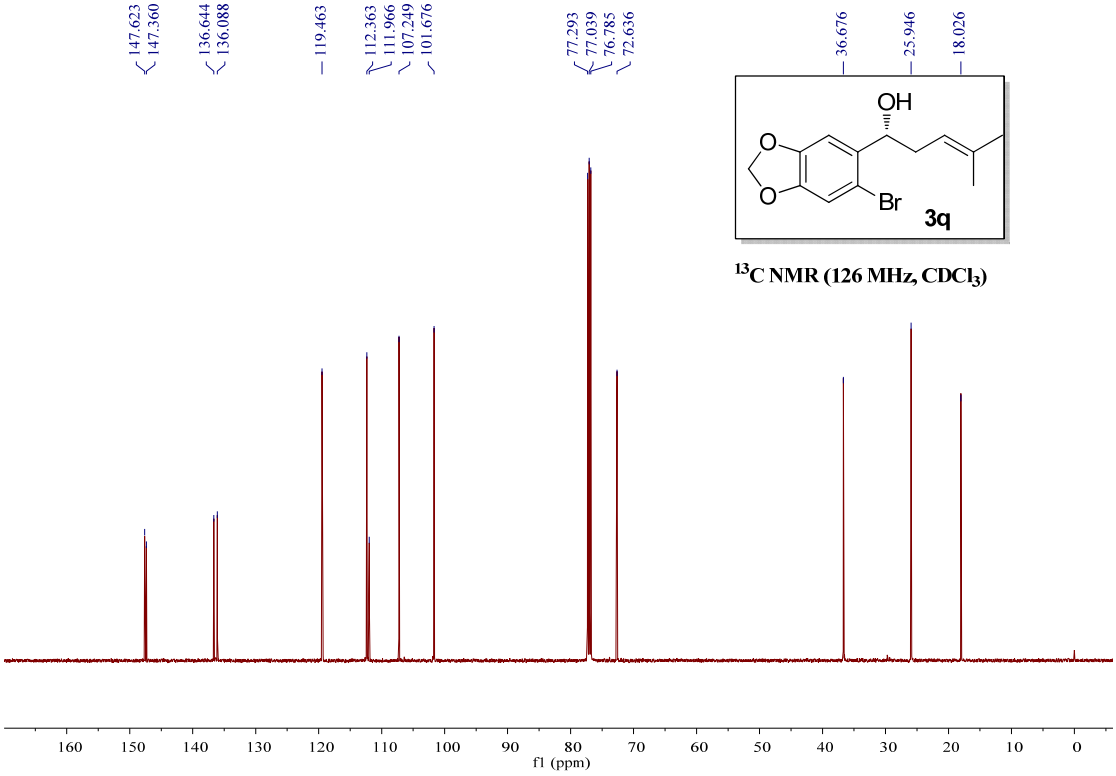
^{13}C NMR (126 MHz, $CDCl_3$)



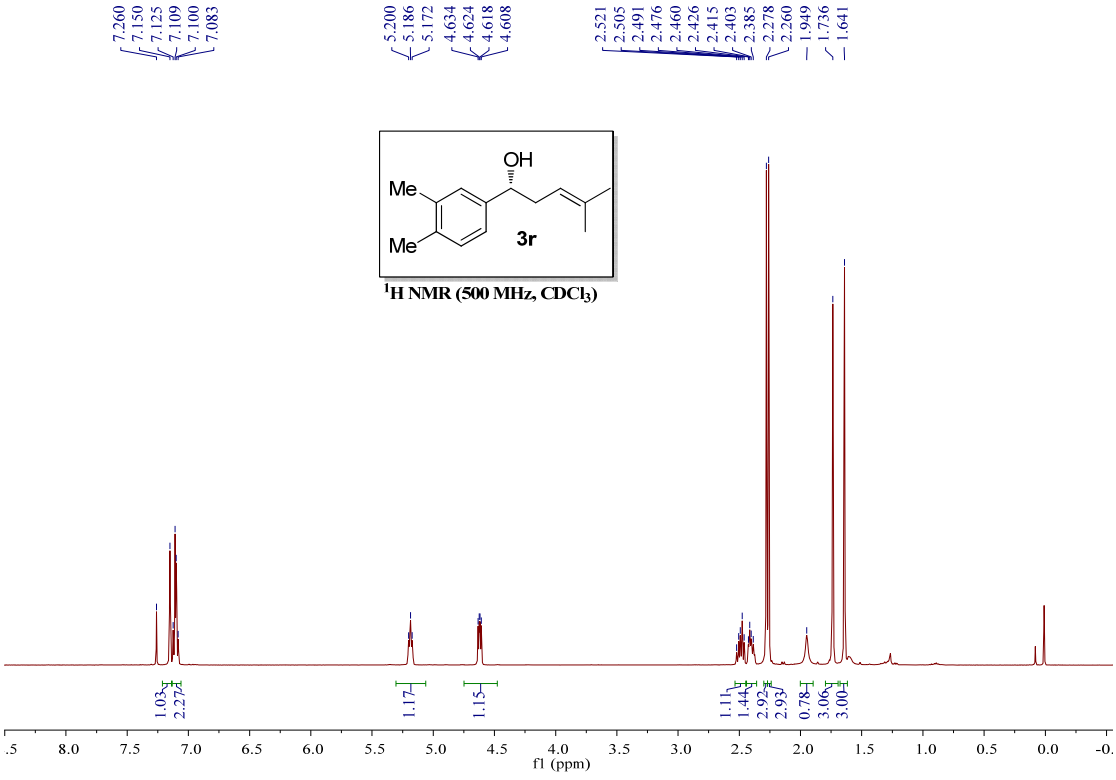
^{19}F NMR (471 MHz, $CDCl_3$)



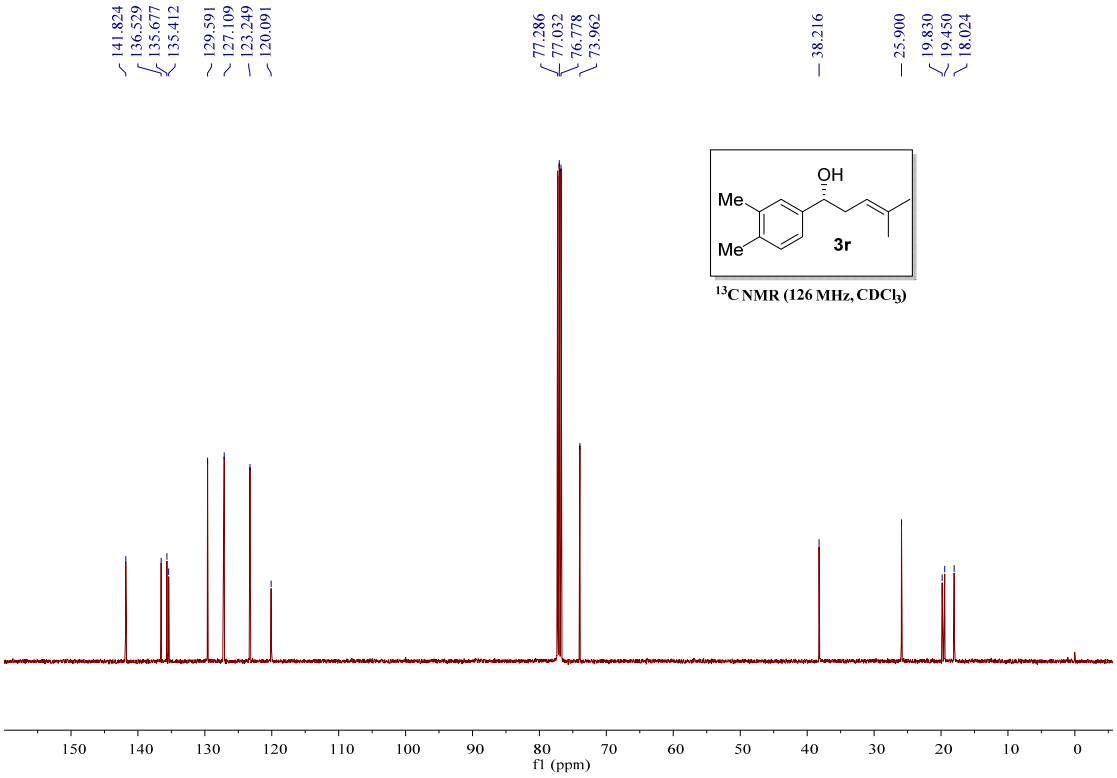
^{1}H NMR (500 MHz, $CDCl_3$)



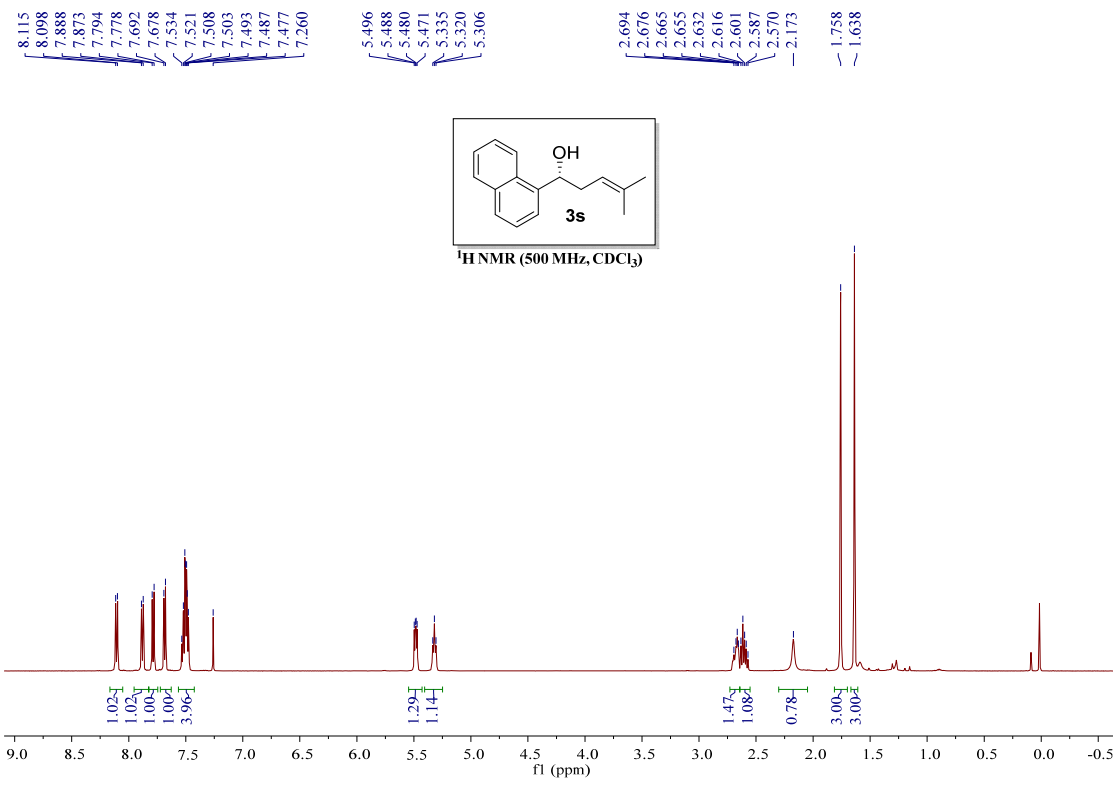
^{13}C NMR (126 MHz, $CDCl_3$)



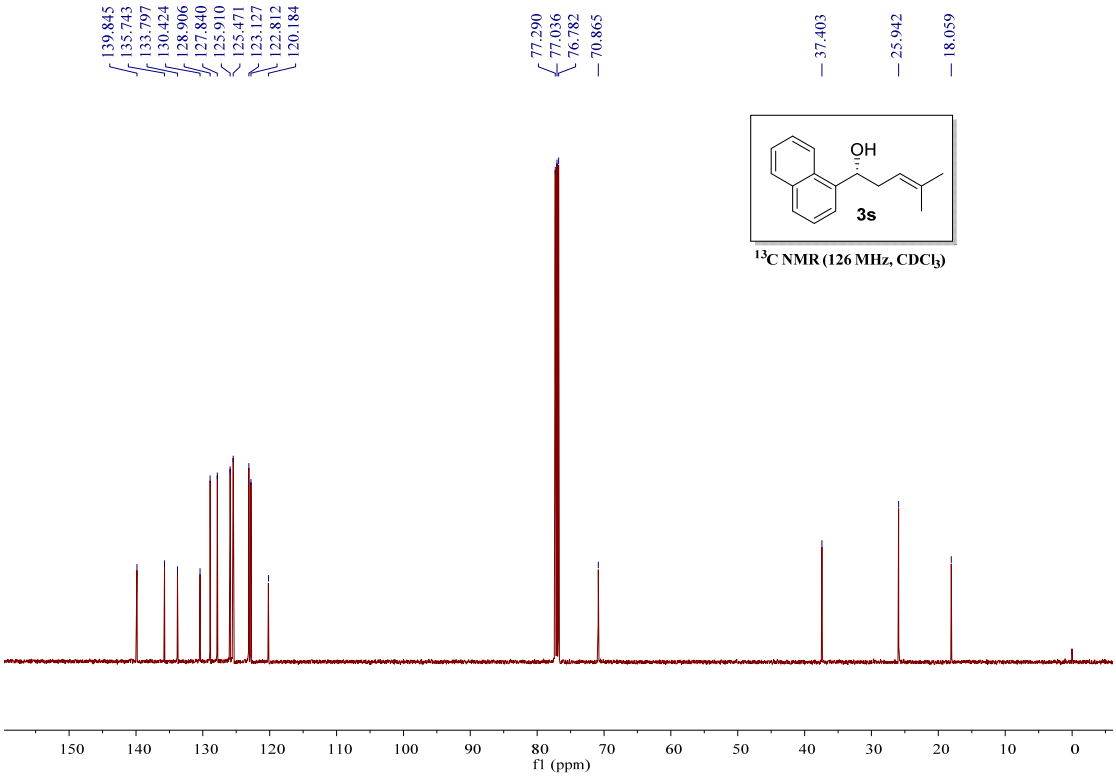
^{1}H NMR (500 MHz, $CDCl_3$)



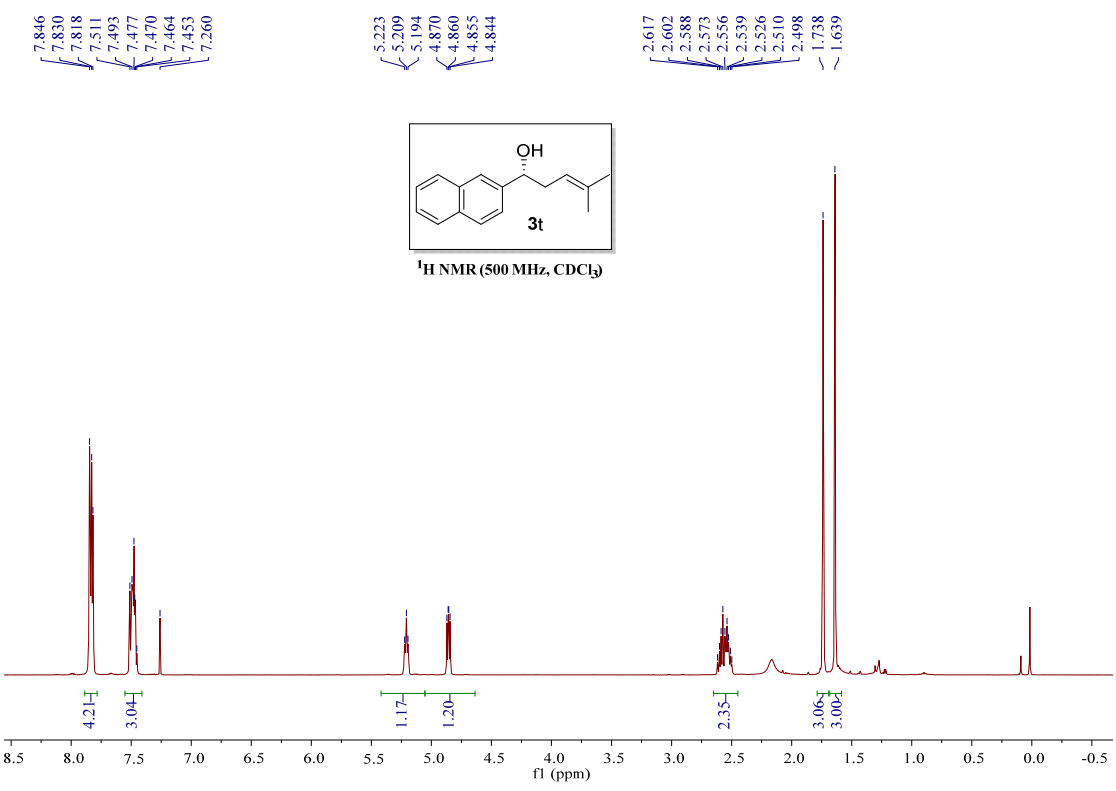
^{13}C NMR (126 MHz, $CDCl_3$)



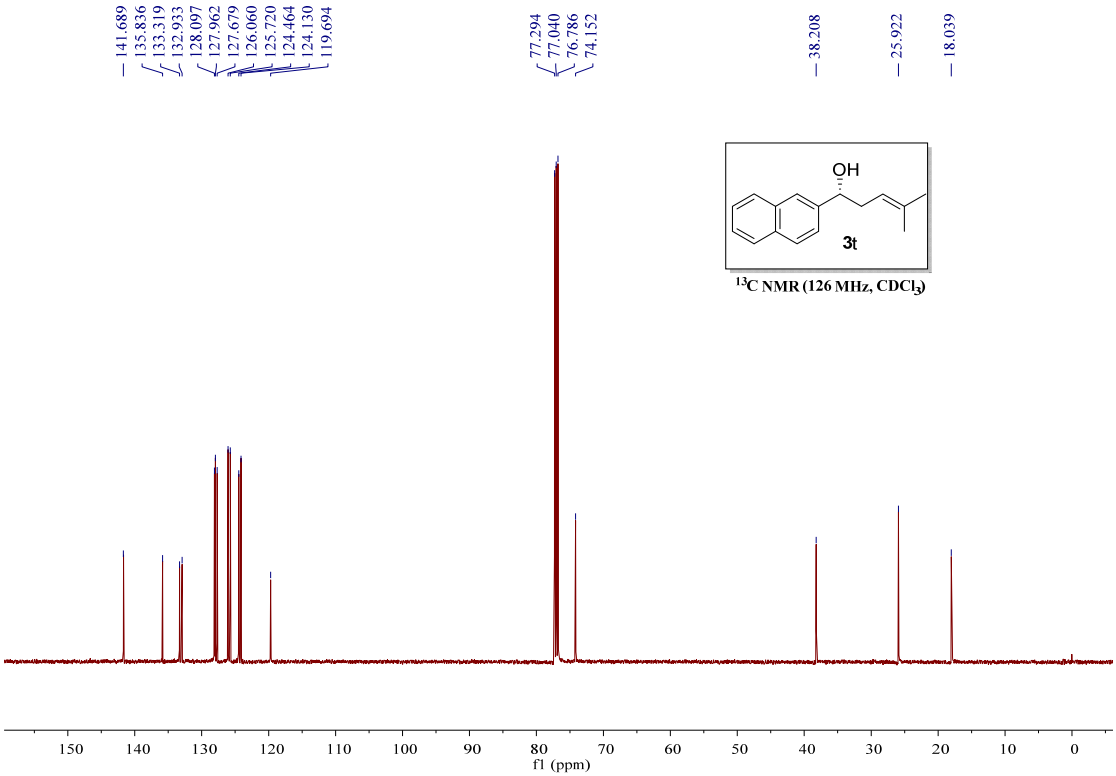
^{1}H NMR (500 MHz, $CDCl_3$)



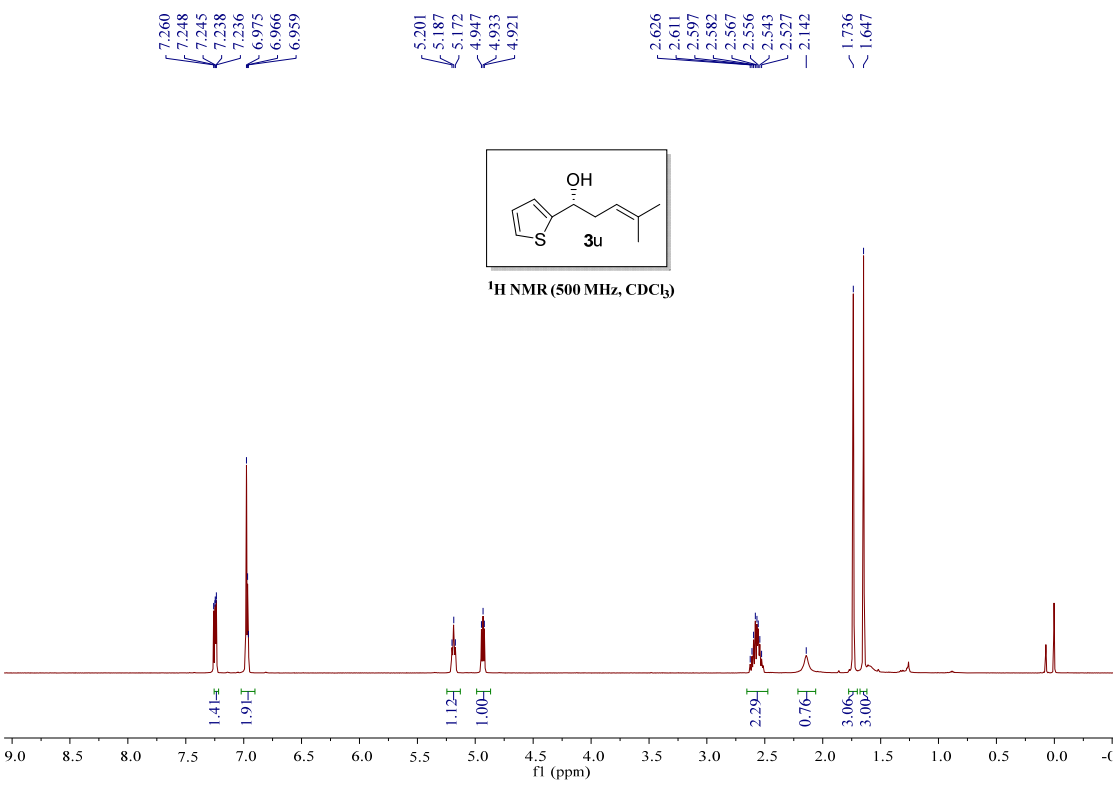
^{13}C NMR (126 MHz, $CDCl_3$)



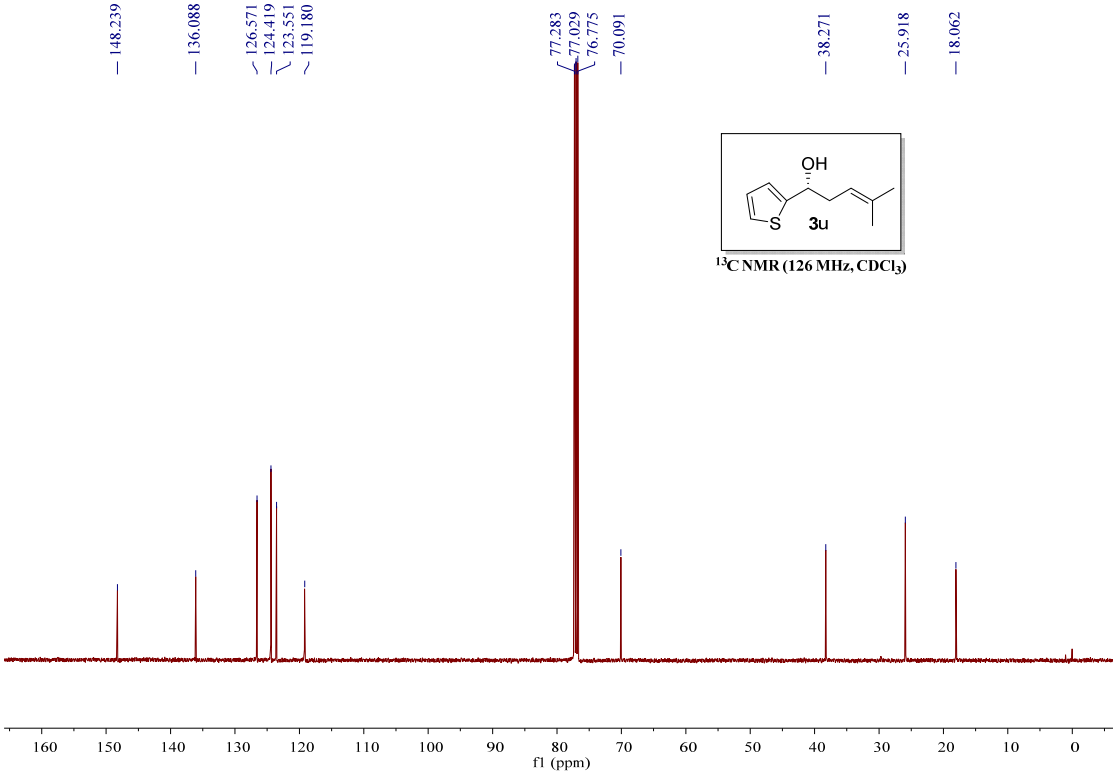
^{1}H NMR (500 MHz, $CDCl_3$)



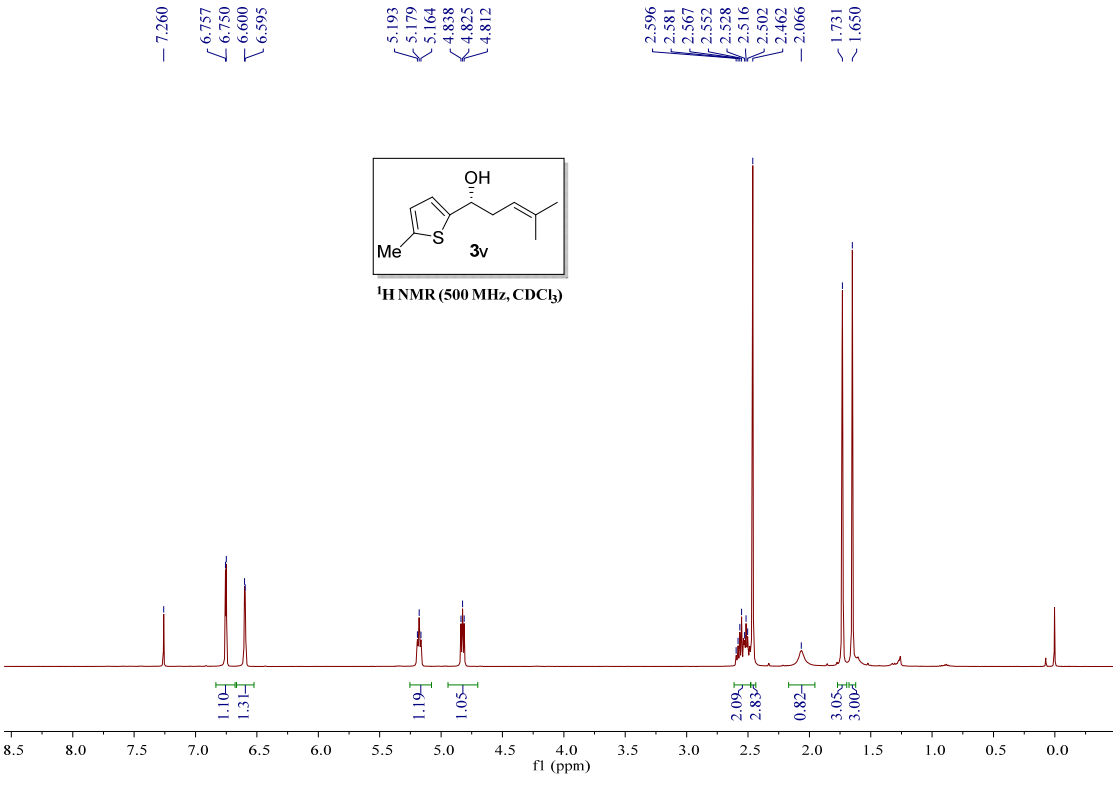
^{13}C NMR (126 MHz, $CDCl_3$)



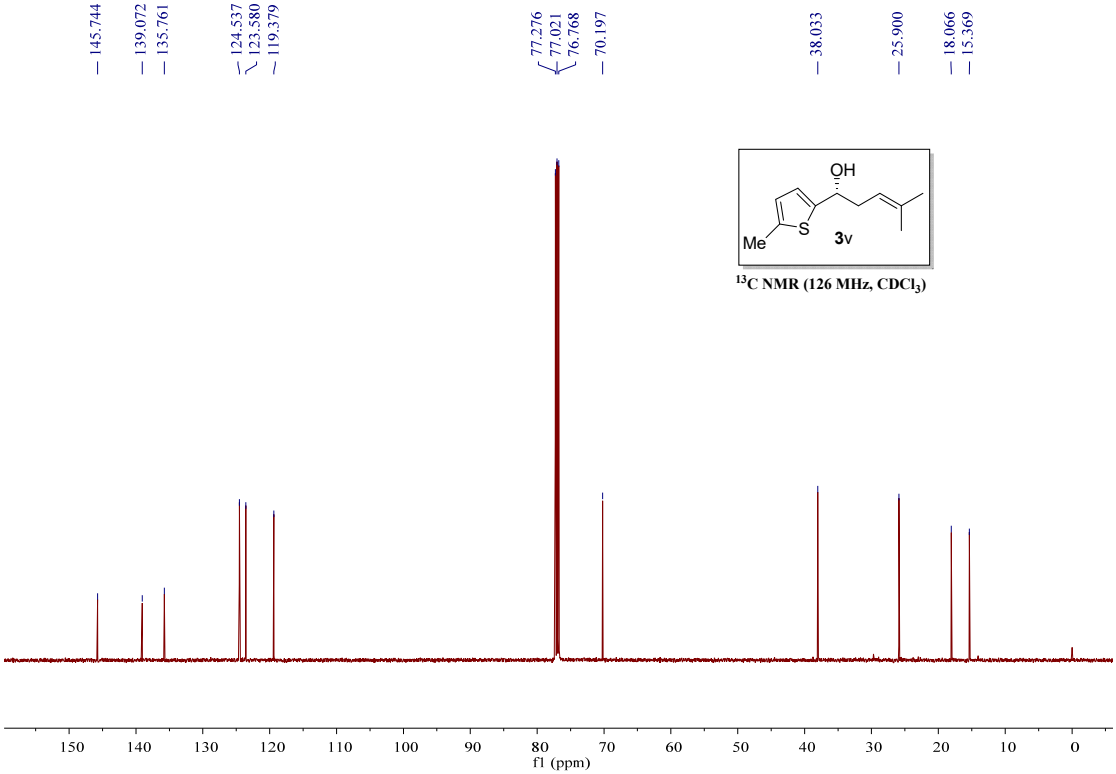
^{1}H NMR (500 MHz, $CDCl_3$)



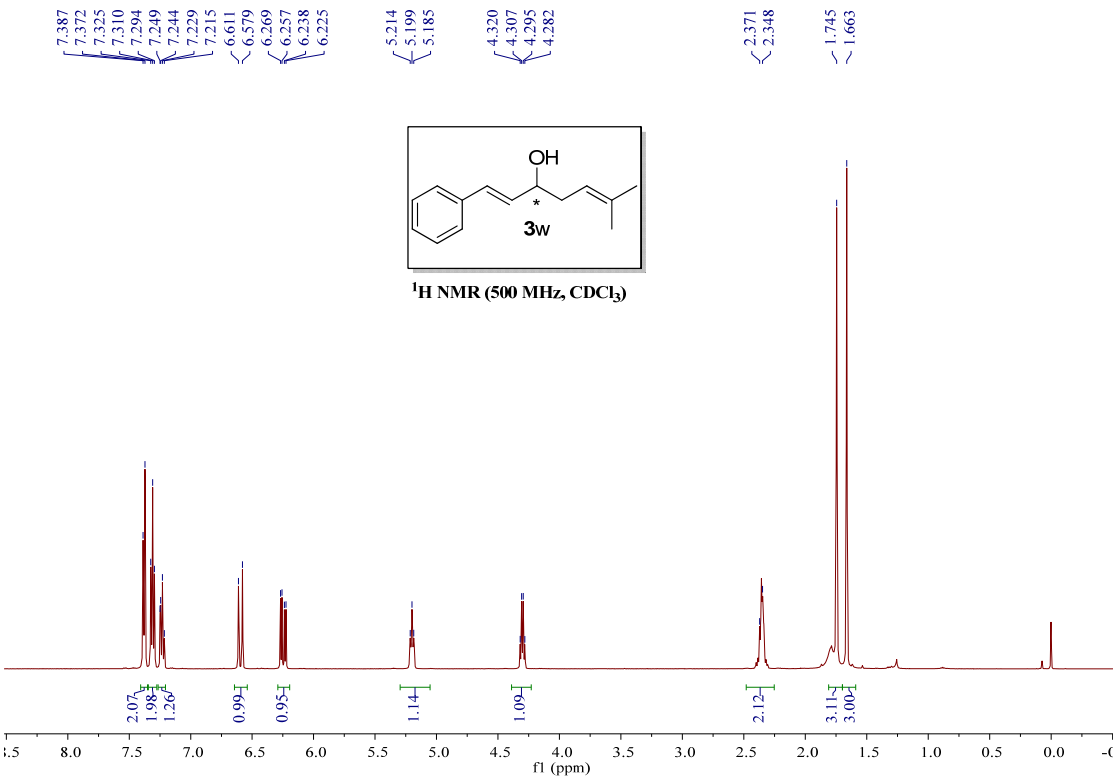
^{13}C NMR (126 MHz, $CDCl_3$)



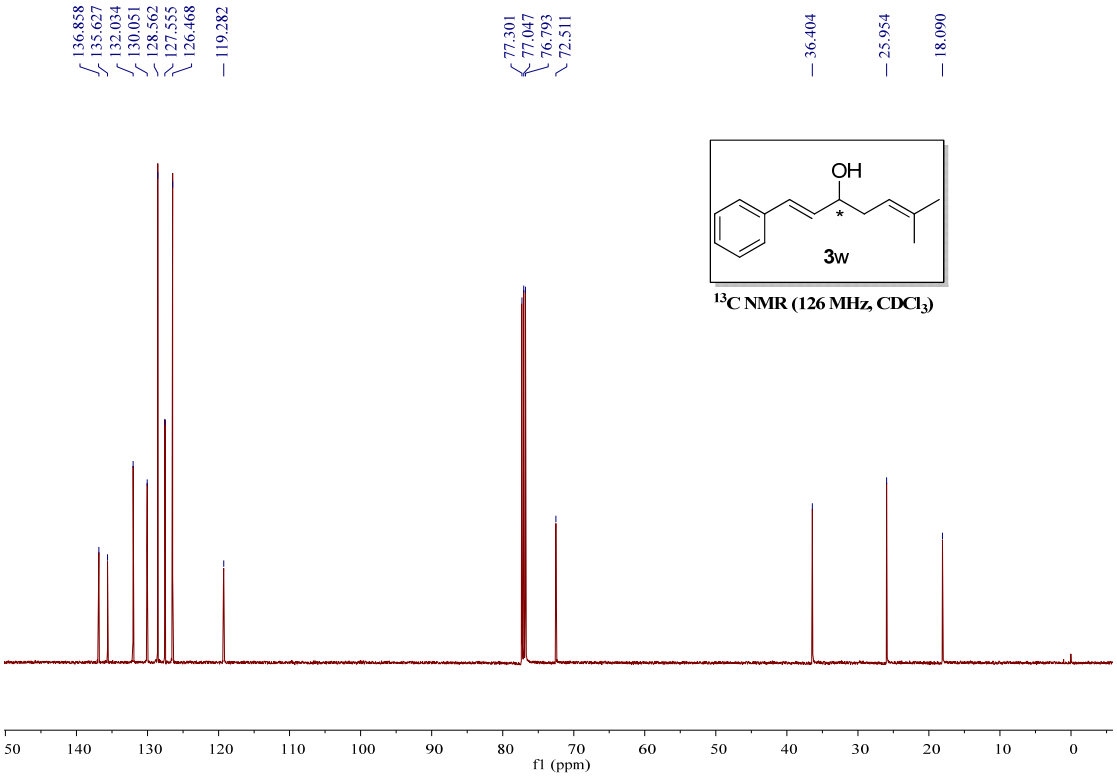
^{1}H NMR (500 MHz, $CDCl_3$)



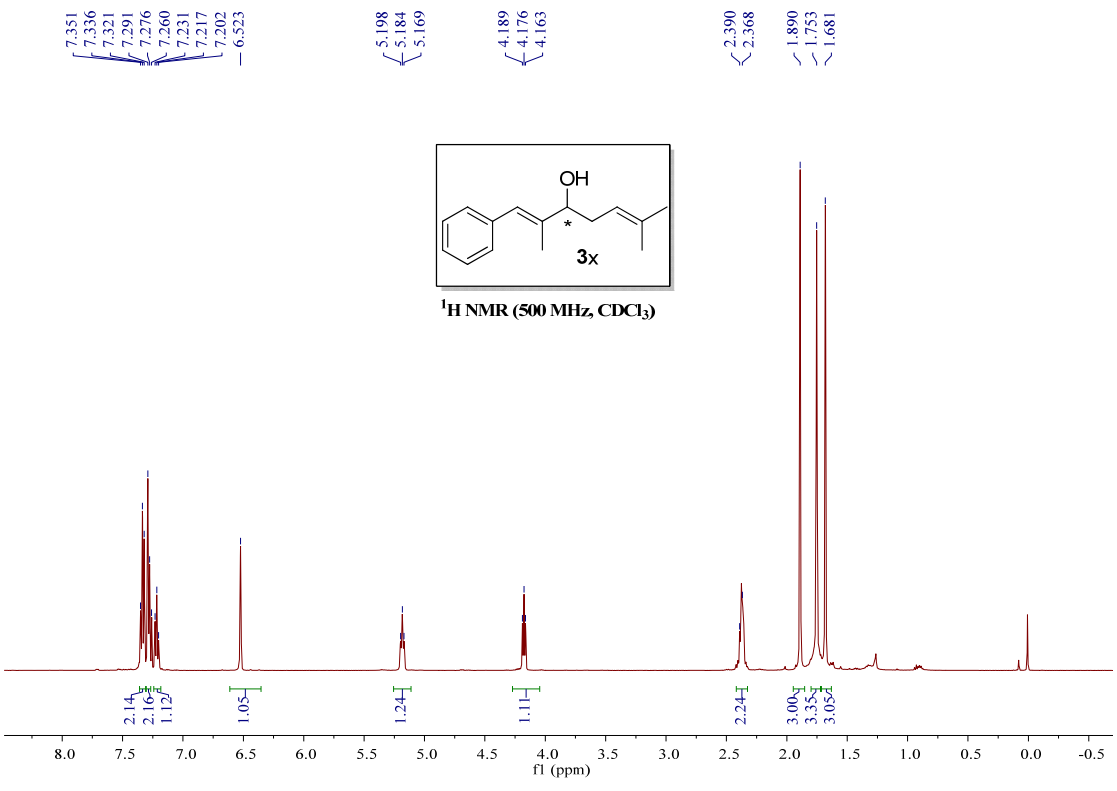
^{13}C NMR (126 MHz, $CDCl_3$)



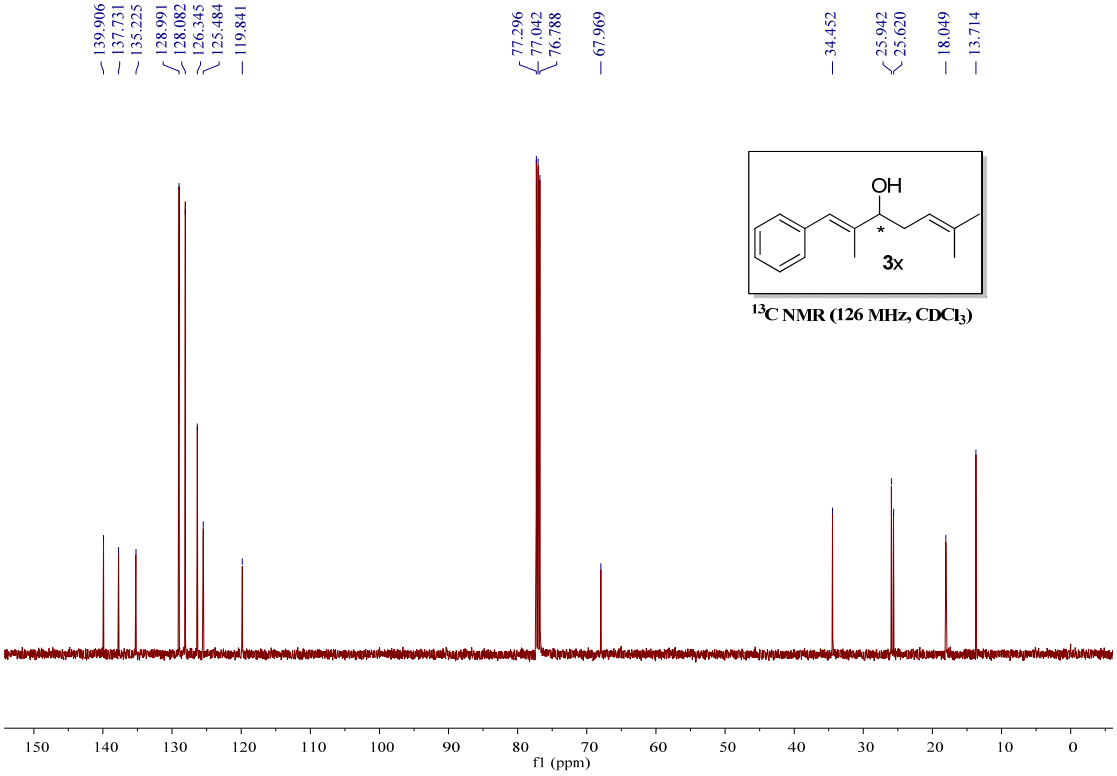
^{1}H NMR (500 MHz, $CDCl_3$)



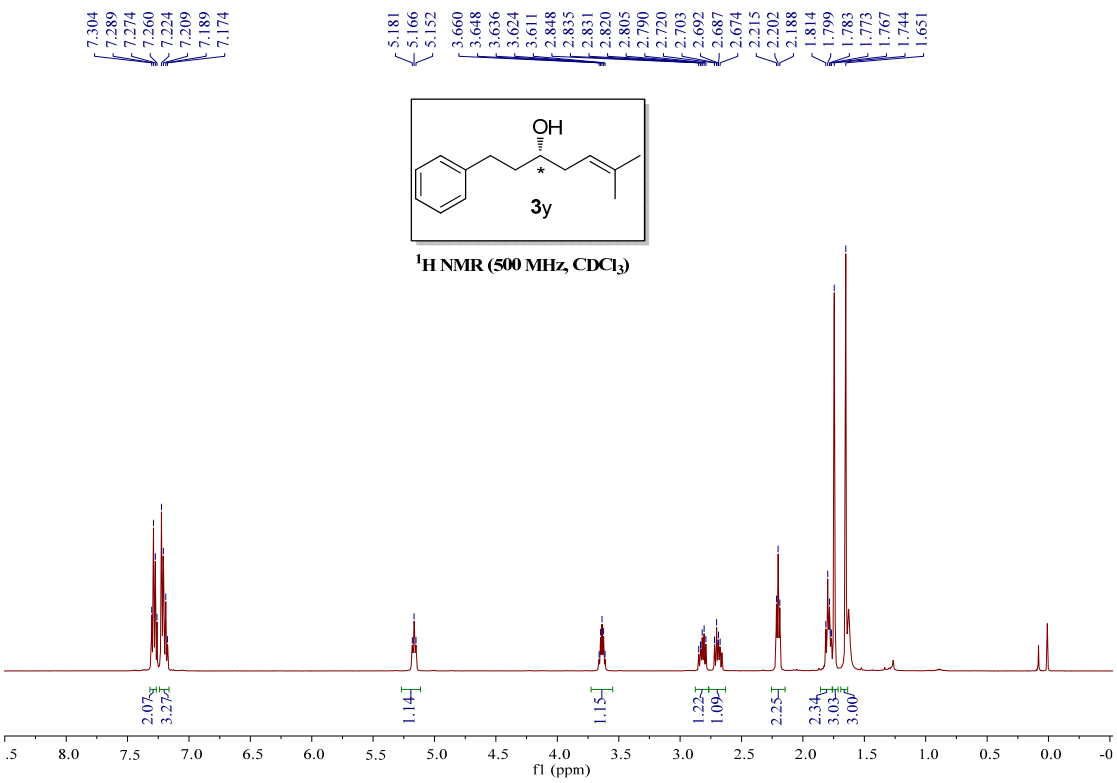
^{13}C NMR (126 MHz, $CDCl_3$)



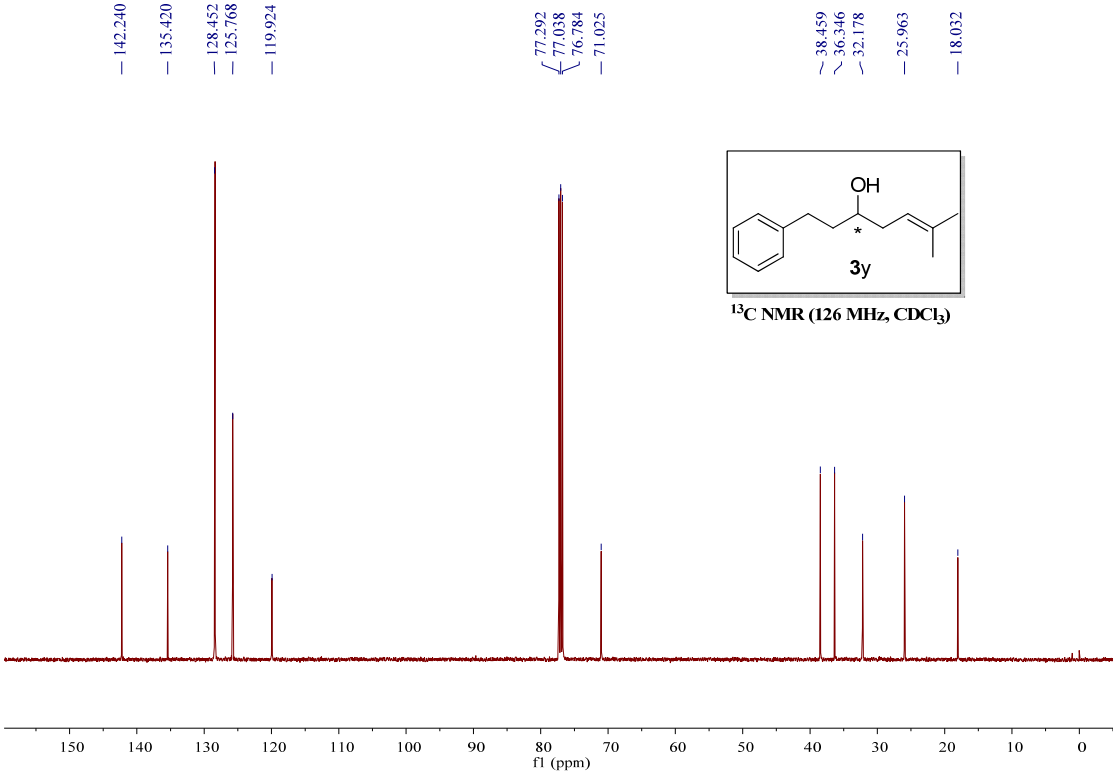
^{1}H NMR (500 MHz, $CDCl_3$)



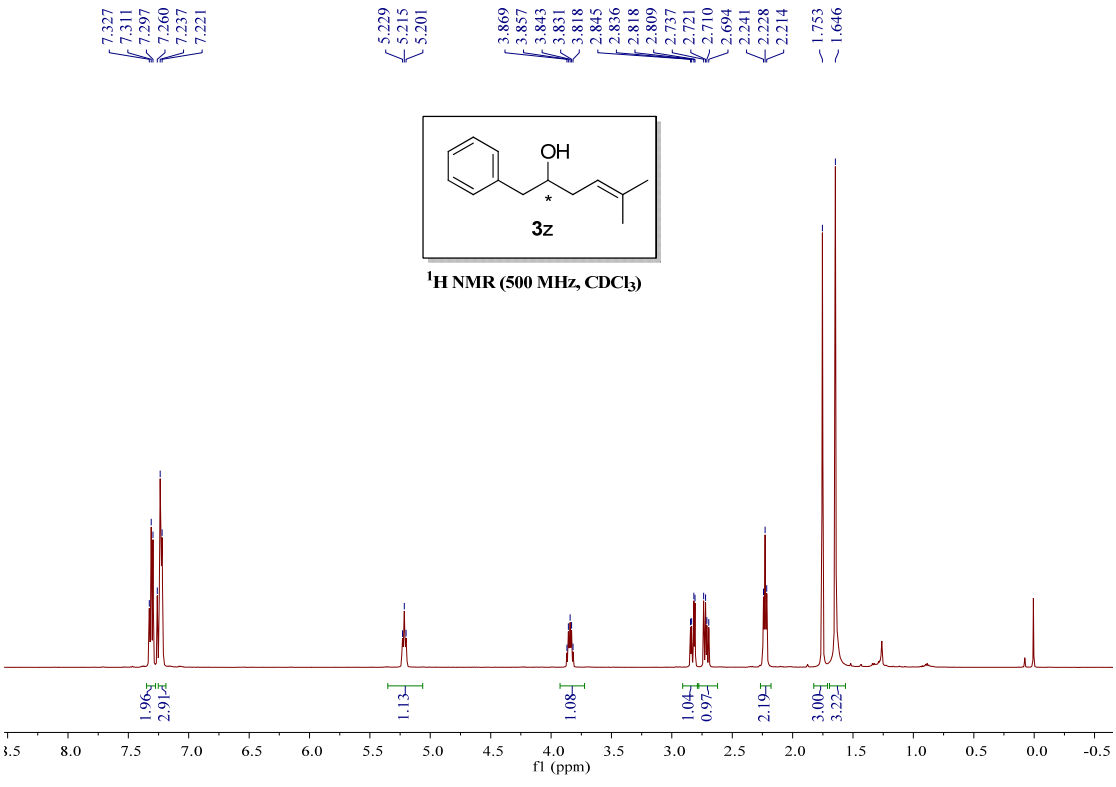
^{13}C NMR (126 MHz, $CDCl_3$)



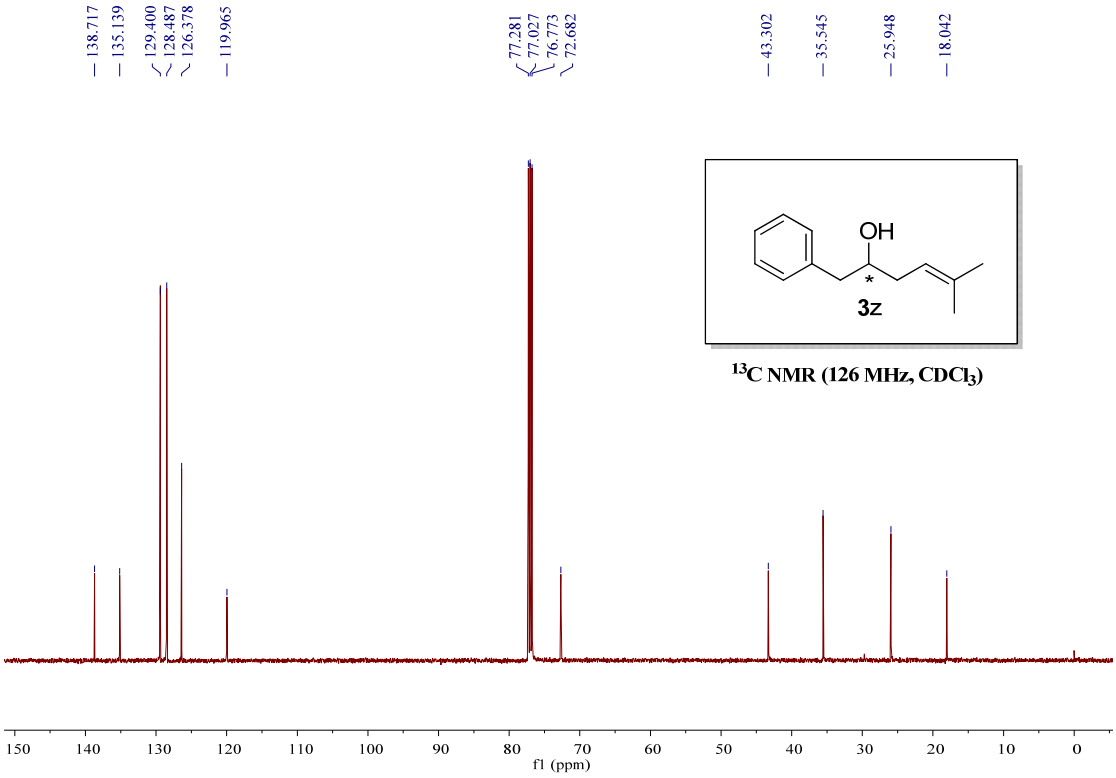
^{1}H NMR (500 MHz, $CDCl_3$)



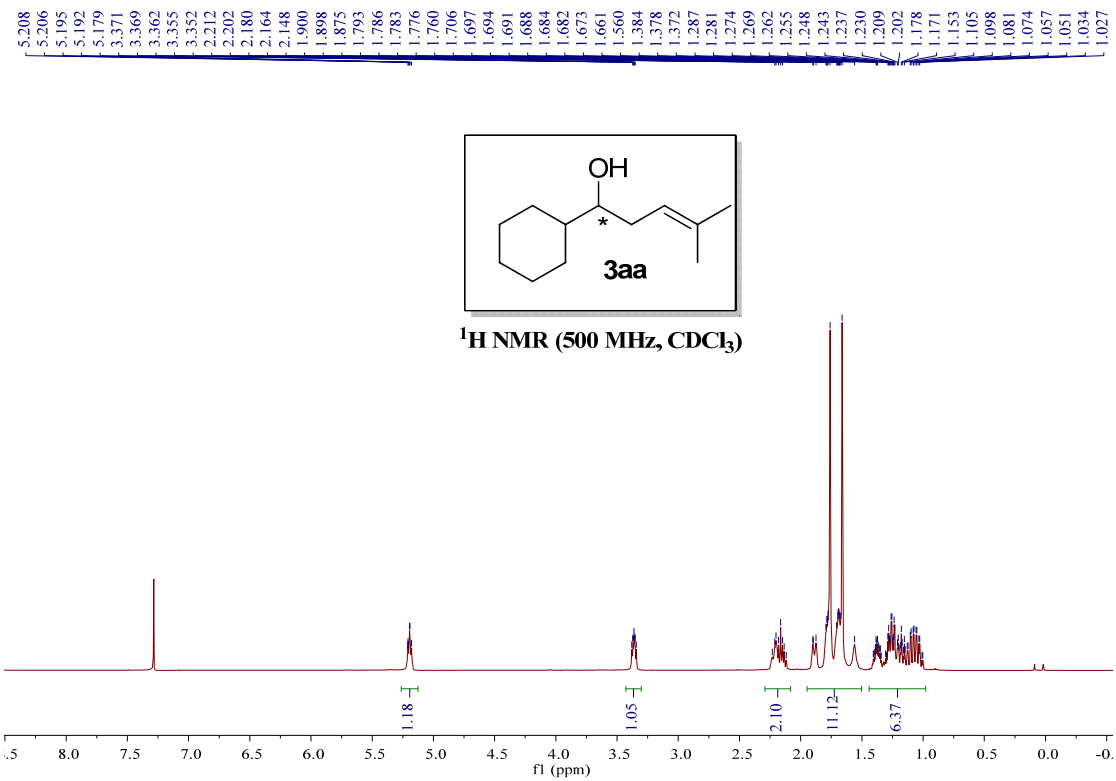
^{13}C NMR (126 MHz, $CDCl_3$)



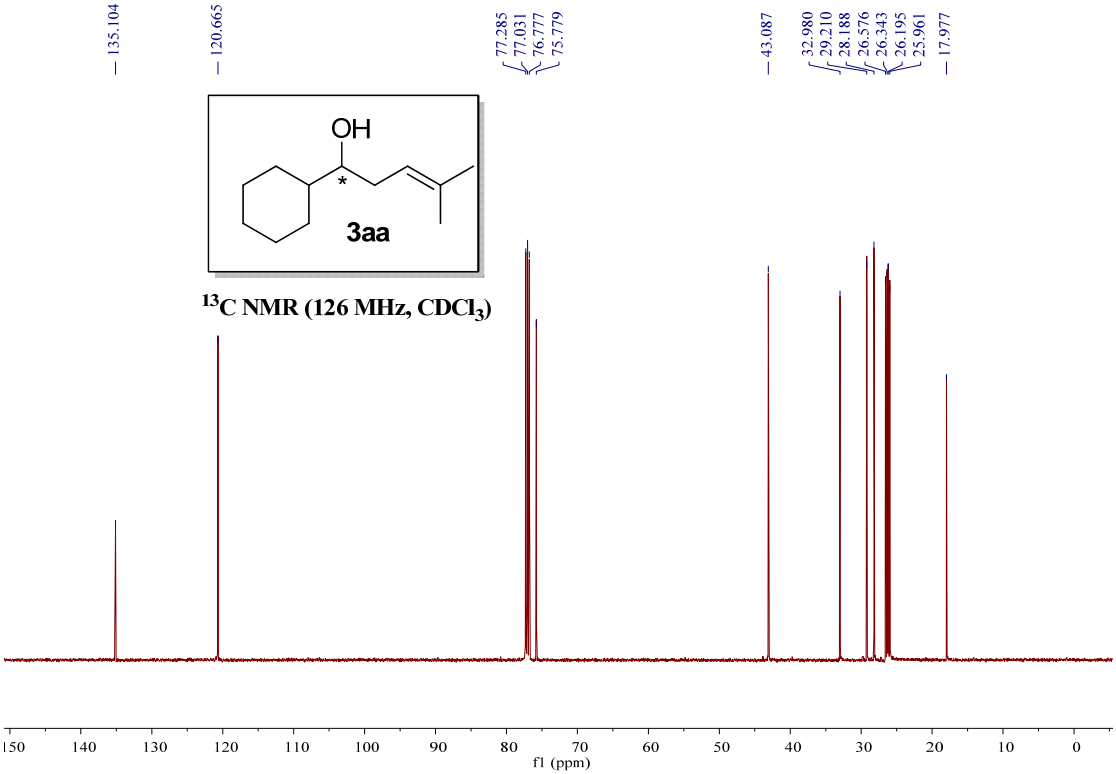
^{1}H NMR (500 MHz, $CDCl_3$)



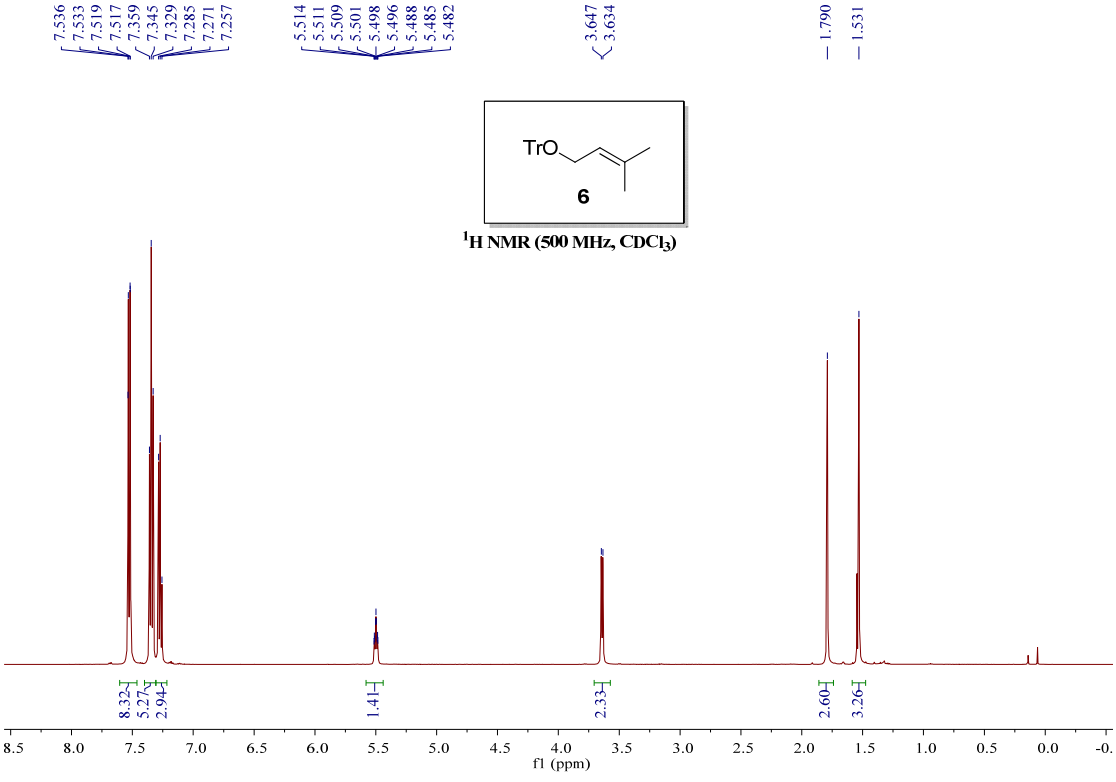
^{13}C NMR (126 MHz, $CDCl_3$)



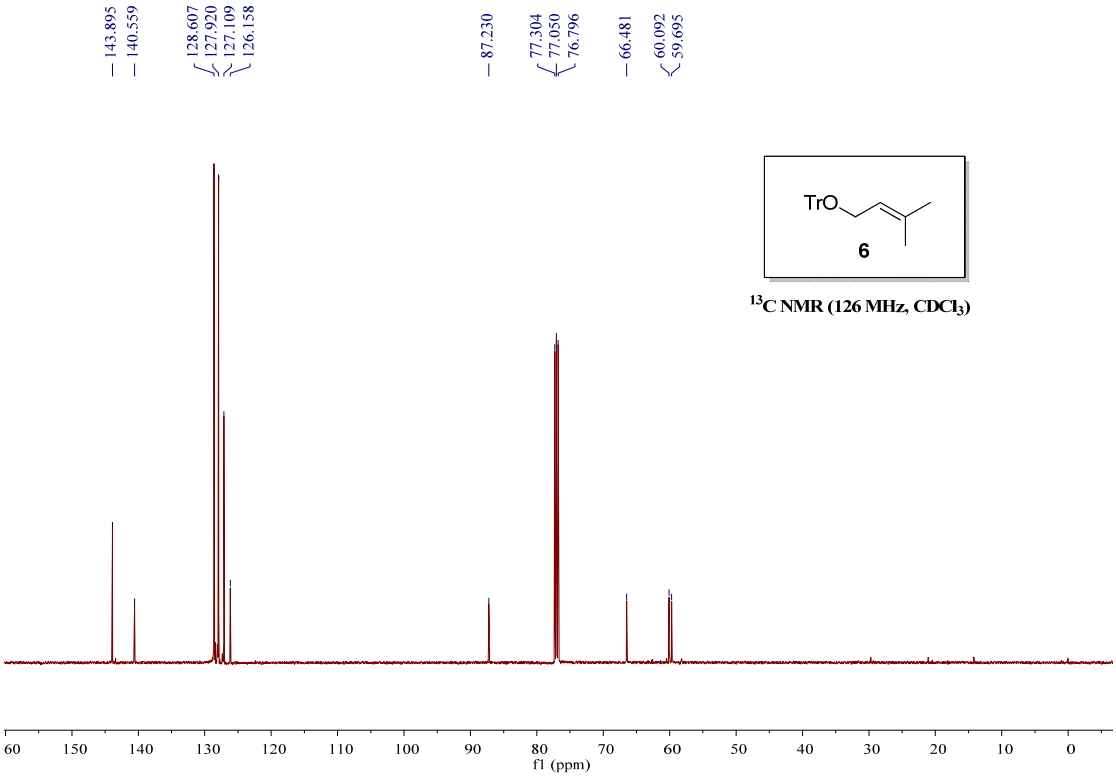
^{1}H NMR (500 MHz, $CDCl_3$)



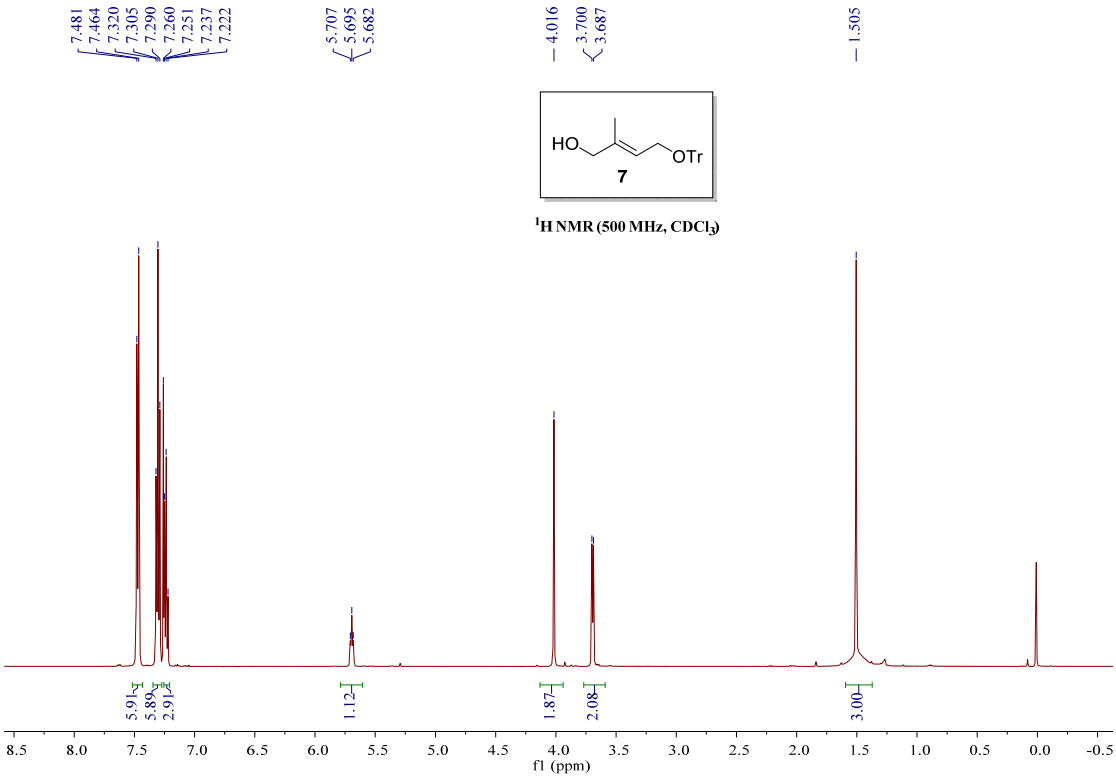
^{13}C NMR (126 MHz, $CDCl_3$)



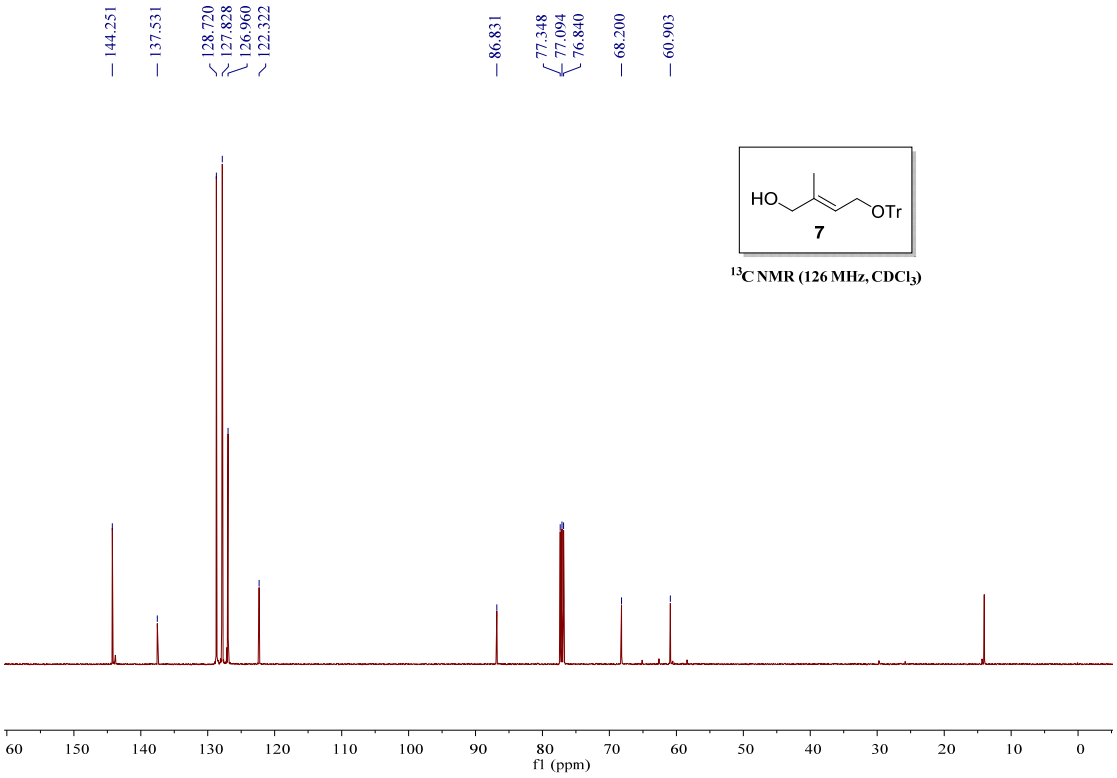
^{1}H NMR (500 MHz, $CDCl_3$)



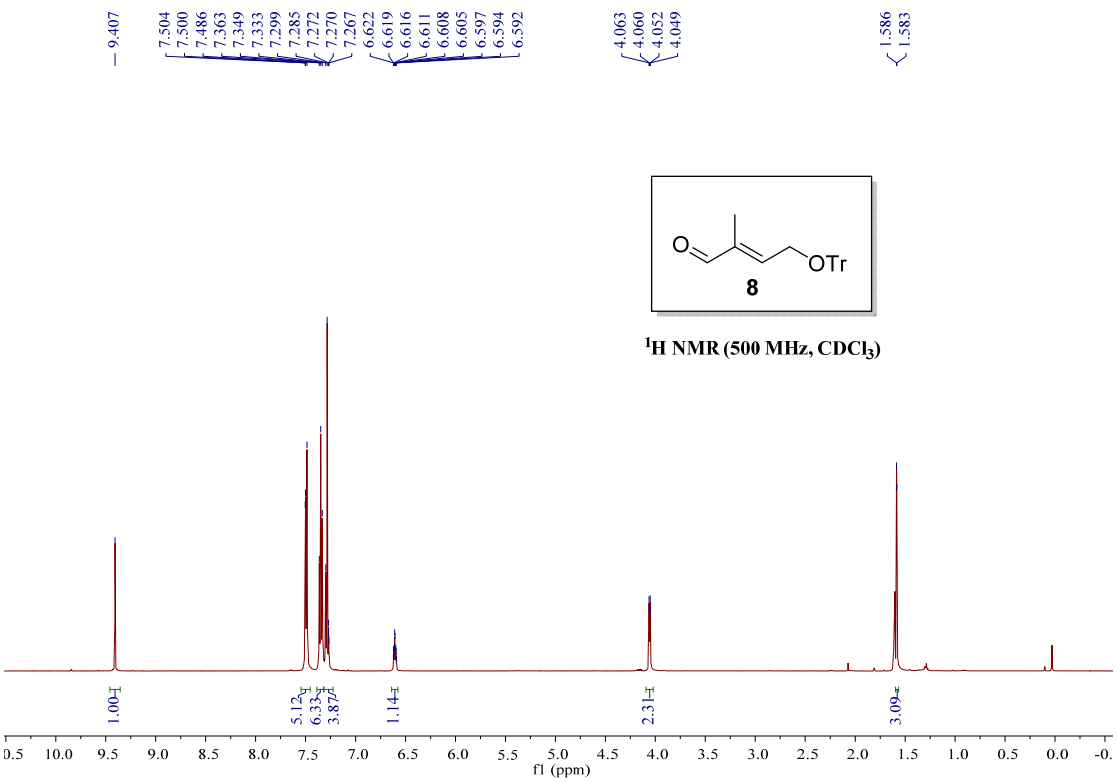
^{13}C NMR (126 MHz, $CDCl_3$)



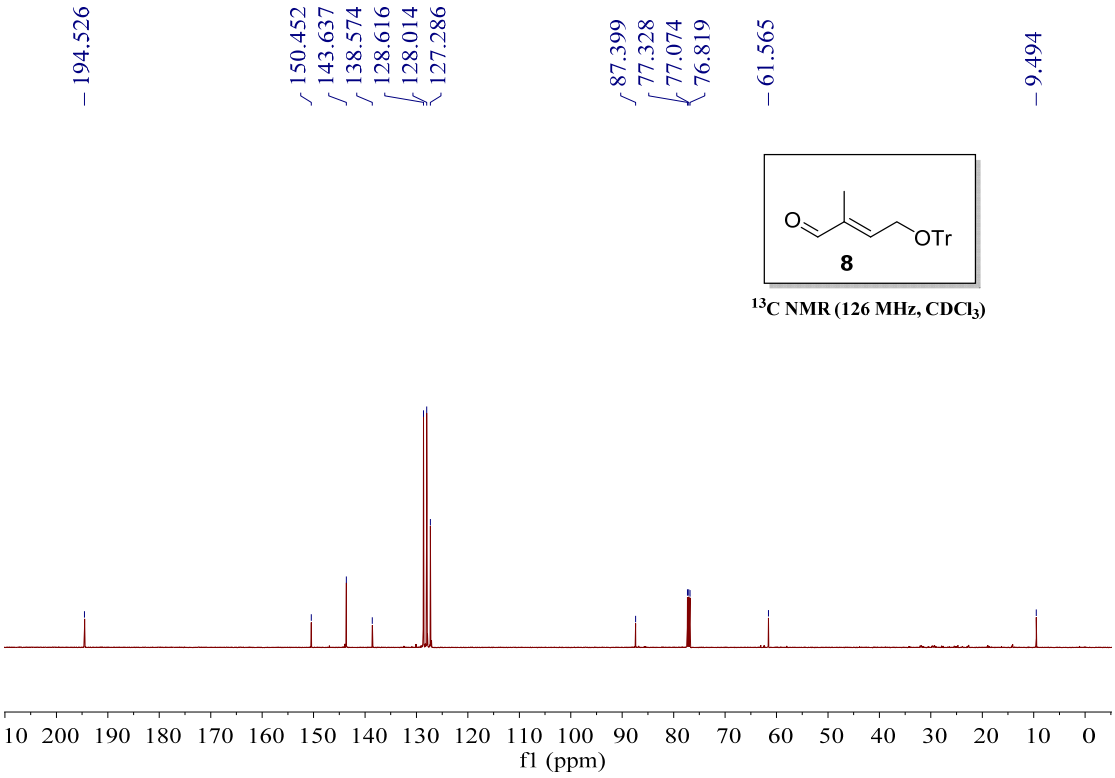
^{1}H NMR (500 MHz, $CDCl_3$)



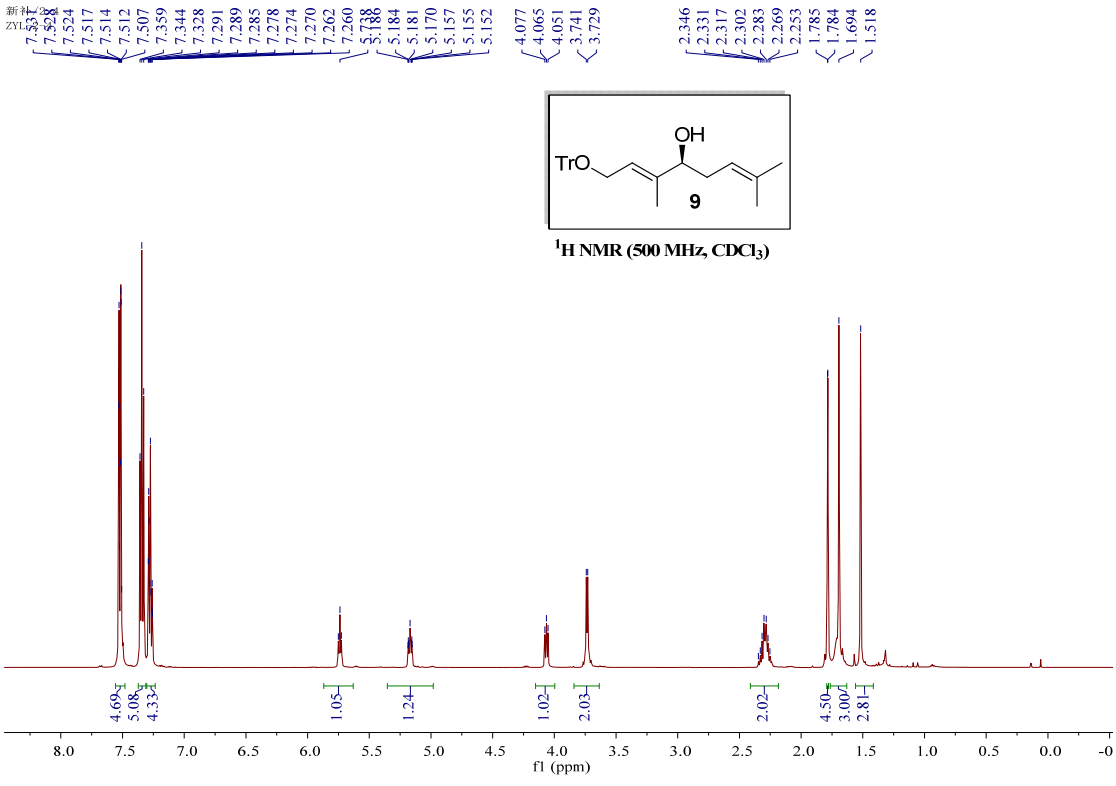
^{13}C NMR (126 MHz, $CDCl_3$)



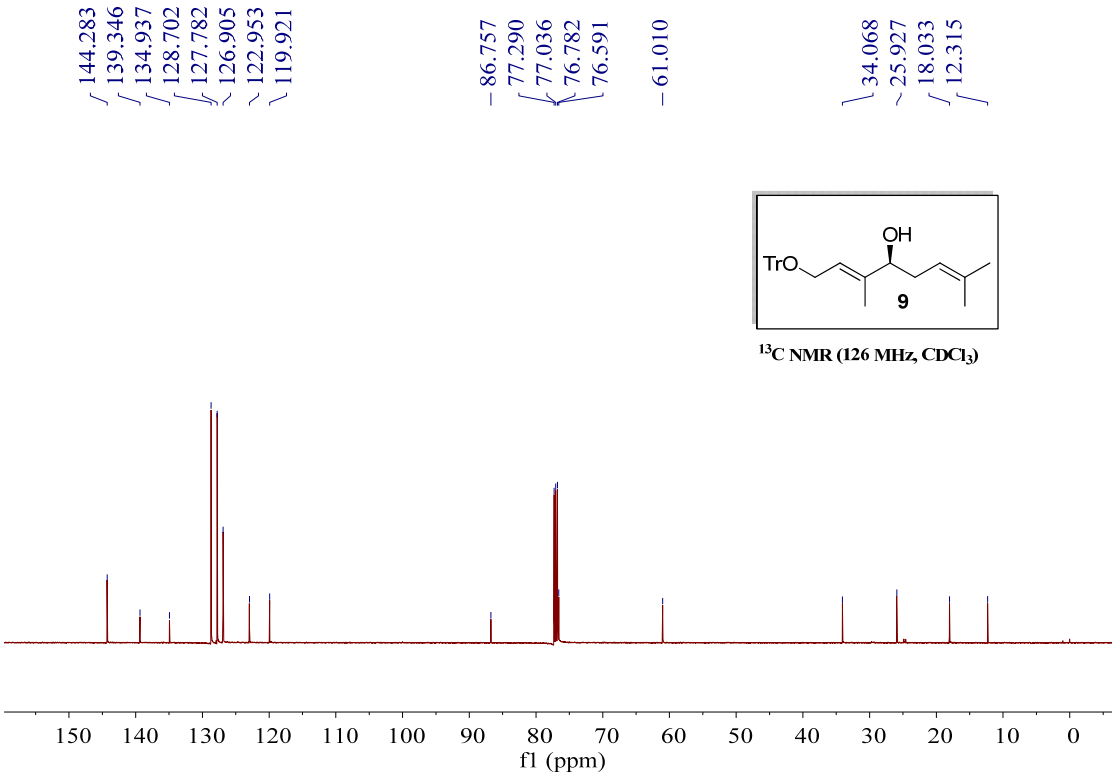
^{1}H NMR (500 MHz, $CDCl_3$)



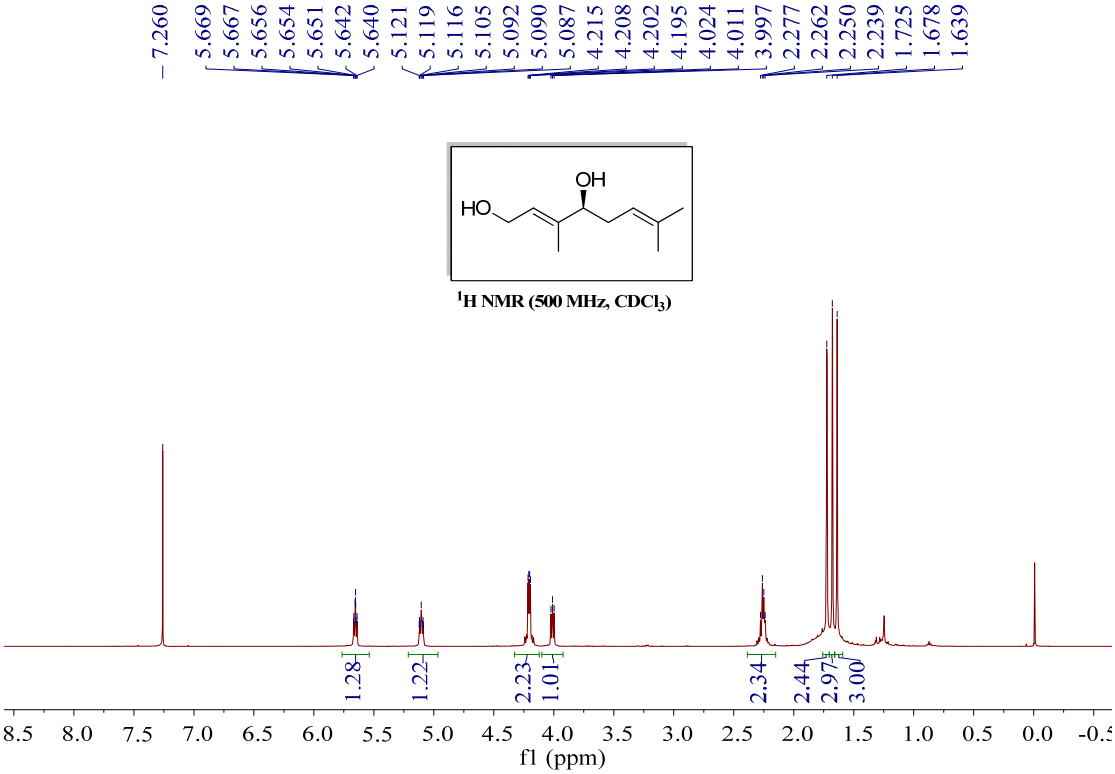
^{13}C NMR (126 MHz, $CDCl_3$)



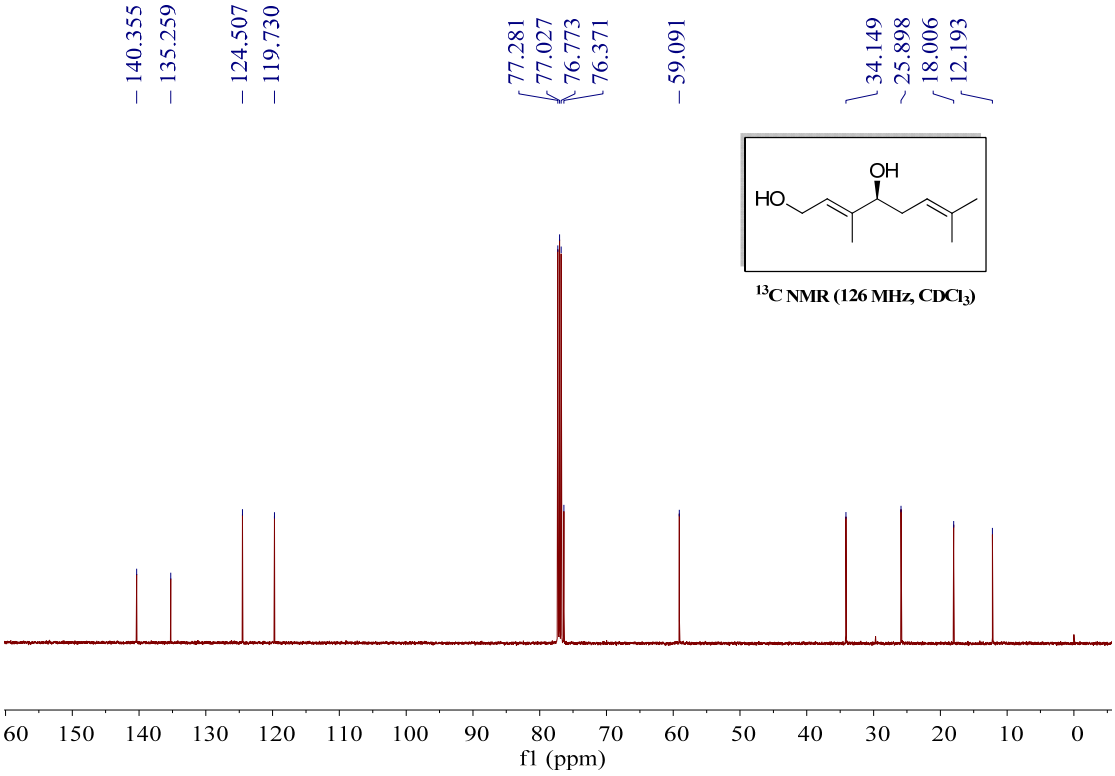
^{1}H NMR (500 MHz, $CDCl_3$)



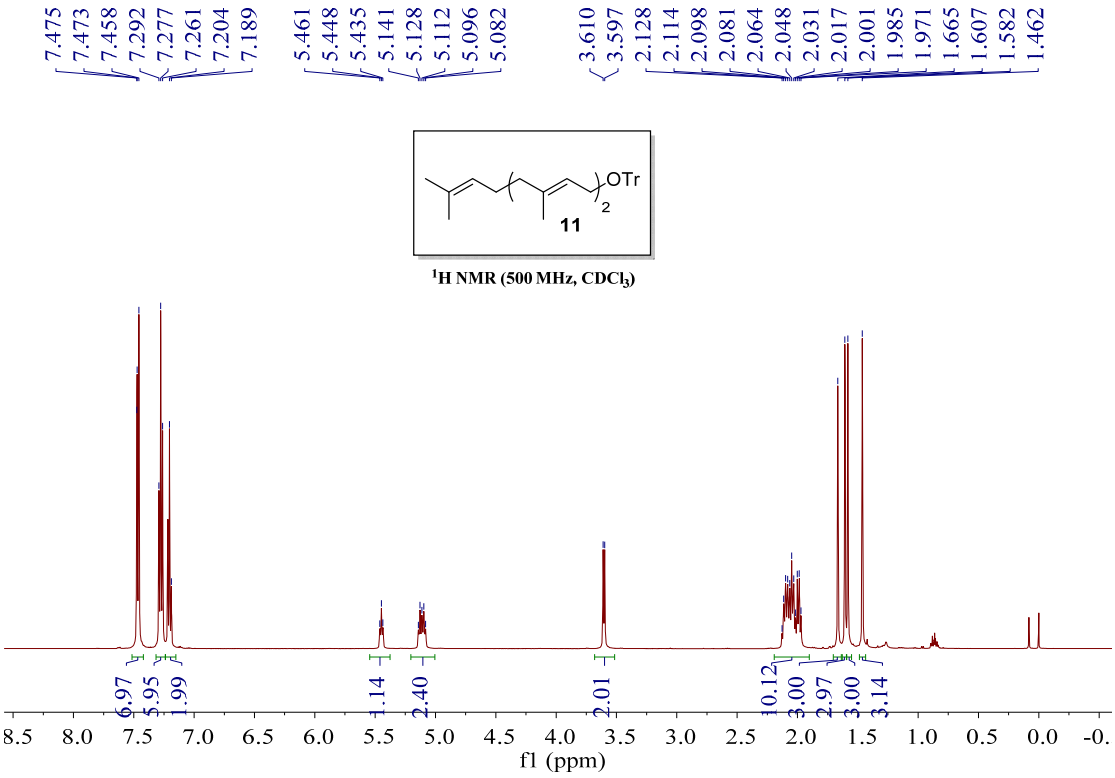
^{13}C NMR (126 MHz, $CDCl_3$)



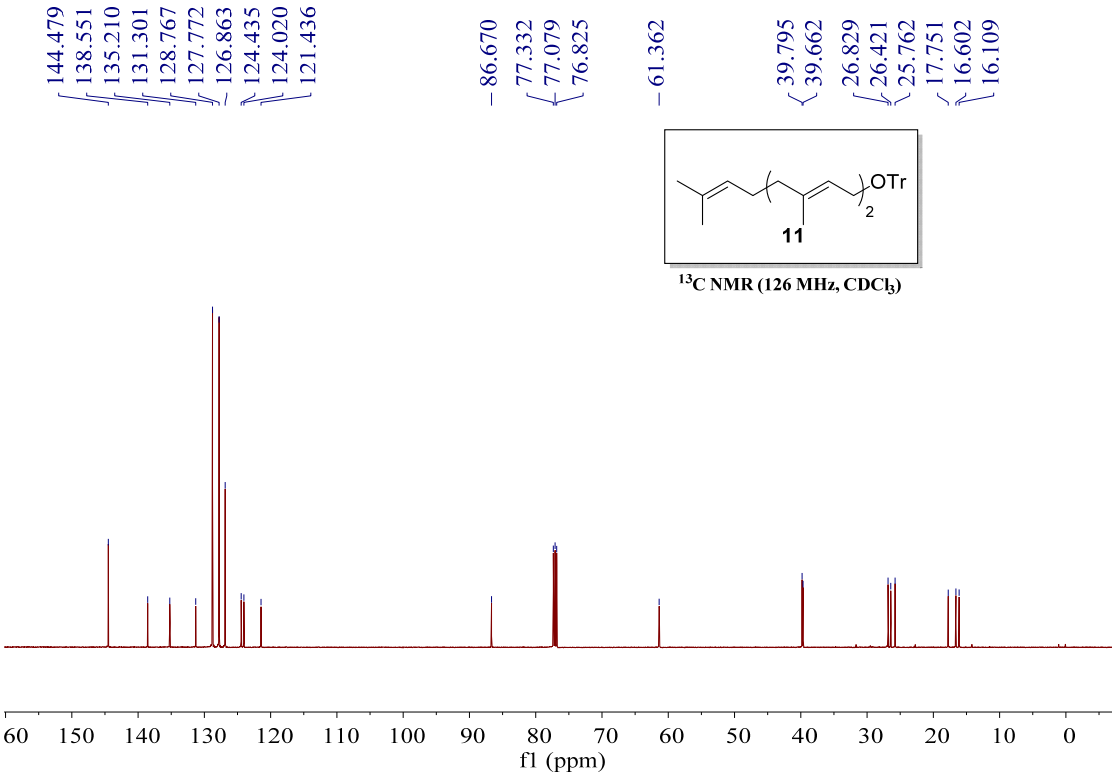
^{1}H NMR (500 MHz, $CDCl_3$)



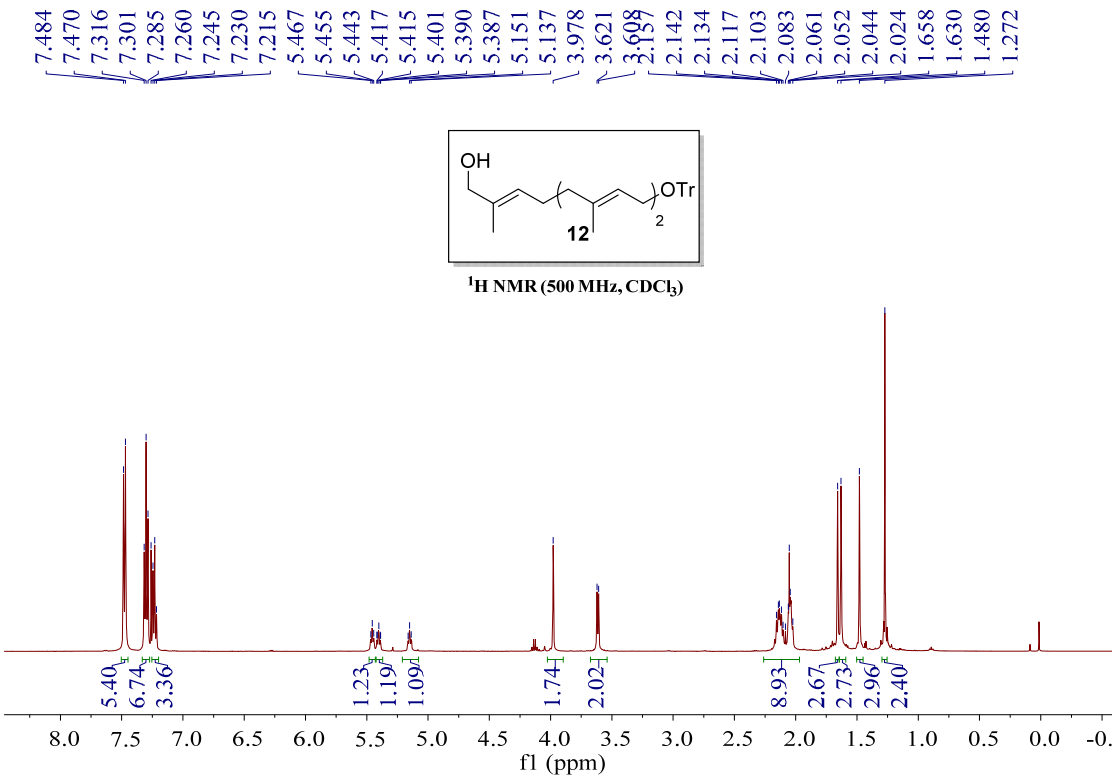
^{13}C NMR (126 MHz, $CDCl_3$)



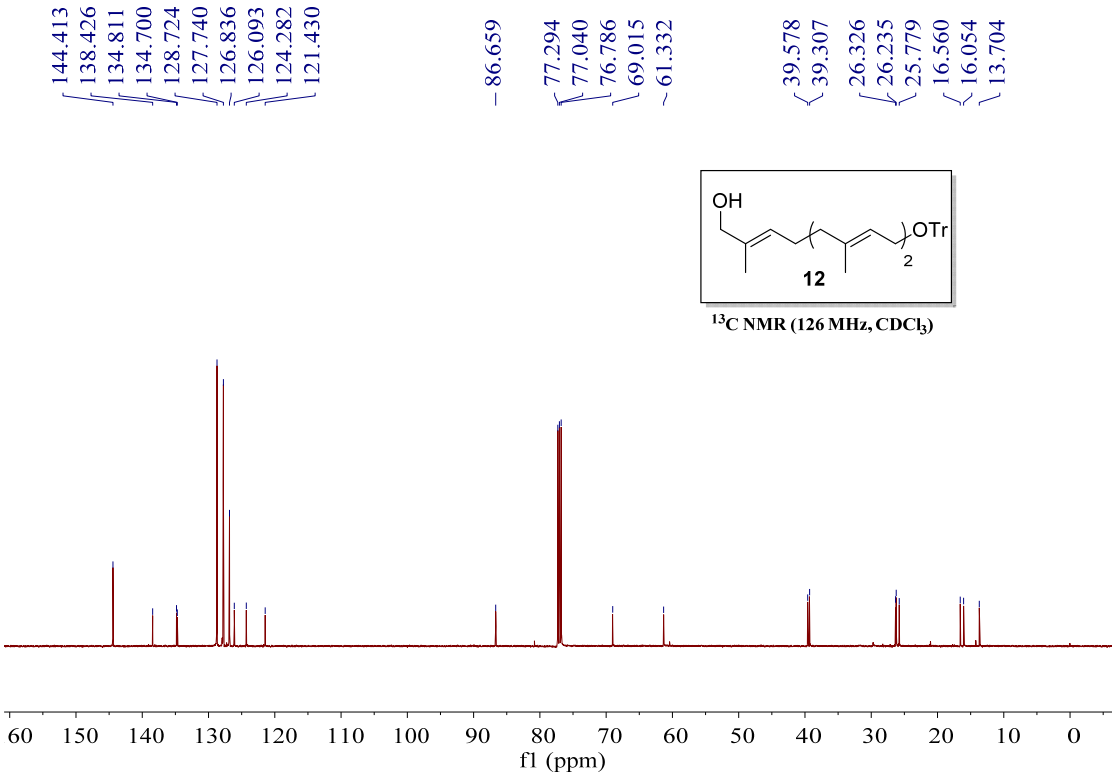
^{1}H NMR (500 MHz, $CDCl_3$)



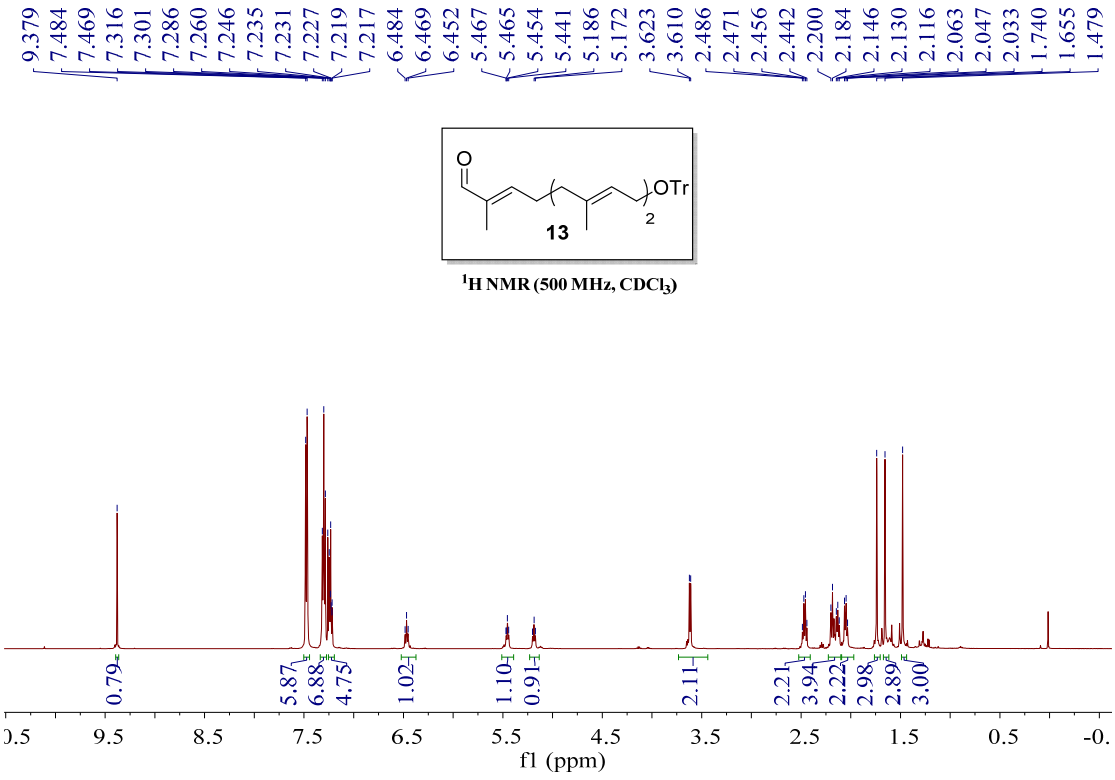
^{13}C NMR (126 MHz, $CDCl_3$)



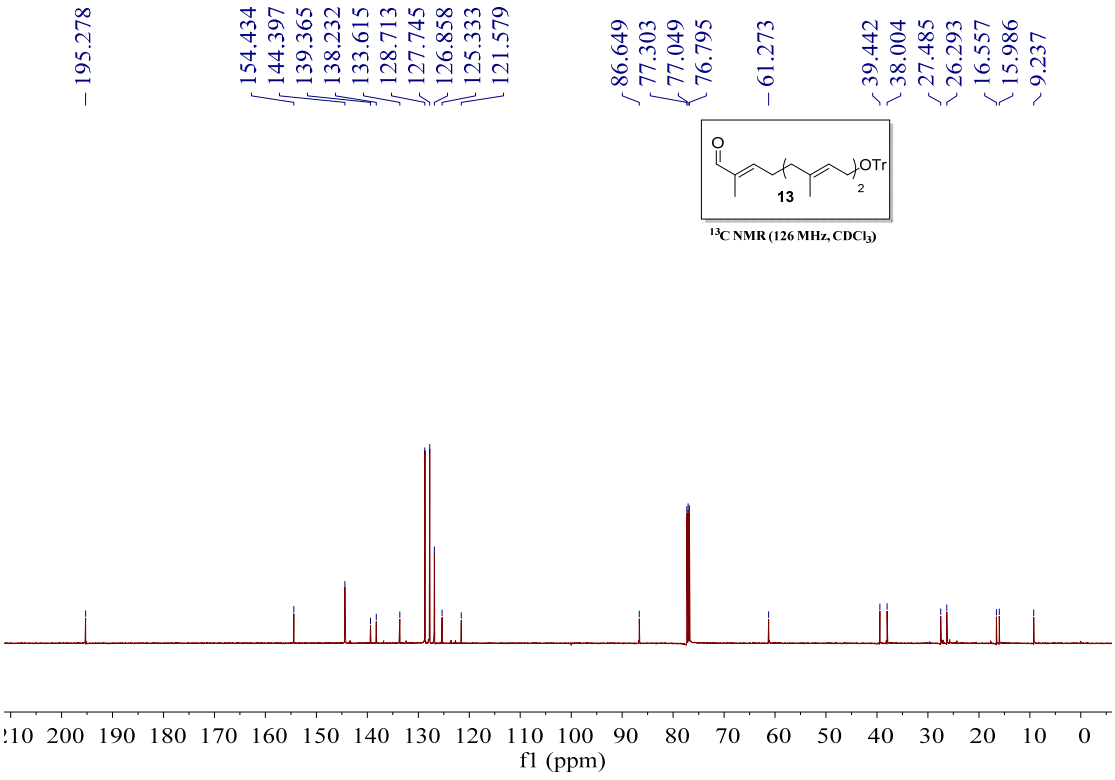
^{1}H NMR (500 MHz, $CDCl_3$)



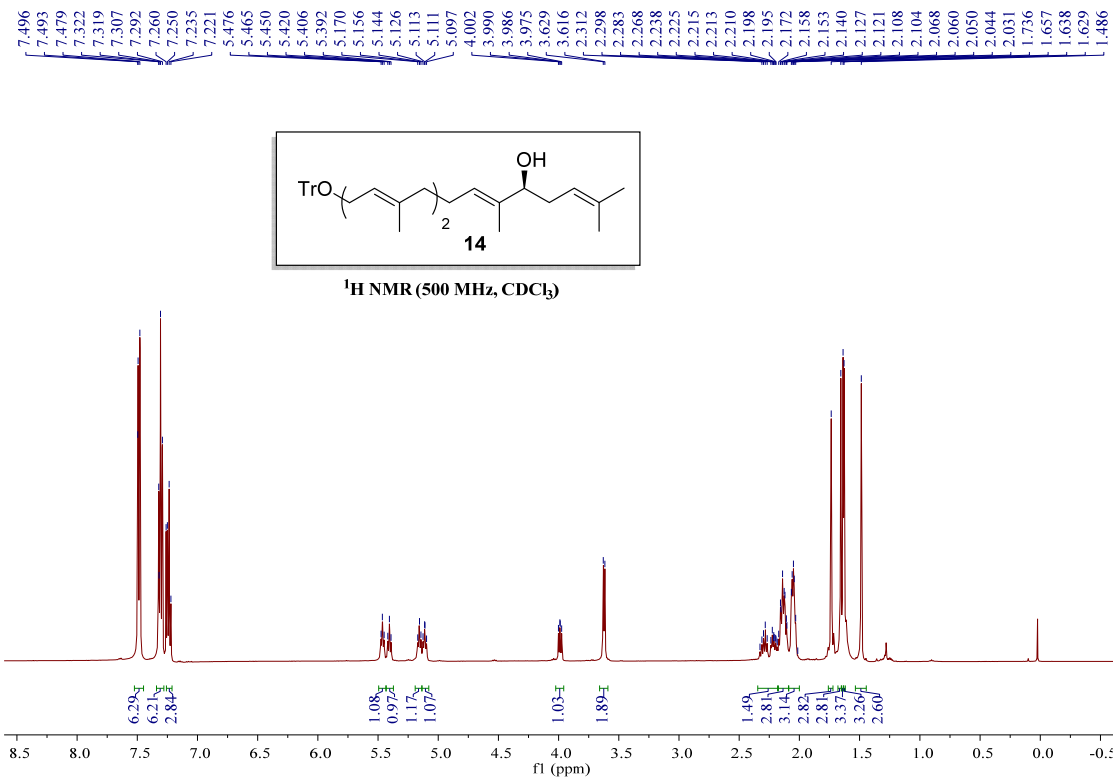
^{13}C NMR (126 MHz, $CDCl_3$)



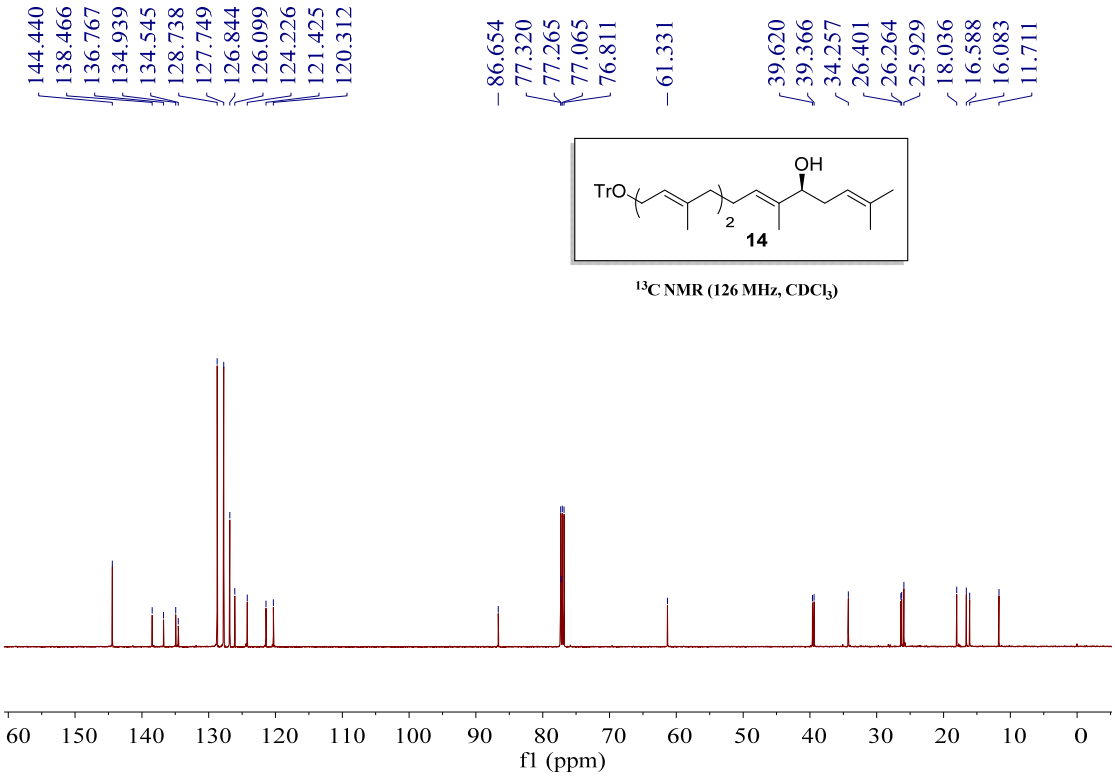
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



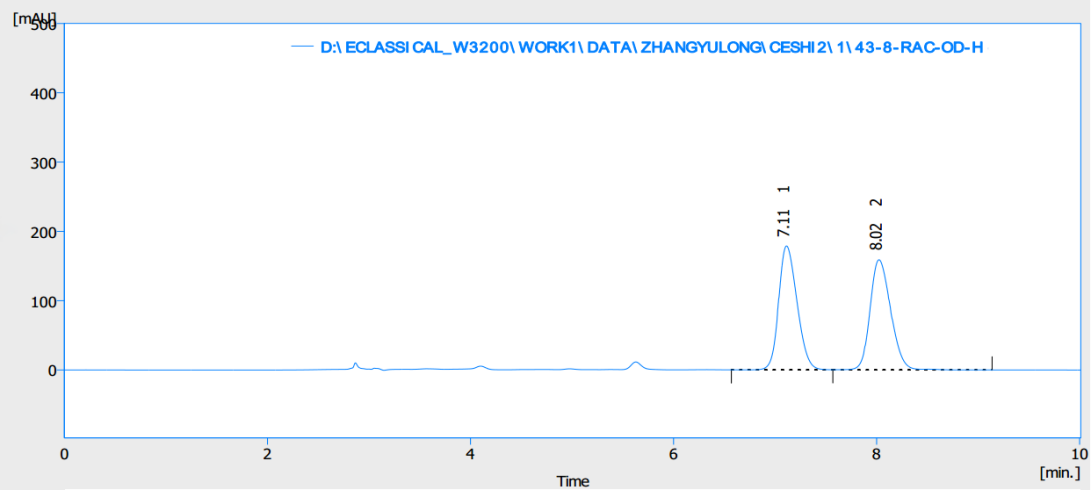
^{1}H NMR (500 MHz, $CDCl_3$)

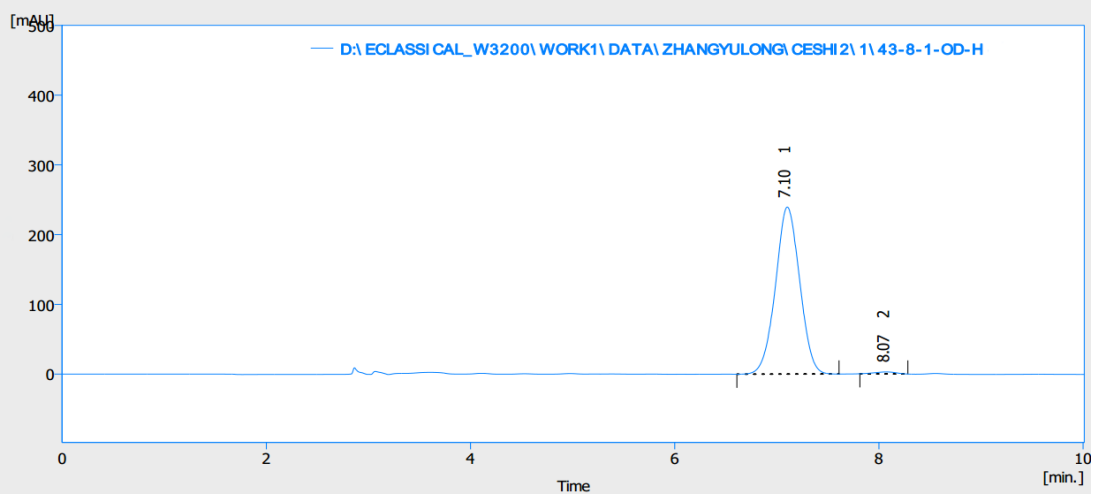


^{13}C NMR (126 MHz, $CDCl_3$)

Copies of HPLC charts

3a, 98% *ee* (Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm)

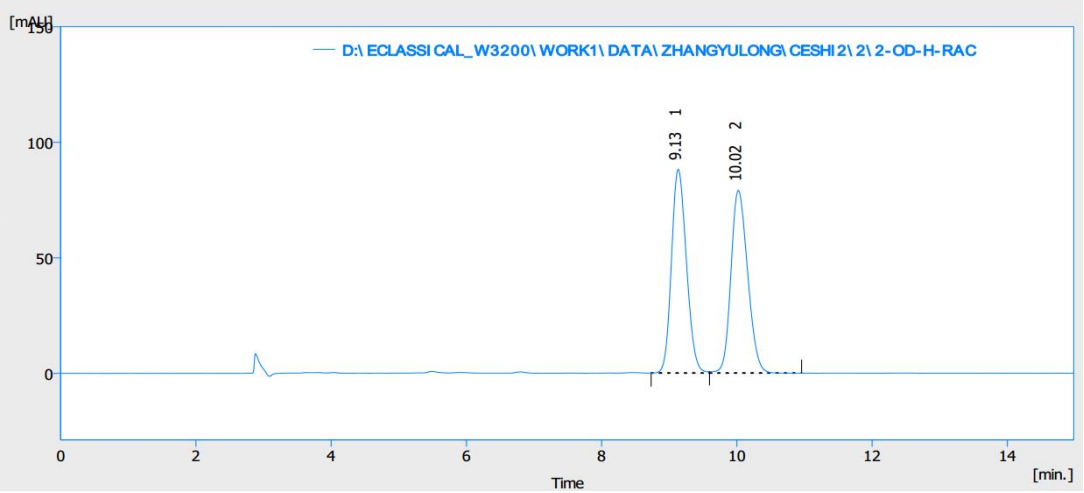


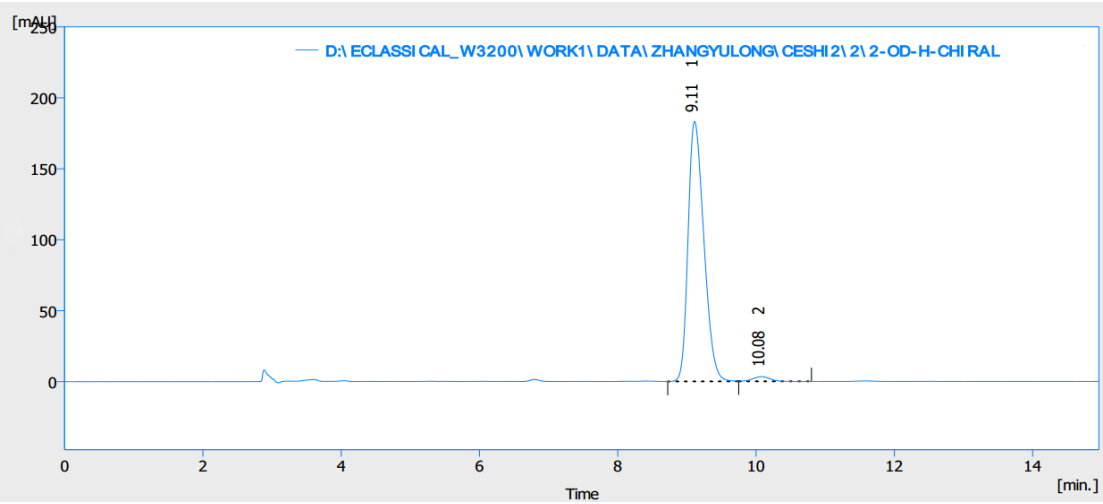


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	7.11	178.77	2248.36	50.0
2	8.02	158.89	2246.12	50.0
Total		337.66	4494.48	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	7.10	239.56	3956.76	99.0
2	8.07	2.82	40.38	1.0
Total		242.39	3997.14	100.0

3b, 96% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm)

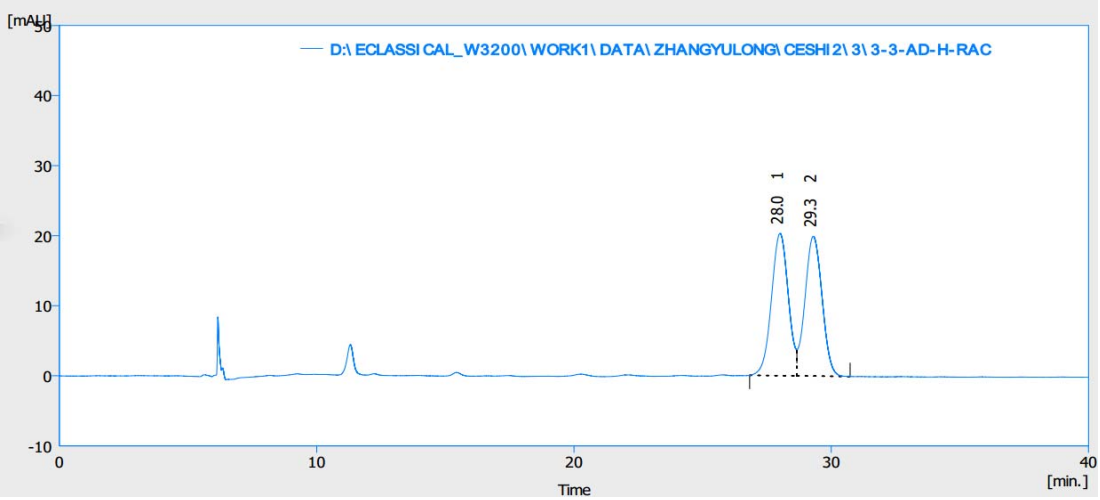


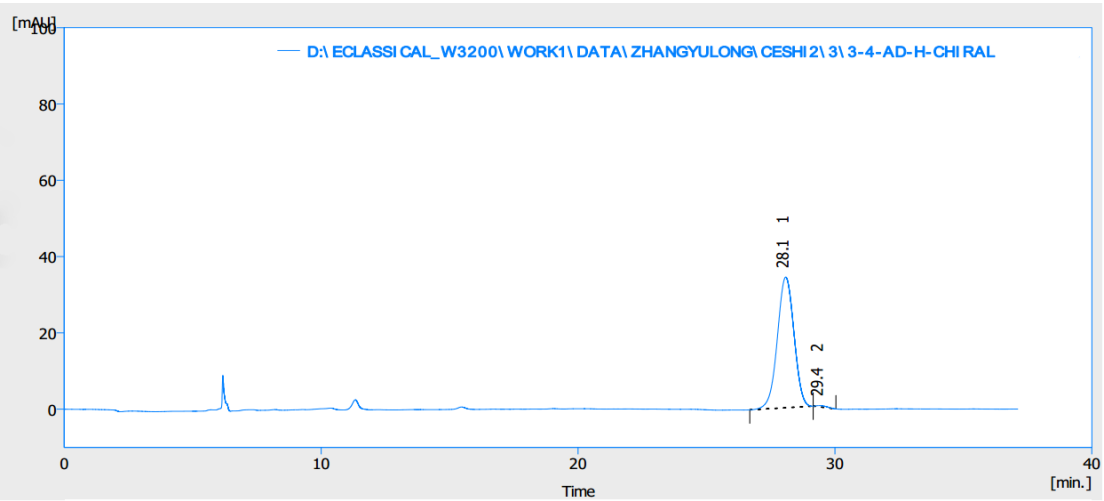


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	9.13	88.17	1357.69	49.9
2	10.02	79.10	1361.28	50.1
Total		167.27	2718.97	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	9.11	183.20	2908.75	98.0
2	10.07	3.38	59.56	2.0
Total		186.58	2968.32	100.0

3c, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm)

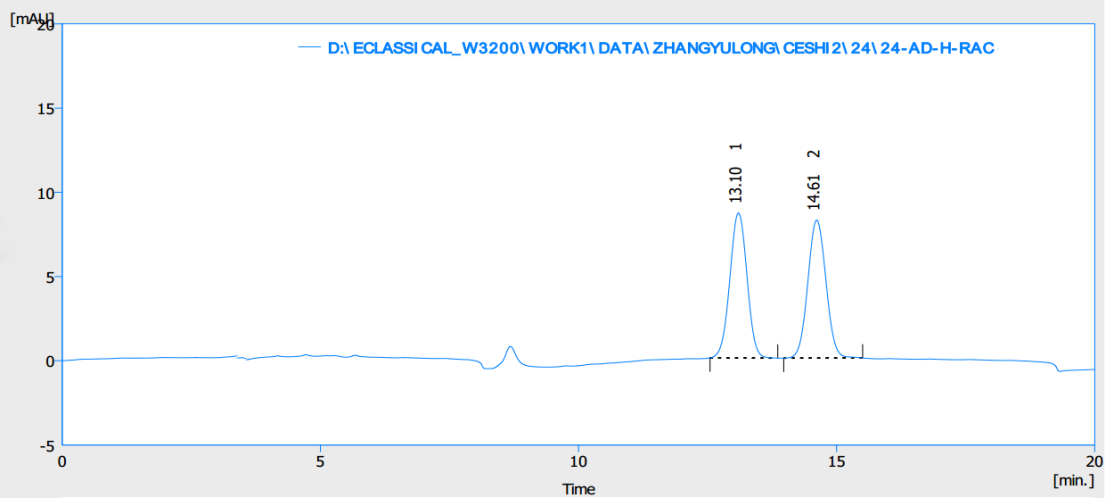


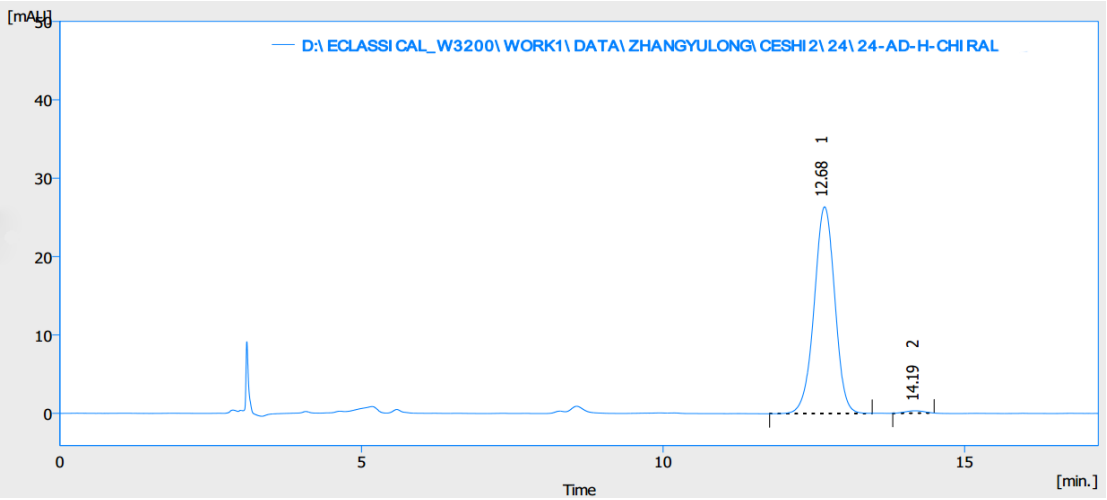


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	28.00	20.31	924.27	50.1
2	29.30	19.95	922.07	49.9
Total		40.26	1846.34	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	28.08	34.24	1539.32	99.3
2	29.41	0.35	10.60	0.7
Total		34.59	1549.92	100.0

3d, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

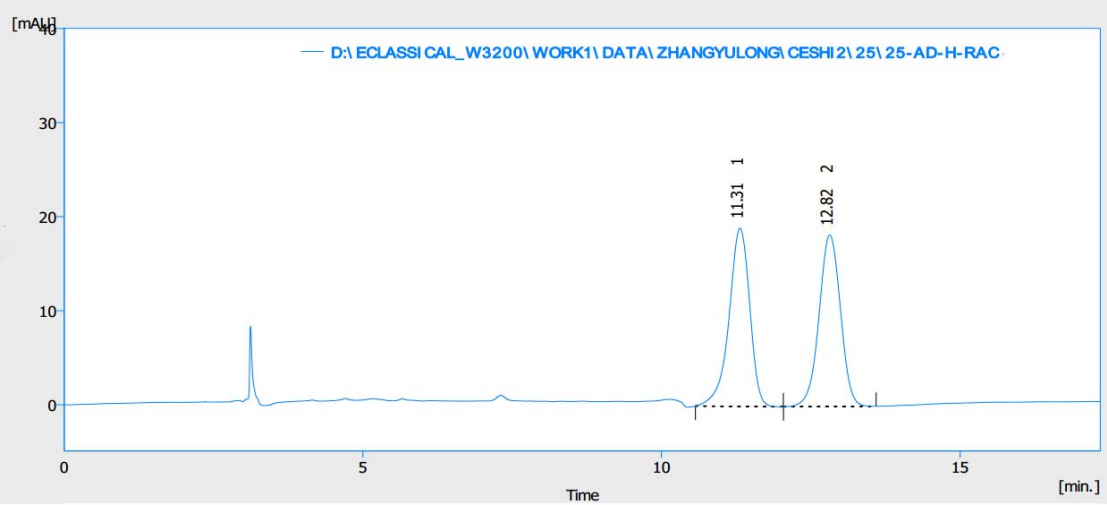


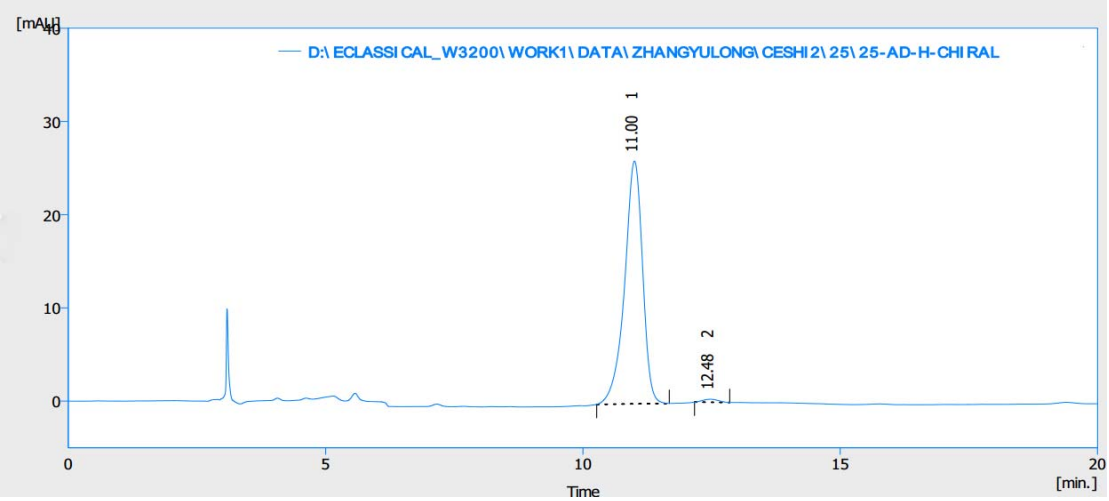


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	13.09	8.62	199.64	49.9
2	14.61	8.19	200.55	50.1
Total		16.81	400.20	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	12.67	26.38	627.04	99.0
2	14.18	0.30	6.52	1.0
Total		26.68	633.57	100.0

3e, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

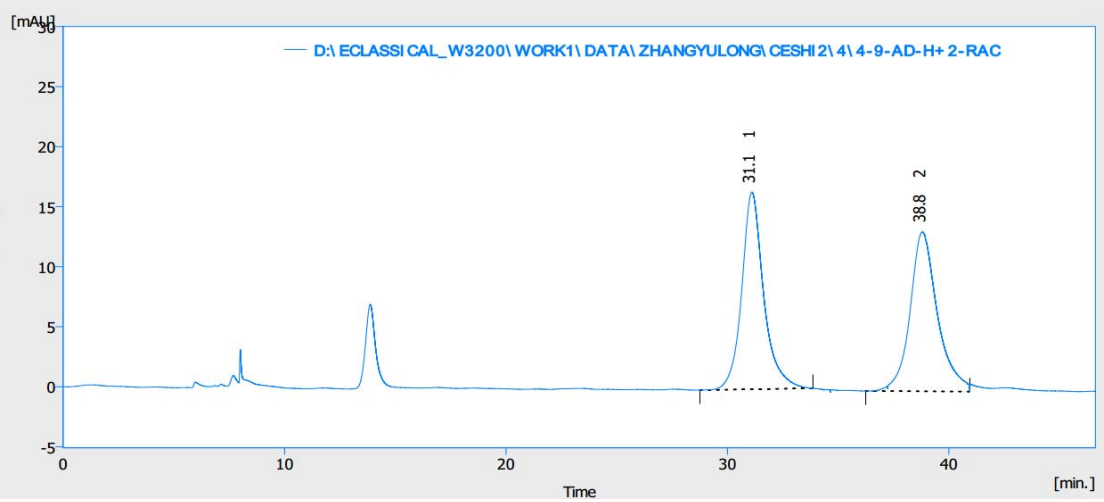


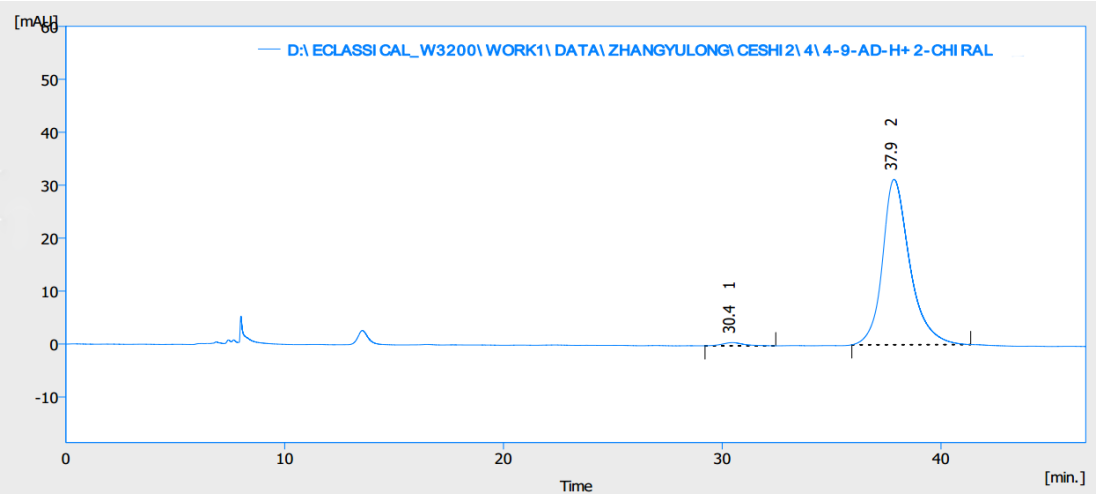


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	11.31	18.93	456.85	50.1
2	12.81	18.22	455.10	49.9
Total		37.16	911.96	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	11.00	26.05	632.48	98.9
2	12.47	0.32	6.86	1.1
Total		26.37	639.34	100.0

3f, 97% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm)

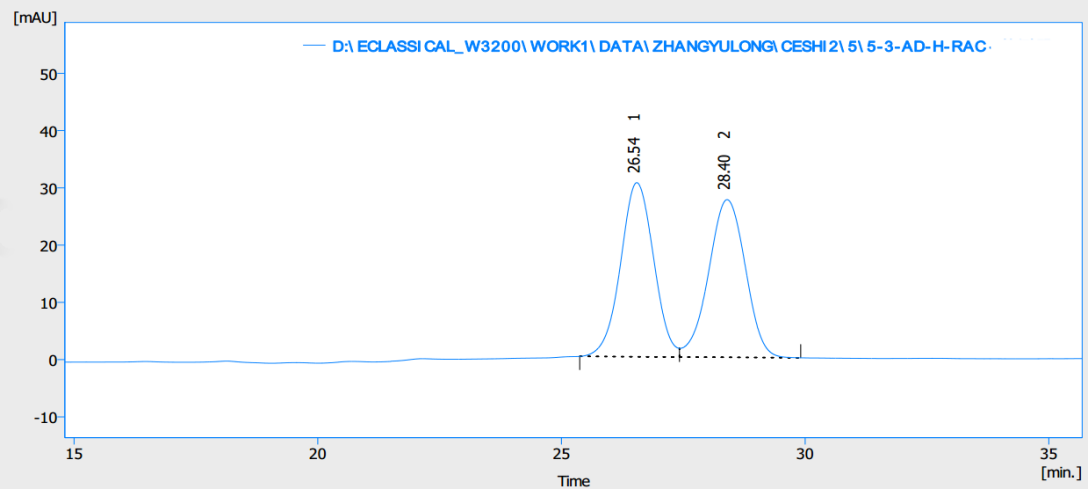


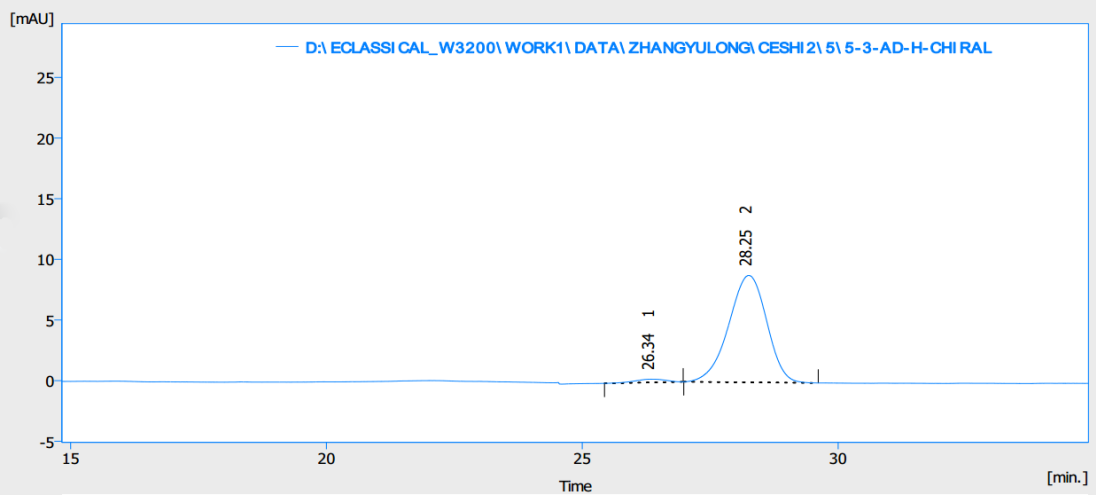


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	31.10	16.42	1133.12	49.8
2	38.80	13.28	1142.33	50.2
Total		29.71	2275.45	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	30.44	0.60	40.20	1.5
2	37.85	31.23	2711.86	98.5
Total		31.83	2752.07	100.0

3g, 95% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm)

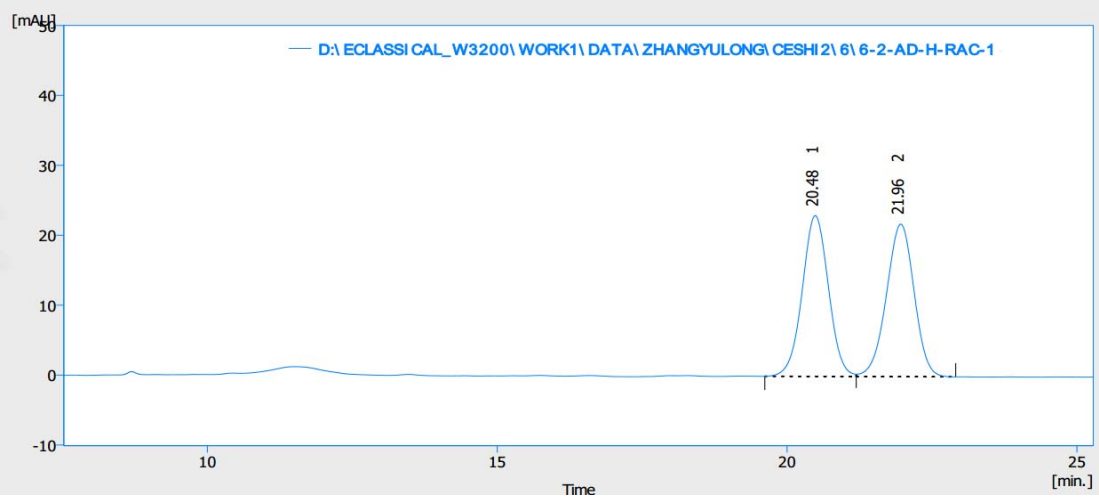


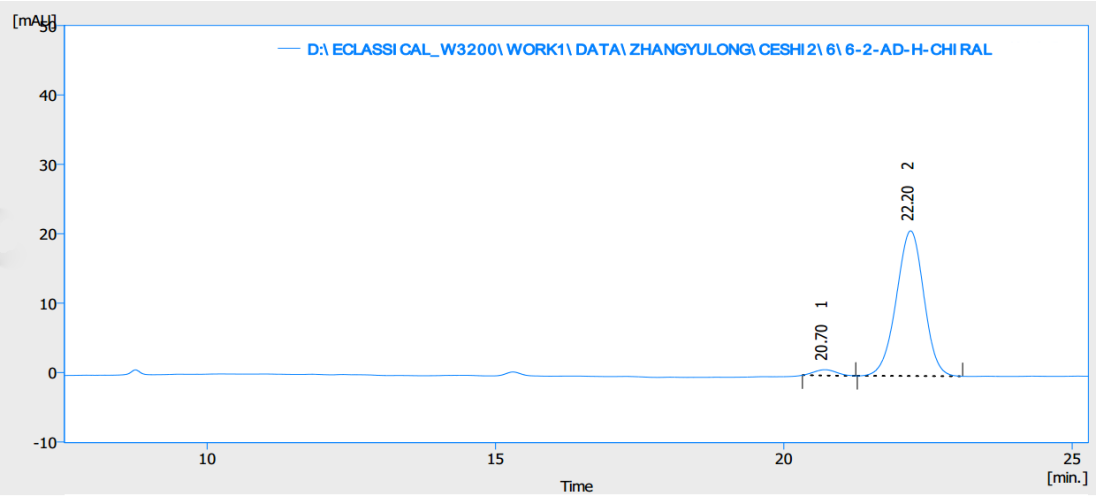


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	26.54	30.41	1437.02	49.8
2	28.39	27.54	1446.36	50.2
Total		57.96	2883.38	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	26.34	0.27	11.15	2.4
2	28.25	8.81	455.33	97.6
Total		9.08	466.49	100.0

3h, 94% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

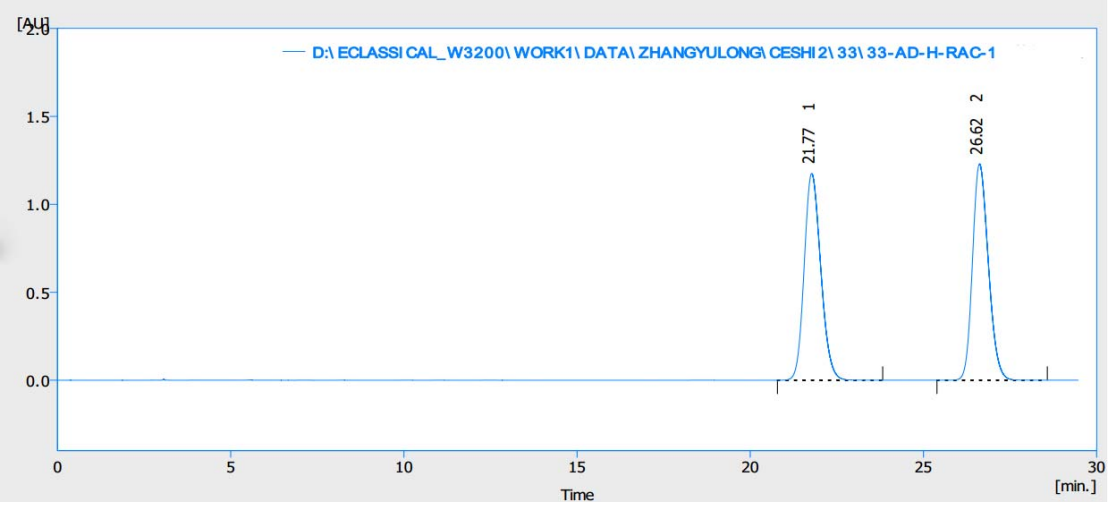


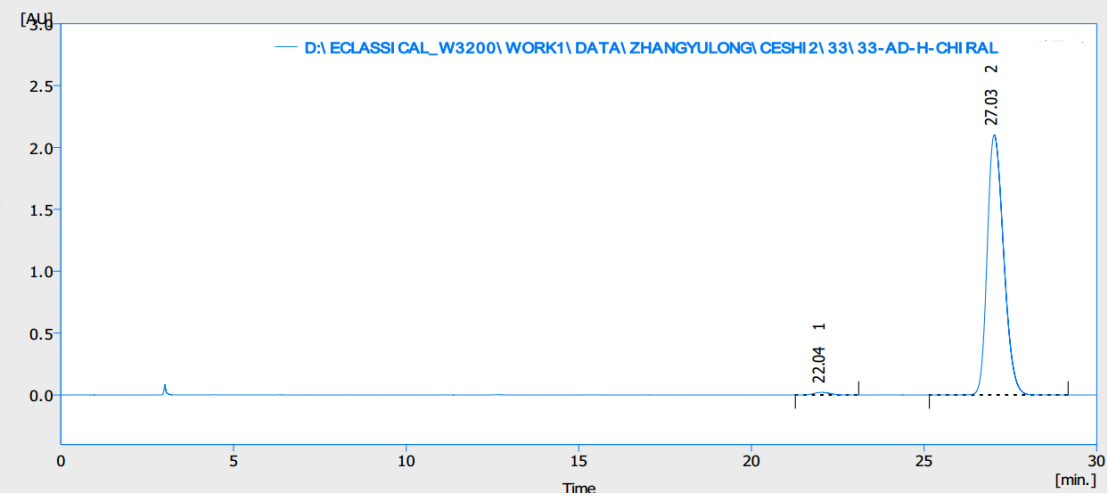


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	20.48	22.99	723.25	49.9
2	21.95	21.81	725.26	50.1
Total		44.81	1448.52	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	20.70	0.83	22.24	3.1
2	22.19	20.92	695.56	96.9
Total		21.76	717.80	100.0

3i, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

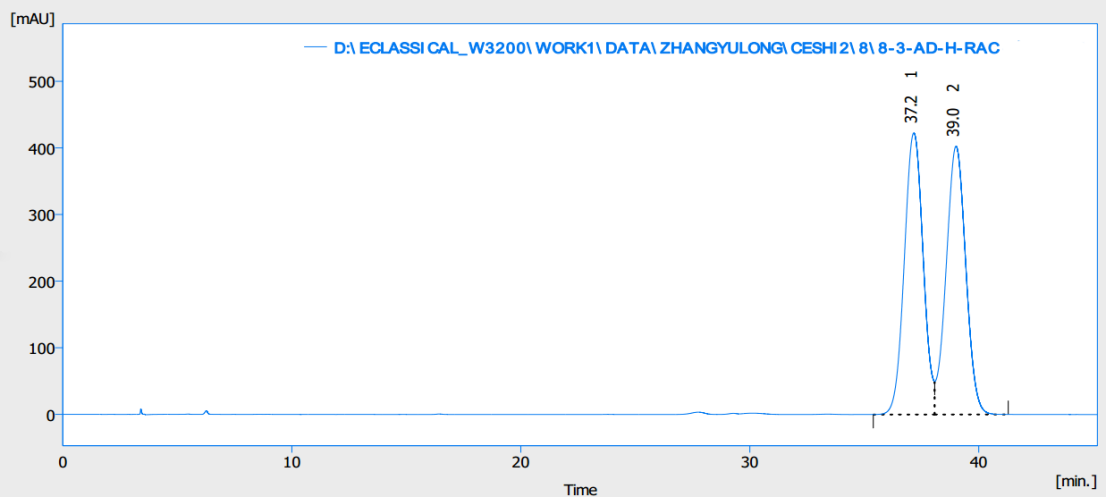


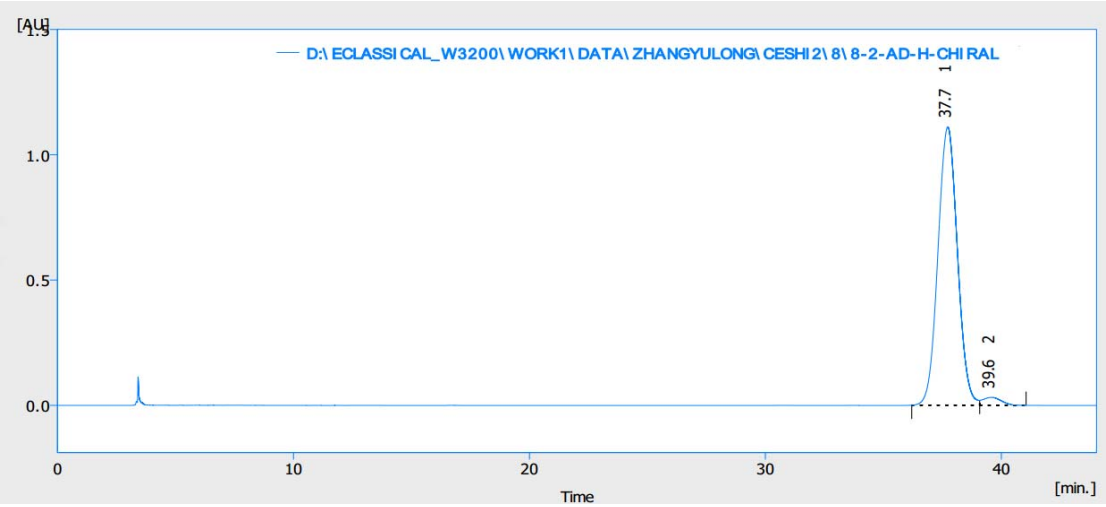


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	21.77	1175.06	39113.71	50.0
2	26.61	1229.91	39117.30	50.0
Total		2404.97	78231.02	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	22.03	21.28	705.43	1.0
2	27.03	2101.78	69219.20	99.0
Total		2123.06	69924.64	100.0

3j, 95% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

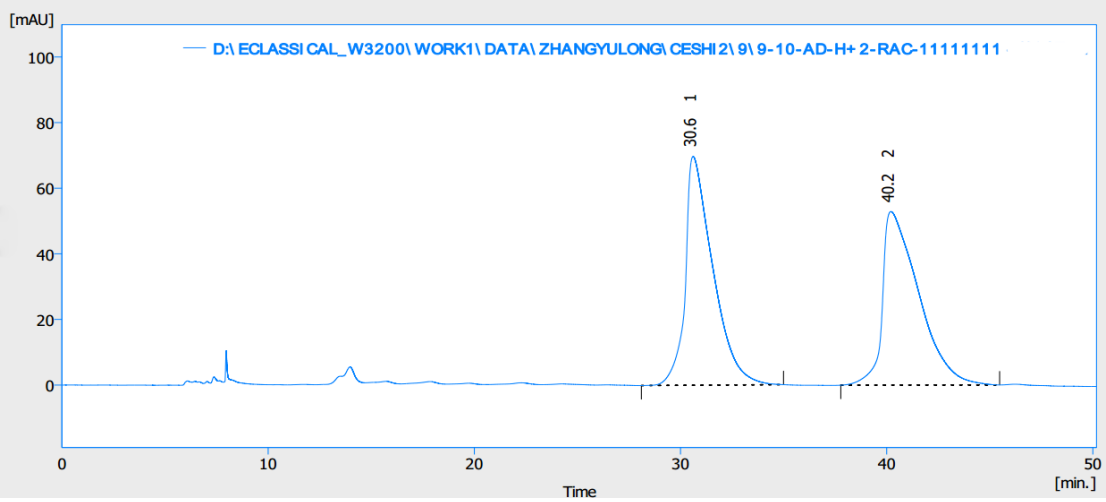


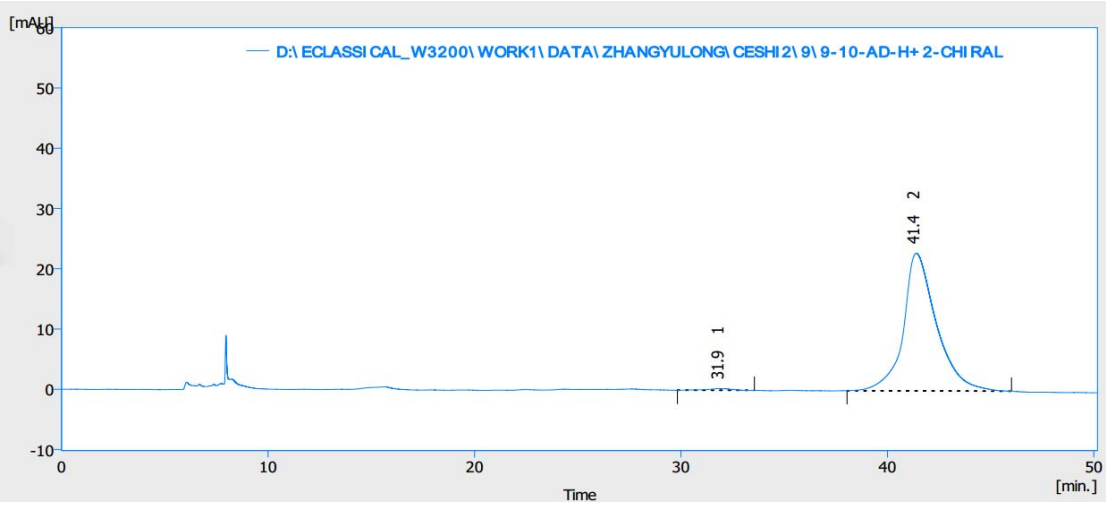


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	37.16	422.68	24120.21	50.1
2	39.00	402.75	24043.51	49.9
Total		825.44	48163.72	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	37.72	1111.19	63742.88	97.4
2	39.57	31.71	1722.72	2.6
Total		1142.90	65465.61	100.0

3k, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

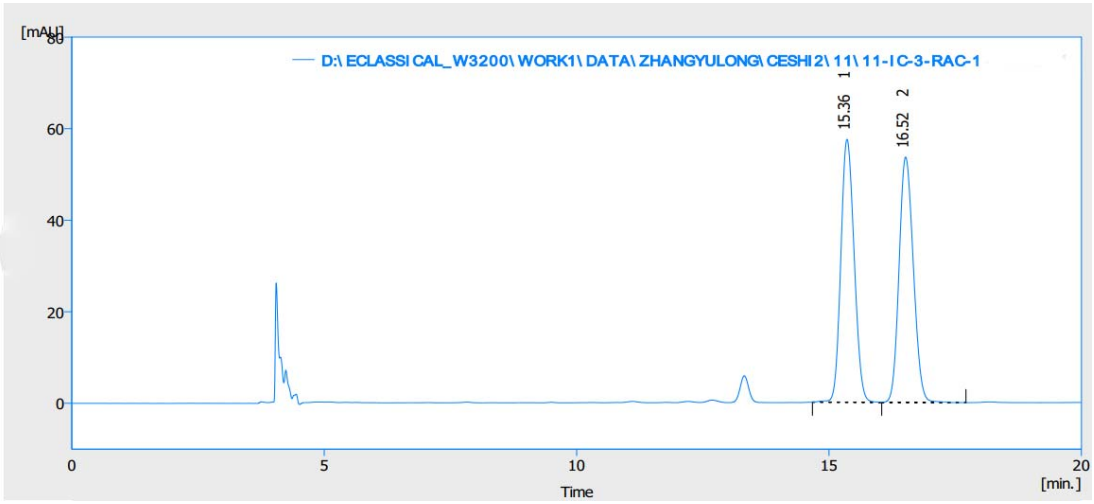


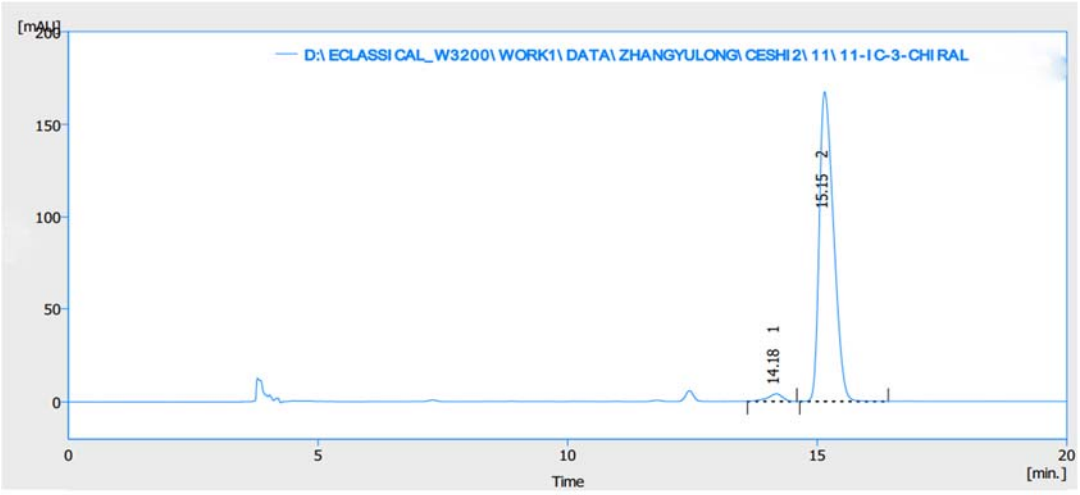


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	30.60	69.75	6506.51	50.2
2	40.20	52.91	6459.71	49.8
Total		122.66	12966.23	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	31.91	0.29	24.61	1.0
2	41.39	22.84	2542.27	99.0
Total		23.14	2566.88	100.0

3l, 95% *ee* (Chiralcel IC-3 column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm)

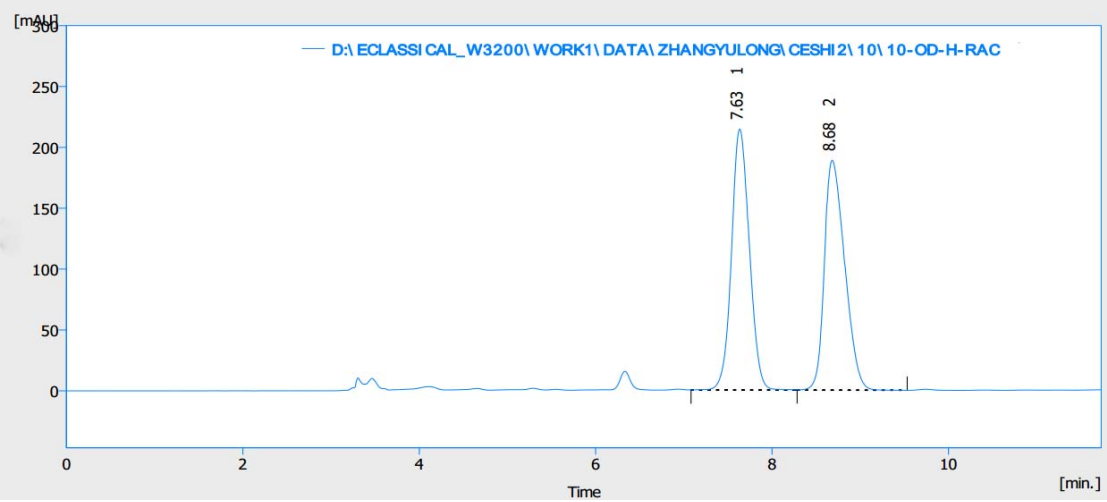


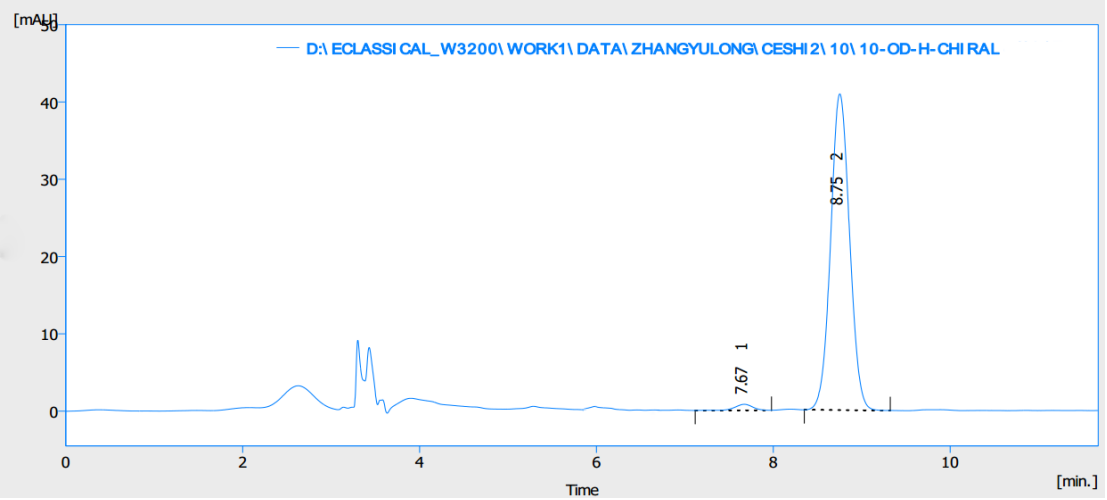


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	15.35	57.45	1055.47	50.0
2	16.51	53.62	1055.10	50.0
Total		111.07	2110.58	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	14.17	4.05	83.61	2.5
2	15.14	167.16	3326.35	97.5
Total		171.22	3409.97	100.0

3m, 97% *ee* (Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm)

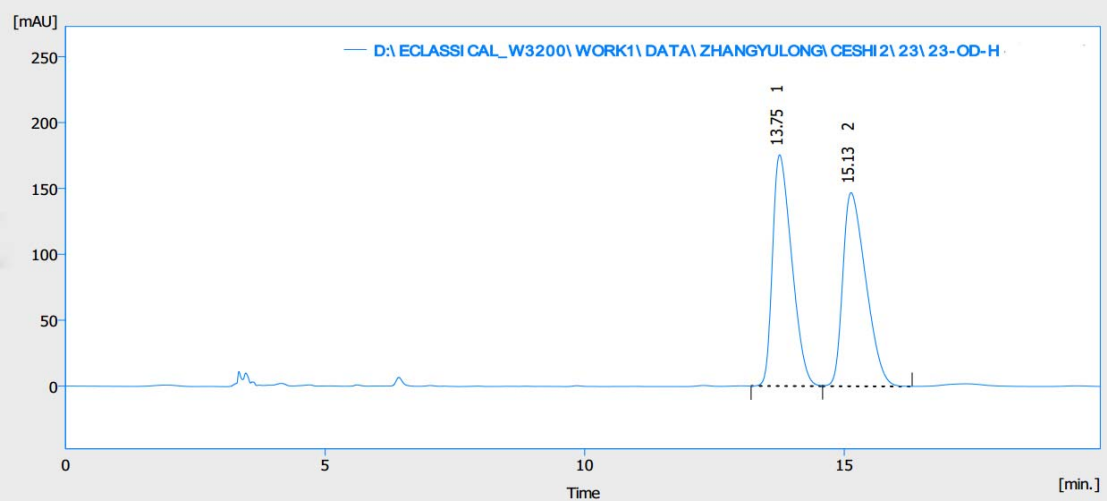


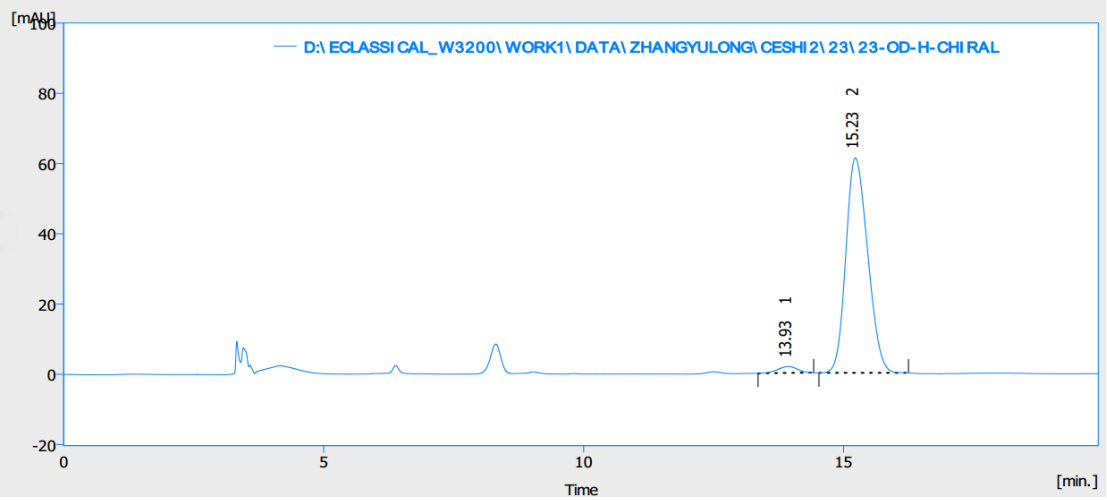


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	7.63	214.26	3024.84	50.0
2	8.68	188.72	3030.57	50.0
Total		402.98	6055.41	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	7.67	0.78	10.84	1.7
2	8.75	40.91	610.18	98.3
Total		41.69	621.03	100.0

3n, 95% *ee* (Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm)

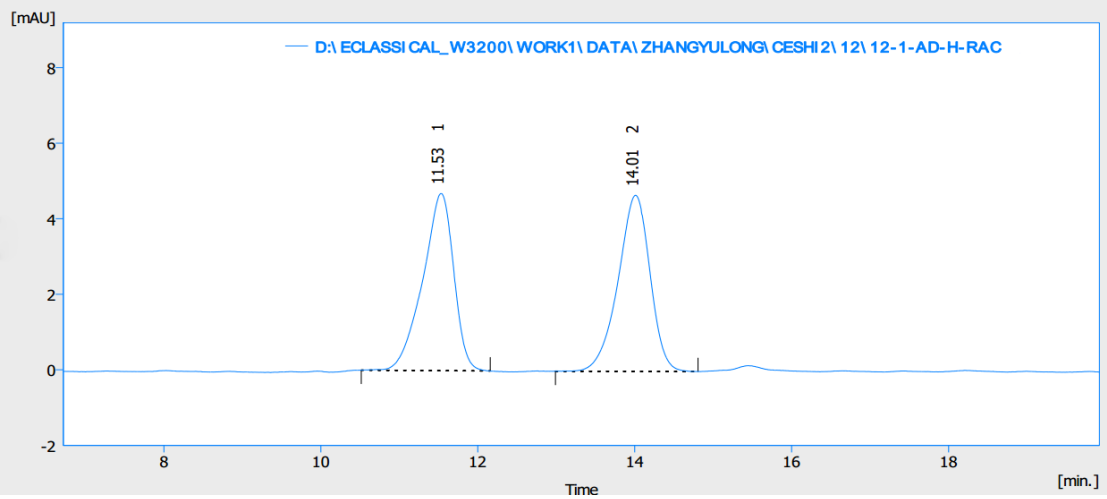


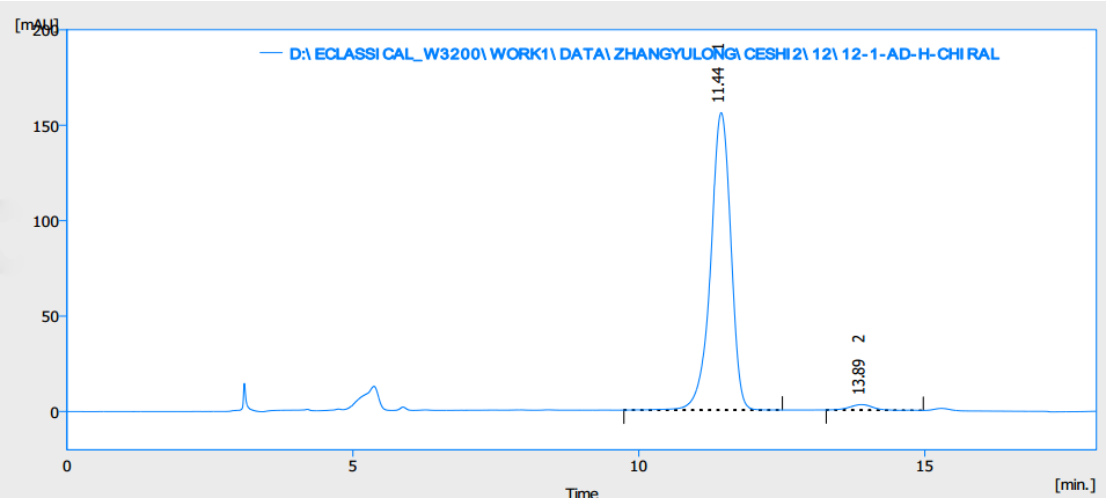


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	13.75	175.51	4518.24	49.9
2	15.13	146.89	4529.66	50.1
Total		322.40	9047.91	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	13.93	1.84	48.77	2.7
2	15.22	61.23	1790.10	97.3
Total		63.08	1838.87	100.0

3o, 96% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

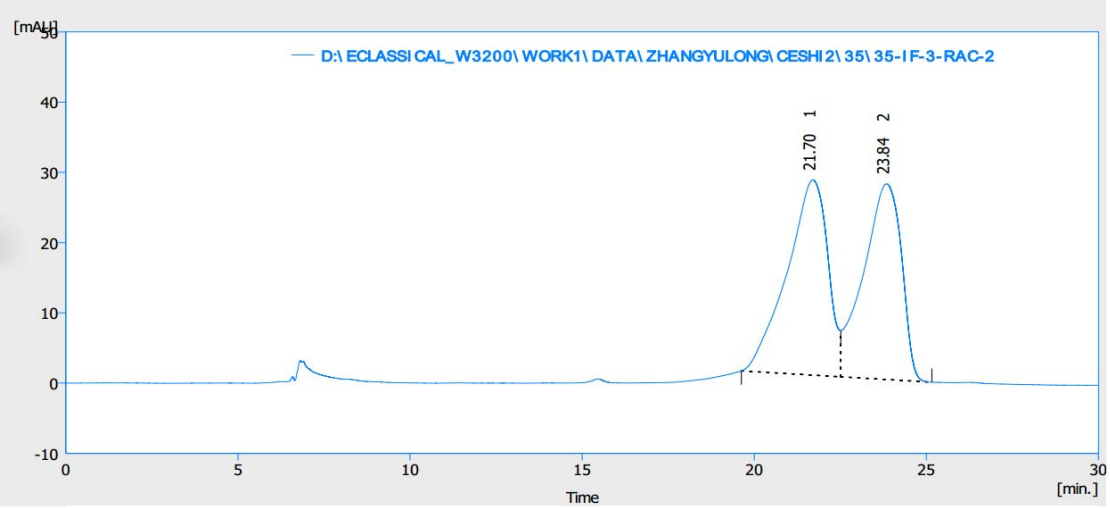


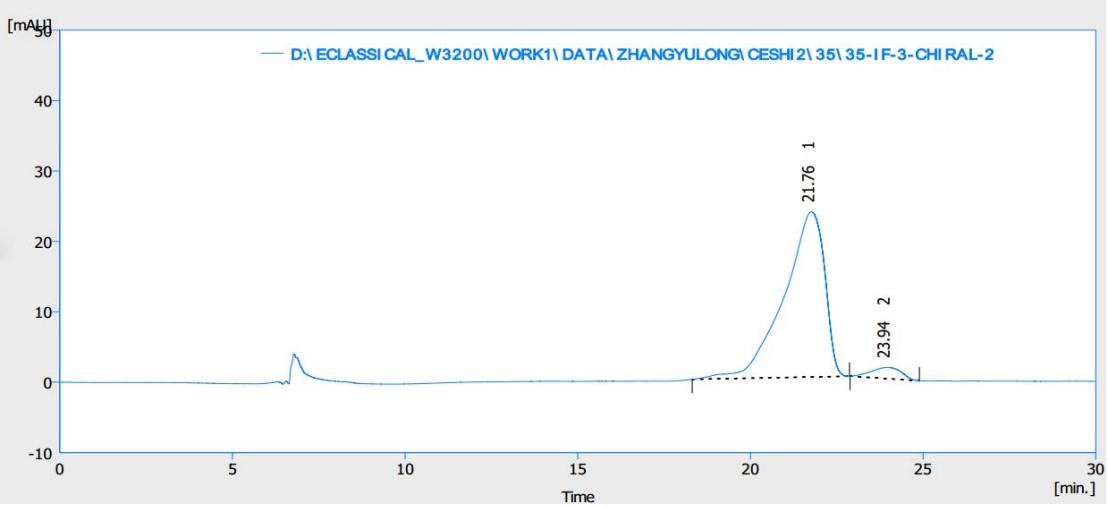


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	11.52	4.68	128.93	49.4
2	14.00	4.66	132.11	50.6
Total		9.35	261.04	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	11.43	155.79	3828.38	98.0
2	13.89	2.86	79.83	2.0
Total		158.66	3908.21	100.0

3p, 90% *ee* (Chiralcel IF-3 column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm)

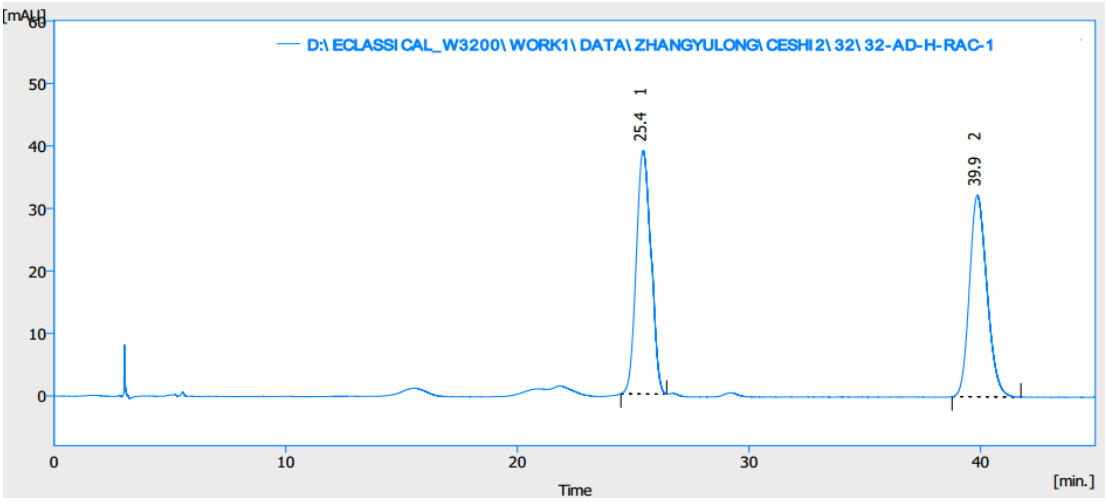


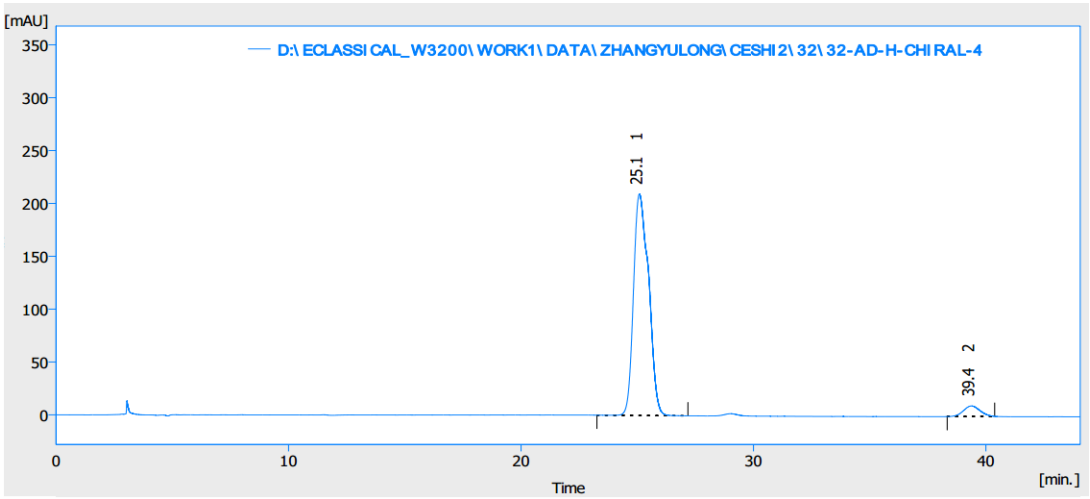


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	21.69	27.80	2301.57	51.8
2	23.83	27.86	2141.39	48.2
Total		55.66	4442.97	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	21.76	23.47	1925.20	95.2
2	23.94	1.59	96.17	4.8
Total		25.06	2021.37	100.0

3q, 90% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

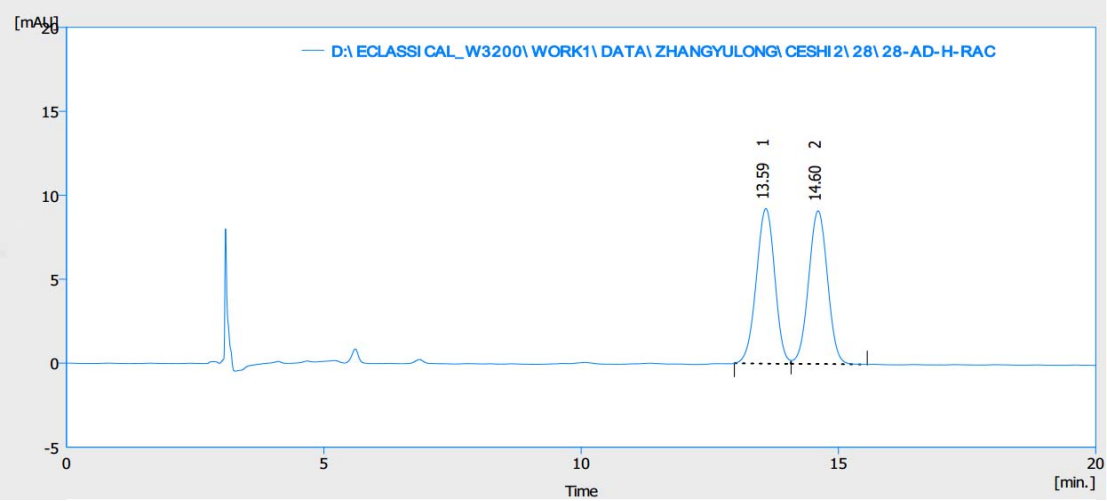


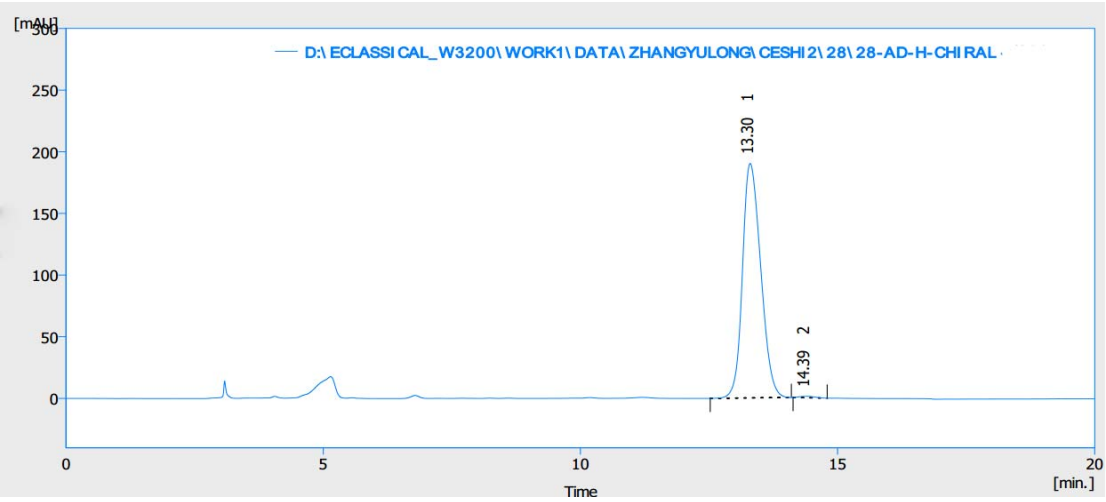


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	25.43	38.89	1720.30	50.5
2	39.86	32.23	1688.51	49.5
Total		71.13	3408.81	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	25.09	1193.31	9470.15	95.1
2	39.37	130.18	486.44	4.9
Total		1323.50	9956.59	100.0

3r, 99% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

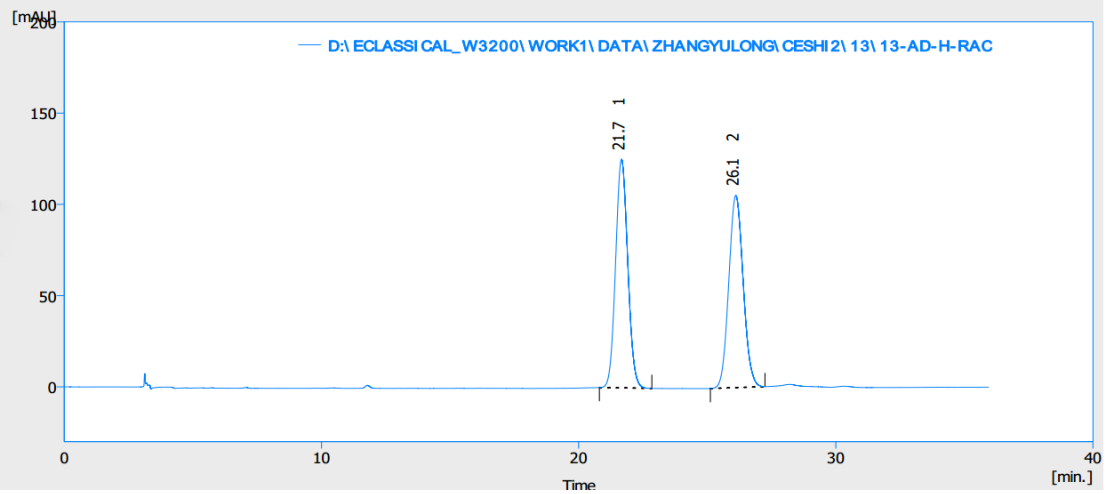


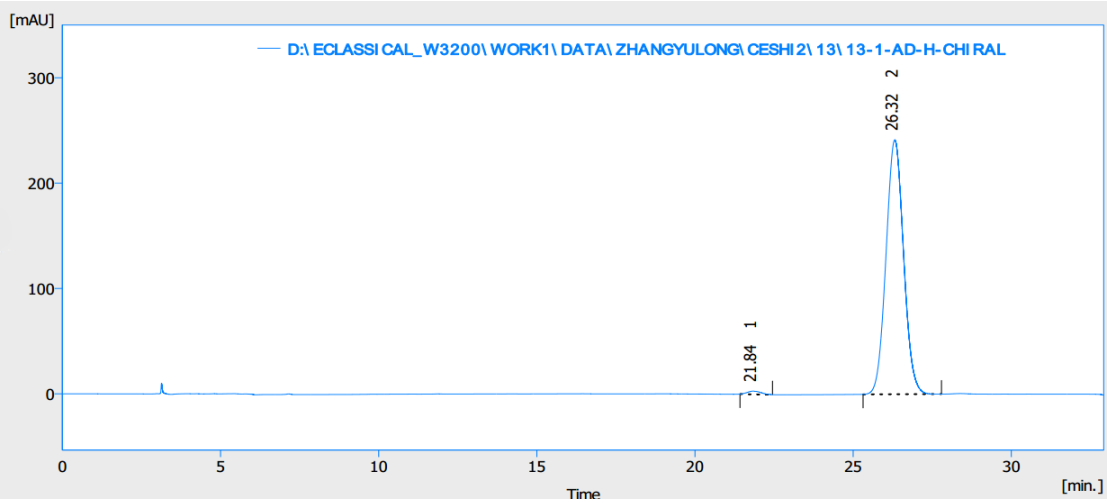


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	13.58	9.23	230.86	49.8
2	14.60	9.12	232.91	50.2
Total		18.36	463.77	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	13.30	190.18	4694.99	99.5
2	14.39	1.19	23.66	0.5
Total		191.37	4718.65	100.0

3s, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

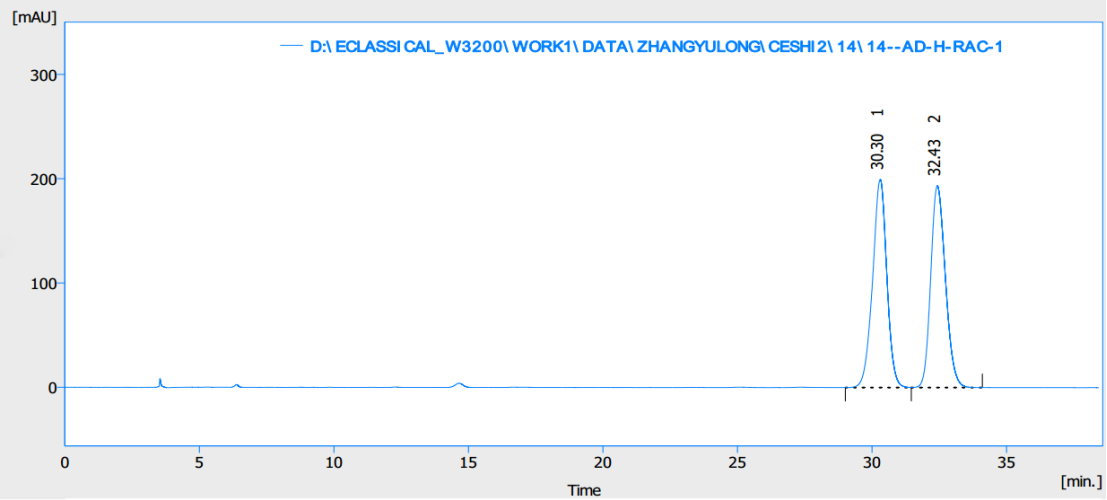


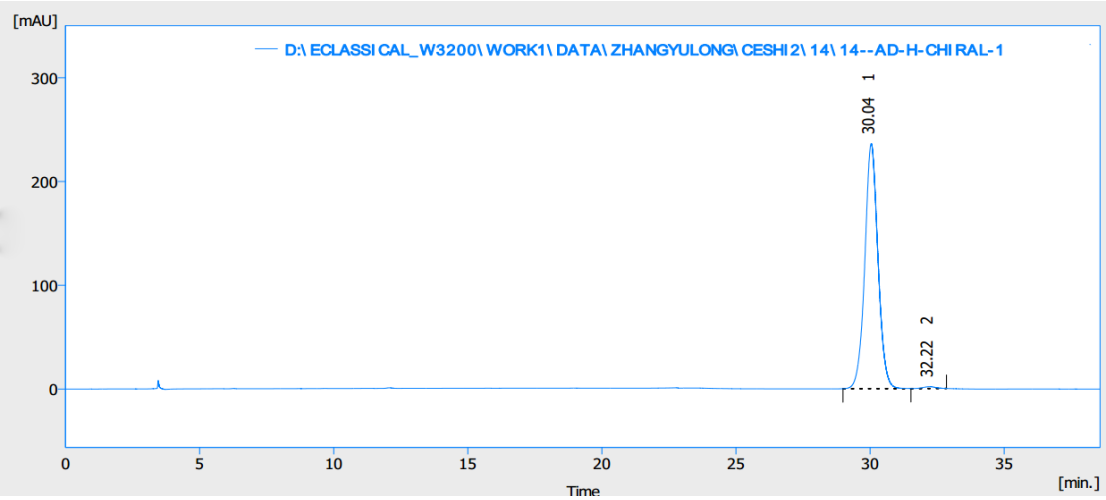


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	21.66	125.34	4111.30	50.1
2	26.11	105.26	4096.92	49.9
Total		230.60	8208.22	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	21.83	3.04	87.61	0.9
2	26.31	241.43	9317.28	99.1
Total		244.47	9404.90	100.0

3t, 98% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

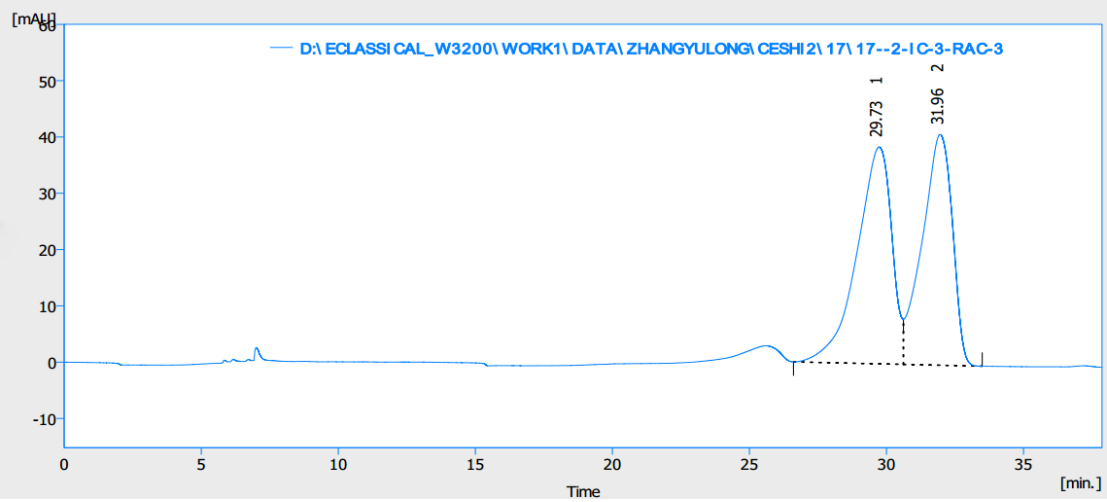


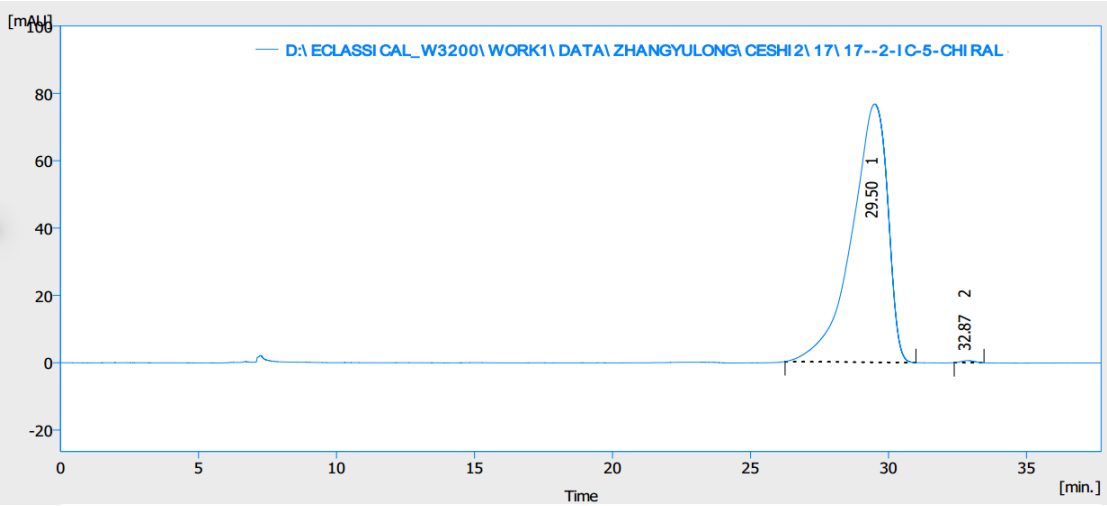


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	30.30	199.48	7342.23	50.0
2	32.42	193.54	7332.83	50.0
Total		393.03	14675.06	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	30.04	236.10	8052.29	99.3
2	32.22	1.74	58.90	0.7
Total		237.85	8111.20	100.0

3u, 99% *ee* (Chiralcel IC-3 column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm)

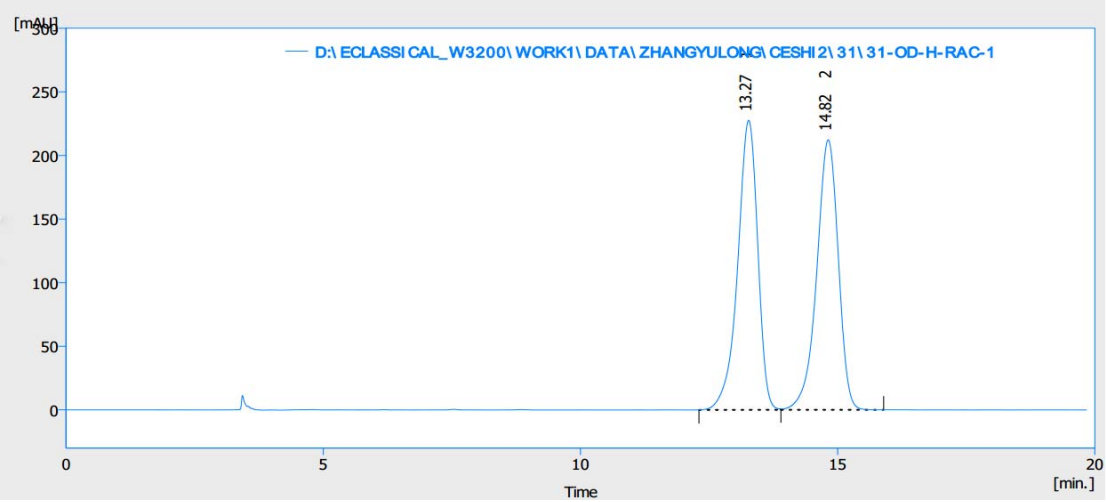


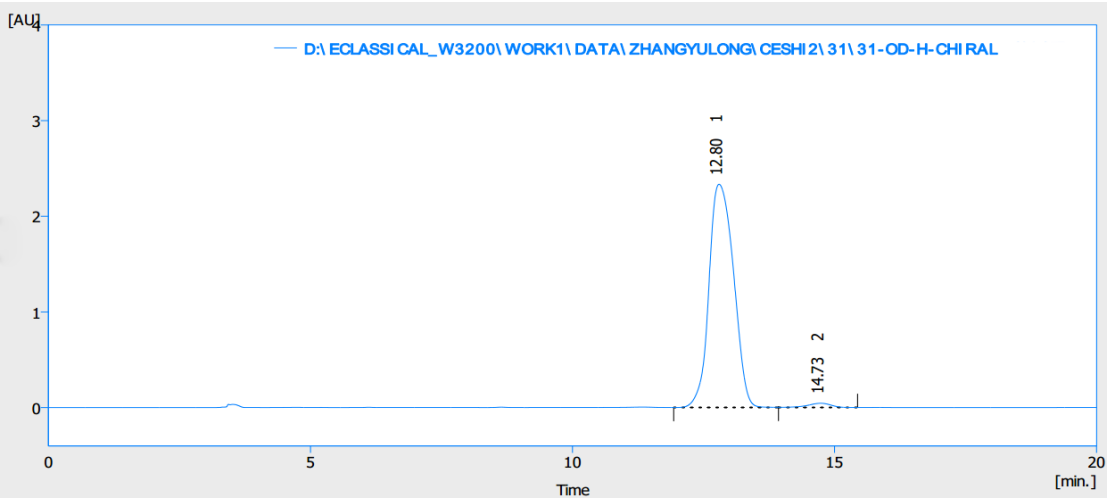


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	29.73	38.51	3414.38	52.0
2	31.95	41.00	3147.50	48.0
Total		79.51	6561.88	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	29.49	76.68	6949.17	99.7
2	32.86	0.62	20.66	0.3
Total		77.31	6969.84	100.0

3v, 96% *ee* (Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

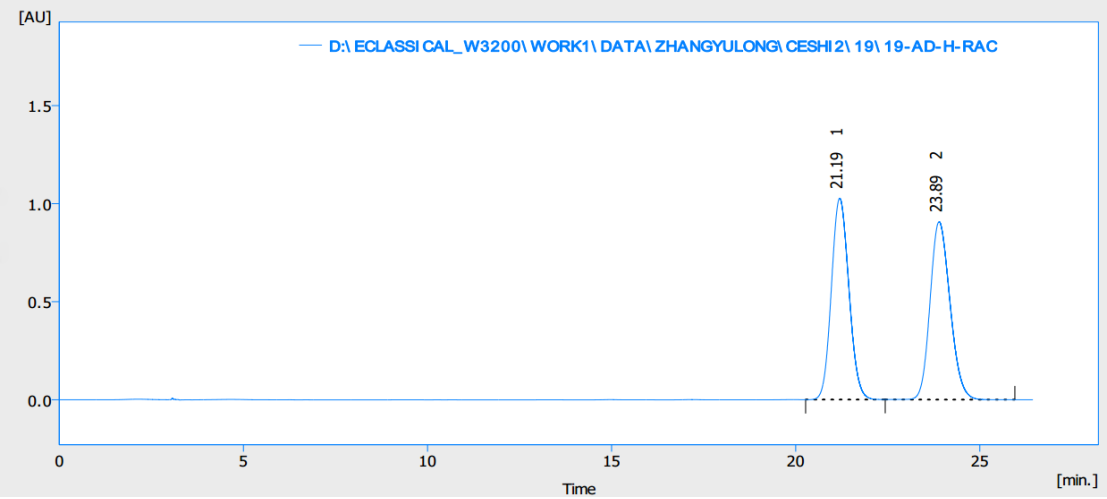


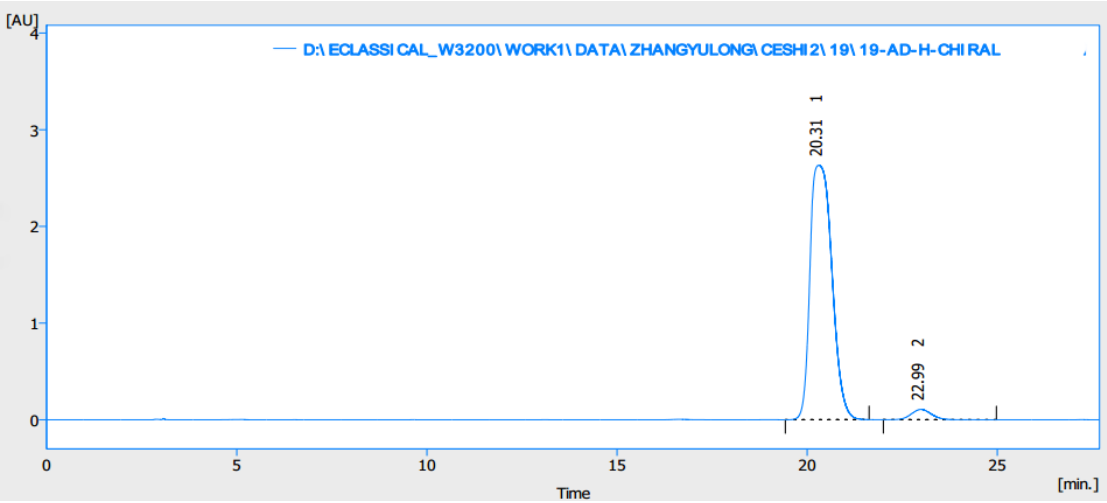


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	13.26	227.57	6167.70	49.9
2	14.81	212.28	6186.84	50.1
Total		439.85	12354.54	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	12.79	2333.95	76234.34	98.2
2	14.73	44.39	1385.11	1.8
Total		2378.35	77619.46	100.0

3w, 93% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

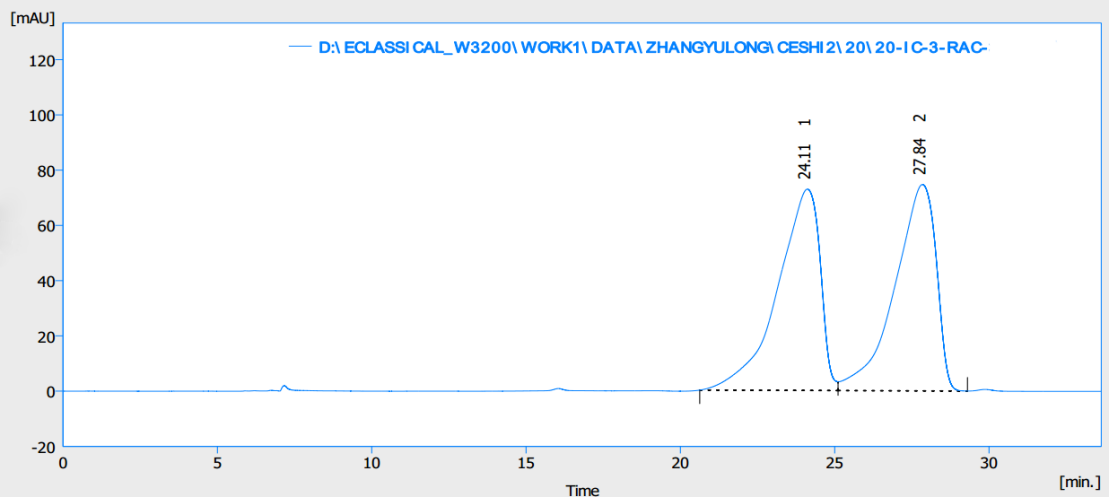


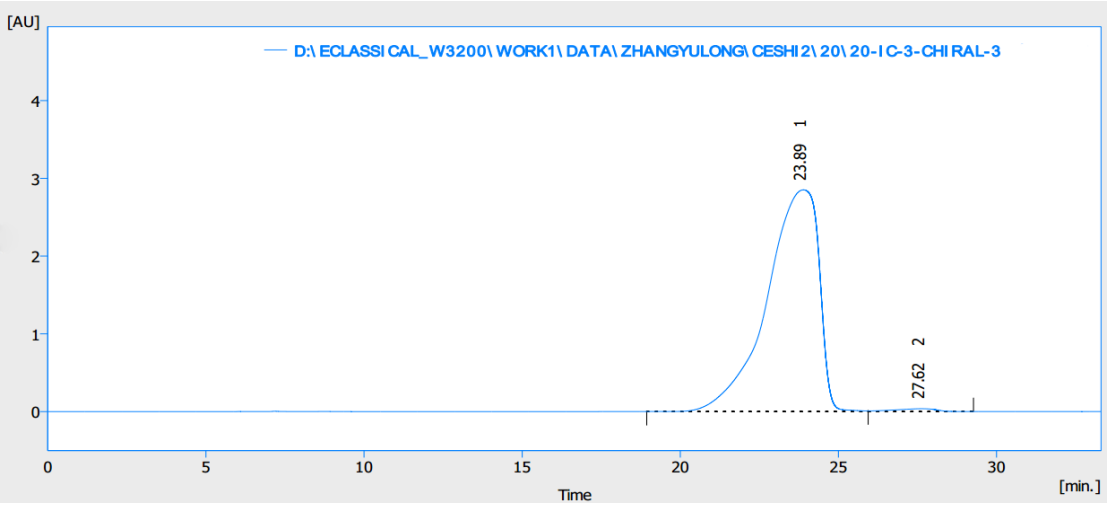


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	21.19	1027.53	34065.10	49.9
2	23.89	907.61	34261.56	50.1
Total		1935.15	68326.66	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	20.30	2631.40	105307.20	96.4
2	22.99	106.15	3914.86	3.6
Total		2737.55	109222.06	100.0

3x, 98% *ee* (Chiralcel IC-3 column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm)

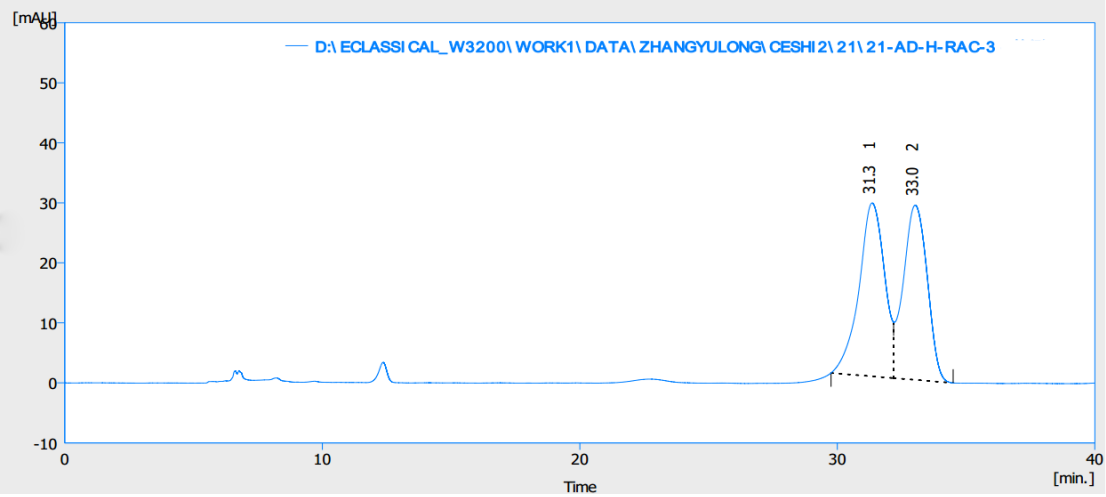


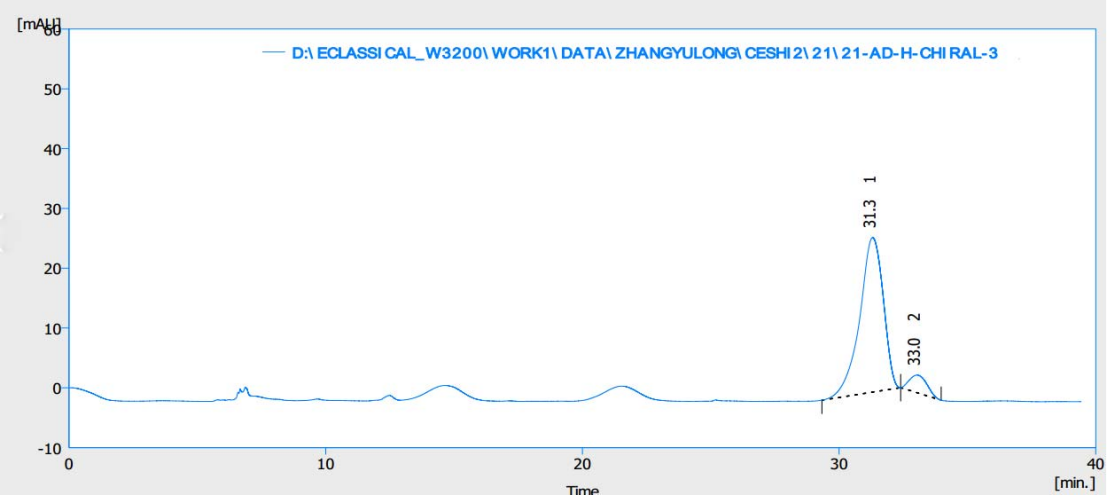


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	24.11	72.91	7005.78	50.1
2	27.84	74.72	6963.96	49.9
Total		147.63	13969.74	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	23.88	2850.63	326373.14	99.0
2	27.62	36.38	3327.61	1.0
Total		2887.01	329700.75	100.0

3y, 84% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm)

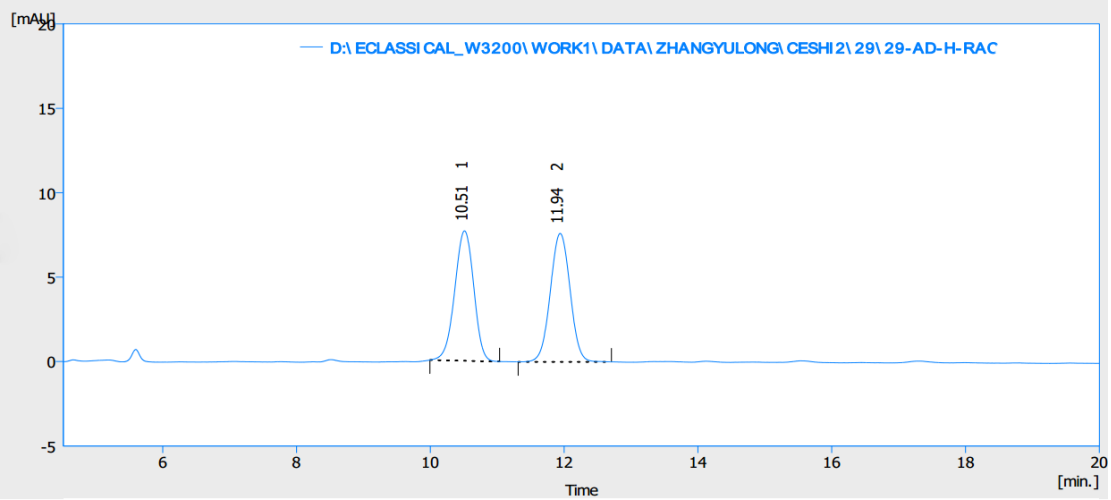


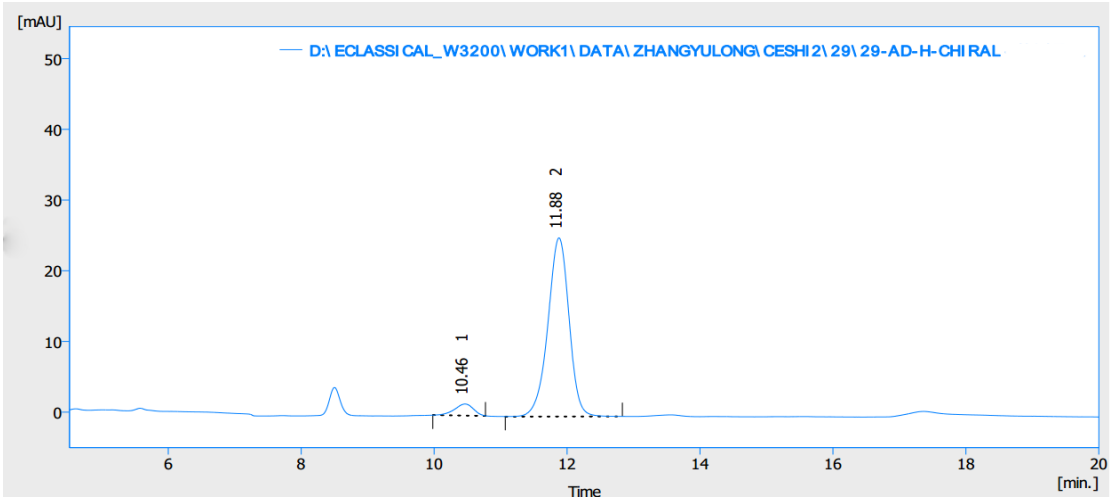


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	31.34	28.89	1998.82	51.3
2	33.01	29.11	1894.40	48.7
Total		58.00	3893.23	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	31.30	25.86	1648.76	92.0
2	33.02	2.94	142.43	8.0
Total		28.80	1791.20	100.0

3z, 89% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

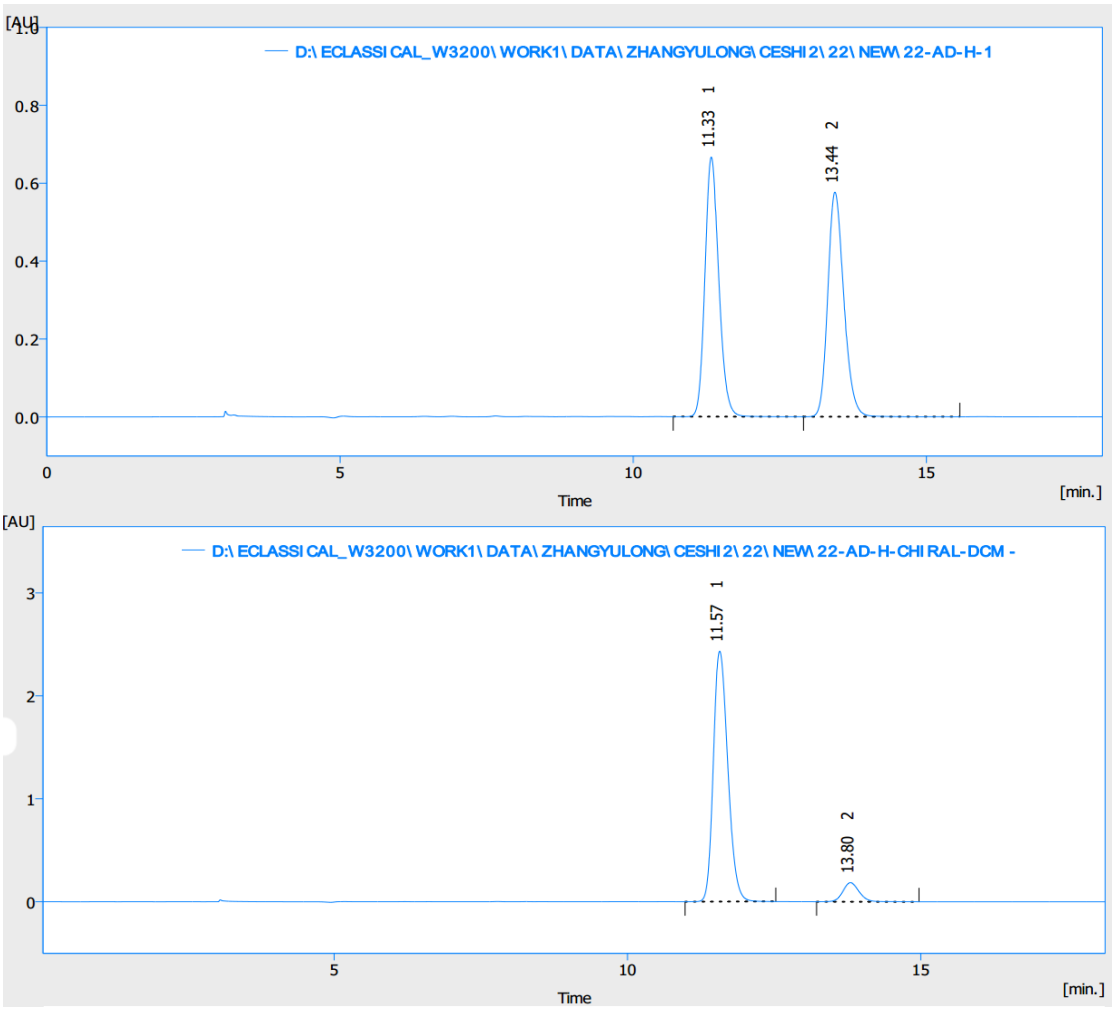




Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	10.50	7.70	152.14	49.3
2	11.93	7.61	156.38	50.7
Total		15.31	308.53	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	10.45	1.62	31.98	5.4
2	11.87	25.26	557.90	94.6
Total		26.88	589.89	100.0

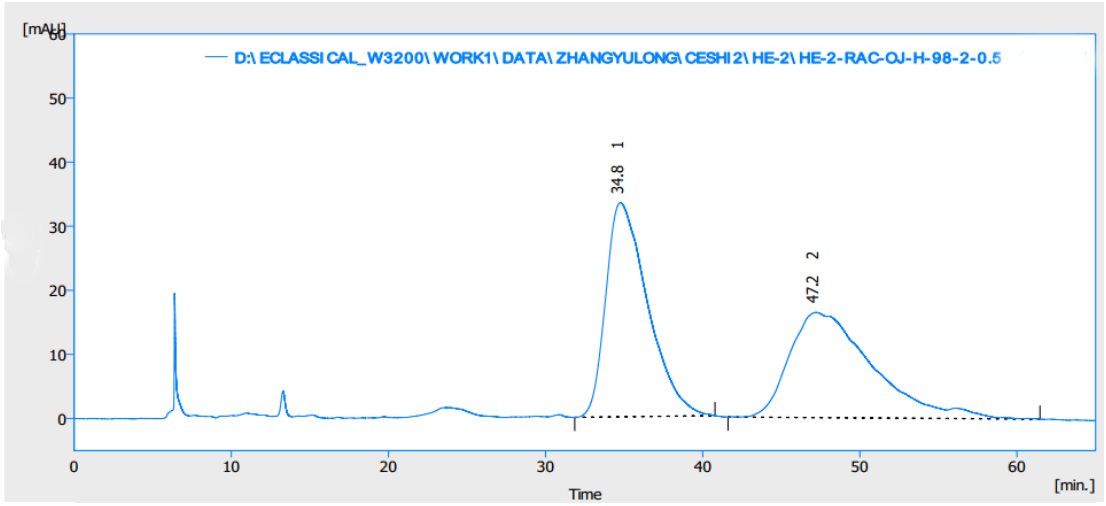
3aa, 84% *ee* (Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm)

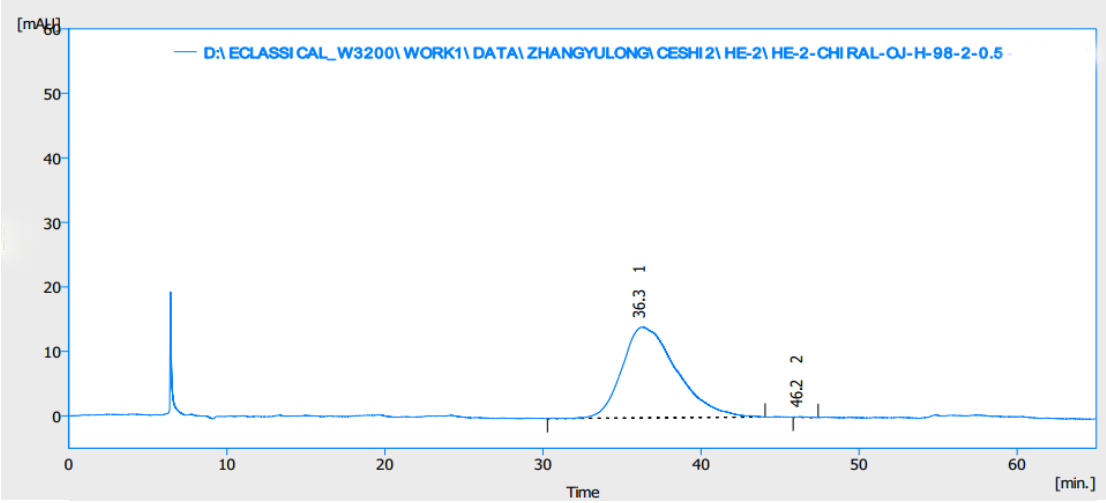


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	11.33	666.43	10951.09	49.9
2	13.43	576.47	10985.29	50.1
Total		1242.90	21936.39	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	11.57	2432.46	41884.65	92.1
2	13.80	184.89	3576.44	7.9
Total		2617.35	3997.14	100.0

9, 99% *ee* (Two connected chiralcel AD-H columns, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm)

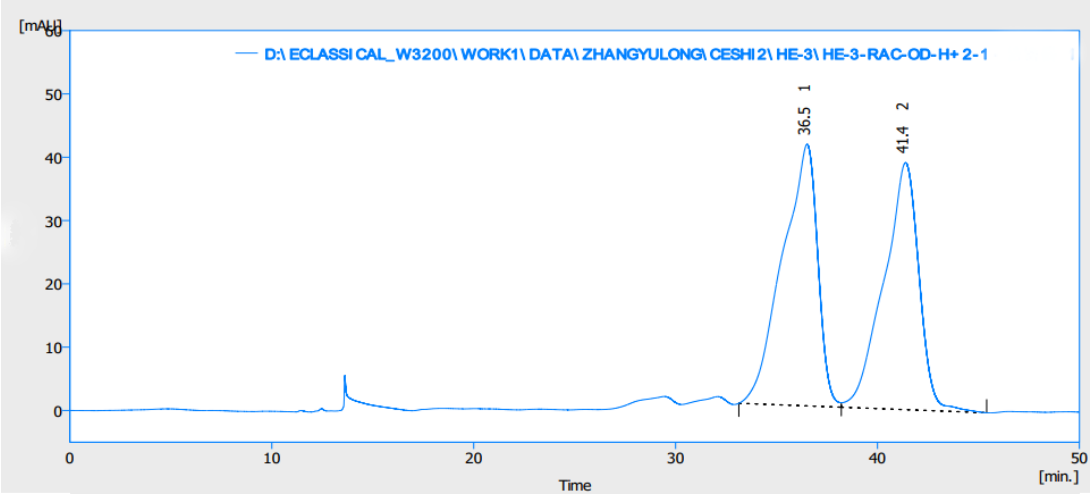


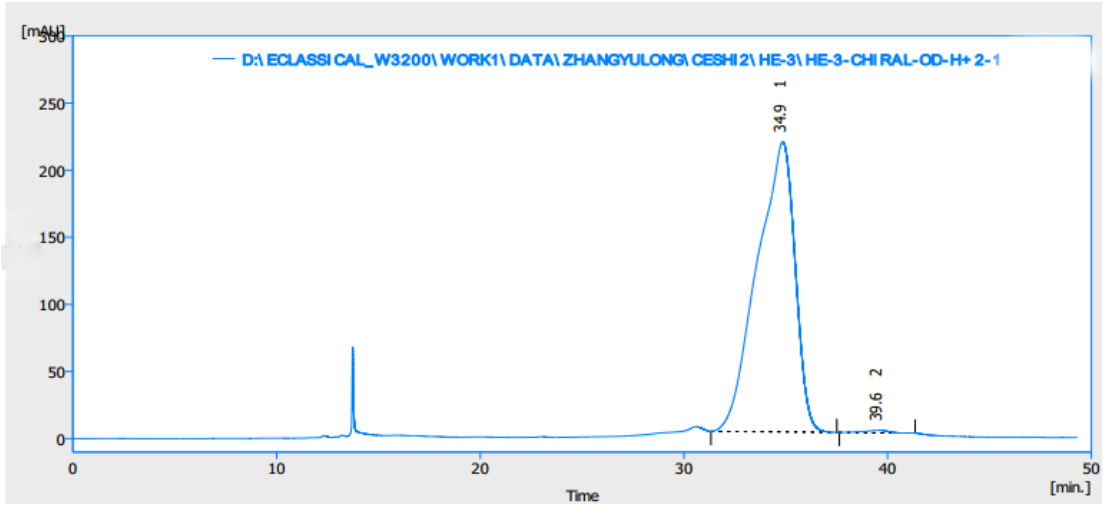


Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	34.75	33.42	6189.46	50.6
2	47.17	16.42	6040.82	49.4
Total		49.85	12230.28	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	36.27	14.07	3391.13	99.8
2	46.22	0.07	8.03	0.2
Total		14.15	3399.1	100.0

14, 99% *ee* (Two connected chiralcel AD-H columns, *n*-hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, λ = 254 nm)

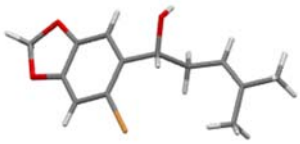




Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	36.51	41.32	5016.04	51.5
2	41.38	39.02	4722.42	48.5
Total		80.34	9738.46	100.0

Index	t_R / (min)	Height / (mv)	Area /	Area / (%)
1	34.85	216.30	27943.12	99.5
2	39.57	1.85	153.62	0.5
Total		218.15	28096.75	100.0

X-ray crystal structure of 3q



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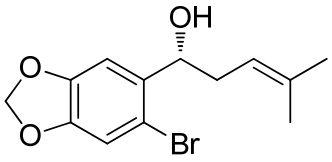

Deposition No. CCDC 1969342

Crystal data for compound **3q**

Identification code	cu_190531b_0m	
Empirical formula	C13 H15 Br O3	
Formula weight	299.16	
Temperature	296.15 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.8308(5) Å	α= 90°.
	b = 4.8800(2) Å	β= 111.046(2)°.
	c = 12.3237(6) Å	γ = 90°.
Volume	664.04(5) $Å^3$	
Z	2	
Density (calculated)	1.496 Mg/m^3	
Absorption coefficient	4.184 mm^{-1}	
F(000)	304	
Crystal size	0.12 x 0.12 x 0.1 mm^3	
Theta range for data collection	3.843 to 63.911°.	
Index ranges	-13<=h<=13, -4<=k<=5, -13<=l<=14	
Reflections collected	4261	
Independent reflections	1931 [R(int) = 0.0646]	
Completeness to theta = 63.911°	96.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.1807	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1931 / 1 / 157	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.1703	
R indices (all data)	R1 = 0.0710, wR2 = 0.1724	

Absolute structure parameter	0.19(4)
Extinction coefficient	n/a
Largest diff. peak and hole	1.150 and -0.908 e.Å^{-3}

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