Supplementary Information

Guerbet upgrading of ethanol to n-butanol using Ru(III) catalysts under air

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1. General Information

Materials

Organic precursors, reagents and solvents (including deuterated solvents for NMR analysis) used in various stages of the experiments were obtained from Sigma Aldrich and were used as received unless otherwise mentioned. $RuCl_3.3H_2O$ was also obtained from Sigma Aldrich and used without further purification. Ethanol (~ 99.5% assay) was obtained from CS chemicals, dried by refluxing over magnesium for overnight and stored over 3Å molecular sieves for three days before use.

Methods

^{1}H and ^{13}C NMR spectra of the ligands (L1-L3) were recorded AVH D 500 AVANCE III HD 500 MHz OneBay NMR Spectrometer. NMR chemical shifts are reported with respect to the standard TMS and referenced to the residual solvent peaks.

Elemental analysis (C, H, N) was carried out on a Thermo Scientific Flash 2000 Organic Elemental Analyzer under air free conditions.

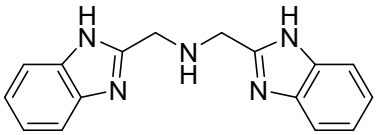
GC-MS spectra were recorded on a Shimadzu QP-2010 SE instrument equipped with an AOC-20i auto injector and a Rtx-5MS column (thickness = 0.25 µm, length = 30.0 m, diameter = 0.25 µm), Initial column oven temp = 50 °C, Injection temp = 250 °C, Column flow = 1.19 mL/min, split ratio 10:1, Temperature program: 1 min at 50 °C, then increase at 5 °C/min to 200 °C and hold for 1 min, then increase at 15 °C/min to 260 °C and hold for 5 min.

GC chromatograms were recorded on a Mayura Analytical Gas Chromatograph instrument (Model 1100) equipped with an AB-InoWax column (thickness = 0.25 µm, length = 30.0 m, diameter = 0.25 µm), Initial column oven temperature = 40 ℃, Injection temperature 225 ℃, split ratio 10:1, pressure 10.5 psi, Temperature program: 20 min at 40 °C, then increase at 10 °C/min to 100 °C and hold for 15 min.

2. Synthesis of Ligands

The ligands used in this work were prepared by following the reported procedures[1] with some modifications as shown below and dully characterized.

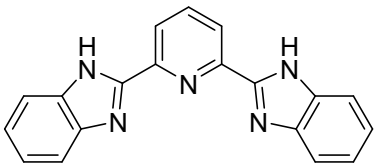
Bis((benzimidazol-2-yl)methyl)amine (L1)



L1

3.3 g of iminodiacetic acid and 5.4 g of 1,2-diaminobenzene were mixed in 50 ml of 18% HCl solution and the mixture was refluxed at 150 ^{o}C for three days. A green solid formed was dissolved in 200 ml of water and ammonia solution (25%) was slowly added upon stirring to adjust the pH of the solution to 9. A light brown solid formed was separated by filtration, washed thoroughly with water and recrystallized using methanol. An off-white solid obtained after charcoal treatment was dried under vacuum. Yield 82%; M.P. 247-250 ^{o}C; ^{1}H NMR (DMSO-d6, 500 MHz, 298 K, ppm) δ 7.53 (4H, m, CH_{ph}), 7.18 (4H, m, CH_{ph}), 4.11 (4H, s, CH_2); ^{13}C{^{1}H} NMR (DMSO-d6, 125 MHz, 298 K, ppm) δ 152.9, 138.7, 124.5, 114.7, 46.1; Analysis for $C_{16}H_{15}N_5$ Calcd (found) C 69.29 (69.12), H 5.45 (5.32), N 25.25 (25.82)%

2,6-bis(benzimidazol-2-yl)pyridine (L2)

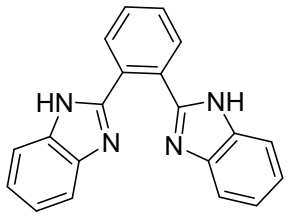


L2

3.0 g of dipicolinic acid and 3.88 g of 1,2-diaminobenzene were dissolved in 20 ml of 85% ortho phosphoric acid and heated for 4 hours at 220 ^{o}C with vigorous stirring. After

cooling to room temperature, the reaction mixture was slowly added into 100 ml of ice-cold water with constant stirring to obtain a blue precipitate, which was then separated by filtration and treated with 200 ml of hot aq. Na_2CO_3 solution. The blue precipitate obtained was dispersed in cold water and acidified with 10% HCl solution to adjust the pH to 4. The resulting white precipitate was collected, recrystallized with methanol and dried under vacuum. Yield 80%; M.P. > 300 ^oC; ^1H NMR (DMSO-d6, 500 MHz, 298 K, ppm) δ 13.01 (2H, s, N*H*), 8.35 (2H, d (J = 10 Hz), m-CH_{py}), 8.17 (1H, t (J = 10 Hz), p-CH_{py}), 7.76 (4H, b, CH_{ph}), 7.32 (4H, b, CH_{ph}); $^{13}C\{^1H\}$ NMR (DMSO-d6, 125 MHz, 298 K, ppm) δ 150.4, 147.7, 139.1, 121.3; Analysis for $C_{19}H_{13}N_5$ Calcd (found) C 73.30 (73.47), H 4.21 (4.38), N 22.49 (22.87)%

1,2-bis(benzimidazol-2-yl)benzene (L3)

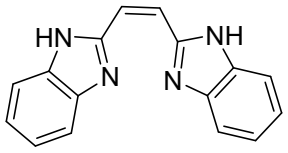


L3

Similar to L2, 3.0 g of phthalic anhydride and 4.32 g of 1,2-diaminobenzene were dissolved in 20 ml 85% ortho phosphoric acid and heated at 200 ^oC for one day. The dark blue colored reaction mixture was cooled and added to ice-cold water to obtain a sky-blue colored precipitate. To which 5M NaOH solution was added to get alkaline pH (~ 9), which changes the color of the precipitate to colorless. The solid was collected by filtration, washed with water, recrystallized using methanol and dried under vacuum. Yield 85%; M.P. > 300 ^oC; ^1H NMR ($CDCl_3$, 500 MHz, 298 K, ppm) δ 12.5 (2H, s, N*H*), 7.90 (1H, d (J = 10Hz), CH_{ph}), 7.82 (2H, d (J = 10 Hz), CH_{ph}), 7.62 – 7.58 (4H, b, CH_{ph}),

7.28 – 7.24 (4H, b, CH_{ph}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K, ppm) δ 151.4, 138.1, 133.6, 132.0, 129.6, 123.8, 116.0; Analysis for $C_{20}H_{14}N_4$ Calcd (found) C 77.40 (77.68), H 4.55 (4.38), N 18.05 (18.36)%

1.3-bis(benzimidazol-2-yl)ethene (L4)



L4

Similar to L3, 3.0 g of maleic anhydride and 4.7 g of 1,2-diaminobenzene were dissolved in 20 ml of 85% orthophosphoric acid and heated at 200 C for one day. After cooling, the mixture was added to ice water and neutralized using 5M NaOH until the pH of solution turns basic (pH~9). The yellow precipitate formed was separated by filtration, washed with water, recrystallized with methanol and dried under vacuum. Yield 80%; M.P. 280-283 ^{o}C;

^{1}H NMR (DMSO-d_6, 500 MHz, 298 K, ppm) δ 12.32 (2H, s, N*H*), 7.68 – 7.62 (4H, b, CH_{ph}), 7.32 – 7.28 (4H, b, CH_{ph}), 6.85 (2H, b, *H*C=C*H*); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 298 K, ppm) δ 151.2, 142.7, 140.0, 123.7, 118.6; Analysis for $C_{20}H_{12}N_2O_2$ Calcd (found) C 73.83 (74.12), H 4.65 (4.78), N 21.52 (21.78)%

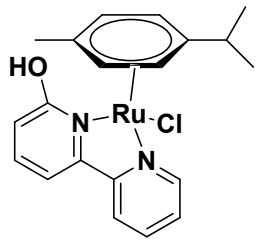
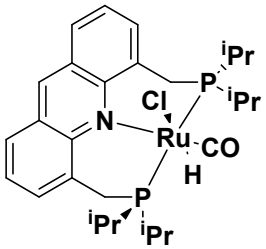
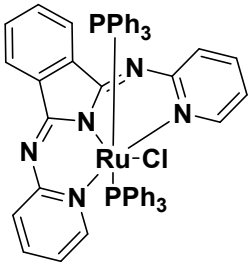
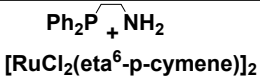
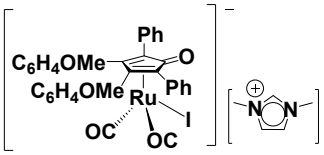
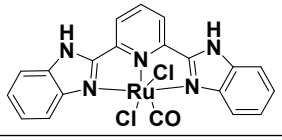
3. **General procedure for catalytic reaction**

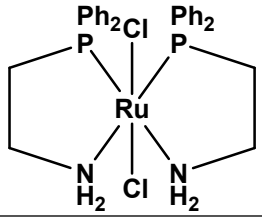
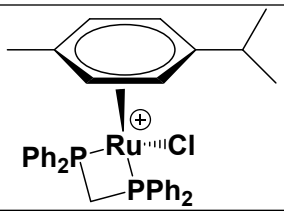
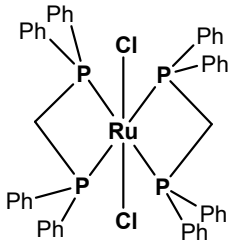
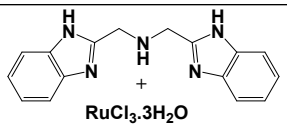
In a typical catalytic reaction, an oven-dried Schlenk bomb (5mL capacity) equipped with a large bore Teflon plug valve was loaded with ligand (0.1 mol %) and $RuCl_3.3H_2O$ (0.1 mol%) under air. Dry ethanol (0.4 mL, 6.85 mmol) was added to this mixture via a

syringe and the resulting mixture was stirred for 0.5h. A base (10 mole%) was then added to the mixture and the sealed Schlenk bomb was placed in an oil bath set at 150 ^{o}C for a specified period of time. After the reaction, the Schlenk bomb was allowed to cool to room temperature and then kept in an ice-water bath for 10 min. Gases were released into the fume hood by cautiously opening the valve. The catalytic mixture was added with 8 mL of diethyl ether, filtered through a short plug of Celite and analyzed using GC/GCMS.

Note: Explosion hazard! The catalytic reactions are carried at high temperature (150 ^{o}C) and could produce large amount of gases. These reactions must be carried out in an isolated, closed hood. Use of protective barriers i.e., shields, barricades, and guards is highly recommended.

4. Catalytic data of the other ruthenium-based catalysts from the literature

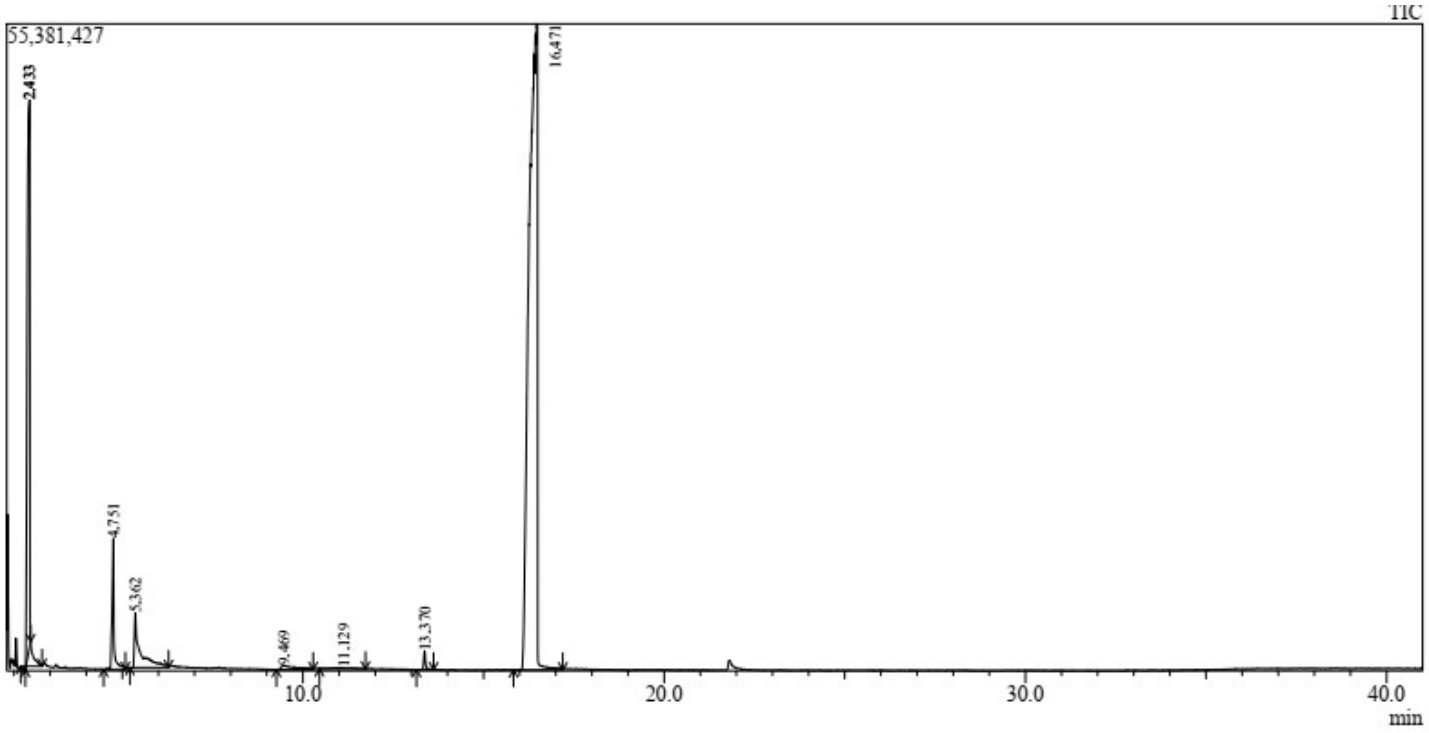
Sl. No	Catalyst	Reaction Condition	Butanol (%)	Selectivity (%)	Higher Alcohol (%)	Ref.
1		Temp: 80 °C Time:18 h Base: KOtBu, 60 mol% [Catalyst] – 2 mol% Water: Ethanol -84:16	28	57	10	2
2		Temp: 150 °C Time: 16 h Base: EtONa, 20 mol% [Catalyst] – 0.02 mol%	35.8	60.3	37.6	3
3		Temp: 150 °C Time: 2 h Base: NaOEt, 5 mol% [Catalyst] – 0.1 mol%	38	84	11	4
4		Temp: 150 °C Time: 4 h Base: EtONa, 5 mol% [Ru] – 0.1 mol% [Ligand] - 0.1 mol%	21.9	91.1	3.1	5
5		Temp: 150 °C Time 8 h Base: NaOEt, 40 mol% [Catalyst] – 0.2 mol% Co-Catalyst – Benzoquinone – 1.5mol%	39	44.3	46	6
6		Temp 110 °C, M.W -75W Time – 2 h Base - KO^{t}Bu, 10 mol % [Catalyst] – 0.025 mol%	34	74		7

7		Temp: 150 °C Time – 20 h Base - NaOEt, 5mol % [Catalyst] – 0.1 mol%	17	94	1.5	8
8		Temp: 150 °C Time – 20 h Base - NaOEt, 5 mol % [Catalyst] – 0.1 mol%	20	91	2.8	8
9		Temp: 150 °C Time – 20 h Base - NaOEt, 5 mol % [Catalyst] – 0.1 mol%	9.6	94	1.9	8
10		Temp: 150°C Time – 24 h Base - K^{t}OBu, 10 mol % [Catalyst] – 0.1mol%	28		12	This Work

5. **Selected GC analysis data**

Shimadzu QP-2010 SE instrument with Rtx-5MS column	
Average retention time	**Compound**
2.4	n-butanol
4.8	2-ethyl butanol
5.2	1-hexanol
9.82	2-ethyl-4-methyl-1-pentanol
10.2	1-octanol
13.3	impurity from tridecane
16.3	tridecane (standard)

Entry 1, Table 1



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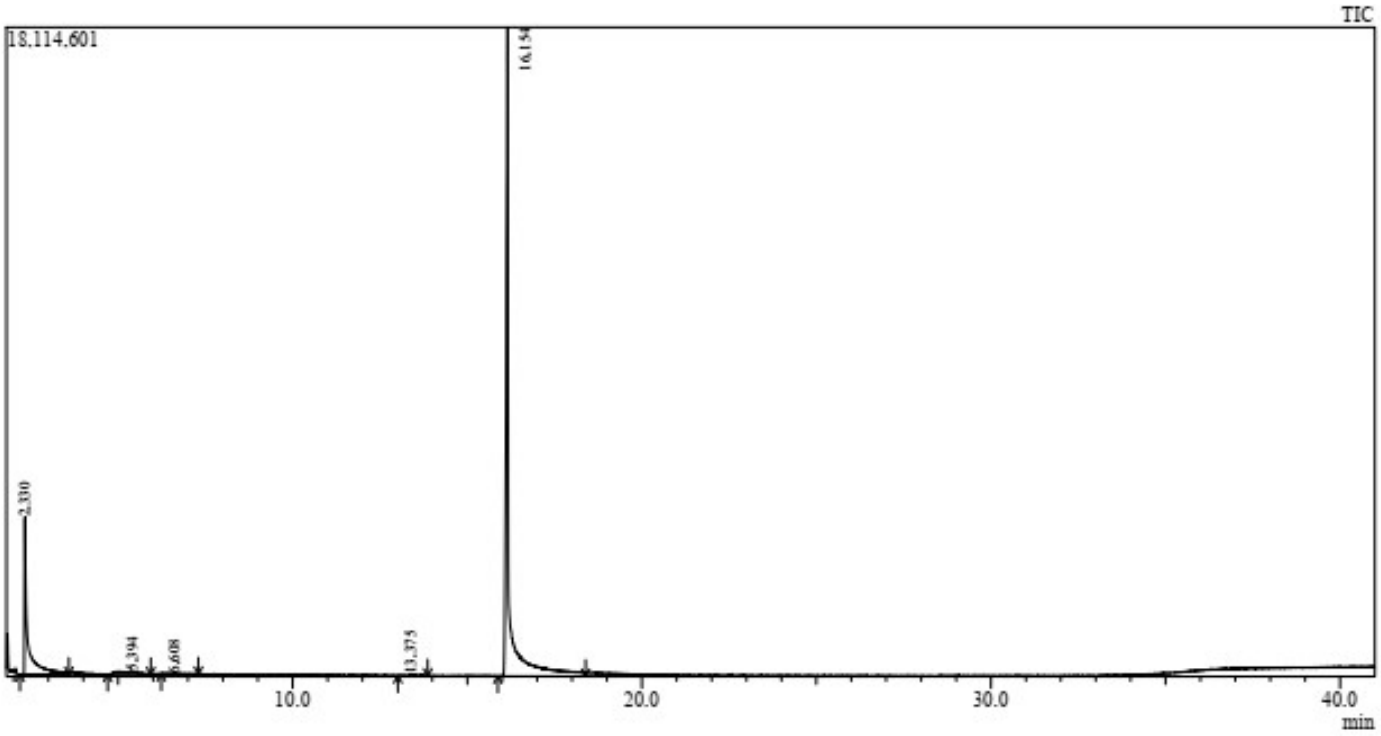

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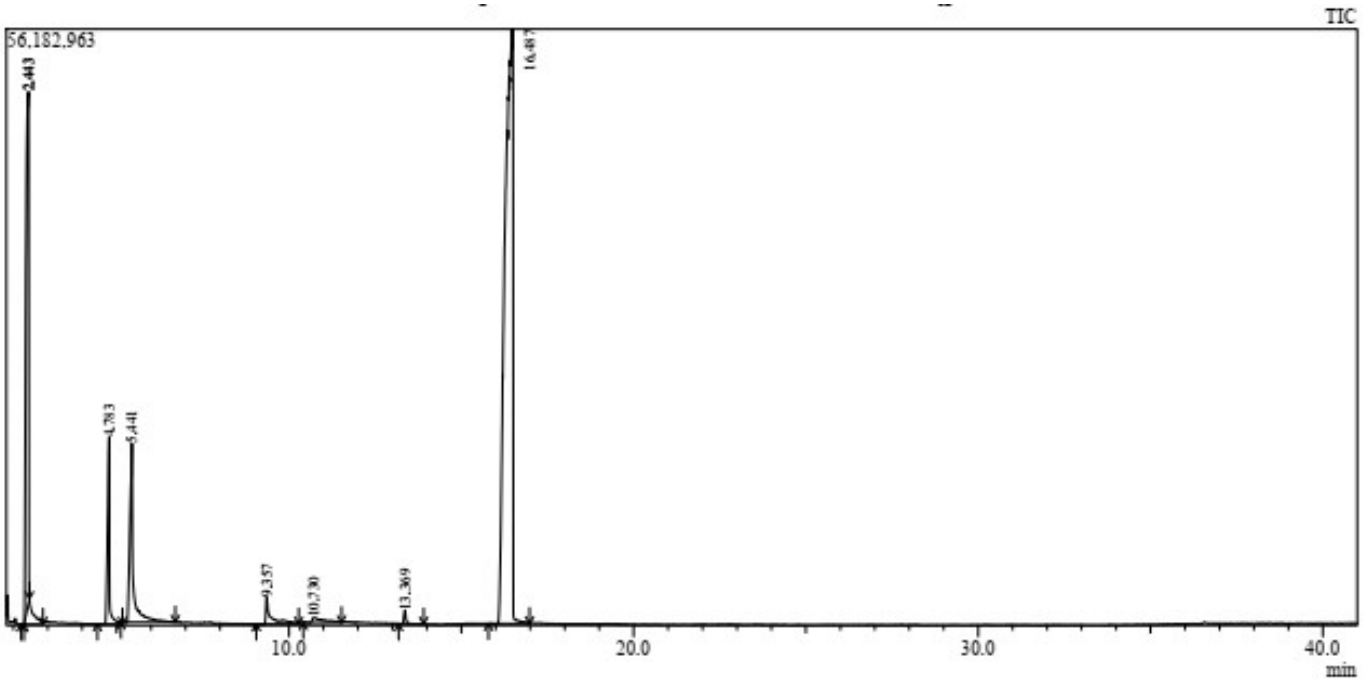
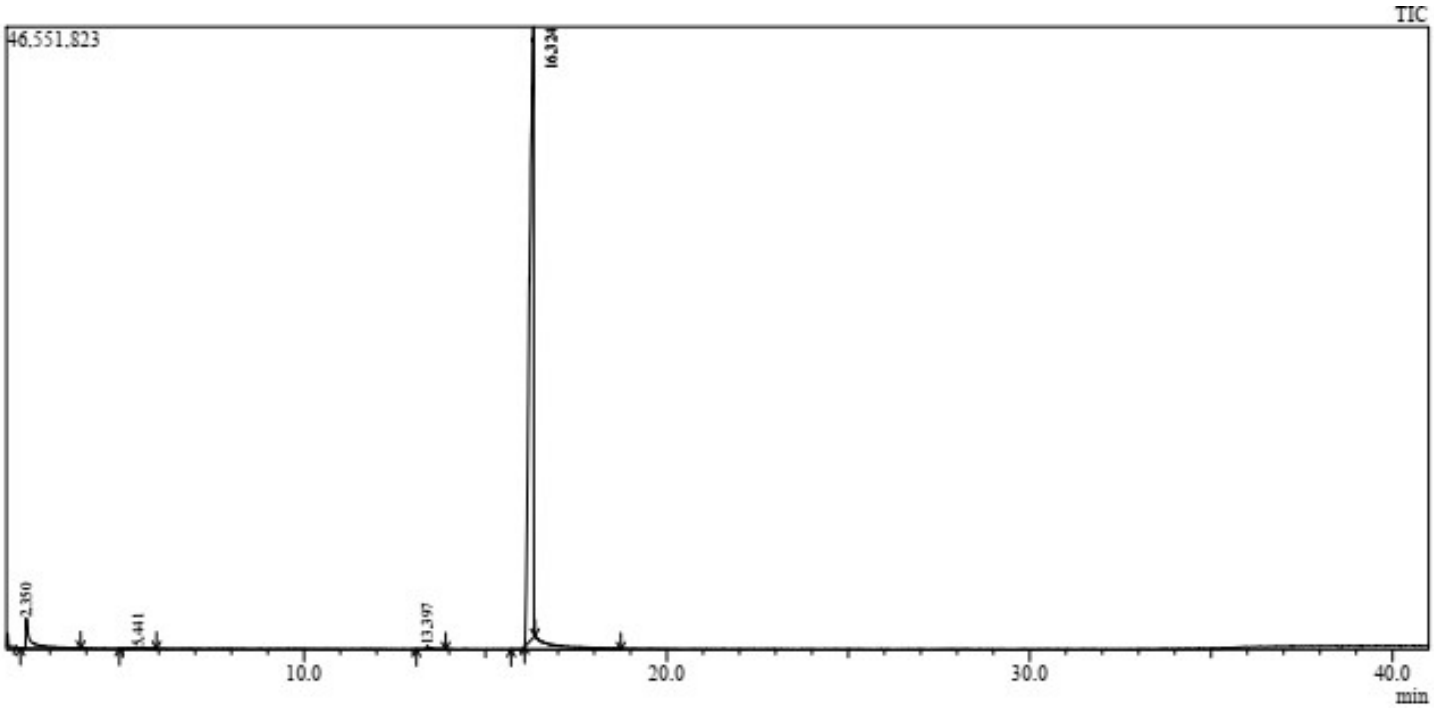


Entry 5, Table 1



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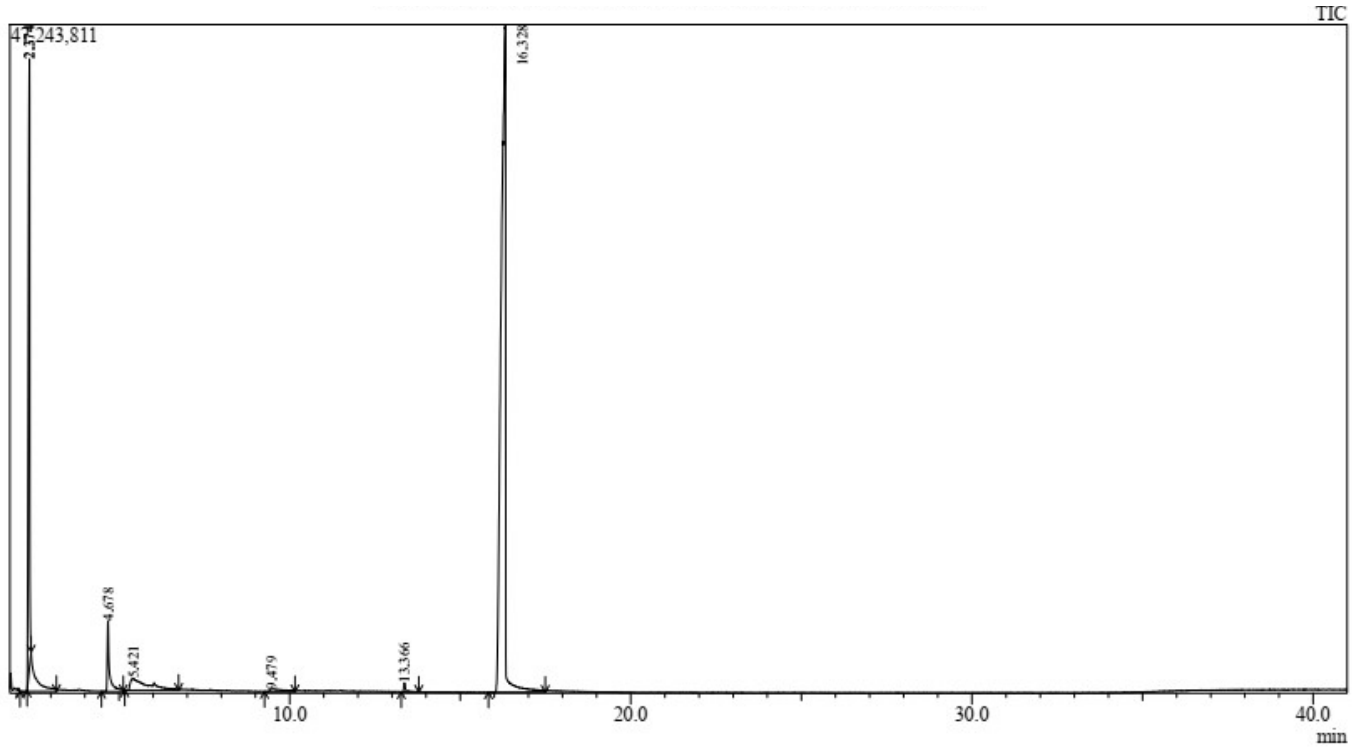

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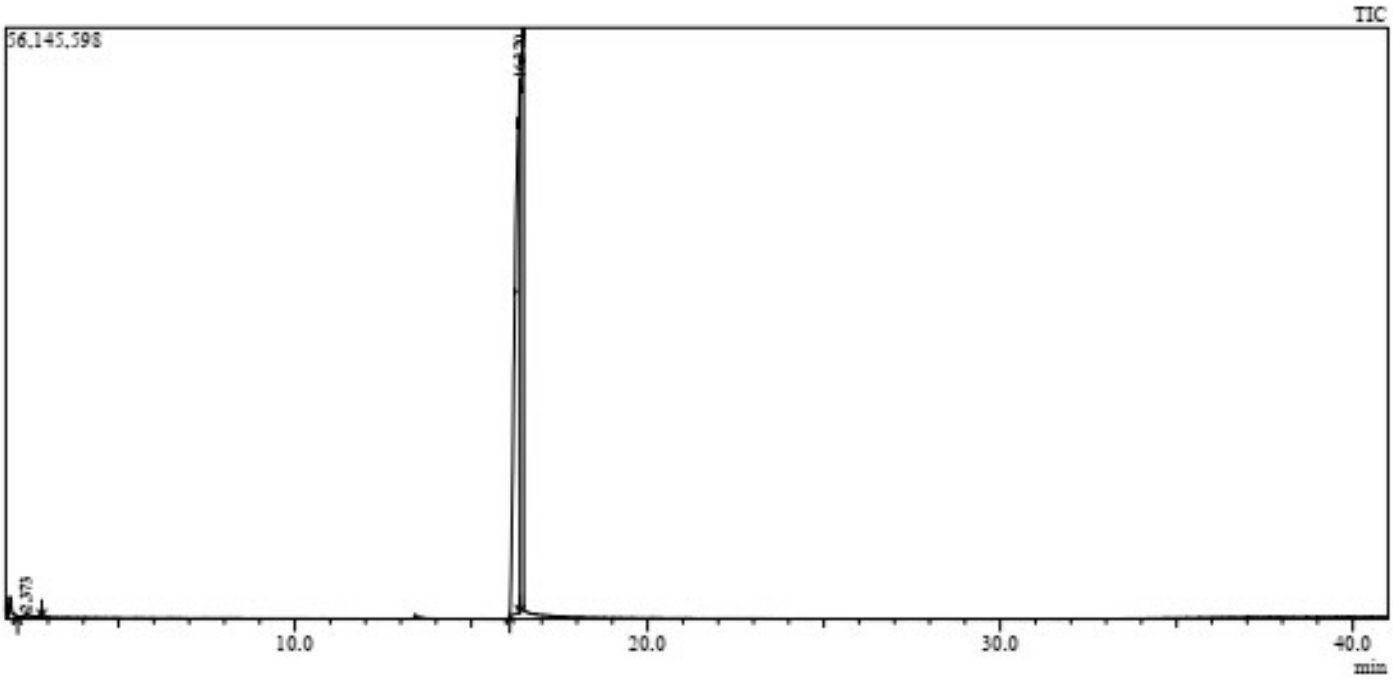

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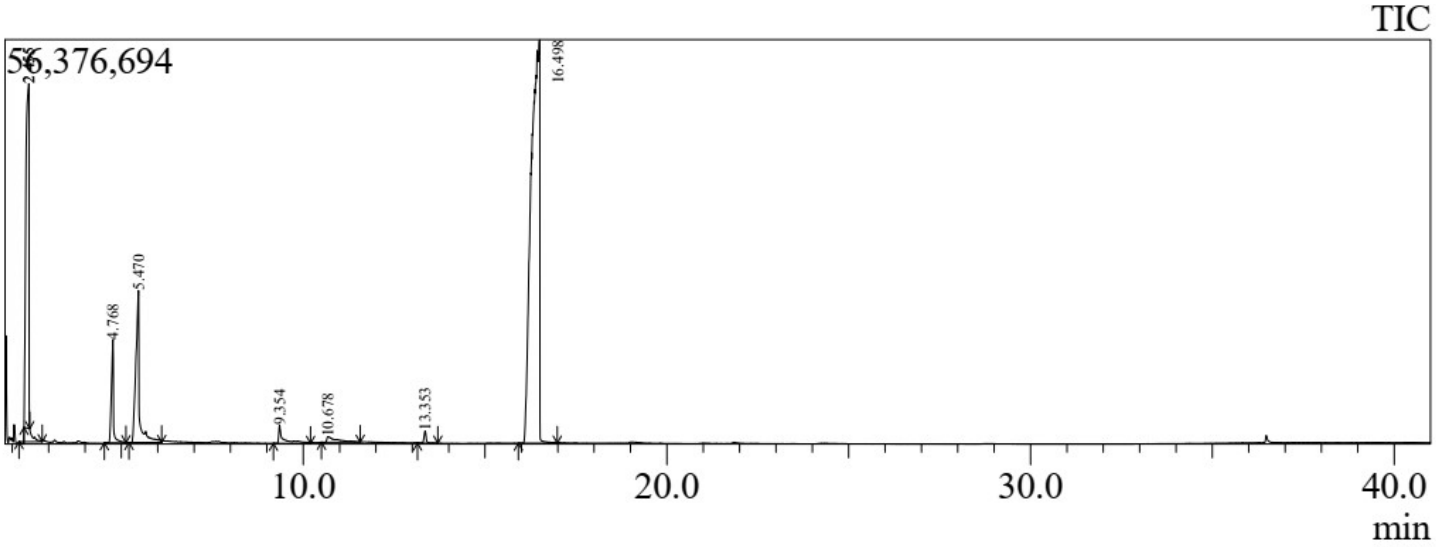

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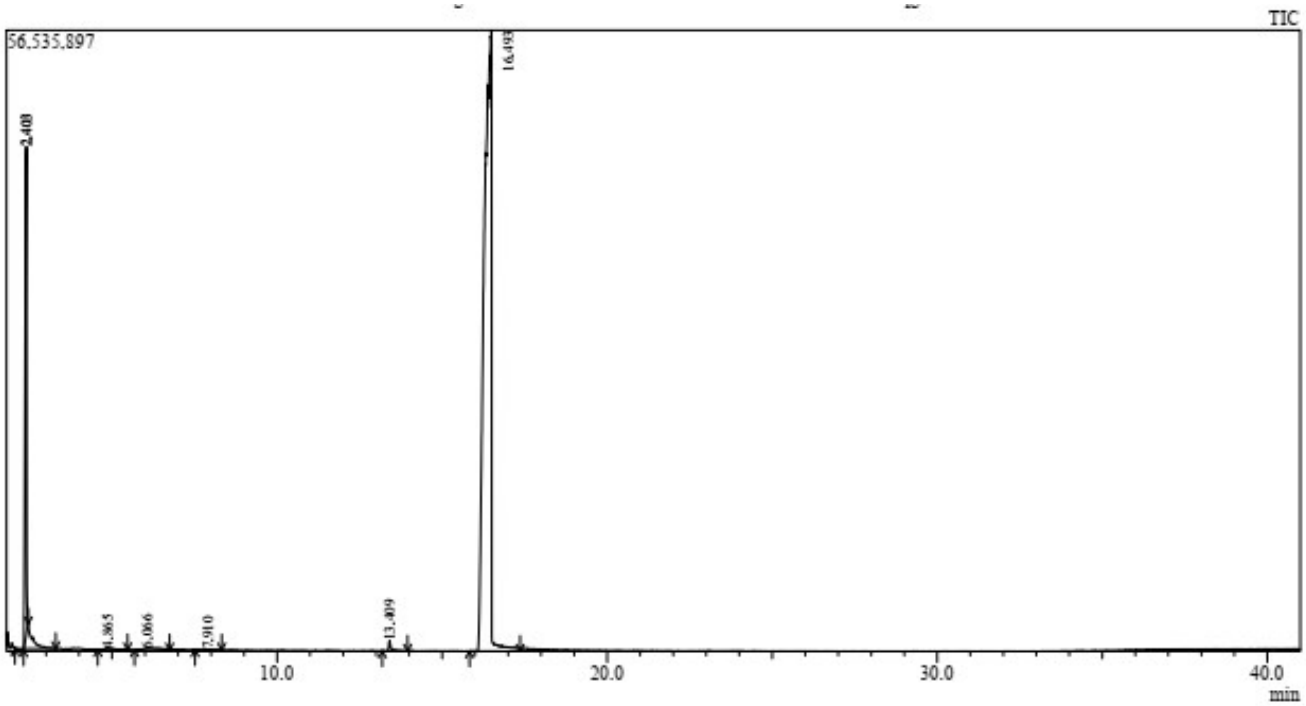

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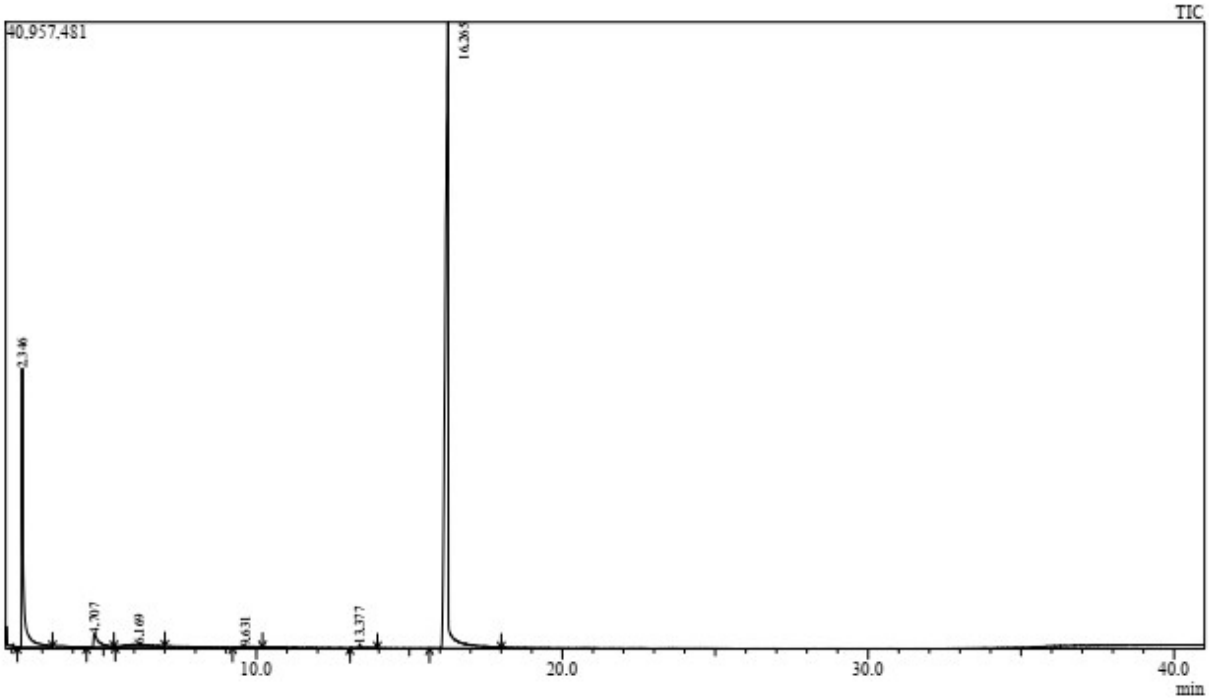

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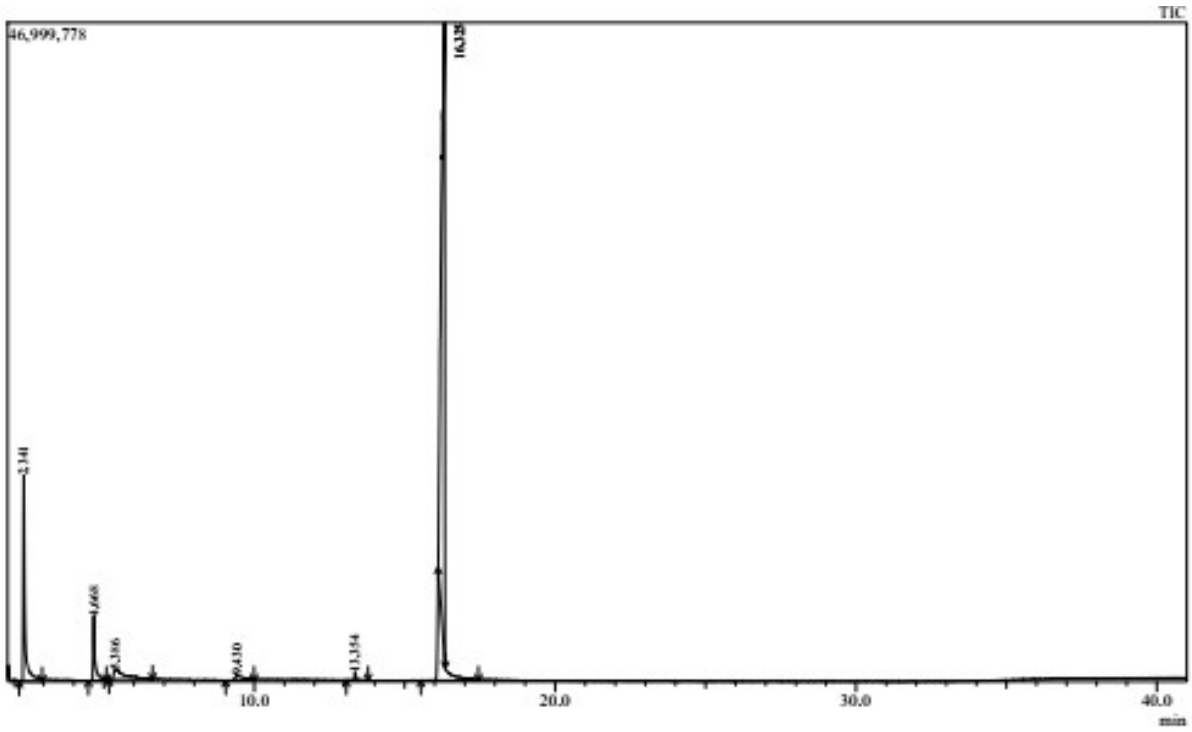

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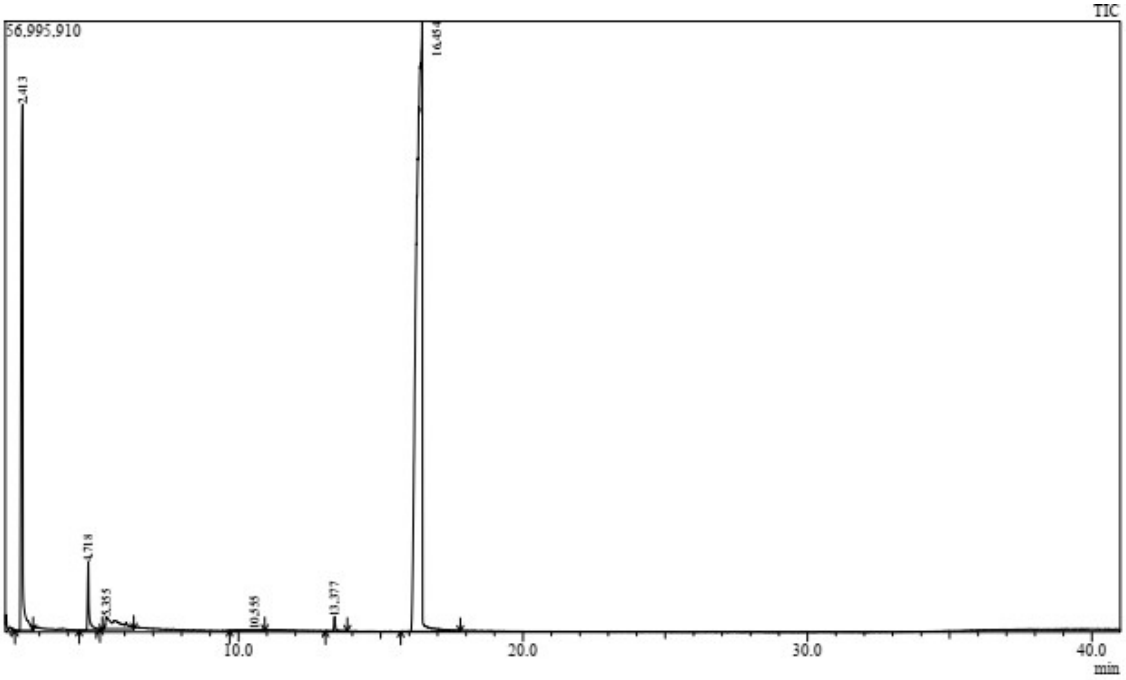

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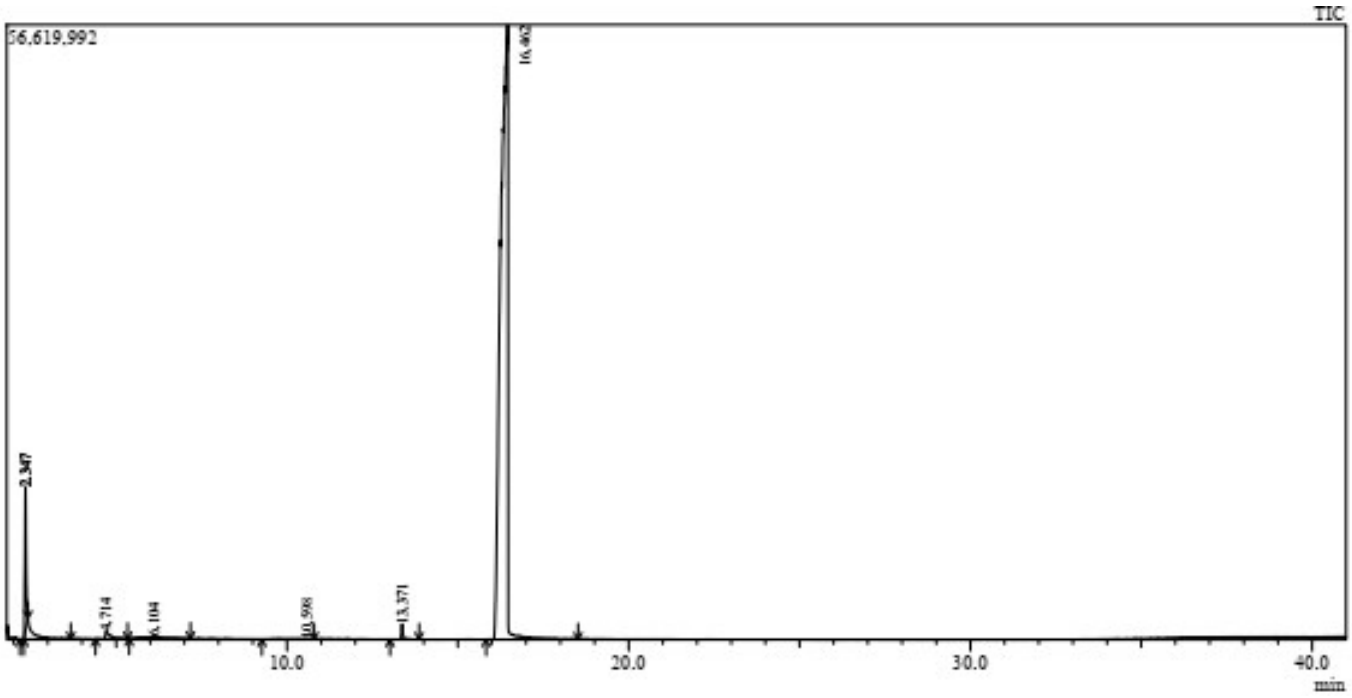

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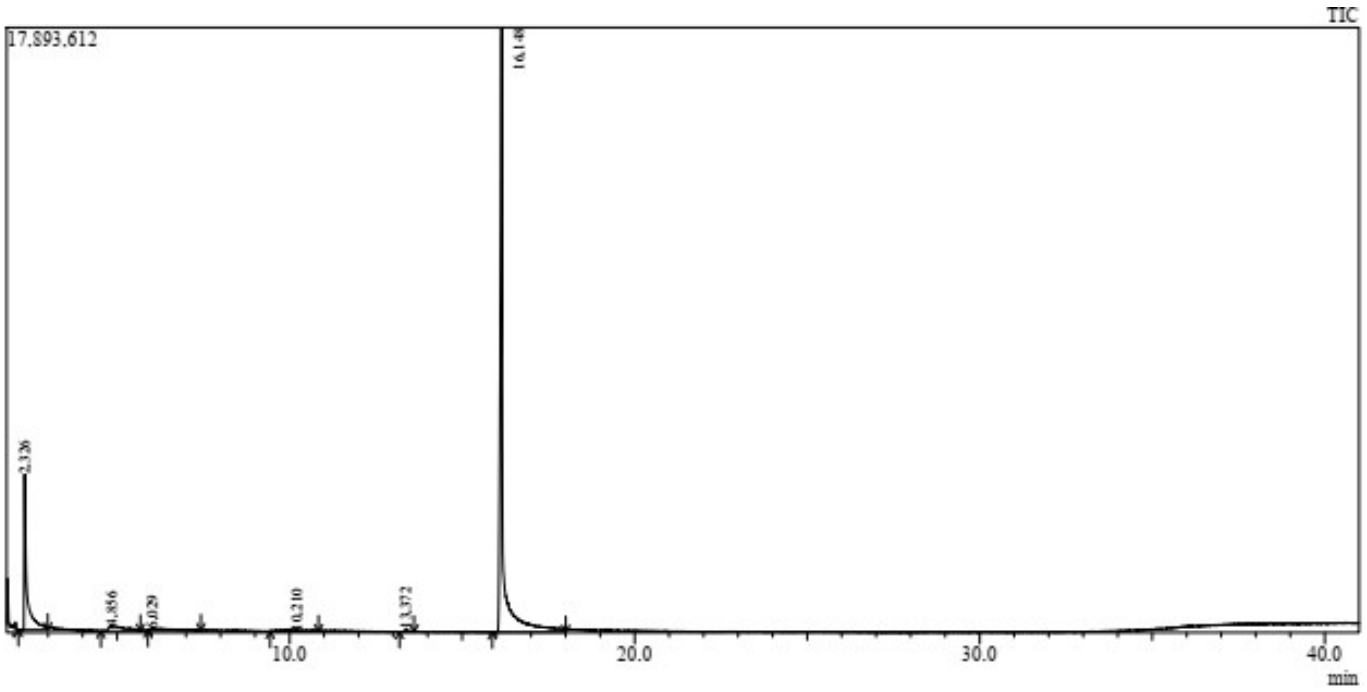

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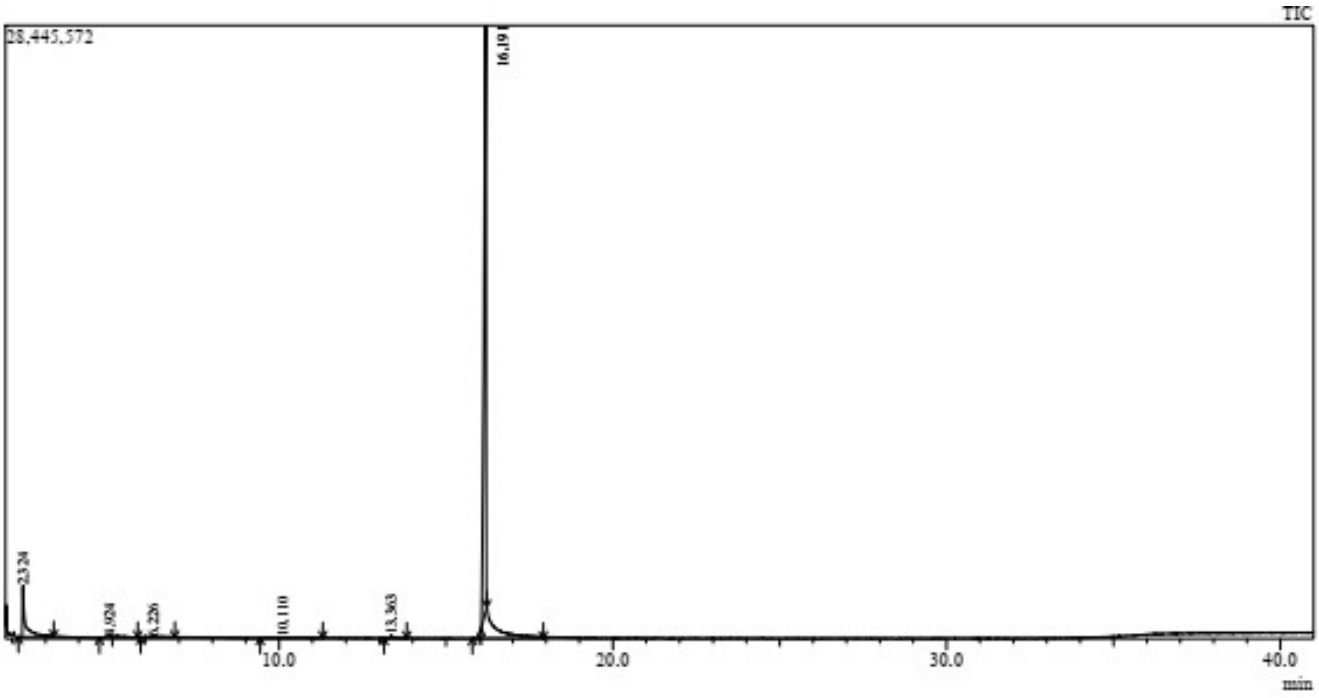

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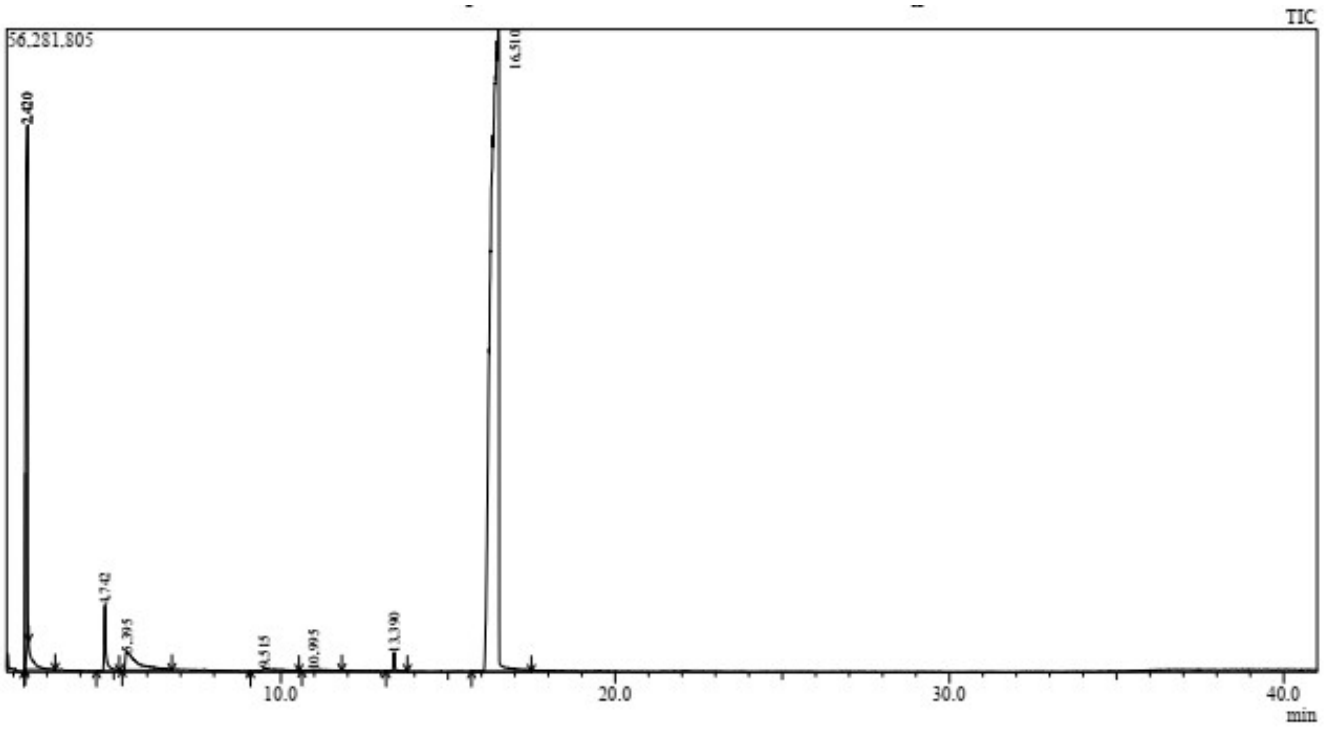

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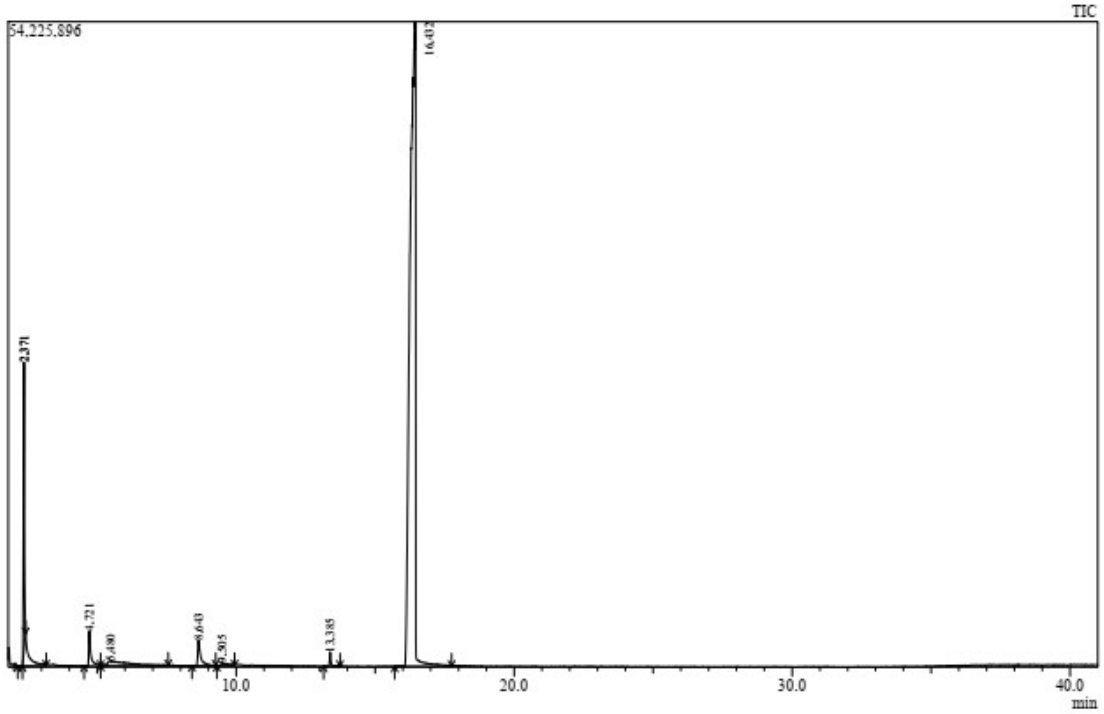

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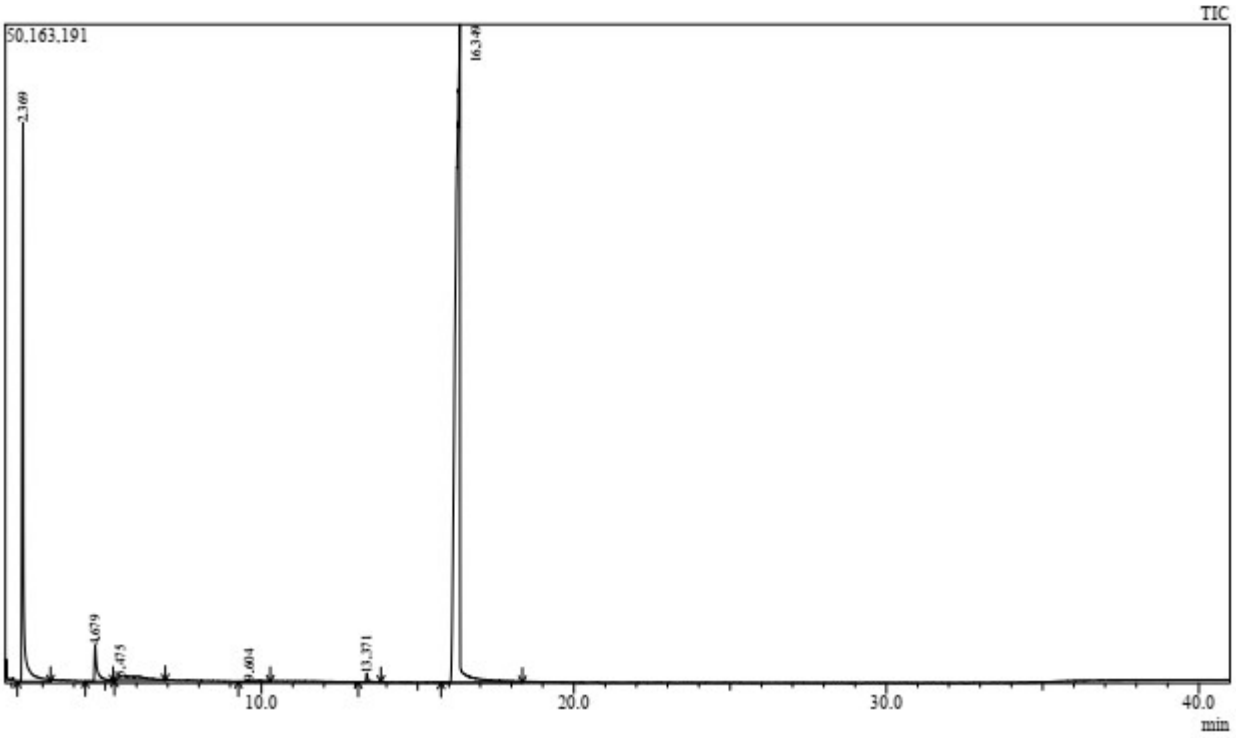

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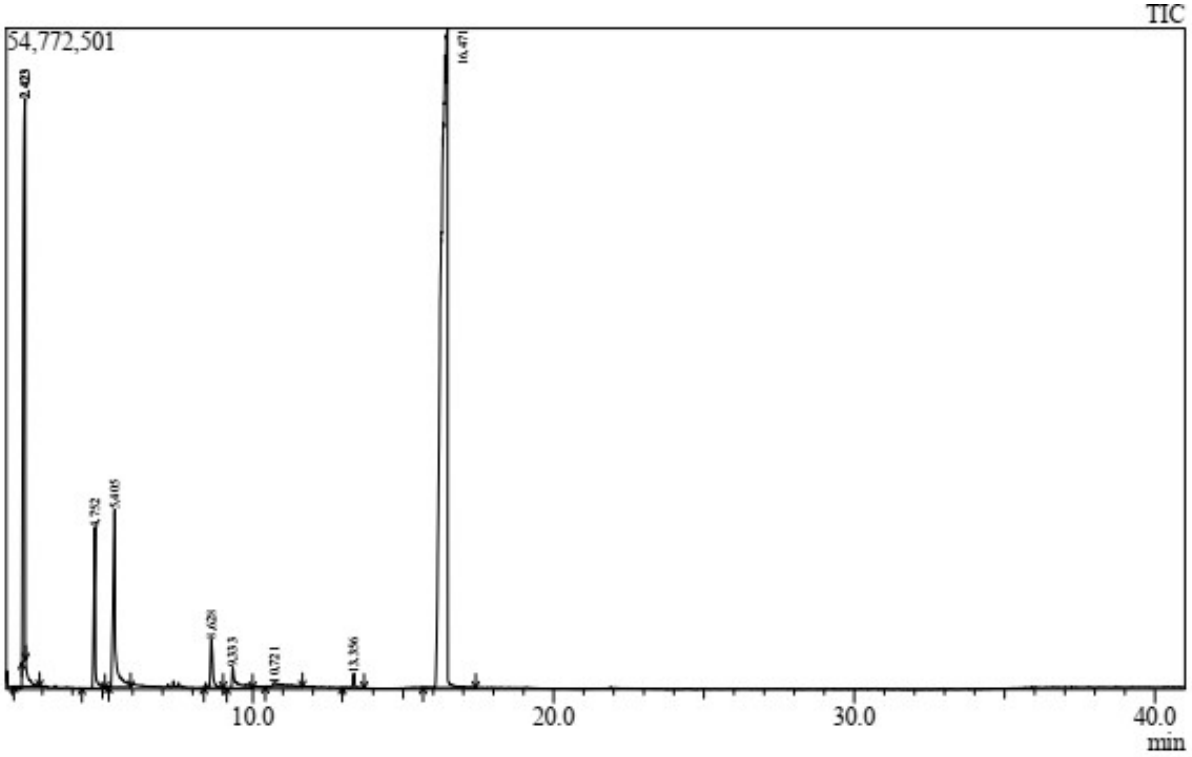
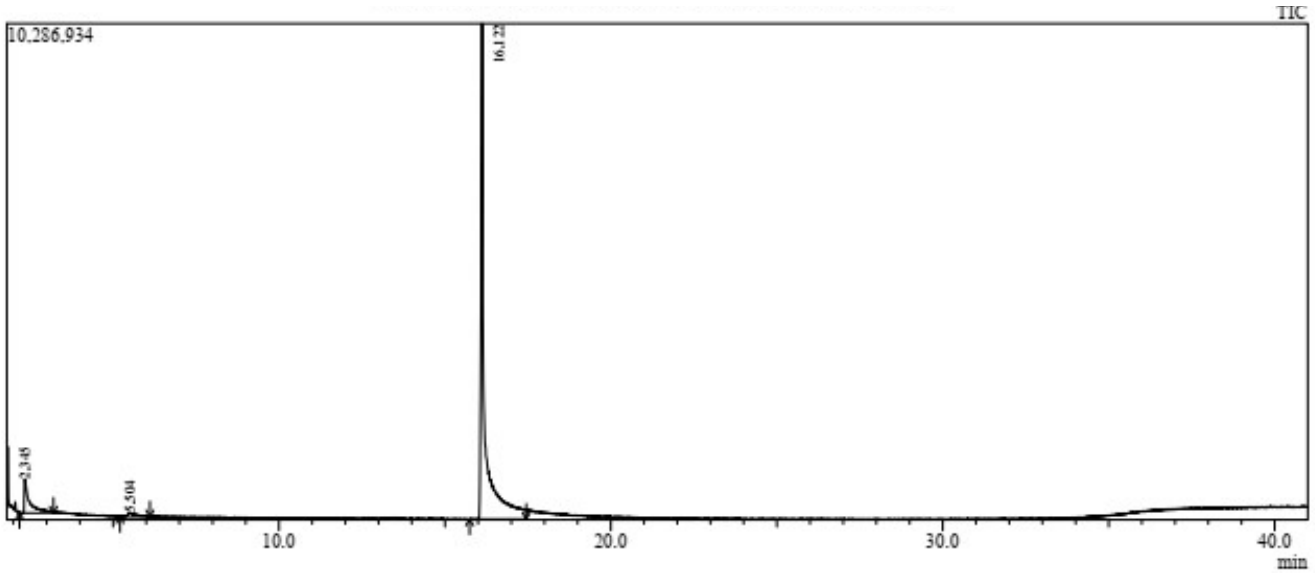


Entry 2, Table 3



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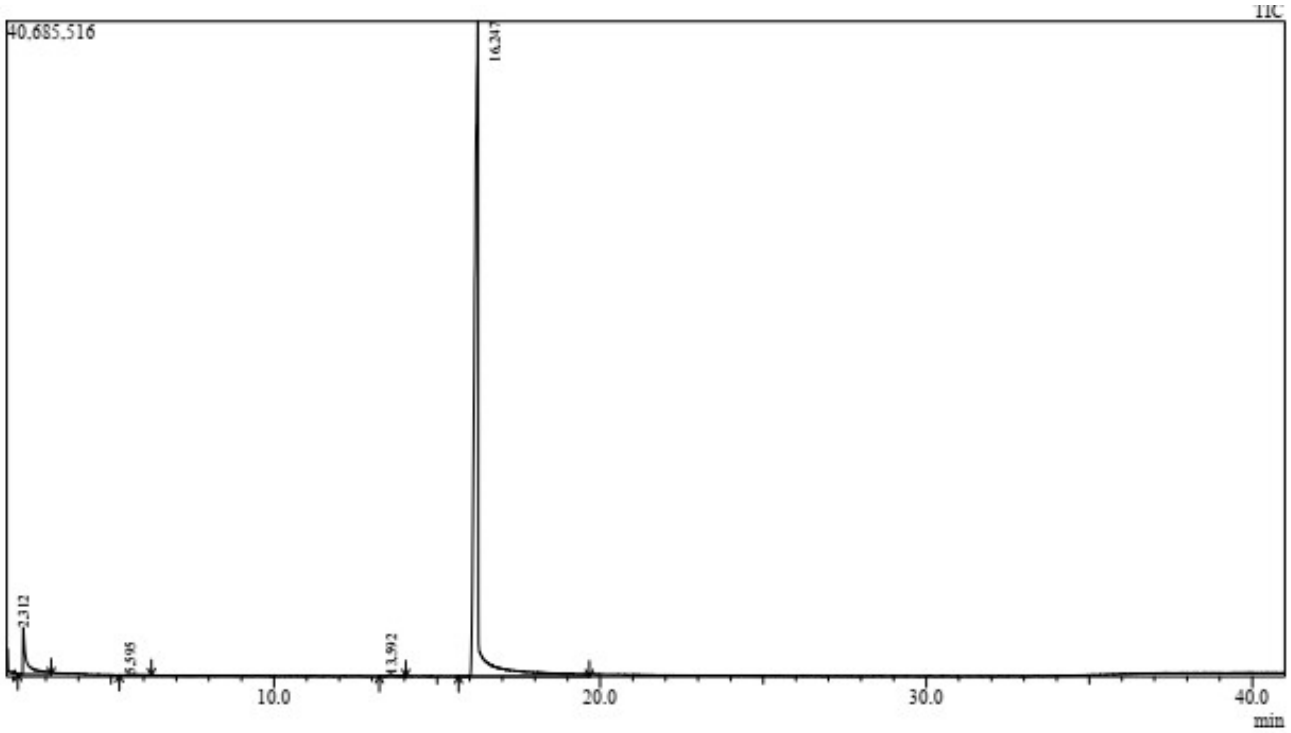

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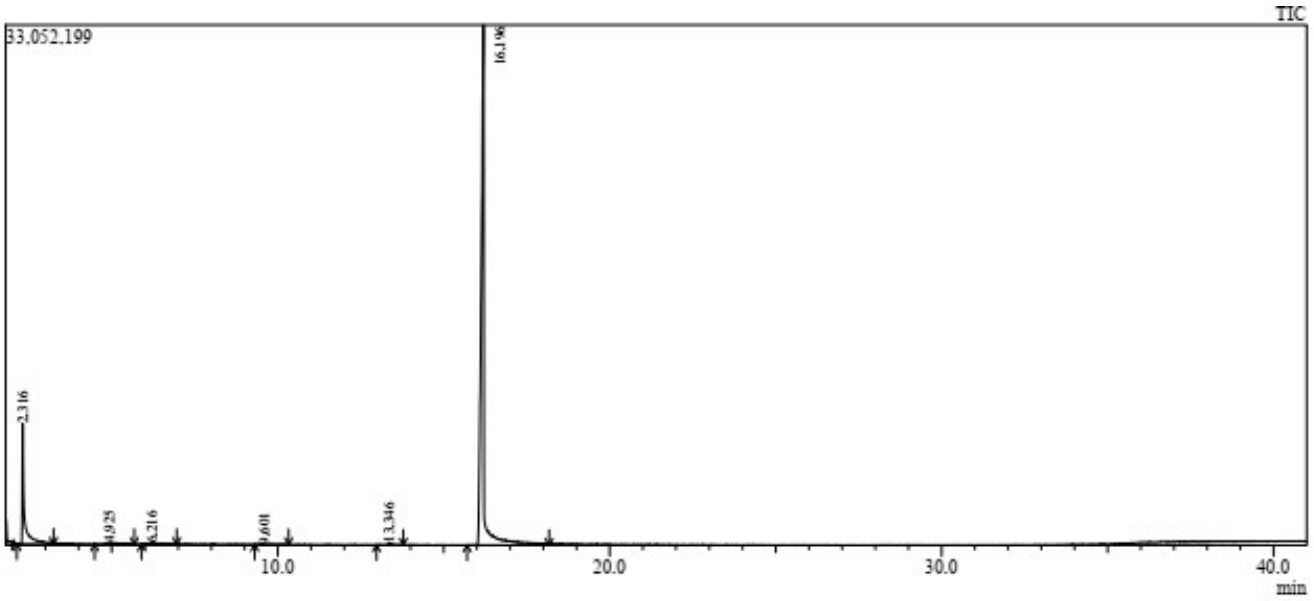

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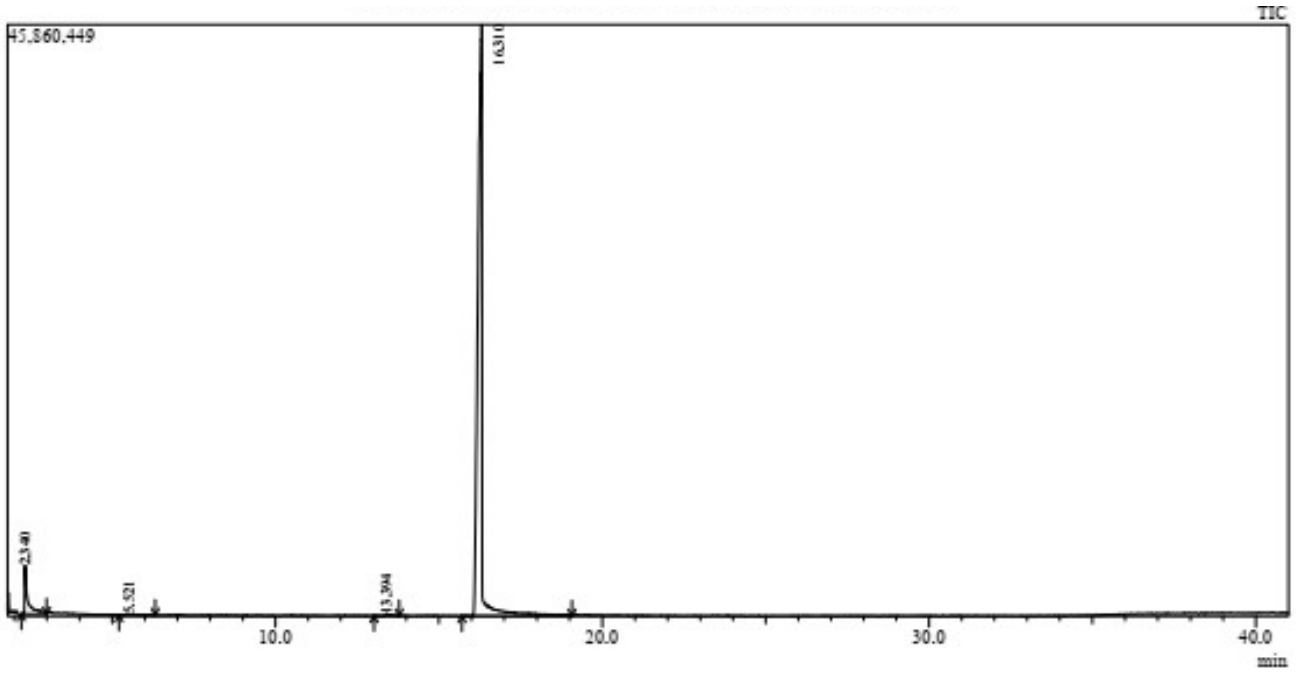
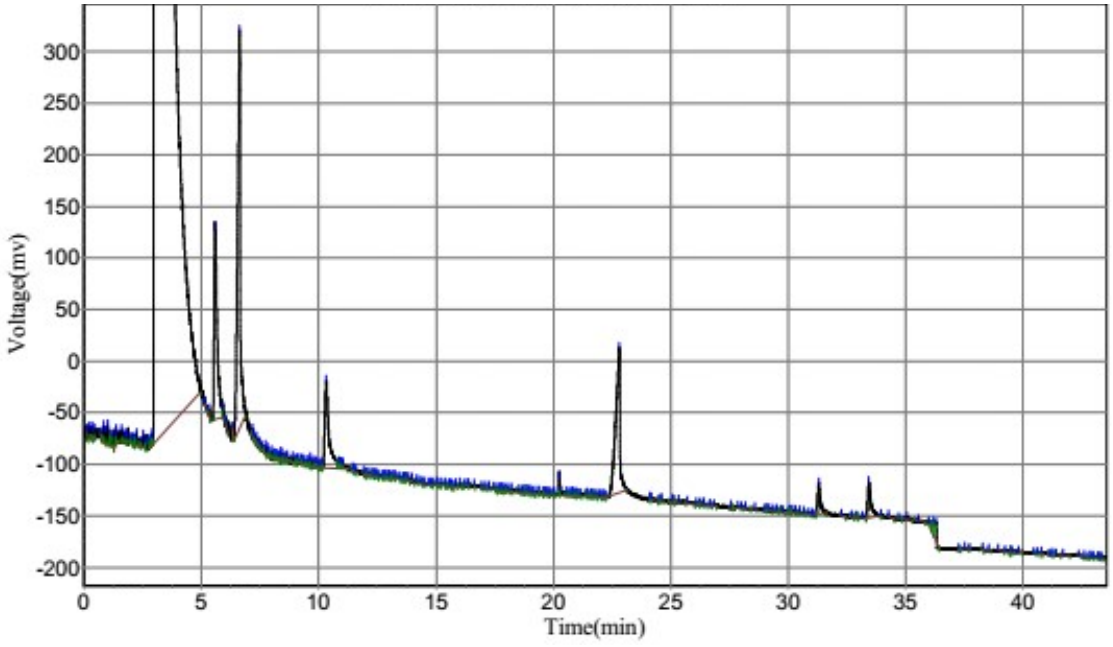
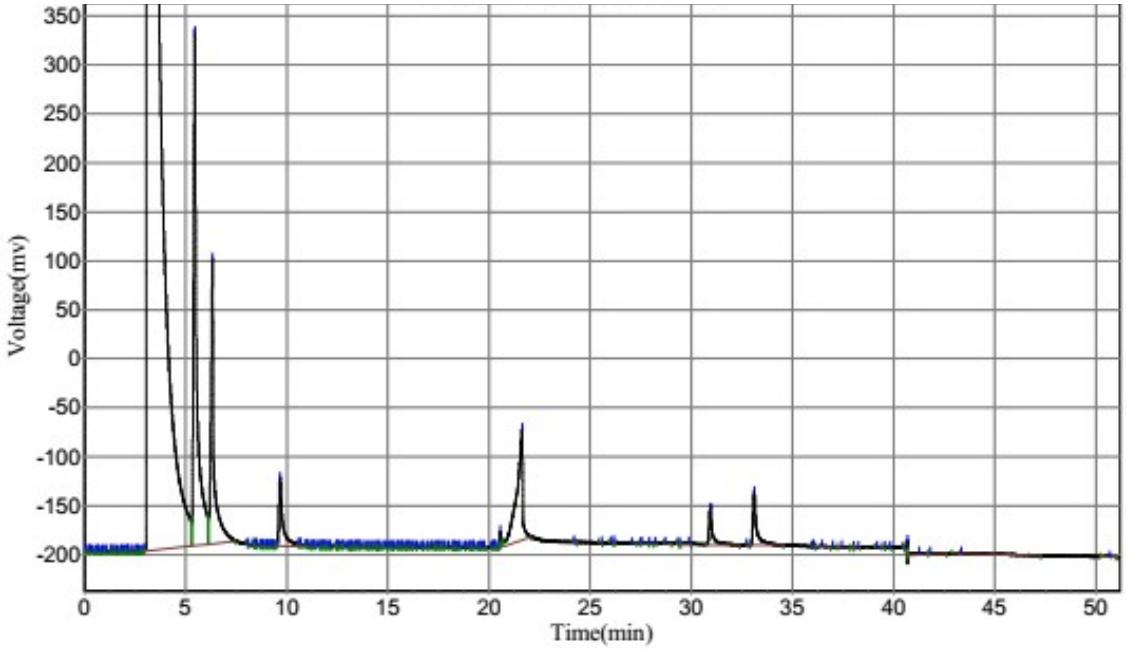


Mayura Analytical (Model 1100) instrument with AB-InoWax column	
Average retention time	**Compound**
3.0	diethyl ether
5.5	t-butanol
6.5	ethanol
9.9	chloroform (standard)
23.2	n-butanol

Entry 2, Table 1



Entry 3, Table 1



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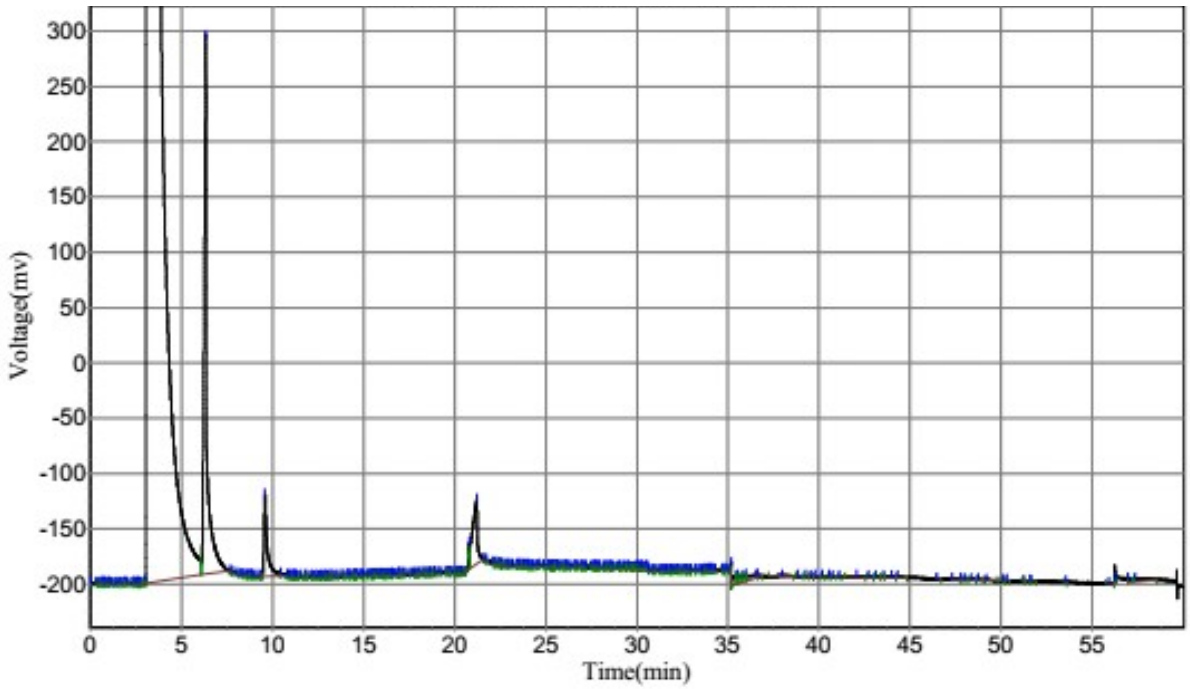

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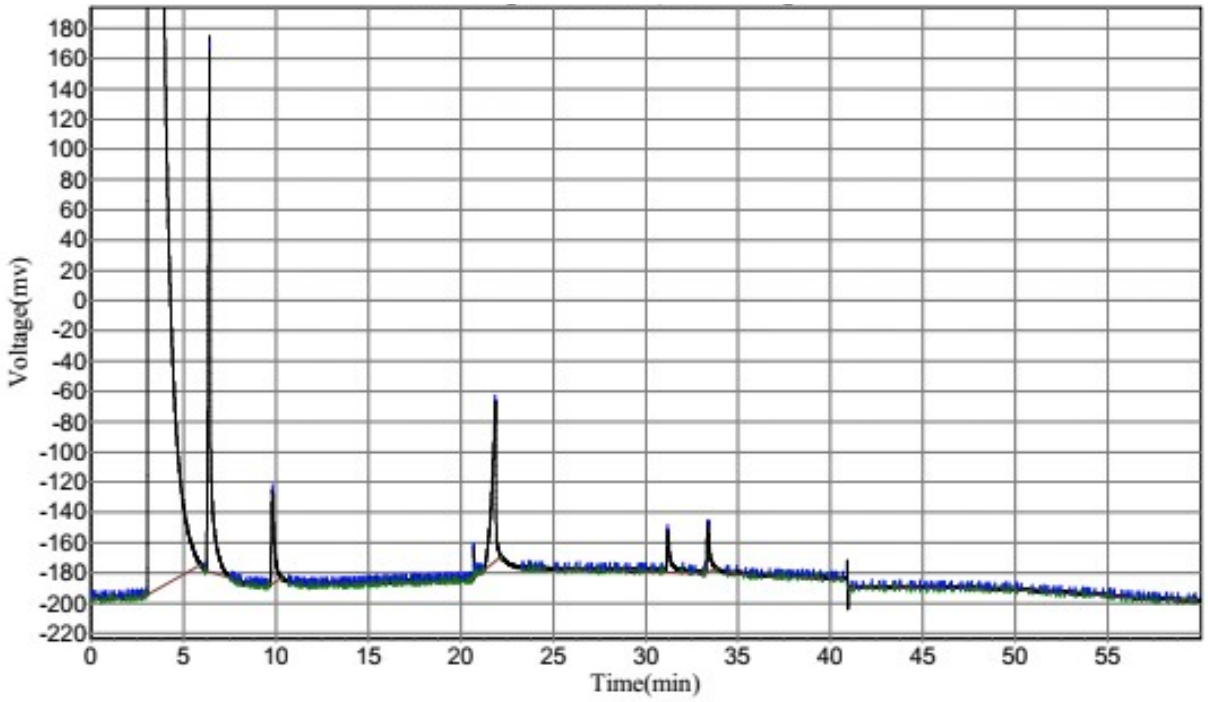

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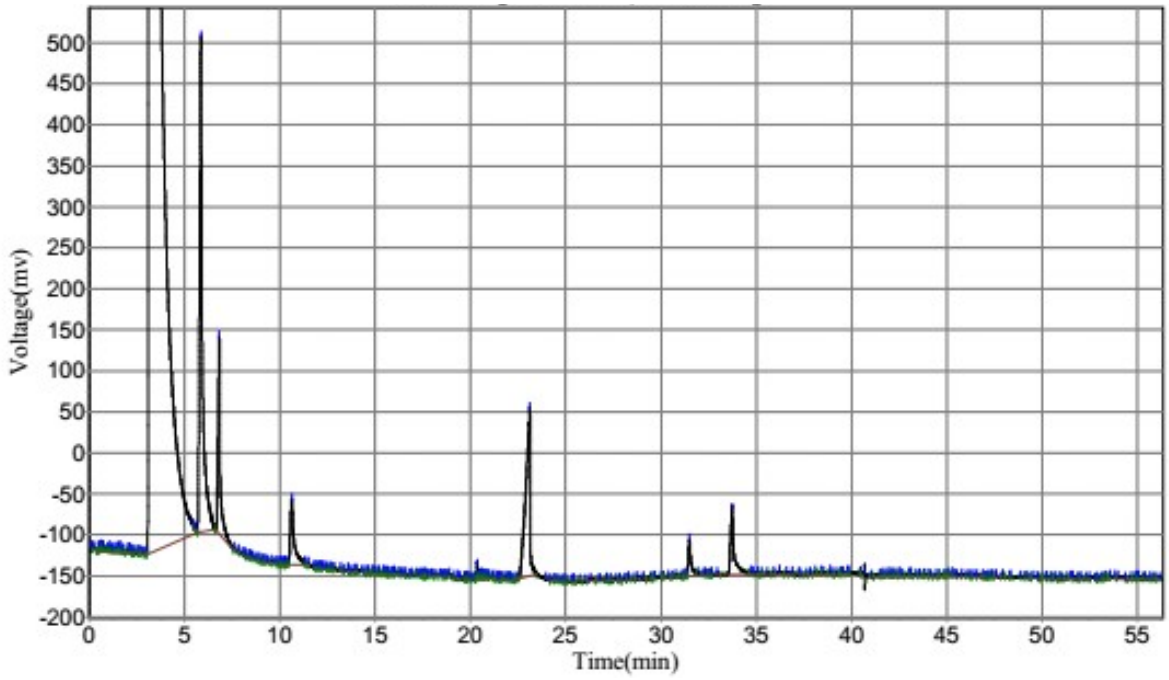

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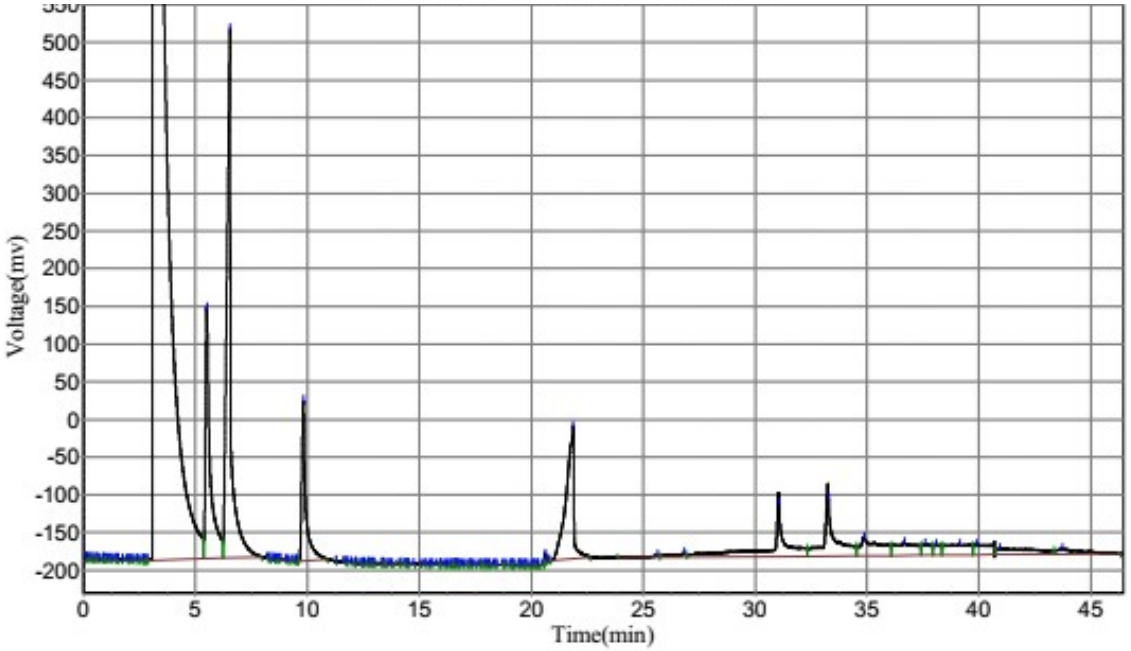

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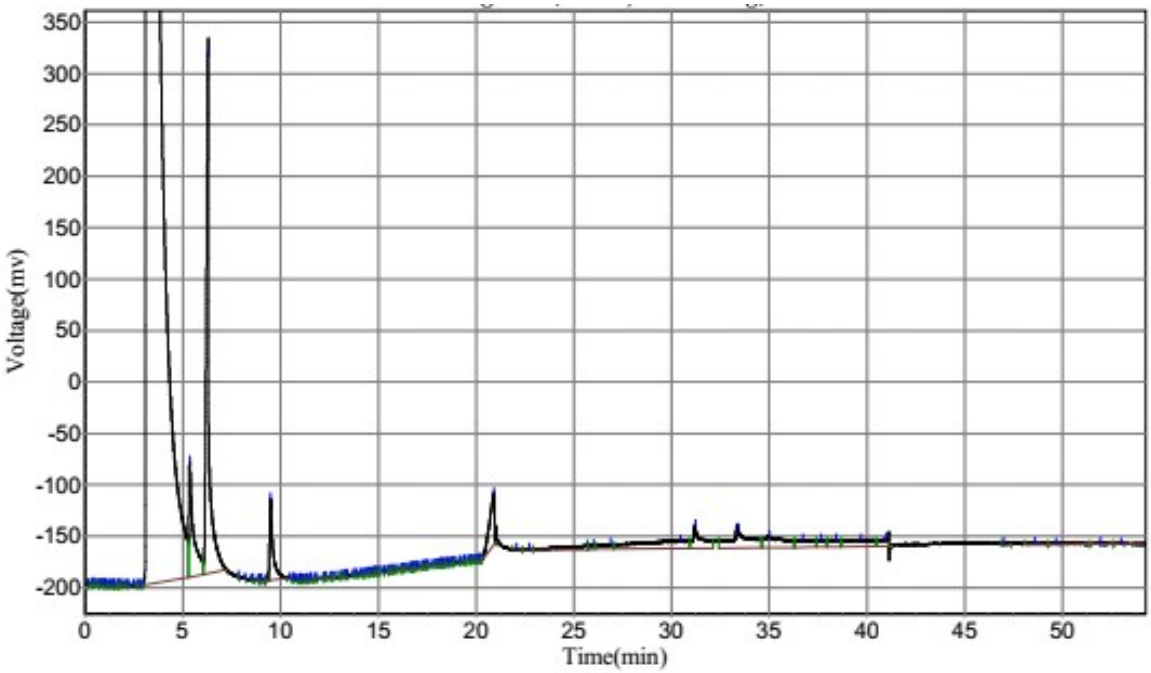
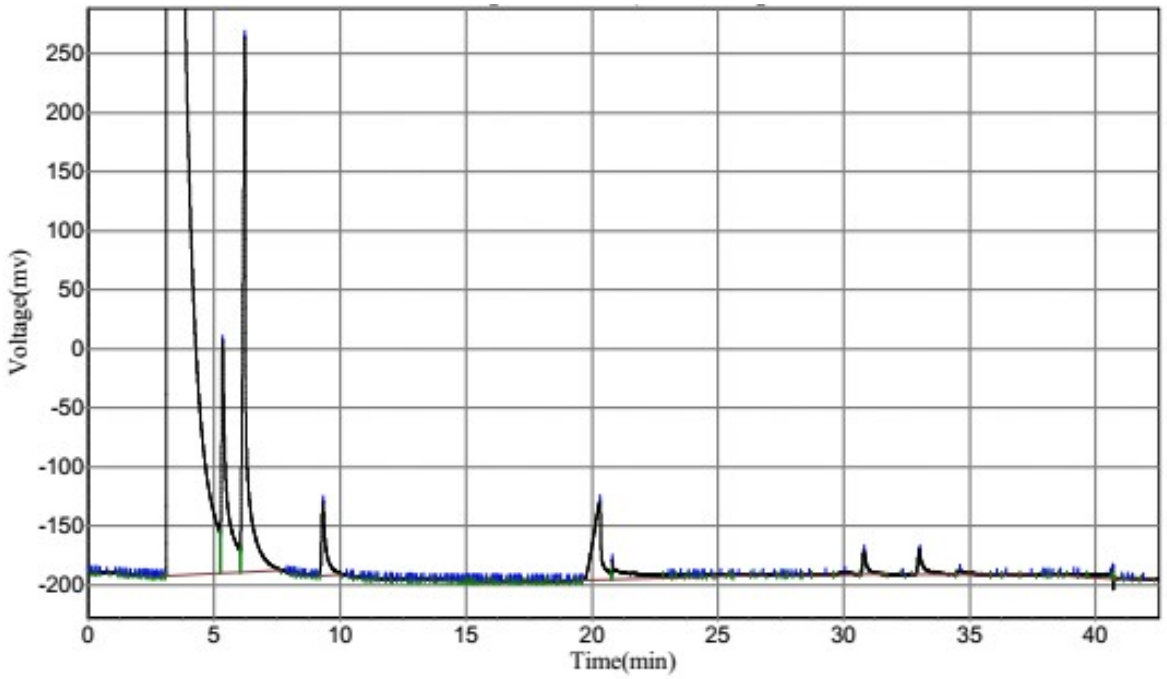
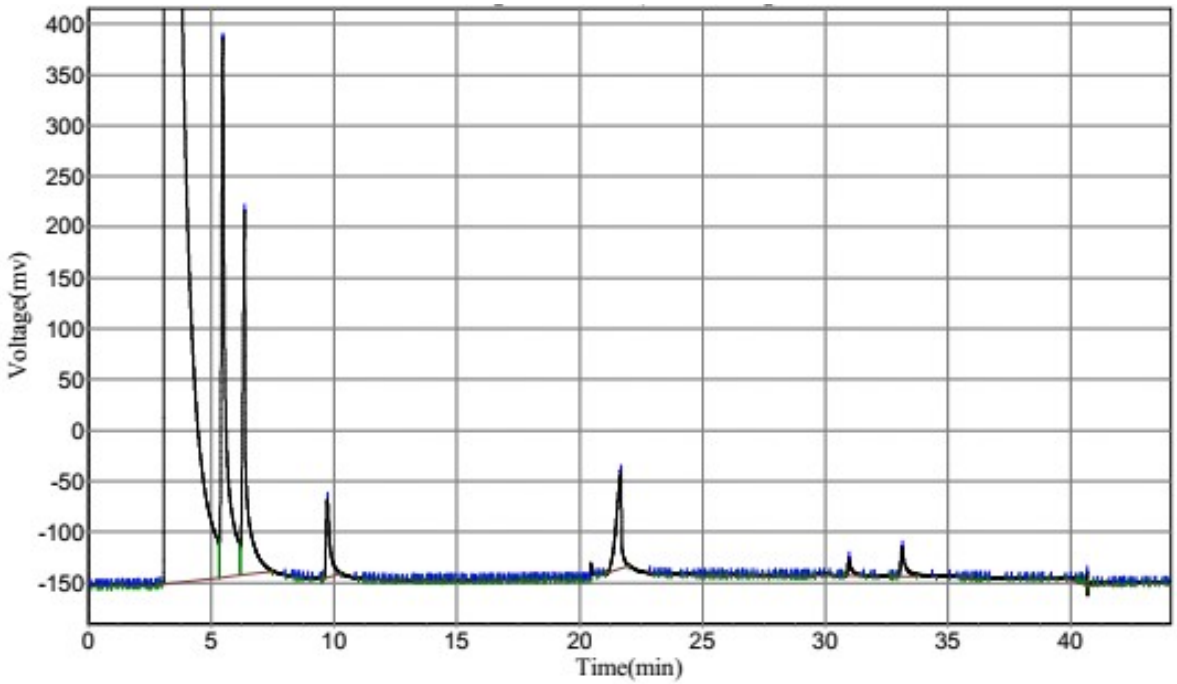


Entry 14, Table 1



Entry 2, Table 2



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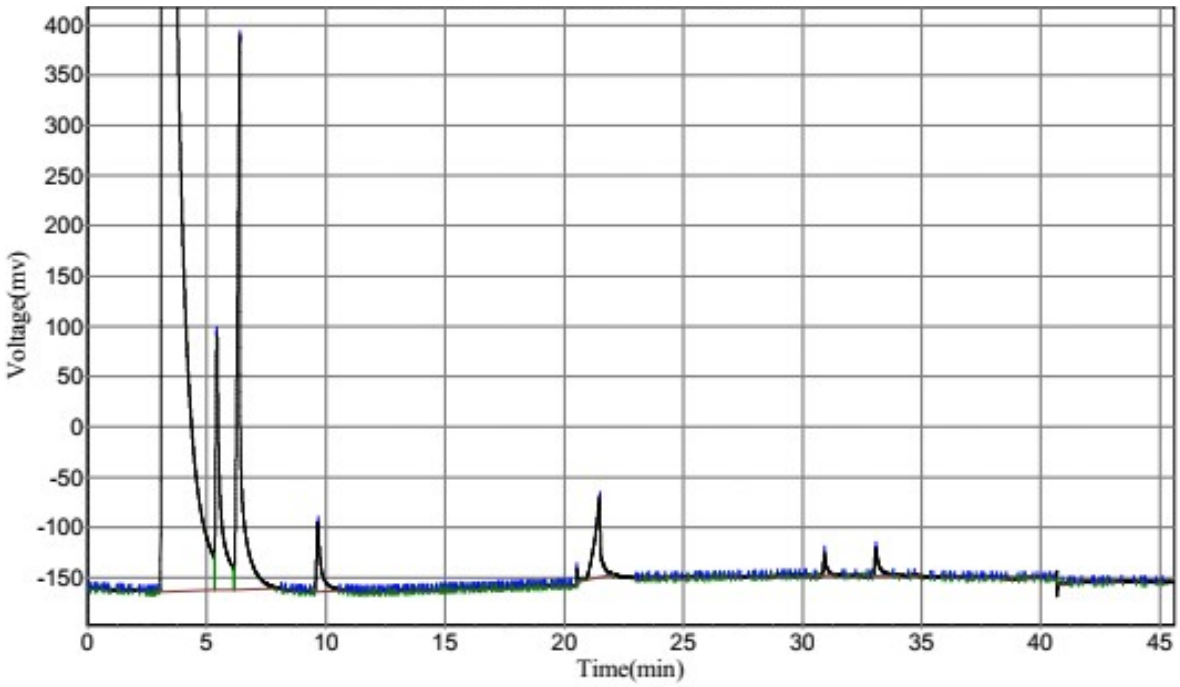

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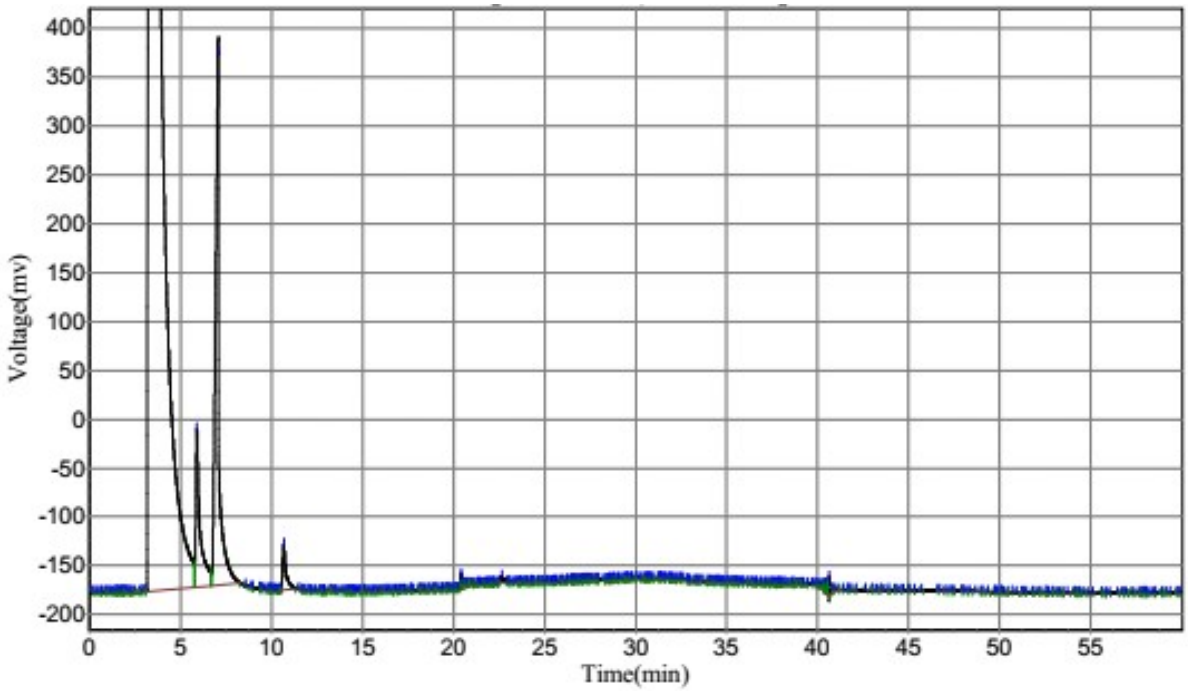

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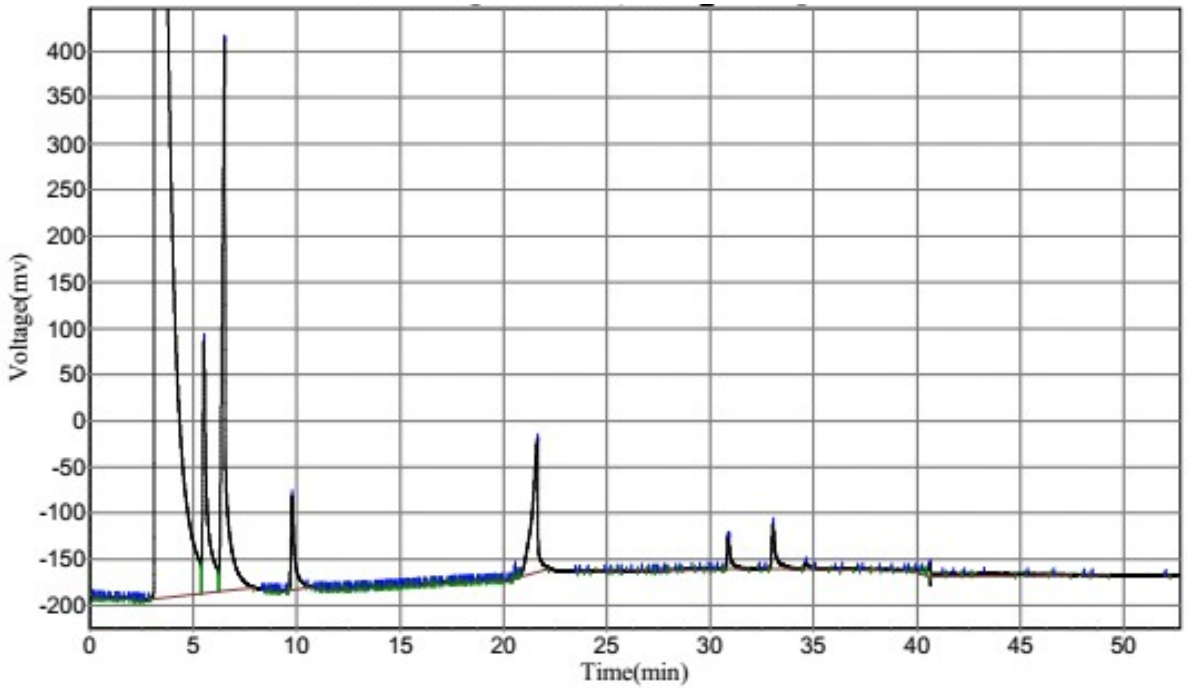
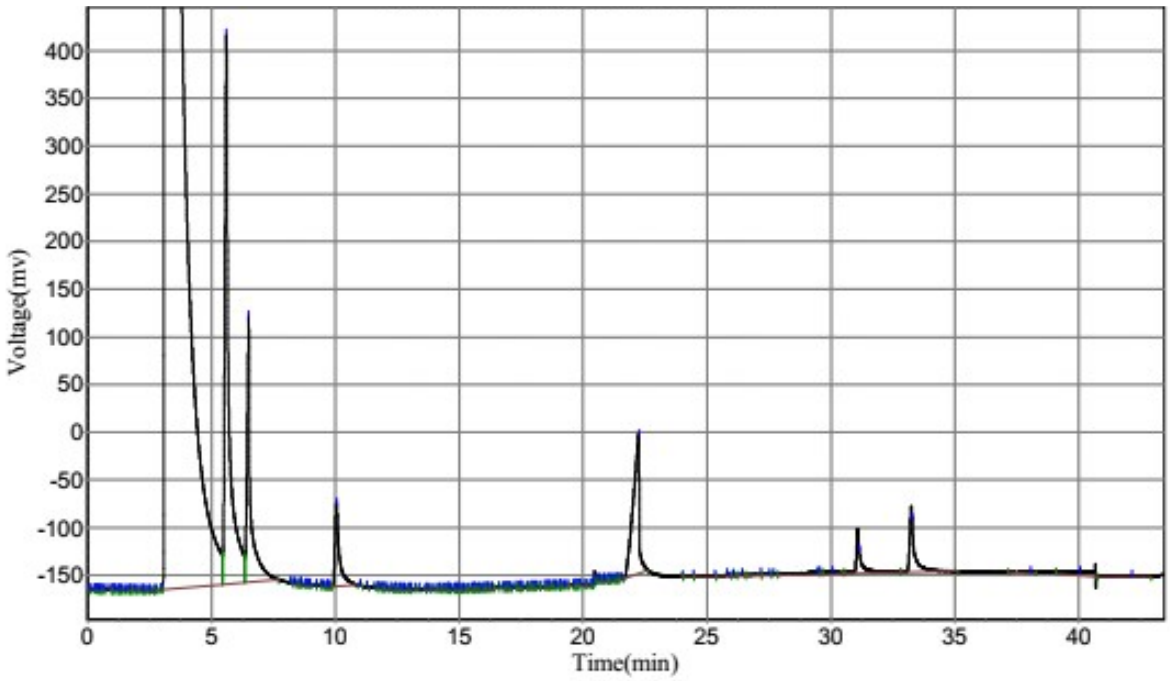


Entry 1, Table 3



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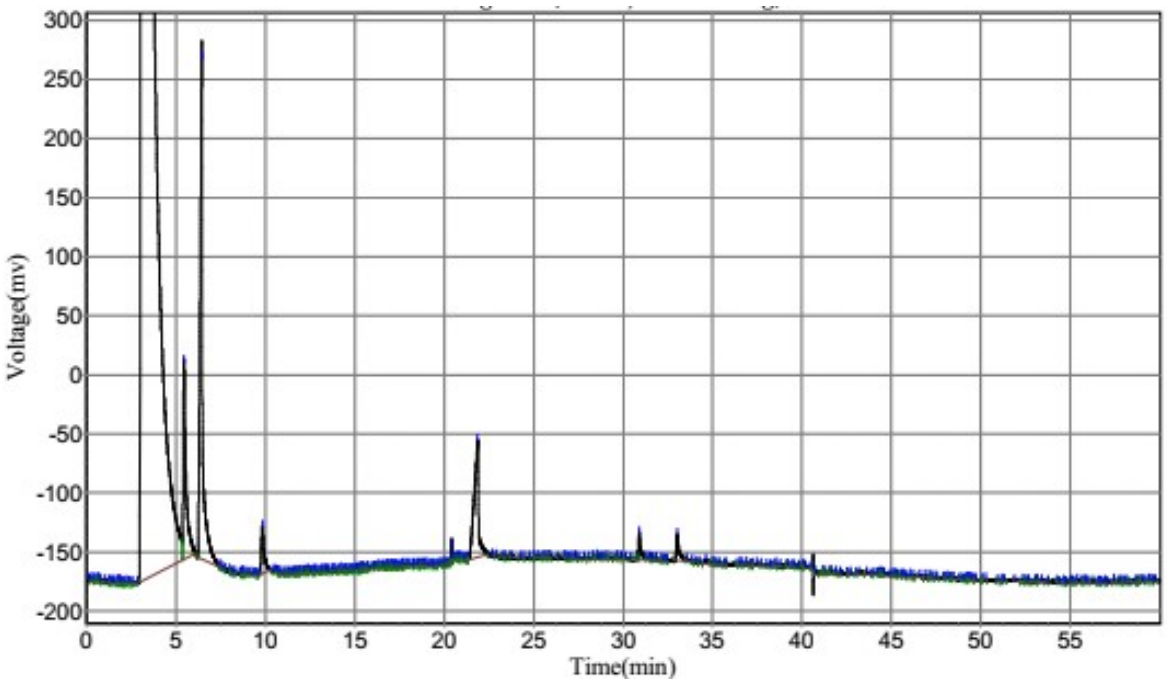

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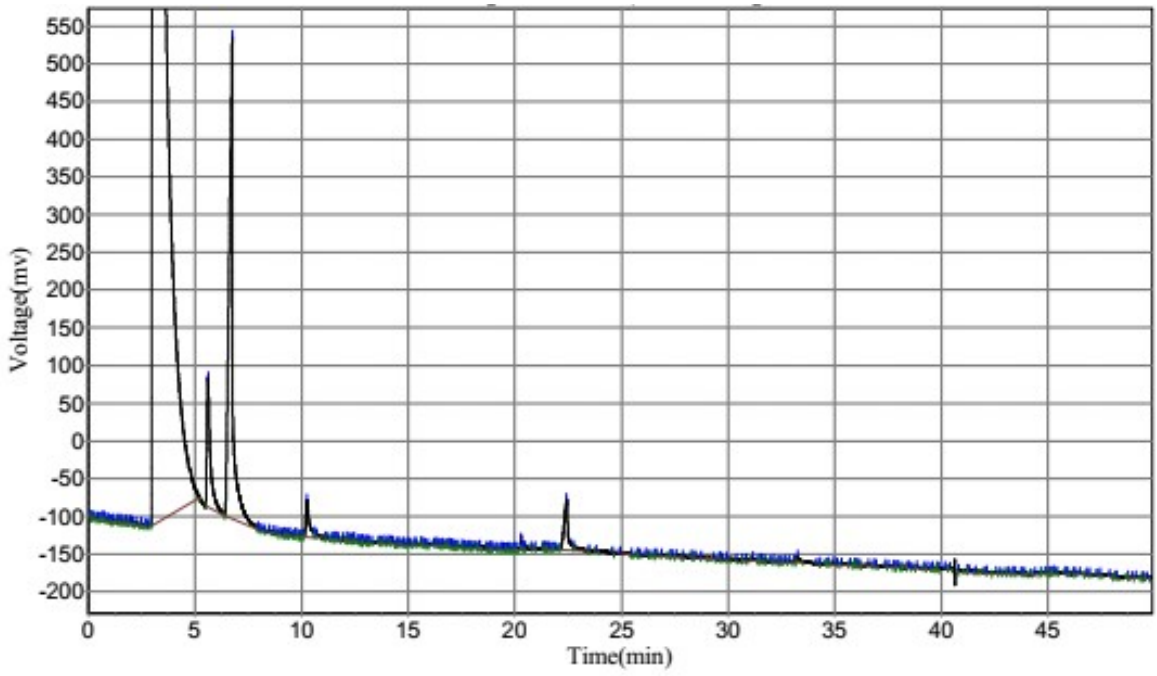

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