

Supporting information

Rational design of mimetic peptides based on aldo-ketoreductase enzyme as asymmetric organocatalyst in aldol reactions

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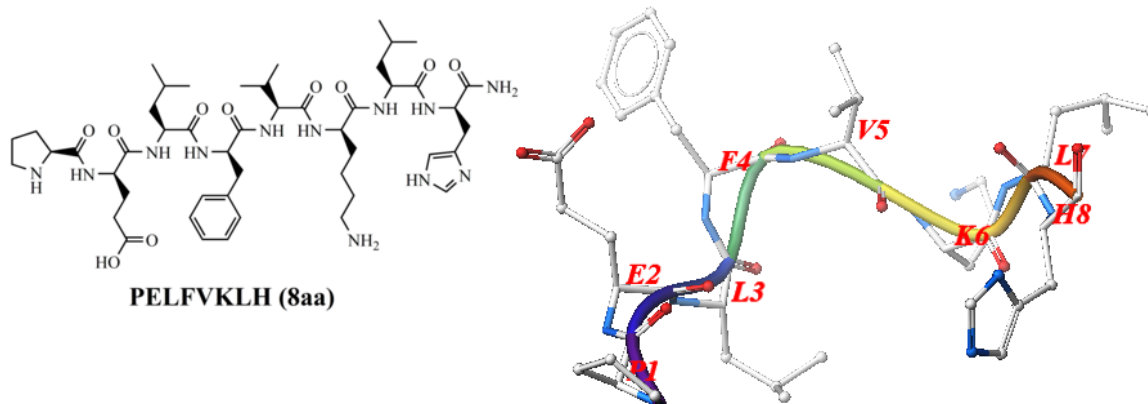
General

All chemicals were purchased and used without further purification. Recombinant Human AKR1A1 aldehyde reductase (Homo sapiens, freeze-dried CFE, in 20 mM sodium phosphate, cat.no. = Pro-E0601) was purchased from Prozomix company to employ as a control promiscuous asymmetry biocatalyst in the aldol reaction. Analytical thin layer chromatography (TLC) was performed using Merck 60 F₂₅₄ precoated silica gel plate (0.2 mm thickness). Flash chromatography was performed using Merck silica gel 60 (70-230 mesh). Fourier transforms infrared spectroscopy (FTIR); Perkin Elmer Spectrum 100 was used for identification of functional groups. NMR data were recorded on 700

MHz (Bruker), 500 MHz (JEOL) for ^1H NMR and 127 MHz (Bruker) 100 MHz (JEOL JNM ECA) for ^{13}C NMR spectrometer. The relative and absolute configurations (dr) of the Aldol reactions were determined by comparison with ^1H NMR spectroscopic analysis. Mass spectra (MS) were measured with a spectrometer (DIMS QP5050A SHIMADZU). Optical rotations were measured on a JASCO P-2000 Polarimeter. Enantioselectivity were determined by HPLC (Waters 1525 Binary Pump and UV-Water 2489) analysis employing a Daicel ChiralCel OD-H, and ChiralPak AD-H columns (4.6mm×250mm). CD spectra were measured on a JASCO J-810 automatic recording spectropolarimeter.

➤ Experimental method

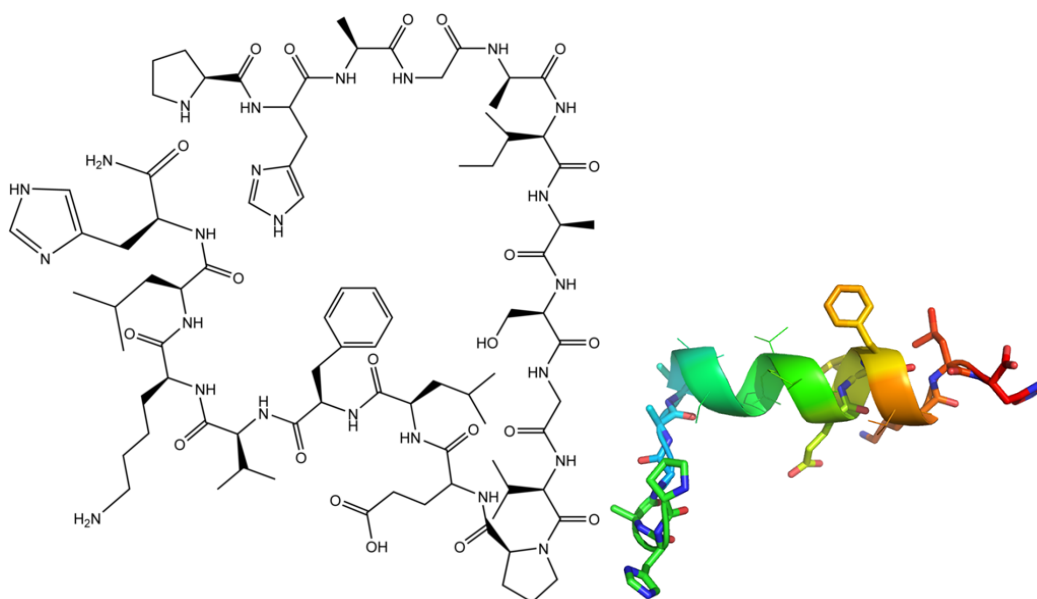
Characterizations of peptide 8aa



IR (neat) $\nu = 3280, 3103, 2966, 2902, 1635, 1546, 1195, 1139, \text{cm}^{-1}$; **^1H NMR** (700 MHz, $\delta = \text{ppm}$); $\delta = 8.71$ (d, $J = 7.09$ Hz, 1H), 8.6 (s, 2H), 8.48 (d, $J = 8.17$, 1H), 8.33 (d, $J = 7.0$ Hz, 1H), 8.19 (d, $J = 7.45$ Hz, 1H), 8.28 (d, $J = 7.19$ Hz, 1H), 8.26 (d, $J = 6.84$ Hz, 1H), 7.97 (d, $J = 7.89$ Hz, 1H), 7.53 (bs, 1H), 7.33 (m, 3H), 7.29 (m, 2H), 7.23 (d, $J = 7.70$ Hz, 3H), 7.18 (s, 1H), 4.63 (m, 2H), 4.40 (t, $J = 7.14$ Hz, 1H), 4.33 (m, 2H), 4.25 (m, 3H), 4.02 (t, $J = 7.50$ Hz, 1H), 3.04 (m, 2H), 3.28 (dd, $J = 15.48, 5.78$ Hz, 1H), 3.16 (dd, $J = 15.50, 8.90, \text{Hz}$, 1H), 3.09 (dd, $J = 14.16, 6.55$ Hz, 1H), 3.00 (m, 4H), 2.45 (m,

2H), 2.39 (m, 2H), 2.34 (m, 2H), 1.99 (m, 6H), 1.79 (m, 1H), 1.70 (m, 3H), 1.58 (m, 1H), 1.5 (m, 2H), 1.45 (m, 2H), 0.89 (d, $J = 5.00$ Hz, 12 H), 0.83 (d, $J = 6.23$ Hz, 6H). ^{13}C NMR (125.70 MHz, D_2O , 25°C) $\delta = 20.52, 20.96, 23.27, 23.56, 24.60, 24.70, 24.79, 26.36, 26.85, 26.93, 28.87, 28.91, 32.50, 32.78, 34.06, 39.58, 42.11, 42.39, 42.58, 54.95, 55.25, 55.80, 56.15, 57.64, 62.09, 62.26, 118.13, 119.80, 120.04, 121.50, 129.75, 131.31, 131.35, 131.81, 136.25, 138.81, 165.50, 165.70, 167.60, 172.3, 175.14, 175.33, 176.27, 176.57, 176.67, 177.10, 179.80$. MS (Accurate Q-TOF LC/HRMS): m/z (%): 981.5887 (100) [M+H].

Spectroscopic data of peptide PH16aa



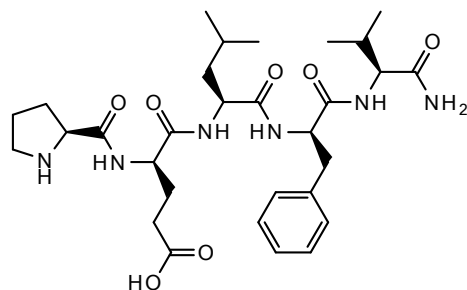
IR (neat) $\nu = 3262, 3046, 2925, 2856, 1624, 1523, 1170, 1130, \text{cm}^{-1}$; **^1H NMR** (700 MHz, $\delta = \text{ppm}$); $\delta = 8.48$ (s, 2H), 8.45 (s, 2H), 8.40 (d, $J = 6.15$ Hz, 1H), 8.38 (d, $J = 6.15$ Hz, 1H), 8.26 (d, $J = 6.50$ Hz, 1H), 8.20 (d, $J = 6.50$ Hz, 1H), 8.19 (d, $J = 6.55$ Hz, 1H), 8.15 (d, $J = 7.55$ Hz, 1H), 8.12 (m, 2H), 7.97 (d, $J = 7.55$ Hz, 1H), 7.89 (d, $J = 7.29$ Hz, 1H), 7.53 (bs, 1H), 7.32 (t, $J = 7.15$ Hz, 3H), 7.27 (d, $J = 7.00$ Hz, 2H), 7.26 (bs, 2H), 7.22 (m, 3H), 7.17 (bs, 1H), 4.41 (t, $J = 7.06$ Hz, 1H), 4.35 (m, 4H), 4.24 (m, 3H), 4.17 (dd, $J = 14.75, 5.70$ Hz, 1H), 4.13 (t, $J = 7.50$ Hz, 1H), 3.97 (m, 2H), 3.94 (d, $J = 5.00$ Hz, 2H), 3.89 (dd, $J = 12, 5.22$ Hz, 1H), 3.84 (dd, $J = 11.5, 4.80$ Hz, 1H), 3.68 (q, $J = 9.25$ Hz, 1H), 3.39 (m, 2H), 3.26 (d, $J = 5.40$ Hz, 1H), 3.24 (t, $J = 6.54$ Hz, 1H), 3.18 (dd, $J = 15.00, 8.00$ Hz, 1H),

(t, $J = 7.12$ Hz, 1H), 4.35 (m, 2H), 4.23 (m, 3H), 4.02 (t, $J = 7.52$ Hz, 1H), 3.08 (m, 2H), 3.27 (dd, $J = 15.48, 5.78$ Hz, 1H), 3.14 (dd, $J = 15.50, 8.91$ Hz, 1H), 3.10 (dd, $J = 14.12, 6.65$ Hz, 1H), 3.06 (m, 4H), 2.42 (m, 2H), 2.32 (m, 2H), 2.31 (m, 2H), 1.94 (m, 6H), 1.71 (m, 1H), 1.72 (m, 3H), 1.58 (m, 1H), 1.53 (m, 2H), 1.43 (m, 2H), 0.85 (d, $J = 5.00$ Hz, 12.00 H), 0.81 (d, $J = 6.20$ Hz, 6H).

^{13}C NMR (125.7 MHz, CD_3OD , 25°C) $\delta = 18.29, 19.78, 21.63, 22.15, 22.77, 23.55, 24.31, 24.36, 26.39, 26.65, 27.91, 28.15, 28.17, 30.62, 31.03, 31.55, 32.21, 38.18, 41.29, 41.69, 47.57, 53.59, 54.03, 54.54, 54.66, 55.86, 57.45, 61.06, 61.92, 67.44, 118.73, 128.08, 128.82, 129.09, 129.58, 129.72, 130.38, 131.39, 134.87, 138.10, 138.58, 169.99, 173.93, 174.33, 174.39, 174.90, 175.19, 176.44$.

MS (Accurate Q-TOF LC/HRMS): m/z (%): 1115.6262 (100) $[\text{M}+\text{H}]^+$

Spectroscopic data of PELFV-NH₂ (5aa)

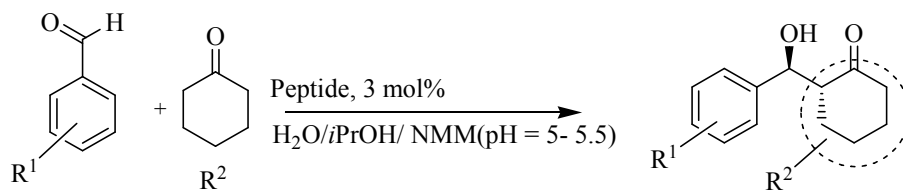


IR (neat) $\nu = 3342, 3125, 3085, 2975, 2846, 1665, 1546, 1187, 1135, \text{cm}^{-1}$; ^1H NMR (700 MHz, $\delta = \text{ppm}$); $\delta = 8.74$ (s, 1H), 8.35 (d, $J = 7.01$ Hz, 1H), 8.33 (d, $J = 7.50$ Hz, 1H), 7.99 (d, $J = 8.32$ Hz, 1H), 7.35 (t, $J = 7.50$ Hz, 2H), 7.29 (t, $J = 7.02$ Hz, 1H), 7.25 (d, $J = 7.60$ Hz), 7.16 (bs, 1H), 6.90 (bs, 1H), 4.30 (m, 2H), 4.03 (t, $J = 7.78$ Hz, 2H), 3.70 (s, 1H), 3.41 (m, 3H), 3.06 (m, 3H), 3.06 (dd, $J = 13.52, 7.50$ Hz, 3H), 2.40 (m, 1H), 2.23 (m, 1H), 2.01 (m, 3H), 1.87 (m, 1H), 1.50 (m, 1H), 1.46 (m, 1H), 1.16 (dd, $J = 6.25, 0.50$ Hz, 2H), 0.89 (d, $J = 6.50$ Hz, 6H), 0.87 (d, $J = 6.72$ Hz, 3H), 0.83 (d, $J = 6.23$ Hz, 3H).

^{13}C NMR (125.7 MHz, D_2O , 25°C) $\delta = 18.51, 19.78, 22.17, 23.42, 25.00, 25.30, 25.80, 28.55, 31.07, 31.60, 32.05, 38.62, 42.31, 47.55, 52.35, 53.16, 54.46, 56.04, 59.71, 61.01, 64.81, 66.95, 127.85, 129.54, 130.43, 138.32, 169.80, 173.04, 173.24, 174.25, 174.82, 175.71, 176.71$.

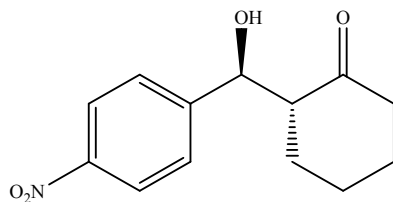
MS (Accurate Q-TOF LC/HRMS): m/z (%): 603.3515 (100) $[\text{M}+\text{H}]^+$

➤ **General procedure for aldol reaction catalyzed by peptide**



To H₂O (0.6 mL) was added the corresponding catalyst (0.005 mmol, 5 mg), NMM (1 drop), and *i*PrOH (0.4 mL). The reaction mixture was stirred for 20 min followed by addition of the corresponding ketone (0.168 mmol, 1.2 eq). Then, the requisite aldehyde (0.14 mmol, 1 eq) was added to the reaction mixture. The resulting mixture was stirred at RT for 24 h. The reaction was monitored by TLC. Then treated with saturated ammonium chloride solution and the mixture was extracted with ethyl acetate (3×2mL). The combined organic extract was washed with brine, dried (Na₂SO₄), and concentrated in vacuo. After NMR analysis to determine diastereomeric ratio, the residue was purified by flash column chromatography with hexanes/ethyl acetate (3:1) to afford the aldol products that were subjected to chiral HPLC analysis to determine enantiomeric excesses.

1- (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone



The resulting pure product was examined by ¹H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 ×250mm), yield: 97%; The *ee* was determined by chiral HPLC (Chiral OD-H, *i*PrOH/*n*-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): *t*_{major}= 35.488 min, *t*_{minor}= 47.551 min, *ee* = 97%, dr = 90:10 (anti/syn).

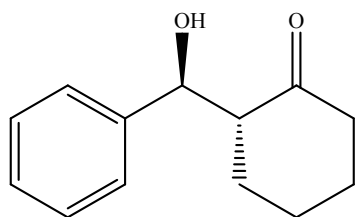
FT-IR (cm⁻¹): 3510, 2938, 2901, 2875, 1686, 1603, 1507, 1339; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.26-1.35 (m, 1H), 1.44-1.65 (m, 4H), 1.77 (d, *J* = 13.7 Hz, 1H), 2.06-2.11 (m, 1H), 2.30-2.37 (td, *J* = 13.75Hz, *J* = 6.9 Hz, 1H), 2.54-2.62 (m, 1H), 4.83 (d, *J* = 8 Hz, 1H), 7.44 (d, *J* = 9.15 Hz, 2H), 8.15 (d, *J* = 9.15 Hz, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ = 24.62, 27.59, 30.69, 42.62, 57.12, 73.74, 123.40, 123.52, 126.56, 127.86, 147.49, 148.30, 214.78

DEPT 90 and 135 deg show four methylene groups (negative) and 6 methine groups (positive) which in the aromatic area two of CH groups have been overlapped together.

MS (DI) = 249

2 *(R)*-2-*(S)*-hydroxy(phenyl)methyl)cyclohexanone

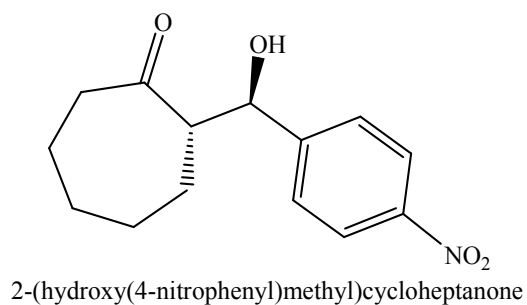


FT-IR (cm^{-1}): 3508, 3112, 2935, 2862, 1692, 1510, 1338; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 1.73- 1.79 (m, 3H), 1.89- 1.94 (m, 3H), 2.51- 2.55 (t, J = 6.85 Hz, 2H), 2.83 (td, J = 12.2Hz, J = 5.4 Hz, 1H) - 2.91- 2.94 (m, 1H), 4.78 (d, J = 9.2 Hz, 1H), 7.4, (m, 5H)

^{13}C NMR (100 MHz, CDCl_3) δ = 23.86, 28.4, 28.92, 40.29, 60.48, 74.54, 128.32, 128.47, 129.2, 130.19, 130.29, 133.78, 215.18

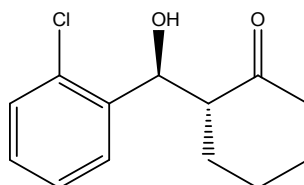
MS(DI) = 204

3 2-(XXXhydroxyl(4-nitrophenyl)methyl)cycloheptanone



FT-IR (cm⁻¹): 3100, 2928, 2860, 1704, 1603, 1346, 1117; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.20- 1.45 (m, 4H), 1.65-1.92 (m, 4H), 2.40- 2.59 (m, 2H), 2.98 (m, 1H), 3.74 (d, *J* = 4.8 Hz, 1H), 4.92 (dd, *J* = 6.9, *J* = 5.2 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 8.21(d, *J* = 9.1Hz, 2H).

4 *S*-2-((*S*)-(2-chlorophenyl)(XXXhydroxyl)methyl)cyclohexanone



The resulting pure product was examined by ¹H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 ×250mm), yield: 95%; The *ee* was determined by chiral HPLC (Chiral OD-H, ⁱPrOH/n-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): *t*_{major}= 13.055 min, *t*_{minor}= 15.552 min, *ee* = 99.9%, dr = 96:4 (anti/syn).

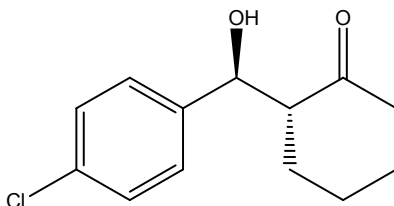
FT-IR (cm⁻¹): 3437, 2940, 2864, 1696, 1438, 1030, 756; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.54-1.64 (m, 5H), 1.79-1.81 (m, 1H), 2.04-2.08 (m, 1H), 2.29-2.35 (td, *J* = 13.75 Hz, *J* = 6.85 Hz 1H), 2.43-2.46 (m, 1H), 2.63-2.68 (m, 1H), 5.33 (d, *J*= 8 Hz, 1H), 7.19 (dd, *J* = 8, *J* = 5.7 Hz, 1H), 7.27-7.31 (m, 2H), 7.52 (dd, *J* = 8, *J* = 2.3 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ = 24.89, 27.79, 30.37, 42.71, 57.56, 70.43, 127.23, 128.20, 128.73, 129.19, 132.94, 139.02, 215.32.

DEPT⁹⁰ and ¹³⁵ deg demonstrate four methylene groups (negative) and 6 methine groups (positive).

MS(DI) = 238

5 (*S*)-2-((*S*)-(4-chlorophenyl)(XXXhydroxyl)methyl)cyclohexanone



The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 \times 250mm). Yield: 95%; The *ee* was determined by chiral HPLC (Chiral OD-H, *i*PrOH/n-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): t_{major} = 13.831 min, t_{minor} = 17.452 min, *ee* = 96.54 %, dr = 93:7 (anti/syn).

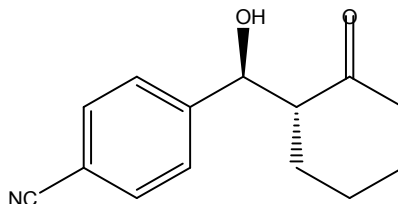
FT-IR (cm^{-1}): 2828, 2663, 2552, 1678, 1418, 1284, 926; ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 1.25-1.27 (m, 2H), 1.52-1.55 (m, 2H), 1.56-1.60 (m, 1H), 1.60-1.63 (m, 1H), 2.07-2.08 (m, 1H), 2.31-2.37 (td, J = 13.7 Hz, J = 6.8 Hz, 1H), 2.46-2.53 (m, 1H), 2.54-2.55 (m, 1H), 4.76 (d, J = 9.15 Hz, 1H), 7.25 (d, J = 9.15 Hz, 2H), 7.32 (d, J = 9.15 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ = 24.67, 27.71, 30.74, 42.64, 57.30, 74.15, 128.48, 128.54, 129.26, 130.19, 133.79, 171.97, 215.44.

DEPT 90 and 135 deg demonstrate four methylene groups (negative) and 6 methine groups (positive).

MS (DI) = 238

6 2-[Hydroxy-(4-cyano-phenyl)-methyl]-cyclohexanone



The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 \times 250mm), yield: 95%; The *ee* was determined by chiral HPLC (Chiral OD-H, *i*PrOH/hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): t_{major} = 18.801 min, t_{minor} = 26.323 min, *ee* = 86 %, dr = 99:1 (anti/syn).

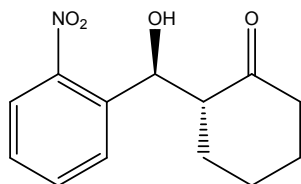
FT-IR (cm^{-1}): 3425, 3356, 2932, 2860, 1688, 1481, 1053, 824; ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 1.61-1.71(m, 3H), 1.89-1.99 (m, 2H), 2.06-2.13 (m, 2H), 2.16-2.24 (m, 1H), 2.29-2.43 (m, 1H), 4.75 (d, J = 9.15 Hz, 1H), 5.31 (d, J = 2.3 Hz, 1H) 7.41 (dd, J = 2.3, J = 8 Hz, 2H), 7.58 (dd, J = 4.6, J = 8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ = 20.25, 22.24, 26.66, 38.94, 55.97, 74.43, 110.82, 118.71, 126.19, 127.17, 132.11, 148.30, 219.91.

DEPT⁹⁰ and ¹³⁵ deg demonstrate four methylene groups (negative) and 6 methine groups (positive).

MS(DI) = 229

7 *(R)*-2-((*S*)-hydroxy(2-nitrophenyl)methyl)cyclohexanone



The resulting pure product was examined by ¹H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 ×250mm). yield: 95%; The *ee* was determined by chiral HPLC (Chiral OD-H, ^tPrOH/n-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): *t*_{major} = 11.508 min, *t*_{minor} = 16.098 min, *ee* = 88.8 %, dr = 98: 2 (anti/syn).

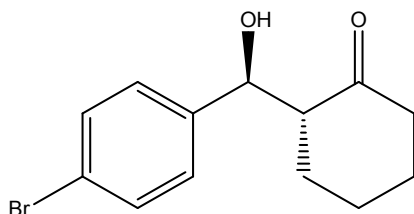
FT-IR (cm⁻¹): 3411, 2942, 2866, 1703, 1524, 1349; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.57-1.75(m, 5H), 1.80-1.83 (m, 1H), 2.04-2.09 (m, 1H), 2.27-2.34 (td, *J* = 13.75 Hz, *J* = 5.75 Hz, 1H), 2.40-2.43 (m, 1H), 5.42 (d, *J* = 6.85 Hz, 1H), 7.40 (t, *J* = 8 Hz, 1H), 7.60 (t, *J* = 8 Hz, 1H), 7.74 (d, *J* = 8 Hz, 1H), 7.81 (d, *J* = 8 Hz, 1H)

¹³C NMR (100 MHz, CDCl₃) δ = 24.93, 27.72, 31.06, 42.78, 57.24, 69.70, 124.04, 128.36, 128.95, 133.05, 136.54, 148.67, 214.96.

DEPT⁹⁰ and ¹³⁵ deg demonstrate four methylene groups (negative) and 6 methine groups (positive).

MS(DI) = 249

8 *(R)*-2-((*S*)-(4-bromophenyl)(hydroxy)methyl)cyclohexanone



The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 \times 250mm). yield: 95%; The *ee* was determined by chiral HPLC (Chiral OD-H, *i*PrOH/n-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): *t*_{major} = 22.316 min, *t*_{minor} = 29.783 min, *ee* = 85.8 %, dr = 90: 10 (anti/syn).

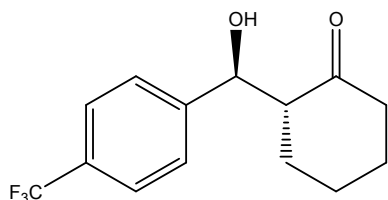
FT-IR (cm⁻¹): 2941, 2833, 2659, 2550, 1678, 1415, 1281, 925; ^1H NMR (500 MHz, CDCl₃): δ (ppm) = 1.24-1.32 (m, 1H), 1.49-1.70 (m, 4H), 1.77-1.85 (m, 1H), 2.06-2.11 (m, 1H), 2.31-2.37 (td, *J* = 13.7 Hz, *J* = 5.7 Hz, 1H), 2.43-2.48 (m, 1H), 2.51- 2.57 (m, 1H), 4.74 (d, *J* = 9.2 Hz, 1H), 7.19 (d, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl₃) δ = 24.68, 27.69, 30.73, 42.64, 57.29, 74.14, 121.70, 127.50, 128.71, 131.24, 131.47, 139.95, 215.30.

DEPT⁹⁰ and ¹³⁵ deg demonstrate four methylene groups (negative) and 6 methine groups (positive).

MS(DI) = 282

9 (*R*)-2-((*S*)-(4-(trifluoromethyl)phenyl)(hydroxy)methyl)cyclohexanone



The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. OD-H ChiralCel Column (4.6 \times 250mm). Yield: 95%; The *ee* was determined by chiral HPLC (Chiral OD-H, *i*PrOH/n-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): *t*_{major} = 13.407 min, *t*_{minor} = 15.682 min, *ee* = 79.5 %, dr = 92: 8 (anti/syn).

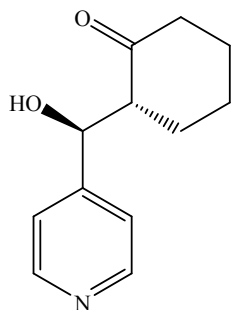
FT-IR (cm⁻¹): 3065, 2828, 2663, 2552, 1678, 1418, 1285, 928; ^1H NMR (500 MHz, CDCl₃): δ (ppm) = 1.25-1.31 (m, 2H), 1.49-1.53 (m, 2H), 1.55-1.64 (m, 1H), 1.73-1.75 (m, 1H), 2.00- 2.06 (m, 1H), 2.26-2.32 (td, *J* = 5.7 Hz, *J* = 13.7 Hz, 1H), 2.40-2.43 (m, 1H), 2.50-2.55 (m, 1H), 4.77 (d, *J* = 8 Hz, 1H), 7.37 (d, *J* = 8 Hz, 2H), 7.53 (d, *J* = 8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl₃) δ = 24.70, 27.69, 30.74, 42.66, 57.24, 74.26, 125.58, 125.32, 127.35, 129.94, 130.20, 144.93, 215.12.

DEPT⁹⁰ and ¹³⁵ deg demonstrate four methylene groups (negative) and 6 methine groups (positive).

MS(DI) = 272

10 (R)-2-((S)-hydroxy(pyridin-4-yl)methyl)cyclohexanone



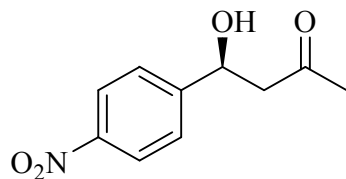
The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. AD-H ChiralPak Column (4.6 \times 250mm). Yield: 95%; The *ee* was determined by chiral HPLC (Chiral AD-H, *i*PrOH/*n*-hexane 5/95, flow rate = 0.8 mL/min, λ = 254 nm): t_{major} = 12.228 min, t_{minor} = 16.668 min, *ee* = 98 %, dr = 99:1 (anti/syn).

FT-IR (cm^{-1}): 3100, 2928, 2860, 1704, 1603, 1413, 1117; ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 1.66-1.71 (m, 2H), 1.93- 2.02 (m, 2H), 2.09-2.16 (m, 1H), 2.3- 2.40 (m, 1H), 4.38 (bs, 1H), 5.29 (d, J = 2.3 Hz 1H), 7.28 (d, J = 4.55 Hz, 2H), 7.43 (d, J = 4.55 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 20.38, 22.14, 39.01, 55.67, 69.50, 120.83, 129.06, 153.18, 219.51.

DEPT⁹⁰ and ¹³⁵ deg demonstrate four methylene groups (negative) and 6 methine groups (positive two overlapped). MS(DI) = 272

11 (S)-4-hydroxy-4-(4-nitrophenyl)butan-2-one



The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. AD-H ChiralPak Column

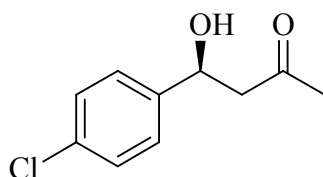
(4.6 ×250mm). The ee was determined by chiral HPLC (Chiral AD-H, ⁱPrOH/n-hexane 10/90, flow rate = 0.8 mL/min, λ = 254 nm).

FT-IR (cm⁻¹): 3430, 3068, 2922, 1700, 1414, 1281. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 2.14 (s, 3H), 2.78 (d, *J* = 5.7 Hz, 2H), 3.96 (bs, 1H), 5.19 (dd, *J* = 6.9, 5.7 Hz, 1H), 7.46 (d, *J* = 8 Hz, 2H), 8.11 (d, *J* = 8 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ = 30.61, 51.48, 68.50, 123.66, 126.36, 128.36, 130.01, 147.4, 150.04, 208.44.

DEPT⁹⁰ and ¹³⁵ deg demonstrate one methylene groups (negative) and five methine groups (positive).

12 (*S*)-4-(4-chlorophenyl)-4-hydroxybutan-2-one



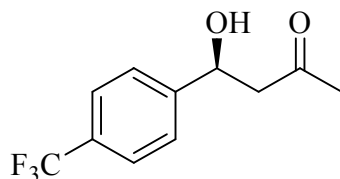
The resulting pure product was examined by ¹H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their ee. AD-H ChiralPak Column (4.6 ×250mm). The ee was determined by chiral HPLC (Chiral AD-H, ⁱPrOH/n-hexane 10/90, flow rate = 0.5 mL/min, λ = 254 nm).

FT-IR (cm⁻¹): 3425, 3077, 2919, 1703, 1515, 1340. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 2.17(s, 3H), 2.78 (d, *J* = 4.6 Hz, 2H), 3.36 (bs, 1H), 5.10 (dd, *J* = 8.9, 3.7 Hz, 1H), 7.27-7.30 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ = 30.74, 51.76, 69.15, 127.00, 128.65, 133.32, 141.14, 208.93.

DEPT⁹⁰ and ¹³⁵ deg demonstrate one methylene groups (negative) and five methine groups (positive).

13 (*S*)-4-(4-(trifluoromethyl)phenyl)-4-hydroxybutan-2-one



The resulting pure product was examined by ¹H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their ee. AD-H ChiralPak Column

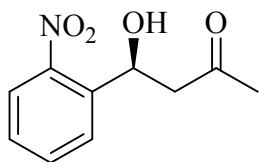
(4.6 × 250mm). The ee was determined by chiral HPLC (Chiral AD-H, *i*PrOH/n-hexane 10/90, flow rate = 1 mL/min, λ = 254 nm).

FT-IR (cm⁻¹): 3420, 3078, 2914, 1705, 1515, 1341. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 2.17 (s, 3H), 2.81 (d, *J* = 4.55 Hz, 2H), 3.54 (bs, 1H), 5.18 (dd, *J* = 7.4, 3.45 Hz, 1H), 7.44 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 9.15 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ = 30.65, 51.45, 68.80, 125.45, 125.87, 129.61, 129.94, 146.94, 208.79.

DEPT⁹⁰ and ¹³⁵ deg demonstrate one methylene groups (negative) and five methine groups (positive).

14 (*S*)-4-hydroxy-4-(2-nitrophenyl)butan-2-one



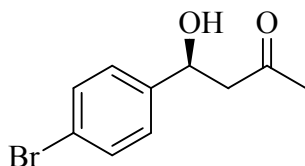
The resulting pure product was examined by ¹H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. AD-H ChiralPak Column (4.6 × 250mm). The ee was determined by chiral HPLC (Chiral AD-H, *i*PrOH/n-hexane 5/95, flow rate = 0.5 mL/min, λ = 254 nm)

FT-IR (cm⁻¹): 3418, 3077, 2922, 1706, 1520, 1344. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 2.21 (s, 3H), 2.70 (dd, *J* = 17.7, 10.3 Hz, 2H), 3.7 (bs, 1H), 5.65 (dd, *J* = 9.15, 2.3 Hz, 1H), 7.41 (d, *J* = 8 Hz, 2H), 7.64 (t, *J* = 8 Hz, 1H), 7.86 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H)

¹³C NMR (100 MHz, CDCl₃) δ = 30.41, 51.04, 65.57, 124.41, 128.15, 128.25, 133.80, 138.37, 147.11, 208.80.

DEPT⁹⁰ and ¹³⁵ deg demonstrate one methylene groups (negative) and five methine groups (positive).

15 (*S*)-4-(4-bromophenyl)-4-hydroxybutan-2-one



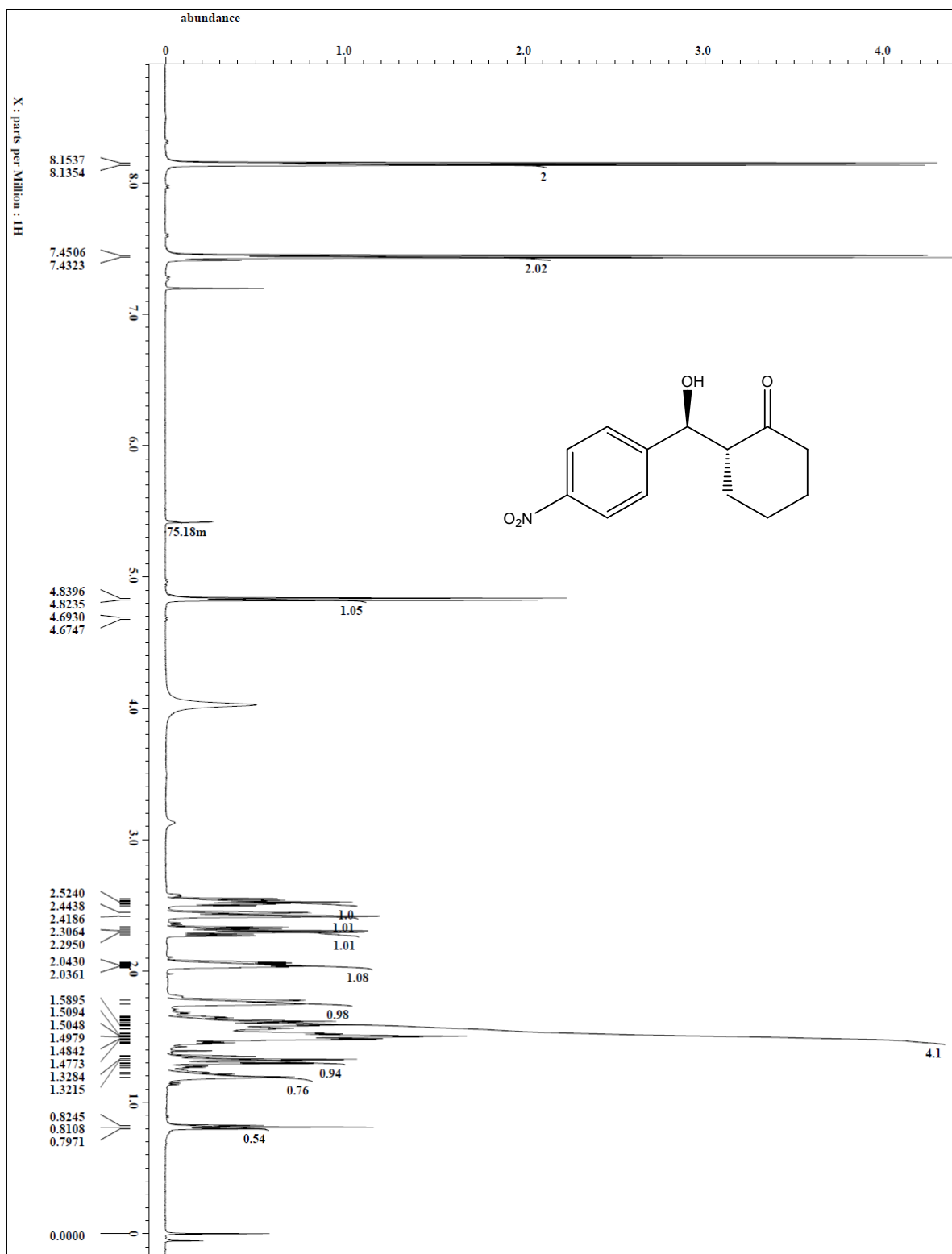
The resulting pure product was examined by ^1H NMR to determine the dr. The chromatography purified aldol products were then examined by HPLC to determine their *ee*. AD-H ChiralPak Column ($4.6 \times 250\text{mm}$). The *ee* was determined by chiral HPLC (Chiral AD-H, $i\text{PrOH/n-hexane } 10/90$, flow rate = 1 mL/min , $\lambda = 254 \text{ nm}$).

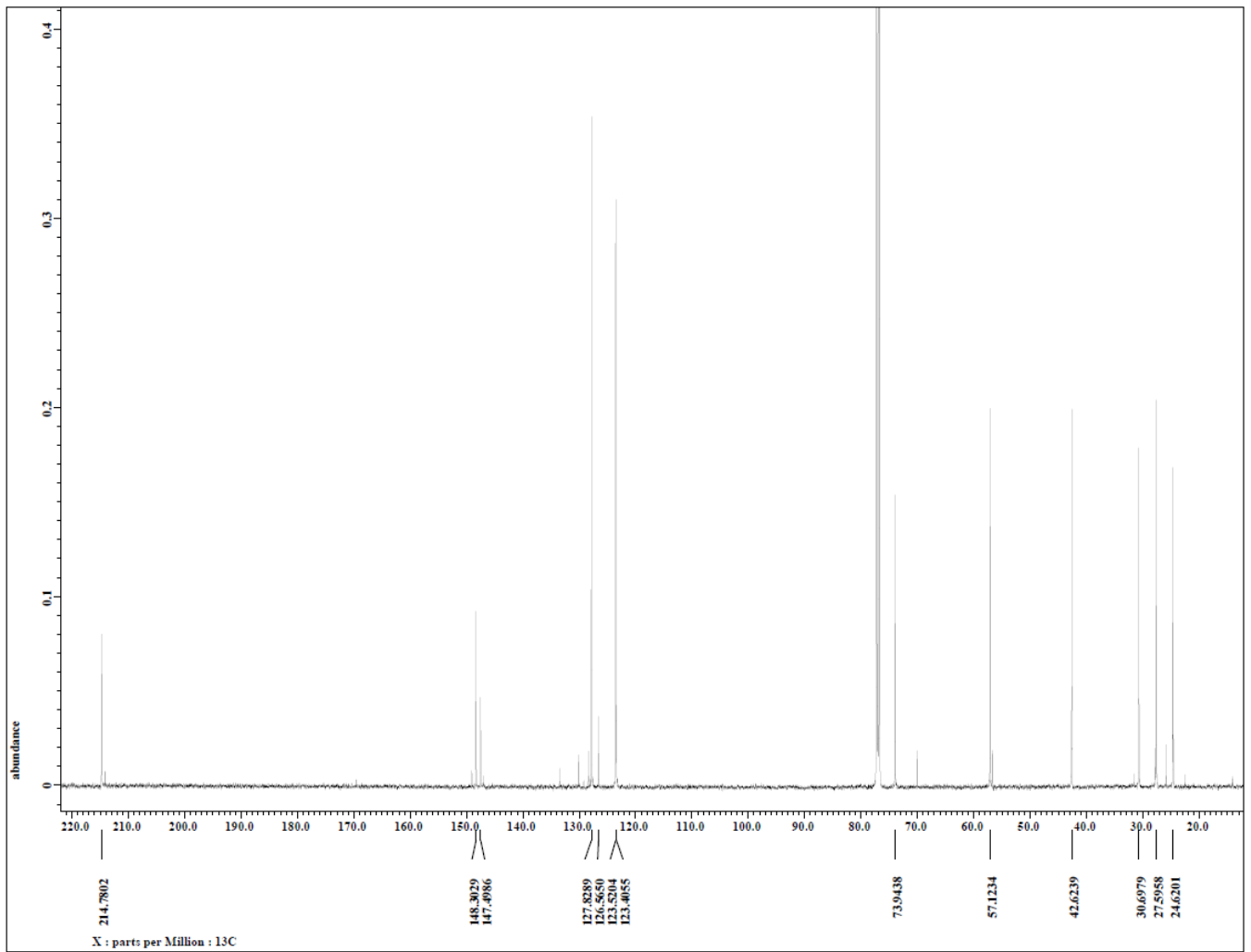
FT-IR (cm^{-1}): 3418, 2921, 2855, 1705, 1490, 1352. ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 2.18 (s, 3H), 2.81 (d, $J = 4.55 \text{ Hz}$, 2H), 3.69 (bs, 1H), 5.22 (dd, $J = 7.4, 3.45 \text{ Hz}$, 1H), 7.49 (d, $J = 8 \text{ Hz}$, 2H), 8.15(d, $J = 9.15 \text{ Hz}$, 2H).

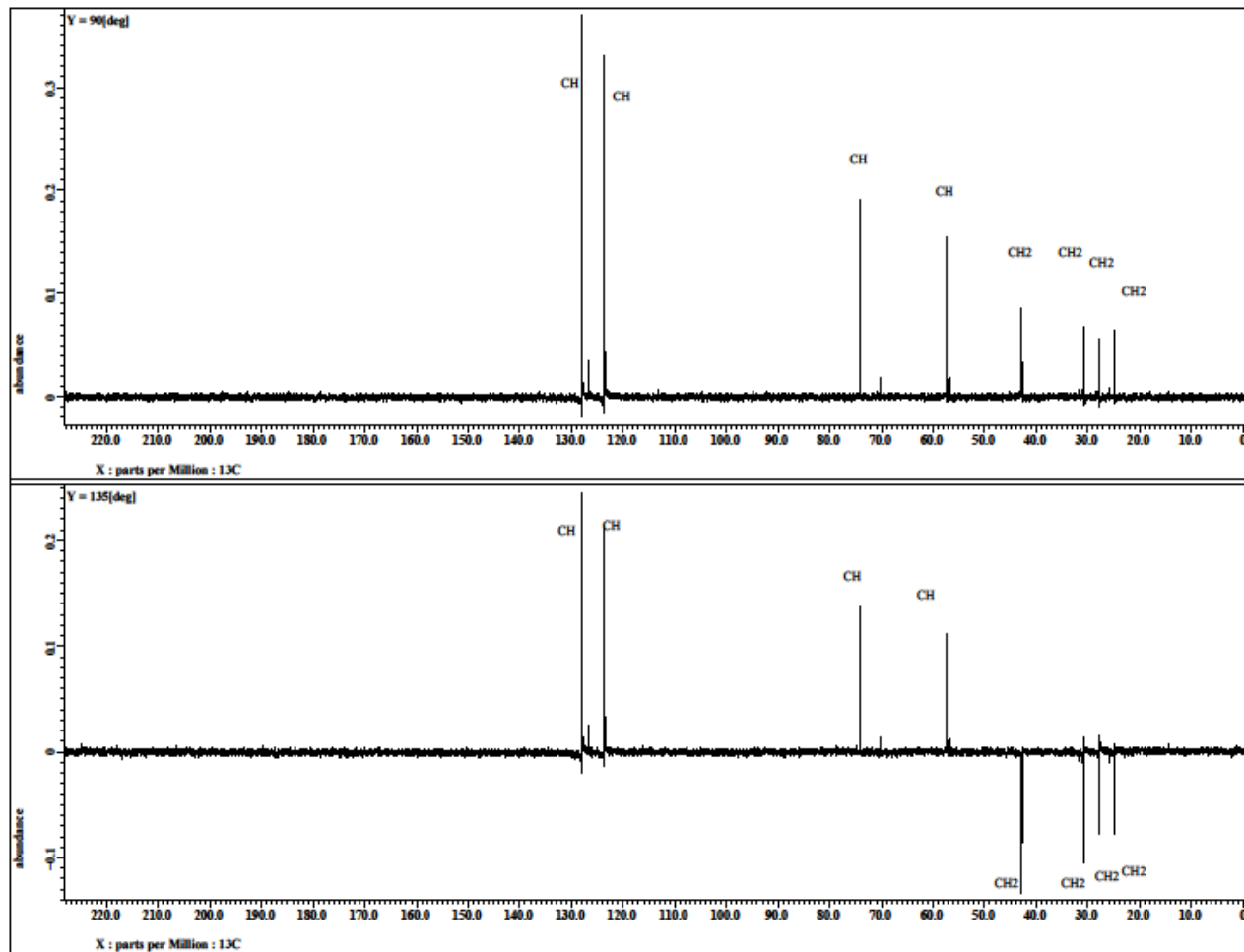
^{13}C NMR (100 MHz, CDCl_3) $\delta = 30.65, 51.45, 68.80, 123.68, 126.36, 147.21, 150.01, 208.47$.

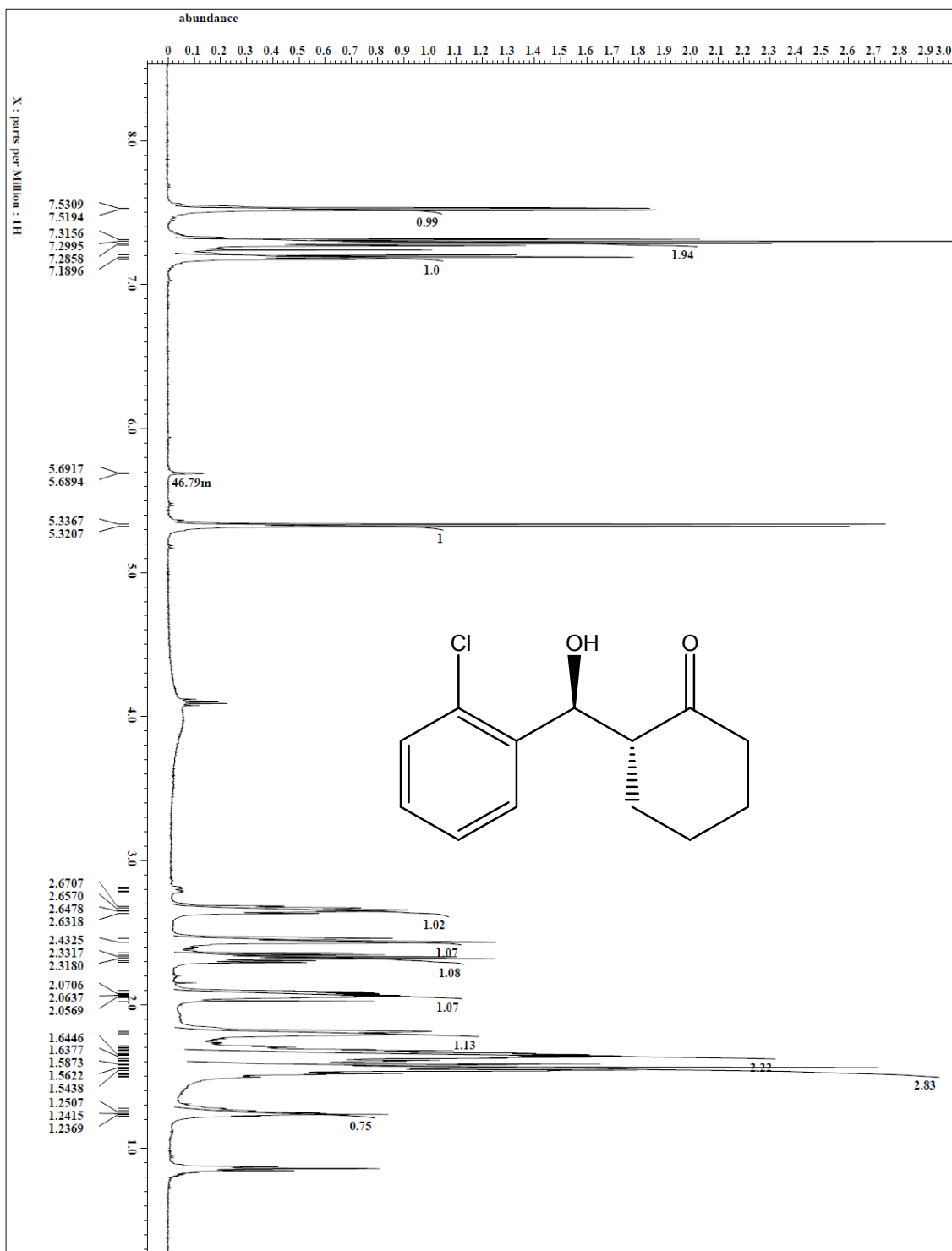
DEPT 90 and 135 deg demonstrate one methylene groups (negative) and five methine groups (positive).

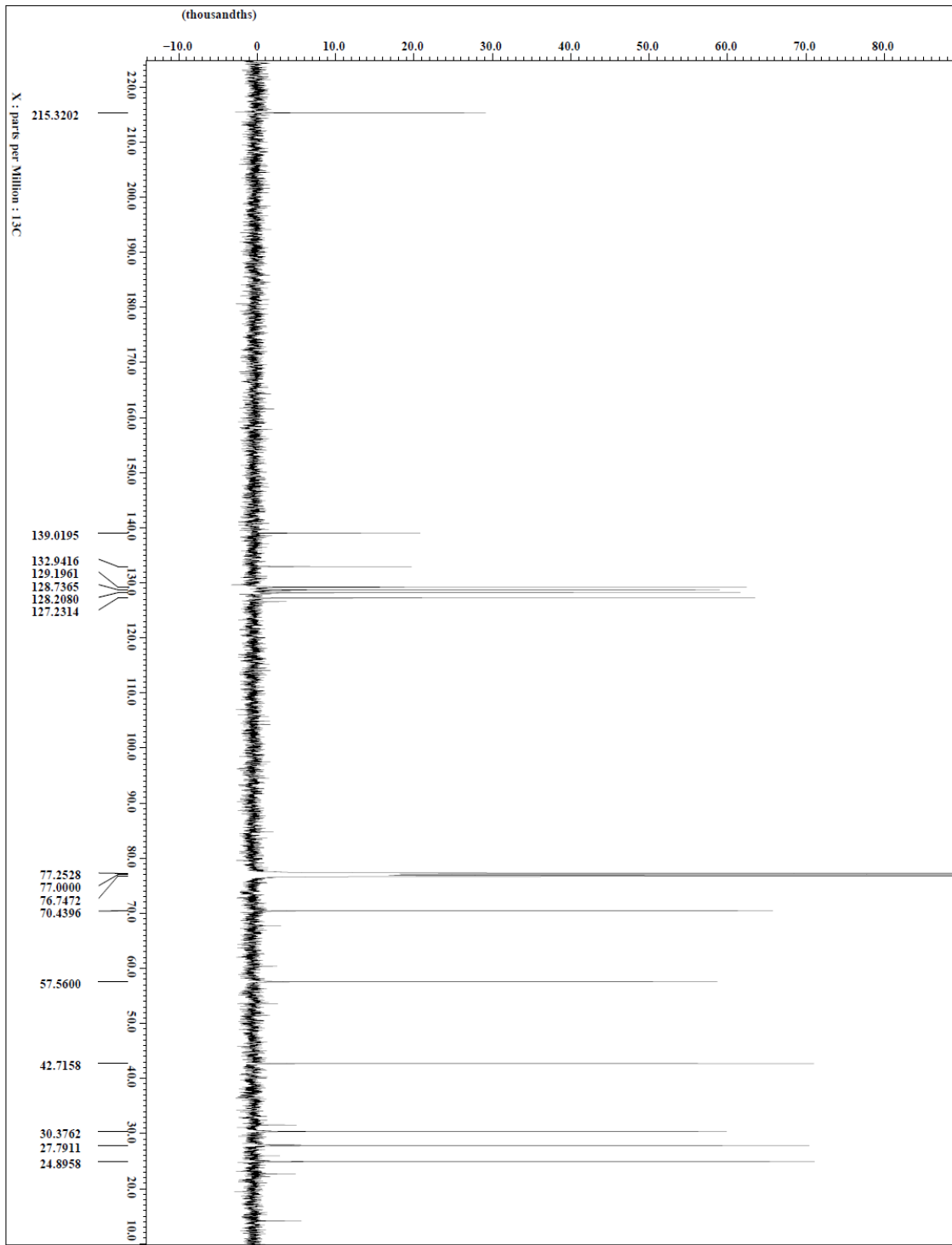
➤ **NMR spectra of corresponding aldol compounds**

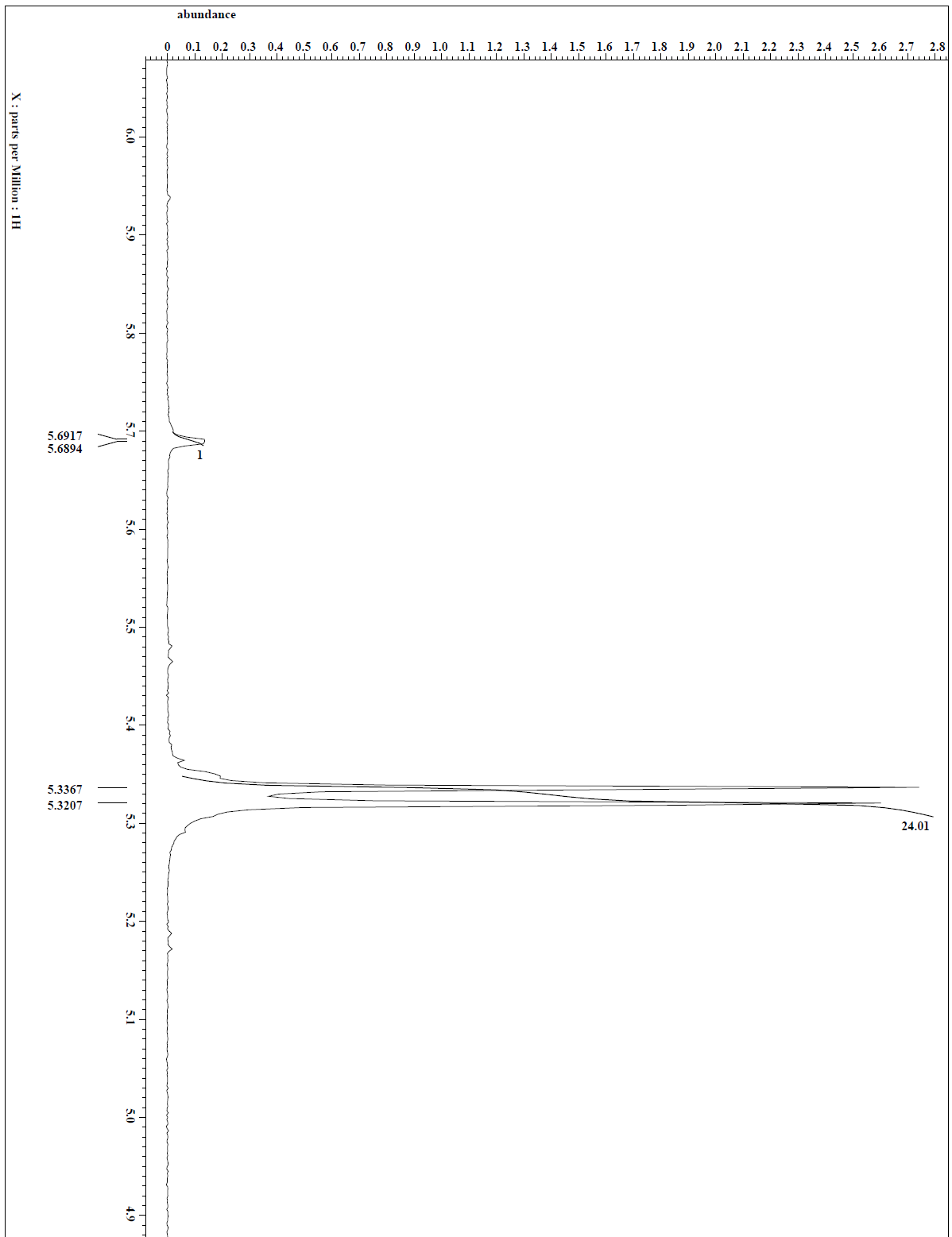


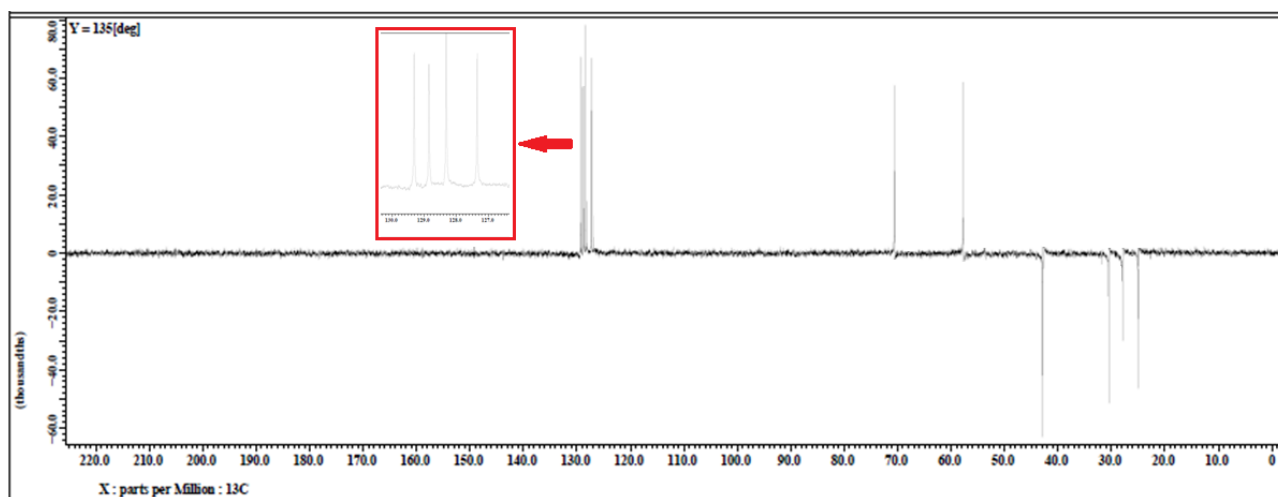
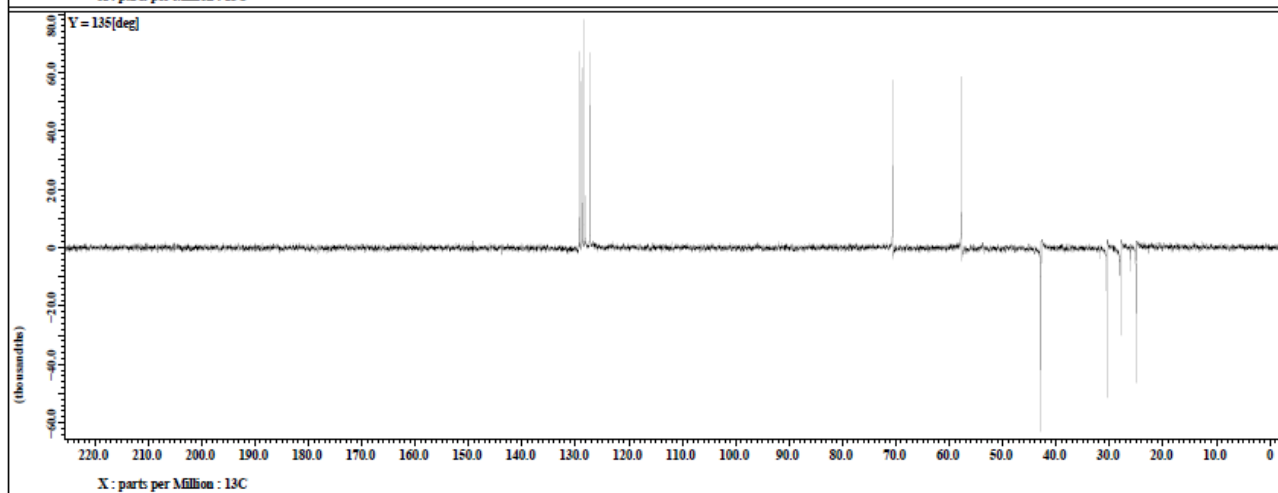
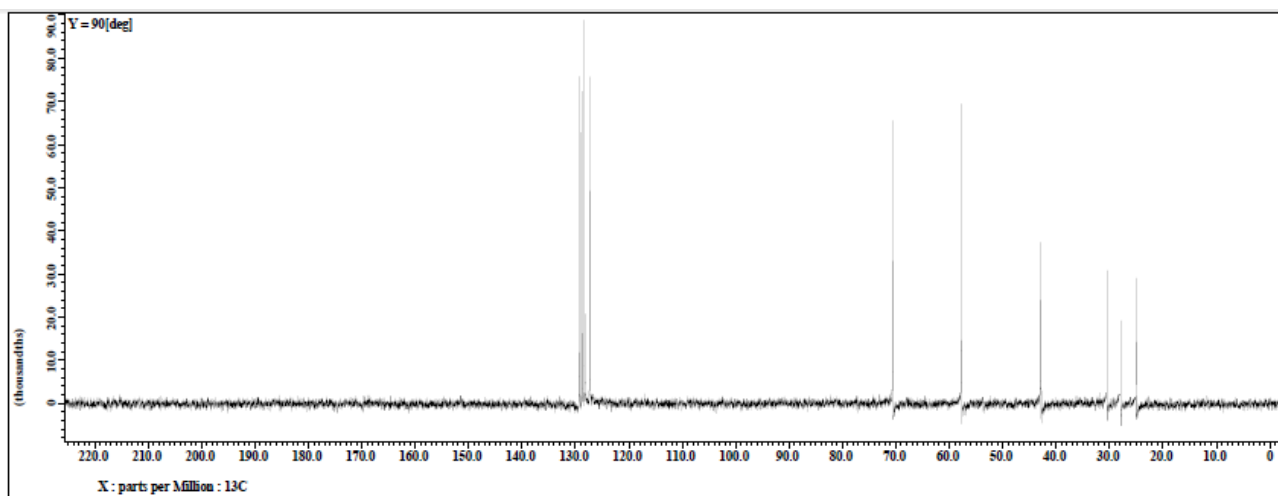


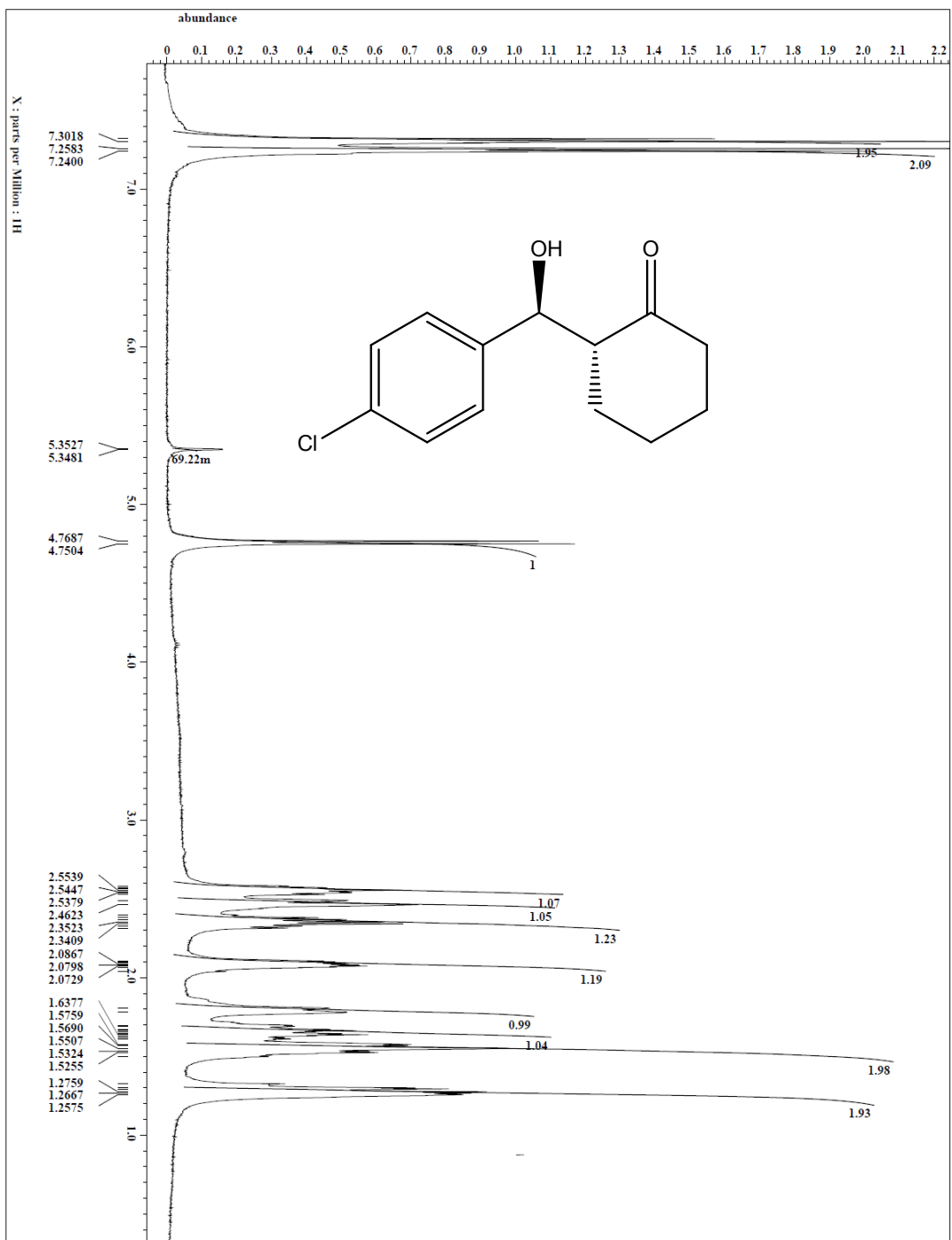


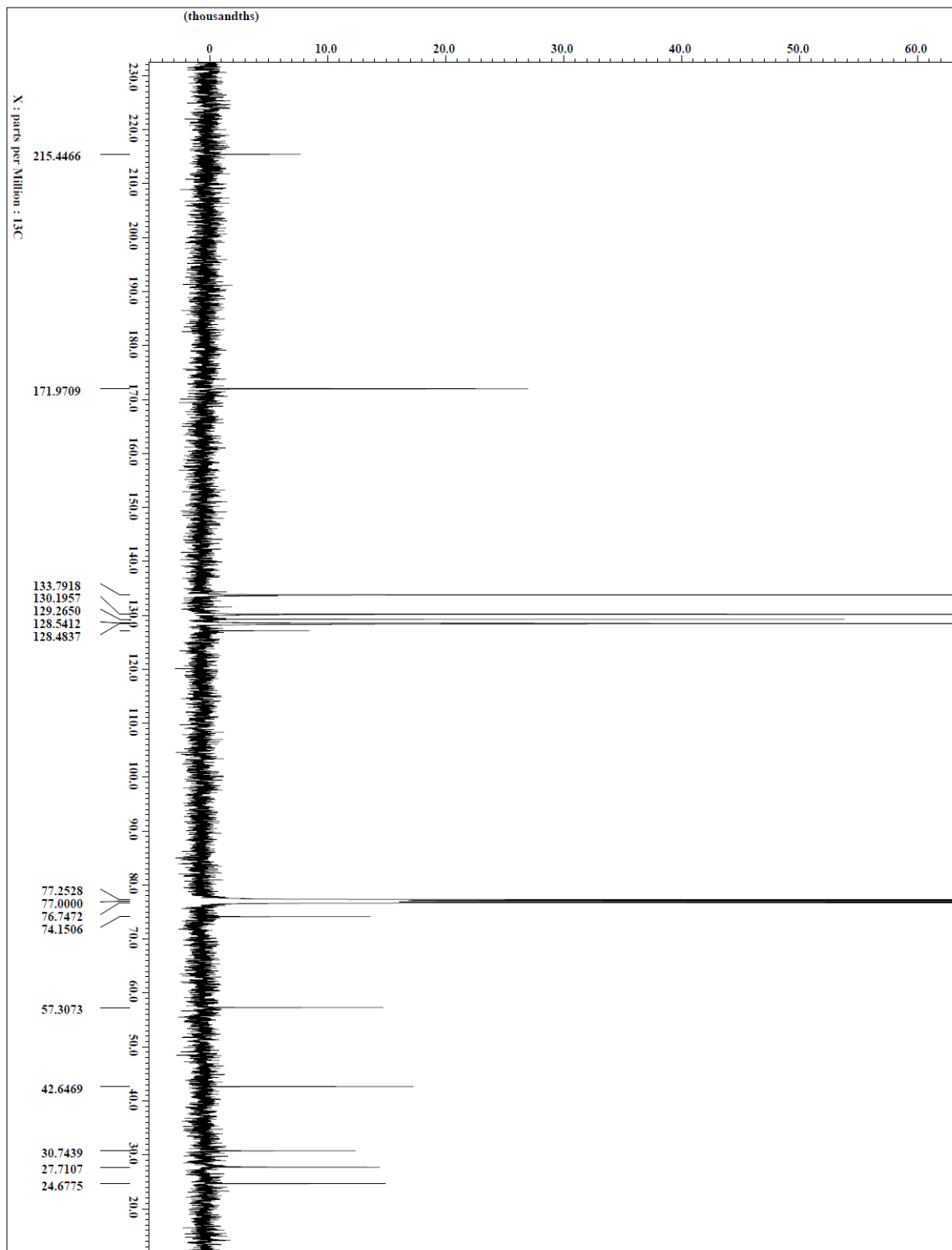


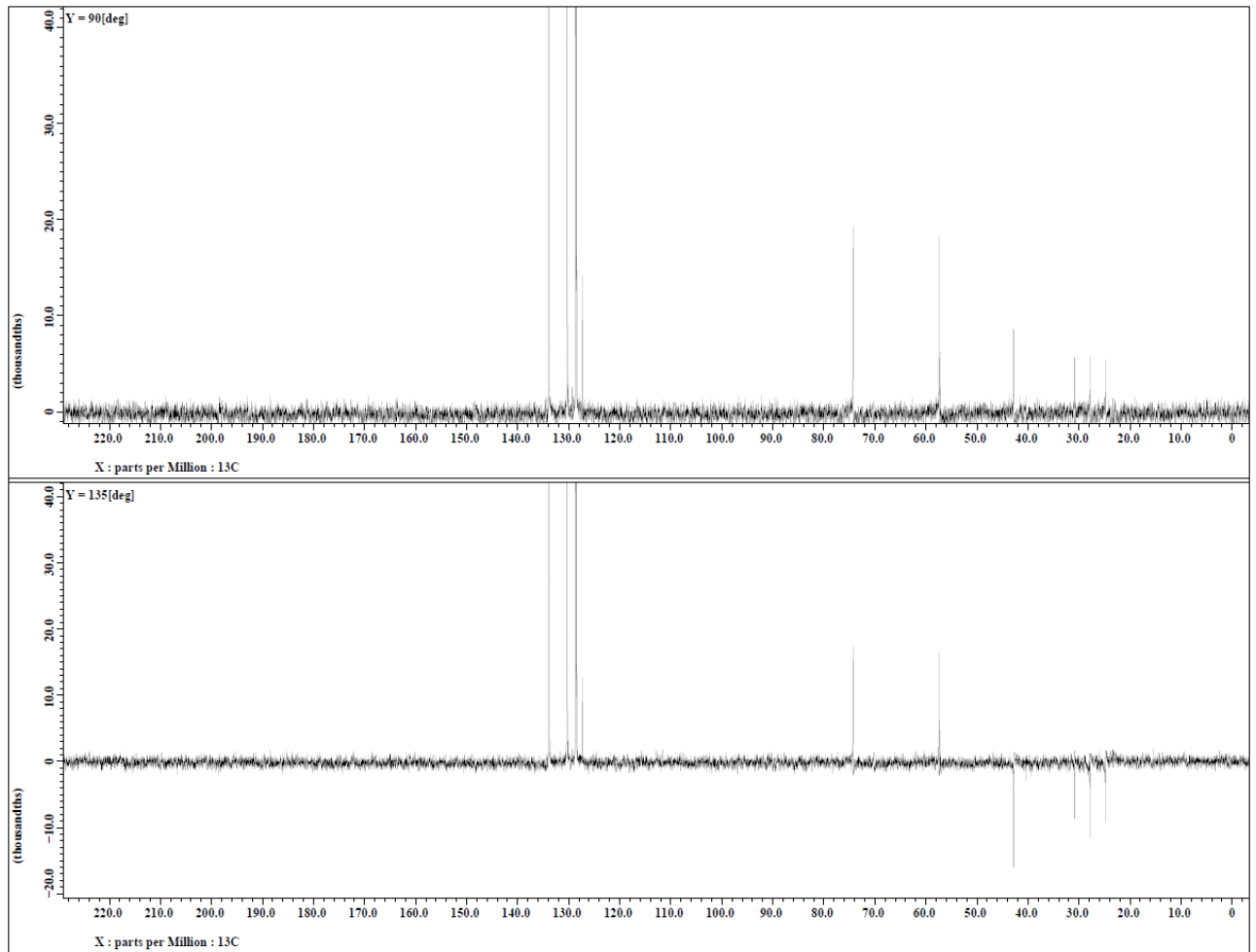




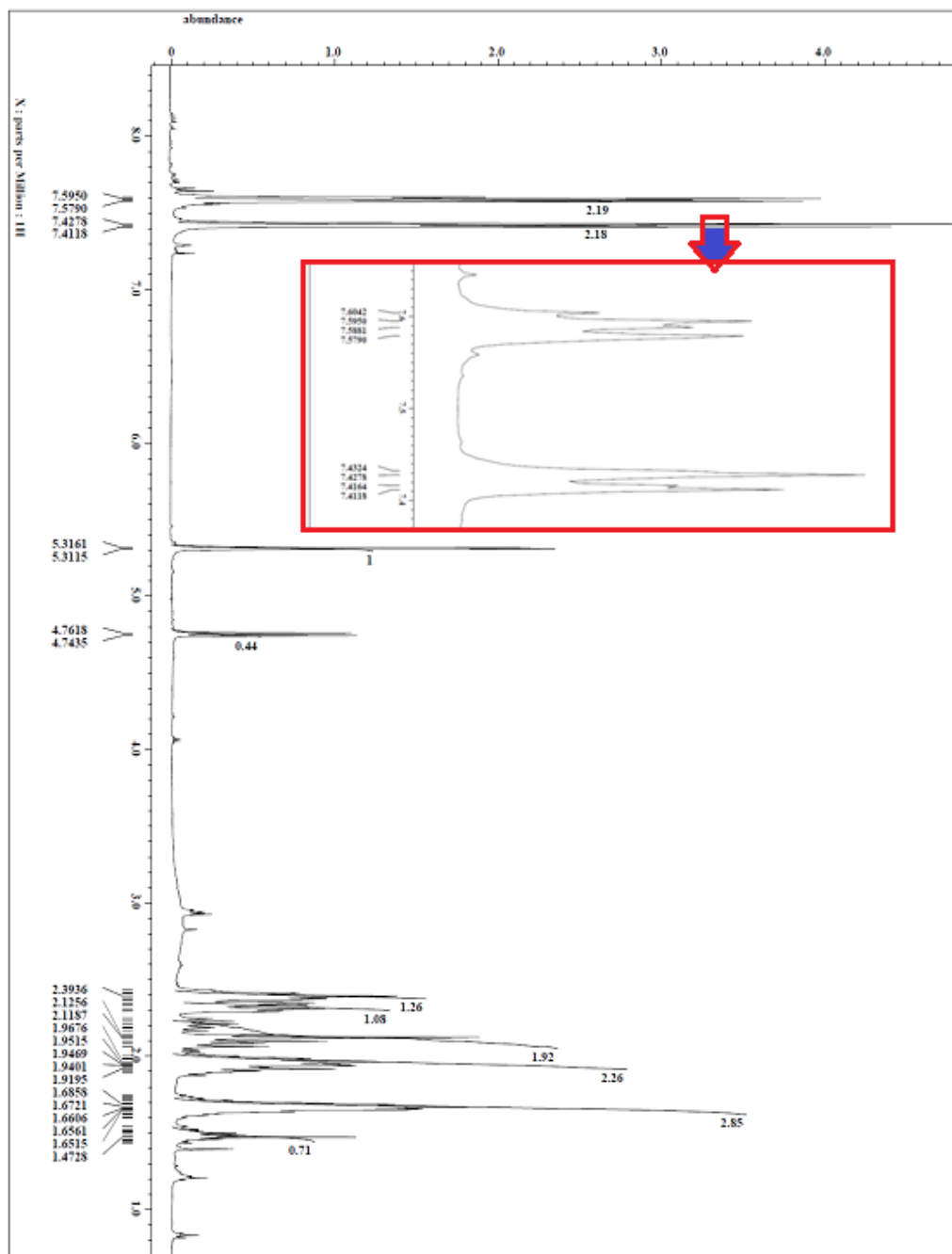


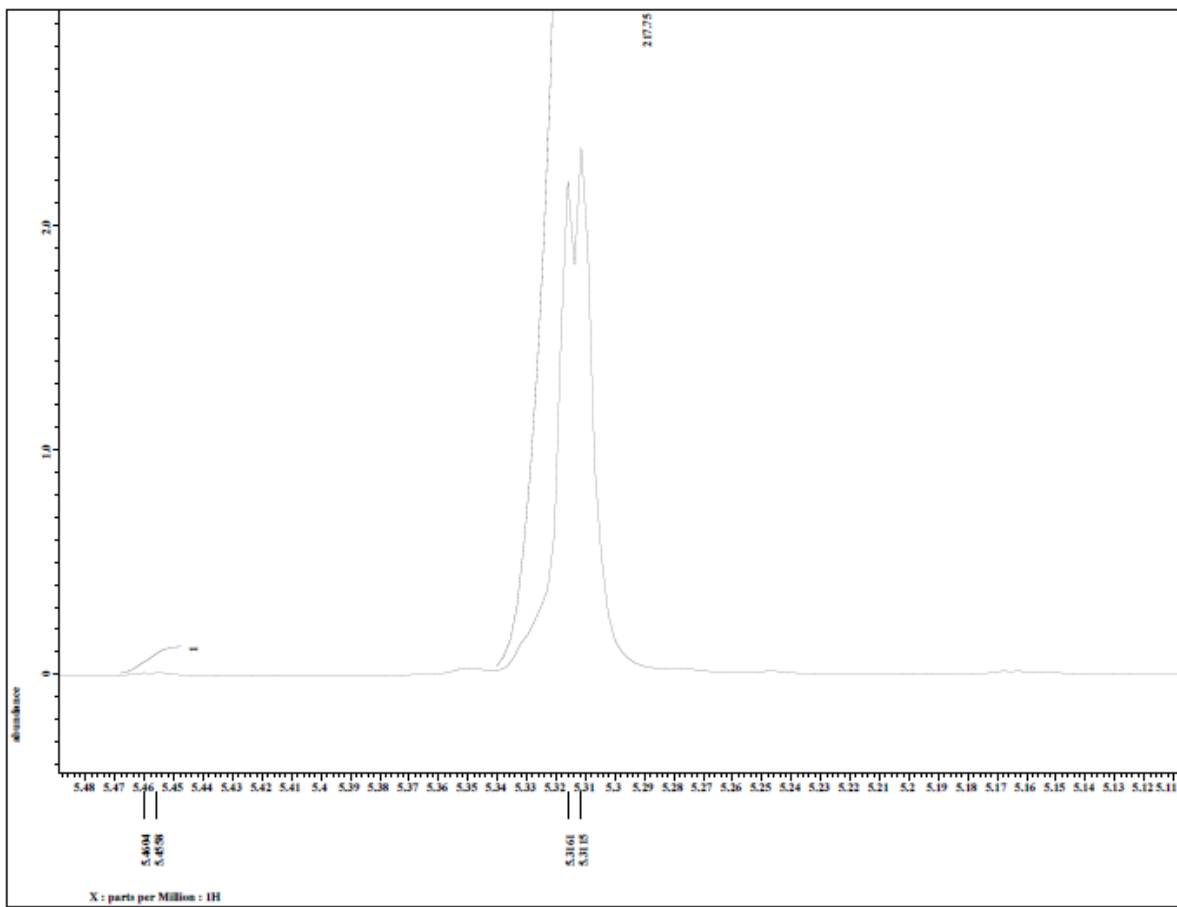


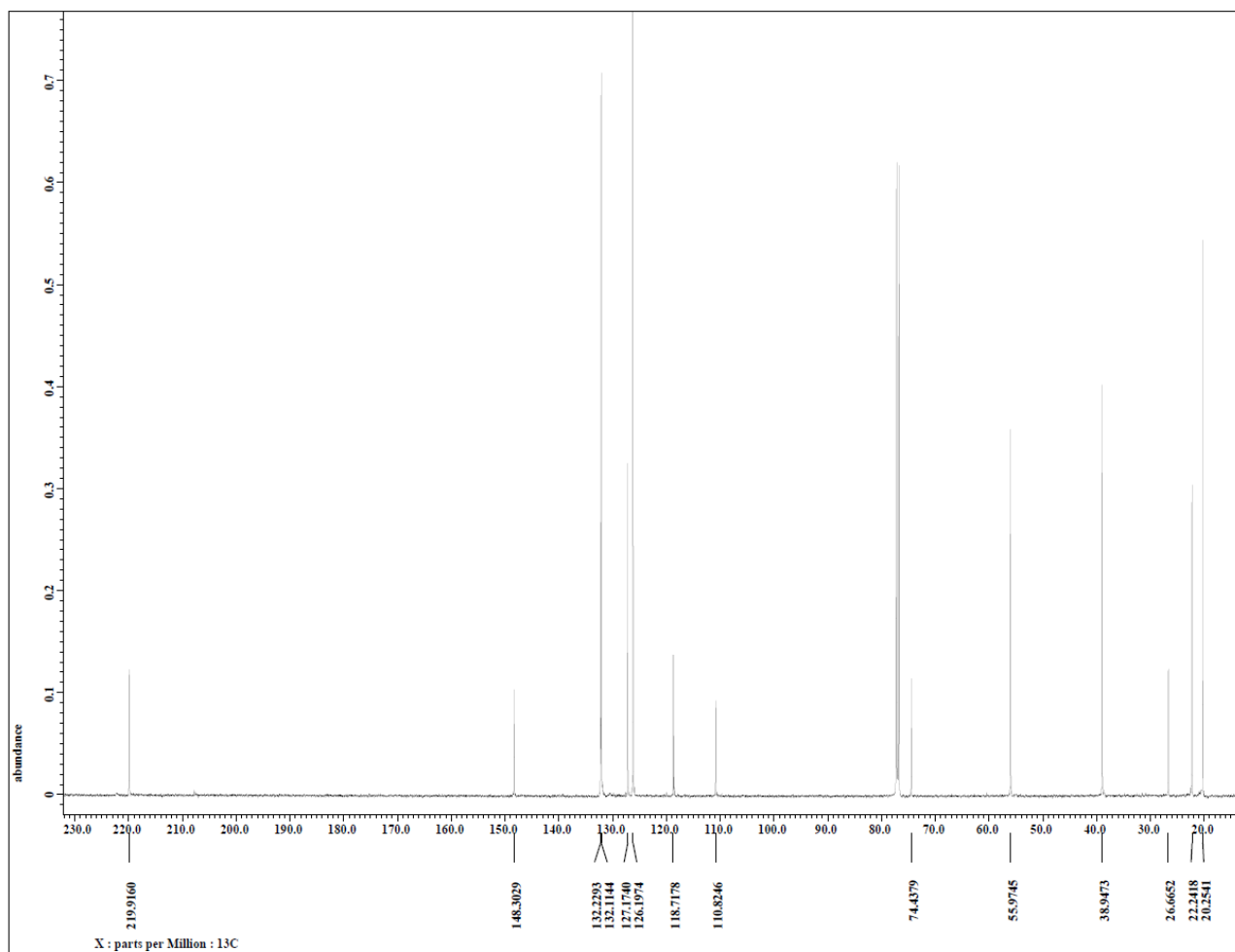


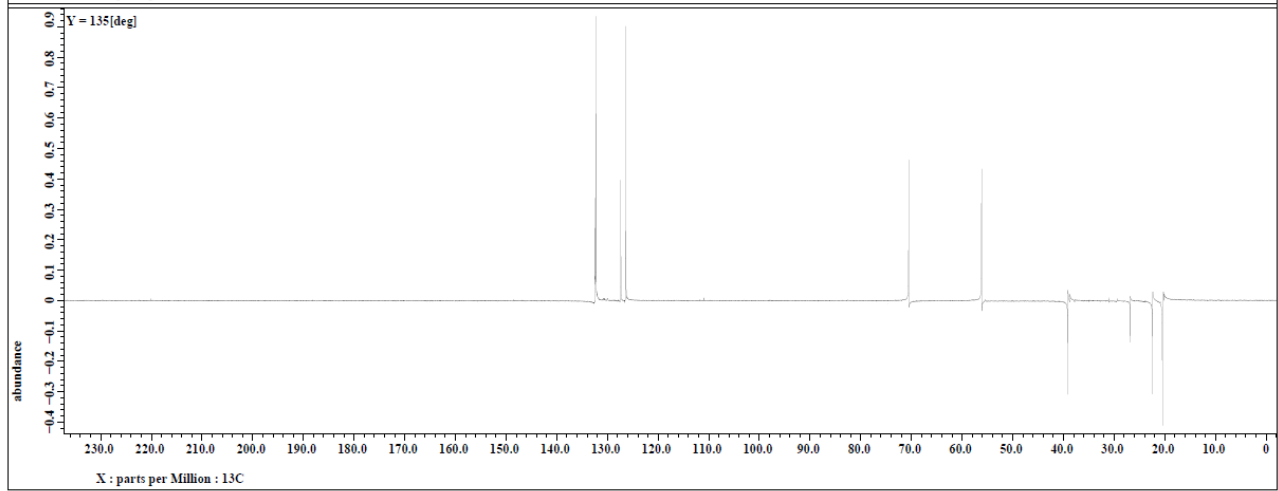
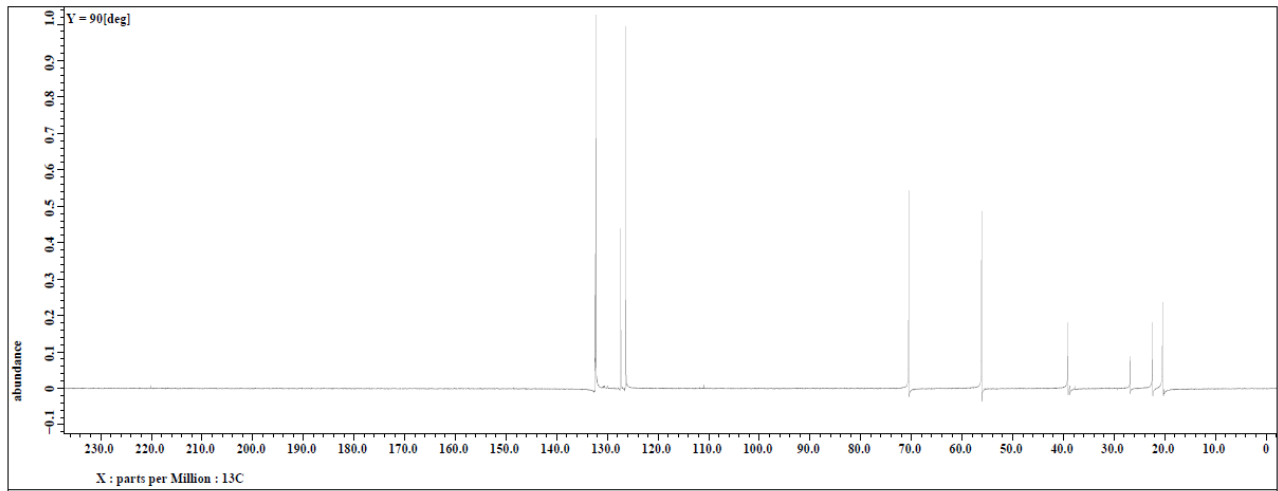


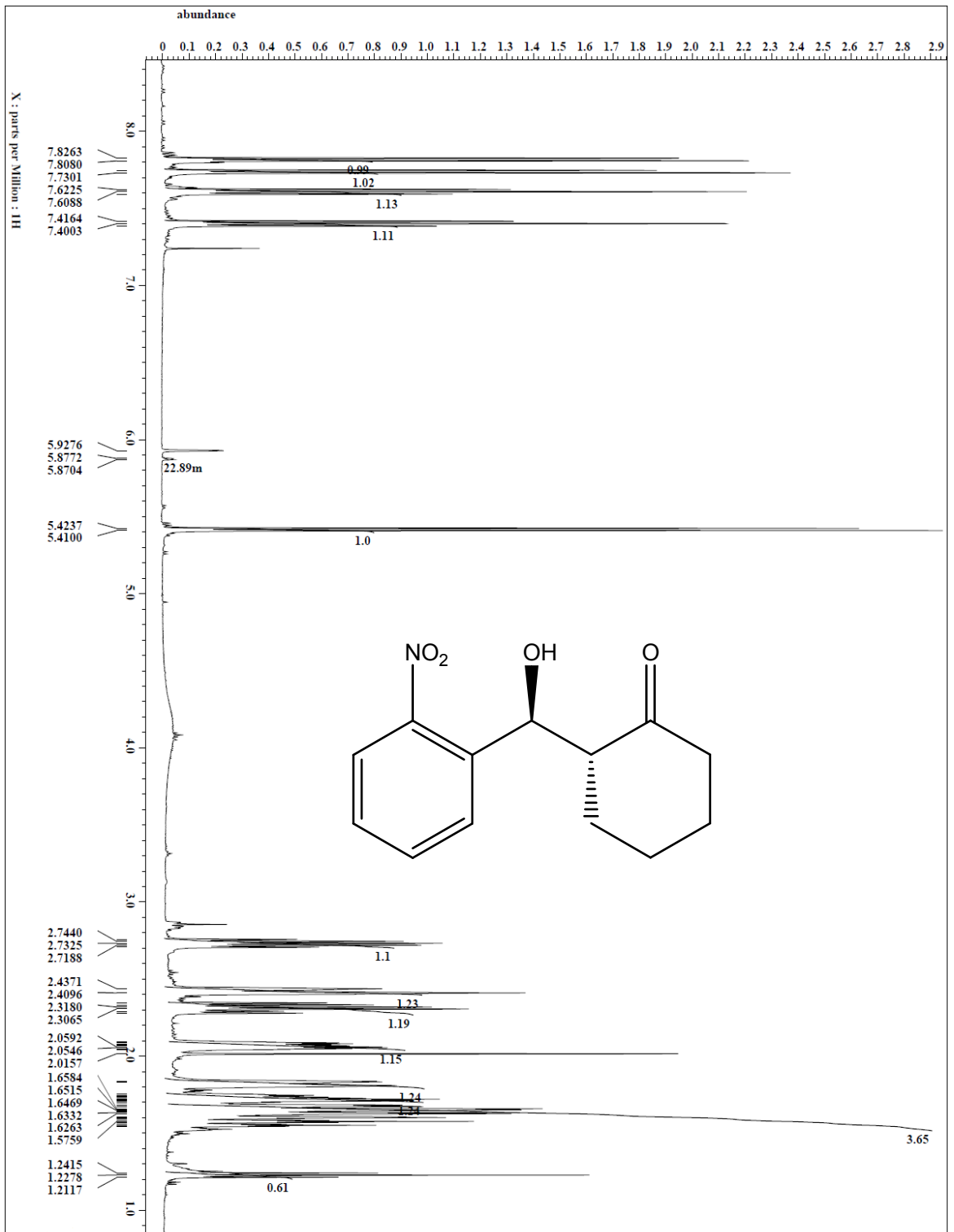


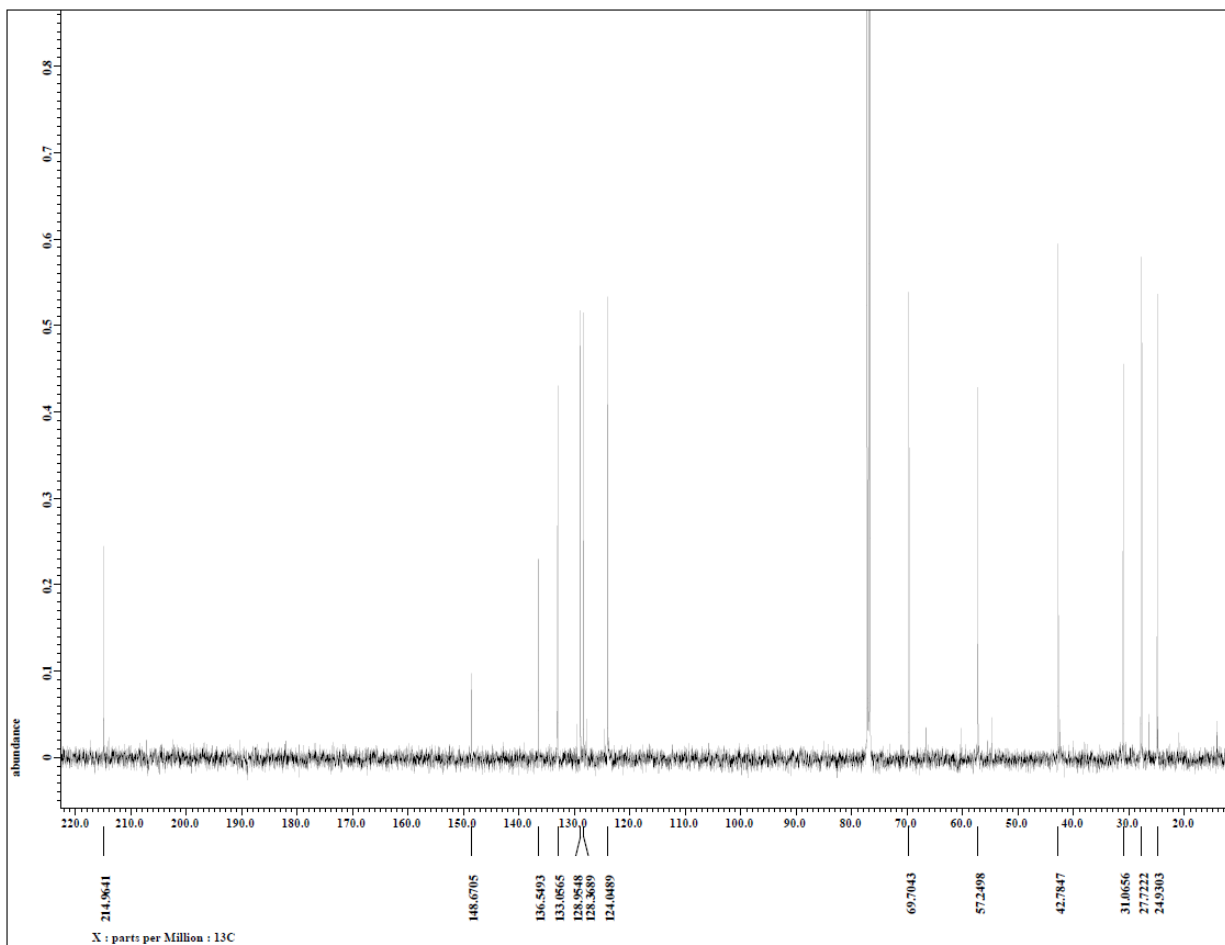


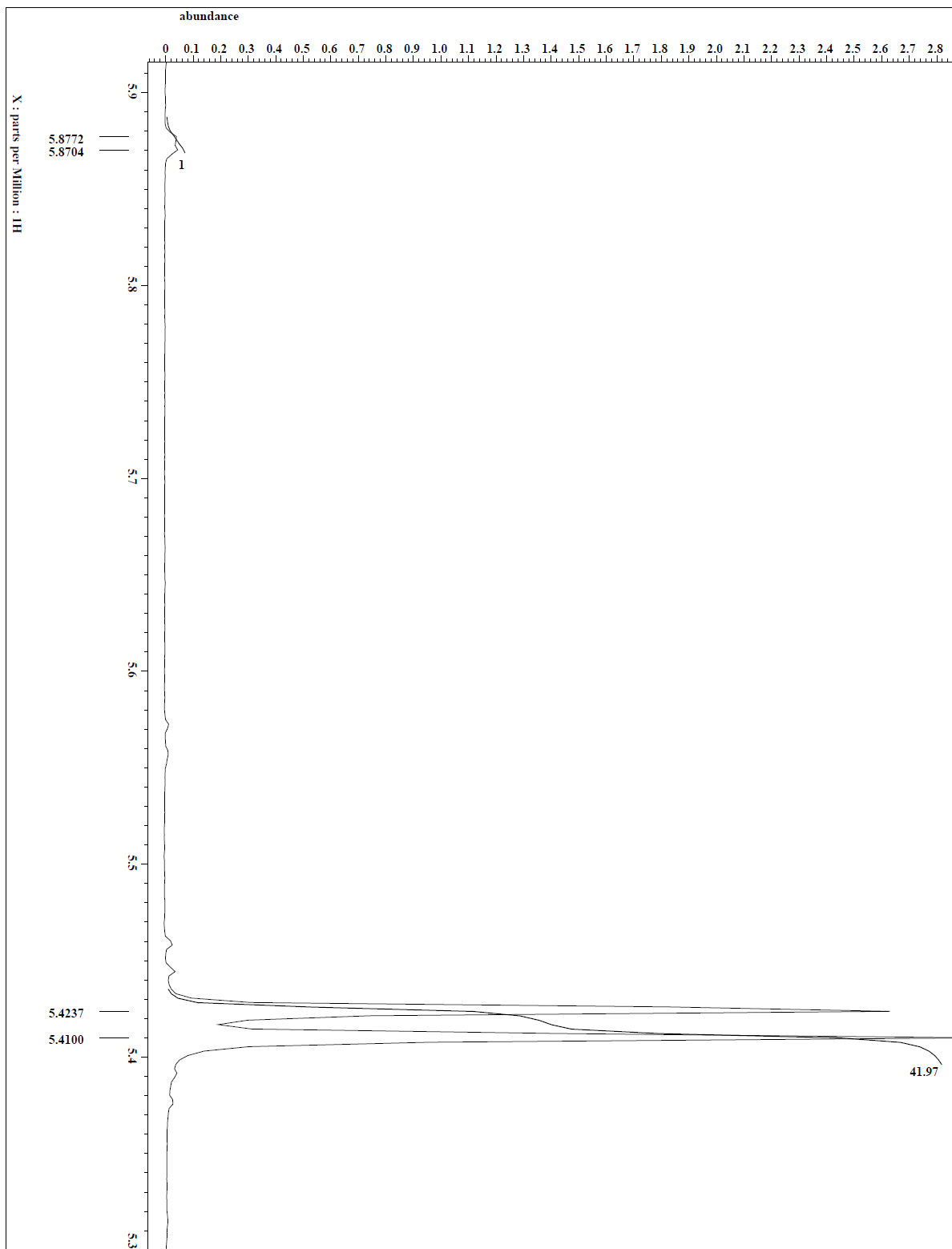


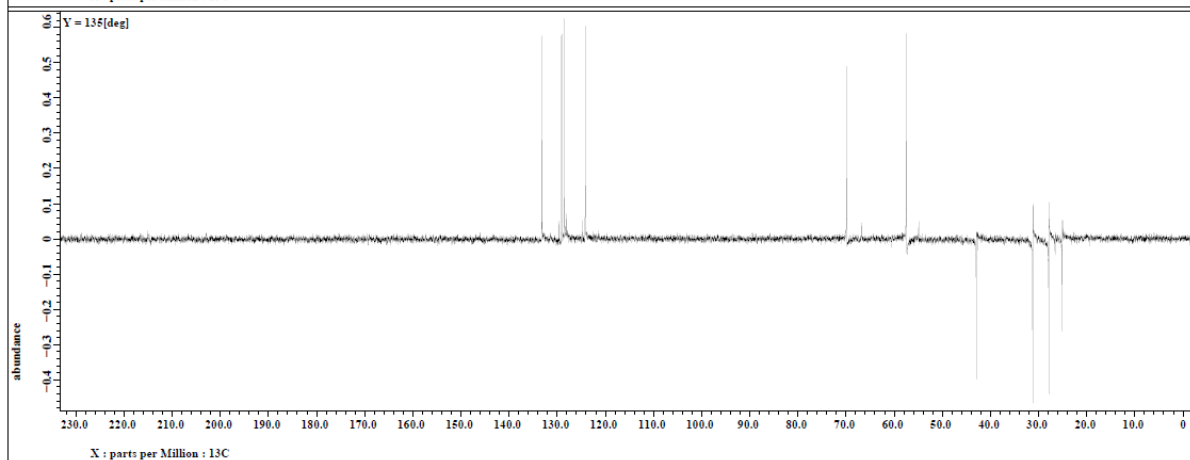
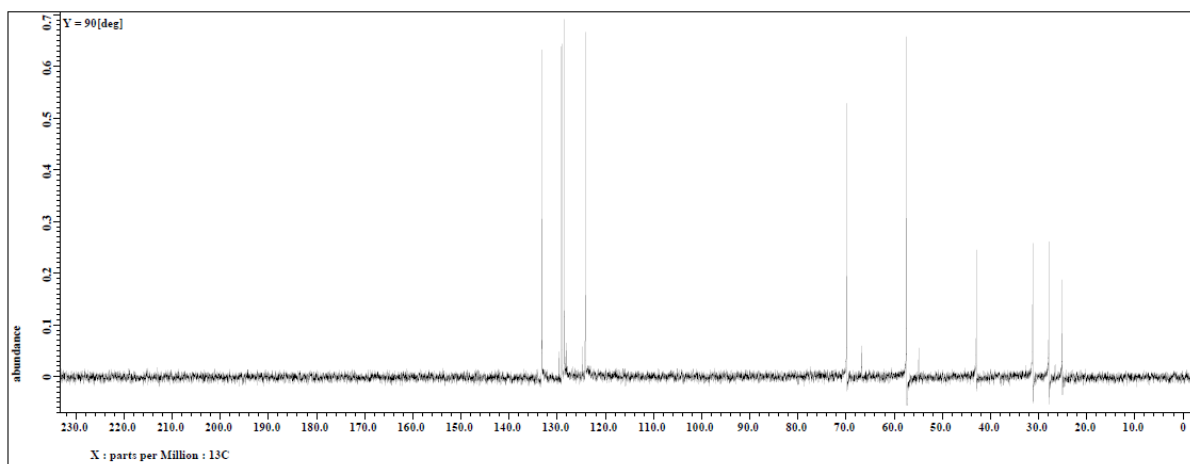


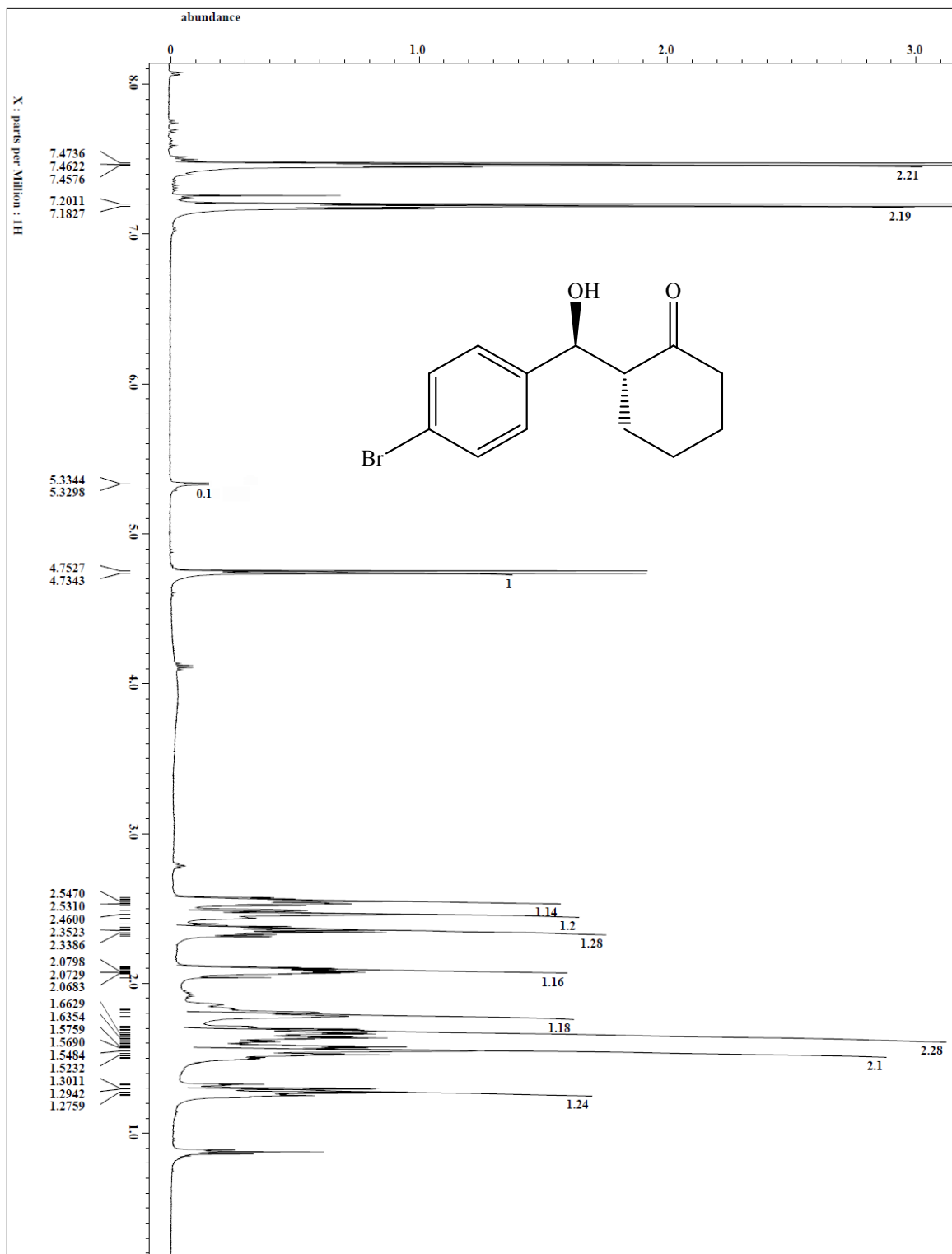


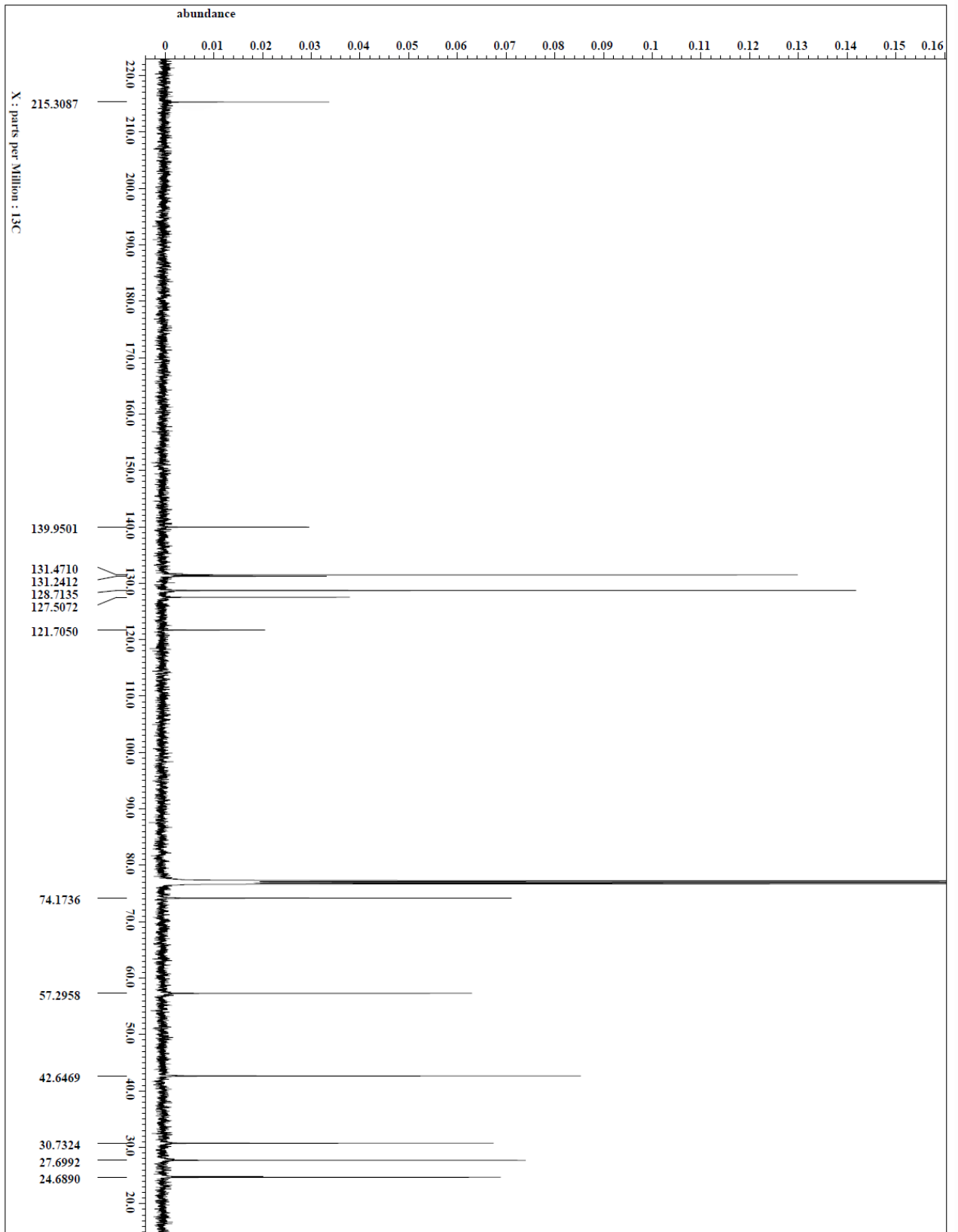


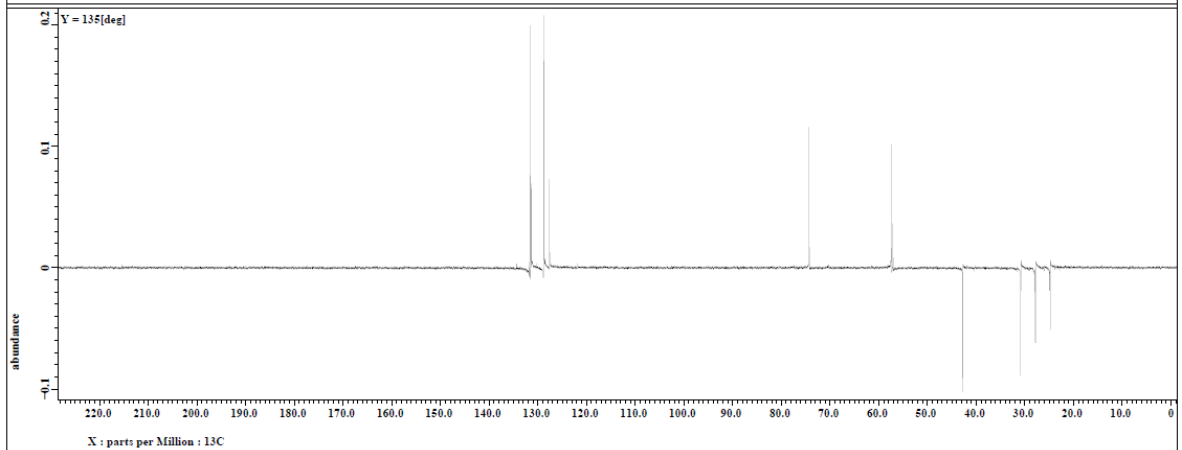
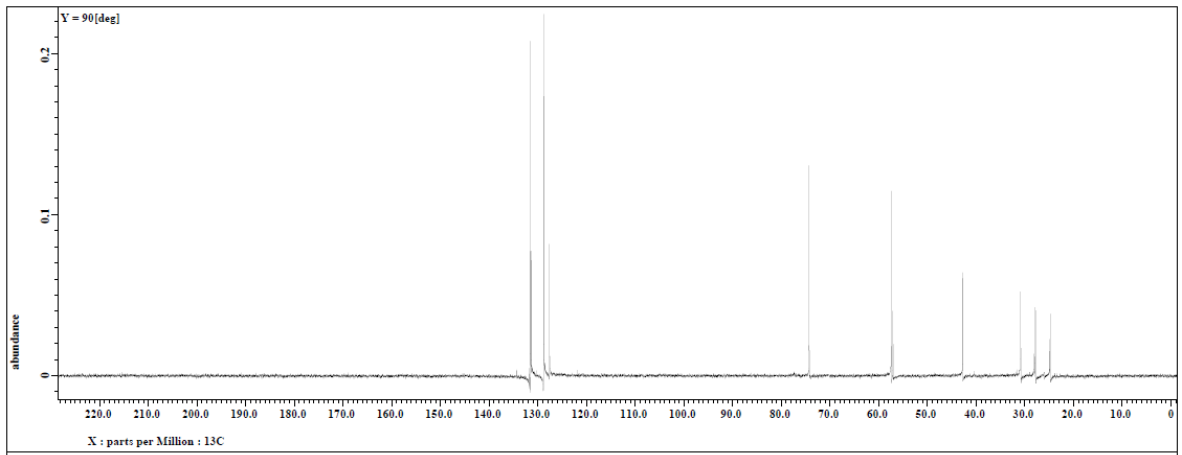


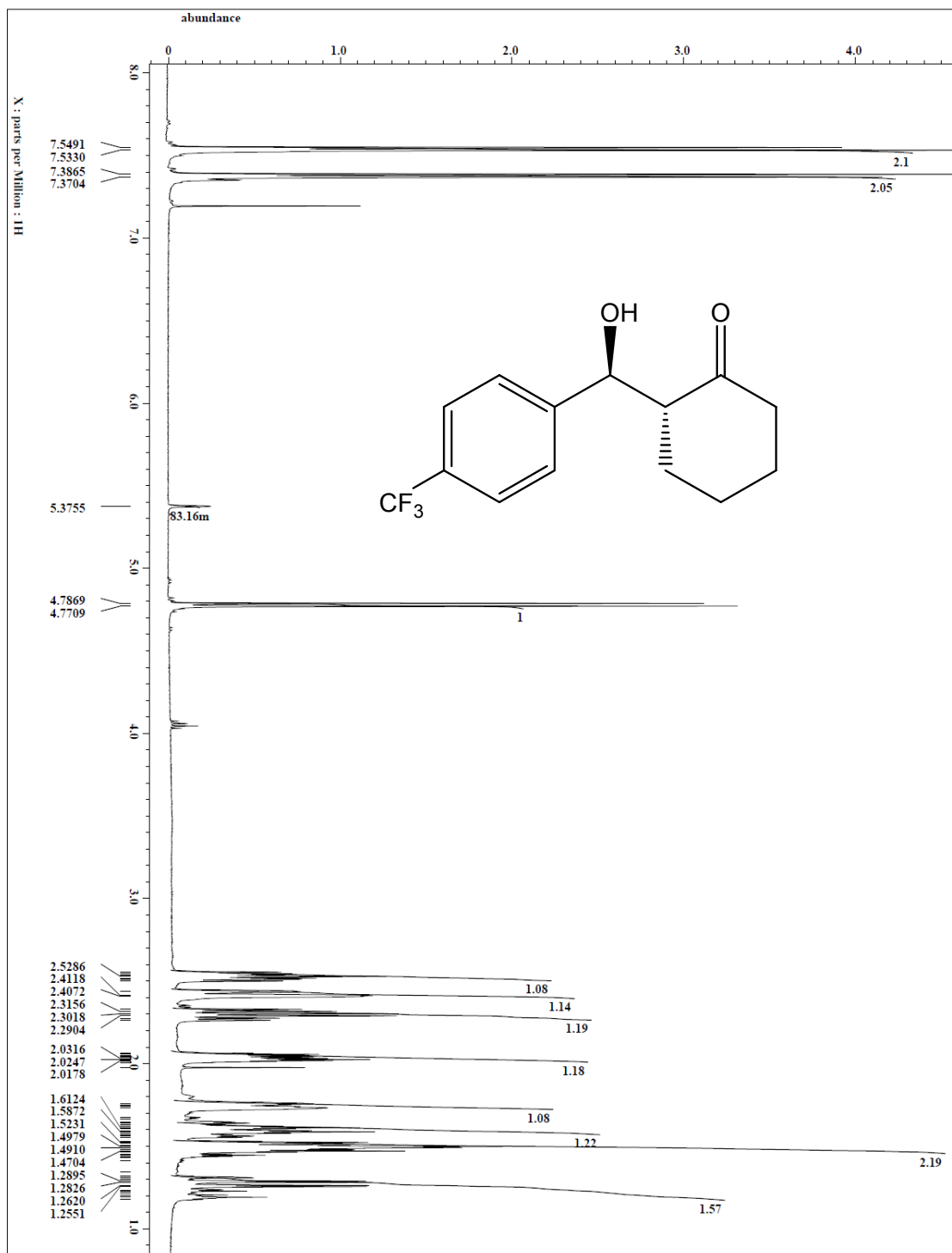


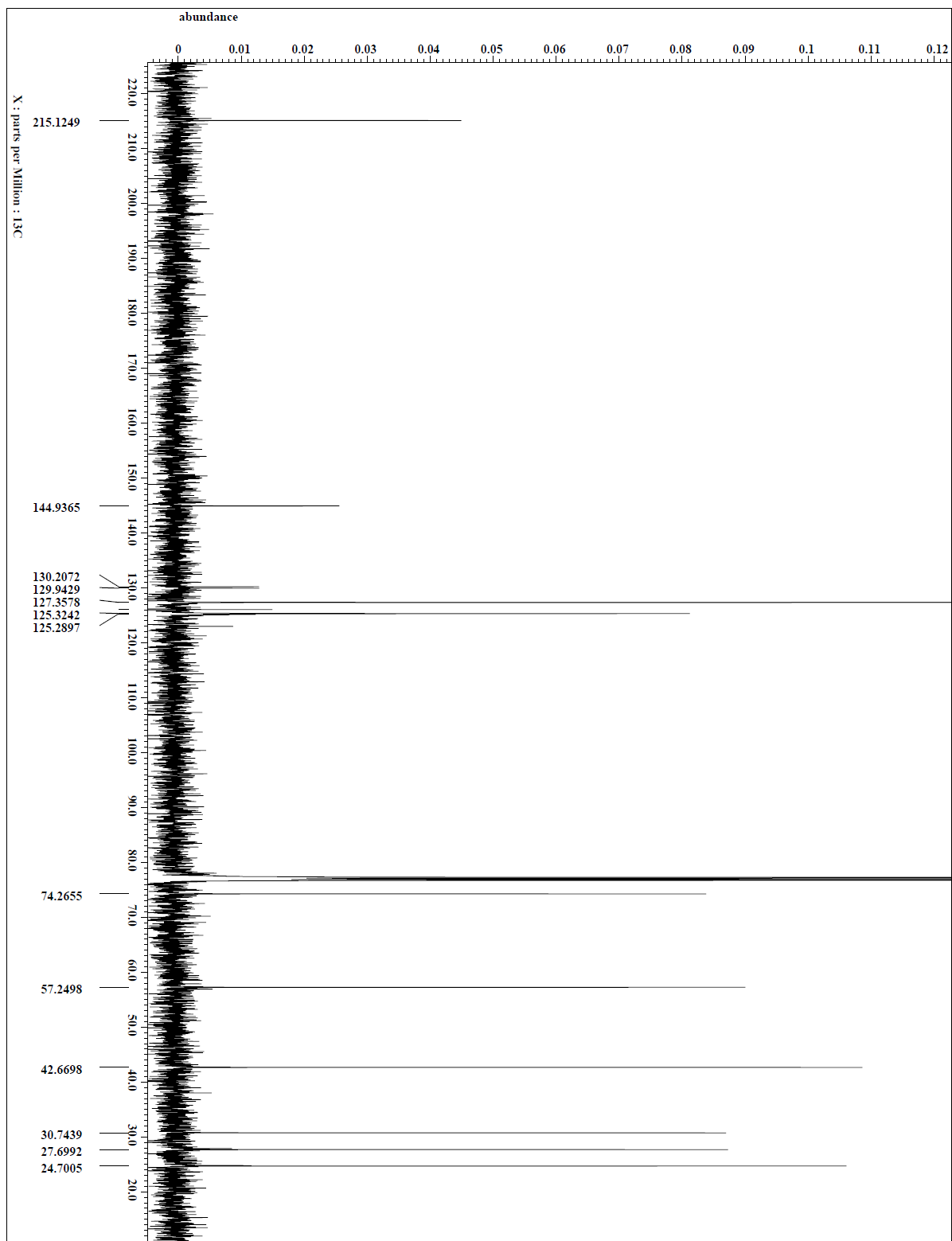


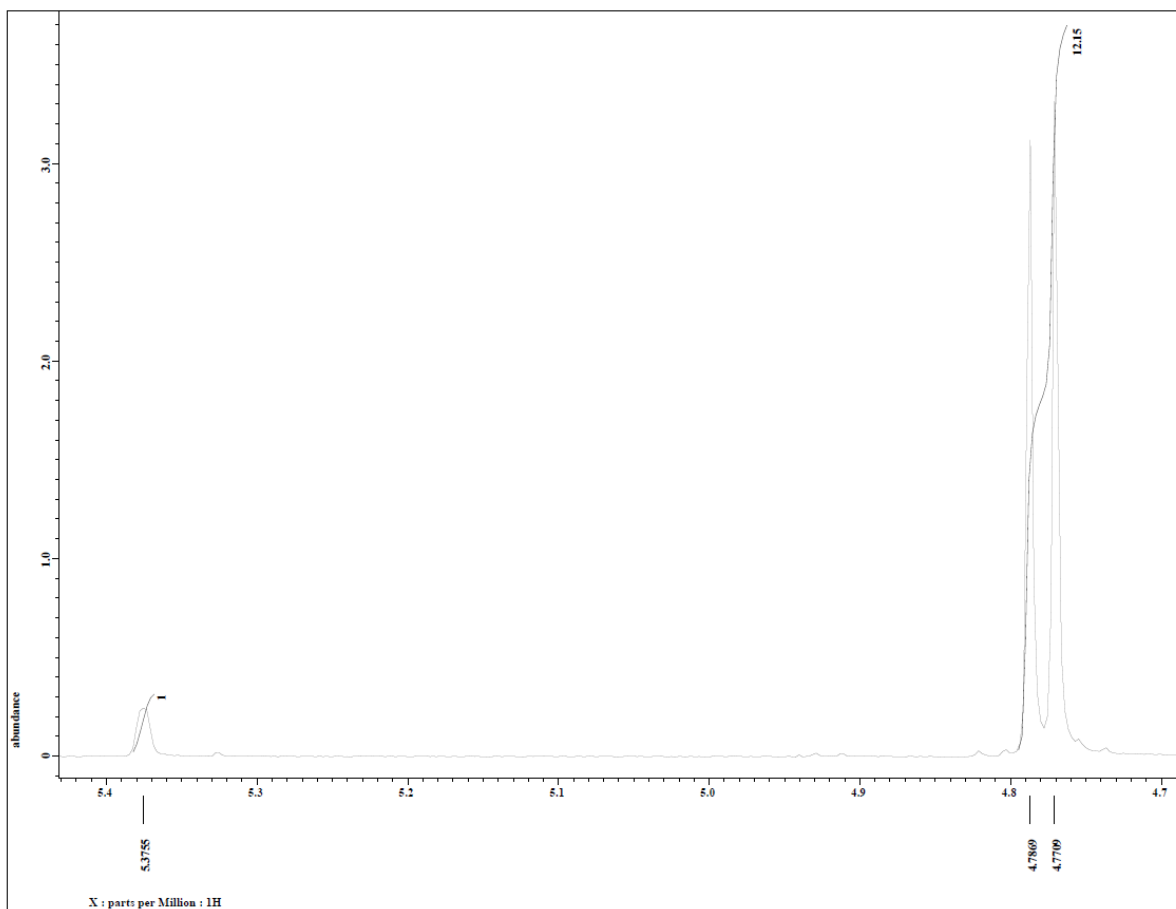


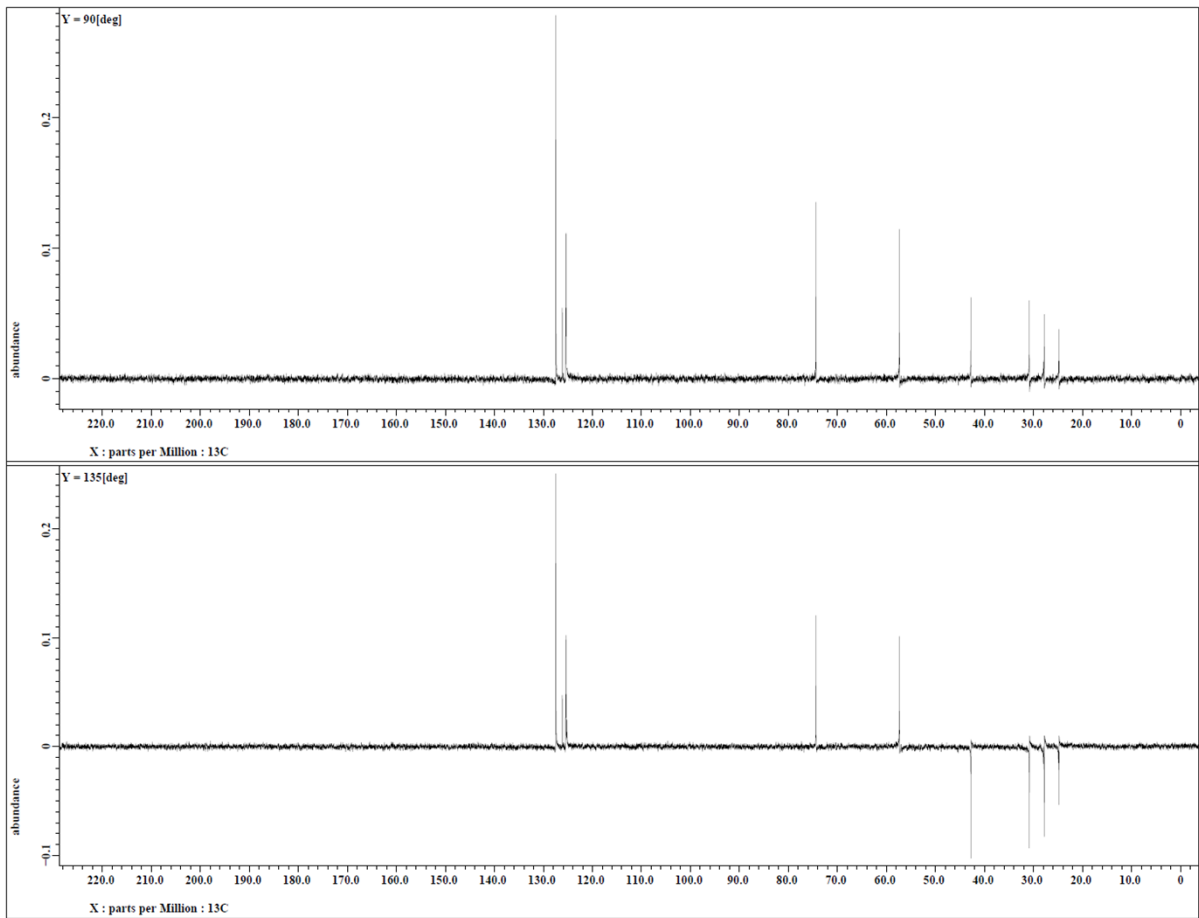


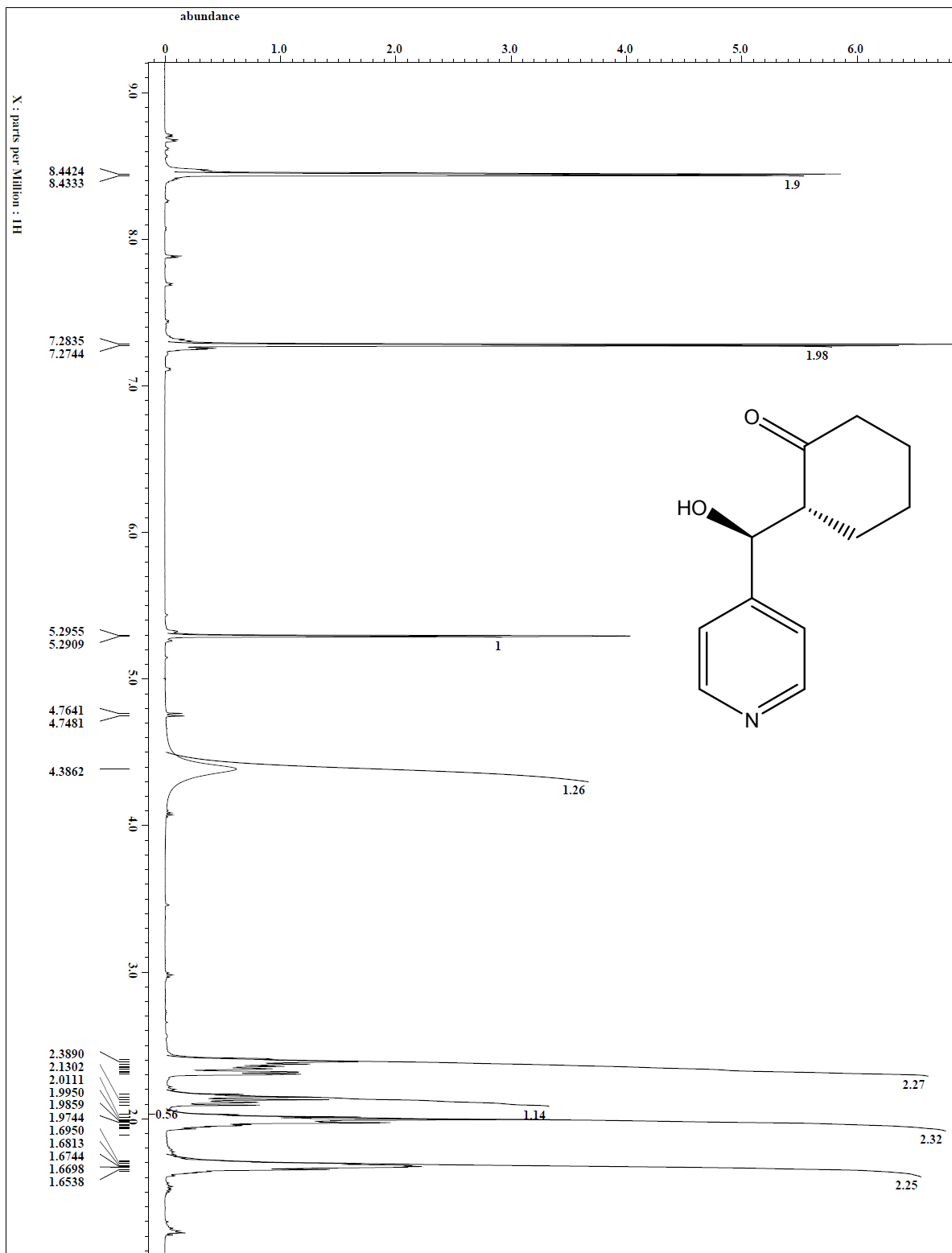


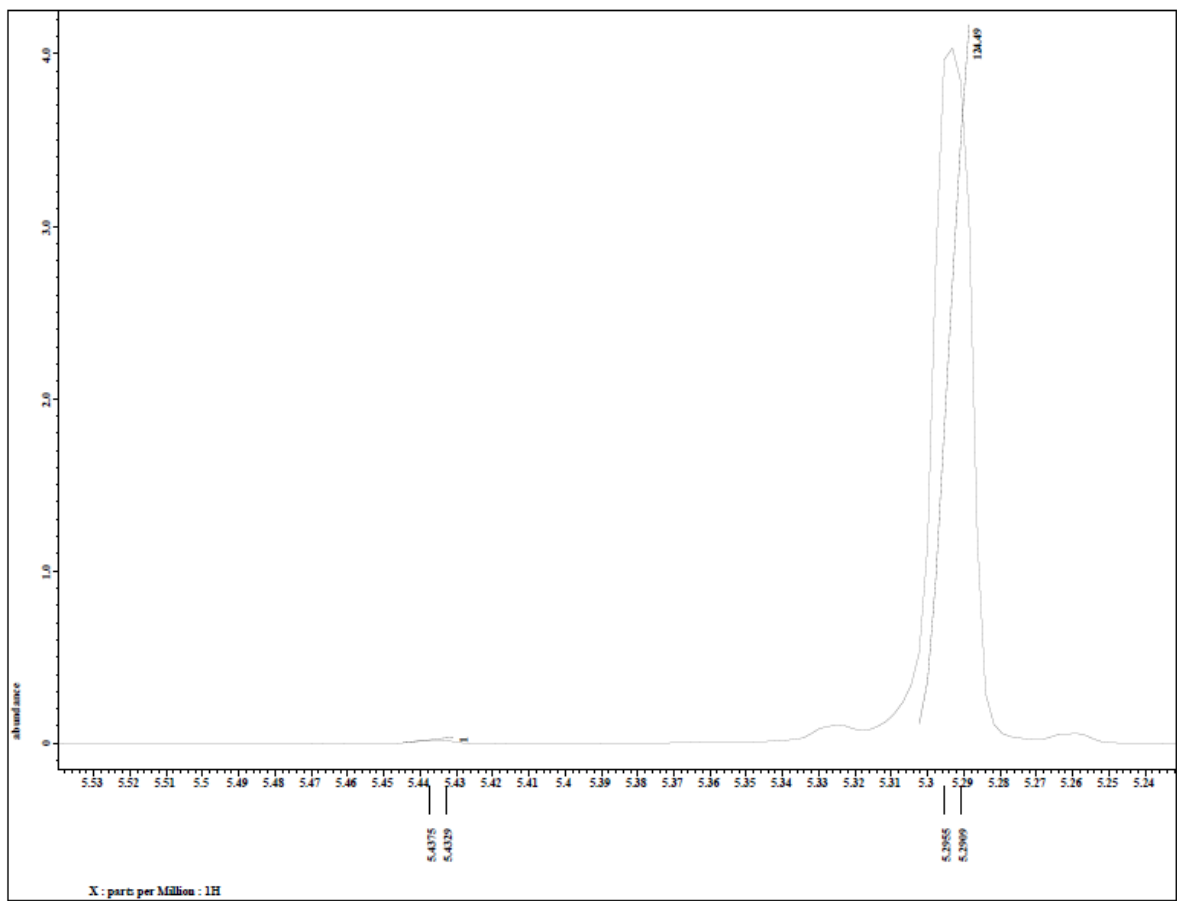


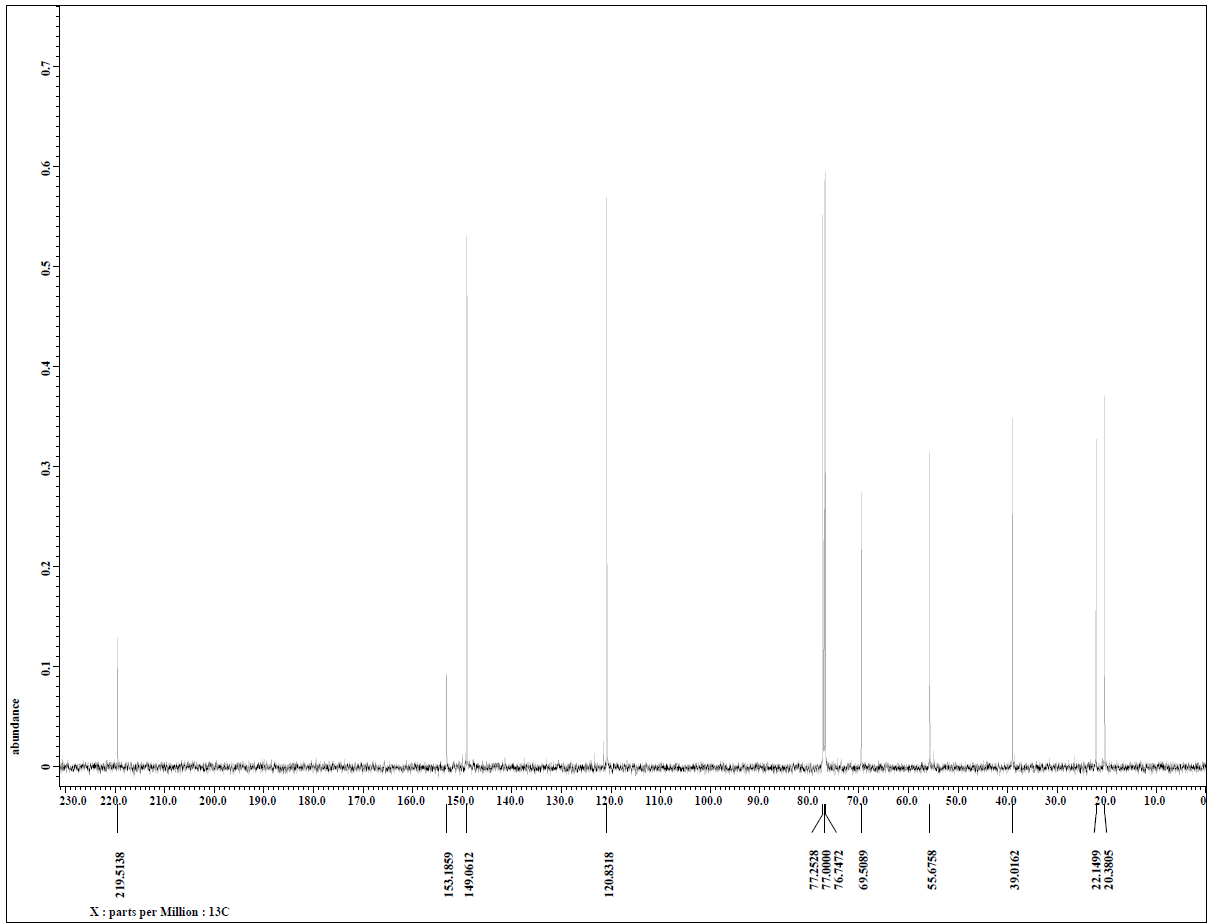


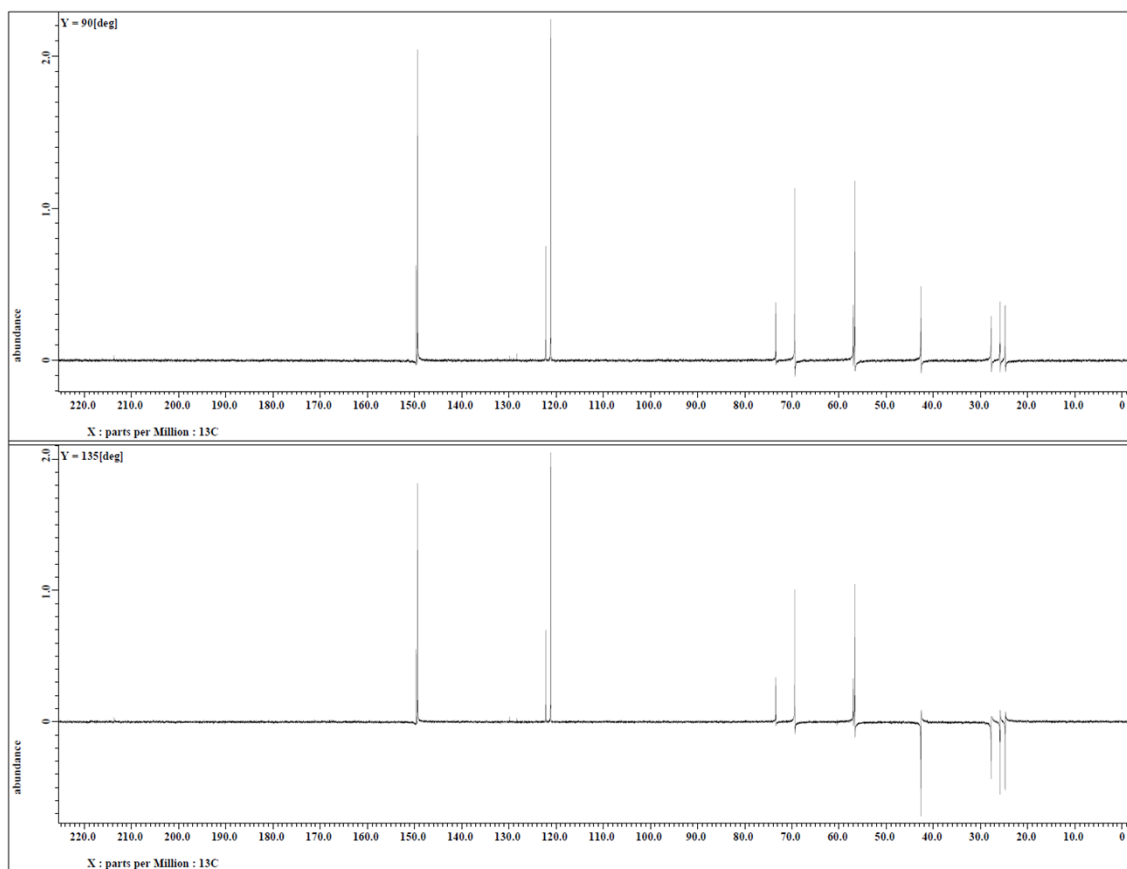


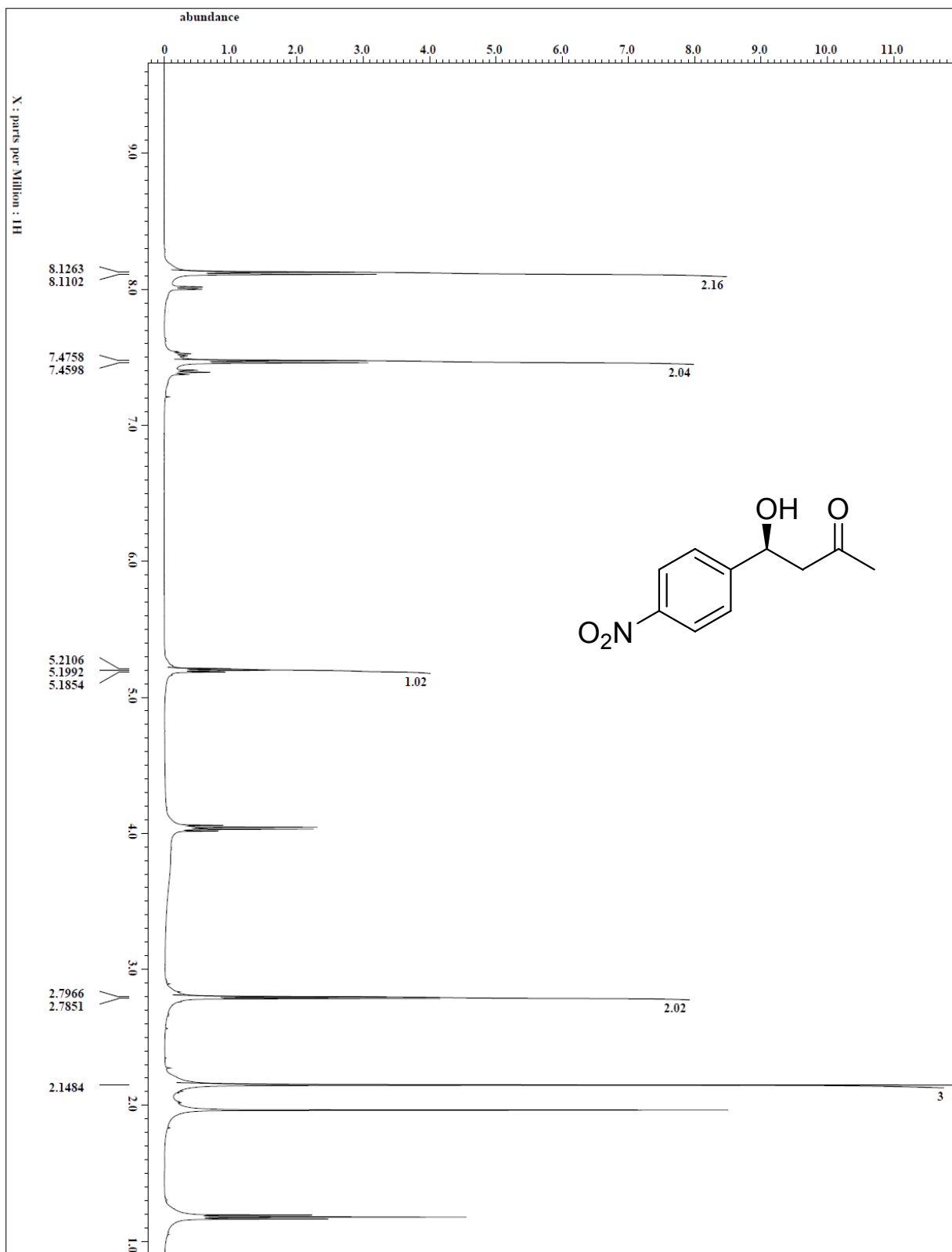


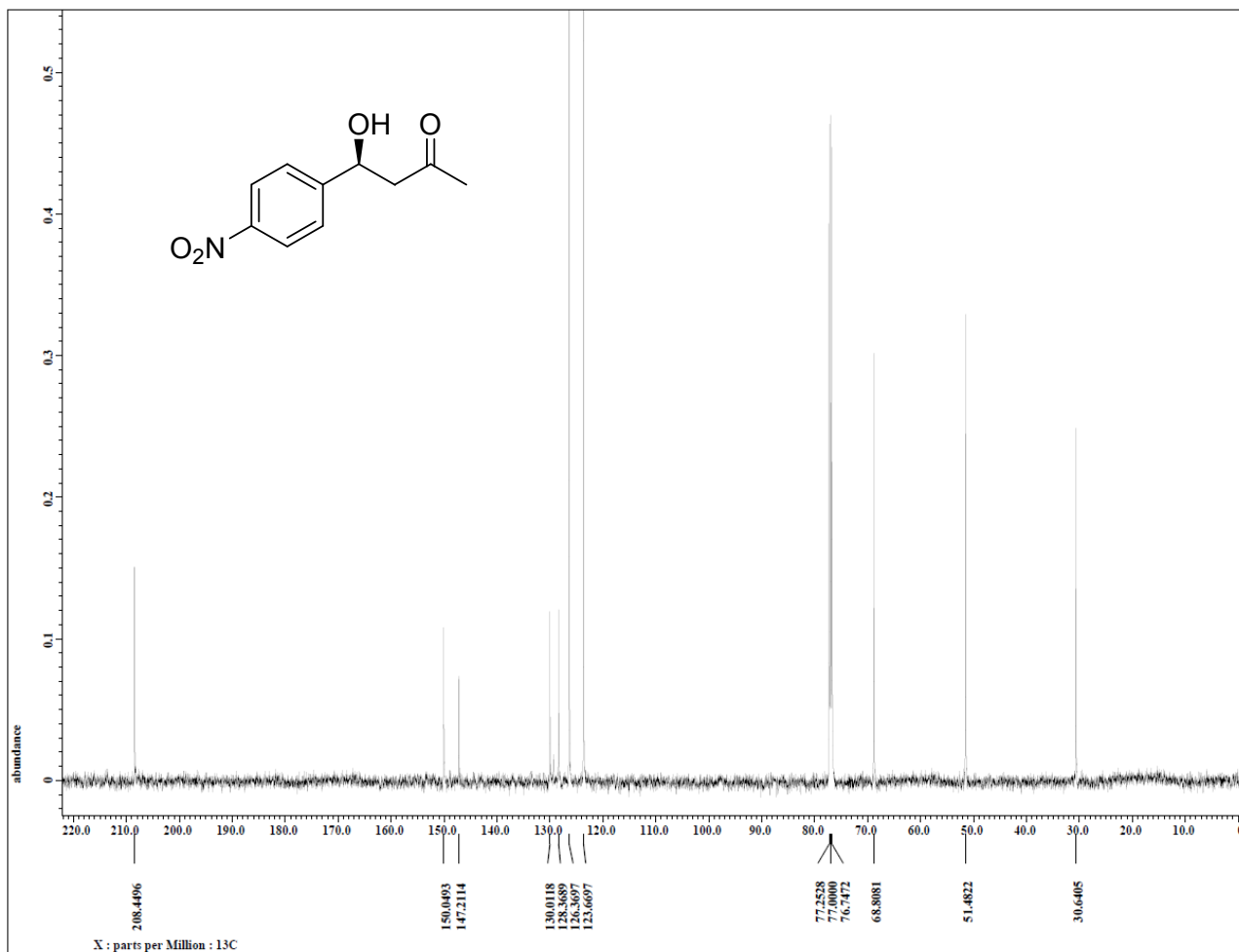


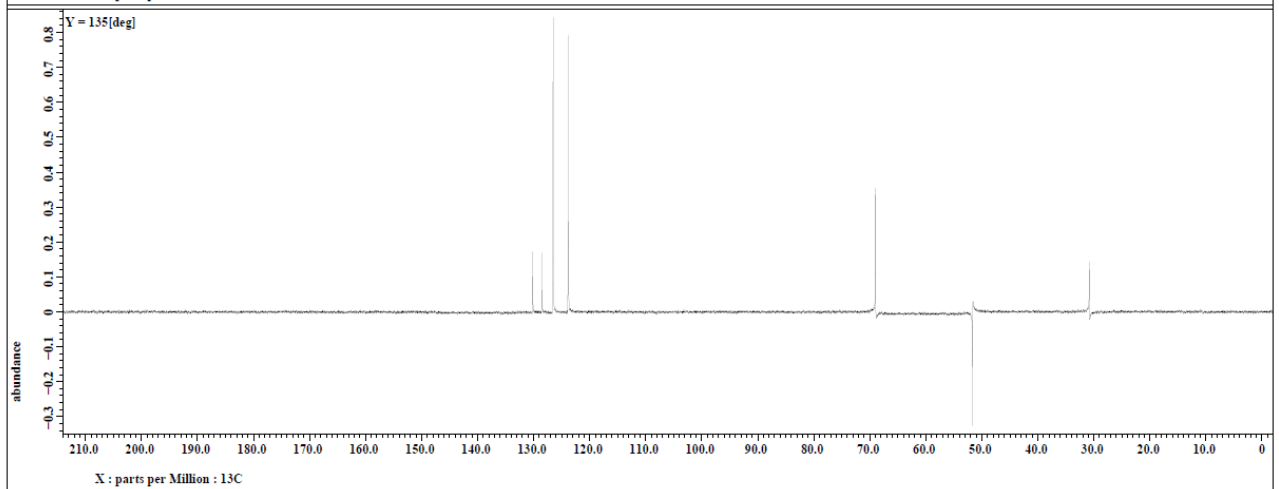
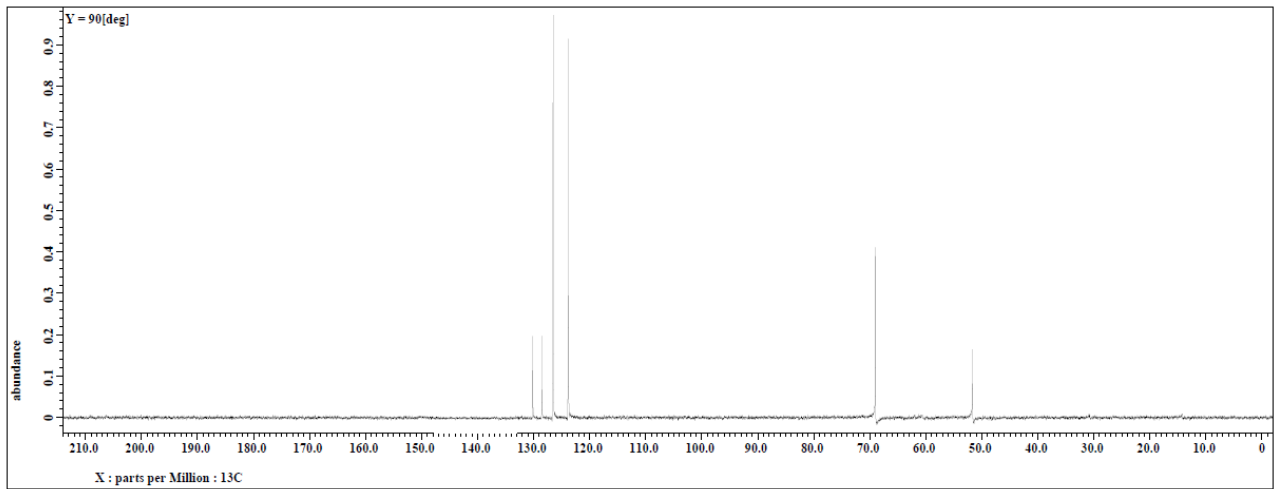


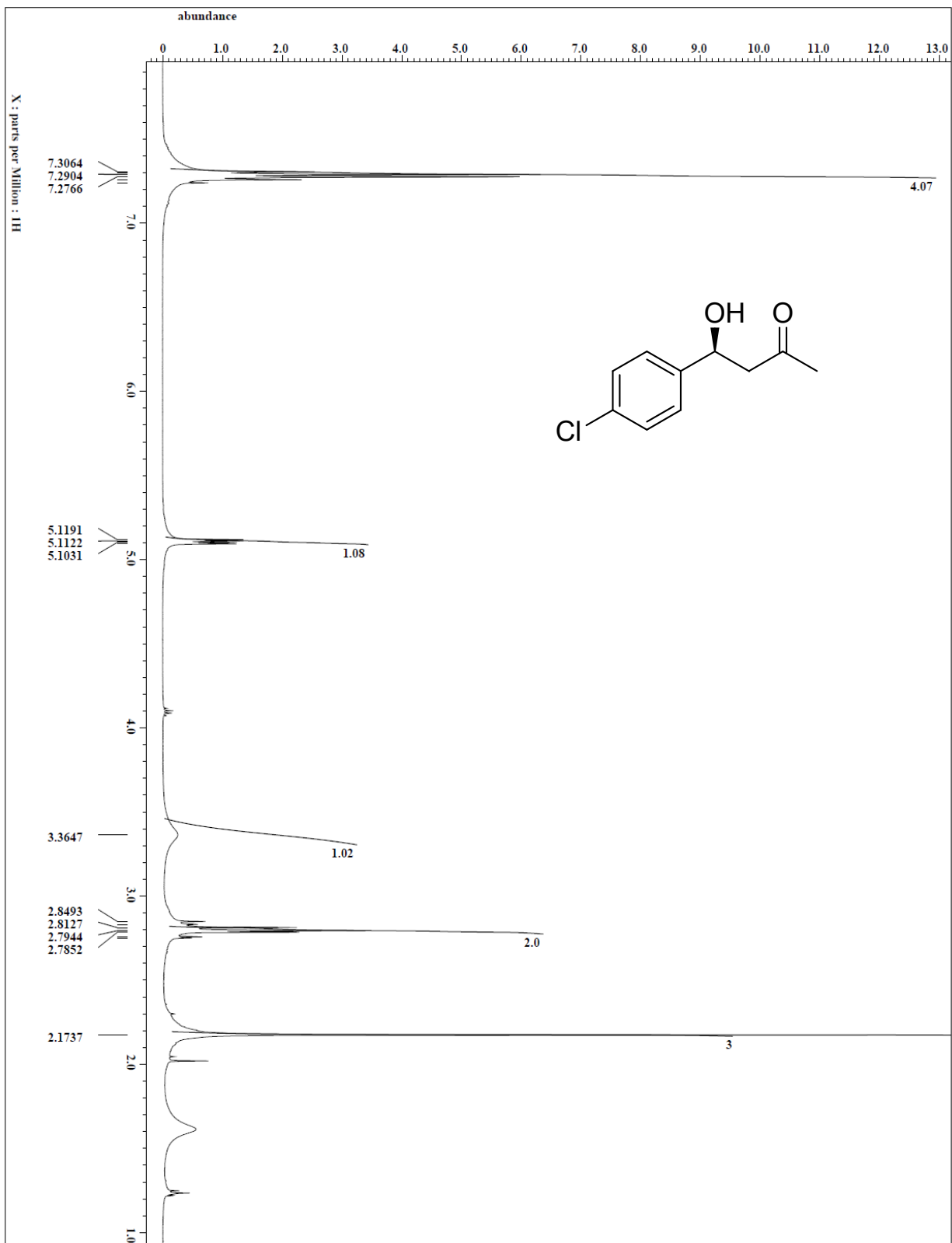


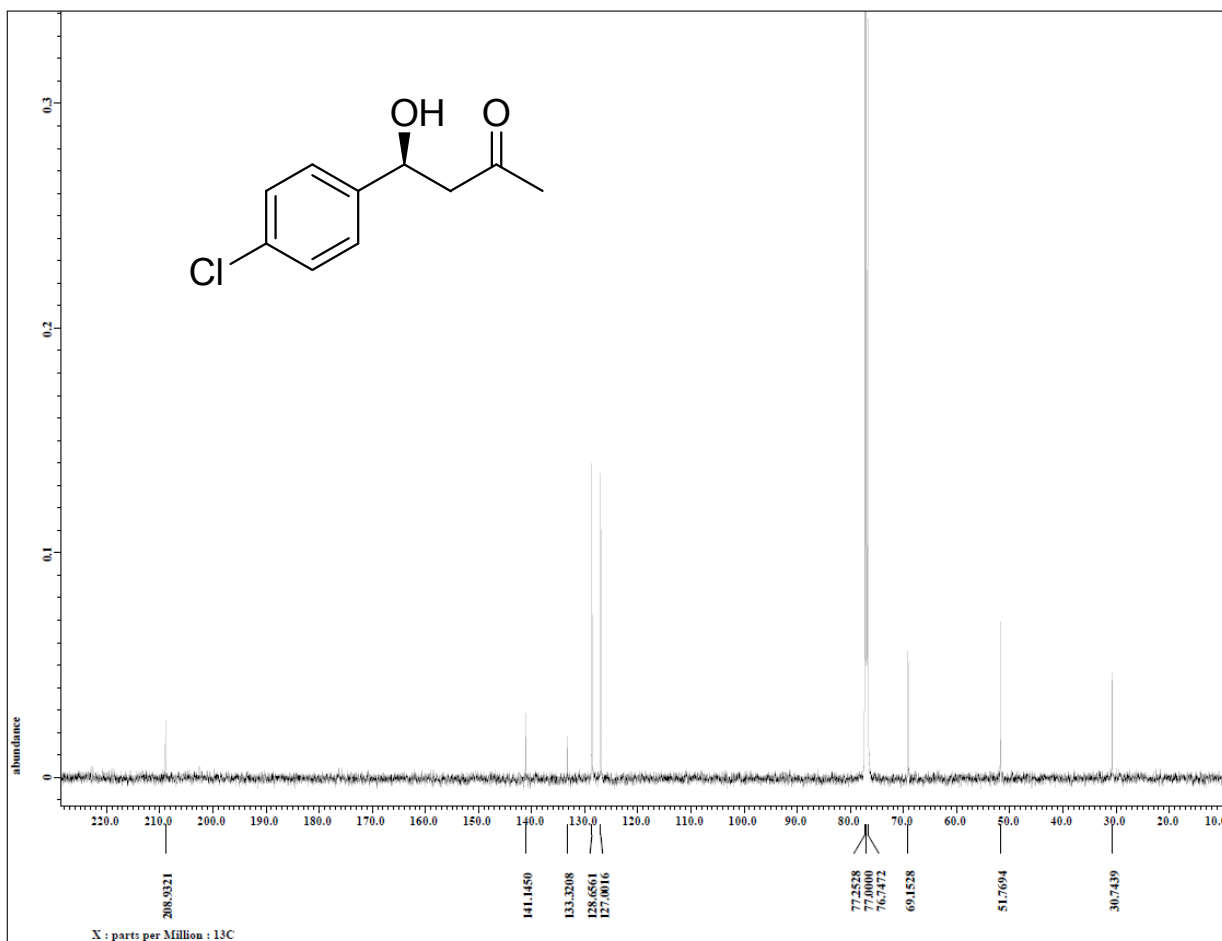


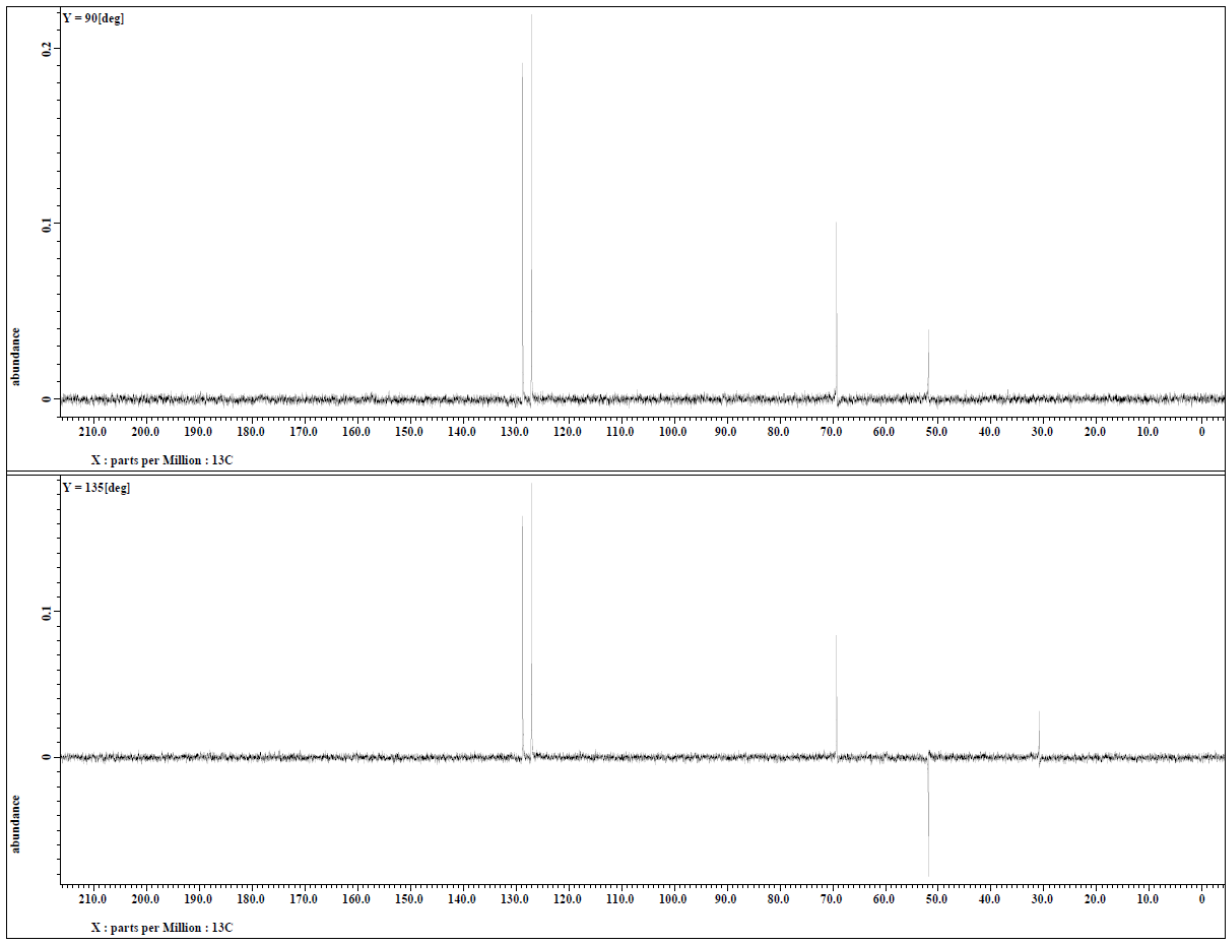


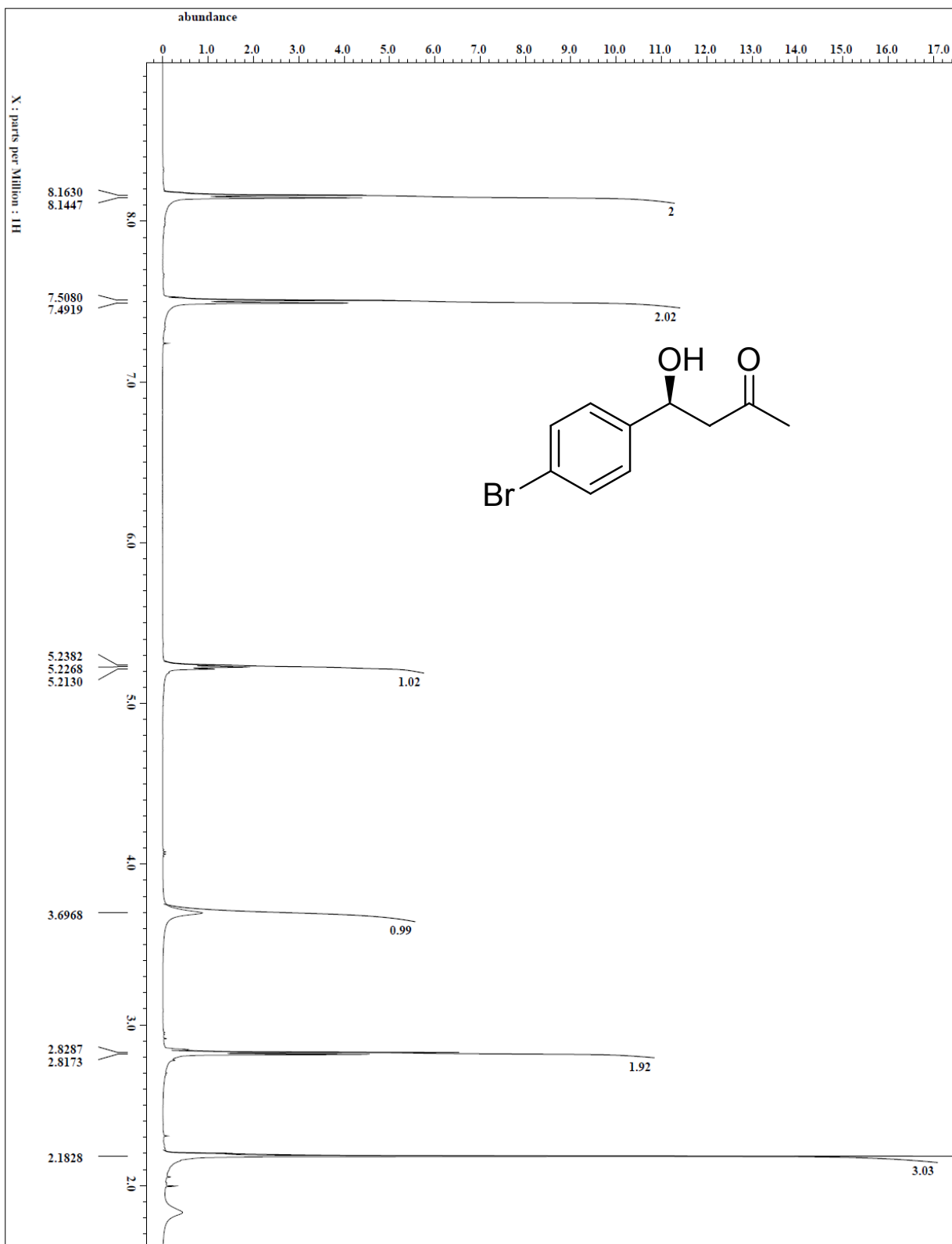


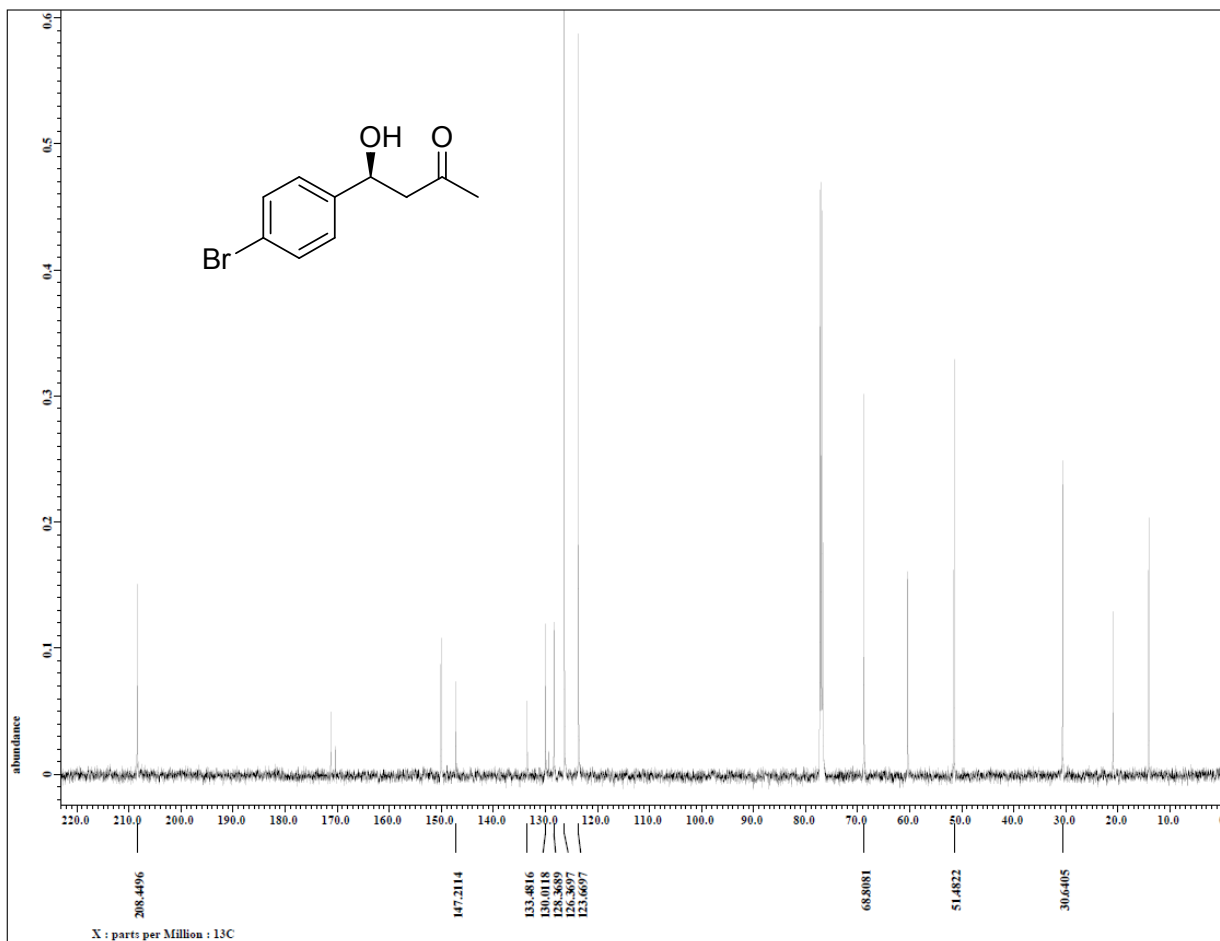


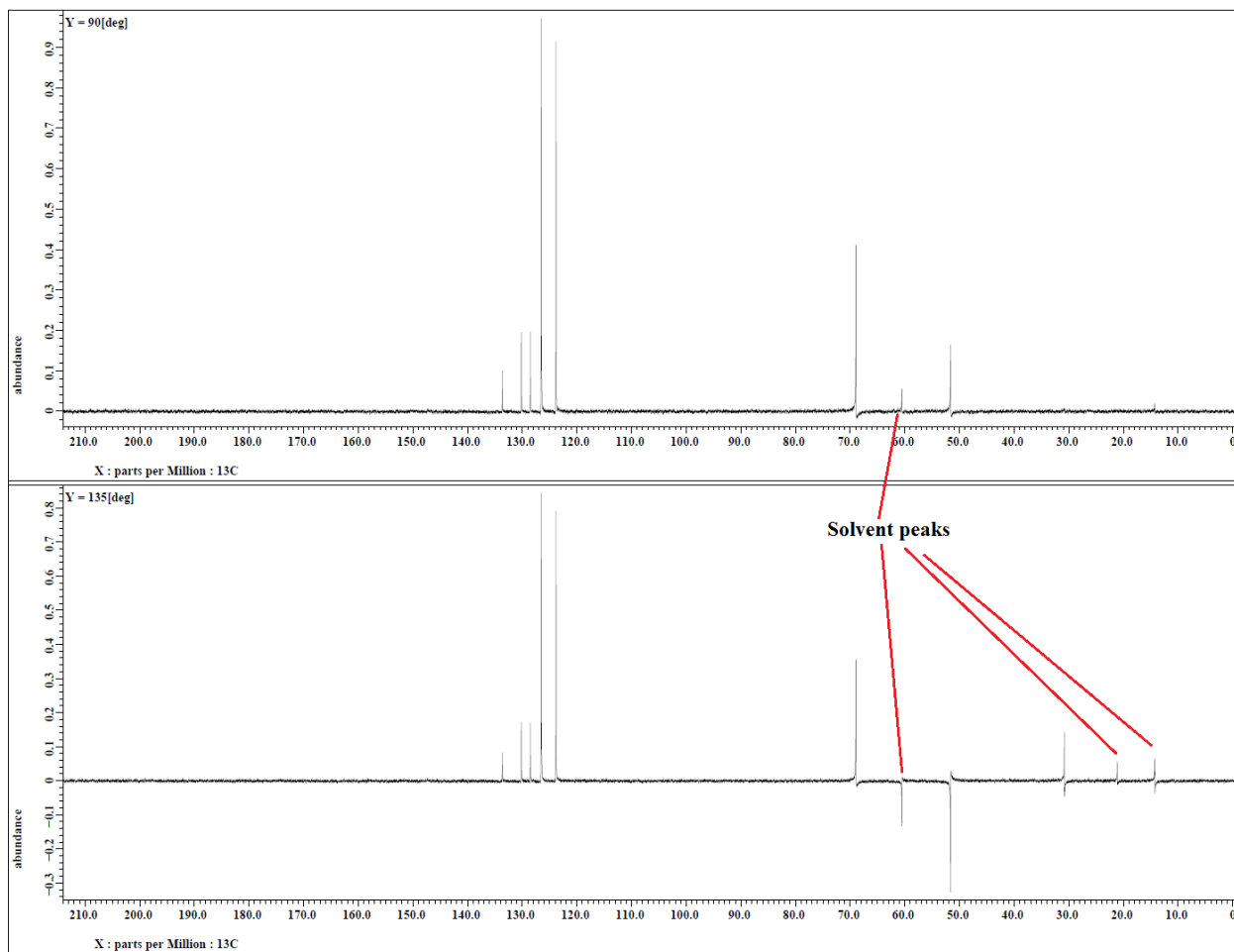


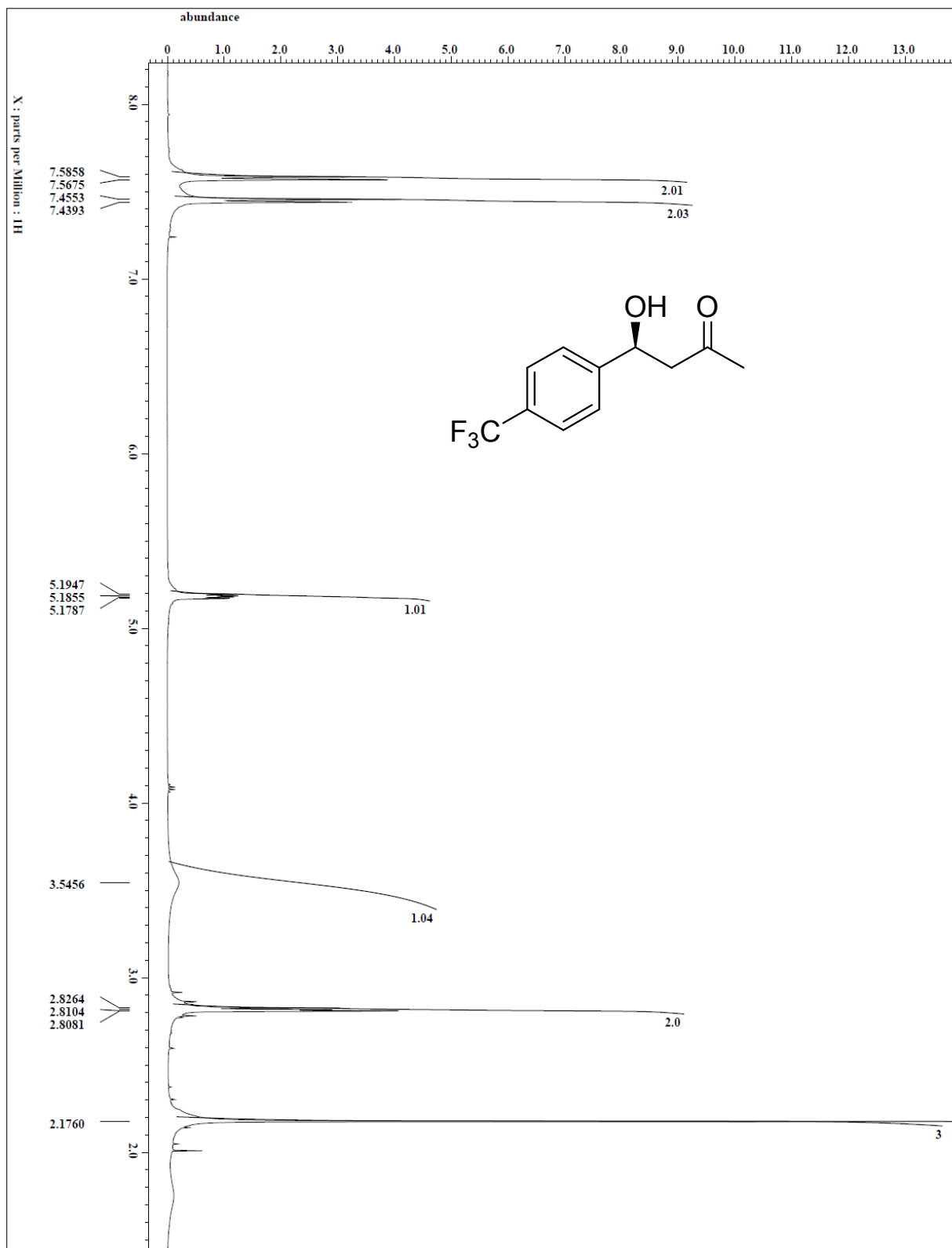


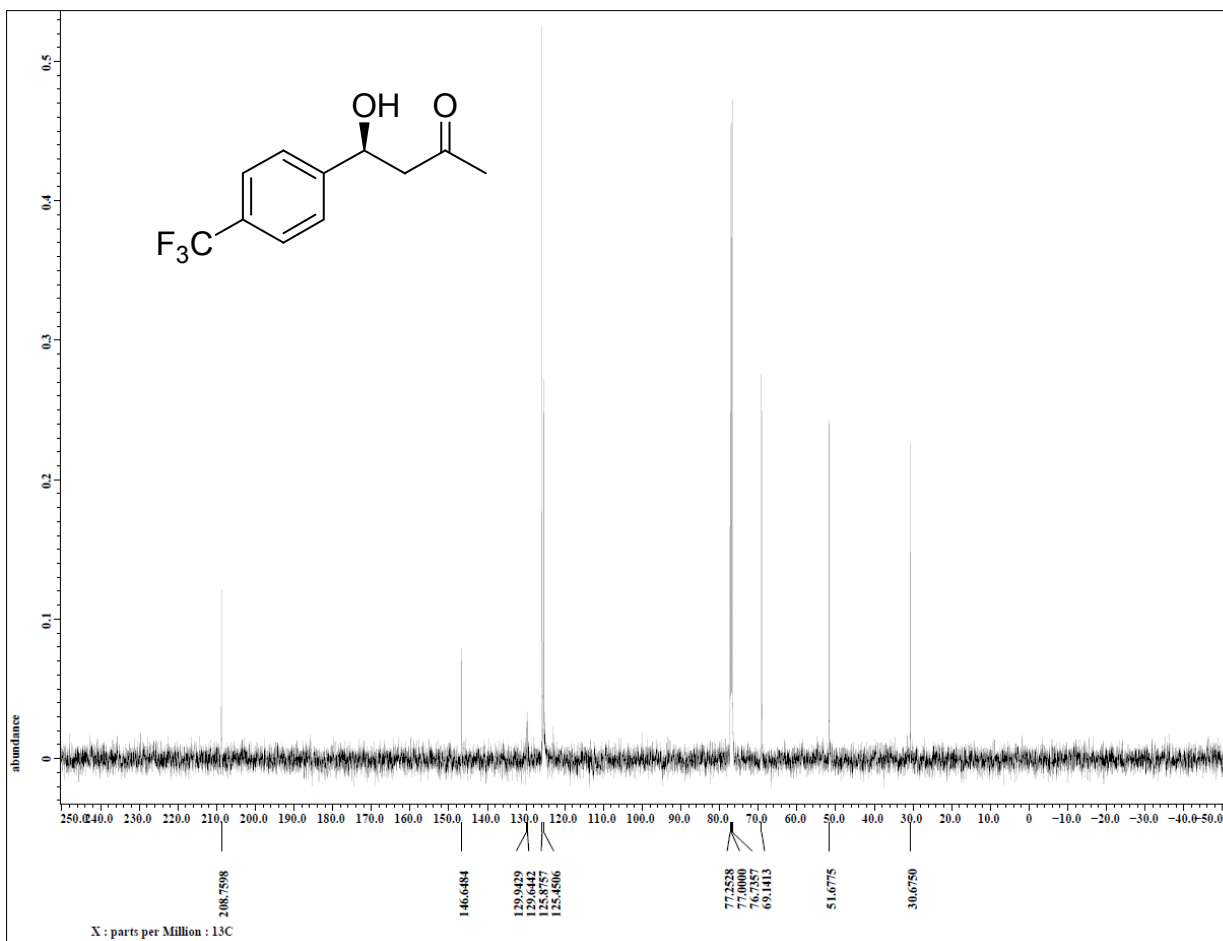


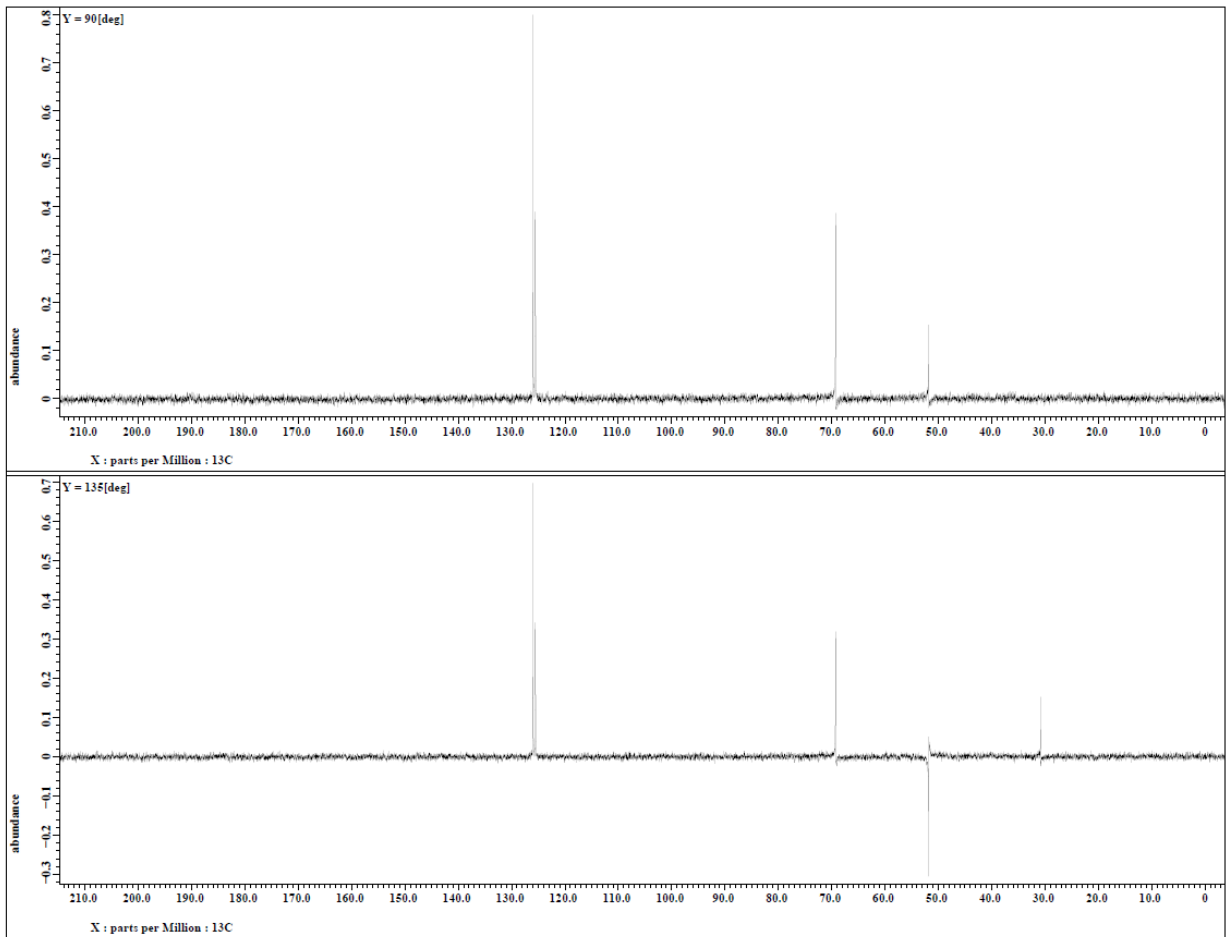


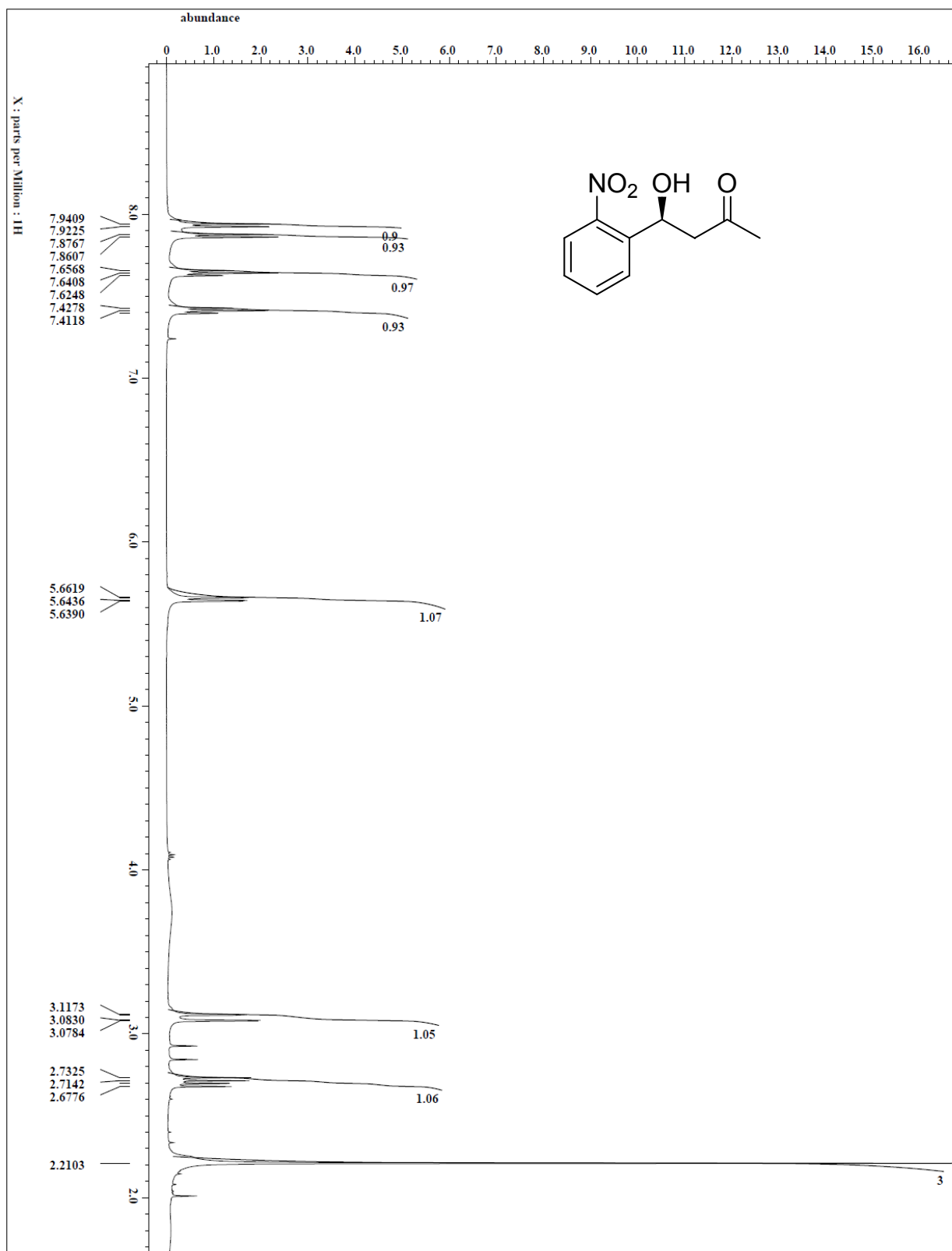


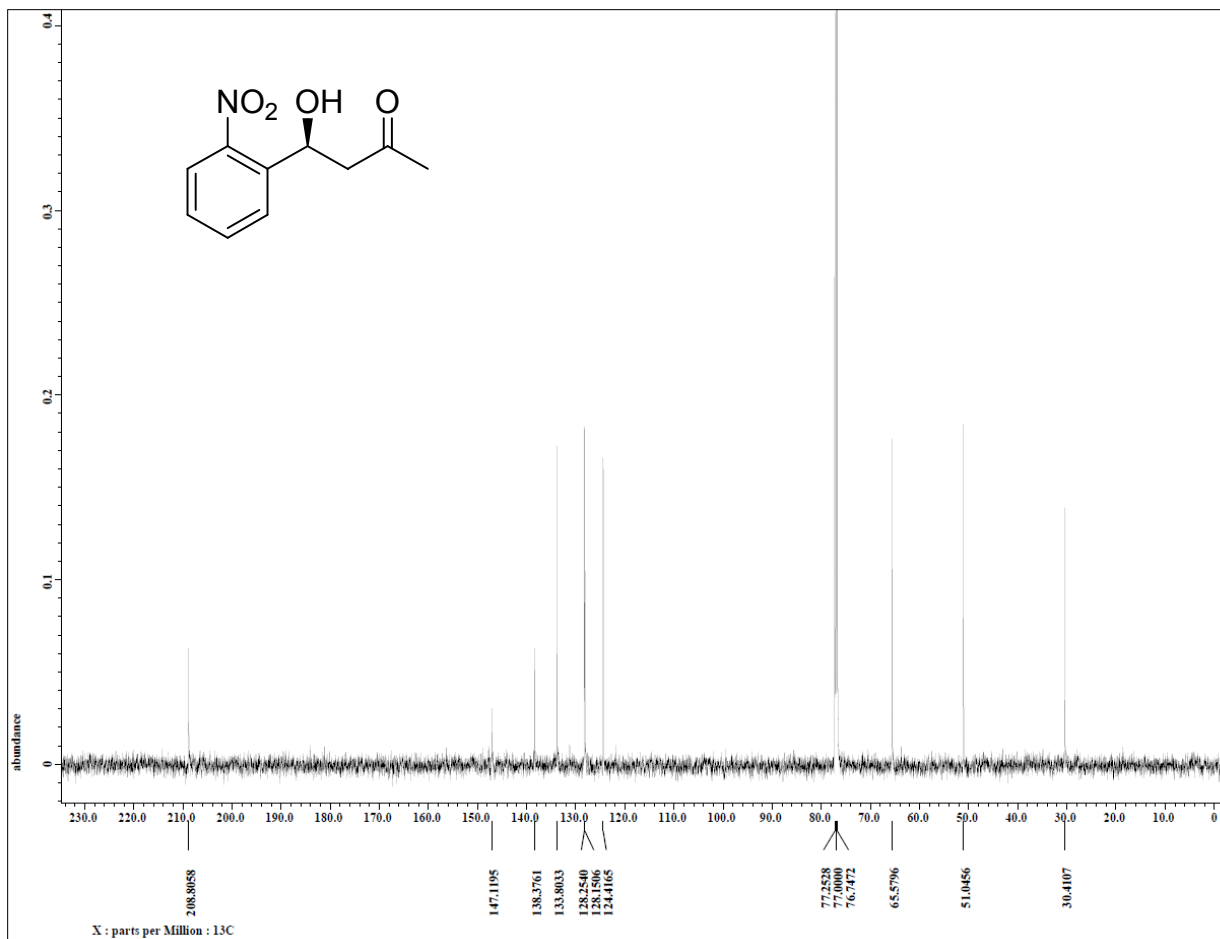


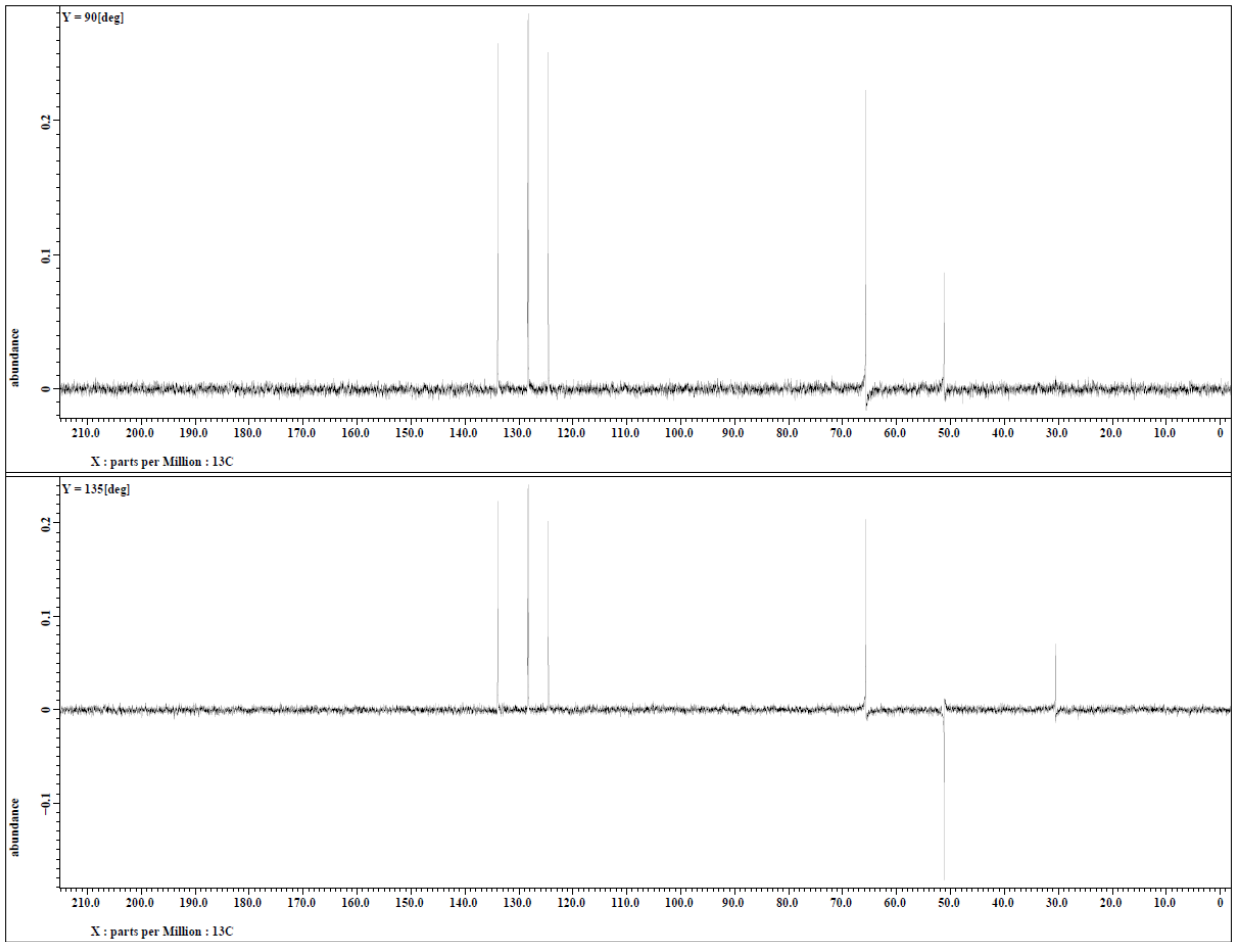




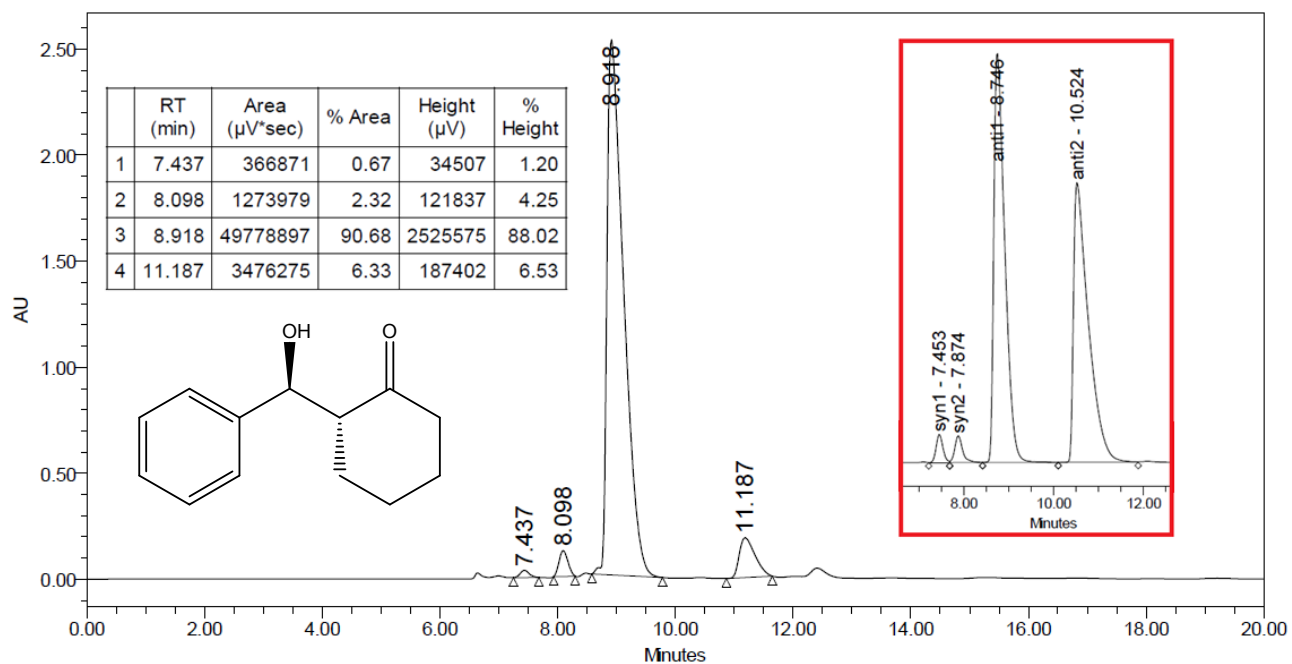
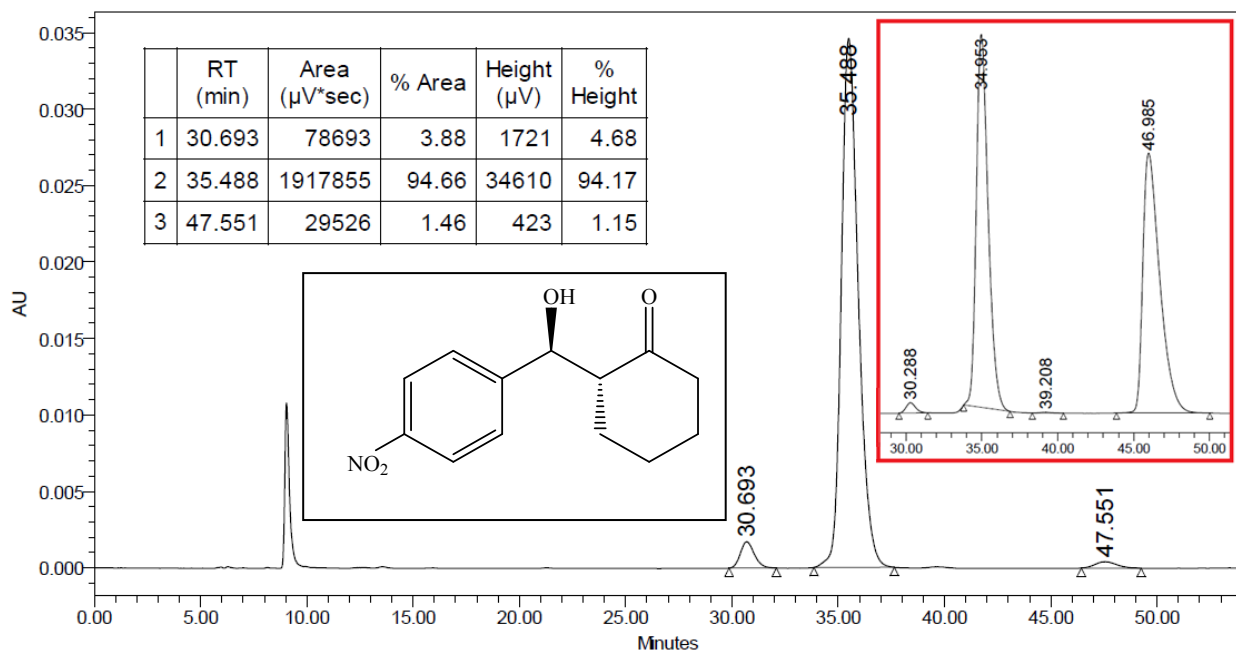


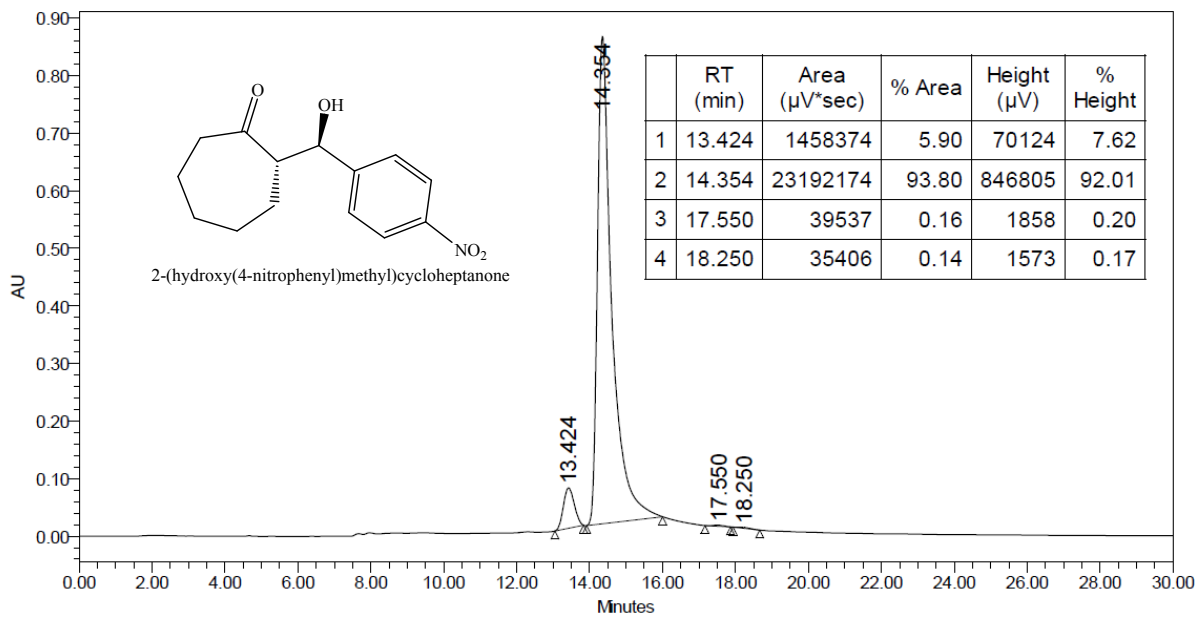
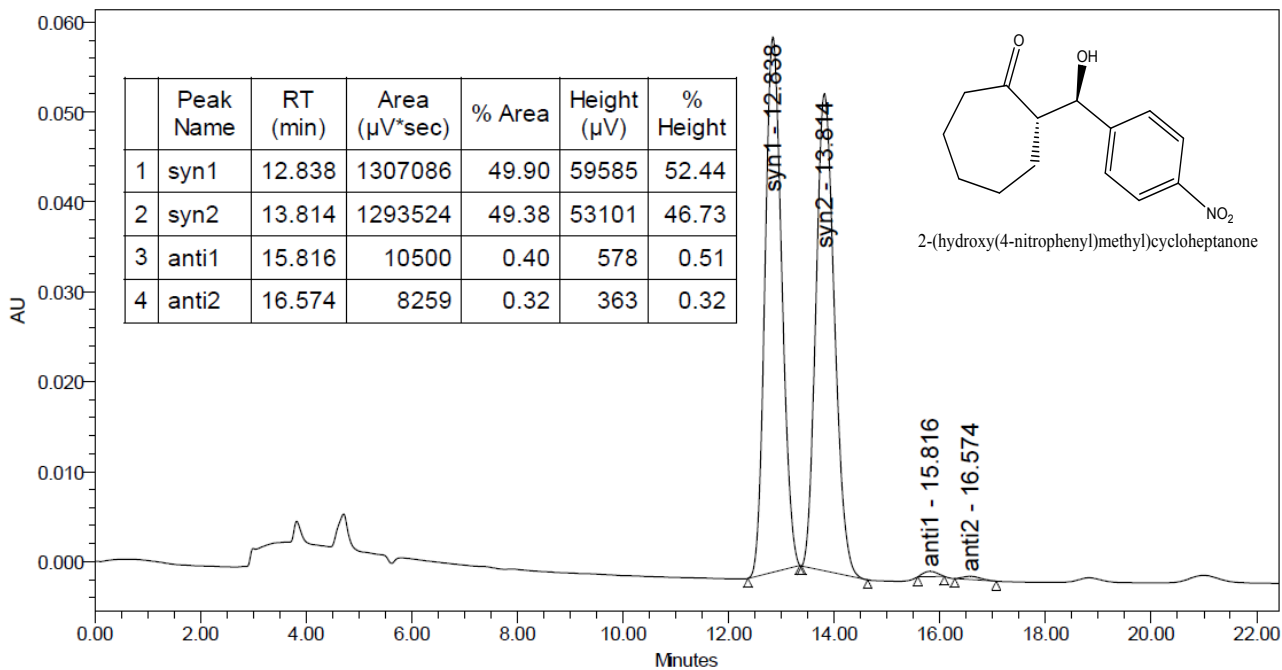


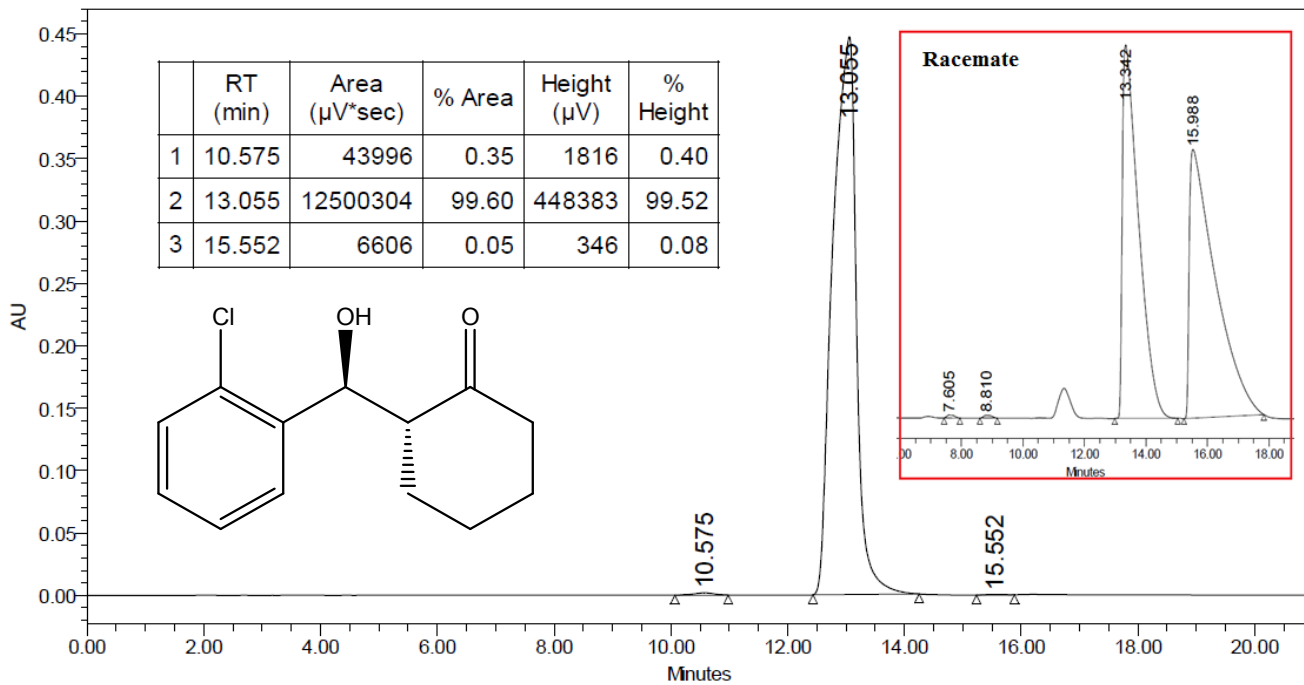


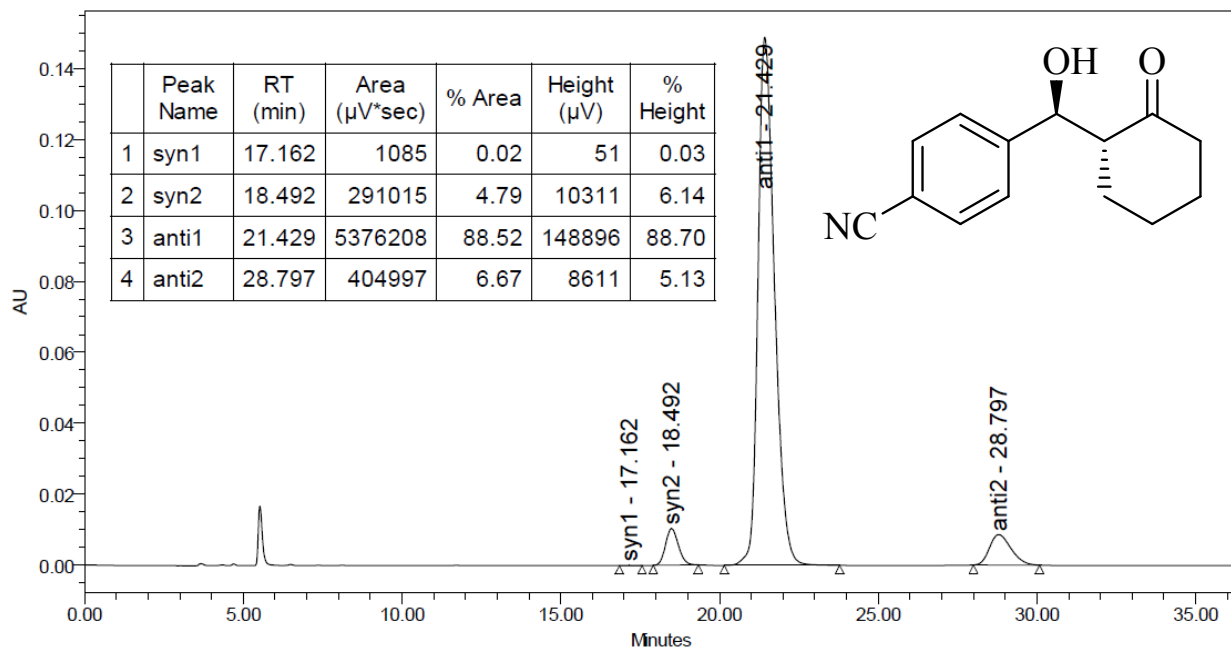
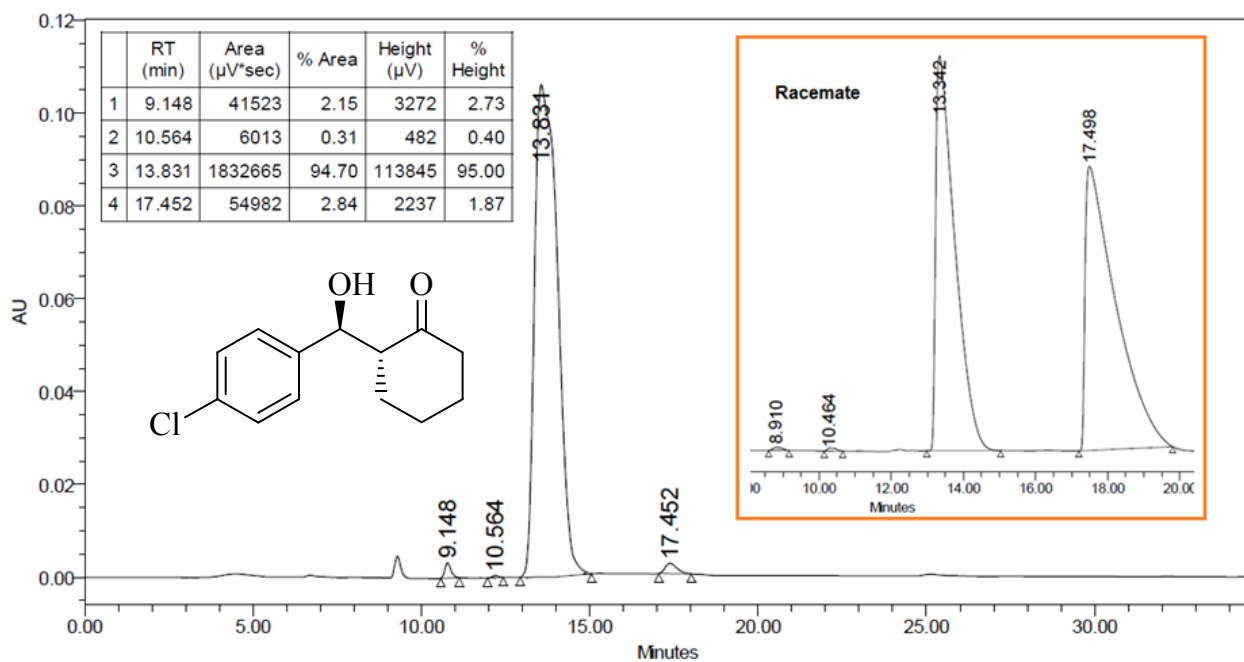


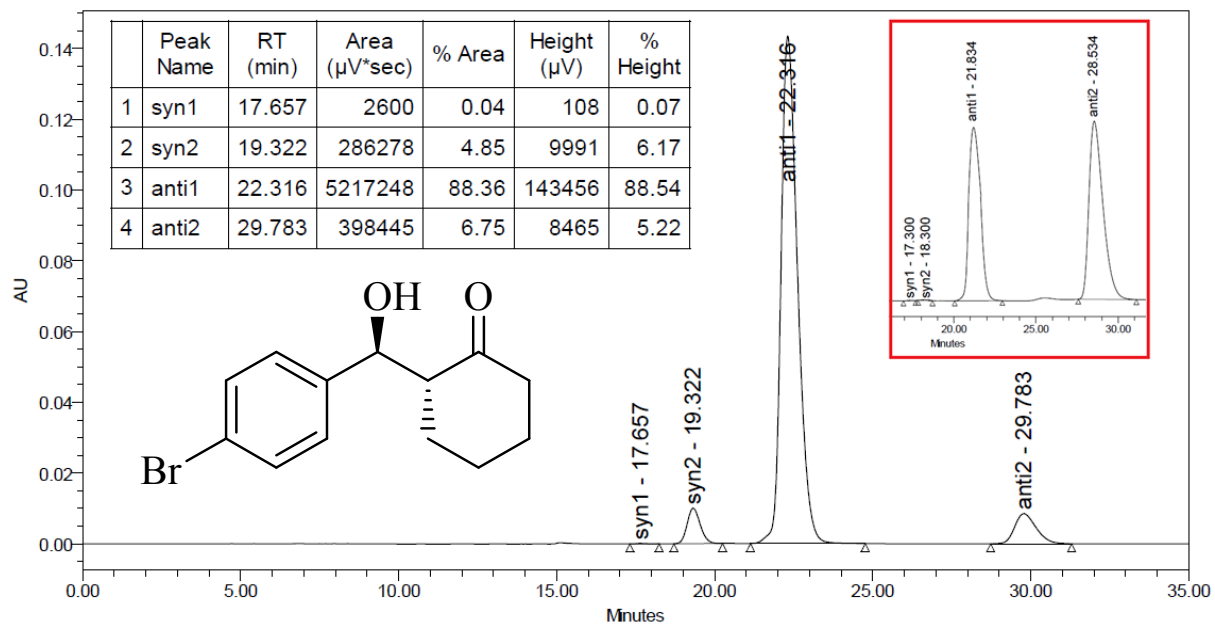
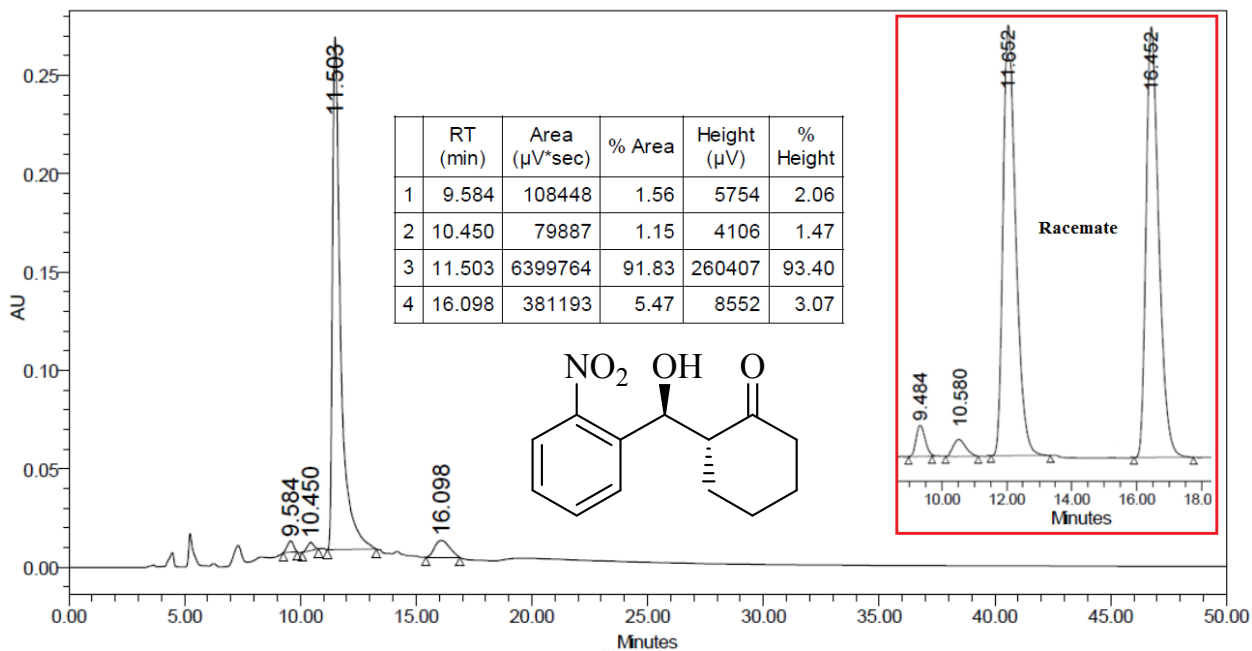
➤ HPLC of corresponding aldol compounds Catalyzed by 8aa taken by chiral column

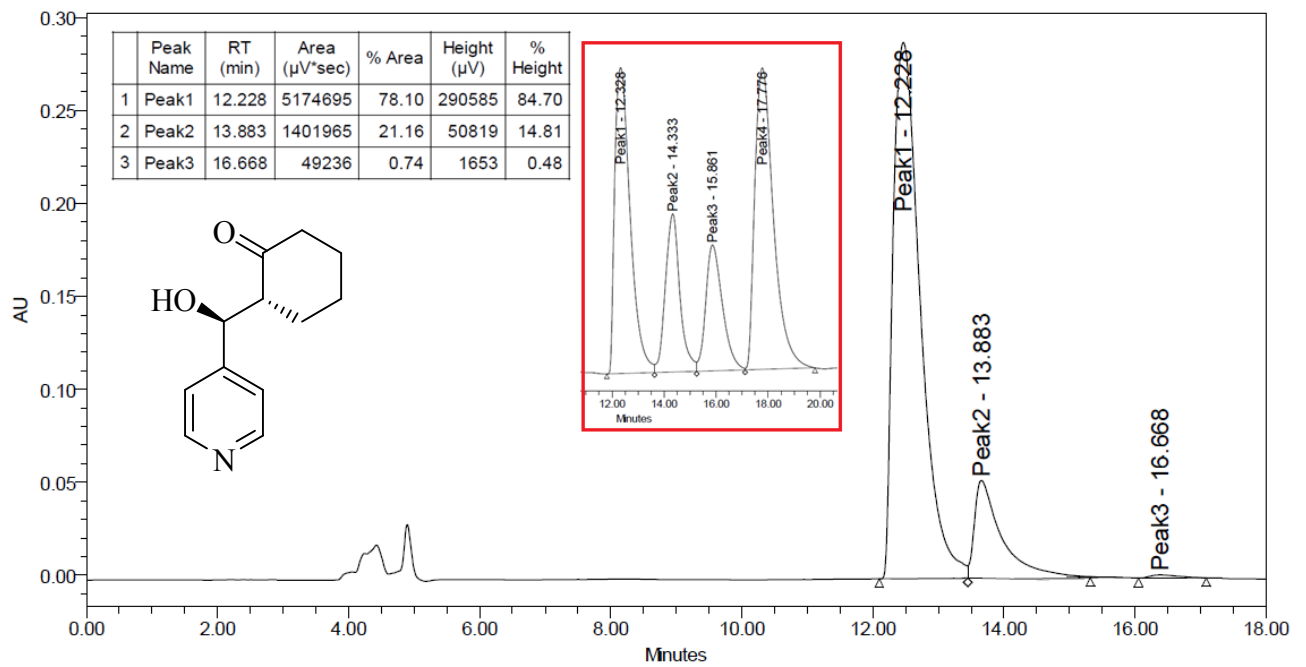
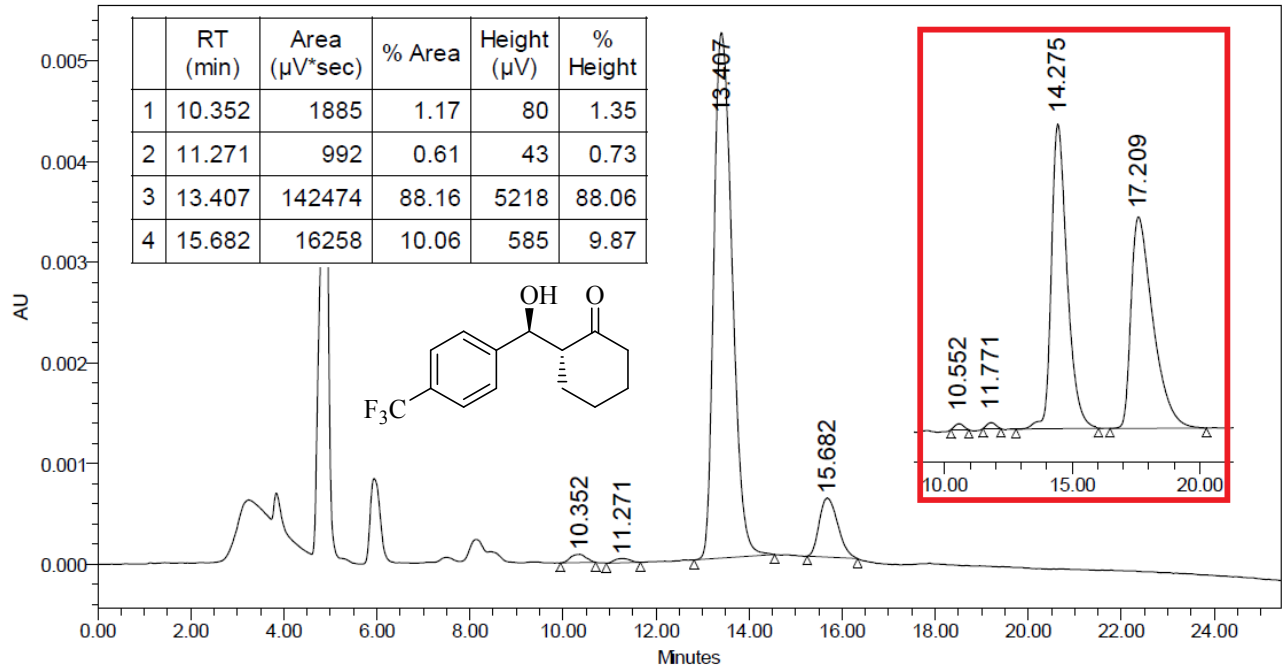




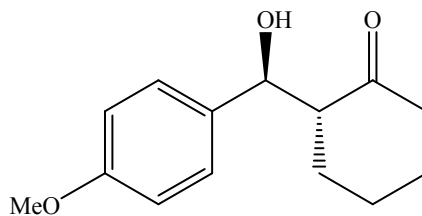




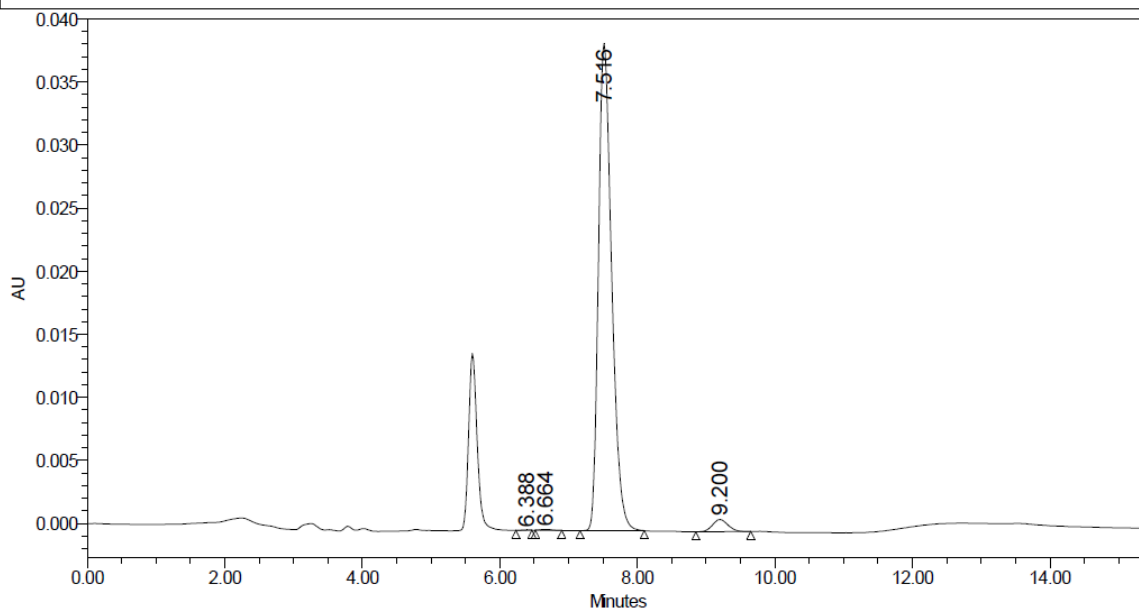




➤ (R)-2-((S)-hydroxy(4-methoxyphenyl)methyl)cyclohexanone cat. 8aa

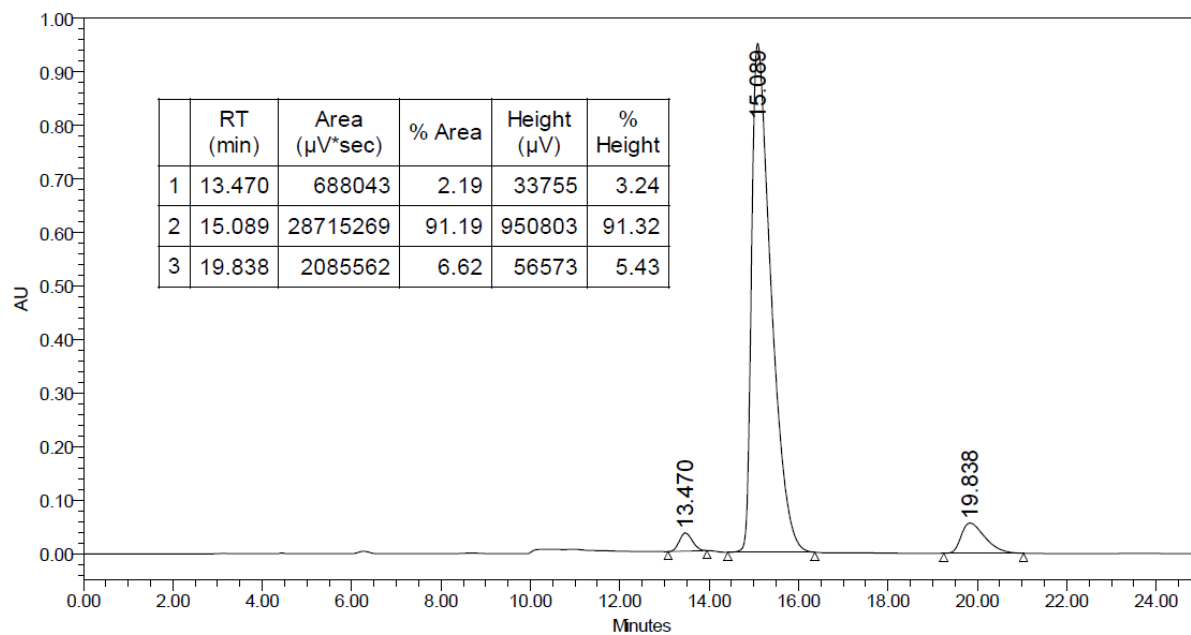
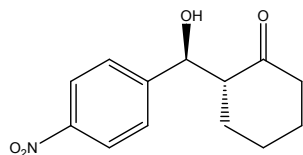


SAMPLE INFORMATION			
Sample Name:	p-Anisaldehyde+Cyhex(8aa)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	5/21/2013 11:55:13 AM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	3	Date Processed:	5/21/2013 12:43:30 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.00 Minutes	Sample Set Name:	

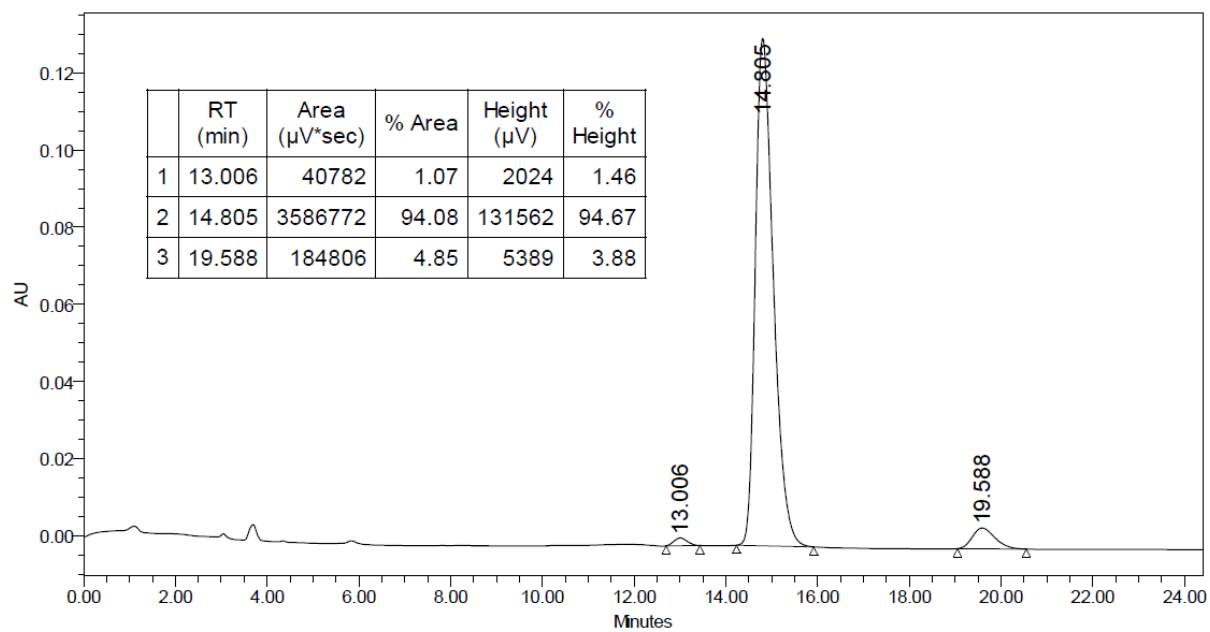
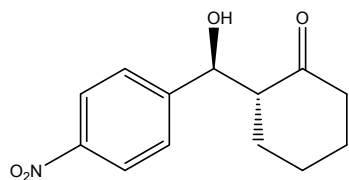


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.388	163	0.03	26	0.06
2	6.664	788	0.15	66	0.17
3	7.516	515357	97.00	38623	97.34
4	9.200	14995	2.82	963	2.43

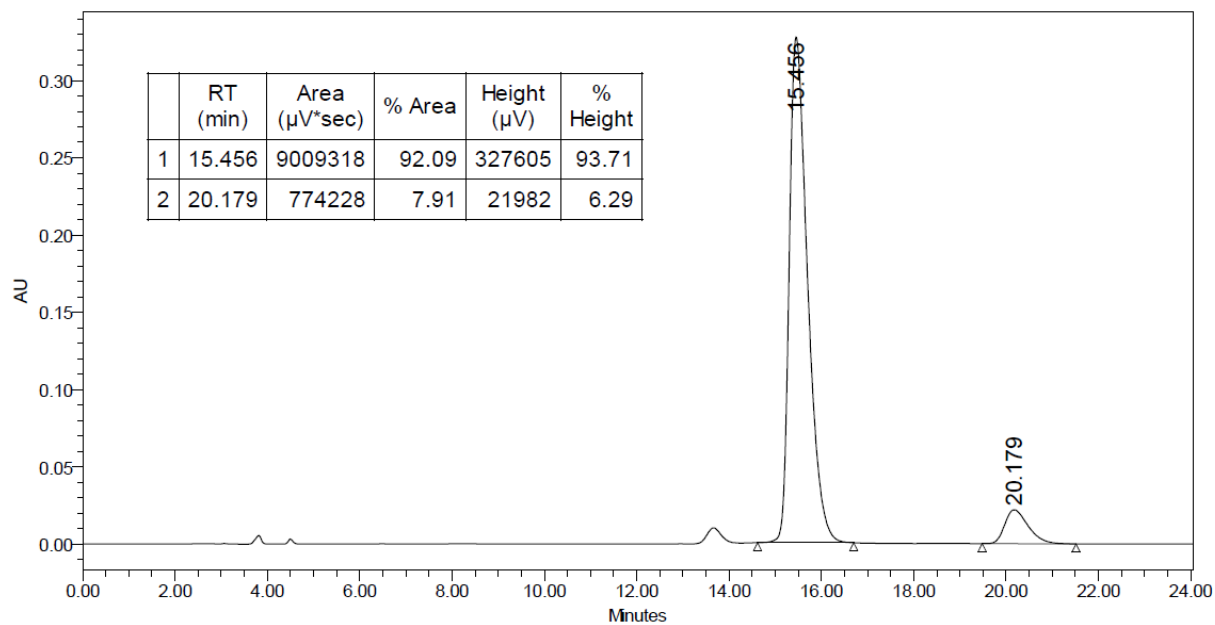
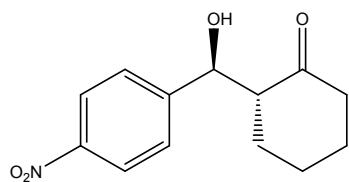
1) (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone catalyzed by cat. **8aa(z)**



2) (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone catalyzed by cat.5aa

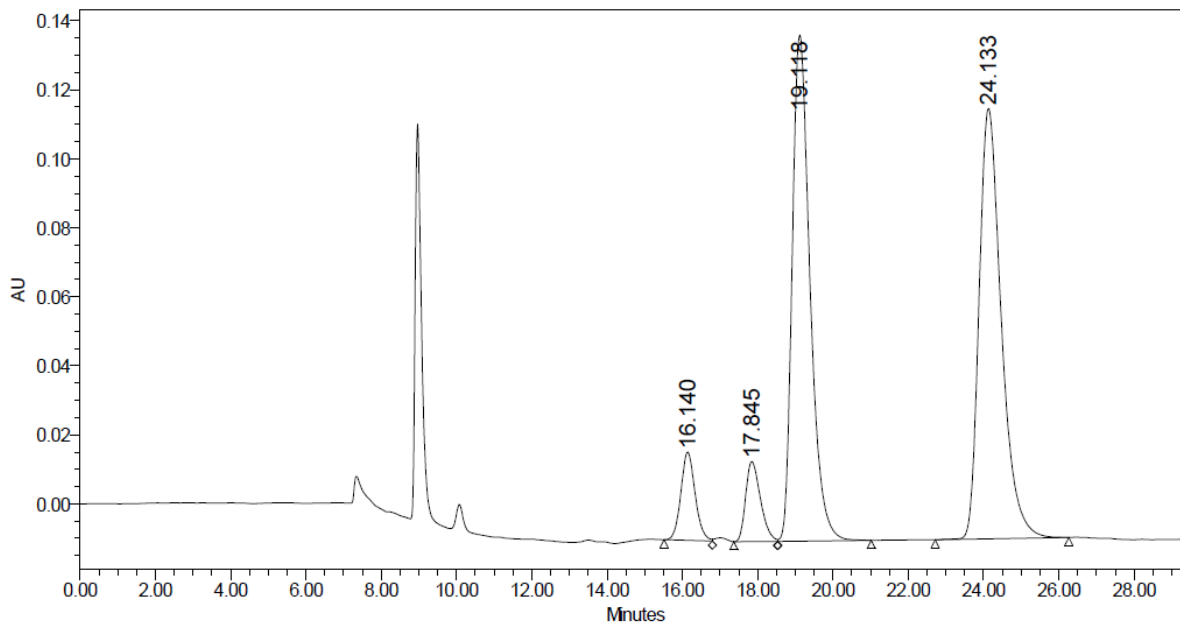


3) (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone catalyzed by cat.3aa



➤ Aldol reaction Catalyzed by Fmoc-3aa-Resin

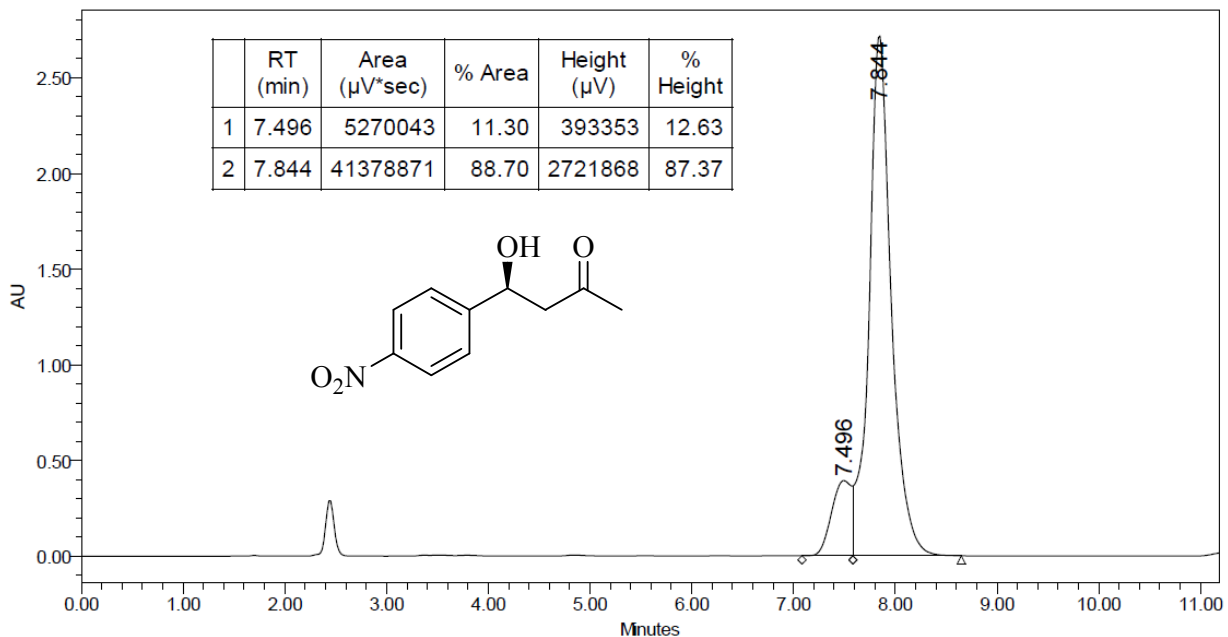
SAMPLE INFORMATION					
Sample Name:	4Nitro+cyhex(Fmoc-K.L.H-Resin)	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	11/9/2012 4:55:38 PM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	11	Date Processed:	11/9/2012 5:47:50 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB		
Run Time:	60.00 Minutes	Sample Set Name:			



	RT (min)	Area ($\mu\text{V} \cdot \text{sec}$)	% Area	Height (μV)	% Height
1	16.140	673921	6.00	25616	8.00
2	17.845	633131	5.64	23222	7.25
3	19.118	4813702	42.84	146662	45.79
4	24.133	5114696	45.52	124758	38.96

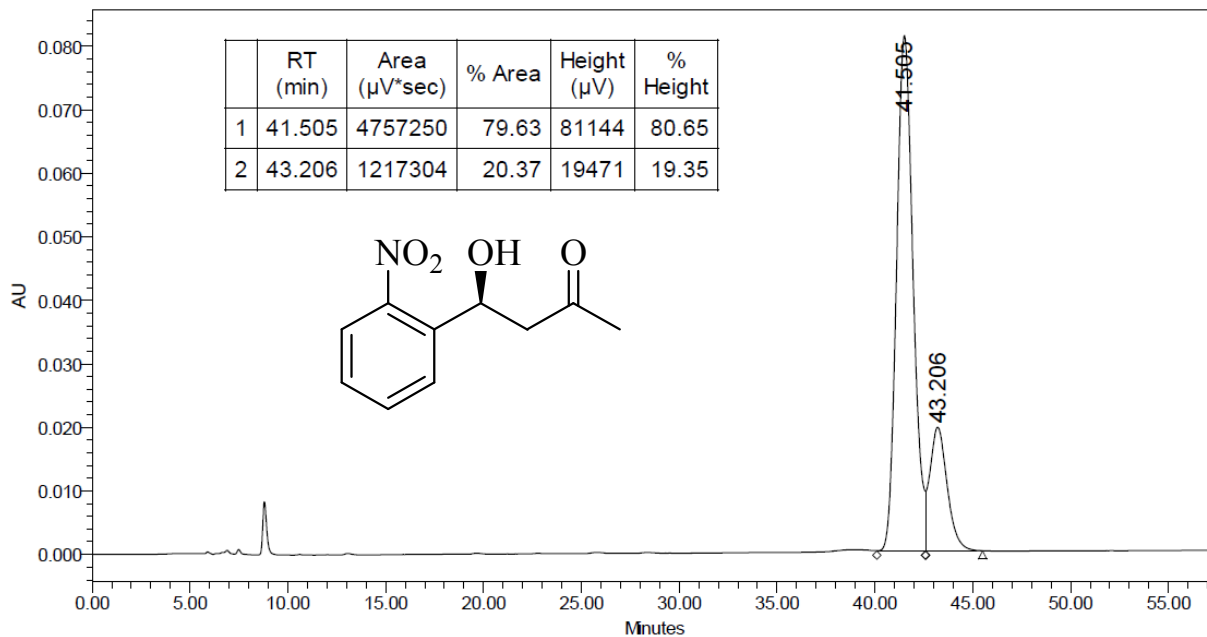
SAMPLE INFORMATION

Sample Name: 4NitroBen+acetone	Acquired By: Breeze
Sample Type: Unknown	Date Acquired: 4/12/2013 11:20:31 AM MYT
Vial: 1	Acq. Method: Saadi
Injection #: 3	Date Processed: 4/12/2013 12:08:00 PM MYT
Injection Volume: 0.00 ul	Channel Name: W2489 ChA
Run Time: 60.00 Minutes	Sample Set Name:



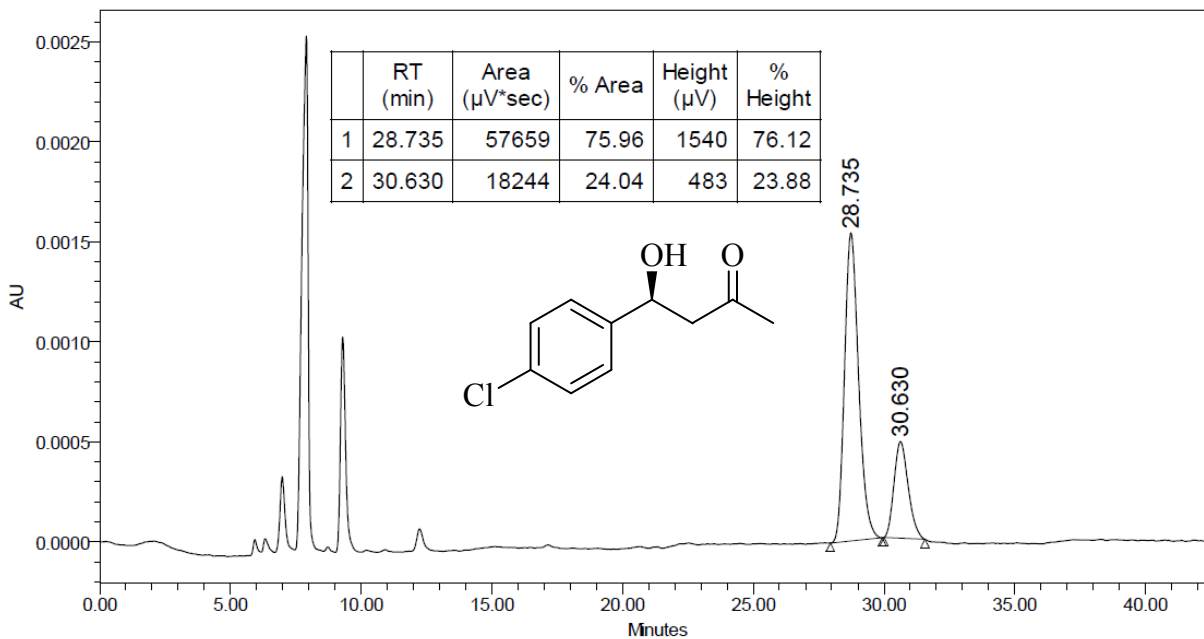
SAMPLE INFORMATION

Sample Name:	2Nitrobenz +acetone(8aa)ADH	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	3/29/2013 10:12:32 AM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	2	Date Processed:	3/29/2013 12:25:52 PM MYT
Injection Volume:	0.00 ul	Channel Name:	W2489 ChA
Run Time:	60.00 Minutes	Sample Set Name:	



SAMPLE INFORMATION

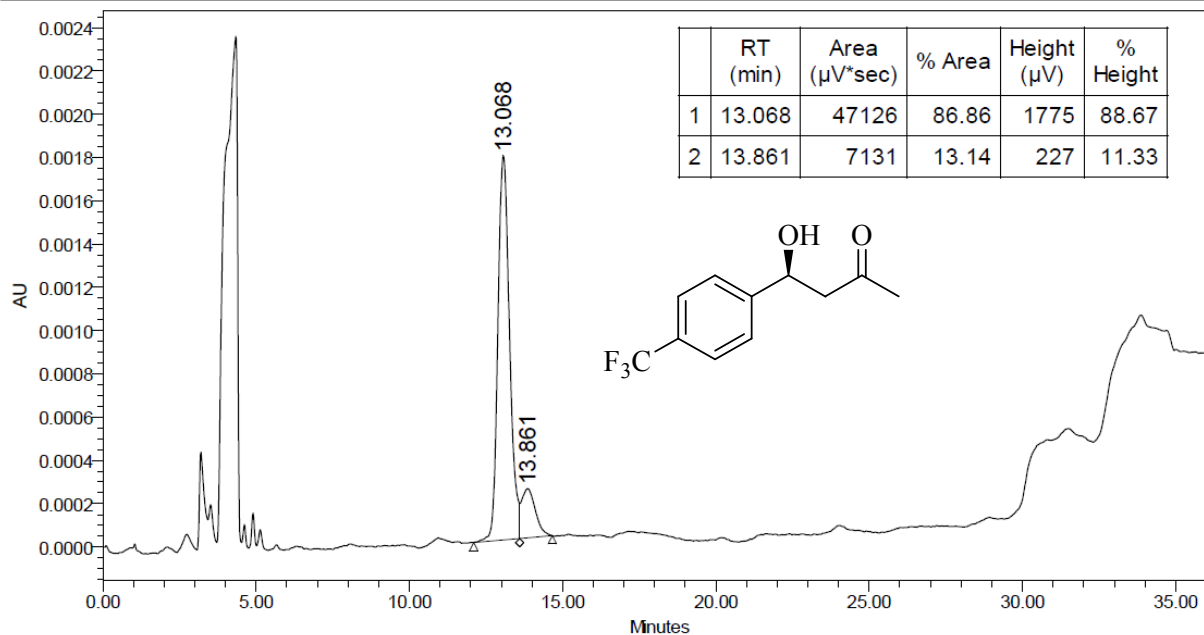
Sample Name:	4Cl-benz +acetone(8aa)ADH	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	3/29/2013 1:15:31 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	5	Date Processed:	3/29/2013 2:09:04 PM MYT
Injection Volume:	0.00 ul	Channel Name:	W2489 ChA
Run Time:	60.00 Minutes	Sample Set Name:	



SAMPLE INFORMATION

Sample Name: 4CF3Ben+acetone
 Sample Type: Unknown
 Vial: 1
 Injection #: 5
 Injection Volume: 0.00 ul
 Run Time: 60.00 Minutes

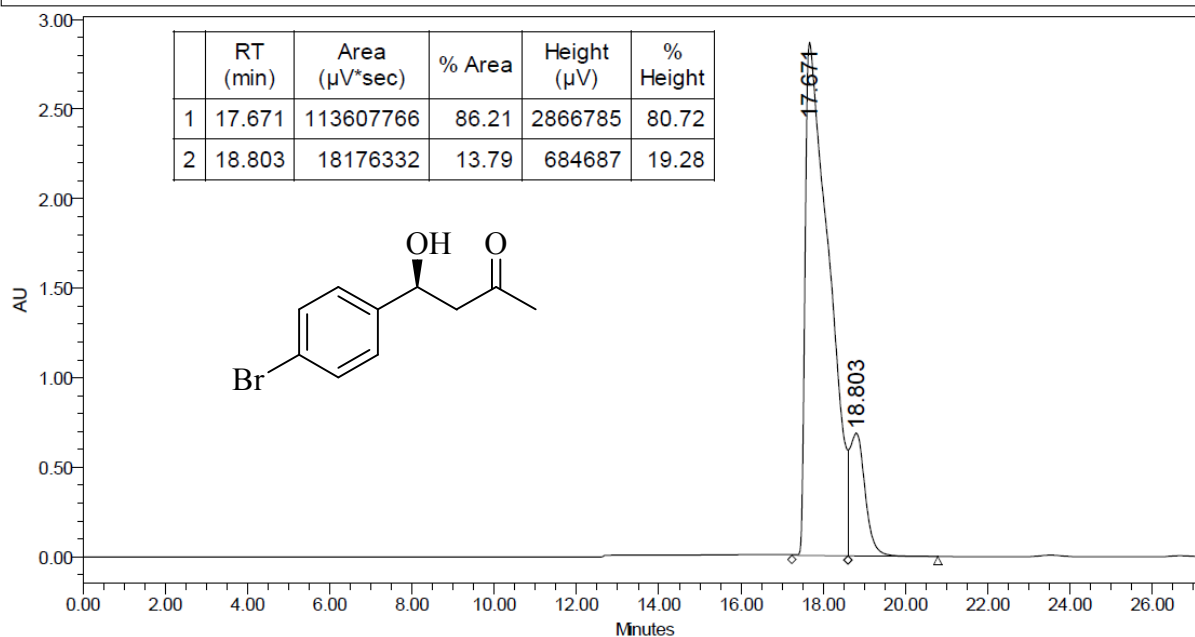
Acquired By: Breeze
 Date Acquired: 4/1/2013 12:30:28 PM MYT
 Acq. Method: Saadi
 Date Processed: 4/1/2013 5:17:38 PM MYT
 Channel Name: W2489 ChA
 Sample Set Name:



SAMPLE INFORMATION

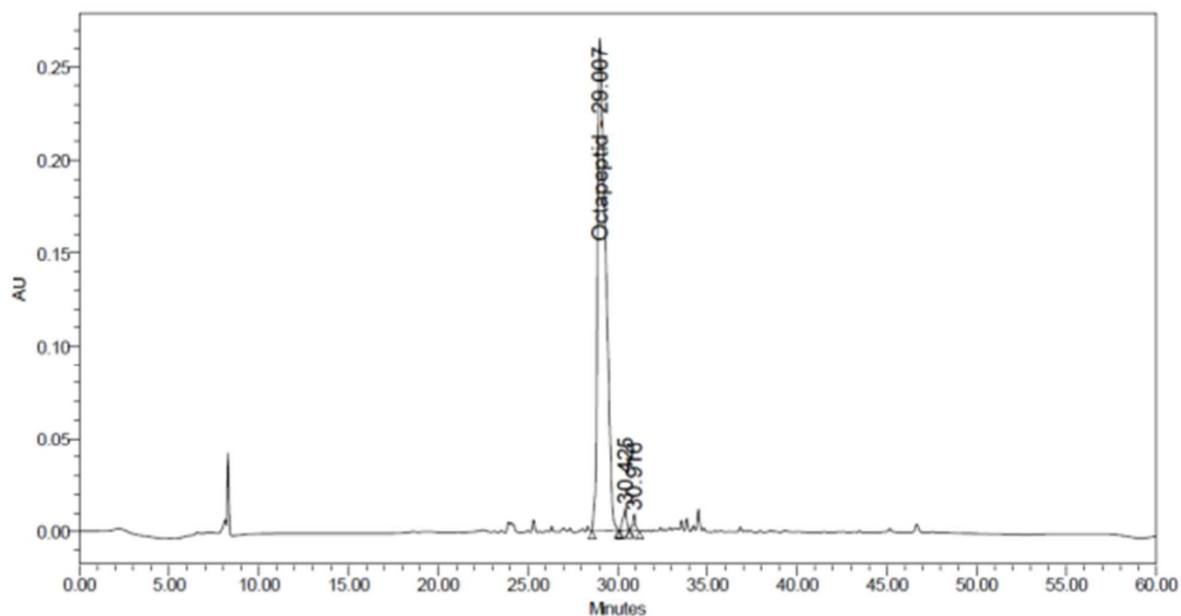
Sample Name: 4BrBen+acetone
 Sample Type: Unknown
 Vial: 1
 Injection #: 9
 Injection Volume: 0.00 ul
 Run Time: 60.00 Minutes

Acquired By: Breeze
 Date Acquired: 3/29/2013 3:41:04 PM MYT
 Acq. Method: Saadi
 Date Processed: 4/3/2013 6:29:39 PM MYT
 Channel Name: W2489 ChA
 Sample Set Name:



4) Octapeptide purity:

Pro-Glu-Leu-Phe-Val-Lys-Leu-His-NH₂



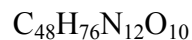
	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Octapeptid	29.007	8319498	97.13	265520	92.84
2		30.425	158948	1.86	11822	4.13
3		30.916	86726	1.01	8662	3.03

Octapeptide Mass:

$$[\alpha]_{\text{Na589}}^{20} = + 2.86 \text{ (c= 5 mg/25ml H}_2\text{O)}$$

Pro-Glu-Leu-Phe-Val-Lys-Leu-His-NH₂

Theory Mol. Wt. calculated by Chemoffice software:

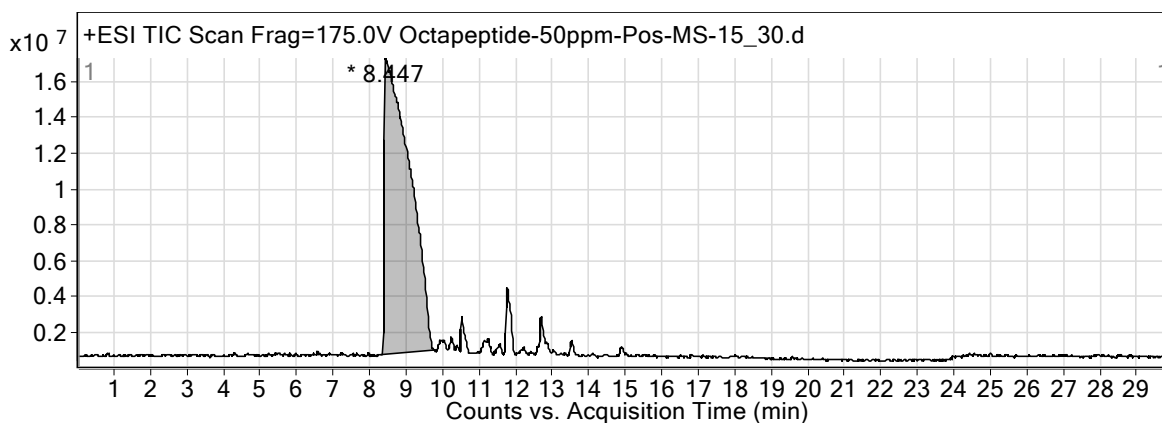


Exact Mass: 980.58

Mol. Wt.: 981.19

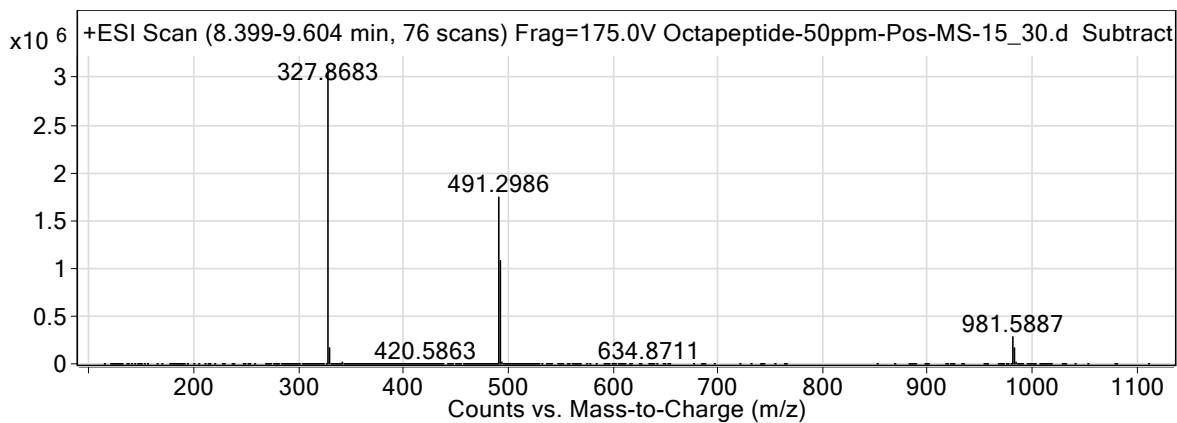
m/e: 980.58 (100.0%), 981.58 (56.7%), 982.59 (13.9%), 982.58 (4.4%), 983.59 (3.5%)

And experimental LC- Mass:

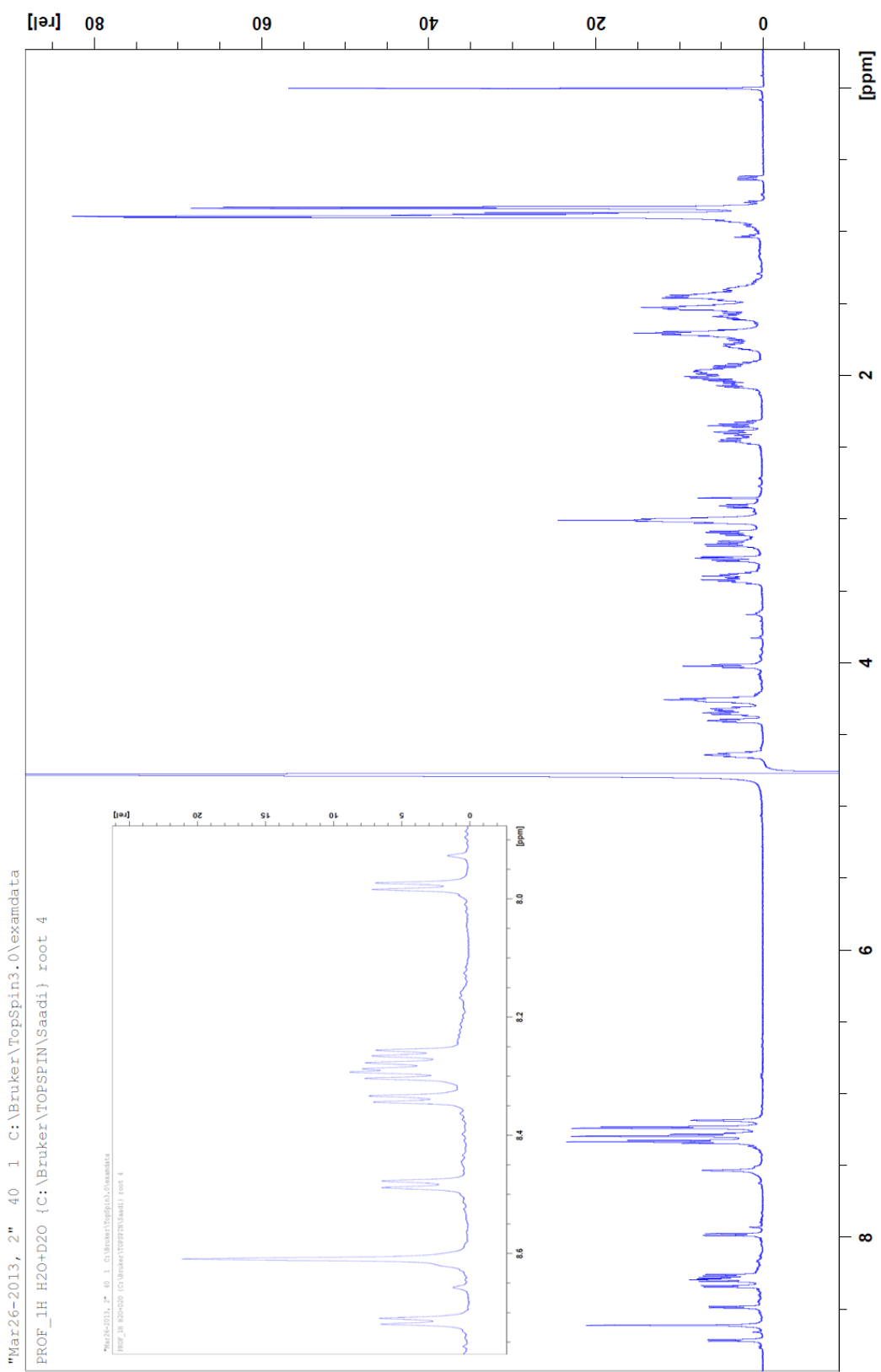


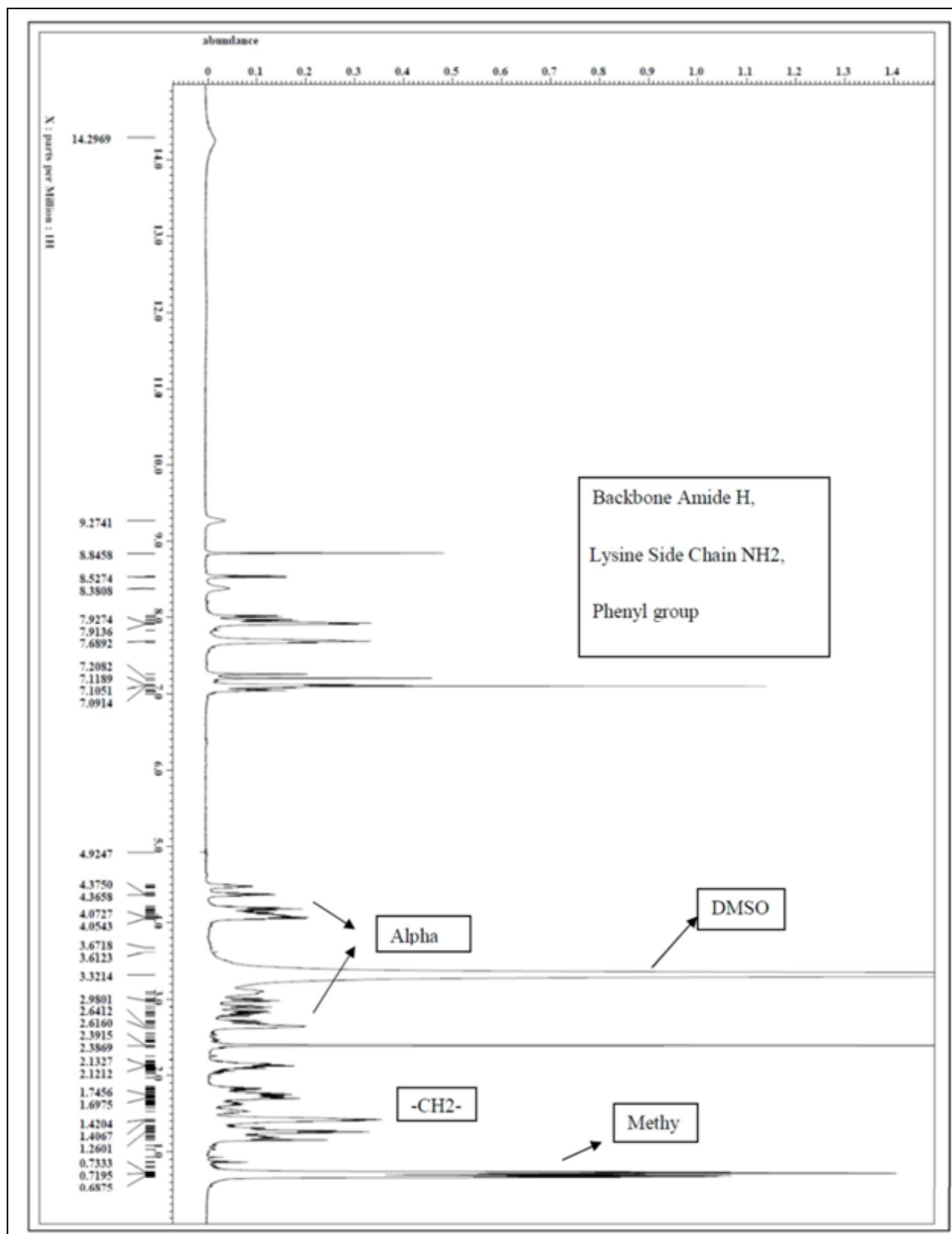
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	8.302	8.447	9.845	16515438	793998057	100



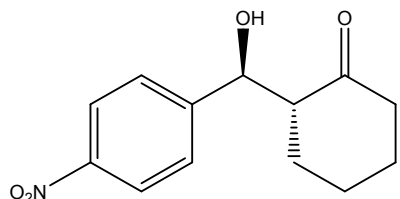
<i>m/z</i>	<i>z</i>	Abund
327.8683	3	3069294
328.0218	3	201133
328.2025	3	1918582
328.5367	3	680737
328.8709	3	168530
491.2986	2	1749495
491.8	2	1076452
492.3018	2	336858
981.5887	1	290675
982.5915	1	172135





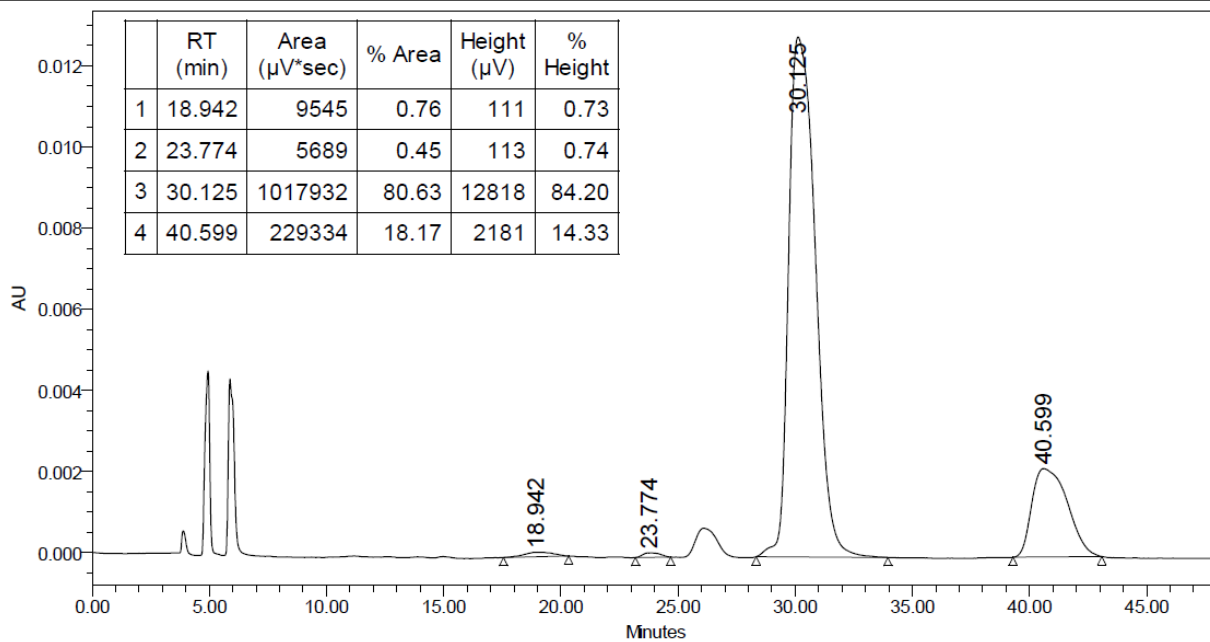
2- Aldol reaction catalyzed by PE-16aa

1-1 (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone Catalyzed by PE-16aa

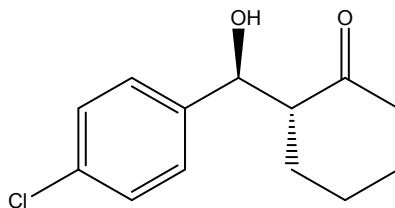


SAMPLE INFORMATION

Sample Name:	4.NitroBe+Cyhex	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/30/2012 2:04:55 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	9	Date Processed:	9/11/2012 10:22:37 AM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.10 Minutes	Sample Set Name:	

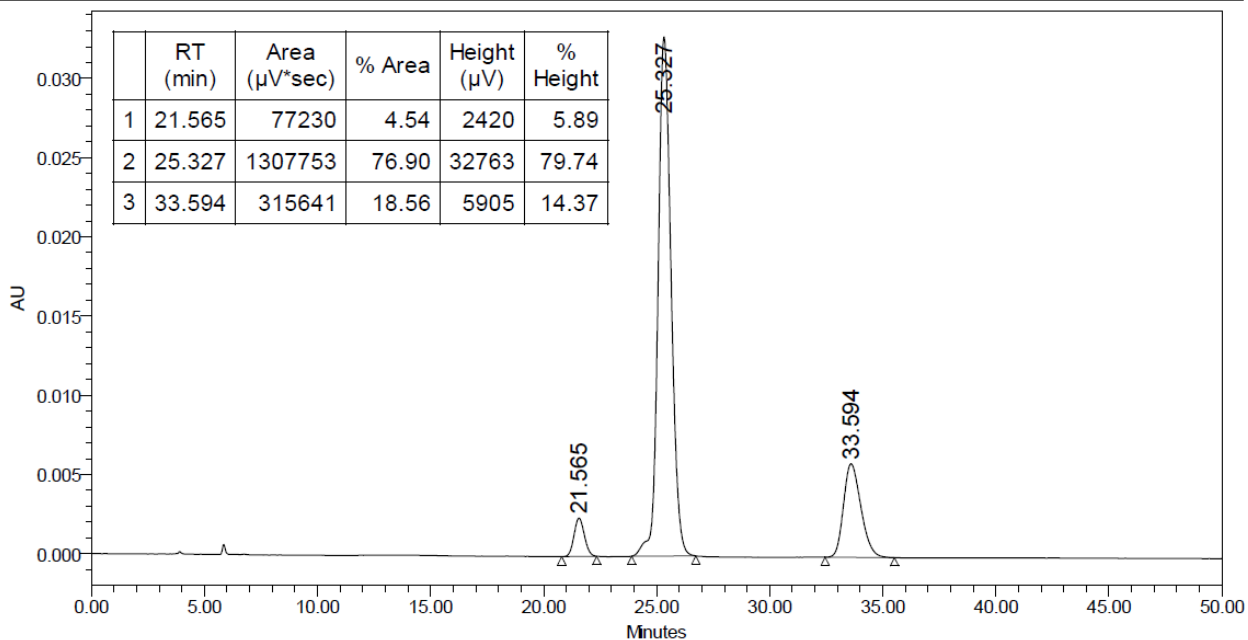


1-2 (S)-2-((S)-(4-chlorophenyl)(XXXydroxyl)methyl)cyclohexanone

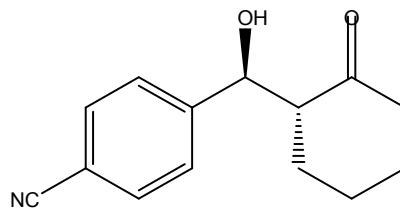


SAMPLE INFORMATION

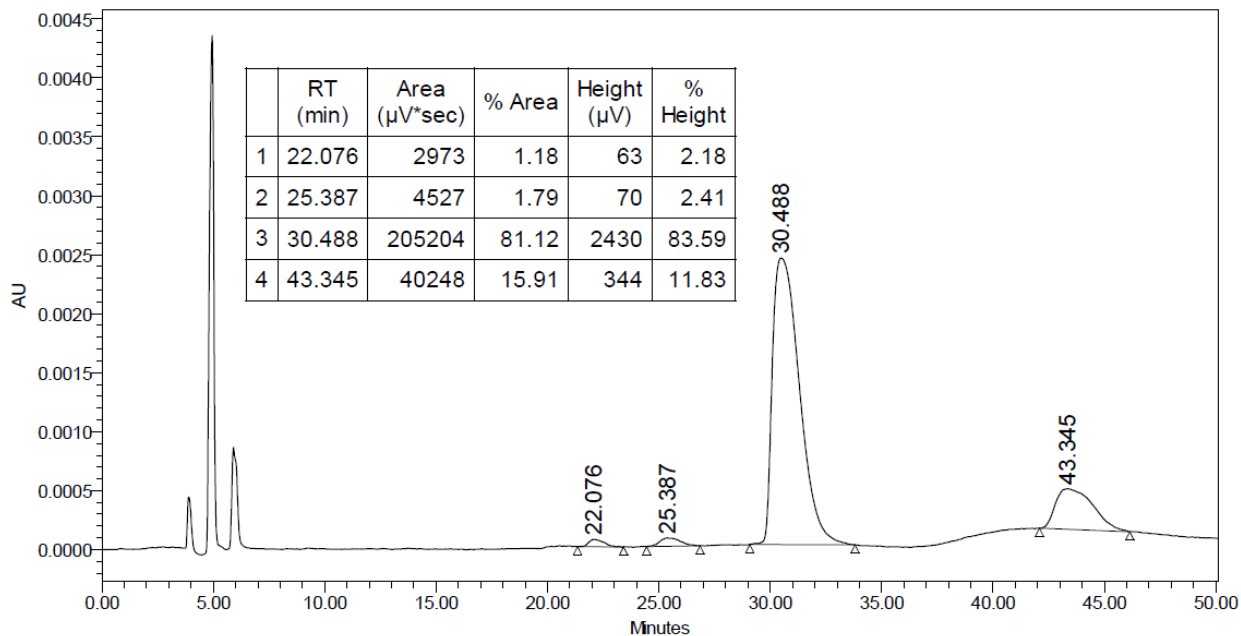
Sample Name:	4Cl-benz+Cyhex	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	7/11/2012 1:48:35 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	5	Date Processed:	7/27/2012 5:48:53 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.00 Minutes	Sample Set Name:	



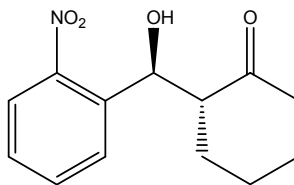
1-3 2-[Hydroxy-(4-cyano-phenyl)-methyl]-cyclohexanone



SAMPLE INFORMATION					
Sample Name:	4.CN-Be+Cyhex	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	8/30/2012 2:54:24 PM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	10	Date Processed:	8/30/2012 4:29:15 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA		
Run Time:	50.10 Minutes	Sample Set Name:			

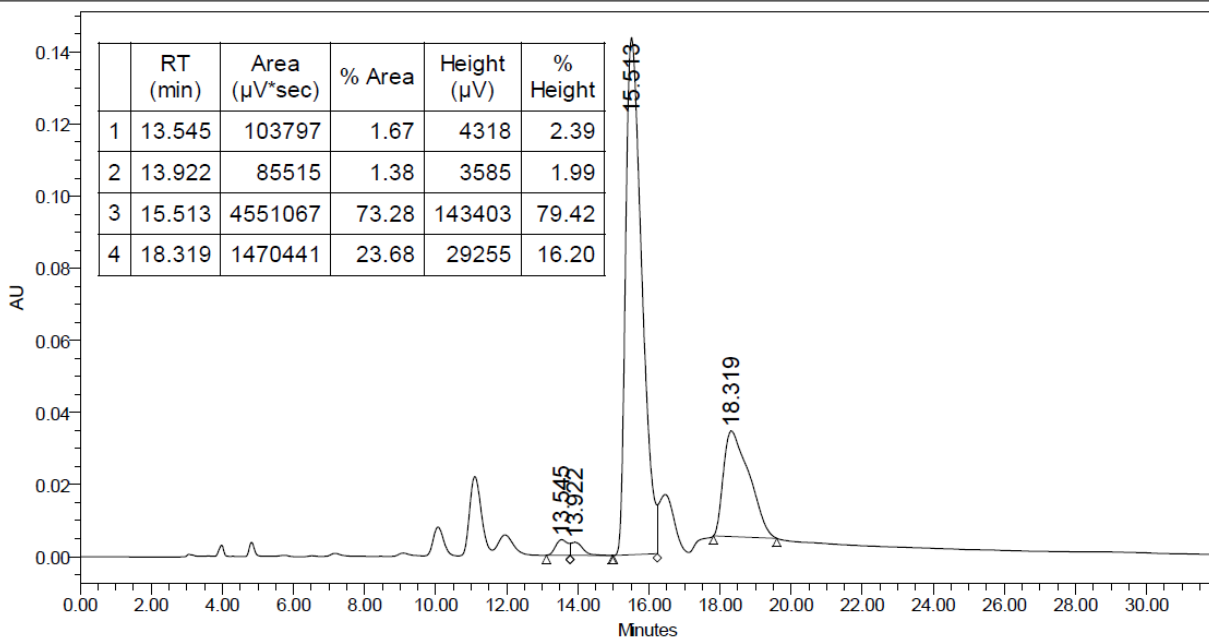


1-4 (R)-2-((S)-hydroxy(2-nitrophenyl)methyl)cyclohexanone

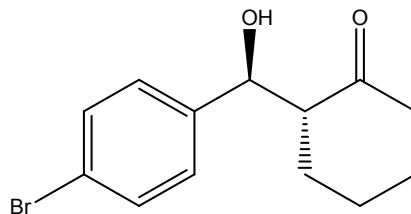


SAMPLE INFORMATION

Sample Name:	2.NitroBenz+Cyhex	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/11/2012 4:37:25 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	5	Date Processed:	9/12/2012 12:59:33 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.00 Minutes	Sample Set Name:	

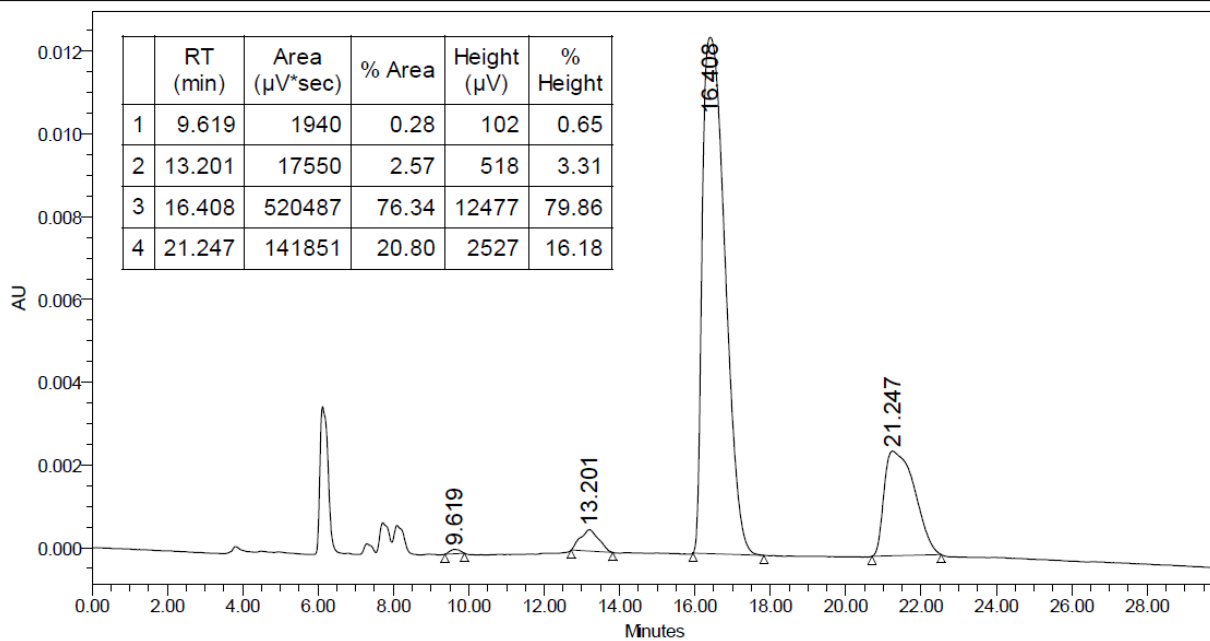


1-5 (R)-2-((S)-(4-bromophenyl)(hydroxy)methyl)cyclohexanone

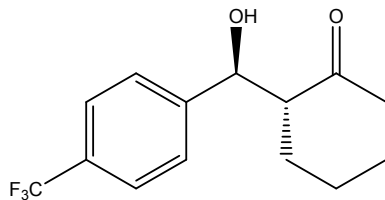


SAMPLE INFORMATION

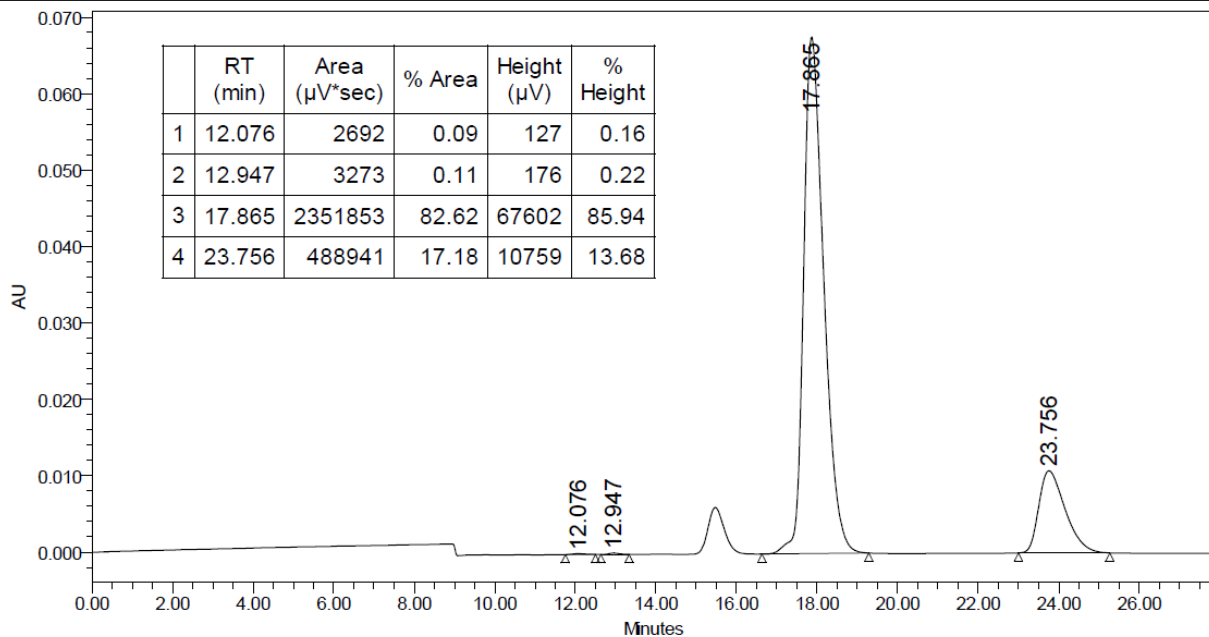
Sample Name:	4Brbenz+Cyhex	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/30/2012 11:52:41 AM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	5	Date Processed:	8/30/2012 1:08:58 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	45.00 Minutes	Sample Set Name:	



1-6 (R)-2-((S)-4-(trifluoromethyl)phenyl)(hydroxy)methyl)cyclohexanone

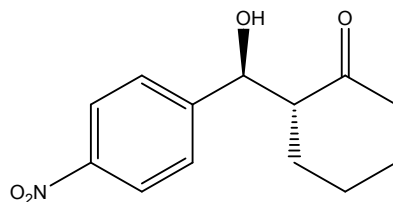


SAMPLE INFORMATION					
Sample Name:	p.CF3Ben+Cyhex	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	10/16/2012 10:44:26 AM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	2	Date Processed:	10/16/2012 3:03:42 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA		
Run Time:	30.00 Minutes	Sample Set Name:			



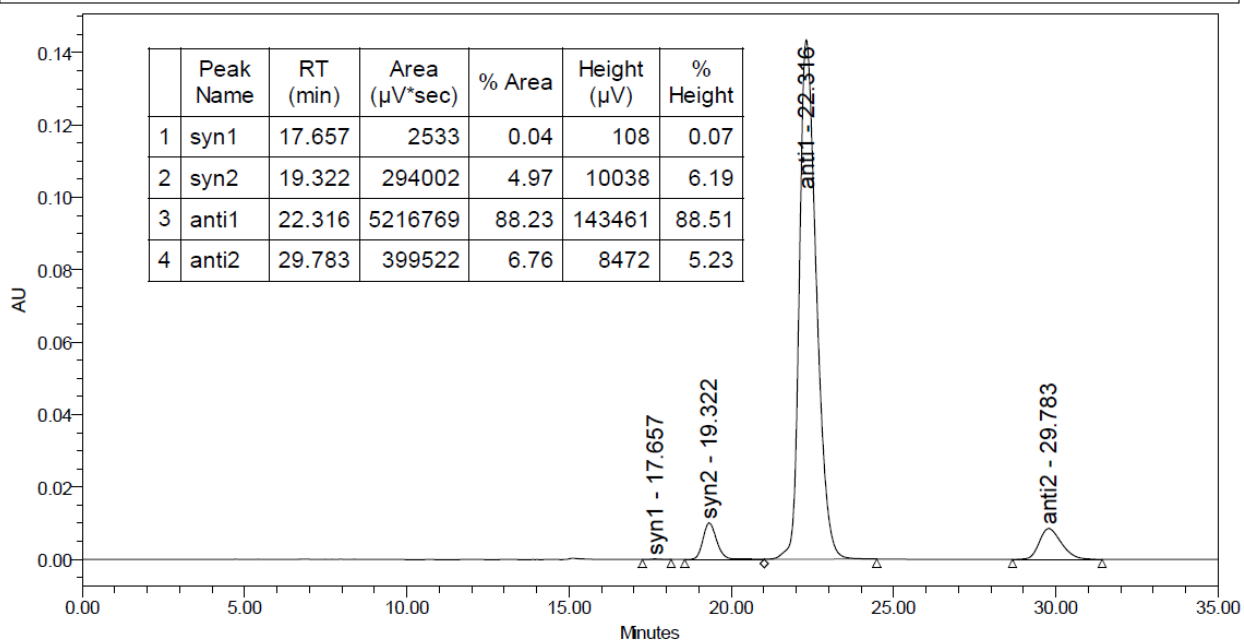
2 - Aldol reaction catalyzed by PH-18aa

2-1 (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone



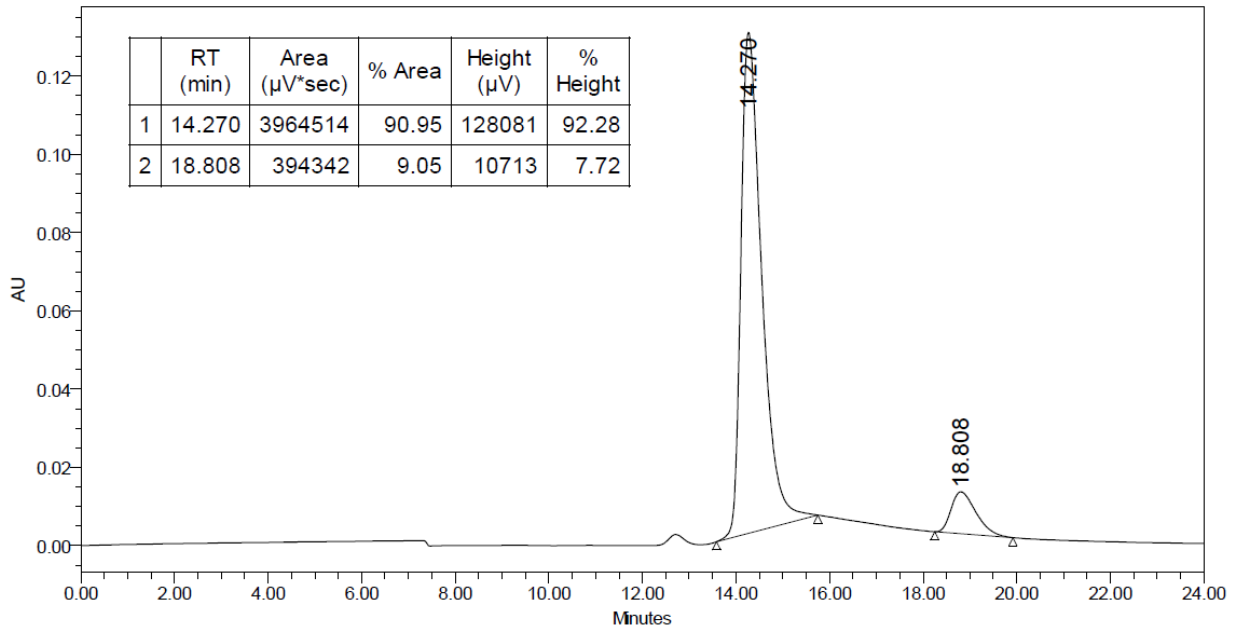
SAMPLE INFORMATION

Sample Name:	4Nitro.Ben-Cyhex	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	7/17/2012 2:21:18 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	2	Date Processed:	7/17/2012 3:15:08 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.00 Minutes	Sample Set Name:	

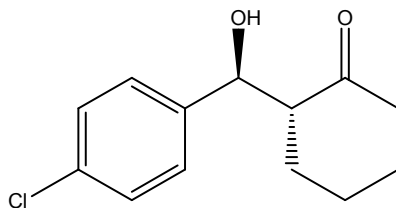


2-2 (R)-2-((S)-hydroxy(4-nitrophenyl)methyl)cyclohexanone (in 1%SDS/iPrOH)

SAMPLE INFORMATION					
Sample Name:	4-nitroben+Chex(8aa.1%SDS)	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	10/19/2012 5:09:53 PM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	5	Date Processed:	10/22/2012 5:42:43 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB		
Run Time:	24.00 Minutes	Sample Set Name:			

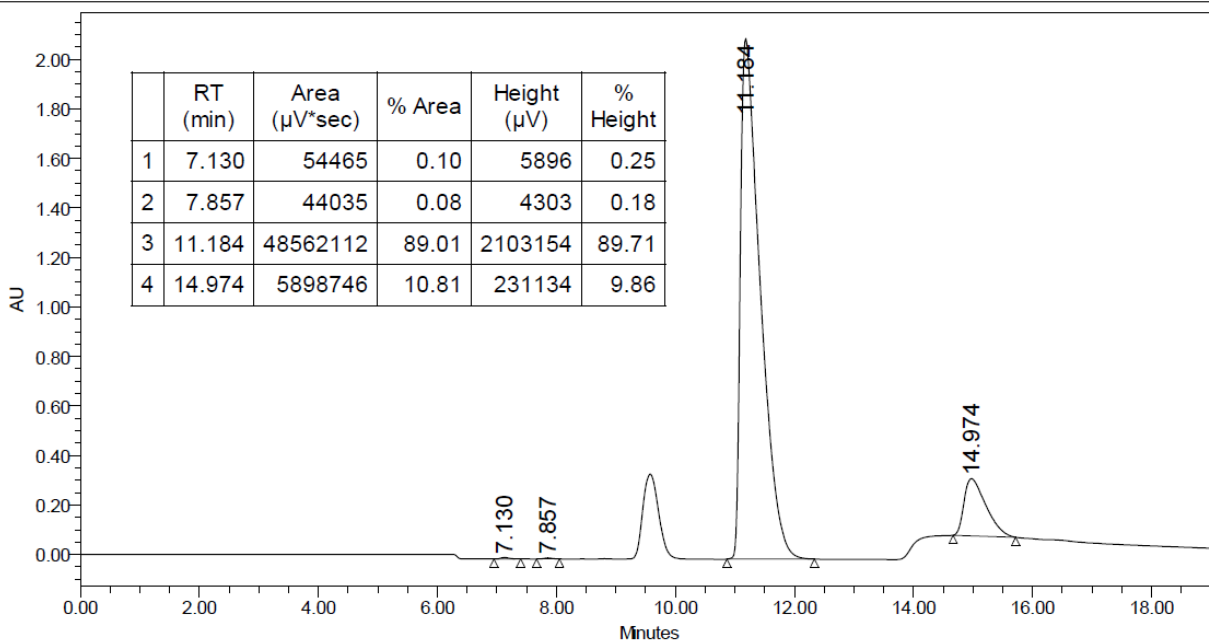


2-3 (S)-2-((S)-(4-chlorophenyl)(XXXhydroxyl)methyl)cyclohexanone

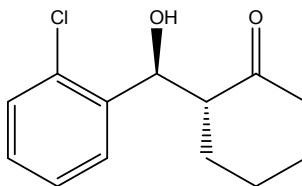


SAMPLE INFORMATION

Sample Name:	4Cl.Ben-Cyhex(P.H-16aa,aq)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	10/12/2012 4:16:29 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	7	Date Processed:	10/15/2012 2:52:05 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.00 Minutes	Sample Set Name:	

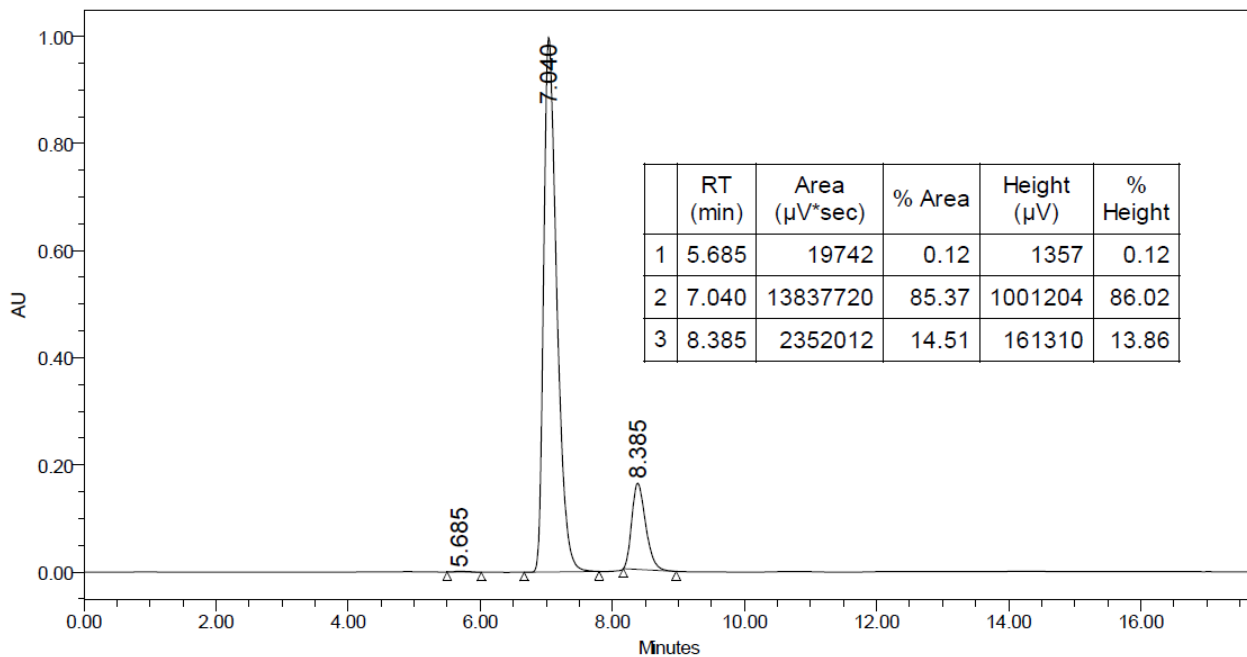


2-4 (S)-2-((S)-(2-chlorophenyl)(XXXhydroxyl)methyl)cyclohexanone

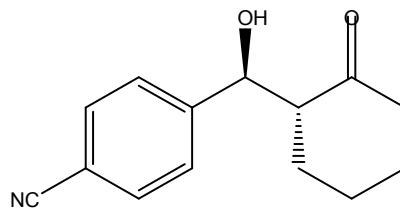


SAMPLE INFORMATION

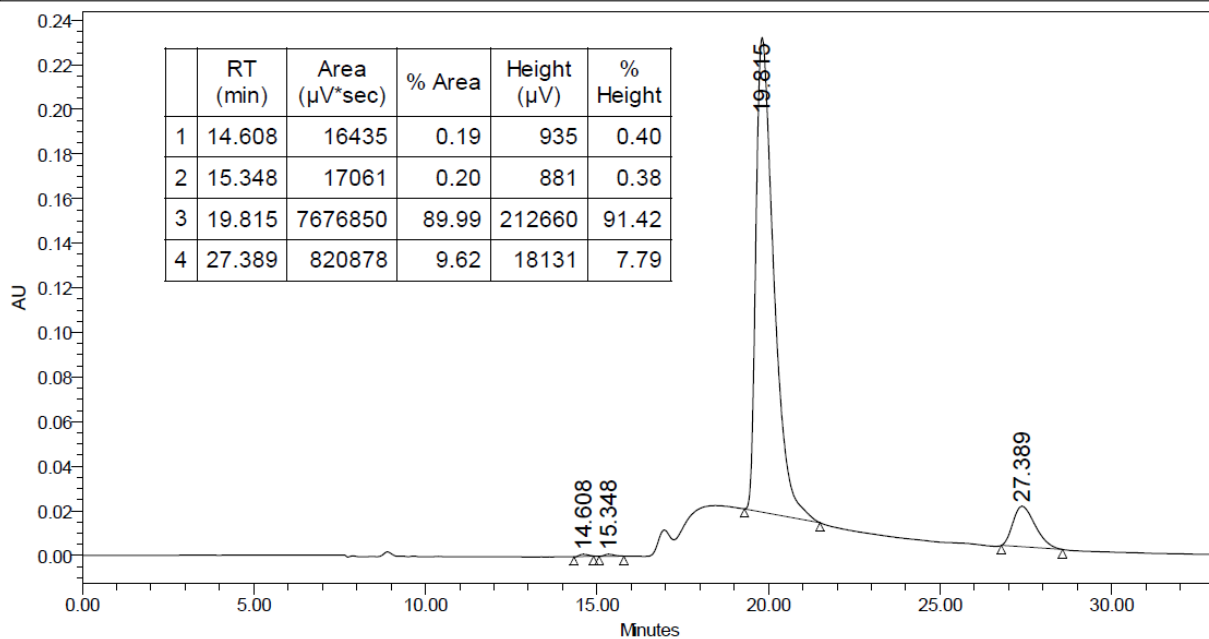
Sample Name:	2-Clbenz+Cyhex(P.H-16aa)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	10/17/2012 2:31:46 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	3	Date Processed:	10/17/2012 2:53:44 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.00 Minutes	Sample Set Name:	



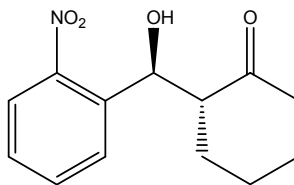
2-5 2-[Hydroxy-(4-cyano-phenyl)-methyl]-cyclohexanone



SAMPLE INFORMATION					
Sample Name:	4CN.Ben-Cyhex(P.H-16aa,aq)	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	10/12/2012 5:29:09 PM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	9	Date Processed:	10/15/2012 2:55:34 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA		
Run Time:	40.00 Minutes	Sample Set Name:			

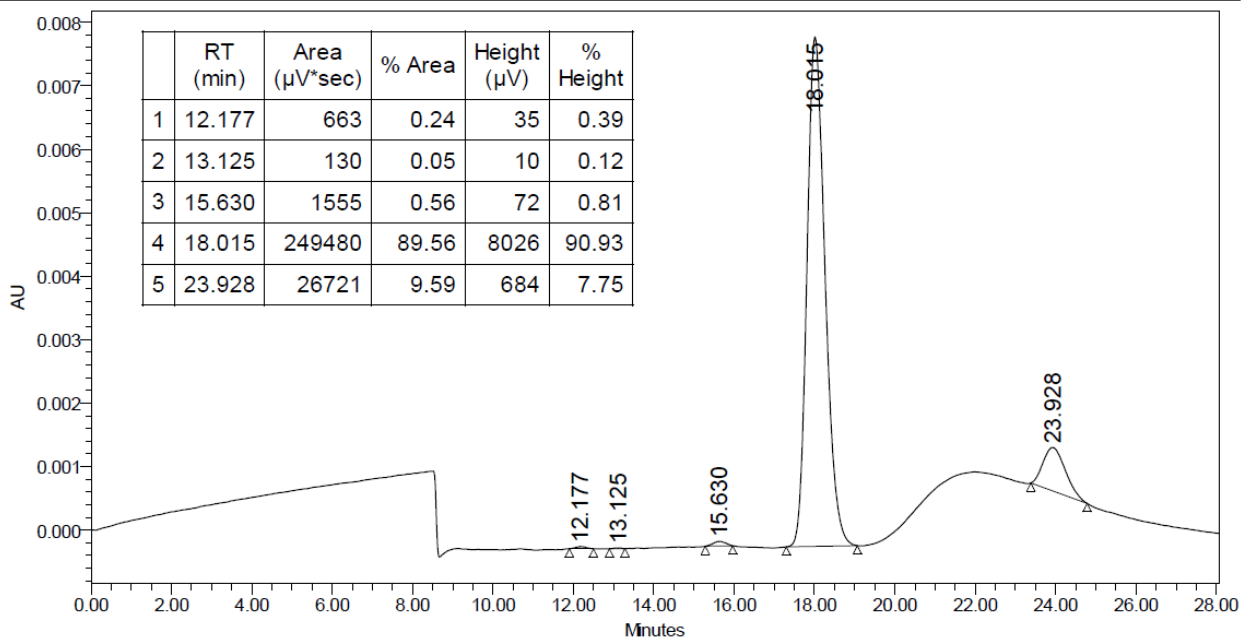


2-6 (R)-2-((S)-hydroxy(2-nitrophenyl)methyl)cyclohexanone

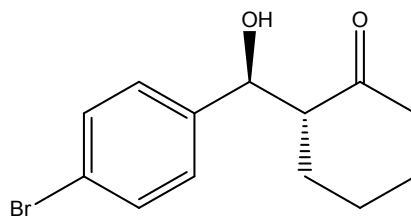


SAMPLE INFORMATION

Sample Name:	2Nitro.Ben-Cyhex(P.H-16aa,aq)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	10/15/2012 4:26:01 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	6	Date Processed:	10/15/2012 4:55:48 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.00 Minutes	Sample Set Name:	

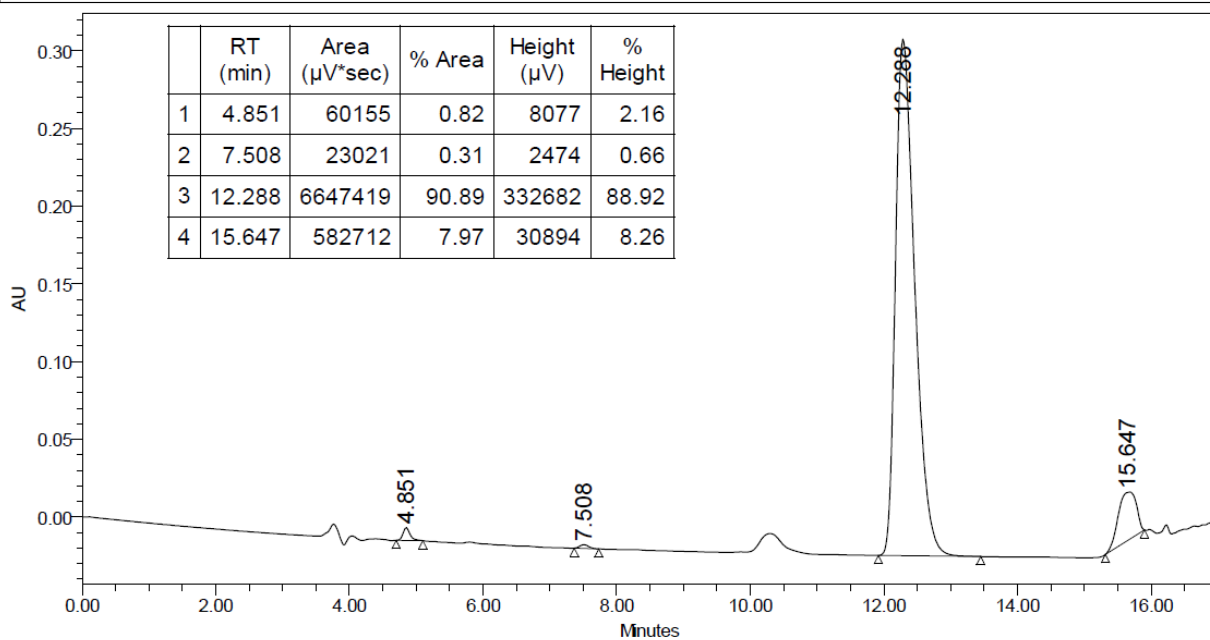


2-7 (R)-2-((S)-(4-bromophenyl)(hydroxy)methyl)cyclohexanone

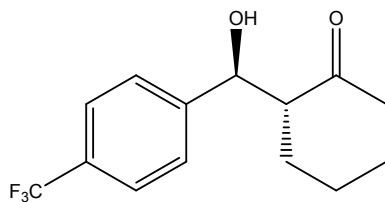


SAMPLE INFORMATION

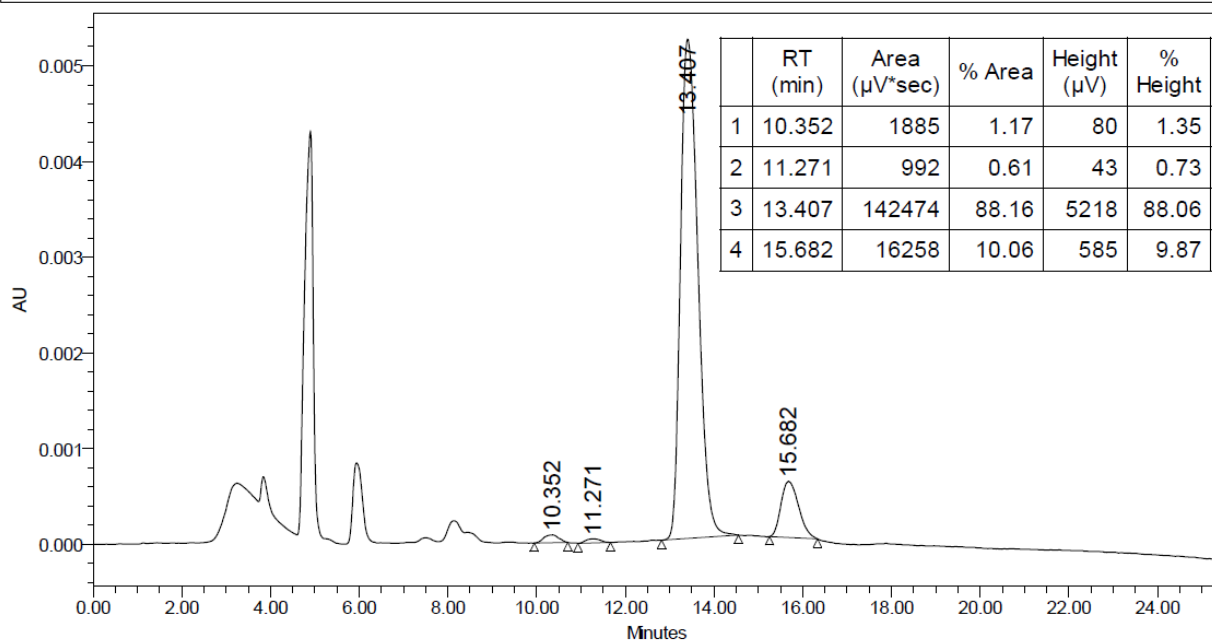
Sample Name:	4Br.Ben-Cyhex(P.H-16aa,aq)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	10/12/2012 3:29:47 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	4	Date Processed:	10/15/2012 2:48:10 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	17.00 Minutes	Sample Set Name:	



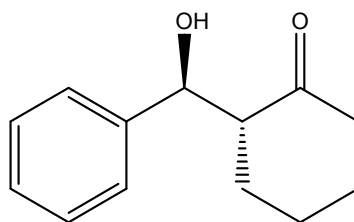
2-8 (R)-2-((S)-4-(trifluoromethyl)phenyl)(hydroxy)methyl)cyclohexanone



SAMPLE INFORMATION					
Sample Name:	4-CF3Benz+Cyhex(P.H-16aa,aq)	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	9/13/2012 1:18:26 PM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	7	Date Processed:	9/13/2012 2:17:05 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA		
Run Time:	50.00 Minutes	Sample Set Name:			

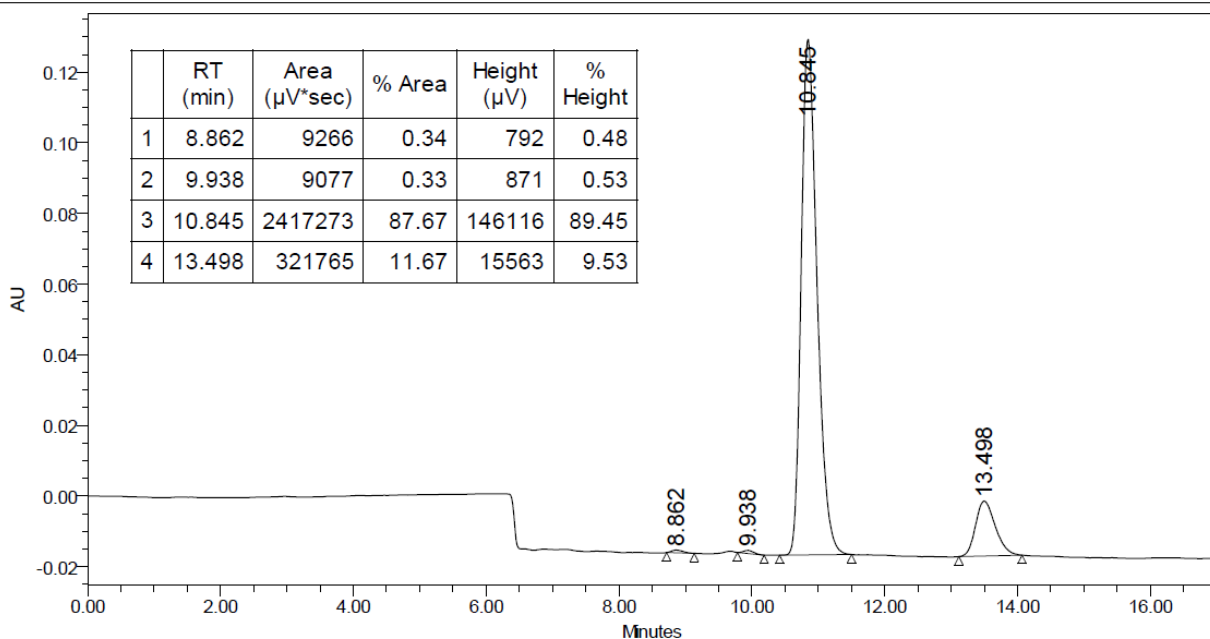


2-9 (R)-2-((S)-hydroxy(phenyl)methyl)cyclohexanone

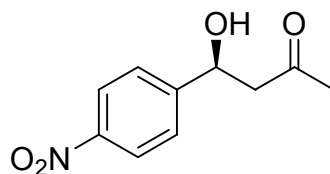


SAMPLE INFORMATION

Sample Name:	Benz+Cyhex(P.H-16aa)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	10/18/2012 12:20:42 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	4	Date Processed:	10/18/2012 1:10:34 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	17.00 Minutes	Sample Set Name:	

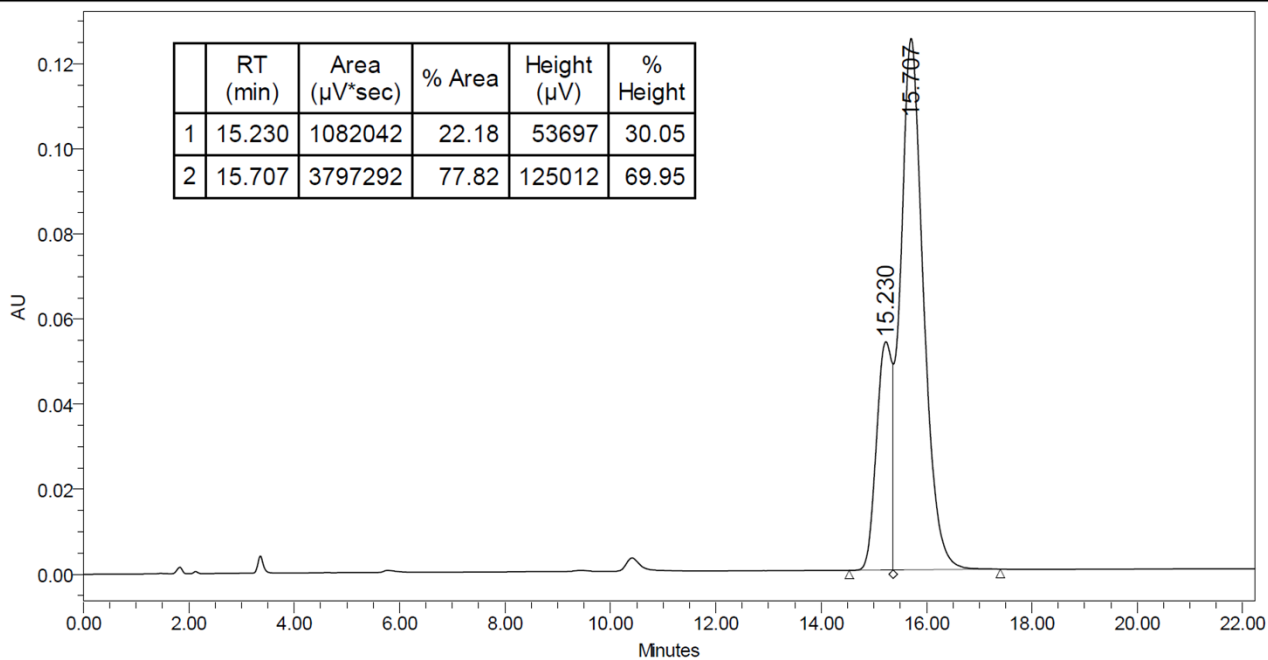


2-10 (S)-4-hydroxy-4-(4-nitrophenyl)butan-2-one

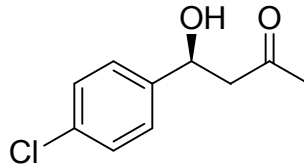


SAMPLE INFORMATION

Sample Name:	4NitroBen+acetone (PH16aa)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	4/15/2013 10:12:28 AM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	1	Date Processed:	4/15/2013 11:43:59 AM MYT
Injection Volume:	0.00 ul	Channel Name:	W2489 ChA
Run Time:	60.00 Minutes	Sample Set Name:	

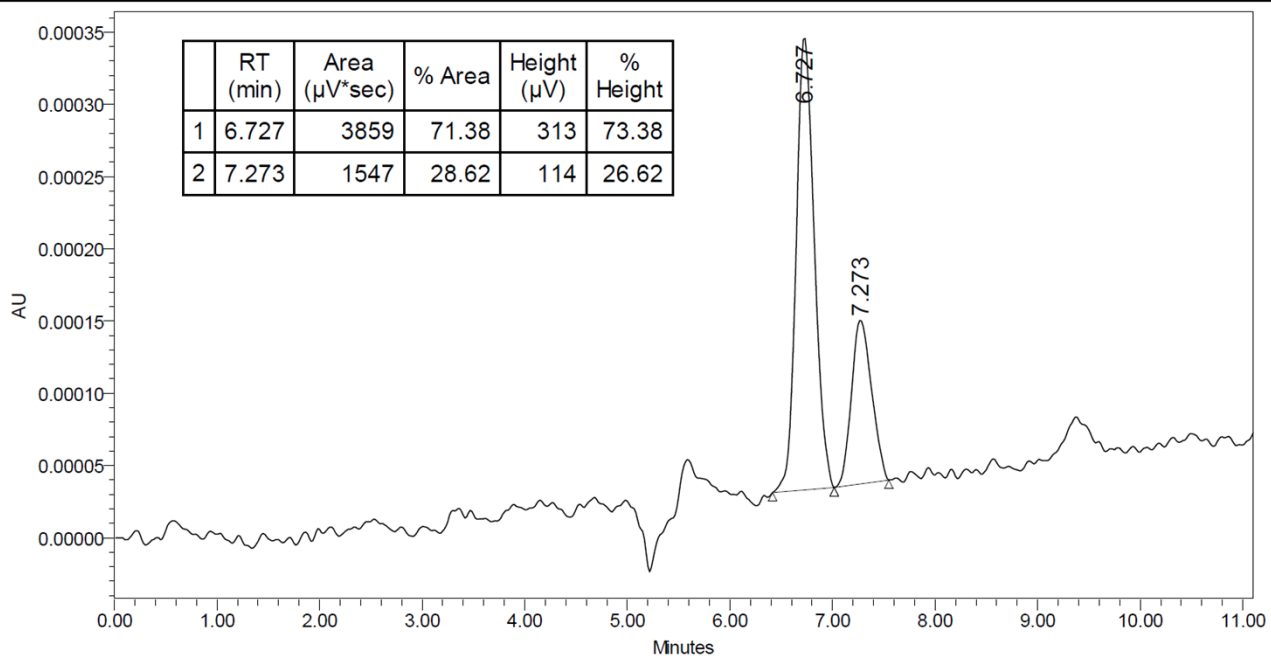


2-11 (S)-4-(4-chlorophenyl)-4-hydroxybutan-2-one

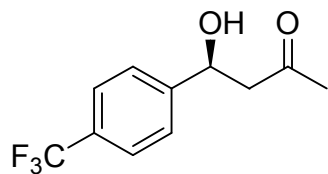


SAMPLE INFORMATION

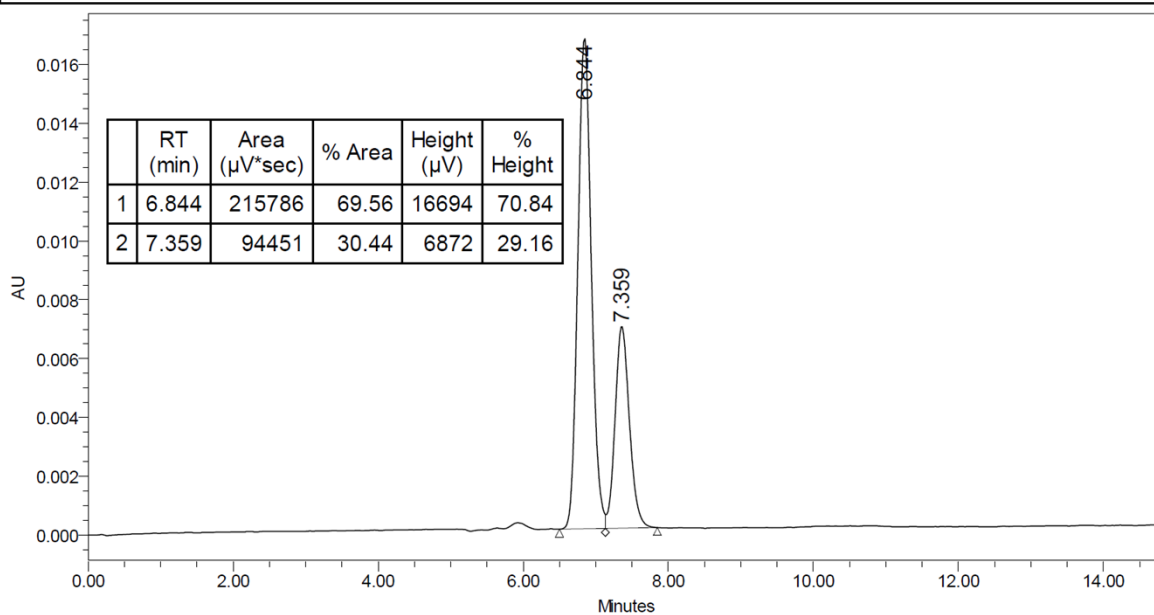
Sample Name:	4ClBen+acetone (PH16aa)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	4/15/2013 1:20:30 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	10	Date Processed:	4/15/2013 1:36:36 PM MYT
Injection Volume:	0.00 ul	Channel Name:	W2489 ChB
Run Time:	60.00 Minutes	Sample Set Name:	



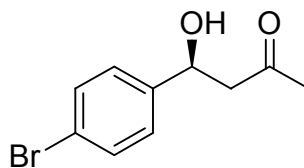
2-12 (S)-4-(4-(trifluoromethyl)phenyl)-4-hydroxybutan-2-one



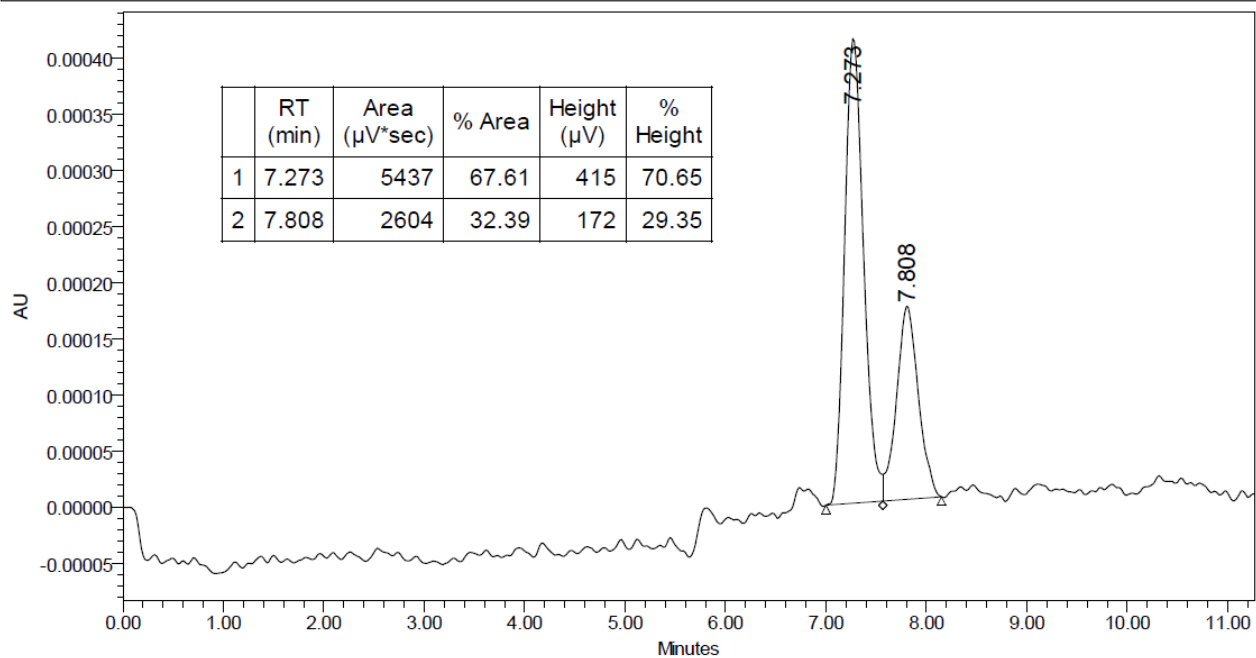
SAMPLE INFORMATION					
Sample Name:	4CF3Ben+acetone	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	4/15/2013 10:57:19 AM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	3	Date Processed:	4/15/2013 11:44:37 AM MYT		
Injection Volume:	0.00 ul	Channel Name:	W2489 ChB		
Run Time:	60.00 Minutes	Sample Set Name:			



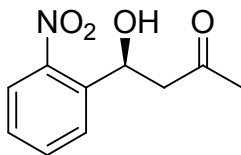
2-13 (S)-4-(4-bromophenyl)-4-hydroxybutan-2-one



SAMPLE INFORMATION					
Sample Name:	4BrBen+acetone (PH16aa)	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	4/15/2013 3:18:22 PM MYT		
Vial:	1	Acq. Method:	Saadi		
Injection #:	15	Date Processed:	4/15/2013 3:31:52 PM MYT		
Injection Volume:	0.00 ul	Channel Name:	W2489 ChB		
Run Time:	60.00 Minutes	Sample Set Name:			

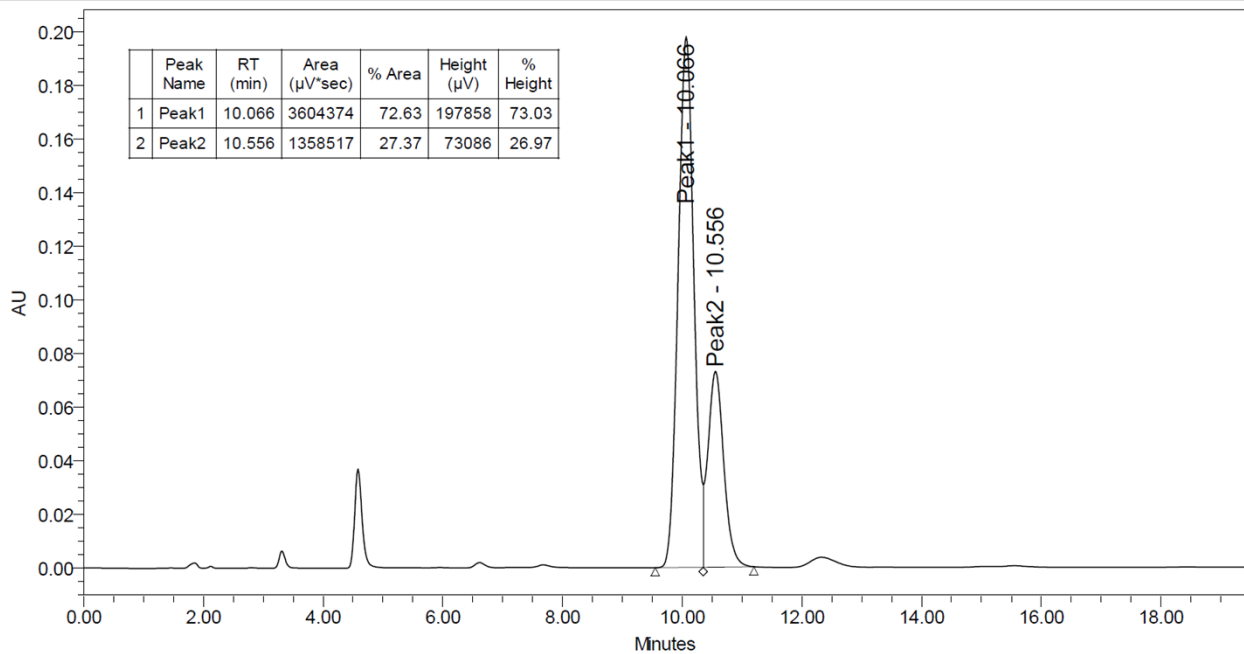


2-14 (S)-4-hydroxy-4-(2-nitrophenyl)butan-2-one



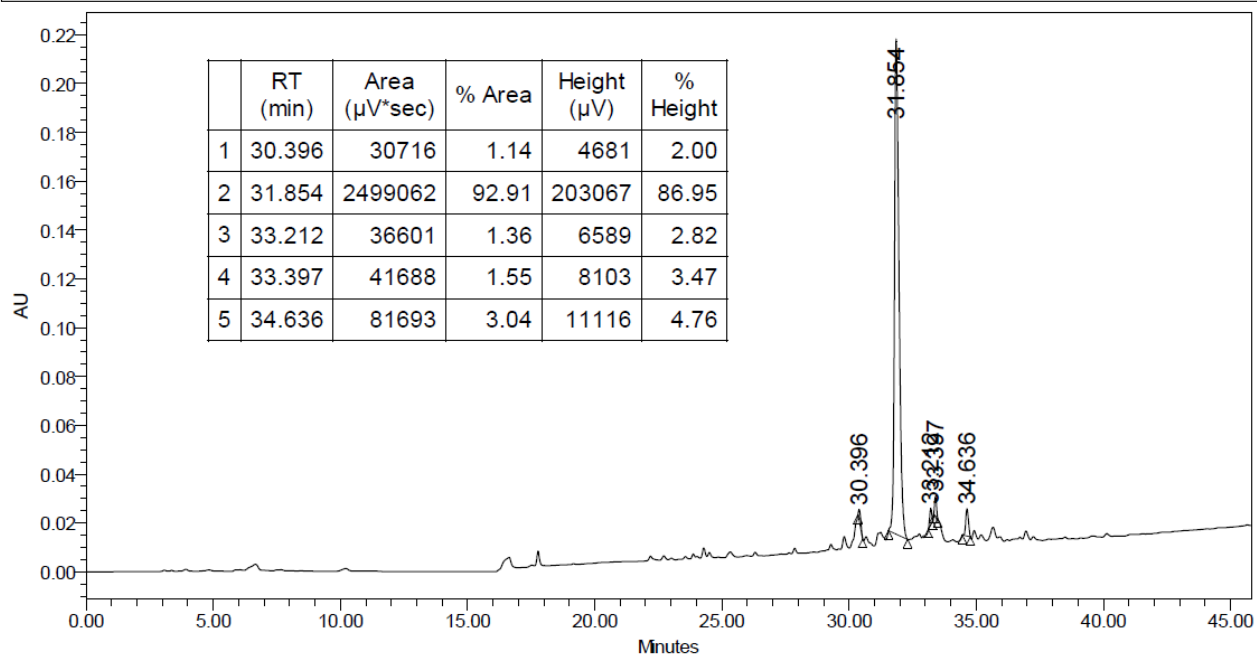
SAMPLE INFORMATION

Sample Name:	2NitroBen+acetone (PH16aa)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	4/15/2013 11:12:45 AM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	4	Date Processed:	4/15/2013 11:46:57 AM MYT
Injection Volume:	0.00 ul	Channel Name:	W2489 ChA
Run Time:	60.00 Minutes	Sample Set Name:	

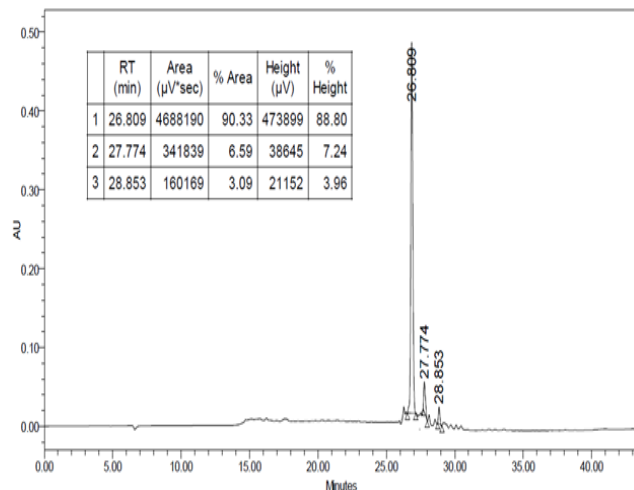
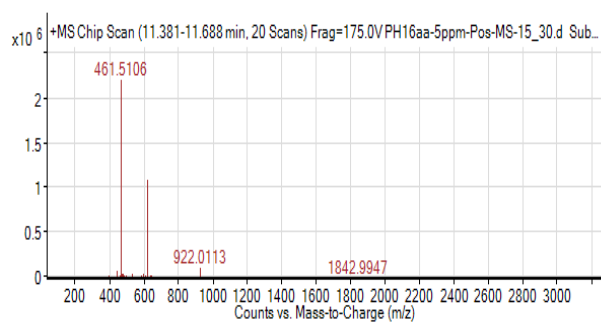
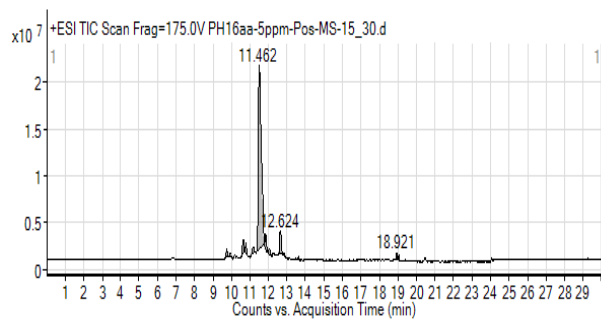


➤ HPLC of peptide (PH16aa)

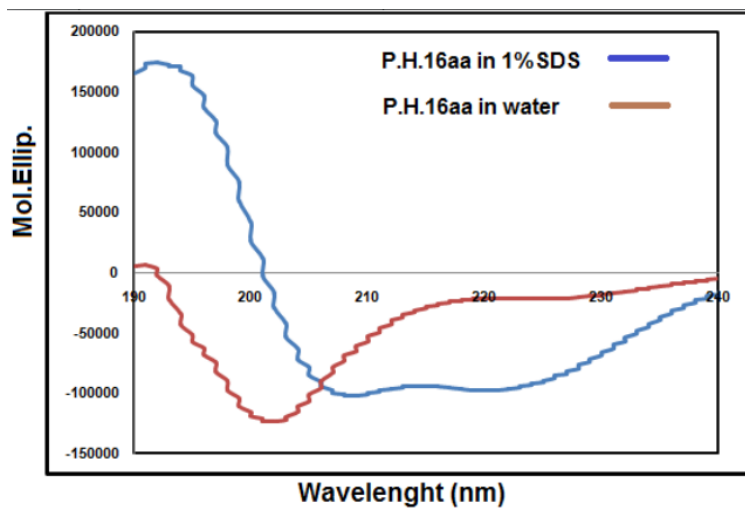
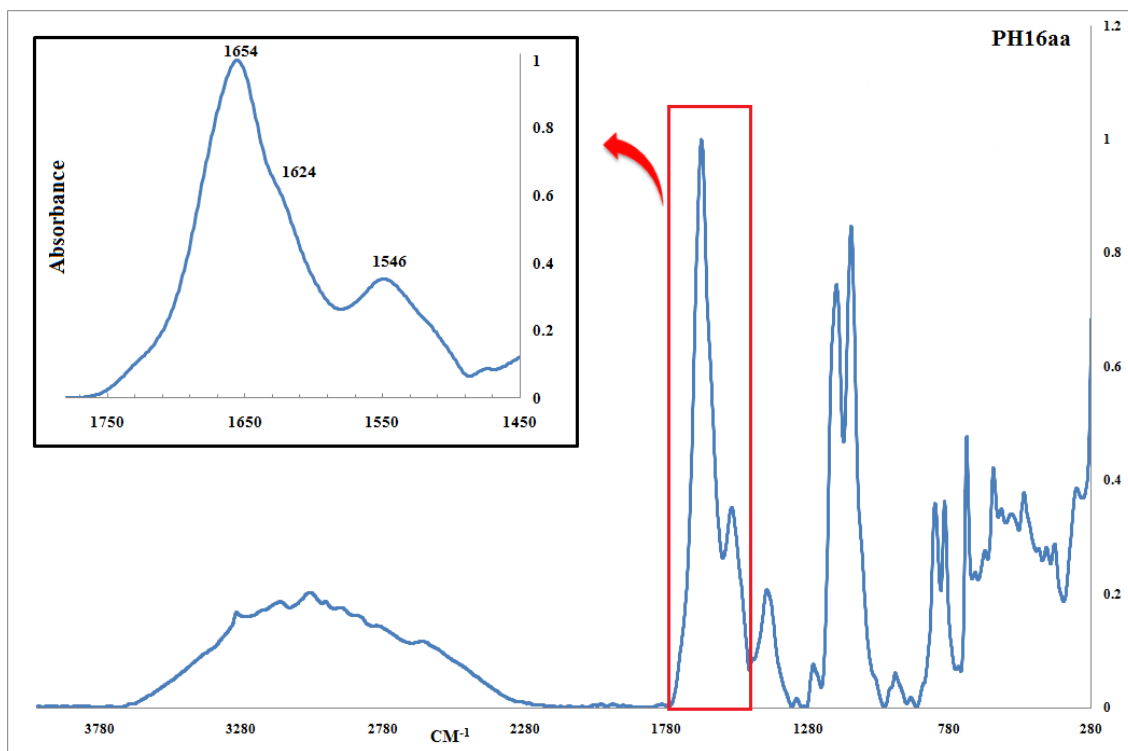
SAMPLE INFORMATION					
Sample Name:	P-H-16aa (0.5mmol/gr resin)	Acquired By:	Breeze		
Sample Type:	Unknown	Date Acquired:	9/10/2012 4:03:07 PM MYT		
Vial:	1	Acq. Method:	Saadi RP		
Injection #:	4	Date Processed:	9/18/2012 12:39:52 PM MYT		
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB		
Run Time:	70.00 Minutes	Sample Set Name:			



➤ LC-Mass spectra of PH16aa



➤ FT-IR and CD spectrum of PH16aa



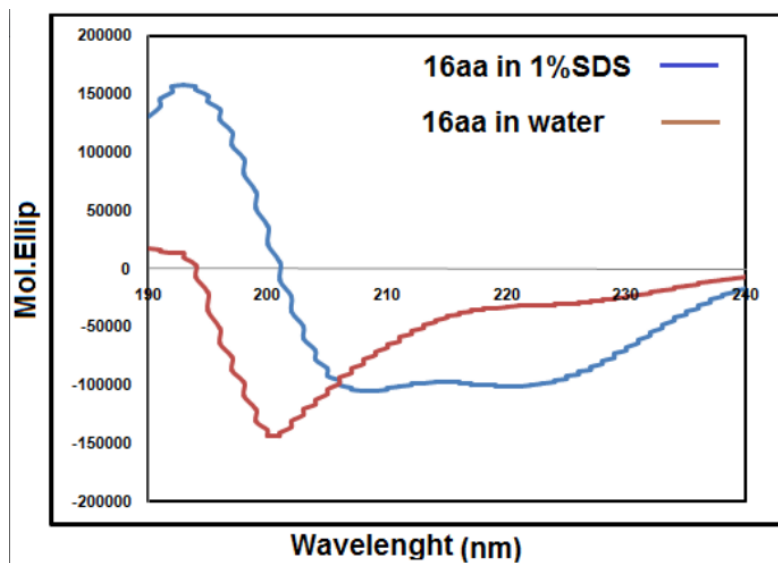
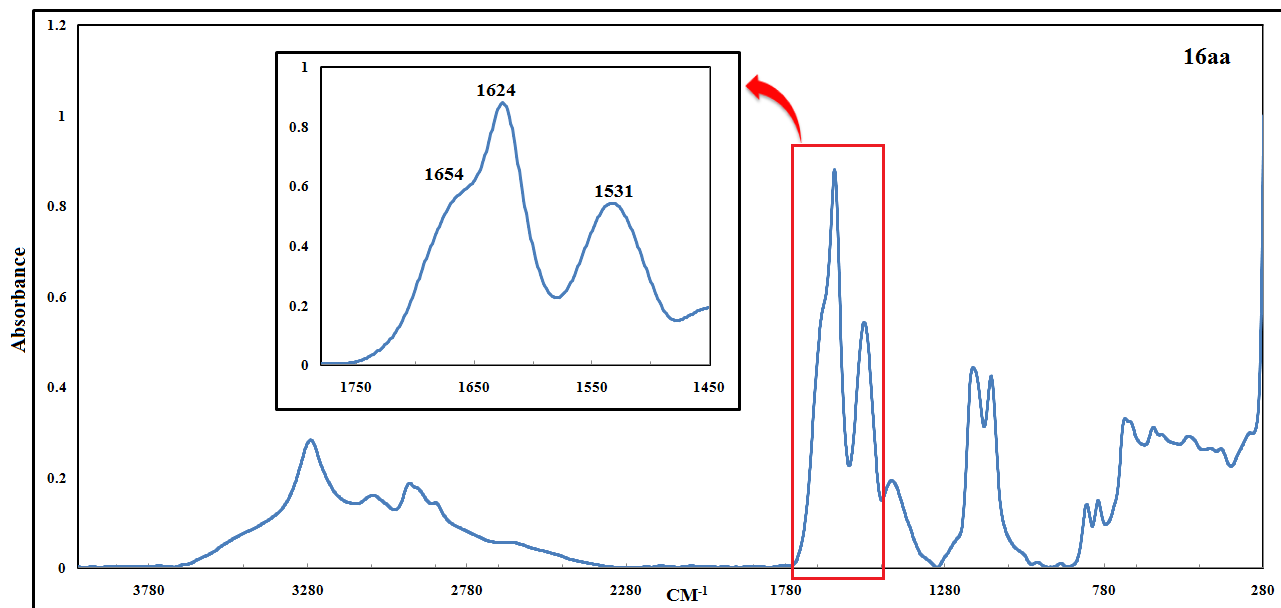
CD spectra in SDS (1%)

- Helix (%): 38.0
- Beta (%): 12.3
- Turn (%): 12.5
- Random (%): 31.6

CD spectra in water

- Helix (%): 15.2
- Beta (%): 28.1
- Turn (%): 12.5
- Random (%): 39.7

➤ FT-IR and CD spectrum of 16aa



CD spectra in 1% SDS

{	Helix (%)	: 34.1
{	Beta (%)	: 13.8
{	Turn (%)	: 12.5
{	Random (%)	: 32.7
{	-----	
{	Sum (%)	: 93.2

CD spectra in water

{	Helix (%)	: 18.5
{	Beta (%)	: 29.5
{	Turn (%)	: 12.5
{	Random (%)	: 38.5
{	-----	
{	Sum (%)	: 99.0

➤ **Characterization of PE16aa**

- **HPLC of PE16aa**

UPM

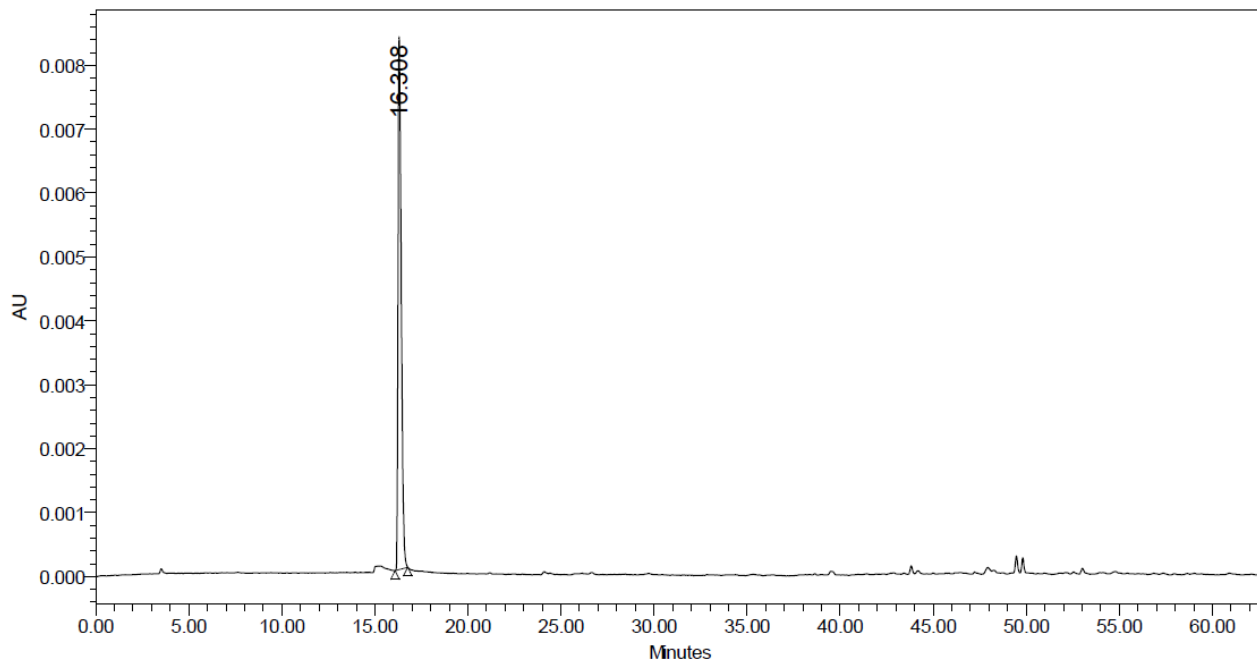
Project Name: Saadi RP.

Reported by User: Breeze user (Breeze)



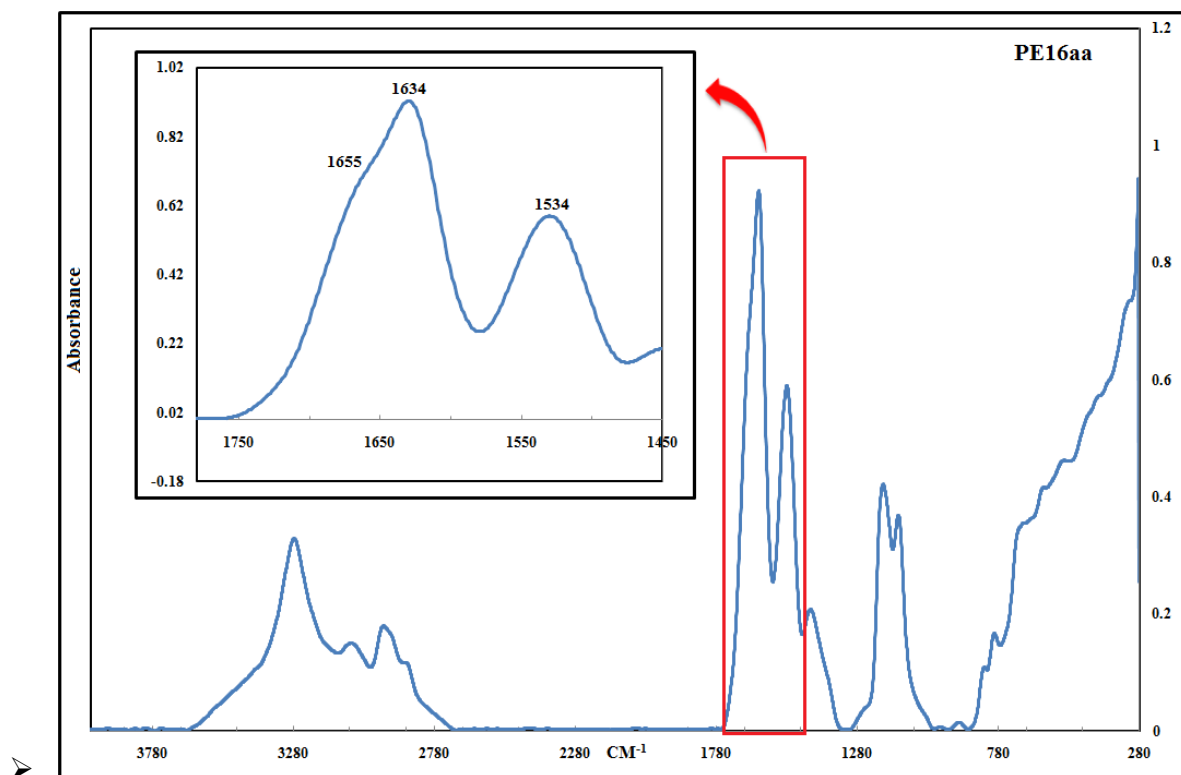
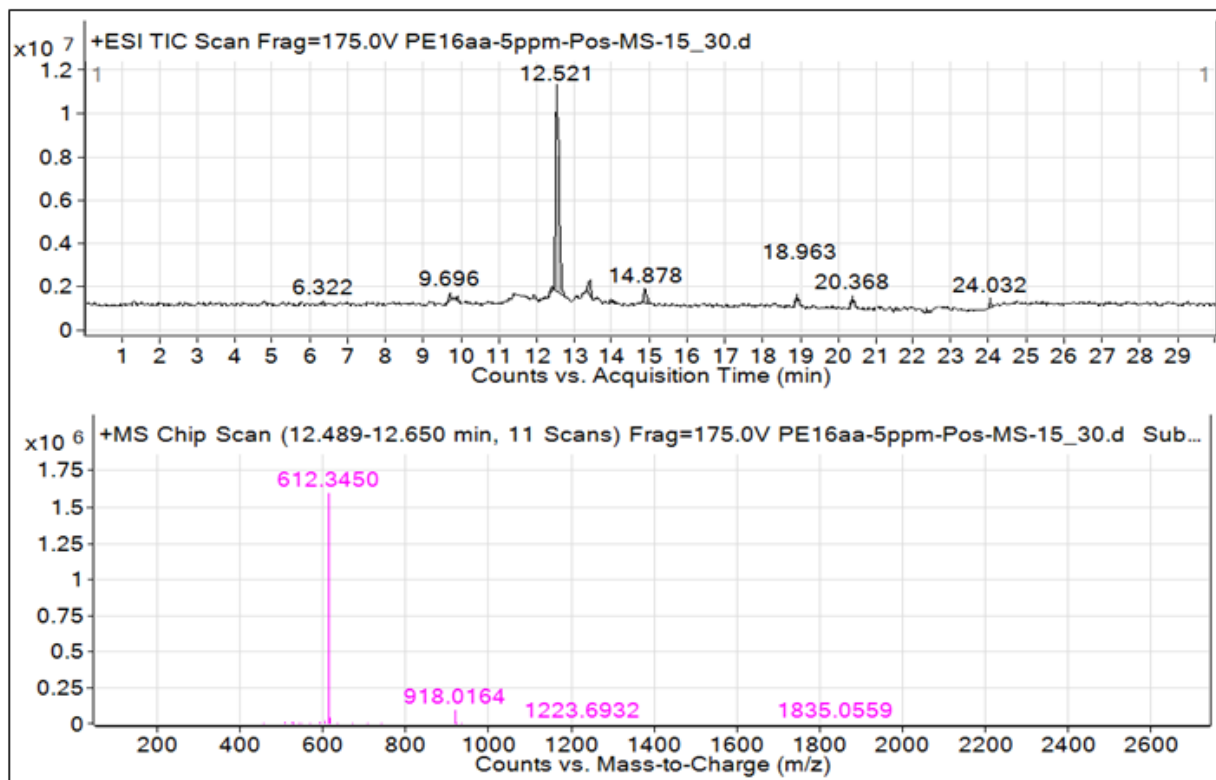
SAMPLE INFORMATION

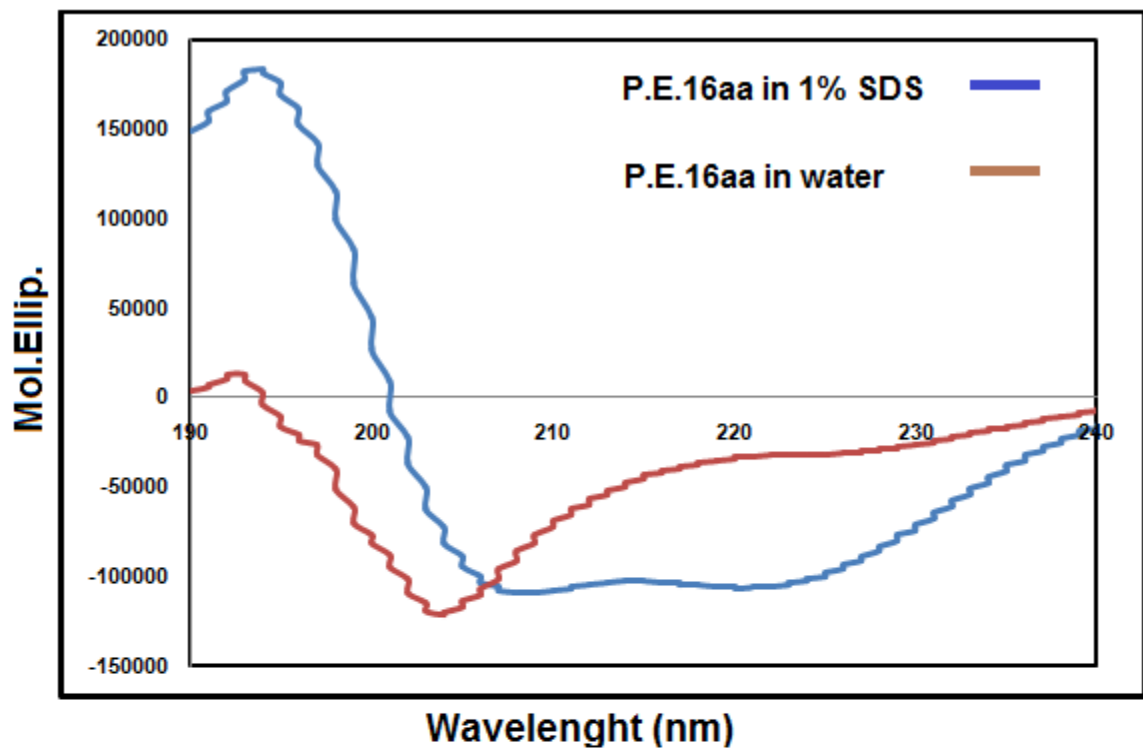
Sample Name:	Pro-Glu-16AA. HPLC	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	7/5/2012 4:28:55 PM MYT
Vial:	1	Acq. Method:	Saadi RP
Injection #:	2	Date Processed:	9/18/2012 12:28:44 PM MYT
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	90.00 Minutes	Sample Set Name:	



	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.308	100019	100.00	8391	100.00

- Spectroscopics data of PE-16aa



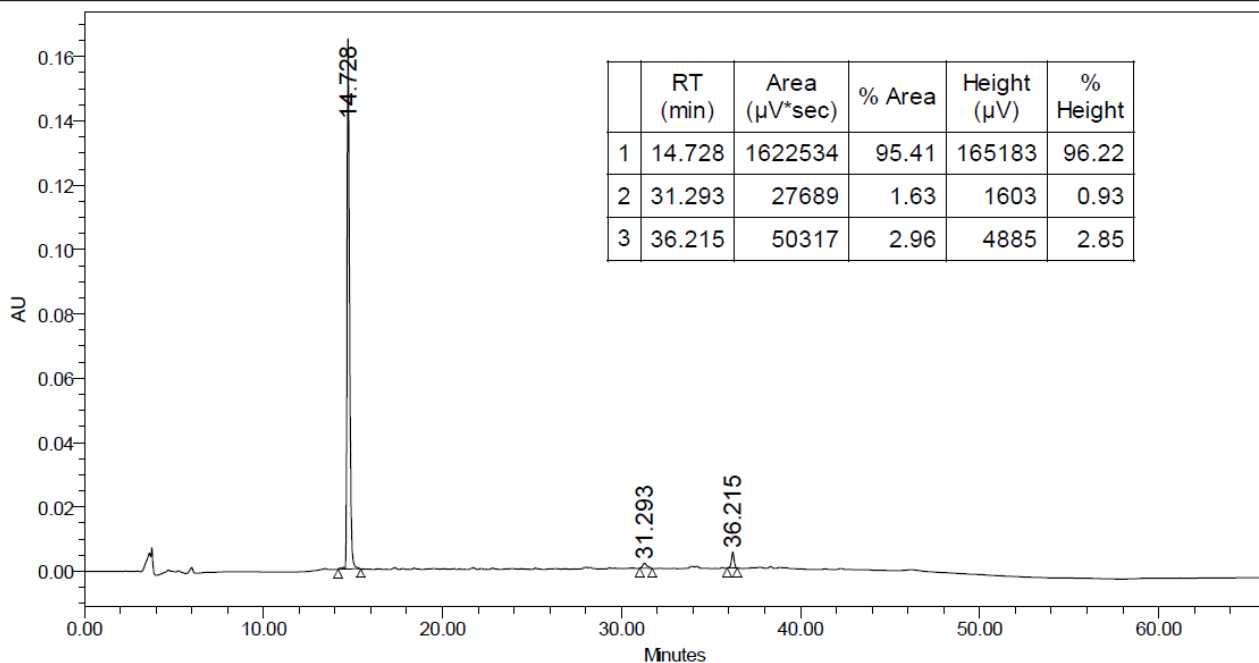


CD spectra in 1% SDS	{	Helix (%):	36.5
		Beta (%):	11.5
		Turn (%):	12.5
		Random (%):	32.1
CD spectra in water	{	Helix (%):	19.1
		Beta (%):	22.9
		Turn (%):	12.5
		Random (%):	38.6

➤ HPLC analysis of 5aa

SAMPLE INFORMATION

Sample Name:	PELFV.NH2	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	2/6/2013 2:44:03 PM MYT
Vial:	1	Acq. Method:	Saadi
Injection #:	2	Date Processed:	2/7/2013 1:27:59 PM MYT
Injection Volume:	20.00 ul	Channel Name:	W2489 ChA
Run Time:	66.00 Minutes	Sample Set Name:	



➤ HPLC analysis of 8aa(z)

UPM

Project Name: Saadi
Reported by User: Breeze user (Breeze)



SAMPLE INFORMATION

Sample Name:	8aa (Lys-Z)	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	2/5/2013 4:58:26 PM MYT
Vial:	1	Acq. Method:	Test
Injection #:	18	Date Processed:	2/5/2013 5:18:08 PM MYT
Injection Volume:	0.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Sample Set Name:	

