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Article

Solvent-free Mizoroki-Heck reaction applied to the synthesis of abscisic acid and analogues

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Experimental Section

1. Materials and Methods

1. Materials and Methods

1.1. General Methods

All reagents were purchased from commercial suppliers and were used without further purification. THF was dried with a dry station GT S100 instantaneously prior to use. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F254) plates. Compounds were visualized by UV irradiation. Flash column chromatography was performed on silica gel 60 (230 - 400 mesh, 0.040 - 0.063 mm). Melting points (mp [°C]) were taken on samples in open capillary tubes and are uncorrected. The infrared spectra of compounds were recorded on a Thermo Scientific Nicolet iS10. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker avance II spectrometer at 250 MHz (^{13}C, 62.9 MHz) and on a Bruker avance III HD nanobay 400 MHz (^{13}C 100.62 MHz). Chemical shifts are given in parts per million from tetramethylsilane (TMS) or deterred solvent (MeOH-d_4, Chloroform-d) as internal standard. The following abbreviations are used for the proton spectra multiplicities: b : broad, s: singlet, d: doublet, t: triplet, q: quartet, p: pentuplet, m: multiplet. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS (ESI)) were performed on a Maxis Bruker 4G by the "Federation de Recherche" ICOA/CBM (FR2708) platform.

1.2 Procedure for synthesis of 1-Ethenyl-3-methylcyclohex-2-en-1-ol

1-Ethenyl-3-methylcyclohex-2-en-1-ol 1:To a solution of vinylmagnesium bromide (22.7 mL, 22.7 mmol) 2.5 equiv) in dry THF (10 mL), was added the corresponding ketone (1.000 g, 9.1 mmol 1 equiv) at 0 °C. The mixture was stirred at this temperature for 2 – 3 hours. Then a saturated solution of NH_4Cl (50 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 40 mL). The organic phases were combined, dried on $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel PE-AE: (8:2, v/v), to provide 1 (1.065 g, 85 %) as a pale yellow oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ 5.93 (dd, J = 17.3, 10.6 Hz, 1H, $H_{1'}$), 5.29 (q, J =1.6 Hz, 1H, H_2), 5.21 (dd, J = 17.3, 1.4 Hz, 1H, $H_{2'}$), 5.06 (dd, J = 10.6, 1.5 Hz, 1H, $H_{2'}$), 1.97 – 1.88 (m, 2H, H_4), 1.80 – 1.59 (m, 8H, H_6, H_5, H_7, OH); ^{13}C NMR (63 MHz, Chloroform-*d*) δ 144.7 ($C_{1'}$), 138.5 (C_3), 125.6 (C_2), 112.5 ($C_{2'}$), 71.4 (C_1), 36.0 (C_6), 30.0 (C_4), 23.7 (C_7), 19.3 (C_5); IR (ATR, cm^{-1}): 3355, 2966, 2866, 1669, 1638, 1436, 988; HRMS (ESI): *m/z* $[M+Li]^+$ calc for $C_9H_{14}LiO$ 145.1199, found 145.1195.

1.3 Procedures for synthesis of Methyl (2Z)-3-iodobut-2-enoate, (2Z)-3-Iodobut-2-enenitrile, Methyl (2Z)-3-iodoacrylate and 4-Nitrophenyl (2Z)-3-iodo-2-methylprop-2-enoate, Methyl (2Z,4E)-3-methyl-5-(4′,4′,6′-trimethyl-1′,3′,2′-dioxaborinan-2′-yl)penta-2,4-dienoate, Methyl (2Z,4E)-5-iodo-3-methylpenta-2,4-dienoate.

Methyl (2*Z*)-3-iodobut-2-enoate (2). [1]: To a solution of methyl butynoate (2.0 g, 20 mmol) in AcOH (18 mL), was added NaI (4.89 g, 33 mmol). The mixture was under reflux for 2 hours. After completion, the reaction was quenched with water (10 mL), treated with a saturated solution of sodium carbonate (100 mL) and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried with $MgSO_4$ then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **2** (3.8 g, 83 %) as a brown oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ 6.30 (q, J = 1.5 Hz, 1H, H_2), 3.75 (s, 3H, H_5), 2.73 (d, J = 1.4 Hz, 3H, H_4); ^{13}C NMR (63 MHz, Chloroform-*d*) δ 164.9 (C_1), 125.3 (C_2), 113.8 (C_3), 51.7 (C_5), 36.7 (C_4).

(2*Z*)-3-Iodobut-2-enenitrile (2a). [2]: To a solution of (2*Z*)-3-iodobut-2-enamide (537 mg; 2.5 mmol) in DCM (2mL) at 0°C, were added triethyamine (369 µL; 3.3 mmol) and trichloroacetyle chloride (711 µL; 5.1 mmol). The mixture was stirred at 0°C for 1.5 h. After

completion, the reaction was quenched with water (10 mL), treated with a saturated solution of sodium carbonate (100 mL) and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried with $MgSO_4$ then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **2a** (453 mg, 92 %) as a brown oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.13 (s, 1H, H_2), 2.70 (s, 3H, H_4); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 122.6 (C_3), 118.1 (C_1), 110.2 (C_2), 34.6 (C_4).

Methyl (2*Z*)-3-iodoacrylate (2b). [3]: To a solution of methyl propynoate (500 mg; 5.9 mmol) in AcOH (5 mL), was added NaI (1.43 g; 9.4 mmol). The mixture was stirred under reflux for 2 h. After completion, the reaction was quenched with water (20 mL), treated with a saturated solution of sodium carbonate (100 mL) and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried with $MgSO_4$ then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **2b** (635 mg, 50 %) as a brown oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ 7.44 (d, J = 8.9 Hz, 1H, H_3), 6.89 (d, J = 8.9 Hz, 1H, H_2), 3.76 (s, 3H, H_4).

4-Nitrophenyl (2*Z*)-3-iodo-2-methylprop-2-enoate (2c). To a solution of (*Z*)-3-iodobut-2-enoic acid (147 mg; 0.7 mmol) in Toluene (10 mL) at 0 °C, was added $SOCl_2$ (251 µL; 3.5 mmol) and *p*-nitrophenol (124 mg; 1.0 mmol). The mixture was stirred at 0 °C for 30 min. After completion, the reaction was quenched with water (20 mL), treated with a saturated solution of sodium carbonate (100 mL) and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried with $MgSO_4$ then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **2c** (159 mg, 69 %) as a yellow solid. mp: 129 - 130 °C ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, J = 8.7 Hz, 2H, $H_{2'}$), 7.33 (d, J = 8.7 Hz, 2H, $H_{3'}$), 6.57 (d, J = 2.4 Hz, 1H, H_2), 2.85 (s, 3H, H_4); ^{3}C RMN (101 MHz, Chloroform-*d*) δ 161.7(C_1) 155.2 ($C_{4'}$), 145.4 ($C_{1'}$), 125.3 ($C_{2'}$), 124.1 (C_2), 122.5 ($C_{3'}$), 119.3 (C_3), 37.3 (C_4). HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{10}H_9INO_4$: 333.9571, found: 333.9577.

Methyl (2Z,4E)-3-methyl-5-(4′,4′,6′-trimethyl-1′,3′,2′-dioxaborinan-2′-yl)penta-2,4-dienoate (2d). To a solution of **2** (500 mg; 0.7 mmol) in ACN (10 mL) were successively added the 2′-ethenyl-4,4,6-trimethyl-1,3,2-dioxoborinane (572 µl; 3.32 mmol), AgOAc (554 mg; 3.32 mmol), P(*o*-tolyl)$_3$ (741 mg; 2.43 mmol) and $Pd(OAc)_2$ (248 mg; 0.5 mmol). The mixture was stirred at 60 °C for 6 h. After completion, the reaction was quenched with water (20 mL), treated with a saturated solution of sodium carbonate (100 mL) and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried with $MgSO_4$ then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **2d** (464 mg, 83 %) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, J = 18.2 Hz, 1H, H_4), 5.93 (d, J = 18.3 Hz, 1H, H_5), 5.76 (s, 1H, H_2), 4.25 (dqd, J = 12.2, 6.1, 2.8 Hz, 1H, $H_{5'}$), 3.72 (s, 3H, H_7), 1.99 (s, 3H, H_6), 1.81 (dd, J = 13.9, 2.9 Hz, 1H, $H_{4'}$), 1.51 (d, J = 13.9 Hz, 1H, $H_{4'}$), 1.32 (d, J = 4.1 Hz, 6H, $H_{7'}$), 1.29 (d, J = 6.2 Hz, 3H, $H_{8'}$); ^{3}C RMN (101 MHz, Chloroform-*d*) δ 166.4 (C_1), 151.6 (C_3), 142.4 (C_4), 118.4 (C_2), 71.1 ($C_{3'}$), 64.9 ($C_{5'}$), 51.1 (C_7), 46.0 ($C_{4'}$), 31.2 ($C_{7'}$), 28.1 ($C_{7'}$), 23.1 ($C_{8'}$), 20.7 (C_6). HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{13}H_{22}BO_4$: 253.1608, found: 253,1607.

Methyl (2Z,4E)-5-iodo-3-methylpenta-2,4-dienoate (2e). To a solution of **2d** (200 mg; 0.79 mmol) in THF (10 mL) at -78 °C was added a solution of NaOMe 0.5M in MeOH (2 mL; 1 mmol). The mixture was stirred for 30 min then a solution of ICl (133 mg; 0.82 mmol) was added at – 78 °C The mixture was still stirred for 1 h then the temperature is allowed to rise to room temperature. The reaction was quenched with water (20 mL), treated with a saturated solution of sodium carbonate

(100 mL) and extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried with $MgSO_4$ then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **2e** (464 mg, 83 %) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, 1H, *J* = 16 Hz, H4 or H5), 5.65 (m, 1H, H2), 6.94 (d, 1H, *J* = 16 Hz, H4 or H5) , 3.71 (s, 3H, H7), 1.98 (s, 3H, H6); ^{3}C RMN (101 MHz, Chloroform-*d*) δ 166.3 (C1), 149.4 (C3), 142.7 (C4 or C5), 117.4 (C4 or C5), 102.9 (C3), 51.4 (C7), 20.4 (C6). HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_7H_{10}IO_2$: 252.9720, found: 252.9724.

1.4. General procedure for Mizoroki-Heck optimized reaction

Iodinated substrate (0.53 mmol), vinylic compound (0.44 mmol), silver carbonate (0.66 mmol) and palladium acetate (5 % mol) were placed in a round bottom flask, stirred at 50 °C for the corresponding time. After completion, the reaction mixture was diluted in EtOAc (5 mL) and a saturated solution of ammonium chloride (5 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL). Then the combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel to provide the expected product.

Methyl (2*Z*,4*E*)-5-(1-hydroxy-3-methylcyclohex-2-en-1-yl)-3-methylpenta-2,4-dienoate 3a

PE-AE: (8:2, v/v), pale yellow oil (59 mg, 63 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 16.2 Hz, 1H, H_5), 6.18 (d, *J* = 16.2 Hz, 1H, H_4), 5.69 (s, 1H, H_2), 5.36 (d, *J* = 1.4 Hz, 1H, $H_{2'}$), 3.70 (s, 3H, H_7), 2.01 (d, *J* = 1.3 Hz, 3H, H_6), 1.99 – 1.93 (m, 2H, $H_{4'}$), 1.82 – 1.64 (m, 8H, $H_{5'}$ $H_{6'}$ $H_{7'}$ OH); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6 (C_1), 150.8 (C_3), 143.6 (C_4), 139.1 ($C_{3'}$), 125.2 (C_5, $C_{2'}$), 117.2 (C_2), 71.3 ($C_{1'}$), 51.0 (C_7), 36.0 ($C_{6'}$), 30.0 ($C_{4'}$), 23.8 ($C_{7'}$), 21.1 (C_6), 19.2 ($C_{5'}$); IR (ATR, cm^{-1}): 3459, 2947, 1713, 1436, 1157; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{13}H_{18}NaO_3$ 245.1148, found 245.1145.

Methyl (2*Z*,4*E*)-5-(1-hydroxy-3,5-dimethylcyclohex-2-en-1-yl)-3-methylpenta-2,4-dienoate 3b

PE-AE: (8:2, v/v), pale yellow oil (84 mg, 76 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 16.1, 0.9 Hz, 1H, H_4), 6.17 (d, *J* = 16.1 Hz, 1H, H_5), 5.70 (s, 1H, H_2), 5.29 (q, *J* = 1.4 Hz, 1H, $H_{2'}$), 3.71 (s, 3H, H_7), 2.01 (d, *J* = 1.3 Hz, 3H, H_6), 2.00 – 1.96 (m, 1H, $H_{6'}$), 1.91 (ddt, *J* = 12.5, 2.8, 1.6 Hz, 1H, $H_{4'}$), 1.75 (d, *J* = 1.4 Hz, 3H, $H_{7'}$), 1.69 – 1.58 (m, 3H, OH, H5', H6'), 1.46 – 1.33 (m, 1H, $H_{4'}$), 0.99 (d, *J* = 6.5 Hz, 3H, $H_{8'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (C_1), 150.8 (C_3), 142.8 (C_5), 137.7 ($C_{3'}$), 126.0 (C_4), 125.7 ($C_{2'}$), 117.6 (C_2), 73.7 ($C_{1'}$), 51.2 (C_7), 45.4 ($C_{4'}$), 39.1 ($C_{6'}$), 27.3 ($C_{5'}$), 23.4 ($C_{7'}$), 21.9 ($C_{8'}$), 21.3 (C_6); IR (ATR, cm^{-1}): 3427, 2967, 1717, 1436, 1157; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{15}H_{22}NaO_3$ 273.1461, found 273.1458.

Methyl (2*Z*,4*E*)-5-(1-hydroxy-2-methylcyclohex-2-en-1-yl)-3-methylpenta-2,4-dienoate 3c

PE-AE: (8:2, v/v), colorless oil (84 mg, 76 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 16.3, 0.9 Hz, 1H, H_4), 6.12 (d, *J* = 16.1 Hz, 1H, H_5), 5.69 (s, 1H, H_2), 5.63 (t, *J* = 1.8 Hz, 1H, $H_{3'}$), 3.70 (s, 3H, H_7), 2.07 – 2.00 (m, 5H, H_6, $H_{4'}$), 1.88 – 1.76 (m, 2H, $H_{6'}$), 1.72 (bs, 1H, OH), 1.67 (q, *J* = 1.9 Hz, 5H, $H_{7'}$, $H_{5'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6 (C_1), 150.5 (C_3), 142.4 (C_4), 135.5 ($C_{2'}$), 126.5 ($C_{3'}$), 126.2 (C_5), 117.1 (C_2), 73.7 ($C_{1'}$), 51.0 (C_7), 37.9 ($C_{6'}$), 25.5 ($C_{4'}$), 21.2 (C_6), 19.2 ($C_{5'}$), 18.1 ($C_{7'}$); IR (ATR, cm^{-1}): 3459, 2947, 1713, 1436, 1157; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{14}H_{20}NaO_3$ 259.1304, found 259.1304.

Methyl (2*Z*,4*E*)-5-(1-hydroxycyclohexyl)-3-methylpenta-2,4-dienoate 3d

PE-AE: (9:1, v/v), colorless oil (47 mg, 47 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 16.2 Hz, 1H, H_4), 6.20 (d, *J* = 16.2 Hz, 1H, H_5), 5.70 (s, 1H, H_2), 3.70 (s, 3H, H_7), 2.01 (d, *J* = 1.3 Hz, 3H, H_6), 1.70 – 1.52 (m, 10H), 1.47 (s, 1H, OH), 1.35 – 1.23 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (C_1), 150.9 (C_3), 144.8 (C_5), 124.6 (C_4), 117.1 (C_2), 71.8 ($C_{1'}$), 51.0 (C_7), 37.5 ($C_{2'}$), 25.5 ($C_{4'}$), 21.9 ($C_{3'}$), 21.0 (C_6); IR (ATR, cm^{-1}): 3401, 2929, 1698, 1447, 1157; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{13}H_{20}NaO_3$ 247.1304, found 247.1297.

Methyl (2*Z*,4*E*)-5-(1-hydroxy-3,5-dimethylcyclohexyl)-3-methylpenta-2,4-dienoate 3e

PE-AE: (8:2, v/v), colorless oil (59.9 mg, 63 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 16.2 Hz, 1H, H_4), 6.17 (d, *J* = 16.2 Hz, 1H, H_5), 5.68 (s, 1H, H_2), 3.70 (s, 3H, H_7), 1.99 (s, 3H, H_6), 1.91 – 1.79 (m, 2H, $H_{3'}$, $H_{5'}$), 1.72 – 1.61 (m, 3H), 1.52 (s, 1H, OH), 1.08 (t, *J* = 12.8 Hz, 2H), 0.91 (d, *J* = 1.3 Hz, 3H), 0.89 (s, 3H), 0.55 (q, *J* = 12.2 Hz, 1H, $H_{4'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9 (C_1), 151.1 (C_3), 145.8 (C_5), 123.9 (C_4), 117.1 (C_2), 73.2 ($C_{1'}$), 51.2 (C_7), 45.4 ($C_{6'}$, $C_{2'}$), 43.4 ($C_{4'}$), 27.7 ($C_{3'}$, $C_{5'}$), 22.4 ($C_{7'}$, $C_{8'}$), 21.3 (C_6); IR (ATR, cm^{-1}): 3411, 2946, 1698, 1434, 1155; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{15}H_{24}NaO_3$ 275.1617, found 275.1617.

Methyl (2*Z*,4*E*)-5-(1-hydroxy-3,3-dimethylcyclohexyl)-3-methylpenta-2,4-dienoate 3f

PE-AE: (8:2, v/v), colorless oil (70 mg, 64 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 16.2 Hz, 1H, H_4), 6.17 (d, *J* = 16.1 Hz, 1H, H_5), 5.71 (s, 1H, H_2), 3.72 (s, 3H, H_7), 2.02 (s, 3H, H_6), 1.90 – 1.80 (m, 1H, $H_{5'}$), 1.70 – 1.61 (m, 1H, $H_{4'}$), 1.61 – 1.38 (m, 5H, $H_{4'}$, $H_{6'}$, $H_{2'}$), 1.33 (s, 1H, OH), 1.23 – 1.17 (m, 1H, $H_{6'}$), 1.13 (s, 3H, $H_{7'}$), 0.92 (s, 3H, $H_{7'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (C_1), 150.9 (C_3), 146.0 (C_5), 123.8 (C_4), 117.1 (C_2), 72.9 ($C_{1'}$), 51.0 (C_7), 49.3 ($C_{2'}$), 38.9 ($C_{6'}$), 37.2 ($C_{4'}$), 33.1 ($C_{7'}$), 30.8 ($C_{3'}$), 27.9 ($C_{7'}$), 21.1 (C_6), 18.5 ($C_{5'}$); IR (ATR, cm^{-1}): 3443, 2948, 1716, 1455, 1190; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{15}H_{24}NaO_3$ 275.1617, found 275.1618.

Methyl (2*Z*,4*E*)-5-(1-hydroxycyclopentyl)-3-methylpenta-2,4-dienoate 3g

PE-AE: (9:1, v/v), dark yellow oil (25 mg, 27 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 16.1 Hz, 1H, H_4), 6.28 (d, *J* = 16.2 Hz, 1H, H_5), 5.69 (s, 1H, H_2), 3.70 (s, 3H, H_7), 2.02 (d, *J* = 1.3 Hz, 3H, H_6), 1.96 – 1.85 (m, 2H, $H_{3'}$), 1.81 – 1.70 (m, 6H, $H_{2'}$, $H_{3'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (C_1), 150.7 (C_3), 143.5 (C_5), 124.1 (C_4), 116.9 (C_2), 82.2 ($C_{1'}$), 51.0 (C_7), 40.7 ($C_{2'}$), 23.8 ($C_{3'}$), 21.1 (C_6); IR (ATR, cm^{-1}): 3472, 2965, 1687, 1452, 1164; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{12}H_{18}NaO_3$ 233.1148, found 233.1147.

Methyl (2*Z*,4*E*)-6-cyclohexyl-6-hydroxy-3-methylhexa-2,4-dienoate 3h

PE-AE: (8:2, v/v), pale yellow oil (74 mg, 70 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 16.0 Hz, 1H, H_4), 6.10 (d, *J* = 16.0 Hz, 1H, H_5), 5.70 (s, 1H, H2), 4.02 (t, *J* = 6.8 Hz, 1H, H_6), 3.70 (s, 3H, H_8), 2.01 (s, 3H, H_7), 1.88 (d, *J* = 13.1 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.66 (dd, *J* = 17.7, 5.6 Hz, 3H), 1.47 (tdd, *J* = 11.9, 6.4, 3.2 Hz, 1H, $H_{1'}$), 1.30 – 1.11 (m, 3H), 1.08 – 0.96 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6 (C_1), 150.4 (C_3), 138.8 (C_5), 128.2 (C_4), 117.2 (C_2), 77.4 (C_6), 51.1 (C_8), 43.8 ($C_{1'}$), 28.9 (CH_2), 28.5 (CH_2), 26.5 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 21.1 (C_7); IR (ATR, cm^{-1}): 3399, 2923, 1714, 1449, 1157; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{14}H_{22}NaO_3$ 261.1461, found 261.1463.

Methyl (2*Z*,4*E*)-5-cyclohexyl-3-methylpenta-2,4-dienoate 3i

PE-AE: (8:2, v/v), pale yellow oil (195 mg, 42 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 16.3 Hz, 1H, H_4), 6.08 (dd, *J* = 16.0, 7.0 Hz, 1H, H_5), 5.61 (s, 1H, H_2), 3.69 (s, 3H, H_7), 2.14 (dtt, *J* = 11.4, 7.6, 3.7 Hz, 1H, $H_{1'}$), 1.98 (s, 3H, H6), 1.81 – 1.70 (m, 4H, $H_{2'}$), 1.34 – 1.10 (m, 6H, $H_{3'}$, $H_{4'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9 (C_1), 152.0 (C_3), 144.7 (C_4), 125.3 (C_5), 115.3 (C_2), 50.9 (C_7), 41.4 ($C_{1'}$), 32.6 ($C_{2'}$), 26.1 ($C_{4'}$), 25.9 ($C_{3'}$), 21.1 (C_6); IR (ATR, cm^{-1}): 2923, 1713, 1448, 1157; HRMS (ESI): *m*/*z* [M+H]$^+$ calcd. for $C_{13}H_{21}O_2$ 209.1536, found 209.1535.

Methyl (2*Z*,4*E*)-3-methyl-5-phenylpenta-2,4-dienoate 3j [4]

PE-AE: (8:2, v/v), white solid (208 mg, 76 %). mp: 36 - 38 °C (litt 38 – 40 °C)[31]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 16.4, 1H, H_5), 7.59 – 7.52 (m, 2H, $H_{2'}$), 7.38 – 7.32 (m, 2H, $H_{3'}$), 7.31 – 7.27 (m, 1H, $H_{4'}$), 6.93 (d, *J* = 16.3 Hz, 1H, H_4), 5.77 – 5.74 (s, 1H, H_2), 3.74 (s, 3H, H_7), 2.14 (d, *J* = 1.3 Hz, 3H, H_6); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8 (C_1), 151.1 (C_3), 136.7 ($C_{1'}$), 135.5 (C_4), 128.7 ($C_{3'}$), 128.7 ($C_{4'}$), 127.4 ($C_{2'}$), 125.9 (C_5), 117.2 (C_2), 51.1 (C_7), 20.9 (C_6); IR (ATR, cm^{-1}): 2999, 1706, 1619, 1598, 1457, 1148; HRMS (ESI): *m*/*z* [M+H]$^+$ calcd. for $C_{13}H_{15}O_2$ 203.1066, found 203.1063.

Methyl (2*Z*,4*E*)-3-methyl-5-phenylpenta-2,4-dienoate 3k

PE-AE: (8:2, v/v), pale yellow oil (46 mg, 44 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 15.5, 11.3 Hz, 1H, H_4), 6.59 (td, *J* = 11.3, 0.8 Hz, 1H, H_3), 6.12 (d, *J* = 15.5 Hz, 1H, H_5),

5.69 – 5.64 (s, 1H, H_2), 5.34 (s, 1H, $H_{2'}$), 3.73 (s, 3H, H_6), 2.02 – 1.88 (m, 2H, $H_{4'}$), 1.81 – 1.62 (m, 8H, $H_{5'}$, $H_{6'}$, $H_{7'}$, OH); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8 (C_1), 149.8 (C_5), 144.7 (C_3), 139.3 ($C_{3'}$), 124.8 ($C_{2'}$), 124.1 (C_4), 117.1 (C_2), 71.1 ($C_{1'}$), 51.2 (C_6), 35.9 ($C_{6'}$), 30.0 ($C_{4'}$), 23.8 ($C_{7'}$), 19.2 ($C_{5'}$); IR (ATR, cm^{-1}): 3436, 2950, 1716, 1437, 1173; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{13}H_{18}NaO_3$ 245.1148, found 245.1145.

Methyl (2*Z*,4*E*)-5-cyclohexyl-3-methylpenta-2,4-dienoate 3l

PE-AE: (9:1, v/v), dark yellow oil (50 mg, 49 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 15.7 Hz, 1H, H_5), 6.21 (d, *J* = 15.7 Hz, 1H, H_4), 5.32 (s, 1H, $H_{2'}$), 5.16 (s, 1H, H_2), 2.01 (d, *J* = 1.3 Hz, 3H, H_6), 2.00 – 1.94 (m, 2H, $H_{4'}$), 1.81 – 1.65 (m, 8H, $H_{5'}$, $H_{6'}$, $H_{7'}$, OH); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.2 (C_3), 145.0 (C_4), 139.9 ($C_{3'}$), 125.4 (C_5), 124.6 (C_2), 116.7 (C_1), 96.6 ($C_{2'}$), 71.1 ($C_{1'}$), 36.1 ($C_{6'}$), 29.9 ($C_{4'}$), 23.8 ($C_{7'}$), 19.6 (C_6), 19.1 ($C_{5'}$); IR (ATR, cm^{-1}): 3438, 2935, 2211, 1165; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{13}H_{17}NNaO$ 226.1202, found 226.1199.

4-Nitrophenyl-(2*Z*,4*E*)-5-(1-hydroxy-3-methylcyclohex-2-en-1-yl)-3-methylpenta-2,4-dienoate 3m

PE-AE: (8:2, v/v), yellow oil (60 mg, 58 %). ^{1}H NMR (250 MHz, Chloroform-*d*) δ 8.33 – 8.21 (m, 2H, H_8), 7.74 (d, *J* = 16.8 Hz, 1H, H_5), 7.36 – 7.26 (m, 2H, H_9), 6.32 (d, *J* = 16.7 Hz, 1H, H_4), 5.90 (s, 1H, H_2), 5.33 (p, *J* = 1.3 Hz, 1H, $H_{2'}$), 2.13 (d, *J* = 1.2 Hz, 3H, H_6), 1.99 – 1.90 (m, 2H, $H_{4'}$), 1.80 – 1.62 (m, 8H, $H_{5'}$, $H_{6'}$, $H_{7'}$, OH); ^{13}C NMR (63 MHz, Chloroform-*d*) δ 163.1 (C_1), 155.6 (C_{10}), 155.4 (C_3), 145.7 (C_7), 145.1 (C_4), 139.5 ($C_{3'}$), 125.1 (C_8), 124.8 ($C_{2'}$), 124.8 (C_5), 122.6 (C_9), 115.2 (C_2), 71.3 ($C_{1'}$), 36.0 ($C_{6'}$), 30.0 ($C_{4'}$), 23.8 ($C_{7'}$), 21.4 (C_6), 19.1 ($C_{5'}$); IR (ATR, cm^{-1}): 3389, 2932, 1731, 1632, 1613, 1521, 1111; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{19}H_{21}NNaO_5$ 366.1311, found 366.113.

Methyl (2*Z*,4*E*,6*E*)-7-(1-hydroxy-3-methylcyclohex-2-en-1-yl)-3-methylhepta-2,4,6-trienoate 3n

PE-AE: (85:15, v/v), yellow oil (64 mg, 56 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 15.5 Hz, 1H, H_4), 6.60 (dd, *J* = 15.6, 10.6 Hz, 1H, H5), 6.40 (dd, *J* = 15.3, 10.6 Hz, 1H, H_6), 5.97 (d, *J* = 15.3 Hz, 1H, H_7), 5.66 (s, 1H, H_2), 5.31 (q, *J* = 1.6 Hz, 1H, $H_{2'}$), 3.70 (s, 3H, H_9), 2.02 (d, *J* = 1.2 Hz, 3H, H_8), 1.94 (dt, *J* = 10.8, 5.8 Hz, 2H, $H_{4'}$), 1.81 – 1.57 (m, 8H, $H_{5'}$, $H_{6'}$, $H_{7'}$, OH); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (C_1), 151.0 (C_3), 143.8 (C_4), 138.9 ($C_{3'}$), 135.6 (C_6), 129.6 (C_7), 129.0 (C_5), 125.3 (C_2), 116.7 ($C_{2'}$), 71.4 ($C_{1'}$), 51.0 (C_9), 36.3 ($C_{6'}$), 30.0 ($C_{4'}$), 23.7 ($C_{7'}$), 20.8 (C_8), 19.3 ($C_{5'}$); IR (ATR, cm^{-1}): 3391, 2932, 1711, 1609, 1613, 1450, 1378, 1155, 993; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{16}H_{22}NaO_3$ 285.1461, found 285.1462.

Methyl (2*Z*,4*E*)-5-(3-hydroxy-3-methylcyclohex-1-en-1-yl)-3-methylpenta-2,4-dienoate 4

PE-AE: (8:2, v/v), yellow oil (17.0 mg, 20 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 16.2 Hz, 1H, H_5), 6.56 (d, *J* = 16.2 Hz, 1H, H_4), 5.81 (s, 1H, $H_{2'}$), 5.68 (s, 1H, H_2), 3.70 (s, 3H, H_7), 2.40 – 2.30 (m, 1H, $H_{4'}$), 2.24 – 2.16 (m, 1H, $H_{4'}$), 2.04 (t, *J* = 1.6 Hz, 3H, H_6), 1.85 – 1.64 (m, 5H, $H_{5'}$, $H_{6'}$, OH), 1.33 (s, 3H, $H_{7'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8 (C_1), 151.3 (C_3), 138.2 (C_4), 138.0 ($C_{2'}$), 137.5 ($C_{1'}$), 125.5 (C_5), 116.8 (C_2), 68.8 ($C_{3'}$), 51.0 (C_7), 37.8 ($C_{7'}$), 29.2 ($C_{6'}$), 24.5 ($C_{4'}$), 20.8 (C_6), 19.4 ($C_{5'}$); IR (ATR, cm^{-1}): 3459, 2950, 1717, 1445, 1157; HRMS (ESI): *m*/*z* [M+Na]$^+$ calcd. for $C_{14}H_{20}NaO_3$ 259.1304, found 259.1302.

(2*S*,3*S*)-7,9,9-trimethyl-2,3-diphenyl-1,4-dioxaspiro[4.5]dec-6-en-8-one 6

To a solution of (*S*,*S*)-(-)-hydrobenzoin (2.000 g, 9.3 mmol, 1 equiv) in cyclohexane (50 mL), was added the 2,6,6-trimethyl-2-cyclohexene-1,4-dione (3.552 g, 23.3 mmol, 2.5 equiv) and pyridinium p-toluensulfonate (258 mg, 1.0 mmol, 0.11 equiv). Then, the reaction mixture was heated under reflux overnight using a *Dean Stark* trap to remove water. The reaction was cooled, diluted with EtOAc/H_2O (30 mL/ 20 mL) and extracted with EtOAc (2 x 30 mL). The organic phases were combined, dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (9:1, v/v), to provide **6** (3.130 g, 96 %) as a pale yellow oil. ^{1}H NMR (250 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 6H, $H_{3'}$, $H_{4'}$), 7.25 – 7.20 (m, 4H, $H_{2'}$), 6.63 (t, *J* = 1.2, 1H, H2'), 4.78 (m, 2H, H_2, H_3), 2.45 (d, *J* = 14.0 Hz, 1H, H_{10}), 2.36 (dd, *J* = 14.0, 1.4 Hz, 1H, H_{10}), 1.89 (d, *J* = 1.4 Hz, 3H,

H_{11}), 1.30 (s, 3H, H_{12}), 1.28 (s, 3H, H_{12}); ^{13}C NMR (63 MHz, Chloroform-*d*) δ 204.2 (C_8), 140.4 (C_6), 136.1 (C_7), 135.9 ($C_{1'}$), 135.9 ($C_{1'}$), 128.5 ($C_{3'}$, $C_{4'}$), 126.7 ($C_{2'}$), 126.7 ($C_{2'}$), 104.4 (C_5), 85.2 (CH), 85.2 (CH), 47.4 (C_{10}), 42.3 (C_9), 27.0 (C_{12}), 26.3 (C_{12}), 16.4 (C_{11}); IR (ATR, cm^{-1}): 3032, 2922, 1674, 1094, 896; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{23}H_{24}NaO_3$ 371.1618, found 371.1617.

(2*S*,3*S*)-8-ethenyl-7,9,9-trimethyl-2,3-diphenyl-1,4-dioxaspiro[4.5]dec-6-en-8-ol 7

To a solution of 1M vinylmagnesium bromide (4.3 mL, 4.3 mmol 5 equiv) in dry THF (10, mL) at 0 °C, was added **6** (300 mg, 0.86 mmol, 1 equiv). The reaction mixture was stirred at 0 °C for 1 hour under inert atmosphere. Then a saturated solution of NH_4Cl (50 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 40 mL). The organic phases were combined, dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-AE: (8:2, v/v), to provide **7** (316 mg, 100 %) as a colorless gum. ^{1}H NMR (250 MHz, Chloroform-*d*) δ 7.34 – 7.30 (m, 6H, $H_{3'}$, $H_{4'}$), 7.25 – 7.20 (m, 4H, $H_{2'}$), 5.94 (dd, *J* = 17.3, 10.7 Hz, 1H, H_{11}), 5.78 – 5.73 (m, 1H, H_6), 5.40 – 5.23 (m, 2H, H_{12}), 4.84 – 4.69 (m, 2H, H_2, H_3), 2.31 – 1.97 (m, 2H, H_{10}), 1.77 (d, *J* = 1.4 Hz, 3H, H_{14}), 1.58 (s, 1H, OH), 1.18 (s, 3H, H_{13}), 1.01 (s, 3H, H_{13}); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8 (C_7), 138.9 (C_{11}), 136.8 ($C_{1'}$), 136.6 ($C_{1'}$), 128.6 (CH_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}), 127.0 (CH_{Ar}), 127.0 (CH_{Ar}), 126.9 (CH_{Ar}), 126.8 (CH_{Ar}), 125.0 (C_6), 114.8 (C_{12}), 105.7 (C_5), 85.0 (CH), 84.7 (CH), 79.5 (C_8), 46.1 (C_{10}), 38.9 (C_9), 24.8 (C_{13}), 23.2 (C_{13}), 17.9 (C_{14}); IR (ATR, cm^{-1}): 3499, 2969, 2875, 1666, 1604, 1439, 1093, 972; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{25}H_{28}NaO_3$ 399.1930, found 399.1928. HLPC: Hitachi Chiralpack IA+pre-colomn 250X4.6 mm; det DAD 254 nm; Mobile phase: 95% acetonitrile, 5% Ethanol, flow: 0,9 $mLmin^{-1}$; T = 30 °C; P = 40 bar; sample preparation: conc. 0.5 $mgmL^{-1}$ in Acetonitrile/Ethanol (95/5), 10 µL injected. Retention time: t1 = 4.096 min for 66.88 %, t2 = 4.338 min for 33.12 %.

Methyl(2*Z*,4*E*)-5-[(2*S*,3*S*)-8-hydroxy-7,9,9-trimethyl-2,3-diphenyl-1,4-dioxaspiro[4.5]dec-6-en-8-yl]-3-methylpenta-2,4-dienoate 8

2 (100 mg, 0.44 mmol), **7** (250 mg, 0.53 mmol), silver carbonate (153 mg, 0.55 mmol) and palladium acetate (10 mg, 5 % mmol) were placed in a round bottom flask, stirred at 50 °C for 17 h. After completion, the reaction mixture was diluted in EtOAc (5 mL) and in a saturated solution of ammonium chloride (5 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL). Then the combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-EA: (8:2, v/v), to provide **8** (88 mg, 96 %) as a pale yellow gum. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 16.0, 11.8 Hz, 1H, H_5), 7.36 – 7.27 (m, 5H, H_{Ar}), 7.28 – 7.18 (m, 5H, H_{Ar}), 6.16 (d, *J* = 15.9 Hz, 1H, H_4), 5.80 – 5.68 (m, 2H, H_2, $H_{6'}$), 4.85 – 4.68 (m, 2H, $H_{2'}$, $H_{3'}$), 3.68 (s, 3H, H_7), 2.33 – 2.01 (m, 2H, $H_{10'}$), 2.00 (s, 3H, H_6), 1.78 (s, 3H, $H1_{2'}$), 1.19 (s, 3H, $H_{11'}$), 1.01 (s, 3H, $H_{11'}$); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7 (C_1), 150.2 ($C_{7'}$), 141.9 (C_3), 138.4 (C_4), 136.9 (C_{Ar}), 136.7 (C_{Ar}), 128.6 (CH_{Ar}), 128.6 (CH_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 127.3 (CH_{Ar}), 127.0 (CH_{Ar}), 127.0 (CH_{Ar}), 126.9 (CH_{Ar}), 126.7 (CH_{Ar}), 125.1 (C_2), 117.4 ($C_{6'}$), 105.7 ($C_{5'}$), 85.1 (CH), 84.8 (CH), 79.3 ($C_{8'}$), 51.2 (C_7), 46.4 ($C_{10'}$), 39.6 ($C_{9'}$), 25.3 ($C_{11'}$), 23.6 ($C_{11'}$), 21.5 (C_6), 18.0 ($C_{12'}$); IR (ATR, cm^{-1}): 3460, 2969, 2875, 1717, 1666, 1604, 1439, 1157, 1093, 972; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{30}H_{24}NaO_5$ 497.2298, found 497.2292.

(2*Z*,4*E*)-5-(1-hydroxy-2,6,6-trimethyl-4-oxocyclohex-2-en-1-yl)-3-methylpenta-2,4-dienoic acid (abscisic acid, ABA). [5,6]

To **8** (178.3 mg, 0.38 mmol, 1 eq) in THF (2 ml), was added a 1N solution of sodium hydroxide (300 µL, 4 equiv) and tetrabutylammonium chloride (2 drops). The mixture was stirred at 40 °C for 2 hours. After completion the reaction was concentrated under reduced pressure. The crude mixture was placed at 0 °C and a 1N solution of HCl (4 mL, 10 equiv) was added. The reaction was stirred at room temperature for 1 hour. Next, the reaction mixture was diluted in EtOAc (5 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL). Then the combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel PE-EA-AcOH: (7:2.9:0.1, v/v/v) to provide **ABA** as a grey solid, which was recrystallized in a mixture of

heptane-EA: (9:1, v/v) to provide **ABA** (62 mg, 62 %) as a white solid. mp: 159 – 162 °C (Litt 161 – 163 °C);[25b] ^{1}H NMR (400 MHz, Methanol-*d4*) δ 7.77 (d, *J* = 16.2 Hz, 1H, H_4), 6.23 (d, *J* = 16.1 Hz, 1H, H_5), 5.92 (s, 1H, $H_{3'}$), 5.75 (s, 1H, H_2), 2.53 (d, *J* = 17.0 Hz, 1H, $H_{5'}$), 2.26 (s, 1H, OH), 2.18 (d, *J* = 16.9 Hz, 1H, $H_{5'}$), 2.03 (s, 3H, H_6), 1.92 (s, 3H, $H_{7'}$), 1.06 (s, 3H, $H_{8'}$), 1.03 (s, 3H, $H_{8'}$); ^{13}C NMR (101 MHz, Methanol-*d4*) δ 201.0 ($C_{4'}$), 169.7 (C_1), 166.6 ($C_{2'}$), 150.6 (C_3), 137.7 (C_5), 129.5 (C_4), 127.5 ($C_{3'}$), 120.0 (C_2), 80.6 ($C_{1'}$), 50.7 ($C_{5'}$), 42.8 ($C_{6'}$), 24.7 ($C_{8'}$), 23.6 ($C_{8'}$), 21.2 (C_6), 19.6 ($C_{7'}$). IR (ATR, cm^{-1}): 3389, 2957, 1676, 1643, 1597, 1196, 1023, 979; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd. for $C_{15}H_{20}NaO_4$ 287.1253, found 287.1254. HLPC: Hitachi Chiralpack IA+pre-colomn 250X4.6 mm; det DAD max plot; Mobile phase: 90% heptane, 10% Ethanol, flow: 1 $mLmin^{-1}$; T = 30 °C; P = 40 bar; sample preparation: conc. 0.5 $mgmL^{-1}$ in Heptane/Ethanol (90/10), 20 μL injected. Retention time: t1 = 10.713 min for 35.69 %, t2 = 23.773 min for 61.79 %.

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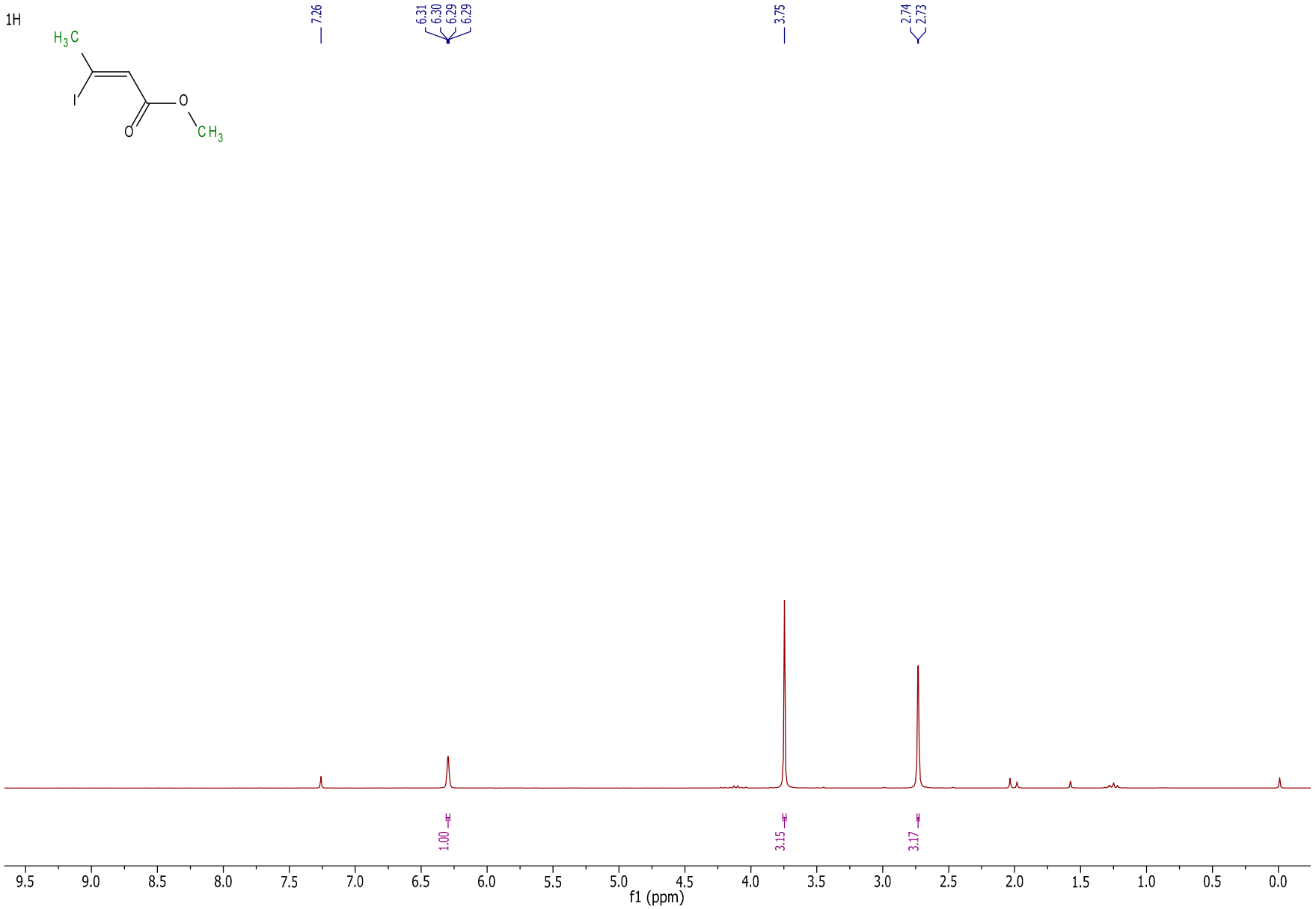
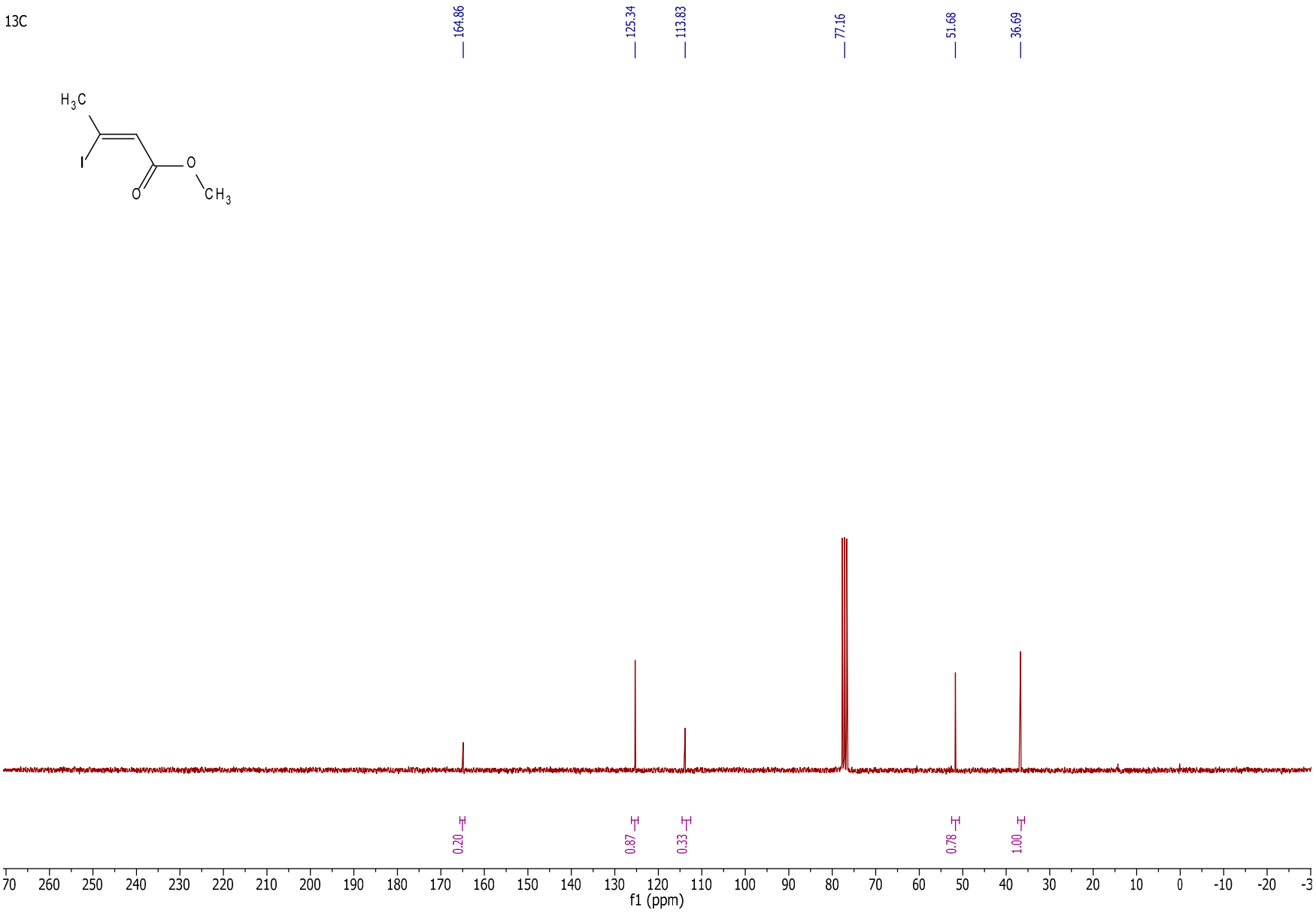
1.5 ^{1}H NMR and ^{13}C NMR Spectra of all Products

NMR Spectra – Iodine compounds

Compound 2 :

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77.16
51.68
36.69
H3C
I
O
O
CH3
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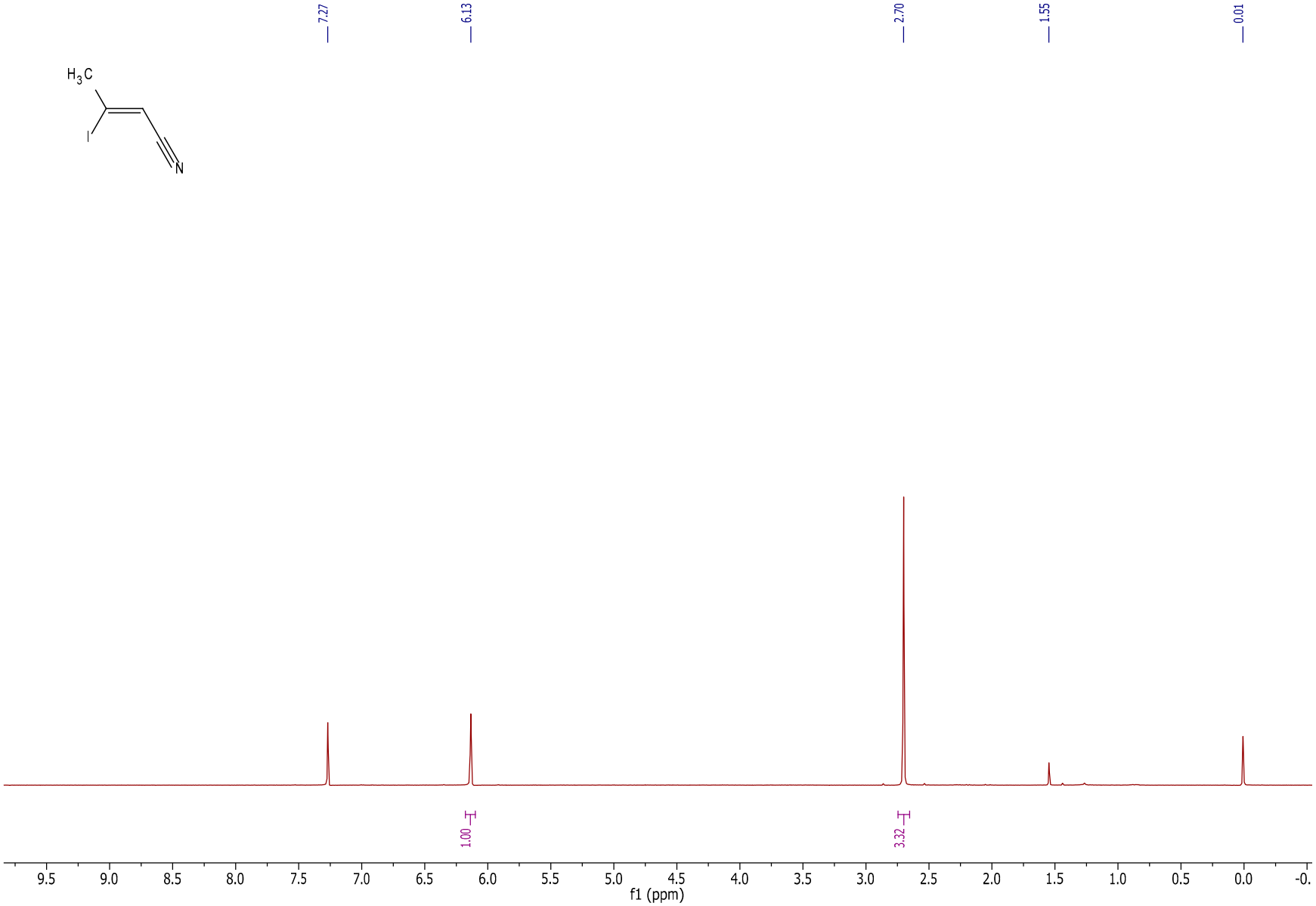
0.87
0.33
0.78
1.00
70 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
f1 (ppm)

Compound 2a :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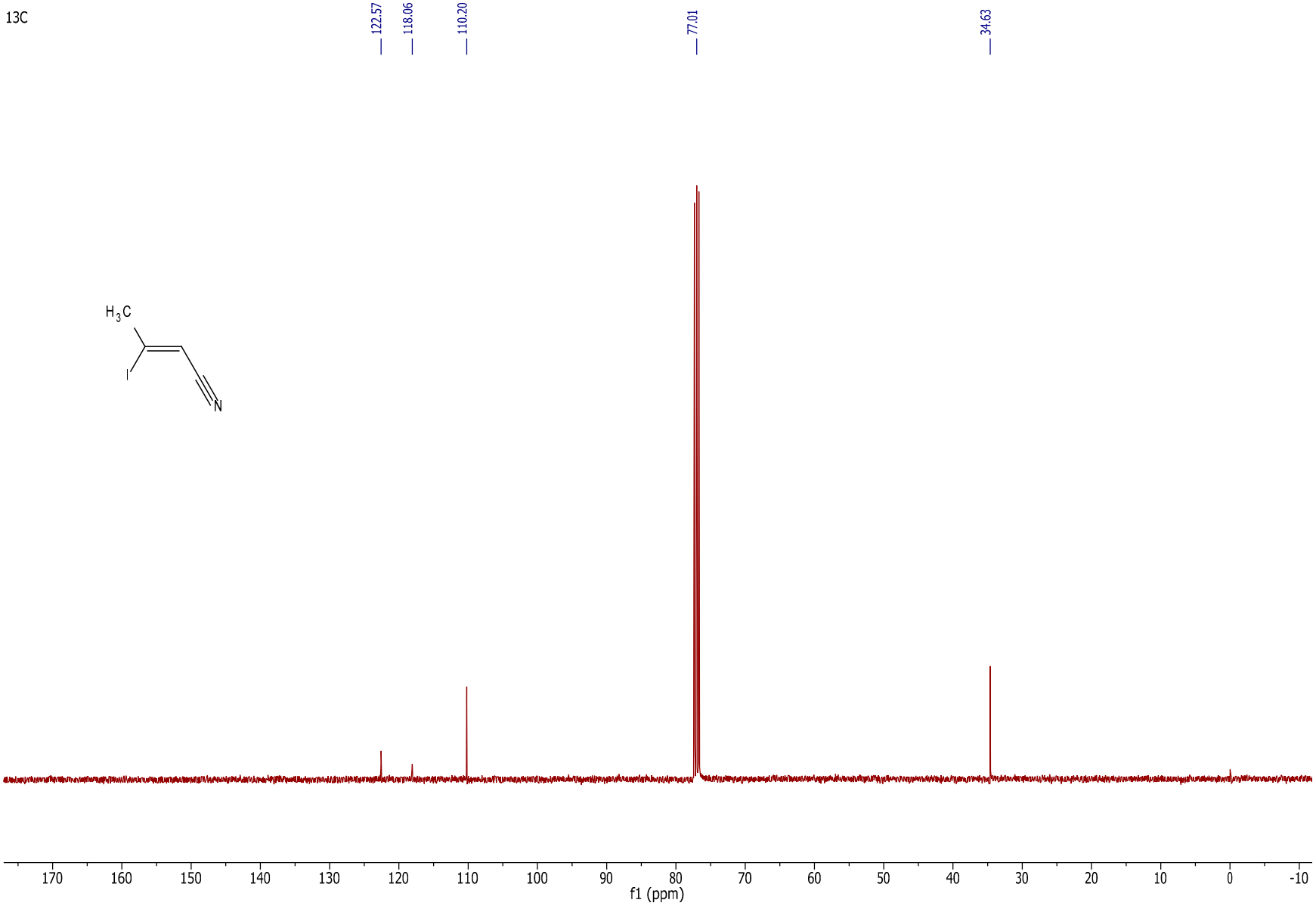
6.13
2.70
1.55
0.01
H3C
I
N
1.00
3.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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34.63
H3C
N
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160
150
140
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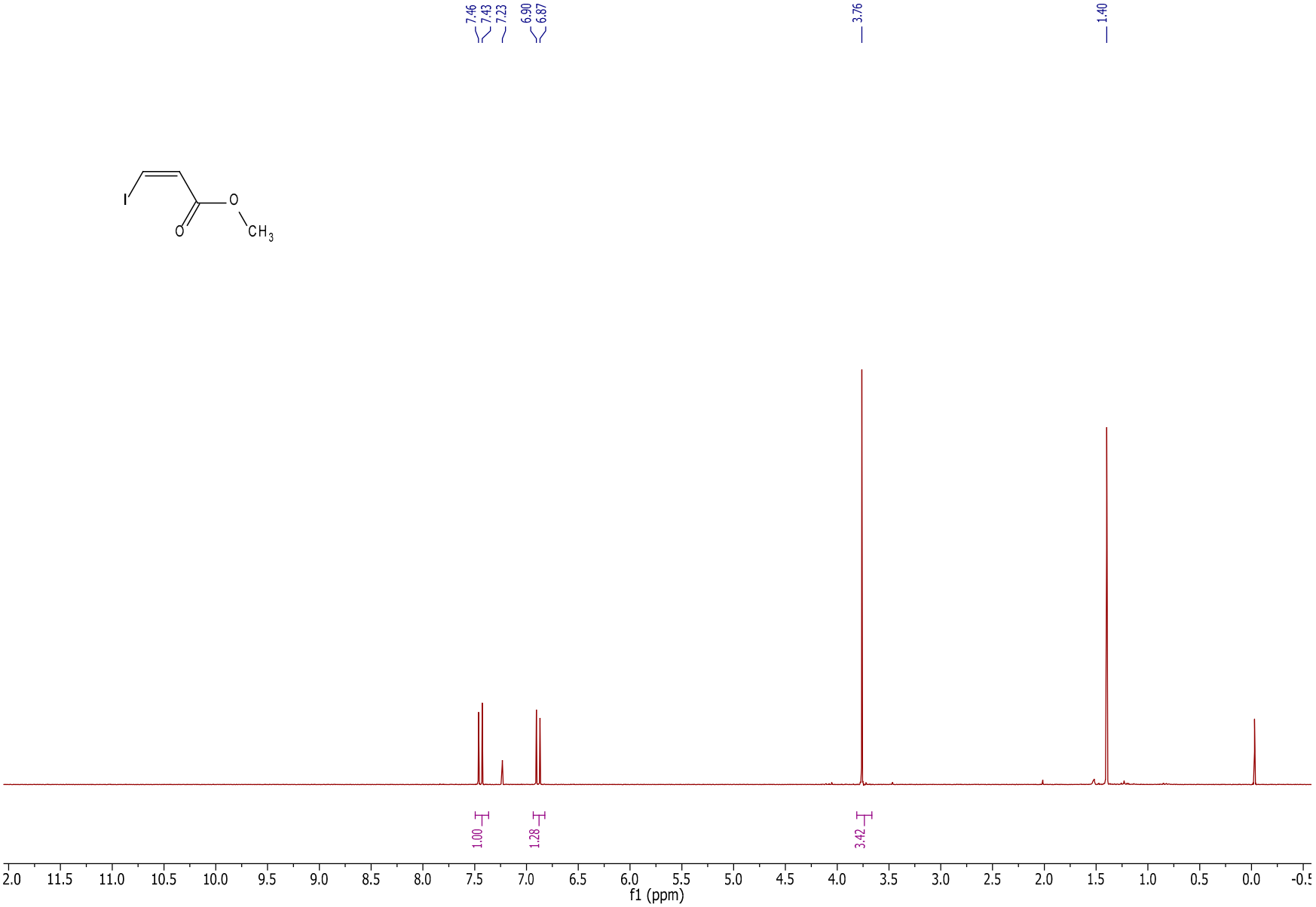
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 2b :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6.87
3.76
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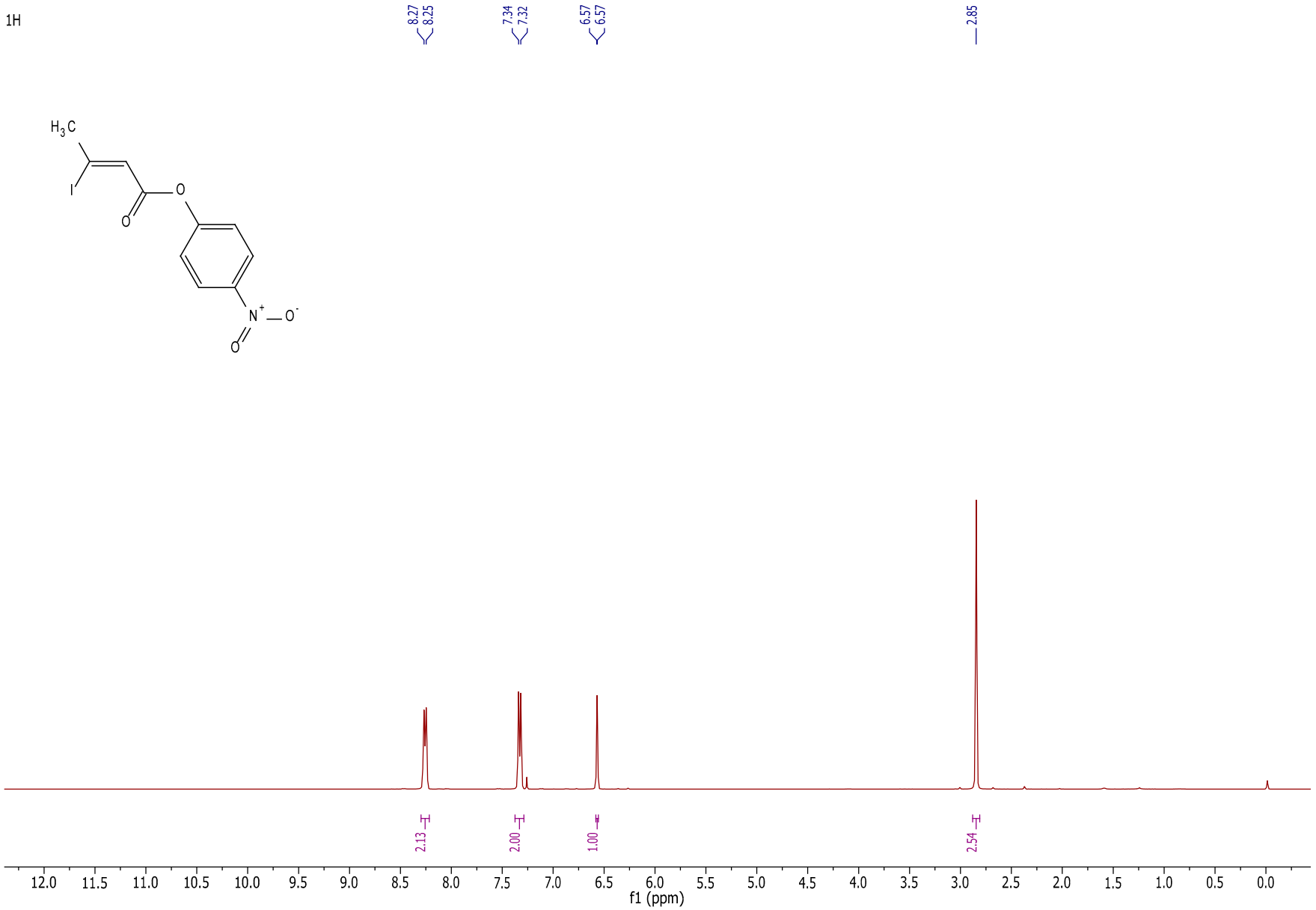
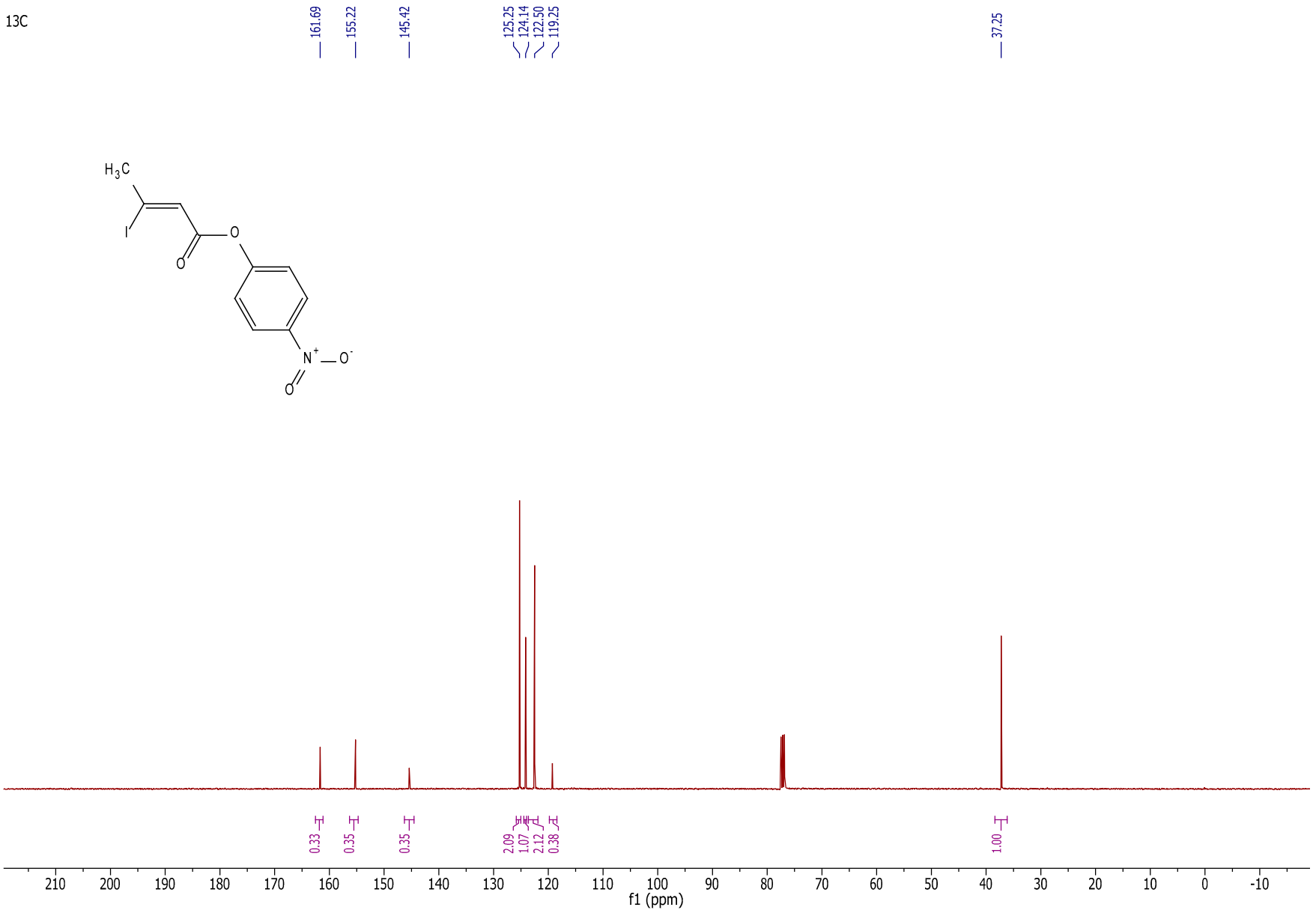
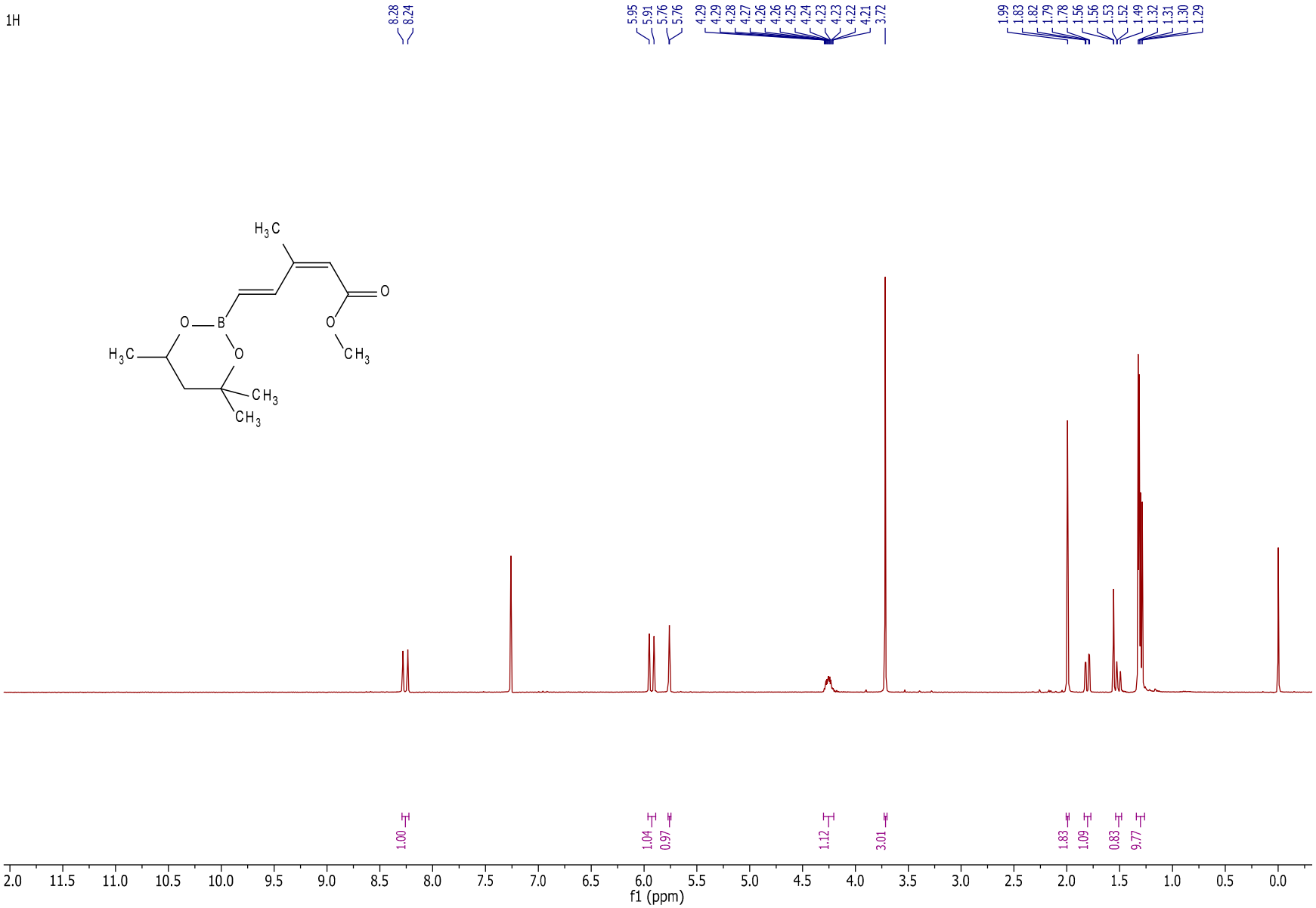
I
O
O
CH3
1.00
1.28
3.42
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

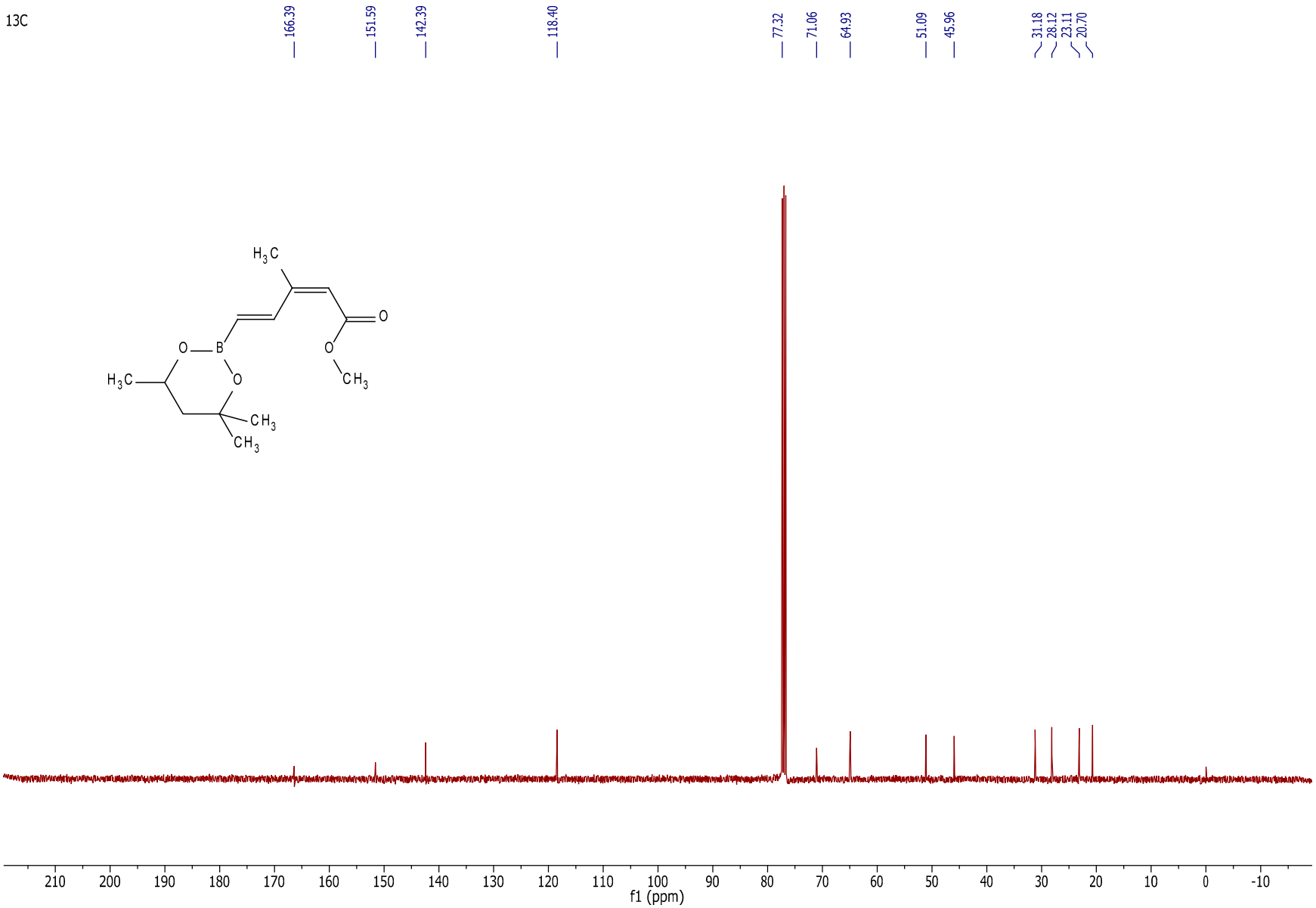
Compound 2c :


1H
8.27
8.25
7.34
7.32
6.57
6.57
2.85
H3C
I
O
O
N+
O-
O
2.13
2.00
1.00
2.54
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

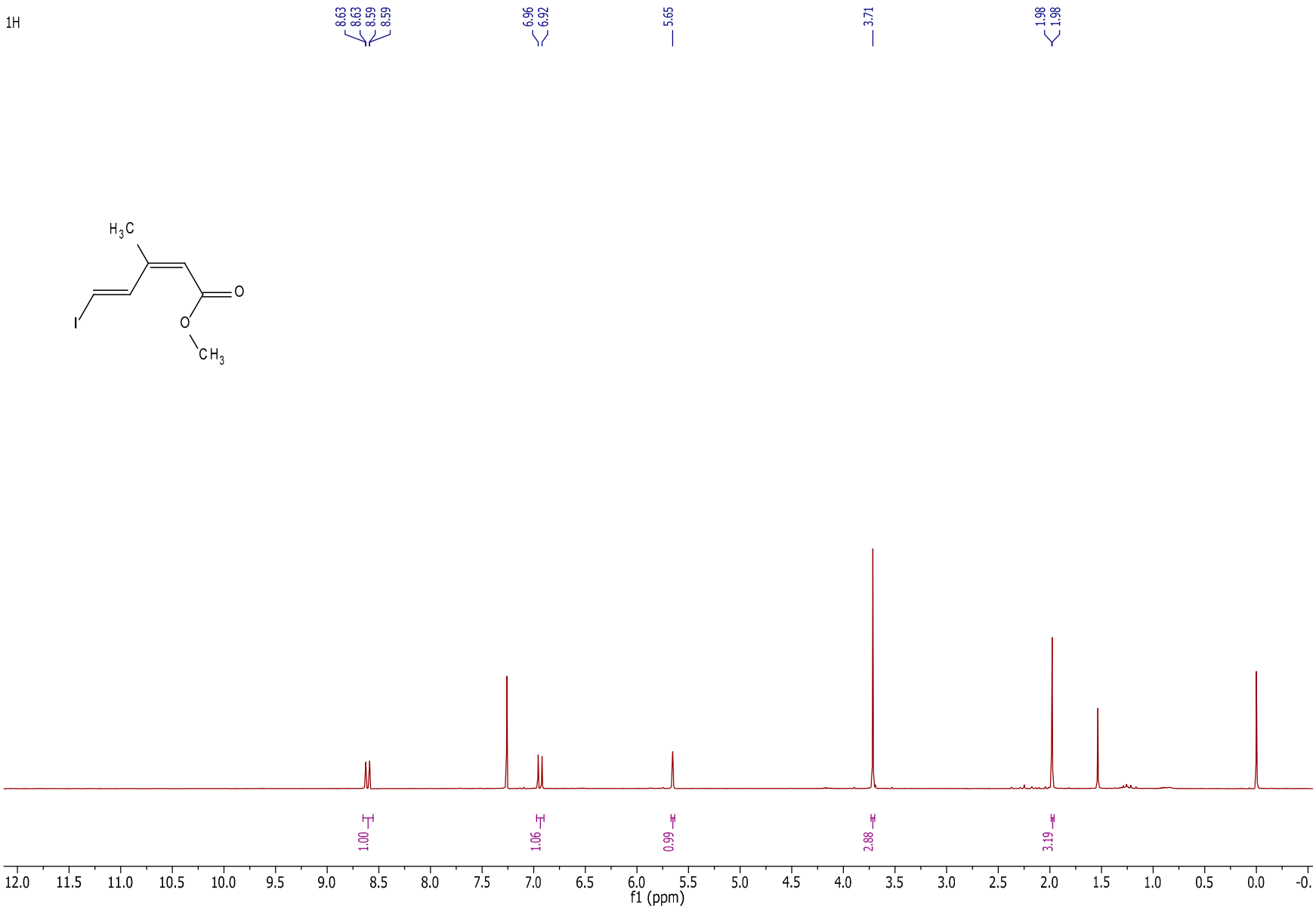

13C
161.69
155.22
145.42
125.25
124.14
122.50
119.25
37.25
H3C
I
O
O
N+
O-
O
0.33
0.35
0.35
2.09
1.07
2.12
0.38
1.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

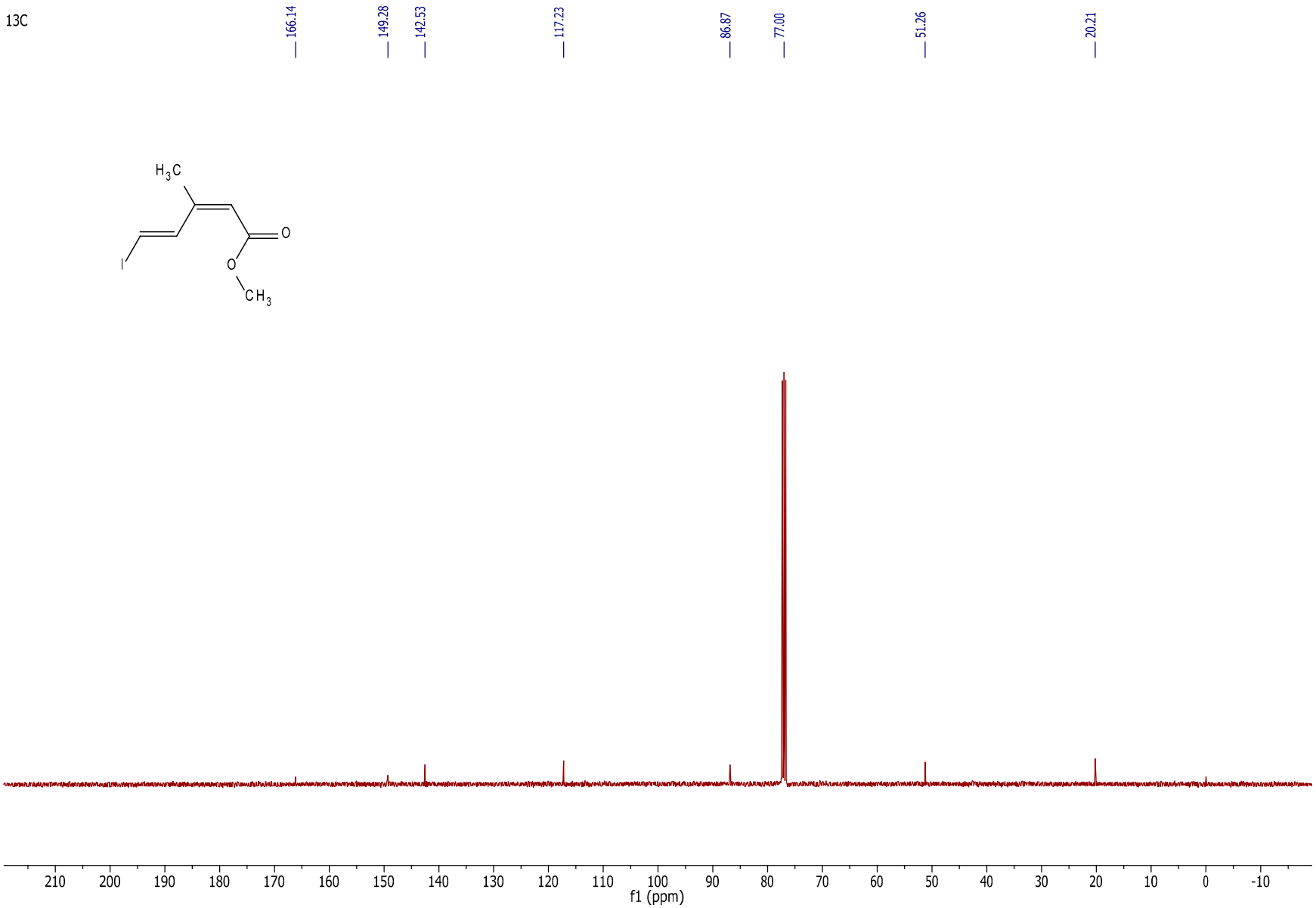
Compound 2d :


1H
8.28
8.24
5.95
5.91
5.76
5.76
4.29
4.29
4.28
4.27
4.26
4.26
4.25
4.24
4.23
4.23
4.22
4.21
3.72
1.99
1.83
1.82
1.79
1.78
1.56
1.56
1.53
1.52
1.49
1.32
1.31
1.30
1.29
H3C
O
B
O
O
H3C
O
CH3
CH3
CH3
1.00
1.04
0.97
1.12
3.01
1.83
1.09
0.83
9.77
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

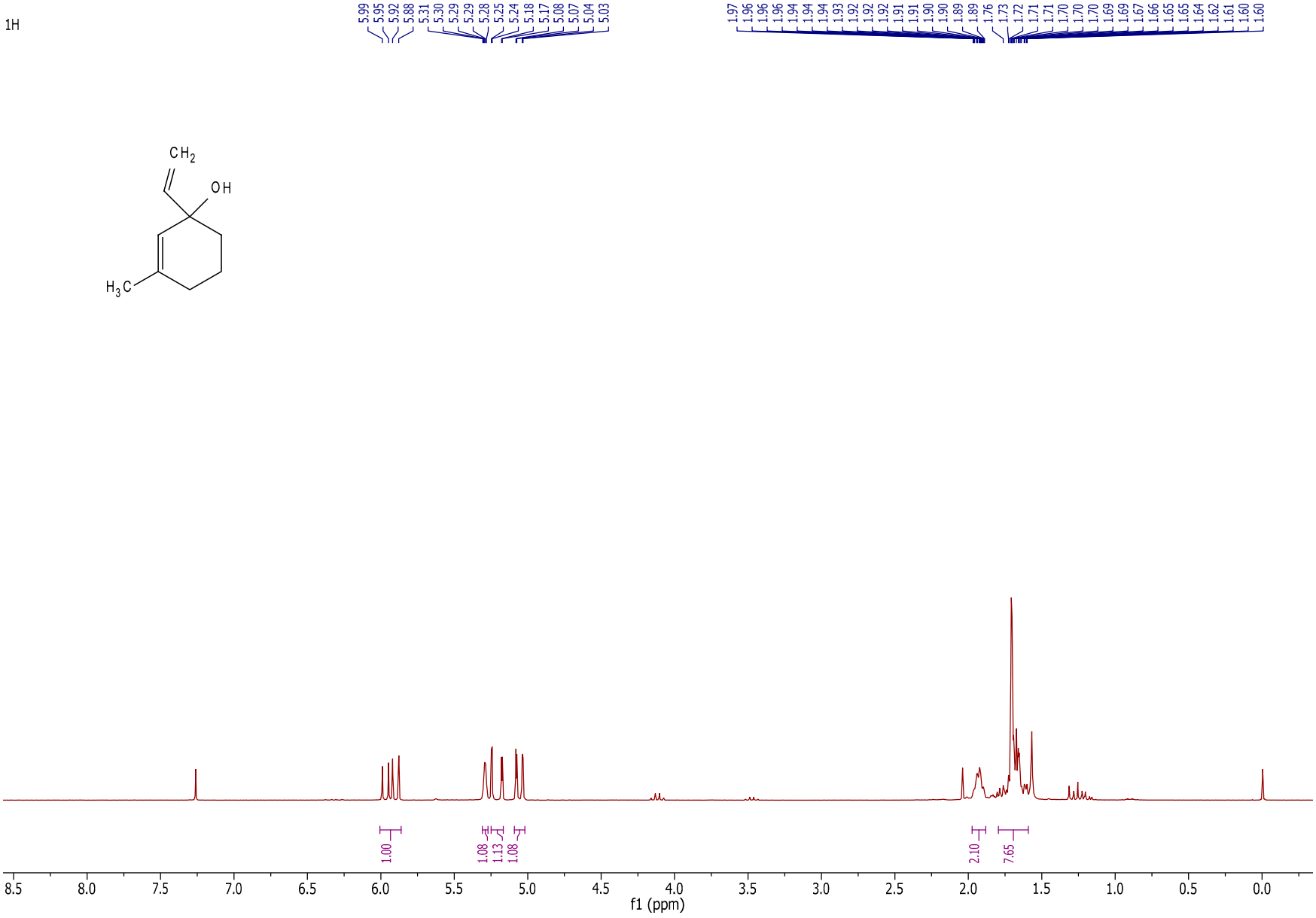

13C
166.39
151.59
142.39
118.40
77.32
71.06
64.93
51.09
45.96
31.18
28.12
23.11
20.70
H3C
O
B
O
O
H3C
O
CH3
CH3
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

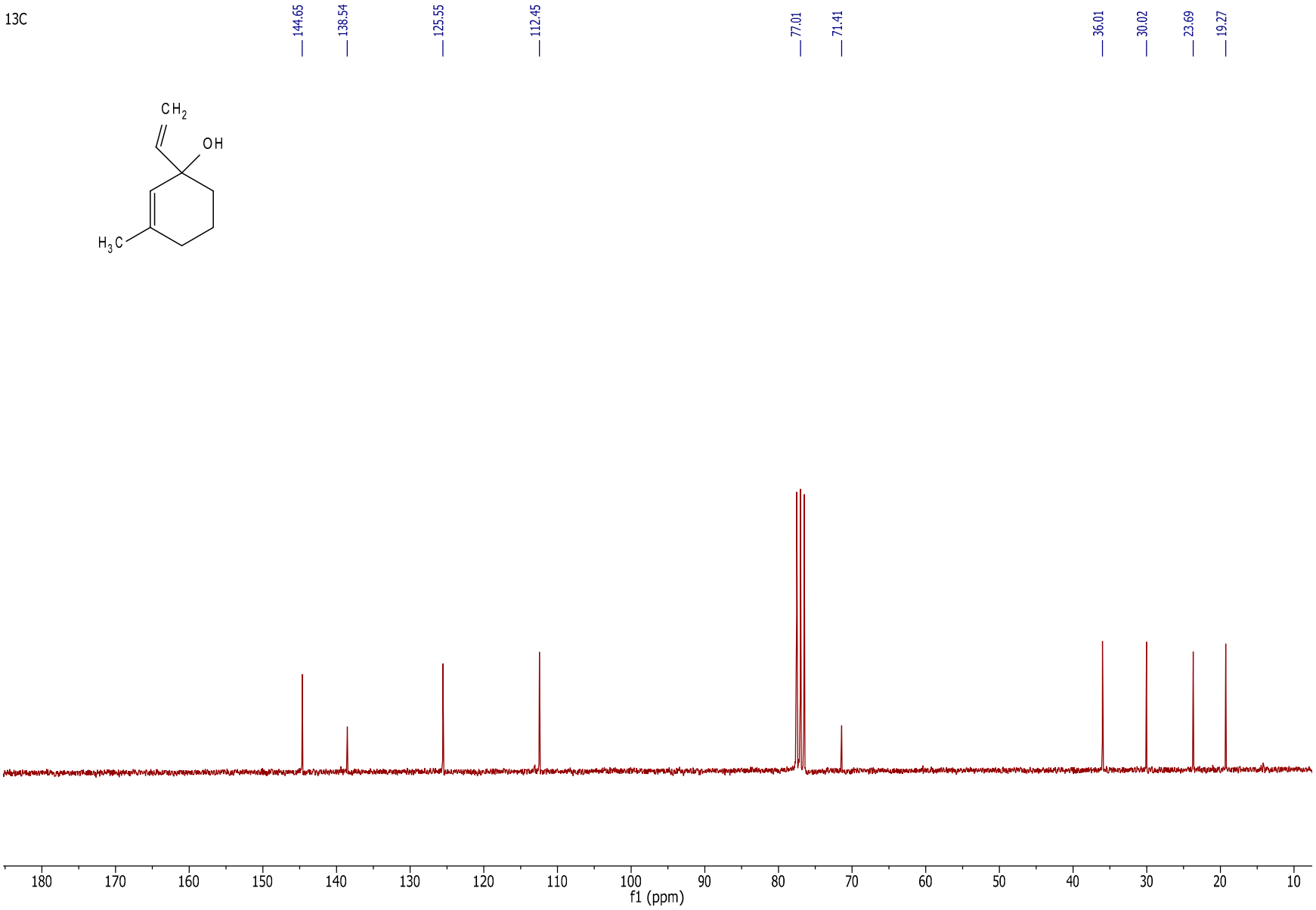
Compound 2e :

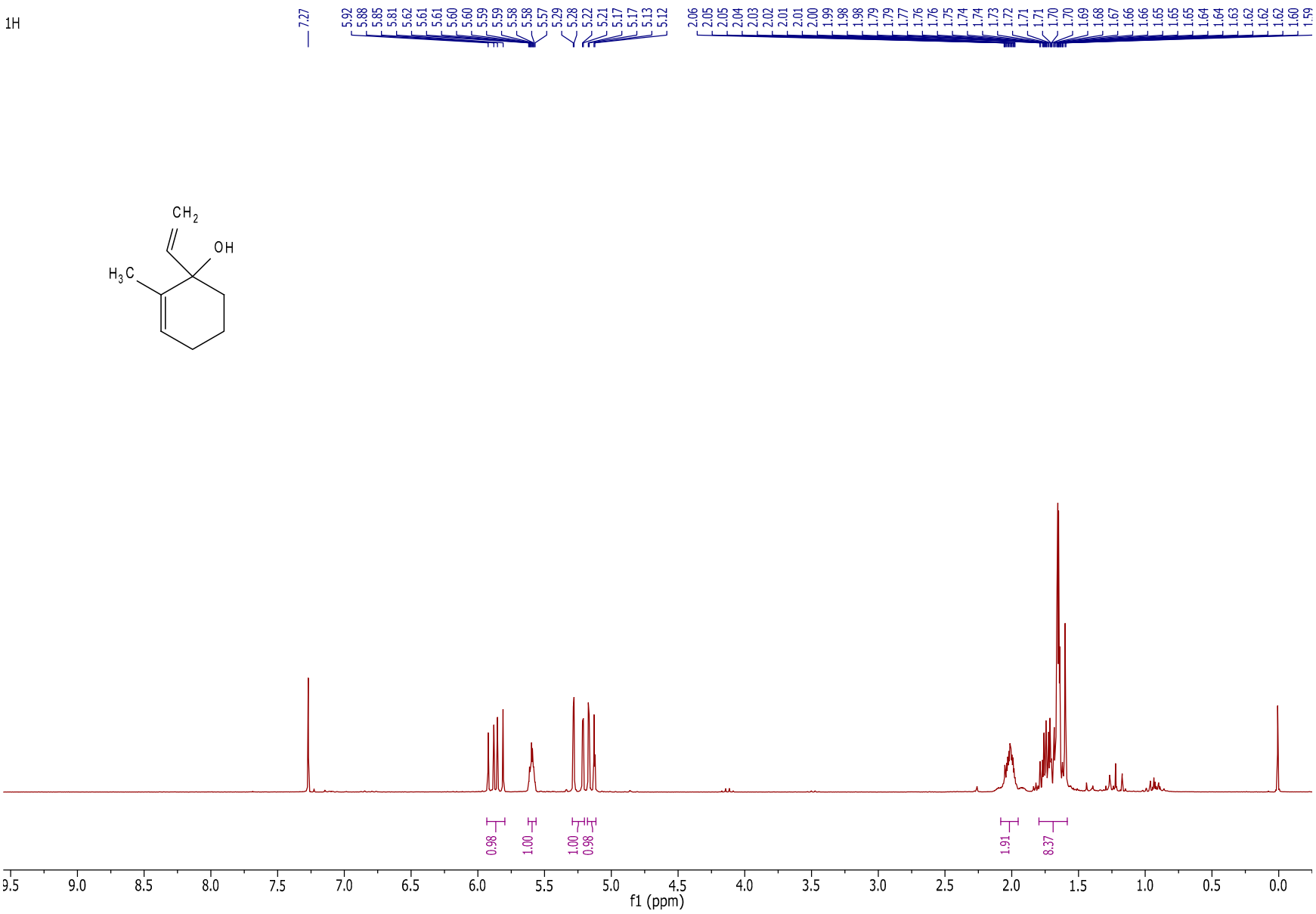

1H
8.63
8.63
8.59
8.59
6.96
6.92
5.65
3.71
1.98
1.98
H3C
O
O
I
CH3
1.00
1.06
0.99
2.88
3.19
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

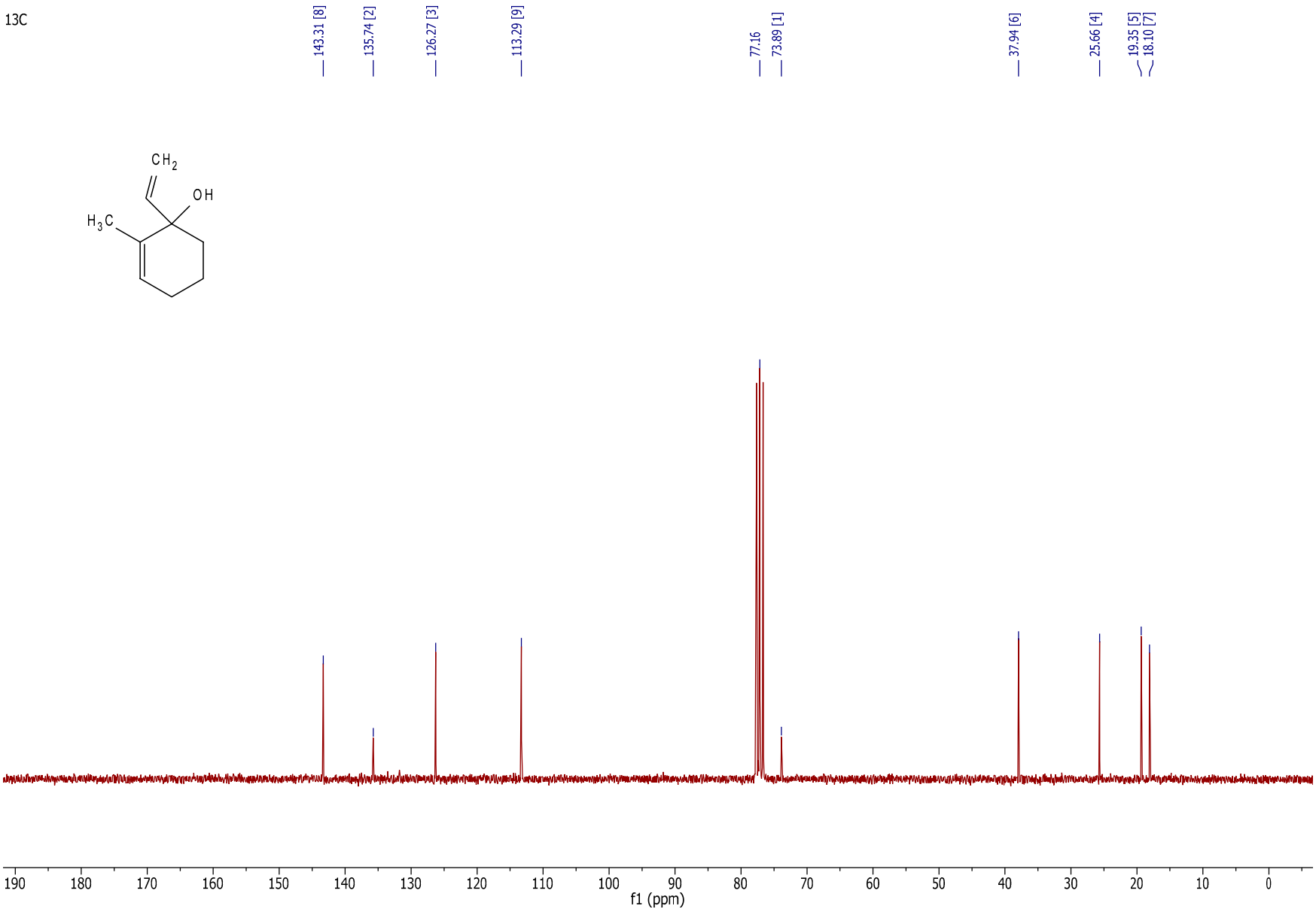

13C
166.14
149.28
142.53
117.23
86.87
77.00
51.26
20.21
H3C
O
O
CH3
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

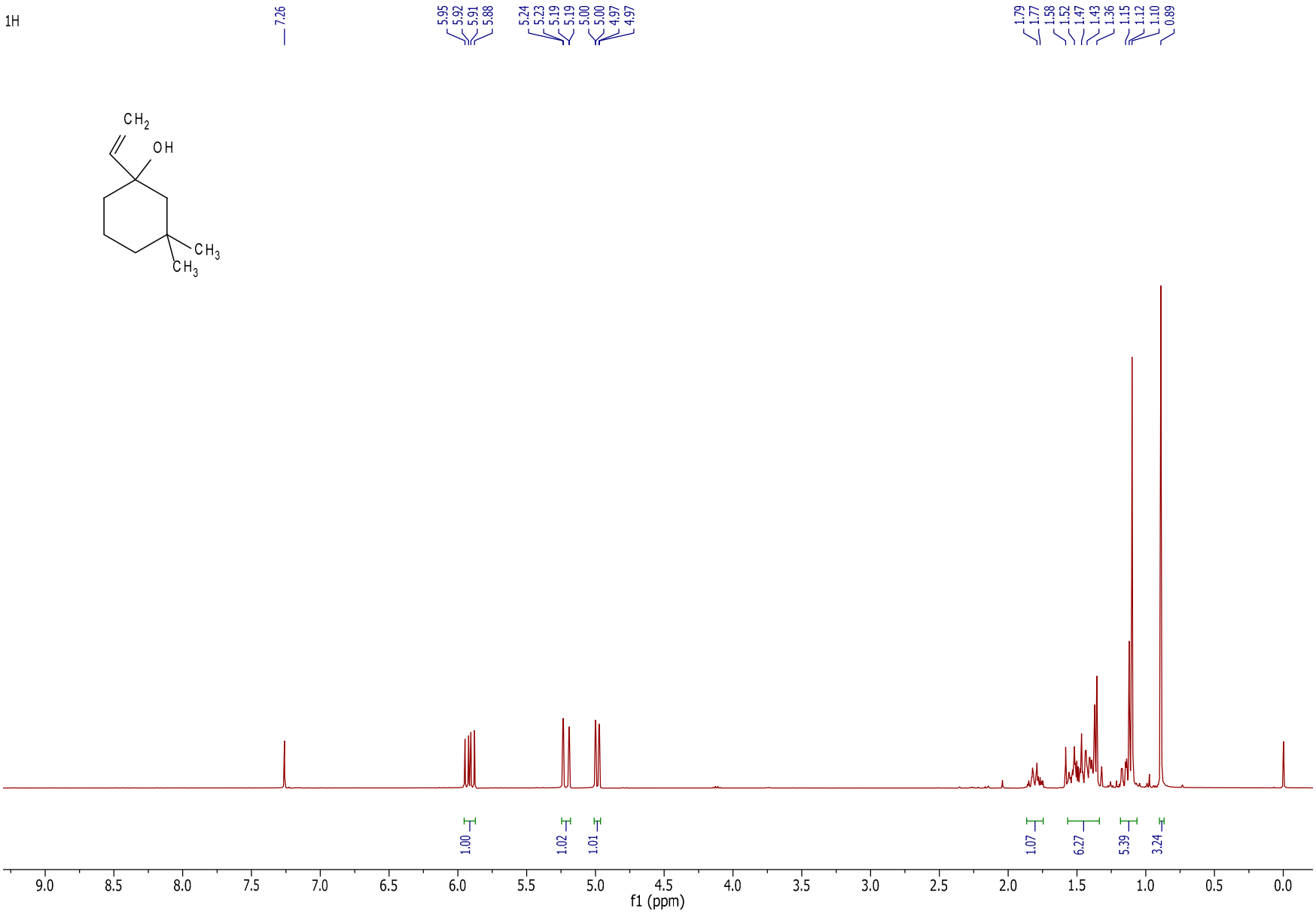
NMR Spectra – Vinyl compounds

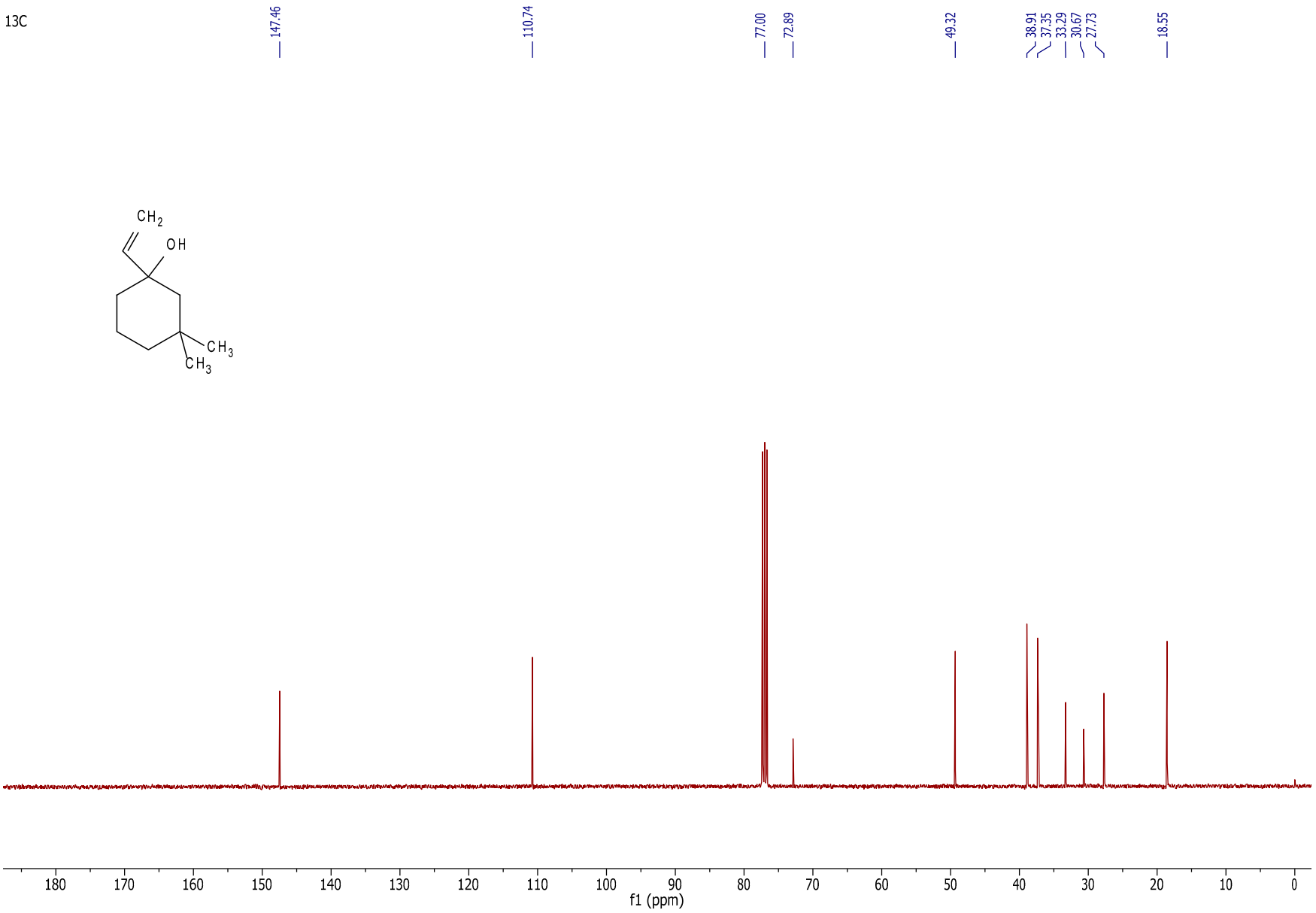


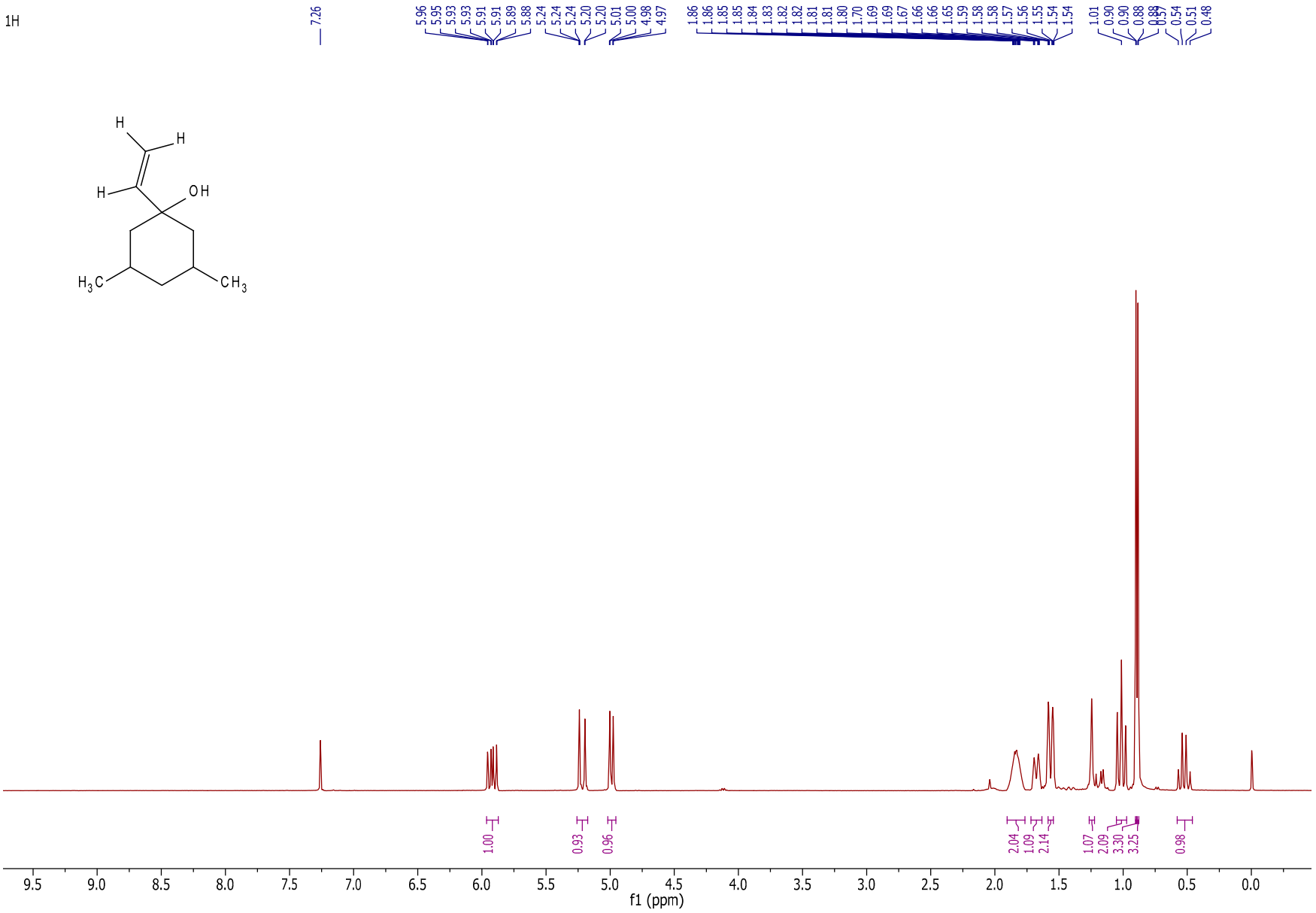

13C
144.65
138.54
125.55
112.45
77.01
71.41
36.01
30.02
23.69
19.27
CH2
OH
H3C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

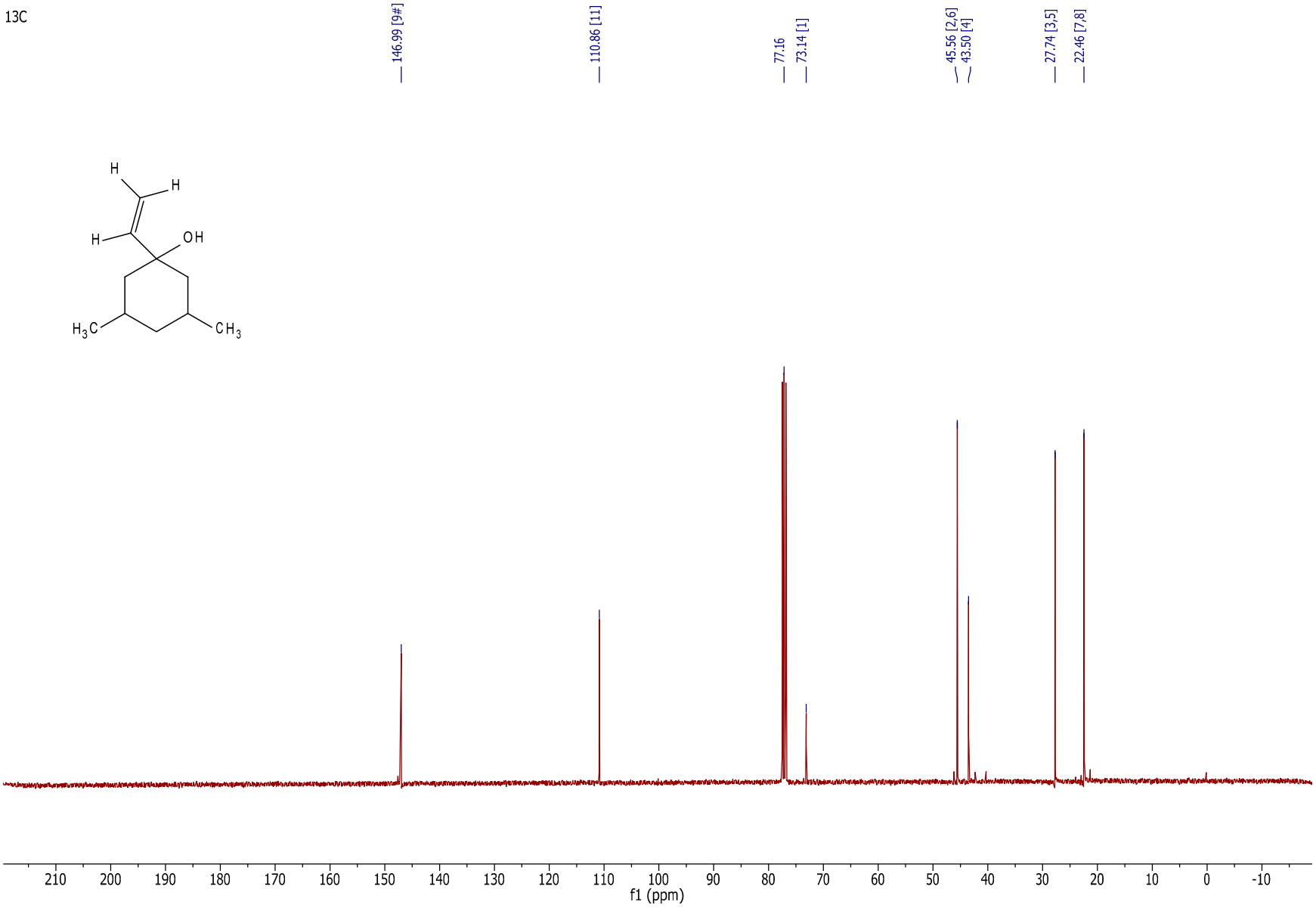

1H
7.27
5.92
5.88
5.85
5.81
5.62
5.61
5.61
5.60
5.60
5.59
5.59
5.58
5.58
5.57
5.29
5.28
5.22
5.21
5.17
5.17
5.13
5.12
2.06
2.05
2.05
2.04
2.03
2.02
2.01
2.01
2.00
1.99
1.98
1.98
1.79
1.79
1.77
1.76
1.76
1.75
1.74
1.74
1.73
1.72
1.71
1.71
1.70
1.70
1.69
1.68
1.67
1.66
1.66
1.65
1.65
1.65
1.64
1.64
1.63
1.62
1.62
1.62
1.60
1.59
CH2
OH
H3C
0.98
1.00
1.00
0.98
1.91
8.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

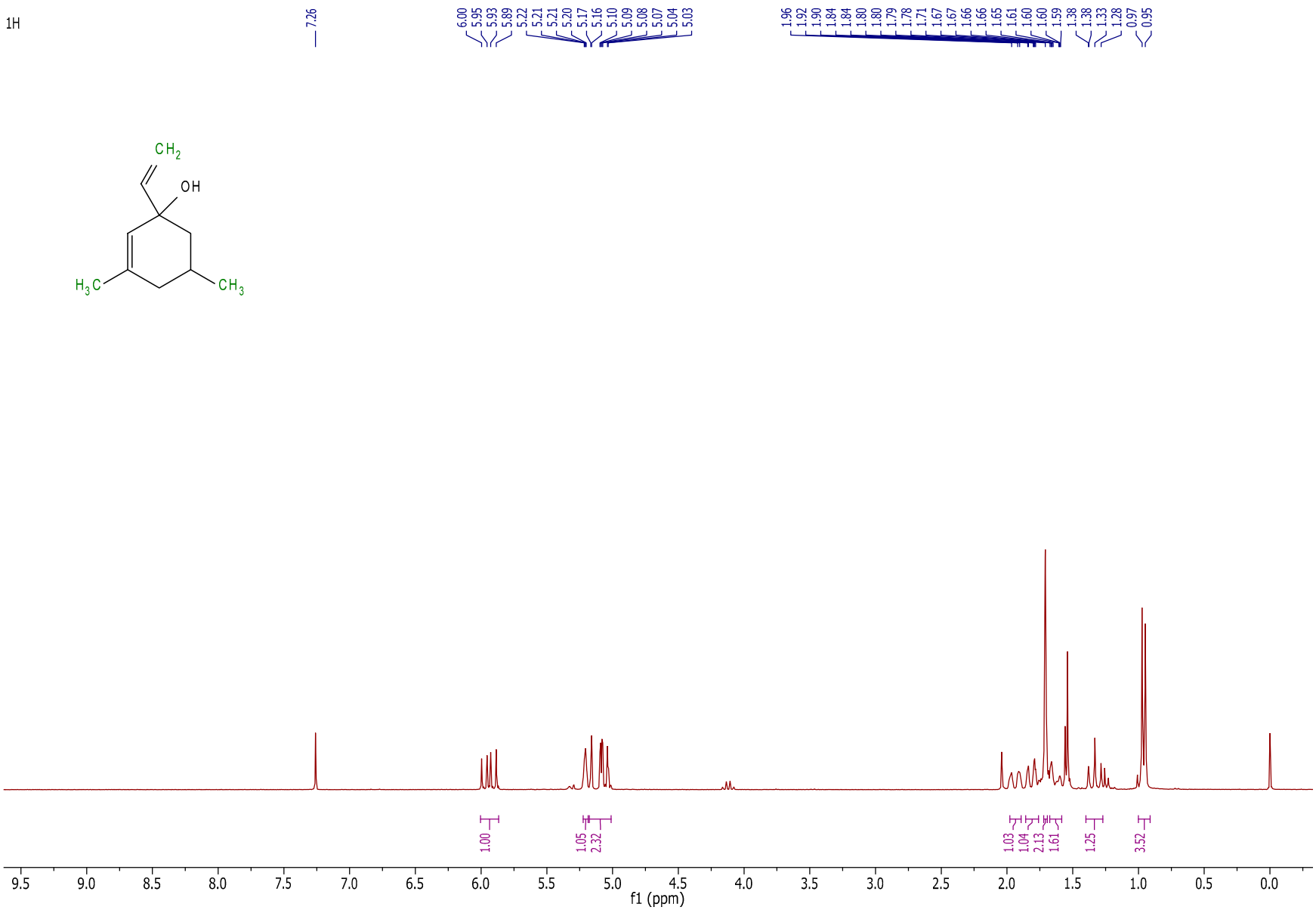

13C
143.31 [8]
135.74 [2]
126.27 [3]
113.29 [9]
77.16
73.89 [1]
37.94 [6]
25.66 [4]
19.35 [5]
18.10 [7]
CH2
OH
H3C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

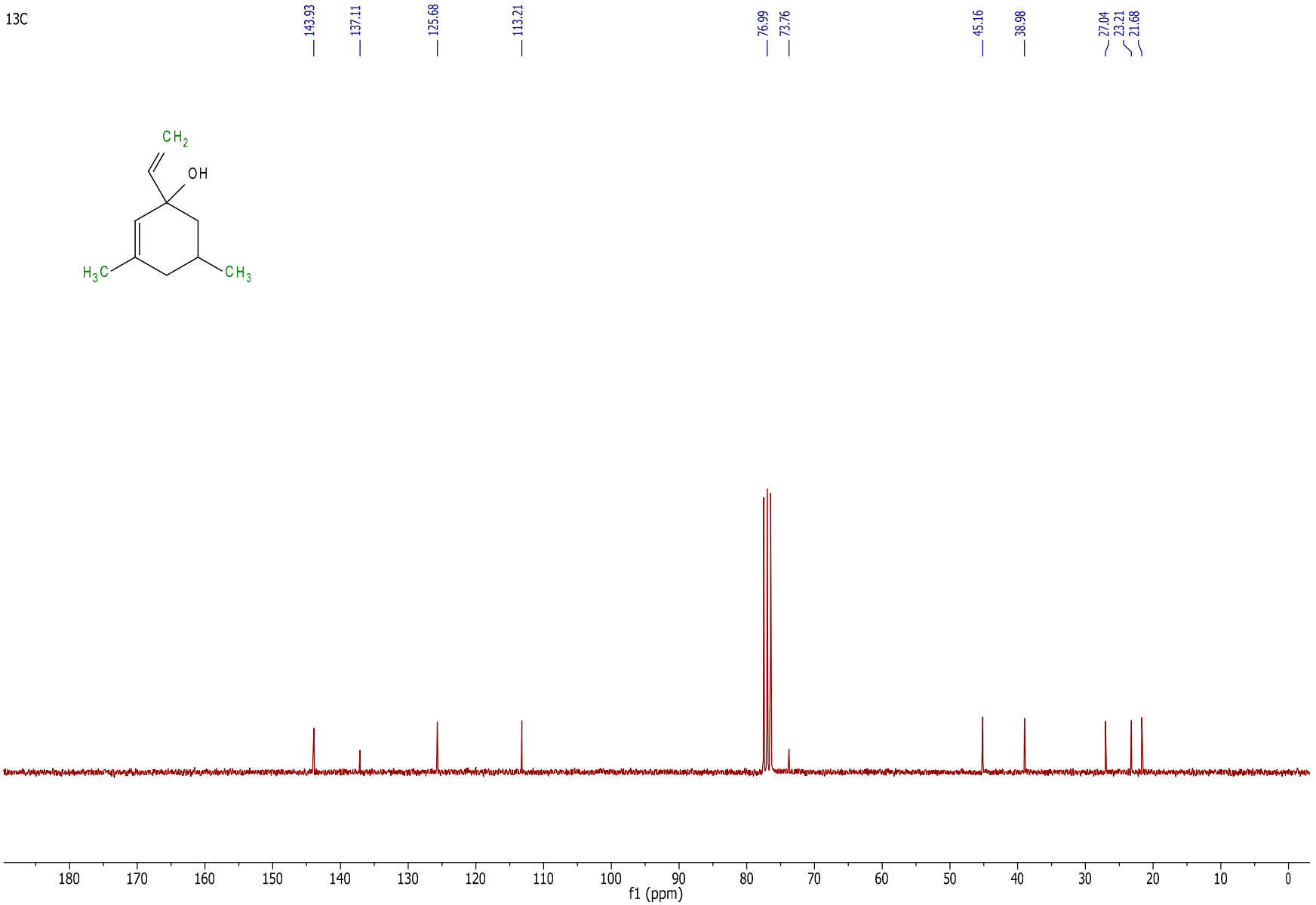

1H
7.26
5.95
5.92
5.91
5.88
5.24
5.23
5.19
5.19
5.00
5.00
4.97
4.97
1.79
1.77
1.58
1.52
1.47
1.43
1.36
1.15
1.12
1.10
0.89
CH2
OH
CH3
CH3
1.00
1.02
1.01
1.07
6.27
5.39
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

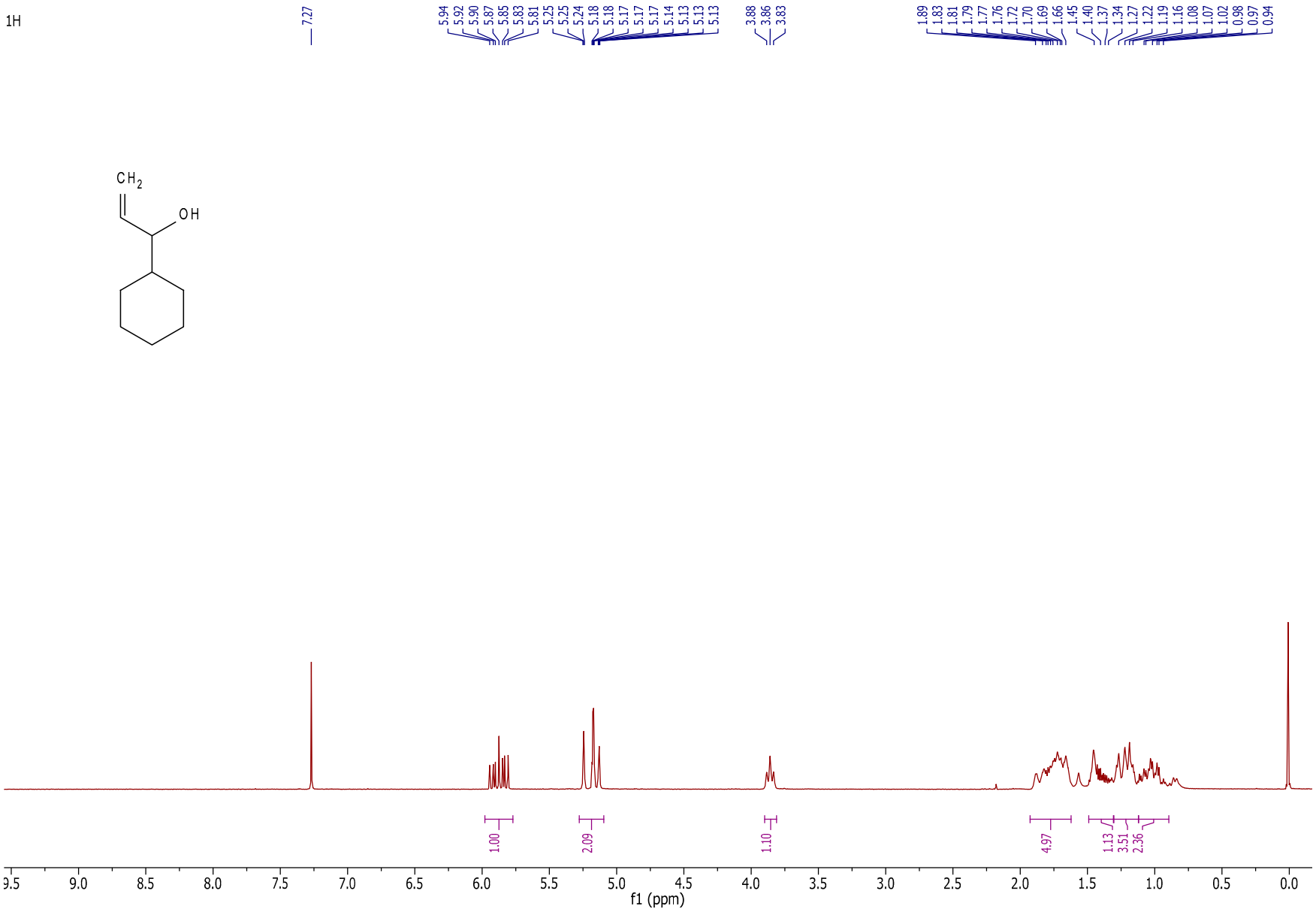

13C
147.46
110.74
77.00
72.89
49.32
38.91
37.35
33.29
30.67
27.73
18.55
CH2
OH
CH3
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

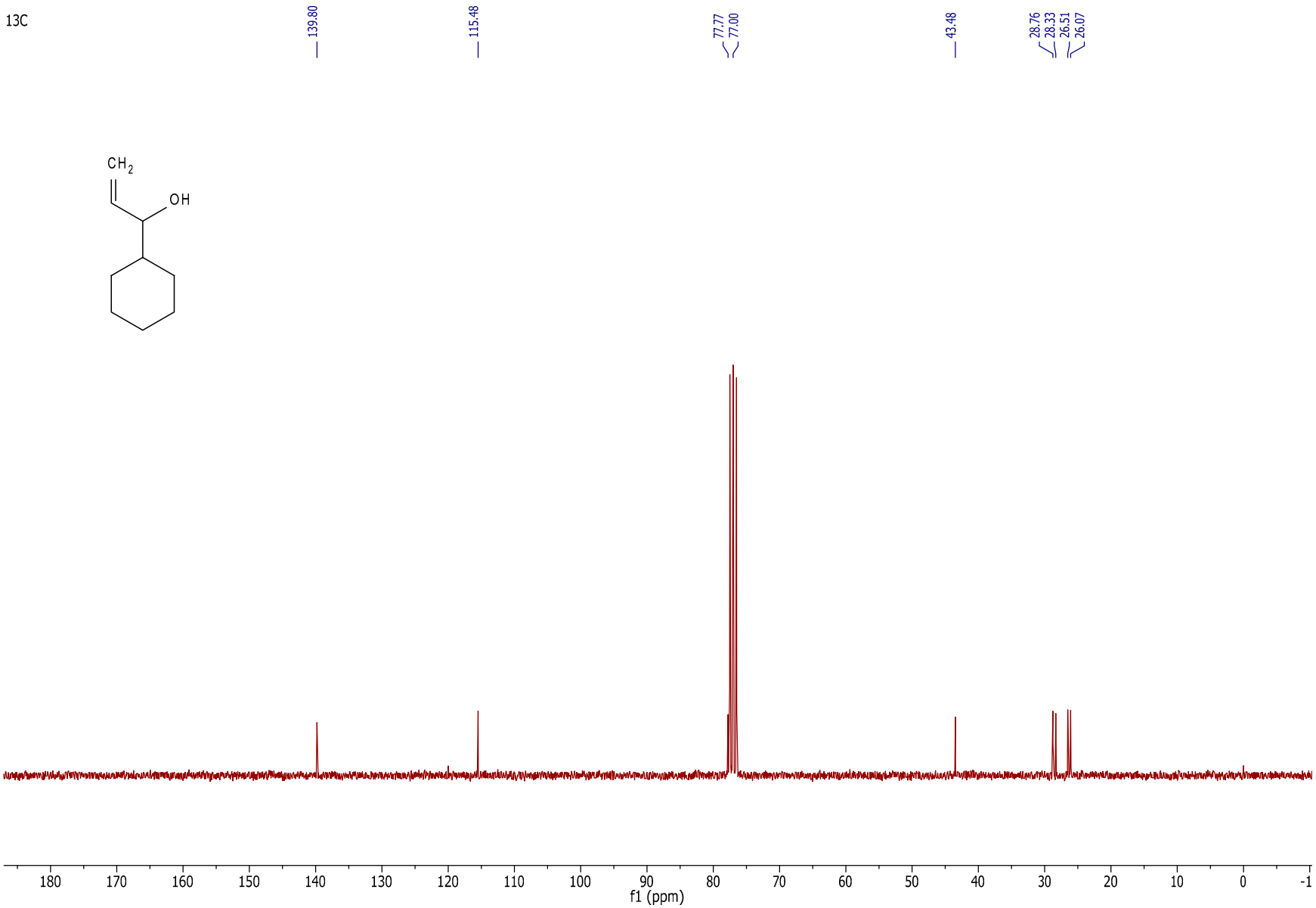

1H
7.26
5.96
5.95
5.93
5.93
5.91
5.91
5.89
5.88
5.24
5.24
5.24
5.20
5.20
5.01
5.00
4.98
4.97
1.86
1.86
1.85
1.85
1.84
1.83
1.82
1.82
1.81
1.81
1.80
1.70
1.69
1.69
1.67
1.66
1.66
1.65
1.59
1.58
1.58
1.57
1.56
1.55
1.54
1.54
1.01
0.90
0.90
0.88
0.57
0.54
0.51
0.48
H
H
H
OH
H3C
CH3
1.00
0.93
0.96
2.04
1.09
2.14
1.07
2.09
3.30
3.25
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

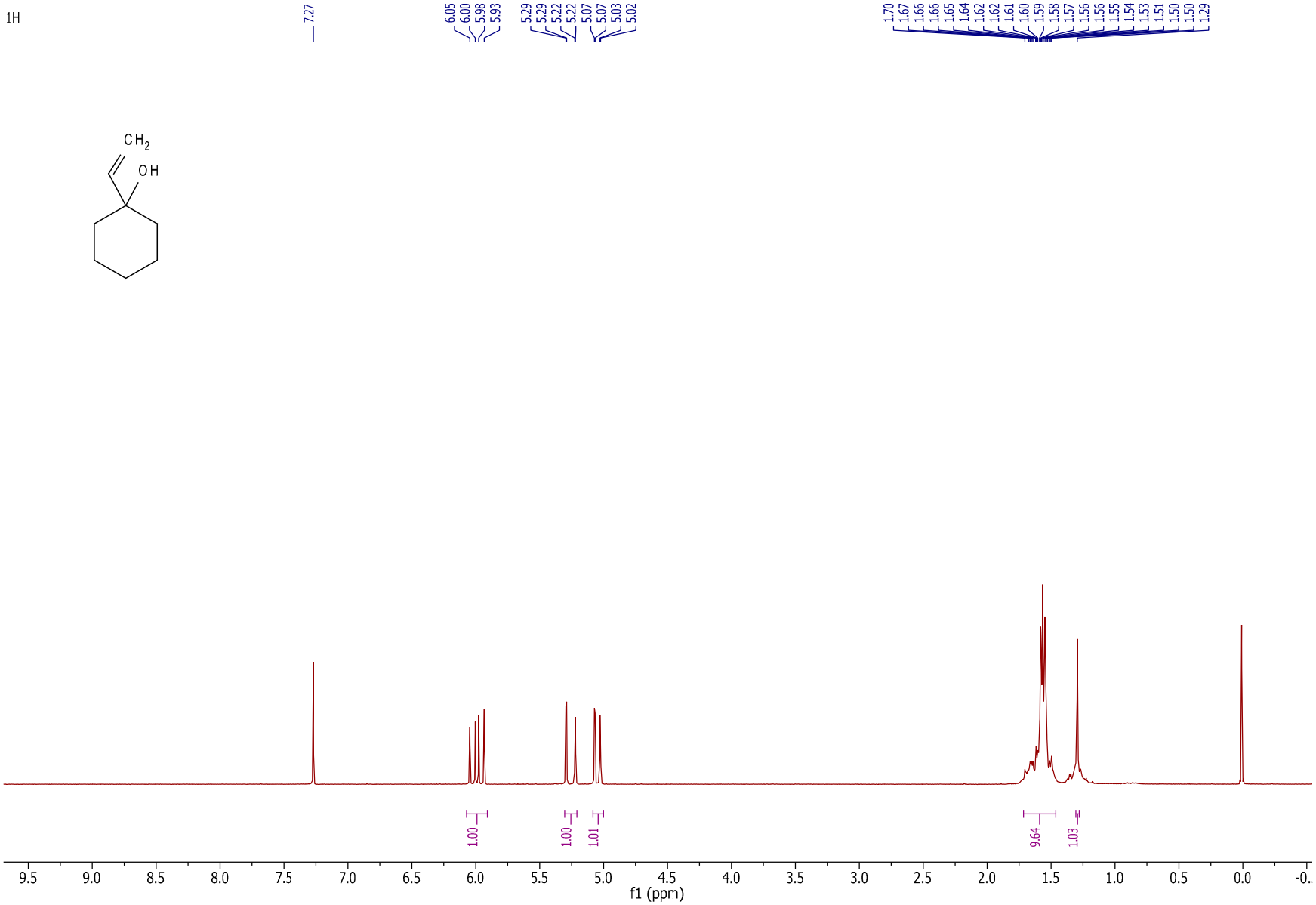

13C
146.99 [9#]
110.86 [11]
77.16
73.14 [1]
45.56 [2,6]
43.50 [4]
27.74 [3,5]
22.46 [7,8]
H
H
H
OH
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

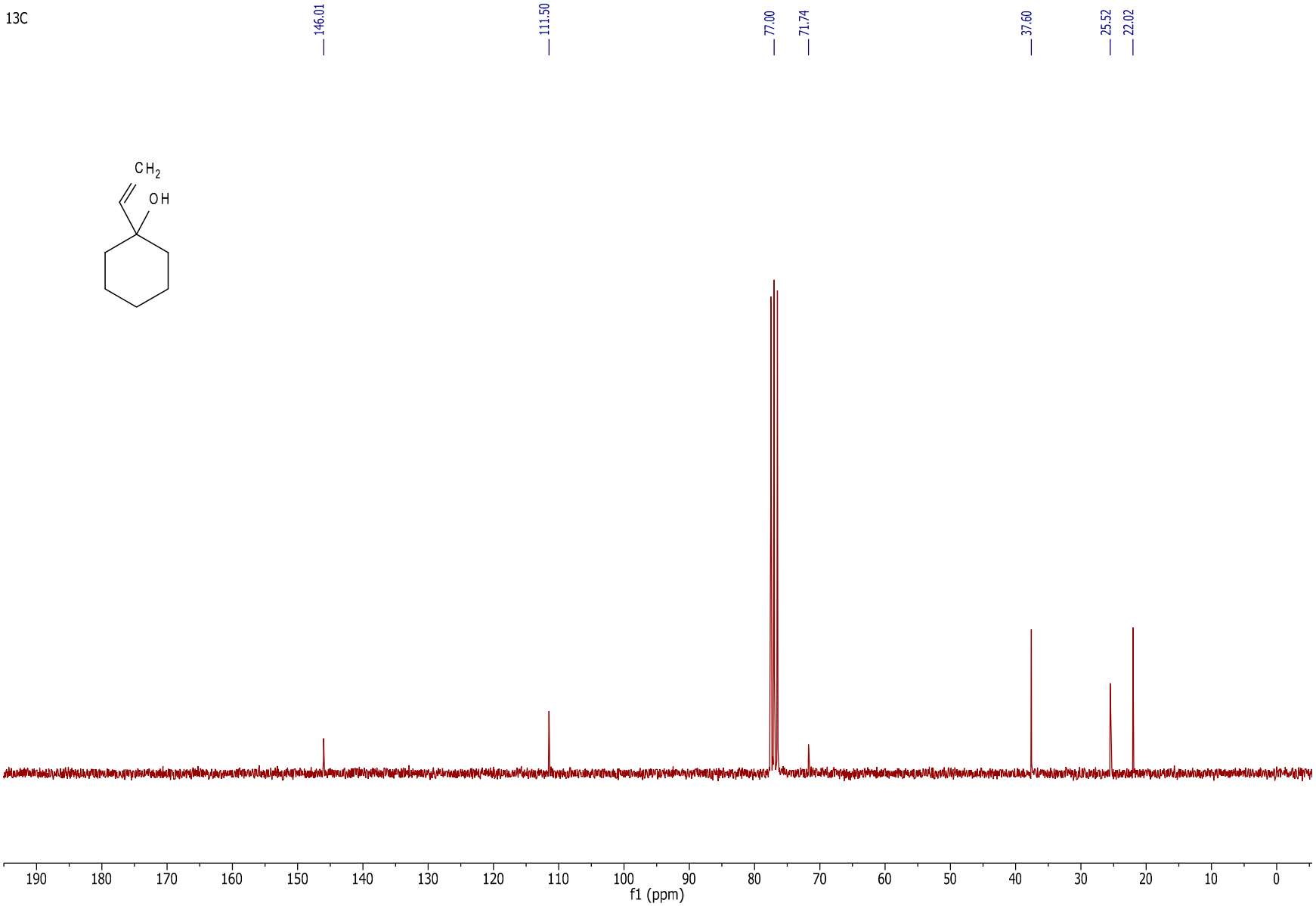

1H
7.26
6.00
5.95
5.93
5.89
5.22
5.21
5.21
5.20
5.17
5.16
5.10
5.09
5.08
5.07
5.04
5.03
1.96
1.92
1.90
1.84
1.84
1.80
1.80
1.79
1.78
1.71
1.67
1.67
1.66
1.66
1.65
1.61
1.60
1.60
1.59
1.38
1.38
1.33
1.28
0.97
0.95
CH2
OH
H3C
CH3
1.00
1.05
2.32
1.03
1.04
2.13
1.61
1.25
3.52
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


13C
143.93
137.11
125.68
113.21
76.99
73.76
45.16
38.98
27.04
23.21
21.68
CH2
OH
H3C
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H
7.27
5.94
5.92
5.90
5.87
5.85
5.83
5.81
5.25
5.25
5.24
5.18
5.18
5.17
5.17
5.17
5.14
5.13
5.13
5.13
3.88
3.86
3.83
1.89
1.83
1.81
1.79
1.77
1.76
1.72
1.70
1.69
1.66
1.45
1.40
1.37
1.34
1.27
1.22
1.19
1.16
1.08
1.07
1.02
0.98
0.97
0.94
CH2
OH
1.00
2.09
1.10
4.97
1.13
3.51
2.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

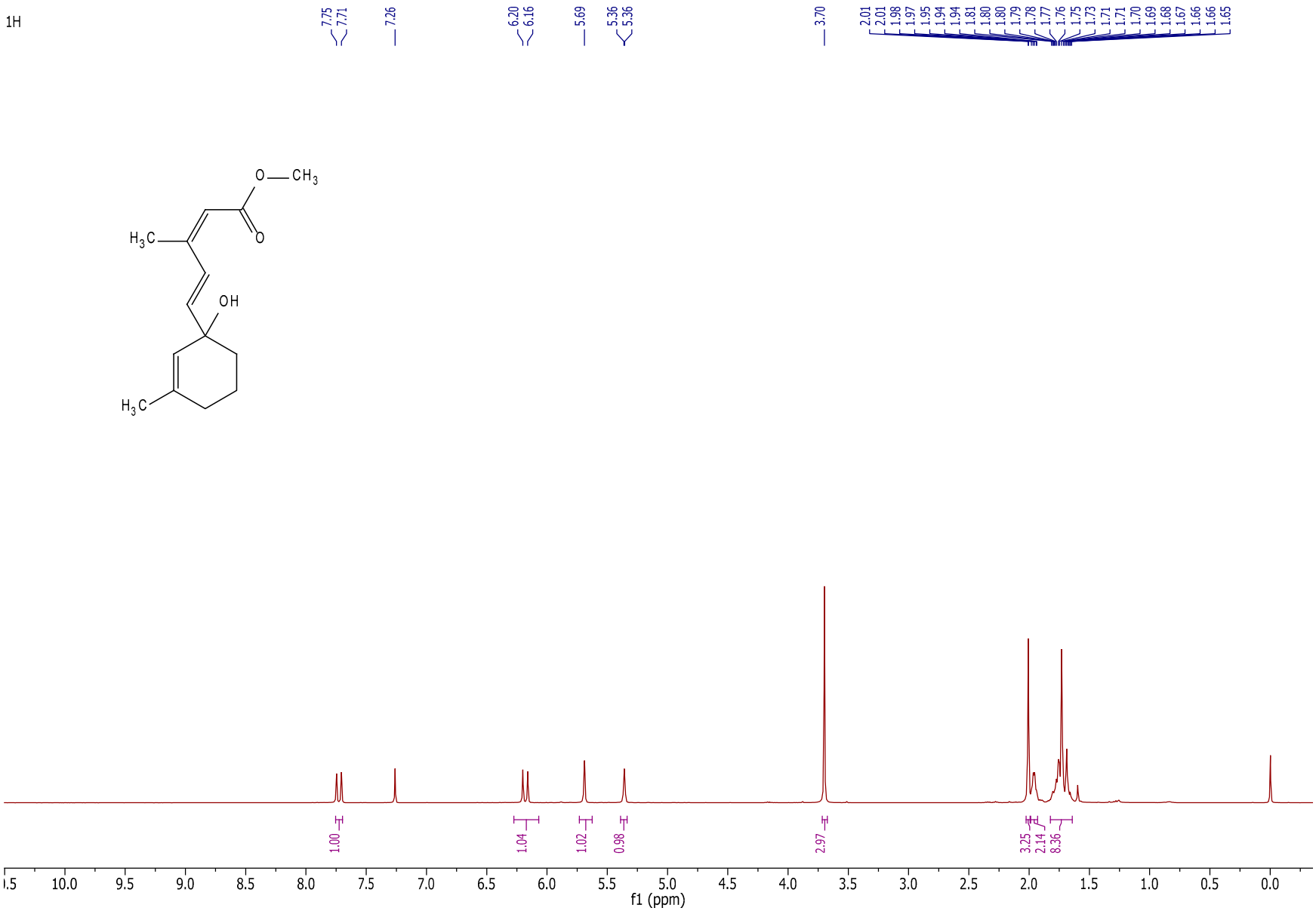

13C
139.80
115.48
77.77
77.00
43.48
28.76
28.33
26.51
26.07
CH2
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

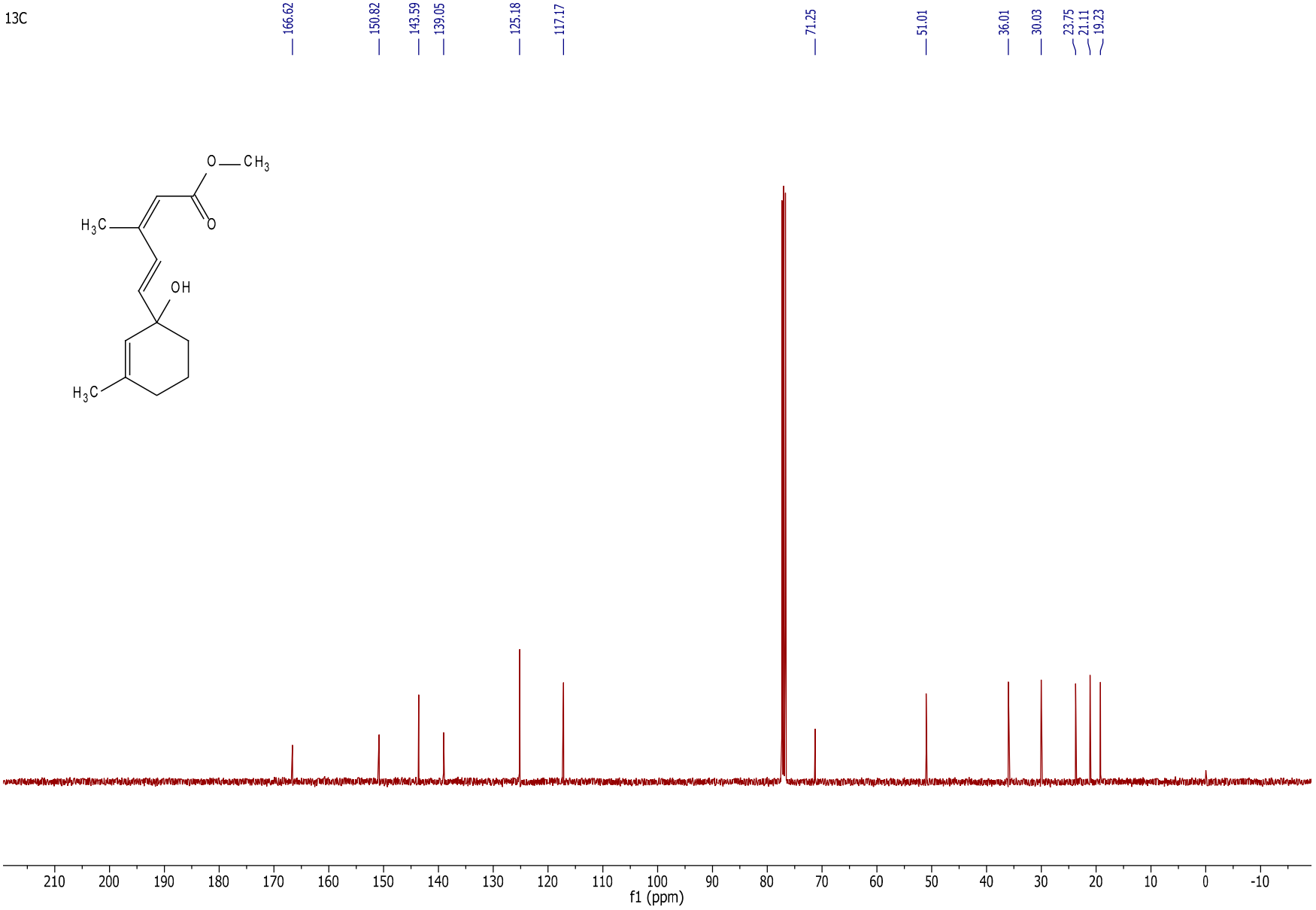

1H
7.27
6.05
6.00
5.98
5.93
5.29
5.29
5.22
5.22
5.07
5.07
5.03
5.02
1.70
1.67
1.66
1.66
1.65
1.64
1.62
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.56
1.55
1.54
1.53
1.51
1.50
1.50
1.29
CH2
OH
1.00
1.00
1.01
9.64
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


13C
146.01
111.50
77.00
71.74
37.60
25.52
22.02
CH2
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

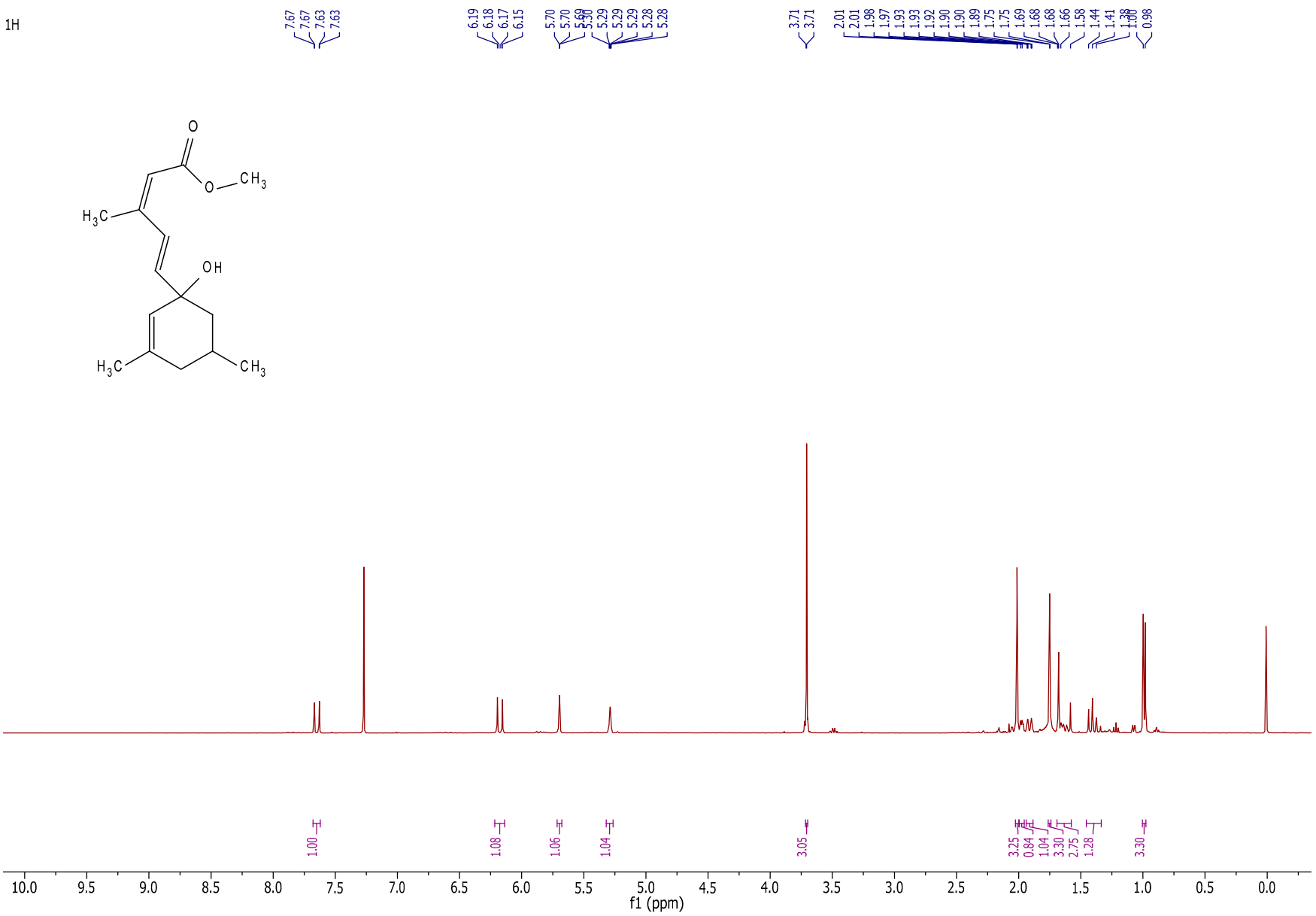
NMR Spectra – Compounds 3a-3n, 4

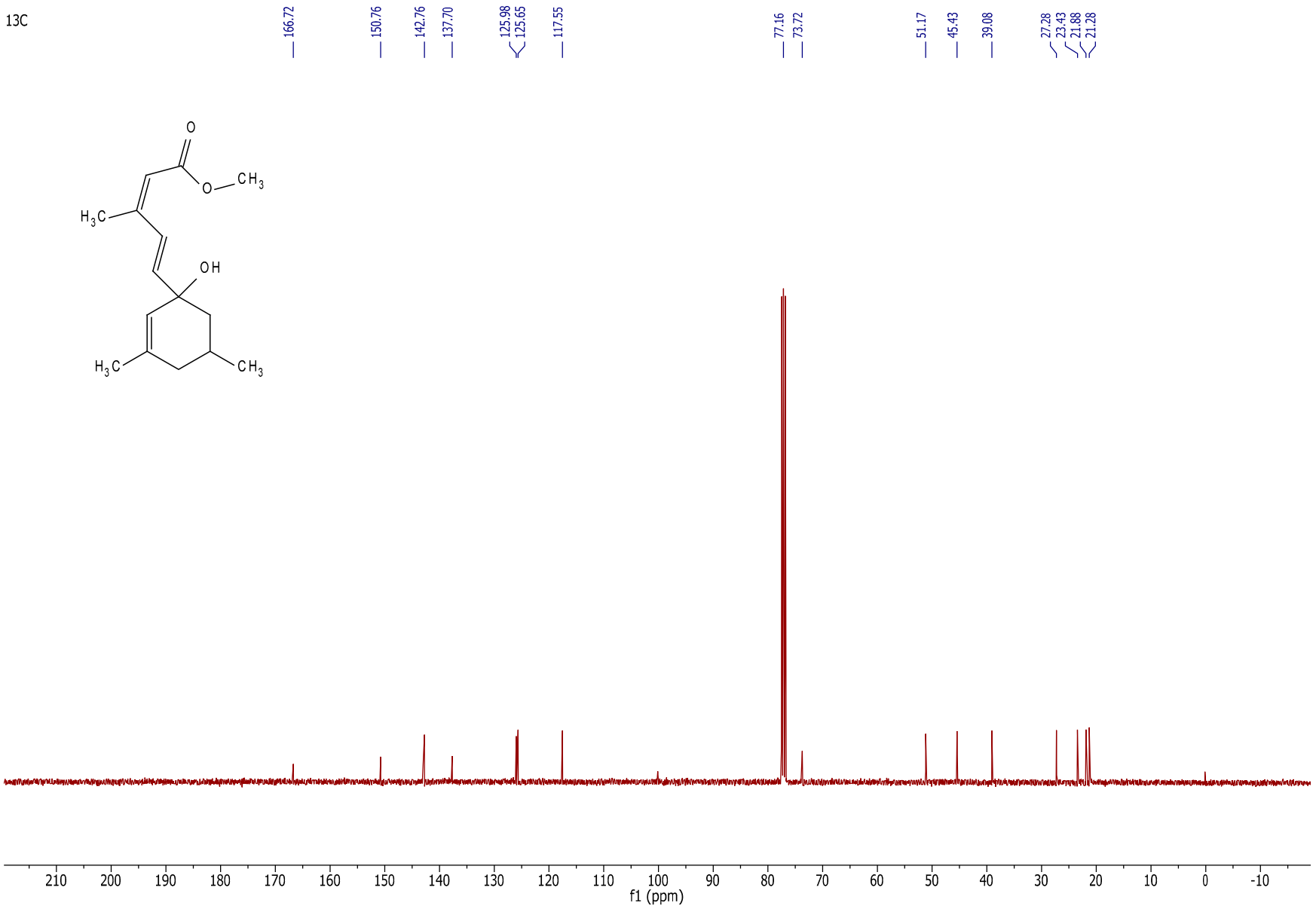
Compound 3a :



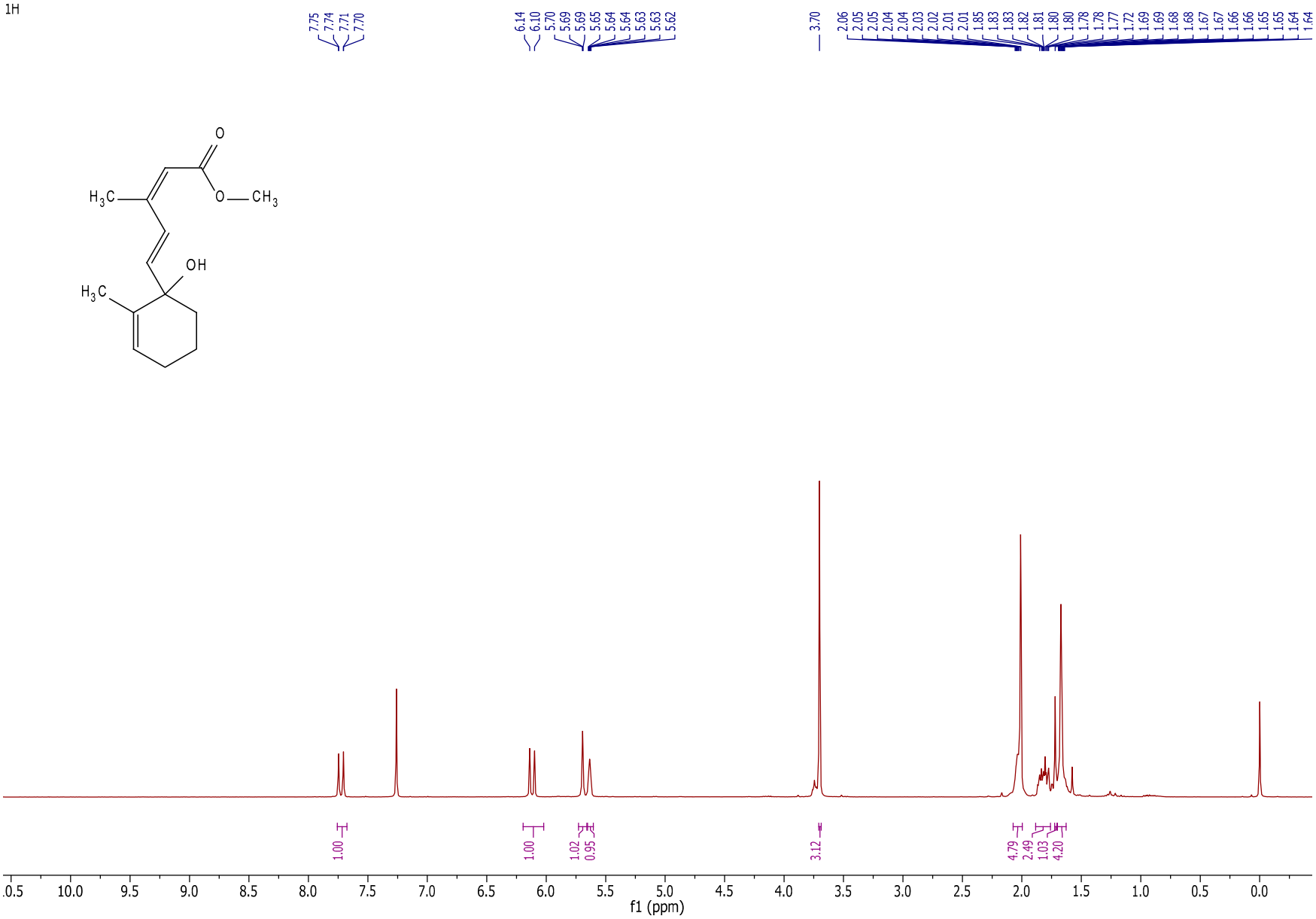

13C
166.62
150.82
143.59
139.05
125.18
117.17
71.25
51.01
36.01
30.03
23.75
21.11
19.23
O
CH3
H3C
O
OH
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

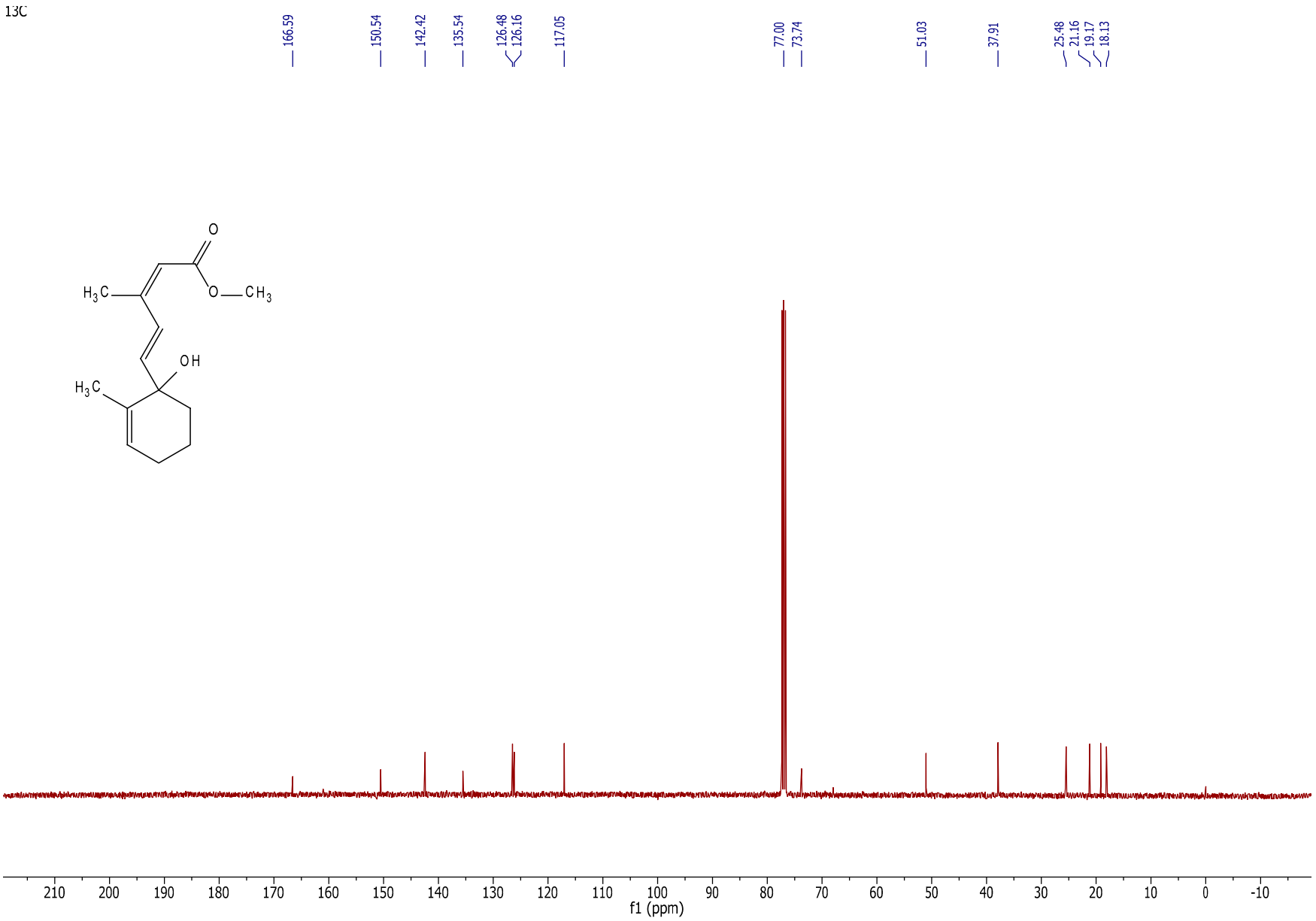
Compound 3b :


1H
7.67
7.67
7.63
7.63
6.19
6.18
6.17
6.15
5.70
5.70
5.69
5.30
5.29
5.29
5.29
5.28
5.28
3.71
3.71
2.01
2.01
1.98
1.97
1.93
1.93
1.92
1.90
1.90
1.89
1.75
1.75
1.69
1.68
1.68
1.66
1.58
1.44
1.41
1.38
1.00
0.98
O
O
CH3
H3C
OH
H3C
CH3
1.00
1.08
1.06
1.04
3.05
3.25
0.84
1.04
3.30
2.75
1.28
3.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

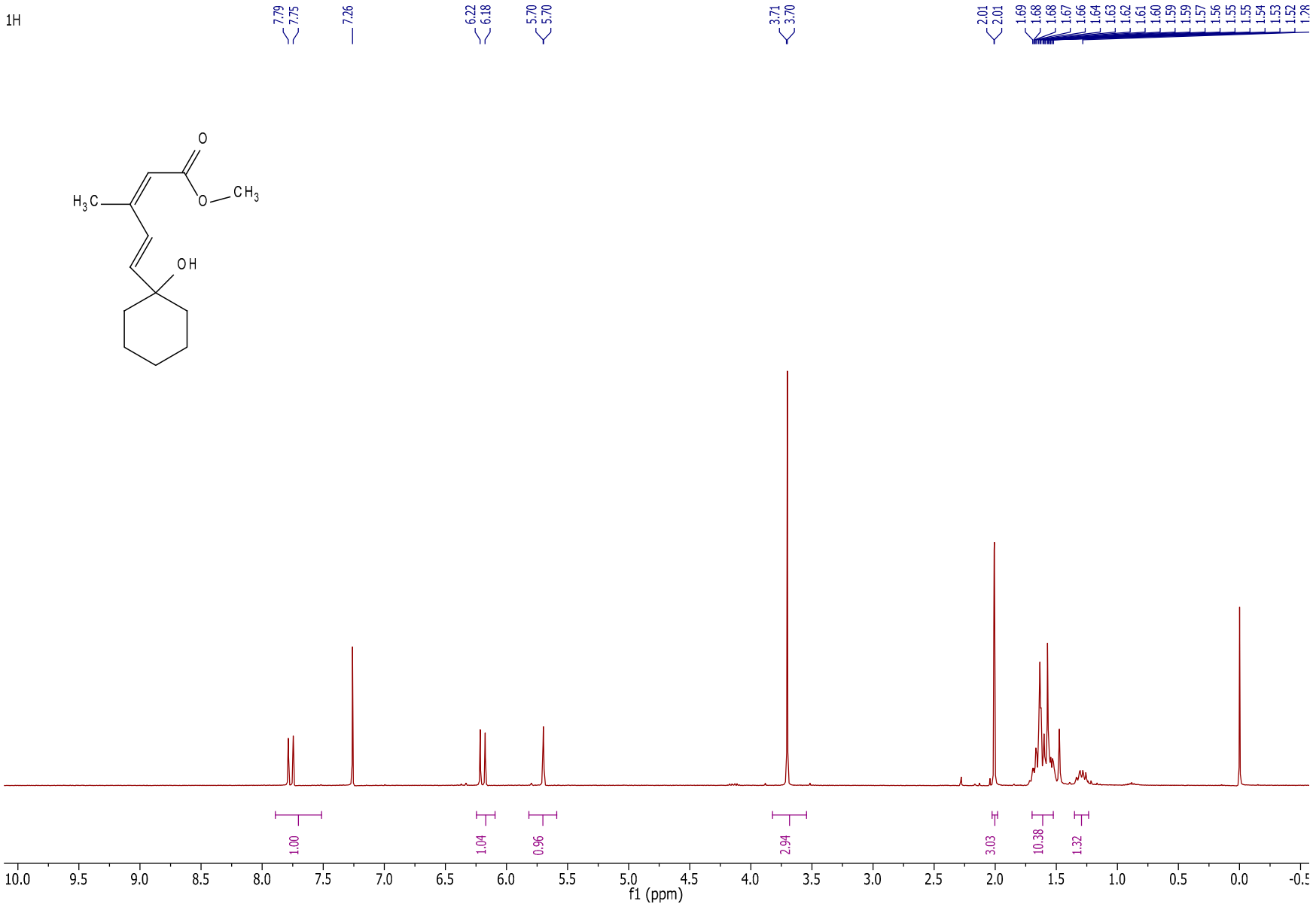

13C
166.72
150.76
142.76
137.70
125.98
125.65
117.55
77.16
73.72
51.17
45.43
39.08
27.28
23.43
21.88
21.28
O
O
CH3
H3C
OH
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

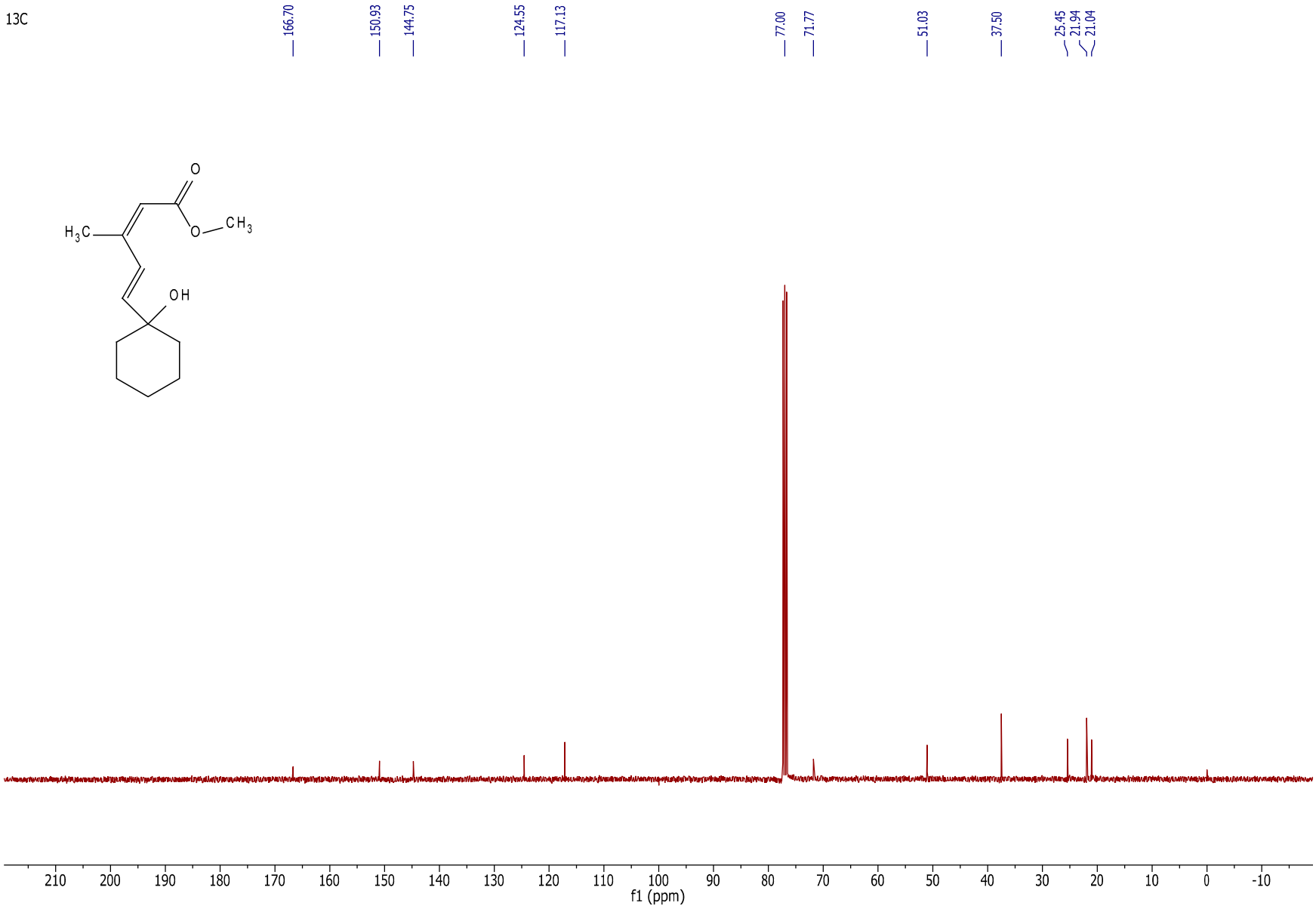
Compound 3c :


1H
7.75
7.74
7.71
7.70
6.14
6.10
5.70
5.69
5.69
5.65
5.64
5.64
5.63
5.63
5.62
3.70
2.06
2.05
2.05
2.04
2.04
2.03
2.02
2.01
2.01
1.85
1.83
1.83
1.82
1.81
1.80
1.80
1.78
1.78
1.77
1.72
1.69
1.69
1.68
1.68
1.67
1.67
1.66
1.66
1.65
1.65
1.64
1.64
O
H3C
O
CH3
OH
H3C
1.00
1.00
1.02
0.95
3.12
4.79
2.49
1.03
4.20
f1 (ppm)

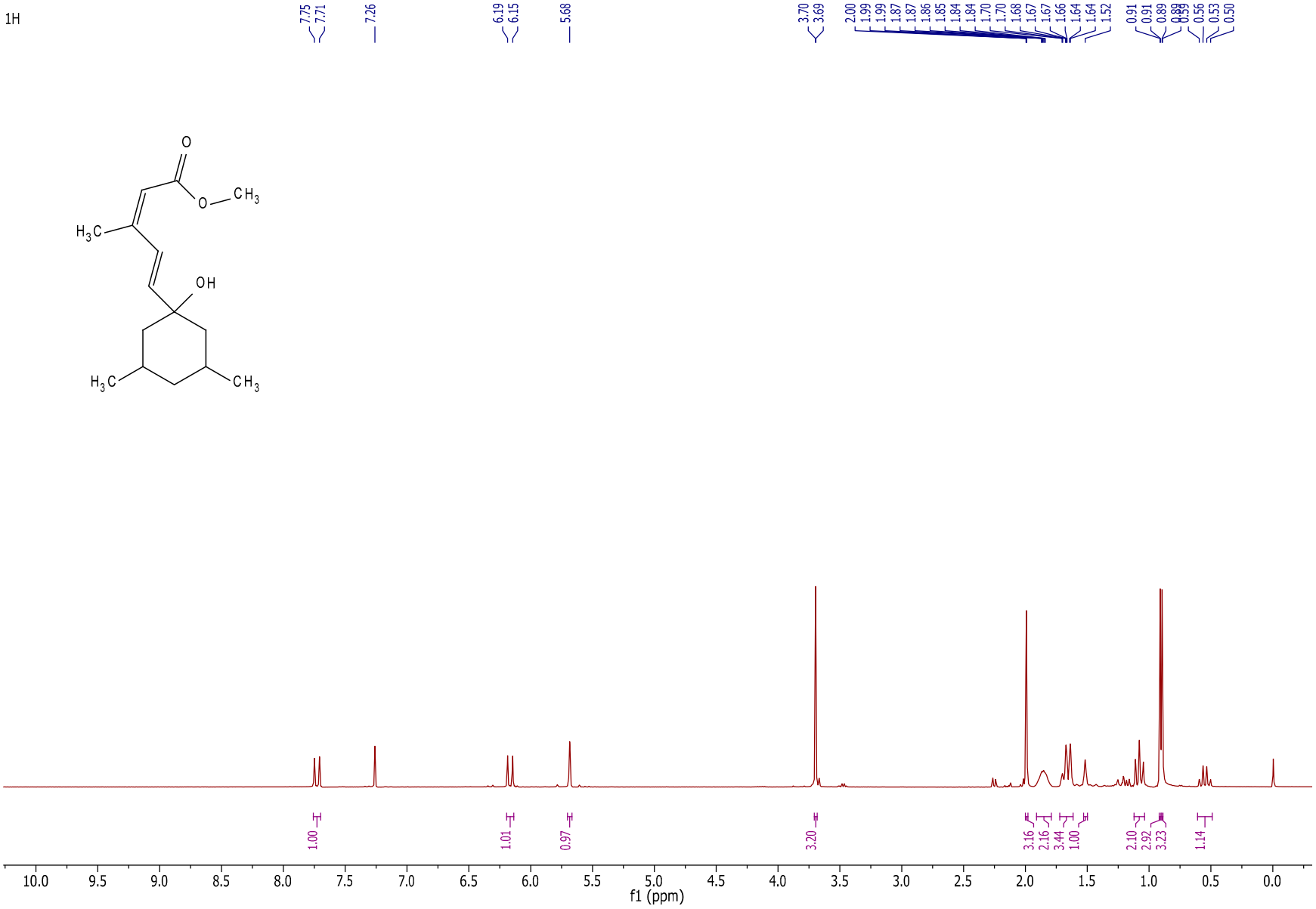

13C
166.59
150.54
142.42
135.54
126.48
126.16
117.05
77.00
73.74
51.03
37.91
25.48
21.16
19.17
18.13
O
H3C
O
CH3
OH
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

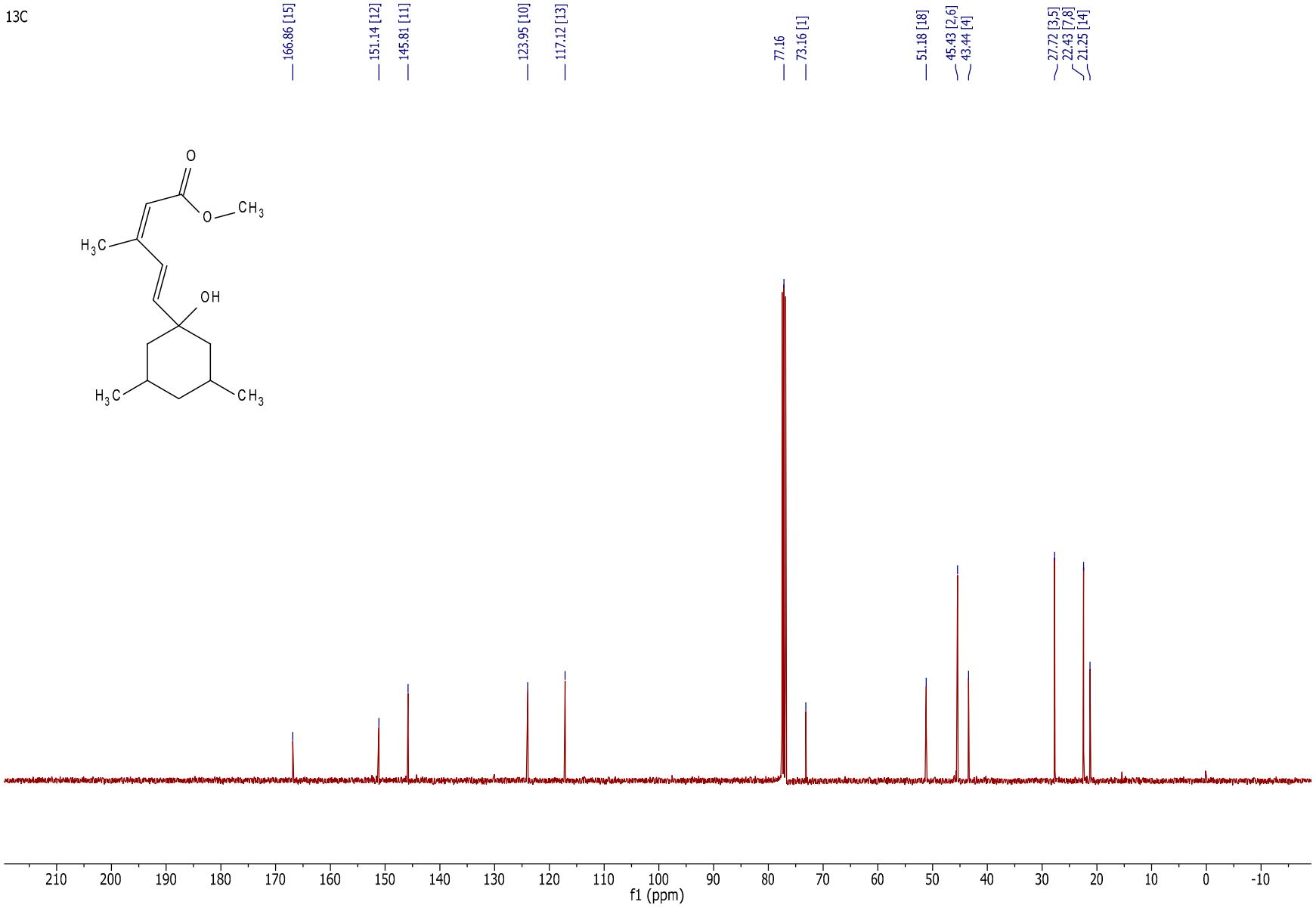
Compound 3d :


1H
7.79
7.75
7.26
6.22
6.18
5.70
5.70
3.71
3.70
2.01
2.01
1.69
1.68
1.68
1.67
1.66
1.64
1.63
1.62
1.61
1.60
1.59
1.59
1.57
1.56
1.55
1.55
1.54
1.53
1.52
O
O
CH3
H3C
OH
1.00
1.04
0.96
2.94
3.03
10.38
1.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

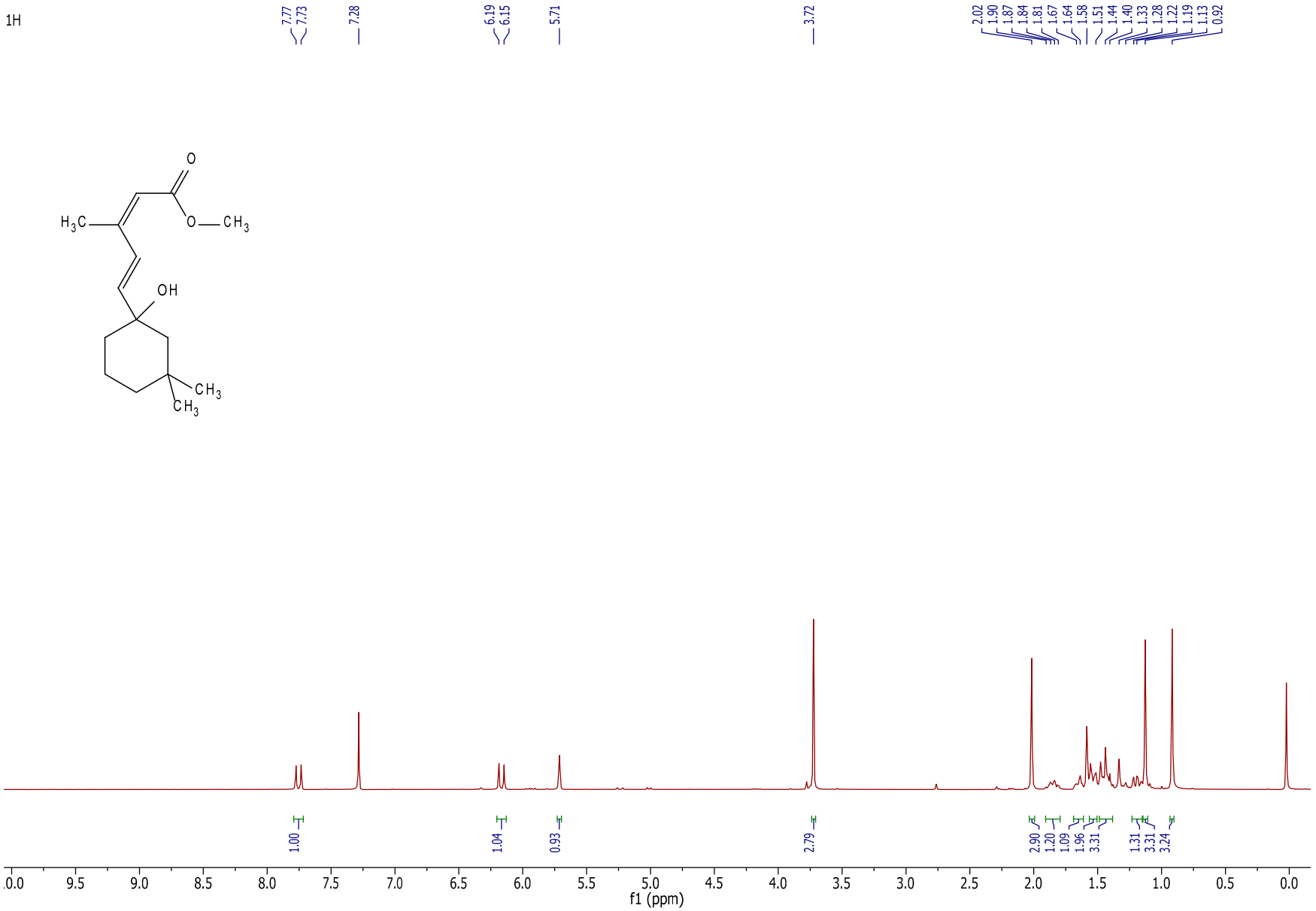

13C
166.70
150.93
144.75
124.55
117.13
77.00
71.77
51.03
37.50
25.45
21.94
21.04
O
H3C
O
CH3
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

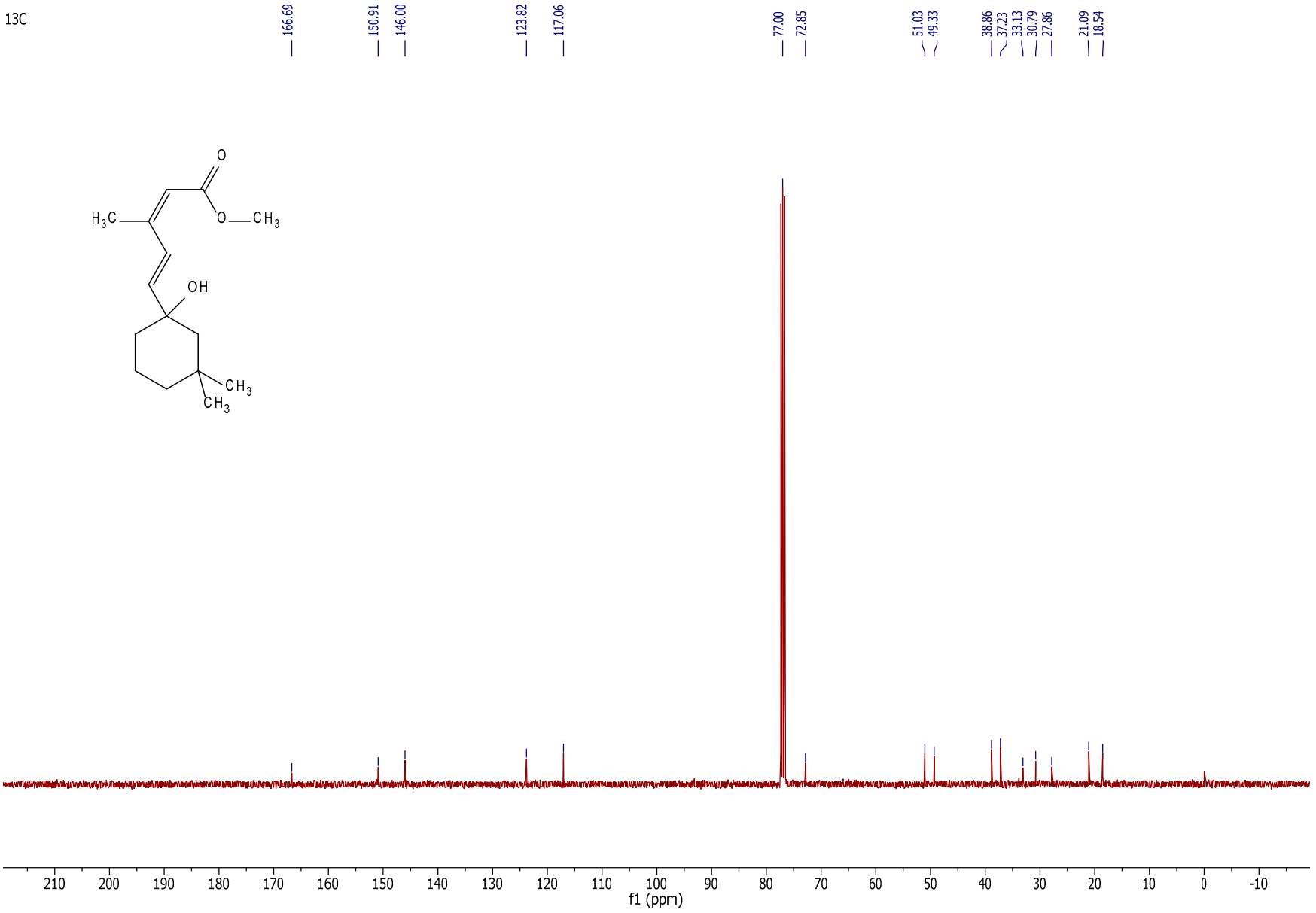
Compound 3e :


1H
7.75
7.71
7.26
6.19
6.15
5.68
3.70
3.69
2.00
1.99
1.99
1.87
1.87
1.86
1.85
1.84
1.84
1.70
1.70
1.68
1.67
1.67
1.66
1.64
1.64
1.52
0.91
0.91
0.89
0.56
0.53
0.50
O
O
CH3
H3C
OH
H3C
CH3
1.00
1.01
0.97
3.20
3.16
2.16
3.44
1.00
2.10
2.92
3.23
1.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

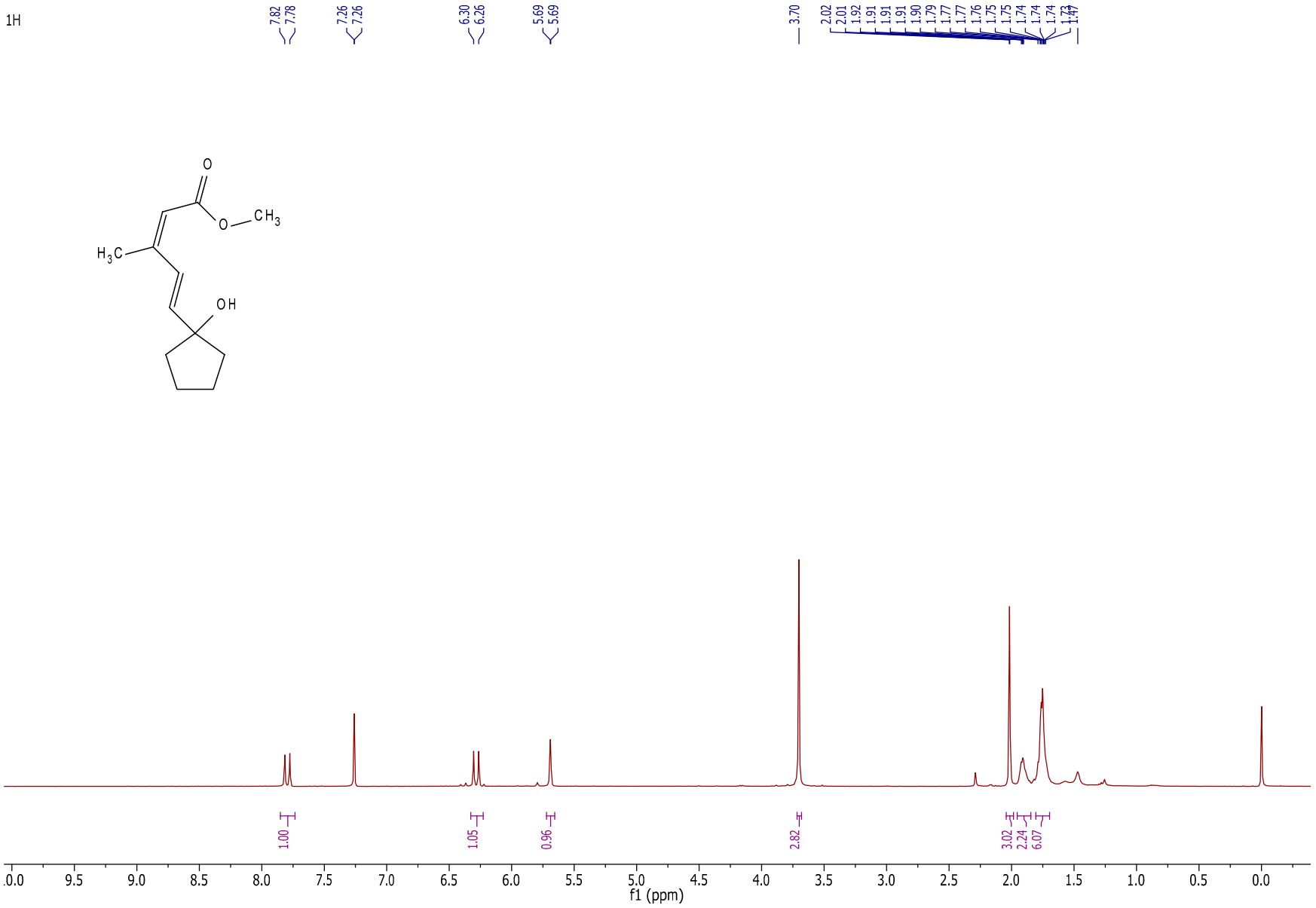

13C
166.86 [15]
151.14 [12]
145.81 [11]
123.95 [10]
117.12 [13]
77.16
73.16 [1]
51.18 [18]
45.43 [2,6]
43.44 [4]
27.72 [3,5]
22.43 [7,8]
21.25 [14]
O
O
CH3
H3C
OH
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

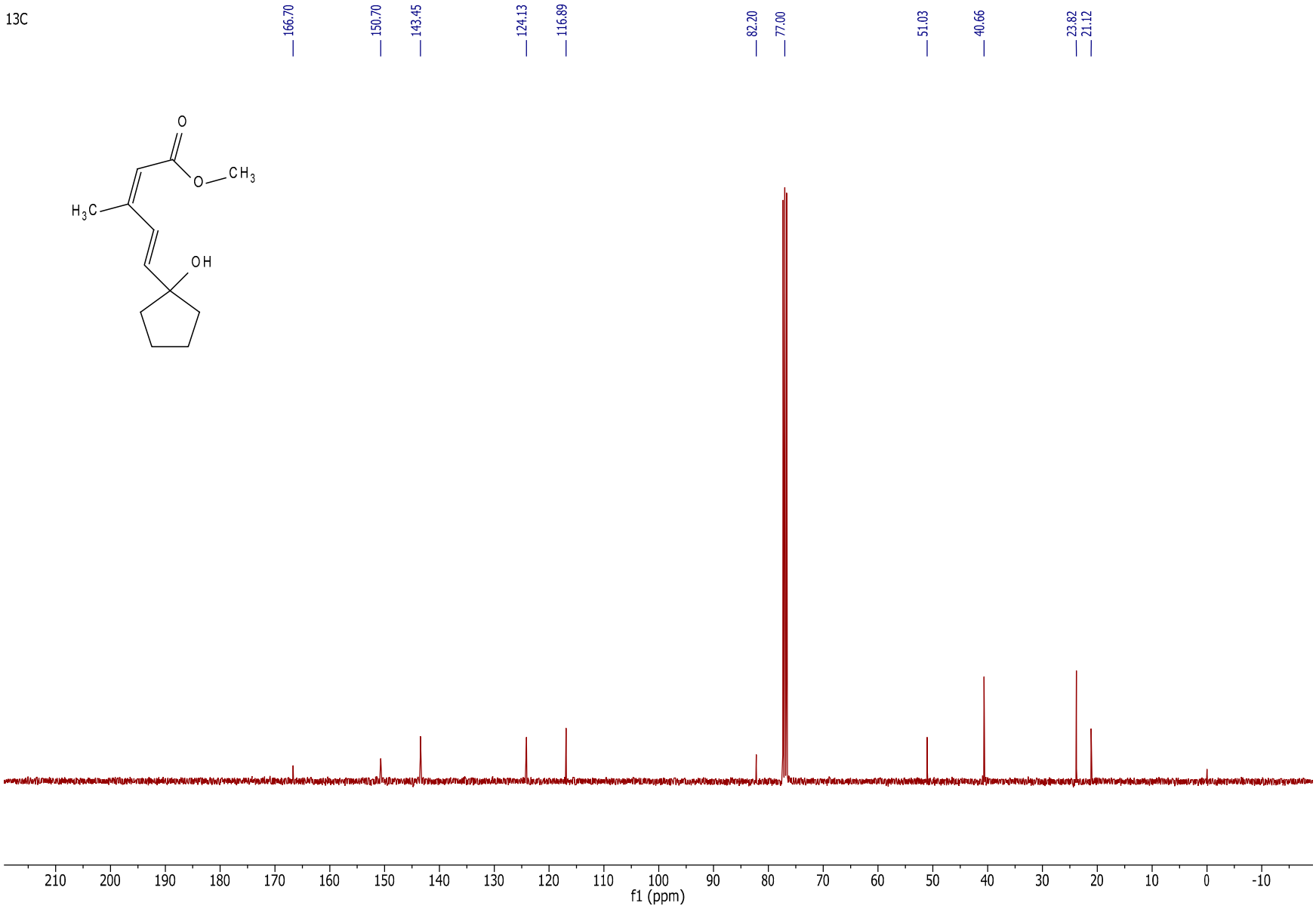
Compound 3f :


1H
7.77
7.73
7.28
6.19
6.15
5.71
3.72
2.02
1.90
1.87
1.84
1.81
1.67
1.64
1.58
1.51
1.44
1.40
1.33
1.28
1.22
1.19
1.13
0.92
O
H3C
O
CH3
OH
CH3
CH3
1.00
1.04
0.93
2.79
2.90
1.20
1.09
1.96
3.31
1.31
3.31
3.24
f1 (ppm)

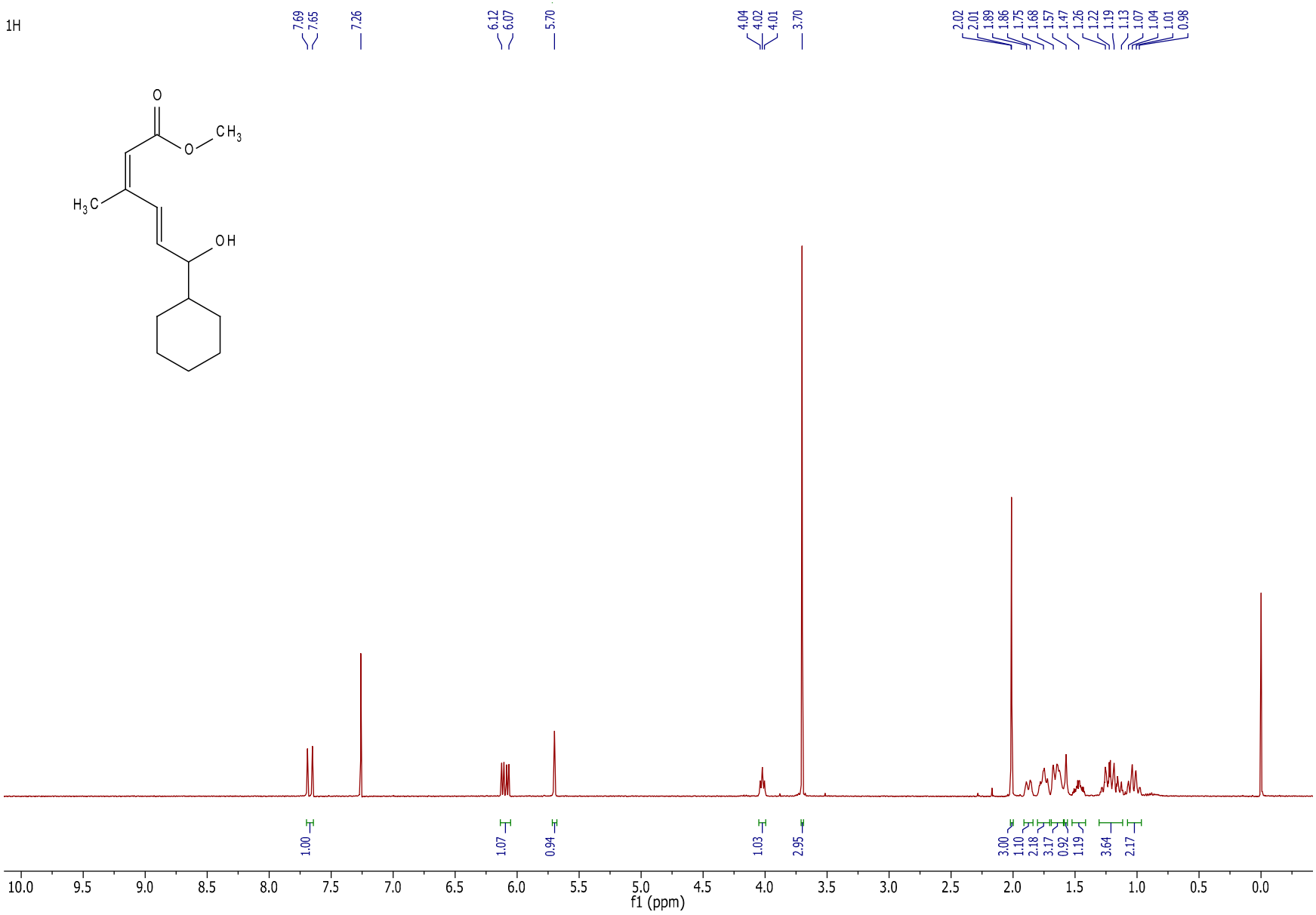

13C
166.69
150.91
146.00
123.82
117.06
77.00
72.85
51.03
49.33
38.86
37.23
33.13
30.79
27.86
21.09
18.54
O
H3C
O
CH3
OH
CH3
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

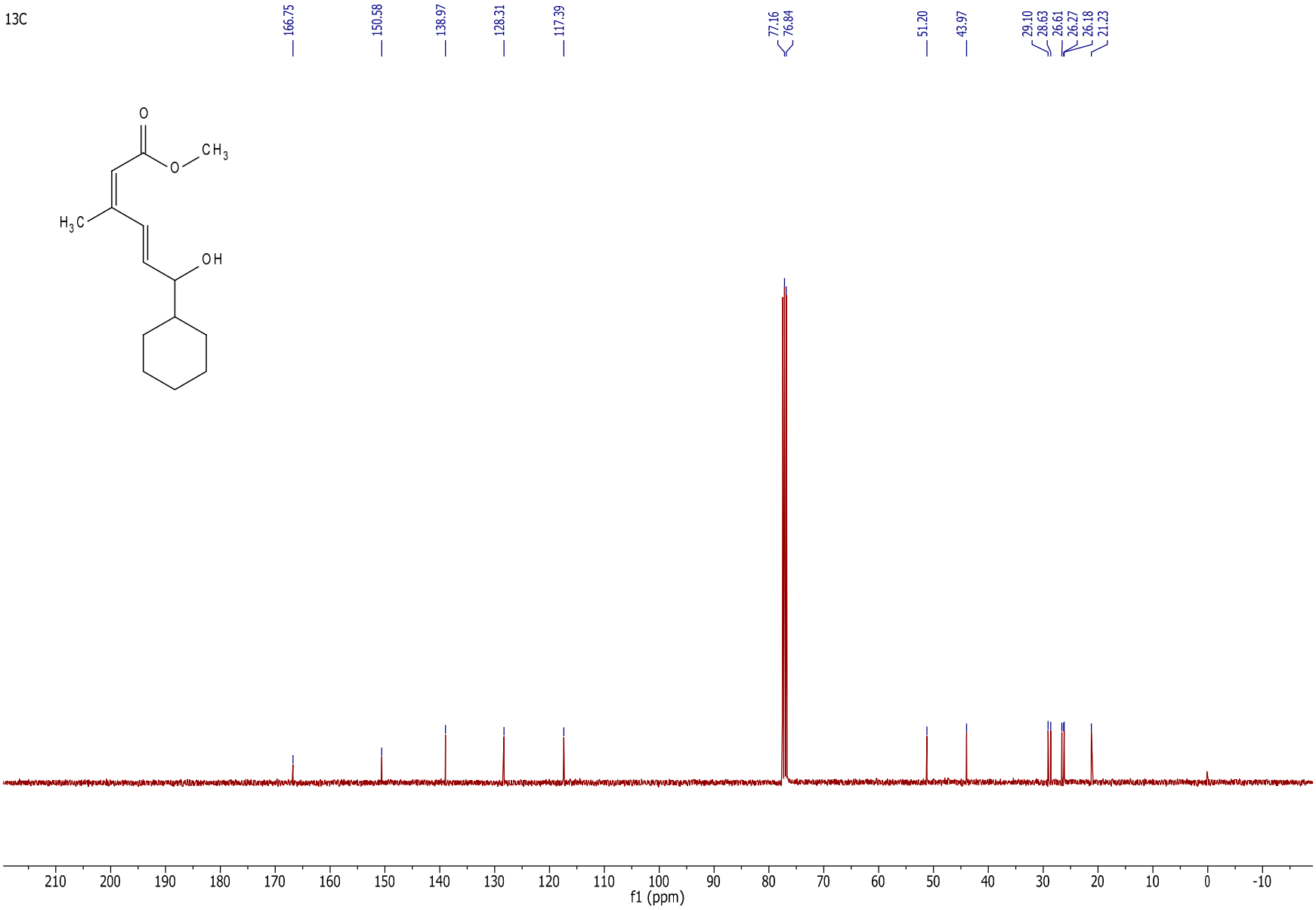
Compound 3g :


1H
7.82
7.78
7.26
7.26
6.30
6.26
5.69
5.69
3.70
2.02
2.01
1.92
1.91
1.91
1.91
1.90
1.79
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.74
1.73
1.47
O
O
CH3
H3C
OH
1.00
1.05
0.96
2.82
3.02
2.24
6.07
f1 (ppm)

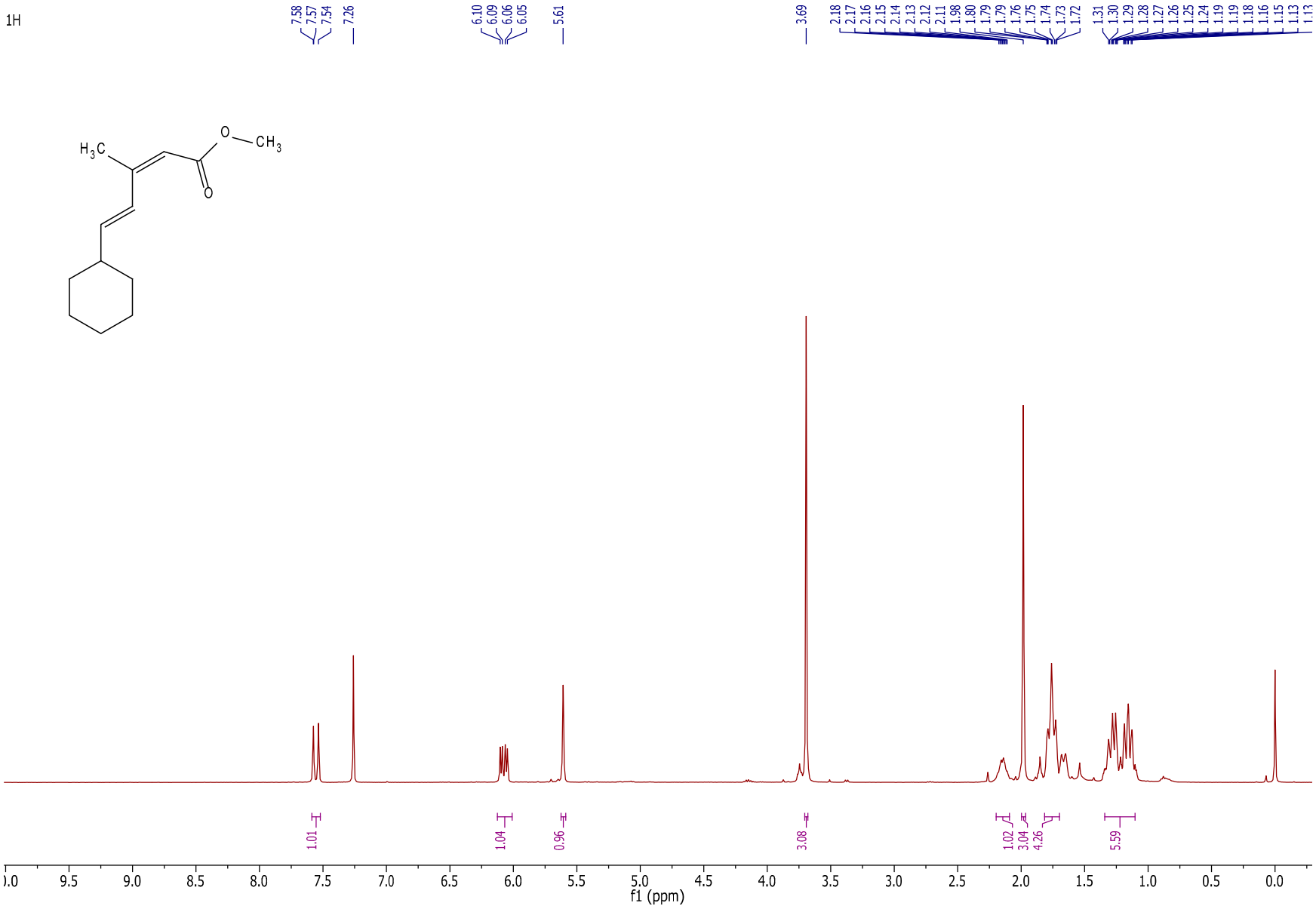

13C
166.70
150.70
143.45
124.13
116.89
82.20
77.00
51.03
40.66
23.82
21.12
O
O
CH3
H3C
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

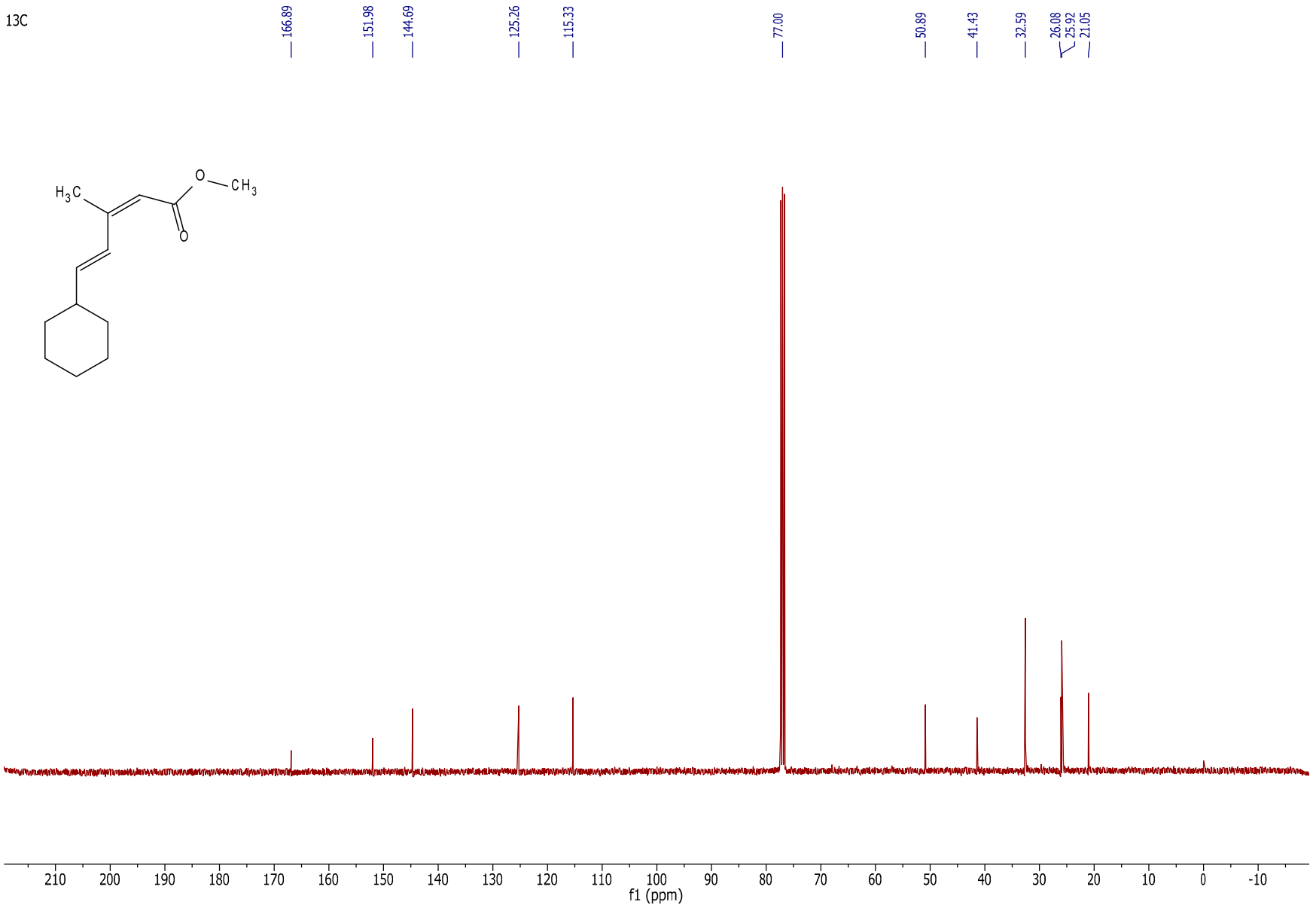
Compound 3h :


1H
7.69
7.65
7.26
6.12
6.07
5.70
4.04
4.02
4.01
3.70
2.02
2.01
1.89
1.86
1.75
1.68
1.57
1.47
1.26
1.22
1.19
1.13
1.07
1.04
1.01
0.98
O
O
CH3
H3C
OH
1.00
1.07
0.94
1.03
2.95
3.00
1.10
2.18
3.17
0.92
1.19
3.64
2.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

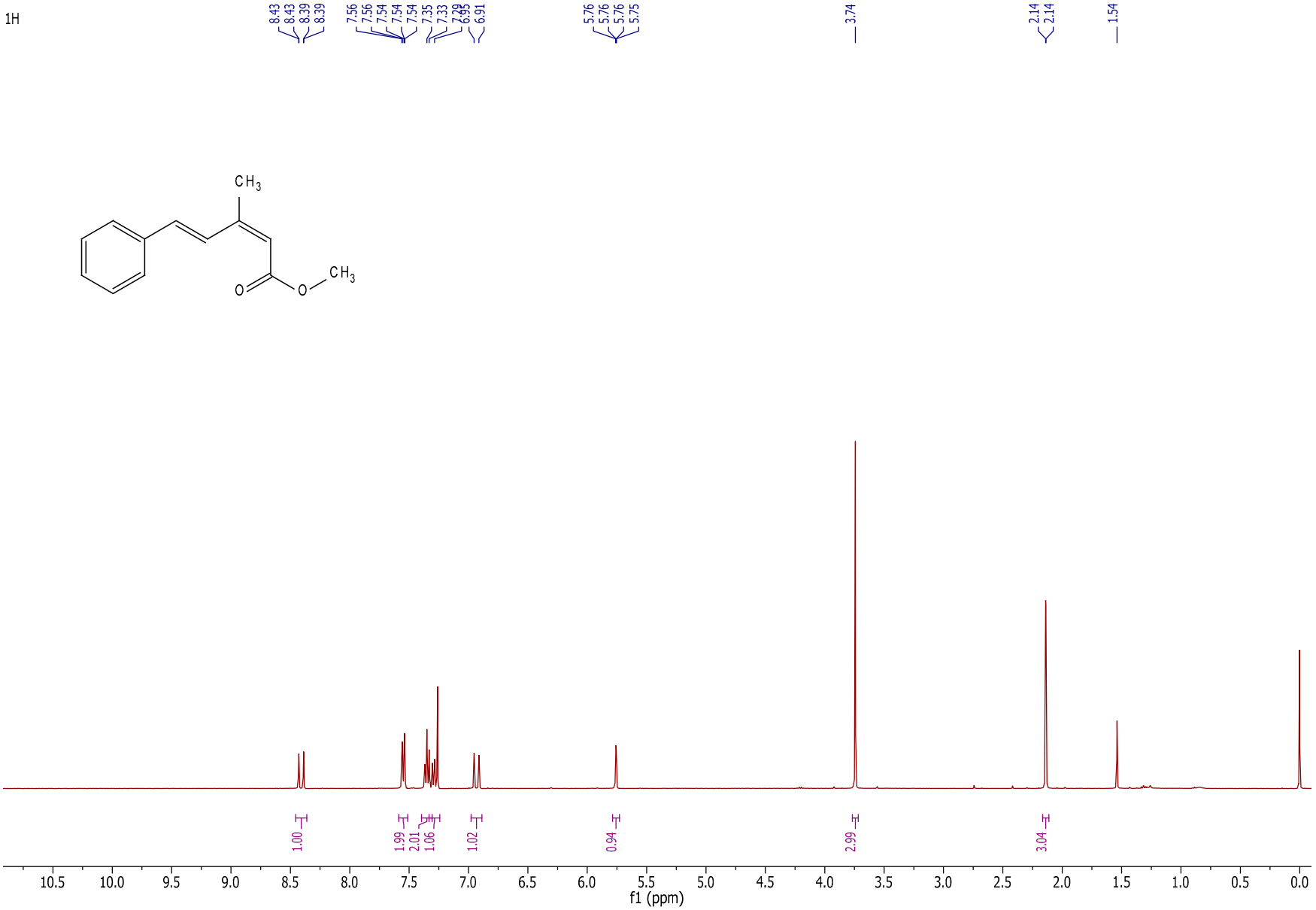

13C
166.75
150.58
138.97
128.31
117.39
77.16
76.84
51.20
43.97
29.10
28.63
26.61
26.27
26.18
21.23
O
O
CH3
H3C
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

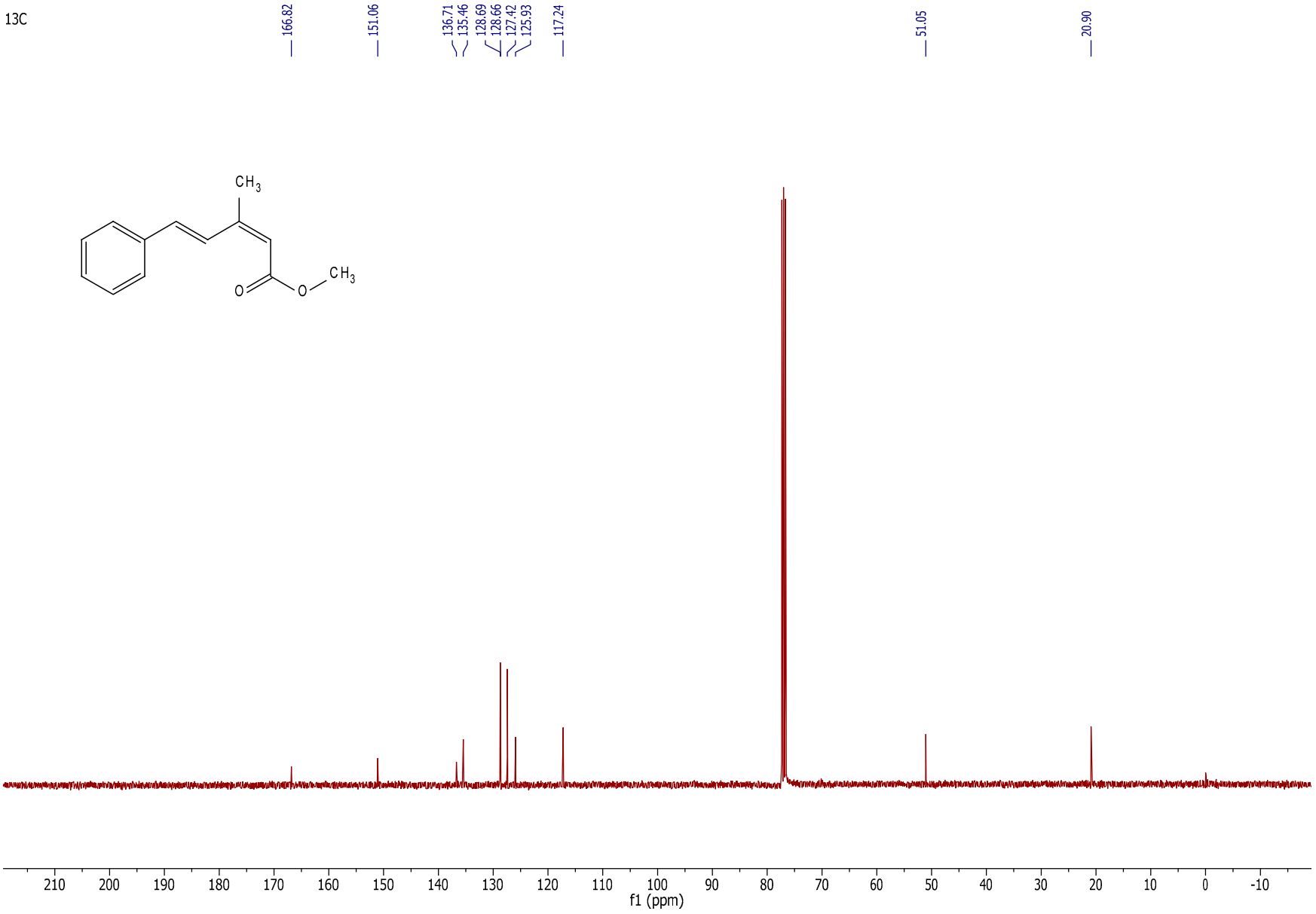
Compound 3i :


1H
7.58
7.57
7.54
7.26
6.10
6.09
6.06
6.05
5.61
3.69
2.18
2.17
2.16
2.15
2.14
2.13
2.12
2.11
1.98
1.80
1.79
1.79
1.76
1.75
1.74
1.73
1.72
1.31
1.30
1.29
1.28
1.27
1.26
1.25
1.24
1.19
1.19
1.18
1.16
1.15
1.13
1.13
H3C
O
CH3
O
1.01
1.04
0.96
3.08
1.02
3.04
4.26
5.59
f1 (ppm)

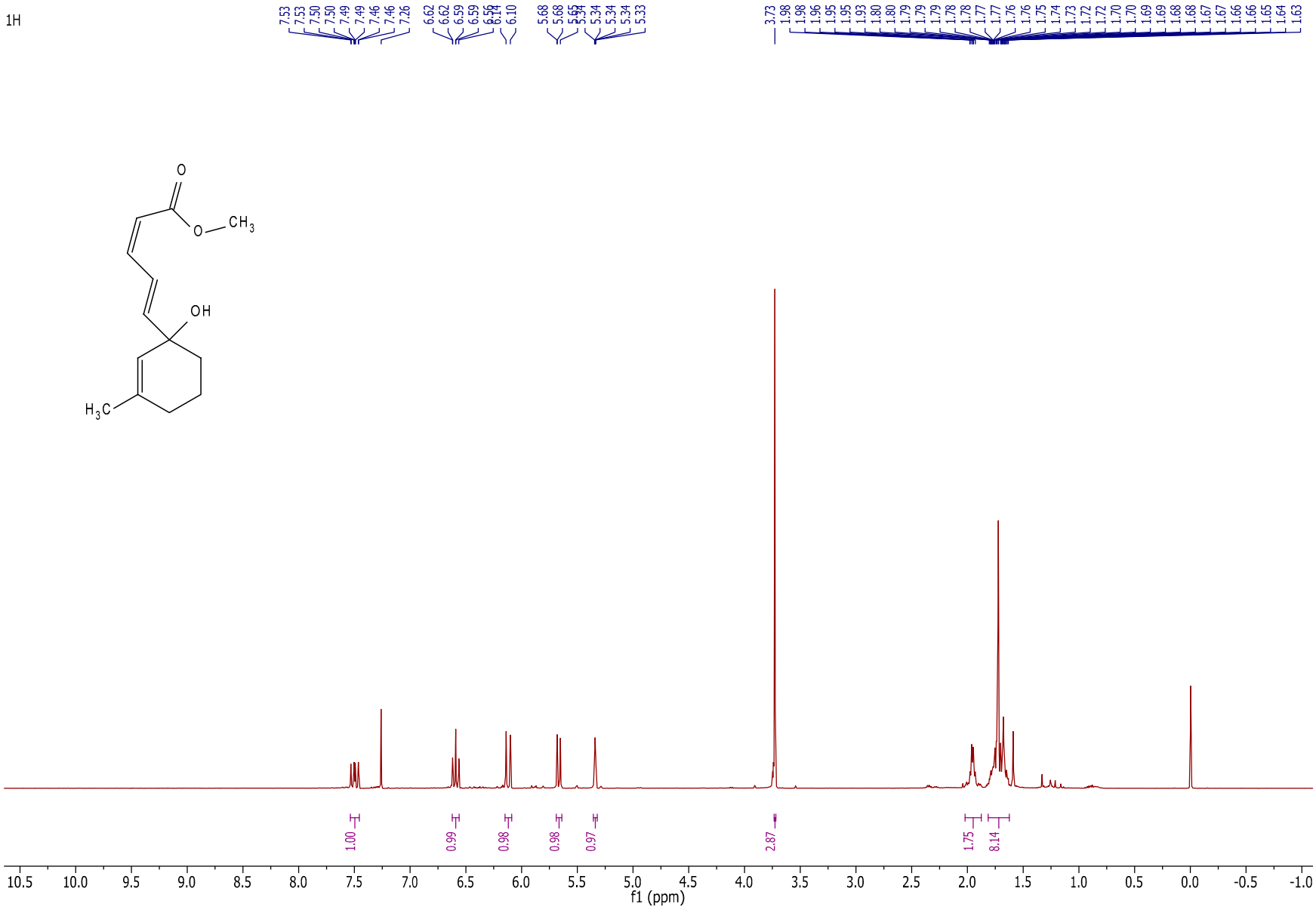

13C
166.89
151.98
144.69
125.26
115.33
77.00
50.89
41.43
32.59
26.08
25.92
21.05
H3C
O
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

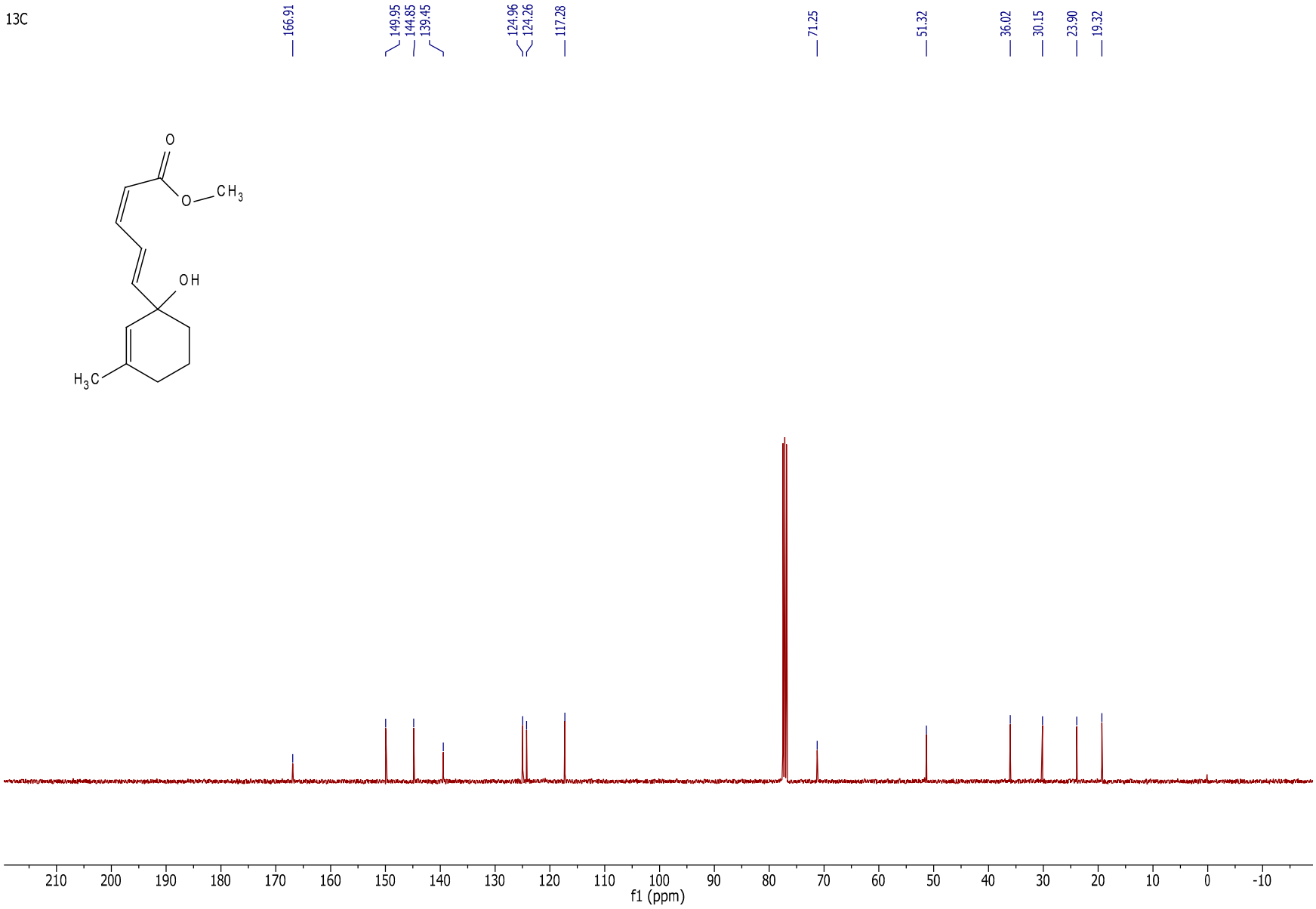
Compound 3j :


1H
8.43
8.43
8.39
8.39
7.56
7.56
7.54
7.54
7.54
7.35
7.33
6.95
6.91
5.76
5.76
5.76
5.75
3.74
2.14
2.14
1.54
CH3
O
O
CH3
1.00
1.99
2.01
1.06
1.02
0.94
2.99
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

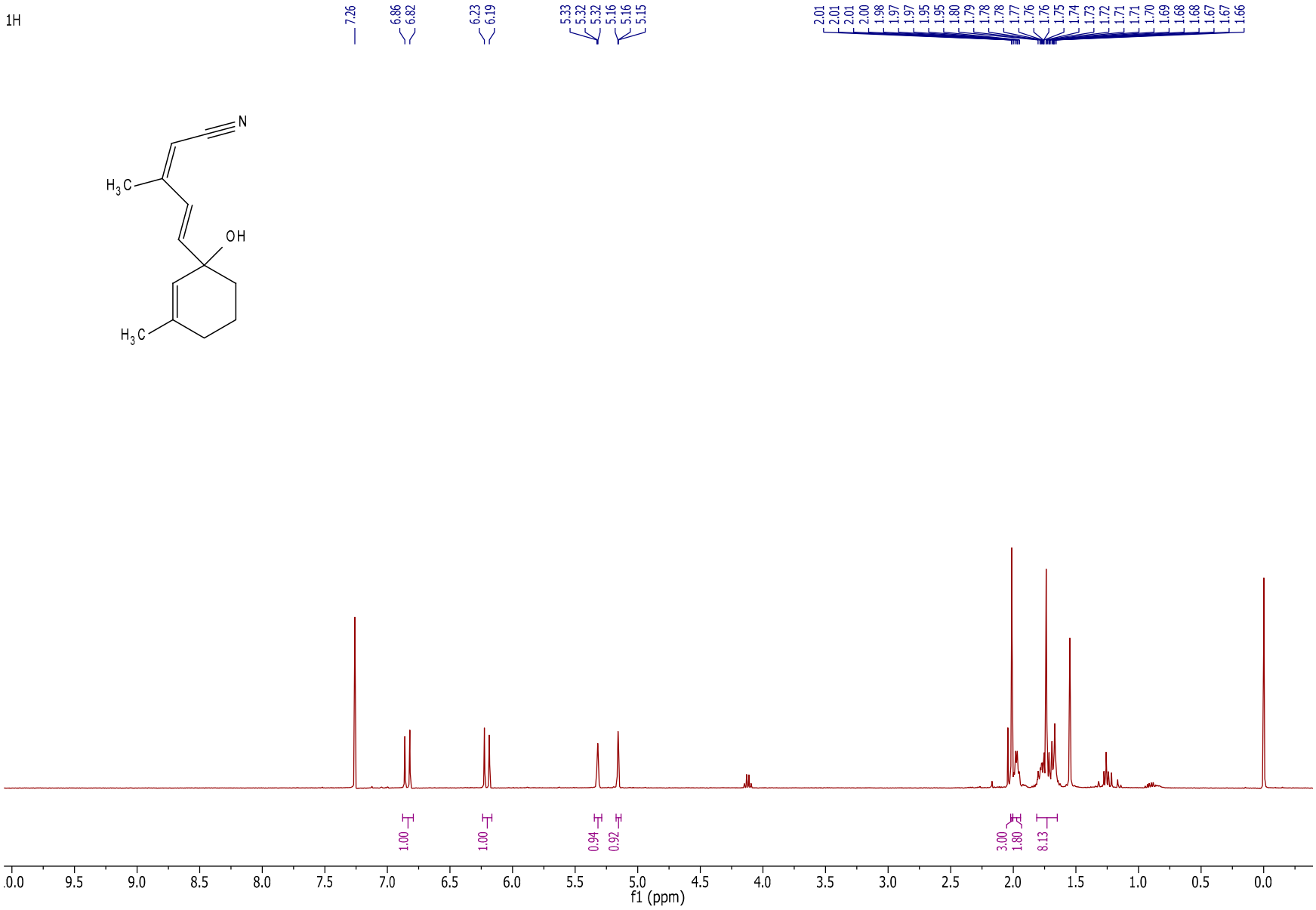

13C
166.82
151.06
136.71
135.46
128.69
128.66
127.42
125.93
117.24
51.05
20.90
CH3
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

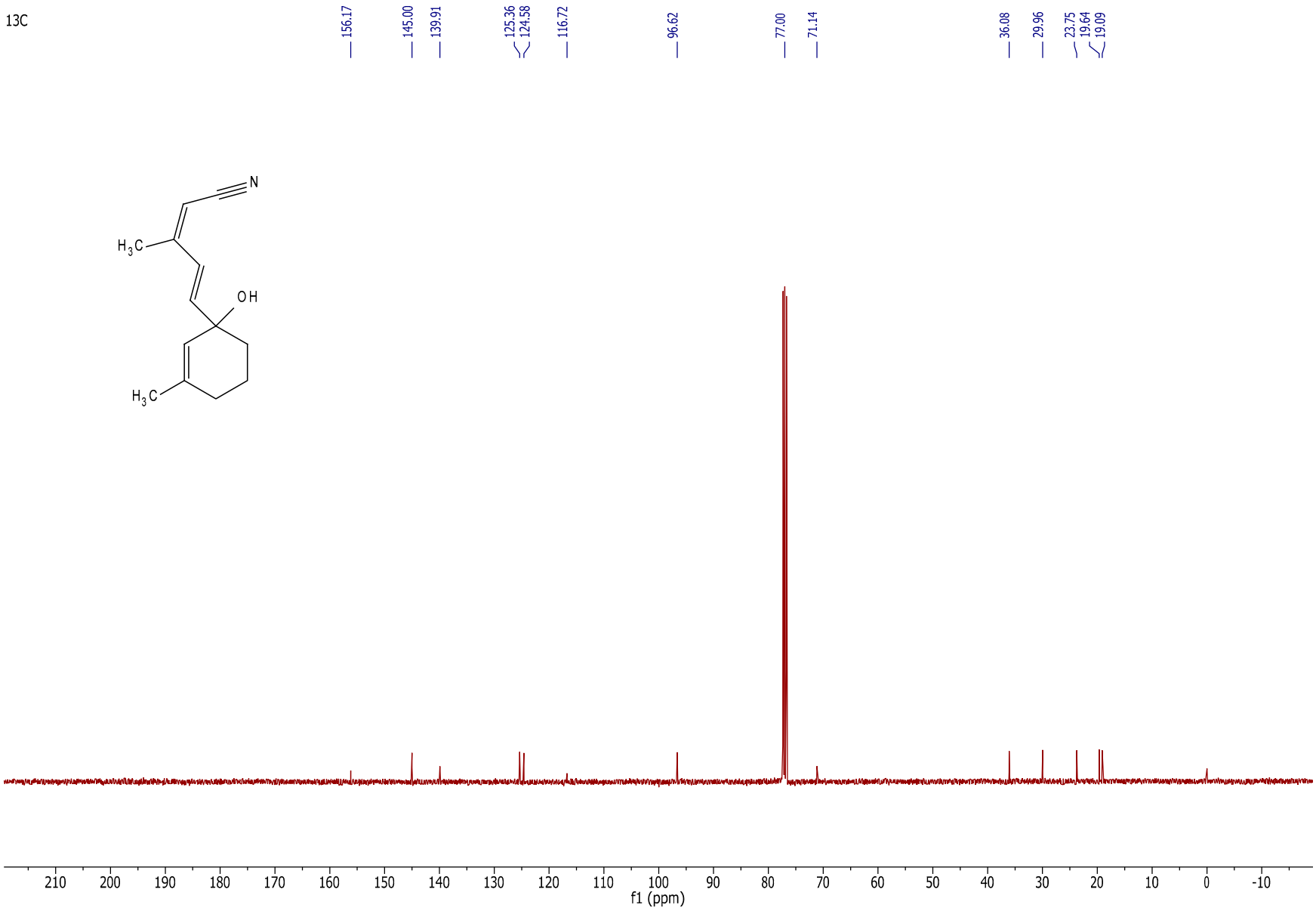
Compound 3k :


1H
O
O
CH3
OH
H3C
7.53 7.53 7.50 7.50 7.49 7.49 7.46 7.46 7.26
6.62 6.62 6.59 6.59 6.10
5.68 5.68 5.34 5.34 5.34 5.33
3.73
1.98 1.98 1.96 1.95 1.95 1.93 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.73 1.72 1.72 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.65 1.64 1.63
1.00
0.99
0.98
0.98
0.97
2.87
1.75
8.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

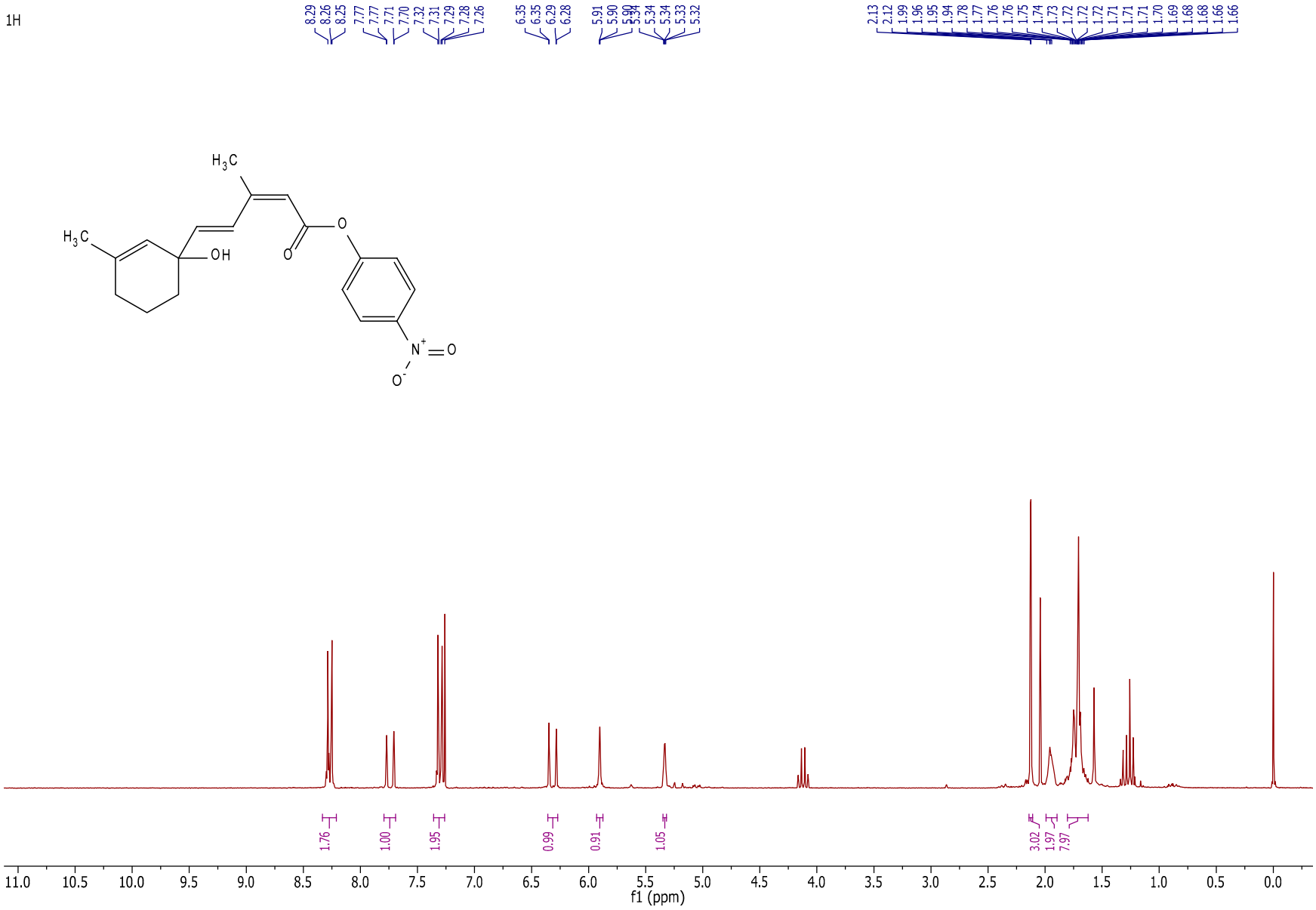

13C
166.91
149.95
144.85
139.45
124.96
124.26
117.28
71.25
51.32
36.02
30.15
23.90
19.32
O
O
CH3
OH
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

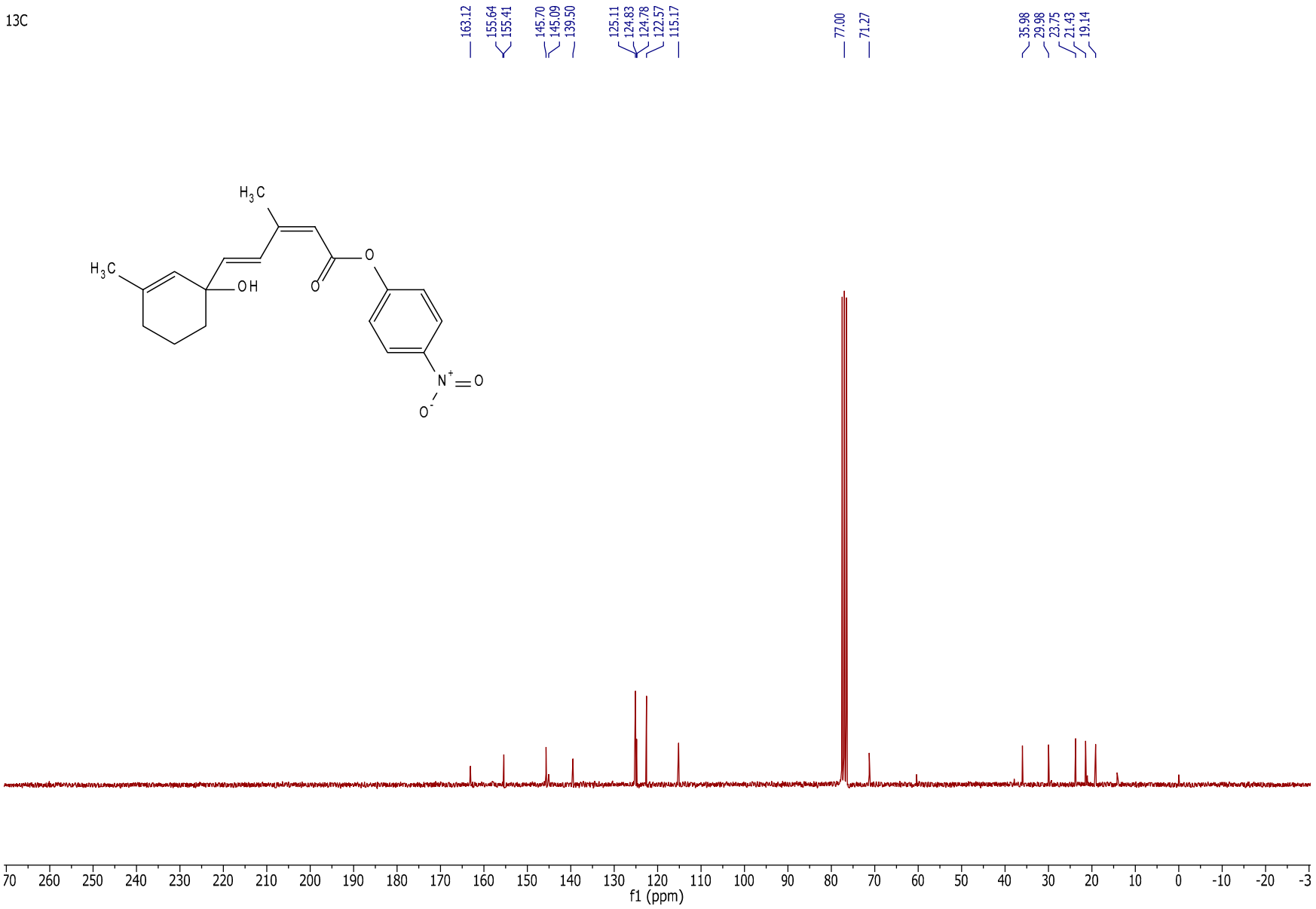
Compound 3l :


1H
7.26
6.86
6.82
6.23
6.19
5.33
5.32
5.32
5.16
5.16
5.15
2.01
2.01
2.01
2.00
1.98
1.97
1.97
1.95
1.95
1.80
1.79
1.78
1.78
1.77
1.76
1.76
1.75
1.74
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.68
1.67
1.67
1.66
N
H3C
OH
H3C
1.00
1.00
0.94
0.92
3.00
1.80
8.13
f1 (ppm)

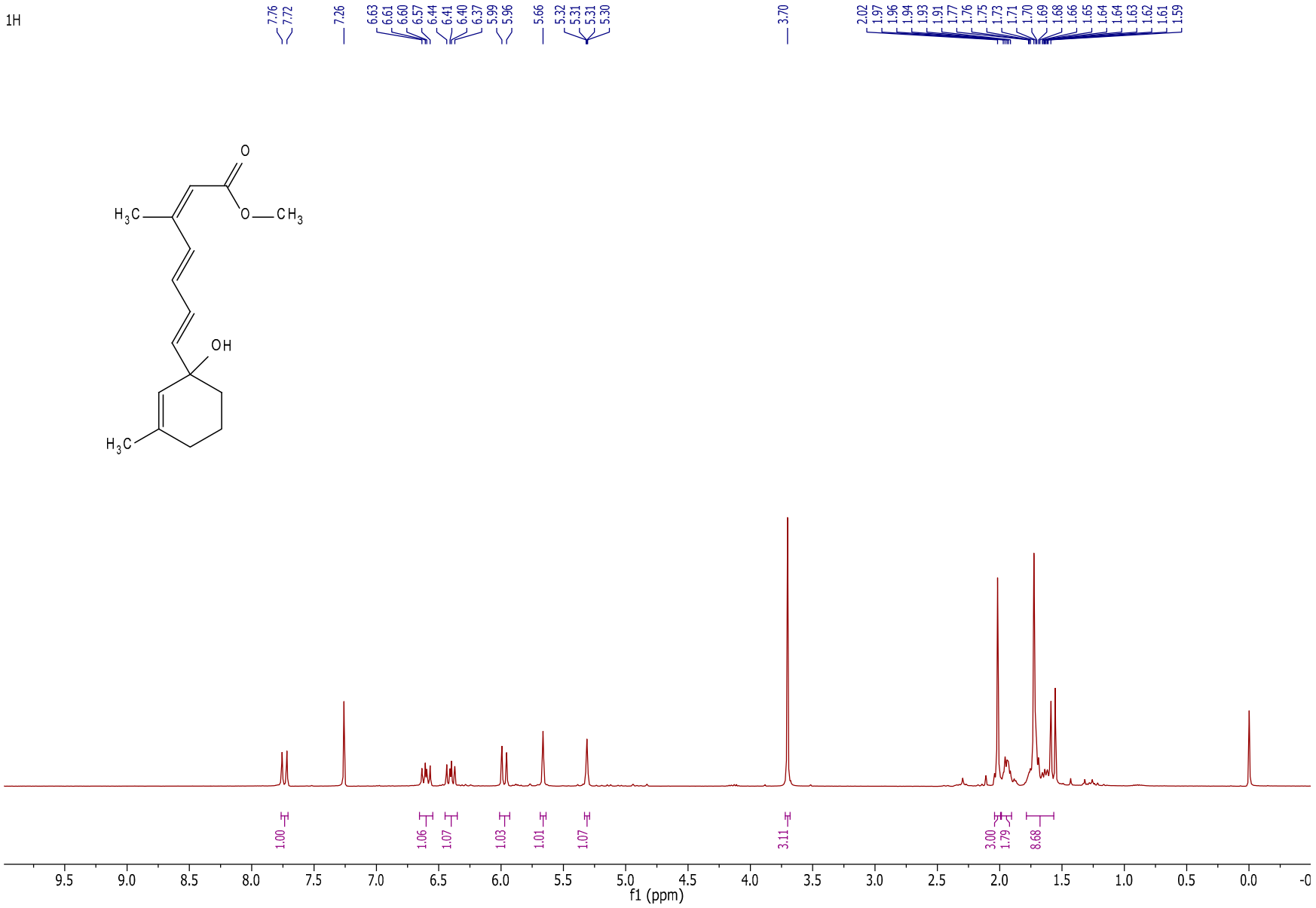

13C
156.17
145.00
139.91
125.36
124.58
116.72
96.62
77.00
71.14
36.08
29.96
23.75
19.64
19.09
N
H3C
OH
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

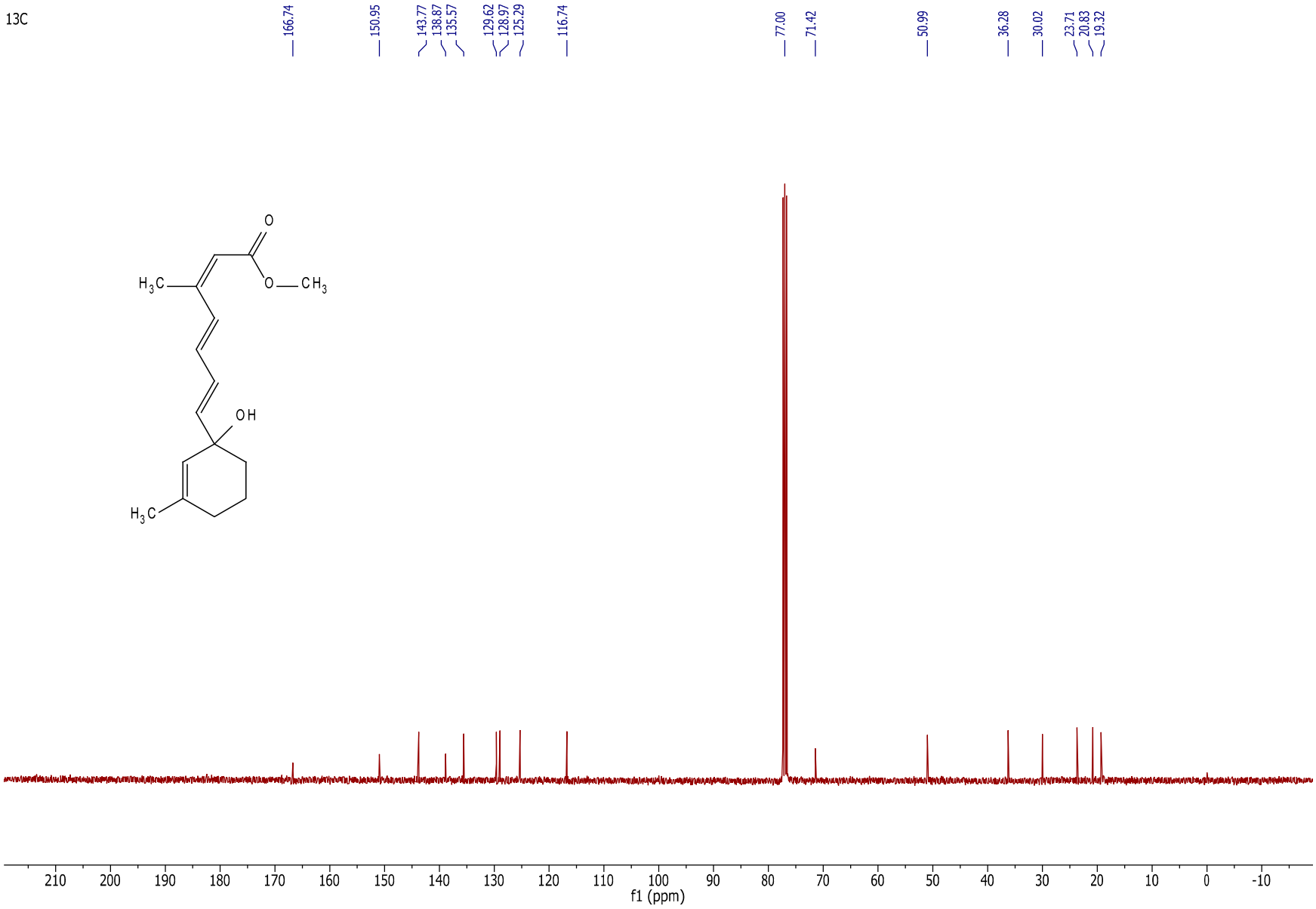
Compound 3m :


1H
8.29
8.26
8.25
7.77
7.77
7.71
7.70
7.32
7.31
7.29
7.28
7.26
6.35
6.35
6.29
6.28
5.91
5.90
5.34
5.34
5.33
5.32
2.13
2.12
1.99
1.96
1.95
1.94
1.78
1.77
1.76
1.76
1.75
1.74
1.73
1.72
1.72
1.72
1.71
1.71
1.71
1.70
1.69
1.68
1.68
1.66
1.66
H3C
H3C
OH
O
O
N+
O
O-
1.76
1.00
1.95
0.99
0.91
1.05
3.02
1.97
7.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

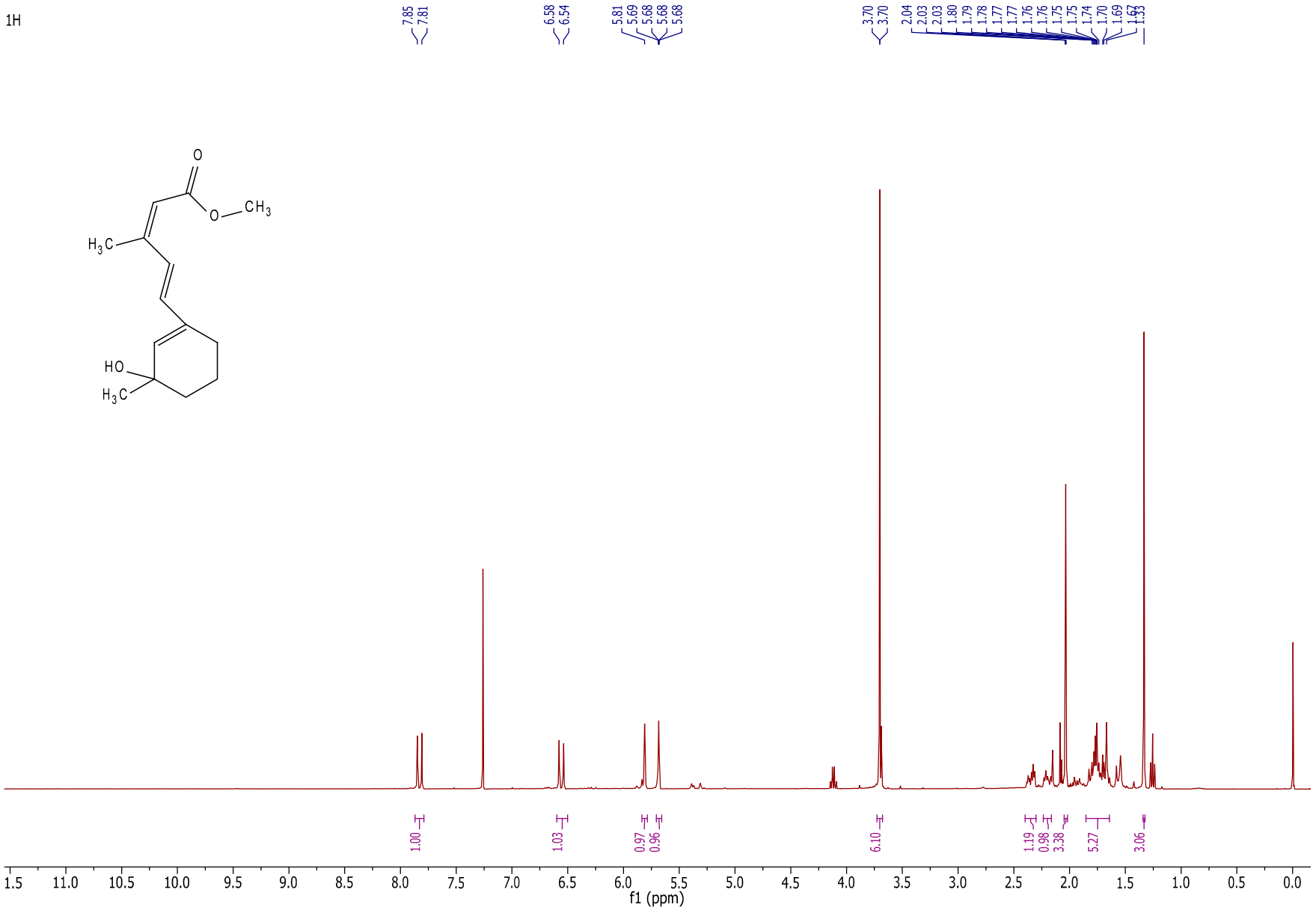

13C
163.12
155.64
155.41
145.70
145.09
139.50
125.11
124.83
124.78
122.57
115.17
77.00
71.27
35.98
29.98
23.75
21.43
19.14
H3C
H3C
OH
O
O
N+
O
O-
70 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
f1 (ppm)

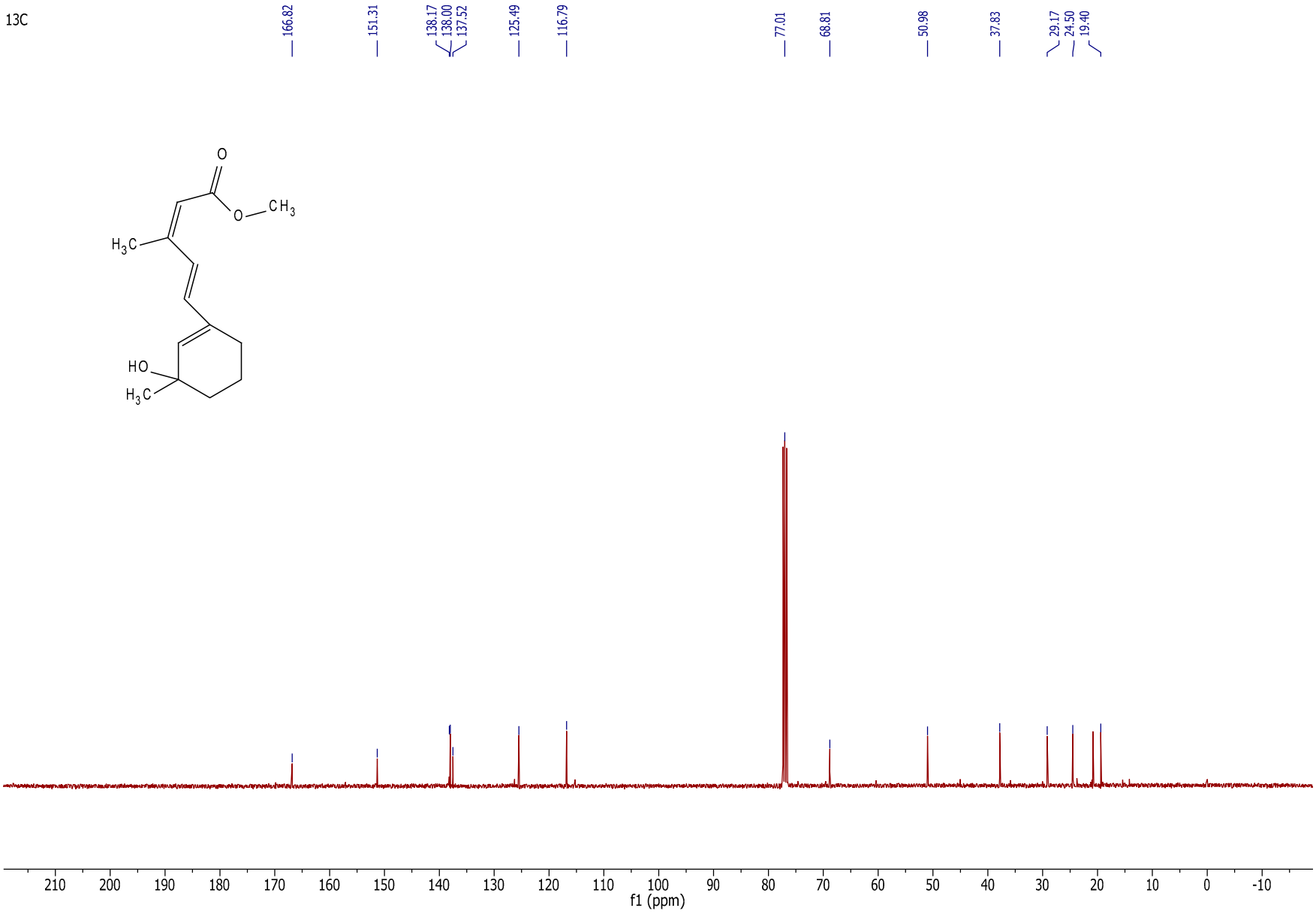
Compound 3n :


1H
7.76
7.72
7.26
6.63
6.61
6.60
6.57
6.44
6.41
6.40
6.37
5.99
5.96
5.66
5.32
5.31
5.30
3.70
2.02
1.97
1.96
1.94
1.93
1.91
1.77
1.76
1.75
1.73
1.71
1.70
1.69
1.68
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.59
O
H3C
O
CH3
OH
H3C
1.00
1.06
1.07
1.03
1.01
1.07
3.11
3.00
1.79
8.68
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


13C
166.74
150.95
143.77
138.87
135.57
129.62
128.97
125.29
116.74
77.00
71.42
50.99
36.28
30.02
23.71
20.83
19.32
O
H3C
O
CH3
OH
H3C
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)

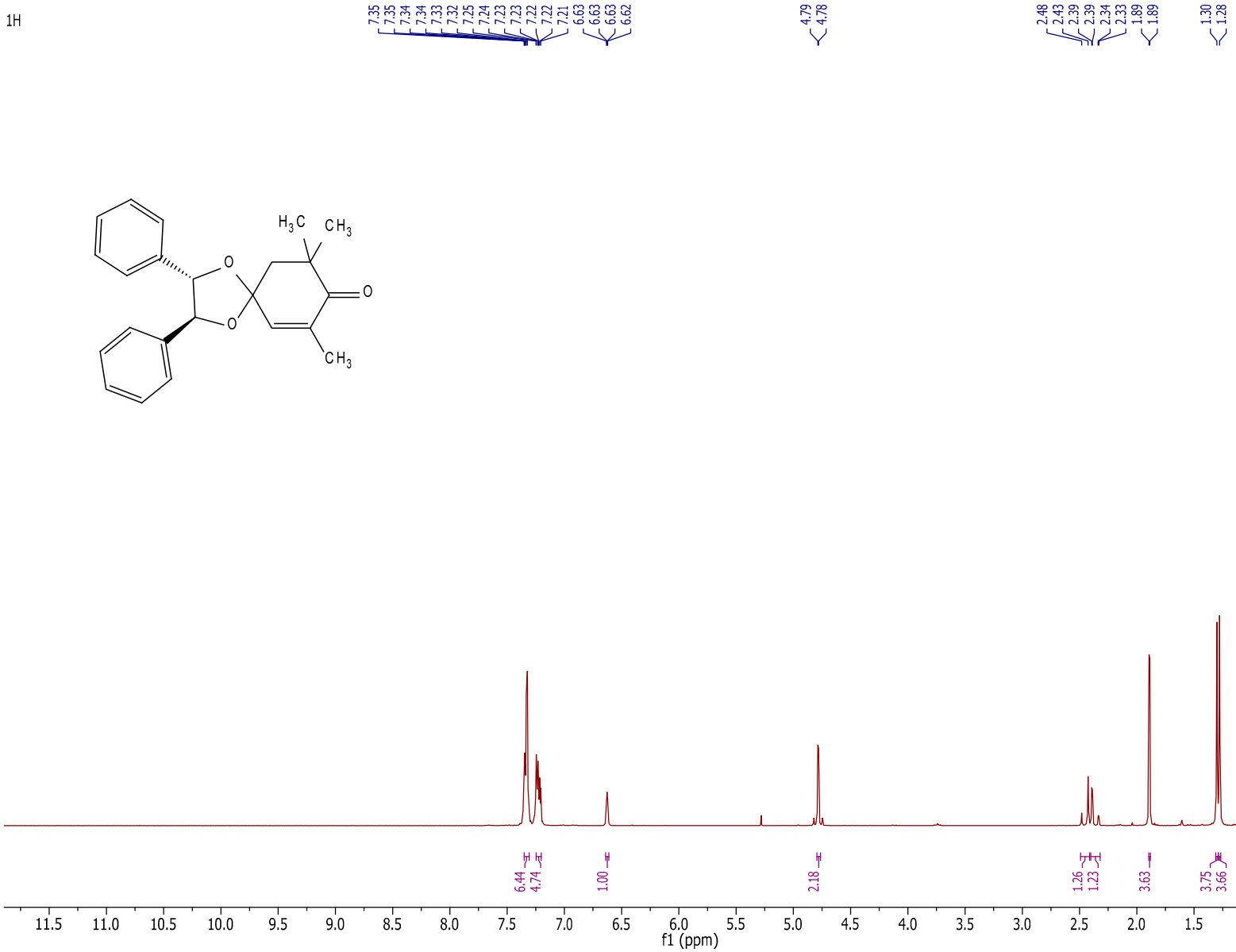
Compound 4 :

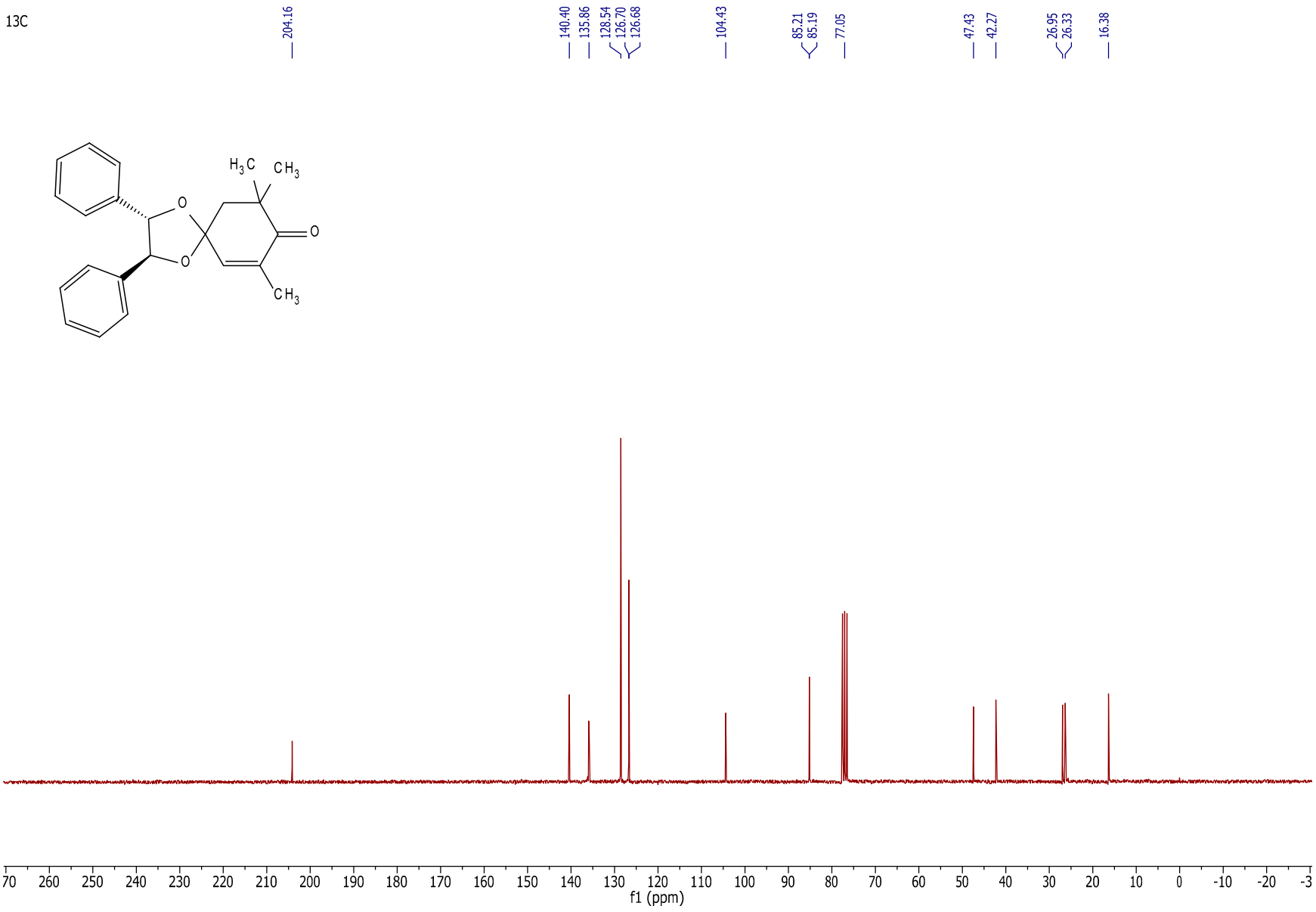

1H
7.85
7.81
6.58
6.54
5.81
5.69
5.68
5.68
5.68
3.70
3.70
2.04
2.03
2.03
1.80
1.79
1.78
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.70
1.69
1.67
1.33
O
O
CH3
H3C
HO
H3C
1.00
1.03
0.97
0.96
6.10
1.19
0.98
3.38
5.27
3.06
f1 (ppm)


13C
166.82
151.31
138.17
138.00
137.52
125.49
116.79
77.01
68.81
50.98
37.83
29.17
24.50
19.40
O
O
CH3
H3C
HO
H3C
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)

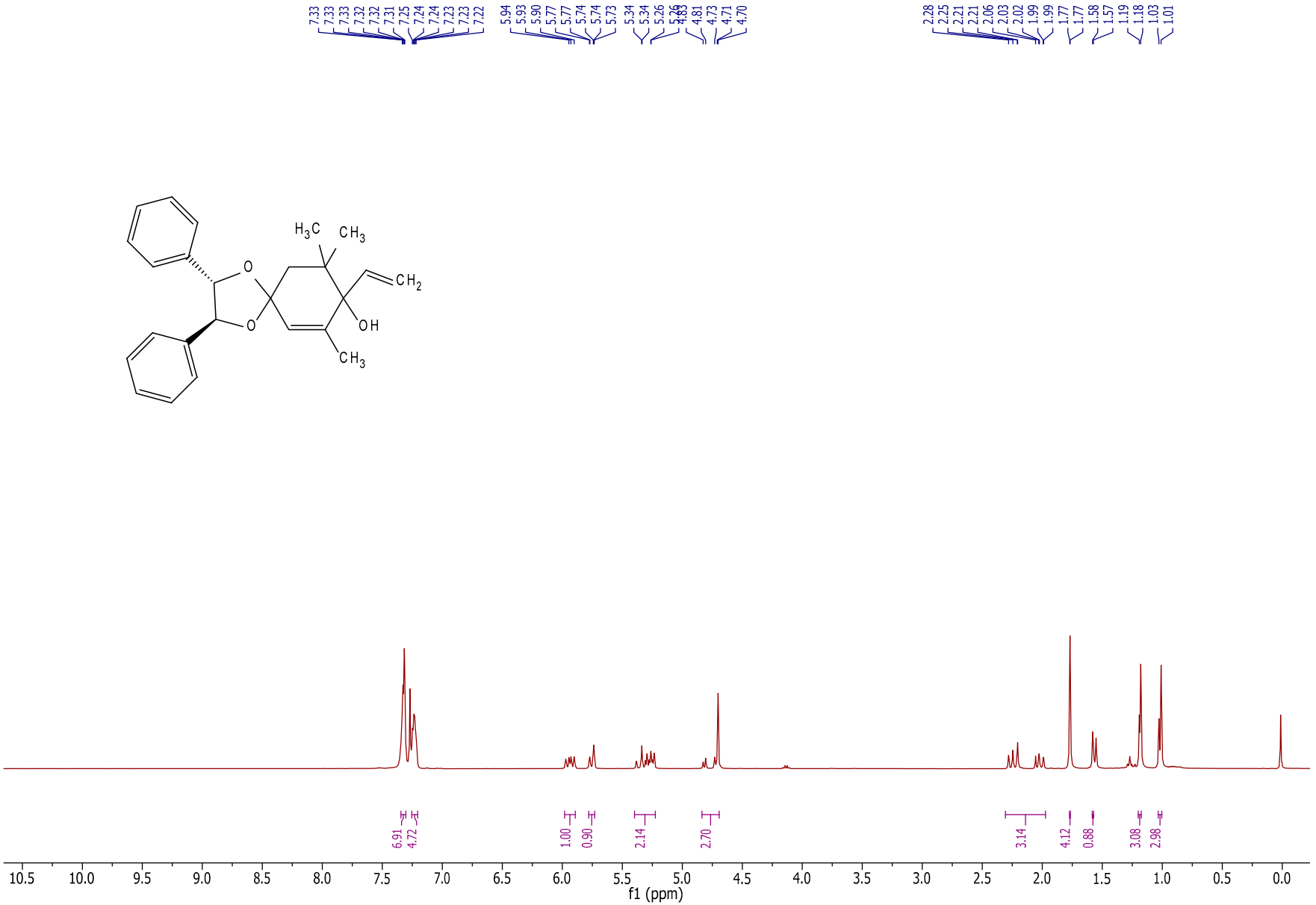
NMR spectra – Synthesis of ABA

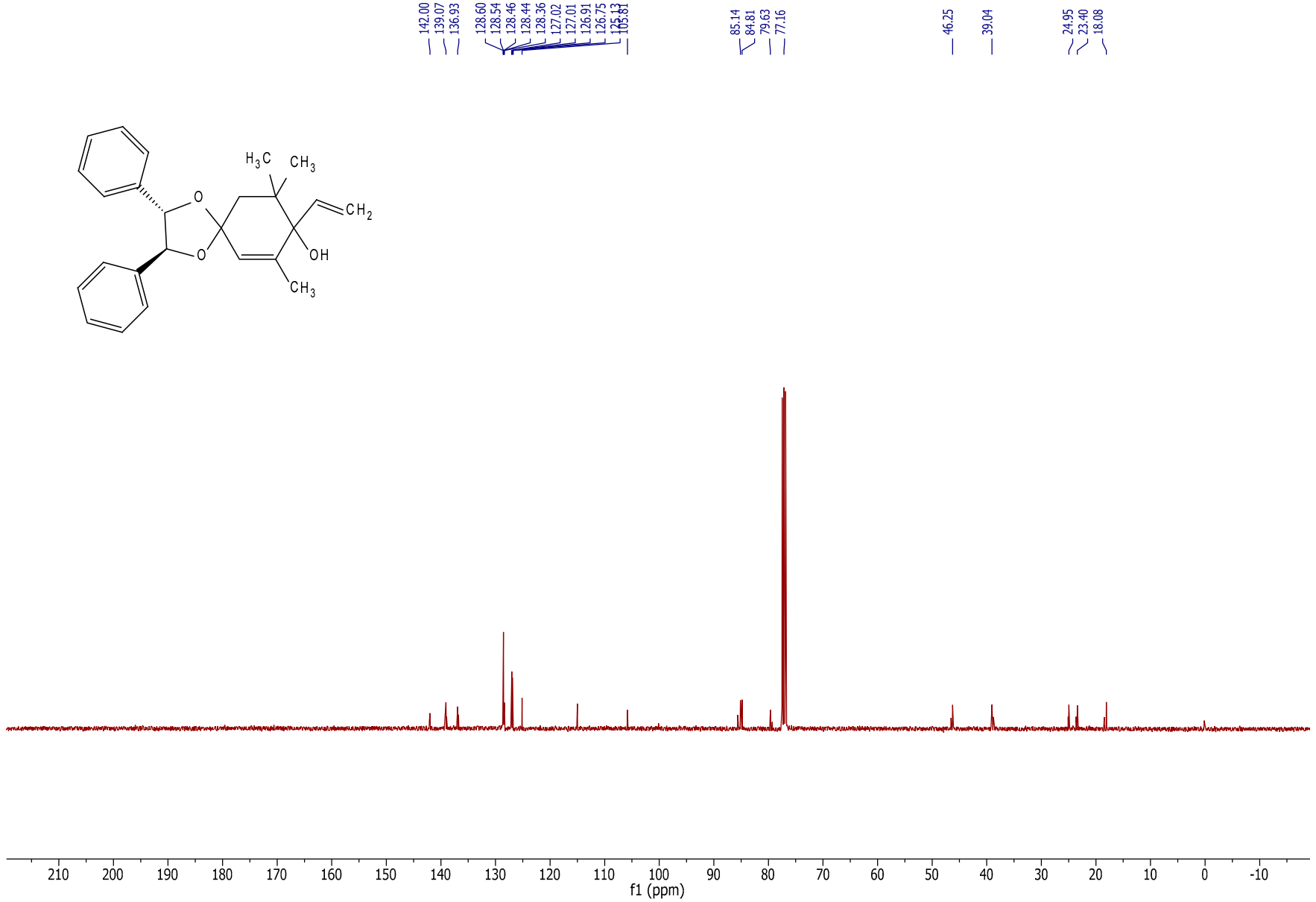
Compound 6 :



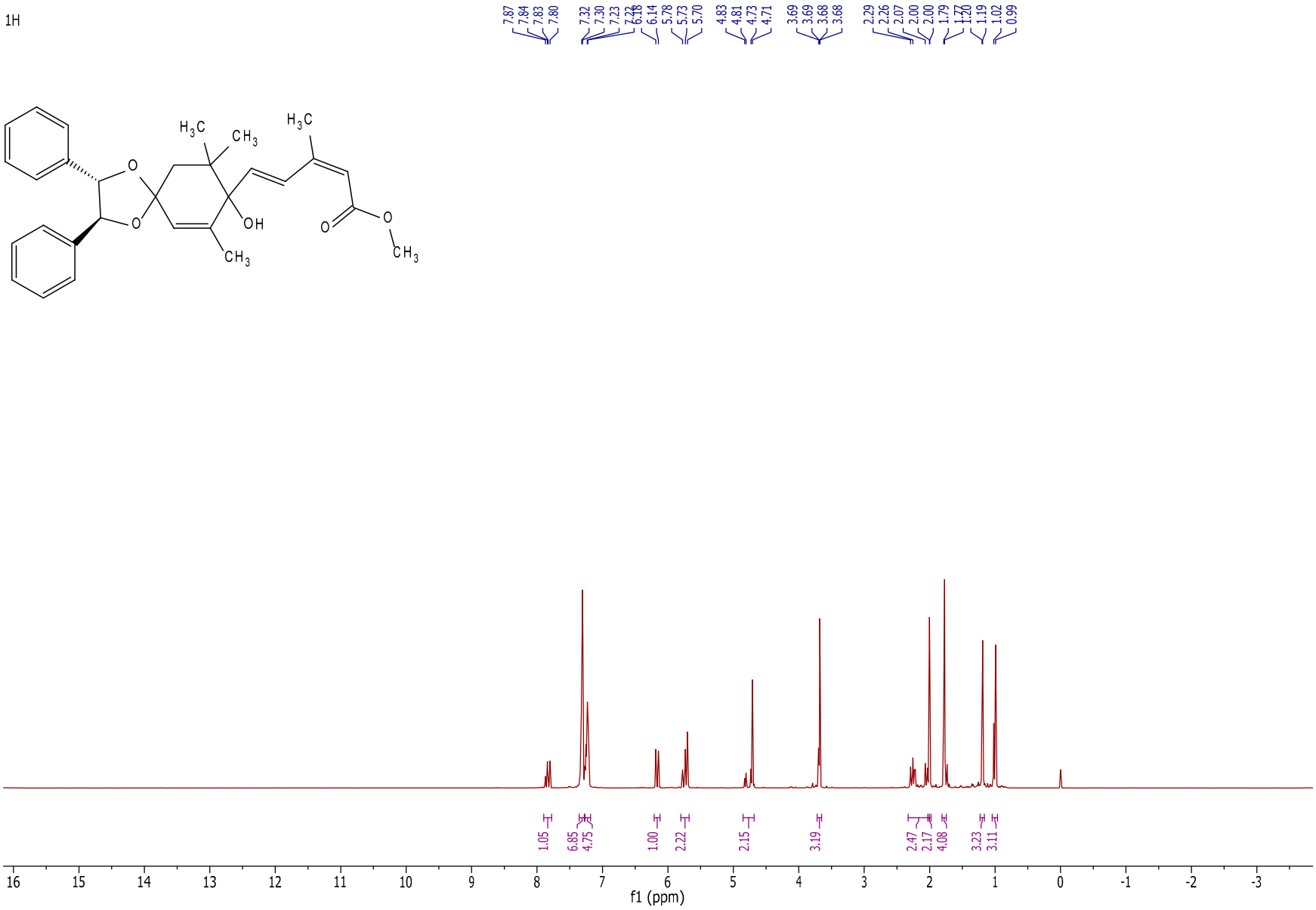

13C
204.16
140.40
135.86
128.54
126.70
126.68
104.43
85.21
85.19
77.05
47.43
42.27
26.95
26.33
16.38
H3C
CH3
O
O
O
CH3
f1 (ppm)

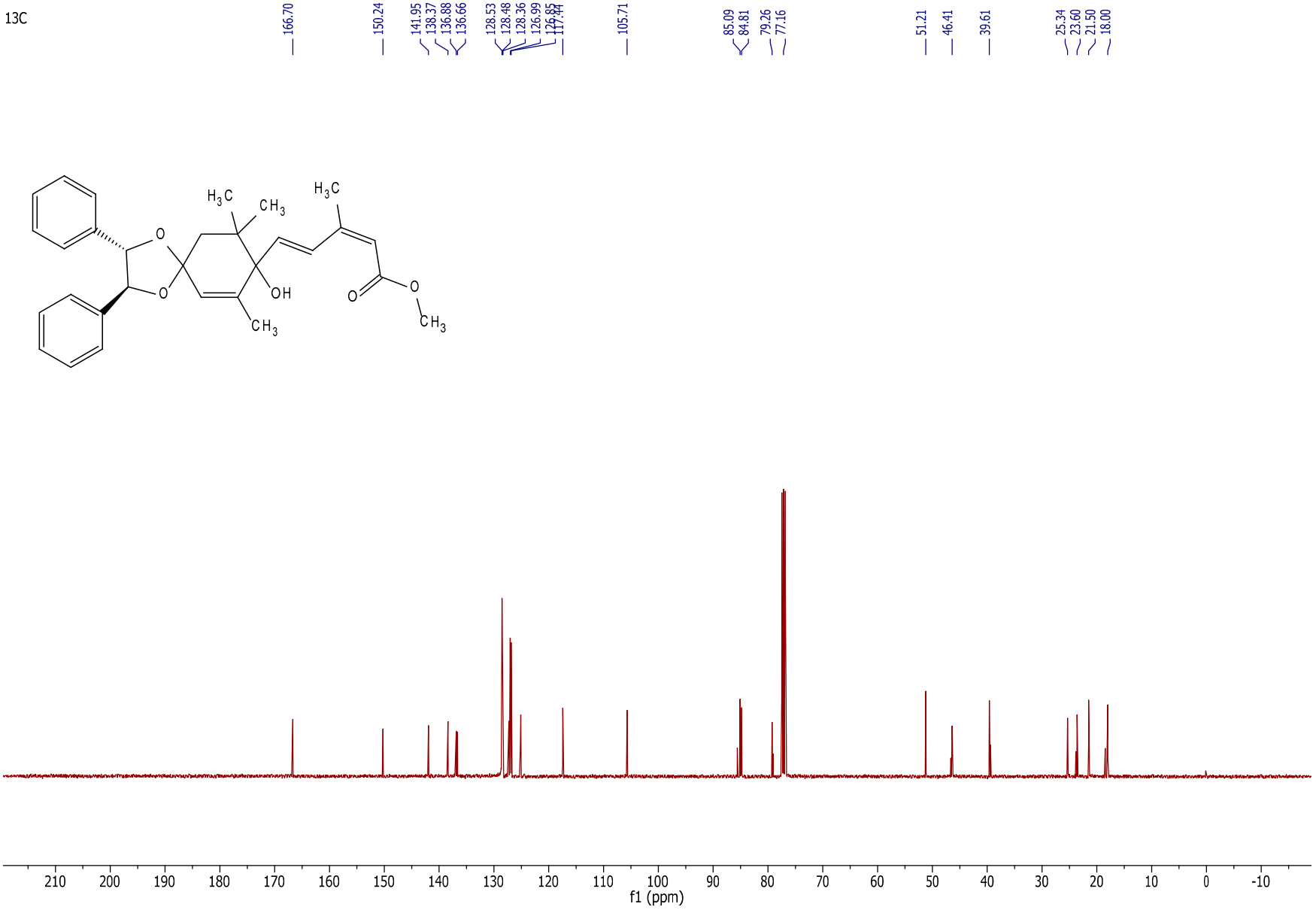
Compound 7 :


7.33
7.33
7.33
7.32
7.32
7.31
7.25
7.24
7.24
7.23
7.23
7.22
5.94
5.93
5.90
5.77
5.77
5.74
5.74
5.73
5.34
5.34
5.26
4.81
4.73
4.71
4.70
2.28
2.25
2.21
2.21
2.06
2.03
2.02
1.99
1.99
1.77
1.77
1.58
1.57
1.19
1.18
1.03
1.01
H3C
CH3
O
O
CH2
OH
CH3
6.91
4.72
1.00
0.90
2.14
2.70
3.14
4.12
0.88
3.08
2.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

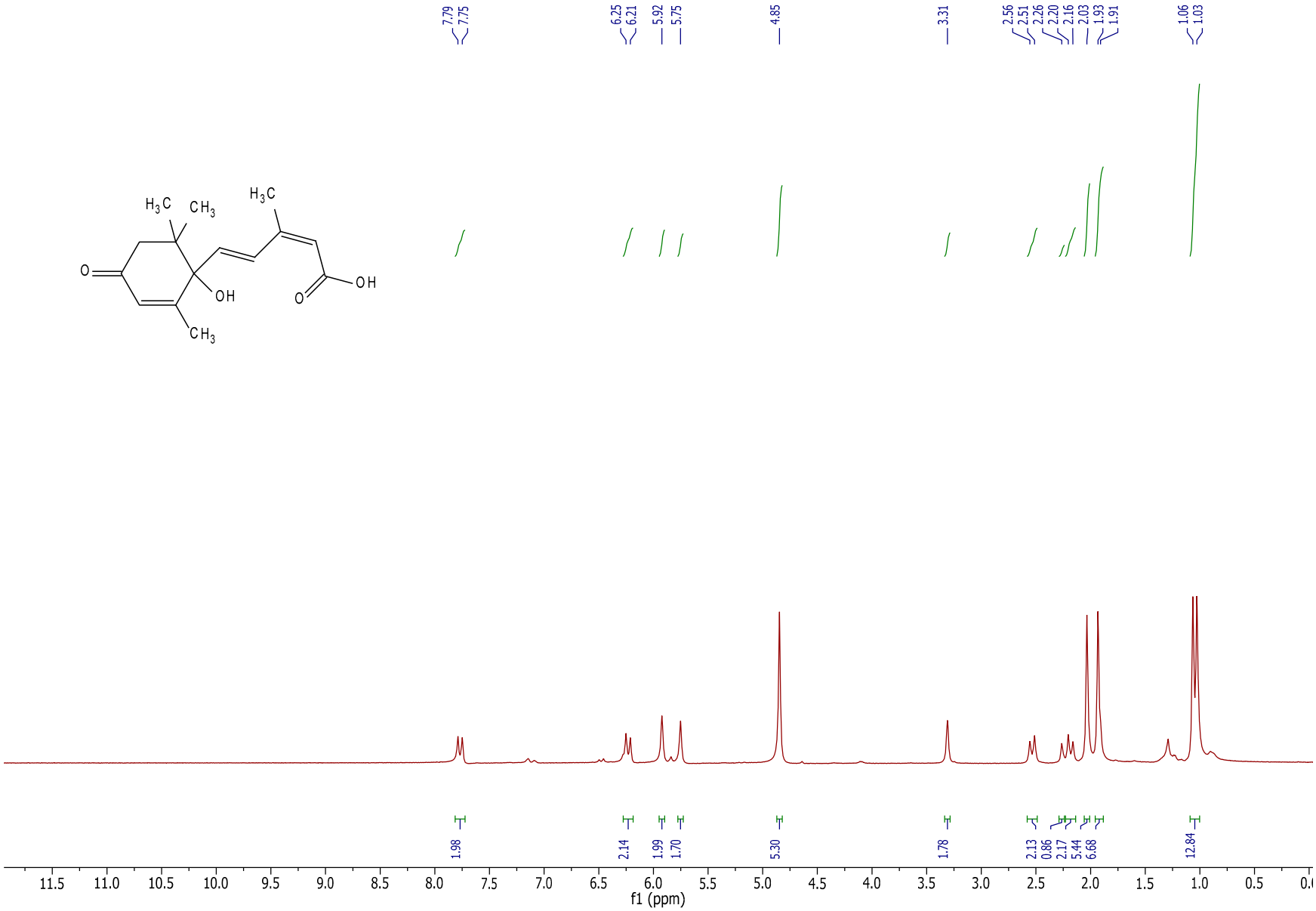

142.00
139.07
136.93
128.60
128.54
128.46
128.44
128.36
127.02
127.01
126.91
126.75
125.13
125.81
85.14
84.81
79.63
77.16
46.25
39.04
24.95
23.40
18.08
H3C
CH3
CH2
O
O
OH
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

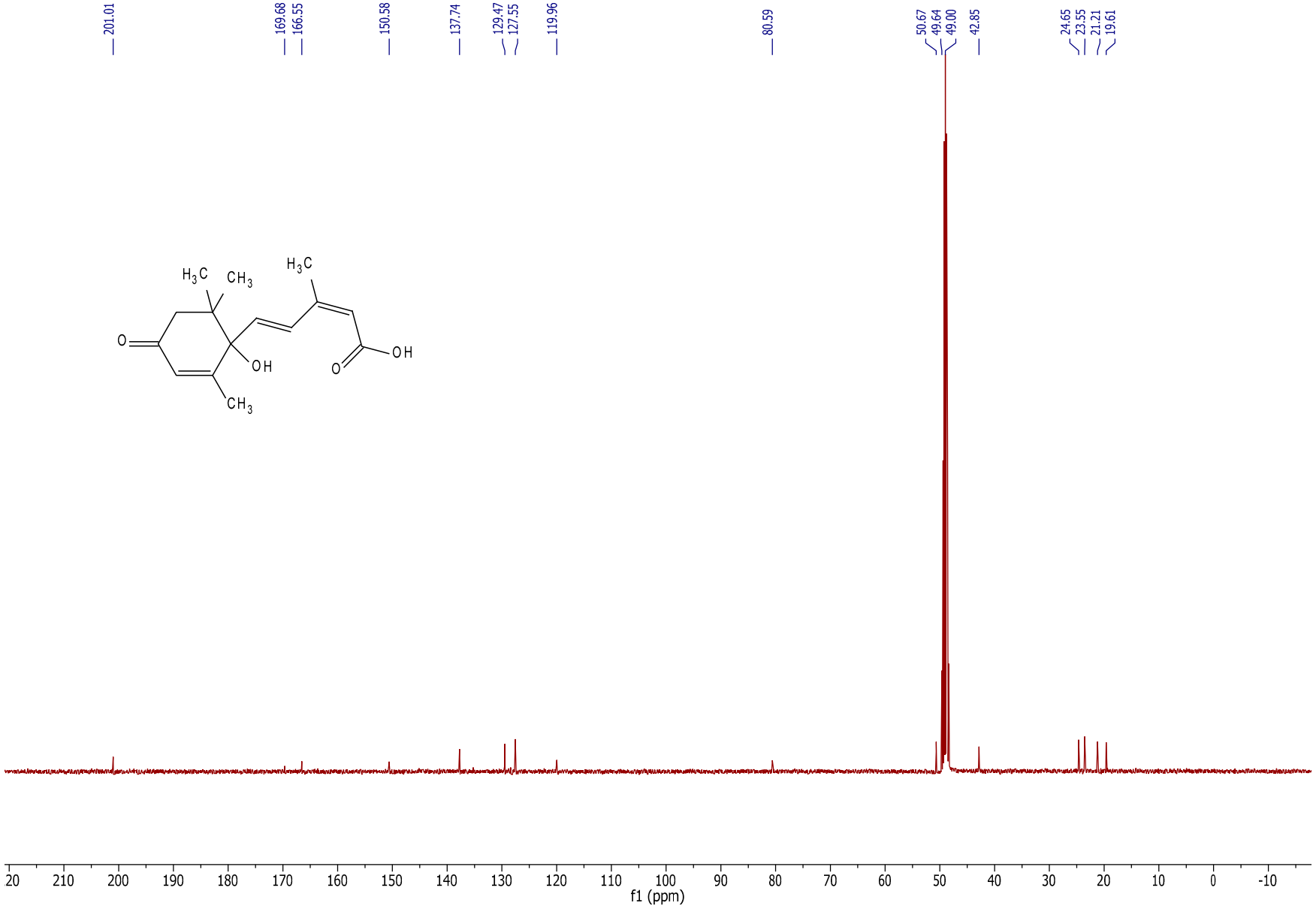
Compound 8 :


1H
7.87
7.84
7.83
7.80
7.32
7.30
7.23
6.14
5.78
5.73
5.70
4.83
4.81
4.73
4.71
3.69
3.68
2.29
2.26
2.07
2.00
1.79
1.19
1.02
0.99
H3C
CH3
H3C
O
O
OH
O
O
CH3
CH3
1.05
6.85
4.75
1.00
2.22
2.15
3.19
2.47
2.17
4.08
3.23
3.11
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


13C
166.70
150.24
141.95
138.37
136.88
136.66
128.53
128.48
128.36
126.99
105.71
85.09
84.81
79.26
77.16
51.21
46.41
39.61
25.34
23.60
21.50
18.00
H3C
CH3
H3C
O
O
OH
O
O
CH3
CH3
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)

Compound ABA :




201.01
169.68
166.55
150.58
137.74
129.47
127.55
119.96
80.59
50.67
49.64
49.00
42.85
24.65
23.55
21.21
19.61
H3C
CH3
H3C
O
OH
O
OH
CH3
20
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)