

Supporting Information

Novel Synthesis of 3-Substituted 2,3-Dihydrobenzofurans via *ortho*-Quinone Methide Intermediates Generated *in Situ*

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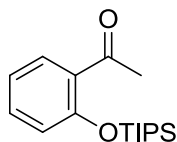
1. General Information

Unless otherwise noted, reactions were carried out under argon atmosphere, in flame dried, three-neck, with magnetic stirring. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 15 Torr. Melting points were taken on a Büchi 510 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured in CDCl_3 or $\text{DMSO-}d_6$ on a 250 or 400 MHz Brüker spectrometer. ^1H chemical shifts are reported in ppm from an internal standard TMS, residual chloroform (7.26 ppm) or $\text{DMSO-}d_6$ (2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from an internal standard TMS, residual chloroform (77.00 ppm) or $\text{DMSO-}d_6$ (39.43 ppm). High resolution ESI mass spectra were measured on a ThermoFisher Scientific Orbitrap XL system. Low resolution ESI spectra were measured with an Agilent 1100 LC-MS/MS spectrometer. IR spectra were acquired on a Perkin-Elmer GX FTIR spectrophotometer as liquids between sodium chloride discs or KBr discs and are reported in wave numbers (cm^{-1}). Analytical thin layer chromatography (TLC) was performed with TLC plates (Merck 70-230 mesh silica gel). TLC visualisation took place under a 254 nm UV light source and by immersion in acidic aqueous-ethanolic vanillin solution or in basic aqueous potassium permanganate (KMnO_4) solution, followed by heating using a heat gun. Purification of reaction products was generally done by dry-column flash chromatography¹ using Merck silica gel 60 and/or flash chromatography² using Carlo Erba Reactifs-SDS silica gel 60.

Solvents, reagents and catalysts were used as received from the manufacturers (Acros, Aldrich, Alfa-Aesar, Fluka and Merk) except for tetrahydrofuran, dichloromethane, ethanol, methanol, ethyl acetate, hexane and toluene that were purified and dried according to recommended procedures.

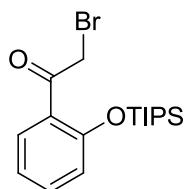
2. Preparation of starting materials

1-{2-[(Triisopropylsilyl)oxy]phenyl}ethanone **2**



To a stirred solution of 2-hydroxyacetophenone **1** (500 mg, 10 mmol) in CH_2Cl_2 (10 mL) diisopropylamine (816 mg, 22 mmol), DMAP (90 mg, 2 mmol) was added, followed by the dropwise addition of triisopropylsilyl chloride (850 mg, 12 mmol) and the reaction mixture was left stirring for 1 h at 25 °C. After TLC analysis had shown complete conversion of the starting materials, water (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×8 mL). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (5% ethyl acetate in hexane) to give **2** (1.1 g, 94%) as a yellow oil. $R_f = 0.42$ (10% ethyl acetate in hexane). ^1H NMR (250 MHz, CDCl_3) δ : 7.61 (d, 1H, $J = 7.7$ Hz), 7.32 (t, 1H, $J = 7.3$ Hz), 6.96 (t, 1H, $J = 7.4$ Hz), 6.87 (d, 1H, $J = 8.2$ Hz), 2.63 (s, 3H), 1.42-1.27 (m, 3H), 1.13 (d, 18H, $J = 7.2$ Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 201.01, 155.30, 132.98, 131.04, 130.14, 120.95, 119.59, 31.43, 18.02 (6C), 13.41 (3C). IR: 2950, 2870, 1688, 1598, 1480, 1266, 904, 738 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{29}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 293.1931, found: 293.1929.

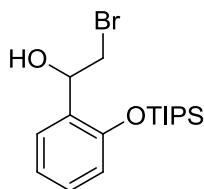
2-Bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethanone **3**



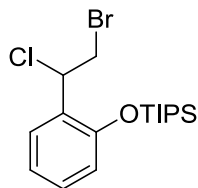
A mixture of 1-{2-[(triisopropylsilyl)oxy]phenyl}ethanone **2** (500 mg, 10 mmol), NBS (304 mg, 10 mmol) and 4-toluenesulfonic acid (32 mg, 1 mmol) was triturated for about 3 h in a mortar and pestle. After TLC analysis had shown complete conversion of the starting materials, water (20 mL) was added, the mixture was extracted with CH_2Cl_2 (3×8 mL). The

combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (5% ethyl acetate in hexane) to give **3** (415 mg, 65%) as a colorless oil. $R_f = 0.58$ (5% *tert*-butylmethyl ether in hexane, two runs). ^1H NMR (250 MHz, CDCl_3) δ : 7.66 (d, 1H, $J = 7.7$ Hz), 7.38 (t, 1H, $J = 8.0$ Hz), 7.00 (t, 1H, $J = 7.46$ Hz), 6.89 (d, 1H, $J = 8.3$ Hz), 4.62 (s, 2H), 1.43-1.28 (m, 3H), 1.13 (d, 18H, $J = 7.2$ Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 193.84, 155.20, 133.93, 131.14, 127.64, 121.35, 119.37, 36.73, 18.02 (6C), 13.39 (3C). IR: 2948, 2868, 1690, 1596, 1480, 1298, 1260, 1158, 996, 906, 758, 680 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{28}\text{BrO}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 371.1036, found: 371.1035.

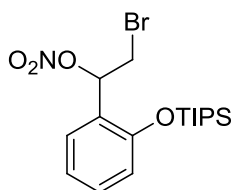
2-Bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethanol **4**



To a solution of NaBH_4 (122 mg, 12 mmol) in THF (25 mL) under nitrogen was added 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethanone **3** (1 g, 10 mmol) and the mixture was refluxed for 4 h. After TLC analysis had shown complete conversion of the starting materials, water (10 mL) was added and the mixture was extracted with EtOAc (3×10 mL). The organic layer was dried with sodium sulphate, filtered and the solvent was removed *in vacuo*. The residue was purified by flash chromatography (10% ethyl acetate in hexane) to give **4** (730 mg, 73%) as a colorless oil. $R_f = 0.24$ (10% ethyl acetate in hexane). ^1H NMR (250 MHz, CDCl_3) δ : 7.49 (d, 1H, $J = 6.7$ Hz), 7.17 (t, 1H, $J = 7.8$ Hz), 6.98 (t, 1H, $J = 7.4$ Hz), 6.81 (d, 1H, $J = 8.0$ Hz), 5.27 (ddd, 1H, $J = 1.9$ Hz, 3.0 Hz, 3.5 Hz), 3.77 (dd, 1H, $J = 2.7$ Hz, 7.4 Hz), 3.45 (t, 1H, $J = 10.0$ Hz), 2.76 (d, 1H, $J = 3.9$ Hz), 1.41-1.26 (m, 3H), 1.13 (dd, 18H, $J = 3.0$ Hz, 4.2 Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 152.77, 130.08, 129.02, 126.83, 121.22, 117.91, 69.64, 39.62, 18.22 (6C), 13.18 (3C). IR: 3438, 2868, 1642, 1492, 1272, 1260, 1144, 920, 876, 754, 664 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{28}\text{OBrSi}$ $[\text{M}-\text{OH}]^+$ 355.1087, found: 355.1083.

[2-(2-Bromo-1-chloroethyl)phenoxy](triisopropyl)silane 5

A solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethanol **4** (6 g, 10 mmol) in freshly distilled thionyl chloride (20 mL) under nitrogen was refluxed for 6 h. After TLC analysis had shown complete conversion of the starting materials, thionyl chloride was removed by distillation, water (30 mL) was added to the residue and the mixture was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **5** (5.3 g, 84%) as a colorless oil. *R*_f = 0.64 (10% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ: 7.44 (d, 1H, *J* = 7.5 Hz), 7.20 (t, 1H, *J* = 7.5 Hz), 6.98 (t, 1H, *J* = 7.9 Hz), 6.83 (d, 1H, *J* = 1.6 Hz, 2.5 Hz), 5.63 (t, 1H, *J* = 4.9 Hz, 8.2 Hz), 3.92 (dd, 1H, *J* = 4.9 Hz, 8.2 Hz), 3.83 (dd, 1H, *J* = 4.9 Hz, 8.2 Hz), 1.40-1.30 (m, 3H), 1.14 (dd, 18H, *J* = 3.0 Hz, 4.2 Hz). ¹³C NMR (63 MHz, CDCl₃) δ: 153.39, 129.97, 127.98, 121.25, 119.38, 118.26, 56.15, 35.66, 18.20 (6C), 13.18 (3C). IR: 2948, 2870, 1596, 1480, 1298, 1260, 1158, 906, 758, 680, 610 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₇H₂₉OBrSi [M-Cl]⁺ 356.1165, found: 356.1165.

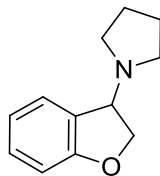
2-Bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate 6

To a solution of [2-(2-bromo-1-chloroethyl)phenoxy](triisopropyl)silane **5** (100 mg, 10 mmol) in acetonitrile (10 mL) under nitrogen was added AgNO₃ (81 mg, 20 mmol) and the reaction mixture was stirred for 12 h. After TLC analysis had shown complete conversion of the starting materials, the solvent was removed *in vacuo* and water (20 mL) was added to the residue and the mixture was extracted with CH₂Cl₂ (3 × 8 mL). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was removed *in vacuo*. The

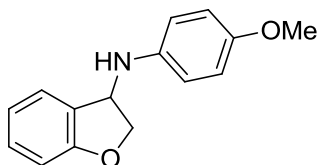
residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **6** (100 g, 94%) as a yellow oil. $R_f = 0.16$ (hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.31 (d, 1H, $J = 7.7$ Hz), 7.23 (t, 1H, $J = 7.8$ Hz), 6.96 (t, 1H, $J = 7.5$ Hz), 6.86 (d, 1H, $J = 8.2$ Hz), 6.52 (dd, 1H, $J = 3.8$ Hz, 5.0 Hz), 3.66 (dd, 1H, $J = 3.9$ Hz, 7.4 Hz), 3.57 (dd, 1H, $J = 2.3$ Hz, 9.0 Hz), 1.41-1.32 (m, 3H), 1.15 (dd, 18H, $J = 3.4$ Hz, 4.0 Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 153.29, 130.51, 126.33, 125.62, 121.36, 118.27, 79.47, 30.09, 18.17 (6C), 13.18 (3C). IR: 2984, 2918, 1596, 1484, 1370, 1234, 1260, 1154, 1022, 978, 802, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{30}\text{BrO}_2\text{Si}$ $[\text{M}-\text{NO}_2+2\text{H}]^+$ 373.1193, found: 373.1196.

3. Preparation of 2,3-dihydrobenzofurans

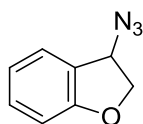
1-(2,3-Dihydro-1-benzofuran-3-yl)pyrrolidine **7a**



To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (200 mg, 0.48 mmol) in THF (10 mL) at -78°C under nitrogen, pyrrolidine (41 mg, 0.58 mmol) was added followed by dropwise addition of TBAF (1M in THF) (0.96 mL, 250 mg, 0.96 mmol). The reaction mixture was stirred at -78°C for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4 \times 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (40% ethyl acetate in hexane) to give **7a** (73 mg, 82%) as a brown oil. $R_f = 0.29$ (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.34 (d, 1H, $J = 7.3$ Hz), 7.21 (t, 1H, $J = 7.5$ Hz), 6.88 (t, 1H, $J = 7.4$ Hz), 6.84 (d, 1H, $J = 8.0$ Hz), 4.60 (dd, 1H, $J = 7.5$ Hz, 9.0 Hz), 4.43 (dd, 2H, $J = 7.6$ Hz, 8.5 Hz, 9.0 Hz), 2.73-2.69 (m, 2H), 2.57-2.52 (m, 2H), 1.80-1.73 (m, 4H). ^{13}C NMR (63 MHz, CDCl_3) δ : 160.70, 129.73, 126.50, 126.04, 120.31, 110.28, 74.29, 63.31, 49.59 (2C), 23.33 (2C). IR: 2966, 2940, 1480, 1320, 1232, 982, 824, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$ 190.1226, found: 190.1222.

2,3-Dihydro-1-benzofuran-3-yl(4-methoxyphenyl)amine 7b

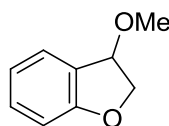
To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen, 4-methoxy aniline (35 mg, 0.29 mmol) was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4×5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7b** as a yellow solid (43 mg, 74%), m.p. $37\text{--}39\text{ }^{\circ}\text{C}$. $R_f = 0.44$ (20% ethyl acetate in hexane). ^1H NMR (400 MHz, DMSO- d_6) δ : 7.32 (d, 1H, $J = 7.3$ Hz), 7.21 (t, 1H, $J = 7.3$ Hz), 6.89–6.83 (m, 2H), 6.74 (d, 2H, $J = 8.9$ Hz), 6.66 (d, 2H, $J = 9.0$ Hz), 5.65 (d, 1H, $J = 8.2$ Hz), 5.19 (ddd, 1H, $J = 2.9$ Hz, 5.0 Hz, 7.9 Hz), 4.72 (dd, 1H, $J = 1.4$ Hz, 7.8 Hz), 4.19 (dd, 1H, $J = 4.6$ Hz, 4.8 Hz), 3.65 (s, 3H). ^{13}C NMR (63 MHz, CDCl_3) δ : 160.27, 152.86, 140.67, 130.17, 127.78, 125.41, 120.99, 115.18 (2C), 115.01 (2C), 110.44, 77.66, 56.49, 55.87. IR: 3250, 2942, 2928, 1512, 1480, 1290, 1236, 1036, 970, 752, 668 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{14}\text{NO}_2$ $[\text{M}-\text{H}]^+$ 240.1030, found: 240.1024.

2,3-Dihydro-1-benzofuran-3-yl azide 7c

To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen, sodium azide (19 mg, 0.29 mmol) was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent

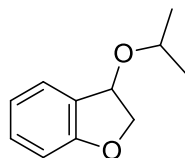
was evaporated *in vacuo*, water (15 mL) was added, the mixture was extracted with EtOAc (4 × 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7c** as a pale yellow oil (30 mg, 79%). R_f = 0.50 (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.42 (d, 1H, J = 7.5 Hz), 7.32 (t, 1H, J = 7.8 Hz), 6.99 (t, 1H, J = 7.4 Hz), 6.93 (d, 1H, J = 8.2 Hz), 5.03 (dd, 1H, J = 2.3 Hz, 4.3 Hz), 4.57 (dd, 1H, J = 3.4 Hz, 7.0 Hz, 9.0 Hz), 4.50 (dd, 1H, J = 2.9 Hz, 7.6 Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 160.33, 131.31, 125.46, 123.95, 121.34, 110.87, 76.39, 62.10. IR: 2956, 2920, 2360, 2096, 1644, 1478, 1234, 1164, 934, 750, 668 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_8\text{H}_8\text{O}$ $[\text{M}-\text{N}_3]^+$ 120.0570, found: 120.0567.

3-Methoxy-2,3-dihydro-1-benzofuran **7d**



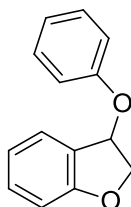
To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in MeOH (10 mL) at $-78\text{ }^\circ\text{C}$ under nitrogen was added dropwise TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4 × 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (20% ethyl acetate in hexane) to give **7d** as colorless oil (31 mg, 88%). R_f = 0.36 (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.41 (d, 1H, J = 7.3 Hz), 7.27 (t, 1H, J = 7.7 Hz), 6.93 (t, 1H, J = 7.4 Hz), 6.89 (d, 1H, J = 8.0 Hz), 5.00 (dd, 1H, J = 2.0 Hz, 4.3 Hz), 4.55 (dd, 1H, J = 2.2 Hz, 8.5 Hz), 4.43 (dd, 1H, J = 4.2 Hz, 6.4 Hz), 3.34 (s, 3H). ^{13}C NMR (63 MHz, CDCl_3) δ : 160.88, 130.86, 126.24, 125.67, 120.63, 110.72, 80.03, 76.11, 55.09. IR: 2986, 2940, 1612, 1480, 1364, 1232, 1168, 1090, 1016, 950, 880, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_{10}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 173.0573, found: 173.0577.

3-Isopropoxy-2,3-dihydro-1-benzofuran **7e**



To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in 2-propanol (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen was added dropwise TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc ($4 \times 5\text{ mL}$), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (20% ethyl acetate in hexane) to give **7e** as a colorless oil (29 mg, 68%). $R_f = 0.57$ (20% ethyl acetate in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.36 (d, 1H, $J = 7.3\text{ Hz}$), 7.23 (t, 1H, $J = 7.8\text{ Hz}$), 6.91 (t, 1H, $J = 7.5\text{ Hz}$), 6.86 (d, 1H, $J = 8.1\text{ Hz}$), 5.16 (dd, 1H, $J = 3.1\text{ Hz}$), 4.50 (dd, 1H, $J = 3.9\text{ Hz}$, 6.3 Hz), 4.45 (dd, 1H, $J = 3.1\text{ Hz}$, 7.1 Hz), 3.84 (sep, 1H, $J = 6.1\text{ Hz}$), 1.21 (d, 6H, $J = 6.1\text{ Hz}$). $^{13}\text{C NMR}$ (63 MHz, CDCl_3) δ : 160.60, 130.47, 126.88, 126.02, 120.73, 110.65, 77.49, 76.54, 70.22, 22.84, 22.76. IR: 2972, 2928, 1600, 1482, 1466, 1378, 1232, 1078, 980, 752, 618 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{14}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 201.0886, found: 201.0877.

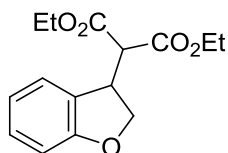
3-Phenoxy-2,3-dihydro-1-benzofuran **7f**



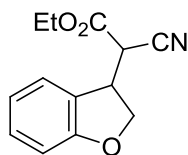
To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen, phenol (27 mg, 0.29 mmol) was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was

evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4 × 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7f** as a colorless oil (29 mg, 59%). $R_f = 0.63$ (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.40 (d, 1H, $J = 7.6$ Hz), 7.33-7.28 (m, 3H), 7.01 (t, 1H, $J = 7.4$ Hz), 6.95-6.89 (m, 4H), 5.89 (dd, 1H, $J = 2.7$ Hz, 3.5 Hz), 4.67 (dd, 1H, $J = 3.0$ Hz, 4.5 Hz, 6.4 Hz), 4.62 (dd, 1H, $J = 2.9$ Hz, 7.9 Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 161.02, 157.22, 131.23, 129.84 (2C), 128.41, 126.39, 121.67, 121.04, 115.91 (2C), 110.75, 77.22, 76.17. IR: 2928, 2892, 1614, 1482, 1228, 1174, 1062, 968, 750, 692 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 235.0730, found: 235.0727.

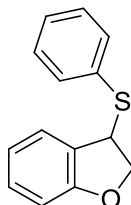
Diethyl 2,3-dihydro-1-benzofuran-3-ylmalonate **7g**



To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in THF (10 mL) at -78 °C under nitrogen, diethyl malonate (45 mg, 0.29 mmol) [it was reacted first with sodium hydride (6.5 mg, 0.31 mmol) in THF (8 mL) to generate the anion] was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at -78 °C for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4 × 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7g** as a colorless oil (32 mg, 76%). $R_f = 0.38$ (20% ethyl acetate in hexane). ^1H NMR (250 MHz, CDCl_3) δ : 7.10 (t, 2H, $J = 7.5$ Hz), 6.82-6.73 (m, 2H), 4.66 (t, 1H, $J = 9.4$ Hz), 4.46 (dd, 1H, $J = 4.7$ Hz, 5.0 Hz), 4.23-4.05 (m, 5H), 3.62 (d, 1H, $J = 8.6$ Hz), 1.22 (t, 6H, $J = 7.1$ Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 165.32, 165.19, 157.63, 126.55, 123.79, 122.45, 117.83, 107.21, 71.99, 59.09, 53.38, 38.75 (2C), 11.38, 11.30. IR: 2984, 2918, 1732, 1596, 1484, 1370, 1234, 1180, 1096, 1022, 978, 864, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{18}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$ 301.1046, found: 301.1042.

Ethyl cyano(2,3-dihydro-1-benzofuran-3-yl)acetate 7h

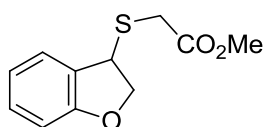
To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (100 mg, 0.24 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen, ethyl cyanoacetate (32 mg, 0.29 mmol) [it was reacted first with sodium hydride (6.5 mg, 0.31 mmol) in THF (8 mL) to generate the anion] was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc ($4 \times 5\text{ mL}$), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7h** as a brown oil (37 mg, 67%). $R_f = 0.36$ (20% ethyl acetate in hexane). ^1H NMR (250 MHz, CDCl_3) δ : 7.21-7.14 (m, 2H), 6.89-6.81 (m, 2H), 4.46 (dd, 1H, $J = 5\text{ Hz}$), 4.23-4.05 (m, 4H), 3.62 (d, 1H, $J = 7.5\text{ Hz}$), 1.22 (t, 3H, $J = 7.1\text{ Hz}$). ^{13}C NMR (63 MHz, CDCl_3) δ : 165.19, 157.63, 126.55, 123.79, 122.45, 117.83, 115.06, 107.21, 71.99, 59.09, 42.10, 38.75, 11.38. IR: 2984, 2918, 2360, 1742, 1598, 1484, 1370, 1234, 1180, 1096, 1022, 978, 864, 802, 754 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{13}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 254.0788, found: 254.0785.

3-(Phenylthio)-2,3-dihydro-1-benzofuran 7i

To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (200 mg, 0.48 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen, thiophenol (32 mg, 0.29 mmol) was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was

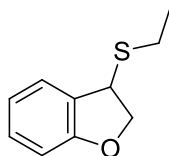
evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4 × 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7i** as a colorless oil (46 mg, 85%). $R_f = 0.56$ (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.35-7.33 (m, 2H), 7.28-7.23 (m, 4H) 7.15 (t, 1H, $J = 7.5$ Hz), 6.87 (t, 1H, $J = 7.48$ Hz), 6.77 (d, 1H, $J = 8.0$ Hz), 4.89 (dd, 1H, $J = 3.8$ Hz, 4.0 Hz), 4.73 (dd, 1H, $J = 1.7$ Hz, 8.1 Hz), 4.55 (dd, 1H, $J = 4.0$ Hz, 5.6 Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 159.91, 133.87, 132.40 (2C), 129.75, 129.14 (2C), 127.74, 126.46, 125.44, 121.0, 110.14, 77.55, 48.85. ESI MS (m/z): 251.3 $[\text{M}+\text{Na}]^+$. IR: 2998, 2884, 2098, 1478, 1320, 1332, 1162, 1088, 988, 808, 736, 682 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 251.0501, found: 251.0499.

Methyl (2,3-dihydro-1-benzofuran-3-ylthio)acetate **7j**



To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (200 mg, 0.48 mmol) in THF (10 mL) at -78°C under nitrogen, methyl thioglycolate (30 mg, 0.29 mmol) was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at -78°C for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc (4 × 5 mL), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7j** as a colorless oil (43 mg, 80%). $R_f = 0.41$ (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.31 (d, 1H, $J = 7.5$ Hz), 7.18 (t, 1H, $J = 7.7$ Hz), 6.91 (t, 1H, $J = 7.5$ Hz), 6.82 (d, 1H, $J = 8.0$ Hz), 4.78 (dd, 1H, $J = 1.5$ Hz, 8.2 Hz), 4.66 (dd, 1H, $J = 4.0$ Hz), 4.57 (dd, 1H, $J = 4.0$ Hz, 5.6 Hz), 3.70 (s, 3H), 3.22 (d, 2H, $J = 2.0$ Hz). ^{13}C NMR (63 MHz, CDCl_3) δ : 170.70, 159.88, 129.80, 125.81, 125.46, 121.09, 110.14, 77.86, 52.55, 45.99, 32.13. IR: 2964, 2854, 1644, 1478, 1434, 1276, 1230, 1140, 1008, 918, 734 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{12}\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 247.0399, found: 247.0390.

3-(Ethylthio)-2,3-dihydro-1-benzofuran **7k**

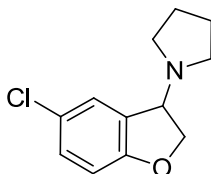


To a solution of 2-bromo-1-{2-[(triisopropylsilyl)oxy]phenyl}ethyl nitrate **6** (200 mg, 0.48 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ under nitrogen, ethyl mercaptan (18 mg, 0.29 mmol) [it was reacted first with sodium hydride (6.5 mg, 0.31 mmol) in THF (8 mL) to generate the anion] was added followed by dropwise addition of TBAF (1M in THF) (0.48 mL, 125 mg, 0.48 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at room temperature for 30 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, and the mixture was extracted with EtOAc ($4 \times 5\text{ mL}$), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (10% ethyl acetate in hexane) to give **7k** as a colorless oil (32 mg, 76%). $R_f = 0.48$ (20% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.30 (d, 1H, $J = 7.0\text{ Hz}$), 7.17 (t, 1H, $J = 7.5\text{ Hz}$), 6.84 (t, 1H, $J = 7.2\text{ Hz}$), 6.80 (d, 1H, $J = 7.8\text{ Hz}$), 4.83 (dd, 1H, $J = 2.5\text{ Hz}$, 6.0 Hz), 4.71 (dd, 1H, $J = 1.5\text{ Hz}$, 5.0 Hz), 4.62 (dd, 1H, $J = 3.0\text{ Hz}$, 6.0 Hz), 2.60 (q, 2H, $J = 7.5\text{ Hz}$), 1.34 (t, 3H, $J = 7.5\text{ Hz}$). ^{13}C NMR (63 MHz, CDCl_3) δ : 161.03, 130.95, 126.96, 126.61, 122.24, 111.29, 78.11, 53.69, 33.27, 17.58. IR: 2956, 2854, 1478, 1436, 1276, 1230, 1128, 1098, 988, 744 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_{13}\text{OS}$ $[\text{M}+\text{H}]^+$ 181.0682, found: 181.0677.

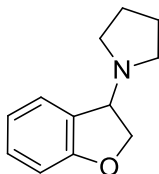
Preparation of 1-(5-chloro-2,3-dihydro-1-benzofuran-3-yl)pyrrolidine **8** and 1-(2,3-dihydro-1-benzofuran-3-yl)pyrrolidine **7a**

To a stirred solution of [2-(2-bromo-1-chloroethyl)phenoxy](triisopropyl)silane **5** (200 mg, 0.50 mmol) in THF (10 mL) at $0\text{ }^{\circ}\text{C}$ under nitrogen, pyrrolidine (43 mg, 0.60 mmol) was added followed by dropwise addition of TBAF (1M in THF) (1 mL, 260 mg, 1 mmol) and the reaction was stirred at $0\text{ }^{\circ}\text{C}$ for 30 min and then room temperature for 10 min. After TLC analysis had shown complete conversion of the starting materials, water (15 mL) was added, the mixture was extracted with EtOAc ($3 \times 10\text{ mL}$), the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash

column chromatography (20% methanol in dichloromethane) to give compound **8** in the first fraction and compound **7a** in the second fraction.

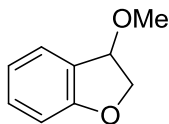


Compound **8** (6 mg, 5%) was isolated as a colorless oil. $R_f = 0.18$ (10% methanol in dichloromethane). ^1H NMR (250 MHz, CDCl_3) δ : 7.30 (d, 1H, $J = 2.0$ Hz), 7.15 (dd, 1H, $J = 2.1$ Hz, 6.4 Hz), 6.76 (d, 1H, $J = 8.6$ Hz), 4.60 (dd, 1H, $J = 6.2$ Hz, 7.1 Hz), 4.43 (dd, 2H, $J = 5.7$ Hz, 7.5 Hz), 2.69-2.66 (m, 2H), 2.53-2.50 (m, 2H), 1.78-1.75 (m, 4H). ^{13}C NMR (63 MHz, CDCl_3) δ : 159.30, 129.59, 126.52, 126.37, 125.01, 111.19, 74.76, 63.09, 49.46 (3C), 23.29 (3C). IR: 2990, 2974, 1478, 1366, 1266, 1224, 896, 738, 704, 666 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{15}\text{ClNO}$ $[\text{M}+\text{H}]^+$ 224.0837, found: 224.0832.



Compound **7a** (9 mg, 10% yield) was isolated as a brown oil. $R_f = 0.29$ (20% ethyl acetate in hexane). The corresponding spectroscopic data matched those reported for the authentic sample (refer to page S7).

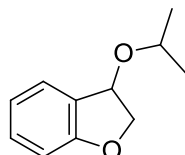
3-Methoxy-2,3-dihydro-1-benzofuran **7d**



[2-(2-Bromo-1-chloroethyl)phenoxy](triisopropyl)silane **5** (200 mg, 0.50 mmol) was dissolved in MeOH (10 mL) under nitrogen, cooled at 0 °C and then TBAF (1M in THF) (1 mL, 260 mg, 1 mmol) was added dropwise while maintaining that temperature. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 10 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, the mixture was extracted with EtOAc (4 \times 5 mL) and the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in*

vacuo. The residue was purified by flash column chromatography (20% ethyl acetate in hexane) to give **7d** as a colorless oil (9 mg, 12%). $R_f = 0.36$ (20% ethyl acetate in hexane). The corresponding spectroscopic data matched those reported for the authentic sample (refer to page S8).

3-Isopropoxy-2,3-dihydro-1-benzofuran **7e**



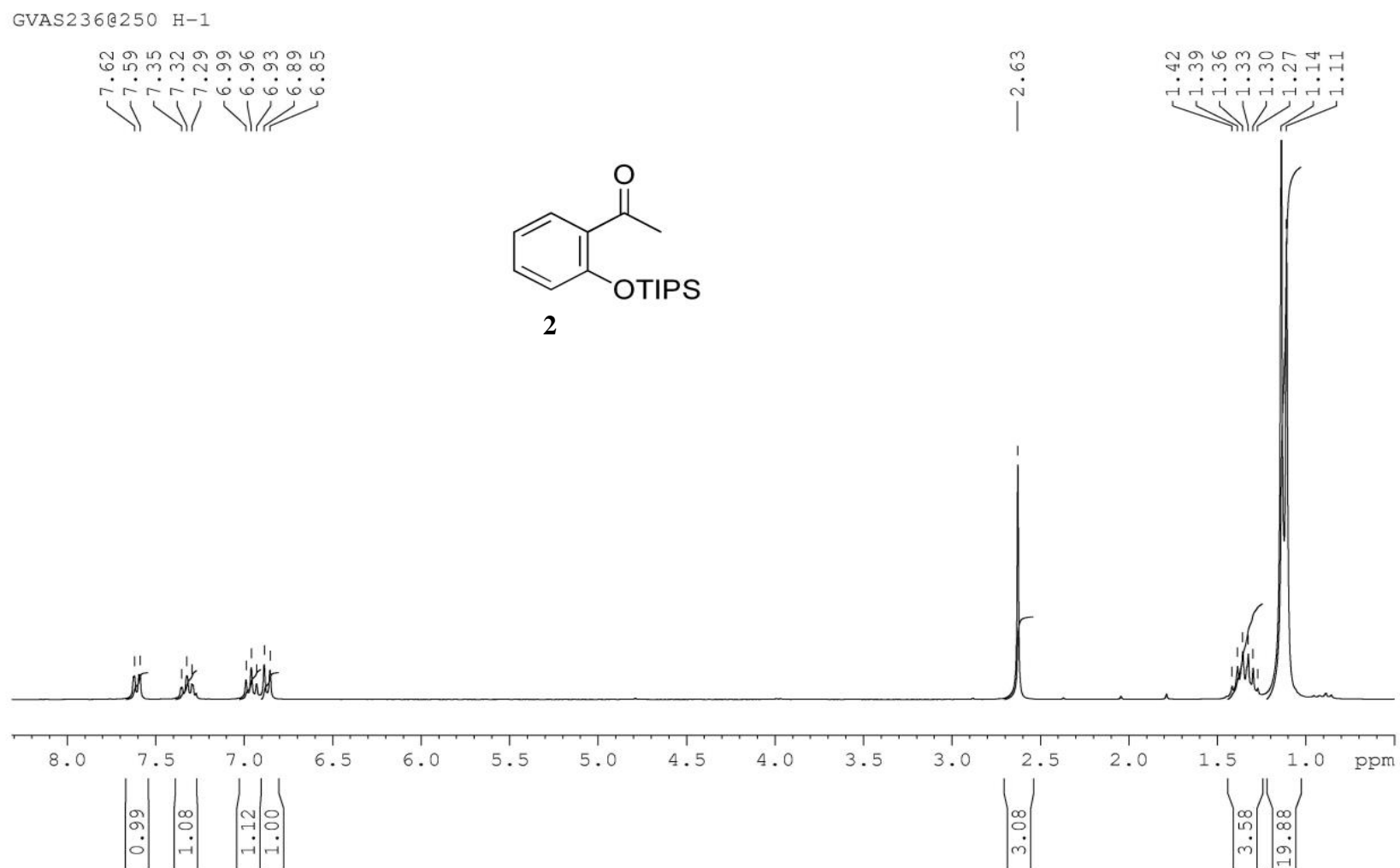
[2-(2-Bromo-1-chloroethyl)phenoxy](triisopropyl)silane **5** (200 mg, 0.50 mmol) was dissolved in 2-propanol (10 mL) under nitrogen, cooled at 0 °C and then TBAF (1M in THF) (1 mL, 260 mg, 1 mmol) was added dropwise while maintaining that temperature. The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 10 min. After TLC analysis had shown complete conversion of the starting materials, the solvent was evaporated *in vacuo*, water (15 mL) was added, the mixture was extracted with EtOAc (4 × 5 mL) and the combined organic extracts dried with sodium sulphate, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (20% ethyl acetate in hexane) to give **7e** as a colorless oil (7.5 mg, 8%). $R_f = 0.57$ (20% ethyl acetate in hexane). The corresponding spectroscopic data matched those reported for the authentic sample (refer to page S9).

4. References

- (1) Leonard, J.; Lygo, B.; Procter, G. *Advanced Practical Organic Chemistry*, Nelson Thornes Ltd. UK, 2001.
- (2) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

5. Copies of ^1H and ^{13}C NMR and HRMS spectra

^1H NMR of compound **2** in CDCl_3 at 250 MHz



^{13}C NMR of compound **2** in CDCl_3 at 63 MHz

GVAS236@250 C-13

—201.01

—155.30

—132.98

—131.04

—130.14

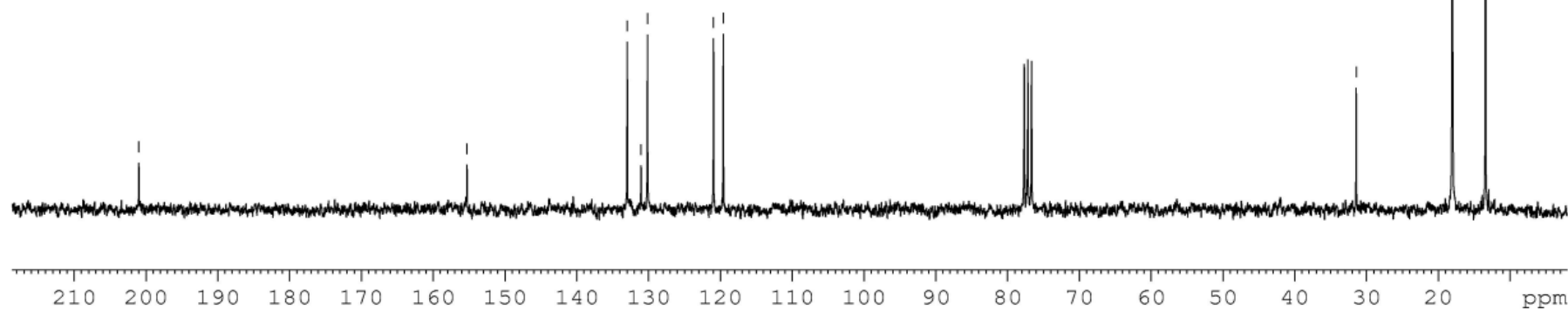
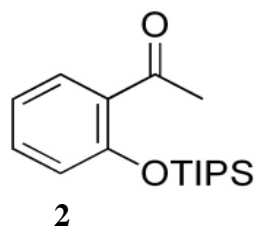
—120.95

—119.59

—31.43

—18.02

—13.41



HRMS of Compound 2



ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ
ΔΙΚΤΥΟ ΕΡΓΑΣΤΗΡΙΩΝ ΥΠΟΣΤΗΡΙΞΗΣ ΕΡΕΥΝΑΣ (Δ.Ε.Υ.Ε.Π.Ι.)
ΜΟΝΑΔΑ ΠΕΡΙΒΑΛΛΟΝΤΙΚΗΣ, ΟΡΓΑΝΙΚΗΣ ΚΑΙ ΒΙΟΧΗΜΙΚΗΣ ΑΝΑΛΥΣΗΣ-ORBITRAP-LC-MS

Διεύθυνση: Κτίριο Β', Αίθουσα Χ2-083, Τμήμα Χημείας, Πανεπιστήμιο Ιωαννίνων, 45110
Τηλέφωνο/fax: +30 26510 08317-8706/26510 08074
e-mail: orbitrap@uoi.gr

Scan mode: FTMS +p ESI full ms [150-2000]
FT resolution: 100000

Data file: GVAS236_21_10_13

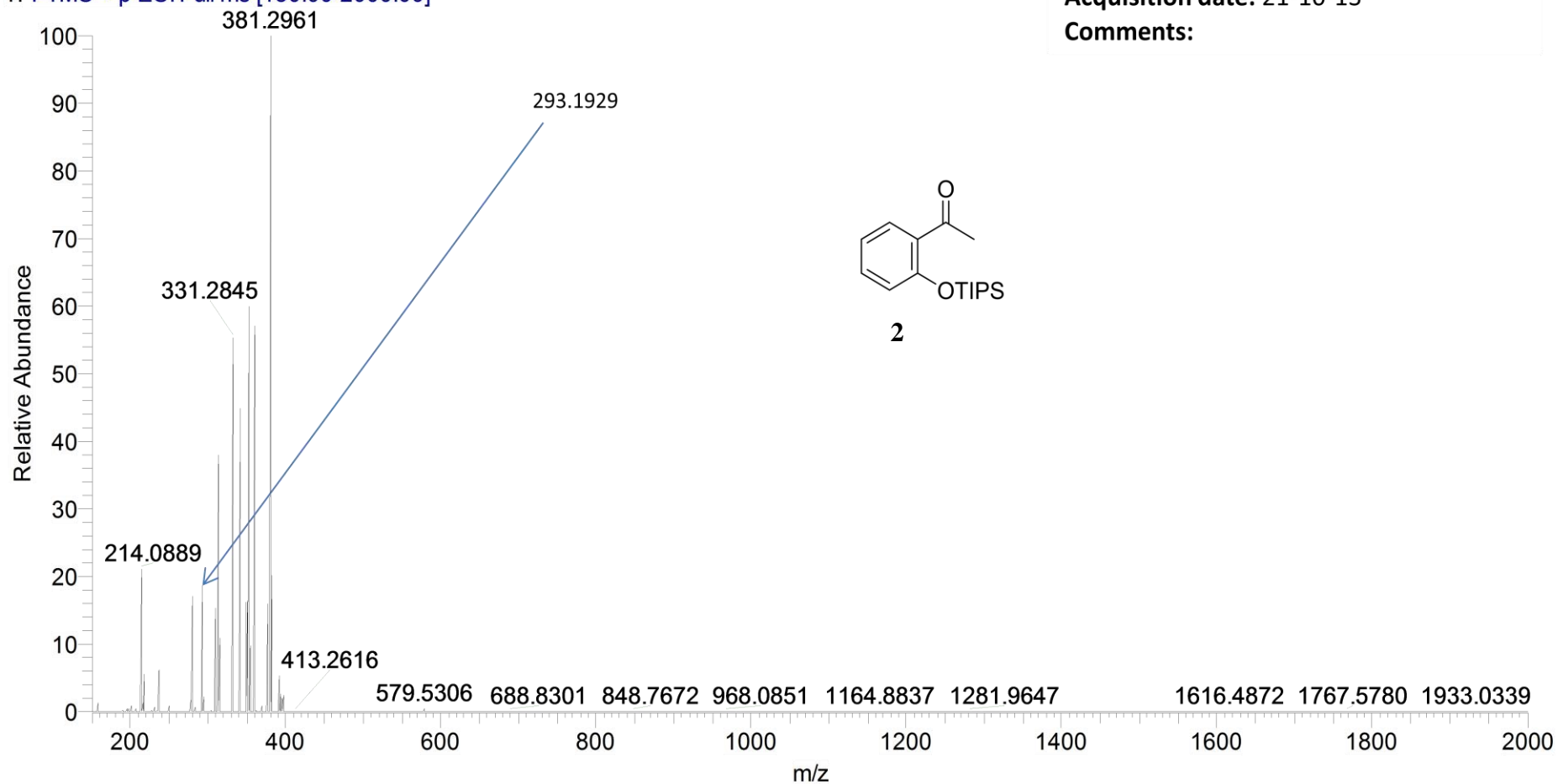
Sample ID: GVAS236

Operator: Θ. Καρκαμπούνας

Acquisition date: 21-10-13

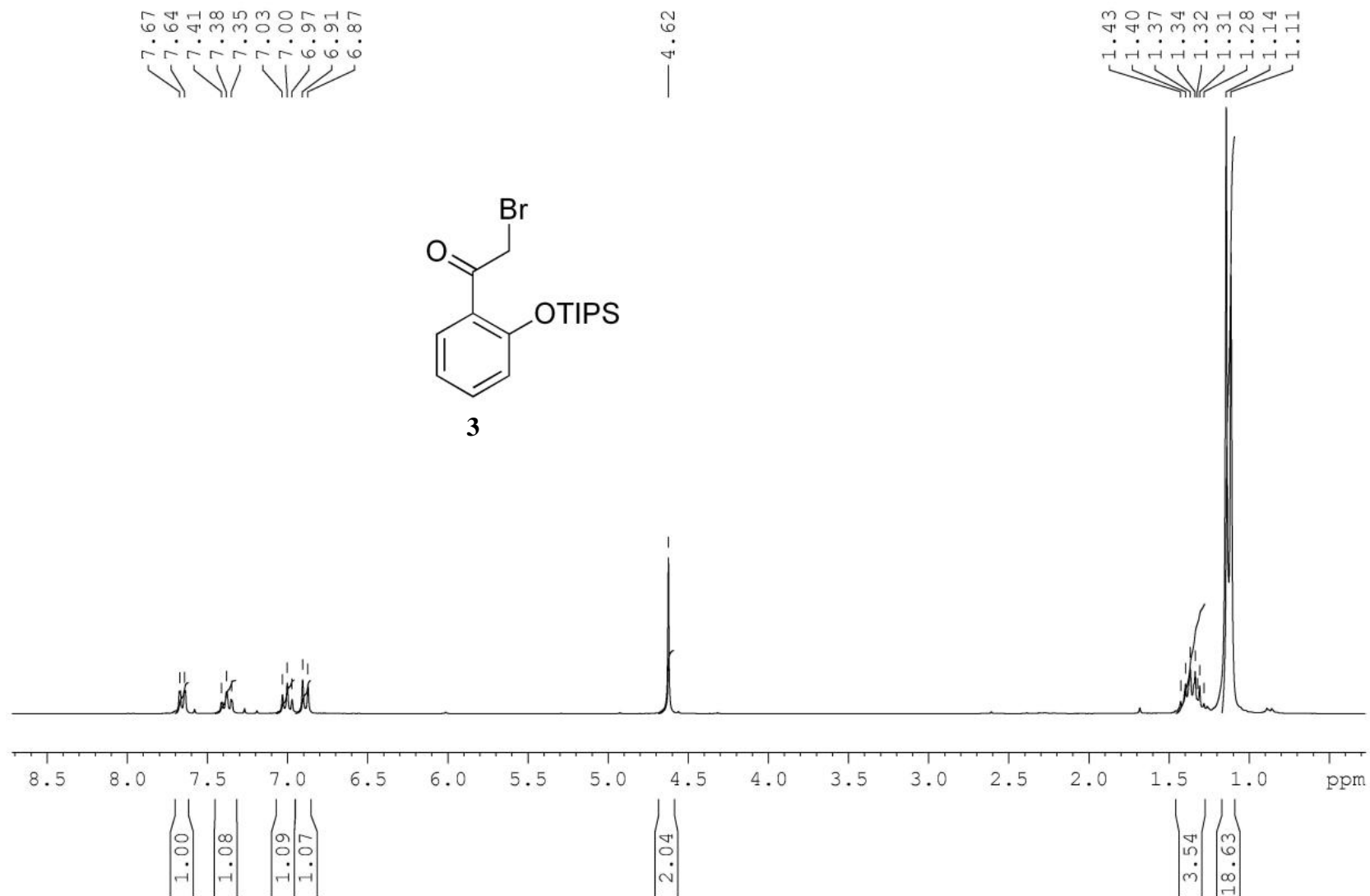
Comments:

GVAS236_21_10_13_131021123627 #3 RT: 0.06 AV: 1 NL: 4.08E7
T: FTMS + p ESI Full ms [150.00-2000.00]



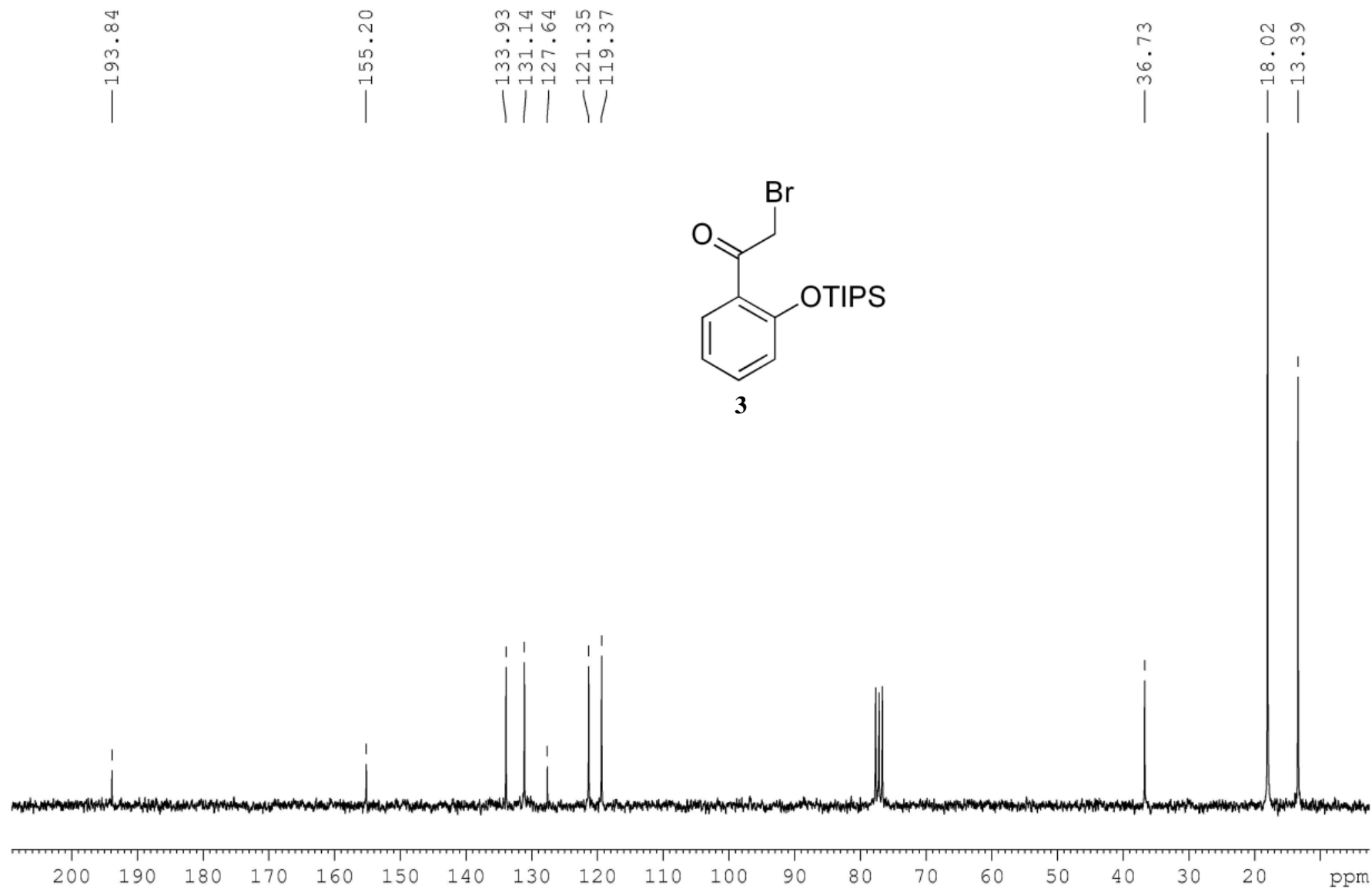
^1H NMR of compound **3** in CDCl_3 at 250 MHz

GVAS259@250 H-1



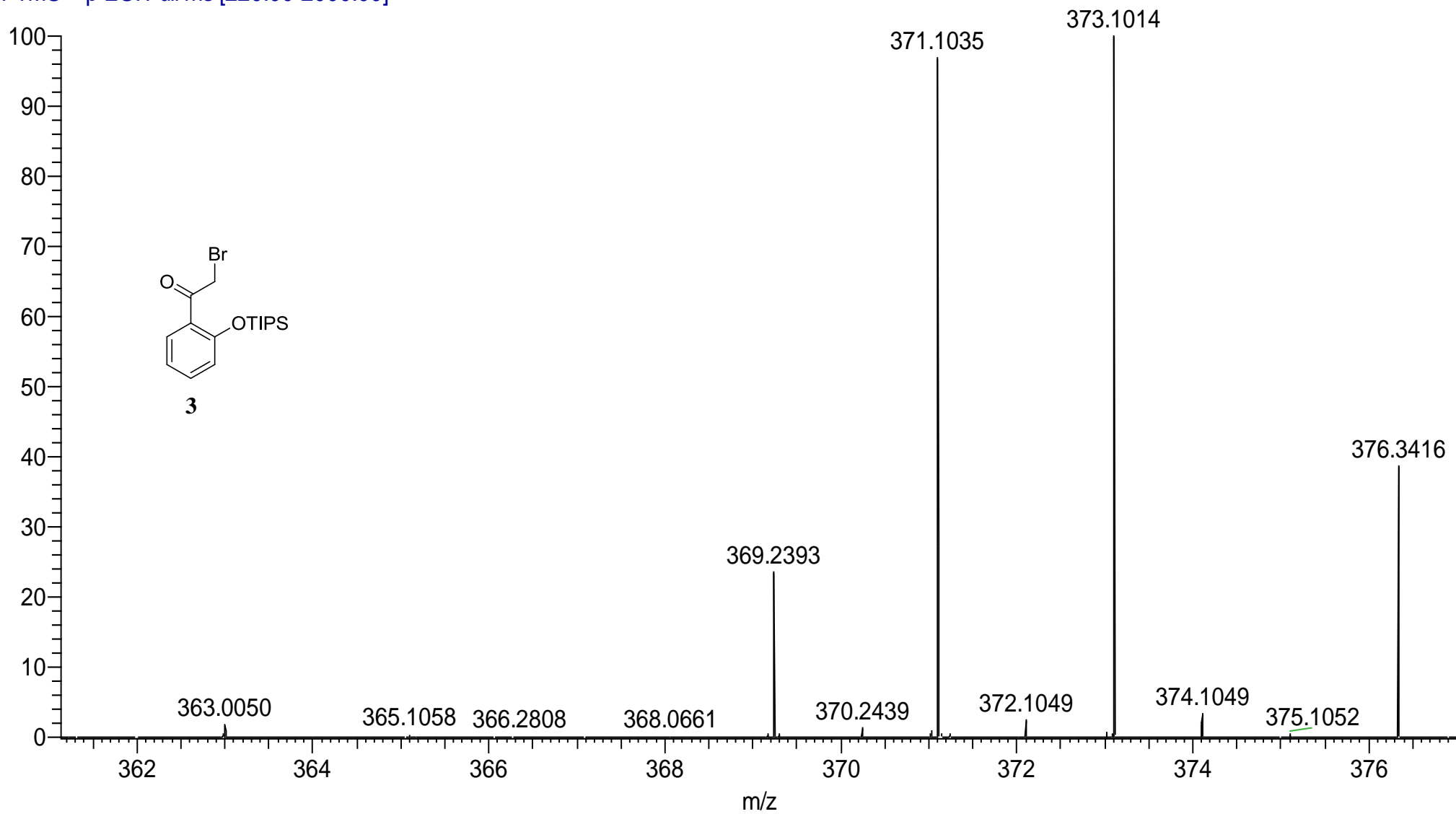
^{13}C NMR of compound **3** in CDCl_3 at 63 MHz

GVAS259@250 C-13



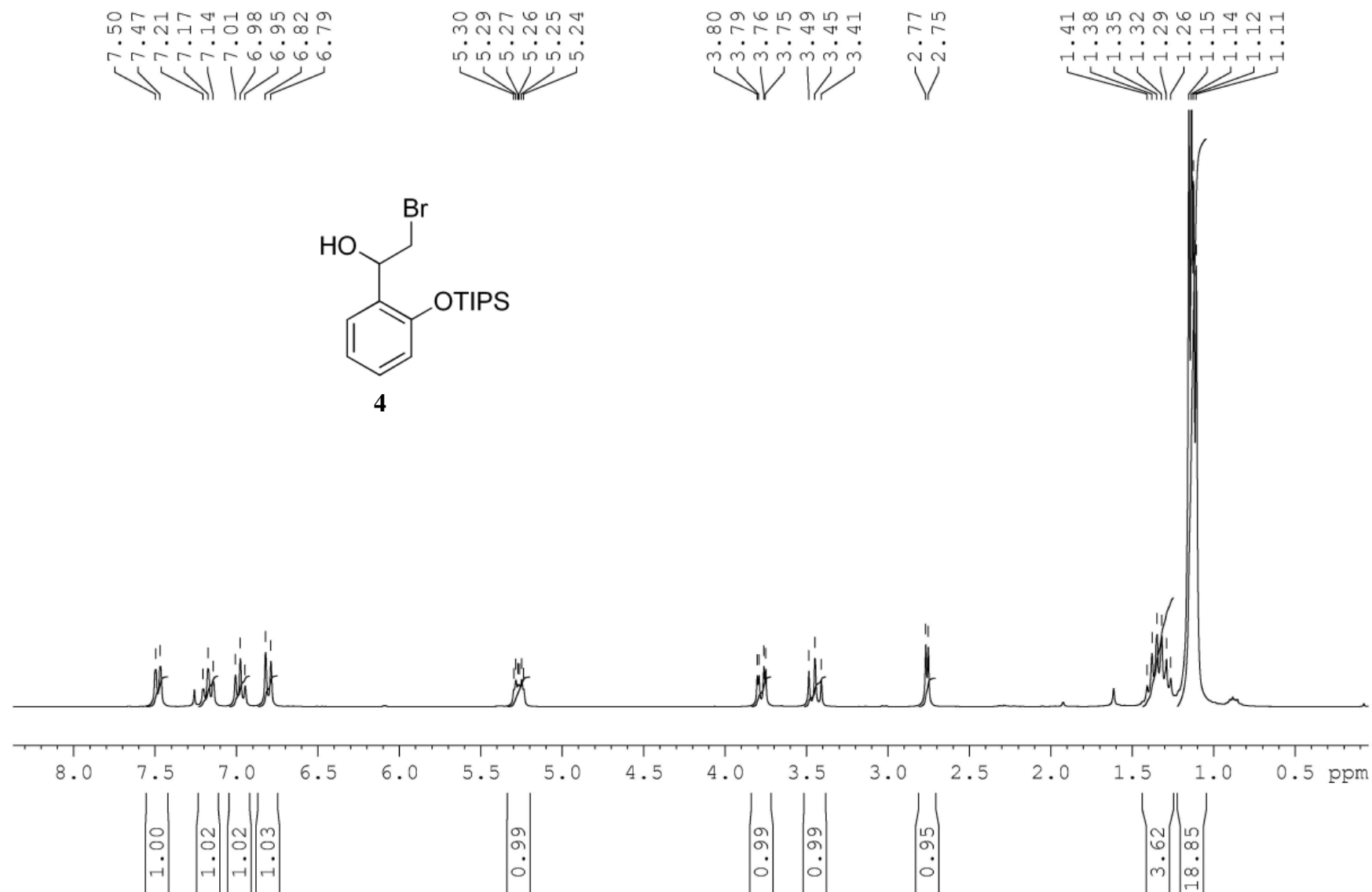
HRMS of compound **3**

GVAS259_21_10_13_131021135802 #3 RT: 0.08 AV: 1 NL: 4.41E5
T: FTMS + p ESI Full ms [220.00-2000.00]



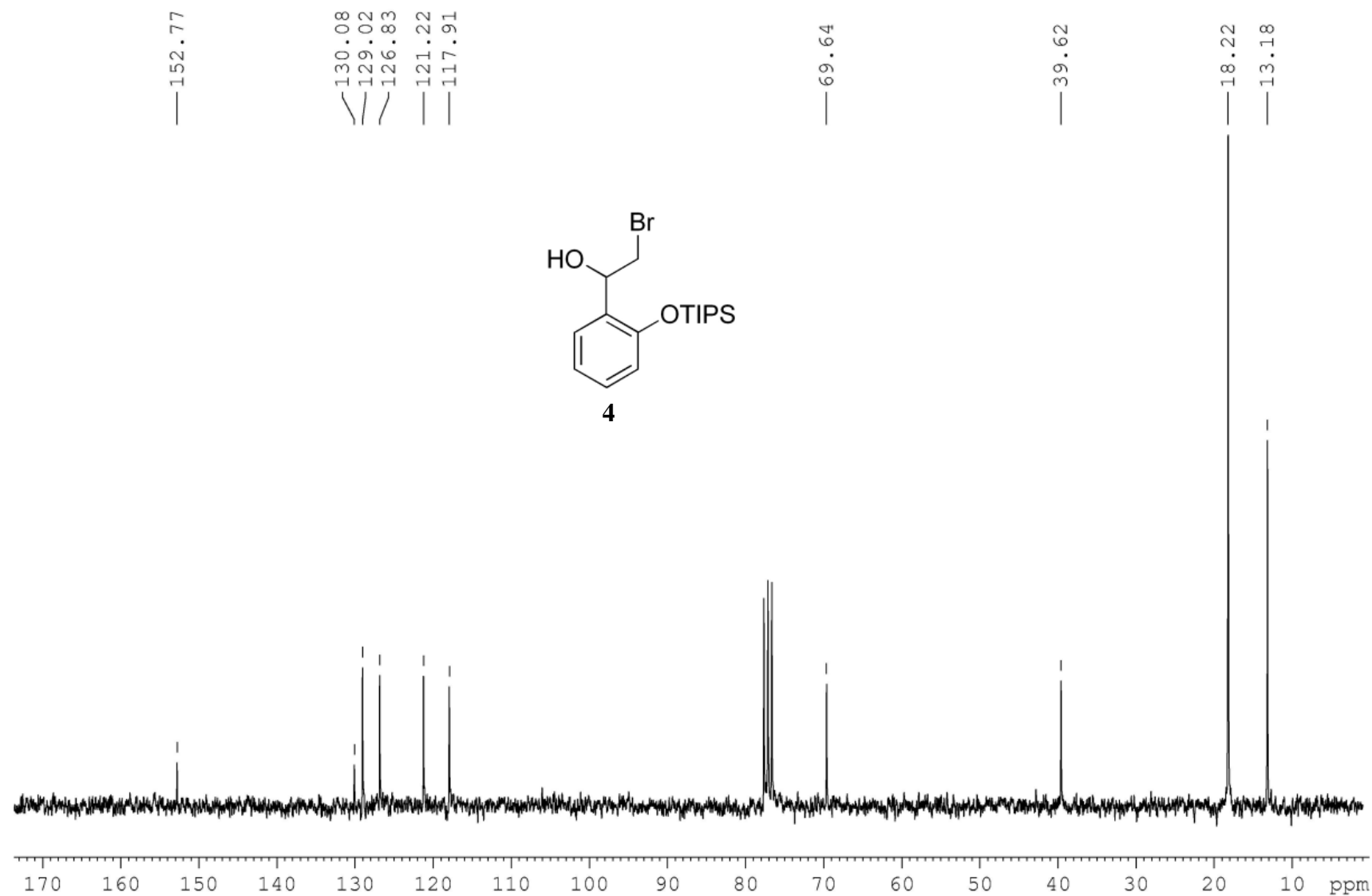
^1H NMR of compound **4** in CDCl_3 at 250 MHz

GVAS260-B@250 H-1



^{13}C NMR of compound **4** in CDCl_3 at 63 MHz

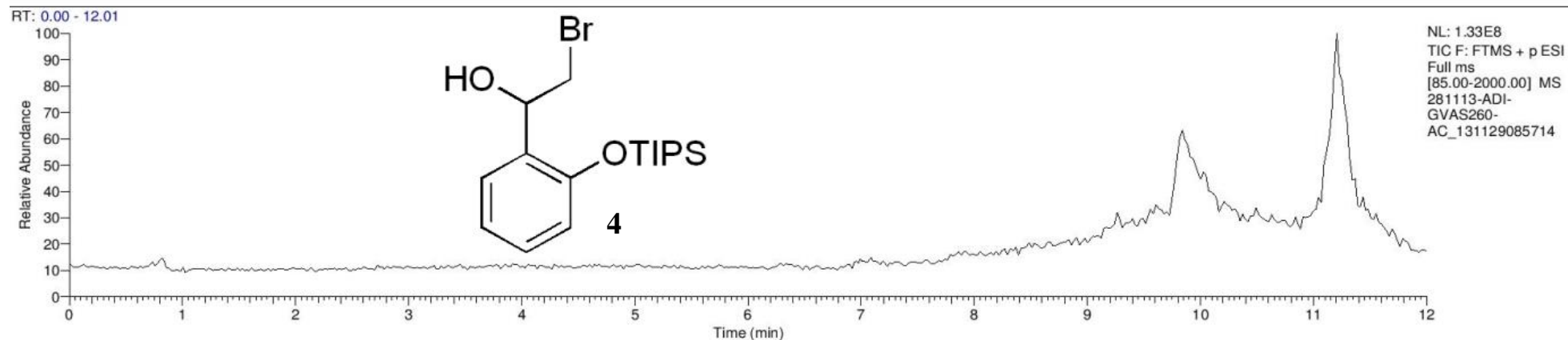
GVAS260-B@250 C-13



HRMS of compound 4

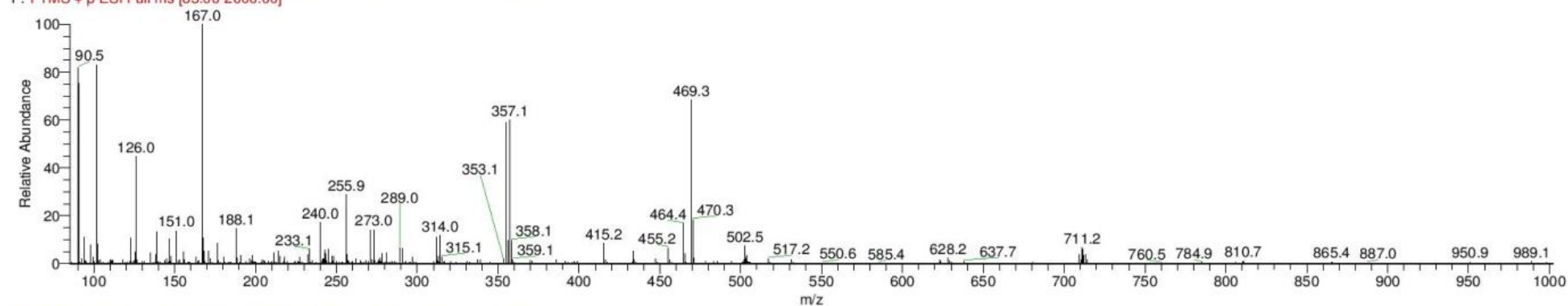
281113-ADI-GVAS260-AC_131129085714

29 Nov 13 08:57:14



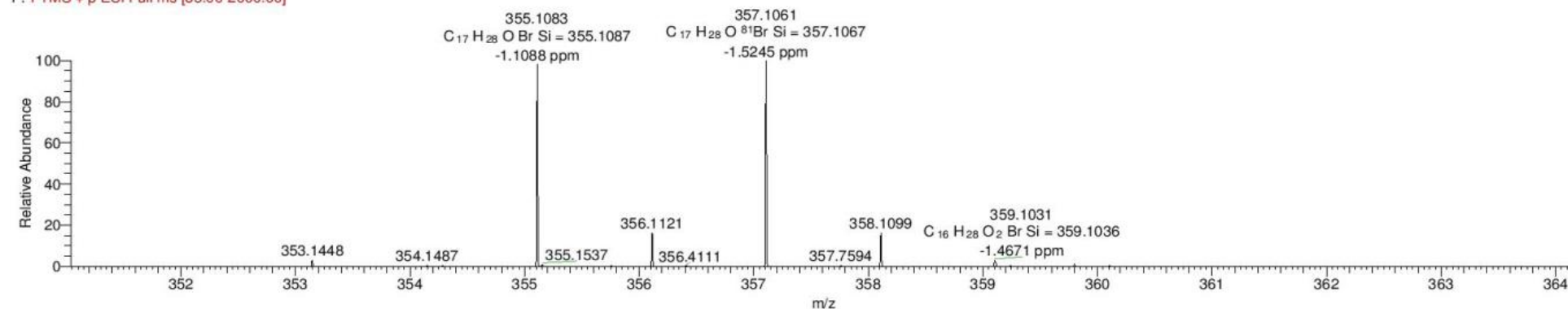
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F: FTMS + p ESI Full ms [85.00-2000.00]



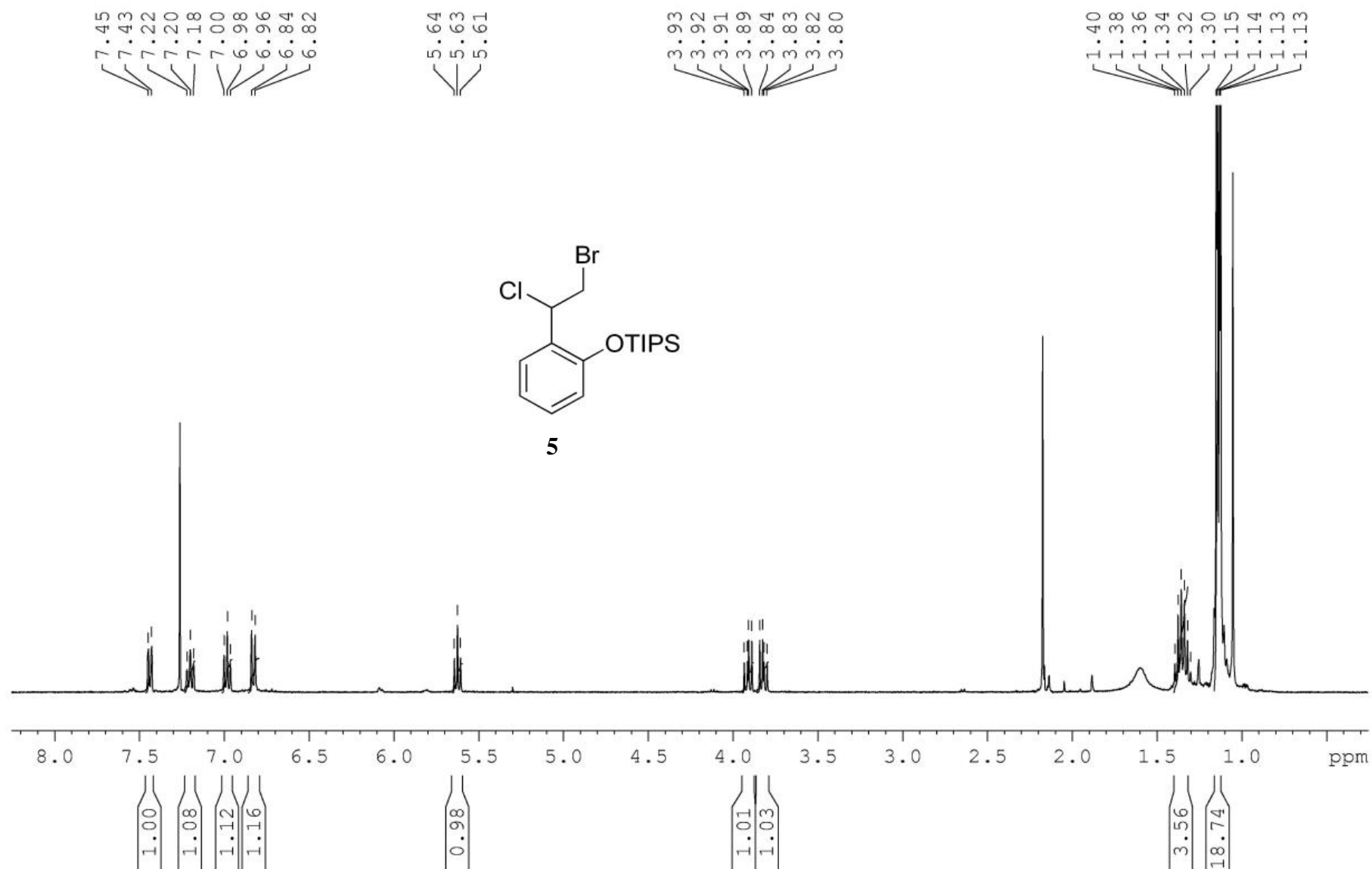
281113-ADI-GVAS260-AC_131129085714 #919 RT: 9.84 AV: 1 NL: 3.10E6

F: FTMS + p ESI Full ms [85.00-2000.00]



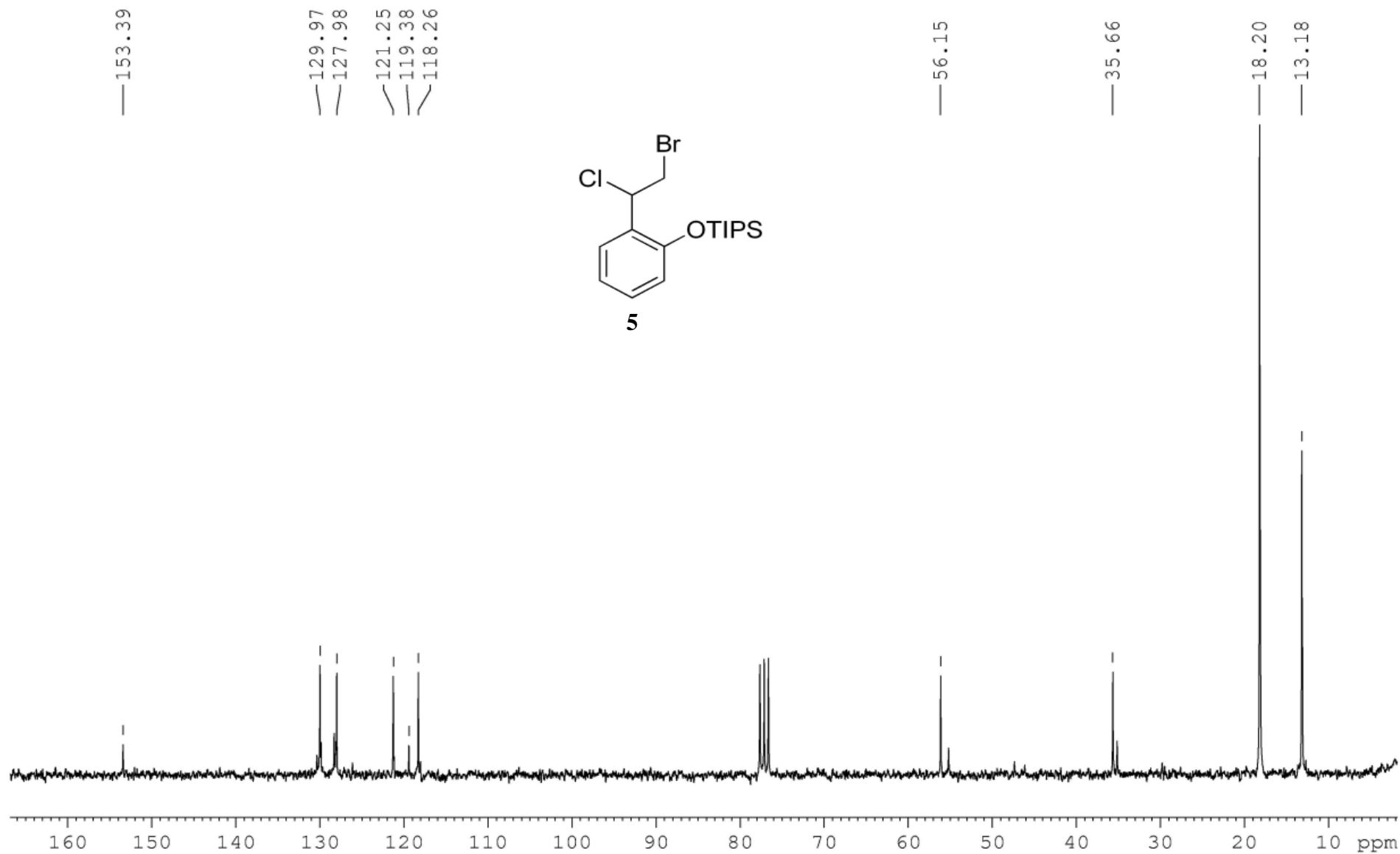
^1H NMR of compound **5** in CDCl_3 at 400 MHz

GVAS261@400 Hz



^{13}C NMR of compound **5** in CDCl_3 at 63 MHz

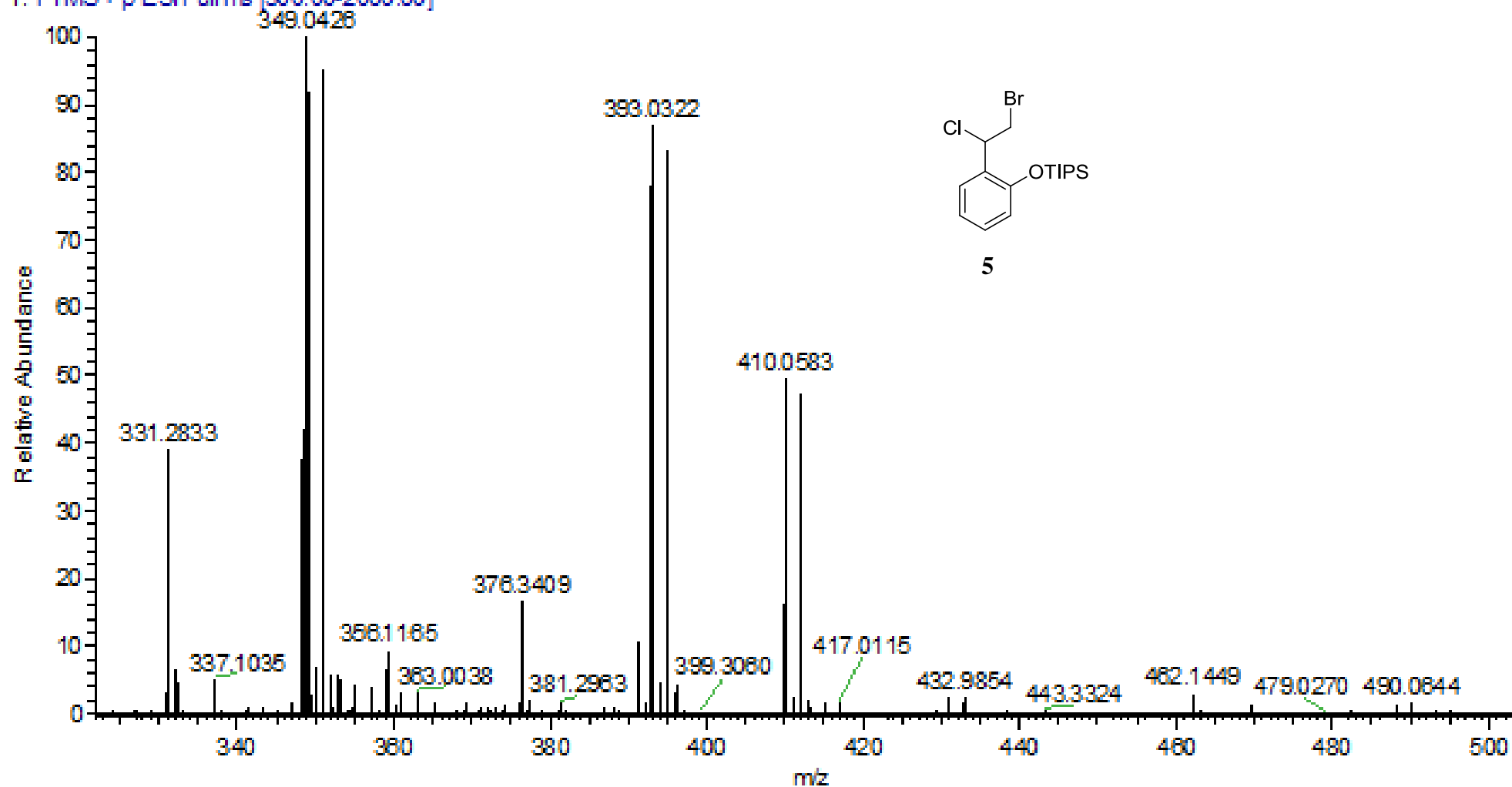
GVAS261@250 C-13



HRMS of compound 5

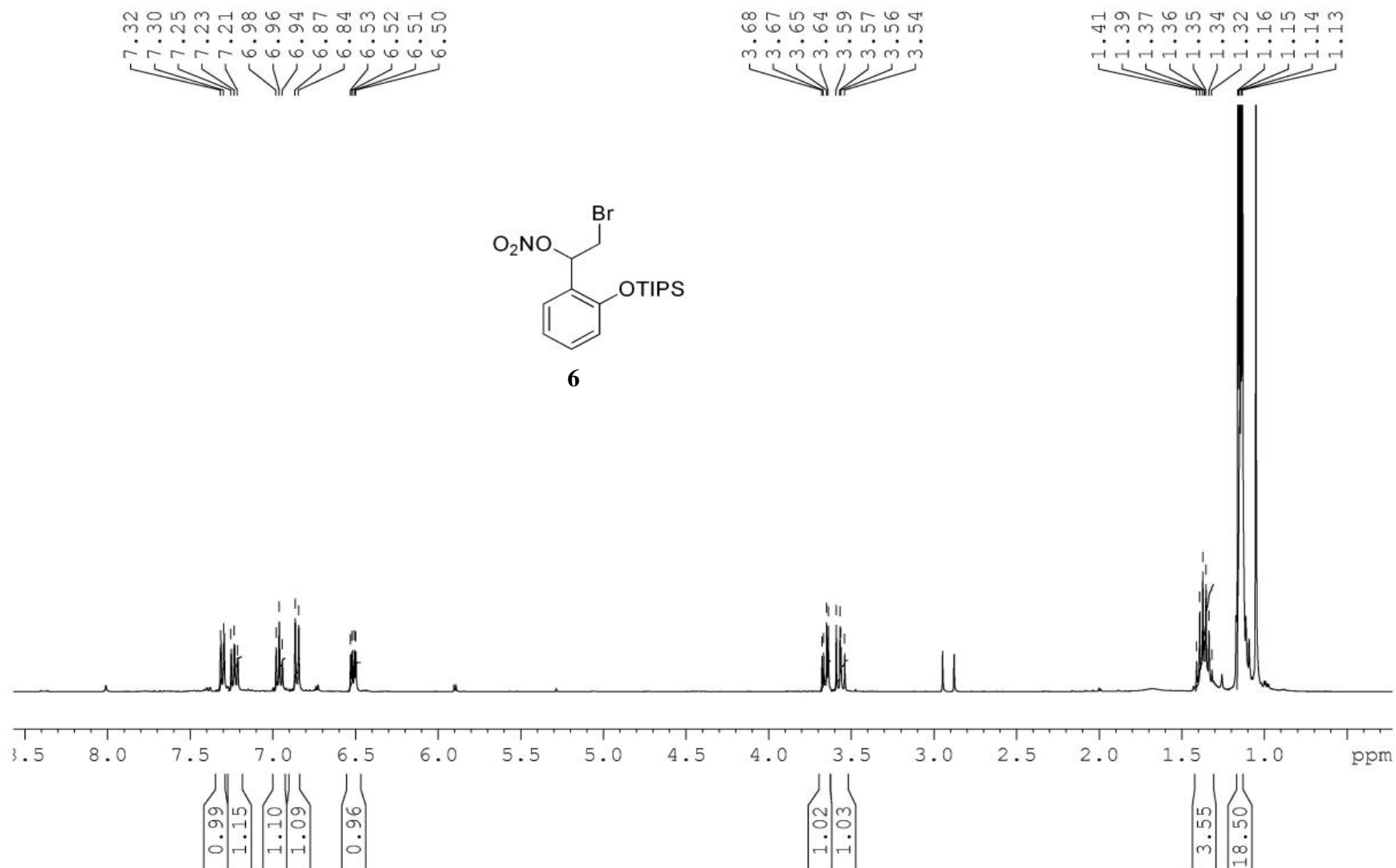
GVAS261 21 10 13 131021141943 #9-35 RT: 0.24-0.99 AV: 27 NL: 2.01E5

T: FTMS + p ESI Full ms [300.00-2000.00]



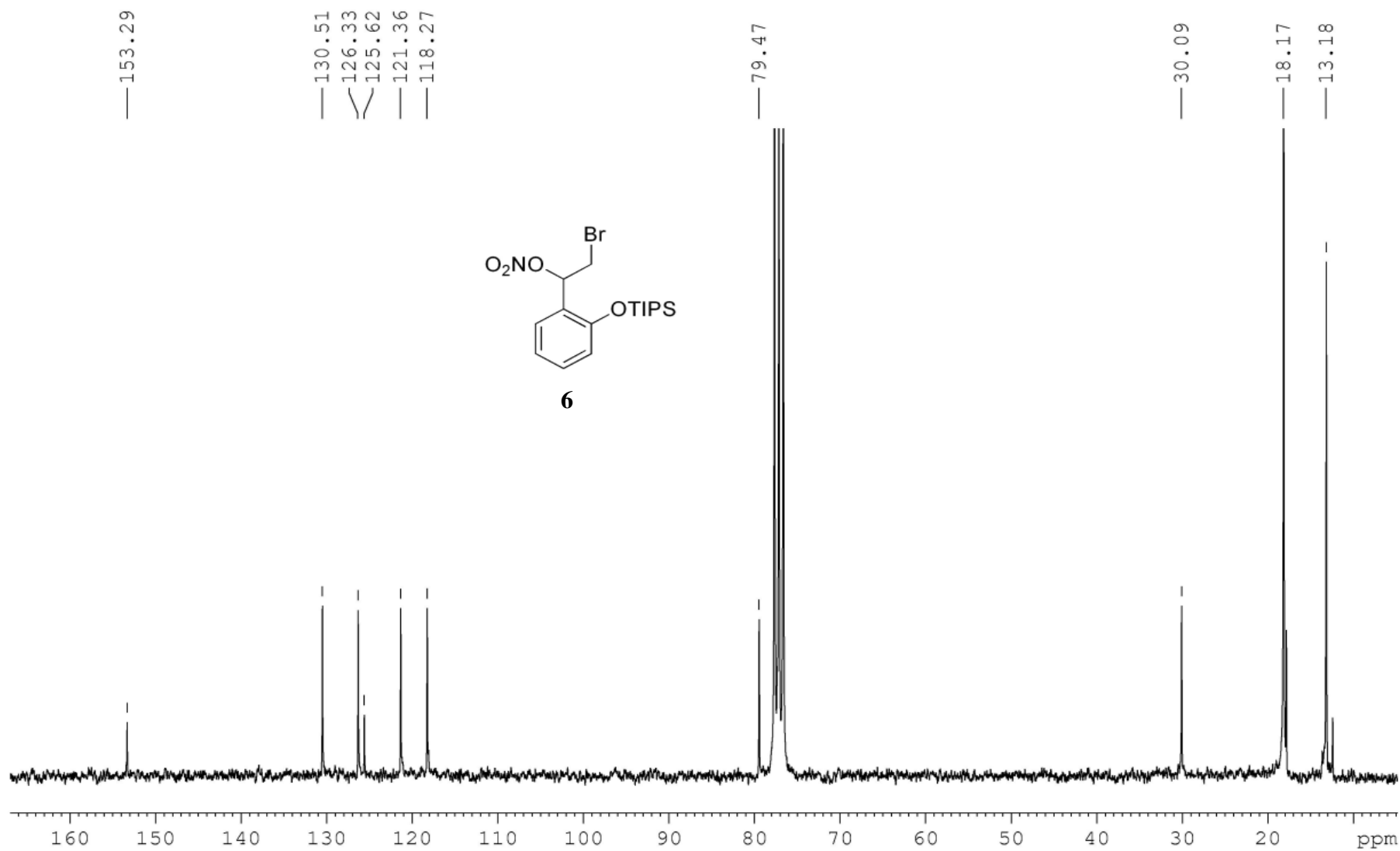
^1H NMR of compound **6** in CDCl_3 at 400 MHz

GVAS280@400 Hz



¹³C NMR of compound **6** in CDCl₃ at 63 MHz

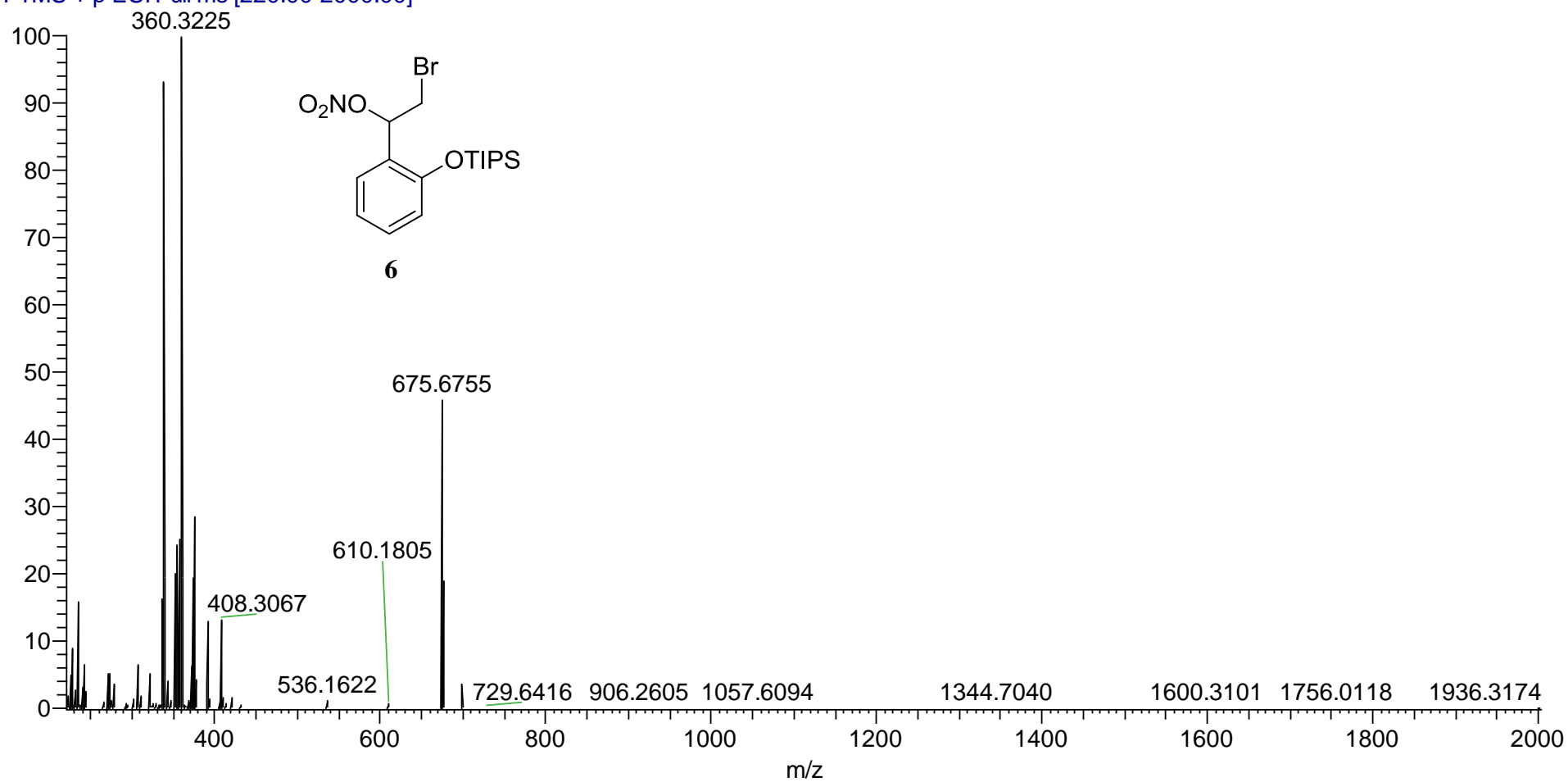
GVAS280@250 C-13



HRMS of compound **6**

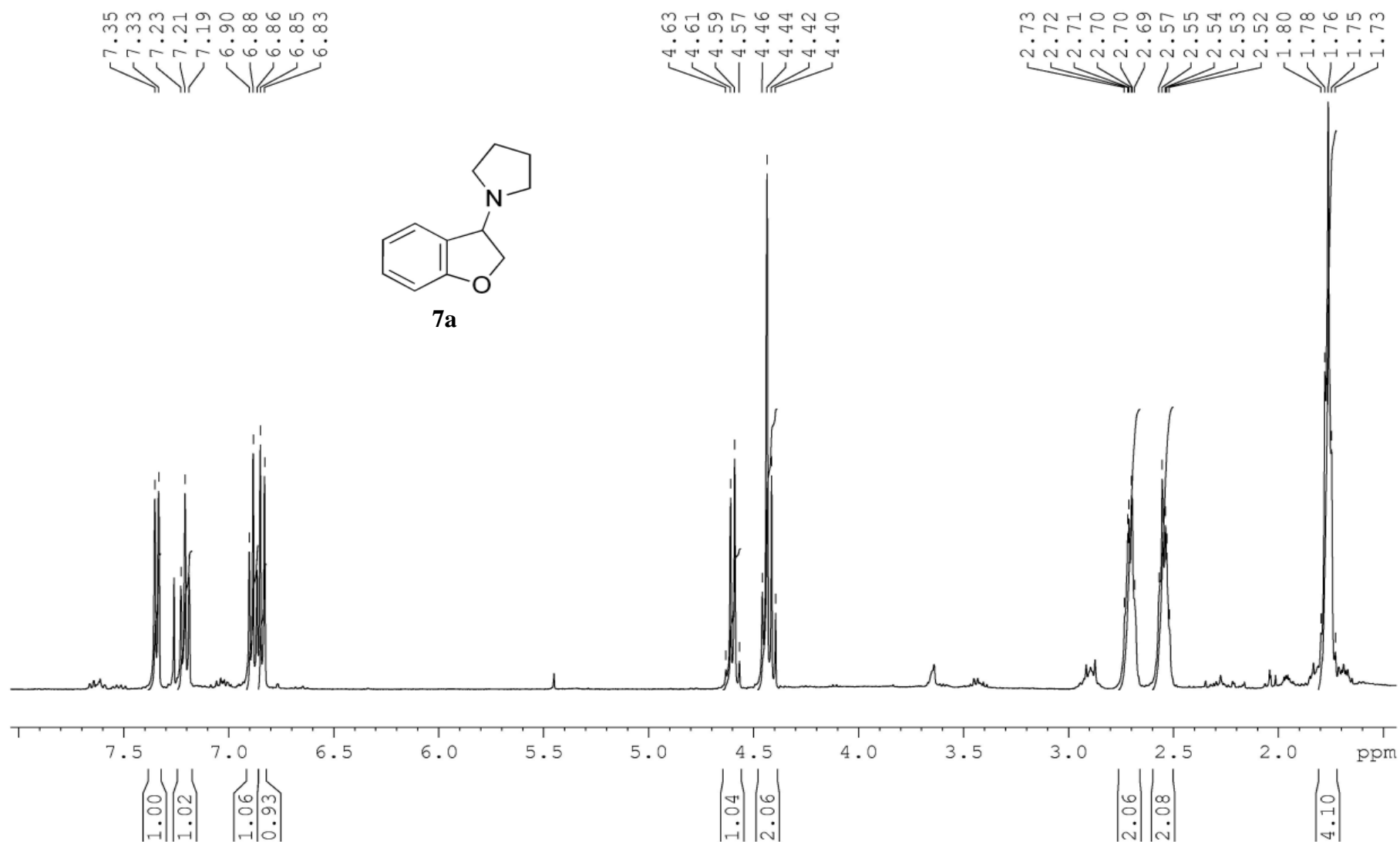
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T: FTMS + p ESI Full ms [220.00-2000.00]



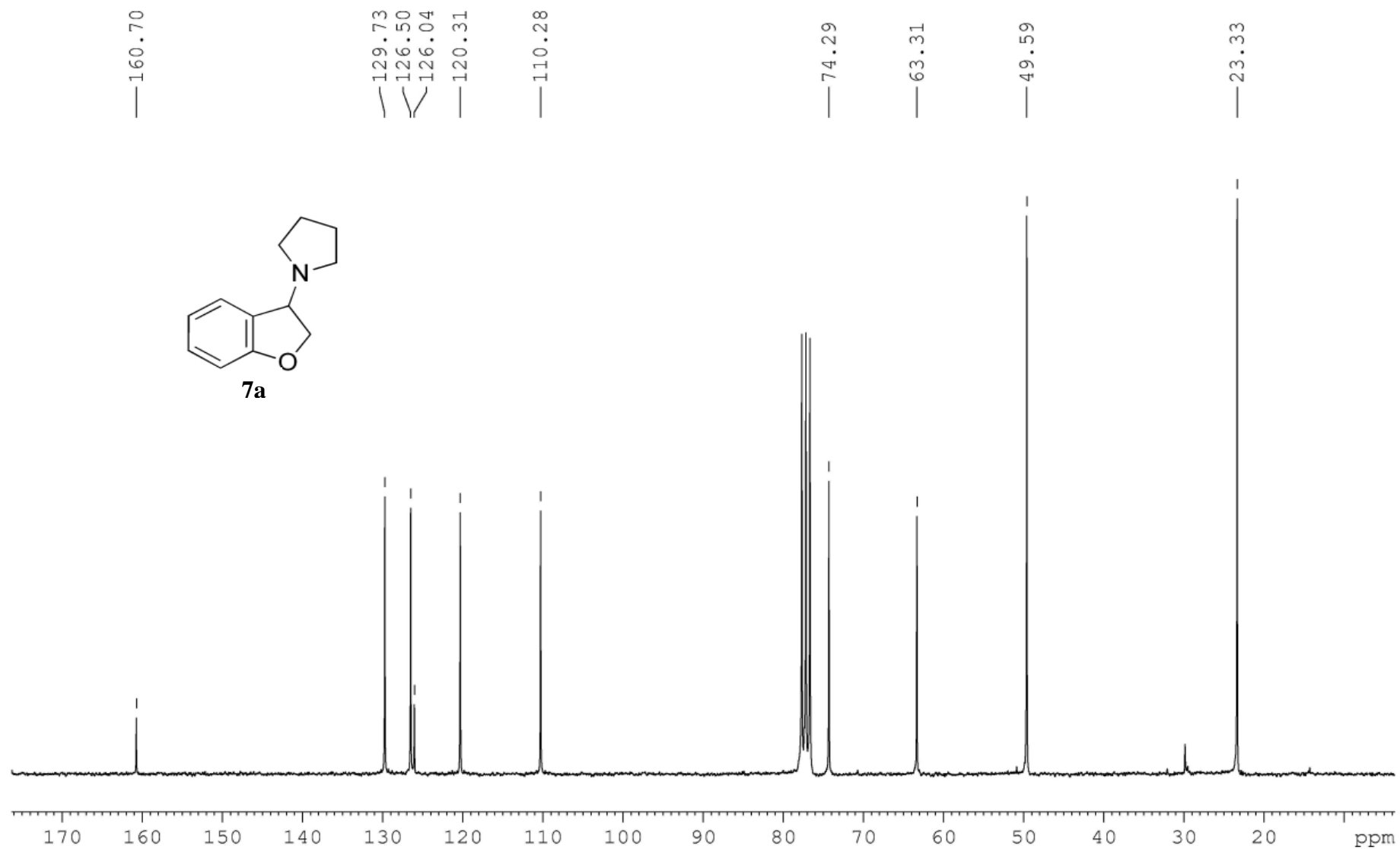
^1H NMR of compound **7a** in CDCl_3 at 400 MHz

GVAS281@400 Hz



¹³C NMR of compound **7a** in CDCl₃ at 63 MHz

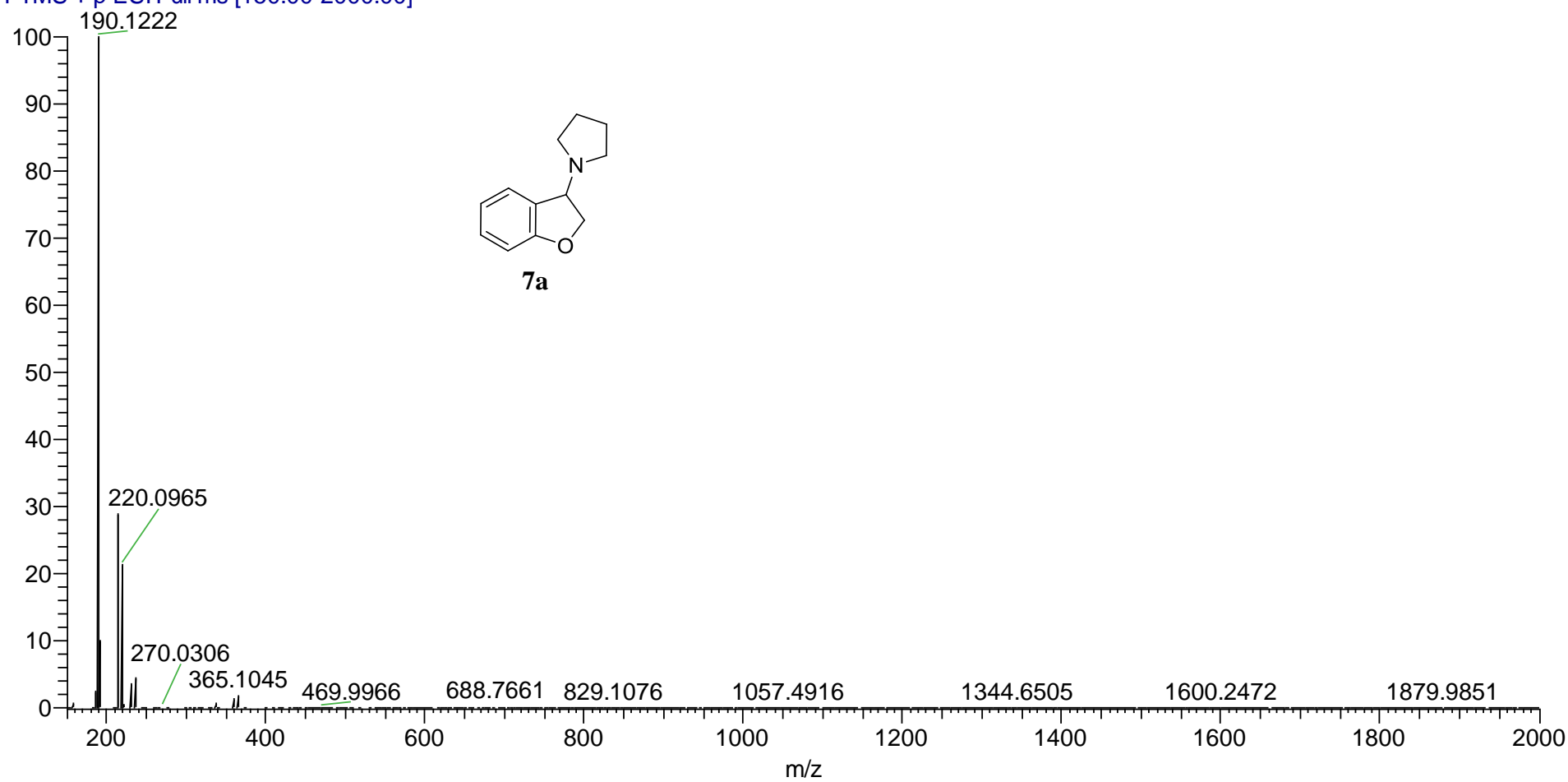
GVAS281@250 C-13



HRMS of compound **7a**

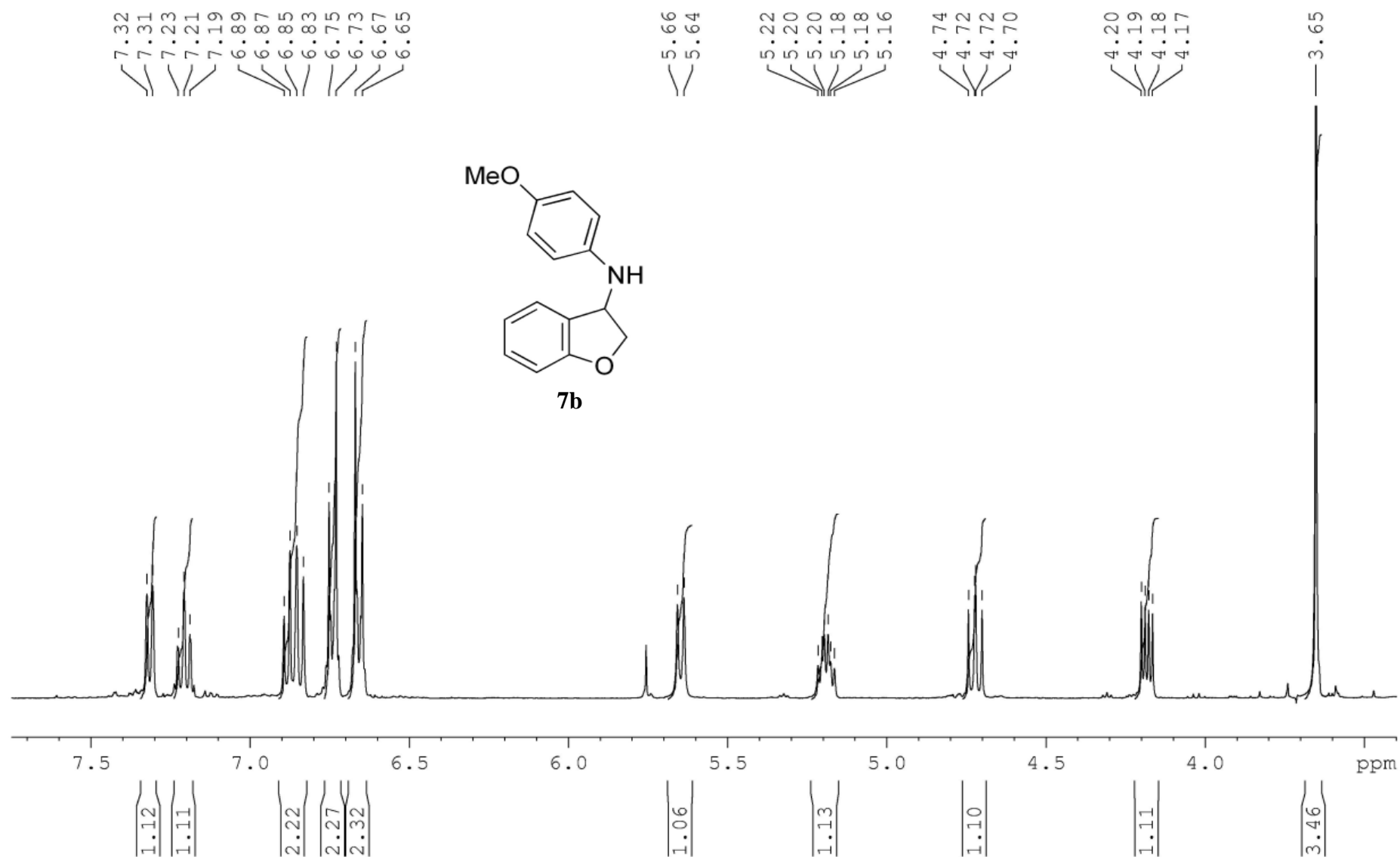
GVAS281_22_10_13_131022111402 #3 RT: 0.07 AV: 1 NL: 3.82E6

T: FTMS + p ESI Full ms [150.00-2000.00]



^1H NMR of compound **7b** in DMSO at 400 MHz

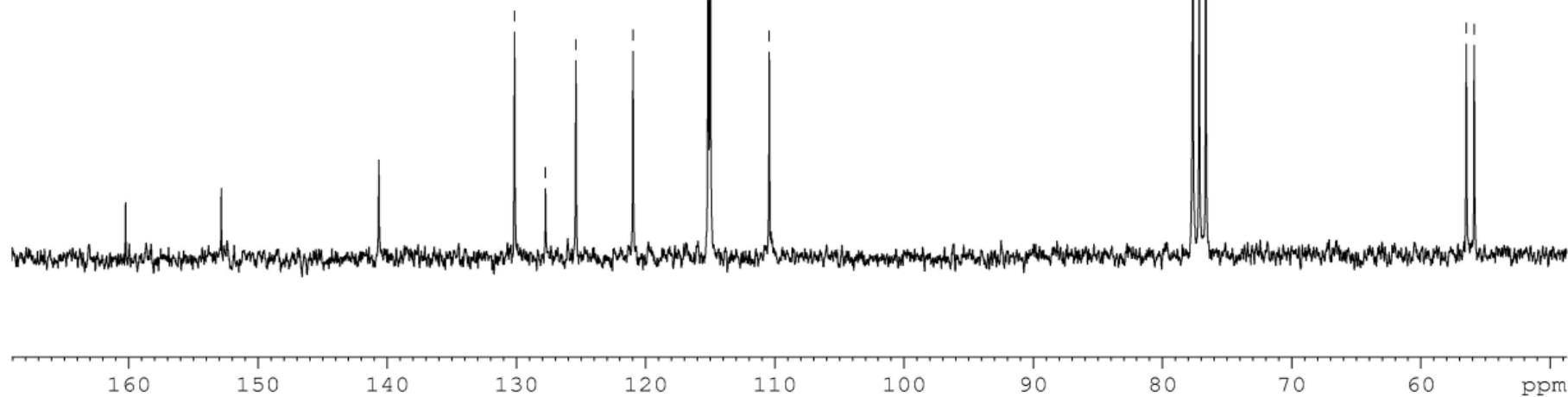
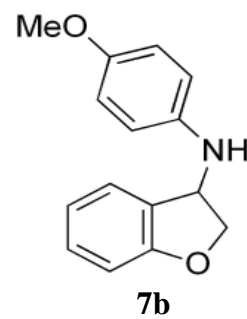
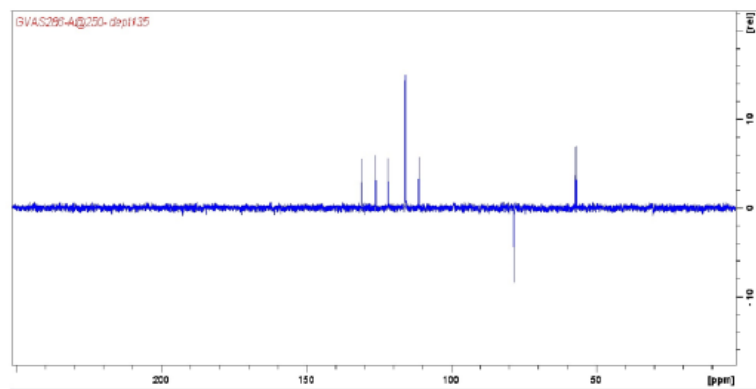
GVAS286-dmsO@400 Hz



^{13}C NMR of compound **7b** in CDCl_3 at 63 MHz

GVAS286-A@250 C-13

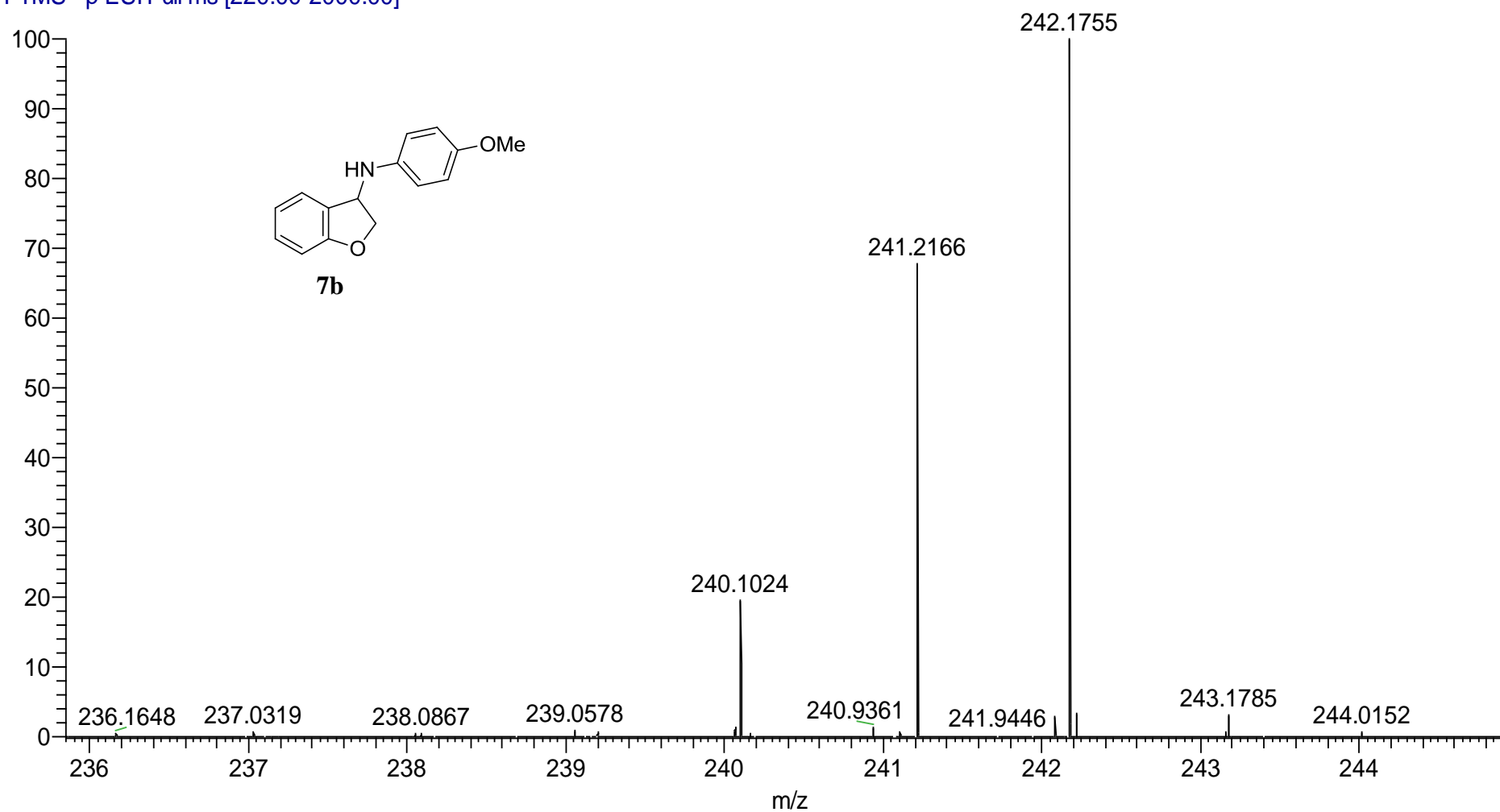
— 160.27 — 152.86 — 140.67 — 130.17 — 127.78 — 125.41 — 120.99 — 115.18 — 115.01 — 110.44 — 77.66 — 56.49 — 55.87



HRMS of compound **7b**

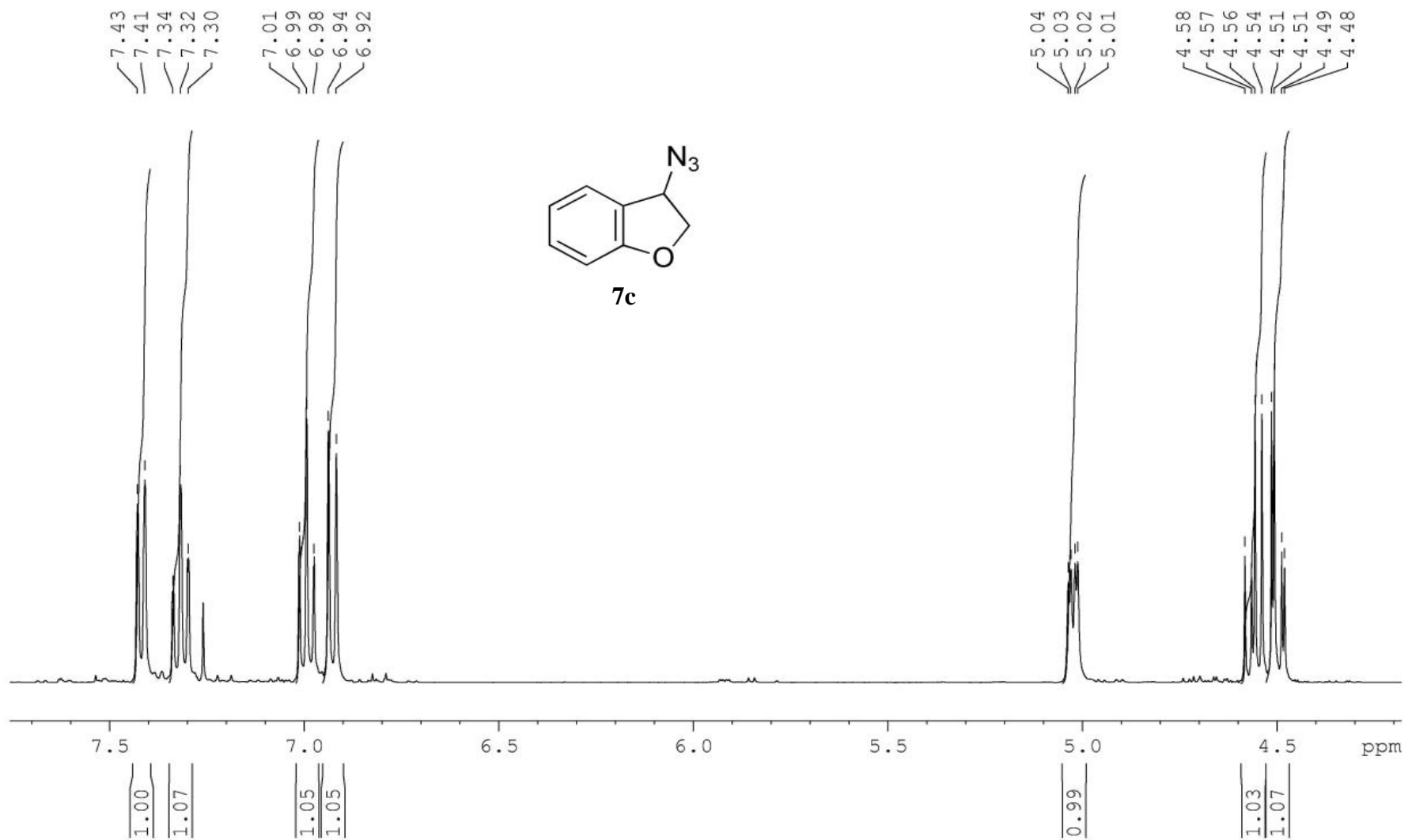
GVAS_anis_24_10_13_131024143622 #41 RT: 1.17 AV: 1 NL: 9.80E5

T: FTMS - p ESI Full ms [220.00-2000.00]



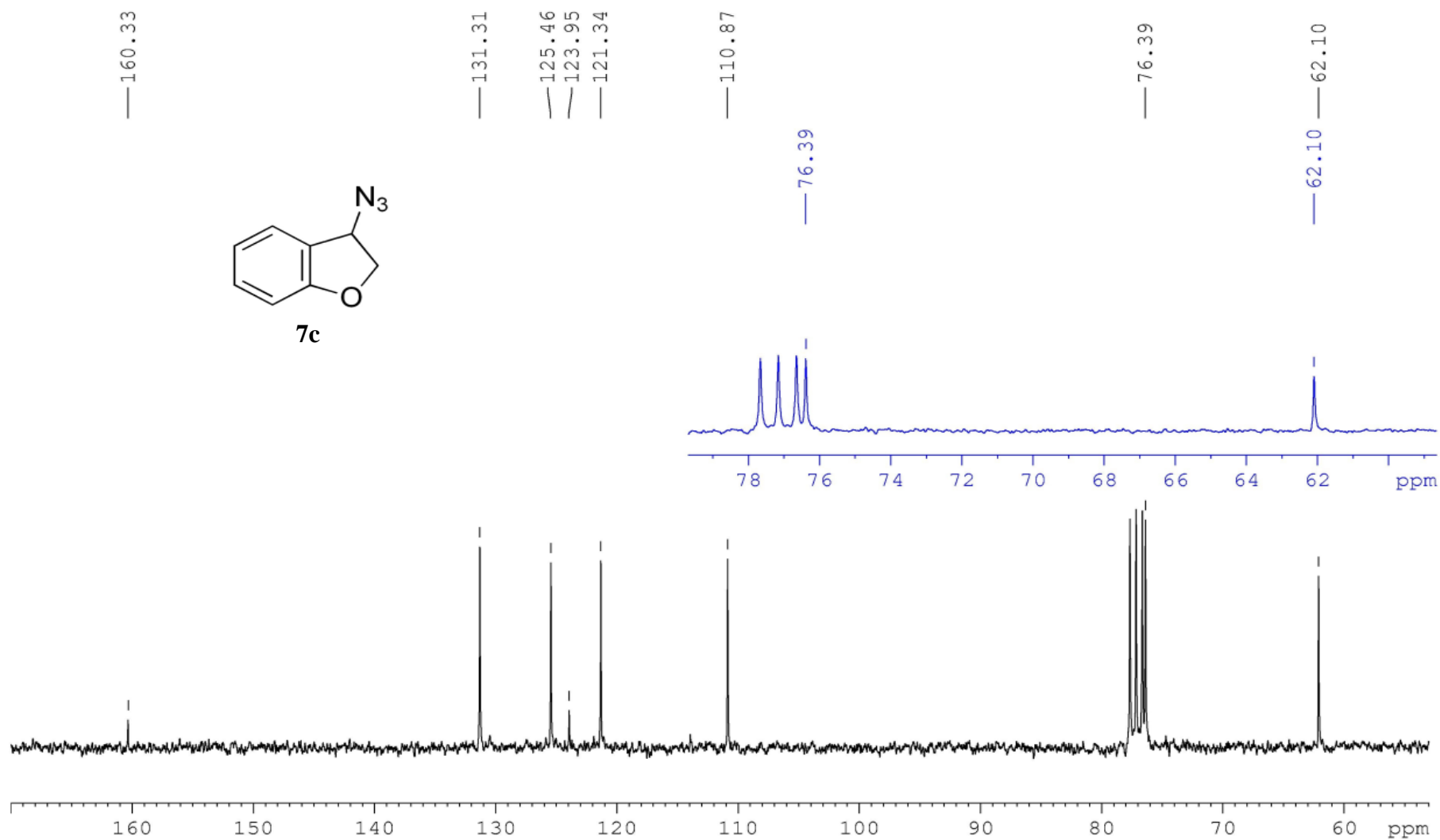
^1H NMR of compound **7c** in CDCl_3 at 400 MHz

GVAS285@400 Hz



^{13}C NMR of compound **7c** in CDCl_3 at 63 MHz

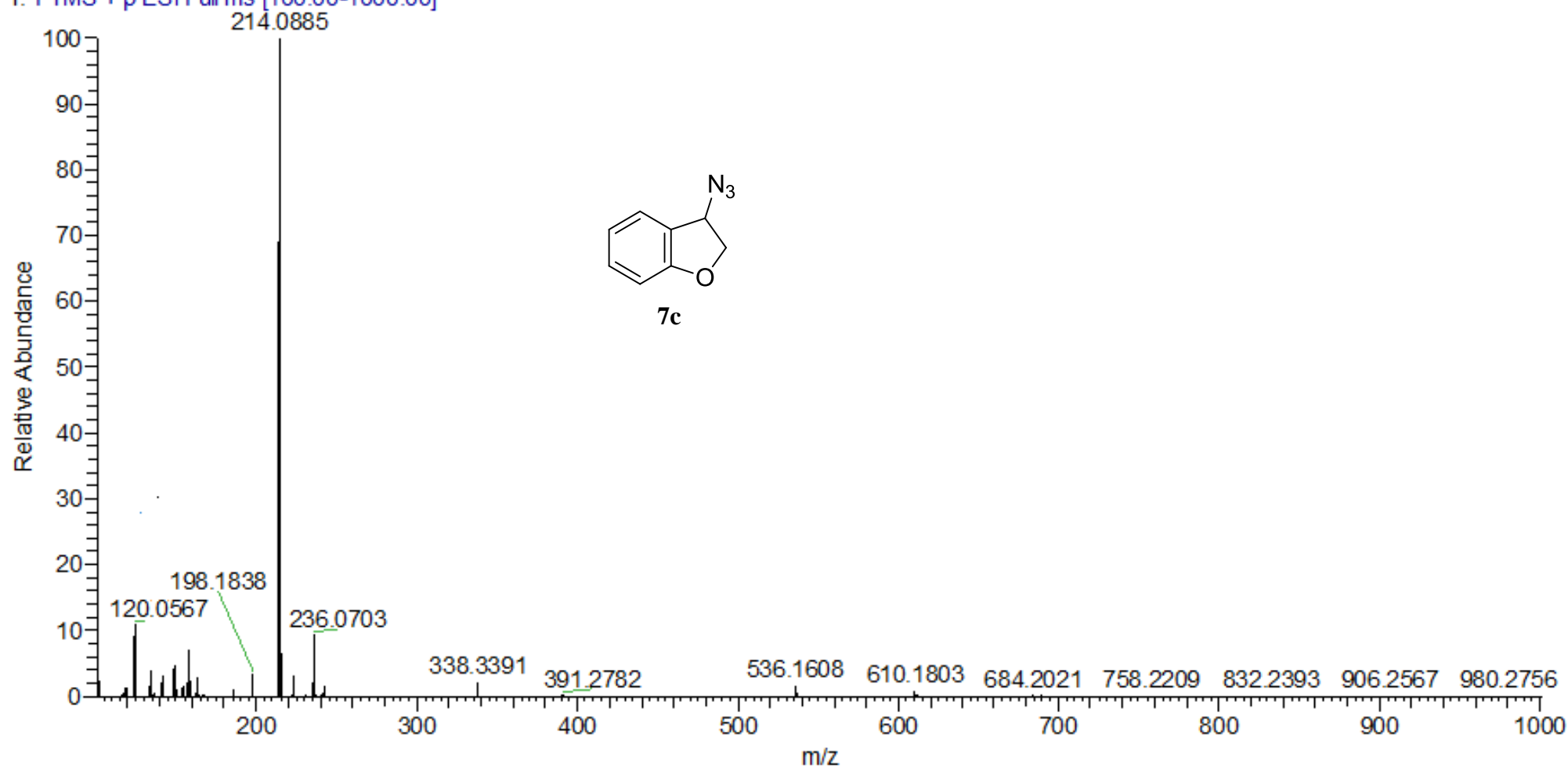
GVAS285-A@250 C-13



HRMS of compound 7c

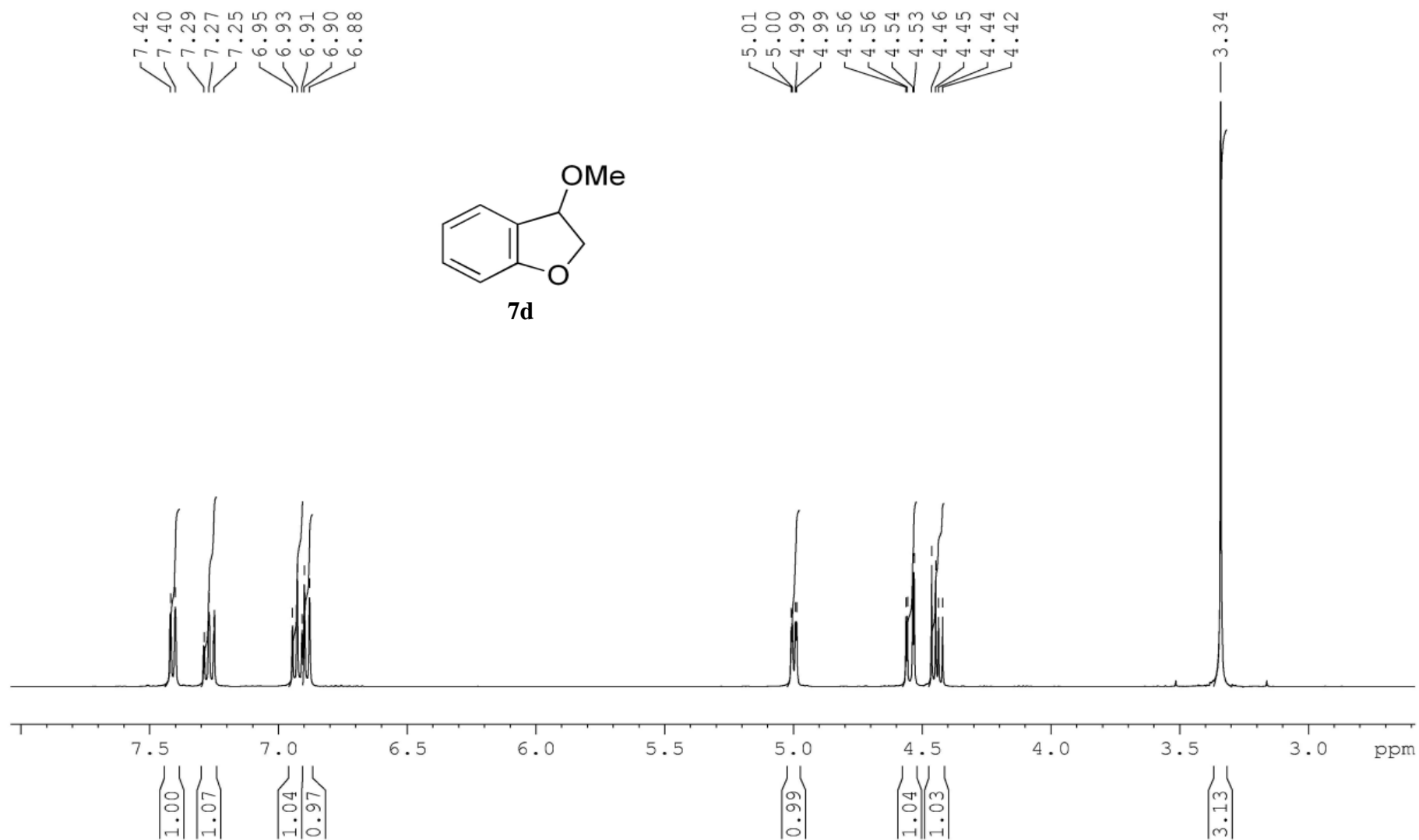
GVAS285 22 10 13 131022113551 #73-91 RT: 2.10-2.49 AV: 15 NL: 1.48E7

T: FTMS + p ESI Full ms [100.00-1000.00]



^1H NMR of compound **7d** in CDCl_3 at 400 MHz

GVAS283@400 Hz



^{13}C NMR of compound **7d** in CDCl_3 at 63 MHz

GVAS283@250 C-13

—160.88

—130.86

—126.24

—125.67

—120.63

—110.72

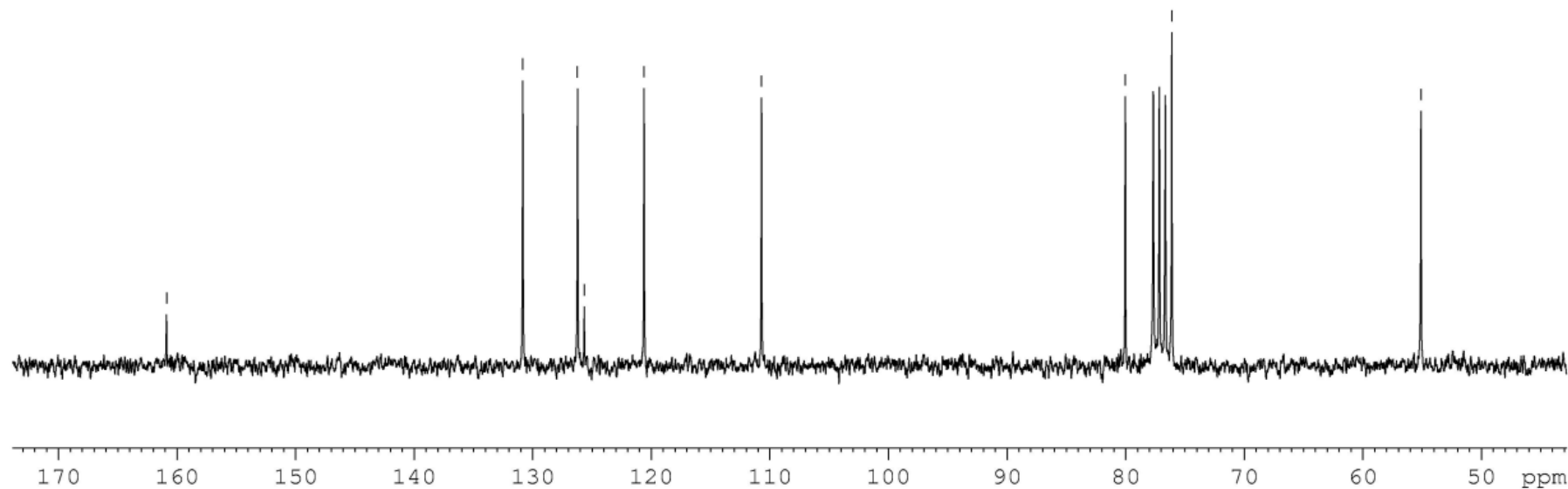
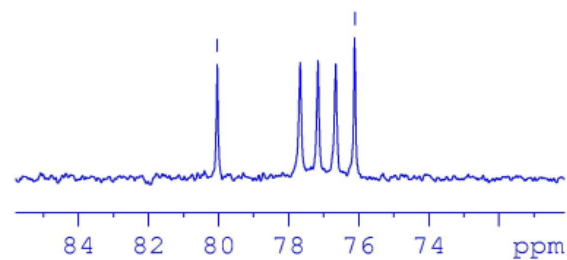
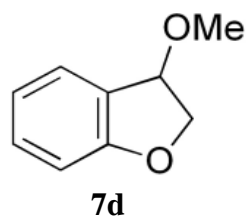
—80.03

—76.11

—80.03

—76.11

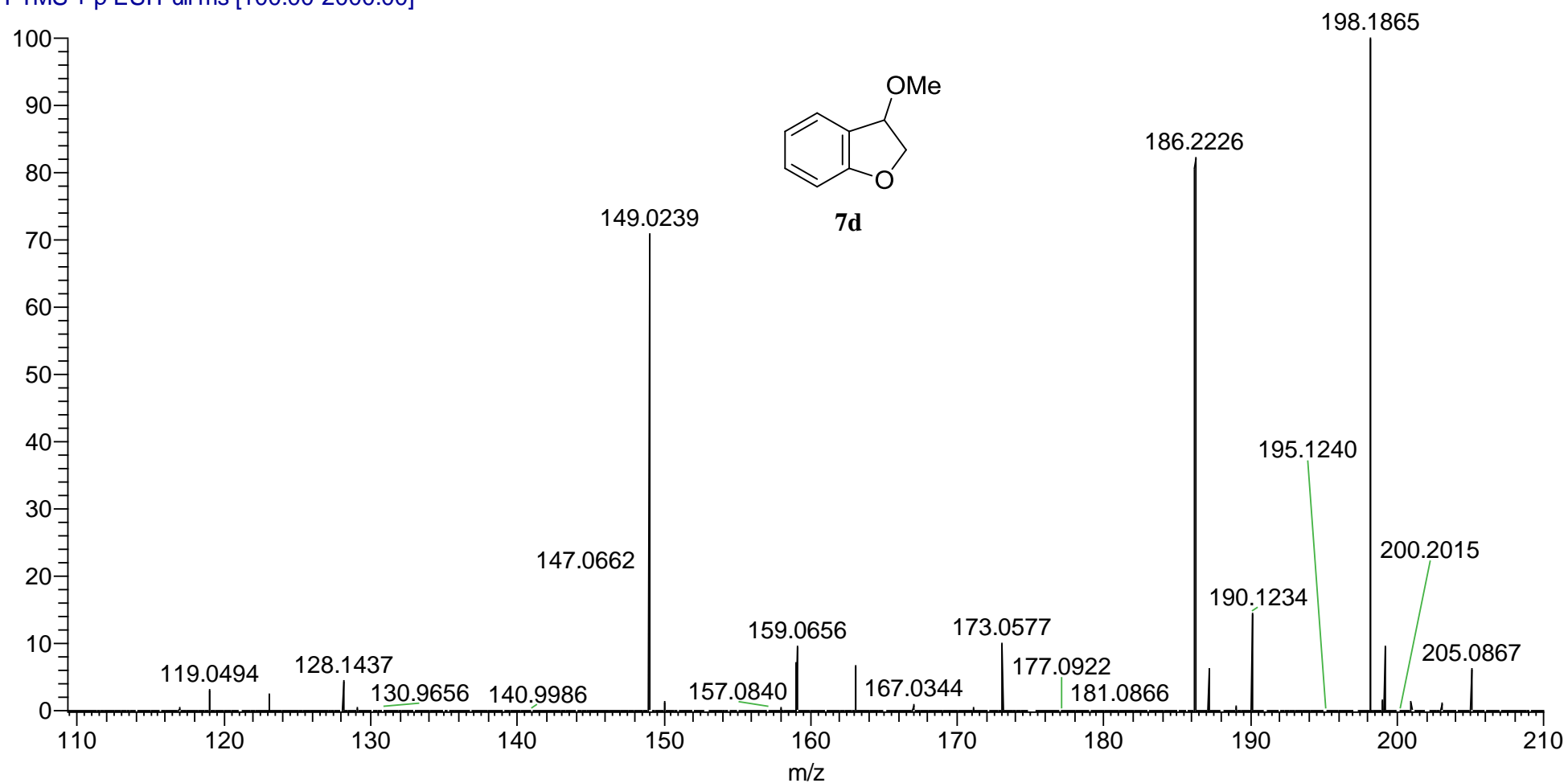
—55.09



HRMS of compound **7d**

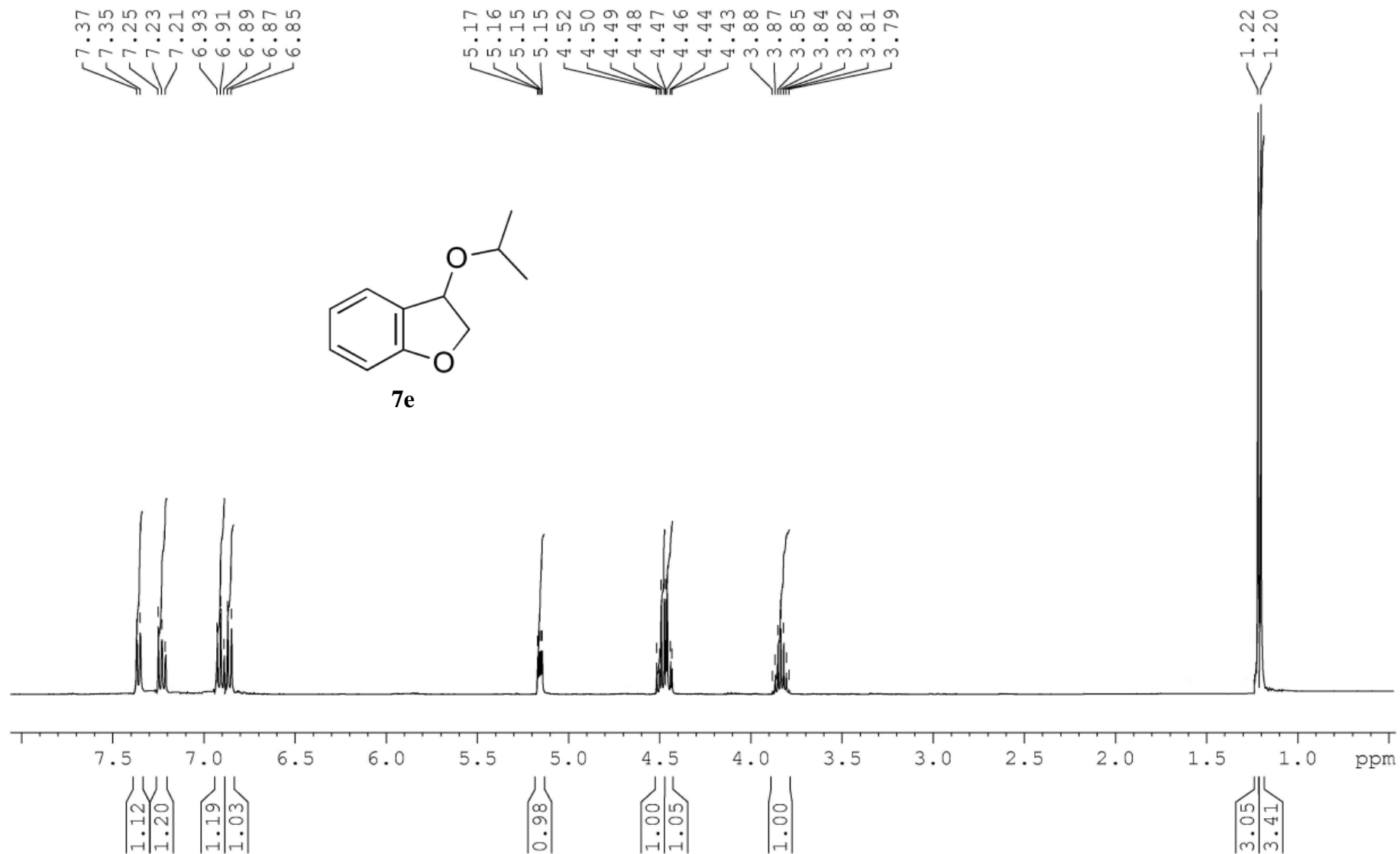
GVAS283_22_10_13_131022113551 #169 RT: 4.77 AV: 1 NL: 1.73E6

T: FTMS + p ESI Full ms [100.00-2000.00]



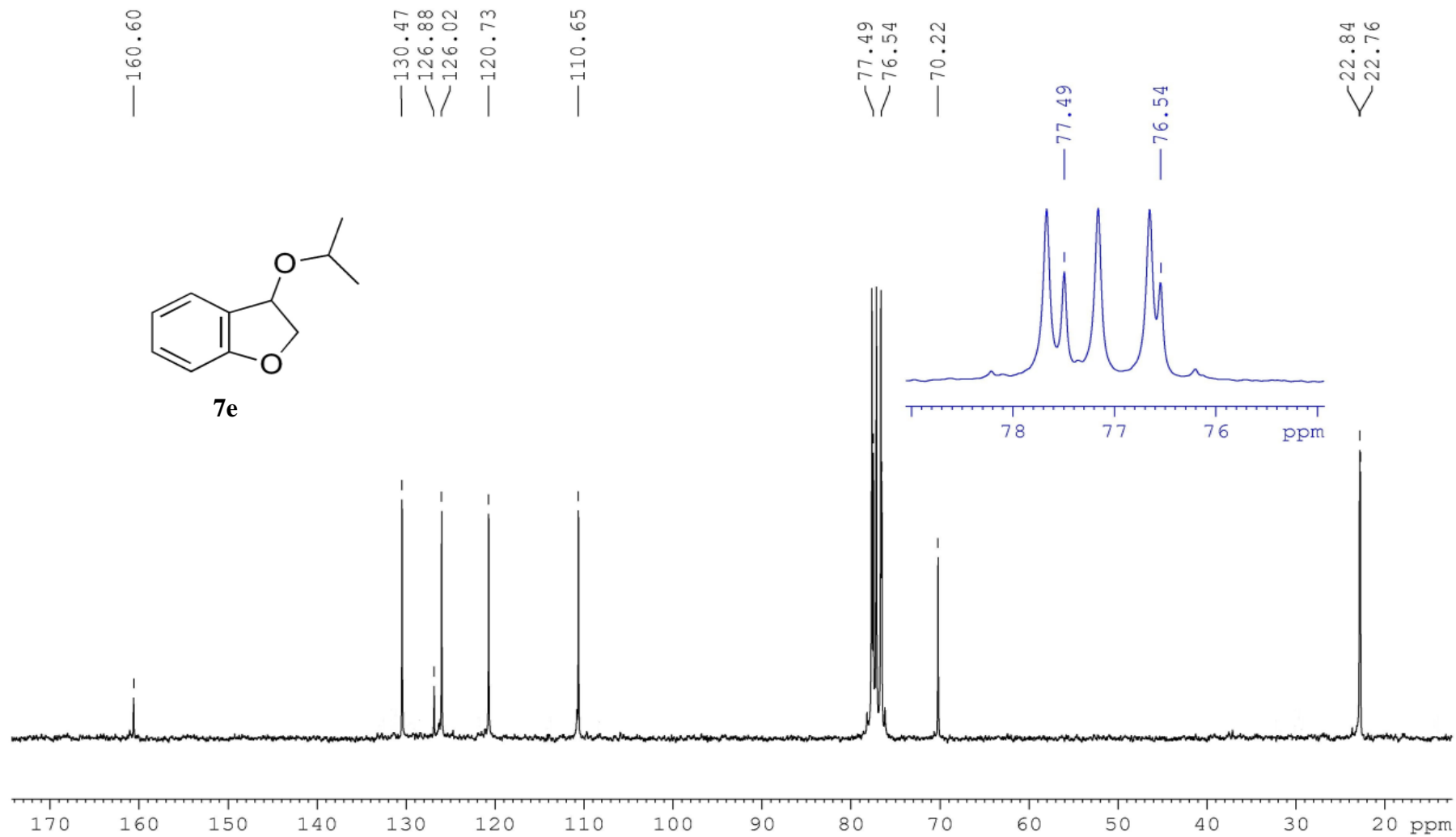
^1H NMR of compound **7e** in CDCl_3 at 400 MHz

GVAS284@400 Hz



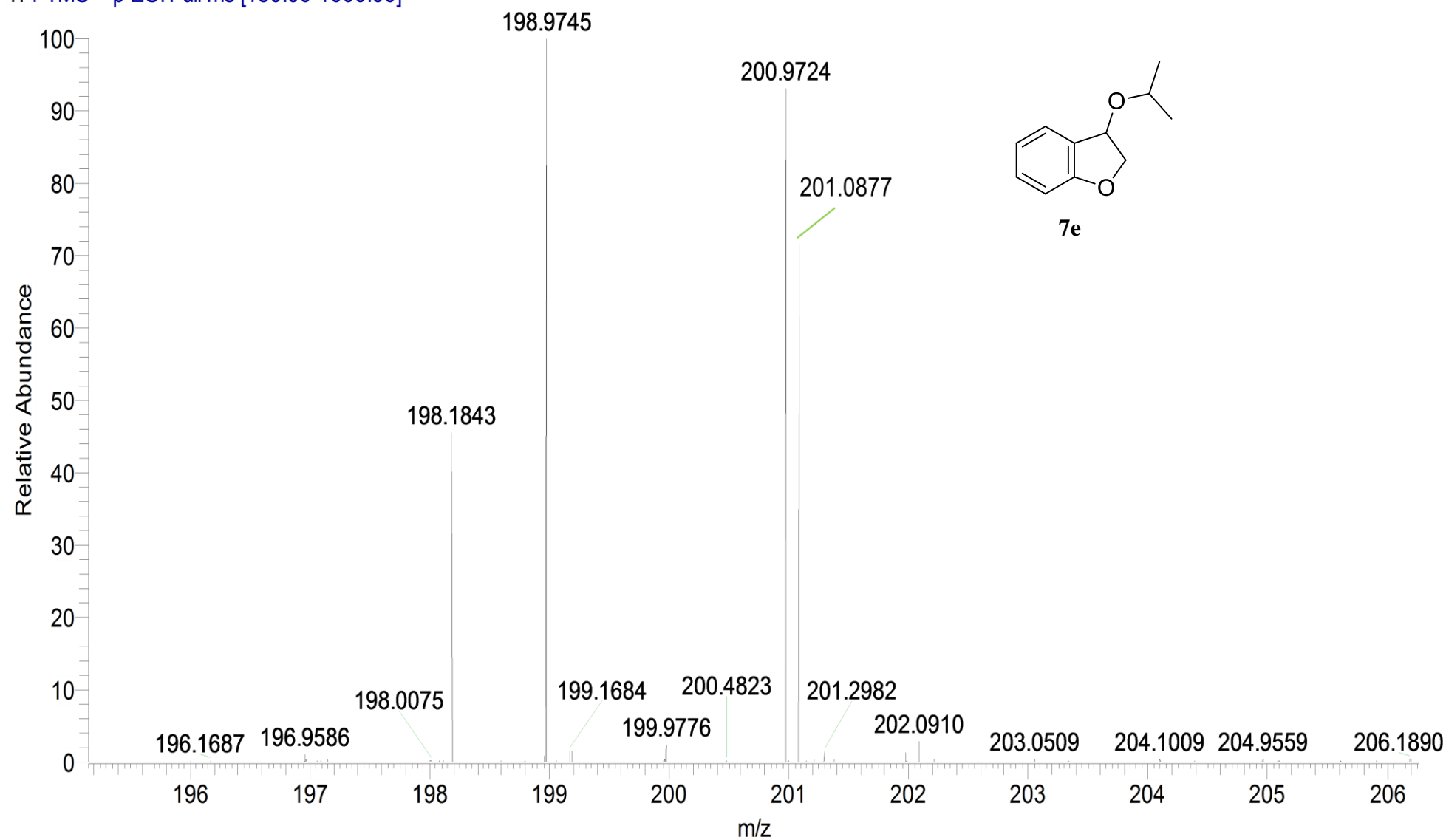
^{13}C NMR of compound **7e** in CDCl_3 at 63 MHz

GVAS284-A@250 C-13



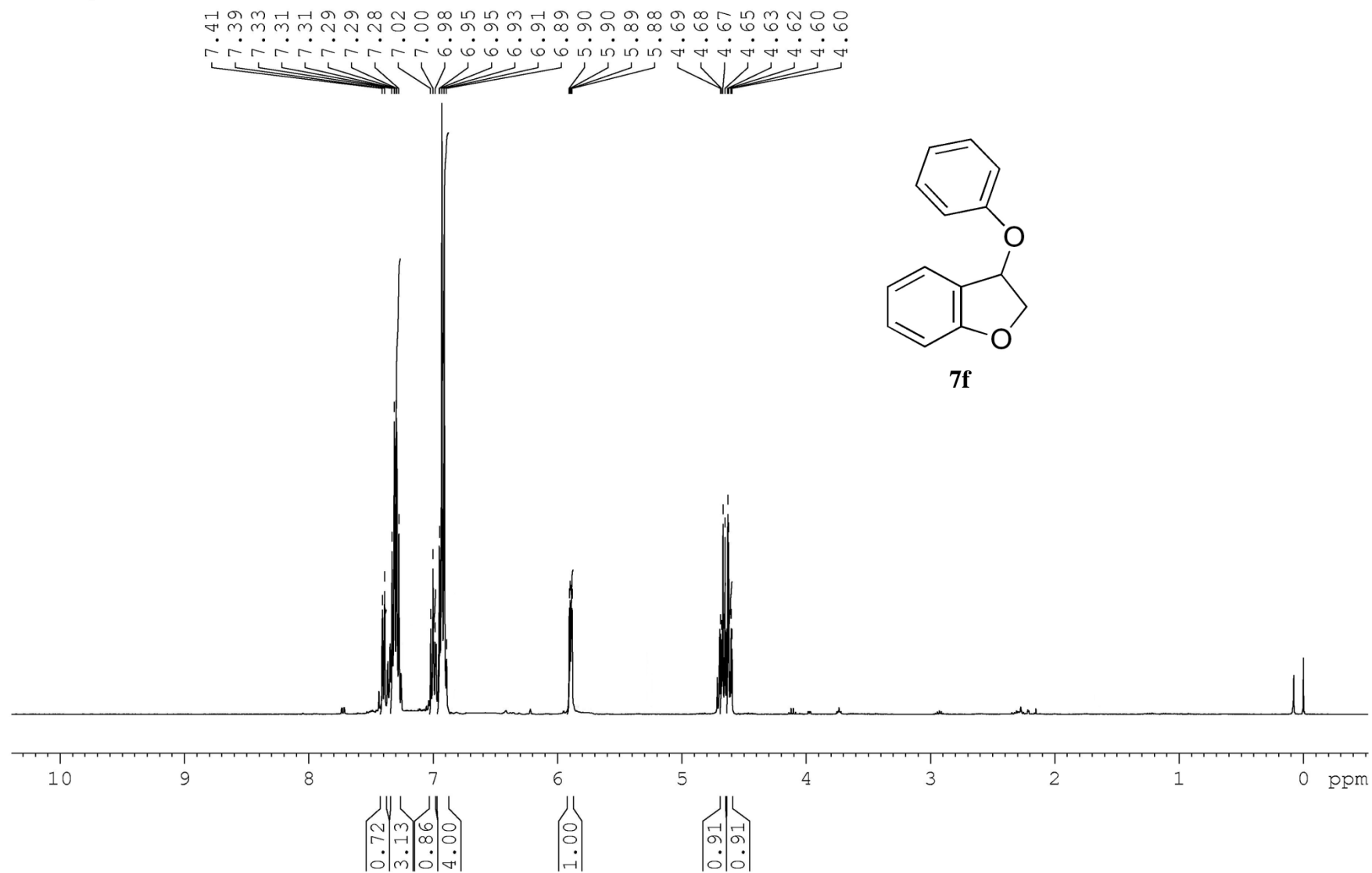
HRMS of compound **7e**

GVAS284_22_10_13_131022113551 #81 RT: 2.22 AV: 1 NL: 2.35E6
T: FTMS +p ESI Full ms [150.00-1000.00]



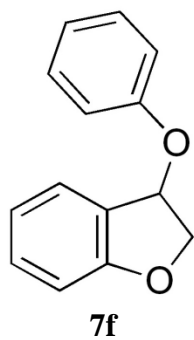
¹H NMR of compound **7f** in CDCl₃ at 400 MHz

GVAS287@400 Hz



^{13}C NMR of compound **7f** in CDCl_3 at 63 MHz

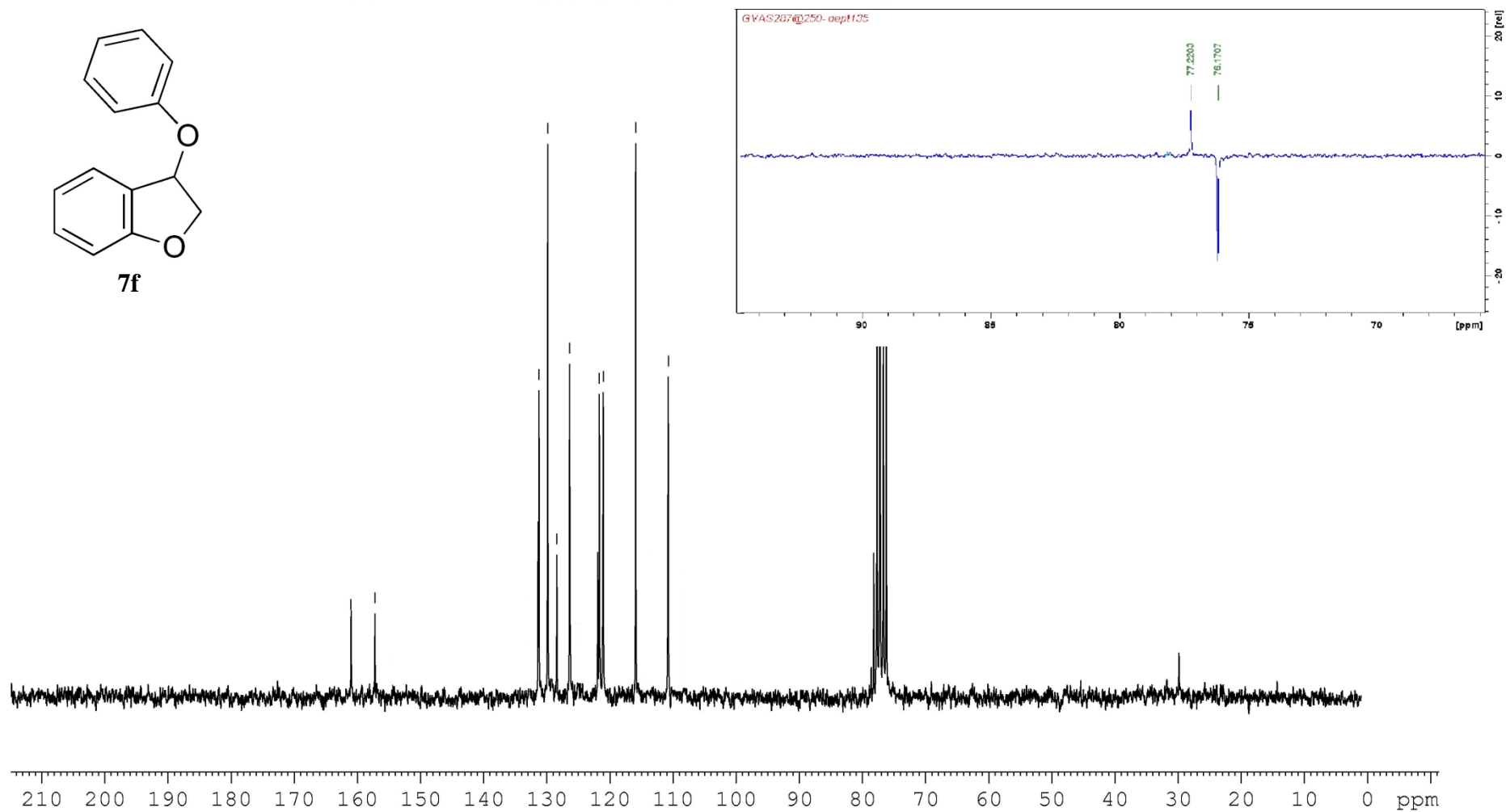
GVAS287@250 C-13



161.02
157.22

131.23
129.84
128.41
126.39
121.67
121.04
115.91
110.75

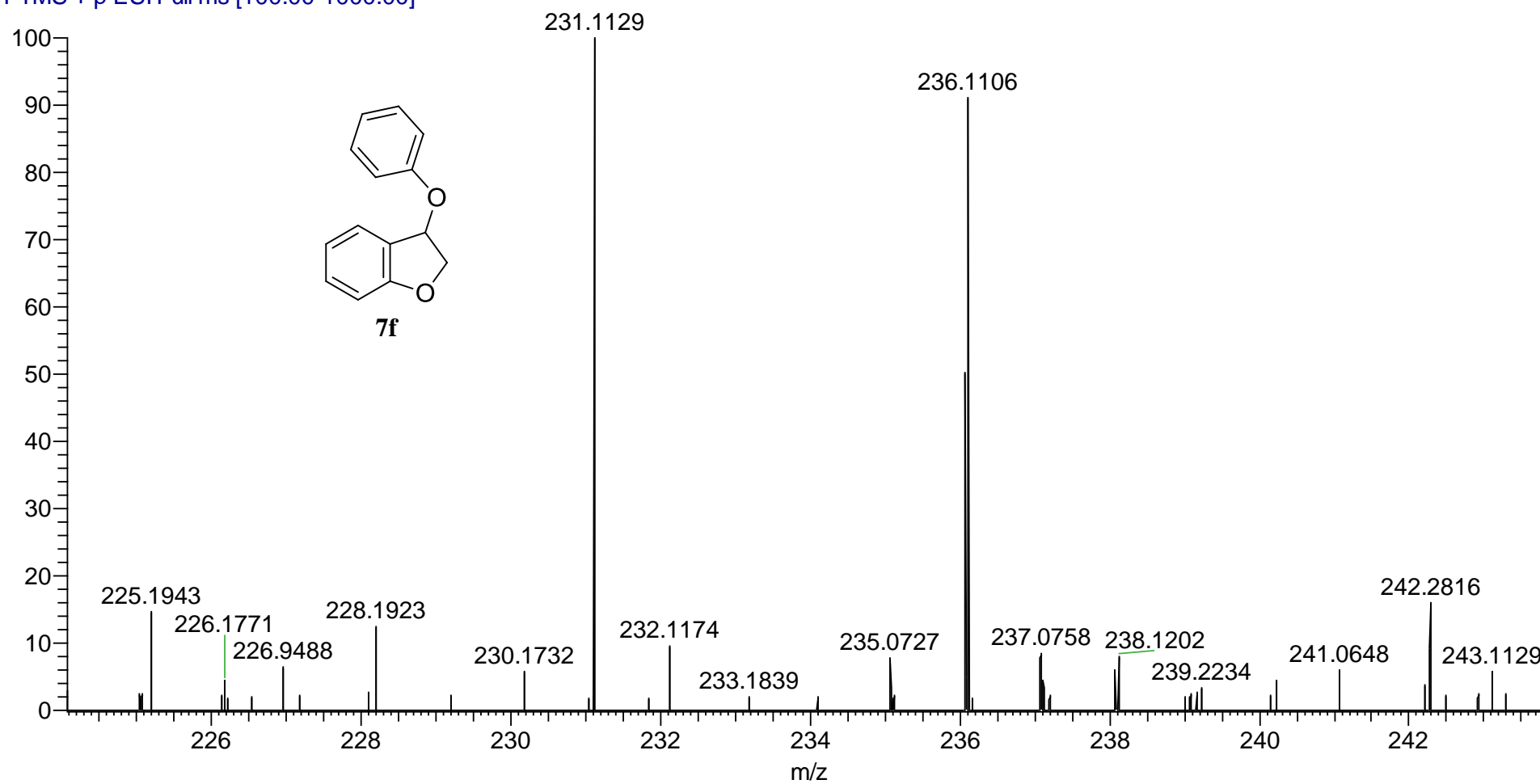
77.22
76.17



HRMS of compound **7f**

GVAS287_22_10_13_131022113551 #35 RT: 0.94 AV: 1 NL: 4.83E5

T: FTMS + p ESI Full ms [100.00-1000.00]



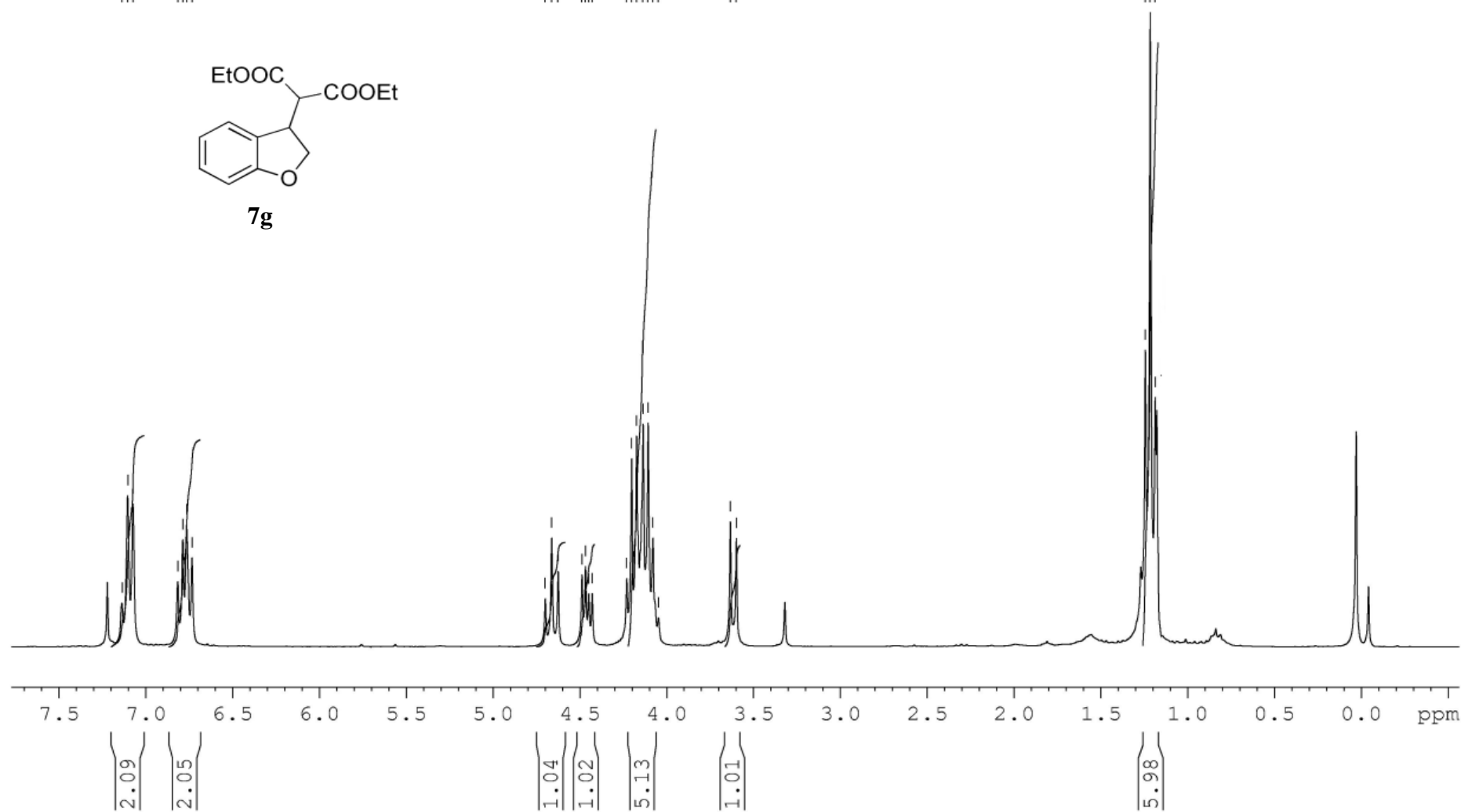
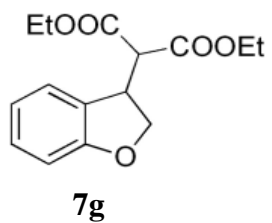
^1H NMR of compound **7g** in CDCl_3 at 250 MHz

GVAS291@250 H-1

7.14
7.10
7.07
6.82
6.79
6.76
6.73

4.70
4.66
4.63
4.49
4.47
4.45
4.43
4.23
4.20
4.17
4.14
4.11
4.08
4.05
3.63
3.60

1.24
1.22
1.19



^{13}C NMR of compound **7g** in CDCl_3 at 63 MHz

GVAS291@250 C-13

165.32
165.19

157.63

126.55

123.79

122.45

117.83

107.21

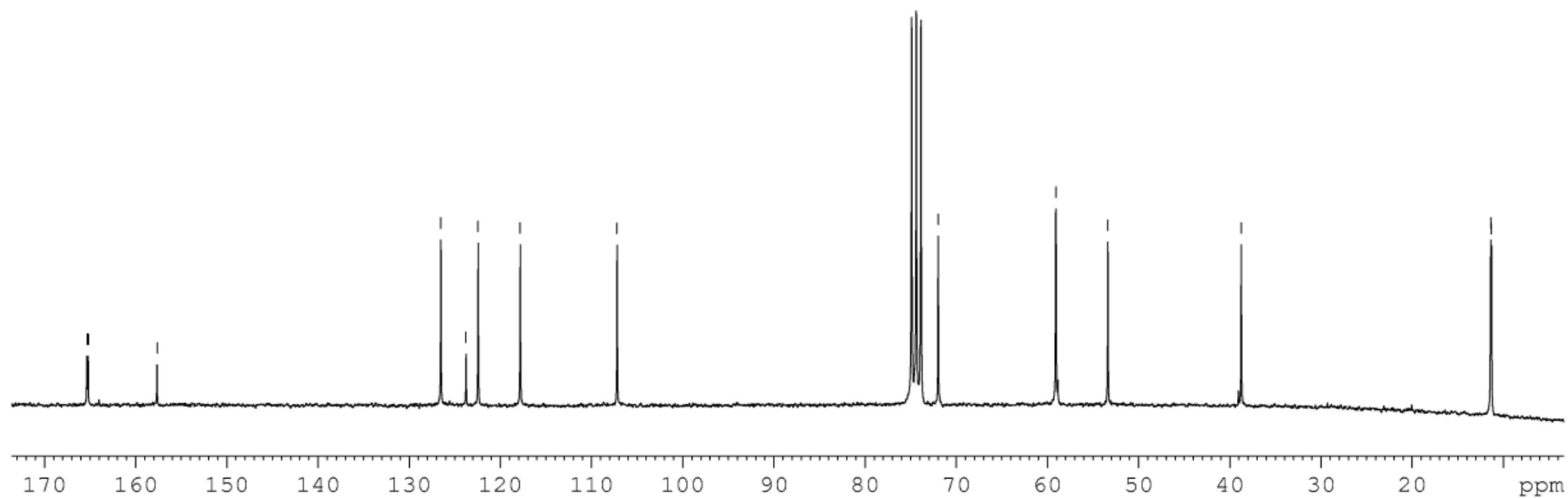
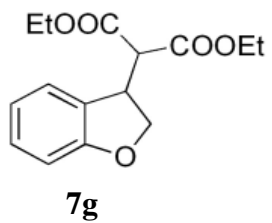
71.99

59.09

53.38

38.75

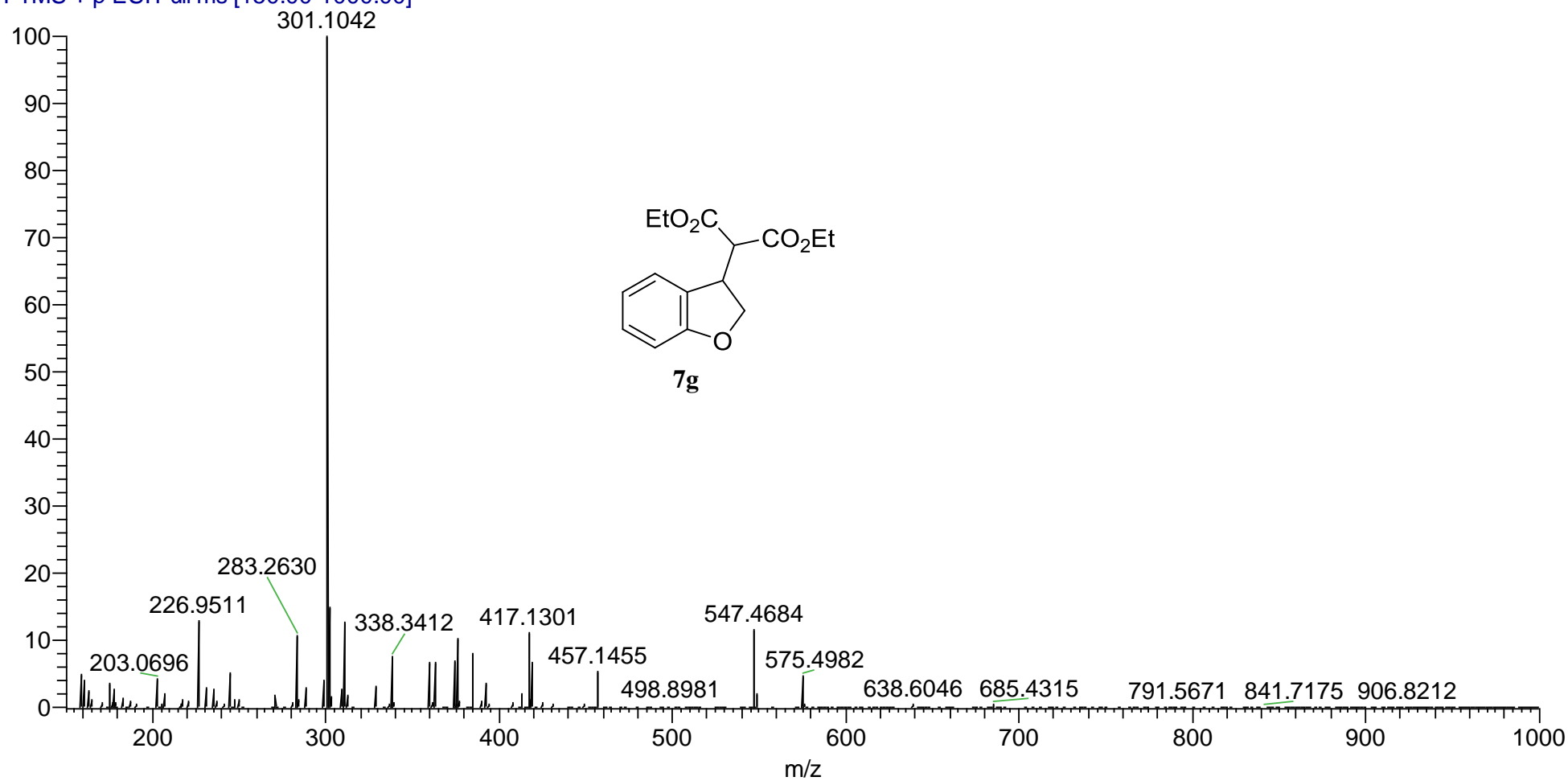
11.38
11.30



HRMS of compound **7g**

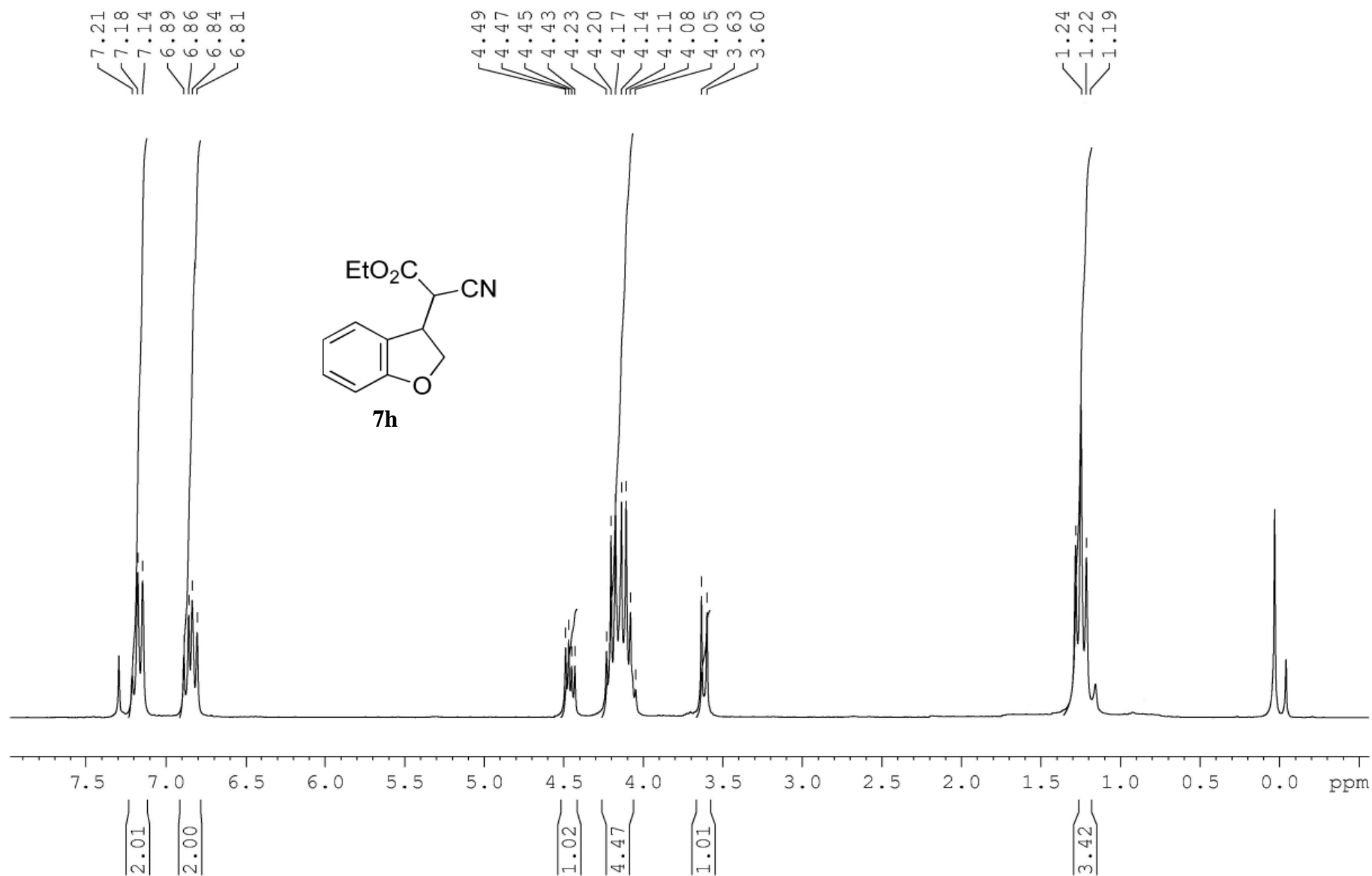
GVAS291_22_10_13_131022130033 #26 RT: 0.70 AV: 1 NL: 8.18E6

T: FTMS + p ESI Full ms [150.00-1000.00]



¹H NMR of compound **7h** in CDCl₃ at 250 MHz

GVAS301@250 H-1



^{13}C NMR of compound **7h** in CDCl_3 at 63 MHz

GVAS301@250 C-13

—165.19

—157.63

—126.55

—123.79

—122.45

—117.83

—115.06

—107.21

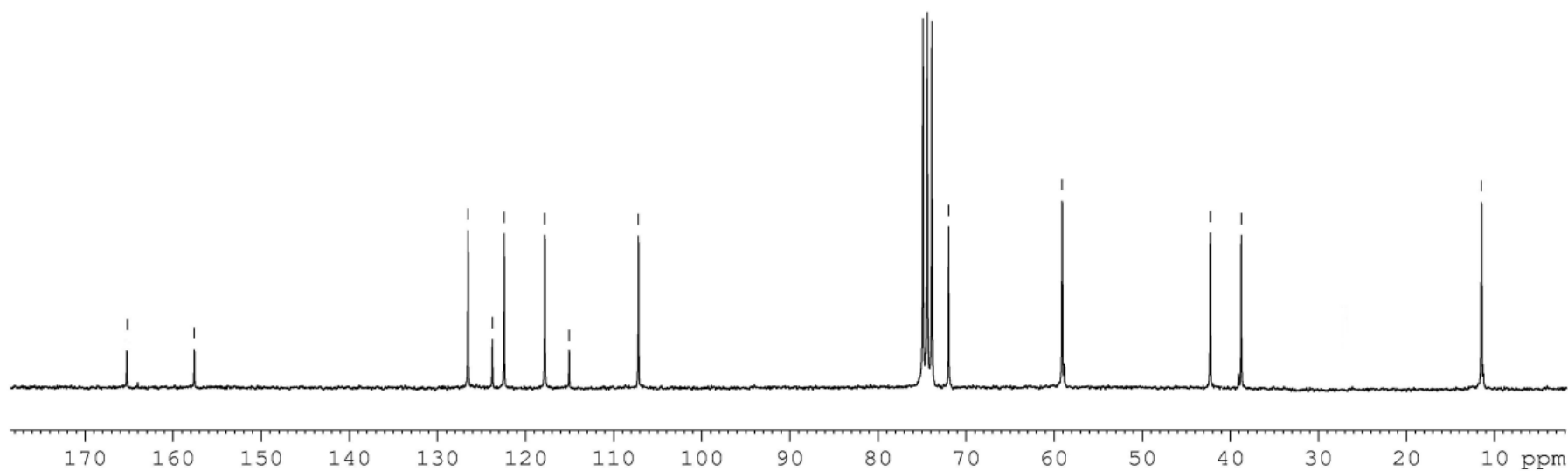
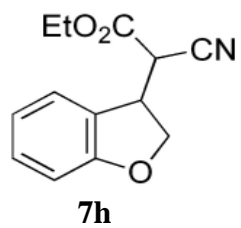
—71.99

—59.09

—42.10

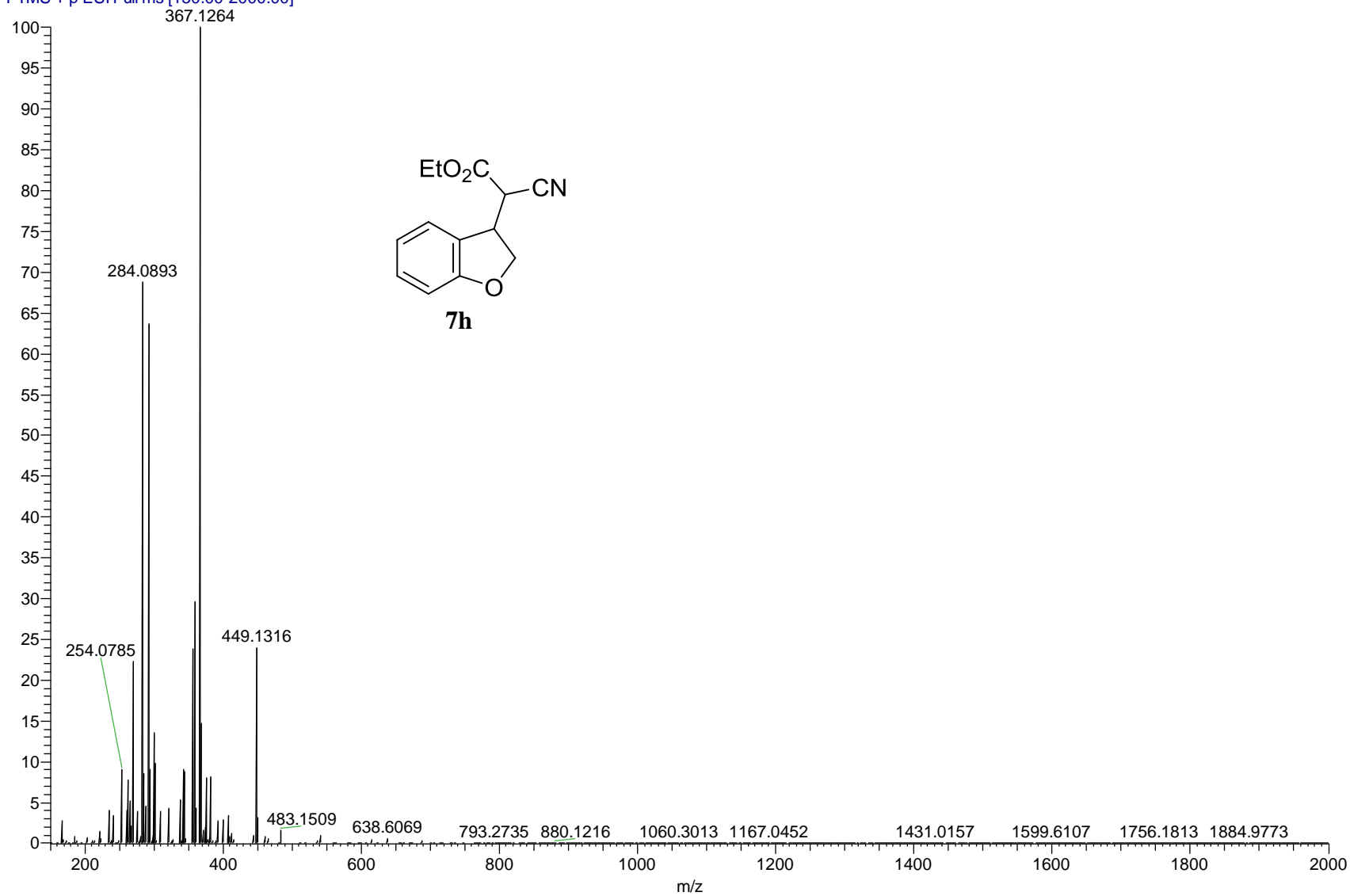
—38.75

—11.38



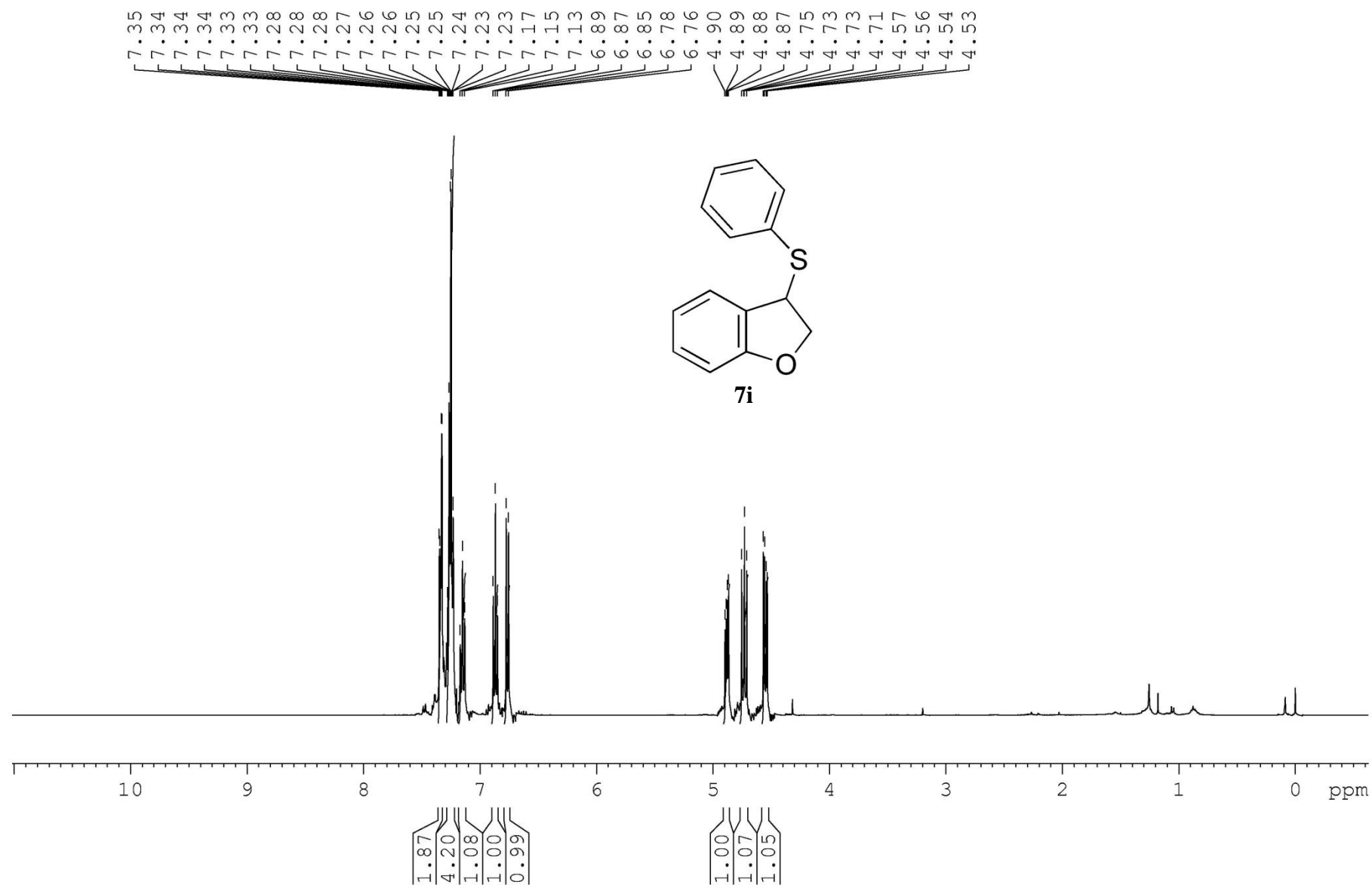
HRMS of compound **7h**

GVAS301_26_11_13_131125162028 #13 RT: 0.35 AV: 1 NL: 2.08E7
T: FTMS + p ESI Full ms [150.00-2000.00]



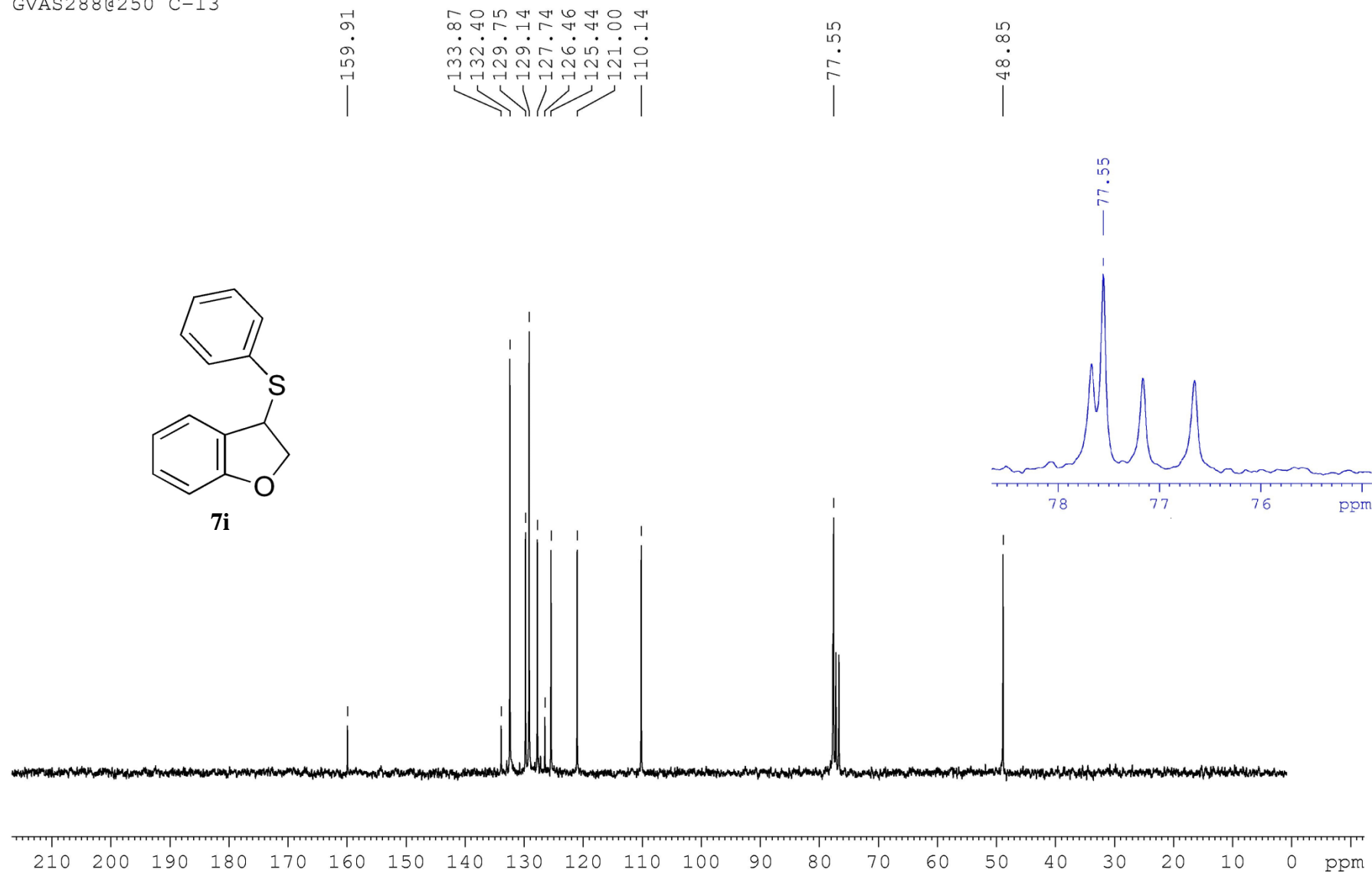
^1H NMR of compound **7i** in CDCl_3 at 400 MHz

GVAS288-B@400 Hz



^{13}C NMR of compound **7i** in CDCl_3 at 63 MHz

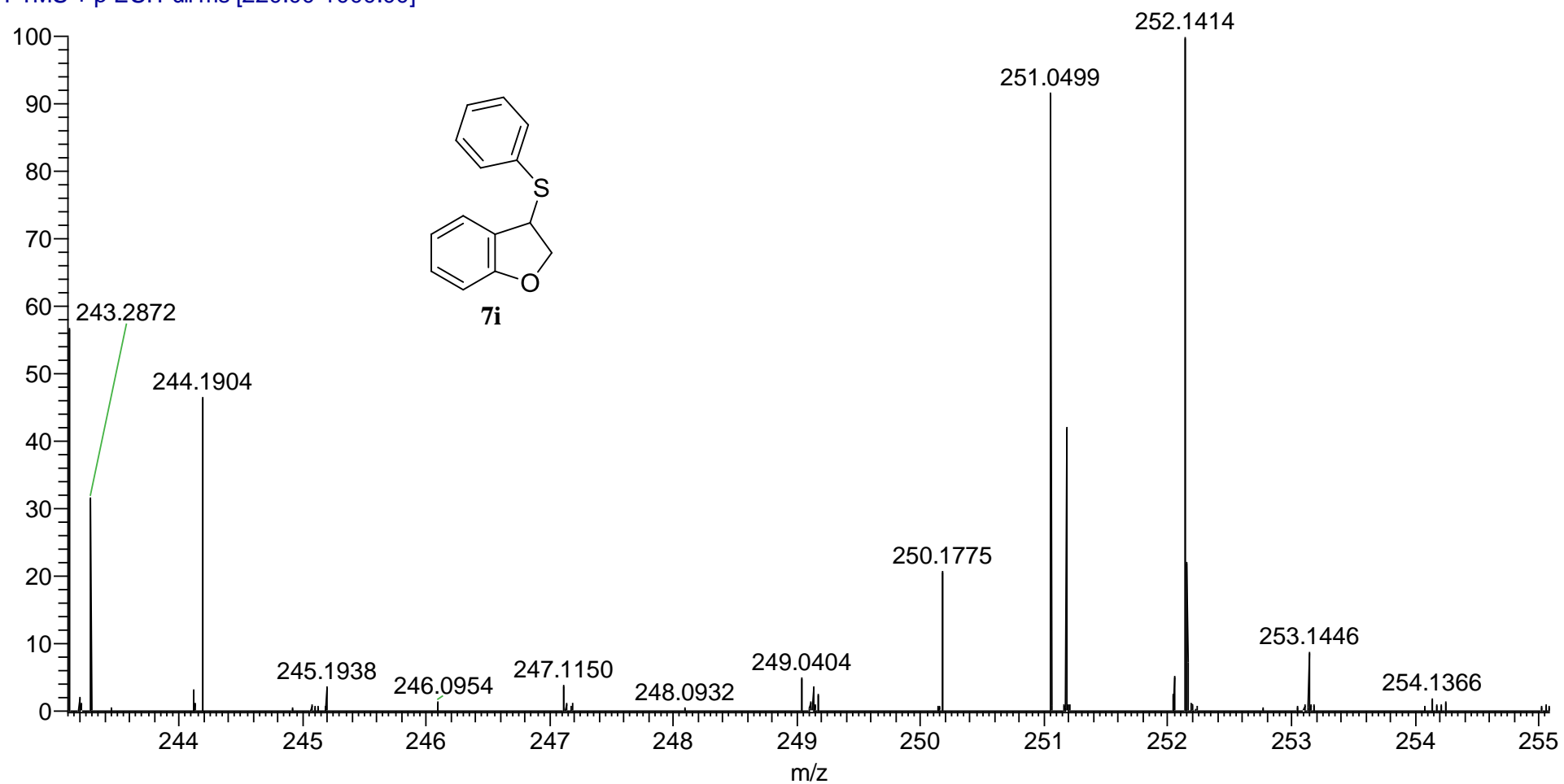
GVAS288@250 C-13



HRMS of compound **7i**

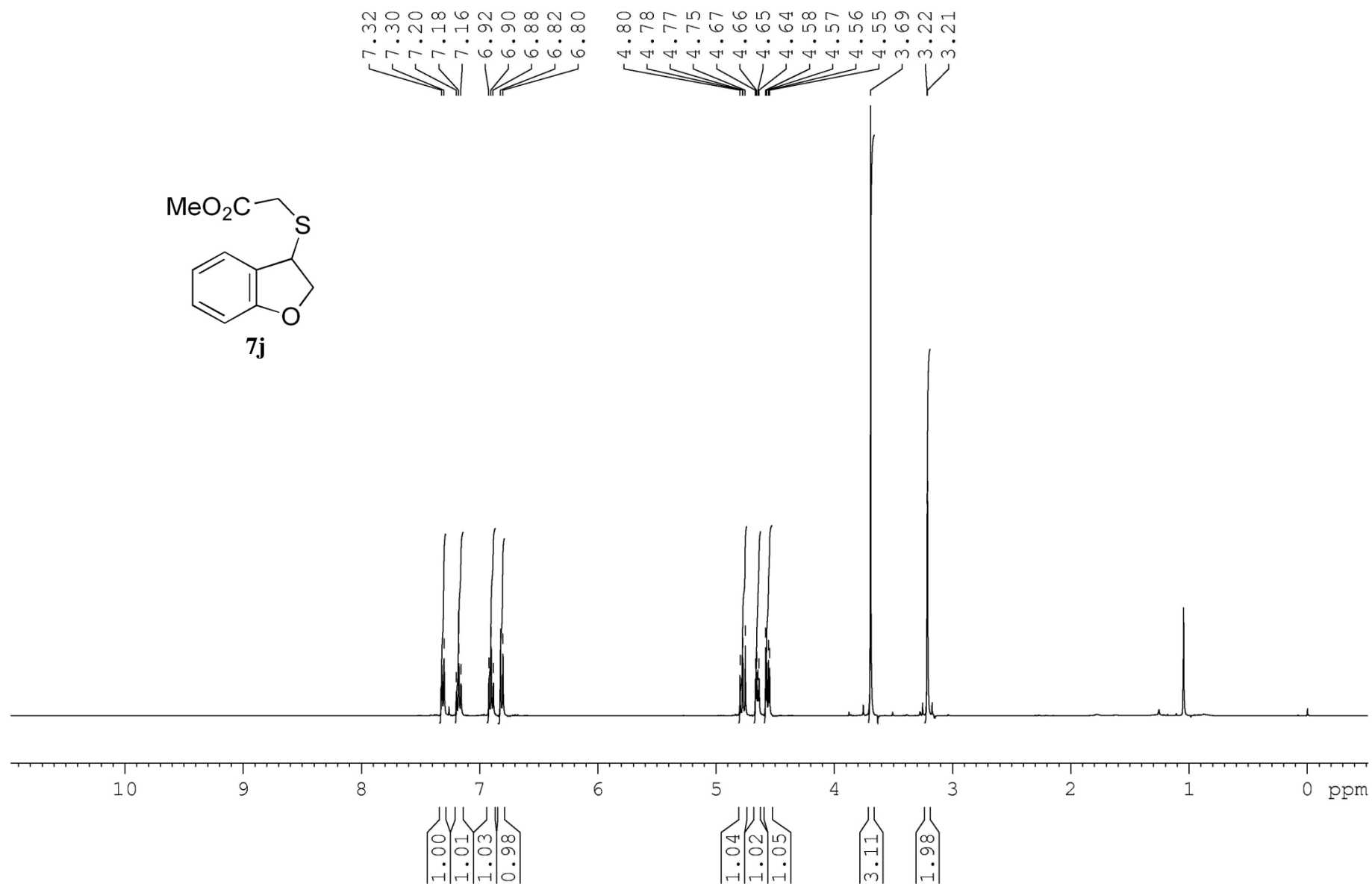
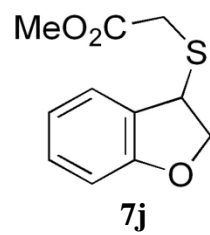
GVAS288_22_10_13_131022113551 #29 RT: 0.78 AV: 1 NL: 8.13E5

T: FTMS + p ESI Full ms [220.00-1000.00]



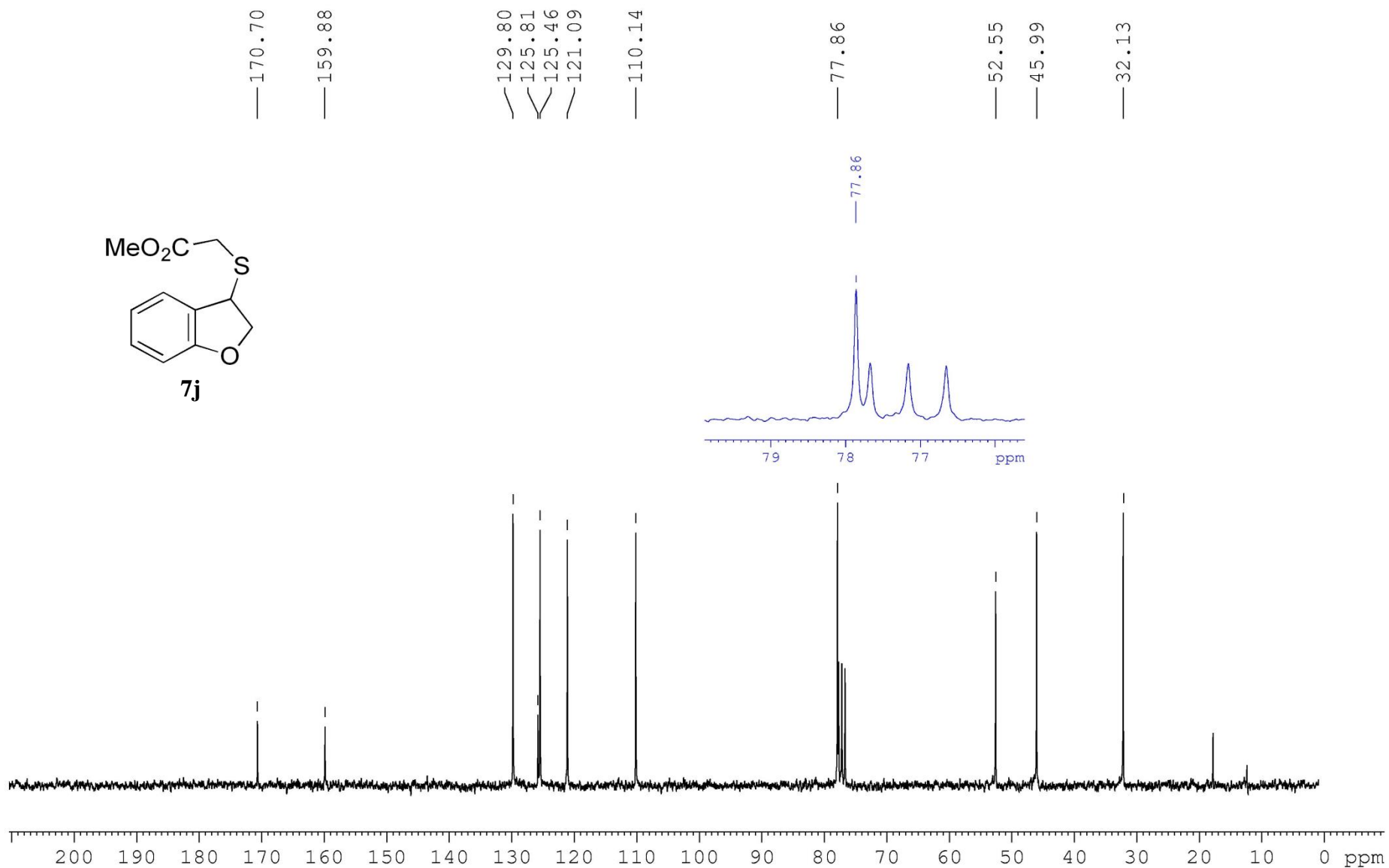
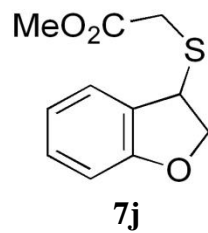
¹H NMR of compound **7j** in CDCl₃ at 400 MHz

GVAS289@400 Hz



^{13}C NMR of compound **7j** in CDCl_3 at 63 MHz

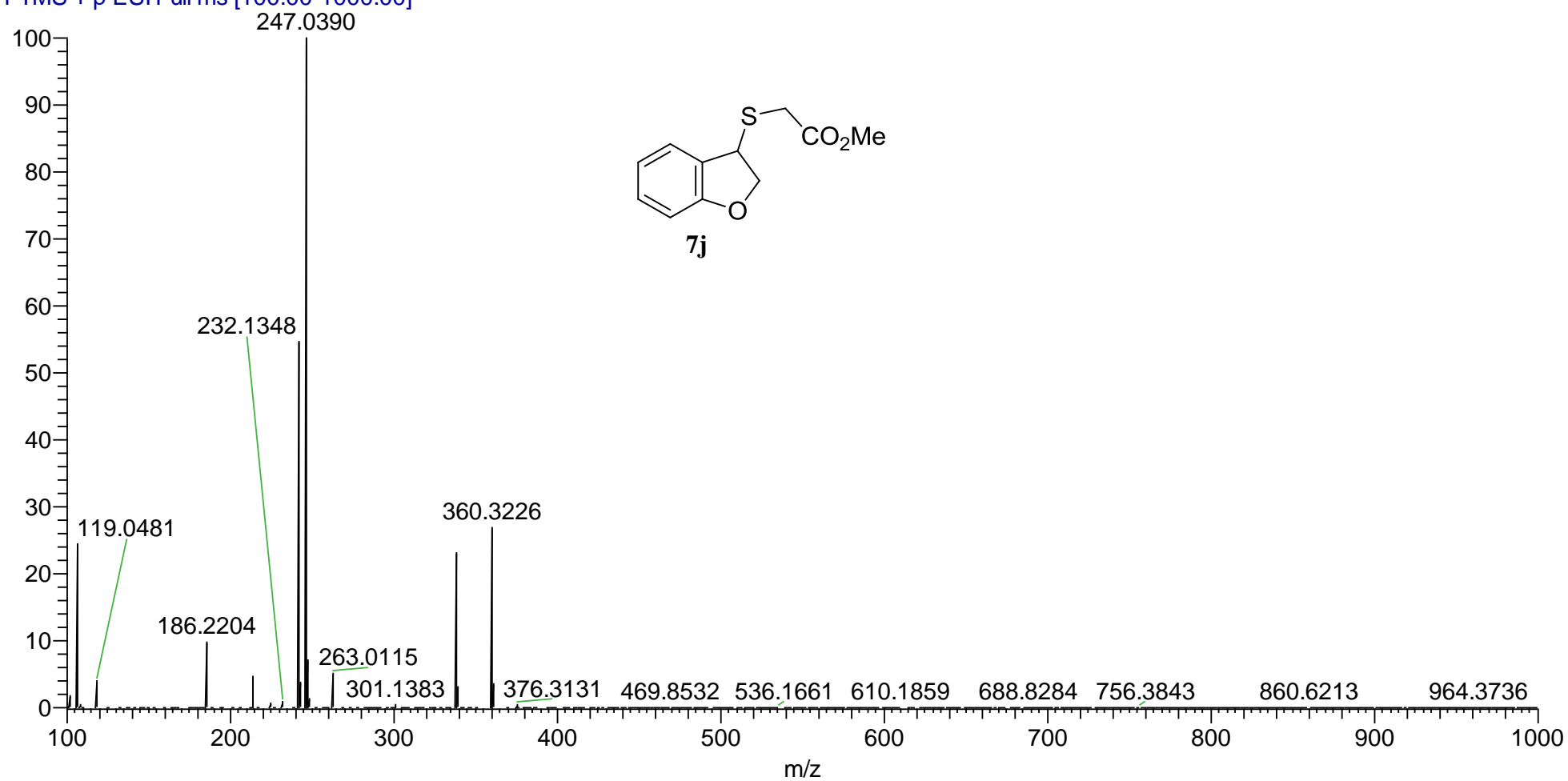
GVAS289-A@250 C-13



HRMS of compound **7j**

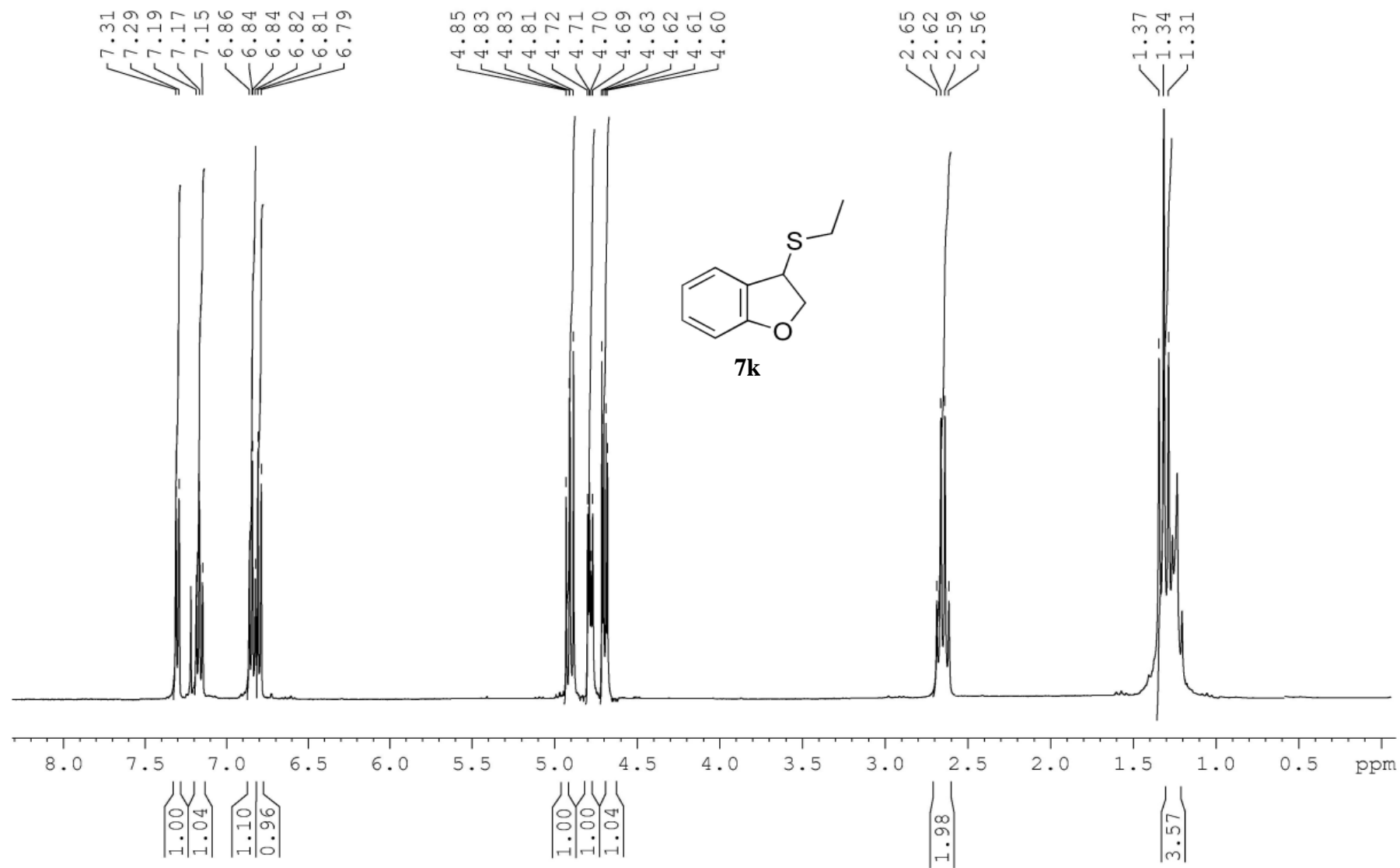
GVAS289_22_10_13_131022130033 #32 RT: 0.87 AV: 1 NL: 2.95E7

T: FTMS + p ESI Full ms [100.00-1000.00]



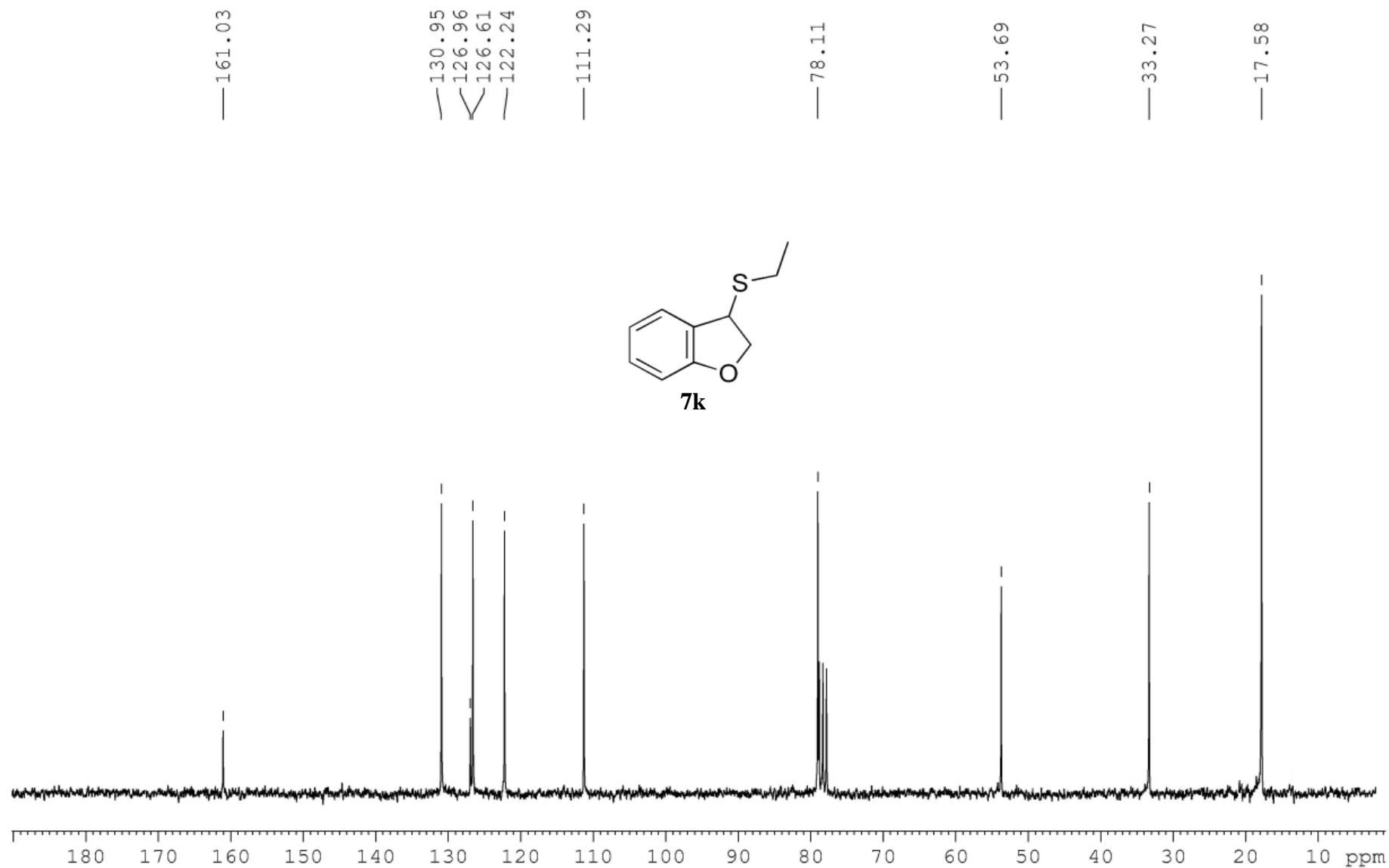
¹H NMR of compound **7k** in CDCl₃ at 400 MHz

GVAS290@400 Hz



^{13}C NMR of compound **7k** in CDCl_3 at 63 MHz

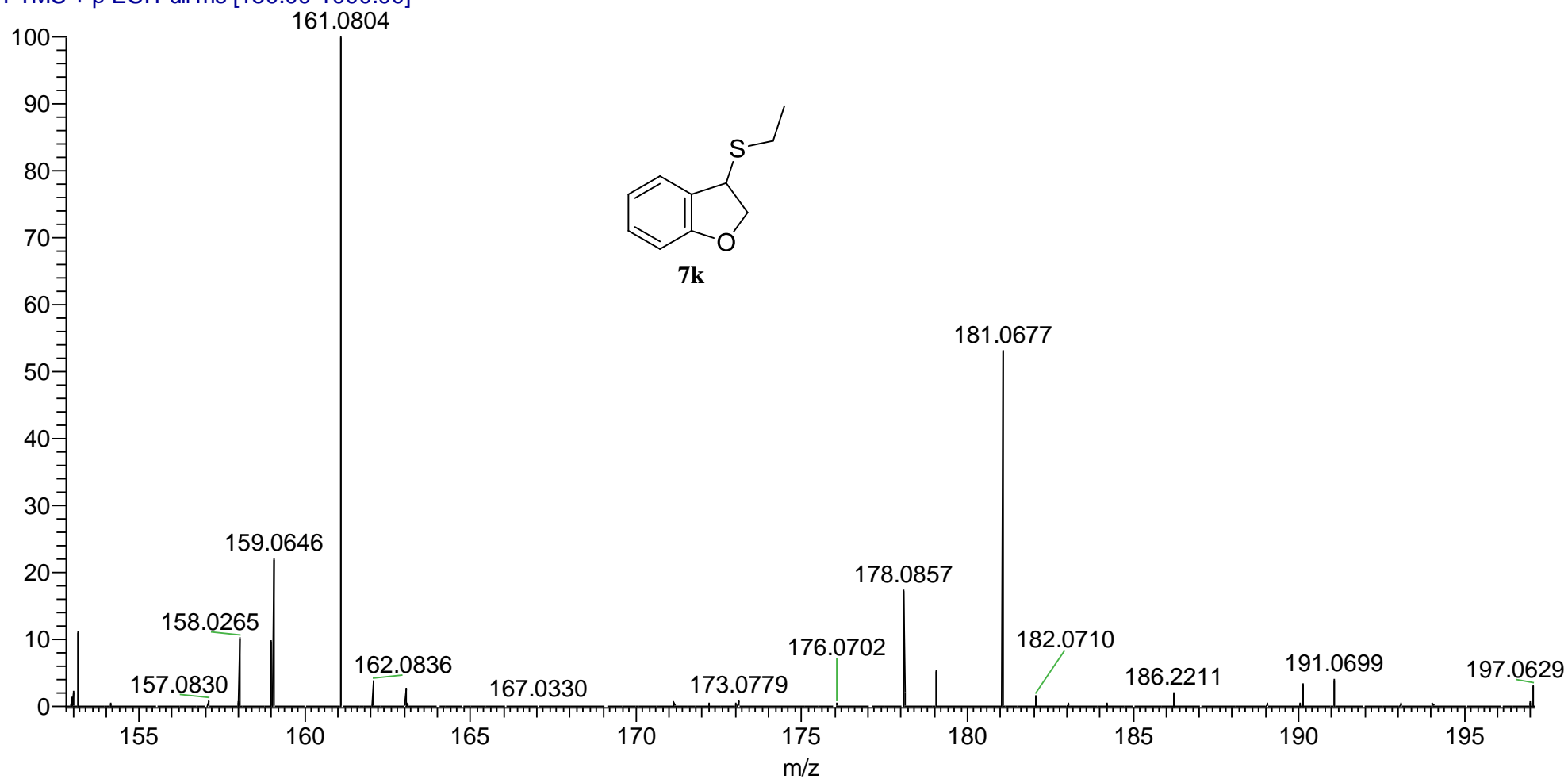
GVAS290-NaH@250 C-13



HRMS of compound **7k**

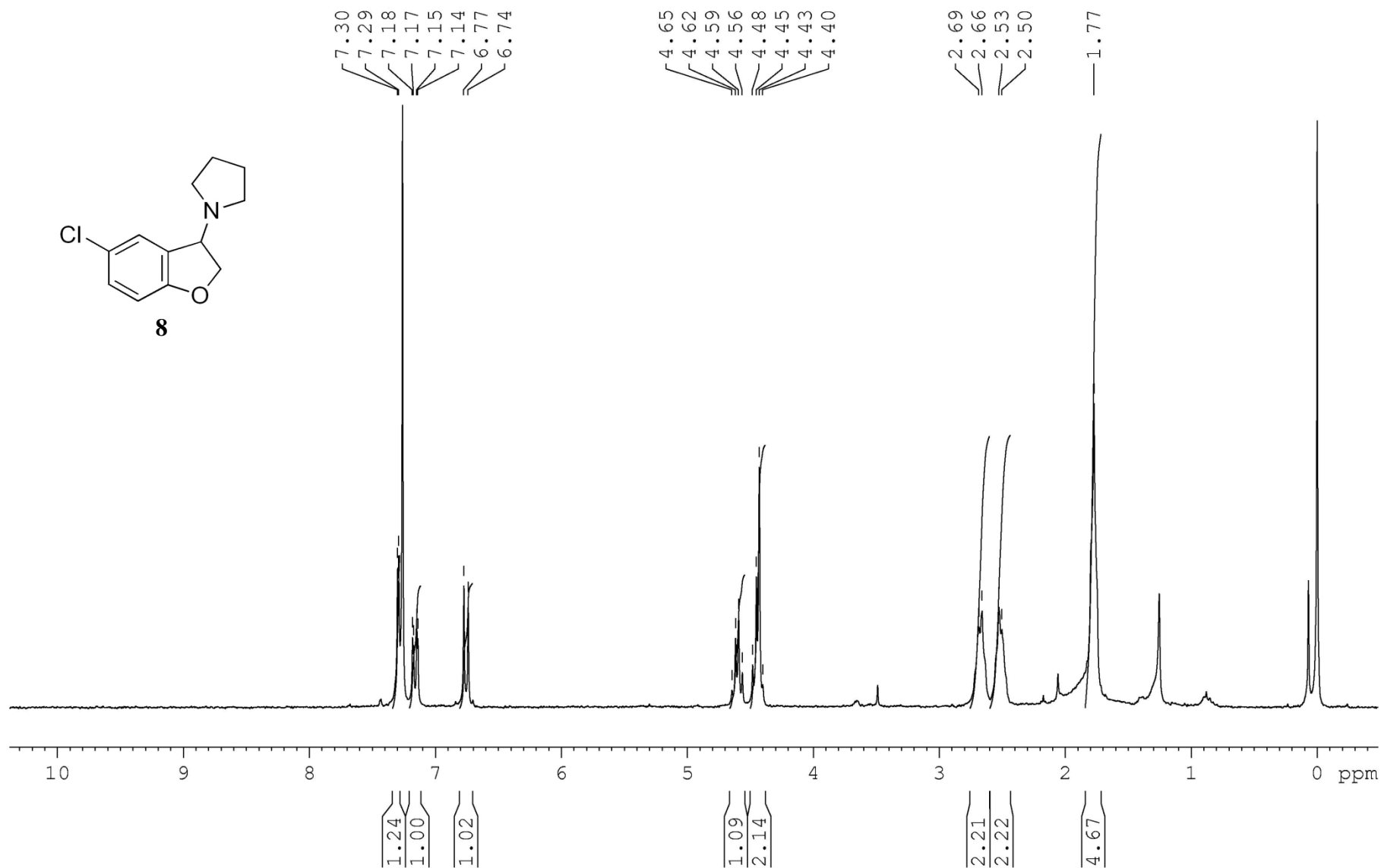
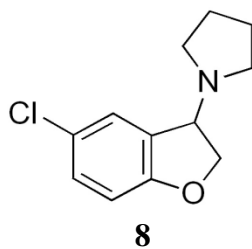
GVAS290_22_10_13_131022130033 #29 RT: 0.77 AV: 1 NL: 4.52E6

T: FTMS + p ESI Full ms [150.00-1000.00]



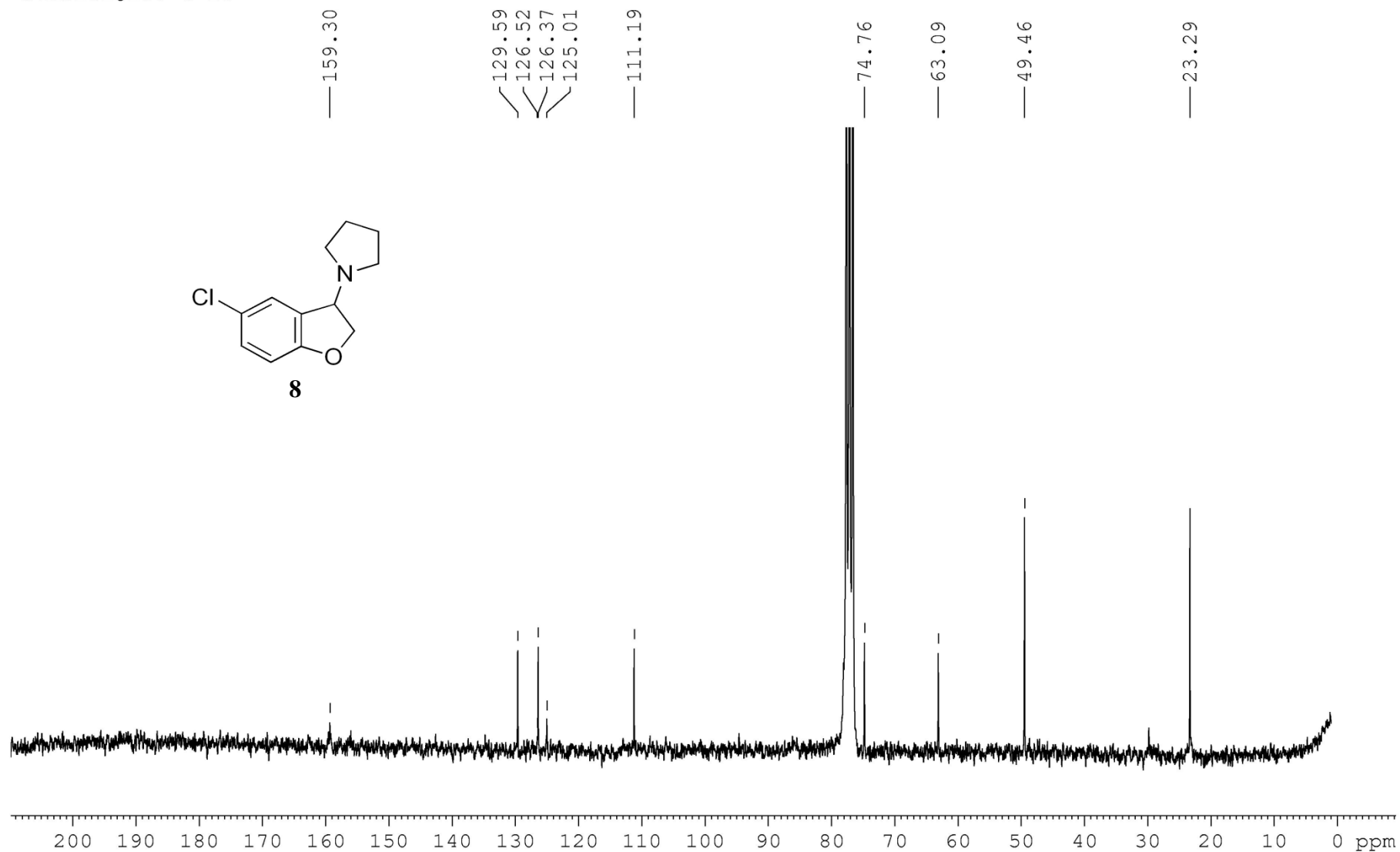
¹H NMR of compound **8** in CDCl₃ at 250 MHz

GVAS262-B@250 H-1



^{13}C NMR of compound **8** in CDCl_3 at 63 MHz

GVAS262@250 C-13



HRMS of compound **8**

GVAS262_22_10_13_131021141943 #14 RT: 0.37 AV: 1 NL: 4.76E7

T: FTMS + p ESI Full ms [150.00-2000.00]

