Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

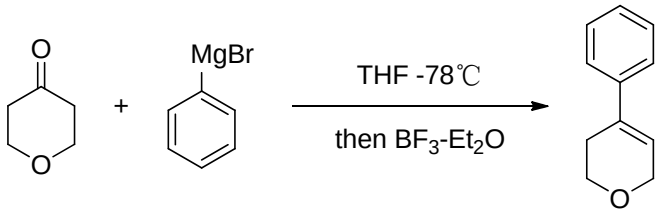
Supporting Information

Table of Contents

General information

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 600 MHz and 151 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, C_6D_6 = 7.15 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23, C_6D_6 = 128.62. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel (200–300 mesh). HRMS were carried out on an Orbitrap analyzer. Optical rotations were measured using a 1.0 mL cell with a 10 cm path length on ANTON PAAR MCP 200 polarimeter and concentrations (c) were reported in g×(100 mL)$^{-1}$. Enantiomeric excesses were determined by HPLC using a Daicel Chiralpak AD-H, OJ-H, AS-H or OD-H column with hexane/*i*-PrOH as the eluent.

General procedure for synthesis 4-aryl-3,6-dihydro-2*H*-pyrans



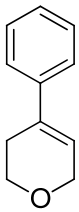
A solution of arylmagnesium bromide (0.5 M in THF, 6 mL, 12 mmol) was added to a stirred solution of tetrahydro-4*H*-pyran-4-one (1g, 10 mmol) in THF (40 mL) at -78 ^{o}C. The reaction mixture was stirred at rt for 2 h. The total procedure was monitored by TLC until the reaction was completed. Without further purification, BF_3-OEt_2 (10 mL) was added to a stirred solution of the resulting reaction mixture at 0 ^{o}C. The reaction mixture was stirred at rt for 15 min. Saturated aqueous $NaHCO_3$ solution (10 mL) was added to the reaction mixture and the solvent was removed under reduced pressure. Water (20 mL) and AcOEt (30 mL) was added to the residue and the mixture was filtered through a short plug of Celite. The filtrate was concentrated under reduced pressure. The residue was extracted with AcOEt (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification by column on SiO_2 (hexane/AcOEt = 6/1) afforded 4-aryl-3,6-dihydro-2*H*-pyrans.

4-Methyl-3,6-dihydro-2*H*-pyran was prepared following the reported method [1].

General procedure for the one-pot asymmetric alkylation of 4-aryl-3,6-dihydro-2*H*-pyrans with aldehydes

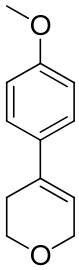
To a solution of 4-aryl-3,6-dihydro-2*H*-pyrans (0.2 mmol, 1.0 equiv.) in CH_2Cl_2 (2.0 mL) was added DDQ (0.19 mmol, 0.95 equiv.) at room temperature. The reaction was monitored by TLC and, upon starting material consumption, 90% solvent was evaporated and CH_3NO_2 (1.8 mL) was added to the mixture. Subsequently, $Zn(OTf)_2$ (0.1 mmol, 0.5 equiv.), B·TFA (0.04 mmol, 20 mol %), aldehyde (0.8 mmol, 4.0 equiv.), and H_2O (12.0 mmol, 60 equiv.) were successively added at 0 °C. The reaction mixture was stirred at 0 °C until TLC analysis showed complete consumption of starting material. The reaction mixture was then poured into the suspension of excess $NaBH_4$ (0.4 mmol, 2.0 equiv.) in MeOH (1.0 mL) at 0 °C, and after stirring for 20 min, the solution was treated with saturated aqueous $NaHCO_3$. The mixture was extracted with Et_2O (10 mL × 3), and the combined organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography to give the desired product.

Analytical data



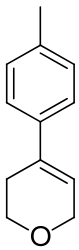
4-Phenyl-3,6-dihydro-2*H*-pyran (1a)

Yield: 0.966 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.14 (m, 5H), 6.15–6.02 (m, 1H), 4.29 (q, *J* = 2.7 Hz, 2H), 3.90 (t, *J* = 5.5 Hz, 2H), 2.49 (ddt, *J* = 8.0, 5.3, 2.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 134.4, 128.6, 127.5, 124.9, 122.6, 66.1, 64.7, 27.4; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{11}H_{13}O$: 161.0961, found 161.0952.



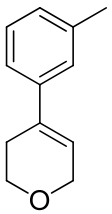
4-(4-Methoxyphenyl)-3,6-dihydro-2*H*-pyran (1b)

Yield: 1.237 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.10–5.98 (m, 1H), 4.32 (dd, *J* = 5.3, 2.6 Hz, 2H), 3.94 (t, *J* = 5.5 Hz, 2H), 3.82 (s, 3H), 2.51 (dd, *J* = 4.3, 2.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 133.7, 133.1, 126.0, 120.9, 114.0, 66.1, 64.7, 55.5, 27.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{12}H_{15}O_2$: 191.1067, found 191.1065.



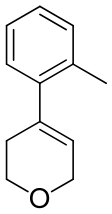
4-(*p*-Tolyl)-3,6-dihydro-2*H*-pyran (1c)

Yield: 1.083 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.26–5.98 (m, 1H), 4.34 (dd, *J* = 5.4, 2.6 Hz, 2H), 3.95 (t, *J* = 5.5 Hz, 2H), 2.53 (dt, *J* = 7.0, 2.6 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.2, 134.1, 129.3, 124.7, 121.7, 66.1, 64.7, 27.4, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{12}H_{15}O$: 175.1117, found 175.1136.



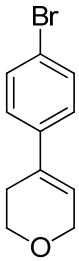
4-(*m*-Tolyl)-3,6-dihydro-2*H*-pyran (1d)

Yield: 1.046 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.02 (m, 4H), 6.21–6.05 (m, 1H), 4.35 (dd, *J* = 5.4, 2.7 Hz, 2H), 3.96 (t, *J* = 5.5 Hz, 2H), 2.55 (dt, *J* = 7.0, 2.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.1, 134.4, 128.5, 128.2, 125.7, 122.5, 122.0, 66.1, 64.7, 27.5, 21.7; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{12}H_{15}O$: 175.1117, found 175.1107.



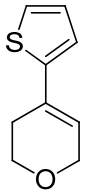
4-(*o*-Tolyl)-3,6-dihydro-2*H*-pyran (1e)

Yield: 0.905 g (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.03 (m, 4H), 5.63 (d, *J* = 1.5 Hz, 1H), 4.31 (q, *J* = 2.7 Hz, 2H), 3.94 (t, *J* = 5.4 Hz, 2H), 2.44–2.28 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 136.7, 135.1, 130.4, 128.3, 127.2, 125.9, 124.5, 65.7, 64.7, 30.2, 20.1; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{12}H_{15}O$: 175.1117, found 175.1128.



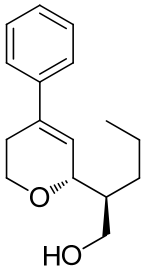
4-(4-Bromophenyl)-3,6-dihydro-2*H*-pyran (1f)

Yield: 1.189 g (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.17–6.08 (m, 1H), 4.32 (q, *J* = 2.7 Hz, 2H), 3.94 (t, *J* = 5.5 Hz, 2H), 2.49 (dt, *J* = 7.0, 2.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 133.5, 131.7, 126.6, 123.3, 121.4, 66.1, 64.6, 27.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{11}H_{12}BrO$: 239.0066, found 239.0079.



4-(Thiophen-2-yl)-3,6-dihydro-2*H*-pyran (1g)

Yield: 0.885 g (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.11 (m, 1H), 6.99 (d, *J* = 3.4 Hz, 2H), 6.19–6.01 (m, 1H), 4.31 (dd, *J* = 5.4, 2.7 Hz, 2H), 3.93 (t, *J* = 5.5 Hz, 2H), 2.54 (td, *J* = 5.4, 2.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 129.0, 127.4, 123.7, 121.9, 121.5, 65.6, 64.3, 27.7; HRMS (EI) m/z $[M + H]^+$ calculated for $C_9H_{11}OS$: 167.0525, found 167.0523.



(*S*)-2-((*R*)-4-Phenyl-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (3a)

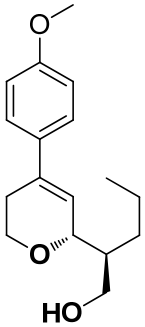
Major diastereomer:

Colorless oil. Yield: 39.4 mg (80%, d.r. = 2.4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ

7.46–7.23 (m, 5H), 6.07 (s, 1H), 4.37 (s, 1H), 4.23 (ddd, *J* = 11.2, 5.8, 1.2 Hz, 1H), 3.86 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.81–3.54 (m, 2H), 2.74 (dddd, *J* = 9.5, 5.9, 4.8, 2.5 Hz, 1H), 2.51 (s, 1H), 2.40–2.28 (m, 1H), 1.68 (dd, *J* = 4.8, 2.6 Hz, 1H), 1.61–1.36 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 135.9, 128.7, 127.7, 125.6, 125.0, 78.7, 64.8, 63.6, 44.9, 30.5, 27.5, 20.8, 14.5; HRMS (EI) m/z [M + H]$^+$ calculated for $C_{16}H_{23}O_2$: 247.1693, found 247.1682; $[\alpha]^{25}_D$= -52.6 (c = 0.93, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 15.070 min, t_{major} = 7.860 min, ee = 98%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.19 (m, 5H), 6.02 (s, 1H), 4.54 (s, 1H), 4.23 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.89–3.55 (m, 3H), 2.85–2.65 (m, 1H), 2.36 (t, *J* = 21.9 Hz, 2H), 2.01–1.86 (m, 1H), 1.49–1.30 (m, 4H), 0.94 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 136.5, 128.7, 127.7, 125.0, 123.8, 78.7, 64.9, 64.7, 44.7, 28.5, 27.5, 21.1, 14.5; HRMS (EI) m/z [M + H]$^+$ calculated for $C_{16}H_{23}O_2$: 247.1693, found 247.1699; $[\alpha]^{25}_D$= +64.5 (c = 0.72, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 6.45 min, t_{major} = 7.19 min, ee = 98%.



(*S*)-2-((*R*)-4-(4-Methoxyphenyl)-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (3b)

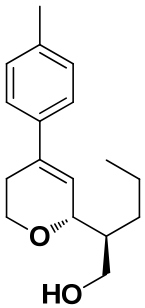
Major diastereomer:

Colorless oil. Yield: 42.5 mg (77%, d.r. = 2.5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.28 (m, 2H), 6.93–6.80 (m, 2H), 5.97 (s, 1H), 4.35 (s, 1H), 4.22 (ddd, *J* = 11.2, 5.8, 1.2 Hz, 1H), 3.93–3.77 (m, 4H), 3.75–3.56 (m, 2H), 2.80–2.62 (m, 1H), 2.50 (s,

1H), 2.38–2.24 (m, 1H), 1.71–1.35 (m, 5H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 135.2, 132.9, 126.1, 123.9, 114.0, 78.8, 64.8, 63.7, 55.5, 44.9, 30.5, 27.6, 20.8, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{25}O_3$: 277.1798, found 277.1797; $[\alpha]^{25}_D$= -48.3 (c = 0.44, $CHCl_3$); HPLC: (Chiralcel OJ-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 15.78 min, t_{major} = 12.14 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.30 (m, 2H), 6.95–6.83 (m, 2H), 5.92 (s, 1H), 4.52 (s, 1H), 4.21 (dd, *J* = 11.3, 5.3 Hz, 1H), 3.83 (s, 3H), 3.78–3.62 (m, 3H), 2.78–2.57 (m, 2H), 2.31 (dd, *J* = 11.2, 8.3 Hz, 1H), 1.93 (dd, *J* = 7.0, 3.4 Hz, 1H), 1.47–1.30 (m, 4H), 0.93 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 135.8, 133.0, 126.1, 122.0, 114.0, 78.8, 64.9, 64.7, 55.5, 44.7, 28.5, 27.6, 21.1, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{25}O_3$: 277.1798, found 277.1784; $[\alpha]^{25}_D$= +48.3 (c = 0.62, $CHCl_3$); HPLC: (Chiralcel OJ-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 13.57 min, t_{major} = 14.67 min, ee = 98%.



(*S*)-2-((*R*)-4-(*p*-Tolyl)-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (3c)

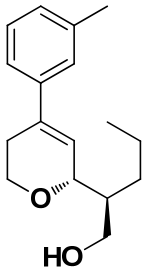
Major diastereomer:

Colorless oil. Yield: 45.8 mg (88%, d.r. = 2.2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.03 (s, 1H), 4.36 (s, 1H), 4.22 (ddd, *J* = 11.2, 5.8, 1.2 Hz, 1H), 3.86 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.78–3.57 (m, 2H), 2.80– 2.64 (m, 1H), 2.57 (d, *J* = 1.9 Hz, 1H), 2.39–2.26 (m, 4H), 1.67 (dd, *J* = 11.0, 5.5 Hz, 1H), 1.59–1.34 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5,

135.7, 129.3, 124.9, 124.7, 78.7, 64.8, 63.6, 44.9, 30.5, 27.5, 21.3, 20.8, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{25}O_2$: 261.1849, found 261.1857; $[\alpha]^{25}_D$= -84.4 (c = 0.43, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 210 nm), retention time: t_{minor} = 9.12 min, t_{major} = 5.66 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.98 (s, 1H), 4.53 (s, 1H), 4.22 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.85–3.61 (m, 3H), 2.82–2.56 (m, 2H), 2.40–2.25 (m, 4H), 2.00–1.87 (m, 1H), 1.50–1.30 (m, 4H), 0.94 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 137.5, 136.3, 129.3, 124.9, 122.9, 78.7, 64.9, 64.7, 44.7, 28.4, 27.5, 21.3, 21.1, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{25}O_2$: 261.1849, found 261.1846; $[\alpha]^{25}_D$= +77.5 (c = 0.22, $CHCl_3$); HPLC: (Chiralcel OJ-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 210 nm), retention time: t_{minor} = 12.49 min, t_{major} = 10.15 min, ee = 98%.



(*S*)-2-((*R*)-4-(*m*-Tolyl)-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (3d)

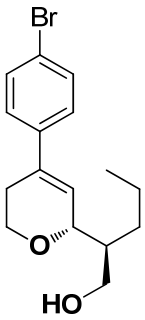
Major diastereomer:

Colorless oil. Yield: 43.2 mg (83%, d.r. = 2.3:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.17 (m, 3H), 7.10 (d, *J* = 6.9 Hz, 1H), 6.04 (s, 1H), 4.35 (s, 1H), 4.21 (ddd, *J* = 11.2, 5.8, 1.3 Hz, 1H), 3.85 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.79–3.54 (m, 2H), 2.89–2.61 (m, 1H), 2.41–2.28 (m, 5H), 1.71–1.36 (m, 5H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.2, 136.0, 128.6, 128.5, 125.8, 125.5, 122.2, 78.7, 64.8, 63.6, 44.9, 30.5, 27.6, 21.7, 20.8, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{25}O_2$: 261.1849, found 261.1857; $[\alpha]^{25}_D$= -64.5 (c = 0.72, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor}

= 7.80 min, t_{major} = 5.95 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.17 (m, 3H), 7.11 (d, *J* = 6.9 Hz, 1H), 6.00 (s, 1H), 4.53 (s, 1H), 4.27–4.15 (m, 1H), 3.84–3.56 (m, 3H), 2.85–2.60 (m, 1H), 2.40–2.28 (m, 5H), 2.00–1.87 (m, 1H), 1.49–1.30 (m, 4H), 0.94 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.2, 136.6, 128.6, 128.5, 125.8, 123.6, 122.2, 78.8, 64.9, 64.7, 44.7, 28.5, 27.6, 21.7, 21.1, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{25}O_2$: 261.1849, found 261.1846; $[\alpha]^{25}_D$= +54.6 (c = 0.52, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 10.12 min, t_{major} = 6.40 min, ee = 99%.



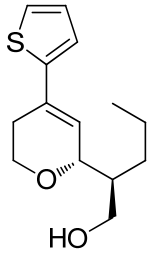
(*S*)-2-((*R*)-4-(4-Bromophenyl)-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (3f)

Major diastereomer:

Colorless oil. Yield: 45.3 mg (70%, d.r. = 2.1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.34 (m, 2H), 7.19 (dd, *J* = 6.4, 2.2 Hz, 2H), 5.99 (s, 1H), 4.27 (s, 1H), 4.15 (ddd, *J* = 11.3, 5.9, 1.1 Hz, 1H), 3.76 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.69–3.49 (m, 2H), 2.76–2.55 (m, 1H), 2.39 (s, 1H), 2.26–2.15 (m, 1H), 1.60 (dd, *J* = 4.8, 2.8 Hz, 1H), 1.54–1.29 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 134.9, 131.7, 126.6, 126.3, 121.6, 78.6, 64.7, 63.6, 44.8, 30.4, 27.4, 20.8, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{16}H_{22}BrO_2$: 325.0798, found 325.0796; $[\alpha]^{25}_D$= -60.1 (c = 0.77, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.02 min, t_{major} = 6.18 min, ee = 94%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.24–7.16 (m, 2H), 5.94 (s, 1H), 4.43 (s, 1H), 4.14 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.72–3.51 (m, 3H), 2.75–2.57 (m, 1H), 2.44 (s, 1H), 2.17 (dd, *J* = 11.4, 8.4 Hz, 1H), 1.85 (dd, *J* = 6.8, 3.4 Hz, 1H), 1.40–1.22 (m, 4H), 0.86 (dd, *J* = 8.9, 4.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 135.5, 131.7, 126.6, 124.5, 121.6, 78.6, 64.7, 64.6, 44.6, 28.4, 27.4, 21.1, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{16}H_{22}BrO_2$: 325.0782, found 325.0797; $[\alpha]^{25}_D$= +43.6(c = 0.58, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.78 min, t_{major} = 9.65 min, ee = 94%.



(*S*)-2-((*R*)-4-(Thiophen-2-yl)-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (3g)

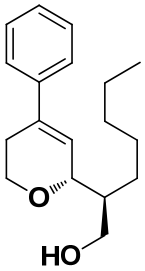
Major diastereomer:

Colorless oil. Yield: 37.8 mg (75%, d.r. = 2.0:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 3.9, 2.3 Hz, 1H), 6.99 (dd, *J* = 4.6, 3.0 Hz, 2H), 6.06 (s, 1H), 4.35 (s, 1H), 4.27–4.13 (m, 1H), 3.84 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.80–3.53 (m, 2H), 2.87–2.50 (m, 2H), 2.43–2.31 (m, 1H), 1.69–1.35 (m, 5H), 0.96 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 130.5, 127.5, 124.3, 124.0, 122.4, 78.4, 64.5, 63.6, 44.8, 30.4, 27.8, 20.8, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{14}H_{21}O_2S$: 253.1257, found 253.1255; $[\alpha]^{25}_D$= -54.7 (c = 0.75, $CHCl_3$); HPLC: (Chiralcel OJ-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.70 min, t_{major} = 9.86 min, ee = 98%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.10 (m, 1H), 7.00 (dd, *J* = 4.4, 3.1

Hz, 2H), 6.00 (s, 1H), 4.51 (d, *J* = 2.3 Hz, 1H), 4.19 (dd, *J* = 11.3, 5.5 Hz, 1H), 3.83–3.55 (m, 3H), 2.82–2.64 (m, 2H), 2.42–2.29 (m, 1H), 1.91 (dd, *J* = 6.9, 3.5 Hz, 1H), 1.47–1.29 (m, 4H), 0.94 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 131.0, 127.6, 124.0, 122.6, 122.3, 78.4, 64.6, 64.6, 44.6, 28.4, 27.8, 21.1, 14.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{14}H_{21}O_2S$: 253.1257, found 253.1239; $[\alpha]^{25}_D$= +73.4 (c = 0.37, $CHCl_3$); HPLC: (Chiralcel OJ-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.89 min, t_{major} = 7.57 min, ee = 96%.



(*S*)-2-((*R*)-4-Phenyl-5,6-dihydro-2*H*-pyran-2-yl)heptan-1-ol (4a)

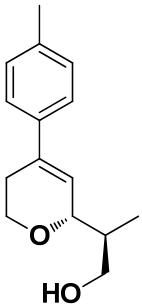
Major diastereomer:

Colorless oil. Yield: 44.3 mg (81%, d.r. = 2.4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.28 (m, 5H), 6.07 (s, 1H), 4.37 (s, 1H), 4.23 (ddd, *J* = 11.2, 5.8, 1.2 Hz, 1H), 3.86 (dd, *J* = 11.2, 2.3 Hz, 1H), 3.78–3.59 (m, 2H), 2.84–2.66 (m, 1H), 2.42–2.28 (m, 2H), 1.64–1.30 (m, 9H), 0.91 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 135.9, 128.7, 127.7, 125.6, 125.0, 78.8, 64.8, 63.7, 45.1, 32.3, 28.3, 27.5, 27.4, 22.9, 14.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{18}H_{27}O_2$: 275.2006, found 275.2017; $[\alpha]^{25}_D$= -39.5 (c = 0.51, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 12.25 min, t_{major} = 7.61 min, ee = 98%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.29 (m, 5H), 6.02 (s, 1H), 4.54 (s, 1H), 4.23 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.83–3.59 (m, 3H), 2.86–2.63 (m, 1H), 2.36–2.24 (m, 2H), 1.98–1.87 (m, 1H), 1.34 (dd, *J* = 13.1, 9.4 Hz, 8H), 0.89 (t, *J* = 6.7 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 136.6, 128.7, 127.7, 125.1, 123.8, 78.8,

64.9, 64.8, 45.0, 32.3, 27.7, 27.6, 26.2, 22.8, 14.2; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{18}H_{27}O_2$: 275.2006, found 275.2007; $[\alpha]^{25}_D$= +40.1 (c = 0.30, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 11.02 min, t_{major} = 7.05 min, ee = 97%.



(*S*)-2-((*R*)-4-(*p*-Tolyl)-5,6-dihydro-2*H*-pyran-2-yl)propan-1-ol (4b)

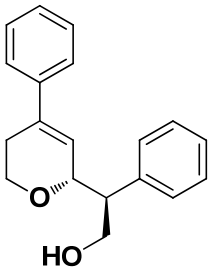
Major diastereomer:

Colorless oil. Yield: 35.7 mg (77%, d.r. = 2.1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.20 (ddd, *J* = 11.2, 5.8, 1.8 Hz, 2H), 3.76–3.61 (m, 3H), 2.79–2.64 (m, 1H), 2.41–2.28 (m, 5H), 1.94–1.87 (m, 1H), 1.08 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.5, 135.6, 129.4, 124.9, 124.1, 80.0, 66.9, 64.4, 40.1, 27.5, 21.3, 13.9; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{15}H_{21}O_2$: 233.1536, found 233.1556; $[\alpha]^{25}_D$= -24.7 (c = 0.62, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.68 min, t_{major} = 6.67 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 1H), 4.48 (s, 1H), 4.20 (dd, *J* = 11.2, 5.9 Hz, 1H), 3.72 (ddd, *J* = 9.4, 7.8, 3.0 Hz, 3H), 2.78–2.61 (m, 1H), 2.42–2.25 (m, 5H), 2.10–2.01 (m, 1H), 0.96 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.5, 136.2, 129.3, 124.9, 123.2, 78.3, 66.6, 64.7, 39.9, 27.5, 21.3, 11.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{15}H_{21}O_2$: 233.1536, found 233.1535; $[\alpha]^{25}_D$= +32.5 (c = 0.21, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor}

= 10.33 min, t_{major} = 8.22 min, ee = 99%.



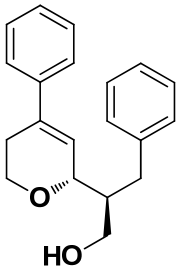
(*S*)-2-Phenyl-2-((*R*)-4-phenyl-5,6-dihydro-2*H*-pyran-2-yl)ethanol (4c)

Major diastereomer:

Colorless oil. Yield: 40.9 mg (73%, d.r. = 2.6:1). ^{1}H NMR (400 MHz, C_6D_6) δ 7.25–6.95 (m, 10H), 5.87 (d, *J* = 0.8 Hz, 1H), 4.55–4.40 (m, 1H), 4.29–4.11 (m, 1H), 4.06–3.93 (m, 1H), 3.80 (ddd, *J* = 11.2, 5.7, 2.2 Hz, 1H), 3.37 (ddd, *J* = 11.1, 10.3, 3.7 Hz, 1H), 3.01 (ddd, *J* = 9.0, 7.0, 4.7 Hz, 1H), 2.74 (s, 1H), 2.46–2.21 (m, 1H), 1.92–1.78 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 140.5, 140.4, 135.3, 128.9, 128.9, 128.6, 128.5, 128.2, 128.0, 127.9, 127.8, 127.6, 127.2, 125.1, 124.8, 78.8, 66.6, 63.9, 53.5, 27.2; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{19}H_{21}O_2$: 281.1536, found 281.1532; $[\alpha]^{25}_D$= -54.6 (c = 0.45, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 22.02 min, t_{major} = 16.90 min, ee = 89%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.23–7.18 (m, 2H), 7.14–7.00 (m, 8H), 5.90 (t, *J* = 1.6 Hz, 1H), 4.67–4.44 (m, 1H), 4.16 (t, *J* = 8.8 Hz, 1H), 3.93 (d, *J* = 4.9 Hz, 1H), 3.81 (ddd, *J* = 11.1, 5.8, 1.3 Hz, 1H), 3.34 (td, *J* = 11.1, 3.4 Hz, 1H), 3.17–2.99 (m, 1H), 2.36–2.14 (m, 1H), 2.04–1.73 (m, 2H); ^{13}C NMR (101 MHz, C_6D_6) δ 141.4, 140.4, 136.8, 130.0, 129.3, 128.9, 128.1, 127.5, 125.8, 125.1, 77.4, 64.9, 64.7, 53.4, 28.0; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{19}H_{21}O_2$: 281.1536, found 281.1527; $[\alpha]^{25}_D$= +46.2 (c = 0.15, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 17.48 min, t_{major} = 12.90 min, ee = 80%.



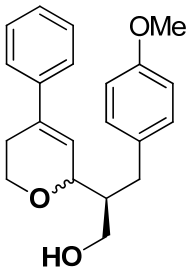
(*S*)-3-Phenyl-2-((*R*)-4-phenyl-5,6-dihydro-2*H*-pyran-2-yl)propan-1-ol (4d)

Major diastereomer:

Colorless oil. Yield: 41.2 mg (70%, d.r. = 2.0:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.12 (m, 10H), 5.93 (s, 1H), 4.30 (s, 1H), 4.19 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.80 (dd, *J* = 11.2, 2.7 Hz, 1H), 3.61 (ddd, *J* = 8.8, 7.2, 3.0 Hz, 1H), 3.49 (dd, *J* = 11.2, 4.5 Hz, 1H), 2.87 (d, *J* = 7.7 Hz, 2H), 2.73–2.61 (m, 1H), 2.25 (dd, *J* = 13.7, 3.0 Hz, 2H), 1.85 (ddd, *J* = 9.0, 5.0, 2.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 140.2, 136.2, 129.5, 128.7, 128.6, 127.7, 126.3, 125.5, 125.0, 77.5, 64.9, 62.9, 47.1, 34.8, 27.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{20}H_{23}O_2$: 295.1693, found 295.1685; $[\alpha]^{25}_D$= -61.2 (c = 0.73, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 7.13 min, t_{major} = 7.82 min, ee = 99%.

Minor diastereomer:

HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 10.96 min, t_{major} = 7.34 min, ee = 98%.



(2*S*)-3-(4-Methoxyphenyl)-2-(4-phenyl-5,6-dihydro-2*H*-pyran-2-yl)propan-1-ol (4e)

Colorless oil. Yield: 42.8 mg (66%, d.r. = 1.8:1). Mixture of 1.8:1 diastereomers. ^{1}H

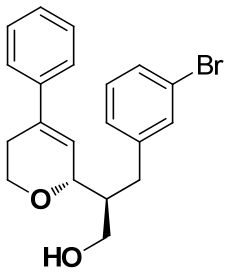
NMR (500 MHz, $CDCl_3$) δ 7.44–7.33 (m, 11.4H), 7.31–7.27 (m, 2.3H), 7.21–7.16 (m, 6.6H), 7.15–7.09 (m, 2.3H), 6.88–6.78 (m, 4.3H), 6.07 (t, *J* = 1.7 Hz, 1.8H), 6.00 (d, *J* = 1.6 Hz, 1H), 4.58–4.51 (m, 1.8H), 4.35 (d, *J* = 15.3 Hz, 1H), 4.29–4.20 (m, 3.1H), 3.80 (s, 3.0H), 3.77 (s, 5.4H), 3.73–3.65 (m, 6.5H), 2.89 (d, *J* = 7.6 Hz, 2.1H), 2.66 (dd, *J* = 14.2, 8.4 Hz, 4.8H), 2.33 (d, *J* = 16.8 Hz, 3.5H), 2.18–2.07 (m, 3.5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 158.1, 140.3, 136.6, 136.1, 132.7, 132.6, 130.4, 130.2, 129.5, 128.7, 127.8, 127.8, 125.6, 125.1, 125.0, 124.1, 114.1, 77.9, 64.9, 64.8, 64.2, 62.9, 62.5, 55.5, 47.3, 47.3, 34.7, 33.9, 31.4, 27.5; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{21}H_{25}O_3$: 325.1798, found 325.1789.

Major diastereomer:

HPLC: (Chiralcel AS-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 15.44 min, t_{major} = 21.16 min, ee = 96%.

Minor diastereomer:

HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 28.15 min, t_{major} = 17.69 min, ee = 97%.



(*S*)-3-(3-Bromophenyl)-2-((*R*)-4-phenyl-5,6-dihydro-2*H*-pyran-2-yl)propan-1-ol (4f)

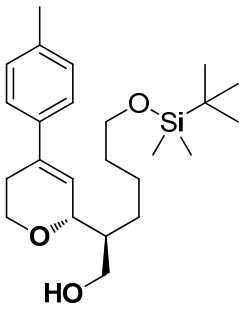
Major diastereomer:

Colorless oil. Yield: 48.4 mg (65%, d.r. = 2.0:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 7.32–7.27 (m, 2H), 7.17–7.11 (m, 2H), 6.03 (t, *J* = 1.7 Hz, 1H), 4.58 (s, 1H), 4.24 (dd, *J* = 11.2, 5.1 Hz, 1H), 3.83–3.60 (m, 3H), 2.79–2.66 (m, 3H), 2.41–2.27 (m, 1H), 2.09 (ddd, *J* = 9.2, 5.9, 2.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 140.1, 136.8, 132.3, 130.1, 129.3, 128.7, 128.1, 127.9, 125.0, 124.1, 122.7,

77.8, 64.7, 63.9, 47.0, 31.6, 27.4; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{20}H_{22}BrO_2$: 373.0798, found 373.0807; $[\alpha]^{25}_D$= -78.2 (c = 0.35, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 15.50 min, t_{major} = 11.32 min, ee = 98%.

Minor diastereomer:

HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 12.15 min, t_{major} = 13.56 min, ee = 98%.



(*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-2-((*R*)-4-(*p*-tolyl)-5,6-dihydro-2*H*-pyran-2-yl) hexan-1-ol (4g)

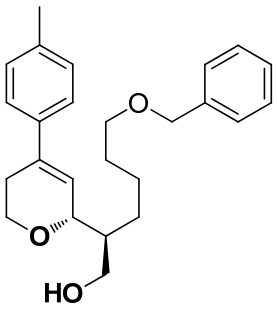
Major diastereomer:

Colorless oil. Yield: 54.9 mg (68%, d.r. = 2.1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 4.37 (s, 1H), 4.21 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.86 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.75–3.58 (m, 4H), 2.80–2.63 (m, 1H), 2.39–2.20 (m, 5H), 2.02 (d, *J* = 5.3 Hz, 1H), 1.67–1.50 (m, 6H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 137.5, 135.8, 129.4, 124.9, 124.7, 78.7, 64.9, 63.6, 63.3, 45.1, 33.3, 28.1, 27.5, 26.2, 23.9, 21.3, 18.6, -5.0; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{24}H_{41}O_3Si$: 405.2819, found 405.2835; $[\alpha]^{25}_D$= -40.3 (c = 0.67, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 210 nm), retention time: t_{minor} = 10.26 min, t_{major} = 6.84 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0

Hz, 2H), 5.96 (s, 1H), 4.53 (s, 1H), 4.21 (dd, *J* = 11.2, 5.5 Hz, 1H), 3.81–3.60 (m, 5H), 2.80–2.64 (m, 1H), 2.37–2.27 (m, 4H), 1.92 (s, 2H), 1.52 (dd, *J* = 8.8, 3.4 Hz, 3H), 1.38 (dd, *J* = 9.3, 3.8 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.5, 136.4, 129.3, 124.9, 122.8, 78.8, 64.9, 64.7, 63.2, 44.9, 33.2, 27.5, 26.2, 26.0, 24.3, 21.3, 18.6, -5.1; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{24}H_{41}O_3Si$: 405.2819, found 405.2814; $[\alpha]^{25}_D$= +48.3 (c = 0.33, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 5/95, 1.0 mL/min, 210 nm), retention time: t_{minor} = 9.11 min, t_{major} = 6.20 min, ee = 98%.



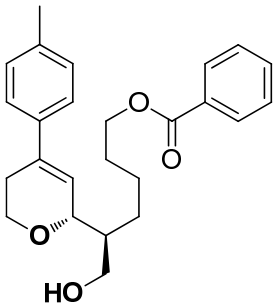
(*S*)-6-(Benzyloxy)-2-((*R*)-4-(*p*-tolyl)-5,6-dihydro-2*H*-pyran-2-yl)hexan-1-ol (4h)

Major diastereomer:

Colorless oil. Yield: 53.2 mg (70%, d.r. = 2.0:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.4 Hz, 4H), 7.30 (d, *J* = 8.1 Hz, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 4.52 (s, 2H), 4.37 (s, 1H), 4.21 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.86 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.70 (td, *J* = 11.1, 3.4 Hz, 1H), 3.62 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.51 (t, *J* = 6.5 Hz, 1H), 2.80–2.66 (m, 1H), 2.41–2.28 (m, 2H), 1.67 (dt, *J* = 12.0, 5.9 Hz, 2H), 1.57–1.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.5, 137.5, 135.8, 129.4, 128.6, 127.9, 127.7, 124.9, 124.7, 78.6, 73.1, 70.5, 64.9, 63.5, 45.1, 30.2, 28.1, 27.6, 24.4, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{25}H_{33}O_3$: 381.2424, found 381.2420; $[\alpha]^{25}_D$= -33.1 (c = 0.52, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 10.41 min, t_{major} = 8.41 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 7H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.94 (s, 1H), 4.50 (d, *J* = 9.5 Hz, 3H), 4.20 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.71 (qd, *J* = 11.0, 5.5 Hz, 3H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.77–2.65 (m, 1H), 2.40–2.23 (m, 5H), 1.89 (s, 1H), 1.64–1.58 (m, 2H), 1.39 (dd, *J* = 10.9, 5.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.5, 137.5, 136.4, 129.4, 128.6, 127.8, 127.7, 124.9, 122.9, 78.7, 73.1, 70.4, 64.9, 64.7, 44.9, 30.2, 27.5, 26.0, 24.7, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{25}H_{33}O_3$: 381.2424, found 381.2431; $[\alpha]^{25}_D$= +47.2 (c = 0.30, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 12.00 min, t_{major} = 7.29 min, ee = 99%.



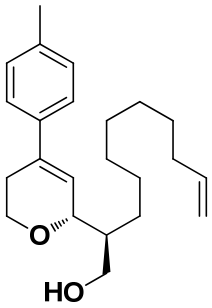
(*S*)-6-Hydroxy-5-((*R*)-4-(*p*-tolyl)-5,6-dihydro-2*H*-pyran-2-yl)hexyl benzoate (4i)

Major diastereomer:

Colorless oil. Yield: 52.8 mg (67%, d.r. = 2.0:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–7.97 (m, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 4.22 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.87 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.75–3.58 (m, 1H), 2.80–2.66 (m, 1H), 2.39–2.28 (m, 2H), 2.13 (s, 1H), 1.89–1.80 (m, 1H), 1.74–1.53 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 137.6, 137.4, 135.9, 133.0, 130.7, 129.8, 129.4, 128.5, 124.9, 124.5, 78.5, 65.1, 64.9, 63.3, 45.0, 29.2, 28.0, 27.5, 24.3, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{25}H_{31}O_4$: 395.2217, found 395.2213; $[\alpha]^{25}_D$= -24.2 (c = 0.43, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 10.79 min, t_{major} = 12.53 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.63–7.51 (m, 1H), 7.43 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.96 (s, 1H), 4.54 (s, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 4.21 (dd, *J* = 11.2, 5.4 Hz, 1H), 3.73 (ddd, *J* = 11.3, 6.9, 2.9 Hz, 3H), 2.82–2.62 (m, 1H), 2.39–2.21 (m, 5H), 1.91 (d, *J* = 3.2 Hz, 1H), 1.84–1.74 (m, 2H), 1.60–1.39 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 137.6, 137.4, 136.4, 133.0, 130.6, 129.7, 129.4, 128.5, 124.9, 122.8, 78.7, 65.1, 64.8, 64.6, 44.9, 29.2, 27.5, 25.7, 24.6, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{25}H_{31}O_4$: 395.2217, found 395.2226; $[\alpha]^{25}_D$= +24.8 (c = 0.23, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 16.18 min, t_{major} = 9.53 min, ee = 99%.



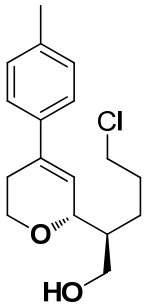
(*S*)-2-((*R*)-4-(*p*-Tolyl)-5,6-dihydro-2*H*-pyran-2-yl)undec-10-en-1-ol (4j)

Major diastereomer:

Colorless oil. Yield: 49.3 mg (72%, d.r. = 2.0:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.07–4.87 (m, 2H), 4.36 (s, 1H), 4.22 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.85 (dd, *J* = 11.2, 2.1 Hz, 1H), 3.75–3.57 (m, 2H), 2.80–2.62 (m, 1H), 2.43–2.28 (m, 4H), 2.16–1.98 (m, 4H), 1.61–1.48 (m, 2H), 1.41–1.29 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 137.5, 137.5, 135.7, 129.4, 124.9, 124.8, 114.3, 78.8, 64.8, 63.7, 45.1, 34.0, 30.0, 29.7, 29.3, 29.1, 28.3, 27.7, 27.6, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{23}H_{35}O_2$: 343.2632, found 343.2635; $[\alpha]^{25}_D$= -44.7 (c = 0.63, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 7.64 min, t_{major} = 5.30 min, ee = 99%.

Minor diastereomer:

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 1H), 5.89–5.74 (m, 1H), 5.08–4.83 (m, 2H), 4.53 (s, 1H), 4.21 (dd, *J* = 11.3, 5.3 Hz, 1H), 3.79–3.60 (m, 3H), 2.89–2.61 (m, 1H), 2.42–2.26 (m, 4H), 2.04 (dd, *J* = 14.1, 6.8 Hz, 2H), 1.95–1.87 (m, 1H), 1.47–1.28 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 137.5, 136.3, 129.4, 124.9, 122.9, 114.3, 78.8, 64.9, 64.8, 44.9, 34.0, 30.0, 29.6, 29.3, 29.1, 28.0, 27.5, 26.2, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{23}H_{35}O_2$: 343.2632, found 343.2638; $[\alpha]^{25}_D$= +49.2 (c = 0.27, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.38 min, t_{major} = 6.05 min, ee = 97%.



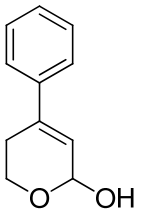
(*S*)-5-Chloro-2-((*R*)-4-(*p*-tolyl)-5,6-dihydro-2*H*-pyran-2-yl)pentan-1-ol (4k)

Major diastereomer:

Colorless oil. Yield: 47.1 mg (80%, d.r. = 1.9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 4.38 (s, 1H), 4.22 (dd, *J* = 11.3, 5.2 Hz, 1H), 3.87 (dd, *J* = 11.3, 2.4 Hz, 1H), 3.76–3.53 (m, 4H), 2.81–2.65 (m, 1H), 2.41–2.29 (m, 4H), 2.18 (s, 1H), 2.00–1.69 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.3, 136.1, 1294, 124.9, 124.3, 78.5, 64.9, 63.1, 45.4, 44.5, 30.8, 27.5, 25.7, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{24}ClO_2$: 295.1459, found 295.1462; $[\alpha]^{25}_D$= -22.4 (c = 0.31, $CHCl_3$); HPLC: (Chiralcel OD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 8.66 min, t_{major} = 5.66 min, ee = 99%.

Minor diastereomer:

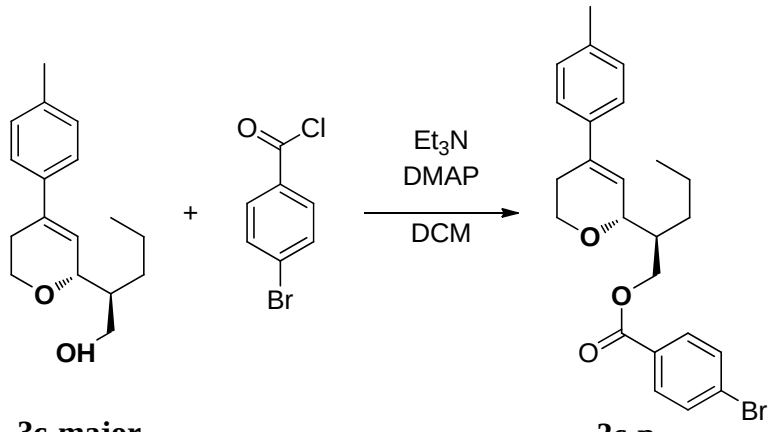
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.88 (s, 1H), 4.46 (s, 1H), 4.13 (dd, *J* = 11.3, 5.2 Hz, 1H), 3.76–3.59 (m, 3H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.63 (tdd, *J* = 11.9, 5.9, 3.7 Hz, 1H), 2.31–2.15 (m, 5H), 1.87–1.67 (m, 3H), 1.53–1.41 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 137.3, 136.5, 129.4, 124.9, 122.8, 78.6, 64.8, 64.5, 45.3, 44.4, 31.0, 27.4, 23.3, 21.3; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{17}H_{24}ClO_2$: 295.1459, found 295.1455; $[\alpha]^{25}_D$= +48.9 (c = 0.14, $CHCl_3$); HPLC: (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 210 nm), retention time: t_{minor} = 9.24 min, t_{major} = 6.53 min, ee = 99%.



4-Phenyl-5,6-dihydro-2*H*-pyran-2-ol (5)

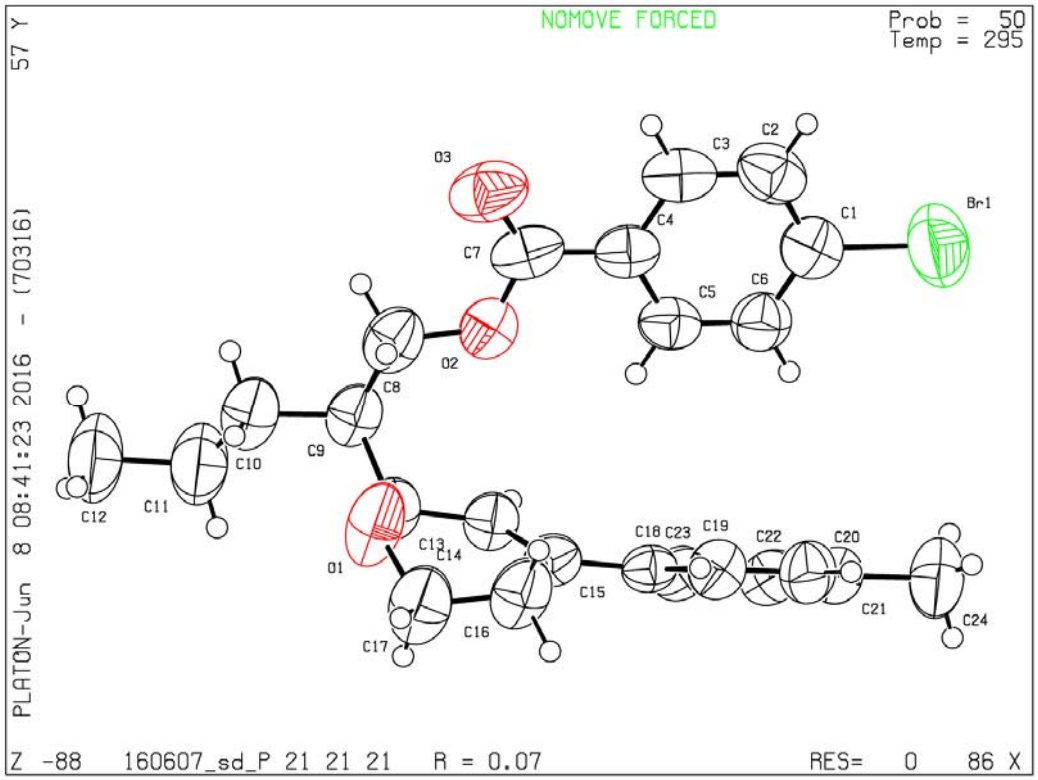
Colorless oil. ^{1}H NMR (600 MHz, C_6D_6) δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.19 (s, 1H), 5.94 (s, 1H), 4.10 (td, *J* = 11.4, 3.2 Hz, 1H), 3.74 (dd, *J* = 10.9, 5.9 Hz, 1H), 2.62–2.36 (m, 1H), 1.95–1.88 (m, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 140.1, 138.7, 128.6, 128.3, 125.5, 122.6, 91.1, 58.0, 27.1; HRMS (EI) m/z $[M + H]^+$ calculated for $C_{11}H_{13}O_2$: 177.0910, found 177.0916.

Absolute stereochemistry determination



3c-major **3c-p**

To a solution of **3c-major** (0.2 mmol, 52 mg), Et_3N (0.4 mmol, 55.6 μL), DMAP (0.02 mmol, 2.5 mg) in DCM (1 mL) was added dropwise a solution of 4-bromobenzoyl chloride (0.3 mmol, 66 mg) in DCM at 0 °C. The resulted mixture was vigorously stirred at room temperature and the reaction was monitored by TLC. After the completion of the reaction, it was treated with saturated aqueous $NaHCO_3$ (2 mL). After stirring at room temperature for 20 min, the mixture was diluted with ethyl acetate, and the organic layer was separated and washed with water and brine, dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash chromatography to give the desired product **3c-p**. Colorless solid. Yield: 75.2 mg (85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.73 (m, 2H), 7.51–7.40 (m, 2H), 7.28–7.23 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.08 (s, 1H), 4.47 (dd, *J* = 11.2, 6.5 Hz, 1H), 4.39 (s, 1H), 4.37–4.28 (m, 1H), 4.18 (ddd, *J* = 11.1, 5.7, 1.4 Hz, 1H), 3.74 (td, *J* = 10.9, 3.4 Hz, 1H), 2.77–2.58 (m, 1H), 2.36 (s, 3H), 2.35–2.00 (m, 1H), 2.20–2.08 (m, 1H), 1.65–1.55 (m, 2H), 1.55–1.40 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 137.6, 137.4, 135.3, 131.8, 131.3, 129.5, 129.3, 128.0, 124.7, 124.4, 75.0, 65.4, 64.5, 43.1, 31.0, 27.5, 21.3, 20.9, 14.5; HRMS (EI) *m/z* $[M + H]^+$ calculated for $C_{24}H_{28}BrO_3$: 443.1216, found 443.1217; $[\alpha]^{25}_D$= -33.6 (c = 0.23, $CHCl_3$).



The absolute stereochemistry (the **major** diastereomer from the reaction) was determined by the X-ray diffraction. A suitable crystal was selected and analyzed on an Xcalibur, Eos, Gemini diffractometer. Further information is contained in the CCDC file **1484800**.

CCDC file 1484800

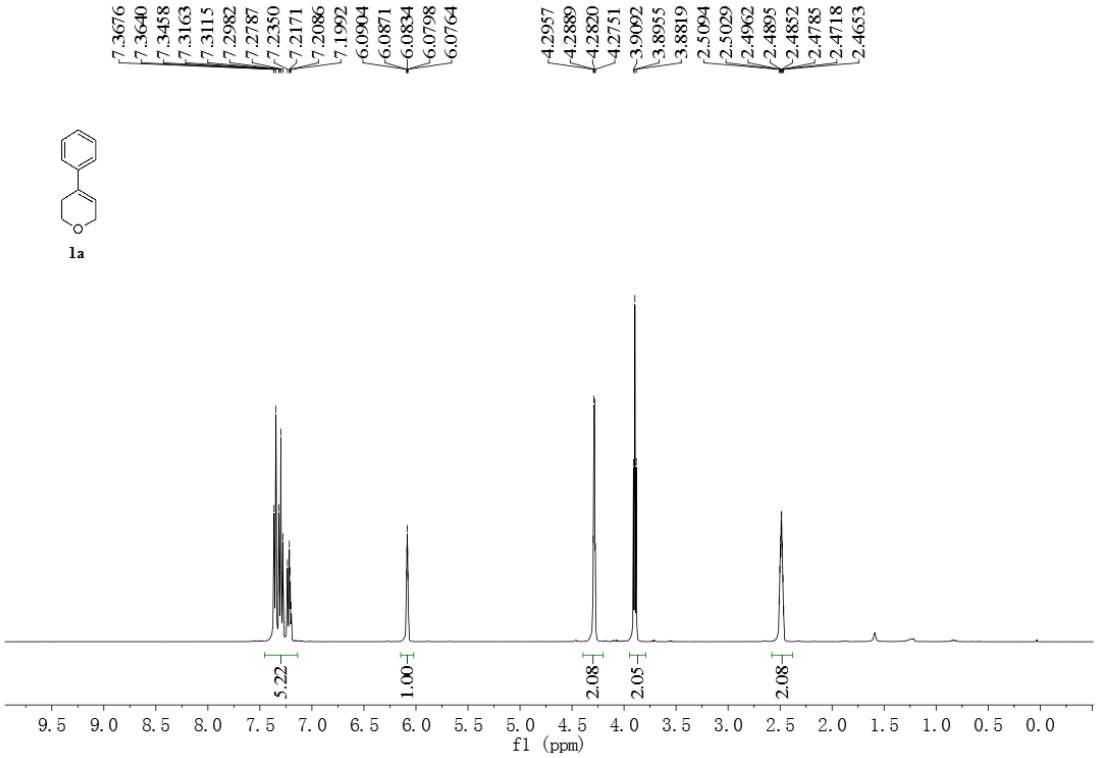
Identification code	160607_SD_1
Empirical formula	$C_{24}H_{27}BrO_3$
Formula weight	443.37
Temperature/K	295.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.4590(3)
b/Å	7.8884(3)
c/Å	51.7461(18)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2228.33(16)
Z	4

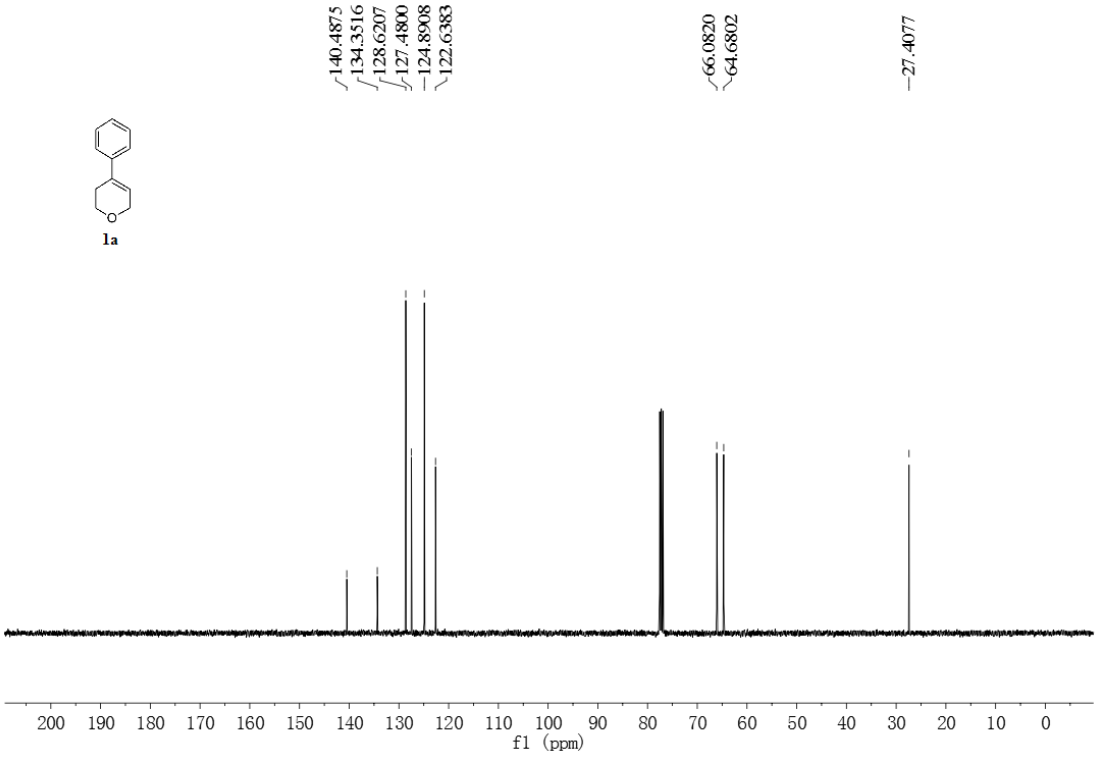
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	2.672
F(000)	920.0
Crystal size/mm^3	0.46 × 0.24 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.84 to 133.06
Index ranges	$-6 \leq h \leq 6$, $-9 \leq k \leq 9$, $-50 \leq l \leq 61$
Reflections collected	15055
Independent reflections	3945 [R_{int} = 0.0420, R_{sigma} = 0.0245]
Data/restraints/parameters	3945/0/255
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0680, wR_2 = 0.1962
Final R indexes [all data]	R_1 = 0.0752, wR_2 = 0.2027
Largest diff. peak/hole / e Å^{-3}	0.58/-0.60
Flack parameter	0.03(4)

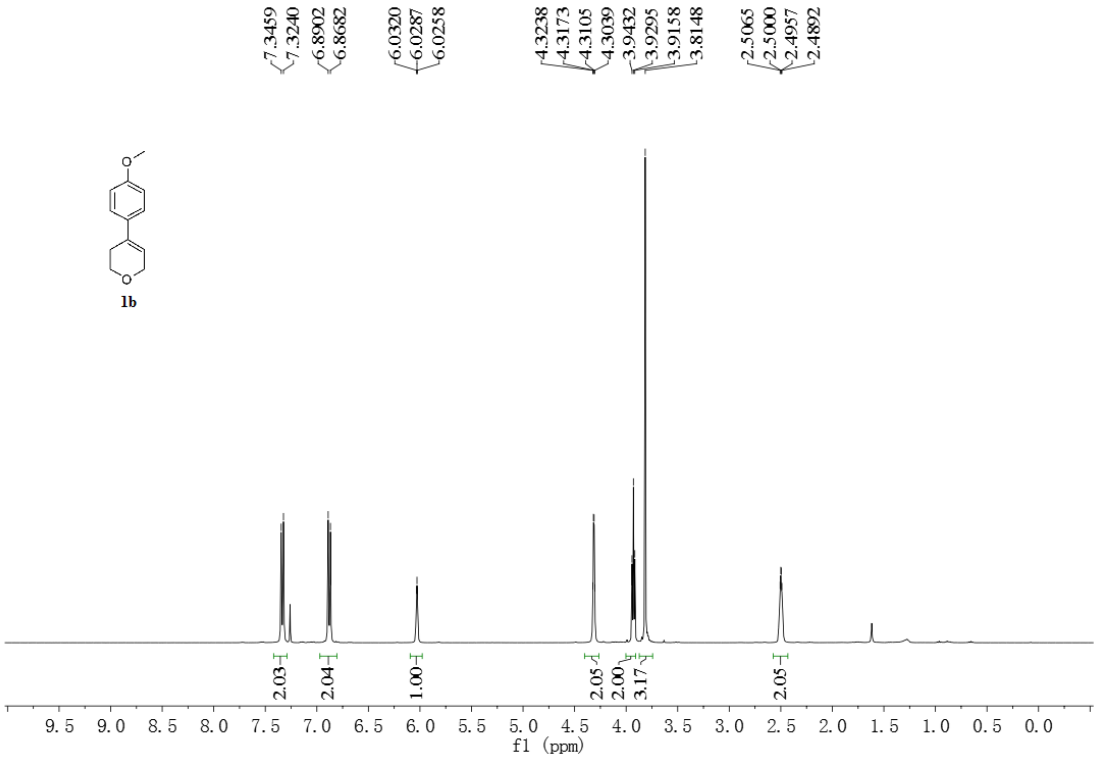
Reference

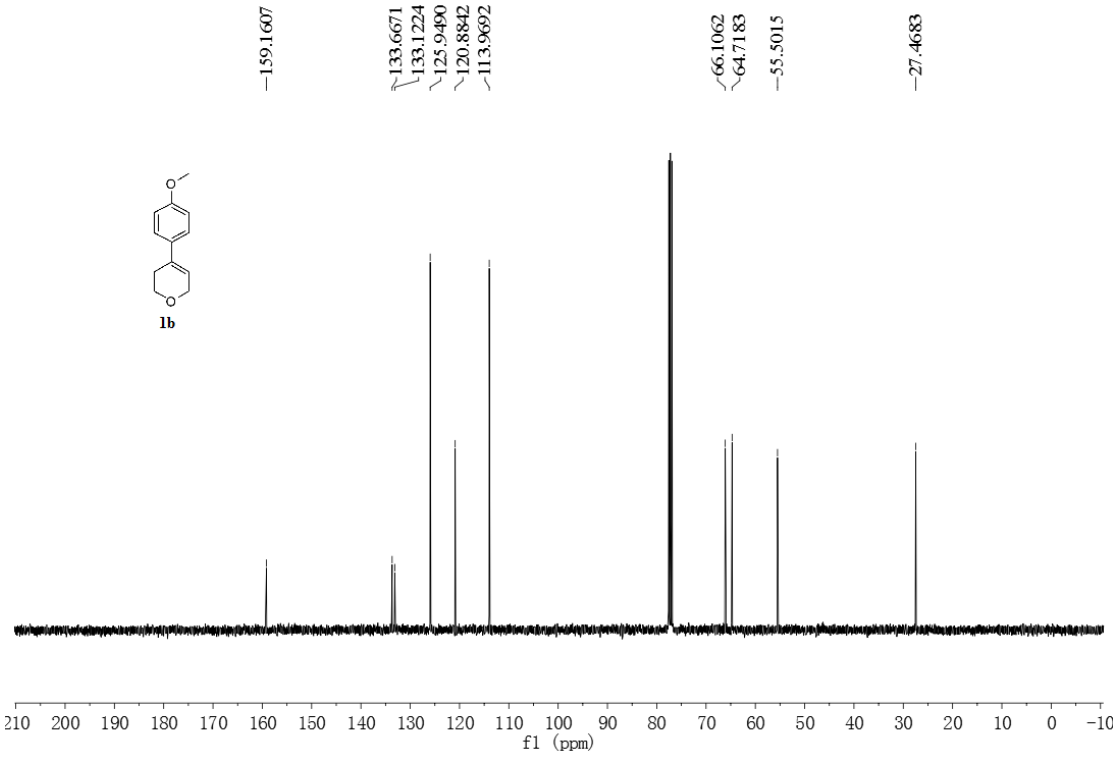
1：M. Chini, P. Crotti, C. Gardelli, F. Macchia, *Tetrahedron*, 1994, **50**, 1261.

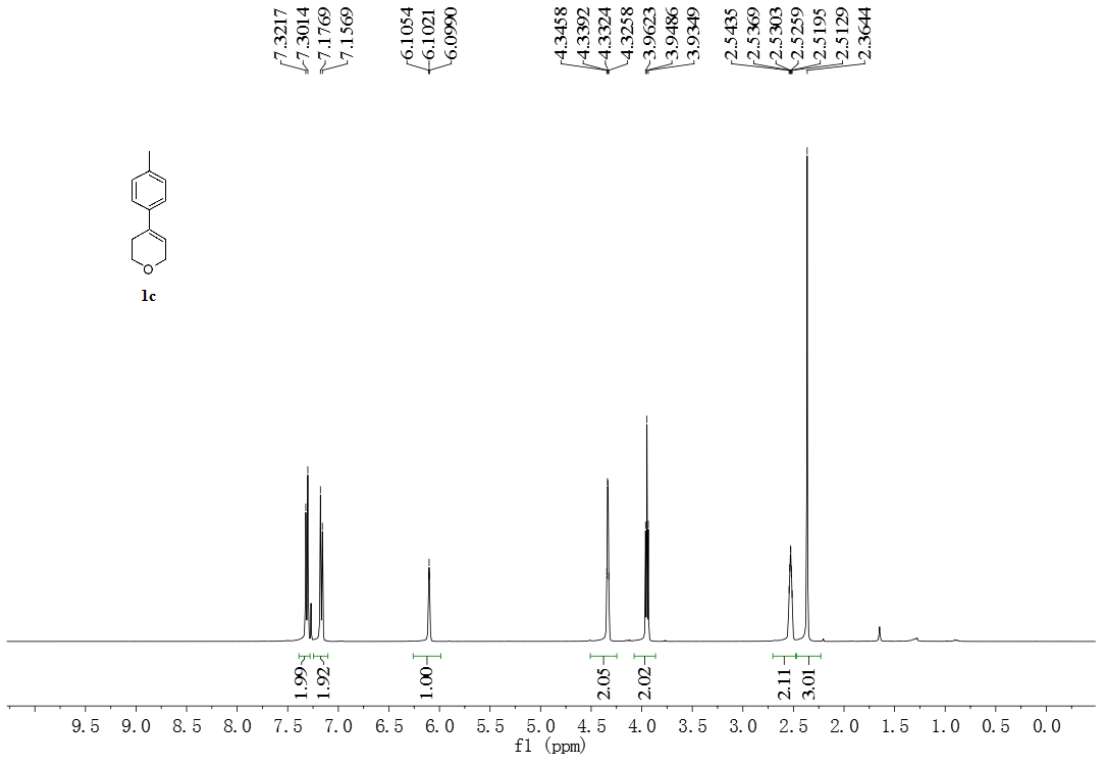
NMR spectra

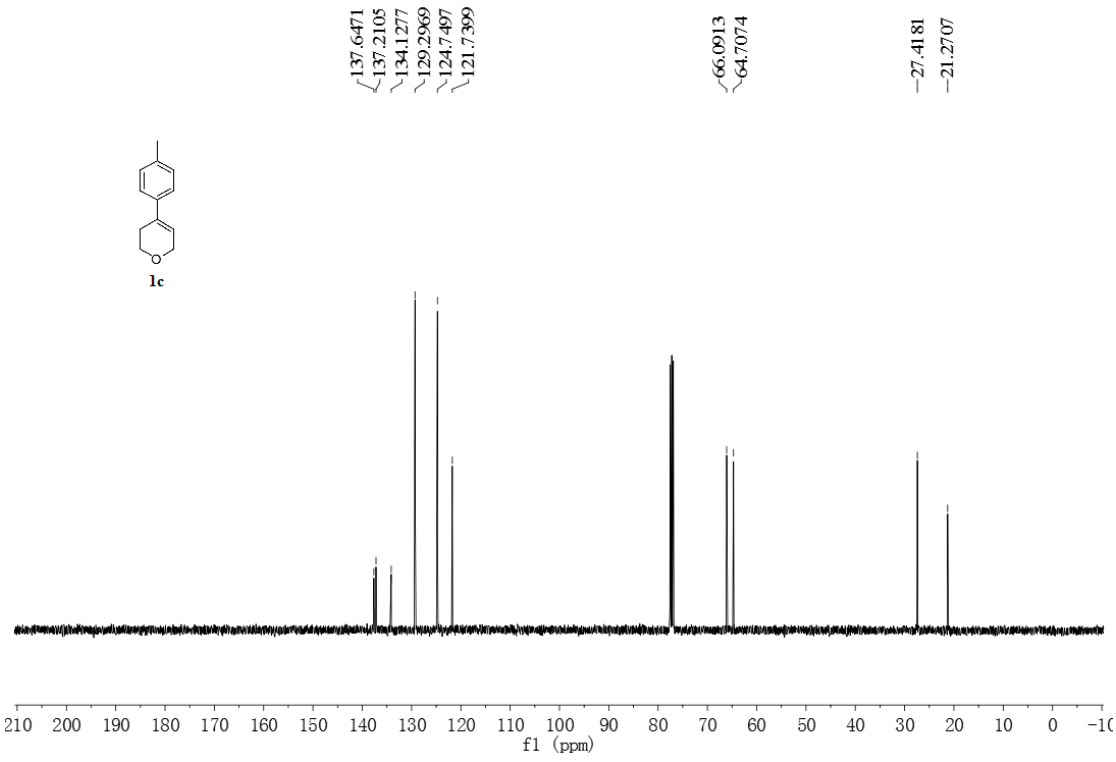

7.3676
7.3640
7.3458
7.3163
7.3115
7.2982
7.2787
7.2350
7.2171
7.2086
7.1992
6.0904
6.0871
6.0834
6.0798
6.0764
4.2957
4.2889
4.2820
4.2751
3.9092
3.8955
3.8819
2.5094
2.5029
2.4962
2.4895
2.4852
2.4785
2.4718
2.4653
1a
5.22
1.00
2.08
2.05
2.08
f1 (ppm)

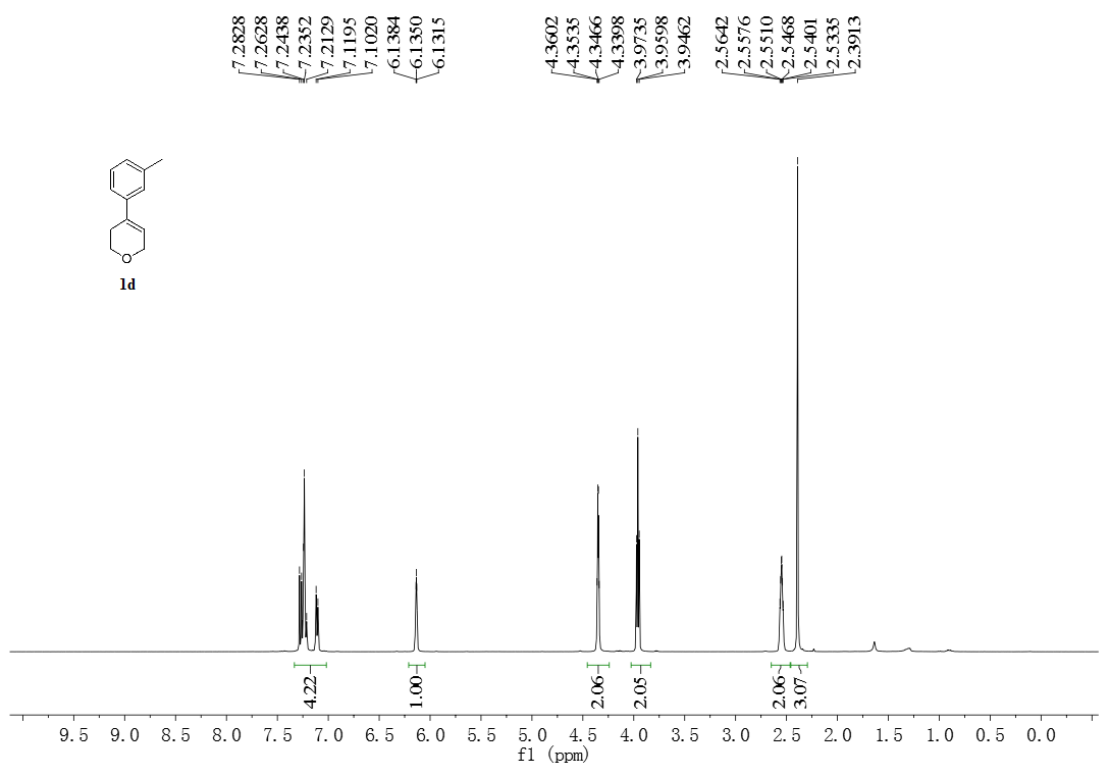

140.4875
134.3516
128.6207
127.4800
124.8908
122.6383
66.0820
64.6802
27.4077
1a
f1 (ppm)

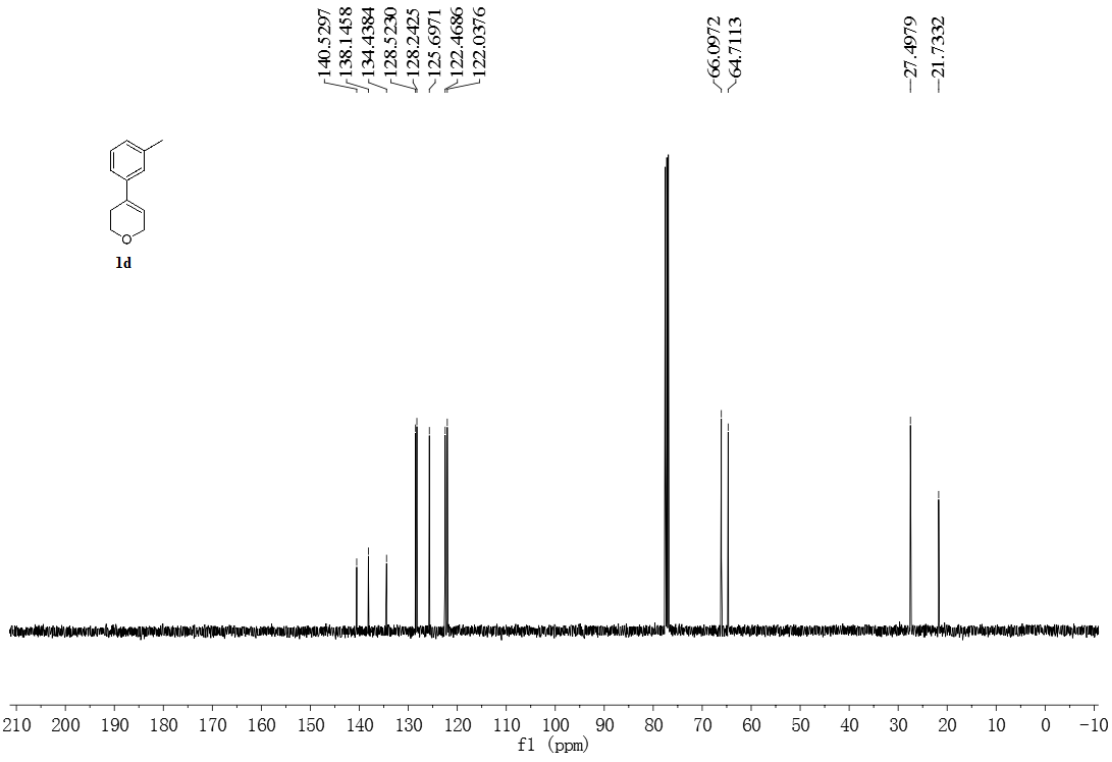

7.3459
7.3240
6.8902
6.8682
6.0320
6.0287
6.0258
4.3238
4.3173
4.3105
4.3039
3.9432
3.9295
3.9158
3.8148
2.5065
2.5000
2.4957
2.4892
1b
2.03
2.04
1.00
2.05
2.00
3.17
2.05
f1 (ppm)

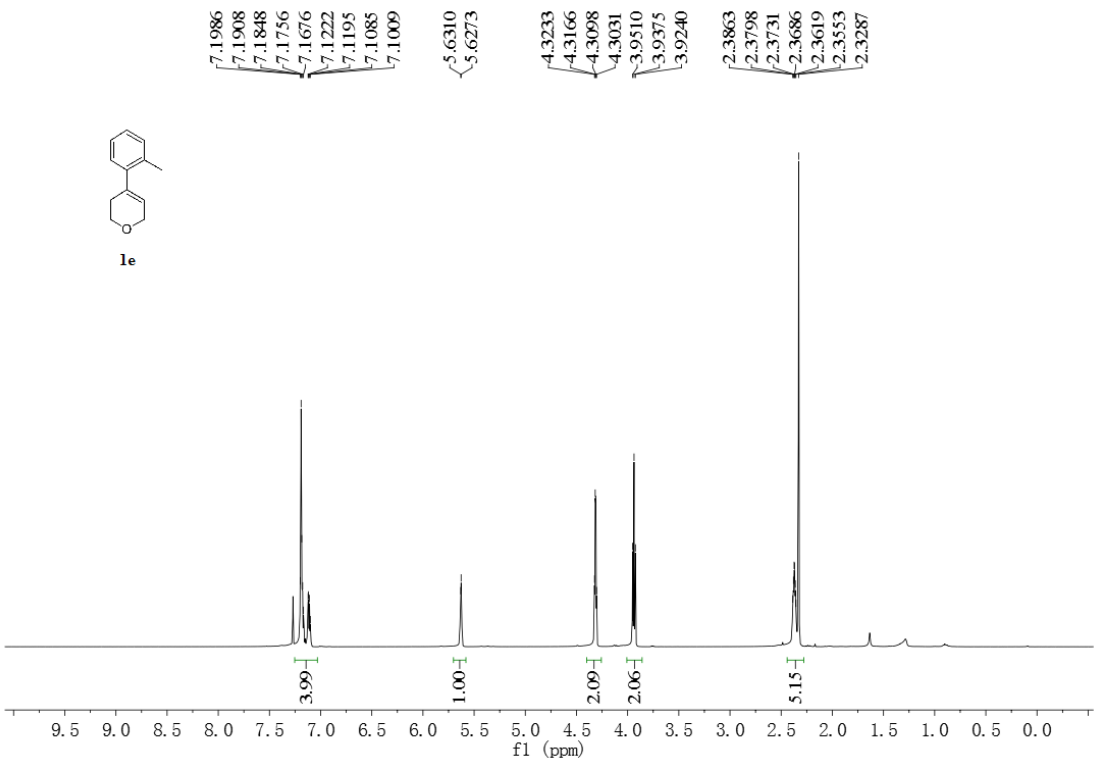

159.1607
133.6671
133.1224
125.9490
120.8842
113.9692
66.1062
64.7183
55.5015
27.4683
1b
f1 (ppm)

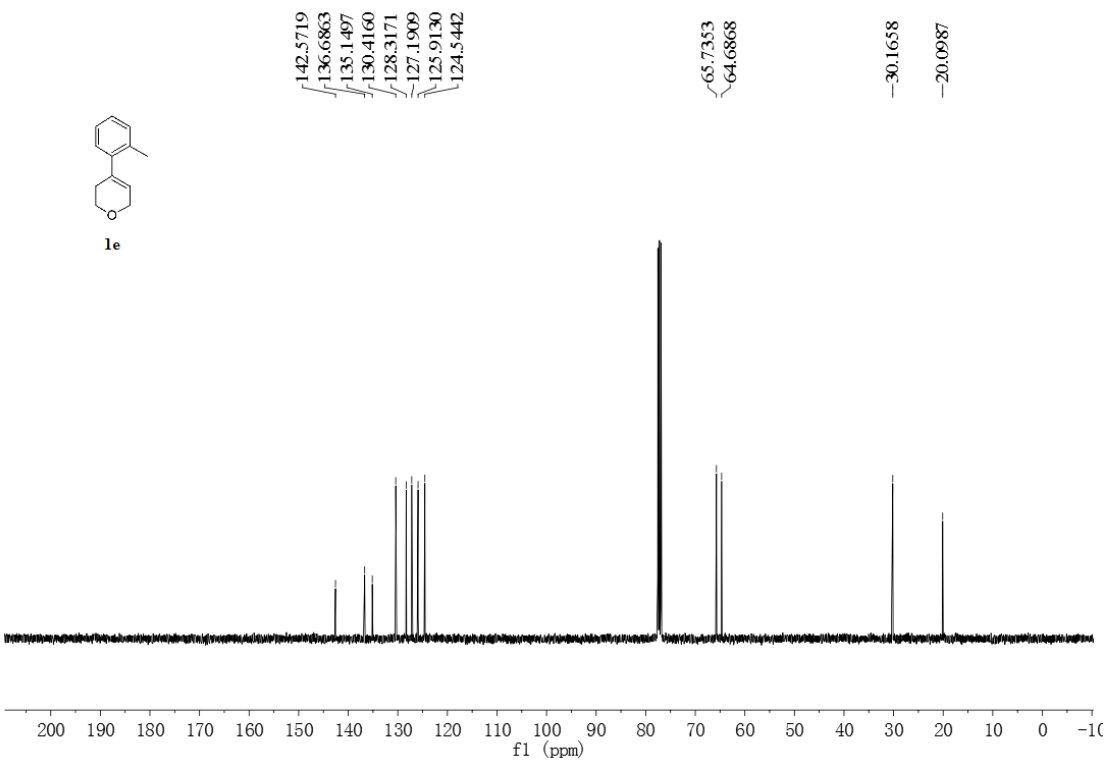

7.3217
7.3014
7.1769
7.1569
6.1054
6.1021
6.0990
4.3458
4.3392
4.3324
4.3258
3.9623
3.9486
3.9349
2.5435
2.5369
2.5303
2.5259
2.5195
2.5129
2.3644
1c
1.99
1.92
1.00
2.05
2.02
2.11
3.01
f1 (ppm)

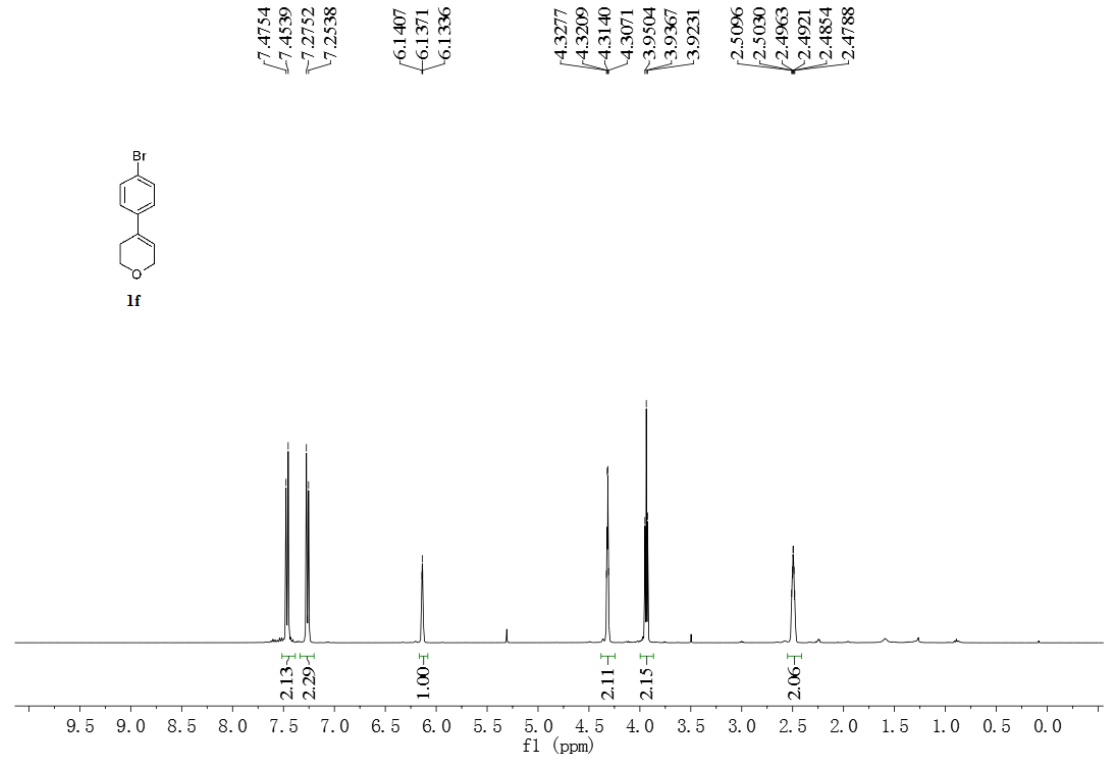

137.6471
137.2105
134.1277
129.2969
124.7497
121.7399
66.0913
64.7074
27.4181
21.2707
1c
f1 (ppm)

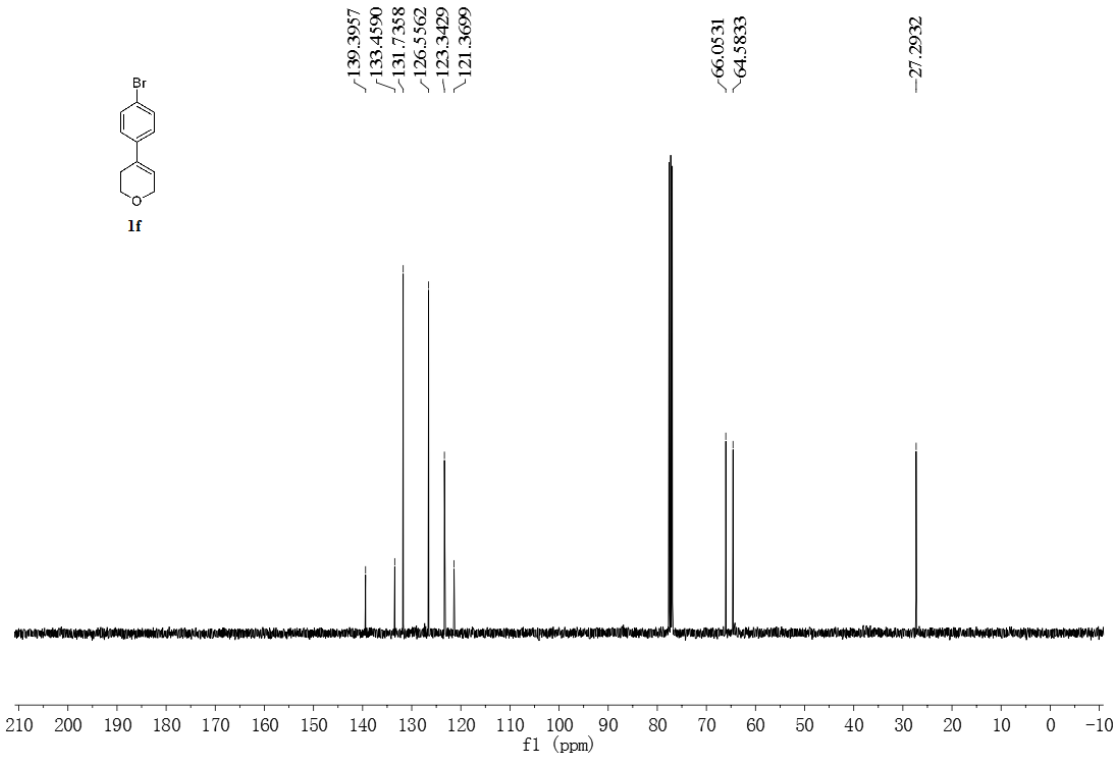

7.2828
7.2628
7.2438
7.2352
7.2129
7.1195
7.1020
6.1384
6.1350
6.1315
4.3602
4.3535
4.3466
4.3398
3.9735
3.9598
3.9462
2.5642
2.5576
2.5510
2.5468
2.5401
2.5335
2.3913
1d
4.22
1.00
2.06
2.05
2.06
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

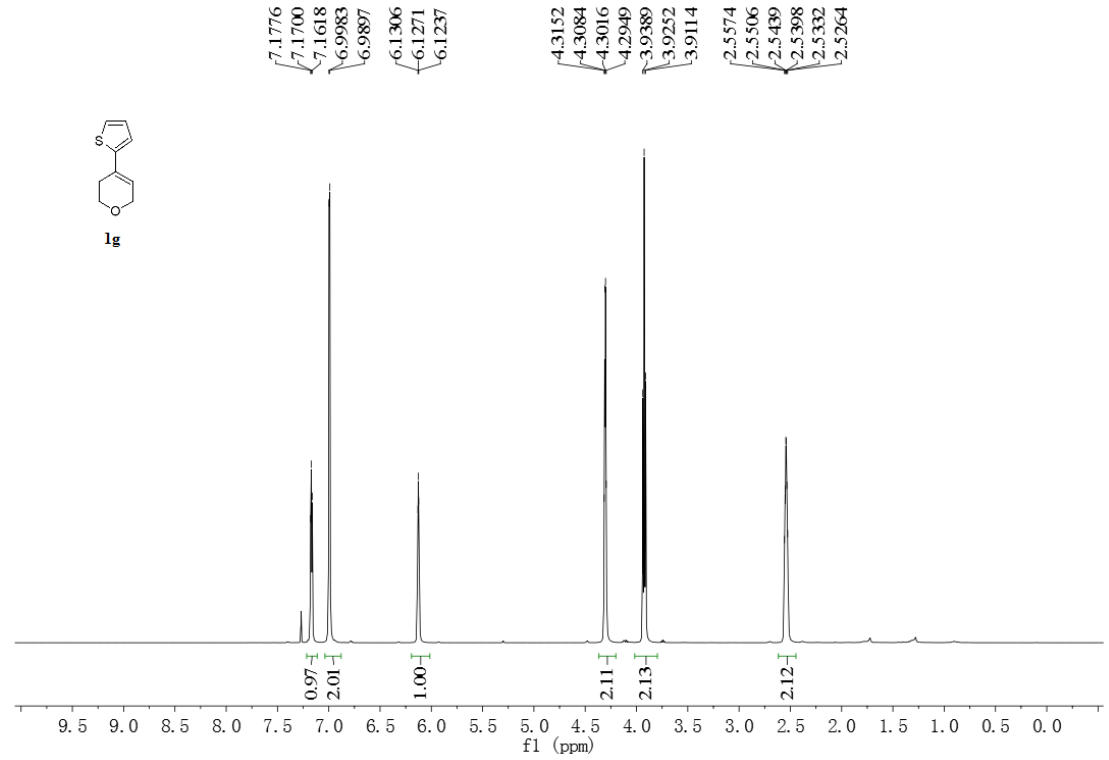

140.5297
138.1458
134.4384
128.5230
128.2425
125.6971
122.4686
122.0376
66.0972
64.7113
27.4979
21.7332
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

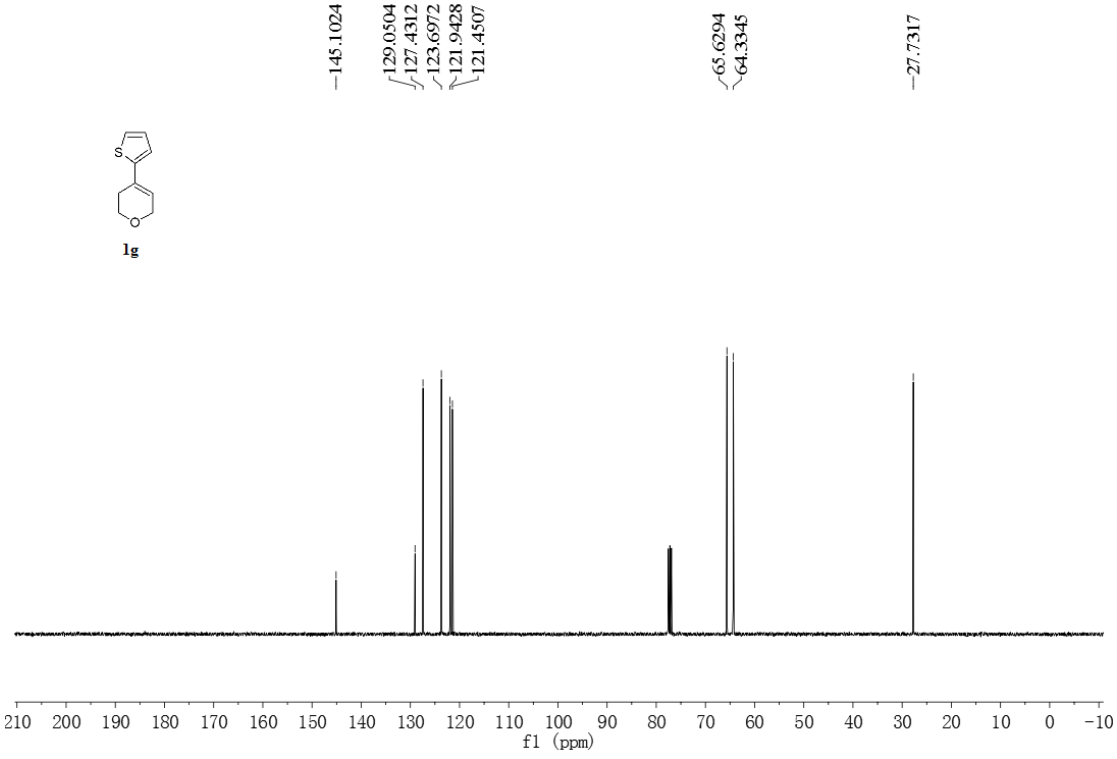

7.1986
7.1908
7.1848
7.1756
7.1676
7.1222
7.1195
7.1085
7.1009
5.6310
5.6273
4.3233
4.3166
4.3098
4.3031
3.9510
3.9375
3.9240
2.3863
2.3798
2.3731
2.3686
2.3619
2.3553
2.3287
1e
3.99
1.00
2.09
2.06
5.15
f1 (ppm)

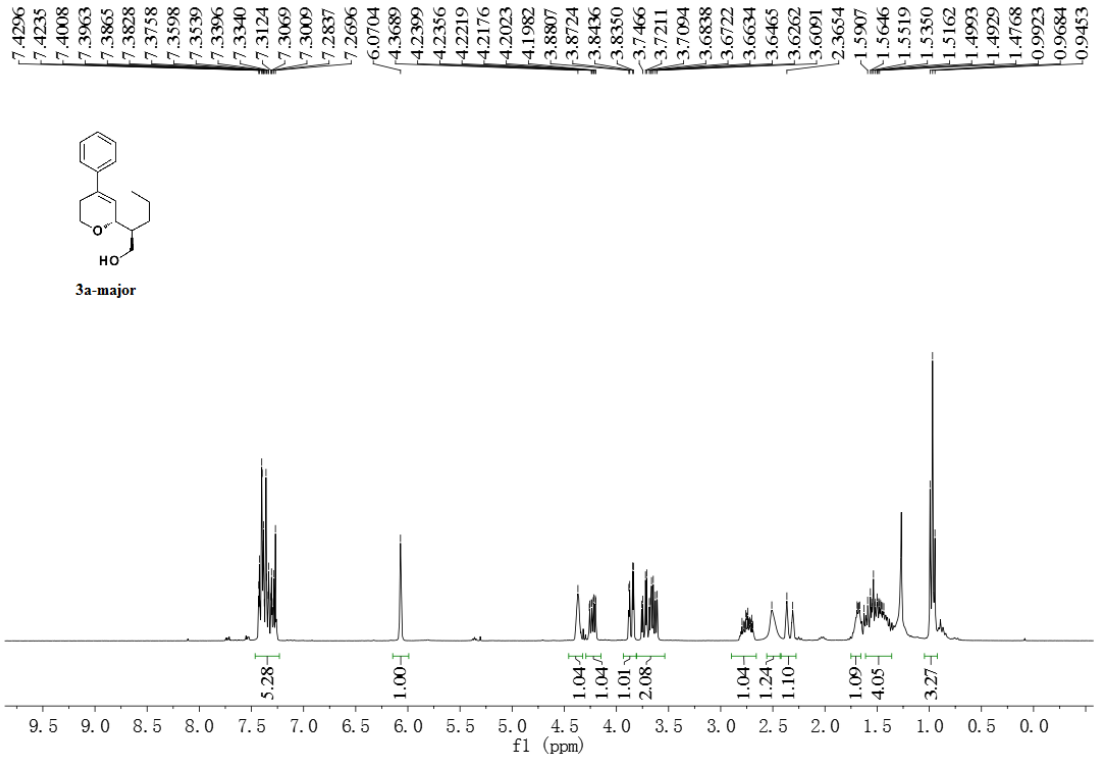

142.5719
136.6863
135.1497
130.4160
128.3171
127.1909
125.9130
124.5442
65.7353
64.6868
30.1658
20.0987
1e
f1 (ppm)

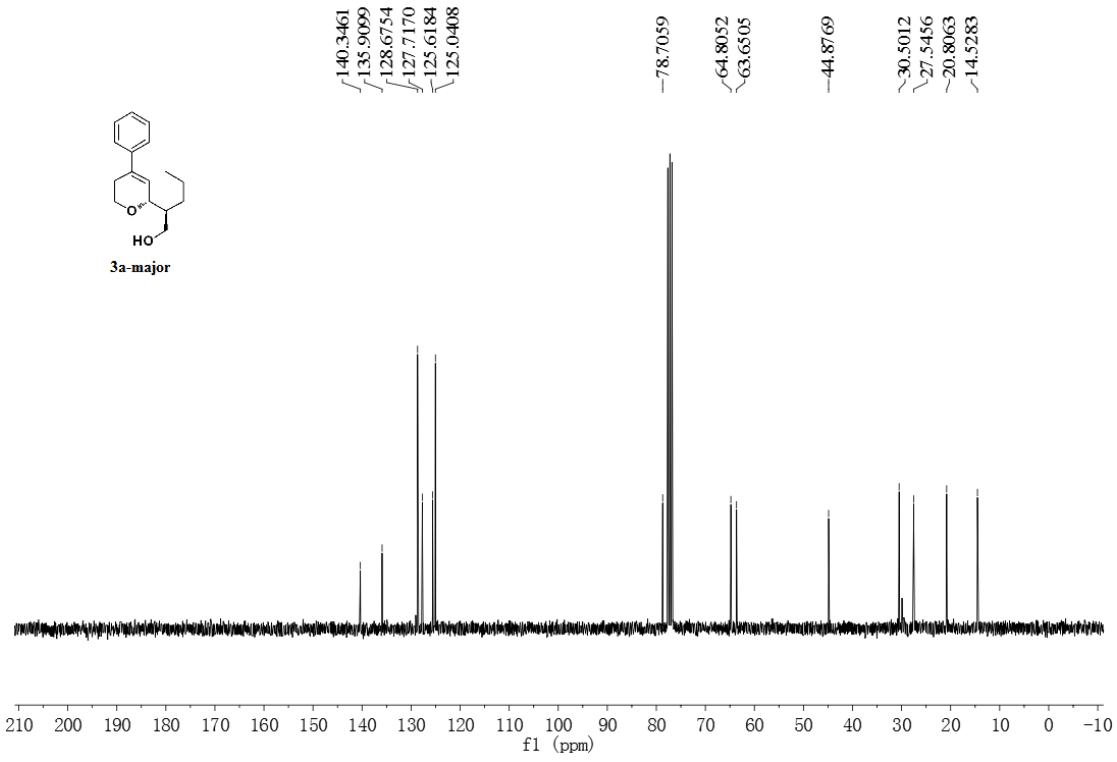

7.4754
7.4539
7.2752
7.2538
6.1407
6.1371
6.1336
4.3277
4.3209
4.3140
4.3071
3.9504
3.9367
3.9231
2.5096
2.5030
2.4963
2.4921
2.4854
2.4788
Br
O
1f
2.13
2.29
1.00
2.11
2.15
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

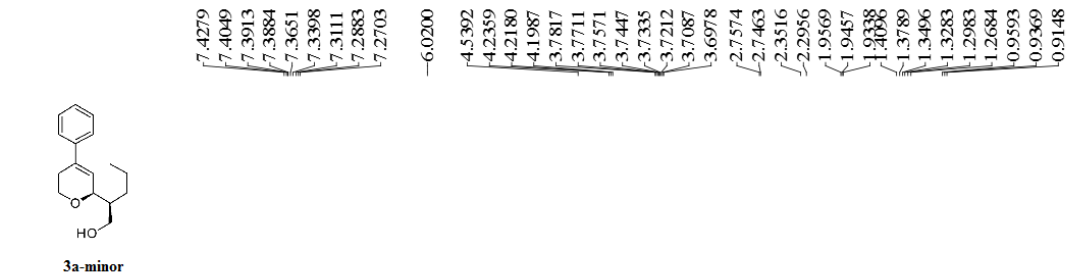

139.3957
133.4590
131.7358
126.5562
123.3429
121.3699
66.0531
64.5833
27.2932
Br
O
1f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

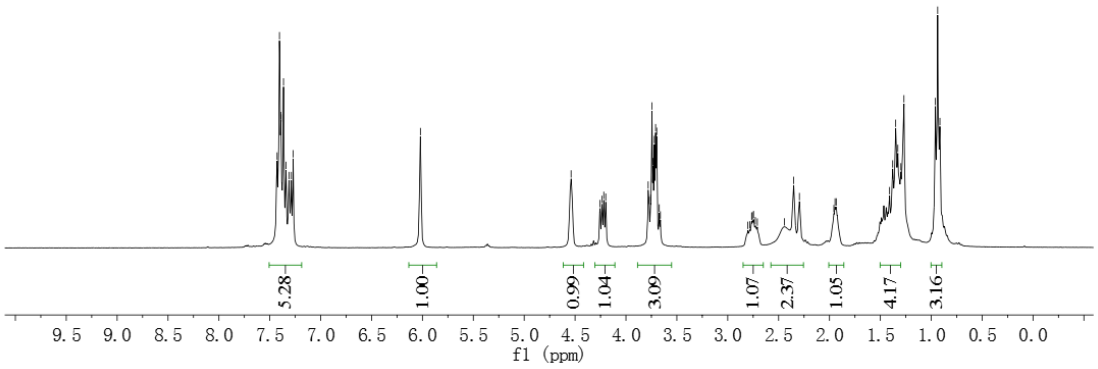

7.1776
7.1700
7.1618
6.9983
6.9897
6.1306
6.1271
6.1237
4.3152
4.3084
4.3016
4.2949
3.9389
3.9252
3.9114
2.5574
2.5506
2.5439
2.5398
2.5332
2.5264
1g
0.97
2.01
1.00
2.11
2.13
2.12
f1 (ppm)

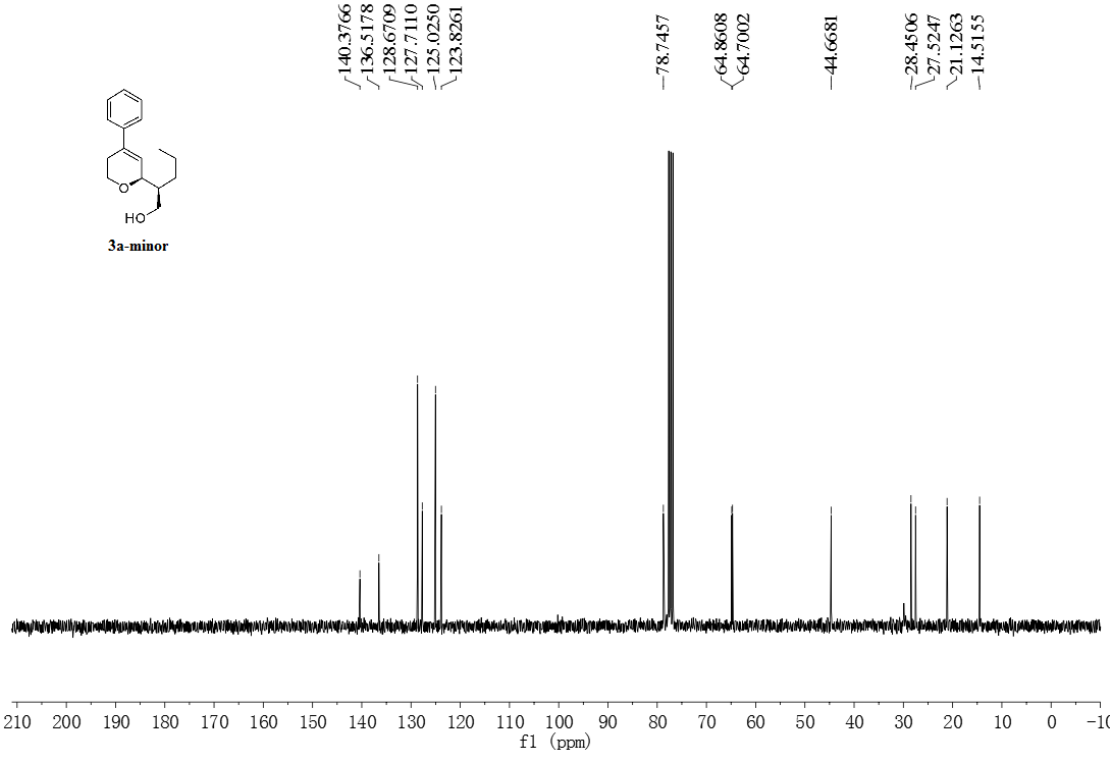

145.1024
129.0504
127.4312
123.6972
121.9428
121.4507
65.6294
64.3345
27.7317
1g
f1 (ppm)

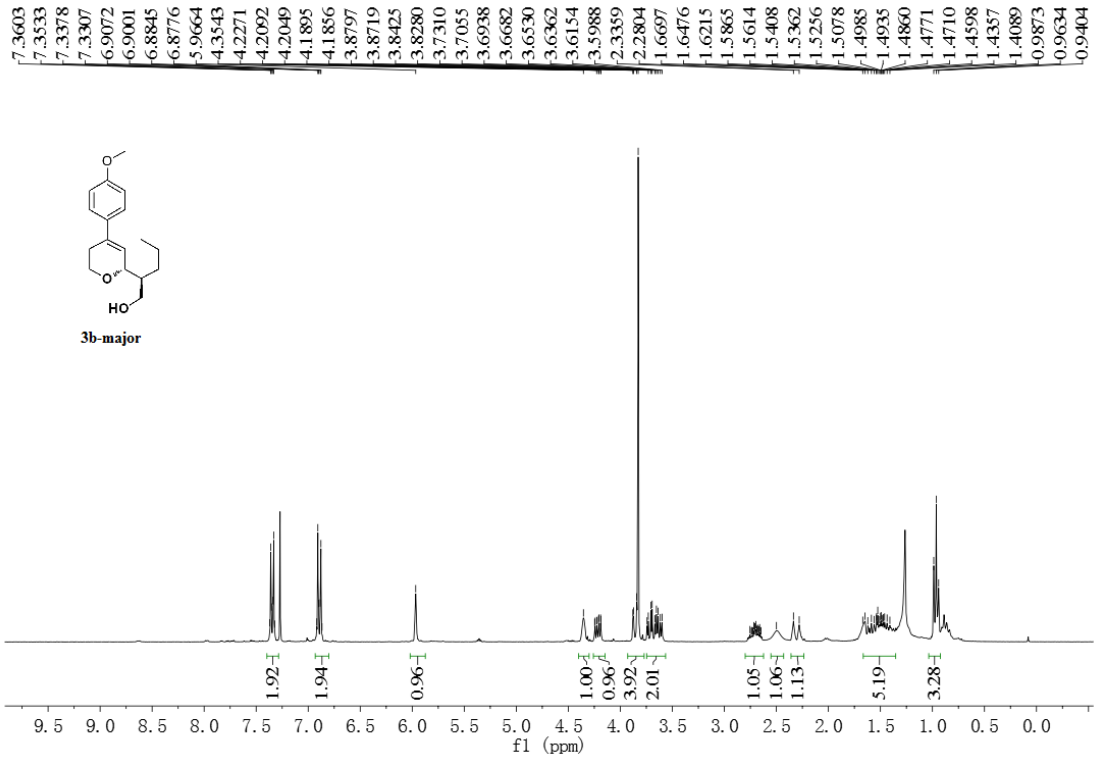

7.4296
7.4235
7.4008
7.3963
7.3865
7.3828
7.3758
7.3598
7.3539
7.3396
7.3340
7.3124
7.3069
7.3009
7.2837
7.2696
6.0704
4.3689
4.2399
4.2356
4.2219
4.2176
4.2023
4.1982
3.8807
3.8724
3.8436
3.8350
3.7466
3.7211
3.7094
3.6838
3.6722
3.6634
3.6465
3.6262
3.6091
2.3654
1.5907
1.5646
1.5519
1.5350
1.5162
1.4993
1.4929
1.4768
0.9923
0.9684
0.9453
HO
3a-major
5.28
1.00
1.04
1.04
1.01
2.08
1.04
1.24
1.10
1.09
4.05
3.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

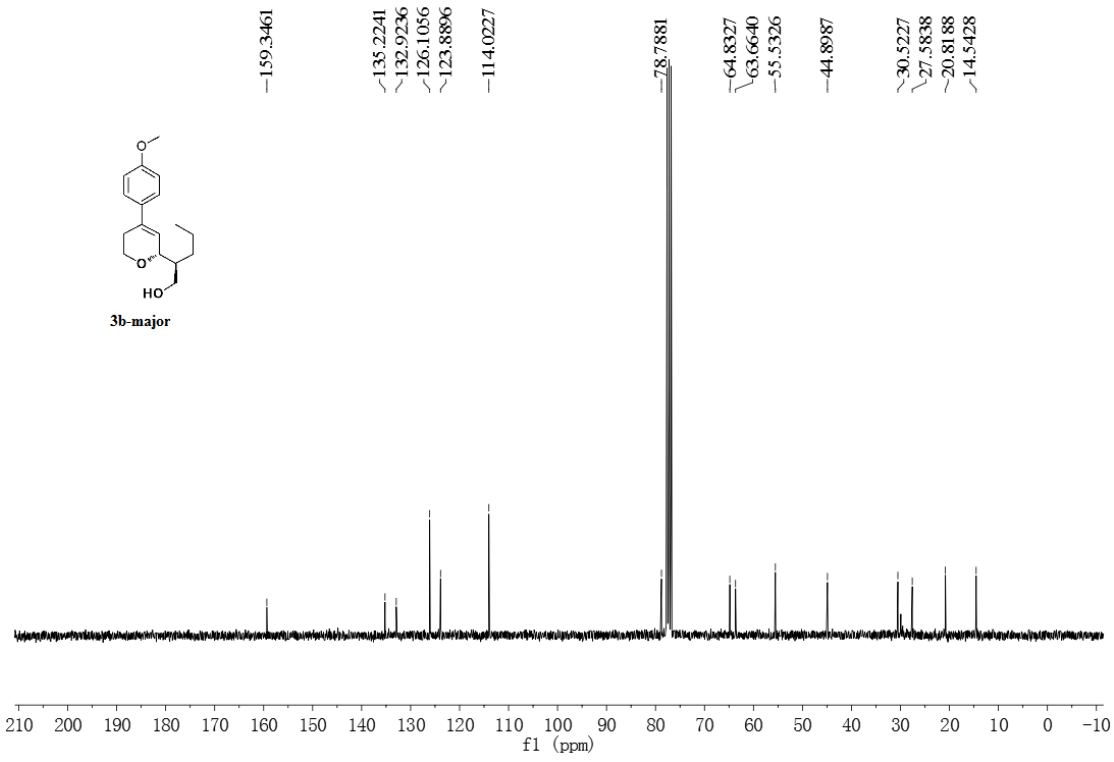

140.3461
135.9099
128.6754
127.7170
125.6184
125.0408
78.7059
64.8052
63.6505
44.8769
30.5012
27.5456
20.8063
14.5283
HO
3a-major
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

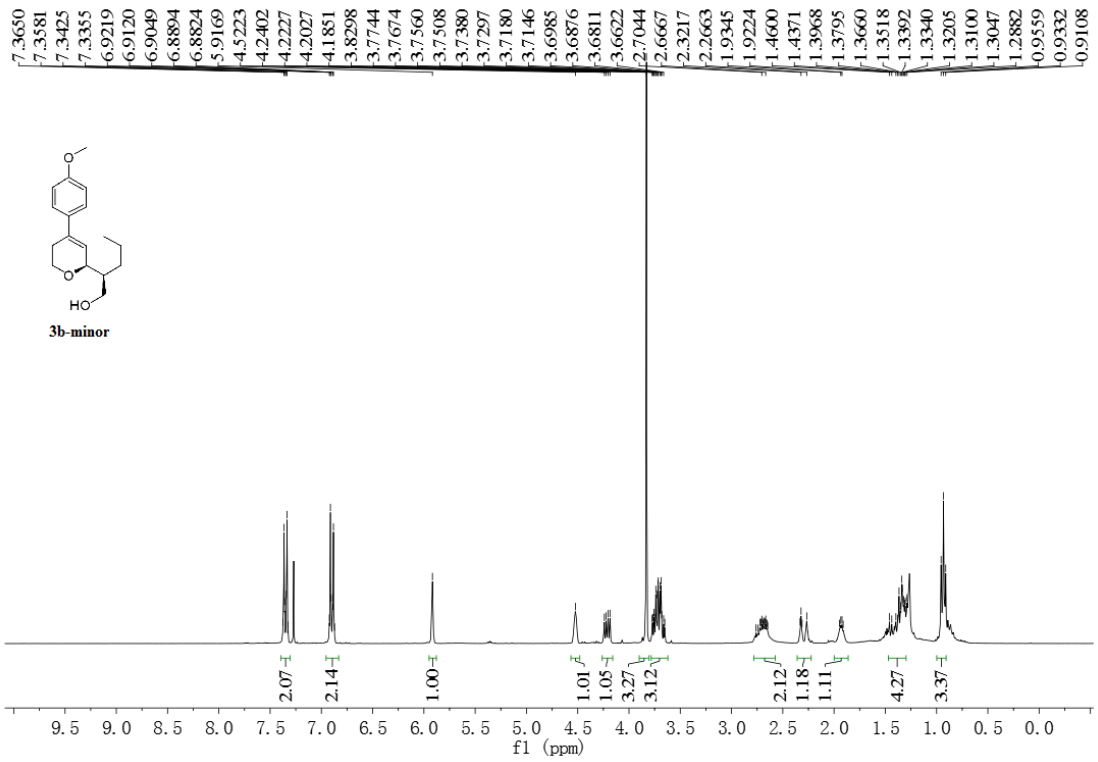

7.4279
7.4049
7.3913
7.3884
7.3651
7.3398
7.3111
7.2883
7.2703
6.0200
4.5392
4.2359
4.2180
4.1987
3.7817
3.7711
3.7571
3.7447
3.7335
3.7212
3.7087
3.6978
2.7574
2.7463
2.3516
2.2956
1.9569
1.9457
1.3789
1.3496
1.3283
1.2983
1.2684
0.9593
0.9369
0.9148
HO
3a-minor

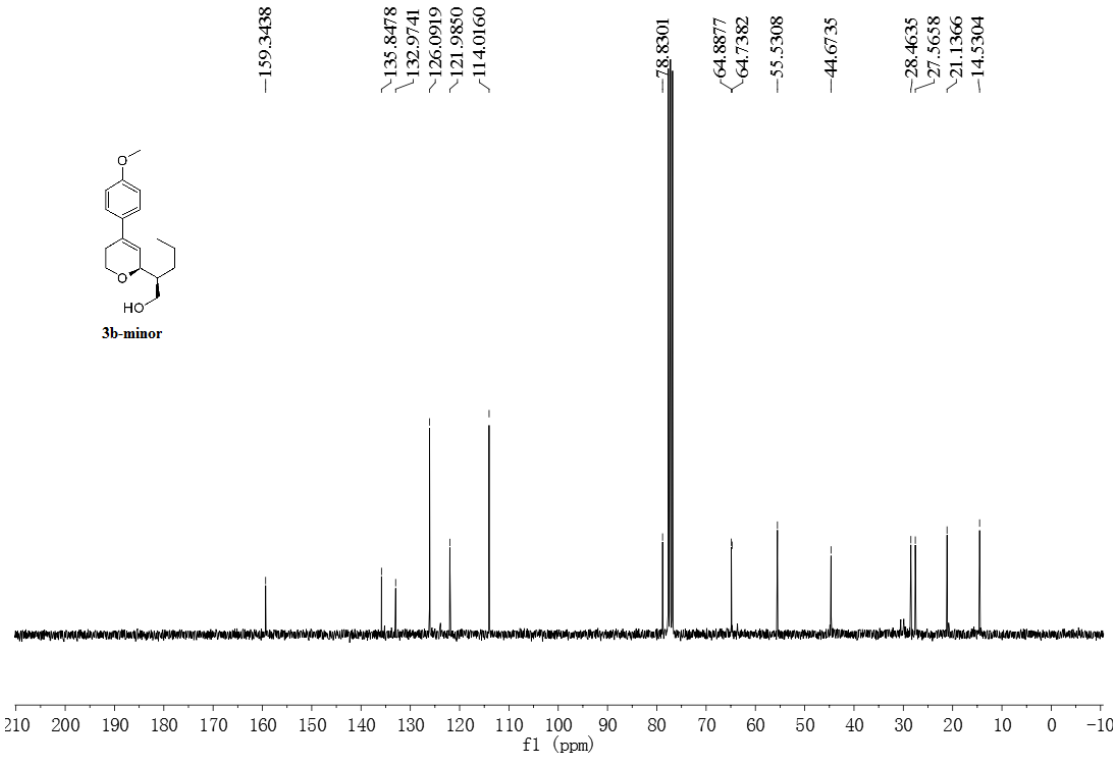

5.28
1.00
0.99
1.04
3.09
1.07
2.37
1.05
4.17
3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

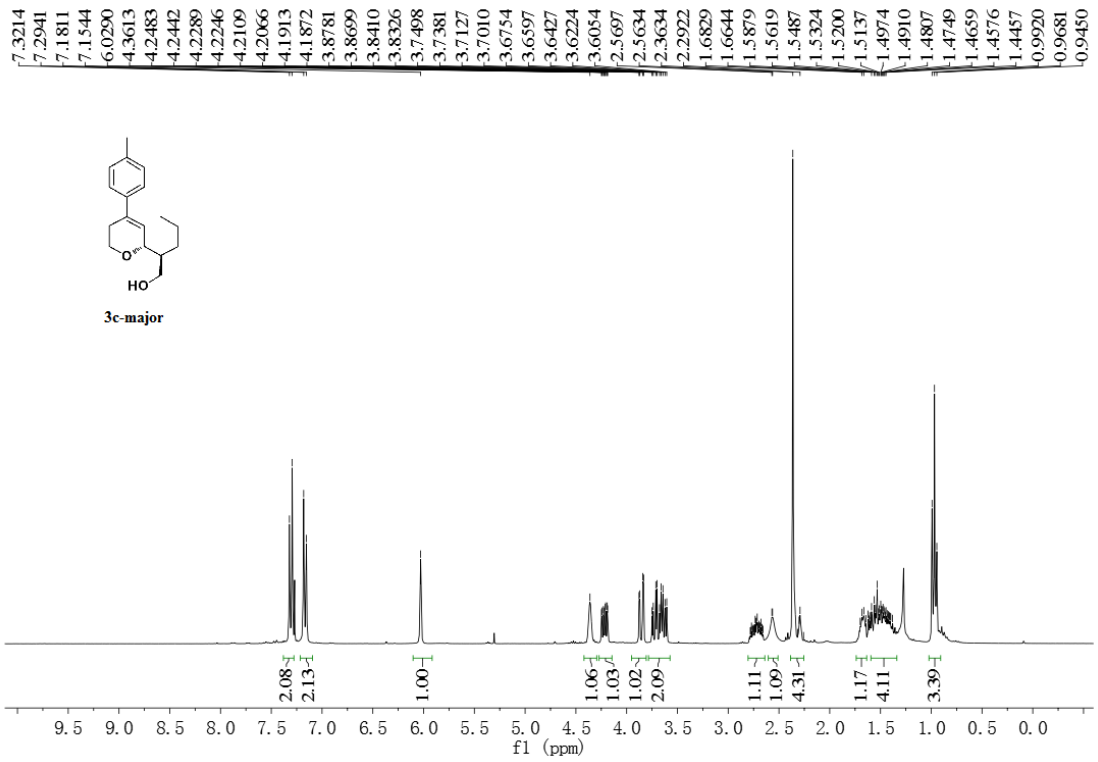

140.3766
136.5178
128.6709
127.7110
125.0250
123.8261
78.7457
64.8608
64.7002
44.6681
28.4506
27.5247
21.1263
14.5155
HO
3a-minor
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

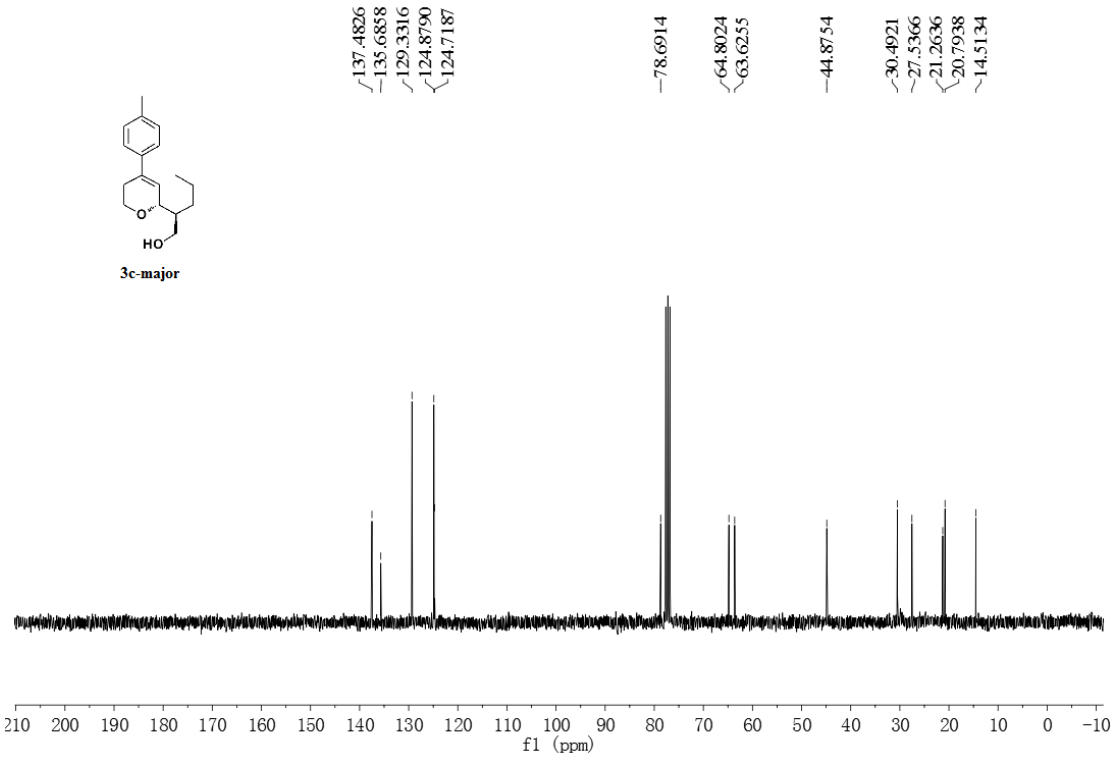

7.3603
7.3533
7.3378
7.3307
6.9072
6.9001
6.8845
6.8776
5.9664
4.3543
4.2271
4.2092
4.2049
4.1895
4.1856
3.8797
3.8719
3.8425
3.8280
3.7310
3.7055
3.6938
3.6682
3.6530
3.6362
3.6154
3.5988
2.3359
2.2804
1.6697
1.6476
1.6215
1.5865
1.5614
1.5408
1.5362
1.5256
1.5078
1.4985
1.4935
1.4860
1.4771
1.4710
1.4598
1.4357
1.4089
0.9873
0.9634
0.9404
3b-major
1.92
1.94
0.96
1.00
0.96
3.92
2.01
1.05
1.06
1.13
5.19
3.28
f1 (ppm)

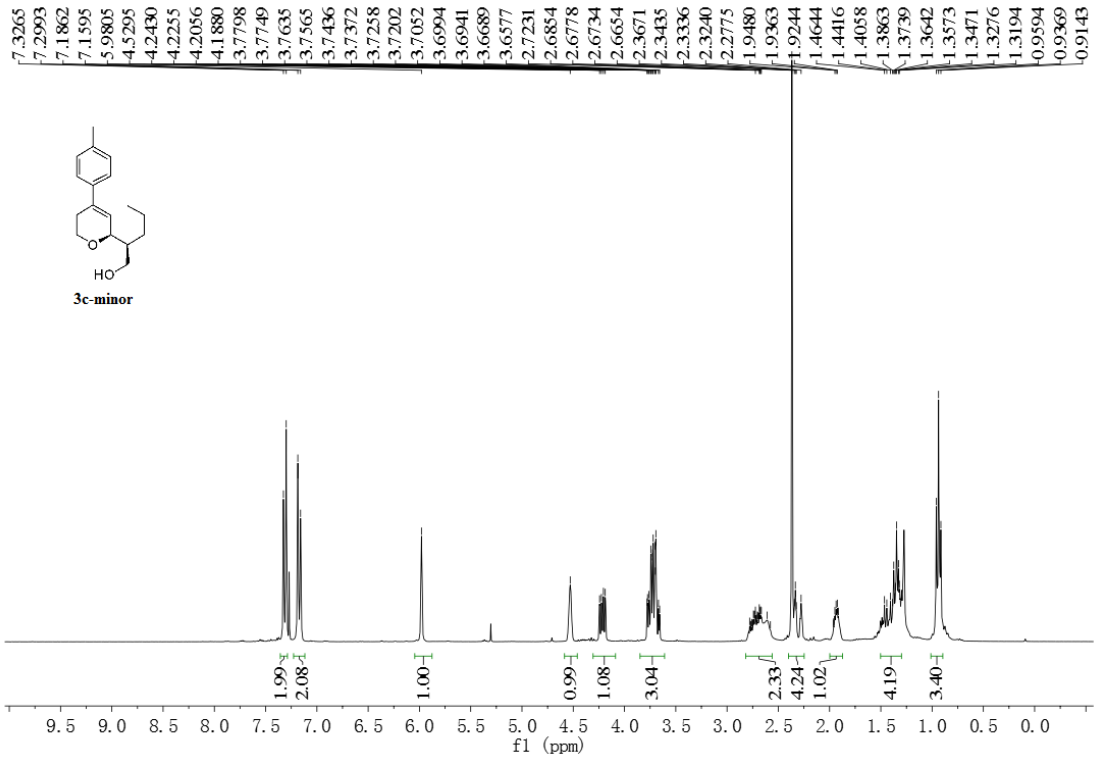

159.3461
135.2241
132.9236
126.1056
123.8896
114.0227
78.7881
64.8327
63.6640
55.5326
44.8987
30.5227
27.5838
20.8188
14.5428
3b-major
f1 (ppm)

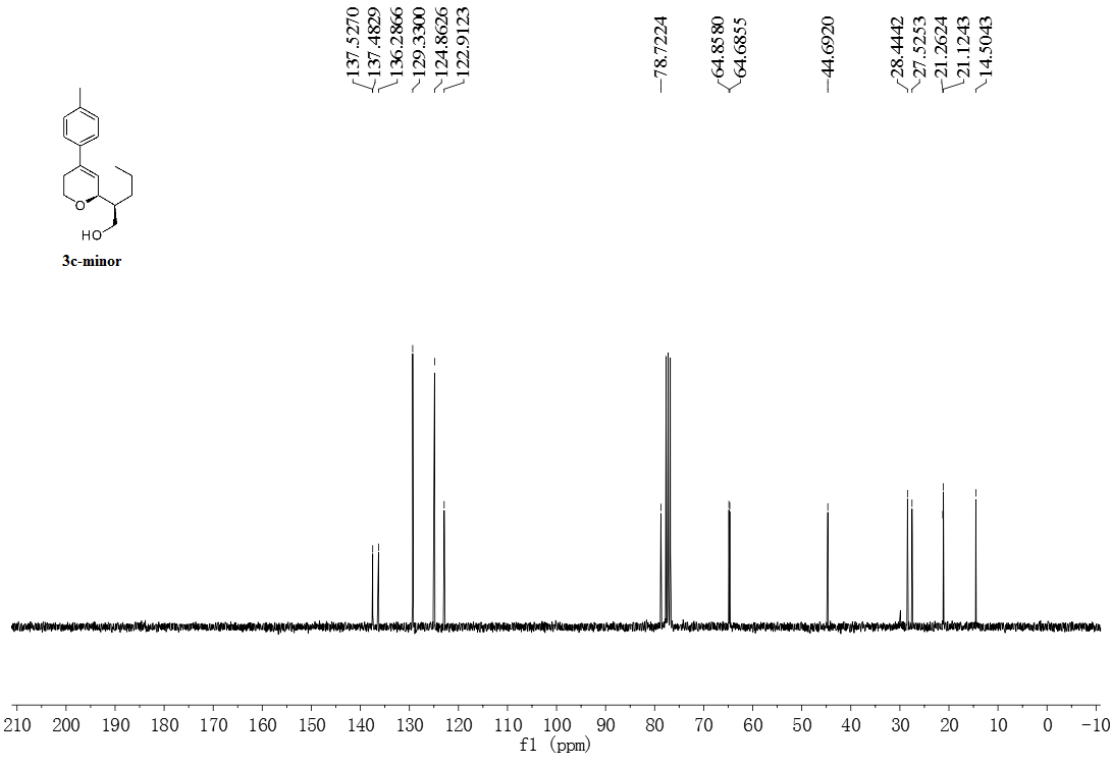

7.3650
7.3581
7.3425
7.3355
6.9219
6.9120
6.9049
6.8894
6.8824
5.9169
4.5223
4.2402
4.2227
4.2027
4.1851
3.8298
3.7744
3.7674
3.7560
3.7508
3.7380
3.7297
3.7180
3.7146
3.6985
3.6876
3.6811
3.6622
2.7044
2.6667
2.3217
2.2663
1.9345
1.9224
1.4600
1.4371
1.3968
1.3795
1.3660
1.3518
1.3392
1.3340
1.3205
1.3100
1.3047
1.2882
0.9559
0.9332
0.9108
O
O
HO
3b-minor
2.07
2.14
1.00
1.01
1.05
3.27
3.12
2.12
1.18
1.11
4.27
3.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

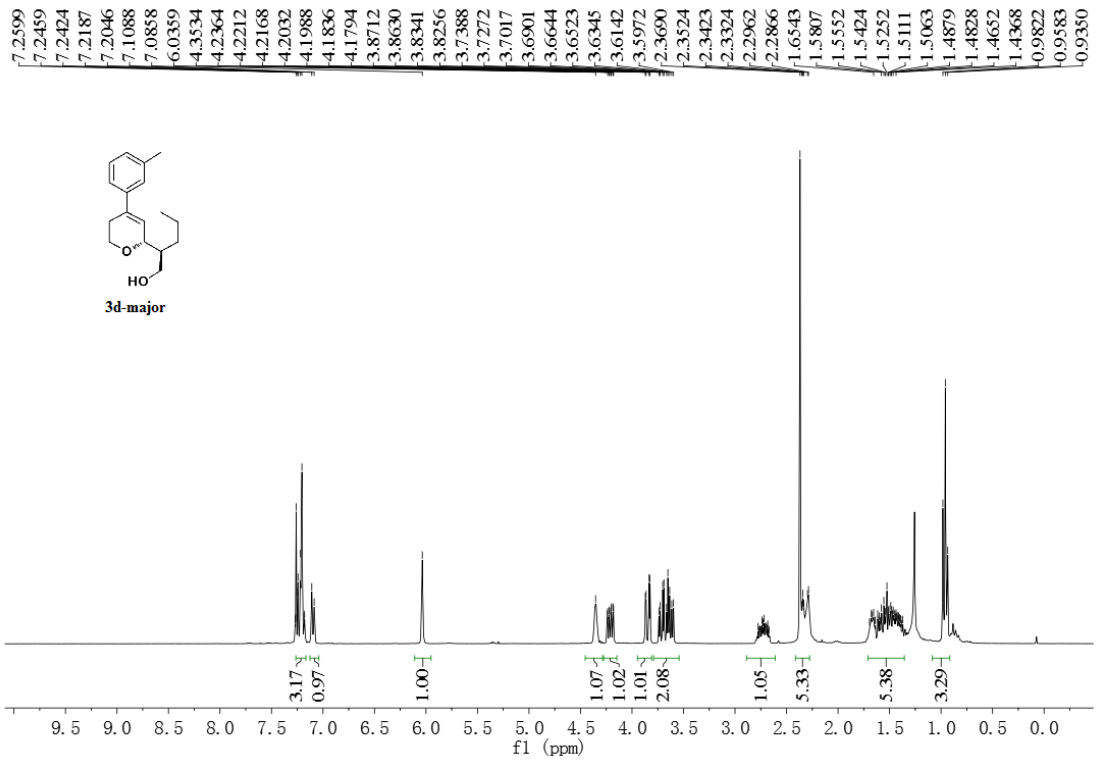

159.3438
135.8478
132.9741
126.0919
121.9850
114.0160
78.8301
64.8877
64.7382
55.5308
44.6735
28.4635
27.5658
21.1366
14.5304
O
O
HO
3b-minor
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

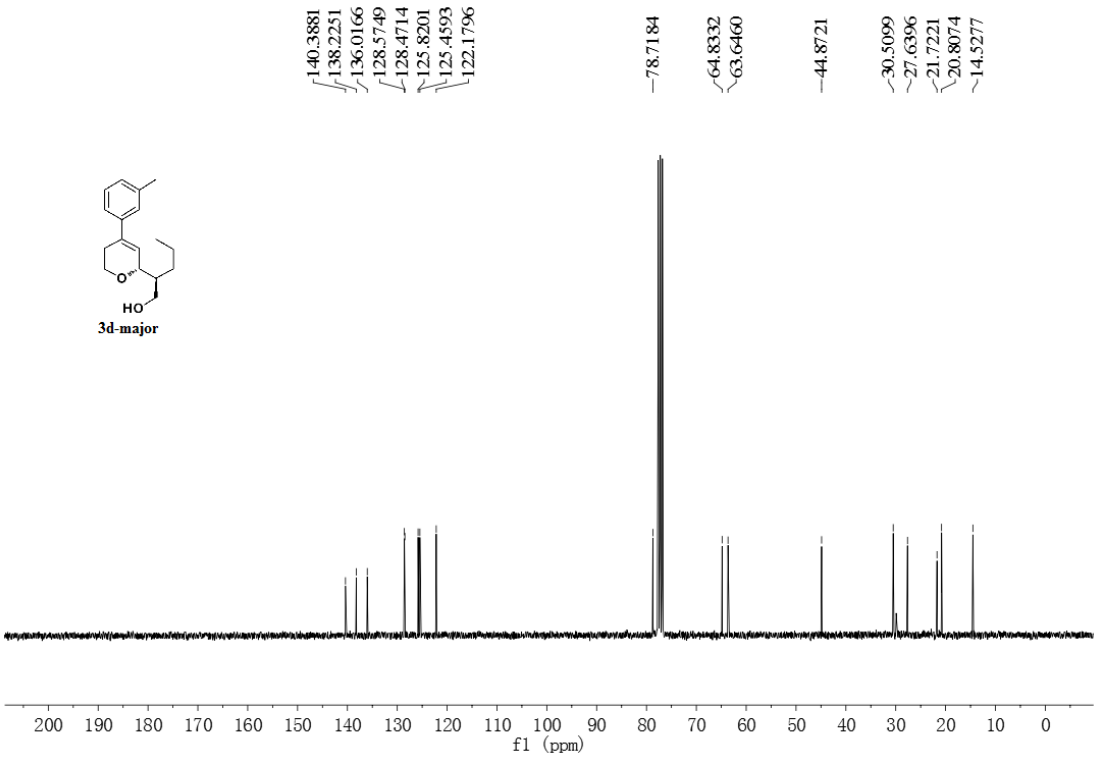

7.3214
7.2941
7.1811
7.1544
6.0290
4.3613
4.2483
4.2442
4.2289
4.2246
4.2109
4.2066
4.1913
4.1872
3.8781
3.8699
3.8410
3.8326
3.7498
3.7381
3.7127
3.7010
3.6754
3.6597
3.6427
3.6224
3.6054
2.5697
2.5634
2.3634
2.2922
1.6829
1.6644
1.5879
1.5619
1.5487
1.5324
1.5200
1.5137
1.4974
1.4910
1.4807
1.4749
1.4659
1.4576
1.4457
0.9920
0.9681
0.9450
HO
3c-major
2.08
2.13
1.00
1.06
1.03
1.02
2.09
1.11
1.09
4.31
1.17
4.11
3.39
f1 (ppm)

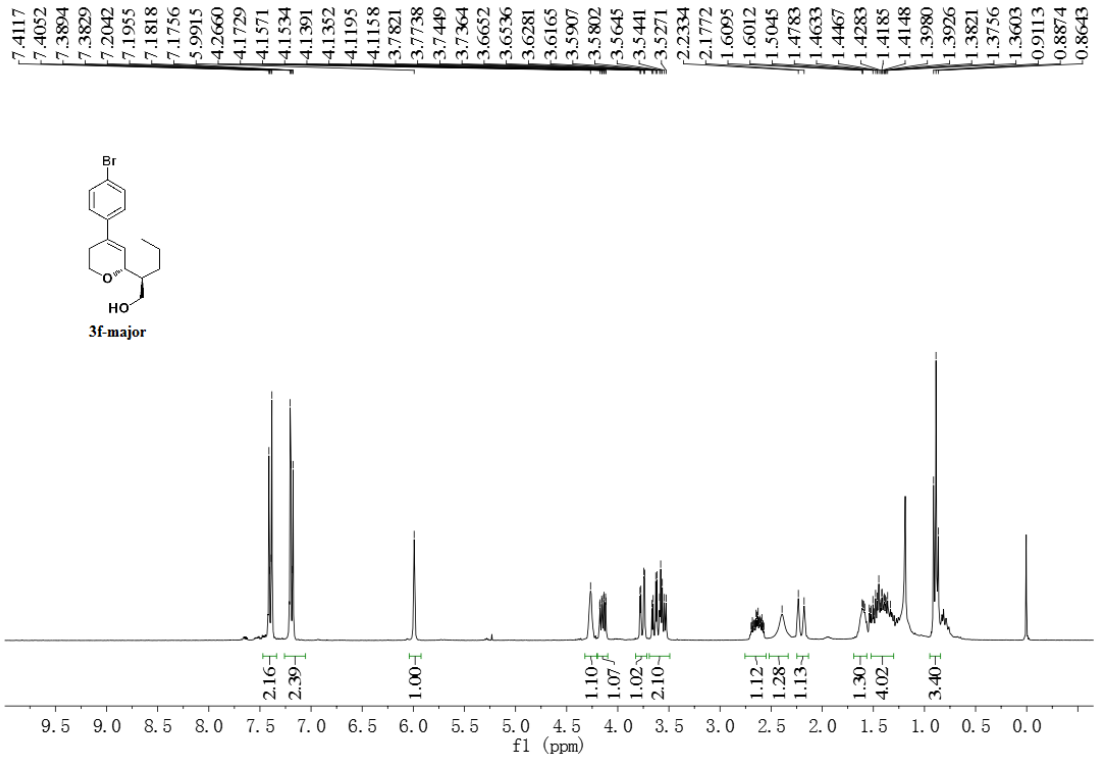

137.4826
135.6858
129.3316
124.8790
124.7187
78.6914
64.8024
63.6255
44.8754
30.4921
27.5366
21.2636
20.7938
14.5134
HO
3c-major
f1 (ppm)

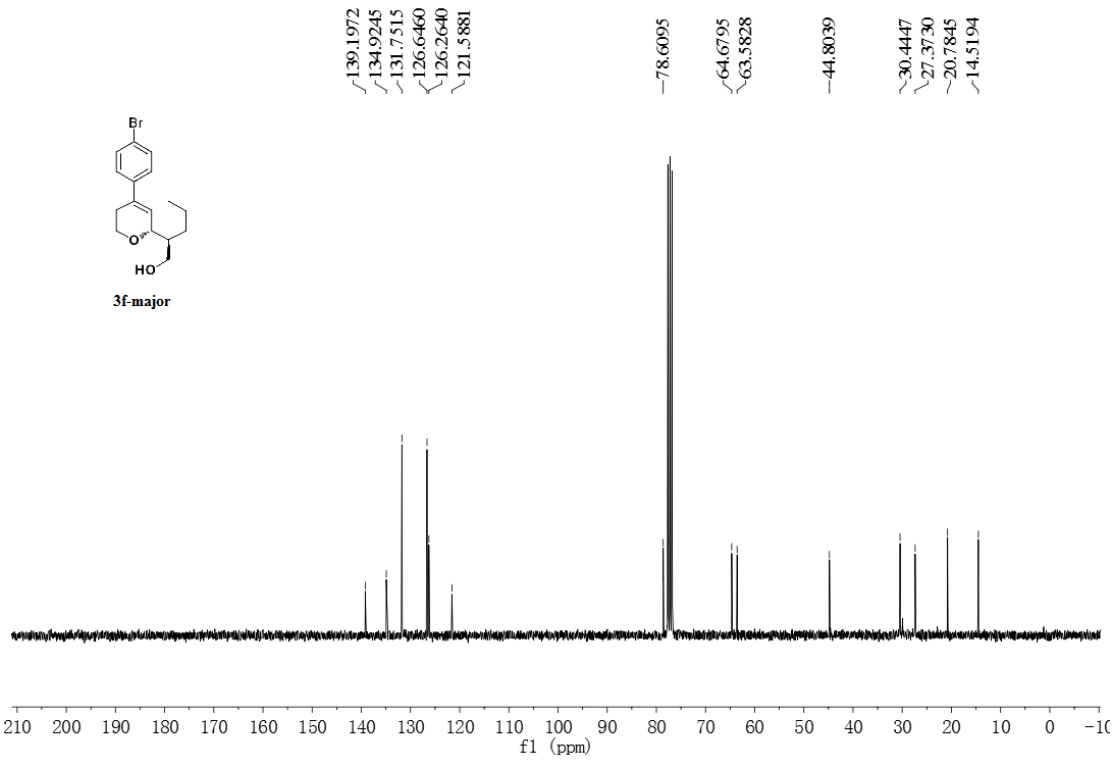

7.3265
7.2993
7.1862
7.1595
5.9805
4.5295
4.2430
4.2255
4.2056
4.1880
3.7798
3.7749
3.7635
3.7565
3.7436
3.7372
3.7258
3.7202
3.7052
3.6994
3.6941
3.6689
3.6577
2.7231
2.6854
2.6778
2.6734
2.6654
2.3671
2.3435
2.3336
2.3240
2.2775
1.9480
1.9363
1.9244
1.4644
1.4416
1.4058
1.3863
1.3739
1.3642
1.3573
1.3471
1.3276
1.3194
0.9594
0.9369
0.9143
HO
3c-minor
1.99
2.08
1.00
0.99
1.08
3.04
2.33
4.24
1.02
4.19
3.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

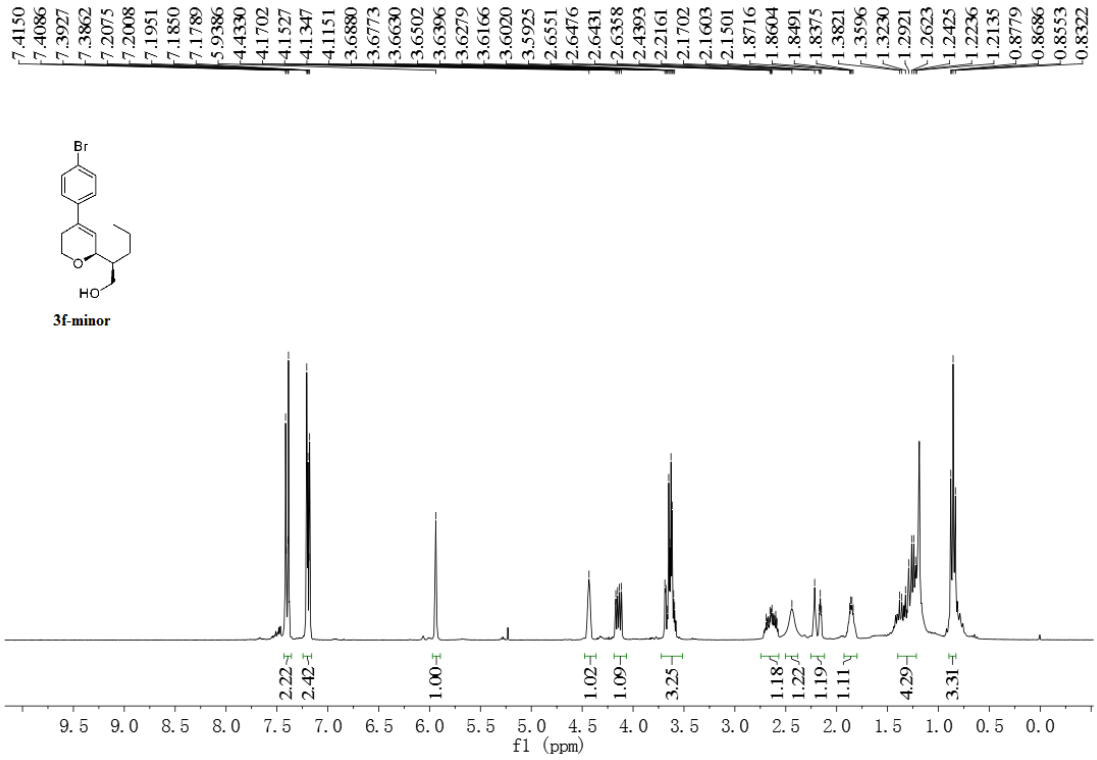

137.5270
137.4829
136.2866
129.3300
124.8626
122.9123
78.7224
64.8580
64.6855
44.6920
28.4442
27.5253
21.2624
21.1243
14.5043
HO
3c-minor
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

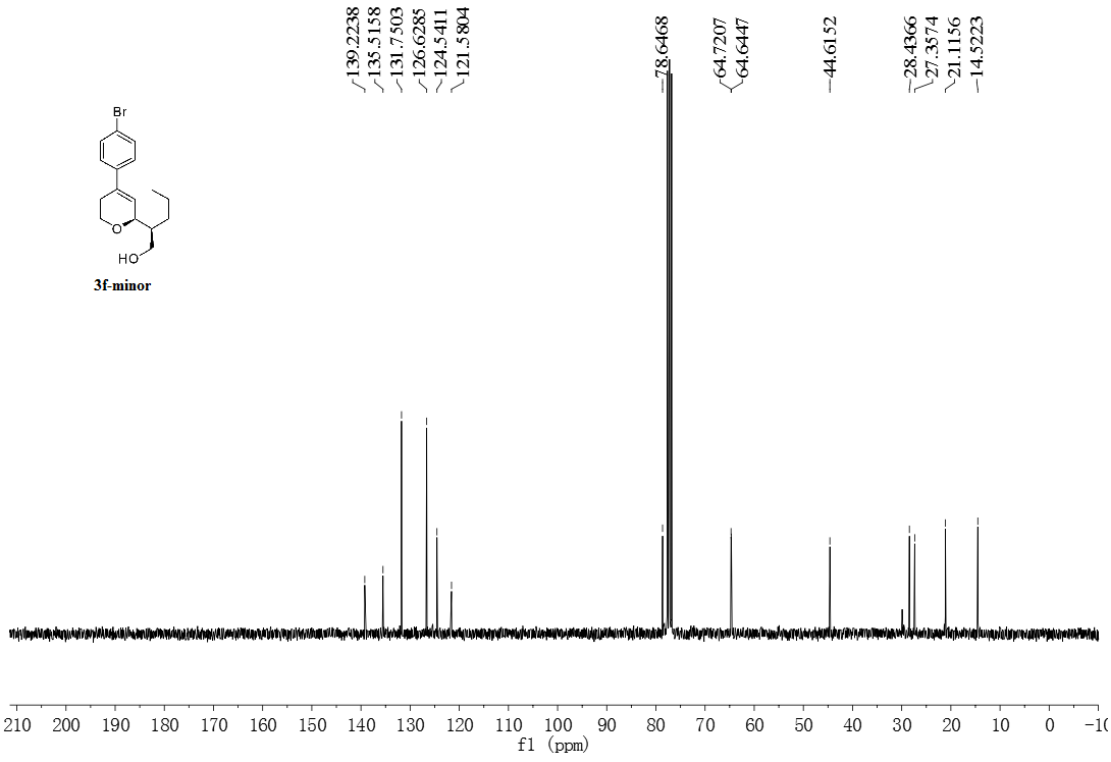

7.2599
7.2459
7.2424
7.2187
7.2046
7.1088
7.0858
6.0359
4.3534
4.2364
4.2212
4.2168
4.2032
4.1988
4.1836
4.1794
3.8712
3.8630
3.8341
3.8256
3.7388
3.7272
3.7017
3.6901
3.6644
3.6523
3.6345
3.6142
3.5972
3.3690
2.3524
2.3423
2.3324
2.2962
2.2866
1.6543
1.5807
1.5552
1.5424
1.5252
1.5111
1.5063
1.4879
1.4828
1.4652
1.4368
0.9822
0.9583
0.9350
3d-major
3.17
0.97
1.00
1.07
1.02
1.01
2.08
1.05
5.33
5.38
3.29
f1 (ppm)

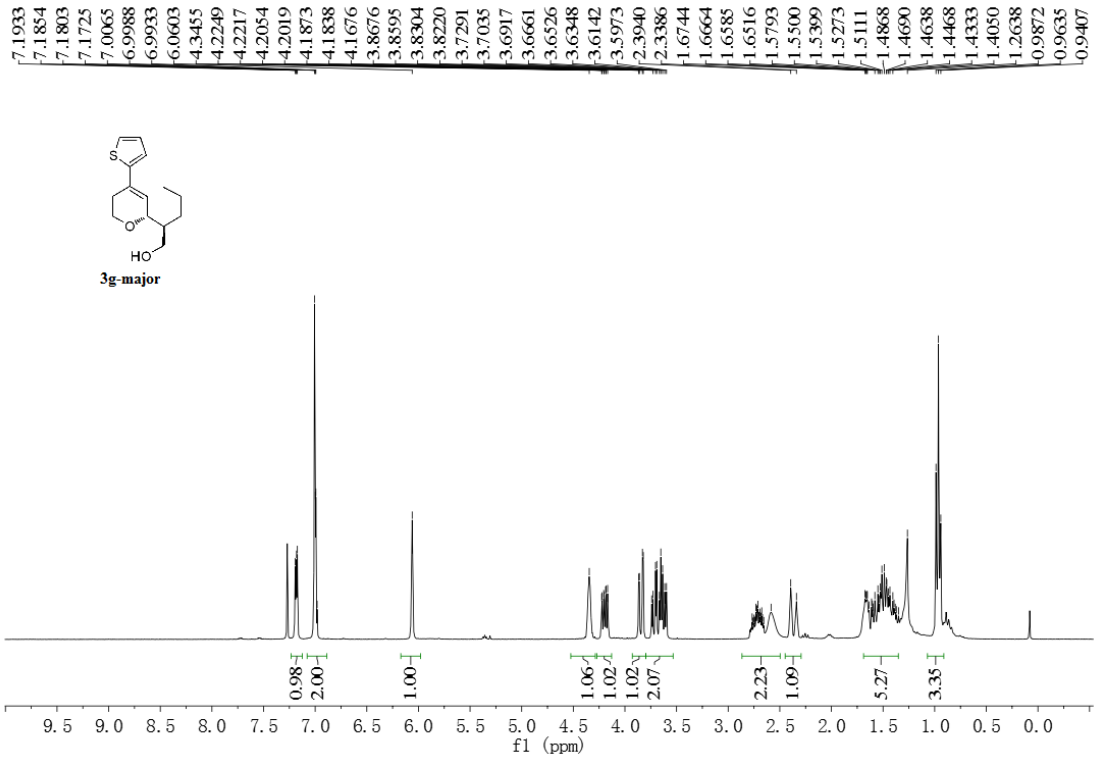

140.3881
138.2251
136.0166
128.5749
128.4714
125.8201
125.4593
122.1796
78.7184
64.8332
63.6460
44.8721
30.5099
27.6396
21.7221
20.8074
14.5277
3d-major
f1 (ppm)

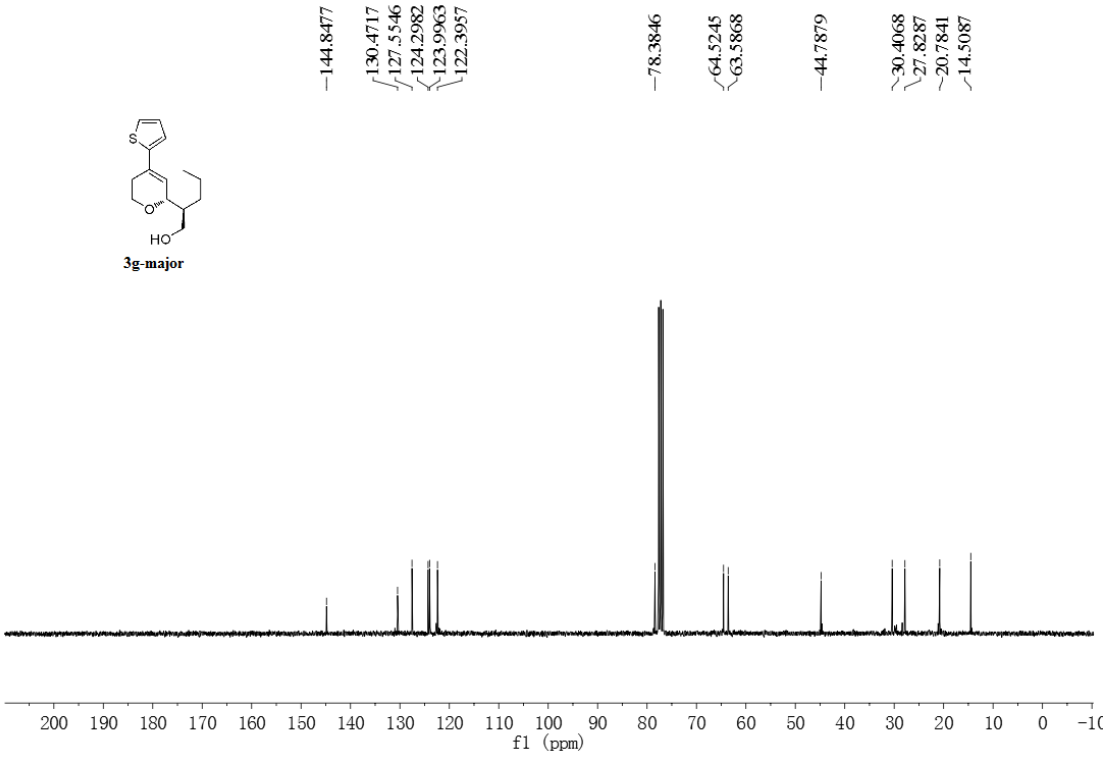

7.4117
7.4052
7.3894
7.3829
7.2042
7.1955
7.1818
7.1756
5.9915
4.2660
4.1729
4.1571
4.1534
4.1391
4.1352
4.1195
4.1158
3.7821
3.7738
3.7449
3.7364
3.6652
3.6536
3.6281
3.6165
3.5907
3.5802
3.5645
3.5441
3.5271
2.2334
2.1772
1.6095
1.6012
1.5045
1.4783
1.4633
1.4467
1.4283
1.4185
1.4148
1.3980
1.3926
1.3821
1.3756
1.3603
0.9113
0.8874
0.8643
Br
O
HO
3f-major
2.16
2.39
1.00
1.10
1.07
1.02
2.10
1.12
1.28
1.13
1.30
4.02
3.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

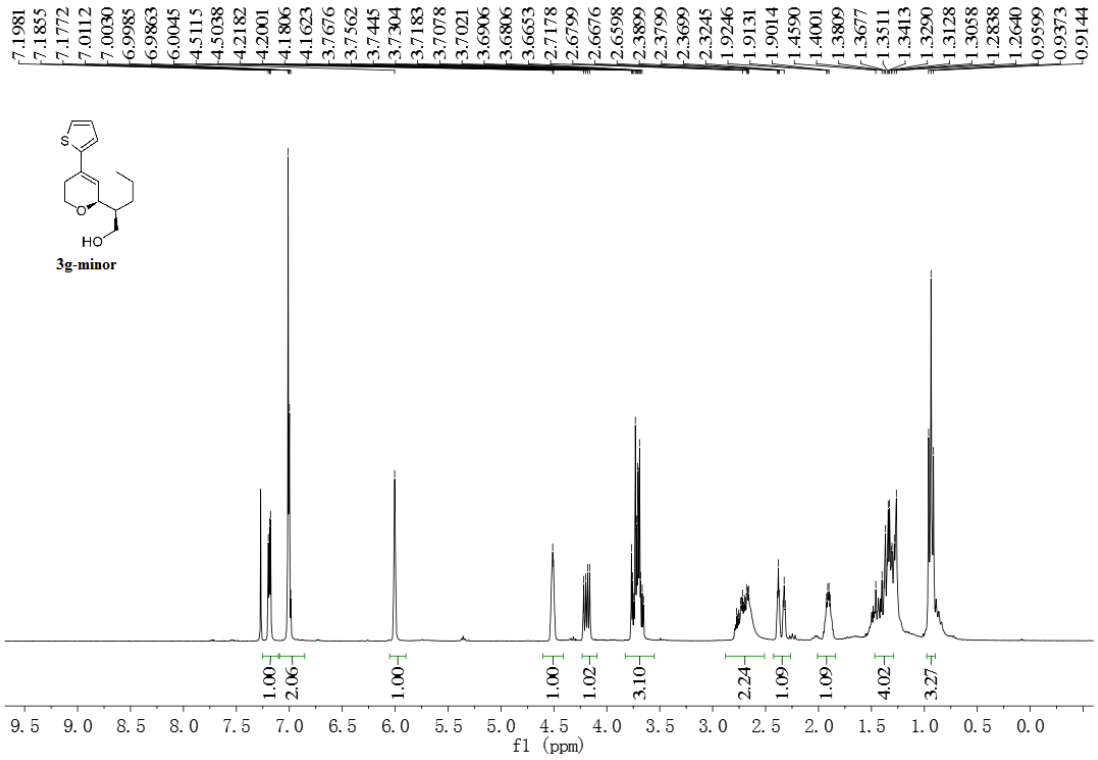

139.1972
134.9245
131.7515
126.6460
126.2640
121.5881
78.6095
64.6795
63.5828
44.8039
30.4447
27.3730
20.7845
14.5194
Br
O
HO
3f-major
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

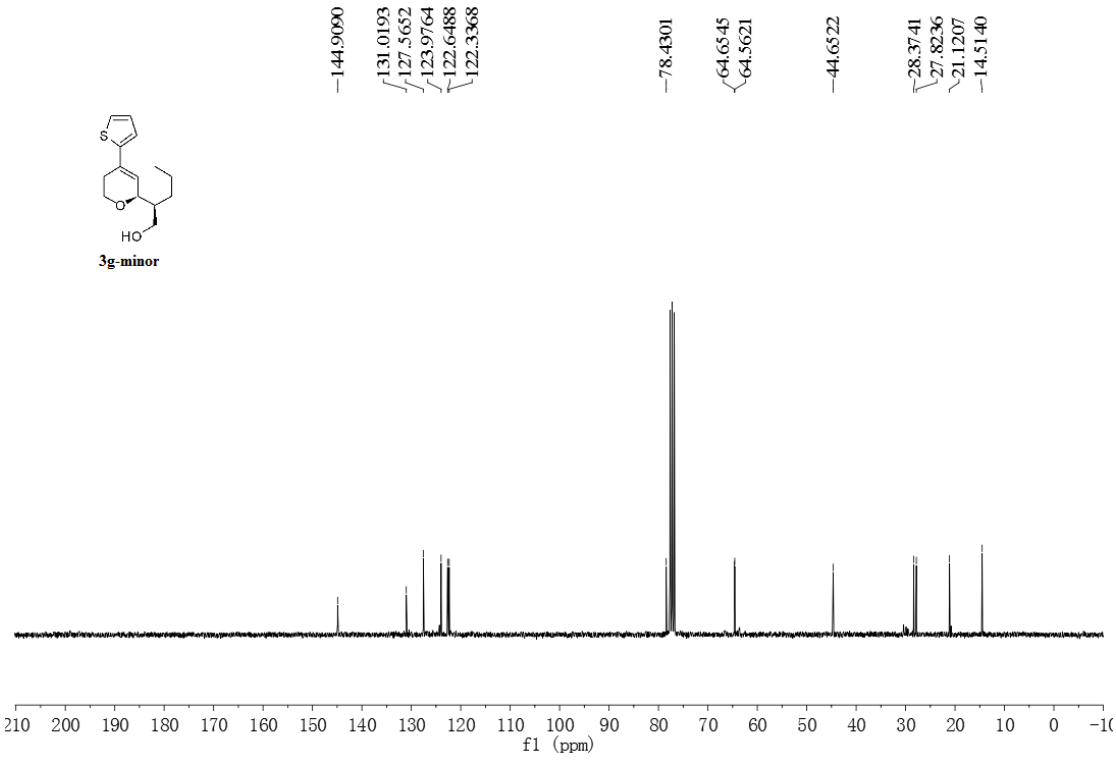

7.4150
7.4086
7.3927
7.3862
7.2075
7.2008
7.1951
7.1850
7.1789
5.9386
4.4330
4.1702
4.1527
4.1347
4.1151
3.6880
3.6773
3.6630
3.6502
3.6396
3.6279
3.6166
3.6020
3.5925
2.6551
2.6476
2.6431
2.6358
2.4393
2.2161
2.1702
2.1603
2.1501
1.8716
1.8604
1.8491
1.8375
1.3821
1.3596
1.3230
1.2921
1.2623
1.2425
1.2236
1.2135
0.8779
0.8686
0.8553
0.8322
Br
O
HO
3f-minor
2.22
2.42
1.00
1.02
1.09
3.25
1.18
1.22
1.19
1.11
4.29
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

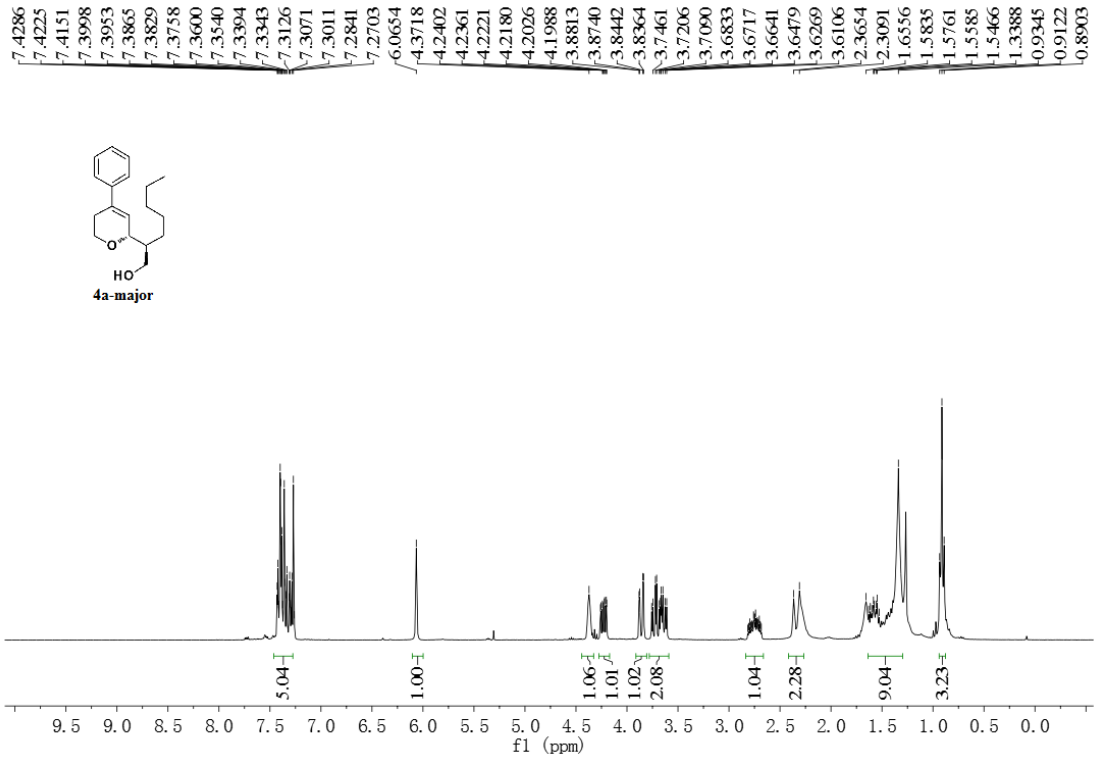

139.2238
135.5158
131.7503
126.6285
124.5411
121.5804
78.6468
64.7207
64.6447
44.6152
28.4366
27.3574
21.1156
14.5223
Br
O
HO
3f-minor
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

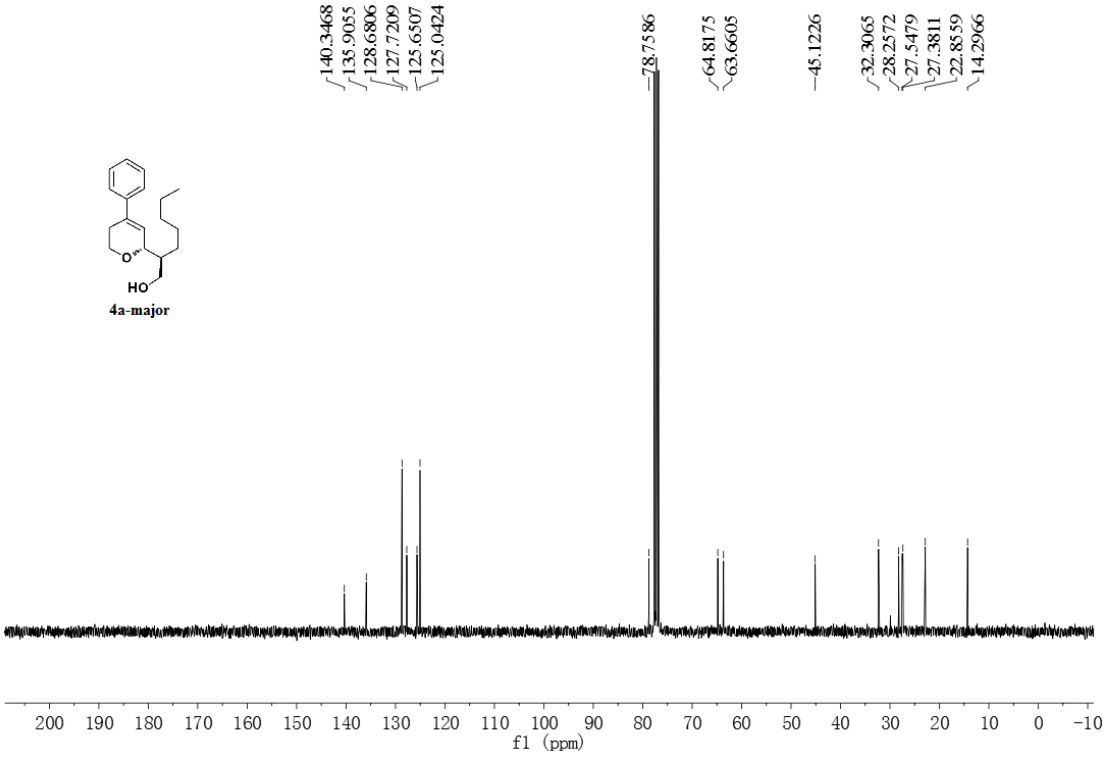

7.1933
7.1854
7.1803
7.1725
7.0065
6.9988
6.9933
6.0603
4.3455
4.2249
4.2217
4.2054
4.2019
4.1873
4.1838
4.1676
3.8676
3.8595
3.8304
3.8220
3.7291
3.7035
3.6917
3.6661
3.6526
3.6348
3.6142
3.5973
2.3940
2.3386
1.6744
1.6664
1.6585
1.6516
1.5793
1.5500
1.5399
1.5273
1.5111
1.4868
1.4690
1.4638
1.4468
1.4333
1.4050
1.2638
0.9872
0.9635
0.9407
S
O
HO
3g-major
0.98
2.00
1.00
1.06
1.02
1.02
2.07
2.23
1.09
5.27
3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

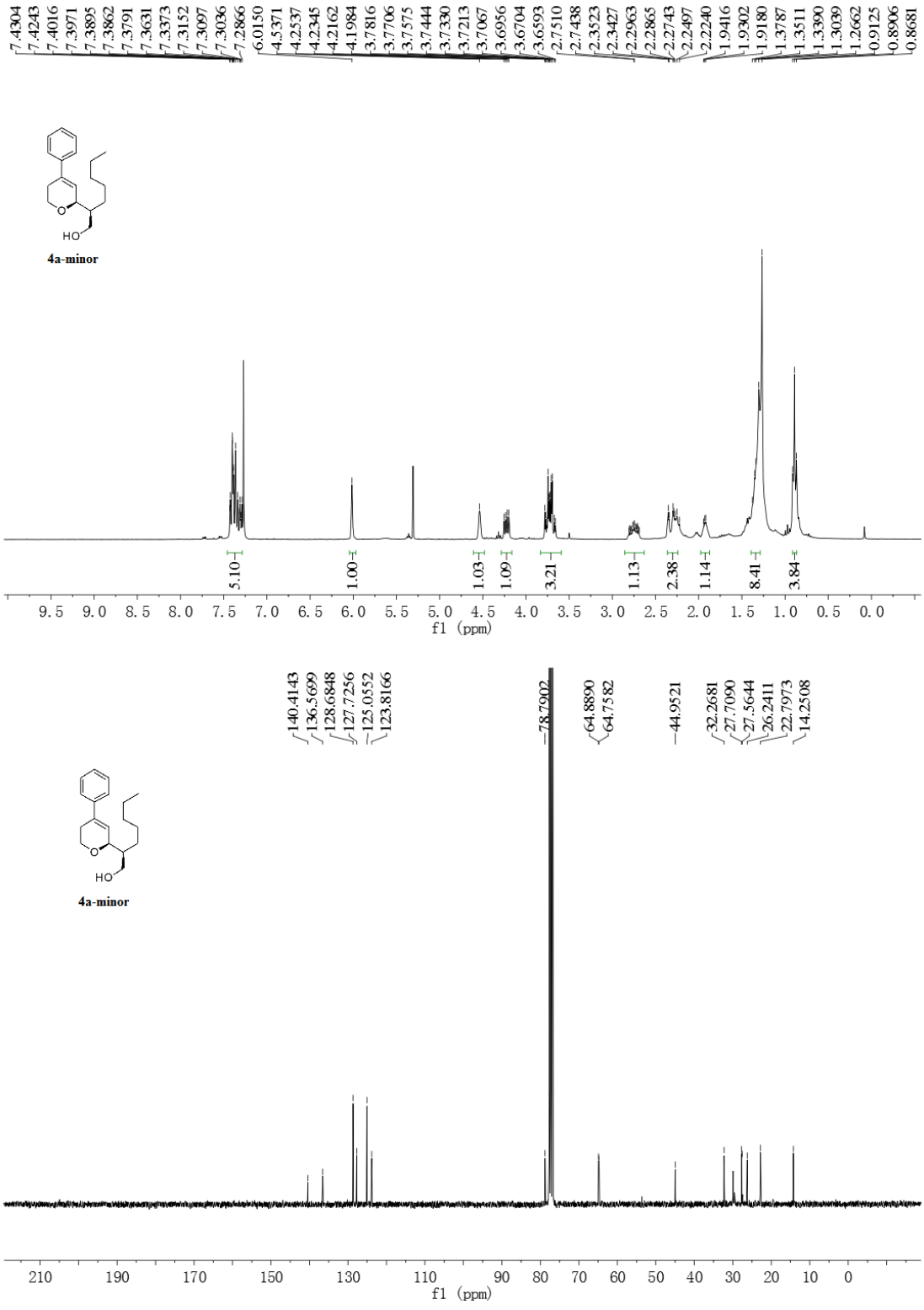

144.8477
130.4717
127.5546
124.2982
123.9963
122.3957
78.3846
64.5245
63.5868
44.7879
30.4068
27.8287
20.7841
14.5087
S
O
HO
3g-major
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

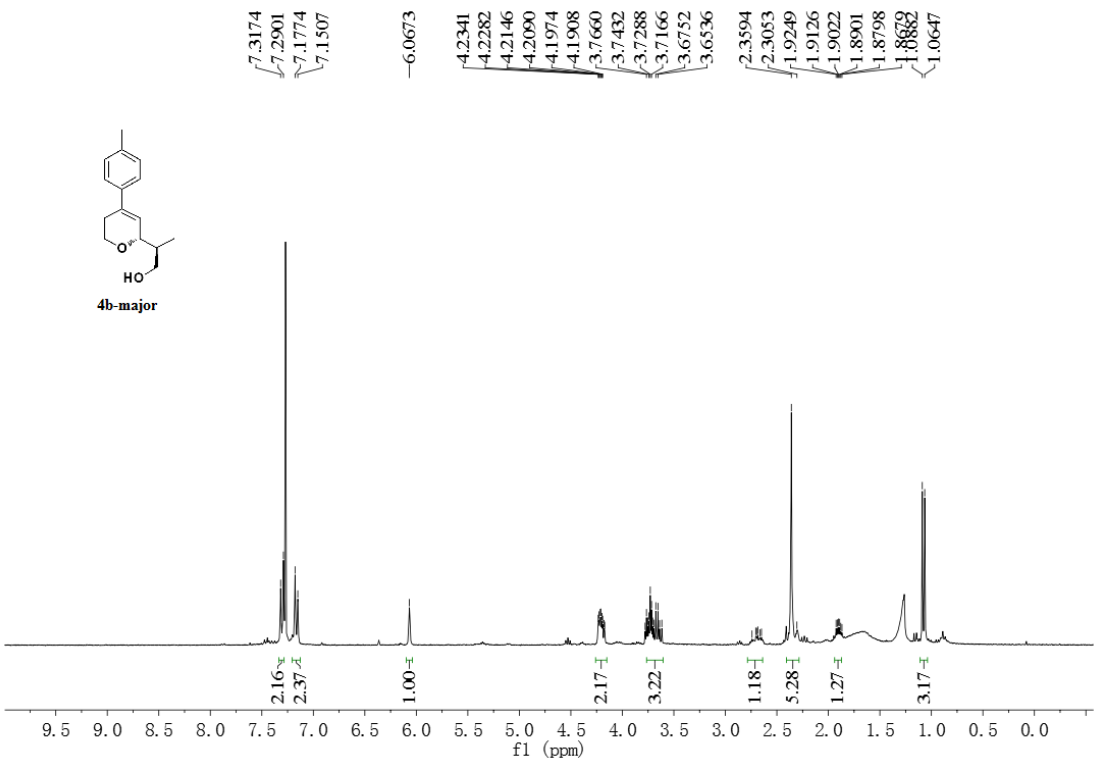

7.1981
7.1855
7.1772
7.0112
7.0030
6.9985
6.9863
6.0045
4.5115
4.5038
4.2182
4.2001
4.1806
4.1623
3.7676
3.7562
3.7445
3.7304
3.7183
3.7078
3.7021
3.6906
3.6806
3.6653
2.7178
2.6799
2.6676
2.6598
2.3899
2.3799
2.3699
2.3245
1.9246
1.9131
1.9014
1.4590
1.4001
1.3809
1.3677
1.3511
1.3413
1.3290
1.3128
1.3058
1.2838
1.2640
0.9599
0.9373
0.9144
3g-minor
1.00
2.06
1.00
1.00
1.02
3.10
2.24
1.09
1.09
4.02
3.27
f1 (ppm)


144.9090
131.0193
127.5652
123.9764
122.6488
122.3368
78.4301
64.6545
64.5621
44.6522
28.3741
27.8236
21.1207
14.5140
3g-minor
f1 (ppm)

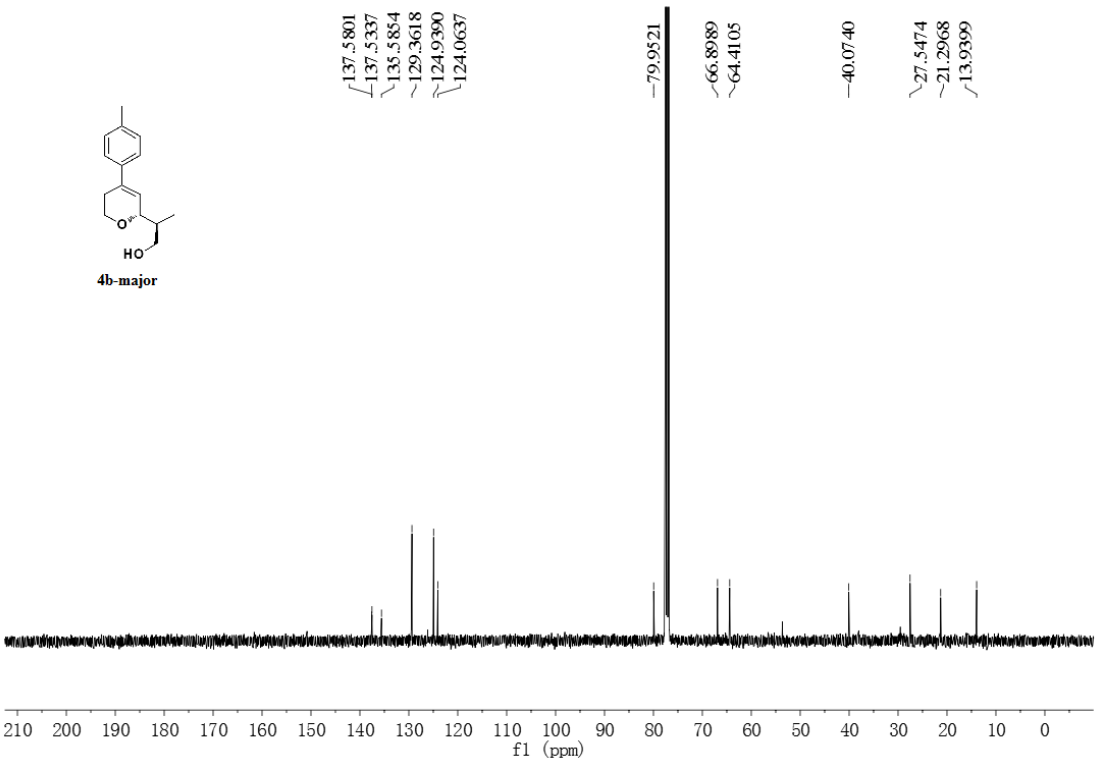

7.4286
7.4225
7.4151
7.3998
7.3953
7.3865
7.3829
7.3758
7.3600
7.3540
7.3394
7.3343
7.3126
7.3071
7.3011
7.2841
7.2703
6.0654
4.3718
4.2402
4.2361
4.2221
4.2180
4.2026
4.1988
3.8813
3.8740
3.8442
3.8364
3.7461
3.7206
3.7090
3.6833
3.6717
3.6641
3.6479
3.6269
3.6106
2.3654
2.3091
1.6556
1.5835
1.5761
1.5585
1.5466
1.3388
0.9345
0.9122
0.8903
HO
4a-major
5.04
1.00
1.06
1.01
1.02
2.08
1.04
2.28
9.04
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.3468
135.9055
128.6806
127.7209
125.6507
125.0424
78.7586
64.8175
63.6605
45.1226
32.3065
28.2572
27.5479
27.3811
22.8559
14.2966
HO
4a-major
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

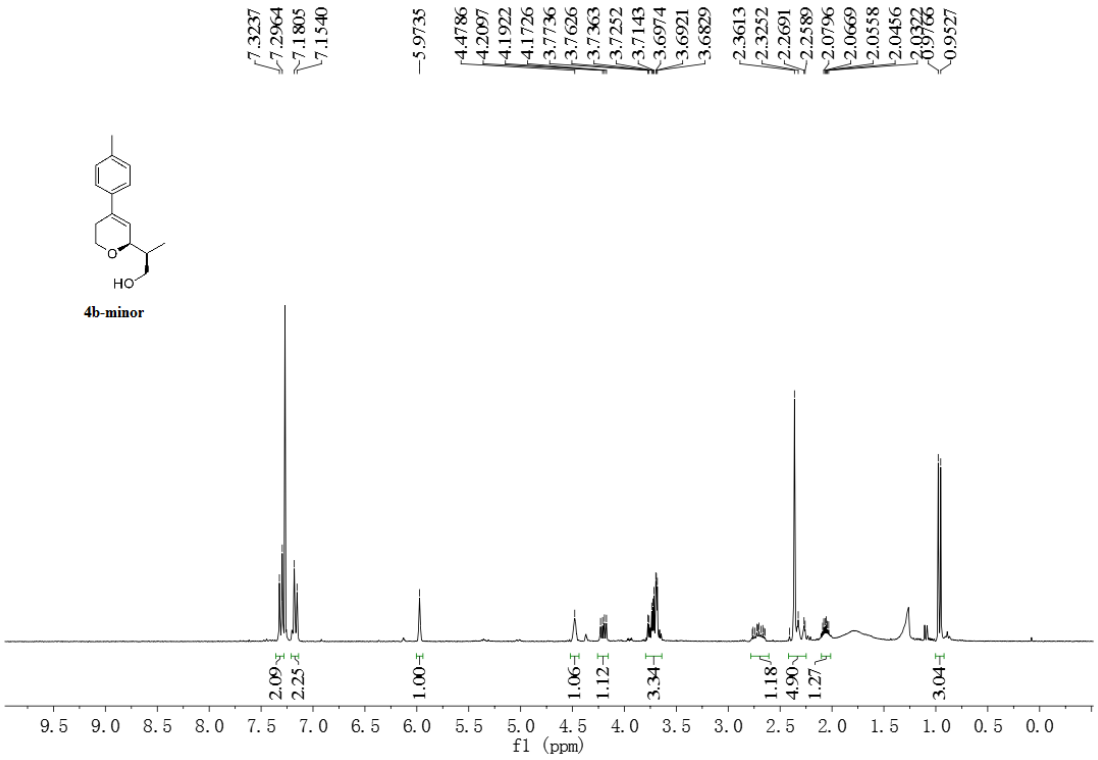

7.4304
7.4243
7.4016
7.3971
7.3895
7.3862
7.3791
7.3631
7.3373
7.3152
7.3097
7.3036
7.2866
6.0150
4.5371
4.2537
4.2345
4.2162
4.1984
3.7816
3.7706
3.7575
3.7444
3.7330
3.7213
3.7067
3.6956
3.6704
3.6593
2.7510
2.7438
2.3523
2.3427
2.2963
2.2865
2.2743
2.2497
2.2240
1.9416
1.9302
1.9180
1.3787
1.3511
1.3390
1.3039
1.2662
0.9125
0.8906
0.8681
HO
4a-minor
5.10
1.00
1.03
1.09
3.21
1.13
2.38
1.14
8.41
3.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
140.4143
136.5699
128.6848
127.7256
125.0552
123.8166
78.7902
64.8890
64.7582
44.9521
32.2681
27.7090
27.5644
26.2411
22.7973
14.2508
HO
4a-minor
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

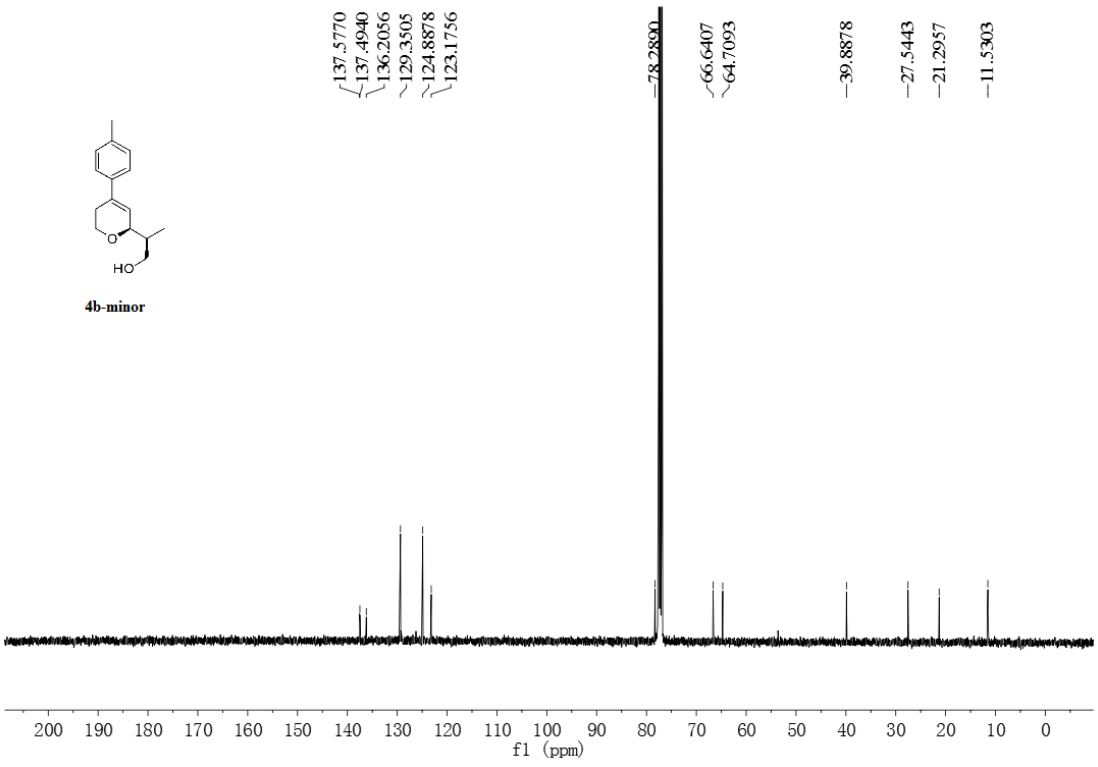


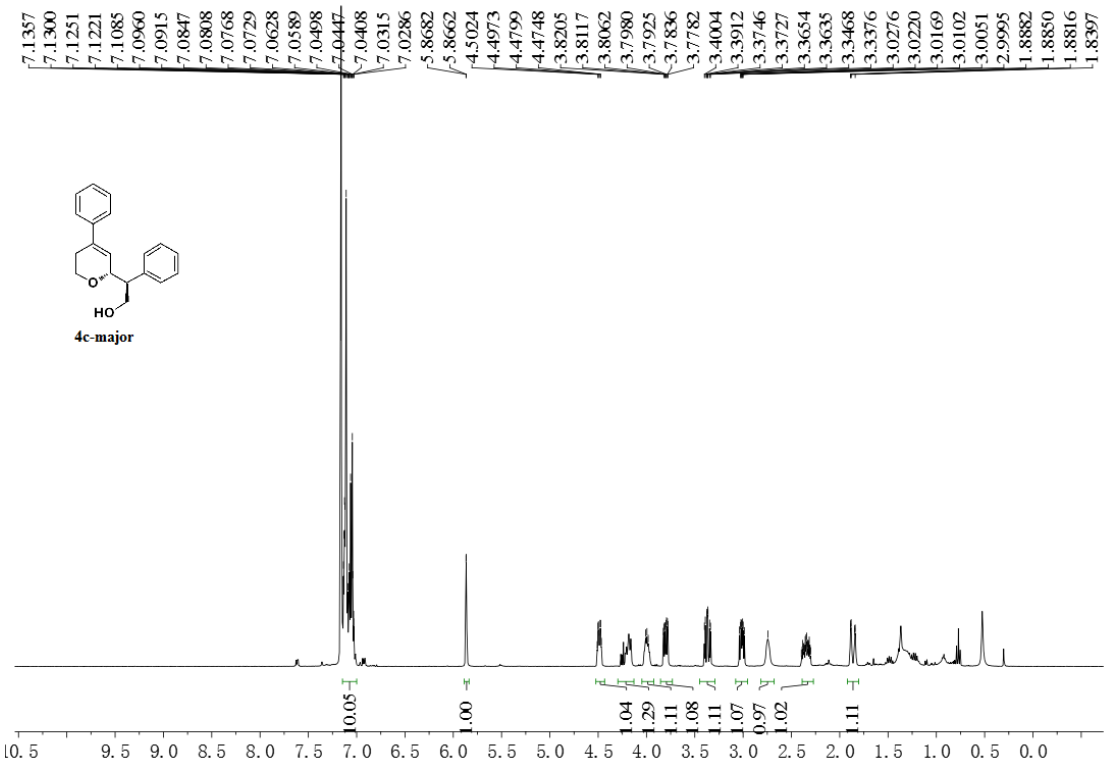
4b-major

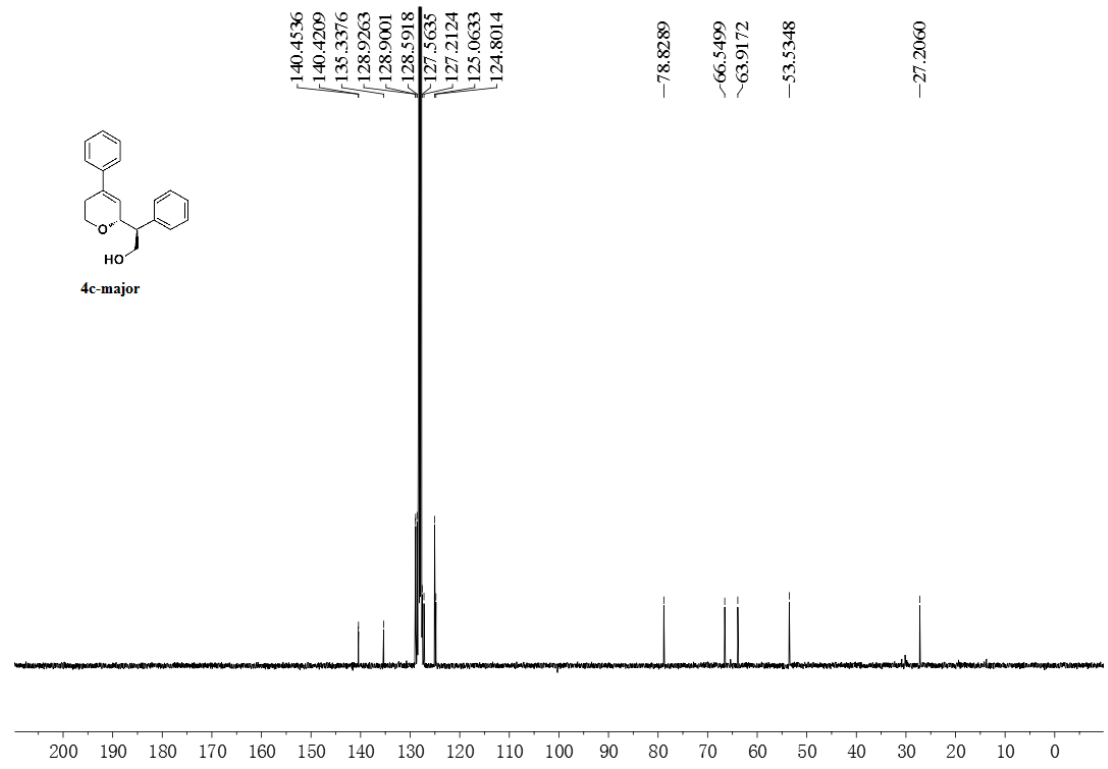


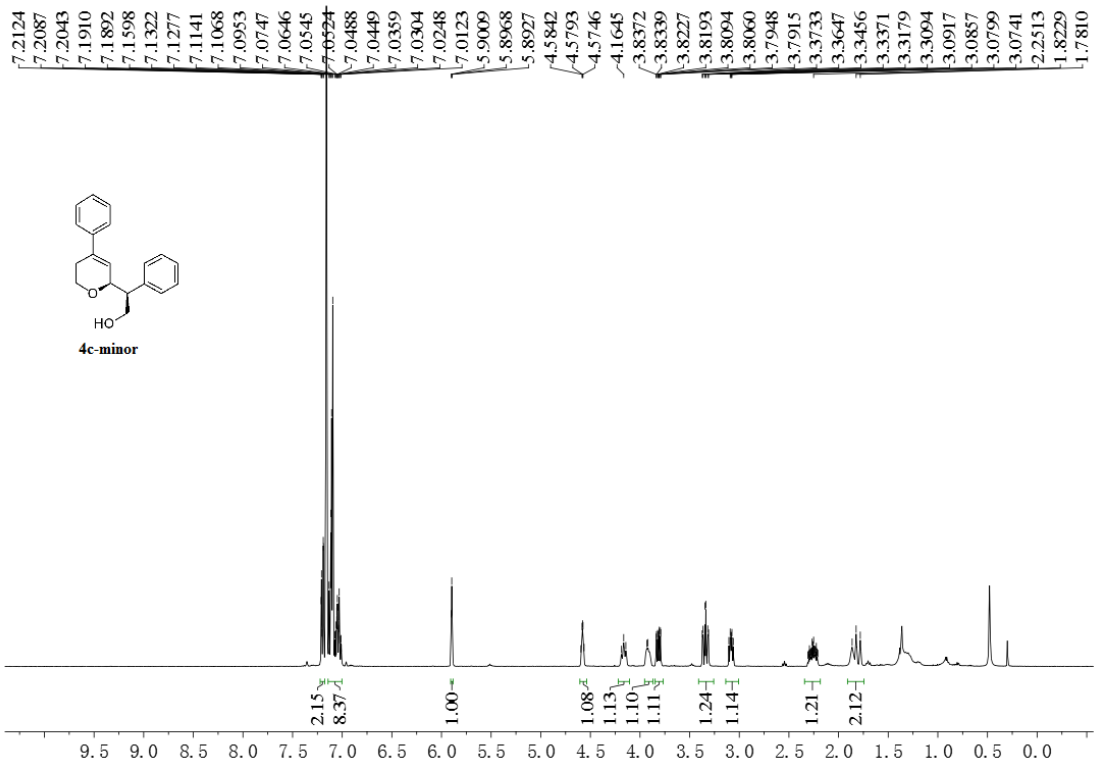
4b-major

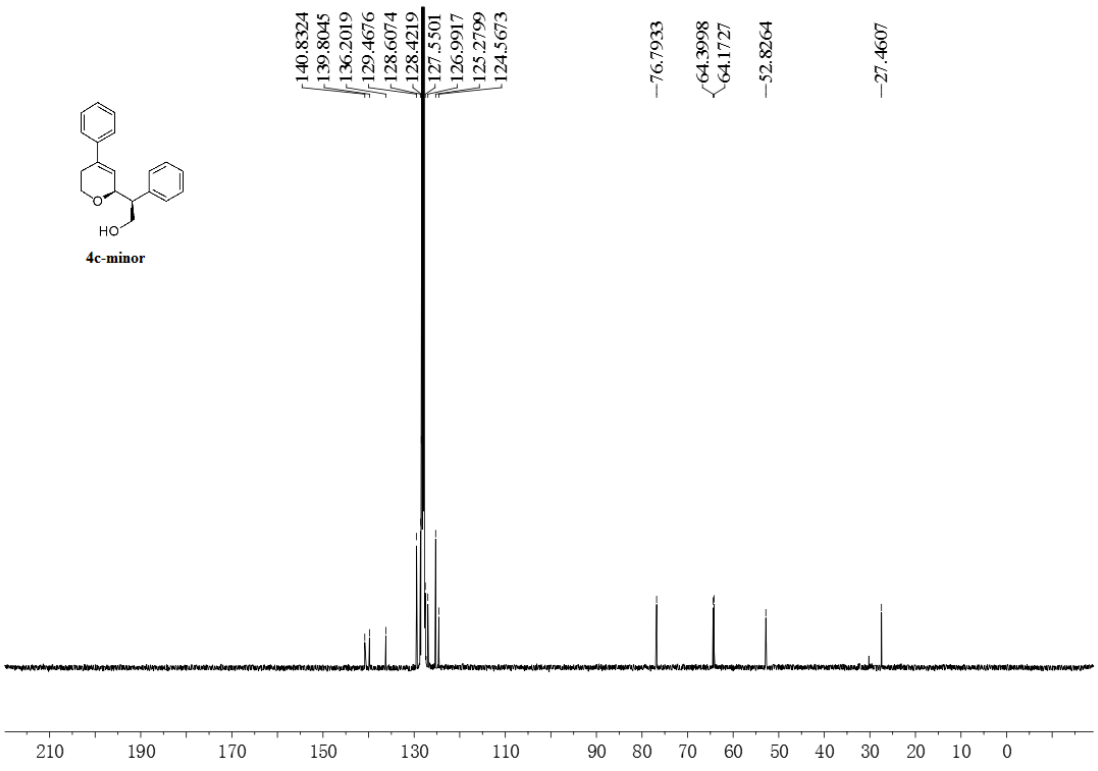

7.3237
7.2964
7.1805
7.1540
5.9735
4.4786
4.2097
4.1922
4.1726
3.7736
3.7626
3.7363
3.7252
3.7143
3.6974
3.6921
3.6829
2.3613
2.3252
2.2691
2.2589
2.0796
2.0669
2.0558
2.0456
0.9768
0.9527
HO
4b-minor
2.09
2.25
1.00
1.06
1.12
3.34
1.18
4.90
1.27
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

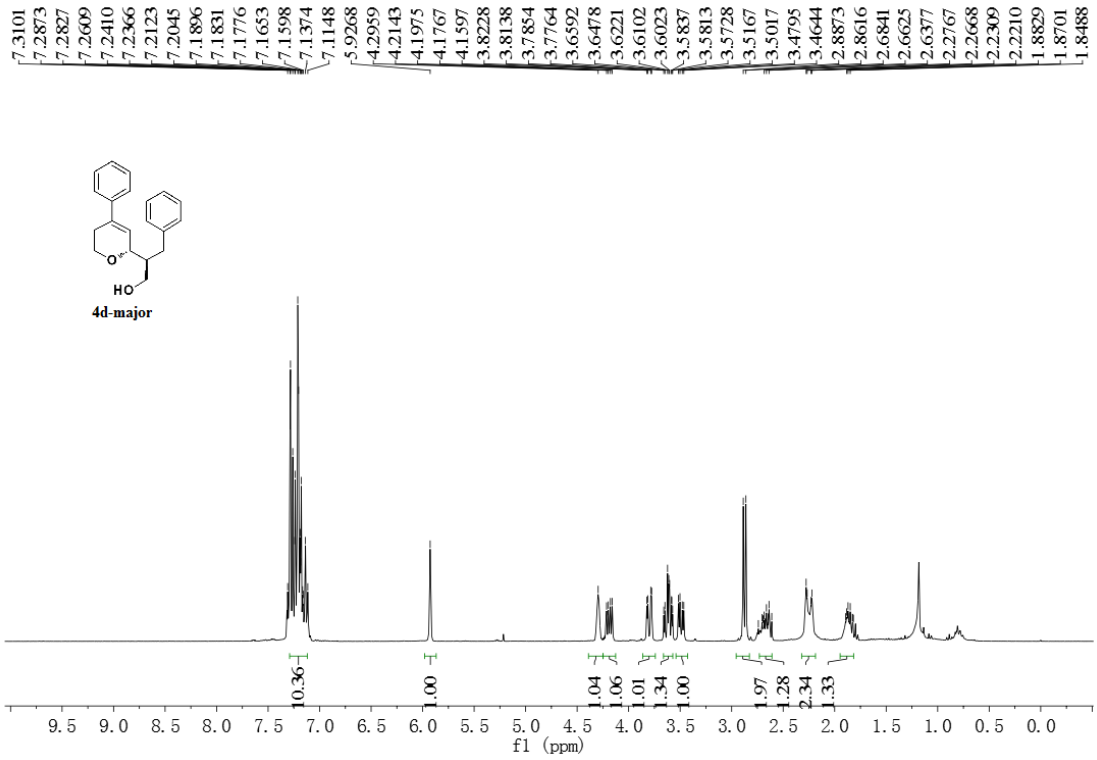

137.5770
137.4940
136.2056
129.3505
124.8878
123.1756
78.2890
66.6407
64.7093
39.8878
27.5443
21.2957
11.5303
HO
4b-minor
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

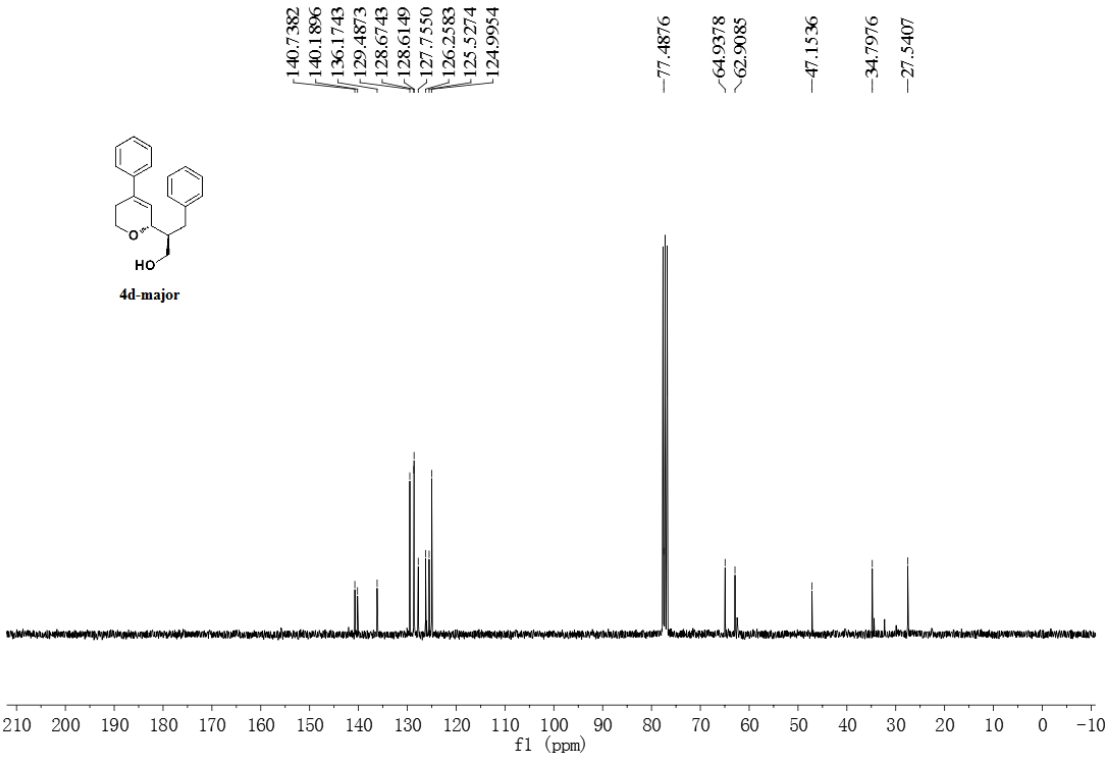

7.1357
7.1300
7.1251
7.1221
7.1085
7.0960
7.0915
7.0847
7.0808
7.0768
7.0729
7.0628
7.0589
7.0498
7.0447
7.0408
7.0315
7.0286
5.8682
5.8662
4.5024
4.4973
4.4799
4.4748
3.8205
3.8117
3.8062
3.7980
3.7925
3.7836
3.7782
3.4004
3.3912
3.3746
3.3727
3.3654
3.3635
3.3468
3.3376
3.0276
3.0220
3.0169
3.0102
3.0051
2.9995
1.8882
1.8850
1.8816
1.8397
HO
4c-major
10.05
1.00
1.04
1.29
1.11
1.08
1.11
1.07
0.97
1.02
1.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

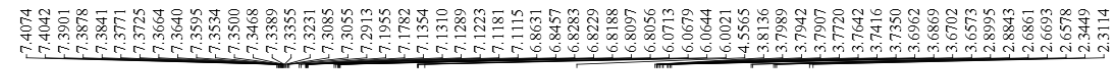

140.4536
140.4209
135.3376
128.9263
128.9001
128.5918
127.5635
127.2124
125.0633
124.8014
78.8289
66.5499
63.9172
53.5348
27.2060
HO
4c-major
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

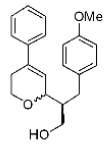

7.2124
7.2087
7.2043
7.1910
7.1892
7.1598
7.1322
7.1277
7.1141
7.1068
7.0953
7.0747
7.0646
7.0545
7.0524
7.0488
7.0449
7.0359
7.0304
7.0248
7.0123
5.9009
5.8968
5.8927
4.5842
4.5793
4.5746
4.1645
3.8372
3.8339
3.8227
3.8193
3.8094
3.8060
3.7948
3.7915
3.3733
3.3647
3.3456
3.3371
3.3179
3.3094
3.0917
3.0857
3.0799
3.0741
2.2513
1.8229
1.7810
HO
4c-minor
2.15
8.37
1.00
1.08
1.13
1.10
1.11
1.24
1.14
1.21
2.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


140.8324
139.8045
136.2019
129.4676
128.6074
128.4219
127.5501
126.9917
125.2799
124.5673
76.7933
64.3998
64.1727
52.8264
27.4607
HO
4c-minor
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

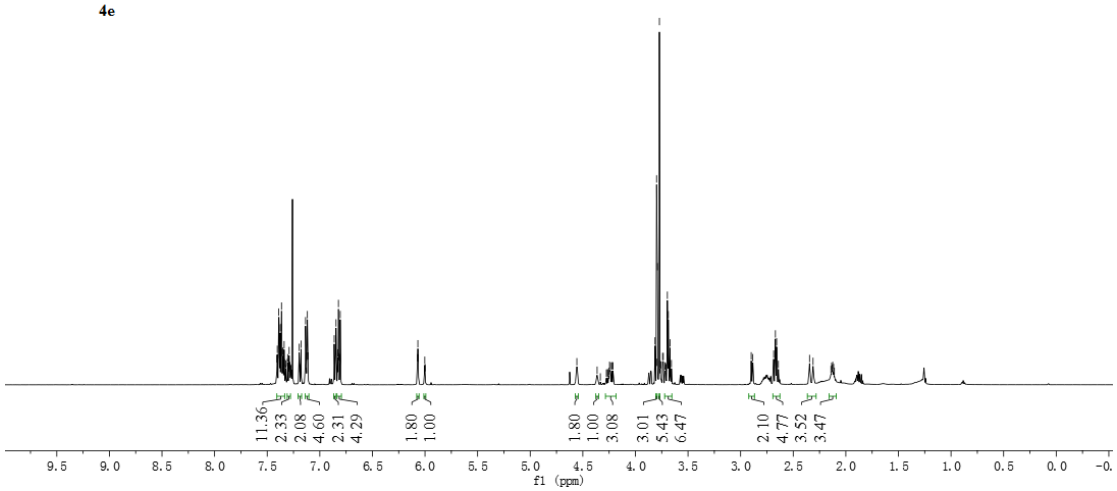

7.3101
7.2873
7.2827
7.2609
7.2410
7.2366
7.2123
7.2045
7.1896
7.1831
7.1776
7.1653
7.1598
7.1374
7.1148
5.9268
4.2959
4.2143
4.1975
4.1767
4.1597
3.8228
3.8138
3.7854
3.7764
3.6592
3.6478
3.6221
3.6102
3.6023
3.5837
3.5813
3.5728
3.5167
3.5017
3.4795
3.4644
2.8873
2.8616
2.6841
2.6625
2.6377
2.2767
2.2668
2.2309
2.2210
1.8829
1.8701
1.8488
HO
4d-major
10.36
1.00
1.04
1.06
1.01
1.34
1.00
1.97
1.28
2.34
1.33
f1 (ppm)

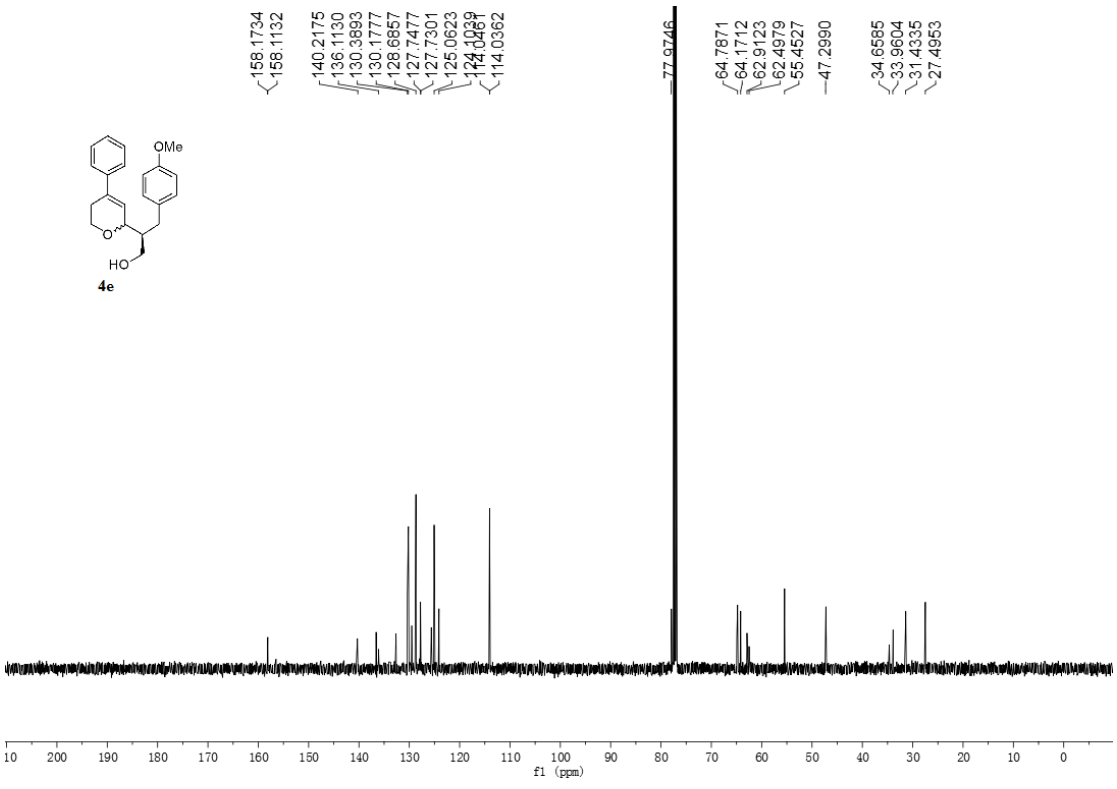

140.7382
140.1896
136.1743
129.4873
128.6743
128.6149
127.7550
126.2583
125.5274
124.9954
77.4876
64.9378
62.9085
47.1536
34.7976
27.5407
HO
4d-major
f1 (ppm)


7.4074
7.4042
7.3901
7.3878
7.3841
7.3771
7.3725
7.3664
7.3640
7.3595
7.3534
7.3500
7.3468
7.3389
7.3355
7.3231
7.3085
7.3055
7.2913
7.1955
7.1782
7.1354
7.1310
7.1289
7.1223
7.1181
7.1115
6.8631
6.8457
6.8283
6.8229
6.8188
6.8097
6.8056
6.0713
6.0679
6.0644
6.0021
4.5565
3.8136
3.7989
3.7942
3.7907
3.7720
3.7642
3.7416
3.7350
3.6962
3.6869
3.6702
3.6573
3.8995
2.8843
2.6861
2.6693
2.6578
2.3449
2.3114


OMe
HO

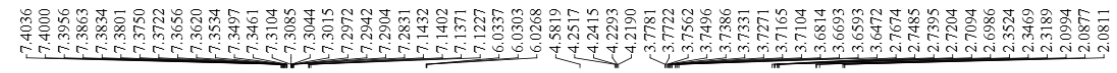
4e

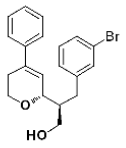

11.36
2.33
2.08
4.60
2.31
4.29
1.80
1.00
1.80
1.00
3.08
3.01
5.43
6.47
2.10
4.77
3.52
3.47
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


158.1734
158.1132
140.2175
136.1130
130.3893
130.1777
128.6857
127.7477
127.7301
125.0623
124.1039
114.0461
114.0362
77.9746
64.7871
64.1712
62.9123
62.4979
55.4527
47.2990
34.6585
33.9604
31.4335
27.4953
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

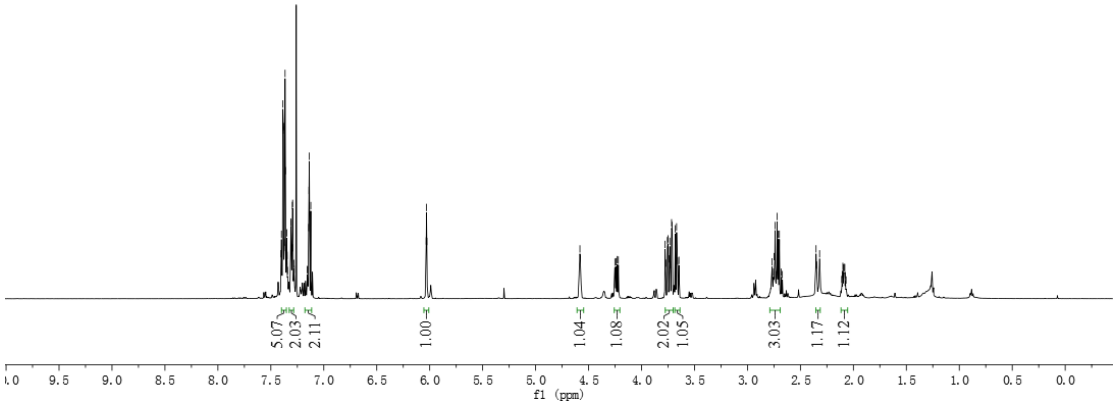
OMe
HO

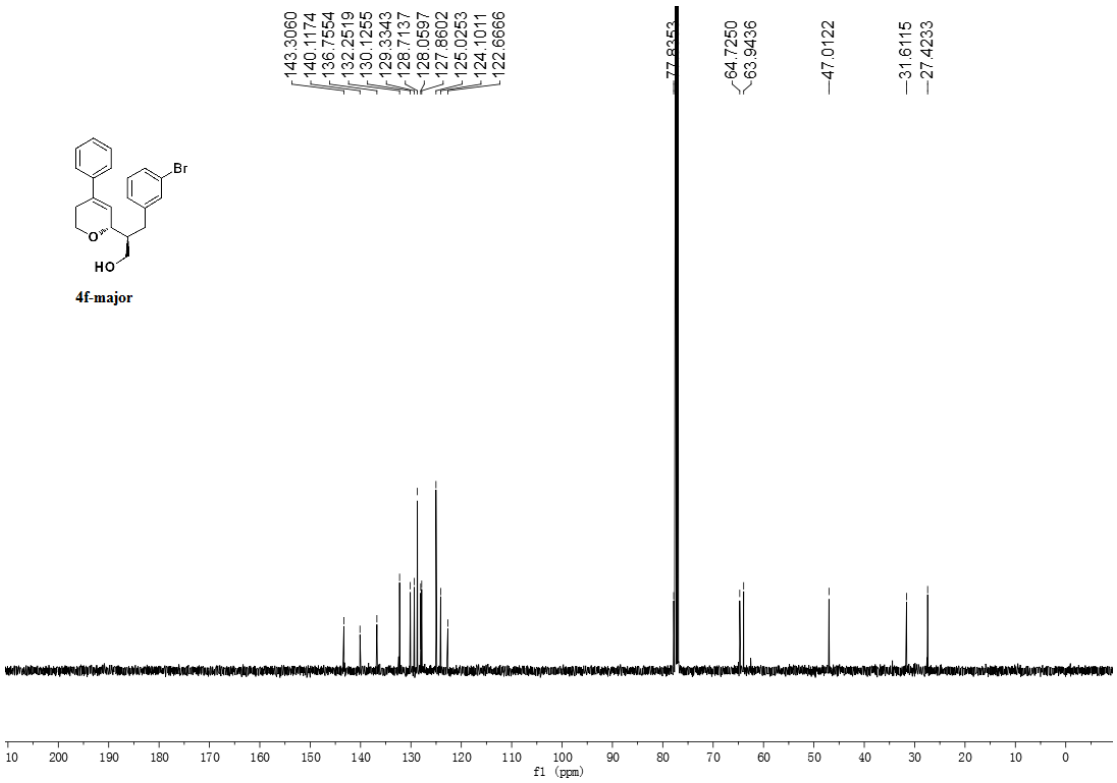
4e



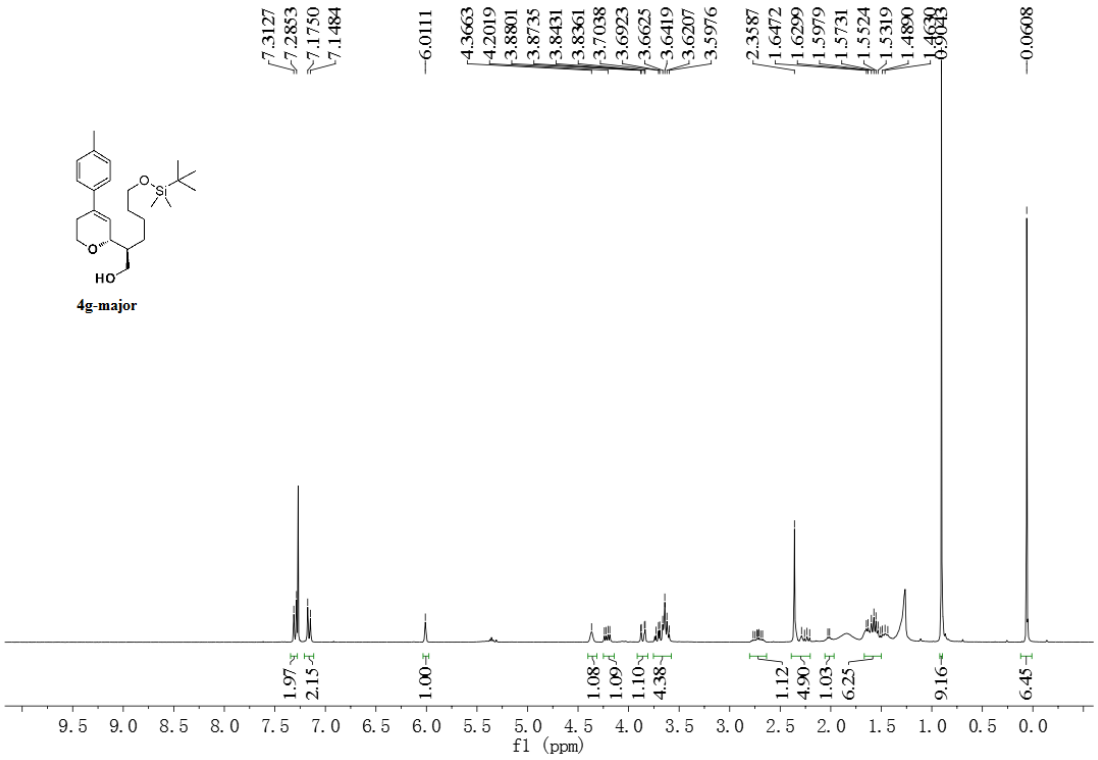


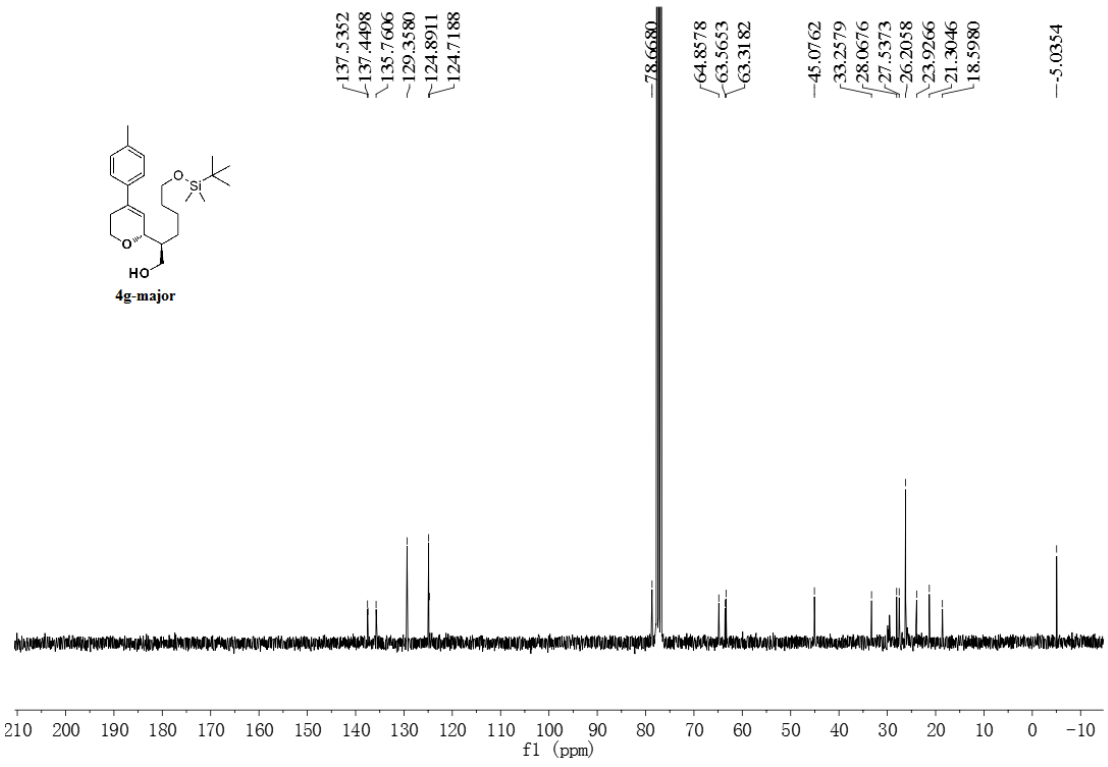
4f-major

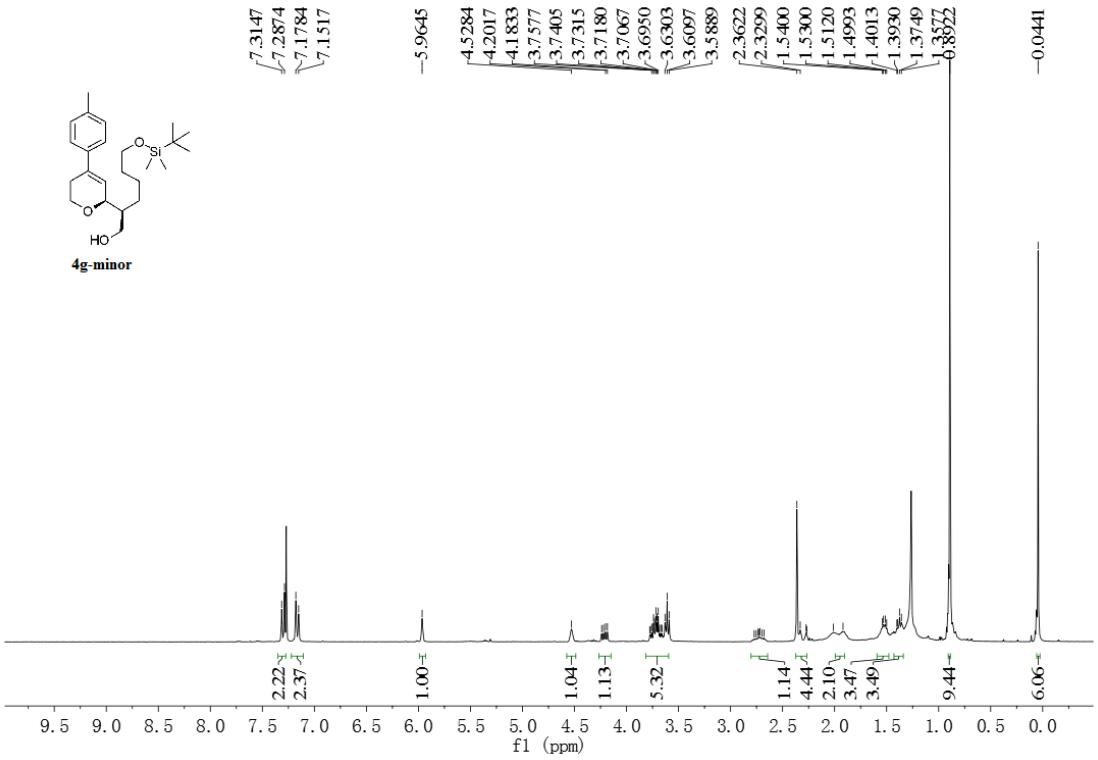


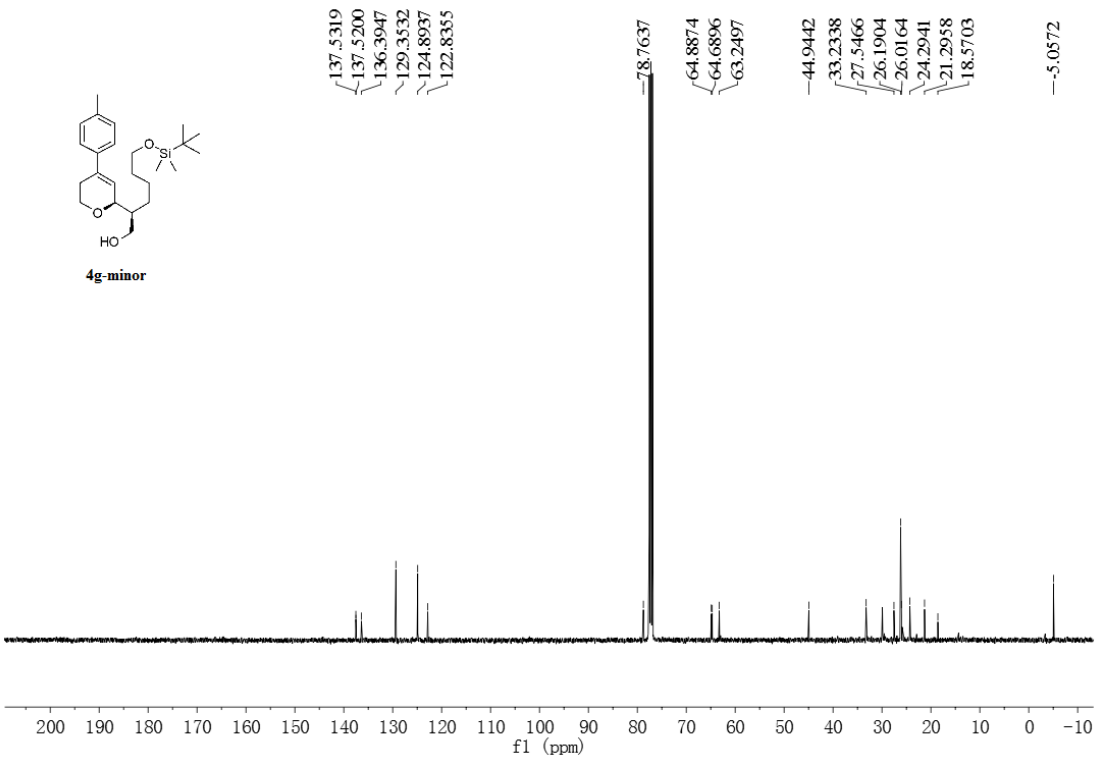


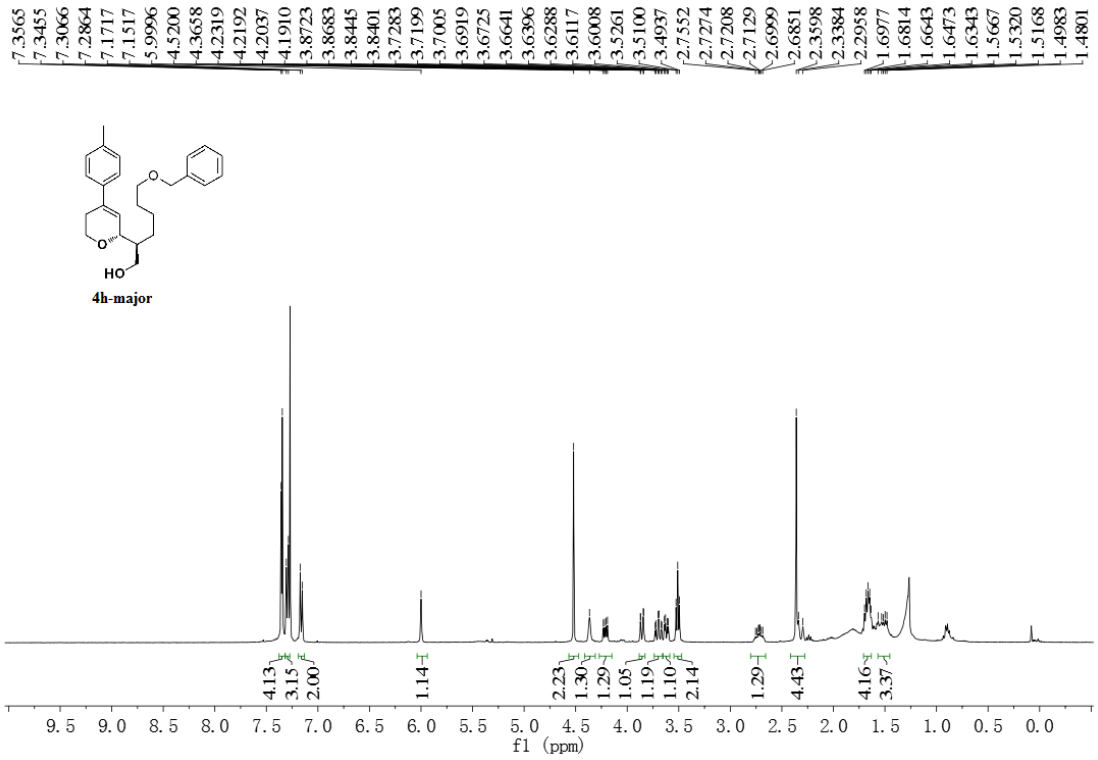
4f-major

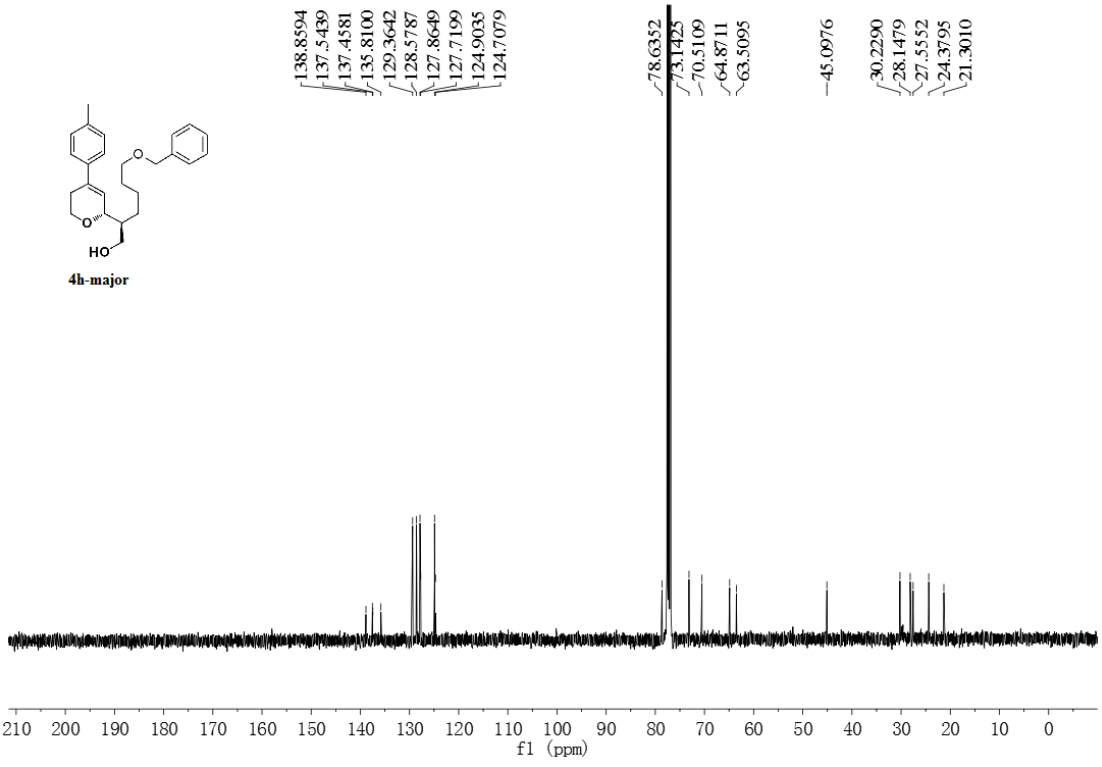

7.3127
7.2853
7.1750
7.1484
6.0111
4.3663
4.2019
3.8801
3.8735
3.8431
3.8361
3.7038
3.6923
3.6625
3.6419
3.6207
3.5976
2.3587
1.6472
1.6299
1.5979
1.5731
1.5524
1.5319
1.4890
0.9043
0.0608
HO
4g-major
1.97
2.15
1.00
1.08
1.09
1.10
4.38
1.12
4.90
1.03
6.25
9.16
6.45
f1 (ppm)

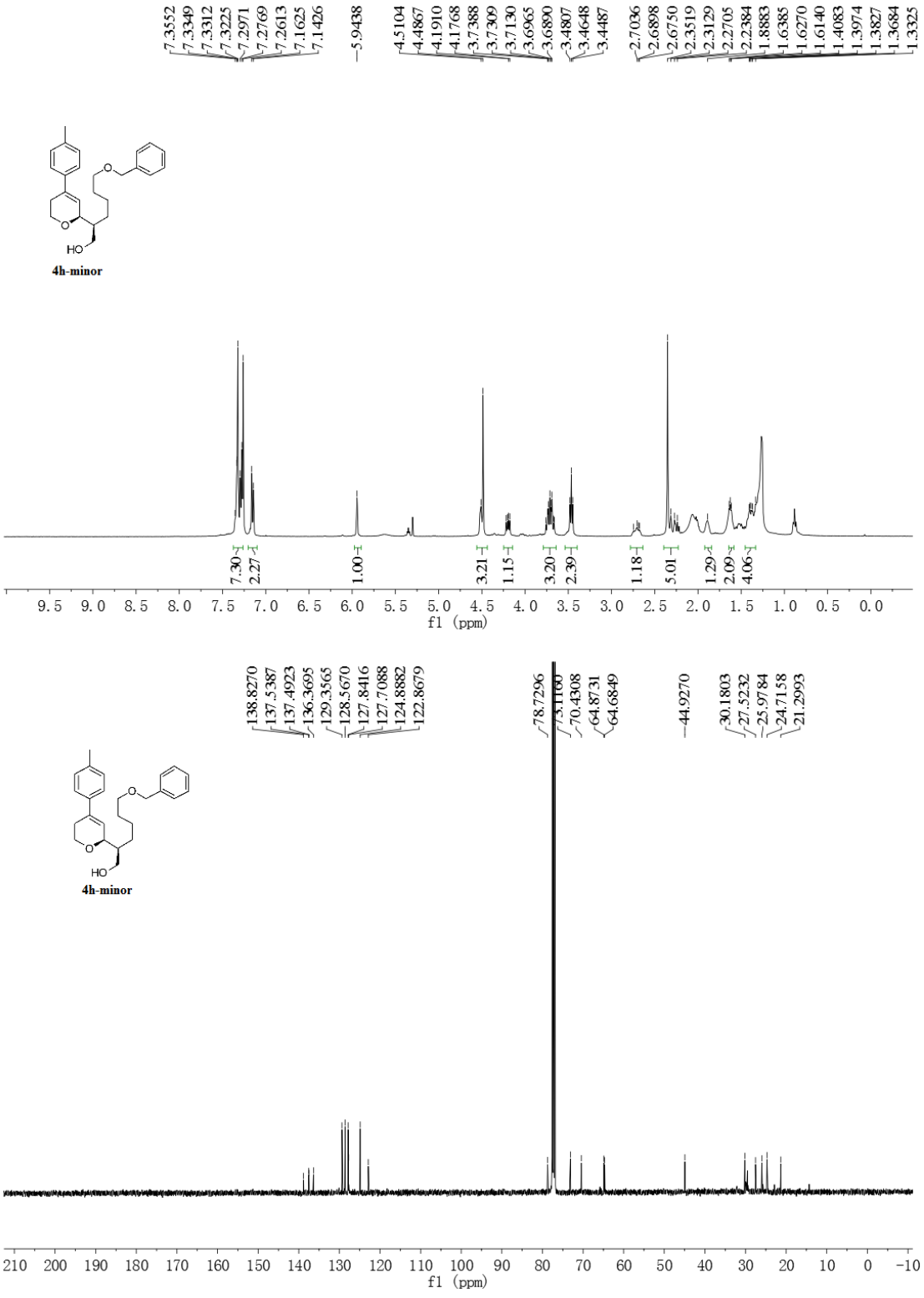

137.5352
137.4498
135.7606
129.3580
124.8911
124.7188
78.6680
64.8578
63.5653
63.3182
45.0762
33.2579
28.0676
27.5373
26.2058
23.9266
21.3046
18.5980
-5.0354
HO
4g-major
f1 (ppm)

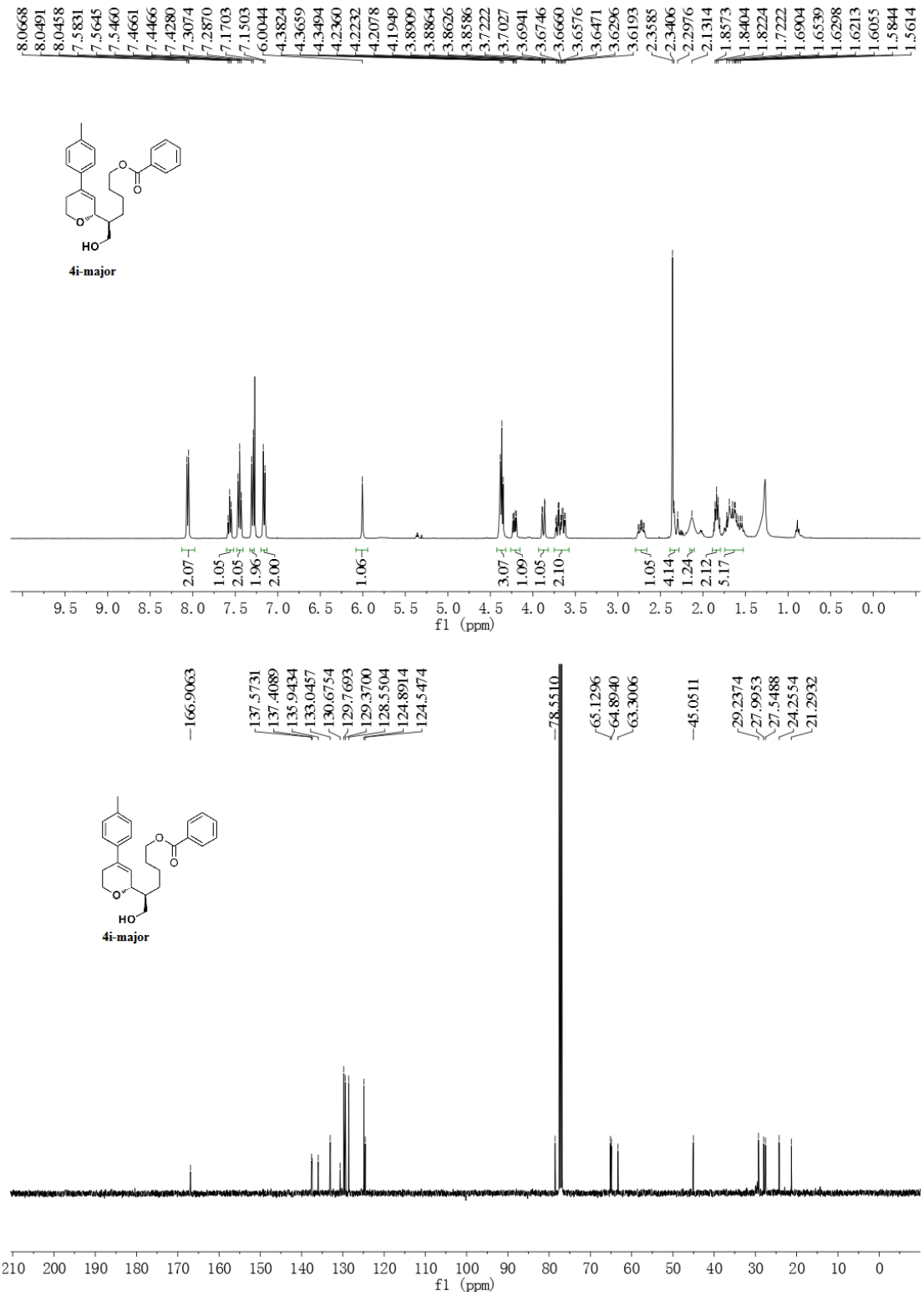

7.3147
7.2874
7.1784
7.1517
5.9645
4.5284
4.2017
4.1833
3.7577
3.7405
3.7315
3.7180
3.7067
3.6950
3.6303
3.6097
3.5889
2.3622
2.3299
1.5400
1.5300
1.5120
1.4993
1.4013
1.3930
1.3749
1.3577
0.8922
0.0441
2.22
2.37
1.00
1.04
1.13
5.32
1.14
4.44
2.10
3.47
3.49
9.44
6.06
f1 (ppm)
4g-minor

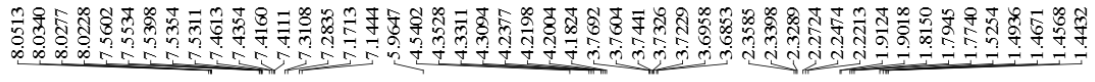

137.5319
137.5200
136.3947
129.3532
124.8937
122.8355
78.7637
64.8874
64.6896
63.2497
44.9442
33.2338
27.5466
26.1904
26.0164
24.2941
21.2958
18.5703
-5.0572
f1 (ppm)
4g-minor

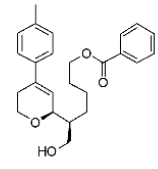

7.3565
7.3455
7.3066
7.2864
7.1717
7.1517
5.9996
4.5200
4.3658
4.2319
4.2192
4.2037
4.1910
3.8723
3.8683
3.8445
3.8401
3.7283
3.7199
3.7005
3.6919
3.6725
3.6641
3.6396
3.6288
3.6117
3.6008
3.5261
3.5100
3.4937
2.7552
2.7274
2.7208
2.7129
2.6999
2.6851
2.3598
2.3384
2.2958
1.6977
1.6814
1.6643
1.6473
1.6343
1.5667
1.5320
1.5168
1.4983
1.4801
HO
4h-major
4.13
3.15
2.00
1.14
2.23
1.30
1.29
1.05
1.19
1.10
2.14
1.29
4.43
4.16
3.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


138.8594
137.5439
137.4581
135.8100
129.3642
128.5787
127.8649
127.7199
124.9035
124.7079
78.6352
73.1425
70.5109
64.8711
63.5095
45.0976
30.2290
28.1479
27.5552
24.3795
21.3010
HO
4h-major
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

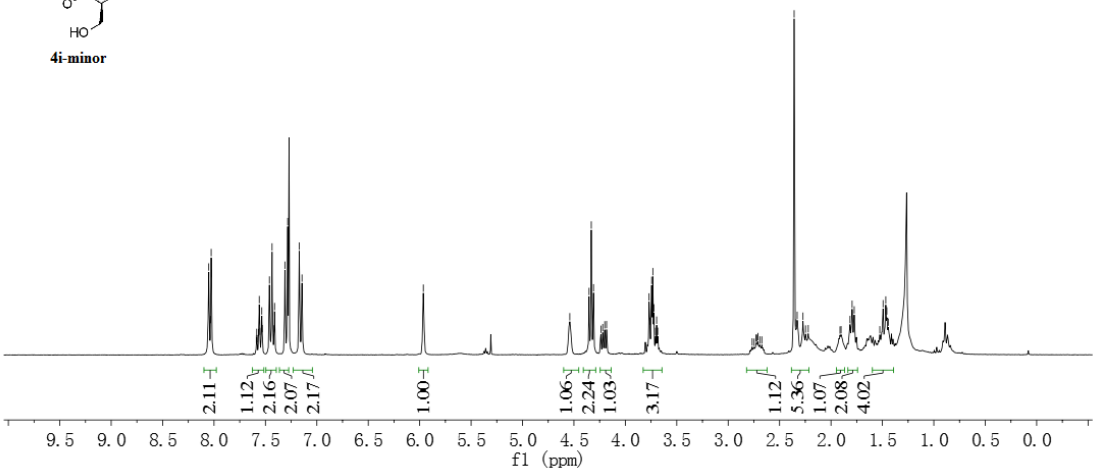

7.3552
7.3349
7.3312
7.3225
7.2971
7.2769
7.2613
7.1625
7.1426
5.9438
4.5104
4.4867
4.1910
4.1768
3.7388
3.7309
3.7130
3.6965
3.6890
3.4807
3.4648
3.4487
2.7036
2.6898
2.6750
2.3519
2.3129
2.2705
2.2384
1.8883
1.6385
1.6270
1.6140
1.4083
1.3974
1.3827
1.3684
1.3325
HO
4h-minor
7.30
2.27
1.00
3.21
1.15
3.20
2.39
1.18
5.01
1.29
2.09
4.06
f1 (ppm)
138.8270
137.5387
137.4923
136.3695
129.3565
128.5670
127.8416
127.7088
124.8882
122.8679
78.7296
70.4308
64.8731
64.6849
44.9270
30.1803
27.5232
25.9784
24.7158
21.2993
HO
4h-minor
f1 (ppm)

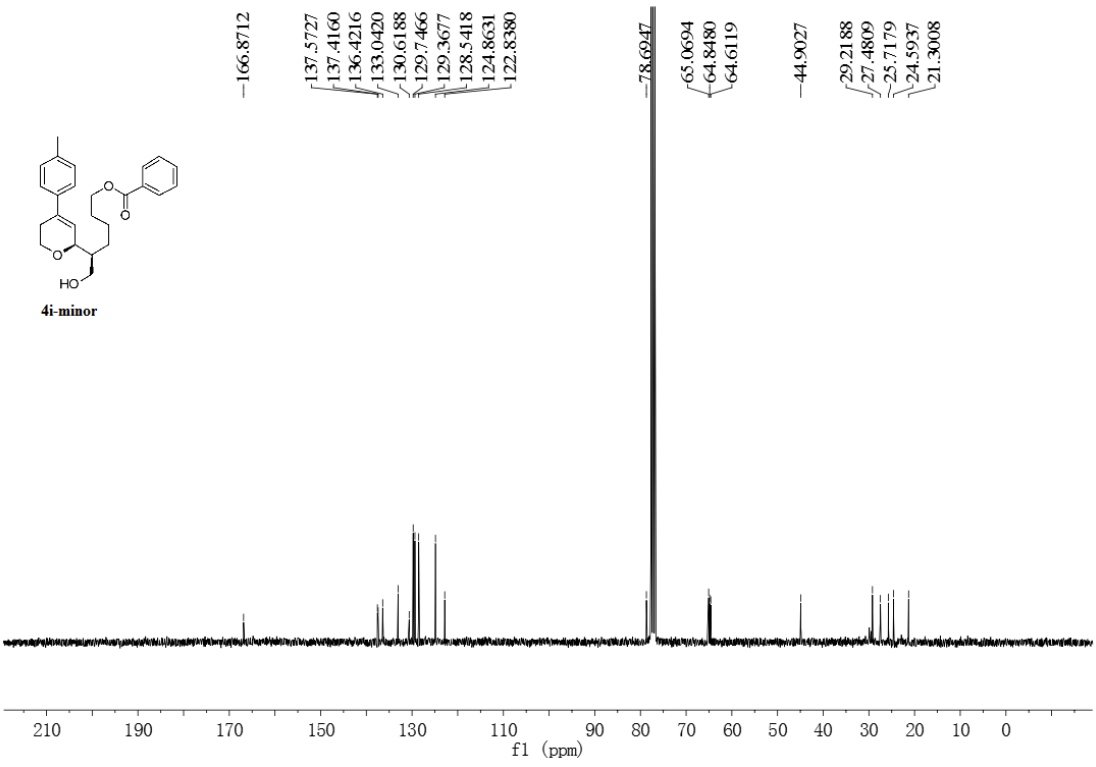

8.0668
8.0491
8.0458
7.5831
7.5645
7.5460
7.4661
7.4466
7.4280
7.3074
7.2870
7.1703
7.1503
6.0044
4.3824
4.3659
4.3494
4.2360
4.2232
4.2078
4.1949
3.8909
3.8864
3.8626
3.8586
3.7222
3.7027
3.6941
3.6746
3.6660
3.6576
3.6471
3.6296
3.6193
2.3585
2.3406
2.2976
2.1314
1.8573
1.8404
1.8224
1.7222
1.6904
1.6539
1.6298
1.6213
1.6055
1.5844
1.5614
4i-major
2.07
1.05
2.05
1.96
2.00
1.06
3.07
1.09
1.05
2.10
1.05
4.14
1.24
2.12
5.17
f1 (ppm)
166.9063
137.5731
137.4089
135.9434
133.0457
130.6754
129.7693
129.3700
128.5504
124.8914
124.5474
78.5510
65.1296
64.8940
63.3006
45.0511
29.2374
27.9953
27.5488
24.2554
21.2932
4i-major
f1 (ppm)



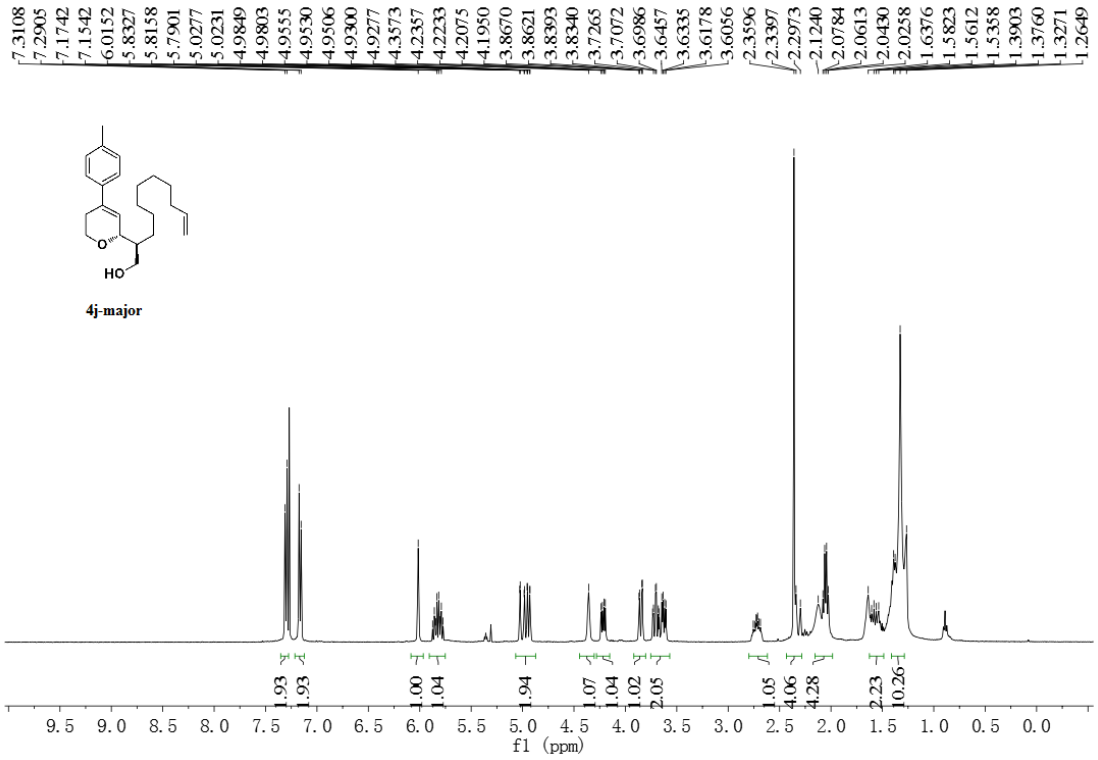


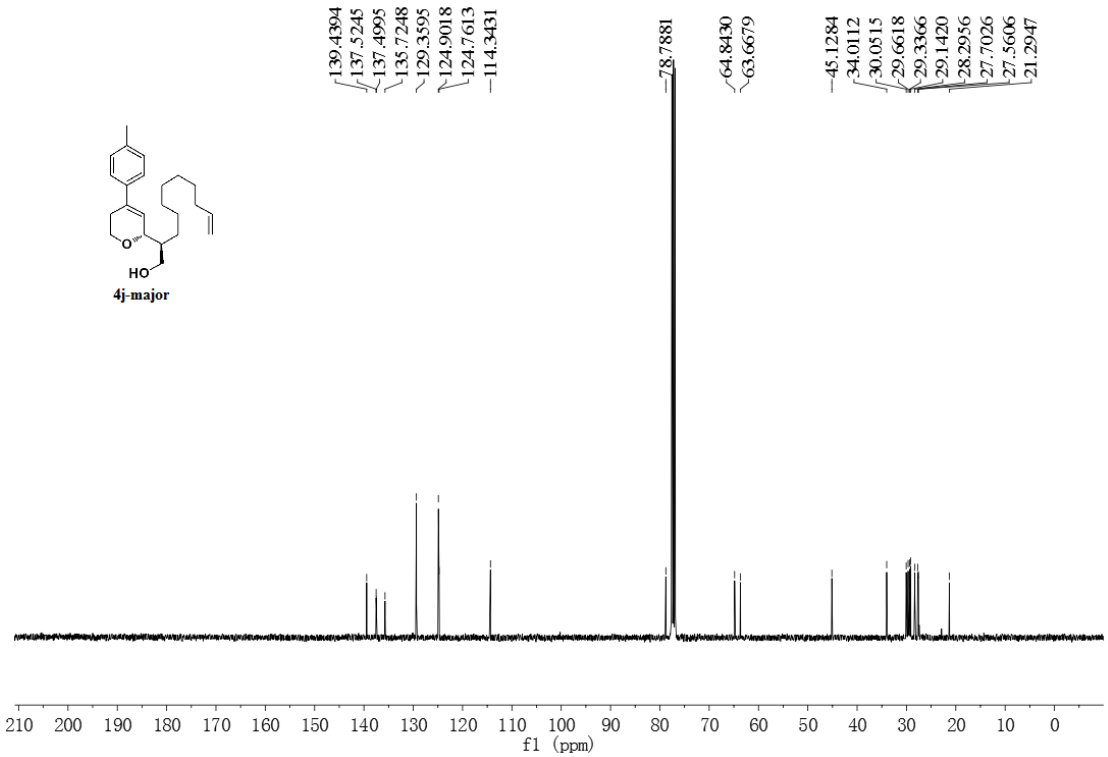
4i-minor

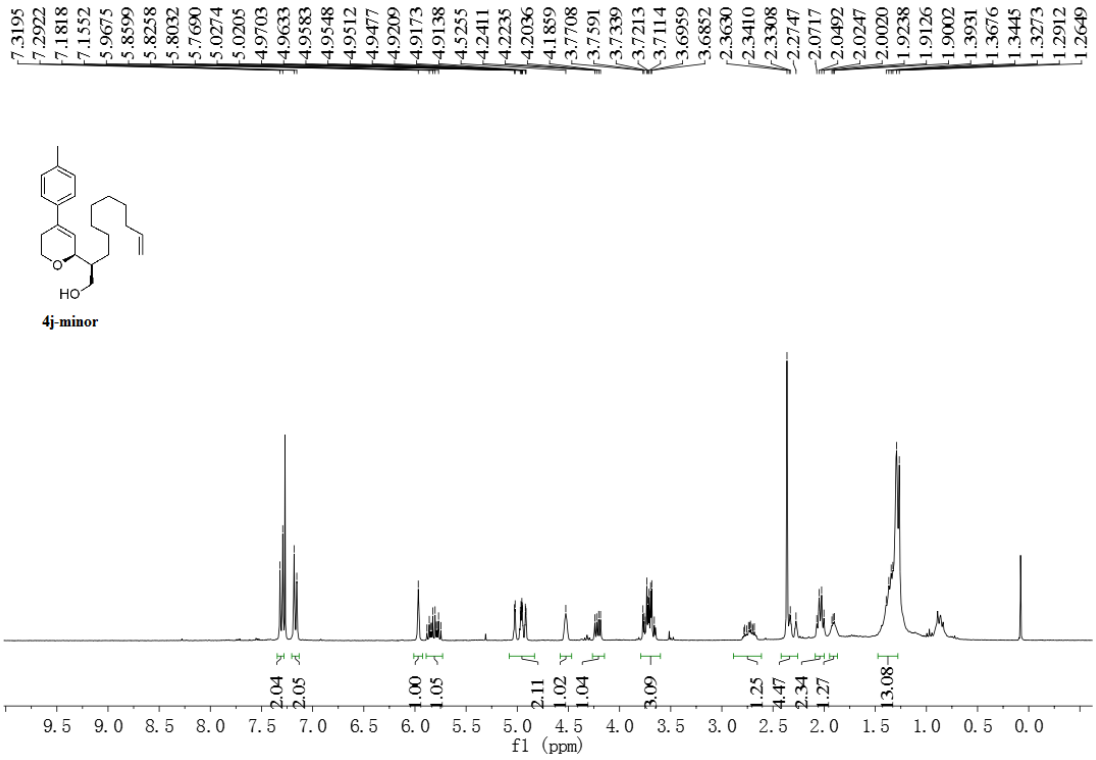


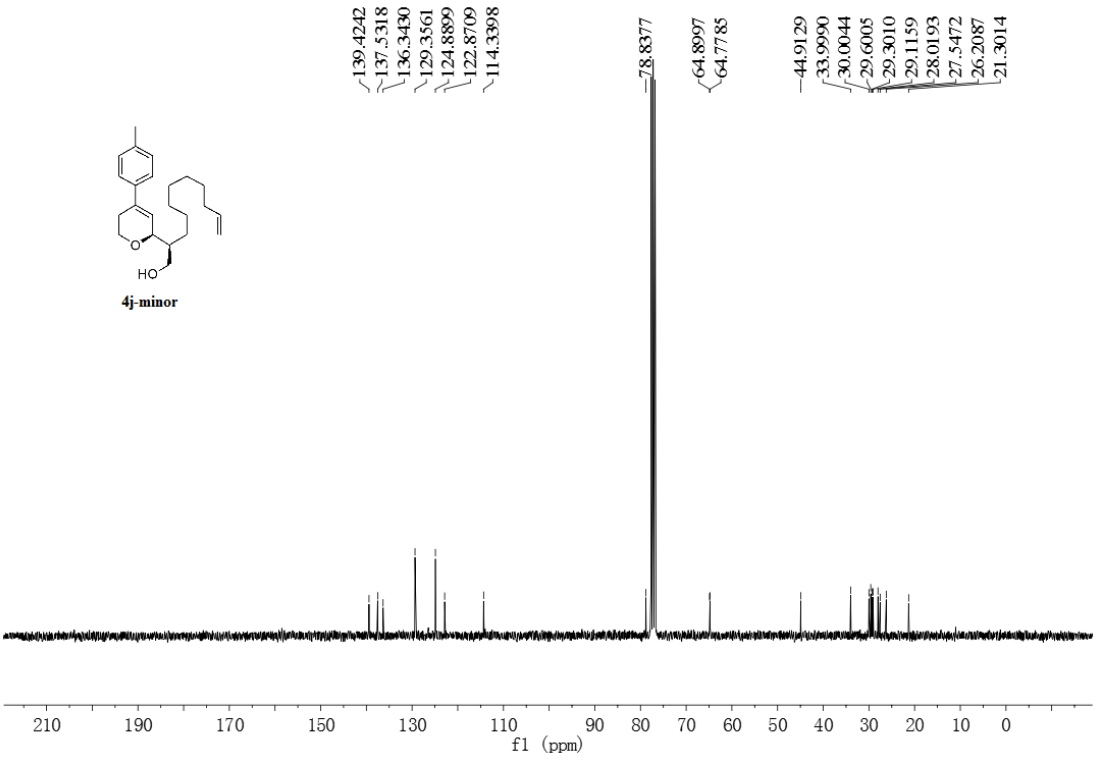


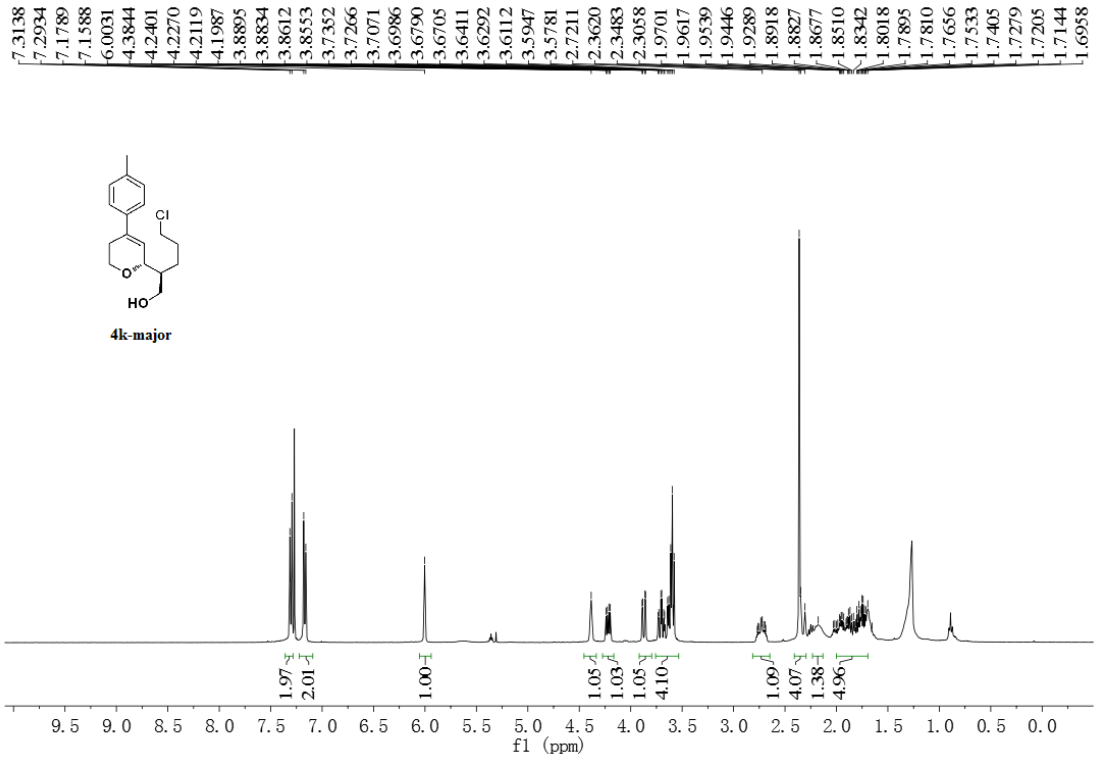
4i-minor

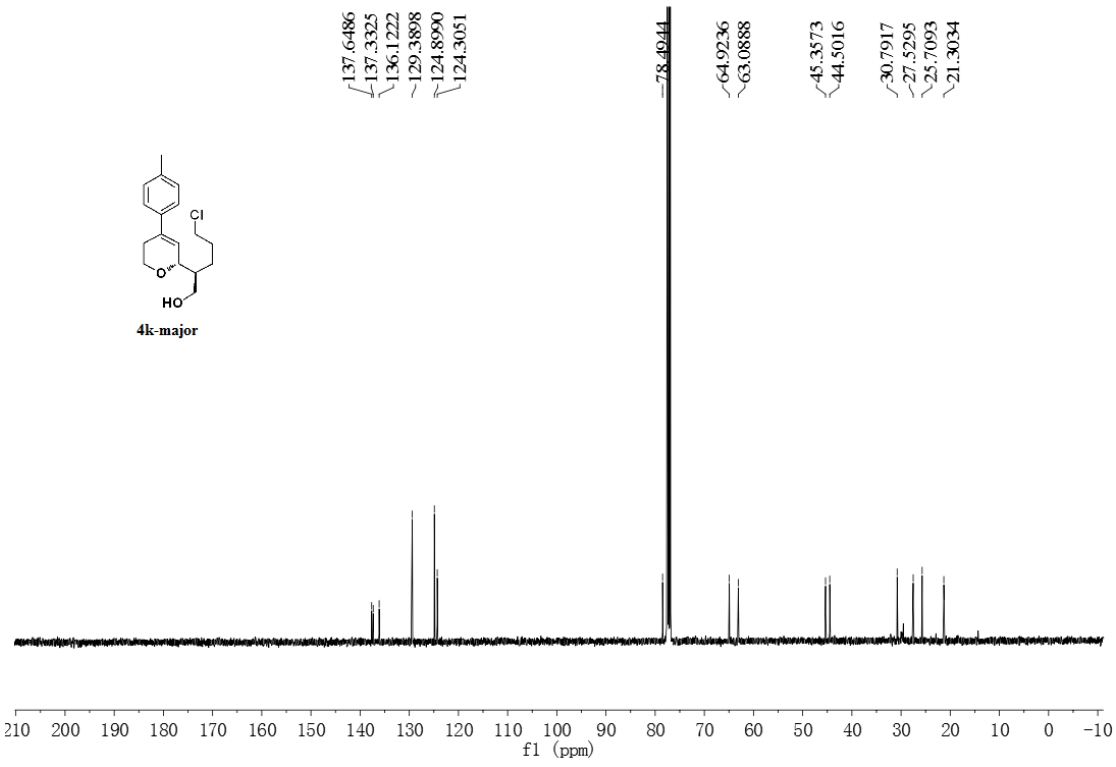

7.3108
7.2905
7.1742
7.1542
6.0152
5.8327
5.8158
5.7901
5.0277
5.0231
4.9849
4.9803
4.9555
4.9530
4.9506
4.9300
4.9277
4.3573
4.2357
4.2233
4.2075
4.1950
3.8670
3.8621
3.8393
3.8340
3.7265
3.7072
3.6986
3.6457
3.6335
3.6178
3.6056
2.3596
2.3397
2.2973
2.1240
2.0784
2.0613
2.0430
2.0258
1.6376
1.5823
1.5612
1.5358
1.3903
1.3760
1.3271
1.2649
HO
4j-major
1.93
1.93
1.00
1.04
1.94
1.07
1.04
1.02
2.05
1.05
4.06
4.28
2.23
10.26
f1 (ppm)

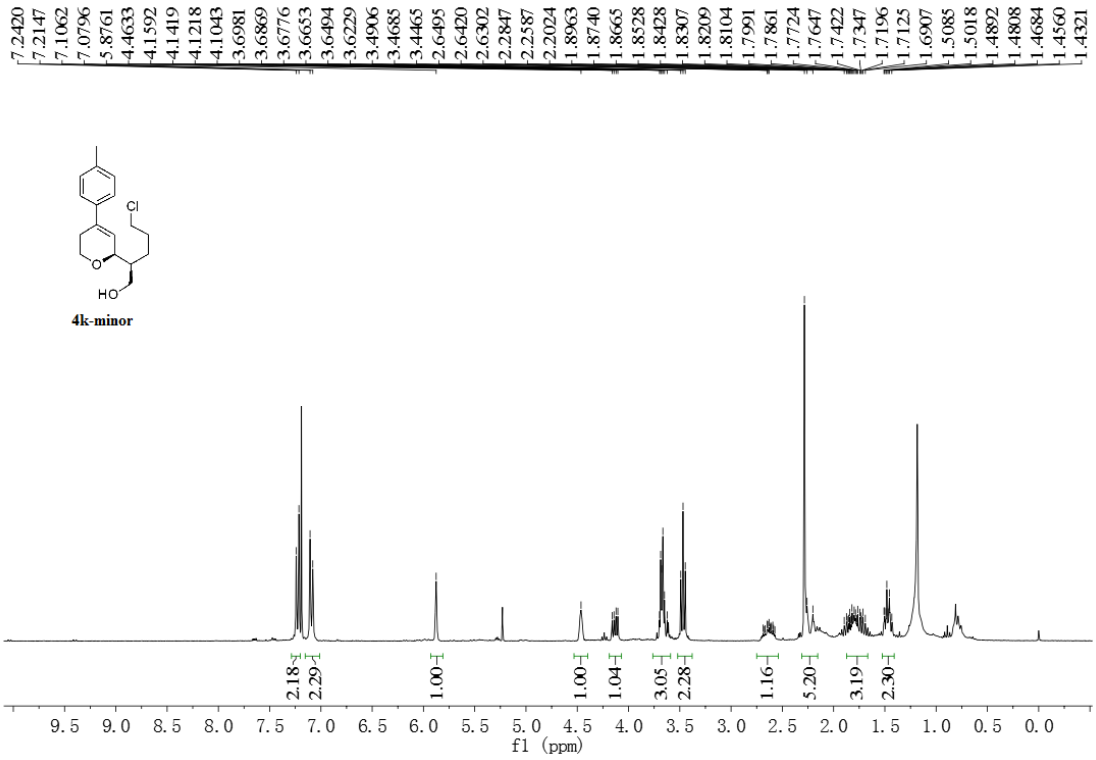

139.4394
137.5245
137.4995
135.7248
129.3595
124.9018
124.7613
114.3431
78.7881
64.8430
63.6679
45.1284
34.0112
30.0515
29.6618
29.3366
29.1420
28.2956
27.7026
27.5606
21.2947
HO
4j-major
f1 (ppm)

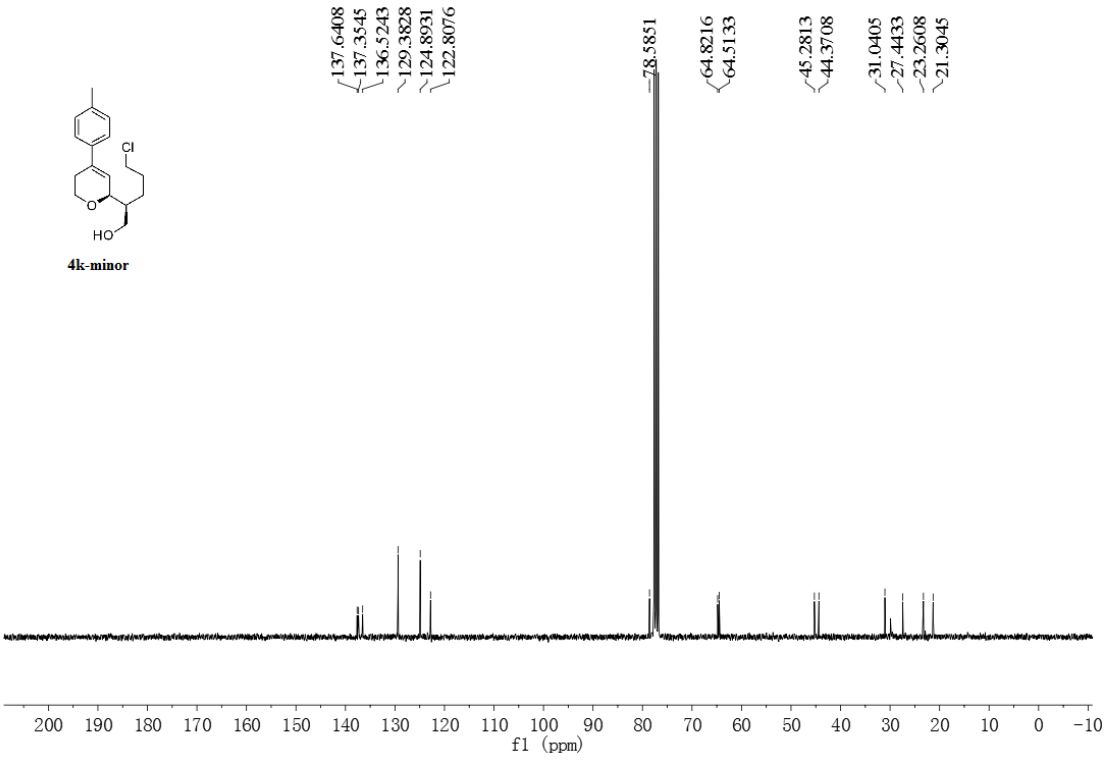

7.3195
7.2922
7.1818
7.1552
5.9675
5.8599
5.8258
5.8032
5.7690
5.0274
5.0205
4.9703
4.9633
4.9583
4.9548
4.9512
4.9477
4.9209
4.9173
4.9138
4.5255
4.2411
4.2235
4.2036
4.1859
3.7708
3.7591
3.7339
3.7213
3.7114
3.6959
3.6852
2.3630
2.3410
2.3308
2.2747
2.0717
2.0492
2.0247
2.0020
1.9238
1.9126
1.9002
1.3931
1.3676
1.3445
1.3273
1.2912
1.2649
HO
4j-minor
2.04
2.05
1.00
1.05
2.11
1.02
1.04
3.09
1.25
4.47
2.34
1.27
13.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

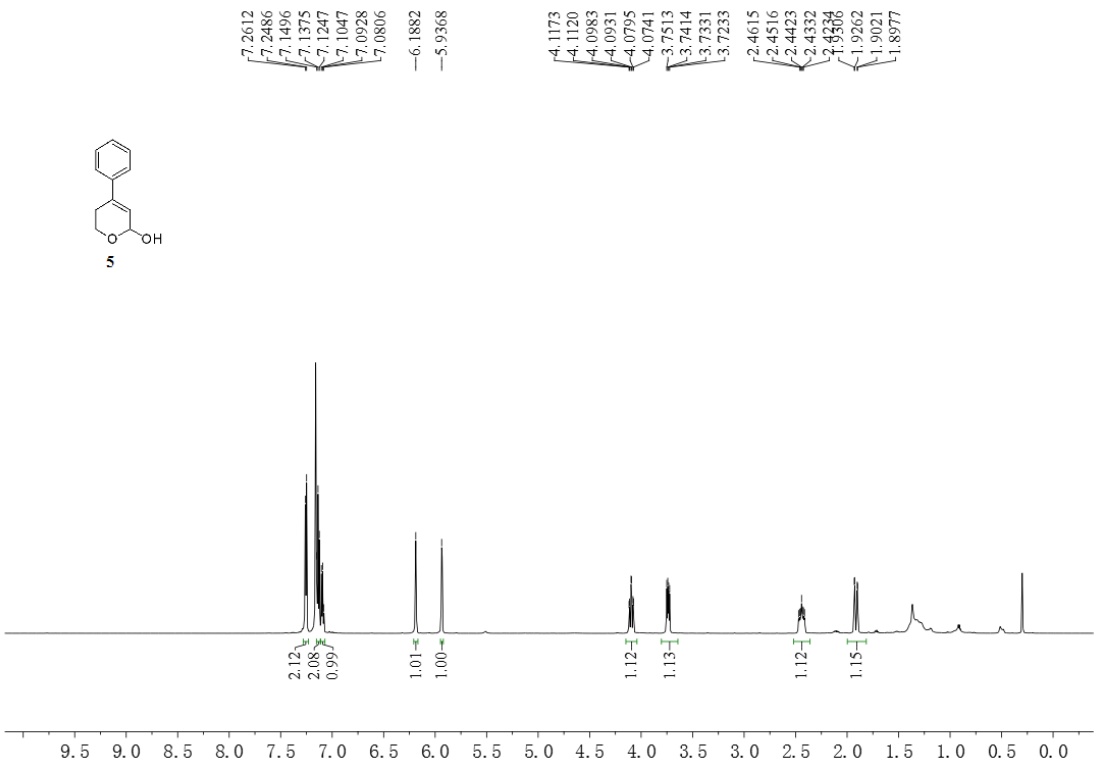

139.4242
137.5318
136.3430
129.3561
124.8899
122.8709
114.3398
78.8377
64.8997
64.7785
44.9129
33.9990
30.0044
29.6005
29.3010
29.1159
28.0193
27.5472
26.2087
21.3014
HO
4j-minor
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

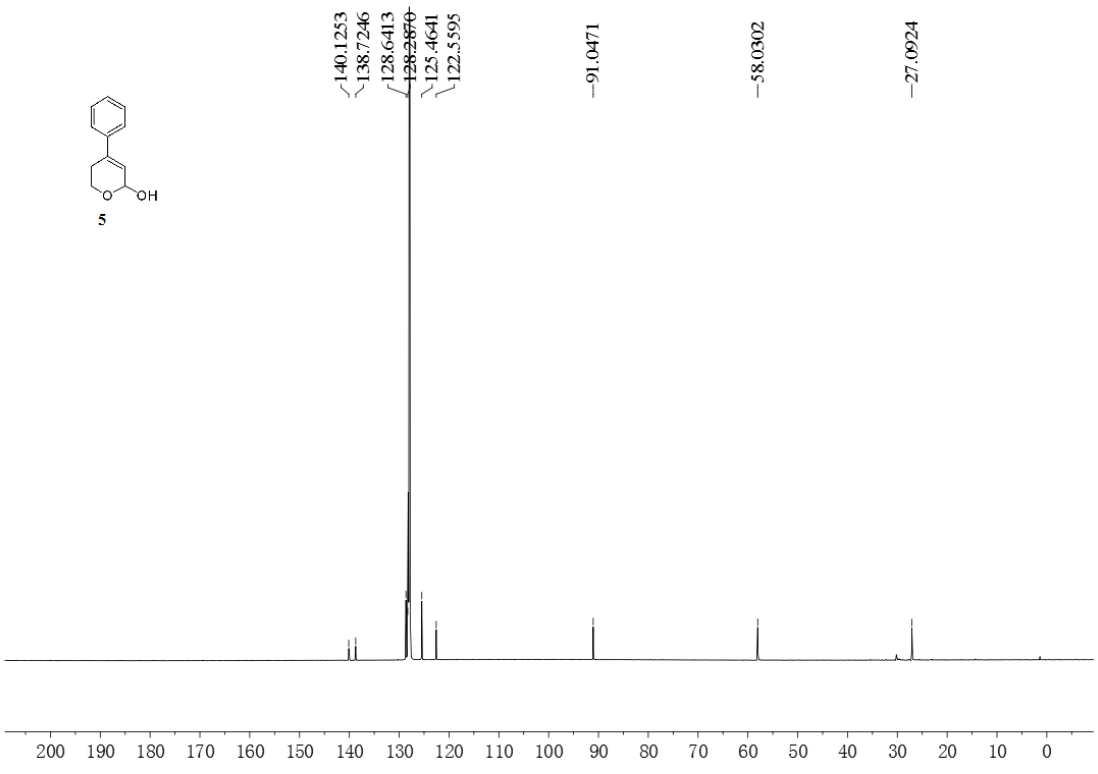

7.3138
7.2934
7.1789
7.1588
6.0031
4.3844
4.2401
4.2270
4.2119
4.1987
3.8895
3.8834
3.8612
3.8553
3.7352
3.7266
3.7071
3.6986
3.6790
3.6705
3.6411
3.6292
3.6112
3.5947
3.5781
2.7211
2.3620
2.3483
2.3058
1.9701
1.9617
1.9539
1.9446
1.9289
1.8918
1.8827
1.8677
1.8510
1.8342
1.8018
1.7895
1.7810
1.7656
1.7533
1.7405
1.7279
1.7205
1.7144
1.6958
Cl
O
HO
4k-major
1.97
2.01
1.00
1.05
1.03
1.05
4.10
1.09
4.07
1.38
4.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

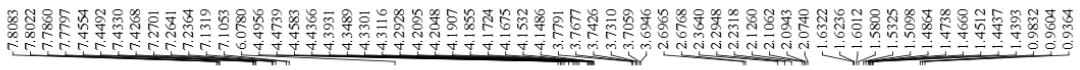

137.6486
137.3325
136.1222
129.3898
124.8990
124.3051
78.4944
64.9236
63.0888
45.3573
44.5016
30.7917
27.5295
25.7093
21.3034
Cl
O
HO
4k-major
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

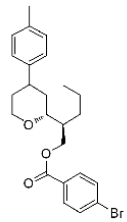

7.2420
7.2147
7.1062
7.0796
5.8761
4.4633
4.1592
4.1419
4.1218
4.1043
3.6981
3.6869
3.6776
3.6653
3.6494
3.6229
3.4906
3.4685
3.4465
2.6495
2.6420
2.6302
2.2847
2.2587
2.2024
1.8963
1.8740
1.8665
1.8528
1.8428
1.8307
1.8209
1.8104
1.7991
1.7861
1.7724
1.7647
1.7422
1.7347
1.7196
1.7125
1.6907
1.5085
1.5018
1.4892
1.4808
1.4684
1.4560
1.4321
Cl
O
HO
4k-minor
2.18
2.29
1.00
1.00
1.04
3.05
2.28
1.16
5.20
3.19
2.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


137.6408
137.3545
136.5243
129.3828
124.8931
122.8076
78.5851
64.8216
64.5133
45.2813
44.3708
31.0405
27.4433
23.2608
21.3045
Cl
O
HO
4k-minor
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

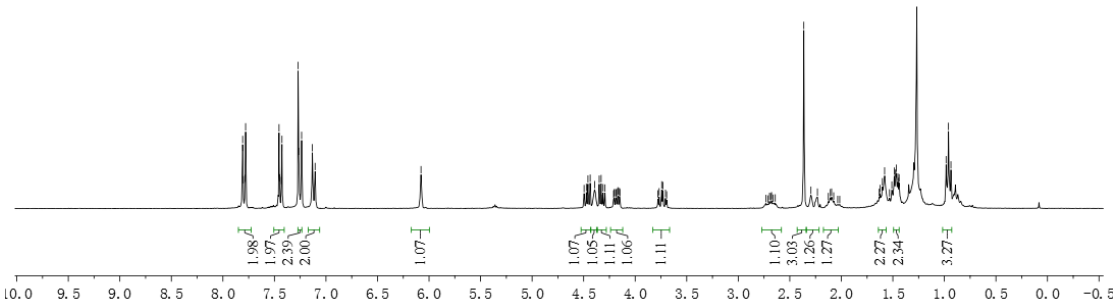

7.2612
7.2486
7.1496
7.1375
7.1247
7.1047
7.0928
7.0806
6.1882
5.9368
4.1173
4.1120
4.0983
4.0931
4.0795
4.0741
3.7513
3.7414
3.7331
3.7233
2.4615
2.4516
2.4423
2.4332
2.4234
1.9306
1.9262
1.9021
1.8977
OH
5
2.12
2.08
0.99
1.01
1.00
1.12
1.13
1.12
1.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

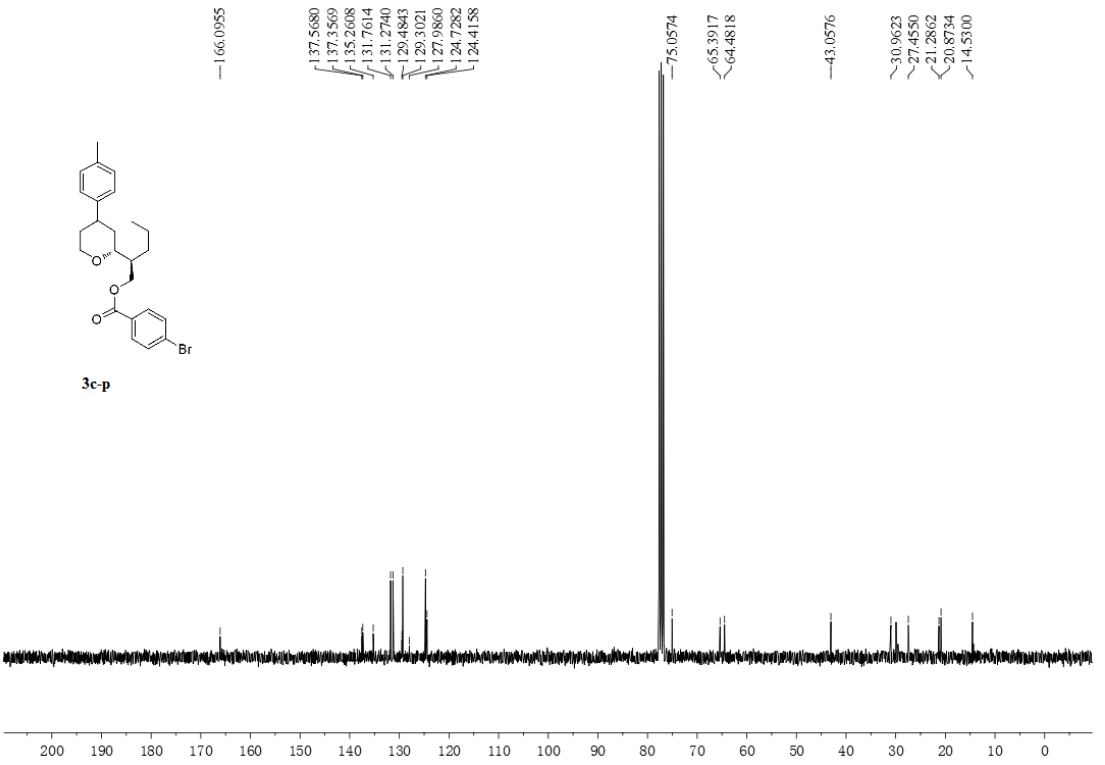

140.1253
138.7246
128.6413
128.2870
125.4641
122.5595
91.0471
58.0302
27.0924
OH
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.8083
7.8022
7.7860
7.7797
7.4554
7.4492
7.4330
7.4268
7.2701
7.2641
7.2364
7.1319
7.1053
6.0780
4.4956
4.4739
4.4583
4.4366
4.3931
4.3489
4.3301
4.3116
4.2928
4.2095
4.2048
4.1907
4.1855
4.1724
4.1675
4.1532
4.1486
3.7791
3.7677
3.7426
3.7310
3.7059
3.6946
2.6965
2.6768
2.3640
2.2948
2.2318
2.1260
2.1062
2.0943
2.0740
1.6322
1.6236
1.6012
1.5800
1.5325
1.5098
1.4864
1.4738
1.4660
1.4512
1.4437
1.4393
0.9832
0.9604
0.9364


O
O
O
Br

3c-p

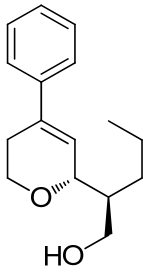

1.98
1.97
2.39
2.00
1.07
1.07
1.05
1.11
1.06
1.11
1.10
3.03
1.26
1.27
2.27
2.34
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


166.0955
137.5680
137.3569
135.2608
131.7614
131.2740
129.4843
129.3021
127.9860
124.7282
124.4158
75.0574
65.3917
64.4818
43.0576
30.9623
27.4550
21.2862
20.8734
14.5300
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

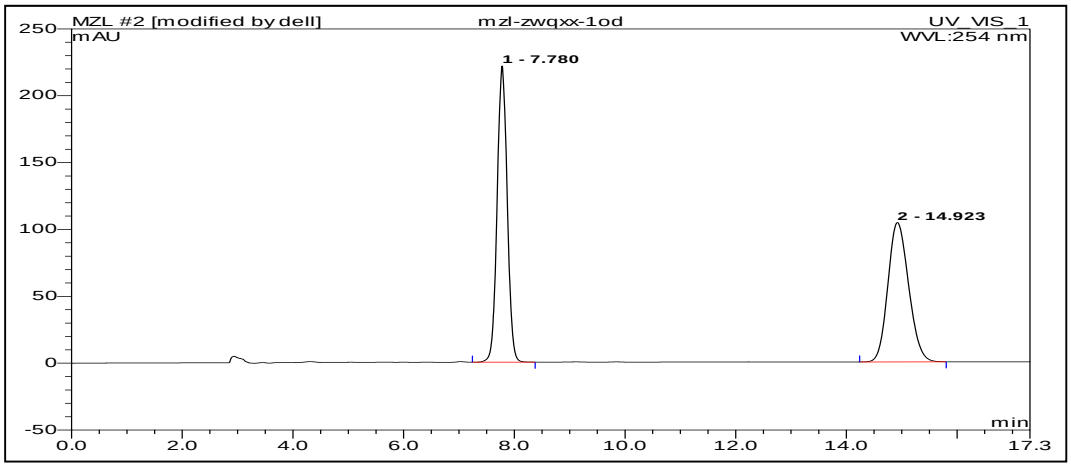
O
O
O
Br

3c-p

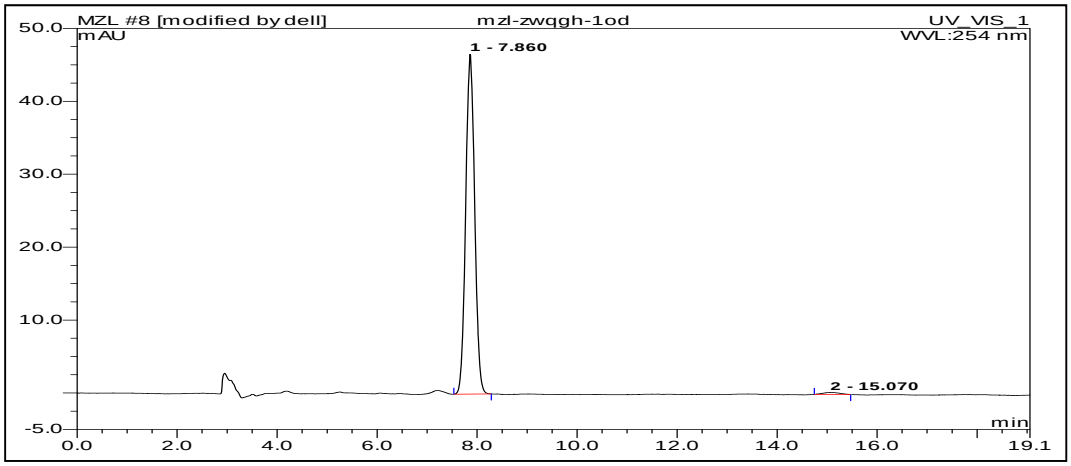
HPLC traces



3a-major

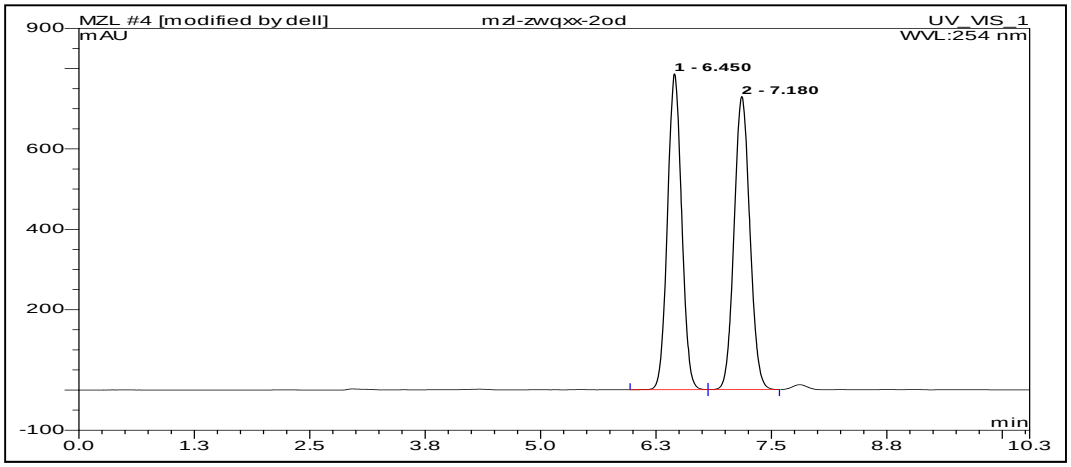


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.78	n.a.	221.491	46.903	50.91	BMB*
2	14.92	n.a.	104.216	45.235	49.09	BMB
Total:			325.707	92.138	100.00	

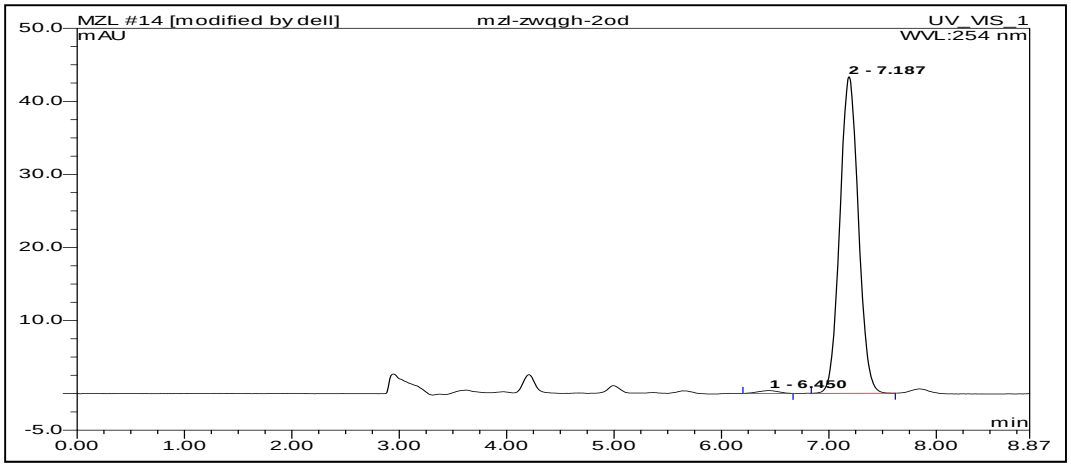


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.86	n.a.	46.607	9.733	98.95	BMB
2	15.07	n.a.	0.272	0.103	1.05	BMB*
Total:			46.879	9.837	100.00	

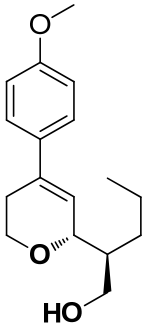
3a-minor



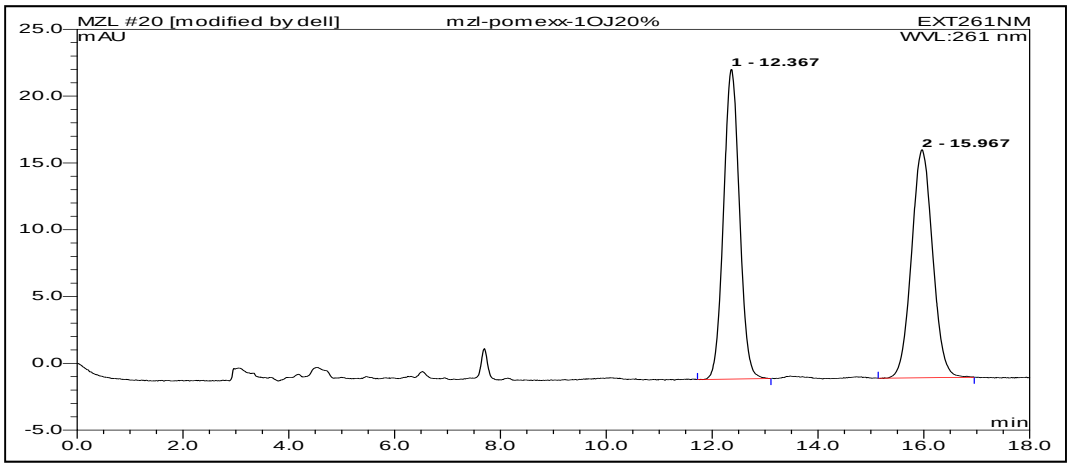
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.45	n.a.	786.124	140.602	49.26	BM *
2	7.18	n.a.	729.557	144.814	50.74	MB*
Total:			1515.680	285.417	100.00	



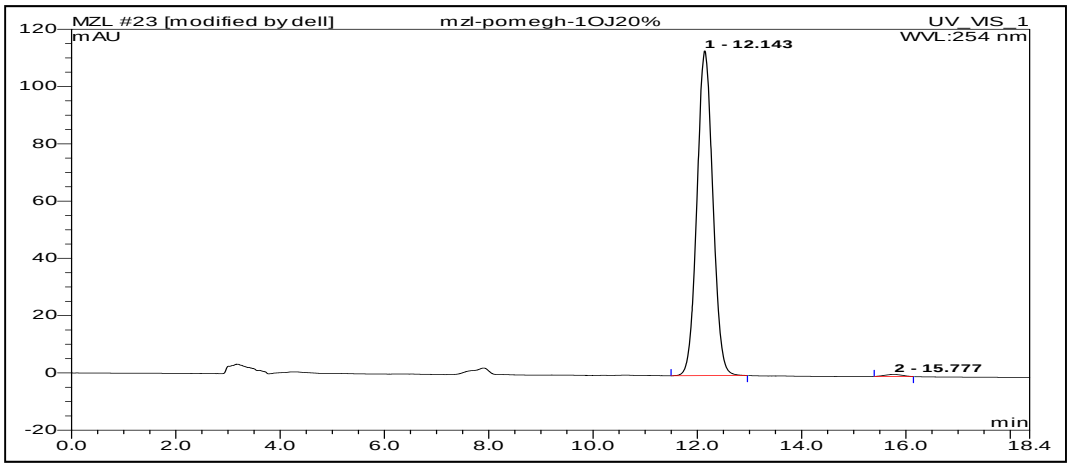
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.45	n.a.	0.370	0.081	0.92	BMB
2	7.19	n.a.	43.311	8.686	99.08	BMB*
Total:			43.681	8.767	100.00	



3b-major

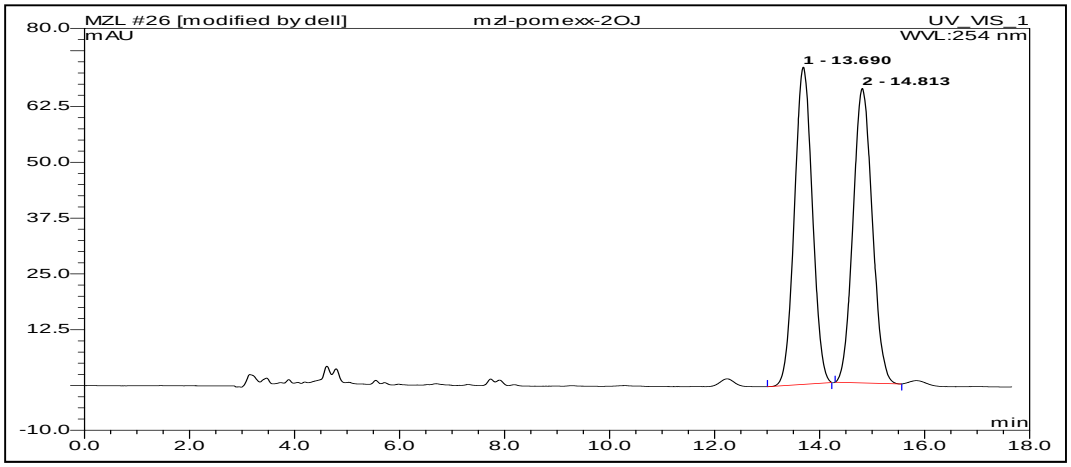


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	12.37	n.a.	23.178	8.109	50.62	BMB*
2	15.97	n.a.	17.075	7.912	49.38	BMB*
Total:			40.253	16.020	100.00	

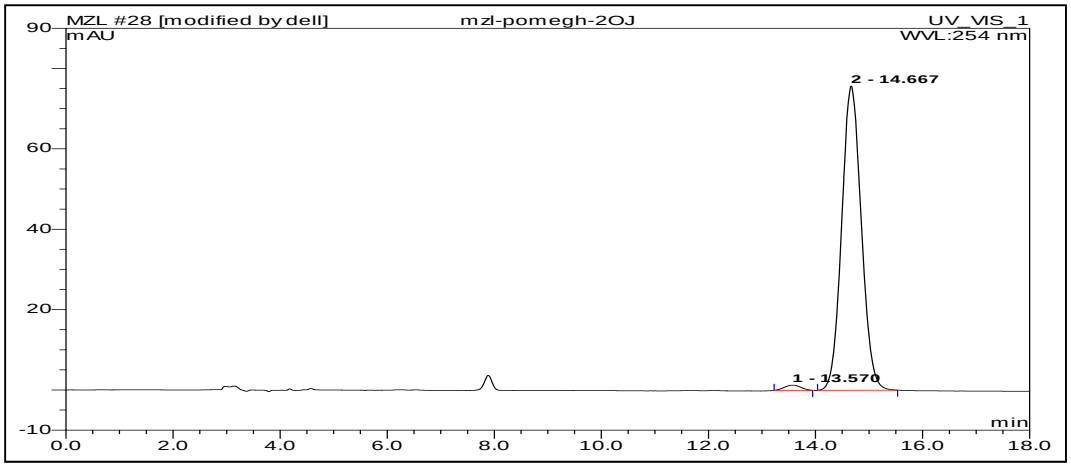


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	12.14	n.a.	113.407	40.088	99.32	BMB*
2	15.78	n.a.	0.702	0.275	0.68	BMB*
Total:			114.110	40.362	100.00	

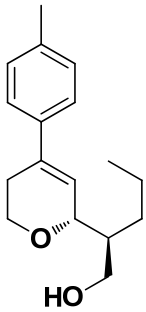
3b-minor



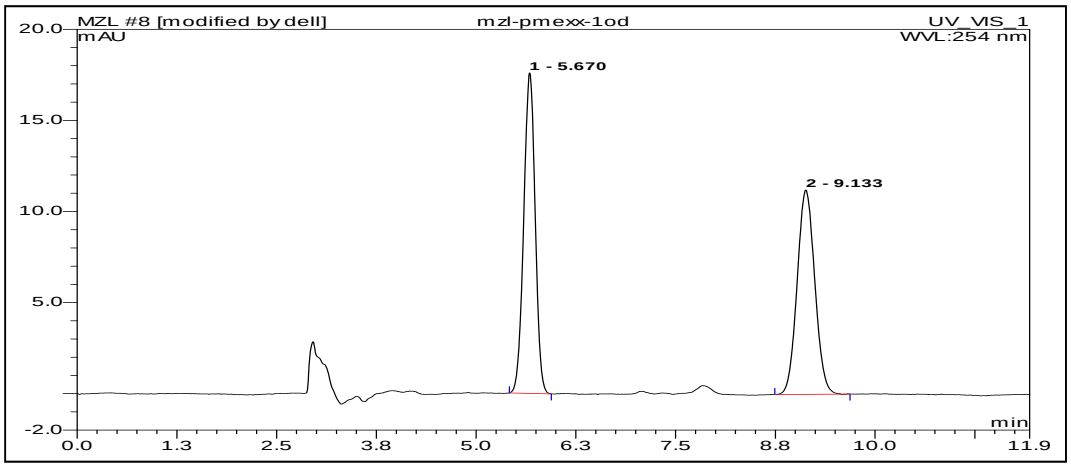
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	13.69	n.a.	71.038	28.148	50.03	BMB*
2	14.81	n.a.	65.954	28.113	49.97	BMB*
Total:			136.992	56.262	100.00	



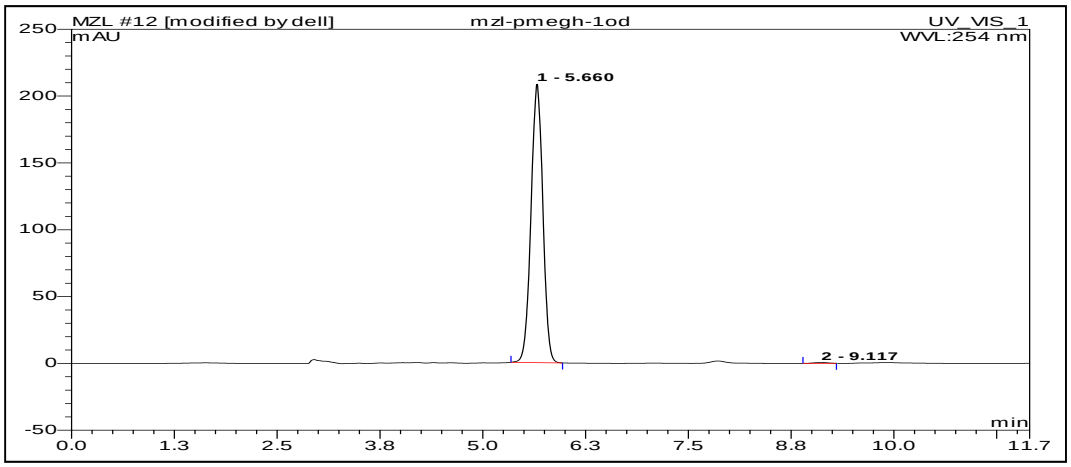
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	13.57	n.a.	1.098	0.337	1.04	BMB*
2	14.67	n.a.	75.705	32.199	98.96	BMB*
Total:			76.803	32.536	100.00	



3c-major

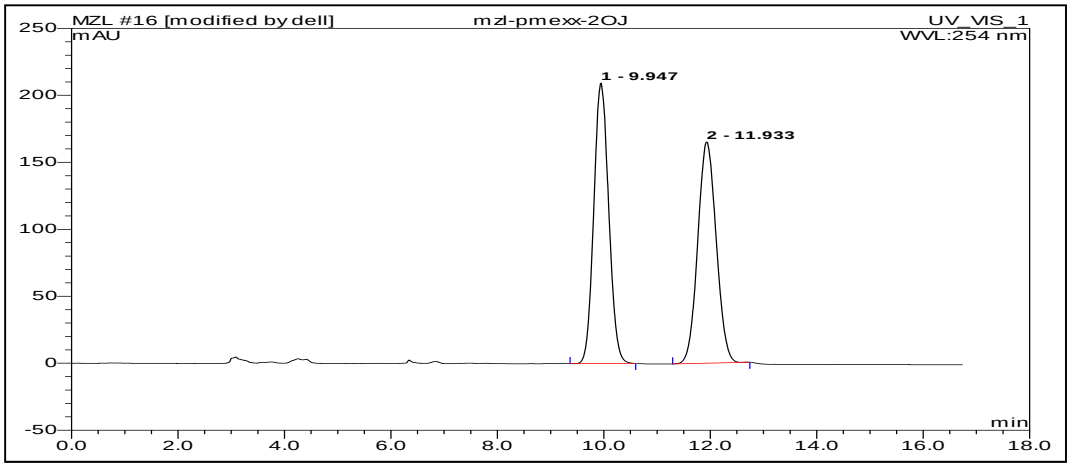


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.67	n.a.	17.592	2.930	50.45	BMB
2	9.13	n.a.	11.216	2.878	49.55	BMB*
Total:			28.808	5.807	100.00	

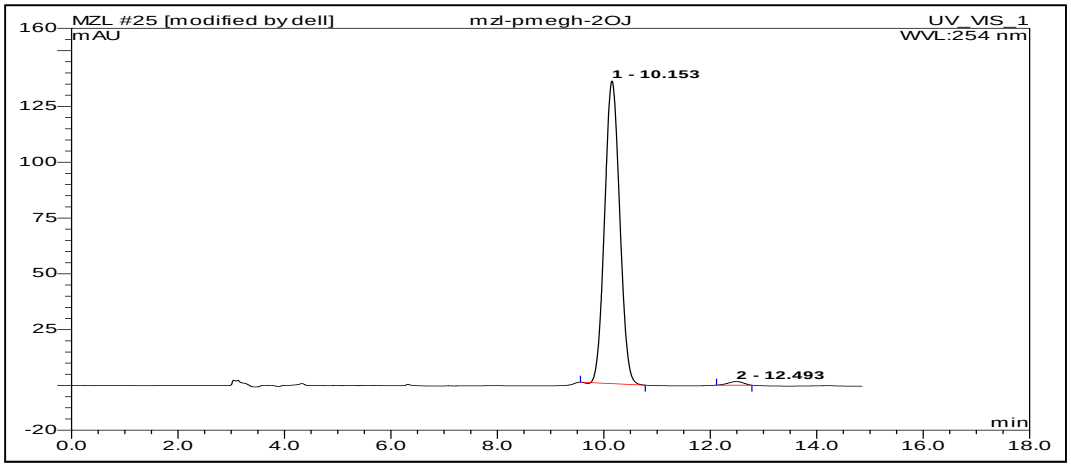


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.66	n.a.	208.368	34.810	99.64	BMB*
2	9.12	n.a.	0.600	0.127	0.36	BMB*
Total:			208.967	34.937	100.00	

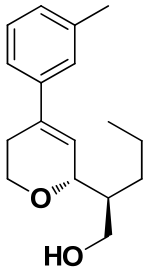
3c-minor



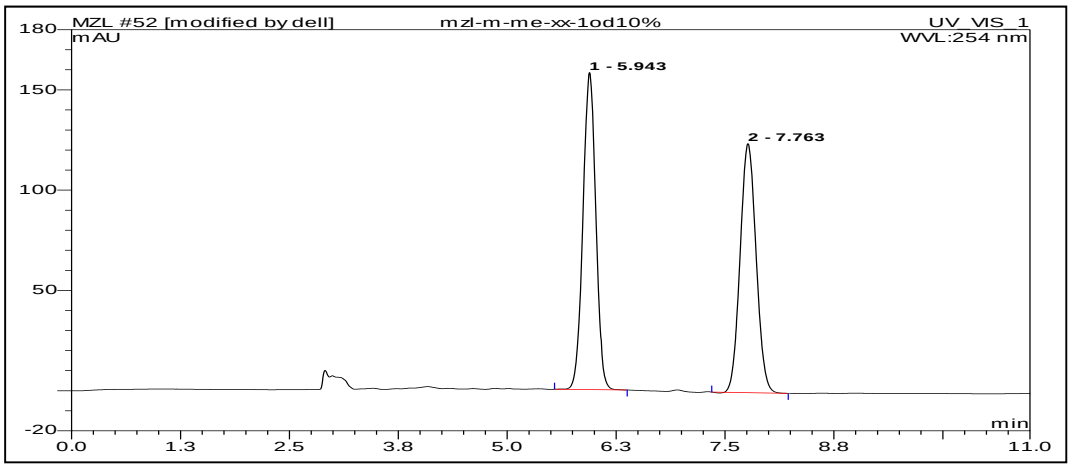
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	9.95	n.a.	209.371	68.165	50.63	BMB*
2	11.93	n.a.	165.152	66.467	49.37	BMB*
Total:			374.523	134.632	100.00	



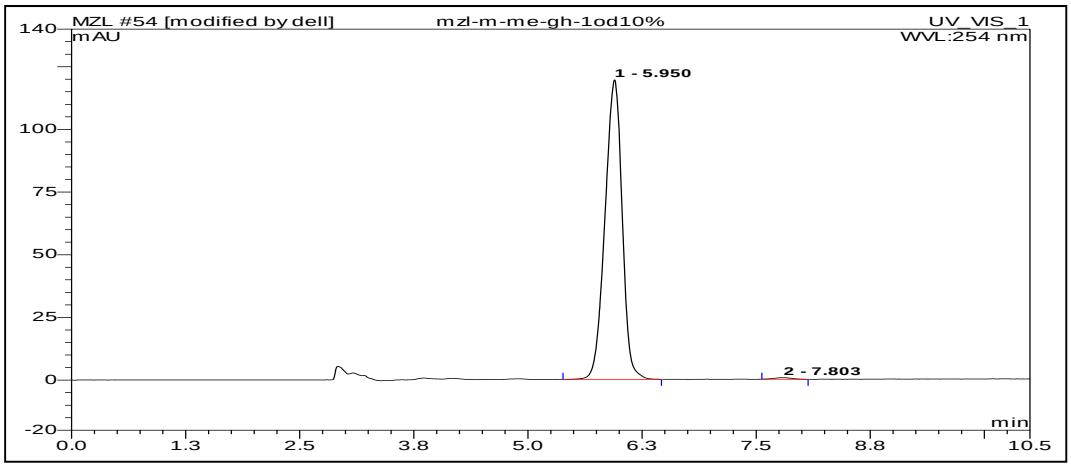
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	10.15	n.a.	135.570	44.597	98.80	BMB*
2	12.49	n.a.	1.647	0.543	1.20	BMB*
Total:			137.217	45.140	100.00	



3d-major

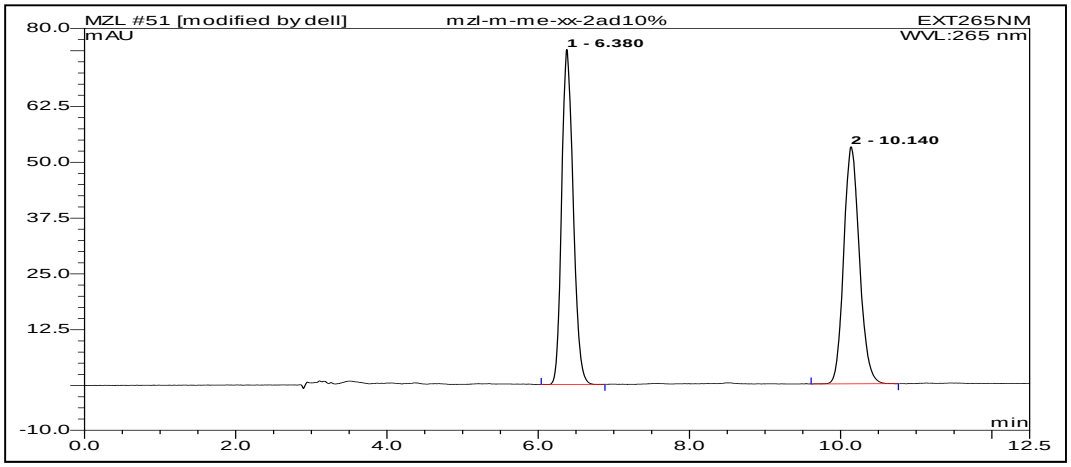


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.94	n.a.	158.012	27.190	50.73	BMB*
2	7.76	n.a.	124.159	26.409	49.27	BMB*
Total:			282.171	53.599	100.00	

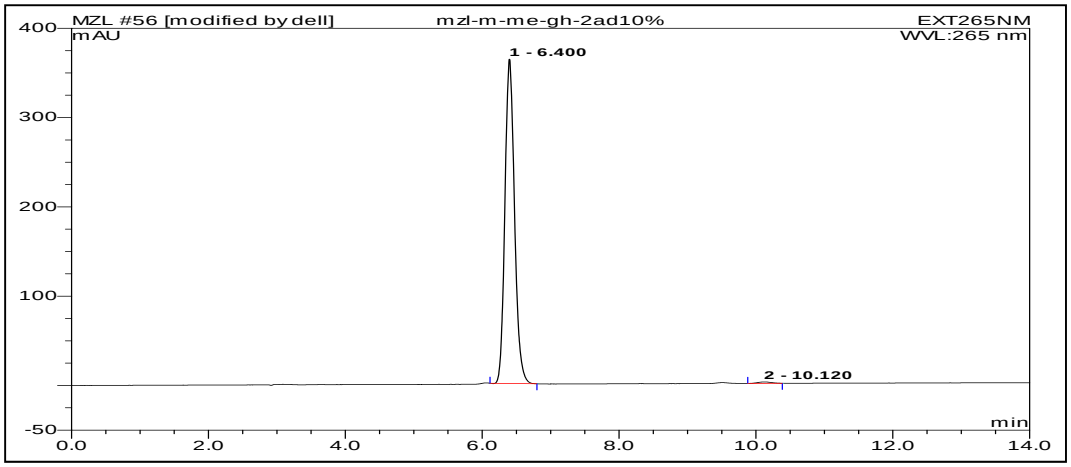


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.95	n.a.	119.404	26.084	99.47	BMB*
2	7.80	n.a.	0.626	0.139	0.53	BMB*
Total:			120.030	26.223	100.00	

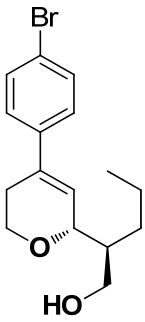
3d-minor



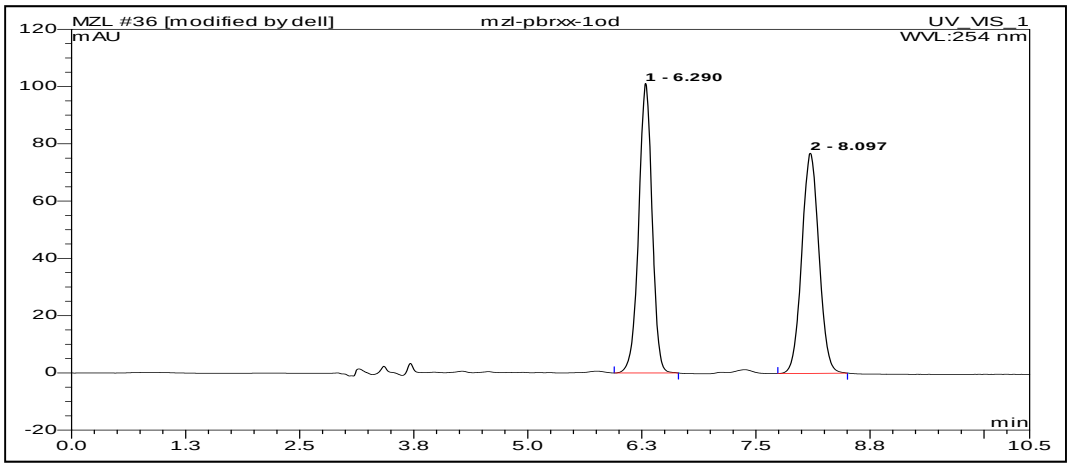
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.38	n.a.	75.025	13.288	50.97	BMB*
2	10.14	n.a.	53.076	12.783	49.03	BMB*
Total:			128.101	26.071	100.00	



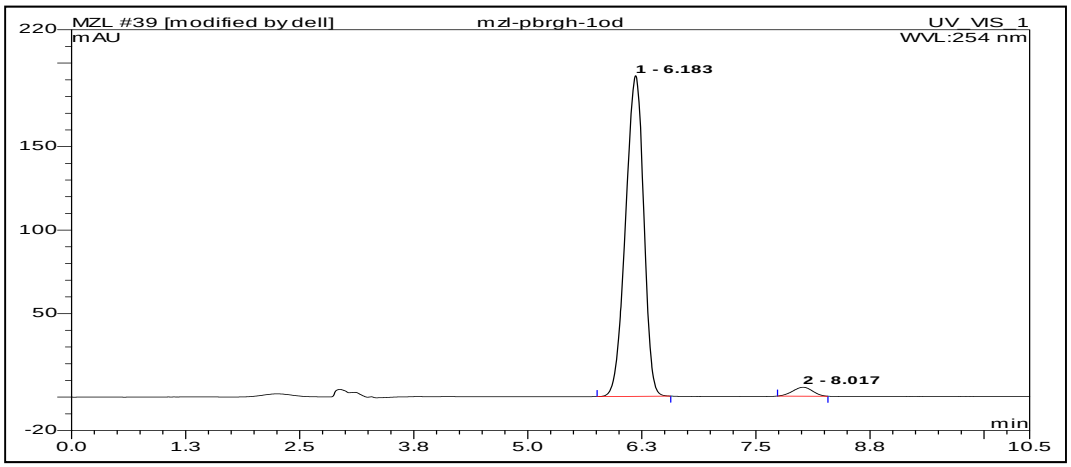
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.40	n.a.	363.206	59.104	99.42	BMB*
2	10.12	n.a.	1.562	0.344	0.58	BMB*
Total:			364.768	59.448	100.00	



3f-major

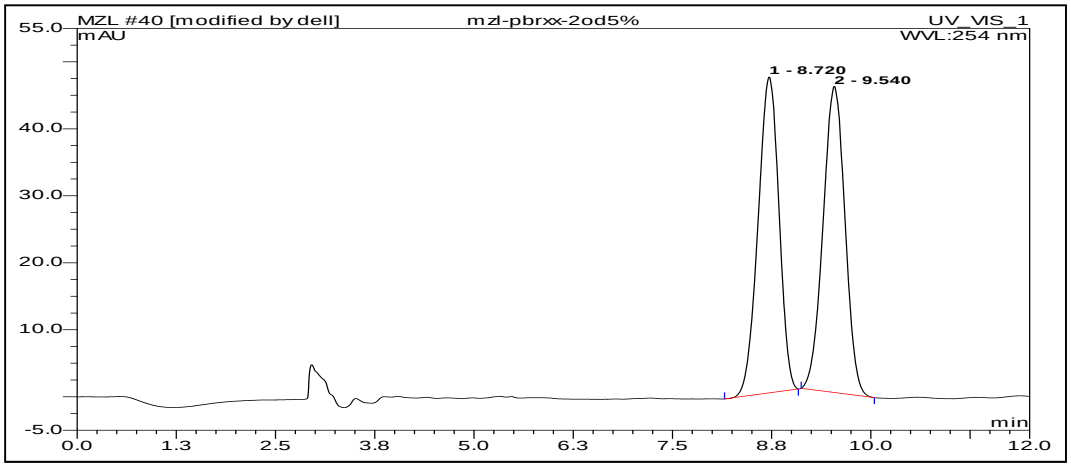


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.29	n.a.	101.102	17.238	50.63	BMB*
2	8.10	n.a.	76.861	16.811	49.37	BMB*
Total:			177.963	34.049	100.00	

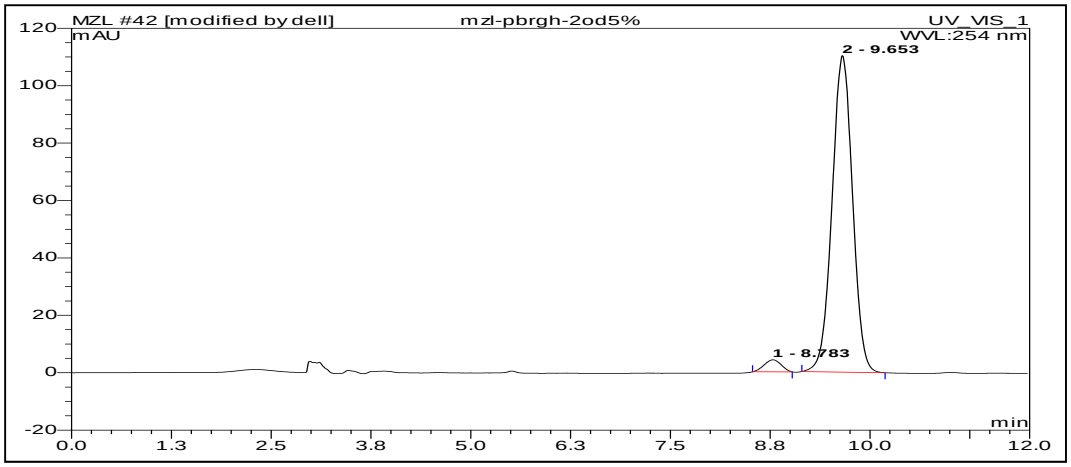


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.18	n.a.	192.016	44.306	97.08	BMB*
2	8.02	n.a.	5.307	1.333	2.92	BMB*
Total:			197.323	45.639	100.00	

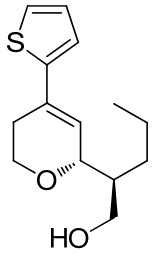
3f-minor



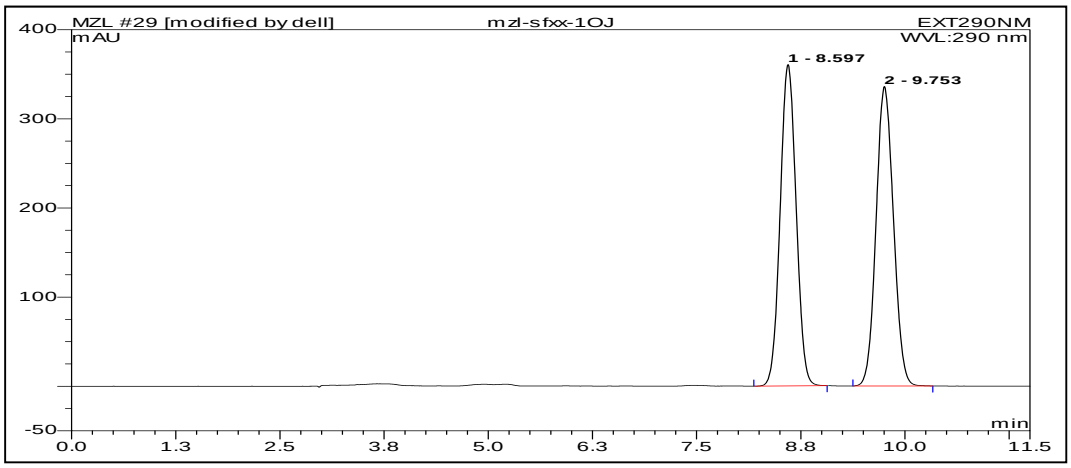
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.72	n.a.	47.170	14.415	49.54	BMB*
2	9.54	n.a.	45.699	14.680	50.46	BMB*
Total:			92.869	29.095	100.00	



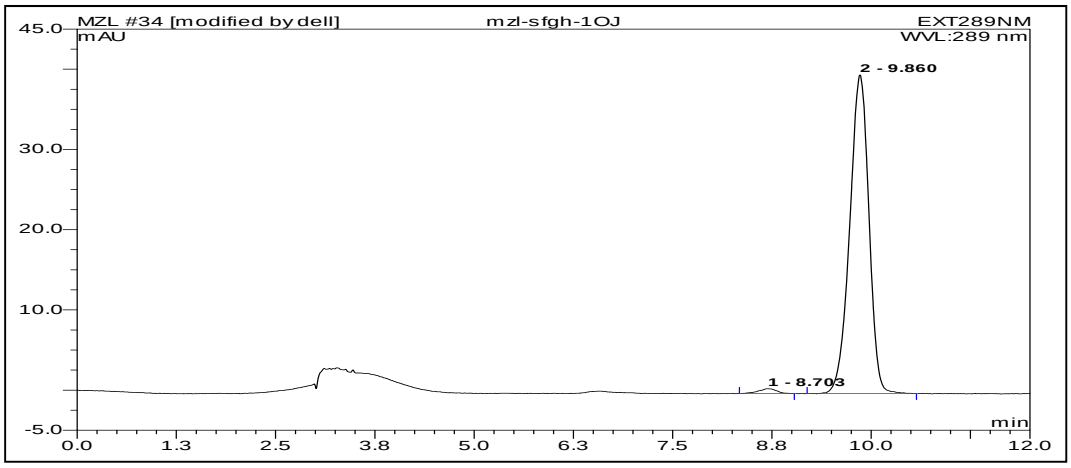
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.78	n.a.	4.181	1.029	3.04	BMB*
2	9.65	n.a.	110.270	32.869	96.96	BMB*
Total:			114.451	33.898	100.00	



3g-major

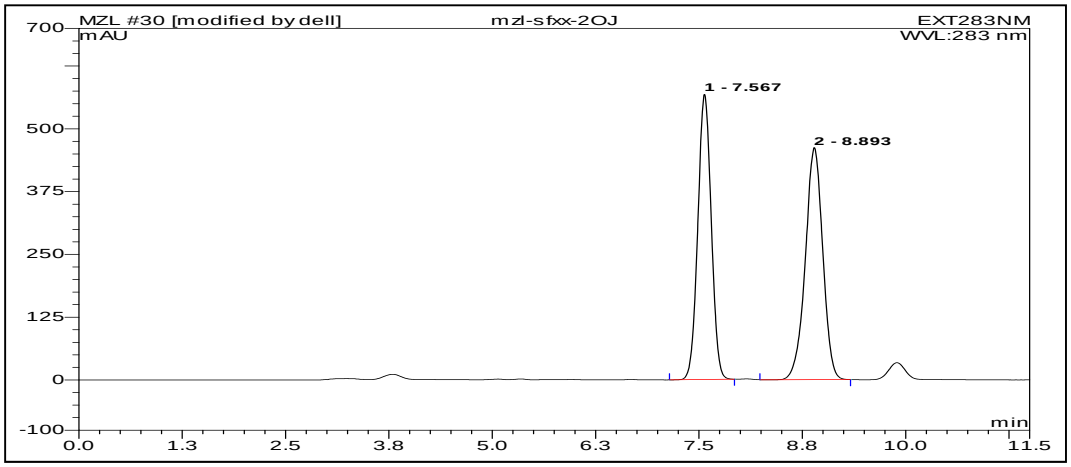


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.60	n.a.	360.435	80.040	49.59	BMB*
2	9.75	n.a.	335.813	81.354	50.41	BMB*
Total:			696.248	161.395	100.00	

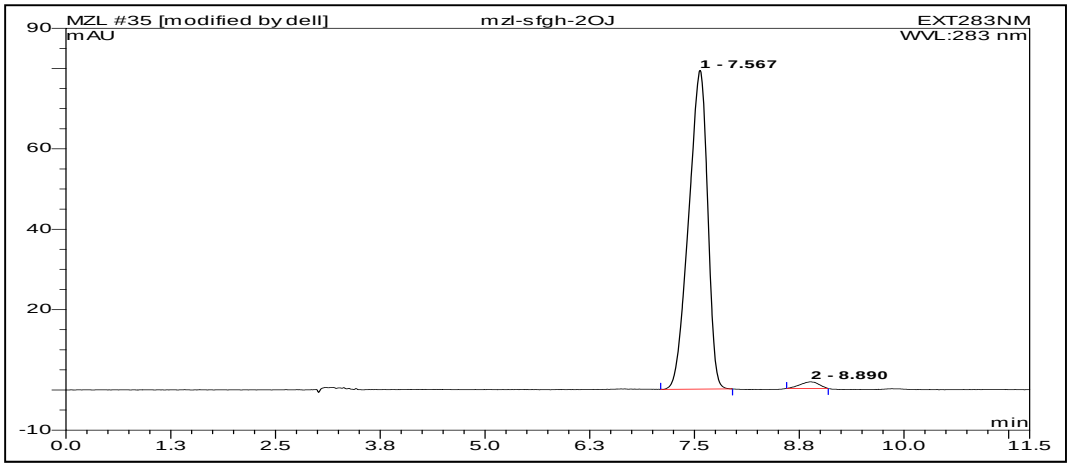


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.70	n.a.	0.526	0.119	1.06	BMB*
2	9.86	n.a.	39.705	11.110	98.94	BMB*
Total:			40.231	11.228	100.00	

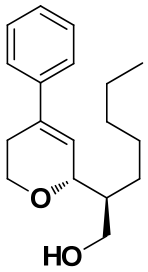
3g-minor



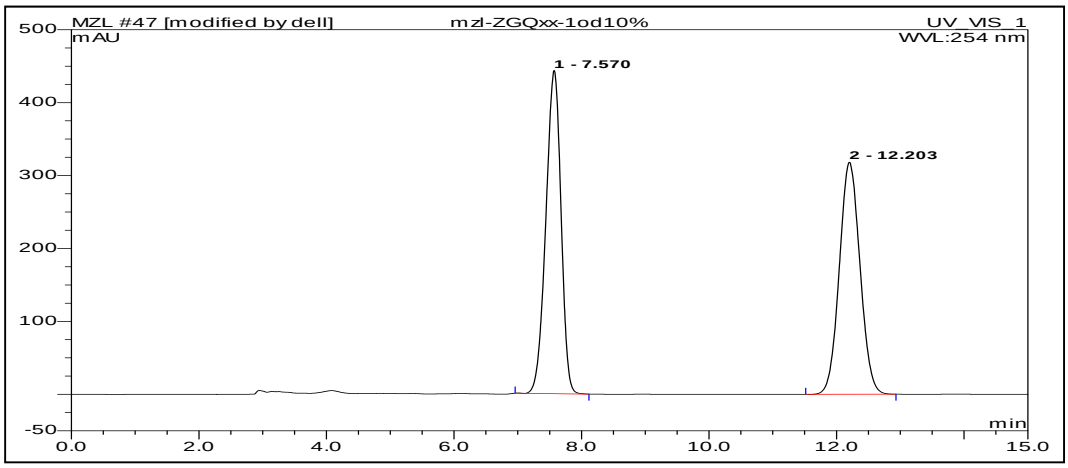
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.57	n.a.	567.881	107.114	48.65	BMB*
2	8.89	n.a.	462.065	113.044	51.35	BMB*
Total:			1029.946	220.158	100.00	



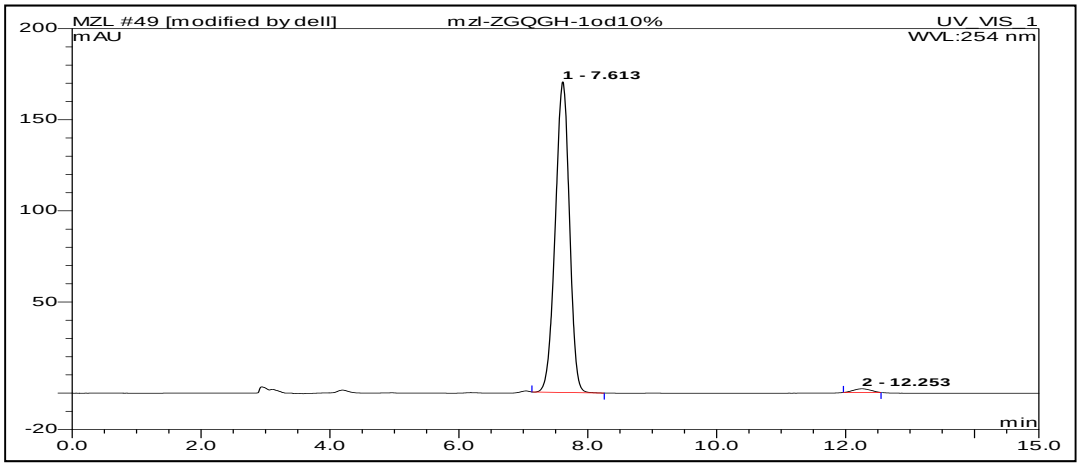
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.57	n.a.	79.310	20.772	97.97	BMB*
2	8.89	n.a.	1.654	0.430	2.03	BMB*
Total:			80.964	21.202	100.00	



4a-major

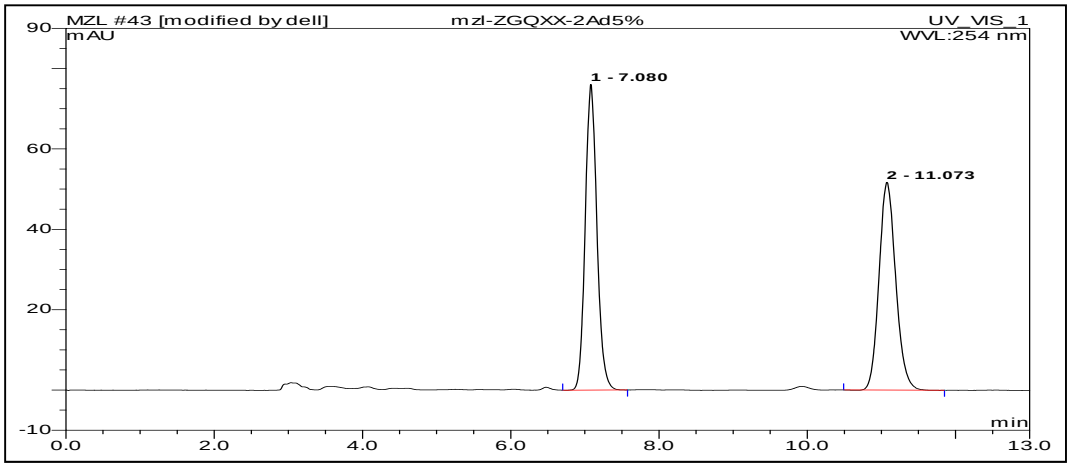


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.57	n.a.	443.023	121.900	50.54	BMB*
2	12.20	n.a.	318.205	119.309	49.46	BMB*
Total:			761.228	241.209	100.00	

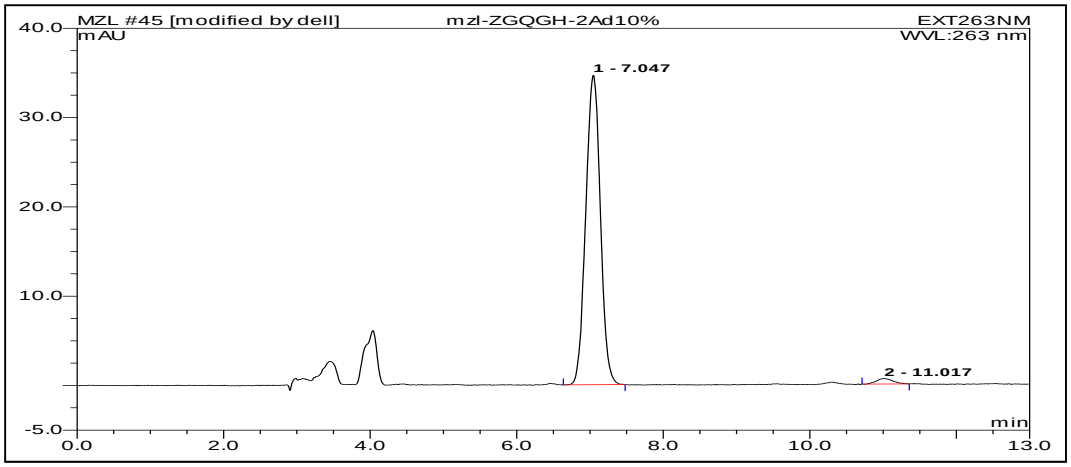


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.61	n.a.	170.456	43.491	98.89	BMB*
2	12.25	n.a.	1.766	0.490	1.11	BMB*
Total:			172.222	43.981	100.00	

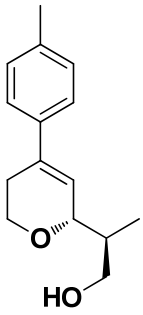
4a-minor



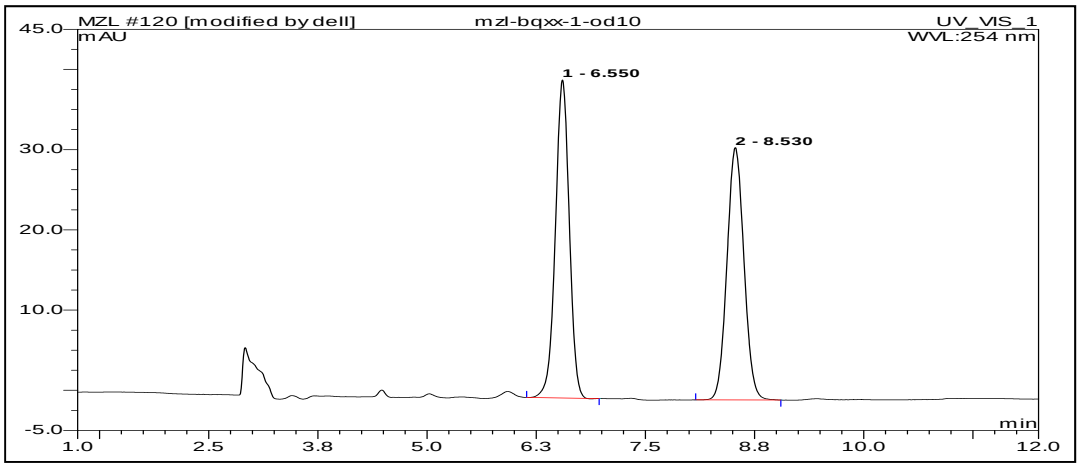
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.08	n.a.	76.060	13.915	50.78	BMB*
2	11.07	n.a.	51.709	13.487	49.22	BMB*
Total:			127.769	27.402	100.00	



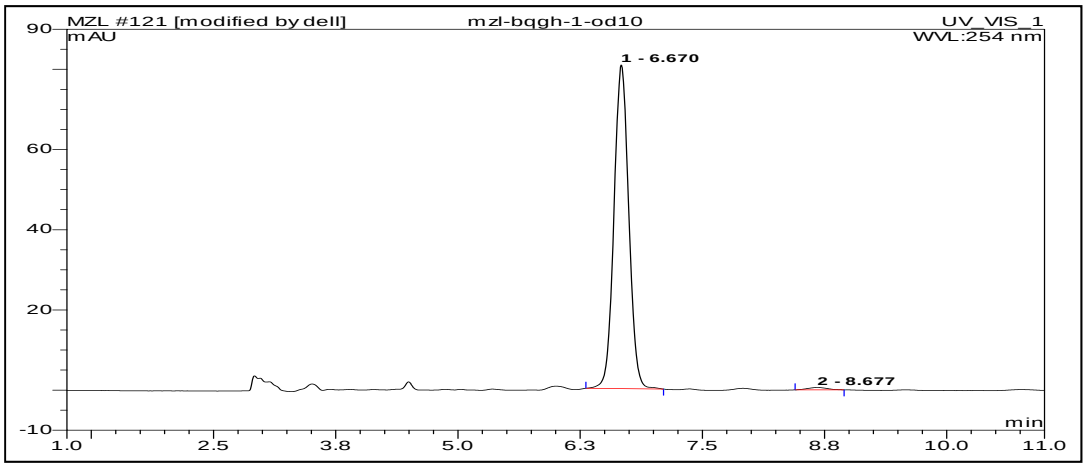
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.05	n.a.	34.670	8.033	98.48	BMB*
2	11.02	n.a.	0.549	0.124	1.52	BMB*
Total:			35.220	8.157	100.00	



4b-major

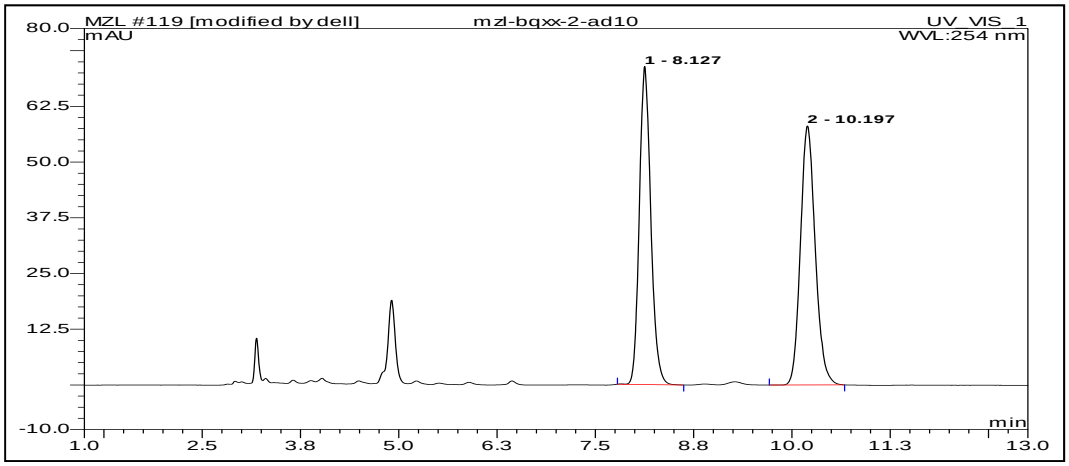


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.55	n.a.	39.640	7.319	50.76	BMB*
2	8.53	n.a.	31.466	7.101	49.24	BMB*
Total:			71.106	14.419	100.00	

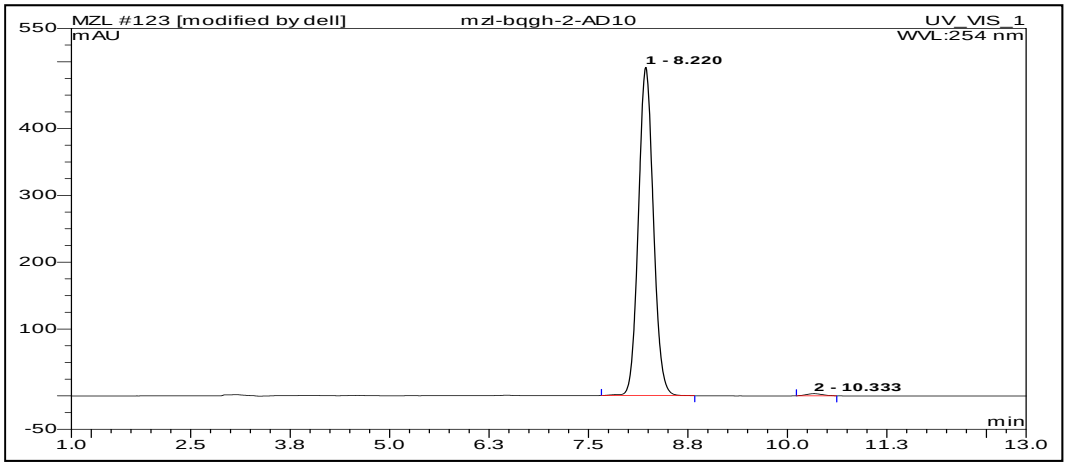


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.67	n.a.	80.720	14.225	99.27	BMB*
2	8.68	n.a.	0.518	0.104	0.73	BMB*
Total:			81.238	14.329	100.00	

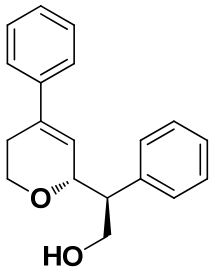
4b-minor



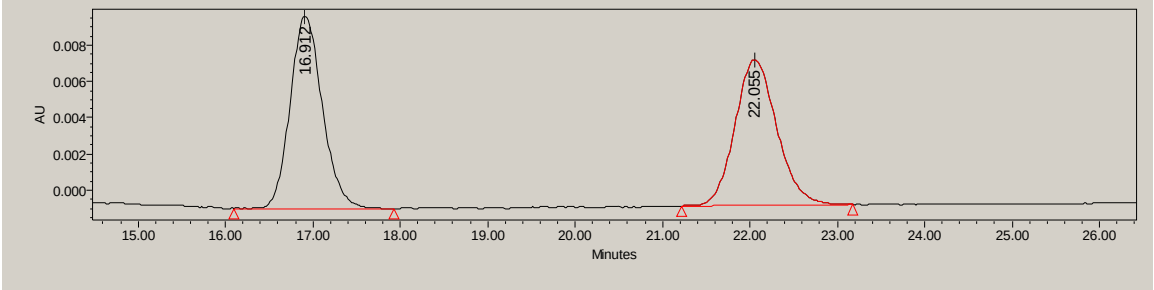
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.13	n.a.	71.334	12.092	48.79	BMB*
2	10.20	n.a.	58.112	12.692	51.21	BMB*
Total:			129.446	24.784	100.00	



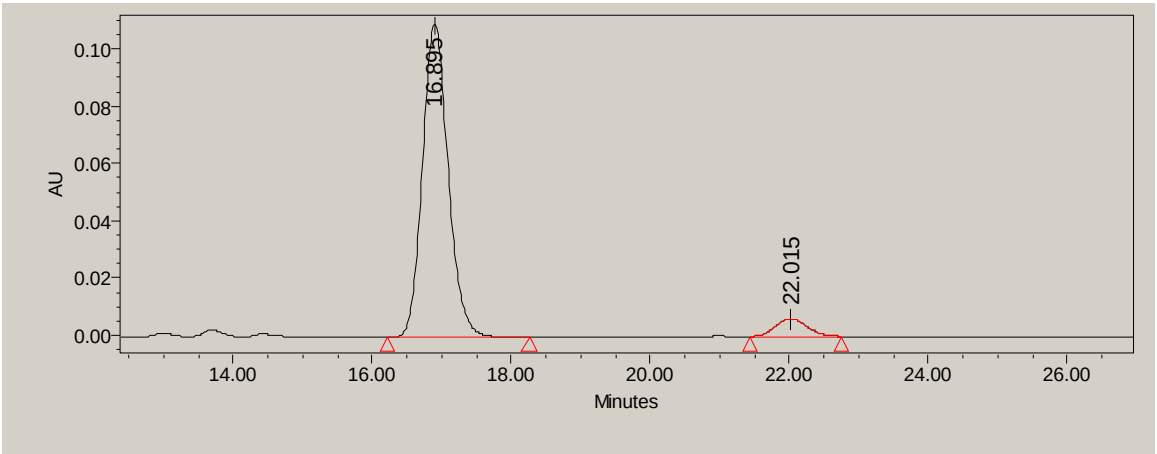
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.22	n.a.	491.222	107.552	99.32	BMB*
2	10.33	n.a.	3.153	0.737	0.68	BMB*
Total:			494.375	108.289	100.00	



4c-major

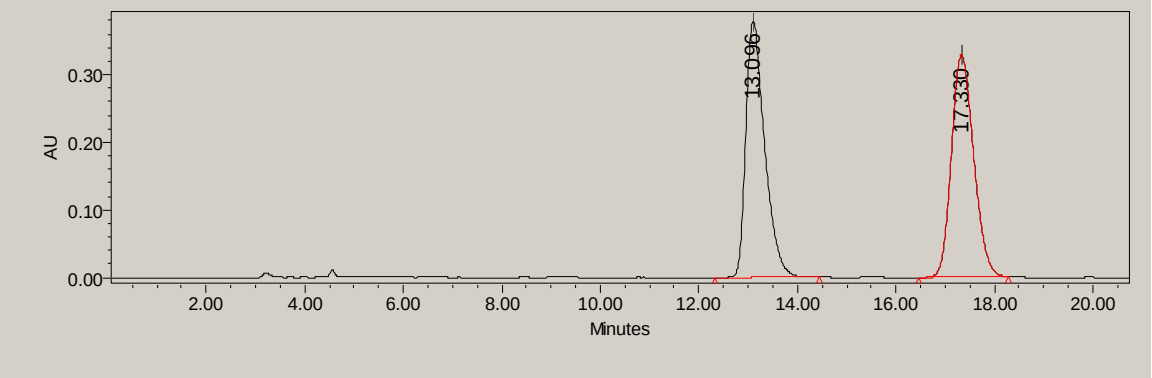


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		16.912	270550	50.76	10577	Bb	Unknown
2		22.055	262491	49.24	7984	Bb	Unknown

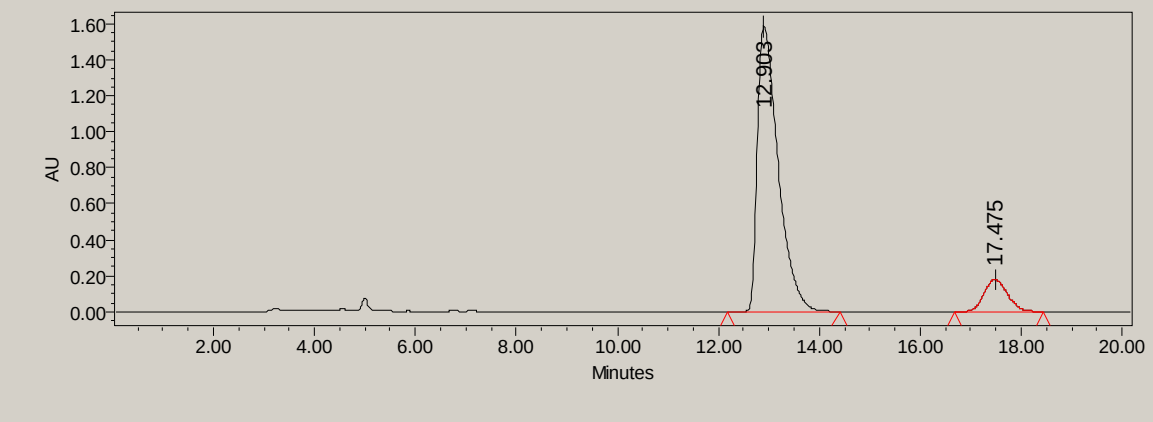


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		16.895	2812256	94.61	109543	bb	Unknown
2		22.015	160187	5.39	5602	bb	Unknown

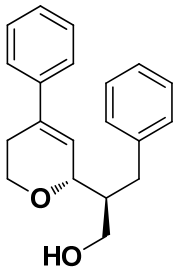
4c-minor



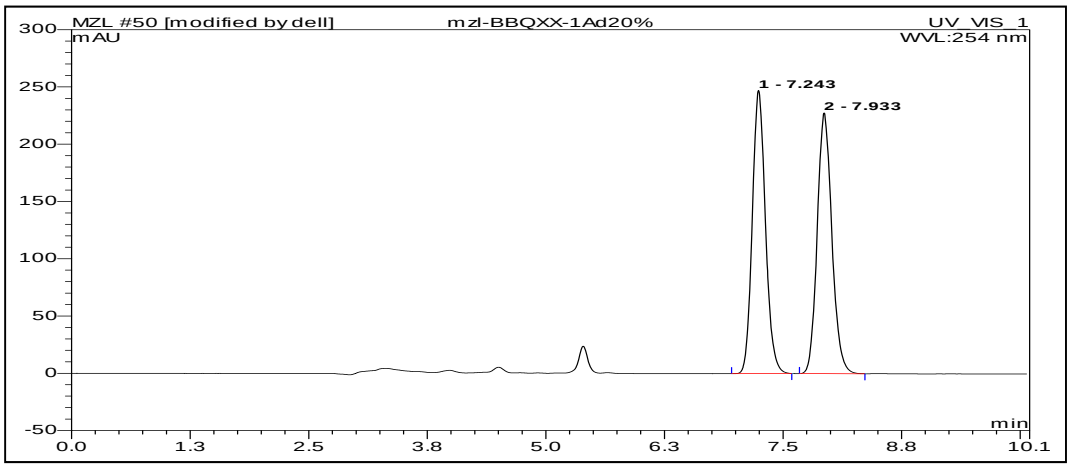
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		13.096	10287062	50.17	378949	bb	Unknown
2		17.330	10215507	49.83	328608	bb	Unknown



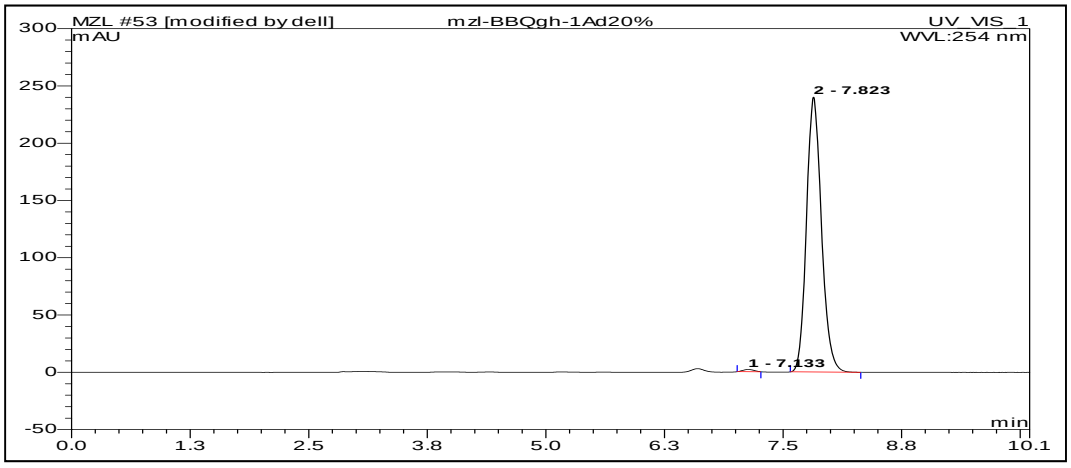
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.903	45658483	90.19	1586356	bb	Unknown
2		17.475	4966891	9.81	167410	bb	Unknown



4d-major

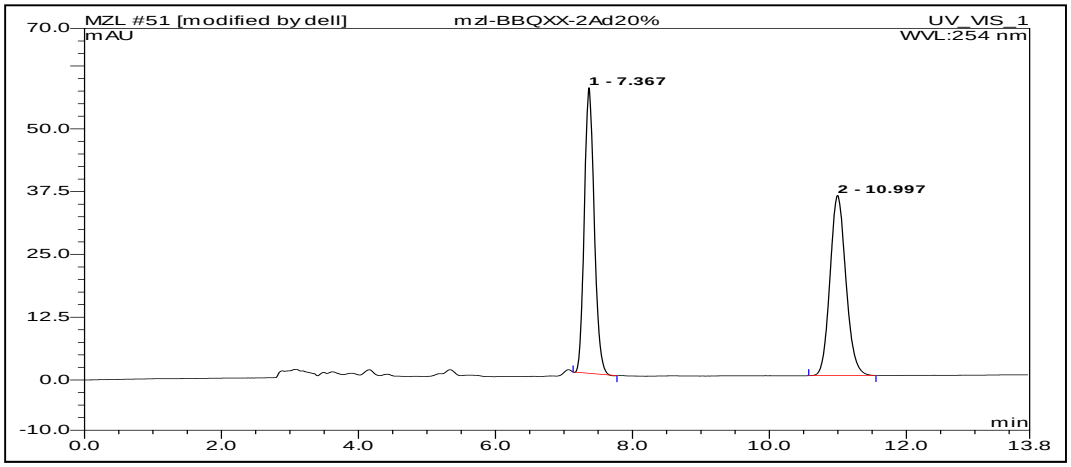


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.24	n.a.	247.128	39.942	49.46	BMB*
2	7.93	n.a.	227.665	40.807	50.54	BMB*
Total:			474.793	80.749	100.00	

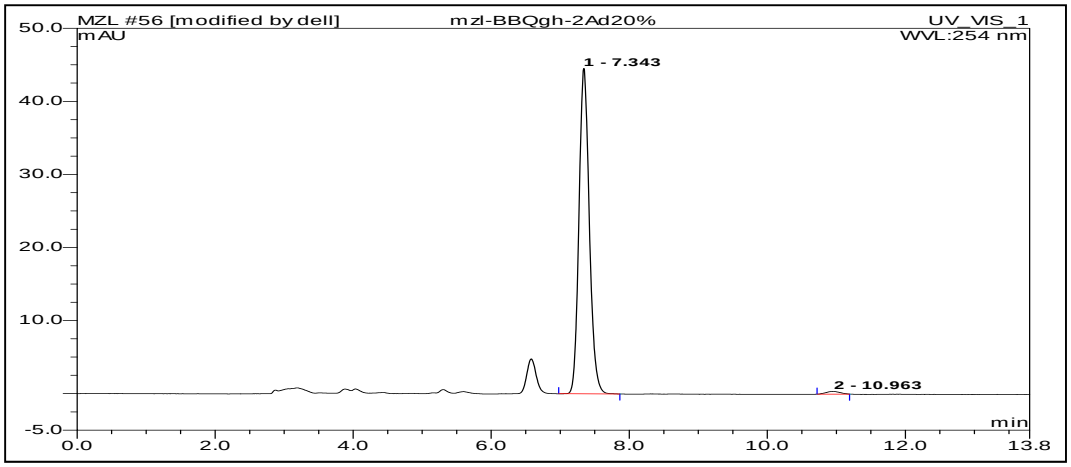


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.13	n.a.	1.967	0.264	0.59	BMB*
2	7.82	n.a.	239.848	44.083	99.41	BMB*
Total:			241.815	44.346	100.00	

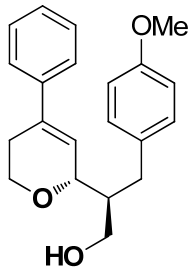
4d-minor



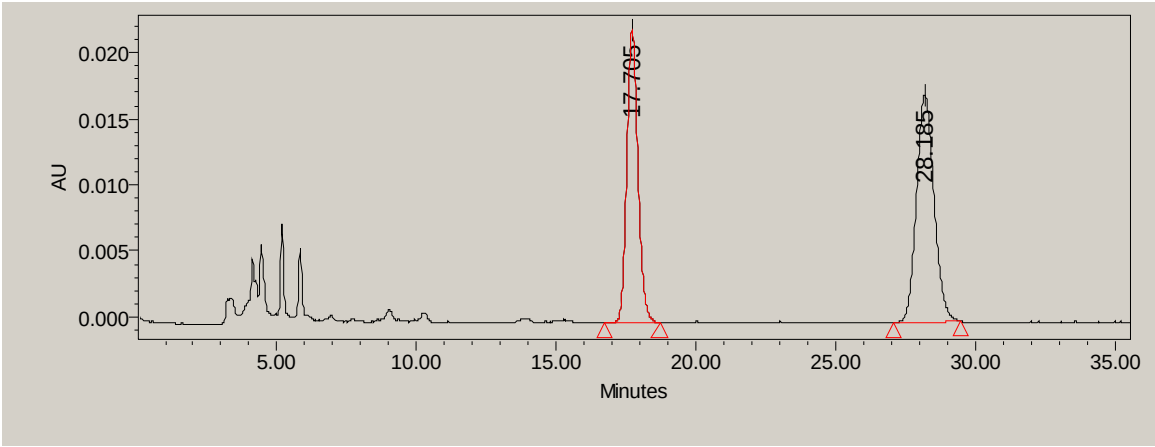
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.37	n.a.	56.867	9.599	49.86	BMB*
2	11.00	n.a.	35.855	9.655	50.14	BMB*
Total:			92.722	19.255	100.00	



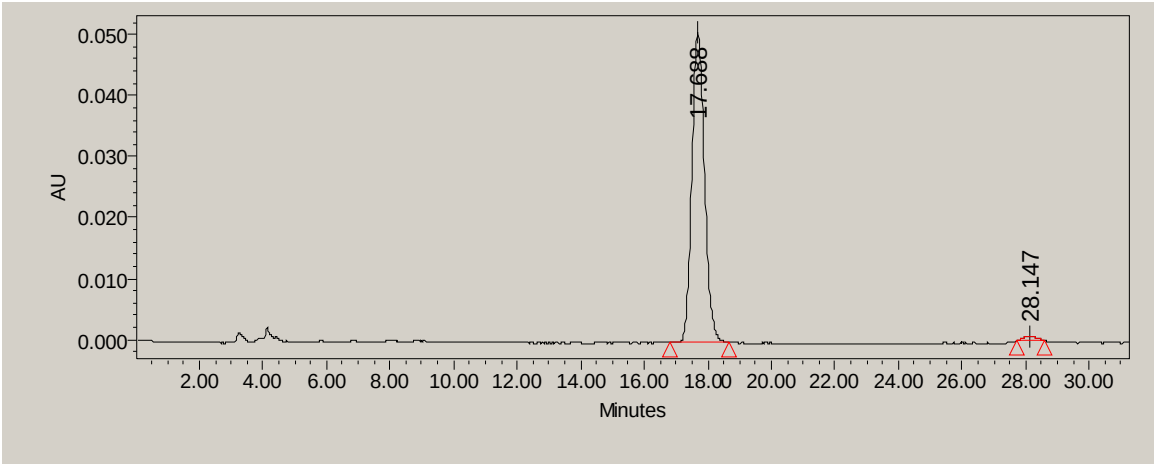
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.34	n.a.	44.540	7.748	98.92	BMB*
2	10.96	n.a.	0.363	0.085	1.08	BMB*
Total:			44.903	7.832	100.00	



4e-major

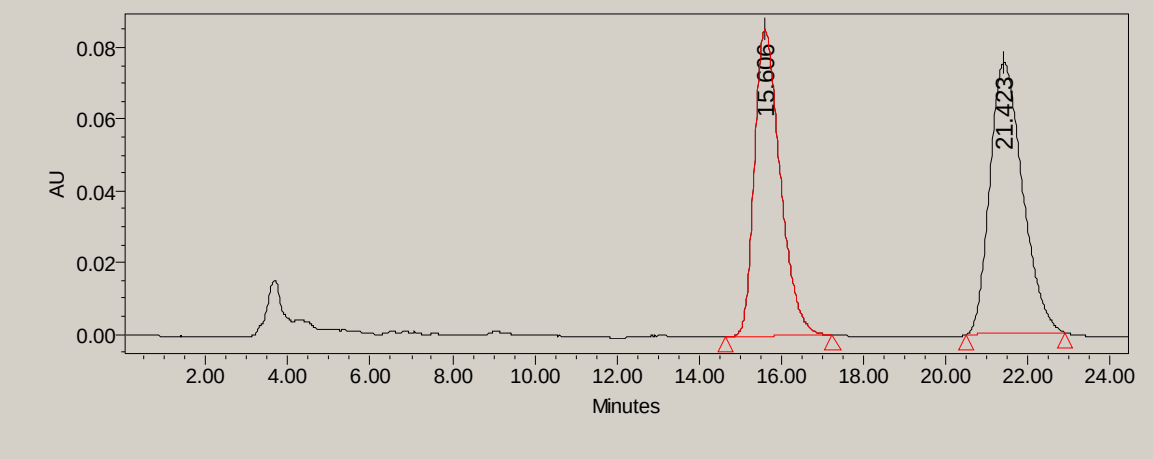


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		17.705	611139	48.15	22135	bb	Unknown
2		28.185	658163	51.85	16287	bb	Unknown

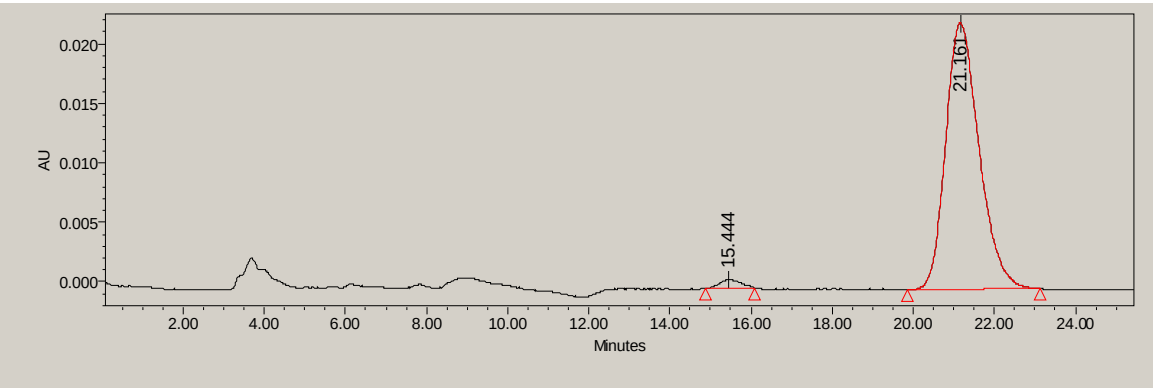


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		17.688	1397610	98.44	51039	bb	Unknown
2		28.147	22111	1.56	766	bb	Unknown

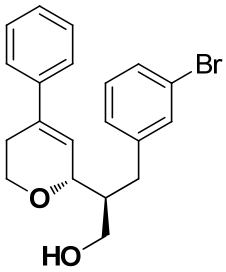
4e-minor



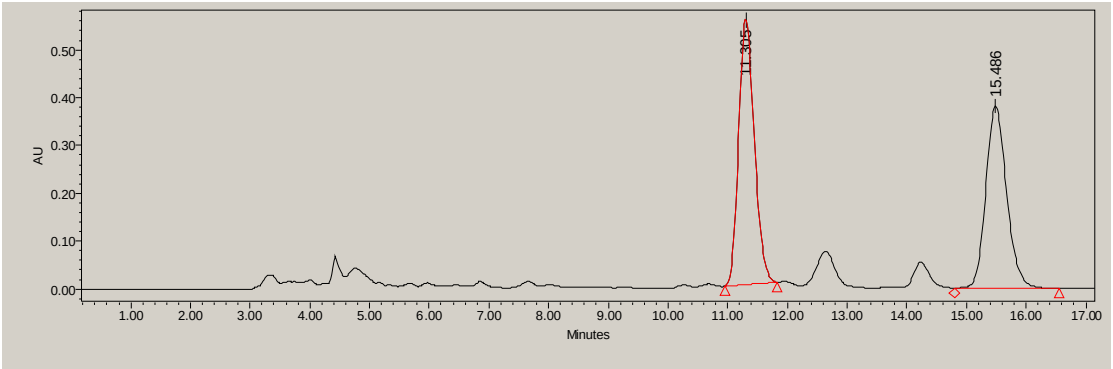
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.606	3713554	48.22	85411	bb	Unknown
2		21.423	3988210	51.78	74043	bb	Unknown



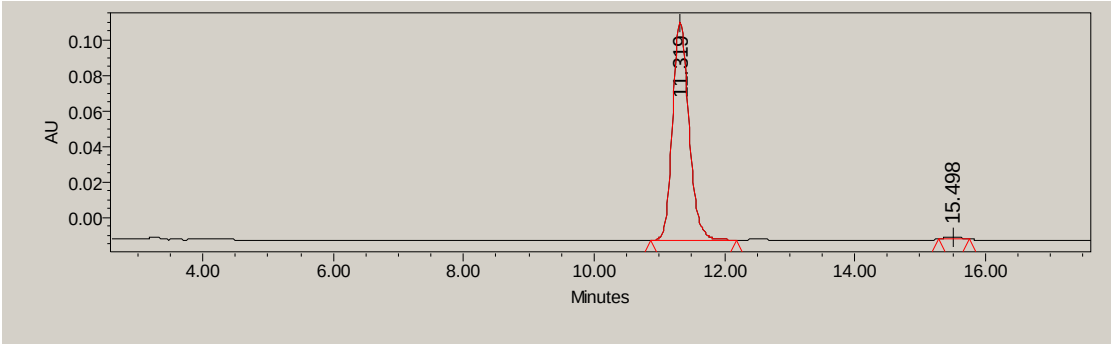
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		15.444	25232	1.94	676	bb	Unknown
2		21.161	1276024	98.06	22343	bb	Unknown



4f-major

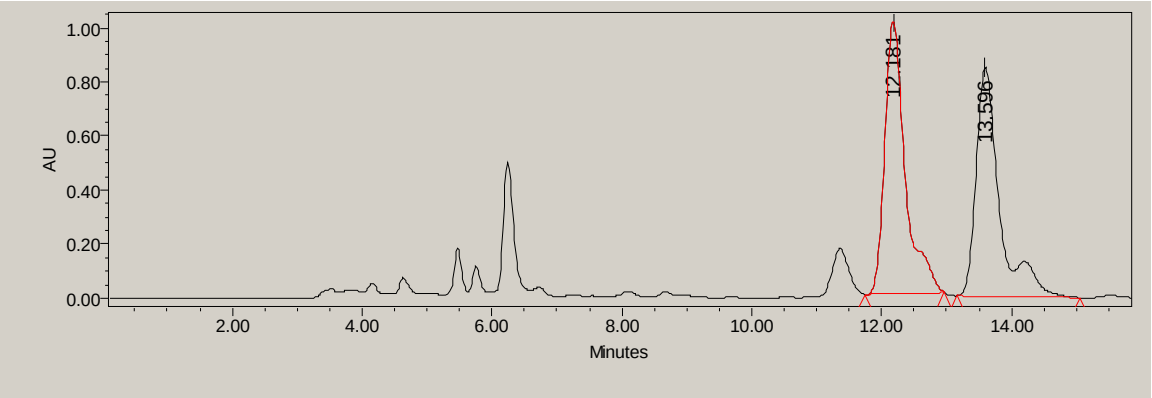


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.305	9513435	50.70	539219	bb	Unknown
2		15.486	9249805	49.30	381010	VB	Unknown

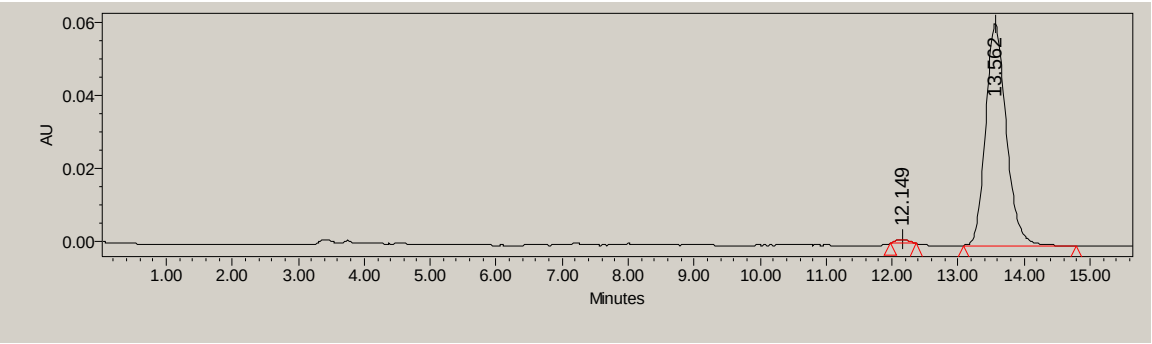


	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		11.319	2153901	99.03	122552	bb	Unknown
2		15.498	21200	0.97	1264	bb	Unknown

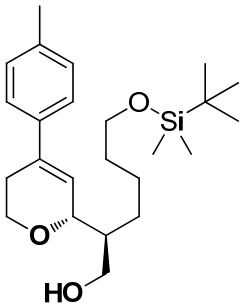
4f-minor



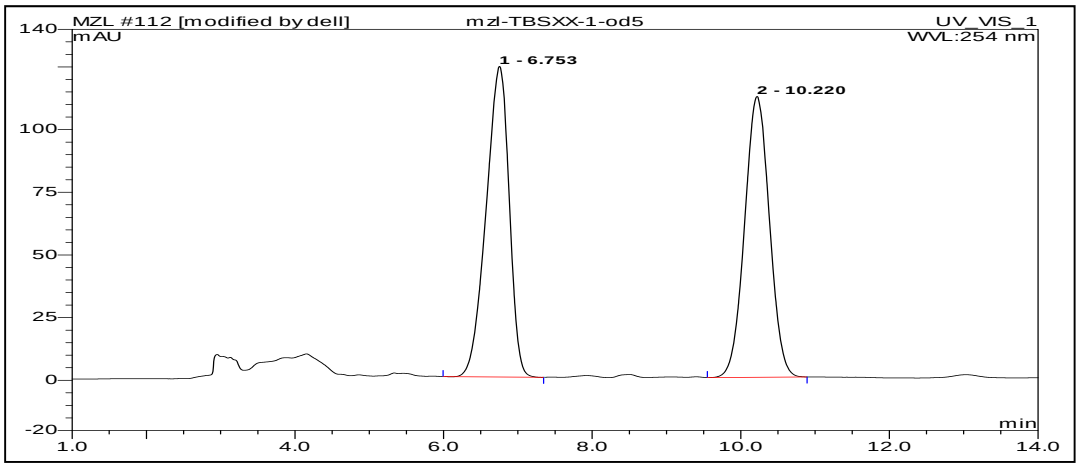
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.181	22029172	50.69	1005877	bb	Unknown
2		13.596	21428176	49.31	847364	bb	Unknown



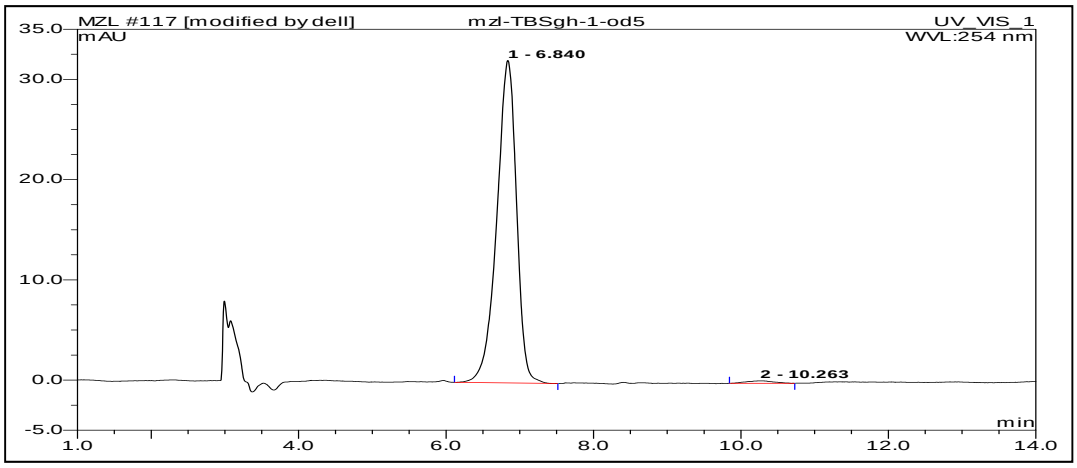
	Name	Retention Time	Area	% Area	Height	Int Type	Peak Type
1		12.149	16376	1.23	1177	bb	Unknown
2		13.562	1311373	98.77	60317	bb	Unknown



4g-major

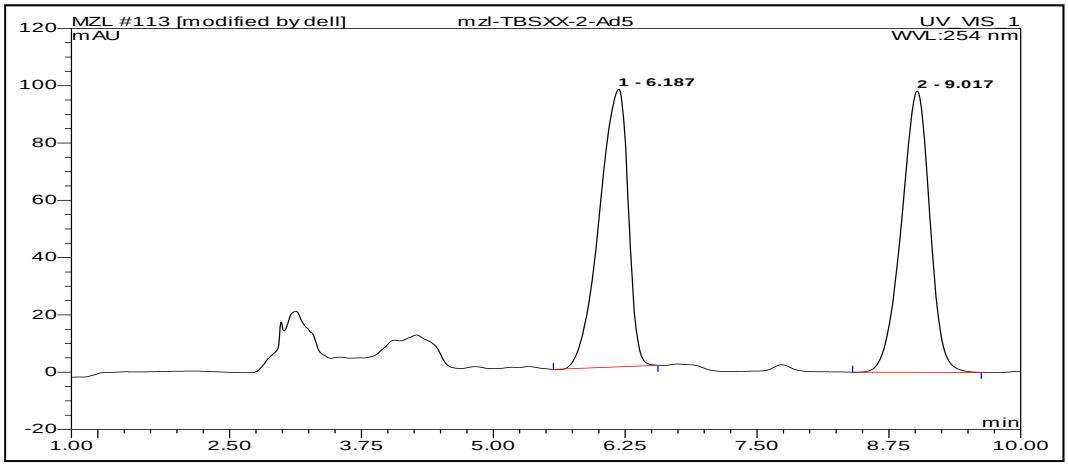


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.75	n.a.	123.897	44.594	50.65	BMB*
2	10.22	n.a.	111.975	43.451	49.35	BMB*
Total:			235.872	88.045	100.00	

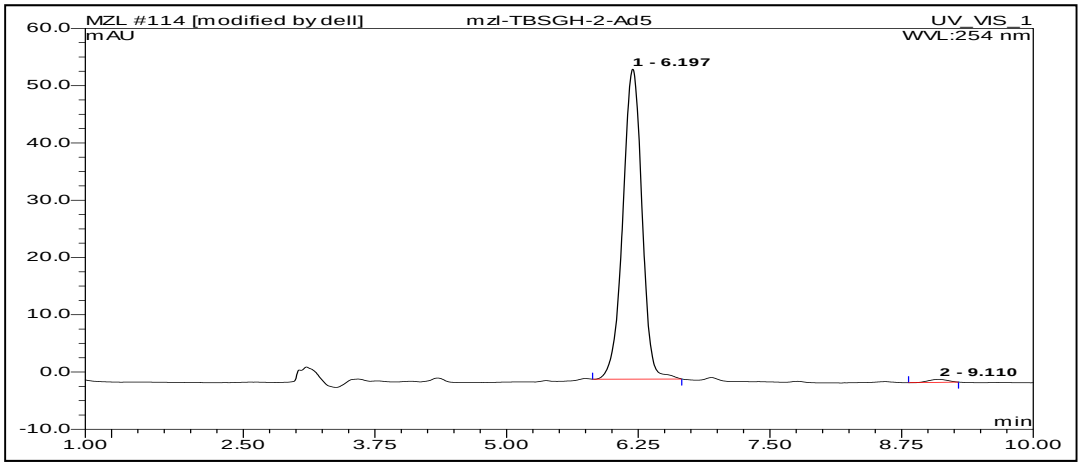


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.84	n.a.	32.163	9.974	99.28	BMB*
2	10.26	n.a.	0.200	0.072	0.72	BMB*
Total:			32.363	10.047	100.00	

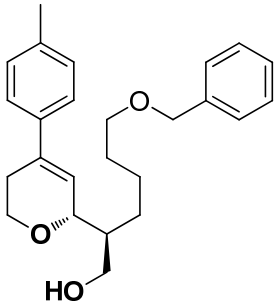
4g-minor



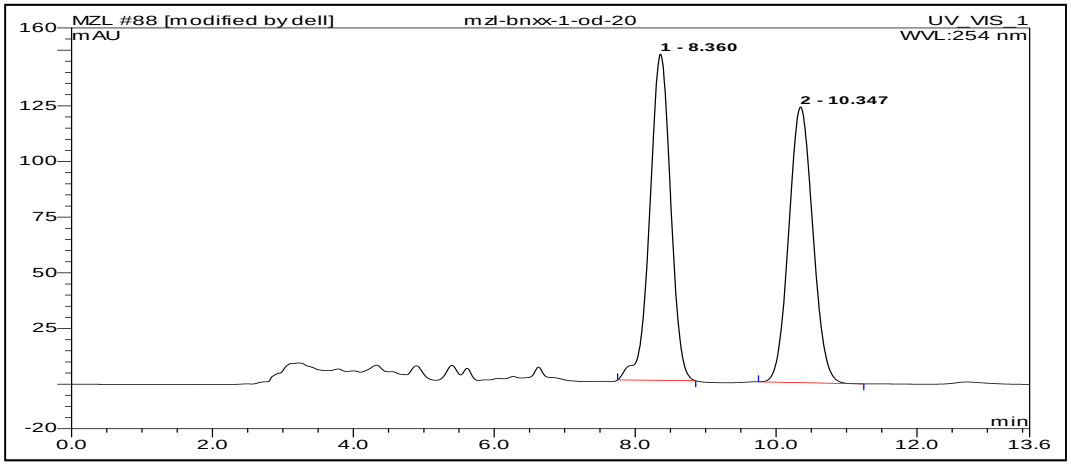
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.19	n.a.	96.912	30.538	49.92	BMB*
2	9.02	n.a.	98.150	30.637	50.08	BMB*
Total:			195.063	61.175	100.00	



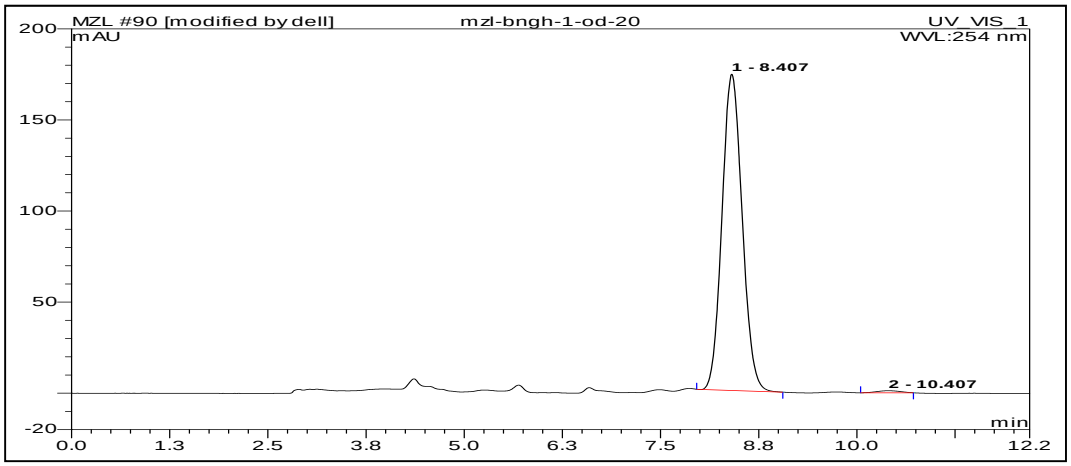
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.20	n.a.	54.111	11.442	99.06	BMB*
2	9.11	n.a.	0.519	0.109	0.94	BMB*
Total:			54.630	11.550	100.00	



4h-major

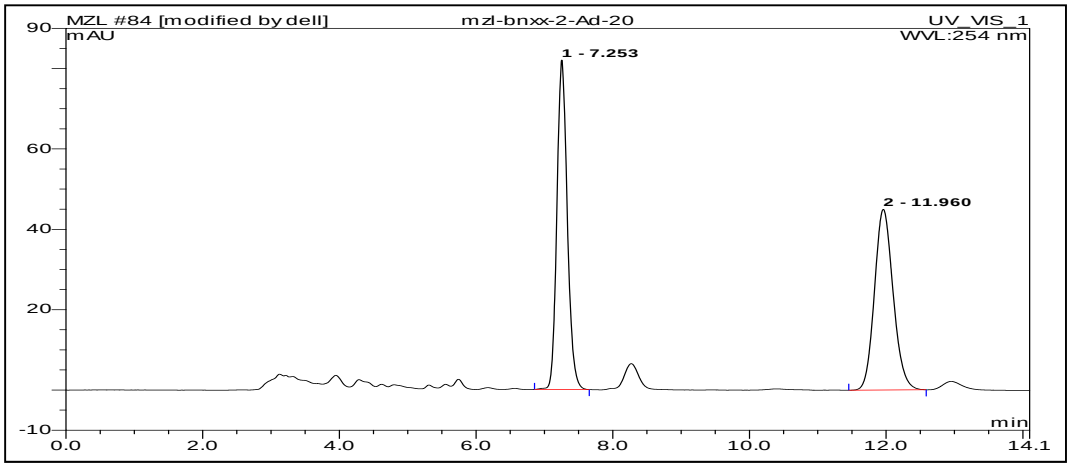


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.36	n.a.	146.558	50.382	50.73	BMB*
2	10.35	n.a.	123.807	48.924	49.27	BMB*
Total:			270.365	99.306	100.00	

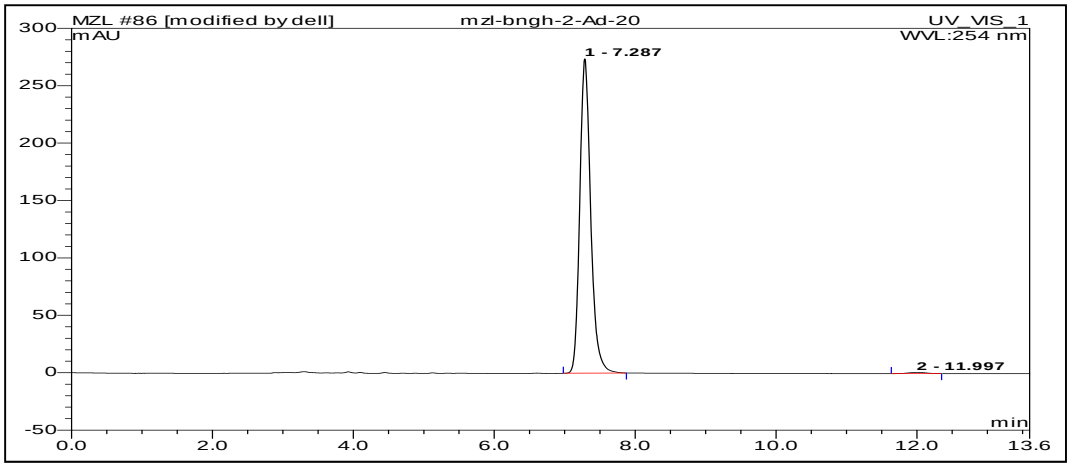


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	8.41	n.a.	173.592	51.670	99.25	BMB*
2	10.41	n.a.	1.141	0.391	0.75	BMB*
Total:			174.733	52.061	100.00	

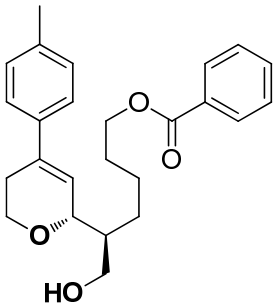
4h-minor



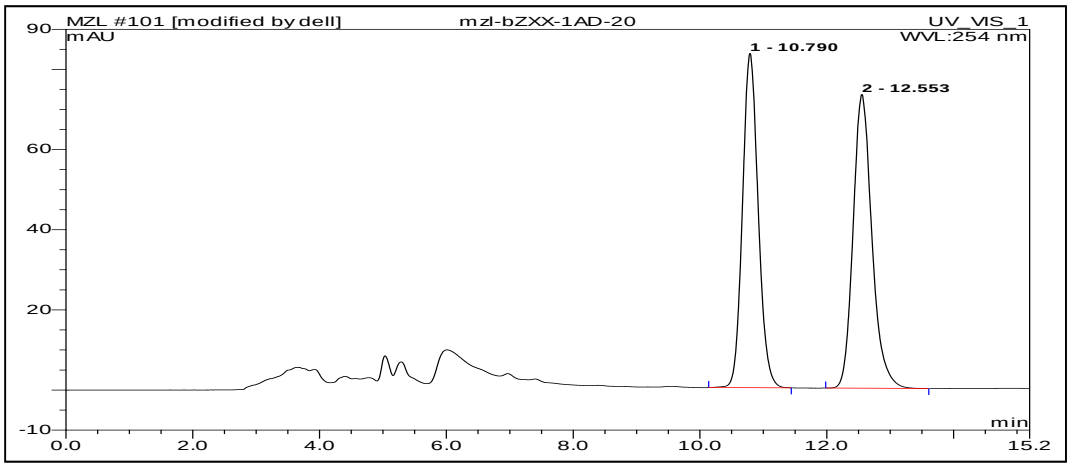
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.25	n.a.	81.974	14.522	50.51	BM *
2	11.96	n.a.	44.957	14.230	49.49	BMB*
Total:			126.931	28.752	100.00	



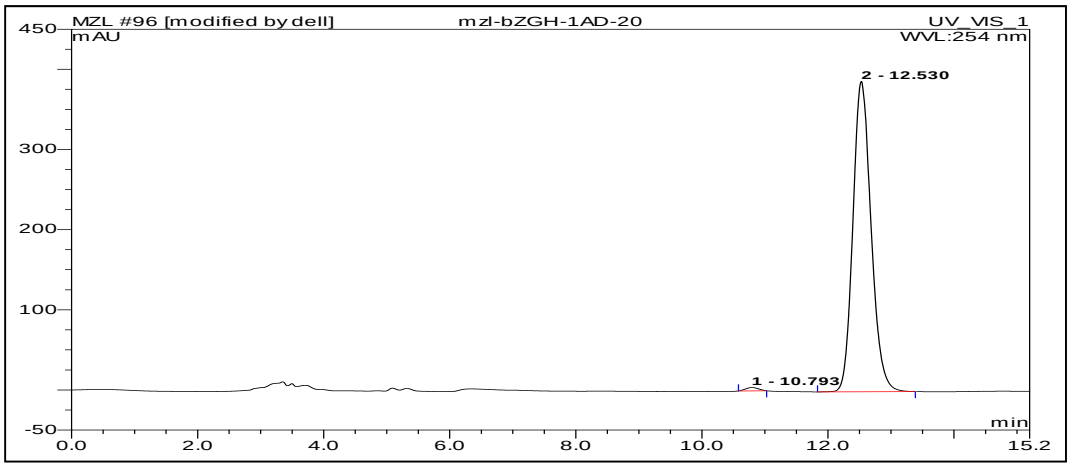
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	7.29	n.a.	273.854	49.356	99.39	BMB*
2	12.00	n.a.	1.019	0.302	0.61	BMB*
Total:			274.872	49.658	100.00	



4i-major

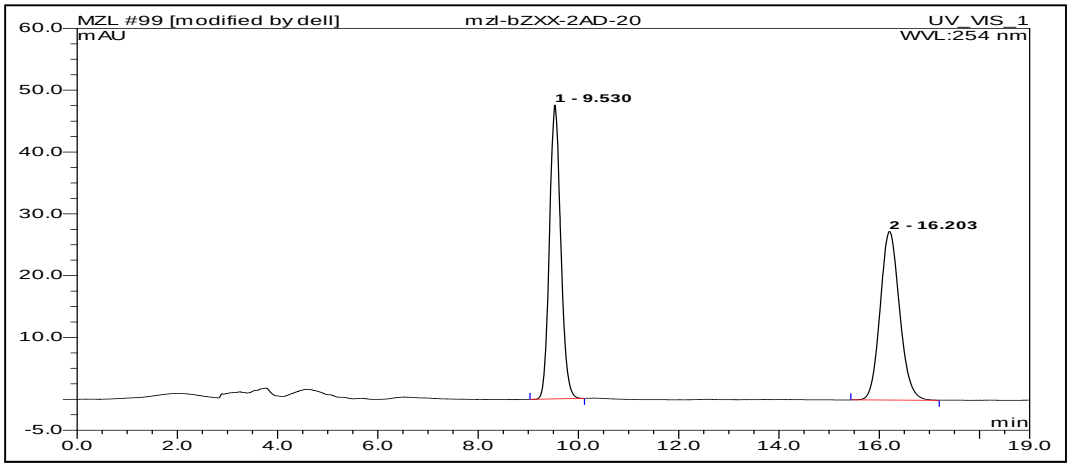


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	10.79	n.a.	83.390	24.022	48.71	BMB*
2	12.55	n.a.	73.283	25.299	51.29	BMB*
Total:			156.673	49.320	100.00	

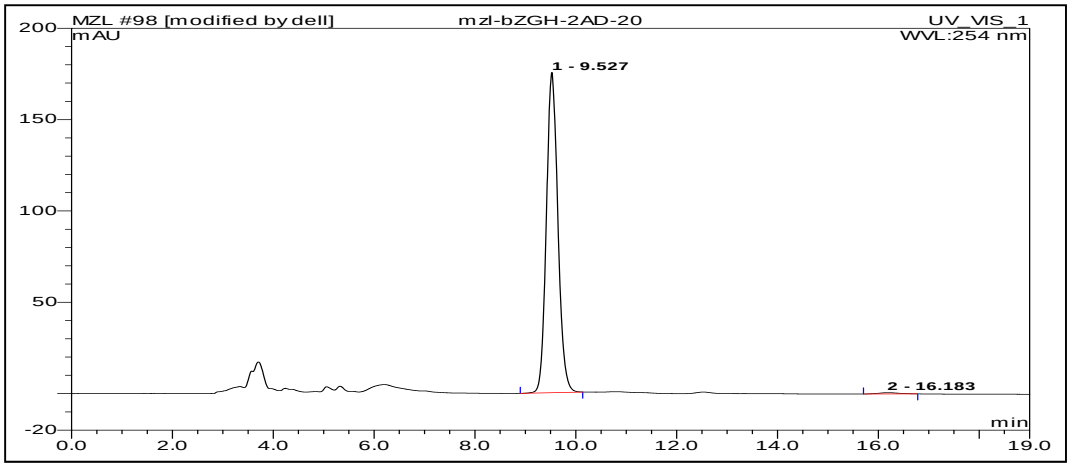


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	10.79	n.a.	4.086	0.967	0.74	BMB*
2	12.53	n.a.	387.024	129.346	99.26	BMB*
Total:			391.111	130.313	100.00	

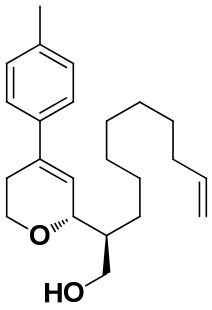
4i-minor



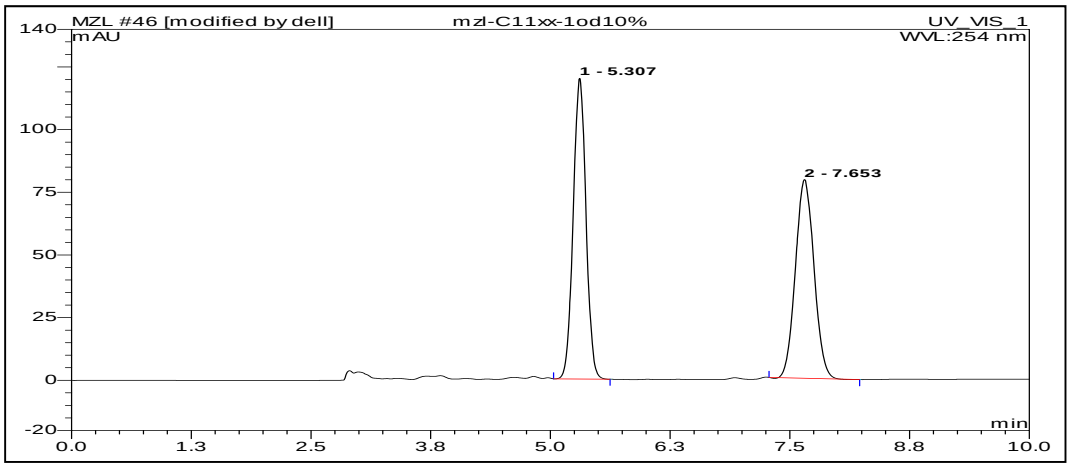
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	9.53	n.a.	47.546	12.436	50.41	BMB*
2	16.20	n.a.	27.273	12.232	49.59	BMB*
Total:			74.819	24.668	100.00	



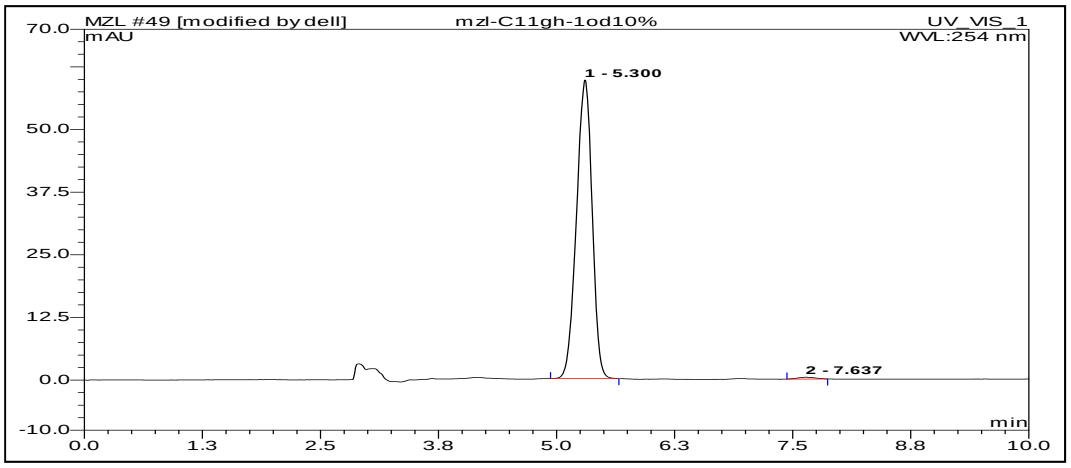
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	9.53	n.a.	175.292	46.527	99.35	BMB*
2	16.18	n.a.	0.685	0.306	0.65	BMB*
Total:			175.977	46.833	100.00	



4j-major

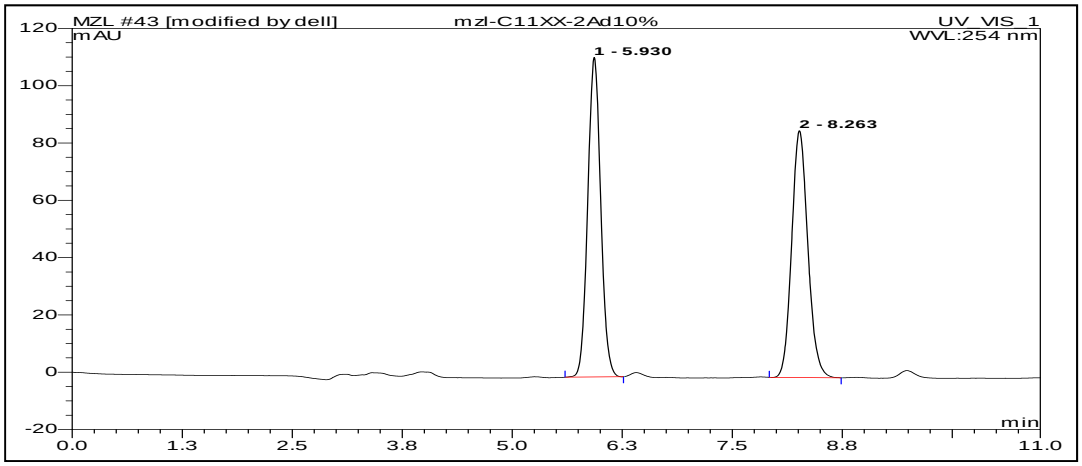


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.31	n.a.	119.977	18.680	51.10	BMB*
2	7.65	n.a.	79.256	17.875	48.90	BMB*
Total:			199.233	36.555	100.00	

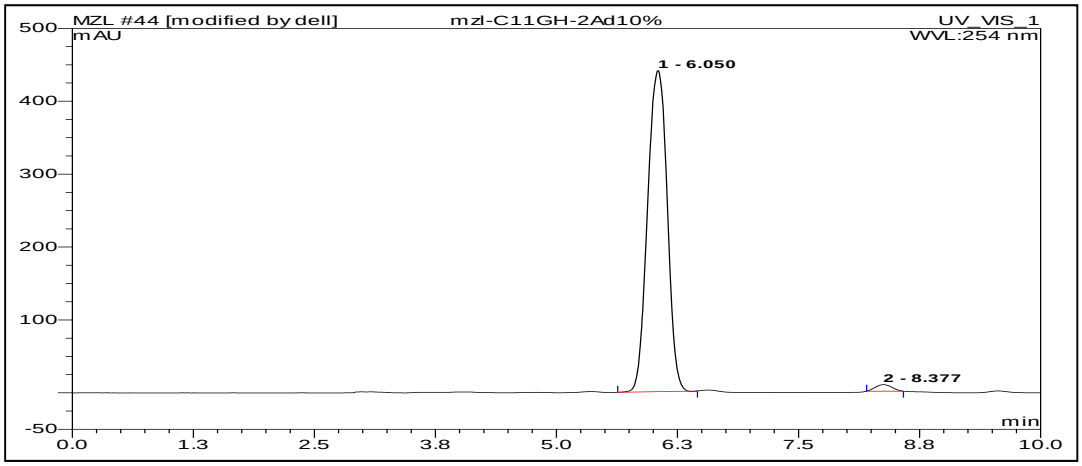


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.30	n.a.	59.560	11.490	99.34	BMB*
2	7.64	n.a.	0.353	0.076	0.66	BMB*
Total:			59.913	11.567	100.00	

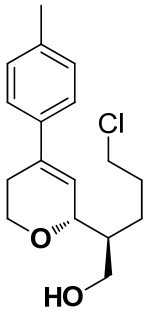
4j-minor



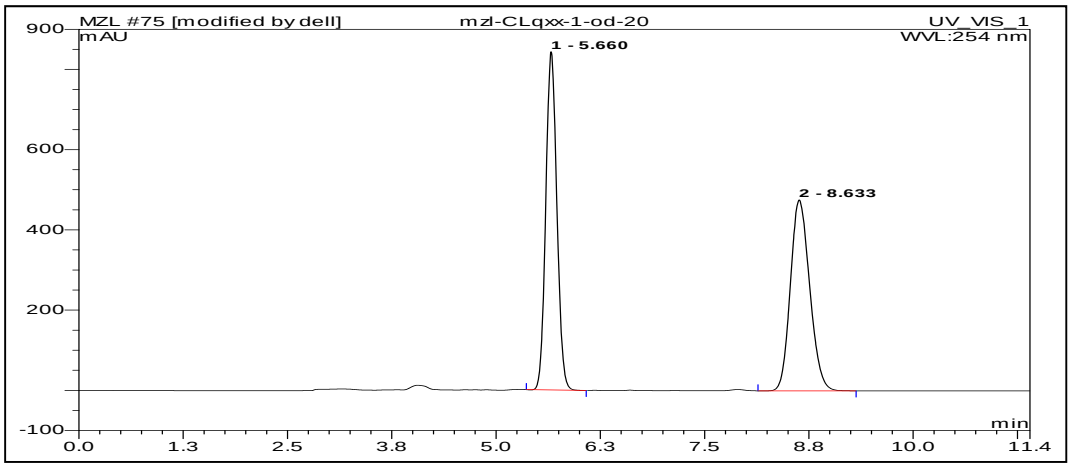
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.93	n.a.	111.534	19.153	51.08	BMB*
2	8.26	n.a.	86.155	18.342	48.92	BMB*
Total:			197.689	37.495	100.00	



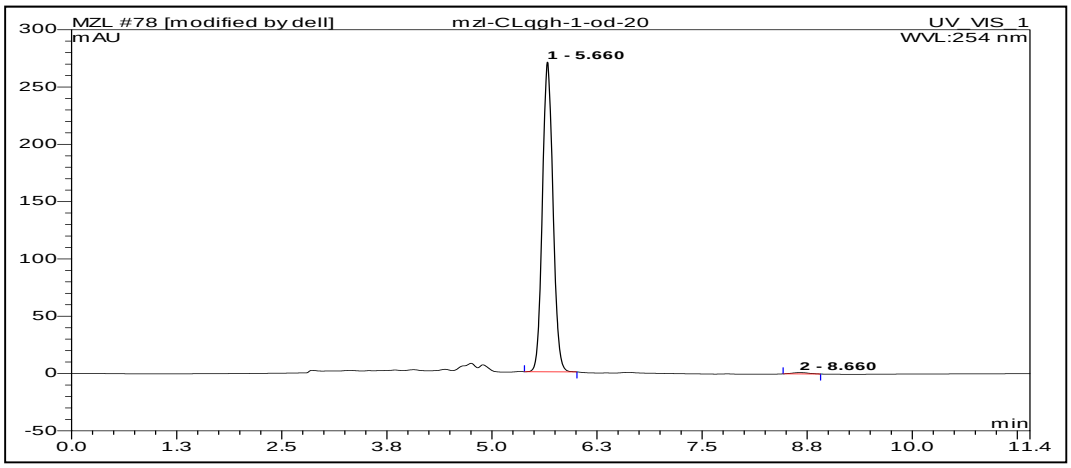
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.05	n.a.	440.514	103.663	98.61	BMB*
2	8.38	n.a.	7.999	1.464	1.39	BMB*
Total:			448.512	105.127	100.00	



4k-major

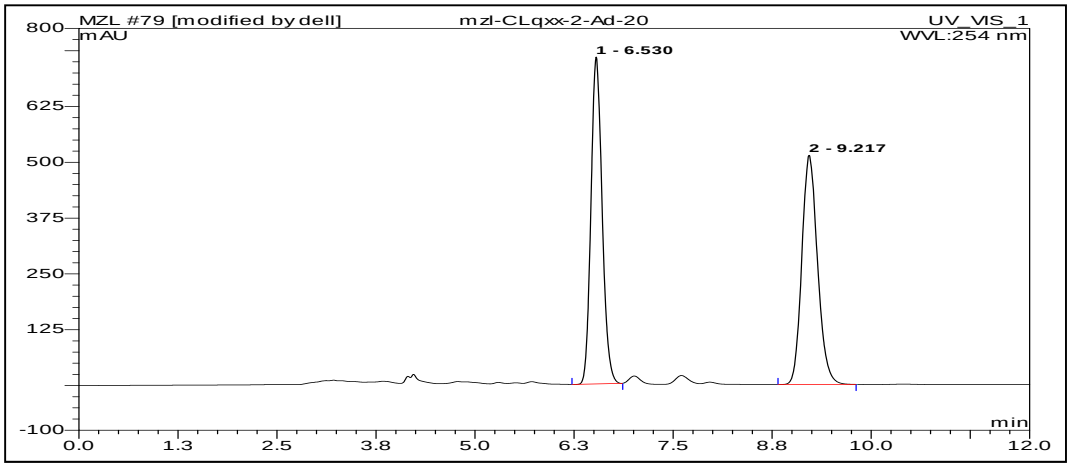


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.66	n.a.	843.343	130.134	50.48	BMB*
2	8.63	n.a.	475.875	127.668	49.52	BMB*
Total:			1319.218	257.802	100.00	

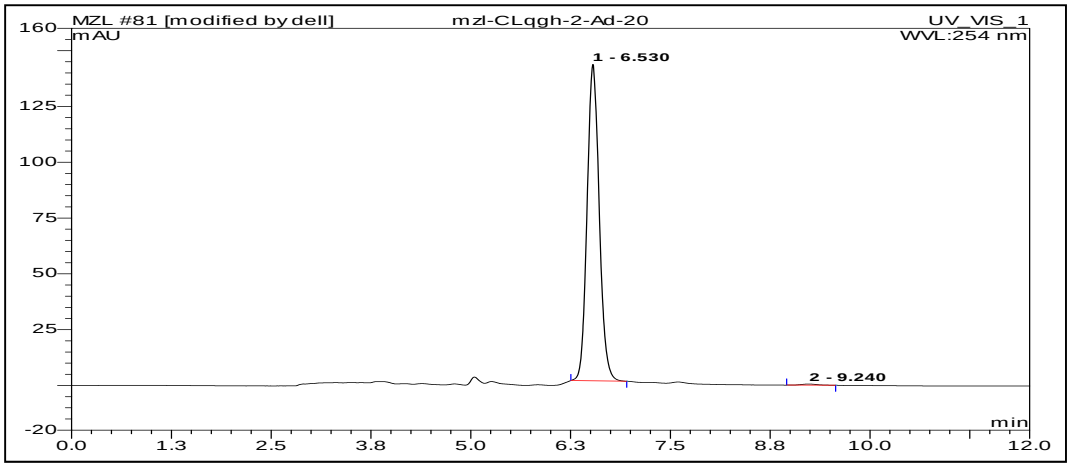


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	5.66	n.a.	270.195	39.460	99.32	BMB*
2	8.66	n.a.	1.170	0.271	0.68	BMB*
Total:			271.365	39.731	100.00	

4k-minor



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.53	n.a.	732.103	119.848	50.32	BMB*
2	9.22	n.a.	513.259	118.330	49.68	BMB*
Total:			1245.362	238.178	100.00	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.53	n.a.	141.723	25.067	99.54	BMB*
2	9.24	n.a.	0.512	0.116	0.46	BMB*
Total:			142.235	25.183	100.00	