Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Aminoborylation / Suzuki-Miyaura tandem cross coupling of aryl iodides as efficient and selective synthesis of unsymmetrical biaryls

Ludovic Marciasini,[a] Nicolas Richy,[b] Michel Vaultier,[a,b] Mathieu Pucheault*[a,b]

[a] *Institut des Sciences Moléculaires, UMR CNRS 5255, Université Bordeaux 1, 351 Cours de la Libération, F-33405 Talence Cedex, France; E-mail: m.pucheault@ism.u-bordeaux1.fr*

[b] *Chimie et Photonique Moléculaires, UMR CNRS 6510, Université Rennes 1, Campus de Beaulieu, 263 Avenue du Général Leclerc, F-35042 Rennes Cedex, France*

I. General Procedures.

Unless specified all reactions were carried out using oven-dried glassware under Argon atmosphere. Toluene was purified by distillation from sodium metal/benzophenone. All reagents were purchased from Sigma-Aldrich, Acros chemicals or Alfa Aesar and used without further purification unless specified. Analytical thin layer chromatography (TLC) was carried out using 0.25 mm silica plates purchased from Merck. Eluted plates were visualized using $KMnO_4$. Silica gel chromatography was performed using 230–400 mesh silica gel purchased from Merck. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker FT NMR instrument (AVANCE 300). NMR spectra are reported as d values in ppm relative to $CDCl_3$ calibrated to 7.26 ppm in ^{1}H NMR and 77.00 in ^{13}C NMR. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q),multiplet (m), doublet of doublet (dd), triplet of doublet (td), doublet of triplet (dt).

GC-MS analysis were performed with a HP 6890 series GC-system equipped with a HP 5973 mass selective detector (EI) using the following method : 40 °C for 2 min then 30 °C/min until 300 °C then 9 min at 300 °C.

A. Preparation of diisopropopylaminoborane

To a stirred solution of diisopropylamine (141 mL, 1 mol, 1 eq) in THF (150 mL) were added at 0 °C 26.64 mL of H_2SO_4 (0.5 mol, 0.5 eq). A white precipitate appears immediately. After 15 min at 0 °C were carefully added 41 g of $NaBH_4$ (1.1 mol, 1.1 eq) in powder. The mixture was allowed to warm to room temperature and stirred for 1h. The crude was filtered under vacuum and the residue washed with THF (3 x 50 mL). The filtrate was concentrated under reduced pressure to give the amine-borane complex as colorless oil. The amine-borane complex was refluxed at 180 °C with a sand bath in the presence of a bubbling device to observe the formation of hydrogen. After the completion of the dehydrogenation (about 1h30), a distillation apparatus was installed and the aminoborane was distillated under argon to give a 102g of colorless liquid (90 % yield).

B. Typical procedure for the synthesis of symmetrical biaryl compounds (procedure A)

To a solution of $Pd(dppp)Cl_2$ (5.6 mg, 10 µmol , 1% mol) and KI (1.6 mg, 10 µmol , 1% mol) under an atmosphere of argon in anhydrous toluene (2 mL), were successively added a solution of aryl iodide (5 eq) in anhydrous toluene (1 mL), and di*iso*propylaminoborane (113 mg, 1 mmol, 1 eq). The mixture was stirred at 110 °C until no starting material is remaining (TLC). The reaction was allowed to cool at 25 °C and was then quenched with a HCl 1M

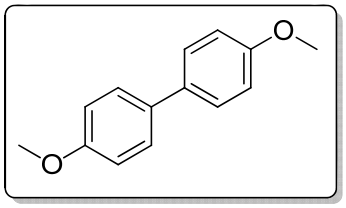
solution (100 mL), extracted with CH_2Cl_2 (4 x 50 mL). The combined organic phases were washed with a 10 % $NaHCO_3$ solution (2 x 50 mL), brine (2 x 100mL) dried over $mgSO_4$ and concentrated under reduced pressure. The obtained crude was purified by flash column chromatography.

C. Typical procedure for the synthesis of unsymmetrical biaryl compounds (procedure B)

To a mixture of $PdCl_2$(dppp) (5.6 mg, 10 µmol , 1% mol) and KI (1.6 mg, 10 µmol , 1% mol) under an atmosphere of argon in anhydrous toluene (2 mL), were successively added a solution of the aryl halide **1** (1eq) in anhydrous toluene (1 mL), and diisopropylaminoborane (226 mg, 2 mmol, 2 eq). The solution was stirred at 110 °C until no starting material is remaining (TLC). The reaction was allowed to cool at 25 °C and were successively added a degassed solution of ethanol (0.6 mL, 10 mmol, 10 eq) and water (0.2 mL, 10 mmol, 10 eq), cesium carbonate (652 mg, 2 mmol, 2 eq) and a solution of the aryl halide **2** (1.5 eq) in toluene (1 mL). The mixture was stirred under refluxing condition (90 °C) for 15 h. The reaction was allowed to cool at 25 °C and was then quenched with a HCl 1M solution (100 mL), extracted with CH_2Cl_2 (4 x 50 mL). The combined organic phases were washed with a 10 % $NaHCO_3$ solution (2 x 50 mL), brine (2 x 100mL) dried over $mgSO_4$ and concentrated under reduced pressure. The obtained crude was purified by flash column chromatography.

II. Analyses

A. 4,4'-dimethoxy-1,1'-biphenyl (4aa) [2132-80-1][1]



Following typical procedure A using 5 mmol of 4-methoxyiodobenzene **2a**, 153 mg of **4aa** were obtained as a white crystalline solid (71% yield).

m.p. : 176 °C

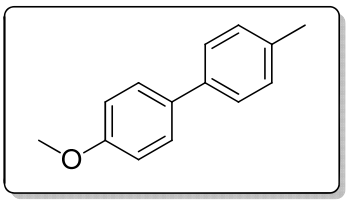
R_f (heptane/dichloromethane 50:50): 0.35.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 4H, *J* = 8.8 Hz), 6.96 (d, 4H, *J* = 8.8 Hz), 3.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) : δ 158.68, 133.47, 127.71, 114.14, 55.33.

MS (EI) t_R = 9.49 min; m/z: 214 ($M^{+\cdot}$, 100%), 199 ($[M-CH_3]^{+\cdot}$, 94%).

B. 4-methoxy-4'-methyl-1,1'-biphenyl (4ab) [53040-92-9][2]



Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 1-iodo-4-methylbenzene **2b**, 198 mg of **4ab** were obtained as a white crystalline solid (quantitative yield)

Following typical procedure B using 1 mmol of 1-iodo-4-methylbenzene **2b** and 1.5 mmol of 1-iodo-4-methoxybenzene **2a**, 111 mg of **4ab** were obtained as a white crystalline solid (56% yield)

---

[1] S. Santra, P. Ranjan, S. K. Mandal and P. K. Ghorai, *Inorg. Chim. Acta*, 2011, **372**, 47-52.

[2] L.-G. Xie and Z.-X. Wang, *Angew. Chem., Int.Ed.*, 2011, **50**, 4901-4904.

m.p. : 106 °C

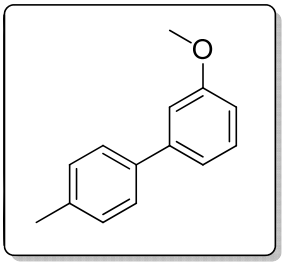
R_f (heptane/dichloromethane 85:25): 0.26

^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.60 – 7.40 (m, 4H), 7.24 (d, 2H, *J* = 7.9 Hz), 6.98 (d, 2H, *J* = 8.9 Hz), 3.86 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.91, 137.95, 136.33, 133.73, 129.41, 127.93, 126.57, 114.14, 55.33, 21.04.

MS (EI) t_R= 8.97 min, m/z: 198 ($M^{+\cdot}$, 100%), 183 ([M-CH3] $^{+\cdot}$, 55%).

C. 3-methoxy-4'-methyl-1,1'-biphenyl (4bc) [24423-07-2][3]



Following typical procedure B using 1 mmol of 1-iodo-4-methylbenzene **2b** and 1.5 mmol of 1-iodo-3-methoxybenzene **2c**, 126 mg of **4bc** were obtained as a colourless oil (64% yield)

R_f (pentane/dichloromethane 95:5): 0.12

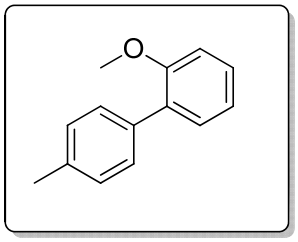
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.26 (t, = *J* = 3.9 Hz, 3H), 7.22 – 7.15 (m, 1H), 7.12 (s, 1H), 6.92 – 6.85 (m, 1H), 3.87 (s, 3H), 2.40 (s 3H,).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.86, 142.60, 138.13, 137.09, 129.63, 129.39, 126.94, 119.41, 112.64, 112.28, 55.13, 21.02.

MS (EI) t_R= 8.85 min, m/z: 198 ($M^{+\cdot}$, 100%), 183 ([M-CH3] $^{+\cdot}$, 4%).

[3] L.-G. Xie and Z.-X. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 4901-4904.

D. 2-methoxy-4'-methyl-1,1'-biphenyl (4bd) [92495-53-9][4]



Following typical procedure B using 1 mmol of 1-iodo-2-methoxybenzene **2b** and 1.5 mmol of 1-iodo-4-methylbenzene **2d** , 166 mg of **4bd** were obtained as a white crystalline solid (84% yield)

m.p. : 77 °C

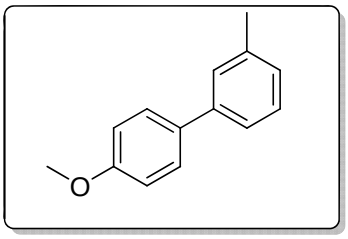
R_f (heptane): 0.13

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 – 7.41 (m, 2H), 7.37 – 7.28 (m, 2H), 7.23 (d, 2H, *J* = 7.9), 7.07 – 6.96 (m, 2H), 3.81 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.39, 136.45, 135.52, 130.68, 130.58, 129.32, 128.65, 128.28, 120.70, 111.06, 55.37, 21.12.

MS (EI) t_R=8.49 min; m/z: 198 ($M^{+\cdot}$, 100%), 183 (=$[M\text{-}CH_3]^{+\cdot}$, 73%), 168 (=$[M\text{-}2CH_3]^{+\cdot}$, 73%), 152 (=$[M\text{-}OCH_3]^{+\cdot}$ and $[CH_3]^{+\cdot}$, 15%)

E. 4'-methoxy-3-methyl-1,1'-biphenyl (4ae) [17171-17-4][5]



Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 1-iodo-3-methylbenzene **2e**, 180 mg of **4ae** were obtained as a white crystalline solid (91% yield)

[4] C. Liu, Q. Ni, P. Hu and J. Qiu, *Org. & Biomol. Chem.*, 2011, **9**, 1054-1060.

[5] A. Joshi-Pangu, C.-Y. Wang and M. R. Biscoe, *J. Am. Chem. Soc.*, 2011, **133**, 8478-8481.

m.p. : 51 °C

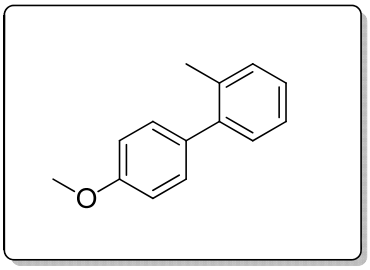
R_f (heptane): 0.10

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, 2H, *J* = 8.9), 7.45 – 7.28 (m, 3H), 7.14 (d, 1H, *J* = 7.2), 6.99 (d, 2H, *J* = 8.9), 3.86 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.02, 140.74, 138.16, 133.78, 128.57, 128.06, 127.45, 127.34, 123.77, 114.06, 55.14, 21.47.

MS (EI) t_R=8.41 min; m/z: 198 ($M^{+\cdot}$, 100%), 183 (=[M-CH_3]$^{+\cdot}$, 66%), 168 (=[M-2CH_3]$^{+\cdot}$, 58%), 152 (=[M-OCH_3]$^{+\cdot}$ and [CH_3]$^{+\cdot}$, 22%)

F. 4'-methoxy-2-methyl-1,1'-biphenyl (4af) [92495-54-0][6]



Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 1-iodo-2-methylbenzene **2f**, 169 mg of **4af** were obtained as a colourless oil (85% yield)

R_f (pentane): 0.23

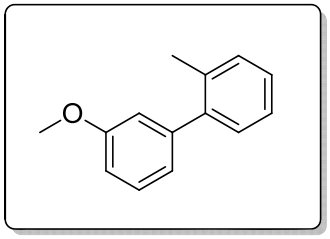
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 – 7.20 (m, 6H), 6.96 (d, 2H, *J* = 8.8 Hz), 3.86 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.44, 141.47, 135.36, 134.28, 130.23, 130.17, 129.83, 126.90, 125.70, 113.41, 55.13, 20.48.

MS (EI) t_R=8.51 min; m/z: 198 (=[$M^{+\cdot}$], 100%), 183 (=[M-CH_3]$^{+\cdot}$, 37%), 165 (=[M-OCH_3]$^{+\cdot}$ and [H]$^{+\cdot}$, 33%), 153 (=[M-OCH_3]$^{+\cdot}$ and [CH_3]$^{+\cdot}$, 34%)

[6] L.-G. Xie and Z.-X. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 4901-4904.

G. 3'-methoxy-2-methyl-1,1'-biphenyl (4cf) [81722-84-1][7]



Following typical procedure B using 1 mmol of 1-iodo-3-methoxybenzene **2c** and 1.5 mmol of 1-iodo-2-methylbenzene **2f**, 159 mg of **4cf** were obtained as a colourless oil (80% yield)

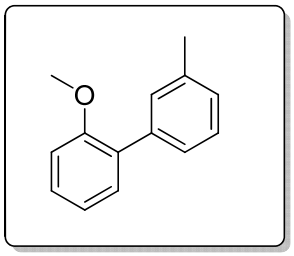
R_f (pentane): 0.22

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.32 (m, 5H, *J* = 11.8, 9.1, 5.7 Hz), 7.09 – 6.96 (m, 3H), 3.92 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.24, 143.32, 141.74, 135.23, 130.23, 129.58, 128.98, 127.24, 125.66, 121.61, 114.79, 112.21, 55.10, 20.39.

MS (EI) t_R=8.40 min; m/z: 198 (=[$M^{+\cdot}$], 100%), 183 (=[M-CH_3] $^{+\cdot}$, 18%), 167 (=[M-OCH_3] $^{+\cdot}$, 58%), 153 (=[M-OCH_3] $^{+\cdot}$, [H] $^{+\cdot}$ and [CH_3] $^{+\cdot}$, 25%)

H. 2-methoxy-3'-methyl-1,1'-biphenyl (4de) [653586-65-3][8]



Following typical procedure B using 1 mmol of 1-iodo-2-methoxybenzene **2d** and 1.5 mmol of 1-iodo-3-methylbenzene **2e**, 172 mg of **4de** were obtained as a colourless oil (87% yield)

R_f (pentane): 0.22

[7] R. Ghosh and A. Sarkar, *J. Org. Chem.*, 2010, **75**, 8283-8286.

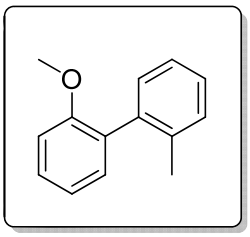
[8] C. Liu, Q. Ni, P. Hu and J. Qiu, *Org. Biomol. Chem.*, 2011, **9**, 1054-1060.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 – 7.38 (m, 5H, *J* = 13.9, 5.6 Hz), 7.28 (d, 1H, *J* = 7.0 Hz), 7.23 – 7.05 (m, 2H), 3.92 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.39, 138.43, 137.39, 130.81, 130.78, 130.16, 128.43, 127.79, 127.63, 126.61, 120.69, 111.07, 55.42, 21.48.

MS (EI) t_R=8.89 min; m/z: 198, 183 (=$[M\text{-}CH_3]^{+\cdot}$, 51%), 165 (=$[M\text{-}OCH_3]^{+\cdot}$ and $[H]^{+\cdot}$, 4%)

I. 2-methoxy-2'-methyl-1,1'-biphenyl (4df) [19853-12-4][9]



Following typical procedure B using 1 mmol of 1-iodo-2-methoxybenzene **2d** and 1.5 mmol of 1-iodo-2-methylbenzene **2f**, 161 mg of **4df** were obtained as a colourless oil (81% yield)

Following typical procedure B using 1 mmol of 1-iodo-2-methylbenzene **2f** and 1.5 mmol of 1-iodo-2-methoxybenzene **2d**, 78 mg of **4df** were obtained as a colourless oil (39% yield)

R_f (pentane): 0.12

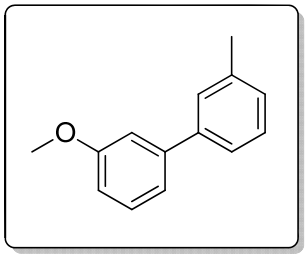
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 – 7.42 (m, 1H), 7.42 – 7.23 (m, 5H), 7.20 – 7.03 (m, 2H), 3.86 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.53, 138.58, 136.74, 130.93, 130.78, 129.94, 129.51, 128.50, 127.23, 125.38, 120.38, 110.57, 55.29, 19.87.

MS (EI) t_R=8.06 min; m/z: 198, 183 (=$[M\text{-}CH_3]^{+\cdot}$, 40%), 165 (=$[M\text{-}OCH_3]^{+\cdot}$ and $[H]^{+\cdot}$, 52%)

[9] L. Ackermann, A. R. Kapdi, S. Fenner, C. Kornhaass and C. Schulzke, *Chem. Eur. J.*, 2011, **17**, 2965-2971.

J. 3-methoxy-3'-methyl-1,1'-biphenyl (4ce) [81722-84-1][10]



Following typical procedure B using 1 mmol of 1-iodo-3-methoxybenzene **2c** and 1.5 mmol of 1-iodo-3-methylbenzene **2e**, 159 mg of **4ce** were obtained as a white colourless oil (80% yield)

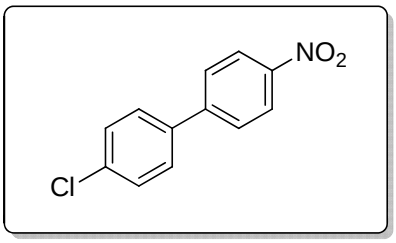
R_f (pentane): 0.23

^{1}H NMR (300 MH, 3Hz, $CDCl_3$): δ 7.57 – 7.36 (m, 4H), 7.32 – 7.18 (m, 3H), 6.98 (d, 1H, *J* = 8.2 Hz), 3.94 (s, 3H), 2.51 (s).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.27, 143.26, 141.46, 138.66, 130.05, 129.01, 128.53, 128.35, 124.67, 120.06, 113.24, 112.97, 55.61, 21.90.

MS (EI) t_R=8.81 min; m/z: 198, 183 (=$[M\text{-}CH_3]^{+\cdot}$, 4%), 167 (=$[M\text{-}OCH_3]^{+\cdot}$, 19%)

K. 4-chloro-4'-nitro-1,1'-biphenyl (4gh) [6242-97-3][11]



Following typical procedure B using 1 mmol of 1-chloro-4-iodobenzene **2g** and 1.5 mmol of 1-iodo-4-nitrobenzene **2h**, 190 mg of **4gh** were obtained as a white crystalline solid (78% yield)

m.p. : 140 °C

R_f (pentane): 0.23

---

[10] R. Ghosh and A. Sarkar, *J. Org. Chem.*, 2010, **75**, 8283-8286.

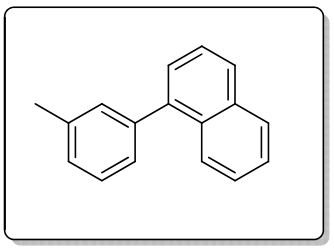
[11] N. Hoshiya, M. Shimoda, H. Yoshikawa, Y. Yamashita, S. Shuto and M. Arisawa, *J Am. Chem. Soc.*, 2010, **132**, 7270-7272.

^{1}H NMR (300MHz, $CDCl_3$): δ 8.35 – 8.26 (m, 2H), 7.76 – 7.66 (m, 2H), 7.61 – 7.51 (m, 2H), 7.51 – 7.42 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.30, 137.17, 135.25, 129.36, 128.61, 127.66, 124.20.

MS (EI) t_R=10.05 min; m/z: 233 (=$[M]^{+\cdot}$, 100%)

L. 1-(m-tolyl)naphthalene (4ei) [27331-44-8][12]



Following typical procedure B using 1 mmol of 1-iodo-3-methylbenzene **2e** and 1.5 mmol of 1-iodonaphthalene **2i**, 159 mg of **4ei** were obtained as a white colourless oil (73% yield)

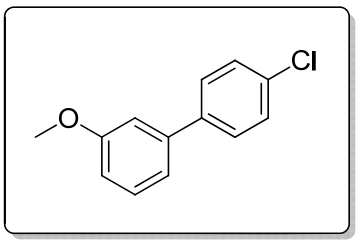
R_f (pentane): 0.50

^{1}H NMR (300MHz, $CDCl_3$): δ 7.97 – 7.88 (m, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.34 (m, 5H), 7.34 – 7.30 (m, 1H), 7.27 (d, *J* = 15.1 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 140.67, 140.35, 137.74, 133.76, 131.64, 130.73, 128.19, 128.08, 127.90, 127.47, 127.13, 126.79, 126.07, 125.89, 125.65, 125.30, 21.45.

MS (EI) t_R=9.60 min; m/z: 218 (=$[M]^{+\cdot}$, 100%), 203 (=$[M\text{-}CH_3]^{+\cdot}$, 100%)

M. 4'-chloro-3-methoxy-1,1'-biphenyl (4cg) [66175-36-8][13]



[12] K. W. Quasdorf, A. Antoft-Finch, P. Liu, A. L. Silberstein, A. Komaromi, T. Blackburn, S. D. Ramgren, K. N. Houk, V. Snieckus and N. K. Garg, *J. Am. Chem. Soc,* 2011, **133**, 6352-6363.

[13] S. E. Denmark, R. C. Smith, W.-T. T. Chang and J. M. Muhuhi, *J. Am. Chem. Soc*, 2009, **131**, 3104-3118

Following typical procedure B using 1 mmol of 1-iodo-3-methoxybenzene **2c** and 1.5 mmol of 1-chloro-4-iodobenzene **2g**, 181 mg of **4cg** were obtained as a white colourless oil (83% yield)

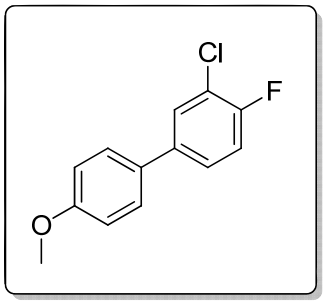
R_f (pentane): 0.18

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.51 (m, 2H), 7.48 – 7.36 (m, 3H), 7.22 – 7.12 (m, 2H), 6.96 (ddd, 1H, *J* = 8.2, 2.6, 0.9 Hz), 3.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.92, 141.32, 139.38, 133.36, 129.80, 128.77, 128.29, 119.34, 112.77, 112.71, 55.13.

MS (EI) t_R=9.17 min; m/z: 218 (=$[M]^{+\cdot}$, 100%)

N. 3-chloro-4-fluoro-4'-methoxy-1,1'-biphenyl (4aj) [22510-30-1][14]



Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 2-chloro-1-fluoro-4-iodobenzene **2j**, 161 mg of **4aj** were obtained as a colourless oil (68% yield)

R_f (pentane): 0.18

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, 1H, *J* = 7.0, 2.3 Hz), 7.49 – 7.42 (m, 2H), 7.38 (ddd, 1H, *J* = 8.6, 4.6, 2.3 Hz), 7.17 (t, 1H, *J* = 8.7 Hz), 7.02 – 6.94 (m, 2H), 3.86 (s, 3H).

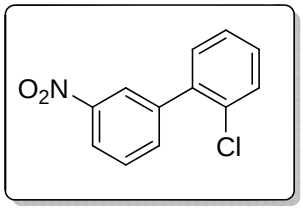
^{13}C NMR (75 MHz, $CDCl_3$): δ 159.45, 131.40, 128.63, 127.96, 127.95, 126.24, 126.15, 116.79, 116.51, 114.30, 55.27.

^{19}F NMR (282 MHz, $CDCl_3$): δ -119.20 (s, 1F).

[14] Application: ZA Pat., 6701021, 1968.

MS (EI) t_R=9.23 min; m/z: 236 (=$[M]^{+\cdot}$, 100%), 221 (=$[M\text{-}CH3]^{+\cdot}$, 48%), 201 (=$[M\text{-}Cl]^{+\cdot}$, 4%)

O. 2-chloro-3'-nitro-1,1'-biphenyl (4kl) [1019-61-0][15]



Following typical procedure B using 1 mmol of 1-iodo-3-nitrobenzene **2k** and 1.5 mmol of 1-chloro-2-iodobenzene **2l**, 149 mg of **4kl** were obtained as a colourless oil (64% yield)

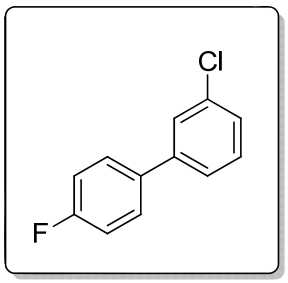
R_f (pentane): 0.125

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 – 8.29 (m, 1H), 8.24 (ddd, 1H, *J* = 8.2, 2.3, 1.1 Hz), 7.79 (ddd, 1H, *J* = 7.7, 1.7, 1.1 Hz), 7.61 (t, 1H, *J* = 7.8 Hz), 7.56 – 7.46 (m, 1H), 7.42 – 7.31 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.98, 140.76, 137.93, 135.59, 132.27, 131.06, 130.16, 129.63, 128.98, 127.18, 124.41, 122.49.

MS (EI) t_R=9.58 min; m/z: 233 (=$[M]^{+\cdot}$, 100%), 187 (=$[M\text{-}NO_2]^{+\cdot}$, 31%), 152 (=$[M\text{-}NO_2\text{-}Cl\text{-}H]^{+\cdot}$, 100%),

P. 3-chloro-4'-fluoro-1,1'-biphenyl (4mn) [80254-79-1][16]



Following typical procedure B using 1 mmol of 1-fluoro-4-iodobenzene **2m** and 1.5 mmol of 1-chloro-3-iodobenzene **2n**, 181 mg of **4mn** were obtained as a colourless oil (88% yield)

R_f (pentane): 0.74

---

[15] D. H. Hey, S. Orman and G. H. Williams, *J. Chem. Soc.* 1965, 101-110.

[16] J. M. A. Miguez, L. A. Adrio, A. Sousa-Pedrares, J. M. Vila and K. K. Hii, *J. Org. Chem.*, 2007, **72**, 7771-7774.

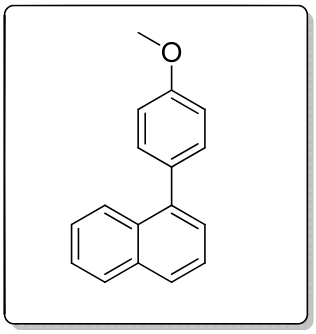
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.48 (m, 3H), 7.47 – 7.31 (m, 3H), 7.22 – 7.11 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.31, 161.03, 141.91, 135.80, 135.76, 134.64, 129.96, 128.66, 128.55, 127.19, 127.04, 125.04, 125.03, 115.85, 115.57.

^{19}F NMR (282 MHz, $CDCl_3$): δ -114.72 (s, 1F).

MS (EI) t_R=8.14 min; m/z: 206, 170 (=$[M-H]^{+\cdot}$ and $[Cl]^-$, 61%)

Q. 1-(4-methoxyphenyl)naphthalene (4ai) [27331-33-5][17]



Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 1-iodonaphthalene **2i**, 194 mg of **4ai** were obtained as a white crystalline solid (89% yield)

m.p. : 115 °C

R_f (pentane): 0.125

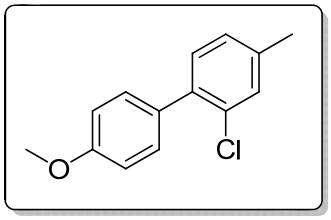
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (t, 2H, *J* = 9.1 Hz), 7.85 (d, 1H, *J* = 8.2 Hz), 7.58 – 7.39 (m, 6H), 7.09 – 7.01 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.92, 139.88, 133.81, 133.10, 131.81, 131.09, 128.23, 127.31, 126.88, 126.05, 125.89, 125.67, 125.38, 113.69, 55.34.

MS (EI) t_R=10.19 min; m/z: 234, 219 (=$[M-CH_3]^{+\cdot}$, 30%)

[17] L.-G. Xie and Z.-X. Wang, *Chem. Eur. J.*, 2011, **17**, 4972-4975.

R. 2-chloro-4'-methoxy-4-methyl-1,1'-biphenyl (4ao)



Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 2-chloro-1-iodo-4-methylbenzene **2o**, 194 mg of **4ao** were obtained as a white crystalline solid (84% yield)

m.p. : 90 °C

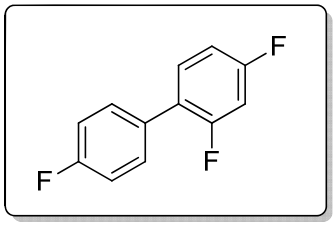
R_f (pentane): 0.125

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 – 7.45 (m, 3H), 7.34 (dd, 1H, *J* = 7.9, 1.9 Hz), 7.26 (d, 2H, *J* = 7.9 Hz), 7.01 – 6.93 (m, 2H), 3.85 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.31, 140.04, 134.67, 134.15, 132.28, 131.15, 127.93, 127.12, 124.80, 114.25, 55.35, 19.65.

MS (EI) t_R=9.68 min; m/z: 232, 217 (=$[M\text{-}CH_3]^{+\cdot}$, 42%)

S. 2,4,4'-trifluoro-1,1'-biphenyl (4mp) [872545-53-4][18]



Following typical procedure B using 1 mmol of 1-fluoro-4-iodobenzene **2m** and 1.5 mmol of 2,4-difluoro-1-iodobenzene **2p**, 127 mg of **4mp** were obtained as a white crystalline solid (61% yield)

m.p. : 86 °C

R_f (pentane): 0.40

[18] C. Heiss, F. Leroux and M. Schlosser, *Eur. J. Org. Chem.*, 2005, 5242-5247.

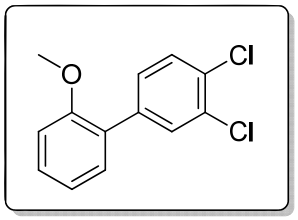
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.42 (m, 2H), 7.42 – 7.31 (m, 1H), 7.20 – 7.08 (m, 2H), 7.02 – 6.86 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 131.37, 130.63, 130.60, 130.53, 130.48, 124.29, 115.64, 115.35, 111.77, 111.72, 111.49, 111.44, 104.76, 104.40, 104.07.

^{19}F NMR (282 MHz, $CDCl_3$): δ -111.29 (d, *J* = 7.5 Hz, 1F), -113.72 (d, *J* = 7.5 Hz, 1F), -114.44 (s, 1F).

MS (EI) t_R=7.10 min; m/z: 208, 188 (=$[M\text{-}F\text{-}H]^{+\cdot}$, 19%)

T. 3',4'-dichloro-2-methoxy-1,1'-biphenyl (4dq) [5243-10-7][19]



Following typical procedure B using 1 mmol of 1-iodo-2-methoxybenzene **2d** and 1.5 mmol of 1,2-dichloro-4-iodobenzene **2q**, 245 mg of **4dq** were obtained as a colourless oil (97% yield)

R_f (pentane): 0.15

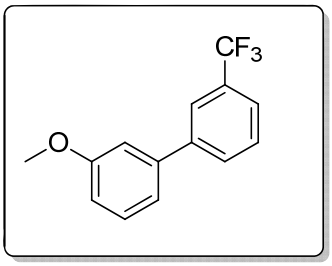
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.31 (dd, *J* = 11.8, 1.8 Hz, 1H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.02 – 6.96 (m, 1H), 3.83 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.27, 138.49, 131.92, 131.35, 130.89, 130.51, 129.85, 129.46, 128.91, 128.16, 120.94, 111.27, 55.54.

MS (EI) t_R=9.53 min; m/z: 252, 217 (=$[M\text{-}H]^{+\cdot}$ and $[Cl]^{-}$, 9%), 202 (=$[M\text{-}Cl\text{-}CH_3]^{+\cdot}$, 100%)

[19] Patent application (1965), GB 1014554 19651231.

U. 3-methoxy-3'-(trifluoromethyl)-1,1'-biphenyl (4cr) [352032-26-9][20]



Following typical procedure B using 1 mmol of 1-iodo-3-methoxybenzene **2c** and 1.5 mmol of 1-iodo-3-(trifluoromethyl)benzene **2r**, 226 mg of **4cr** were obtained as a colourless oil (90% yield)

R_f (pentane/dichloromethane 90:10): 0.29

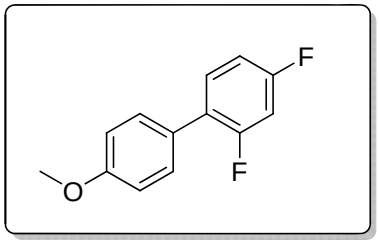
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.57 (dt, *J* = 15.2, 7.8 Hz, 2H), 7.39 (t, *J* = 7.9, 1H), 7.18 (ddd, *J* = 7.7, 1.7, 1.0, 1H), 7.14 – 7.10 (m, 1H), 6.95 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.08, 141.87, 141.25, 130.46, 130.02, 129.18, 124.00, 119.65, 113.33, 113.00, 55.37.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.61 (s, 3F)

MS (EI) t_R=8.22 min; m/z: 252, 222 (=$[M\text{-}OCH_3]^{+\cdot}$ and $[H]^{+\cdot}$, 22%), 183 (=$[M\text{-}CF_3]^{+\cdot}$, 15%)

V. 2,4-difluoro-4'-methoxy-1,1'-biphenyl (4ap) [90101-30-7][21]



[20] T. Nakamura, H. Kinoshita, H. Shinokubo and K. Oshima, *Org. Lett*, 2002, **4**, 3165-3167.

[21] T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc*, 2005, **127**, 4685-4696.

Following typical procedure B using 1 mmol of 1-iodo-4-methoxybenzene **2a** and 1.5 mmol of 2,4-difluoro-1-iodobenzene **2p**, 178 mg of **4ap** were obtained as a white crystalline solid (81% yield)

m.p. : 75 °C

R_f (pentane): 0.125

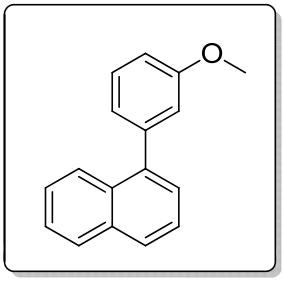
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 1H), 7.03 – 6.95 (m, 2H), 6.95 – 6.85 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.24, 131.20, 131.13, 131.07, 131.01, 130.02, 129.98, 127.32, 113.98, 111.58, 111.53, 111.30, 111.25, 104.61, 104.28, 104.26, 103.92, 55.30.

^{19}F NMR (282 MHz, $CDCl_3$): δ –112.40 (d, *J* = 7.1 Hz, 1F), -113.86 (d, *J* = 7.1 Hz, 1F).

MS (EI) t_R=8.24 min; m/z: 220, 205 (=$[M\text{-}CH_3]^{+\cdot}$, 42%), 188 (=$[M\text{-}OCH_3]^{+\cdot}$ and $[H]^{+\cdot}$, 7%), 151 (=$[M\text{-}OCH_3]^{+\cdot}$ and $2[F]^-$, 31%)

W. 1-(3-methoxyphenyl)naphthalene(4ci) [27331-43-7][22]



Following typical procedure B using 1 mmol of 1-iodo-3-methoxybenzene **2c** and 1.5 mmol of 1-iodonaphthalene **2i**, 185 mg of **4ci** were obtained as a colourless oil (79% yield)

R_f (pentane): 0.10

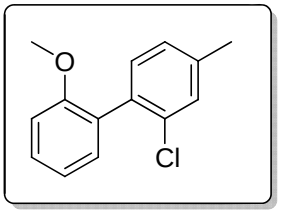
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (ddd, *J* = 20.3, 7.0, 4.4 Hz, 3H), 7.58 – 7.35 (m, 5H), 7.09 (ddd, *J* = 7.5, 1.5, 1.0 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.99 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 3.86 (s, 3H).

[22] C. F. R. A. C. Lima, J. E. Rodriguez-Borges and L. M. N. B. F. Santos, *Tetrahedron*, 2011, **67**, 689-697.

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.44, 142.15, 133.74, 131.56, 129.20, 128.22, 127.67, 126.75, 126.04, 126.01, 125.76, 125.31, 122.57, 115.60, 112.86, 55.31.

MS (EI) t_R=10.09 min; m/z: 234, 218 (=$[M\text{-}CH_3\text{-}H]^{+\cdot}$, 22%), 203 (=$[M\text{-}OCH_3]^{+\cdot}$, 57%)

X. 2-chloro-2'-methoxy-4-methyl-1,1'-biphenyl (4do)



Following typical procedure B using 1 mmol of 1-iodo-2-methoxybenzene **2d** and 1.5 mmol of 2-chloro-1-iodo-4-methylbenzene **2o**, 219 mg of **4do** were obtained as a colourless oil (94% yield)

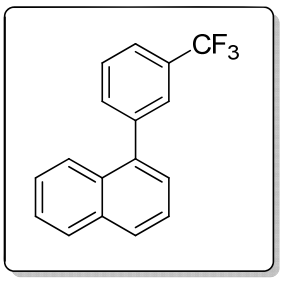
R_f (pentane): 0.125

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 1.6, 1H), 7.37 – 7.29 (m, 2H), 7.27 (dd, *J* = 6.6, 4.9 Hz, 2H), 7.04 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.37, 137.64, 134.49, 133.89, 130.63, 130.43, 129.93, 129.22, 128.89, 127.74, 120.83, 111.18, 55.54, 19.78.

MS (EI) t_R=9.20 min; m/z: 232, 197 (=$[M\text{-}Cl\text{-}H]^{+\cdot}$, 16%),

Y. 1-(3-(trifluoromethyl)phenyl)naphthalene (4ir) [194874-05-0][23]



[23] D. Badone, M. Baroni, R. Cardamone, A. Ielmini and U. Guzzi, *J. Org. Chem.*, 1997, **62**, 7170-7173.

Following typical procedure B using 1 mmol of 1-iodo-3-(trifluoromethyl)benzene **2r** and 1.5 mmol of 1-iodonaphthalene **2i**, 185 mg of **4ir** were obtained as a colourless oil (83% yield)

R_f (pentane): 0.10

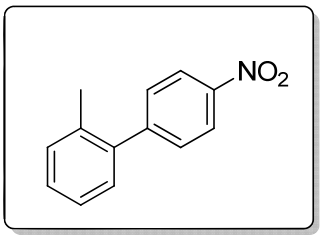
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (td, *J* = 7.8, 4.3 Hz, 2H), 7.82 – 7.75 (m, 2H), 7.75 – 7.66 (m, 2H), 7.66 – 7.51 (m, 3H), 7.51 – 7.45 (m, 1H), 7.43 (dd, *J* = 7.1, 1.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 141.54, 138.58, 133.81, 133.38, 133.36, 131.33, 131.00, 130.57, 128.71, 128.44, 128.35, 127.13, 126.82, 126.77, 126.72, 126.67, 126.46, 126.07, 126.00, 125.38, 125.32, 124.13, 124.08, 124.03, 123.98, 122.46.

^{19}F NMR (282 MHz, $CDCl_3$): δ –62.50 (s, 3F).

MS (EI) t_R=9.05 min; m/z: 272, 203 (=$[M\text{-}CF_3]^{+\cdot}$, 57%)

Z. 2-methyl-4'-nitro-1,1'-biphenyl (4fh) [33350-73-1][24]



Following typical procedure B using 1 mmol of 1-iodo-2-methylbenzene **2f** and 1.5 mmol of 1-iodo-4-nitrobenzene **2h**, 193 mg of **4fh** were obtained as a colourless oil (91% yield)

R_f (pentane/dichloromethane 80:20): 0.29

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 – 8.25 (m, 2H), 7.56 – 7.46 (m, 2H), 7.40 – 7.19 (m, 4H), 2.29 (s, 3H).

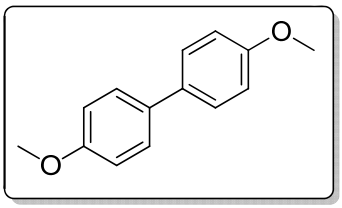
^{13}C NMR (75 MHz, $CDCl_3$): δ 148.65, 146.68, 139.46, 134.91, 130.61, 129.97, 129.28, 128.35, 126.01, 123.26, 20.20.

MS (EI) t_R=9.27 min; m/z: 213

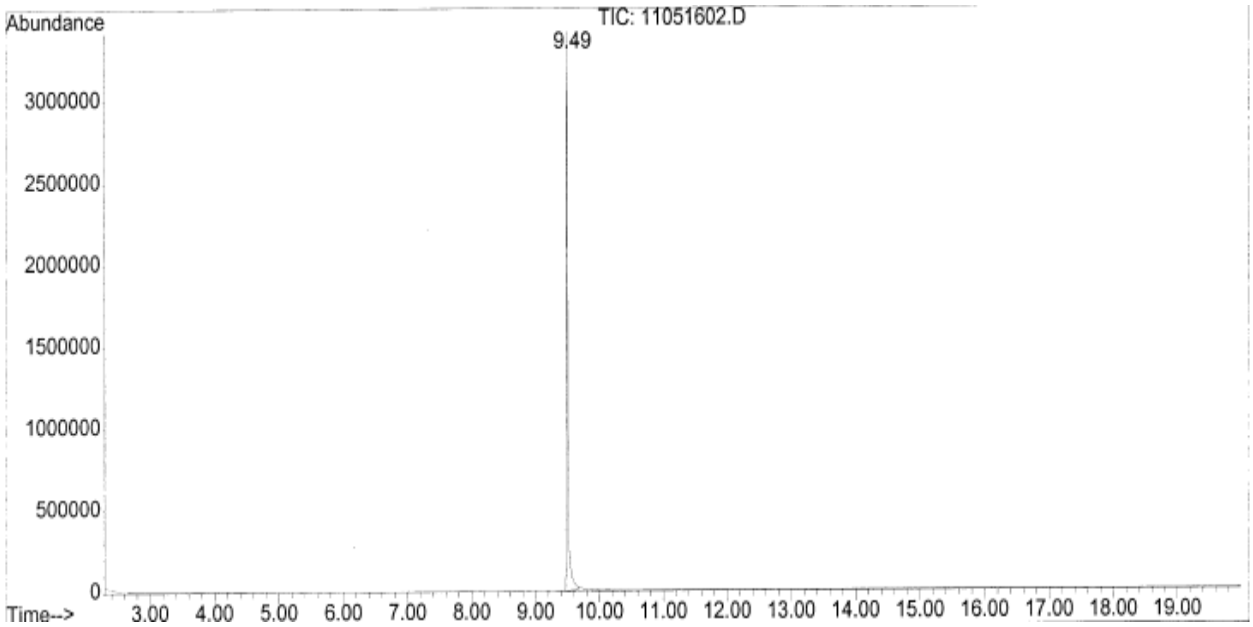
[24] J. L. Bolliger and C. M. Frech, *Chem. Eur. J.*, 2010, **16**, 11072-11081.

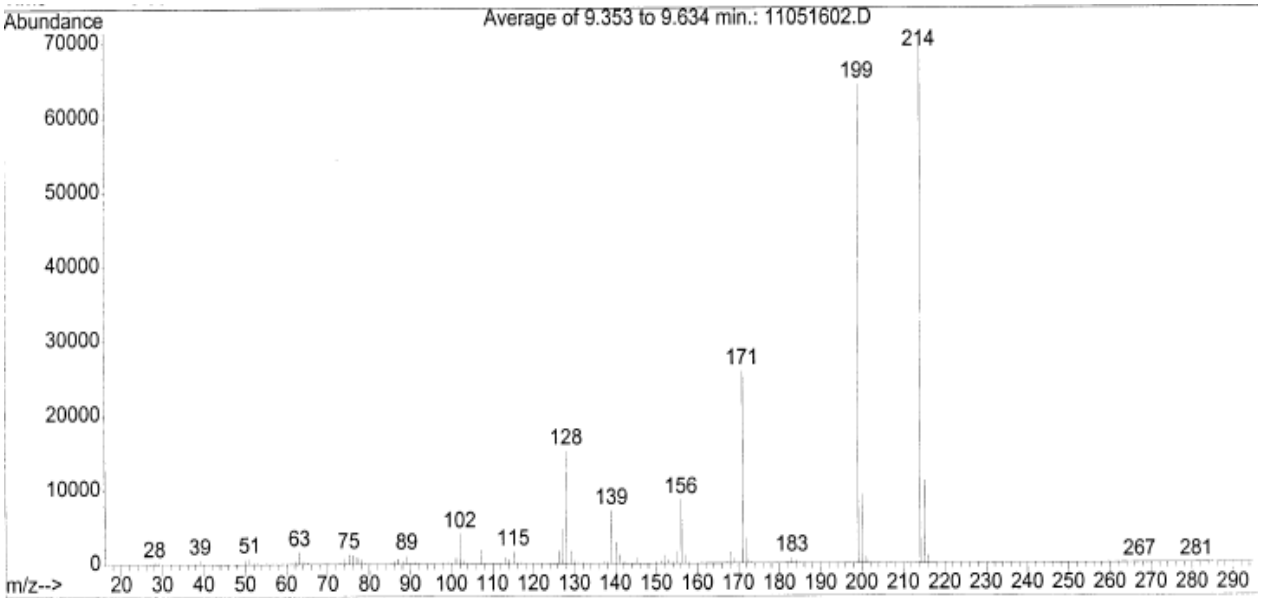
III. Spectra

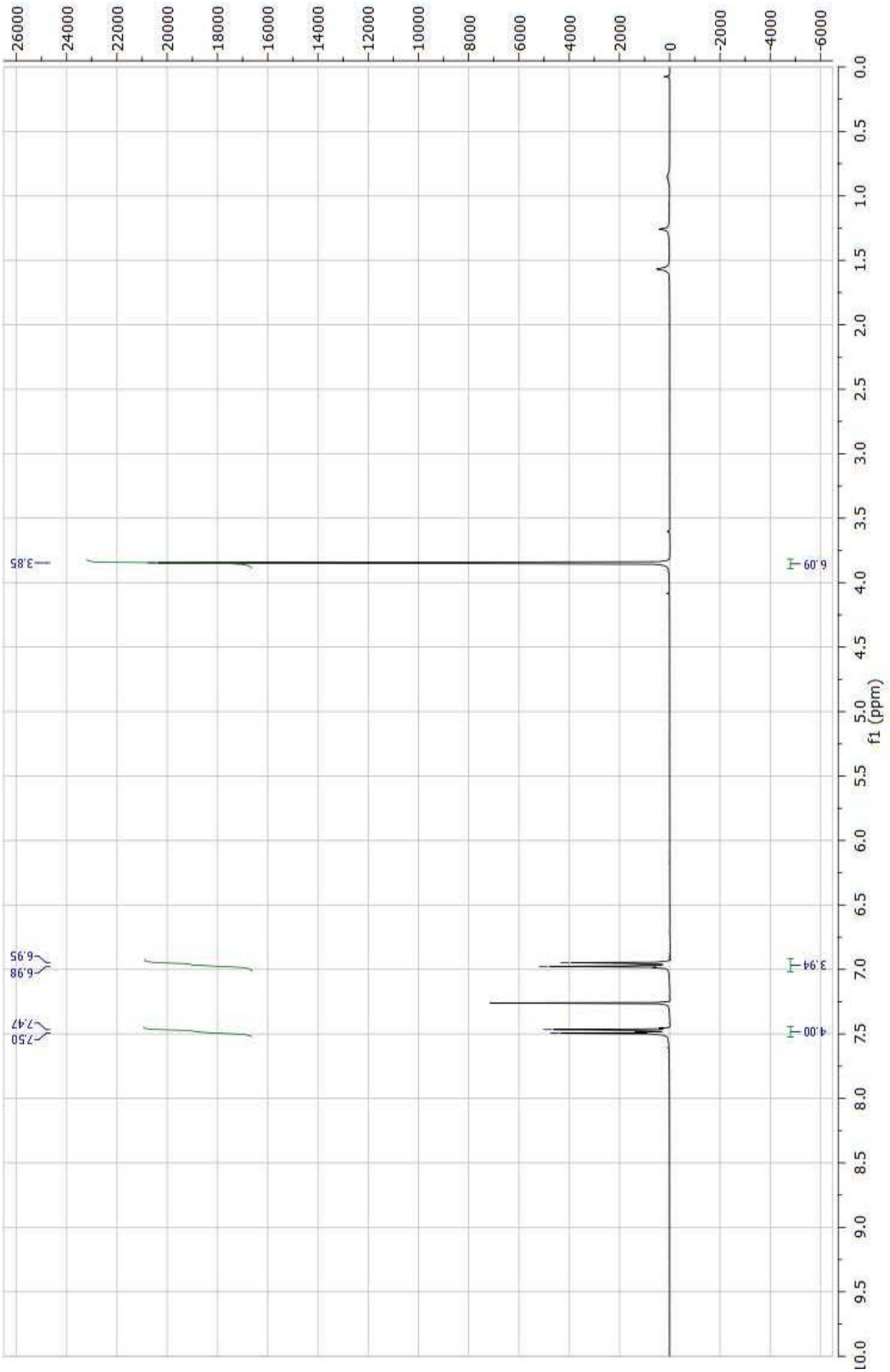
A. 4aa

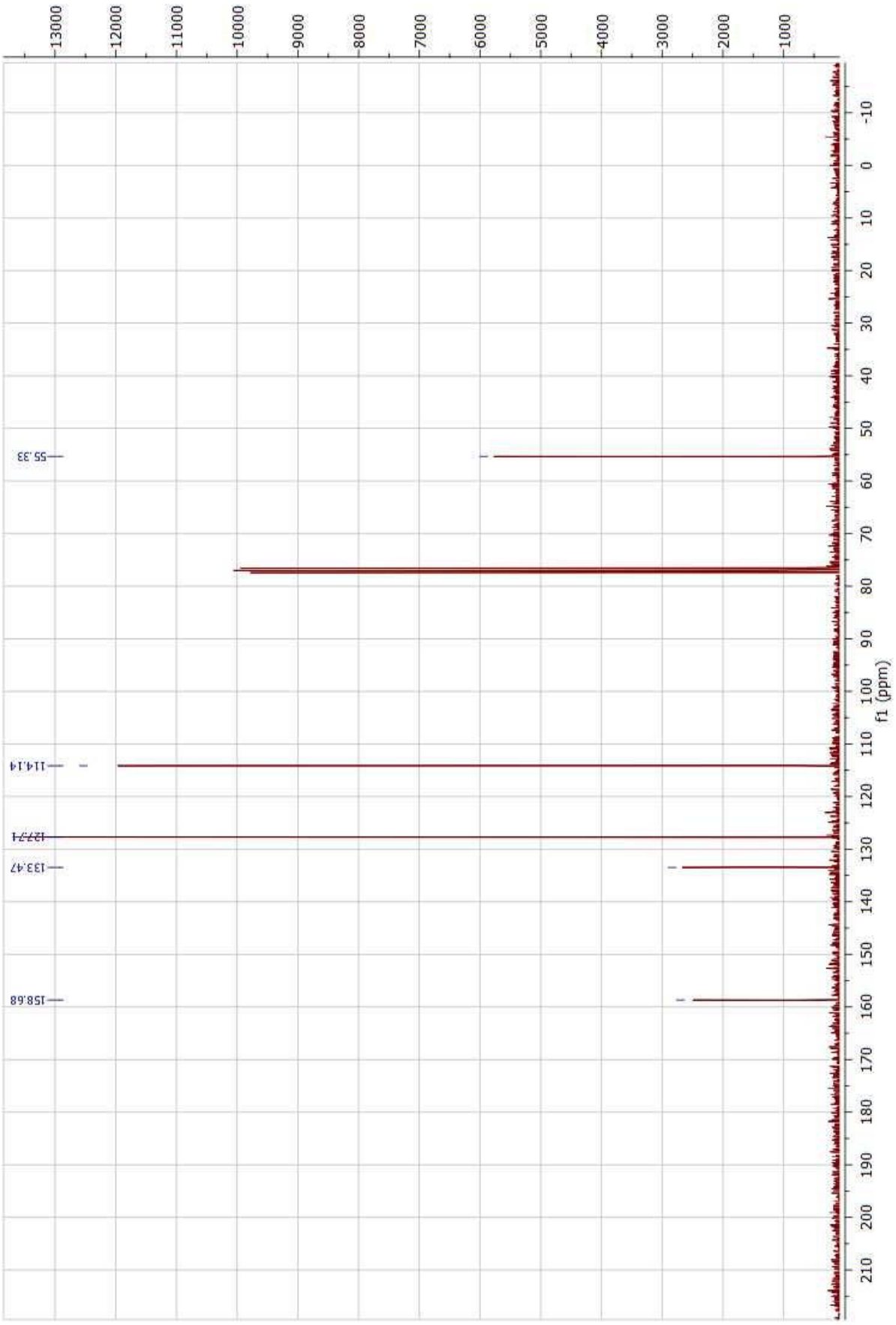


GC/MS Analysis

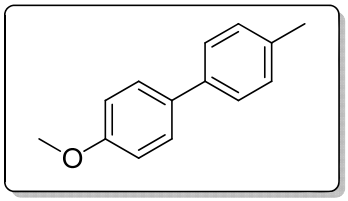




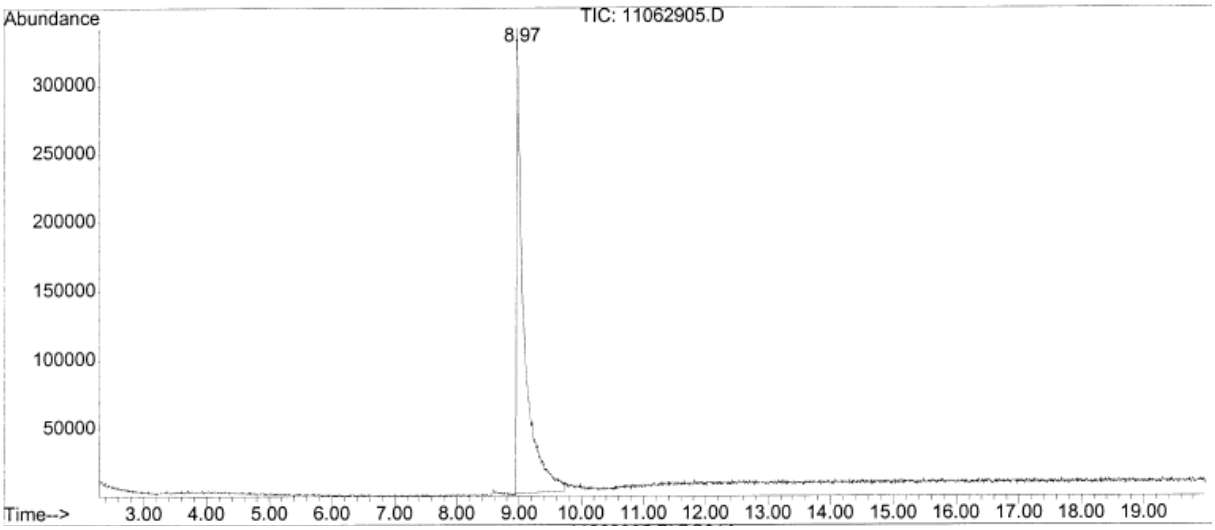

f1 (ppm)
3.85
6.09
6.98
6.95
7.50
7.47
3.94
4.00

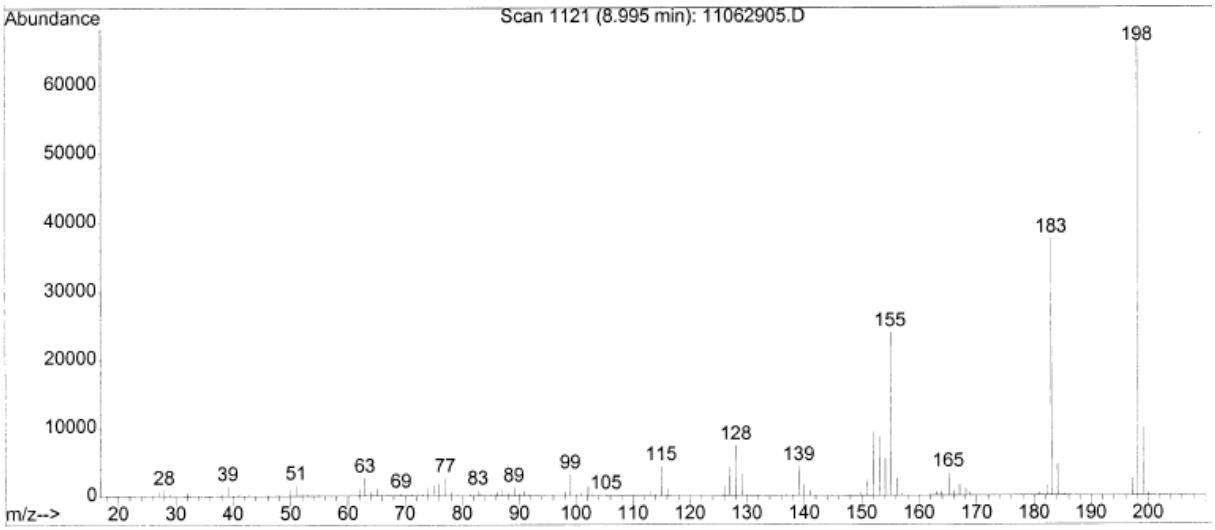

13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
55.33
114.14
127.71
133.47
158.68

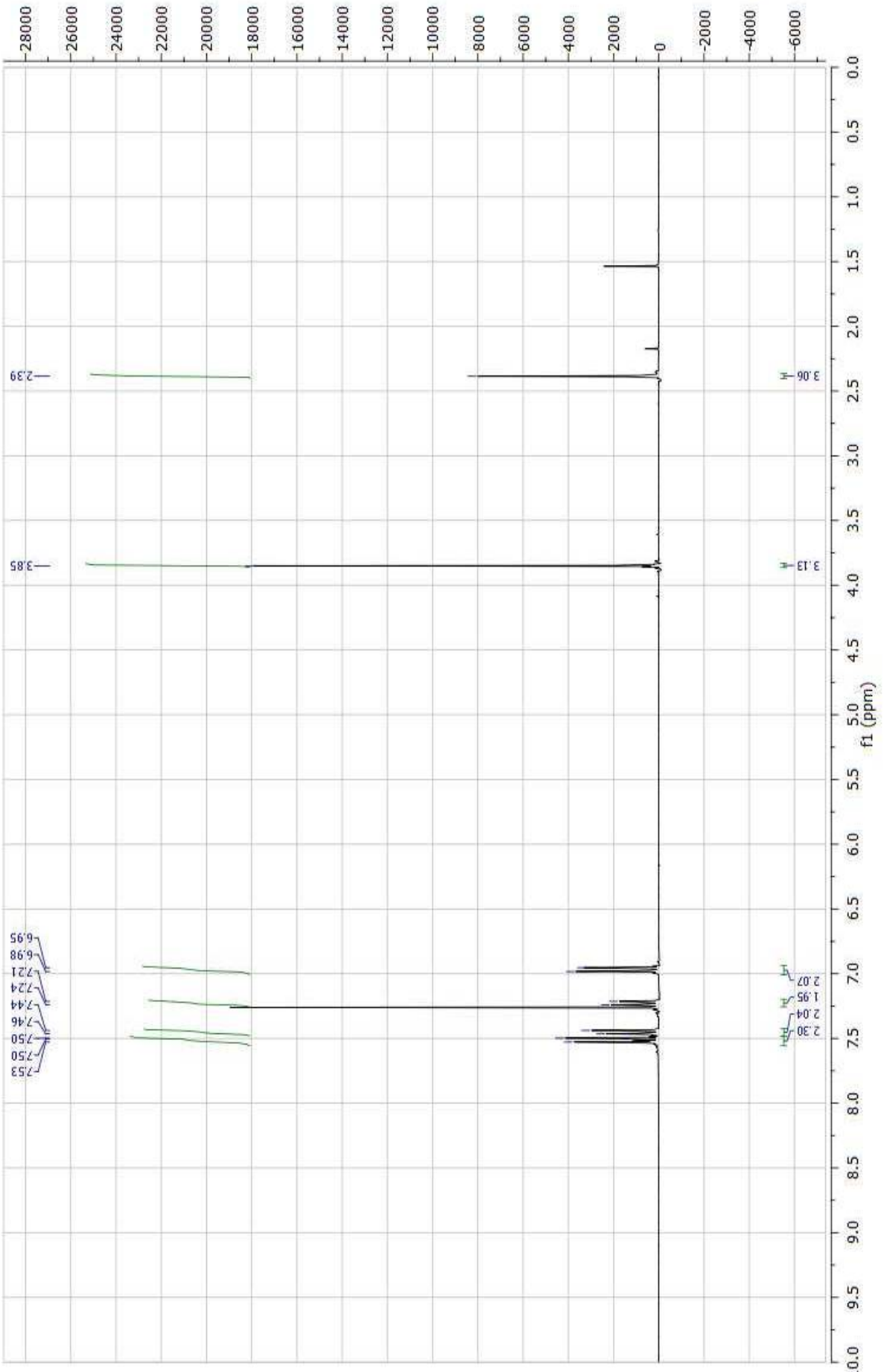
B. 4ab

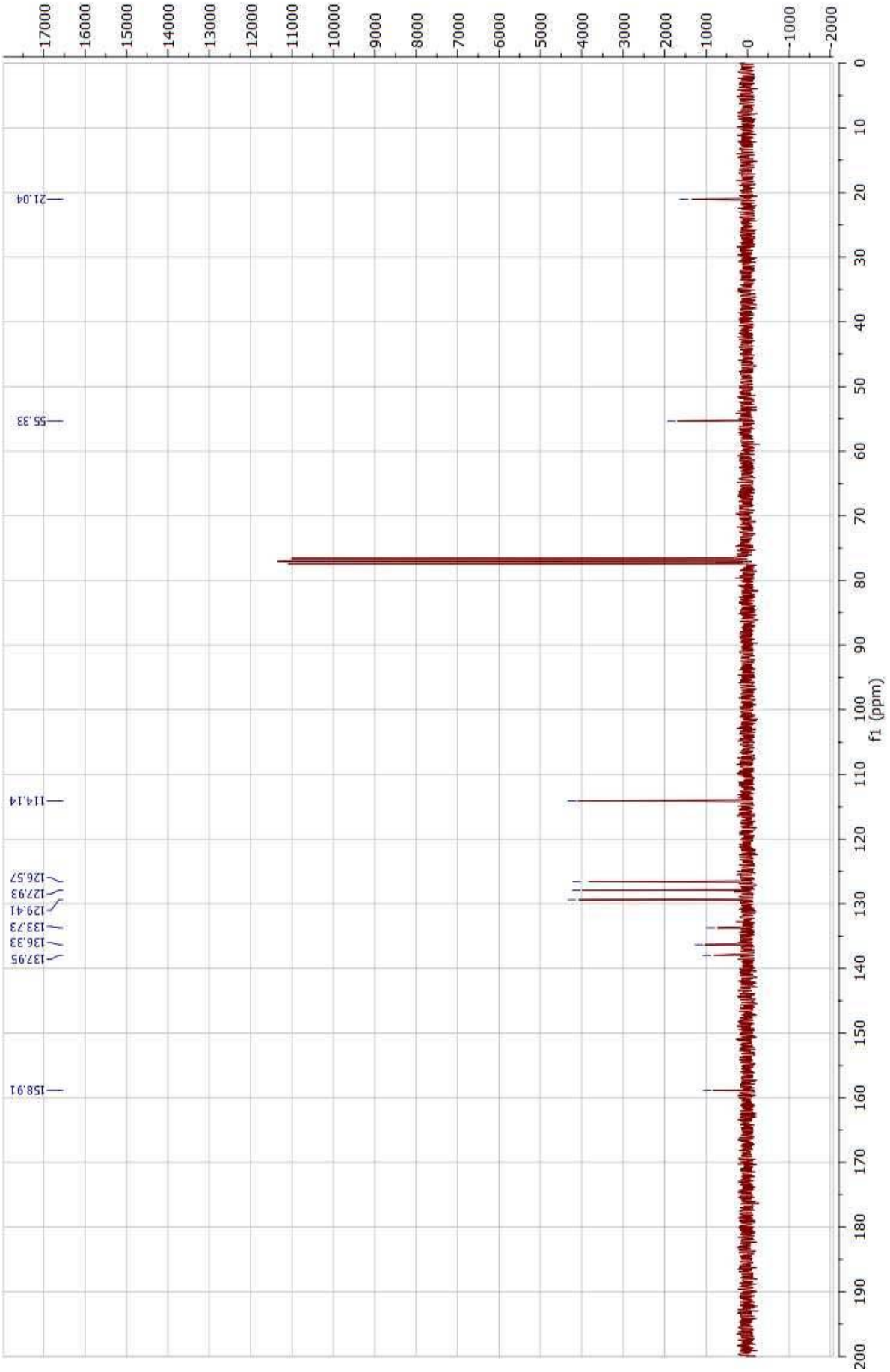


GC/MS Analysis

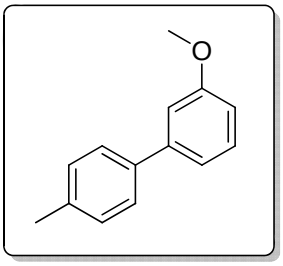




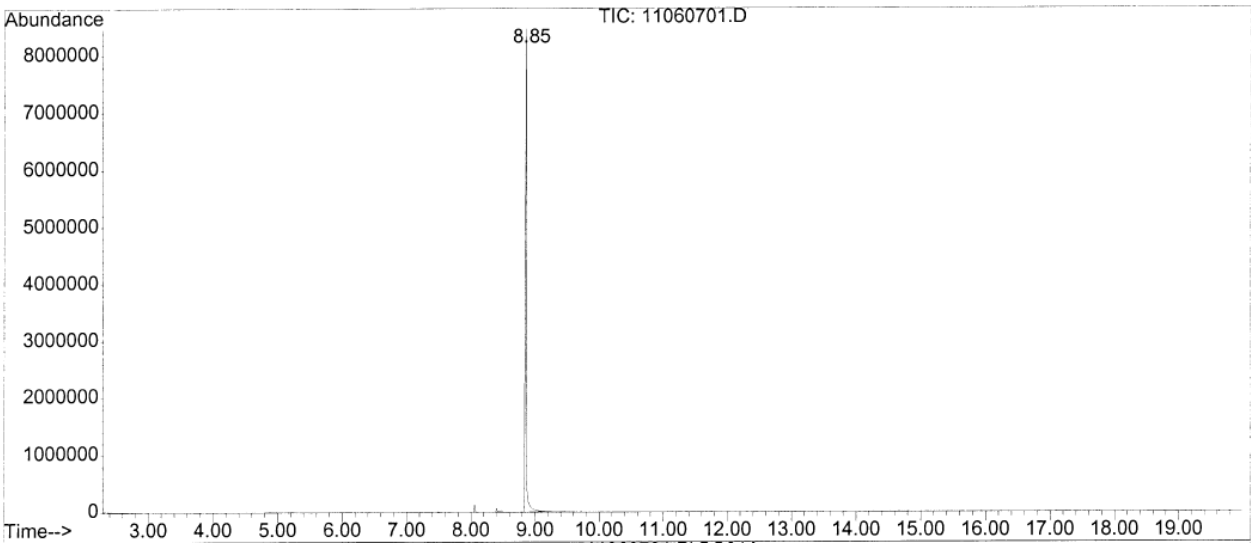

f1 (ppm)
2.39
3.85
6.95
6.98
7.21
7.24
7.44
7.46
7.50
7.50
7.53
3.06
3.13
2.07
1.95
2.04
2.30

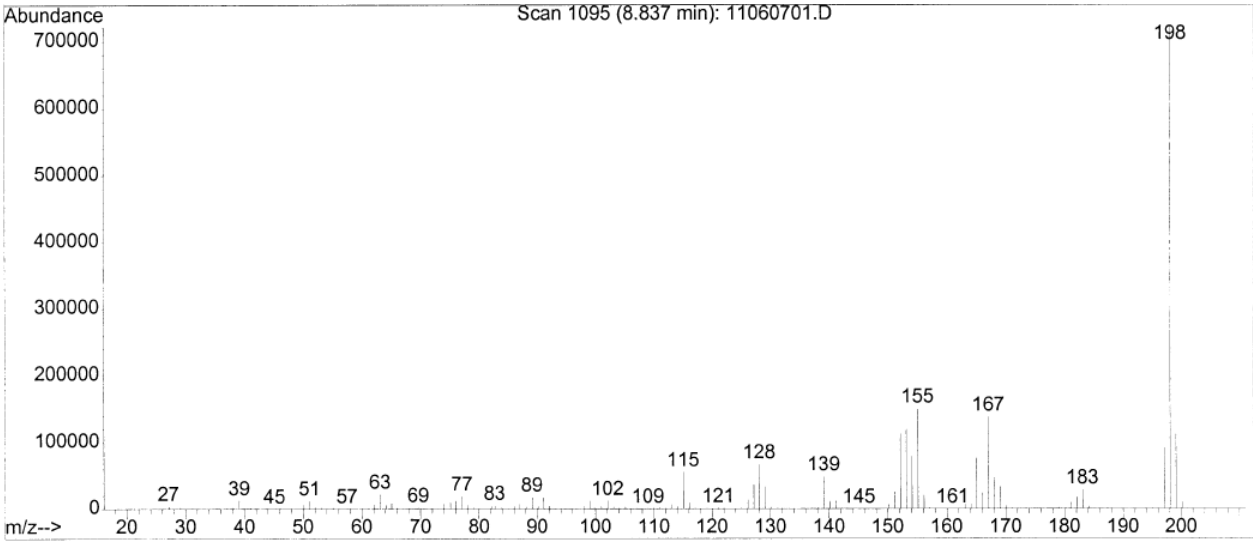

21.04
55.33
114.14
126.57
127.93
129.41
133.73
136.33
137.95
158.91
f1 (ppm)

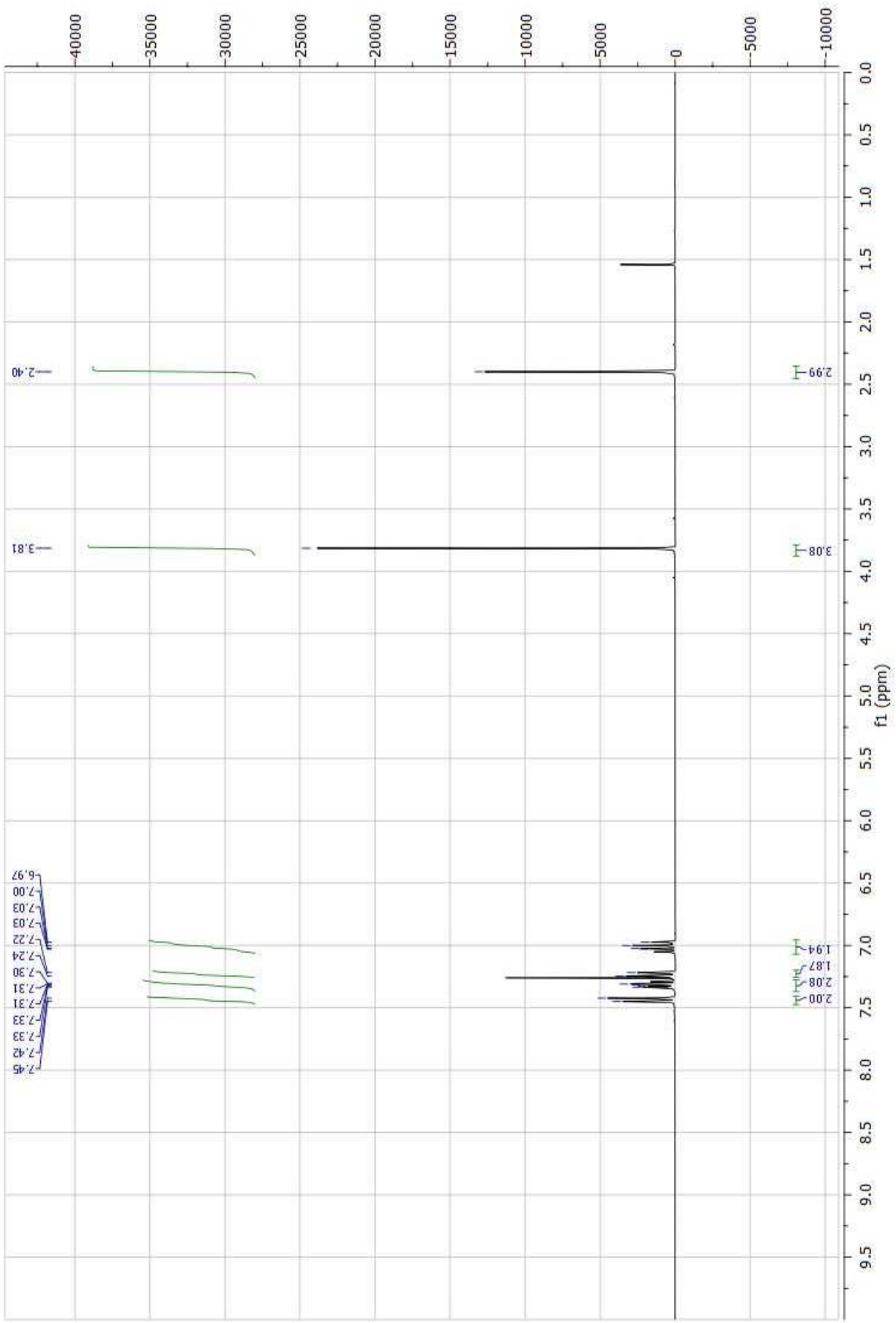
C. 4bc

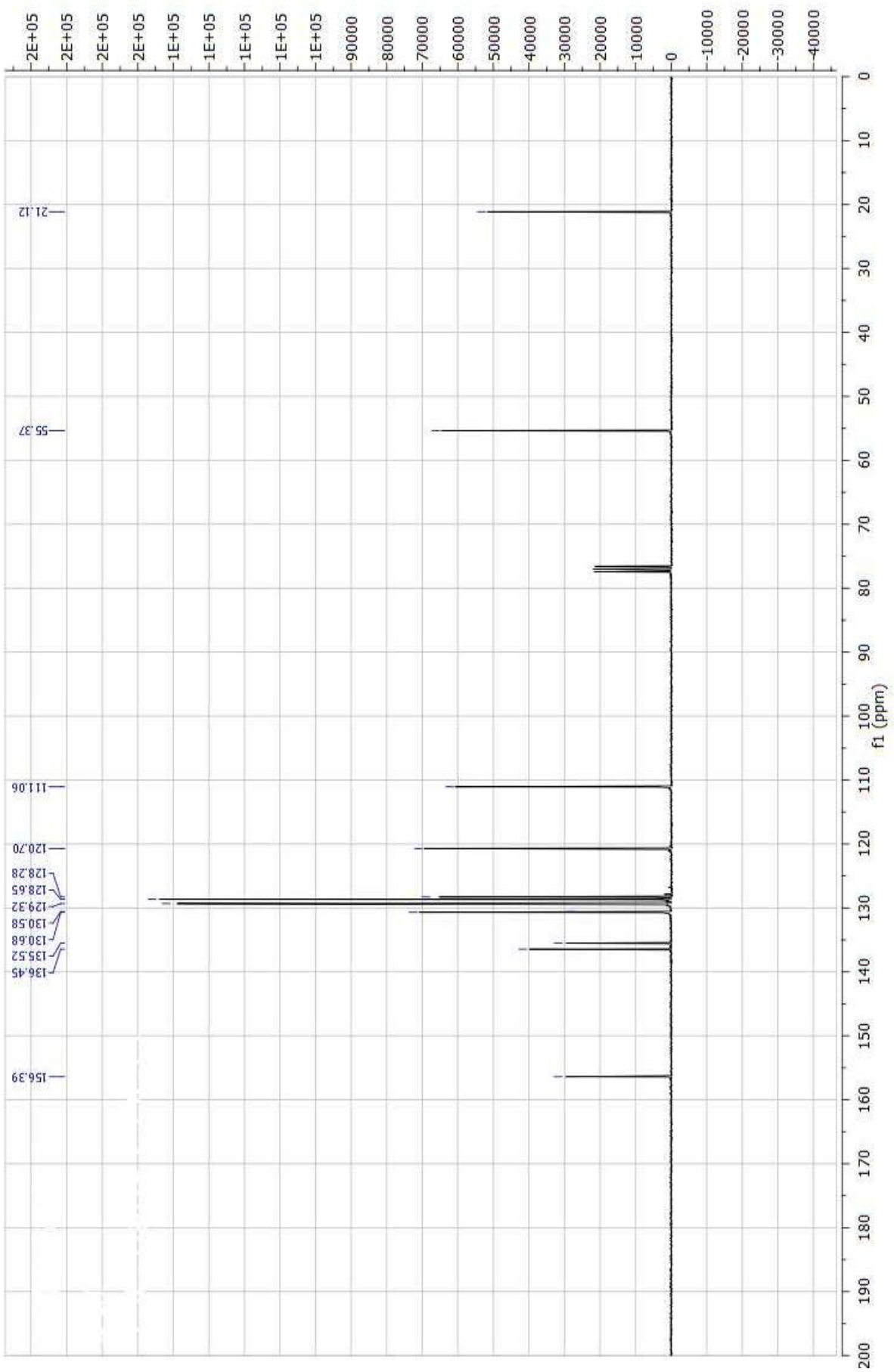


GC/MS Analysis

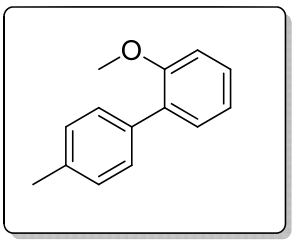




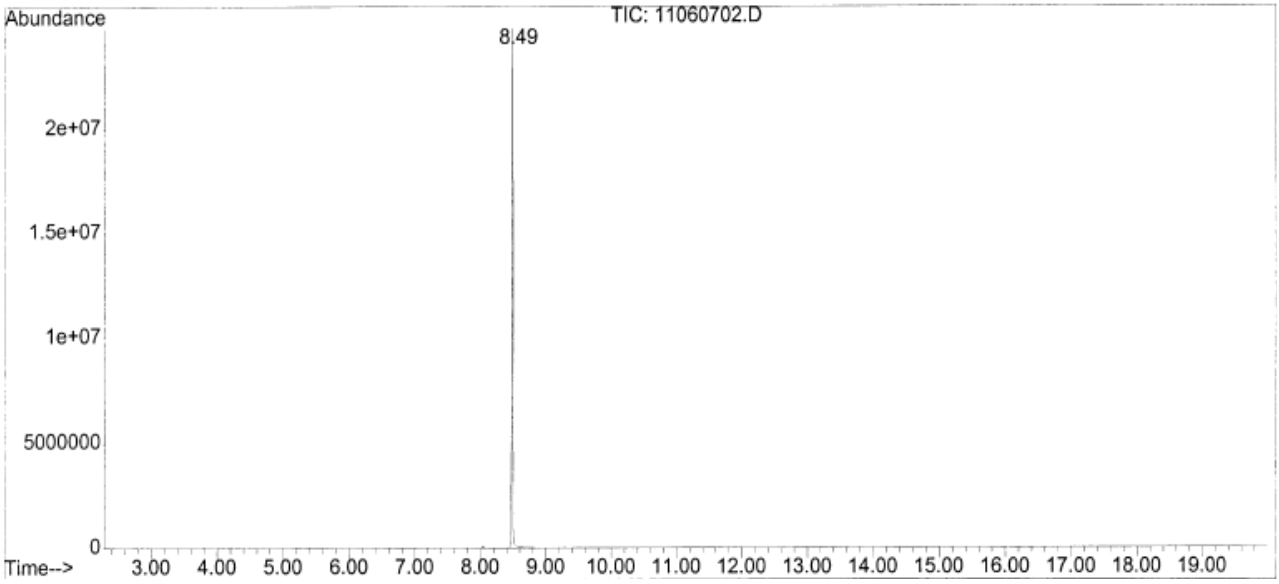

40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)
2.40
3.81
2.99
3.08
1.94
1.87
2.08
2.00
6.97
7.00
7.03
7.03
7.22
7.24
7.30
7.31
7.31
7.33
7.33
7.42
7.45

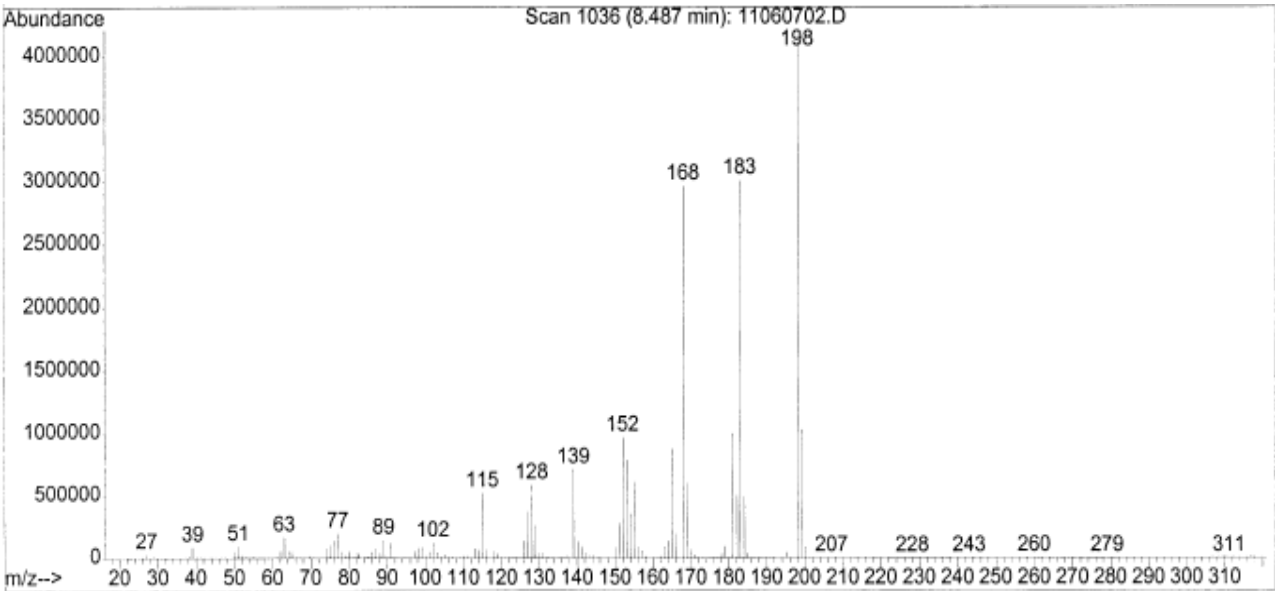

21.12
55.37
111.06
120.70
128.28
128.65
129.32
130.58
130.68
135.52
136.45
156.39
f1 (ppm)

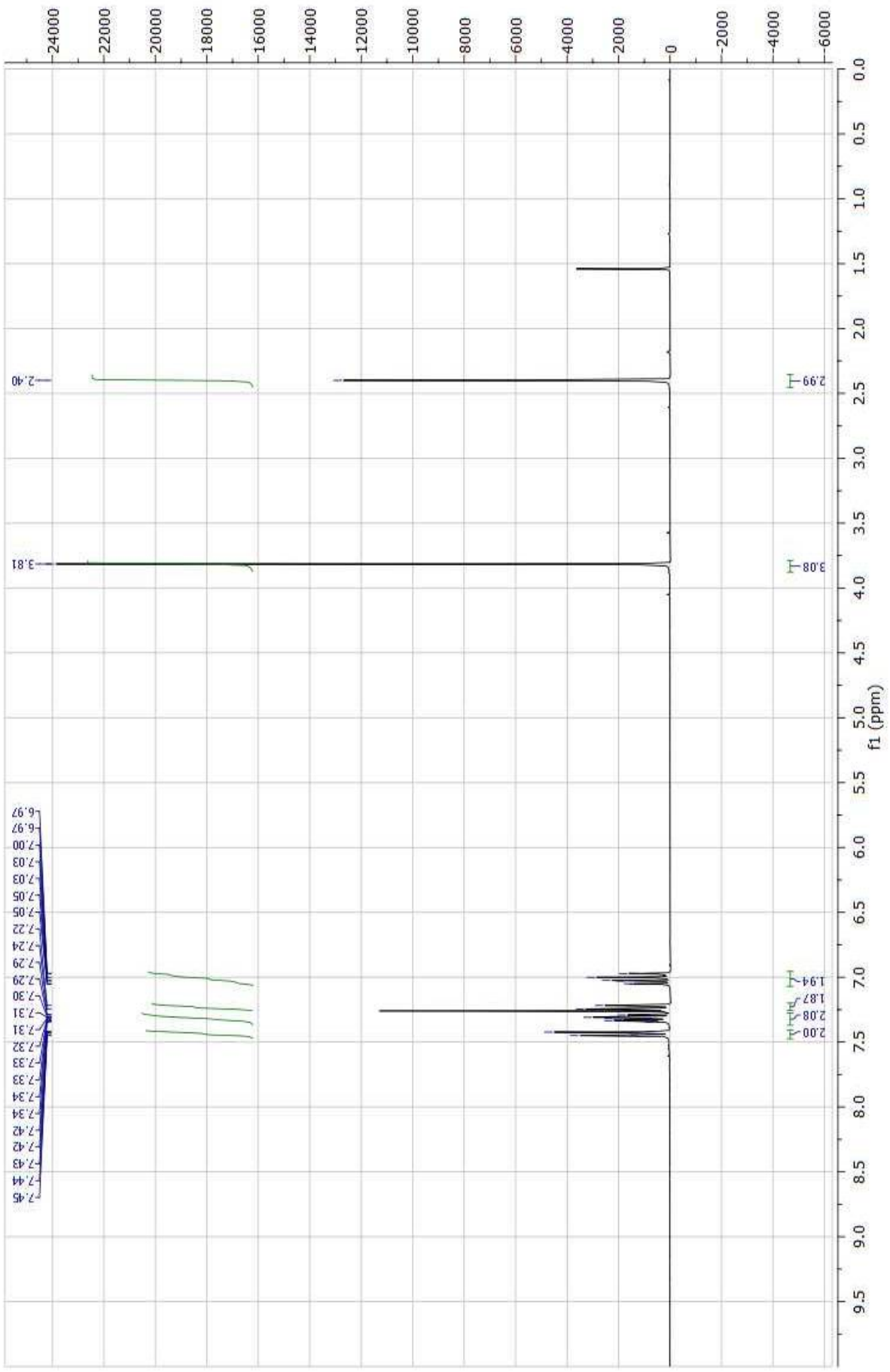
D. 4bd

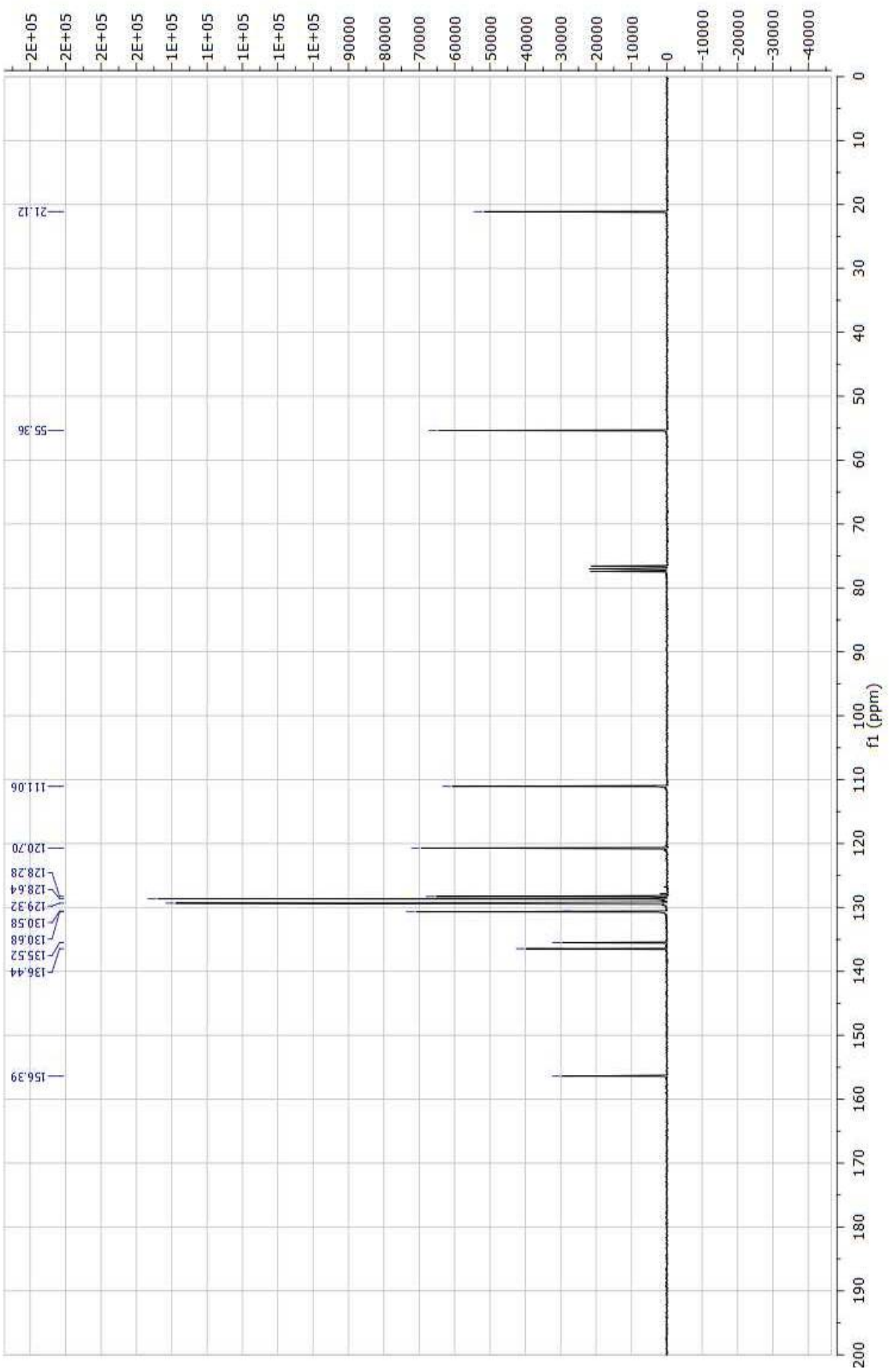


GC/MS Analysis

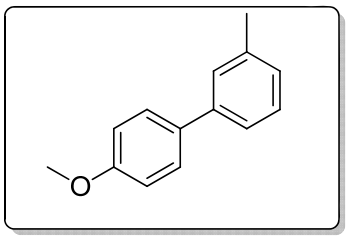




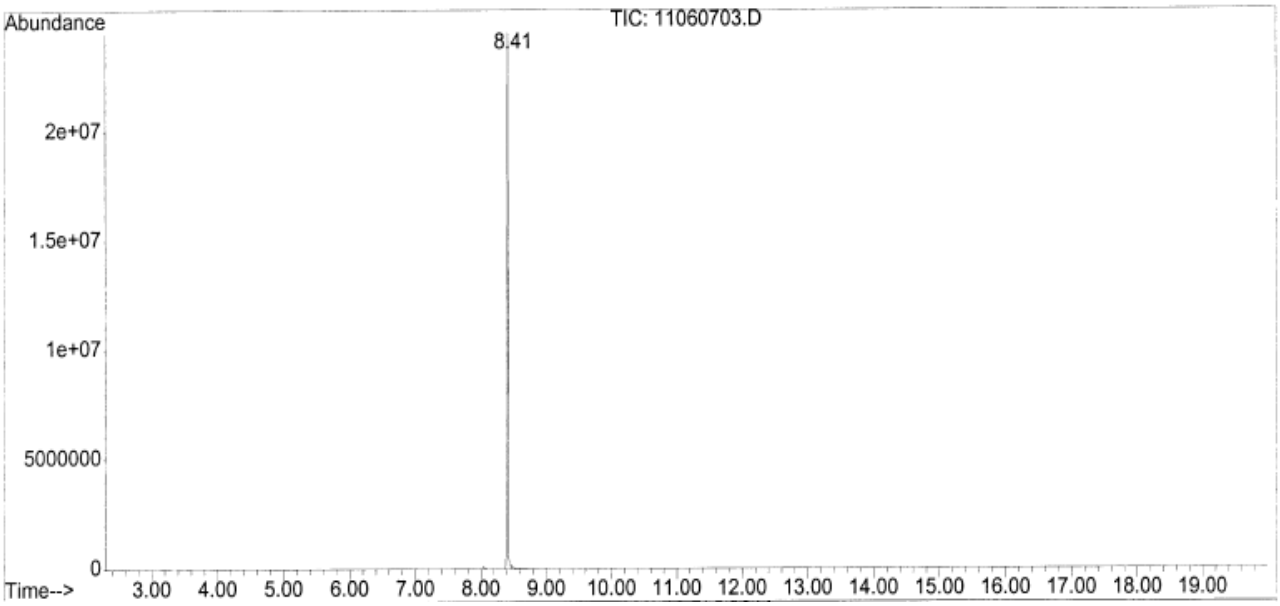

f1 (ppm)
2.40
3.81
2.99
3.08
1.94
1.87
2.08
2.00

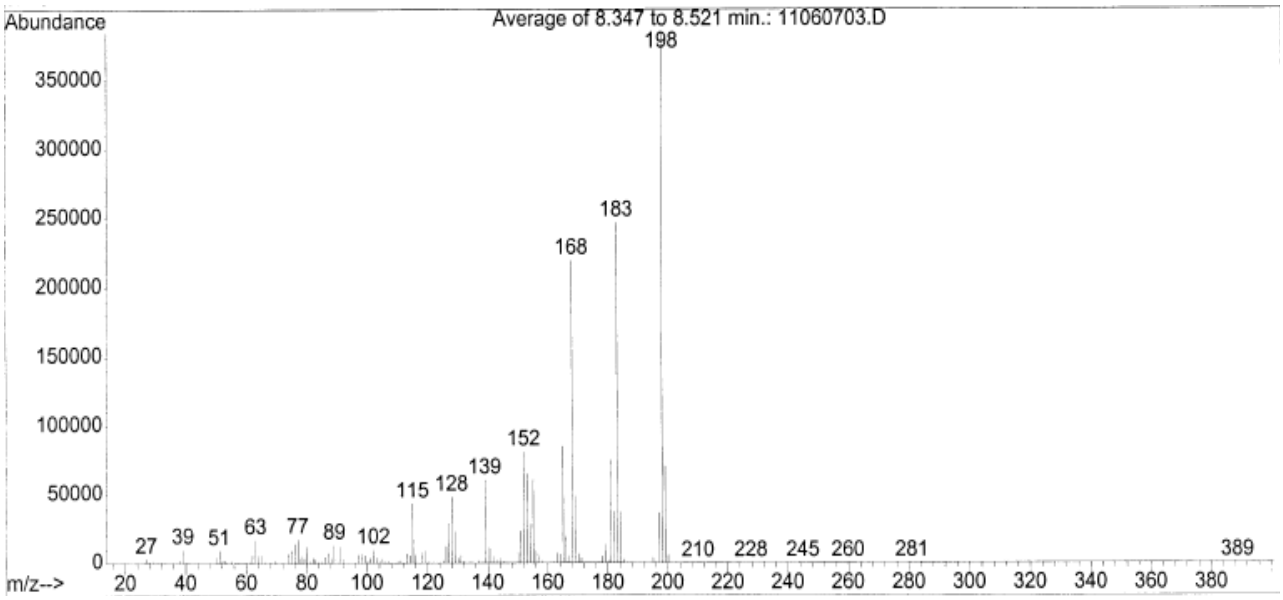

21.12
55.36
111.06
120.70
128.28
128.64
129.32
130.58
130.68
135.52
136.44
156.39
f1 (ppm)

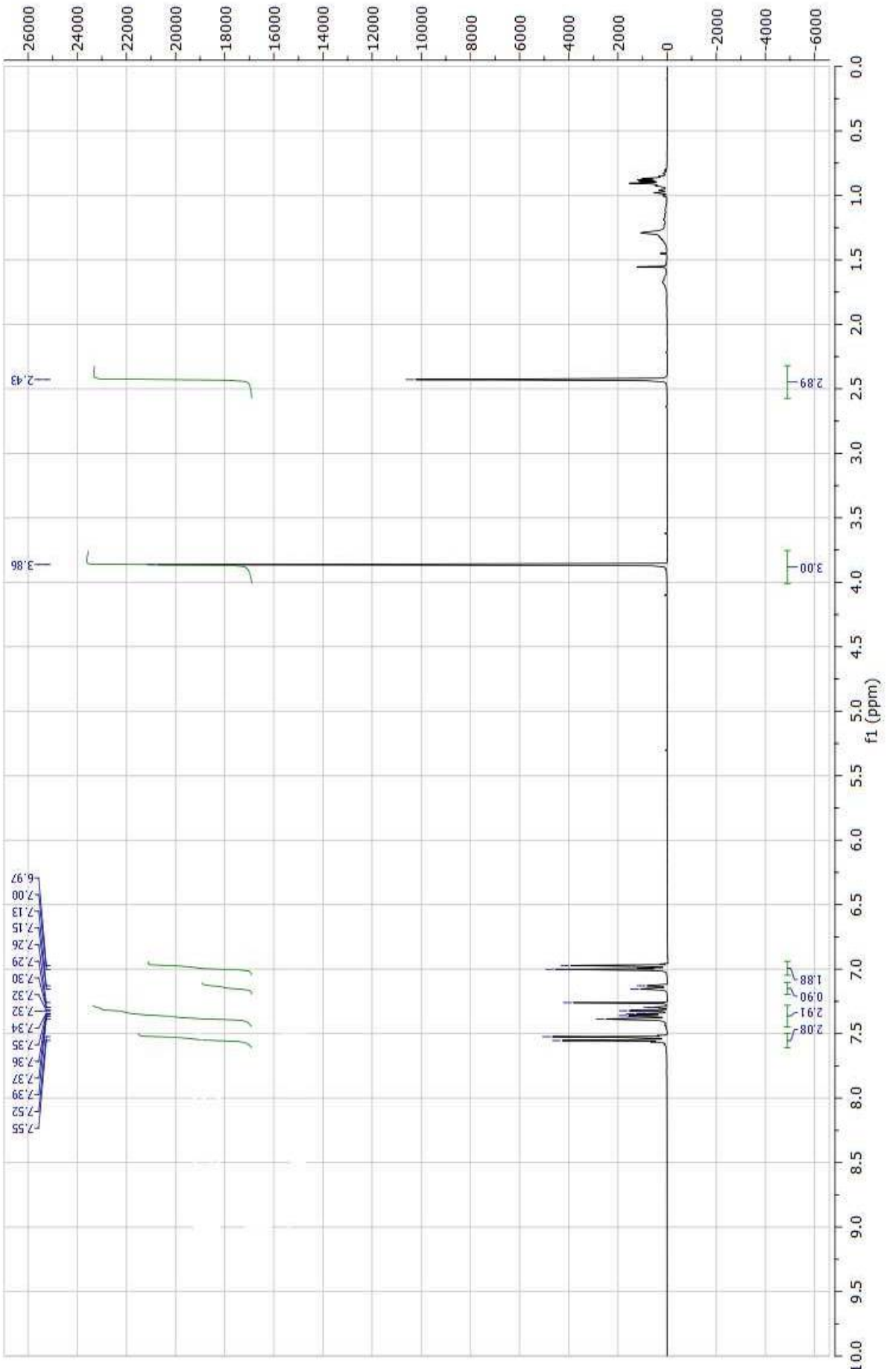
E. 4ae

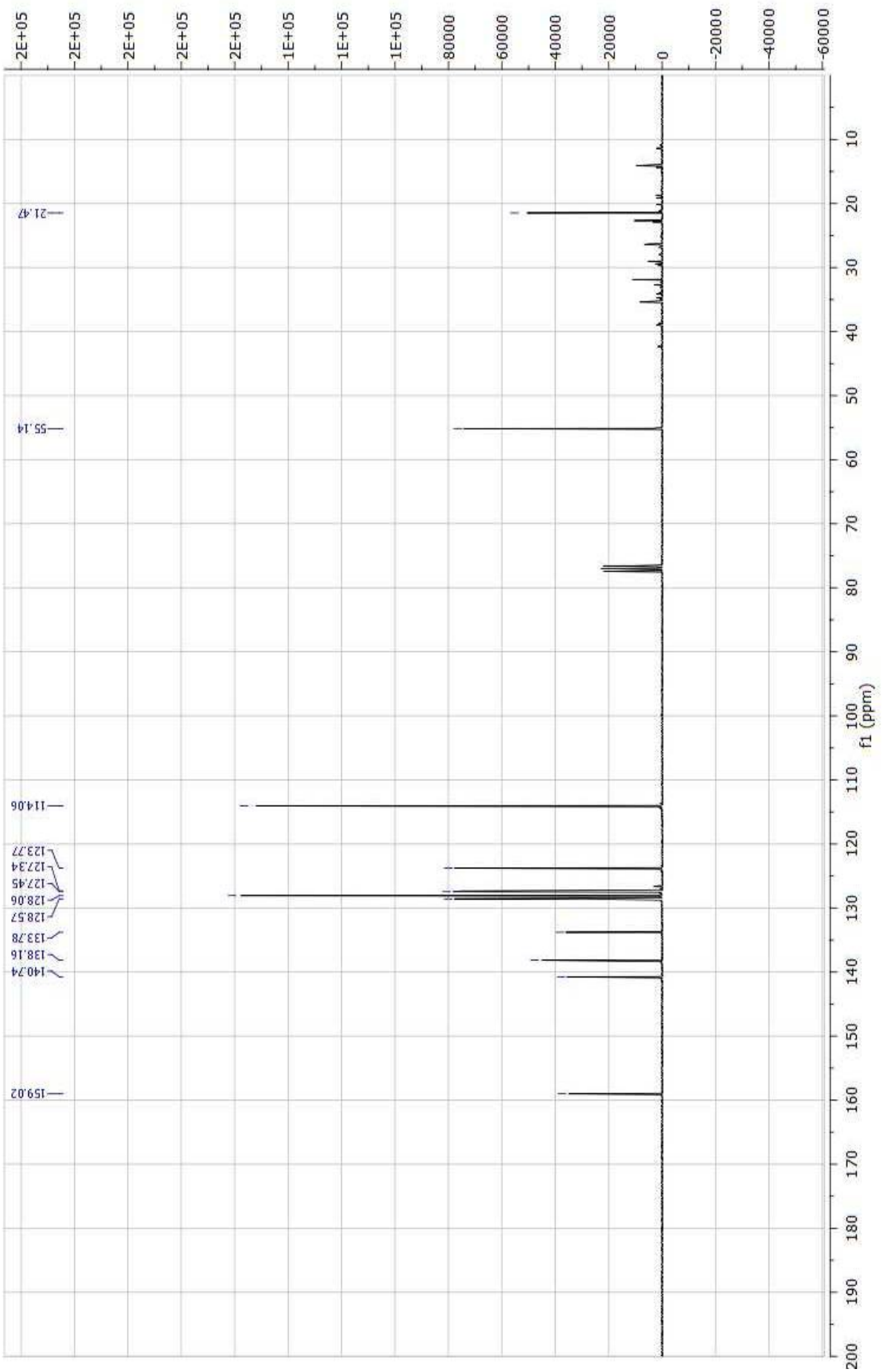


GC/MS Analysis

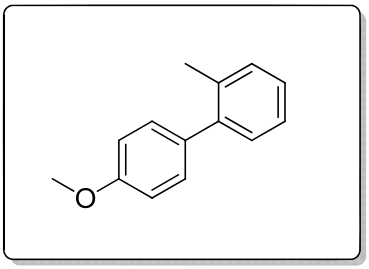




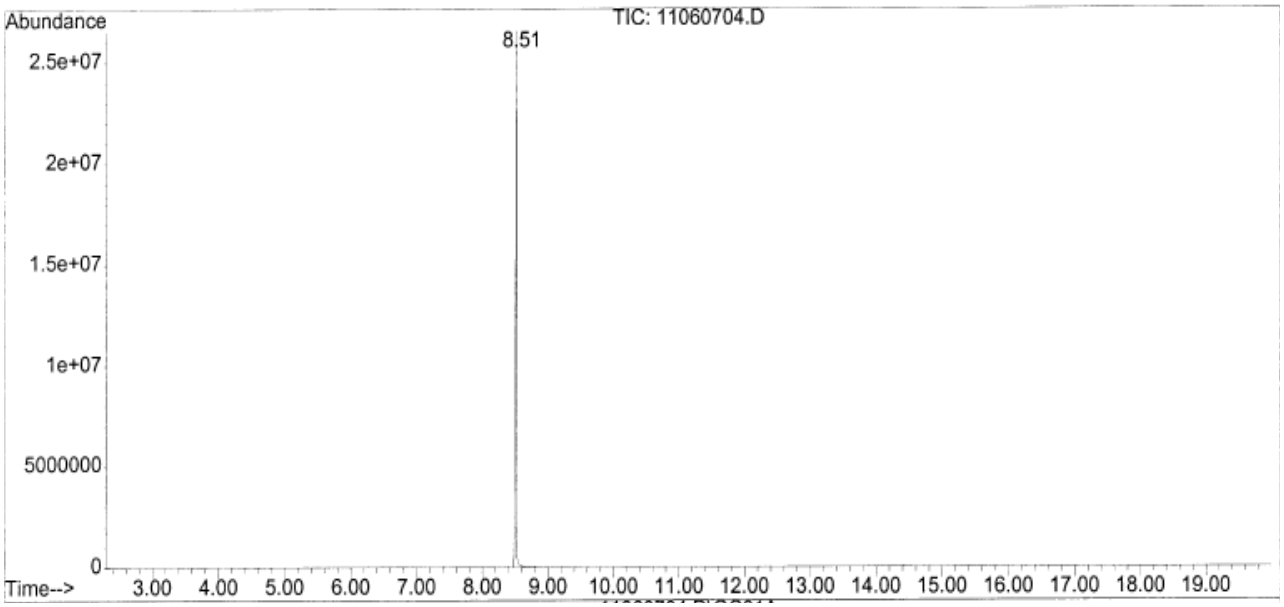

f1 (ppm)
2.43
3.86
6.97
7.00
7.13
7.15
7.26
7.29
7.30
7.32
7.32
7.34
7.35
7.36
7.37
7.39
7.52
7.55
2.89
3.00
1.88
0.90
2.91
2.08

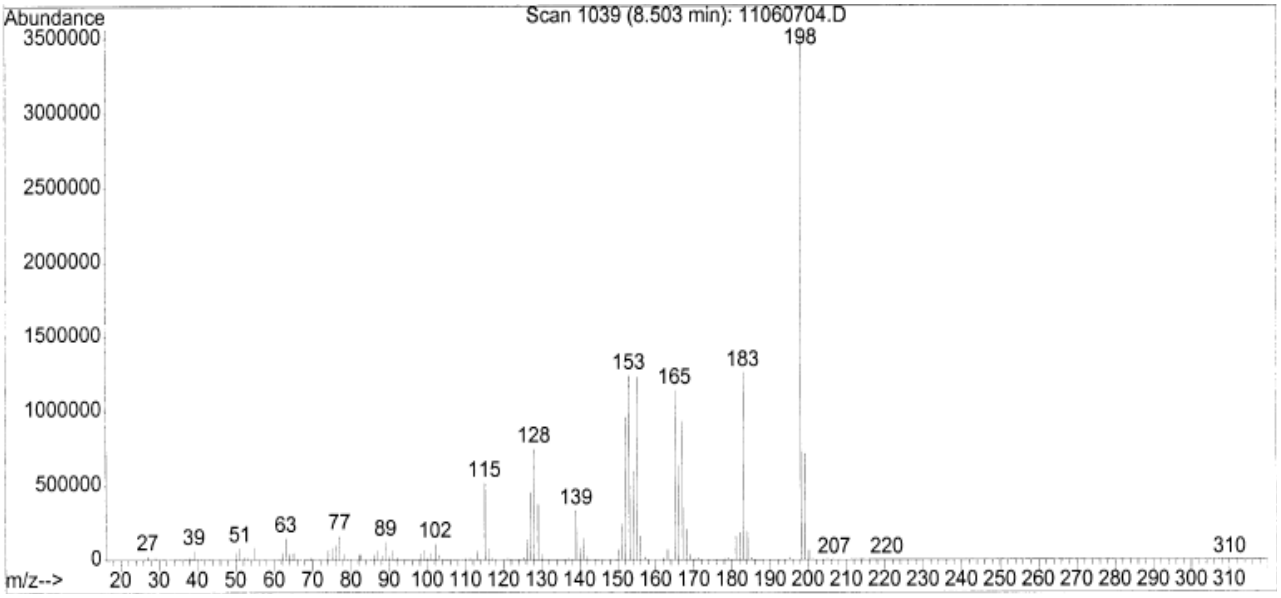

21.47
55.14
114.06
123.77
127.34
127.45
128.06
128.57
133.78
138.16
140.74
159.02
f1 (ppm)

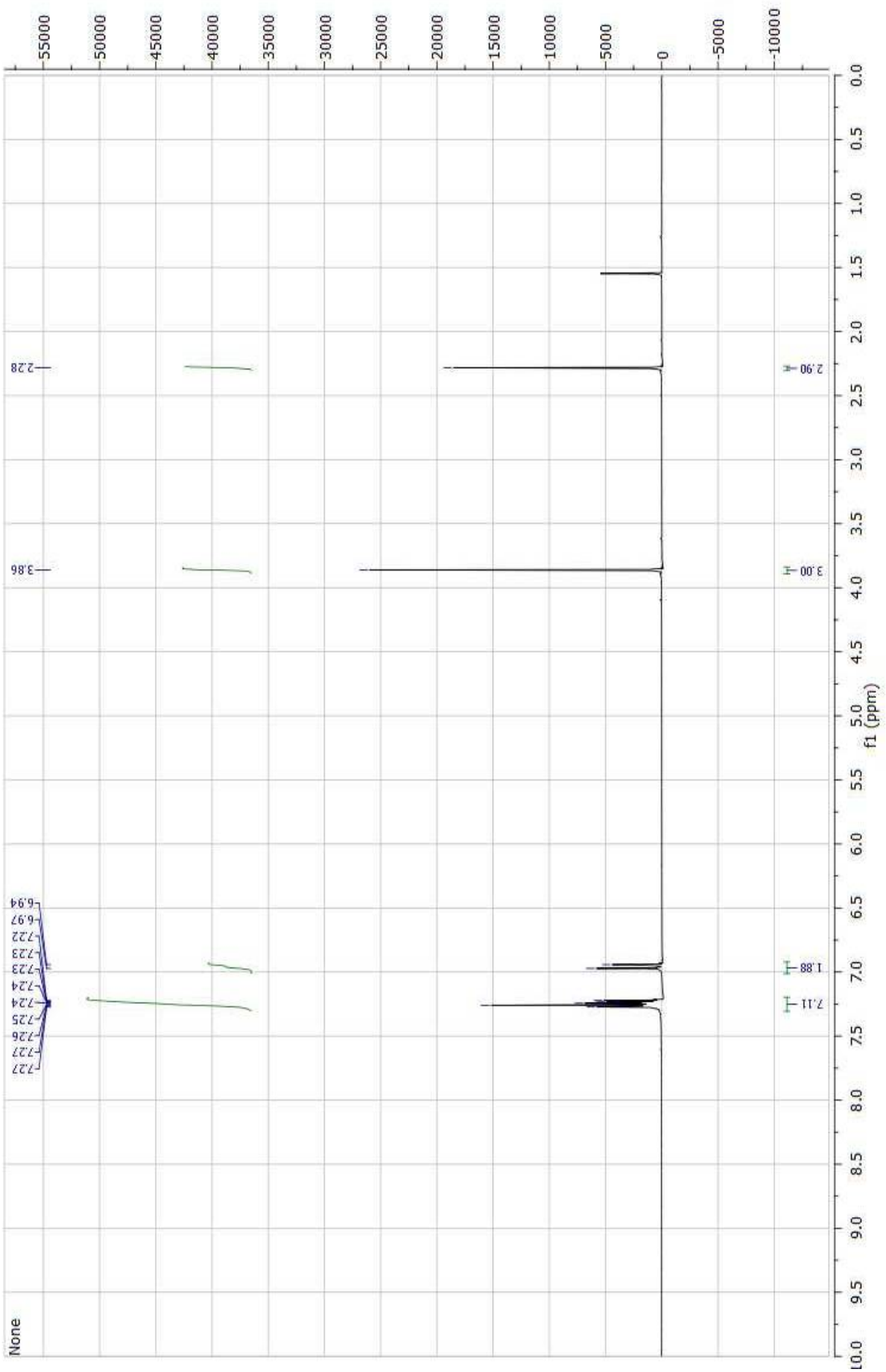
F. 4af

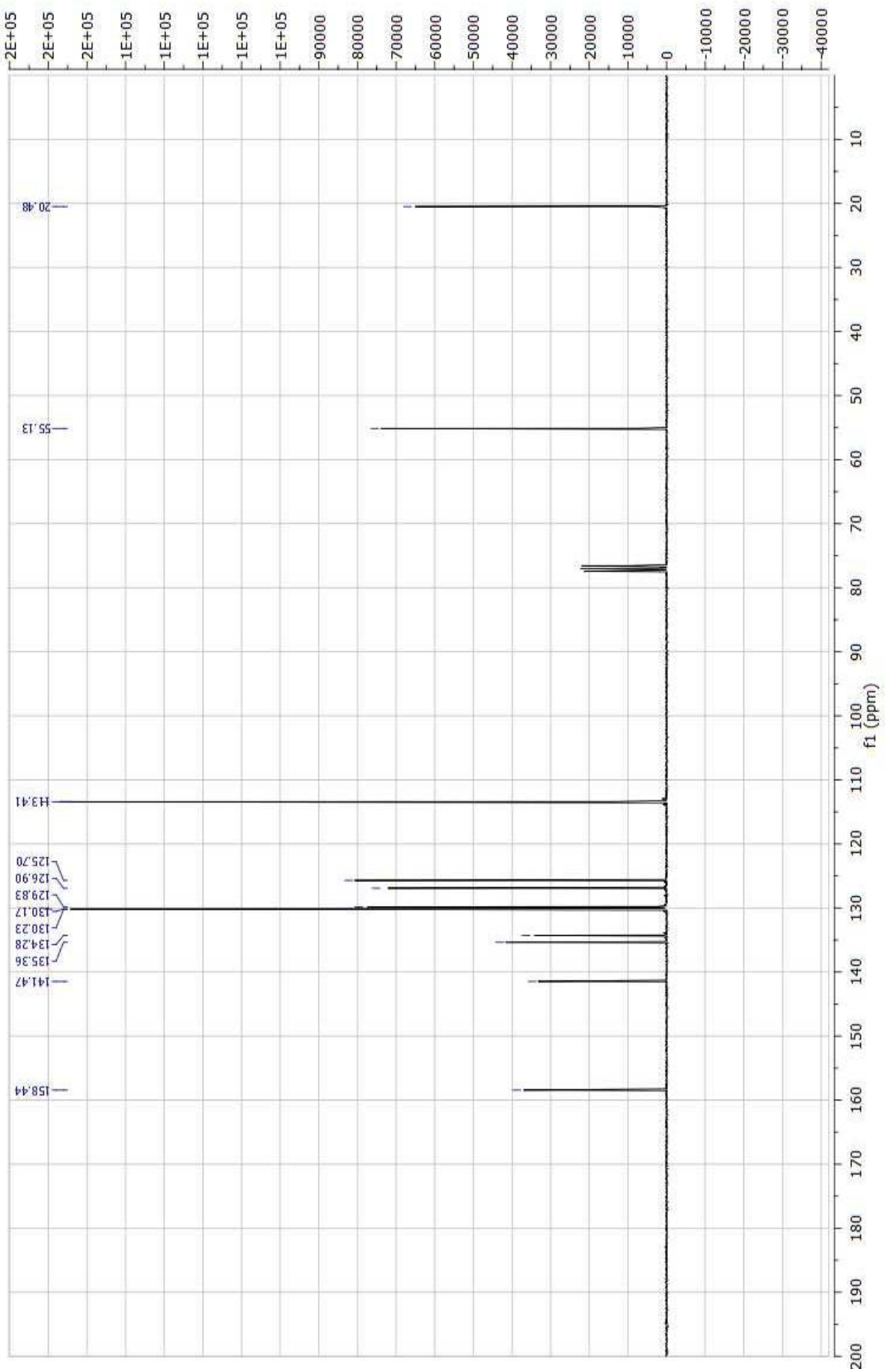


GC/MS Analysis

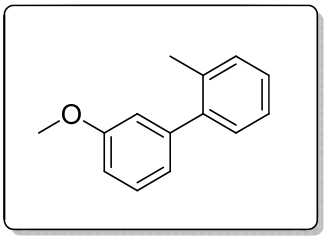




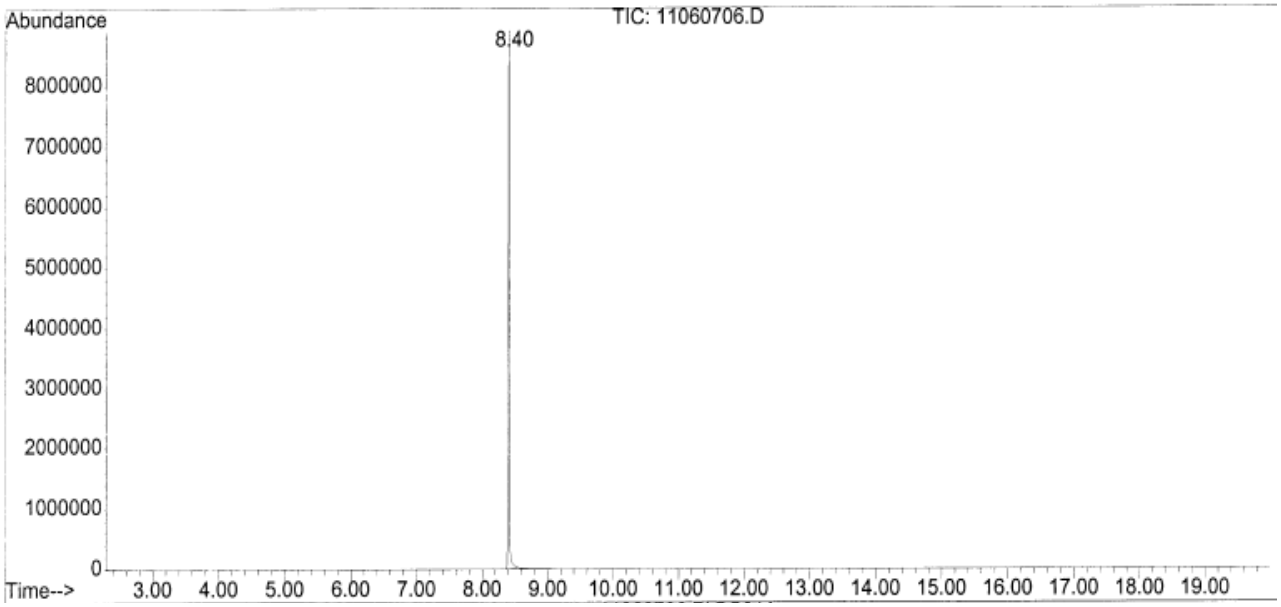

55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)
2.28
3.86
6.94
6.97
7.22
7.23
7.23
7.24
7.24
7.25
7.26
7.27
7.27
2.90
3.00
1.88
7.11
None

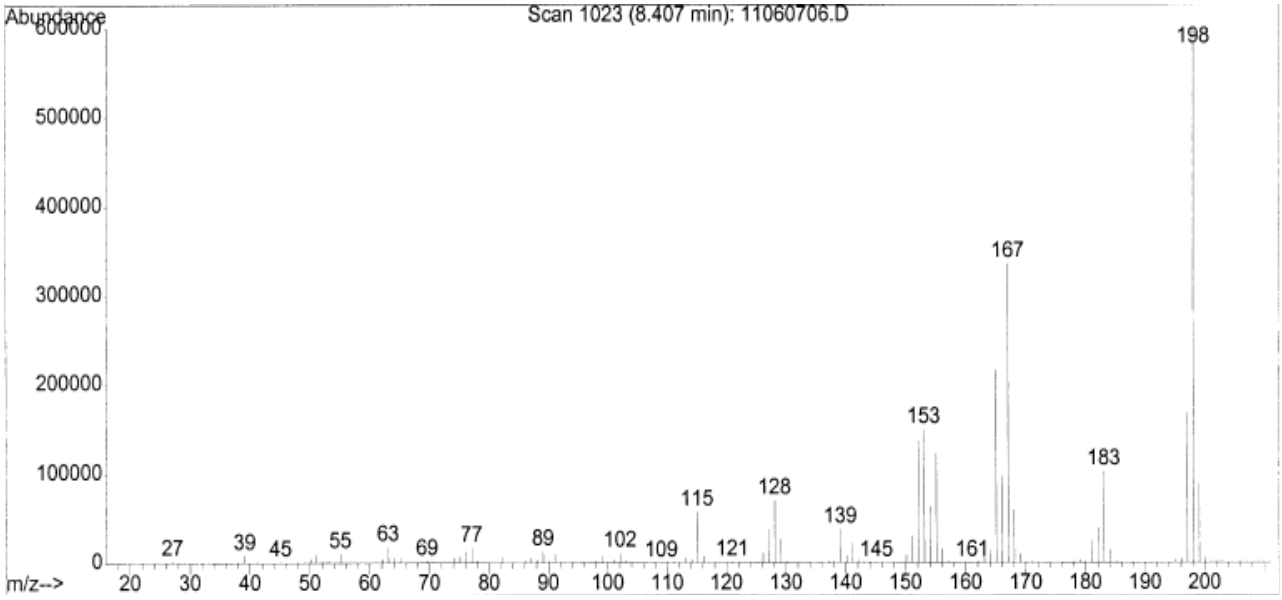

20.48
55.13
113.41
125.70
126.90
129.83
130.17
130.23
134.28
135.36
141.47
158.44
f1 (ppm)

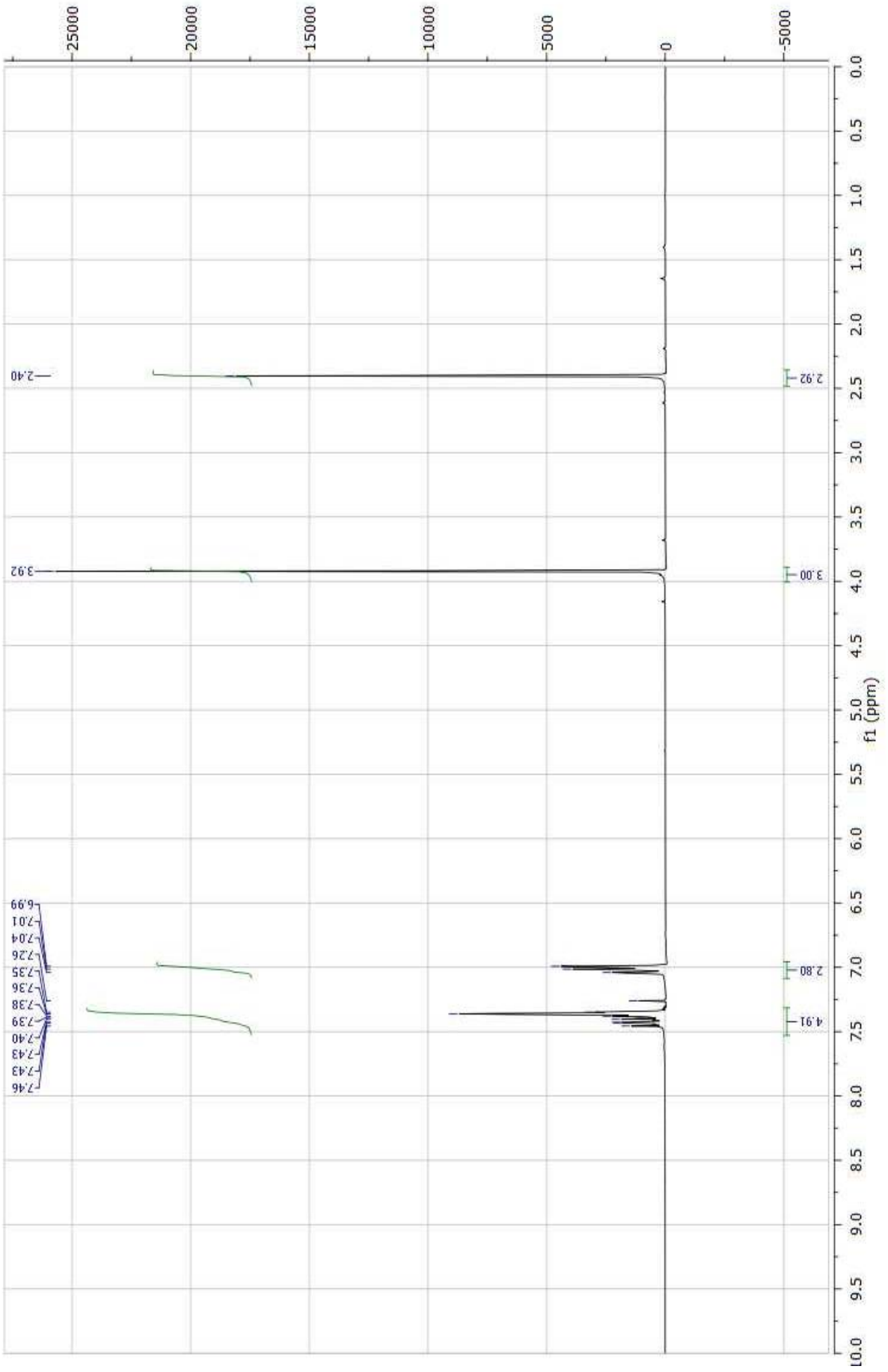
G. 4cf

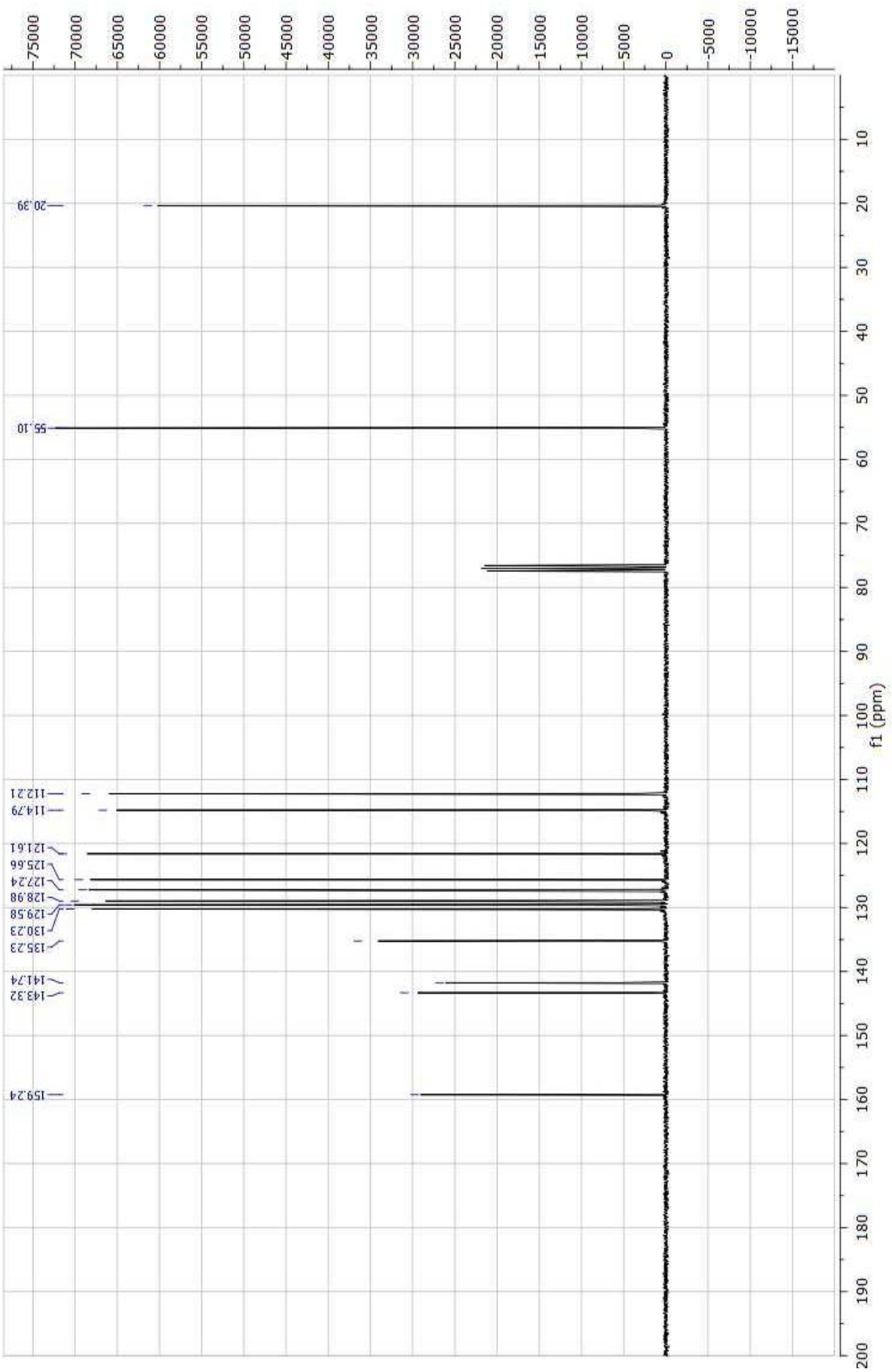


GC/MS Analysis

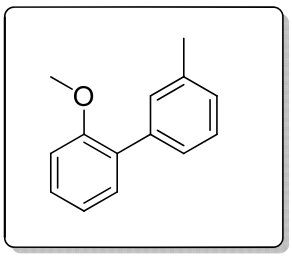




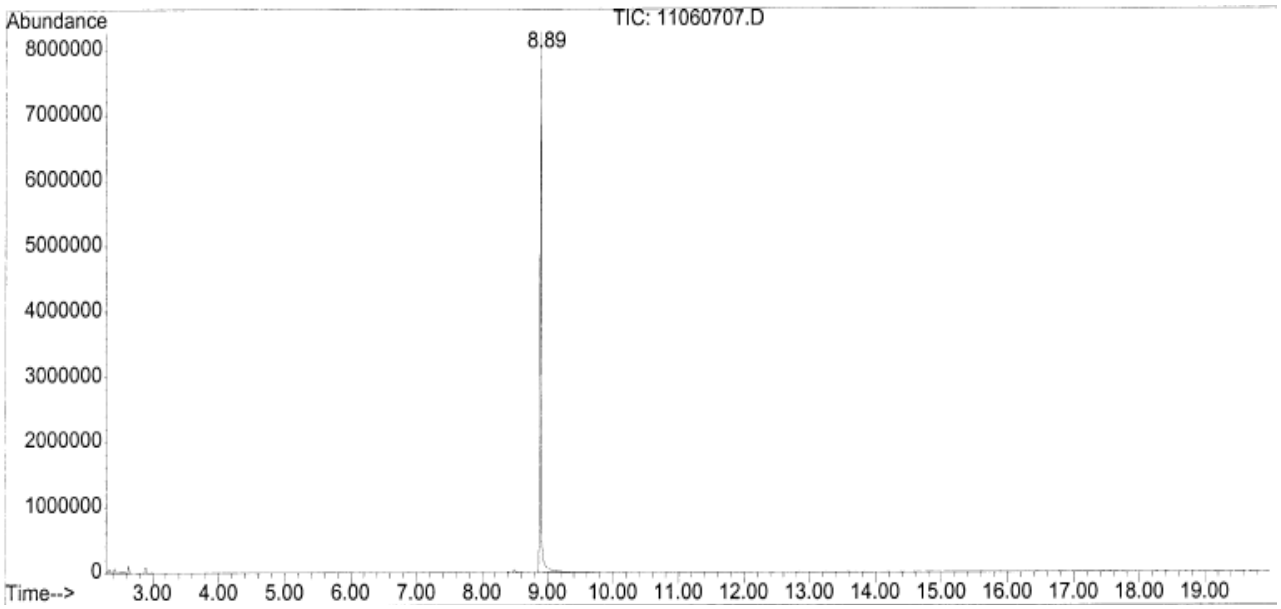

25000
20000
15000
10000
5000
0
-5000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)
2.40
3.92
6.99
7.01
7.04
7.26
7.35
7.36
7.38
7.39
7.40
7.43
7.43
7.46
2.92
3.00
2.80
4.91

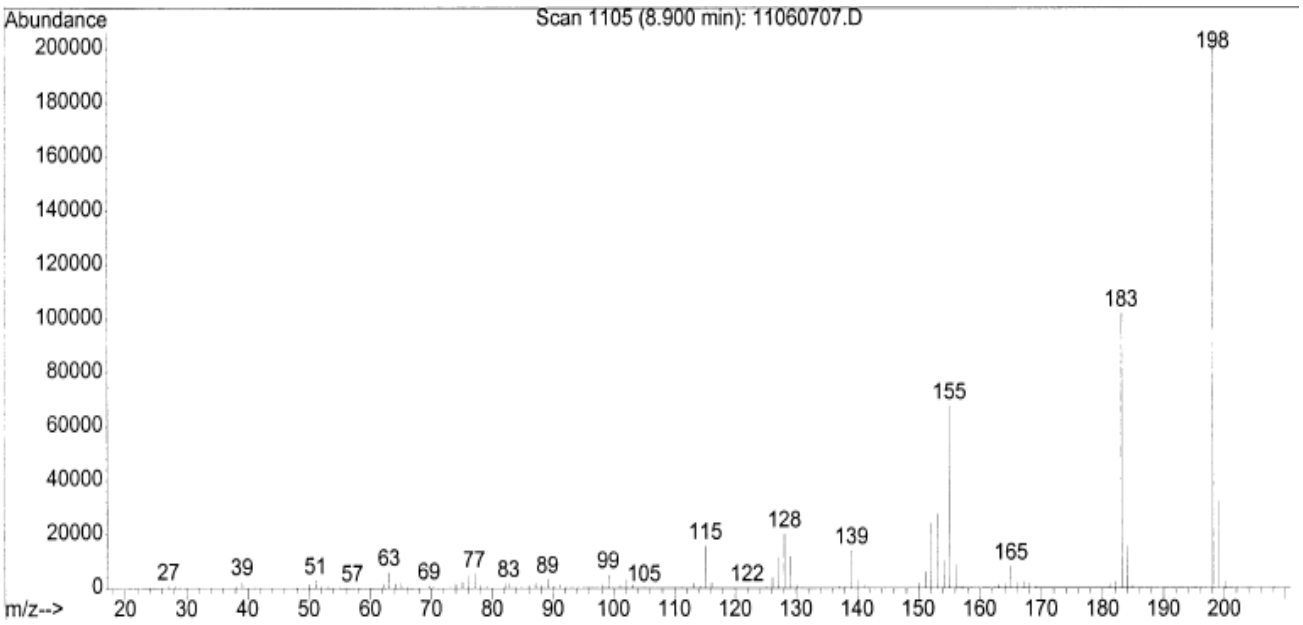

75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
20.39
55.10
112.21
114.79
121.61
125.66
127.24
128.98
129.58
130.23
135.23
141.74
143.32
159.24
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

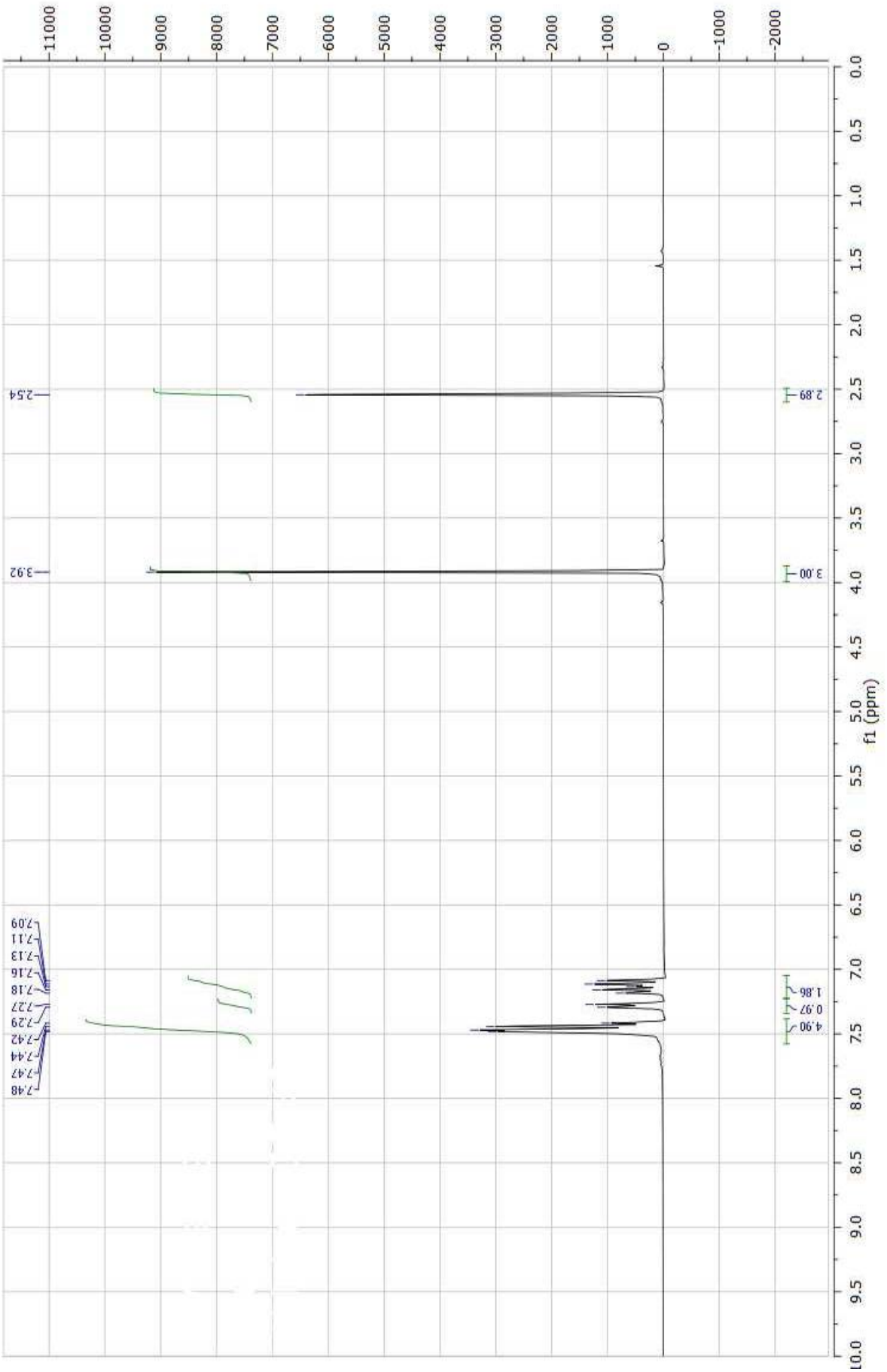
H. 4de

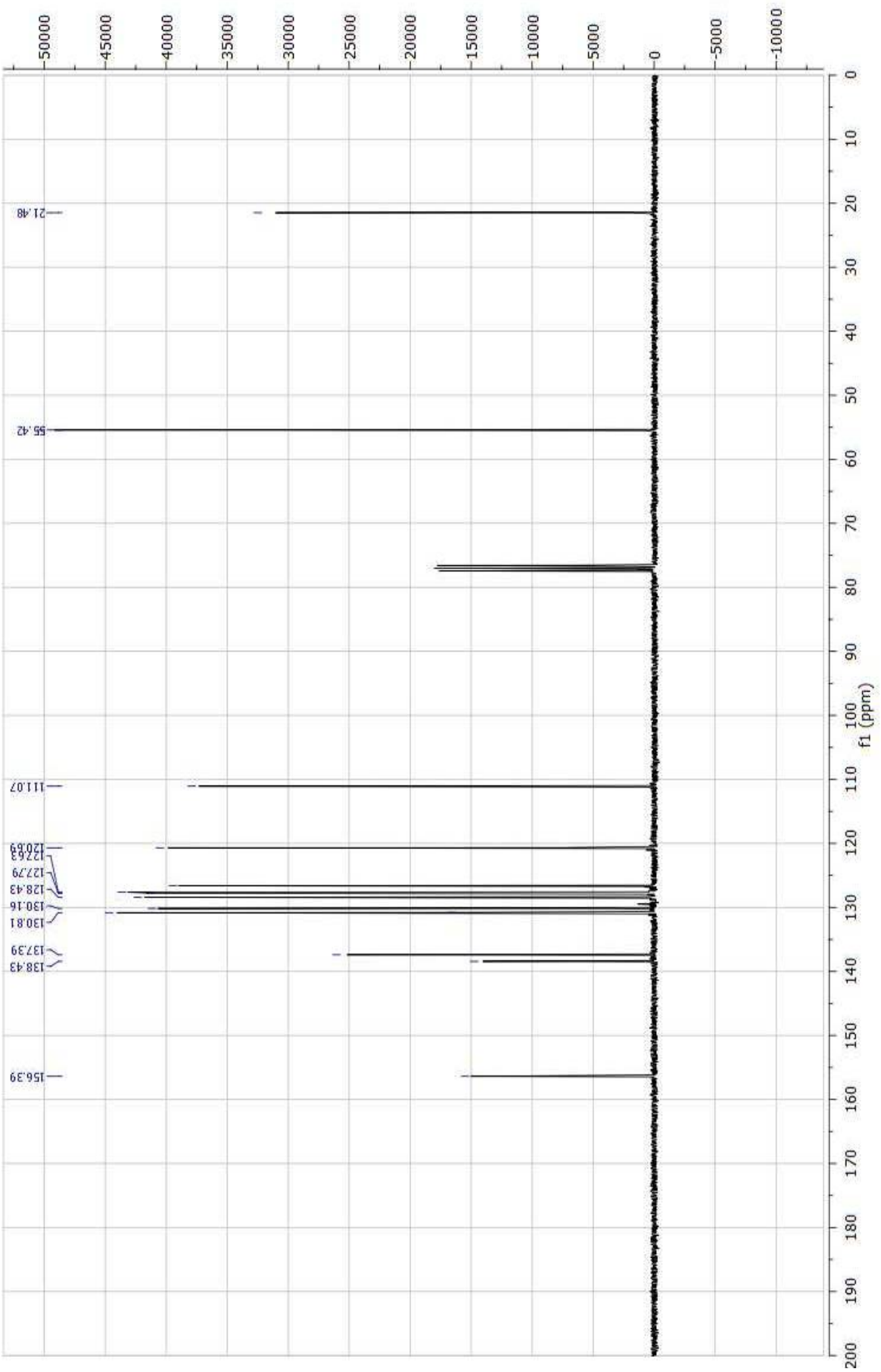


GC/MS Analysis

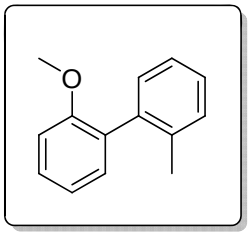




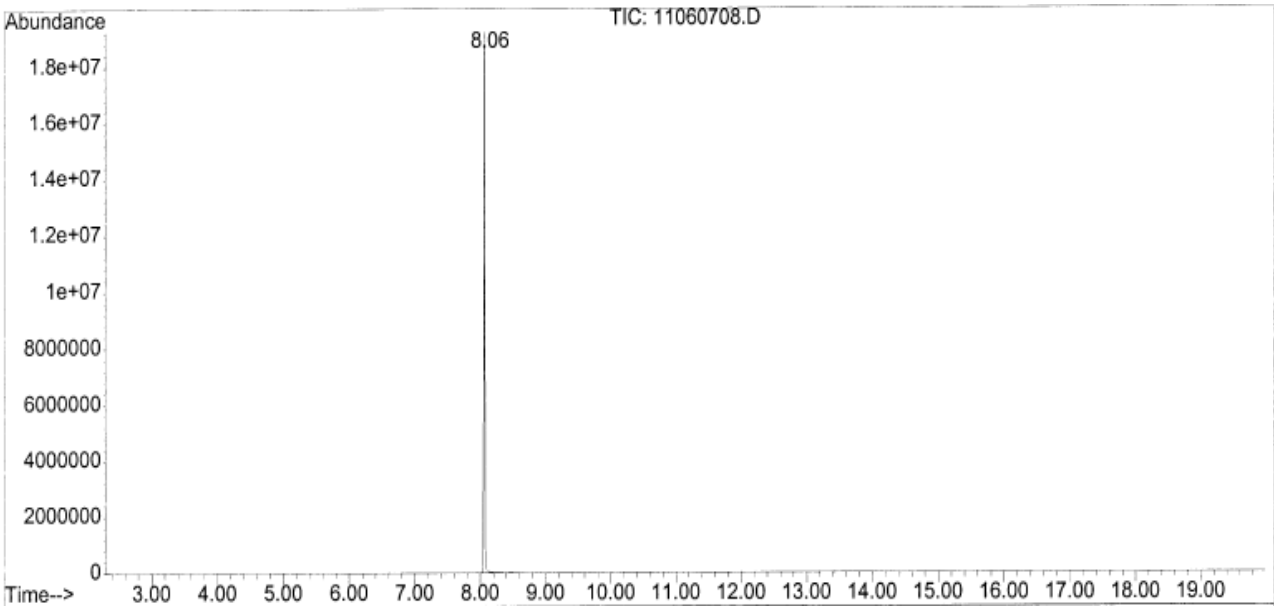

11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)
2.54
3.92
7.09
7.11
7.13
7.16
7.18
7.27
7.29
7.42
7.44
7.47
7.48
2.89
3.00
1.86
0.97
4.90

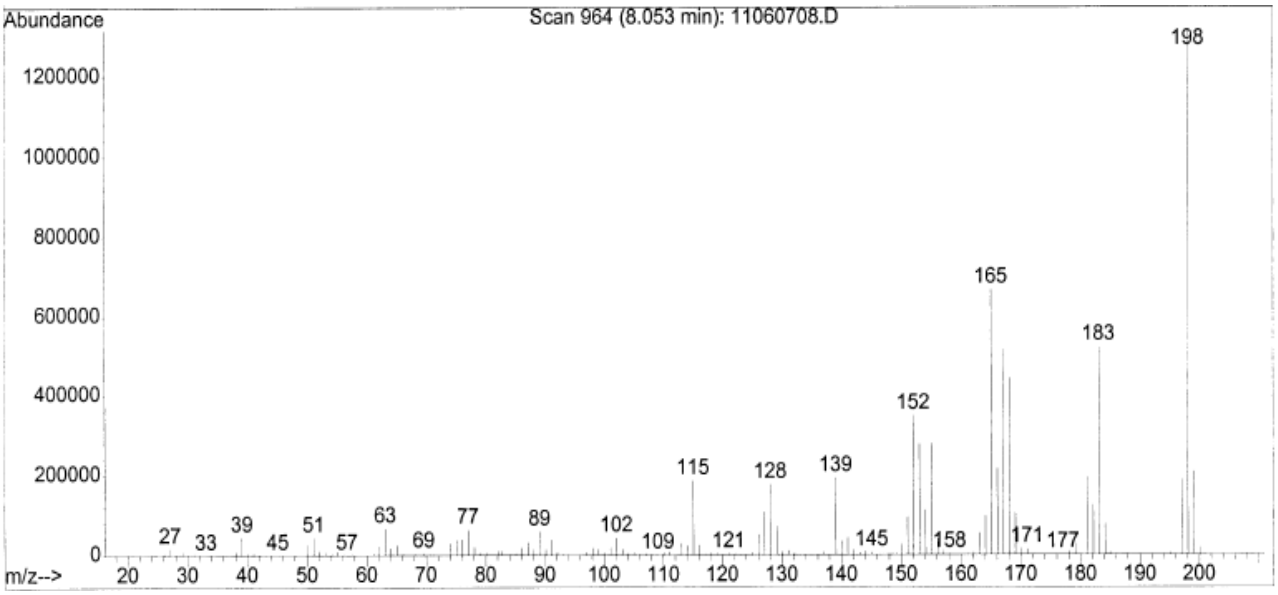

21.48
55.42
111.07
120.69
127.63
127.79
128.43
130.16
130.81
137.39
138.43
156.39
f1 (ppm)

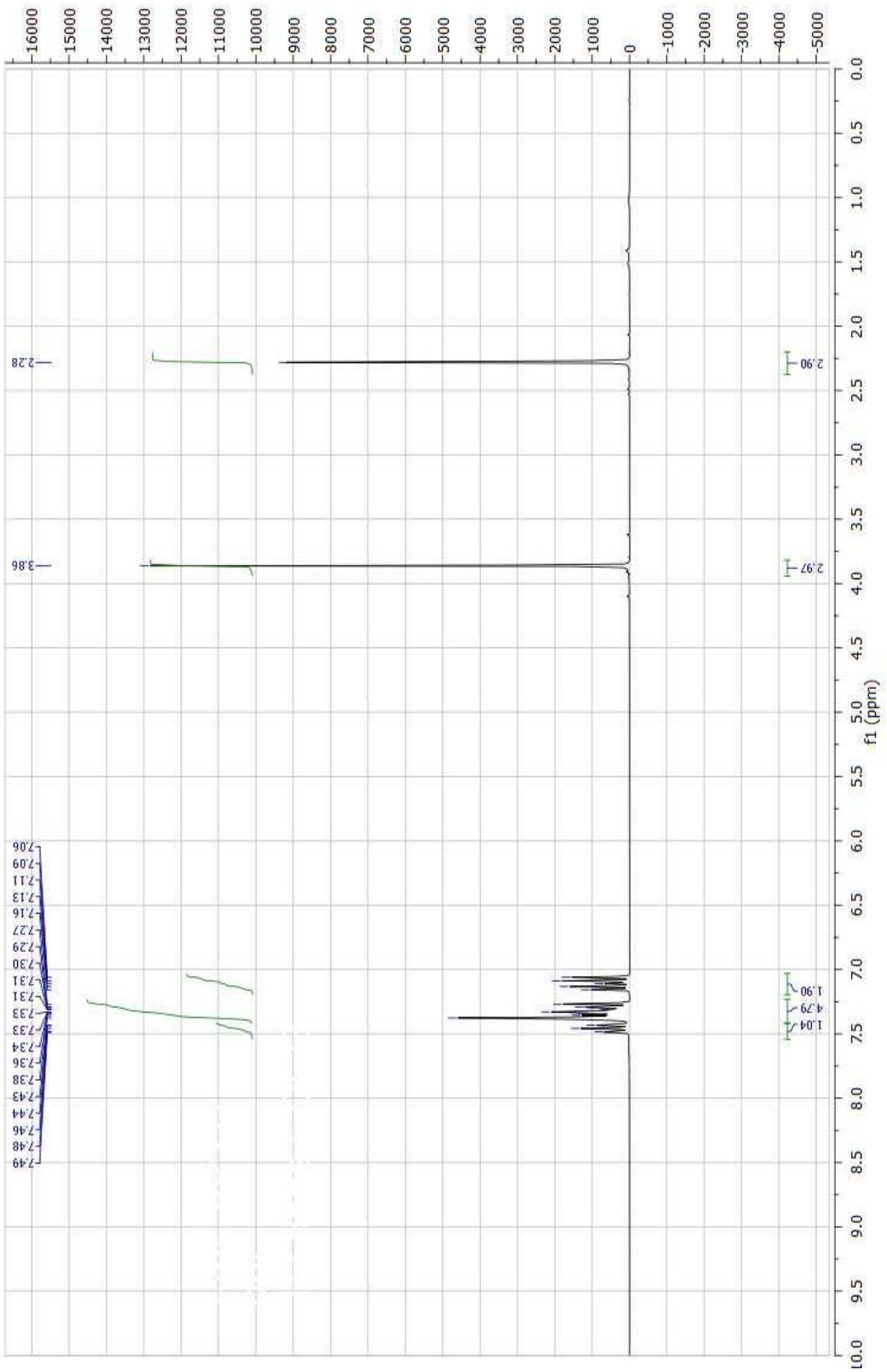
I. 4df

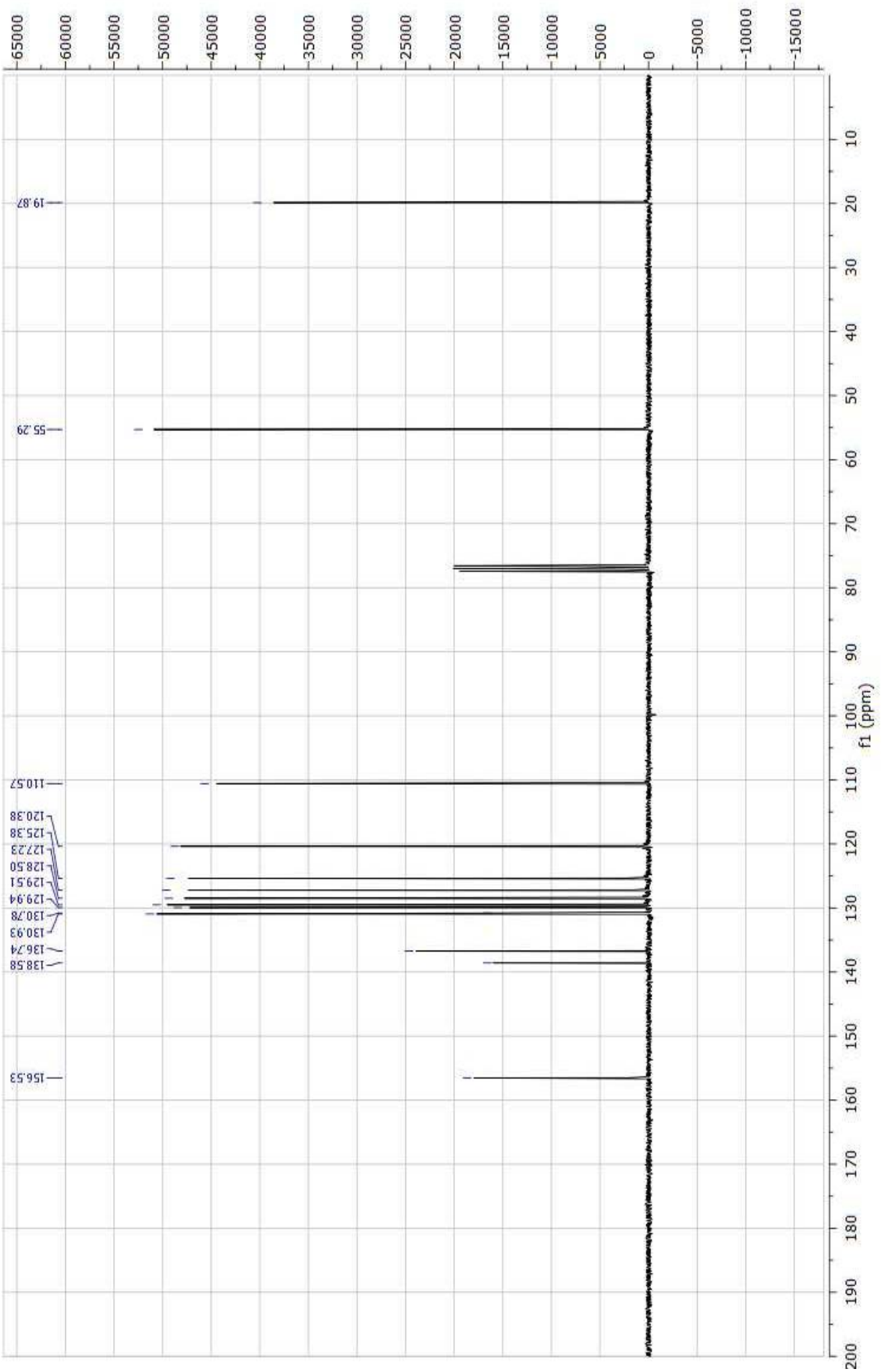


GC/MS Analysis

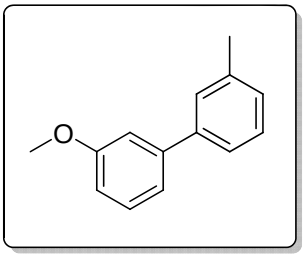




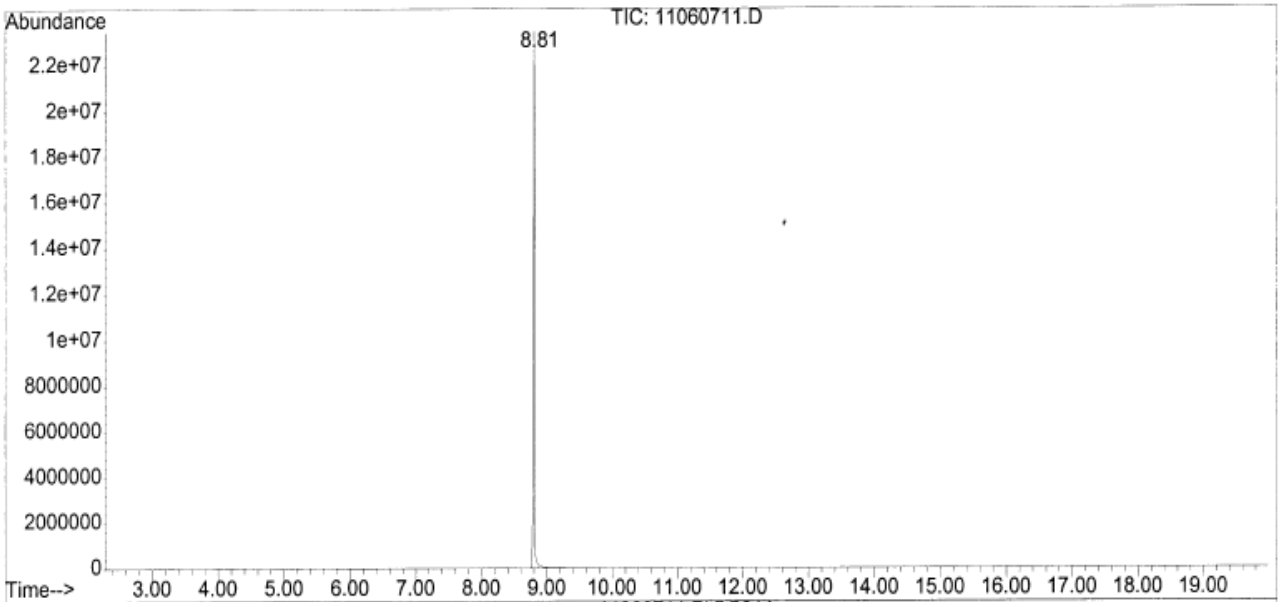

f1 (ppm)
2.28
3.86
2.90
2.97
1.90
4.79
1.04

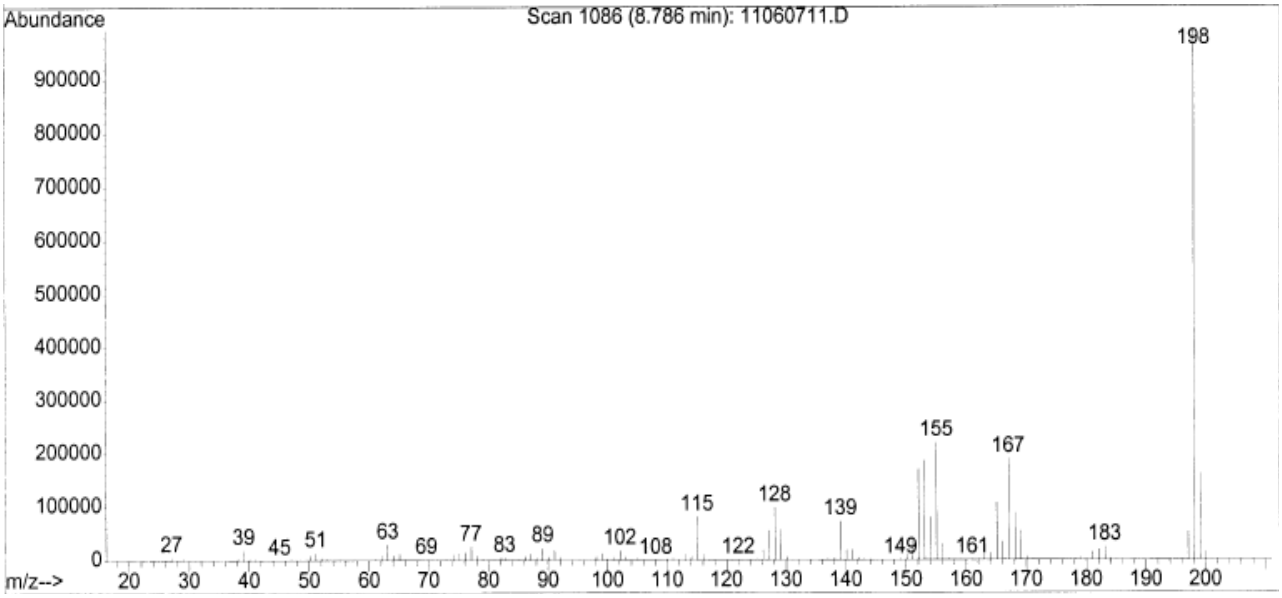

19.87
55.29
110.57
120.38
125.38
127.23
128.50
129.51
129.94
130.78
130.93
136.74
138.58
156.53
f1 (ppm)

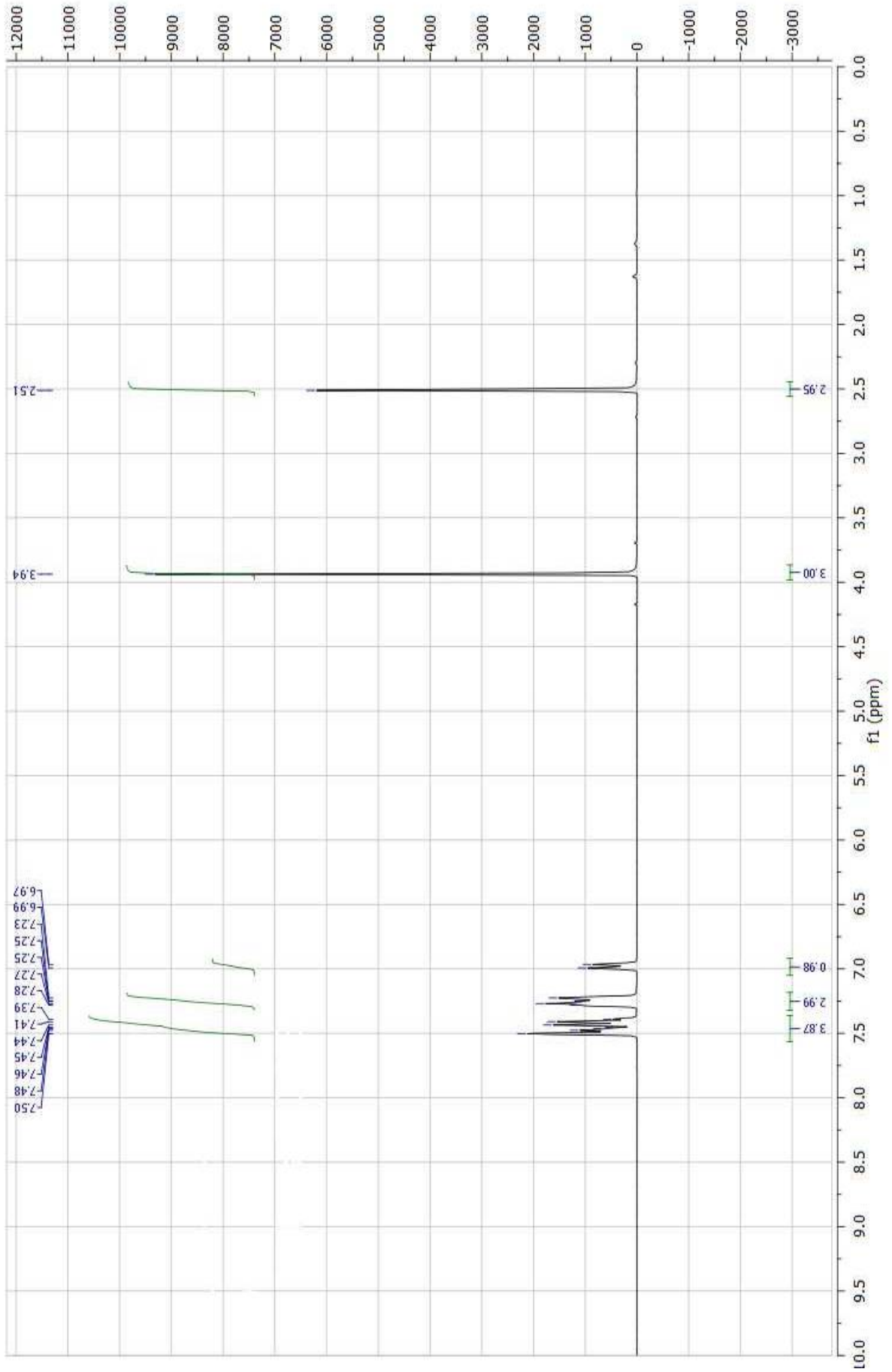
J. 4ce

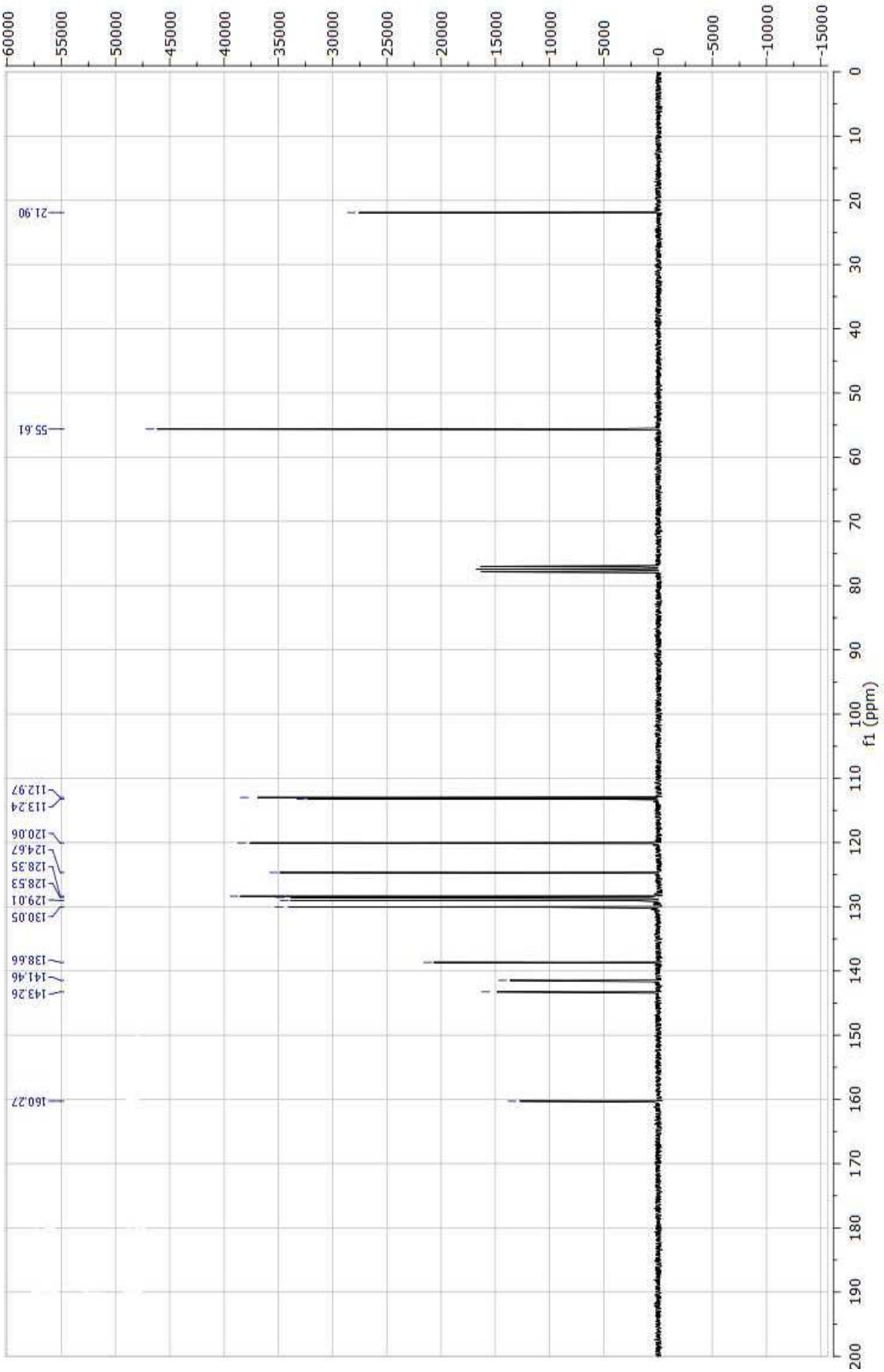


GC/MS Analysis

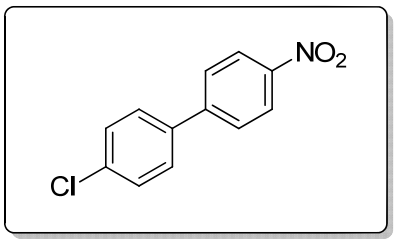




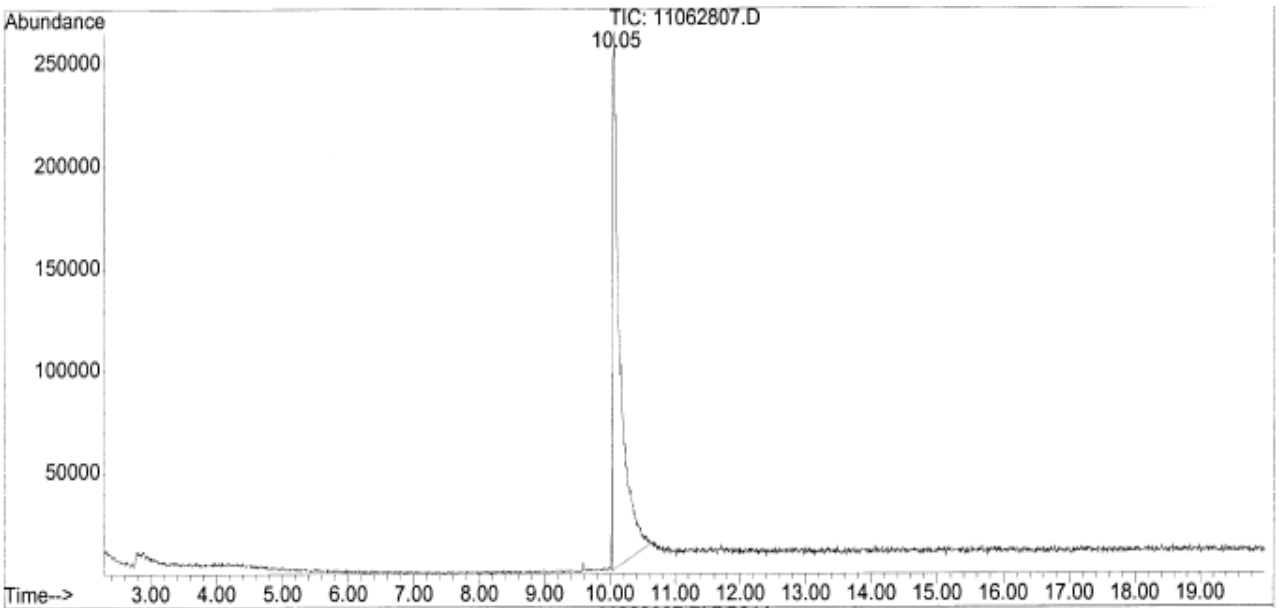

f1 (ppm)
2.51
3.94
6.97
6.99
7.23
7.25
7.25
7.27
7.28
7.39
7.41
7.44
7.45
7.46
7.48
7.50
2.95
3.00
0.98
2.99
3.87

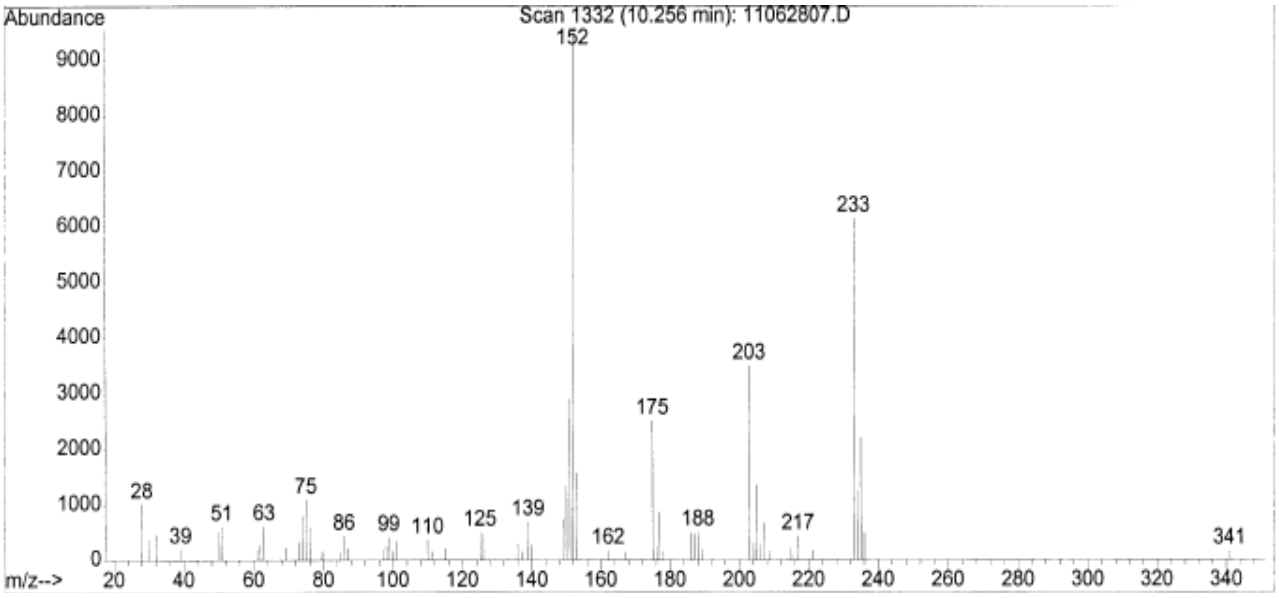

21.90
55.61
112.97
113.24
120.06
124.67
128.35
128.53
129.01
130.05
138.66
141.46
143.26
160.27
f1 (ppm)

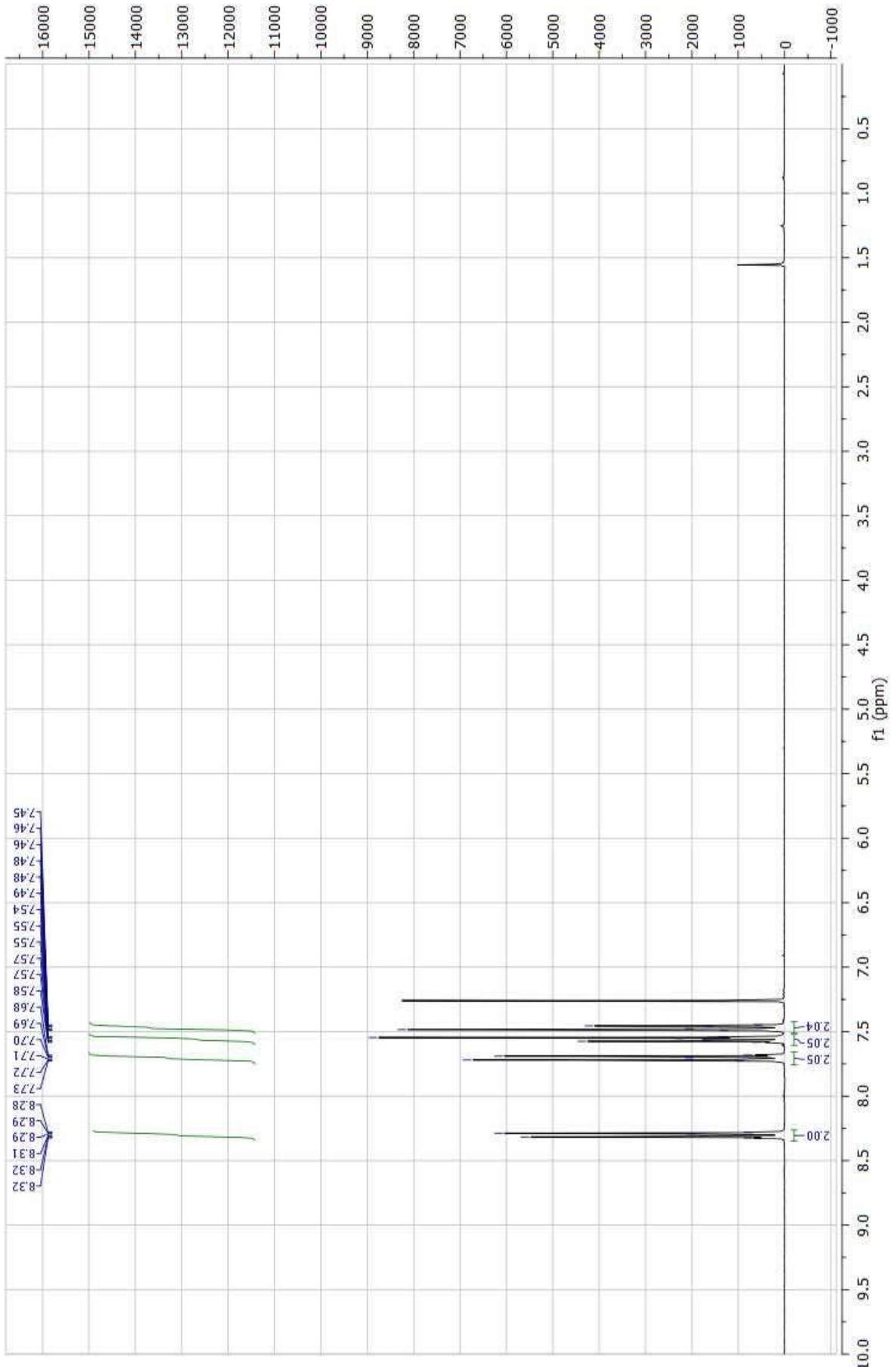
K. 4gh

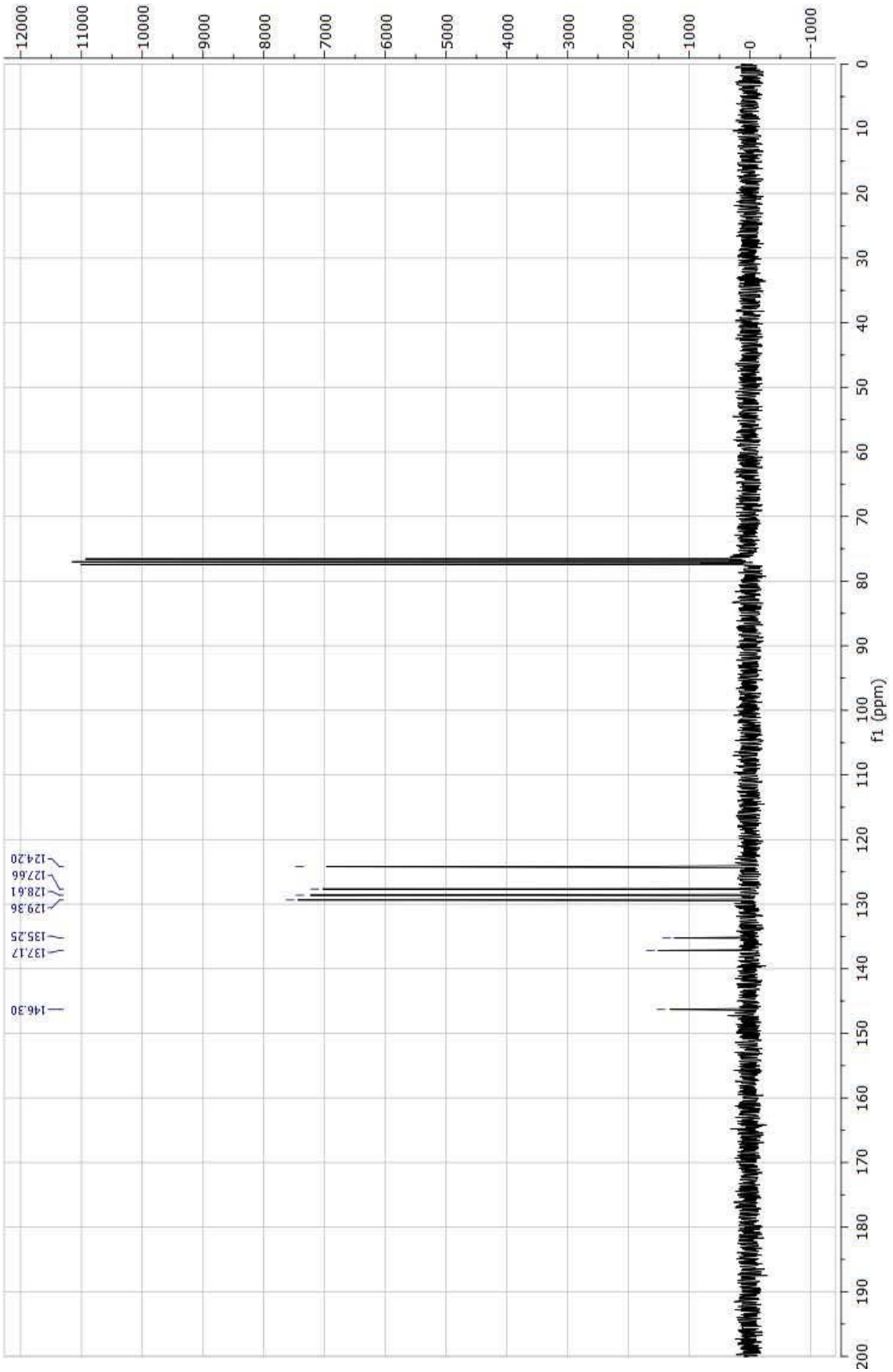


GC/MS Analysis

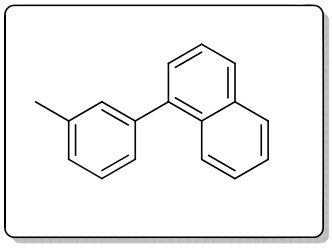




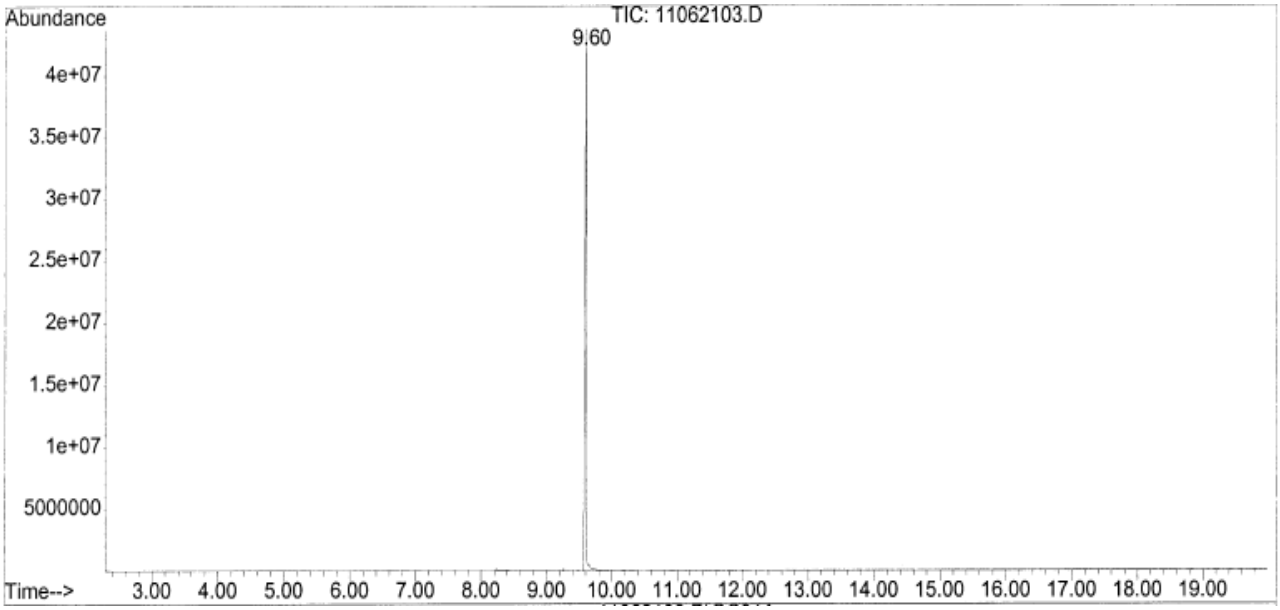

f1 (ppm)
2.00
2.05
2.05
2.04

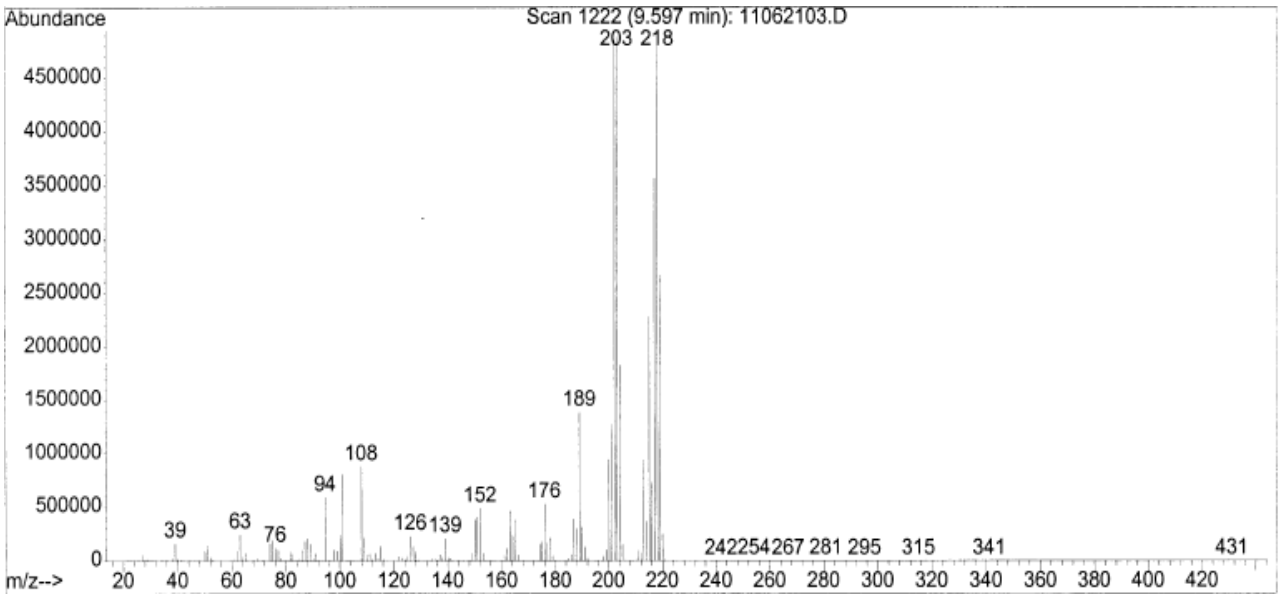

12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
124.20
127.66
128.61
129.36
135.25
137.17
146.30

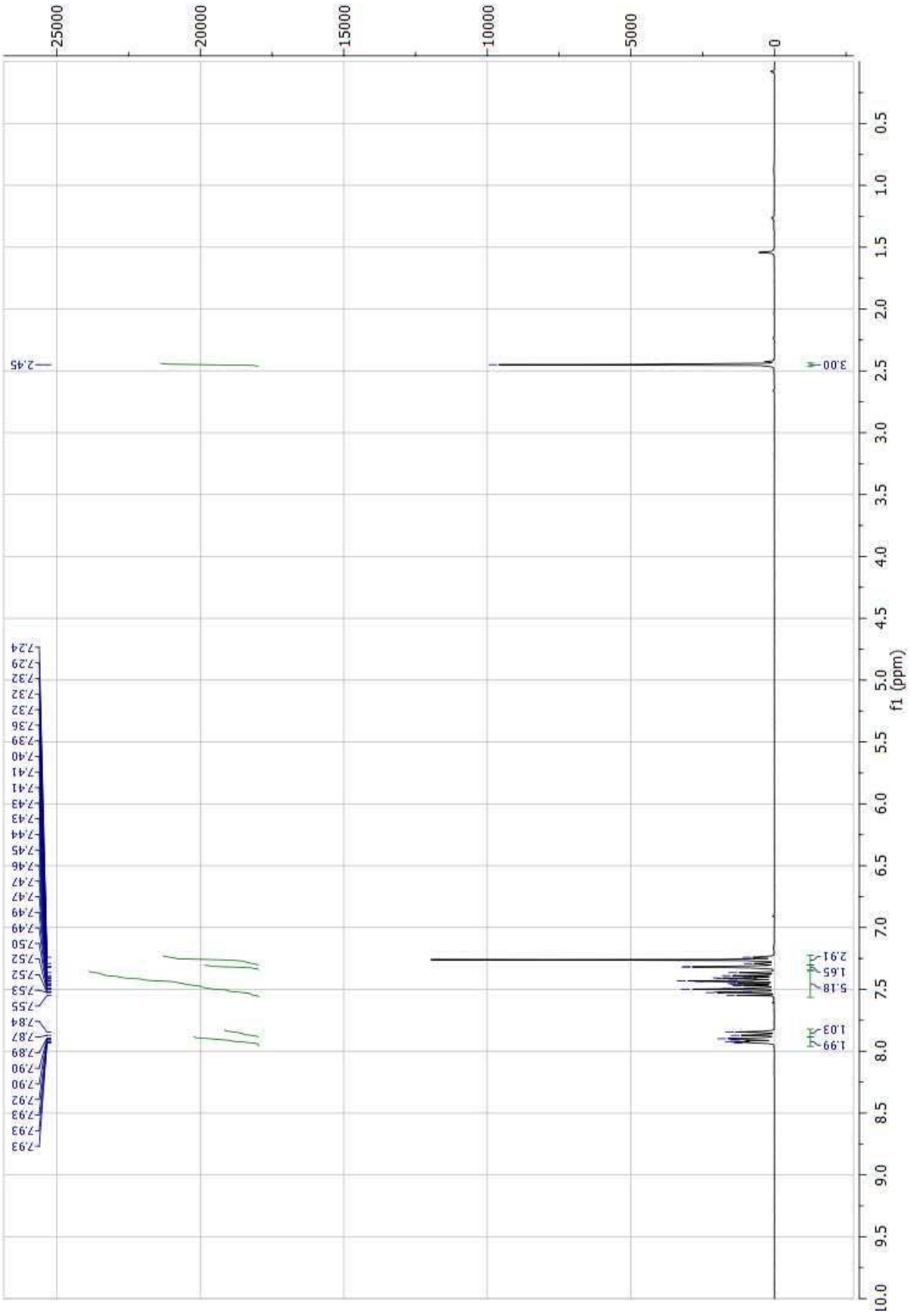
L. 4ei

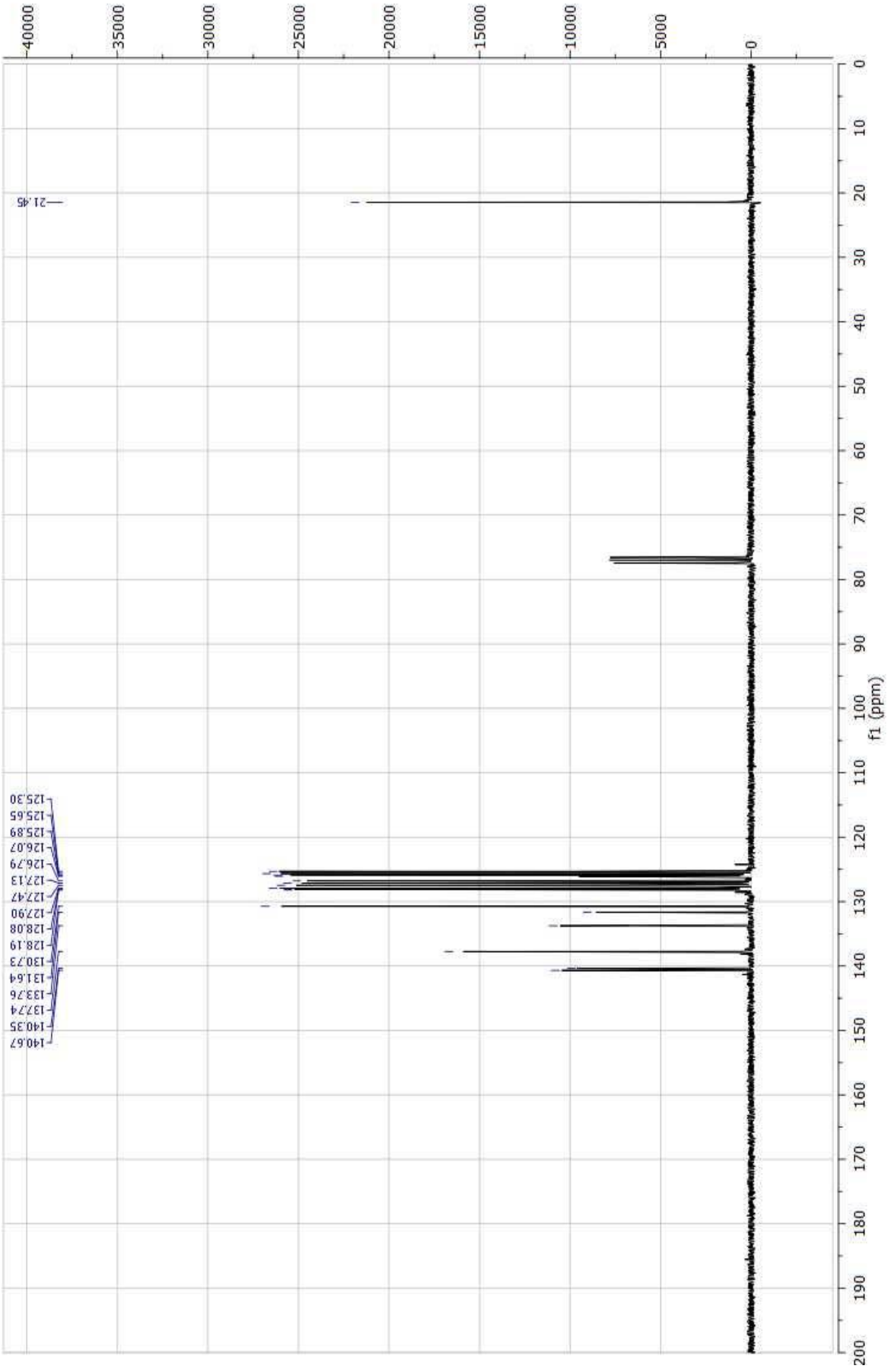


GC/MS Analysis

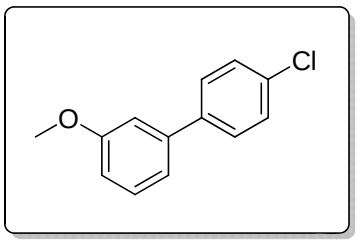




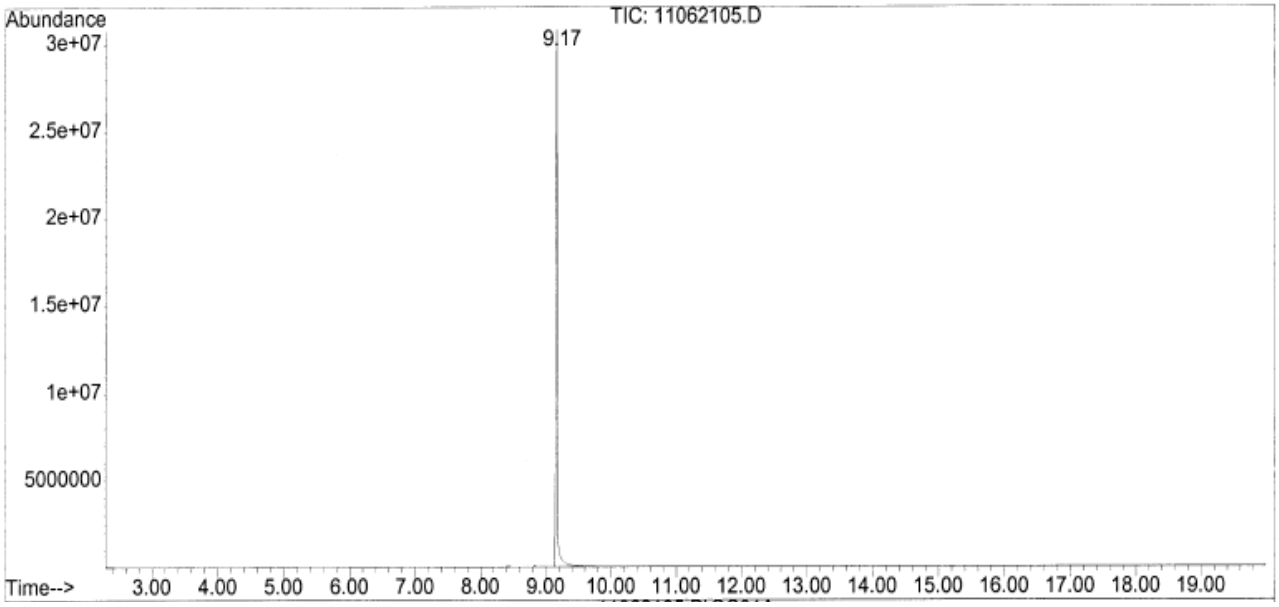

25000
20000
15000
10000
5000
0
2.45
3.00
2.91
1.65
5.18
1.03
1.99
f1 (ppm)

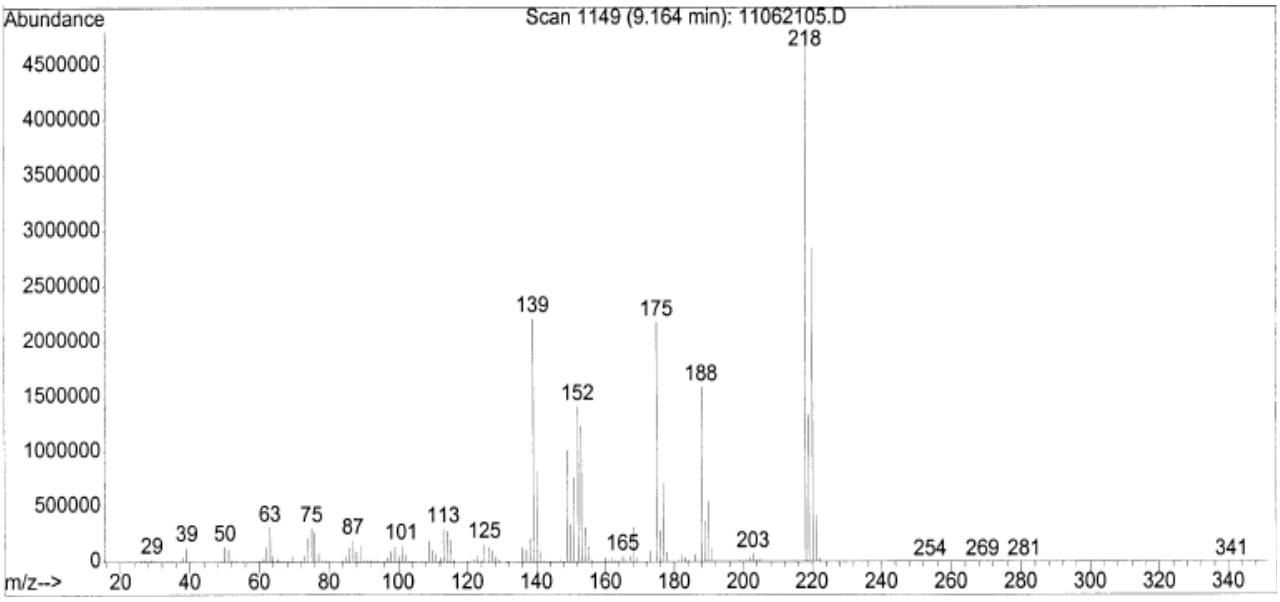

21.45
125.30
125.65
125.89
126.07
126.79
127.13
127.47
127.90
128.08
128.19
130.73
131.64
133.76
137.74
140.35
140.67
f1 (ppm)

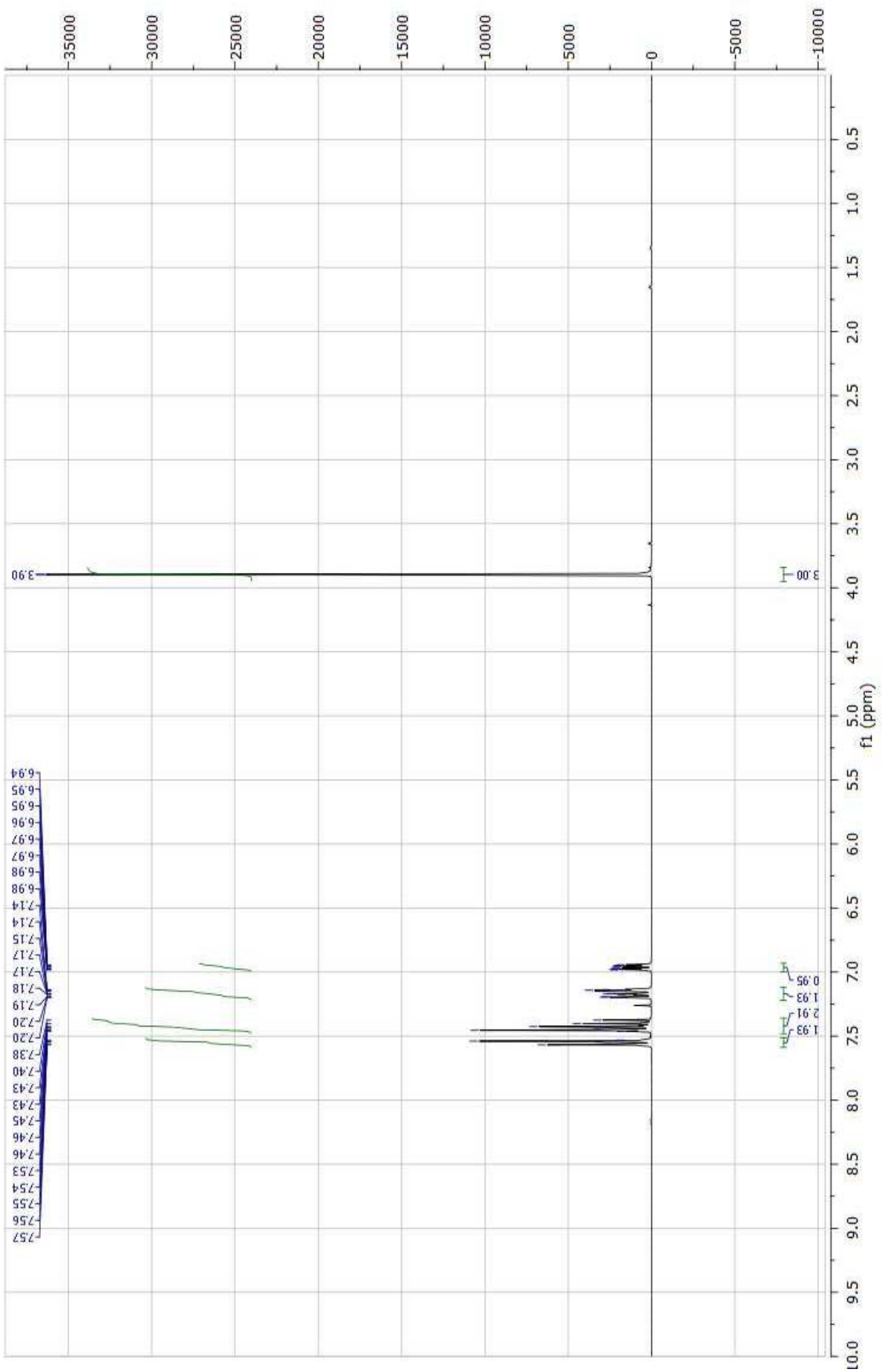
M. 4cg

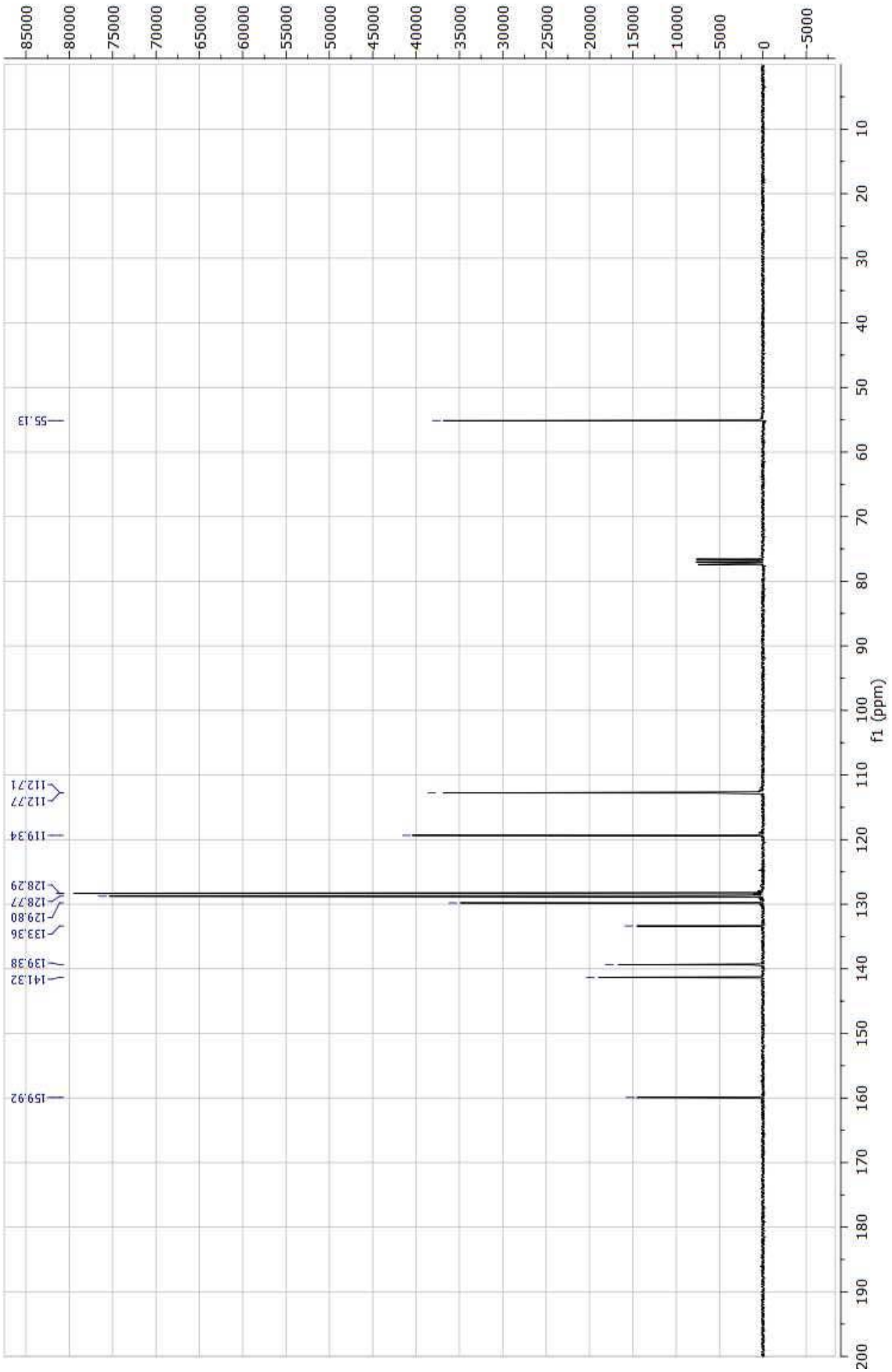


GC/MS Analysis

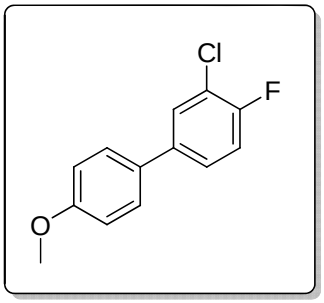




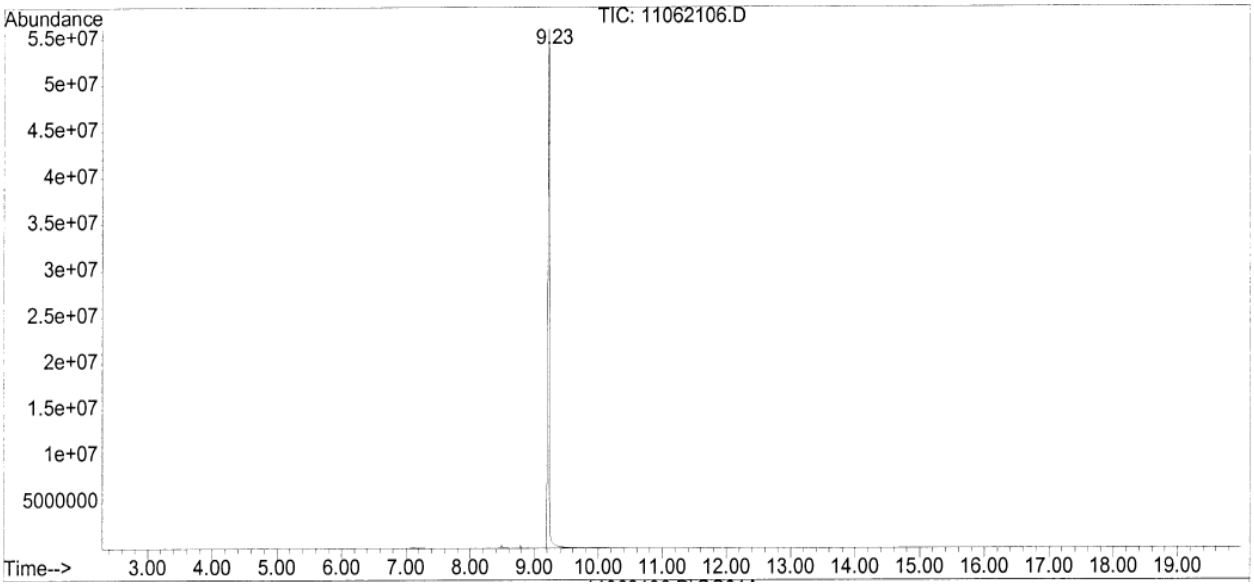

f1 (ppm)
3.90
3.00
0.95
1.93
2.91
1.93

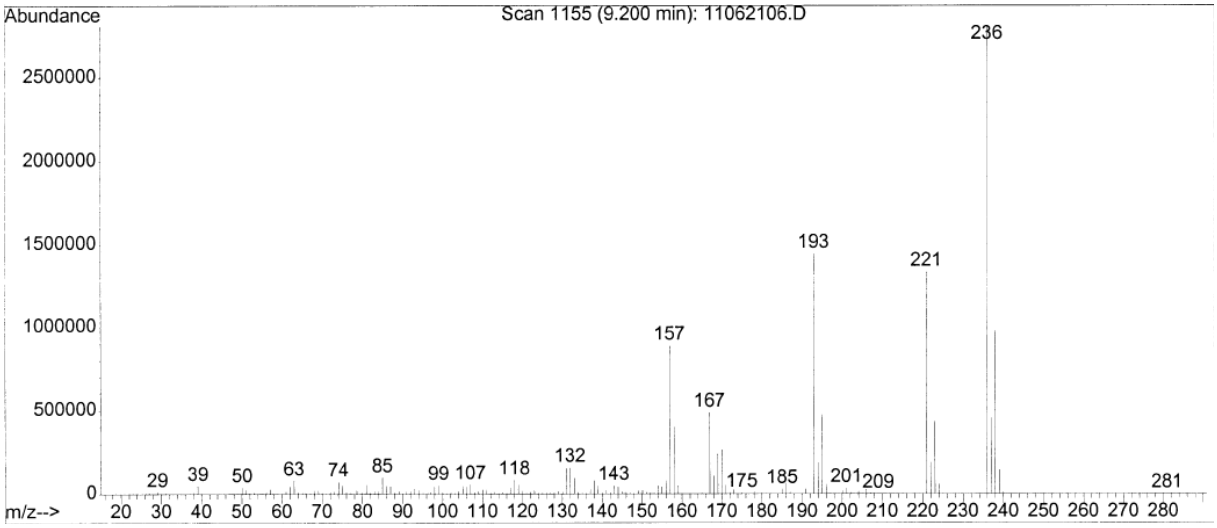

85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
55.13
112.71
112.77
119.34
128.29
128.77
129.80
133.36
139.38
141.32
159.92
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

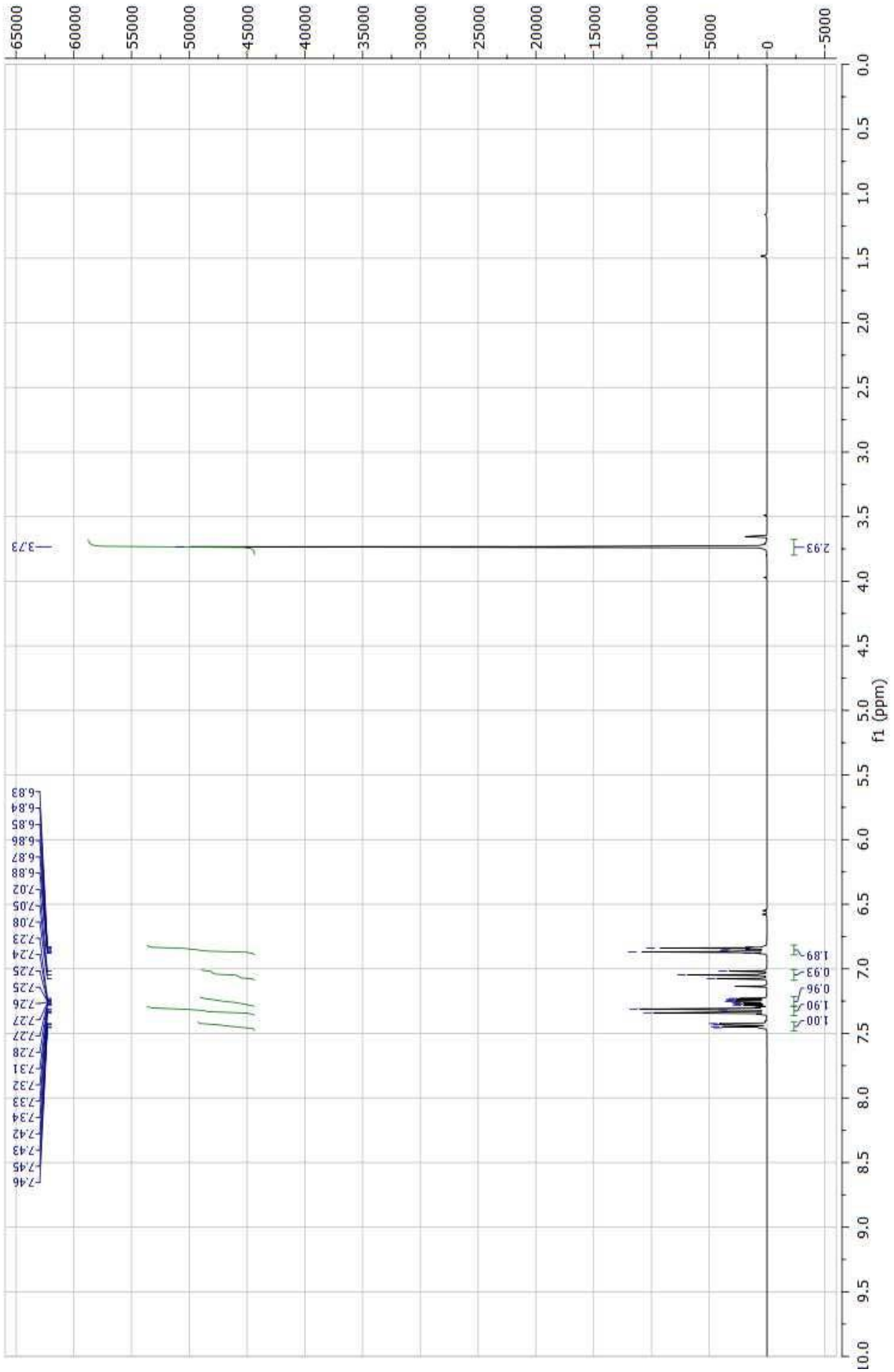
N. 4aj

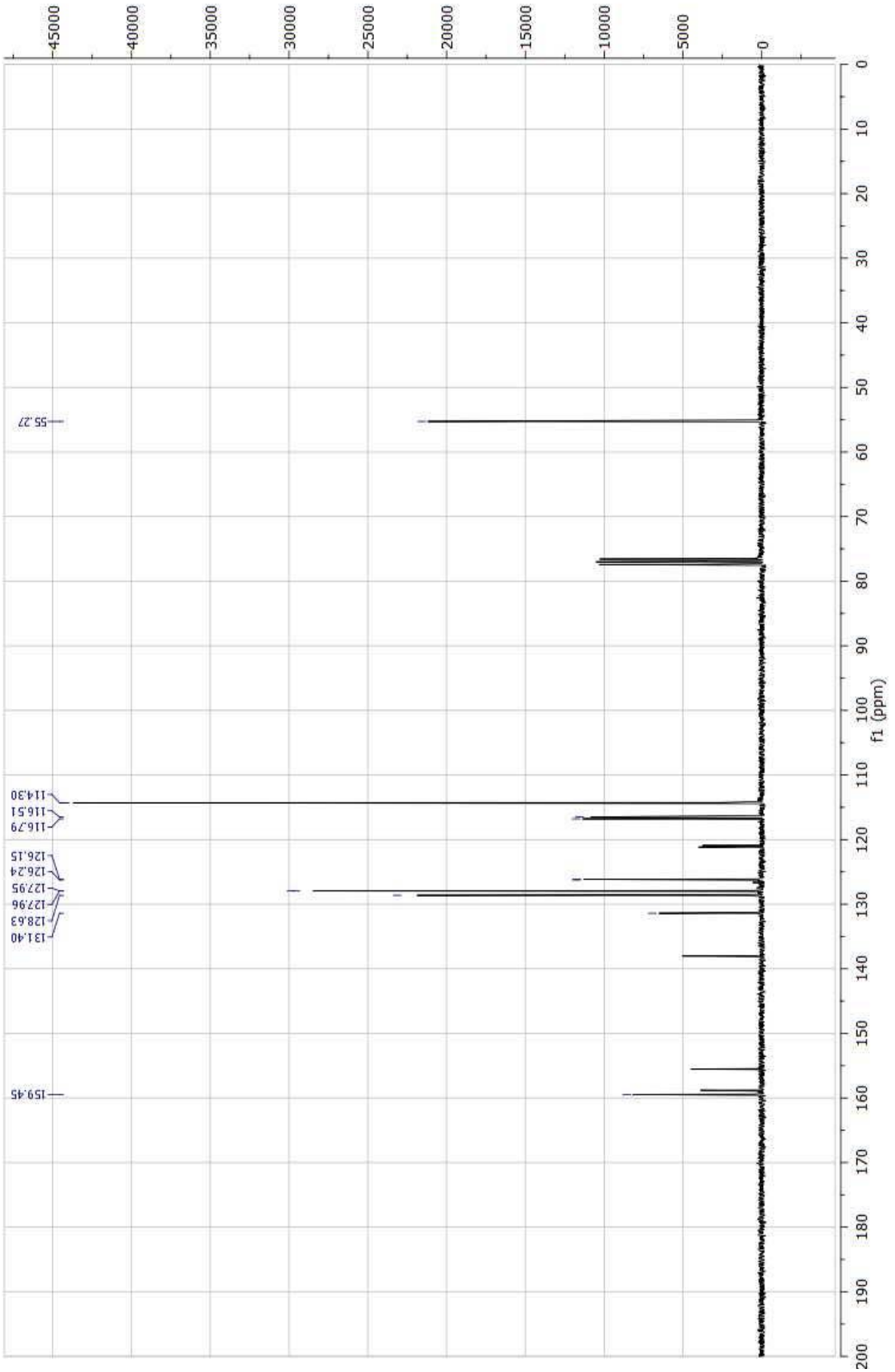


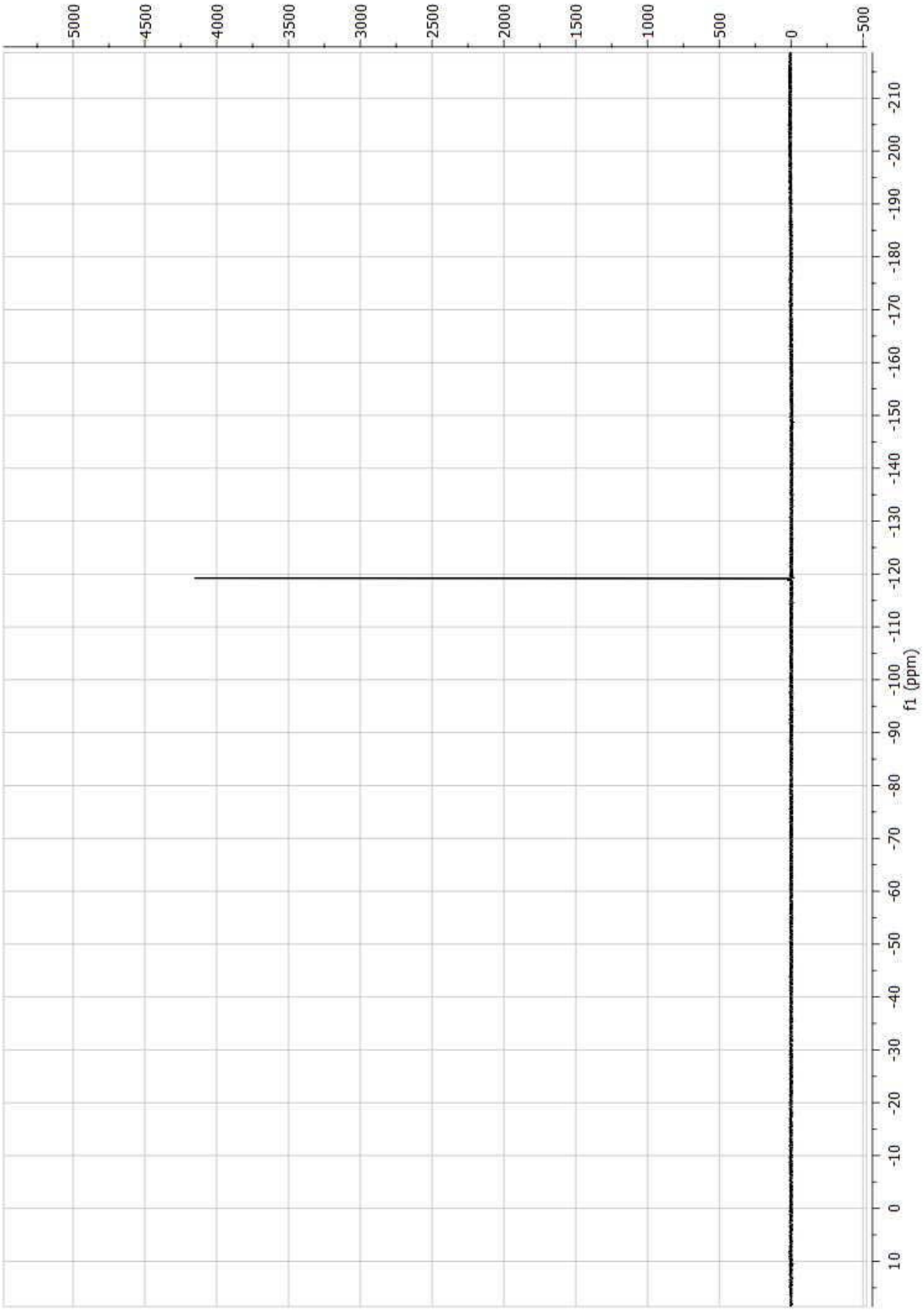
GC/MS Analysis



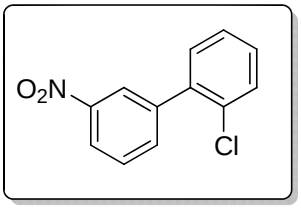



f1 (ppm)
3.73
2.93
1.89
0.93
0.96
1.90
1.00

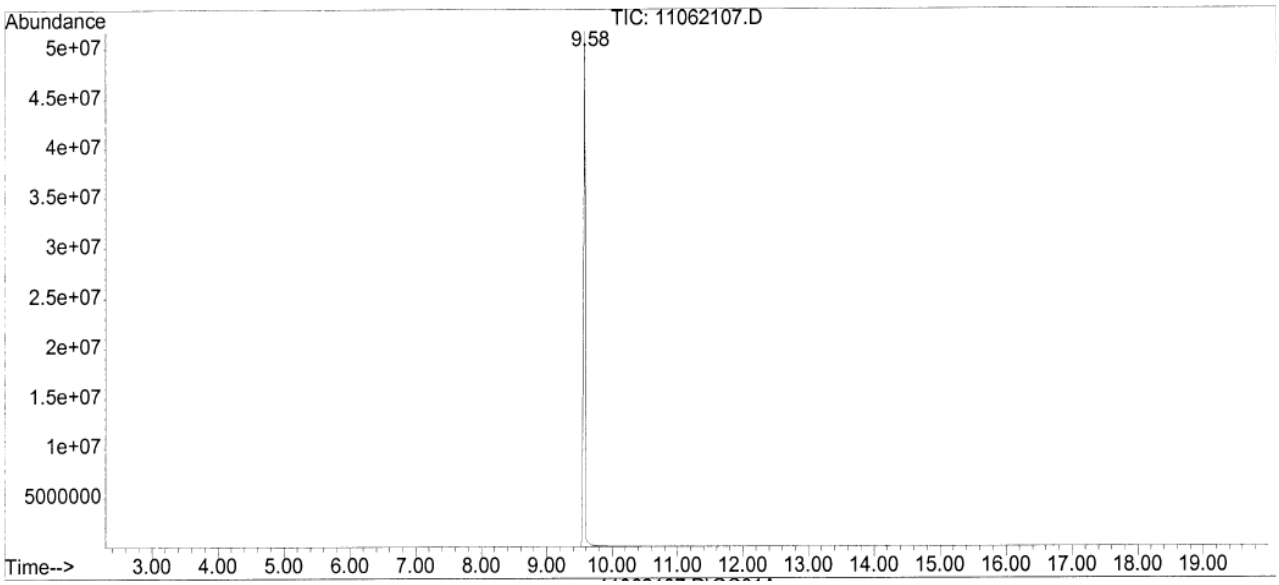

45000
40000
35000
30000
25000
20000
15000
10000
5000
0
55.27
114.30
116.51
116.79
126.15
126.24
127.95
127.96
128.63
131.40
159.45
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

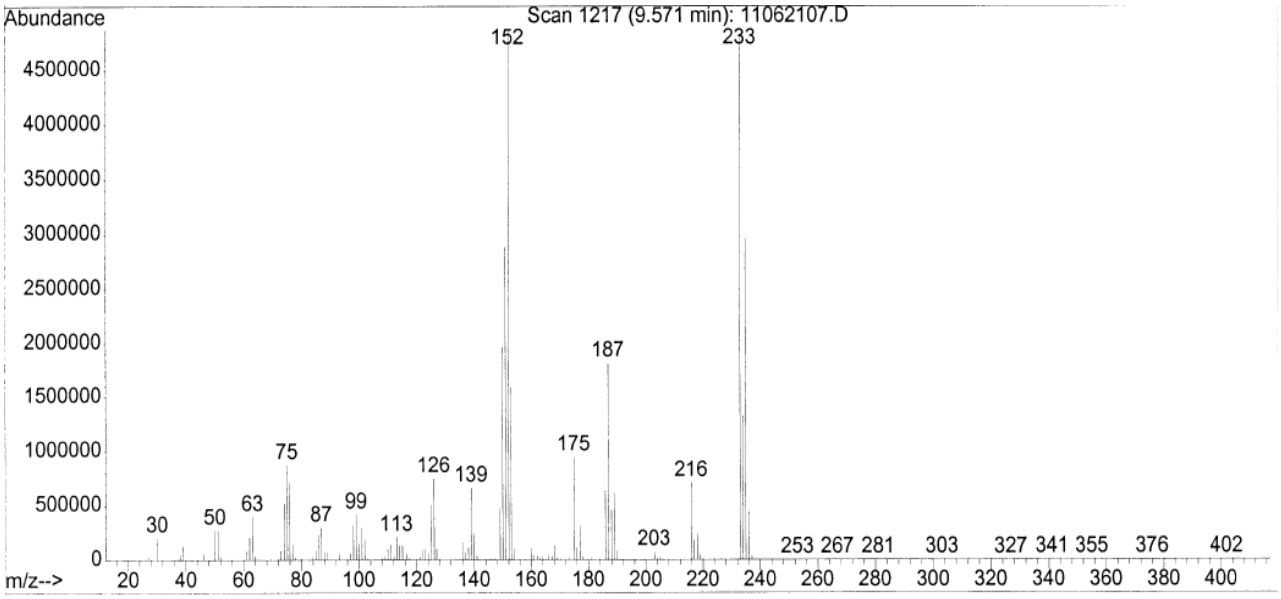

5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-210
-200
-190
-180
-170
-160
-150
-140
-130
-120
-110
-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
f1 (ppm)

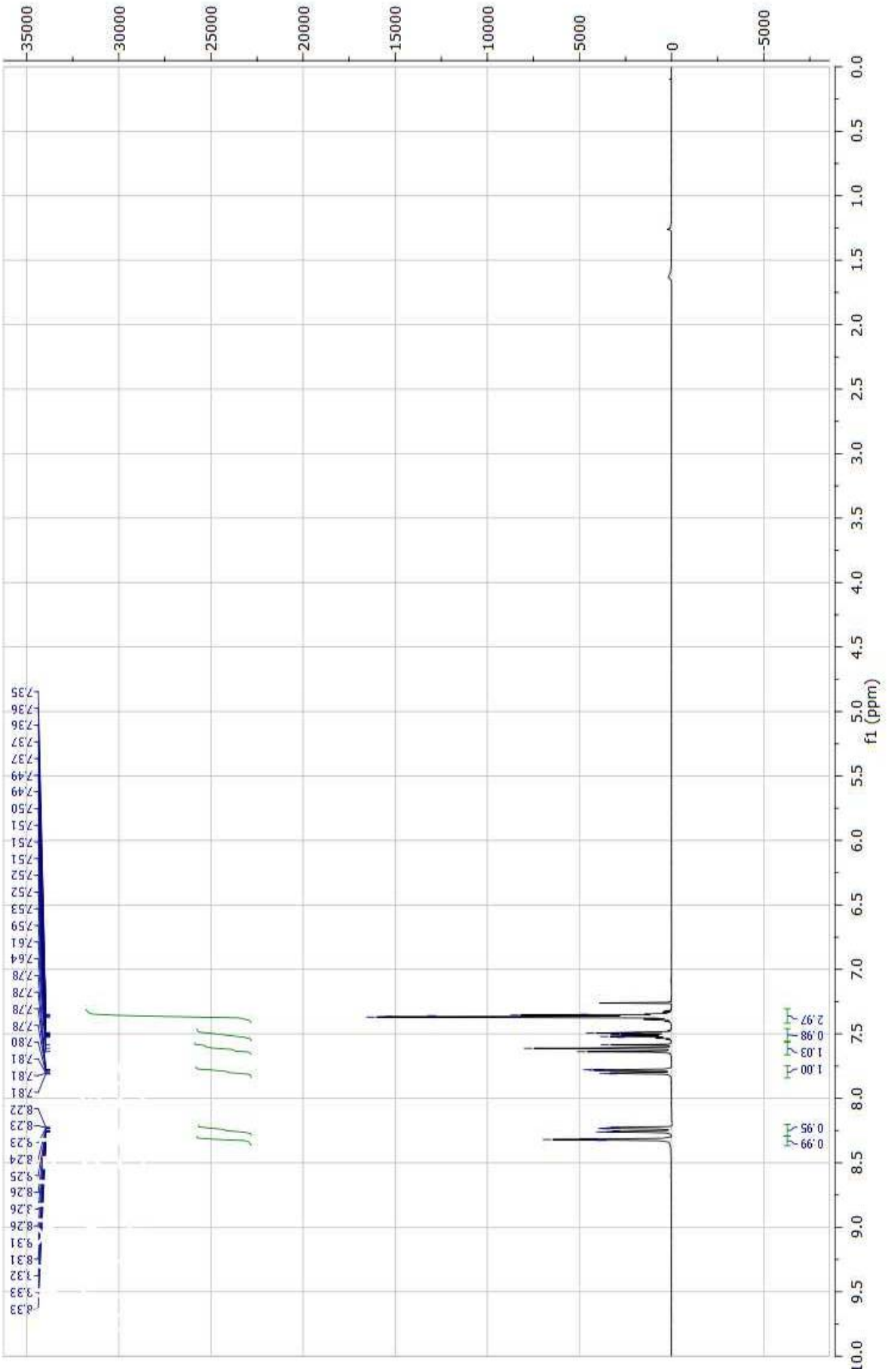
0. 4kl

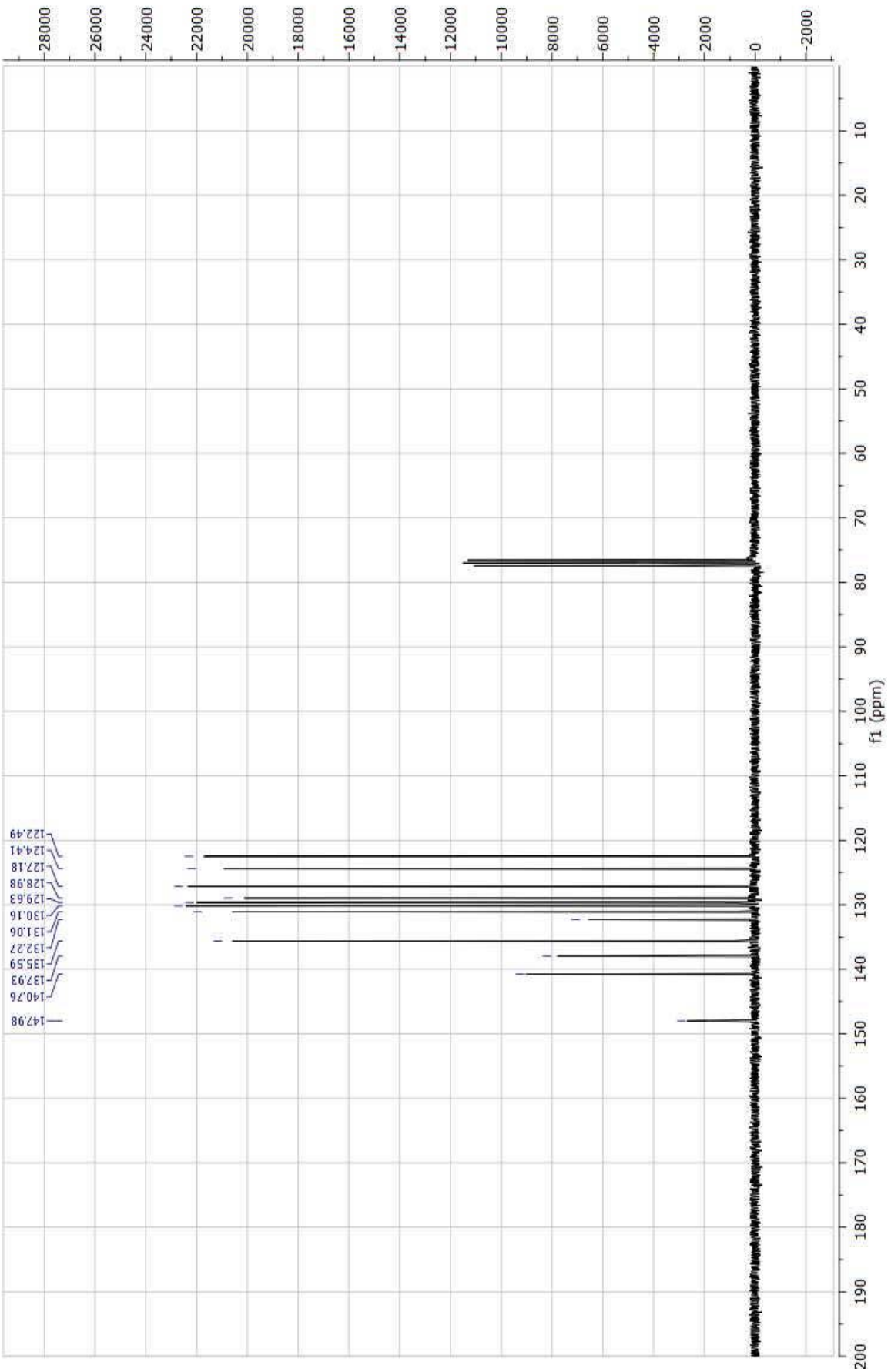


GC/MS Analysis

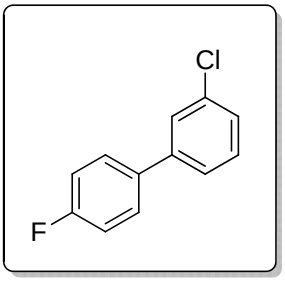




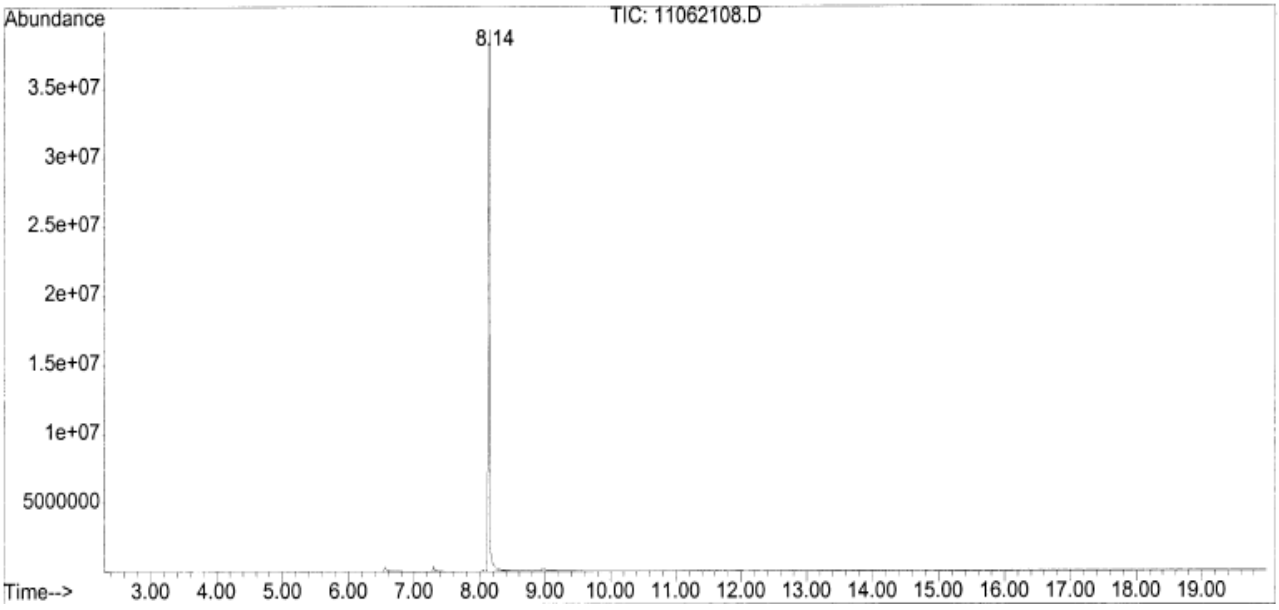

f1 (ppm)
2.97
0.98
1.03
1.00
0.95
0.99

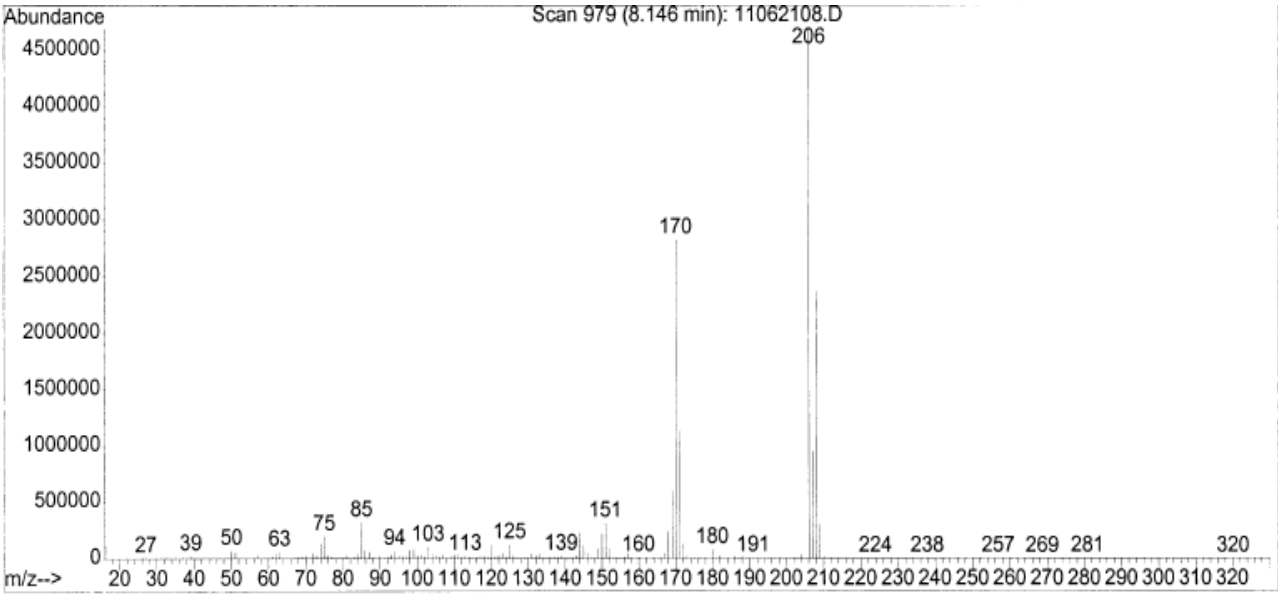

f1 (ppm)
122.49
124.41
127.18
128.98
129.63
130.16
131.06
132.27
135.59
137.93
140.76
147.98

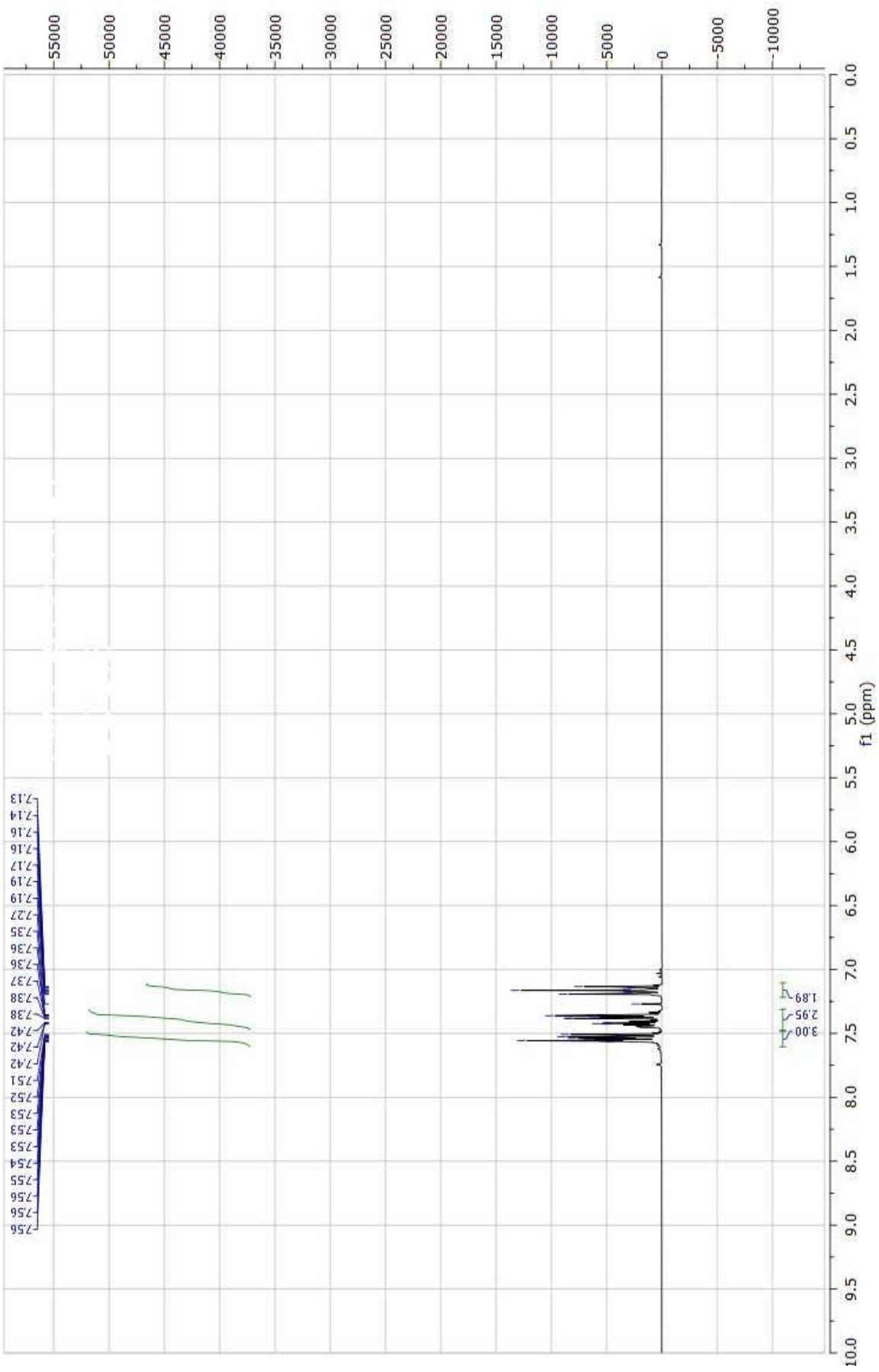
P. 4mn

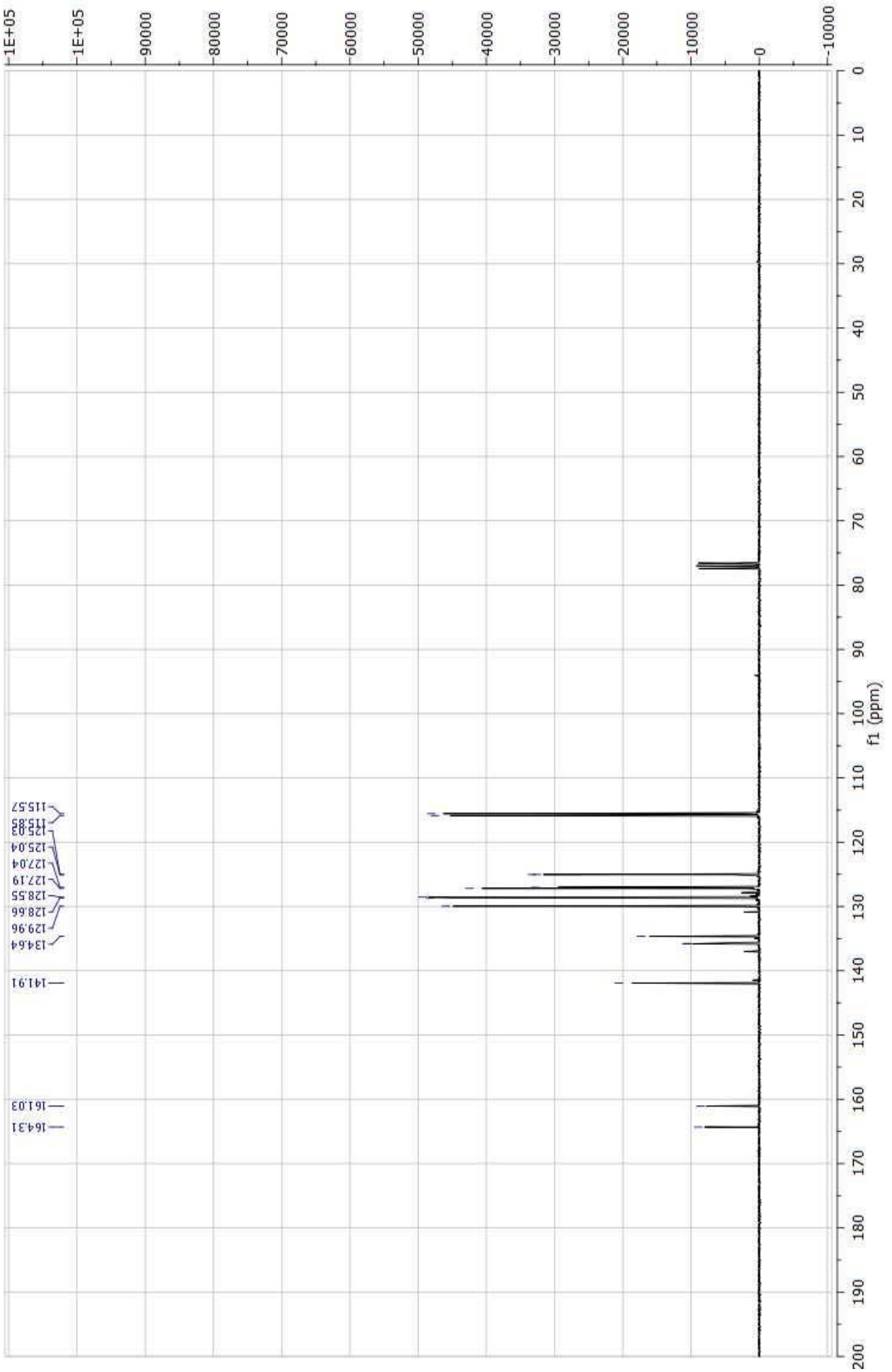


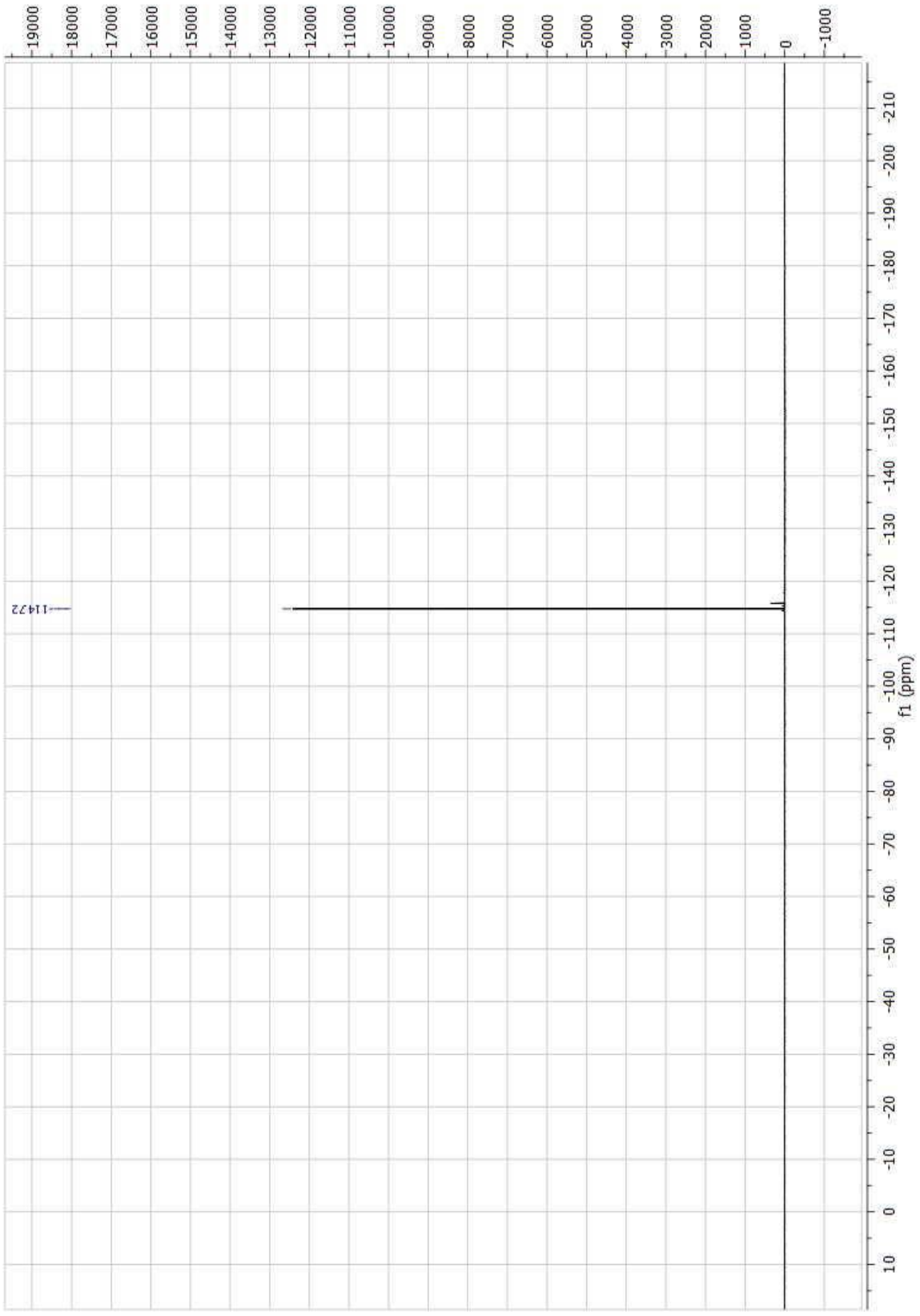
GC/MS Analysis



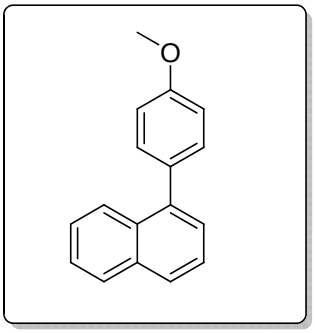



f1 (ppm)
1.89
2.95
3.00

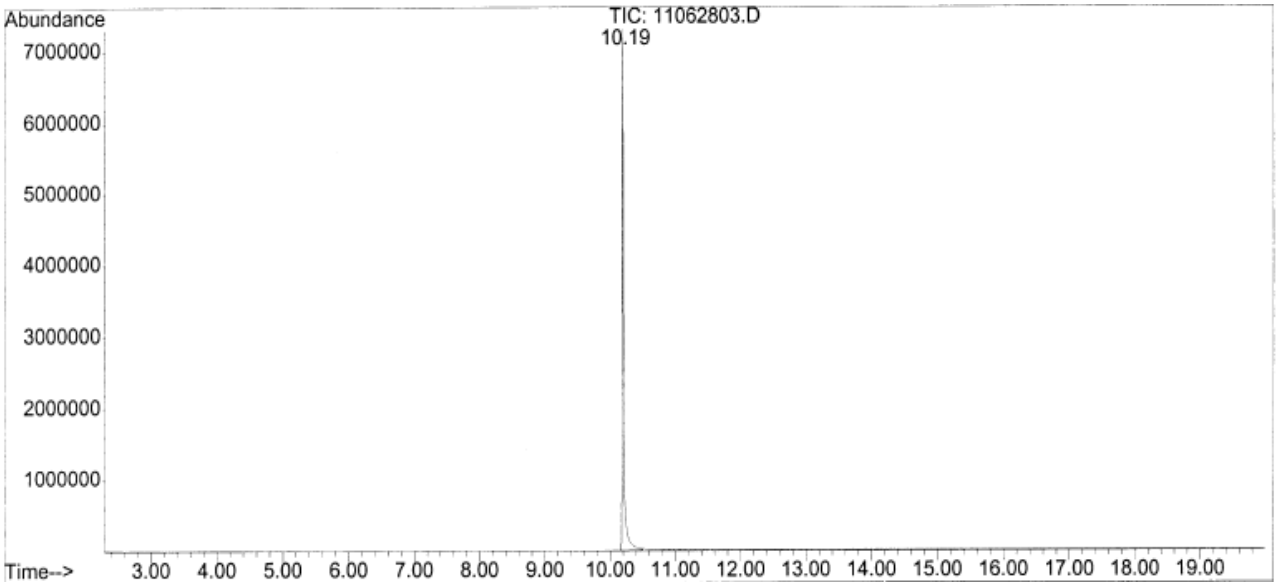

1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
115.57
115.85
125.03
125.04
127.04
127.19
128.55
128.66
129.96
134.64
141.91
161.03
164.31

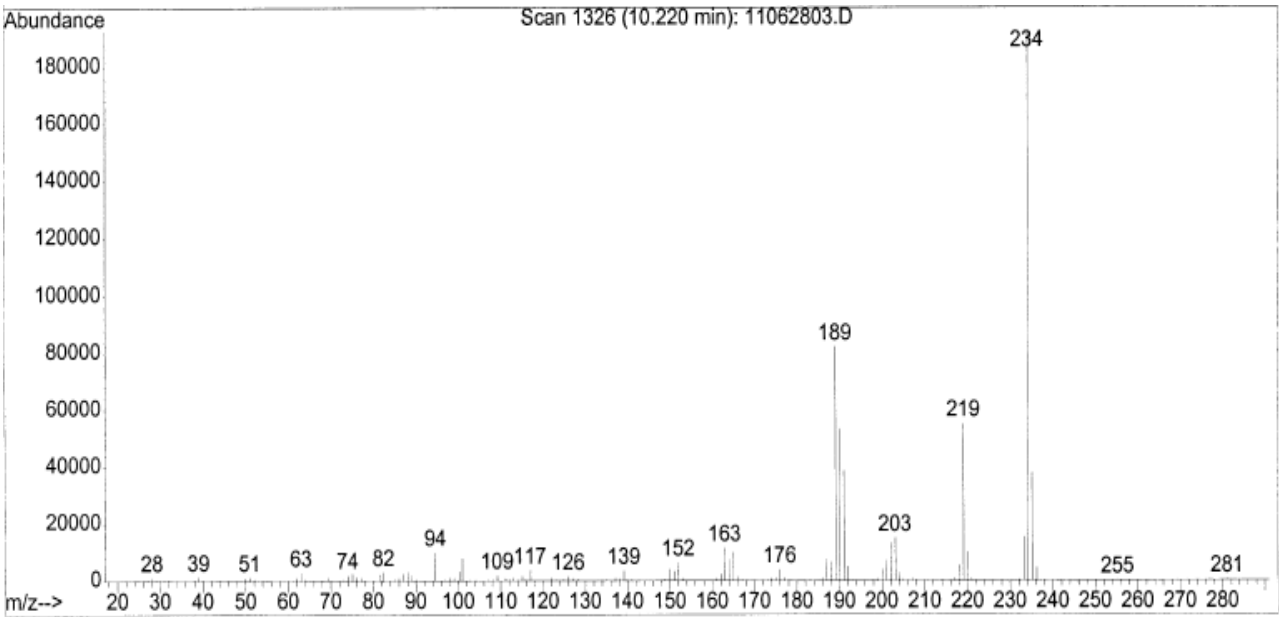


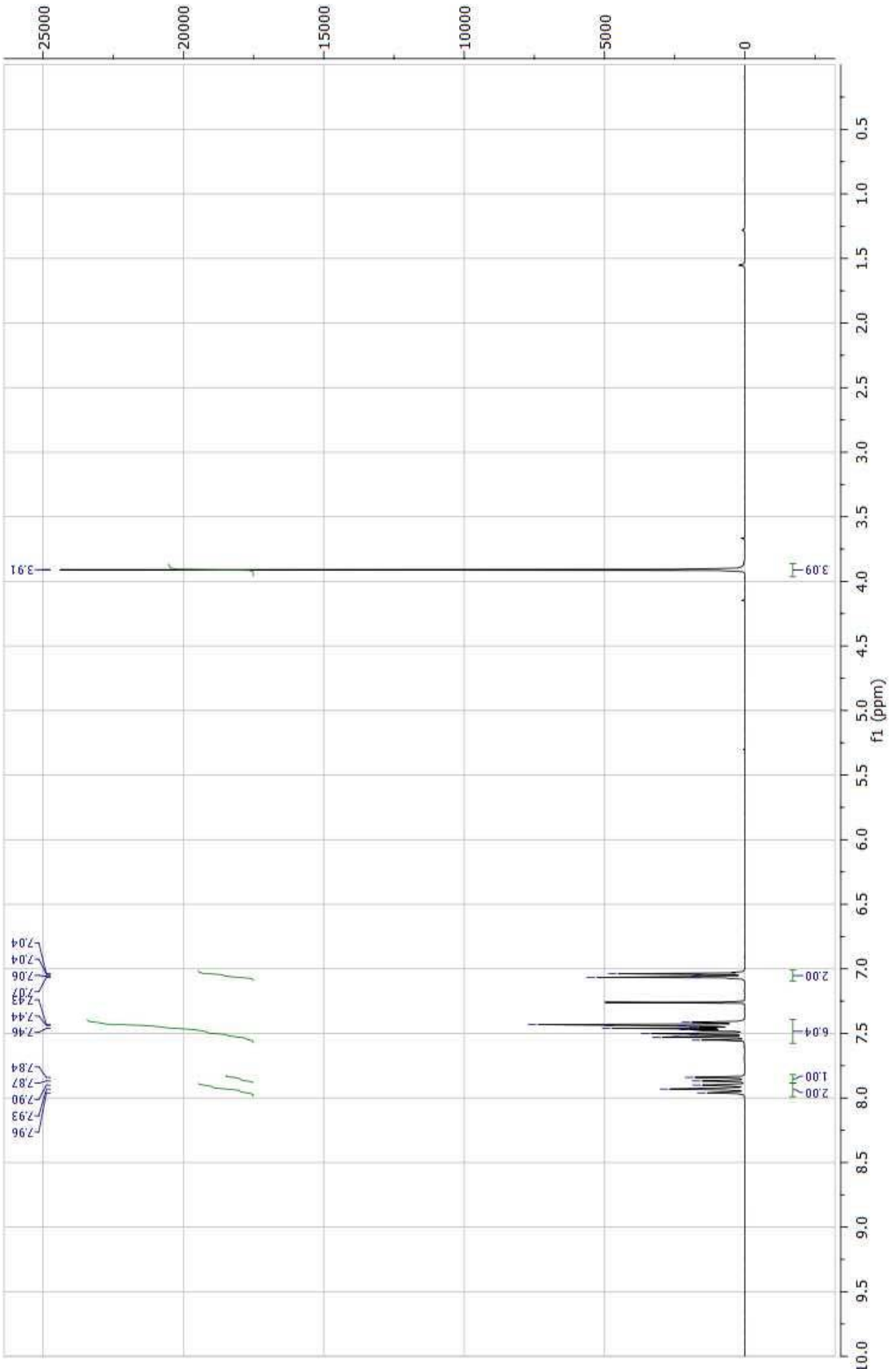
Q. 4ai

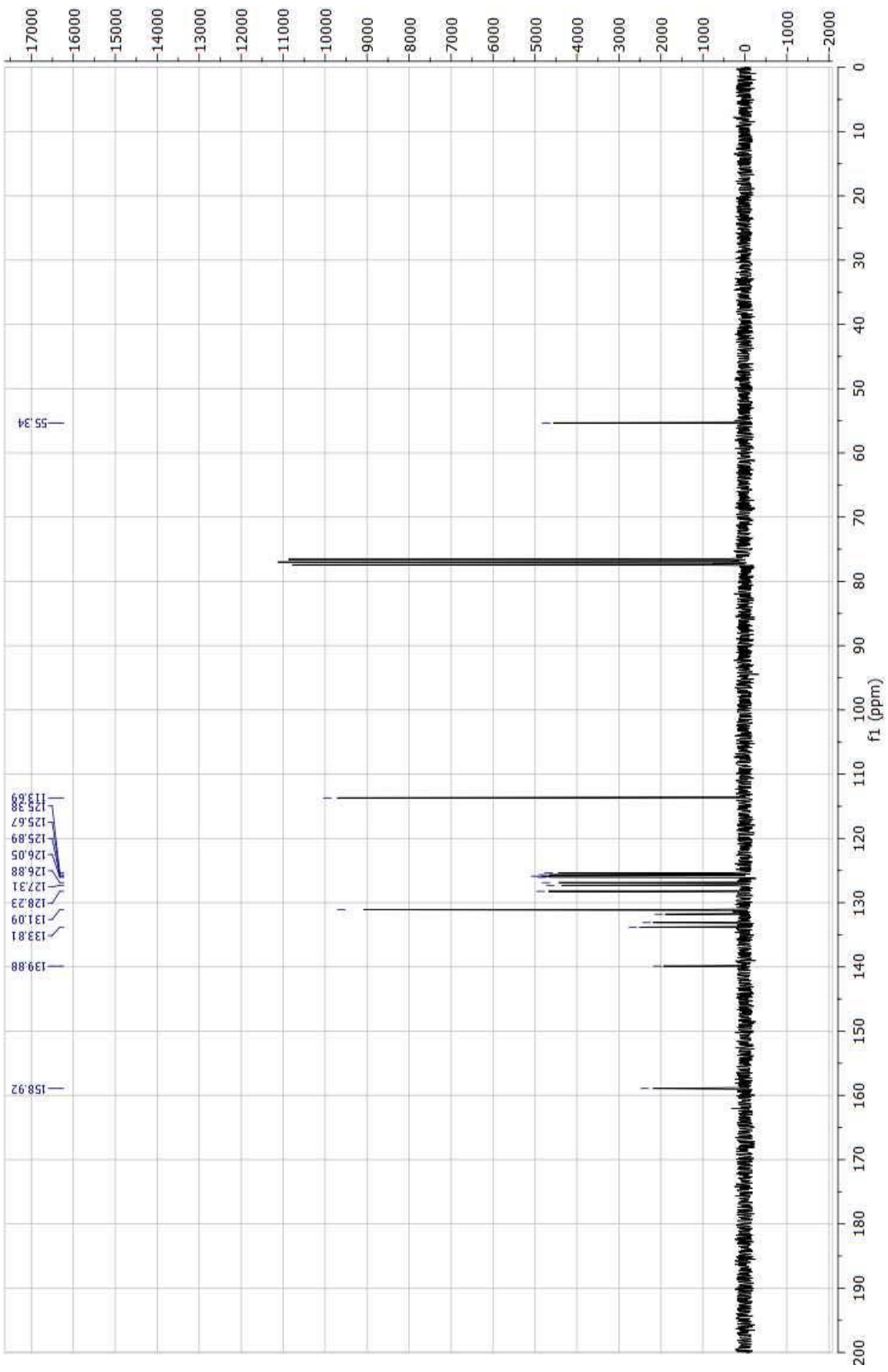


GC/MS Analysis

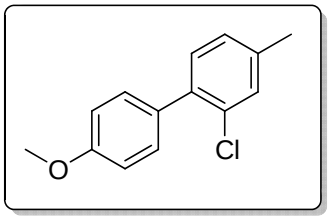




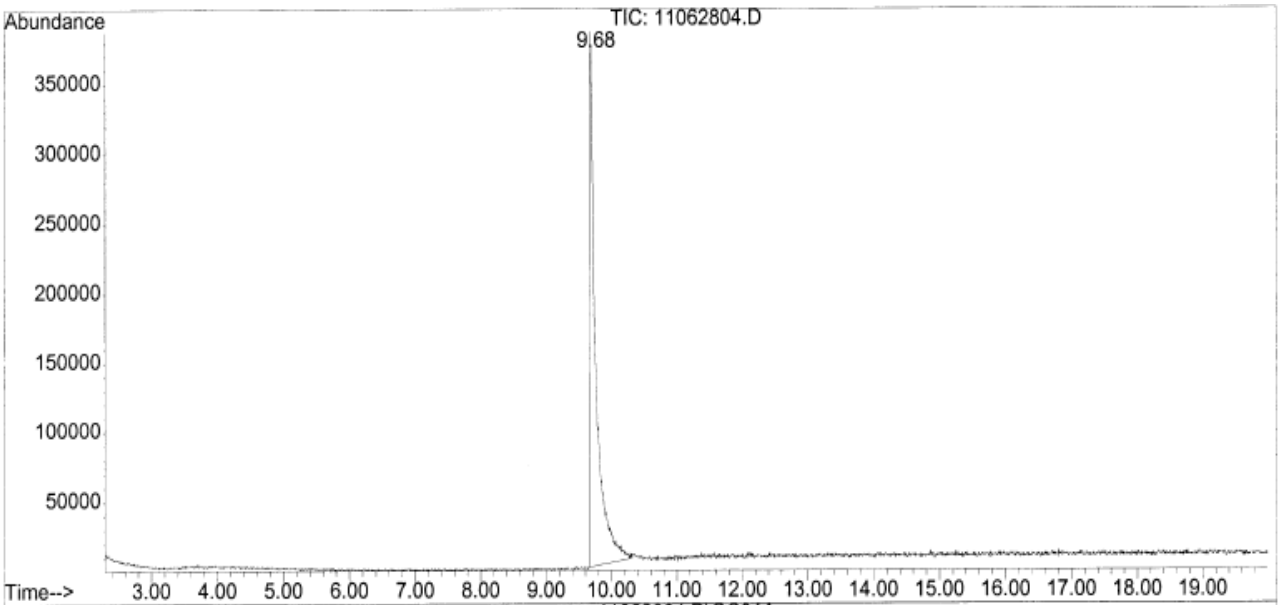

25000
20000
15000
10000
5000
0
3.91
3.09
2.00
6.04
1.00
2.00
7.96
7.93
7.90
7.87
7.84
7.46
7.44
7.43
7.07
7.06
7.04
7.04
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)

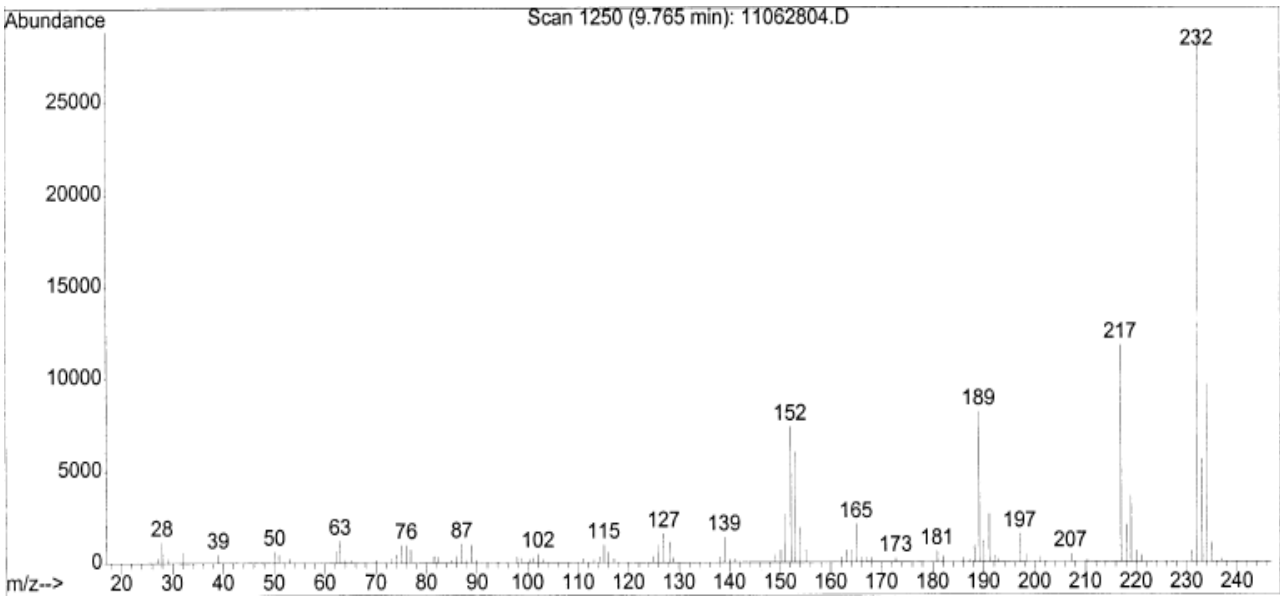

55.34
113.69
125.38
125.67
125.89
126.05
126.88
127.31
128.23
131.09
133.81
139.88
158.92
f1 (ppm)

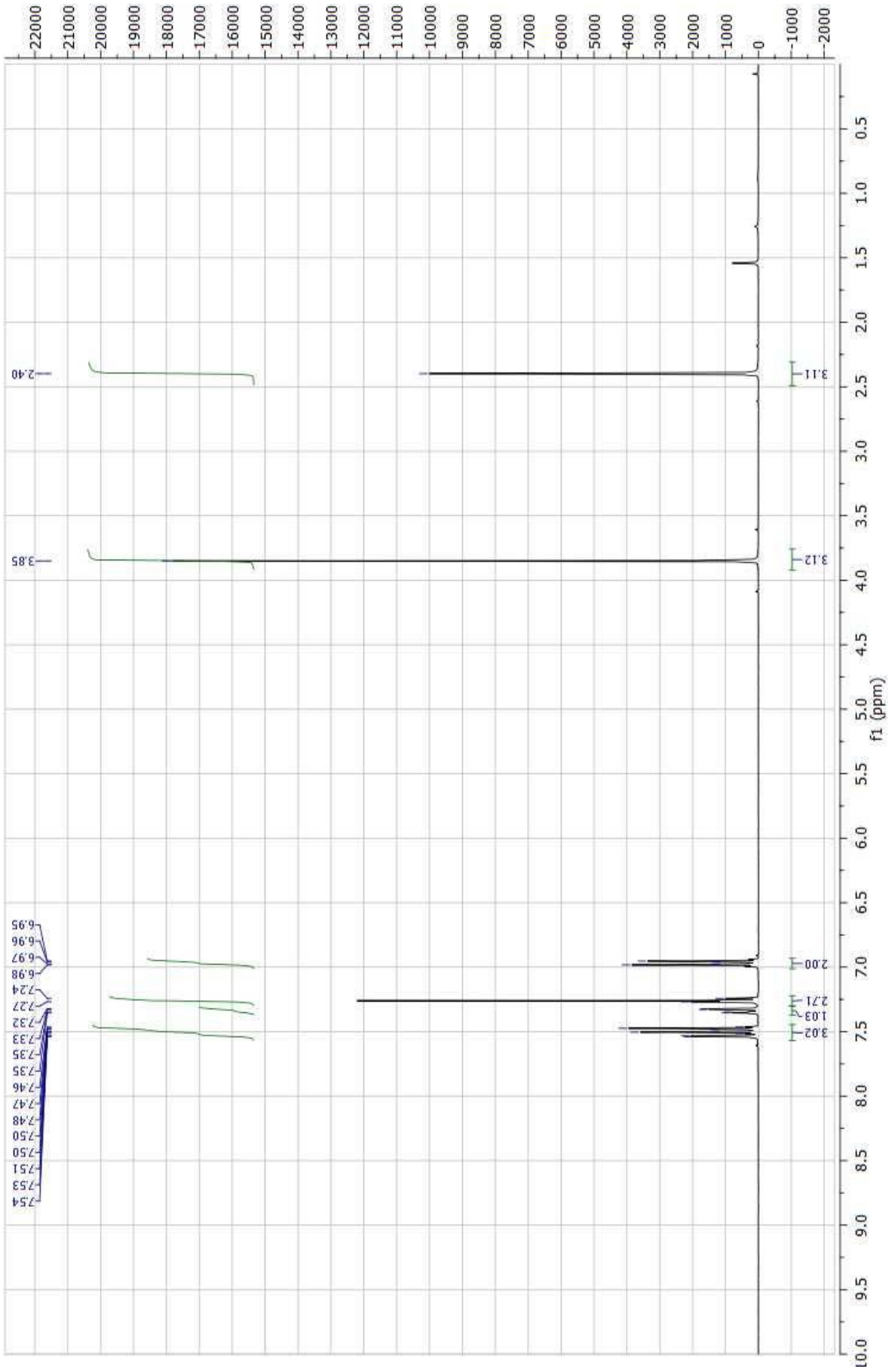
R. 4ao

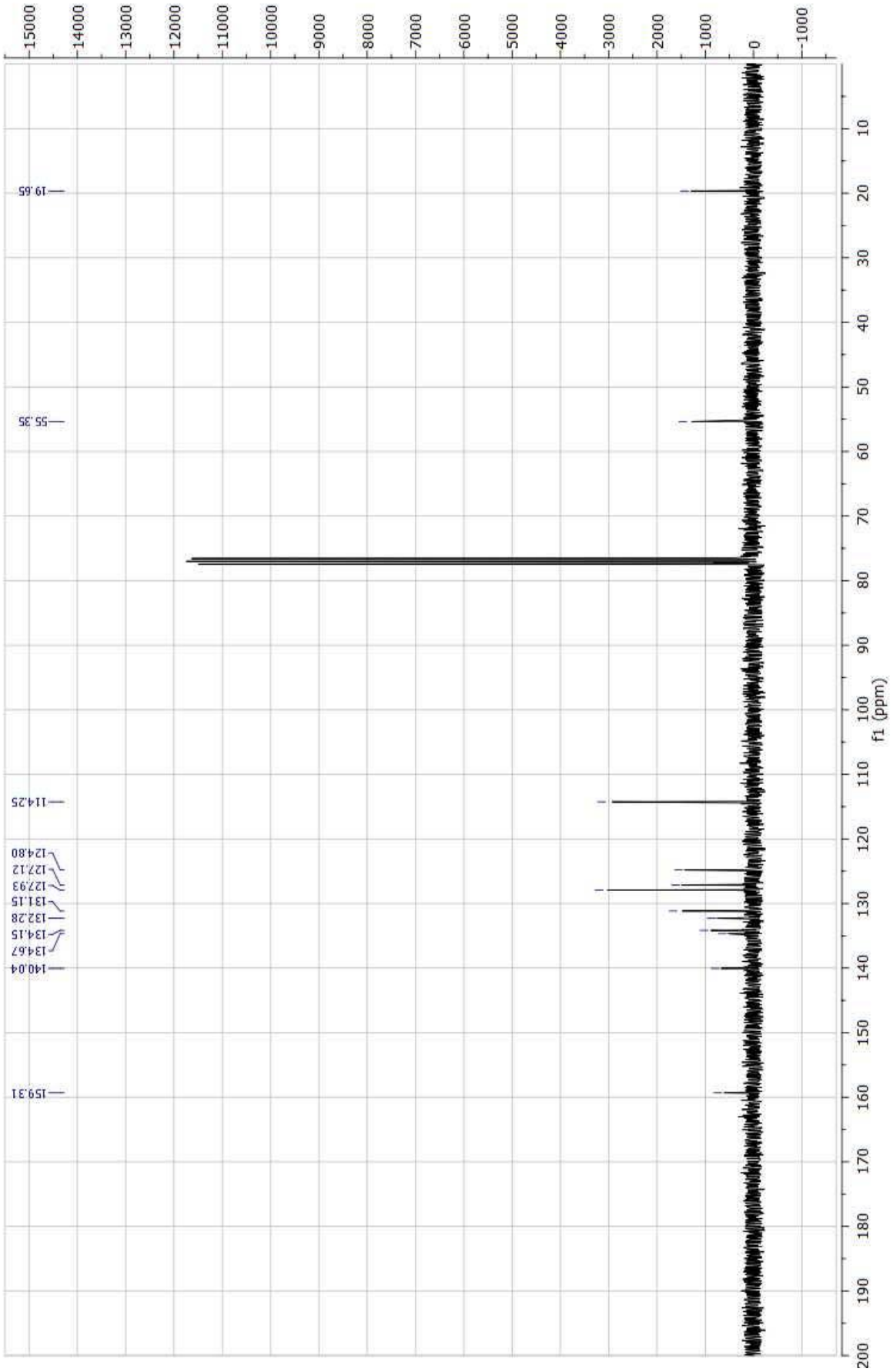


GC/MS Analysis

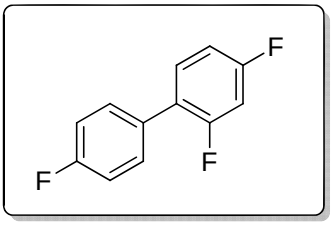




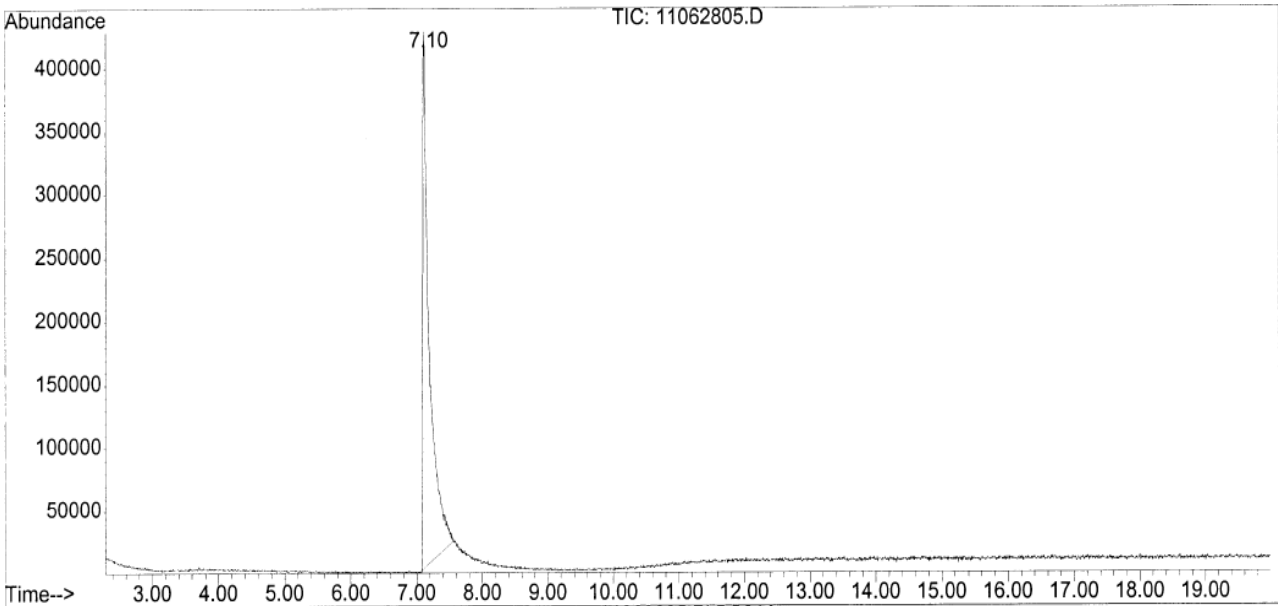

f1 (ppm)
2.40
3.85
6.95
6.96
6.97
6.98
7.24
7.27
7.32
7.33
7.35
7.35
7.46
7.47
7.48
7.50
7.50
7.51
7.53
7.54
3.11
3.12
2.00
2.71
1.03
3.02

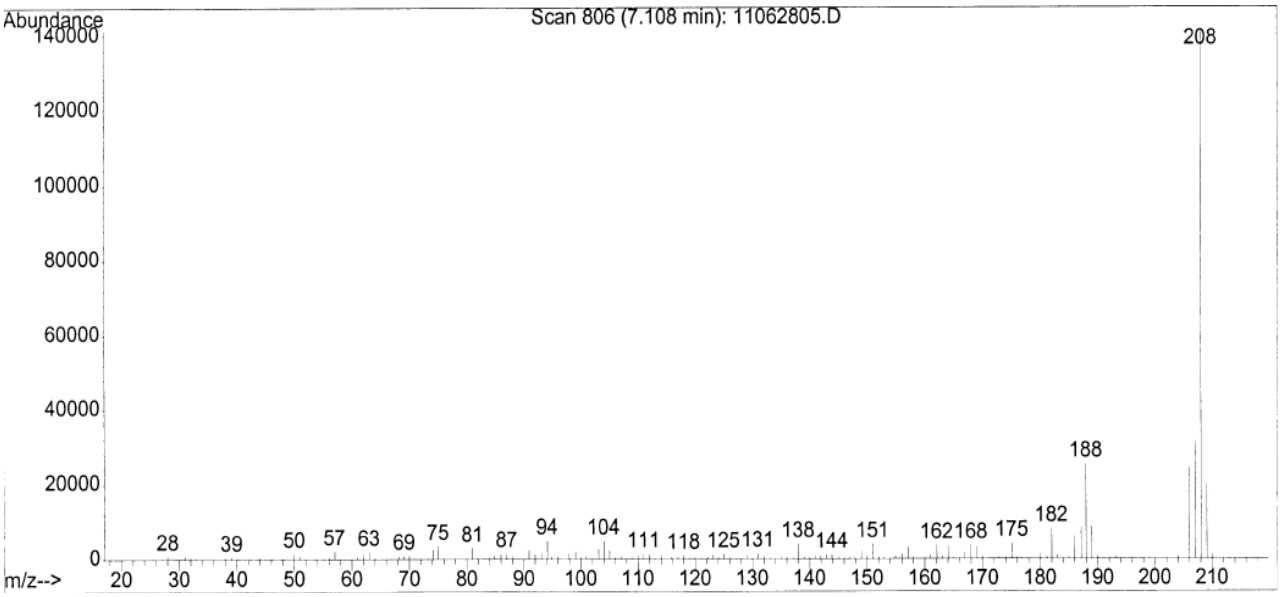

19.65
55.35
114.25
124.80
127.12
127.93
131.15
132.28
134.15
134.67
140.04
159.31
f1 (ppm)

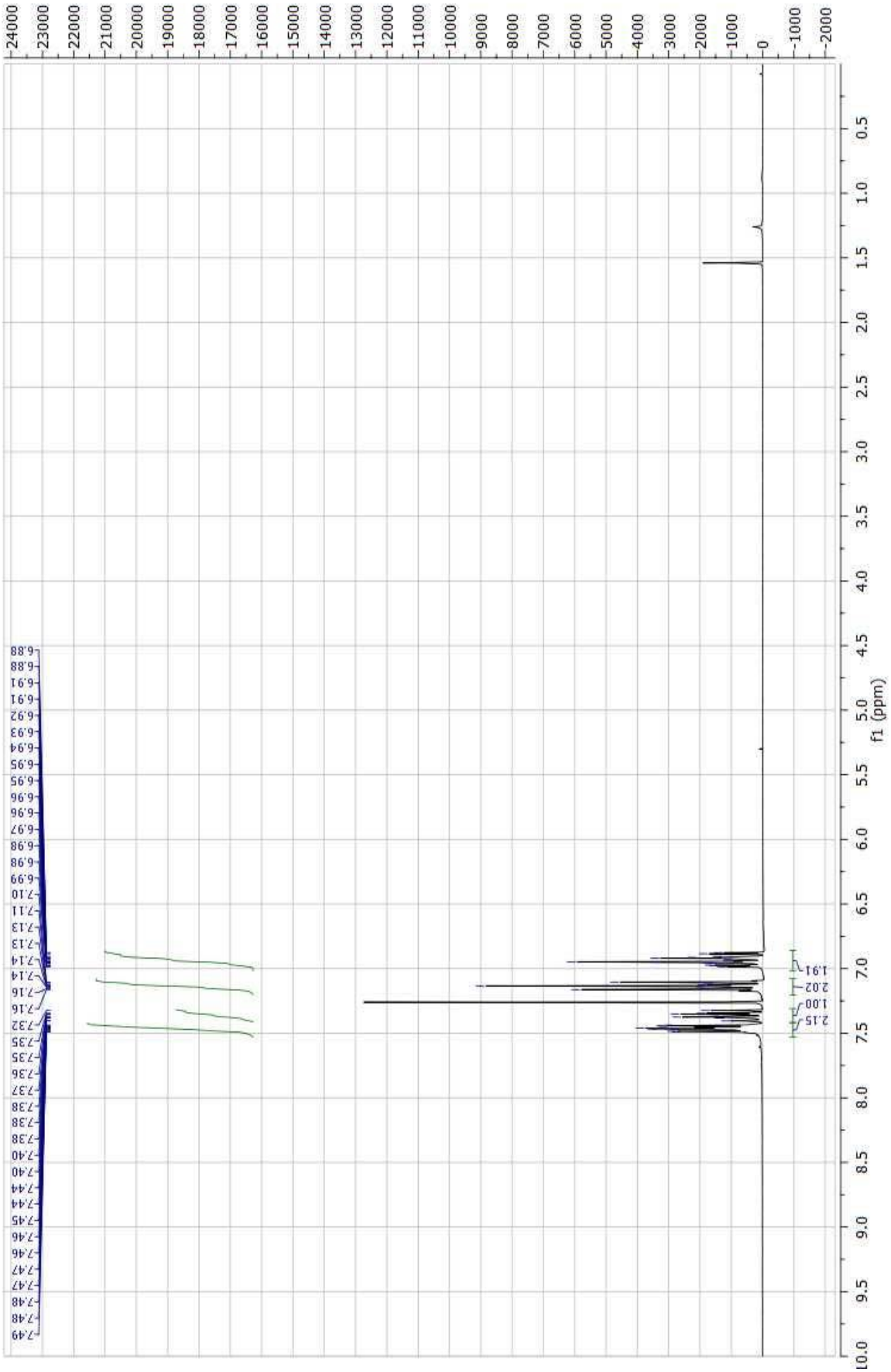
S. 4mp

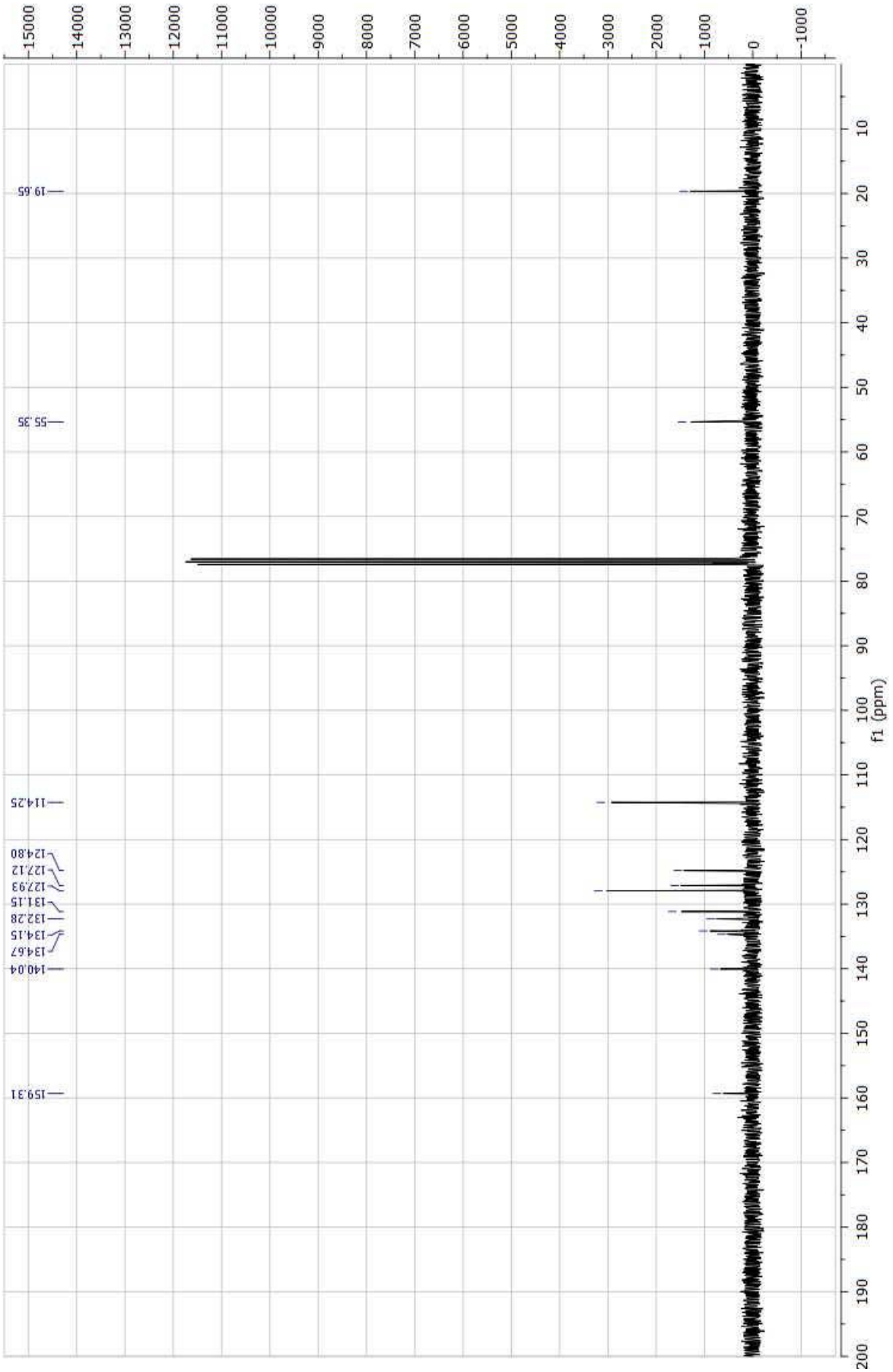


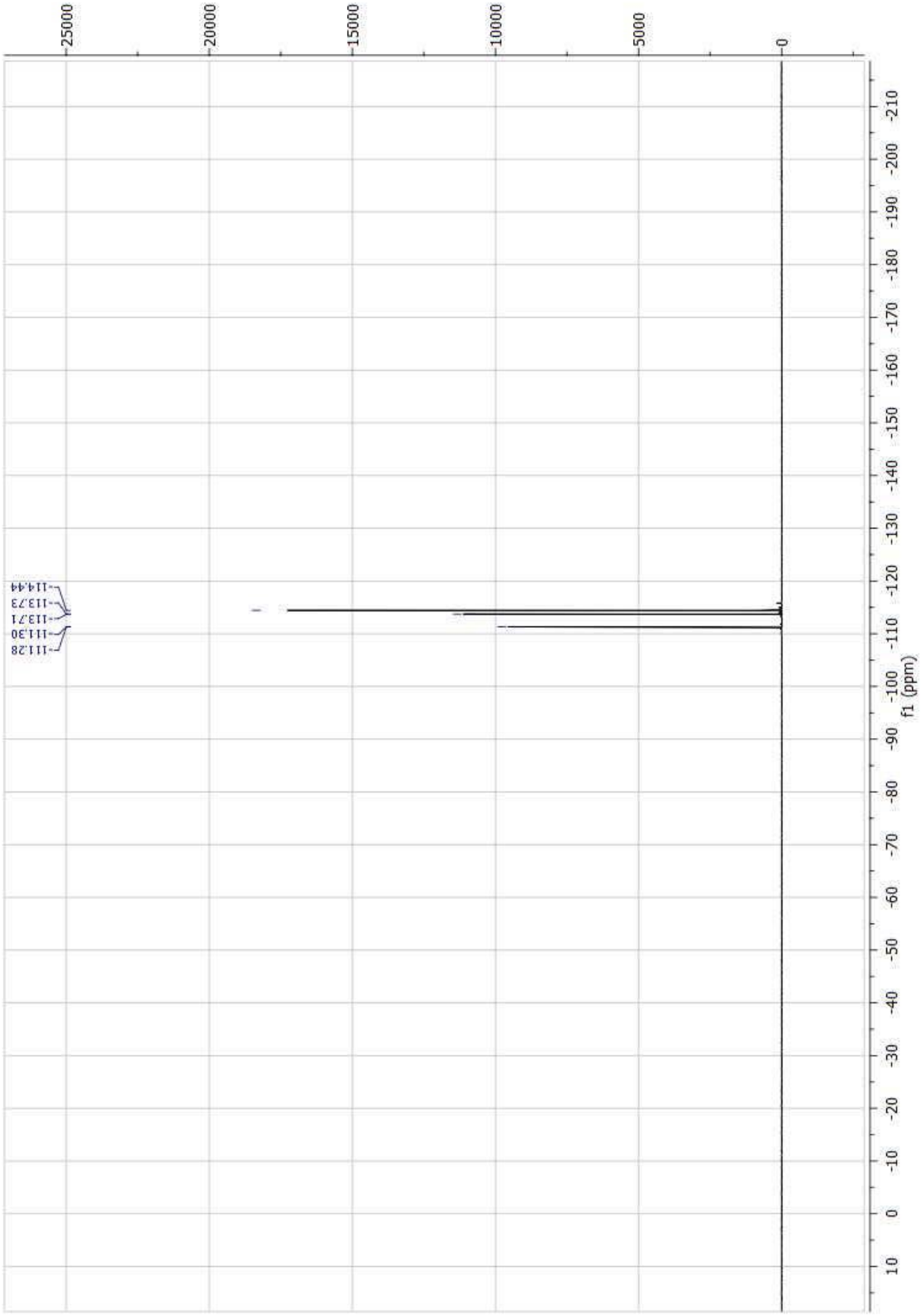
GC/MS Analysis



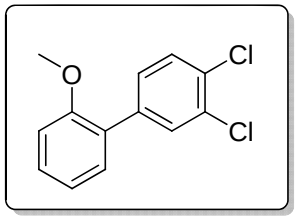


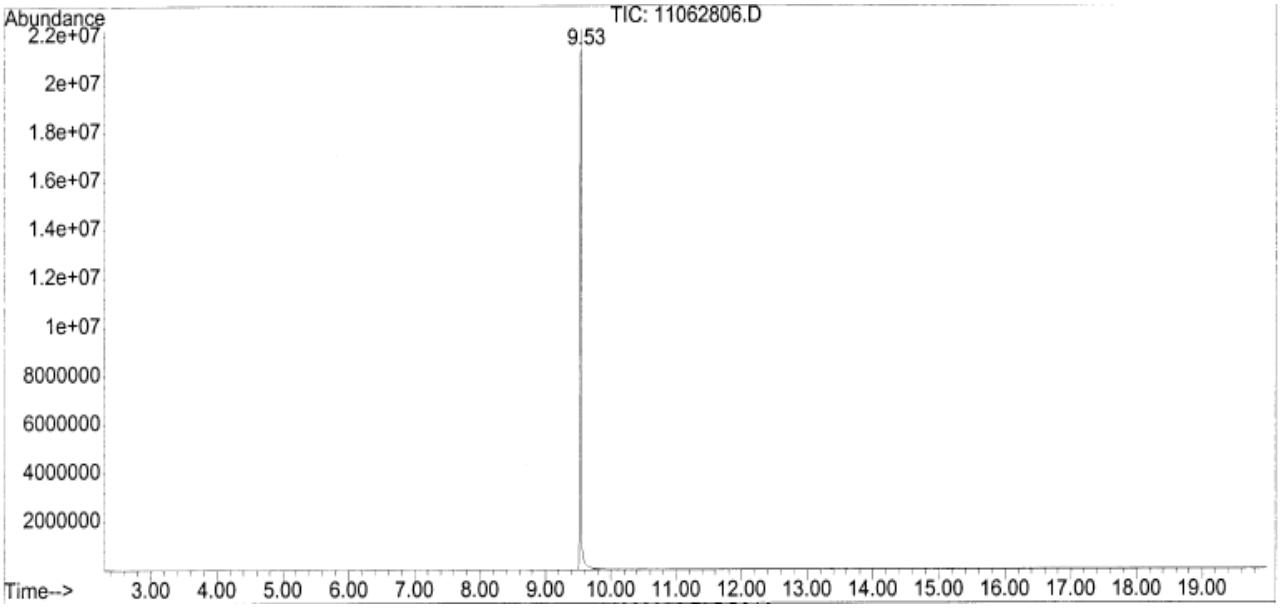

f1 (ppm)
1.91
2.02
1.00
2.15

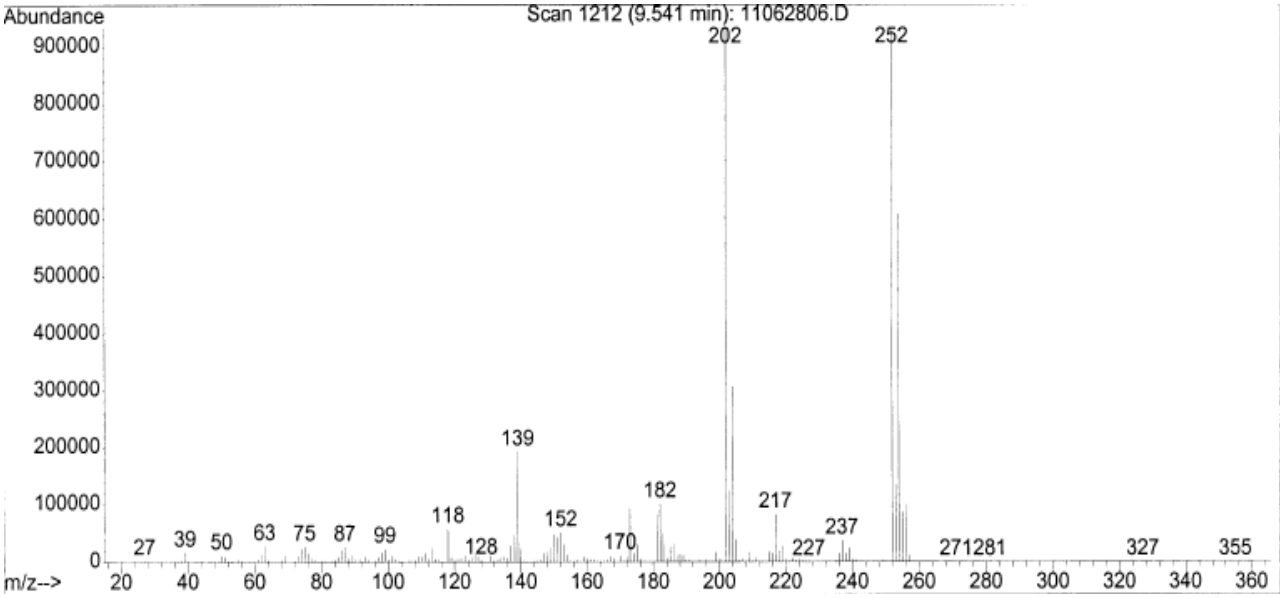

19.65
55.35
114.25
124.80
127.12
127.93
131.15
132.28
134.15
134.67
140.04
159.31
f1 (ppm)

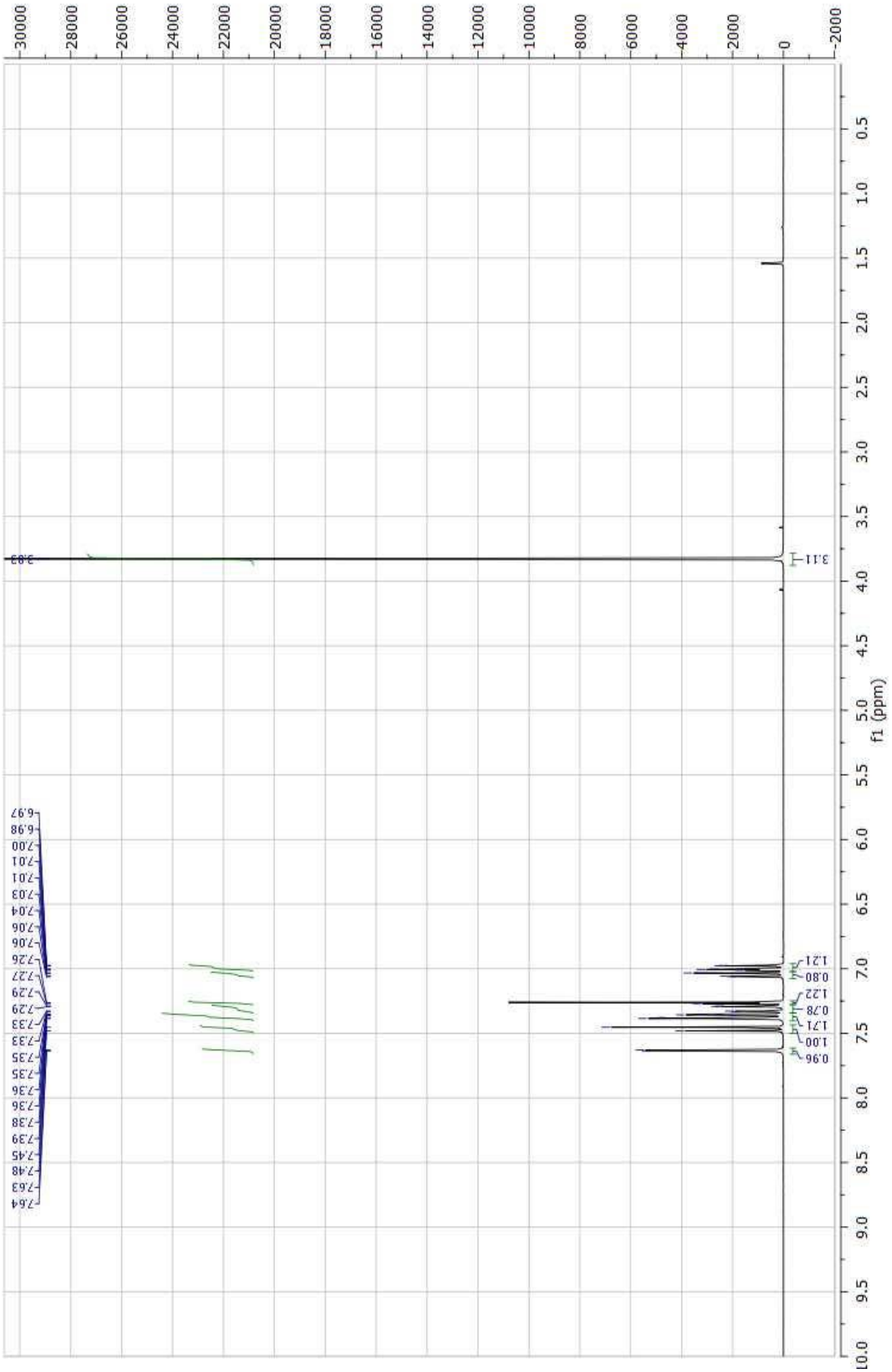


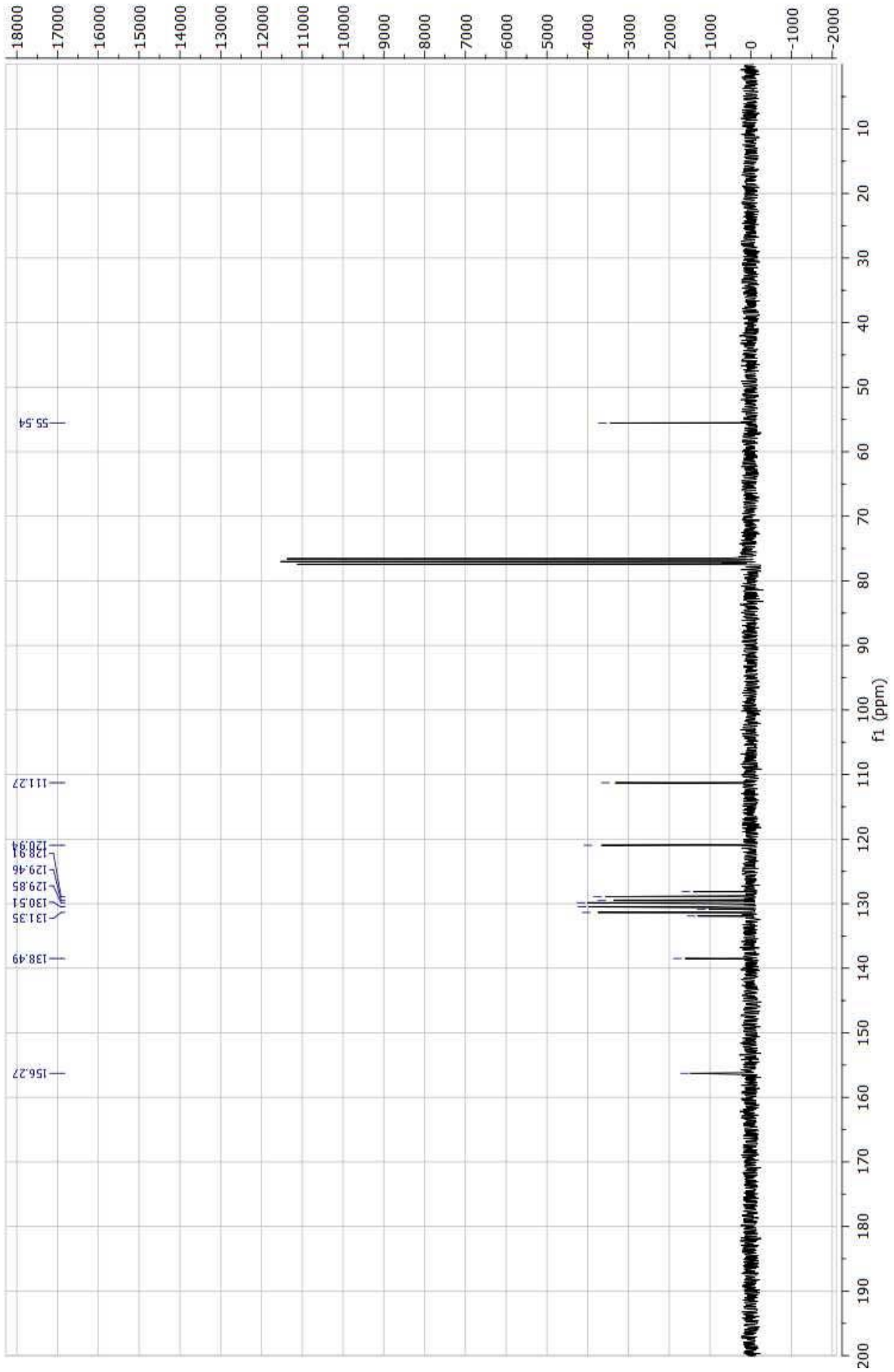
T. 4dq


O
Cl
Cl

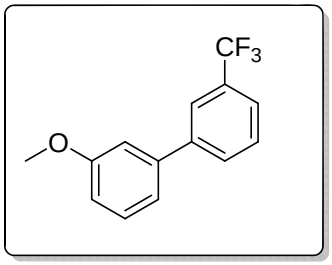

Abundance
TIC: 11062806.D
9.53
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
Time-->
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00

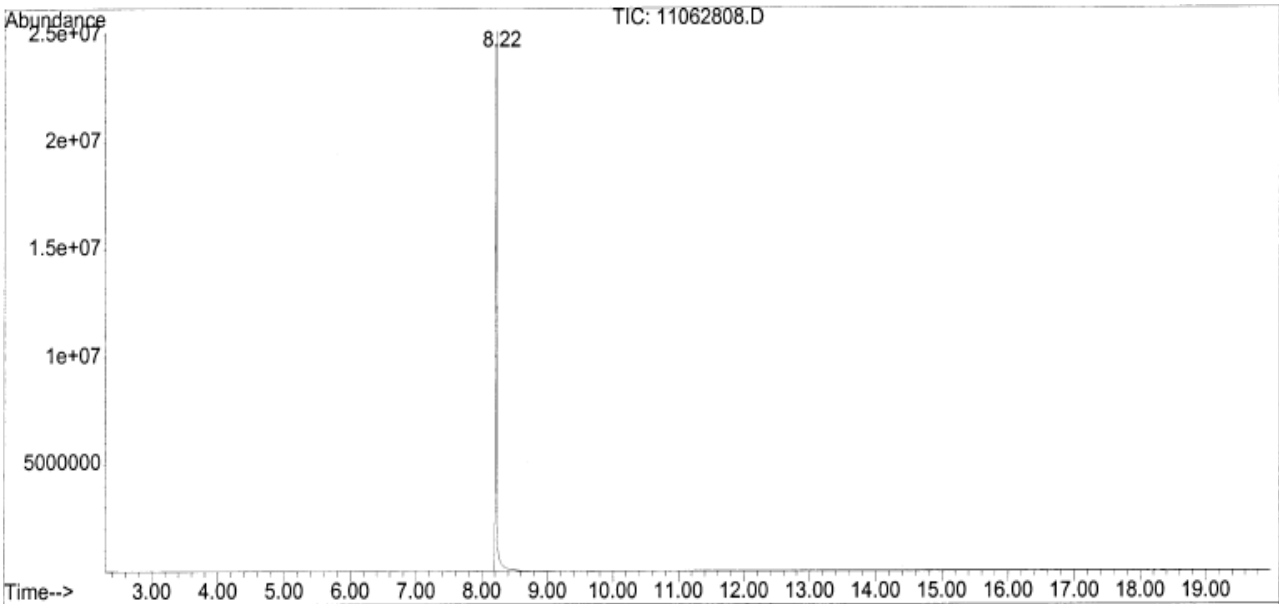

Abundance
Scan 1212 (9.541 min): 11062806.D
202
252
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
139
182
217
118
152
237
27 39 50 63 75 87 99
128
170
227
271281
327
355
m/z-->
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

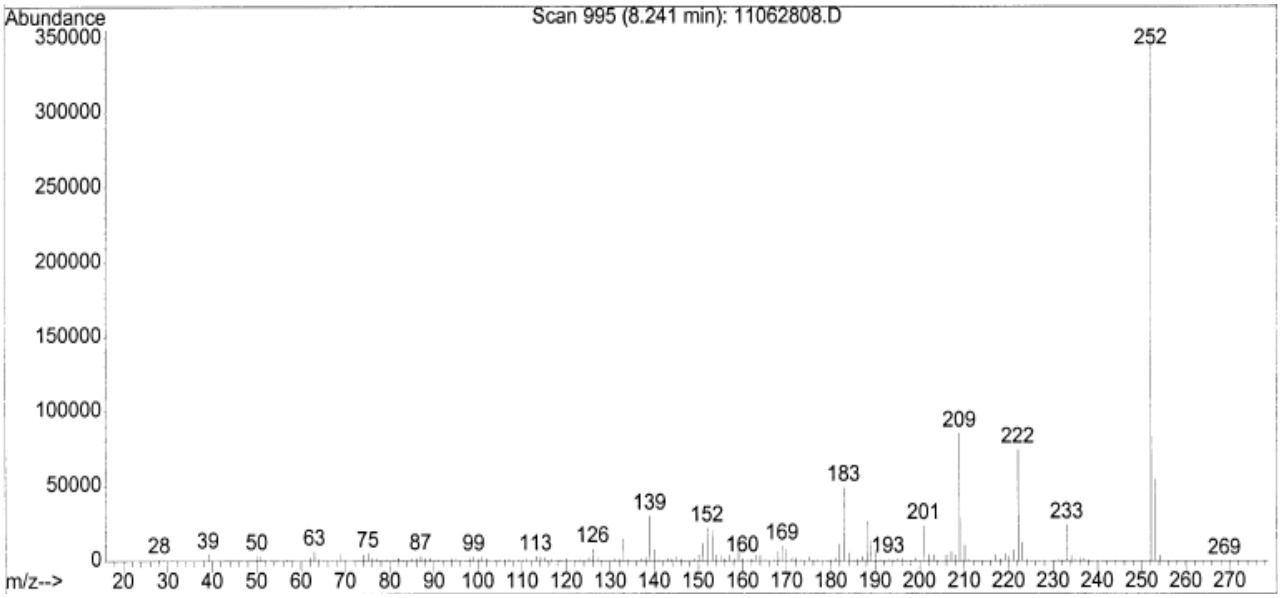

f1 (ppm)
3.11
1.21
0.80
1.22
0.78
1.71
1.00
0.96

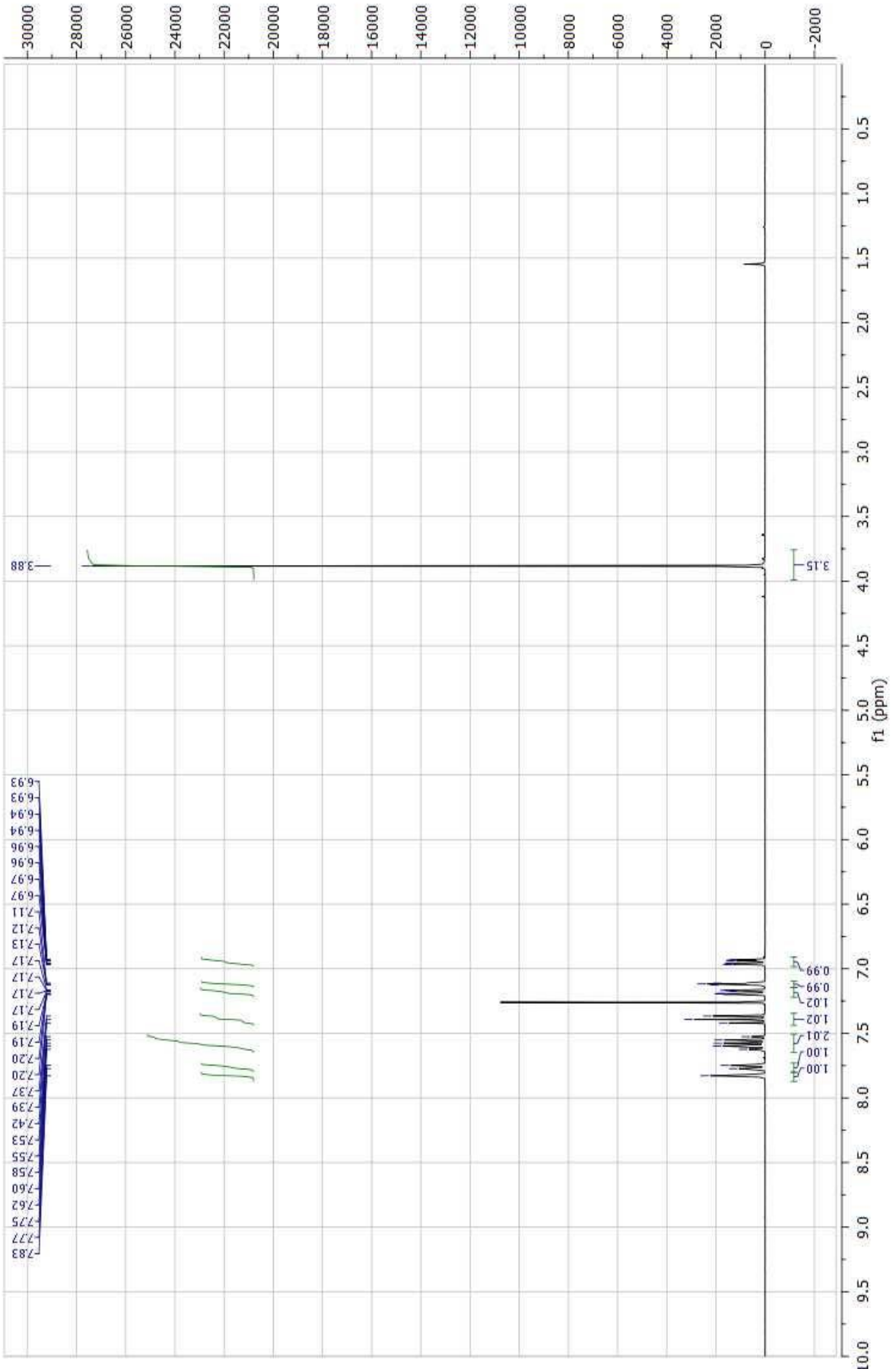

55.54
111.27
120.94
128.91
129.46
129.85
130.51
131.35
138.49
156.27
f1 (ppm)

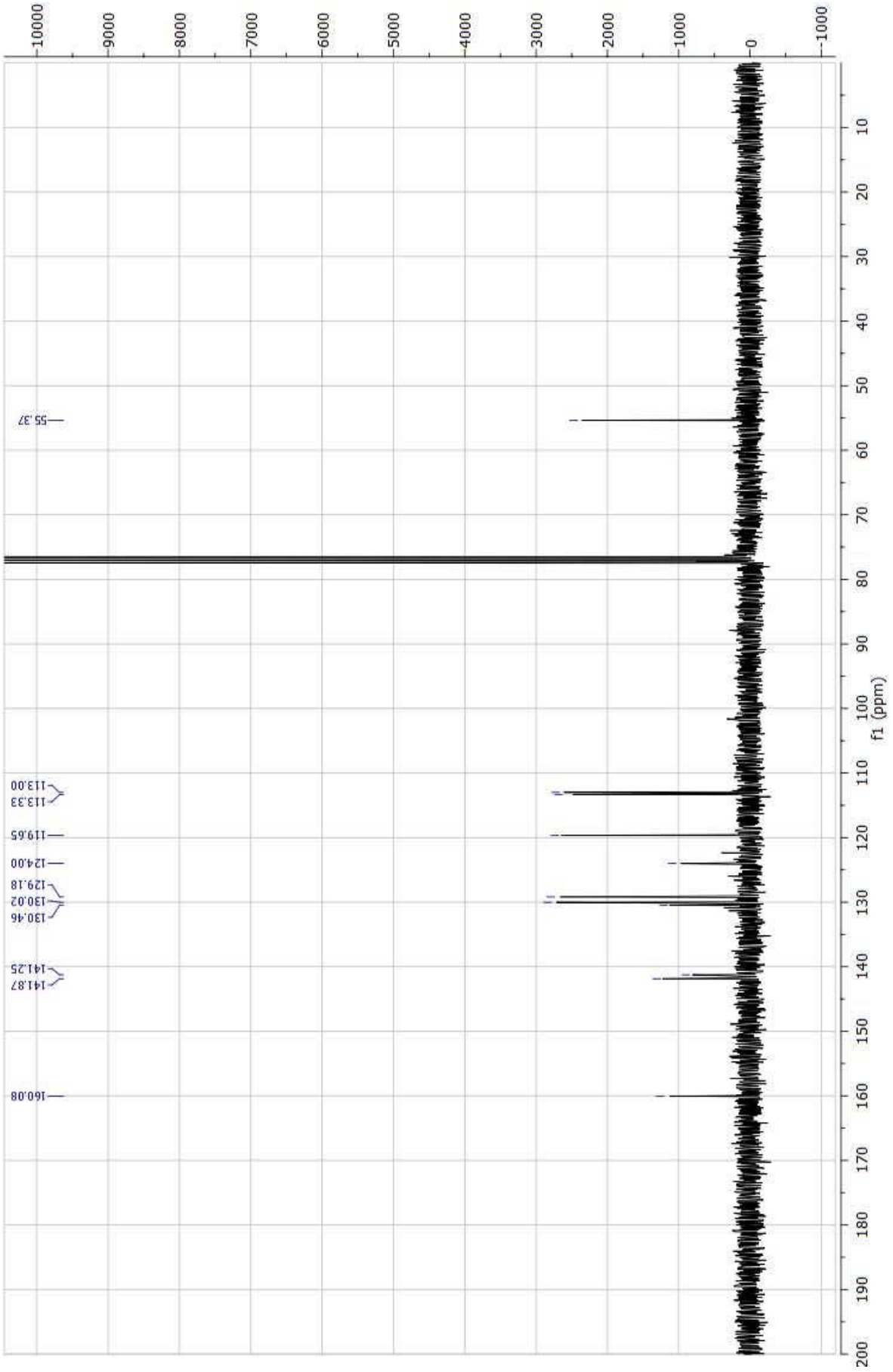
U. 4cr

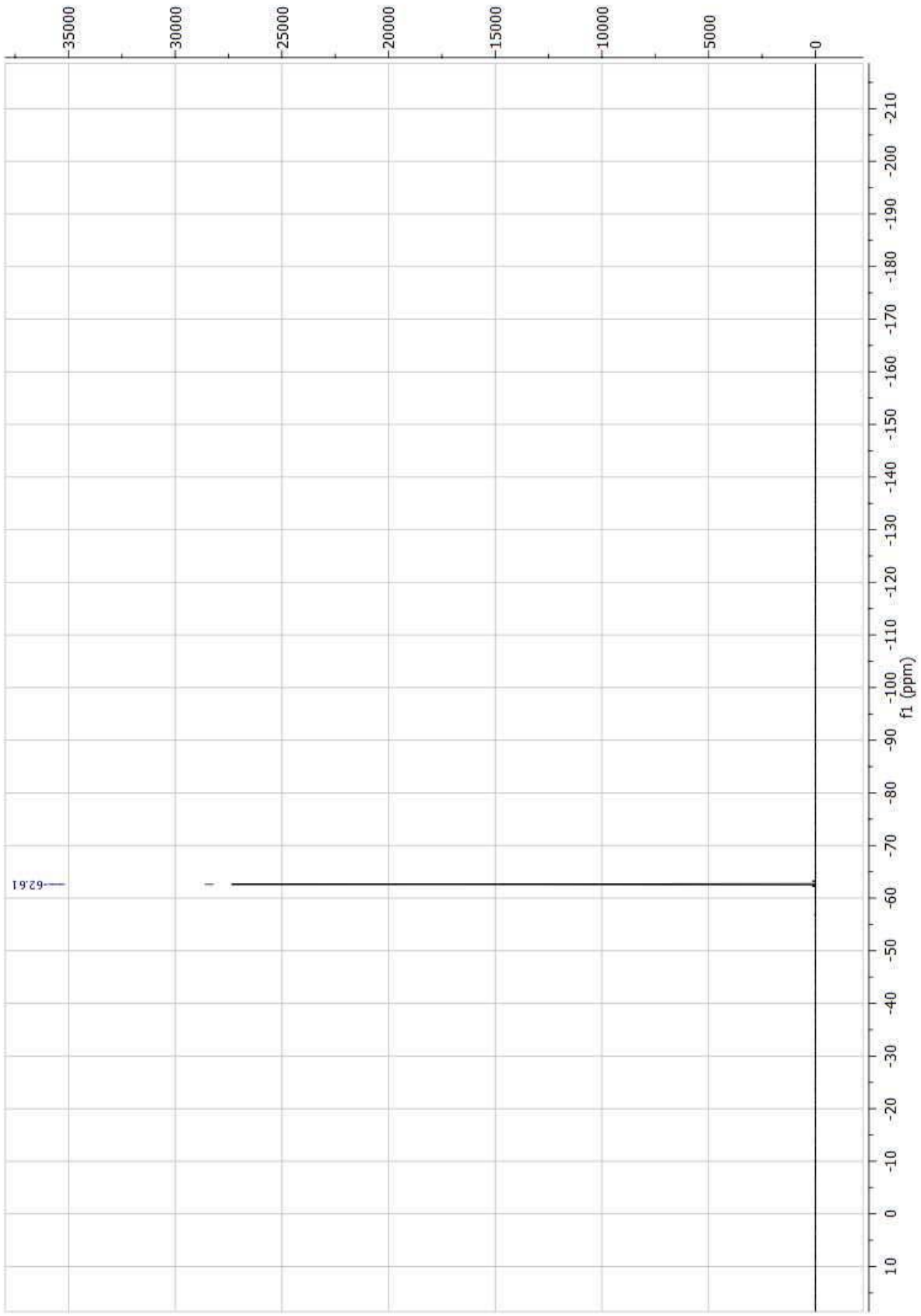

CF3
O


TIC: 11062808.D
Abundance
2.5e+07
2e+07
1.5e+07
1e+07
5000000
8.22
Time-->
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00

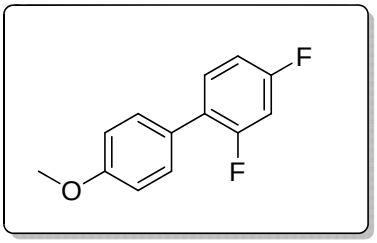

Scan 995 (8.241 min): 11062808.D
Abundance
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
252
209
222
183
139
152
201
233
269
28 39 50 63 75 87 99 113 126 160 169 193
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270


f1 (ppm)
3.88
3.15
1.00
2.01
1.00
1.02
1.02
0.99
0.99

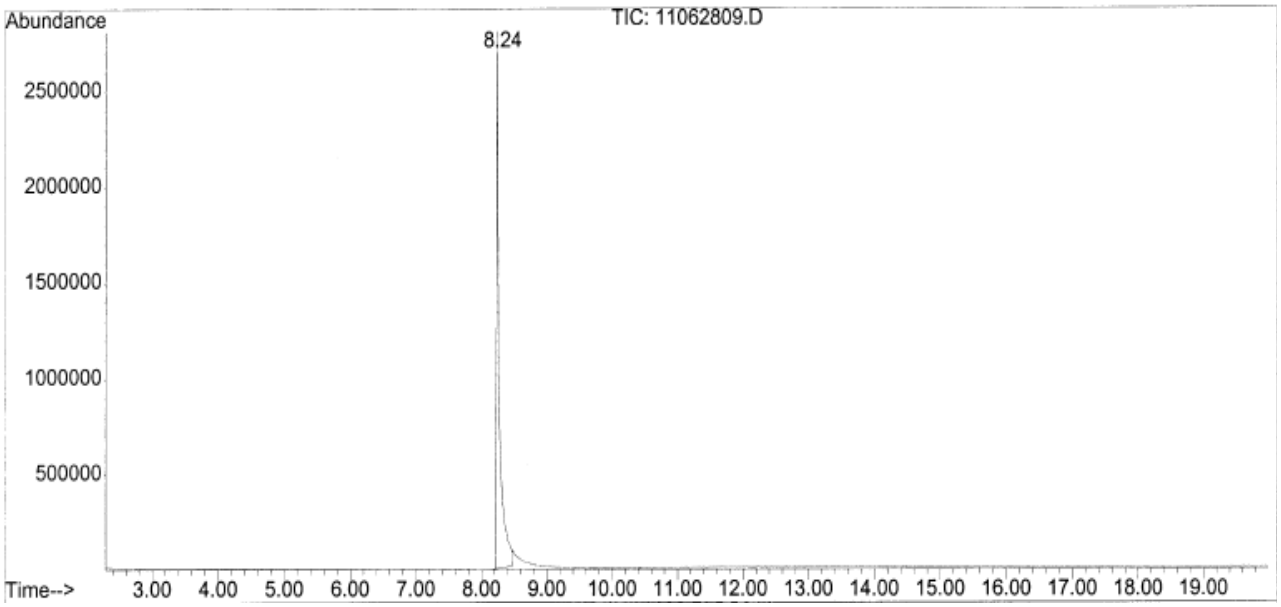

55.37
113.00
113.33
119.65
124.00
129.18
130.02
130.46
141.25
141.87
160.08
f1 (ppm)

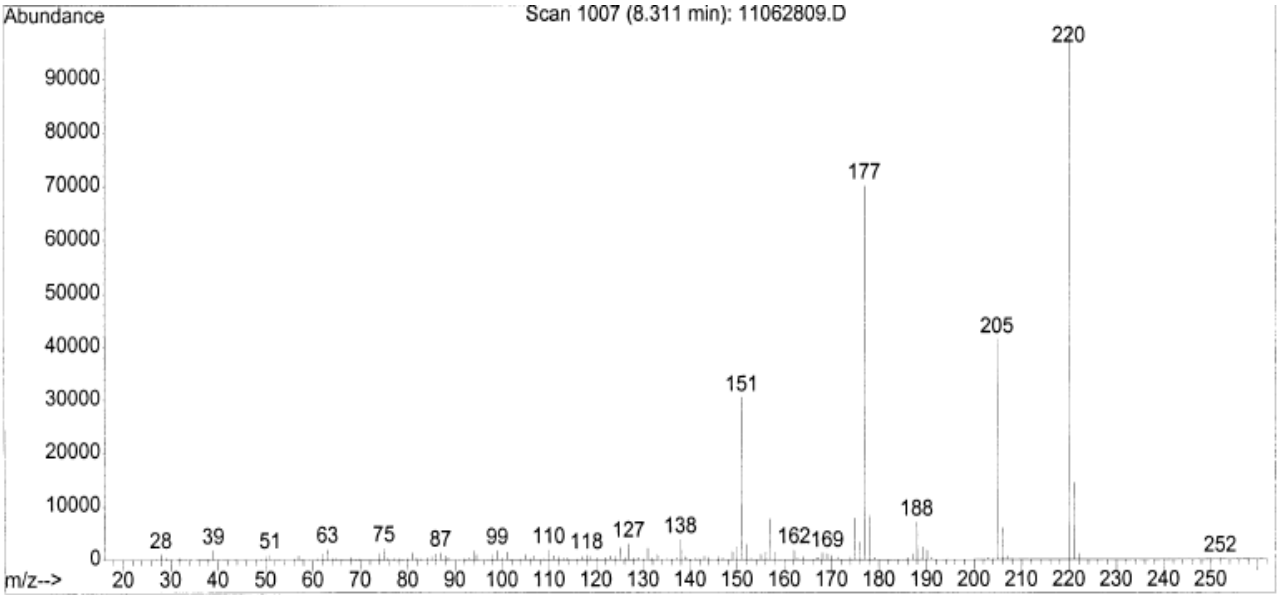

35000
30000
25000
20000
15000
10000
5000
0
-210
-200
-190
-180
-170
-160
-150
-140
-130
-120
-110
-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
f1 (ppm)
62.61

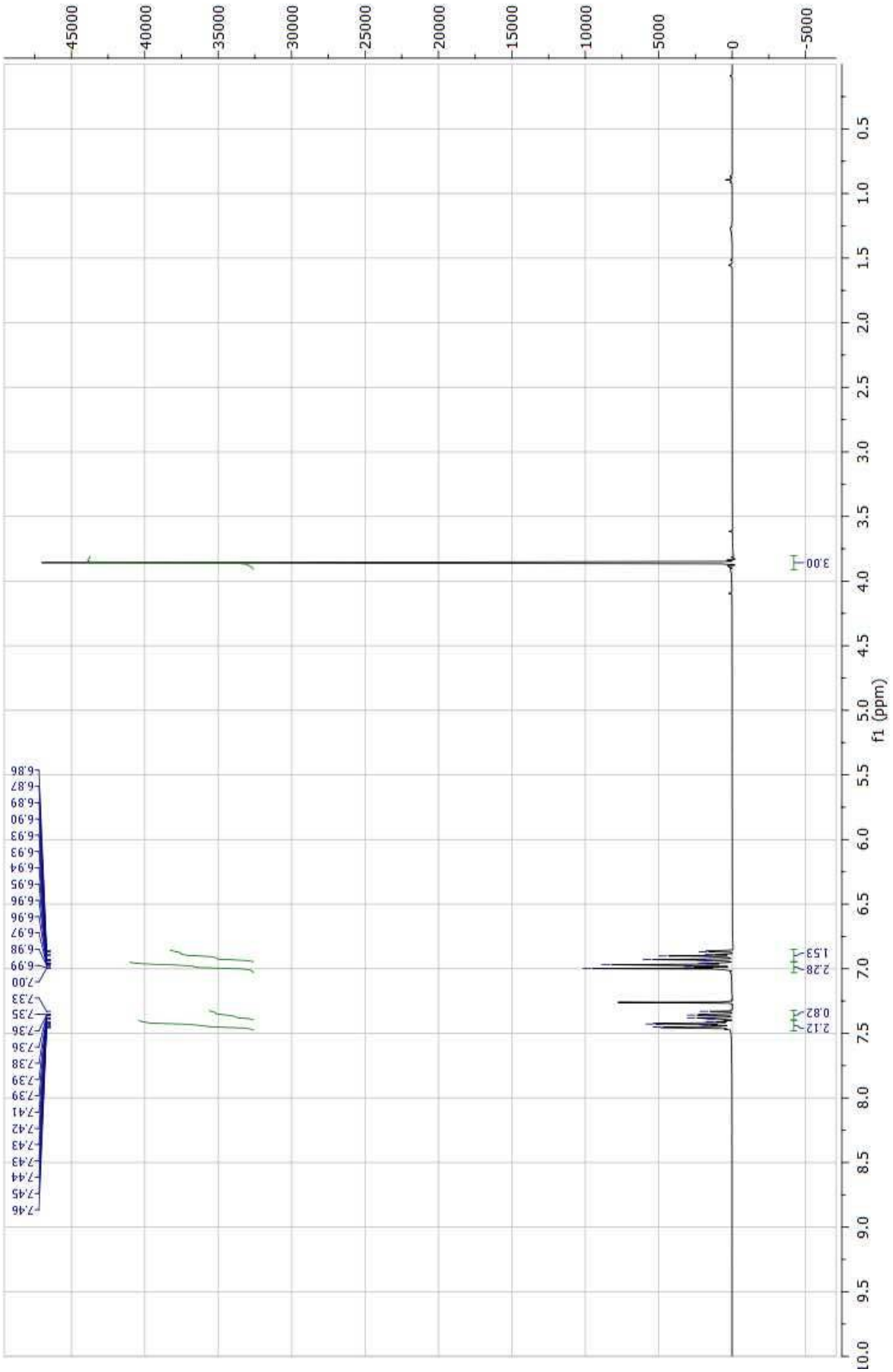
V. 4ap

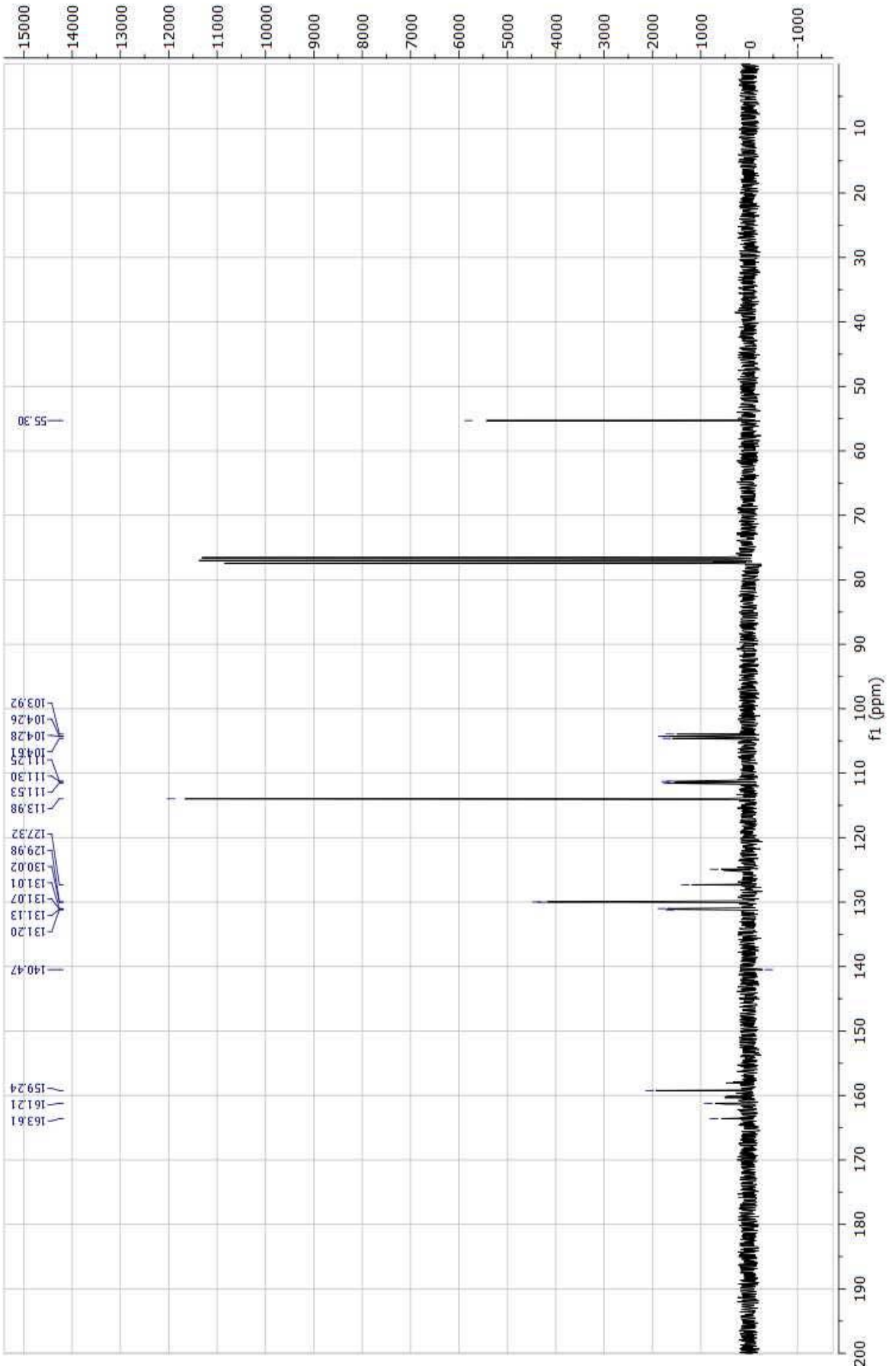


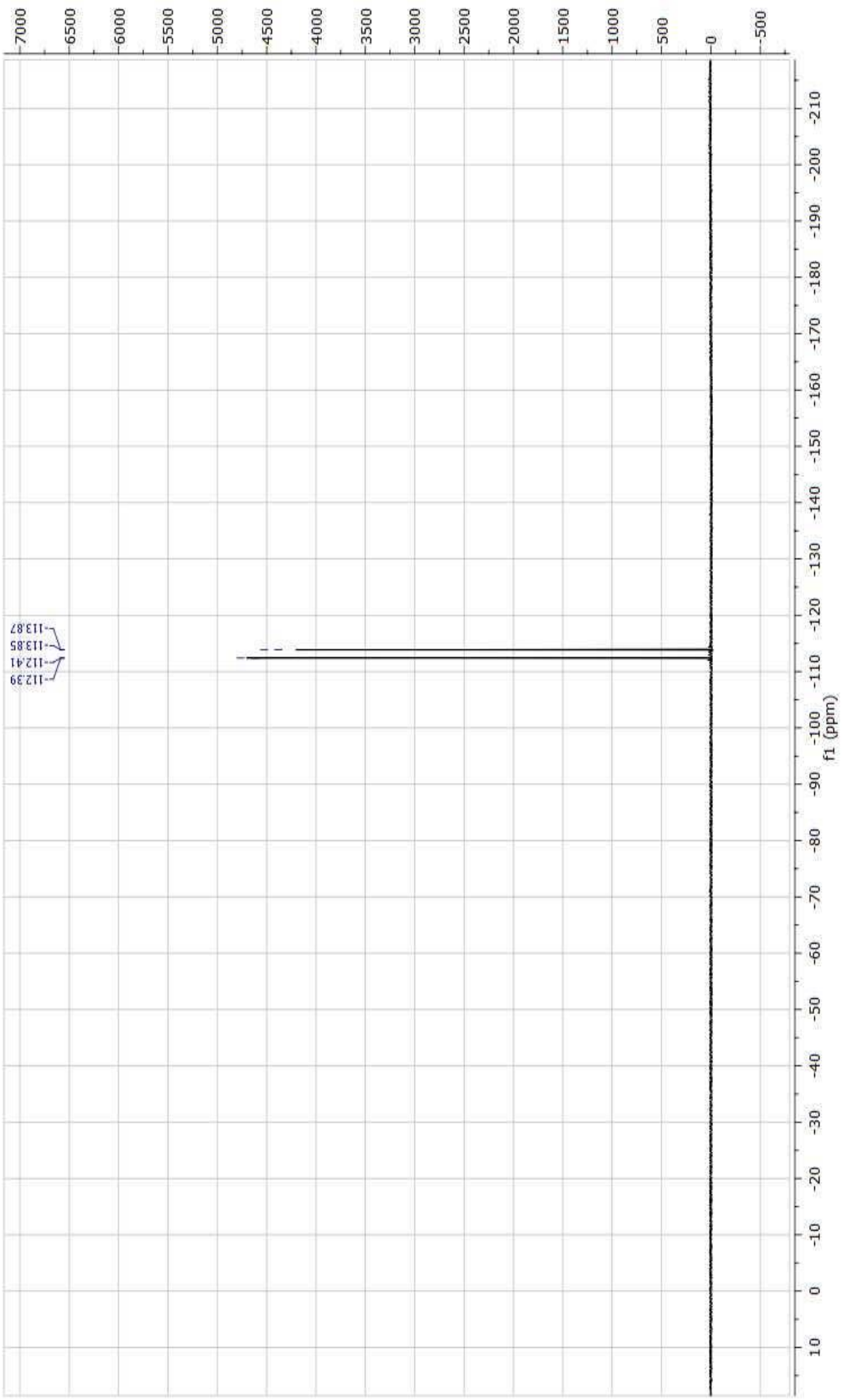
GC/MS Analysis



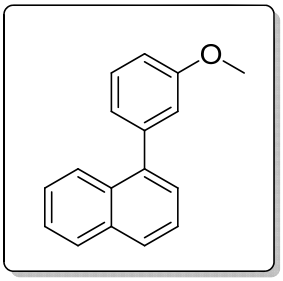


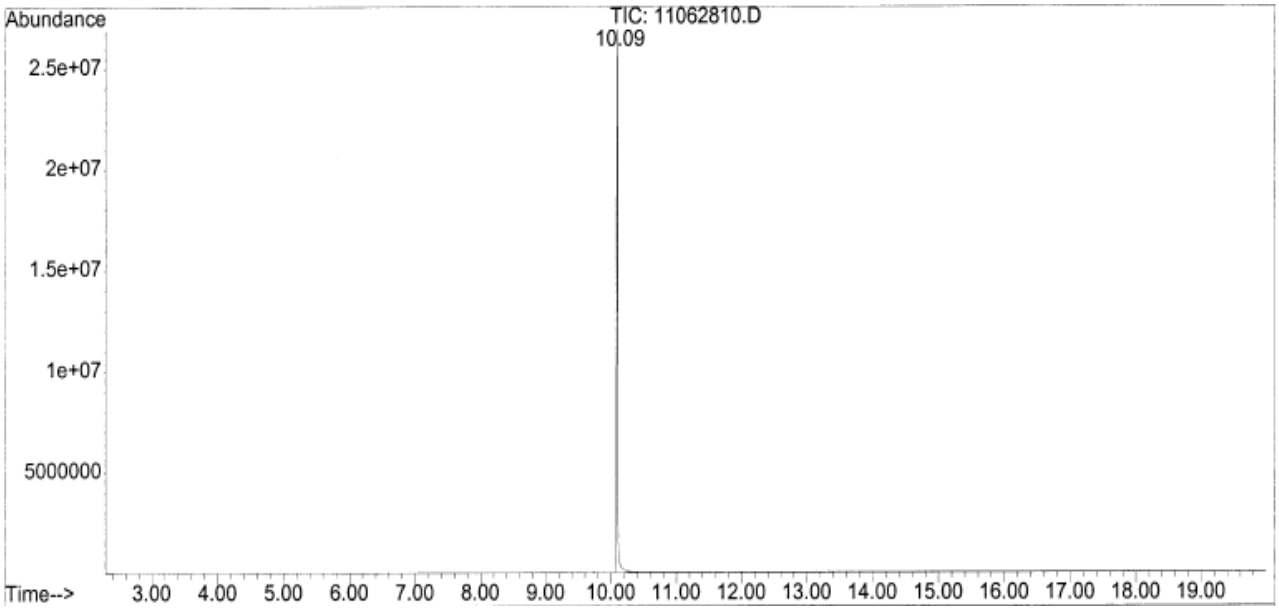

45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)
3.00
1.53
2.28
0.82
2.12
6.86
6.87
6.89
6.90
6.93
6.93
6.94
6.95
6.96
6.96
6.97
6.98
6.99
7.00
7.33
7.35
7.36
7.36
7.38
7.39
7.39
7.41
7.42
7.43
7.43
7.44
7.45
7.46

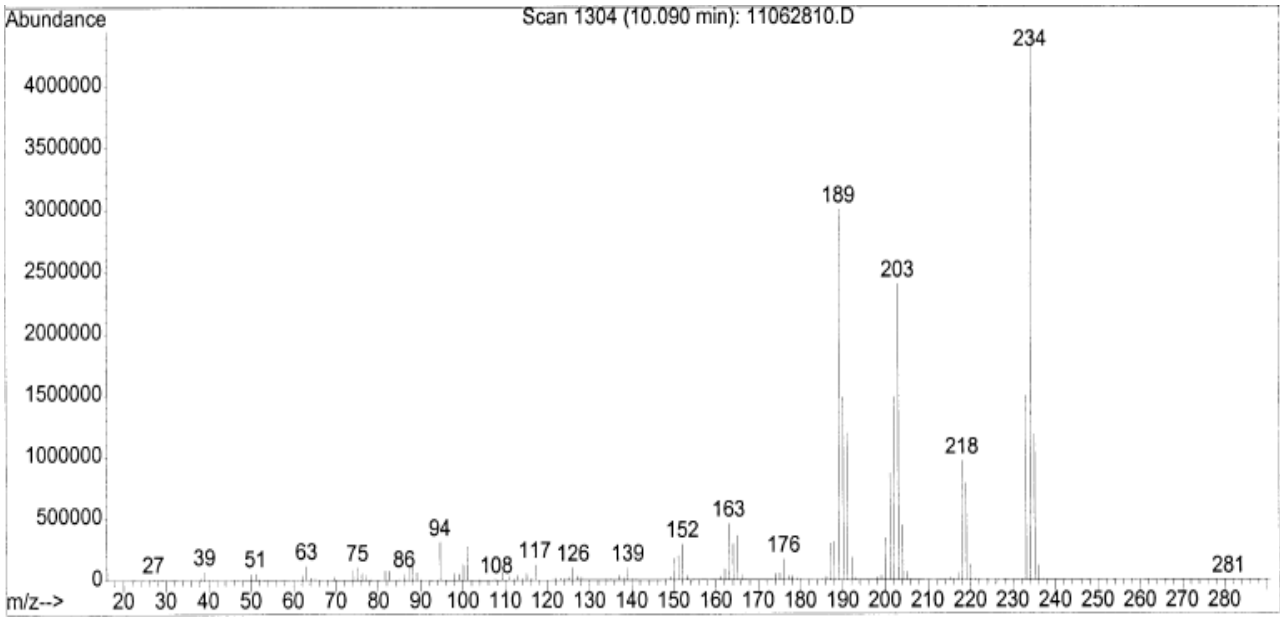

55.30
103.92
104.26
104.28
104.61
111.25
111.30
111.53
113.98
127.32
129.98
130.02
131.01
131.07
131.13
131.20
140.47
159.24
161.21
163.61
f1 (ppm)

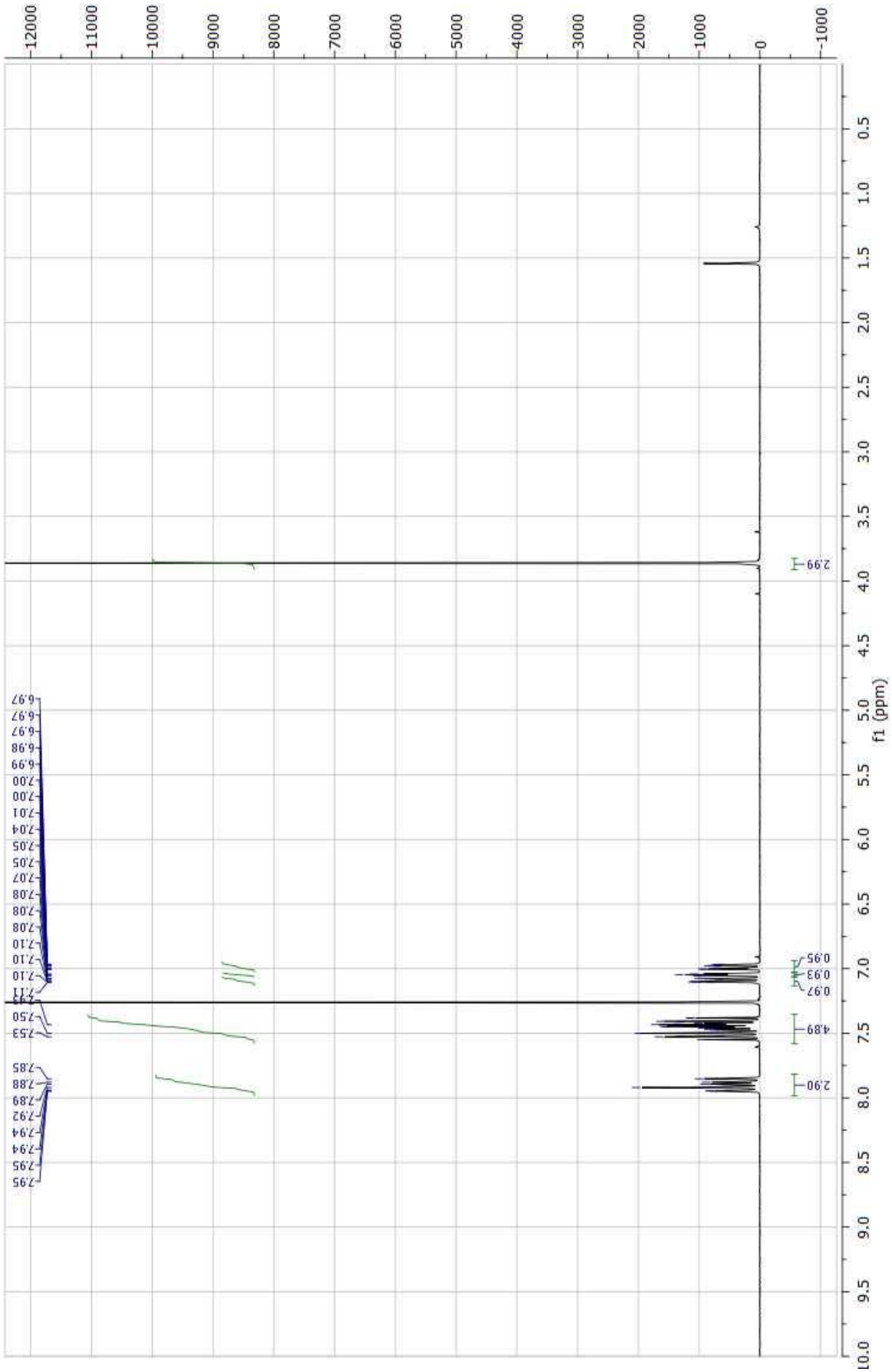

-112.39
-112.41
-113.85
-113.87
f1 (ppm)

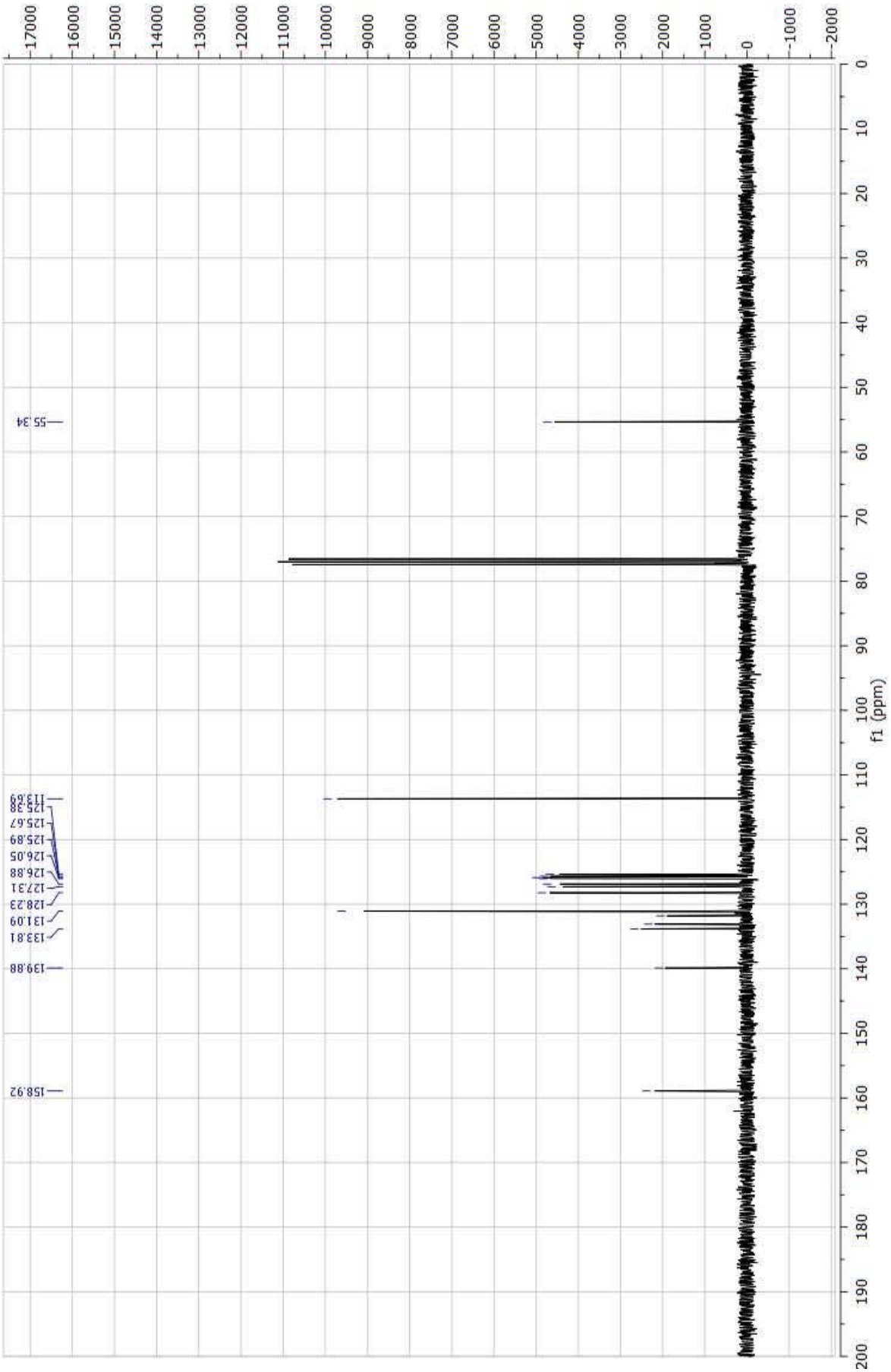
W. 4ci


O

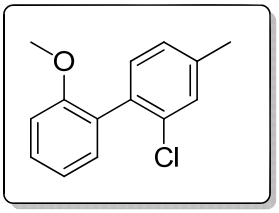

Abundance
TIC: 11062810.D
10.09
2.5e+07
2e+07
1.5e+07
1e+07
5000000
Time-->
3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00


Abundance
Scan 1304 (10.090 min): 11062810.D
234
4000000
3500000
189
3000000
203
2500000
2000000
218
1500000
1000000
500000
163
94
152
176
27 39 51 63 75 86 108 117 126 139
281
0
m/z-->
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280

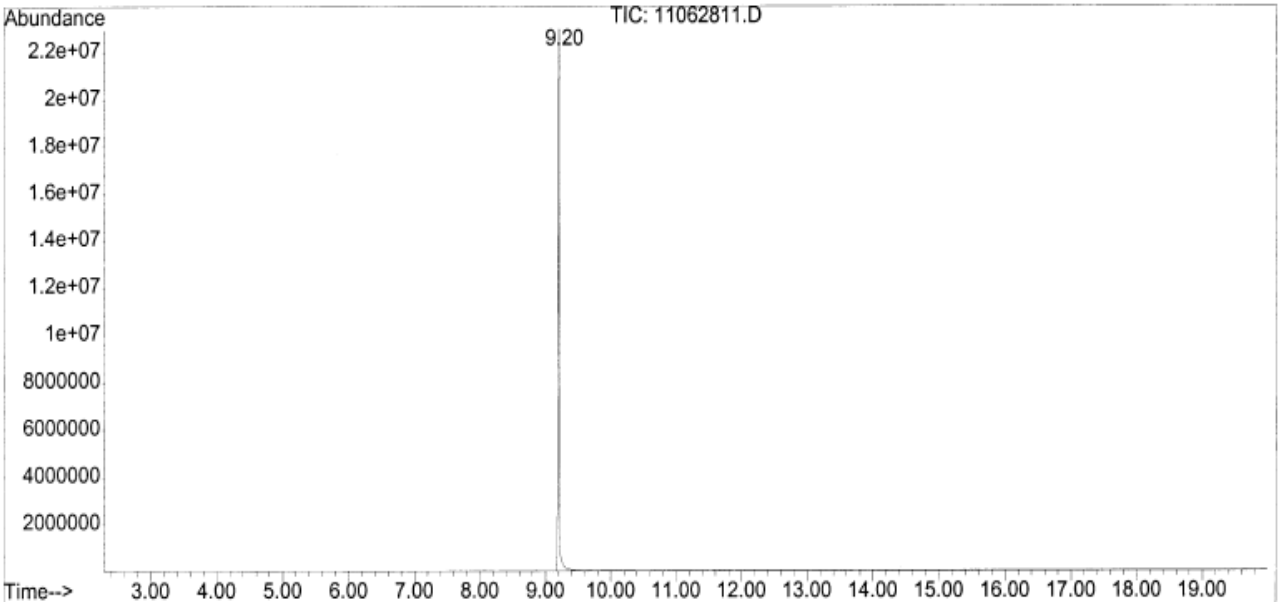

f1 (ppm)
2.99
0.95
0.93
0.97
4.89
2.90

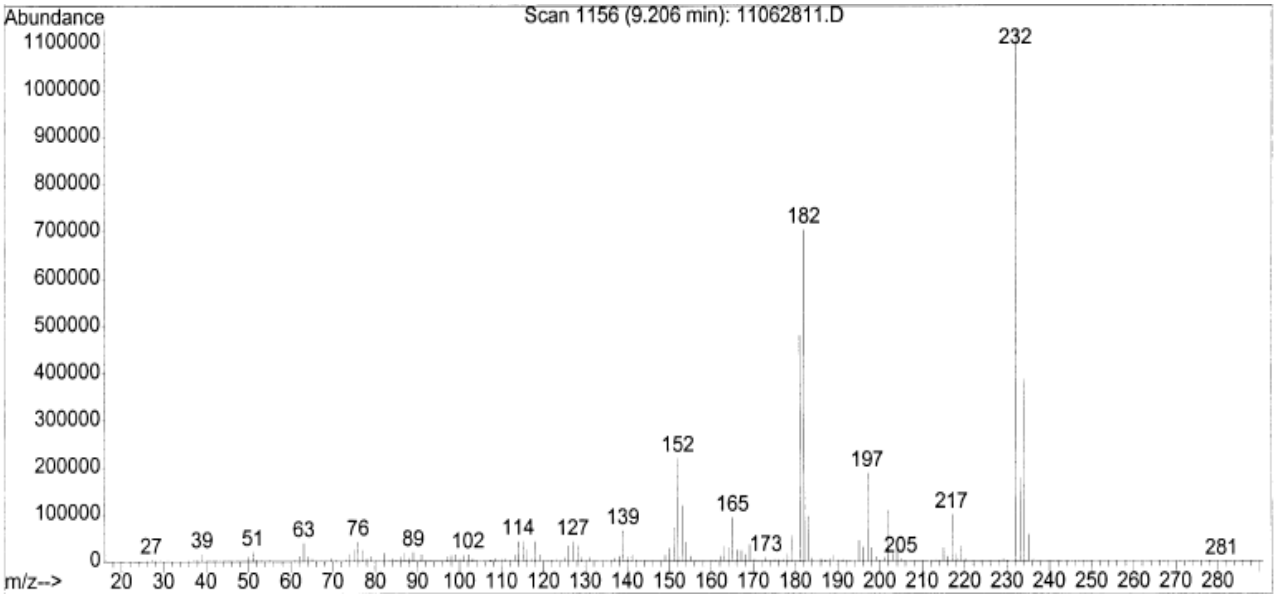

55.34
113.69
125.38
125.67
125.89
126.05
126.88
127.31
128.23
131.09
133.81
139.88
158.92
f1 (ppm)

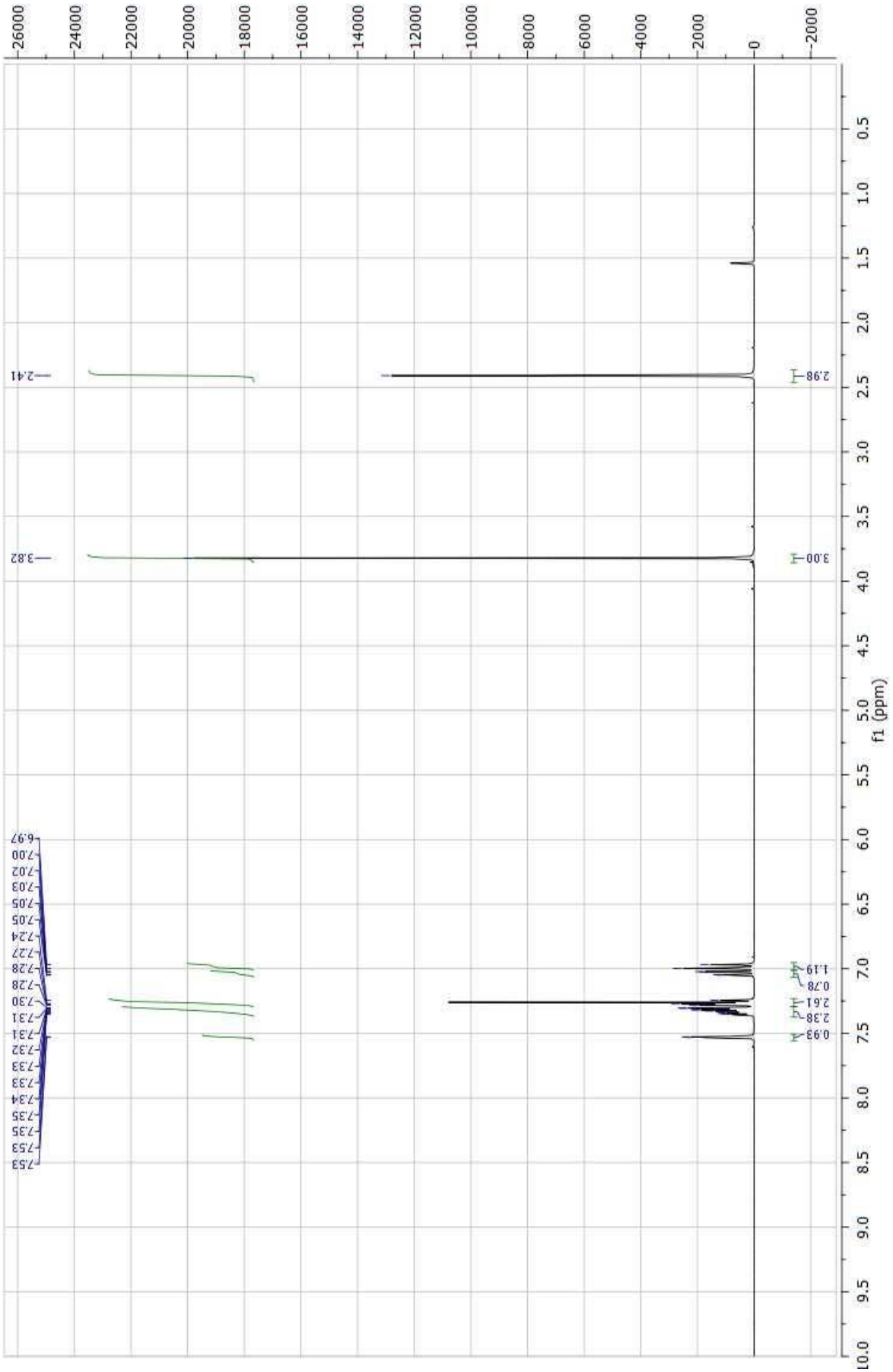
X. 4dl

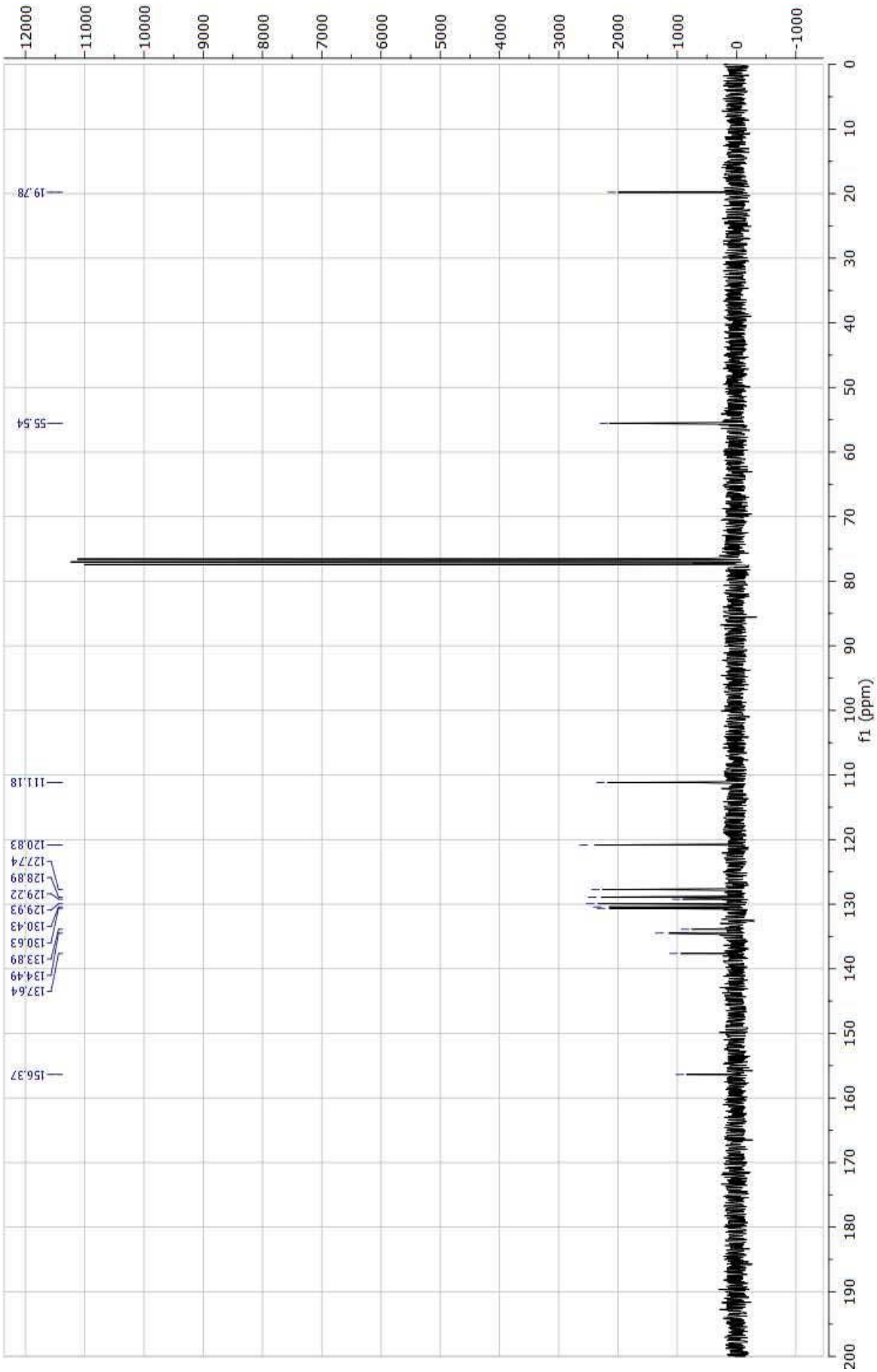


GC/MS Analysis

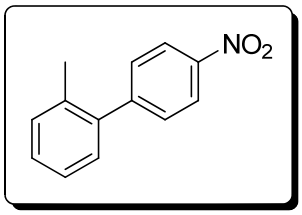




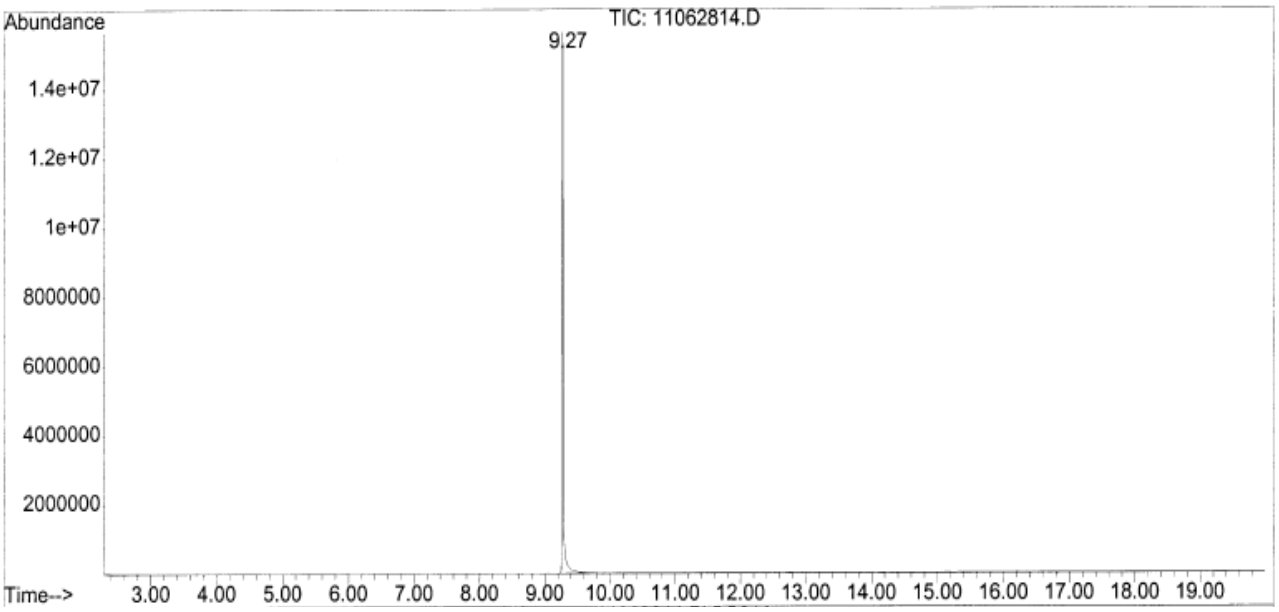

f1 (ppm)
2.41
3.82
2.98
3.00
1.19
0.78
2.61
2.38
0.93
6.97

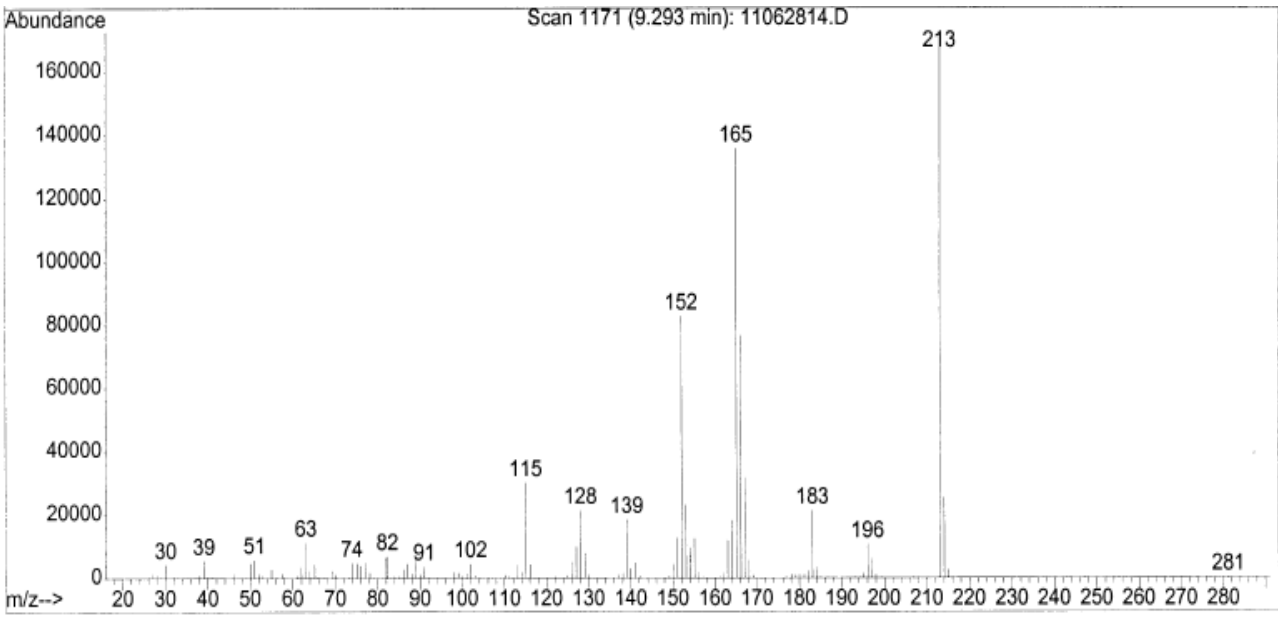

19.78
55.54
111.18
120.83
127.74
128.89
129.22
129.93
130.43
130.63
133.89
134.49
137.64
156.37
f1 (ppm)

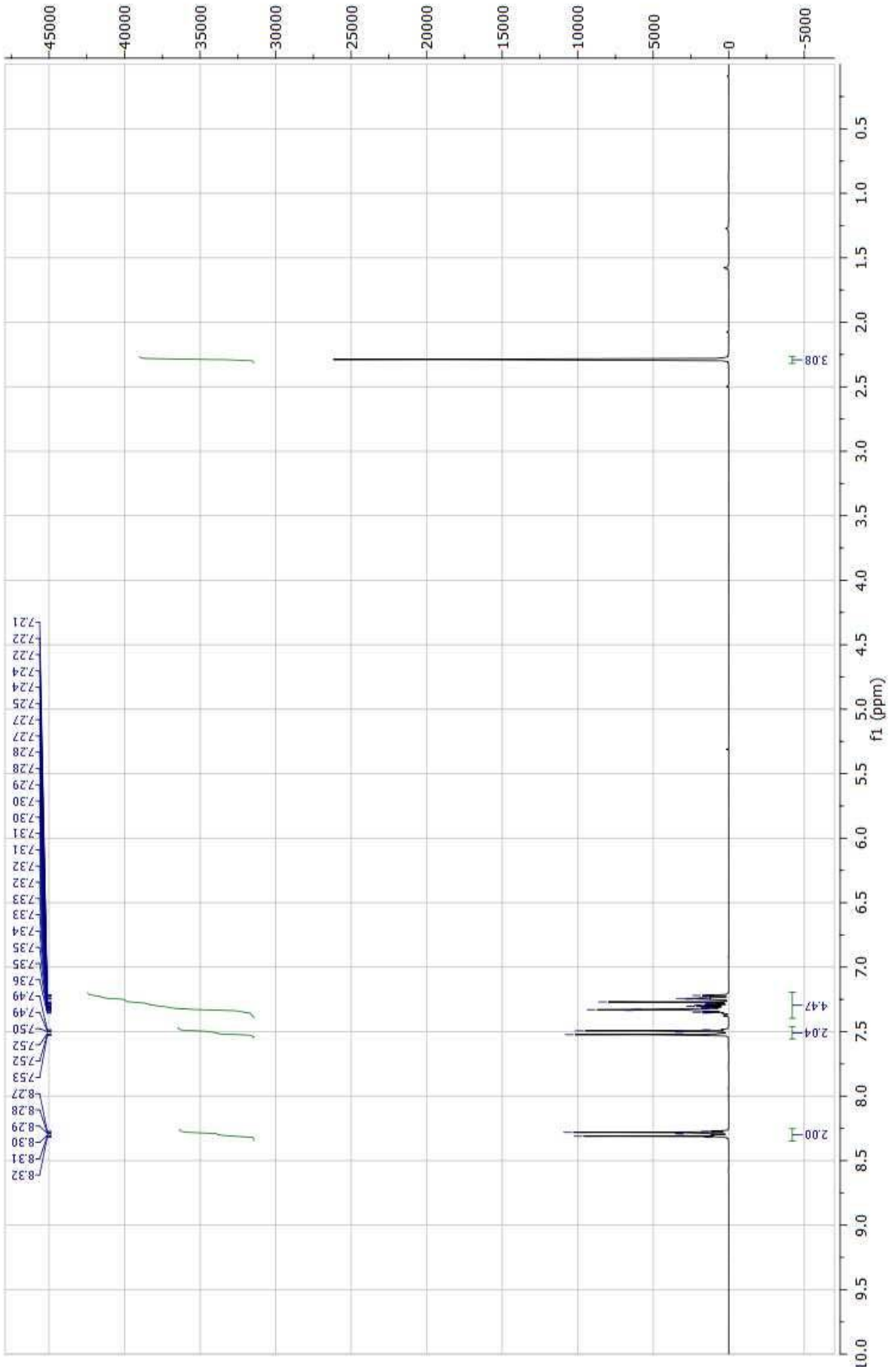
Y. 4fh

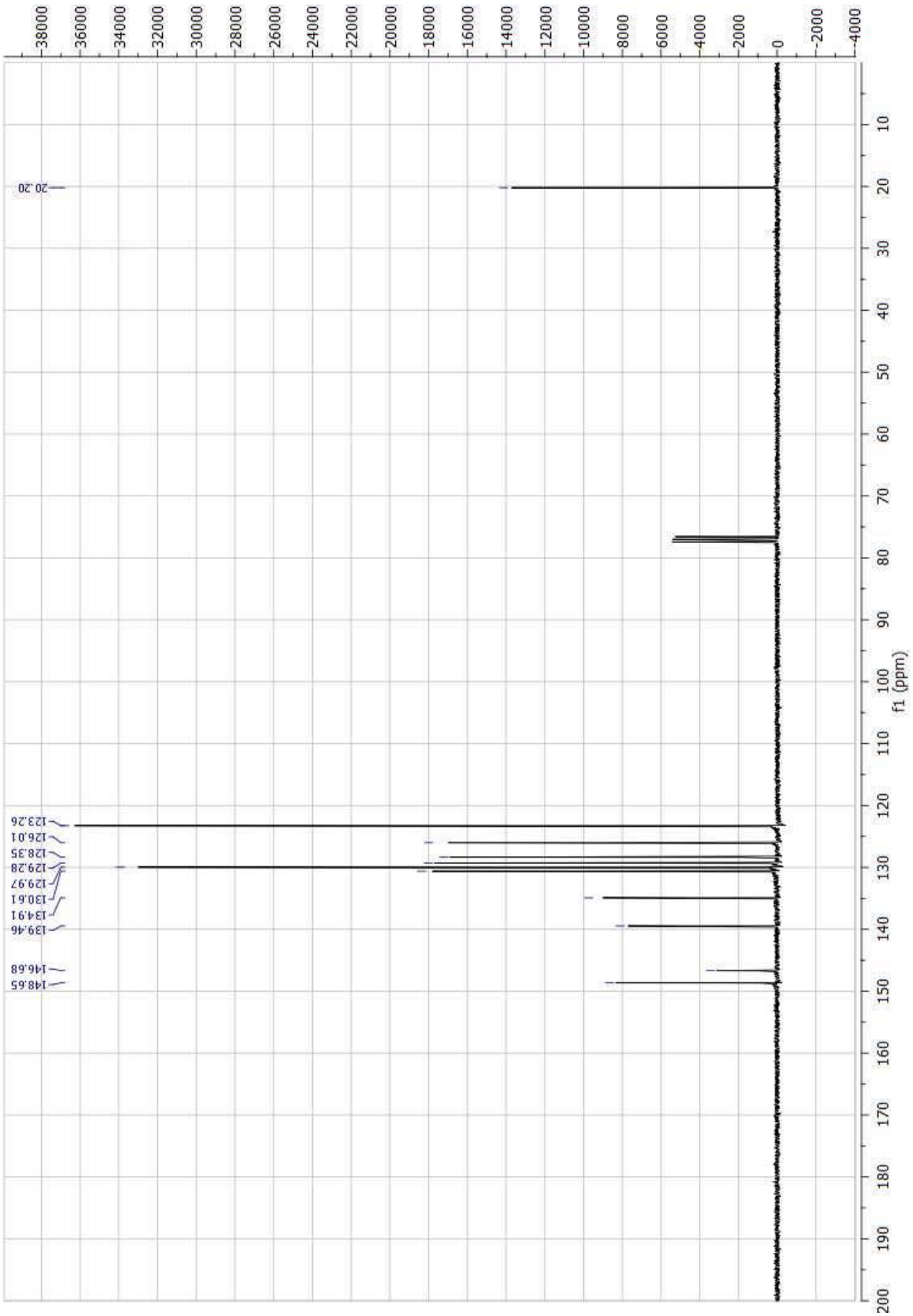


GC/MS Analysis

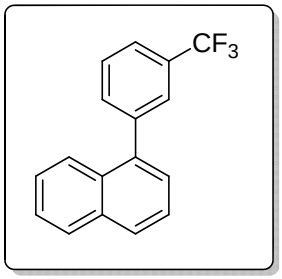




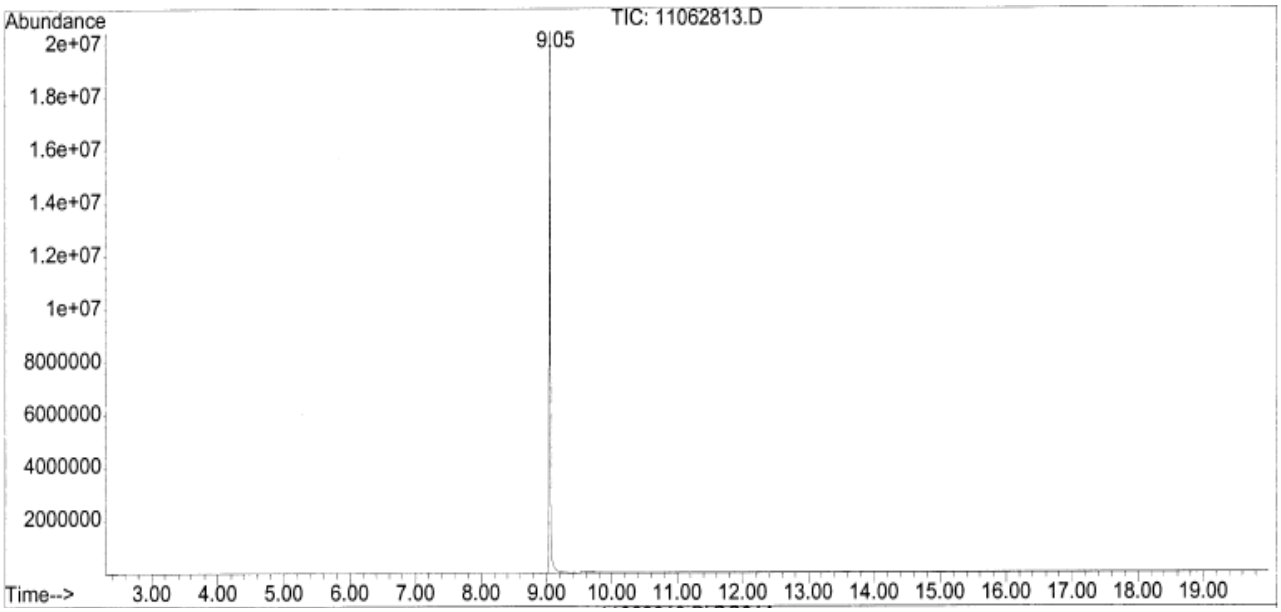

f1 (ppm)
3.08
4.47
2.04
2.00

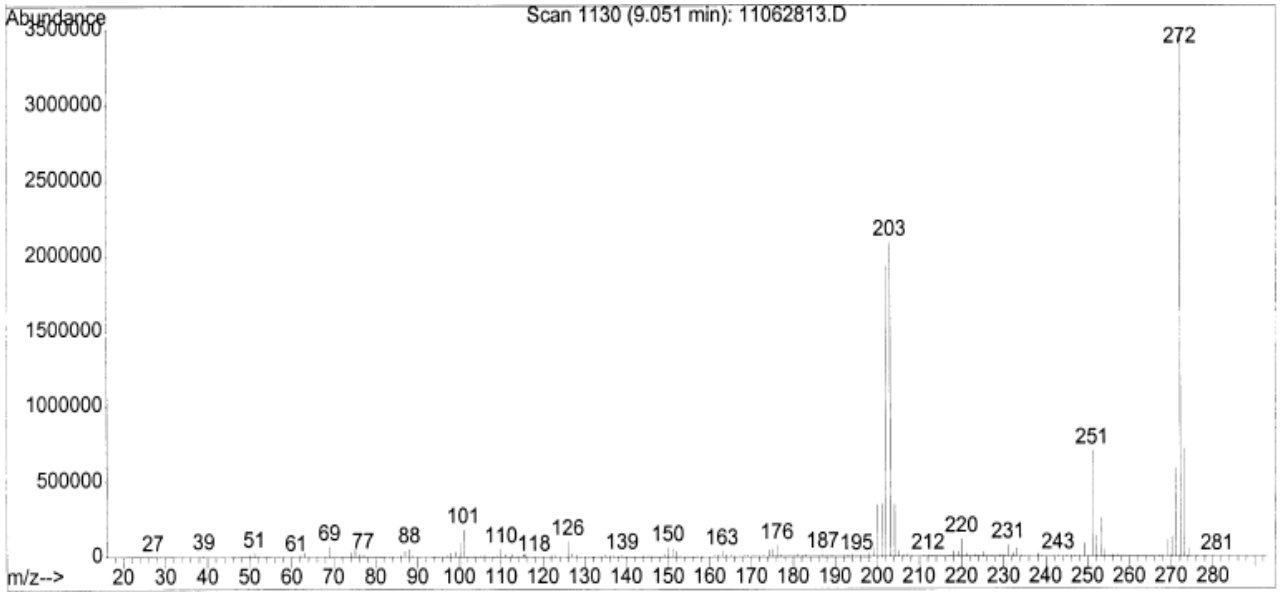

20.20
123.26
126.01
128.35
129.28
129.97
130.61
134.91
139.46
146.68
148.65
f1 (ppm)

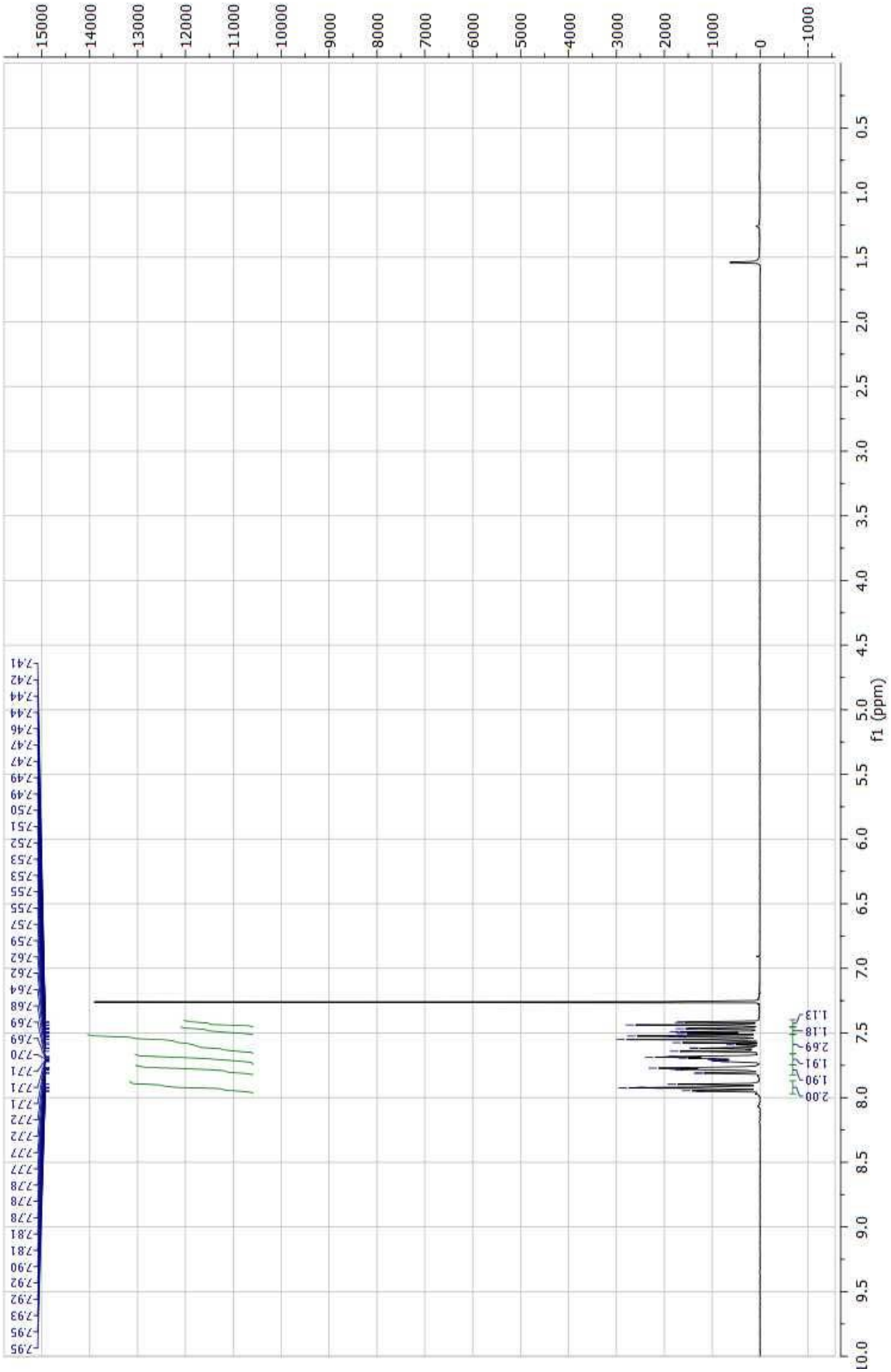
Z. 4ir

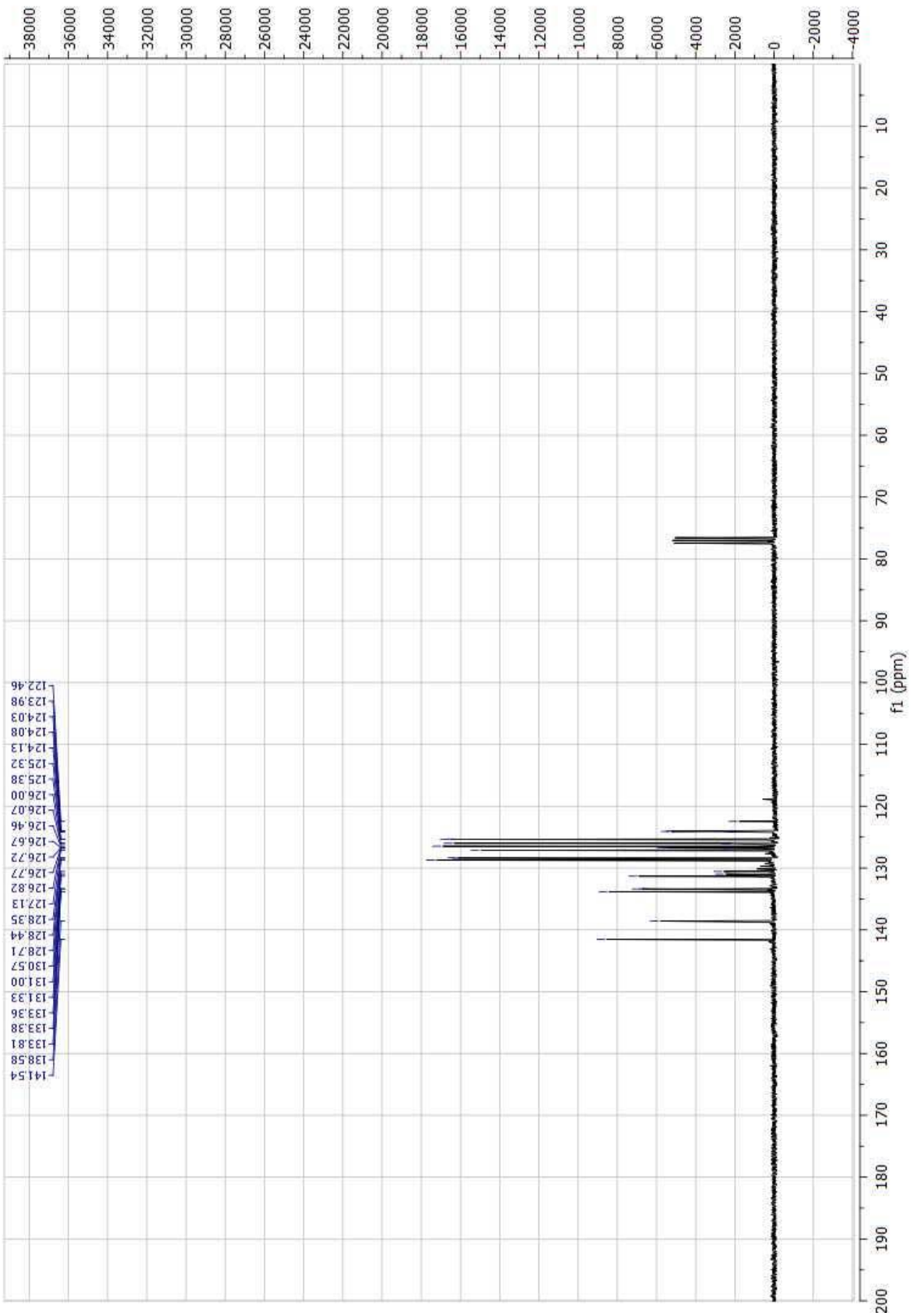


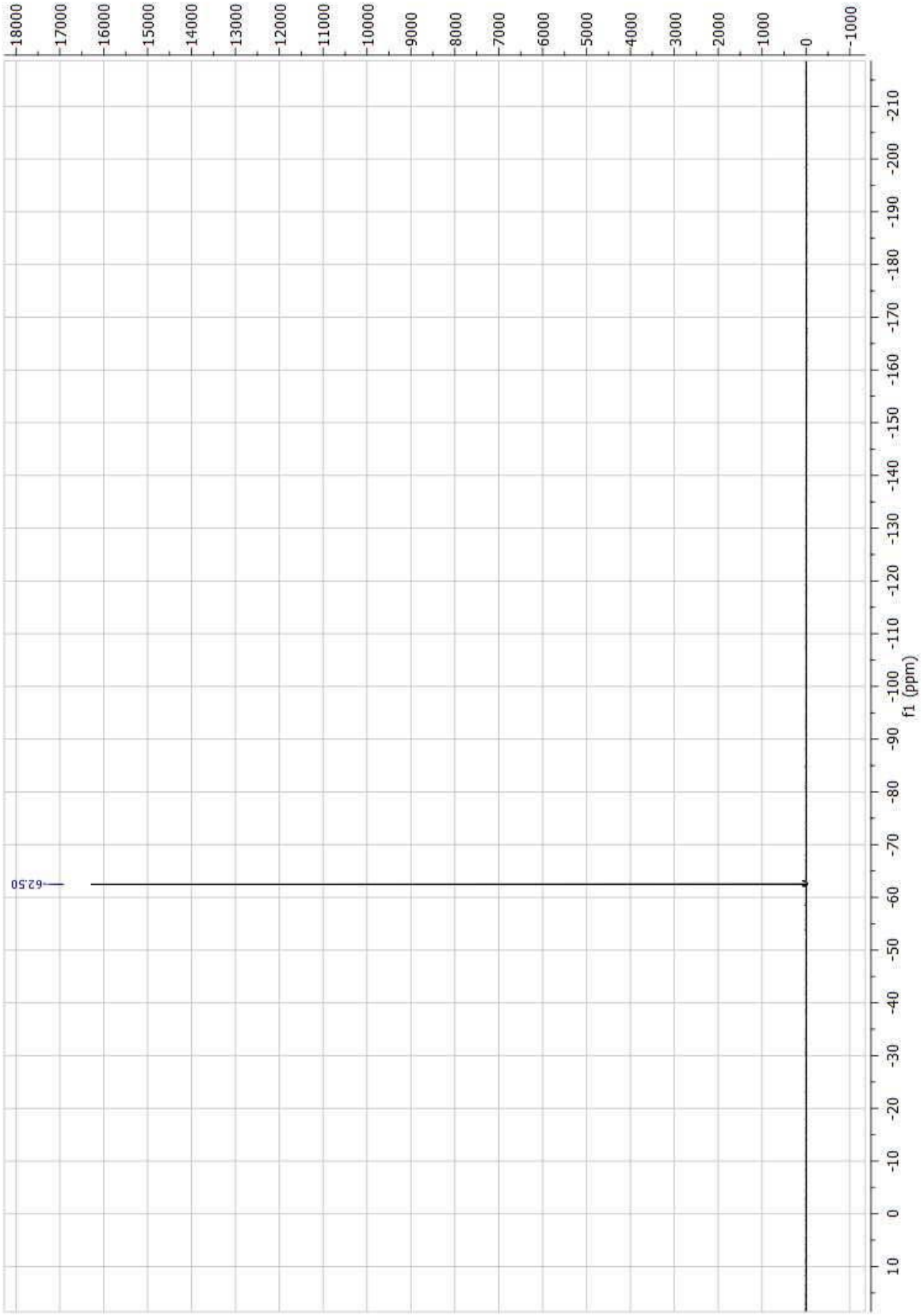
GC/MS Analysis






f1 (ppm)


f1 (ppm)


18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-210
-200
-190
-180
-170
-160
-150
-140
-130
-120
-110
-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
f1 (ppm)
62.50