Supplementary Information

Leveraging Lewis Acid Catalysis for Cascade Construction of Multisubstituted Furans from Active Methylenes and 3-Oxetanone

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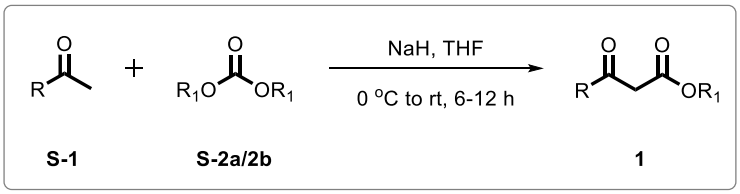
1. General information

All reactions were performed under an argon atmosphere and using an oven (80 ºC) or flame-dried glassware with a septum seal or sealed tubes. Tetrahydrofuran (THF) was distilled from sodium benzophenone under an argon atmosphere immediately before use. All dry solvents were either freshly distilled or purchased from a commercial supplier in extra-dry grade. Anhydrous methanol, acetone, and dichloromethane were purchased from commercial sources. The solvents for workup and column chromatography were purified by distillation before use. A few of the starting materials were commercially available and obtained from Sigma-Aldrich, BLD Pharm, and TCI Chemicals and were used as received without any further purification. Reaction temperatures are reported as the oil bath temperature surrounding the reaction vessel. Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F254. Visualization was accomplished with shortwave UV light, anisaldehyde, or $KMnO_4$ staining solutions, followed by heating. Chromatography purification was performed on silica gel (100−200 mesh) by standard techniques eluting with solvents as indicated. For NMR analysis, MestReNova v14.1.0- 24037 was applied. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400 and 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). The following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; td, triplet of doublet; and br, broad. Coupling constants (*J*) are given in Hertz (Hz) in one decimal place. Structural assignments were made with additional information from gCOSY, gNOESY, gHSQC, and gHMBC experiments. Infrared (IR) spectra were recorded with an FT-IR Bruker Alpha II spectrometer equipped with an ATR unit. HRMS data were recorded on a Thermo Scientific QExactive Accela 1250 pump.

2. General synthesis procedures and analytical data for starting materials

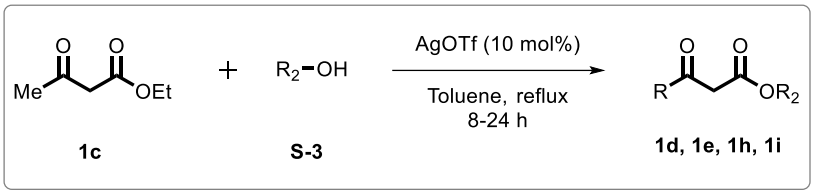
(a) General procedure-1 for the synthesis of *β*-ketoesters (GP1):[1]



A 100 mL two-necked flask was charged with NaH (60% in dispersion oil) (1.5 mmol) in anhydrous THF (7 mL) at 0 ºC (ice bath) and stirred to homogeneity. To it was added a solution

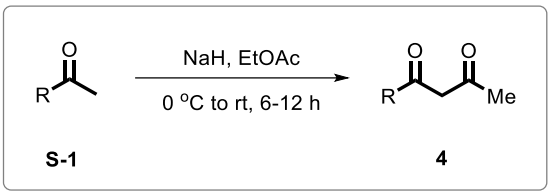
of acetophenone (methyl ketone derivative) (**S-1**, 1 mmol) in anhydrous THF (5 mL) at same temperature, and slowly warmed to rt, and stirred at rt for 45 mins. Then, diethyl carbonate (**S-2a**, 1.2 mmol) OR dimethyl carbonate (**S-2b**, 1.2 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, the reaction was quenched with acetic acid at 0 °C (ice bath) & pH = 6.0 was maintained, and the aqueous layer was extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **1**.

(b) General procedure-2 for the synthesis of *β*-ketoesters (GP2):[2]



A 100 mL round bottom flask containing ethyl acetoacetate (**1c**, 1 mmol) was dissolved in toluene (10 mL) at room temperature. Then, alcohol (**S-3**, 2 mmol) and AgOTf (0.1 mmol) were added and refluxed, connecting to a Dean-Stark apparatus, and the reaction progress was monitored by TLC. After completion of the reaction, the excess solvent was evaporated and was quenched with saturated aqueous solution $NaHCO_3$ (5 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-10% EtOAc/Hexane) to afford the desired product **1d**, **1e**, **1h**, **1i**, respectively.

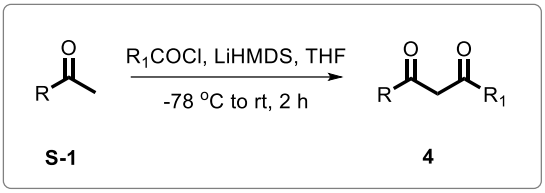
(c) General procedure-3 for the synthesis of *β*-diketones (GP3):[3]



A 100 mL two-necked flask was charged with NaH (60% in dispersion oil) (1.5 mmol) in anhydrous EtOAc (7 mL) at 0 °C (ice bath) and stirred to homogeneity. To it was added a solution of acetophenone OR methyl ketone derivatives (**S-1**, 1 mmol) in anhydrous EtOAc (5 mL), stirred and allowed to warm to room temperature, and stirred at rt for 6-12 h. After completion of the reaction, the reaction was quenched with saturated aqueous NH_4Cl solution

at 0 °C (ice bath) & pH=6 was maintained, and the aqueous layer was extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-10% EtOAc/Hexane) to afford the desired product **4**.

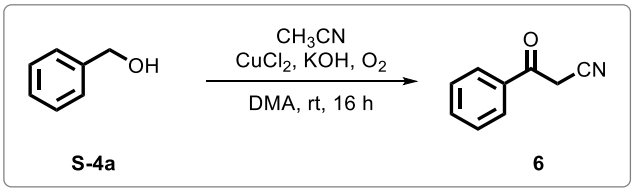
(d) General procedure-4 for the synthesis of *β*-diketones (GP4):[4]



In a 100 mL two-necked flask, acetophenone/methyl ketone derivatives (**S-1**, 1 mmol) in anhydrous THF (30 mL) at –78 °C and stirred to homogeneity. To it was added LiHMDS (1 M solution in THF) (1.5 or 3 mmol) dropwise, and alkyl/aryl acid chloride (1 mmol) was added after 45 mins at the same temperature and stirred to warm to room temperature for 2-6 h, and the reaction progress was monitored by TLC. After completion of the reaction, the reaction was quenched with saturated aqueous NH_4Cl solution at 0 °C (ice bath) & pH=6 was maintained, and the aqueous layer was extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **4**.

(e) Synthesis of 3-oxo-3-phenylpropanenitrile (*β*-ketonitriles):

The synthesis of 3-oxo-3-phenylpropanenitrile (**6**) was carried out according to the procedure described in the literature.[5]

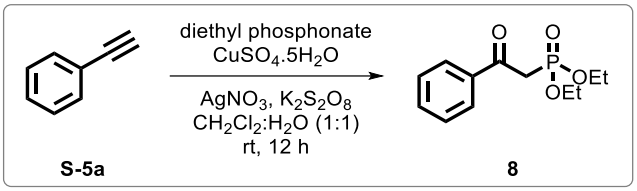


To a 100 mL two-necked flask, benzyl alcohol (**S-4a**, 5 g, 46.23 mmol), anhydrous acetonitrile (24.14 mL, 462.36 mmol), KOH (7.78 g, 138.70 mmol), $CuCl_2$ (0.621 g, 4.62 mmol), and DMA (35 mL) at room temperature were added sequentially under O_2 (1 atm) and stirred for 16 h, and the reaction progress was monitored by TLC. After completion of the reaction, the reaction was quenched with 10% HCl solution (50 mL), and the aqueous layer was extracted with

EtOAc (3 × 50 mL), dried over Na_2SO_4, and filtered; the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-50% EtOAc/Hexane) to afford the desired product **6**.

(f) Synthesis of diethyl (2-oxo-2-phenylethyl)phosphonate (*β*-ketophosphonates):

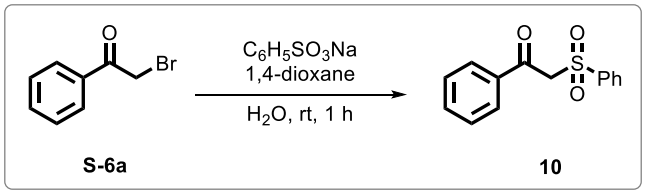
The synthesis of diethyl (2-oxo-2-phenylethyl)phosphonate (**8**) was carried out according to the procedure described in the literature.[6]



To a 100 mL two-necked flask, phenylacetylene (**S-5a**, 5 g, 48.95 mmol), diethyl phosphonate (9.75 mL, 73.42 mmol), $CuSO_4.5H_2O$ (0.78 g, 4.89 mmol), $AgNO_3$ (0.083 g, 0.489 mmol), $K_2S_2O_8$ (0.66 g, 2.44 mmol) and CH_2Cl_2:H_2O (1:1) (55 mL) at room temperature were added sequentially under O_2 (1 atm) and stirred for 12 h, and the reaction progress was monitored by TLC. After completion of the reaction, the reaction was quenched with 1(N) HCl solution (20 mL), and the aqueous layer was extracted with EtOAc (3 × 50 mL), dried over Na_2SO_4, and filtered; the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-50% EtOAc/Hexane) to afford the desired product **8**. The characterization data aligns perfectly with the reported data in the literature.

(g) Synthesis of 1-phenyl-2-(phenylsulfonyl)ethan-1-one (*β*-ketosulfones):

The synthesis of 1-phenyl-2-(phenylsulfonyl)ethan-1-one (**10**) was carried out according to the procedure described in the literature.[7]

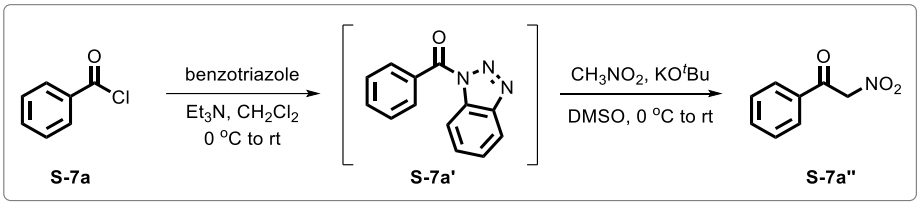


To a 100 mL two-necked flask, 2-bromo-1-phenylethan-1-one derivatives (**S-6a**, 5 g, 25.11 mmol) in 1,4-dioxane (50 mL) was added and stirred to homogeneity. To it was added a solution of sodium benzenesulfonate (4.52 g, 25.11 mmol) in water (50 mL) dropwise and stirred at room temperature for 1 h, and the reaction progress was monitored by TLC. After completion

of the reaction, the excess solvent was evaporated under reduced pressure, and the aqueous layer was extracted with EtOAc (3 × 50 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product obtained as a white solid is the desired product **10**. The characterization data aligns perfectly with the reported data in the literature.

(h) Synthesis of 2-nitro-1-phenylethan-1-one (*β*-nitroketones):

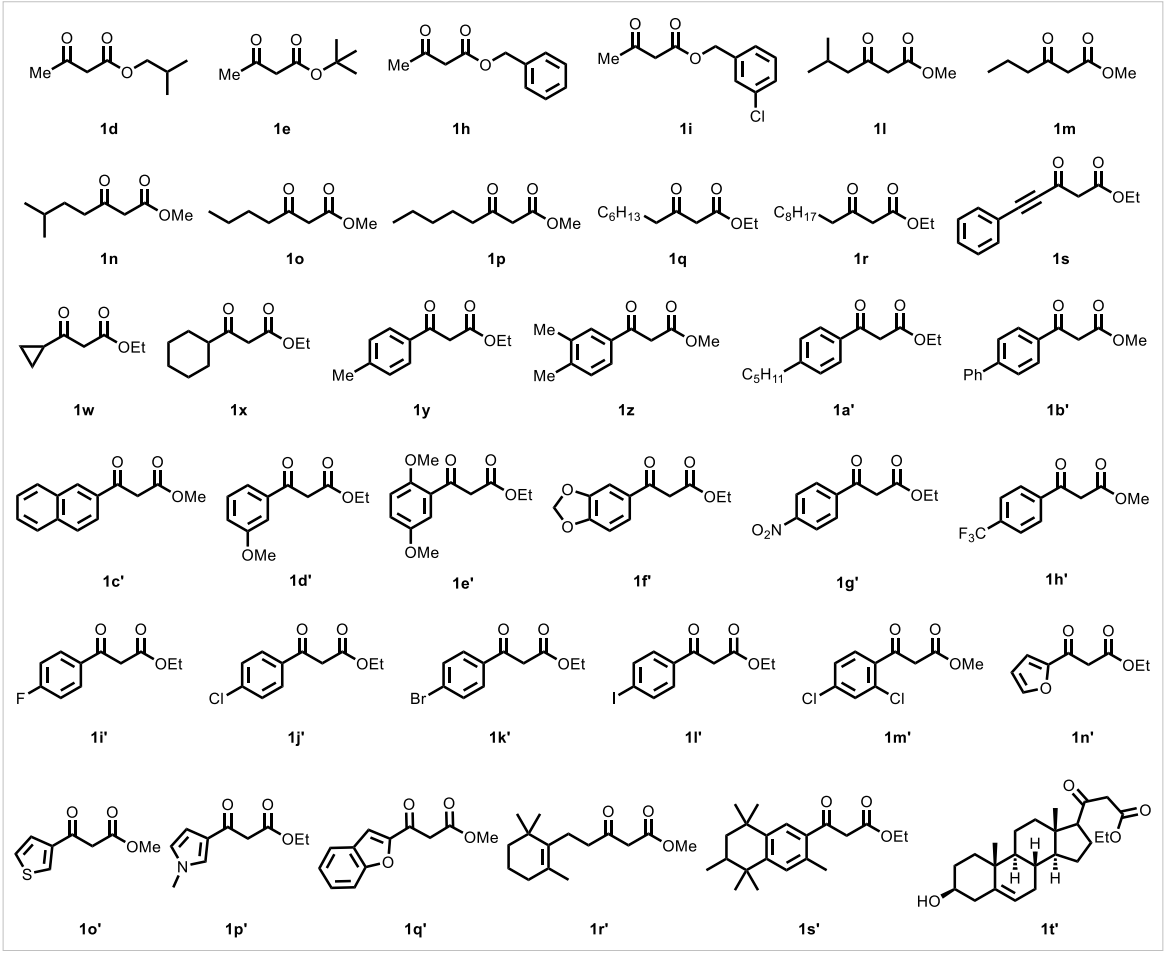
The synthesis of 2-nitro-1-phenylethan-1-one (**S-7a″**) was carried out according to the procedure described in the literature.[8]



Step 1: In a 100 mL two-necked flask, benzotriazole (**S-7a**, 5 g, 41.97 mmol) in anhydrous CH_2Cl_2 (75 mL) was stirred to homogeneity. To it was added Et_3N (7 mL, 50.36 mmol) and benzoyl chloride (5.35 mL, 46.17 mmol) sequentially at 0 °C, and the reaction progress was monitored by TLC. After completion of the reaction, the reaction was quenched with 1(N) HCl solution (50 mL), and the aqueous layer was extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure, and the crude product **S-7a′** obtained (2.67 g) was subjected to the next step without further purification or characterization.

Step 2: In a 100 mL two-necked flask, KO^{t}Bu (2.95 g, 26.31 mmol) in anhydrous DMSO (20 mL) was taken under argon and cooled to 10 °C. To this was added nitromethane (0.64 mL, 11.96 mmol), followed by a solution of the **S-7a′** crude (2.67 g, 11.96 mmol) in anhydrous DMSO (10 mL), and the mixture was allowed to warm up to room temperature and stirred overnight. After completion of the reaction, the reaction was quenched 5 (N) acetic acid, and the aqueous layer was extracted with EtOAc (3 × 50 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product obtained as a white solid is the desired product **S-7a″**. The characterization data aligns perfectly with the reported data in the literature.

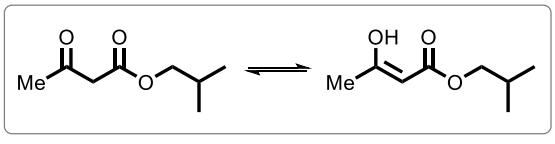
(i) List of *β*-ketoesters synthesized:



All the *β*-ketoesters (**1d**, **1e**, **1h-1i, 1l**–**1s**, **1w**–**1t′**) are synthesized using known literature procedures, **1s** was directly forwarded to next step without any further purification, while substrates (**1a**–**1c**, **1f**, **1g**, **1j-1k**, **1t**–**1v**) are commercially available and purchased from Sigma-Aldrich, BLD Pharm, TCI chemicals and are used as received without further purification.

(j) Analytical data of *β*-ketoesters:

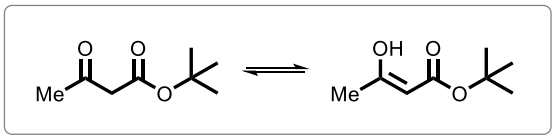
Isobutyl 3-oxobutanoate (1d):



The title compound was synthesized following general procedure GP2, using ethyl acetoacetate (**1c**, 1 g, 7.68 mmol), isobutanol (**S-3a**, 1.42 mL, 15.36 mmol), AgOTf (0.197 g, 0.768 mmol) and toluene (10 mL). The product **1d** was isolated as keto and enol tautomers, as a colorless liquid (0.943 g, 78%). TLC: R_f = 0.3 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3422, 2361, 2105, 1640, 1524, 1477, 1425, 1027, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 0.09H), 4.97 (s, 0.09H), 3.90 (dd, *J* = 6.6,

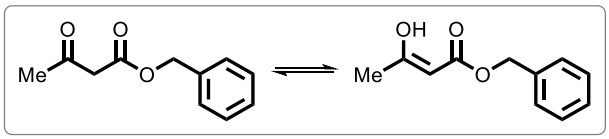
1.2 Hz, 2H), 3.44 (s, 2H), 2.25 (s, 3H), 1.98-1.87 (m, 1H), 0.91 (d, J = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.6, 175.4, 172.8, 167.2, 89.8, 71.5, 70.0, 50.1, 30.2, 27.8, 27.7, 19.1, 19.0; HRMS (ESI): *m/z* calcd for $C_8H_{14}O_3Na$ $[M + Na]^+$ 181.0835, found 181.0833.

Tert-butyl 3-oxobutanoate (1e):



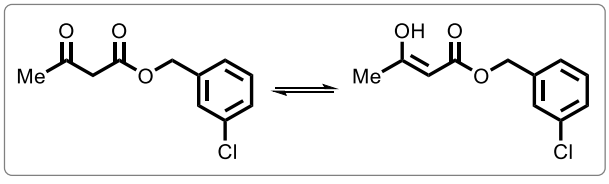
The title compound was synthesized following general procedure GP2, using ethyl acetoacetate (**1c**, 1 g, 7.68 mmol), *tert*-butyl alcohol (**S-3b**, 1.45 mL, 15.36 mmol), AgOTf (0.197 g, 0.768 mmol) and toluene (10 mL). The product **1e** was isolated as keto and enol tautomers, as a colorless liquid (0.915 g, 76%). TLC: R_f = 0.3 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3613, 3429, 2959, 2859, 2361, 1712, 1604, 1521, 1473, 1424, 1372, 1028, 928, 850, 670, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 2H), 2.19 (s, 3H), 1.41 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 201.1, 174.6, 172.6, 166.4, 91.1, 81.9, 80.6, 51.4, 30.0, 28.3, 27.9; HRMS (ESI): *m/z* calcd for $C_8H_{14}O_3Na$ $[M + Na]^+$ 181.0835, found 181.0833.

Benzyl 3-oxobutanoate (1h):



The title compound was synthesized following general procedure GP2, using ethyl acetoacetate (**1c**, 1 g, 7.68 mmol), benzyl alcohol (**S-3c**, 1.59 mL, 15.36 mmol), and AgOTf (0.197 g, 0.768 mmol) in toluene (10 mL). The product **1h** was isolated as a colorless liquid (1.29 g, 88%). TLC: R_f = 0.3 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3776, 3684, 3430, 2361, 1741, 1718, 1649, 1523, 1477, 1422, 1363, 1314, 1152, 1028, 962, 928, 848, 670, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.35 (m, 5H), 5.36 (s, 2H), 4.60 (s, 2H), 2.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 161.0, 138.2, 135.6, 128.7, 128.4, 128.2, 126.0, 112.4, 66.5, 60.7, 55.7, 14.5, 14.2; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}O_3Na$ $[M + Na]^+$ 215.0679, found 215.0679.

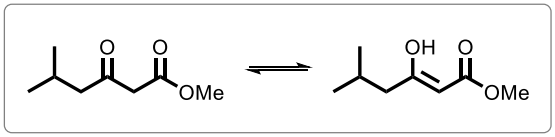
3-Chlorobenzyl 3-oxobutanoate (1i):



The title compound was synthesized following general procedure GP2, using ethyl acetoacetate (**1c**, 1 g, 7.68 mmol), 3-chlorobenzyl alcohol (**S-3d**, 1.59 mL, 15.36 mmol), and AgOTf (0.197 g, 0.768 mmol) in toluene (10 mL). The product **1i** was isolated as

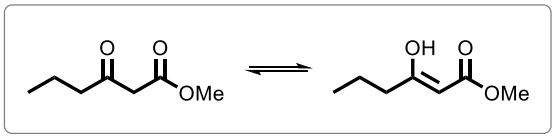
a colorless liquid (1.49 g, 86%). TLC: R_f = 0.3 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3431, 2364, 1745, 1719, 1655, 1602, 1578, 1520, 1476, 1428, 1365, 1314, 1149, 1079, 1031, 971, 928, 873, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.38–7.28 (m, 3H), 5.31 (s, 2H), 4.59 (d, *J* = 6.9 Hz, 2H), 2.57 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 161.2, 138.4, 137.7, 134.6, 130.1, 128.7, 128.3, 126.3, 126.1, 112.3, 65.7, 55.8, 14.7; HRMS (ESI): *m/z* calcd for $C_{11}H_{11}O_3ClNa$ $[M + Na]^+$ 249.0289, found 249.0290.

Methyl 5-methyl-3-oxohexanoate (1l):



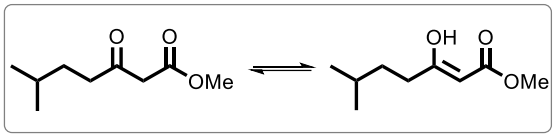
The title compound was synthesized following general procedure GP1, using 4-methyl-2-pentanone (**S-1a**, 1 g, 9.98 mmol), Dimethyl carbonate (**S-2b**, 1.0 mL, 11.98 mmol), NaH (60% in dispersion oil) (0.599 g, 14.97 mmol) in THF (12 mL). The product **1l** was isolated as a yellow liquid (1.26 g, 80%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3780, 3685, 2961, 2874, 2360, 1745, 1715, 1653, 1628, 1523, 1440, 1407, 1367, 1318, 1159, 1058, 1012, 928, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 0.13H), 4.93 (s, 0.13H), 3.69 (s, 3H), 3.39 (s, 2H), 2.37 (d, *J* = 7.0 Hz, 2H), 2.16-2.08 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.4, 178.2, 173.0, 167.7, 89.7, 52.3, 51.9, 51.0, 49.4, 44.3, 26.2, 24.4, 22.4, 22.3; HRMS (ESI): *m/z* calcd for $C_8H_{15}O_3$ $[M + H]^+$ 159.1016, found 159.1013.

Methyl 3-oxohexanoate (1m):



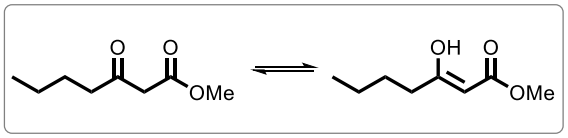
The title compound was synthesized following general procedure GP1, using pentan-2-one (**S-1b**, 1 g, 11.61 mmol), dimethyl carbonate (**S-2b**, 1.17 mL, 13.93 mmol), NaH (60% in dispersion oil) (0.696 g, 17.41 mmol) in THF (12 mL). The product **1m** was isolated as a yellow liquid (1.31 g, 78%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3430, 2961, 2872, 2361, 1745, 1716, 1652, 1627, 1522, 1442, 1408, 1319, 1158, 1077, 1011, 927, 847, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 0.10H), 4.94 (s, 0.10H), 3.69 (s, 3H), 3.67 (s, 0.41H), 3.40 (s, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.15-2.08 (m, 0.28H), 1.62-1.53 (m, 2H), 0.92 (s, 0.17H), 0.88 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.7, 178.8, 173.1, 167.7, 88.8, 52.3, 51.0, 49.0, 45.6, 44.9, 36.9, 19.6, 17.3, 16.9, 13.6, 13.5; HRMS (ESI): *m/z* calcd for $C_7H_{12}O_3Na$ $[M + Na]^+$ 167.0679, found 167.0677.

Methyl 6-methyl-3-oxoheptanoate (1n):



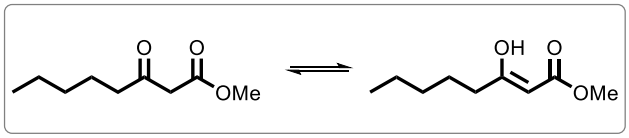
The title compound was synthesized following general procedure GP1, using isoamyl methyl ketone (**S-1c**, 1 g, 8.75 mmol), dimethyl carbonate (**S-2b**, 0.88 mL, 10.50 mmol), NaH (60% in dispersion oil) (0.525 g, 13.13 mmol) in THF (12 mL). The product **1n** isolated as a yellow liquid (1.22 g, 81%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3684, 2959, 2872, 2361, 1745, 1715, 1626, 1523, 1440, 1410, 1367, 1320, 1071, 1013, 927, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 0.08H), 4.93 (s, 0.08H), 3.67 (s, 3H), 3.66 (s, 0.29H), 3.40 (s, 2H), 2.48 (t, *J* = 2.4 Hz, 2H), 1.50 (dd, *J* = 13.2, 6.9 Hz, 1H), 1.47–1.36 (m, 2H), 0.85 (d, *J* = 2.4 Hz, 0.84H), 0.82 (d, *J* = 6.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.2, 202.9, 179.3, 170.5, 167.7, 88.5, 60.3, 57.9, 52.3, 52.2, 51.0, 48.9, 41.1, 36.9, 35.2, 33.0, 32.1, 28.6, 27.5, 22.4, 22.2; HRMS (ESI): *m/z* calcd for $C_9H_{17}O_3$ $[M + H]^+$ 173.1172, found 173.1169.

Methyl 3-oxoheptanoate (1o):



The title compound was synthesized following general procedure GP1, using hexan-2-one (**S-1d**, 1 g, 9.98 mmol), Dimethyl carbonate (**S-2b**, 1.0 mL, 11.98 mmol), NaH (60% in dispersion oil) (0.599 g, 14.97 mmol) in THF (12 mL). The product **1o** was isolated as a yellow liquid (1.22 g, 77%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3684, 3430, 2960, 2872, 2361, 1745, 1715, 1652, 1627, 1522, 1441, 1408, 1319, 1158, 1077, 1012, 927, 847, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 0.09H), 4.94 (s, 0.09H), 3.68 (s, 3H), 3.67 (s, 0.34H), 3.40 (s, 2H), 2.49 (t, *J* = 8.1 Hz, 2H), 1.59–1.45 (m, 2H), 1.28 (dt, *J* = 15.0, 7.4 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.8, 179.1, 170.4, 167.7, 88.6, 60.3, 59.5, 52.2, 51.0, 49.0, 42.7, 34.7, 30.3, 28.7, 28.3, 25.5, 22.1, 20.6, 14.2, 13.7; HRMS (ESI): *m/z* calcd for $C_8H_{15}O_3$ $[M + H]^+$ 159.1016, found 159.1016.

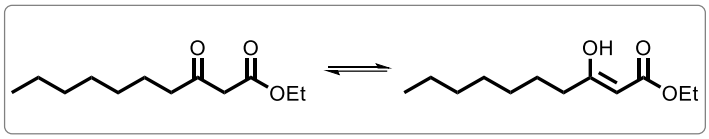
Methyl 3-oxooctanoate (1p):



The title compound was synthesized following general procedure GP1, using heptan-2-one (**S-1e,** 1 g, 8.75 mmol), dimethyl carbonate (**S-2b**, 0.88 mL, 10.50 mmol), NaH (60% in dispersion oil) (0.525 g, 13.13 mmol) in THF (12 mL). The product **1p** was isolated (keto-enol tautomers) as a yellow liquid

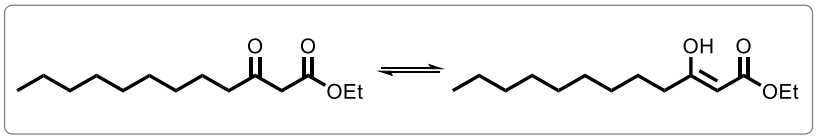
(1.23 g, 82%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 2959, 2867, 2360, 1744, 1713, 1626, 1523, 1437, 1362, 1320, 1018, 926, 849, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.0 (s, 0.11H), 4.97 (s, 0.12H), 3.72 (s, 3H), 3.43 (s, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.58–1.54 (m, 2H), 1.32–1.24 (m, 4H), 0.88 (d, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.0, 173.2, 170.5, 167.8, 88.7, 59.8, 52.4, 51.1, 49.1, 43.1, 35.1, 31.3, 29.6, 28.8, 28.1, 26.0, 23.2, 22.54, 22.50, 13.99, 13.90; HRMS (ESI): *m/z* calcd for $C_9H_{17}O_3$ $[M + H]^+$ 173.1172, found 173.1173.

Ethyl 3-oxodecanoate (1q):



The title compound was synthesized following general procedure GP1, using nonan-2-one (**S-1f**, 1 g, 7.03 mmol), diethyl carbonate (**S-2a**, 1.02 mL, 8.43 mmol), NaH (60% in dispersion oil) (0.421 g, 10.54 mmol), in THF (12 mL) and the product **1q** was isolated (keto-enol tautomers) as a yellow liquid (1.32 g, 88%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3611, 3429, 2959, 2930, 2859, 2361, 1739, 1713, 1605, 1523, 1473, 1423, 1371, 1029, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.0 (s, 0.08H), 4.95(s, 0.08H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.57 (t, *J* = 7.4 Hz, 2H), 1.29–1.24 (m, 11H), 0.88–0.84 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.5, 203.1, 170.0, 167.3, 61.4, 61.3, 60.07, 60.00, 49.4, 43.1, 31.7, 31.6, 29.1, 29.0, 28.3, 27.4, 23.5, 22.69, 22.62, 14.2, 14.15, 14.12; HRMS (ESI): *m/z* calcd for $C_{12}H_{23}O_3$ $[M + H]^+$ 215.1642, found 215.1640.

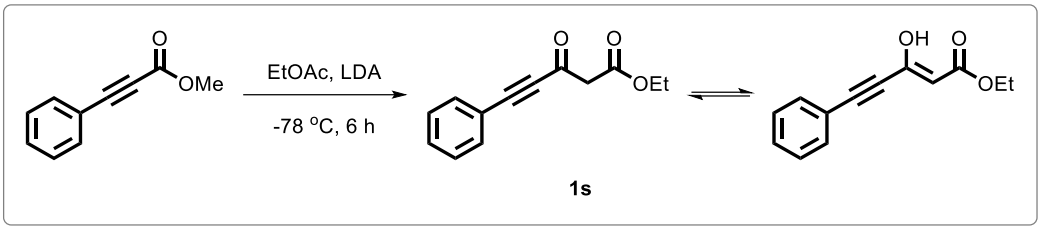
Ethyl 3-oxododecanoate (1r):



The title compound was synthesized following general procedure GP1, using undecan-2-one (**S-1g**, 1 g, 5.87 mmol), diethyl carbonate (**S-2a**, 0.85 mL, 7.04 mmol), NaH (60% in dispersion oil) (0.352 g, 8.80 mmol), in THF (12 mL). The product **1r** was isolated (keto-enol tautomers) as a yellow liquid (1.23 g, 86%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3685, 2929, 2857, 2360, 1739, 1713, 1645, 1523, 1467, 1421, 1370, 1310, 1094, 1029, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 0.08H), 4.94(s, 0.09H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.40 (s, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.56 (t, *J* = 7.4 Hz, 2H), 1.27–1.22 (m, 15H), 0.87–0.83 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.4, 203.0, 170.0, 167.3, 89.0, 61.39, 61.33, 60.0, 59.9, 49.4, 43.1, 31.94, 31.90, 29.49,

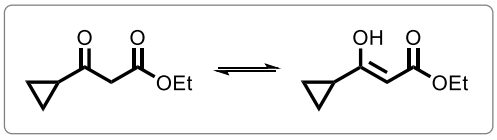
29.45, 29.3, 29.2, 29.1, 28.7, 28.3, 27.4, 26.3, 23.5, 22.7, 14.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{27}O_3$ $[M + H]^+$ 243.1955, found 243.1953.

Ethyl 3-oxo-5-phenylpent-4-ynoate (1s):[9]



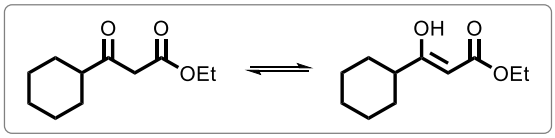
To a flame-dried (100mL) two-neck round-bottom flask, anhydrous THF (20mL) was added under an argon atmosphere and was cooled to -78 °C. To this, diisopropylamine (1.31 mmol, 2.1 equiv) was added, followed by the dropwise addition of *n*-butyl lithium (1.6 M in hexane, 1.25 mmol, 2.0 equiv) at -78 °C, and the mixture was stirred for 45 min. To this LDA solution, ethyl acetate (1.25 mmol, 2.0 equiv) was added. The resulting mixture was stirred for 1 h at −78 °C, and then a solution of phenyl methyl propiolate (0.63 mmol, 1.0 equiv) in THF was added dropwise. Then, the reaction was stirred at the same temperature for 6h. Then, the reaction progress was monitored by TLC; after completion of the reaction, it was quenched with saturated NH_4Cl (50mL), and the aqueous layer was extracted with EtOAc (3×50mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure. Further, the corresponding *β*-ketoester **(1s)** obtained was forwarded without any purifications.

Ethyl 3-cyclopropyl-3-oxopropanoate (1w):



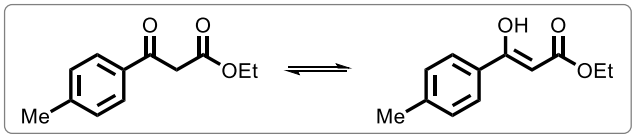
The title compound was synthesized following general procedure GP1, using 1-cyclopropylethan-1-one (**S-1h**, 1 g, 11.88 mmol), diethyl carbonate (**S-2a**, 1.72 mL, 14.26 mmol), NaH (60% in dispersion oil) (0.713 g, 17.83 mmol), in THF (12 mL). The product **1w** isolated (keto-enol tautomers) as a yellow liquid (1.34 g, 72%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3431, 2939, 2360, 2090, 1736, 1699, 1639, 1524, 1471, 1444, 1415, 1384, 1311, 1073, 1027, 930, 907, 852, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.18 (s, 0.02H), 5.02 (s, 0.02H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.13–4.11 (m, 0.08H), 3.50 (s, 2H), 2.03–1.92 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.07–1.00 (m, 2H), 0.93–0.86 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.9, 167.2, 61.2, 49.9, 20.7, 14.0, 11.6; HRMS (ESI): *m/z* calcd for $C_8H_{13}O_3$ $[M + H]^+$ 157.0859, found 157.0858.

Ethyl 3-cyclohexyl-3-oxopropanoate (1x):



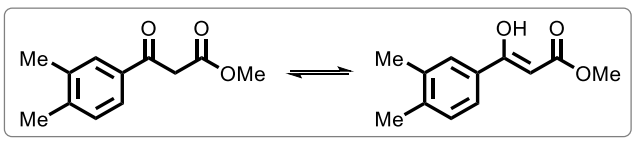
The title compound was synthesized following general procedure GP1, using 1-cyclohexylethan-1-one (**S-1i**, 1 g, 7.92 mmol), diethyl carbonate (**S-2a**, 1.15 mL, 9.50 mmol), NaH (60% in dispersion oil) (0.475 g, 11.88 mmol), in THF (12 mL). The product **1x** was isolated (keto-enol tautomers) as a yellow liquid (1.21 g, 77%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3431, 2934, 2857, 2361, 1739, 1706, 1644, 1523, 1446, 1421, 1371, 1308, 1156, 1030, 929, 847, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.11 (s, 0.12H), 4.92 (s, 0.12H), 4.15 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.44 (d, *J* = 1.1 Hz, 2H), 2.50–2.36 (m, 1H), 2.31–2.26 (m, 0.29H), 1.85 (d, *J* = 12.3 Hz, 2H), 1.75 (d, *J* = 12.5 Hz, 2H), 1.63 (d, *J* = 11.0 Hz, 1H), 1.35–1.18 (m, 8H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 213.5, 206.0, 182.8, 167.5, 87.0, 61.3, 59.9, 51.5, 50.9, 47.4, 43.5, 30.0, 28.2, 25.9, 25.7, 25.6, 25.5, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{11}H_{19}O_3$ $[M + H]^+$ 199.1329, found 199.1330.

Ethyl 3-oxo-3-(p-tolyl)propanoate (1y):



The title compound was synthesized following general procedure GP1, using 1-(*p*-tolyl)ethan-1-one (**S-1j**, 1 g, 7.45 mmol), diethyl carbonate (**S-2a**, 1.08 mL, 8.94 mmol), NaH (60% in dispersion oil) (0.447 g, 11.17 mmol), in THF (12 mL). The product **1y** was isolated (keto-enol tautomers) as a yellow liquid (1.33 g, 87%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3686, 2953, 2359, 1741, 1609, 1572, 1520, 1443, 1412, 1322, 1270, 1146, 1018, 928, 671, 625 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 0.13H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 0.28H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 0.32H), 5.63 (s, 0.14H), 4.28-4.26 (m, 0.24H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 2.41 (s, 3H), 2.39 (s, 0.39H), 1.33 (t, *J* = 7.1 Hz, 0.47H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 173.4, 171.7, 167.7, 144.7, 141.8, 133.7, 129.5, 129.3, 128.7, 128.5, 126.1, 86.7, 61.5, 60.3, 46.0, 21.7, 21.5, 14.4, 14.1; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1016, found 207.1014.

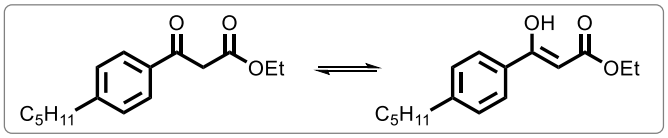
Methyl 3-(3,4-dimethylphenyl)-3-oxopropanoate (1z):



The title compound was synthesized following general procedure GP1, using 1-(3,4-dimethylphenyl)ethan-1-one (**S-1k**, 1

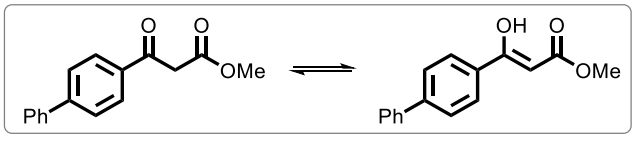
g, 6.74 mmol), dimethyl carbonate (**S-2b**, 0.68 mL, 8.09 mmol), NaH (60% in dispersion oil) (0.404 g, 10.12 mmol), in THF (12 mL). The product **1z** was isolated (keto-enol tautomers) as a yellow liquid (1.26 g, 91%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 2954, 2359, 1742, 1681, 1609, 1572, 1519, 1444, 1411, 1322, 1270, 1146, 1018, 928, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.49 (s, 0.13H), 7.70 (s, 1H), 7.65 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.64 (s, 0.13H), 7.63 (s, 0.14H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.16–7.14 (m, 0.17H), 5.62 (s, 0.14H), 3.96 (s, 2H), 3.87 (s, 0.18H), 3.77 (s, 0.41H), 3.73 (s, 3H), 2.30 (s, 6H), 2.27 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 173.6, 171.9, 168.2, 143.5, 140.5, 137.2, 136.8, 133.9, 130.6, 130.0, 129.8, 129.6, 127.2, 126.3, 123.6, 86.2, 52.4, 51.3, 45.6, 20.09, 20.00, 19.7, 19.6; HRMS (ESI): *m/z* calcd for $C_{12}H_{14}O_3Na$ $[M + Na]^+$ 229.0835, found 229.0832.

Ethyl 3-oxo-3-(4-pentylphenyl)propanoate (1a′):



The title compound was synthesized following general procedure GP1, using 1-(4-pentylphenyl)ethan-1-one (**S-1l**, 1 g, 5.25 mmol), diethyl carbonate (**S-2a**, 0.764 mL, 6.30 mmol), NaH (60% in dispersion oil) (0.315 g, 7.88 mmol), in THF (12 mL). The product **1a′** was isolated (keto-enol tautomers) as a yellow liquid (1.22 g, 89%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3621, 2958, 2928, 2858, 2360, 1737, 1682, 1610, 1568, 1516, 1468, 1426, 1380, 1264, 1078, 1031, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 0.13H), 7.89–7.83 (m, 2H), 7.70–7.67 (m, 0.28H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.25–7.20 (m, 0.30H), 5.60 (s, 0.14H), 4.27–4.26 (m, 0.27H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 2H), 2.69–2.61 (m, 2H), 1.67–1.59 (m, 2H), 1.31 (dd, *J* = 7.2, 2.6 Hz, 4H), 1.24 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 173.3, 171.7, 167.7, 149.6, 146.8, 133.8, 130.9, 128.8, 128.7, 126.1, 86.7, 61.4, 60.2, 46.0, 37.2, 36.0, 32.0, 31.5, 30.9, 30.8, 30.1, 29.8, 22.7, 22.5, 14.4, 14.2, 14.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{16}H_{22}O_3Na$ $[M + Na]^+$ 285.1461, found 285.1456.

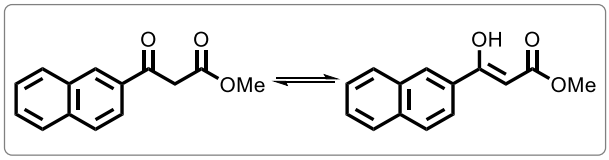
Methyl 3-([1,1'-biphenyl]-4-yl)-3-oxopropanoate (1b′):



The title compound was synthesized following general procedure GP1, using 1-([1,1'-biphenyl]-4-yl)ethan-1-one (**S-1m**, 1 g, 5.09 mmol), dimethyl carbonate (**S-2b**, 0.514 mL, 6.11 mmol), NaH (60% in dispersion

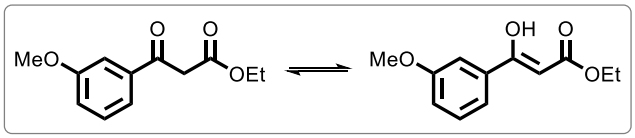
oil) (0.305 g, 7.64 mmol), in THF (12 mL). The product **1b′** was isolated (keto-enol tautomers) as a yellow liquid (1.1 g, 85%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3776, 3684, 3431, 2361, 1742, 1683, 1605, 1522, 1480, 1437, 1324, 1024, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 0.21H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.87–7.84 (m, 0.44H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.64–7.61 (m, 2H), 7.50 (s, 0.34H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.40–7.38 (m, 0.30H), 5.73 (s, 0.21H), 4.04 (s, 2H), 3.82 (s, 0.61H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.0, 173.6, 171.2, 168.1, 146.6, 144.1, 140.1, 139.7, 134.7, 132.2, 129.2, 129.1, 129.0, 128.5, 128.0, 127.5, 127.4, 127.3, 127.2, 126.6, 87.0, 52.6, 51.5, 45.8; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}O_3$ $[M + H]^+$ 255.1016, found 255.1010.

Methyl 3-(naphthalen-2-yl)-3-oxopropanoate (1c′):



The title compound was synthesized following general procedure GP1, using using 1-(naphthalen-2-yl)ethan-1-one (**S-1n**, 1 g, 5.87 mmol), dimethyl carbonate (**S-2b**, 0.59 mL, 7.05 mmol), NaH (60% in dispersion oil) (0.352 g, 8.81 mmol), in THF (12 mL). The product **1c′** was isolated final (keto-enol tautomers) as a yellow liquid (1.12 g, 83%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3910, 3777, 3681, 3428, 3069, 2366, 1742, 1680, 1630, 1526, 1475, 1437, 1322, 1022, 929, 851, 670, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 0.20H), 8.40 (s, 1H), 8.32 (s, 0.21H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.87–7.80 (m, 2H), 7.62–7.55 (m, 1H), 7.52 (t, *J* = 6.9 Hz, 1H), 5.79 (s, 0.21H), 4.11 (s, 2H), 3.80 (s, 0.64H), 3.75 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.3, 173.5, 171.2, 168.0, 135.7, 134.6, 133.2, 132.7, 132.3, 130.5, 130.4, 129.6, 129.0, 128.8, 128.6, 128.2, 127.7, 127.6, 127.5, 126.9, 126.7, 126.6, 123.7, 122.5, 87.5, 52.4, 51.4, 45.6; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_3$ $[M + H]^+$ 229.0859, found 229.0856.

Ethyl 3-(3-methoxyphenyl)-3-oxopropanoate (1d′):



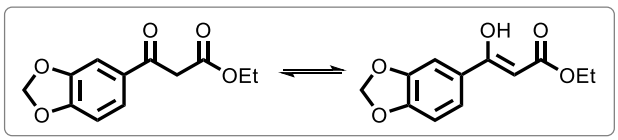
The title compound was synthesized following general procedure GP1, using 1-(3-methoxyphenyl)ethan-1-one (**S-1o**, 1 g, 6.65 mmol), diethyl carbonate (**S-2a**, 0.96 mL, 7.99 mmol), NaH (60% in dispersion oil) (0.399 g, 9.98 mmol), in THF (12 mL). The product **1d′** was isolated (keto-enol tautomers) as a yellow liquid (1.01 g, 69%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3680, 3422, 2838, 1737, 1686, 1595, 1486, 1462, 1432, 1368, 1148, 1093, 1032, 928, 873, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.56 (s, 0.19H), 7.69–7.66 (m, 0.12H), 7.59–7.56 (m, 0.10H),

7.51–7.44 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.33–7.25 (m, 1H), 7.14–7.07 (m, 1H), 6.99–6.96 (m, 0.19H), 5.63 (s, 0.18H), 4.27–4.23 (m, 0.36H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 3.82 (s, 3H), 3.81 (s, 1H), 1.31 (t, *J* = 7.2 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 0.60H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.4, 173.2, 171.3, 167.5, 160.0, 159.7, 137.4, 134.9, 129.8, 129.6, 122.6, 121.2, 120.3, 118.5, 117.3, 112.6, 111.2, 87.7, 61.5, 60.4, 55.5, 55.4, 46.1, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_4$ $[M + H]^+$ 223.0965, found 223.0965.

Ethyl 3-(2,5-dimethoxyphenyl)-3-oxopropanoate (1e′):

The title compound was synthesized following general procedure GP1, using 1-(2,5-dimethoxyphenyl)ethan-1-one (**S-1p**, 1 g, 5.54 mmol), diethyl carbonate (**S-2a**, 0.806 mL, 6.65 mmol), NaH (60% in dispersion oil) (0.332 g, 8.32 mmol), in THF (12 mL). The product **1e′** was isolated (keto-enol tautomers) as a yellow liquid (0.88 g, 63%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3680, 3420, 2838, 1736, 1686, 1591, 1434, 1091, 1032, 929, 874, 673 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.71 (s, 0.07H), 7.42 (d, *J* = 3.3 Hz, 1H), 7.07 (dd, *J* = 9.1, 3.3 Hz, 1H), 6.90 (d, *J* = 9.1 Hz, 1H), 6.06 (s, 0.08H), 4.26–4.22 (m, 0.27H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 0.16H), 3.96 (s, 2H), 3.87 (s, 0.19H), 3.85 (s, 3H), 3.81 (s, 0.14H), 3.79 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 0.36H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.8, 168.3, 153.9, 153.6, 126.4, 122.0, 113.9, 113.1, 61.0, 55.95, 55.90, 50.7, 14.2; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_5$ $[M + H]^+$ 253.1071, found 253.1066.

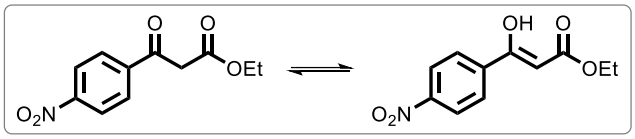
Ethyl 3-(benzo[d][1,3]dioxol-5-yl)-3-oxopropanoate (1f′):



The title compound was synthesized following general procedure GP1, using 3′,4′-(Methylenedioxy)acetophenone (**S-1q**, 1 g, 6.09 mmol), diethyl carbonate (**S-2b**, 0.88 mL, 7.30 mmol), NaH (60% in dispersion oil) (0.365 g, 9.13 mmol), in THF (12 mL). The product **1f′** was isolated (keto-enol tautomers) as a yellow liquid (1.12 g, 78%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 2903, 2784, 2359, 1736, 1678, 1607, 1488, 1443, 1359, 1317, 1105, 1039, 932, 851, 741, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.60 (s, 0.07H), 7.50 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.34–7.33 (m, 0.08H), 7.32–7.31 (m, 0.08H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.18 (s, 0.11H), 6.03 (s, 2H), 5.99 (s, 0.18H), 5.51 (s, 0.08H), 4.25–4.23 (m, 0.14H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 0.29H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101

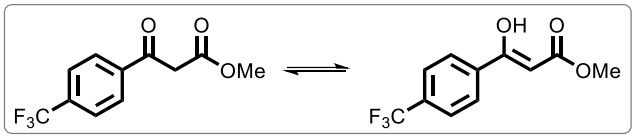
MHz, $CDCl_3$) δ 190.6, 173.3, 171.1, 167.6, 152.4, 150.3, 148.4, 148.0, 130.9, 127.6, 125.2, 121.1, 108.3, 108.1, 108.0, 106.2, 102.1, 101.7, 61.5, 60.3, 45.9, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{12}H_{13}O_5$ $[M + H]^+$ 237.0757, found 237.0755.

Ethyl 3-(4-nitrophenyl)-3-oxopropanoate (1g′):



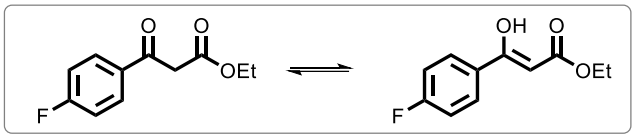
The title compound was synthesized following general procedure GP1, using using 1-(4-nitrophenyl)ethan-1-one (**S-1r**, 1 g, 6.05 mmol), diethyl carbonate (**S-2a**, 0.88 mL, 7.26 mmol), NaH (60% in dispersion oil) (0.363 g, 9.08 mmol) in THF (12 mL). The product **1g′** was isolated (keto-enol tautomers) as a yellow liquid (0.93 g, 65%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3685, 3618, 2361, 1694, 1604, 1529, 1478, 1424, 1348, 1318, 1258, 1110, 1017, 959, 928, 854, 670, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.56 (s, 1H), 8.33 (d, *J* = 8.9 Hz, 2H), 8.26 (d, *J* = 9.1 Hz, 2H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 2H), 5.76 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.2, 172.7, 168.4, 166.8, 150.7, 149.3, 140.4, 139.4, 129.7, 127.1, 124.1, 123.9, 90.3, 62.0, 61.0, 46.3, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{11}H_{11}O_5NNa$ $[M + Na]^+$ 260.0529, found 260.0534.

Methyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (1h′):



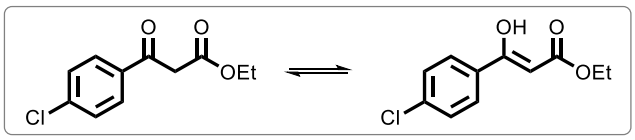
The title compound was synthesized following general procedure GP1, using 1(4-(Trifluoromethyl)phenyl)ethan-1-one (**S-1s**, 1 g, 5.31 mmol), dimethyl carbonate (**S-2b**, 0.53 mL, 6.37 mmol), NaH (60% in dispersion oil) (0.318 g, 7.97 mmol), in THF (12 mL). The product **1h′** was isolated (keto-enol tautomers) as a yellow liquid (0.89 g, 68%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3630, 3417, 2946, 2837, 2360, 1630, 1524, 1474, 1424, 1331, 1019, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.48 (s, 0.60H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 5.72 (s, 0.63H), 4.03 (s, 2H), 3.83 (s, 2H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.5, 173.3, 169.7, 167.5, 138.7, 136.9, 135.3, 129.0, 126.5, 126.09, 126.05, 125.7, 125.6, 88.8, 52.8, 51.8, 45.9; HRMS (ESI): *m/z* calcd for $C_{11}H_9O_3F_3Na$ $[M + Na]^+$ 269.0396, found 269.0391.

Ethyl 3-(4-fluorophenyl)-3-oxopropanoate (1i′):



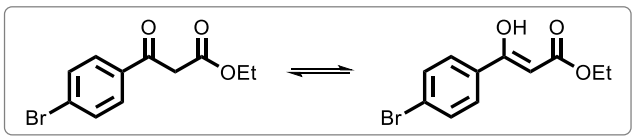
The title compound was synthesized following general procedure GP1, using 1-(4-Fluorophenyl)ethan-1-one (**S-1t**, 1 g, 7.23 mmol), diethyl carbonate (**S-2a**, 1.05 mL, 8.68 mmol), NaH (60% in dispersion oil) (0.434 g, 10.85 mmol) in THF (12 mL). The product **1i′** was isolated (keto-enol tautomers) as a yellow liquid (1.16 g, 76%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3684, 2360, 1737, 1686, 1599, 1509, 1474, 1422, 1369, 1323, 1266, 1155, 1101, 1031, 929, 845, 670, 627 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.60 (s, 0.18H), 8.01–7.92 (m, 2H), 7.95-7.74 (m, 0.37H), 7.18–7.11 (m, 2H), 7.10–7.06 (m, 0.36H), 5.59 (s, 0.18H), 4.27–4.24 (m, 0.34H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 0.59H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.5, 191.0, 173.2, 170.4, 167.4, 164.9, 132.6, 132.5, 131.4, 131.3, 131.0, 130.9, 128.3, 128.2, 116.1, 115.9, 115.8, 115.6, 87.2, 61.6, 60.4, 46.0, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}O_3F$ $[M + H]^+$ 211.0765, found 211.0763.

Ethyl 3-(4-chlorophenyl)-3-oxopropanoate (1j′):



The title compound was synthesized following general procedure GP1, using 1-(4-Chlorophenyl)ethan-1-one (**S-1u**, 1 g, 6.46 mmol), diethyl carbonate (**S-2a**, 0.94 mL, 7.76 mmol), NaH (60% in dispersion oil) (0.388 g, 9.7 mmol), in THF (12 mL). The product **1j′** was isolated (keto-enol tautomers) as a yellow liquid (1.16 g, 79%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3614, 2361, 1736, 1686, 1623, 1566, 1523, 1489, 1425, 1385, 1092, 1023, 928, 843, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.56 (s, 0.26H), 7.91–7.83 (m, 2H), 7.73–7.66 (m, 0.54H), 7.48–7.41 (m, 2H), 7.40–7.34 (m, 0.56H), 5.62 (s, 0.41H), 4.25 (q, *J* = 7.1 Hz, 0.48H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 0.85H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.4, 173.1, 170.2, 167.3, 140.4, 134.4, 130.0, 129.2, 128.9, 127.4, 87.7, 61.7, 60.5, 46.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}O_3Cl$ $[M + H]^+$ 227.0469, found 227.0467.

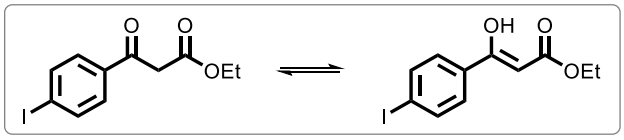
Ethyl 3-(4-bromophenyl)-3-oxopropanoate (1k′):



The title compound was synthesized following general procedure GP1, using 1-(4-bromophenyl)ethan-1-one (**S-1v**, 1 g,

5.02 mmol), diethyl carbonate (**S-2a**, 0.73 mL, 6.02 mmol), NaH (60% in dispersion oil) (0.301 g, 7.53 mmol), in THF (12 mL). The product **1k′** was isolated (keto-enol tautomers) as a yellow liquid (1.03 g, 76%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 2358, 1737, 1686, 1620, 1587, 1483, 1423, 1266, 1073, 1009, 929, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.55 (s, 0.28H), 7.82–7.77 (m, 3H), 7.64–7.56 (m, 4H), 7.55–7.51 (m, 1H), 5.63 (s, 0.29H), 4.26 (t, *J* = 7.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.1, 191.6, 170.2, 167.2, 135.9, 134.8, 132.2, 131.9, 131.8, 130.1, 129.9, 129.1, 128.3, 127.6, 87.8, 61.7, 60.5, 46.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}O_3Br$ $[M + H]^+$ 270.9964, found 270.9963.

Ethyl 3-(4-iodophenyl)-3-oxopropanoate (1l′):



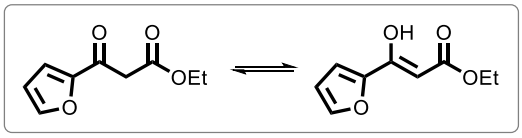
The title compound was synthesized following general procedure GP1, using 1-(4-iodophenyl)ethan-1-one (**S-1w**, 1 g, 4.06 mmol), diethyl carbonate (**S-2a**, 0.59 mL, 4.87 mmol), NaH (60% in dispersion oil) (0.243 g, 6.09 mmol), in THF (12 mL). The product **1l′** was isolated (keto-enol tautomers) as a yellow liquid (0.93 g, 72%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3609, 2933, 2362, 1738, 1688, 1621, 1583, 1523, 1479, 1422, 1390, 1319, 1262, 1151, 1110, 1060, 1030, 1002, 929, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 0.28H), 7.85–7.79 (m, 2H), 7.76–7.68 (m, 0.61H), 7.66–7.58 (m, 2H), 7.50–7.41 (m, 0.64H), 5.62 (s, 0.29H), 4.26–4.21 (m, 0.46H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 0.88H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.8, 173.0, 170.3, 167.2, 138.1, 137.8, 135.3, 129.8, 127.6, 102.0, 98.0, 87.7, 61.6, 60.5, 45.8, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}O_3I$ $[M + H]^+$ 318.9826, found 318.9822.

Methyl 3-(2,4-dichlorophenyl)-3-oxopropanoate (1m′):

The title compound was synthesized following general procedure GP1, using 1-(2,4-dichlorophenyl)ethan-1-one (**S-1x**, 1 g, 5.28 mmol), dimethyl carbonate (**S-2b**, 0.53 mL, 6.34 mmol), NaH (60% in dispersion oil) (0.317 g, 7.93 mmol), in THF (12 mL). The product **1m′** was isolated (keto-enol tautomers) as a yellow liquid (0.63 g, 63%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3685, 2360, 1743, 1653, 1628, 1586, 1524, 1474, 1443, 1327, 1272, 1107, 1014, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 7.61–7.59 (m, 0.43H), 7.53 (d, *J* = 8.4

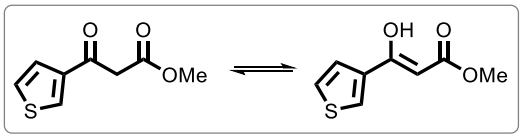
Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.36–7.33 (m, 0.45H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.58 (s, 1H), 4.04 (s, 1H), 3.81 (s, 3H), 3.74 (s, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 193.3, 173.0, 169.3, 167.4, 138.6, 136.7, 135.8, 133.1, 132.8, 132.0, 131.4, 131.1, 130.8, 130.6, 127.7, 127.3, 93.4, 52.6, 51.8, 48.9; HRMS (ESI): *m/z* calcd for $C_{10}H_8O_3Cl_2Na$ $[M + Na]^+$ 268.9743, found 268.9740.

Ethyl 3-(furan-2-yl)-3-oxopropanoate (1n′):



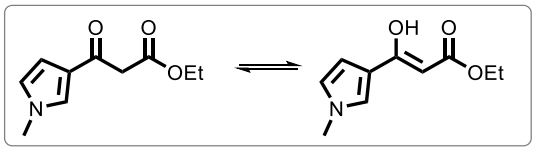
The title compound was synthesized following general procedure GP1, using 2-acetylfuran (**S-1y**, 1 g, 9.08 mmol), diethyl carbonate (**S-2a**, 1.32 mL, 10.89 mmol), NaH (60% in dispersion oil) (0.545 g, 13.62 mmol), in THF (12 mL). The product **1n′** was isolated (keto-enol tautomers) as a yellow liquid (1.17 g, 71%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3685, 2360, 1737, 1678, 1602, 1570, 1523, 1469, 1422, 1324, 1087, 1023, 928, 883, 848, 670, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.13 (s, 0.08H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.46 (s, 0.07H), 7.24 (d, *J* = 3.6 Hz, 1H), 6.90 (s, 0.07H), 6.54 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.46 (s, 0.08H), 5.58 (s, 0.06H), 4.24–4.20 (m, 0.20H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 0.57H), 1.22 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 181.1, 173.1, 167.8, 167.0, 162.0, 152.0, 147.1, 144.9, 130.9, 128.8, 118.3, 112.7, 112.1, 86.3, 68.2, 61.5, 60.3, 45.5, 38.7, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_9H_{11}O_4$ $[M + H]^+$ 183.0652, found 183.0651.

Methyl 3-oxo-3-(thiophen-3-yl)propanoate (1o′):



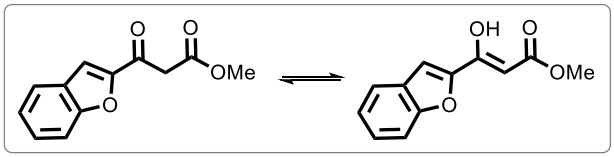
The title compound was synthesized following general procedure GP1. using 3-acetyl thiophene (**S-1z**, 1 g, 7.92 mmol), dimethyl carbonate (**S-2b**, 0.8 mL, 9.51 mmol), NaH (60% in dispersion oil) (0.475 g, 11.88 mmol) in THF (12 mL). The product **1o′** was isolated (keto-enol tautomers) as a yellow liquid (1.24 g, 85%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3612, 2957, 2361, 1743, 1679, 1621, 1513, 1477, 1419, 1318, 1151, 1076, 1013, 928, 875, 848, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 0.14H), 8.09 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.85–7.84 (m,0.12H), 7.52 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.31 (dd, *J* = 5.1, 2.9 Hz, 1H), 5.50 (s, 0.08H) 3.89 (s, 2H), 3.76 (s, 0.42H), 3.72 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 186.2, 173.6, 167.7, 167.1, 141.3, 136.2, 133.5, 127.1, 127.0, 126.9, 126.6, 124.9, 87.1, 52.5, 51.4, 46.9; HRMS (ESI): *m/z* calcd for $C_8H_9O_3S$ $[M + H]^+$ 185.0267, found 185.0265.

Ethyl 3-(1-methyl-1*H*-pyrrol-2-yl)-3-oxopropanoate (1p′):



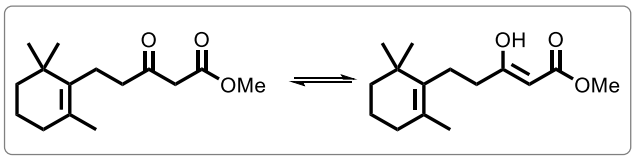
The title compound was synthesized following general procedure GP1, using 1-(1-methyl-1*H*-pyrrol-3-yl)ethan-1-one (**S-1a′**, 1 g, 7.92 mmol), diethyl carbonate (**S-2a**, 0.8 mL, 9.51 mmol), NaH (60% in dispersion oil) (0.475 g, 11.88 mmol), in THF (12 mL). The product **1p′** was isolated (keto-enol tautomers) as a yellow liquid (1.24 g, 85%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 2360, 1734, 1652, 1527, 1473, 1408, 1305, 1265, 1149, 1095, 1067, 1030, 981, 930, 849, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (dd, *J* = 4.2, 1.7 Hz, 1H), 6.78 (t, *J* = 2.2 Hz, 1H), 6.06 (dd, *J* = 4.2, 2.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.72 (s, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 182.1, 167.7, 131.9, 129.7, 120.3, 108.3, 61.0, 46.2, 37.4, 13.9; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_3N$ $[M + H]^+$ 196.0968, found 196.0966.

Methyl 3-(benzofuran-2-yl)-3-oxopropanoate (1q′):



The title compound was synthesized following general procedure GP1 using 2-Benzofuranyl methyl ketone (**S-1b′**, 1 g, 6.24 mmol), dimethyl carbonate (**S-2b**, 0.63 mL, 7.49 mmol), NaH (60% in dispersion oil) (0.374 g, 9.36 mmol), in THF (12 mL). The product **1q′** was isolated (keto-enol tautomers) as a yellow liquid (0.972 g, 71%). TLC: R_f= 0.4 (SiO_2, 30% EtOAc/Hexanes). IR ($CHCl_3$) 3779, 3685, 3620, 2361, 1653, 1523, 1476, 1445, 1352, 1071, 1022, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 0.26H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.63-7.61 (m, 0.35H), 7.60–7.54 (m, 2H), 7.52–7.46 (m, 1H), 7.39–7.37 (m, 0.28H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 18.0 Hz, 1H), 7.25–7.24 (m, 0.60H), 5.86 (s, 0.27), 3.99 (s, 2H), 3.81 (s, 0.83H), 3.75 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 182.9, 175.5, 173.2, 167.3, 161.8, 155.9, 155.4, 151.7, 149.6, 128.8, 128.3, 127.88, 127.83, 127.0, 126.6, 124.2, 123.9, 123.6, 123.3, 122.9, 122.3, 114.2, 112.6, 112.1, 111.8, 111.7, 108.9, 88.3, 52.7, 51.7, 45.6; HRMS (ESI): *m/z* calcd for $C_{12}H_{11}O_4$ $[M + H]^+$ 219.0652, found 219.0650.

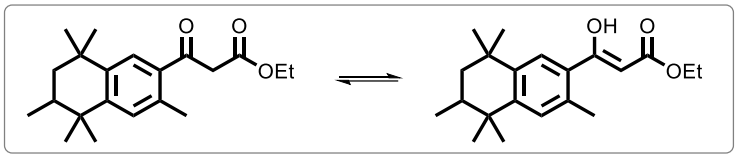
Methyl 3-oxo-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pentanoate (1r′):



The title compound was synthesized following general procedure GP1, using Dihydro-β-ionone (**S-1c′**, 1 g, 5.14 mmol),

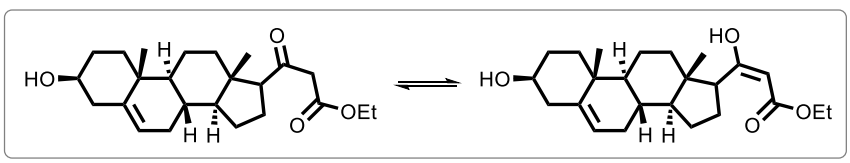
dimethyl carbonate (**S-2b**, 0.51 mL, 6.17 mmol), NaH (60% in dispersion oil) (0.308 g, 7.71 mmol), in THF (12 mL). The product **1r′** was isolated (keto-enol tautomers) as a yellow liquid (0.68 g, 53%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3614, 3533, 2933, 2868, 2362, 1744, 1715, 1652, 1626, 1522, 1472, 1439, 1360, 1319, 1079, 1032, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 0.09H), 4.96(s, 0.10H), 3.69 (d, *J* = 1.0 Hz, 3H), 3.41 (s, 2H), 2.62–2.52 (m, 2H), 2.29–2.18 (m, 2H), 1.85 (t, *J* = 6.3 Hz, 2H), 1.55–1.46 (m, 5H), 1.39–1.33 (m, 2H), 0.93 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.6, 179.0, 173.1, 167.7, 135.6, 128.1, 88.2, 52.3, 51.0, 48.9, 43.8, 39.7, 35.8, 35.0, 32.7, 28.4, 25.6, 22.0, 19.7, 19.4; HRMS (ESI): *m/z* calcd for $C_{15}H_{24}O_3Na$ $[M + Na]^+$ 275.1618, found 275.1612.

Ethyl3-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-3-oxopropanoate (1s′):



The title compound was synthesized following general procedure GP1, using Tonalide (**S-1d′**, 1 g, 5.14 mmol), dimethyl carbonate (**S-2b**, 0.51 mL, 6.17 mmol), NaH (60% in dispersion oil) (0.308 g, 7.71 mmol), in THF (12 mL). The product **1s′** was isolated (keto-enol tautomers) as a yellow liquid (0.68 g, 53%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3684, 3620, 2967, 2929, 2361, 1735, 1678, 1612, 1539, 1500, 1460, 1420, 1368, 1299, 1146, 1114, 1033, 928, 890, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.22 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 2.53 (s, 3H), 1.89–1.86 (m, 1H), 1.68 (s, 1H), 1.43 (s, 1H), 1.34 (s, 6H), 1.27 (s, 3H), 1.08 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 7H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.0, 167.9, 151.0, 142.5, 136.4, 133.5, 131.0, 128.4, 61.4, 48.4, 43.4, 38.0, 34.5, 34.1, 32.5, 32.0, 28.3, 24.7, 21.6, 16.9, 14.2; HRMS (ESI): *m/z* calcd for $C_{21}H_{31}O_3$ $[M + H]^+$ 331.2268, found 331.2264.

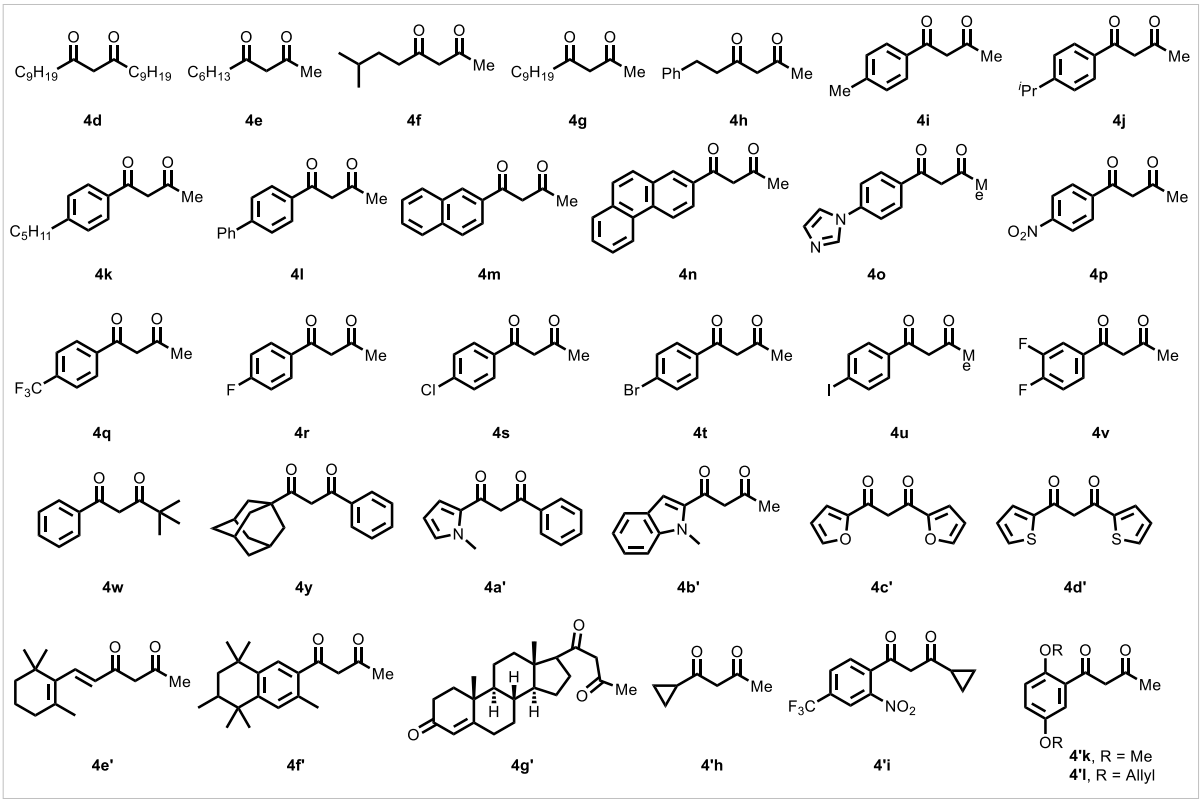
Ethyl 3-((3S,8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxopropanoate (1t′):



The title compound was synthesized following general procedure GP1, using pregnenolone (**S-1e′**, 1 g, 3.15 mmol), diethyl carbonate (**S-2a**, 0.45 mL, 3.79 mmol), NaH (60% in dispersion oil) (0.189 g, 4.73 mmol), in THF (12 mL) and the product **1t′** was

isolated (keto-enol tautomers) as a yellow liquid (0.68 g, 56%). TLC: R_f = 0.4 (SiO_2, 30% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3603, 2953, 2360, 1743, 1707, 1674, 1619, 1523, 1474, 1438, 1310, 1029, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.19 (0.12H), 5.29 (s, 1H), 4.94 (s, 0.10H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.56–3.41 (m, 1H), 3.38 (s, 2H), 2.64–2.51 (m, 1H), 2.34–2.07 (m, 4H), 2.04–1.88 (m, 2H), 1.85–1.72 (m, 3H), 1.71–1.62 (m, 2H), 1.60–1.51 (m, 2H), 1.50–1.36 (m, 5H), 1.25–1.21 (m, 3H), 0.96 (d, *J* = 6.3 Hz, 4H), 0.63 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 206.9, 203.7, 179.5, 167.4, 140.8, 140.5, 121.5, 121.2, 89.3, 63.1, 61.2, 60.6, 56.9, 55.6, 51.7, 50.6, 49.9, 49.4, 46.3, 44.6, 44.5, 42.2, 38.7, 37.29, 37.25, 36.5, 36.4, 34.8, 32.04, 32.02, 31.8, 31.7, 31.5, 26.9, 25.9, 24.8, 24.4, 23.1, 21.0, 20.4, 19.4, 19.3, 14.3, 14.1, 13.4, 12.9; HRMS (ESI): *m/z* calcd for $C_{24}H_{37}O_4$ $[M + H]^+$ 389.2686, found 389.2689.

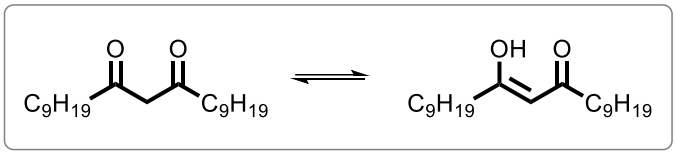
(k) List of *β*-diketones synthesized:



All the *β*-diketones (**4d**–**4w**, **4y**, **4a′**–**4g′**, **4′h**, **4′i**, **4′k**, **4′l**) are synthesized using known literature procedures, while substrates (**4a**–**4c**, **4x**, **4z, 4′a**–**4′g**, **4′m**, **4′n**) are commercially available and purchased from Sigma-Aldrich, BLD Pharm, TCI chemicals, and are used as received without further purification.

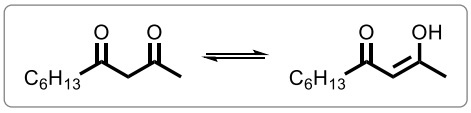
(l) Analytical data of *β*-diketones:

Henicosane-10,12-dione (4d):



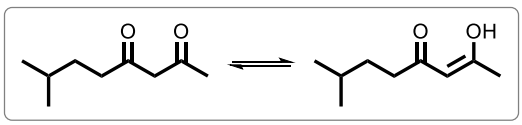
The title compound was synthesized following general procedure GP4, using undecan-2-one (**S1g**, 1 g, 5.87 mmol), decanoyl chloride (1.34 g, 7.05 mmol) and LiHMDS (1 M solution in THF) (8.81 mL, 8.81 mmol). The product **4d** was isolated (keto-enol tautomers) as a yellow liquid (0.9 g, 47%). TLC: R_f= 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3109, 2923, 2852, 1691, 1603, 1520, 1343, 1317, 1259, 1109, 1011, 854, 745, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.54 (s, 1H), 5.47 (s, 1H), 2.49 (t, *J* = 7.4 Hz, 1H), 2.26 (s, 2H), 3.54 (s, 0.37H), 1.85 (d, *J* = 1.4 Hz, 1H), 1.60 (d, *J* = 7.3 Hz, 2H), 1.31–1.24 (m, 28H), 0.88 (d, *J* = 6.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 204.4, 194.5, 144.6, 117.0, 99.0, 57.2, 43.8, 38.4, 34.2, 31.9, 31.8, 29.43, 29.41, 29.3, 29.2, 29.2, 29.1, 29.0, 29.0, 25.7, 25.4, 25.1, 23.4, 22.6, 19.5, 14.0; HRMS (ESI): *m/z* calcd for $C_{21}H_{41}O_2$ $[M + H]^+$ 325.3101, found 325.3097.

Decane-2,4-dione (4e):



The title compound was synthesized following general procedure GP3, using octan-2-one (**S-1f′**, 1 g, 7.8 mmol), NaH (60% in dispersion oil) (1.24 g, 31.19 mmol), in EtOAc (22 mL). The product **4e** was isolated (keto-enol tautomers) as a yellow liquid (0.71 g, 47%). TLC: R_f= 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2961, 2926, 2871, 1606, 1272, 1186, 1054, 1016, 847, 779, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.51 (s, 1H), 5.49 (s, 1H), 3.56 (s, 0.38H), 2.30–2.23 (m, 3H), 2.51–2.48 (t, *J* = 7.38 Hz, 0.41H), 2.05 (s, 3H), 1.65–1.53 (m, 3H), 1.38–1.27 (m, 8H), 0.92–0.86 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 204.4, 202.3, 194.4, 191.6, 99.8, 58.0, 43.9, 38.3, 31.6, 30.9, 29.8, 29.0, 28.8, 25.8, 25.1, 23.4, 22.6, 22.5, 14.1, 14.1; HRMS (ESI): *m/z* calcd for $C_{10}H_{19}O_2$ $[M + H]^+$ 171.1380, found 171.1381.

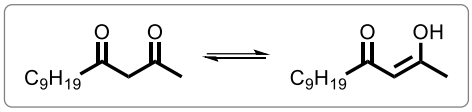
7-Methyloctane-2,4-dione (4f):[10]



The title compound was synthesized following general procedure GP3, using methyl isoamyl ketone (**S-1c**, 1 g, 8.75 mmol), NaH (60% in dispersion oil) (1.4 g, 35.02 mmol), in EtOAc (22 mL). The product **4f** was isolated (keto-enol

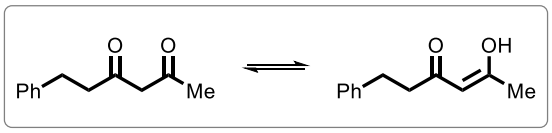
tautomers) as a yellow liquid (0.845 g, 62%). TLC: R_f = 0.7 (SiO_2, 10% EtOAc/Hexanes). The characterization data aligns perfectly with the reported data in the literature.[10]

Tridecane-2,4-dione (4g):



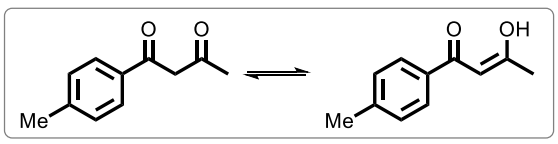
The title compound was synthesized following general procedure GP3, using undecan-2-one (**S-1g**, 1 g, 5.87 mmol), NaH (60% in dispersion oil) (0.93 g, 23.48 mmol), in EtOAc (22 mL). The product **4g** was isolated (keto-enol tautomers) as a yellow liquid (0.964 g, 77%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2961, 2926, 2871, 1606, 1460, 1272, 1186, 1054, 1016, 847, 779, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.48 (s, 1H), 5.46 (s, 1H), 2.27–2.18 (m, 3H), 3.53 (s, 0.44H), 2.46 (t, *J* = 7.38 Hz, 0.41H), 2.11 (d, *J* = 16.7 Hz, 1H), 2.01 (s, 3H), 1.56 (p, *J* = 7.3 Hz, 2H), 1.25 (d, *J* = 12.8 Hz, 14H), 0.85 (t, *J* = 6.7 Hz, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.9, 153.2, 139.8, 121.4, 106.7, 57.9, 34.4, 32.0, 29.5, 29.3, 22.8, 14.2; HRMS (ESI): *m/z* calcd for $C_{13}H_{25}O_2$ $[M + H]^+$ 213.1849, found 213.1852.

6-Phenylhexane-2,4-dione (4h):



The title compound was synthesized following general procedure GP3, using 4-phenylbutan-2-one (**S-1g′**, 1 g, 6.74 mmol), NaH (60% in dispersion oil) (1.07 g, 13.49 mmol) and EtOAc (22 mL). The product **4h** was isolated (keto-enol tautomers) as a yellow liquid (0.87 g, 68%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2923, 2854, 1707, 1606, 1458, 1362, 1237, 1147, 948, 773, 722 cm^{-1}; 15.52 (s, 1H), 7.33–7.28 (m, 2H), 7.24–7.19 (m, 3H), 5.49 (s, 1H), 3.55 (s, 0.4H), 2.99–2.91 (m, 2H), 2.88–2.82 (m, 0.41H), 2.65–2.58 (m, 2H), 2.20 (s, 1H), 2.05 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.2, 201.9, 193.2, 190.9, 140.6, 128.5, 128.5, 128.3, 128.2, 126.2, 126.2, 100.0, 57.9, 45.1, 39.9, 31.4, 30.8, 29.4, 24.7; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1067, found 191.1068.

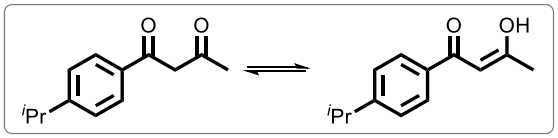
1-(*p*-Tolyl)butane-1,3-dione (4i):



The title compound was synthesized following general procedure GP3, using 1-(*p*-tolyl)ethan-1-one (**S-1j**, 1 g, 7.45 mmol), NaH (60% in dispersion oil) (1.19 g, 29.81 mmol) and EtOAc (22 mL). The product **4i** was isolated (keto-

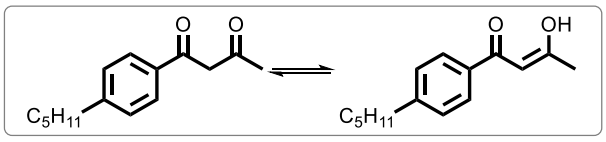
enol tautomers) as a yellow liquid (0.99 g, 76%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3681, 3423, 2925, 2364, 1715, 1610, 1430, 1365, 1277, 1117, 1079, 1021, 989, 929, 848, 772, 669, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.24 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 2.39 (s, 3H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.1, 183.8, 143.1, 132.2, 129.4, 127.1, 96.3, 25.6, 21.6; HRMS (ESI): *m/z* calcd for $C_{11}H_{13}O_2$ $[M + H]^+$ 177.0910, found 177.0908.

1-(4-Isopropylphenyl)butane-1,3-dione (4j):



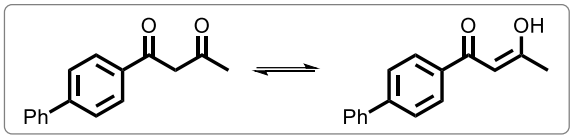
The title compound was synthesized following general procedure GP3, using 1-(4-isopropylphenyl)ethan-1-one (**S-1h′**, 1 g, 6.16 mmol), NaH (60% in dispersion oil) (0.986 g, 24.67 mmol) and EtOAc (22 mL). The product **4j** was isolated (keto-enol tautomers) as a yellow liquid (0.61 g, 71%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2923, 2852, 1691, 1603, 1520, 1343, 1317, 1259, 1109, 1012, 854, 745, 688, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.22 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.15 (s, 1H), 4.06 (s, 0.21H), 2.94 (p, *J* = 6.9 Hz, 1H), 2.27 (s, 0.34H), 2.17 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.2, 183.7, 153.9, 132.6, 129.0, 127.2, 127.0, 126.8, 96.4, 34.2, 25.7, 23.7, 23.6; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1223, found 205.1225.

1-(4-Pentylphenyl)butane-1,3-dione (4k):



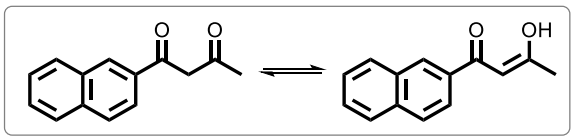
The title compound was synthesized following general procedure GP3, using 1-(4-pentylphenyl)ethan-1-one (**S-1l**, 1 g, 5.25 mmol), NaH (60% in dispersion oil) (0.840 g, 21.02 mmol) and EtOAc (22 mL). The product **4k** was isolated (keto-enol tautomers) as a yellow liquid (0.83 g, 68%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3421, 2960, 2930, 2859, 1607, 1525, 1474, 1428, 928, 850, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.28 (s, 1H), 7.81–7.76 (m, 2H), 7.24–7.20 (m, 2H), 6.15 (s, 1H), 2.68–2.57 (m, 2H), 2.15 (s, 3H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.32 (td, *J* = 6.5, 3.0 Hz, 4H), 0.90 (d, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.4, 193.0, 183.7, 149.6, 148.0, 134.0, 132.4, 128.85, 128.81, 128.6, 127.1, 96.2, 54.6, 35.9, 31.4, 30.8, 30.7, 27.1, 25.6, 22.7, 22.5, 14.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{15}H_{21}O_2$ $[M + H]^+$ 233.1536, found 233.1535.

1-([1,1'-Biphenyl]-4-yl)butane-1,3-dione (4l):



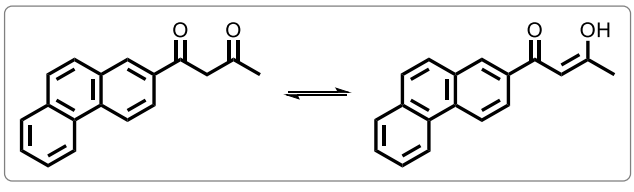
The title compound was synthesized following general procedure GP3, using 1-([1,1'-biphenyl]-4-yl)ethan-1-one (**S-1m**, 1 g, 5.09 mmol), NaH (60% in dispersion oil) (0.815 g, 20.38 mmol) and EtOAc (22 mL). The product **4l** was isolated (keto-enol tautomers) as a yellow liquid (0.91 g, 75%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3421, 1637, 1430, 1028, 928, 851, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.22 (s, 1H), 7.99–7.92 (m, 2H), 7.70–7.66 (m, 2H), 7.64 (dd, *J* = 6.9, 1.6 Hz, 2H), 7.51–7.44 (m, 2H), 7.43–7.36 (m, 1H), 6.22 (s, 1H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.8, 183.0, 145.1, 140.0, 133.7, 129.0, 128.2, 127.6, 127.37, 127.31, 96.7, 26.0; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}O_2$ $[M + H]^+$ 239.1067, found 239.1062.

1-(Naphthalen-2-yl)butane-1,3-dione (4m):



The title compound was synthesized following general procedure GP3, using 1-(naphthalen-2-yl)ethan-1-one (**S-1n**, 1 g, 5.87 mmol), NaH (60% in dispersion oil) (0.94 g, 23.50 mmol) and EtOAc (22 mL). The product **4m** was isolated (keto-enol tautomers) as a yellow liquid (0.88 g, 71%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3420, 2356, 1607, 1525, 1477, 1425, 1024, 928, 850, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.27 (s, 1H), 8.43 (s, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.90–7.83 (m, 3H), 7.61–7.50 (m, 2H), 6.31 (s, 1H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.5, 193.8, 183.1, 135.9, 135.3, 133.7, 132.8, 132.5, 132.1, 131.0, 129.8, 129.3, 129.0, 128.8, 128.4, 128.2, 128.1, 127.88, 127.82, 127.0, 126.8, 123.8, 123.1, 54.8, 30.6, 25.9; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_2$ $[M + H]^+$ 213.0910, found 213.0908.

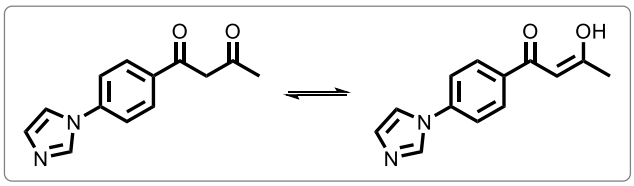
1-(Phenanthren-2-yl)butane-1,3-dione (4n):



The title compound was synthesized following general procedure GP3, using 1-(phenanthren-2-yl)ethan-1-one (**S-1i′**, 1 g, 4.53 mmol), NaH (60% in dispersion oil) (0.72 g, 18.15 mmol) and EtOAc (22 mL). The product **4n** was isolated (keto-enol tautomers) as a yellow liquid 0.83 g, 70%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3045, 3005, 1601, 1458, 1423, 1347, 1240, 996, 918, 899, 818, 775, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.28 (s, 1H), 8.68 (dd, *J* = 9.0, 6.5 Hz, 2H), 8.43 (d, *J* = 1.9 Hz, 1H), 8.07 (dd, *J* =

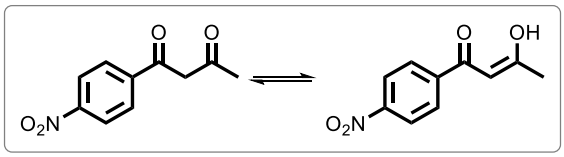
8.8, 1.9 Hz, 1H), 7.95–7.86 (m, 1H), 7.78 (s, 2H), 7.67 (qd, *J* = 6.9, 1.6 Hz, 2H), 4.24 (s, 0.17H), 6.35 (s, 1H), 2.36 (s, 0.27H), 2.26 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 194.00, 183.03, 133.06, 132.9, 132.7, 131.7, 129.8, 128.8, 128.1, 127.9, 127.7, 127.3, 127.1, 124.2, 123.2, 123.2, 97.1, 26.0; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}O_2$ $[M + H]^+$ 263.1067, found 263.1068.

1-(4-(1H-Imidazol-1-yl)phenyl)butane-1,3-dione (4o):



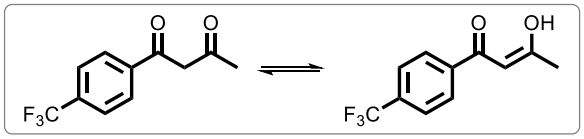
The title compound was synthesized following general procedure GP3, using 1-(4-(1H-imidazol-1-yl)phenyl)ethan-1-one (**S-1j′**, 1 g, 5.37 mmol), NaH (60% in dispersion oil) (0.86 g, 21.48 mmol) and EtOAc (22 mL). The product **4o** was isolated (keto-enol tautomers) as a yellow liquid (0.38 g, 31%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3113, 1606, 1526, 1391, 1304, 1188, 1123, 1050, 936, 845, 780, 736, 607 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.17 (s, 1H), 8.02–7.94 (m, 3H), 7.82–7.74 (m, 3H), 6.51 (dd, *J* = 2.5, 1.8 Hz, 1H), 6.19 (s, 1H), 2.21 (s, 3H), 4.11 (s, 0.12H), 2.31 (s, 0.17H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 193.5, 182.5, 142.9, 142.0, 132.7, 130.5, 128.6, 126.9, 118.6, 118.6, 108.5, 96.6, 25.8; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}O_2N_2$ $[M + H]^+$ 229.0972, found 229.0973.

1-(4-Nitrophenyl)butane-1,3-dione (4p):[12]



The title compound was synthesized following general procedure GP3, using 1-(4-nitrophenyl)ethan-1-one (**S-1r**, 1 g, 6.05 mmol), NaH (60% in dispersion oil) (0.968 g, 24.22 mmol) and EtOAc (22 mL). The product **4p** was isolated (keto-enol tautomers) as a yellow liquid (0.78 g, 62%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2961, 1606, 1272, 1186, 1054, 1016, 847, 780, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.90 (s, 1H), 8.35–8.26 (m, 4H), 8.11 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 6.23 (s, 1H), 2.68 (s, 3H), 2.26 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 196.4, 196.2, 179.3, 141.5, 140.5, 129.4, 128.0, 124.0, 123.9, 98.1, 27.1, 26.6.

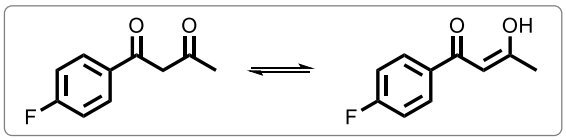
1-(4-(Trifluoromethyl)phenyl)butane-1,3-dione (4q):



The title compound was synthesized following general procedure GP3, using 1-(4-(trifluoromethyl)phenyl)ethan-1-one (**S-1s**, 1

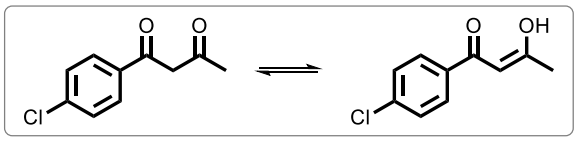
g, 5.31 mmol), NaH (60% in dispersion oil) (0.85 g, 21.25 mmol) and EtOAc (22 mL). The product **4q** was isolated (keto-enol tautomers) as a yellow liquid (0.82 g, 67%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3613, 2362, 1603, 1523, 1477, 1425, 1324, 1023, 928, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.99 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 2H), 6.19 (s, 1H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.3, 181.0, 138.2, 127.4, 125.75, 125.71, 97.4, 29.8, 26.2; HRMS (ESI): *m/z* calcd for $C_{11}H_{10}O_2F_3$ $[M + H]^+$ 231.0627, found 231.0627.

1-(4-Fluorophenyl)butane-1,3-dione (4r):



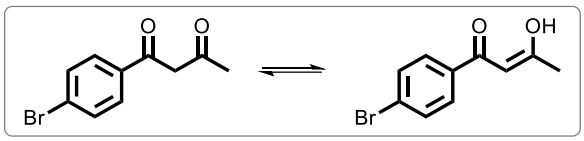
The title compound was synthesized following general procedure GP3, using 1-(4-fluorophenyl)ethan-1-one (**S-1t**, 1 g, 7.23 mmol), NaH (60% in dispersion oil) (1.15 g, 28.95 mmol) and EtOAc (22 mL). The product **4r** was isolated (keto-enol tautomers) as a yellow liquid (0.73 g, 56%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3775, 3685, 3432, 2364, 1882, 1604, 1507, 1429, 1367, 1269, 1157, 1101, 1077, 1016, 928, 851, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.15 (s, 1H), 7.92–7.85 (m, 2H), 7.16–7.07 (m, 2H), 6.12 (s, 1H), 2.18 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.0, 192.3, 183.0, 167.5, 166.6, 164.1, 131.6, 131.5, 131.4, 131.3, 129.6, 129.5, 116.2, 116.0, 115.9, 115.7, 96.4, 54.8, 30.7, 25.6; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}O_2F$ $[M + H]^+$ 181.0659, found 181.0658.

1-(4-Chlorophenyl)butane-1,3-dione (4s):



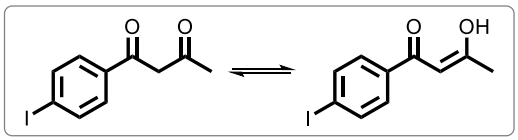
The title compound was synthesized following general procedure GP3, using 1-(4-chlorophenyl)ethan-1-one (**S-1u**, 1 g, 6.46 mmol), NaH (60% in dispersion oil) (1.03 g, 25.87 mmol) and EtOAc (22 mL). The product **4s** was isolated (keto-enol tautomers) as a yellow liquid (0.88 g, 69%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3421, 2357, 1601, 1523, 1479, 1425, 1092, 1019, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.09 (s, 1H), 7.83–7.77 (m, 2H), 7.43–7.38 (m, 2H), 6.13 (s, 1H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.8, 182.3, 138.6, 133.5, 130.2, 129.3, 129.0, 128.4, 96.7, 54.8, 30.7, 25.9; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}O_2Cl$ $[M + H]^+$ 197.0364, found 197.0363.

1-(4-Bromophenyl)butane-1,3-dione (4t):



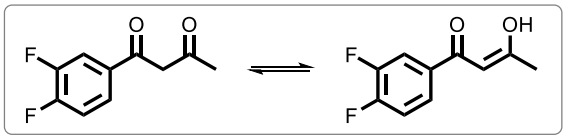
The title compound was synthesized following general procedure GP3, using 1-(4-bromophenyl)ethan-1-one (**S-1v**, 1 g, 5.02 mmol), NaH (60% in dispersion oil) (0.803 g, 20.09 mmol) and EtOAc (22 mL). The product **4t** was isolated (keto-enol tautomers) as a yellow liquid (0.66 g, 54%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3419, 2356, 1598, 1527, 1477, 1426, 1016, 928, 848, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.07 (s, 1H), 7.76–7.70 (m, 2H), 7.60–7.55 (m, 2H), 6.14 (s, 1H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.0, 182.4, 133.9, 132.3, 132.0, 130.2, 128.6, 127.2, 96.7, 54.8, 25.9; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}O_2Br$ $[M + H]^+$ 240.9859, found 240.9859.

1-(4-Iodophenyl)butane-1,3-dione (4u):



The title compound was synthesized following general procedure GP3, using 1-(4-iodophenyl)ethan-1-one (**S-1w**, 1 g, 4.06 mmol), NaH (60% in dispersion oil) (0.647 g, 16.19 mmol) and EtOAc (22 mL). The product **4u** was isolated (keto-enol tautomers) as a yellow liquid (0.83 g, 71%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 1601, 1524, 1477, 1426, 1026, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.06 (s, 1H), 7.82–7.77 (m, 2H), 7.61–7.55 (m, 2H), 6.14 (s, 1H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.1, 182.4, 138.3, 138.0, 134.4, 130.1, 128.5, 99.7, 96.7, 54.7, 30.7, 26.0; HRMS (ESI): *m/z* calcd for $C_{10}H_9O_2INa$ $[M + Na]^+$ 310.9539, found 310.9537.

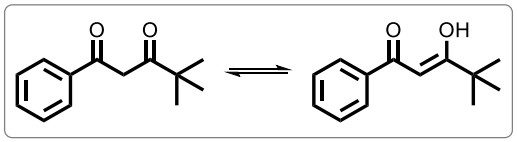
1-(3,4-Difluorophenyl)butane-1,3-dione (4v):



The title compound was synthesized following general procedure GP4, using acetone (**S-1m'**, 1 g, 17.21 mmol), 3,4-difluorobenzyl chloride (2.8 mL, 20.66 mmol) and LiHMDS (1 M solution in THF) (25.82 mL, 25.82 mmol). The product **4v** was isolated (keto-enol tautomers) as a yellow liquid (0.98 g, 29%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3074, 2927, 1515, 1302, 1111, 934, 882, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.90 (s, 1H), 7.62–7.48 (m, 2H), 7.16–7.05 (m, 1H), 5.97 (s, 1H), 3.94 (s, 0.11H), 2.94 (s, 0.17H), 2.18 (s, 0.17H), 2.07 (s, 3H), 2.99 (s, 0.24H), 1.99 (s, 0.24H), 1.70 (s, 0.26H), 1.55 (s, 0.51H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.6, 193.2,

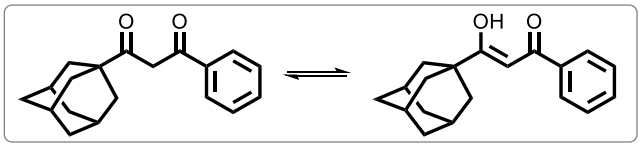
181.8, 181.8, 181.8, 156.0, 154.3, 154.2, 151.8, 151.7, 149.3, 149.2, 132.4, 132.3, 132.3, 132.3, 125.1, 123.8, 123.8, 123.8, 123.7, 117.7, 117.5, 116.6, 116.5, 116.4, 116.4, 96.6, 82.5, 54.6, 53.0, 30.7, 27.6, 26.7, 25.5, 20.8; HRMS (ESI): *m/z* calcd for $C_{10}H_9O_2F_2[M + H]^+$ 199.0565, found 199.0559.

4,4-Dimethyl-1-phenylpentane-1,3-dione (4w):



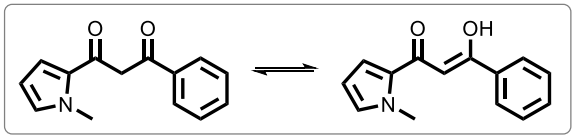
The title compound was synthesized following general procedure GP4, using acetophenone (**S-1n'**, 1 g, 8.32 mmol), pivaloyl chloride (1.2 g, 9.98 mmol) and LiHMDS (1 M solution in THF) (12.48 mL, 12.48 mmol). The product **4w** was isolated (keto-enol tautomers) as a yellow liquid (1.0 g, 59%). TLC: R_f = 0.8 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2966, 2870, 1599, 1562, 1479, 1458, 1363, 1283, 1130, 1076, 1027, 847, 766, 691, 650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.86 (m, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.48–7.43 (m, 2H), 6.31 (s, 1H), 1.26 (s, 9H), 1.23 (s, 0.44H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.0, 184.7, 135.6, 132.2, 128.7, 127.1, 92.2, 39.9, 27.5, 26.3; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1223, found 205.1226.

1-((3r,5r,7r)-Adamantan-1-yl)-3-phenylpropane-1,3-dione (4y):



The title compound was synthesized following general procedure GP4, using 1-((3r,5r,7r)-adamantan-1-yl)ethan-1-one (**S-1o'**, 1 g, 7.23 mmol), benzoyl chloride (0.434 mL, 10.85 mmol) and LiHMDS (1 M solution in THF) (mL, 3 mmol). The product **4y** was isolated (keto-enol tautomers) as a yellow liquid (1.16 g, 76%). TLC: R_f= 0.6 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3684, 3611, 2911, 2853, 2362, 1710, 1601, 1571, 1527, 1478, 1451, 1425, 1362, 1322, 1264, 1103, 1026, 976, 928, 849, 670, 622 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.83 (m, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 6.27 (s, 1H), 2.08 (s, 3H), 1.92 (d, *J* = 3.3 Hz, 6H), 1.82–1.70 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 201.4, 185.6, 135.8, 132.1, 128.6, 127.1, 91.9, 41.6, 39.1, 36.6, 28.1; HRMS (ESI): *m/z* calcd for $C_{19}H_{23}O_2$ $[M + H]^+$ 283.1693, found 283.1692.

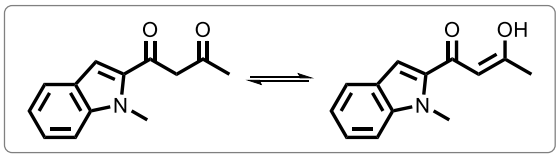
1-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylpropane-1,3-dione (4a′):



The title compound was synthesized following general procedure GP4, using 1-(1-methyl-1*H*-pyrrol-2-yl)ethan-1-one (**S-1a′**, 1 g, 7.23

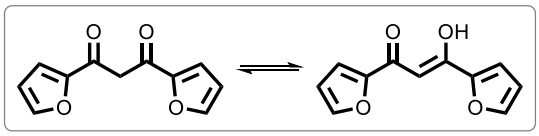
mmol), benzoyl chloride (0.434 mL, 10.85 mmol) and LiHMDS (1 M solution in THF) (mL, 3 mmol). The product **4a′** was isolated (keto-enol tautomers) as a yellow solid (1.16 g, 76%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3774, 3684, 3423, 2364, 1606, 1569, 1527, 1458, 1428, 1372, 1326, 1055, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.26 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.48–7.45 (m, 2H), 7.03 (dd, *J* = 4.1, 1.8 Hz, 1H), 6.88–6.81 (m, 1H), 6.61 (s, 1H), 6.20 (dd, *J* = 4.2, 2.4 Hz, 1H), 4.43 (s, 1H), 4.02 (s, 3H), 3.91 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.5, 184.1, 183.5, 175.6, 136.5, 134.6, 133.4, 132.1, 131.4, 131.3, 129.8, 128.9, 128.7, 128.5, 126.3, 121.0, 117.8, 108.66, 108.61, 94.0, 51.0, 37.8; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}O_2N$ $[M + H]^+$ 228.1019, found 228.1017.

1-(1-methyl-1*H*-indol-2-yl)butane-1,3-dione (4b′):



The title compound was synthesized following general procedure GP3, using 1-(1-methyl-1*H*-indol-2-yl)ethan-1-one (**S-1p'**, 1 g, 5.77 mmol), NaH (60% in dispersion oil) (0.923 g, 23.09 mmol) and EtOAc (22 mL). The product **4b′** was isolated (keto-enol tautomers) as a yellow liquid (1.02 g, 82%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$)) 3055, 2915, 1526, 1468, 1359, 1227, 1128, 1093, 1012, 939, 811, 788, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.32 (s, 1H), 8.39–8.31 (m, 1H), 8.29–8.19 (m, 1H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.33–7.24 (m, 5H), 5.93 (s, 1H), 3.89 (s, 2H), 3.74 (dt, *J* = 6.4, 2.2 Hz, 5H), 2.28 (s, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.4, 187.1, 186.0, 184.6, 137.7, 137.5, 137.1, 133.8, 126.2, 126, 123.7, 123.1, 123.0, 122.4, 122.2, 122.0, 116.1, 113.2, 109.9, 109.8, 96.7, 57.1, 33.6, 33.4, 30.2, 24.1; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}O_2N$ $[M + H]^+$ 216.1019, found 216.1019.

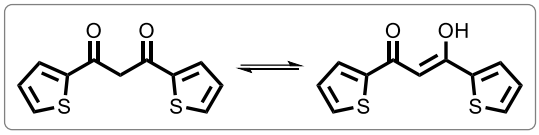
1,3-Di(furan-2-yl)propane-1,3-dione (4c′):



The title compound was synthesized following general procedure GP4, using 2-acetylfuran (**S-1y**, 1 g, 9.08 mmol), furan-2-carbonyl chloride (1.42 g, 10.90 mmol) and LiHMDS (1 M solution in THF) (13.63 mL, 13.63 mmol). The product **4c′** was isolated (keto-enol tautomers) as a yellow liquid (1.0 g, 54%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2955, 2926, 2856, 1605, 1457, 1363, 1238, 950, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.60 (s, 1H), 7.61 (s, 2H), 7.38–7.12 (m, 2H), 6.72–6.51 (m, 3H),

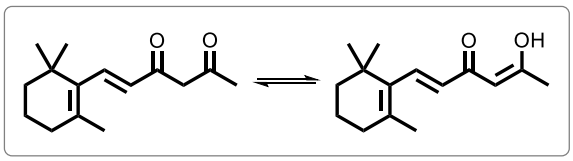
4.34 (s, 0.19H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 174.8, 150.4, 147.2, 146.2, 118.9, 115.6, 112.8, 112.7, 92.2; HRMS (ESI): *m/z* calcd for $C_{11}H_9O_4$ $[M + H]^+$ 205.0495, found 205.0504.

1,3-Di(thiophen-2-yl)propane-1,3-dione (4d′):



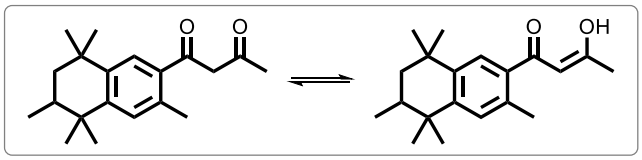
The title compound was synthesized following general procedure GP4, using 1-(thiophen-2-yl)ethan-1-one (**S-1q′**, 1 g, 7.92 mmol), thiophene-2-carbonyl chloride (1.39 g, 9.51 mmol) and LiHMDS (1 M solution in THF) (11.88 mL, 11.88 mmol). The product **4d′** was isolated (keto-enol tautomers) as a yellow liquid (1.2 g, 65%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3103, 1526, 1403, 1283, 1235, 1088, 1060, 858, 777, 751, 714, 627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.20 (s, 1H), 7.88-7.7.84 (m, 0.39H), 7.75 (dd, *J* = 3.8, 1.2 Hz, 2H), 7.70-7.7.64 (m, 0.41H), 7.59 (dd, *J* = 5.0, 1.2 Hz, 2H), 7.18–7.08 (m, 2H), 6.53 (s, 1H), 4.46 (s, 0.40H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 185.6, 178.8, 143.4, 140.6, 135.2, 134.3, 132.1, 130.0, 128.5, 128.4, 92.6, 52.2; HRMS (ESI): *m/z* calcd for $C_{11}H_9O_2S_2$ $[M + H]^+$ 237.0038, found 237.0041.

(*E*)-6-(2,6,6-Trimethylcyclohex-1-en-1-yl)hex-5-ene-2,4-dione (4e′):



The title compound was synthesized following general procedure GP3, using β-ionone (**S-1r′**, 1 g, 52.0 mmol), NaH (60% in dispersion oil) (0.83 g, 20.80 mmol) and EtOAc (22 mL). The product **4e′** was isolated (keto-enol tautomers) as a brown liquid (1.0 g, 81%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2928, 2871, 1717, 1650, 1585, 1449, 1363, 1259, 1223, 1160, 976, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.46 (s, 1H), 7.37–7.29 (m, 1H), 5.84 (d, *J* = 16.0 Hz, 1H), 5.52 (s, 1H), 5.52 (s, 1H), 3.73 (s, 0.13H), 2.24 (s, 0.21H), 2.11 (s, 3H), 2.05 (t, *J* = 6.4 Hz, 2H), 1.76 (d, *J* = 1.1 Hz, 3H), 1.67 (s, 0.27H), 1.65–1.56 (m, 2H), 1.49–1.43 (m, 2H), 1.06 (s, 6H), 0.99 (d, 0.36H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 196.7, 178.5, 139.9, 136.6, 135.4, 126.7, 100.4, 39.9, 34.2, 33.7, 28.9, 26.7, 21.8, 19.0; HRMS (ESI): *m/z* calcd for $C_{15}H_{23}O_2$ $[M + H]^+$ 235.1693, found 235.1705.

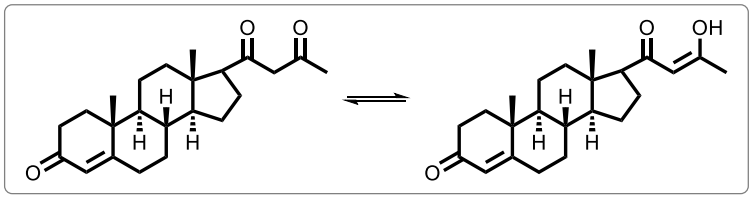
1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)butane-1,3-dione (4f′):



The title compound was synthesized following general procedure GP3, using tonalide (**S-1d′**, 1 g, 5.14 mmol), NaH

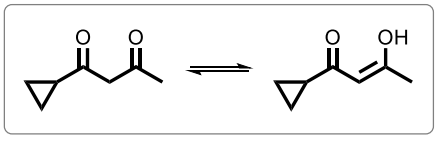
(60% in dispersion oil) (0.61 g, 15.47 mmol) and EtOAc (22 mL). The product **4f′** was isolated (keto-enol tautomers) as a yellow liquid (0.82 g, 70%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2961, 2926, 1594, 1454, 1363, 1258, 1114, 1086, 969, 826, 790 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.08 (s, 1H), 7.42 (s, 1H), 7.21 (s, 1H), 5.86 (d, *J* = 0.6 Hz, 1H), 4.04 (s, 0.19H), 2.53 (s, 0.28H), 2.47 (s, 3H), 2.47 (s, 3H), 2.29 (s, 0.25H), 1.88 (ddd, *J* = 12.9, 6.7, 2.6 Hz, 1H), 1.64 (t, *J* = 13.2 Hz, 1H), 1.41 (d, *J* = 2.6 Hz, 1H), 1.38 (d, *J* = 2.6 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H), 1.08 (s, 3H), 1.00 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.8, 188.4, 149.2, 142.5, 133.9, 133.3, 130.1, 126.8, 100.6, 43.6, 37.9, 34.5, 34.1, 32.5, 32.0, 28.5, 25.7, 24.9, 20.6, 16.9; HRMS (ESI): *m/z* calcd for $C_{20}H_{29}O_2$ $[M + H]^+$ 301.1262, found 323.1977.

1-((8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)butane-1,3-dione (4g′):



The title compound was synthesized following general procedure GP3, using progesterone (**S-1s′**, 1 g, 3.17 mmol), NaH (60% in dispersion oil) (0.508 g, 12.71 mmol) and EtOAc (22 mL). The product **4g′** was isolated (keto-enol tautomers) as a yellow liquid (0.56 g, 49%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2940, 2903, 1730, 1606, 1365, 1246, 1035, 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.73 (s, 1H), 5.73 (s, 1H), 5.42 (s, 0.09H), 5.44 (s, 1H), 5.29 (s, 0.11H), 3.55 (s, 0.2H), 2.44–2.35 (m, 3H), 2.31 – 2.25 (m, 2H), 2.18–2.10 (m, 1H), 2.05 (s, 3H), 2.03–1.96 (m, 2H), 1.89–1.83 (m, 1H), 1.73 (dtd, *J* = 11.4, 6.3, 2.2 Hz, 3H), 1.57 (ddd, *J* = 13.0, 7.9, 2.8 Hz, 2H), 1.42 (dt, *J* = 12.7, 3.5 Hz, 1H), 1.29 (dd, *J* = 12.4, 4.1 Hz, 2H), 1.18 (s, 3H), 1.15–1.09 (m, 1H), 1.08–1.03 (m, 1H), 1.02–0.95 (m, 1H), 0.69 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.6, 194.4, 190.8, 171.2, 124.0, 100.7, 58.6, 56.0, 53.9, 45.1, 38.7, 38.3, 35.8, 34.0, 32.9, 32.0, 25.1, 24.5, 22.7, 21.0, 17.5, 13.3; HRMS (ESI): *m/z* calcd for $C_{23}H_{33}O_3$ $[M + H]^+$ 357.2424, found 357.2435.

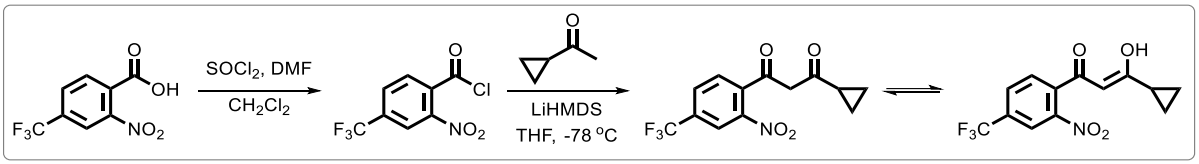
1-Cyclopropylbutane-1,3-dione (4h′):



The title compound was synthesized following general procedure GP3 using 1-cyclopropylethan-1-one (**S-1h**, 1 g, 11.88 mmol), NaH (60% in dispersion oil) (1.9 g, 47.55 mmol) and EtOAc (22 mL) and the product **4h′** isolated acquired with both keto and enol

tautomers as a yellow liquid (1.11 g, 74%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3470, 2926, 2855, 2365, 1721, 1690, 1620, 1425, 1384, 1362, 1139, 1087, 1028, 930, 849, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.60 (s, 1H), 5.57 (s, 1H), 3.66 (s, 1H), 2.21 (s, 1H), 1.98 (s, 3H), 1.59 (td, *J* = 8.0, 4.7 Hz, 1H), 1.06 (p, *J* = 4.0 Hz, 2H), 0.95–0.91 (m, 1H), 0.87 (dq, *J* = 7.4, 3.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 204.2, 202.2, 198.8, 185.0, 99.5, 58.6, 30.7, 23.2, 21.4, 18.5, 11.7, 10.1; HRMS (ESI): *m/z* calcd for $C_7H_{11}O_2$ $[M + H]^+$ 127.0754, found 127.0755.

1-Cyclopropyl-3-(2-nitro-4-(trifluoromethyl)phenyl)propane-1,3-dione (4i′):



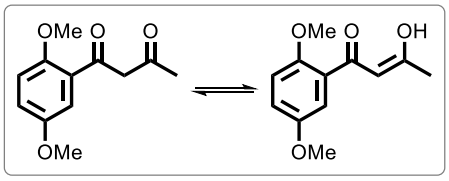
The compound **4i′** was synthesized in two steps using the known literature procedures.[13]

Step 1: To a 100 mL round-bottomed flask containing 2-nitro-4-(trifluoromethyl)benzoic acid (2 g, 8.5 mmol) was suspended in anhydrous CH_2Cl_2, and DMF (5 drops) & thionyl chloride (0.92 mL, 12.75 mmol) was added dropwise, and the reaction mixture was stirred at 55 °C until completion of starting material. After completion of the reaction, the solvents and excess thionyl chloride were removed under vacuum. The crude benzoyl chloride was used without further purification.

Step 2: To 100 mL two-necked flask, cyclopropyl methyl ketone (0.74 mL, 7.88 mmol) in anhydrous THF (30 mL) at –78 °C (ice bath) and stirred to homogeneity. To it was added LiHMDS (1 M solution in THF) (23.66 mL, 23.66 mmol) dropwise, and benzoyl chloride derivative (2 g, 7.88 mmol) was added after 45 mins at the same temperature and stirred to warm to room temperature for 2-6 h, and the reaction progress was monitored by TLC. After completion of the reaction, the reaction was quenched with saturated aqueous NH_4Cl solution & pH=6 was maintained, and the aqueous layer was extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product. The isolated product **4i′** acquired with both keto and enol tautomers as a yellow solid (1.16 g, 76%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3417, 2361, 1601, 1543, 1427, 1359, 1323, 1148, 1083, 1026, 928, 849, 670, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 15.54 (s, 1H), 8.17 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H),

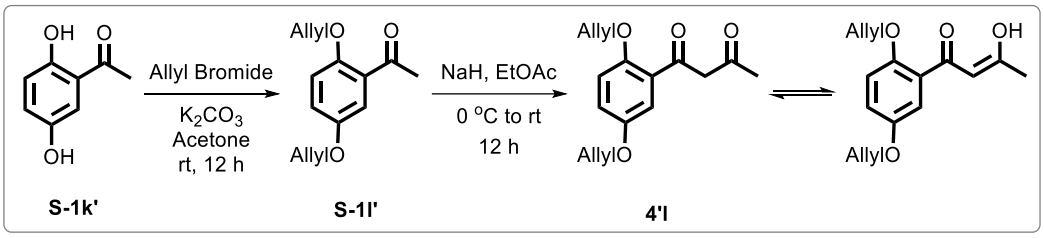
7.73 (d, *J* = 7.9 Hz, 1H), 5.95 (s, 1H), 1.73 (dq, *J* = 8.0, 4.4 Hz, 1H), 1.26 (d, *J* = 3.4 Hz, 2H), 1.11–1.03 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 203.8, 198.0, 194.9, 180.2, 148.2, 135.3, 133.6, 133.2, 130.4, 129.65, 129.62, 123.9, 121.9, 121.8, 121.2, 99.5, 21.6, 18.7, 12.3, 11.5; HRMS (ESI): *m/z* calcd for $C_{13}H_{10}O_4NF_3Na$ $[M + Na]^+$ 324.0454, found 324.0473.

1-(2,5-Dimethoxyphenyl)butane-1,3-dione (4k′):



The title compound was synthesized following general procedure GP3, using 1-(2,5-dimethoxyphenyl)ethan-1-one (**S-1p**, 1 g, 5.54 mmol), NaH (60% in dispersion oil) (0.887 g, 22.19 mmol) and EtOAc (22 mL). The product **4k′** was isolated (keto-enol tautomers) as a yellow liquid (0.99 g, 80%). TLC: R_f = 0.7 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2941, 2837, 1715, 1573, 1496, 1219, 1169, 1149, 1039, 811, 728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.22 (s, 1H), 7.37 (dd, *J* = 19.1, 3.2 Hz, 1H), 6.95 (dd, *J* = 8.9, 3.2 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.45 (s, 1H), 4.02 (s, 0.5H), 3.81 (dd, *J* = 8.9, 0.8 Hz, 4H), 3.75 (dd, *J* = 3.1, 0.9 Hz, 4H), 2.21 (s, 1H), 2.14 (d, *J* = 0.9 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 202.7, 194.4, 194.3, 180.9, 153.5, 153.5, 153.4, 152.8, 126.5, 124.4, 121.6, 119.0, 114.1, 113.7, 113.2, 113.0, 101.8, 58.7, 56.1, 55.8, 55.7, 30.2, 26.0; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_4$ $[M + H]^+$ 223.0965, found 223.0966.

1-(2,5-Bis(allyloxy)phenyl)butane-1,3-dione (4l′):



The compound **4l′** was synthesized in two-steps using the known literature procedures.

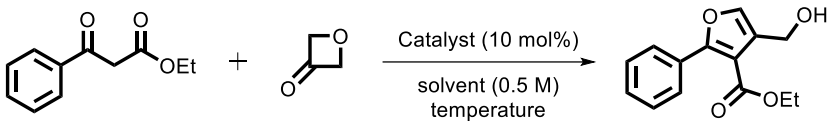
Step 1: To 1-(2,5-dihydroxyphenyl)ethan-1-one (**S-1k'**, 2 g, 13.14 mmol) in anhydrous acetone (20 mL), K_2CO_3 (7.26 g, 52.57 mmol) and allyl bromide (3.4 mL, 39.43 mmol) were added, and the reaction was stirred at room temperature for 24 h. After completion of the reaction, it was filtered through celite. The residue was washed with CH_2Cl_2. The filtrate was evaporated under reduced pressure, and the crude product was purified using silica gel column chromatography to afford the desired product (2.83 g, 93%) as a white solid. The analytical data was found to be in complete agreement with reported literature data.[11]

Step 2: Further, in the next step the title compound was synthesized following the general procedure GP3, using 1-(2,5-bis(allyloxy)phenyl)ethan-1-one (**S-1l′**, 1 g, 4.30 mmol), NaH (60% in dispersion oil) (0.689 g, 43.10 mmol) and EtOAc (22 mL). The product **4l′** was isolated (keto-enol tautomers) as a yellow liquid (0.76 g, 64%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 1720, 1577, 1496, 1423, 1023, 929, 851, 670, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.15 (s, 1H), 7.44 (d, *J* = 3.3 Hz, 1H), 6.98 (dd, *J* = 9.0, 3.3 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.54 (s, 1H), 6.09–6.00 (m, 2H), 5.47–5.38 (m, 2H), 5.29 (td, *J* = 10.8, 1.5 Hz, 2H), 4.58–4.55 (m, 2H), 4.52 (dt, *J* = 5.3, 1.6 Hz, 2H), 2.23 (s, 1H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.0, 194.7, 194.4, 180.9, 152.8, 152.77, 152.73, 152.0, 133.3, 133.1, 133.0, 132.6, 127.3, 125.2, 122.4, 120.0, 119.0, 117.9, 117.8, 117.7, 115.2, 115.07, 115.04, 114.5, 102.1, 70.3, 70.2, 69.56, 69.53, 58.9, 30.6, 26.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_4$ $[M + H]^+$ 275.1278, found 275.1275.

3. Optimization of reaction conditions

(a) Optimization tables for the synthesis of ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):

Table S1. Optimization of various catalysts[a,b]



1a 2 3a

entry	catalyst	solvent	temp	time	yield[b]
Evaluation of metal triflate-based Lewis acids					
1.	No Catalyst	CH_2Cl_2	rt	24 h	N.R[c]
2.	TfOH	CH_2Cl_2	rt	24 h	N.R[c]
3.	$Sc(OTf)_3$	CH_2Cl_2	rt	1 h	99
4.	$Fe(OTf)_3$	CH_2Cl_2	rt	5 min	98
5.	$Fe(OTf)_2$	CH_2Cl_2	rt	5 h	93
6.	$Cu(OTf)_2$	CH_2Cl_2	rt	2.5 h	81
7.	AgOTf	CH_2Cl_2	rt	24 h	33
8.	$Zn(OTf)_2$	CH_2Cl_2	rt	24 h	51
9.	$In(OTf)_3$	CH_2Cl_2	rt	10 min	95
10.	$Yb(OTf)_3$	CH_2Cl_2	rt	10 h	68

11.	$Bi(OTf)_3$	CH_2Cl_2	rt	3.5 h	89
12.	$La(OTf)_3$	CH_2Cl_2	rt	3 h	64
13.	$Ni(OTf)_2$	CH_2Cl_2	rt	7 h	56
Evaluation of other Lewis acids					
1.	$BF_3.Et_2O$	CH_2Cl_2	0 °C-rt	2 h	72
2.	$TiCl_4$ (1 M Solution)	CH_2Cl_2	0 °C-rt	2 h	68
3.	TMSOTf	THF	rt	1.5 h	81
4.	TMSCl	THF	rt	24 h	N.R[c]
5.	ZnI_2	CH_2Cl_2	rt	24 h	trace
6.	$FeCl_3$	CH_2Cl_2	rt	10 min	92
7.	$Fe(ClO_4)_2$	CH_2Cl_2	rt	2.5 h	94
8.	$FeSO_4.7H_2O$	CH_2Cl_2	rt	24 h	N.R[c]
Evaluation of Brønsted acid catalysts					
1.	CPA-1	CH_2Cl_2	rt	24 h	N.R[c]
2.	HCl (2 M in Et_2O)	CH_2Cl_2	rt	24 h	N.R[c]
3.	CF_3CO_2H	CH_2Cl_2	rt	24 h	49
4.	AcOH	CH_2Cl_2	rt	24 h	N.R[c]
5.	CH_3SO_3H	CH_2Cl_2	rt	24 h	32
6.	Amberlyst-15	CH_2Cl_2	rt	24 h	N.R[c]
7.	*p*-TsOH	CH_2Cl_2	rt	24 h	N.R[c]
8.	PPTS	CH_2Cl_2	rt	6 h	59
9.	$HNTf_2$	CH_3CN	rt	3 h	67

[a]Reaction conditions unless otherwise specified: **1a** (0.5 mmol), **2** (0.5 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **3a**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2). CPA-1 = (*R*)-(-)-1,1'-Binaphthyl-2,2'-diyl Hydrogen Phosphate.

Table S2. Optimization of solvents[a,b]

entry	catalyst	solvent	temp	time	yield[b]
1.	$Fe(OTf)_3$	CH_2Cl_2	rt	5 min	98
2.	$Fe(OTf)_3$	1, 2-DCE	rt	5 min	88
3.	$Fe(OTf)_3$	PhF	rt	10 min	63
4.	$Fe(OTf)_3$	CH_3CN	rt	10 min	77
5.	$Fe(OTf)_3$	Toluene	rt	1 h	47

6.	$Fe(OTf)_3$	DMF	rt	24 h	N.R[c]
7.	$Fe(OTf)_3$	THF	rt	3 h	34
8.	$Fe(OTf)_3$	1,4-Dioxane	rt	2 h	41
9.	$Fe(OTf)_3$	MeOH	rt	5 h	48
10.	$Fe(OTf)_3$	EtOH	rt	5 h	51

[a]Reaction conditions unless otherwise specified: **1a** (0.5 mmol), **2** (0.5 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **3a**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2).

Table S3. Optimization of metal-salts[a,b]

entry	catalyst	solvent	temp	time	yield[b]
1.	$Fe(OTf)_3$	CH_2Cl_2	rt	5 min	98
2.	$Fe(NO)_3.9H_2O$	CH_2Cl_2	rt	1 h	76
3.	$FeBr_3$	CH_2Cl_2	rt	15 min.	91
4.	Fe_2O_3	CH_2Cl_2	rt	24 h	N.R[c]
5.	$Fe(OAc)_2$	CH_2Cl_2	rt	24 h	N.R[c]
6.	$FeCl_2$	CH_2Cl_2	rt	2 h	58
7.	$FeCl_2.4H_2O$	CH_2Cl_2	rt	3 h	79
8.	$FeCl_3.6H_2O$	CH_2Cl_2	rt	2 h	73

[a]Reaction conditions unless otherwise specified: **1a** (0.5 mmol), **2** (0.5 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **3a**. [c]N.R = no reaction.

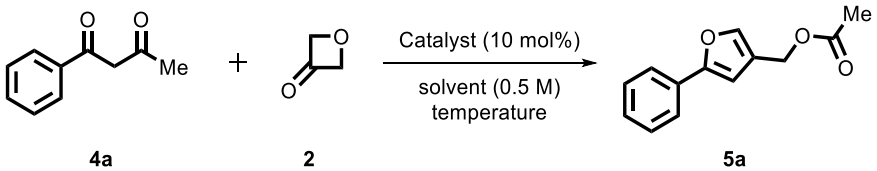
Table S4. Optimization of catalyst loading[a,b]

entry	Catalyst (mol%)	solvent	temp	time	yield[b]
1.	$Fe(OTf)_3$ (10 mol%)	CH_2Cl_2	rt	5 min	98
2.	$Fe(OTf)_3$ (5 mol%)	CH_2Cl_2	rt	5 min	72
3.	$Fe(OTf)_3$ (2 mol%)	CH_2Cl_2	rt	5 min	53

[a]Reaction conditions unless otherwise specified: **1a** (1 mmol), **2** (1 mmol) and solvent (0.5 M). [b]Isolated yield of **3a**. Tf = triflate (CF_3SO_2).

(b) Optimization tables for synthesis of (5-phenylfuran-3-yl)methyl acetate (5a):

Table S5. Optimization of various catalysts[a,b]



4a **2** **5a**

entry	catalyst	solvent	temp	time	yield[b]
Evaluation of metal triflate-based Lewis acids					
1.	No Catalyst	CH_2Cl_2	rt	24 h	N.R[c]
2.	TfOH	CH_2Cl_2	rt	24 h	N.R[c]
3.	$Sc(OTf)_3$	CH_2Cl_2	rt	2 h	74
4.	$Fe(OTf)_3$	CH_2Cl_2	rt	3 h	71
5.	$Fe(OTf)_2$	CH_2Cl_2	rt	24 h	42
6.	$Cu(OTf)_2$	CH_2Cl_2	rt	4.5 h	52
7.	AgOTf	CH_2Cl_2	rt	24 h	66
8.	$Zn(OTf)_2$	CH_2Cl_2	rt	24 h	54
9.	$In(OTf)_3$	CH_2Cl_2	rt	4 h	55
10.	$Yb(OTf)_3$	CH_2Cl_2	rt	10 h	65
11.	$Bi(OTf)_3$	CH_2Cl_2	rt	1.5 h	86
12.	$La(OTf)_3$	CH_2Cl_2	rt	5 h	74
13.	$Ni(OTf)_2$	CH_2Cl_2	rt	7 h	67
Evaluation of other Lewis acids					
1.	$BF_3.Et_2O$	CH_2Cl_2	0 °C-rt	2 h	47
2.	$TiCl_4$ (1 M Solution)	CH_2Cl_2	0 °C-rt	2 h	36
3.	TMSOTf	THF	rt	2 h	61
4.	TMSCl	THF	rt	24 h	N.R[c]
5.	ZnI_2	CH_2Cl_2	rt	24 h	trace
6.	$FeCl_3$	CH_2Cl_2	rt	10 min	83
7.	$Fe(ClO_4)_2$	CH_2Cl_2	rt	2.5 h	65
8.	$FeSO_4.7H_2O$	CH_2Cl_2	rt	24 h	N.R[c]
Evaluation of Brønsted acid catalysts					
1.	CPA-1	CH_2Cl_2	rt	24 h	N.R[c]
2.	HCl (2 M in Et_2O)	CH_2Cl_2	rt	24 h	N.R[c]
3.	CF_3CO_2H	CH_2Cl_2	rt	24 h	32
4.	AcOH	CH_2Cl_2	rt	24 h	N.R[c]
5.	CH_3SO_3H	CH_2Cl_2	rt	24 h	26
6.	Amberlyst-15	CH_2Cl_2	rt	24 h	N.R[c]
7.	*p*-TsOH	CH_2Cl_2	rt	24 h	N.R[c]
8.	PPTS	CH_2Cl_2	rt	24 h	N.R[c]

9.	$HNTf_2$	CH_3CN	rt	6 h	19

[a]Reaction conditions unless otherwise specified: **4a** (0.5 mmol), **2** (0.5 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **5a**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2). CPA-1 = (*R*)-(-)-1,1'-Binaphthyl-2,2'-diyl Hydrogen Phosphate.

Table S6. Optimization of solvents[a,b]

entry	catalyst	solvent	temp	time	yield[b]
1.	$FeCl_3$	CH_2Cl_2	rt	15 min	83
2.	$FeCl_3$	1, 2-DCE	rt	15 min	74
3.	$FeCl_3$	PhF	rt	20 min	56
4.	$FeCl_3$	CH_3CN	rt	20 min	76
5.	$FeCl_3$	Toluene	rt	1.5 h	39
6.	$FeCl_3$	DMF	rt	24 h	N.R[c]
7.	$FeCl_3$	THF	rt	4 h	42
8.	$FeCl_3$	1,4-Dioxane	rt	3 h	49
9.	$FeCl_3$	MeOH	rt	5 h	34
10.	$FeCl_3$	EtOH	rt	5 h	38

[a]Reaction conditions unless otherwise specified: **4a** (1 mmol), **2** (1 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **5a**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2).

Table S7. Optimization of metal-salts[a,b]

entry	catalyst	solvent	temp	time	yield[b]
1.	$FeCl_3$	CH_2Cl_2	rt	10 min	83
2.	$FeCl_2$	CH_2Cl_2	rt	2 h	51
3.	$FeBr_3$	CH_2Cl_2	rt	15 min.	76
4.	$FeCl_2.4H_2O$	CH_2Cl_2	rt	4 h	64
5.	$FeCl_3.6H_2O$	CH_2Cl_2	rt	4 h	61
6.	$Fe(NO)_3.9H_2O$	CH_2Cl_2	rt	2 h	64
7.	Fe_2O_3	CH_2Cl_2	rt	24 h	N.R[c]
8.	$Fe(OAc)_2$	CH_2Cl_2	rt	24 h	N.R[c]

[a]Reaction conditions unless otherwise specified: **4a** (1 mmol), **2** (1 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **5a**. [c]N.R = no reaction.

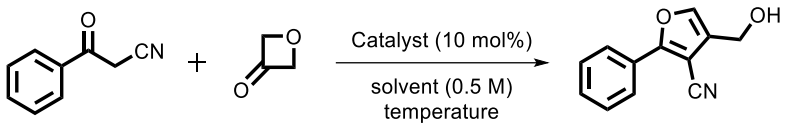
Table S8. Optimization of catalyst loading[a,b]

entry	Catalyst (mol%)	solvent	temp	time	yield[b]
1.	$Fe(OTf)_3$ (10 mol%)	CH_2Cl_2	rt	10 min	83
2.	$Fe(OTf)_3$ (5 mol%)	CH_2Cl_2	rt	10 min	59
3.	$Fe(OTf)_3$ (2 mol%)	CH_2Cl_2	rt	10 min	32

[a]Reaction conditions unless otherwise specified: **4a** (1 mmol), **2** (1 mmol) and solvent (0.5 M). [b]Isolated yield of **5a**. Tf = triflate (CF_3SO_2).

(c) Optimization table for synthesis of 4-(Hydroxymethyl)-2-phenylfuran-3-carbonitrile (7):

Table S9. Optimization of various catalysts[a,b]



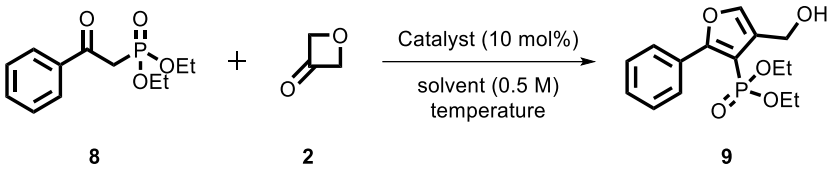
6 **2** **7**

entry	catalyst	solvent	temp	time	yield[b]
1.	No Catalyst	CH_2Cl_2	rt	24 h	N.R[c]
2.	TfOH	CH_2Cl_2	rt	24 h	N.R[c]
3.	$Sc(OTf)_3$	CH_2Cl_2	rt	24 h	23
4.	$Sc(OTf)_3$	1, 2-DCE	80 °C	24 h	19
5.	$Fe(OTf)_3$	CH_2Cl_2	rt	24 h	31
6.	$Fe(OTf)_3$	1, 2-DCE	80 °C	24 h	23
7.	$FeCl_3$	CH_2Cl_2	rt	8 h	0
8.	$FeCl_3$	1, 2-DCE	80 °C	8 h	0
9.	$FeBr_3$	CH_2Cl_2	rt	8 h	0
10.	$Fe(NO)_3.9H_2O$	CH_2Cl_2	rt	24 h	N.R[c]
11.	$In(OTf)_3$	CH_2Cl_2	rt	24 h	18
12.	$Bi(OTf)_3$	CH_2Cl_2	rt	24 h	25
13.	$Bi(OTf)_3$	1, 2-DCE	80 °C	24 h	25
14.	TMSOTf	THF	rt	6 h	0

[a]Reaction conditions unless otherwise specified: **6** (1 mmol), **2** (1 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **7** b.r.s.m. [c]N.R = no reaction. Tf = triflate (CF_3SO_2).

(d) Optimization table for the synthesis of Diethyl (4-(hydroxymethyl)-2-phenylfuran-3-yl)phosphonate (9):

Table S10. Optimization of various catalysts[a,b]



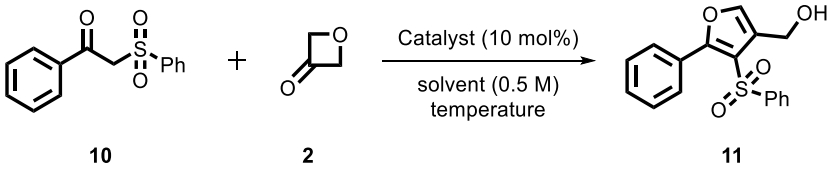
8 **2** **9**

entry	catalyst	solvent	temp	time	yield[b]
1.	No Catalyst	CH_2Cl_2	rt	24 h	N.R[c]
2.	TfOH	CH_2Cl_2	rt	24 h	N.R[c]
3.	$Sc(OTf)_3$	CH_2Cl_2	rt	6 h	26
4.	$Fe(OTf)_3$	CH_2Cl_2	rt	2.5 h	28
5.	$FeCl_3$	CH_2Cl_2	rt	4 h	18
6.	AgOTf	CH_2Cl_2	rt	24 h	N.R[c]
7.	$In(OTf)_3$	CH_2Cl_2	rt	24 h	9
8.	$Bi(OTf)_3$	CH_2Cl_2	rt	4 h	20
9.	$BF_3.OEt_2$	CH_2Cl_2	rt	24 h	N.R[c]
10.	TMSOTf	THF	rt	24 h	N.R[c]
11.	PPTS	CH_2Cl_2	rt	24 h	N.R[c]

[a]Reaction conditions unless otherwise specified: **8** (1 mmol), **2** (1 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **9**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2).

(e) Optimization table for the synthesis of (5-Phenyl-4-(phenylsulfonyl)furan-3-yl)methanol (11):

Table S11. Optimization of various catalysts[a,b]



10 **2** **11**

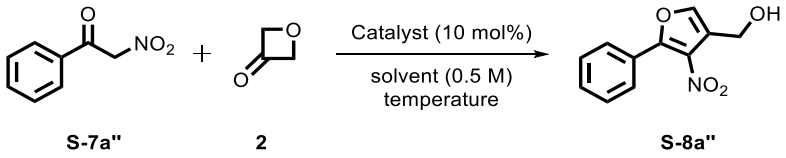
entry	catalyst	solvent	temp	time	yield[b]
1.	No Catalyst	CH_2Cl_2	rt	24 h	N.R[c]
2.	TfOH	CH_2Cl_2	rt	24 h	N.R[c]

3.	$Sc(OTf)_3$	CH_2Cl_2	rt	24 h	5
4.	$Fe(OTf)_3$	CH_2Cl_2	rt	24 h	5
5.	$FeCl_3$	CH_2Cl_2	rt	24 h	5
6.	$FeBr_3$	CH_2Cl_2	rt	24 h	6
7.	AgOTf	CH_2Cl_2	rt	24 h	N.R[c]
8.	$Bi(OTf)_3$	CH_2Cl_2	rt	24 h	5
9.	$Fe(OTf)_3$	1,2-DCE	60 °C	24 h	7
10.	$FeCl_3$	1,2-DCE	60 °C	24 h	12
11.	$FeBr_3$	1,2-DCE	60 °C	24 h	16

[a]Reaction conditions unless otherwise specified: **10** (1 mmol), **2** (1 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **11**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2).

(f) Optimization table for the synthesis of (4-Nitro-5-phenylfuran-3-yl)methanol (13a):

Table S12. Optimization of various catalysts[a,b]



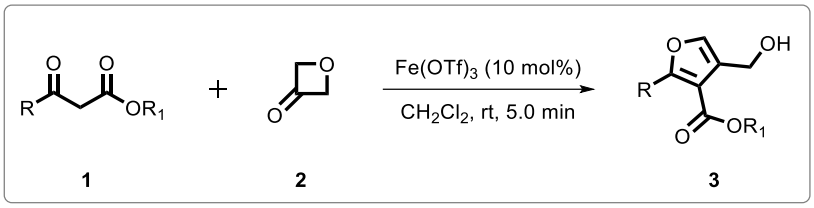
S-7a'' **2** **S-8a''**

entry	catalyst	solvent	temp	time	yield[b]
1.	No Catalyst	CH_2Cl_2	rt	24 h	N.R[c]
2.	TfOH	CH_2Cl_2	rt	24 h	N.R[c]
3.	$Sc(OTf)_3$	CH_2Cl_2	rt	24 h	N.R[c]
4.	$Fe(OTf)_3$	CH_2Cl_2	rt	24 h	N.R[c]
5.	$FeCl_3$	CH_2Cl_2	rt	24 h	N.R[c]
6.	$FeBr_3$	CH_2Cl_2	rt	24 h	N.R[c]
7.	$Fe(NO)_3.9H_2O$	CH_2Cl_2	rt	24 h	N.R[c]
8.	$In(OTf)_3$	CH_2Cl_2	rt	24 h	N.R[c]
9.	$Bi(OTf)_3$	CH_2Cl_2	rt	24 h	N.R[c]
10.	$BF_3.OEt_2$	CH_2Cl_2	rt	24 h	N.R[c]
11.	TMSOTf	THF	rt	24 h	N.R[c]
12.	*p*TSA.H_2O	CH_2Cl_2	rt	24 h	N.R[c]

[a]Reaction conditions unless otherwise specified: **S-7a''** (1 mmol), **2** (1 mmol) and catalyst (10 mol %), solvent (0.5 M). [b]Isolated yield of **S-8a''**. [c]N.R = no reaction. Tf = triflate (CF_3SO_2).

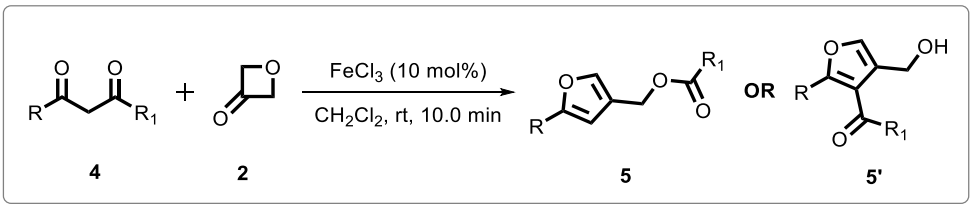
4. General synthesis procedures and analytical data for final substrates

(a) General procedure-5 for synthesis of multi-substituted furan derivatives (3) from *β*-ketoesters (GP5):



A 10 mL two-neck round-bottom flask containing *β*-ketoester (**1**, 0.5 mmol) was evacuated under vacuo and then backfilled with argon. Then, anhydrous CH_2Cl_2 (0.5 mL) and $Fe(OTf)_3$ (0.05 mmol) were added at room temperature, and the mixture was stirred for 5 min. Then, 3-oxetanone (**2**, 0.5 mmol) was added, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (2 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **3**.

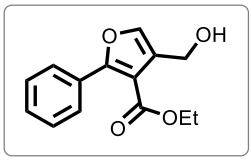
(b) General procedure for the synthesis of multi-substituted furan derivatives from *β*-diketones (GP6):



A 10 mL two-neck round bottom flask containing *β*-Diketones (**4**, 0.5 mmol) was evacuated under vacuo and then backfilled with argon. Then, anhydrous CH_2Cl_2 (0.5 mL) and $FeCl_3$ (0.05 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 0.5 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (2 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **5**.

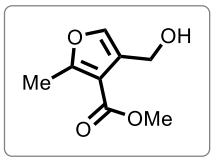
(c) Analytical data for furan carboxylate derivatives:

Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



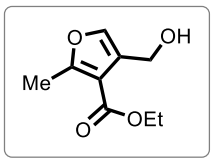
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1a**, 0.096 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3a** was isolated as a colorless liquid (0.119 g, 98%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3432, 1772, 1721, 1602, 1523, 1484, 1422, 1378, 1095, 1065, 1021, 928, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.69 (m, 2H), 7.44 (s, 1H), 7.42–7.40 (m, 2H), 4.63 (d, *J*=6.13 Hz, 2H), 4.29 (q, *J*=7.13 Hz, 2H), 3.66 (t, *J*=6.63 Hz, 1H), 1.26 (t, *J*=7.13 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 159.3, 139.8, 130.1, 129.6, 129.0, 127.9, 127.4, 113.0, 61.1, 56.0, 14.0; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}O_4Na$ [M + Na]$^+$ 269.0784, found 269.0783.

Methyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3b):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1b**, 0.058 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol) in CH_2Cl_2 (0.5 mL). The product **3b** was isolated as a colorless liquid (0.079 g, 93%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3431, 2361, 1718, 1603, 1523, 1476, 1426, 1111, 1031, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 4.50 (d, *J* = 6.1 Hz, 2H), 3.82 (s, 3H), 3.75–3.67 (m, 1H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) 165.6, 160.8, 138.2, 126.0, 112.4, 55.7, 51.7, 14.4; HRMS (ESI): *m/z* calcd for $C_8H_{10}O_4Na$ [M + Na]$^+$ 193.0471, found 193.0468.

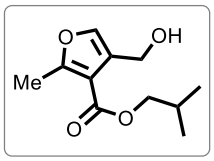
Ethyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3c):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1c**, 0.065 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol) in CH_2Cl_2 (0.5 mL). The product **3c** was isolated as a colorless liquid (0.081 g, 89%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3684, 3434, 2936, 2361, 1765, 1717, 1567, 1523, 1473, 1431, 1380, 1301, 1106, 1039, 929, 850, 670, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 4.53 (br. s., 2H), 4.32 (q, *J* = 7.13 Hz, 2H), 3.72 (br. s., 1H), 2.52 (s, 3H), 1.36 (t, *J* =

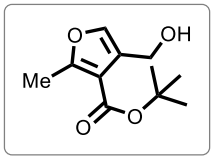
7.13 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4, 160.8, 138.2, 126.0, 112.8, 60.8, 55.8, 14.5, 14.3; HRMS (ESI): *m/z* calcd for $C_9H_{12}O_4Na$ $[M + Na]^+$ 207.0628, found 207.0629.

Isobutyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3d):



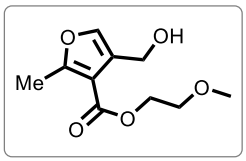
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1d**, 0.079 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3d** was isolated as a colorless liquid (0.090 g, 86%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3681, 3459, 2966, 2878, 2361, 1764, 1689, 1608, 1567, 1466, 1431, 1383, 1303, 1279, 1113, 1010, 969, 934, 851, 669, 627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 4.52 (s, 2H), 4.04 (d, *J* = 6.5 Hz, 2H), 3.76 (br. s., 1H), 2.53 (s, 3H), 2.02 (td, *J* = 6.75, 13.38 Hz, 1H), 0.98 (d, *J* = 6.75 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4, 160.6, 138.1, 126.1, 112.8, 71.0, 55.8, 27.8, 19.3, 14.6; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_4Na$ $[M + Na]^+$ 235.0941, found 235.0947.

Tert-butyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3e):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1e**, 0.079 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3e** isolated as a colorless liquid (0.086 g, 82%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3608, 3432, 2979, 2930, 2361, 1766, 1719, 1603, 1523, 1476, 1425, 1372, 1029, 928, 847, 670, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 4.51 (d, *J* = 6.5 Hz, 2H), 3.88–3.83 (m, 1H), 2.50 (s, 3H), 1.57 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.8, 160.3, 137.9, 126.1, 114.2, 81.9, 55.8, 28.4, 14.5; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_4Na$ $[M + Na]^+$ 235.0941, found 235.0948.

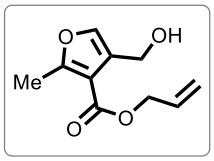
2-Methoxyethyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3f):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1f**, 0.08 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3f** was isolated as a colorless liquid (0.087 g, 81%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3464, 2933, 2891, 2361, 1714, 1608, 1566, 1524, 1430, 1298, 1277, 1112, 1025, 931, 853, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H),

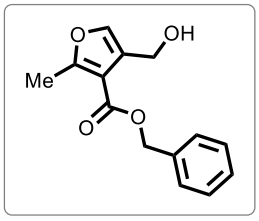
4.48 (s, 2H), 4.41–4.32 (m, 2H), 3.69–3.59 (m, 2H), 3.36 (s, 3H), 2.51 (s, 3H);$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.5, 161.5, 138.5, 125.6, 112.2, 70.2, 62.9, 58.8, 55.5, 14.1; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_5Na$ $[M + Na]^+$ 237.0733, found 237.0744.

Allyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3g):



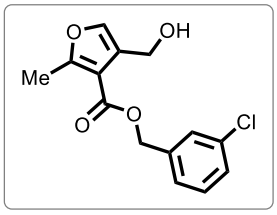
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1g**, 0.071 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3g** was isolated as a colorless liquid (0.086 g, 88%). TLC: R_f = 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3469, 2361, 1765, 1708, 1606, 1567, 1523, 1475, 1424, 1386, 1299, 1114, 1012, 931, 849, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.08–5.92 (m, 1H), 5.37 (qd, *J* = 1.38, 17.13 Hz, 1H), 5.33–5.23 (m, 1H), 4.77 (td, *J* = 1.38, 5.75 Hz, 2H), 4.54 (d, *J* = 3.88 Hz, 2 H), 3.62 (br. s., 1H), 2.54 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 161.1, 138.3, 132.0, 126.1, 118.8, 112.5, 65.4, 55.8, 14.6; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}O_4$ $[M + H]^+$ 197.0808, found 197.0807.

Benzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3h):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1h**, 0.096 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3h** was isolated as a colorless liquid (0.102 g, 83%). TLC: R_f= 0.6 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3457, 2360, 1765, 1712, 1606, 1566, 1523, 1428, 1110, 1014, 930, 848, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.29 (m, 5H), 7.21 (s, 1H), 5.31 (s, 2H), 4.56 (s, 2H), 3.65 (s, 1H), 2.52 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 161.0, 138.2, 135.6, 128.7, 128.4, 128.2, 126.0, 112.4, 66.5, 55.7, 14.5; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}O_4Na$ $[M + Na]^+$ 269.0784, found 269.0783.

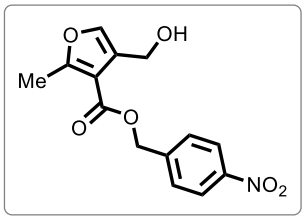
3-Chlorobenzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3i):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1i**, 0.113 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3i** was isolated as a colorless liquid (0.112 g, 80%). TLC: R_f= 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3483, 2880, 2361, 1694,

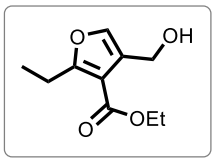
1603, 1570, 1524, 1476, 1427, 1299, 1278, 1109, 1011, 932, 851, 670, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.33–7.25 (m, 3H), 7.22 (s, 1H), 5.28 (s, 2H), 4.55 (d, *J* = 6.9 Hz, 2H), 3.51 (t, *J* = 6.9 Hz, 1H), 2.53 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 161.2, 138.4, 137.7, 134.6, 130.1, 128.7, 128.3, 126.3, 126.1, 112.3, 65.7, 55.8, 14.7; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_4ClNa$ $[M + Na]^+$ 303.0395, found 303.0388.

4-Nitrobenzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3j):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1j**, 0.118 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3j** was isolated as a colorless liquid (0.112 g, 77%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3429, 2360, 1700, 1606, 1525, 1477, 1427, 1348, 1107, 1019, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27–8.20 (m, 2H), 7.61–7.54 (m, 2H), 7.24 (s, 1H), 5.41 (s, 2H), 4.55 (br. s., 2H), 3.40 (br. s., 1H), 2.55 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.7, 161.4, 147.9, 143.0, 138.6, 128.6, 126.0, 124.0, 112.1, 65.1, 55.8, 14.8; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_6NNa$ $[M + Na]^+$ 314.0635, found 314.0634.

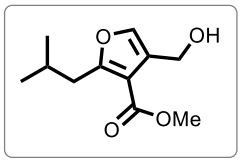
Ethyl 2-ethyl-4-(hydroxymethyl)furan-3-carboxylate (3k):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1k**, 0.072 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3k** was isolated as a colorless liquid (0.086 g, 87%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3448, 2983, 2939, 2361, 1688, 1560, 1524, 1468, 1430, 1307, 1282, 1109, 1019, 928, 849, 670, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.54 (d, *J* = 6.13 Hz, 2H), 4.33 (q, *J* = 7.13 Hz, 2H), 3.72 (t, *J* = 6.75 Hz, 1H), 2.95 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.13 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.7, 165.4, 138.3, 125.9, 111.9, 60.8, 55.8, 22.0, 14.3, 12.2; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_4Na$ $[M + Na]^+$ 221.0784, found 221.0790.

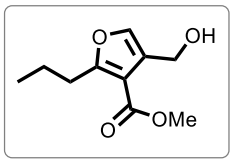
Methyl 4-(hydroxymethyl)-2-isobutylfuran-3-carboxylate (3l):

The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1l**, 0.079 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g,



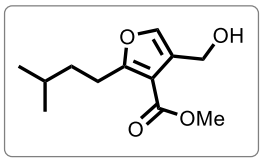
0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3l** was isolated as a colorless liquid (0.09 g, 85%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3419, 2966, 2359, 1723, 1528, 1441, 1029, 928, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.53 (s, 2H), 3.84 (s, 3H), 3.65 (br. s., 1H), 2.79 (d, *J* = 7.25 Hz, 2H), 2.02 (td, *J* = 6.88, 13.63 Hz, 1H), 0.90 (d, *J* = 6.63 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.7, 164.2, 138.5, 125.8, 112.7, 55.8, 51.7, 37.0, 28.4, 22.4; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_4Na$ $[M + Na]^+$ 235.0941, found 235.0940.

Methyl 4-(hydroxymethyl)-2-propylfuran-3-carboxylate (3m):



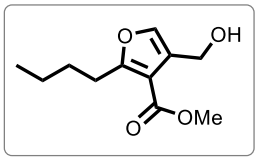
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1m**, 0.072 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3m** isolated as a colorless liquid (0.079 g, 80%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3427, 2360, 1686, 1524, 1475, 1428, 1301, 1114, 1021, 928, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 4.54 (d, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 3.64 (t, *J* = 6.88 Hz, 1H), 2.90 (t, *J* = 7.38 Hz, 2H), 1.73–1.61 (m, 2H), 0.93 (t, *J* = 7.38 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.8, 164.8, 138.4, 125.9, 112.3, 55.8, 51.8, 30.2, 21.4, 13.8; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_4Na$ $[M + Na]^+$ 221.0784, found 221.0785.

Methyl 4-(hydroxymethyl)-2-isopentylfuran-3-carboxylate (3n):



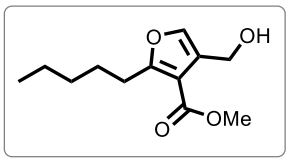
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1n**, 0.086 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3n** was isolated as a colorless liquid (0.093 g, 83%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3417, 2933, 2857, 2360, 1714, 1527, 1440, 1024, 928, 851, 671, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 4.52 (d, *J* = 6.13 Hz, 2H), 3.85 (s, 3H), 3.67 (t, *J* = 6.75 Hz, 1H), 2.96–2.85 (m, 2H), 1.60–1.45 (m, 3H), 0.90 (d, *J* = 6.38 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.7, 165.1, 138.3, 125.9, 111.9, 55.8, 51.7, 37.0, 27.7, 26.3, 22.3; HRMS (ESI): *m/z* calcd for $C_{12}H_{19}O_4$ $[M + H]^+$ 227.1278, found 227.1284.

Methyl 2-butyl-4-(hydroxymethyl)furan-3-carboxylate (3o):



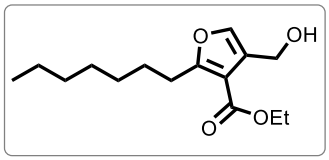
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1o**, 0.079 g, 0.5 mmol), 3-oxetanone (**2**, 0.031 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3o** was isolated as a colorless liquid (0.081 g, 82%). TLC: R_f = 0.5 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3455, 2961, 2872, 2361, 1694, 1604, 1558, 1523, 1446, 1116, 1075, 1017, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.54 (d, *J* = 6.5 Hz, 2H), 3.86 (s, 3H), 3.63 (t, *J* = 6.75 Hz, 1H), 2.92 (t, *J* = 7.63 Hz, 2H), 1.62 (quin, *J* = 7.5 Hz, 2H), 1.34 (quin, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.25 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.8, 165.0, 138.4, 125.9, 112.1, 55.8, 51.8, 30.1, 28.0, 22.3, 13.8; HRMS (ESI): *m/z* calcd for $C_{11}H_{17}O_4$ $[M + H]^+$ 213.1121, found 213.1124.

Methyl 4-(hydroxymethyl)-2-pentylfuran-3-carboxylate (3p):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1p**, 0.086 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3p** was isolated as a colorless liquid (0.086 g, 76%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3433, 2960, 2932, 2869, 2361, 1726, 1523, 1438, 1038, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 3.87 (s, 3H), 3.61 (t, *J* = 6.50 Hz, 1H), 2.92 (t, *J* = 7.75 Hz, 2H), 1.65 (quin, *J* = 7.50 Hz, 3H), 1.35–1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.8, 165.1, 138.4, 125.9, 112.1, 55.8, 51.8, 31.4, 28.3, 27.7, 22.4, 14.0; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}O_4Na$ $[M + Na]^+$ 249.1097, found 249.1098.

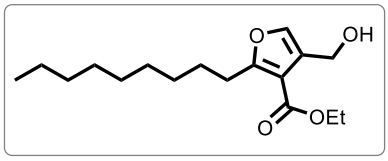
Ethyl 2-heptyl-4-(hydroxymethyl)furan-3-carboxylate (3q):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1q**, 0.107 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3q** was isolated as a colorless liquid (0.105 g, 78%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3479, 2958, 2930, 2859, 2361, 1687, 1603, 1559, 1523, 1465, 1431, 1303, 1115, 1080, 1016, 962, 928, 847, 670, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 4.53 (d, *J* = 6.5 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 6.9 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.63 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.13 Hz, 3H), 1.40–1.18 (m, 8H), 0.86 (t, *J* = 7.01 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.3,

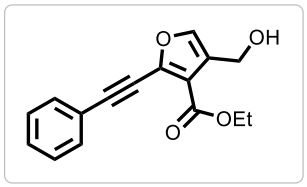
164.9, 138.3, 125.9, 112.3, 60.7, 55.8, 31.8, 29.3, 29.0, 28.4, 28.1, 22.7, 14.3, 14.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{24}O_4Na$ $[M + Na]^+$ 291.1567, found 291.1559.

Ethyl 4-(hydroxymethyl)-2-nonylfuran-3-carboxylate (3r):



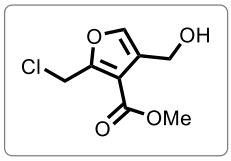
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1r**, 0.121 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3r** was isolated as a colorless liquid (0.107 g, 72%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3684, 3451, 2929, 2857, 2361, 1704, 1603, 1523, 1473, 1427, 1115, 1082, 1023, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.54 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 1.64 (t, *J* = 7.5 Hz, 2H), 1.38 (d, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 14.4 Hz, 12H), 0.87 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4, 165.0, 138.3, 125.9, 112.3, 60.8, 55.8, 31.9, 29.5, 29.3, 28.4, 28.1, 22.7, 14.3, 14.2; HRMS (ESI): *m/z* calcd for $C_{17}H_{28}O_4Na$ $[M + Na]^+$ 319.1880, found 319.1873.

Ethyl 4-(hydroxymethyl)-2-(phenylethynyl)furan-3-carboxylate (3s):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1s**, 0.108 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3s** was isolated as a colorless liquid (0.102 g, 76%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.51 (m, 2H), 7.44–7.33 (m, 4H), 4.61 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 1H), 1.43 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.3, 141.9, 141.0, 131.8, 129.6, 128.7, 126.7, 121.7, 119.9, 98.0, 79.0, 61.4, 55.6, 14.4; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}O_4Na$ $[M + Na]^+$ 293.0784, found 293.0783.

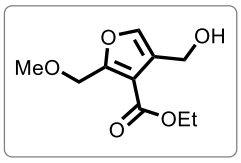
Methyl 2-(chloromethyl)-4-(hydroxymethyl)furan-3-carboxylate (3t):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1t**, 0.075 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3t** was isolated as a colorless liquid (0.079 g, 78%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3684, 3429, 2361, 1722, 1605, 1523, 1476, 1429, 1028, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 4.84 (s, 2H), 4.59 (s, 2H),

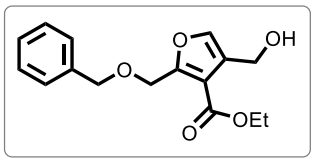
3.92 (s, 3H), 3.39 (br. s., 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.3, 156.4, 140.7, 126.7, 115.0, 55.7, 52.4, 35.9; HRMS (ESI): *m/z* calcd for $C_8H_9O_4ClNa$ $[M + Na]^+$ 227.0082, found 227.0083.

Ethyl 4-(hydroxymethyl)-2-(methoxymethyl)furan-3-carboxylate (3u):



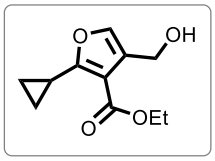
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1u**, 0.080 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3u** was isolated as a colorless liquid (0.089 g, 84%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3684, 3457, 2933, 2361, 1715, 1606, 1523, 1473, 1425, 1377, 1096, 1019, 929, 848, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 4.68 (s, 2H), 4.57 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 1H), 3.38 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.5, 158.4, 140.2, 126.2, 115.4, 65.5, 61.2, 58.6, 55.7, 14.3; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_5Na$ $[M + Na]^+$ 237.0733, found 237.0745.

Ethyl 2-((benzyloxy)methyl)-4-(hydroxymethyl)furan-3-carboxylate (3v):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1v**, 0.118 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3v** was isolated as a colorless liquid (0.131 g, 91%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684,3 3453, 2360, 1697, 1605, 1524, 1475, 1426, 1126, 1096, 1019, 929, 849, 669, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.34–7.27 (m, 5H), 4.78 (s, 2H), 4.58 (s, 4H), 4.30 (q, *J* = 7.13 Hz, 2H), 3.61 (br. s., 1H), 1.30 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.4, 158.3, 140.1, 137.6, 128.4, 127.8, 126.2, 115.4, 72.7, 63.1, 61.1, 55.6, 14.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}O_5Na$ $[M + Na]^+$ 313.1046, found 313.1045.

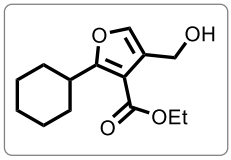
Ethyl 2-cyclopropyl-4-(hydroxymethyl)furan-3-carboxylate (3w):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1w**, 0.078 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3w** was isolated as a colorless liquid (0.082 g, 79%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3425, 2982, 2360, 2077, 1681, 1566, 1525, 1473, 1431, 1345, 1300, 1097, 1053, 1031, 928, 670, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 4.51

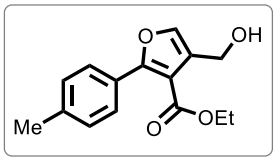
(d, *J* = 6.9 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.73 (t, *J* = 7.0 Hz, 1H), 2.66 (tt, *J* = 8.3, 5.4 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.01 (tt, *J* = 8.4, 2.8 Hz, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.6, 164.7, 137.0, 126.2, 112.2, 60.7, 55.8, 14.4, 9.6, 8.5; HRMS (ESI): *m/z* calcd for $C_{11}H_{15}O_4$ $[M + H]^+$ 211.0965, found 211.0968.

Ethyl 2-cyclohexyl-4-(hydroxymethyl)furan-3-carboxylate (3x):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1x**, 0.099 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3x** was isolated as a colorless liquid (0.103 g, 82%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3428, 2963, 2931, 2869, 2360, 1721, 1604, 1524, 1472, 1425, 1281, 1133, 1074, 1033, 928, 849, 670, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.53 (s, 2H), 4.33 (q, *J* = 7.13 Hz, 2H), 3.70 (br. s., 1H), 3.33 (tt, *J* = 3.13, 11.88 Hz, 1H), 1.85–1.80 (m, 4H), 1.76–1.66 (m, 2 H), 1.60–1.51 (m, 2 H), 1.38 (t, *J* = 7.13, 3H), 1.34–1.31 (m, 1H), 1.29 (m, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 168.3, 165.4, 138.2, 125.7, 111.0, 60.8, 55.8, 37.8, 30.9, 26.4, 25.9, 14.3; HRMS (ESI): *m/z* calcd for $C_{14}H_{20}O_4Na$ $[M + Na]^+$ 275.1254, found 275.1248.

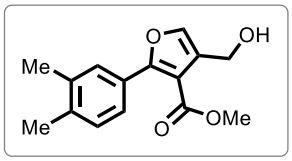
Ethyl 4-(hydroxymethyl)-2-(*p*-tolyl)furan-3-carboxylate (3y):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1y**, 0.103 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3y** was isolated as a colorless liquid (0.12 g, 93%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3435, 2931, 2360, 1770, 1720, 1686, 1608, 1504, 1473, 1422, 1378, 1301, 1135, 1095, 1073, 1019, 929, 670, 626 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.58 (m, *J* = 8.26 Hz, 2H), 7.42 (s, 1H), 7.25–7.18 (m, *J* = 8.13 Hz, 2H), 4.62 (s, 2H), 4.30 (q, *J* = 7.13 Hz, 2H), 3.68 (br. s., 1H), 2.40 (s, 3H), 1.28 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.0, 159.6, 139.7, 139.5, 128.9, 128.7, 127.34, 127.32, 112.5, 61.1, 56.0, 21.5, 14.0; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_4Na$ $[M + Na]^+$ 283.0941, found 283.0940.

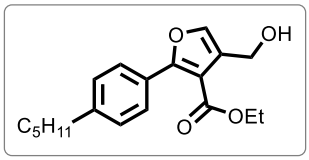
Methyl 2-(3,4-dimethylphenyl)-4-(hydroxymethyl)furan-3-carboxylate (3z):

The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1z**, 0.103 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g,



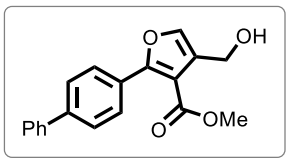
0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3z** was isolated as a colorless liquid (0.098 g, 95%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3609, 3469, 2361, 1689, 1603, 1523, 1440, 1307, 1131, 1077, 1020, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.45 (dd, *J* = 1.88, 7.88 Hz, 1H), 7.42 (s, 1H), 7.19 (d, *J* = 7.63 Hz, 1H), 4.63 (s, 2H), 3.81 (s, 3H), 3.70 (br. s., 1H), 2.31 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4, 159.7, 139.5, 138.5, 136.3, 129.8, 129.3, 127.6, 127.3, 126.4, 112.0, 56.0, 51.7, 19.84, 19.80; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_4Na$ $[M + Na]^+$ 283.0941, found 283.0945.

Ethyl 4-(hydroxymethyl)-2-(4-pentylphenyl)furan-3-carboxylate (3a′):



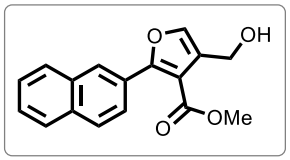
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1a′**, 0.131 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3a′** was isolated as a colorless liquid (0.141 g, 90%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3609, 3457, 2964, 2931, 2862, 2361, 1771, 1719, 1687, 1604, 1523, 1475, 1424, 1072, 1022, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.61 (m, 2H), 7.42 (s, 1H), 7.23 (d, J = 8.38 Hz, 2H), 4.62 (d, *J* = 6.0 Hz, 2H), 4.30 (q, *J* = 7.13 Hz, 2H), 3.66 (t, *J* = 6.5 Hz, 1H), 2.65 (t, *J* = 7.50 Hz, 2H), 1.71–1.59 (m, 2H), 1.38–1.31 (m, 4H), 1.27 (t, *J* = 7.25 Hz, 3H), 0.90 (t, *J* = 6.88 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.0, 159.6, 144.8, 139.5, 128.9, 128.0, 127.4, 127.3, 112.5, 61.1, 56.0, 35.9, 31.5, 31.0, 22.6, 14.1, 14.0; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}O_4$ $[M + H]^+$ 317.1747, found 317.1747.

Methyl 2-([1,1'-biphenyl]-4-yl)-4-(hydroxymethyl)furan-3-carboxylate (3b′):



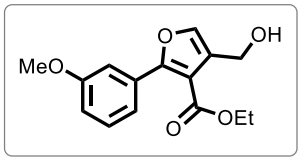
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1b′**, 0.127 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3b′** was isolated as a colorless liquid (0.136 g, 88%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3776, 3684, 3429, 2361, 1688, 1637, 1604, 1523, 1479, 1425, 1024, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.38 Hz, 2H), 7.71–7.61 (m, 4H), 7.52–7.42 (m, 3H), 7.42–7.34 (m, 1H), 4.66 (s, 2H), 3.85 (s, 3H), 3.54 (br. s., 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.3, 159.1, 142.3, 140.4, 140.0, 129.3, 129.0, 128.9, 127.9, 127.5, 127.2, 126.8, 112.7, 56.0, 52.0; HRMS (ESI): *m/z* calcd for $C_{19}H_{16}O_4Na$ $[M + Na]^+$ 331.0941, found 331.0933.

Methyl 4-(hydroxymethyl)-2-(naphthalen-2-yl)furan-3-carboxylate (3c′):



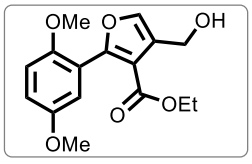
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1c′**, 0.114 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3c′** isolated as a colorless liquid (0.129 g, 92%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3420, 2361, 1692, 1603, 1524, 1475, 1425, 1021, 928, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.88 (q, *J* = 6.3 Hz, 3H), 7.78 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.59–7.52 (m, 2H), 7.51 (s, 1H), 4.67 (s, 2H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4, 159.4, 140.1, 133.7, 132.8, 128.9, 128.7, 127.8, 127.6, 127.5, 127.4, 127.2, 126.6, 126.0, 112.9, 56.0, 52.0; HRMS (ESI): *m/z* calcd for $C_{17}H_{14}O_4Na$ $[M + Na]^+$ 305.0784, found 305.0777.

Ethyl 4-(hydroxymethyl)-2-(3-methoxyphenyl)furan-3-carboxylate (3d′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1d′**, 0.111 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3d′** was isolated as a colorless liquid (0.118 g, 85%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3455, 2360, 1769, 1720, 1689, 1600, 1545, 1467, 1429, 1135, 1089, 1041, 962, 928, 852, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.33 (d, *J* = 6.8 Hz, 1H), 7.28 (s, 1H), 6.97 (dt, *J* = 7.0, 2.6 Hz, 1H), 4.63 (d, *J* = 6.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.59 (t, *J* = 6.9 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 159.2, 158.9, 139.8, 131.2, 129.0, 127.4, 121.6, 115.4, 114.5, 113.2, 61.2, 56.0, 55.4, 14.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}O_5$ $[M + H]^+$ 277.1071, found 277.1079.

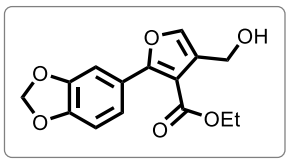
Ethyl 2-(2,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-carboxylate (3e′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1e′**, 0.126 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3e′** was isolated as a colorless liquid (0.128 g, 84%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 2838, 2360, 1734, 1671, 1609, 1497, 1466, 1416, 1370, 1327, 1265, 1033, 928, 880, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 6.99–6.92 (m, 2H), 6.91–6.84 (m, 1H), 4.62 (d, *J* = 6.8 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.82 (t, *J* = 6.9 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101

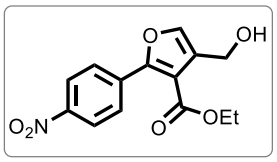
MHz, $CDCl_3$) δ 165.4, 155.8, 153.1, 151.6, 139.7, 126.5, 120.3, 116.4, 116.2, 115.5, 112.2, 60.8, 56.2, 55.9, 55.8, 13.9; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_6$ $[M + H]^+$ 307.1176, found 307.1169.

Ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-4-(hydroxymethyl)furan-3-carboxylate (3f′):



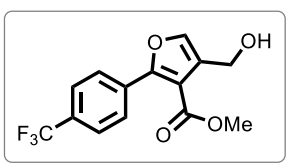
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1f′**, 0.118 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3f′** was isolated as a colorless liquid (0.103 g, 87%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3684, 3473, 2361, 1685, 1603, 1482, 1447, 1341, 1302, 1128, 1088 1040, 960, 931, 867, 670, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.30–7.25 (m, 1H), 7.23 (d, *J* = 1.63 Hz, 1H), 6.86 (d, *J* = 8.13 Hz, 1H), 6.01 (s, 2H), 4.61 (d, *J* = 4.13 Hz, 2H), 4.31 (q, *J* = 7.13 Hz, 2H), 3.58 (br. s., 1H), 1.30 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.8, 159.0, 148.7, 147.3, 139.3, 127.3, 123.9, 123.6, 112.3, 109.5, 108.0, 101.5, 61.1, 56.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}O_6Na$ $[M + Na]^+$ 313.0683, found 313.0673.

Ethyl 4-(hydroxymethyl)-2-(4-nitrophenyl)furan-3-carboxylate (3g′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1g′**, 0.118 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3g′** was isolated as a colorless liquid (0.120 g, 82%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3609, 3448, 2361, 1693, 1603, 1523, 1478, 1424, 1345, 1022, 928, 851, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 9.1 Hz, 2H), 7.54 (s, 1H), 4.66 (s, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.37 (s, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.0, 156.0, 148.0, 141.2, 135.8, 129.6, 128.1, 123.3, 115.2, 61.6, 56.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_6NNa$ $[M + Na]^+$ 314.0635, found 314.0638.

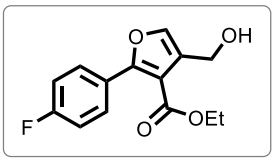
Methyl 4-(hydroxymethyl)-2-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (3h′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1h′**, 0.123 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3h′** was isolated as a colorless liquid (0.121 g, 81%). TLC:

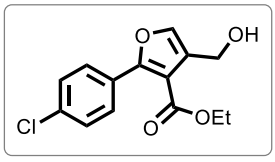
R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3611, 3486, 2361, 1698, 1602, 1514, 1476, 1418, 1325, 1173, 1133, 1067, 1019, 928, 847, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.50 (s, 1H), 4.65 (d, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.39 (t, *J* = 6.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.8, 157.4, 140.7, 133.3, 131.4, 131.1, 129.2, 127.7, 125.17, 125.13, 122.6, 113.9, 56.0, 52.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{11}O_4F_3Na$ $[M + Na]^+$ 323.0502, found 323.0503.

Ethyl 2-(4-fluorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3i′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1i′**, 0.105 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3i′** was isolated as a colorless liquid (0.111 g, 85%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3419, 2359, 1637, 1530, 1439, 1024, 928, 851, 671, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.67 (m, 2H), 7.43 (s, 1H), 7.16–7.05 (m, 2H), 4.63 (d, *J* = 6.5 Hz, 2H), 4.29 (q, *J* = 7.13 Hz, 2H), 3.56 (t, *J* = 6.75 Hz, 1H), 1.27 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.7, 164.6, 162.2, 158.3, 139.8, 131.2, 131.1, 127.4, 126.3, 115.2, 115.0, 112.9, 61.2, 56.0, 14.0; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}O_4F$ $[M + H]^+$ 265.0871, found 265.0896.

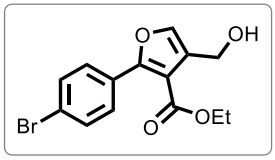
Ethyl 2-(4-chlorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3j′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1j′**, 0.113 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3j′** was isolated as a colorless liquid (0.122 g, 87%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3426, 2361, 1688, 1603, 1524, 1482, 1424, 1301, 1094, 1018, 928, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72–7.64 (m, 2H), 7.44 (s, 1H), 7.42–7.35 (m, 2H), 4.62 (s, 2H), 4.30 (q, *J* = 7.13 Hz, 2H), 3.54 (br. s., 1H), 1.28 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.6, 158.0, 140.0, 135.6, 130.3, 128.5, 128.3, 127.5, 113.3, 61.3, 56.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_4ClNa$ $[M + Na]^+$ 303.0395, found 303.0388.

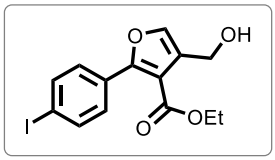
Ethyl 2-(4-bromophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3k′):

The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1k′**, 0.135 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g,



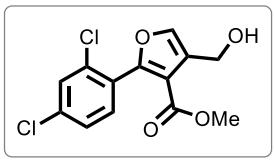
0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3k′** was isolated as a colorless liquid (0.147 g, 91%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3610, 3461, 2361, 1689, 1601, 1523, 1480, 1424, 1072, 1016, 928, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.59 (m, 2H), 7.58–7.52 (m, 2H), 7.45 (s, 1H), 4.63 (d, *J* = 4.5 Hz, 2H), 4.31 (q, *J* = 7.13 Hz, 2H), 3.51 (br. s., 1H), 1.29 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.5, 158.0, 140.1, 131.2, 130.5, 129.0, 127.6, 124.0, 113.4, 61.3, 56.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}O_4Br$ $[M + H]^+$ 325.0070, found 325.0062.

Ethyl 4-(hydroxymethyl)-2-(4-iodophenyl)furan-3-carboxylate (3l′):



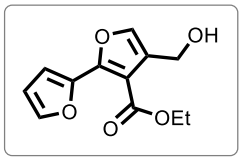
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1l′**, 0.159 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3l′** was isolated as a colorless liquid (0.171 g, 92%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3456, 2360, 1689, 1603, 1526, 1479, 1424, 1300, 1094, 1014, 929, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80–7.73 (m, 2H), 7.51–7.46 (m, 2H), 7.45 (s, 1H), 4.62 (s, 2H), 4.35–4.27 (m, 2H), 3.52 (br. s., 1H), 1.29 (t, *J* = 7.13 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.5, 158.0, 140.1, 137.2, 130.5, 129.5, 129.1, 128.0, 127.6, 113.4, 96.0, 61.3, 56.0, 14.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_4INa$ $[M + Na]^+$ 394.9751, found 394.9749.

Methyl 2-(2,4-dichlorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3m′):



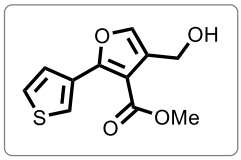
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1m′**, 0.123 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3m′** isolated as a colorless liquid (0.128 g, 82%). TLC: R_f= 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3609, 3488, 2361, 1701, 1586, 1523, 1473, 1441, 1379, 1306, 1132, 1104, 1085, 1047, 1019, 929, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.45 (m, 2H), 7.37–7.33 (m, 1H), 7.32–7.29 (m, 1H), 4.64 (br. s., 2H), 3.69 (s, 3H), 3.68 (br. s., 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.7, 155.2, 140.6, 136.3, 135.0, 132.6, 129.7, 128.4, 126.8, 126.7, 115.8, 55.7, 52.0; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_4Cl_2$ $[M + H]^+$ 315.0185, found 315.0183.

Ethyl 4-(hydroxymethyl)-[2,2'-bifuran]-3-carboxylate (3n′):



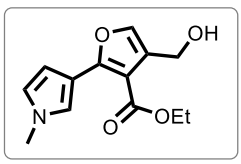
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1n′**, 0.091 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3n′** was isolated as a colorless liquid (0.103 g, 88%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3682, 3431, 2930, 2360, 1689, 1531, 1473, 1422, 1300, 1092, 1018, 956, 928, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.40 (s, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.61 (d, *J* = 5.5 Hz, 2H), 4.38 (d, *J* = 7.0 Hz, 2H), 3.43 (s, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.0, 150.1, 144.4, 143.7, 139.6, 127.2, 113.4, 111.87, 111.83, 61.3, 56.0, 14.3; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}O_5Na$ $[M + Na]^+$ 259.0577, found 259.0576.

Methyl 4-(hydroxymethyl)-2-(thiophen-3-yl)furan-3-carboxylate (3o′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1o′**, 0.092 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3o′** isolated as a colorless liquid (0.1 g, 85%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3609, 3415, 2360, 1690, 1602, 1523, 1477, 1425, 1074, 1021, 928, 851, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 1.25, 3.0 Hz, 1H), 7.57 (dd, *J* = 1.13, 5.13 Hz, 1H), 7.38 (s, 1H), 7.33 (dd, *J* = 3.0, 5.13 Hz, 1H), 4.62 (s, 2H), 3.89 (s, 3H), 3.36 (br. s., 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.0, 155.3, 139.1, 130.8, 127.6, 127.2, 126.8, 125.2, 111.5, 56.2, 51.9; HRMS (ESI): *m/z* calcd for $C_{11}H_{10}O_4SNa$ $[M + Na]^+$ 261.0192, found 261.0187.

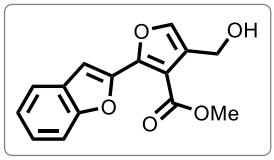
Ethyl 4-(hydroxymethyl)-2-(1-methyl-1*H*-pyrrol-3-yl)furan-3-carboxylate (3p′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1p′**, 0.097 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3p′** was isolated as a colorless liquid (0.101 g, 82%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3418, 2360, 1656, 1564, 1523, 1422, 1077, 1018, 928, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 6.74 (s, 1H), 6.62 (s, 1H), 6.18 (s, 1H), 4.62 (s, 2H), 4.27 (q, *J* = 6.2 Hz, 2H), 3.81 (s, 1H), 3.63 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.5, 152.5, 139.3, 126.7, 125.3, 122.1, 114.5, 113.7,

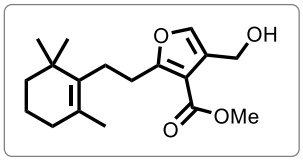
107.9, 60.9, 55.9, 35.6, 14.0; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_4N$ $[M + H]^+$ 250.1074, found 250.1069.

Methyl 2-(benzofuran-2-yl)-4-(hydroxymethyl)furan-3-carboxylate (3q′):



The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1q′**, 0.109 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3q′** was isolated as a colorless liquid (0.113 g, 83%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3609, 3429, 2361, 1603, 1523, 1477, 1425, 1024, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.52 (s, 1H), 7.37 (t, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 4.67 (s, 2H), 3.98 (s, 3H), 3.23 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.2, 154.8, 149.8, 145.5, 140.6, 128.2, 127.6, 126.1, 123.5, 122.1, 113.7, 111.5, 109.5, 56.1, 52.2; HRMS (ESI): *m/z* calcd for $C_{15}H_{12}O_5Na$ $[M + Na]^+$ 295.0577, found 295.0575.

Methyl-4-(hydroxymethyl)-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)furan-3-carboxylate (3r′):

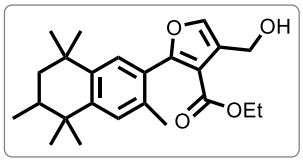


dehydrogenated β-ionone derived

The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1r′**, 0.126 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3r′** was isolated as a colorless liquid (0.123 g, 81%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3458, 2933, 2870, 2360, 1695, 1604, 1523, 1473, 1445, 1120, 1092, 1016, 929, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1 H), 4.55 (br. s., 2 H), 3.87 (s, 3H), 3.70 (br. s., 1H), 3.02–2.95 (m, 2H), 2.34–2.26 (m, 2H), 1.94 (t, *J* = 6.3 Hz, 2H), 1.68 (s, 3H), 1.58 (td, *J* = 3.0, 6.1 Hz, 2H), 1.47–1.43 (m, 2H), 1.04 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.9, 164.7, 138.5, 135.8, 128.7, 126.0, 111.9, 55.8, 51.8, 39.9, 35.1, 32.9, 29.1, 28.5, 27.4, 19.7, 19.5; HRMS (ESI): *m/z* calcd for $C_{18}H_{26}O_4Na$ $[M + Na]^+$ 329.1723, found 329.1719.

Ethyl 2-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-4-(hydroxymethyl) furan-3-carboxylate (3s′):

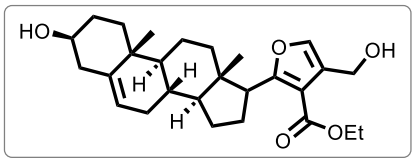
The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1s′**, 0.165 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3s′** was isolated as a colorless liquid (0.142 g,



tonalide derived

74%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3418, 1642, 1441, 1021, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.22 (d, *J* = 6.0 Hz, 2H), 4.65 (s, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 1.96–1.83 (m, 1H), 1.65 (t, *J* = 13.2 Hz, 1H), 1.39 (d, *J* = 13.5 Hz, 1H), 1.34 (s, 3H), 1.27 (s, 3H), 1.24 (s, 3H), 1.09 (s, 3H), 1.02 (q, *J* = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.2, 161.0, 147.7, 141.6, 139.4, 134.4, 128.9, 128.4, 127.6, 126.2, 114.3, 60.7, 55.9, 43.7, 37.8, 34.6, 34.1, 32.5, 32.1, 28.6, 25.0, 19.7, 16.9, 13.8; HRMS (ESI): *m/z* calcd for $C_{24}H_{33}O_4$ $[M + H]^+$ 385.2373, found 385.2365.

Ethyl-2-((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-4-(hydroxymethyl) furan-3-carboxylate (3t′):

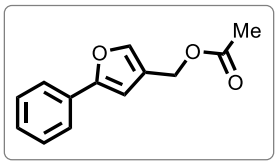


pregnenolone derived

The title compound was synthesized following general procedure 5, using corresponding *β*-ketoester (**1t′**, 0.194 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **3t′** was isolated as a pale yellow liquid (0.169 g, 77%). TLC: R_f = 0.4 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3778, 3685, 3609, 3451, 2975, 2361, 1681, 1603, 1524, 1476, 1426, 1088, 1025, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 5.36 (d, *J* = 5.0 Hz, 1H), 4.56 (s, 2H), 4.33 (dq, *J* = 2.88, 7.13 Hz, 2H), 3.78–3.75 (m, 1H), 3.59–3.46 (m, 2H), 2.35–2.25 (m, 2H), 2.25–2.16 (m, 2H), 2.02 (m, 1H), 1.98–1.88 (m, 1H), 1.87–1.74 (m, 3H), 1.67–1.60 (m, 1H), 1.58 (br. s., 1H), 1.52 (dd, *J* = 4.5, 10.4 Hz, 2H), 1.49–1.44 (m, 1H), 1.42–1.40 (m, 1H), 1.40–1.37 (m, 3H), 1.35–1.30 (m, 1H), 1.29–1.24 (m, 1H), 1.23–1.16 (m, 1H), 1.14–1.03 (m, 1H), 1.00 (s, 3H), 0.95 (s, 1H), 0.62 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.5, 164.0, 141.0, 138.4, 125.9, 121.3, 113.6, 71.6, 60.7, 56.2, 55.9, 50.3, 48.5, 46.9, 42.2, 37.6, 37.3, 36.6, 32.2, 31.9, 31.6, 25.3, 24.7, 20.8, 19.4, 14.4, 13.8; HRMS (ESI): *m/z* calcd for $C_{27}H_{38}O_5Na$ $[M + Na]^+$ 465.2611, found 465.2604.

(g) Analytical data for furan acetate or ethanone derivatives:

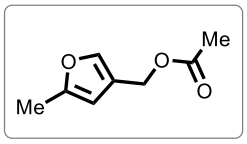
(5-Phenylfuran-3-yl)methyl acetate (5a):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4a**, 0.081 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5

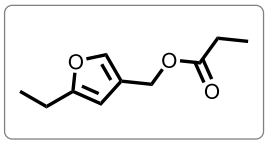
mL). The product **5a** was isolated as a colorless solid (0.089 g, 83%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3684, 2361, 1764, 1601, 1523, 1478, 1423, 1366, 1028, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.61 (m, 2H), 7.49 (s, 1H), 7.41–7.34 (m, 2H), 7.30–7.23 (m, 1H), 6.68 (s, 1H), 5.00 (s, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 154.9, 141.0, 130.6, 128.8, 127.7, 123.9, 122.5, 105.9, 57.9, 21.1; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}O_3$ $[M + H]^+$ 217.0859, found 217.0867.

(5-Methylfuran-3-yl)methyl acetate (5b):



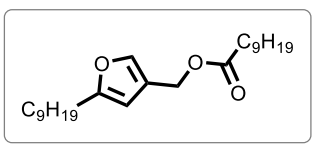
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4b**, 0.050 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5b** was isolated as a colorless liquid (0.061 g, 80%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3421, 1638, 1526, 1476, 1425, 1022, 928, 851, 669, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.01 (s, 1H), 4.91 (s, 2H), 2.27 (s, 3H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 153.3, 139.9, 121.2, 106.6, 58.1, 21.1, 13.6; HRMS (ESI): *m/z* calcd for $C_8H_{10}O_3Na$ $[M + Na]^+$ 177.0522, found 177.0544.

(5-Ethylfuran-3-yl)methyl propionate (5c):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4c**, 0.064 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5c** was isolated as a colorless liquid (0.073 g, 81%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3776, 3685, 3426, 2360, 1638, 1539, 1477, 1425, 1352, 1323, 1150, 1092, 1024, 927, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.01 (s, 1H), 4.92 (s, 2H), 2.61 (q, *J*=7.6 Hz, 2H), 2.34 (q, *J*=7.6 Hz, 2H), 1.21 (t, *J*=7.6 Hz, 3H), 1.14 (t, *J*=7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.4, 158.9, 139.7, 121.1, 105.0, 58.0, 27.6, 21.4, 12.0, 9.1; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}O_3Na$ $[M + Na]^+$ 205.0835, found 205.0839.

(5-Nonylfuran-3-yl)methyl decanoate (5d):

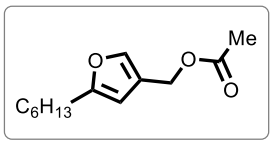


The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**5d**, 0.162 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5d** was isolated as a colorless solid (0.126 g, 67%). TLC: R_f=

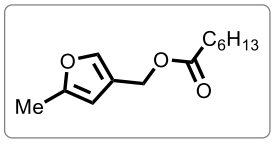
0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2923, 2854, 1738, 1573, 1557, 1462, 1159, 1110, 949, 931, 804, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.00 (s, 1H), 4.92 (s, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.64–1.58 (m, 4H), 1.38–1.26 (m, 24H), 0.88 (t, *J* = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.9, 157.7, 139.6, 121.1, 105.7, 58.0, 34.4, 32.0, 32.0, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.2, 28.1, 28.0, 25.0, 22.8, 14.2.

(5-Hexylfuran-3-yl)methyl acetate (5ea) and (5-Methylfuran-3-yl)methyl heptanoate (5eb):

The title compounds were synthesized following general procedure 6, using corresponding *β*-diketone (**4e**, 0.085 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The regioisomers **5ea** and **5eb** were obtained in respective yields.



The product **5ea** was isolated as a colorless solid (0.046 g, 41%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2928, 2858, 1737, 1557, 1454, 1378, 1228, 1165, 1127, 1024, 953, 917, 806, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.0 Hz, 1H), 6.01 (d, *J* = 1.1 Hz, 1H), 4.91 (d, *J* = 0.8 Hz, 2H), 2.61–2.54 (m, 2H), 2.06 (s, 3H), 1.68–1.58 (m, 2H), 1.31 (tdd, *J* = 10.9, 8.1, 5.0 Hz, 6H), 0.90–0.85 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 157.8, 139.7, 120.9, 105.7, 58.2, 31.6, 28.9, 28.1, 27.9, 22.6, 21.1, 14.17; HRMS (ESI): *m/z* calcd for $C_{13}H_{21}O_3$ $[M + H]^+$ 225.1485, found 225.1481.

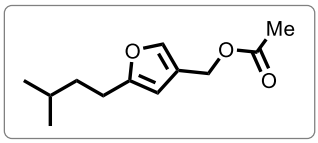


The product **5eb** was isolated as a colorless solid (0.039 g, 35%). TLC: R_f = 0.45 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2955, 2928, 2858, 1738, 1558, 1454, 1378, 1228, 1165, 1127, 1024, 953, 917, 806, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.1 Hz, 1H), 6.01–5.99 (m, 1H), 4.91 (d, *J* = 0.8 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.26 (d, *J* = 1.1 Hz, 3H), 1.62 (q, *J* = 7.4 Hz, 2H), 1.33–1.26 (m, 6H), 0.89–0.84 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.8, 153.2, 139.7, 121.3, 106.6, 57.9, 34.4, 31.5, 28.8, 25.0, 22.5, 14.1, 13.5; HRMS (ESI): *m/z* calcd for $C_{13}H_{21}O_3$ $[M + H]^+$ 225.1485, found 225.1480.

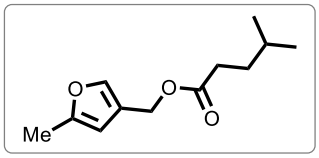
(5-Isopentylfuran-3-yl)methyl acetate (5fa) and (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):

The title compounds were synthesized following general procedure 6, using corresponding *β*-diketone (**4f**, 0.085 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The following regioisomers **5fa** and **5fb** were obtained. Further,

the structures of regioisomers were confirmed using gCOSY, gNOESY, gHSQC, and gHMBC experiments.



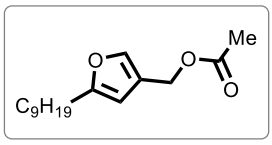
The product **5fa** was isolated as a colorless solid (0.030 g, 28%). TLC: R_f = 0.45 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2956, 2924, 2854, 1742, 1465, 1368, 1227, 1170, 1106, 1045, 927 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.01 (s, 1H), 4.91 (s, 2H), 2.62–2.56 (m, 2H), 2.07 (s, 3H), 1.57 (d, *J* = 8.7 Hz, 1H), 1.54–1.49 (m, 2H), 0.92 (s, 3H), 0.91 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 157.9, 139.7, 120.9, 105.6, 58.2, 36.9, 27.7, 26.0, 22.5, 21.1; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}O_3Na$ $[M + Na]^+$ 233.1148, found 233.1144.



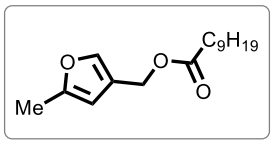
The product **5fb** was isolated as a colorless solid (0.031 g, 29%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2956, 2924, 2870, 2854, 1742, 1465, 1368, 1227, 1170, 1106, 1045, 927 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 6.01 (s, 1H), 4.91 (s, 2H), 2.34–2.29 (m, 2H), 2.27 (s, 3H), 1.54 (dt, *J* = 15.1, 7.0 Hz, 3H), 0.89 (s, 3H), 0.88 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1, 153.2, 139.8, 121.3, 106.6, 58.0, 33.8, 32.5, 27.8, 22.3, 13.6; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}O_3Na$ $[M + Na]^+$ 233.1148, found 233.1144.

(5-Nonylfuran-3-yl)methyl acetate (5ga) and (5-Methylfuran-3-yl)methyl decanoate (5gb):

The title compounds were synthesized following general procedure 6, using corresponding *β*-diketone (**4g**, 0.085 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The regioisomers **5ga** and **5gb** were obtained.



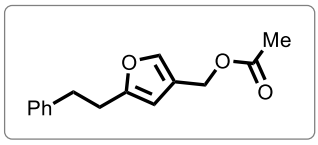
The product **5ga** was isolated as a colorless solid (0.05 g, 34%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2954, 2925, 2855, 1745, 1458, 1376, 1223, 1043, 963, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 0.9 Hz, 1H), 6.01 (d, *J* = 1.0 Hz, 1H), 4.92 (s, 2H), 2.60–2.54 (m, 2H), 2.07 (s, 3H), 1.61 (p, *J* = 7.6 Hz, 2H), 1.37–1.26 (m, 12H), 0.90–0.86 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 157.8, 139.7, 120.9, 105.7, 58.2, 32.0, 29.6, 29.5, 29.4, 29.3, 28.1, 28.0, 22.8, 21.1, 14.2; HRMS (ESI): *m/z* calcd for $C_{16}H_{27}O_3$ $[M + H]^+$ 267.1955, found 267.1943.



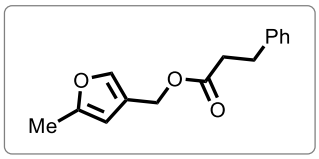
The product **5gb** was isolated as a colorless solid (0.04 g, 30%). TLC: R_f = 0.45 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2954, 2925, 2815, 1745, 1457, 1376, 1223, 1113, 1040, 960 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.1 Hz, 1H), 6.00 (t, *J* = 1.1 Hz, 1H), 4.91 (d, *J* = 0.8 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.26 (d, *J* = 1.1 Hz, 3H), 1.62 (q, *J* = 7.1 Hz, 2H), 1.33–1.25 (m, 12H), 0.88 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.8, 153.2, 139.8, 121.4, 106.6, 57.9, 34.4, 31.9, 29.5, 29.3, 29.2, 25.0, 22.7, 14.2, 13.6; HRMS (ESI): *m/z* calcd for $C_{16}H_{27}O_3$ $[M + H]^+$ 267.1955, found 267.1941.

(5-Phenethylfuran-3-yl)methyl acetate (5ha) and (5-Methylfuran-3-yl)methyl 3-phenylpropanoate (5hb):

The title compounds were synthesized following general procedure 6, using corresponding *β*-diketone (**4h**, 0.085 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The following regioisomers **5ha** and **5hb** were obtained.

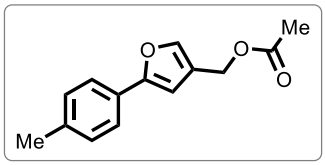


The product **5ha** was isolated as a colorless solid (0.031 g, 42%). TLC: R_f = 0.45 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2954, 2923, 1734, 1557, 1453, 1228, 1160, 1125, 1026, 951, 916, 809, 743, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 1.0 Hz, 1H), 7.33–7.26 (m, 2H), 7.24–7.15 (m, 3H), 6.03 (s, 1H), 4.92 (d, *J* = 0.8 Hz, 2H), 2.99–2.87 (m, 4H), 2.07 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 156.5, 141.1, 140.0, 128.5, 128.4, 126.2, 121.0, 106.3, 58.1, 34.3, 30.0, 21.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_3Na$ $[M + Na]^+$ 267.0992, found 267.0994.



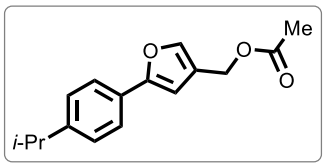
The product **5hb** was isolated as a colorless solid (0.028 g, 38%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2954, 2923, 1735, 1453, 1229, 1126, 1026, 916, 744, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 3H), 7.20 (td, *J* = 7.3, 1.6 Hz, 3H), 5.97 (s, 1H), 4.92 (d, *J* = 0.8 Hz, 2H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.65 (dd, *J* = 8.4, 7.2 Hz, 2H), 2.27 (d, *J* = 1.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.9, 153.2, 140.5, 139.8, 128.6, 128.4, 126.3, 121.2, 106.6, 58.1, 36.0, 31.0, 13.6; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_3Na$ $[M + Na]^+$ 267.0992, found 267.0992.

(5-(*p*-Tolyl)furan-3-yl)methyl acetate (5i):



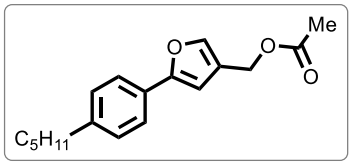
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4i**, 0.088 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5i** was isolated as a colorless solid (0.095 g, 80%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3420, 2066, 1641, 1442, 1021, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.47 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 5.00 (s, 2H), 2.36 (s, 3H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 155.1, 140.6, 137.6, 129.5, 127.9, 123.9, 122.4, 105.2, 58.0, 21.4, 21.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}O_3$ $[M + H]^+$ 231.1016, found 231.1019.

(5-(4-Isopropylphenyl)furan-3-yl)methyl acetate (5j):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4j**, 0.102 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5j** was isolated as a colorless solid (0.104 g, 81%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2960, 2930, 2871, 1741, 1606, 1460, 1418, 1365, 1229, 1052, 1026, 955, 915, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 2H), 7.48 (d, *J* = 1.0 Hz, 1H), 7.27–7.23 (m, 2H), 6.64 (d, *J* = 0.9 Hz, 1H), 5.01 (d, *J* = 0.9 Hz, 2H), 2.92 (p, *J* = 6.9 Hz, 1H), 2.10 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 155.1, 148.6, 140.7, 128.3, 126.8, 124.0, 122.4, 105.2, 58.0, 34.0, 24.0, 21.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_3$ $[M + H]^+$ 259.1329, found 259.1338.

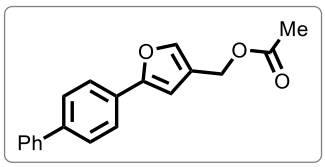
(5-(4-Pentylphenyl)furan-3-yl)methyl acetate (5k):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4k**, 0.116 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5k** was isolated as a colorless solid (0.109 g, 80%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3409, 2961, 2932, 2861, 2360, 1763, 1606, 1519, 1472, 1422, 1375, 1022, 928, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.55 (m, 2H), 7.50–7.44 (m, 1H), 7.20 (d, *J* = 8.38 Hz, 2H), 6.67–6.62 (m, 1H), 5.01 (s, 2H), 2.62 (t, *J* = 7.50 Hz, 2H), 2.10 (s, 3H), 1.69–1.58 (m, 2H), 1.39–1.30 (m, 4H), 0.92 (t, *J* = 6.88 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.9, 155.1, 142.6, 140.6, 128.7, 128.1,

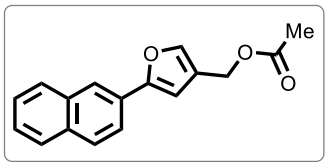
123.8, 122.4, 105.1, 57.9, 35.7, 31.5, 31.0, 22.6, 20.9, 14.0; HRMS (ESI): *m/z* calcd for $C_{18}H_{23}O_3$ $[M + H]^+$ 287.1642, found 287.1635.

(5-([1,1'-Biphenyl]-4-yl)furan-3-yl)methyl acetate (5l):



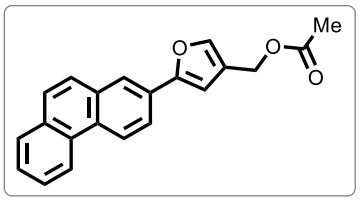
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4l**, 0.119 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5l** was isolated as a colorless solid (0.119 g, 82%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3420, 2361, 1735, 1637, 1523, 1479, 1424, 1027, 927, 847, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76–7.70 (m, 2H), 7.65–7.59 (m, 4H), 7.53 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.73 (s, 1H), 5.03 (s, 2H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 154.7, 141.1, 140.6, 140.4, 129.6, 128.9, 127.57, 127.51, 127.0, 124.4, 122.6, 106.1, 57.9, 21.1; HRMS (ESI): *m/z* calcd for $C_{19}H_{17}O_3$ $[M + Na]^+$ 293.1172, found 293.1169.

(5-(Naphthalen-2-yl)furan-3-yl)methyl acetate (5m):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4m**, 0.106 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5m** was isolated as a colorless solid (0.107 g, 77%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3419, 1736, 1628, 1530, 1436, 1371, 1026, 928, 859, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92–7.78 (m, 4H), 7.75 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.56 (s, 1H), 7.47 (pd, *J* = 6.9, 1.6 Hz, 2H), 6.81 (s, 1H), 5.04 (s, 2H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 155.0, 141.3, 133.6, 132.9, 128.5, 128.3, 127.96, 127.90, 126.6, 126.2, 122.7, 122.5, 122.3, 106.5, 58.0, 21.1; HRMS (ESI): *m/z* calcd for $C_{17}H_{15}O_3$ $[M + H]^+$ 267.1016, found 267.1010.

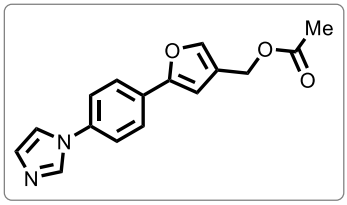
(5-(Phenanthren-2-yl)furan-3-yl)methyl acetate (5n):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4n**, 0.131 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5n** was isolated as a colorless solid (0.124 g, 79%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3023, 2929, 2855, 1738, 1459, 1372, 1243, 1035, 940, 896, 814, 749, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 1.8 Hz, 1H), 7.88 (ddd, *J* = 8.6, 4.4, 1.7 Hz,

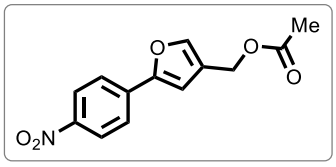
2H), 7.74 (s, 2H), 7.67–7.56, (m, 3H), 6.83 (d, J = 0.8 Hz, 1H), 5.05 (s, 2H), 2.14 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 155.0, 141.3, 133.6, 132.9, 128.5, 128.3, 127.96, 127.90, 126.6, 126.2, 122.7, 122.5, 122.3, 106.5, 58.0, 21.1; HRMS (ESI): *m/z* calcd for $C_{21}H_{17}O_3$ $[M + H]^+$ 317.1172, found 317.1164.

(5-(4-(1*H*-Imidazol-1-yl)phenyl)furan-3-yl)methyl acetate (5o):



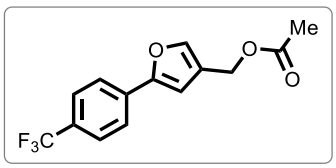
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4o**, 0.114 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5o** was isolated as a colorless solid (0.106 g, 76%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3019, 2929, 1736, 1604, 1393, 1230, 1123, 1024, 914, 841, 743, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 1.8 Hz, 1H), 7.88 (ddd, J = 8.6, 4.4, 1.7 Hz, 2H), 7.74 (s, 2H), 7.67–7.56, (m, 3H), 6.83 (d, J = 0.8 Hz, 1H), 5.05 (s, 2H), 2.14 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 155.0, 141.3, 133.6, 132.9, 128.5, 128.3, 127.96, 127.90, 126.6, 126.2, 122.7, 122.5, 122.3, 106.5, 58.0, 21.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}O_3N_2$ $[M + H]^+$ 283.1077, found 283.1071.

(5-(4-Nitrophenyl)furan-3-yl)methyl acetate (5p):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4p**, 0.103 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5p** was isolated as a yellow solid (0.091 g, 70%). TLC: R_f= 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3109, 2926, 2854, 1735, 1592, 1526, 1497, 1340, 1229, 1160, 1103, 1021, 913, 852, 752, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28–8.22 (m, 2H), 7.81–7.75 (m, 2H), 7.60 (d, J = 1.0 Hz, 1H), 6.91 (d, J = 0.8 Hz, 1H), 5.02 (s, 2H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 152.5, 146.8, 143.0, 136.2, 124.4, 124.2, 123.4, 109.8, 57.5, 21.0.

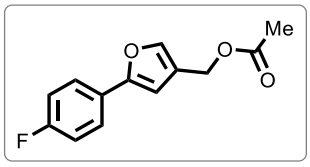
(5-(4-(Trifluoromethyl)phenyl)furan-3-yl)methyl acetate (5q):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4q**, 0.115 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5q** was isolated as a yellow solid (0.101 g, 72%). TLC: R_f=

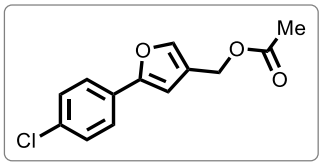
0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3421, 2091, 1640, 1440, 1324, 1068, 928, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 6.80 (s, 1H), 5.01 (s, 2H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 153.3, 142.0, 133.6, 125.9, 125.89, 125.85, 125.81, 123.9, 122.9, 107.9, 57.7, 21.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{12}O_3F_3$ $[M + H]^+$ 285.0733, found 285.0729.

(5-(4-Fluorophenyl)furan-3-yl)methyl acetate (5r):



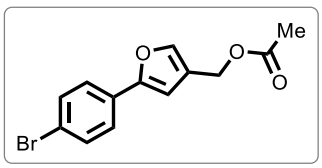
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4r**, 0.090 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5r** was isolated as a pale yellow solid (0.084 g, 70%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3418, 1641, 1441, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.58 (m, 2H), 7.48 (s, 1H), 7.11–7.02 (m, 2H), 6.61 (s, 1H), 4.99 (s, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 163.6, 161.2, 154.0, 141.0, 127.03, 127.00, 125.8, 125.7, 122.6, 115.9, 115.7, 105.65, 105.63, 57.9, 21.1; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}O_3FNa$ $[M + Na]^+$ 257.0584, found 257.0583.

(5-(4-Chlorophenyl)furan-3-yl)methyl acetate (5s):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4s**, 0.098 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5s** was isolated as a yellow solid (0.095 g, 74%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3418, 2359, 1602, 1523, 1425, 1021, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.53 (m, 2H), 7.49 (s, 1H), 7.37–7.30 (m, 2H), 6.67 (s, 1H), 4.99 (s, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 153.8, 141.3, 133.4, 129.1, 129.0, 125.2, 122.7, 106.3, 57.8, 21.0; HRMS (ESI): *m/z* calcd for $C_{13}H_{12}O_3Cl$ $[M + H]^+$ 251.0469, found 251.0465.

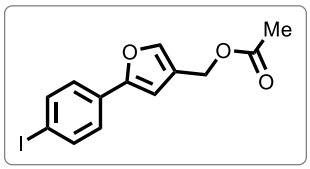
(5-(4-Bromophenyl)furan-3-yl)methyl acetate (5t):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4t**, 0.120 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5t** was isolated as a brown solid (0.108 g, 69%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3775, 3684, 3427, 2361, 1771, 1638, 1595, 1522,

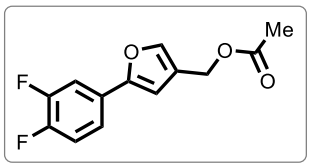
1480, 1424, 1072, 1013, 928, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 5H), 6.68 (s, 1H), 4.99 (s, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 153.8, 141.3, 131.9, 129.5, 125.4, 122.7, 121.6, 106.5, 57.8, 21.1; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}O_3BrNa$ $[M + Na]^+$ 316.9784, found 316.9782.

(5-(4-Iodophenyl)furan-3-yl)methyl acetate (5u):



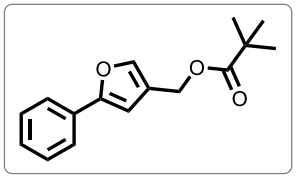
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4u**, 0.096 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5u** was isolated as a brown solid (0.121 g, 75%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3422, 2360, 1729, 1604, 1523, 1477, 1425, 1027, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.50 (s, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.70 (s, 1H), 4.99 (s, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 153.9, 141.4, 137.9, 131.0, 130.0, 125.6, 122.7, 106.6, 57.8, 21.1; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}O_3INa$ $[M + Na]^+$ 364.9645, found 364.9641.

(5-(3,4-Difluorophenyl)furan-3-yl)methyl acetate (5v):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4v**, 0.099 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5v** was isolated as a brown solid (0.109 g, 68%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3385, 3084, 2927, 2854, 1739, 1609, 1512, 1430, 1223, 1114, 1026, 870, 815, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 0.9 Hz, 1H), 7.41 (ddd, *J* = 11.4, 7.5, 2.1 Hz, 1H), 7.33 (ddt, *J* = 8.5, 3.9, 1.7 Hz, 1H), 7.14 (dt, *J* = 10.1, 8.4 Hz, 1H), 6.63 (d, *J* = 0.9 Hz, 1H), 4.98 (d, *J* = 0.9 Hz, 2H), 2.08 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.9, 152.7, 152.7, 152.7, 151.9, 151.8, 151.1, 151.0, 149.4, 149.3, 148.7, 148.5, 141.4, 127.8, 127.7, 127.7, 127.6, 122.8, 120.0, 120.0, 120.0, 119.9, 117.8, 117.6, 113.0, 112.8, 106.6, 106.5, 57.6, 20.9; HRMS (ESI): *m/z* calcd for $C_{13}H_{11}O_3F_2$ $[M + H]^+$ 253.0671, found 253.0674.

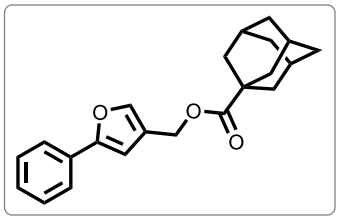
(5-Phenylfuran-3-yl)methyl pivalate (5w):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4w**, 0.102 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in

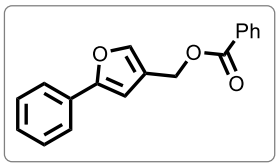
CH_2Cl_2 (0.5 mL). The product **5w** was isolated as a colorless liquid (0.085 g, 66%). TLC: R_f= 0.8 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2966, 2933, 2872, 1724, 1480, 1396, 1365, 1278, 1150, 1132, 1071, 1033, 954, 913, 814, 762, 691, 662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.48 (s, 1H), 7.41-7.35 (m, 2H), 7.30-7.26 (m, 1H), 5.00 (s, 2H), 1.22 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 178.6, 154.8, 140.7, 130.7, 128.8, 127.8, 124.0, 123.0, 105.8, 58.0, 38.9, 27.3; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}O_3$ $[M + H]^+$ 259.1329, found 259.1325.

(5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



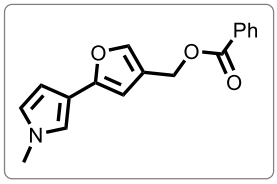
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4y**, 0.141 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5y** was isolated as a colorless liquid (0.092 g, 72%). TLC: R_f= 0.8 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2905, 2851, 1724, 1451, 1425, 1228, 1183, 1103, 1071, 914, 760, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.0 Hz, 2H), 7.47 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.29–7.23 (m, 1H), 6.65 (s, 1H), 4.99 (s, 2H), 2.01 (s, 3H), 1.90 (d, *J* = 3.3 Hz, 6H), 1.72 (d, *J* = 16.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 177.6, 154.7, 140.6, 130.7, 128.8, 127.7, 123.9, 123.0, 105.7, 57.7, 40.8, 38.9, 36.6, 28.0; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}O_3Na$ $[M + Na]^+$ 359.1618, found 359.1617.

(5-Phenylfuran-3-yl)methyl benzoate (5z):



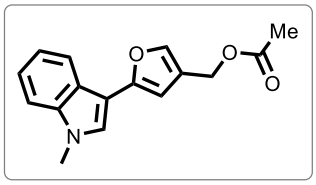
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4z**, 0.112 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5z** was isolated as a colorless solid (0.113 g, 82%). TLC: R_f= 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3685, 3611, 2360, 1771, 1724, 1602, 1523, 1477, 1424, 1025, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11–8.01 (m, 2H), 7.68–7.61 (m, 2H), 7.55 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.27–7.20 (m, 1H), 6.74 (s, 1H), 5.24 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 185.8, 166.6, 154.8, 141.0, 133.1, 132.5, 130.6, 130.2, 129.7, 128.7, 128.4, 127.7, 127.2, 123.9, 122.6, 105.9, 58.4; HRMS (ESI): *m/z* calcd for $C_{18}H_{13}O_3$ $[M – H]^-$ 277.0859, found 277.0854.

(5-(1-Methyl-1*H*-pyrrol-3-yl)furan-3-yl)methyl benzoate (5a′):



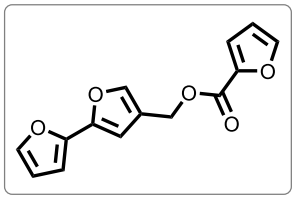
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4a′**, 0.113 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5a′** was isolated as a colorless liquid (0.086 g, 74%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3421, 2360, 1715, 1639, 1524, 1476, 1425, 1108, 1026, 928, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11-8.01 (m, 2H), 7.61–7.54 (m, 1H), 7.54–7.51 (m, 1H), 7.48–7.41 (m, 2H), 6.65 (t, *J* = 2.25 Hz, 1H), 6.45 (s, 1H), 6.43 (dd, *J* = 1.75, 3.63 Hz, 1H), 6.14 (dd, *J* = 2.63, 3.63 Hz, 1H), 5.25 (s, 2H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 149.0, 140.1, 133.1, 130.2, 129.8, 128.7, 128.5, 126.4, 124.7, 124.4, 122.0, 109.2, 108.0, 106.2, 58.5, 35.9; HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_3N$ $[M + H]^+$ 282.1125, found 282.1138.

(5-(1-Methyl-1*H*-indol-3-yl)furan-3-yl)methyl acetate (5b′):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4b′**, 0.107 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5b′** was isolated as a yellow solid (0.095 g, 71%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2923, 2853, 1737, 1465, 1365, 1228, 1023, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.45 (d, *J* = 0.9 Hz, 1H), 7.38 (s, 1H), 7.35 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.29 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.22 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 6.54 (d, *J* = 0.8 Hz, 1H), 5.04 (s, 2H), 3.82 (s, 3H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 149.0, 140.1, 133.1, 130.2, 129.8, 128.7, 128.4, 126.4, 124.7, 124.4, 122.0, 109.2, 108.0, 106.2, 58.5, 35.9; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}O_3NNa$ $[M + Na]^+$ 292.0944, found 292.0937.

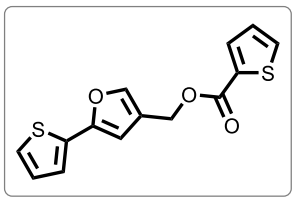
[2,2'-Bifuran]-4-ylmethyl furan-2-carboxylate (5c′):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4c′**, 0.102 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5c′** was isolated as a yellow solid (0.089 g, 61%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3130, 2960, 1715, 1579, 1473, 1395, 1291, 1230, 1176, 1108, 1074, 1005, 945, 881, 803, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 36.4, 8.5 Hz, 2H), 7.42 (t, *J* = 8.2 Hz, 1H), 7.24–7.15 (m, 1H), 6.66 (t, *J* = 7.7 Hz, 1H), 6.61–6.39 (m, 3H), 5.23 (q, *J* = 6.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.6,

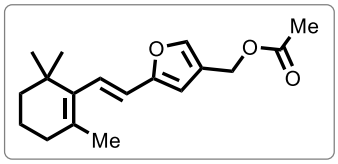
147.5, 146.6, 146.2, 144.5, 142.1, 141.0, 122.0, 118.4, 112.0, 111.5, 106.0, 105.8, 58.1; HRMS (ESI): *m/z* calcd for $C_{14}H_{10}O_5Na$ $[M + Na]^+$ 281.0420, found 281.0413.

(5-(Thiophen-2-yl)furan-3-yl)methyl thiophene-2-carboxylate (5d′):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4d′**, 0.118 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5d′** was isolated as a yellow solid (0.084 g, 58%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3129, 1714, 1579, 1473, 1396, 1290, 1230, 1176, 1106, 1074, 1004, 930, 883, 803, 759, 613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.57 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.50 (t, *J* = 0.9 Hz, 1H), 7.26 (d, *J* = 3.0 Hz, 1H), 7.23 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.03 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.61 (d, *J* = 0.9 Hz, 1H), 5.21 (d, *J* = 0.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.2, 150.4, 140.7, 133.8, 133.6, 133.4, 132.7, 127.9, 127.7, 124.6, 123.1, 122.5, 106.0, 58.4; HRMS (ESI): *m/z* calcd for $C_{14}H_{10}O_2S_2Na$ $[M + Na]^+$ 312.9964, found 312.9962.

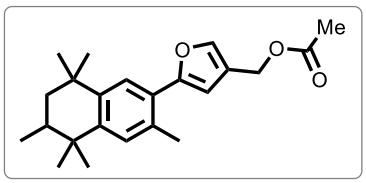
(*E*)-(5-(2-(2,6,6-Trimethylcyclohex-1-en-1-yl)vinyl)furan-3-yl)methyl acetate (5e′):



β-Ionone derived

The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4e′**, 0.117 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5e′** was isolated as a yellow solid (0.089 g, 62%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2990, 2960, 1775, 1440, 1254, 1243, 990, 870 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.63 (d, *J* = 16.3 Hz, 1H), 6.23 (s, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 4.94 (s, 2H), 2.07 (s, 3H), 2.03 (t, *J* = 6.4 Hz, 2H), 1.74 (d, *J* = 1.1 Hz, 3H), 1.67–1.58 (m, 3H), 1.51–1.44 (m, 2H), 1.05 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 154.6, 140.4, 137.2, 130.5, 127.3, 122.1, 120.7, 107.3, 58.0, 39.8, 34.3, 33.3, 29.0, 21.8, 21.1, 19.3, 19.5; HRMS (ESI): *m/z* calcd for $C_{18}H_{25}O_3$ $[M + H]^+$ 289.1798, found 289.1793.

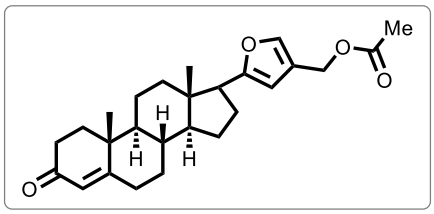
(5-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)furan-3-yl)methyl acetate(5f′):



tonalide derived

The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4f′**, 0.150 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5f′** was isolated as a yellow solid (0.122 g, 69%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3730, 3693, 2961, 2926, 1607, 1456, 1363, 1258, 1200, 1086, 971, 792 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.22 (s, 1H), 6.52 (s, 1H), 5.04 (s, 2H), 2.45 (s, 3H), 2.11 (s, 3H), 1.93-187 (m, 1H), 1.66 (t, *J* = 13.2 Hz, 1H), 1.40 (dd, *J* = 2.6, 13.5 Hz, 1H), 1.35 (d, *J* = 2.75 Hz, 6H), 1.29 (s, 3H), 1.10 (s, 3H), 1.01 (d, *J* = 6.75 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1, 155.0, 146.0, 142.6, 140.4, 131.9, 129.7, 127.5, 125.4, 122.0, 108.7, 58.2, 43.8, 37.7, 34.7, 34.2, 32.5, 32.2, 28.7, 25.0, 21.6, 21.2, 17.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{31}O_3$ $[M + H]^+$ 355.2268 found 355.2272.

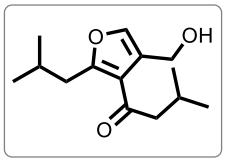
(5-((8S,9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetra decahydro-1*H* cyclopenta[a]phenanthren-17-yl)furan-3-yl)methyl acetate (5g′):



progesterone derived

The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4g′**, 0.178 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5g′** was isolated as a yellow solid (0.129 g, 63%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 2938, 2874, 1738, 1669, 1614, 1449, 1378, 1227, 1025, 953, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 0.9 Hz, 1H), 6.05 (d, *J* = 1.0 Hz, 1H), 5.73 (t, *J* = 1.1 Hz, 1H), 4.92 (s, 2H), 2.63 (t, *J* = 9.8 Hz, 1H), 2.45–2.26 (m, 4H), 2.07 (s, 3H), 2.05–1.95 (m, 3H), 1.93–1.85 (m, 2H), 1.82–1.65 (m, 3H), 1.60–1.55 (m, 1H), 1.45–1.23 (m, 4H), 1.18 (s, 3H), 1.13–1.05 (m, 1H), 1.02–0.94 (m, 1H), 0.54 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.7, 171.4, 171.1, 158.2, 140.0, 124.0, 120.6, 106.6, 58.2, 55.0, 54.0, 49.9, 44.2, 38.8, 37.8, 36.0, 35.8, 34.0, 33.0, 32.1, 25.4, 24.4, 21.1, 20.9, 17.5, 13.2; HRMS (ESI): *m/z* calcd for $C_{26}H_{35}O_4$ $[M + H]^+$ 411.2530, found 411.2519.

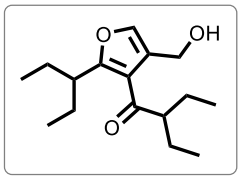
1-(4-(Hydroxymethyl)-2-isobutylfuran-3-yl)-3-methylbutan-1-one (5′a):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′a**, 0.092 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′a** was isolated as a colorless solid (0.090 g, 76%). TLC: R_f = 0.4 (SiO_2, 10%

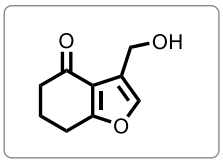
EtOAc/Hexanes). IR ($CHCl_3$) 3427, 2962, 1645, 1538, 1415, 1020, 928, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 4.43 (d, *J* = 6.8 Hz, 2H), 4.07 (t, *J* = 6.9 Hz, 1H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.64 (d, *J* = 6.9 Hz, 2H), 2.22 (dp, *J* = 13.5, 6.7 Hz, 1H), 2.07 (dp, *J* = 13.8, 6.8 Hz, 1H), 0.95 (dd, *J* = 6.7, 3.2 Hz, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.9, 162.2, 138.7, 125.9, 123.1, 55.8, 50.8, 38.0, 28.8, 25.0, 22.7, 22.5; HRMS (ESI): *m/z* calcd for $C_{14}H_{23}O_3$ $[M + H]^+$ 239.1642, found 239.1645.

2-Ethyl-1-(4-(hydroxymethyl)-2-(pentan-3-yl)furan-3-yl)butan-1-one (5′b):



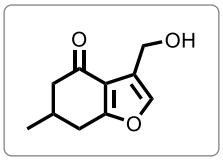
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′b**, 0.106 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′b** was isolated as a colorless solid (0.104 g, 79%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3681, 3426, 2967, 2933, 2875, 2360, 1641, 1535, 1460, 1409, 1340, 1124, 1018, 984, 927, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 4.41 (d, *J* = 6.3 Hz, 2H), 4.15 (t, *J* = 6.9 Hz, 1H), 3.12–2.96 (m, 2H), 1.82–1.67 (m, 6H), 1.59–1.46 (m, 2H), 0.86 (dt, *J* = 20.6, 7.4 Hz, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 204.3, 164.3, 139.0, 125.6, 124.8, 55.8, 52.8, 42.8, 27.3, 24.9, 12.2, 11.9; HRMS (ESI): *m/z* calcd for $C_{16}H_{27}O_3$ $[M + H]^+$ 267.1955, found 267.1957.

3-(Hydroxymethyl)-6,7-dihydrobenzofuran-4(5*H*)-one (5′c):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′c**, 0.056 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL) and the product **5′c** was isolated as a colorless solid (0.065 g, 79%). TLC: R_f = 0.6 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3418, 2360, 1656, 1564, 1523, 1422, 1077, 1018, 928, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 4.68 (d, *J* = 1.13 Hz, 2H), 2.85 (t, *J* = 6.25 Hz, 2H), 2.53–2.44 (m, 2H), 2.17 (quin, *J* = 6.38 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.9, 168.1, 141.1, 121.3, 119.0, 38.0, 36.2, 23.5, 22.7; HRMS (ESI): *m/z* calcd for $C_9H_{11}O_3$ $[M + H]^+$ 167.0703, found 167.0703.

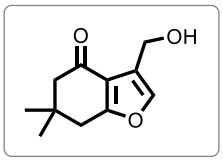
3-(Hydroxymethyl)-6-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (5′d):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′d**, 0.063 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The

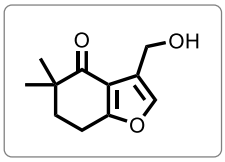
product **5′d** was isolated as a colorless solid (0.069 g, 77%). TLC: R_f = 0.6 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 3421, 2360, 1656, 1603, 1523, 1477, 1425, 1331, 1028, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 4.52 (d, *J* = 5.9 Hz, 2H), 4.32 (t, *J* = 6.9 Hz, 1H), 2.99–2.87 (m, 1H), 2.62–2.47 (m, 2H), 2.26 (dd, *J* = 16.1, 10.7 Hz, 1H), 1.16 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.6, 168.9, 138.4, 123.8, 120.3, 55.3, 45.9, 31.5, 31.0, 21.0; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}O_3$ $[M + H]^+$ 181.0859, found 181.0859.

3-(Hydroxymethyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (5′e):



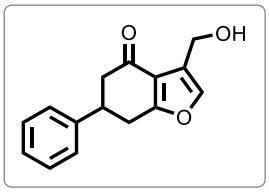
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′e**, 0.070 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′e** was isolated as a colorless solid (0.073 g, 76%). TLC: R_f = 0.6 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3418, 2971, 2867, 2360, 1655, 1560, 1523, 1472, 1443, 1418, 1333, 1295, 1149, 1077, 1007, 970, 928, 849, 670, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 4.56 (s, 2H), 4.31 (s, 1H), 2.74 (s, 2H), 2.42 (s, 2H), 1.15 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.5, 168.4, 138.6, 123.9, 119.6, 55.4, 51.9, 37.5, 35.7, 28.6; HRMS (ESI): *m/z* calcd for $C_{11}H_{15}O_3$ $[M + H]^+$ 195.1016, found 195.1015.

3-(Hydroxymethyl)-5,5-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (5′f):



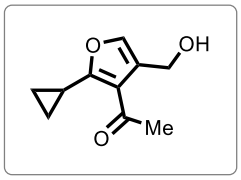
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′f**, 0.070 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′f** was isolated as a colorless solid (0.072 g, 75%). TLC: R_f = 0.6 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3418, 2971, 2867, 2360, 1655, 1560, 1523, 1472, 1443, 1418, 1333, 1295, 1149, 1077, 1007, 970, 928, 849, 670, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.53 (d, *J* = 6.3 Hz, 2H), 4.35 (t, *J* = 6.9 Hz, 1H), 2.64–2.54 (m, 2H), 2.06–1.95 (m, 2H), 1.35 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.0, 175.0, 138.3, 123.7, 118.5, 55.3, 37.9, 35.3, 32.9, 25.8; HRMS (ESI): *m/z* calcd for $C_{11}H_{15}O_3$ $[M + H]^+$ 195.1016, found 195.1016.

3-(Hydroxymethyl)-6-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (5′g):



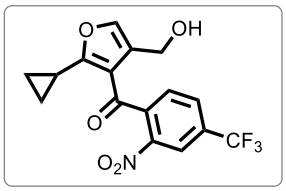
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′g**, 0.094 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL) & two drops of MeOH for solubility. The product **5′g** was isolated as a colorless solid (0.056 g, 63%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.29 (d, *J* = 6.1 Hz, 4H), 4.60 (d, *J* = 6.6 Hz, 2H), 4.27 (t, *J* = 7.2 Hz, 1H), 3.66–3.53 (m, 1H), 3.19 (dd, *J* = 17.2, 5.2 Hz, 1H), 3.07 (dd, *J* = 17.2, 11.1 Hz, 1H), 2.83 (d, *J* = 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.6, 168.4, 142.1, 138.9, 129.1, 127.5, 126.8, 124.0, 55.4, 44.9, 41.6, 31.3; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}O_3Na$ $[M + Na]^+$ 265.0835, found 265.0837.

1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′h**, 0.063 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′h** was isolated as a colorless liquid (0.058 g, 64%). TLC: R_f = 0.5 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3682, 3429, 2875, 2361, 1642, 1553, 1423, 1359, 1119, 1013, 932, 850, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 4.48 (d, *J* = 6.8 Hz, 2H), 4.19 (d, *J* = 7.0 Hz, 1H), 2.65 (s, 3H), 2.36–2.24 (m, 1H), 1.14 (d, *J* = 9.8 Hz, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.2, 164.0, 137.4, 126.1, 122.9, 55.6, 30.5, 10.4, 8.4; HRMS (ESI): *m/z* calcd for $C_{10}H_{12}O_3Na$ $[M + Na]^+$ 203.0679, found 203.0669.

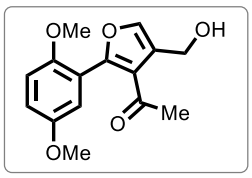
(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl) methanone (5′i):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′i**, 0.150 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′i** was isolated as a yellow solid (0.122 g, 70%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3776, 3685, 3426, 2360, 1638, 1539, 1477, 1425, 1352, 1323, 1150, 1092, 1024, 927, 848, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.20 (s, 1H), 4.56 (s, 2H), 3.58 (s, 1H), 1.09–1.01 (m, 1H), 0.98 (s, 2H), 0.69 (d, *J* = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 188.4, 165.6, 146.7, 140.3, 138.4, 133.8, 133.5, 133.1, 132.8, 131.03,

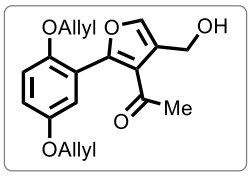
131.00, 129.7, 126.5, 123.8, 122.16, 122.12, 121.0, 55.5, 9.9, 9.1; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}O_5NF_3Na$ $[M + Na]^+$ 378.0560, found 378.0551.

1-(2-(2,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′k):



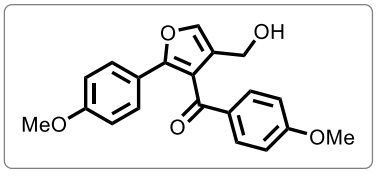
The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′k**, 0.111 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′k** was isolated as a colorless solid (0.102 g, 74%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3023, 2929, 2855, 1738, 1459, 1372, 1243, 1035, 940, 898, 814, 749, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.39 (d, J = 3.0 Hz, 1H), 6.99 (s, 1H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.79 (dd, *J* = 9.0, 3.1 Hz, 1H), 5.01 (s, 2H), 3.90 (s, 3H), 3.82 (s, 3H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 153.7, 150.9, 149.9, 140.2, 122.4, 120.1, 113.8, 112.3, 111.1, 111.0, 58.1, 56.0, 55.9, 21.1; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}O_5Na$ $[M + Na]^+$ 299.0890, found 299.0888.

1-(2-(2,5-Bis(allyloxy)phenyl)-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′l):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′l**, 0.137 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′l** was isolated as a colorless solid (0.125 g, 79%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 2964, 2930, 2359, 1728, 1603, 1501, 1424, 1380, 1029, 929, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.41 (d, *J* = 3.13 Hz, 1H), 7.02 (s, 1H), 6.87 (d, *J* = 9.01 Hz, 1H), 6.79 (dd, *J* = 3.13, 9.01 Hz, 1H), 6.19–6.01 (m, 2H), 5.47–5.40 (m, 2H), 5.34–5.27 (qdd, *J* = 1.3, 10.5, 15.5 Hz, 2H), 5.01 (s, 2H), 4.61 (td, *J* = 1.5, 5.38 Hz, 2H), 4.54 (td, *J* = 1.5, 5.38 Hz, 2H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 152.9, 150.9, 149.0, 140.2, 133.58, 133.51, 122.4, 120.5, 118.0, 117.7, 114.7, 113.9, 112.1, 111.1, 70.0, 69.5, 58.1, 21.1; HRMS (ESI): *m/z* calcd for $C_{19}H_{21}O_5$ $[M + H]^+$ 329.1384, found 329.1375.

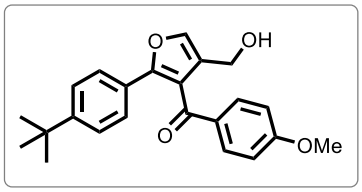
(4-(Hydroxymethyl)-2-(4-methoxyphenyl)furan-3-yl)(4-methoxyphenyl)methanone (5′m):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′m**, 0.142 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g,

0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′m** was isolated as a colorless solid (0.134 g, 80%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3420, 2359, 1599, 1507, 1423, 1305, 1256, 1029, 928, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 2H), 7.50 (s, 1H), 7.23 (d, *J* = 8.9 Hz, 2H), 6.70 (t, *J* = 8.9 Hz, 4H), 4.50 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.6, 163.7, 160.1, 157.1, 139.6, 132.5, 130.2, 129.7, 128.1, 122.5, 119.8, 113.8, 113.6, 55.58, 55.56, 55.3; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}O_5$ $[M + H]^+$ 339.1227, found 339.1225.

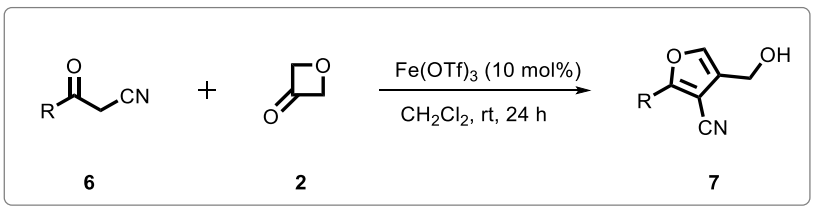
(2-(4-(*tert*-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



The title compound was synthesized following general procedure 6, using corresponding *β*-diketone (**4′n**, 0.155 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeCl_3$ (0.008 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **5′n** was isolated as a colorless solid (0.119 g, 78%). TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3777, 3684, 3450, 2966, 2362, 1691, 1603, 1503, 1468, 1418, 1366, 1304, 1255, 1113, 1074, 1028, 928, 837, 670, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.50 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 4.53 (s, 2H), 3.70 (s, 3H), 1.23 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.0, 160.1, 158.4, 156.8, 139.6, 134.8, 129.96, 129.94, 128.0, 125.1, 122.4, 120.1, 113.6, 55.6, 55.3, 35.1, 31.0; HRMS (ESI): *m/z* calcd for $C_{23}H_{25}O_4$ $[M + H]^+$ 365.1747, found 365.1744.

5. Reactivity of dicarbonyl surrogates and post-synthetic modifications

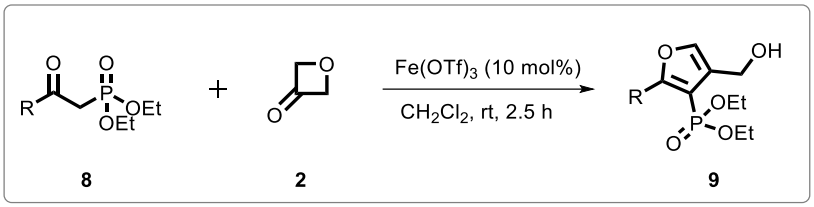
(a) General procedure-7 for synthesis 4-hydroxymethyl phenyl furan carbonitrile derivatives from *β*-ketonitriles (GP7):



A 10 mL two-neck round bottom flask containing *β*-ketonitriles (**6**, 0.5 mmol) was evacuated under vacuo and then backfilled with argon. Then, anhydrous CH_2Cl_2 (0.5 mL) and $Fe(OTf)_3$ (0.05 mmol) were added at room temperature, and the mixture was stirred for 5 min. Then, 3-oxetanone (**2**, 0.5 mmol) was added to it, and the reaction progress was monitored by TLC.

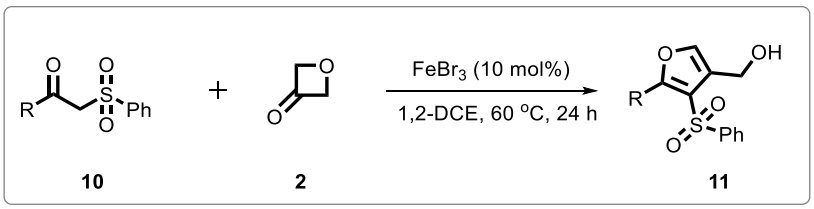
After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (2 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-50% EtOAc/Hexane) to afford the desired product **7**.

(b) General procedure-8 for synthesis 4-Hydroxymethyl phenyl furan diethylphosphonate derivatives from *β*-ketophosphonates (GP8):



A 10 mL two-neck round bottom flask containing *β*-ketophosphonates (**8**, 0.5 mmol) was evacuated under vacuo and then backfilled with argon. Then, anhydrous CH_2Cl_2 (0.5 mL) and $Fe(OTf)_3$ (0.05 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 0.5 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (2 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-60% EtOAc/Hexane) to afford the desired product **9**.

(c) General procedure-9 for synthesis of 4-Hydroxymethyl phenyl furan phenylsulfonyl derivatives from *β*-ketosulfones (GP9):

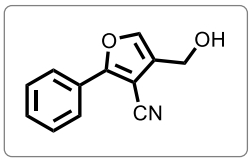


A 10 mL two-neck round bottom flask containing *β*-ketosulfones (**10**, 0.5 mmol) was evacuated under vacuo and then backfilled with argon. Then, anhydrous 1,2-DCE (0.5 mL) and $FeBr_3$ (0.049 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 1 mmol) was added to it and heated at 60℃, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (2

mL), and the aqueous layer was extracted with EtOAc (3 × 2 mL), dried over Na_2SO_4, and filtered; the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-40% EtOAc/Hexane) to afford the desired product **11**.

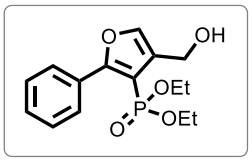
(d) Analytical data for furan derivatives:

4-(Hydroxymethyl)-2-phenylfuran-3-carbonitrile (7):



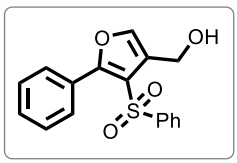
The title compound was synthesized following general procedure 7, using corresponding *β*-ketonitrile (**6**, 0.072 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **7** was isolated as a yellow liquid (0.043 g, 28%). TLC: R_f = 0.3 (SiO_2, 50% EtOAc/Hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.9 Hz, 2H), 7.49-7.41 (m, 4H), 4.70 (s, 2H), 2.23 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.7, 139.7, 130.4, 129.2, 128.1, 128.0, 125.5, 114.3, 91.8, 55.3; HRMS (ESI): *m/z* calcd for $C_{12}H_{10}O_2N$ $[M + H]^+$ 200.0706, found 200.0703.

Diethyl (4-(hydroxymethyl)-2-phenylfuran-3-yl)phosphonate (9):



The title compound was synthesized following general procedure 8, using corresponding *β*-ketophosphonates (**8**, 0.128 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $Fe(OTf)_3$ (0.025 g, 0.05 mmol), in CH_2Cl_2 (0.5 mL). The product **9** isolated as a colorless liquid (0.043 g, 28%). TLC: R_f = 0.4 (SiO_2, 60% EtOAc/Hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.6, 2.2 Hz, 2H), 7.47 (d, *J* = 2.9 Hz, 1H), 7.43–7.36 (m, 3H), 4.57 (s, 2H), 4.19–4.03 (m, 4H), 1.15 (t, *J* = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.3, 139.9, 133.7, 130.4, 129.6, 129.1, 128.6, 128.2, 105.6, 62.57, 62.52, 55.6, 16.0, 15.9; HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_5P$ $[M + H]^+$ 311.1043, found 311.1039.

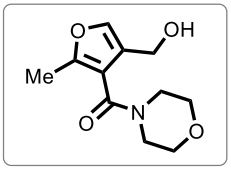
(5-Phenyl-4-(phenylsulfonyl)furan-3-yl)methanol (11):



The title compound was synthesized following general procedure 9, using corresponding *β*-ketosulfones (**10**, 0.137 g, 0.5 mmol), 3-oxetanone (**2**, 0.029 mL, 0.5 mmol), $FeBr_3$ (0.014 g, 0.05 mmol), in 1,2-DCE (0.5 mL). The product **11** was isolated as a yellow liquid (0.025 g, 16%). TLC: R_f = 0.4 (SiO_2, 40% EtOAc/Hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.68 (m, 2H), 7.59–7.55 (m, 2H), 7.52–7.48 (m, 1H), 7.46 (s, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.71–4.66 (m,

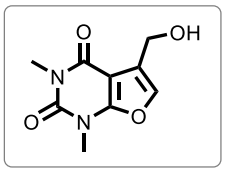
2H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.8, 142.1, 140.8, 140.2, 133.4, 129.4, 129.09, 129.04, 126.7, 126.2, 125.5, 121.7, 55.5, 21.6; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}O_4S$ $[M + H]^+$ 329.0842, found 329.0835.

Synthesis of (4-(Hydroxymethyl)-2-methylfuran-3-yl)(morpholino)methanone (13):



An oven-dried 25 mL round-bottom flask was equipped with a stir bar, then, morpholinobutane-1,3-dione **(12)** (0.086 g, 0.5 mmol) was added, evacuated under vacuum, and then backfilled with argon. Then, anhydrous CH_2Cl_2 (1 mL) and $Fe(OTf)_3$ (0.025 g, 0.05 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 0.029 mL, 0.5 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (5 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-50% EtOAc/Hexane) to afford the desired product **13** brown liquid (0.098 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 4.44 (s, 2H), 4.26 (d, *J* = 2.9 Hz, 1H), 3.86–3.82 (m, 4H), 3.24 (dd, *J* = 5.6, 3.8 Hz, 4H), 2.55 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 195.4, 163.8, 133.9, 126.1, 111.1, 66.6, 56.1, 51.7, 28.2; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}O_4N$ $[M + H]^+$ 226.1074, found 226.1075.

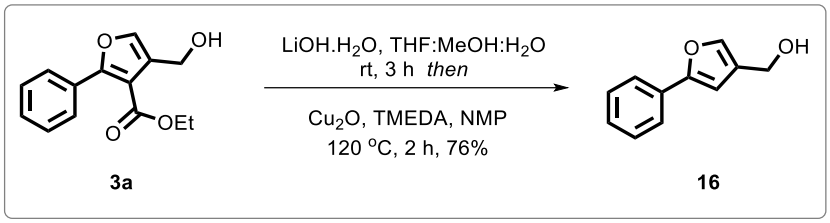
Synthesis of 5-(Hydroxymethyl)-1,3-dimethylfuro[2,3-d]pyrimidine-2,4(1*H*,3*H*)-dione (15):



An oven-dried 25 mL round bottom flask equipped with a stir bar, and 1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione **(14)** (0.078 g, 0.5 mmol) was added, evacuated under vacuum, and then backfilled with argon. Then, anhydrous CH_2Cl_2:THF (9:2) (1 mL) and $Fe(OTf)_3$ (0.025 g, 0.05 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 0.029 mL, 0.5 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (5 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **15** as yellow solid (0.085 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 4.57 (s, 2H), 4.29 (s, 1H), 3.50–3.48 (m, 3H), 3.39–3.29 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.7, 156.0, 150.4,

134.0, 124.7, 96.65, 96.62, 55.2, 29.5, 28.4; HRMS (ESI): *m/z* calcd for $C_9H_{11}O_4N_2$ $[M + H]^+$ 211.0713, found 211.0707.

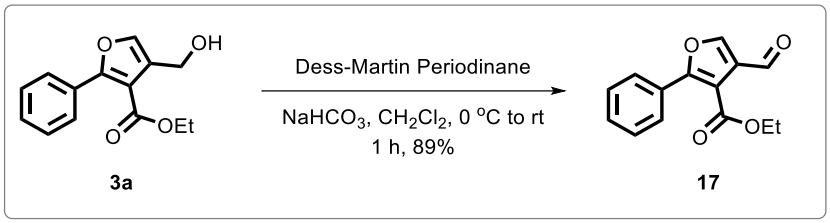
Synthesis of (5-Phenylfuran-3-yl)methanol (16):



To the stirred solution of furan ester (**3a**, 0.5 g, 2.03 mmol) in (1:1:1) ratio of THF:MeOH:H_2O (6 mL), $LiOH.H_2O$ (0.255 g, 6.09 mmol) was added at room temperature. The reaction was stirred for 3 hours at room temperature. After completion of the reaction, it was quenched with saturated aq. solution of NH_4Cl, and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (SiO_2, 0-40% EtOAc/Hexane) to afford the desired product as colorless solid. The crude acid was used without further purification.

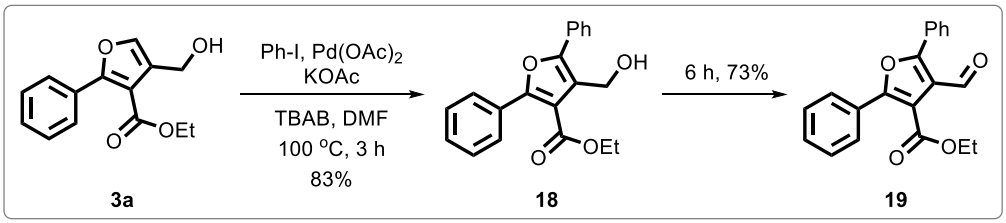
Next, an oven-dried 250 mL round-bottom flask equipped with a stir bar was cooled under vacuum. To it was added a stirred solution, furan carboxylic acid (0.4 g, 1.83 mmol) in NMP (4 mL) and stirred to homogeneity. Then, Cu_2O (0.013 g, 0.091 mmol), TMEDA (0.027 mL, 0.183 mmol) was added sequentially and refluxed the reaction mixture at 120°C for 2 h. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with aqueous 1 N HCl (10 mL), and filtered through a short celite pad, and the aqueous layer was extracted with EtOAc (3 x 10 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography to afford the desired product **16** (0.262 g, 76%) as a white solid. TLC: R_f = 0.7 (SiO_2, 30% EtOAc/ hexanes). IR ($CHCl_3$) 3364, 2944, 2881, 2840, 1762, 1595, 1541, 1476, 1290, 1242, 1214, 1166, 1029, 978, 932, 827, 782, 724, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.19 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.16 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.78 (ddd, *J* = 8.0, 2.6, 1.3 Hz, 1H), 6.63 (s, 1H), 4.50 (s, 2H), 3.79 (s, 3H), 2.34 (s, 1H); $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) δ 159.90, 154.56, 139.36, 132.02, 129.83, 127.26, 116.49, 113.41, 109.18, 105.50, 56.69, 55.31; HRMS (ESI): *m/z* calcd for $C_{12}H_{13}O_3$ $[M+H]^+$ 205.0859, found 205.0858.

Synthesis of ethyl 4-formyl-2-phenylfuran-3-carboxylate (17):



To furan alcohol **3a** (0.5 g, 2.03 mmol) in anhydrous CH_2Cl_2 (8 mL), Dess–Martin periodinane (DMP) (1.03 g, 2.43 mmol), and $NaHCO_3$ (0.187 g, 2.23 mmol) were added at 0 °C, and the reaction mixture was stirred for 1 h at the same temperature. The reaction progress was monitored by TLC. After completion of the reaction, it was quenched with 1:1 ratio of a saturated aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), then the combined organic layers were washed with brine, dried over Na_2SO_4, and filtered, and the solvent was evaporated under reduced pressure. The resulting crude product was purified by silica gel column chromatography to afford the desired product **17** (0.442 g, 89%) as a colorless liquid. TLC: R_f = 0.5 (SiO_2, 40% EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.06 (s, 1H), 7.85–7.77 (m, 2H), 7.49–7.40 (m, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H; ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 186.9, 163.13, 158.88, 146.83, 130.18, 128.80, 128.59, 128.36, 127.85, 112.05, 61.52, 14.16; HRMS (ESI): *m/z* calcd for $C_{14}H_{13}O_4$ $[M+H]^+$ 245.0808, found 205.0805.

Synthesis of ethyl 4-(hydroxymethyl)-2,5-diphenylfuran-3-carboxylate (18) & ethyl 4-formyl-2,5-diphenylfuran-3-carboxylate (19):



To an oven-dried 25 mL sealed tube equipped with a stir bar and DMF solutions (8 mL), furan ester **3a** (0.5 g, 2.03 mmol), iodobenzene (0.79 mL, 7.10 mmol), $Pd(OAc)_2$ (0.045 g, 0.203 mmol), KOAc (0.99 g, 10.15 mmol), and TBAB (1.30 g, 4.06 mmol) were added. The reaction mixture was flushed with N_2 and heated at 100 °C for 3 h, giving **18** along with minor amounts of **19** as visualised on TLC. Prolonged heating for an additional 6 h resulted in the complete conversion of **18** to **19**. After completion, the solvent was removed under reduced pressure, and the crude residue diluted with ice-cold water and was extracted with EtOAc (3 × 15 mL), dried

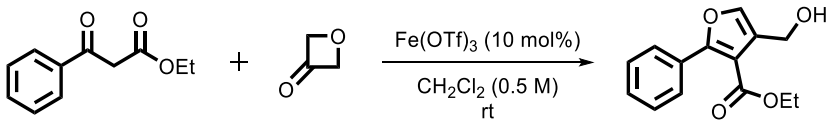
over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-30% EtOAc/Hexane) to afford the desired products.

For **18**: (0.545 g, 83%) as a colorless liquid. TLC: R_f = 0.4 (SiO_2, 30% EtOAc/ hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.76 (m, 2H), 7.74–7.64 (m, 2H), 7.53–7.34 (m, 6H), 4.78 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 165.0, 157.0, 151.2, 130.0, 129.6, 129.5, 129.0, 128.8, 128.7, 128.0, 127.4, 122.0, 115.1, 61.2, 55.9, 14.0; HRMS (ESI): *m/z* calcd for $C_{20}H_{18}O_4Na$ $[M+Na]^+$ 345.1097, found 345.1084.

For **19**: (0.48 g, 73%) as a colorless liquid. TLC: R_f = 0.6 (SiO_2, 30% EtOAc/ hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.96–7.87 (m, 2H), 7.82 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.57–7.48 (m, 3H), 7.48–7.39 (m, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 185.8, 164.1, 158.6, 154.0, 130.7, 129.8, 129.0, 128.7, 128.6, 128.5, 128.4, 127.5, 122.1, 114.4, 61.9, 14.1; HRMS (ESI): *m/z* calcd for $C_{20}H_{17}O_4$ $[M+H]^+$ 321.1121, found 321.1112.

6. Scale-up synthesis

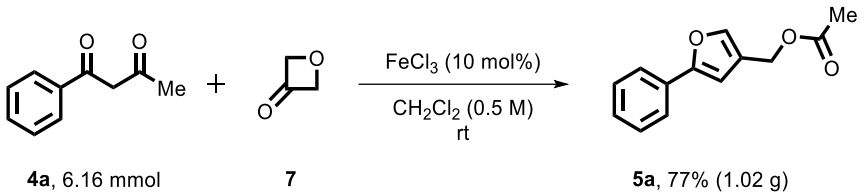
(a) Synthesis of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



1a, 5.20 mmol **2** **3a**, 94% (1.21 g)

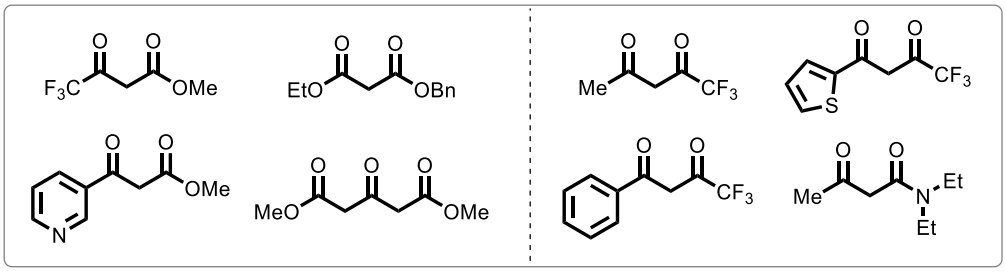
An oven-dried 100 mL round bottom flask equipped with a stir bar, ethyl 3-oxo-3-phenylpropanoate (**1a**, 1 g, 5.20 mmol) was added, evacuated under vacuum, and then backfilled with argon. Then, anhydrous CH_2Cl_2 (10 mL) and $Fe(OTf)_3$ (0.261 g, 0.520 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 0.297 mL, 5.20 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (15 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **3a** (1.21 g, 94%).

(b) Synthesis of (5-Phenylfuran-3-yl)methyl acetate (5a):



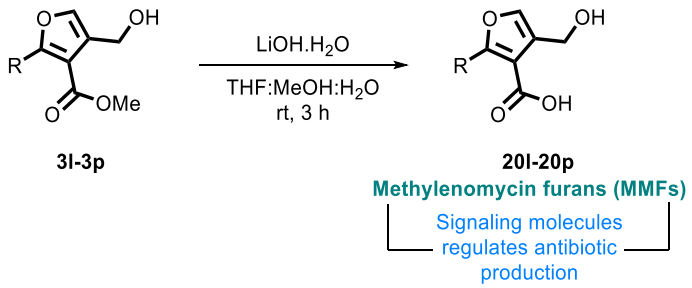
An oven-dried 100 mL round bottom flask equipped with a stir bar. Then, 1-phenylbutane-1,3-dione (**4a**, 1 g, 6.16 mmol) was taken and evacuated under vacuo and then backfilled with argon. Then, anhydrous CH_2Cl_2 (0.5 mL) and $FeCl_3$ (0.1 g, 0.616 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (**2**, 0.352 mL, 6.16 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, it was quenched with saturated aqueous solution $NaHCO_3$ (15 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), dried over Na_2SO_4, and filtered, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO_2, 0-20% EtOAc/Hexane) to afford the desired product **5a** (1.02 g, 77%).

7. Failed substrates



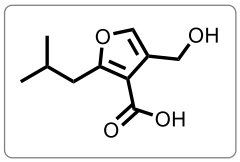
8. Application in total synthesis of natural products

(a) General Procedure-13 for the total synthesis of methylenomycin furans (MMF 1-5) (GP13):



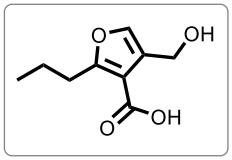
To the stirred solution of MMF ester (**3l-3p**, 1 mmol) in (1:1:1) ratio of THF:MeOH:H_2O (1 mL), LiOH.H_2O (3 mmol) was added at room temperature. The reaction was stirred for 3 hours at room temperature. After completion of the reaction, it was quenched with saturated aq. solution of NH_4Cl, and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (SiO_2, 0-40% EtOAc/Hexane) to afford the desired product **20l-20p**. The characterization data aligns perfectly with the reported data in the literature.[14]

Methylenomycin furan 1 (MMF1) (20l):



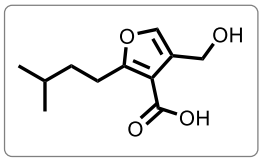
The title compound was synthesized following general procedure 13, using corresponding MMF ester (**3l**, 0.1 g, 0.47 mmol), LiOH.H_2O (0.059 g, 1.41 mmol), in THF:MeOH:H_2O in (1:1:1) ratio of (1 mL). The product **20l** was isolated as a white solid (0.072 g, 77%). TLC: R_f= 0.2 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3608, 2963, 2361, 1668, 1602, 1555, 1523, 1467, 1427, 1120, 1019, 928, 849, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 6.91 (br. s., 1H), 4.61 (s, 2H), 2.89 (d, *J* = 7.3 Hz, 2H), 2.10 (quind, *J* = 6.8, 13.7 Hz, 1H), 0.94 (d, *J* = 6.78 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2, 166.3, 138.9, 125.5, 112.3, 55.7, 36.9, 28.4, 22.5; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}O_4$ $[M - H]^-$ 197.0808, found 197.0810.

Methylenomycin furan 2 (MMF2) (20m):



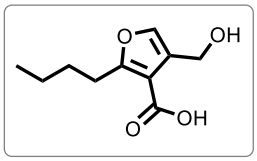
The title compound was synthesized following general procedure 13, using corresponding MMF ester (**3m**, 0.1 g, 0.50 mmol), LiOH.H_2O (0.063 g, 1.51 mmol), in THF:MeOH:H_2O in (1:1:1) ratio of (1 mL). The product **20m** was isolated as a white solid (0.076 g, 82%). TLC: R_f= 0.2 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3488, 2969, 2877, 2361, 1668, 1602, 1557, 1523, 1467, 1426, 1120, 1017, 986, 959, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (br. s., 1H), 7.27 (s, 1H), 4.61 (s, 2H), 2.97 (t, *J* = 7.38 Hz, 2H), 1.81–1.63 (m, 2H), 0.95 (t, *J* = 7.38 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.1, 166.8, 138.8, 125.5, 111.8, 55.7, 30.1, 21.2, 13.8; HRMS (ESI): *m/z* calcd for $C_9H_{11}O_4$ $[M - H]^-$ 183.0652, found 183.0653.

Methylenomycin furan 3 (MMF3) (20n):



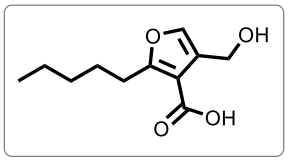
The title compound was synthesized following general procedure 13, using corresponding MMF ester (**3n**, 0.1 g, 0.50 mmol), $LiOH.H_2O$ (0.063 g, 1.51 mmol), in THF:MeOH:H_2O in (1:1:1) ratio of (1 mL). The product **20n** was isolated as a white solid (0.074 g, 80%). TLC: R_f = 0.2 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3425, 2364, 1661, 1604, 1523, 1475, 1425, 1022, 928, 849, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 6.91 (br. s., 1H), 4.60 (s, 2H), 3.00 (t, *J* = 7.38 Hz, 2H), 1.64-1.50 (m, 3H), 0.93 (d, *J* = 5.88 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.1, 167.3, 138.8, 125.6, 111.3, 55.7, 36.8, 27.9, 26.4, 22.4; HRMS (ESI): *m/z* calcd for $C_{11}H_{15}O_4$ $[M - H]^-$ 211.0965, found 211.0969.

Methylenomycin furan 4 (MMF4) (20o):



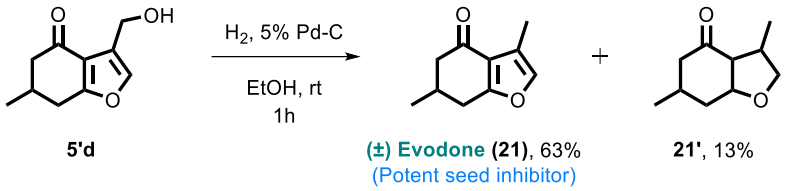
The title compound was synthesized following general procedure 13, using corresponding MMF ester (**3o**, 0.1 g, 0.47 mmol), $LiOH.H_2O$ (0.059 g, 1.41 mmol), in THF:MeOH:H_2O in (1:1:1) ratio of (1 mL). The product **20o** was isolated as a white solid (0.074 g, 80%). TLC: R_f = 0.2 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3683, 3423, 2965, 2932, 1664, 1603, 1525, 1471, 1426, 1020, 928, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 6.54 (br. s., 2H), 4.60 (s, 2H), 3.00 (t, *J* = 7.50 Hz, 2H), 1.66 (quin, *J* = 7.63 Hz, 2H), 1.37 (qd, *J* = 7.41, 15.13 Hz, 2H), 0.93 (t, *J* = 7.25 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.1, 167.1, 138.8, 125.5, 111.6, 55.7, 30.1, 28.0, 22.4, 13.8; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}O_4$ $[M - H]^-$ 197.0808, found 197.0811.

Methylenomycin furan 5 (MMF5) (20p):



The title compound was synthesized following general procedure 13, using corresponding MMF ester (**3p**, 0.1 g, 0.44 mmol), $LiOH.H_2O$ (0.055 g, 1.32 mmol), in THF:MeOH:H_2O in (1:1:1) ratio of (1 mL). The product **20p** was isolated as a white solid (0.081 g, 87%). TLC: R_f = 0.2 (SiO_2, 20% EtOAc/Hexanes). IR ($CHCl_3$) 3684, 3421, 2961, 2932, 2356, 1671, 1602, 1524, 1427, 1120, 1019, 928, 850, 669, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 4.60 (s, 2H), 3.00 (t, *J* = 7.50 Hz, 2H), 1.69 (t, *J* = 7.38 Hz, 2H), 1.40–1.29 (m, 4H), 0.90 (t, *J* = 6.88 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2, 167.2, 138.8, 125.6, 111.5, 55.7, 31.5, 28.3, 27.7, 22.4, 14.0; HRMS (ESI): *m/z* calcd for $C_{11}H_{15}O_4$ $[M - H]^-$ 211.0965, found 211.0969.

(b) Total Synthesis of (±)-evodone (21):



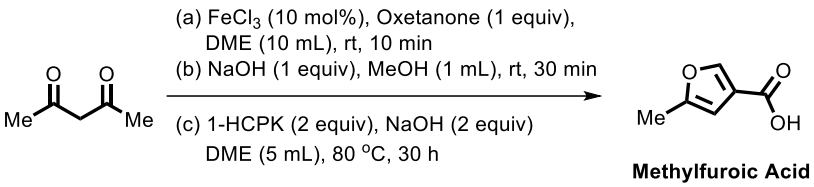
In a 25 mL round bottom flask, was taken a solution of 3-(hydroxymethyl)-6-methyl-6,7-dihydrobenzofuran-4(5H)-one (**5′d**, 0.2 g, 1.10 mmol) in EtOH (2 mL), 5% palladium on charcoal (0.023 g, 0.22 mmol), and the reaction was stirred for 1 h under H_2 atmosphere. The reaction was monitored by TLC until the starting material was consumed entirely (1.5 h). After completion of the reaction, the reaction mixture was filtered through a short celite pad, and the filtrate was concentrated in vacuum. The crude product was purified by silica gel column chromatography using 5% EtOAc/Hexanes to afford the desired product **21** as white solid (0.114 g, 63%) & **21′** as colorless liquid (0.024 g, 13%). The characterization data aligns perfectly with the reported data in the literature.[15]

Note: The natural product **21** *is highly volatile. Precautionary measures must be taken when using the rotary evaporator, preferably at a lower temperature.*

For **21**, TLC: R_f = 0.7 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3682, 3417, 1664, 1526, 1427, 1025, 928, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 2.90 (dd, *J* = 16.3, 4.8 Hz, 1H), 2.54–2.44 (m, 2H), 2.44–2.35 (m, 1H), 2.27–2.20 (m, 1H), 2.18 (s, 3H), 1.15 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.4, 167.3, 139.2, 120.2, 119.1, 46.9, 31.8, 31.0, 21.2, 9.1; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}O_2$ $[M + H]^+$ 165.0910, found 165.0912.

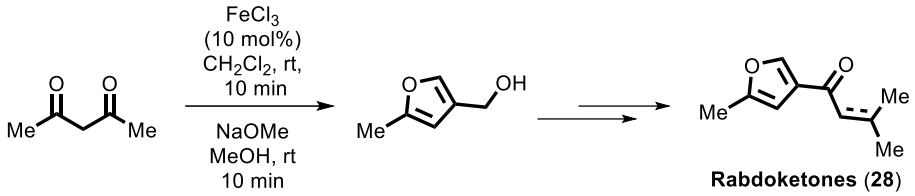
For **21′**, TLC: R_f = 0.4 (SiO_2, 10% EtOAc/Hexanes). IR ($CHCl_3$) 3685, 2360, 1603, 1524, 1477, 1425, 1024, 928, 850, 670, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.31 (ddd, *J* = 10.6, 9.0, 6.5 Hz, 1H), 3.86 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.64 (dd, *J* = 8.6, 3.3 Hz, 1H), 2.97 (t, *J* = 8.8 Hz, 1H), 2.76–2.61 (m, 1H), 2.55–2.42 (m, 1H), 2.22–2.10 (m, 1H), 1.89–1.78 (m, 1H), 1.74 (dd, *J* = 15.8, 12.7 Hz, 1H), 1.27 (d, *J* = 13.3 Hz, 1H), 1.05 (d, *J* = 6.3 Hz, 3H), 1.00 (d, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 212.4, 77.9, 73.8, 54.0, 50.4, 39.1, 37.3, 26.8, 21.9, 16.4; HRMS (ESI): *m/z* calcd for $C_{10}H_{15}O_2$ $[M + H]^+$ 167.1067, found 167.1069.

(c) Scalable Process Synthesis for Methylfuroic acid (27):



A 250 ml sealed tube equipped with a magnetic stir bar was charged with acetylacetone (1 g, 9.98 mmol), evacuated under vacuo, and then backfilled with argon. Then, anhydrous DME (10 mL) and $FeCl_3$ (0.161 g, 0.998 mmol) were added at room temperature, and the mixture was stirred for 5 min. Then, 3-oxetanone (0.585 mL, 9.98 mmol) was added, and the reaction progress was monitored by TLC (10 min). After the reaction was complete, a powder of NaOH solids (0.399 g, 9.98 mmol) was added, along with anhydrous methanol (1 mL). The mixture was stirred for 30 min at room temperature, monitored by TLC until completion. Next, 1-hydroxycyclohexyl phenyl ketone (4 g, 19.97 mmol) and powder of NaOH solids (0.798 g, 19.97 mmol) was added with DME (10 mL). The reaction tube was purged with argon, then sealed with a cap, and the reaction mixture was stirred at 80 °C (note: take suitable precautions while setting of reaction in the sealed tube). The reaction progress was monitored by TLC until no starting material was observed (approximately 30 hours). After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with water (100 mL). The combined layers were then extracted with diethyl ether (3 × 150 mL) to remove 1(hydroxy(phenyl)methyl)cyclohexanol and DME before acidification. The aqueous layer was then neutralized with 12 (N) HCl and extracted with EtOAc (3 × 150 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography to afford desired product as a white solid. (Yield: 0.905 g, 72%). TLC: R_f = 0.5 (SiO_2, 40% EtOAc/hexanes). IR ($CHCl_3$) 3616, 3433, 2896, 1632, 1523, 1426, 1045, 928, 877, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 6.35 (s, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, CDCl3) δ 168.4, 154.2, 147.7, 119.3, 105.6, 13.5; HRMS (ESI): *m/z* calcd for $C_6H_5O_3$ $[M - H]^-$ 125.0233, found 125.0231.

(d) Formal total synthesis of Rabdoketone (28)



An oven-dried 100 mL round bottom flask equipped with a stir bar. Then, acetylacetone (1 g, 9.98 mmol) was taken and evacuated under vacuo and then backfilled with argon. Then, anhydrous CH_2Cl_2 (0.5 mL) and $FeCl_3$ (0.161 g, 0.998 mmol) were added at room temperature and stirred for 5 min. Then, 3-oxetanone (0.585 mL, 9.98 mmol) was added to it, and the reaction progress was monitored by TLC. After completion of the reaction, MeOH (15 mL) was added and stirred to homogeneity. To it was added NaOMe (0.421 g, 7.79 mmol) portion-wise, and then the reaction mixture was stirred for 10 min at room temperature, and the reaction progress was monitored by TLC. After the completion of the reaction, the solvent was evaporated under reduced pressure, and the resulting crude was purified by silica gel column chromatography to afford the desired product. (0.744 g, 85%) TLC: R_f = 0.7 (SiO_2, 40% EtOAc/hexanes). IR ($CHCl_3$) 3616, 3433, 2976, 2896, 1636, 1524, 1427, 1045, 928, 877, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.02 (s, 1H), 4.48 (s, 2H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.3, 138.2, 126.1, 105.9, 57.0, 13.7; HRMS (ESI): m/z calcd for $C_6H_9O_2$ $[M + H]^+$ 113.0597, found 113.0599.

8. References

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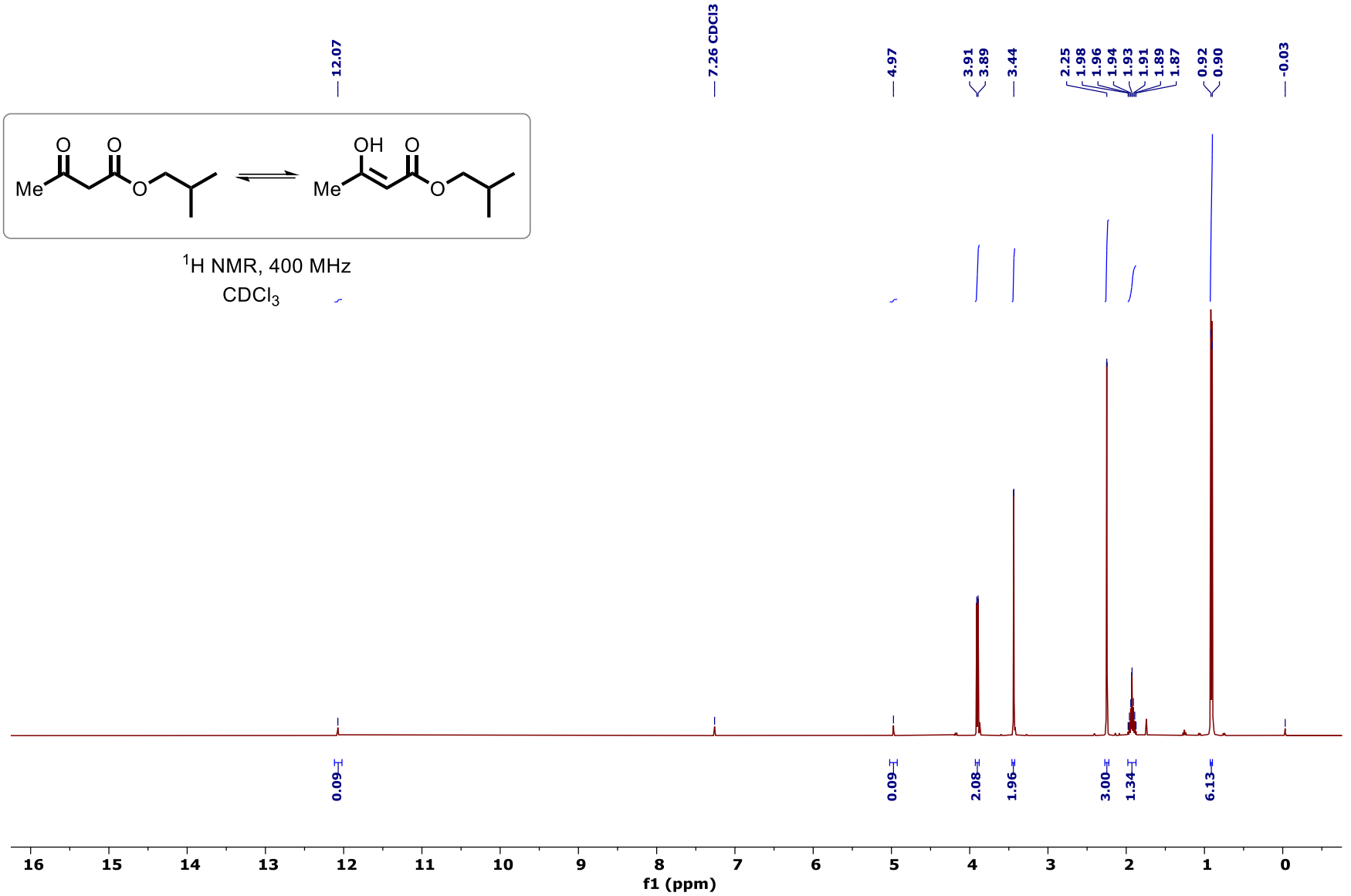
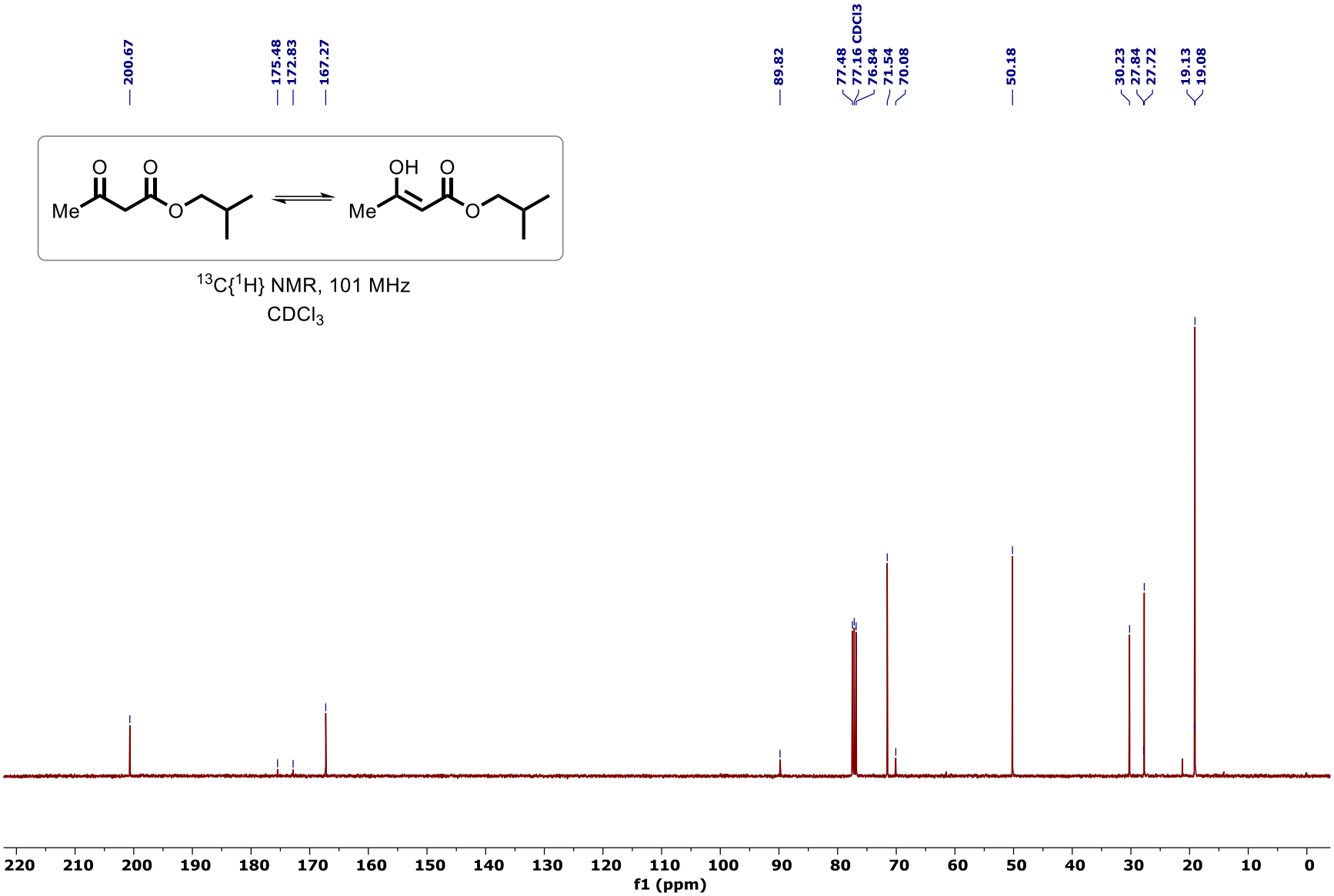
9. ^{1}H, ^{13}C and 2D NMR spectra

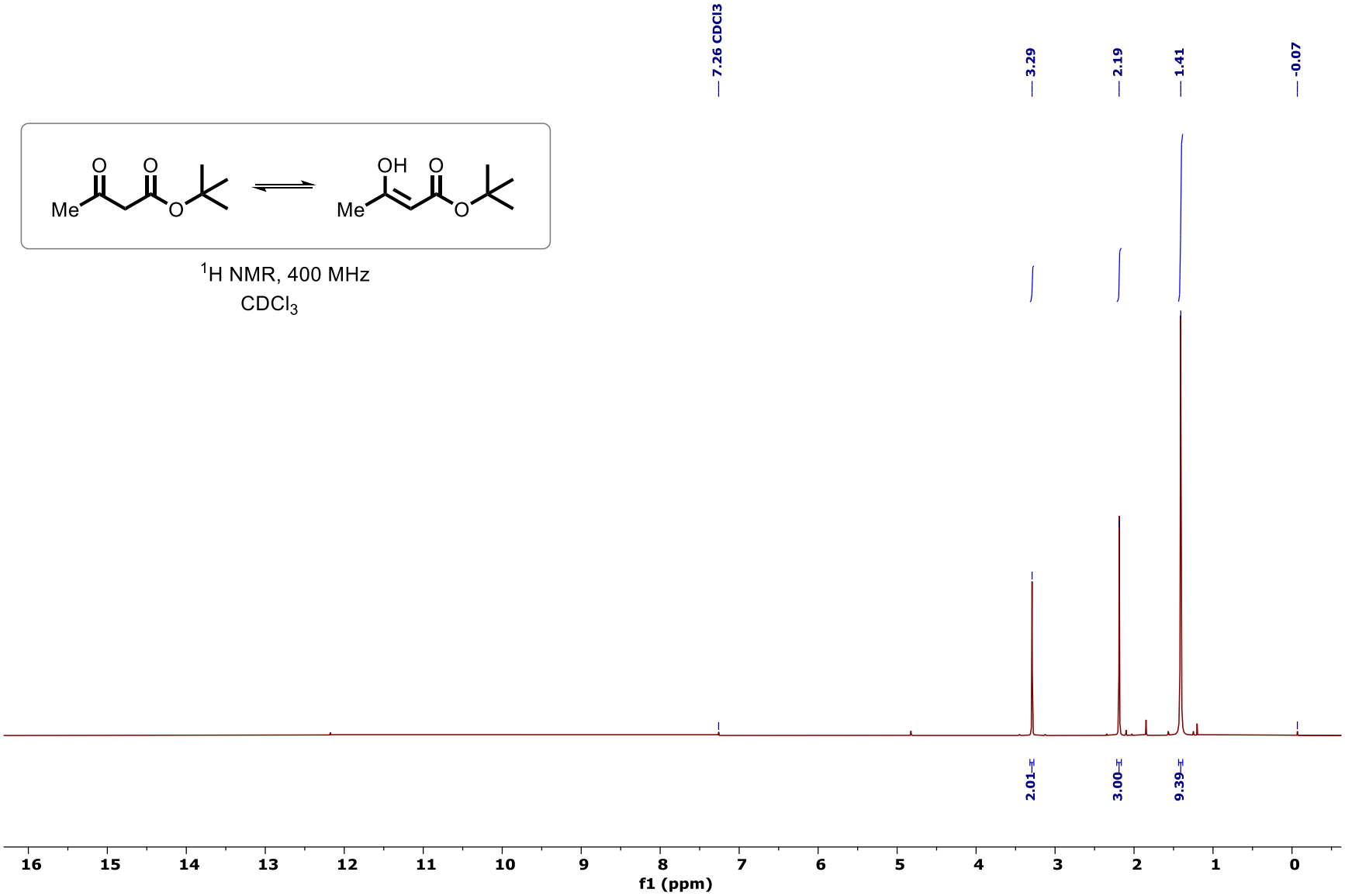
^{1}H NMR spectrum of Isobutyl 3-oxobutanoate (1d):



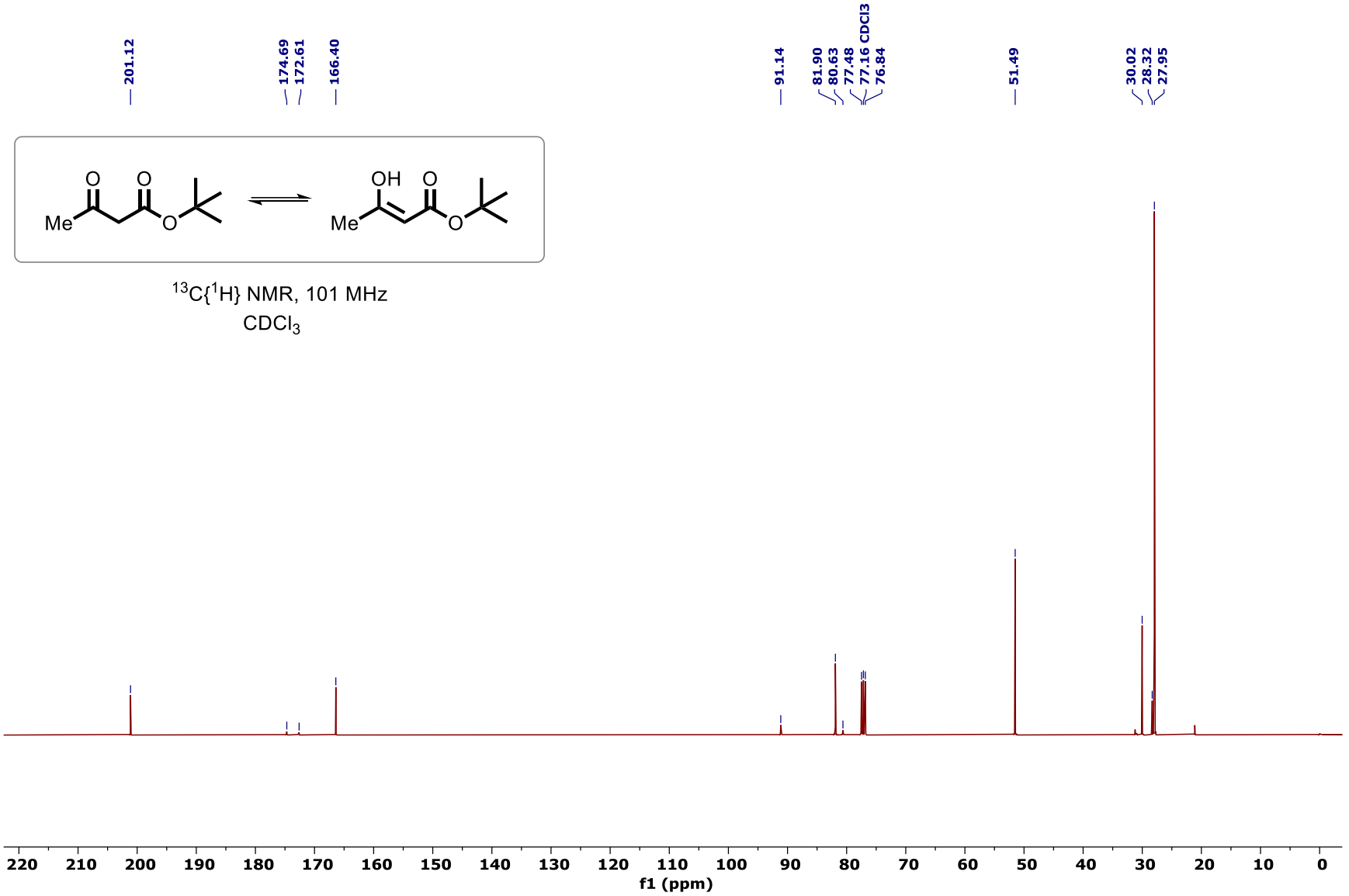
$^{13}C\{^{1}H\}$ NMR spectrum of Isobutyl 3-oxobutanoate (1d):



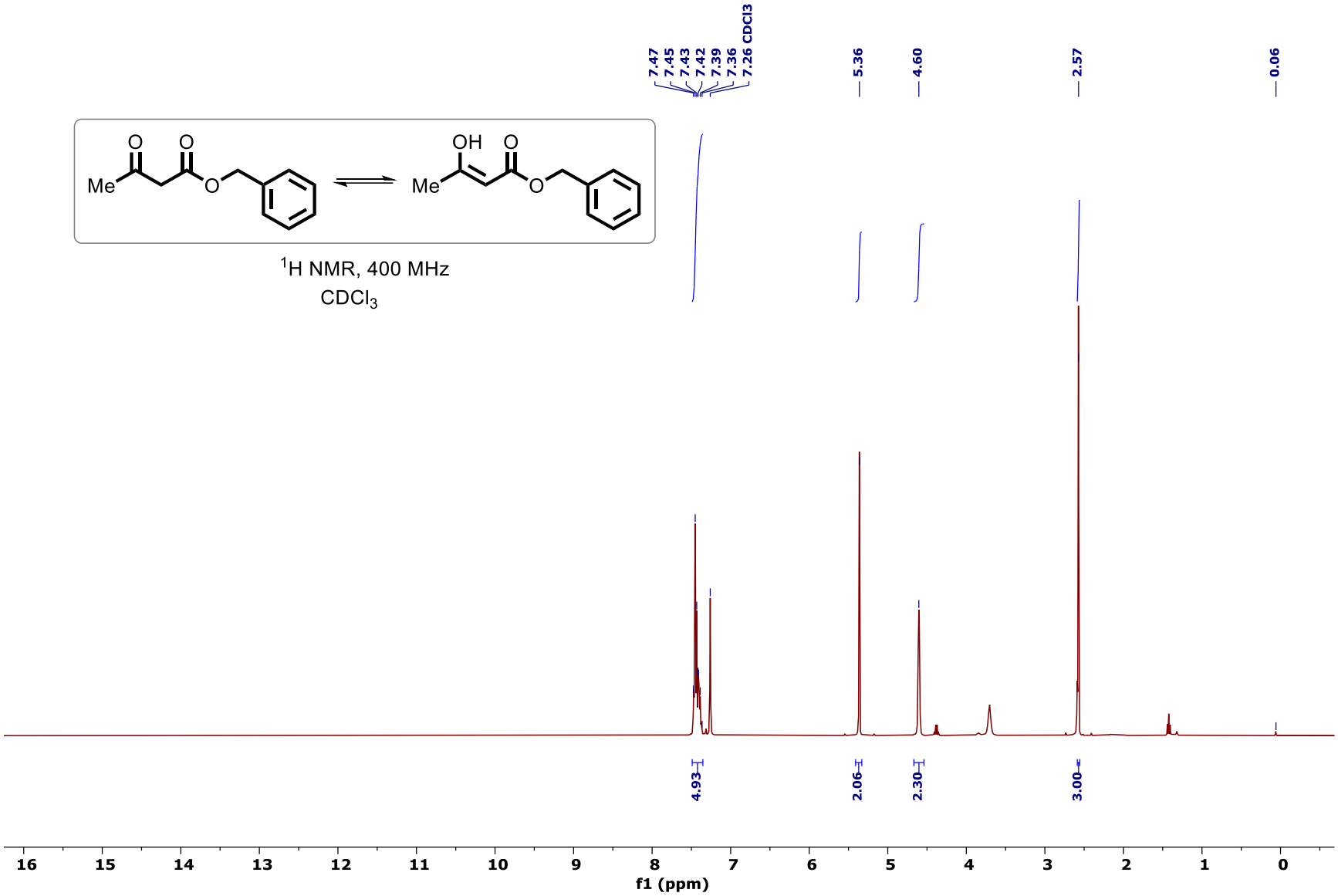
^{1}H NMR spectrum of Tert-butyl 3-oxobutanoate (1e):



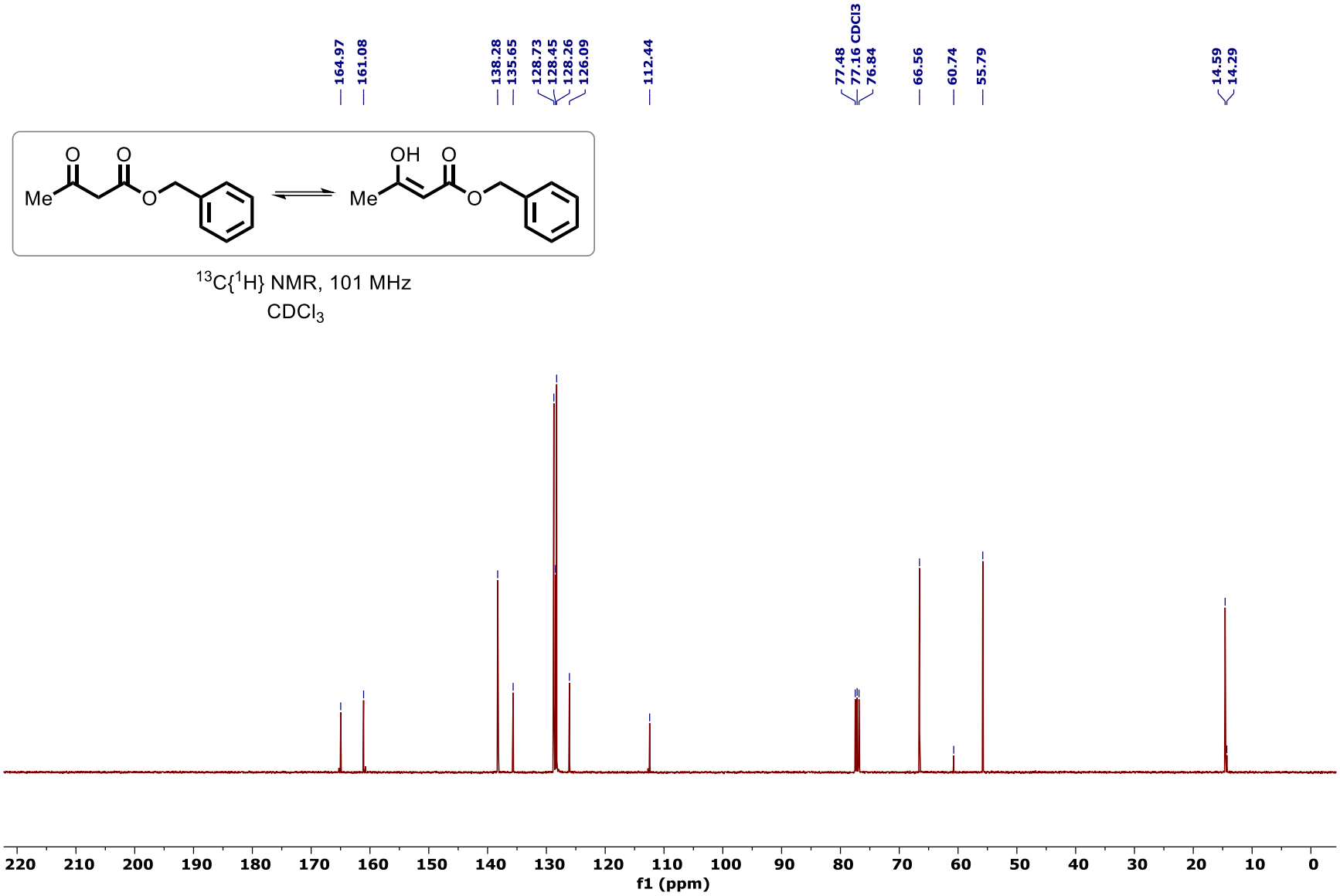
$^{13}C\{^{1}H\}$ NMR spectrum of Tert-butyl 3-oxobutanoate (1e):



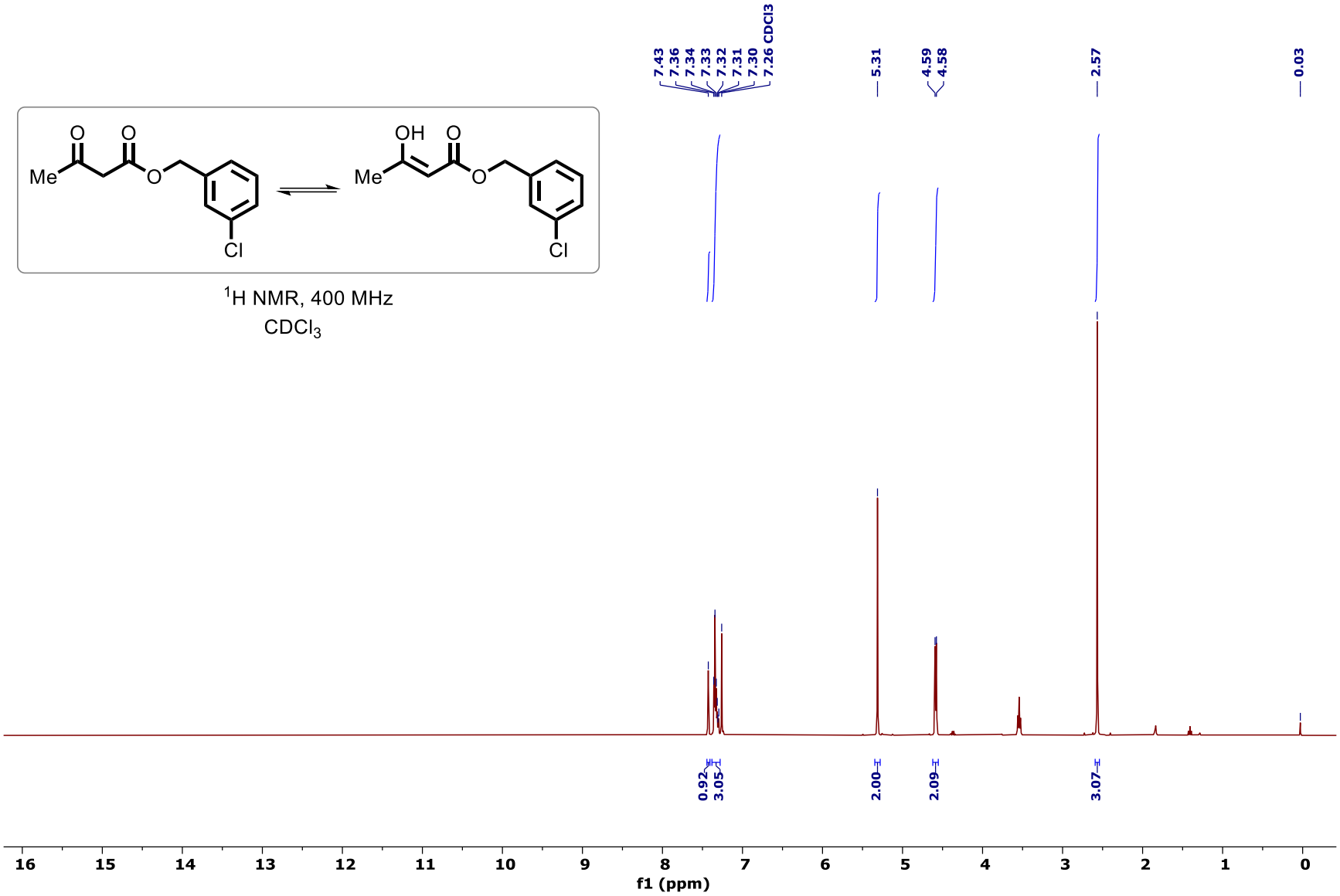
^{1}H NMR spectrum of Benzyl 3-oxobutanoate (1h):



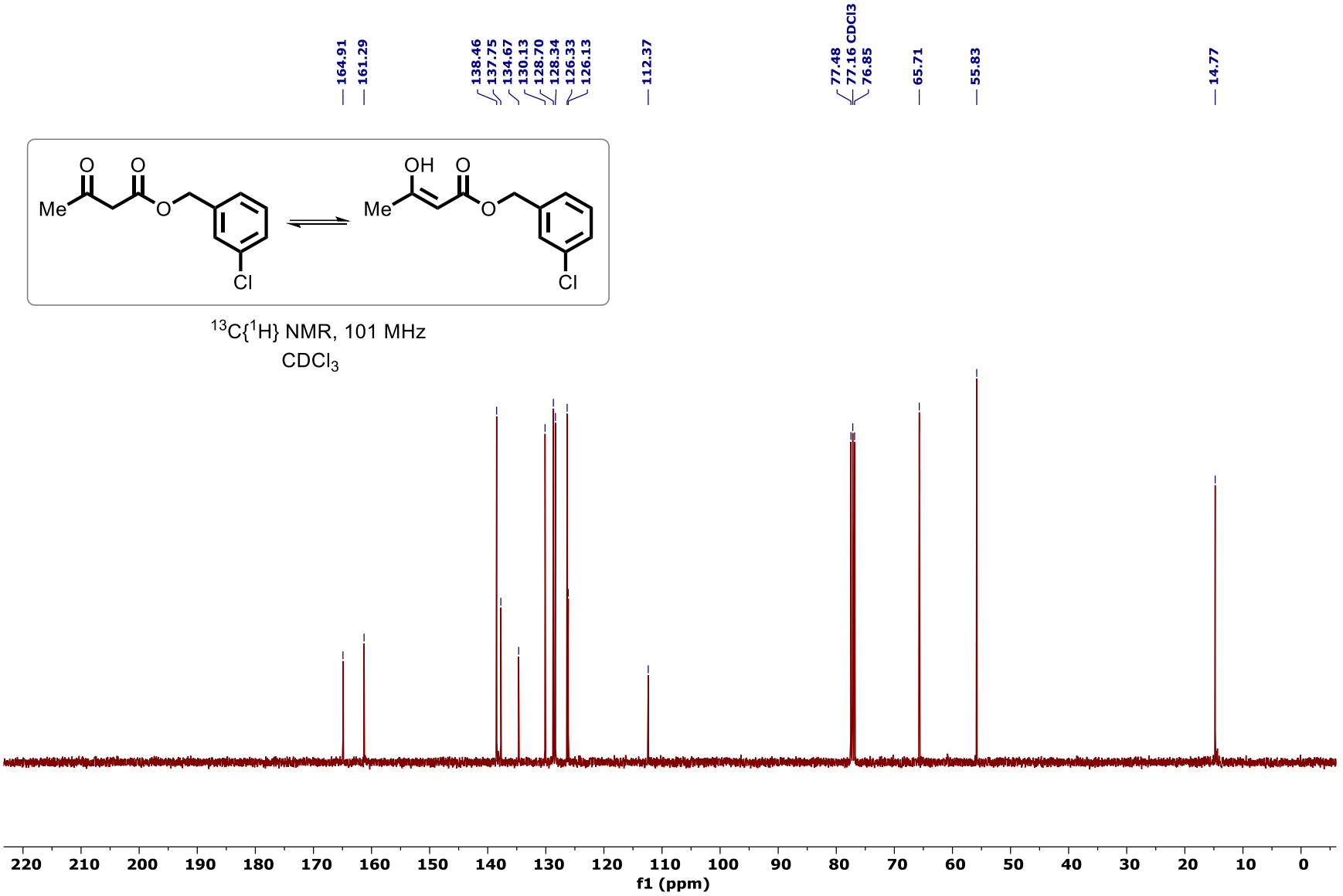
$^{13}C\{^{1}H\}$ NMR spectrum of Benzyl 3-oxobutanoate (1h):



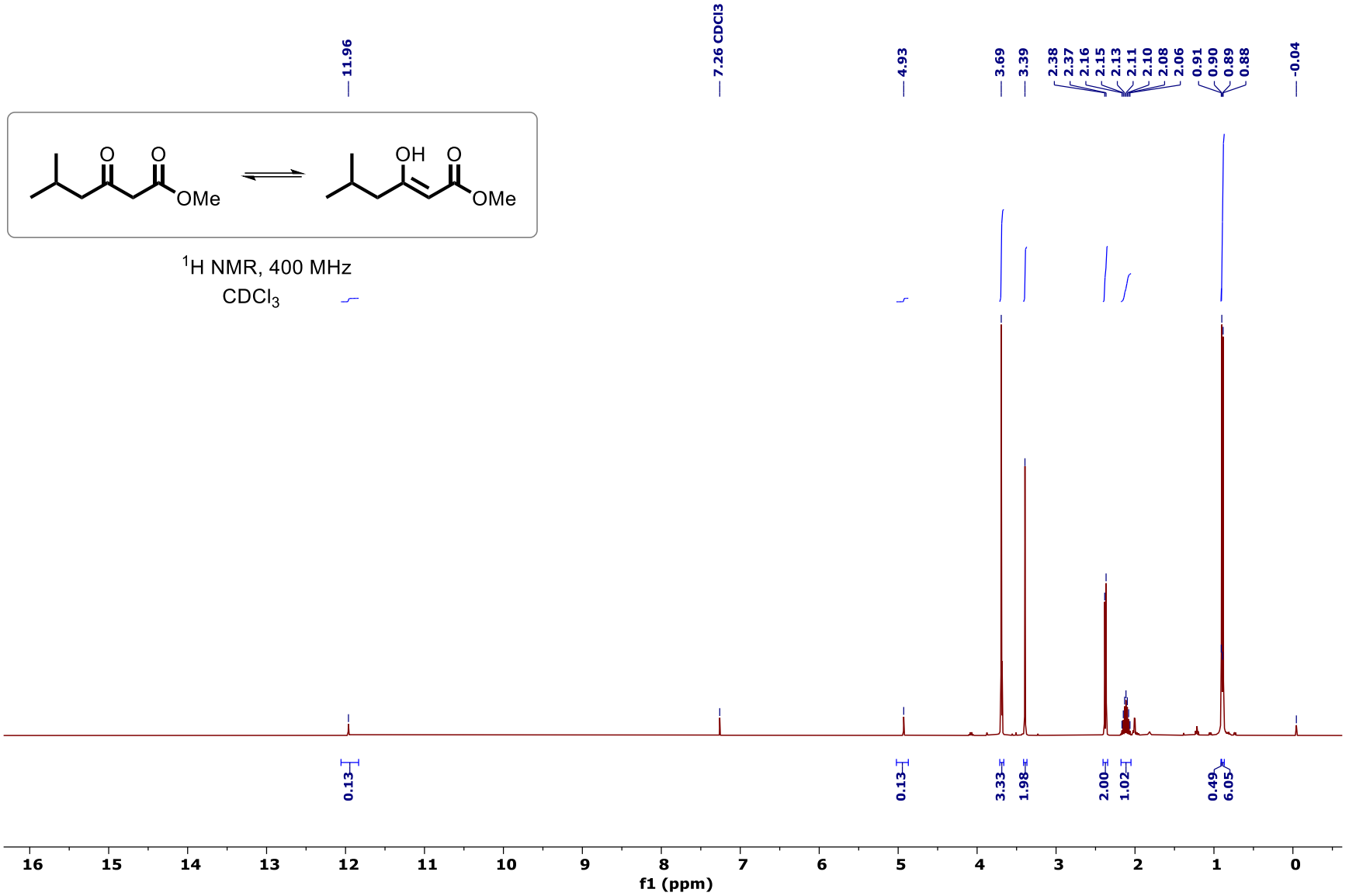
^{1}H NMR spectrum of 3-Chlorobenzyl 3-oxobutanoate (1i):



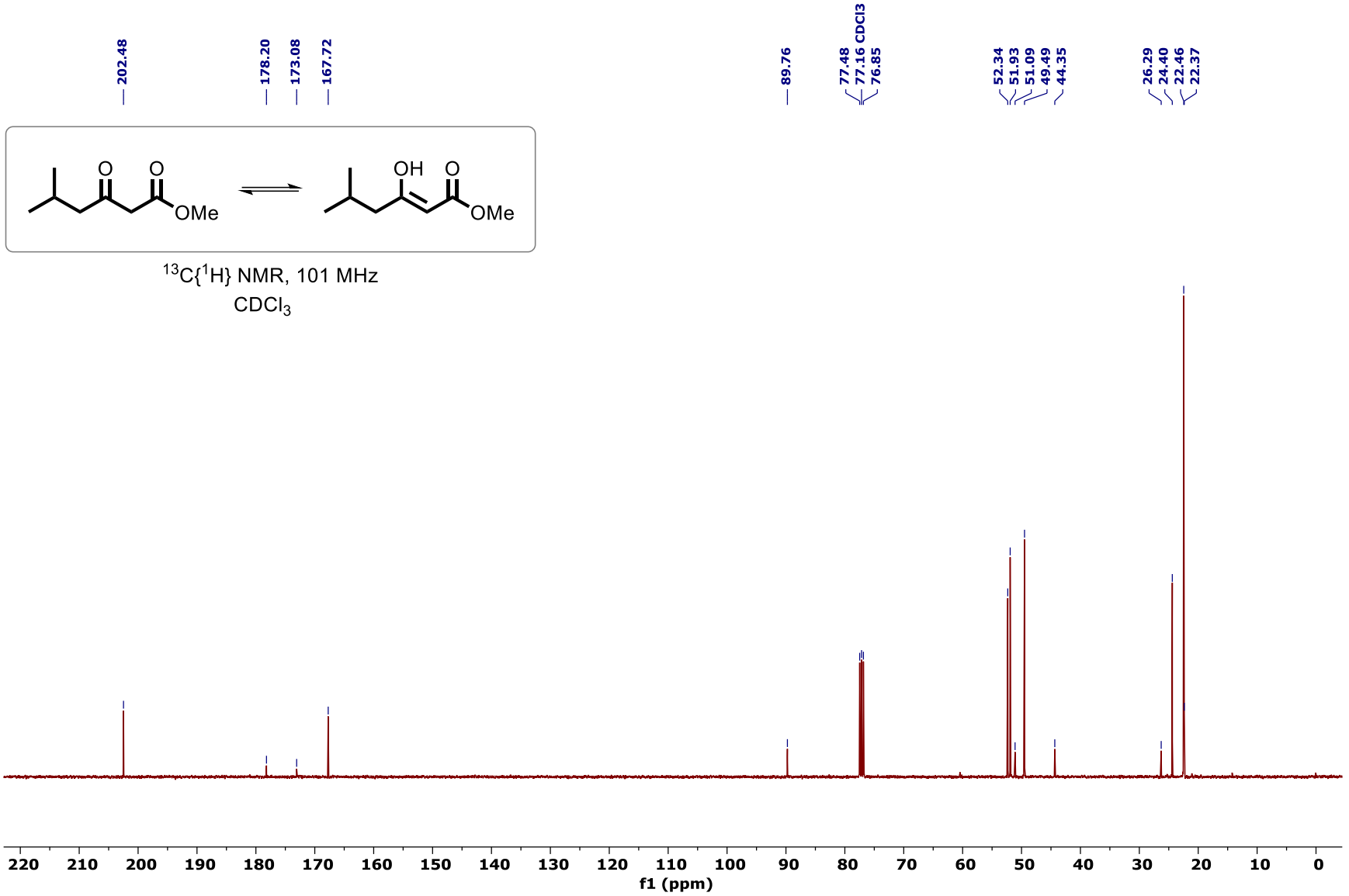
$^{13}C\{^{1}H\}$ NMR spectrum of 3-Chlorobenzyl 3-oxobutanoate (1i):



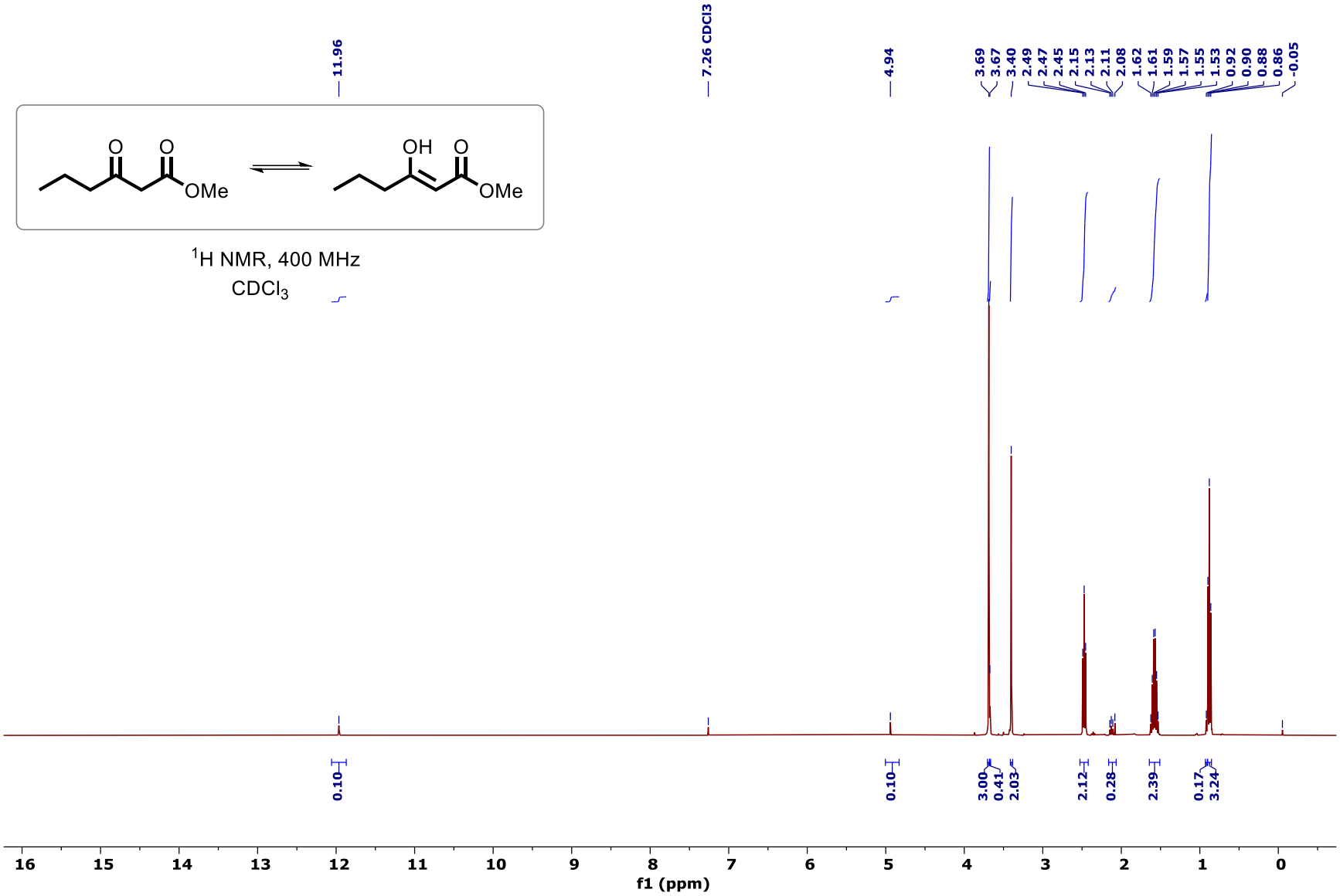
^{1}H NMR spectrum of Methyl 5-methyl-3-oxohexanoate (1l):



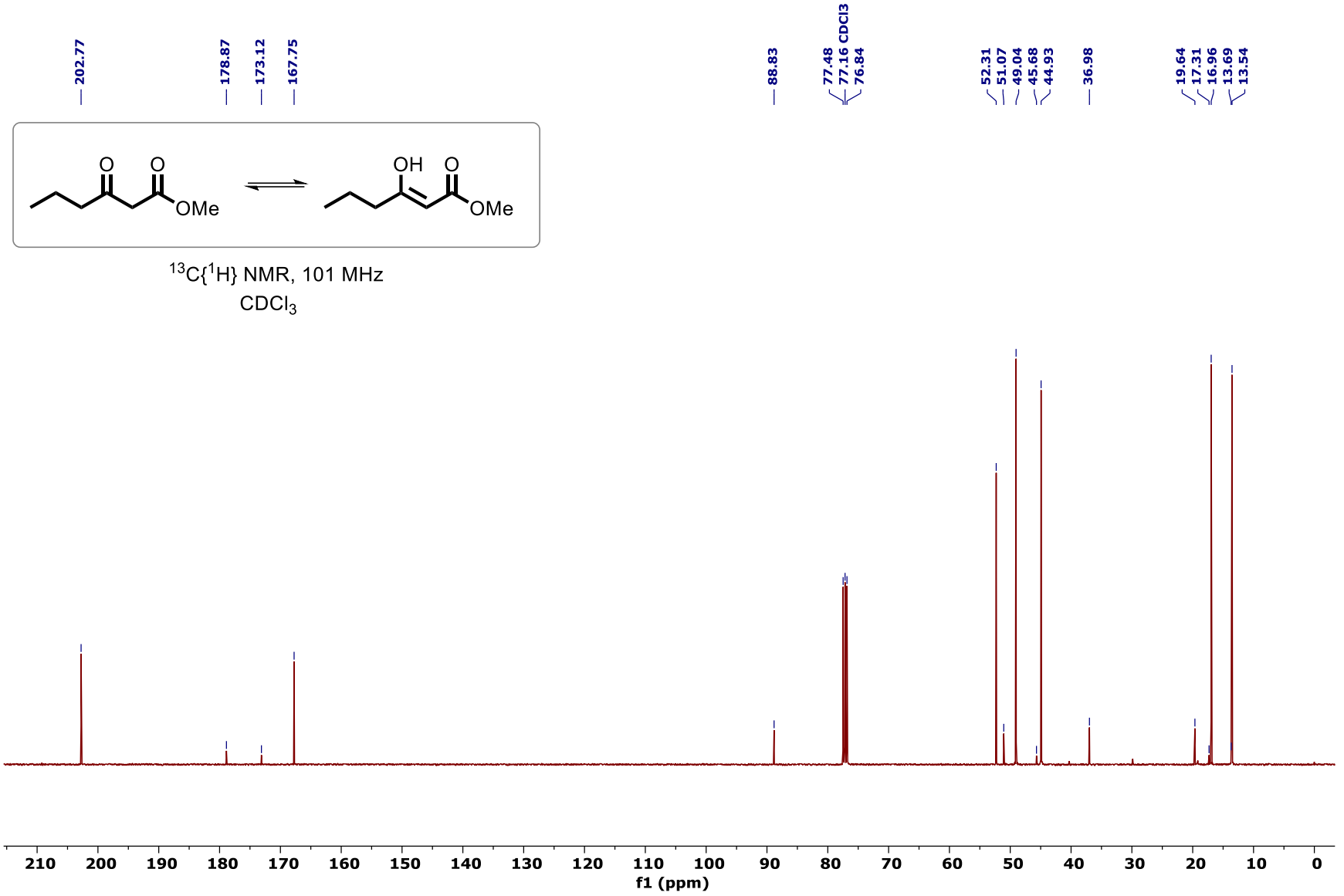
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 5-methyl-3-oxohexanoate (1l):



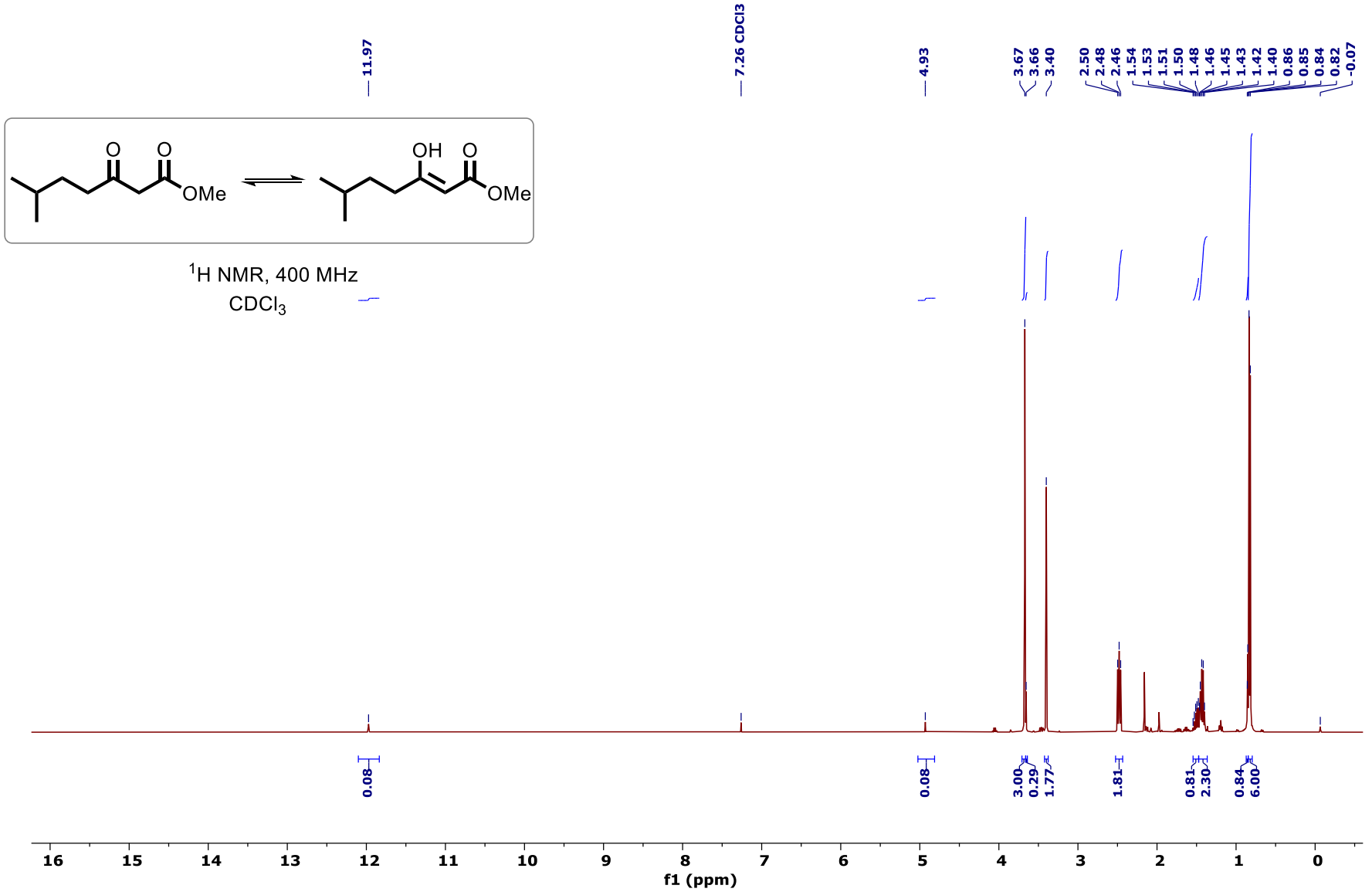
^{1}H NMR spectrum of Methyl 3-oxohexanoate (1m):



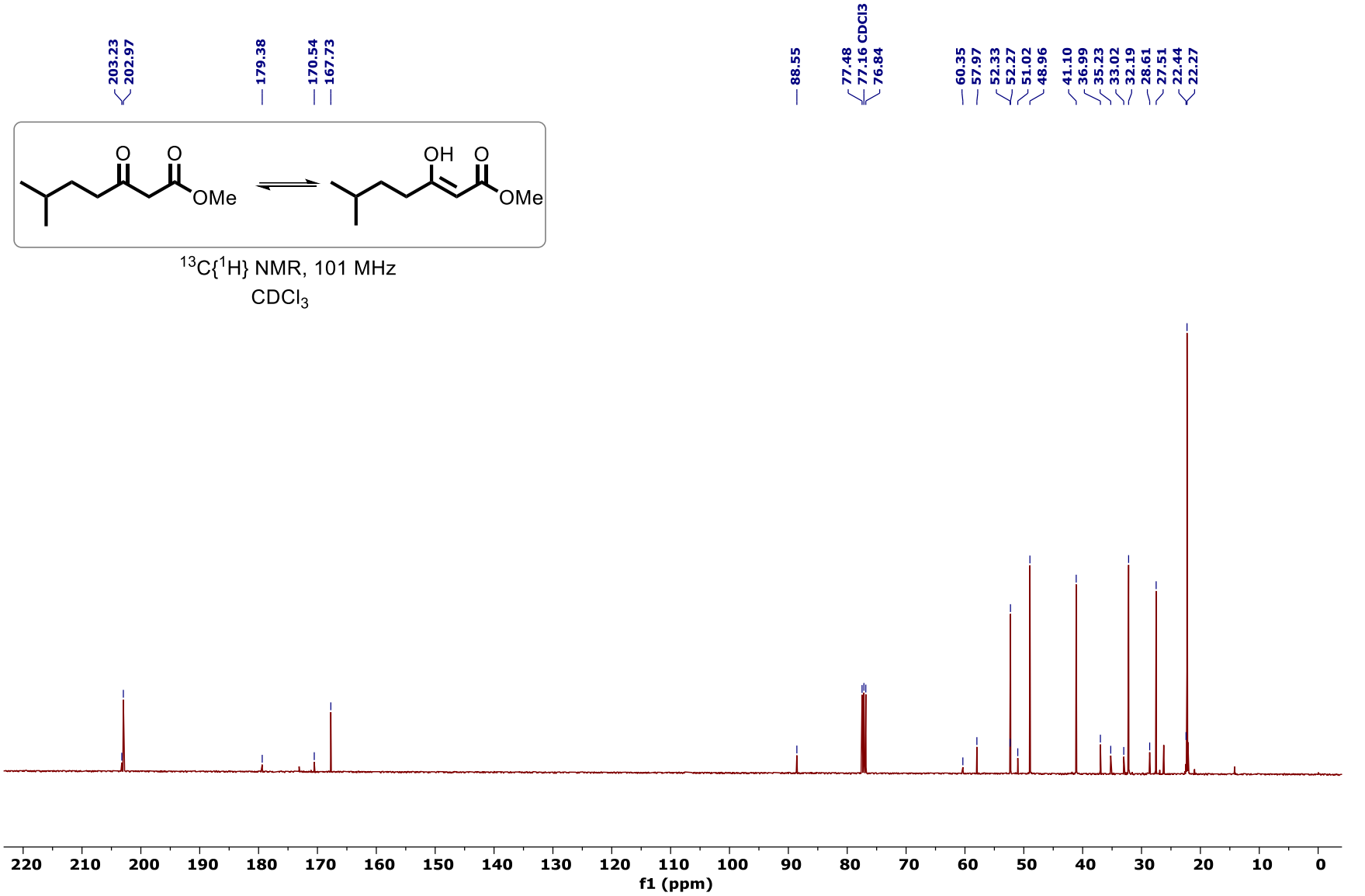
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-oxohexanoate (1m):



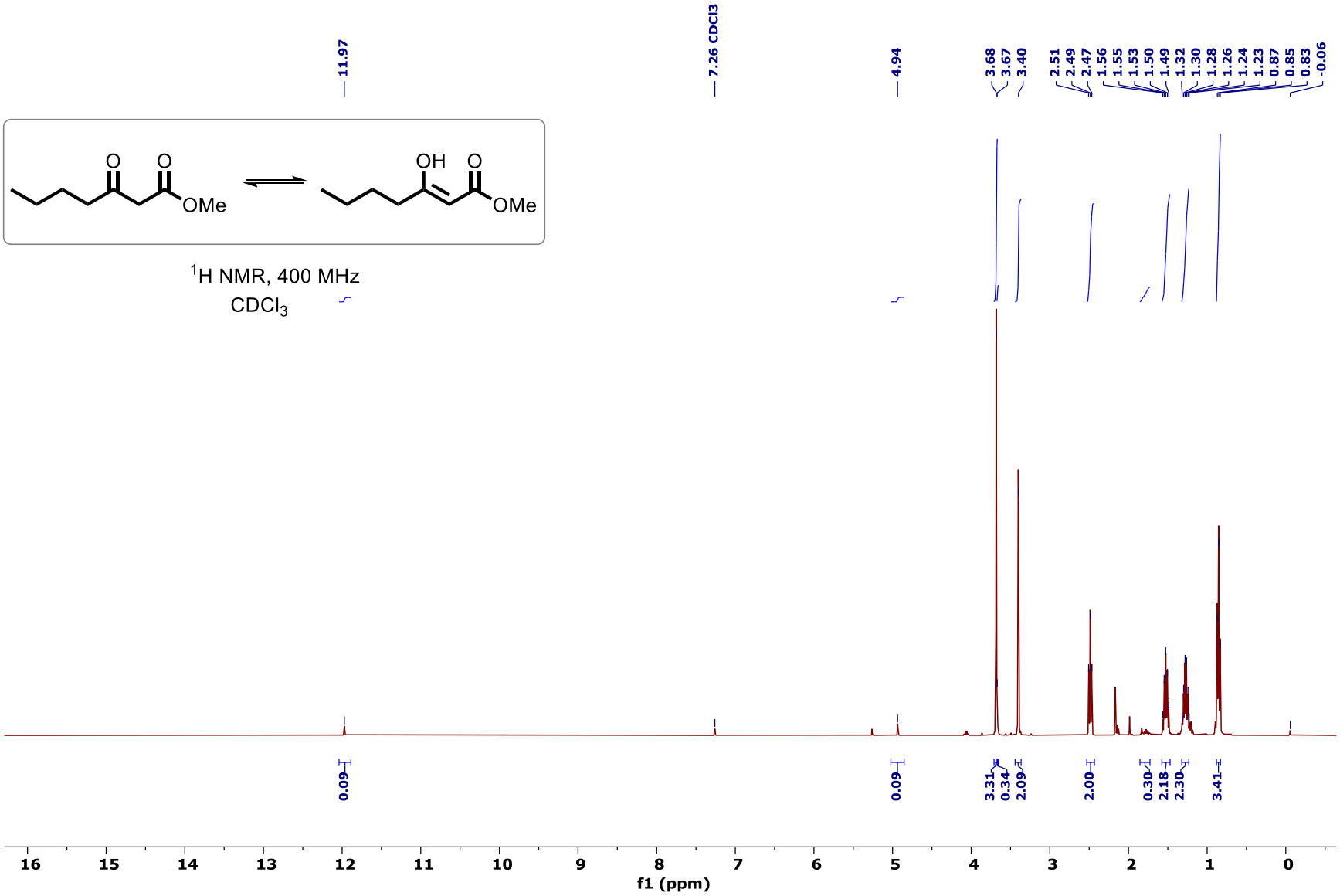
^{1}H NMR spectrum of Methyl 6-methyl-3-oxoheptanoate (1n):



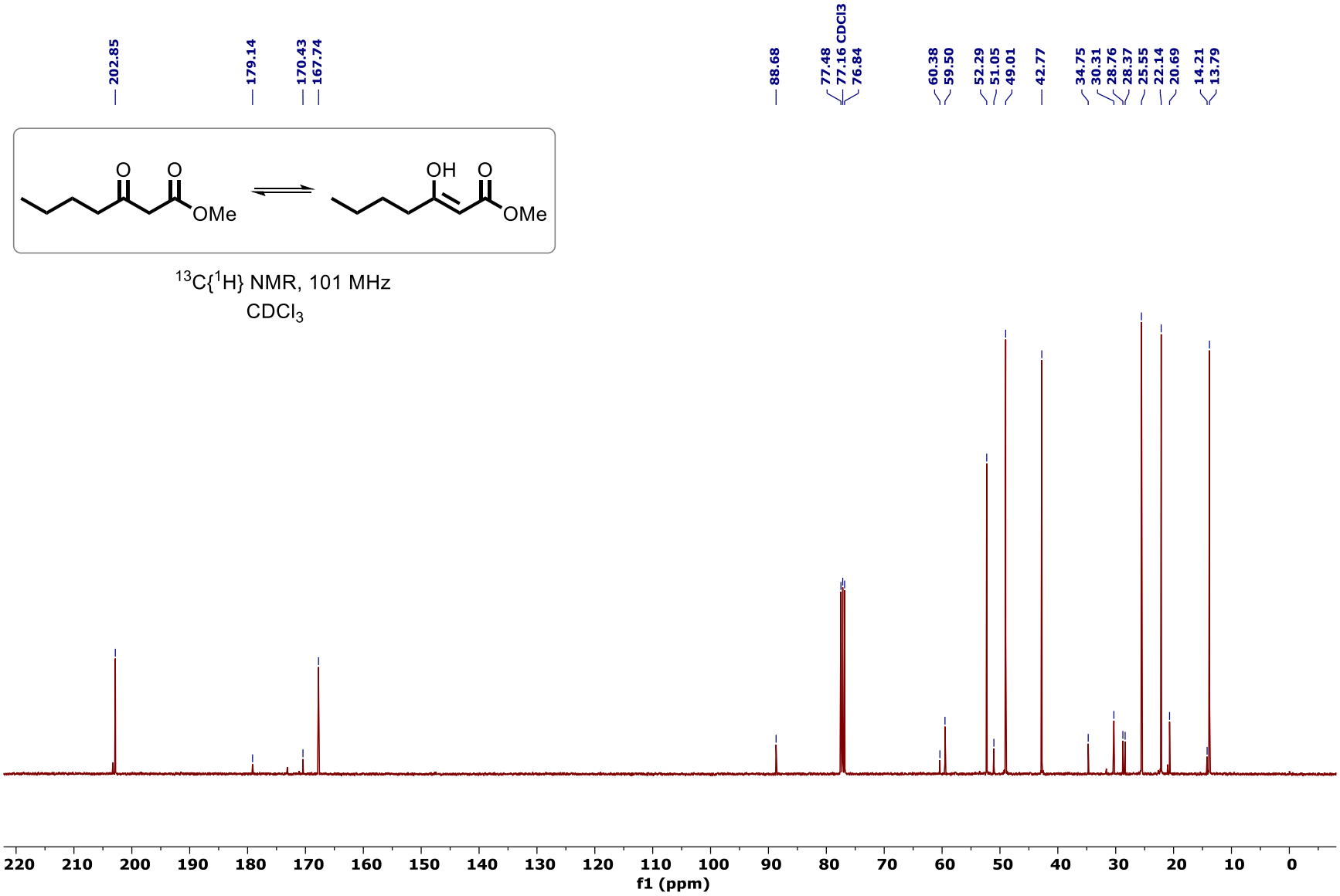
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 6-methyl-3-oxoheptanoate (1n):



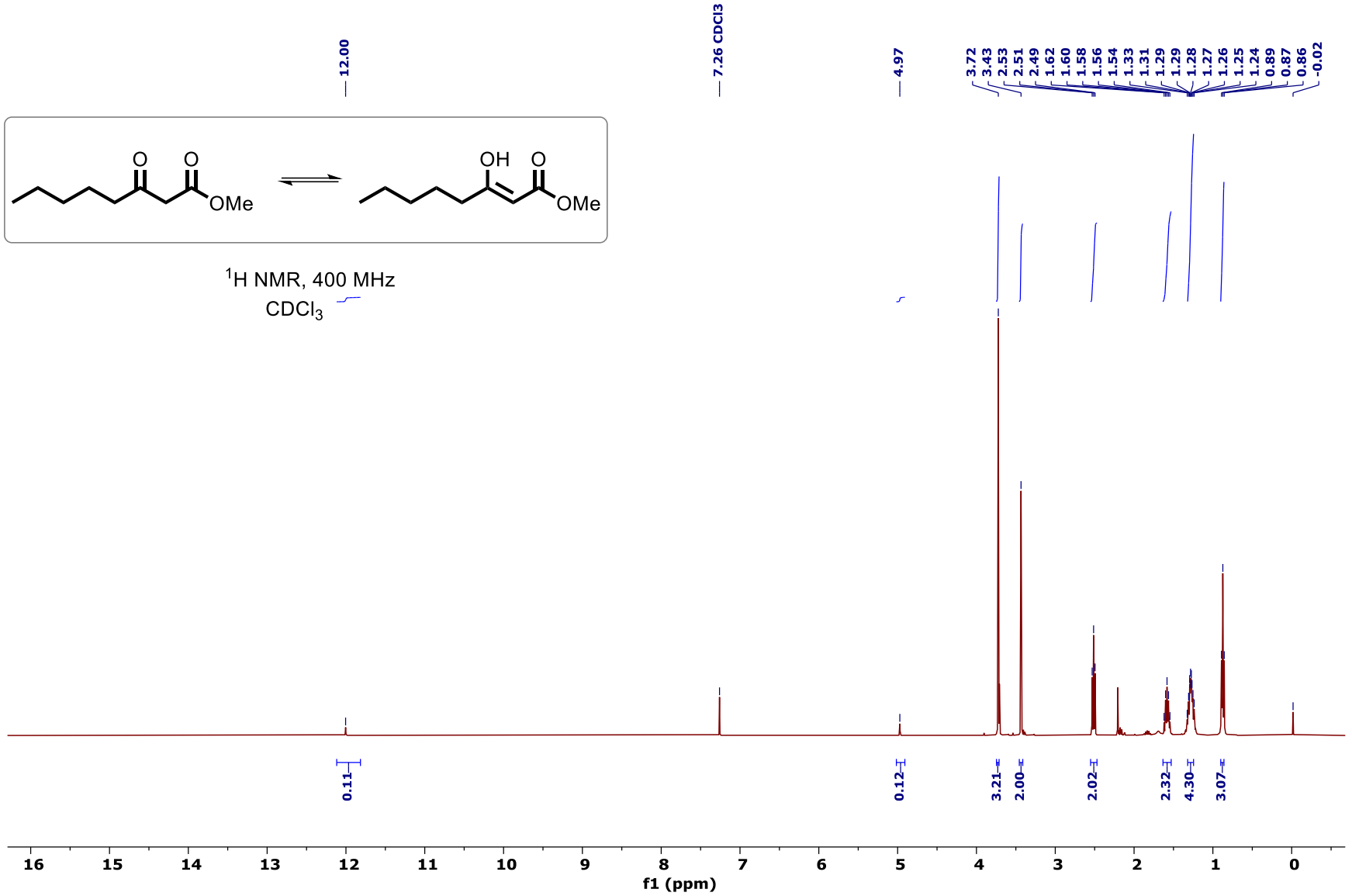
^{1}H NMR spectrum of Methyl 3-oxoheptanoate (1o):



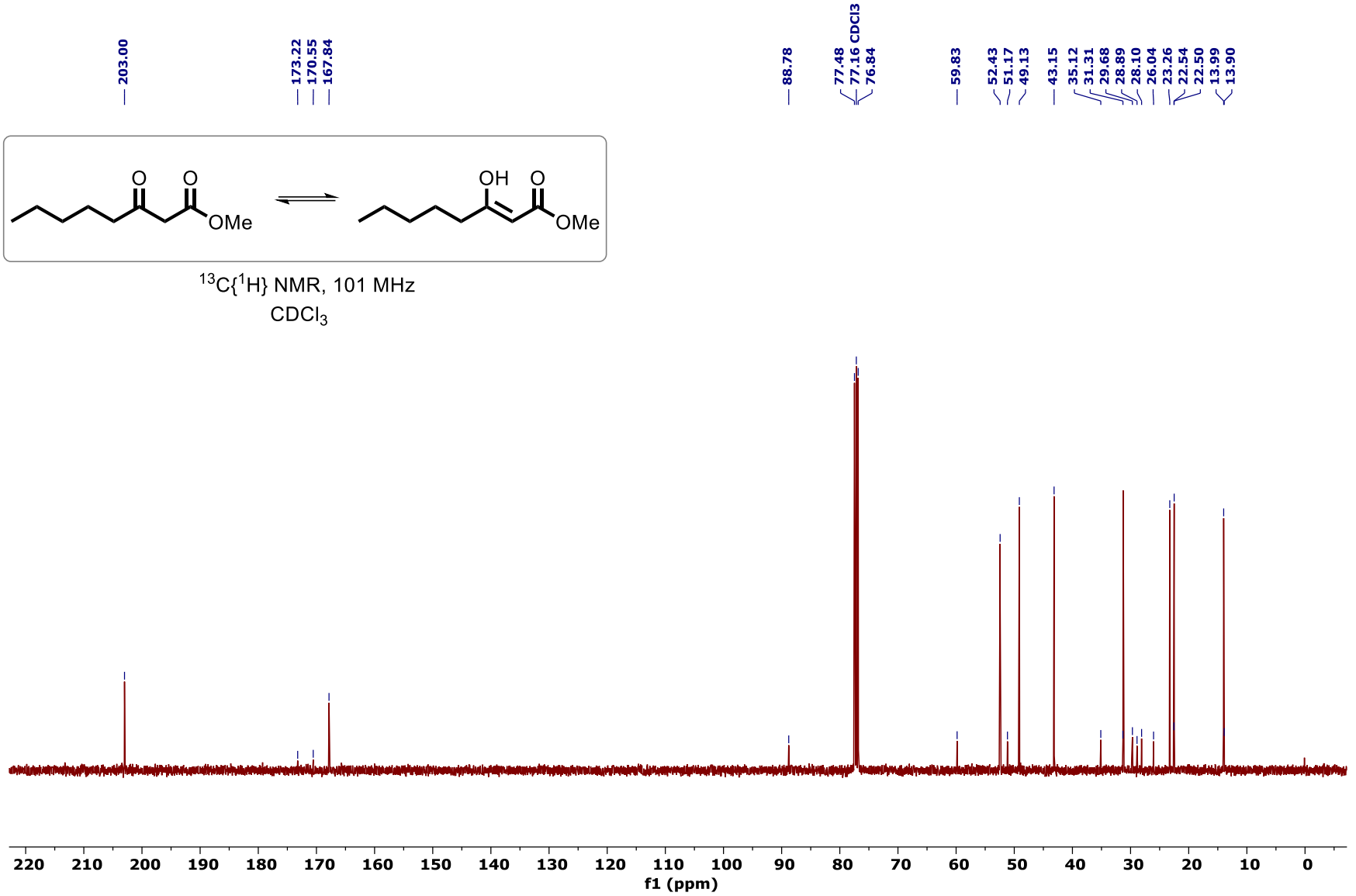
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-oxoheptanoate (1o):



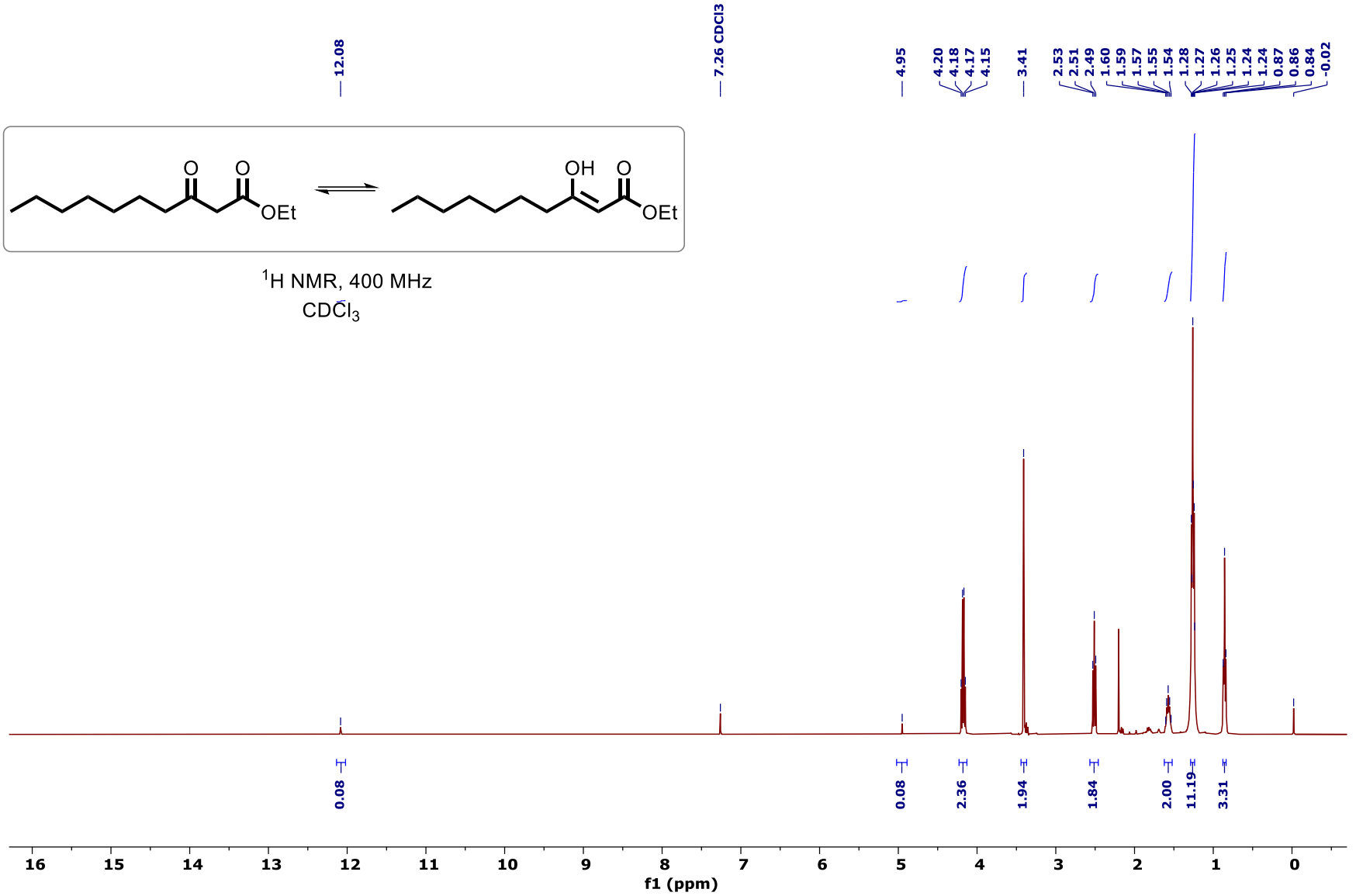
^{1}H NMR spectrum of Methyl 3-oxooctanoate (1p):



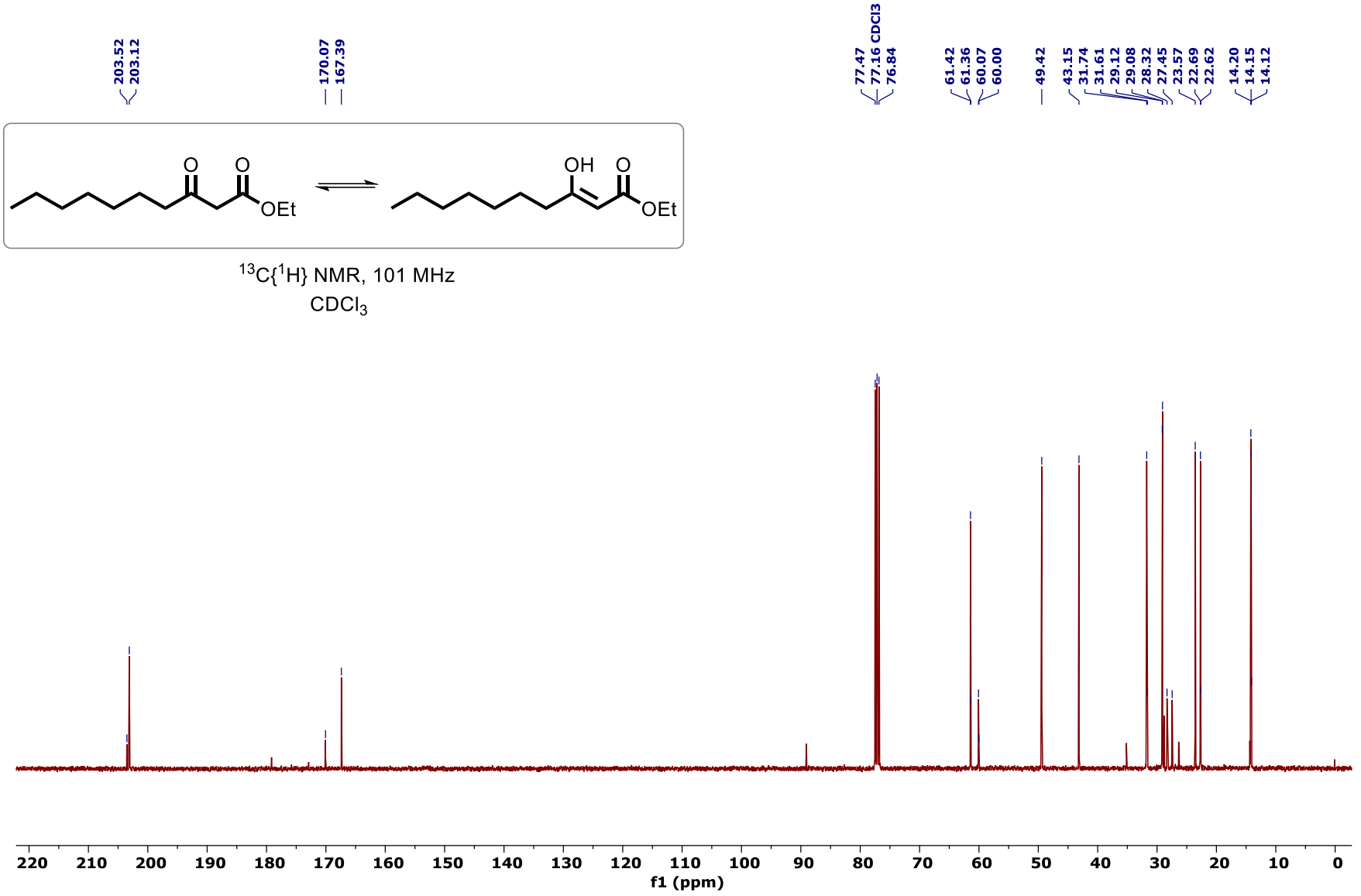
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-oxooctanoate (1p):



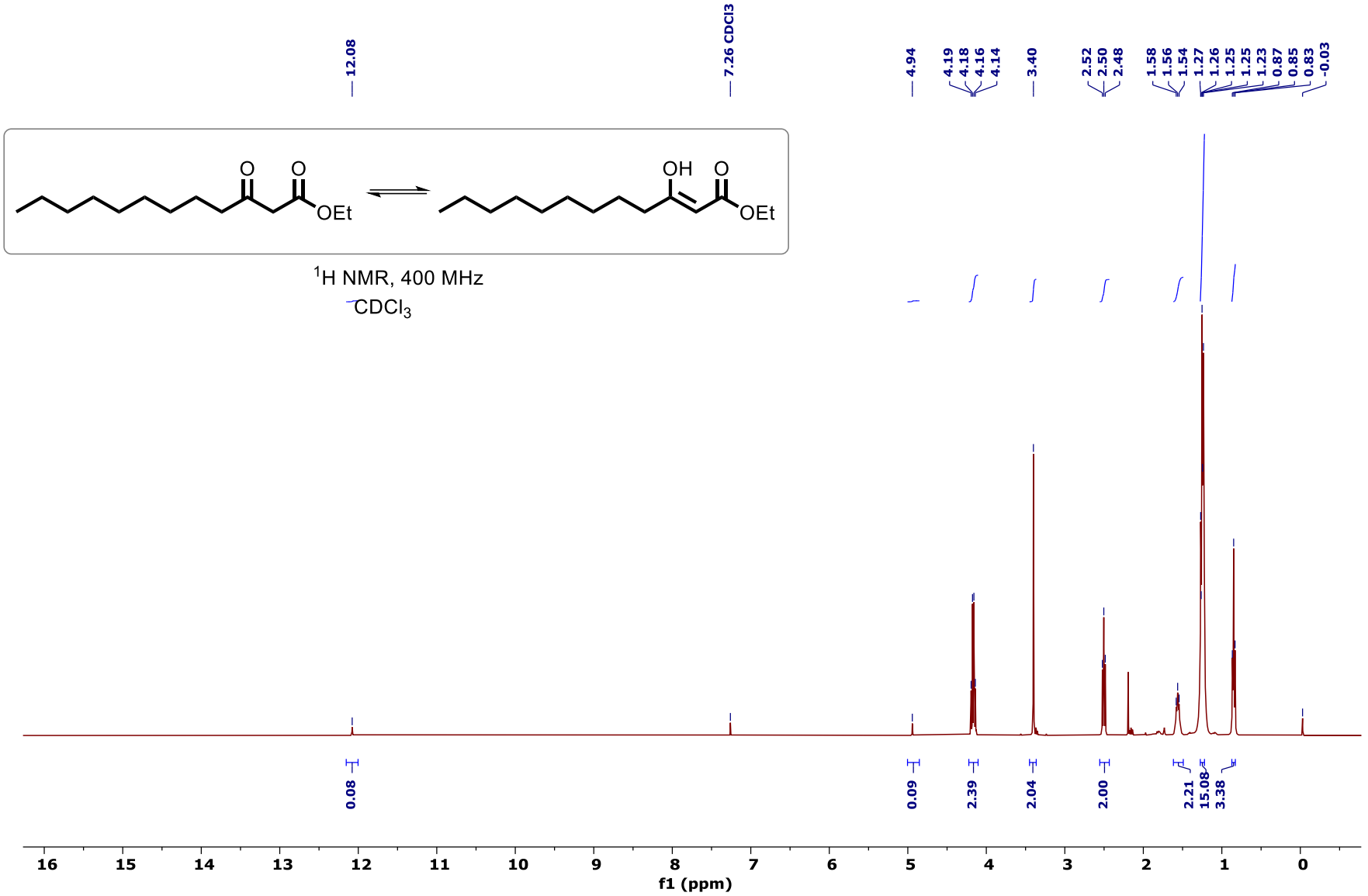
^{1}H NMR spectrum of Ethyl 3-oxodecanoate (1q):



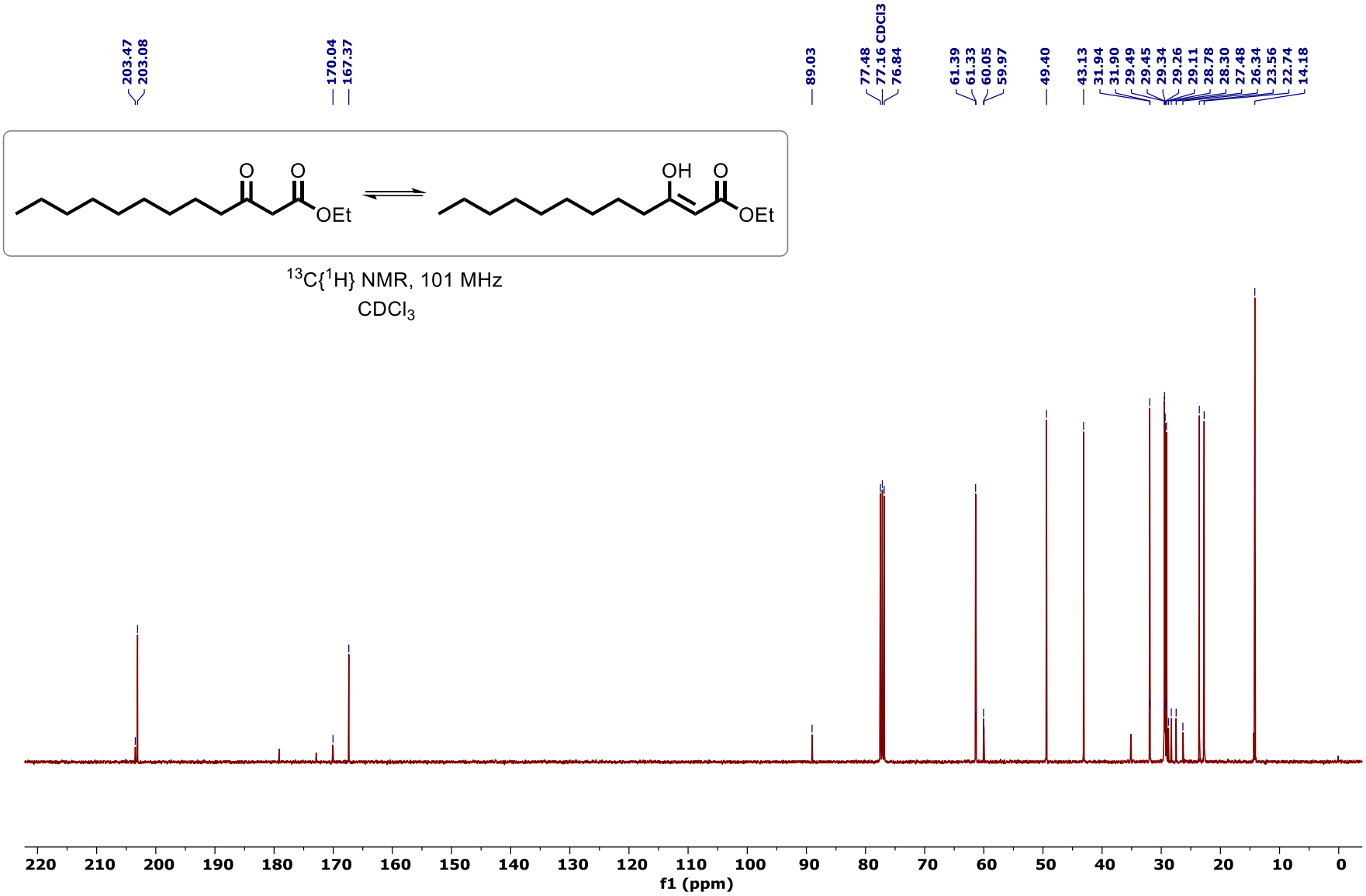
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-oxodecanoate (1q):



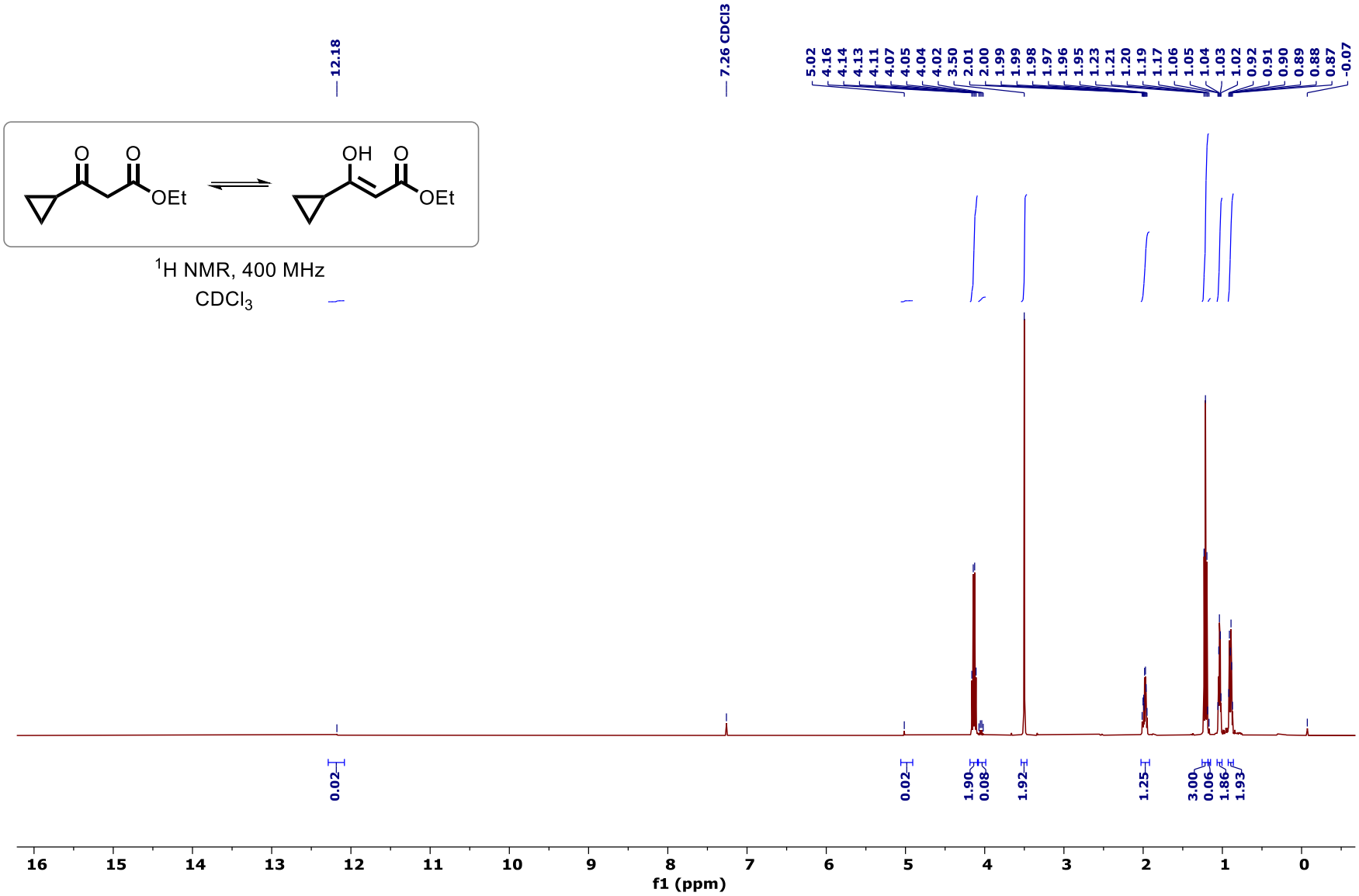
^{1}H NMR spectrum of Ethyl 3-oxododecanoate (1r):



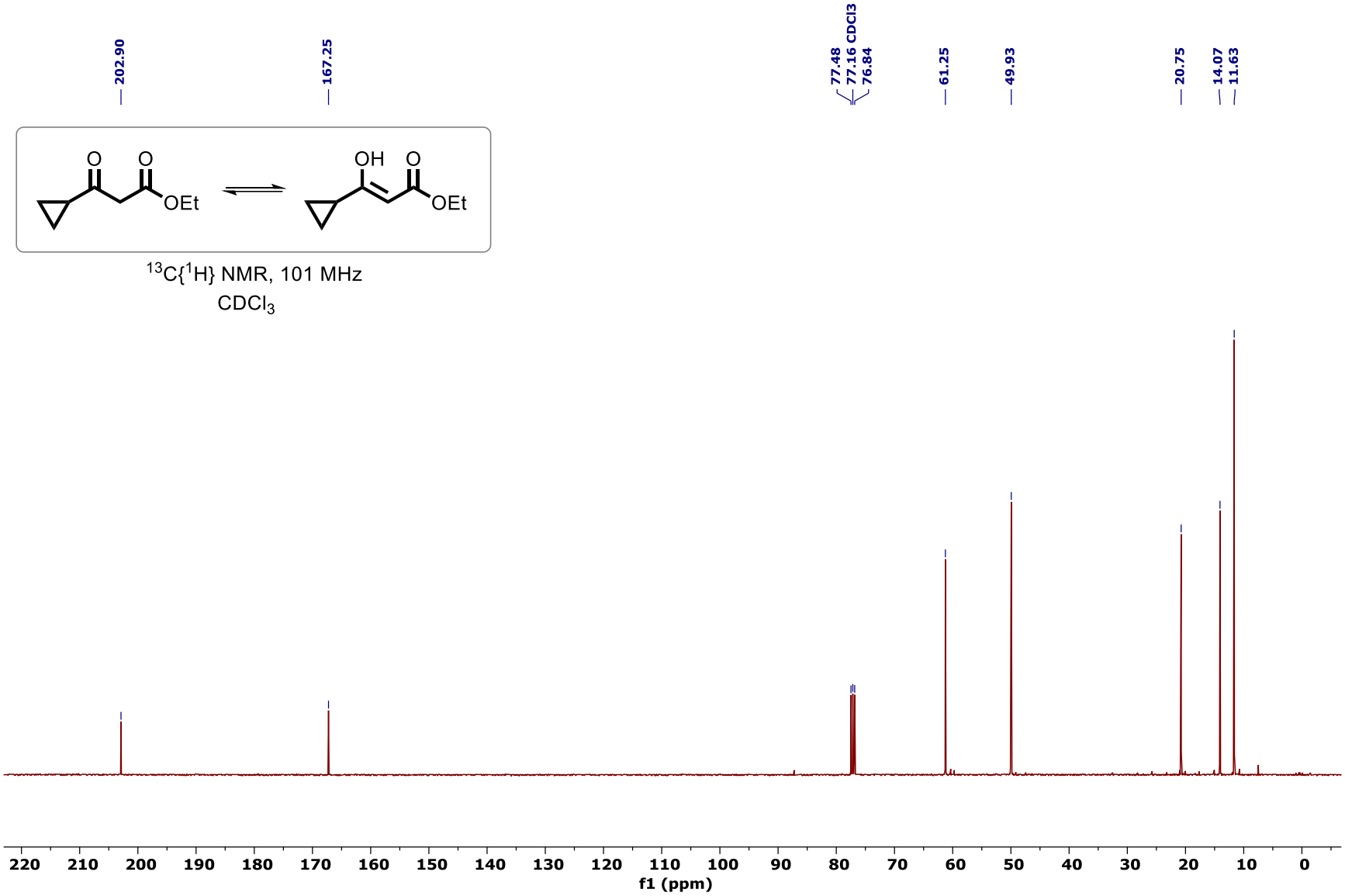
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-oxododecanoate (1r):



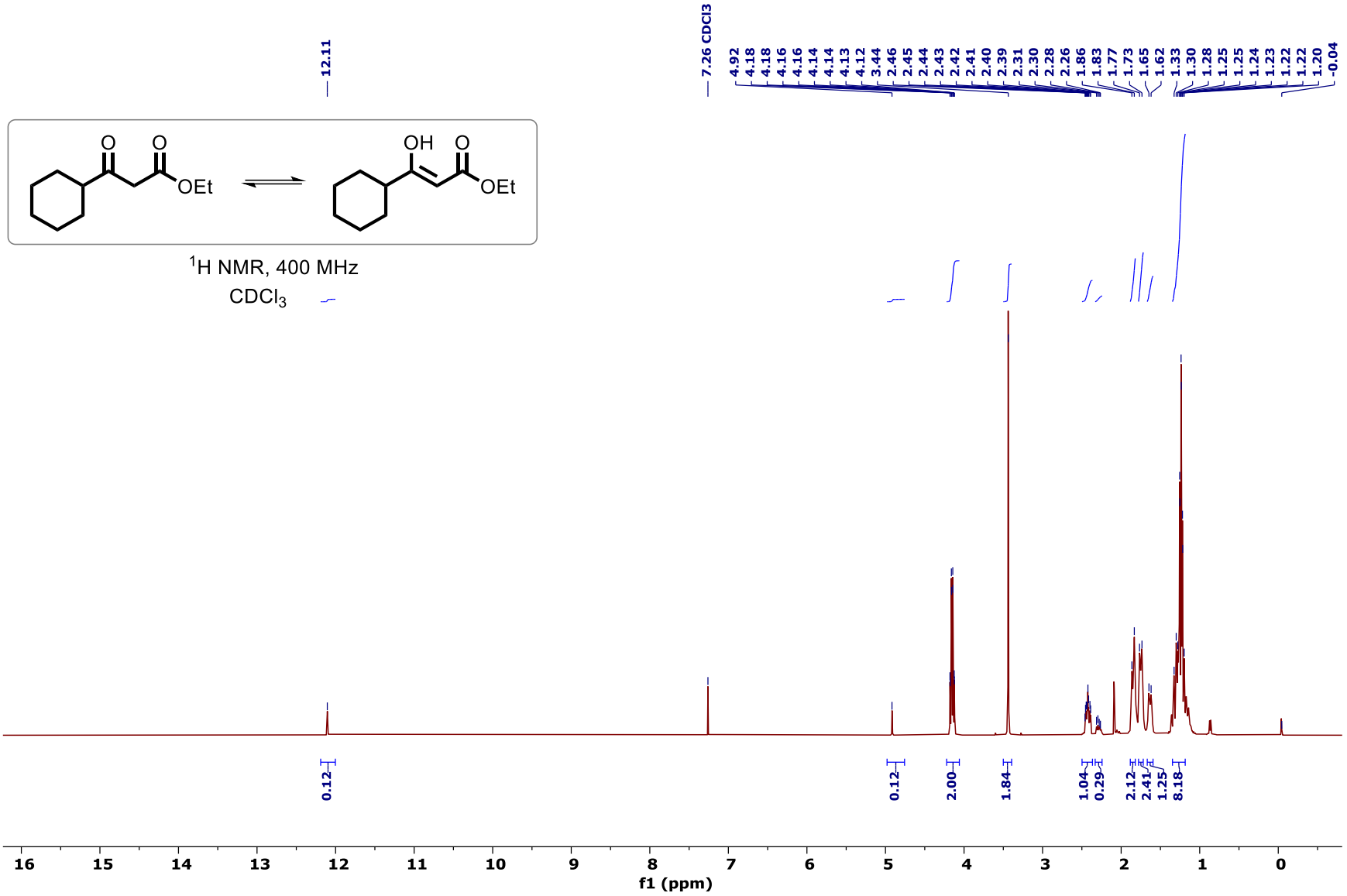
^{1}H NMR spectrum of Ethyl 3-cyclopropyl-3-oxopropanoate (1w):



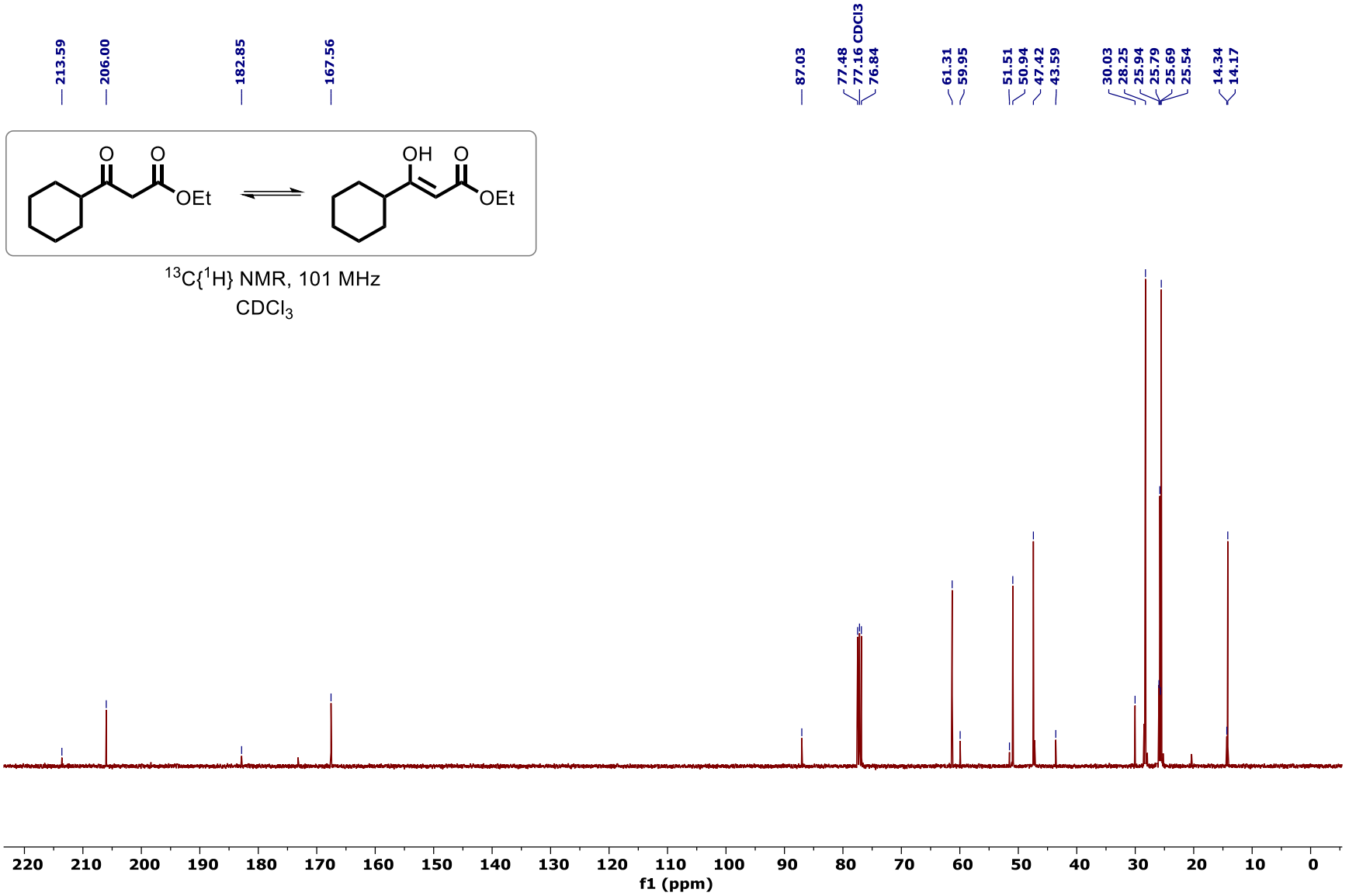
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-cyclopropyl-3-oxopropanoate (1w):



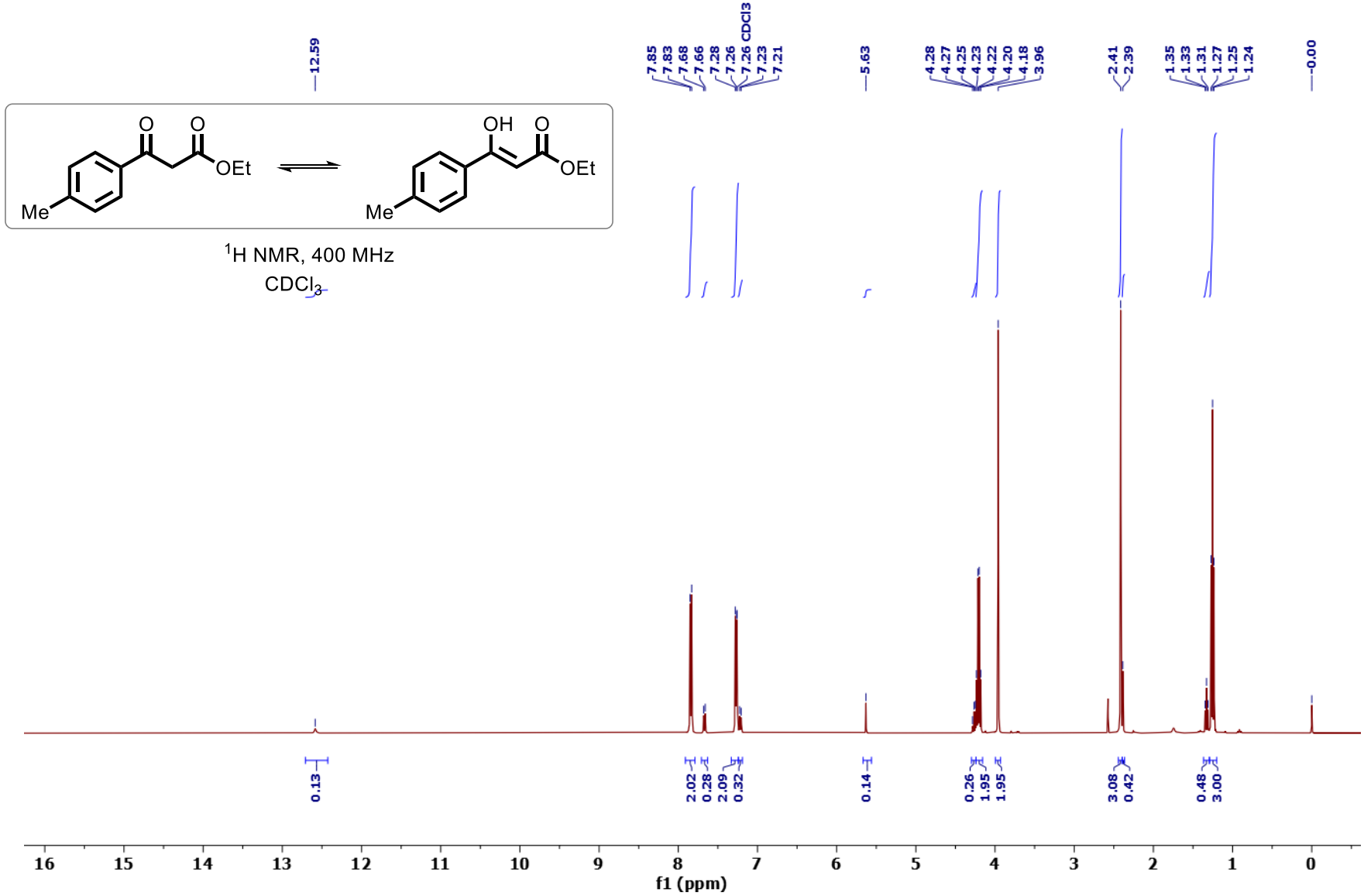
^{1}H NMR spectrum of Ethyl 3-cyclohexyl-3-oxopropanoate (1x):



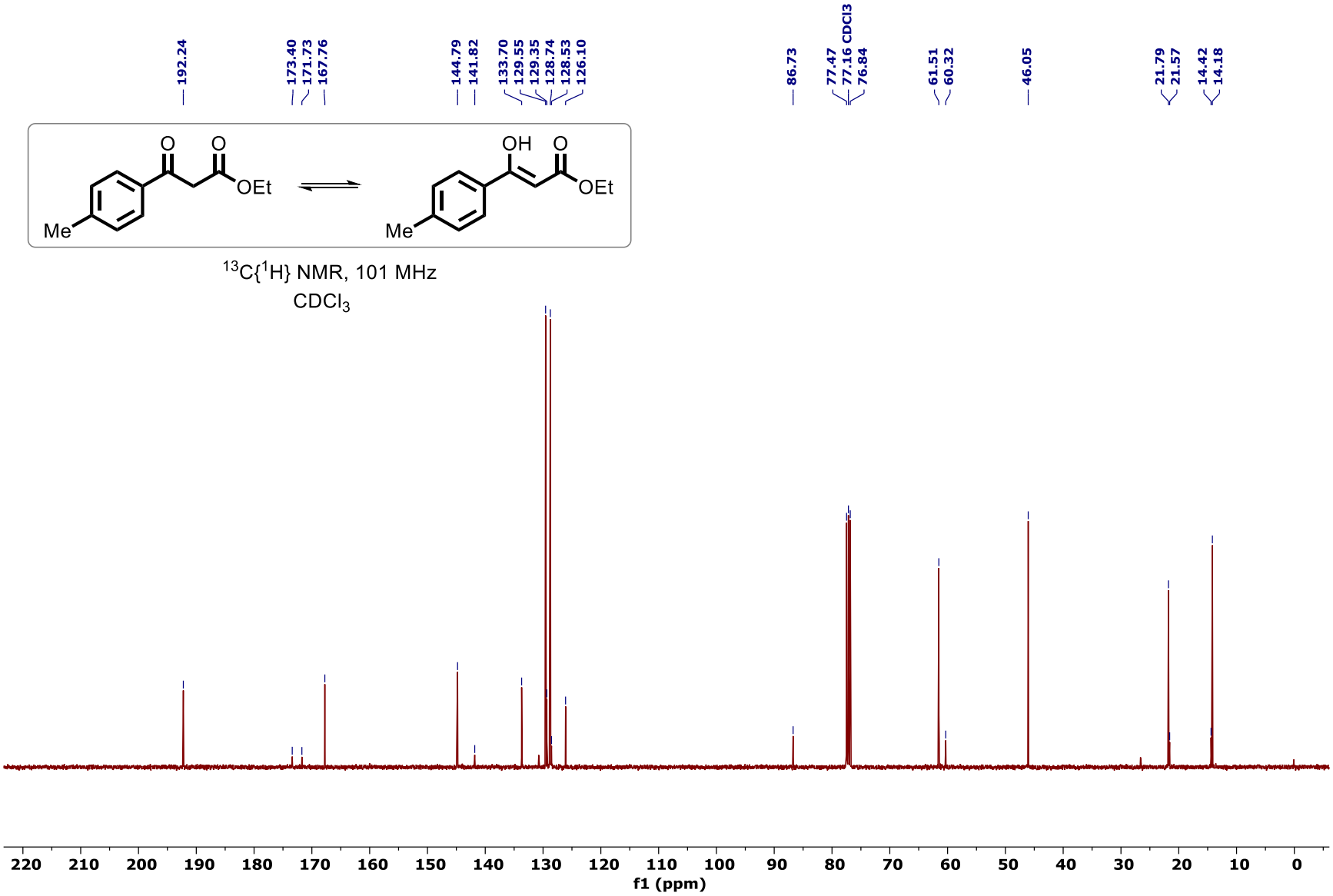
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-cyclohexyl-3-oxopropanoate (1x):



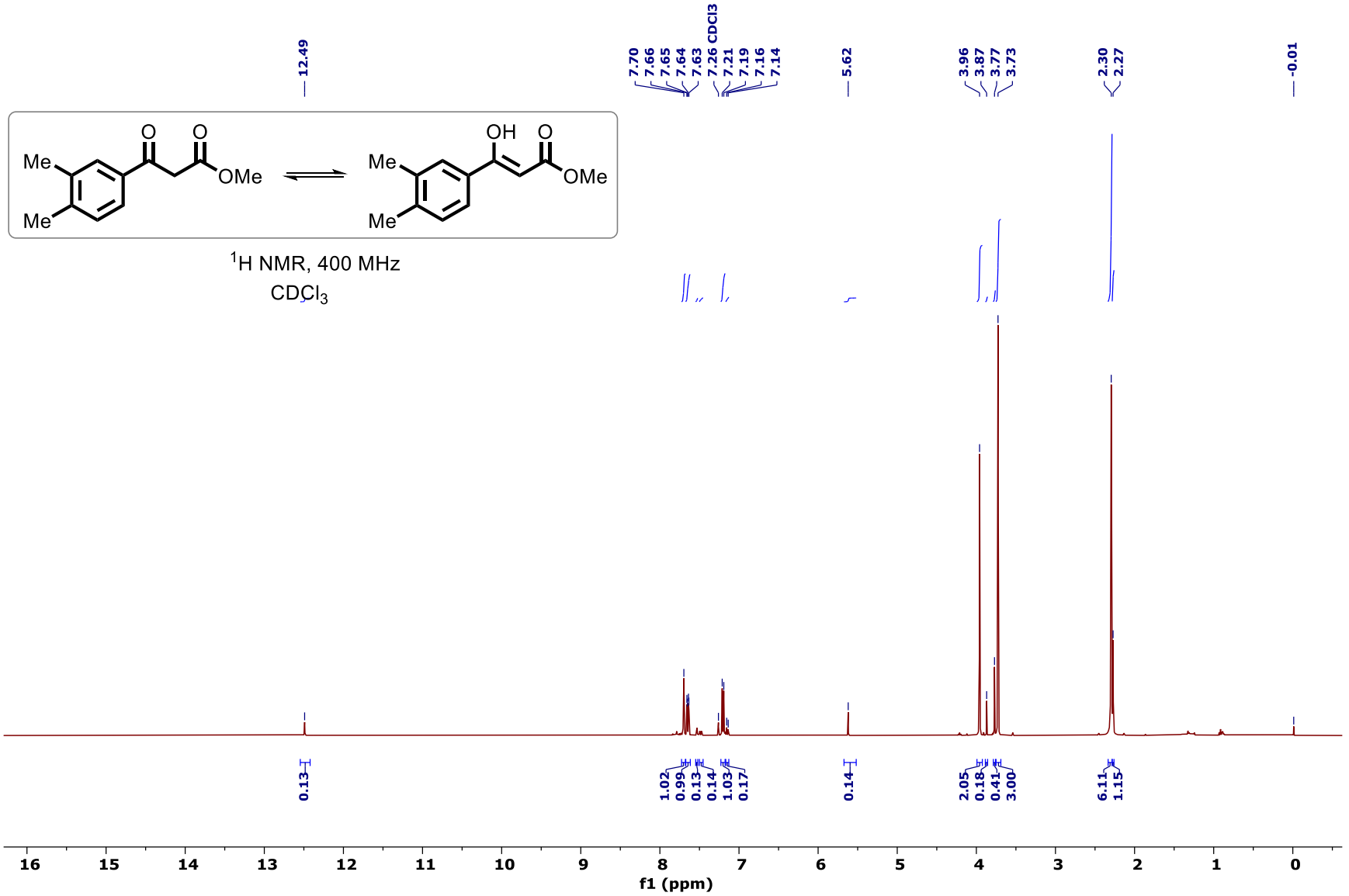
^{1}H NMR spectrum of Ethyl 3-oxo-3-(*p*-tolyl)propanoate (1y):



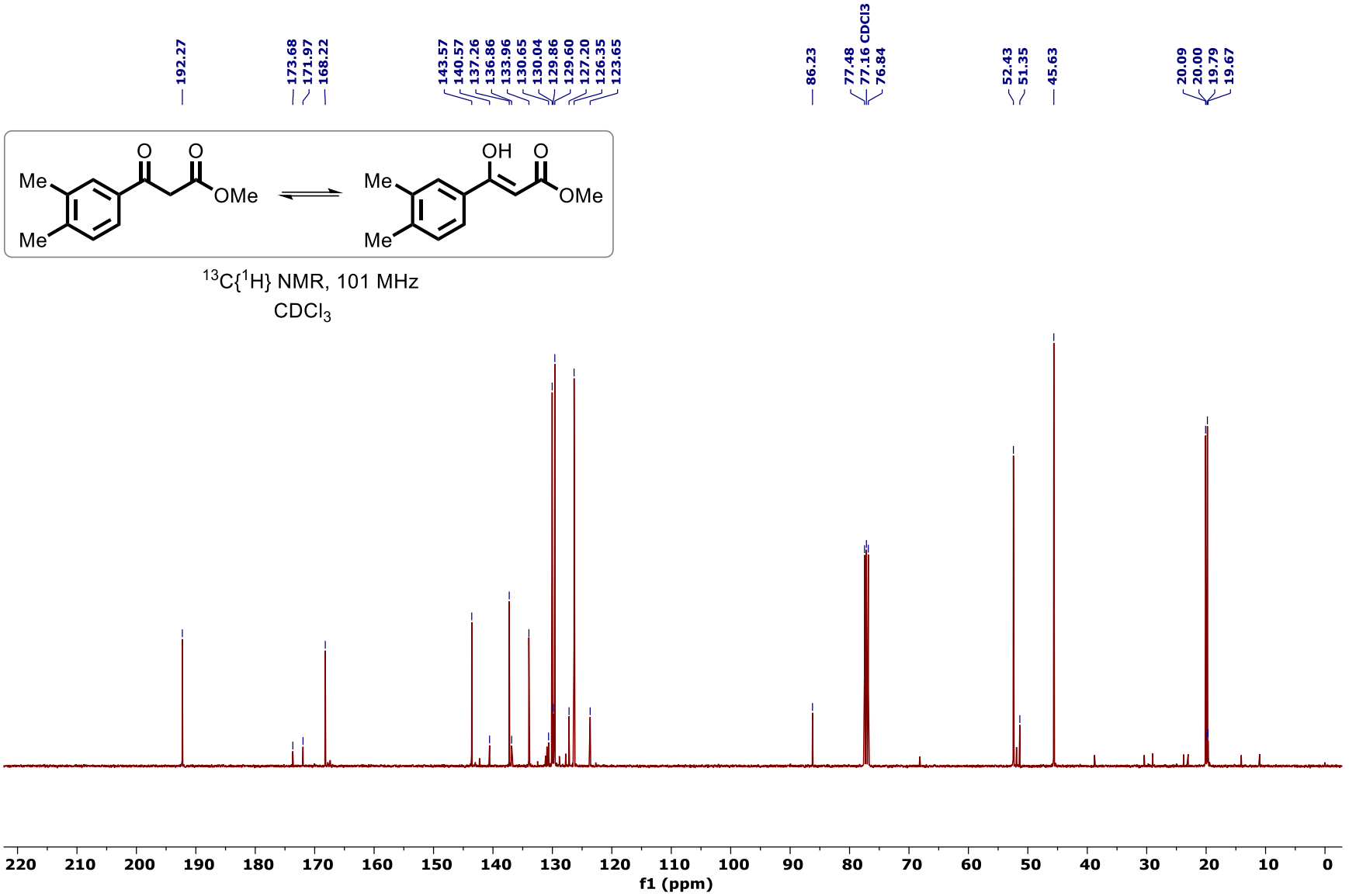
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-oxo-3-(*p*-tolyl)propanoate (1y):



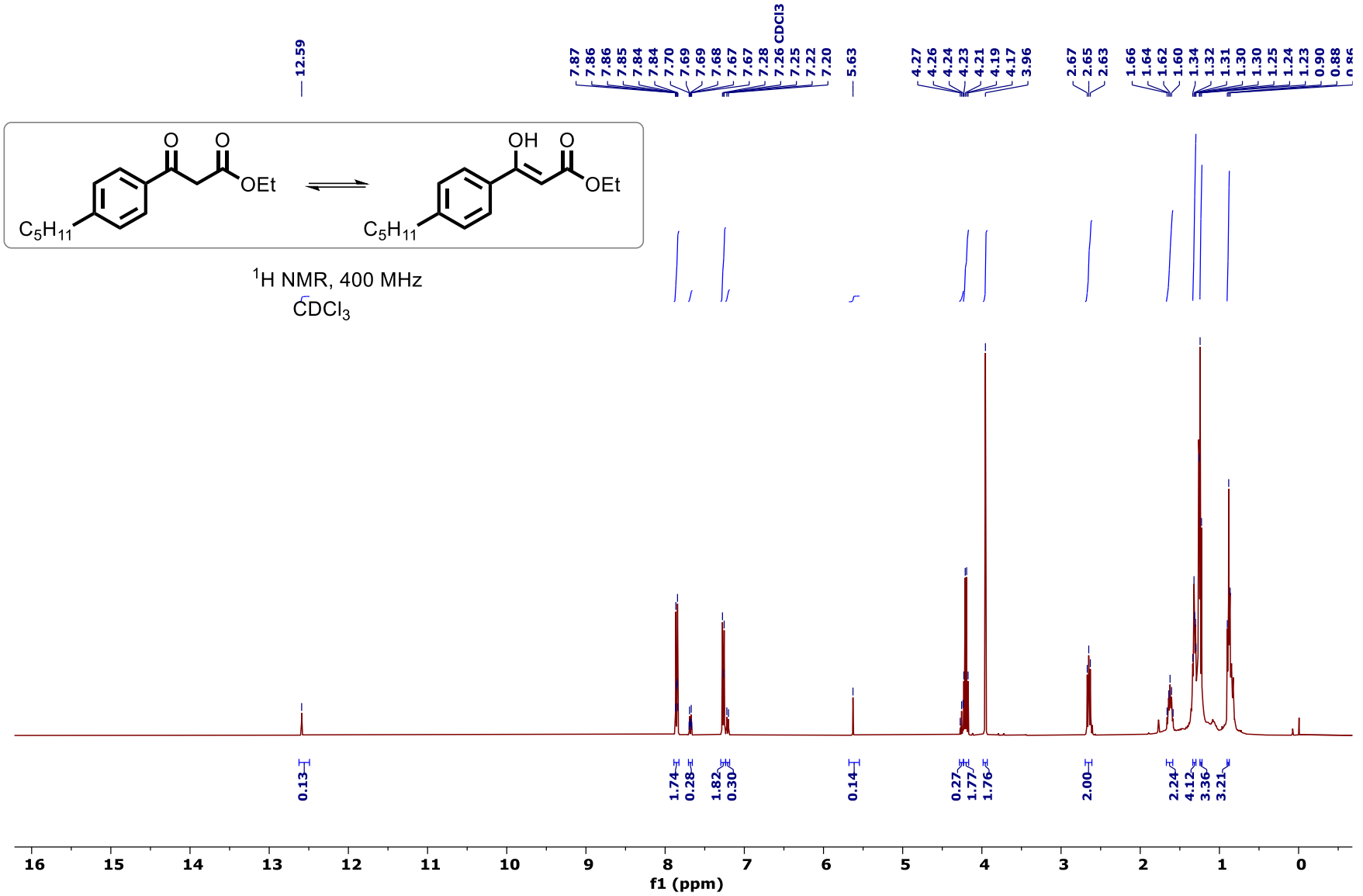
^{1}H NMR spectrum of Methyl 3-(3,4-dimethylphenyl)-3-oxopropanoate (1z):



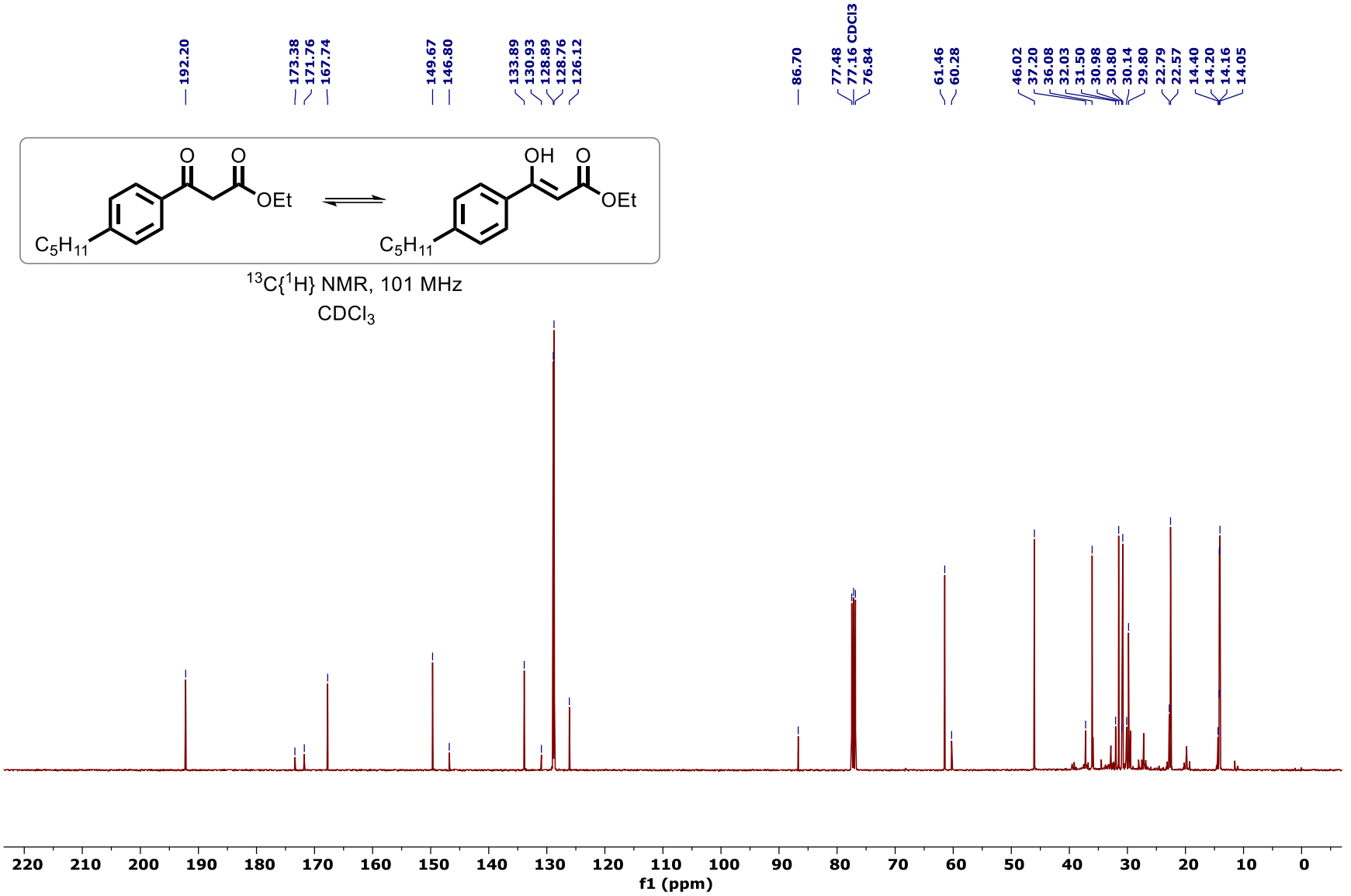
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-(3,4-dimethylphenyl)-3-oxopropanoate (1z):



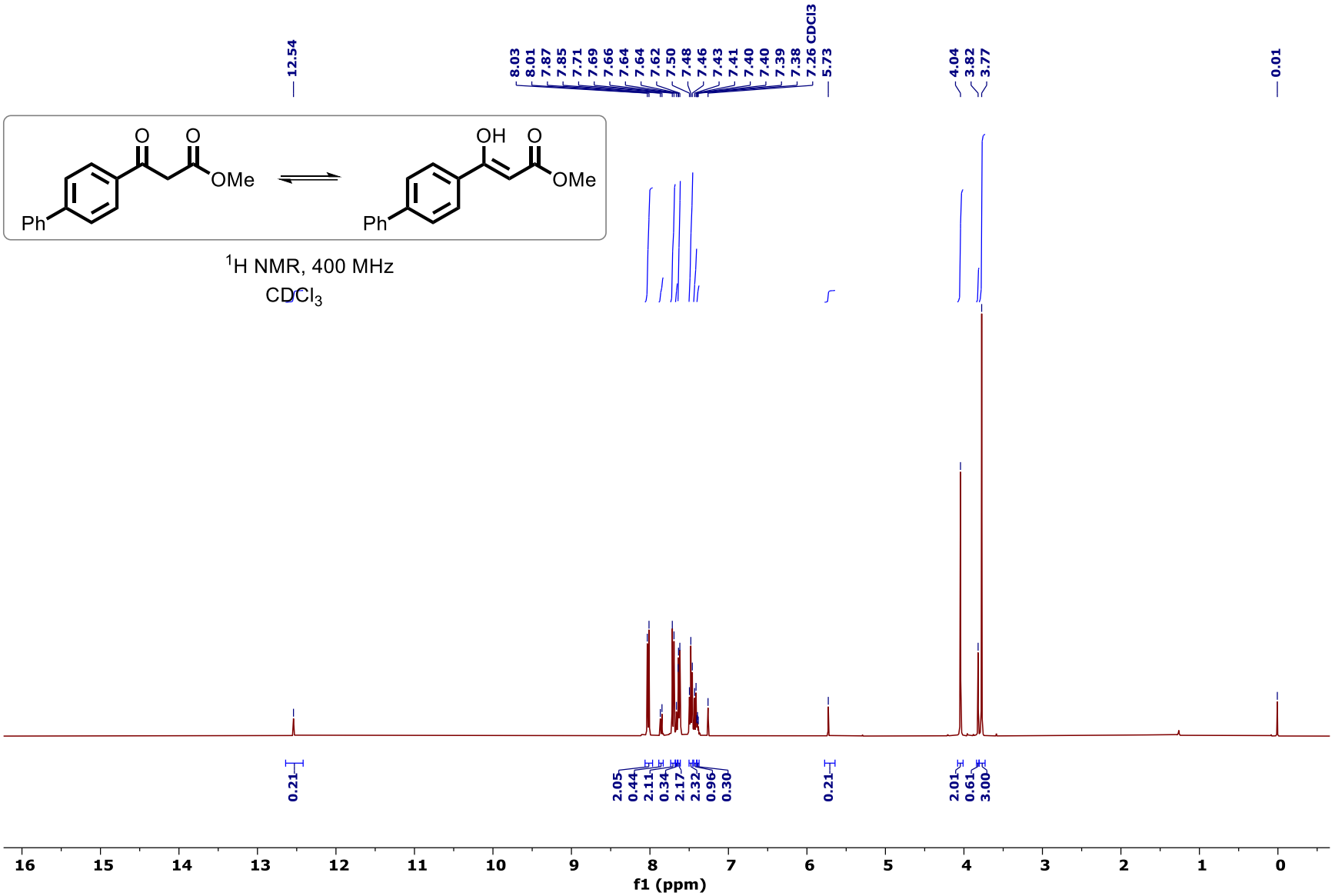
^{1}H NMR spectrum of Ethyl 3-oxo-3-(4-pentylphenyl)propanoate (1a′):



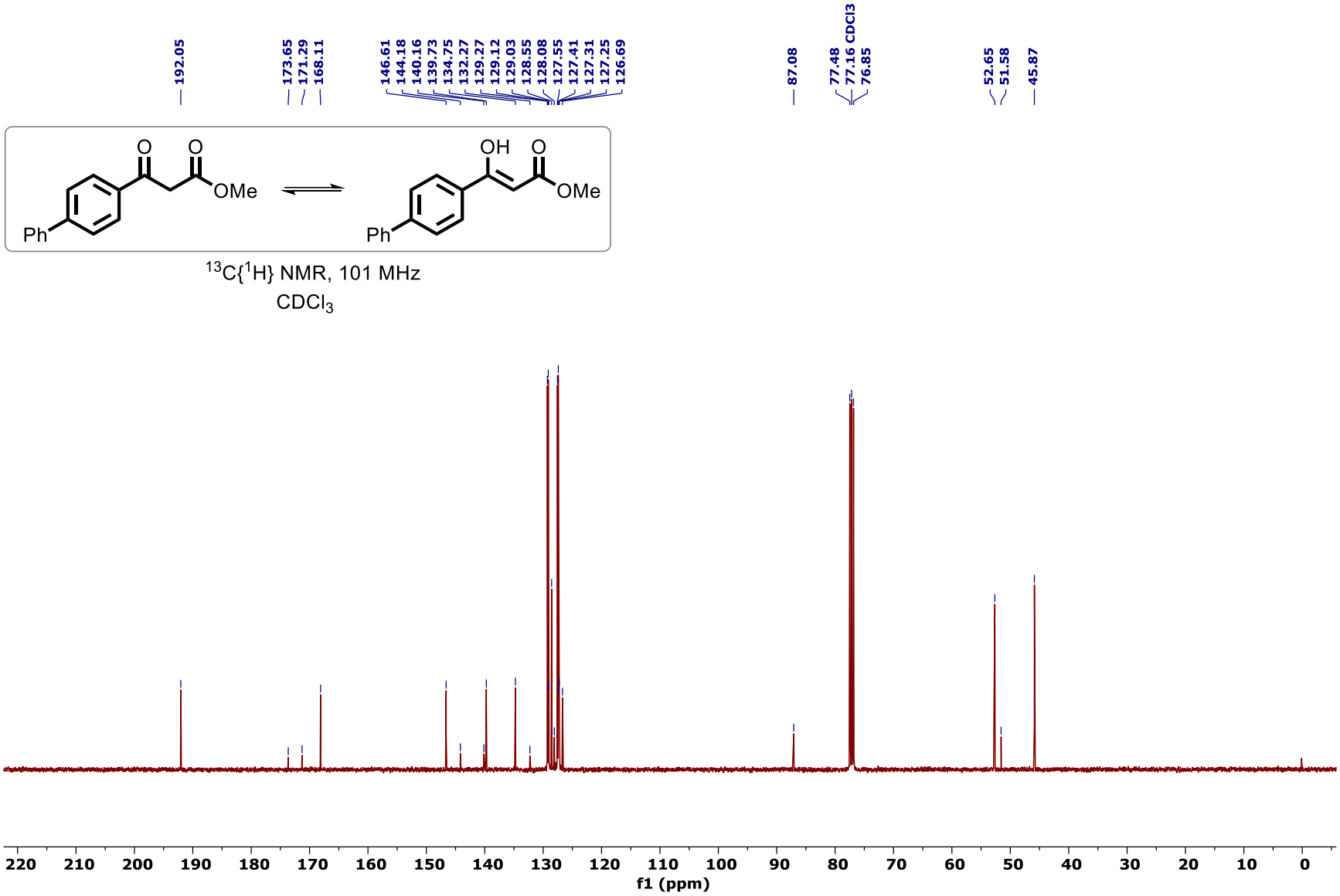
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-oxo-3-(4-pentylphenyl)propanoate (1a′):



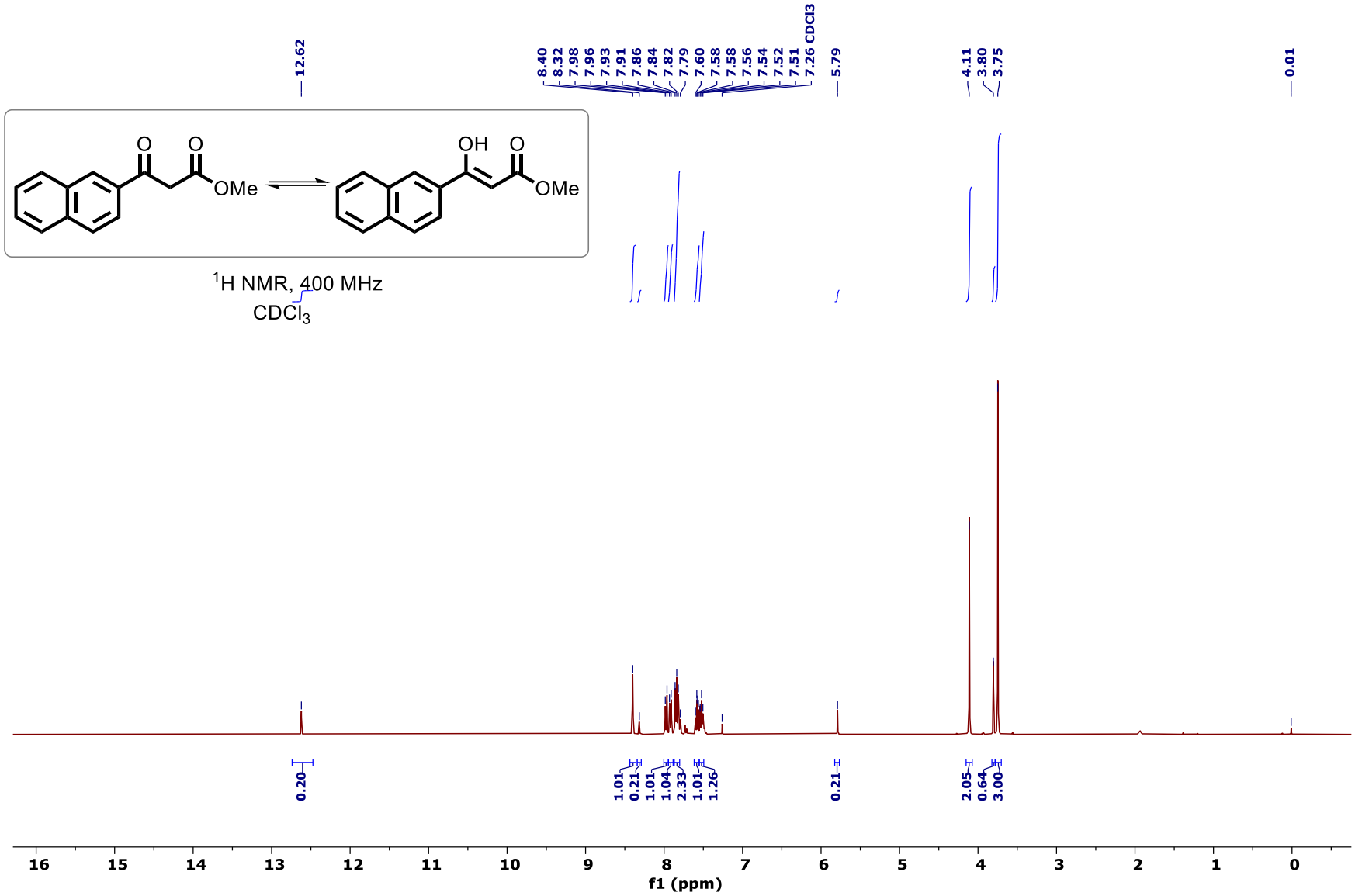
^{1}H NMR spectrum of Methyl 3-([1,1'-biphenyl]-4-yl)-3-oxopropanoate (1b′):



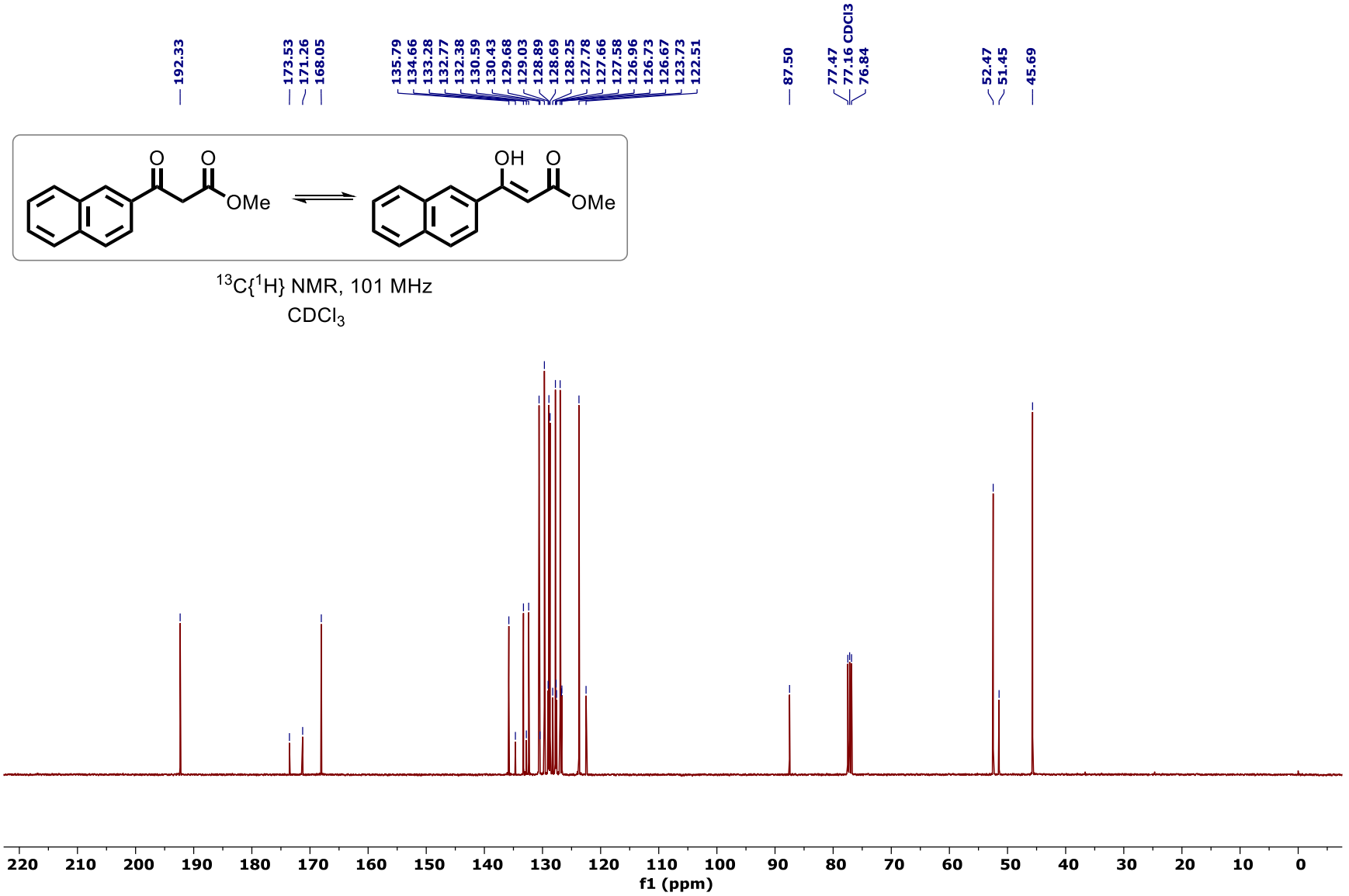
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-([1,1'-biphenyl]-4-yl)-3-oxopropanoate (1b′):



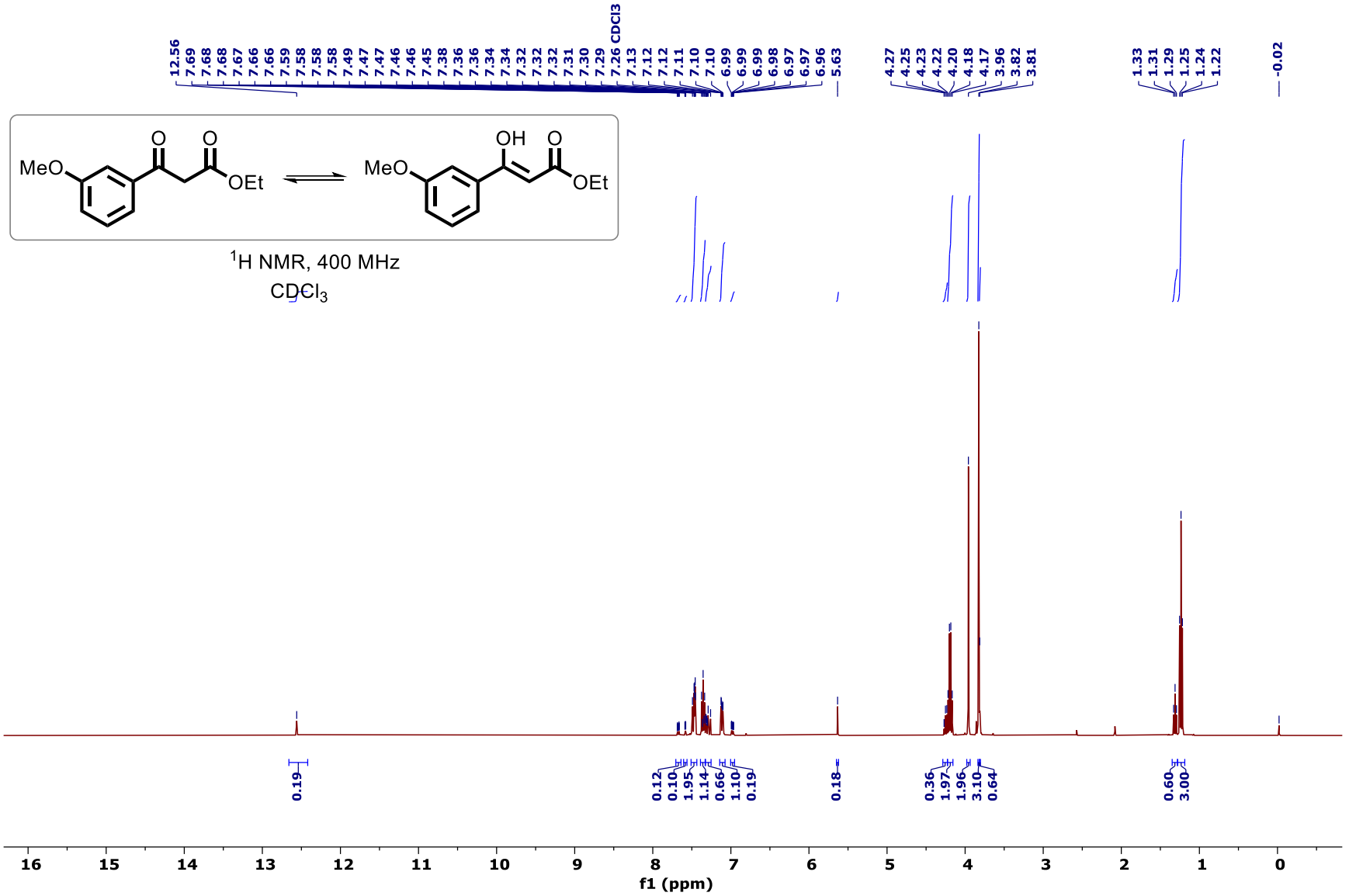
^{1}H NMR spectrum of Methyl 3-(naphthalen-2-yl)-3-oxopropanoate (1c′):



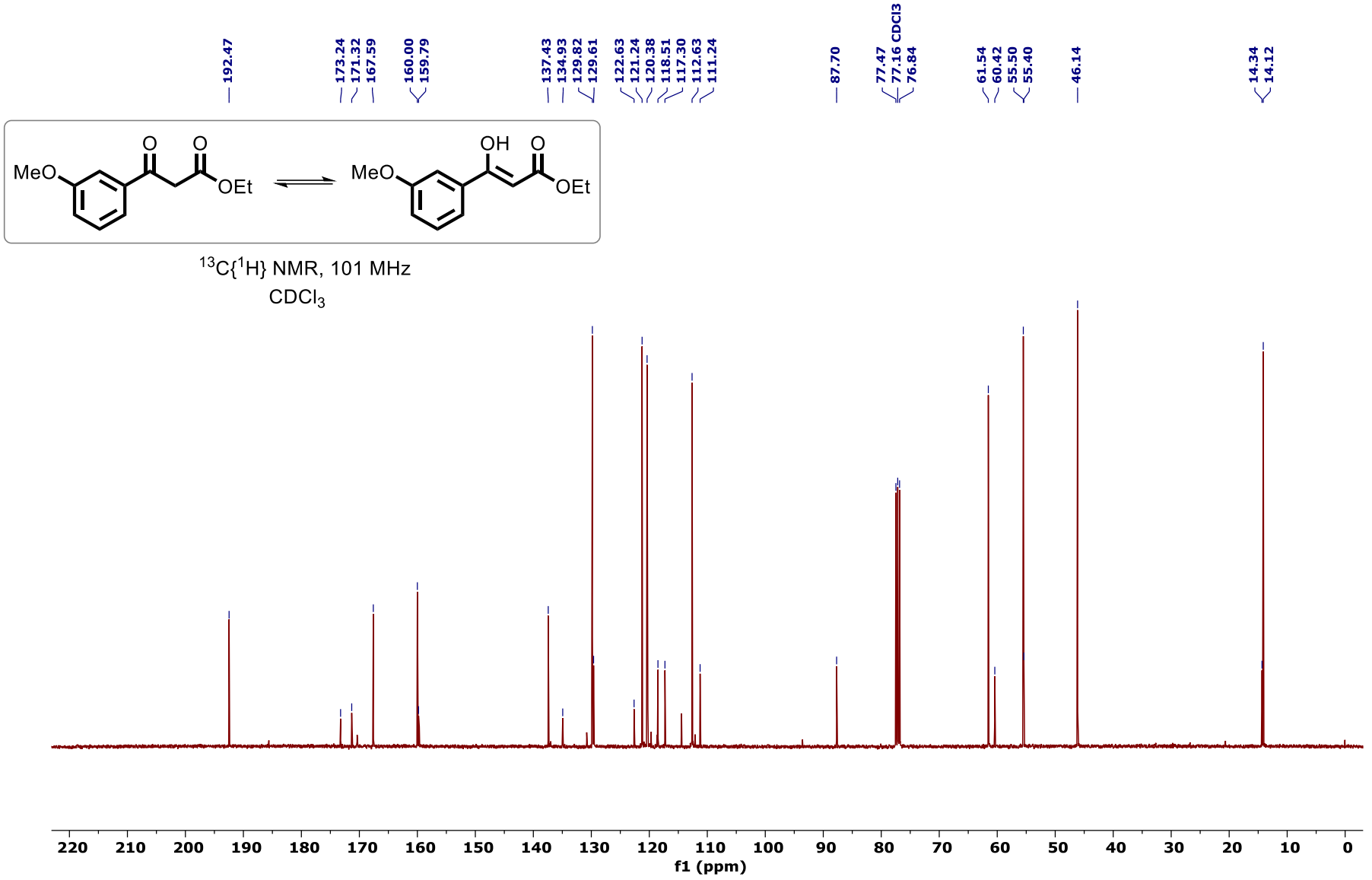
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-(naphthalen-2-yl)-3-oxopropanoate (1c′):



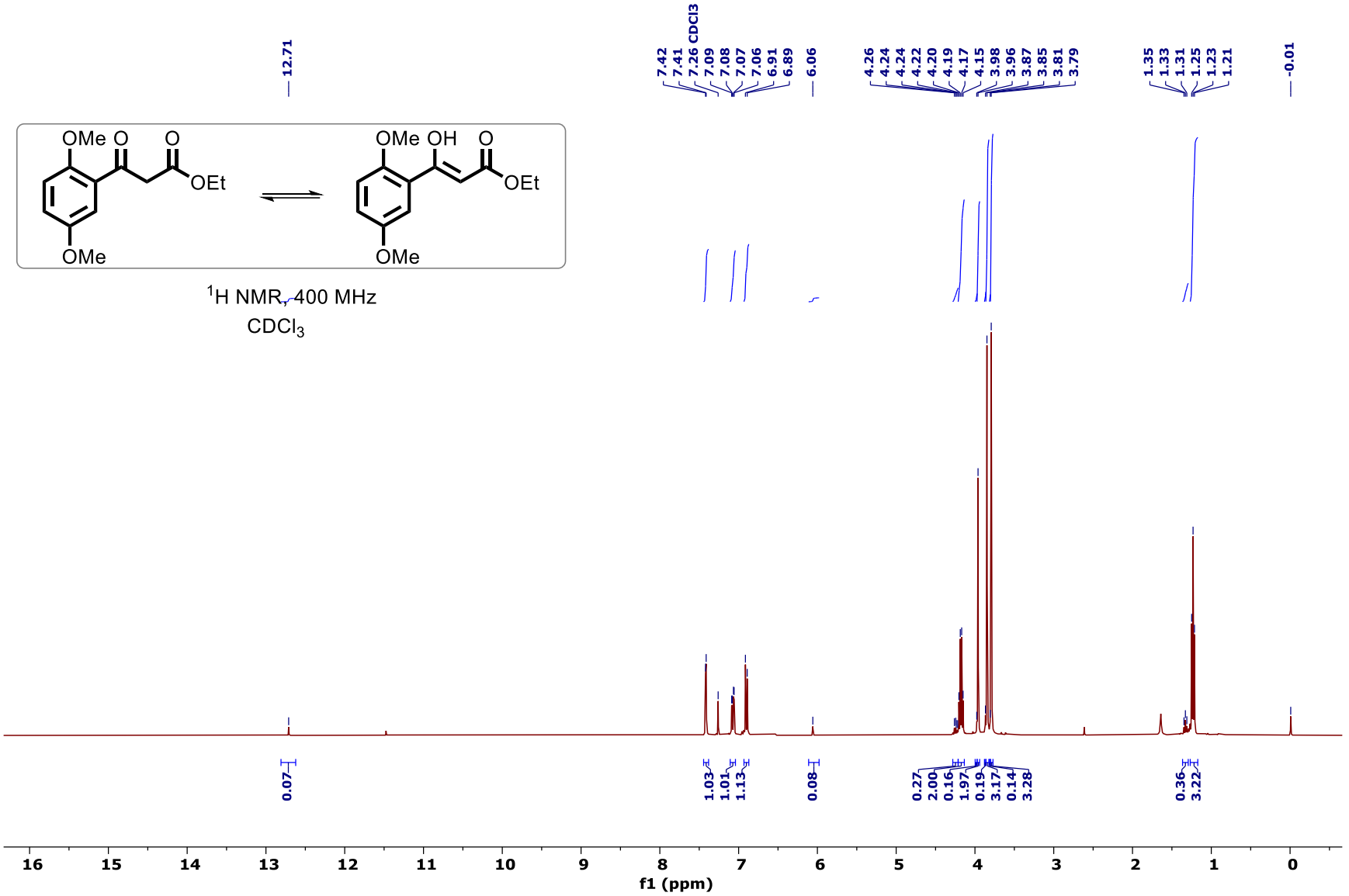
^{1}H NMR spectrum of Ethyl 3-(3-methoxyphenyl)-3-oxopropanoate (1d′):



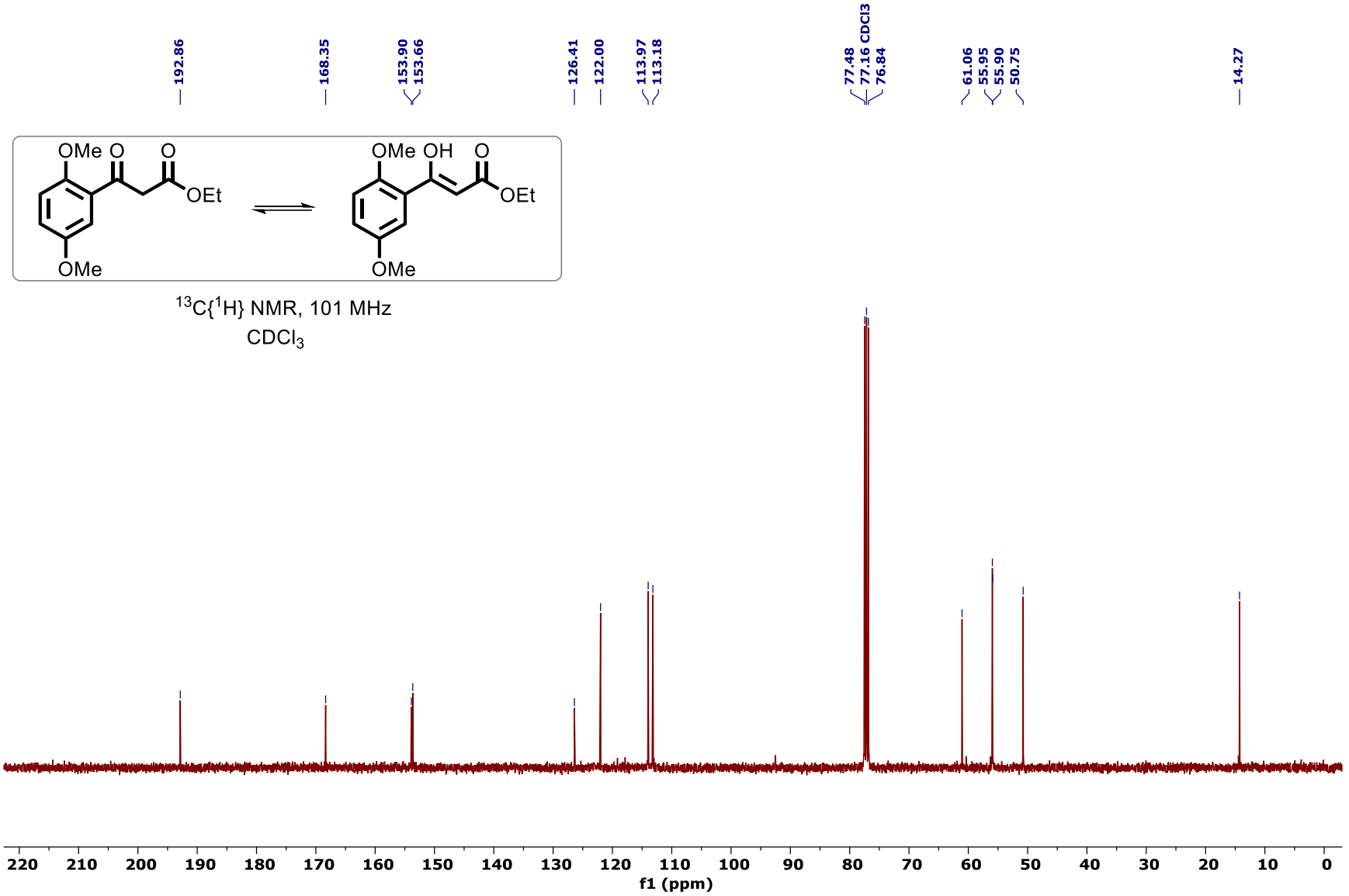
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(3-methoxyphenyl)-3-oxopropanoate (1d′):



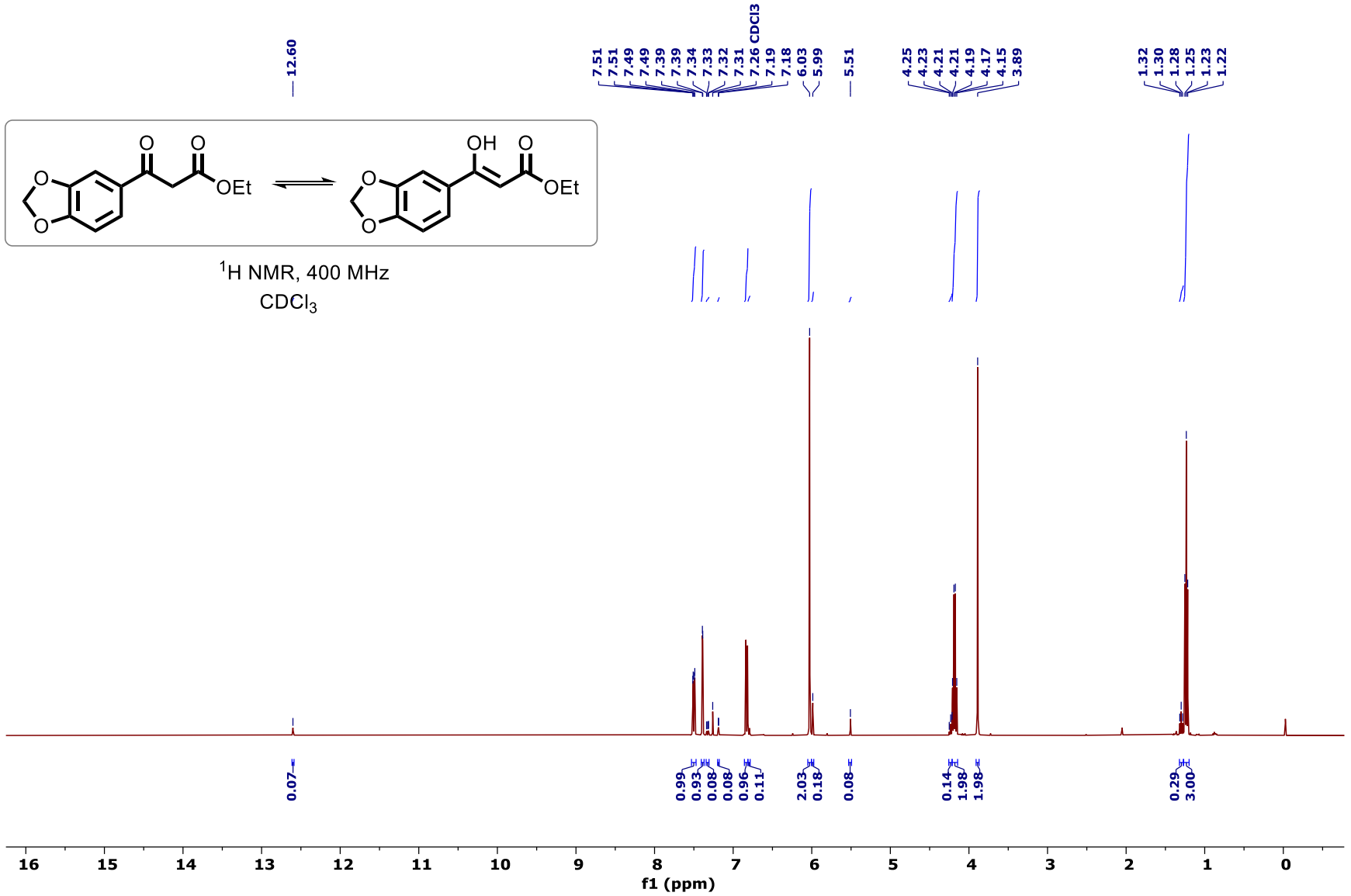
^{1}H NMR spectrum of Ethyl 3-(2,5-dimethoxyphenyl)-3-oxopropanoate (1e′):



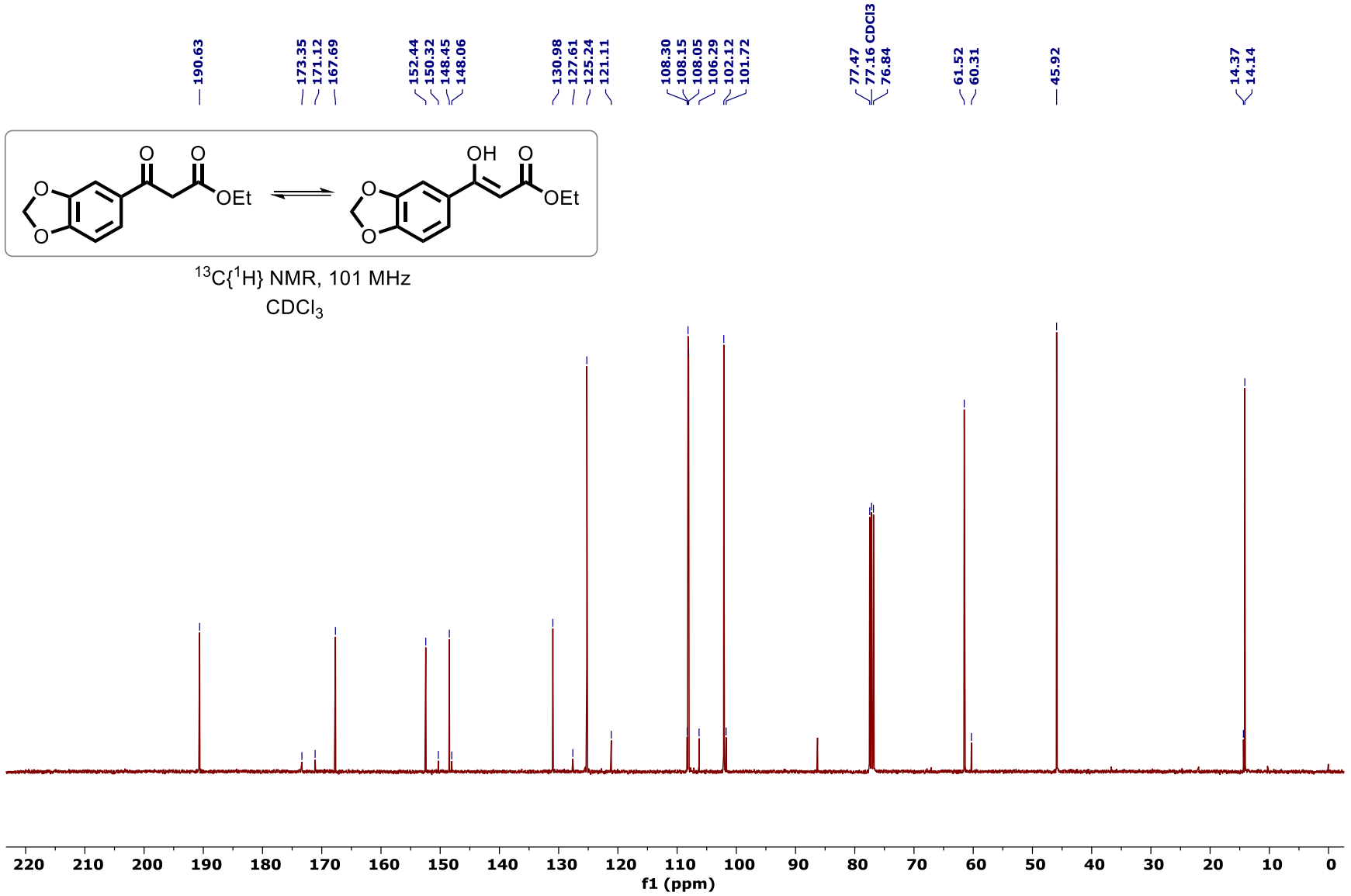
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(2,5-dimethoxyphenyl)-3-oxopropanoate (1e′):



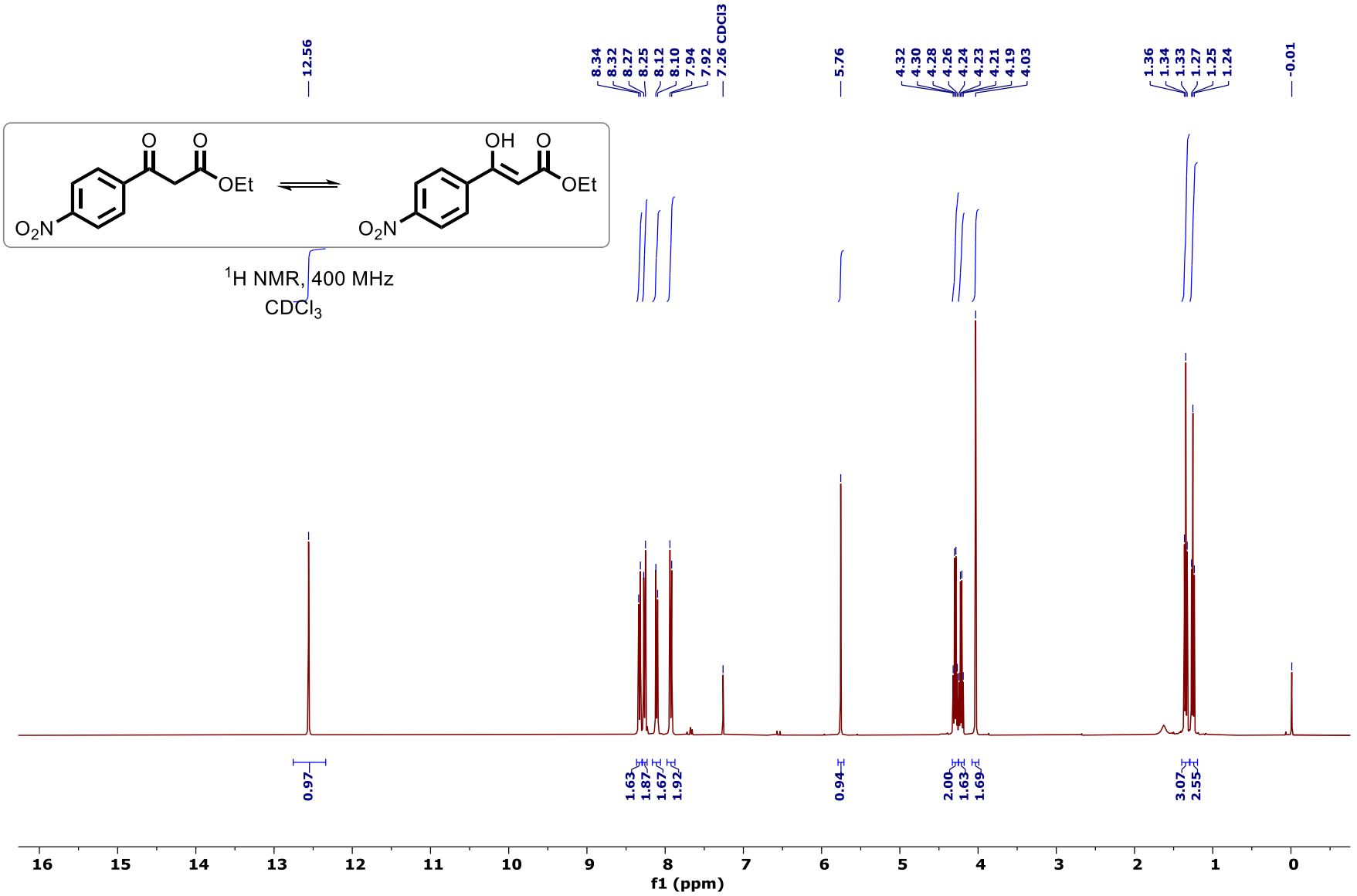
^{1}H NMR spectrum of Ethyl 3-(benzo[*d*][1,3]dioxol-5-yl)-3-oxopropanoate (1f′):



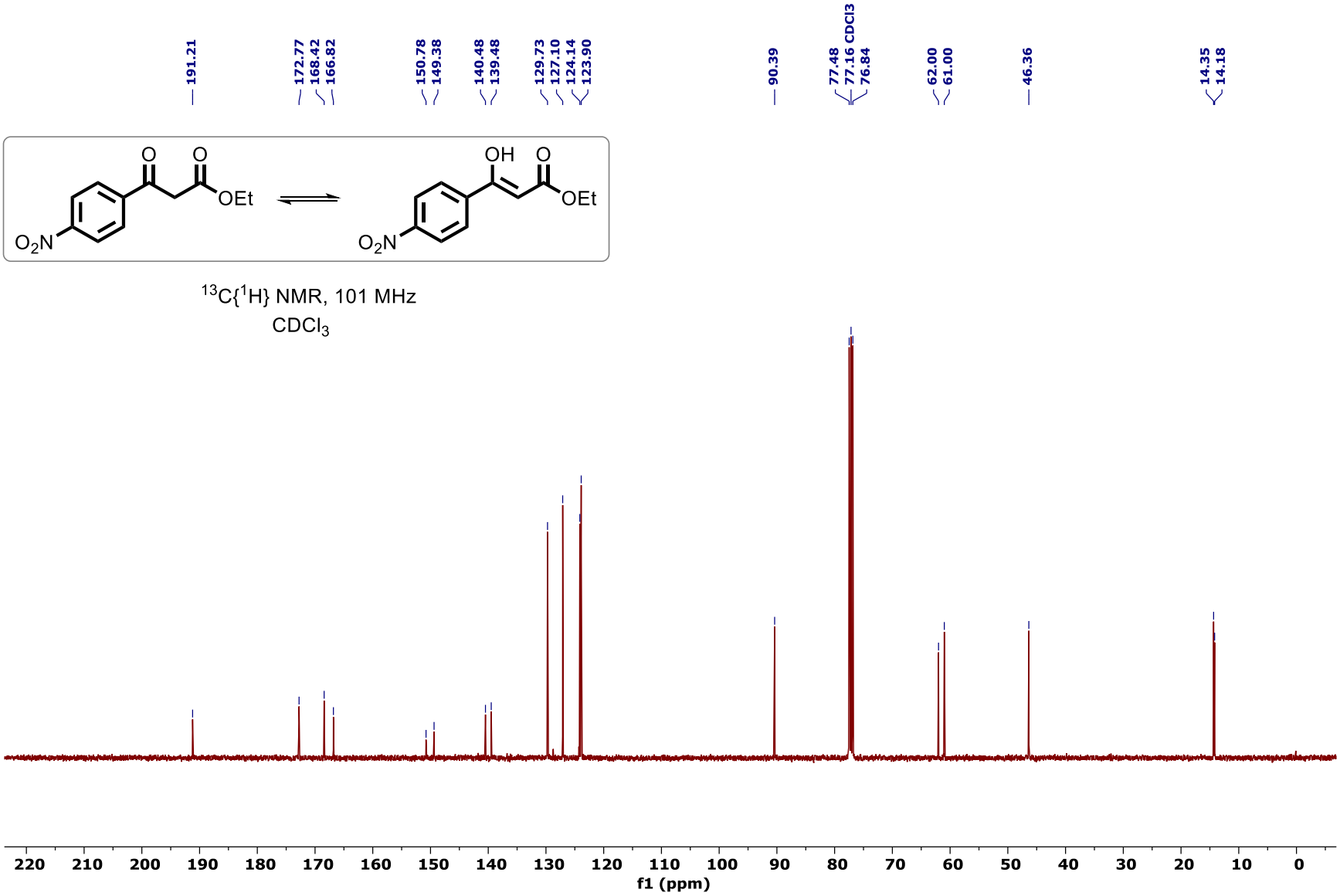
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(benzo[*d*][1,3]dioxol-5-yl)-3-oxopropanoate (1f′):



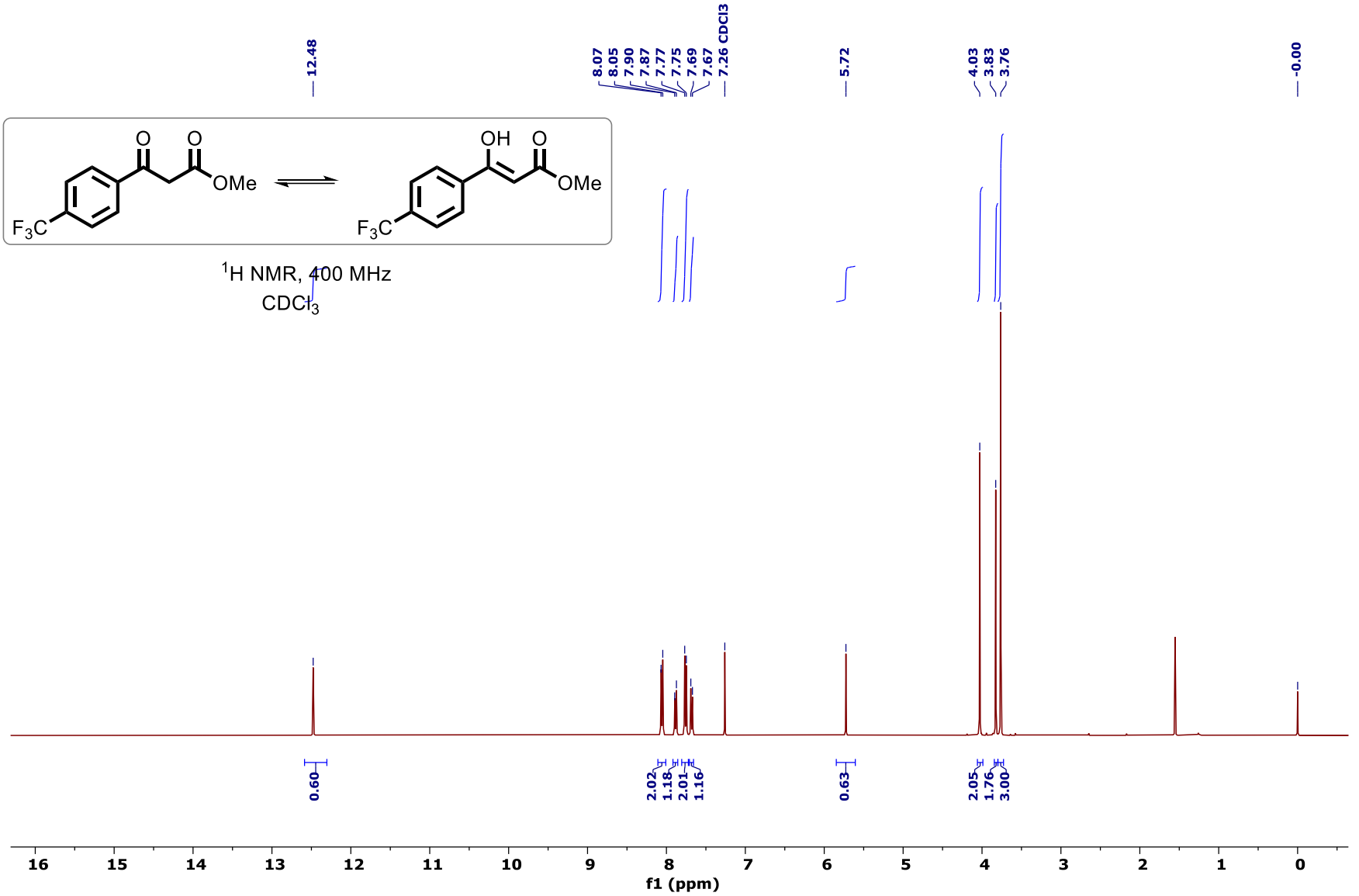
^{1}H NMR spectrum of Ethyl 3-(4-nitrophenyl)-3-oxopropanoate (1g′):



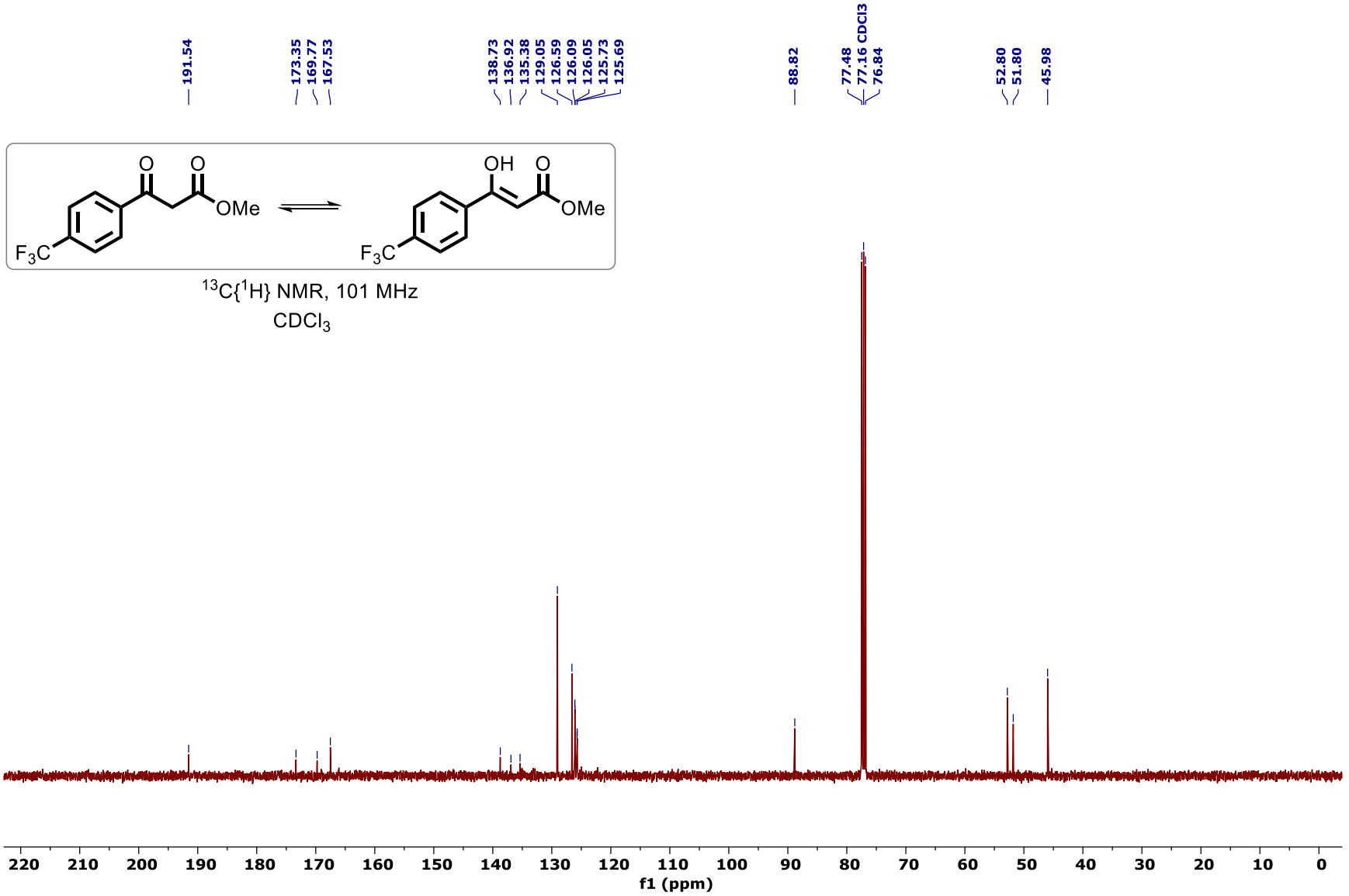
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(4-nitrophenyl)-3-oxopropanoate (1g′):



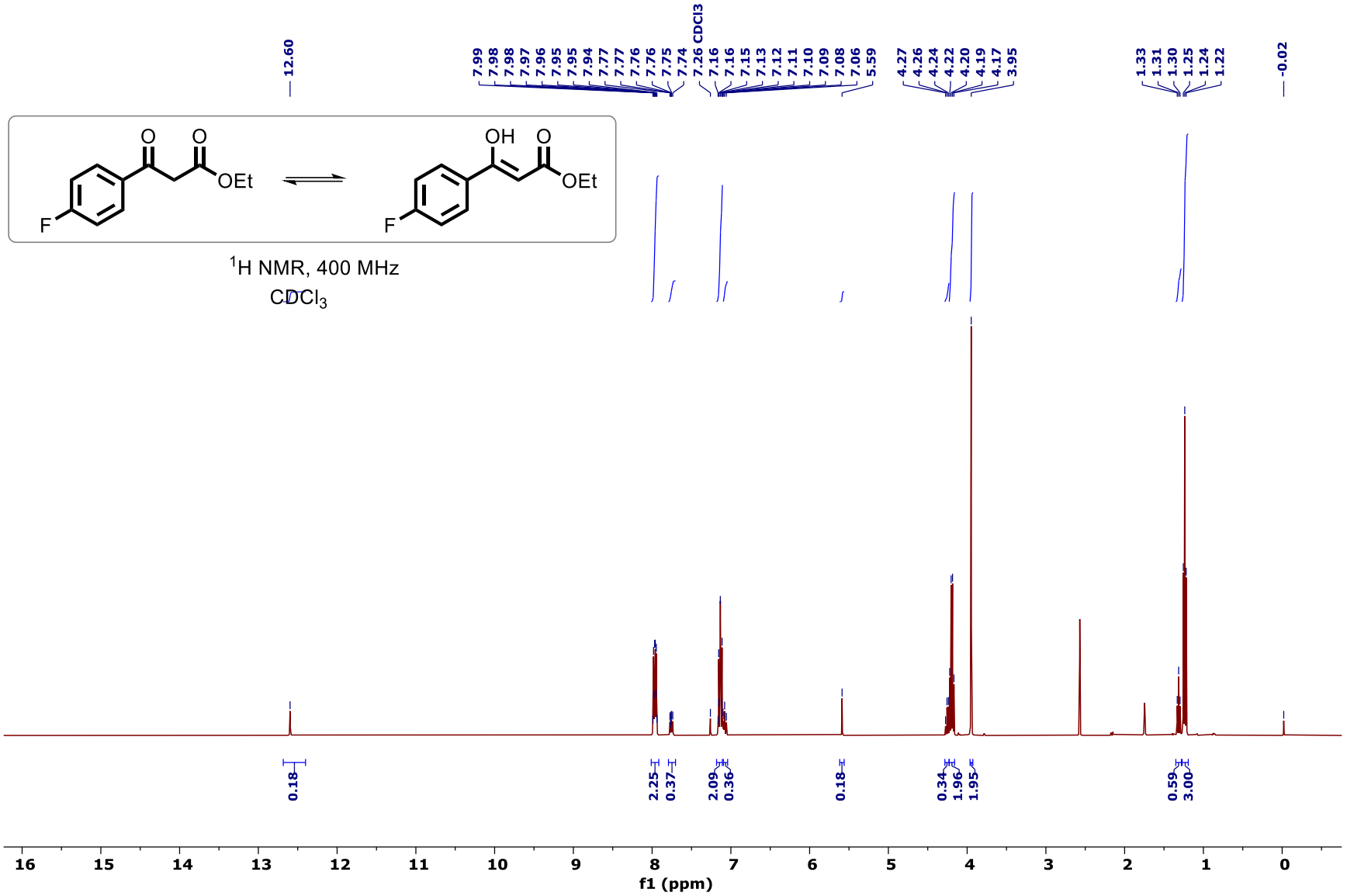
^{1}H NMR spectrum of Methyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (1h′):



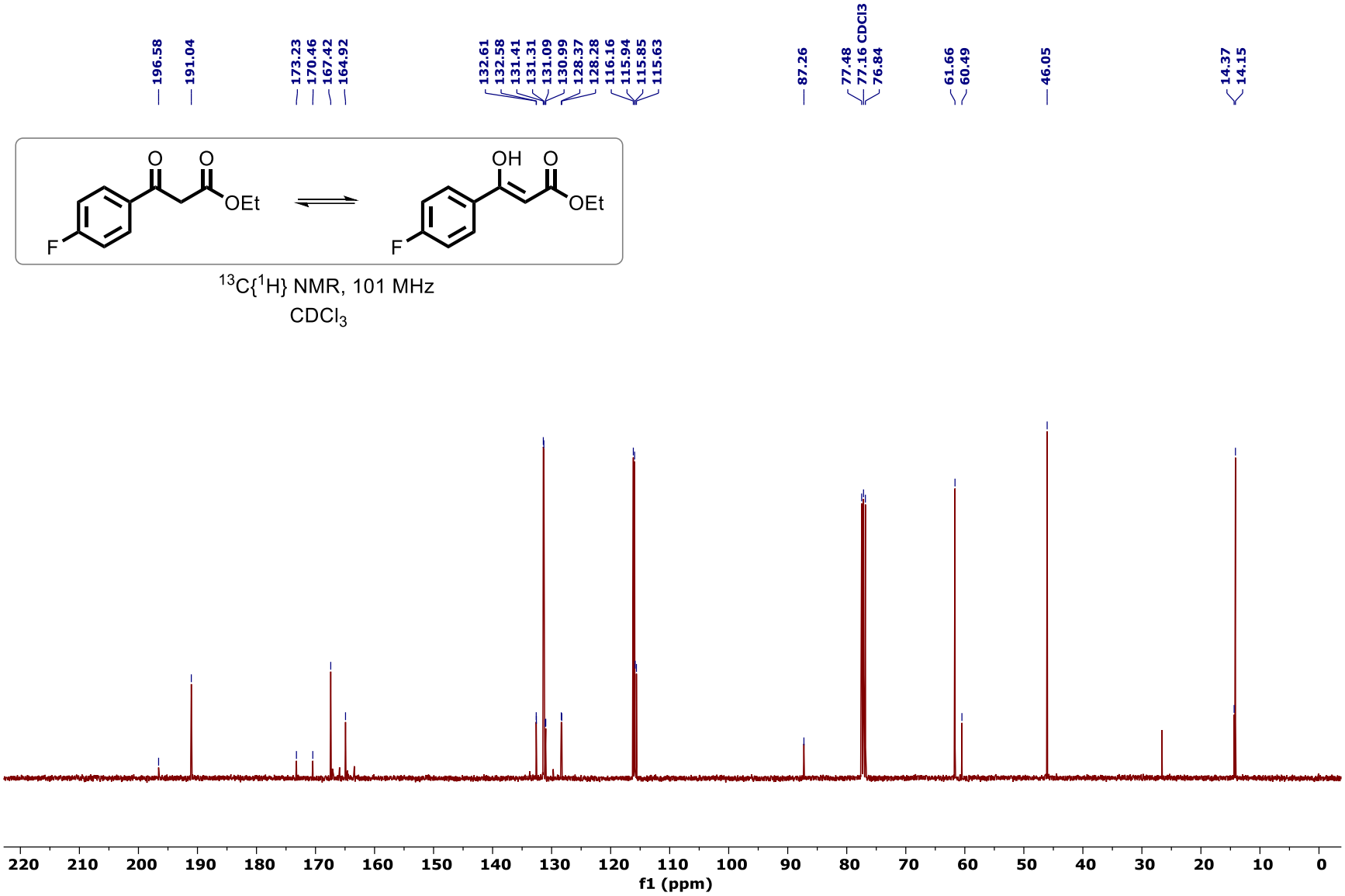
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (1h′):



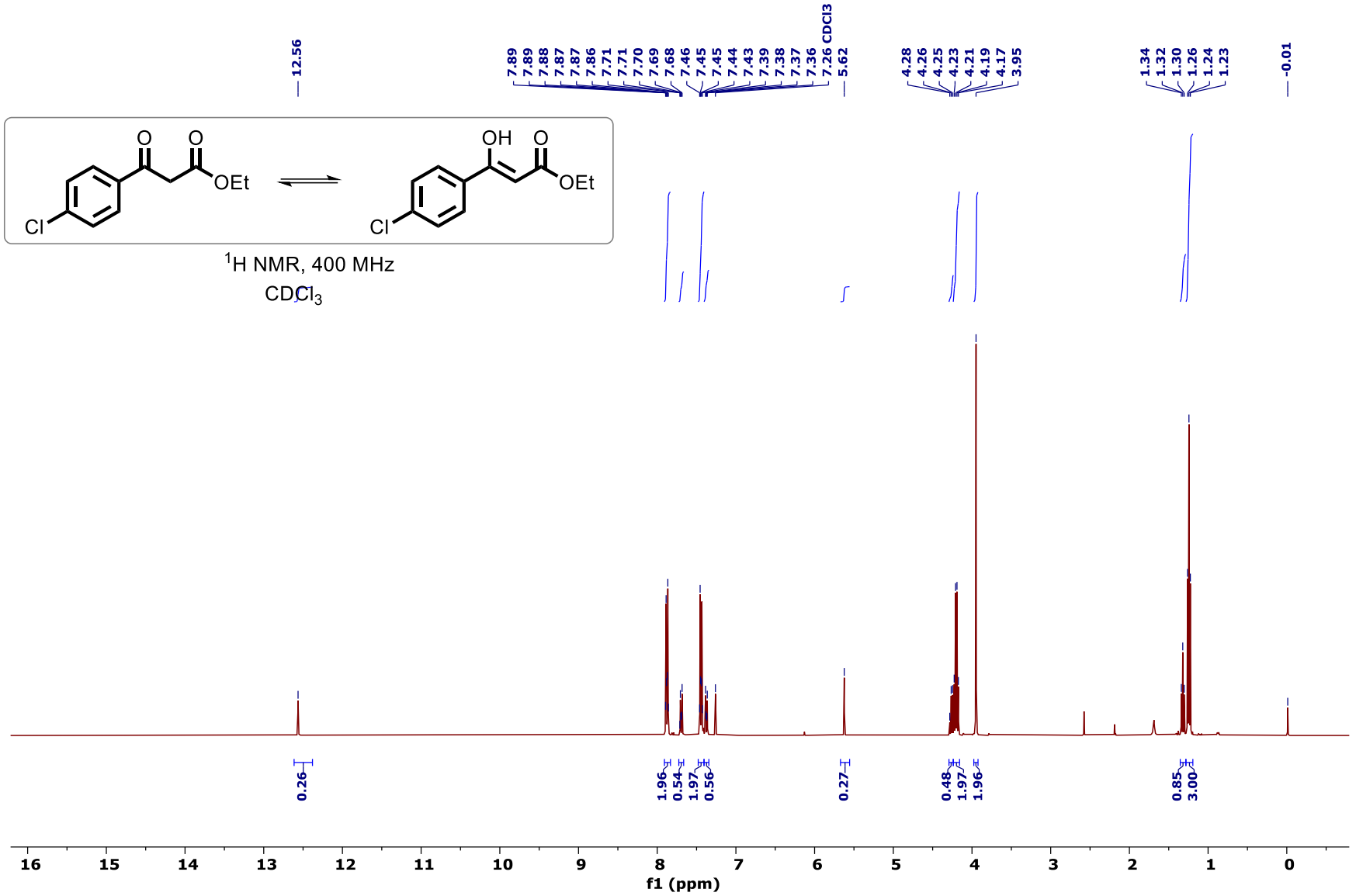
^{1}H NMR spectrum of Ethyl 3-(4-fluorophenyl)-3-oxopropanoate (1i′):



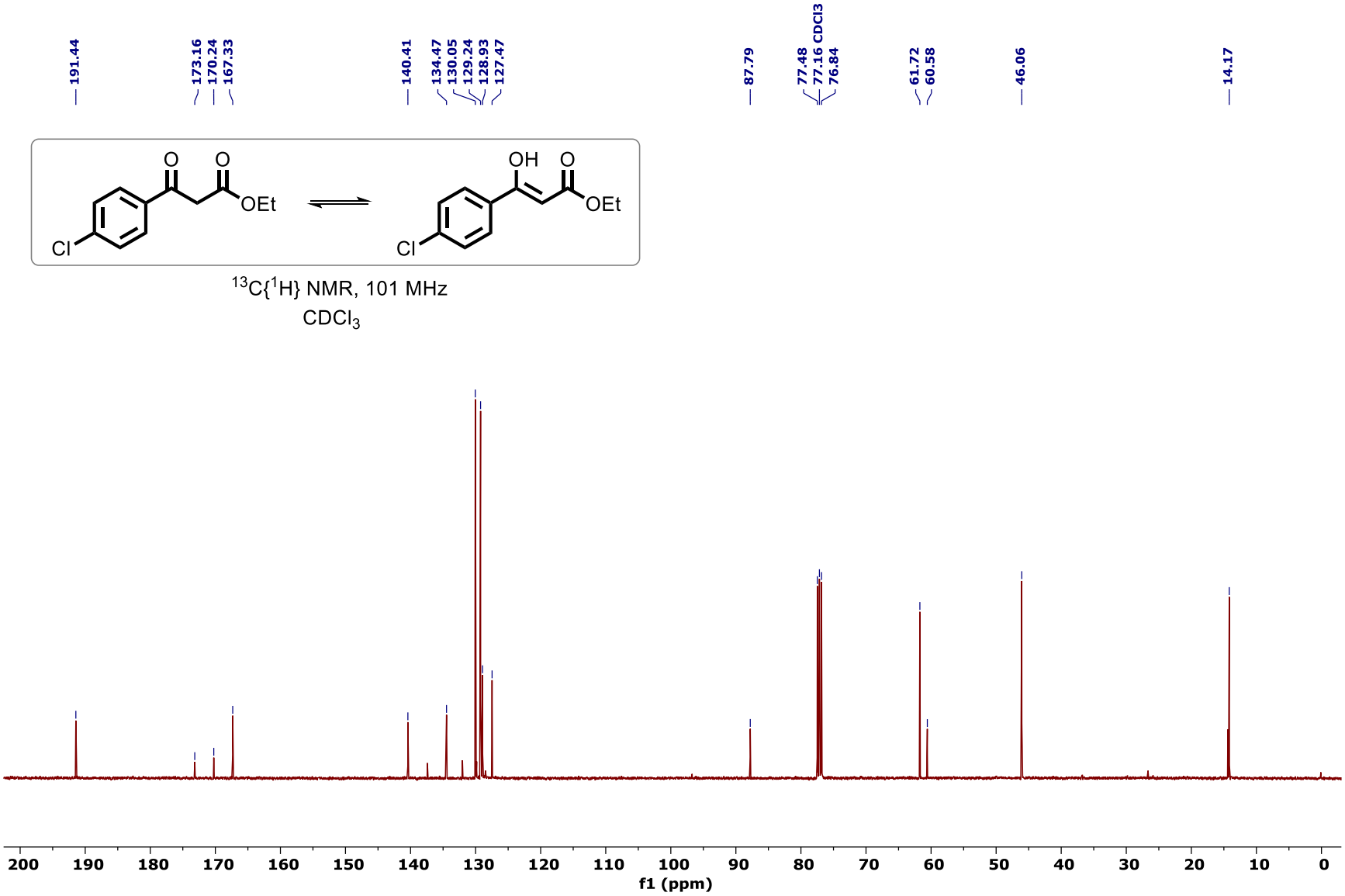
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(4-fluorophenyl)-3-oxopropanoate (1i′):



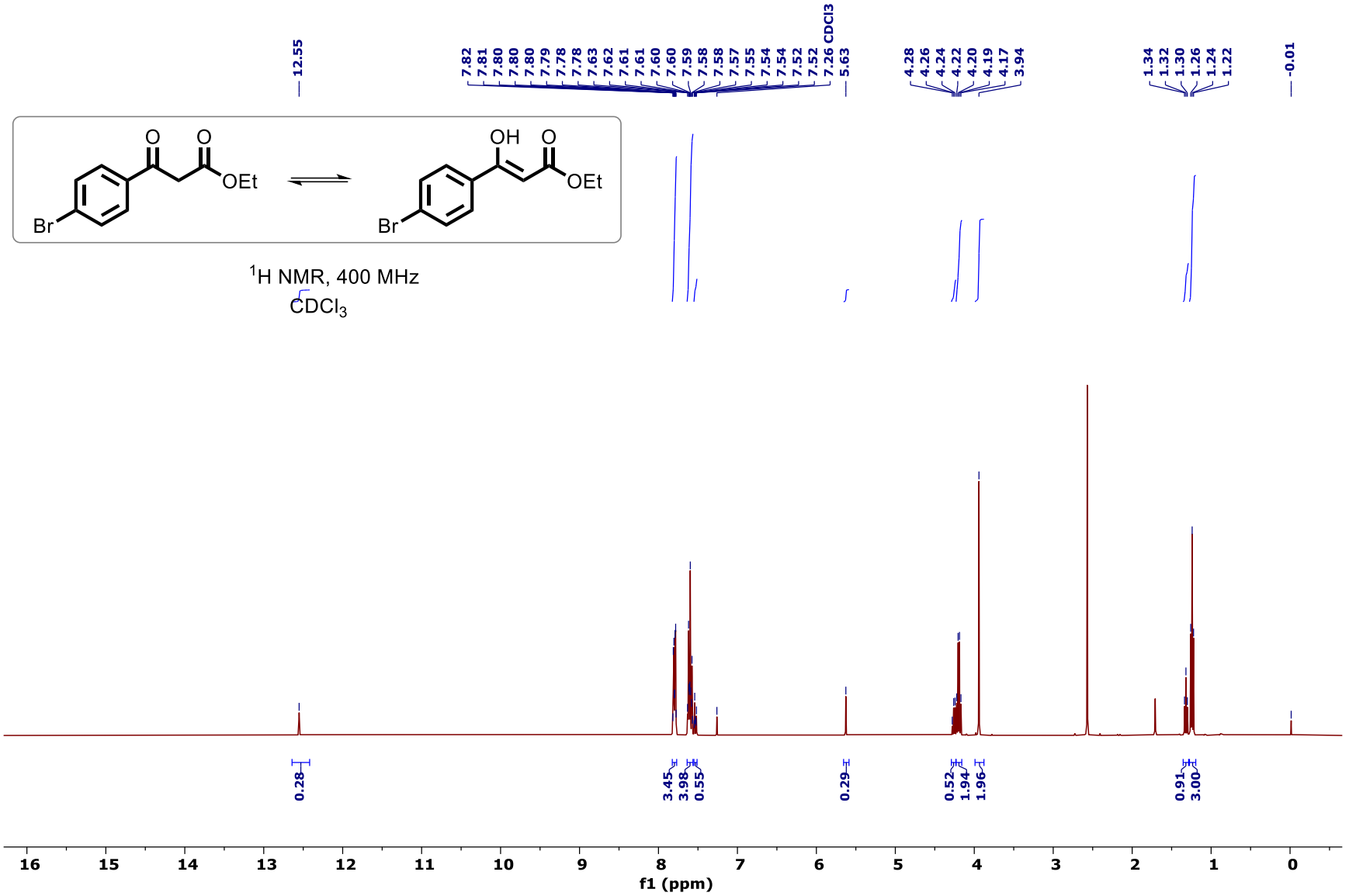
^{1}H NMR spectrum of Ethyl 3-(4-chlorophenyl)-3-oxopropanoate (1j′):



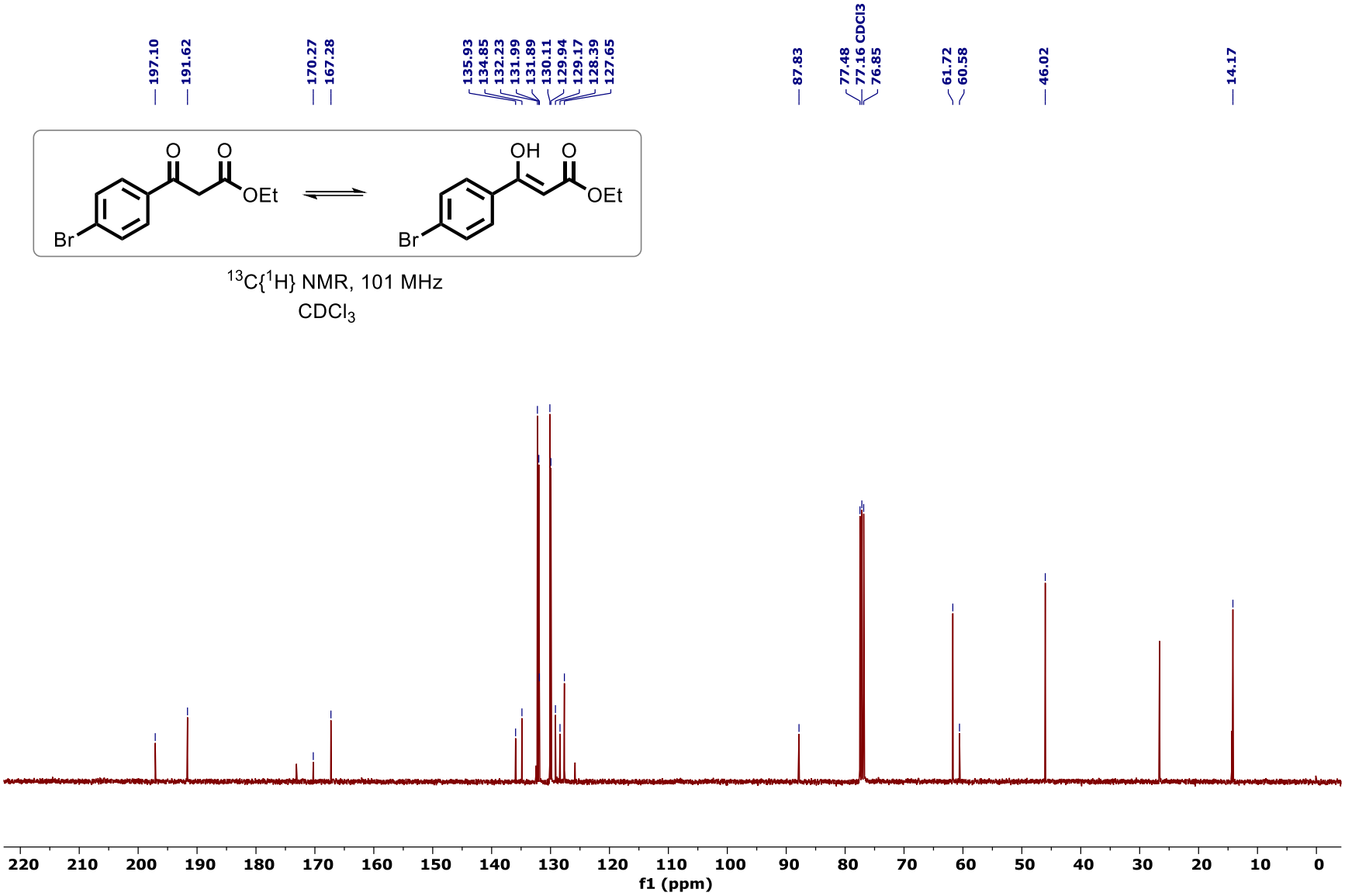
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(4-chlorophenyl)-3-oxopropanoate (1j′):



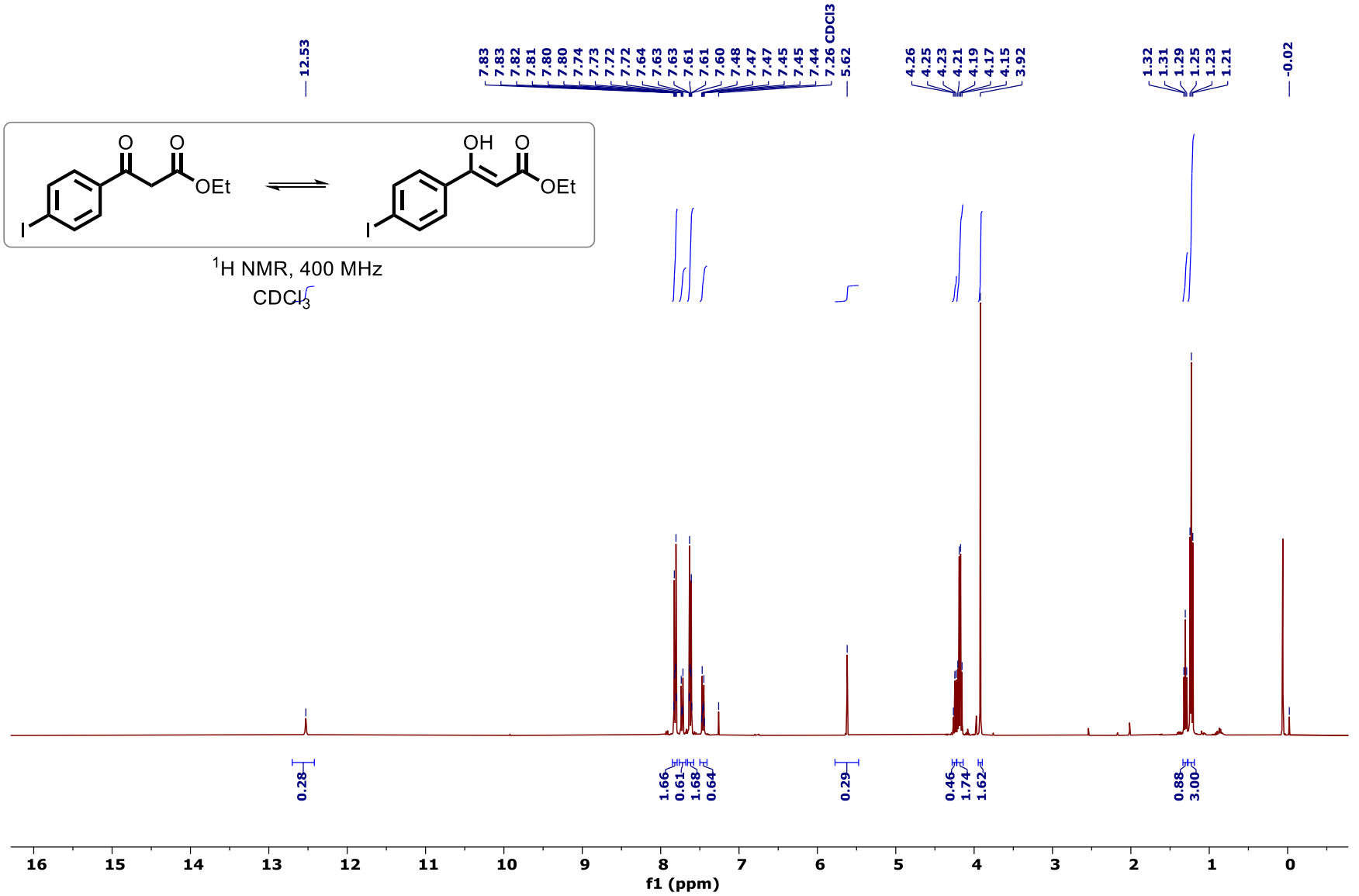
^{1}H NMR spectrum of Ethyl 3-(4-bromophenyl)-3-oxopropanoate (1k′):



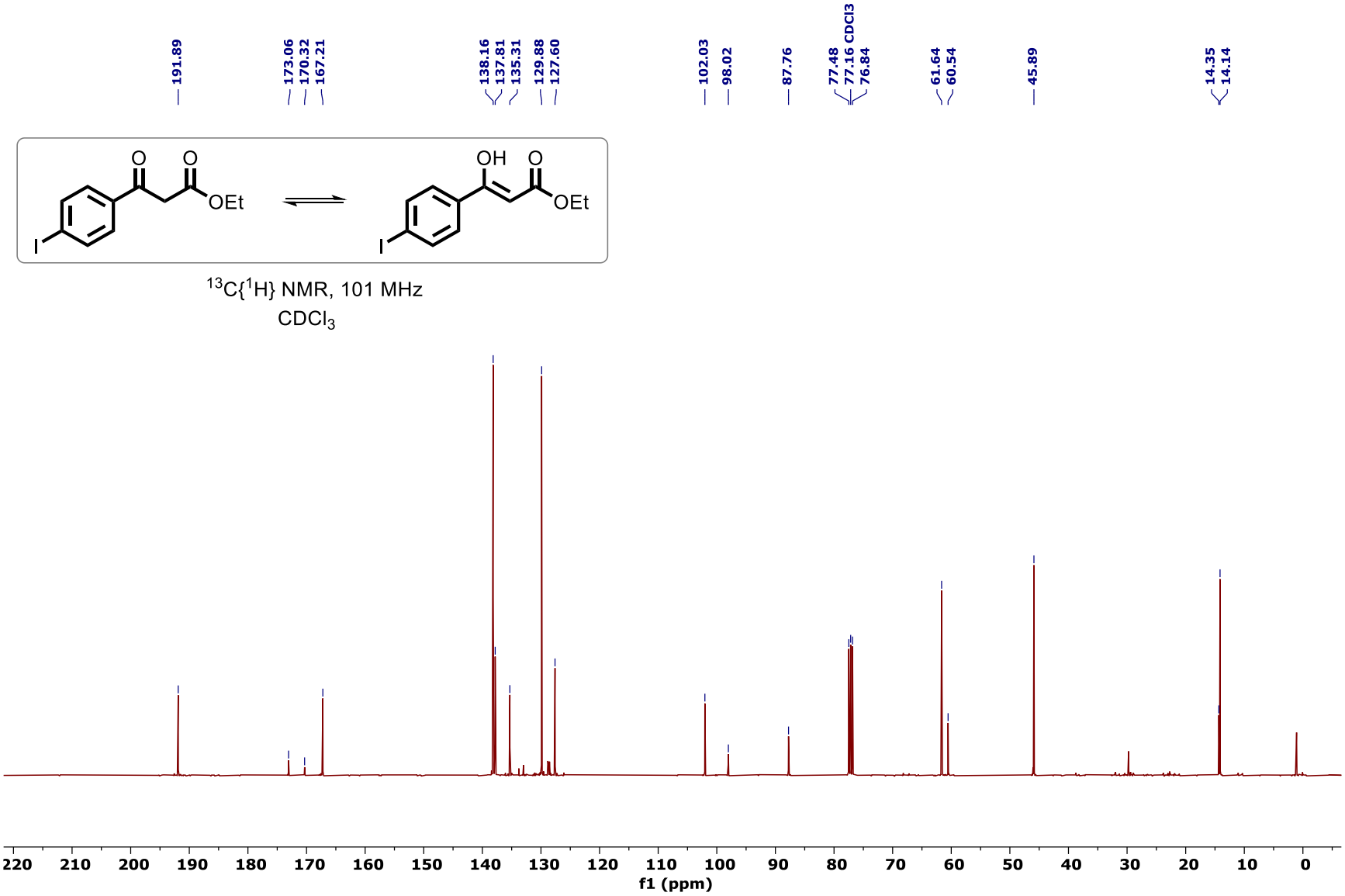
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(4-bromophenyl)-3-oxopropanoate (1k′):



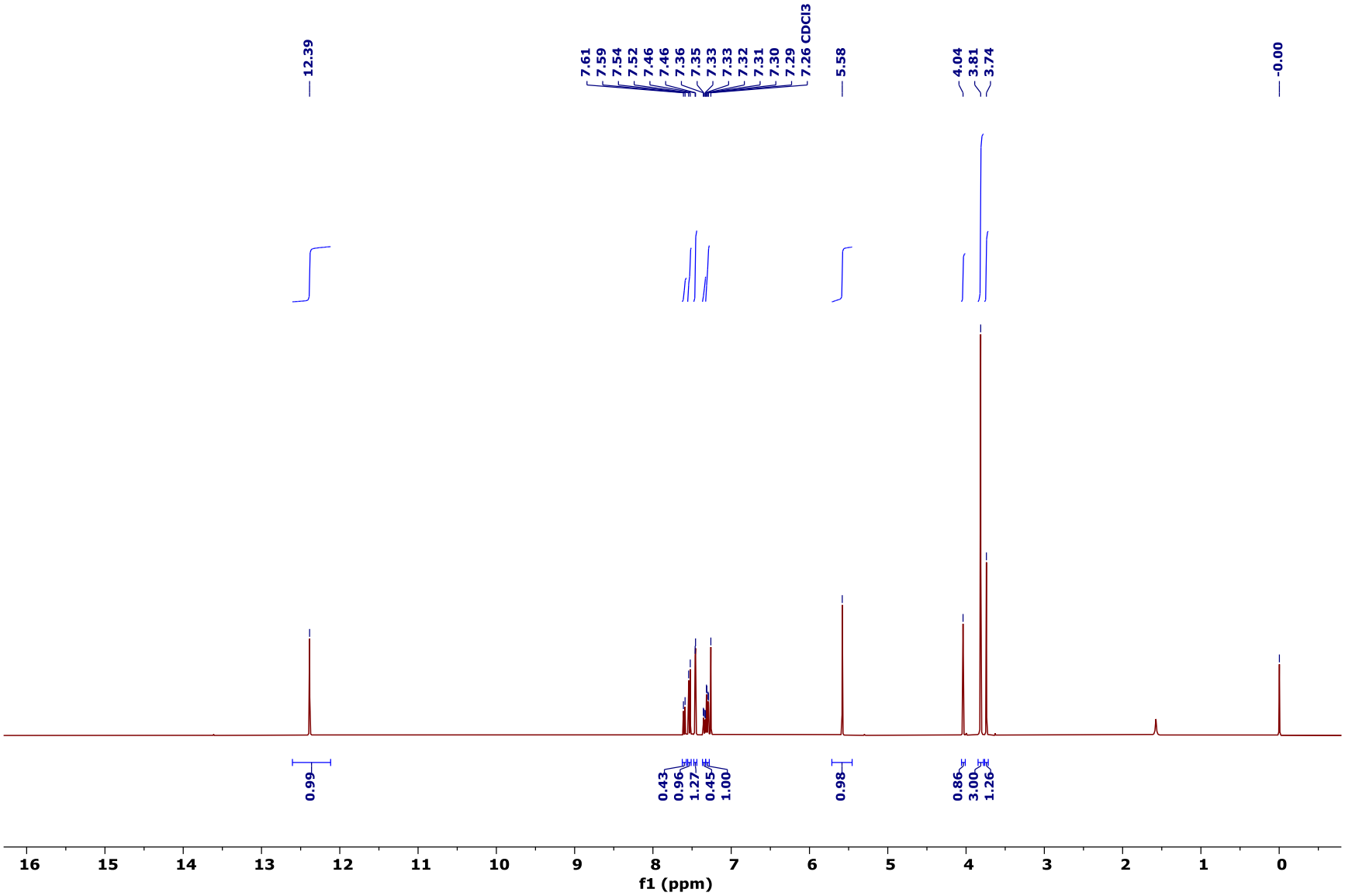
^{1}H NMR spectrum of Ethyl 3-(4-iodophenyl)-3-oxopropanoate (1l′):



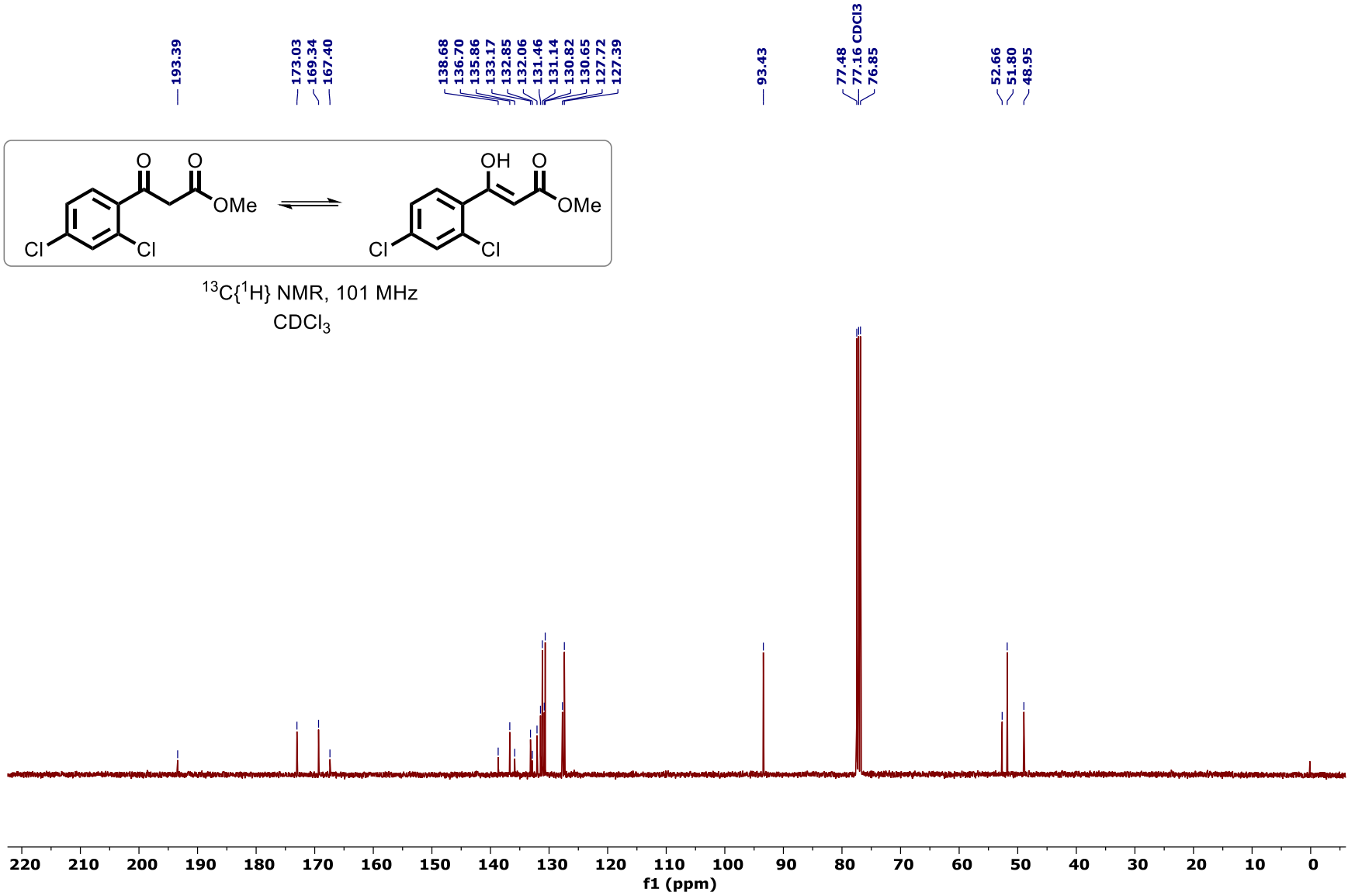
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(4-iodophenyl)-3-oxopropanoate (1l′):



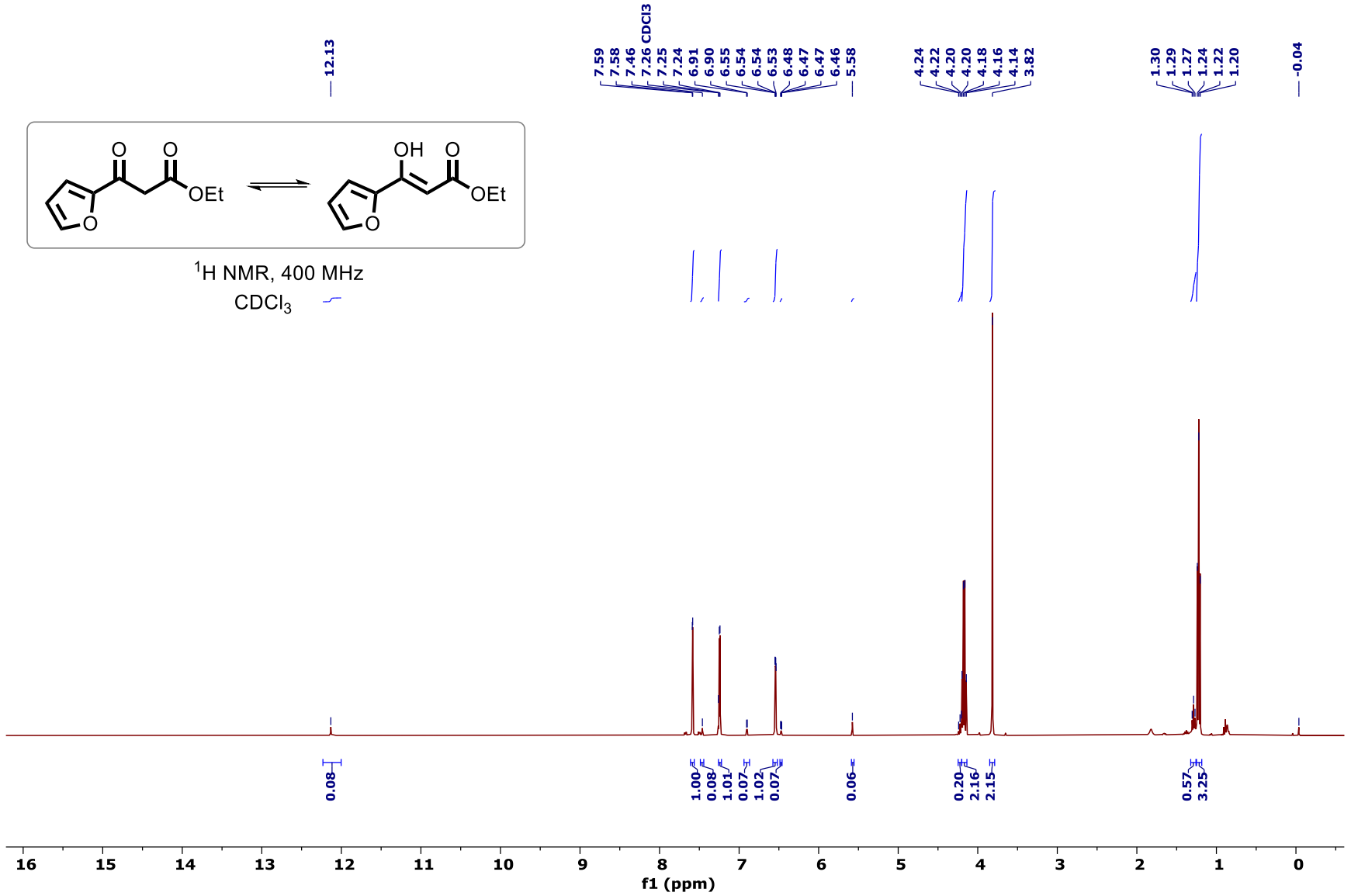
^{1}H NMR spectrum of Methyl 3-(2,4-dichlorophenyl)-3-oxopropanoate (1m′):



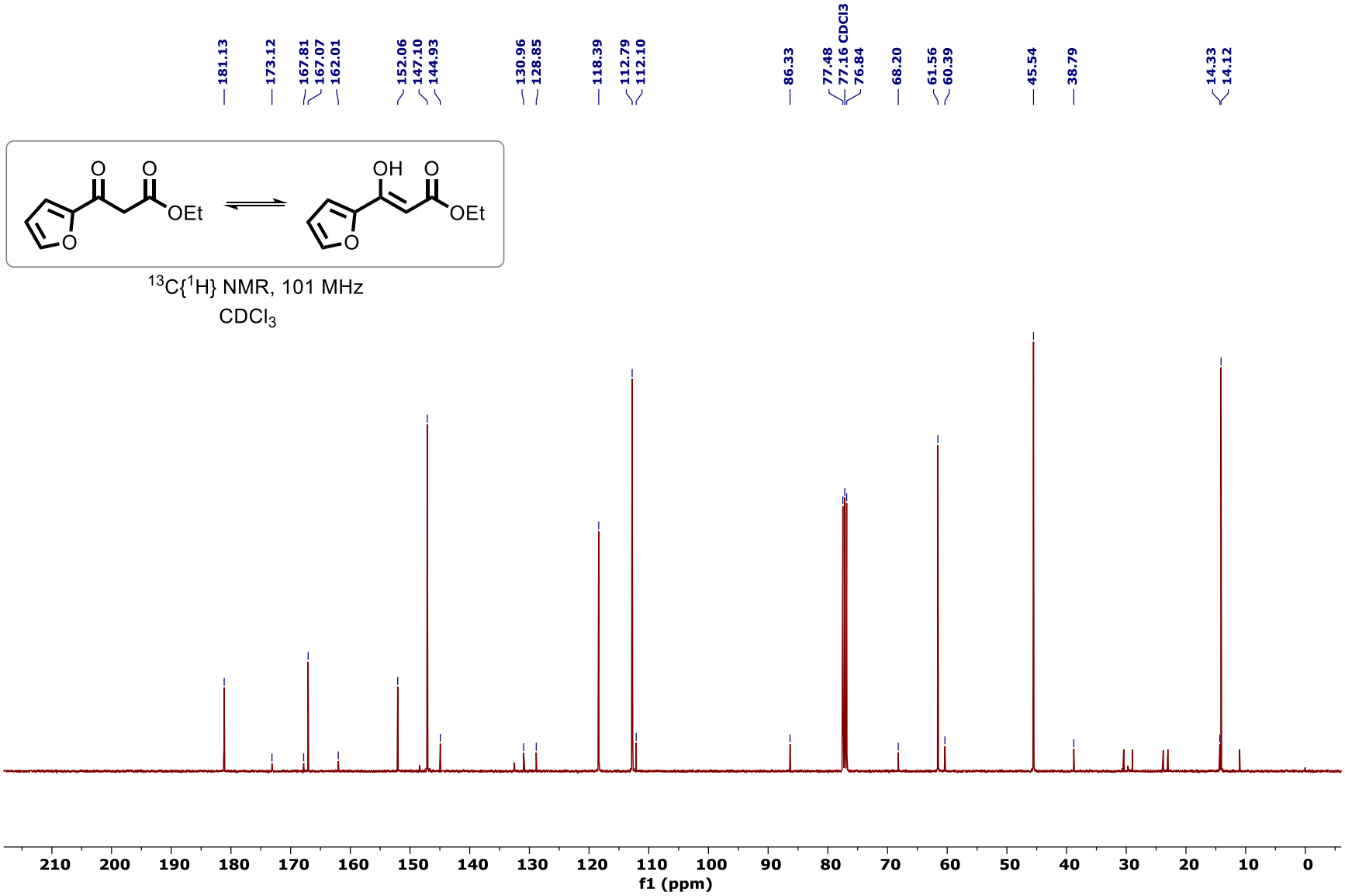
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-(2,4-dichlorophenyl)-3-oxopropanoate (1m′):



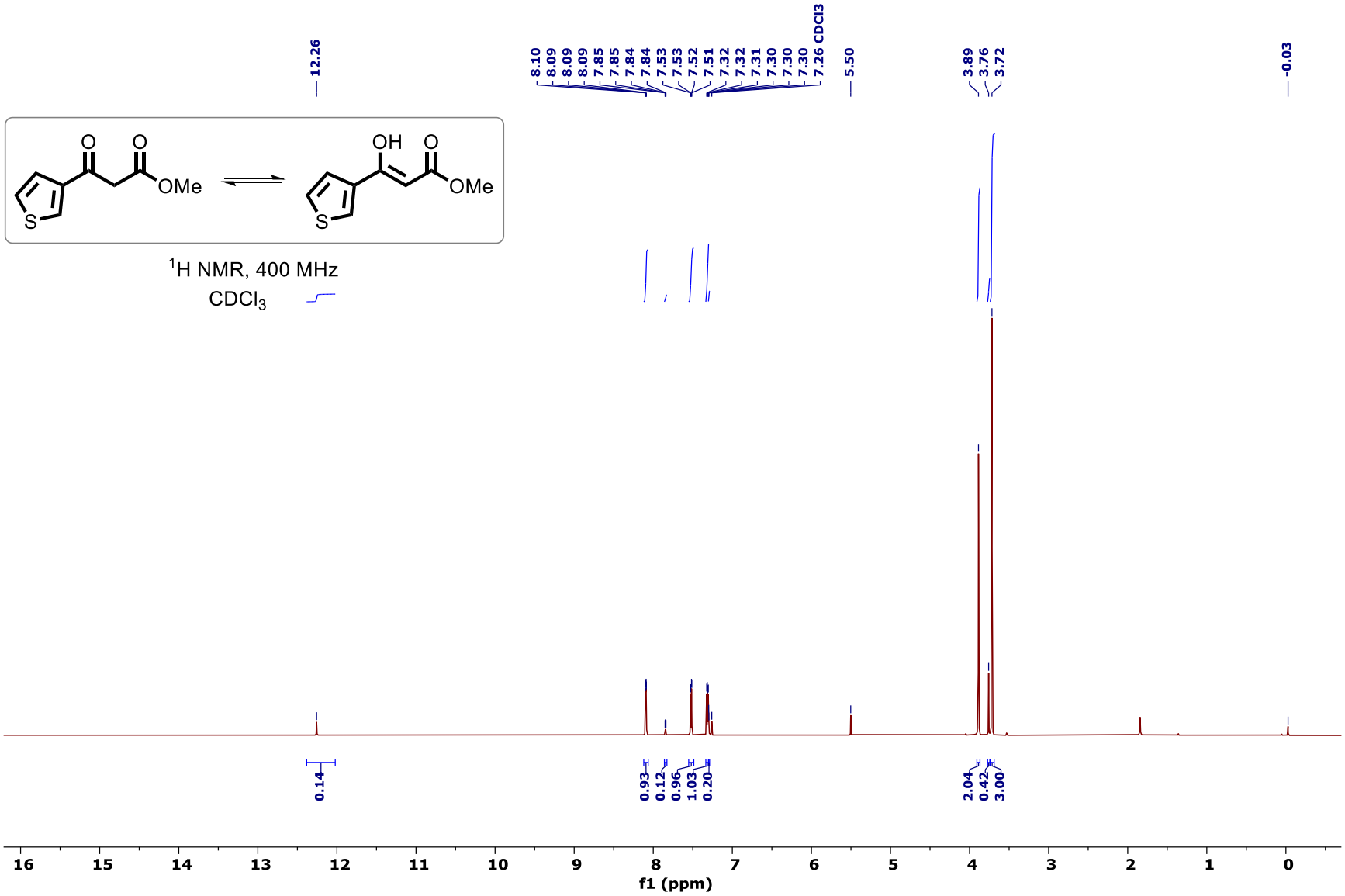
^{1}H NMR spectrum of Ethyl 3-(furan-2-yl)-3-oxopropanoate (1n′):



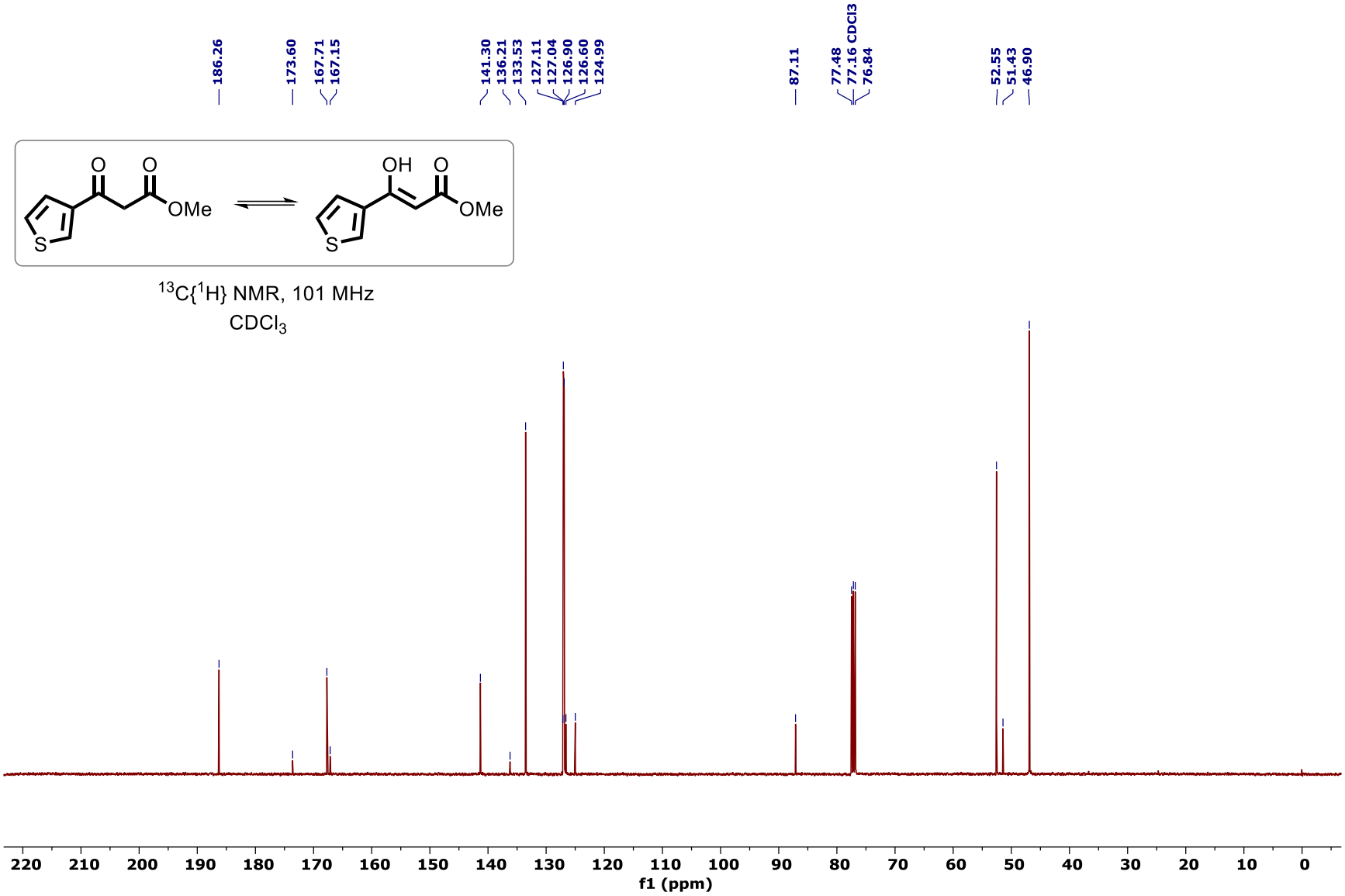
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(furan-2-yl)-3-oxopropanoate (1n′):



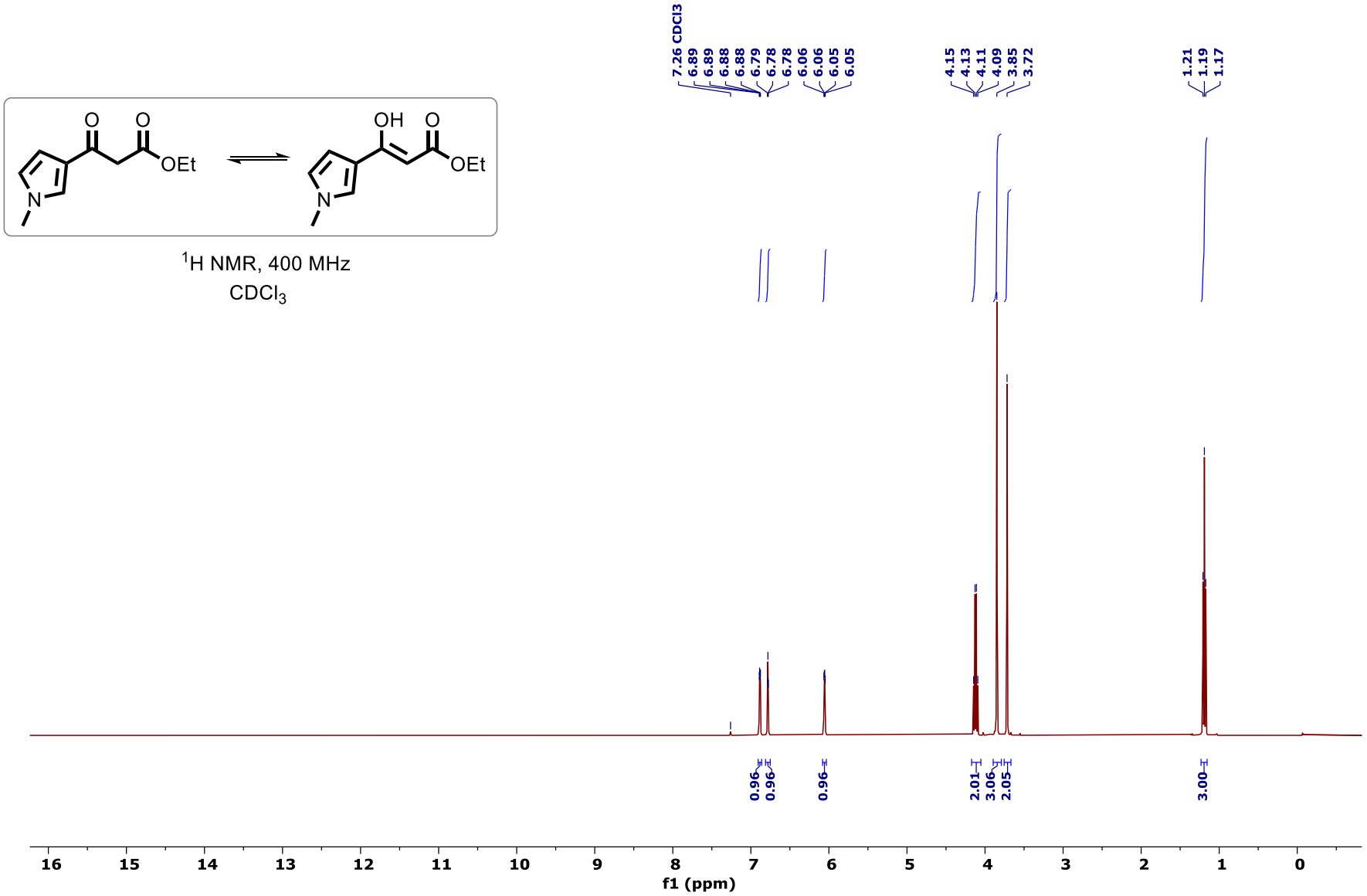
^{1}H NMR spectrum of Methyl 3-oxo-3-(thiophen-3-yl)propanoate (1o′):



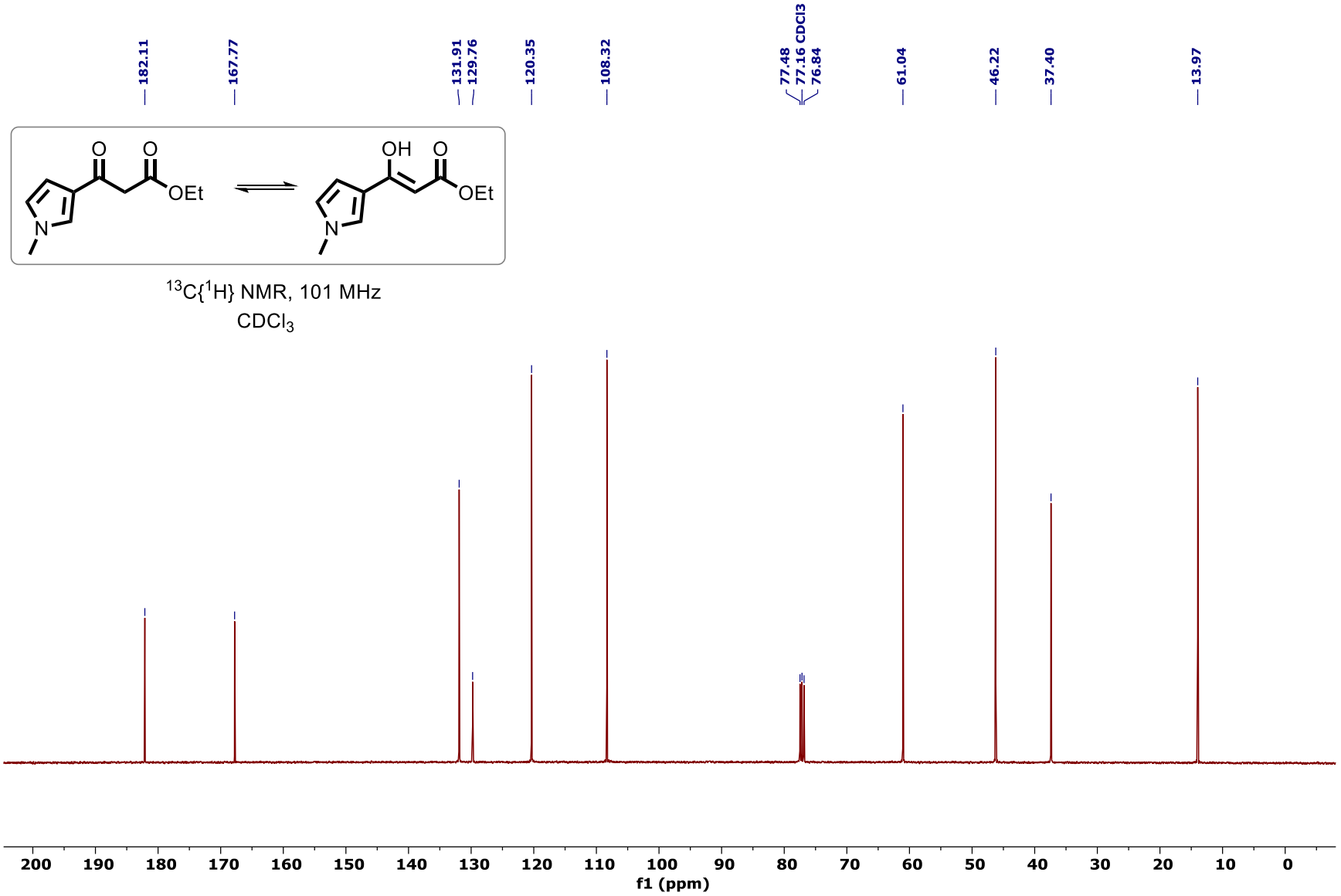
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-oxo-3-(thiophen-3-yl)propanoate (1o′):



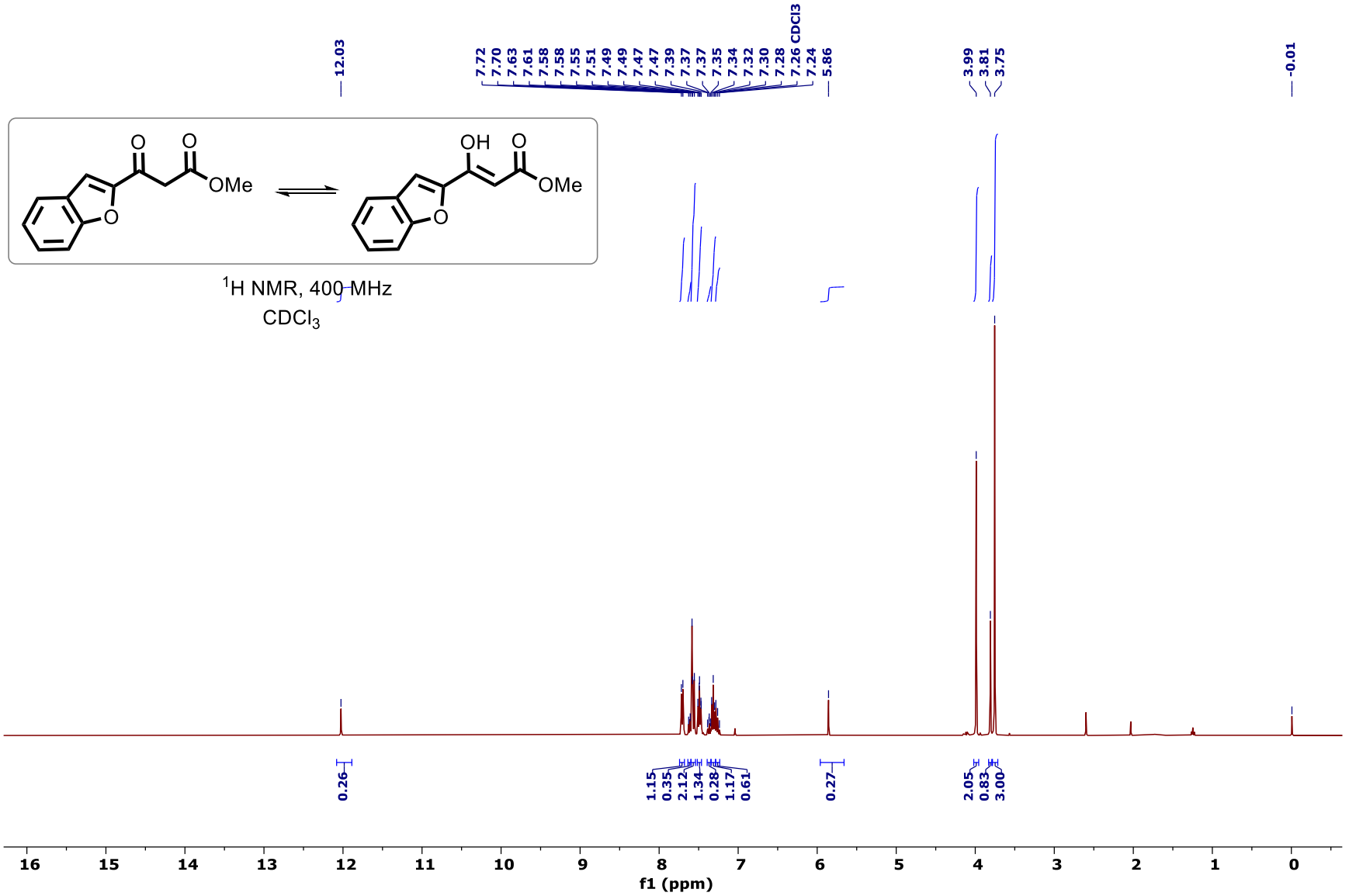
^{1}H NMR spectrum of Ethyl 3-(1-methyl-1*H*-pyrrol-3-yl)-3-oxopropanoate (1p′):



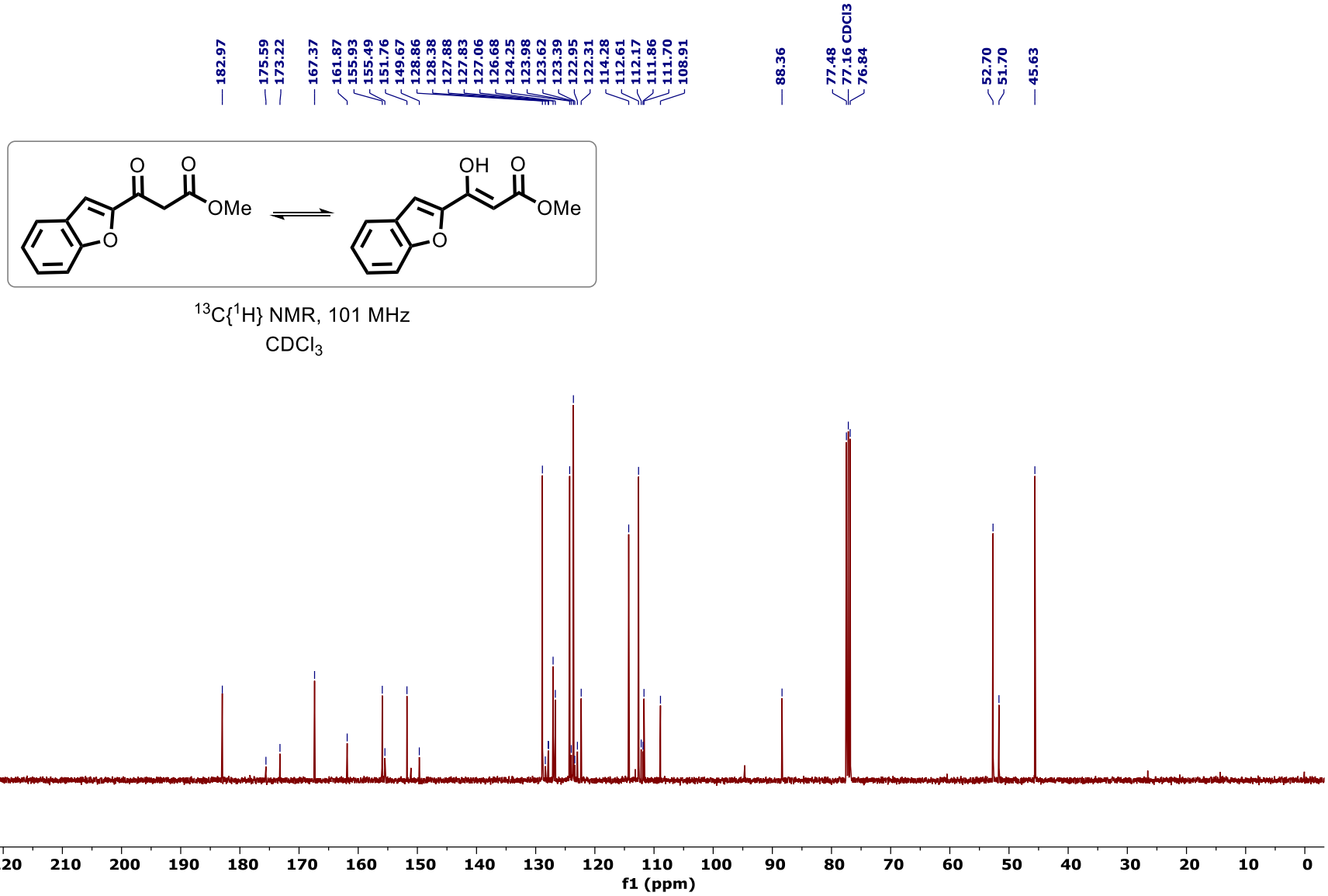
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(1-methyl-1*H*-pyrrol-3-yl)-3-oxopropanoate (1p′):



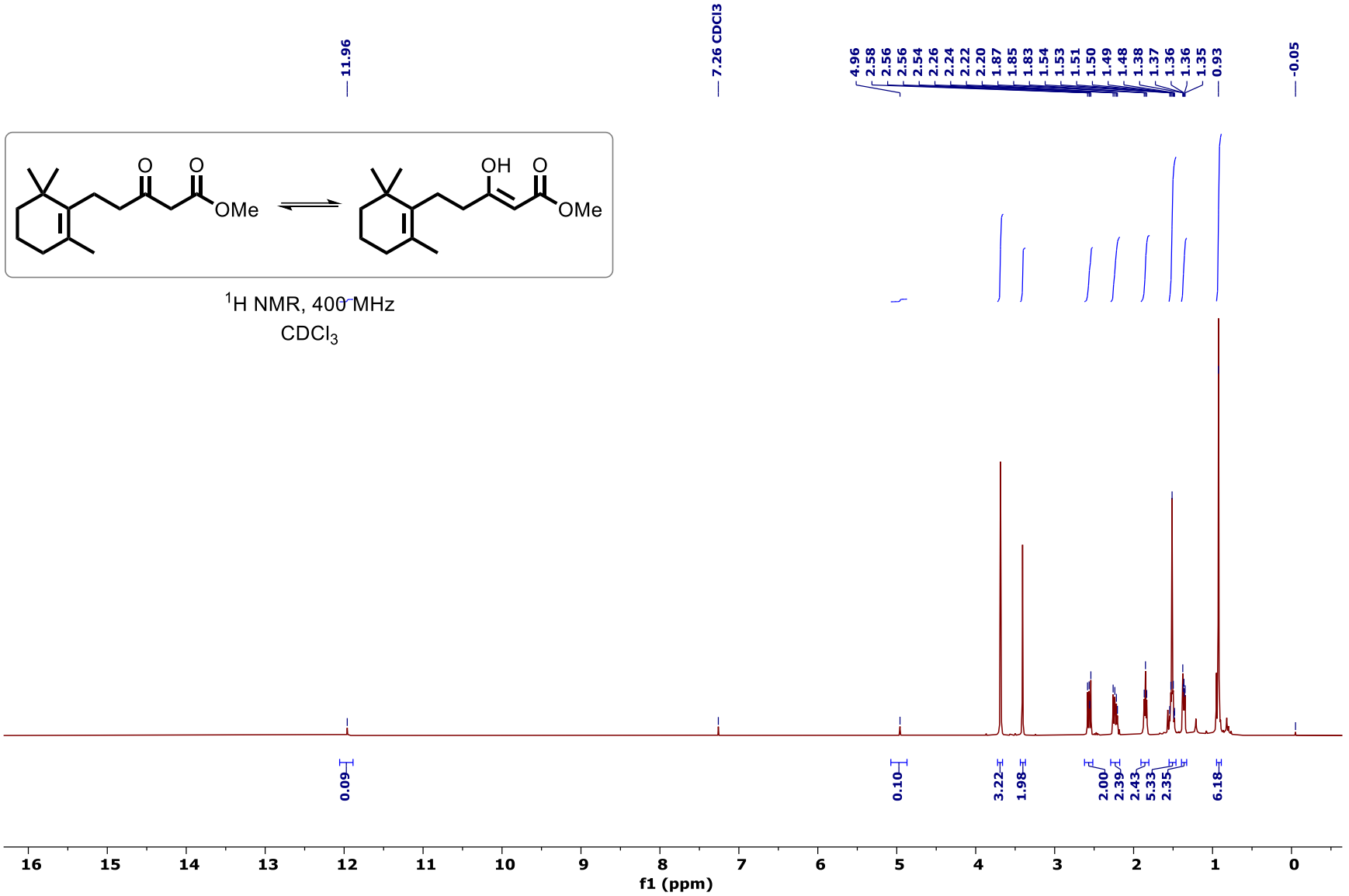
^{1}H NMR spectrum of Methyl 3-(benzofuran-2-yl)-3-oxopropanoate (1q′):



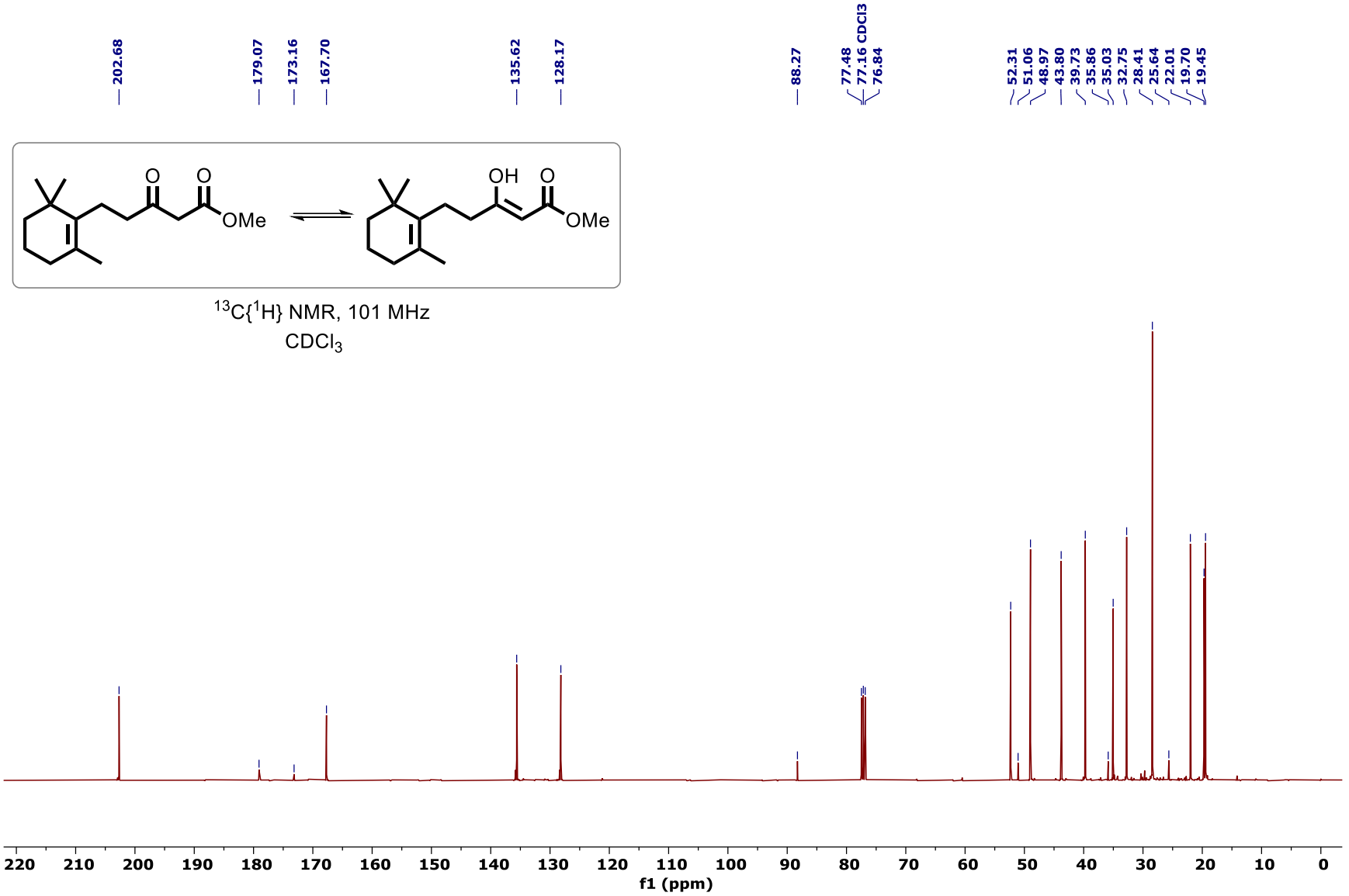
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-(benzofuran-2-yl)-3-oxopropanoate (1q′):



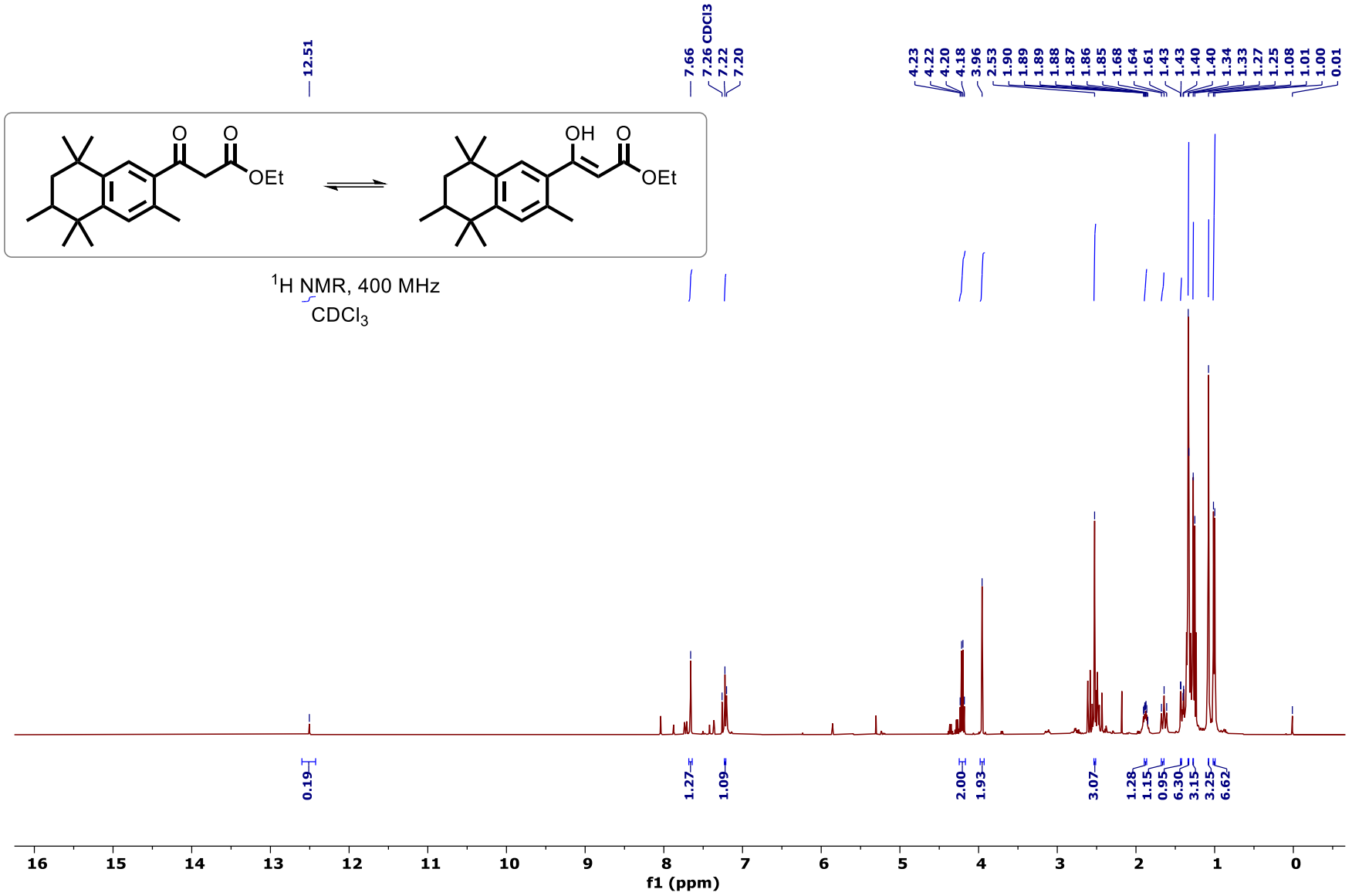
^{1}H NMR spectrum of Methyl 3-oxo-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pentanoate (1r′):



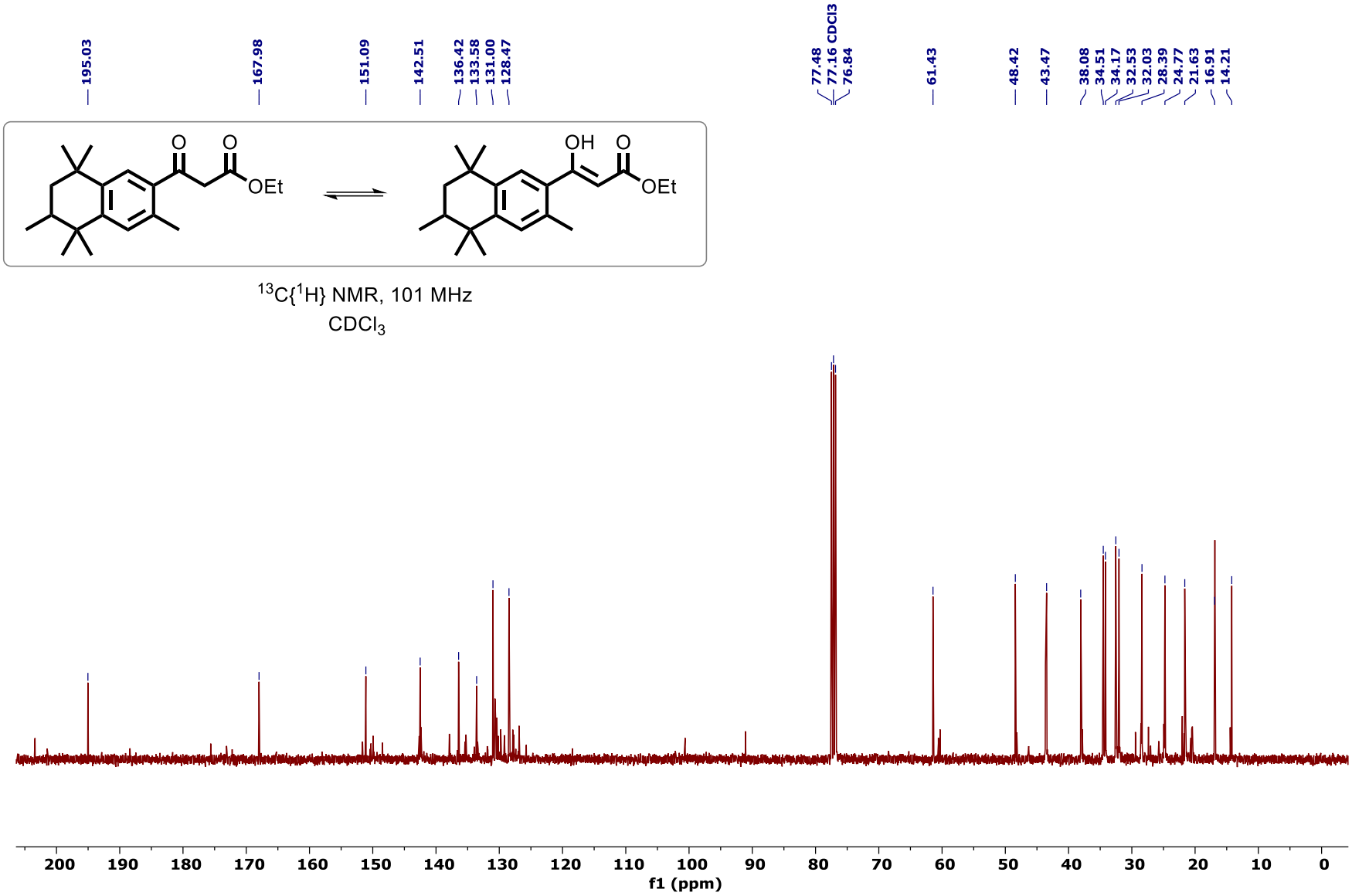
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 3-oxo-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pentanoate (1r′):



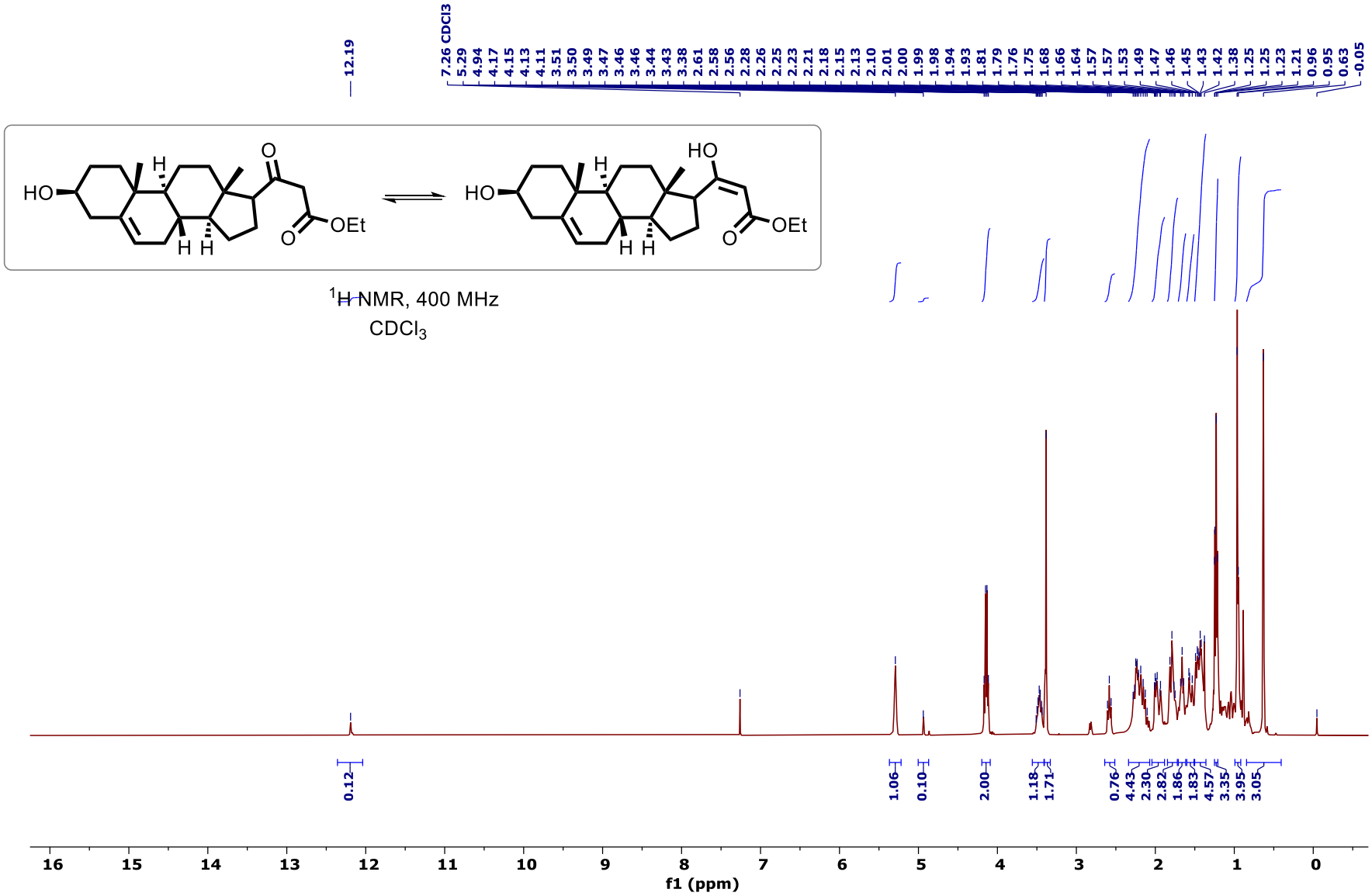
^{1}H NMR spectrum of of Ethyl 3-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-3-oxopropanoate (1s′):



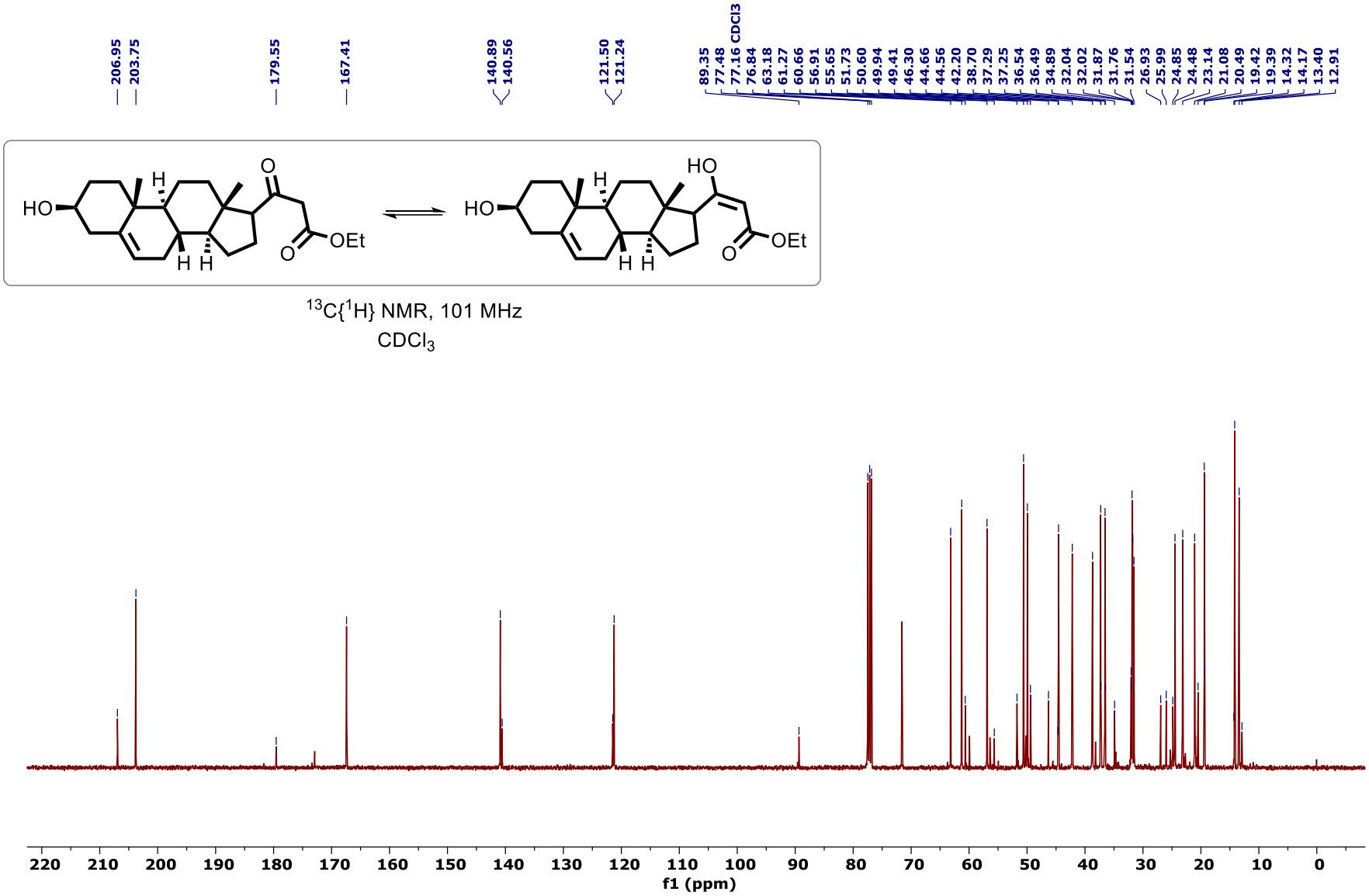
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-3-oxopropanoate (1s′):



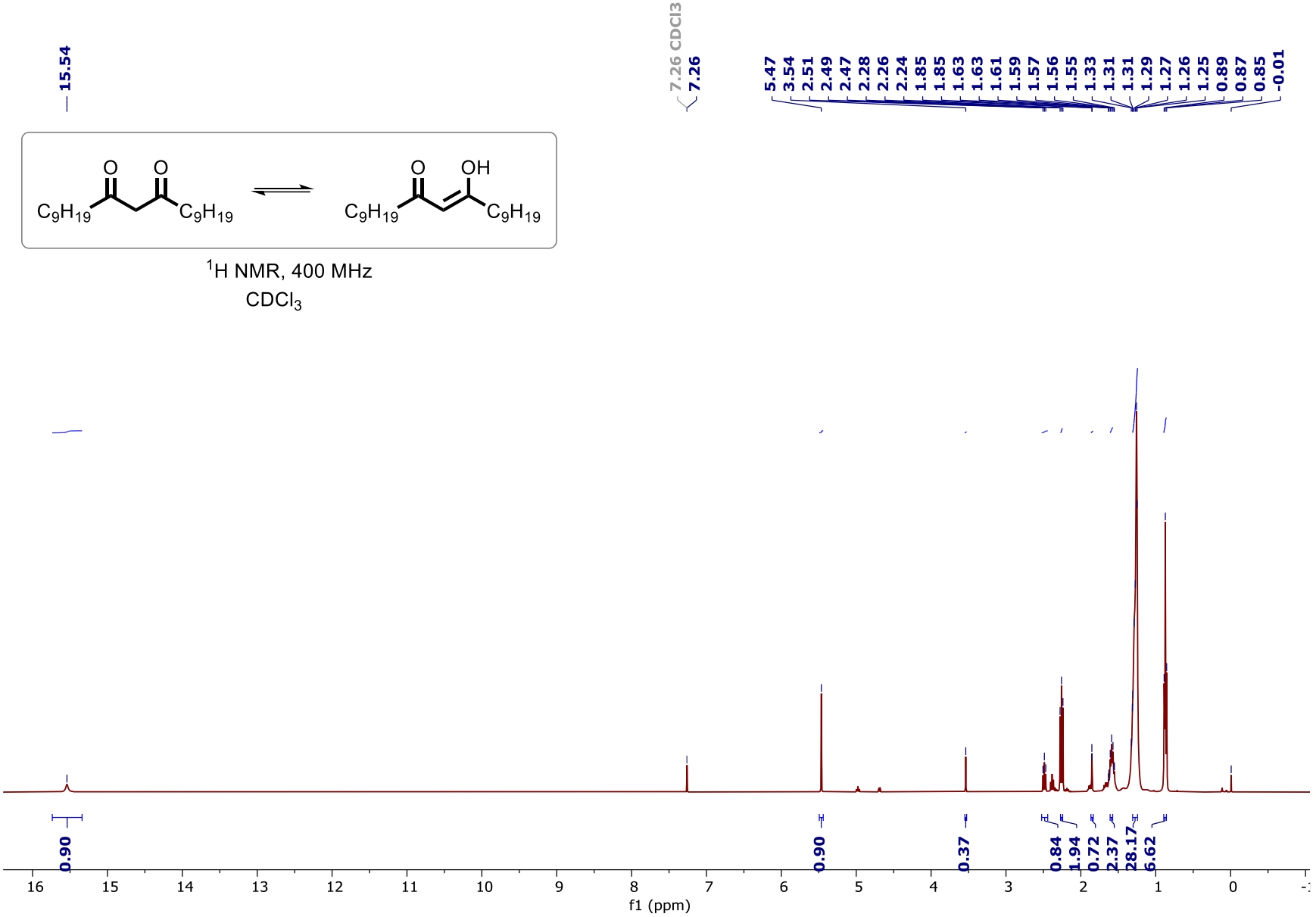
^{1}H NMR spectrum of Ethyl 3-((3S,8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxopropanoate (1t′):



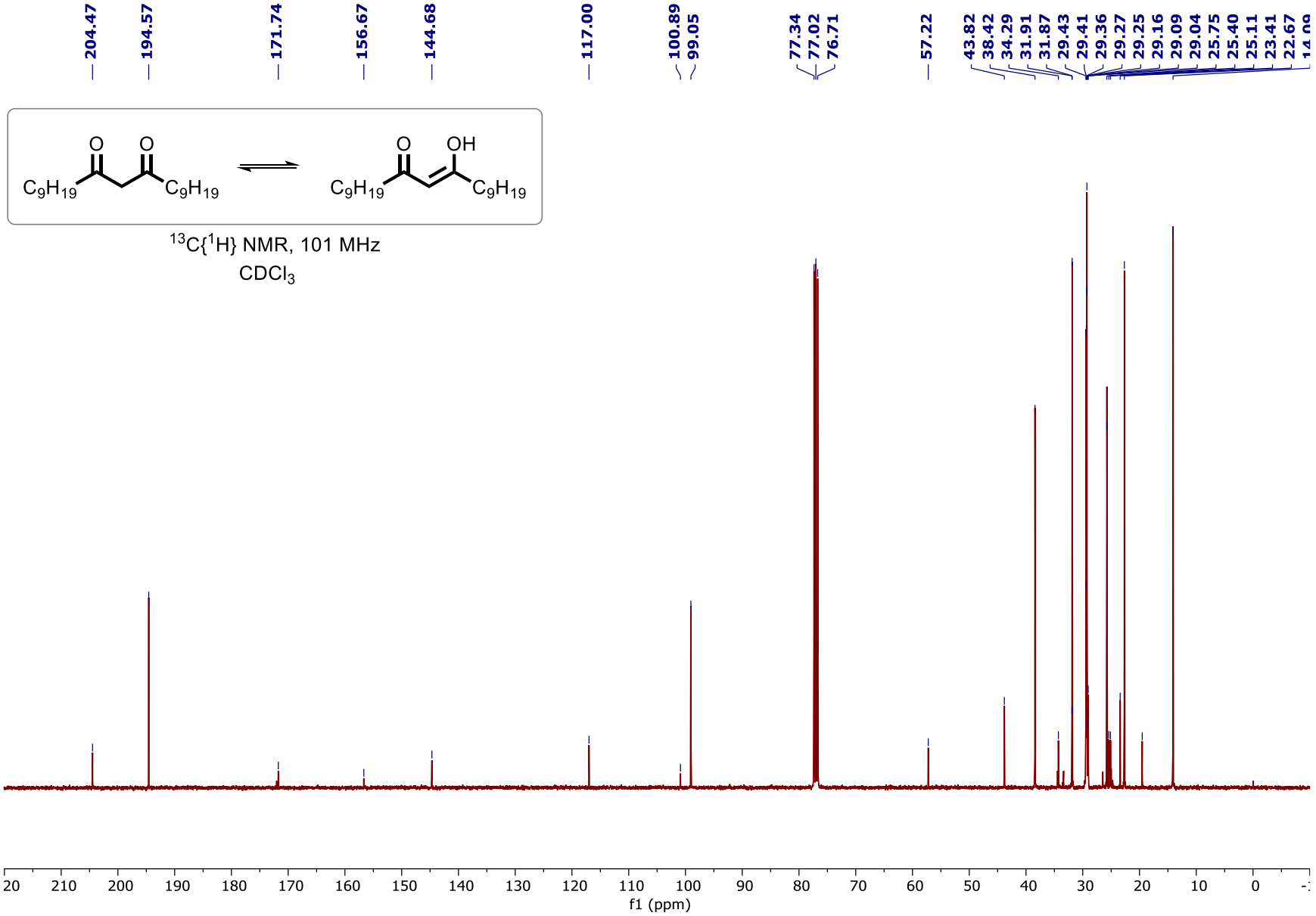
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 3-((3S,8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-oxopropanoate (1t′):



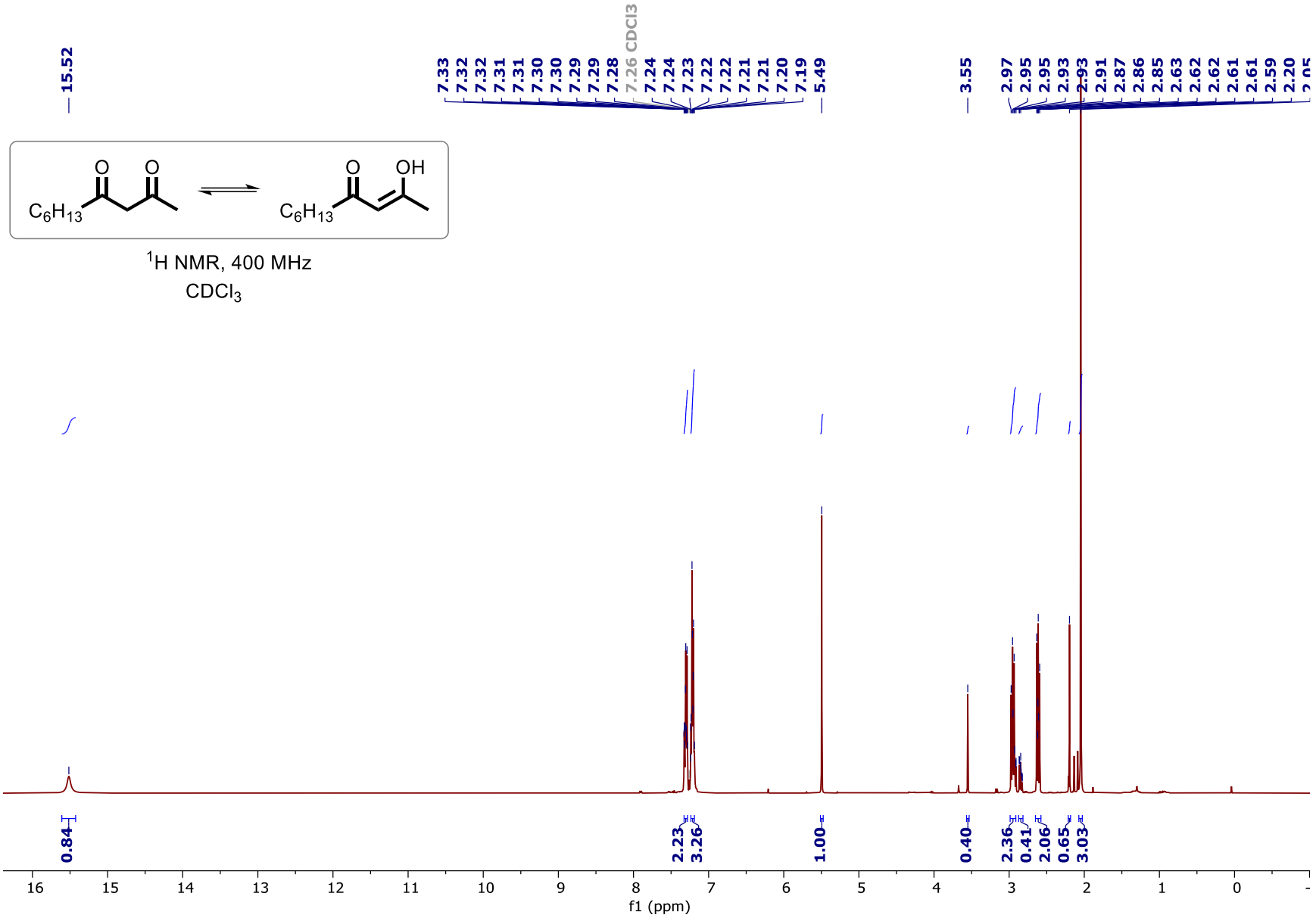
^{1}H NMR spectrum of of Henicosane-10,12-dione (4d):



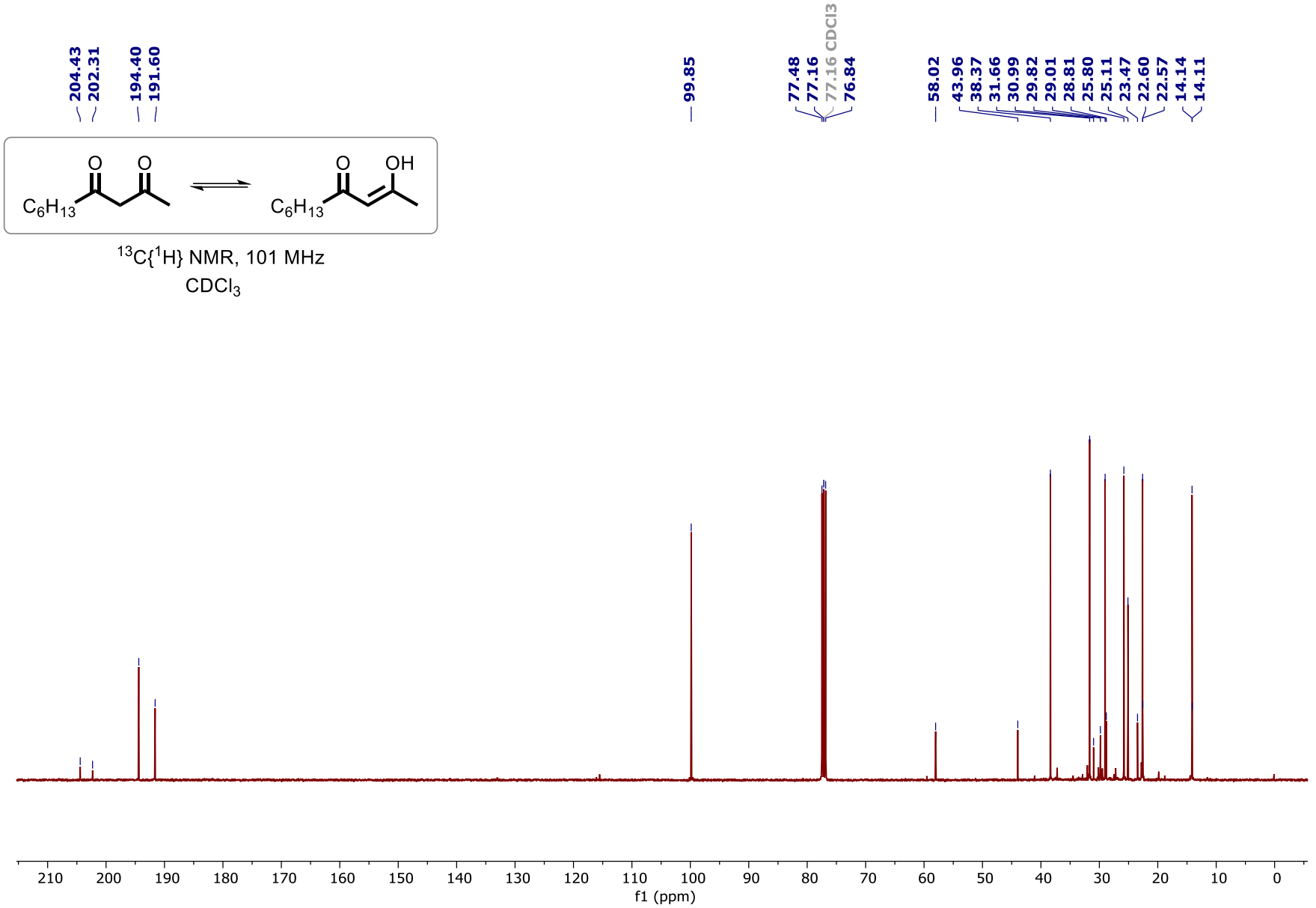
$^{13}C\{^{1}H\}$ NMR spectrum of Henicosane-10,12-dione (4d):



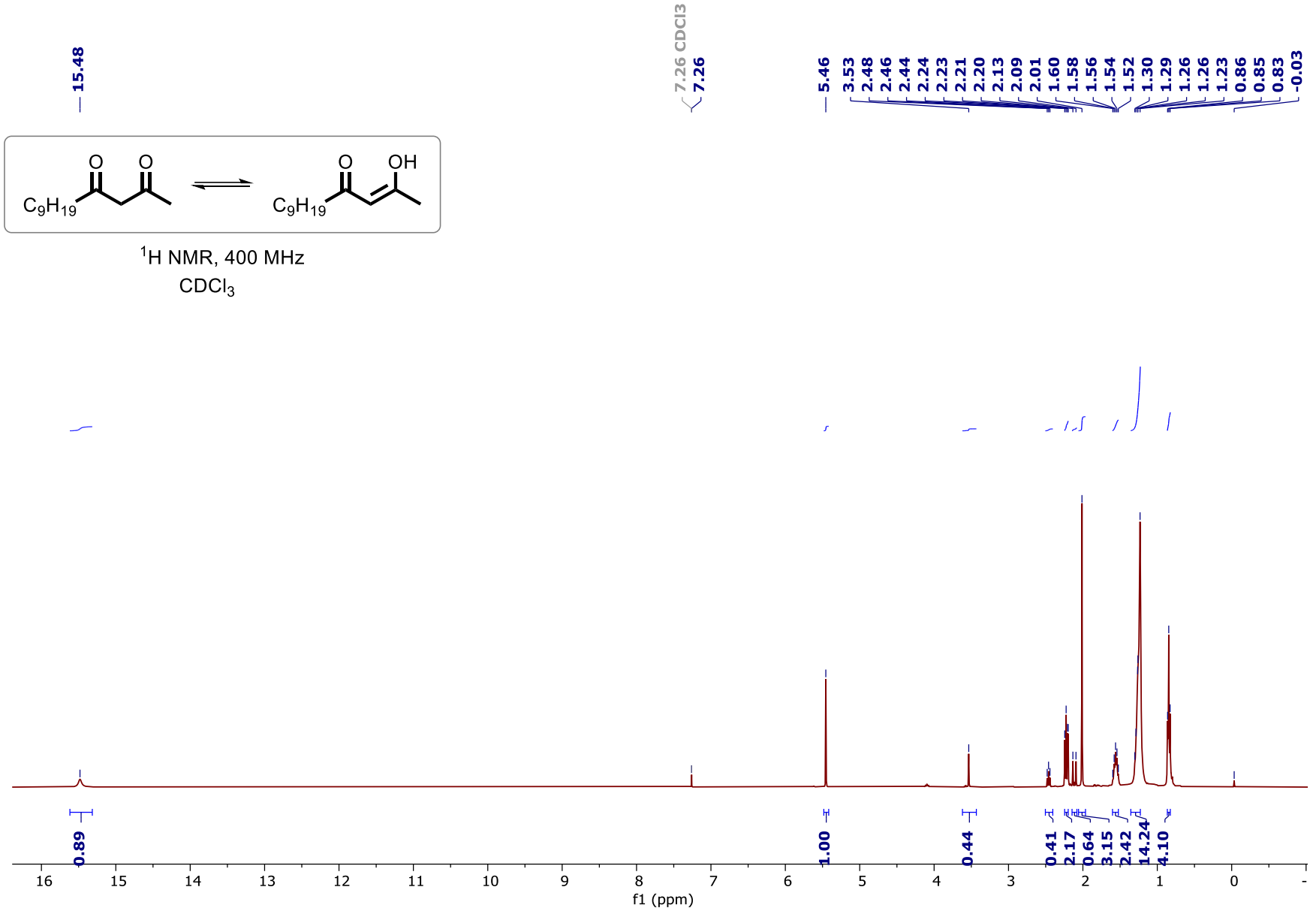
^{1}H NMR spectrum of Decane-2,4-dione (4e):



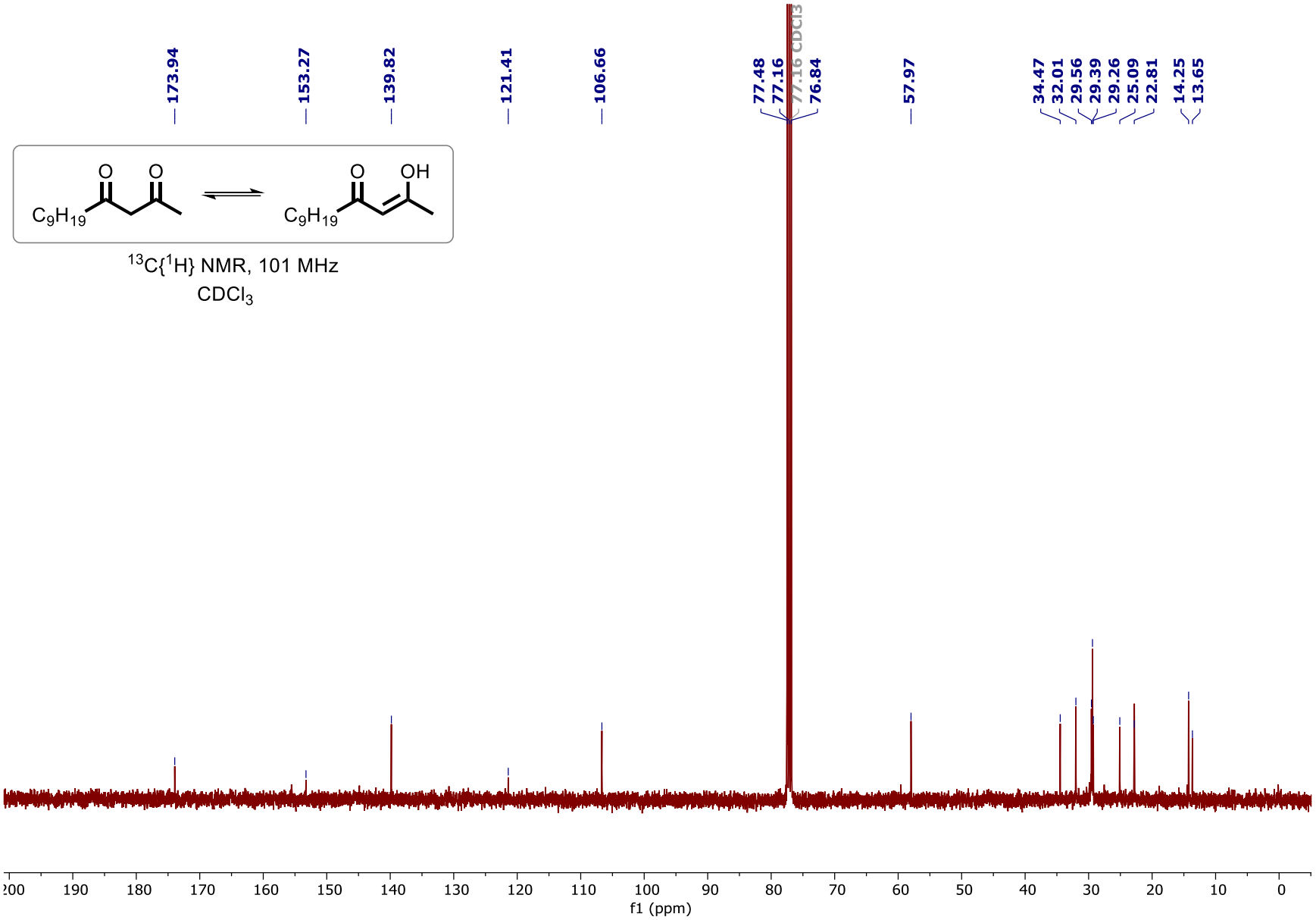
$^{13}C\{^{1}H\}$ NMR spectrum of Decane-2,4-dione (4e):



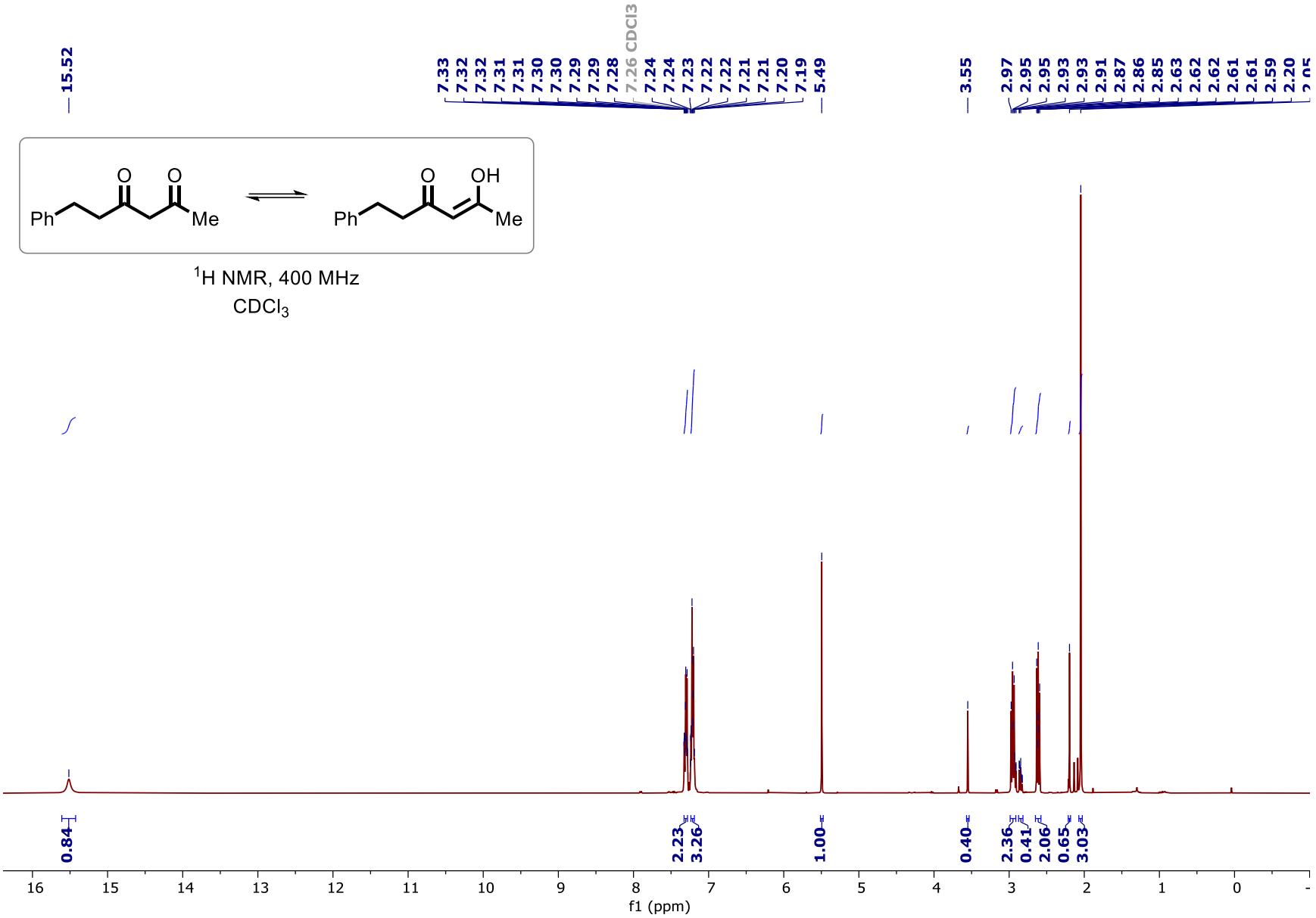
^{1}H NMR spectrum of of Tridecane-2,4-dione (4g):



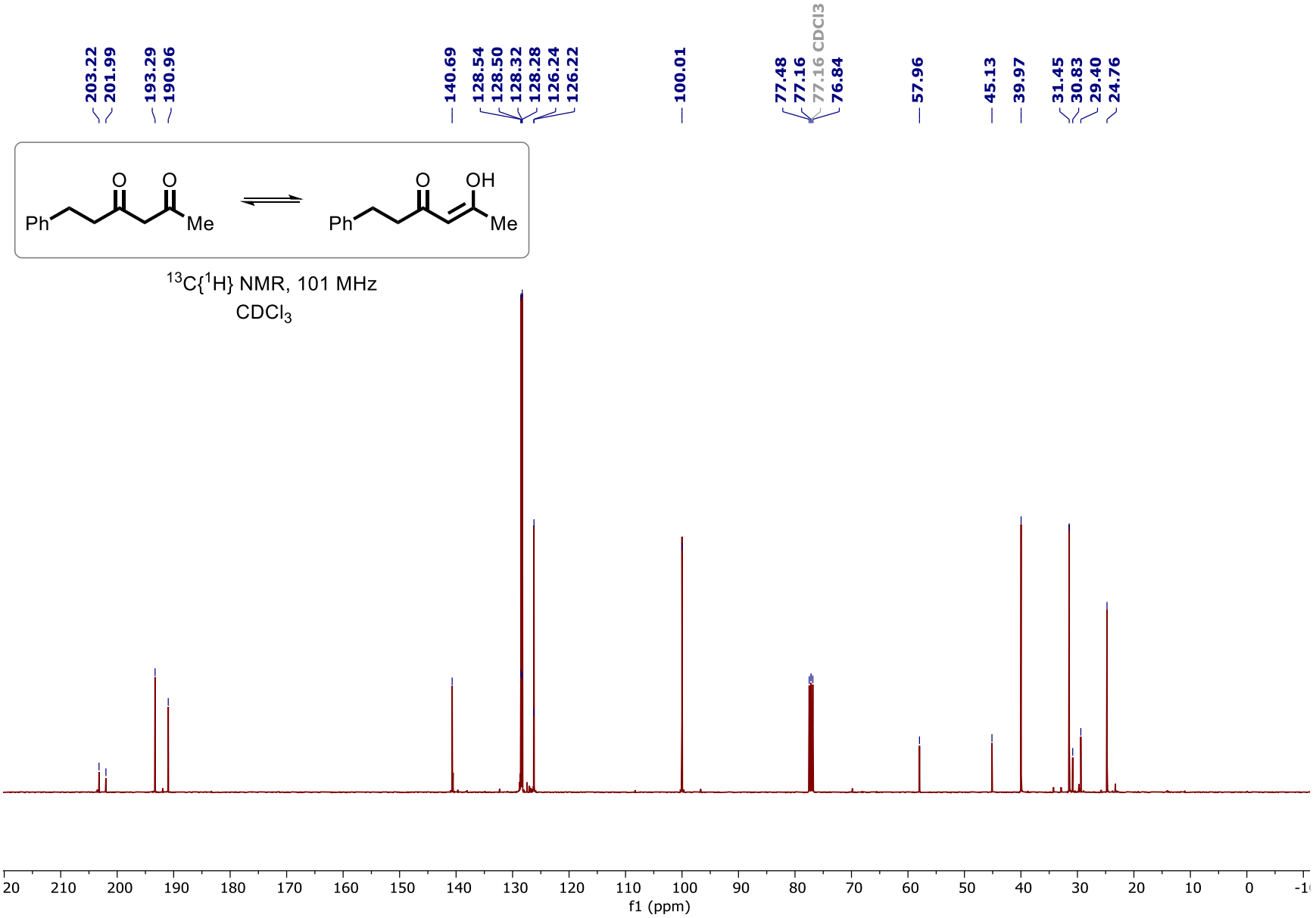
$^{13}C\{^{1}H\}$ NMR spectrum of Tridecane-2,4-dione (4g):



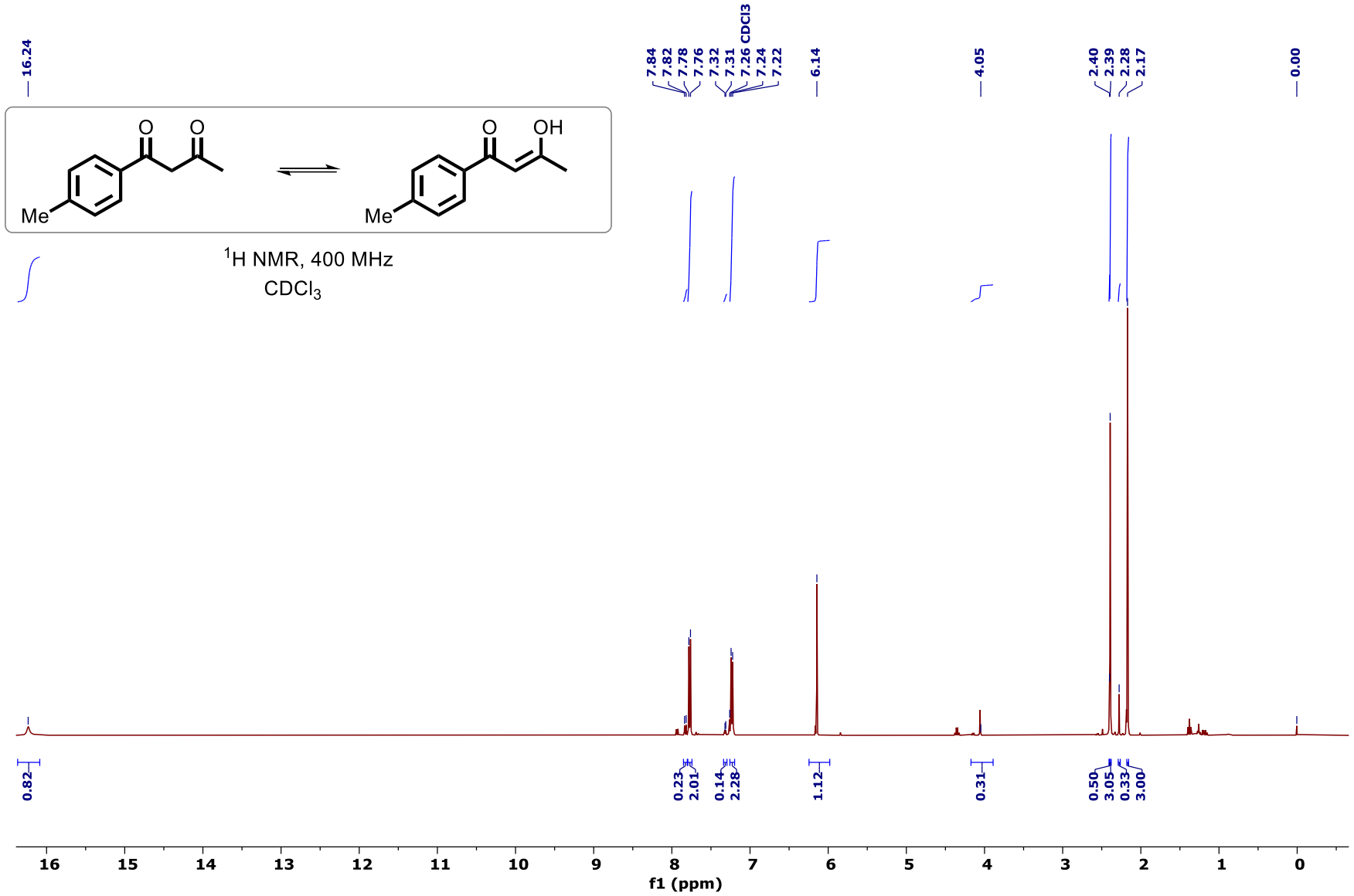
^{1}H NMR spectrum of 6-Phenylhexane-2,4-dione (4h):



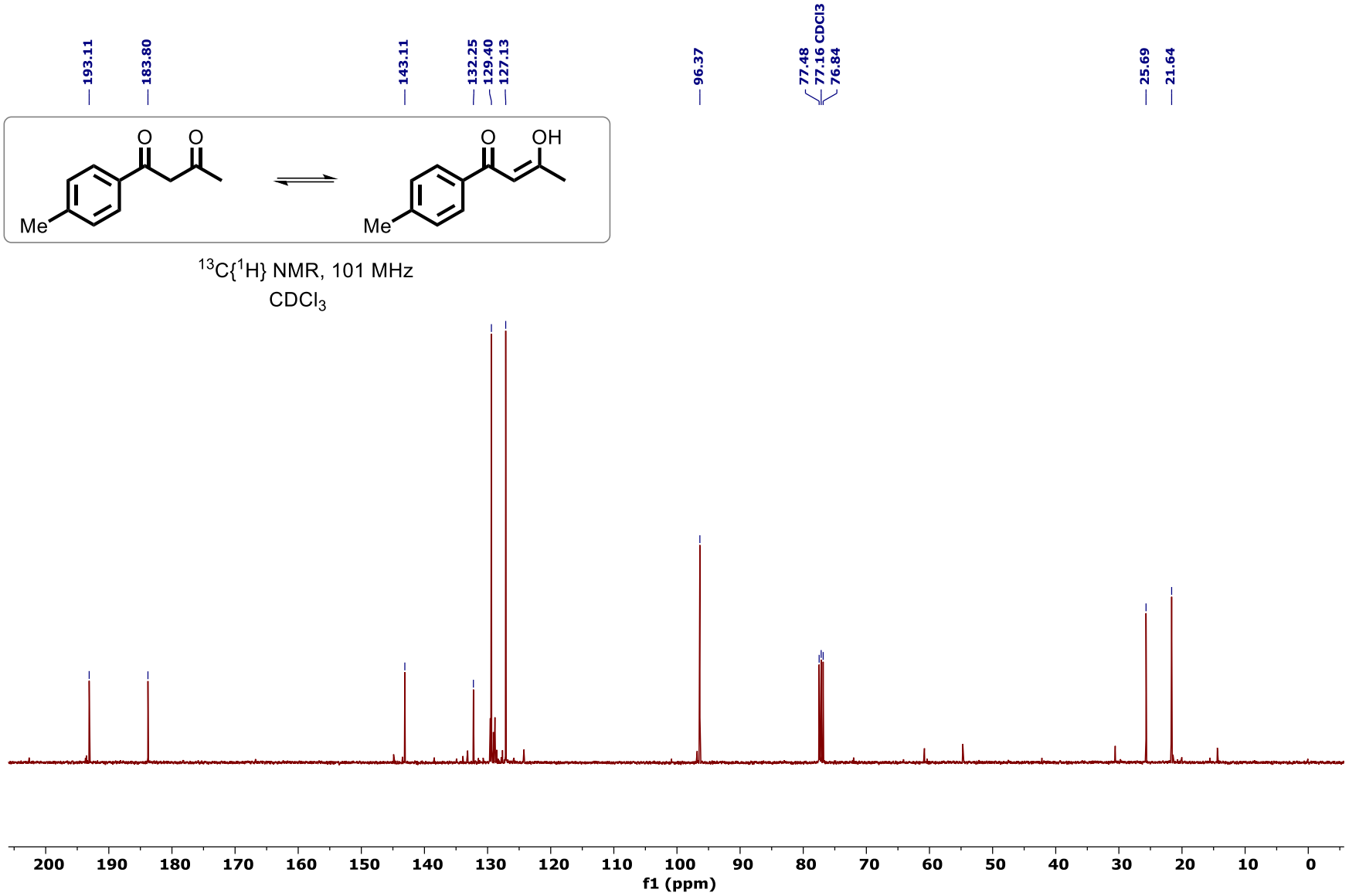
$^{13}C\{^{1}H\}$ NMR spectrum of 6-Phenylhexane-2,4-dione (4h):



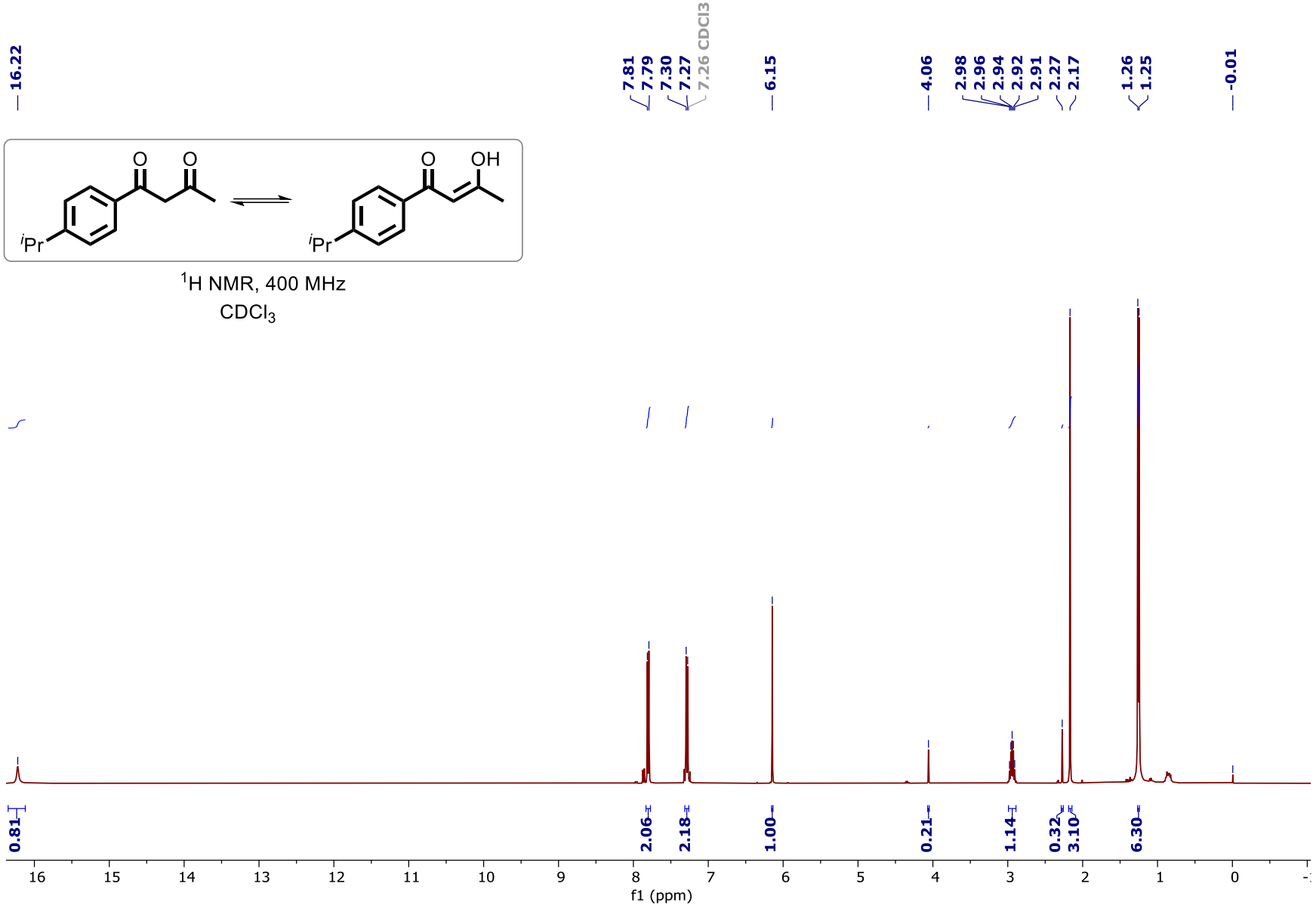
^{1}H NMR spectrum of 1-(*p*-Tolyl)butane-1,3-dione (4i):



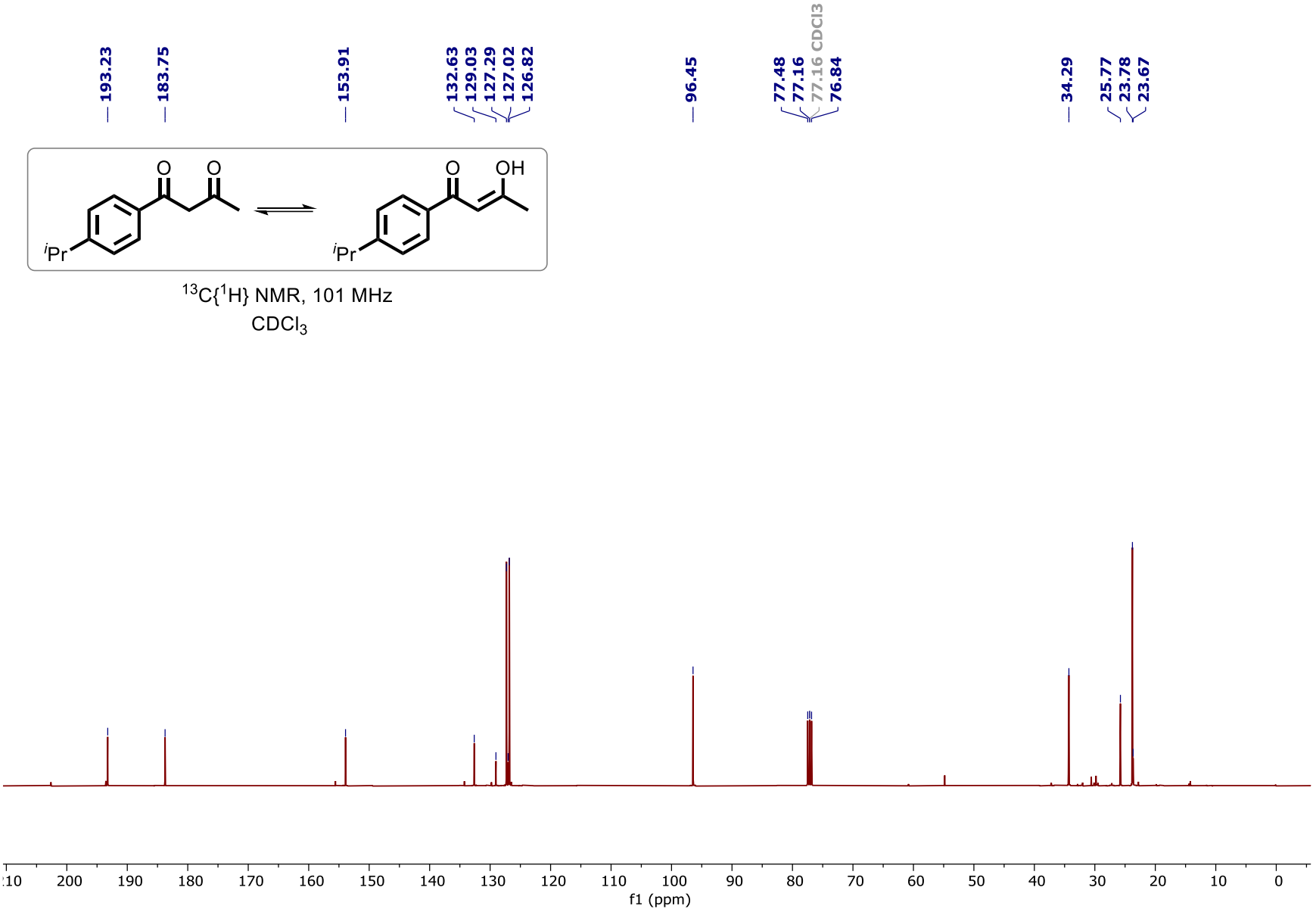
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(*p*-Tolyl)butane-1,3-dione (4i):



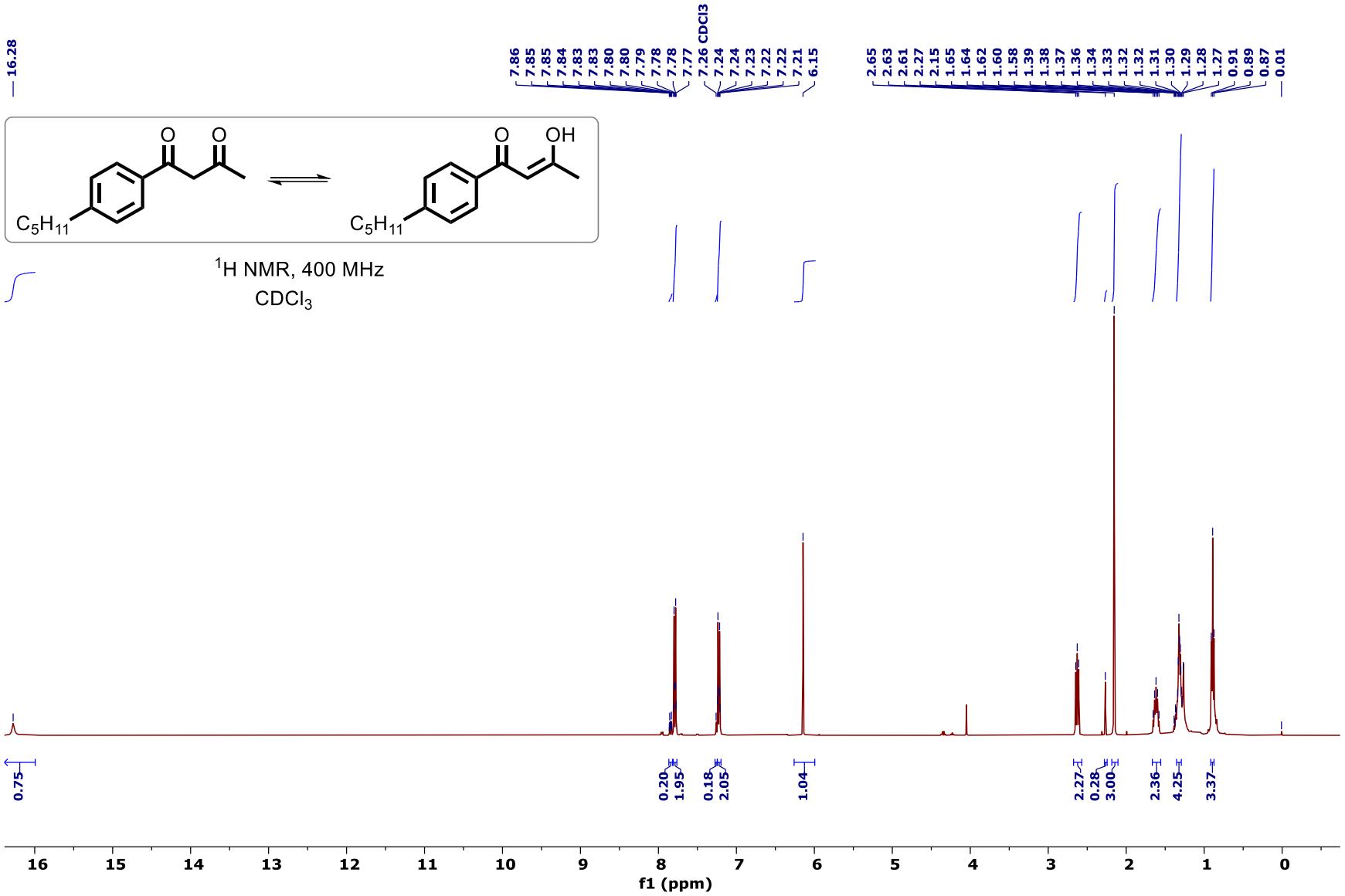
^{1}H NMR spectrum of 1-(4-Isopropylphenyl)butane-1,3-dione (4j):



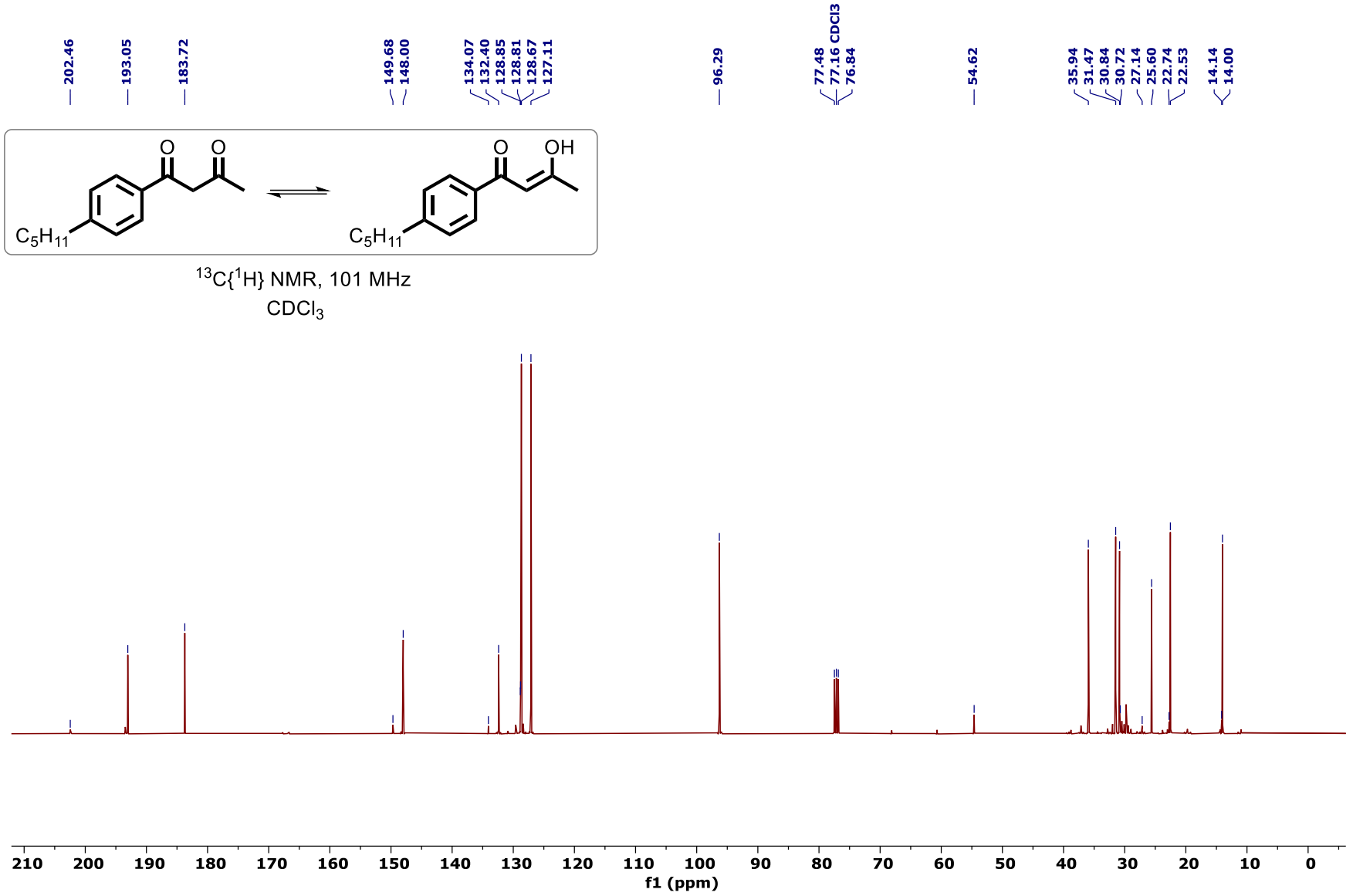
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Isopropylphenyl)butane-1,3-dione (4j):



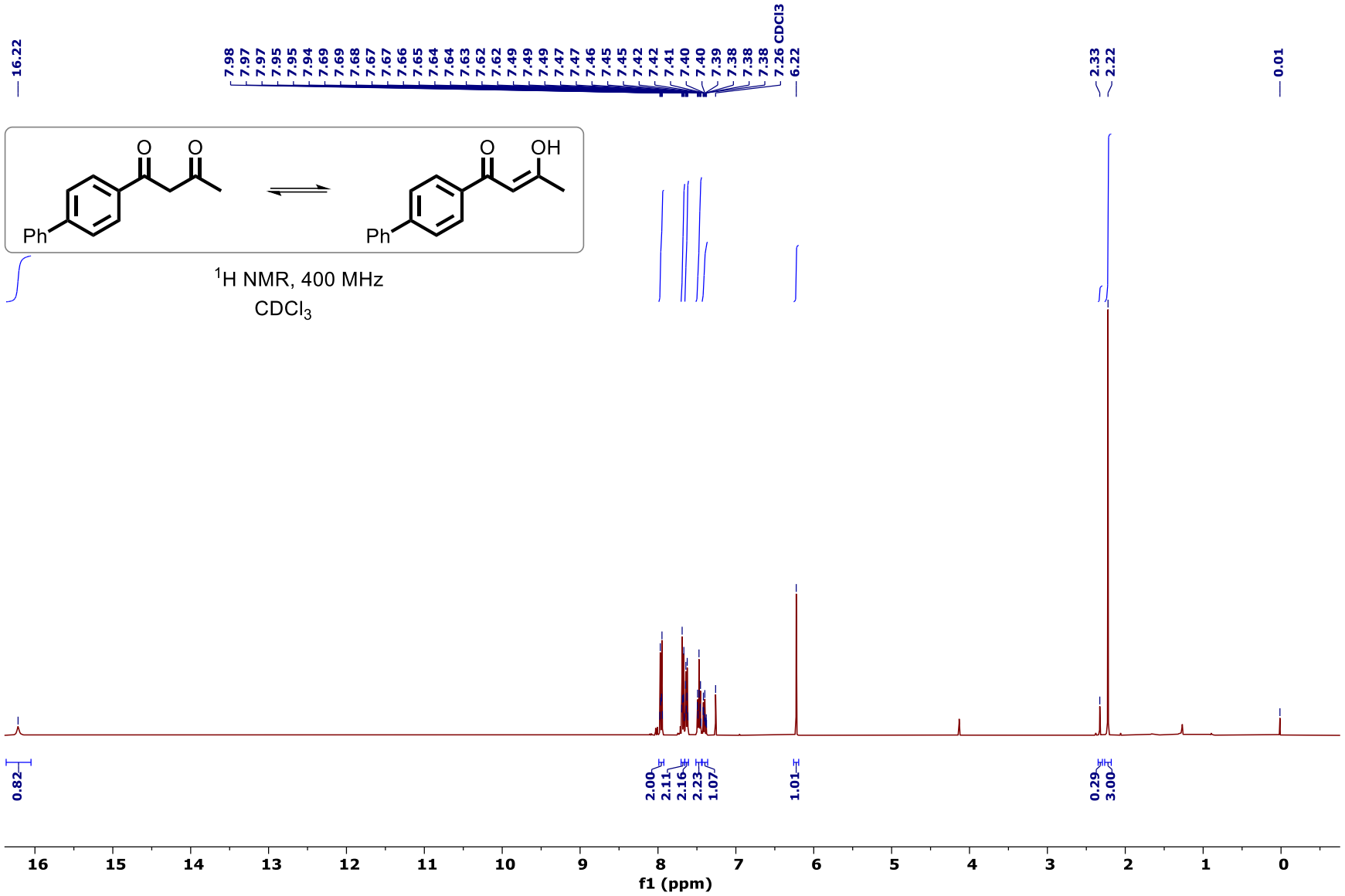
^{1}H NMR spectrum of 1-(4-Pentylphenyl)butane-1,3-dione (4k):



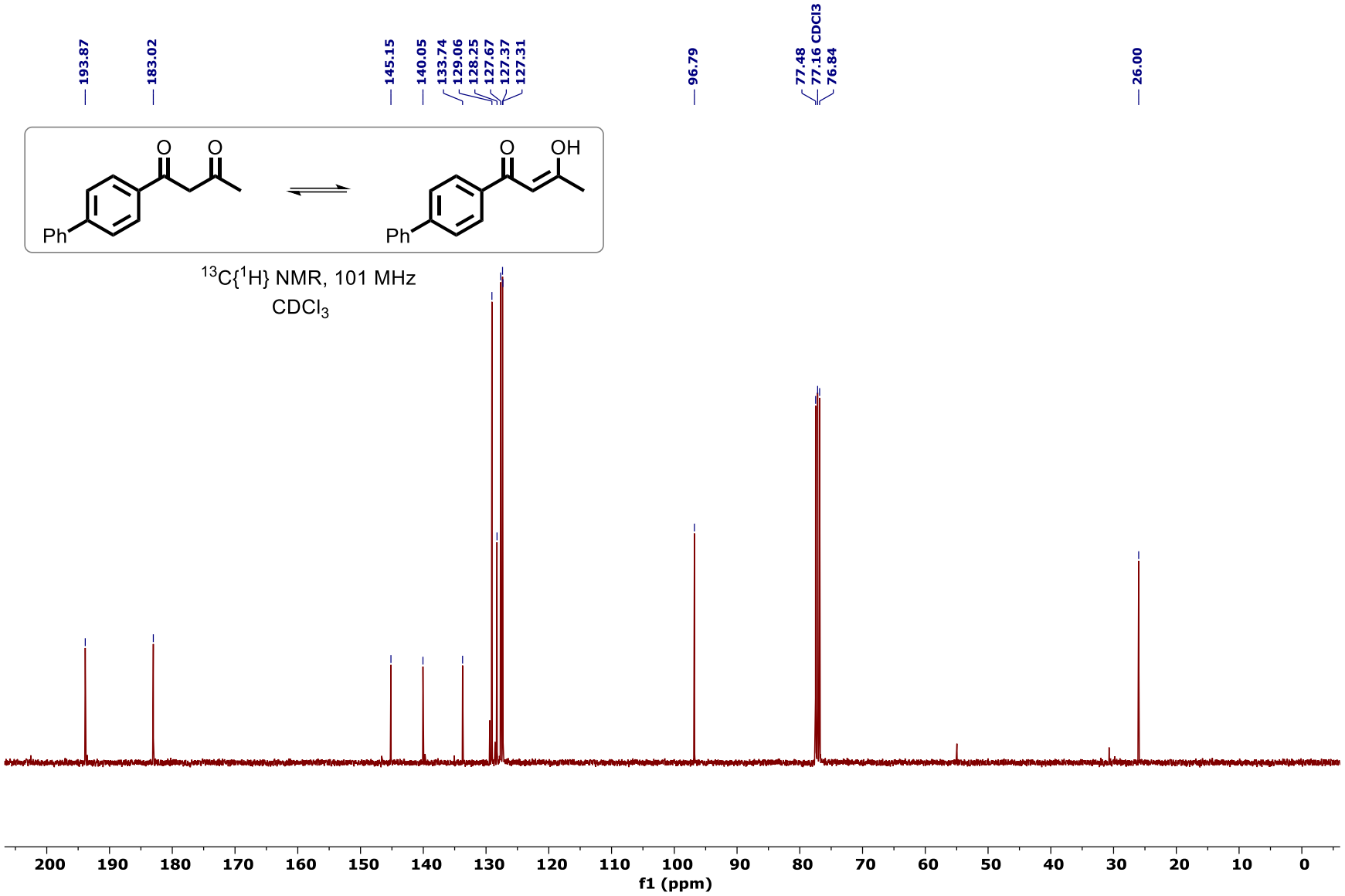
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Pentylphenyl)butane-1,3-dione (4k):



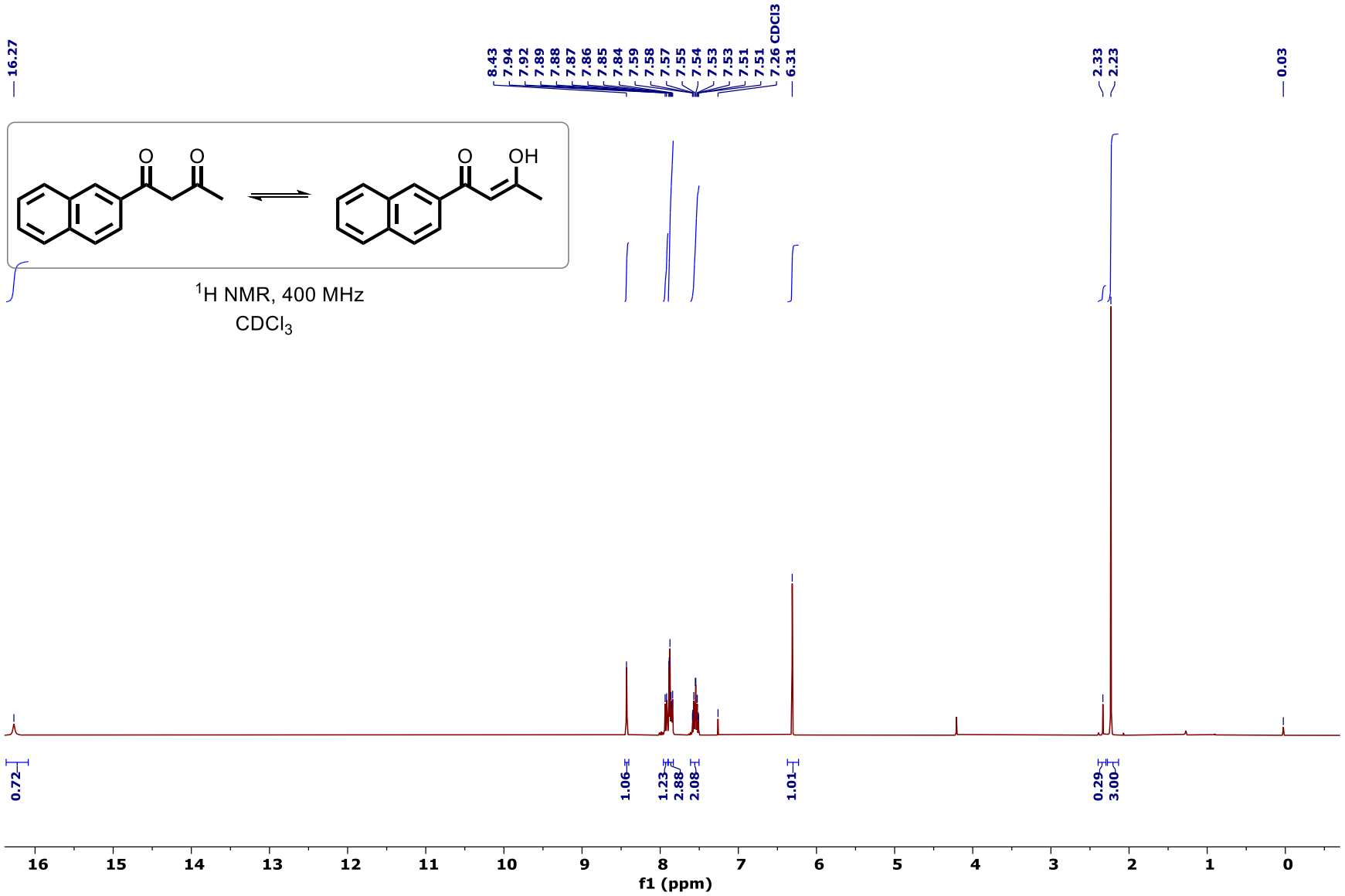
^{1}H NMR spectrum of 1-([1,1'-Biphenyl]-4-yl)butane-1,3-dione (4l):



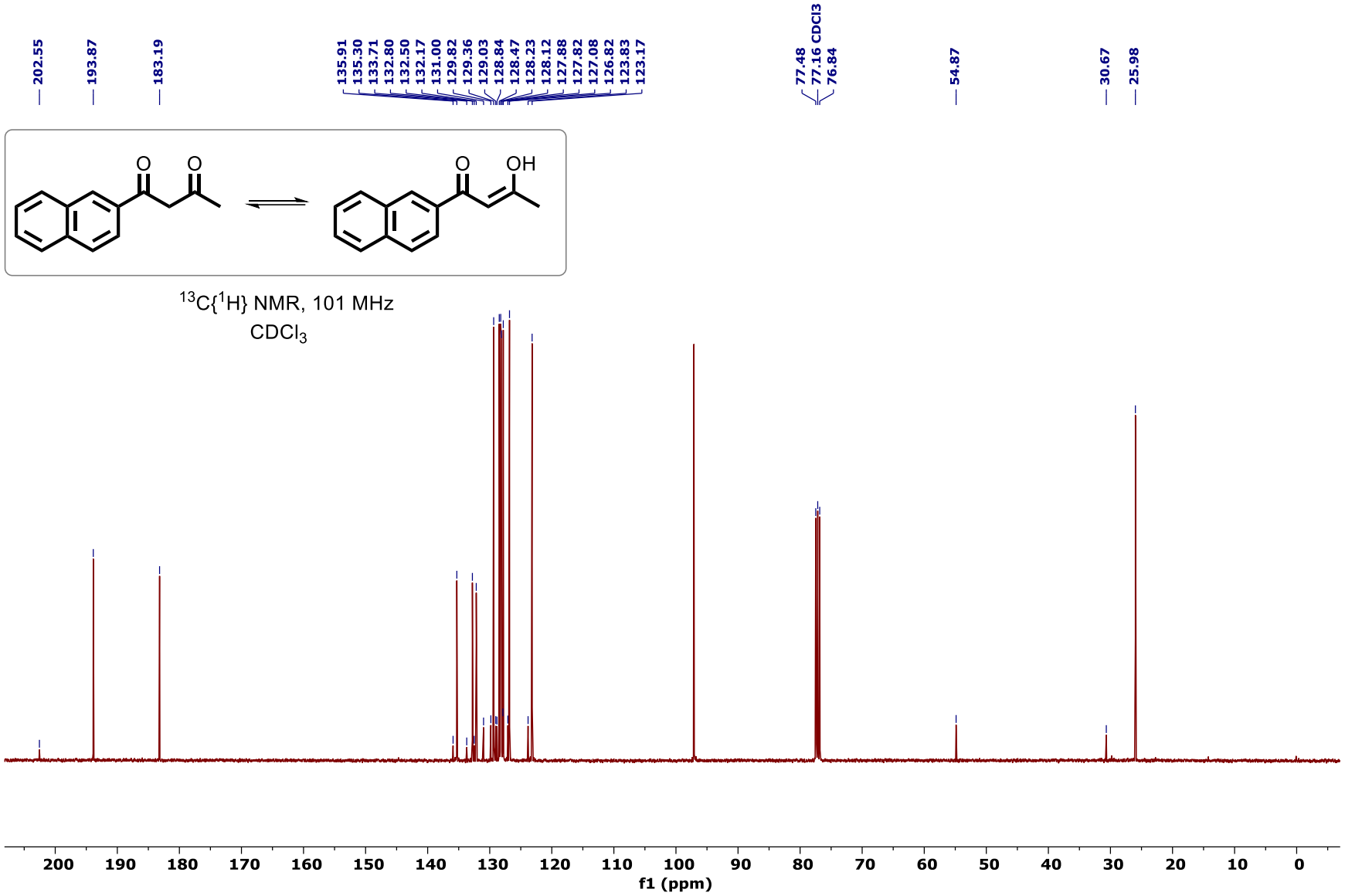
$^{13}C\{^{1}H\}$ NMR spectrum of 1-([1,1'-Biphenyl]-4-yl)butane-1,3-dione (4l):



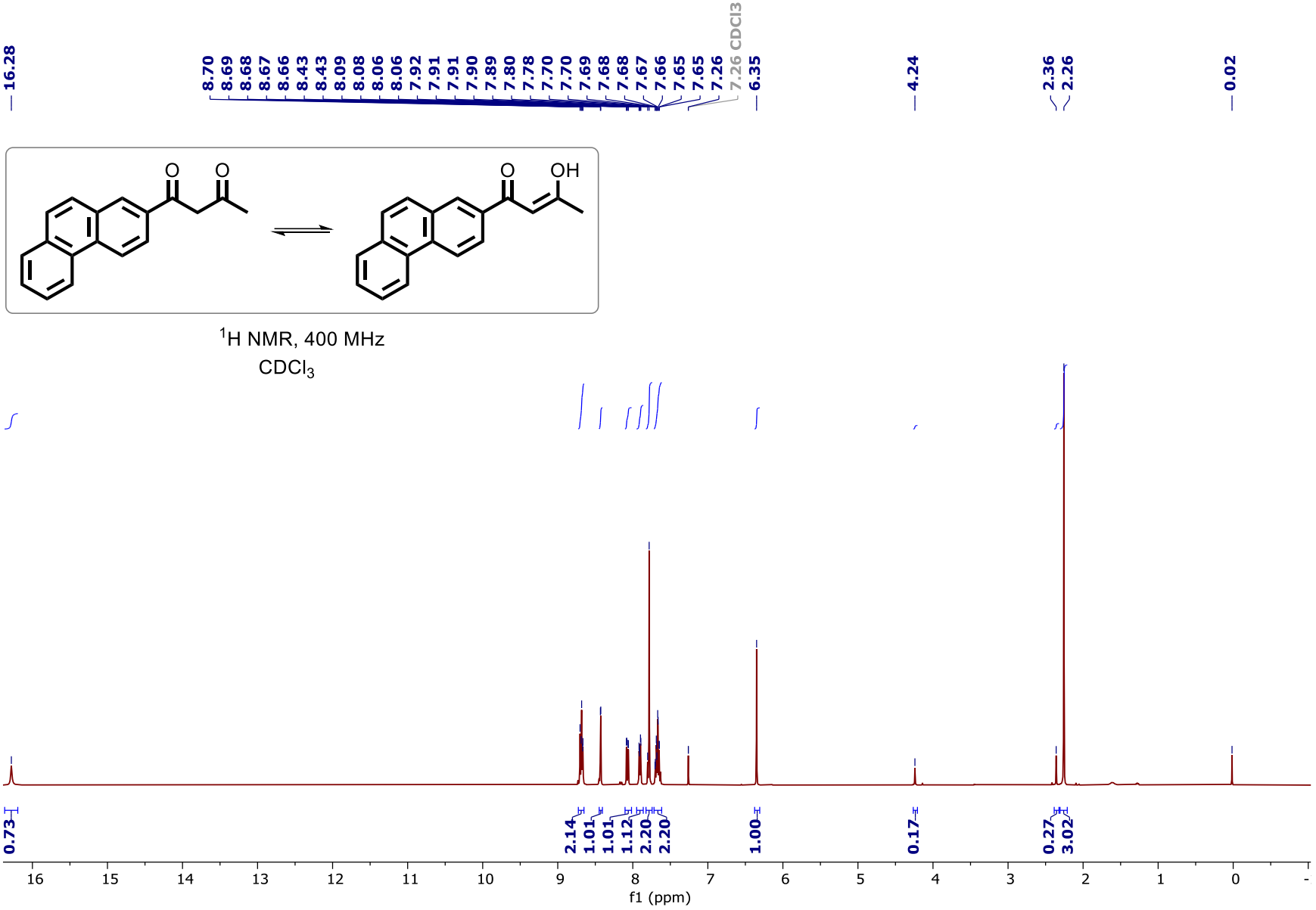
^{1}H NMR spectrum of 1-(Naphthalen-2-yl)butane-1,3-dione (4m):



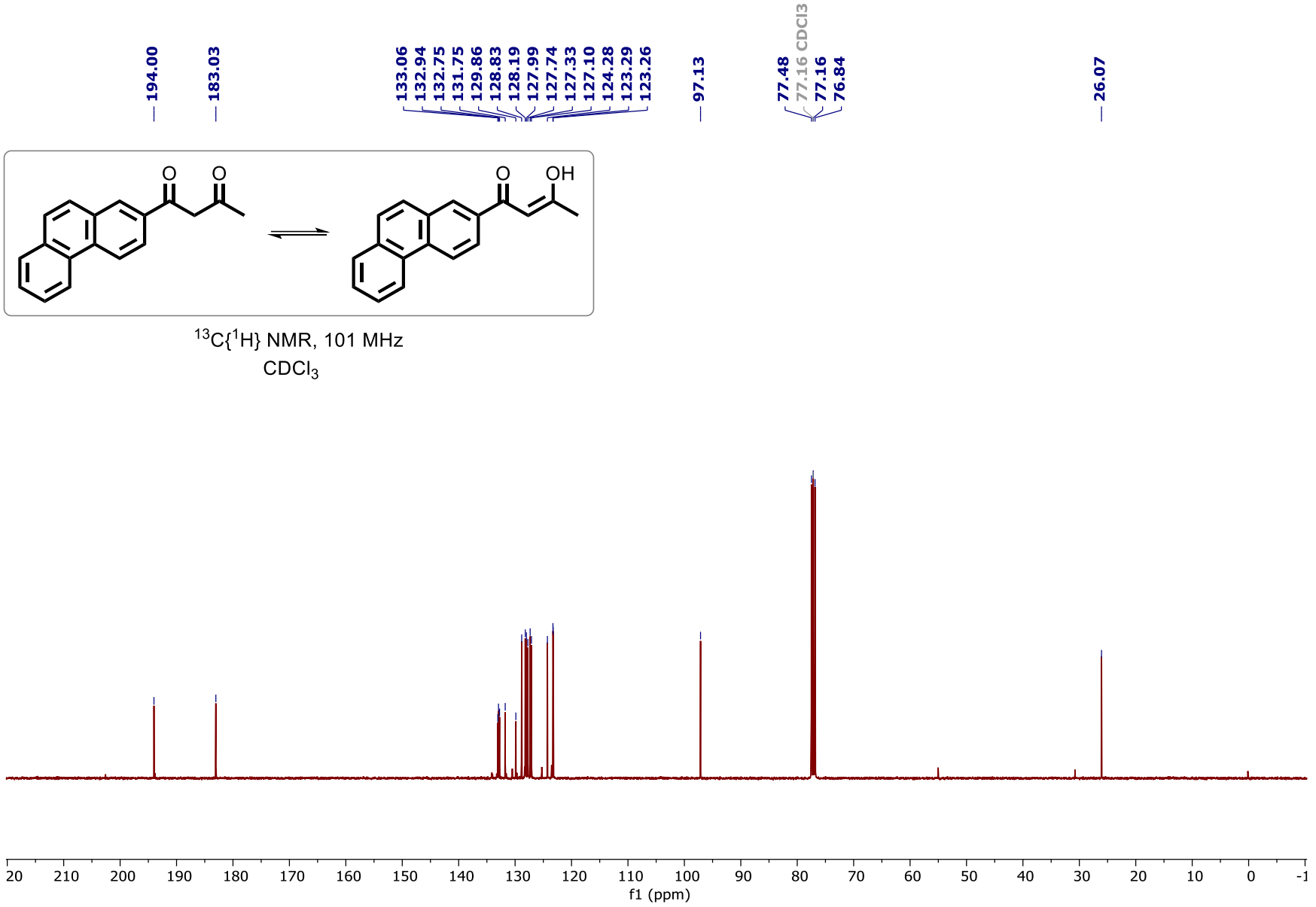
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(Naphthalen-2-yl)butane-1,3-dione (4m):



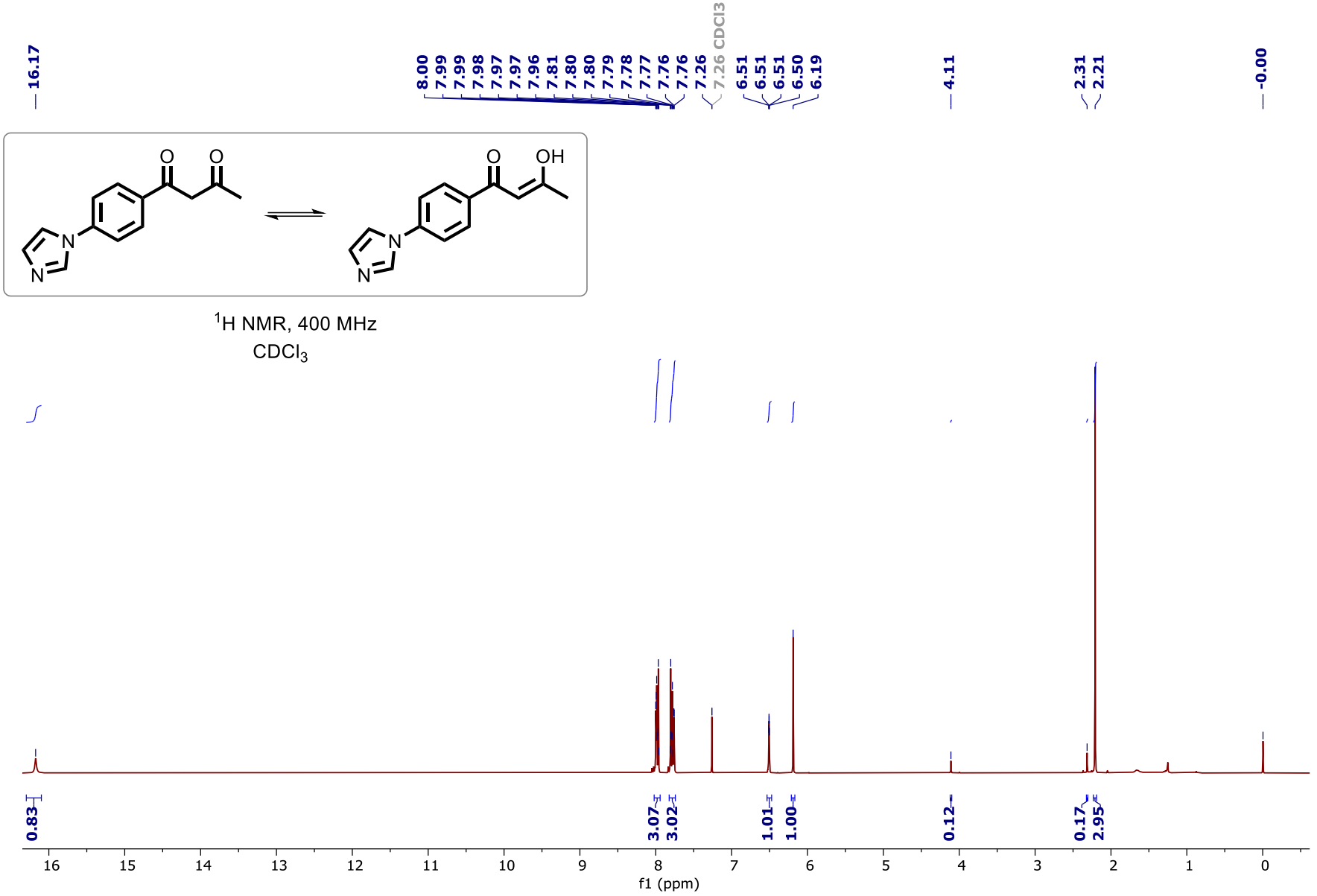
^{1}H NMR spectrum of 1-(Phenanthren-2-yl)butane-1,3-dione (4n):



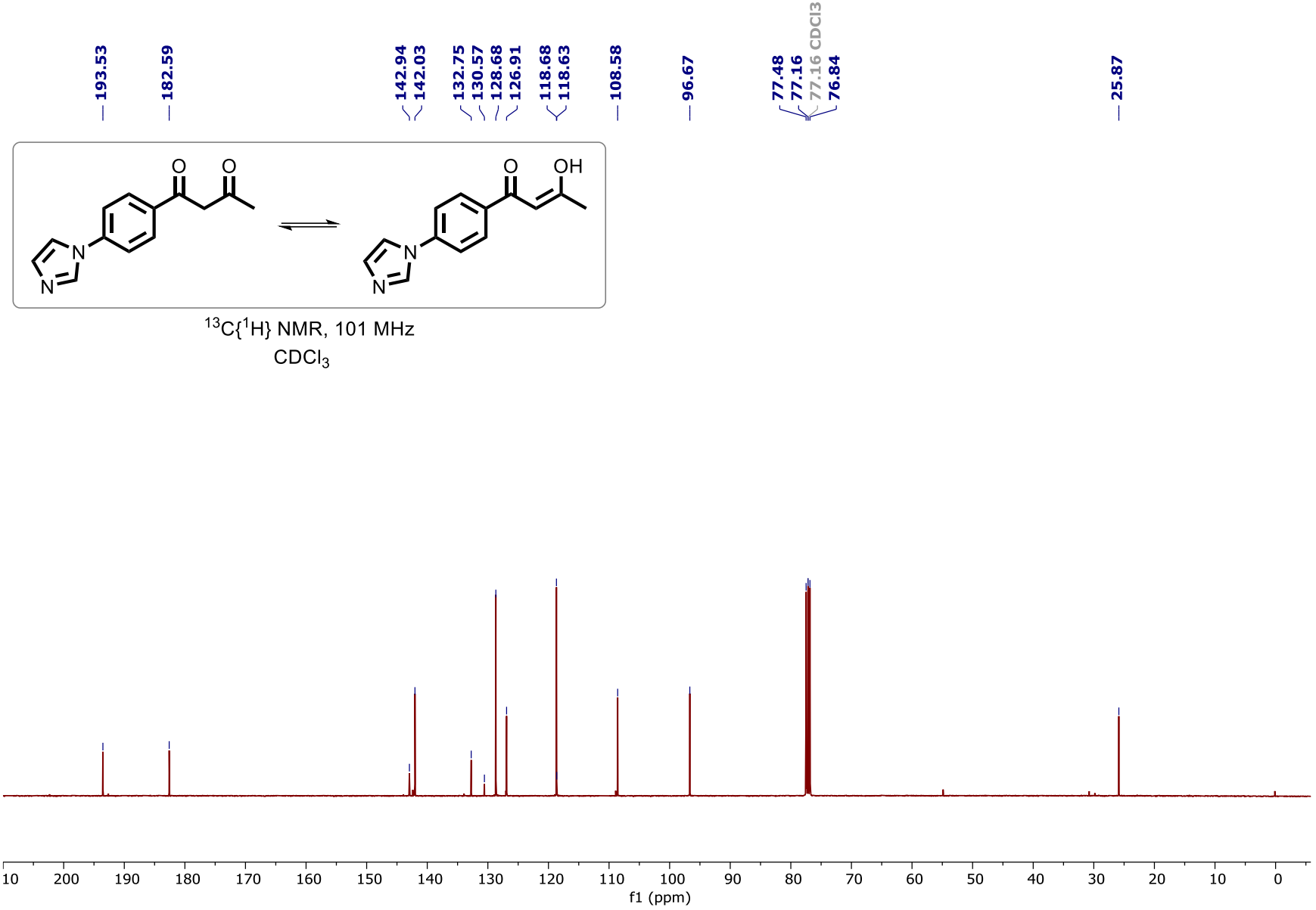
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(Phenanthren-2-yl)butane-1,3-dione (4n):



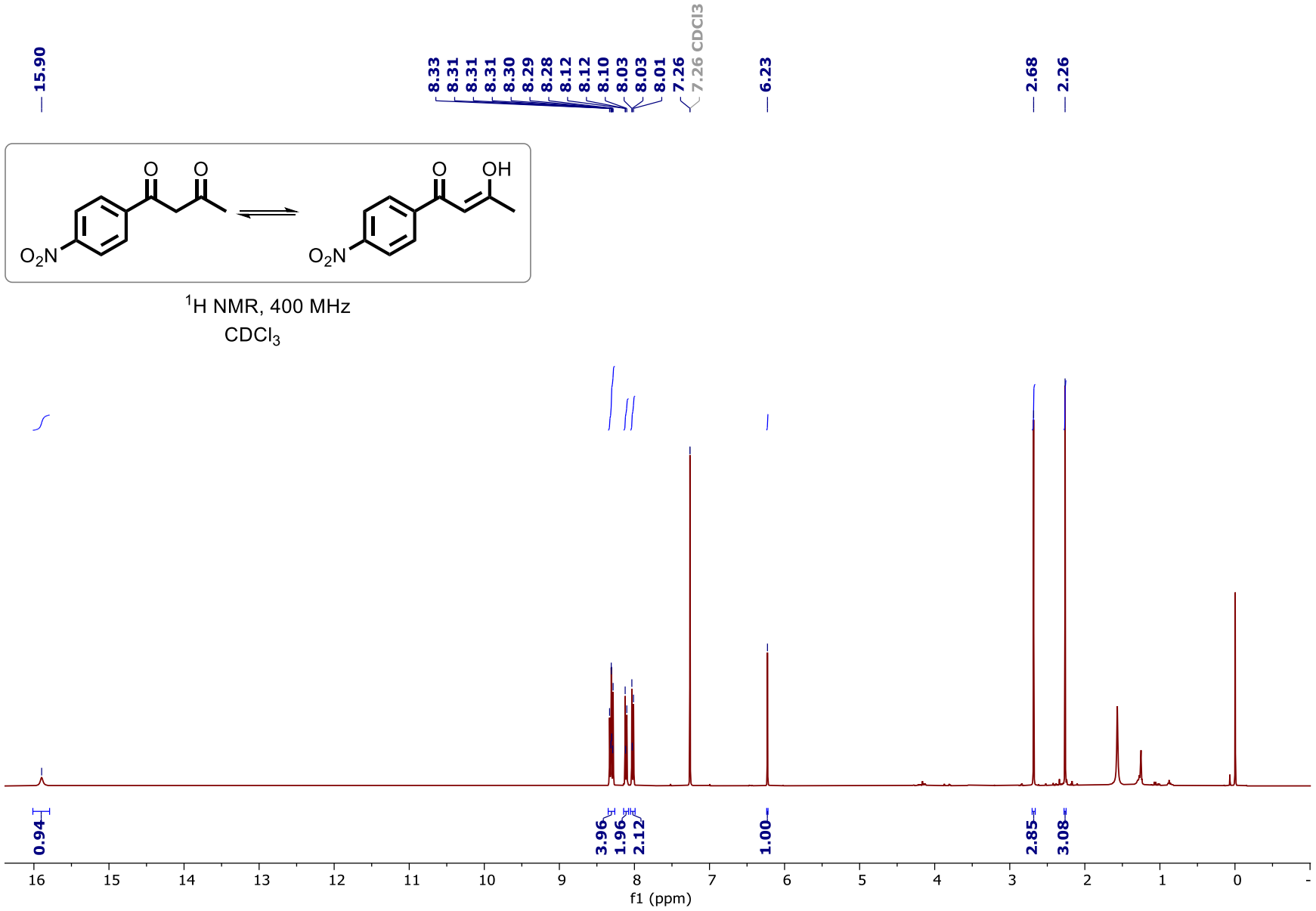
^{1}H NMR spectrum of 1-(4-(1*H*-Imidazol-1-yl)phenyl)butane-1,3-dione (4o):



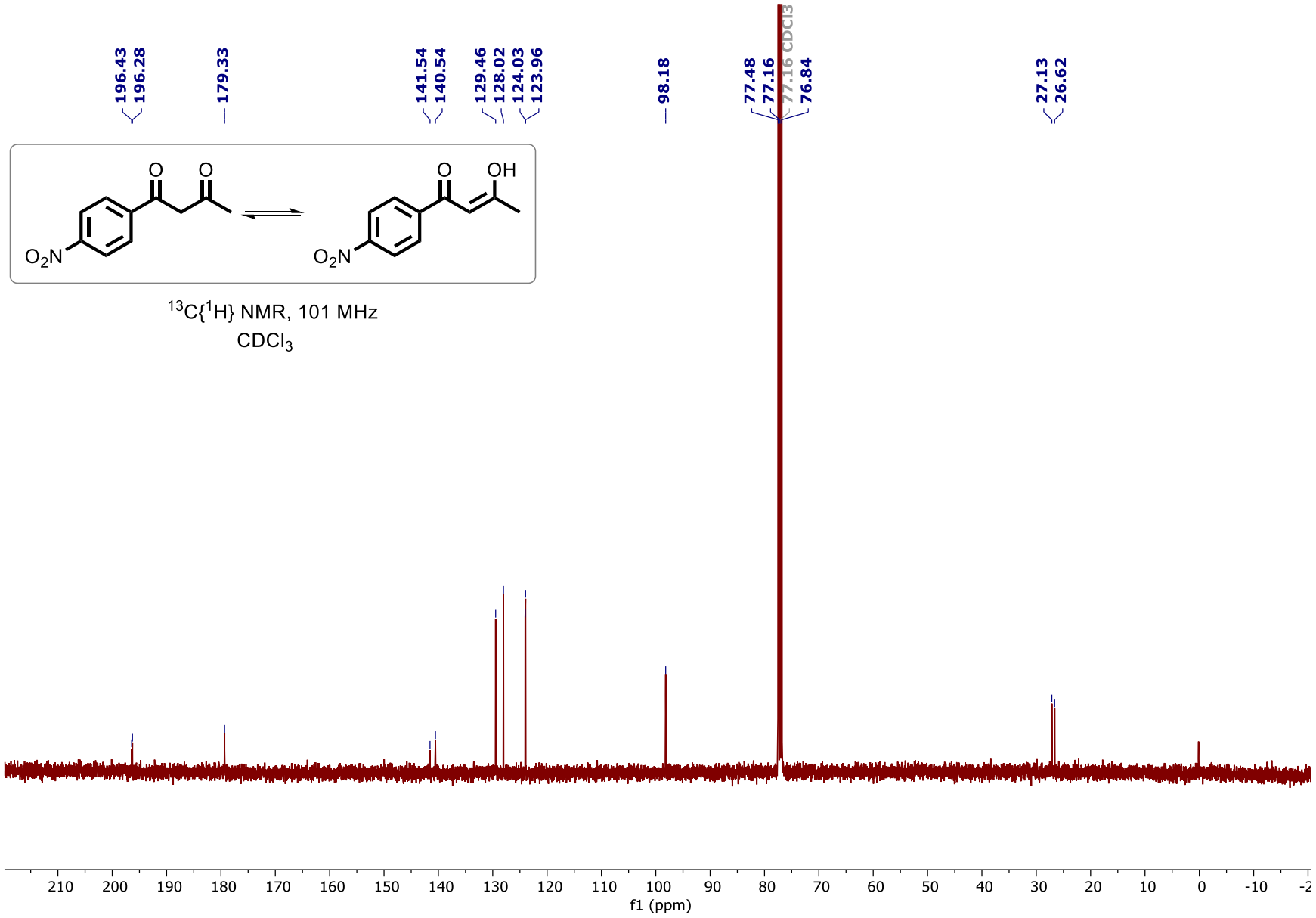
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-(1H-Imidazol-1-yl)phenyl)butane-1,3-dione (4o):



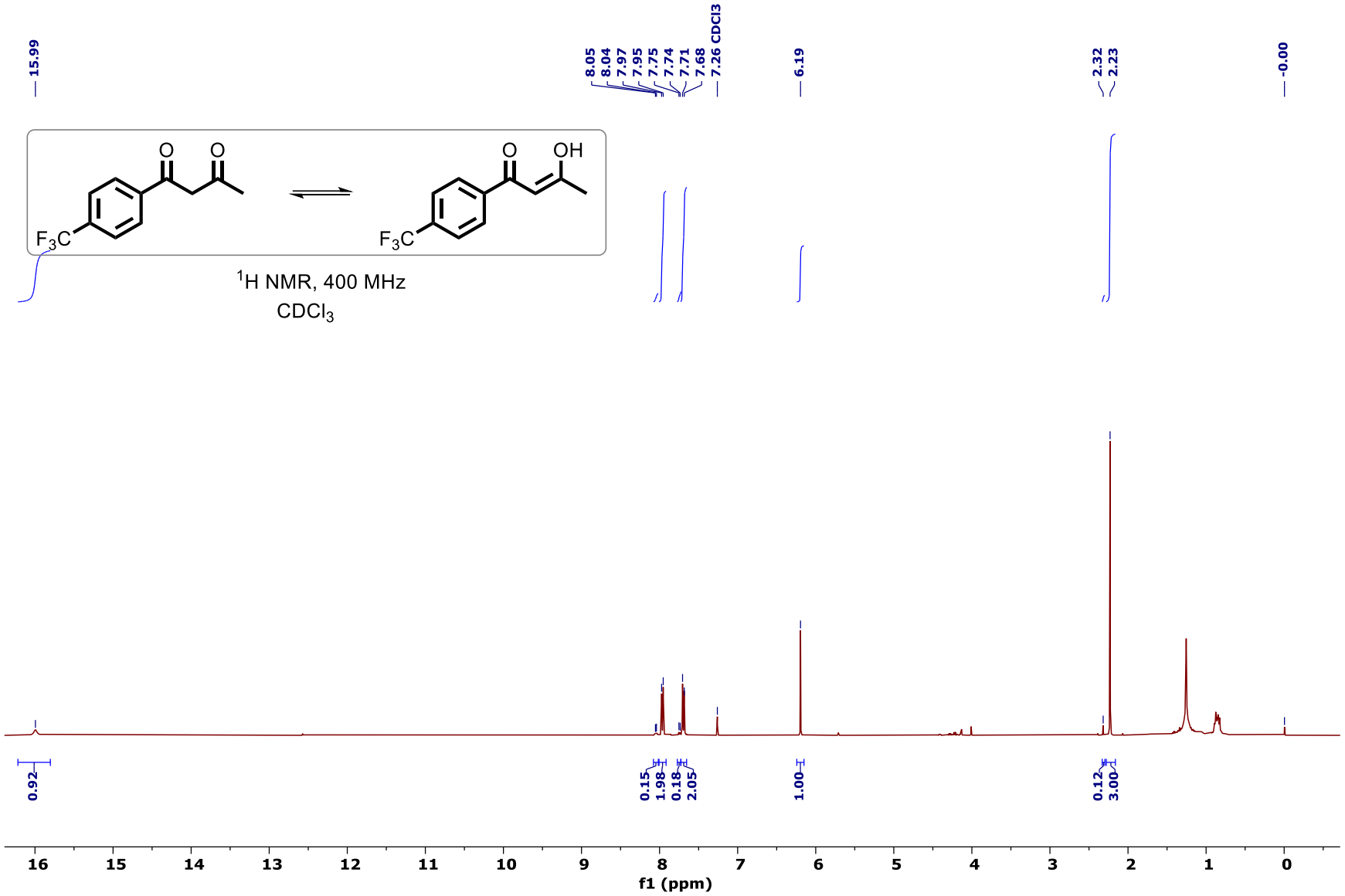
^{1}H NMR spectrum of 1-(4-Nitrophenyl)butane-1,3-dione (4p):



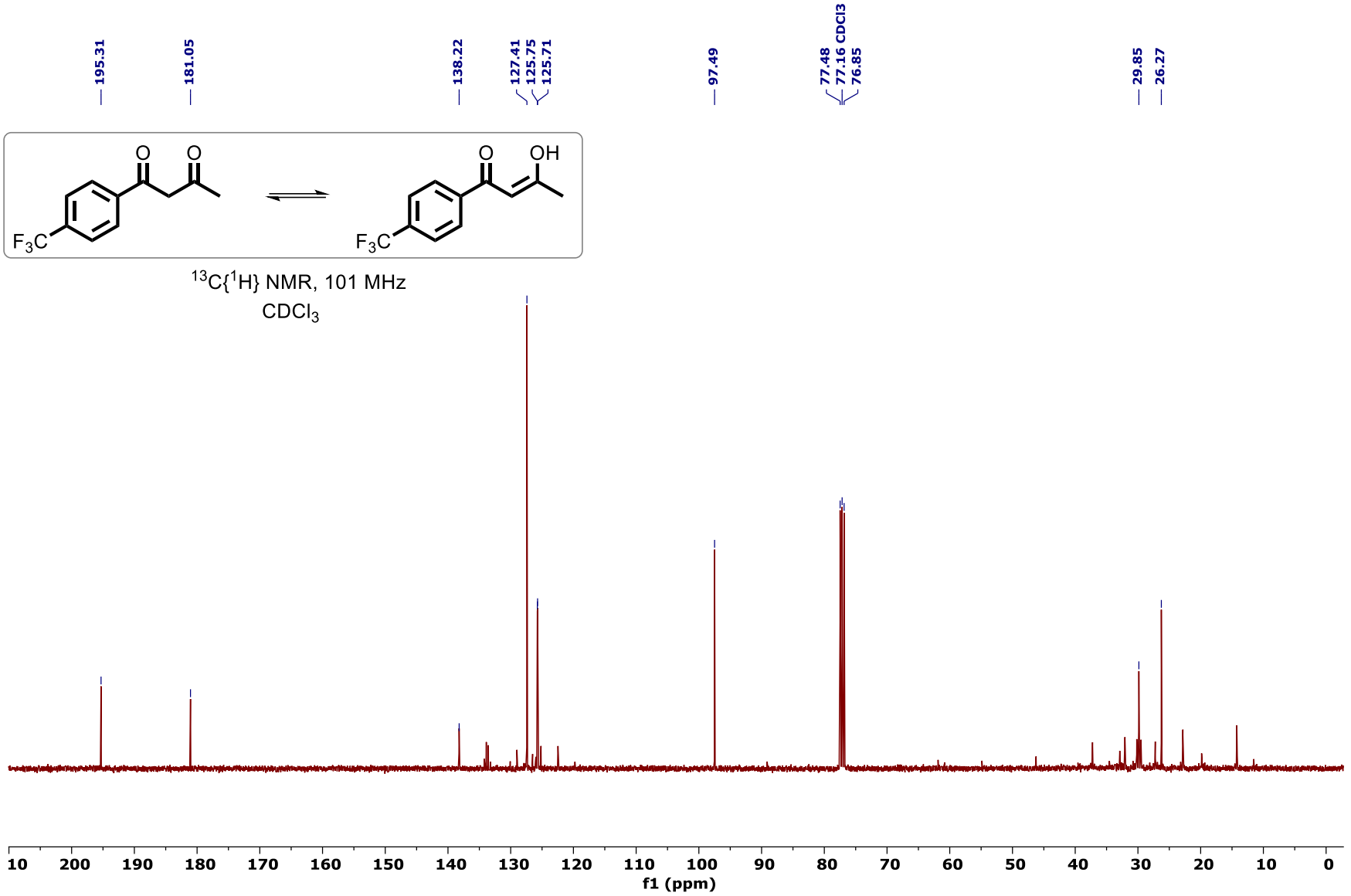
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Nitrophenyl)butane-1,3-dione (4p):



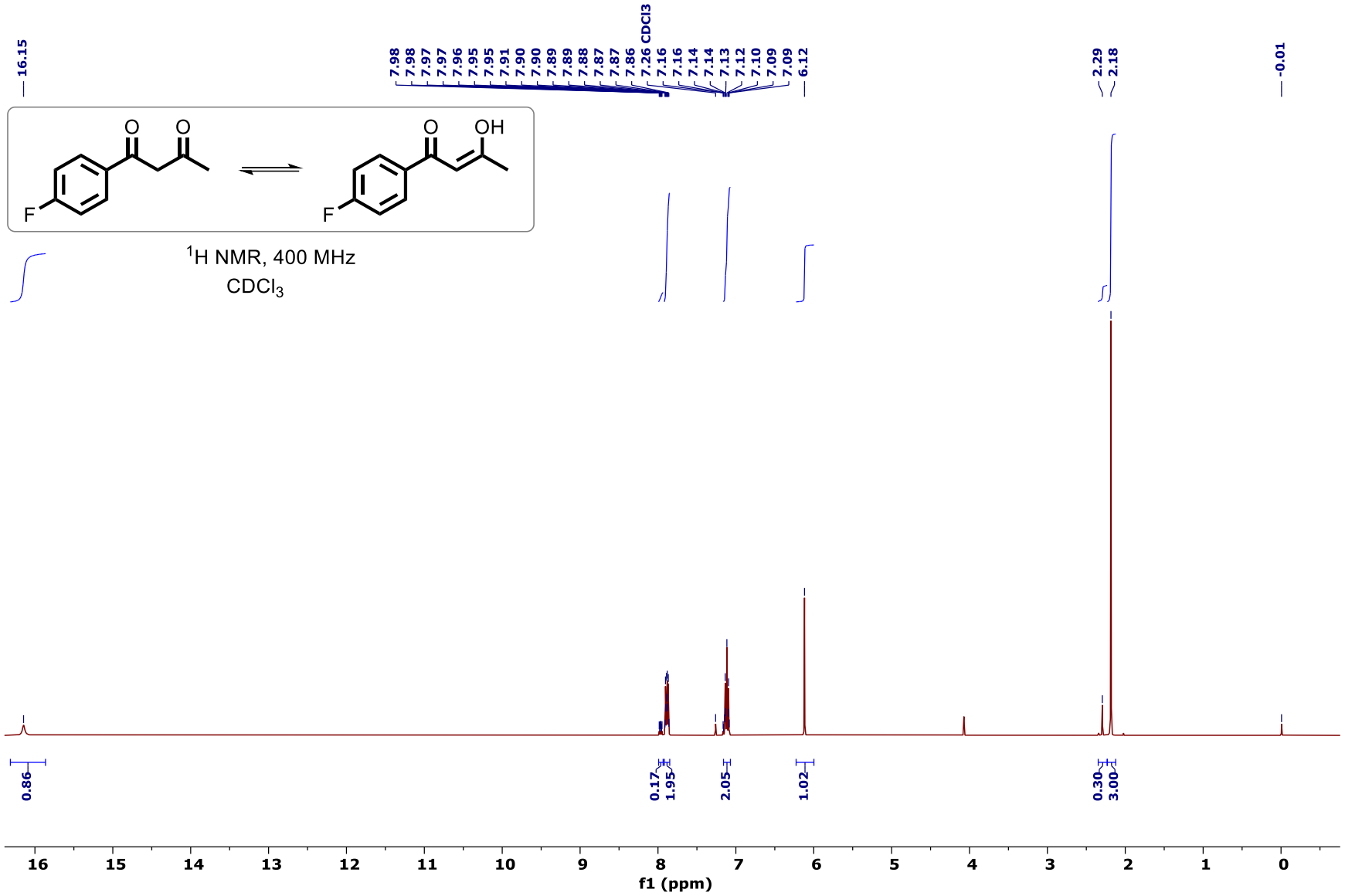
^{1}H NMR spectrum of 1-(4-(Trifluoromethyl)phenyl)butane-1,3-dione (4q):



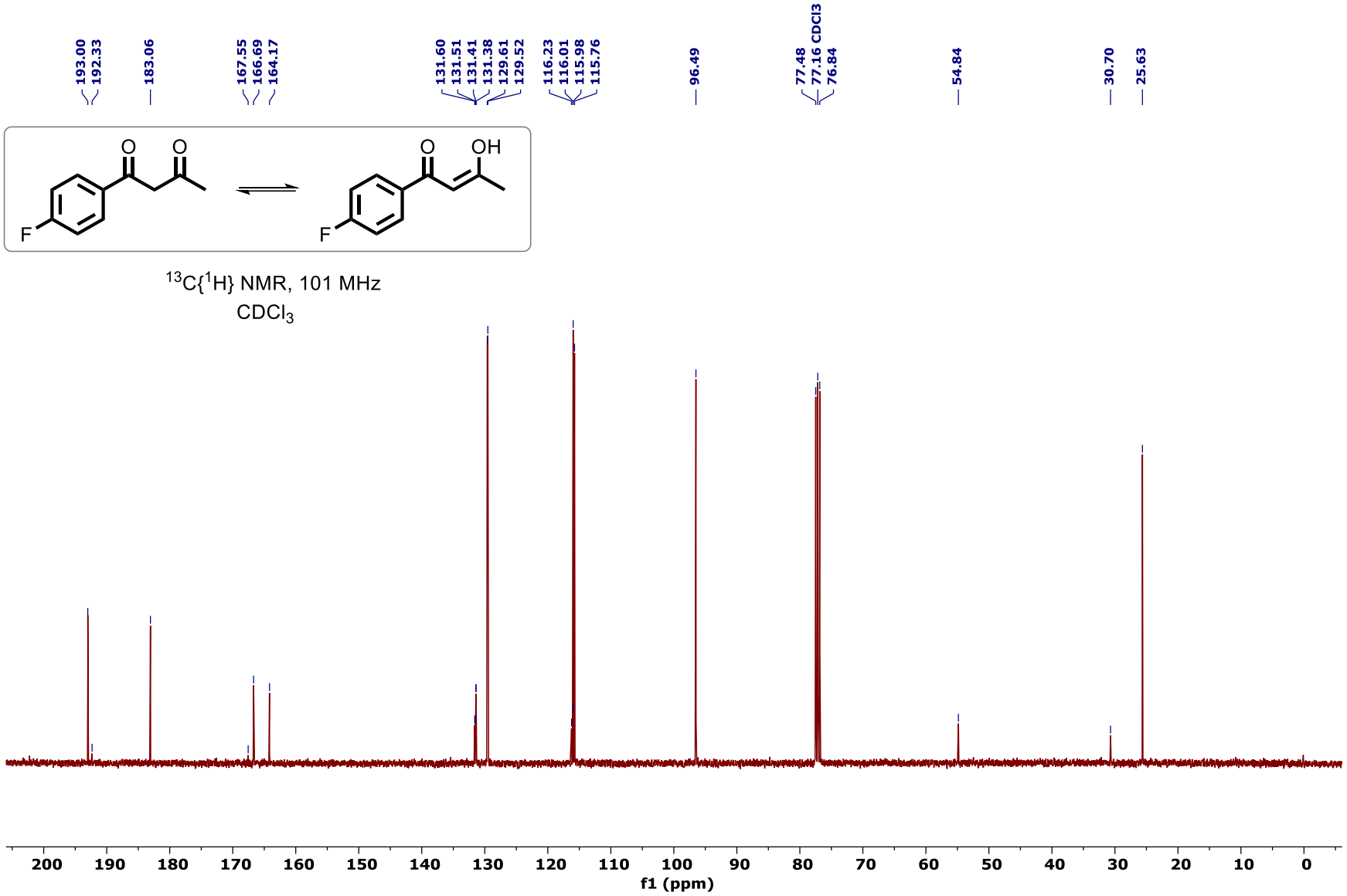
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-(Trifluoromethyl)phenyl)butane-1,3-dione (4q):



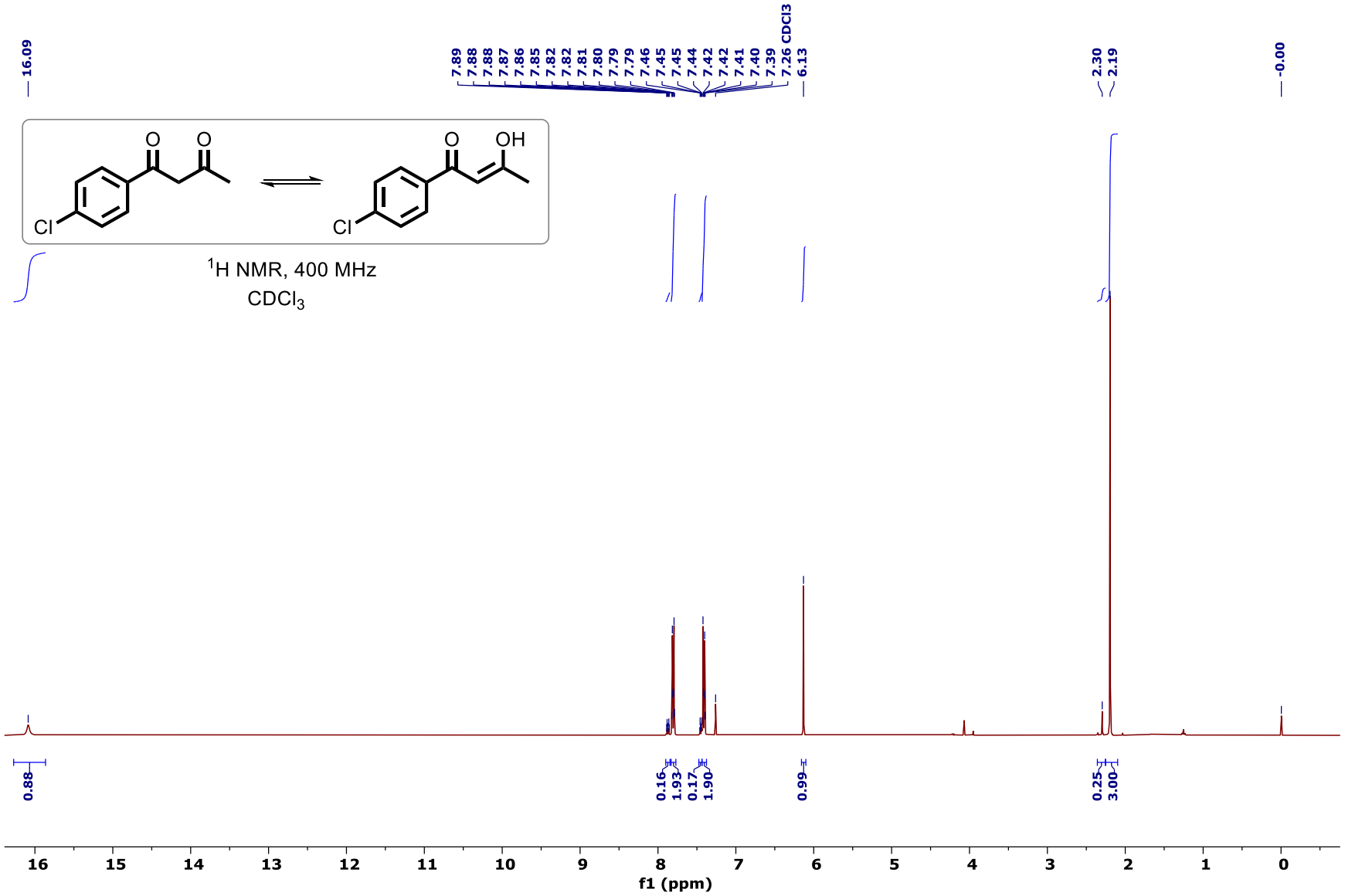
^{1}H NMR spectrum of 1-(4-Fluorophenyl)butane-1,3-dione (4r):



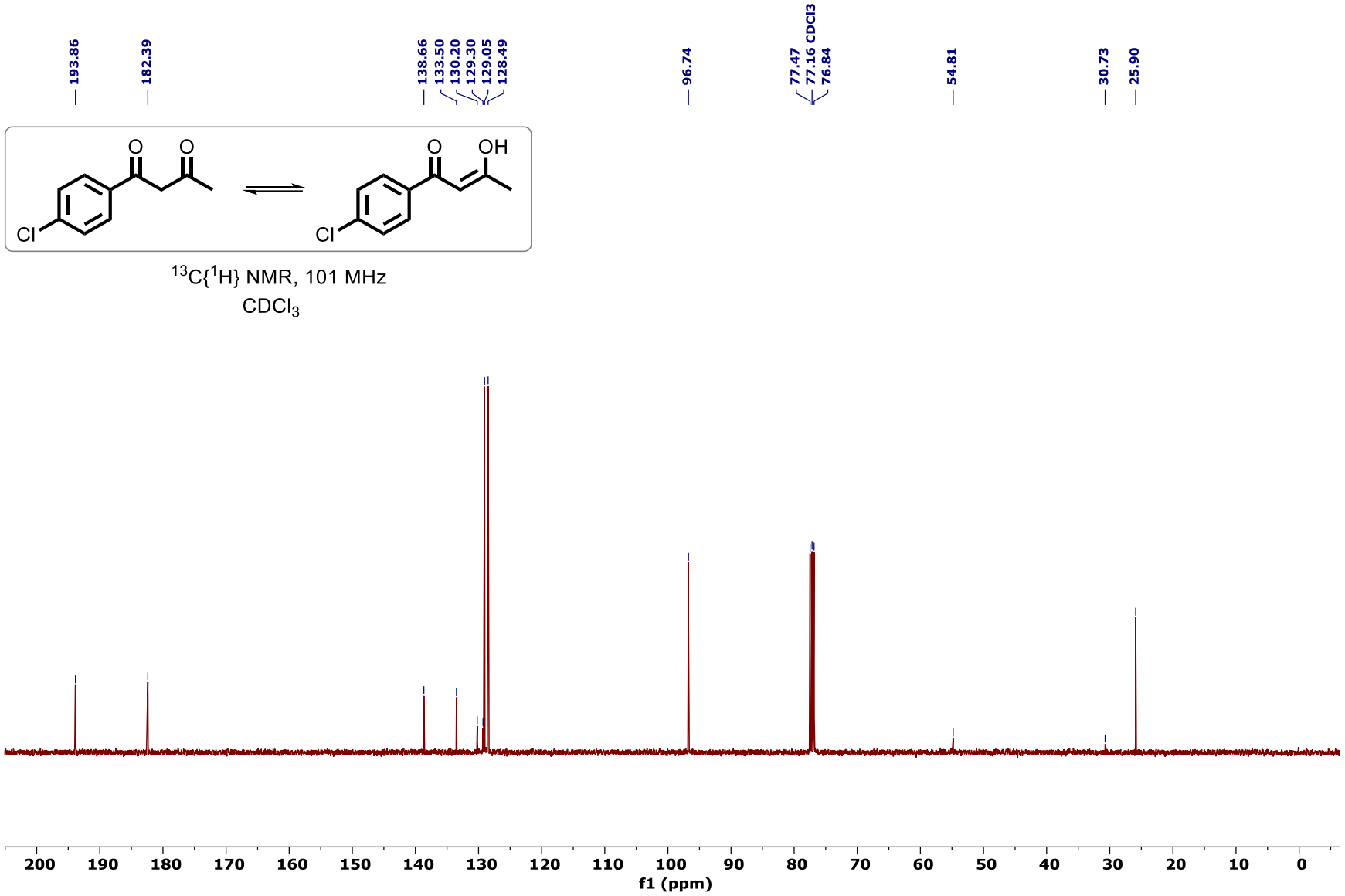
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Fluorophenyl)butane-1,3-dione (4r):



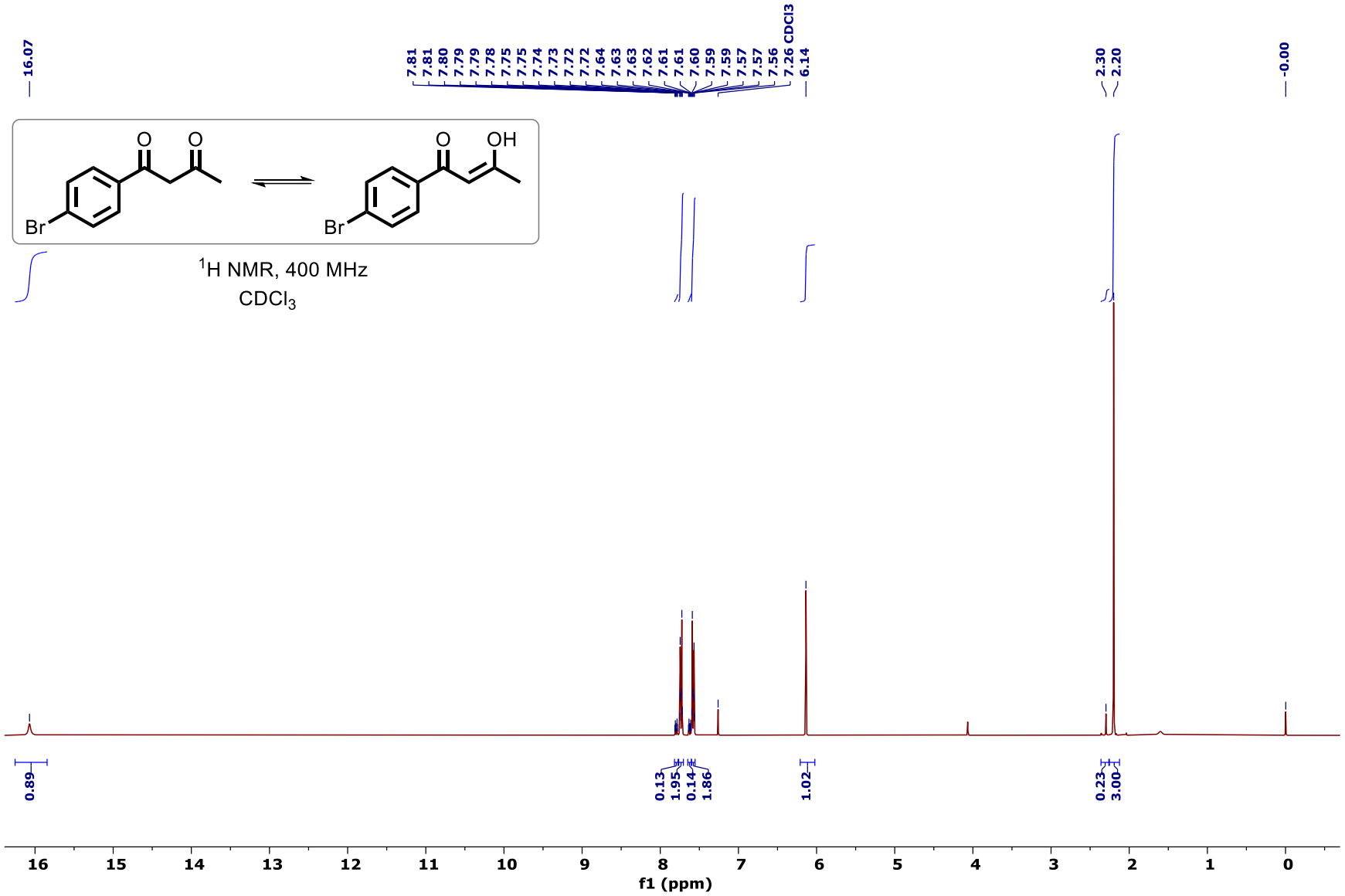
^{1}H NMR spectrum of 1-(4-Chlorophenyl)butane-1,3-dione (4s):



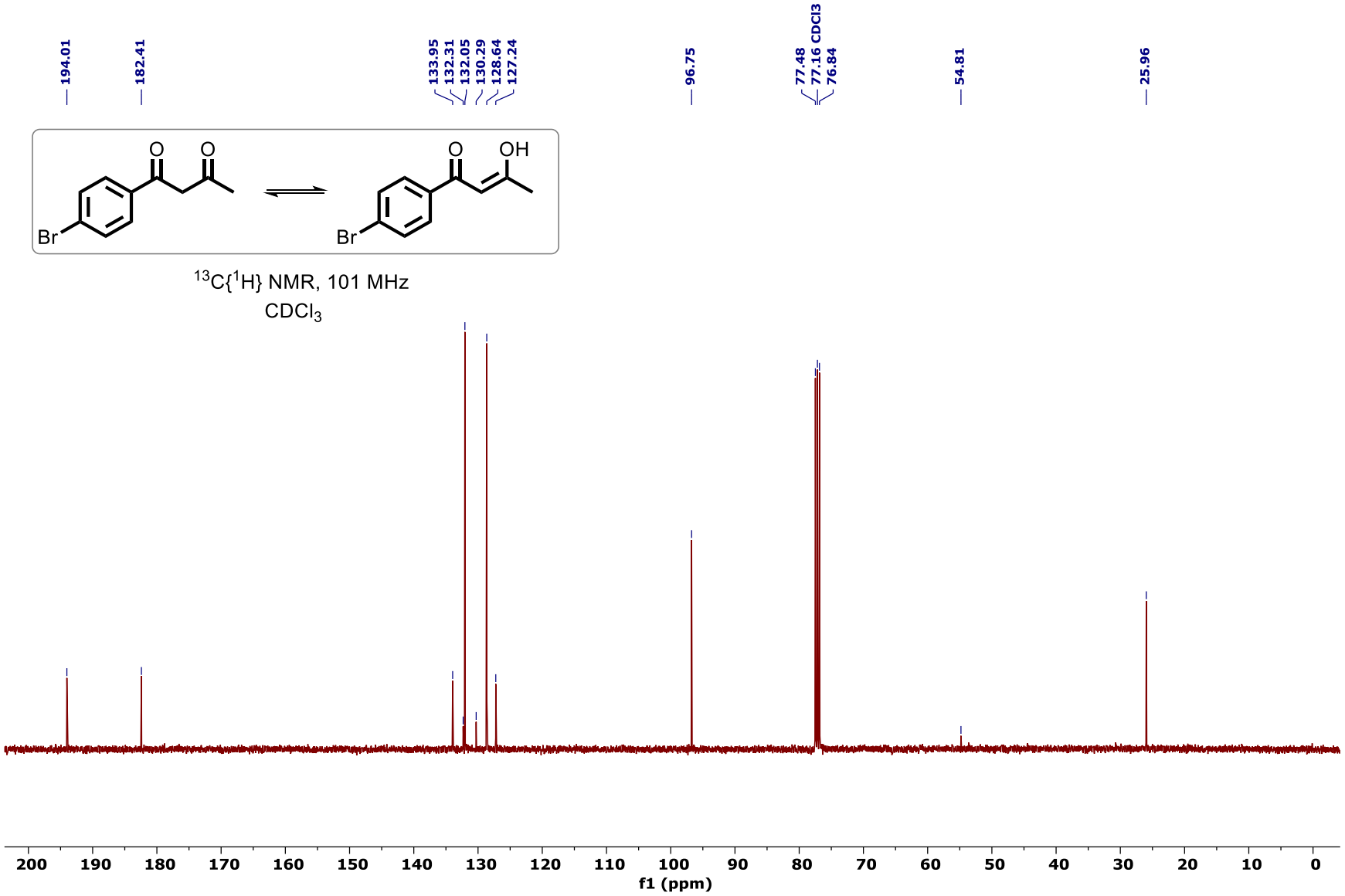
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Chlorophenyl)butane-1,3-dione (4s):



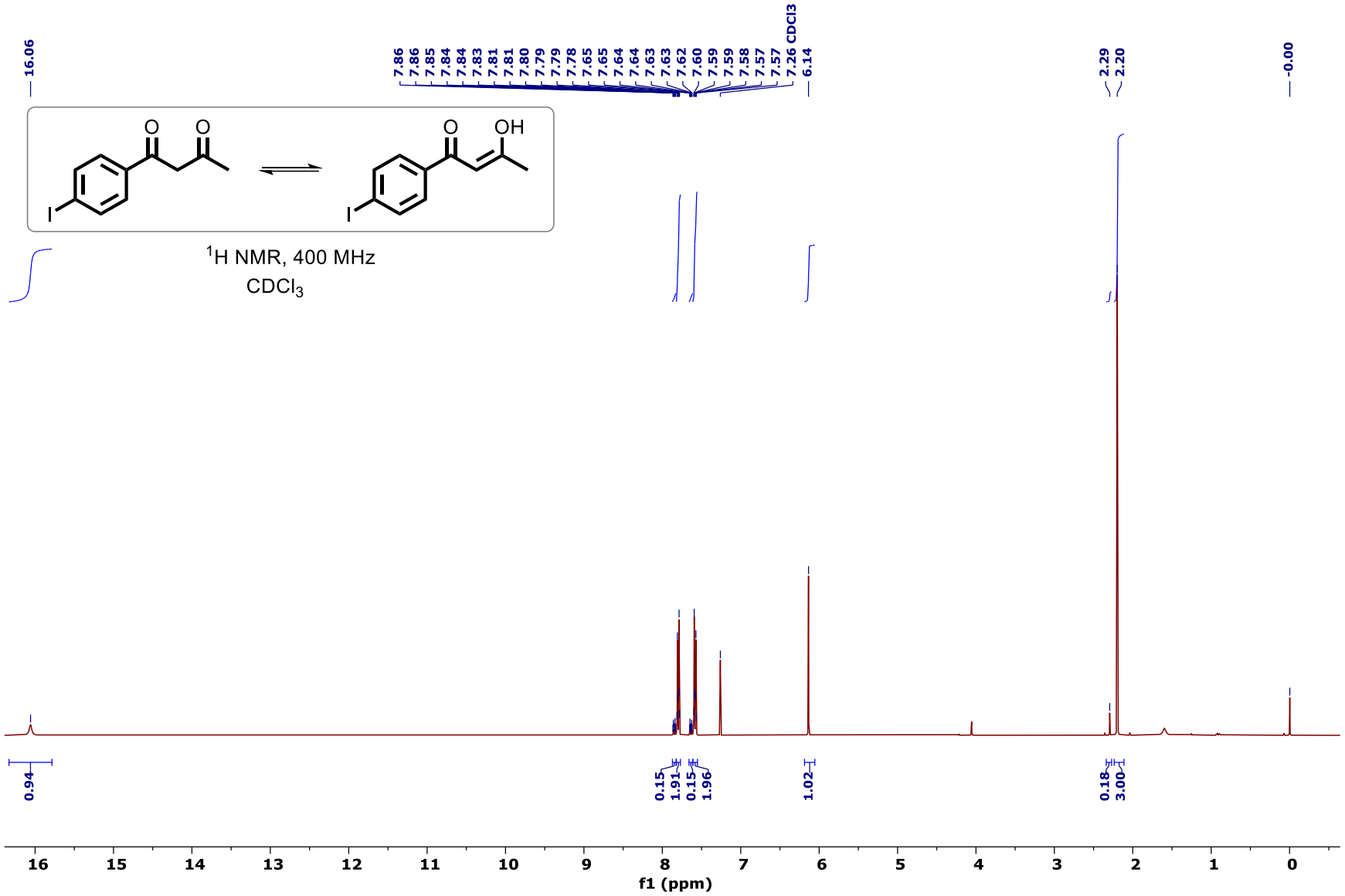
^{1}H NMR spectrum of 1-(4-Bromophenyl)butane-1,3-dione (4t):



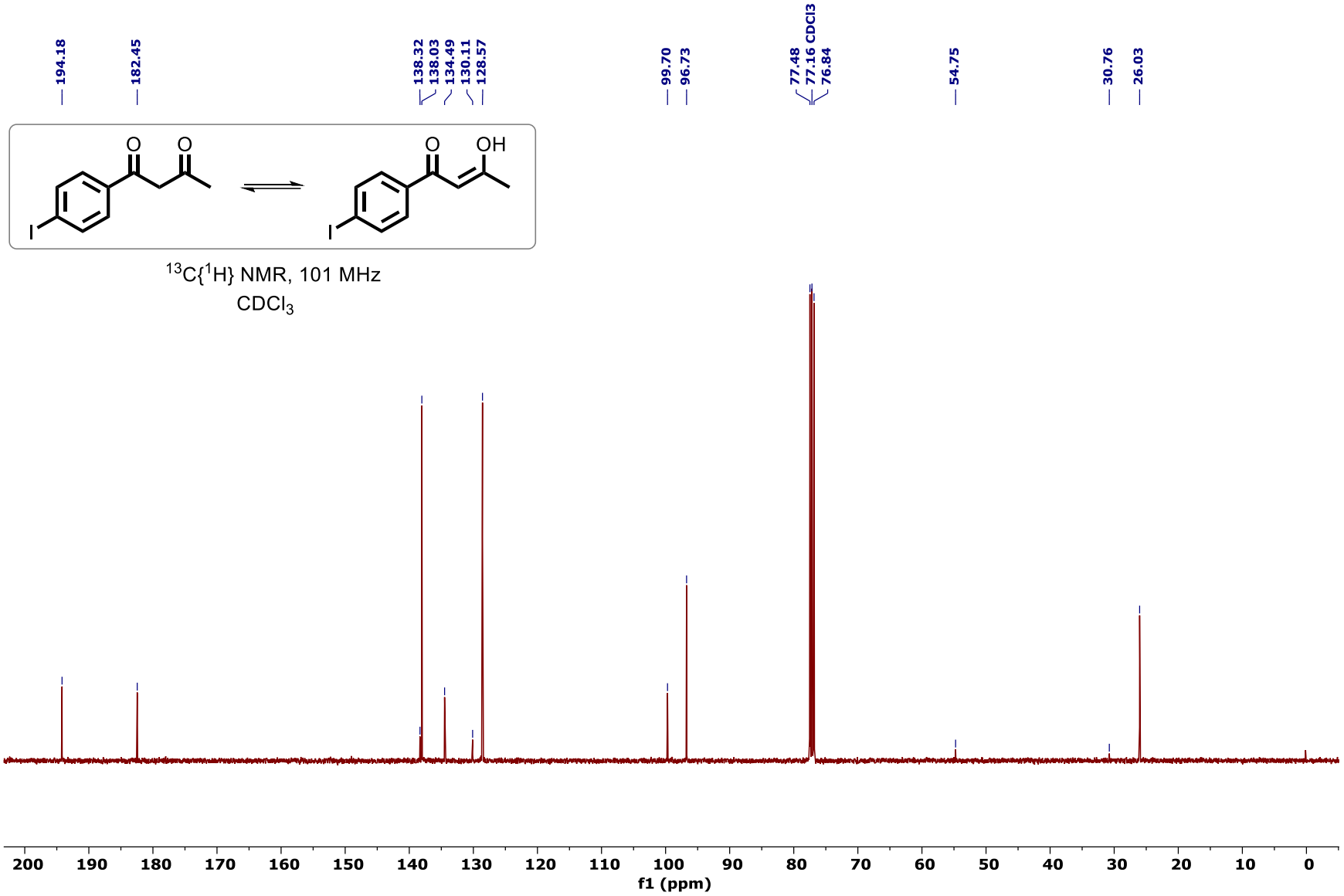
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Bromophenyl)butane-1,3-dione (4t):



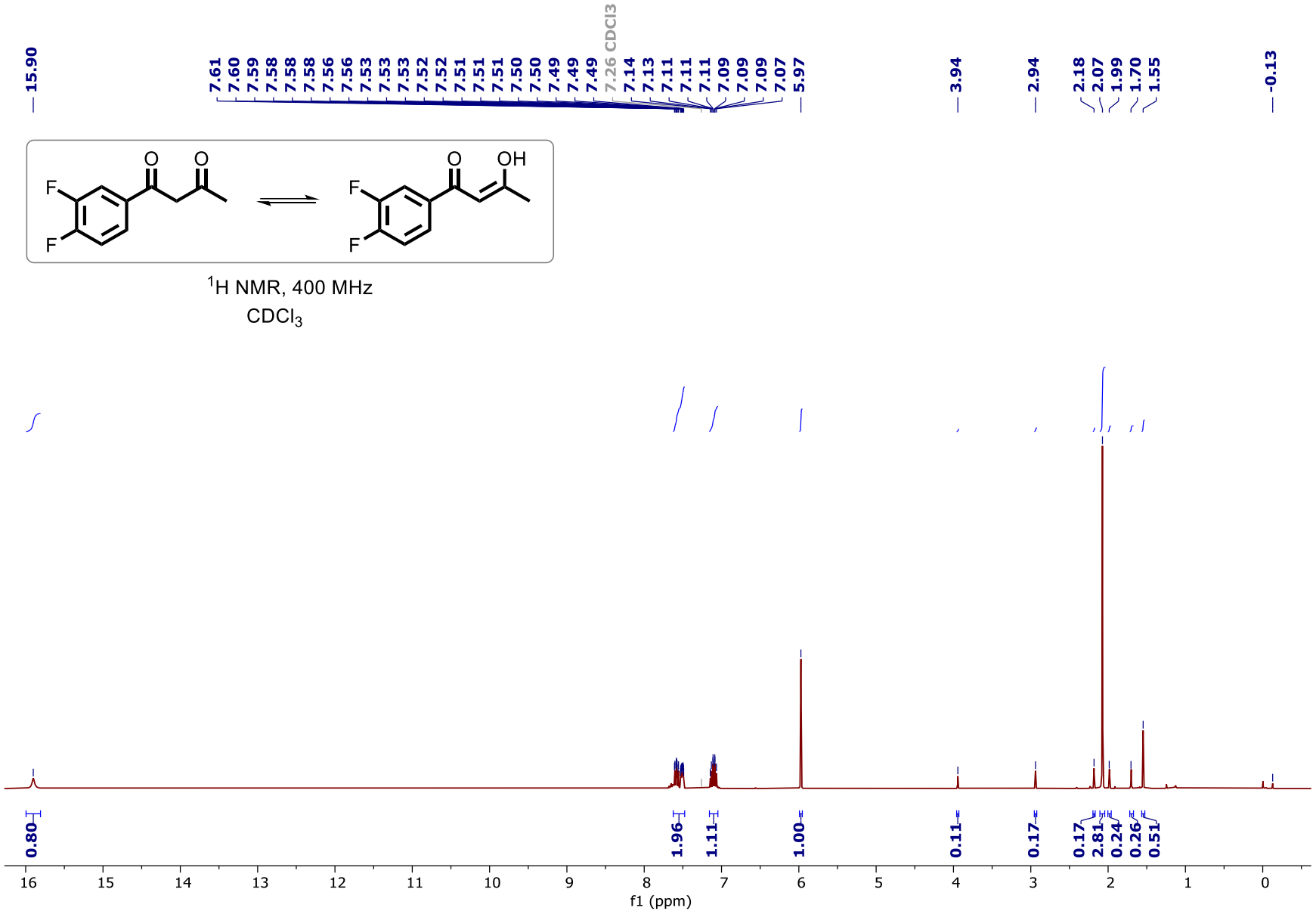
^{1}H NMR spectrum of 1-(4-Iodophenyl)butane-1,3-dione (4u):



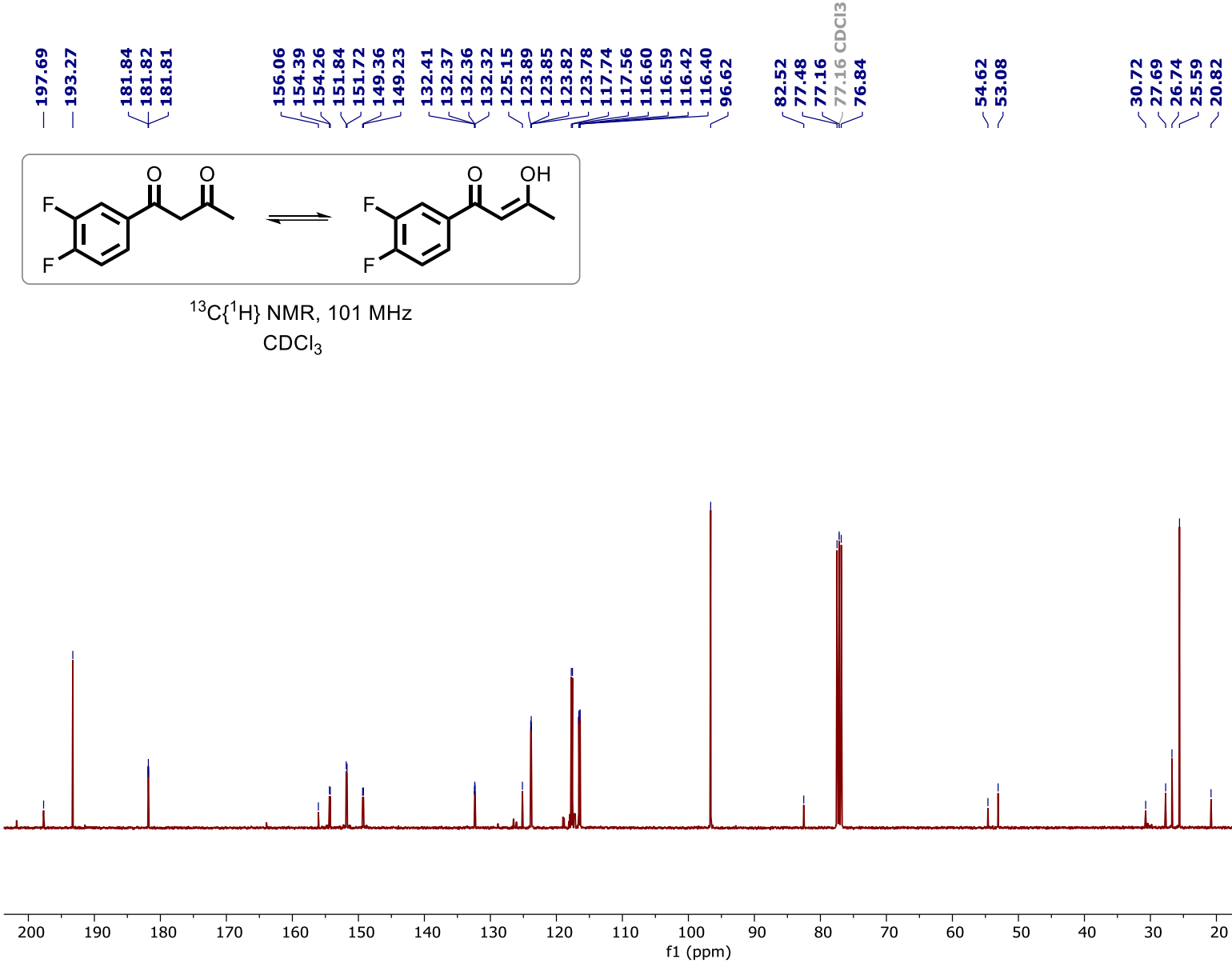
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-Iodophenyl)butane-1,3-dione (4u):



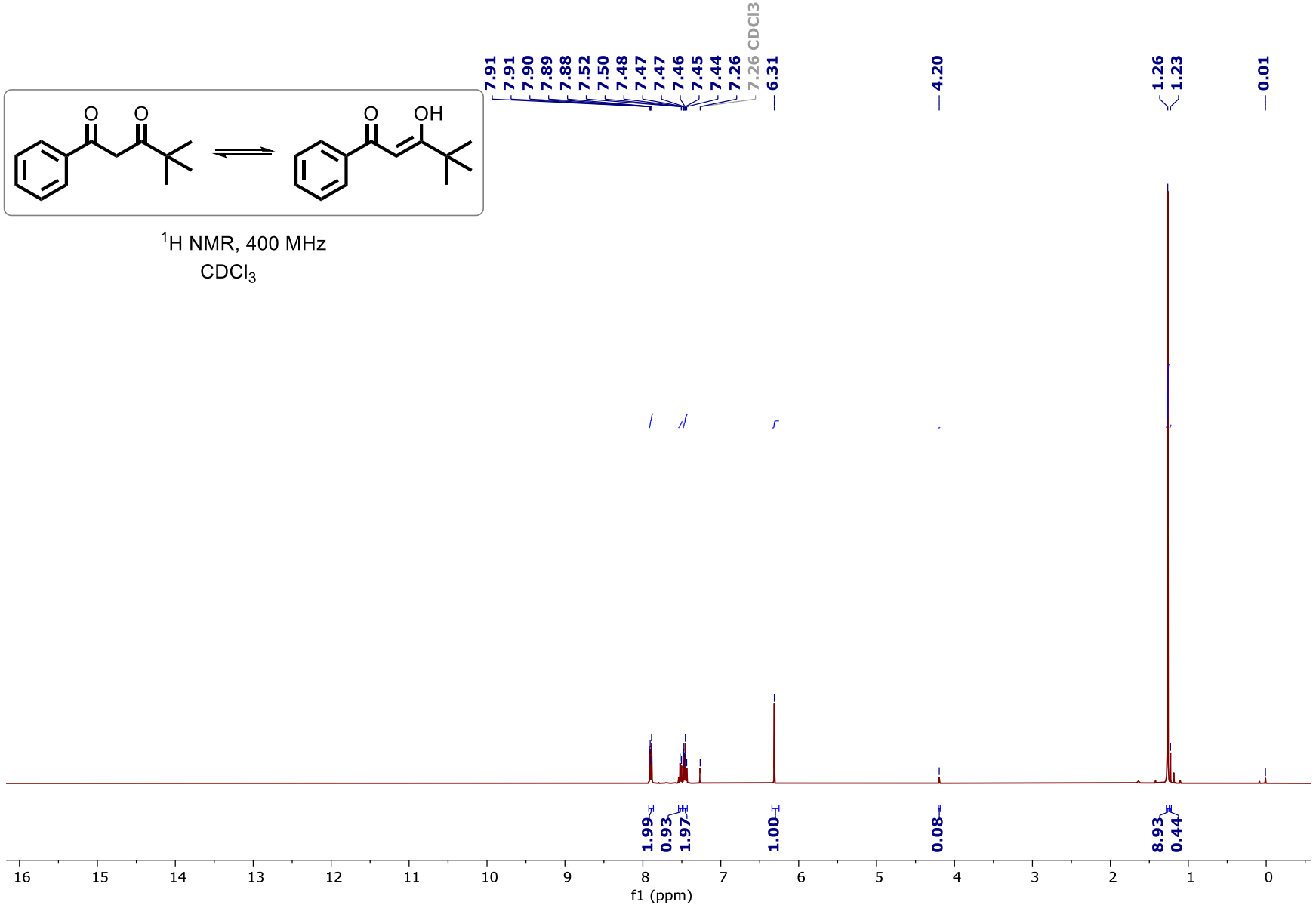
^{1}H NMR spectrum of 1-(3,4-Difluorophenyl)butane-1,3-dione (4v):



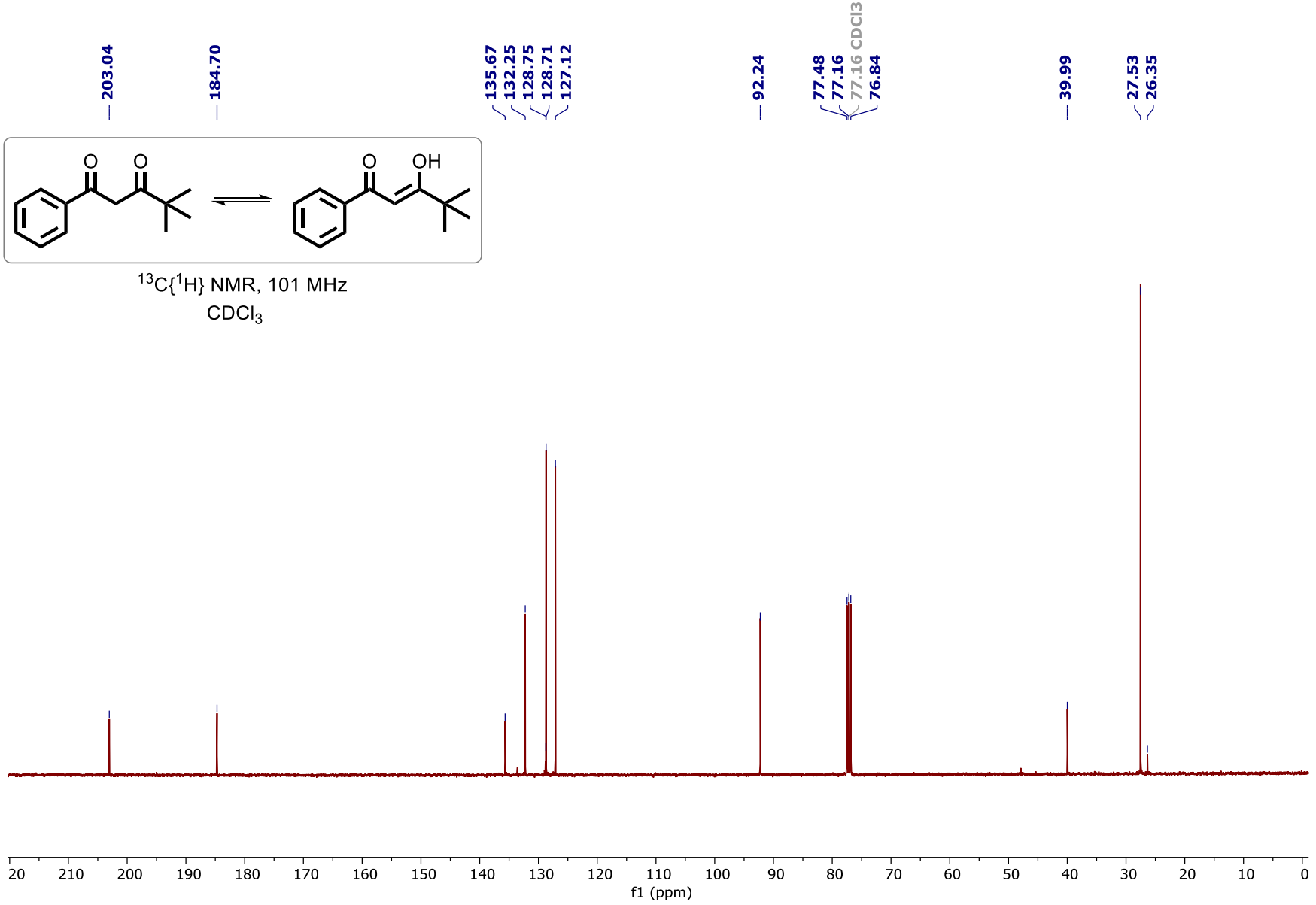
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(3,4-Difluorophenyl)butane-1,3-dione (4v):



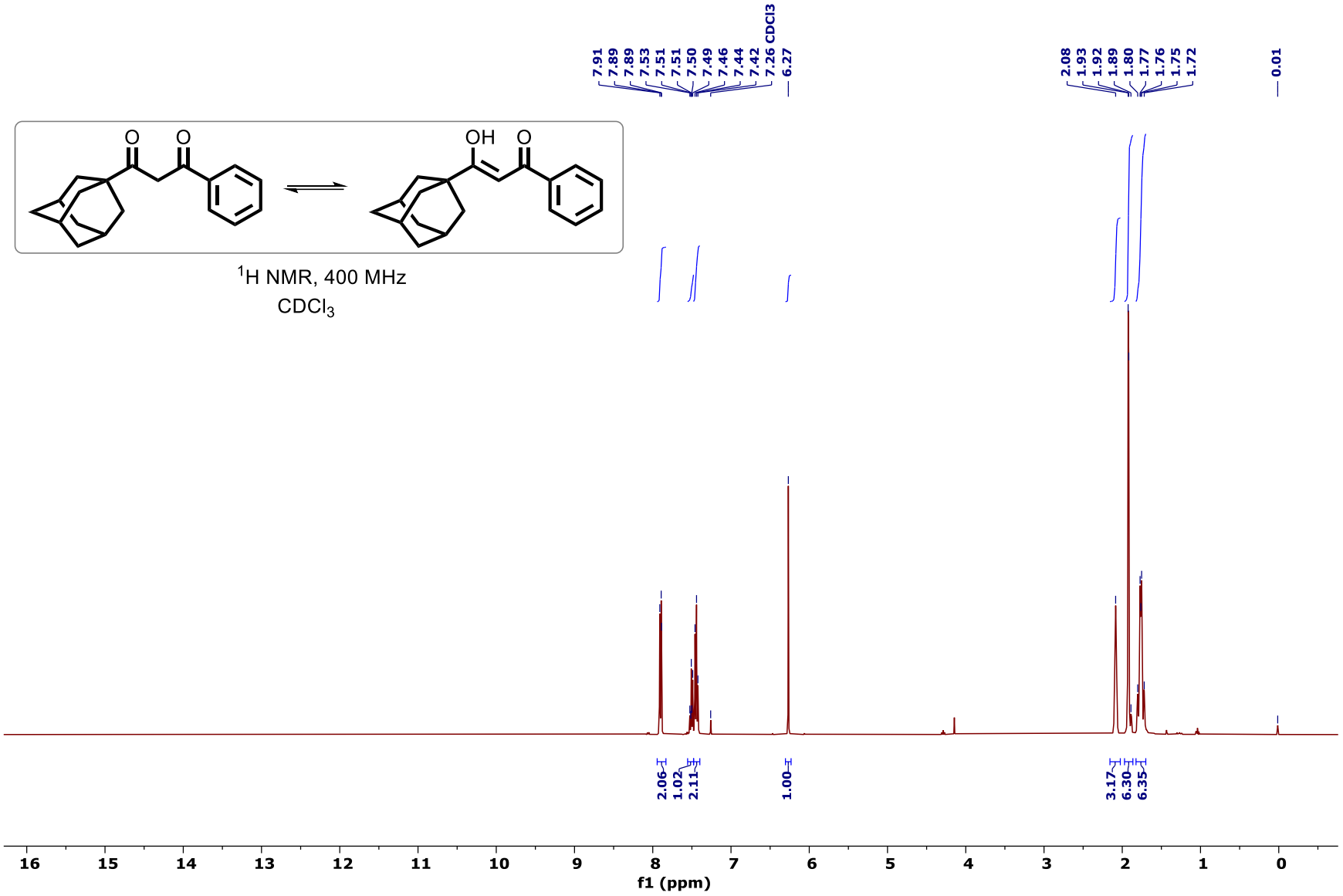
^{1}H NMR spectrum of 4,4-Dimethyl-1-phenylpentane-1,3-dione (4w):



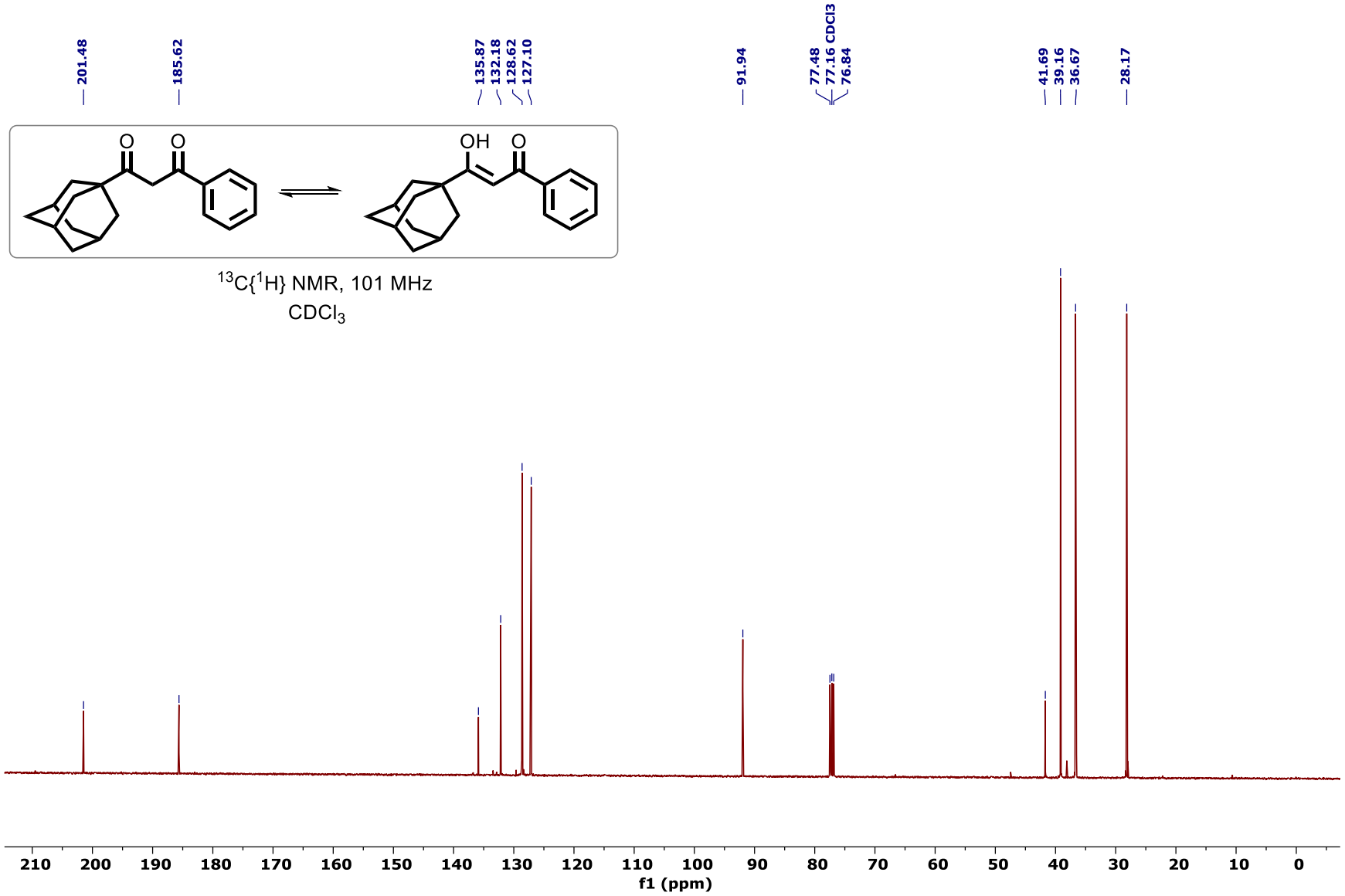
$^{13}C\{^{1}H\}$ NMR spectrum of 4,4-Dimethyl-1-phenylpentane-1,3-dione (4w):



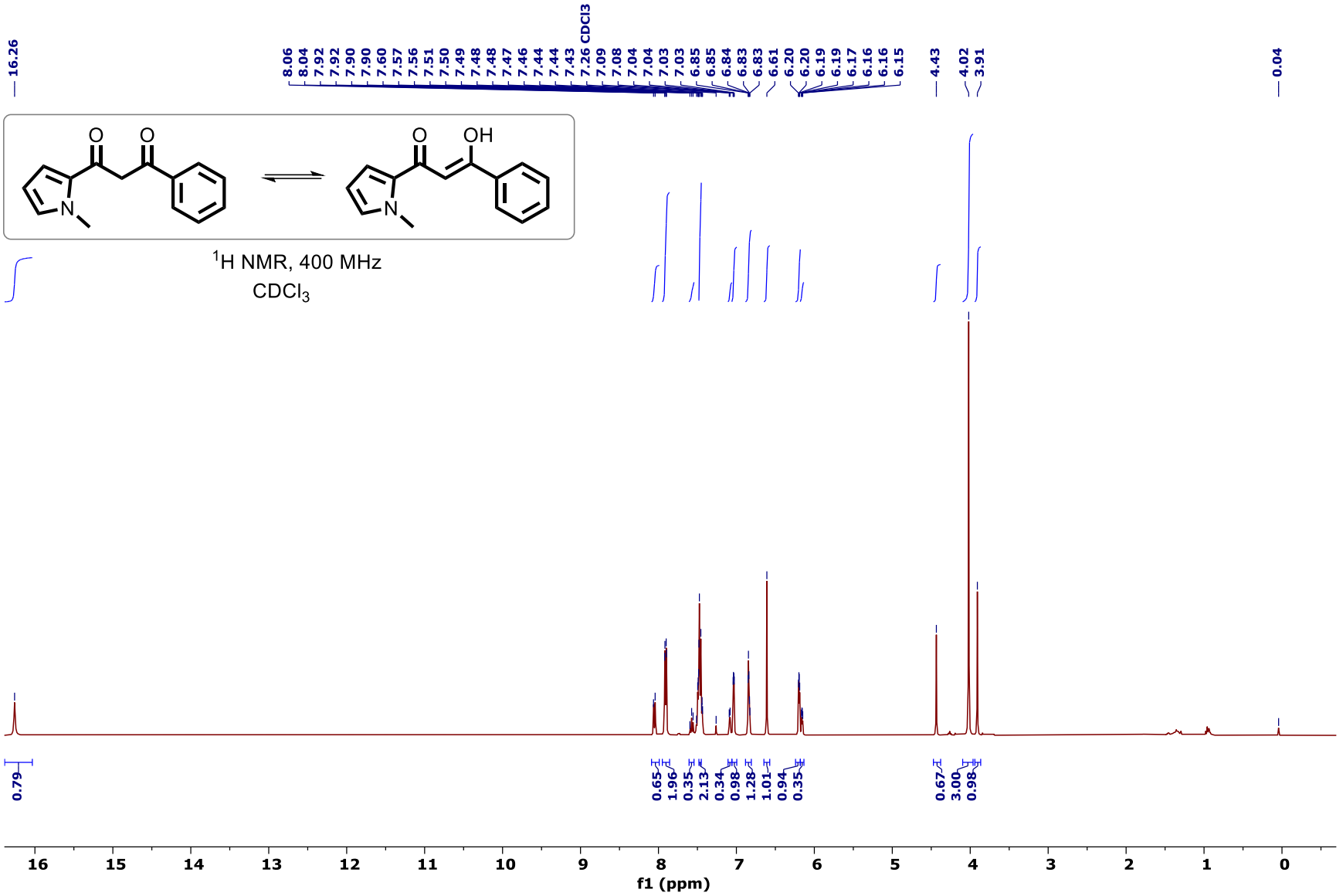
^{1}H NMR spectrum of 1-((3r,5r,7r)-Adamantan-1-yl)-3-phenylpropane-1,3-dione (4y):



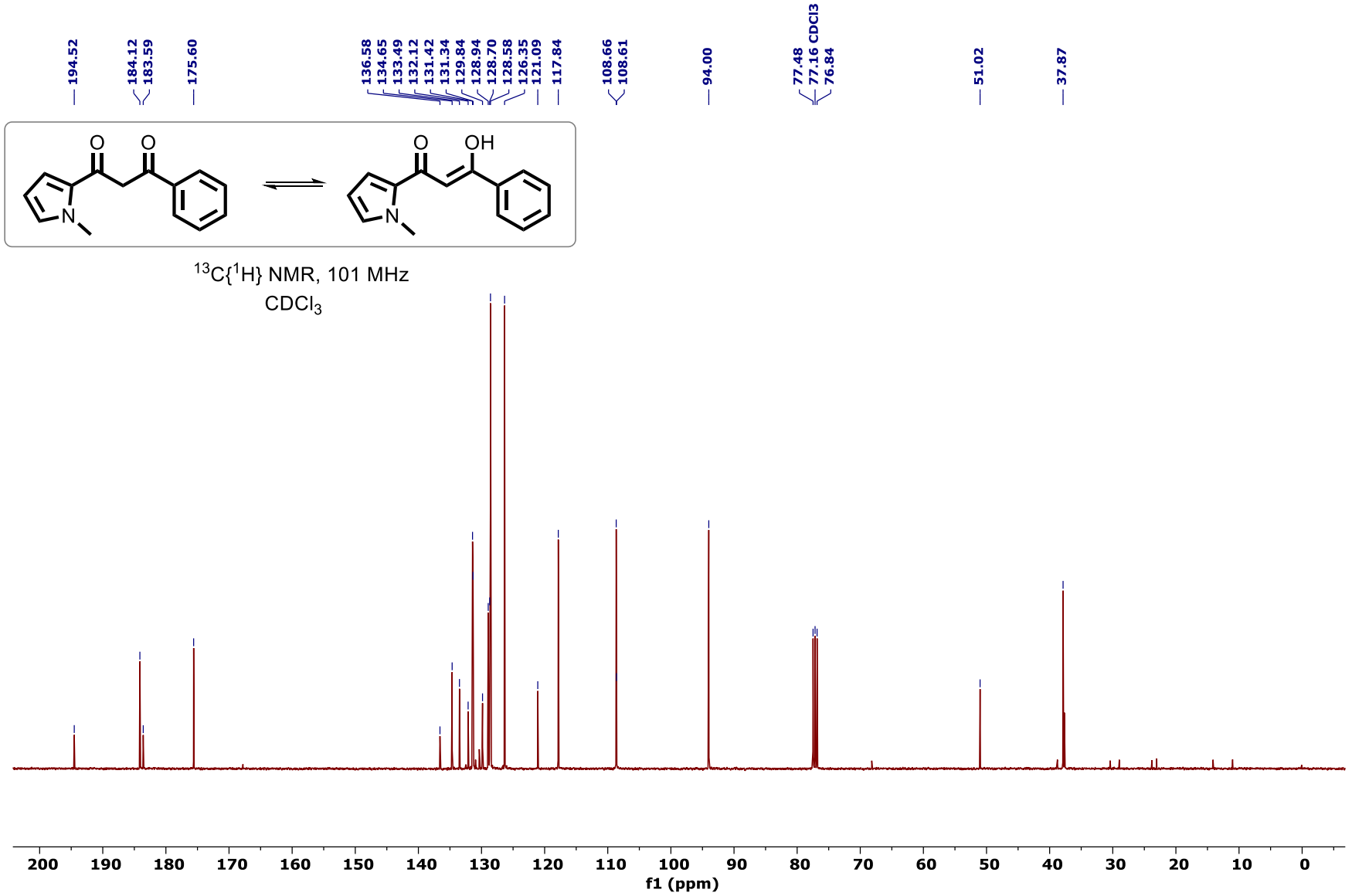
$^{13}C\{^{1}H\}$ NMR spectrum of 1-((3r,5r,7r)-Adamantan-1-yl)-3-phenylpropane-1,3-dione (4y):



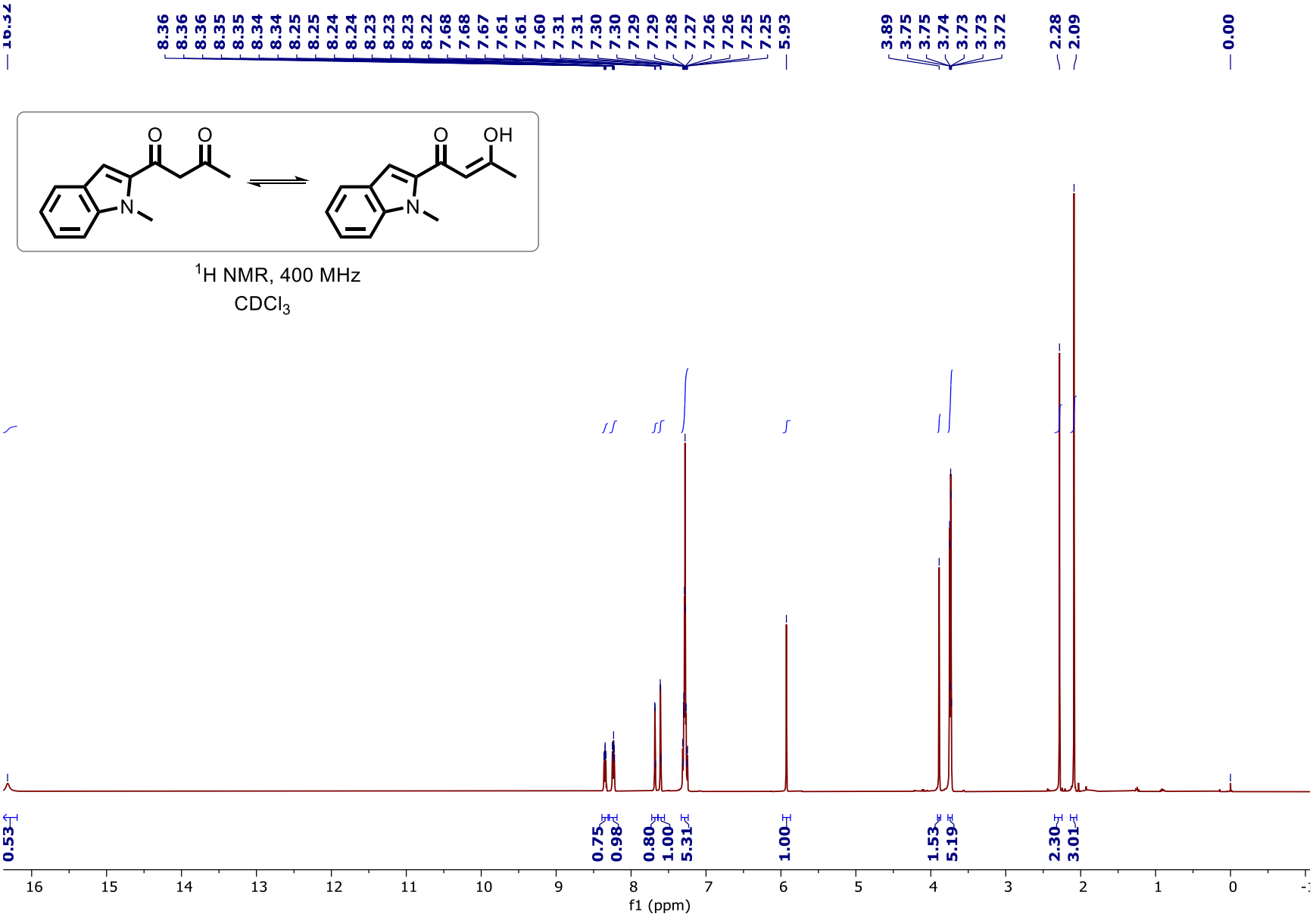
^{1}H NMR spectrum of 1-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylpropane-1,3-dione (4a′):



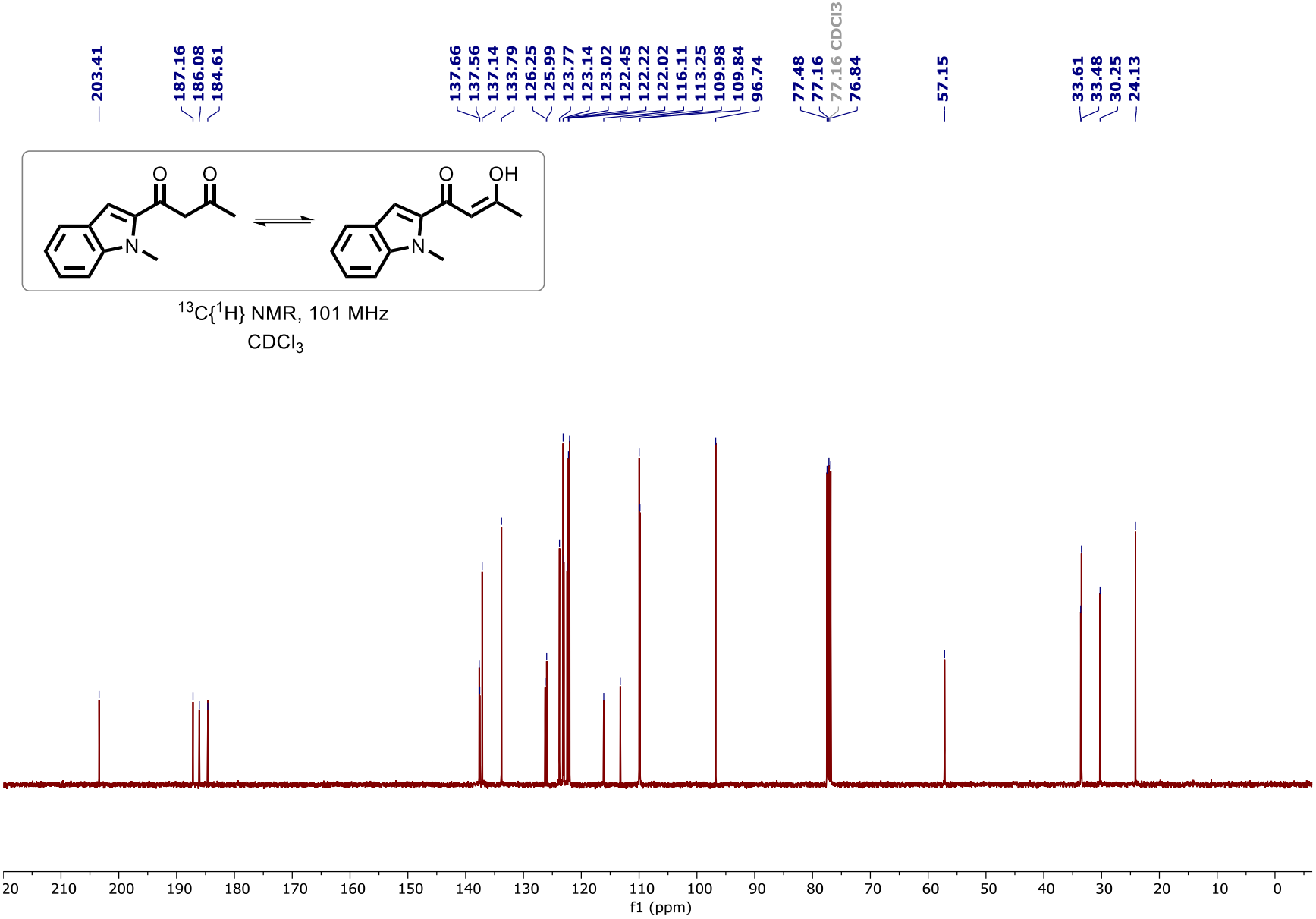
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylpropane-1,3-dione (4a′):



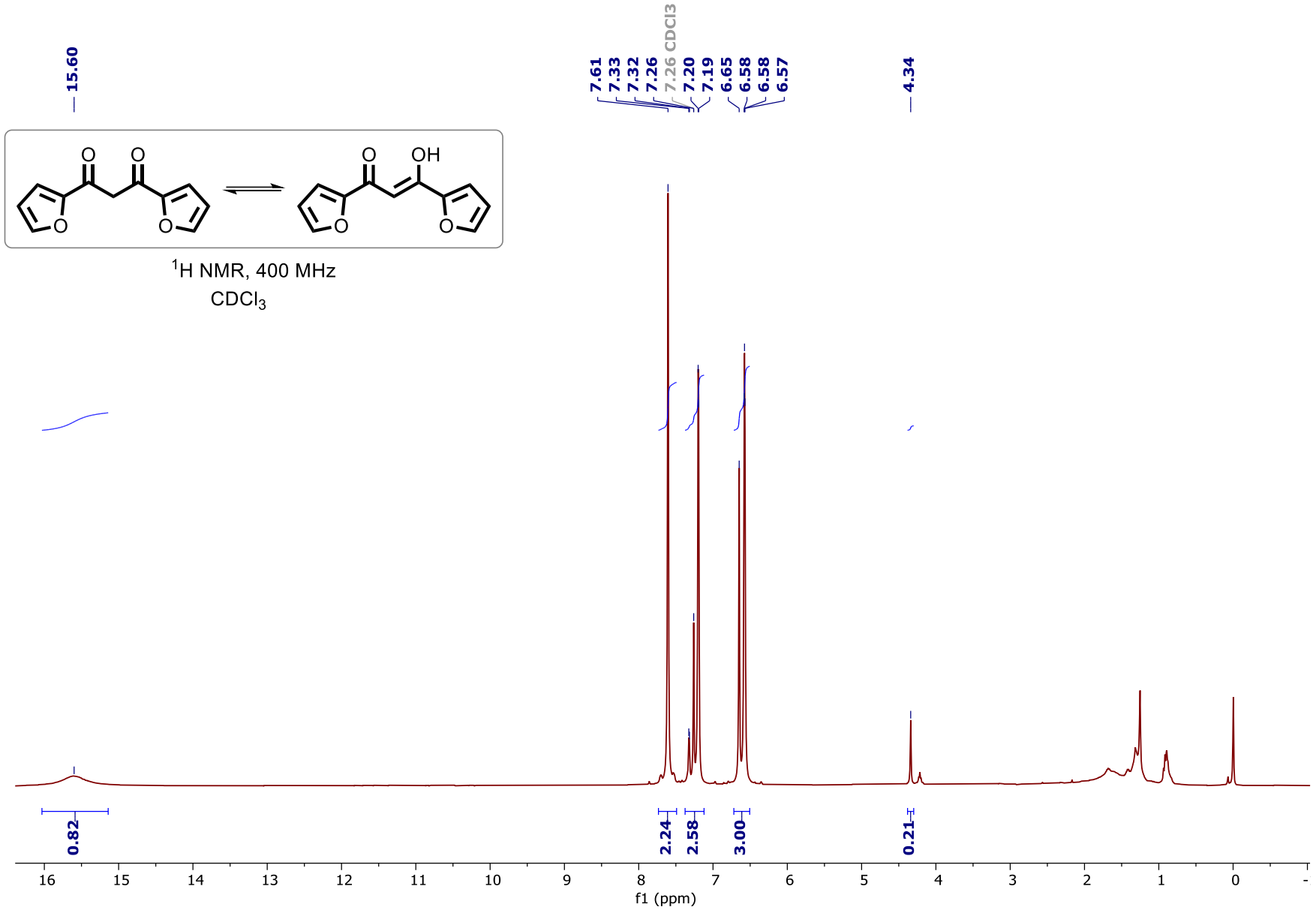
^{1}H NMR spectrum of 1-(1-methyl-1*H*-indol-2-yl)butane-1,3-dione (4b′):



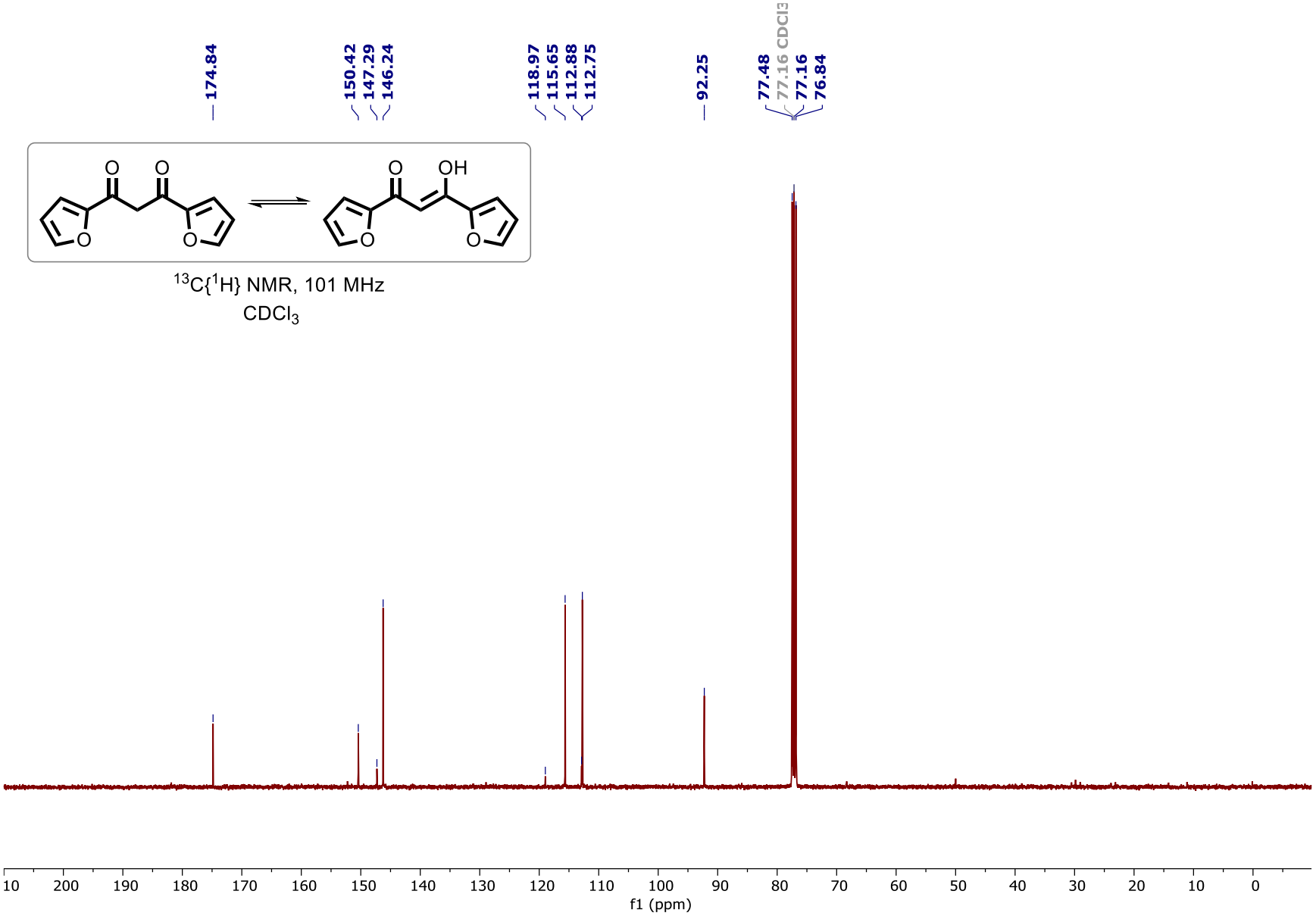
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(1-methyl-1*H*-indol-2-yl)butane-1,3-dione (4b′):



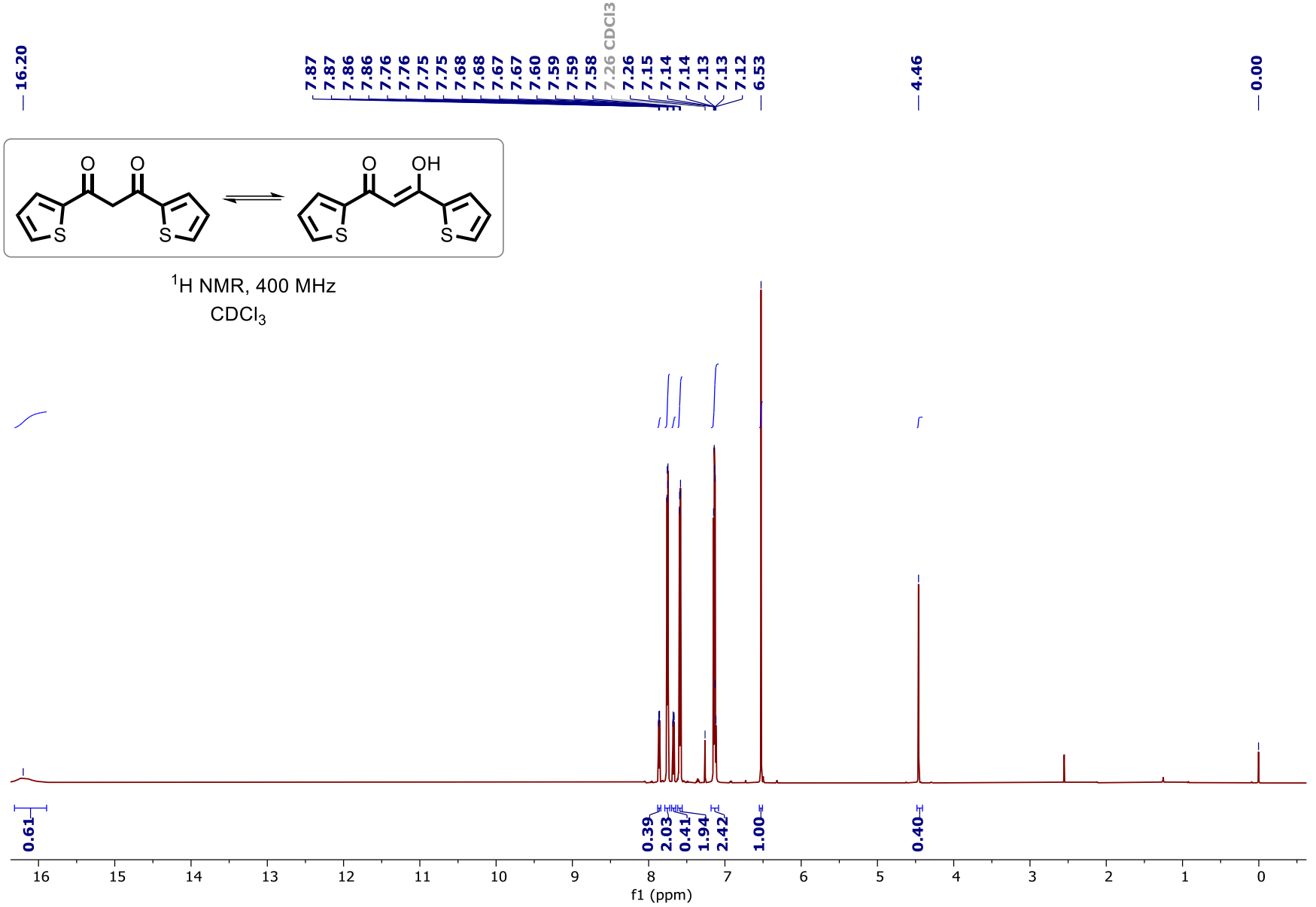
^{1}H NMR spectrum of 1,3-Di(furan-2-yl)propane-1,3-dione (4c′):



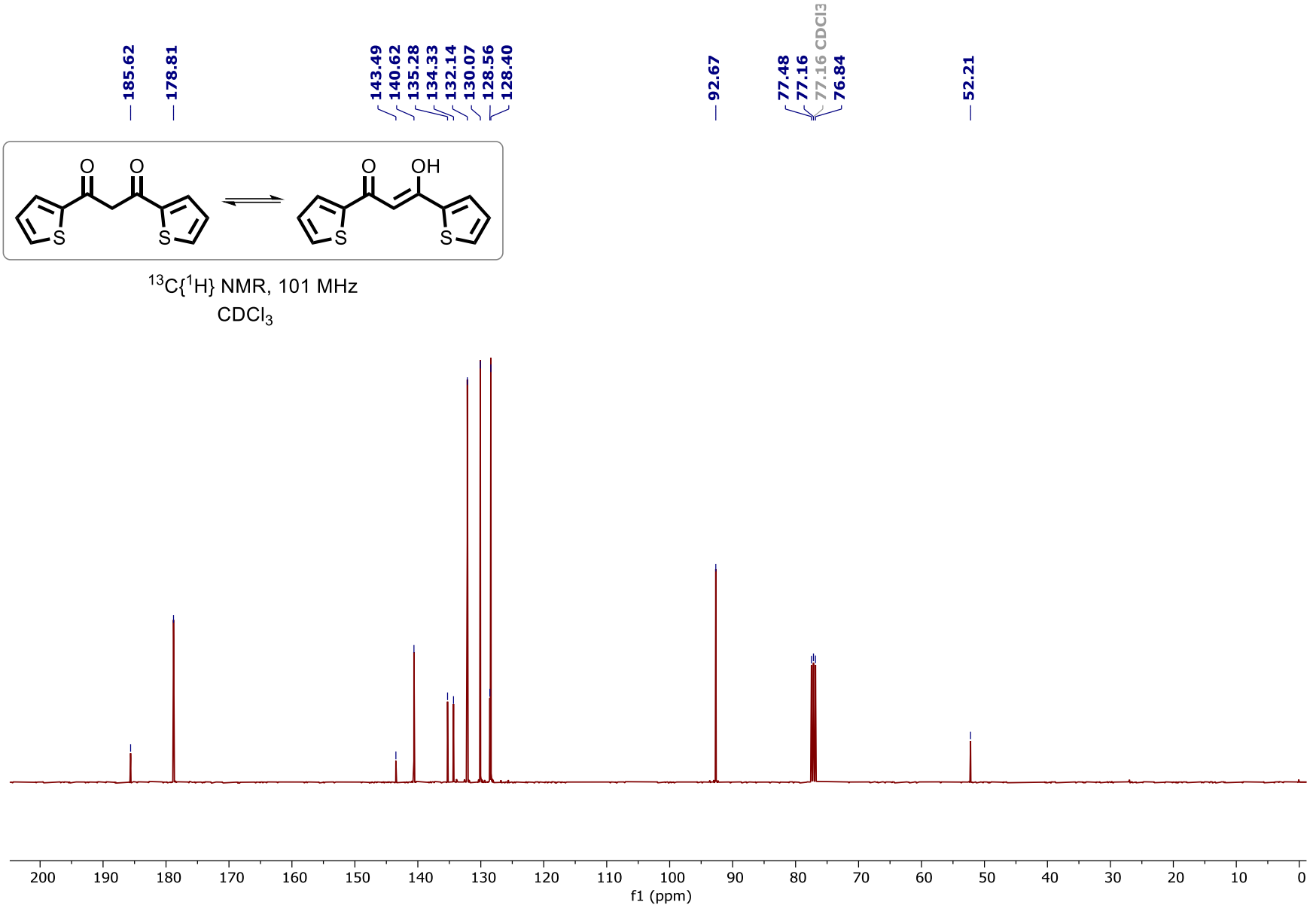
$^{13}C\{^{1}H\}$ NMR spectrum of 1,3-Di(furan-2-yl)propane-1,3-dione (4c′):



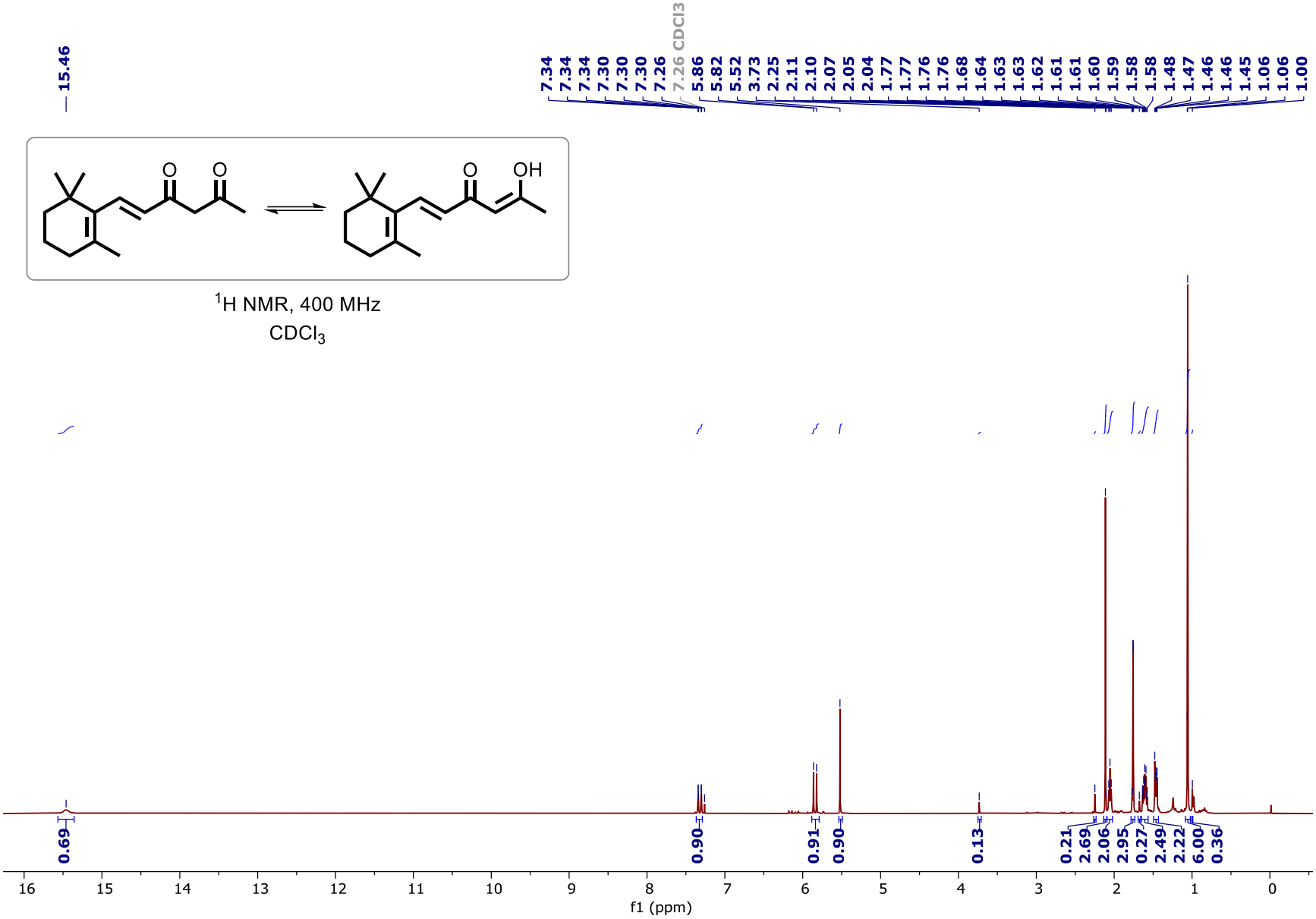
^{1}H NMR spectrum of 1,3-Di(thiophen-2-yl)propane-1,3-dione (4d′):



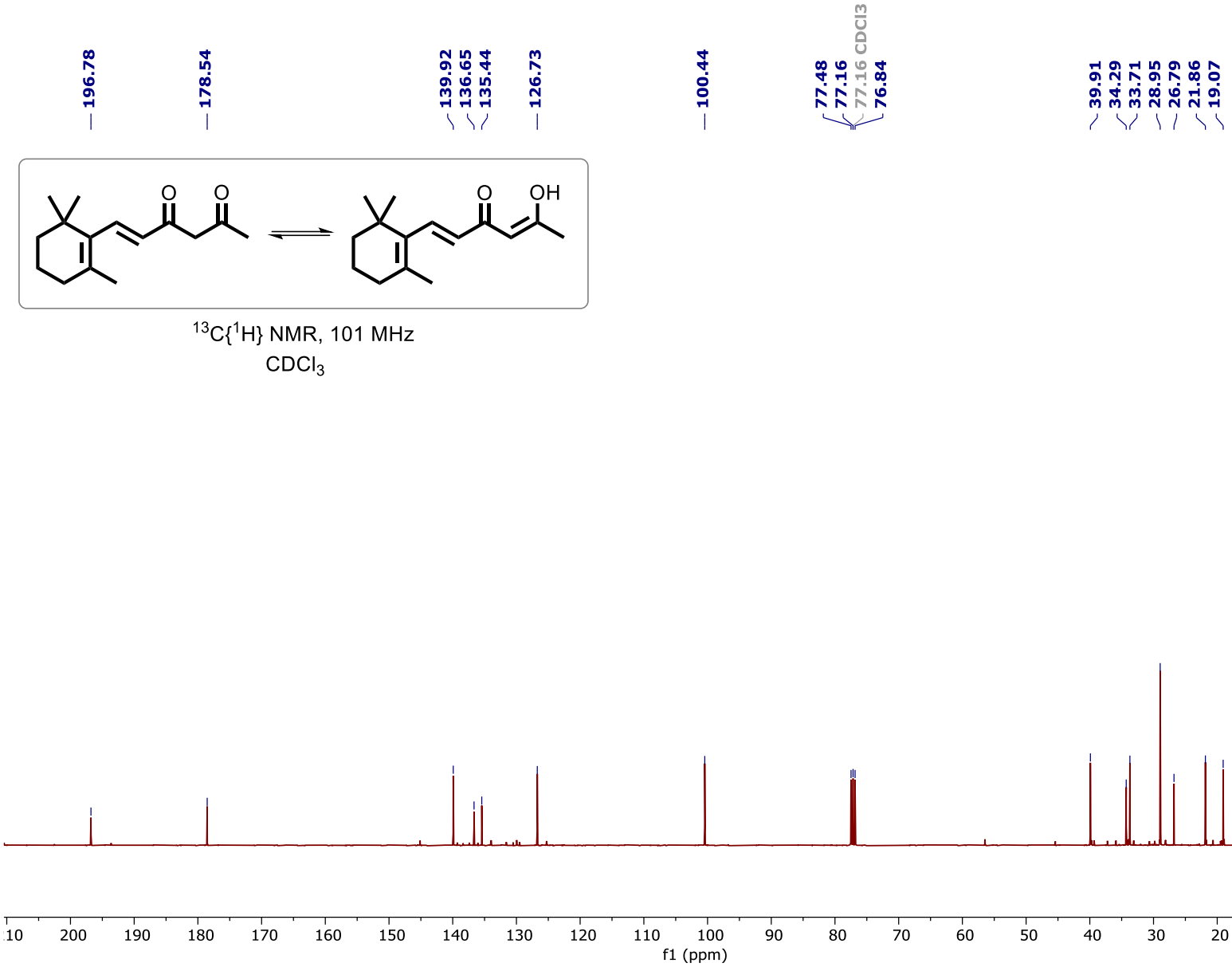
$^{13}C\{^{1}H\}$ NMR spectrum of 1,3-Di(thiophen-2-yl)propane-1,3-dione (4d′):



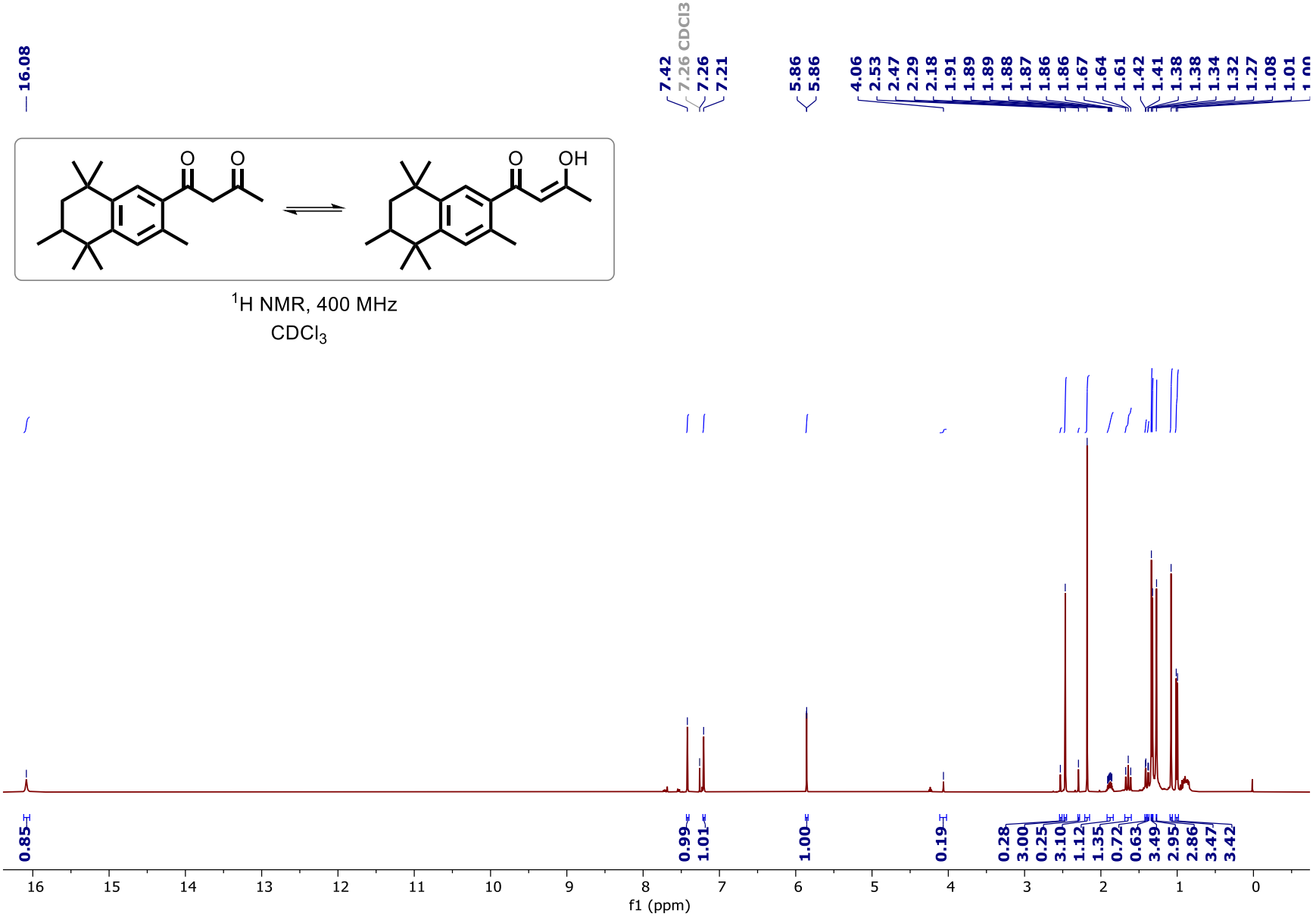
^{1}H NMR spectrum of (*E*)-6-(2,6,6-Trimethylcyclohex-1-en-1-yl)hex-5-ene-2,4-dione (4e′):



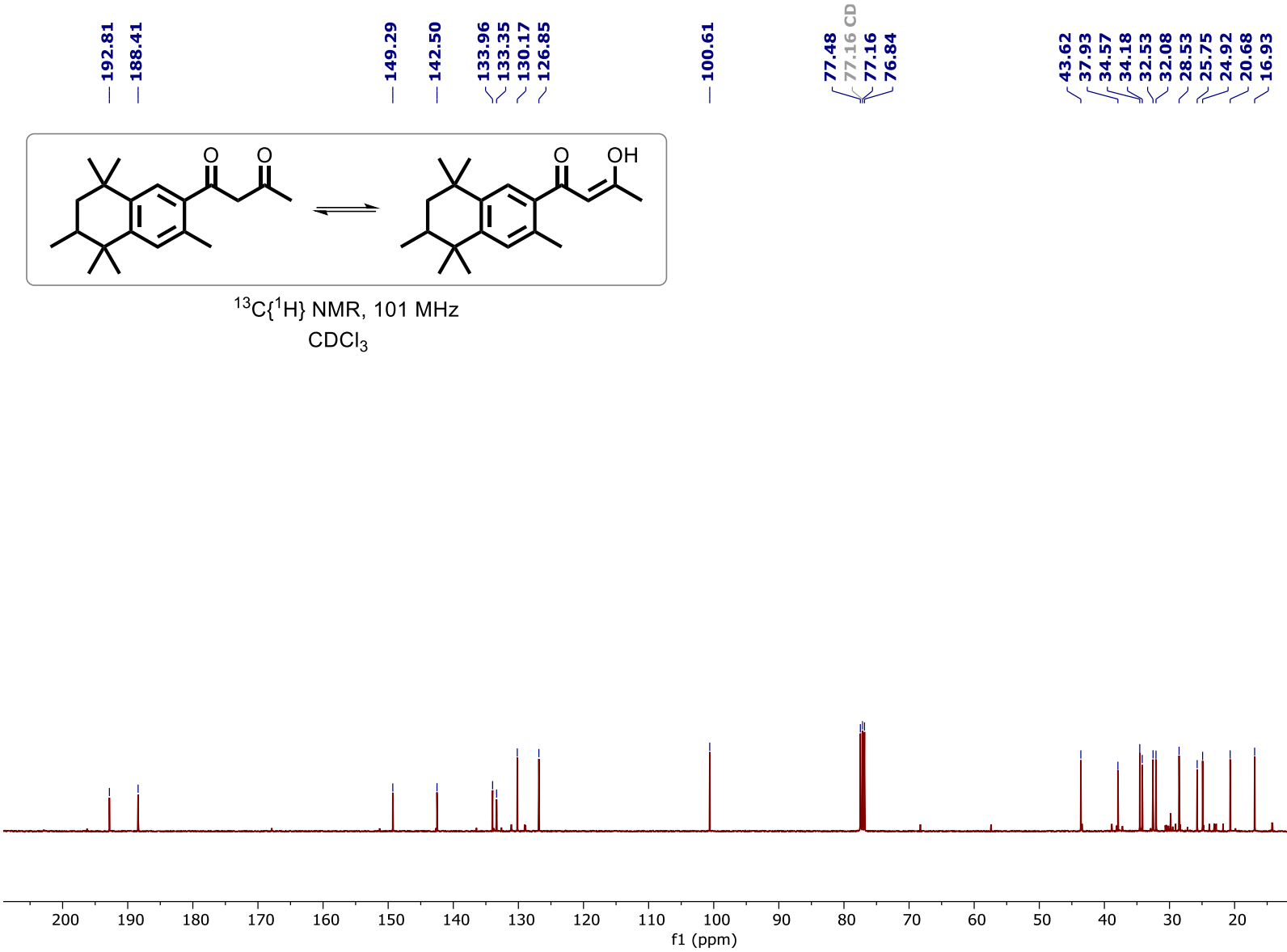
$^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-6-(2,6,6-Trimethylcyclohex-1-en-1-yl)hex-5-ene-2,4-dione (4e′):



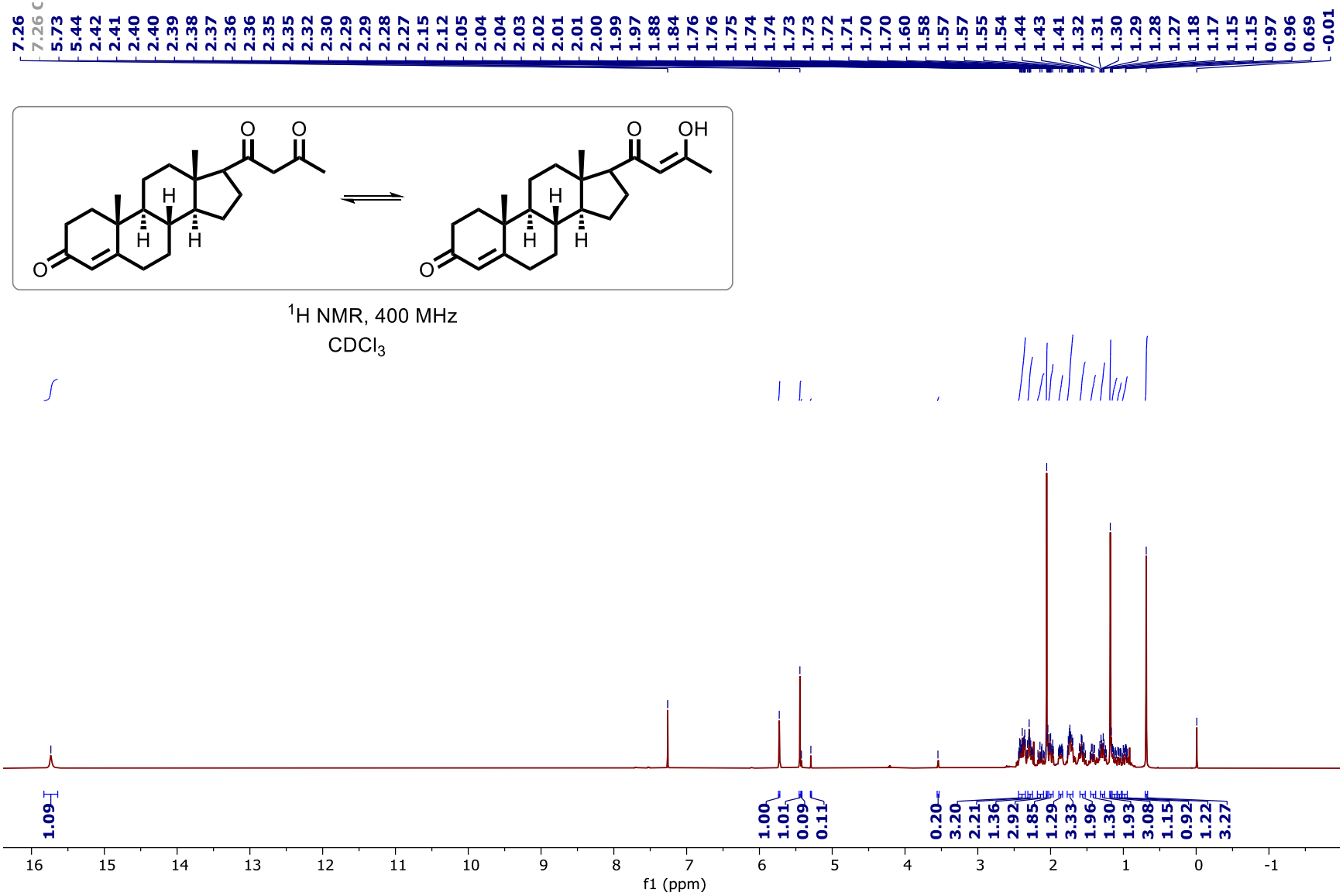
^{1}H NMR spectrum of 1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)butane-1,3-dione (4f′):



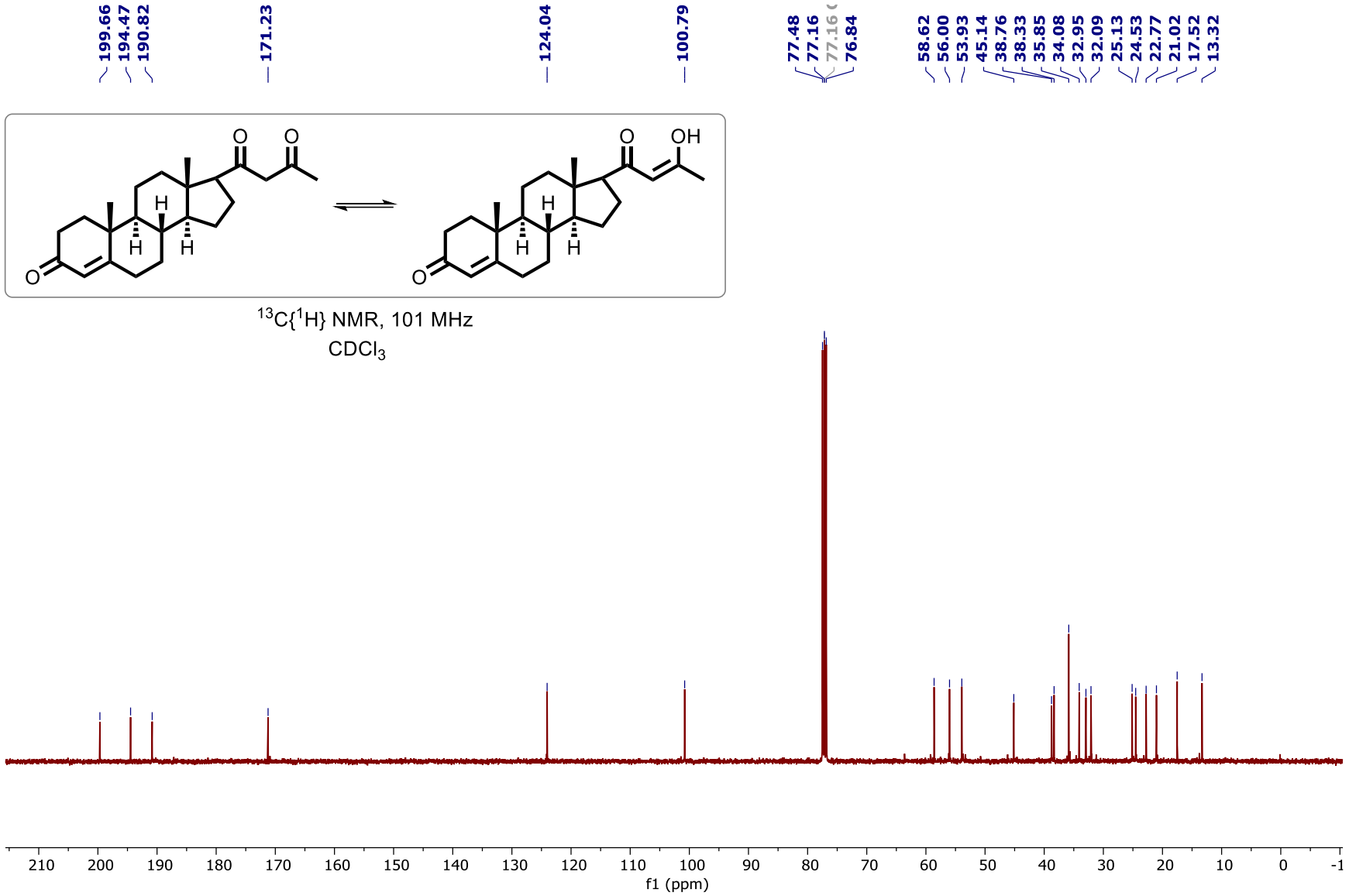
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)butane-1,3-dione (4f′):



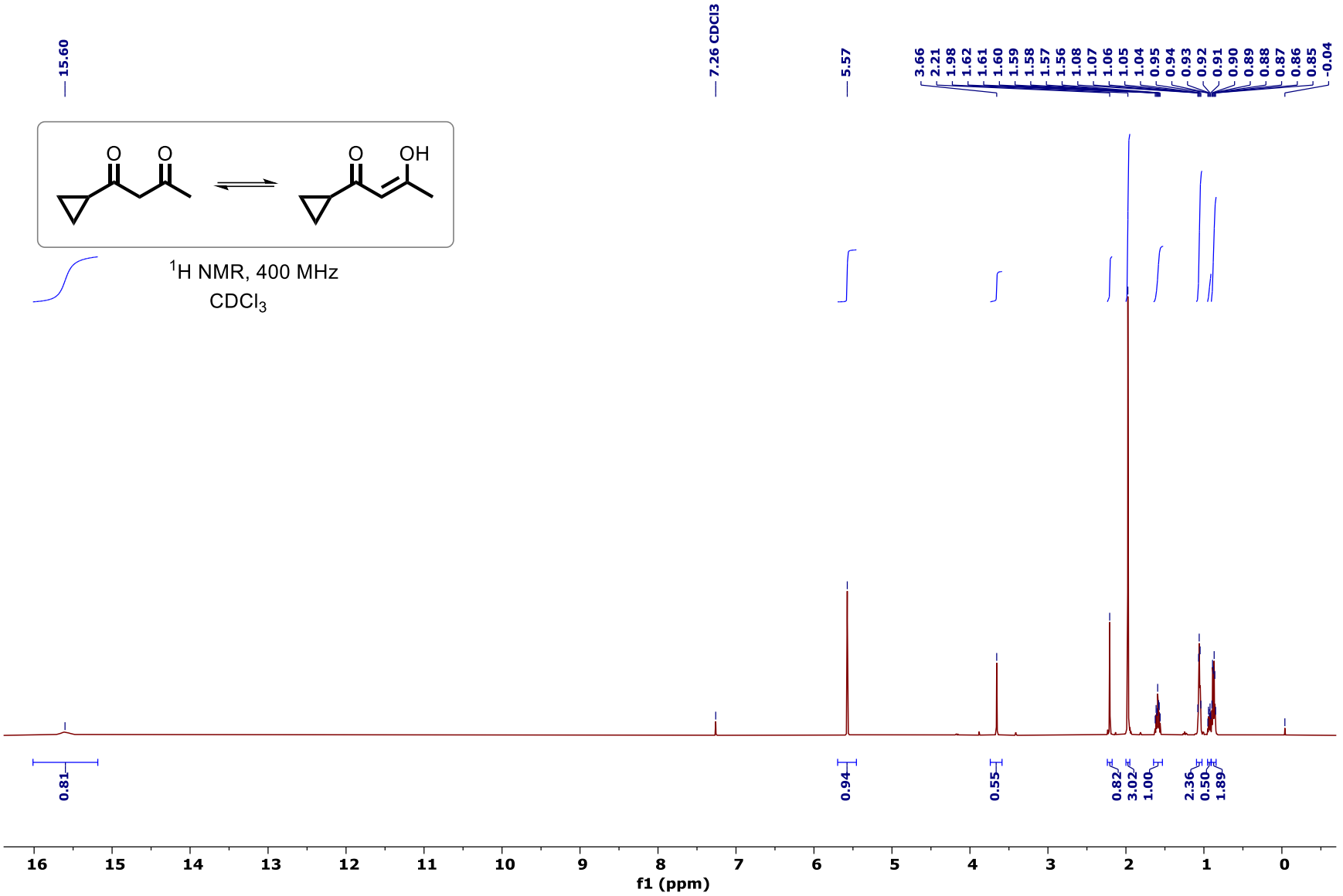
^{1}H NMR spectrum of 1-((8S,9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)butane-1,3-dione (4g′):



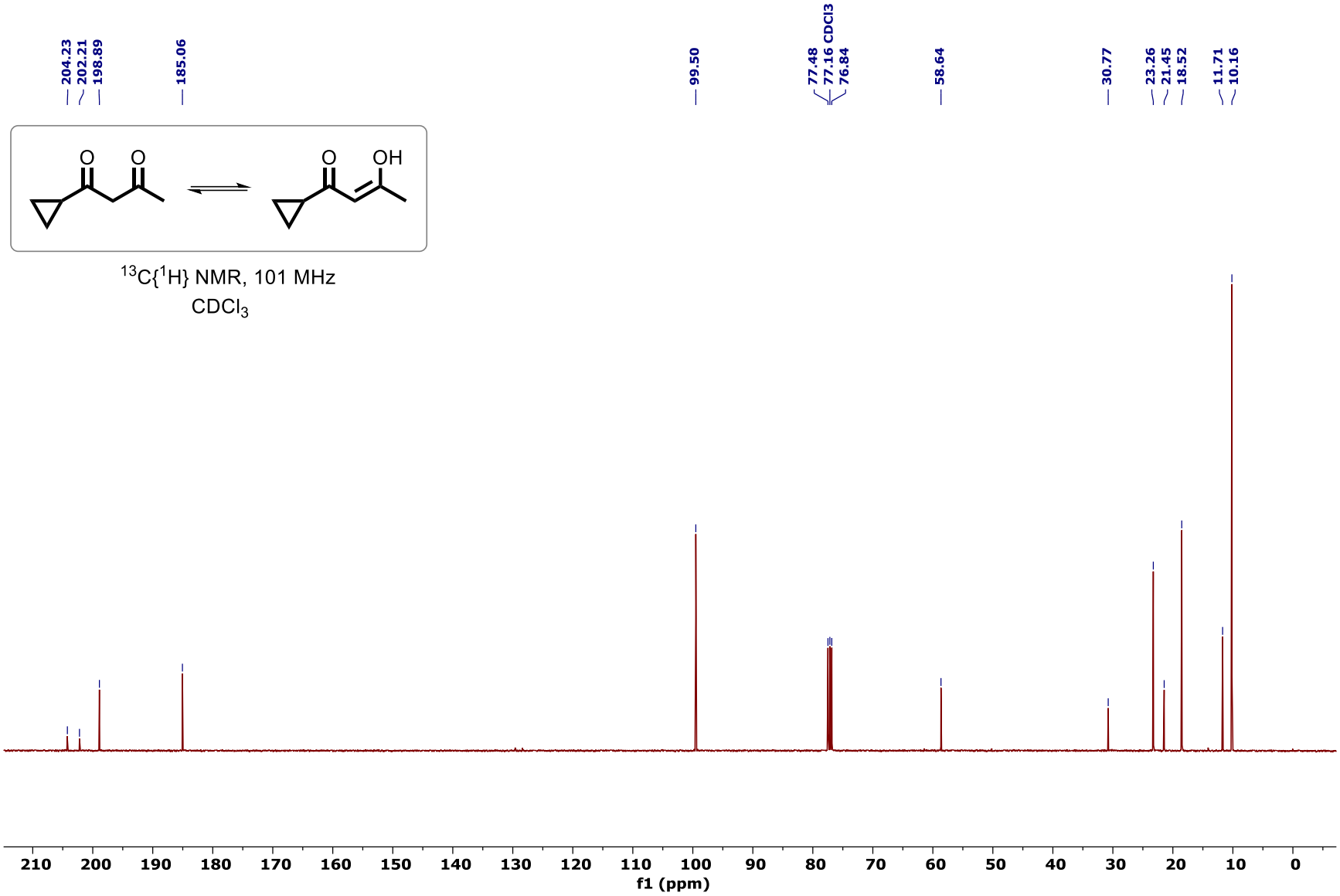
$^{13}C\{^{1}H\}$ NMR spectrum of 1-((8S,9S,10R,13S,14S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)butane-1,3-dione (4g′):



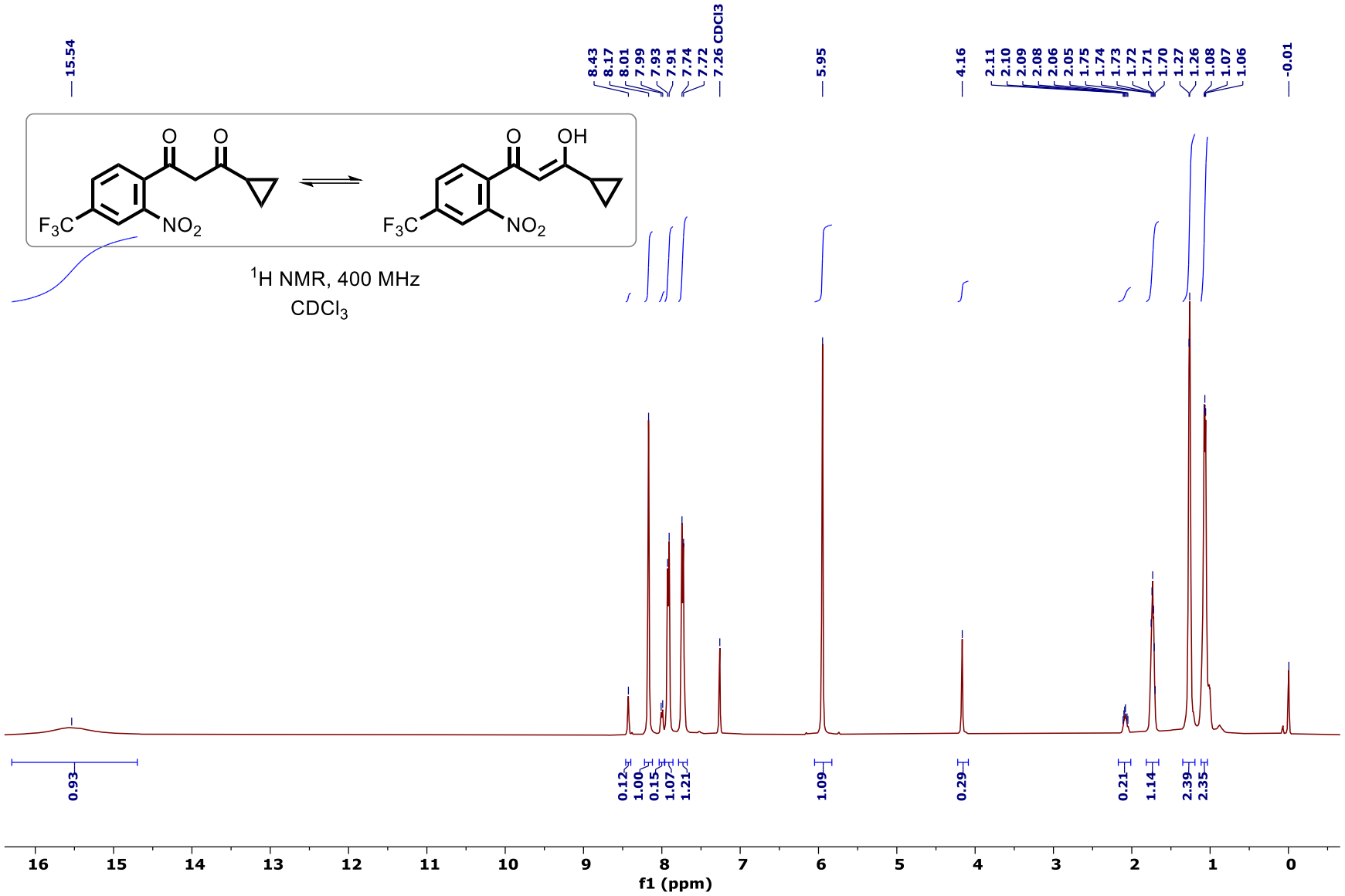
^{1}H NMR spectrum of 1-Cyclopropylbutane-1,3-dione (4′h):



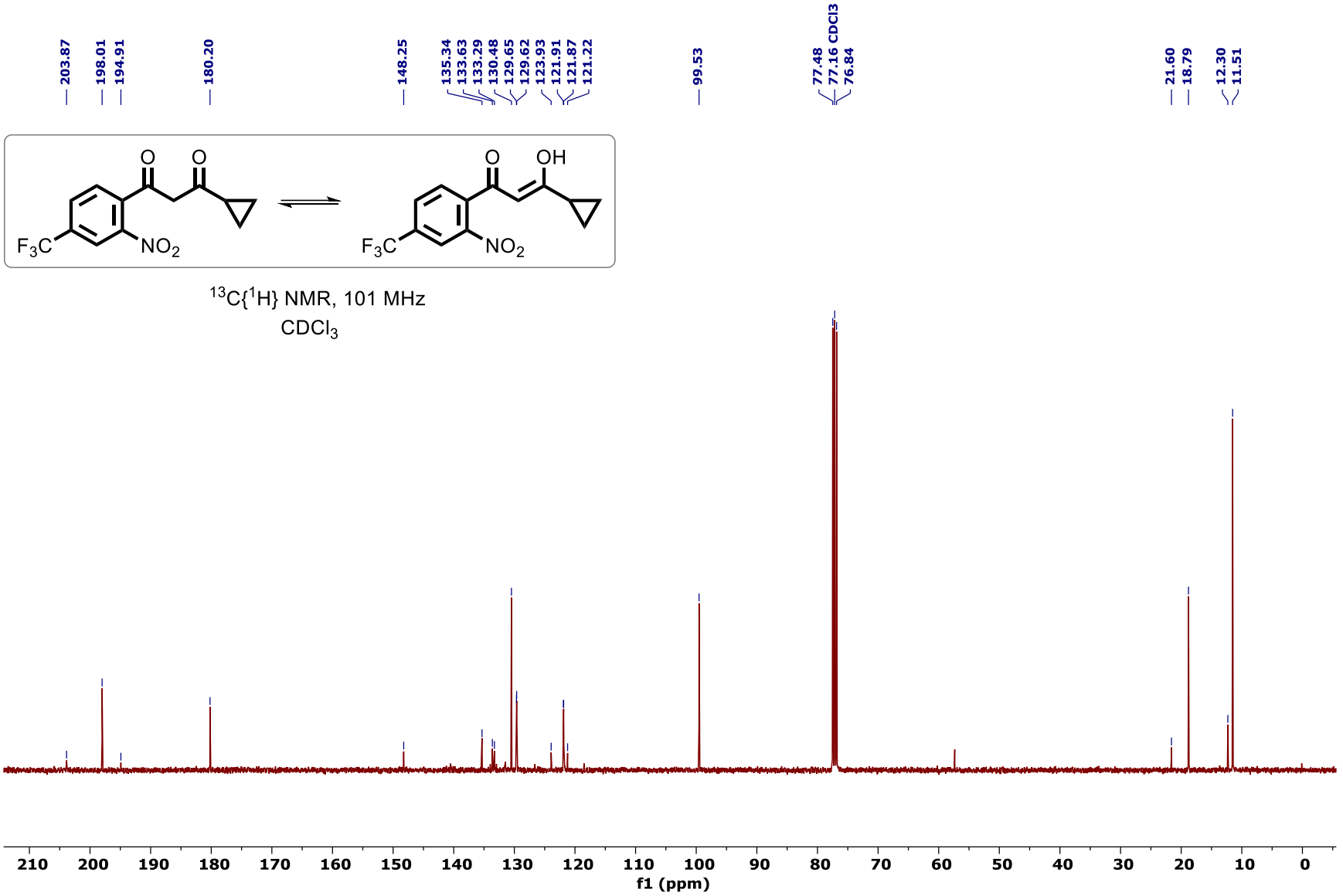
$^{13}C\{^{1}H\}$ NMR spectrum of 1-Cyclopropylbutane-1,3-dione (4′h):



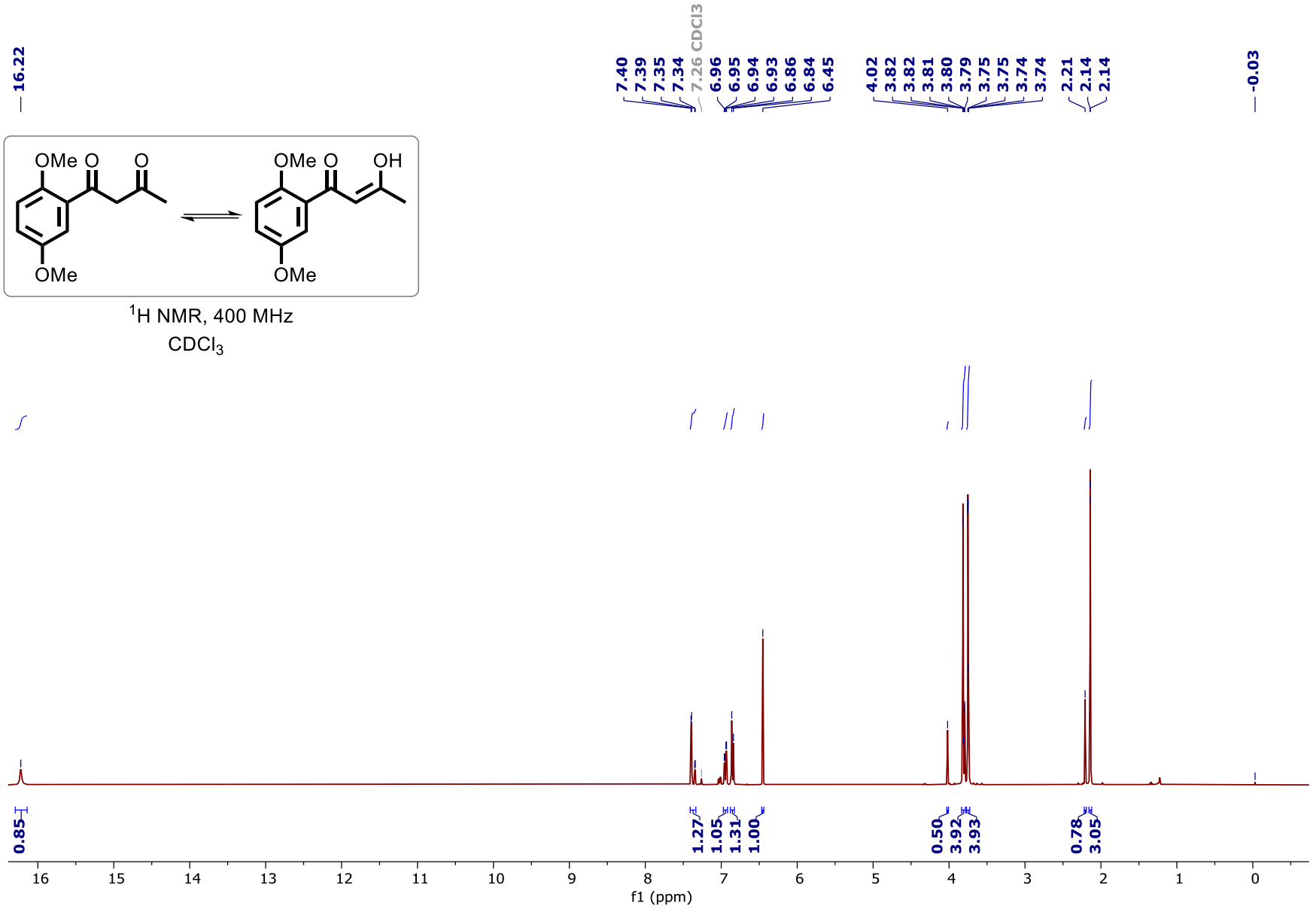
^{1}H NMR spectrum of 1-Cyclopropyl-3-(2-nitro-4-(trifluoromethyl)phenyl)propane-1,3-dione (4′i):



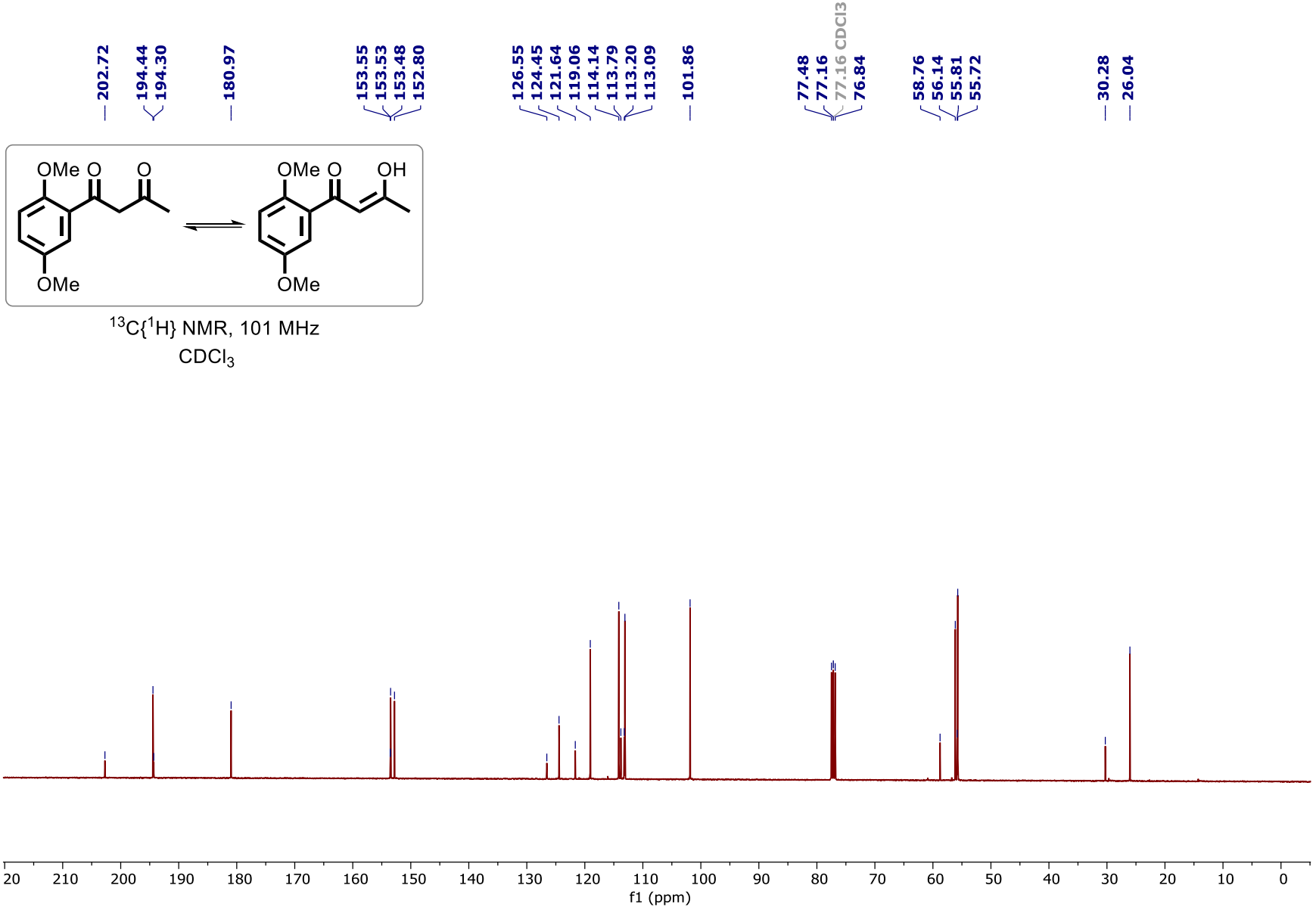
$^{13}C\{^{1}H\}$ NMR spectrum of 1-Cyclopropyl-3-(2-nitro-4-(trifluoromethyl)phenyl)propane-1,3-dione (4′i):



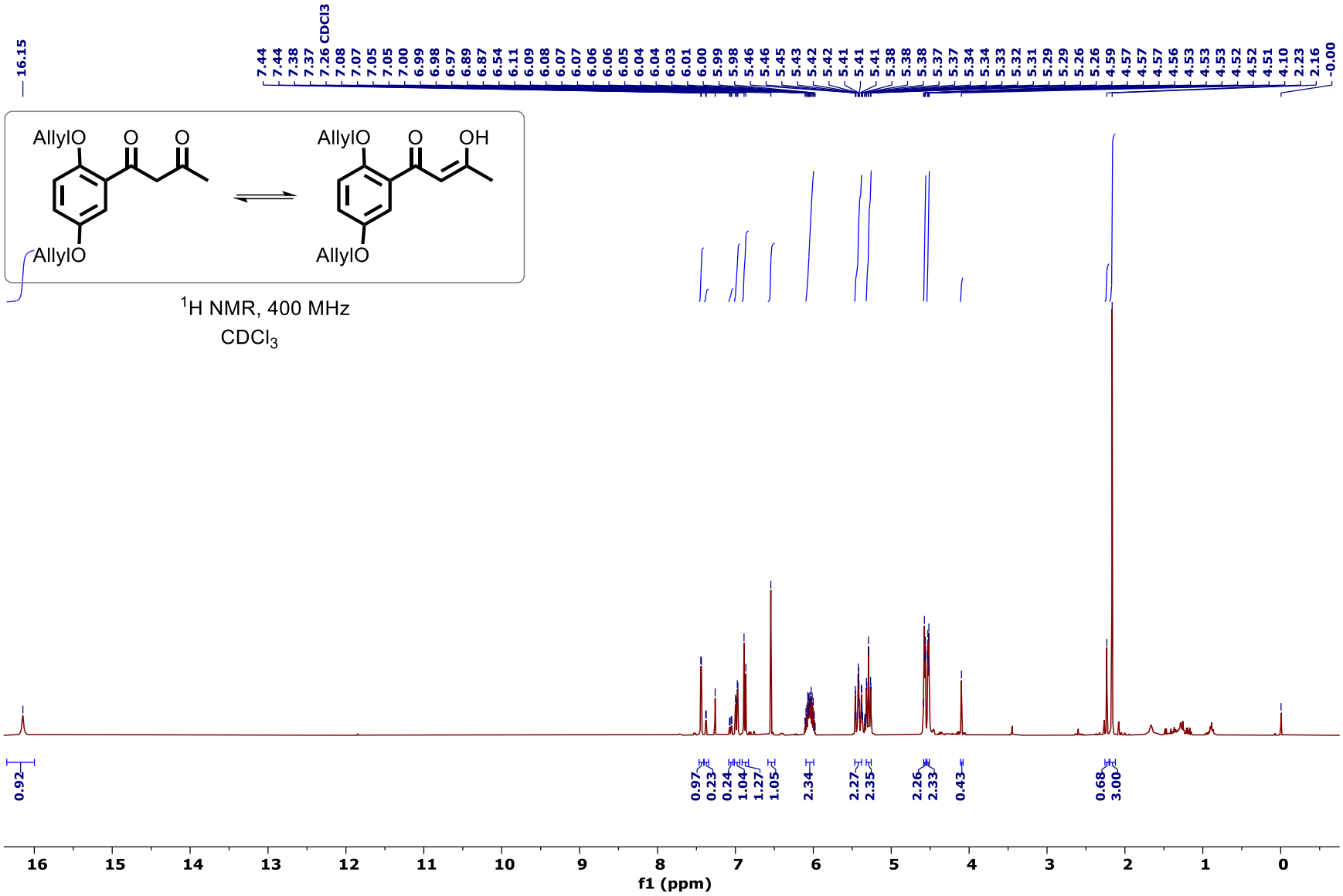
^{1}H NMR spectrum of 1-(2,5-Dimethoxyphenyl)butane-1,3-dione (4′k):



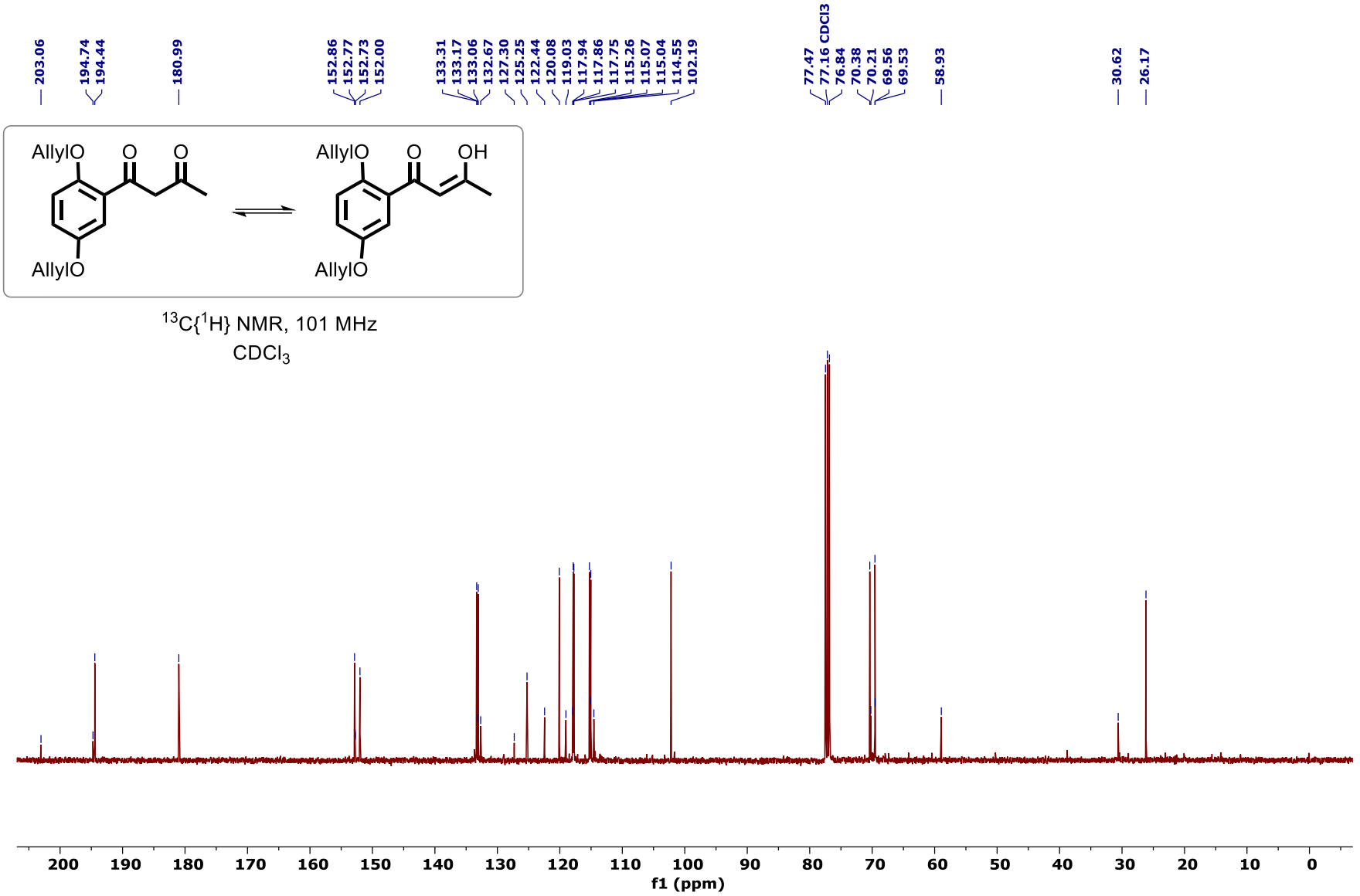
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(2,5-Dimethoxyphenyl)butane-1,3-dione (4′k):



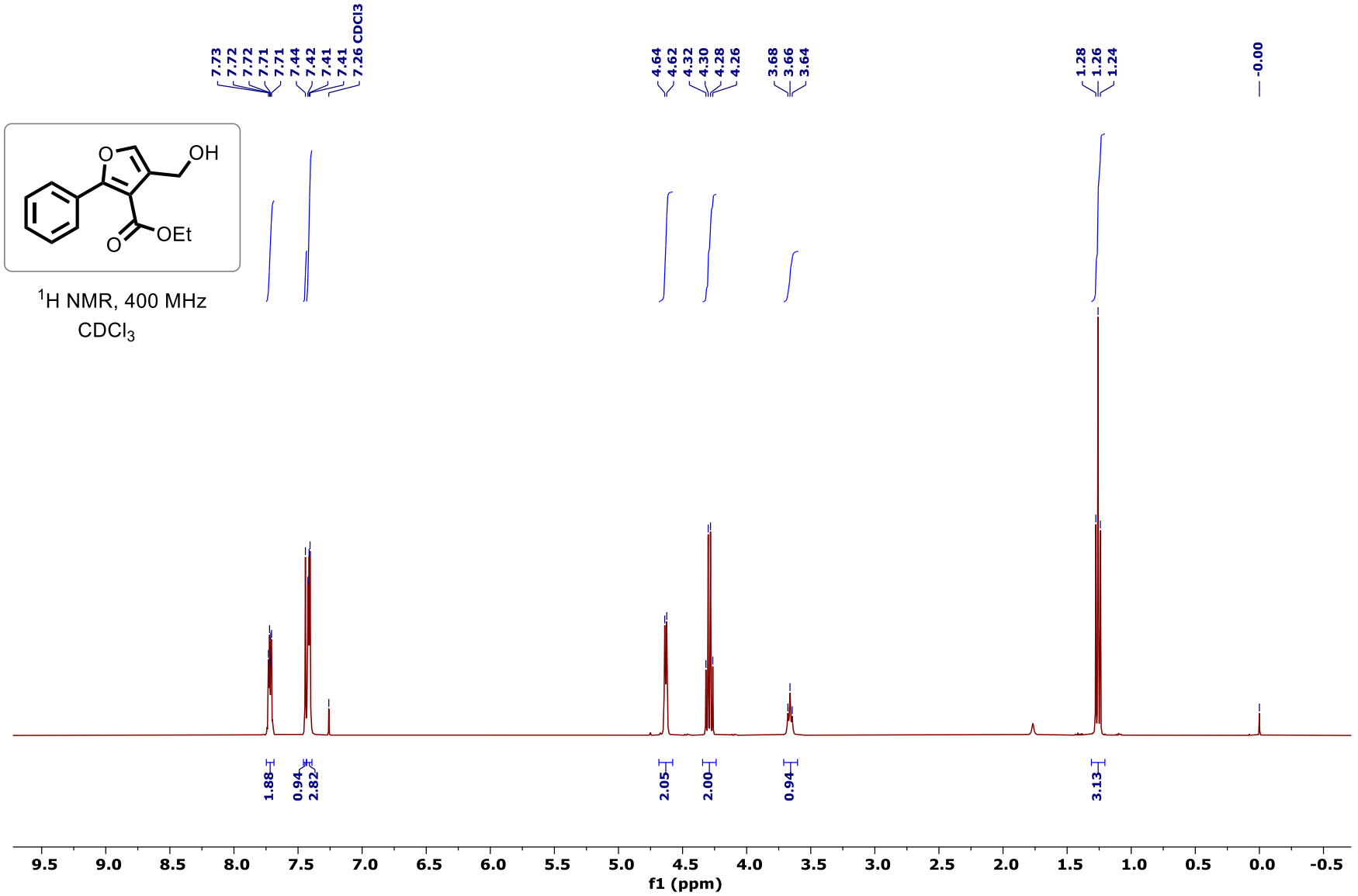
^{1}H NMR spectrum of 1-(2,5-Bis(allyloxy)phenyl)butane-1,3-dione (4′l):



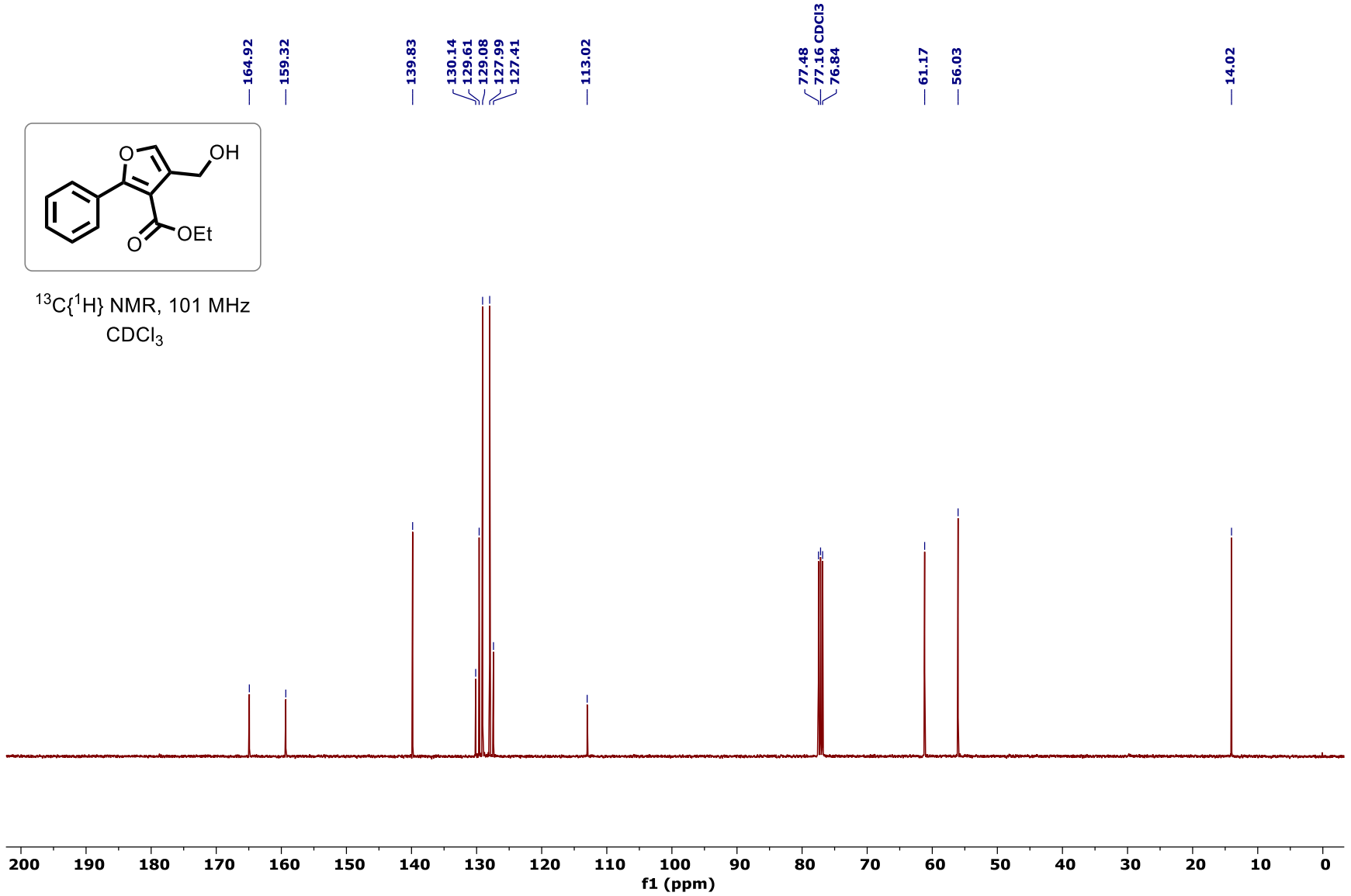
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(2,5-Bis(allyloxy)phenyl)butane-1,3-dione (4′l):



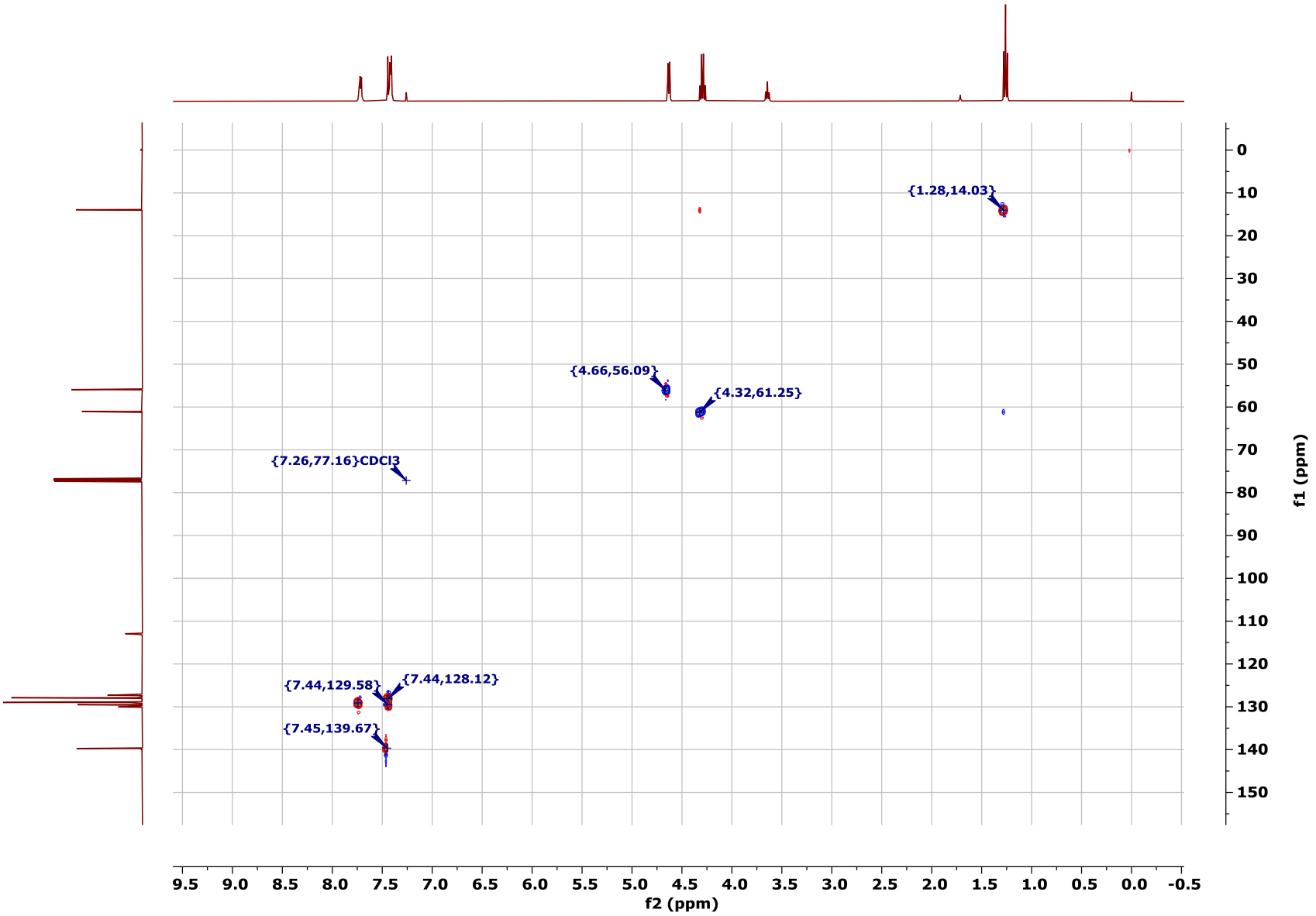
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



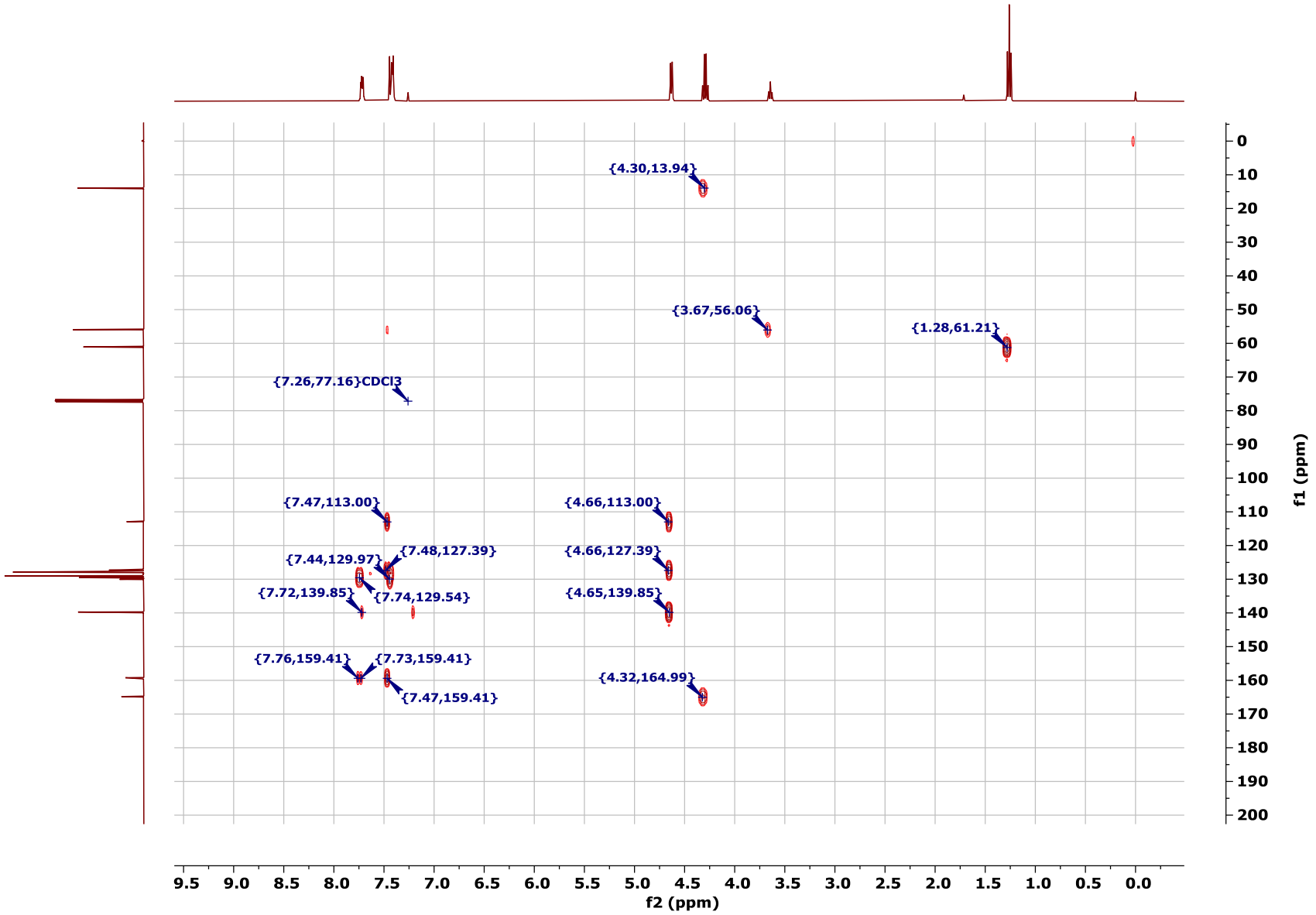
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



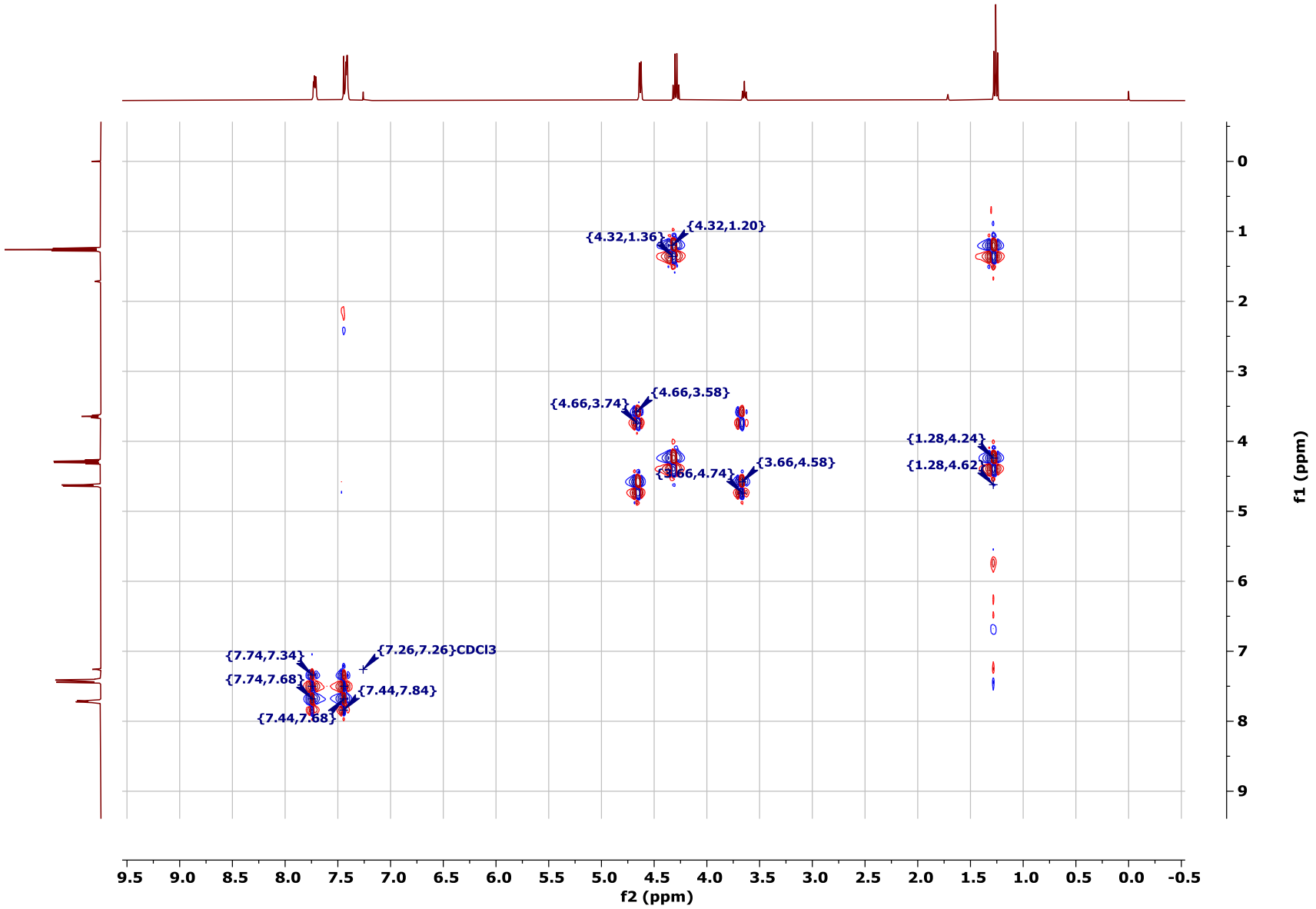
HSQC NMR spectrum of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



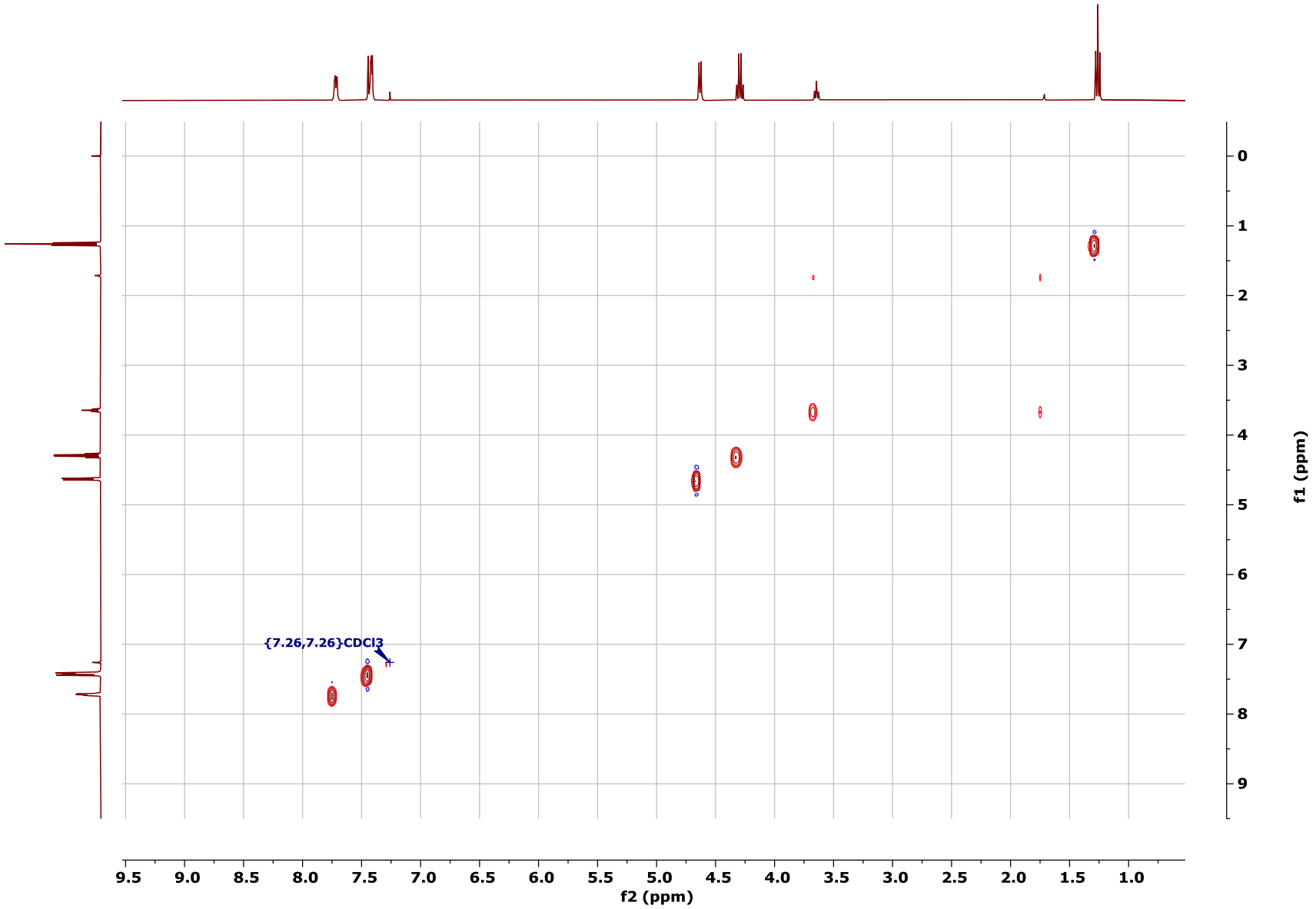
HMBC NMR spectrum of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



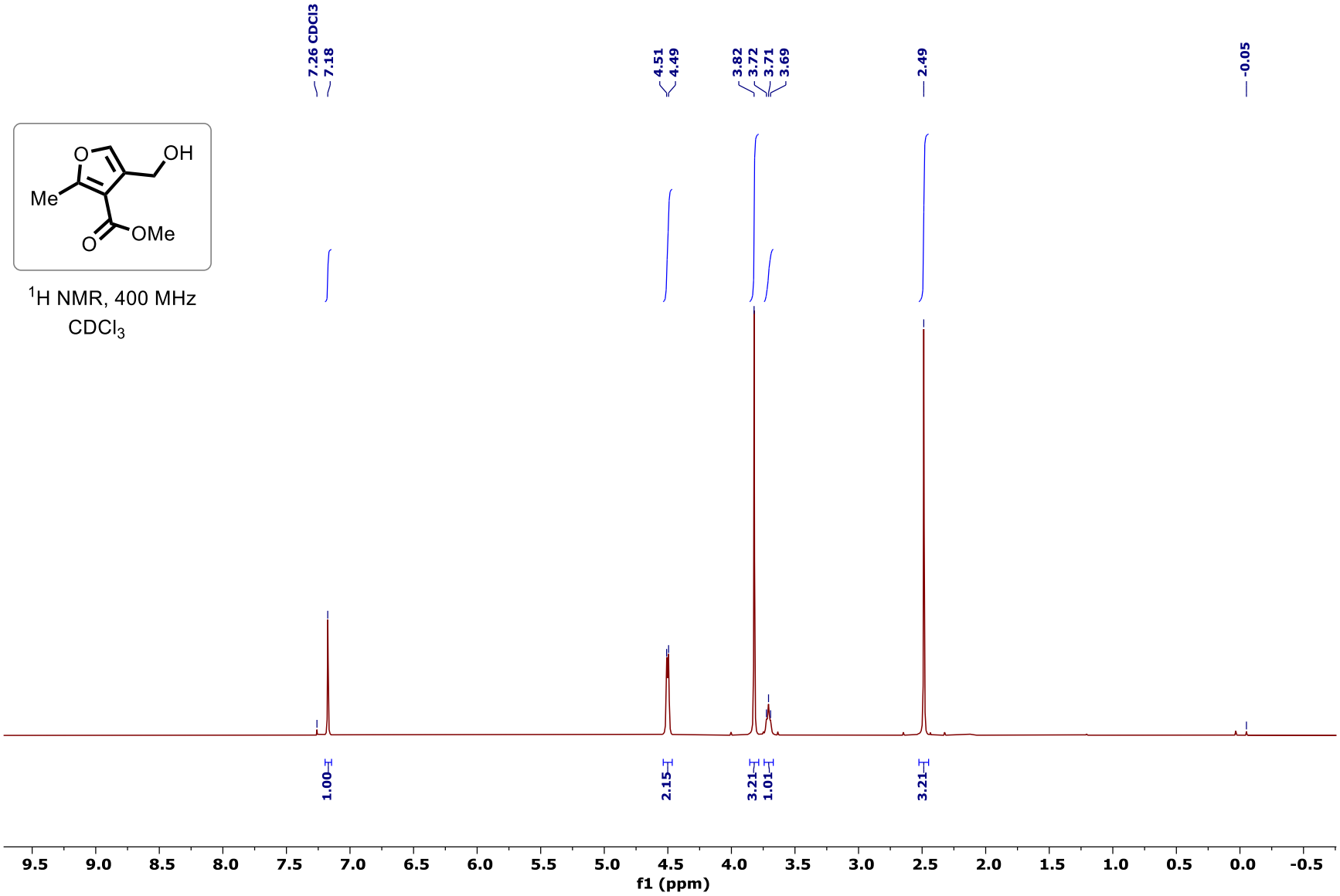
COSY NMR spectrum of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



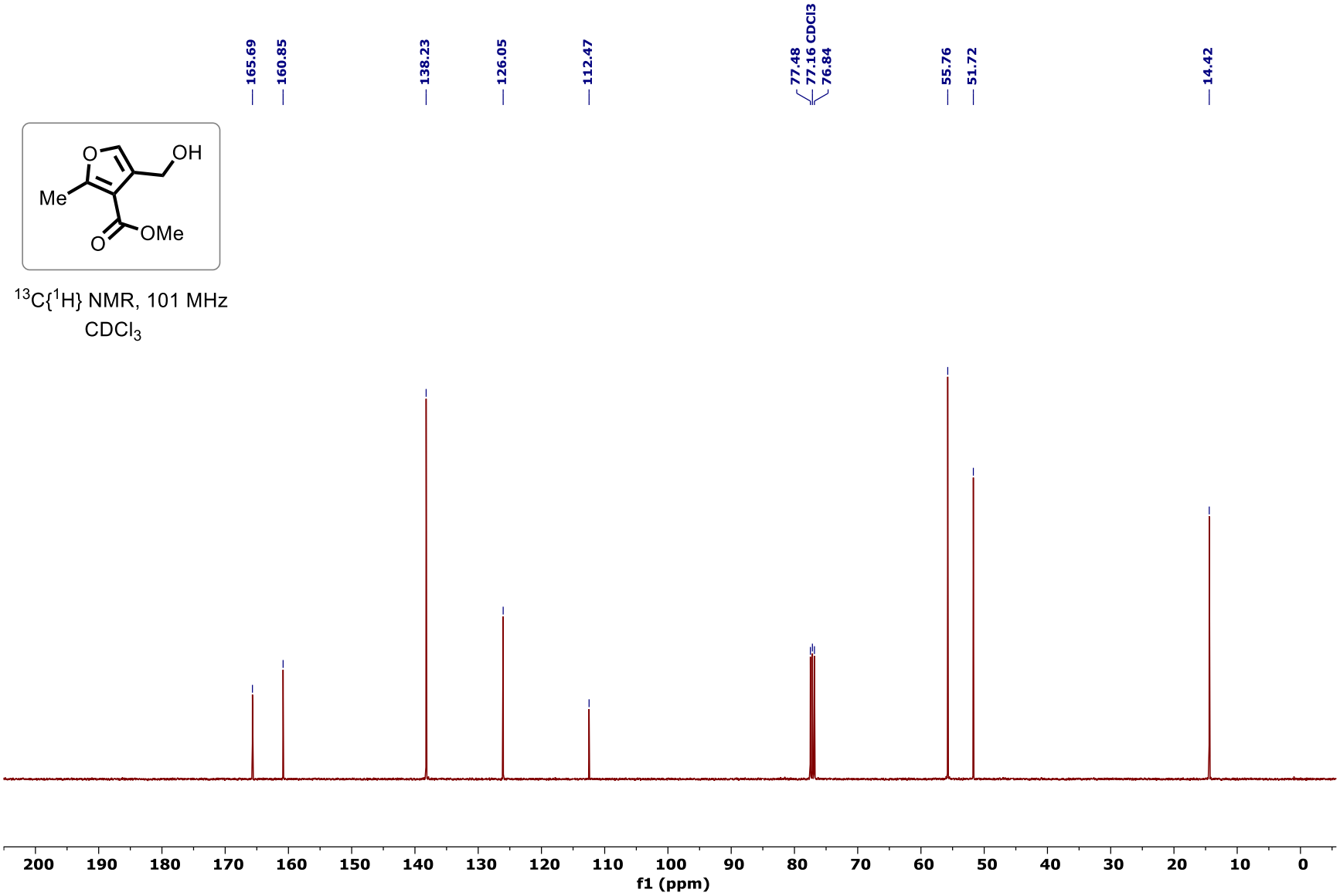
NOESY NMR spectrum of Ethyl 4-(hydroxymethyl)-2-phenylfuran-3-carboxylate (3a):



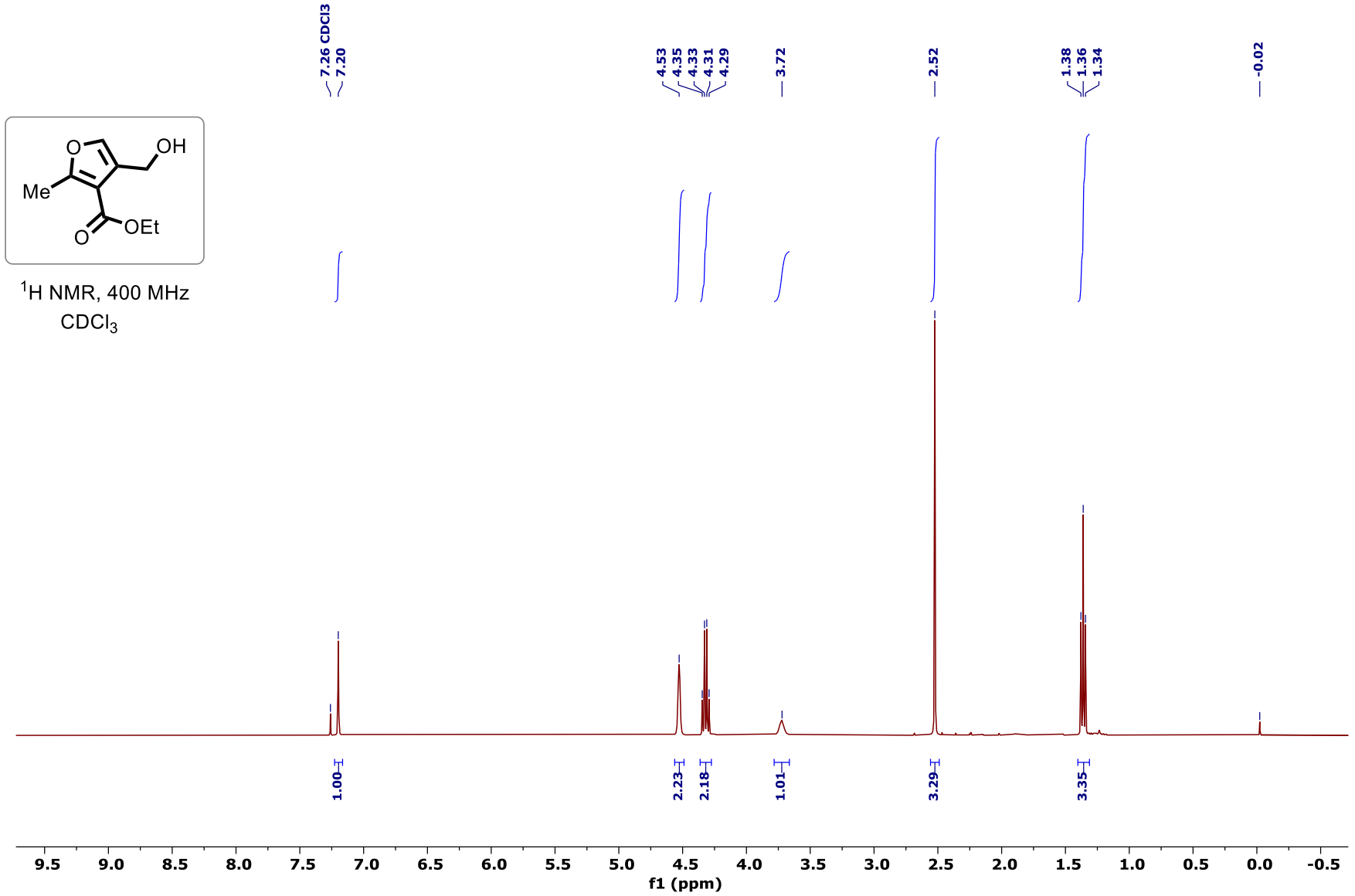
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3b):



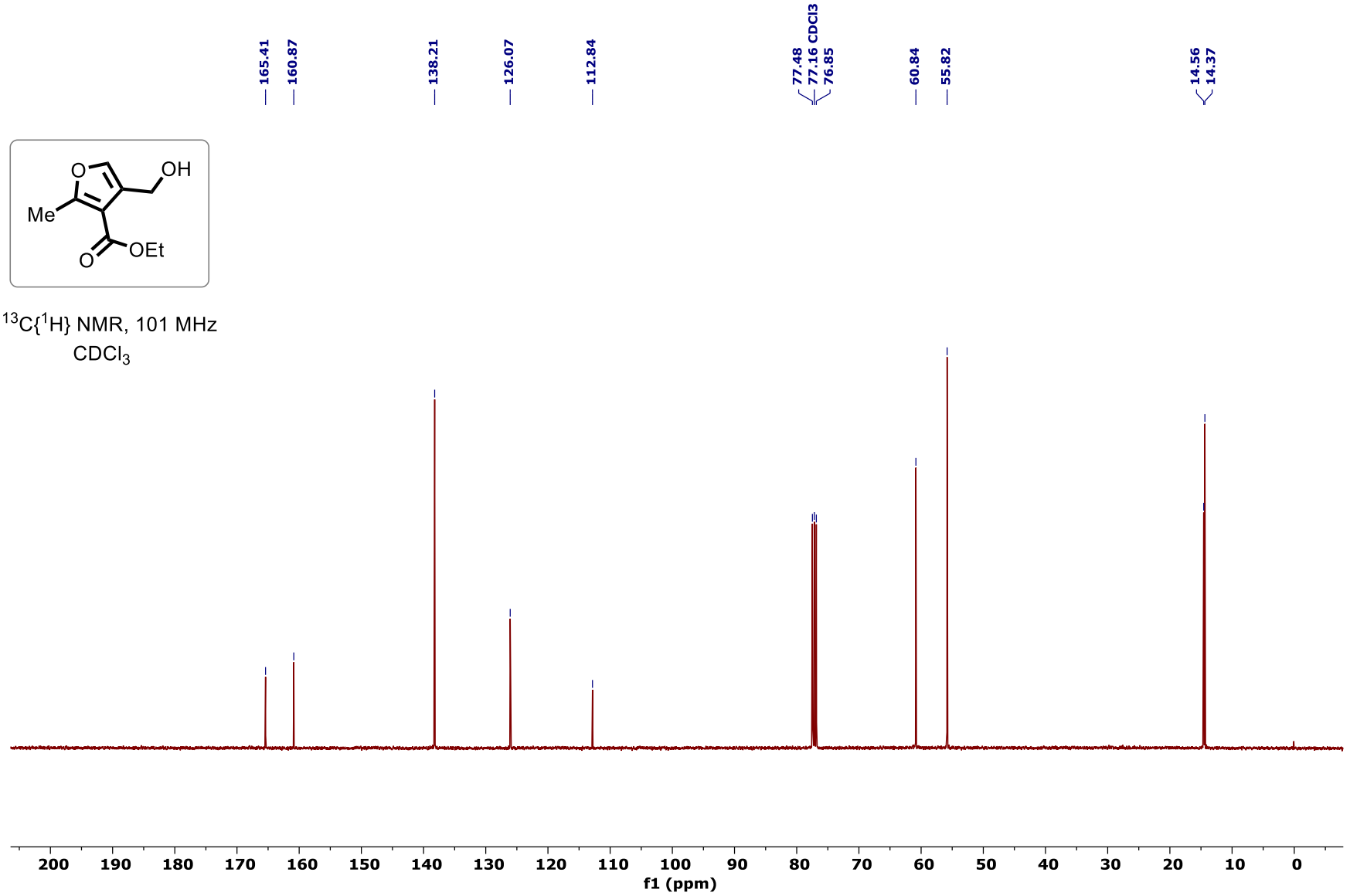
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3b):



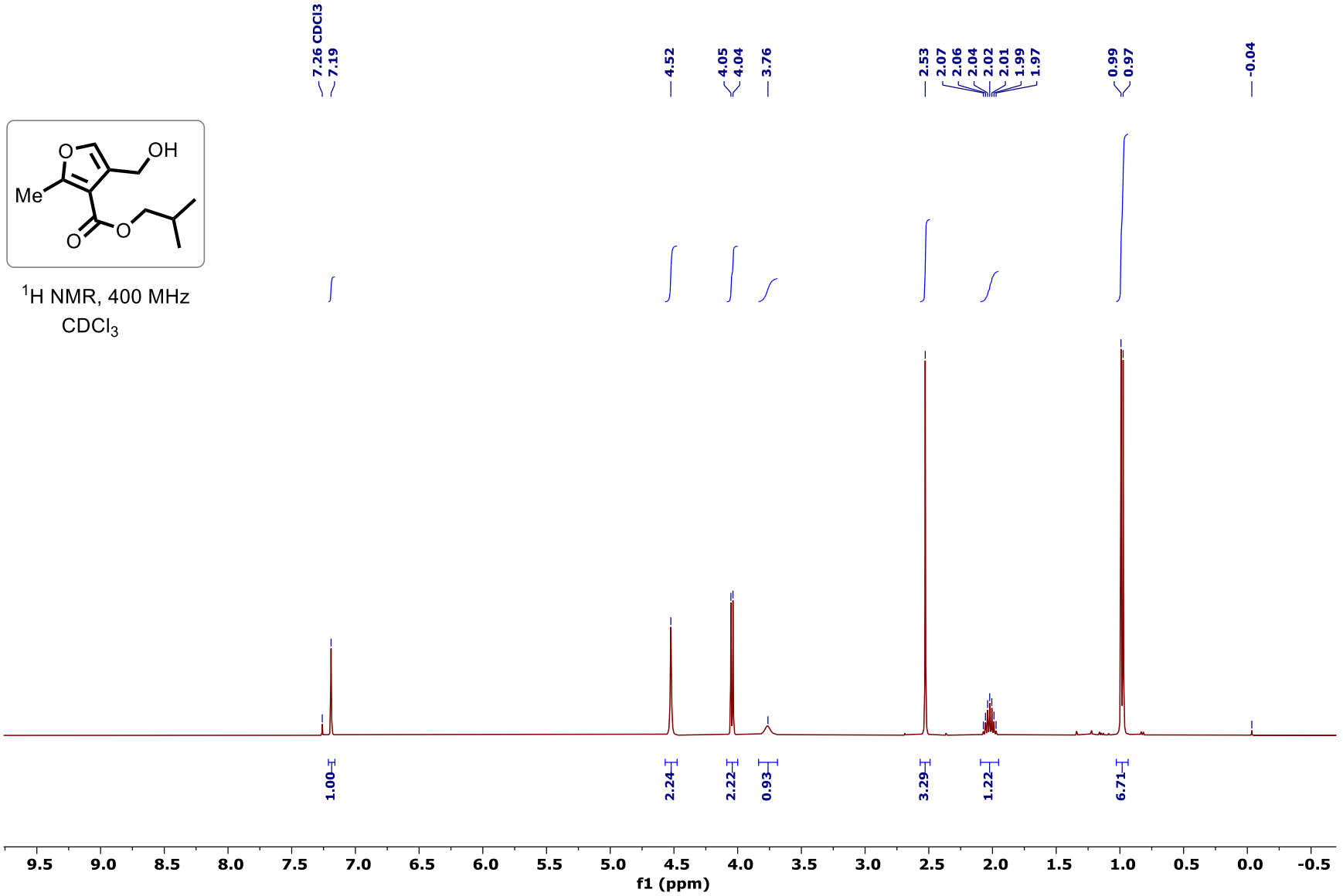
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3c):



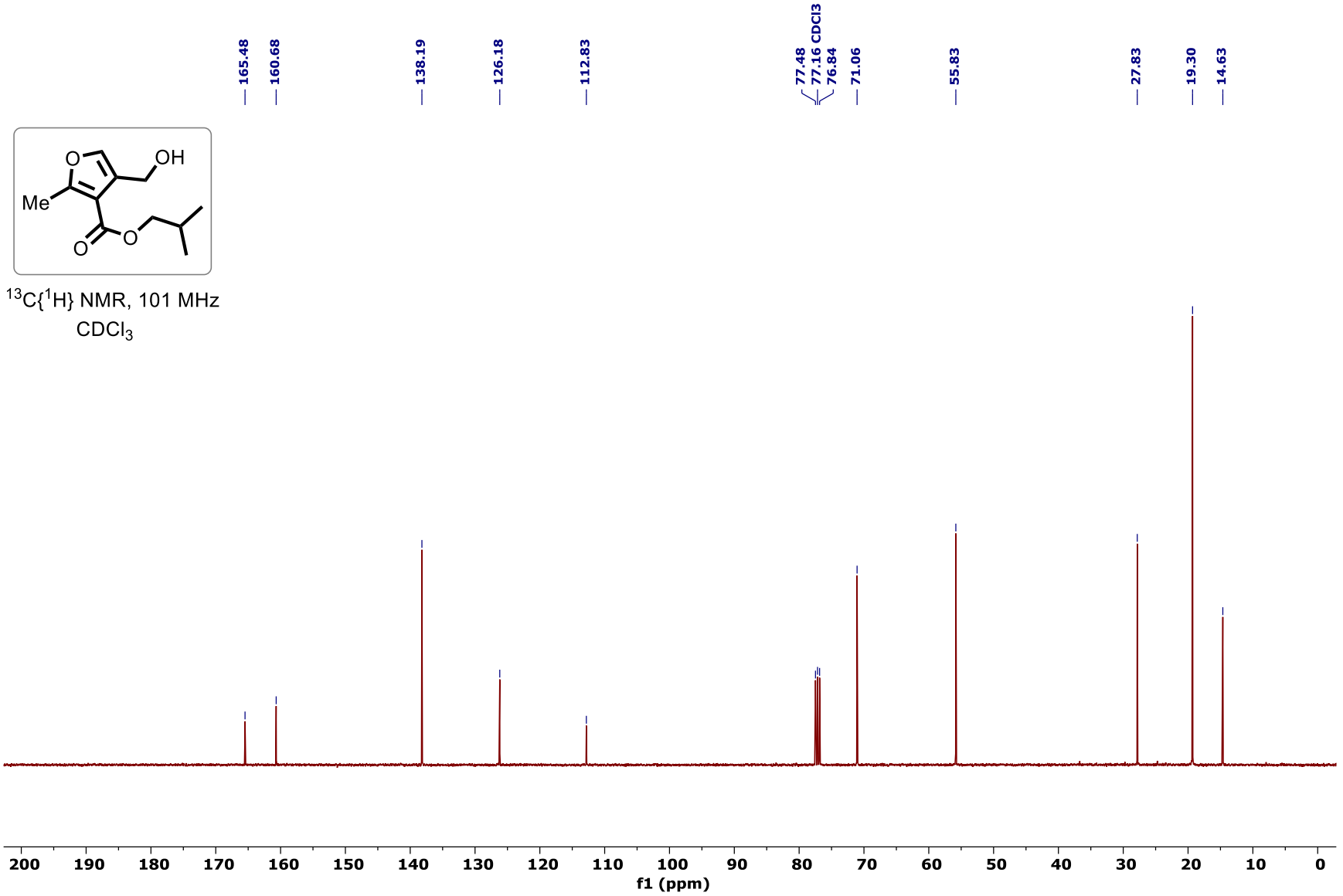
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3c):



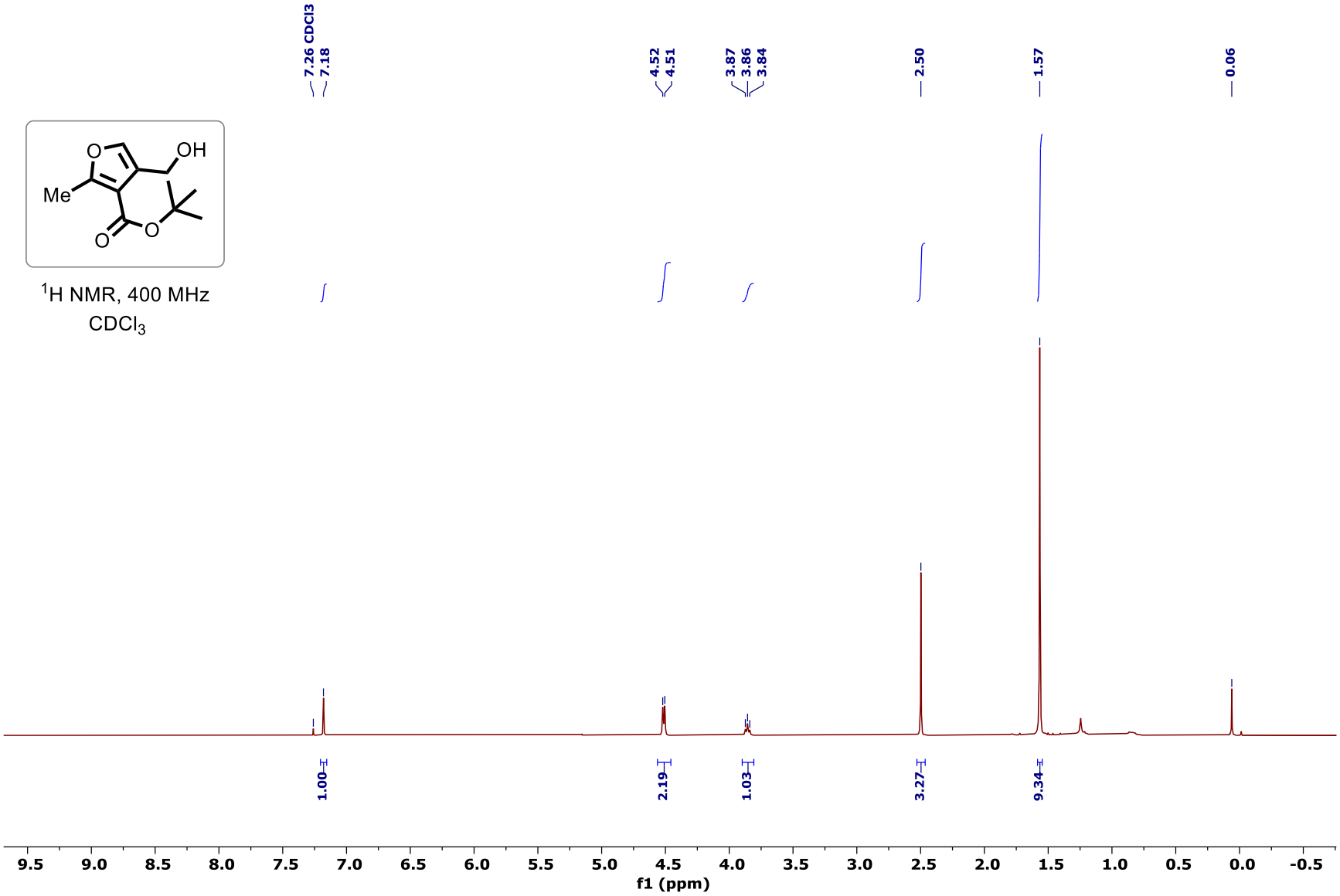
^{1}H NMR spectrum of Isobutyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3d):



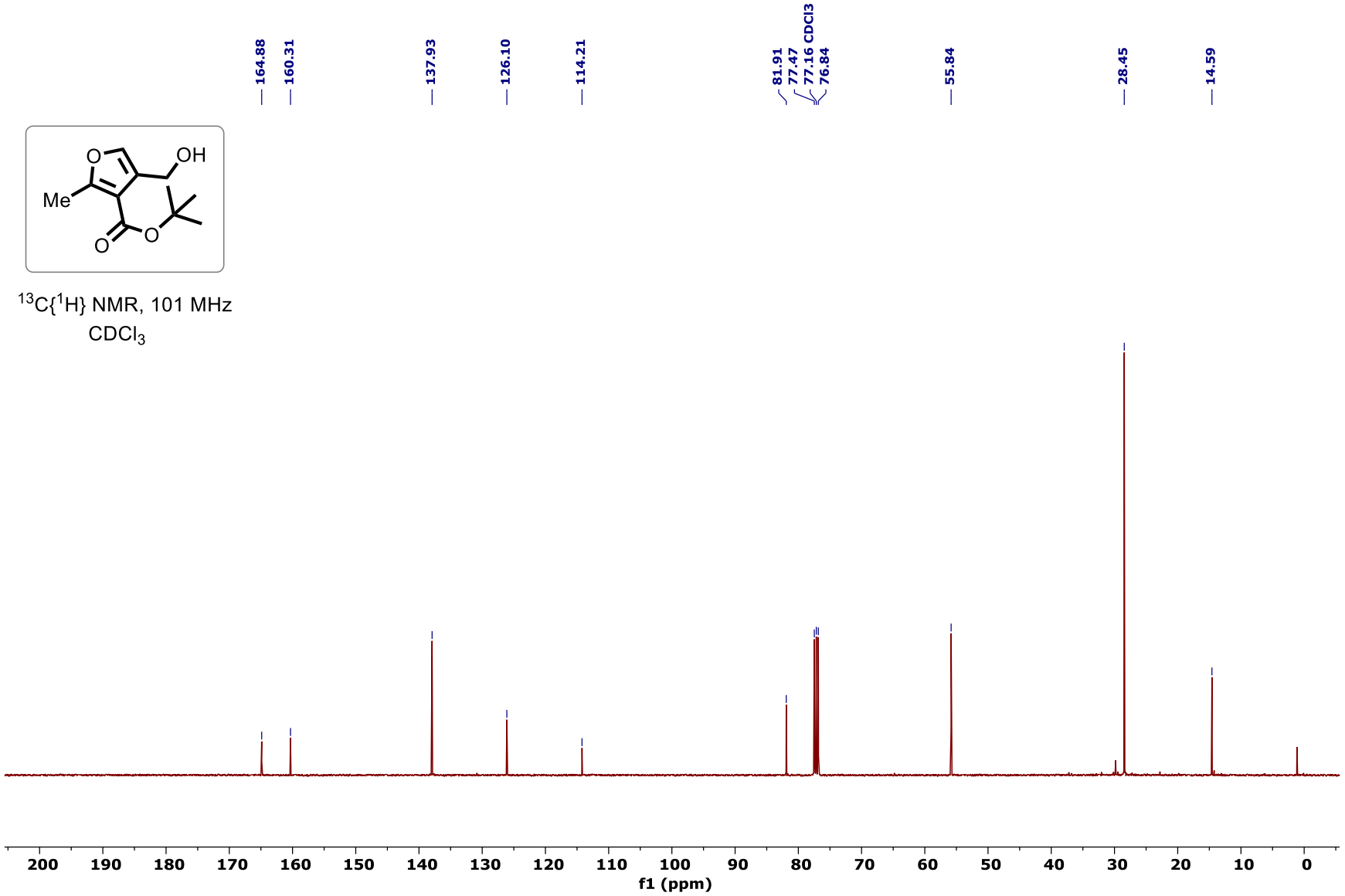
$^{13}C\{^{1}H\}$ NMR spectrum of Isobutyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3d):



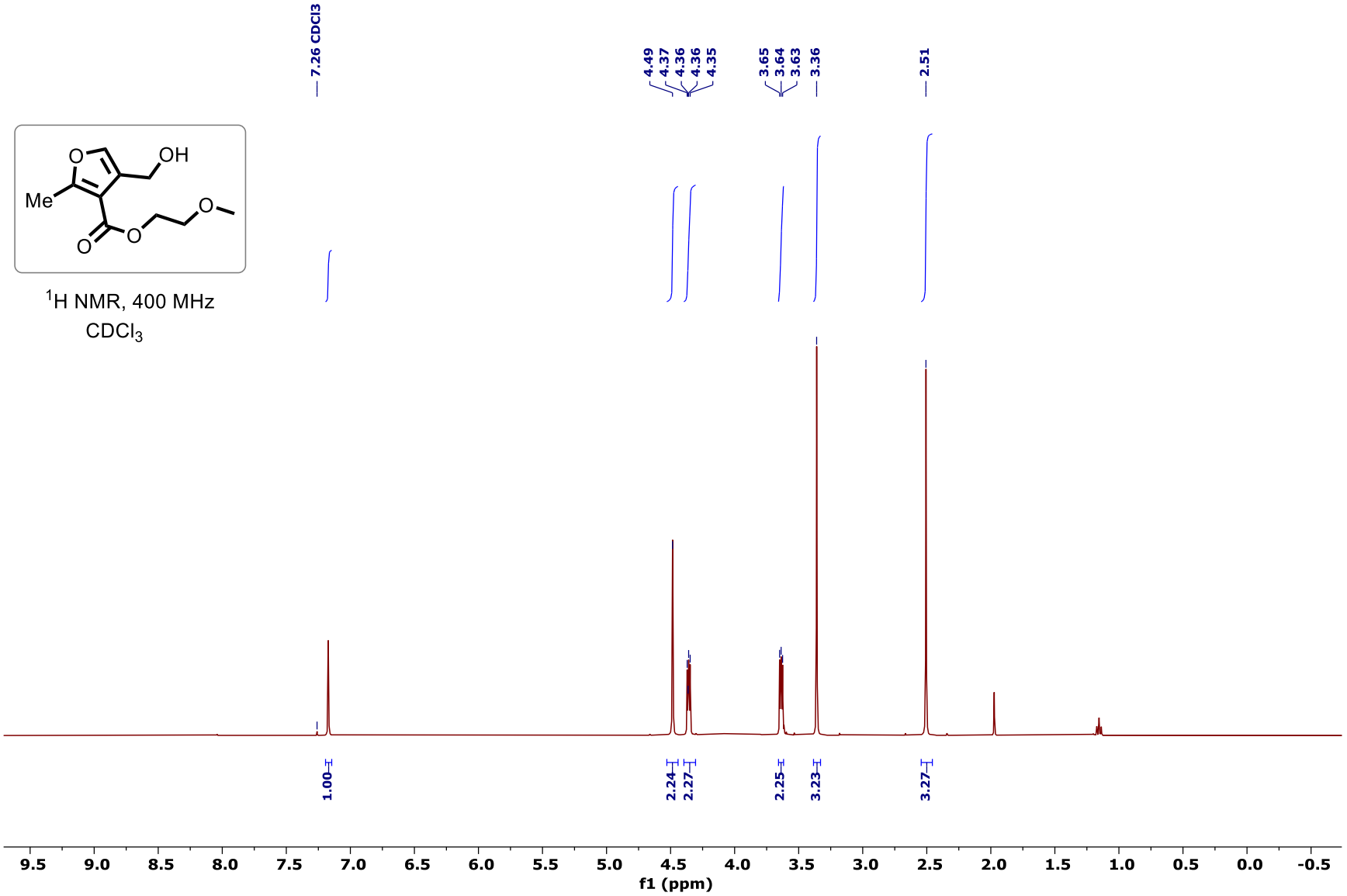
^{1}H NMR spectrum of Tert-butyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3e):



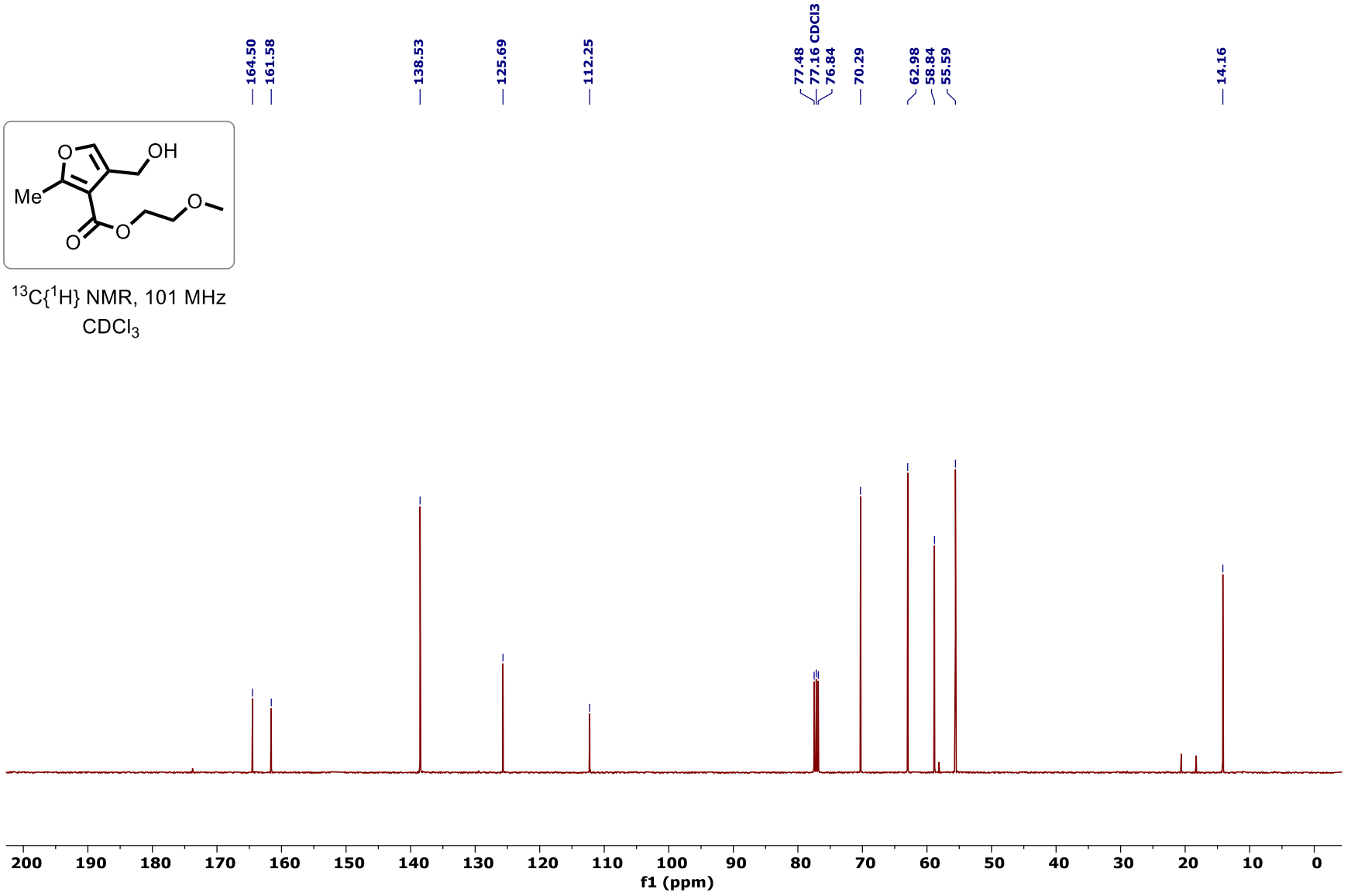
$^{13}C\{^{1}H\}$ NMR spectrum of Tert-butyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3e):



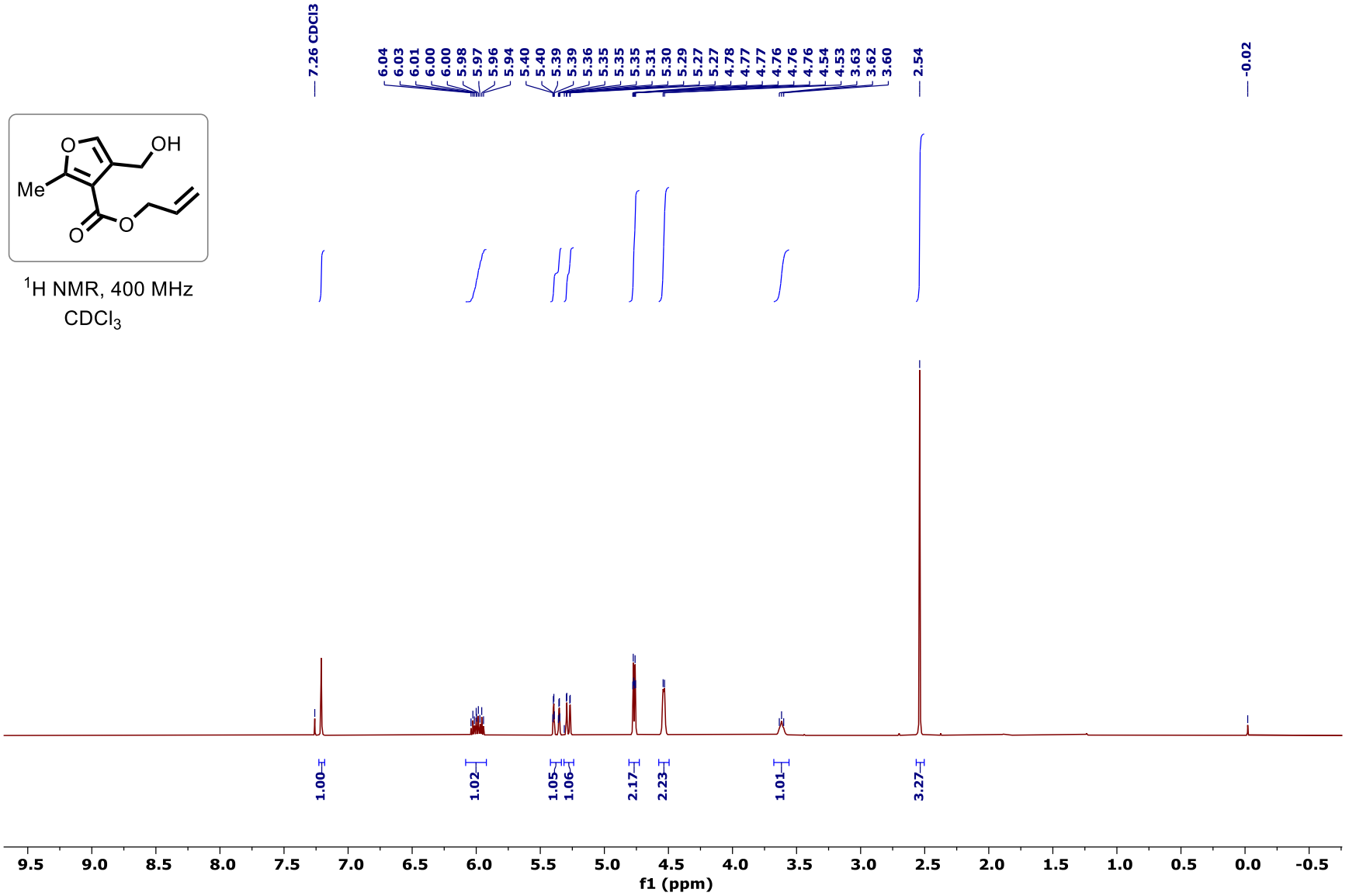
^{1}H NMR spectrum of 2-Methoxyethyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3f):



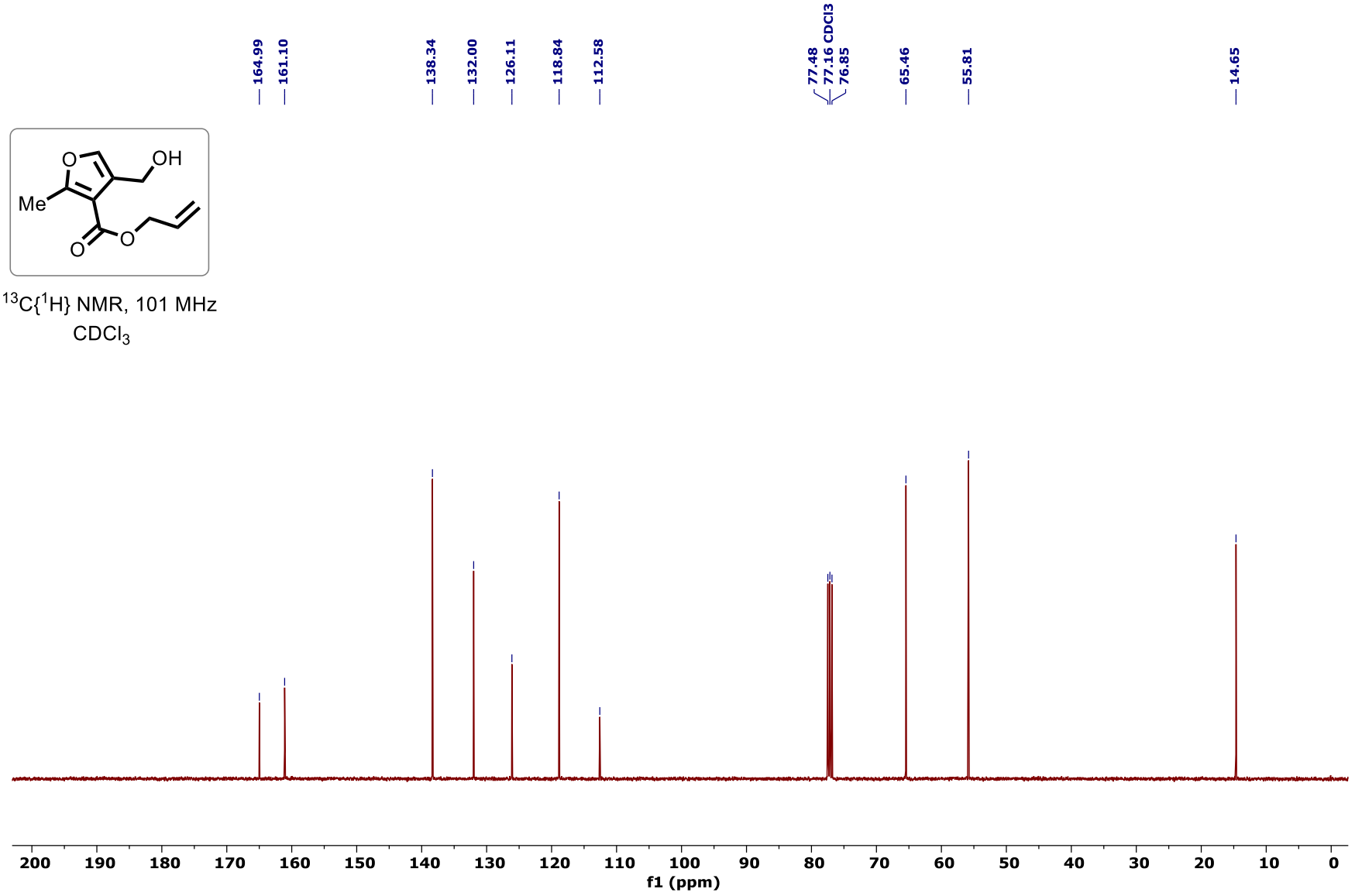
$^{13}C\{^{1}H\}$ NMR spectrum of 2-Methoxyethyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3f):



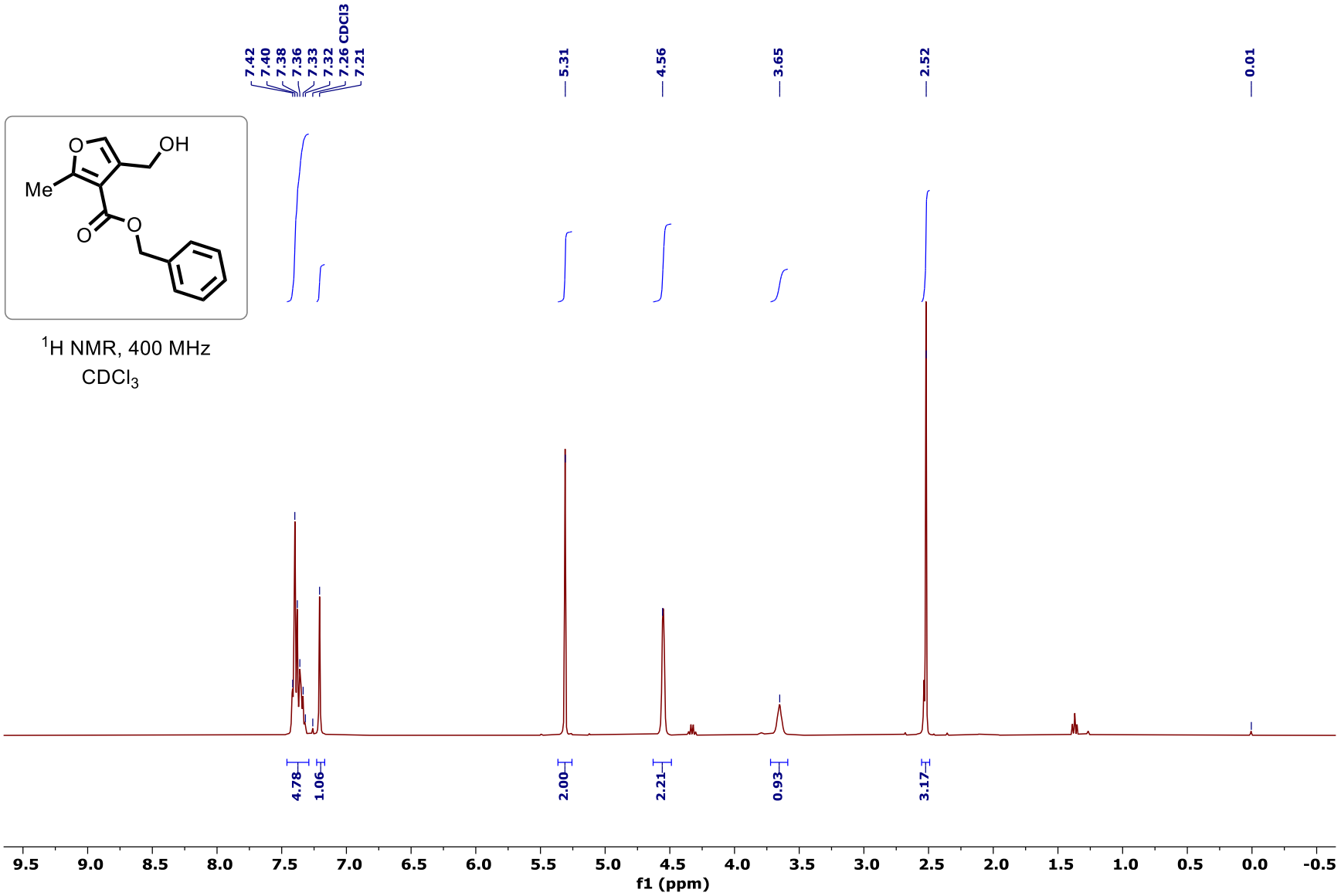
^{1}H NMR spectrum of Allyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3g):



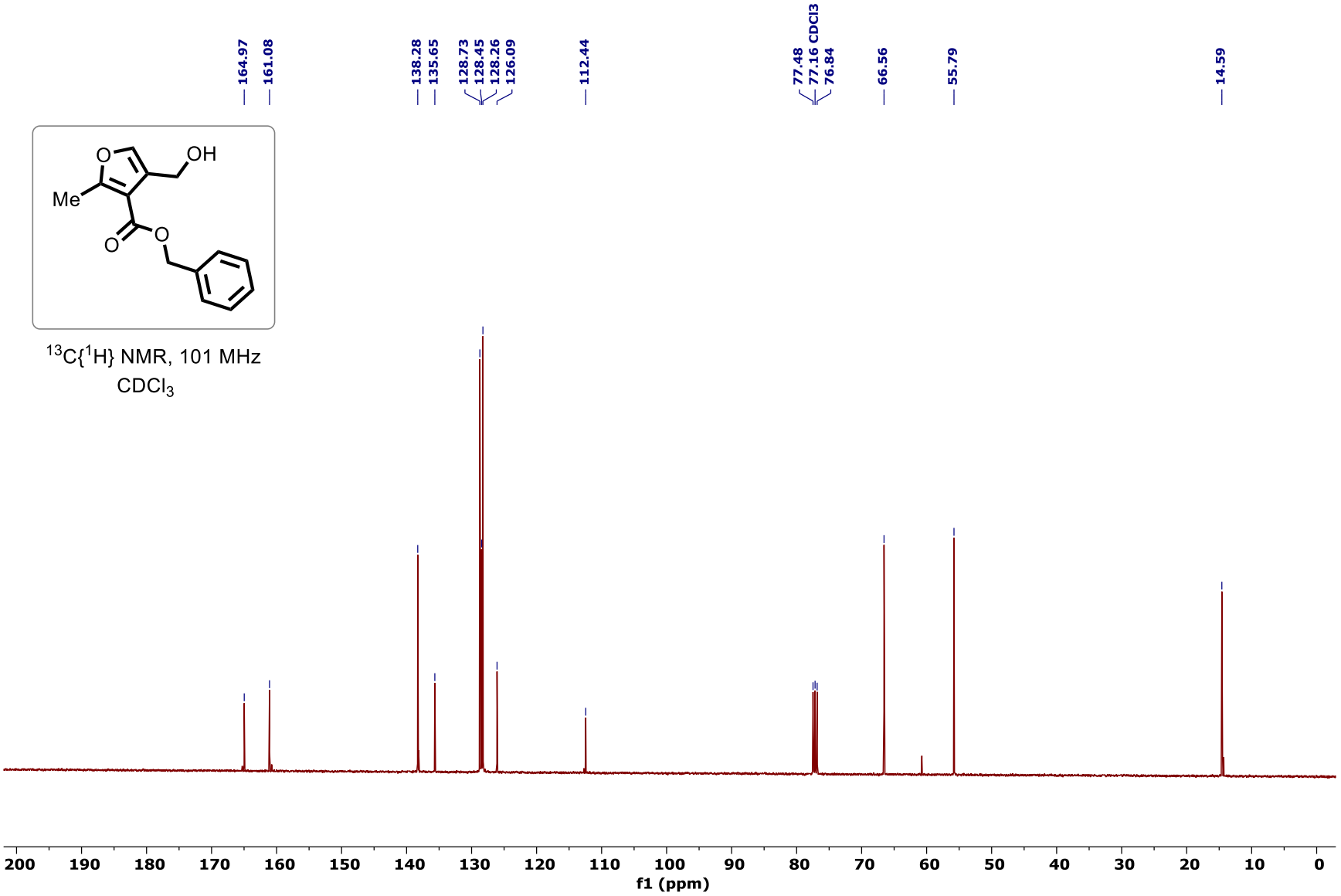
$^{13}C\{^{1}H\}$ NMR spectrum of Allyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3g):



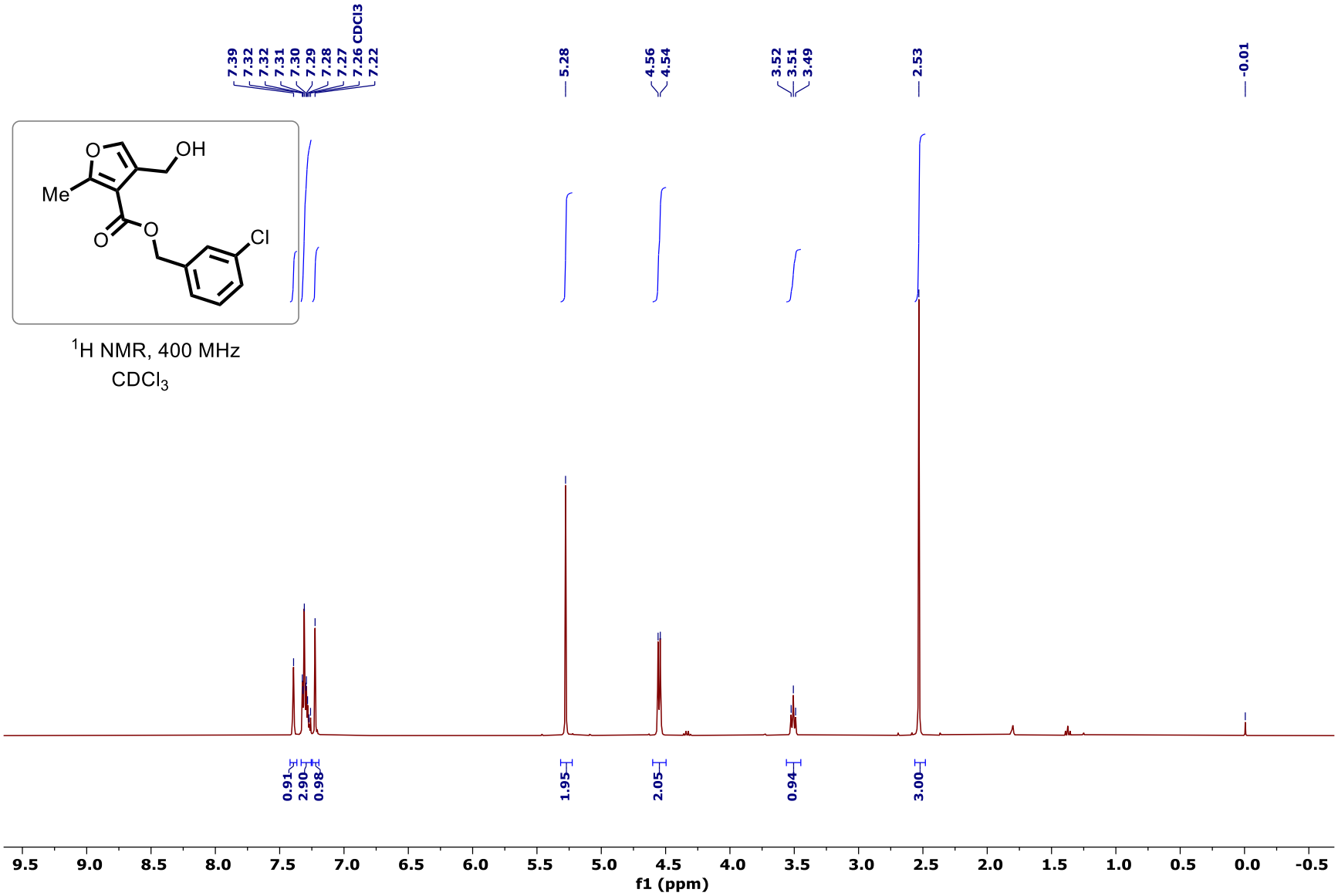
^{1}H NMR spectrum of Benzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3h):



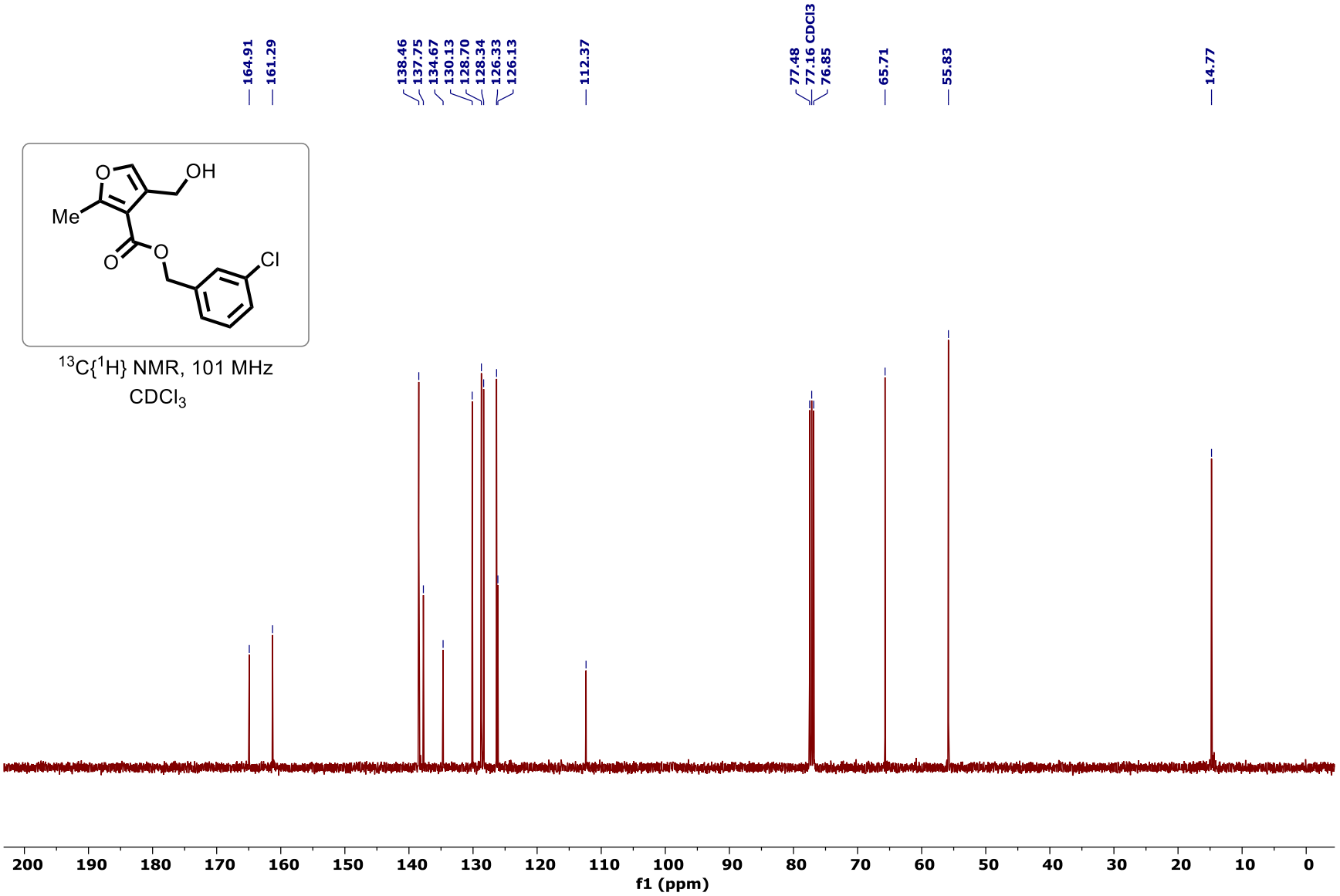
$^{13}C\{^{1}H\}$ NMR spectrum of Benzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3h):



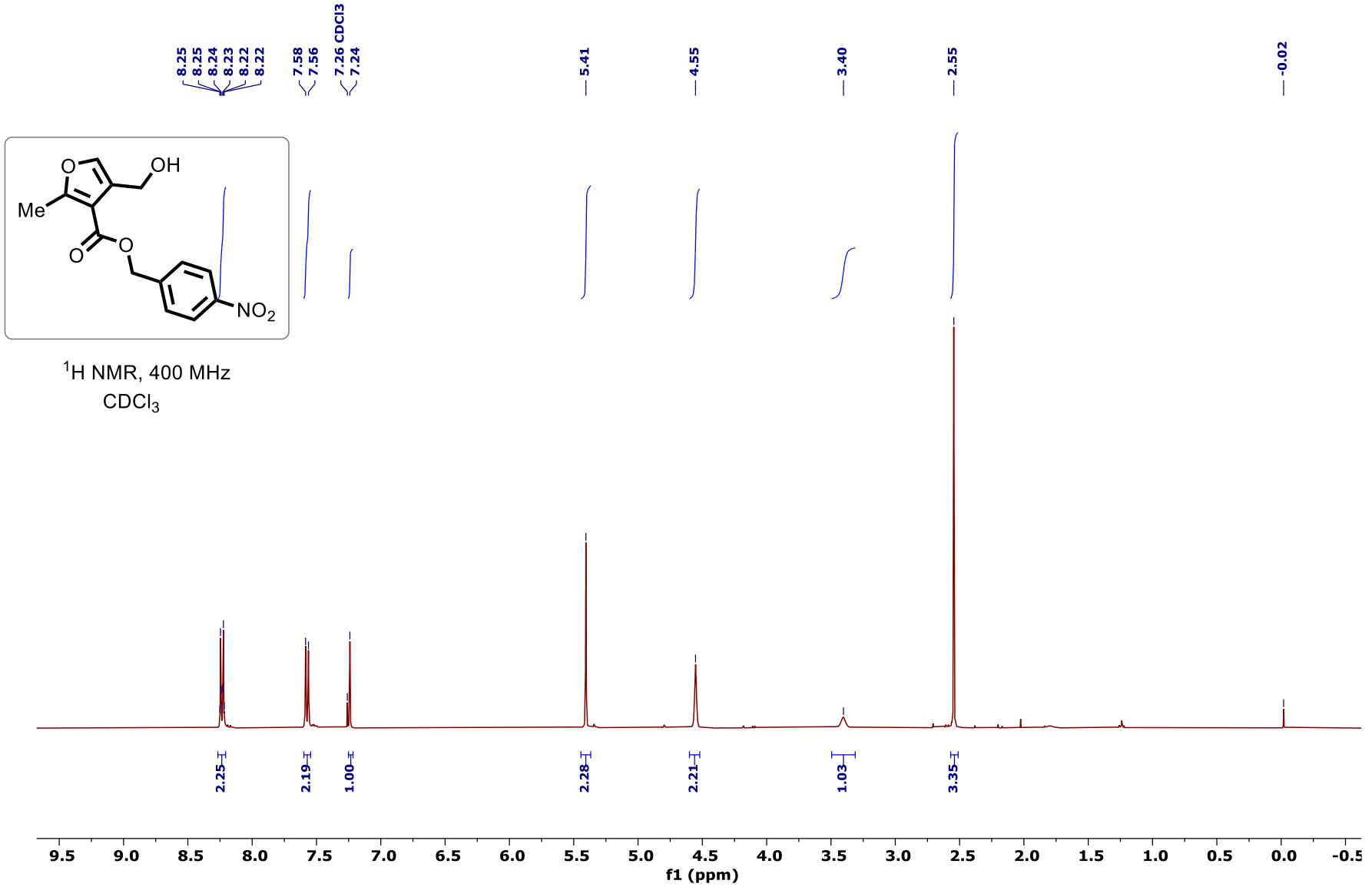
^{1}H NMR spectrum of 4-Chlorobenzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3i):



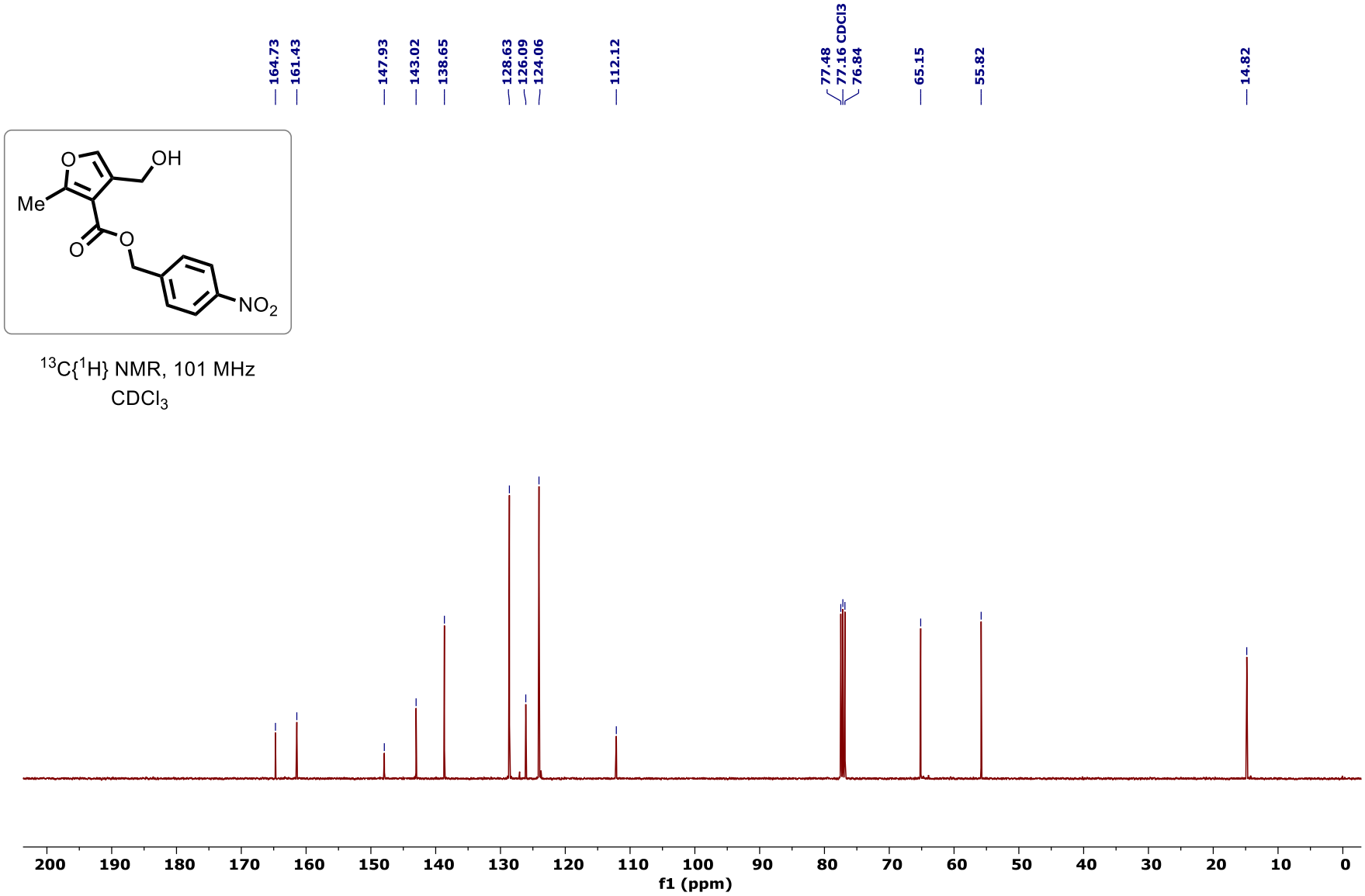
$^{13}C\{^{1}H\}$ NMR spectrum of 4-Chlorobenzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3i):



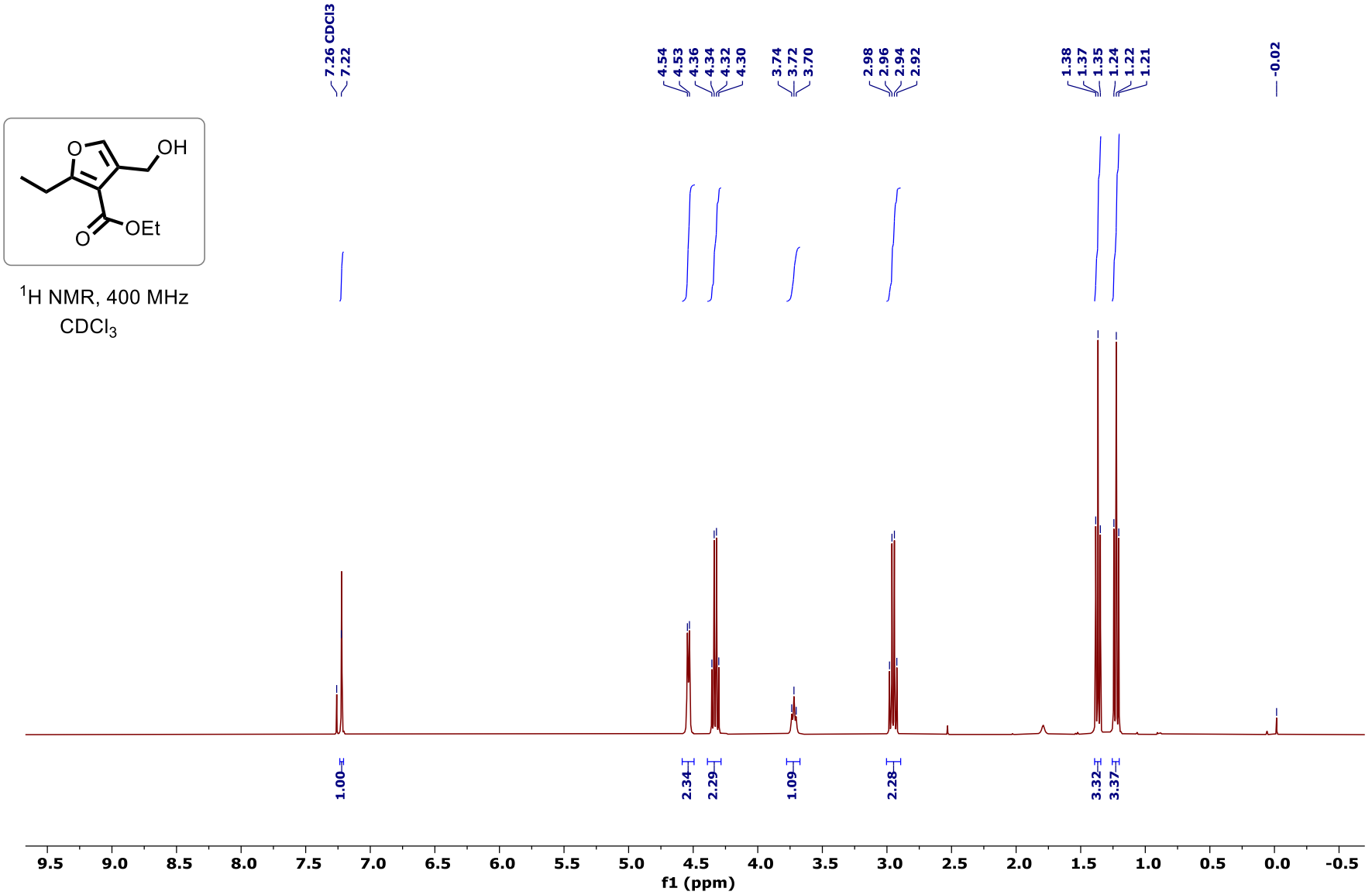
^{1}H NMR spectrum of 4-Nitrobenzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3j):



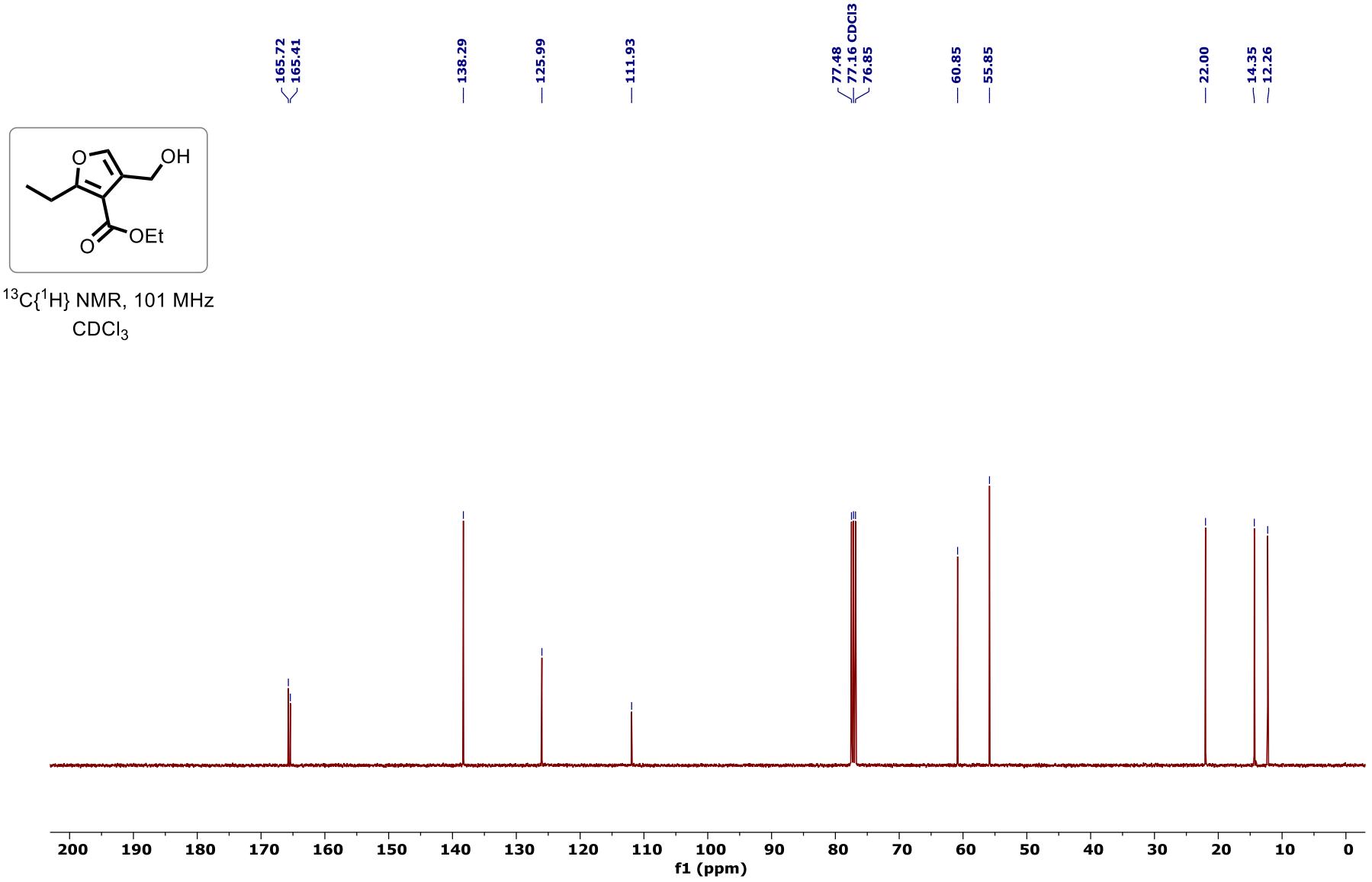
$^{13}C\{^{1}H\}$ NMR spectrum of 4-Nitrobenzyl 4-(hydroxymethyl)-2-methylfuran-3-carboxylate (3j):



^{1}H NMR spectrum of Ethyl 2-ethyl-4-(hydroxymethyl)furan-3-carboxylate (3k):

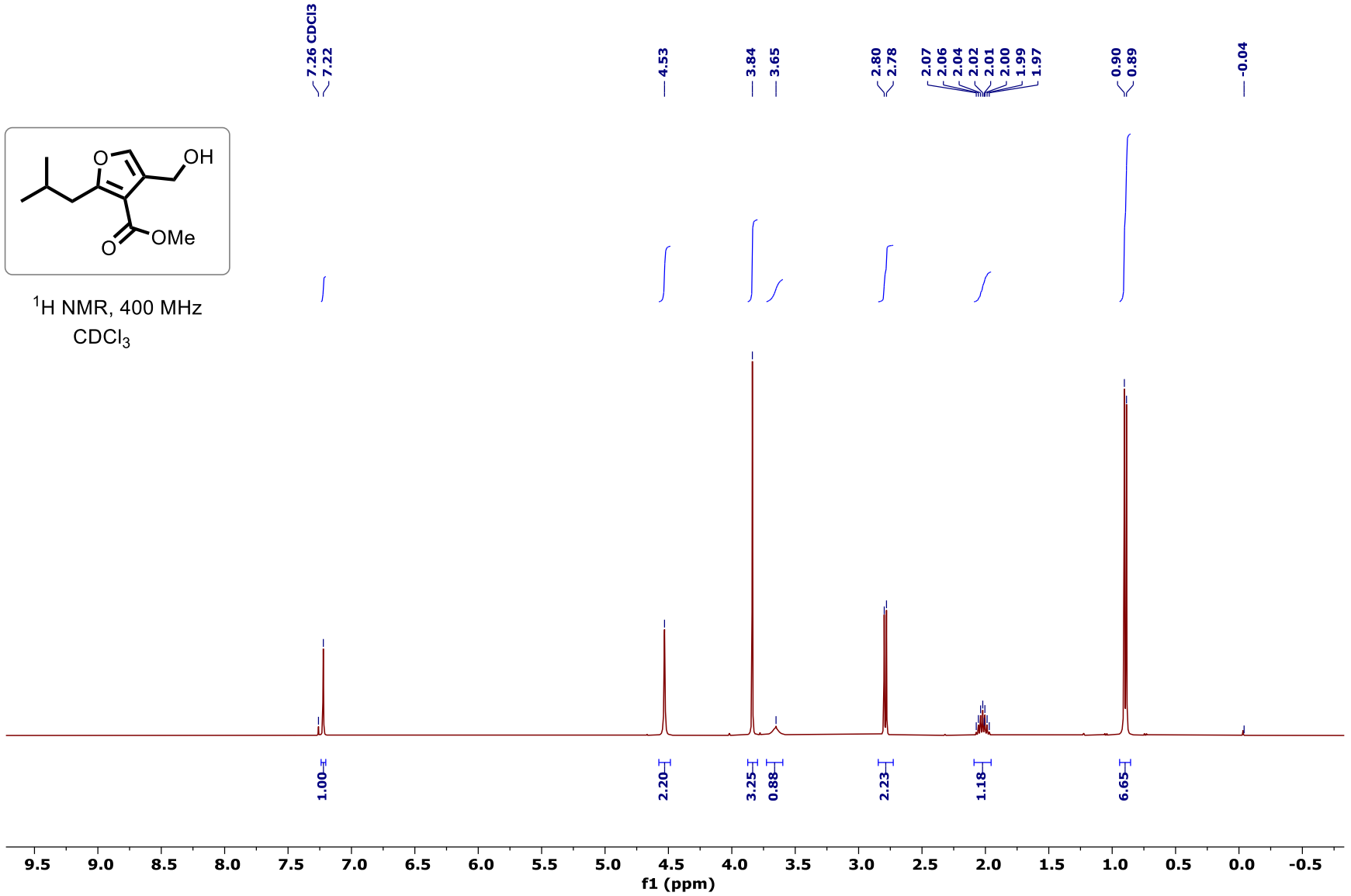


$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-ethyl-4-(hydroxymethyl)furan-3-carboxylate (3k):

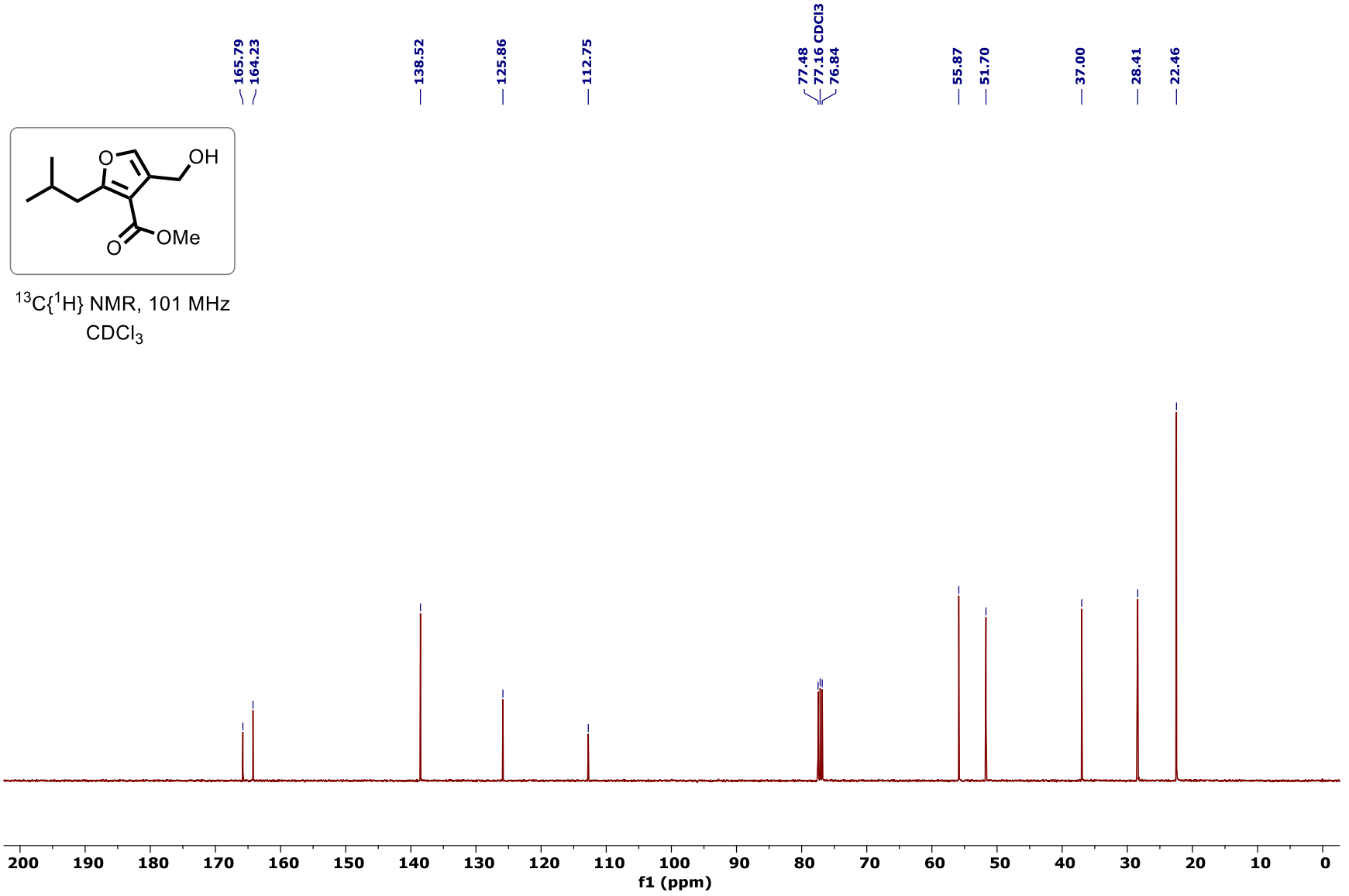


$^{13}C\{^{1}H\}$ NMR, 101 MHz
$CDCl_3$

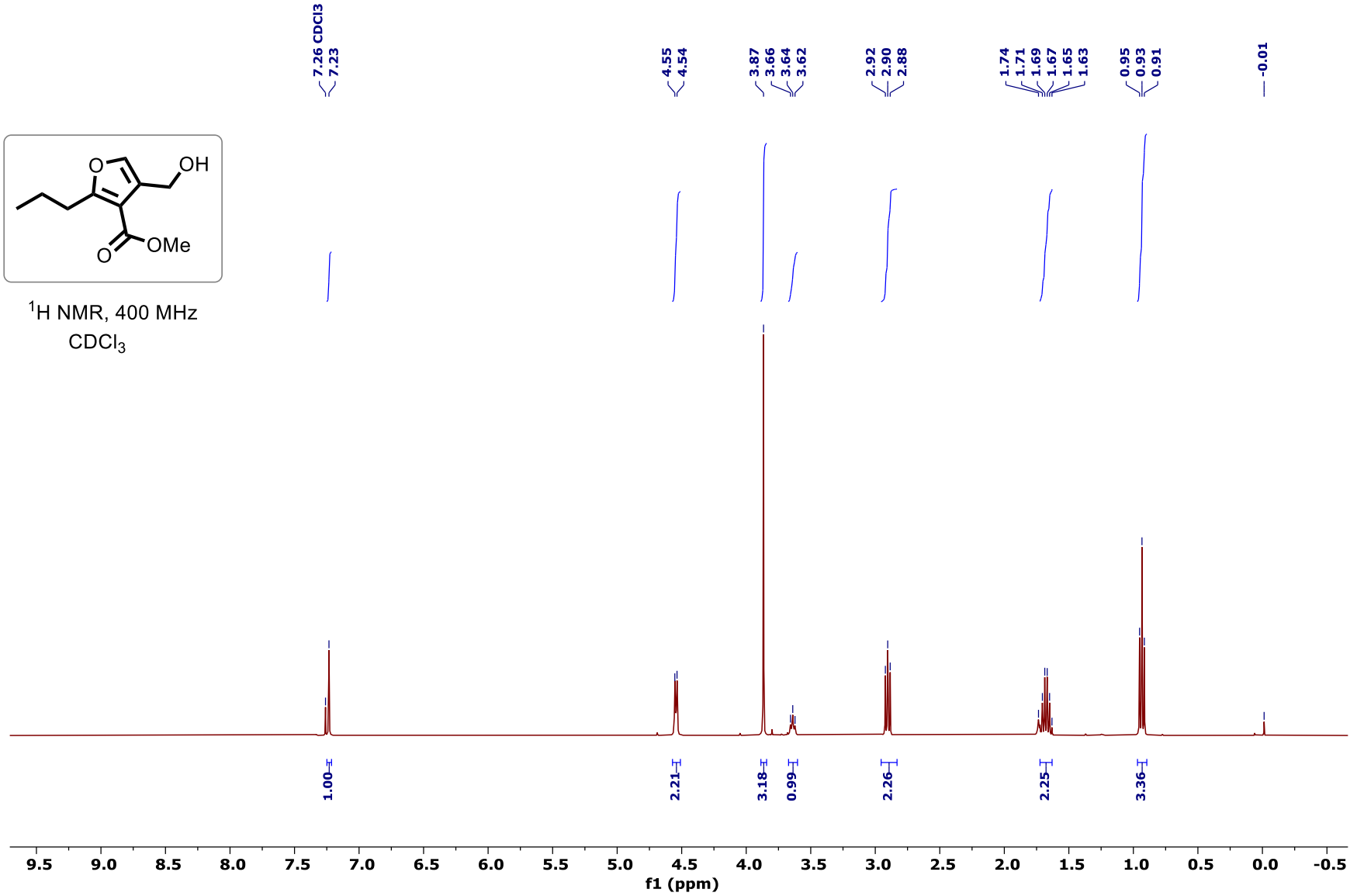
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-isobutylfuran-3-carboxylate (3l):



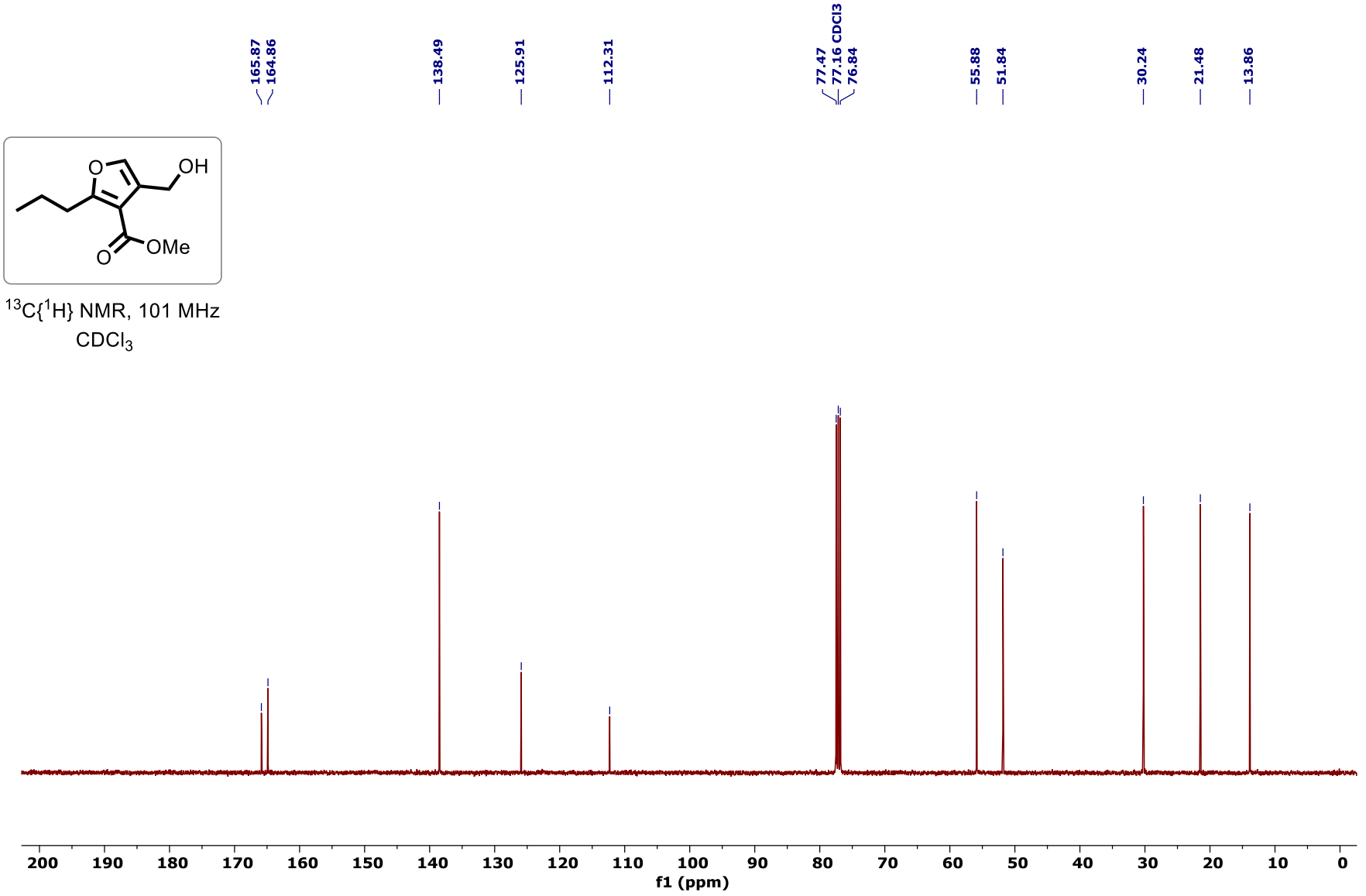
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-isobutylfuran-3-carboxylate (3l):



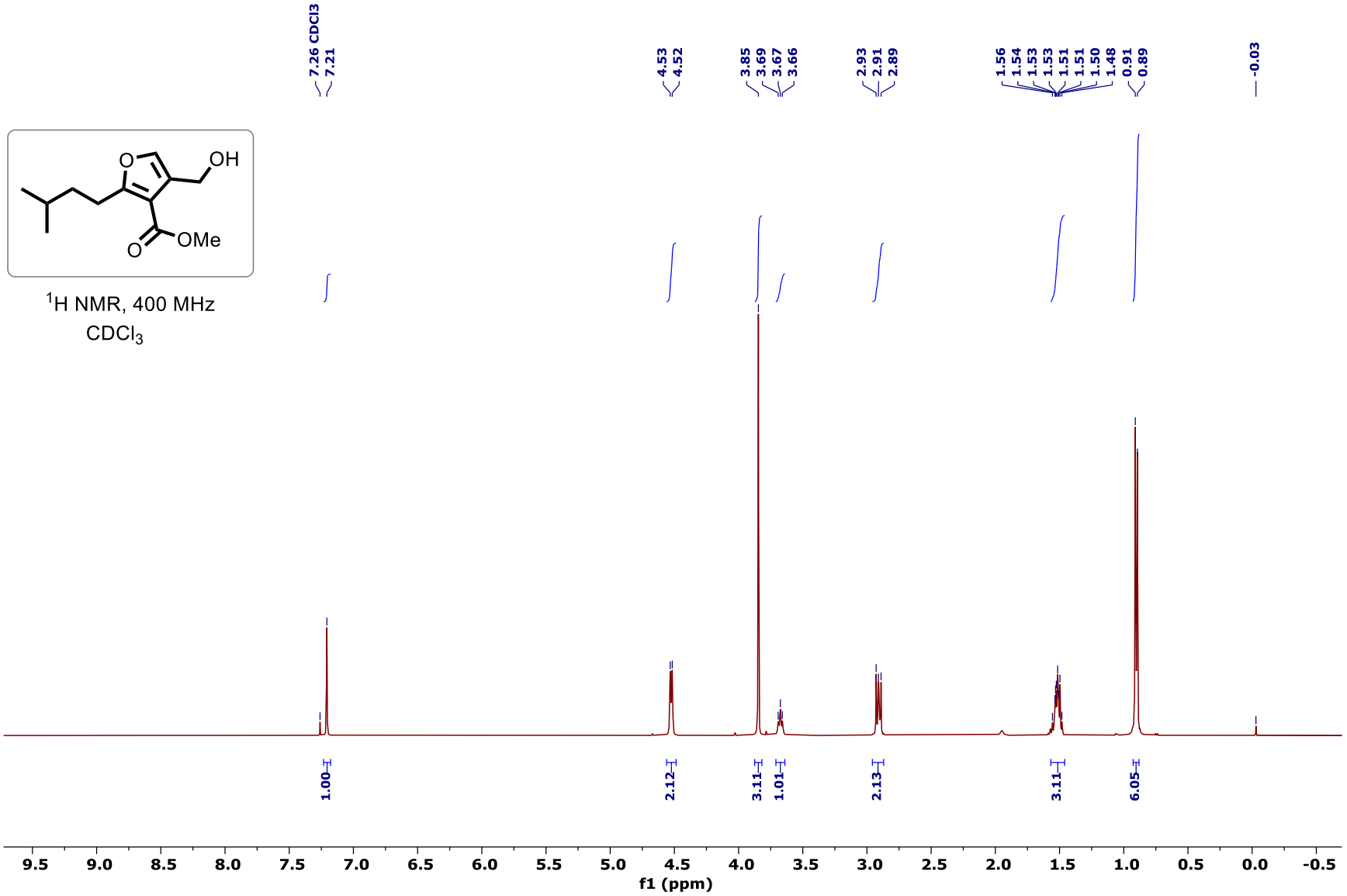
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-propylfuran-3-carboxylate (3m):



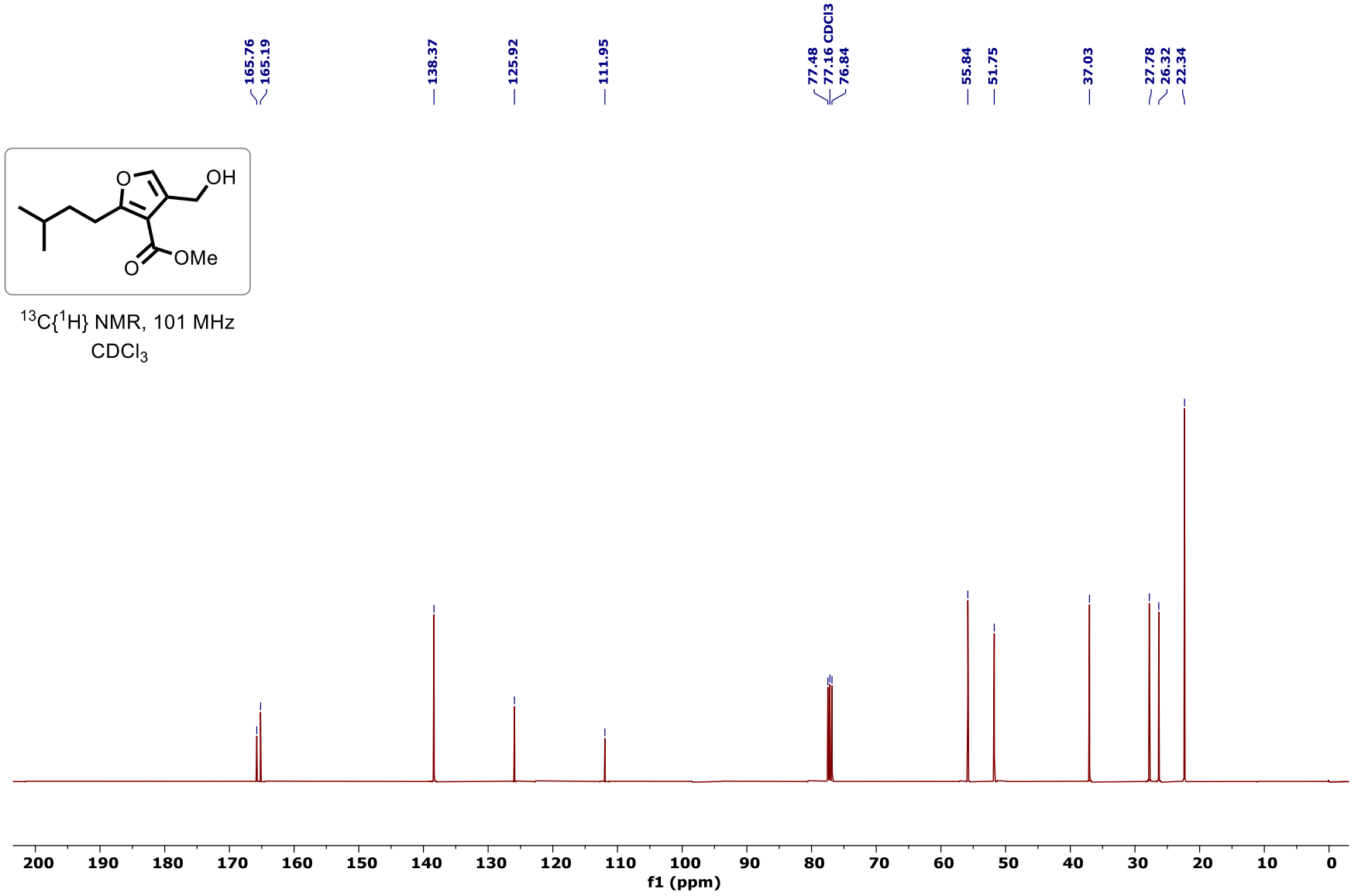
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-propylfuran-3-carboxylate (3m):



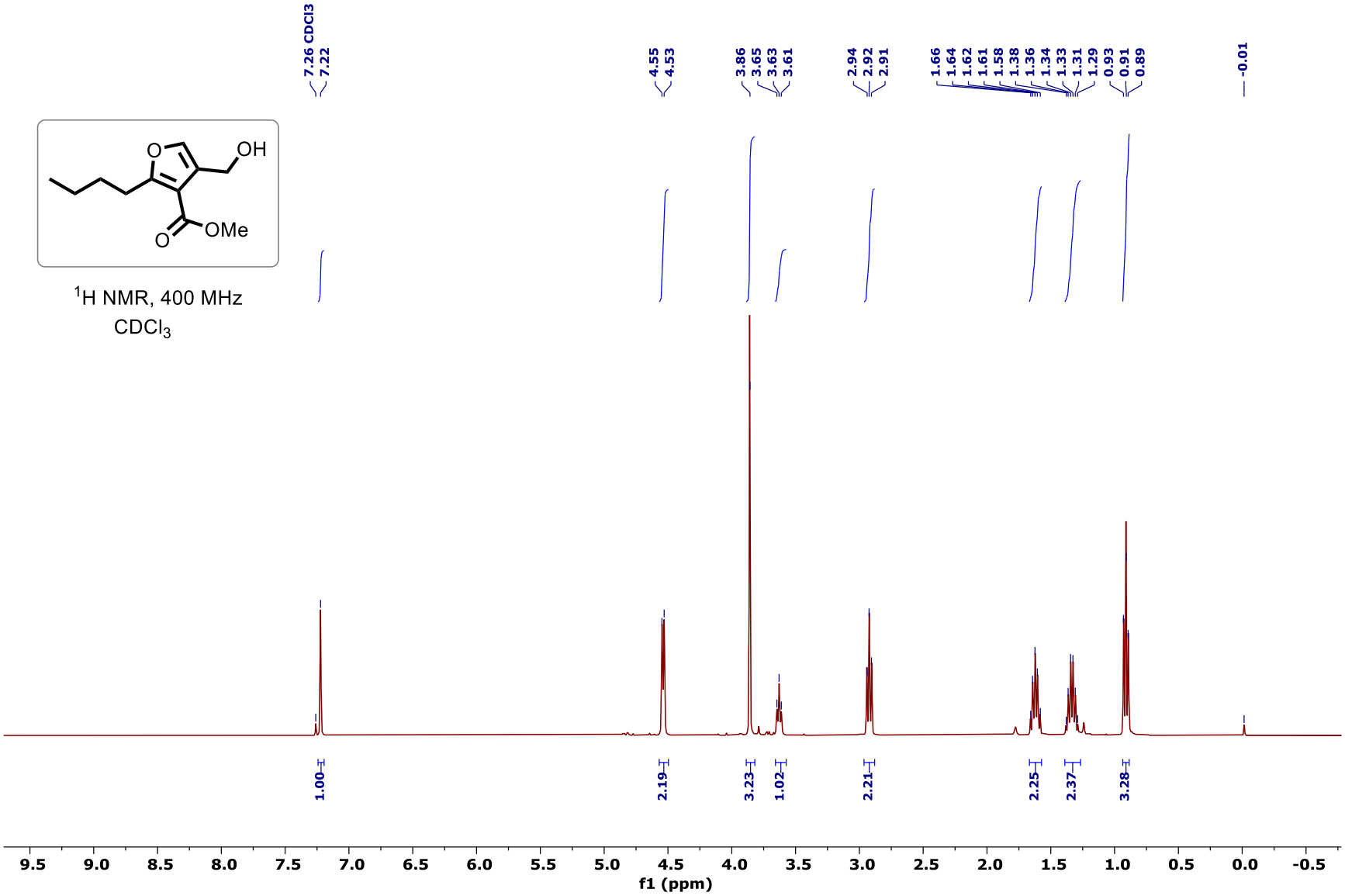
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-isopentylfuran-3-carboxylate (3n):



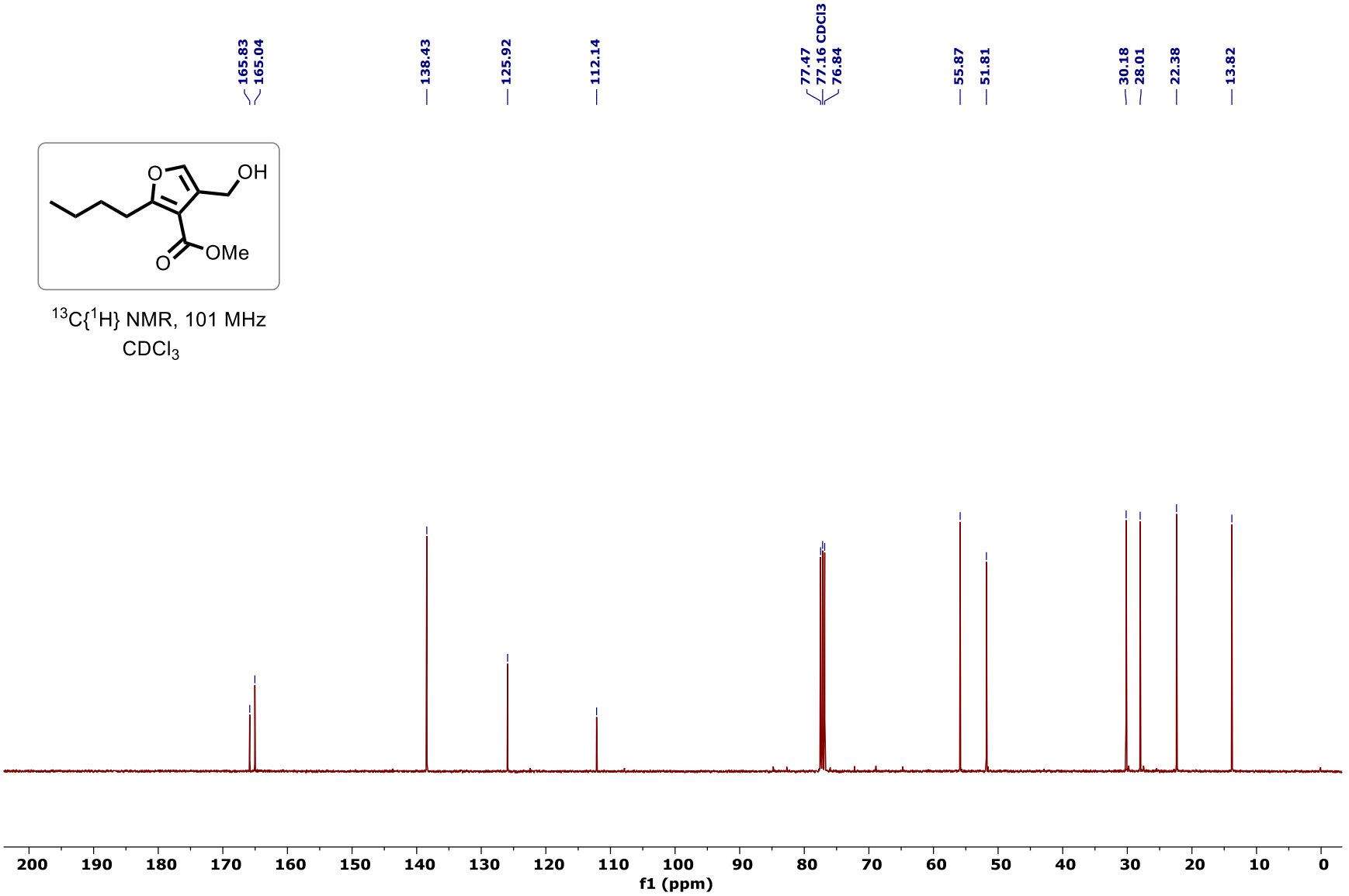
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-isopentylfuran-3-carboxylate (3n):



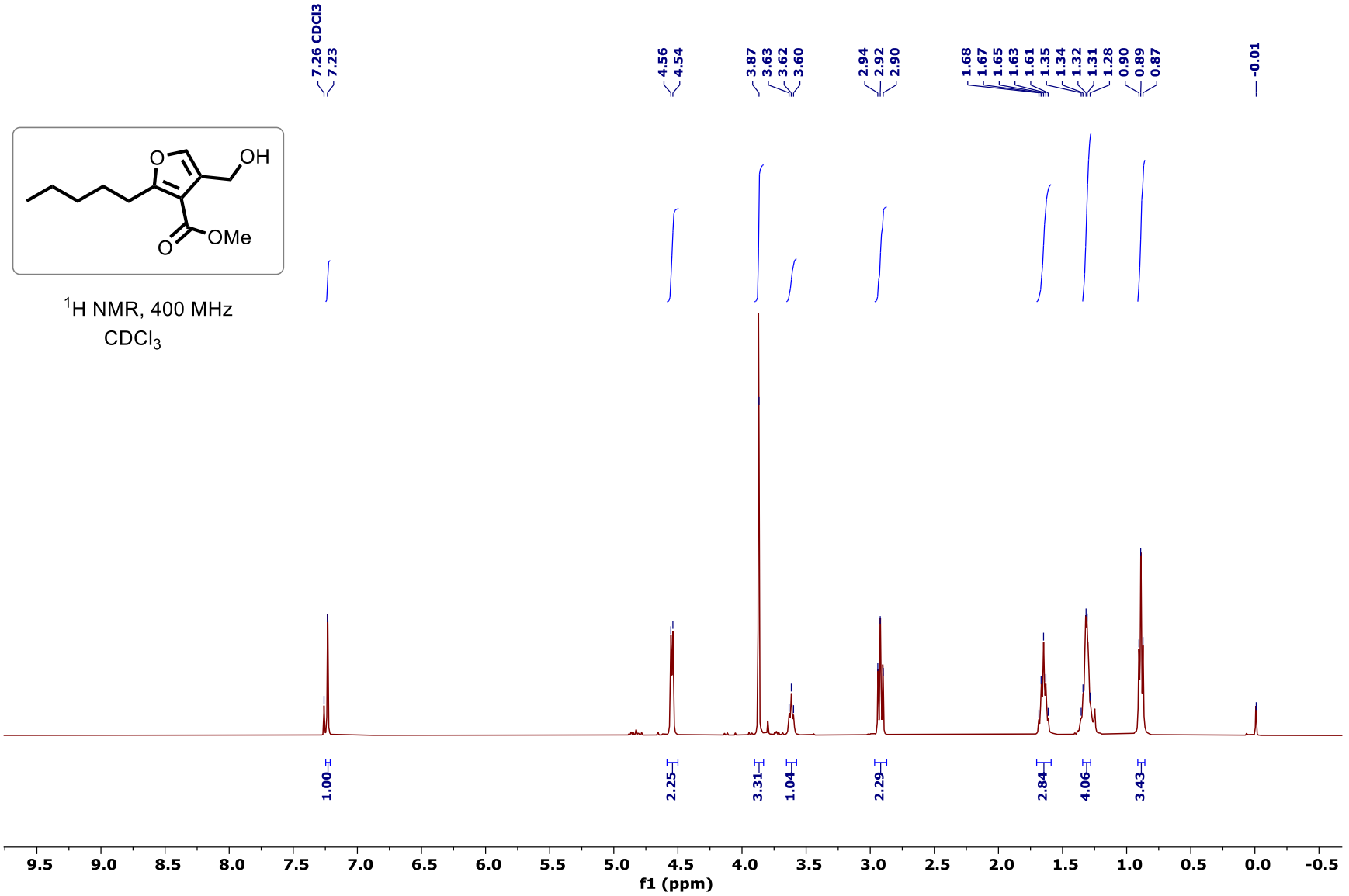
^{1}H NMR spectrum of Methyl 2-butyl-4-(hydroxymethyl)furan-3-carboxylate (3o):



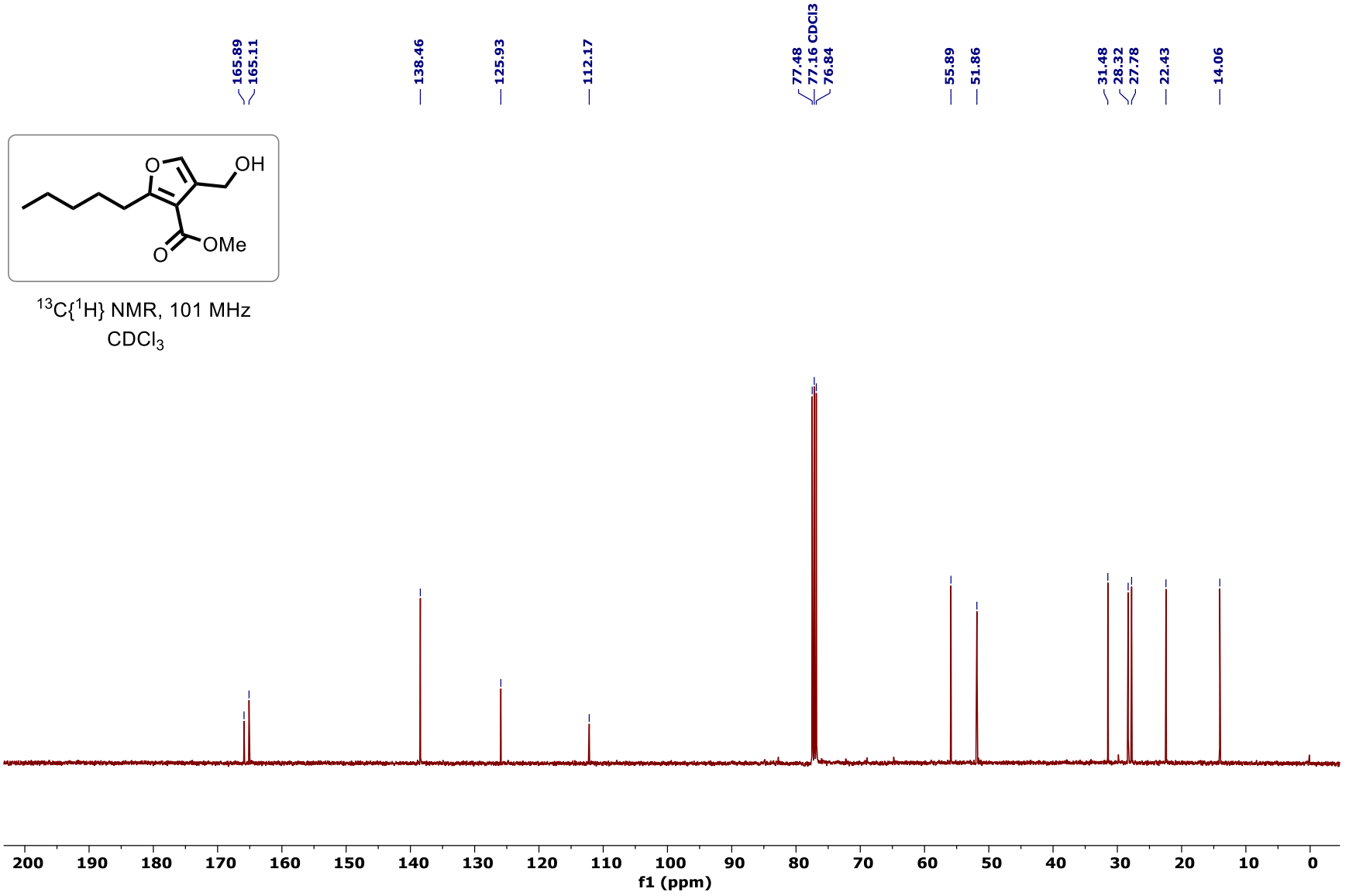
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 2-butyl-4-(hydroxymethyl)furan-3-carboxylate (3o):



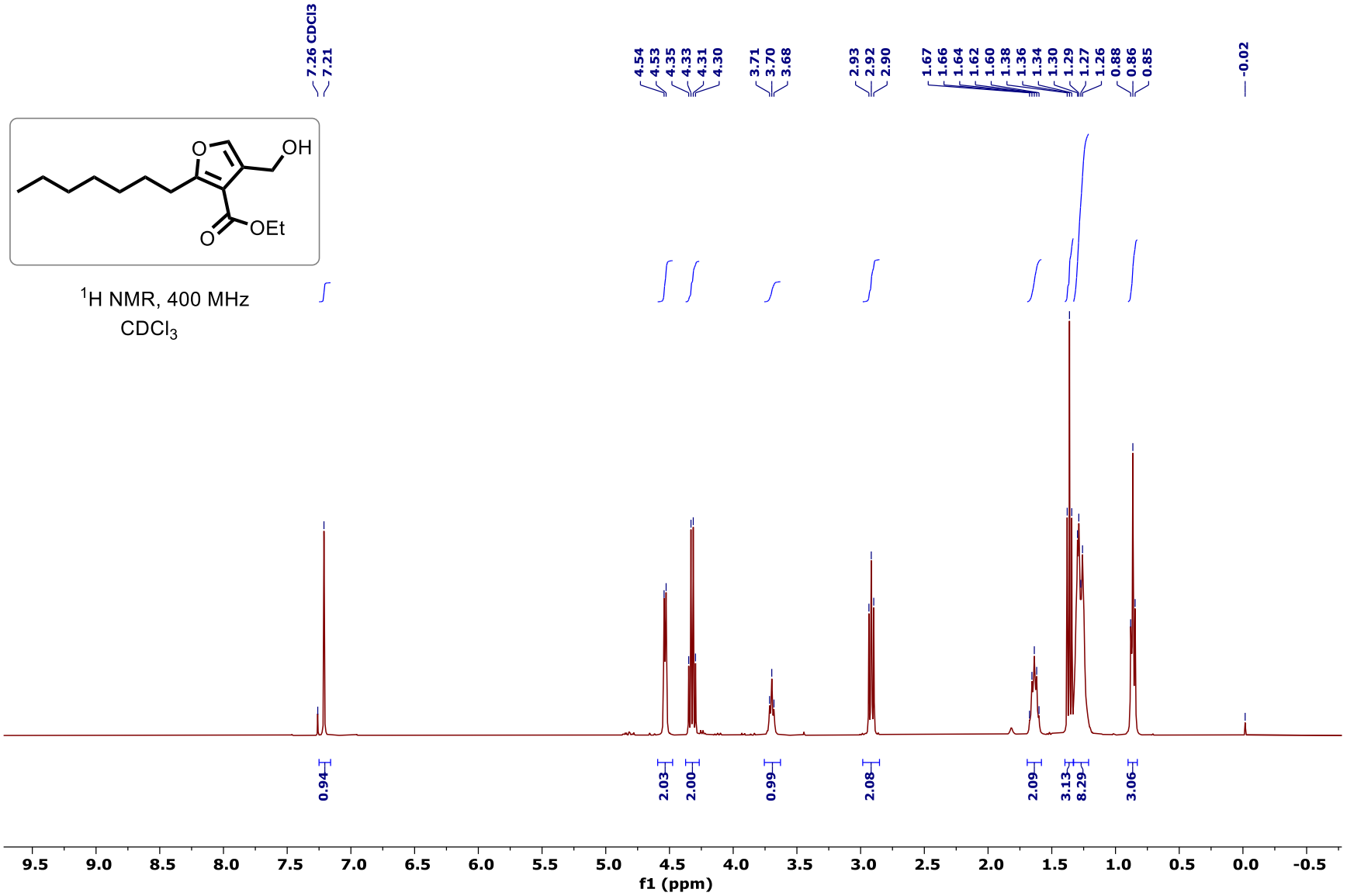
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-pentylfuran-3-carboxylate (3p):



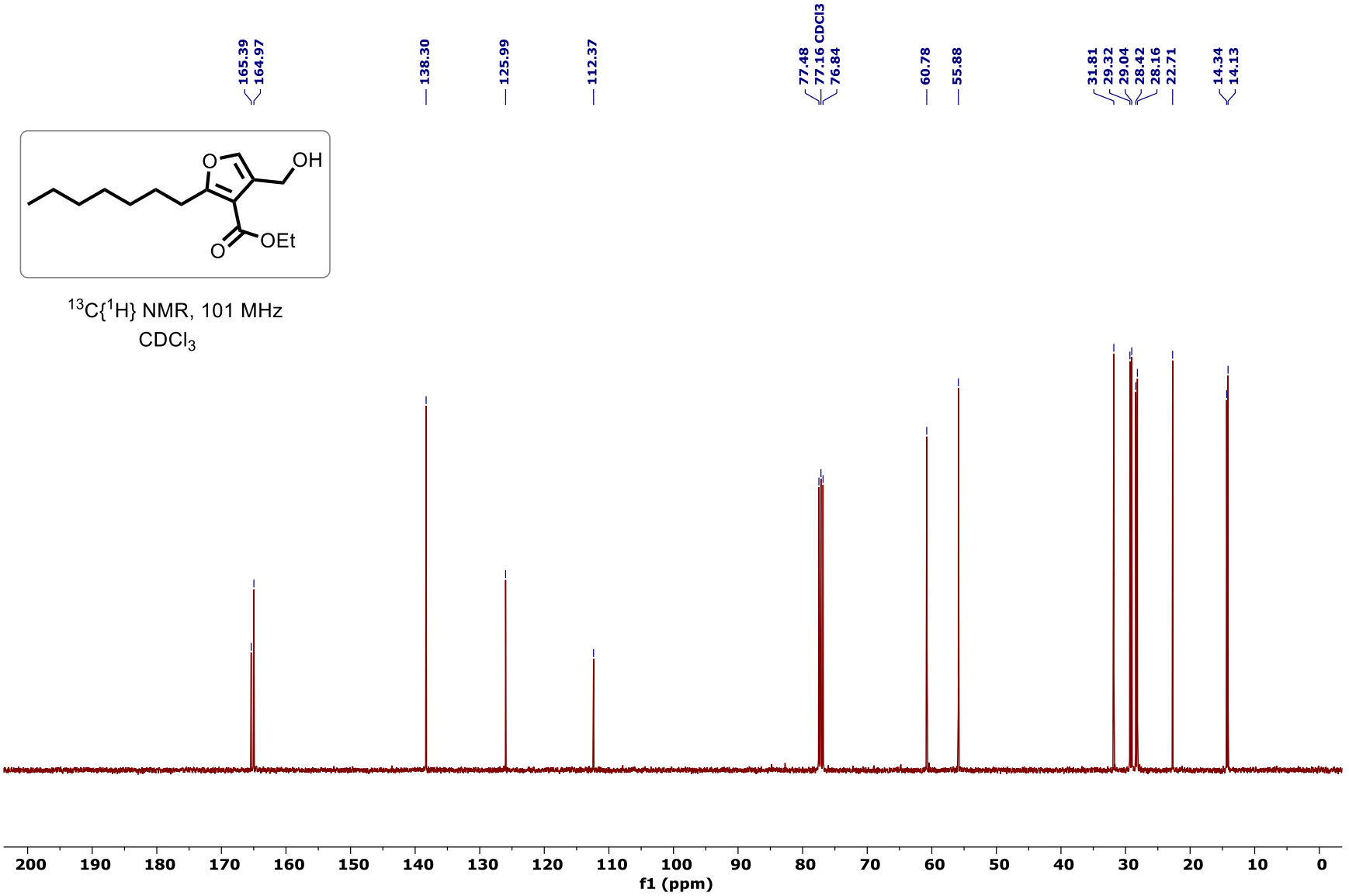
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-pentylfuran-3-carboxylate (3p):



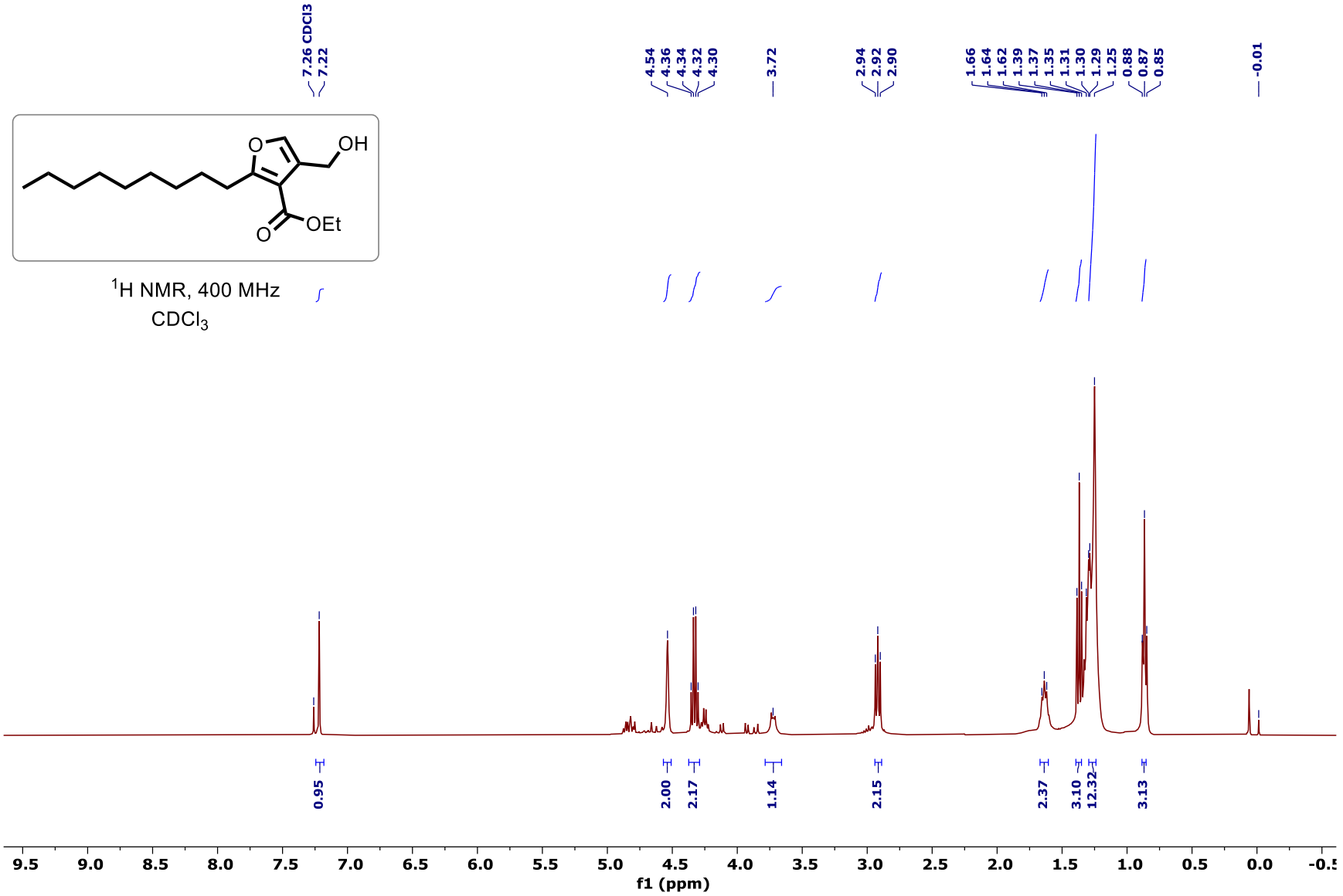
^{1}H NMR spectrum of Ethyl 2-heptyl-4-(hydroxymethyl)furan-3-carboxylate (3q):



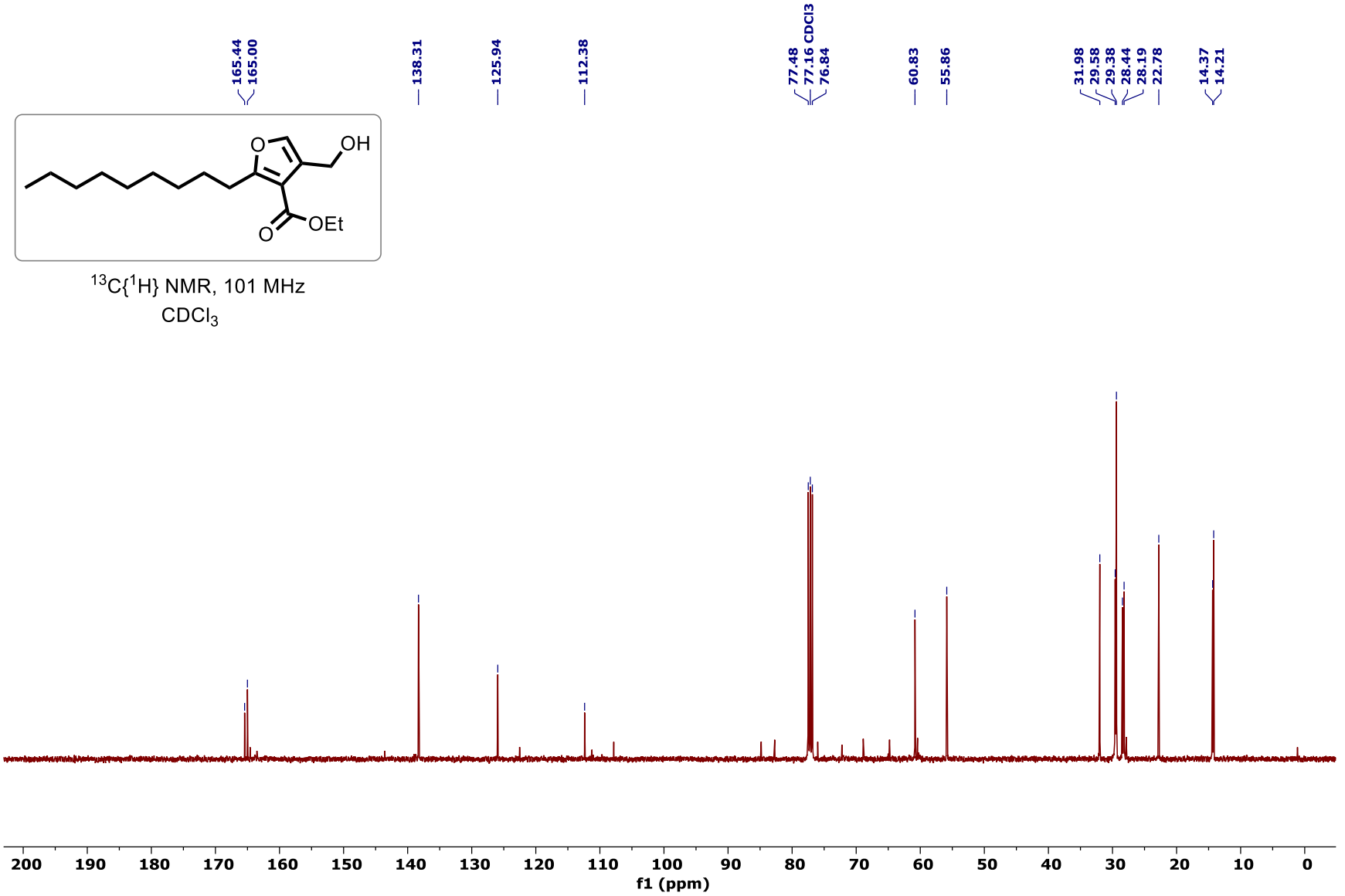
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-heptyl-4-(hydroxymethyl)furan-3-carboxylate (3q):



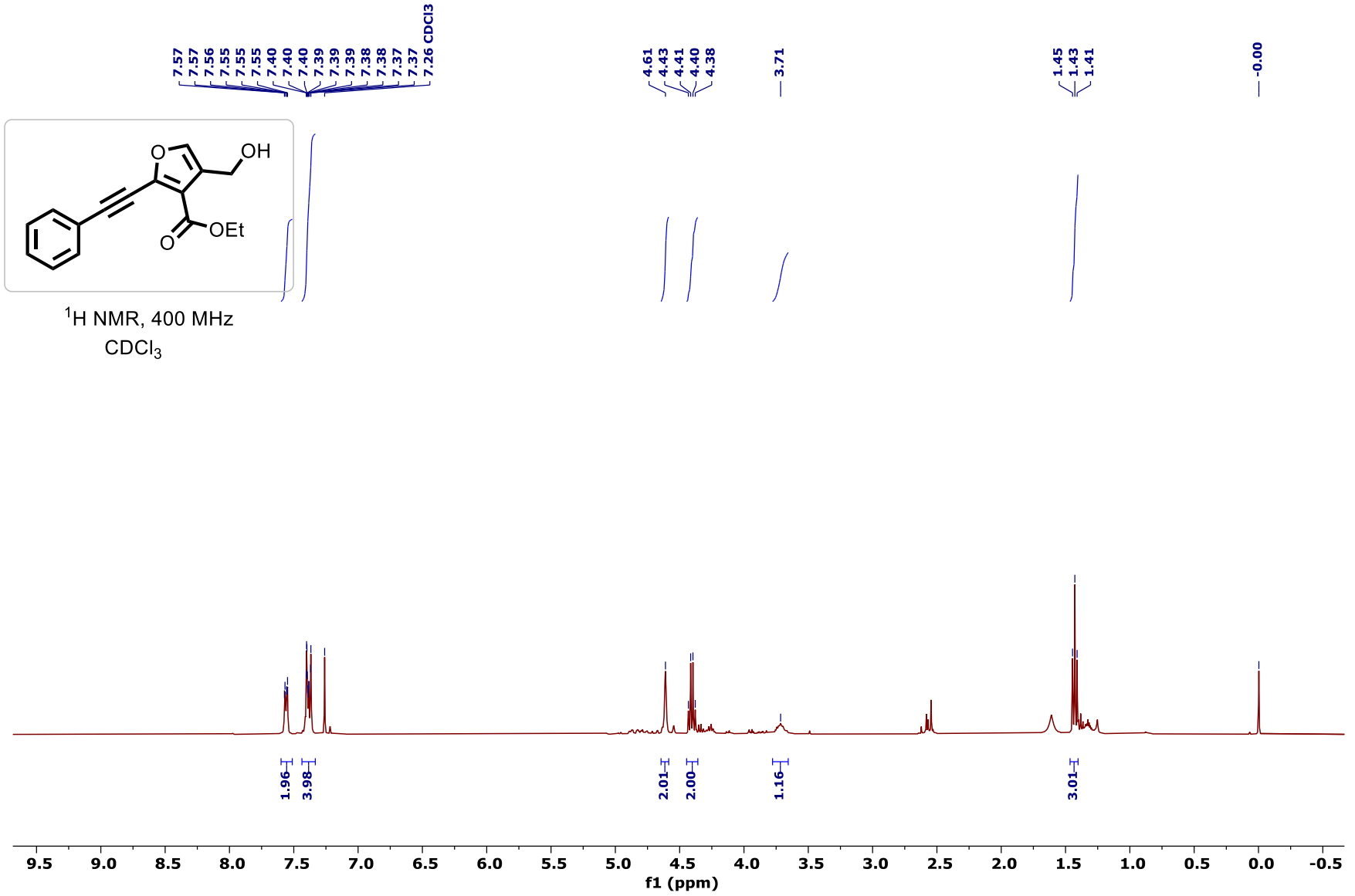
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-nonylfuran-3-carboxylate (3r):



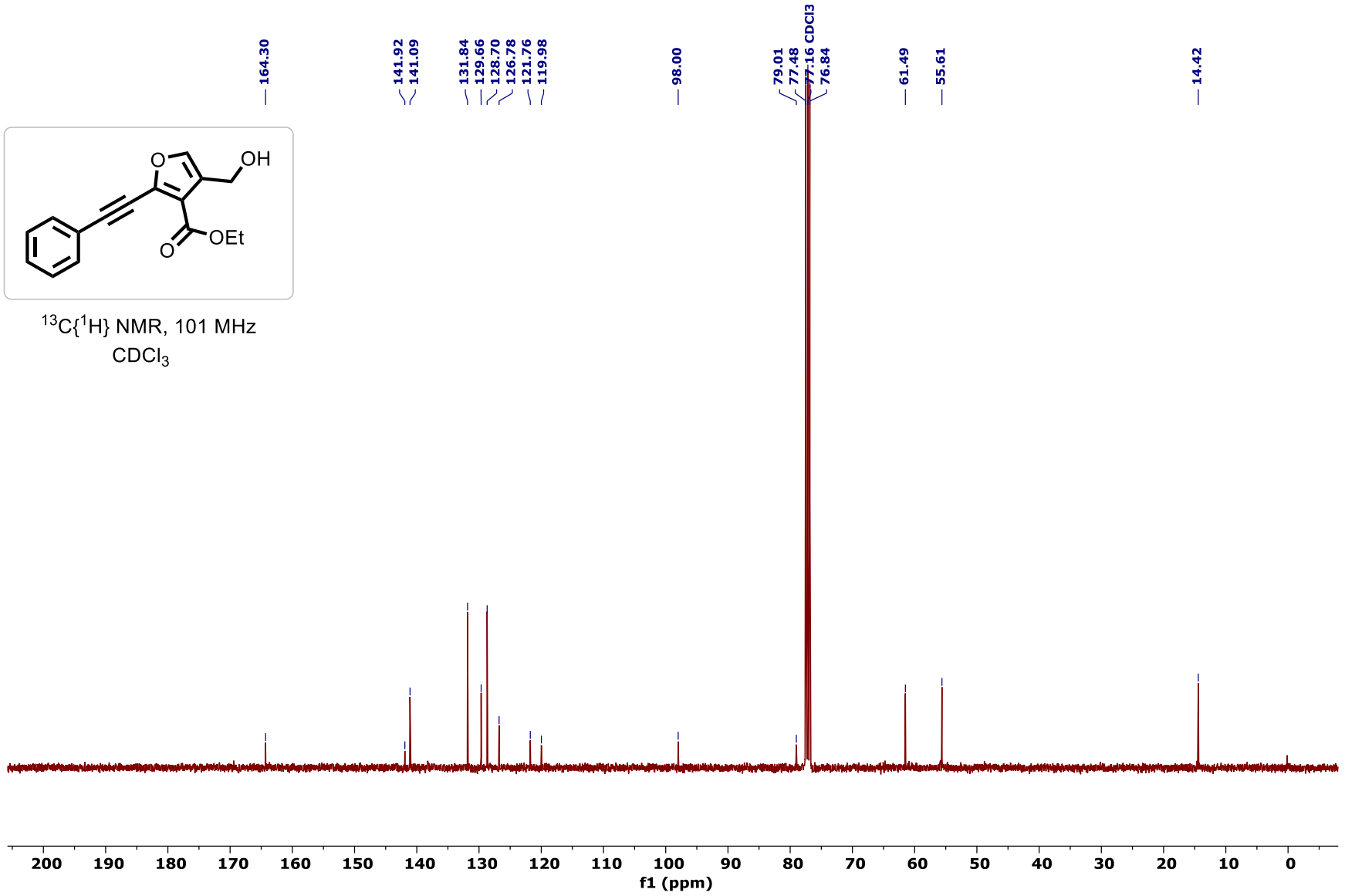
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-nonylfuran-3-carboxylate (3r):



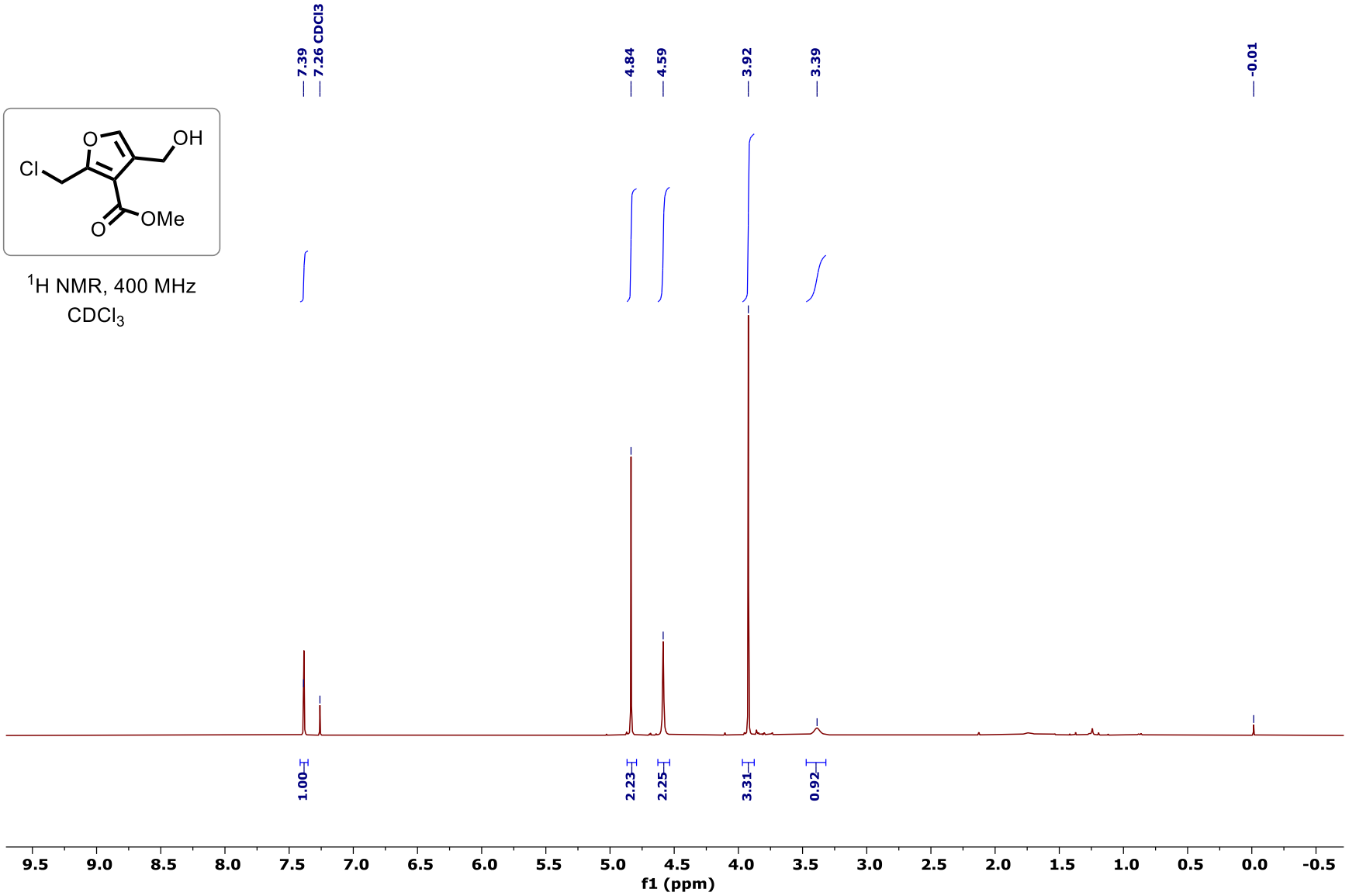
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(phenylethynyl)furan-3-carboxylate (3s):



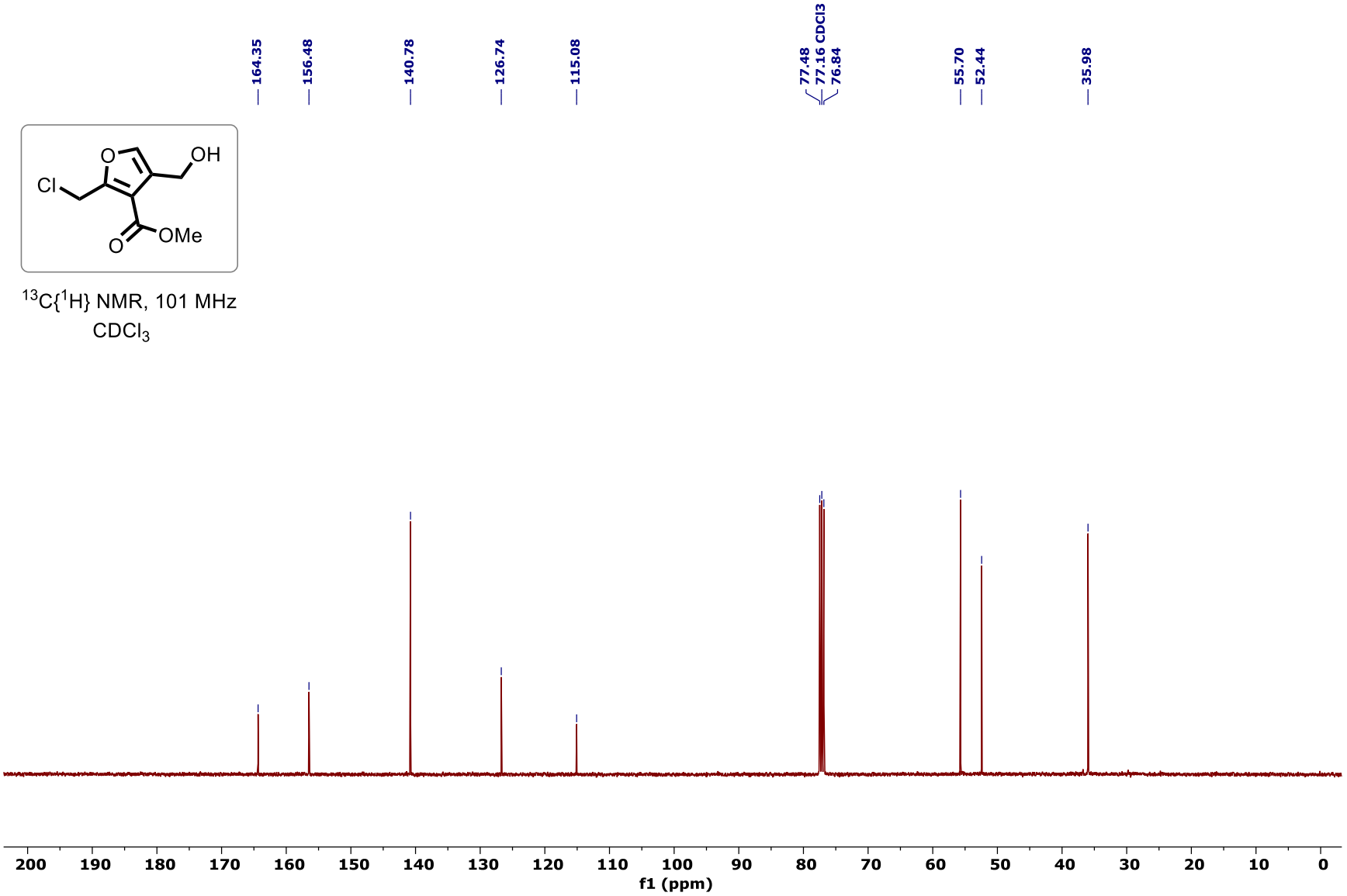
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(phenylethynyl)furan-3-carboxylate (3s):



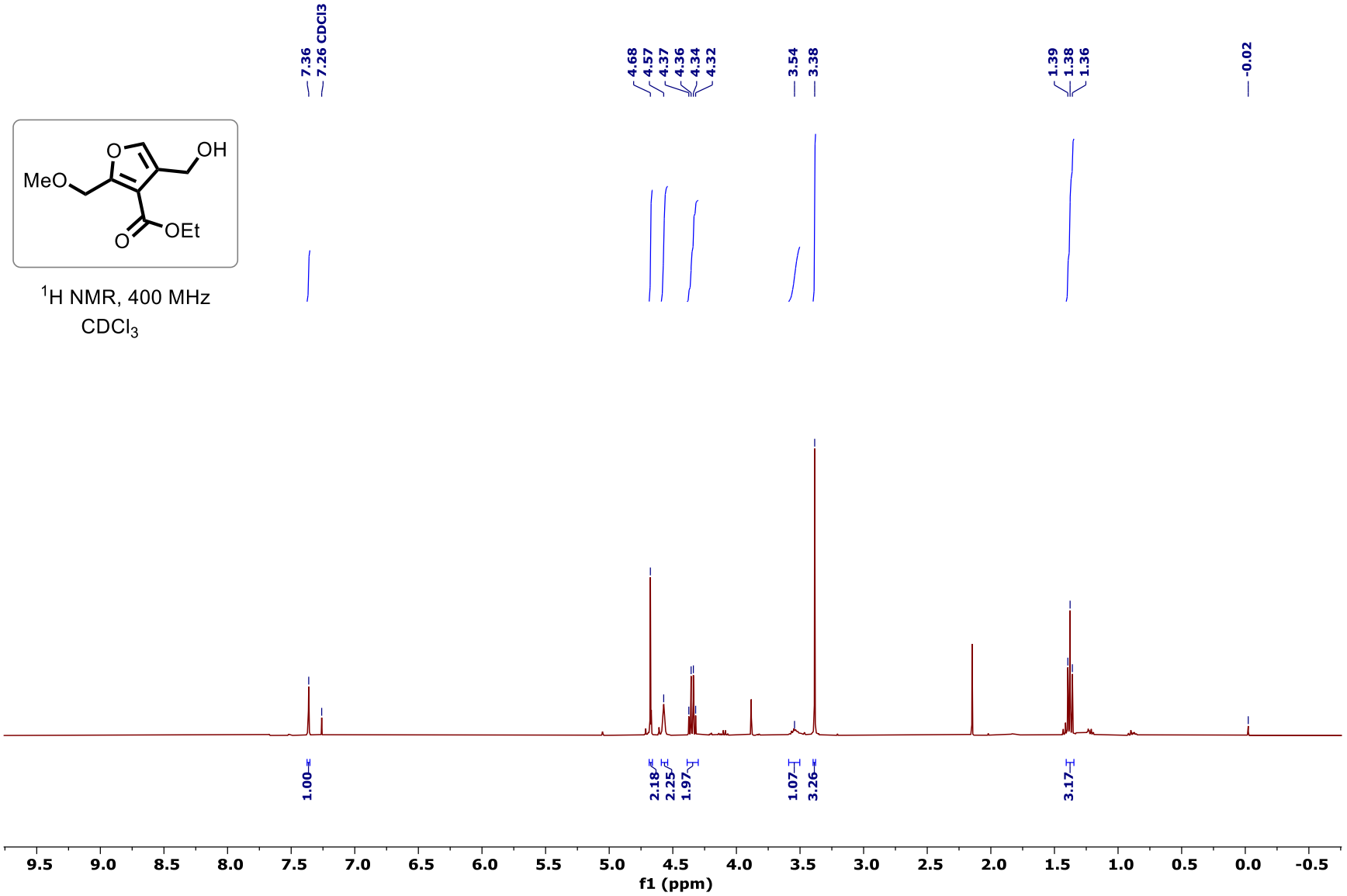
^{1}H NMR spectrum of Methyl 2-(chloromethyl)-4-(hydroxymethyl)furan-3-carboxylate (3t):



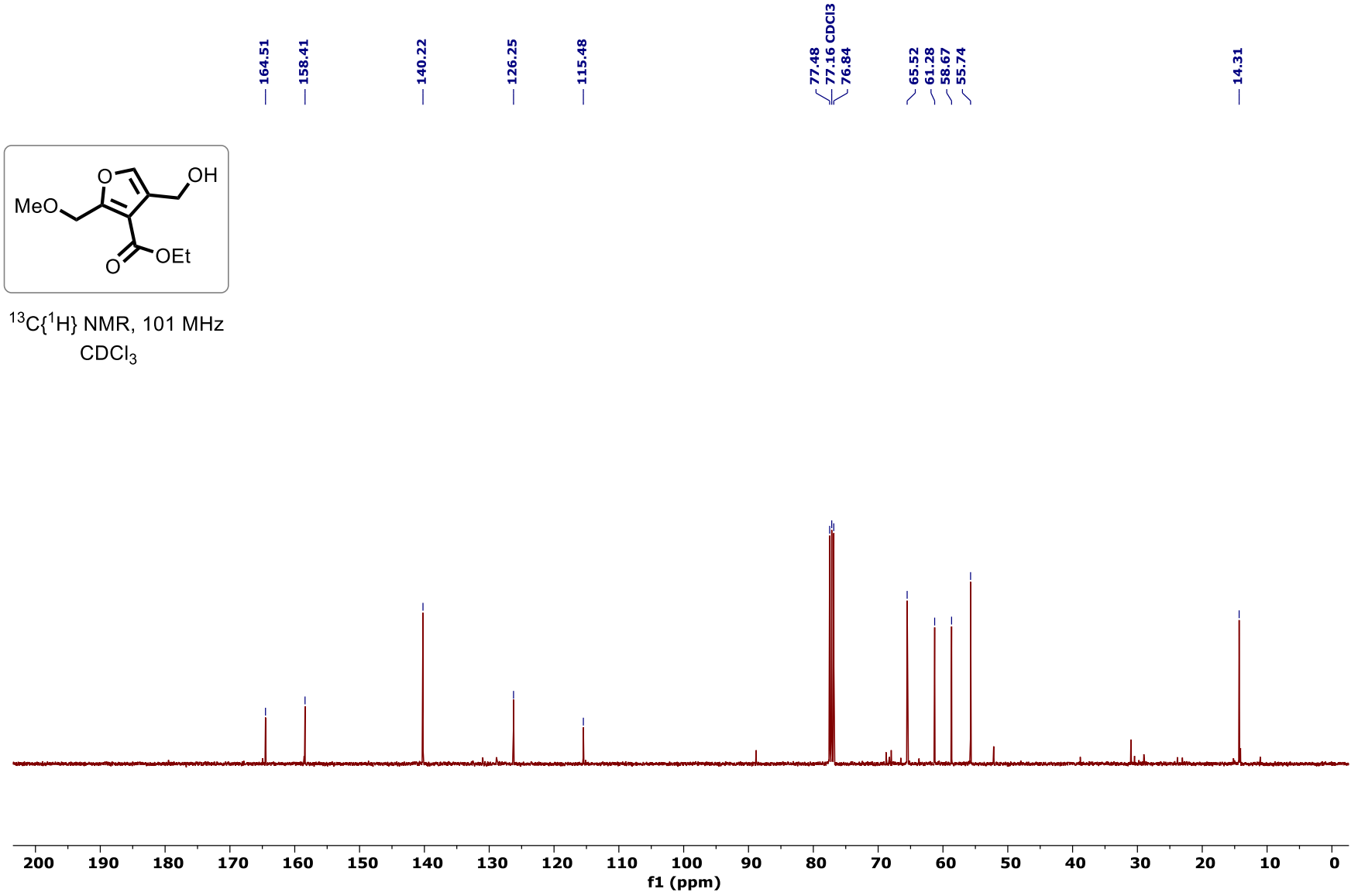
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 2-(chloromethyl)-4-(hydroxymethyl)furan-3-carboxylate (3t):



^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(methoxymethyl)furan-3-carboxylate (3u):

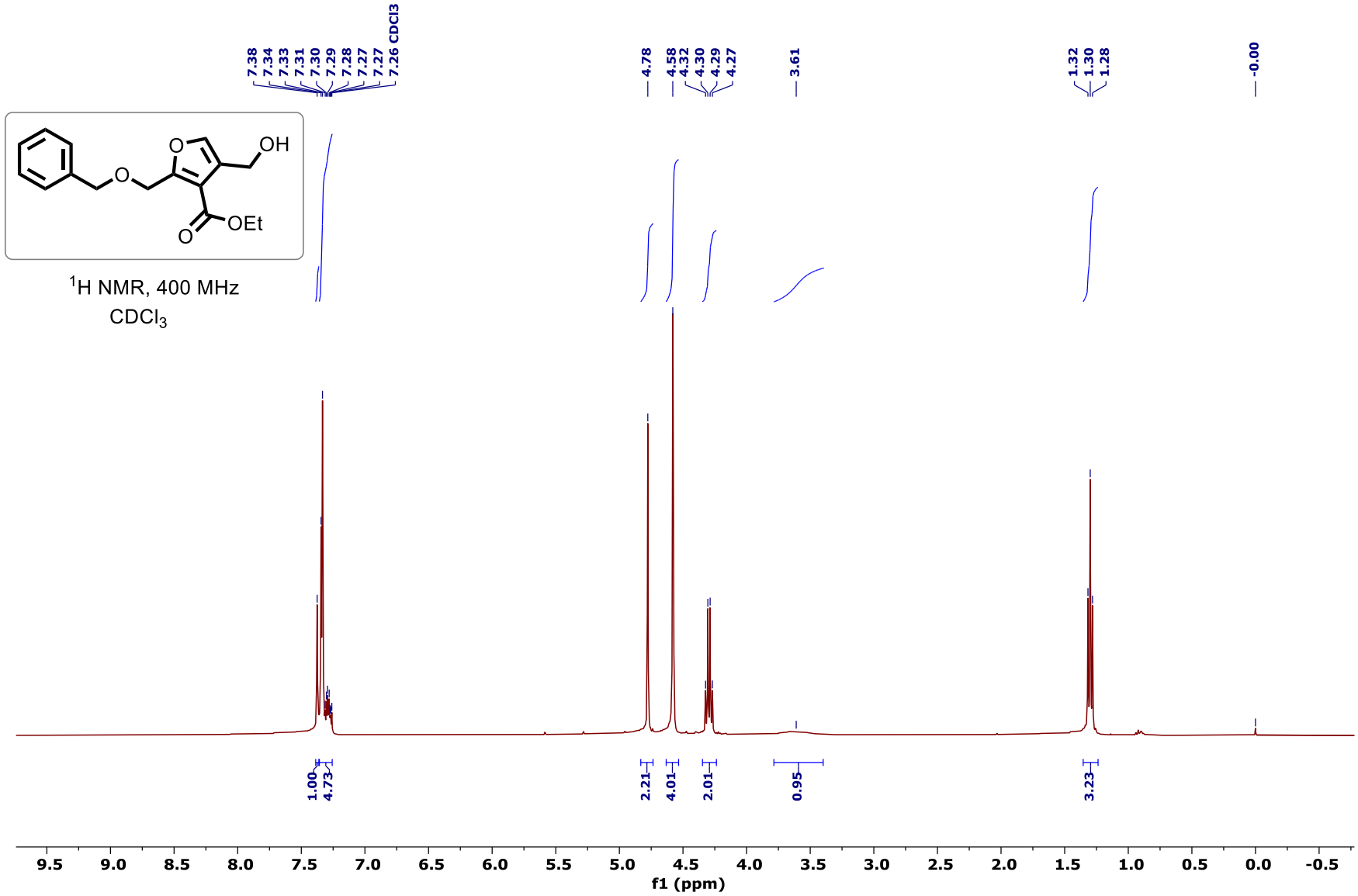


$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(methoxymethyl)furan-3-carboxylate (3u):

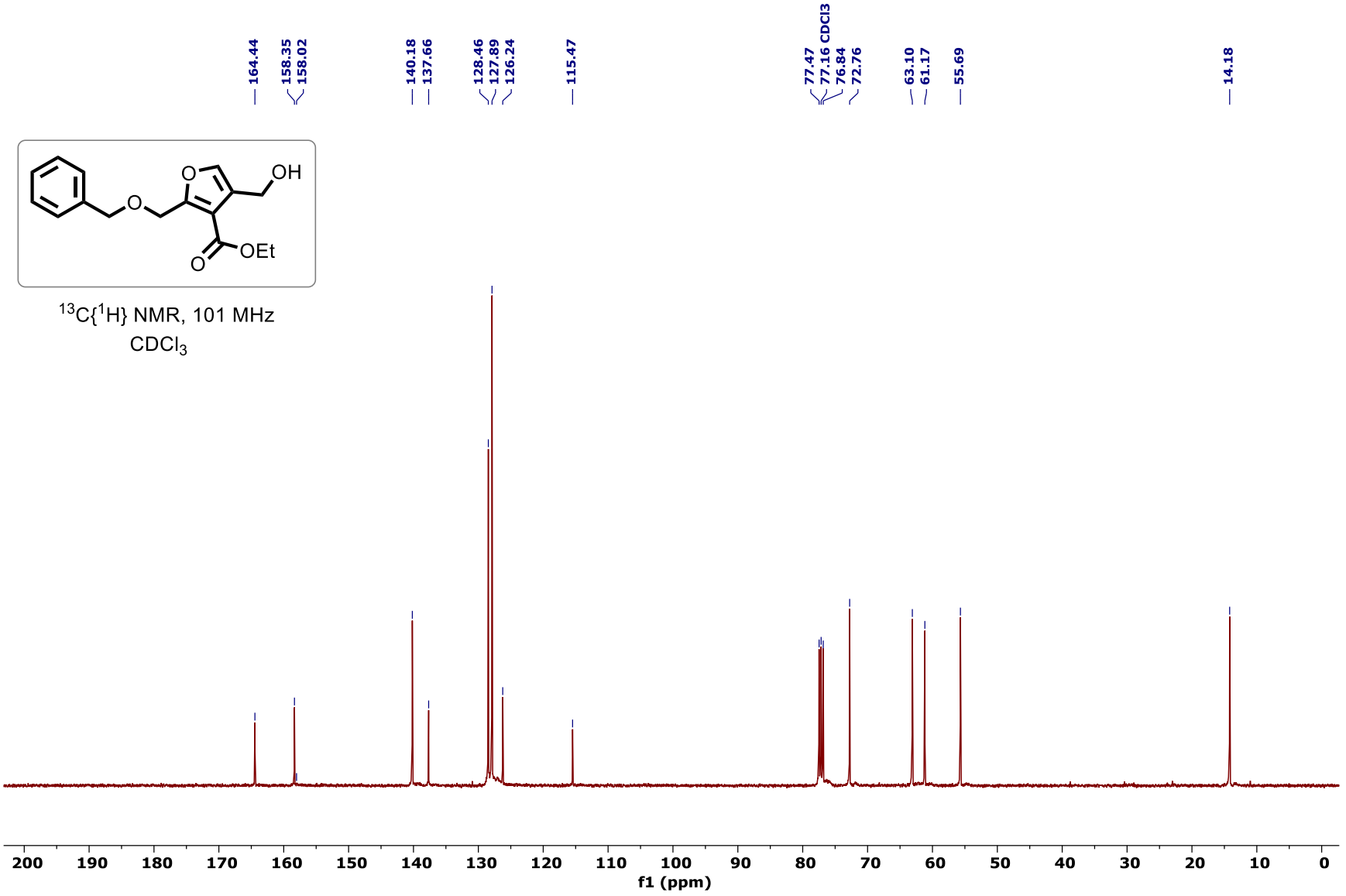


$^{13}C\{^{1}H\}$ NMR, 101 MHz
$CDCl_3$

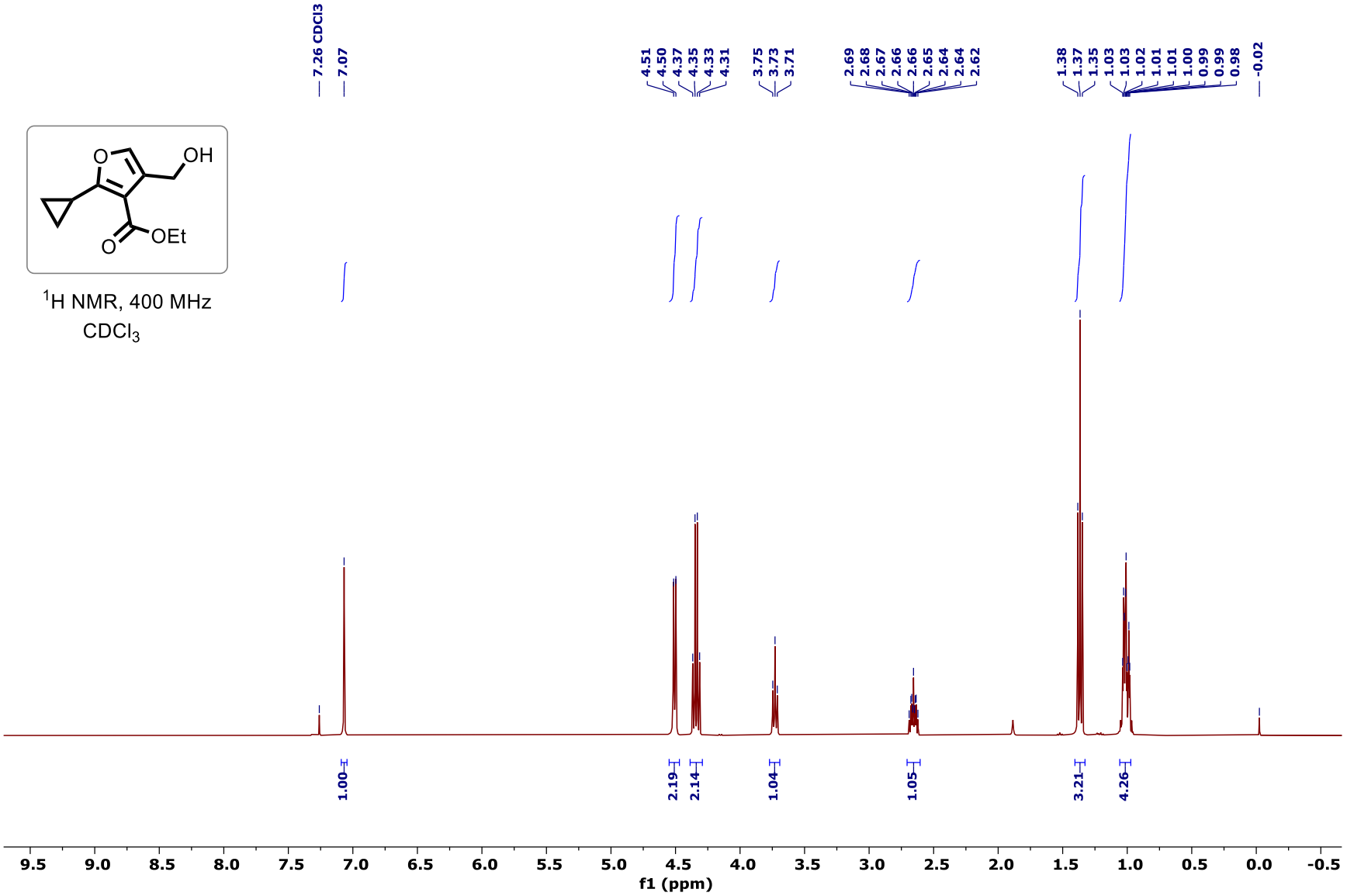
^{1}H NMR spectrum of Ethyl 2-((benzyloxy)methyl)-4-(hydroxymethyl)furan-3-carboxylate (3v):



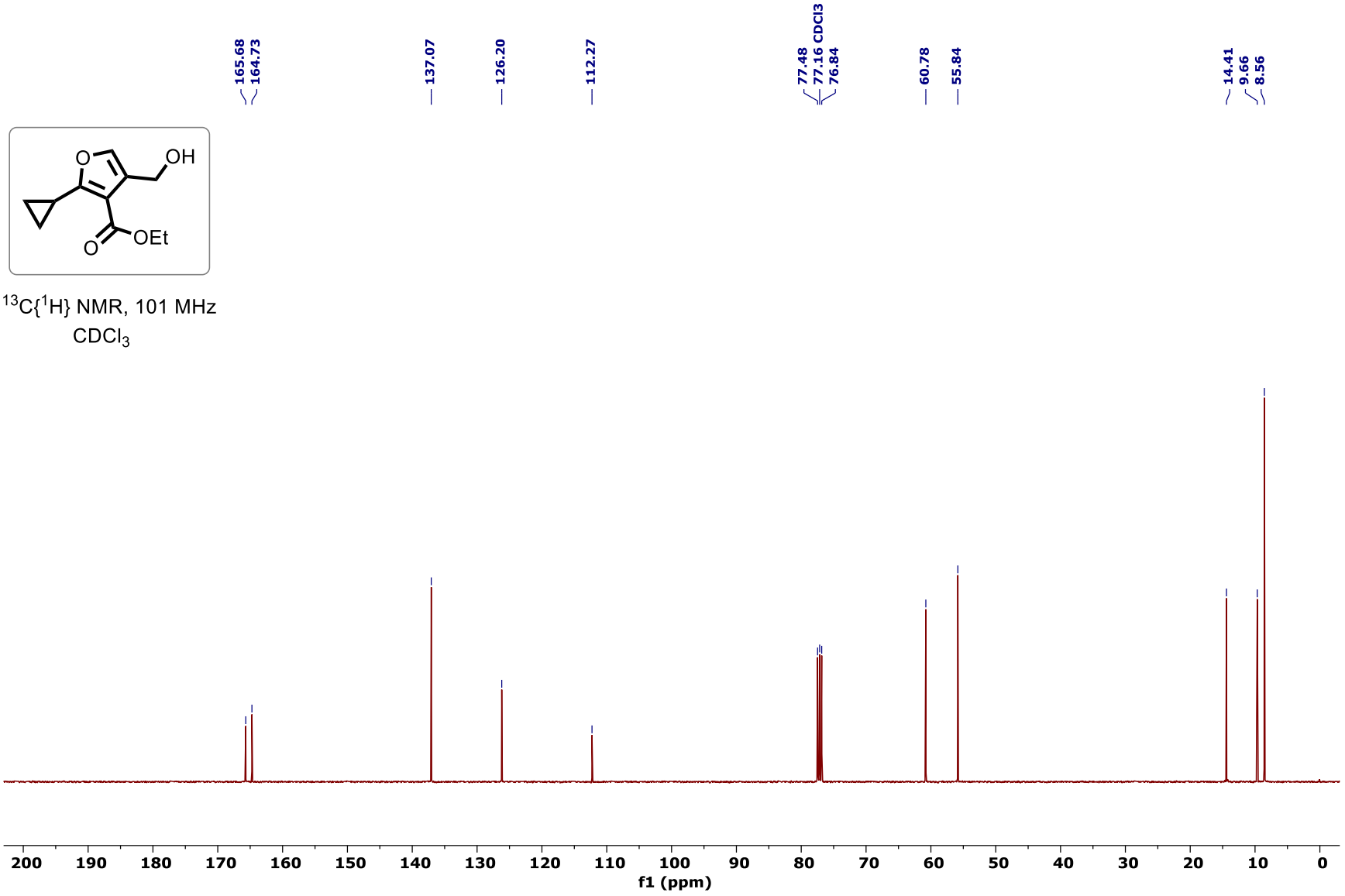
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-((benzyloxy)methyl)-4-(hydroxymethyl)furan-3-carboxylate (3v):



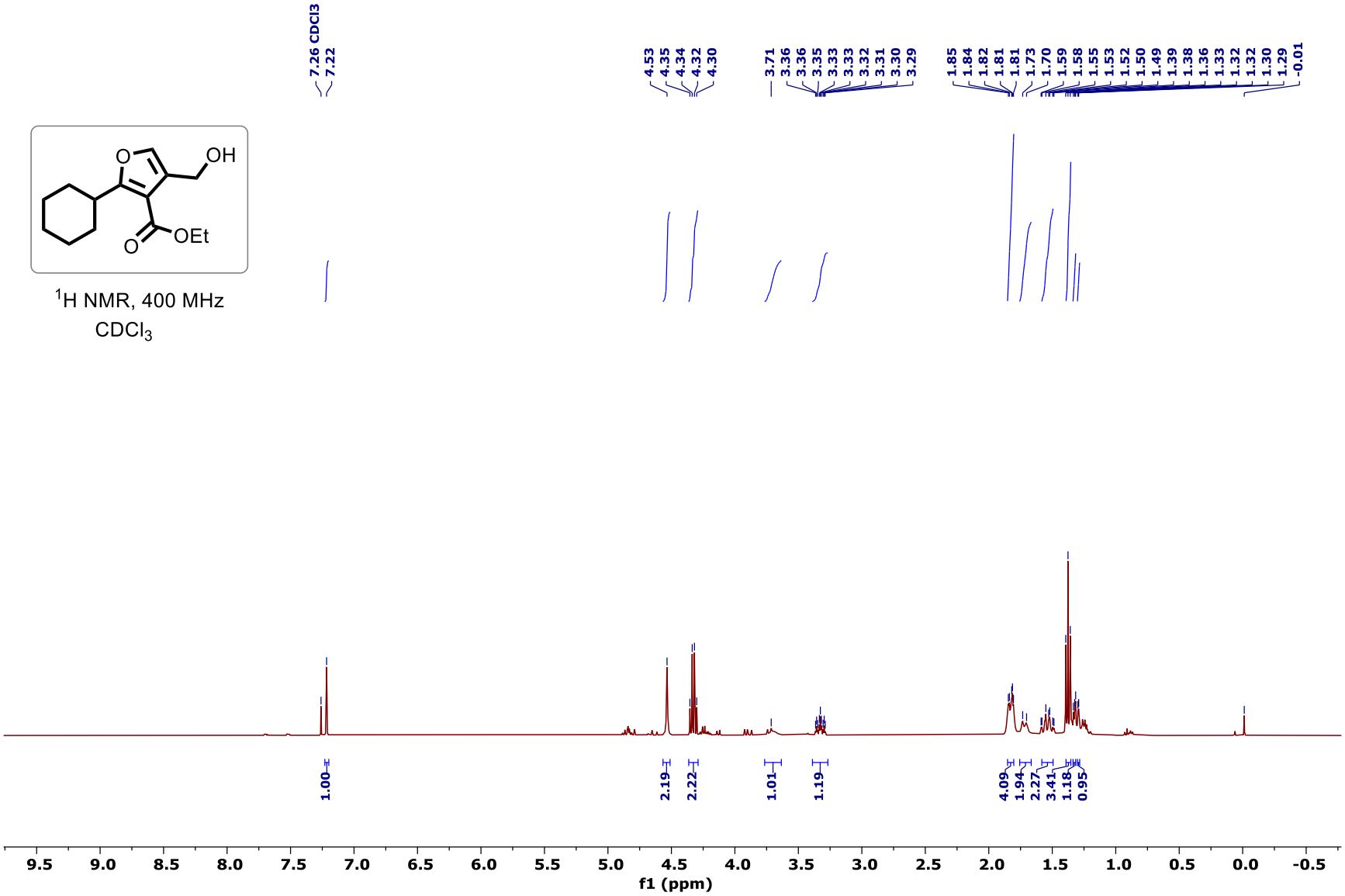
^{1}H NMR spectrum of Ethyl 2-cyclopropyl-4-(hydroxymethyl)furan-3-carboxylate (3w):



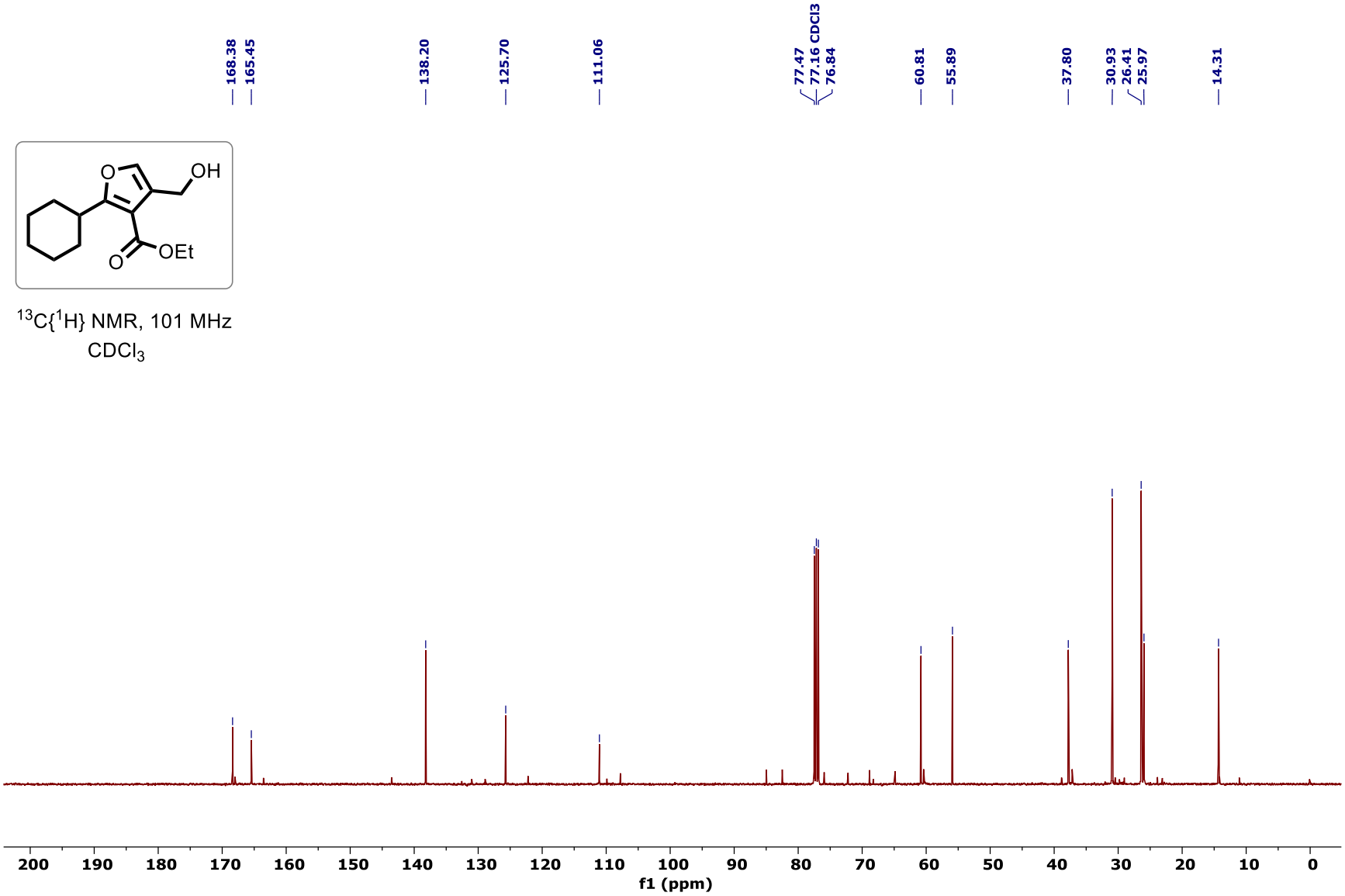
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-cyclopropyl-4-(hydroxymethyl)furan-3-carboxylate (3w):



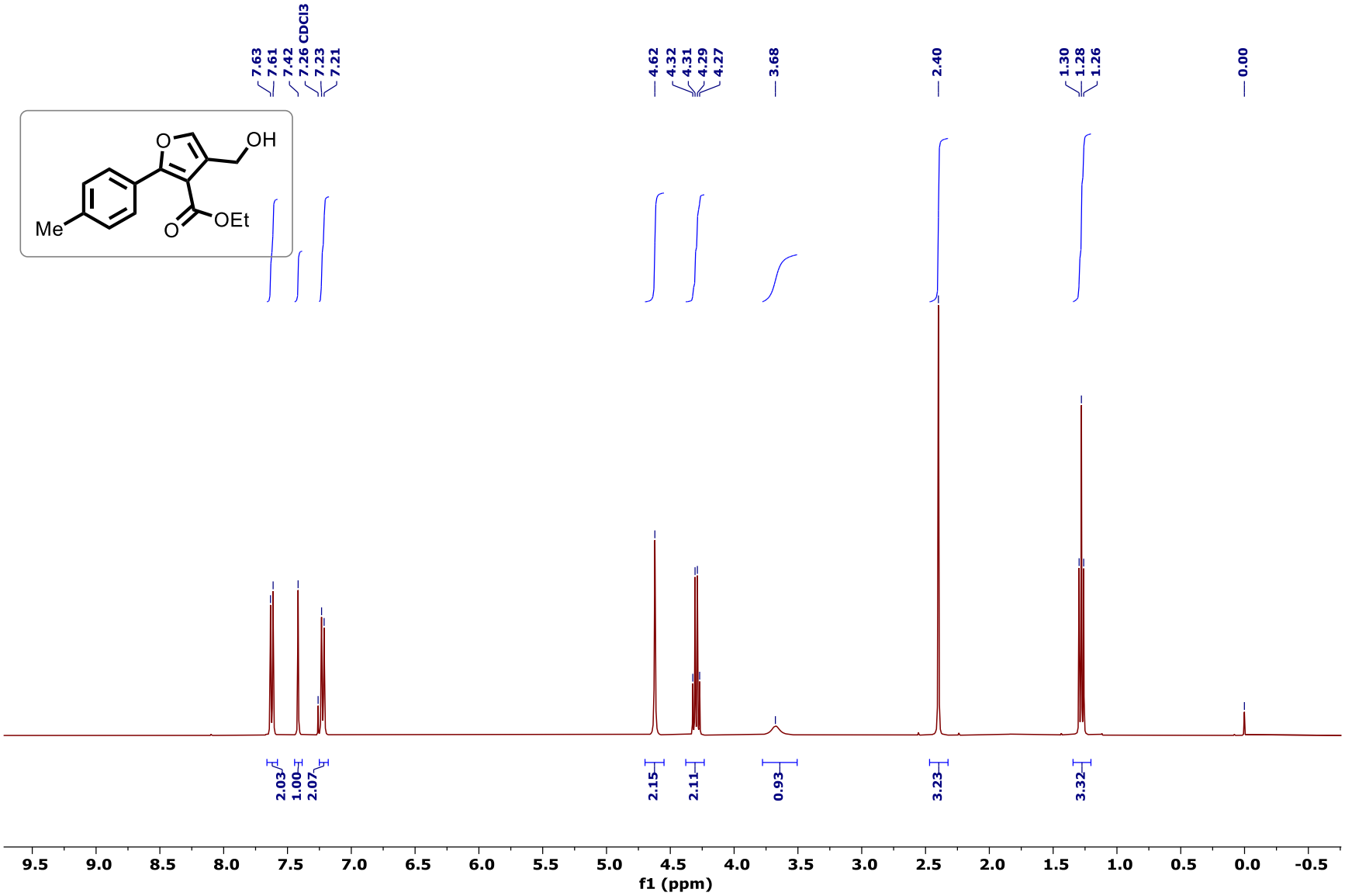
^{1}H NMR spectrum of Ethyl 2-cyclohexyl-4-(hydroxymethyl)furan-3-carboxylate (3x):



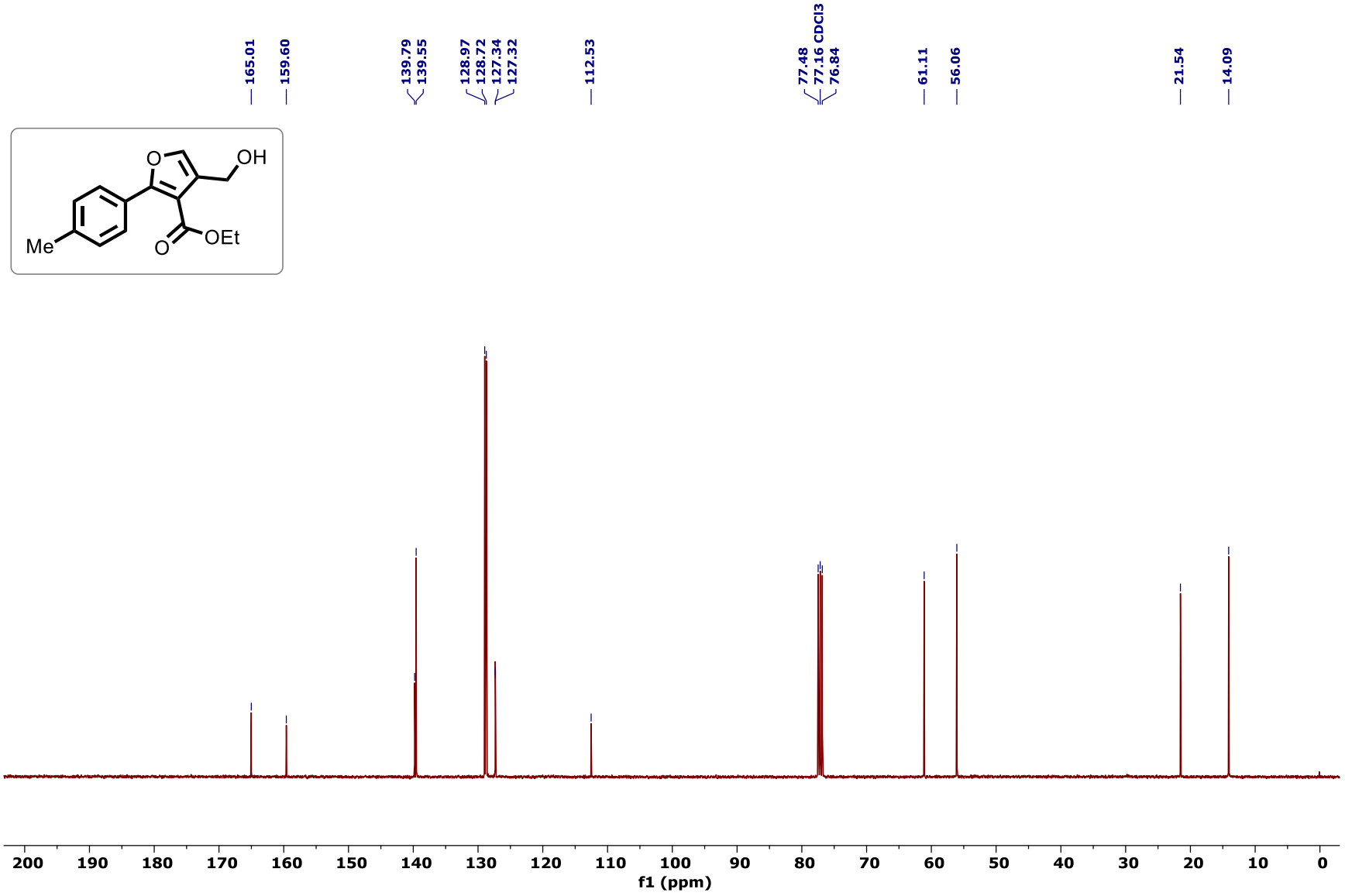
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-cyclohexyl-4-(hydroxymethyl)furan-3-carboxylate (3x):



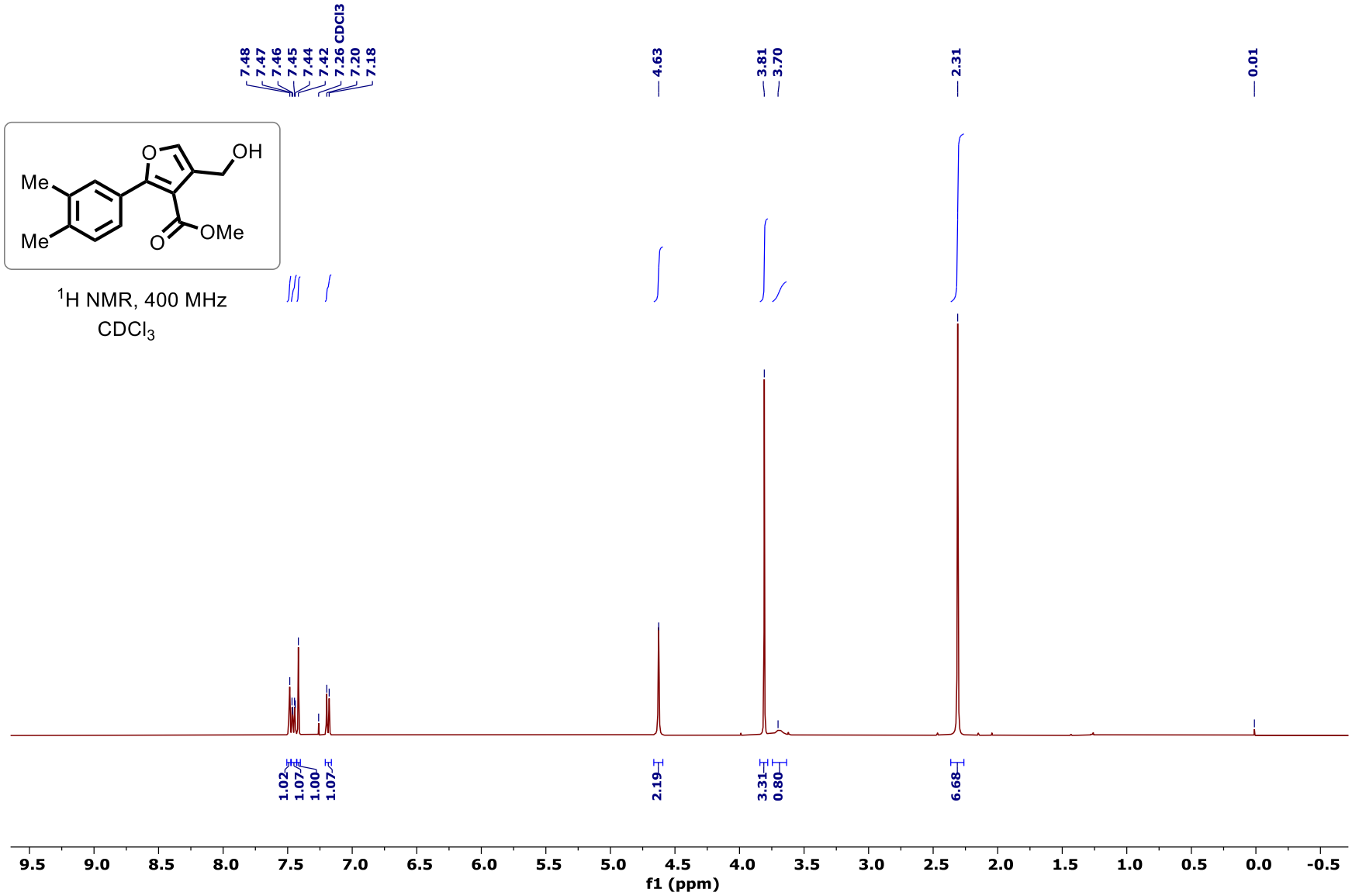
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(*p*-tolyl)furan-3-carboxylate (3y):



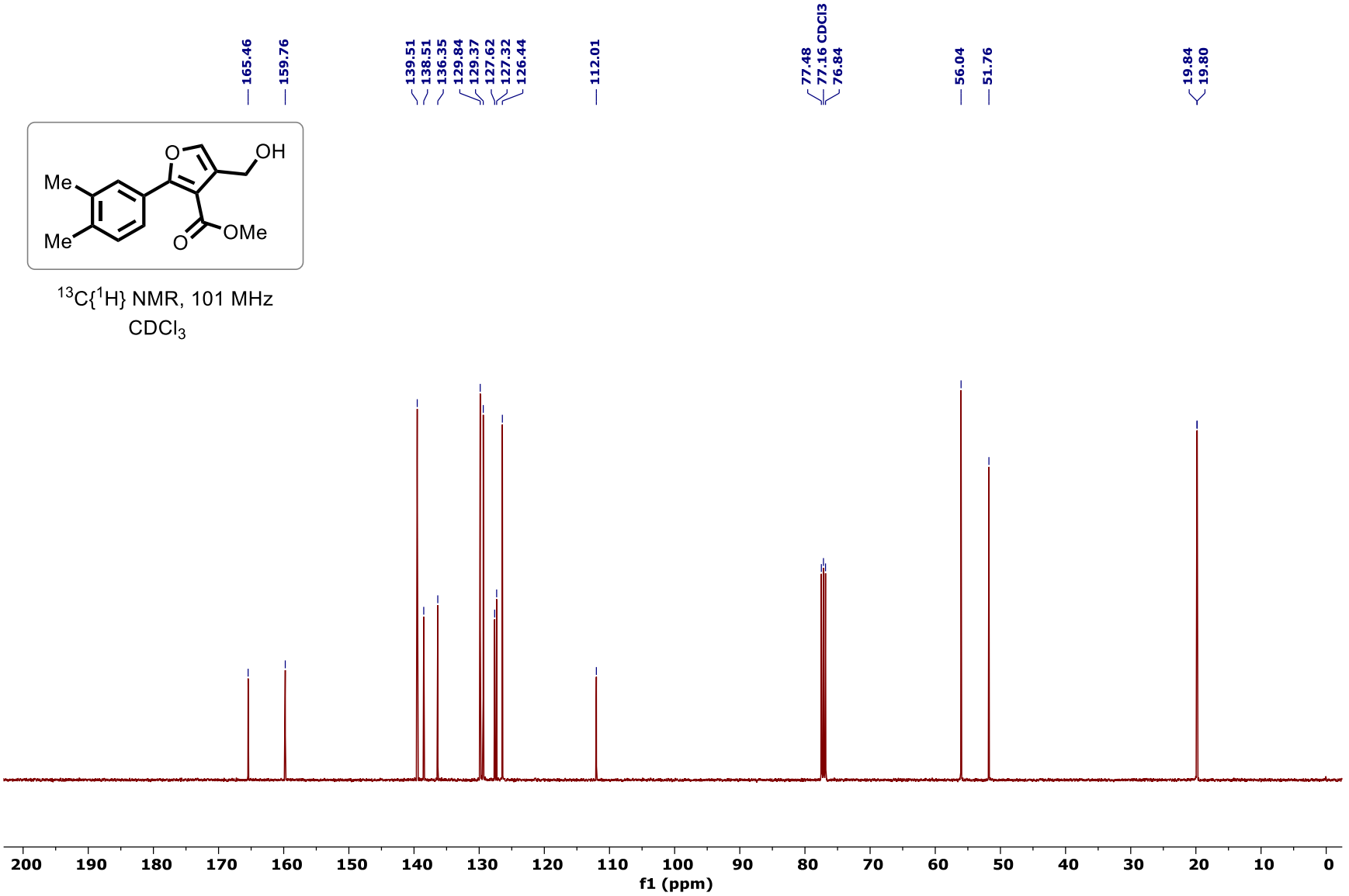
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(*p*-tolyl)furan-3-carboxylate (3y):



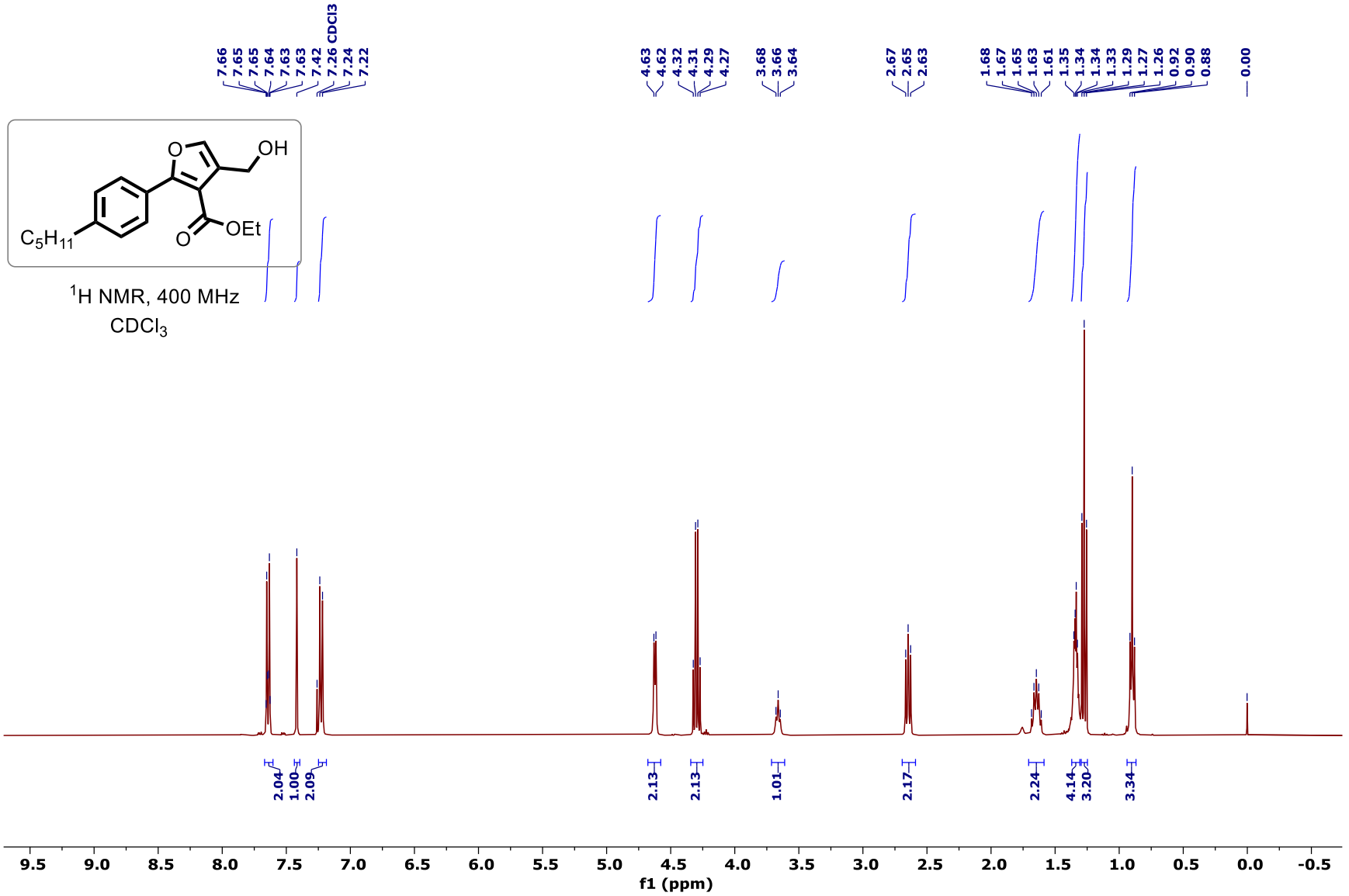
^{1}H NMR spectrum of Methyl 2-(3,4-dimethylphenyl)-4-(hydroxymethyl)furan-3-carboxylate (3z):



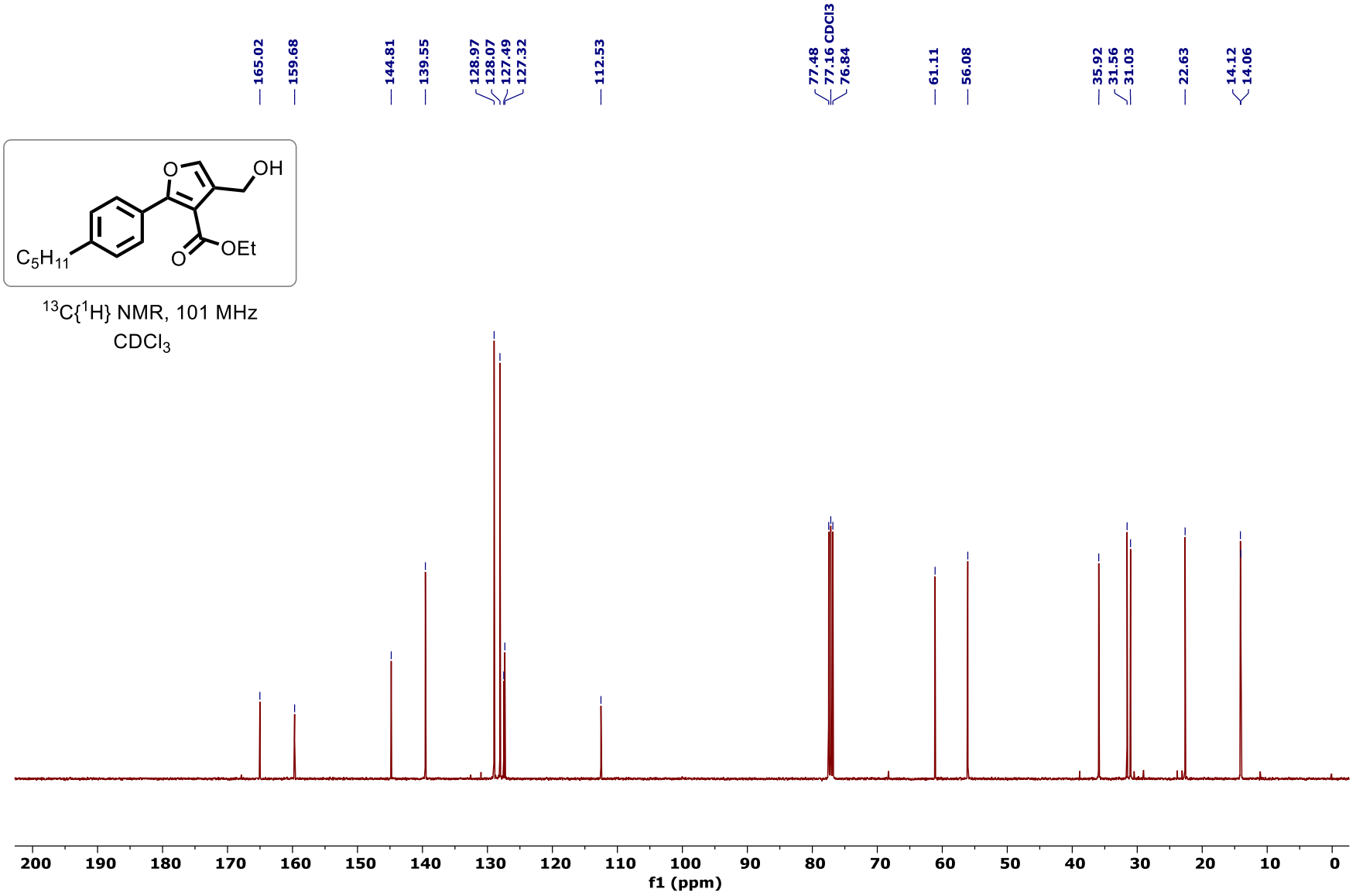
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 2-(3,4-dimethylphenyl)-4-(hydroxymethyl)furan-3-carboxylate (3z):



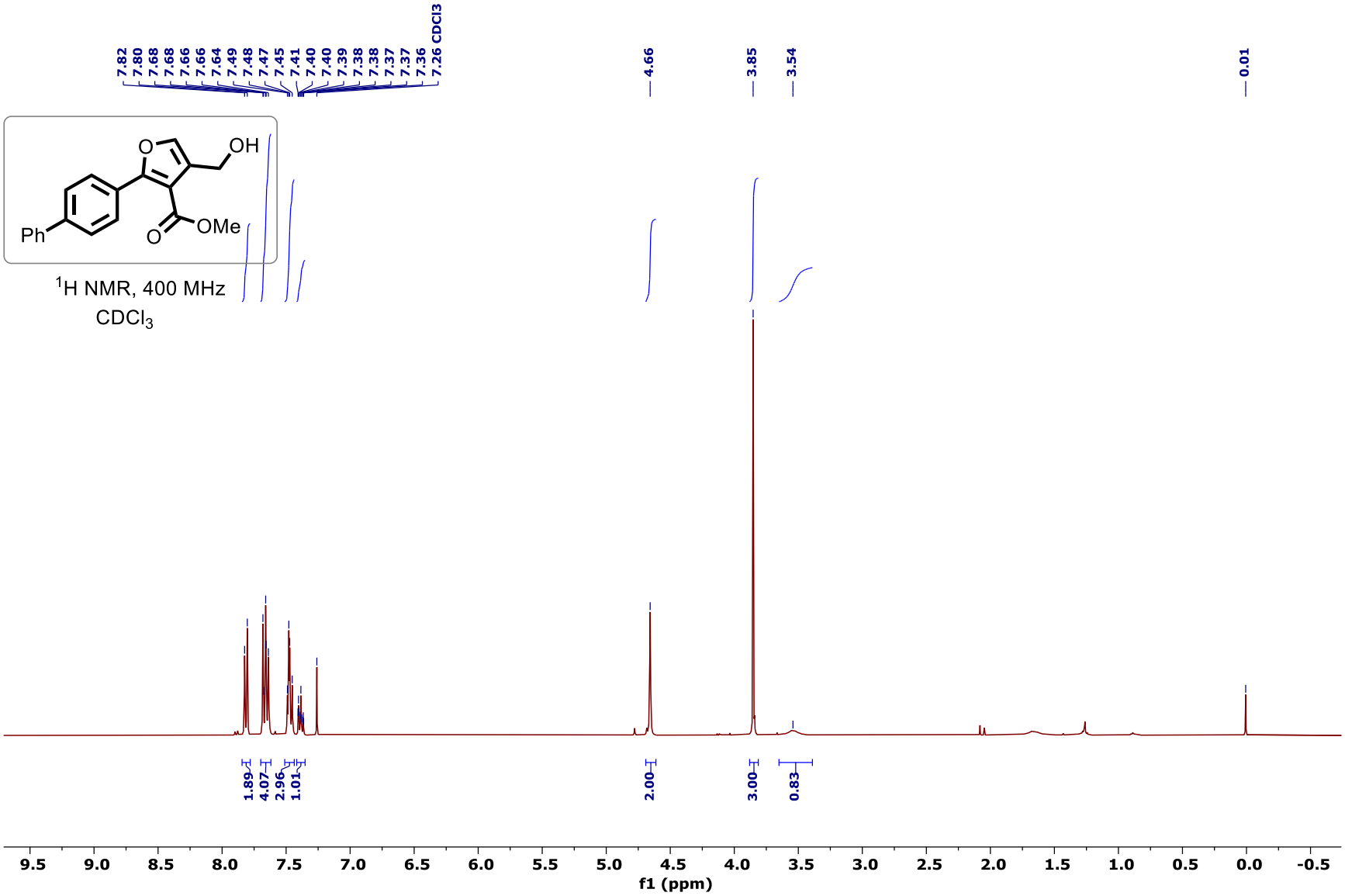
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(4-pentylphenyl)furan-3-carboxylate (3a′):



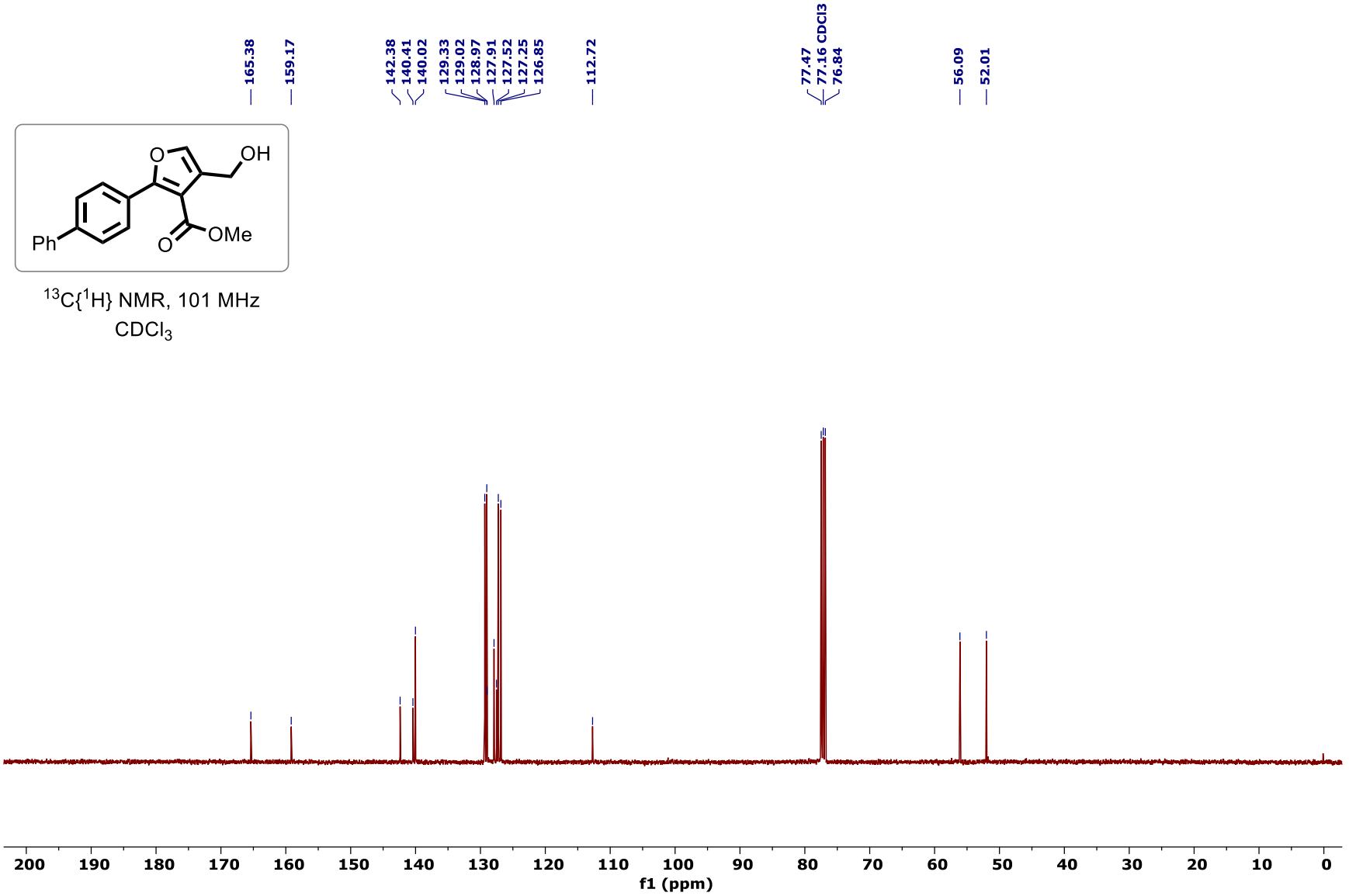
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(4-pentylphenyl)furan-3-carboxylate (3a′):



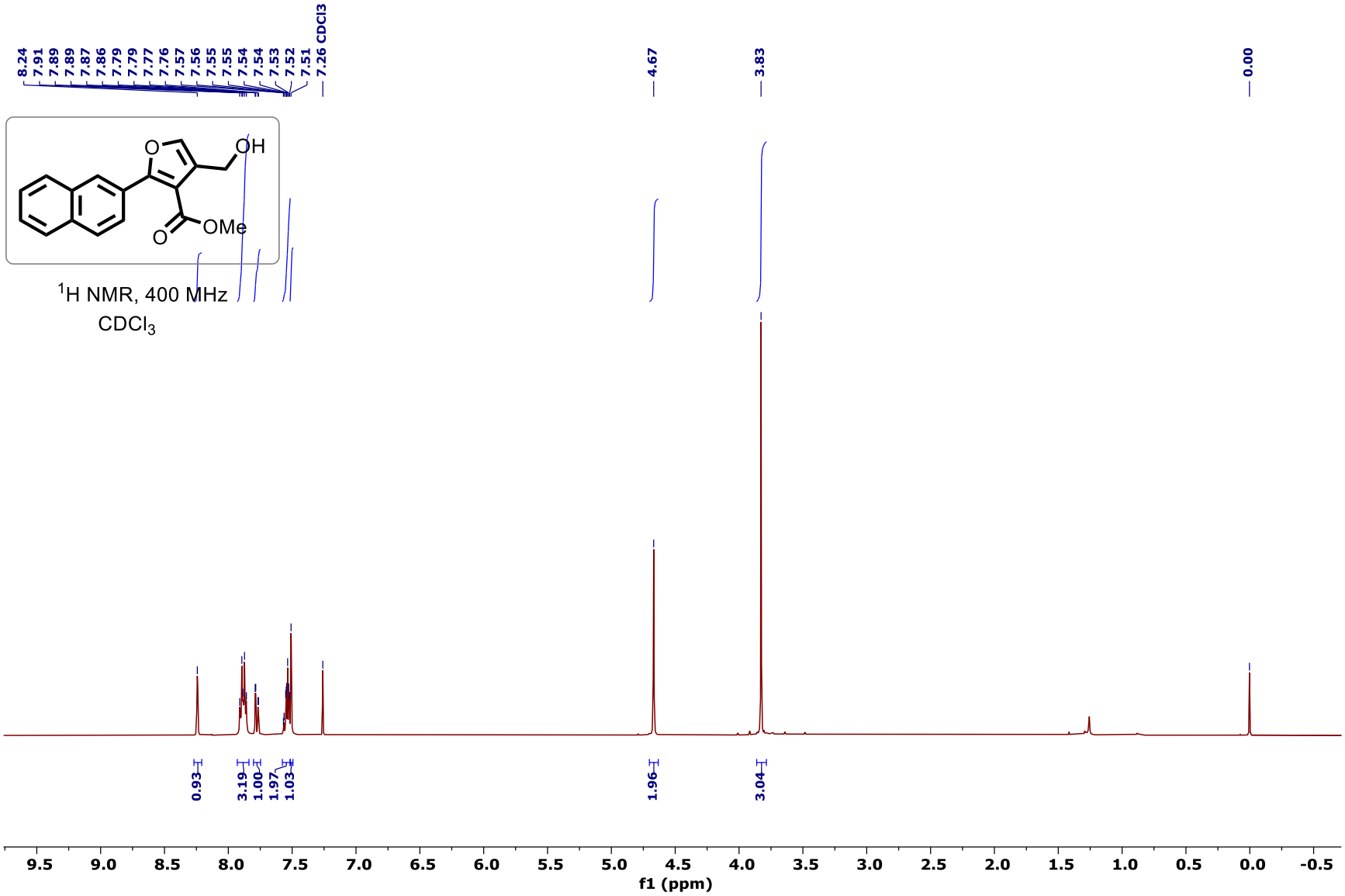
^{1}H NMR spectrum of Methyl 2-([1,1'-biphenyl]-4-yl)-4-(hydroxymethyl)furan-3-carboxylate (3b′):



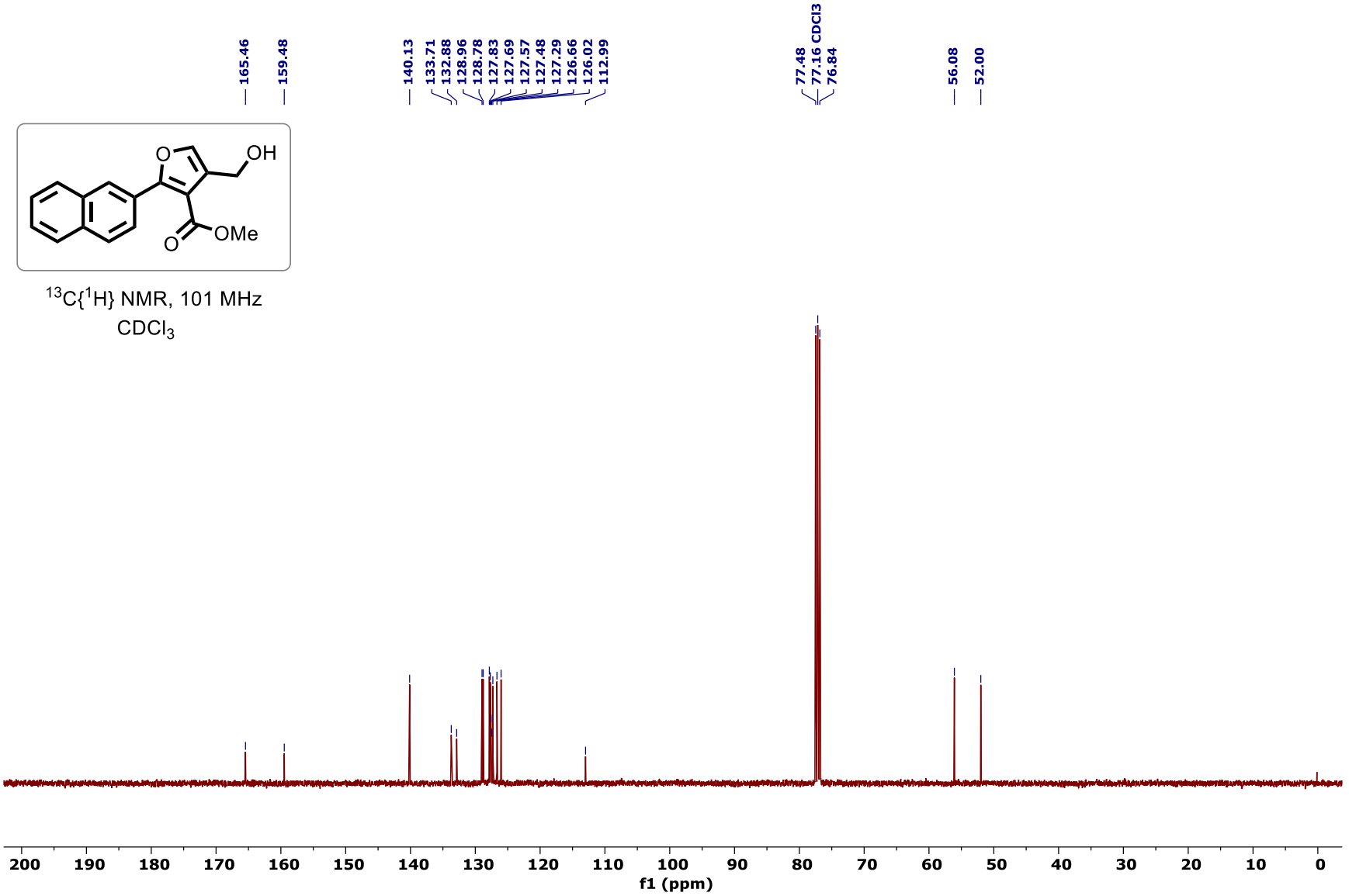
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 2-([1,1'-biphenyl]-4-yl)-4-(hydroxymethyl)furan-3-carboxylate (3b′):



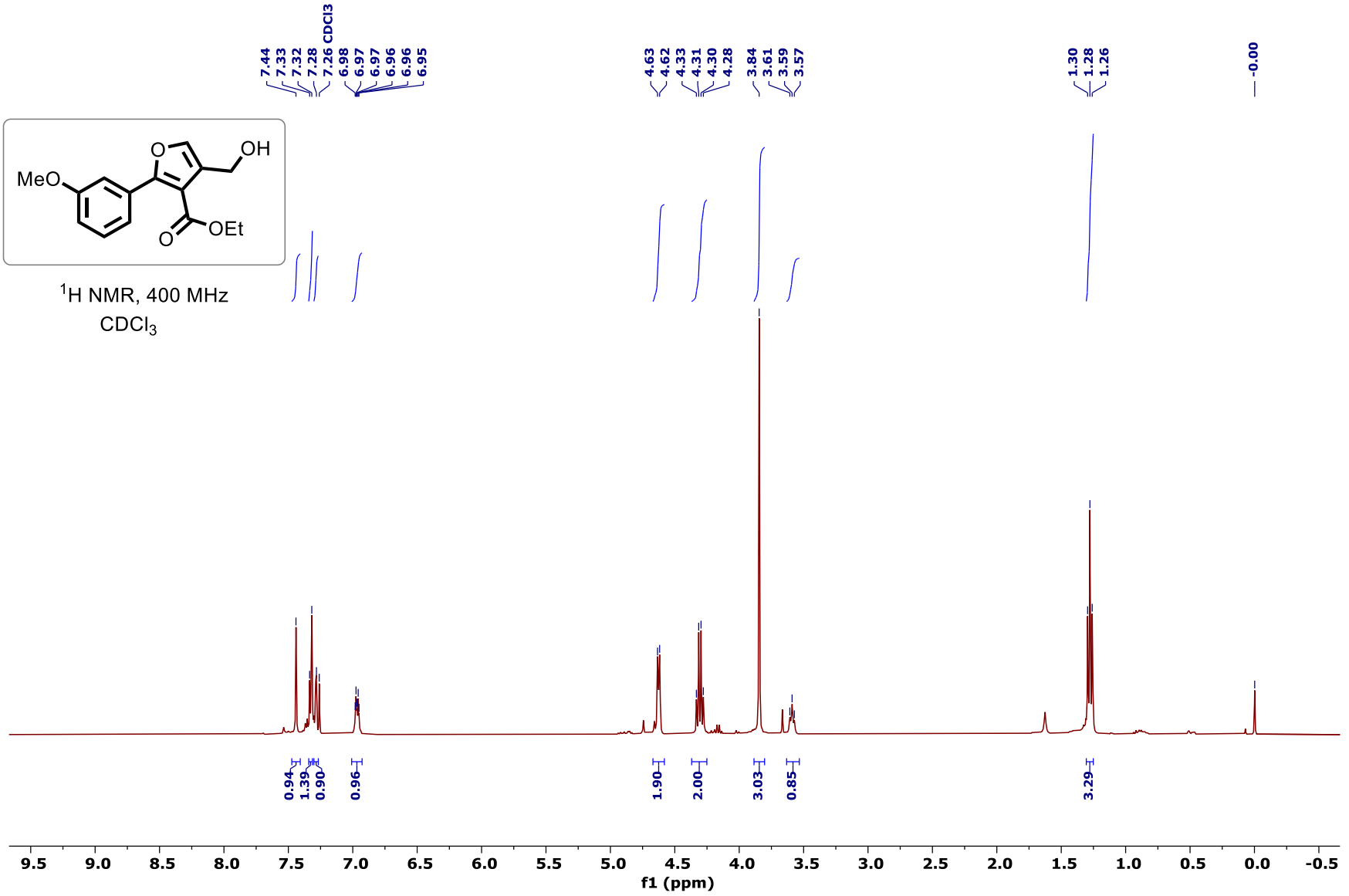
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-(naphthalen-2-yl)furan-3-carboxylate (3c′):



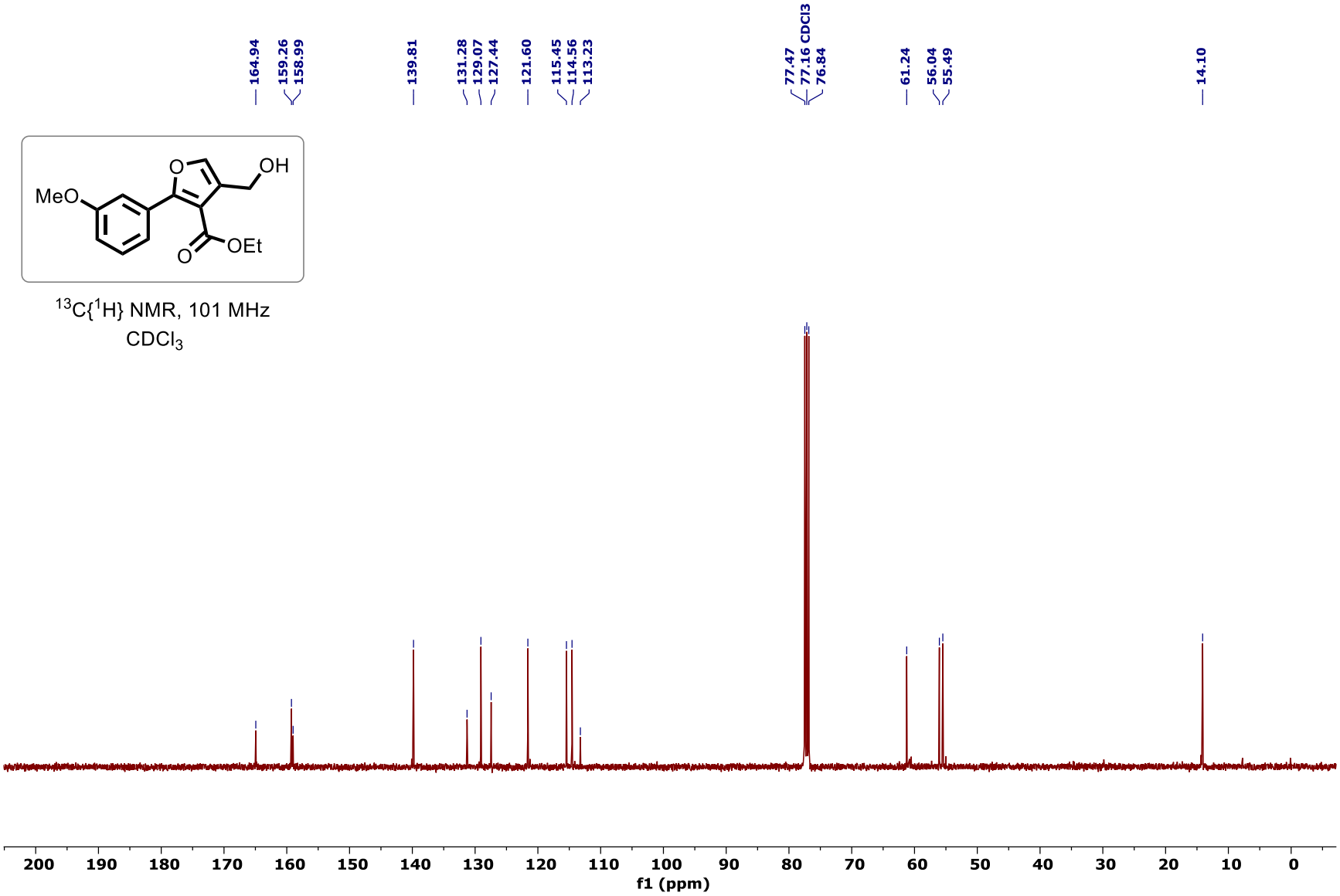
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-(naphthalen-2-yl)furan-3-carboxylate (3c′):



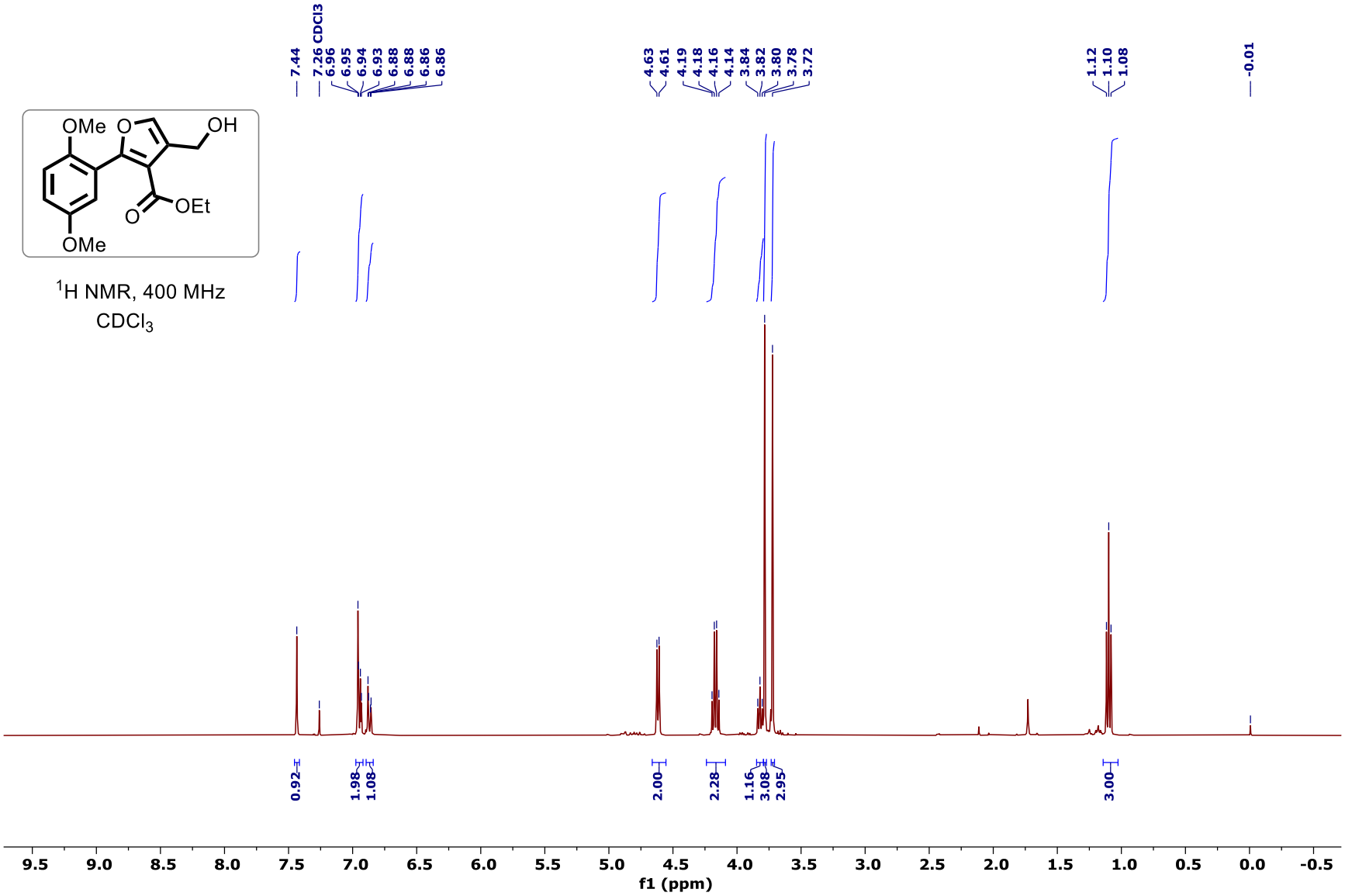
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(3-methoxyphenyl)furan-3-carboxylate (3d′):



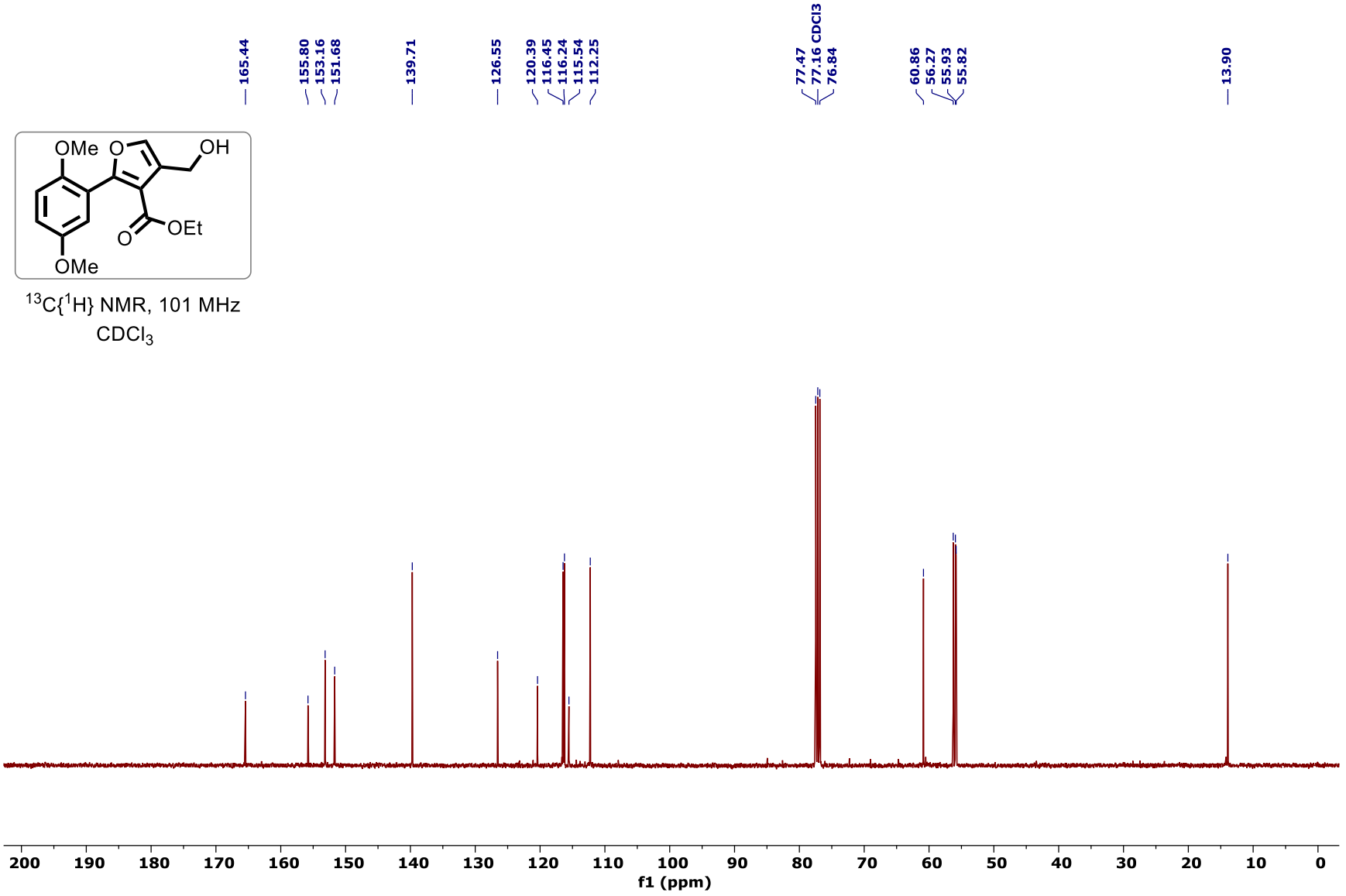
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(3-methoxyphenyl)furan-3-carboxylate (3d′):



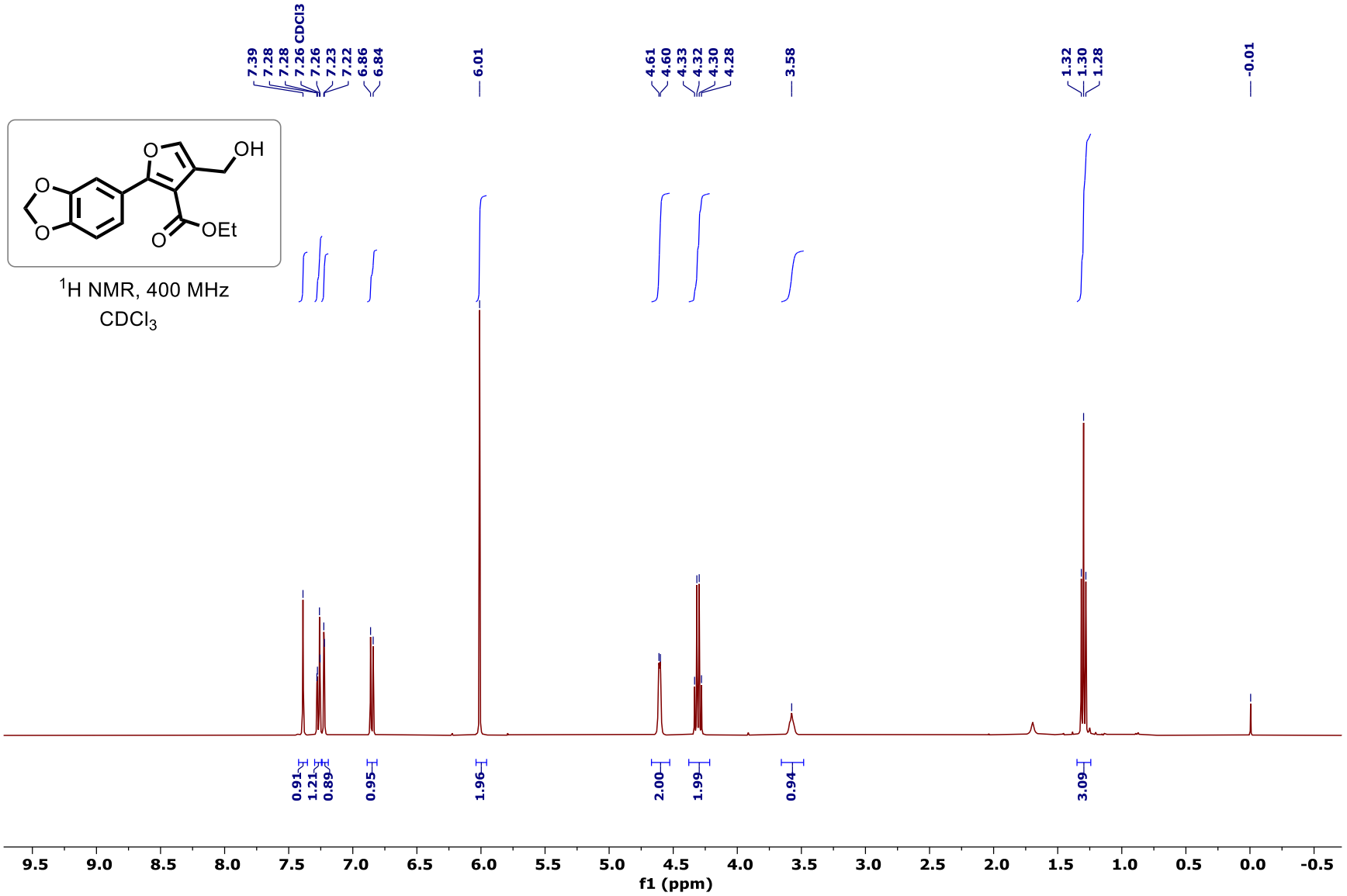
^{1}H NMR spectrum of Ethyl 2-(2,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-carboxylate (3e′):



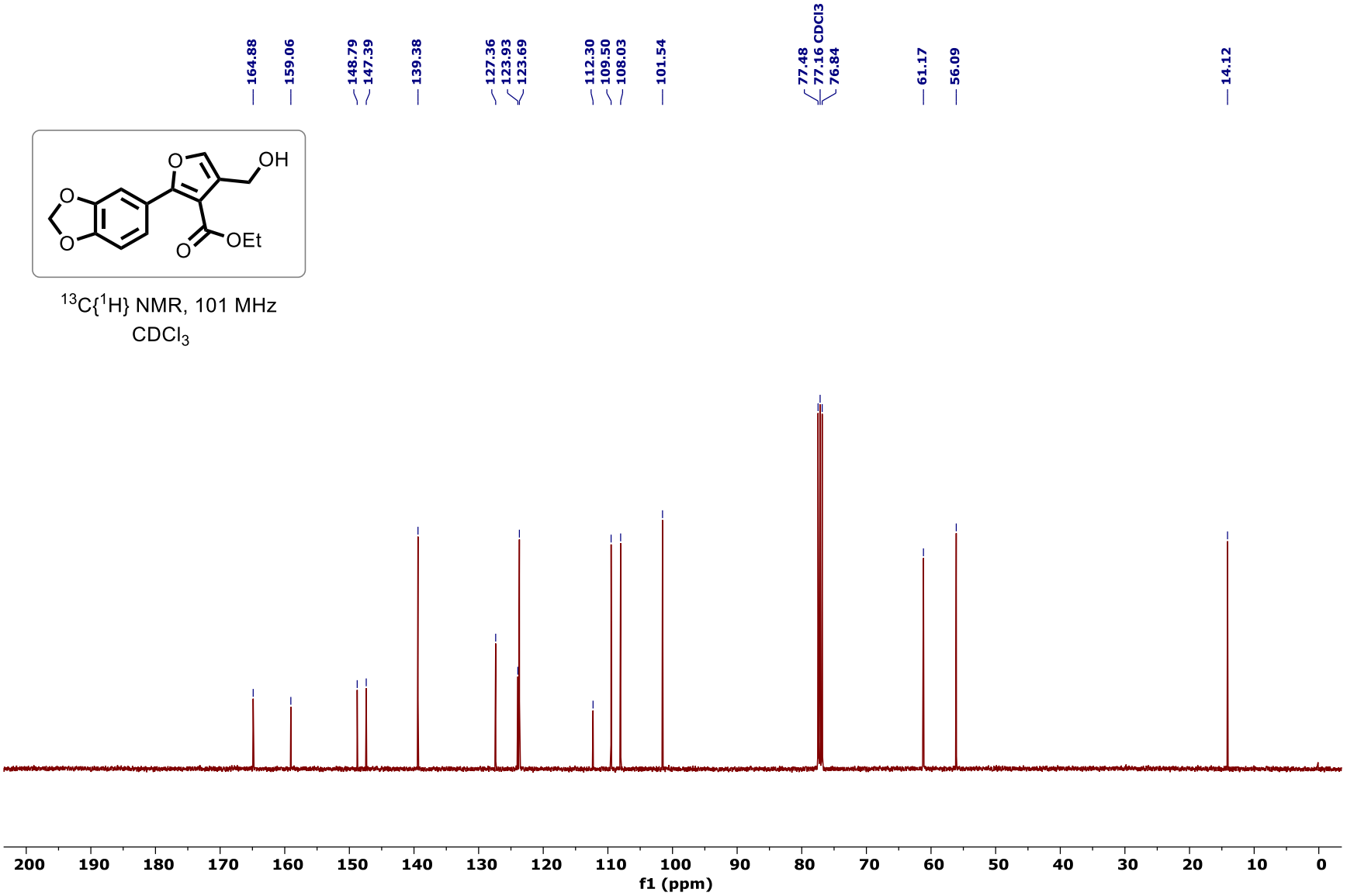
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-(2,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-carboxylate (3e′):



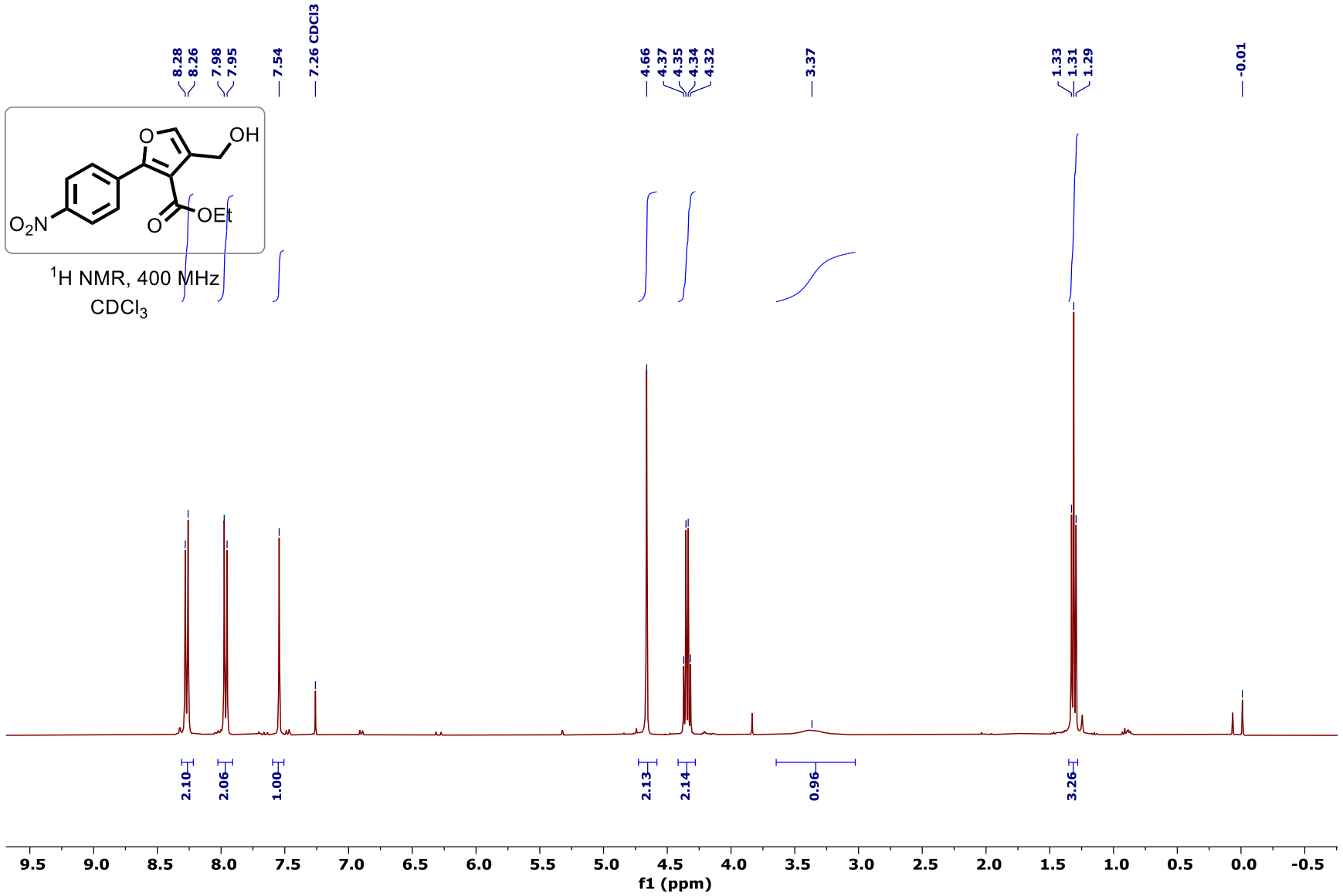
^{1}H NMR spectrum of Ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-4-(hydroxymethyl)furan-3-carboxylate (3f′):



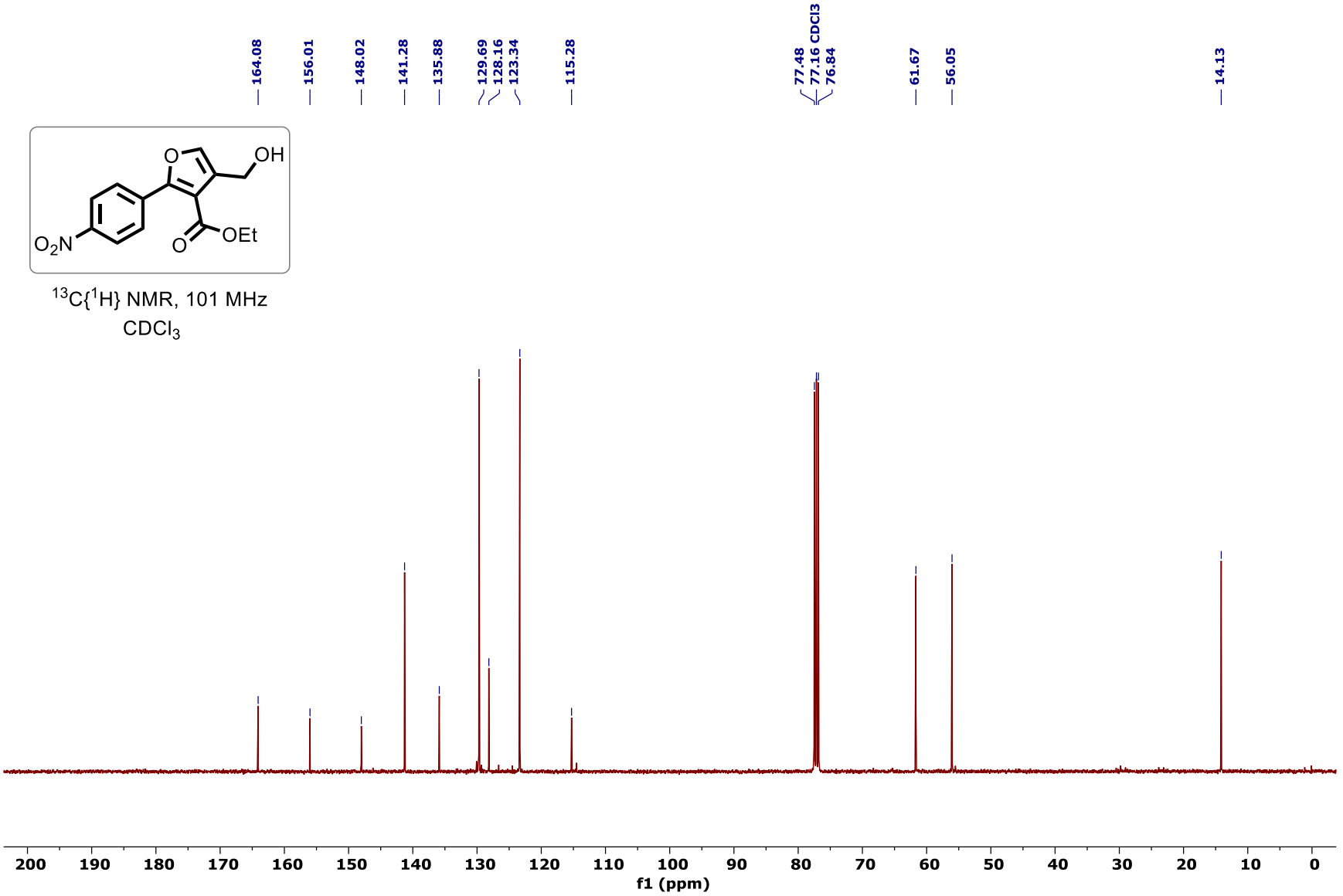
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-4-(hydroxymethyl)furan-3-carboxylate (3f′):



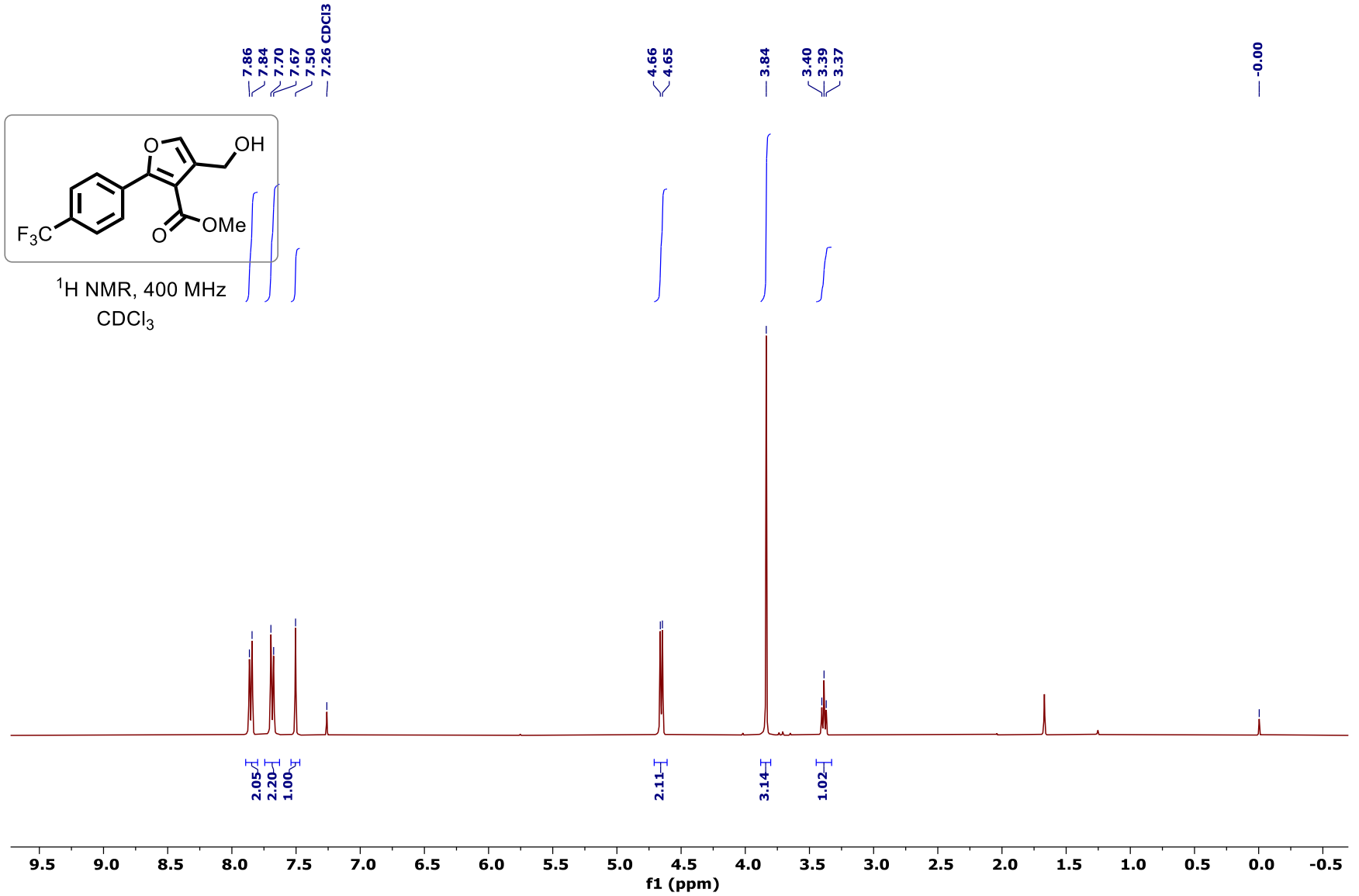
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(4-nitrophenyl)furan-3-carboxylate (3g′):



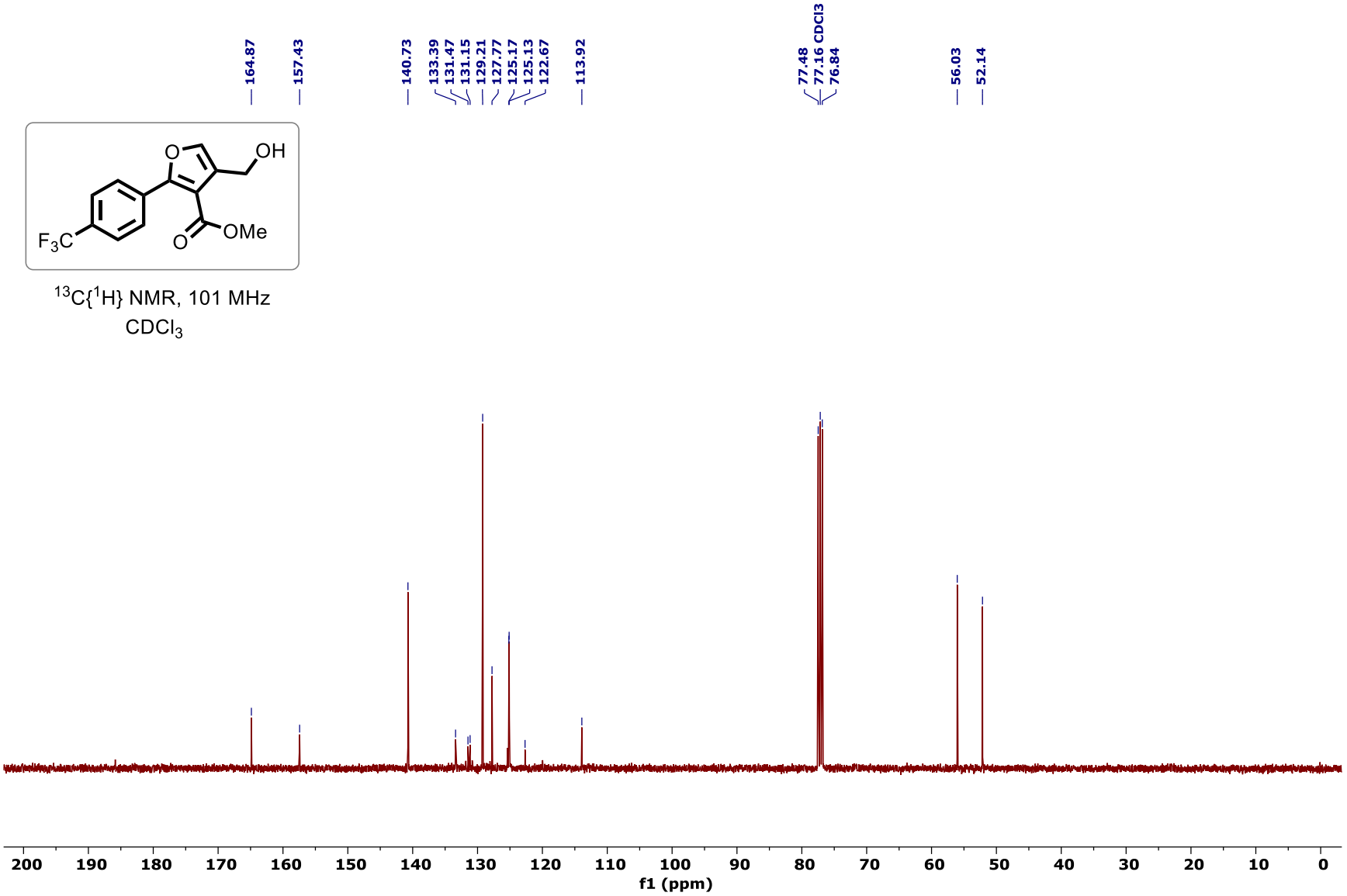
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(4-nitrophenyl)furan-3-carboxylate (3g′):



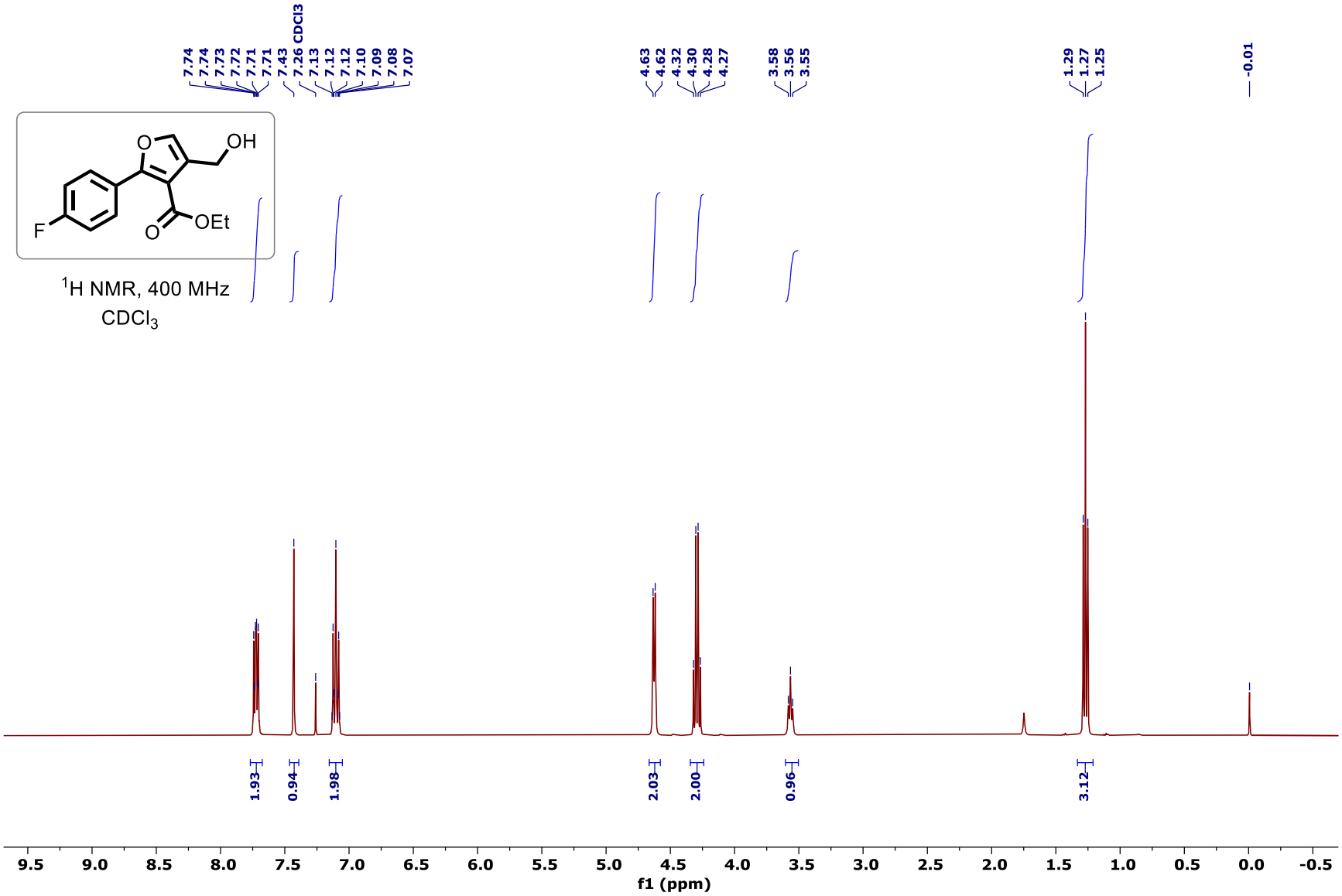
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (3h′):



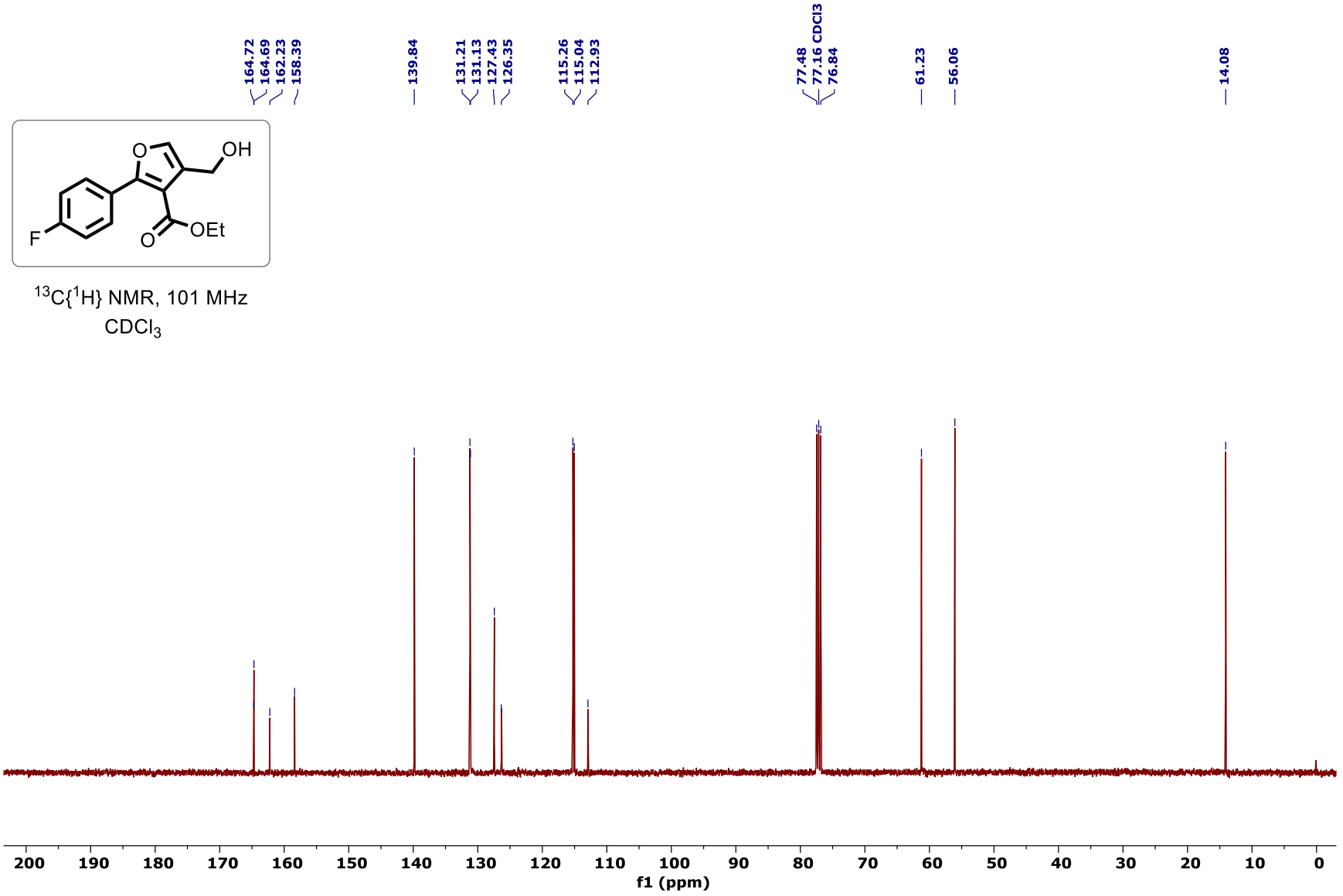
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (3h′):



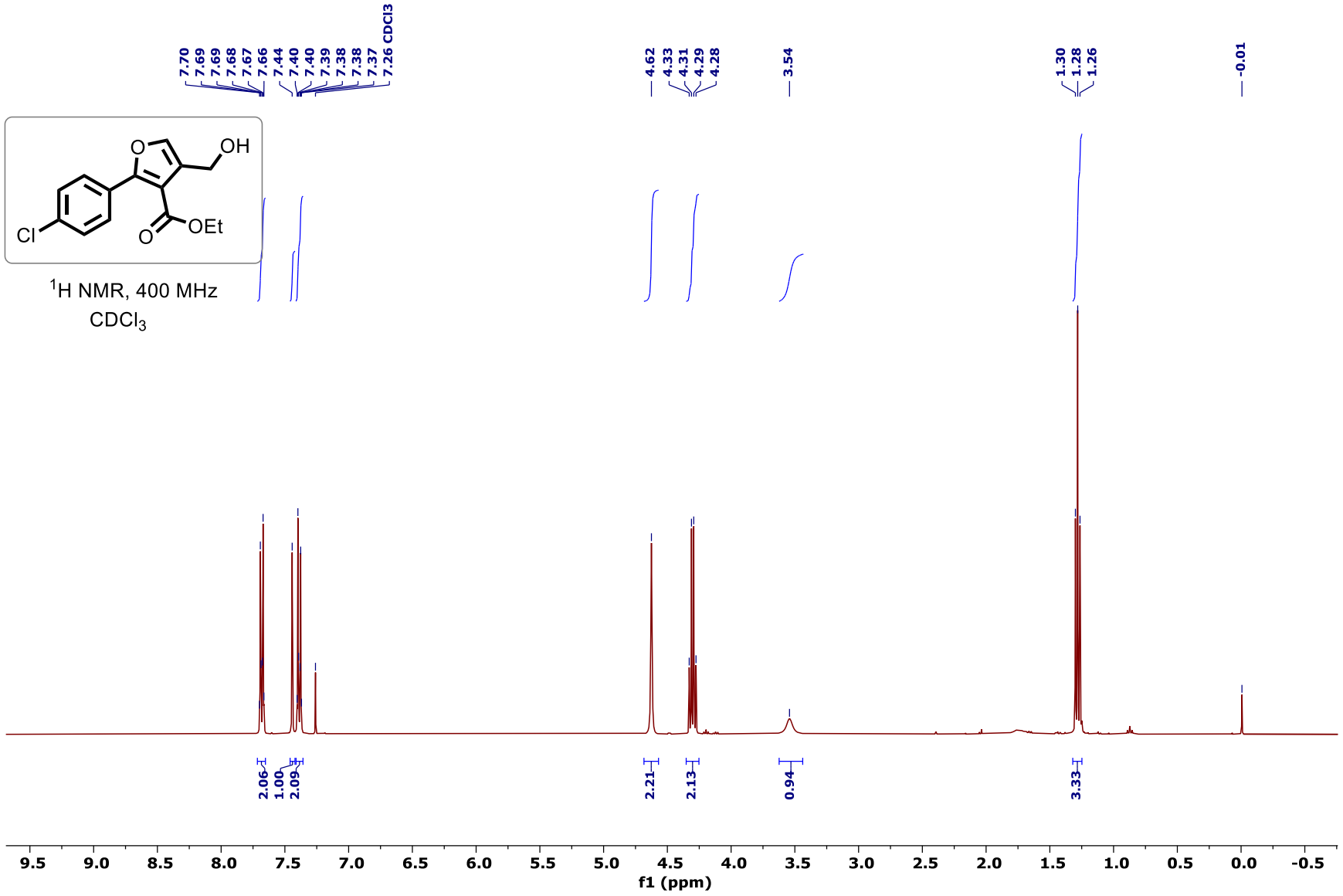
^{1}H NMR spectrum of Ethyl 2-(4-fluorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3i′):



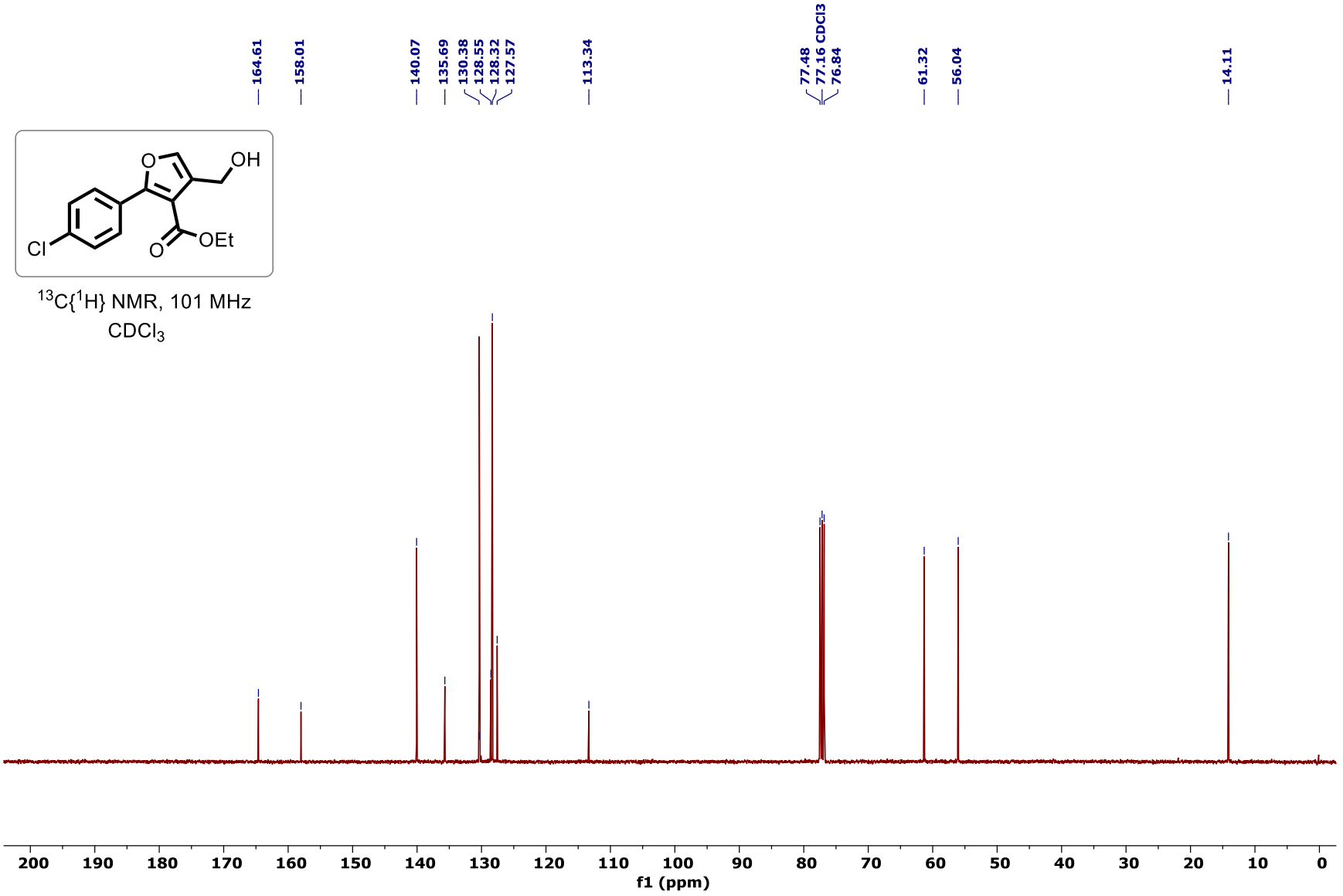
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-(4-fluorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3i′):



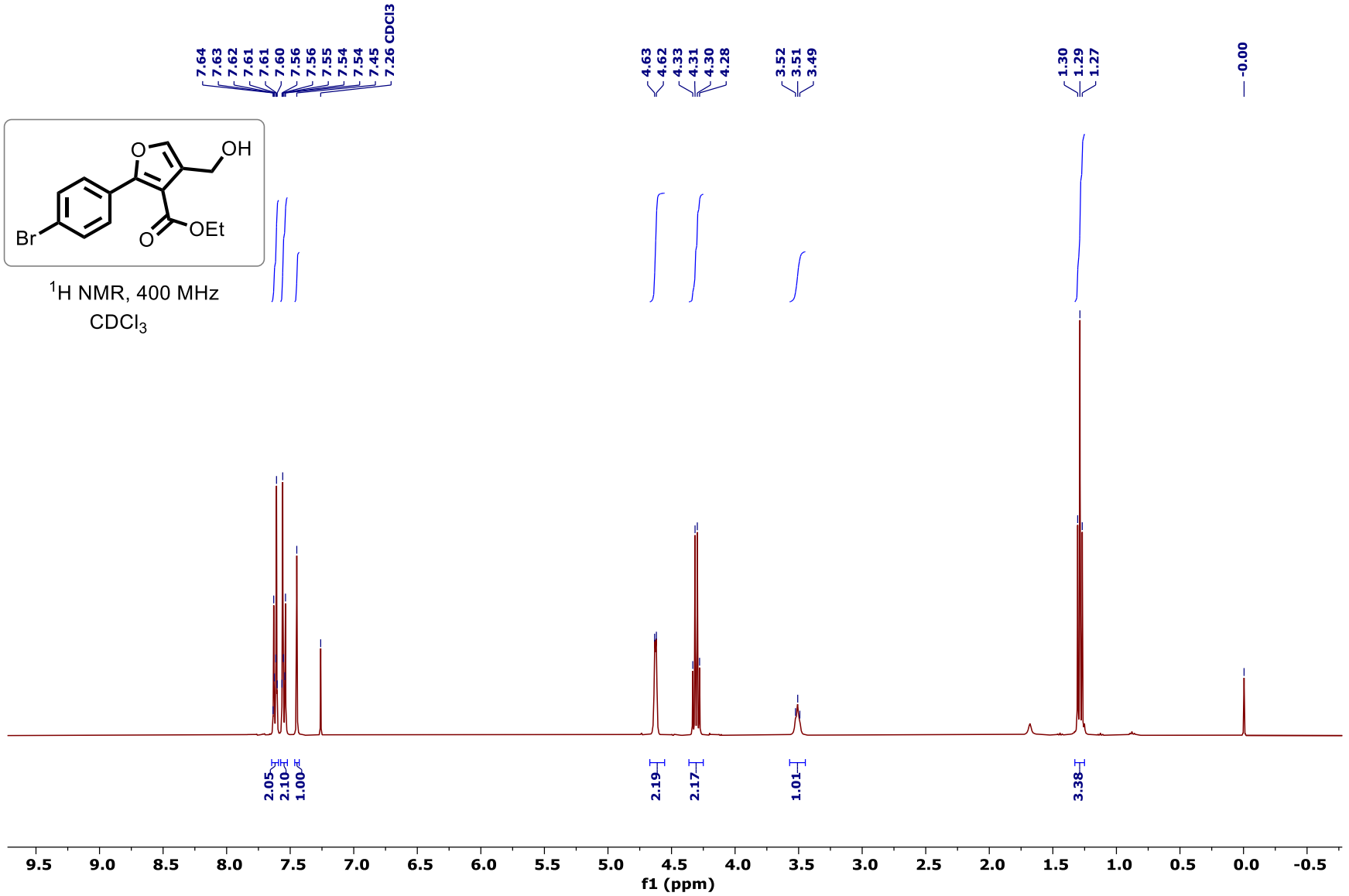
^{1}H NMR spectrum of Ethyl 2-(4-chlorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3j′):



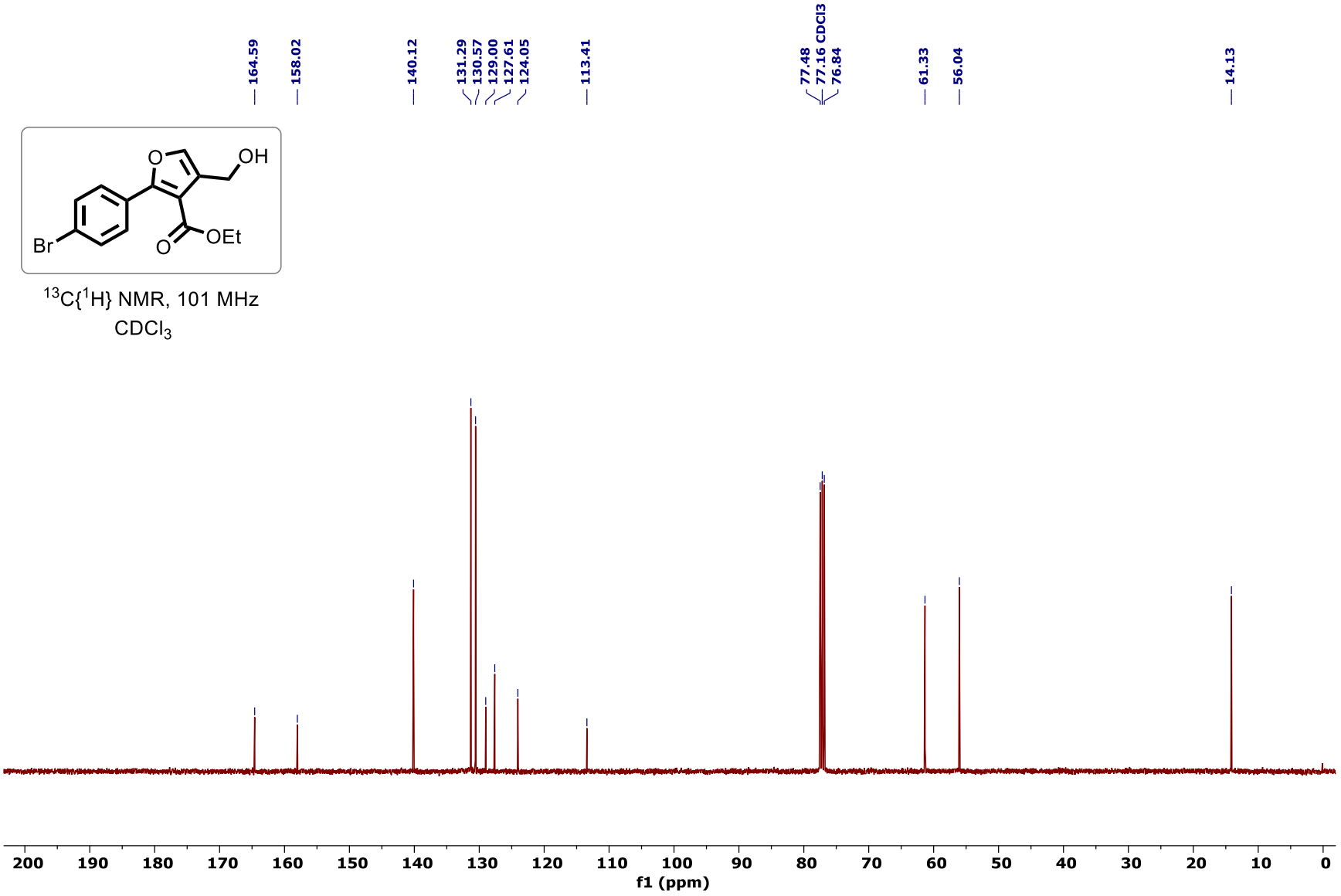
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-(4-chlorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3j′):



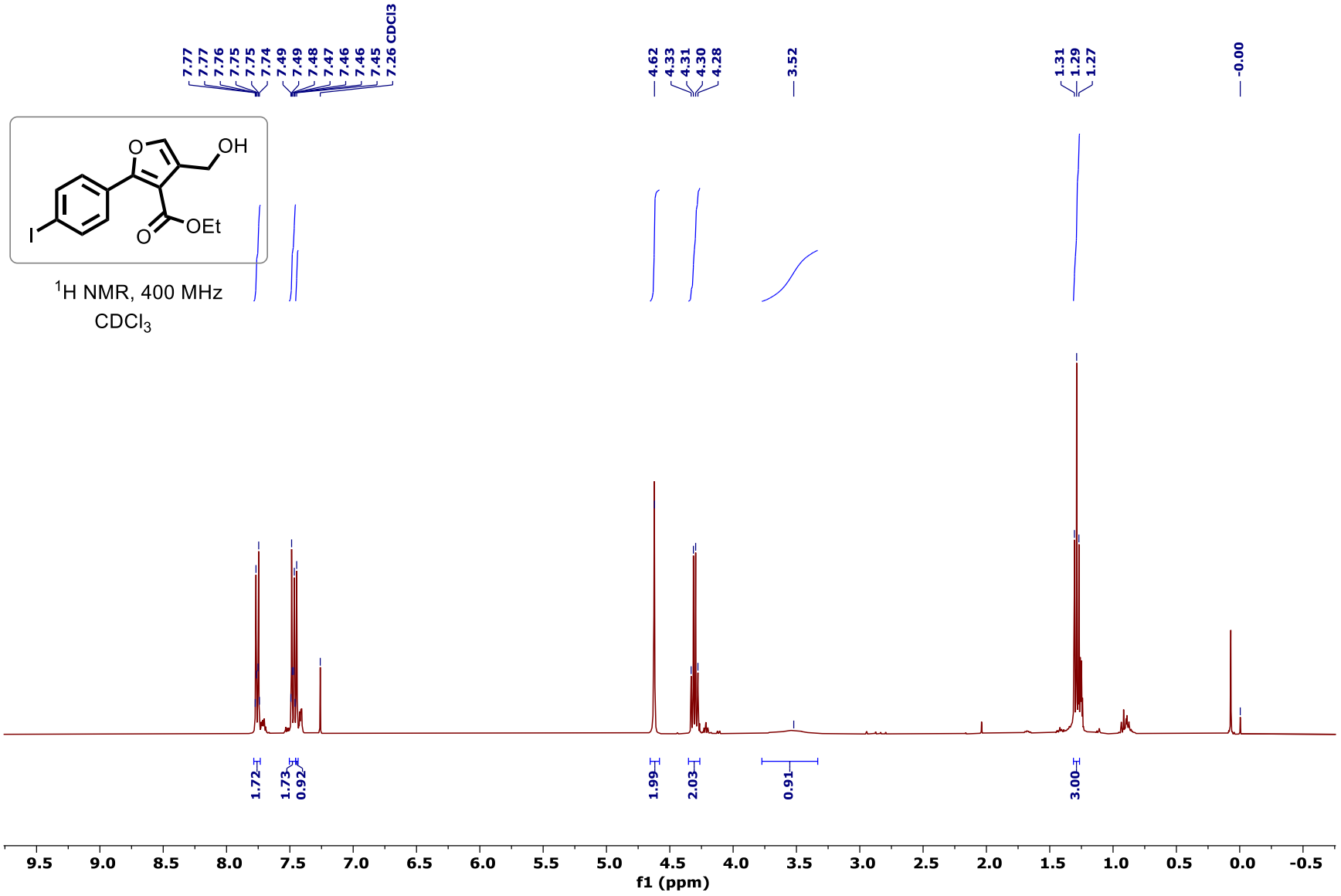
^{1}H NMR spectrum of Ethyl 2-(4-bromophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3k′):



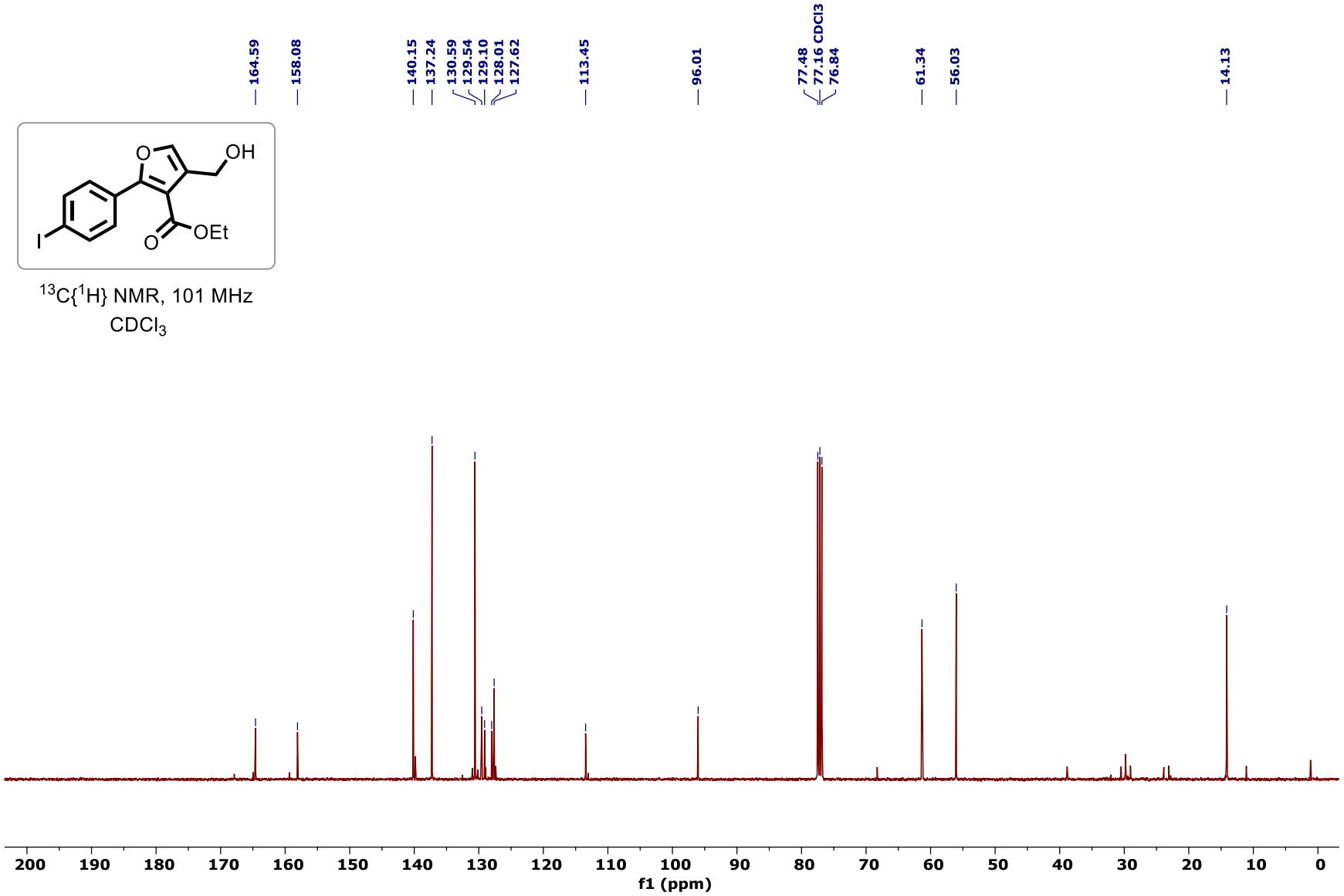
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-(4-bromophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3k′):



^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(4-iodophenyl)furan-3-carboxylate (3l′):

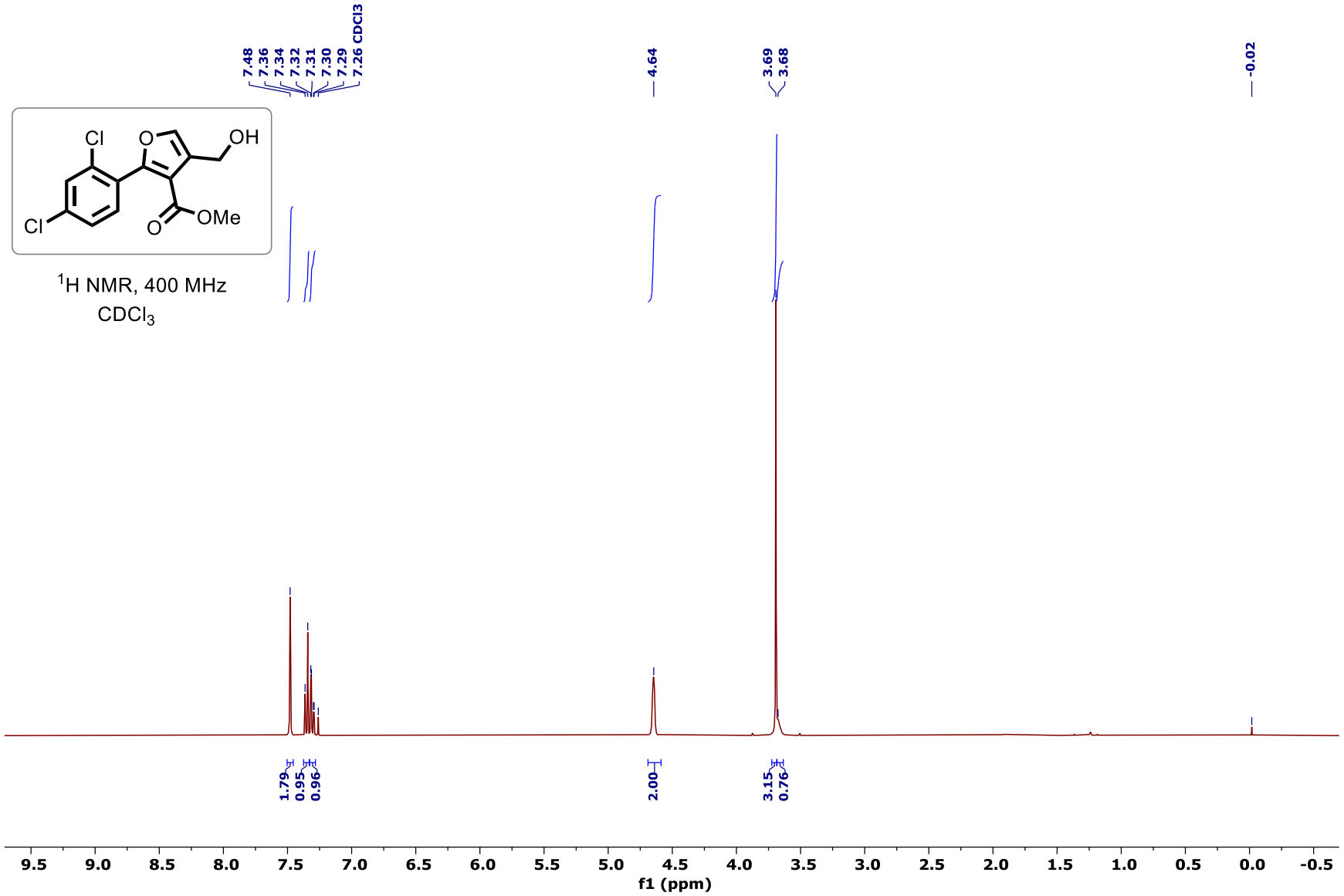


$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(4-iodophenyl)furan-3-carboxylate (3l′):

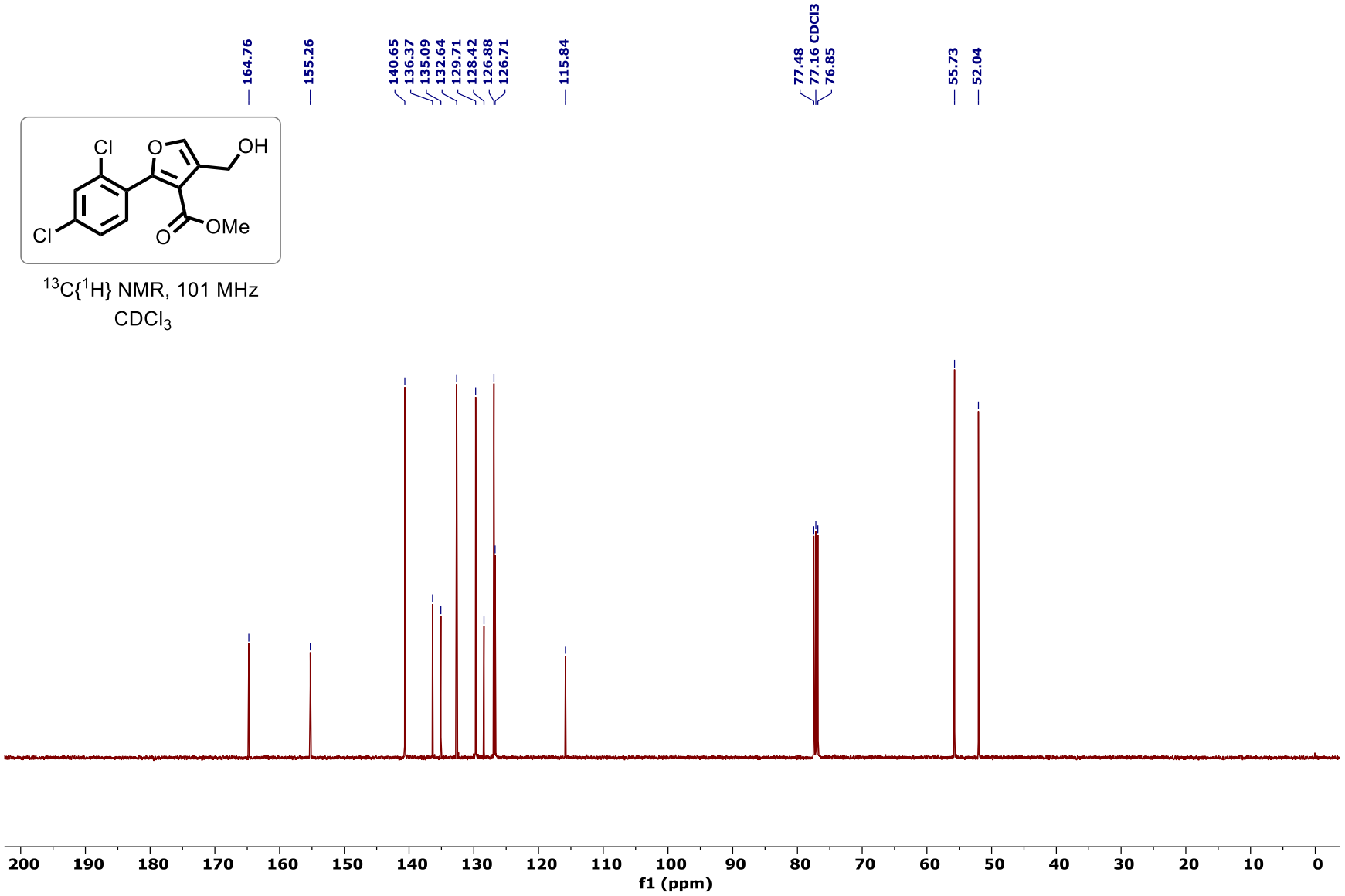


$^{13}C\{^{1}H\}$ NMR, 101 MHz
$CDCl_3$

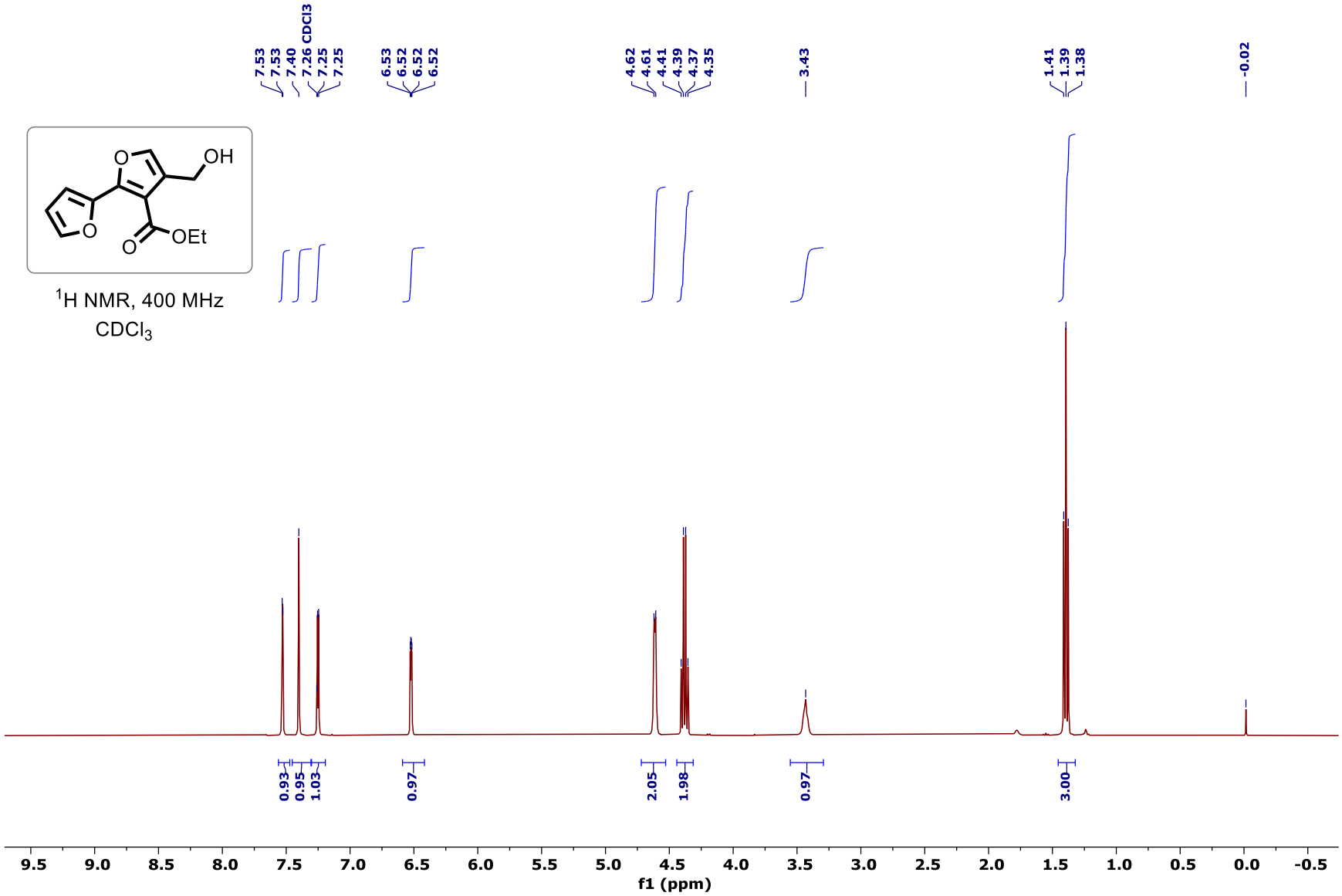
^{1}H NMR spectrum of Methyl 2-(2,4-dichlorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3m′):



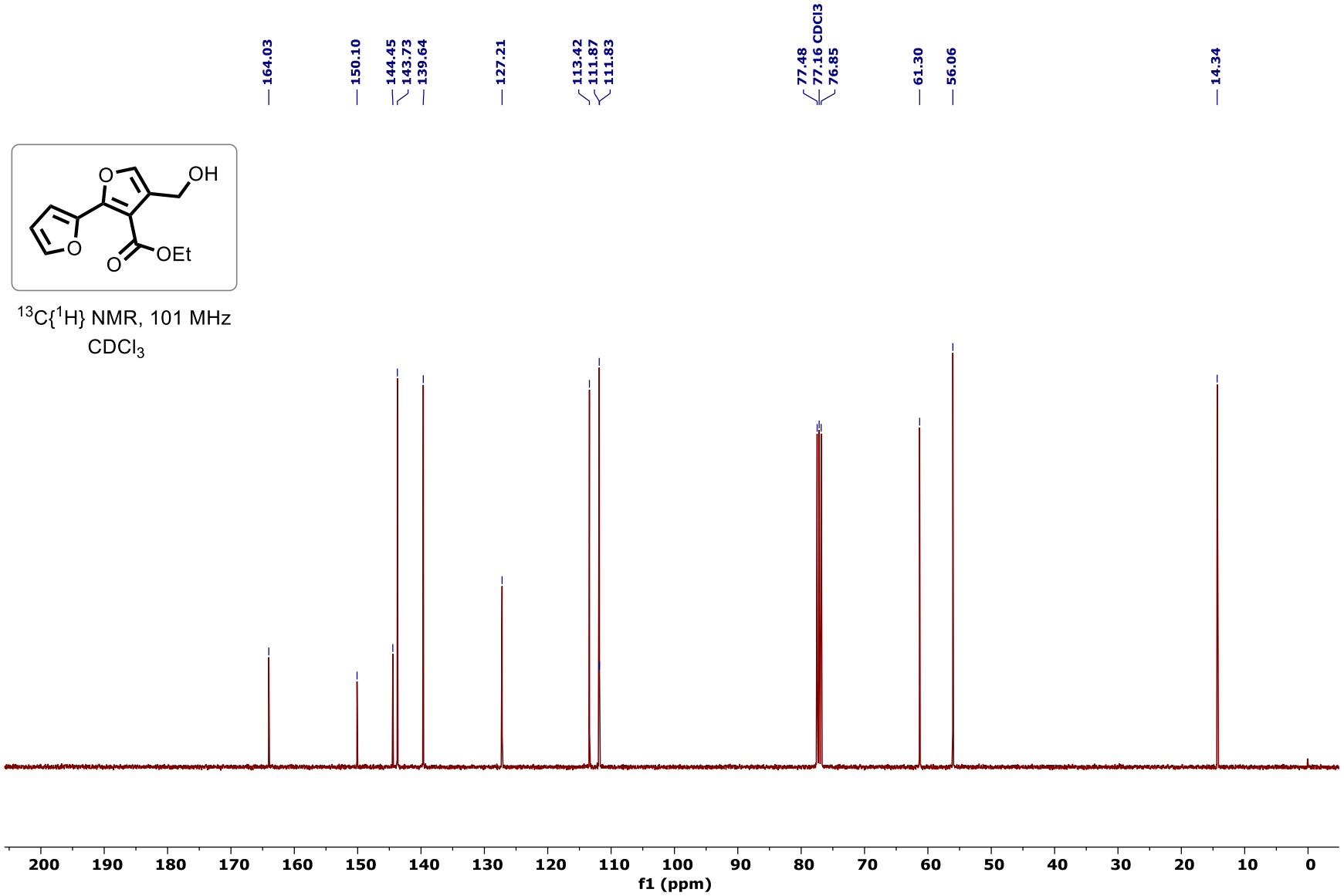
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 2-(2,4-dichlorophenyl)-4-(hydroxymethyl)furan-3-carboxylate (3m′):



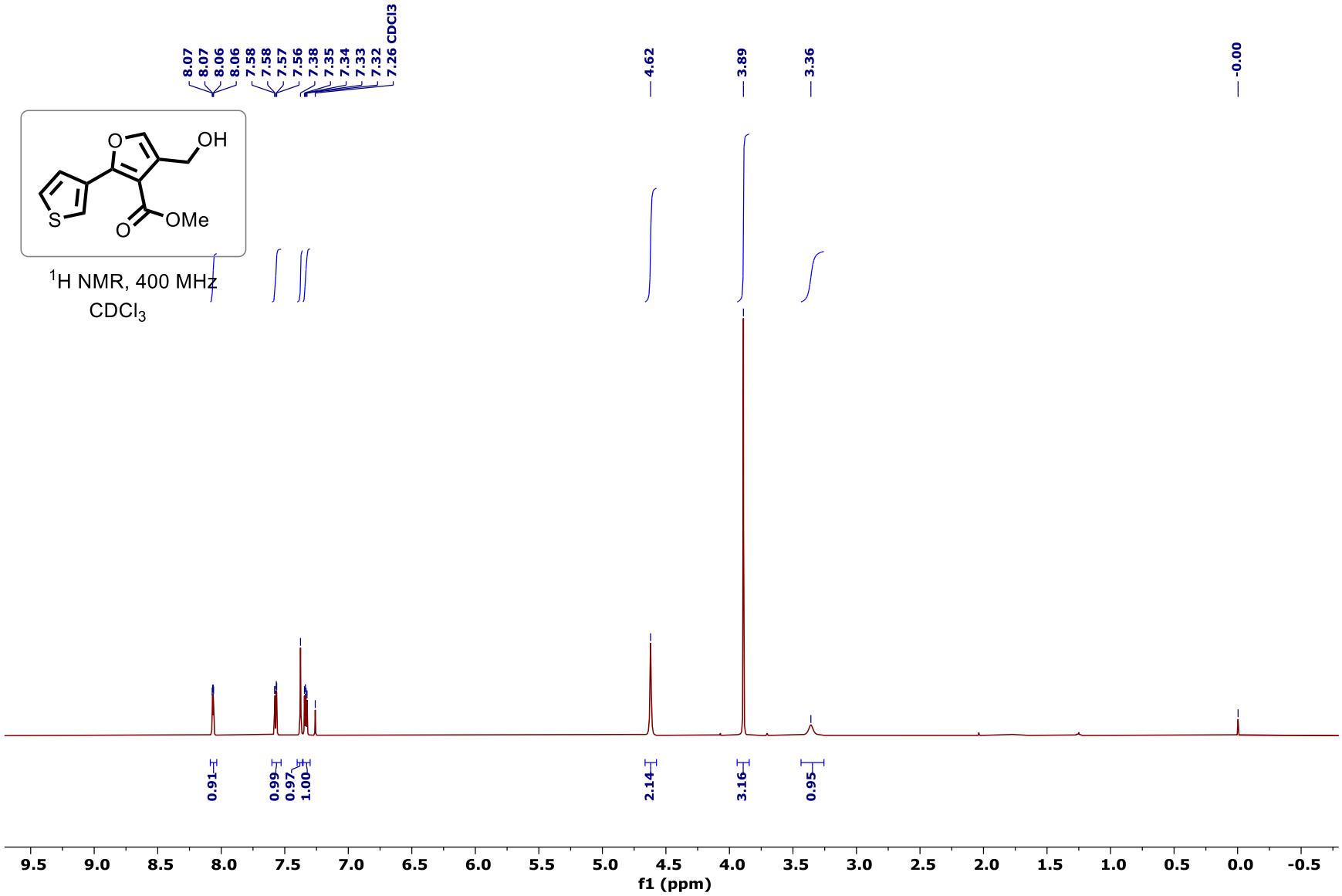
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-[2,2'-bifuran]-3-carboxylate (3n′):



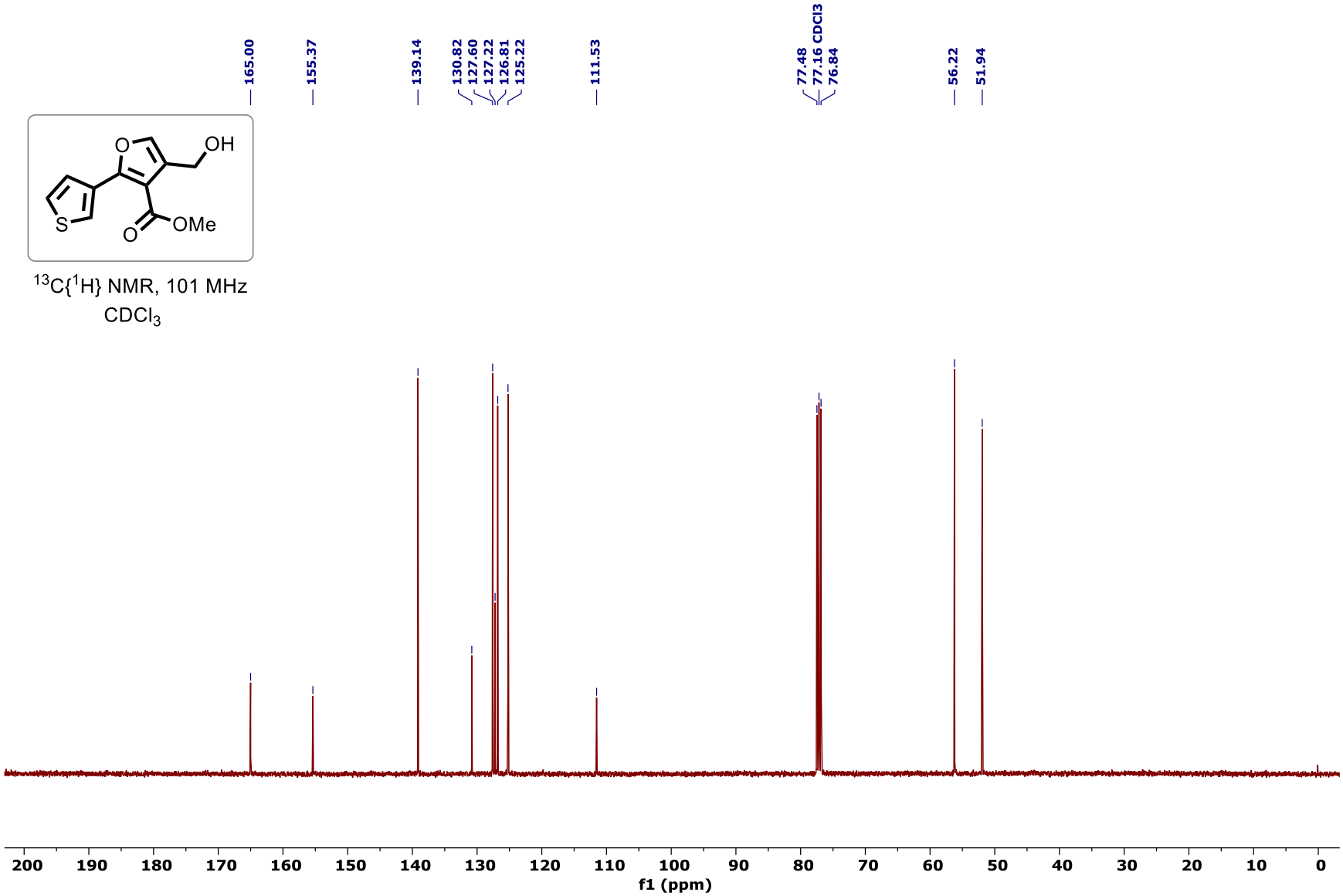
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-[2,2'-bifuran]-3-carboxylate (3n′):



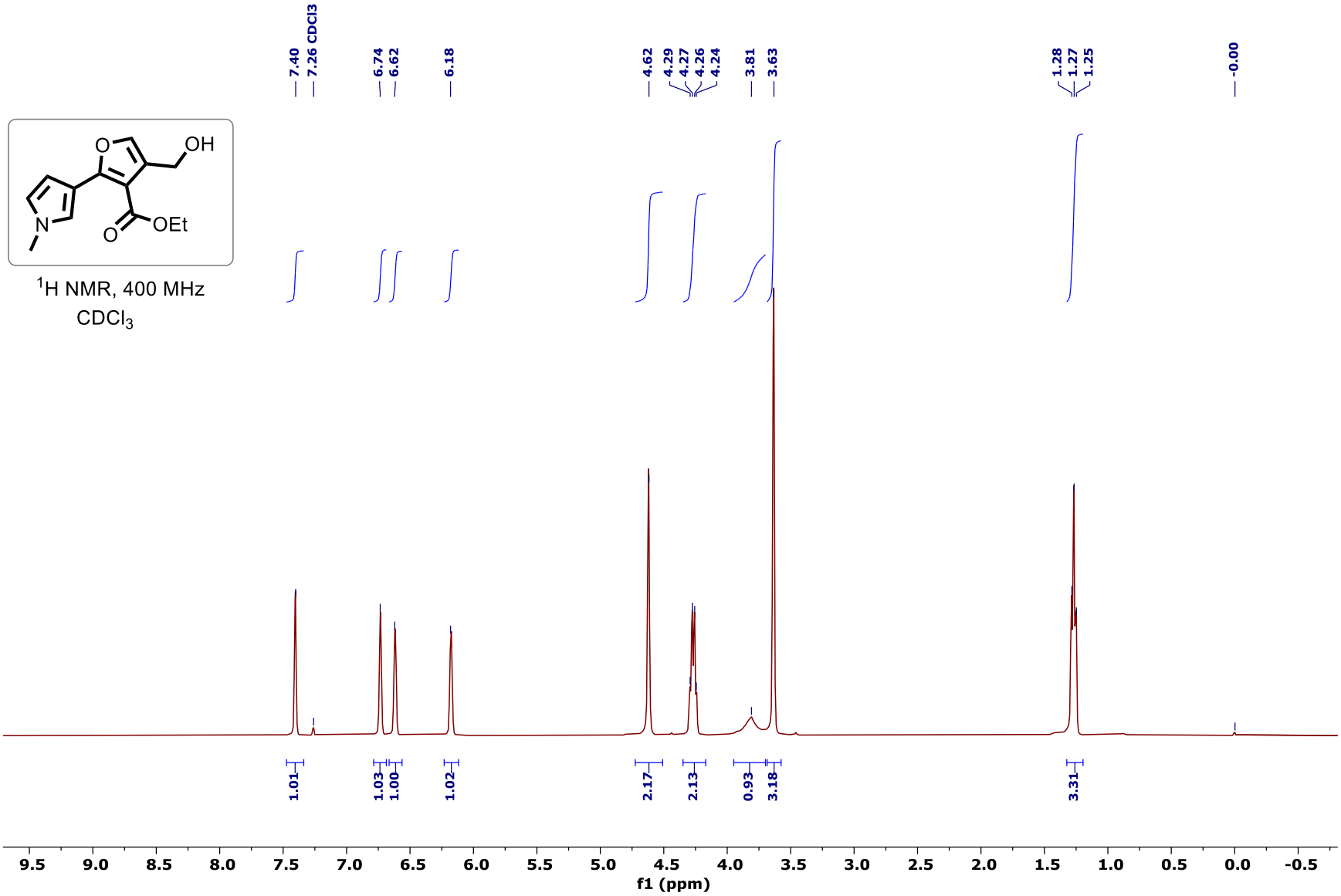
^{1}H NMR spectrum of Methyl 4-(hydroxymethyl)-2-(thiophen-3-yl)furan-3-carboxylate (3o′):



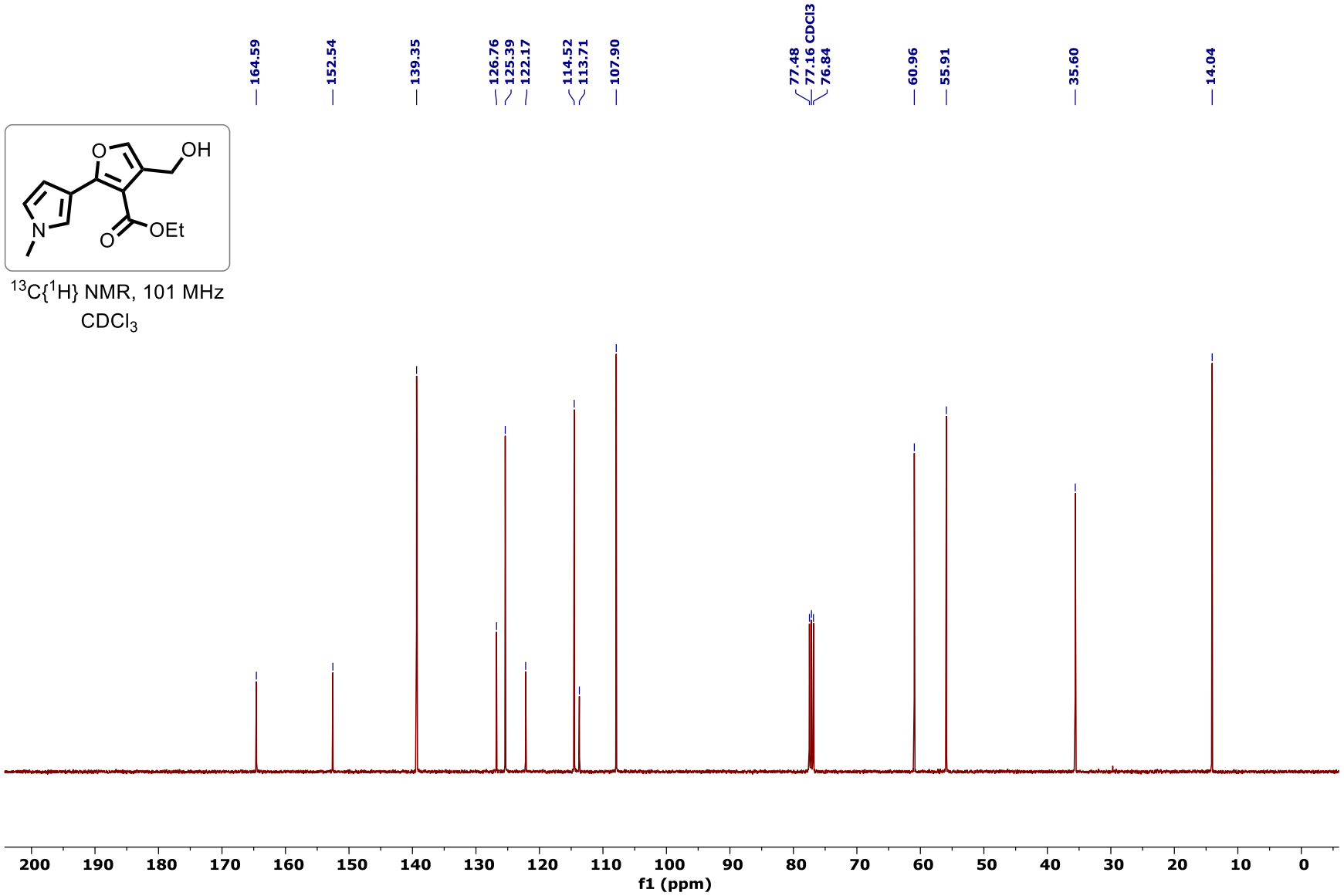
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 4-(hydroxymethyl)-2-(thiophen-3-yl)furan-3-carboxylate (3o′):



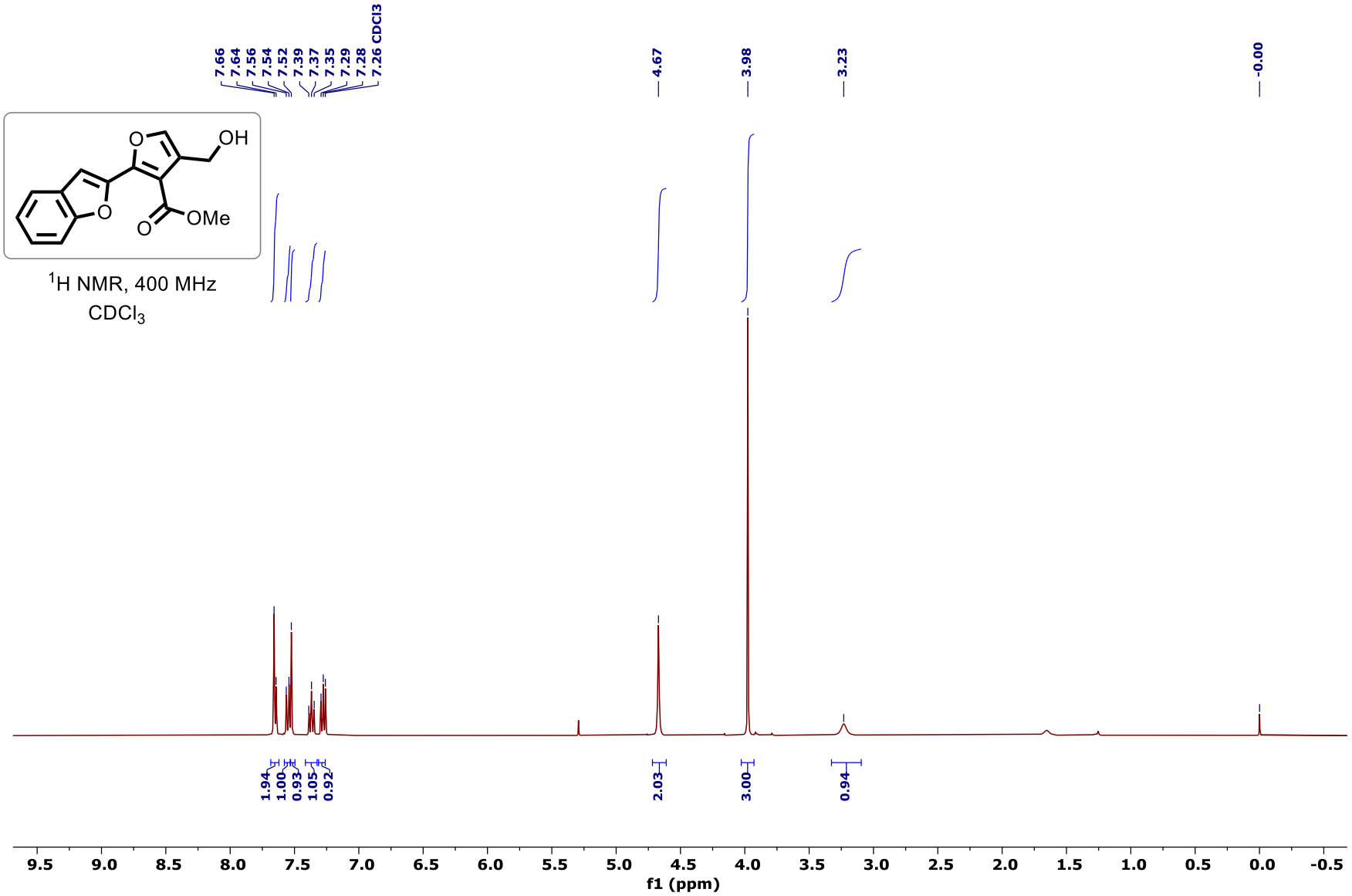
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(1-methyl-1*H*-pyrrol-3-yl)furan-3-carboxylate (3p′):



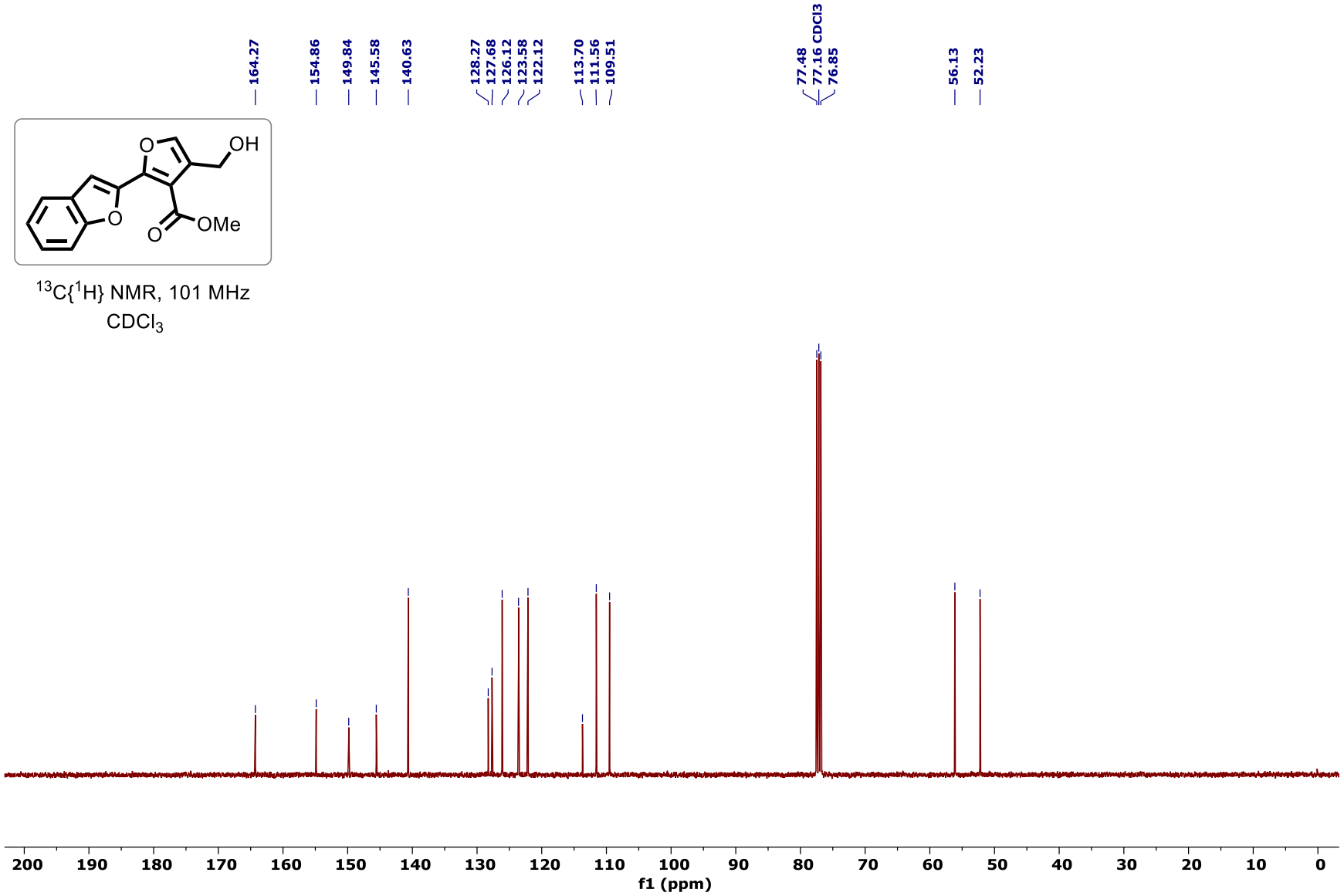
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2-(1-methyl-1*H*-pyrrol-3-yl)furan-3-carboxylate (3p′):



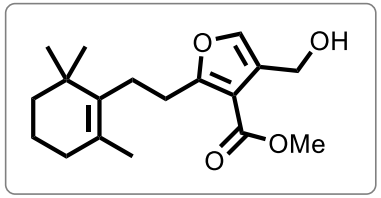
^{1}H NMR spectrum of Methyl 2-(benzofuran-2-yl)-4-(hydroxymethyl)furan-3-carboxylate (3q′):



$^{13}C\{^{1}H\}$ NMR spectrum of Methyl 2-(benzofuran-2-yl)-4-(hydroxymethyl)furan-3-carboxylate (3q′):

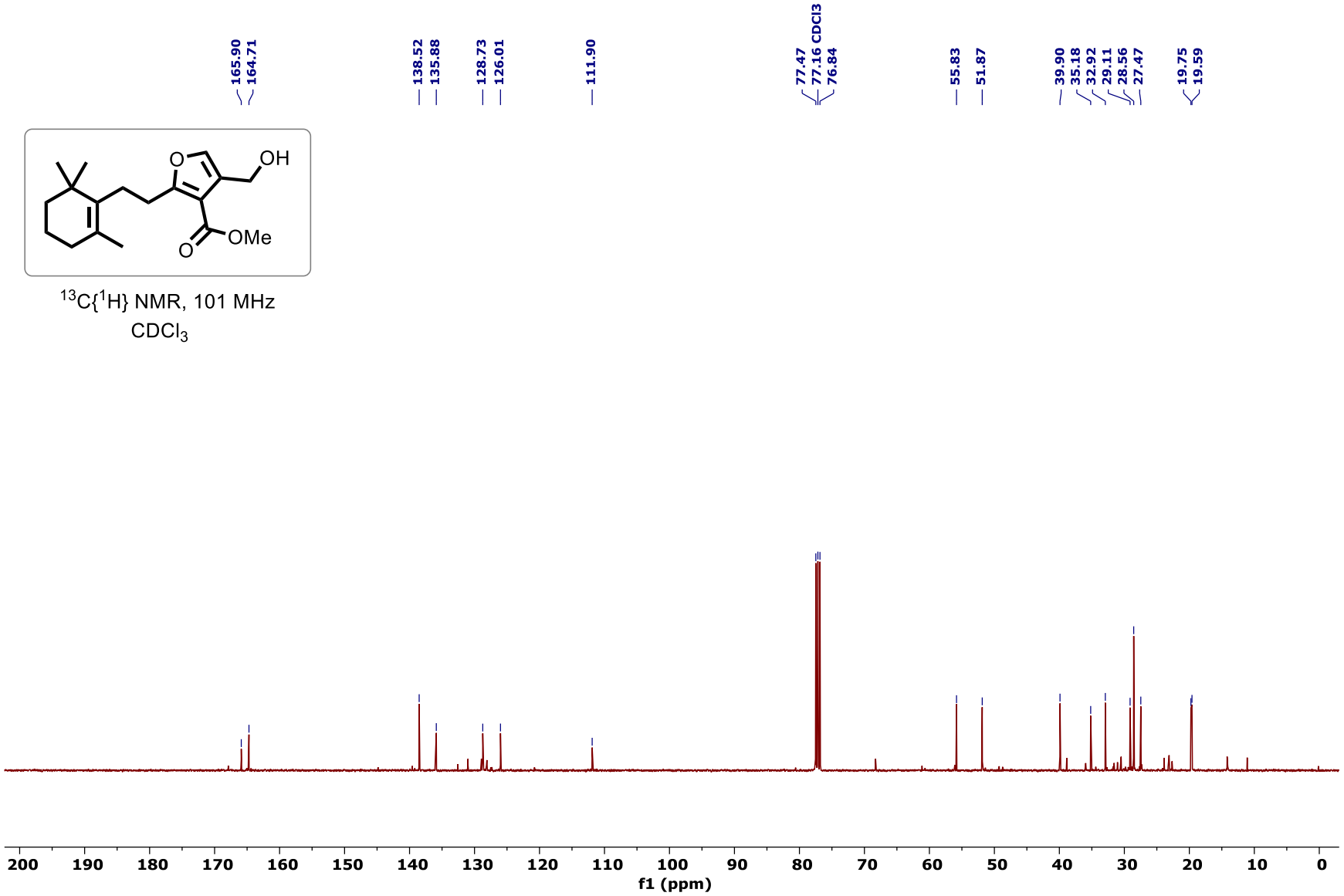


^{1}H NMR spectrum of Methyl-4-(hydroxymethyl)-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)furan-3-carboxylate (3r′):

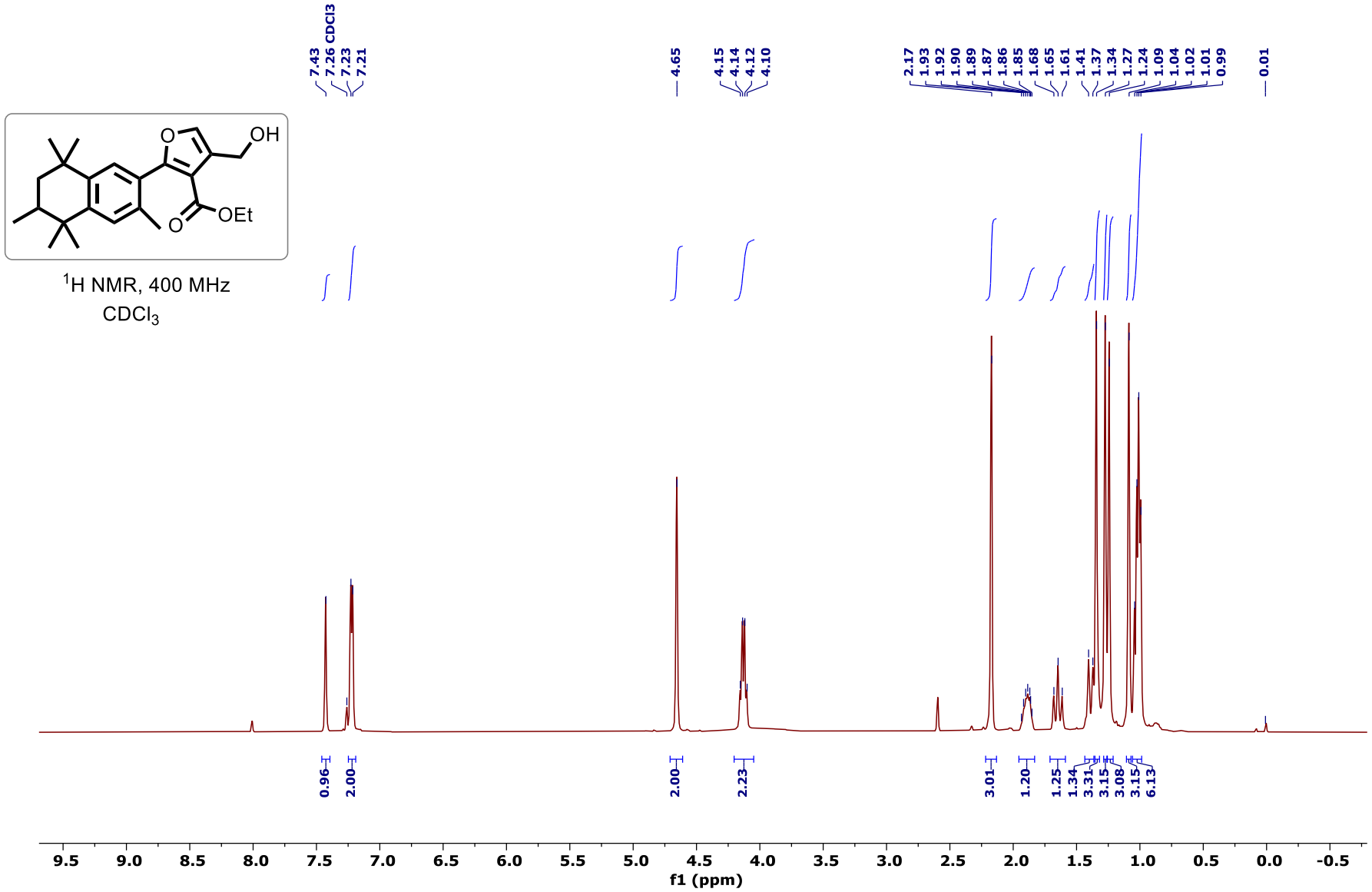


^{1}H NMR, 400 MHz
$CDCl_3$

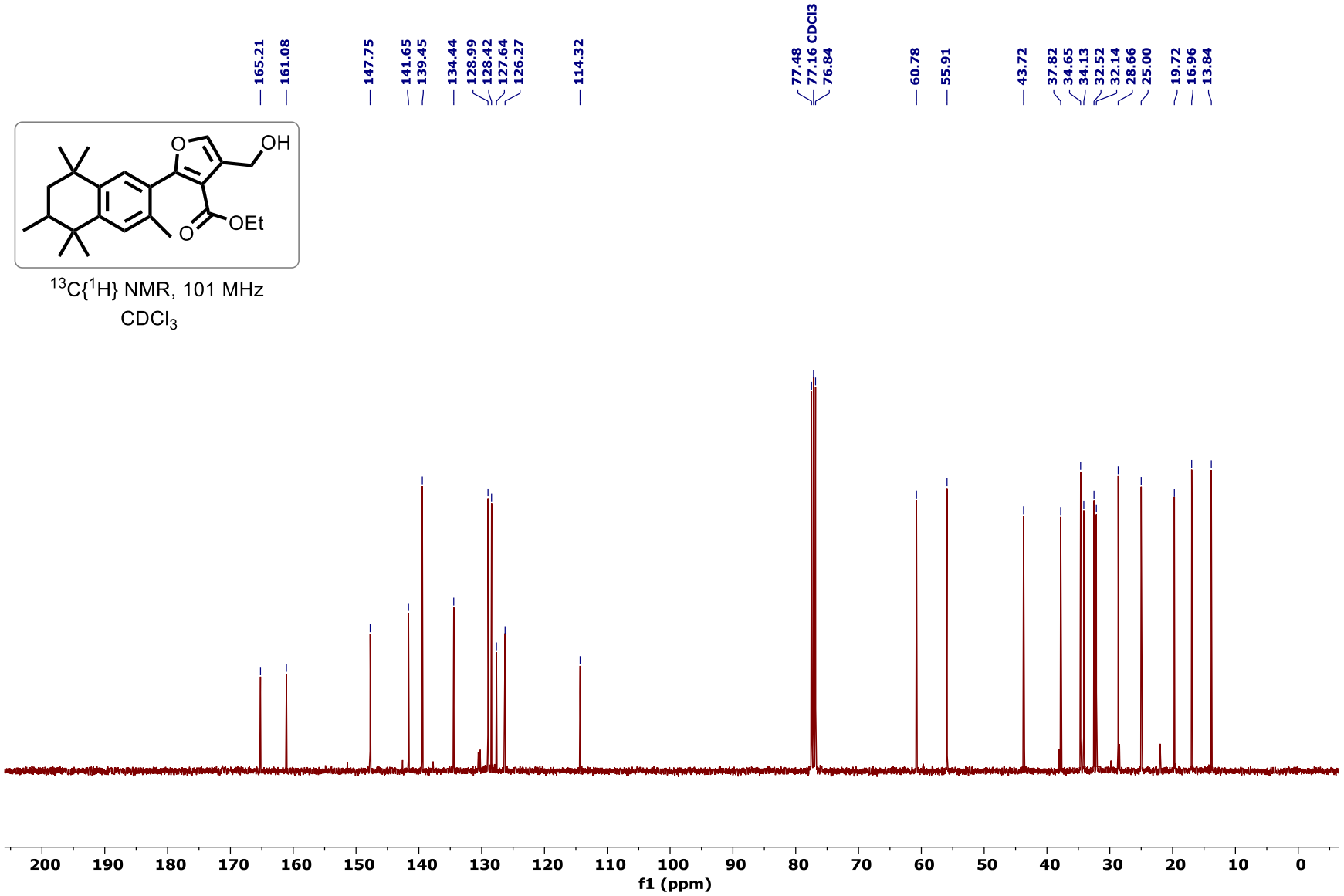
$^{13}C\{^{1}H\}$ NMR spectrum of Methyl-4-(hydroxymethyl)-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)furan-3-carboxylate (3r′):



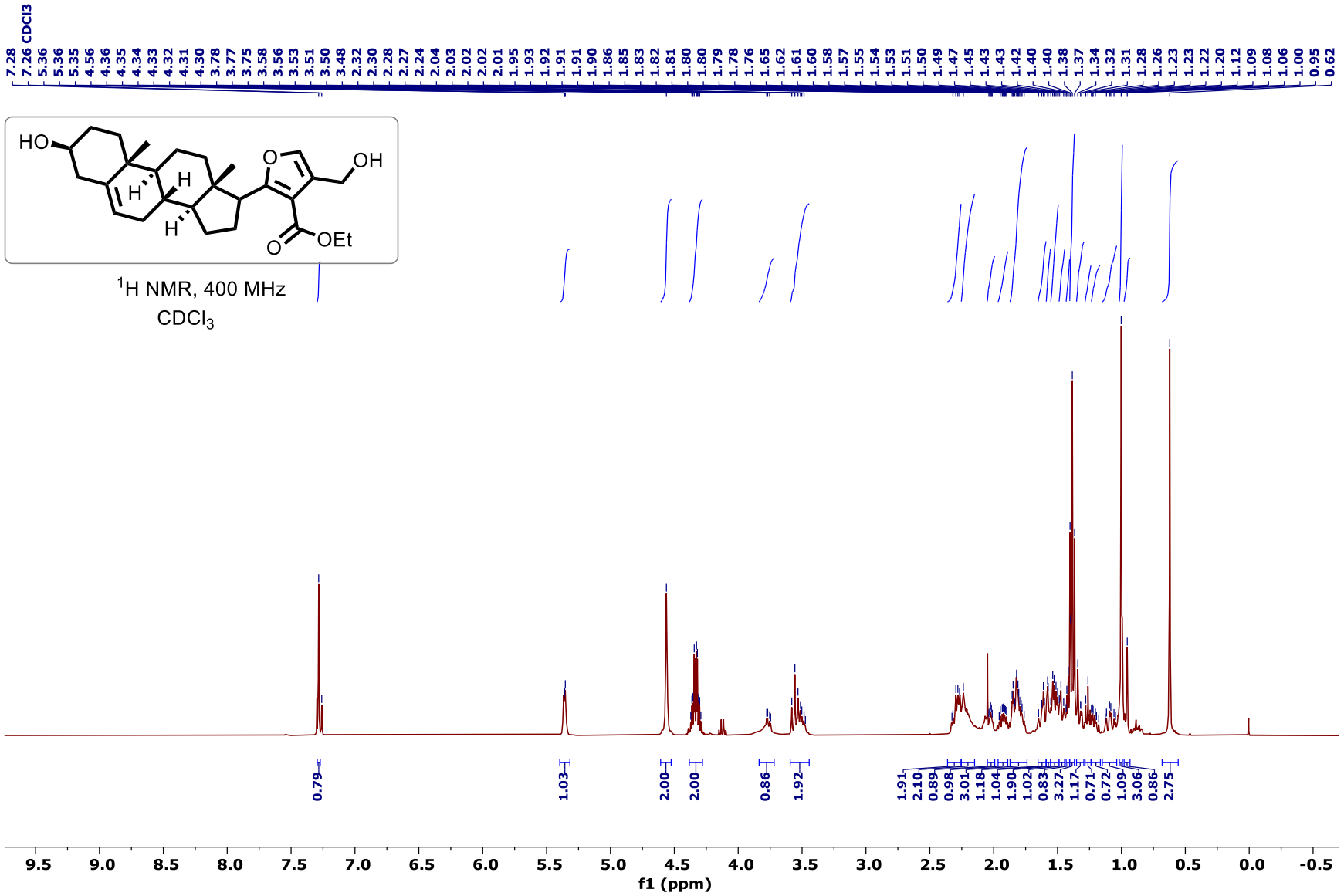
^{1}H NMR spectrum of Ethyl 2-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-4-(hydroxymethyl)furan-3-carboxylate (3s′):



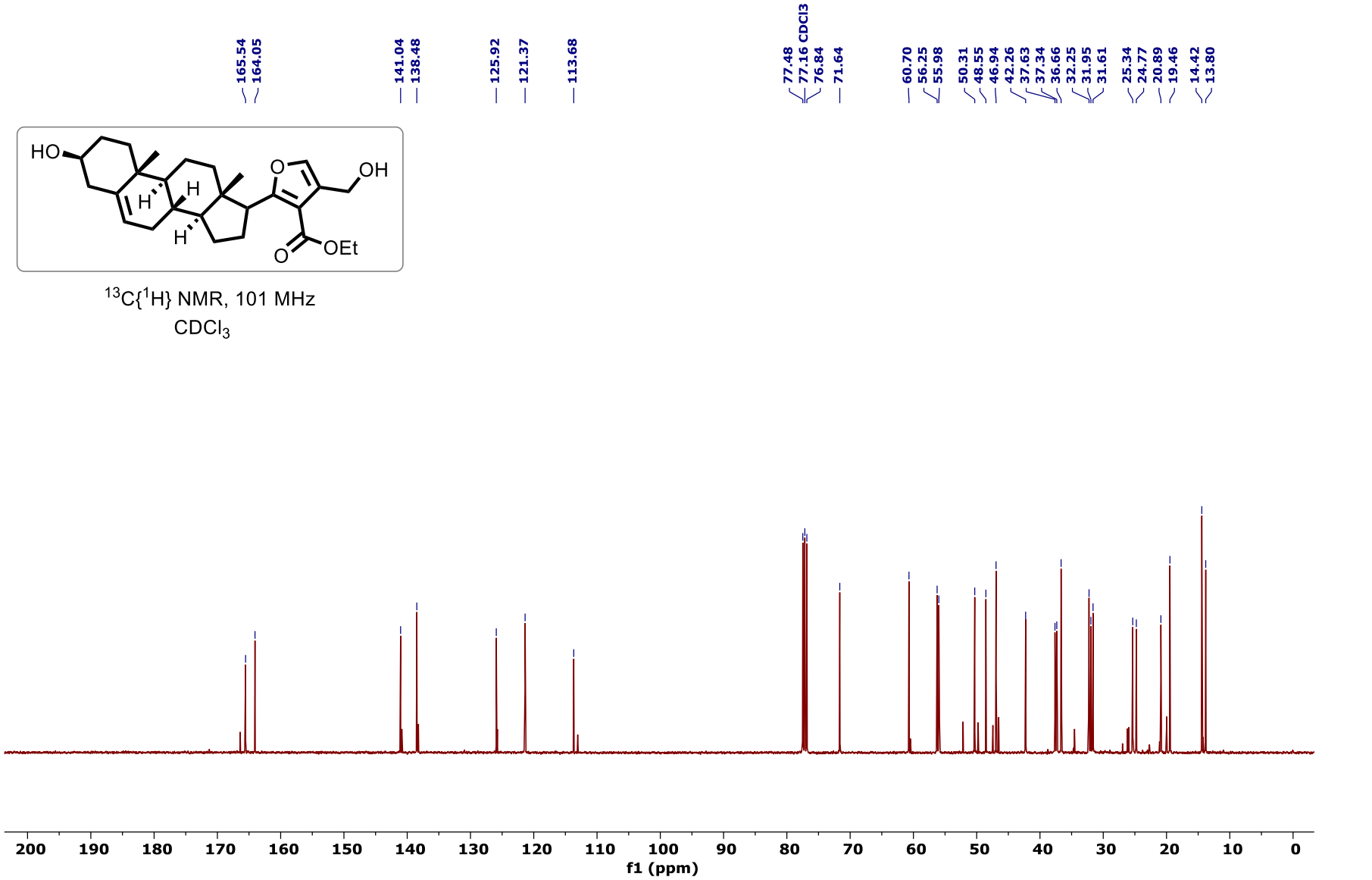
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 2-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-4-(hydroxymethyl)furan-3-carboxylate (3s′):



^{1}H NMR spectrum of Ethyl-2-((3S,8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-4-(hydroxymethyl)furan-3-carboxylate (3t′):

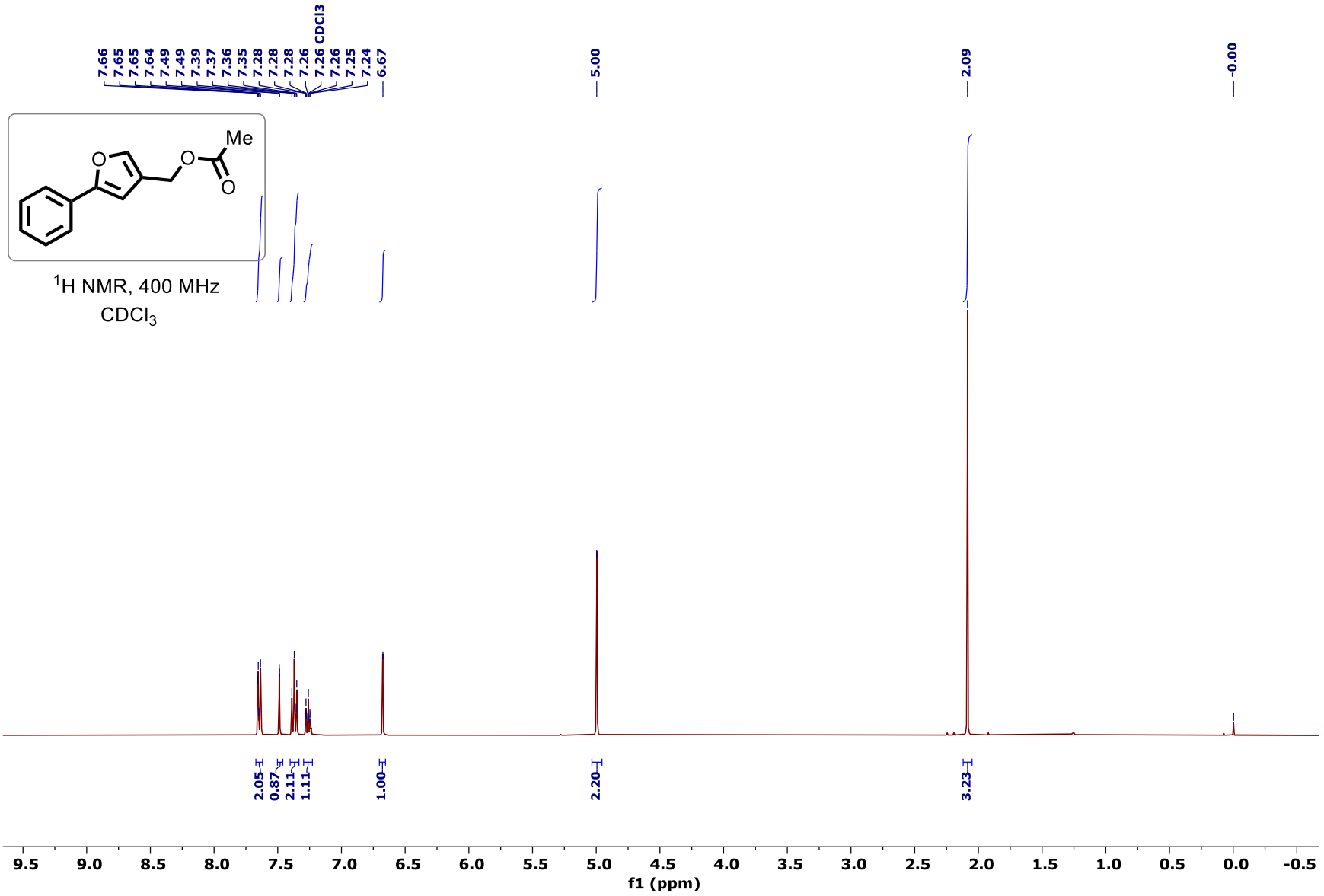


$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl-2-((3S,8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-4-(hydroxymethyl)furan-3-carboxylate (3t′):

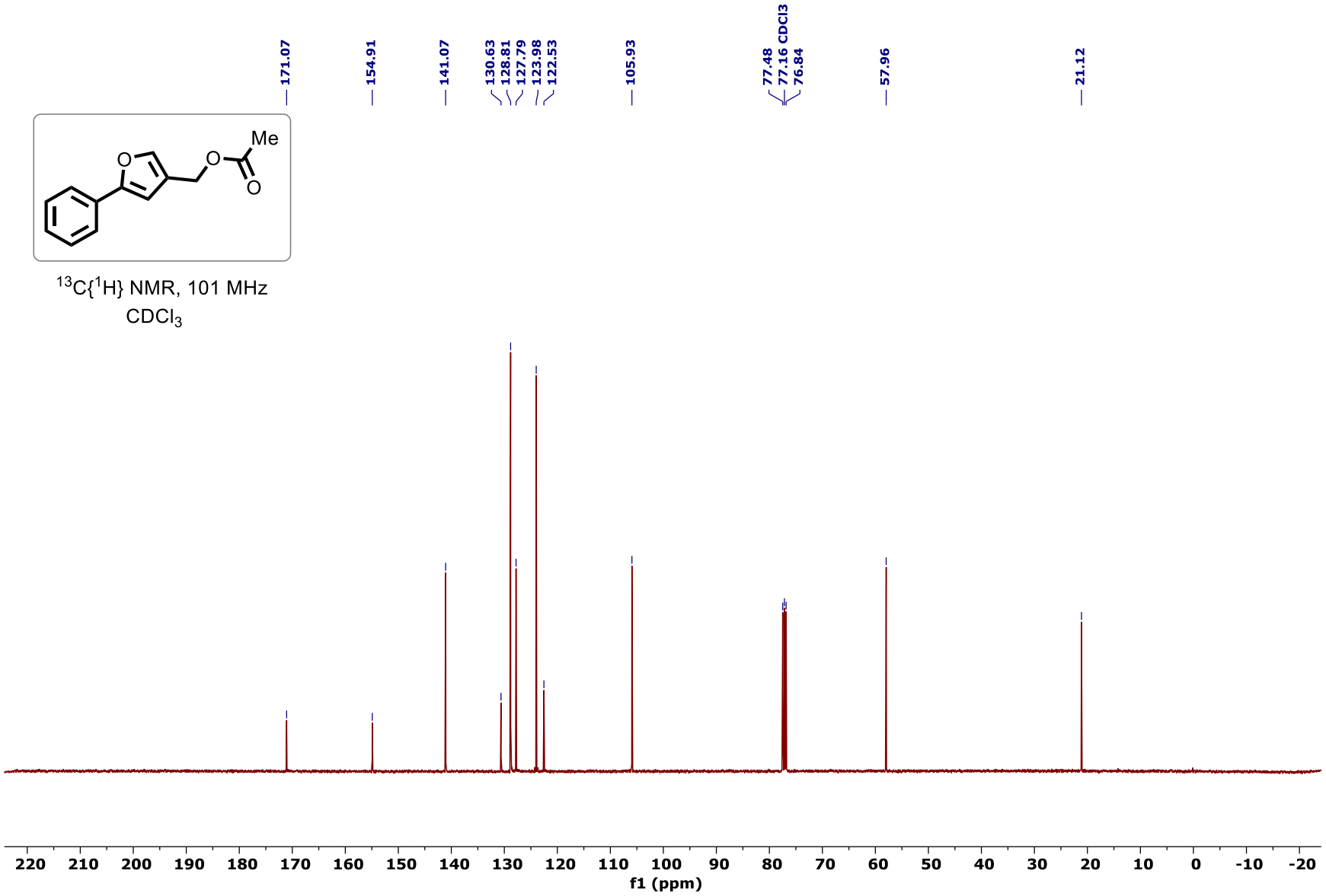


$^{13}C\{^{1}H\}$ NMR, 101 MHz
$CDCl_3$

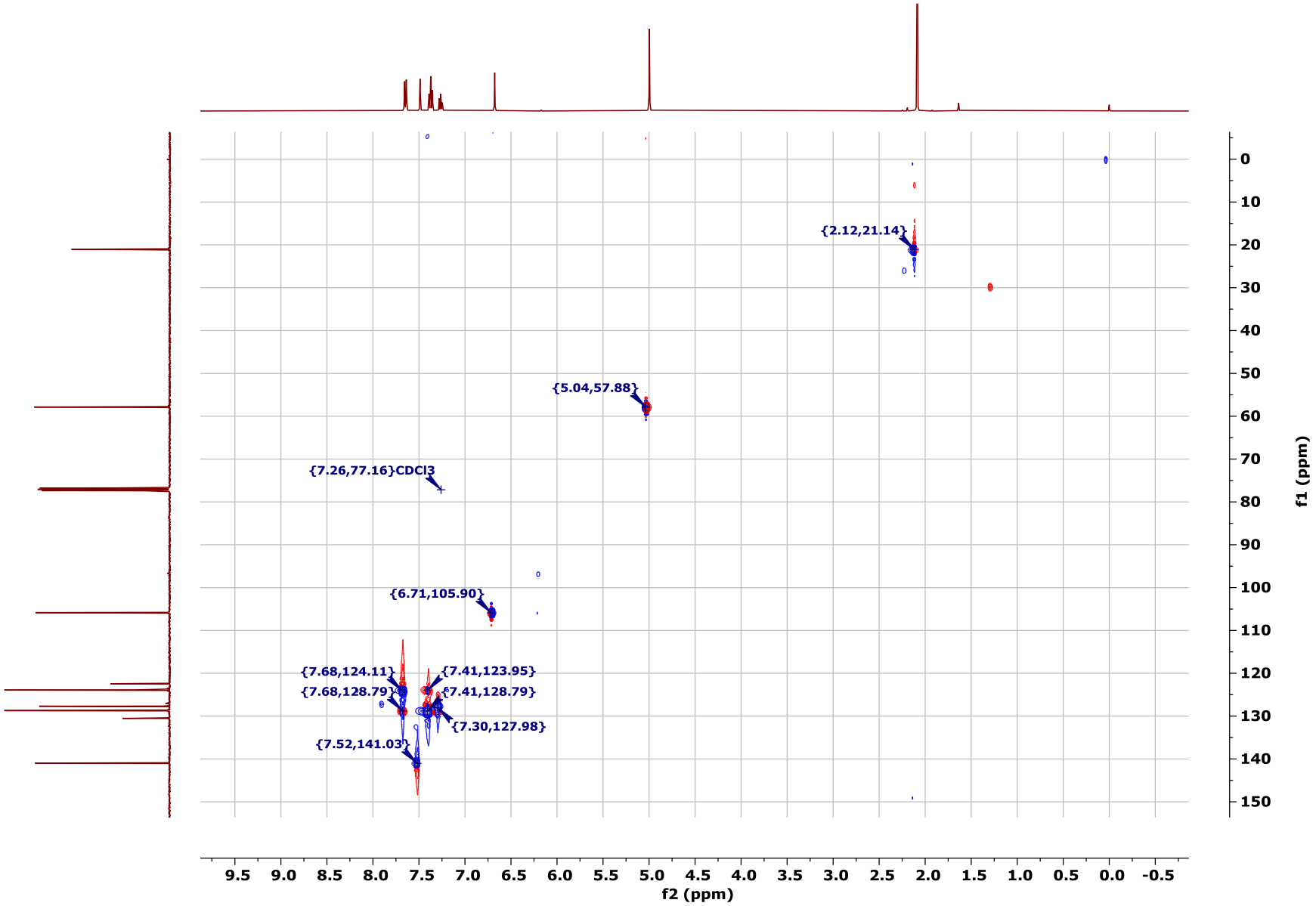
^{1}H NMR spectrum of (5-Phenylfuran-3-yl)methyl acetate (5a):



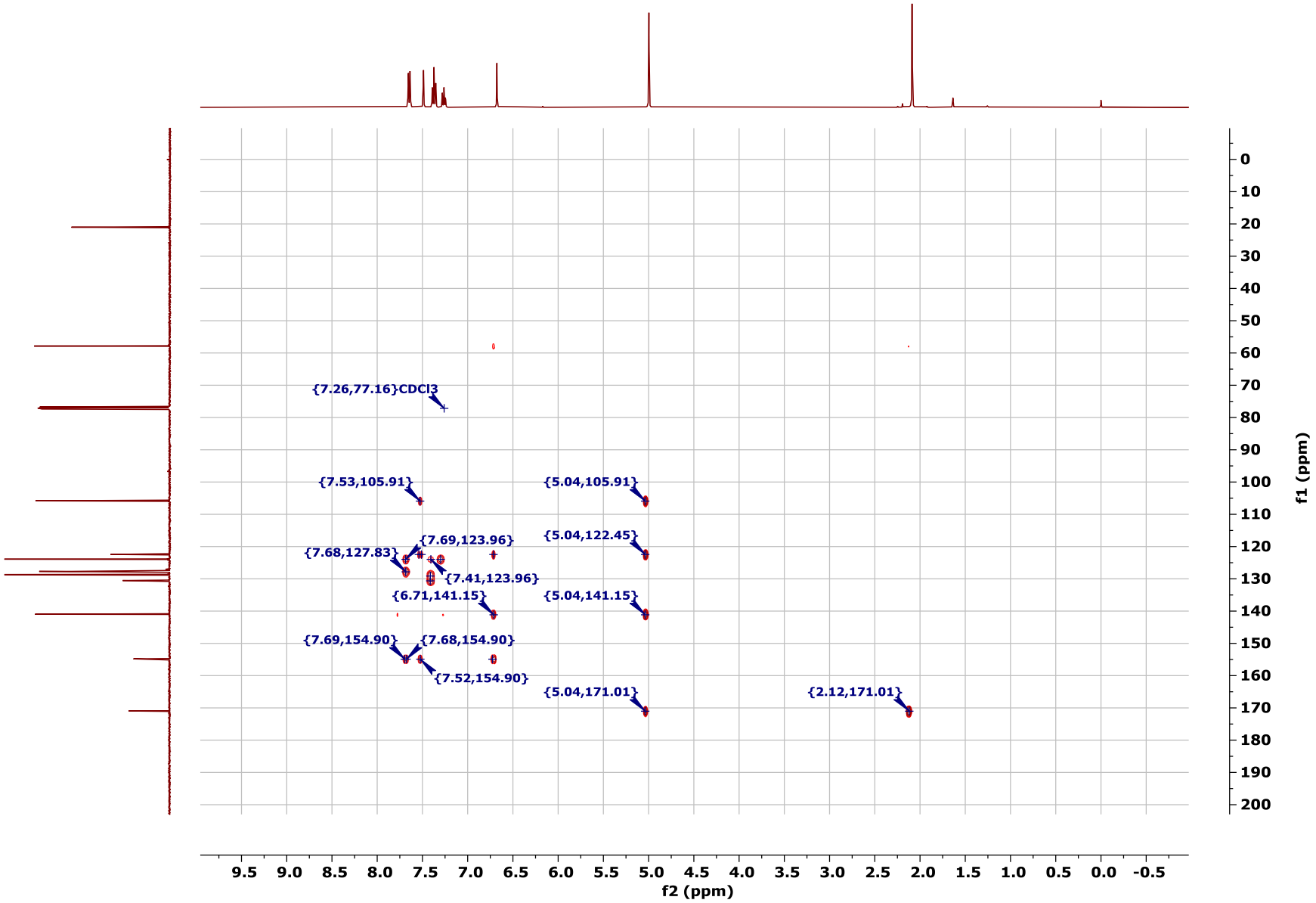
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Phenylfuran-3-yl)methyl acetate (5a):



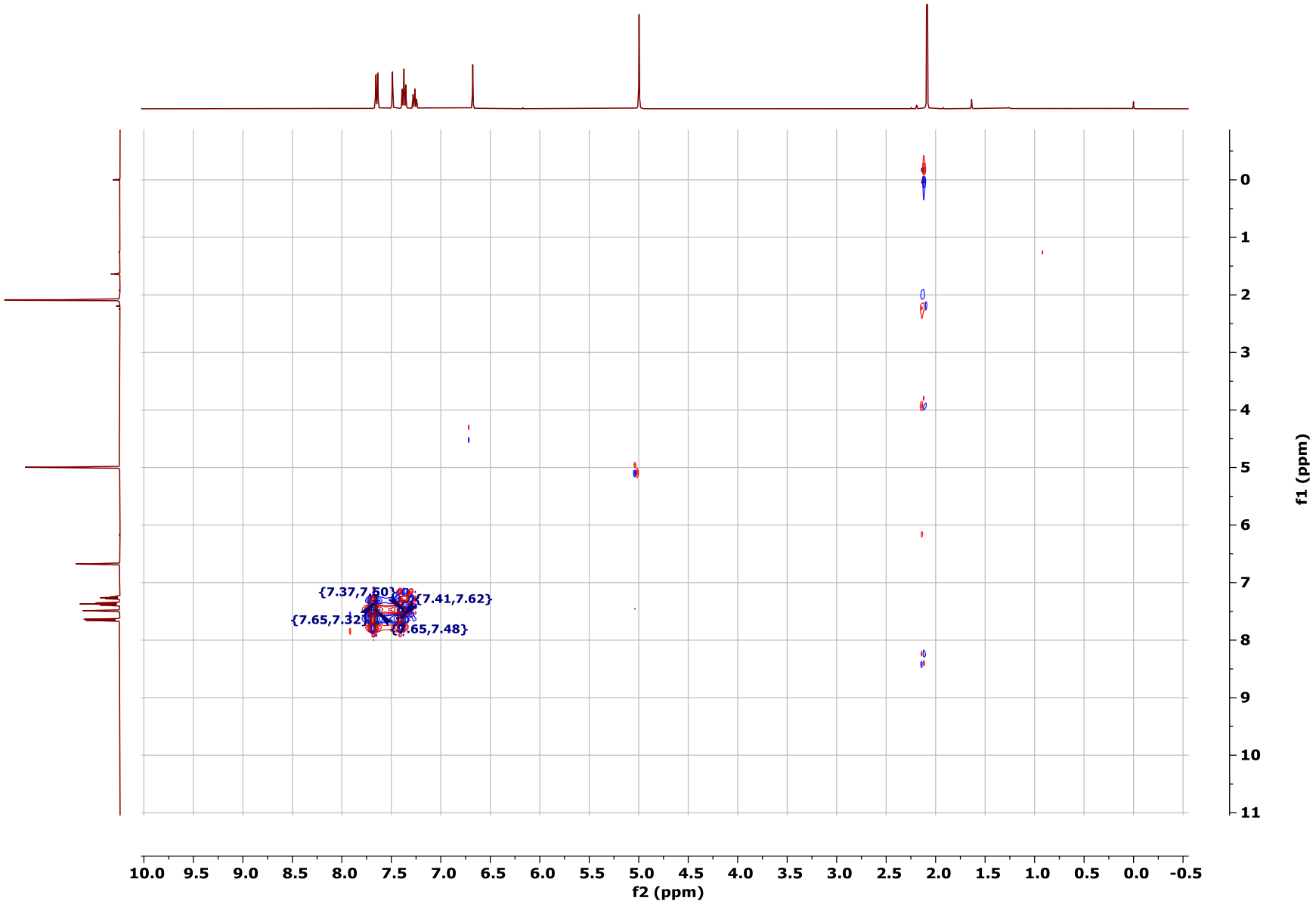
HSQC NMR spectrum of (5-Phenylfuran-3-yl)methyl acetate (5a):



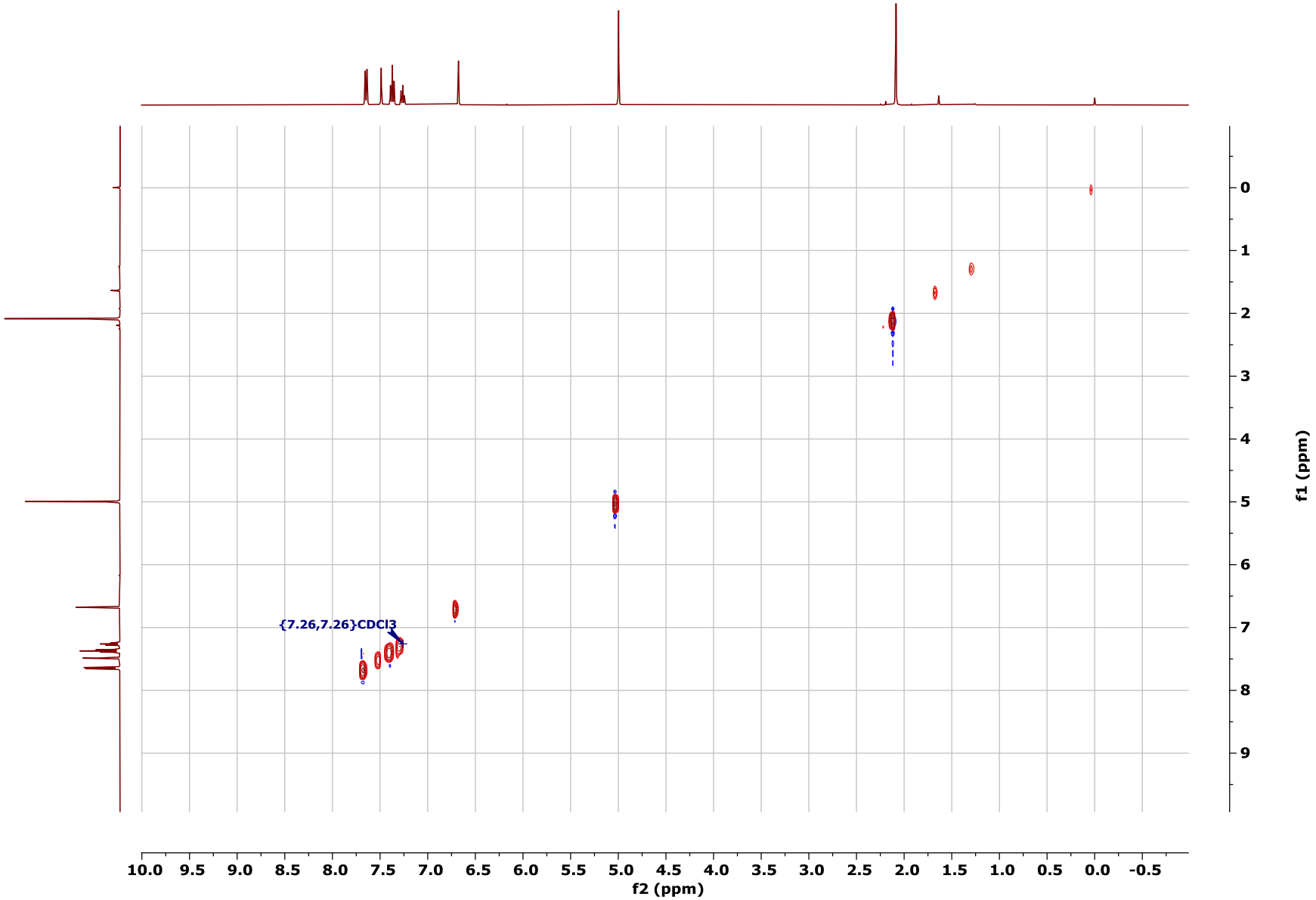
HMBC NMR spectrum of (5-Phenylfuran-3-yl)methyl acetate (5a):



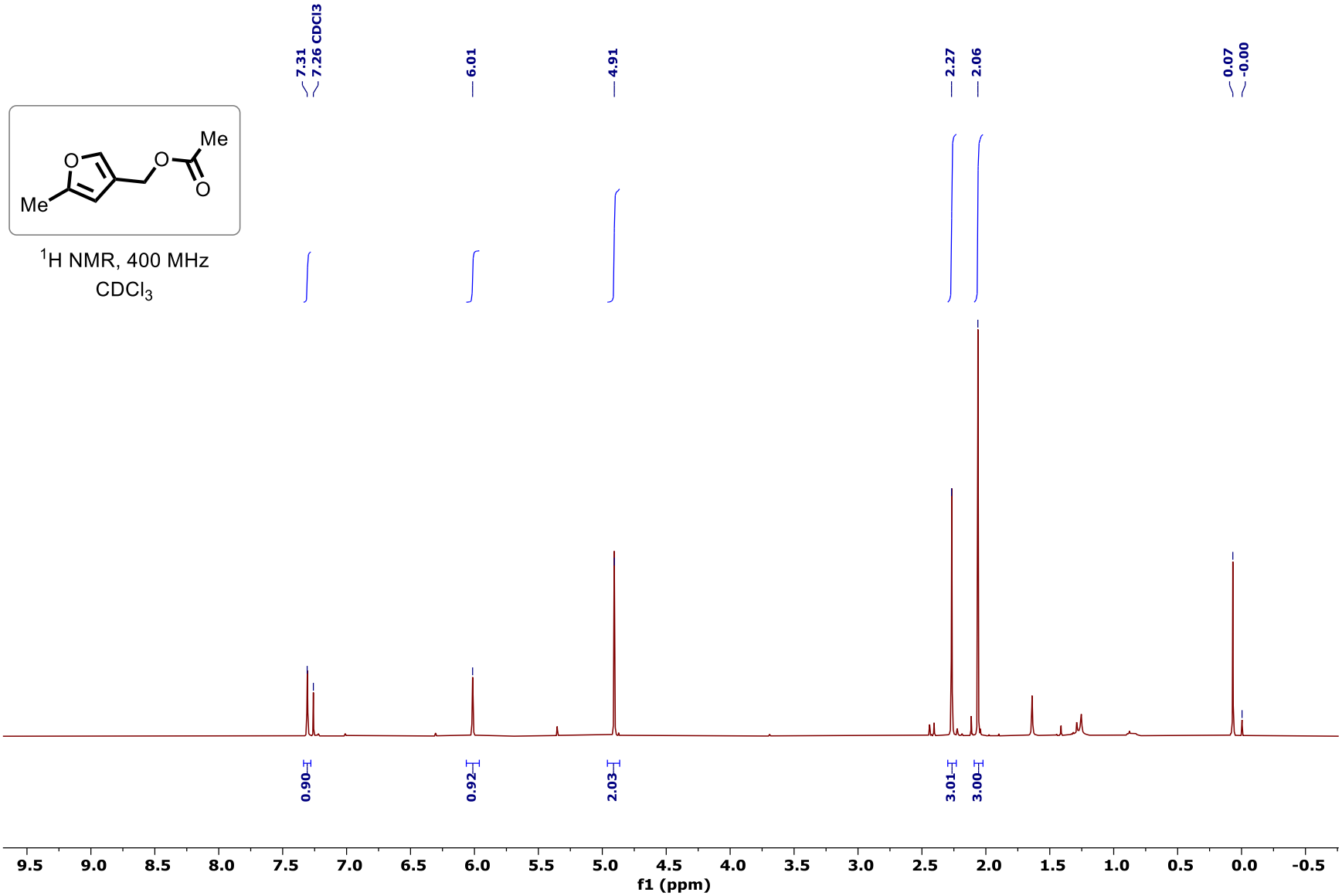
COSY NMR spectrum of (5-Phenylfuran-3-yl)methyl acetate (5a):



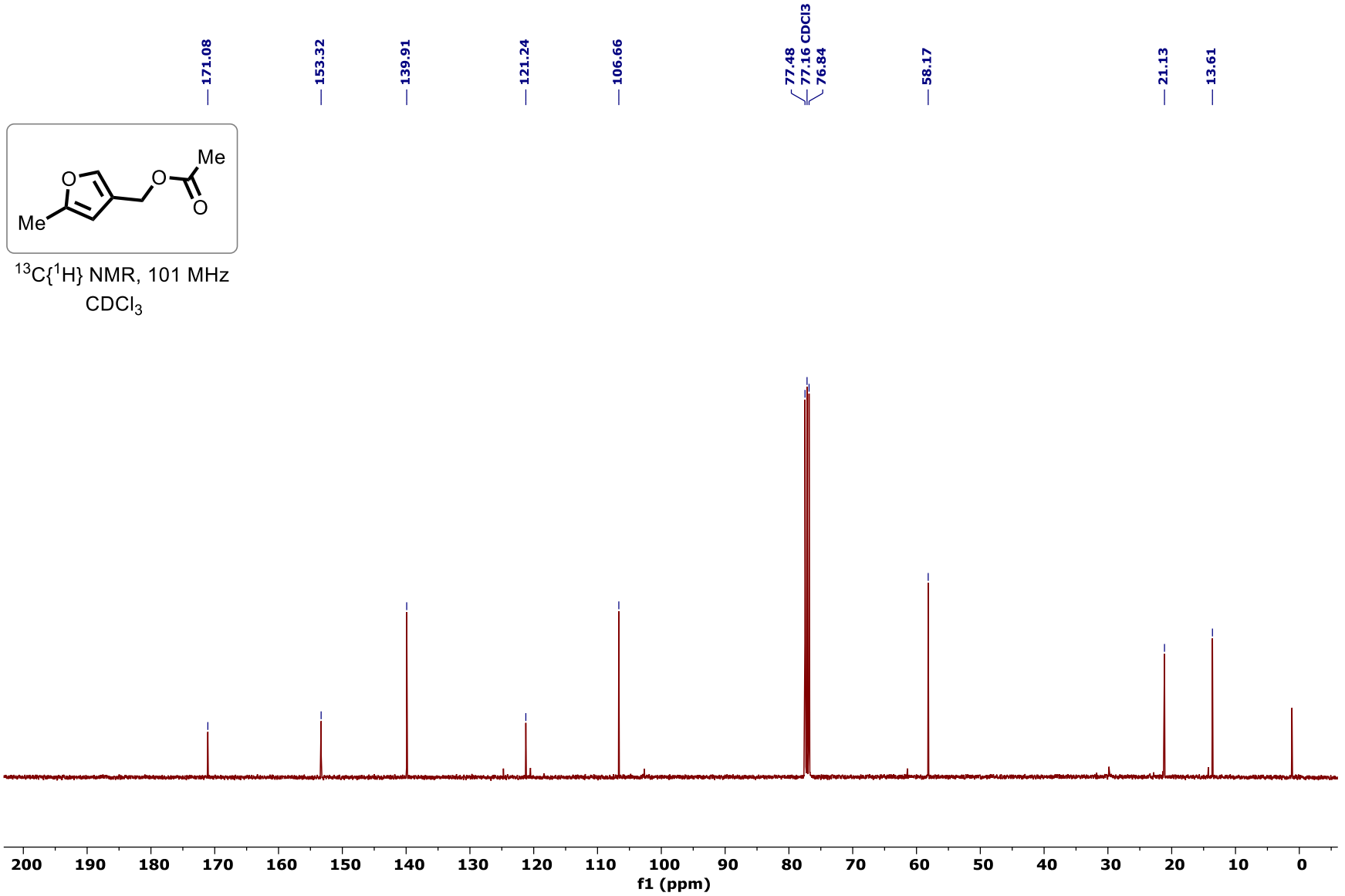
NOESY NMR spectrum of (5-Phenylfuran-3-yl)methyl acetate (5a):



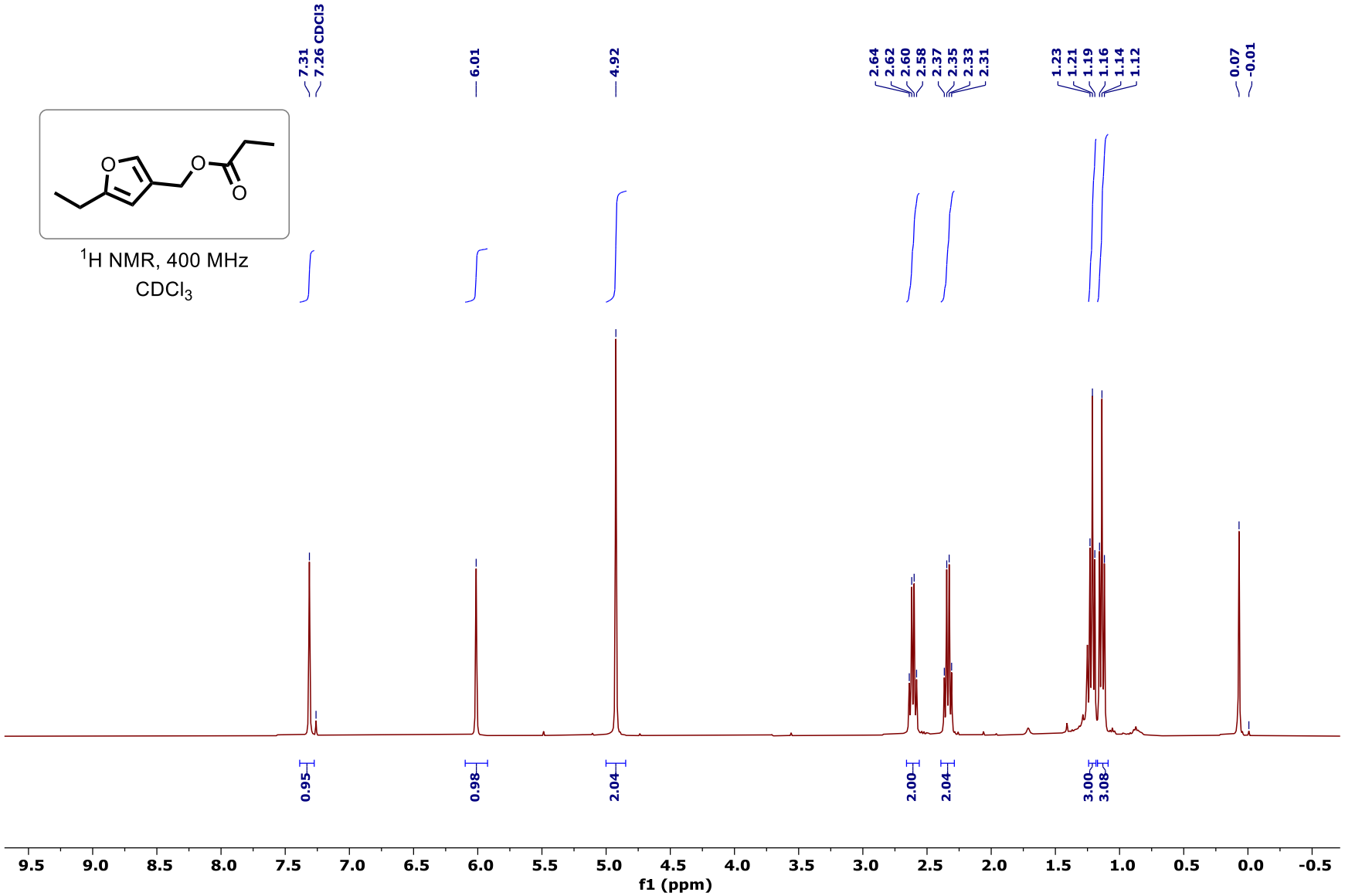
^{1}H NMR spectrum of (5-Methylfuran-3-yl)methyl acetate (5b):



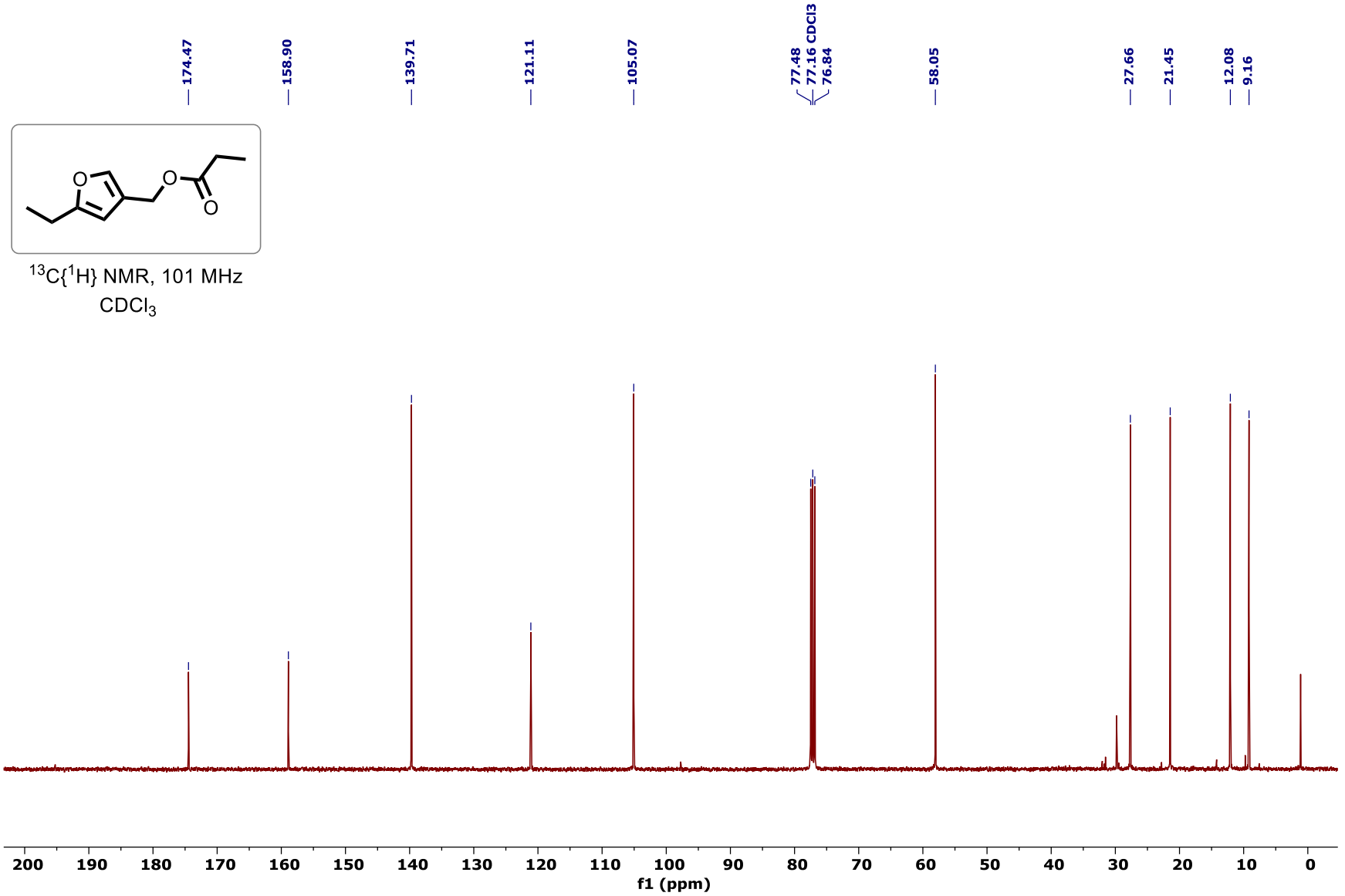
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Methylfuran-3-yl)methyl acetate (5b):



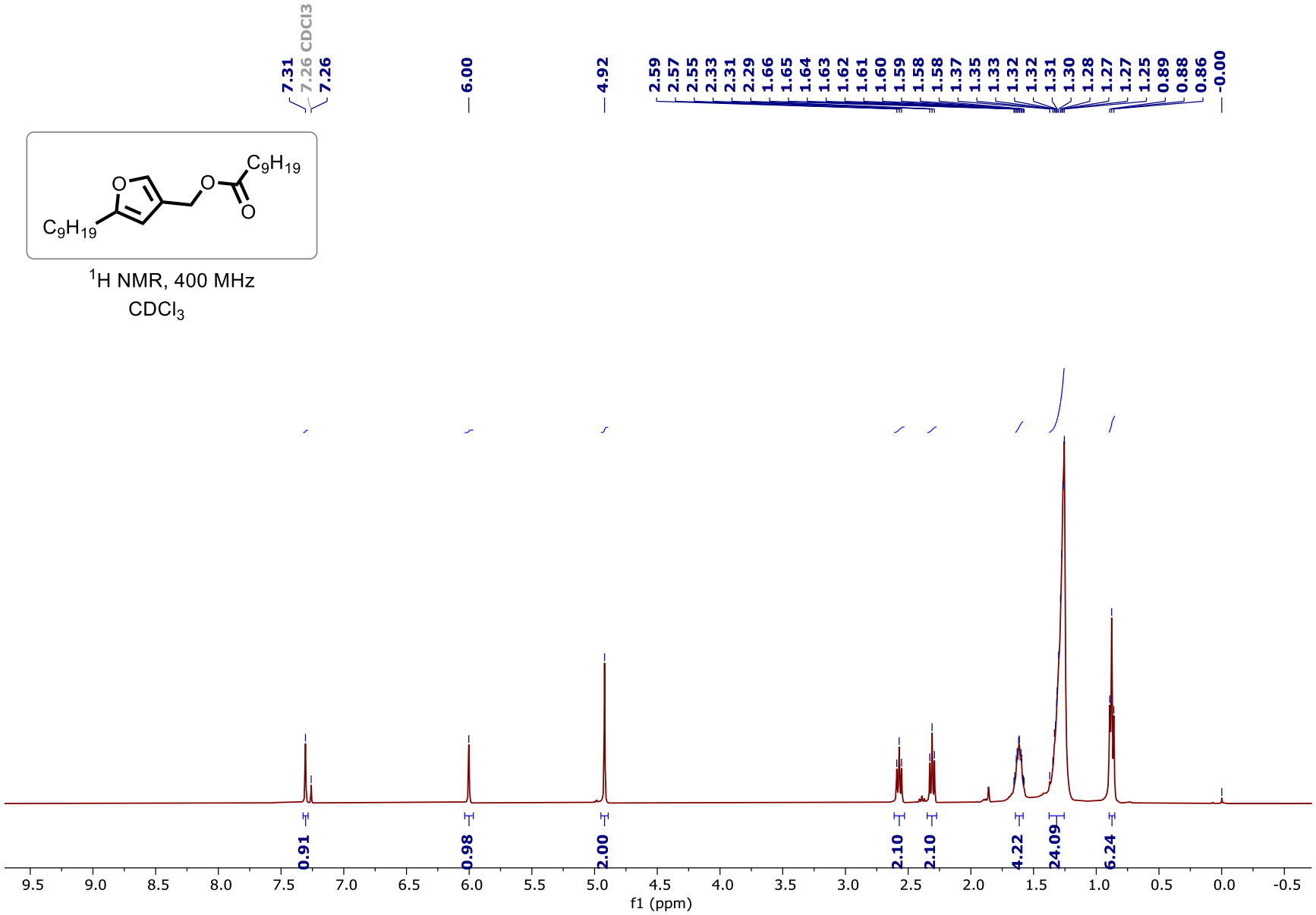
^{1}H NMR spectrum of (5-Ethylfuran-3-yl)methyl propionate (5c):



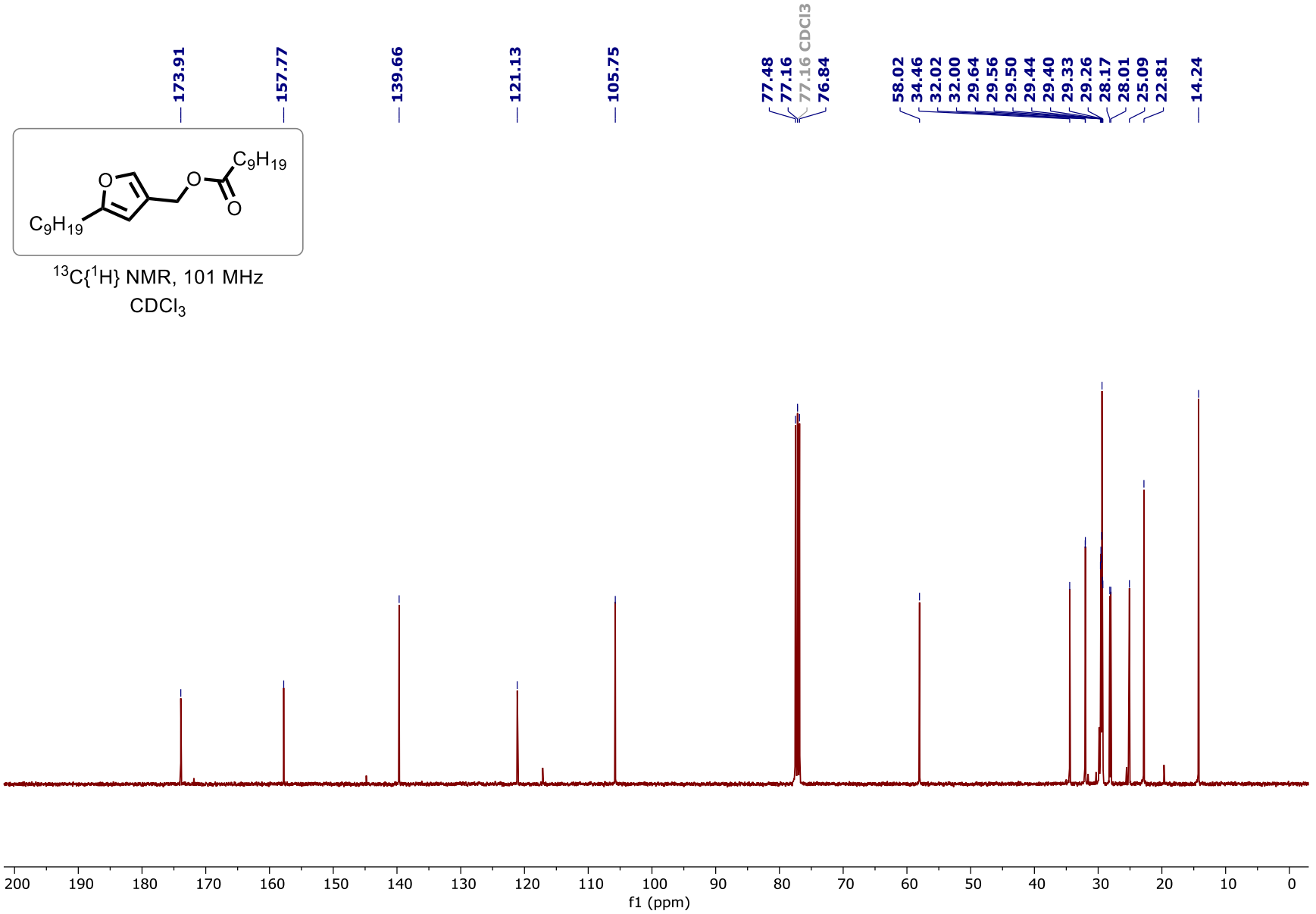
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Ethylfuran-3-yl)methyl propionate (5c):



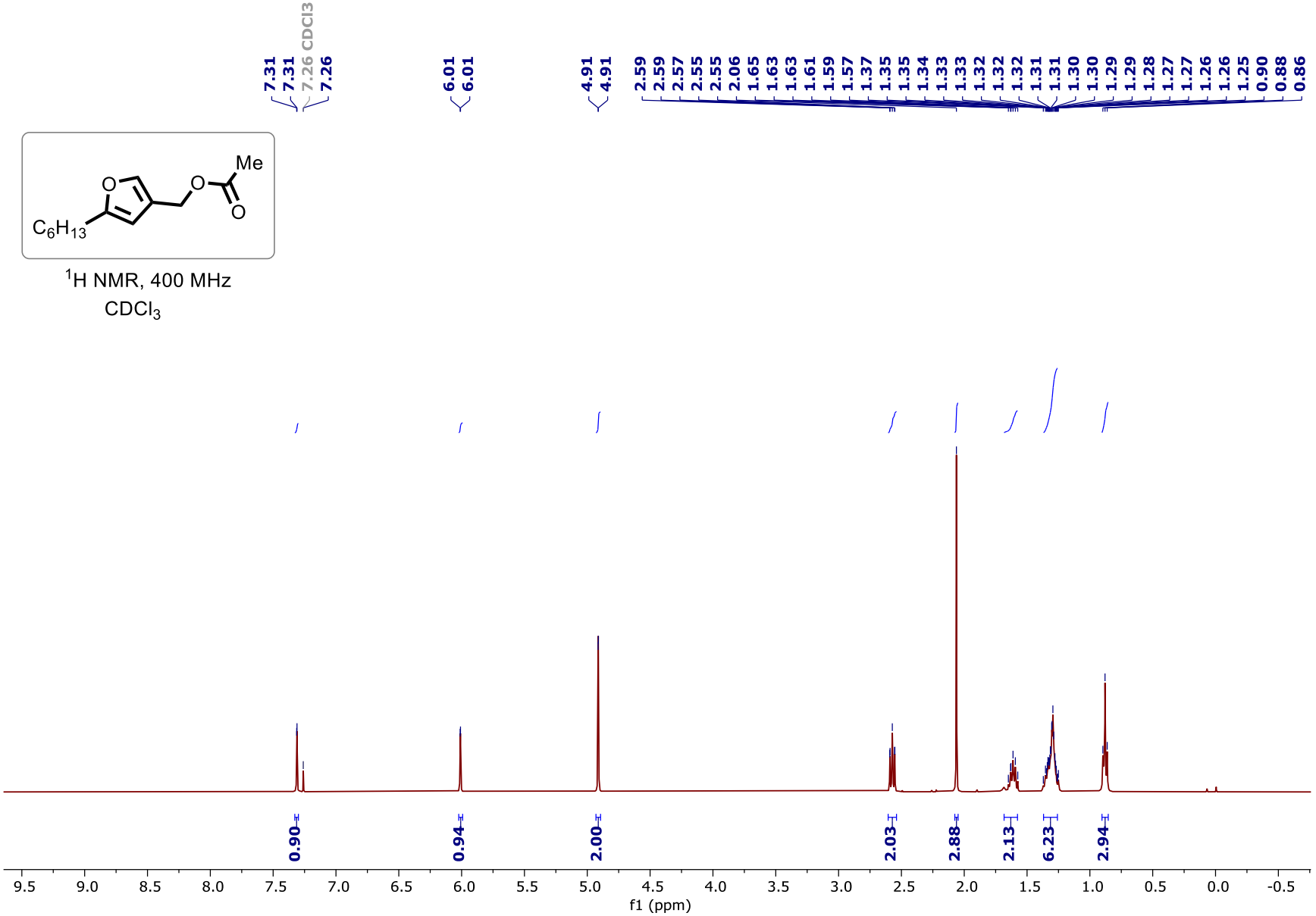
^{1}H NMR spectrum of (5-Nonylfuran-3-yl)methyl decanoate (5d):



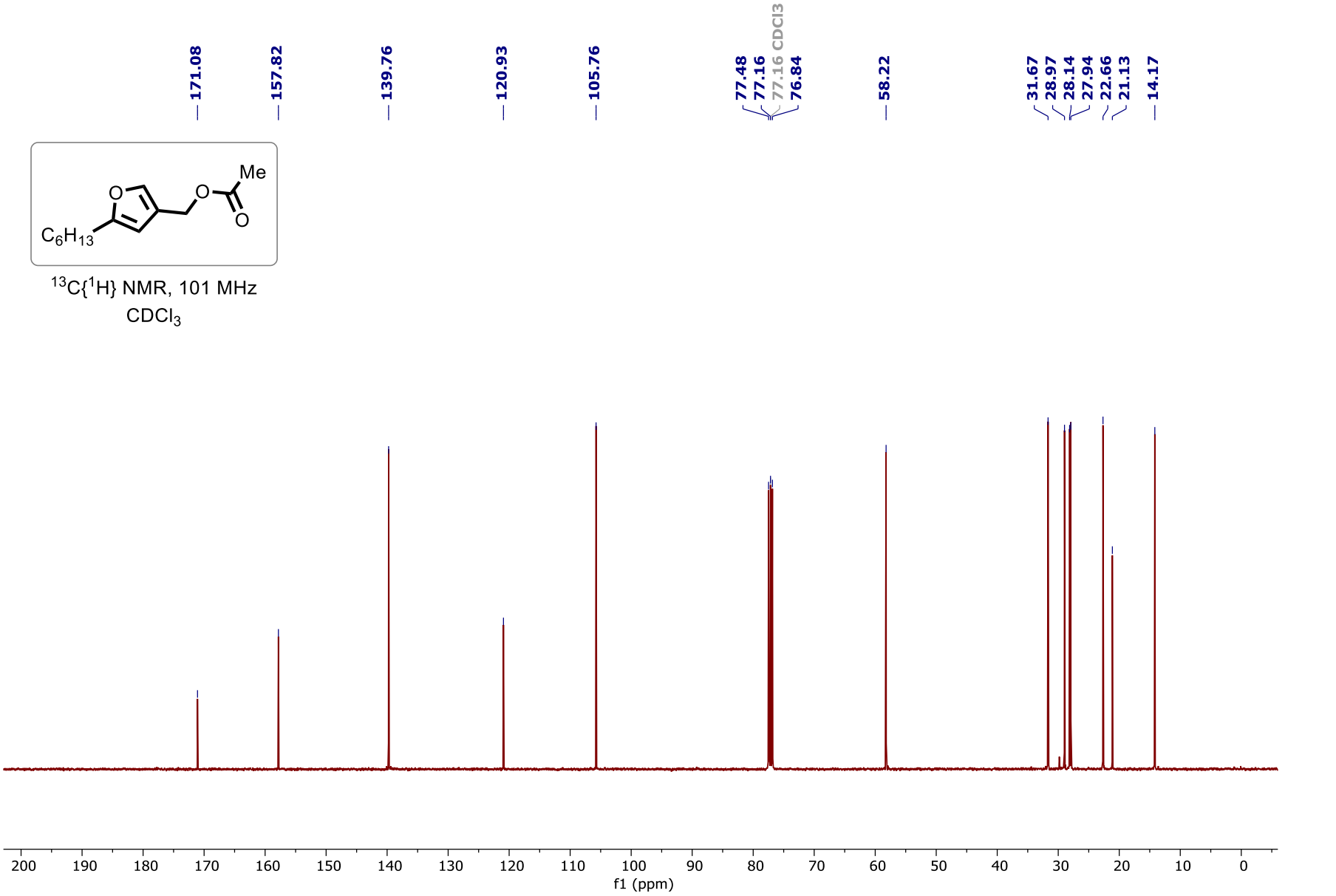
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Nonylfuran-3-yl)methyl decanoate (5d):



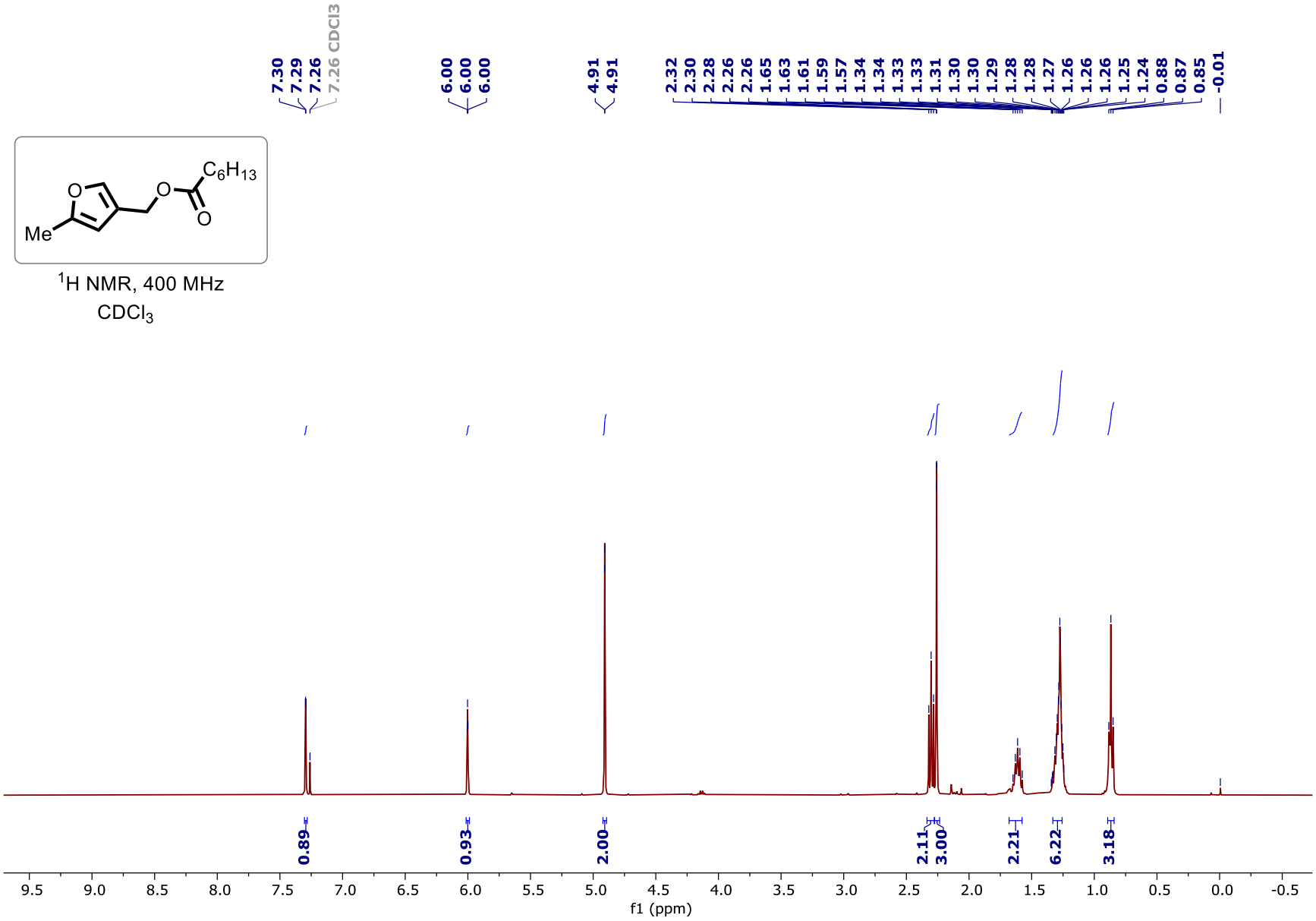
^{1}H NMR spectrum of (5-Hexylfuran-3-yl)methyl acetate (5ea):



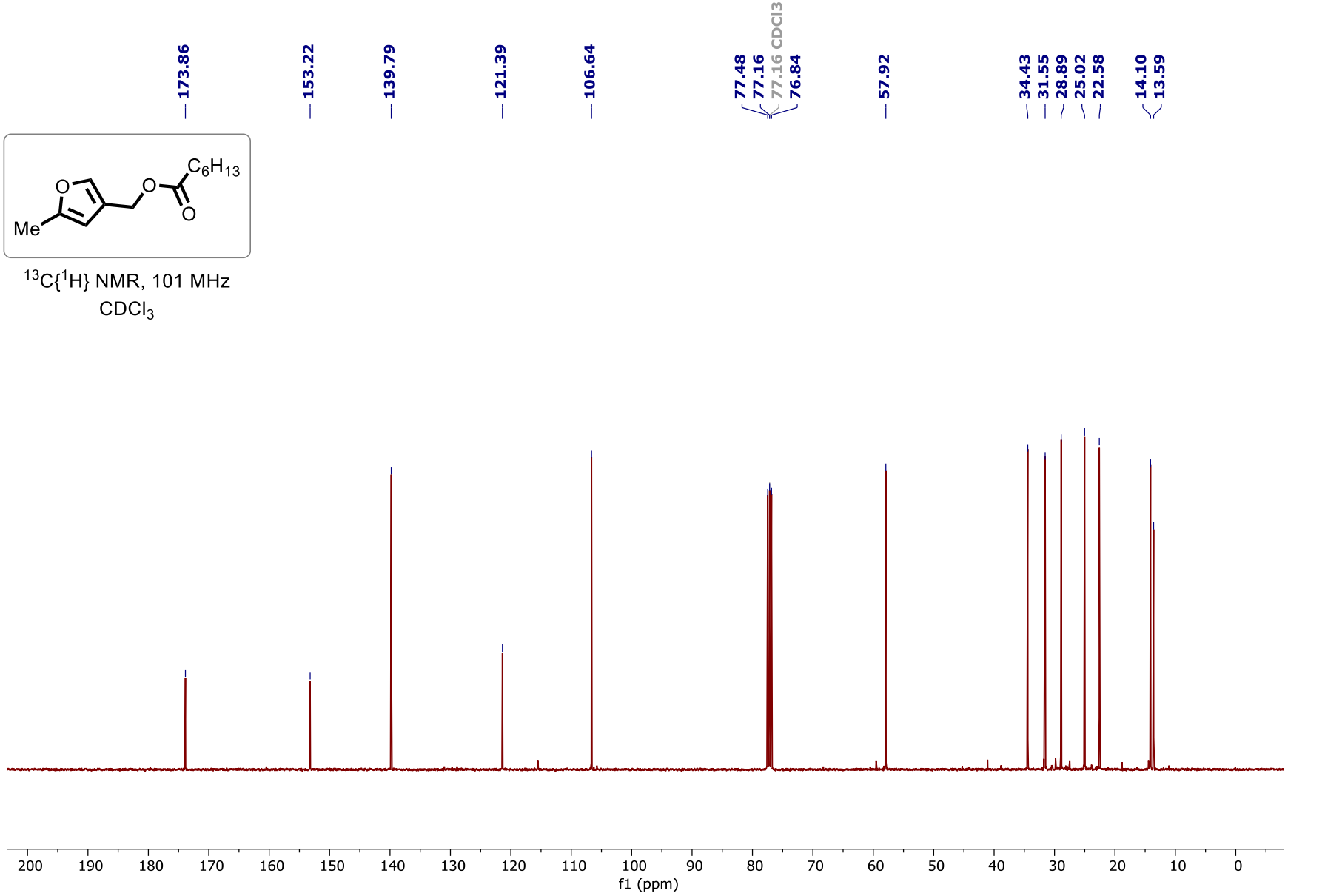
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Hexylfuran-3-yl)methyl acetate (5ea):



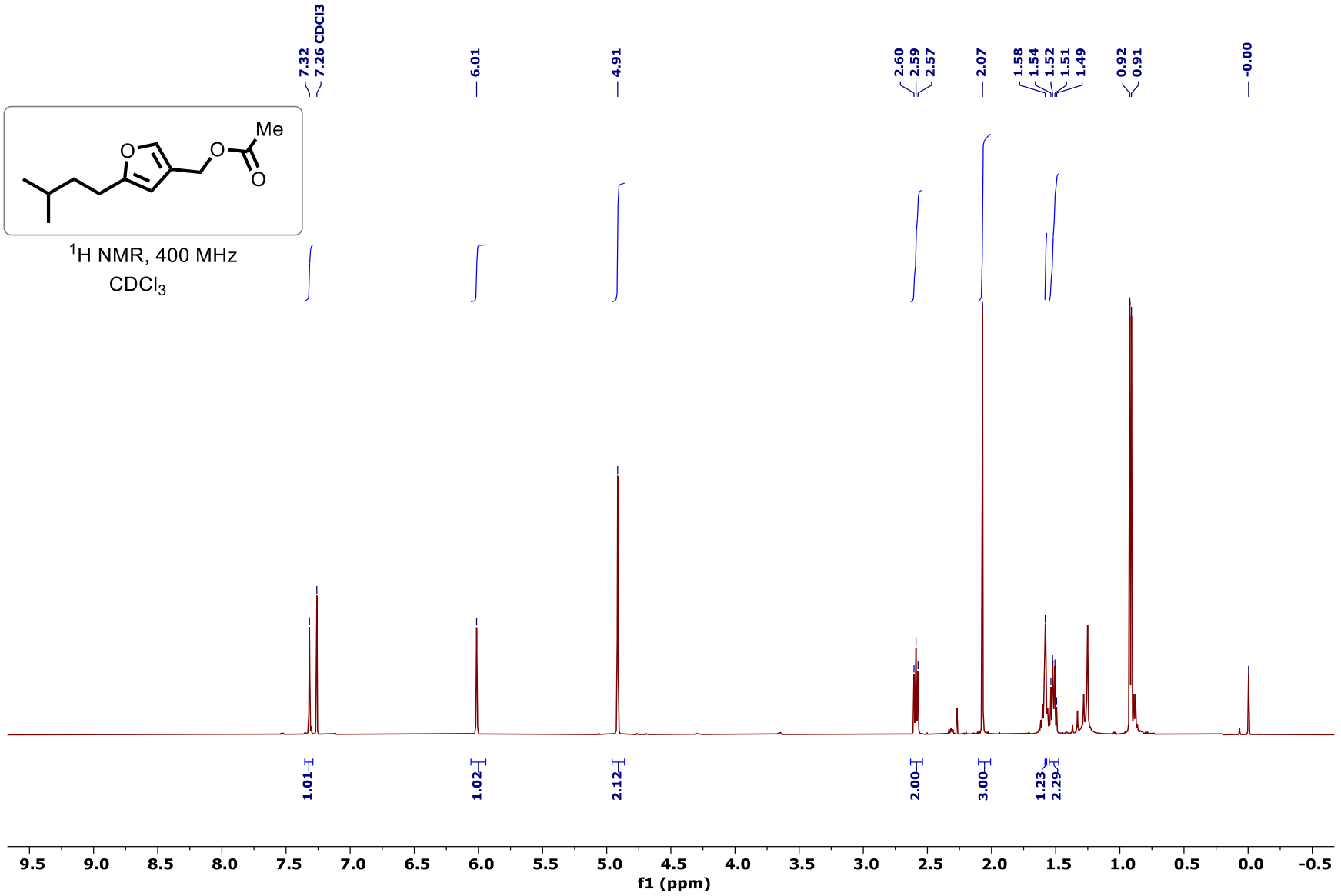
^{1}H NMR spectrum of (5-Methylfuran-3-yl)methyl heptanoate (5eb):



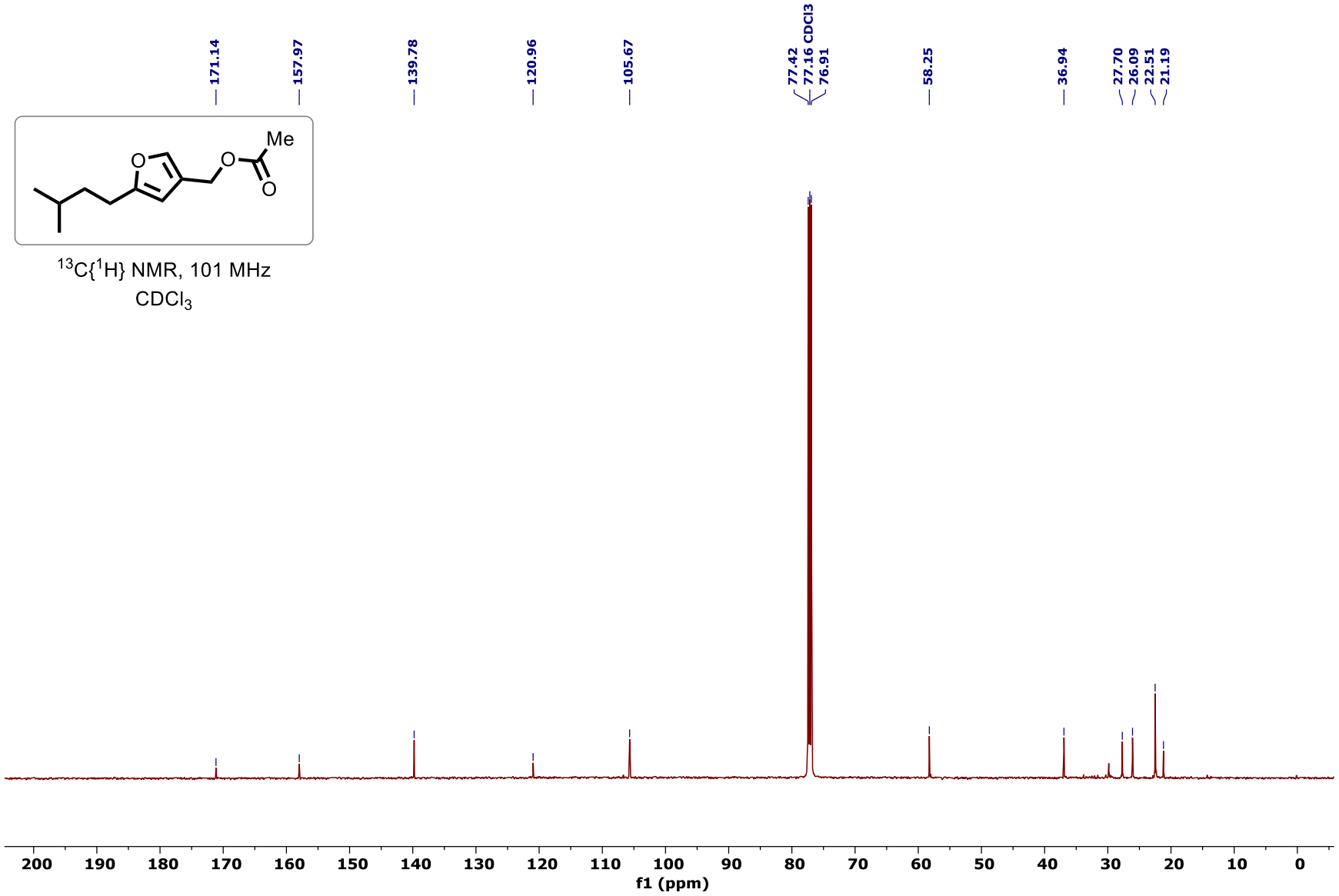
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Methylfuran-3-yl)methyl heptanoate (5eb):



^{1}H NMR spectrum of (5-Isopentylfuran-3-yl)methyl acetate (5fa):

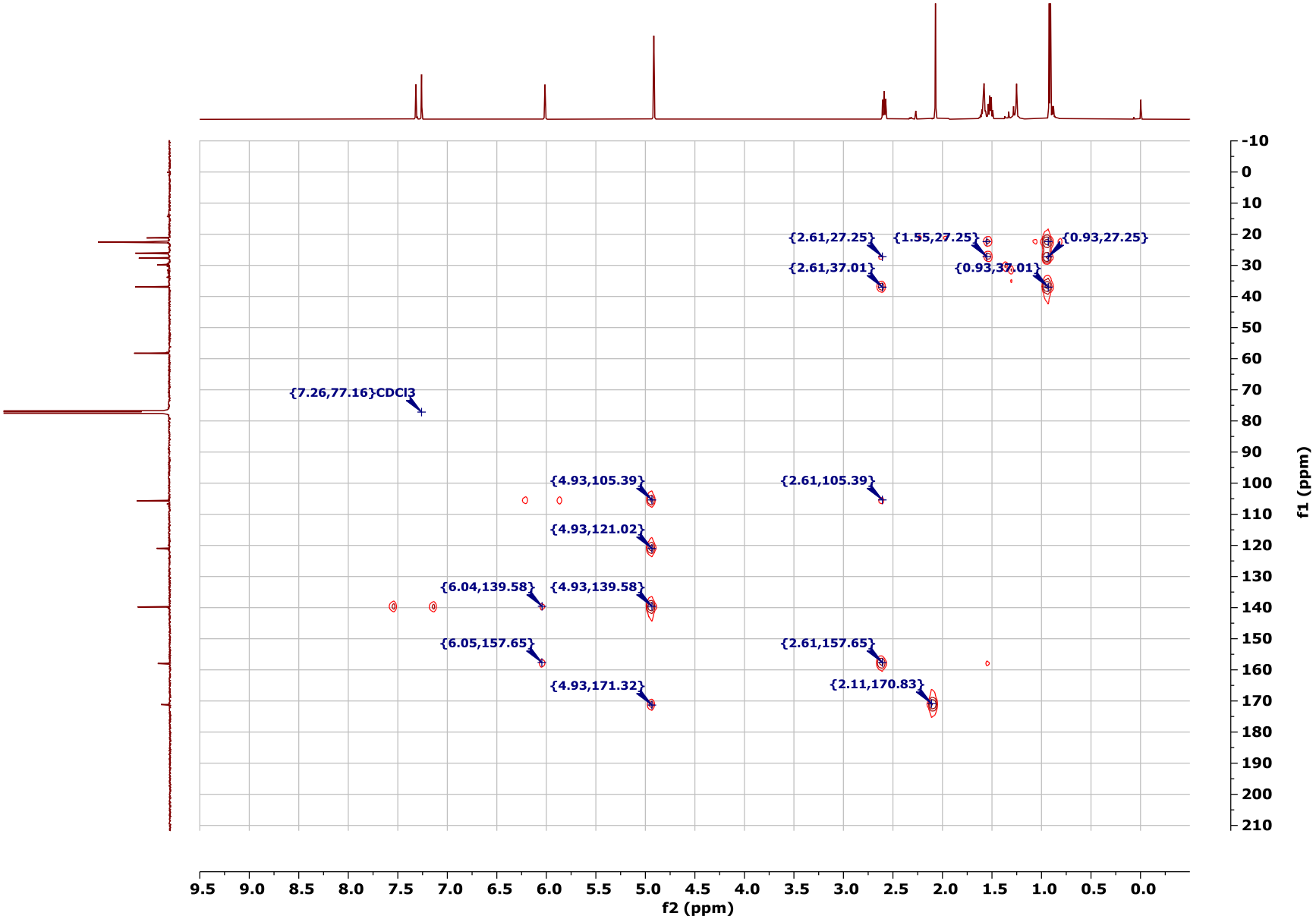


$^{13}C\{^{1}H\}$ NMR spectrum of (5-Isopentylfuran-3-yl)methyl acetate (5fa):

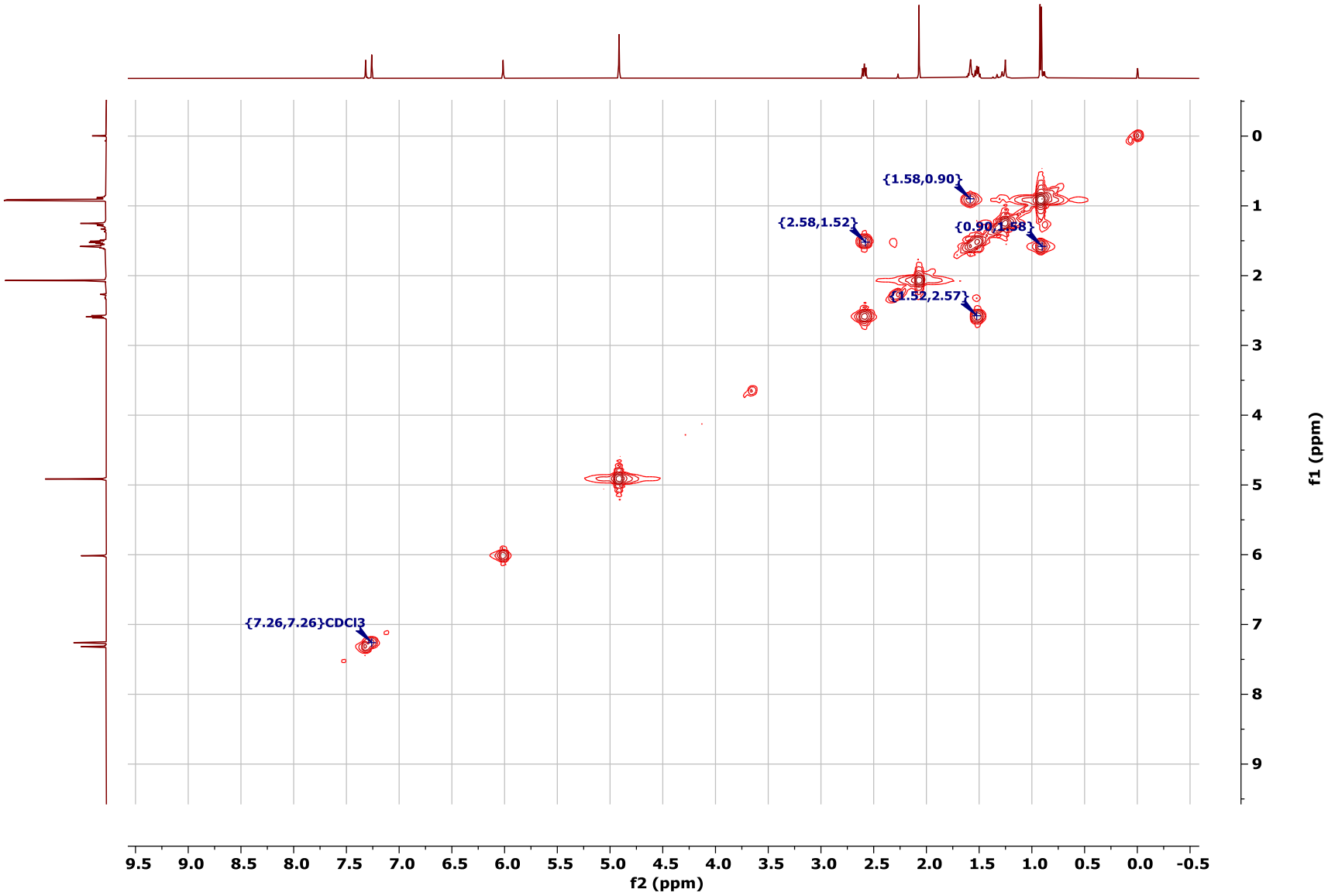


HSQC NMR spectrum of (5-Isopentylfuran-3-yl)methyl acetate (5fa):

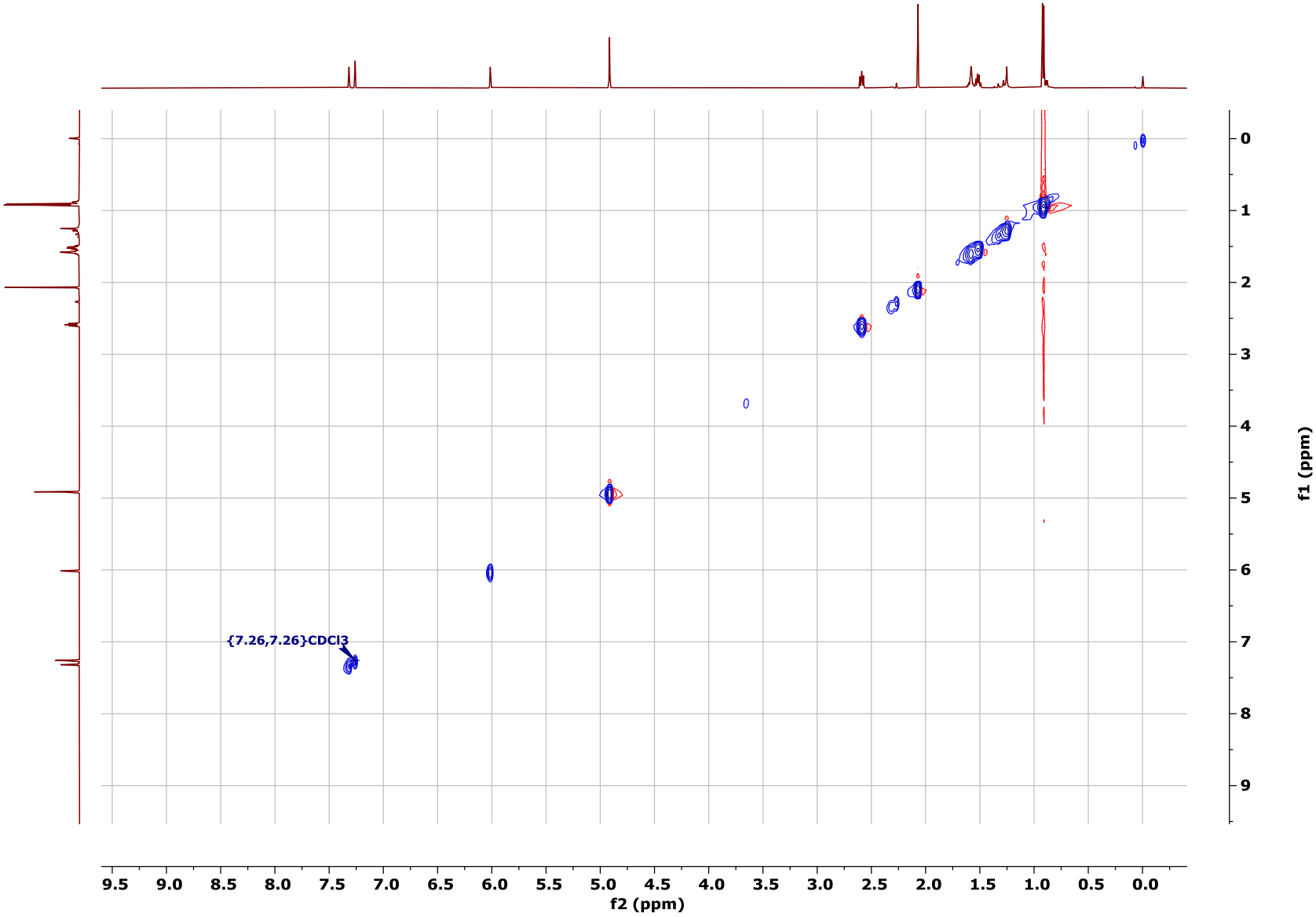
HMBC NMR spectrum of (5-Isopentylfuran-3-yl)methyl acetate (5fa):



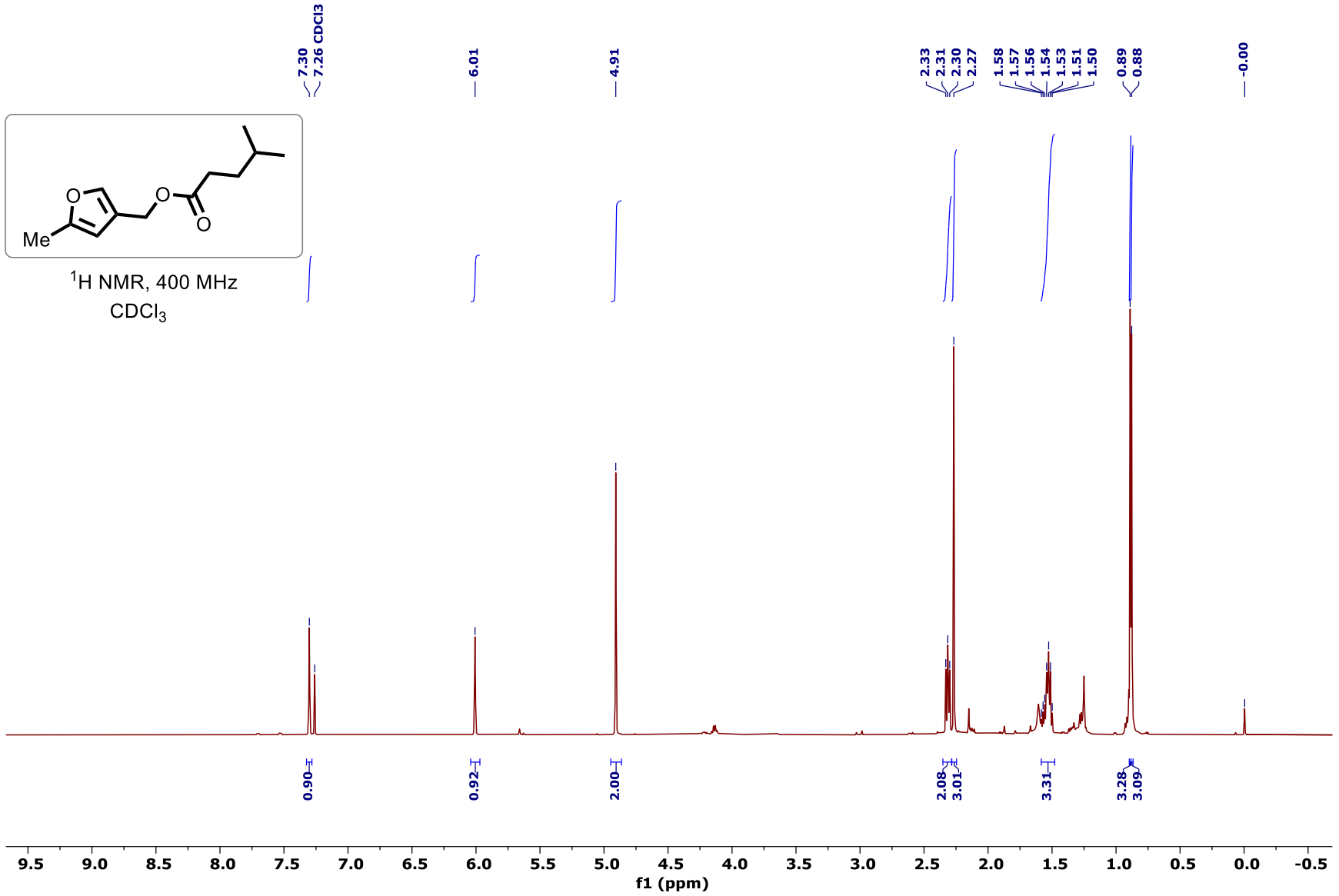
COSY NMR spectrum of (5-Isopentylfuran-3-yl)methyl acetate (5fa):



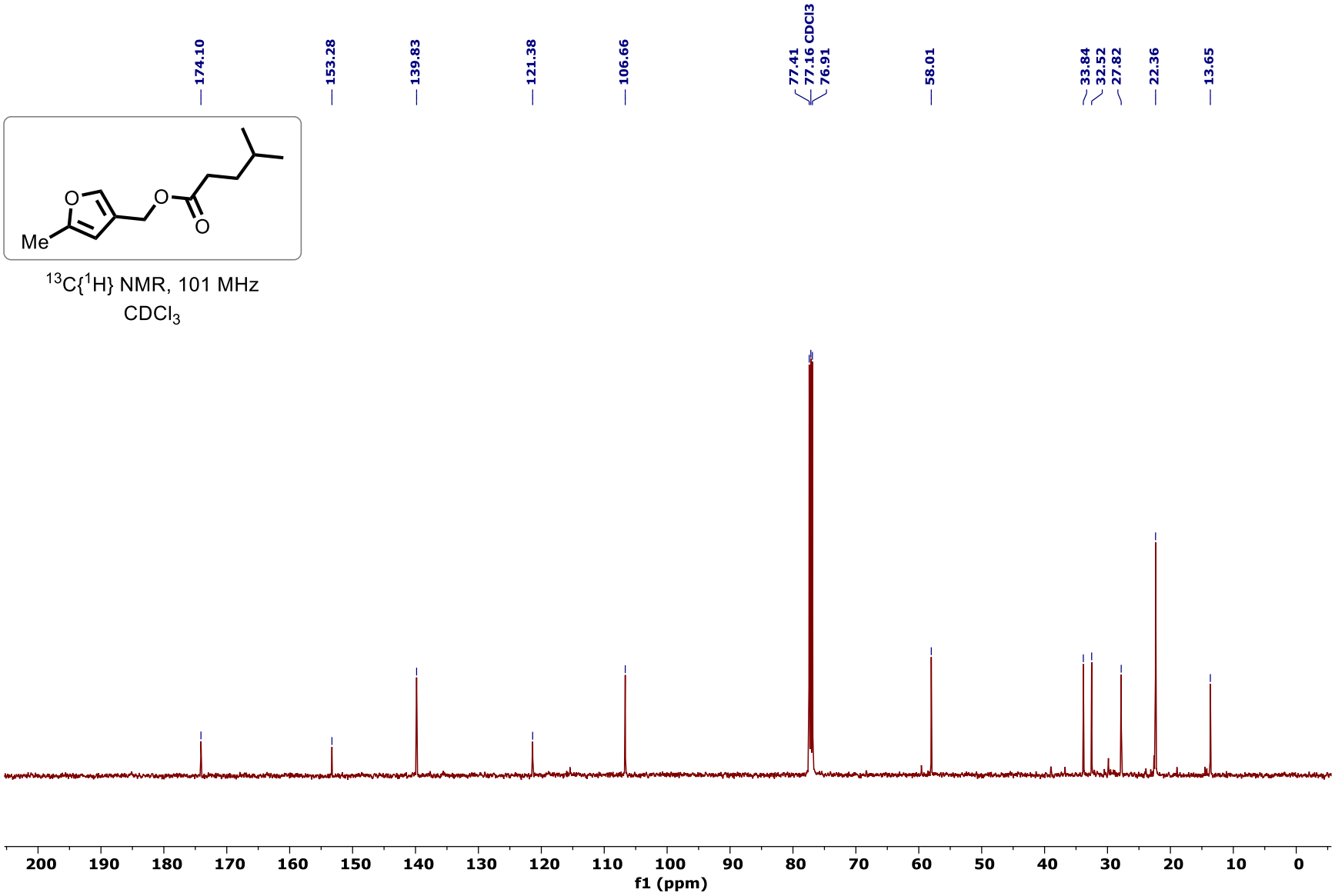
NOESY NMR spectrum of (5-Isopentylfuran-3-yl)methyl acetate (5fa):



^{1}H NMR spectrum of (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):

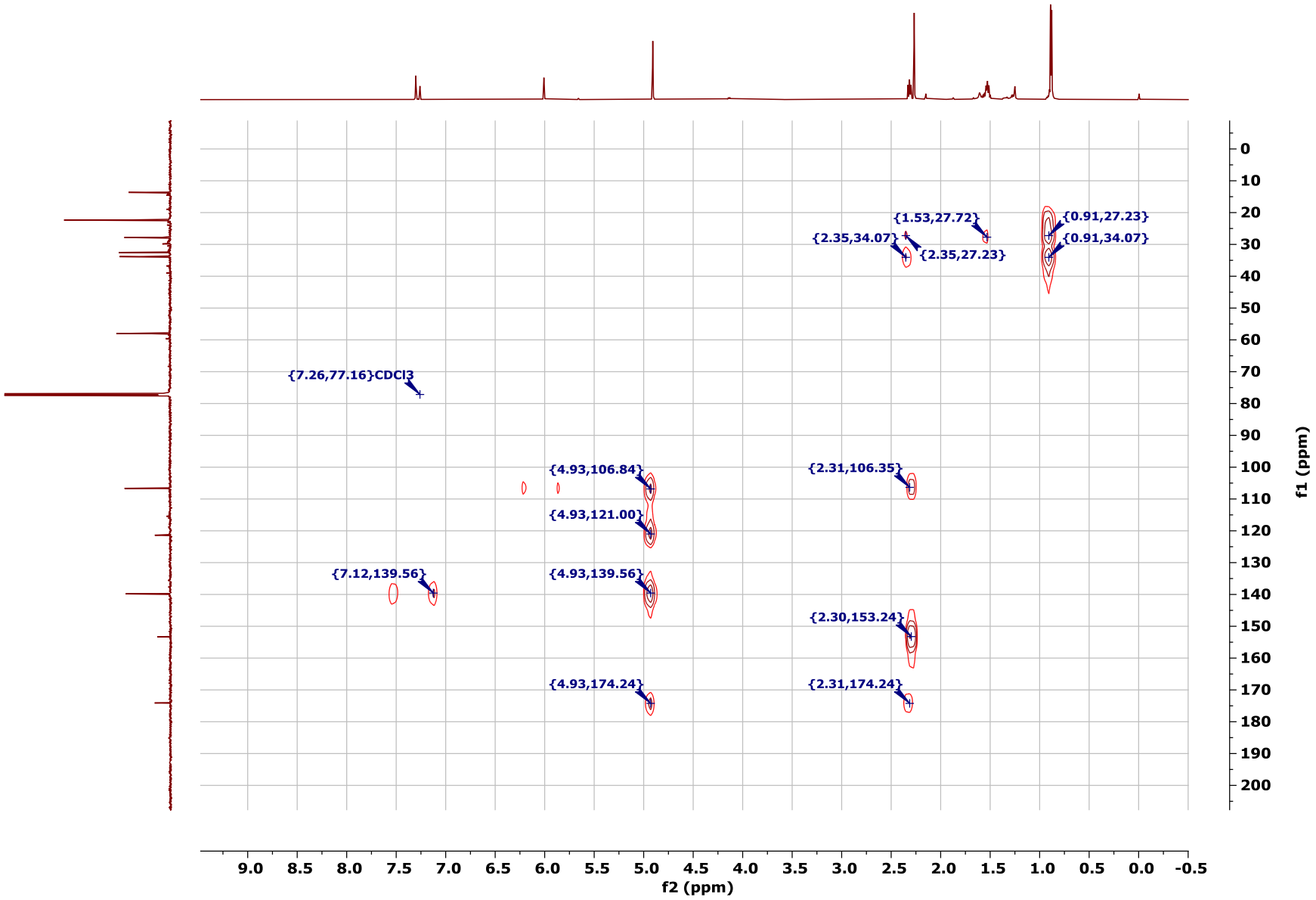


$^{13}C\{^{1}H\}$ NMR spectrum of (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):

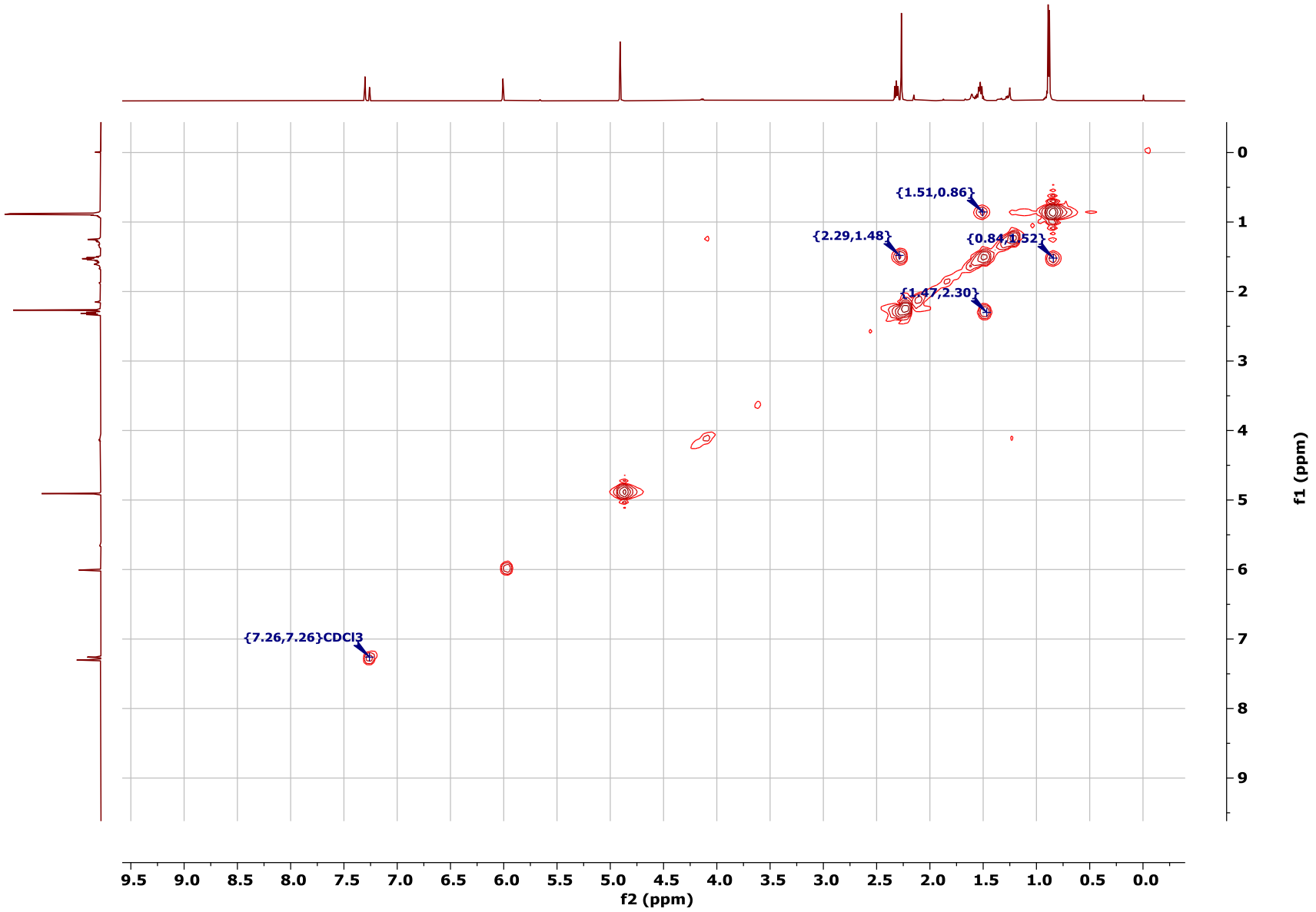


HSQC NMR spectrum of (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):

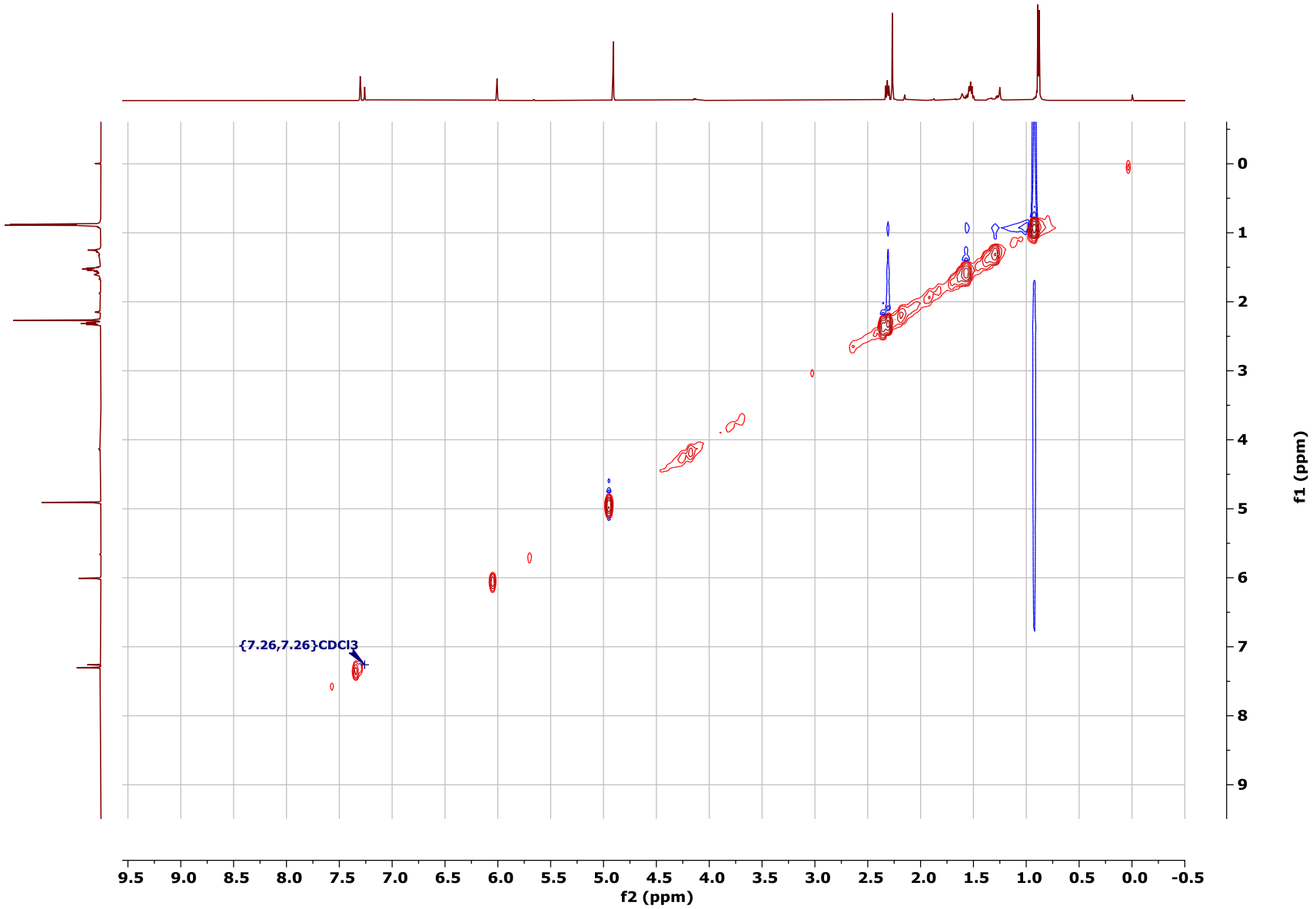
HMBC NMR spectrum of (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):



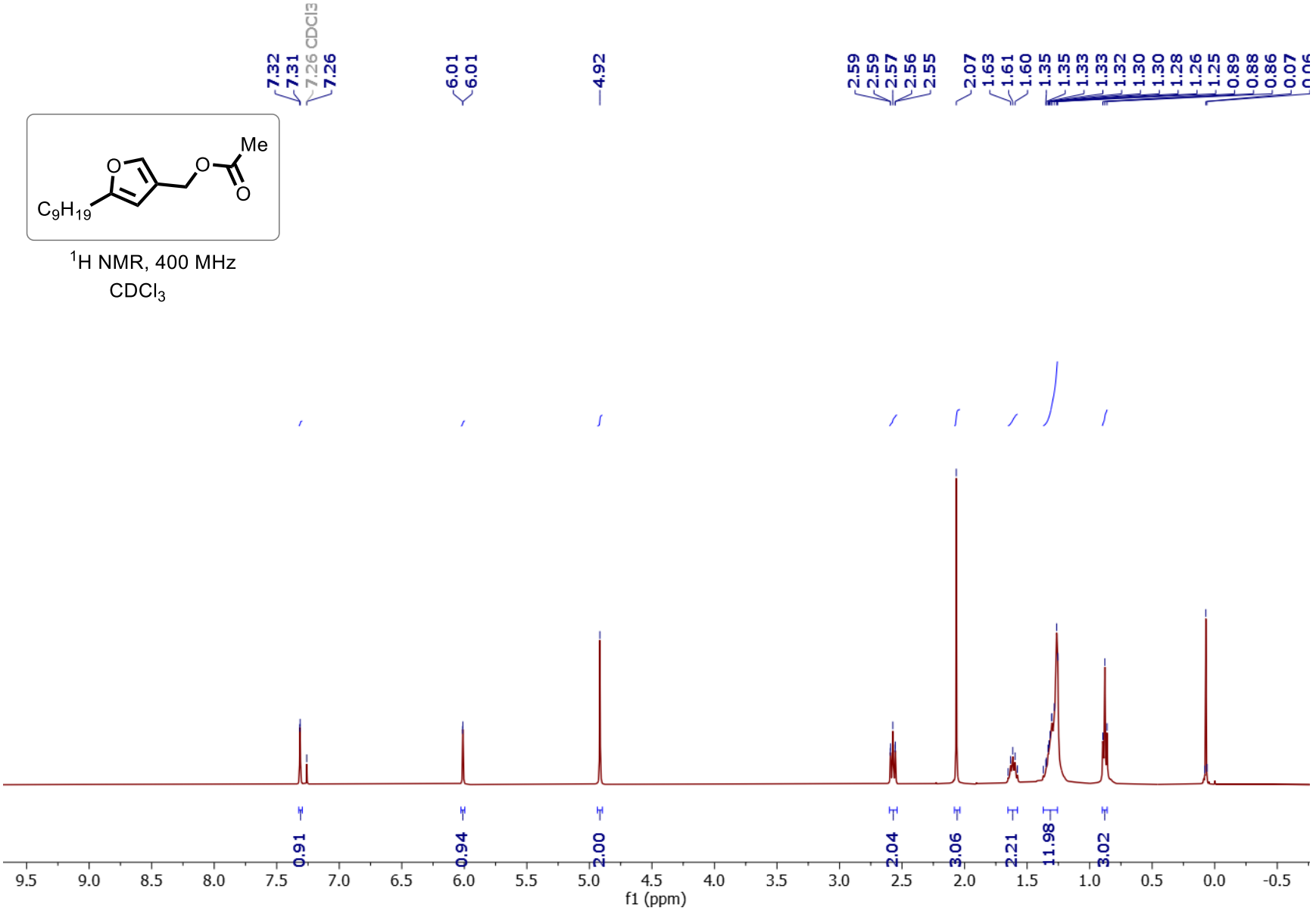
COSY NMR spectrum of (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):



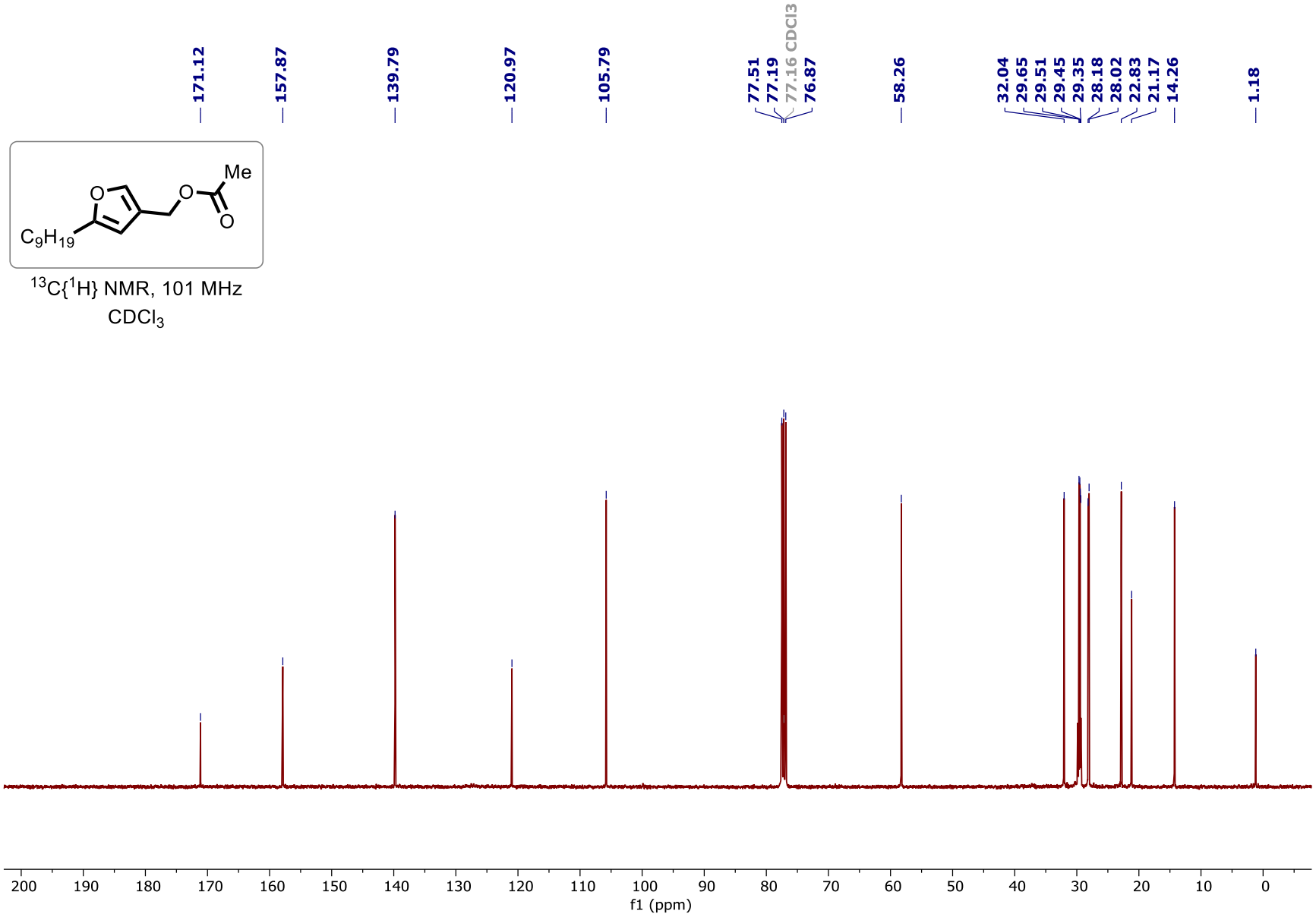
NOESY NMR spectrum of (5-Methylfuran-3-yl)methyl 4-methylpentanoate (5fb):



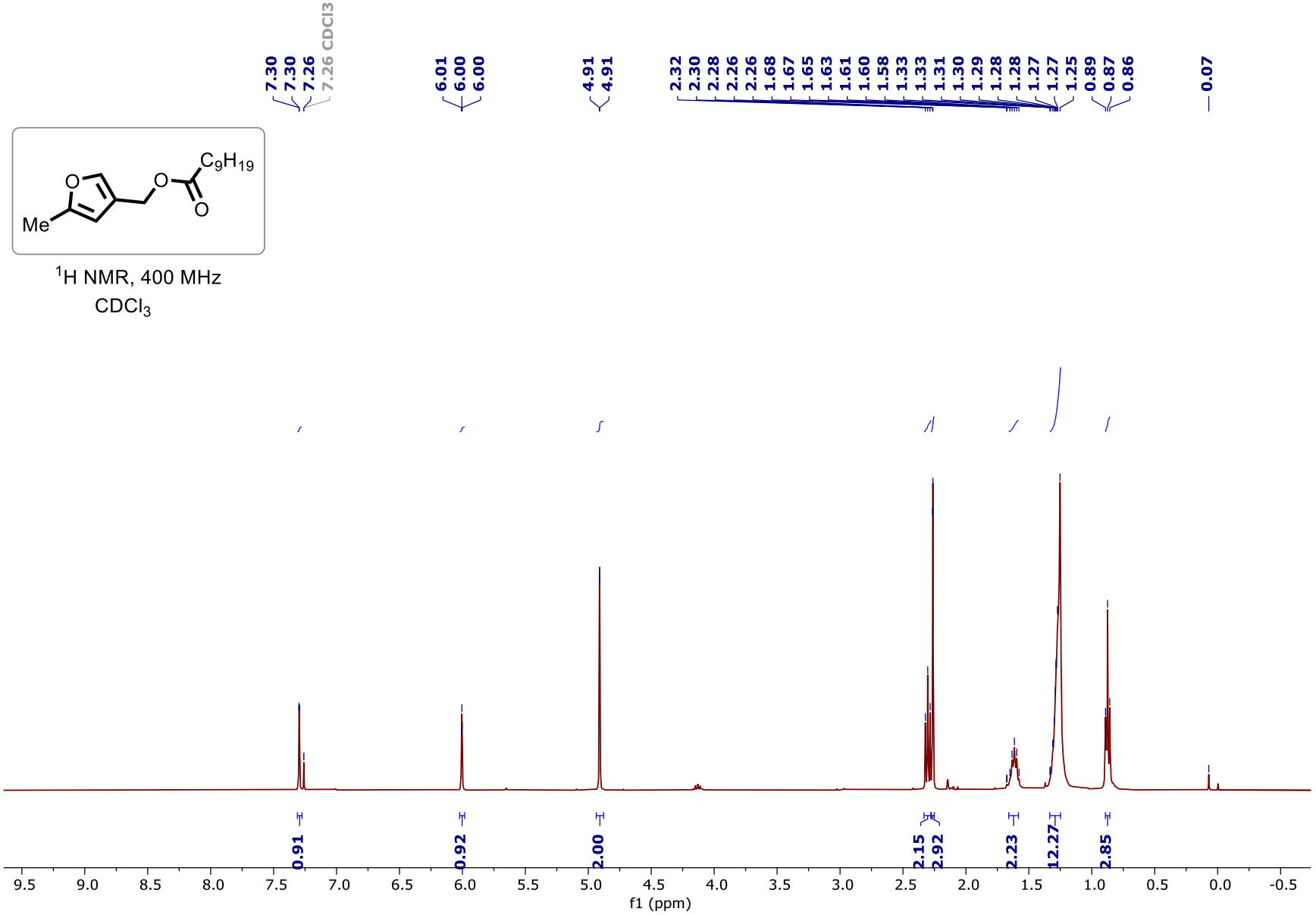
^{1}H NMR spectrum of (5-Nonylfuran-3-yl)methyl acetate (5ga):



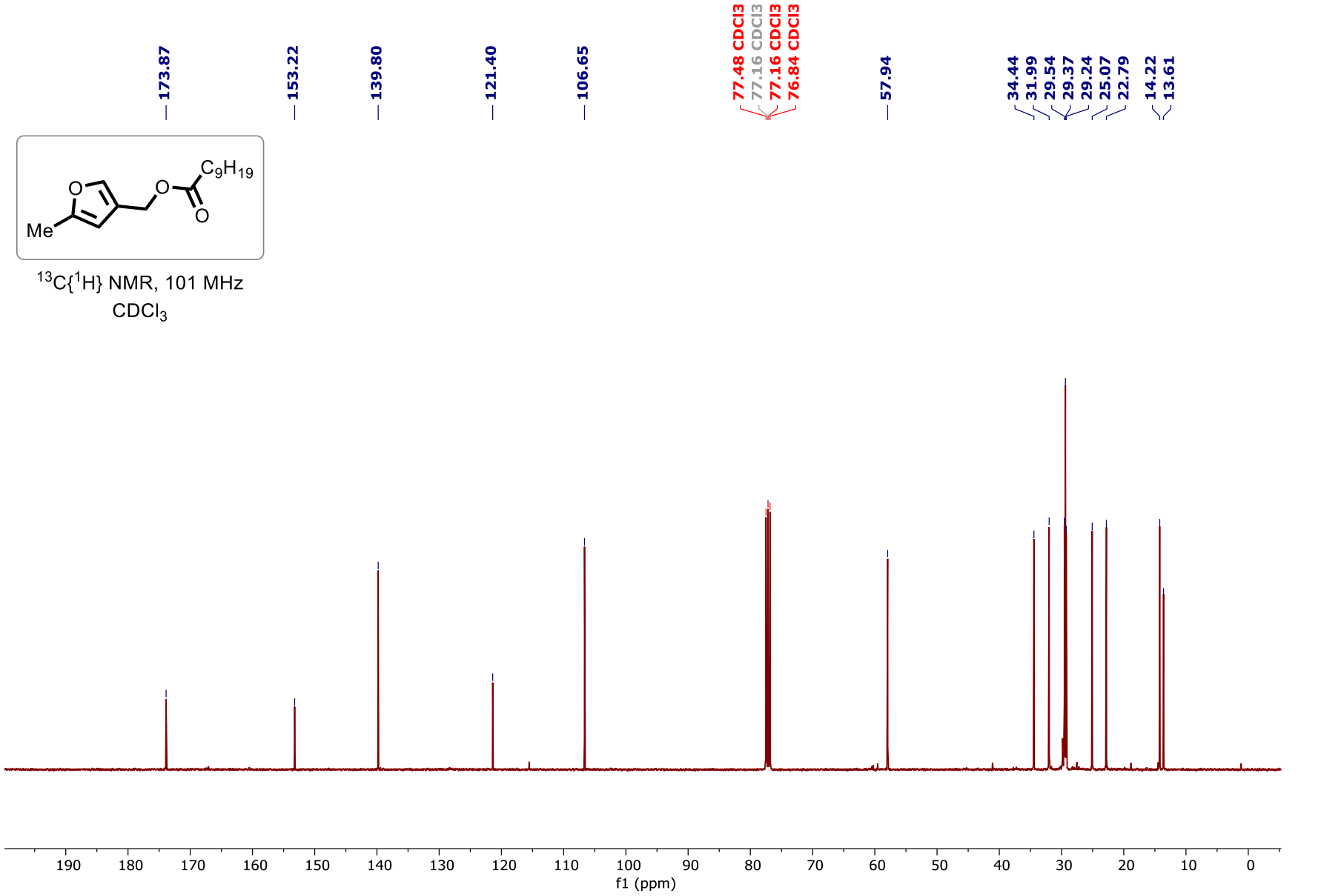
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Nonylfuran-3-yl)methyl acetate (5ga):



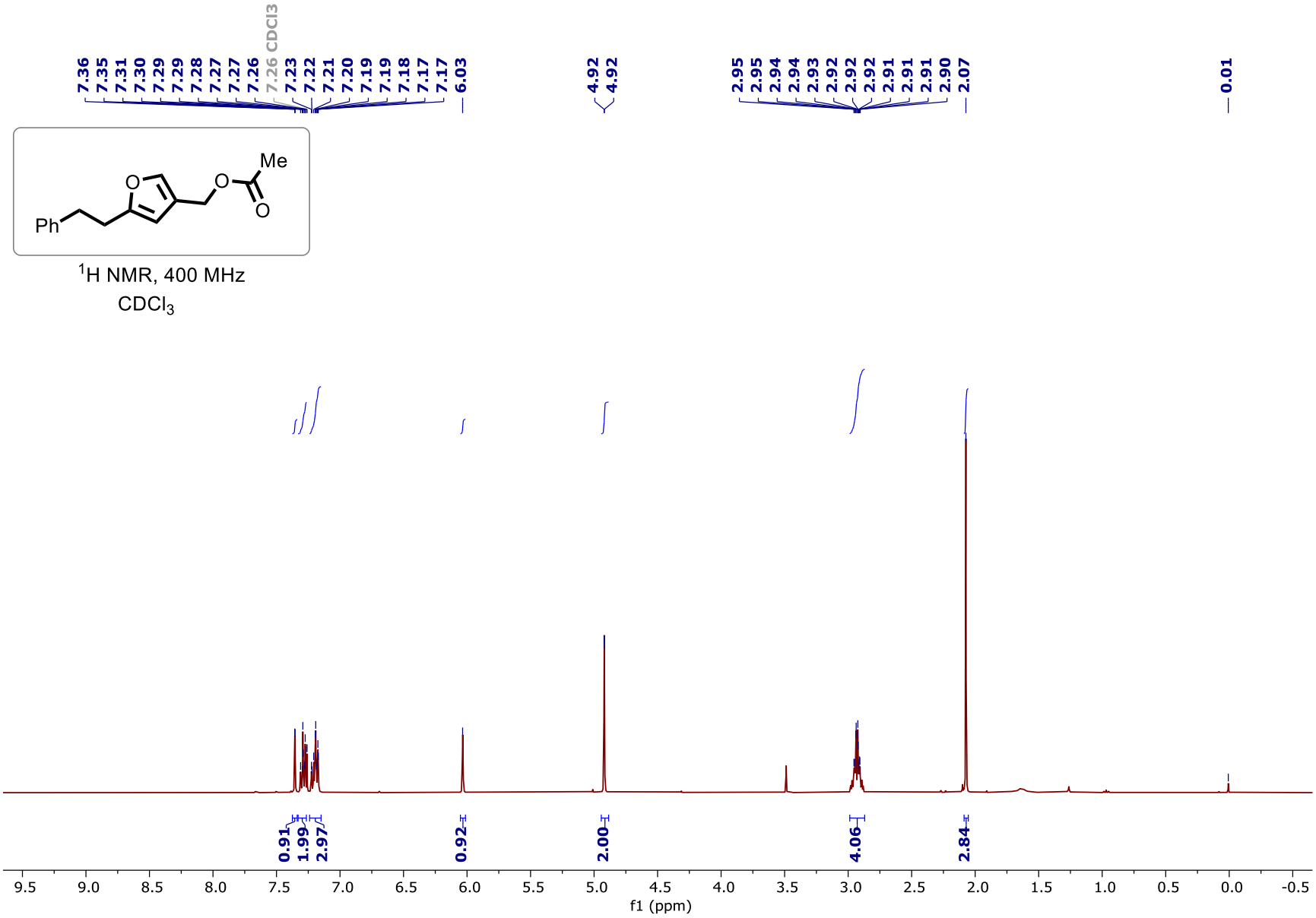
^{1}H NMR spectrum of (5-Methylfuran-3-yl)methyl decanoate (5gb):



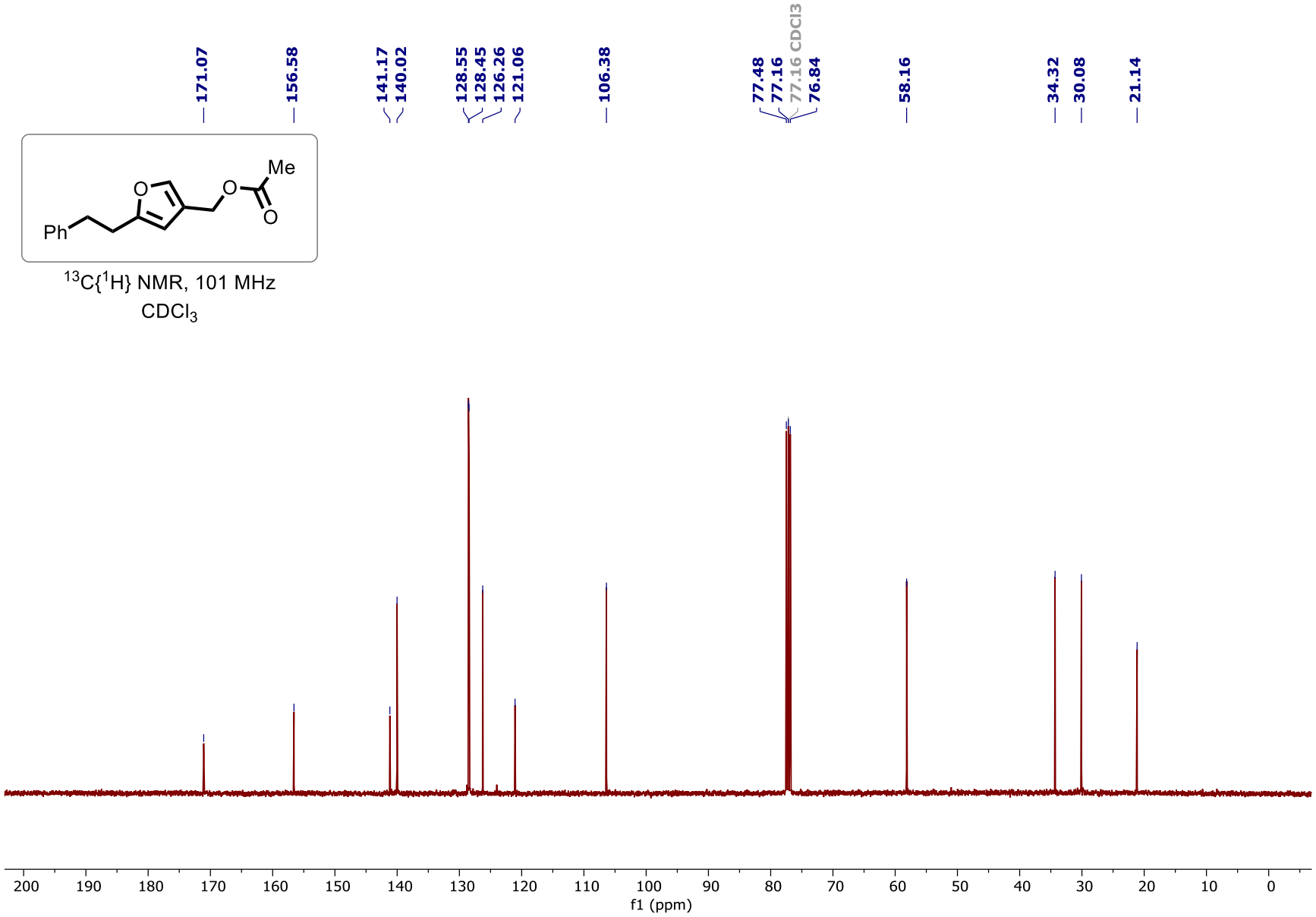
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Methylfuran-3-yl)methyl decanoate (5gb):



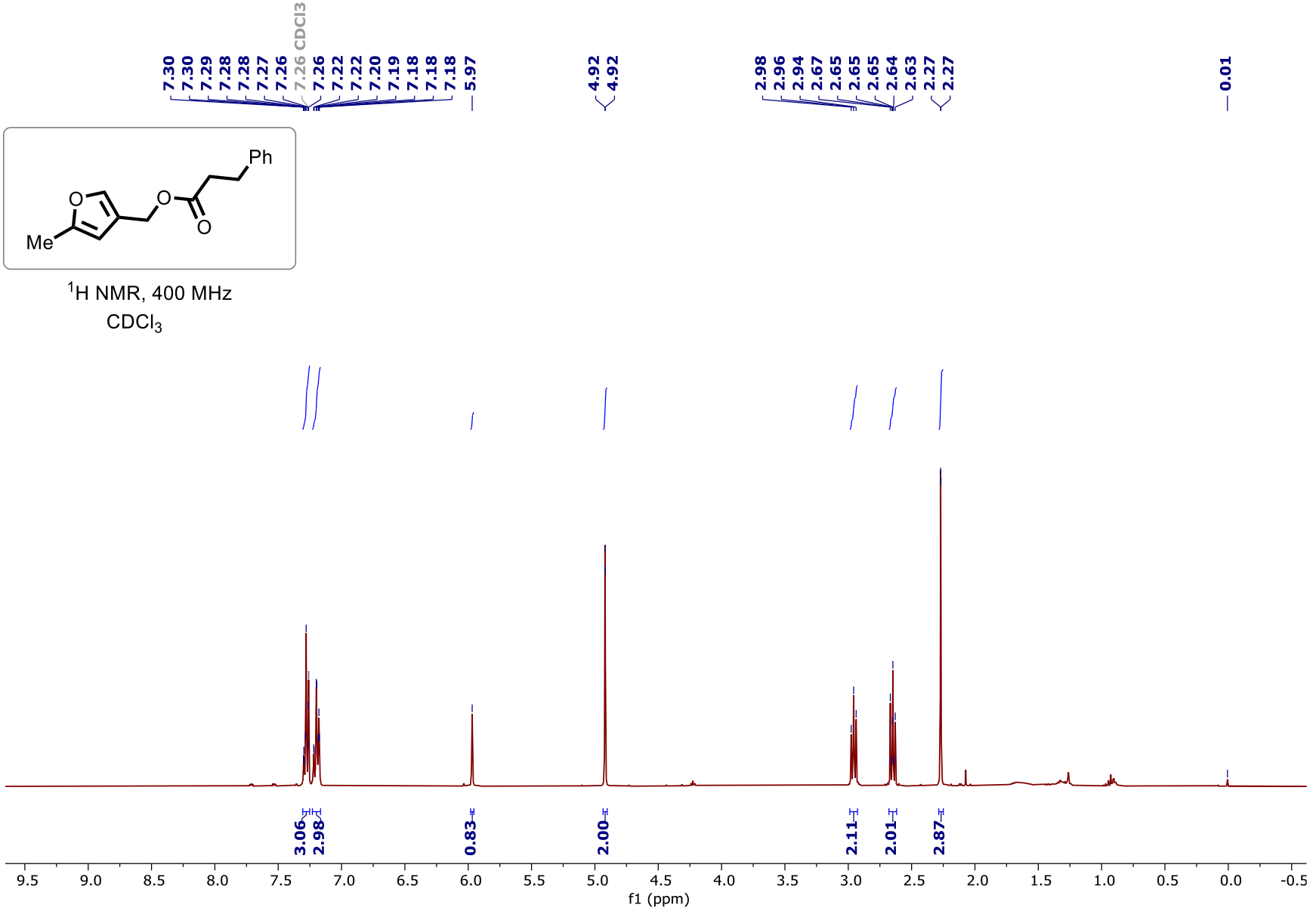
^{1}H NMR spectrum of (5-Phenethylfuran-3-yl)methyl acetate (5ha):



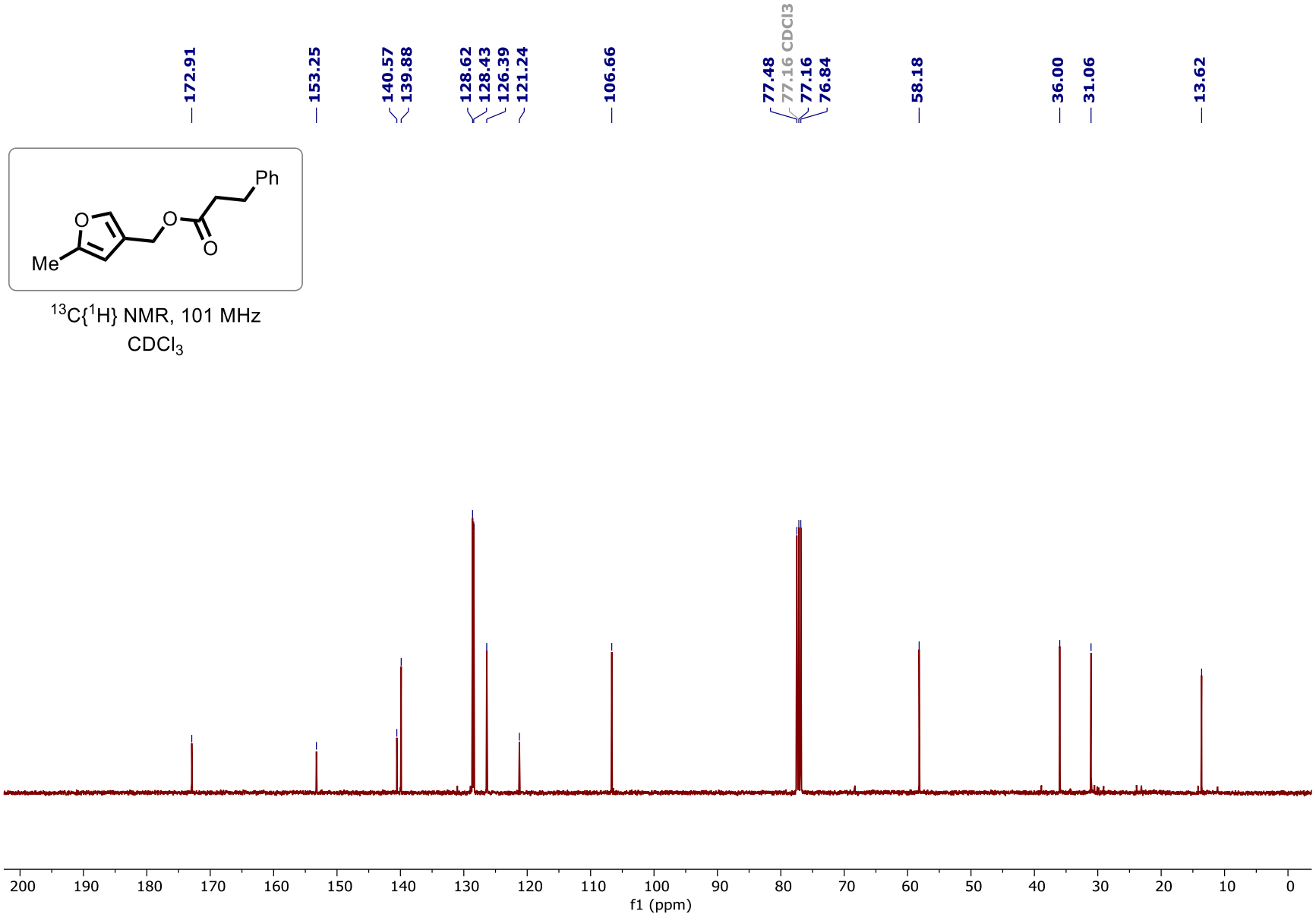
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Phenethylfuran-3-yl)methyl acetate (5ha):



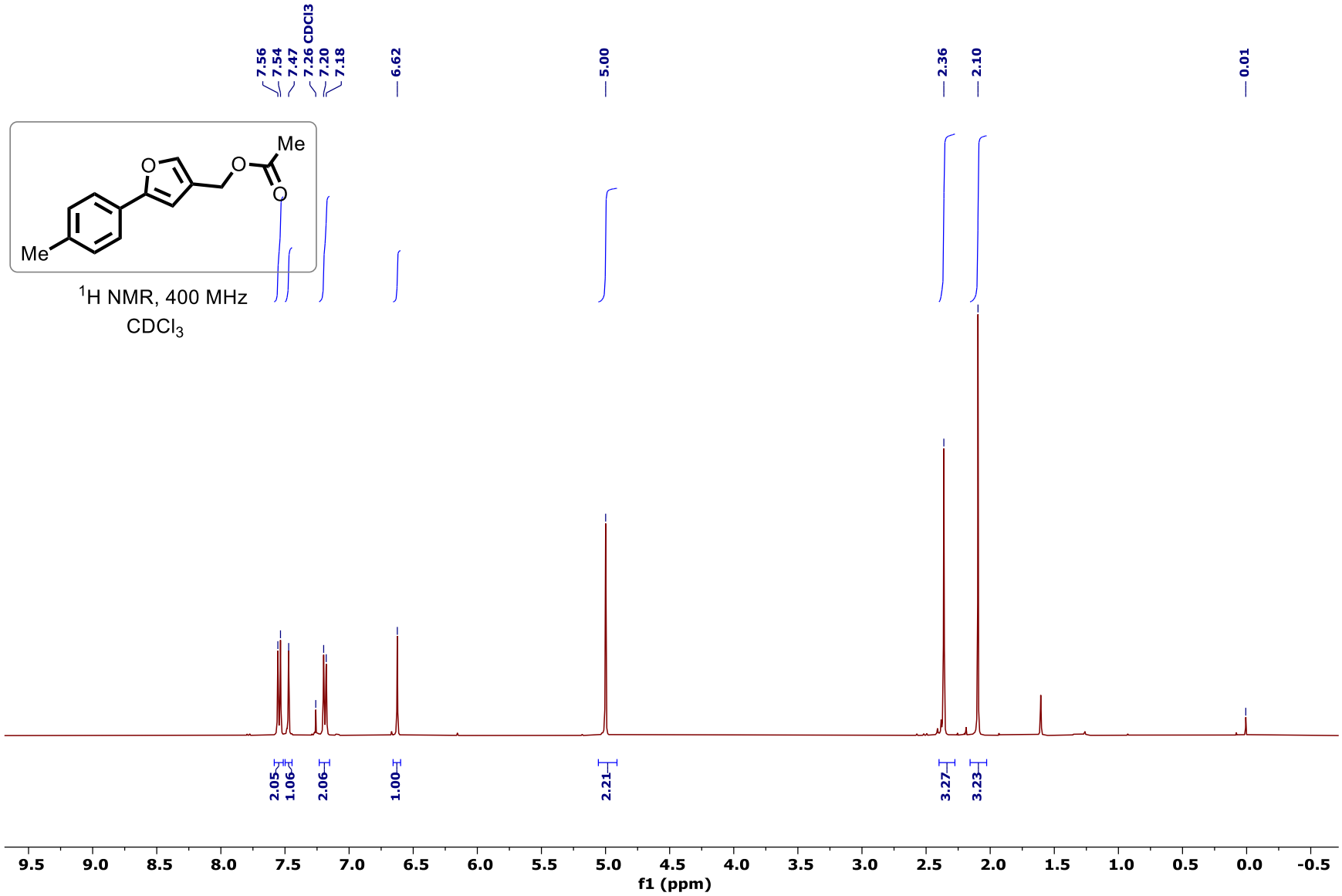
^{1}H NMR spectrum of (5-Methylfuran-3-yl)methyl 3-phenylpropanoate (5hb):



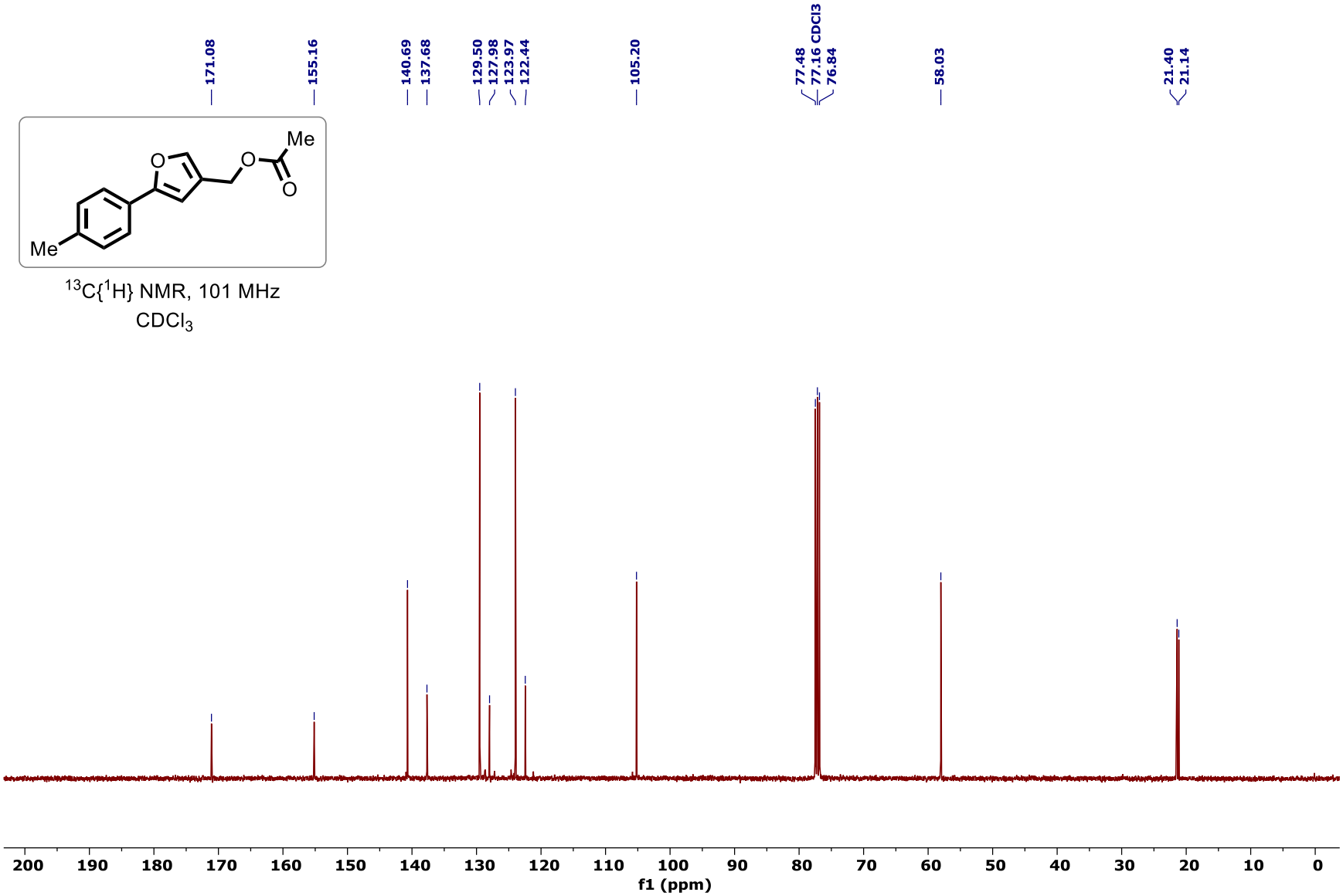
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Methylfuran-3-yl)methyl 3-phenylpropanoate (5hb):



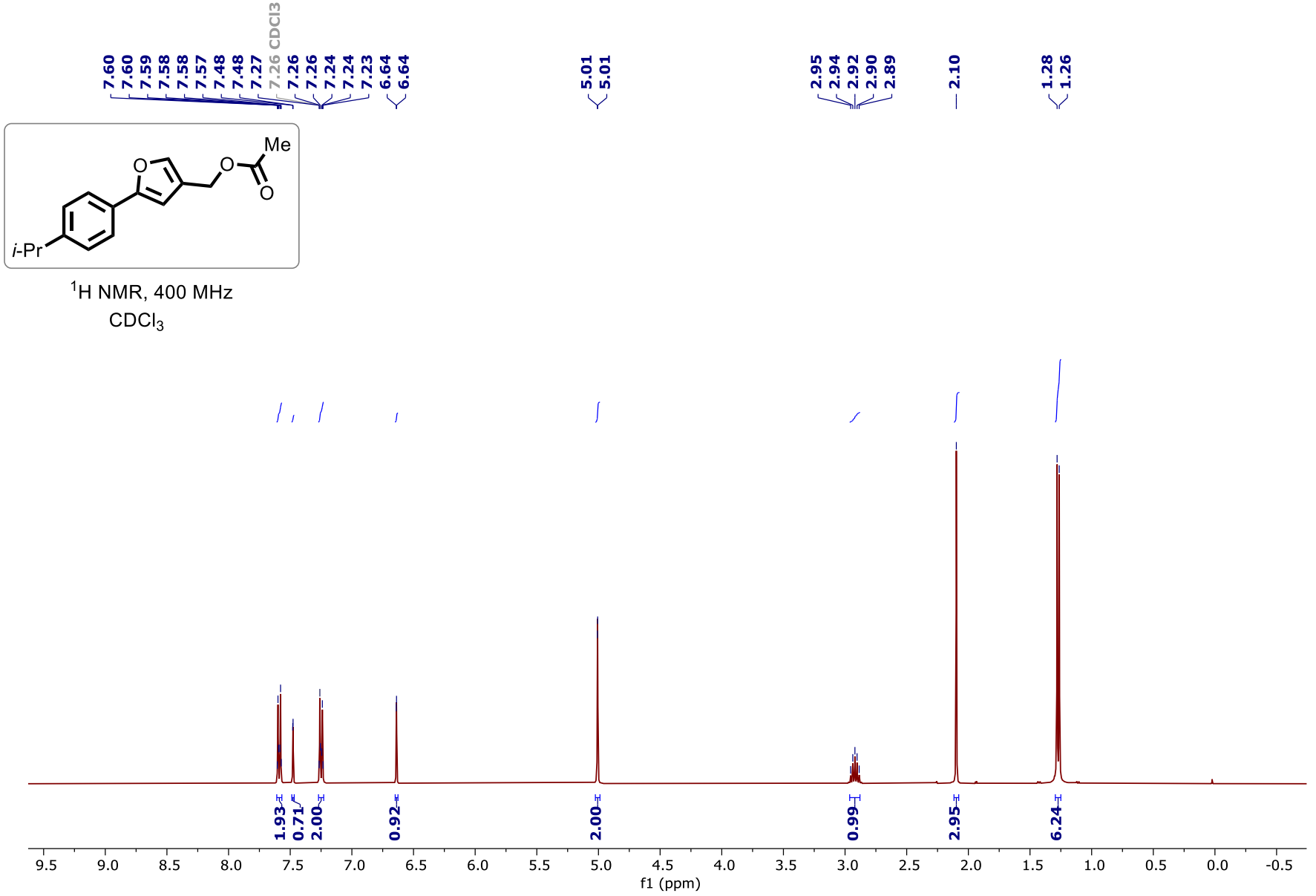
^{1}H NMR spectrum of (5-(*p*-Tolyl)furan-3-yl)methyl acetate (5i):



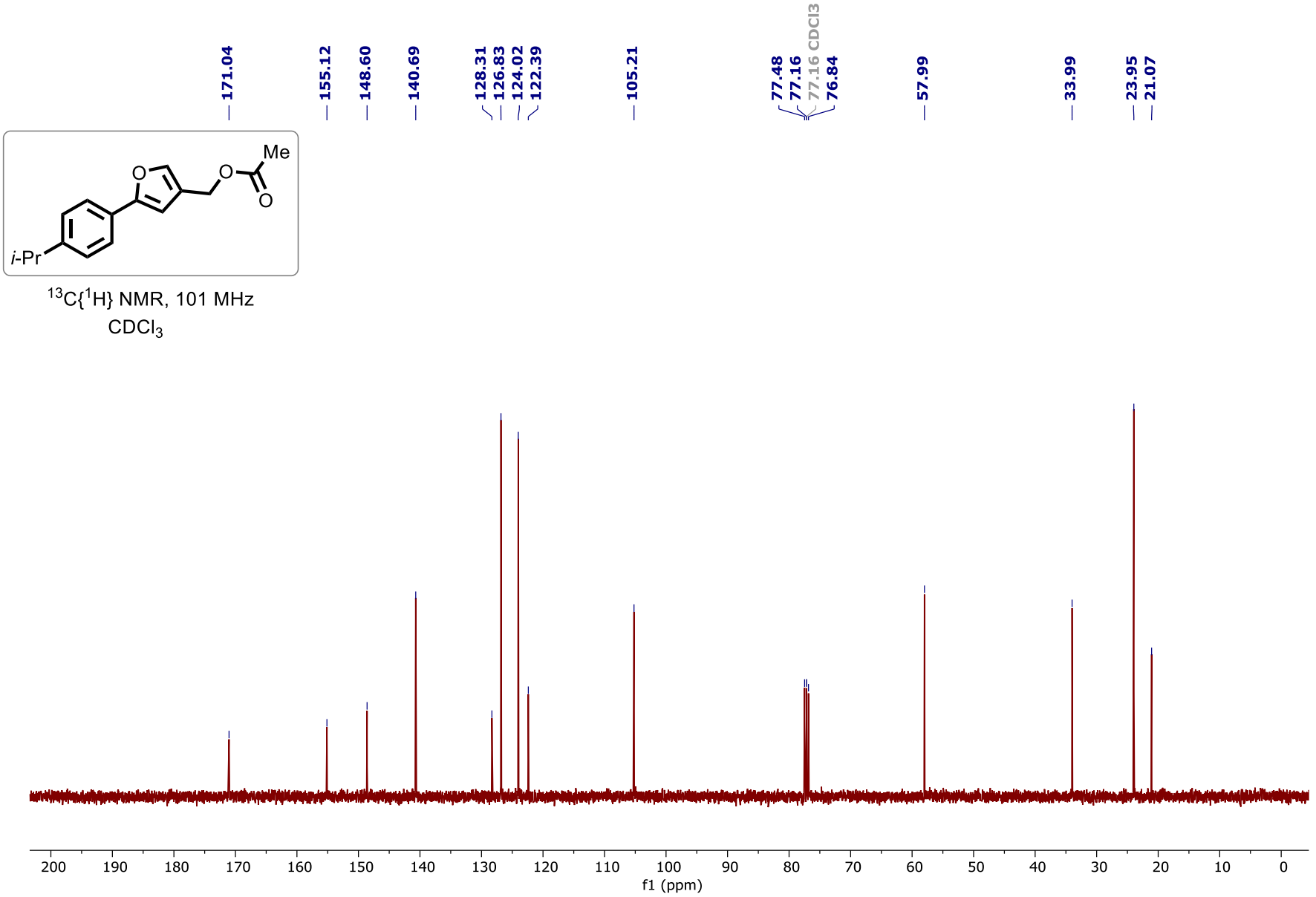
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(*p*-Tolyl)furan-3-yl)methyl acetate (5i):



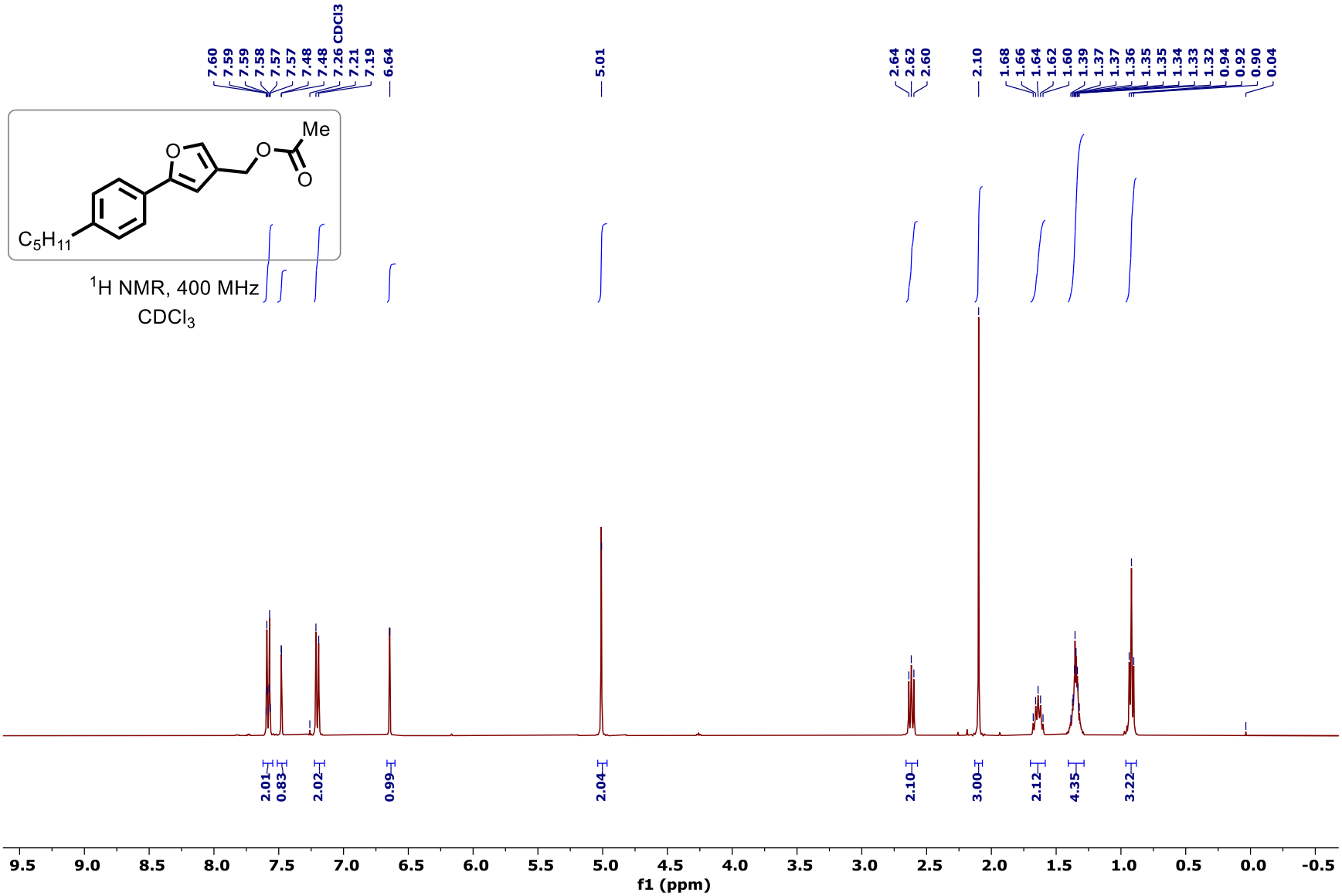
^{1}H NMR spectrum of (5-(4-Isopropylphenyl)furan-3-yl)methyl acetate (5j):



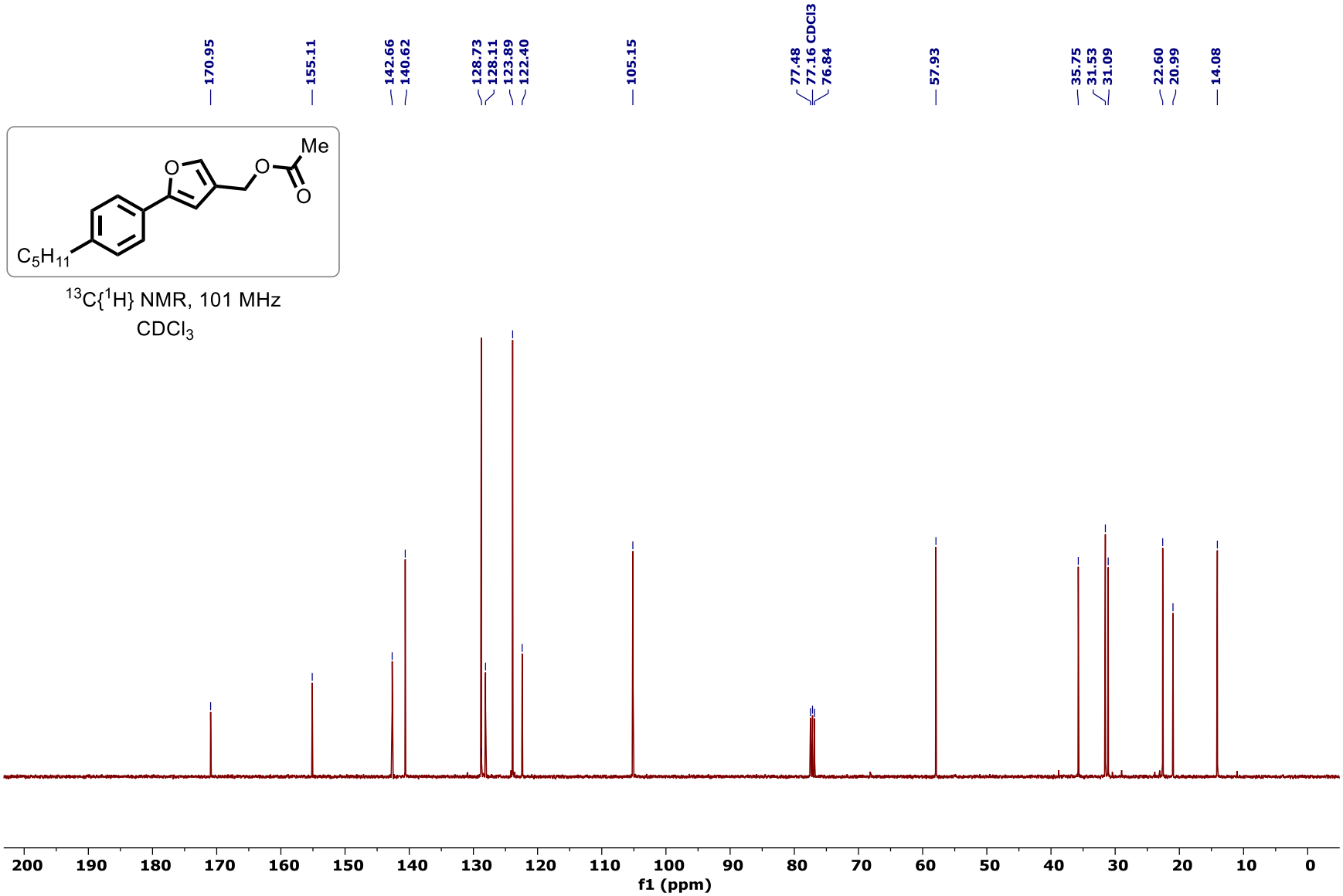
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Isopropylphenyl)furan-3-yl)methyl acetate (5j):



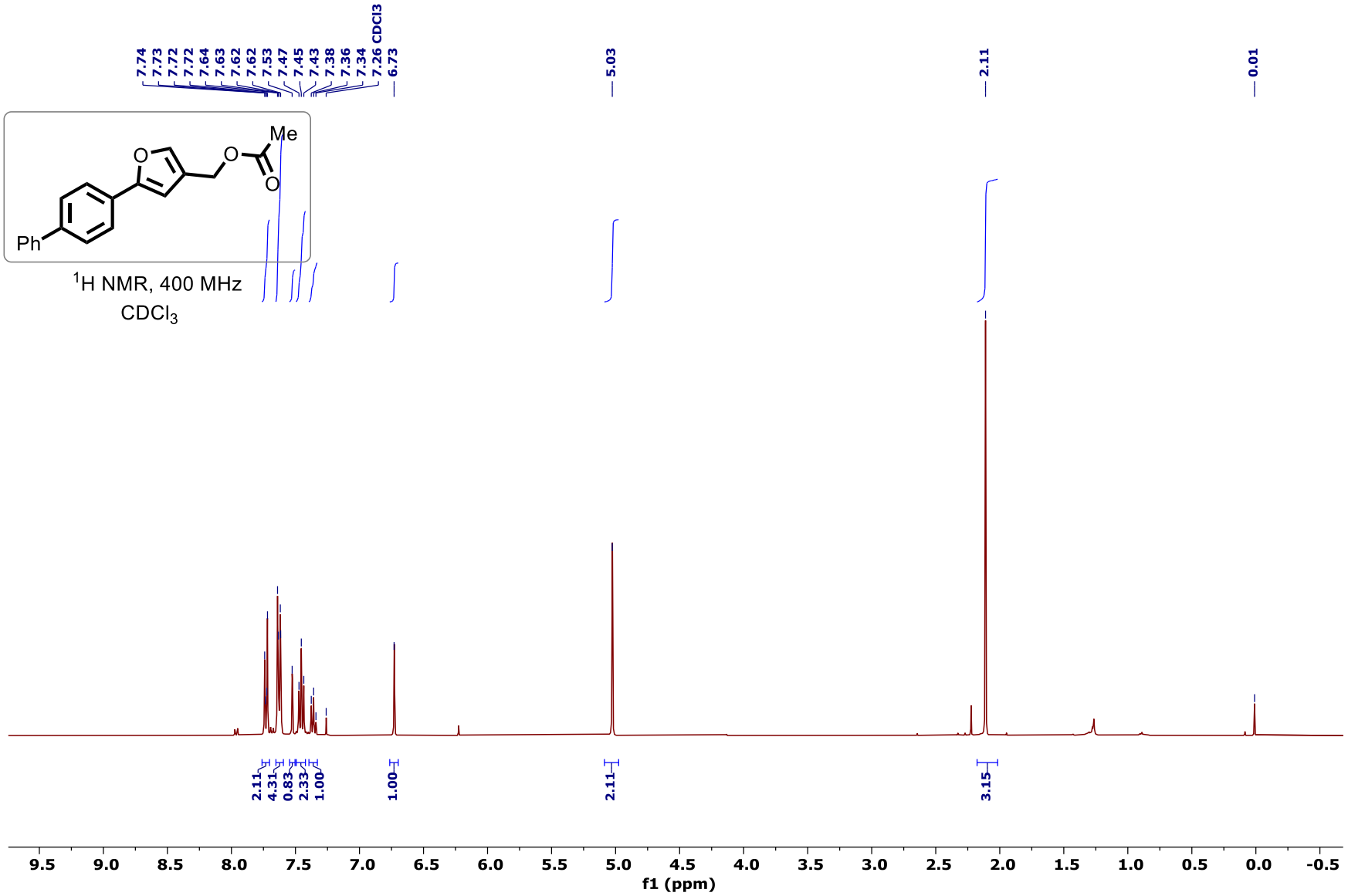
^{1}H NMR spectrum of (5-(4-Pentylphenyl)furan-3-yl)methyl acetate (5k):



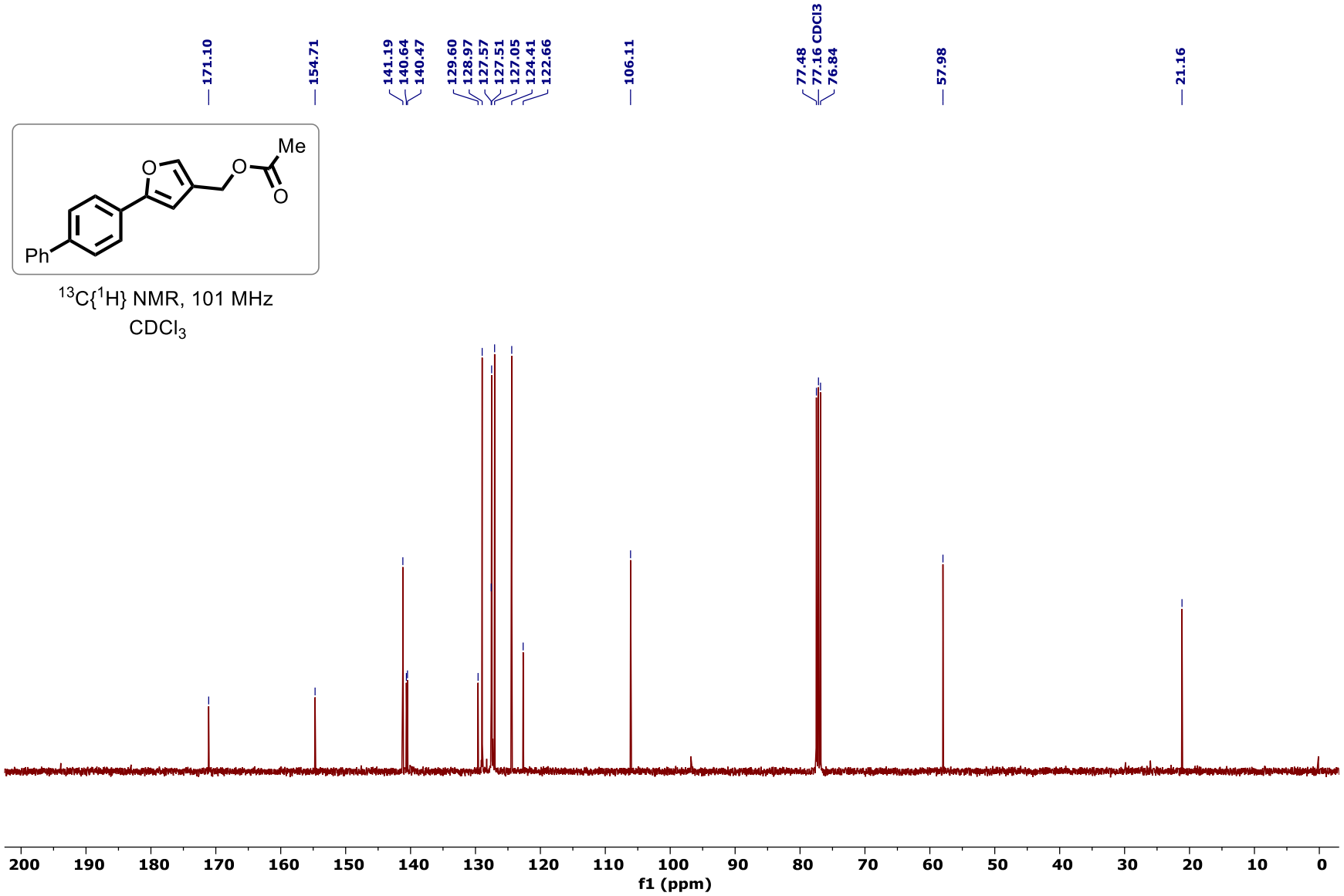
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Pentylphenyl)furan-3-yl)methyl acetate (5k):



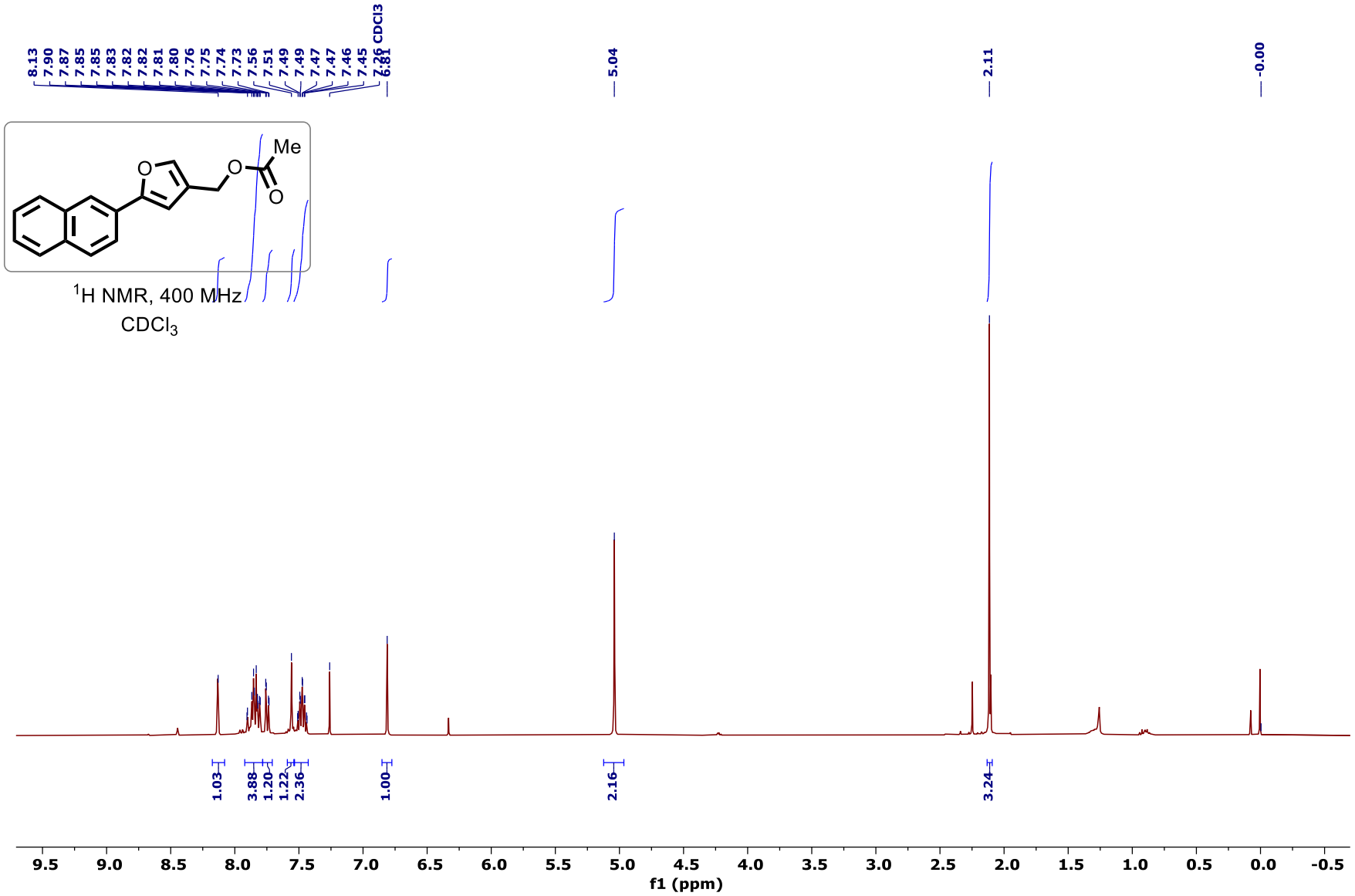
^{1}H NMR spectrum of (5-([1,1'-Biphenyl]-4-yl)furan-3-yl)methyl acetate (5l):



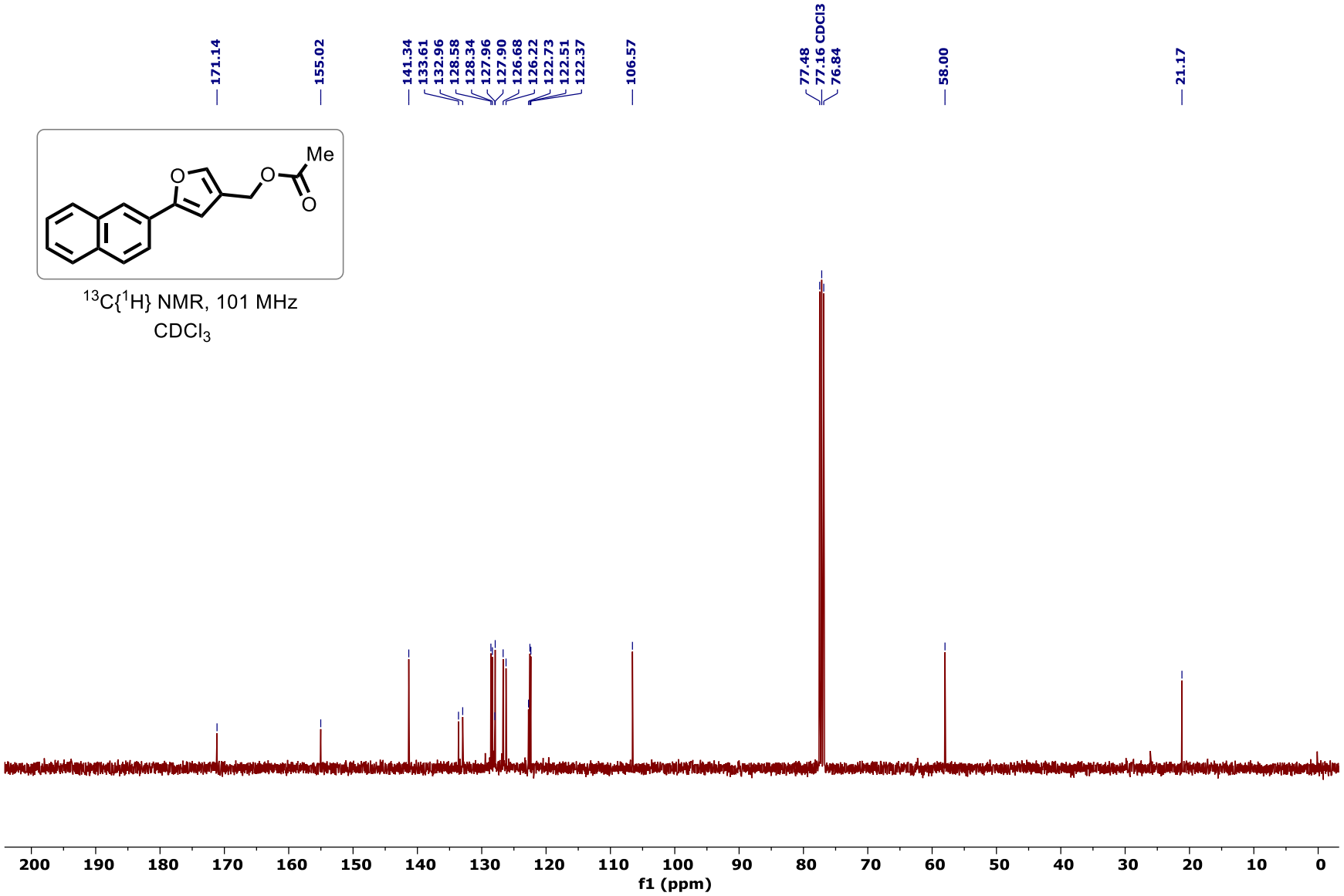
$^{13}C\{^{1}H\}$ NMR spectrum of (5-([1,1'-Biphenyl]-4-yl)furan-3-yl)methyl acetate (5l):



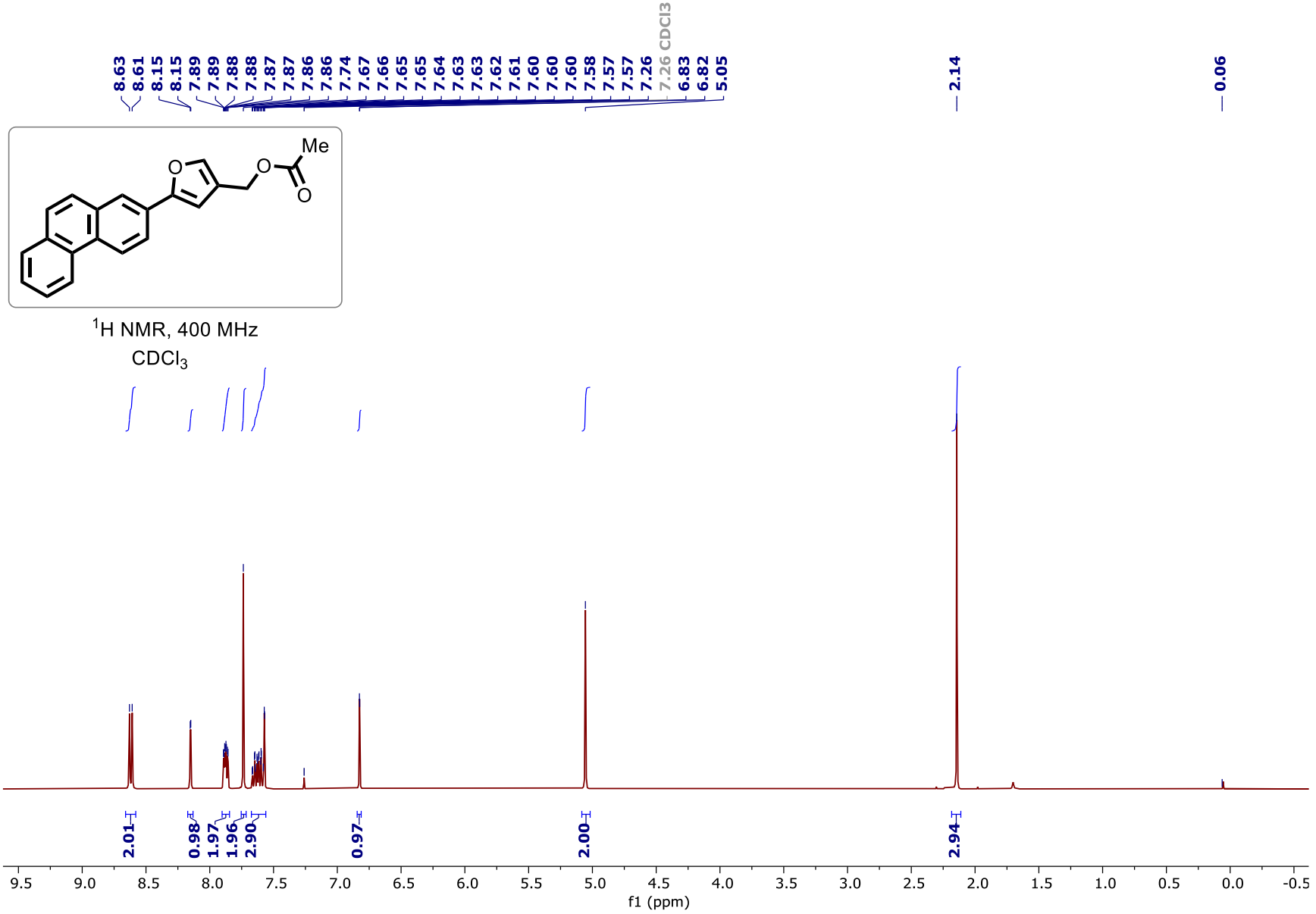
^{1}H NMR spectrum of (5-(Naphthalen-2-yl)furan-3-yl)methyl acetate (5m):



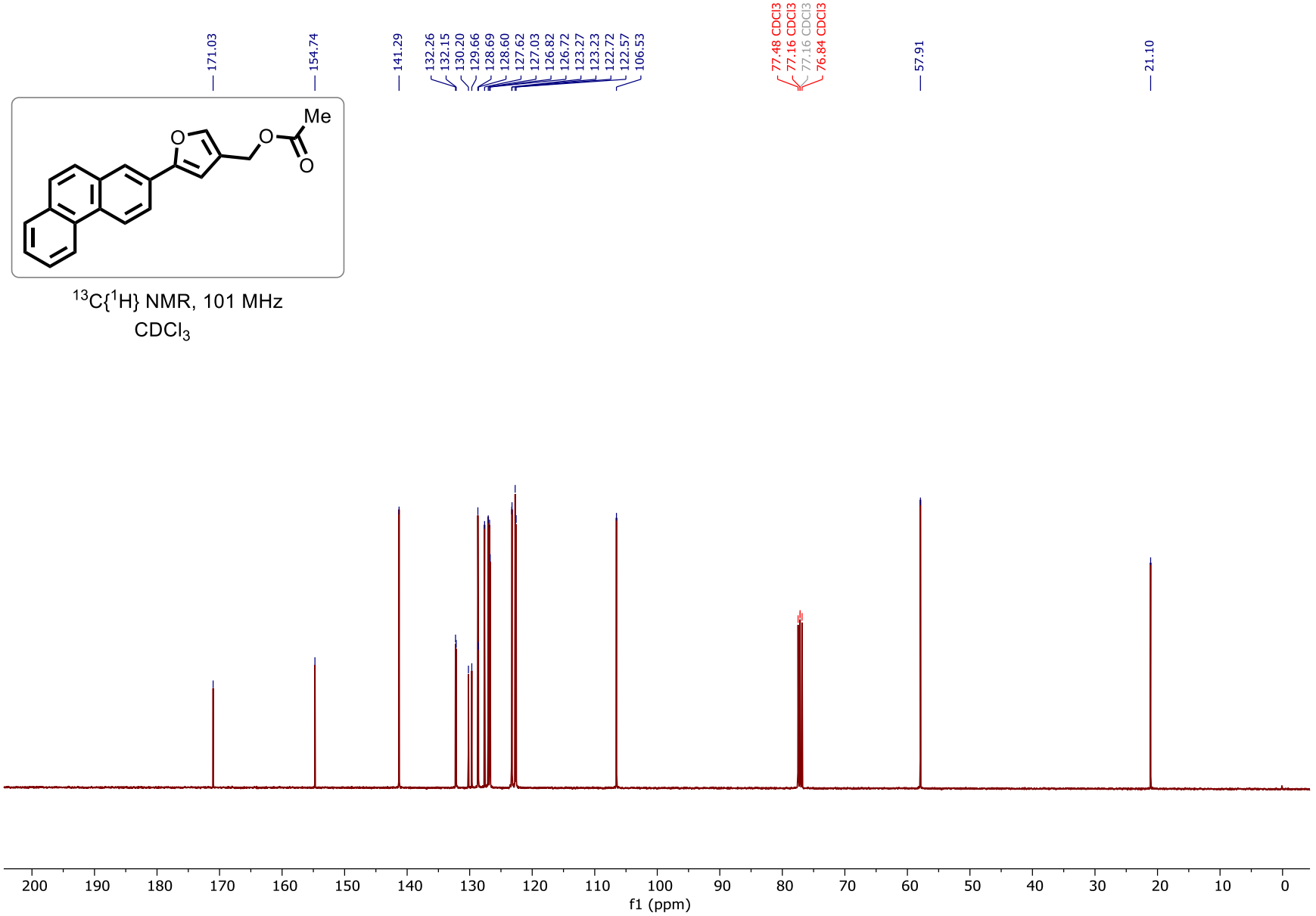
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(Naphthalen-2-yl)furan-3-yl)methyl acetate (5m):



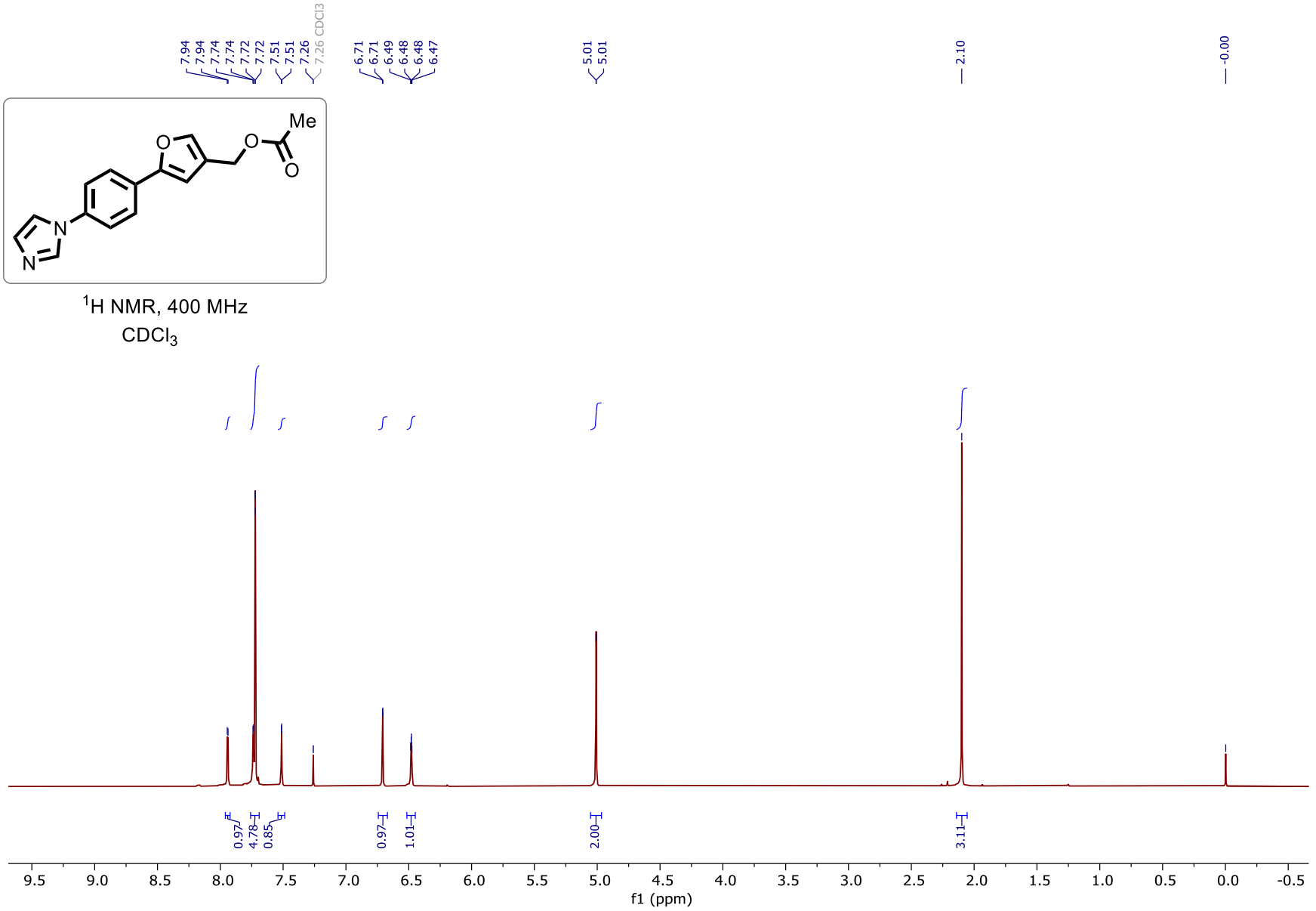
^{1}H NMR spectrum of (5-(Phenanthren-2-yl)furan-3-yl)methyl acetate (5n):



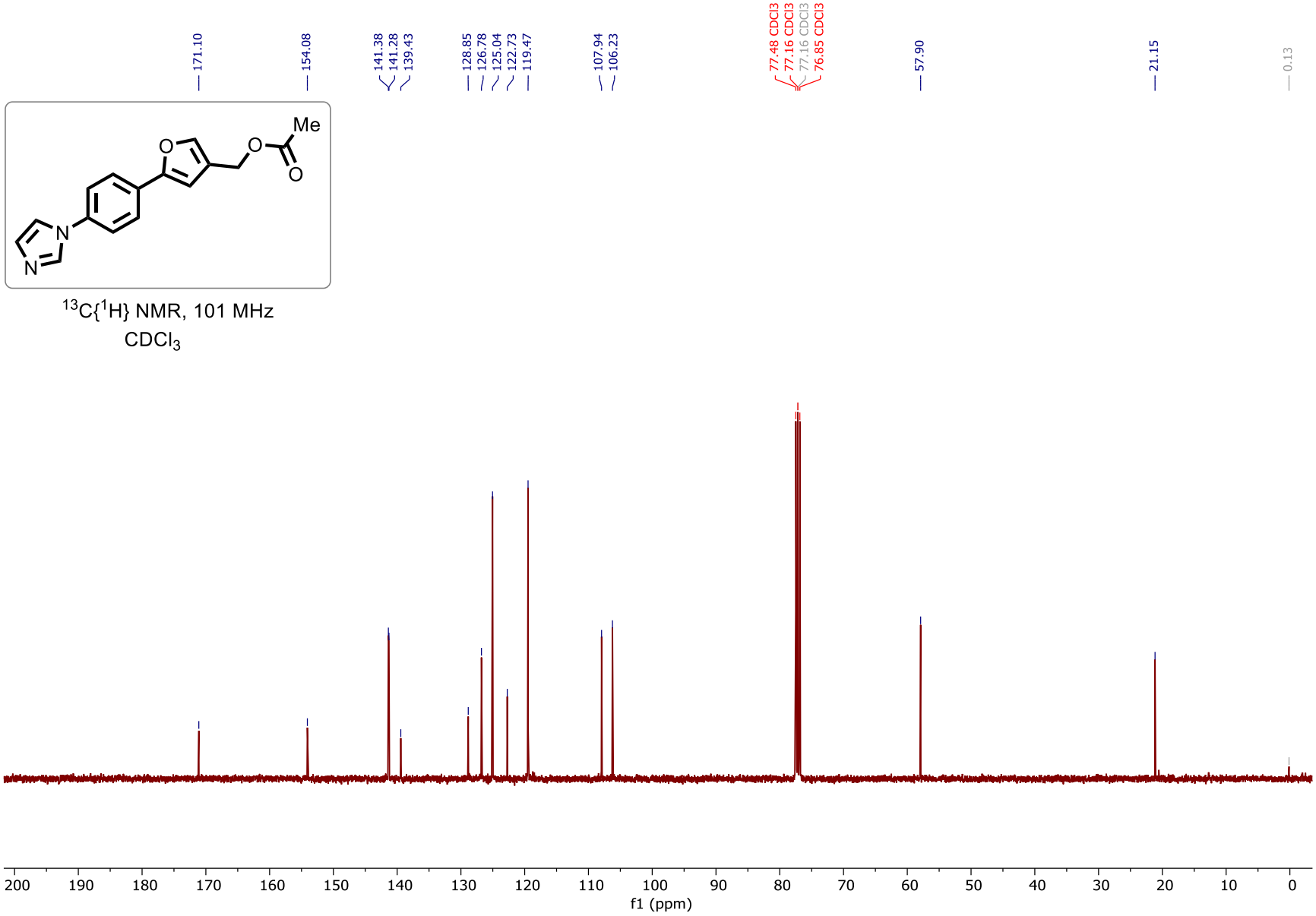
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(Phenanthren-2-yl)furan-3-yl)methyl acetate (5n):



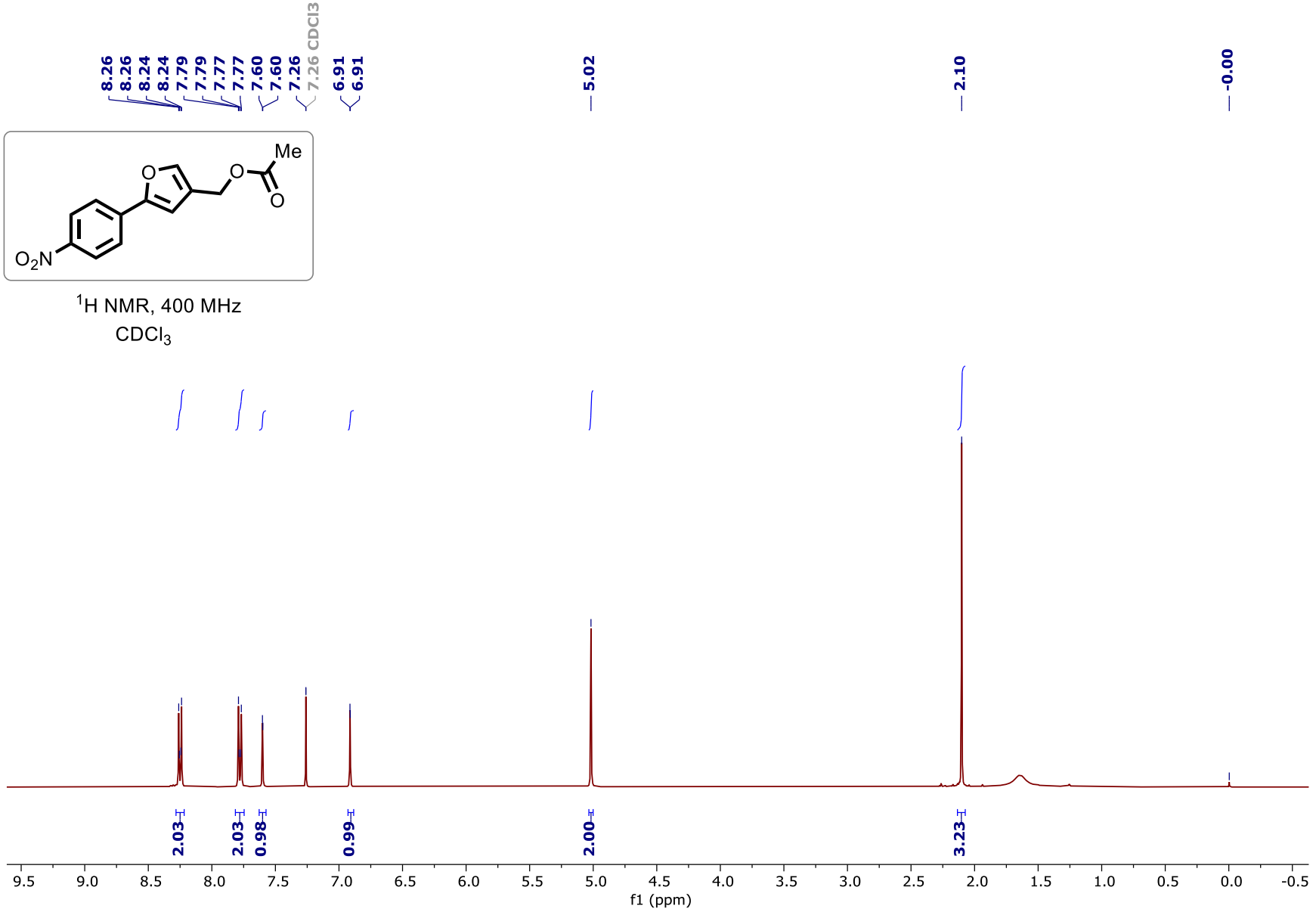
^{1}H NMR spectrum of (5-(4-(1*H*-Imidazol-1-yl)phenyl)furan-3-yl)methyl acetate (5o):



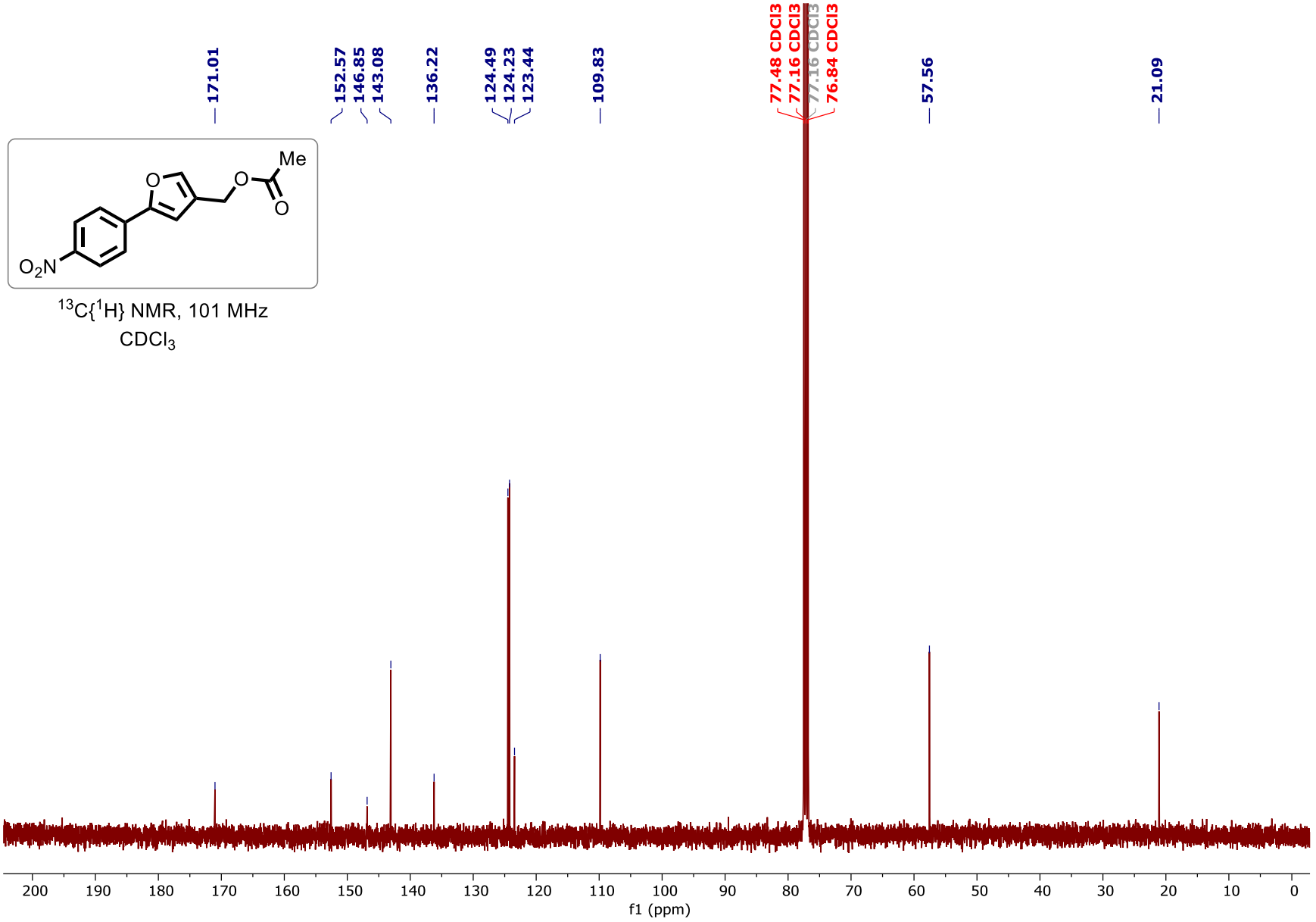
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-(1*H*-Imidazol-1-yl)phenyl)furan-3-yl)methyl acetate (5o):



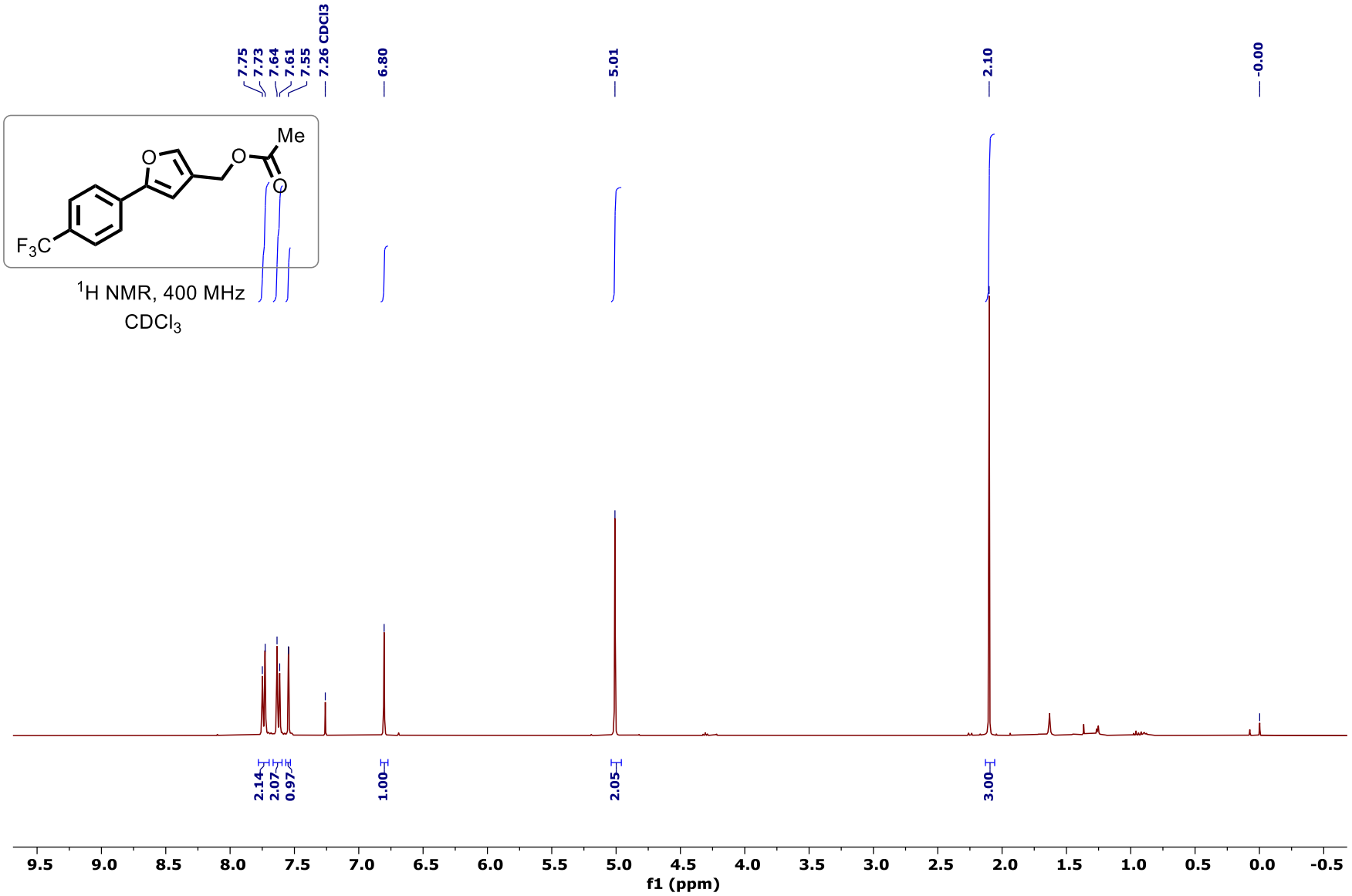
^{1}H NMR spectrum of (5-(4-Nitrophenyl)furan-3-yl)methyl acetate (5p):



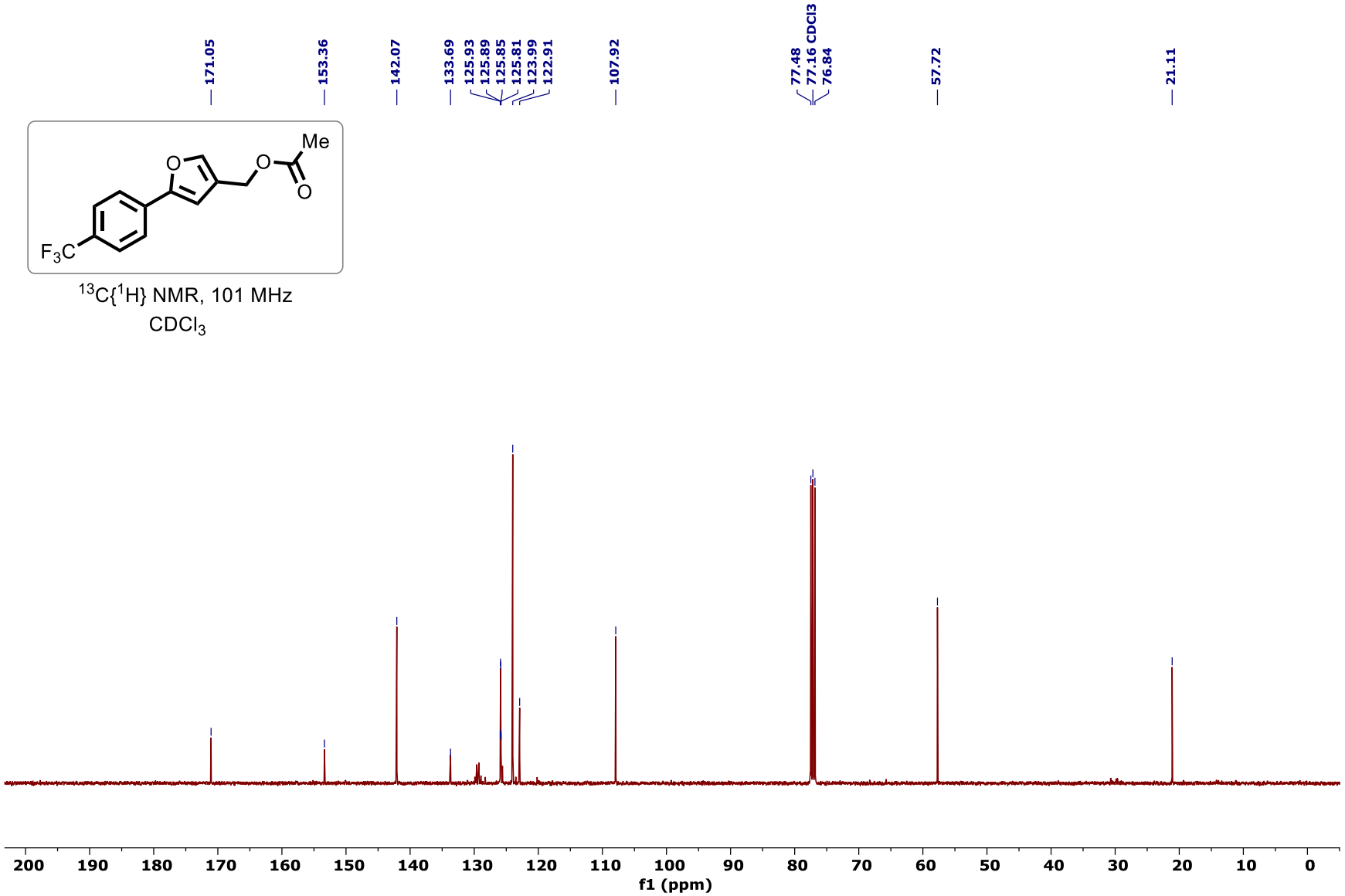
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Nitrophenyl)furan-3-yl)methyl acetate (5p):



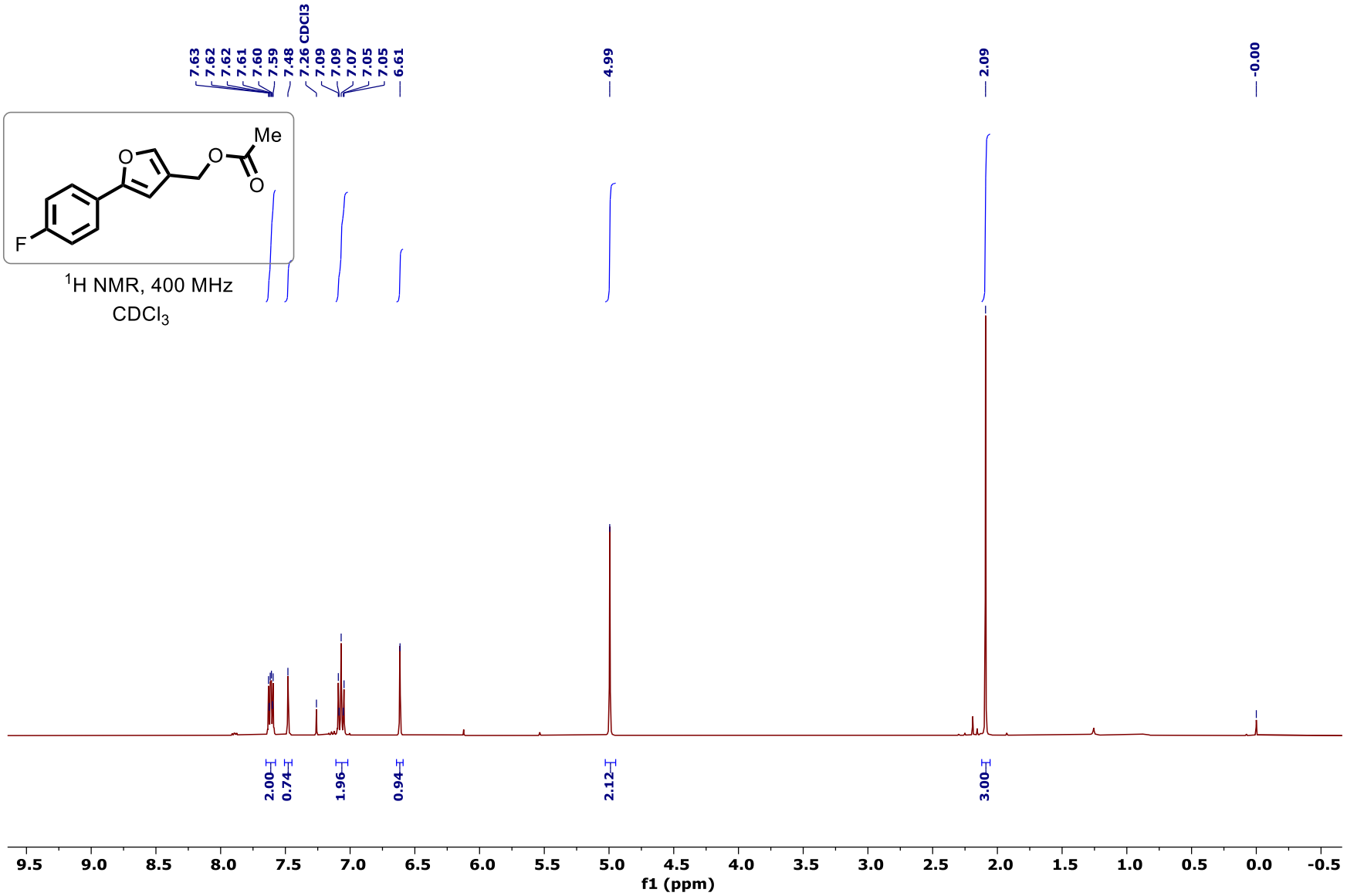
^{1}H NMR spectrum of (5-(4-(Trifluoromethyl)phenyl)furan-3-yl)methyl acetate (5q):



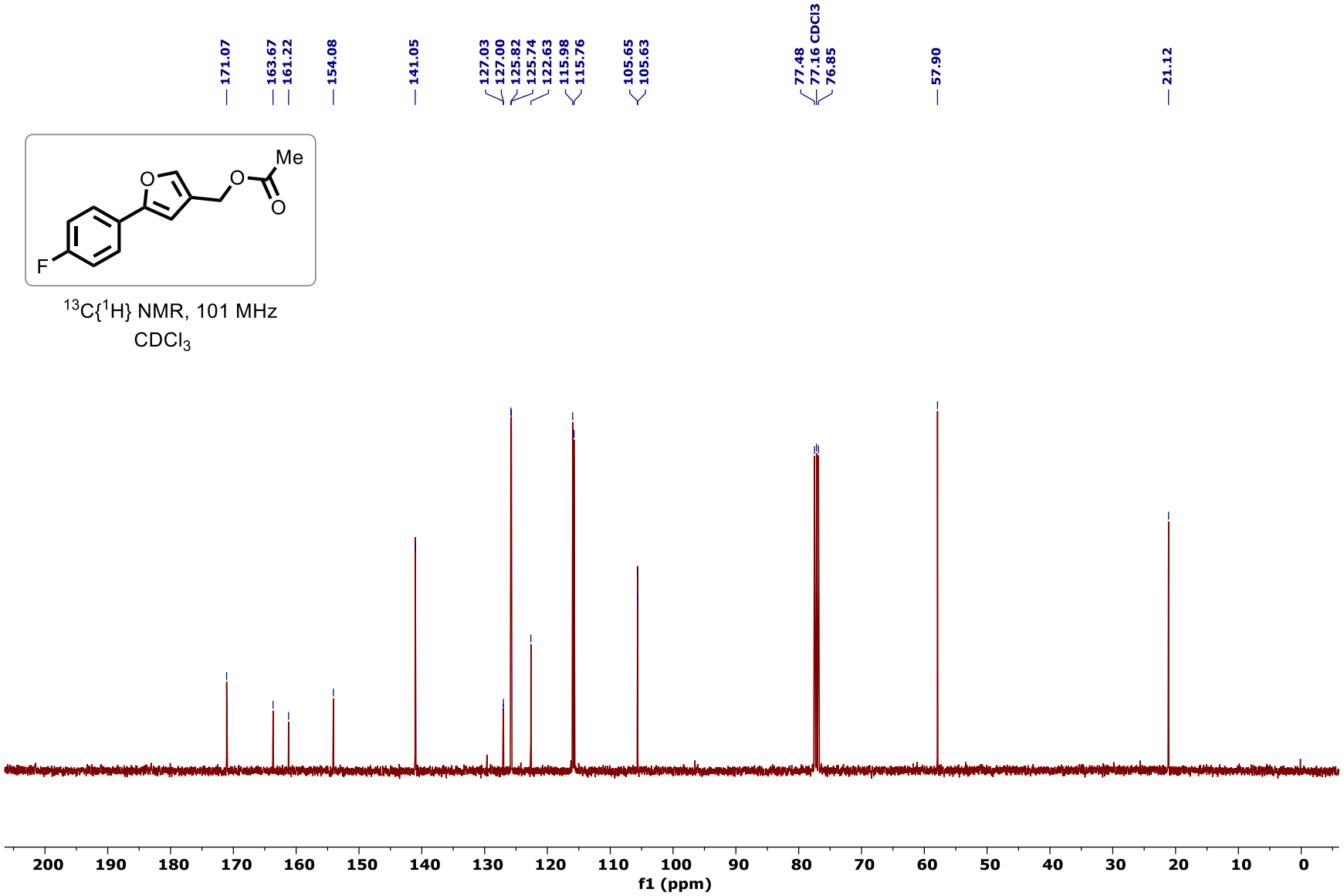
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-(Trifluoromethyl)phenyl)furan-3-yl)methyl acetate (5q):



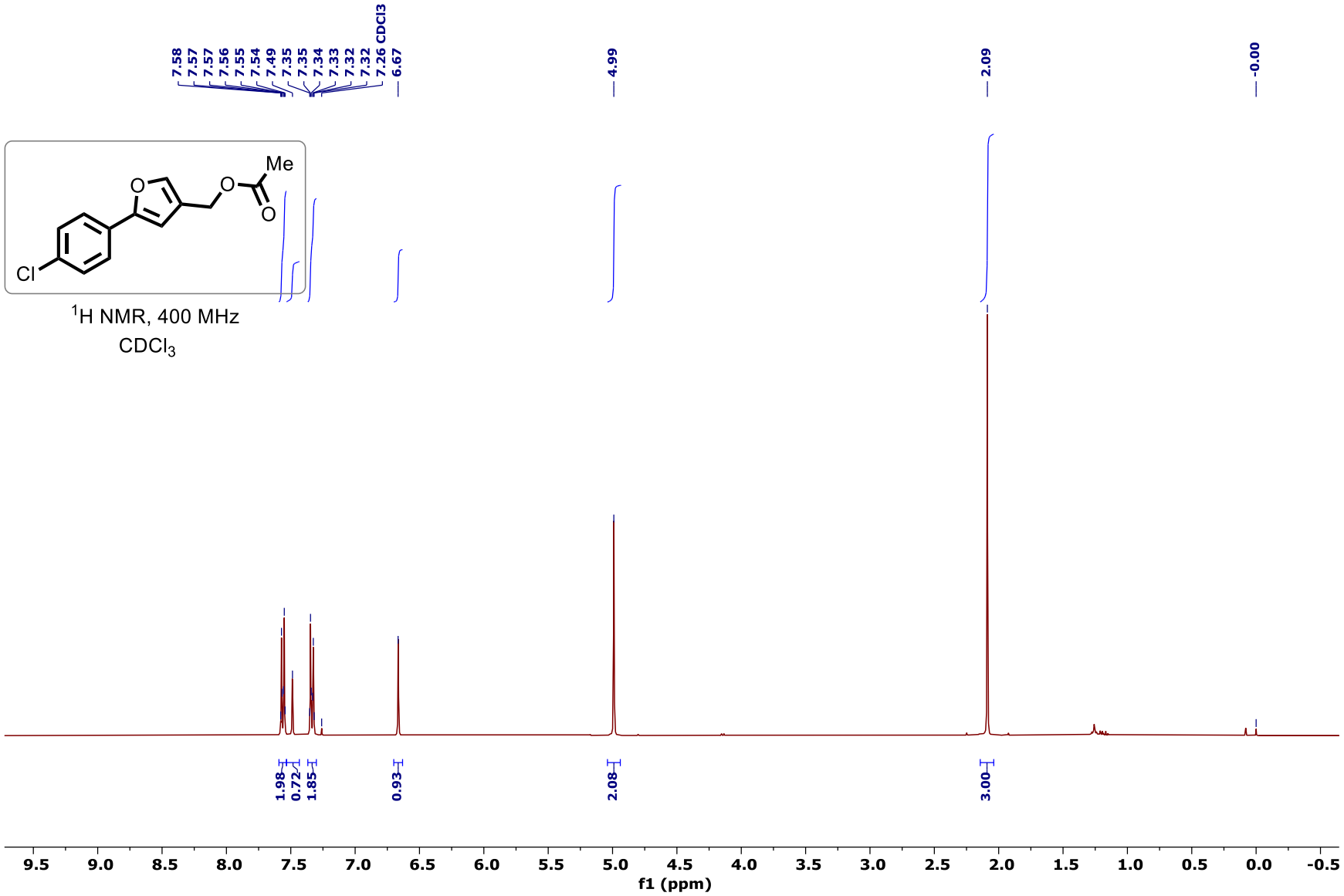
^{1}H NMR spectrum of (5-(4-Fluorophenyl)furan-3-yl)methyl acetate (5r):



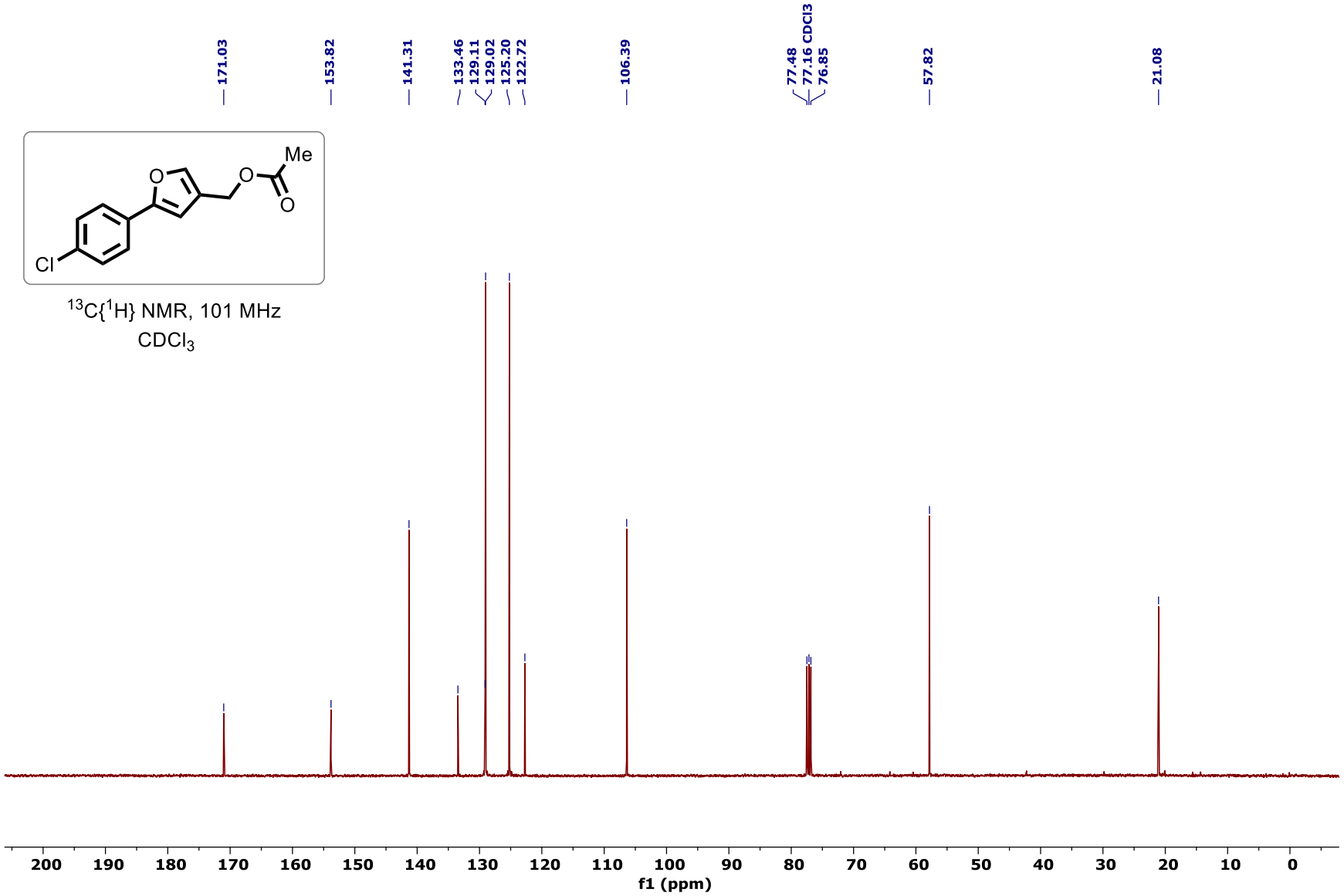
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Fluorophenyl)furan-3-yl)methyl acetate (5r):



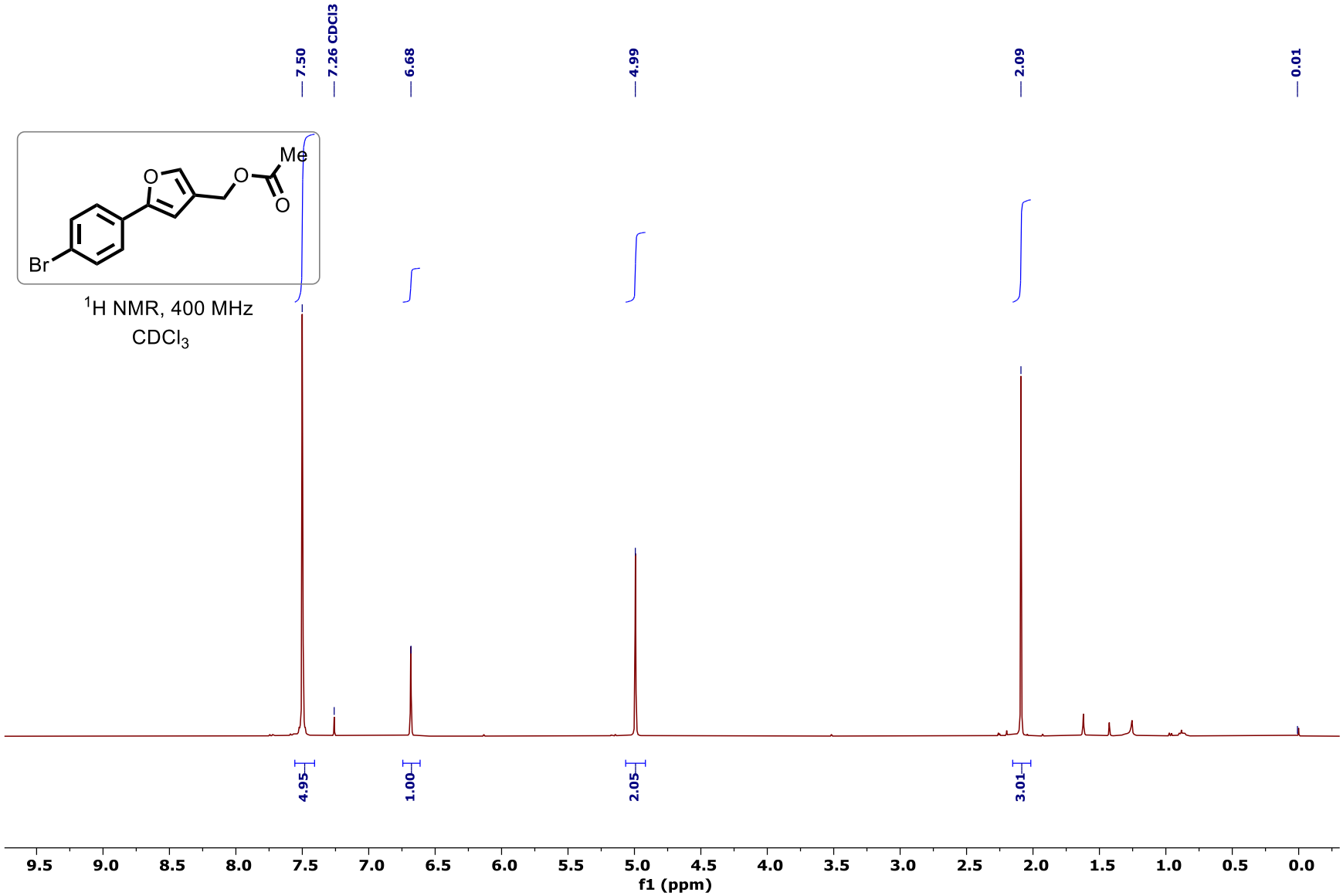
^{1}H NMR spectrum of (5-(4-Chlorophenyl)furan-3-yl)methyl acetate (5s):



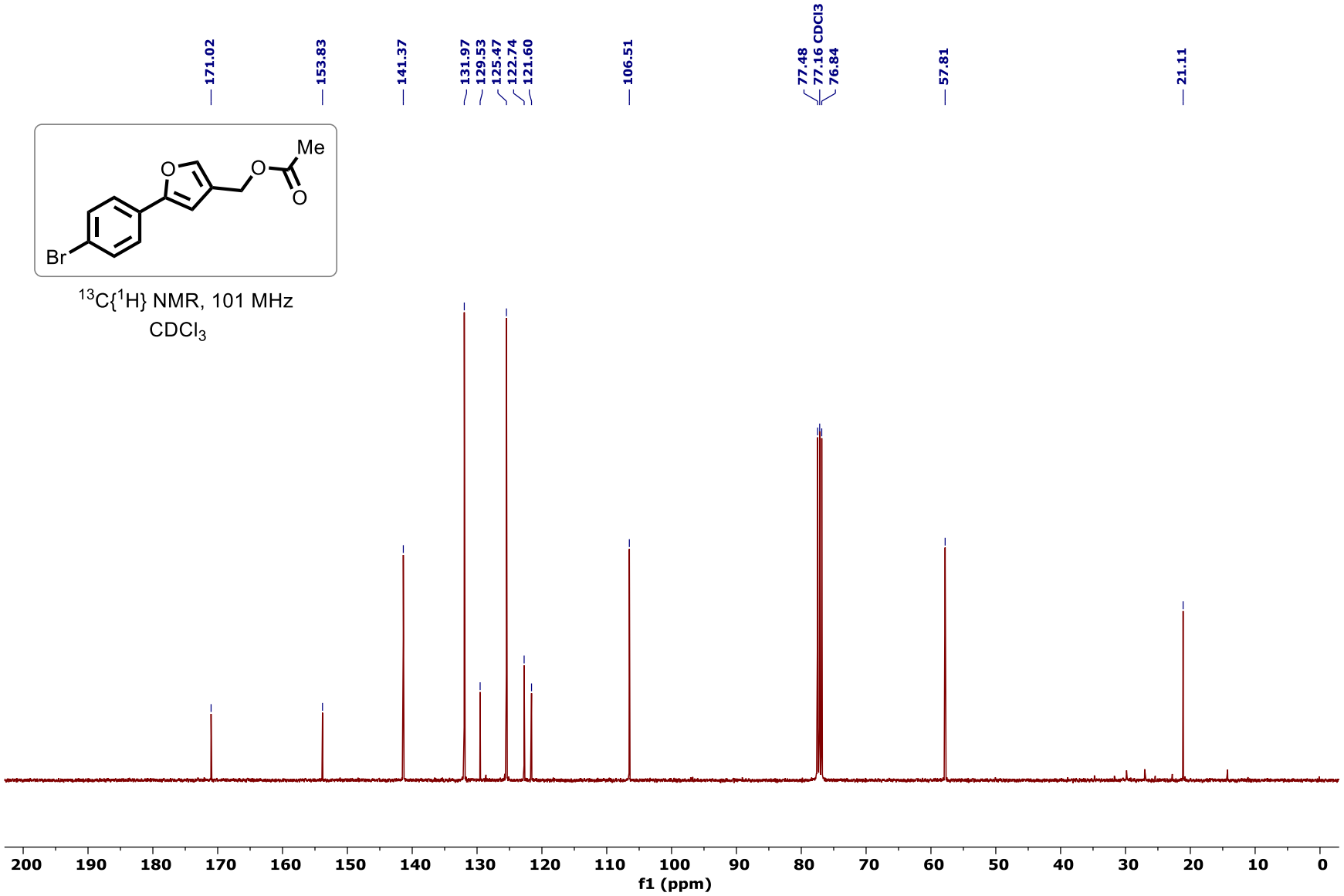
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Chlorophenyl)furan-3-yl)methyl acetate (5s):



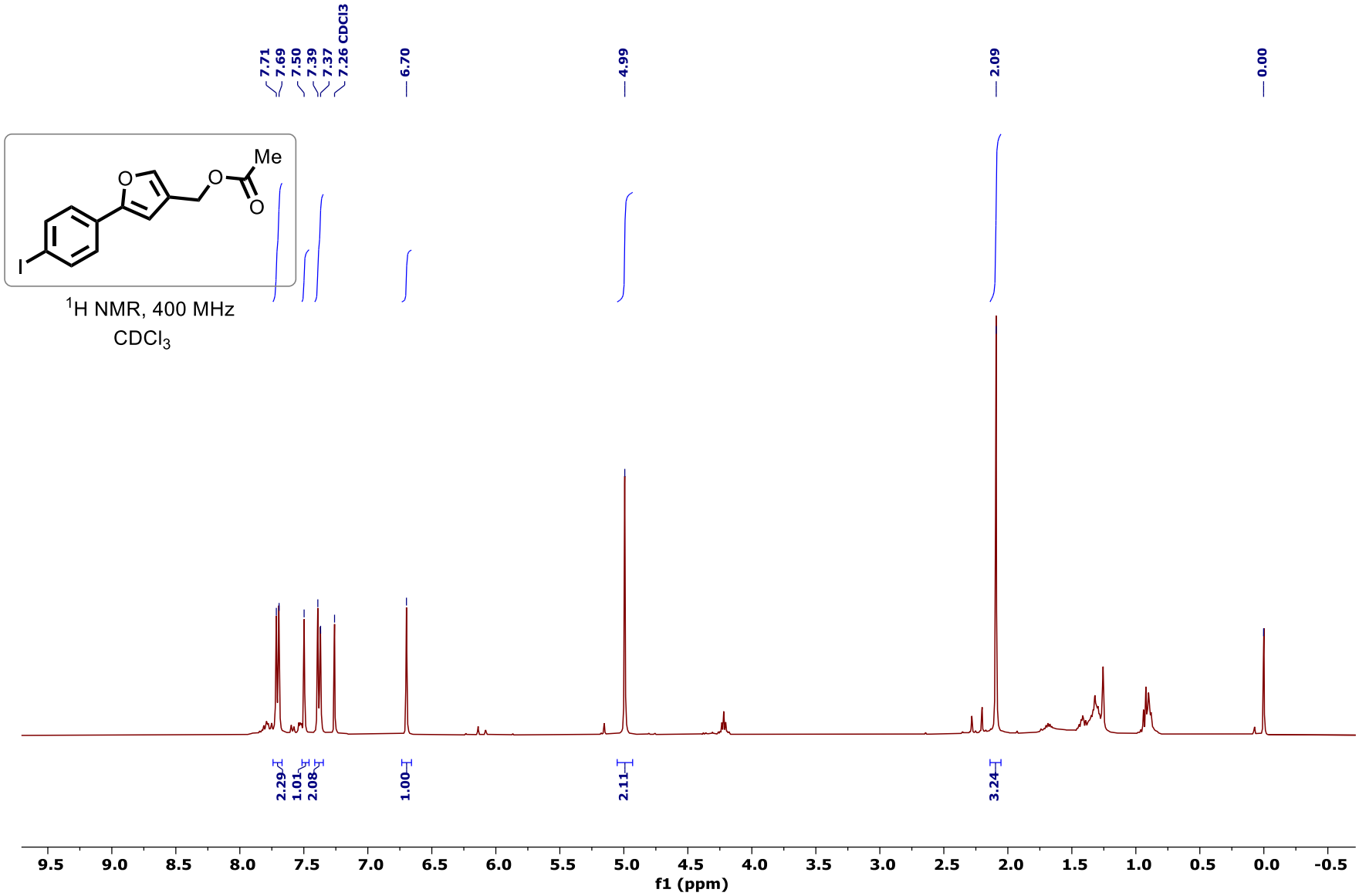
^{1}H NMR spectrum of (5-(4-Bromophenyl)furan-3-yl)methyl acetate (5t):



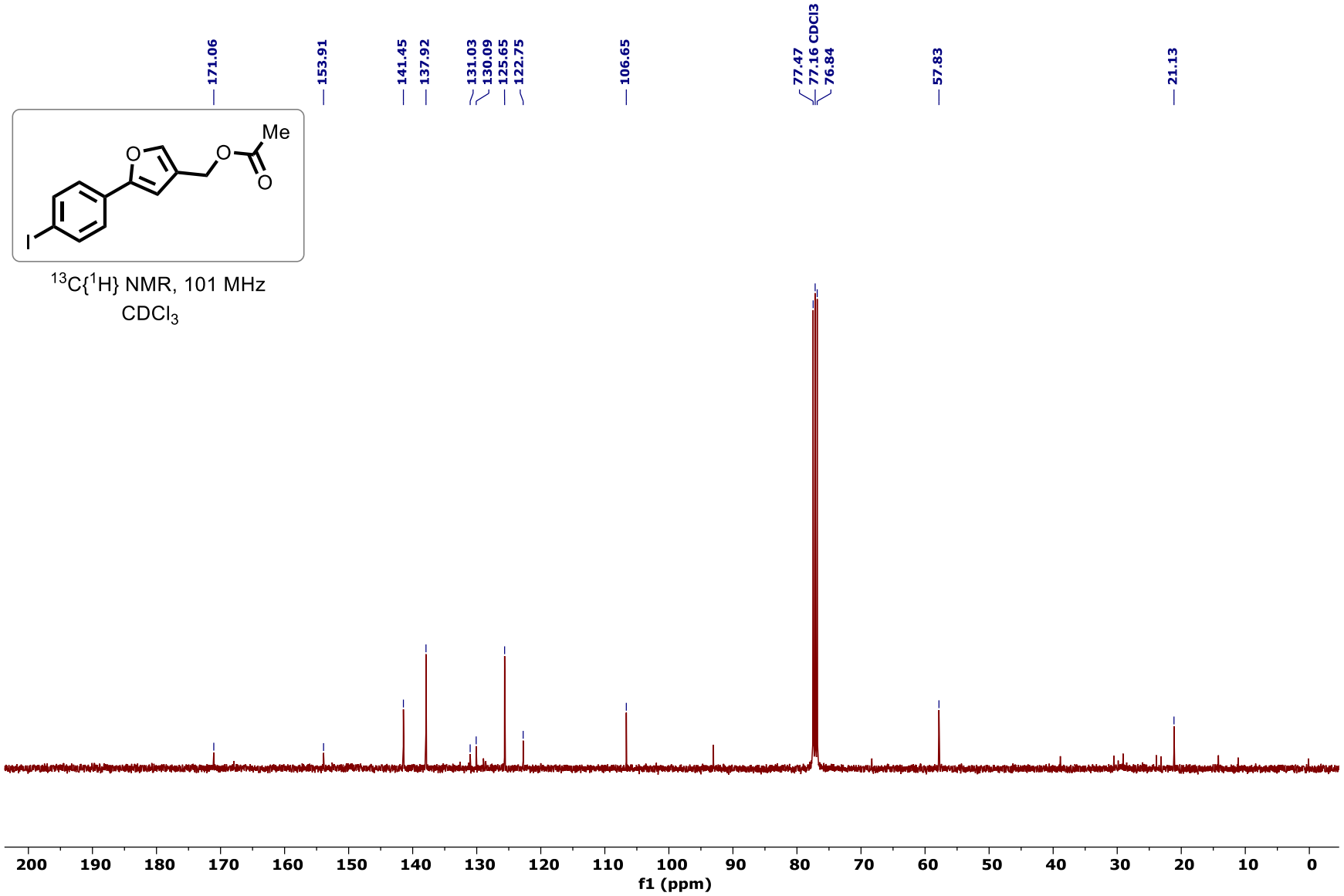
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Bromophenyl)furan-3-yl)methyl acetate (5t):



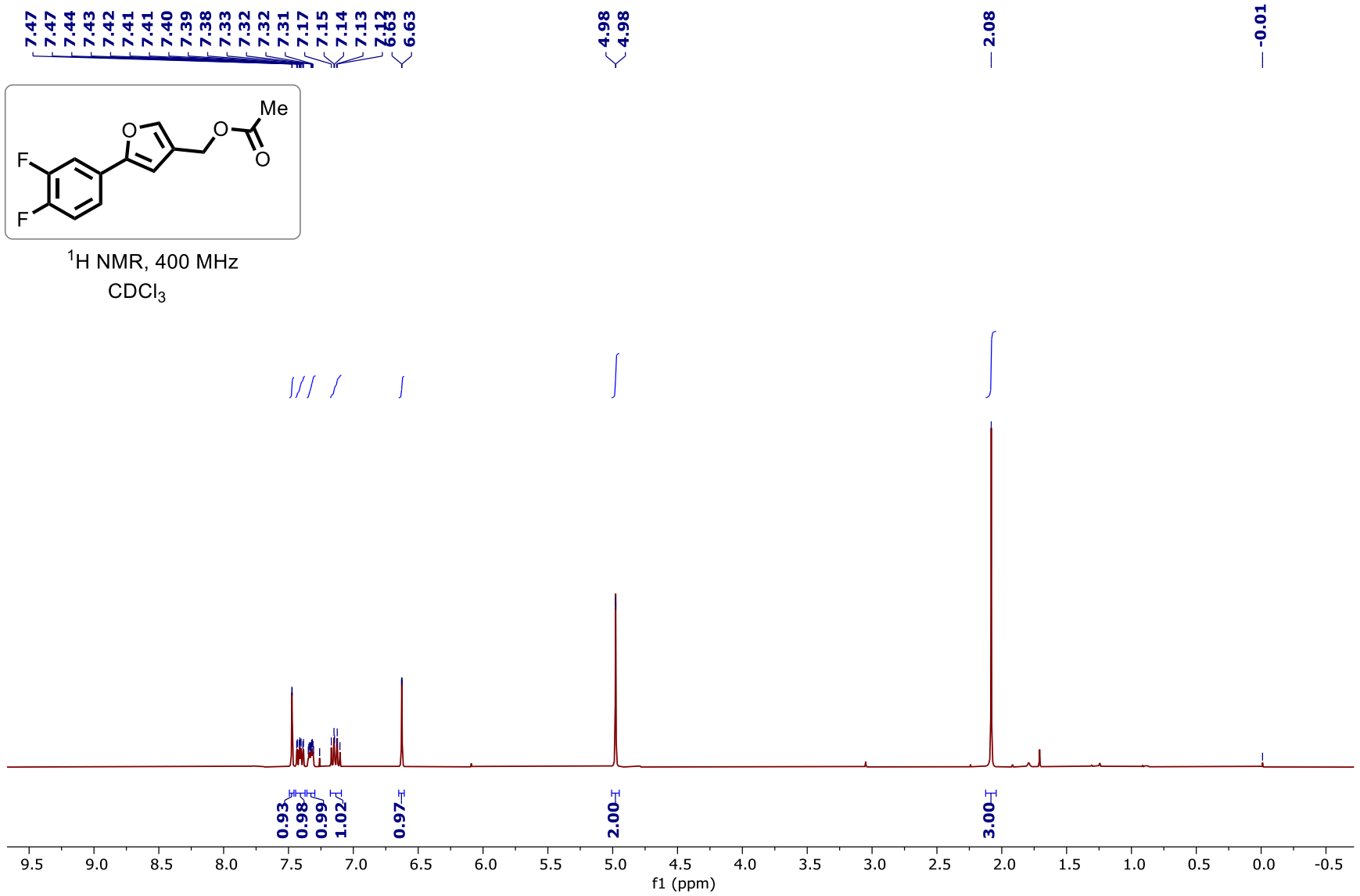
^{1}H NMR spectrum of (5-(4-Iodophenyl)furan-3-yl)methyl acetate (5u):



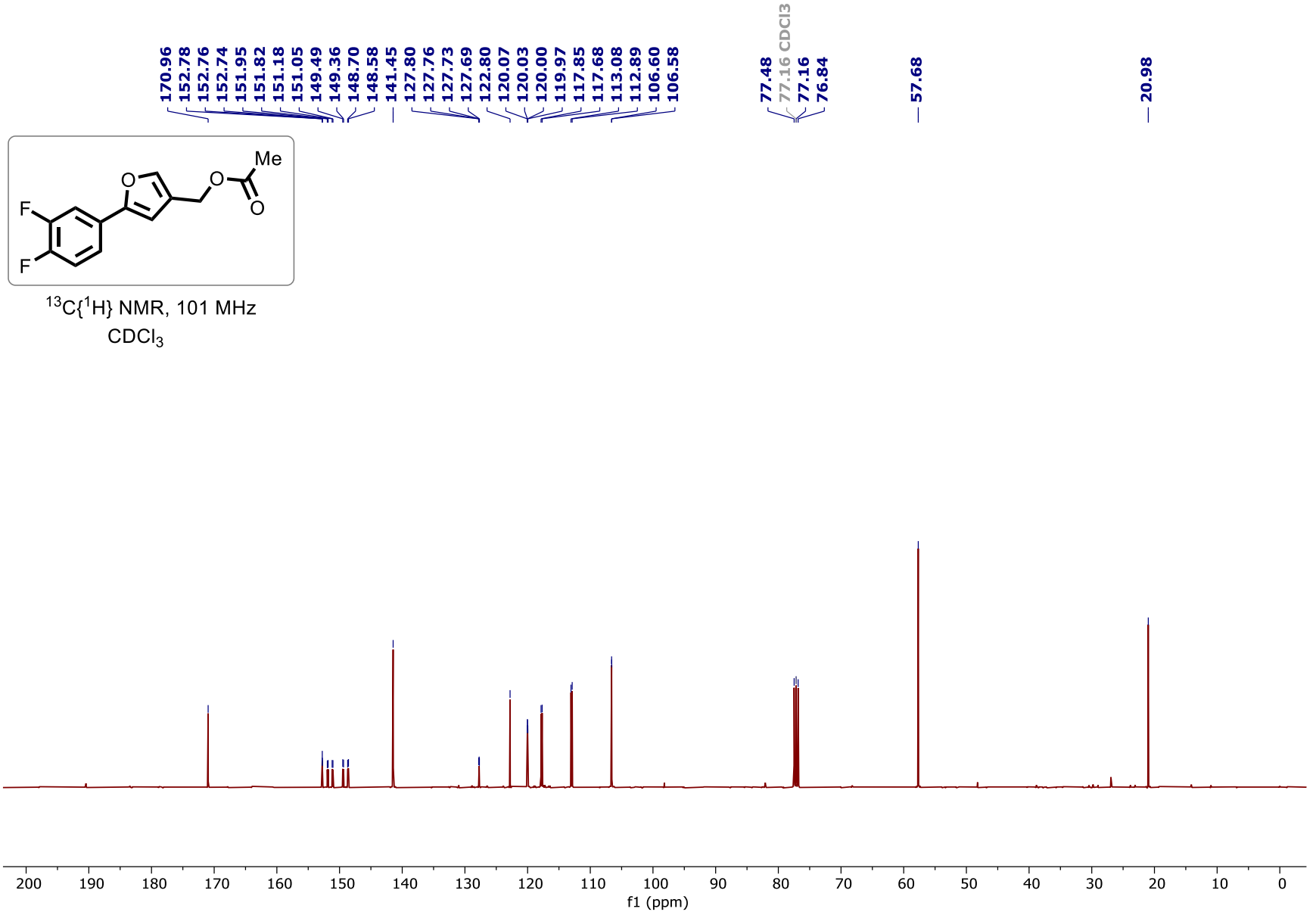
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(4-Iodophenyl)furan-3-yl)methyl acetate (5u):



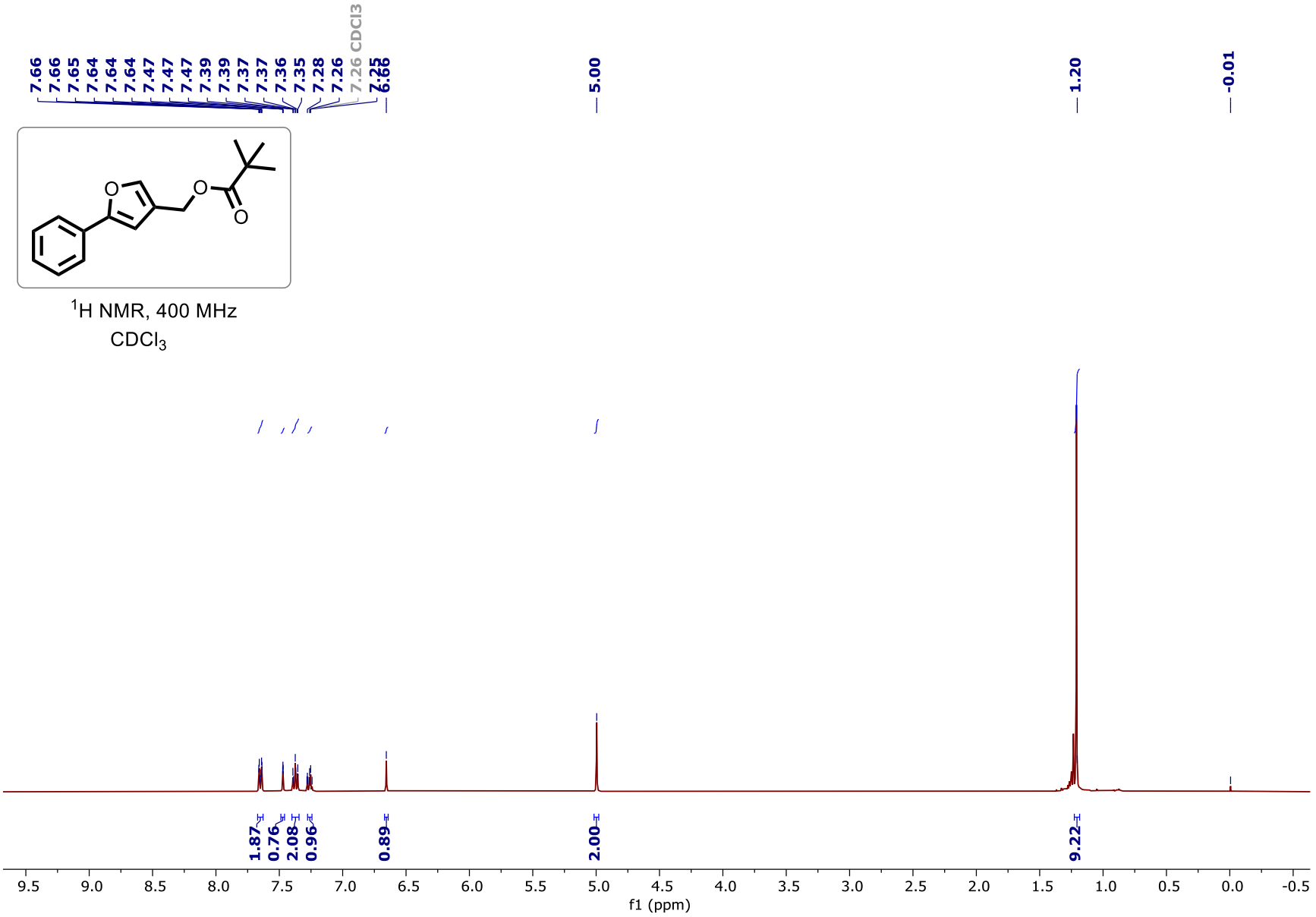
^{1}H NMR spectrum of (5-(3,4-Difluorophenyl)furan-3-yl)methyl acetate (5v):



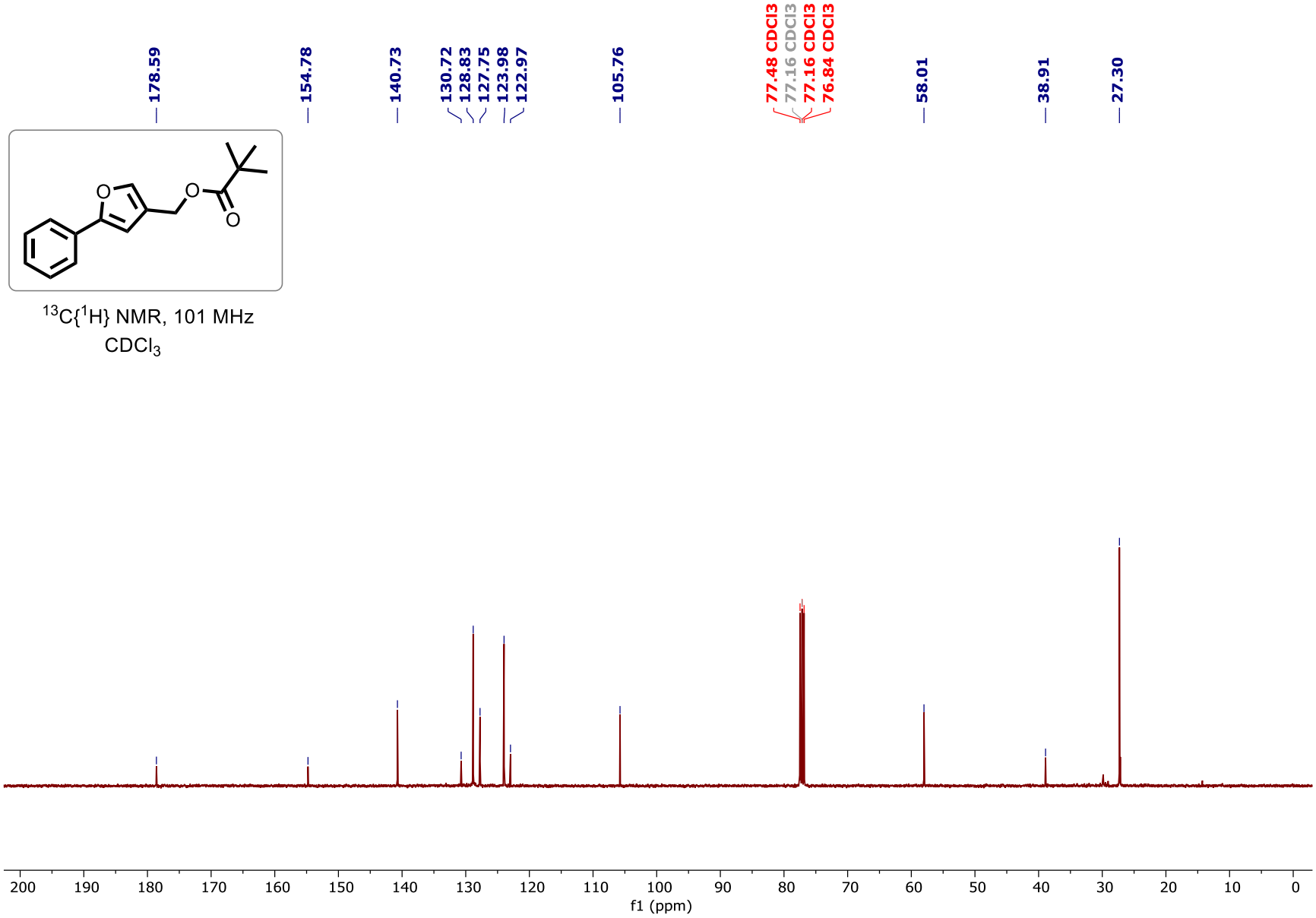
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(3,4-Difluorophenyl)furan-3-yl)methyl acetate (5v):



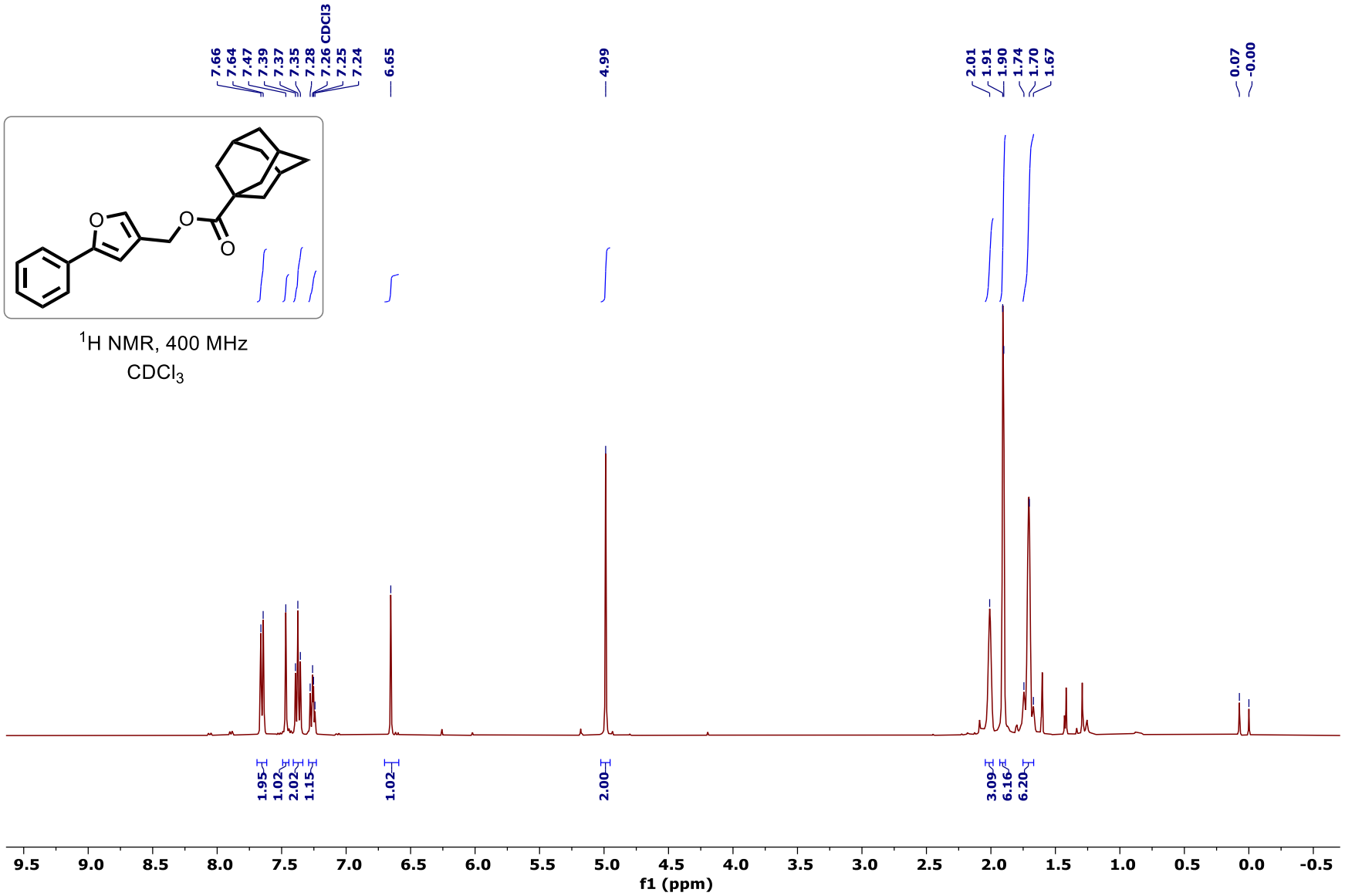
^{1}H NMR spectrum of (5-Phenylfuran-3-yl)methyl pivalate (5w):



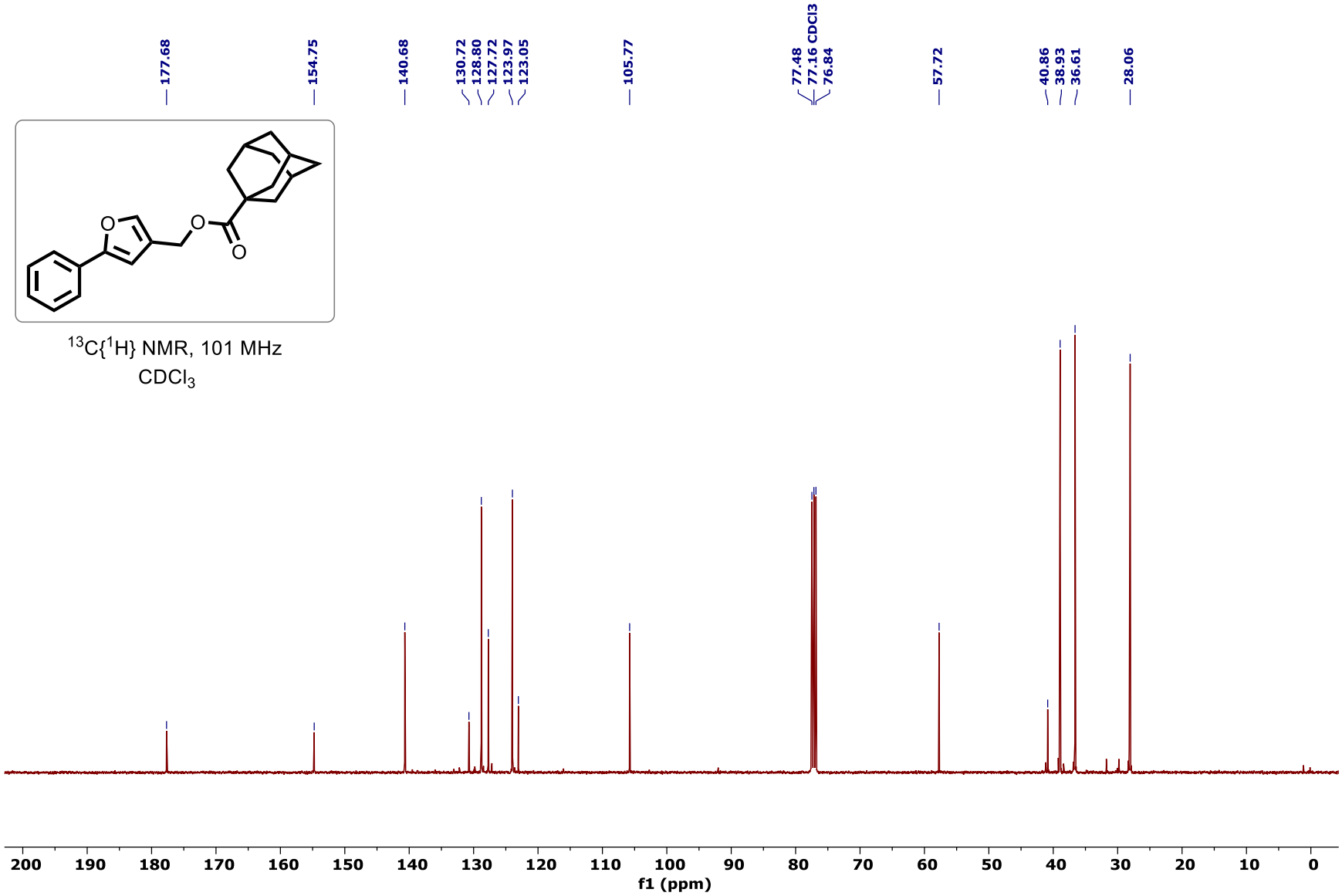
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Phenylfuran-3-yl)methyl pivalate (5w):



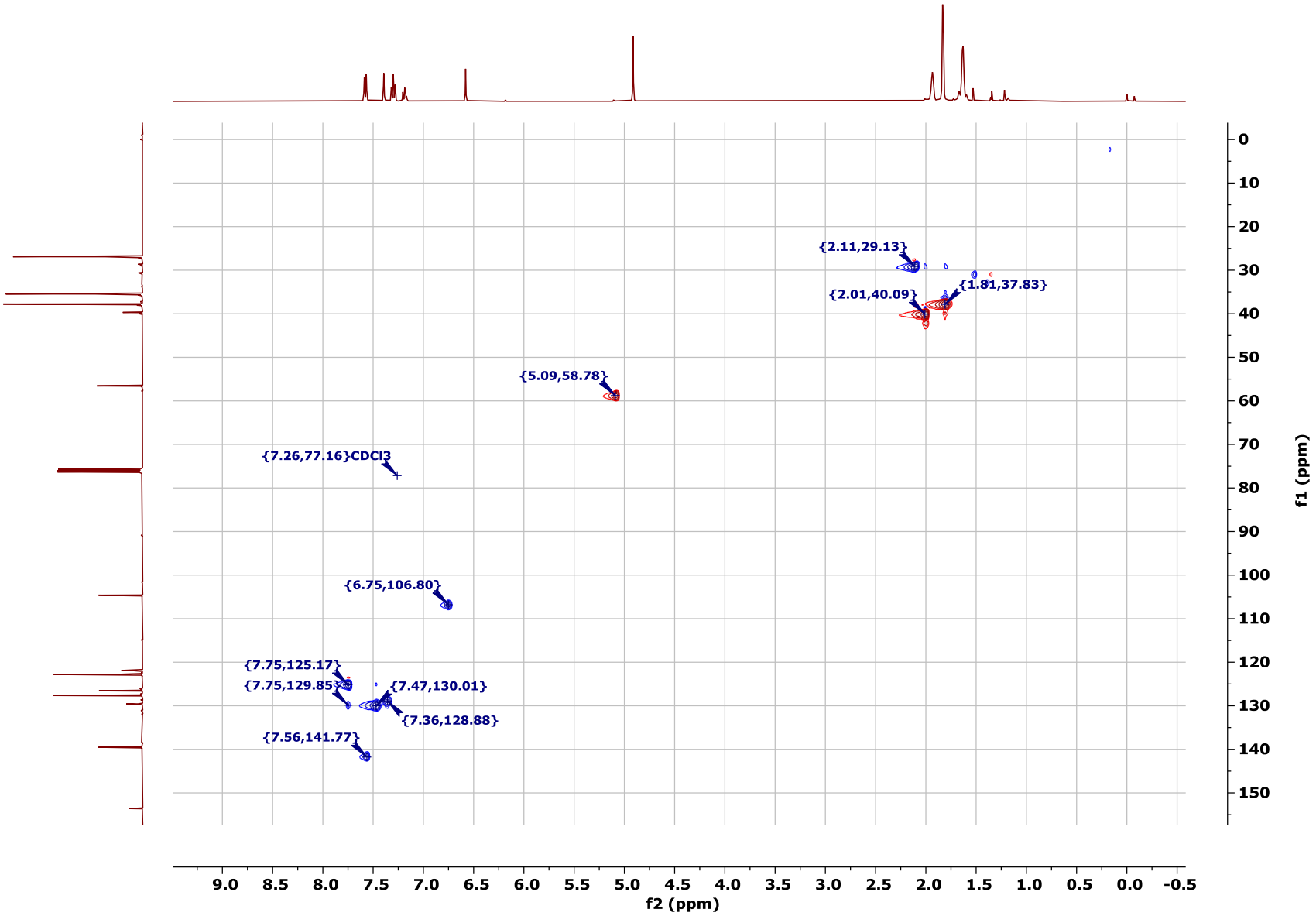
^{1}H NMR spectrum of (5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



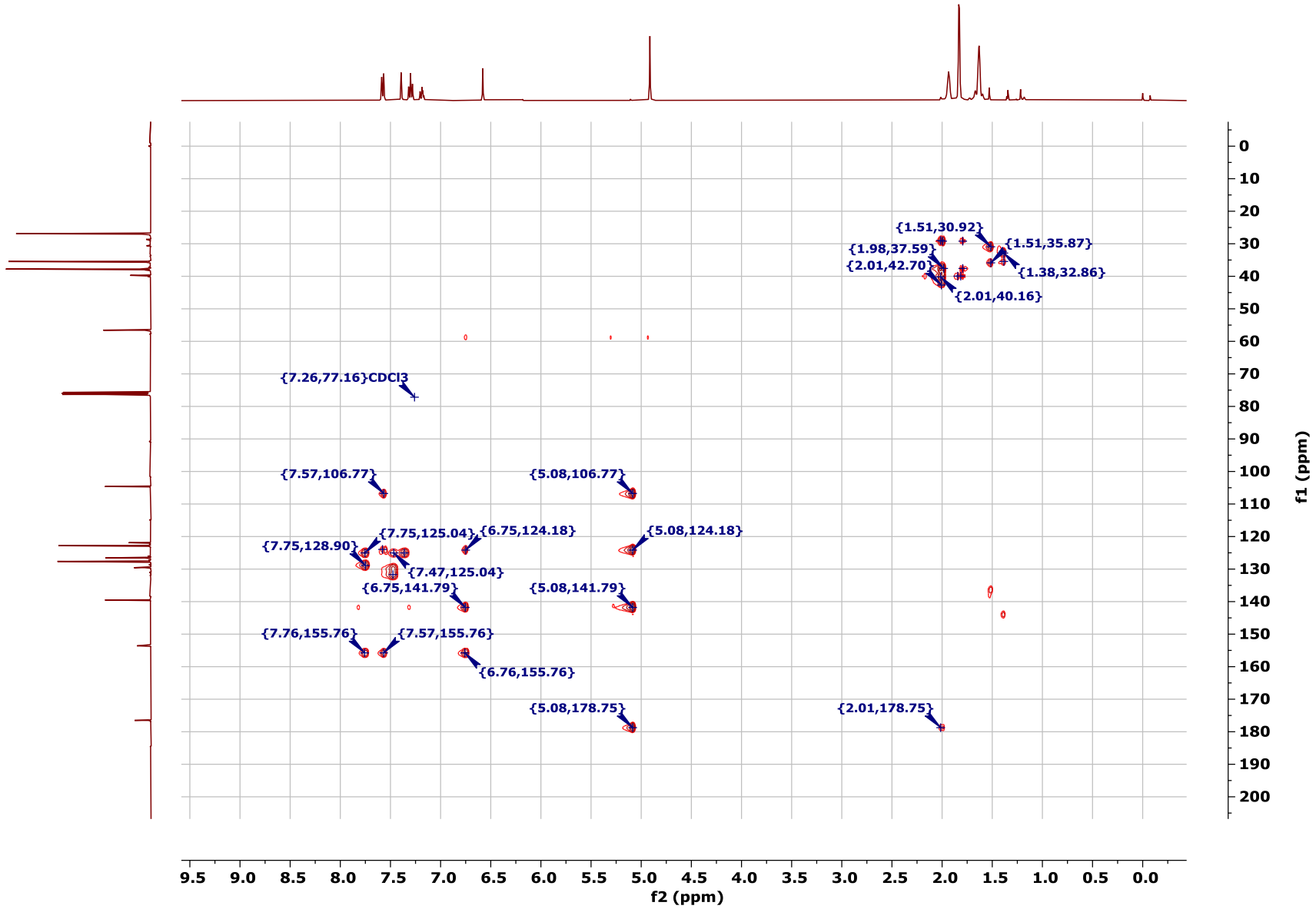
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



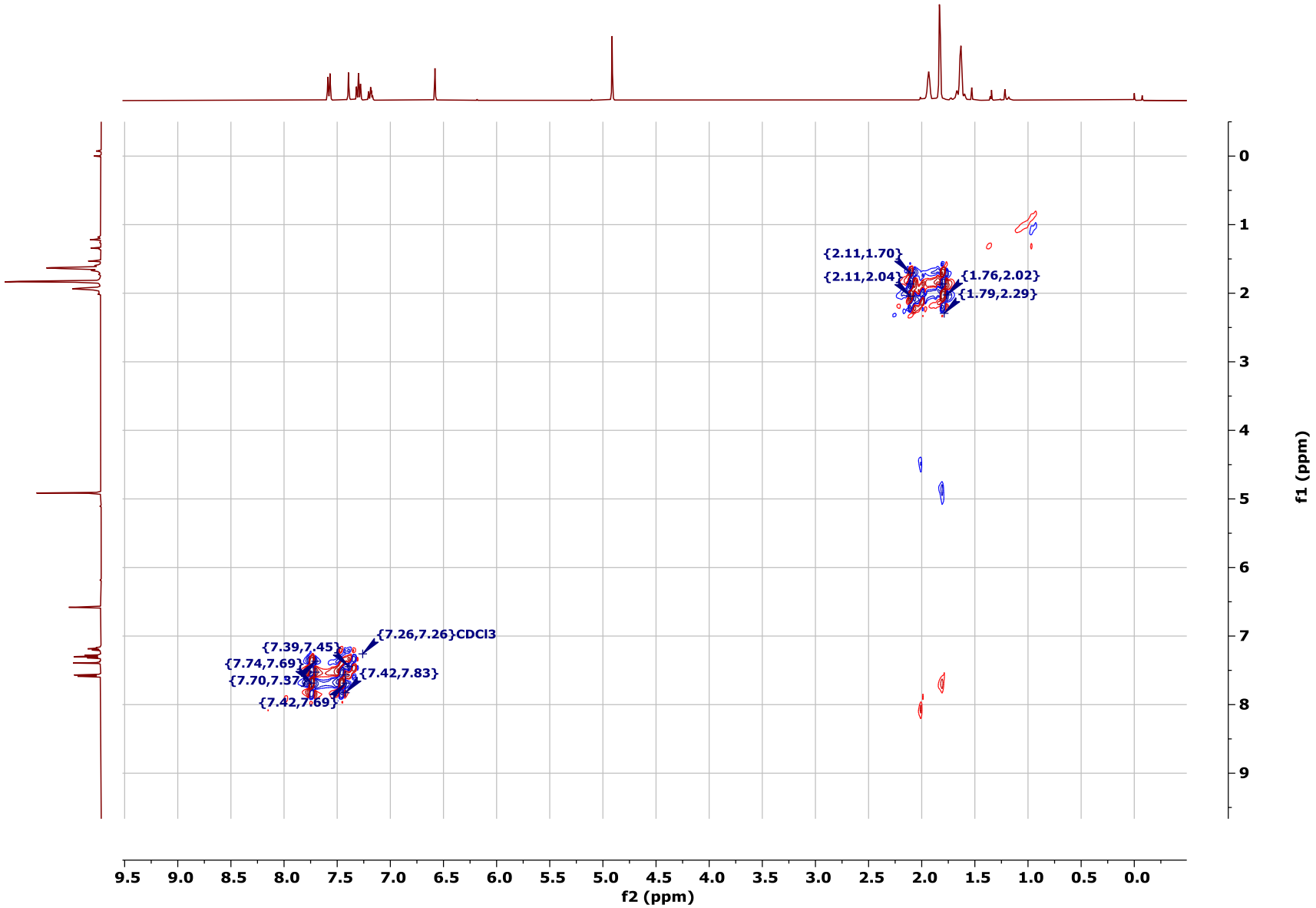
HSQC NMR spectrum of (5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



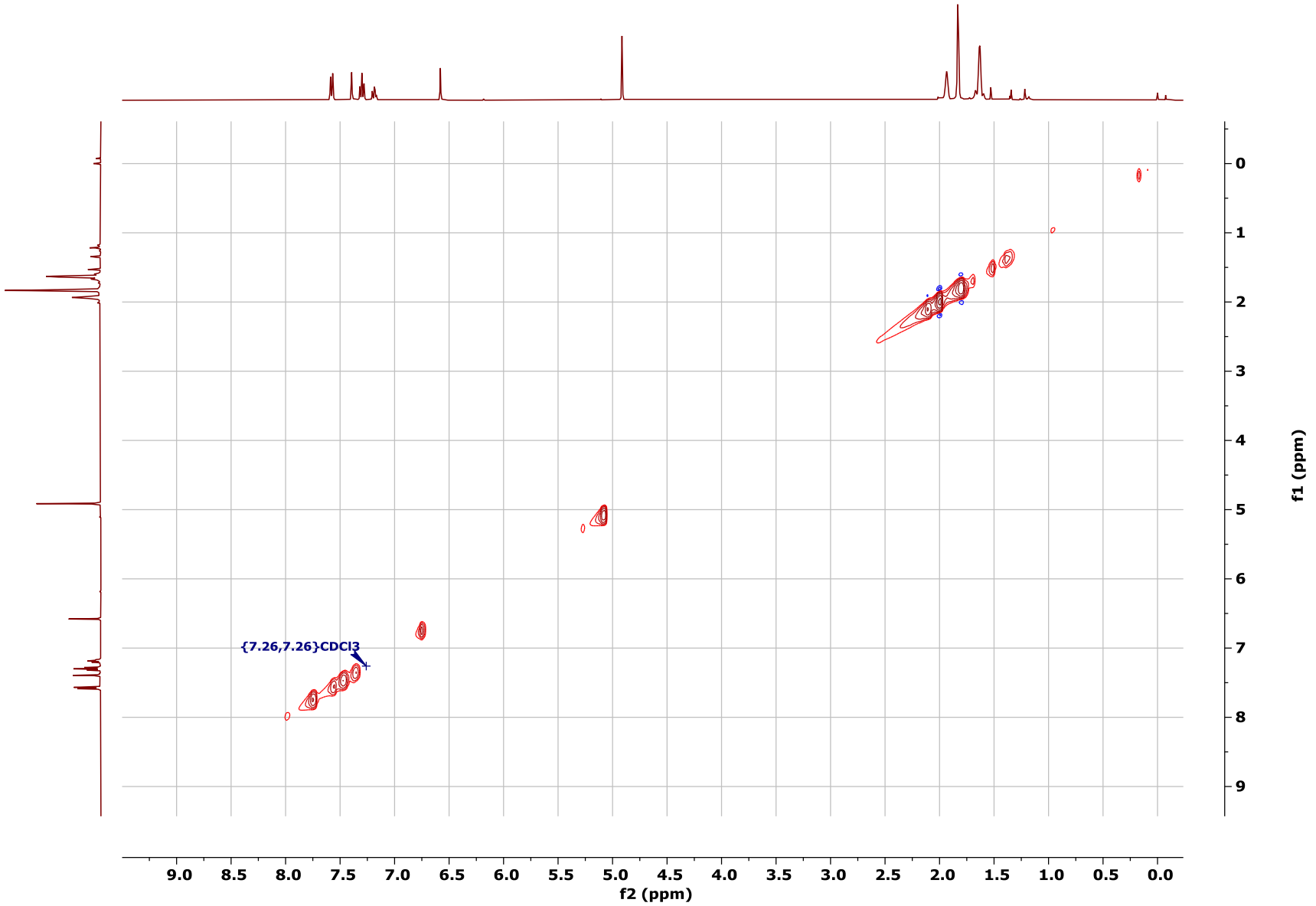
HMBC NMR spectrum of (5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



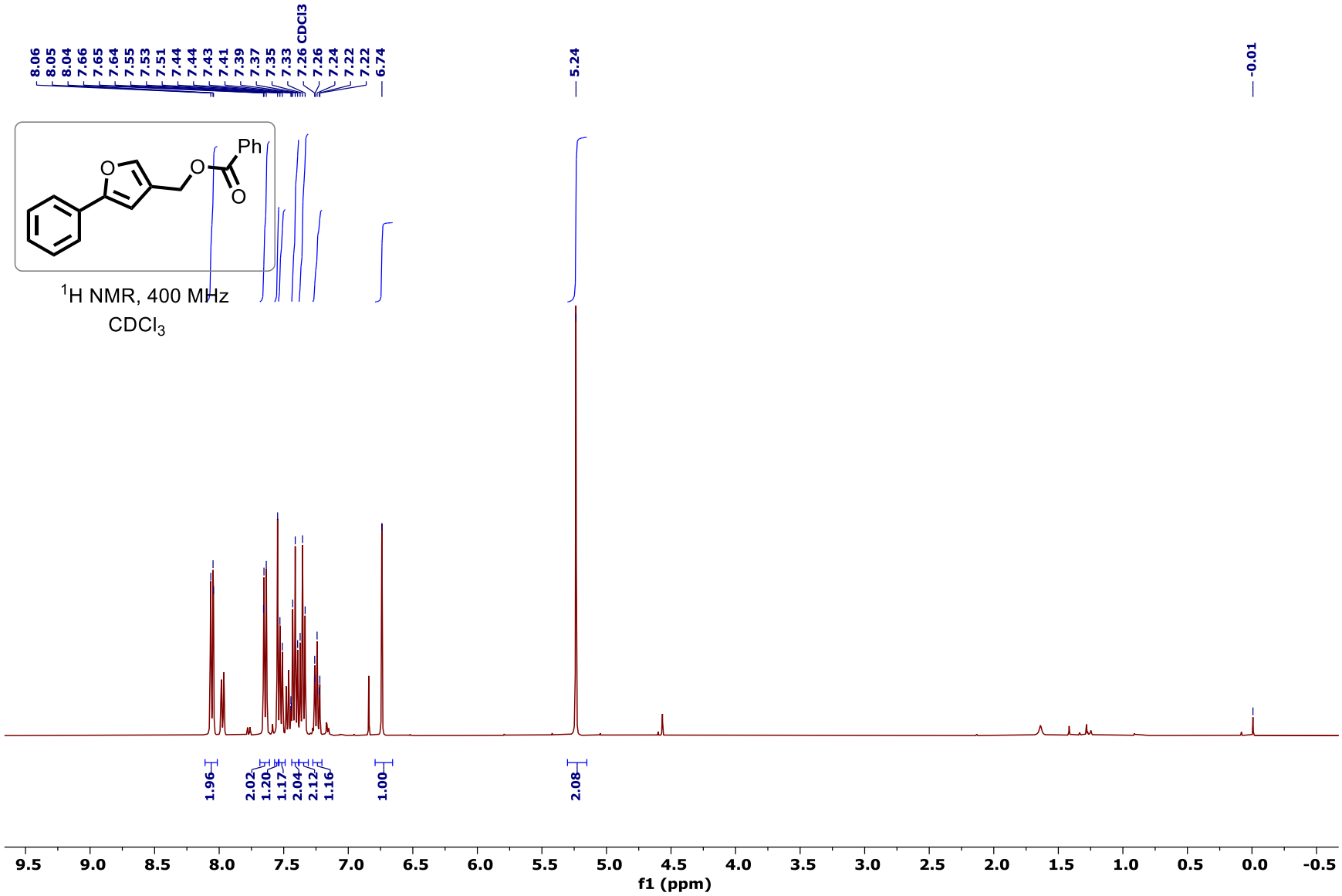
COSY NMR spectrum of (5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



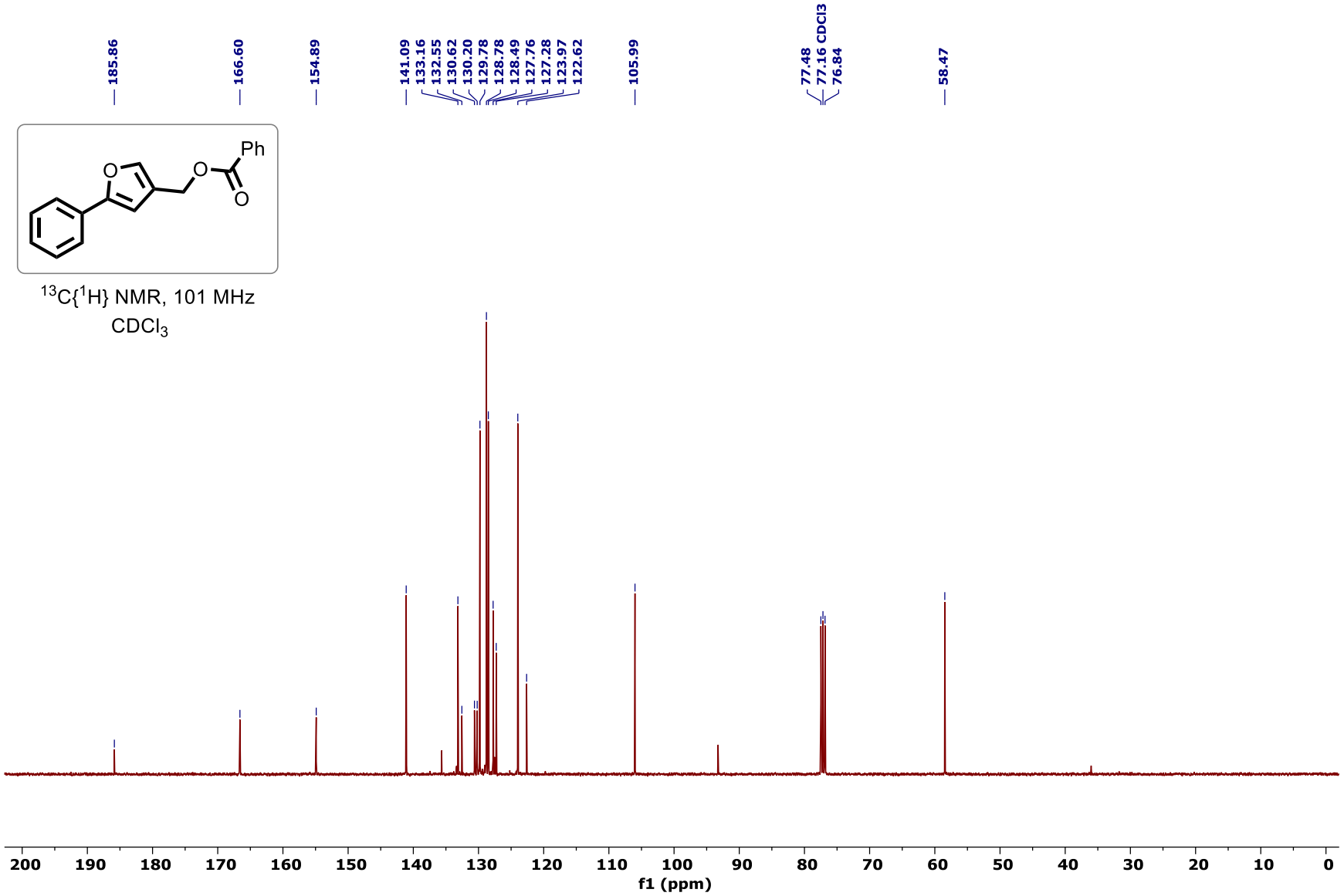
NOESY NMR spectrum of (5-Phenylfuran-3-yl)methyl (3r,5r,7r)-adamantane-1-carboxylate (5y):



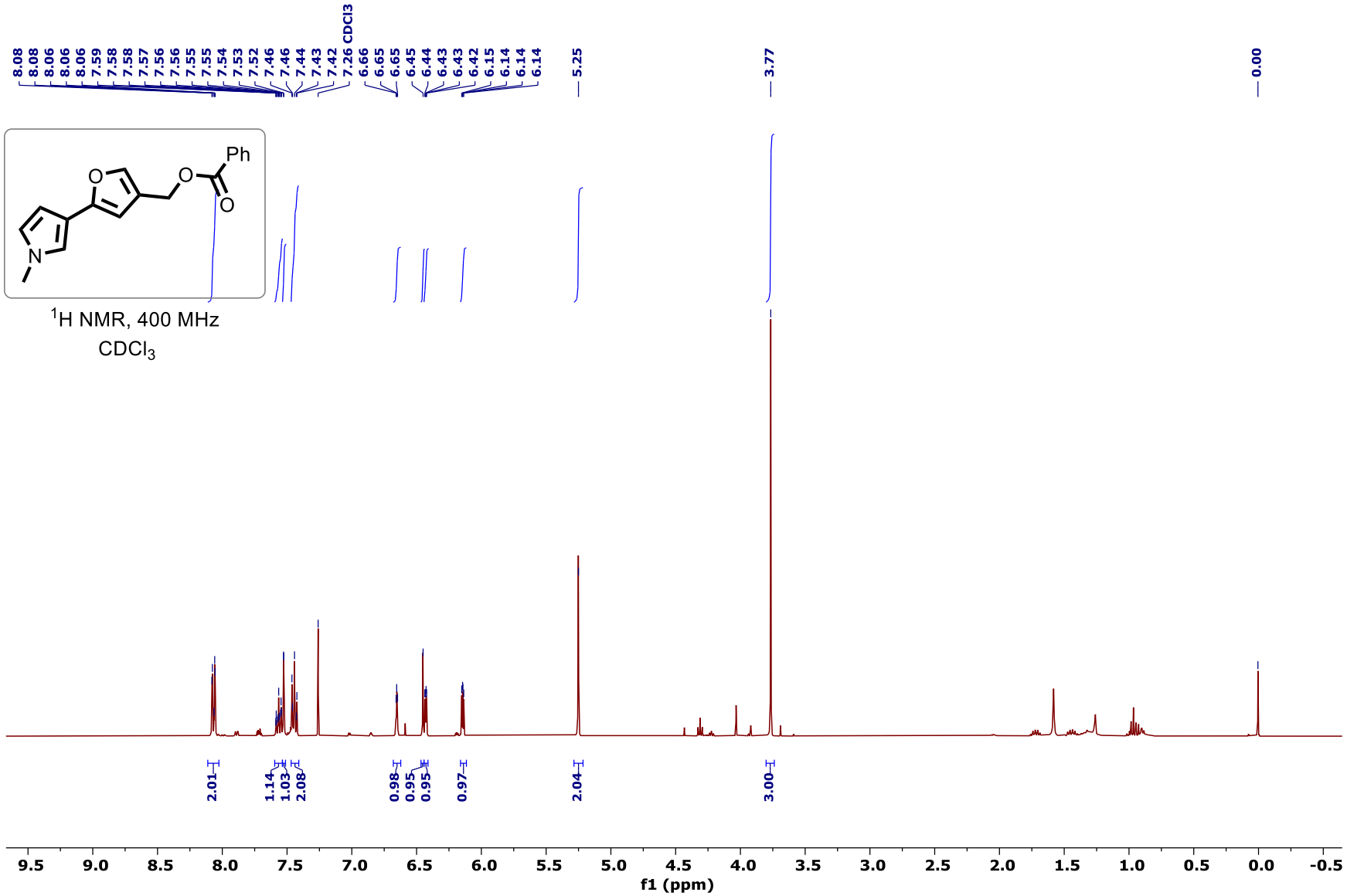
^{1}H NMR spectrum of (5-Phenylfuran-3-yl)methyl benzoate (5z):



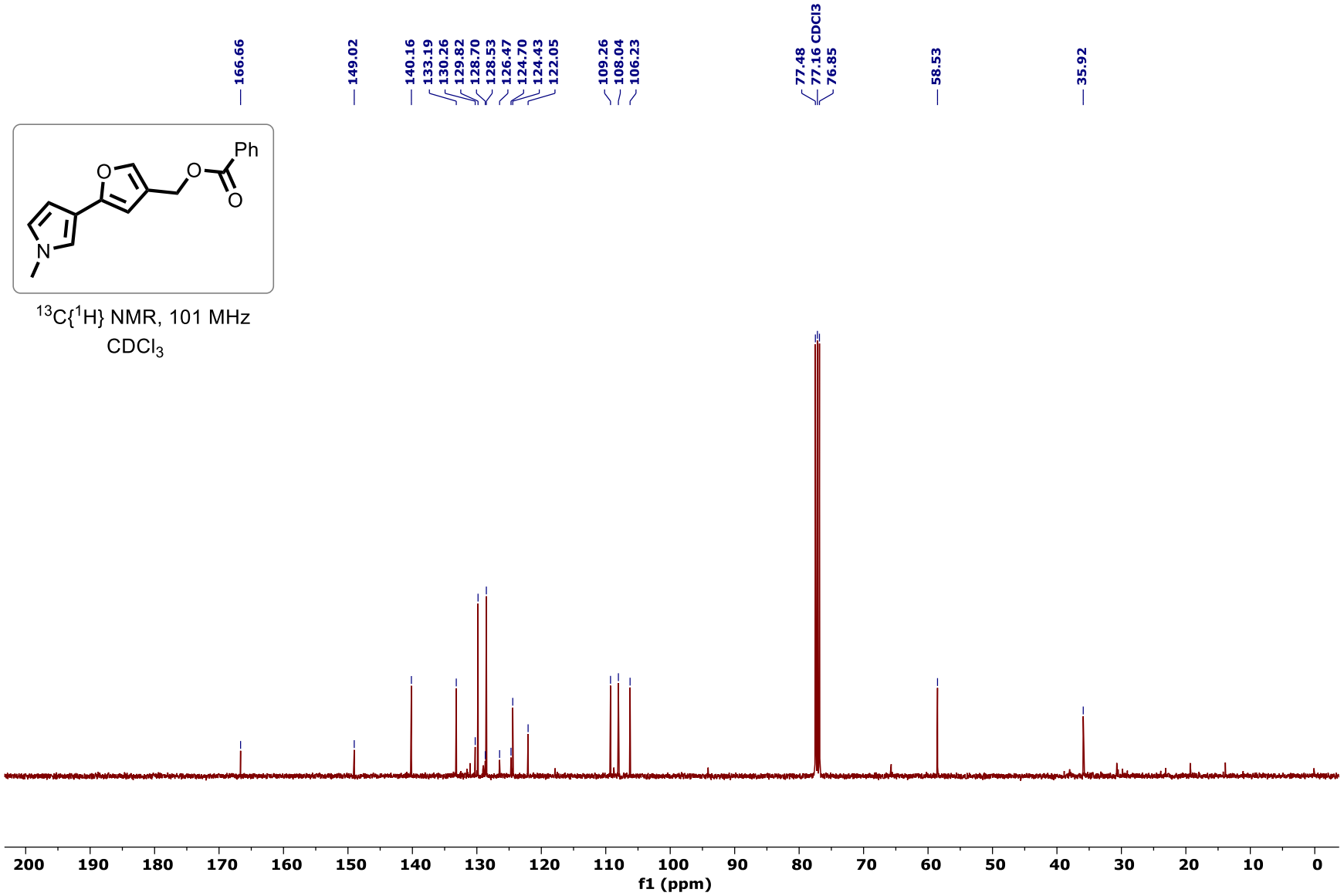
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Phenylfuran-3-yl)methyl benzoate (5z):



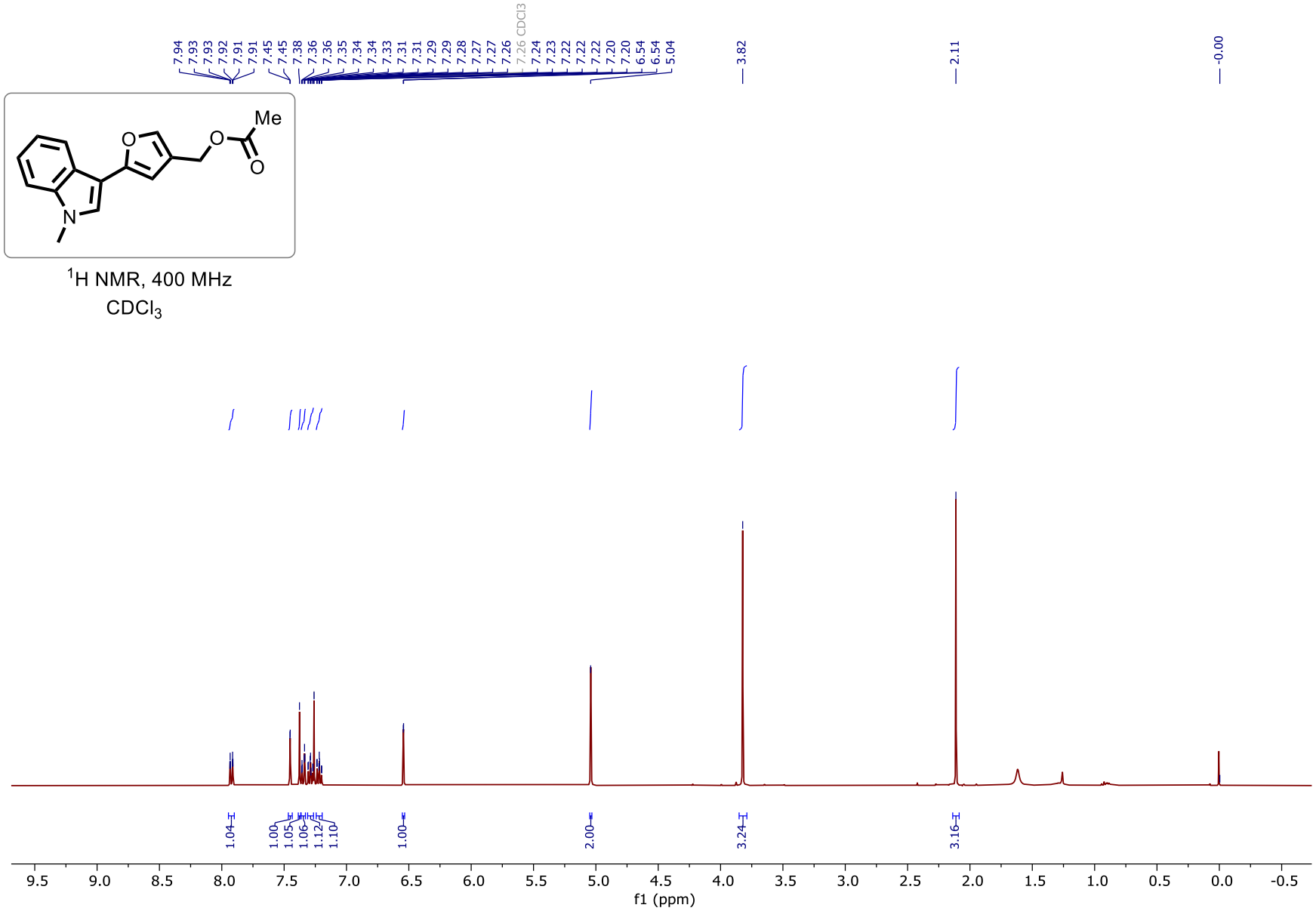
^{1}H NMR spectrum of (5-(1-Methyl-1*H*-pyrrol-3-yl)furan-3-yl)methyl benzoate (5a′):



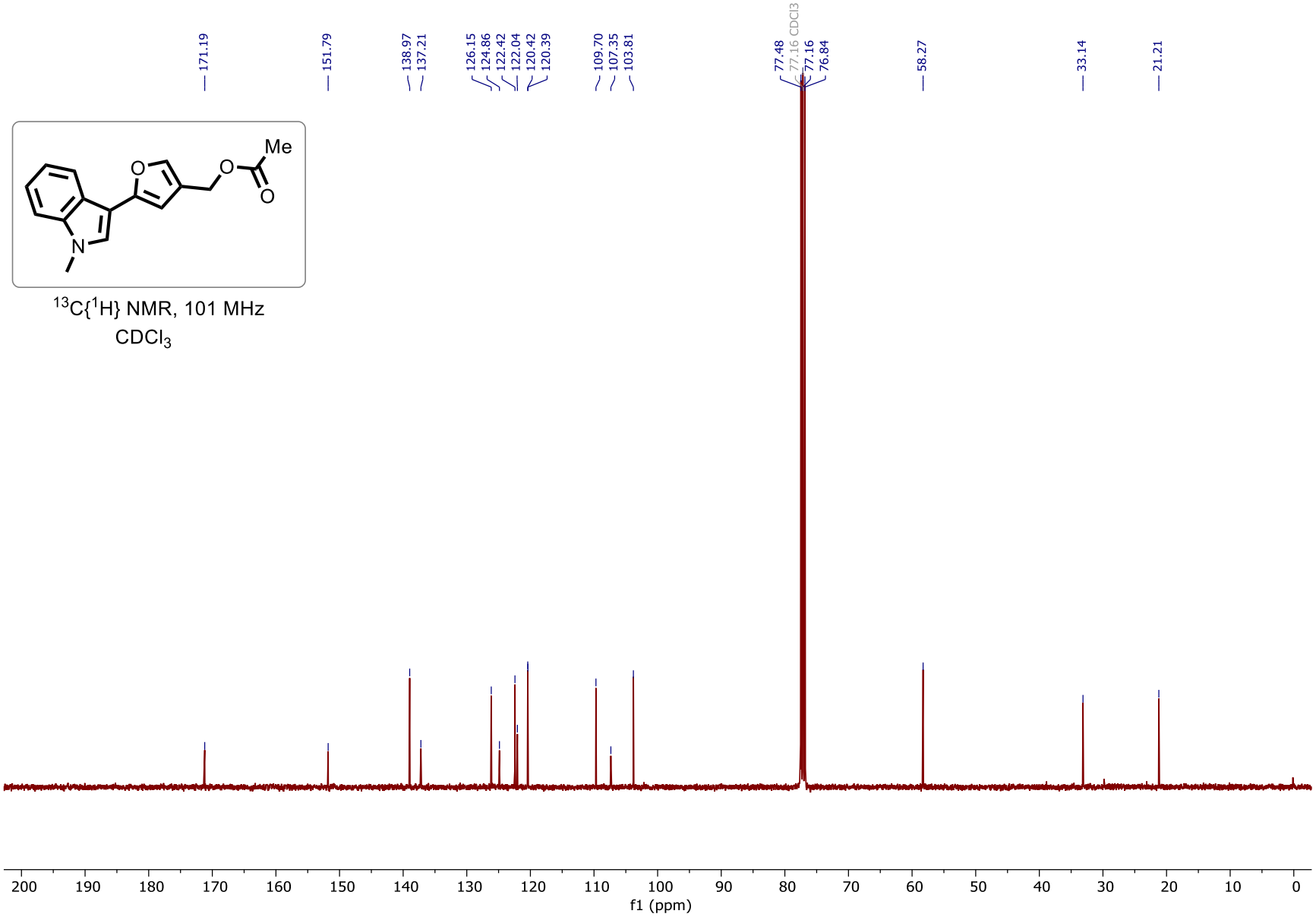
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(1-Methyl-1*H*-pyrrol-3-yl)furan-3-yl)methyl benzoate (5a′):



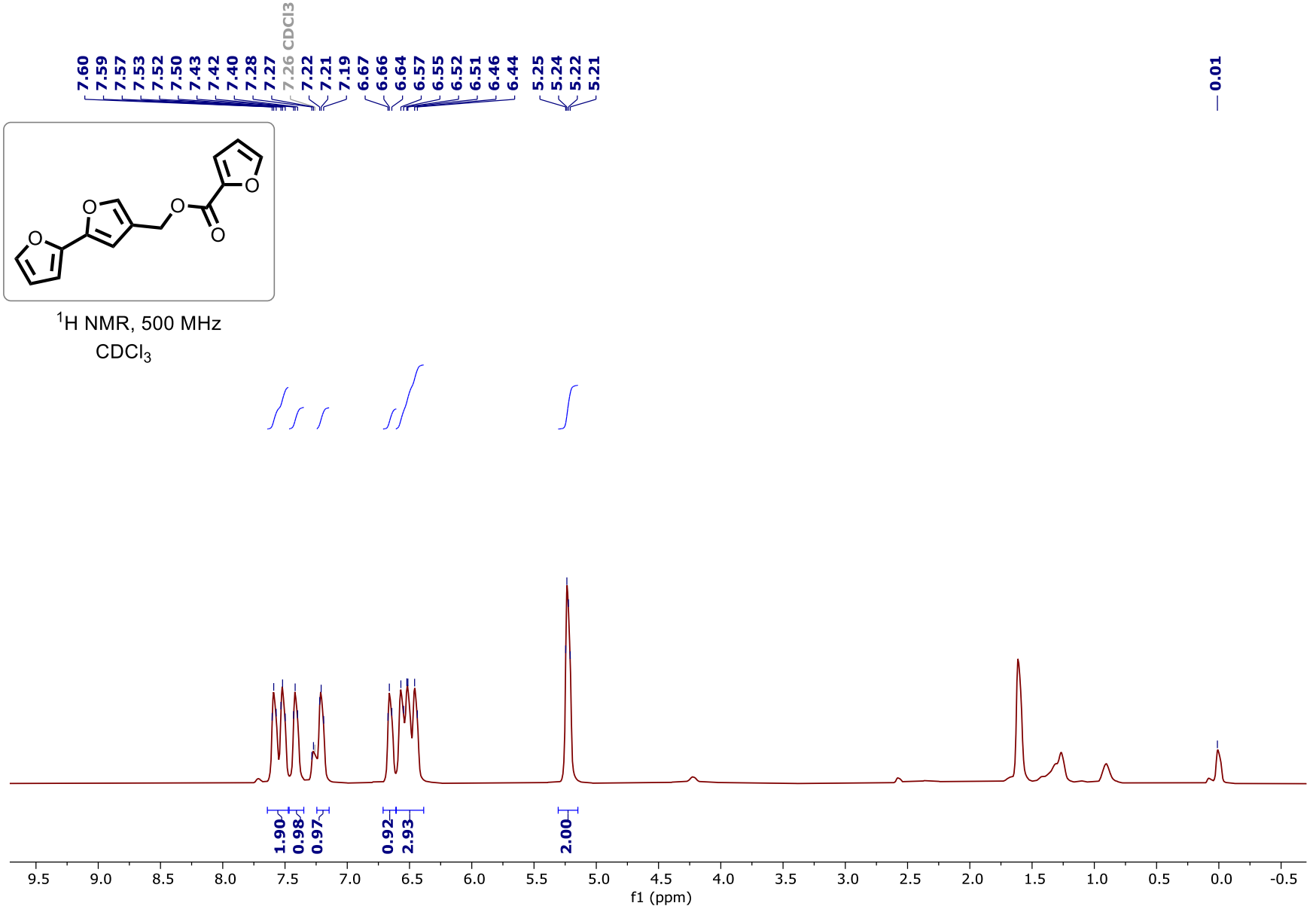
^{1}H NMR spectrum of (5-(1-Methyl-1*H*-indol-3-yl)furan-3-yl)methyl acetate (5b′):



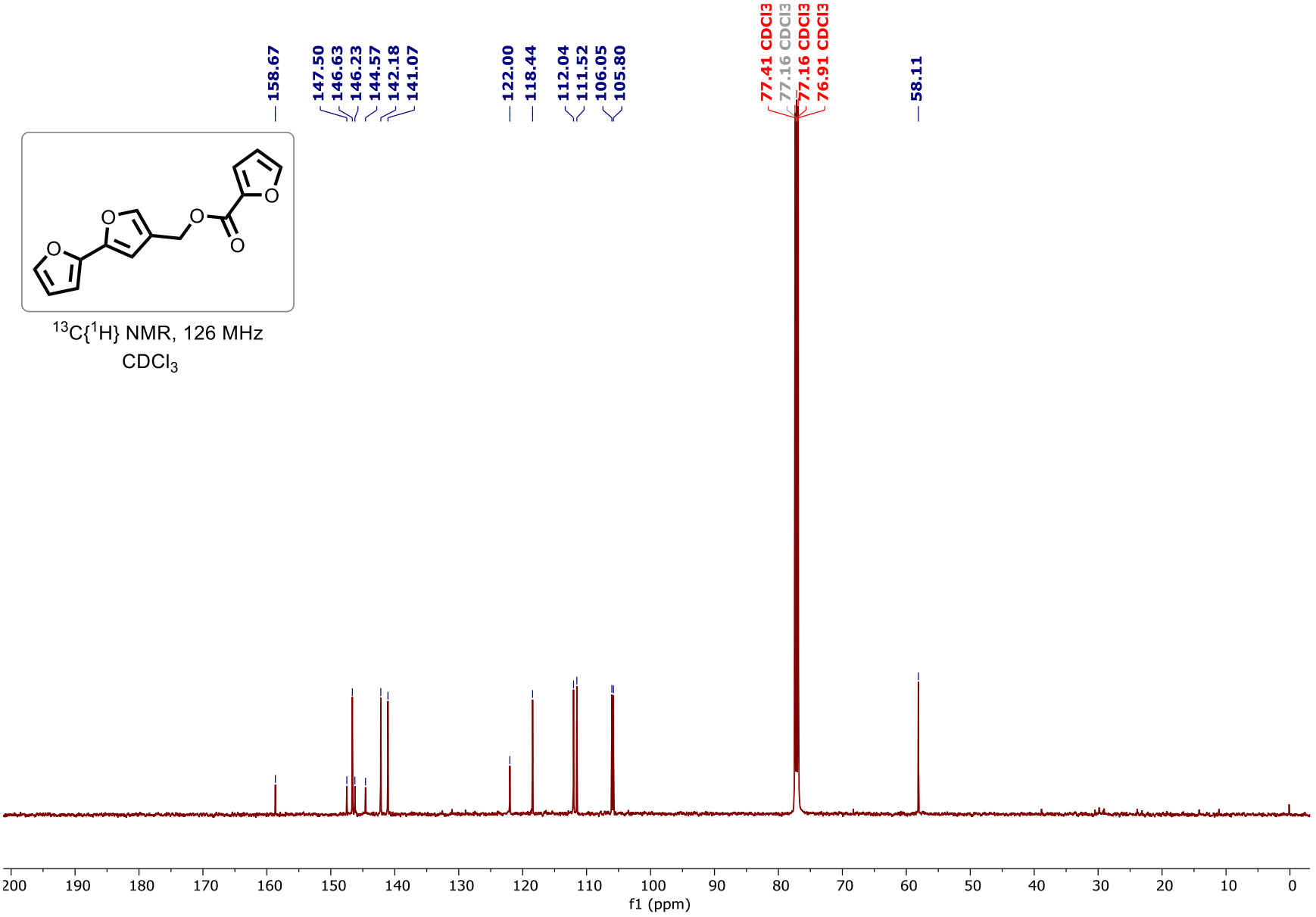
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(1-Methyl-1*H*-indol-3-yl)furan-3-yl)methyl acetate (5b′):



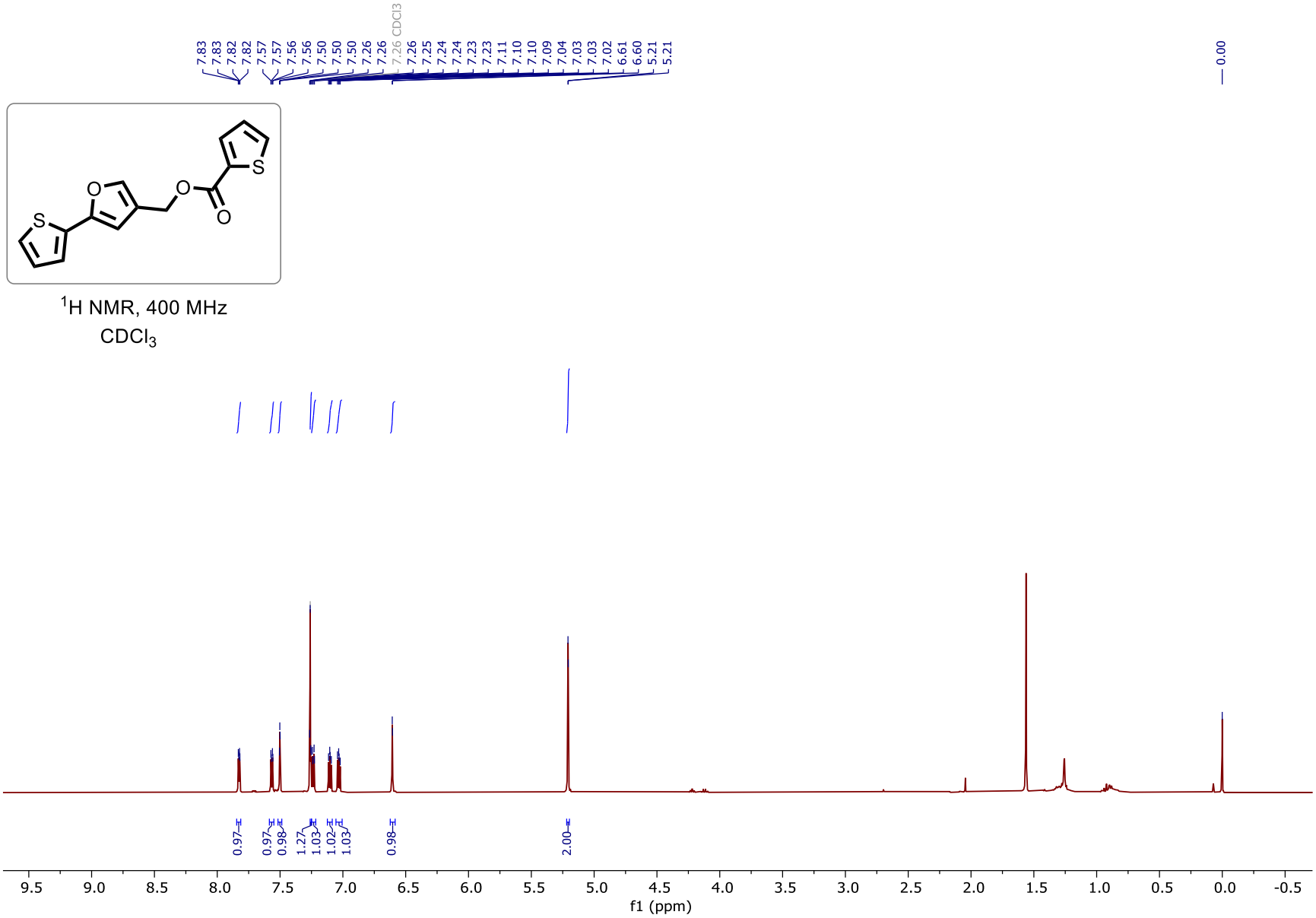
^{1}H NMR spectrum of [2,2'-Bifuran]-4-ylmethyl furan-2-carboxylate (5c′):



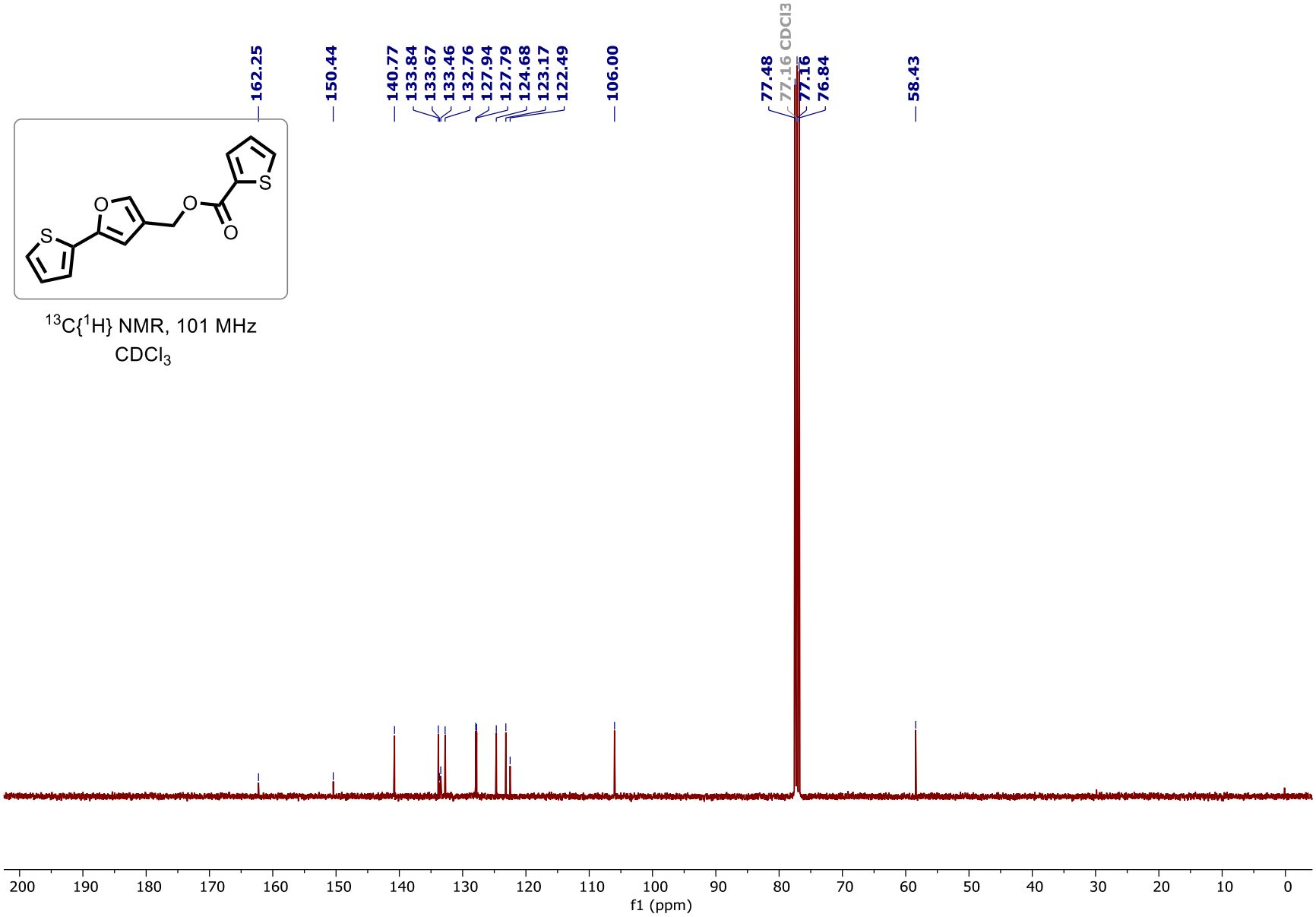
$^{13}C\{^{1}H\}$ NMR spectrum of [2,2'-Bifuran]-4-ylmethyl furan-2-carboxylate (5c′):



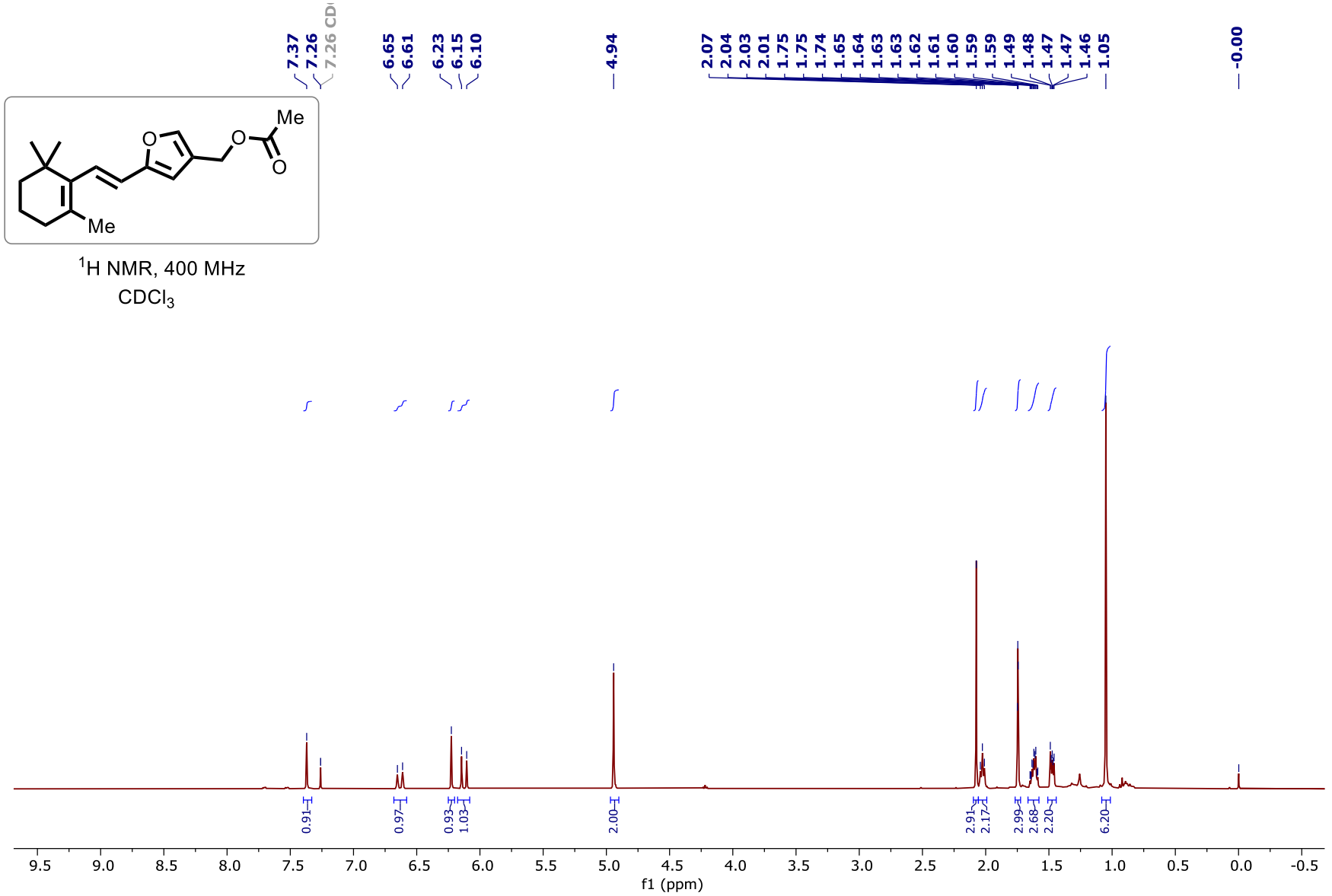
^{1}H NMR spectrum of (5-(Thiophen-2-yl)furan-3-yl)methyl thiophene-2-carboxylate (5d′):



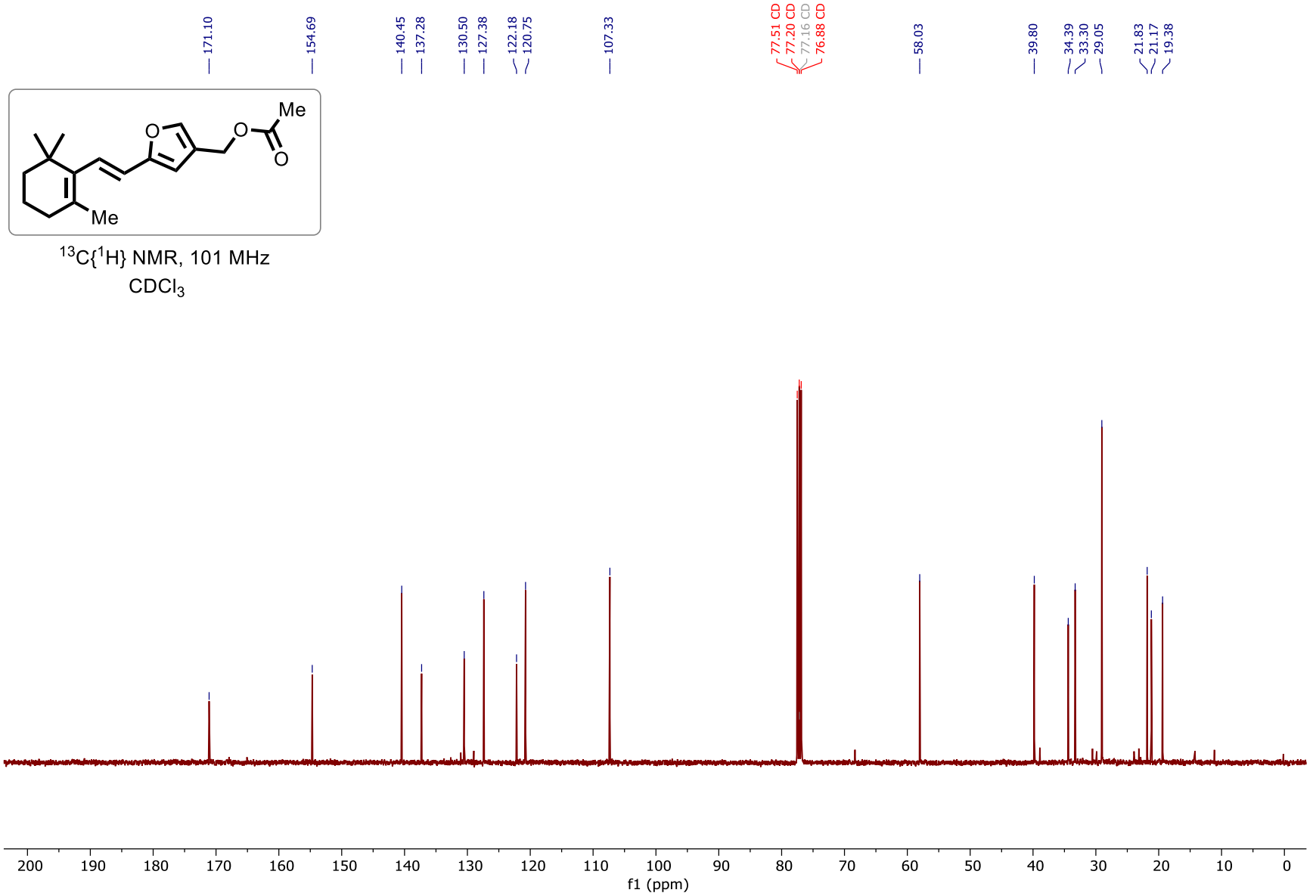
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(Thiophen-2-yl)furan-3-yl)methyl thiophene-2-carboxylate (5d′):



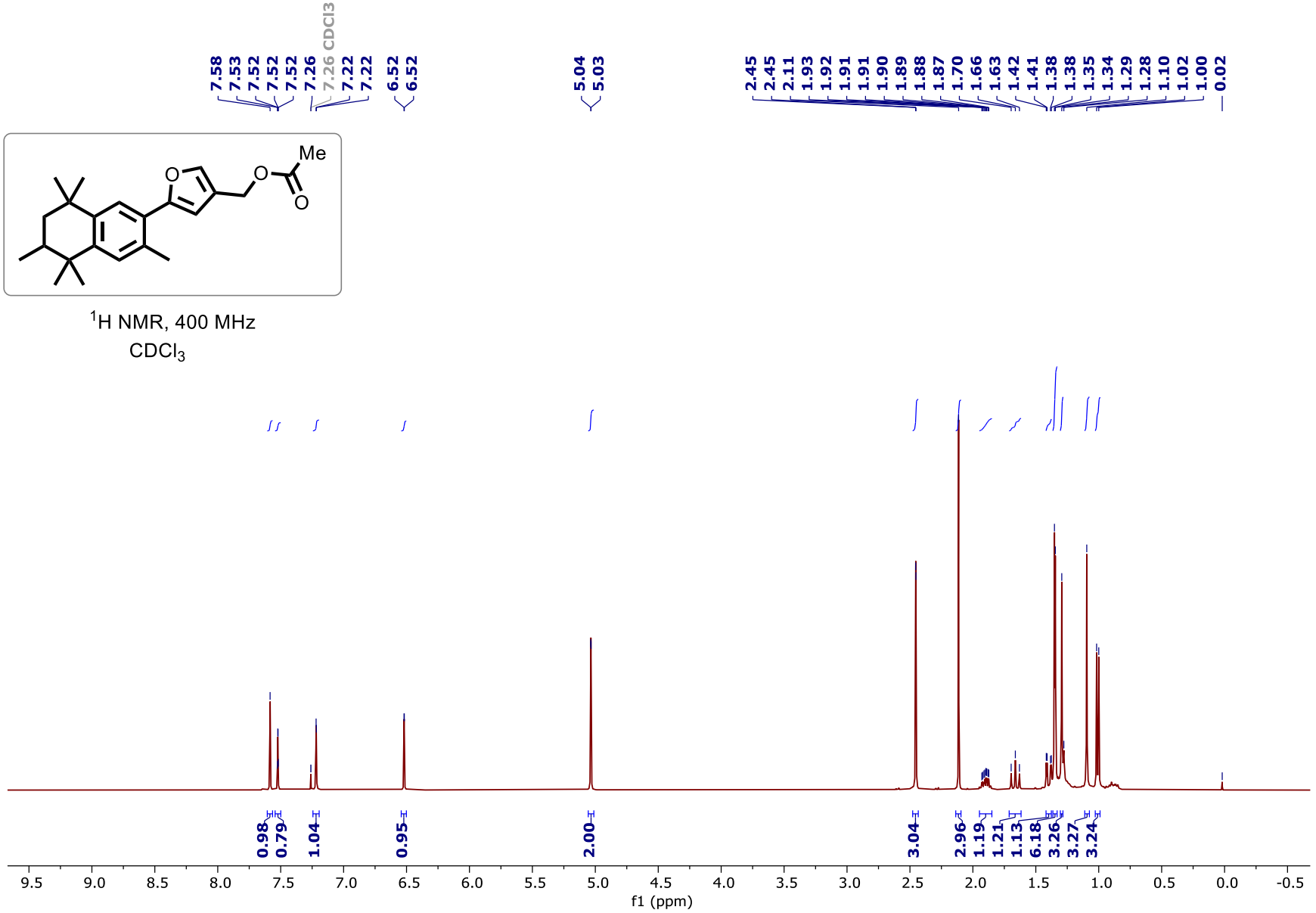
^{1}H NMR spectrum of (*E*)-(5-(2-(2,6,6-Trimethylcyclohex-1-en-1-yl)vinyl)furan-3-yl)methyl acetate (5e′):



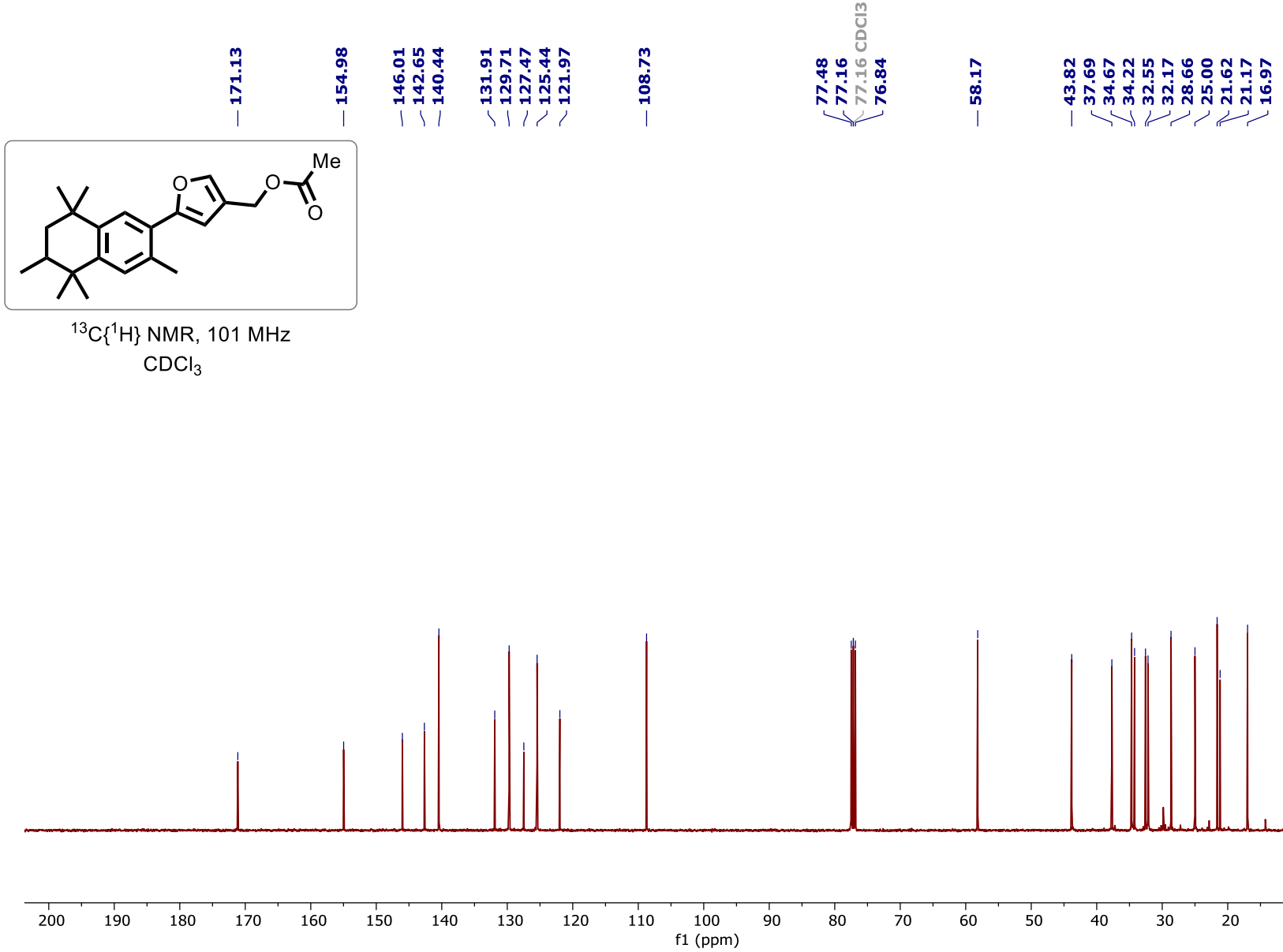
$^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-(5-(2-(2,6,6-Trimethylcyclohex-1-en-1-yl)vinyl)furan-3-yl)methyl acetate (5e′):



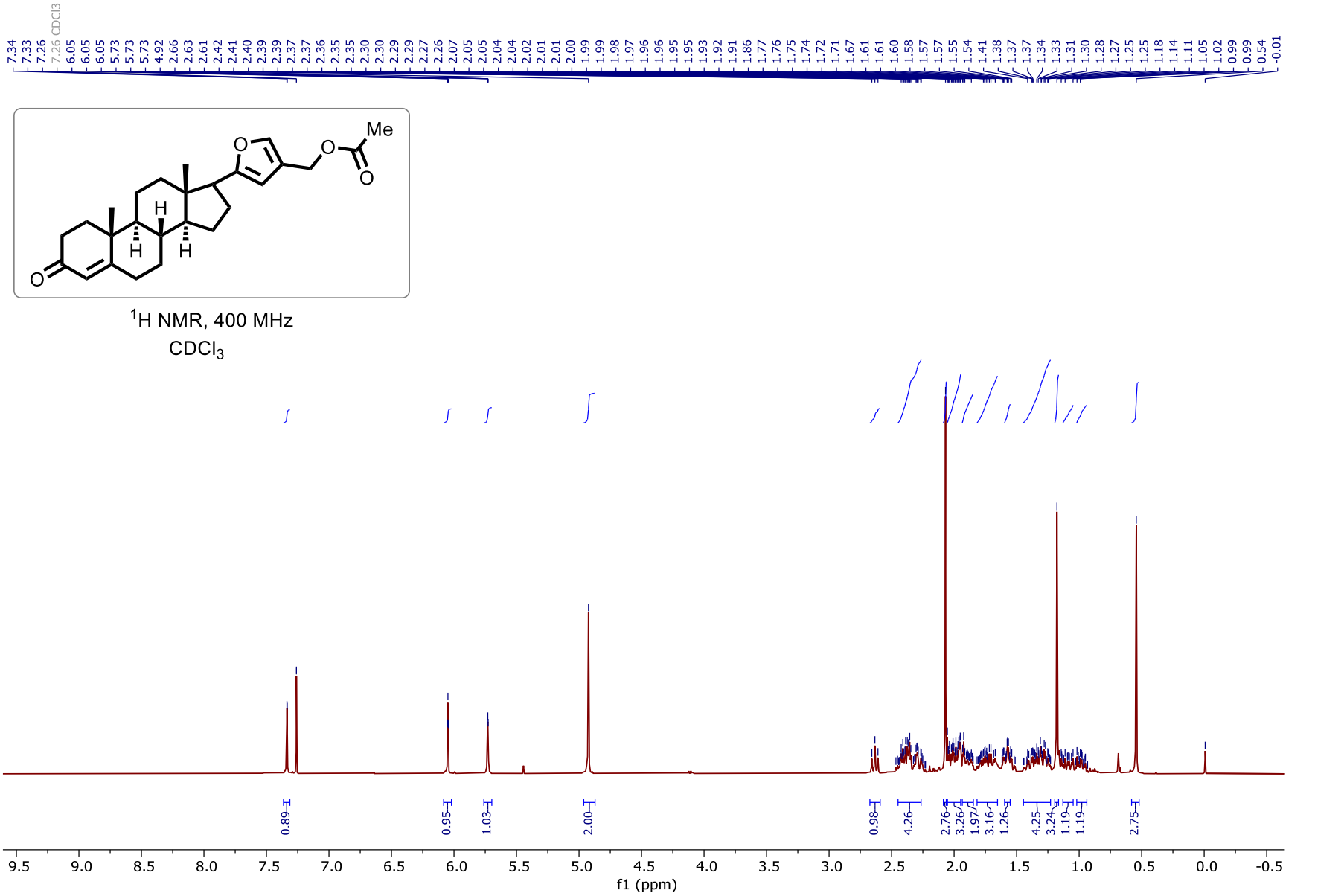
^{1}H NMR spectrum of (5-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)furan-3-yl)methyl acetate (5f′):



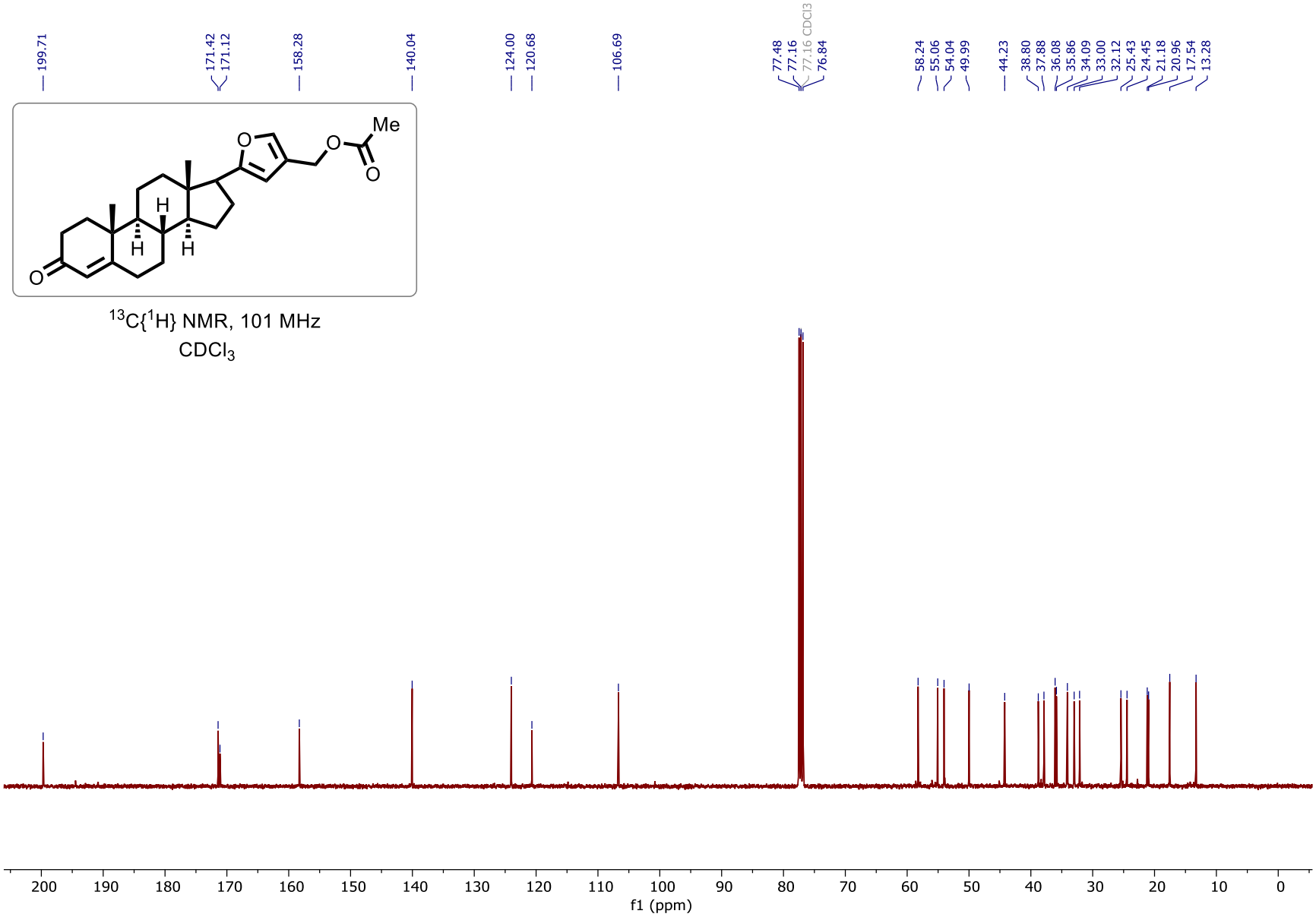
$^{13}C\{^{1}H\}$ NMR spectrum of (5-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)furan-3-yl)methyl acetate (5f′):



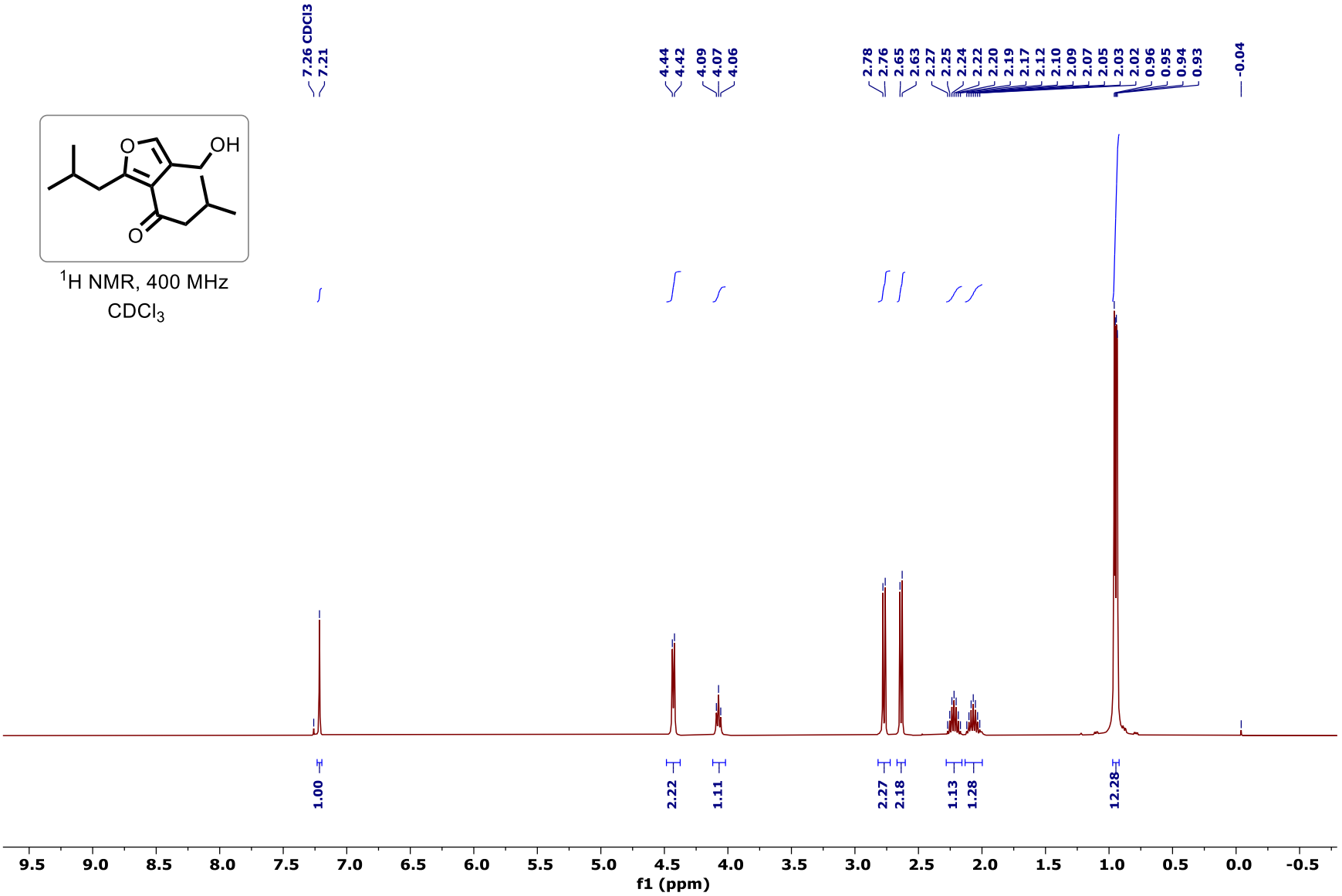
^{1}H NMR spectrum of (5-((8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)furan-3-yl)methyl acetate (5g′):



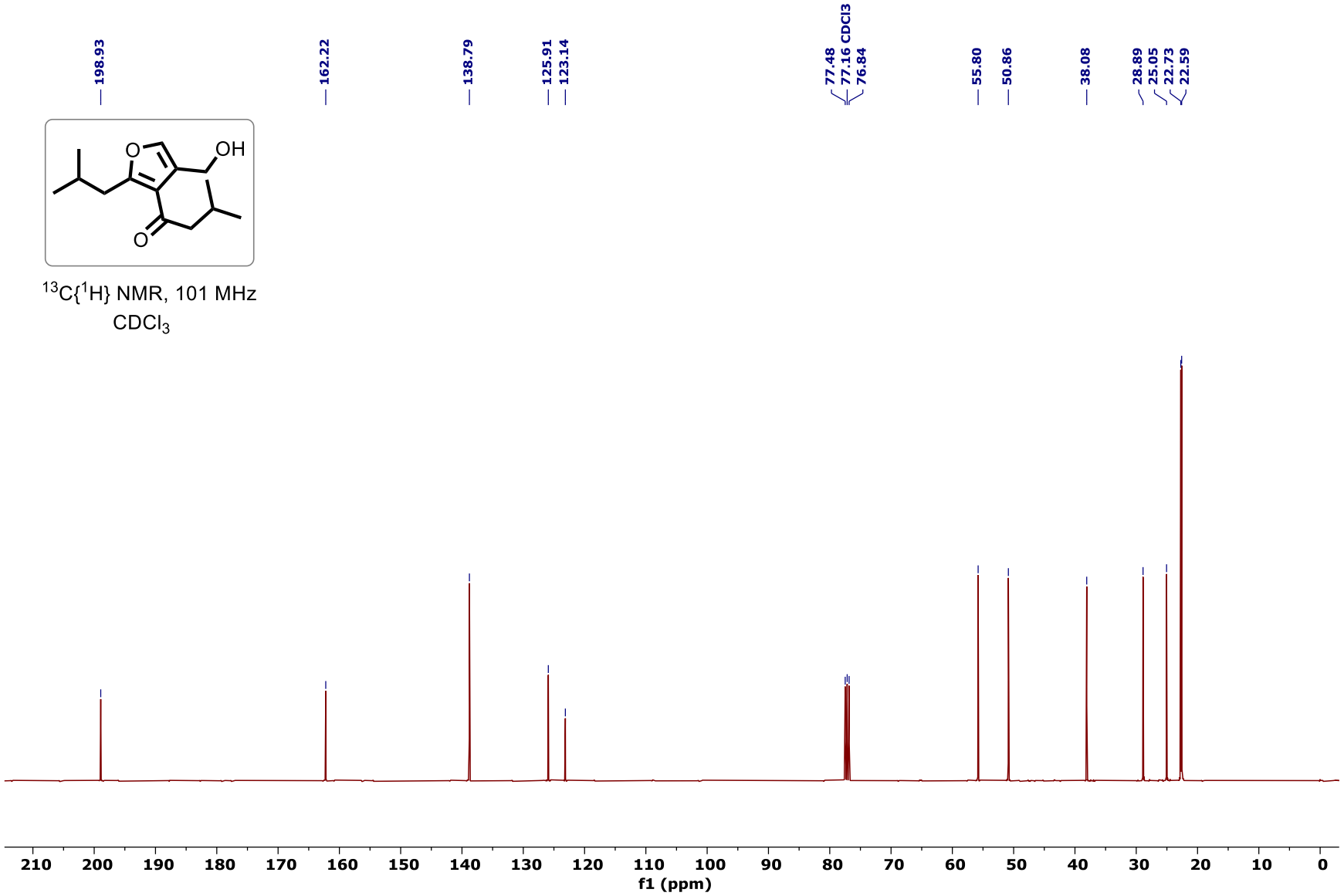
$^{13}C\{^{1}H\}$ NMR spectrum of (5-((8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)furan-3-yl)methyl acetate (5g′):



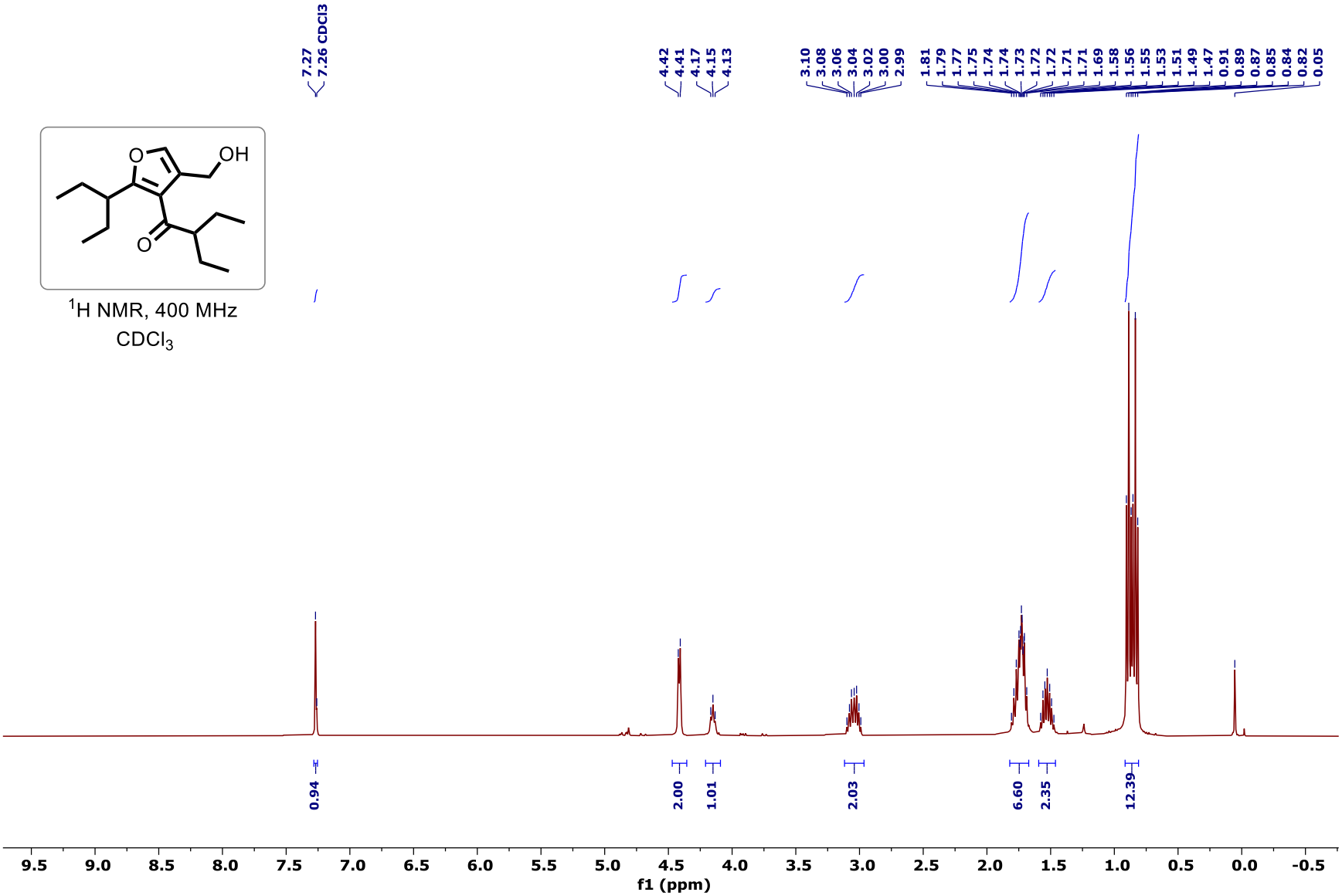
^{1}H NMR spectrum of 1-(4-(Hydroxymethyl)-2-isobutylfuran-3-yl)-3-methylbutan-1-one (5′a):



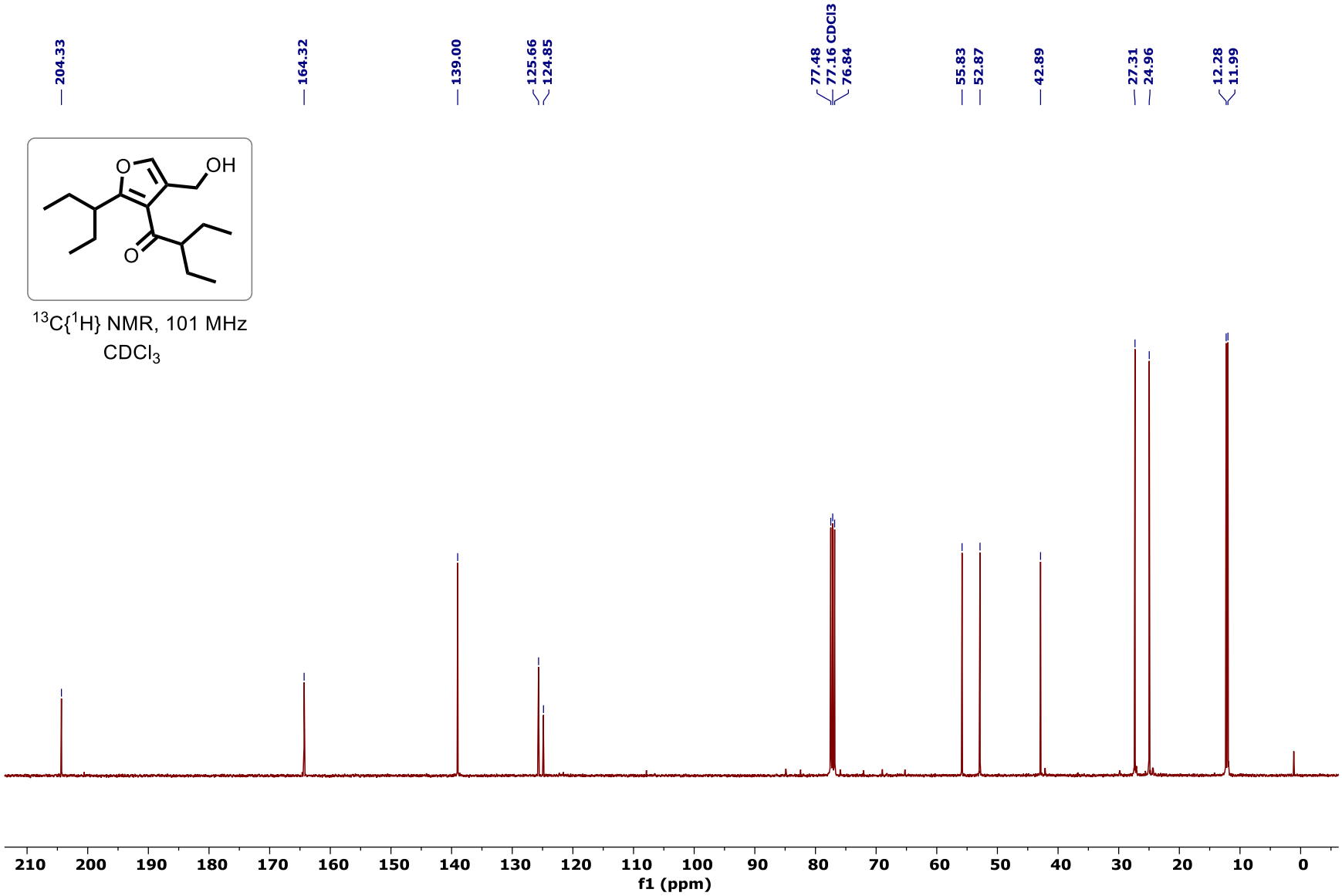
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-(Hydroxymethyl)-2-isobutylfuran-3-yl)-3-methylbutan-1-one (5′a):



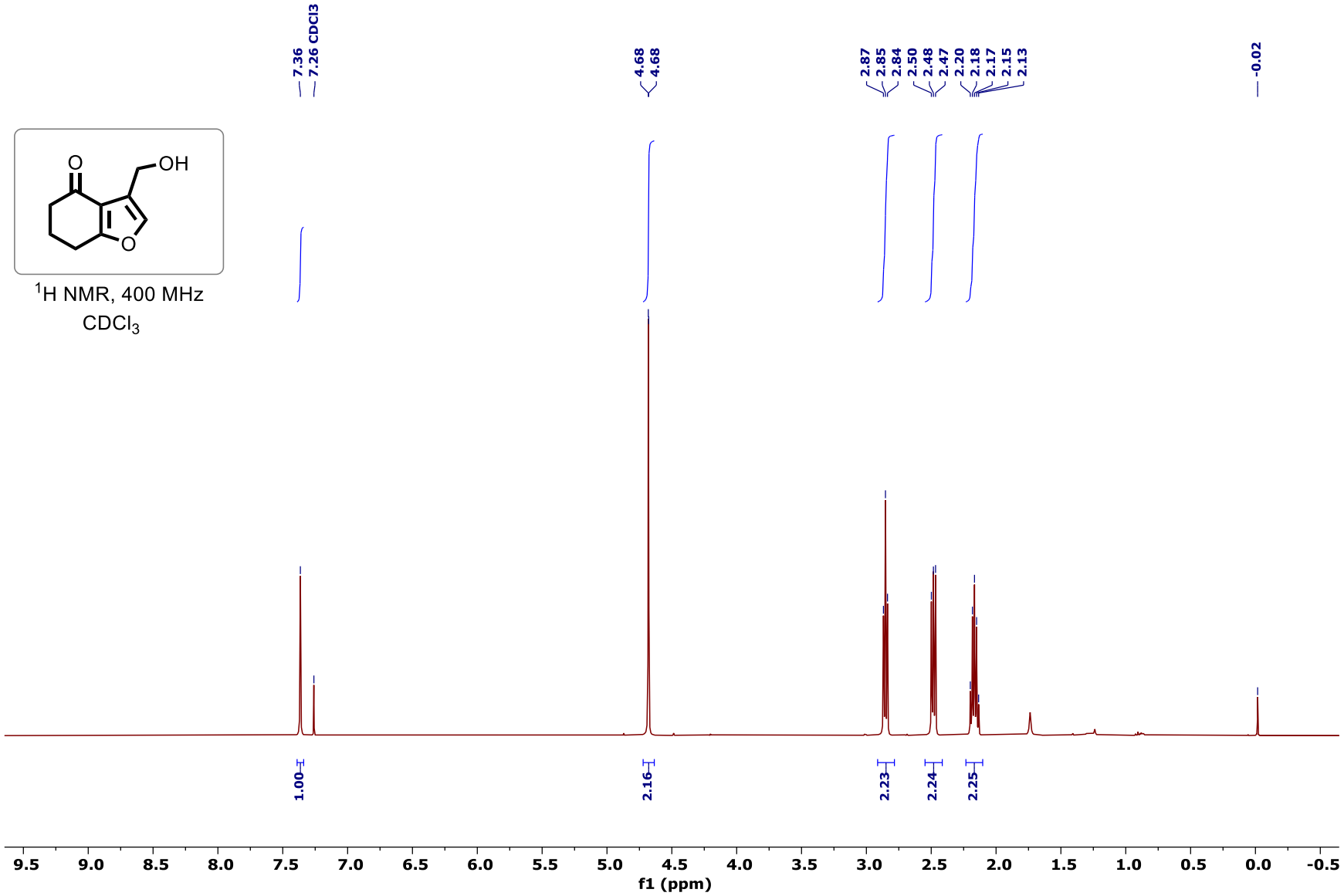
^{1}H NMR spectrum of 2-Ethyl-1-(4-(hydroxymethyl)-2-(pentan-3-yl)furan-3-yl)butan-1-one (5′b):



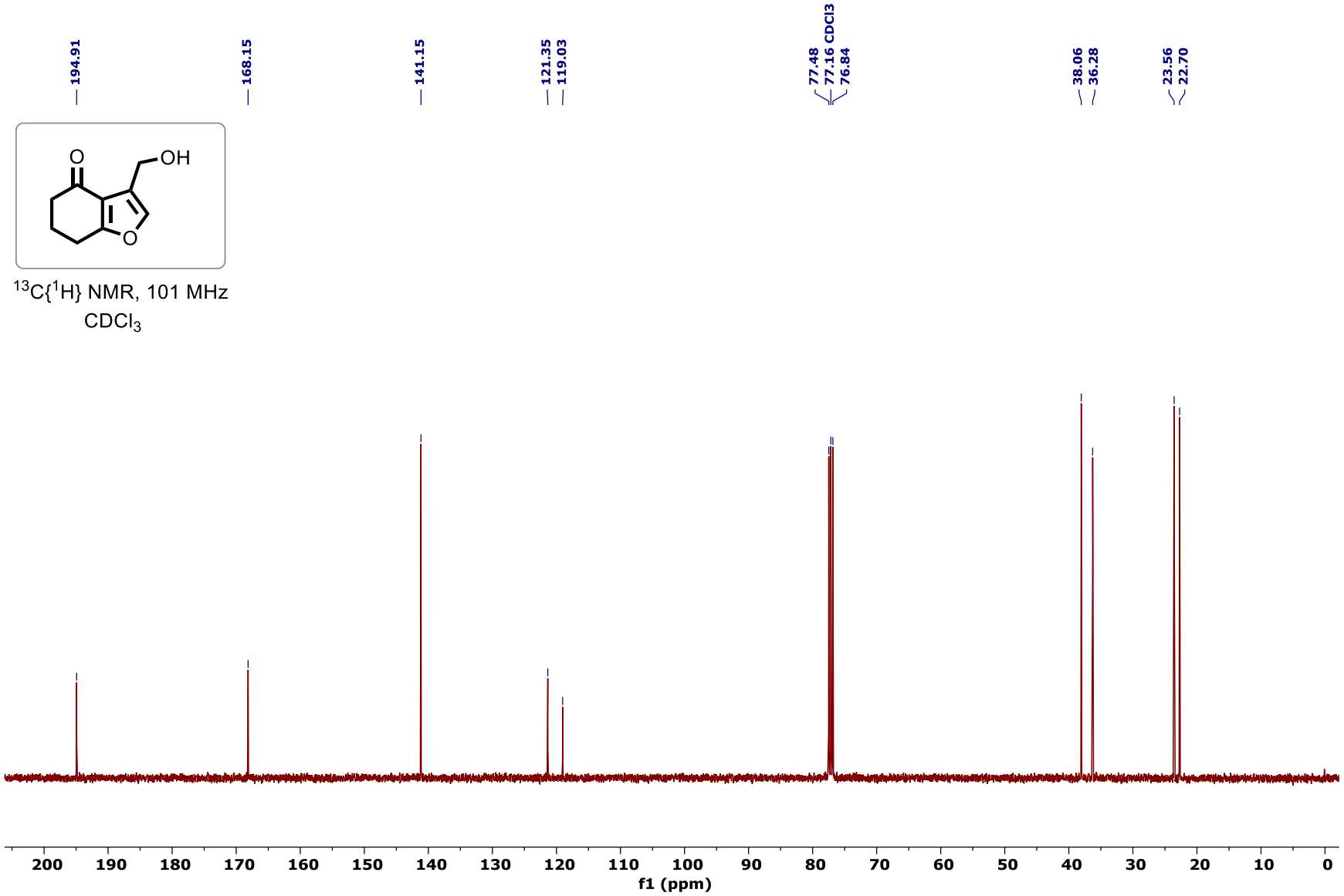
$^{13}C\{^{1}H\}$ NMR spectrum of 2-Ethyl-1-(4-(hydroxymethyl)-2-(pentan-3-yl)furan-3-yl)butan-1-one (5′b):



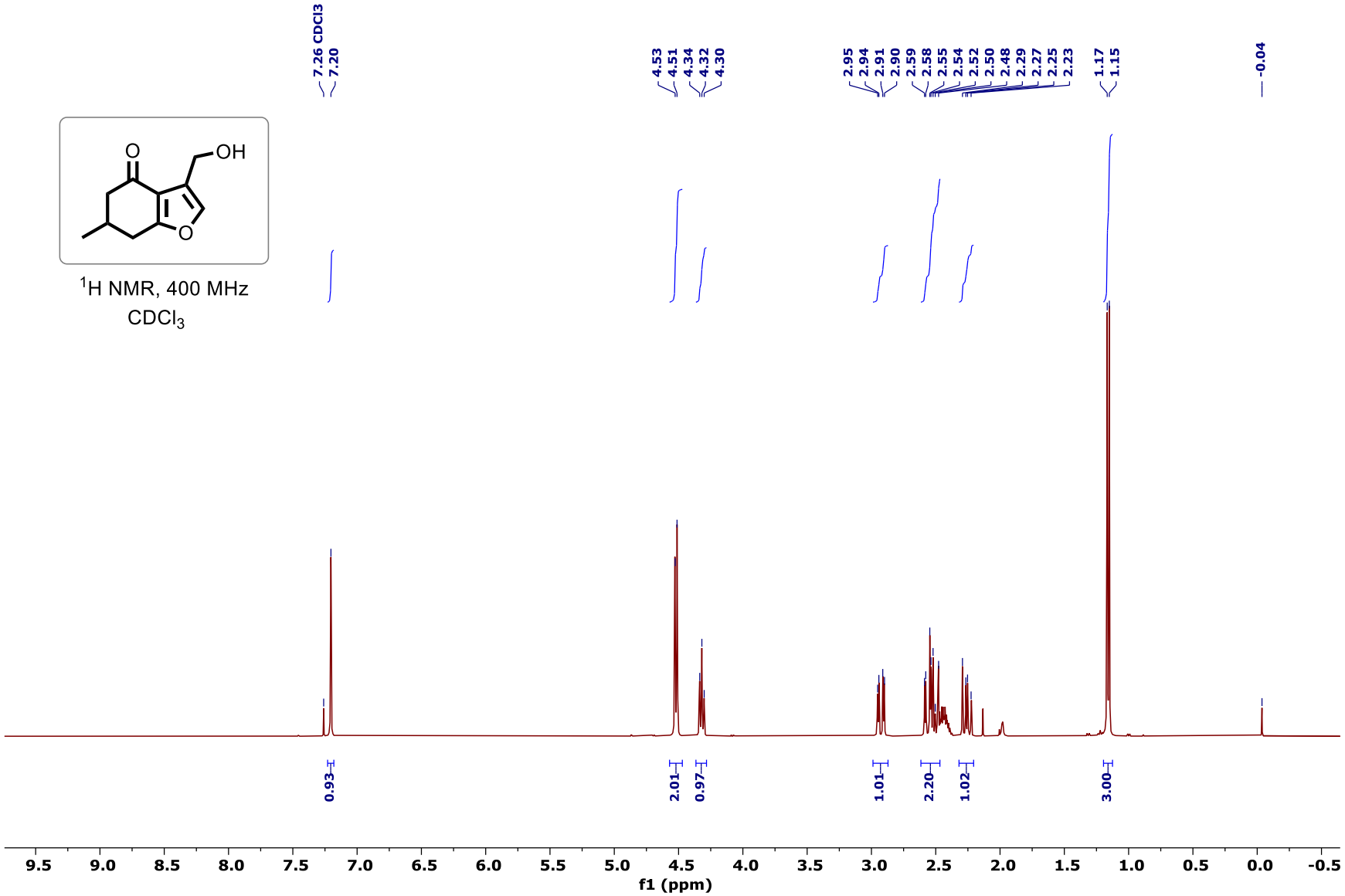
^{1}H NMR spectrum of 3-(Hydroxymethyl)-6,7-dihydrobenzofuran-4(5*H*)-one (5′c):



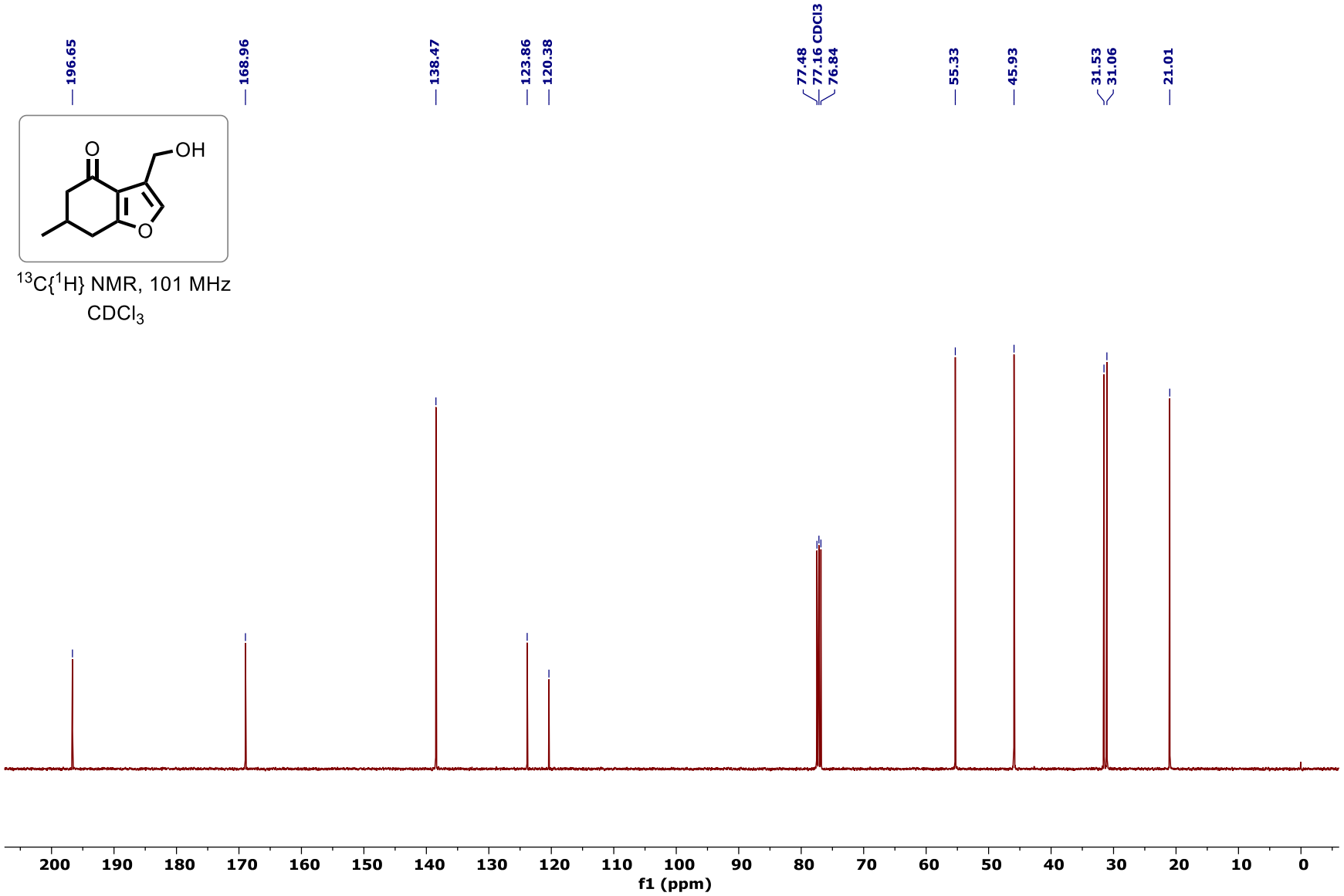
$^{13}C\{^{1}H\}$ NMR spectrum of 3-(Hydroxymethyl)-6,7-dihydrobenzofuran-4(5*H*)-one (5′c):



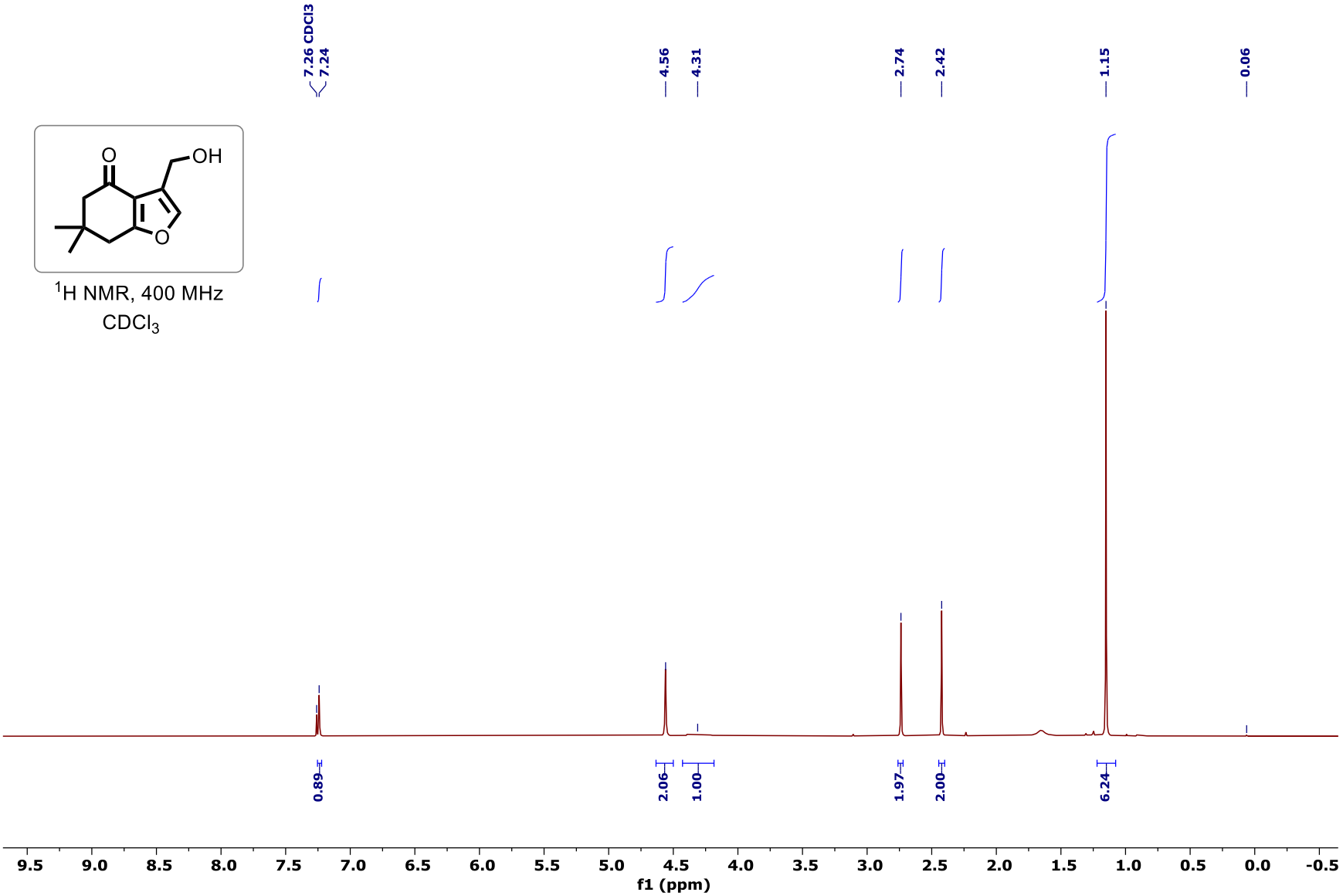
^{1}H NMR spectrum of 3-(Hydroxymethyl)-6-methyl-6,7-dihydrobenzofuran-4(5H)-one (5′d):



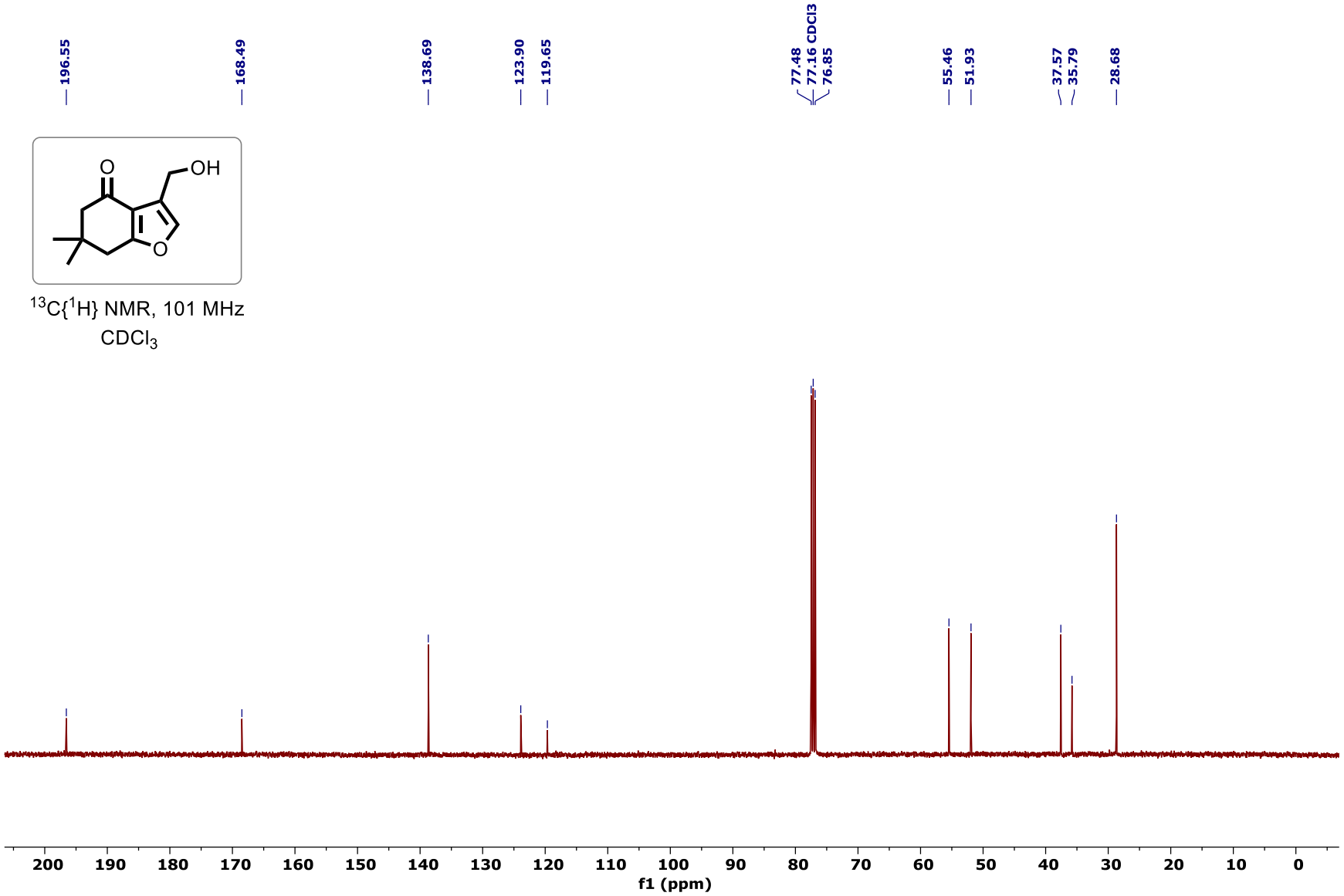
$^{13}C\{^{1}H\}$ NMR spectrum of 3-(Hydroxymethyl)-6-methyl-6,7-dihydrobenzofuran-4(5H)-one (5′d):



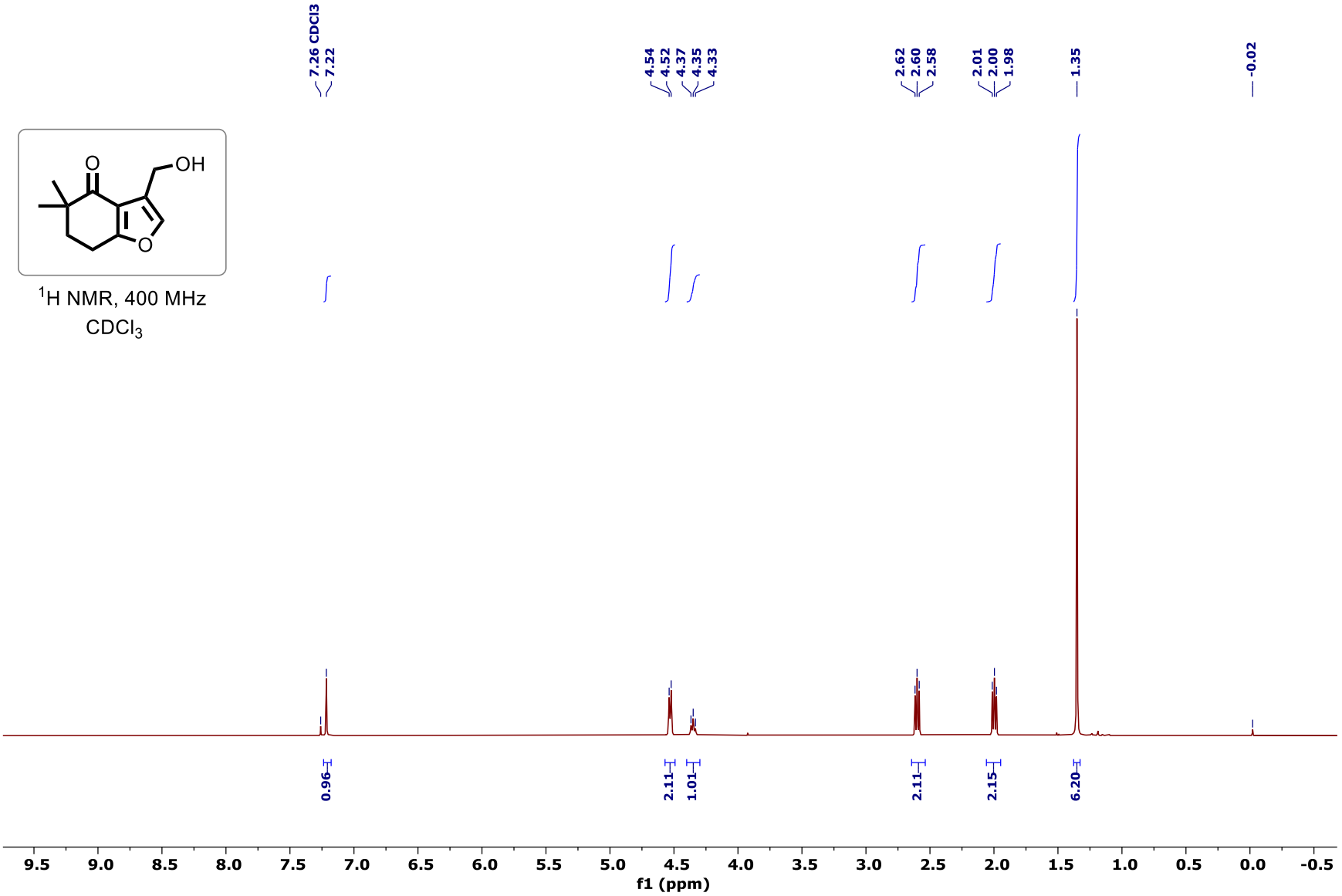
^{1}H NMR spectrum of 3-(Hydroxymethyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (5′e):



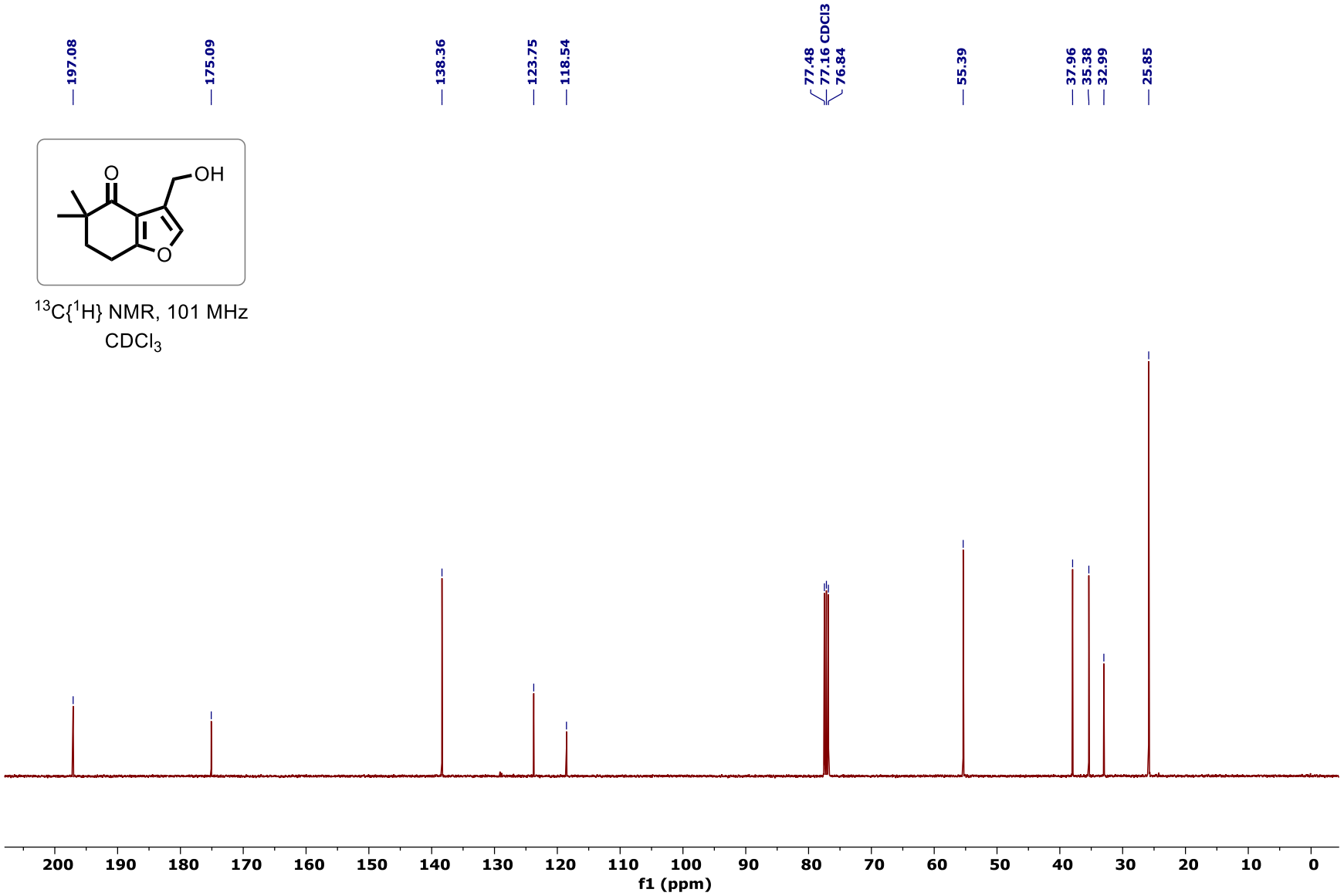
$^{13}C\{^{1}H\}$ NMR spectrum of 3-(Hydroxymethyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (5′e):



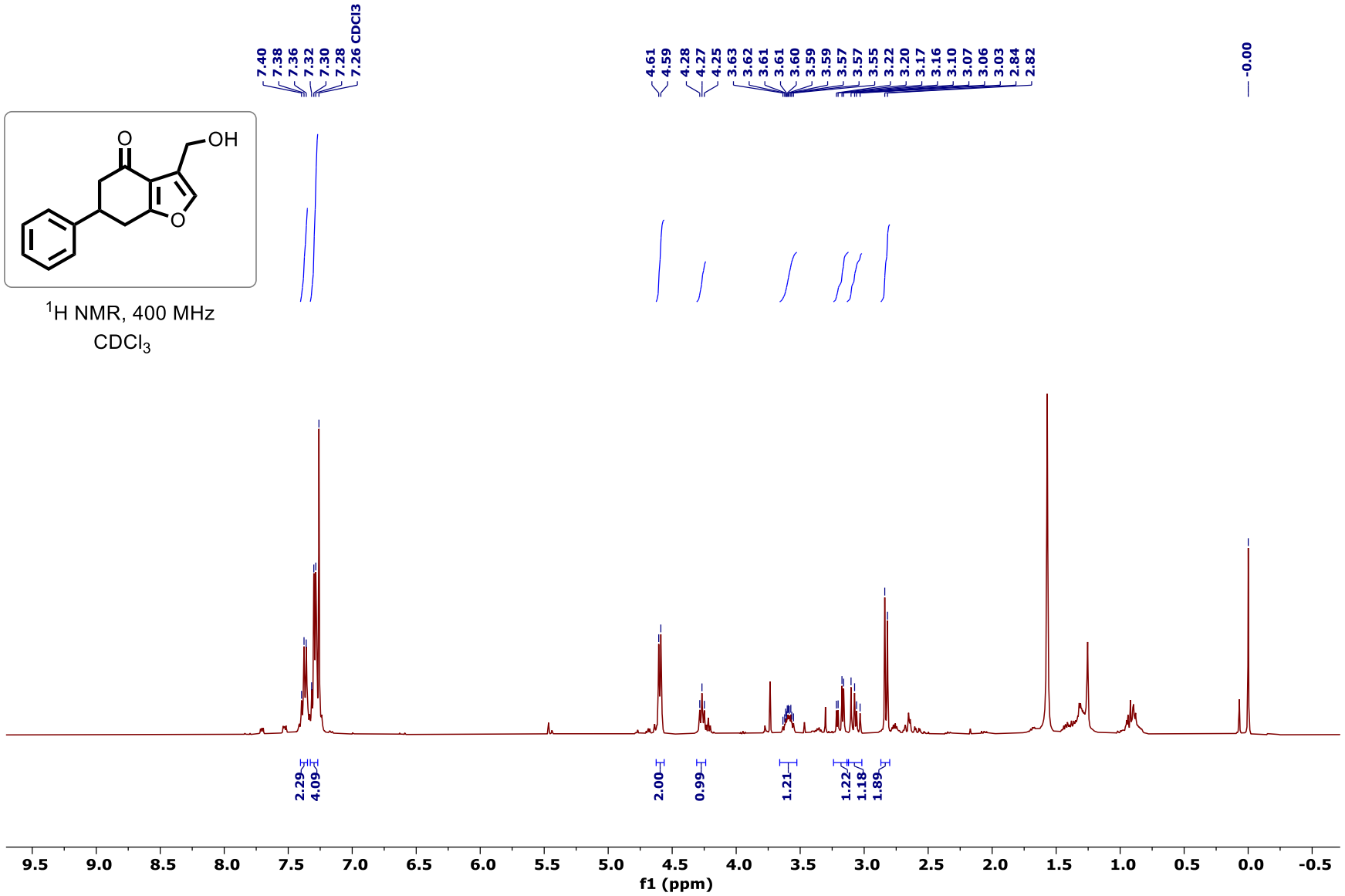
^{1}H NMR spectrum of 3-(Hydroxymethyl)-5,5-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (5′f):



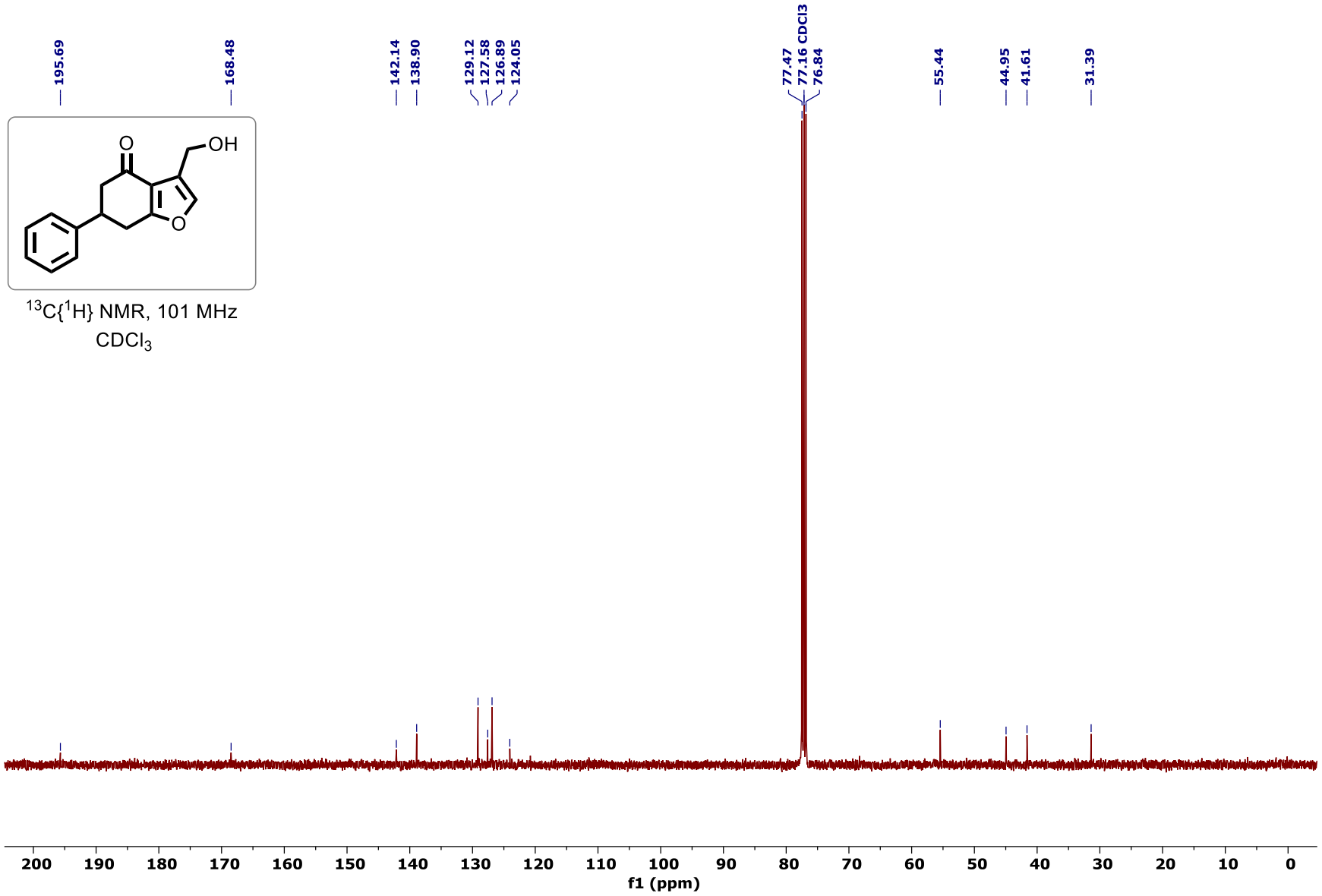
$^{13}C\{^{1}H\}$ NMR spectrum of 3-(Hydroxymethyl)-5,5-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (5′f):



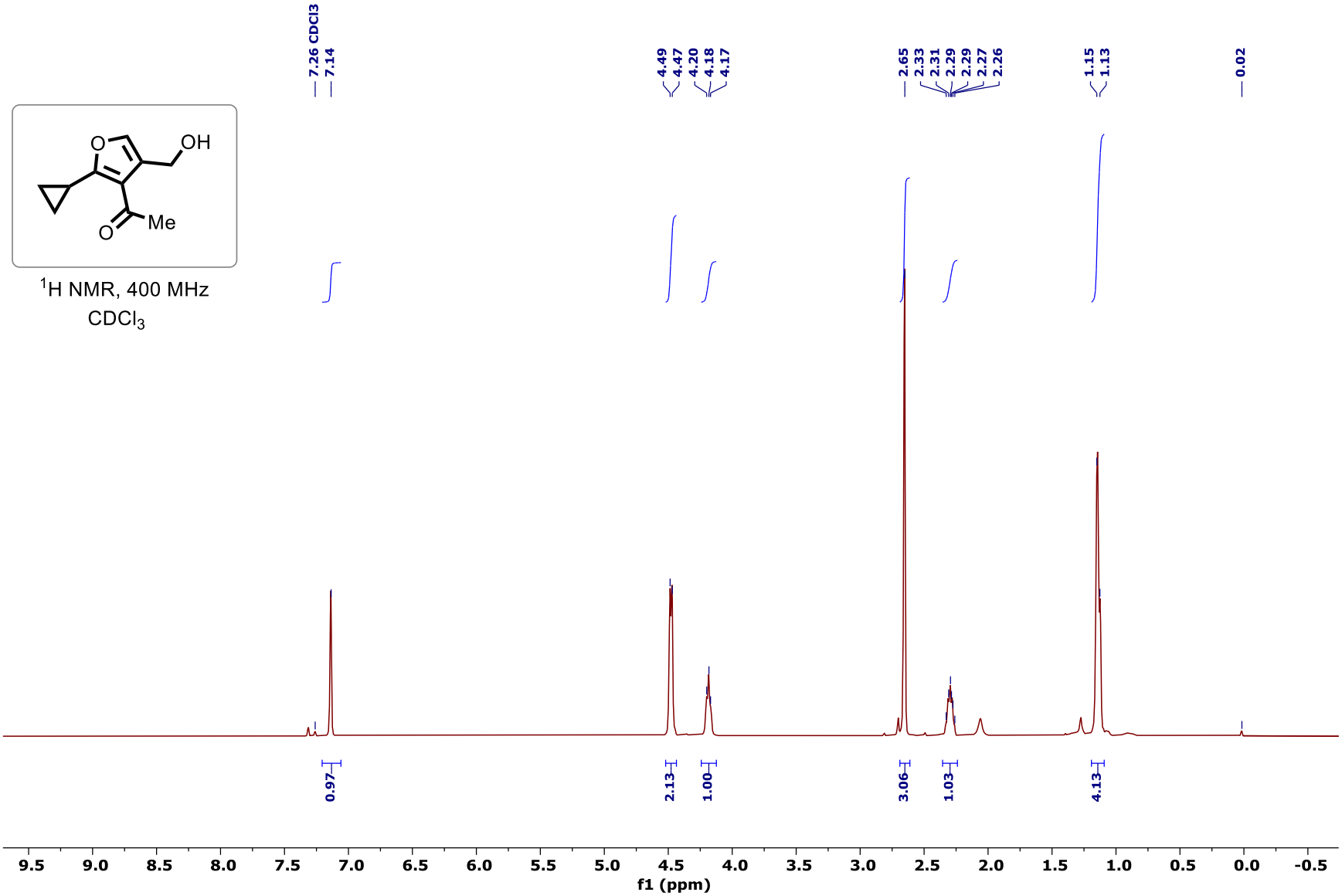
^{1}H NMR spectrum of 3-(Hydroxymethyl)-6-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5′g):



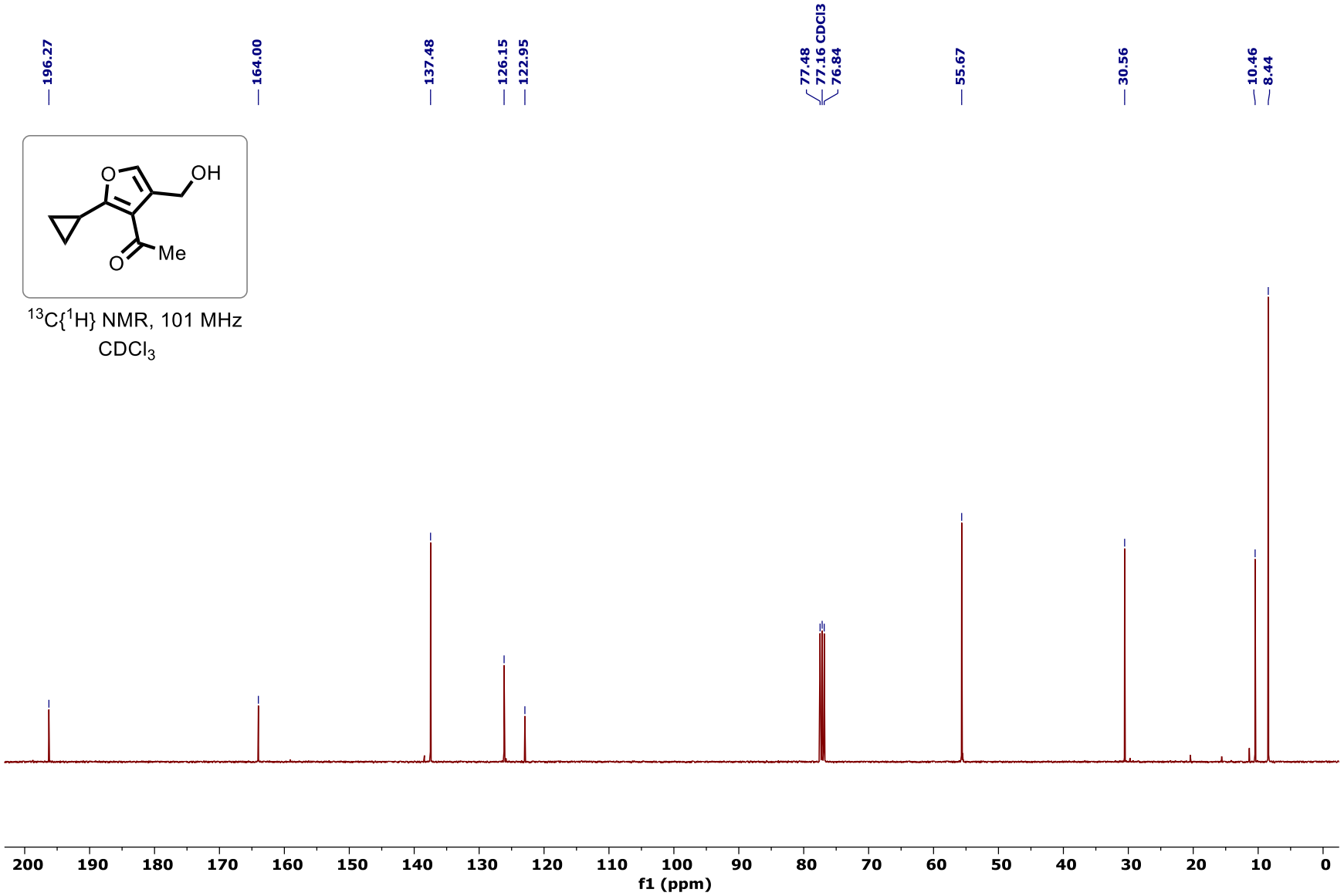
$^{13}C\{^{1}H\}$ NMR spectrum of 3-(Hydroxymethyl)-6-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5′g):



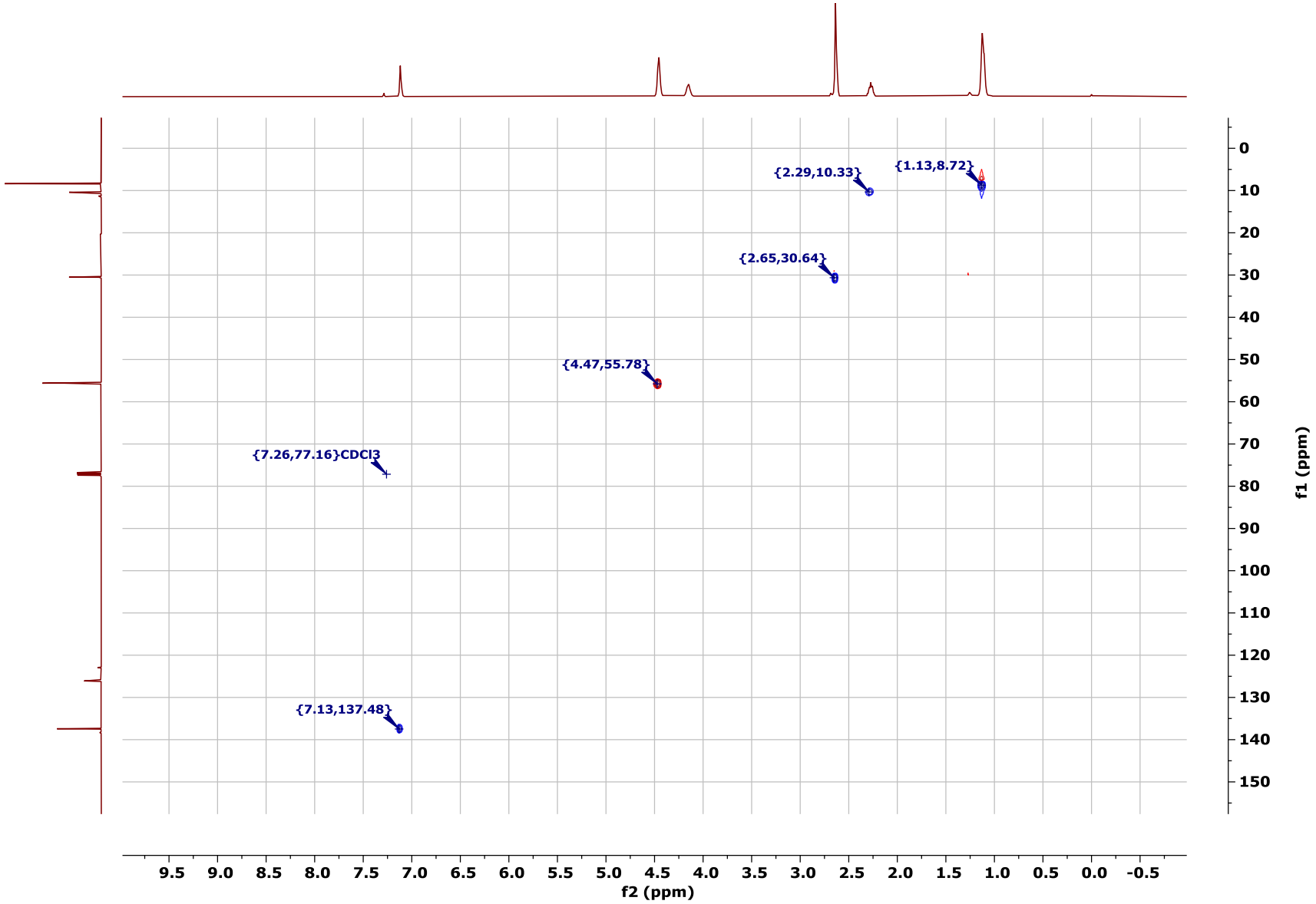
^{1}H NMR spectrum of 1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



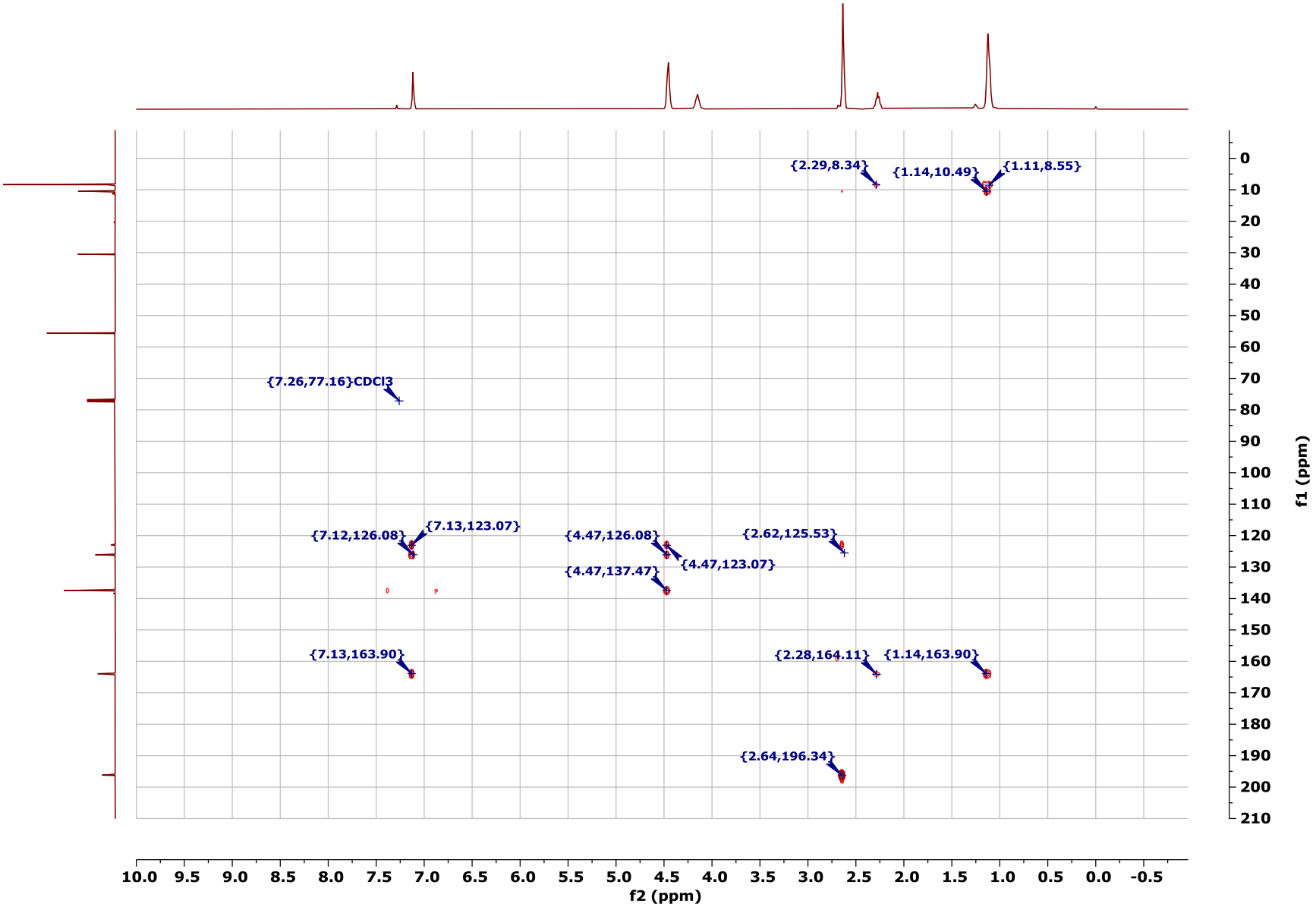
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



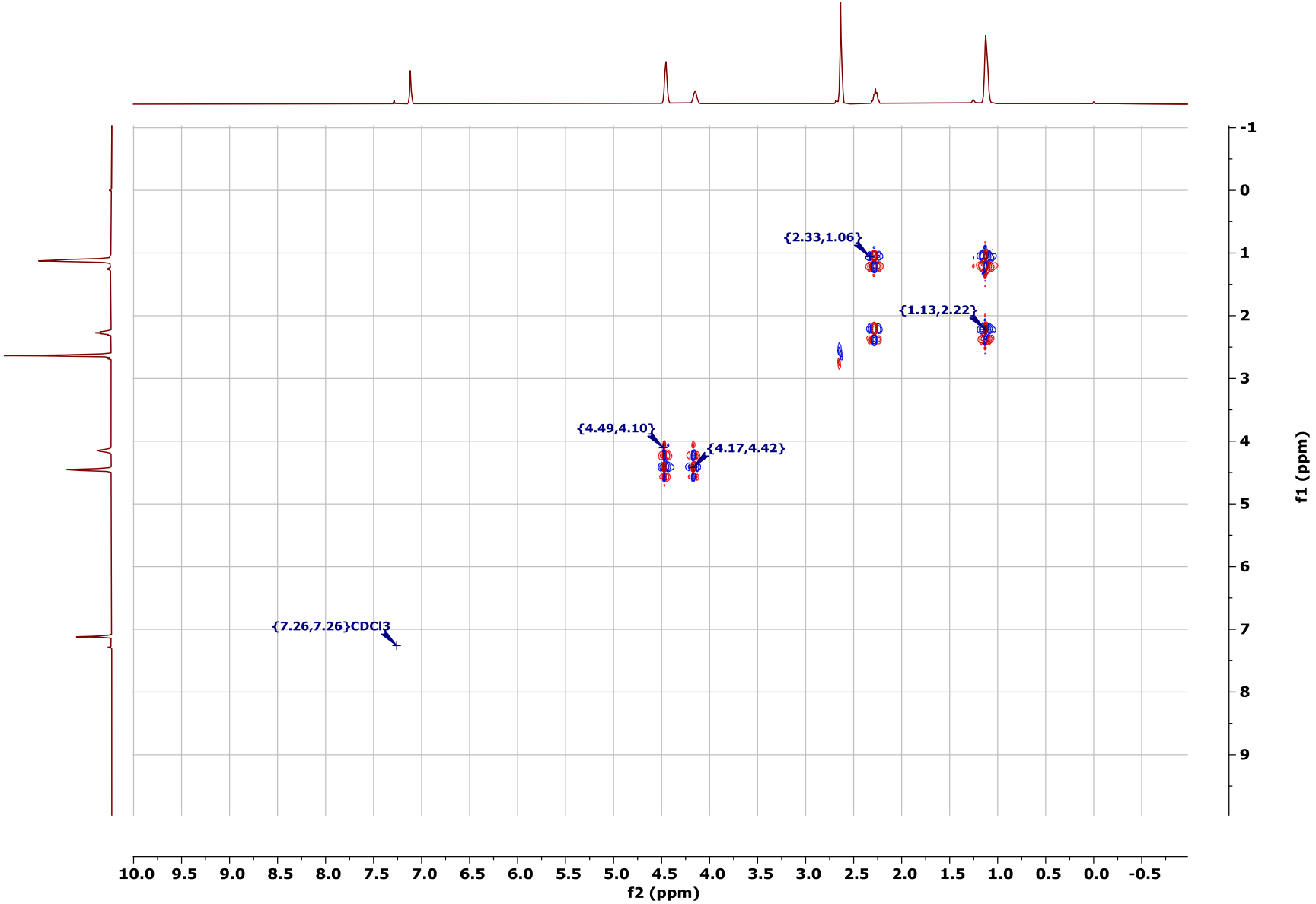
HSQC NMR spectrum of 1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



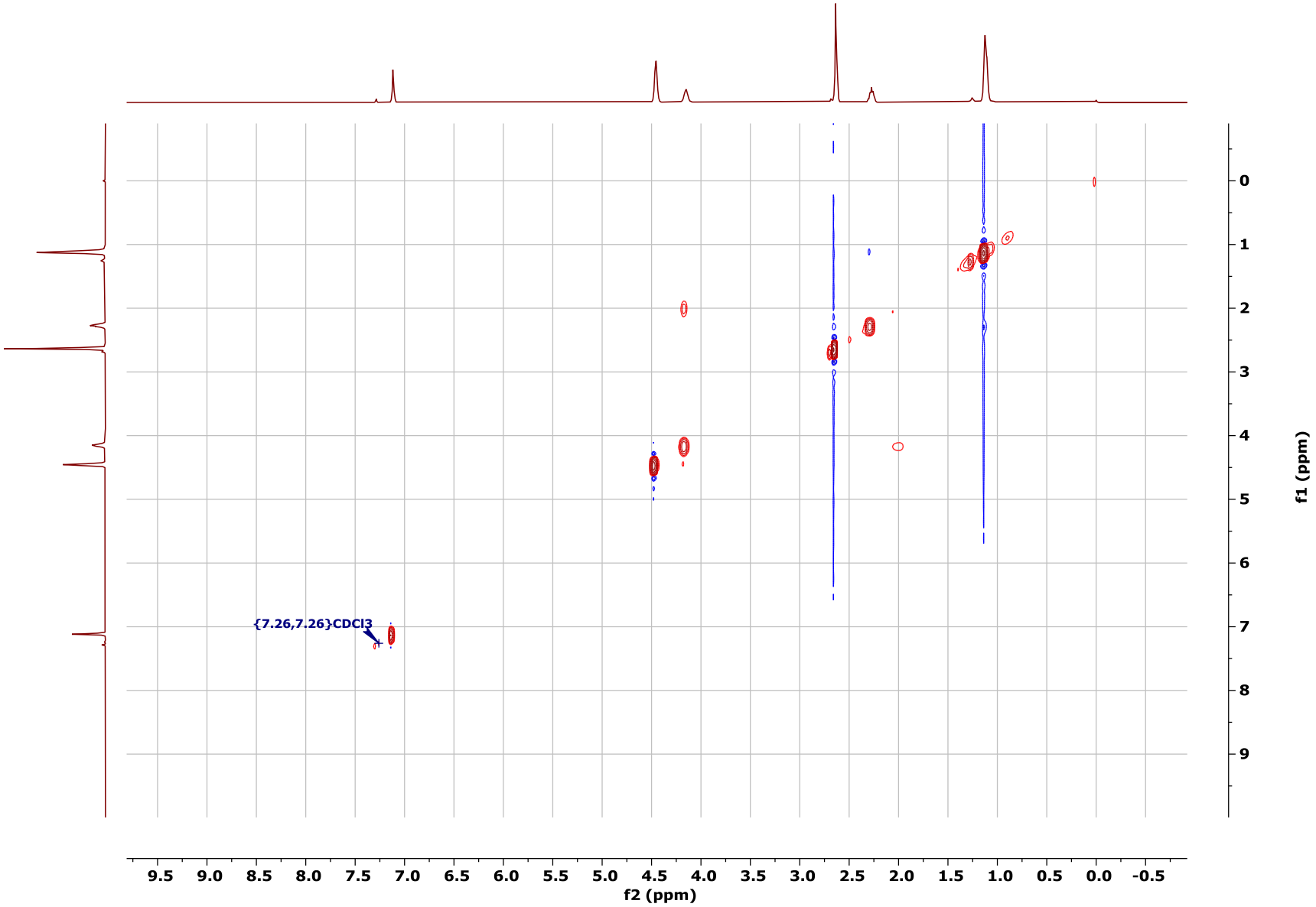
HMBC NMR spectrum of 1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



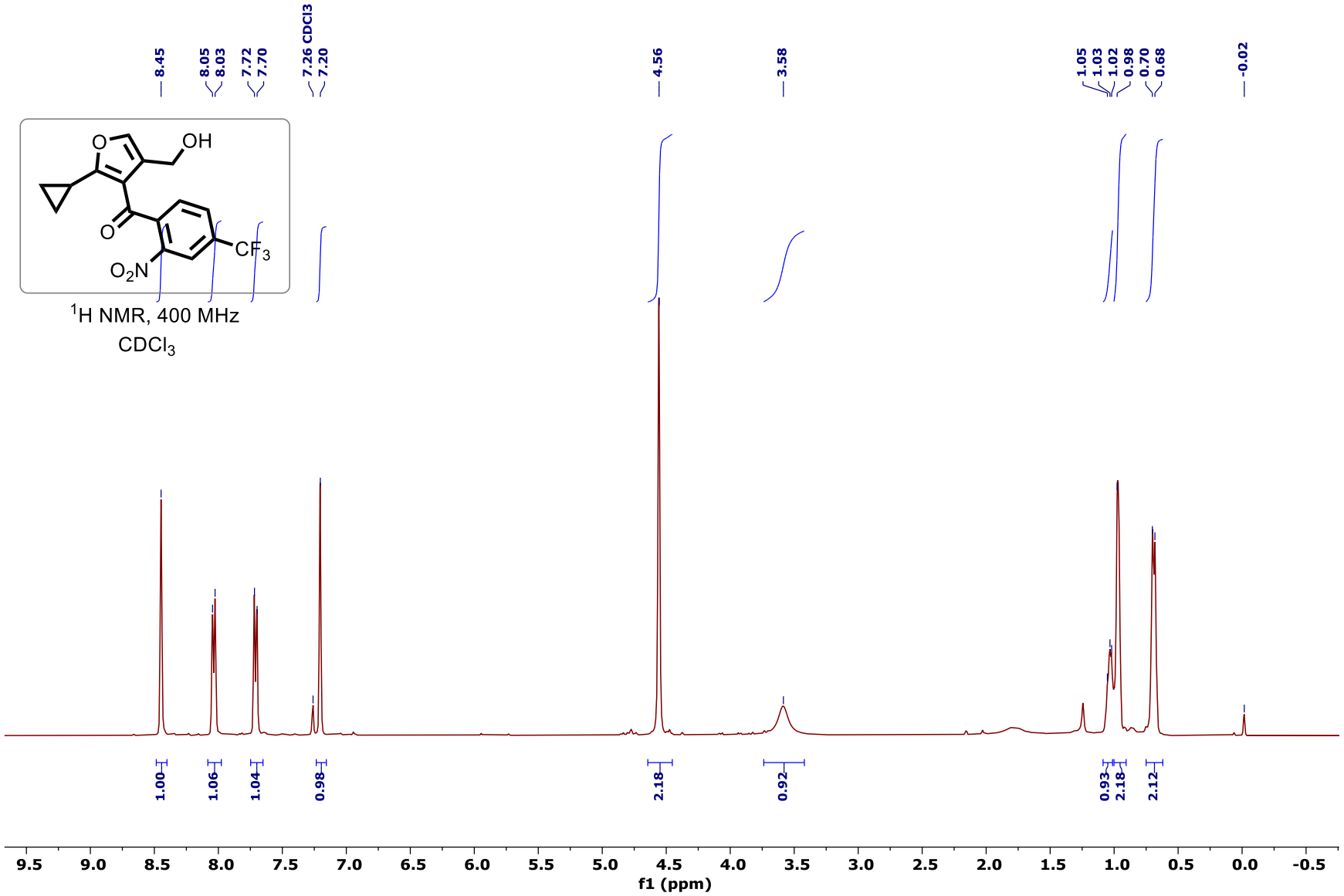
COSY NMR spectrum of 1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



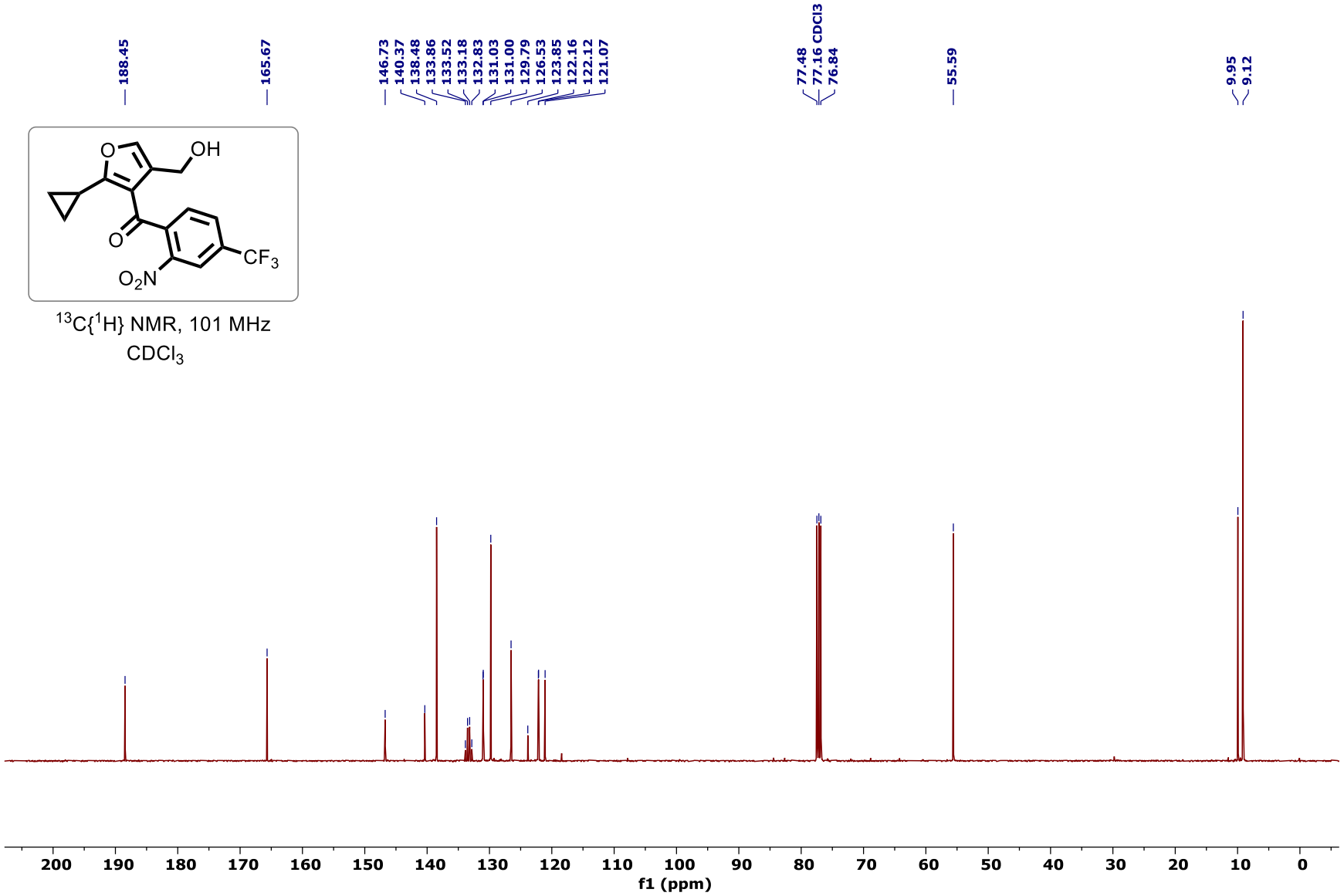
NOESY NMR spectrum of 1-(2-Cyclopropyl-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′h):



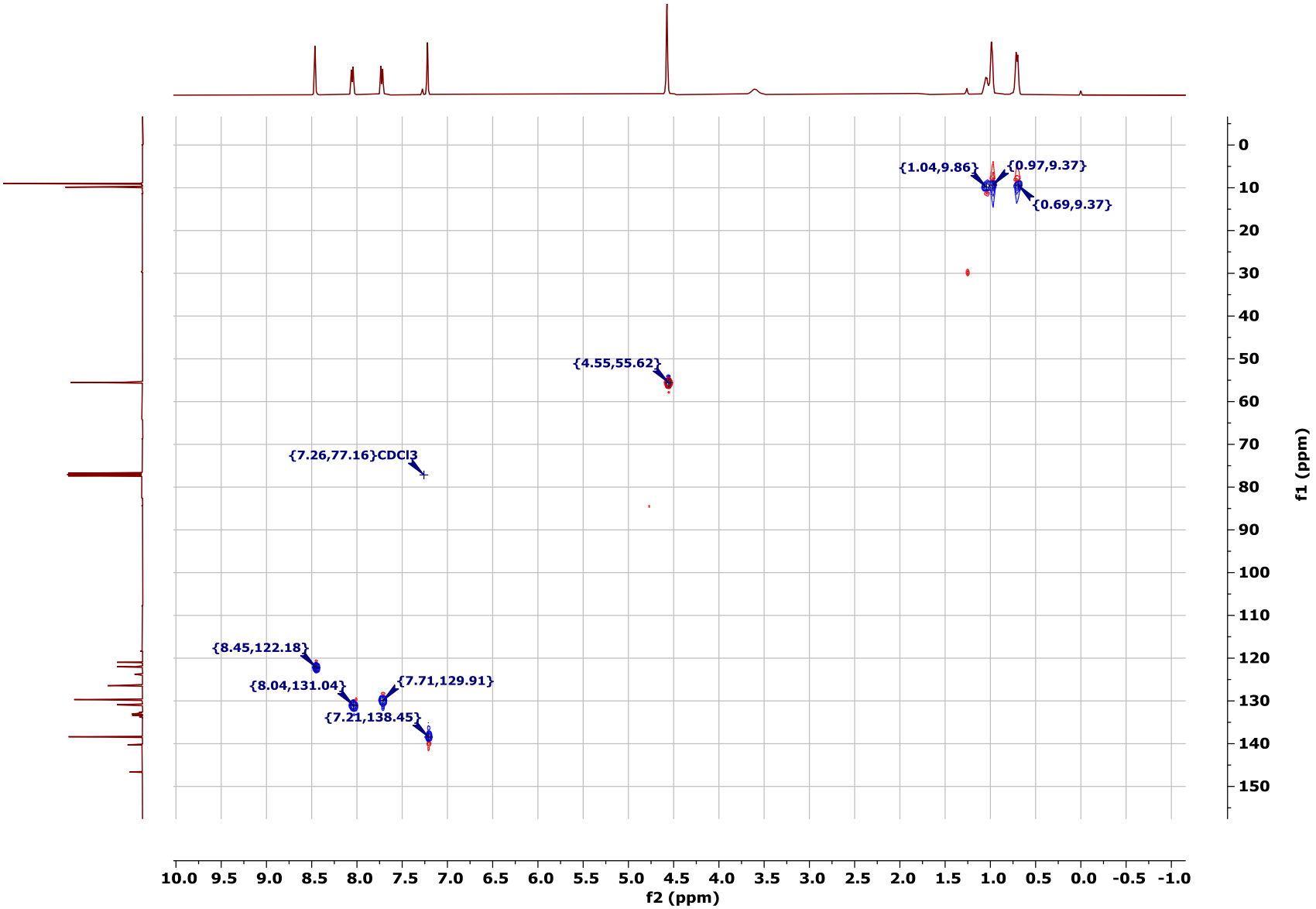
^{1}H NMR spectrum of (2-cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (5′i):



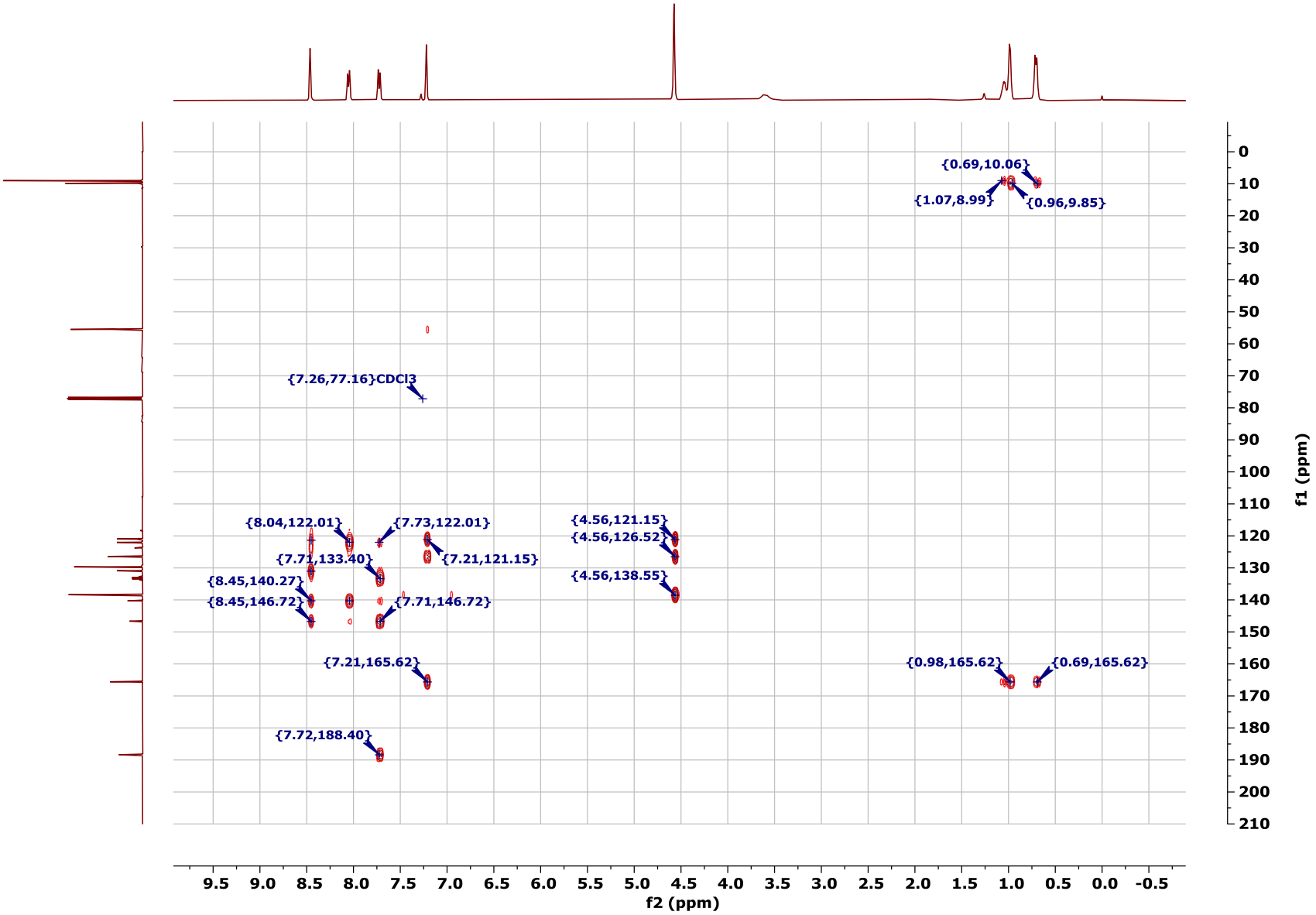
$^{13}C\{^{1}H\}$ NMR spectrum of (2-cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (5′i):



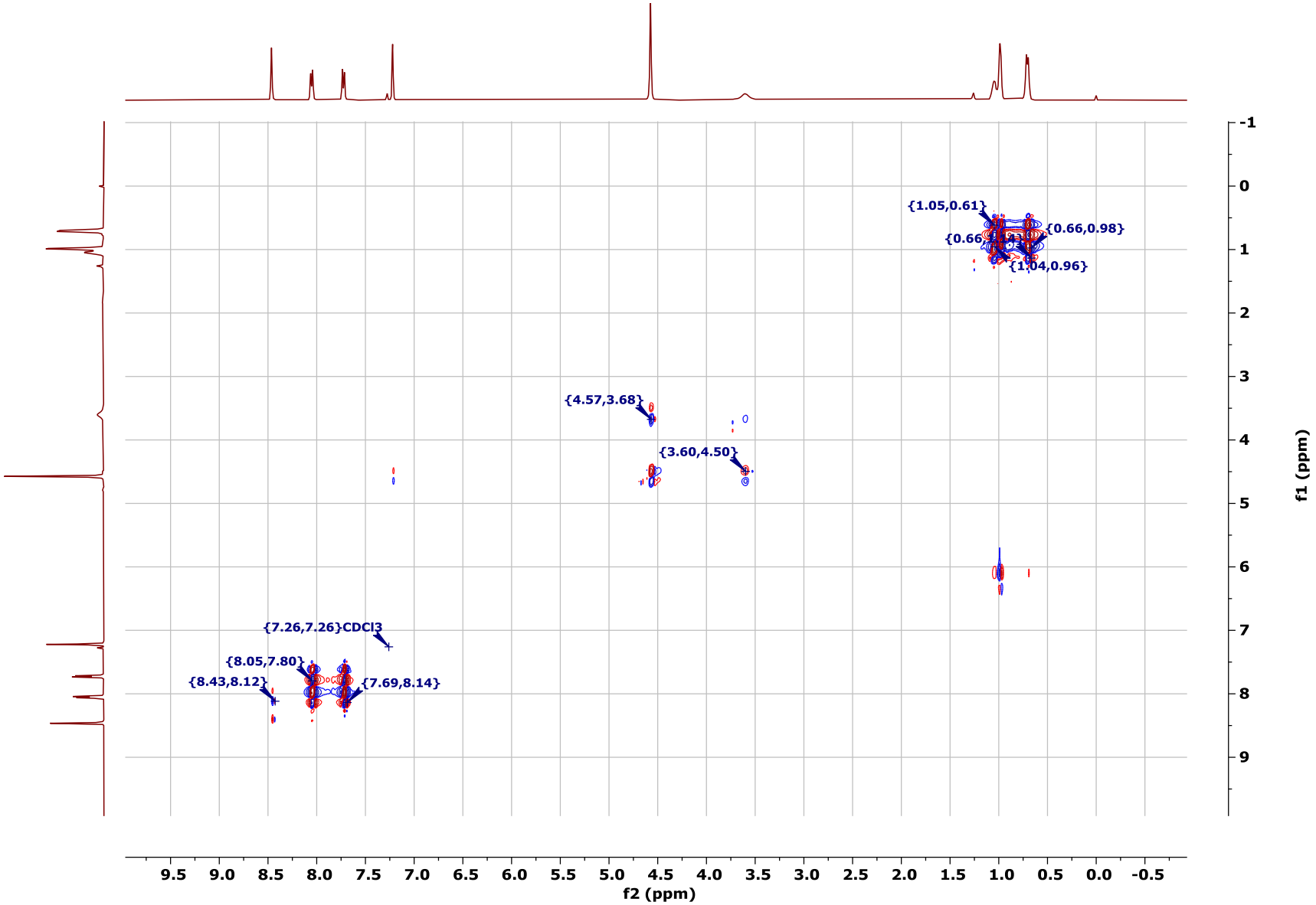
HSQC NMR spectrum of (2-cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (5′i):



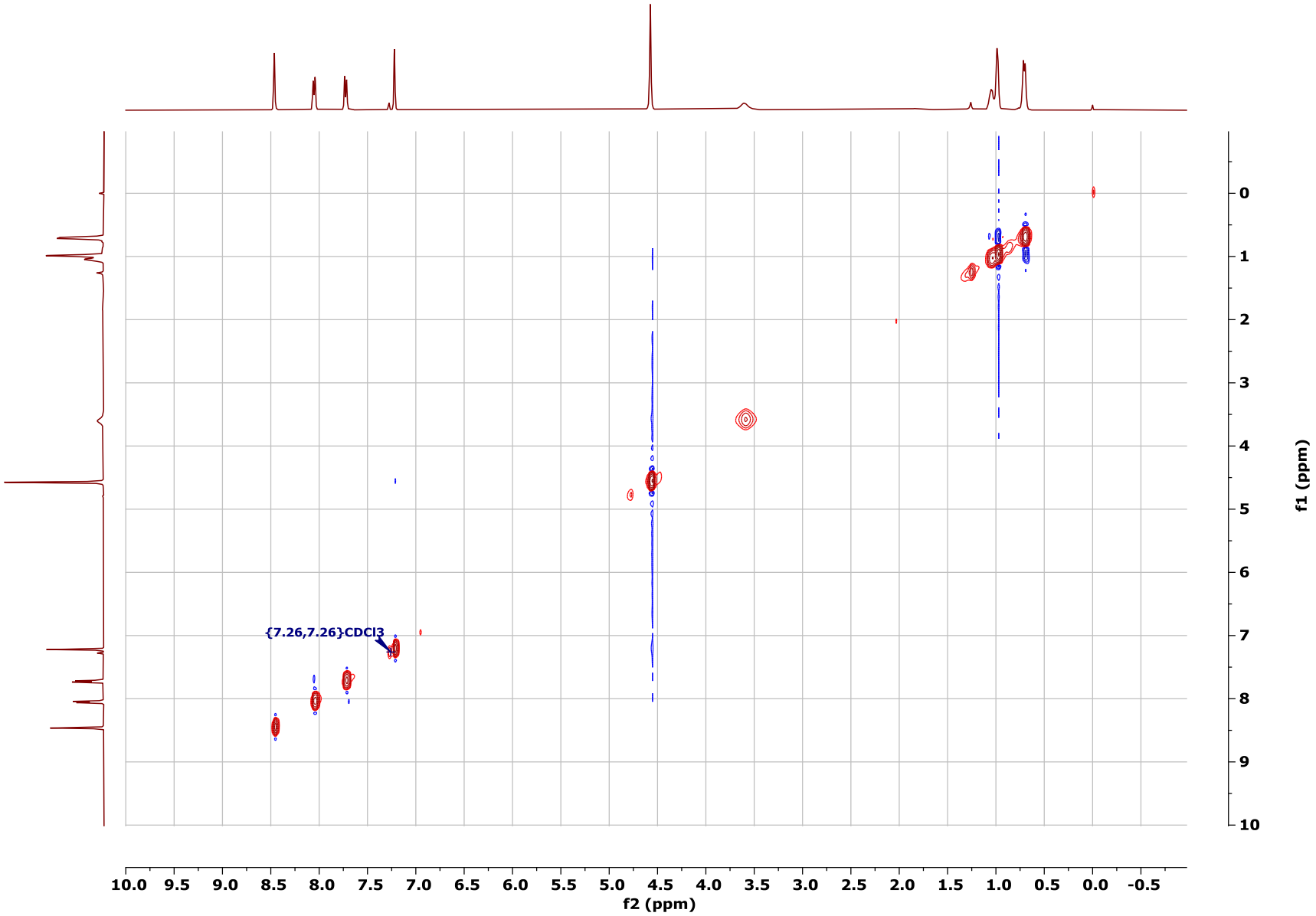
HMBC NMR spectrum of (2-cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (5′i):



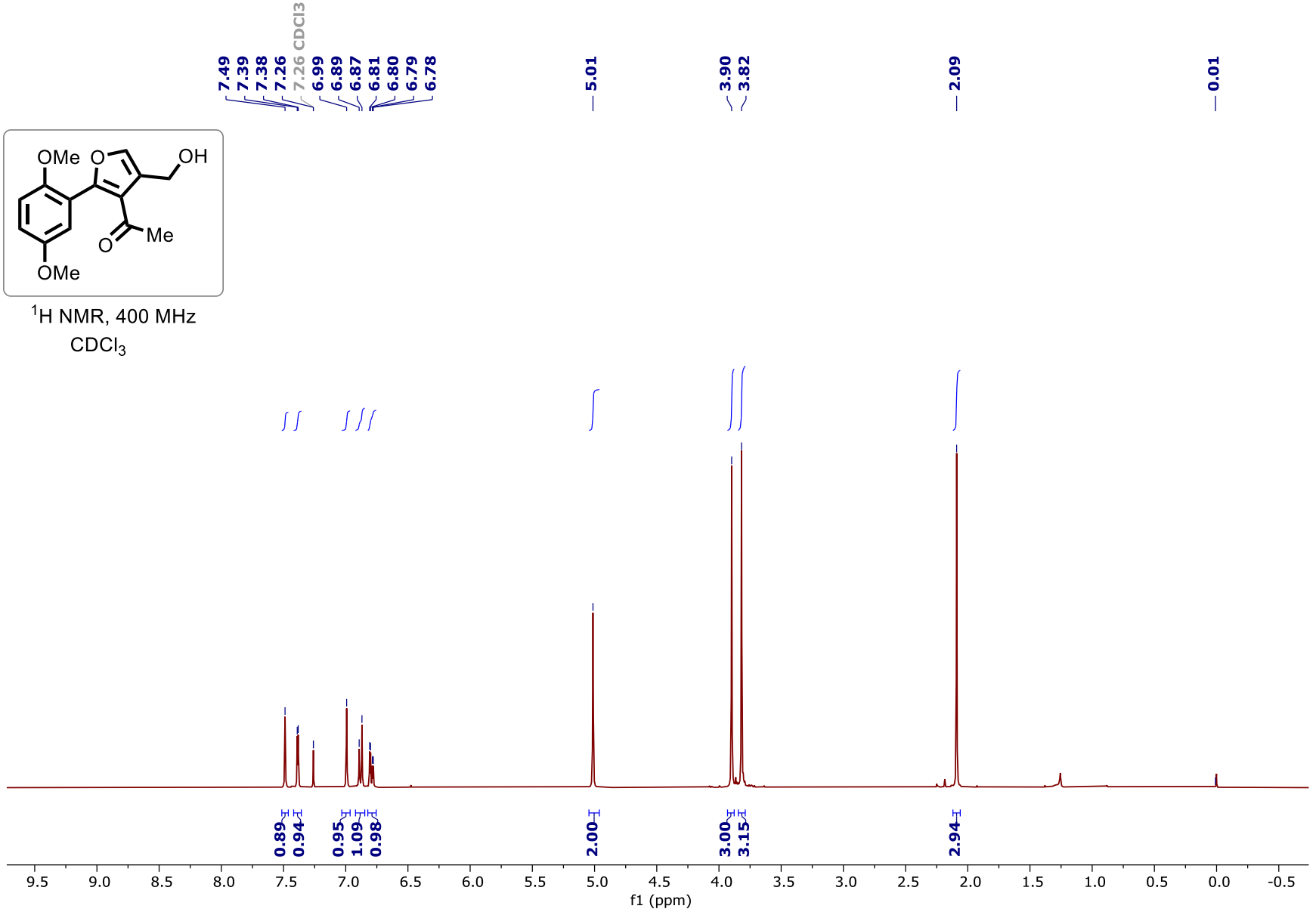
COSY NMR spectrum of (2-cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (5′i):



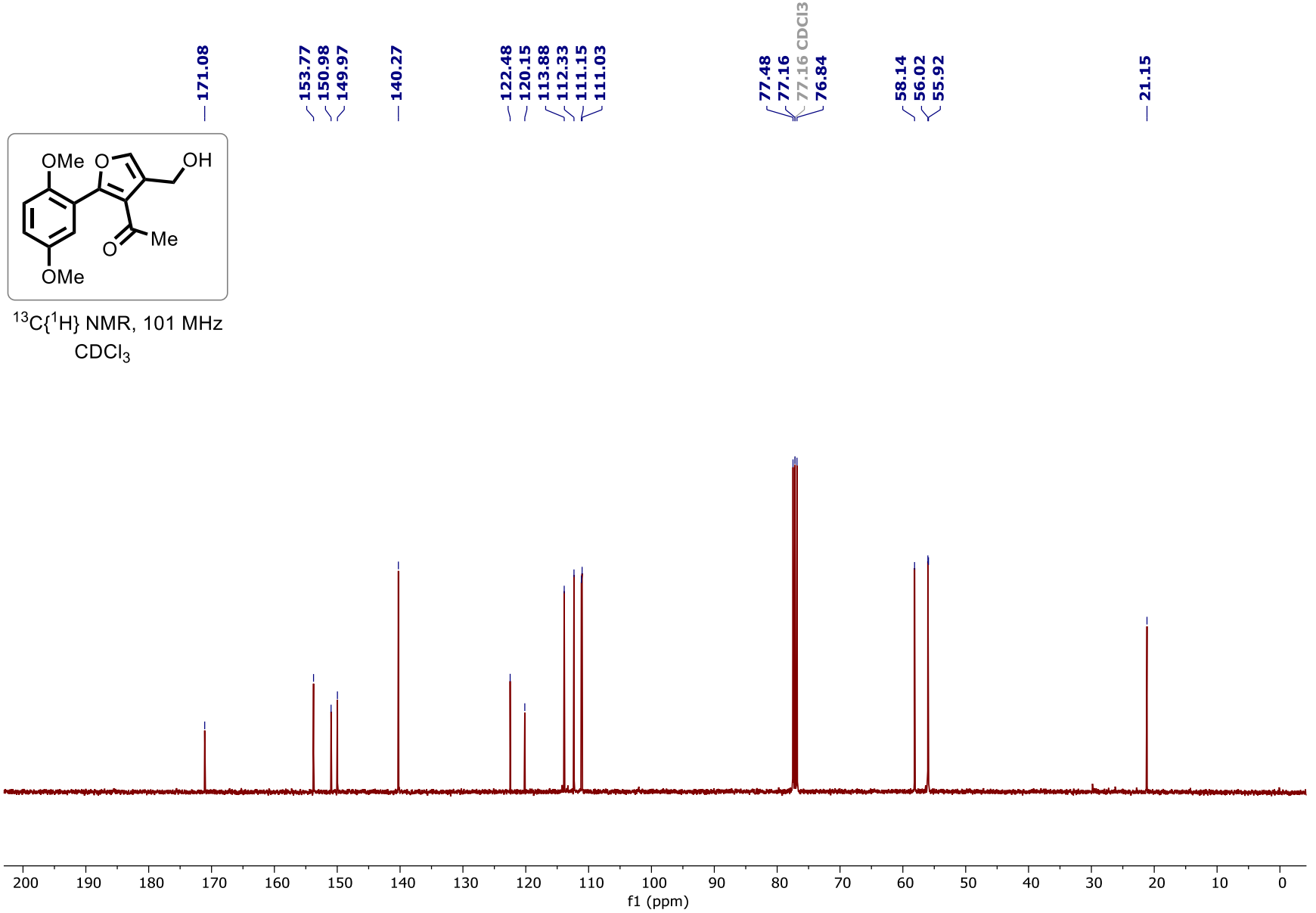
NOESY NMR spectrum of (2-cyclopropyl-4-(hydroxymethyl)furan-3-yl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (5′i):



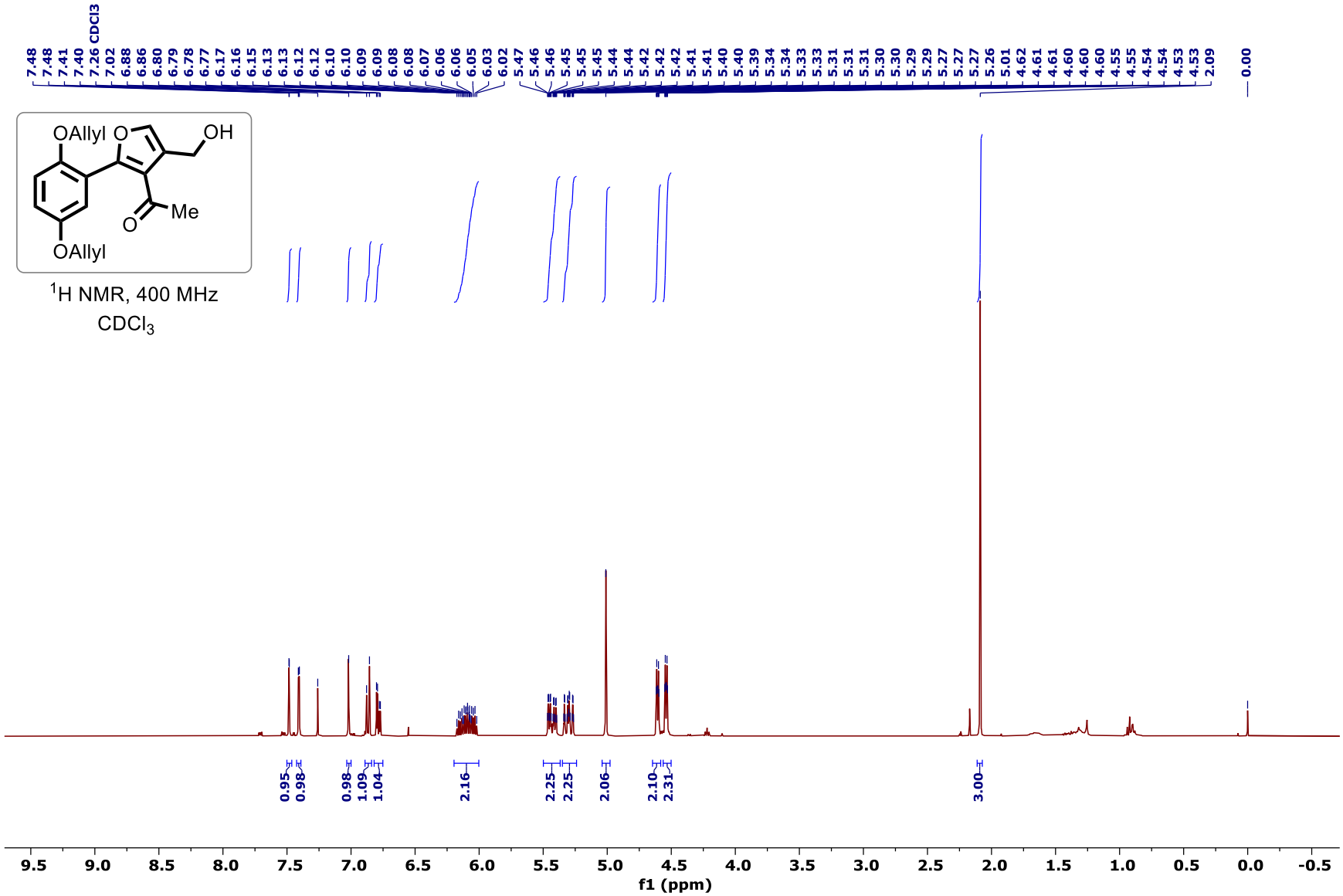
^{1}H NMR spectrum of 1-(2-(2,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′k):



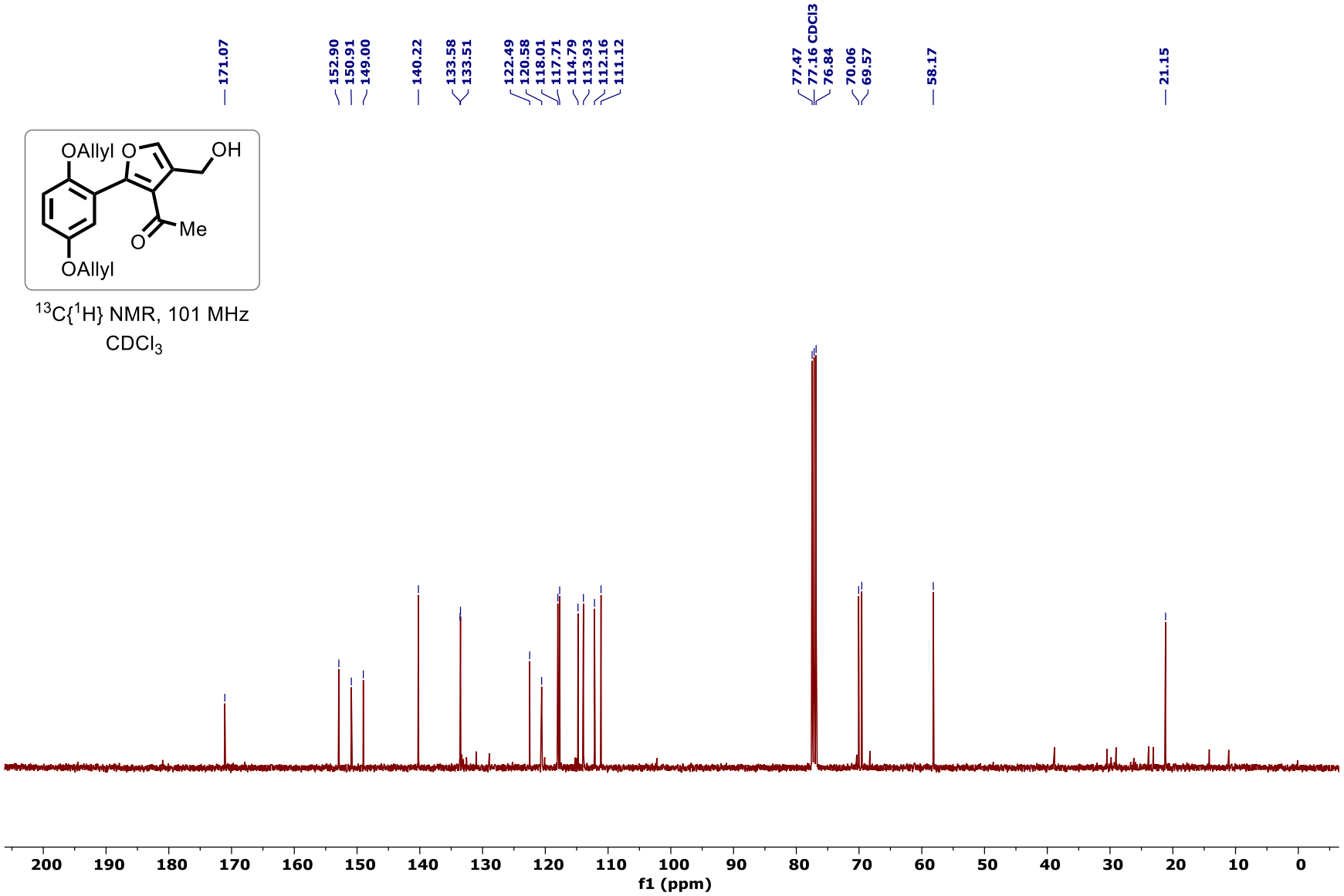
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(2-(2,5-dimethoxyphenyl)-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′k):



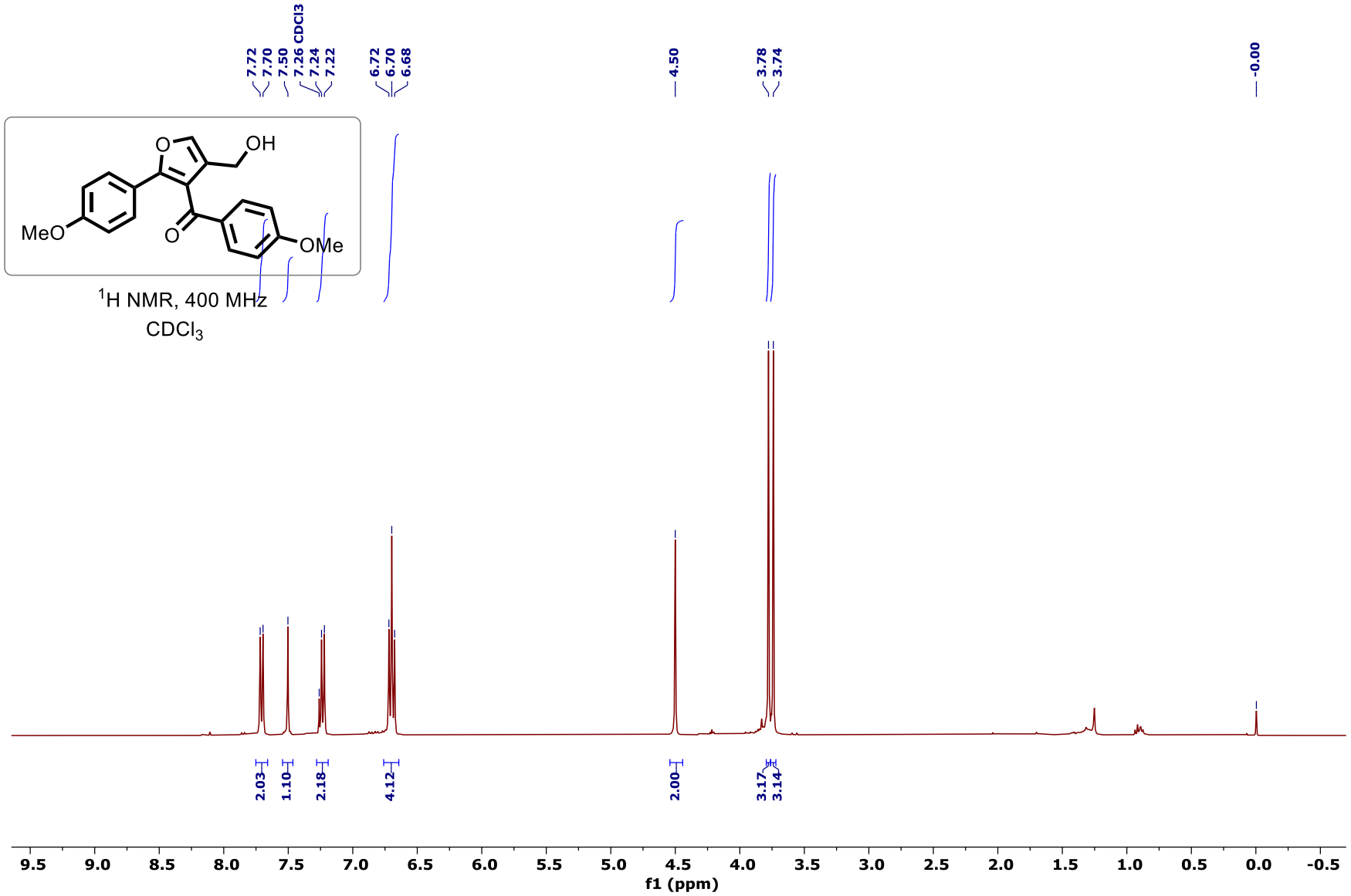
^{1}H NMR spectrum of 1-(2-(2,5-Bis(allyloxy)phenyl)-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′l):



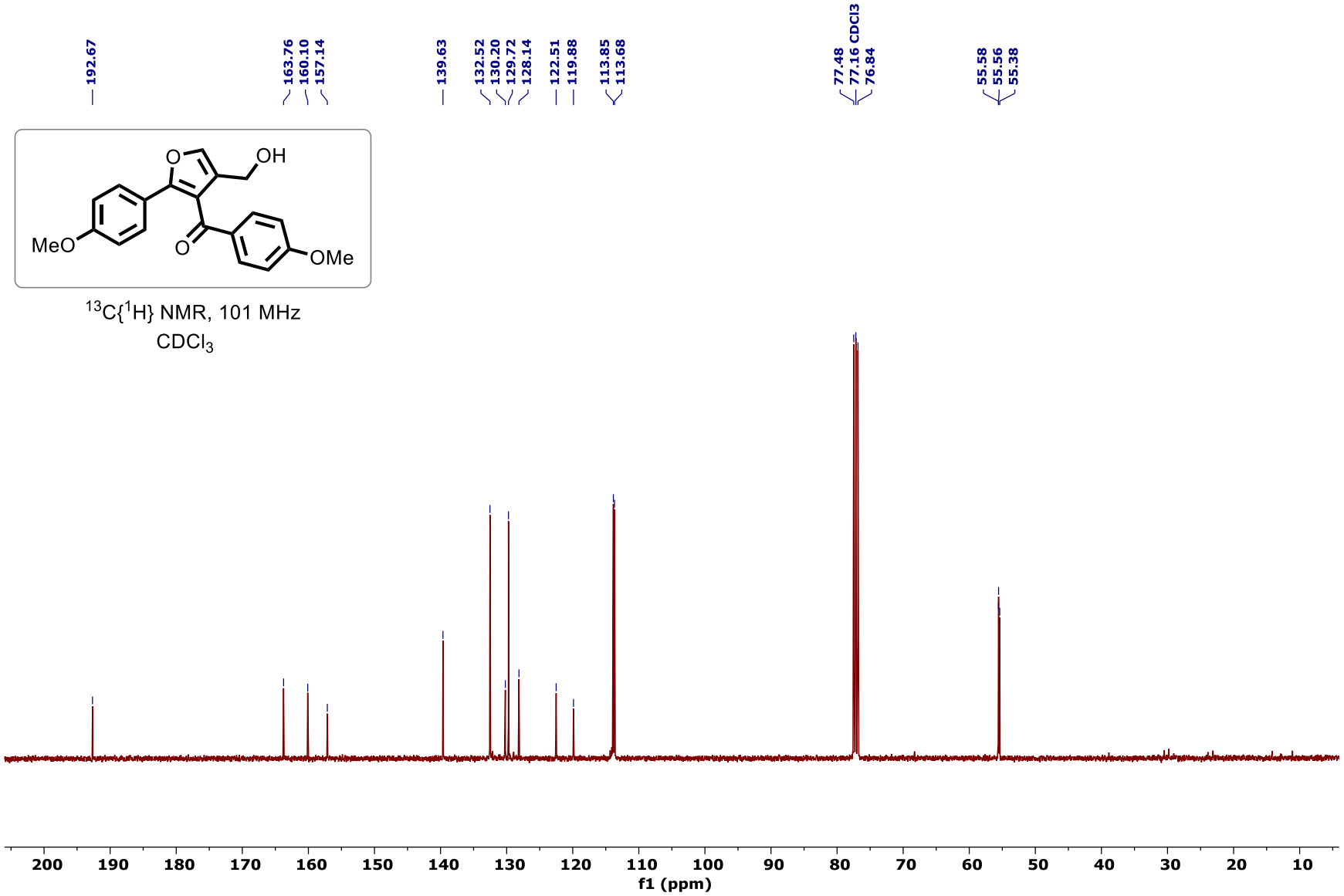
$^{13}C\{^{1}H\}$ NMR spectrum of 1-(2-(2,5-Bis(allyloxy)phenyl)-4-(hydroxymethyl)furan-3-yl)ethan-1-one (5′l):



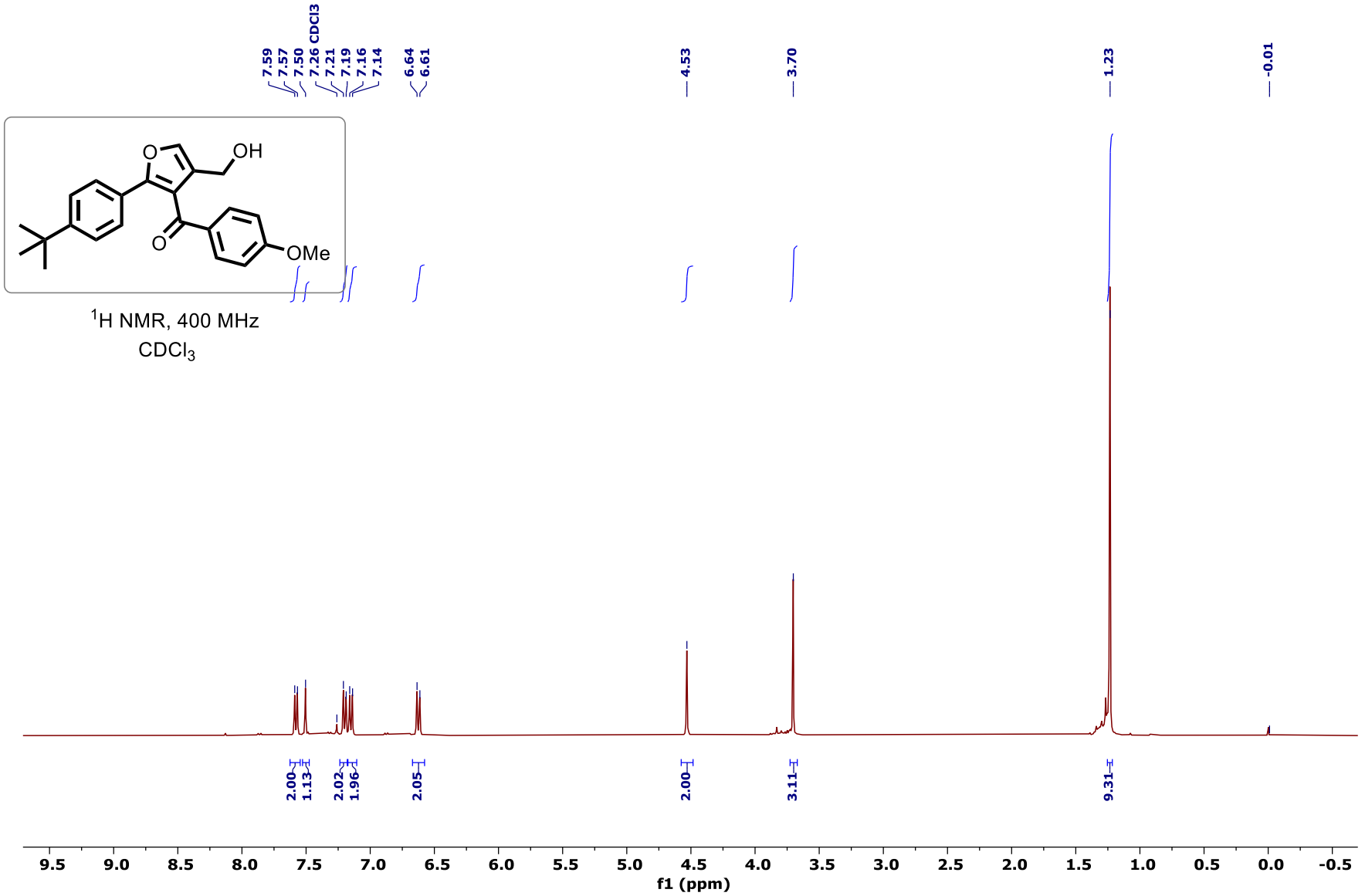
^{1}H NMR spectrum of (4-(hydroxymethyl)-2-(4-methoxyphenyl)furan-3-yl)(4-methoxyphenyl)methanone (5′m):



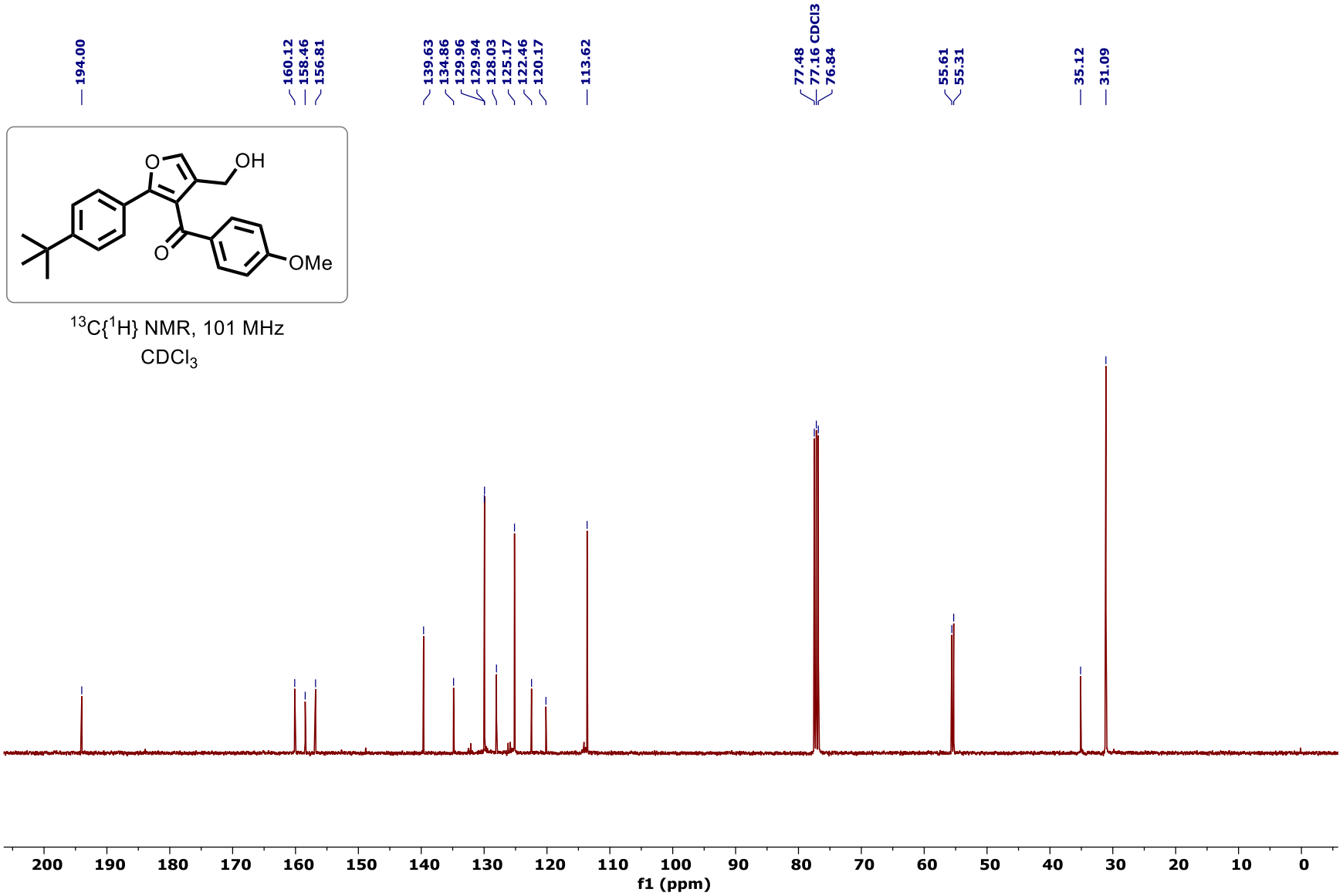
$^{13}C\{^{1}H\}$ NMR spectrum of (4-(Hydroxymethyl)-2-(4-methoxyphenyl)furan-3-yl)(4-methoxyphenyl)methanone (5′m):



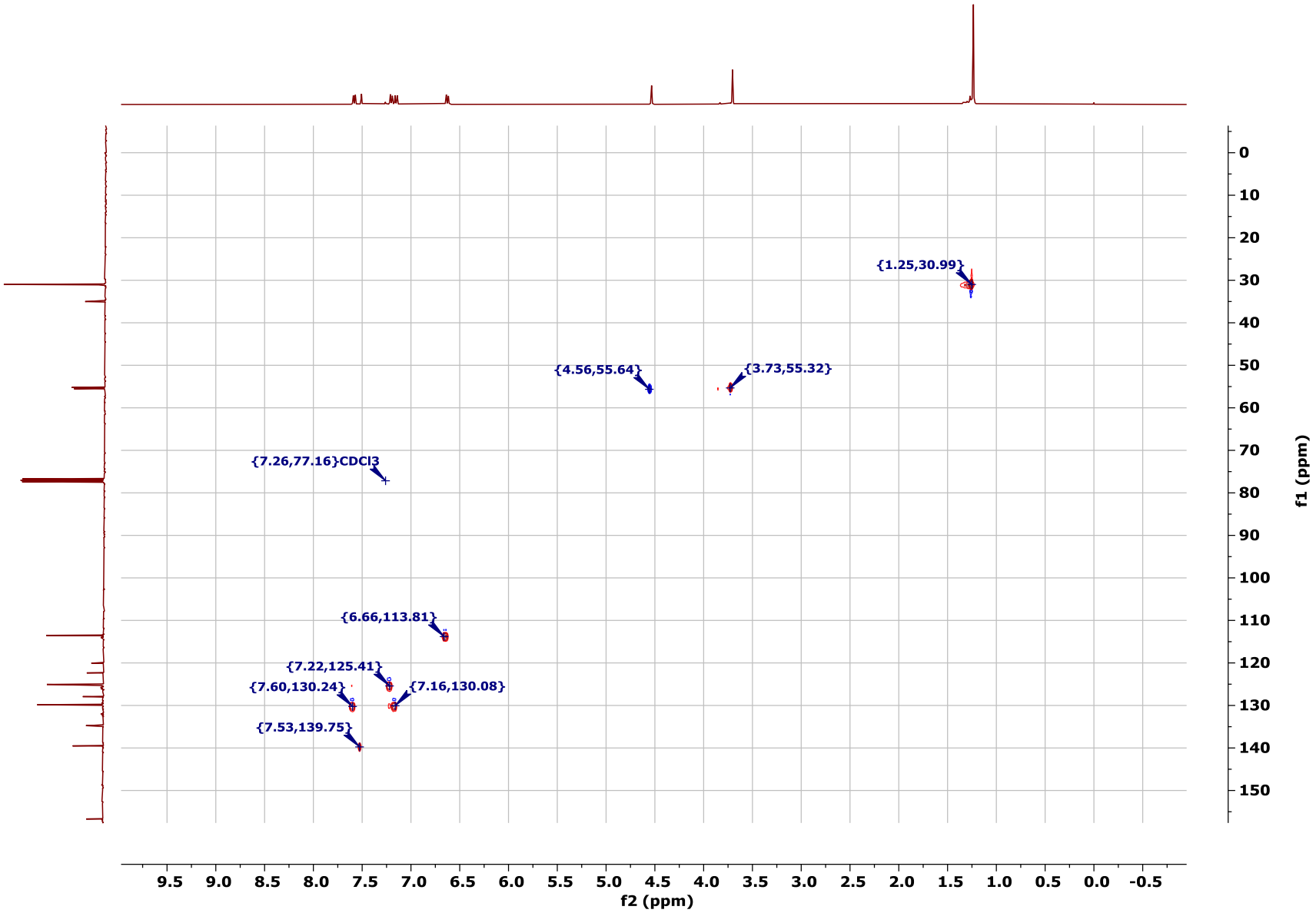
^{1}H NMR spectrum of (2-(4-(tert-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



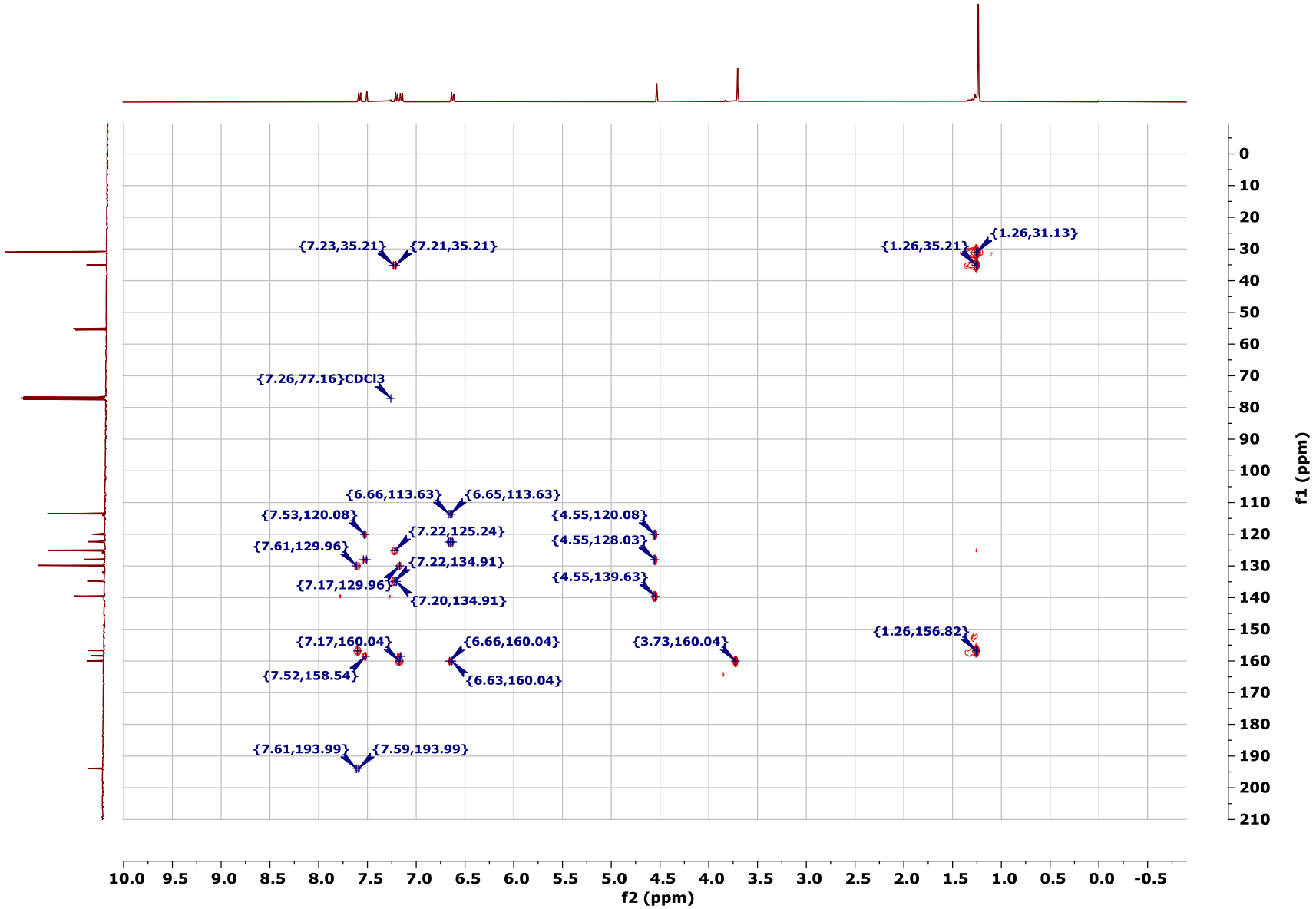
$^{13}C\{^{1}H\}$ NMR spectrum of (2-(4-(tert-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



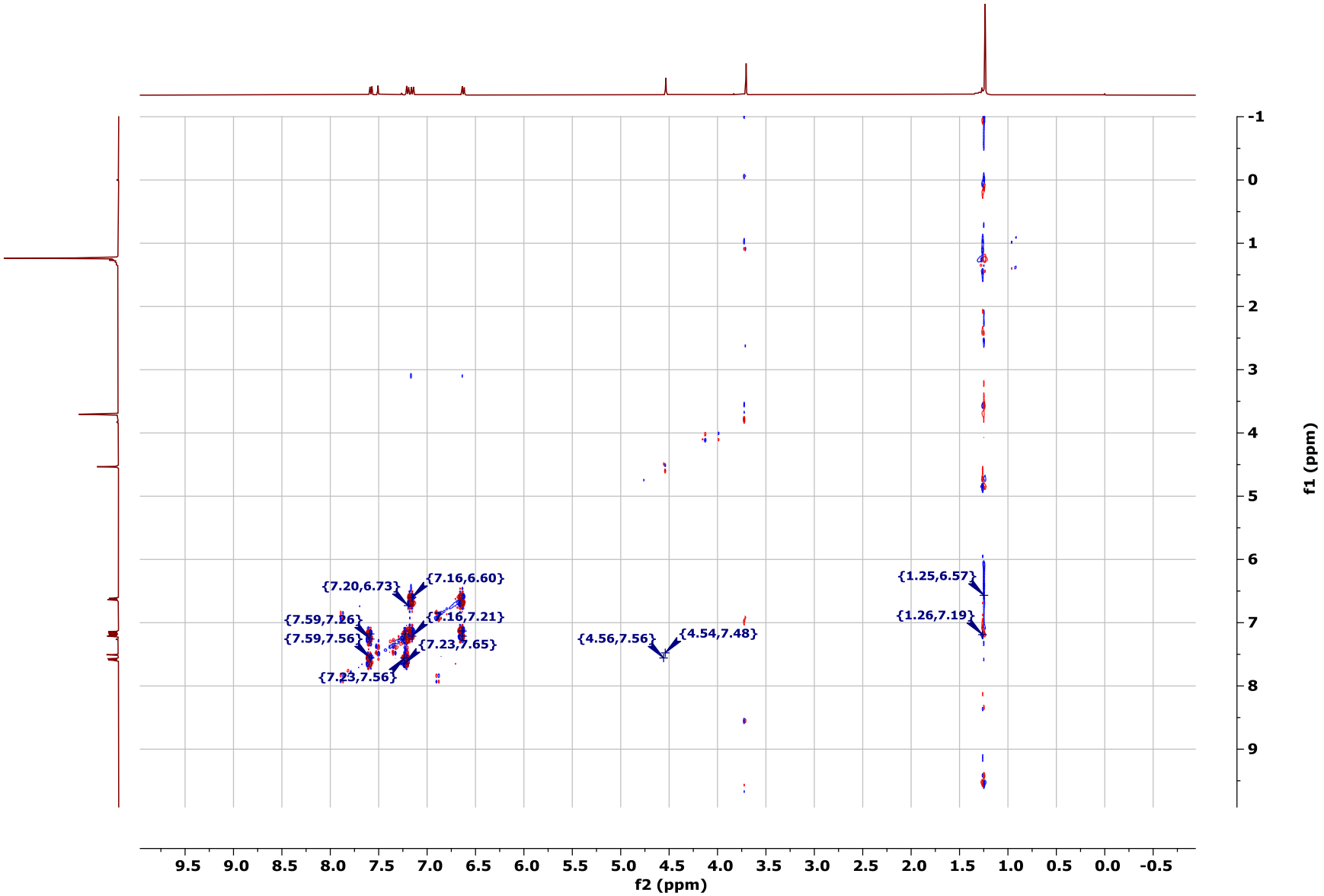
HSQC NMR spectrum of (2-(4-(tert-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



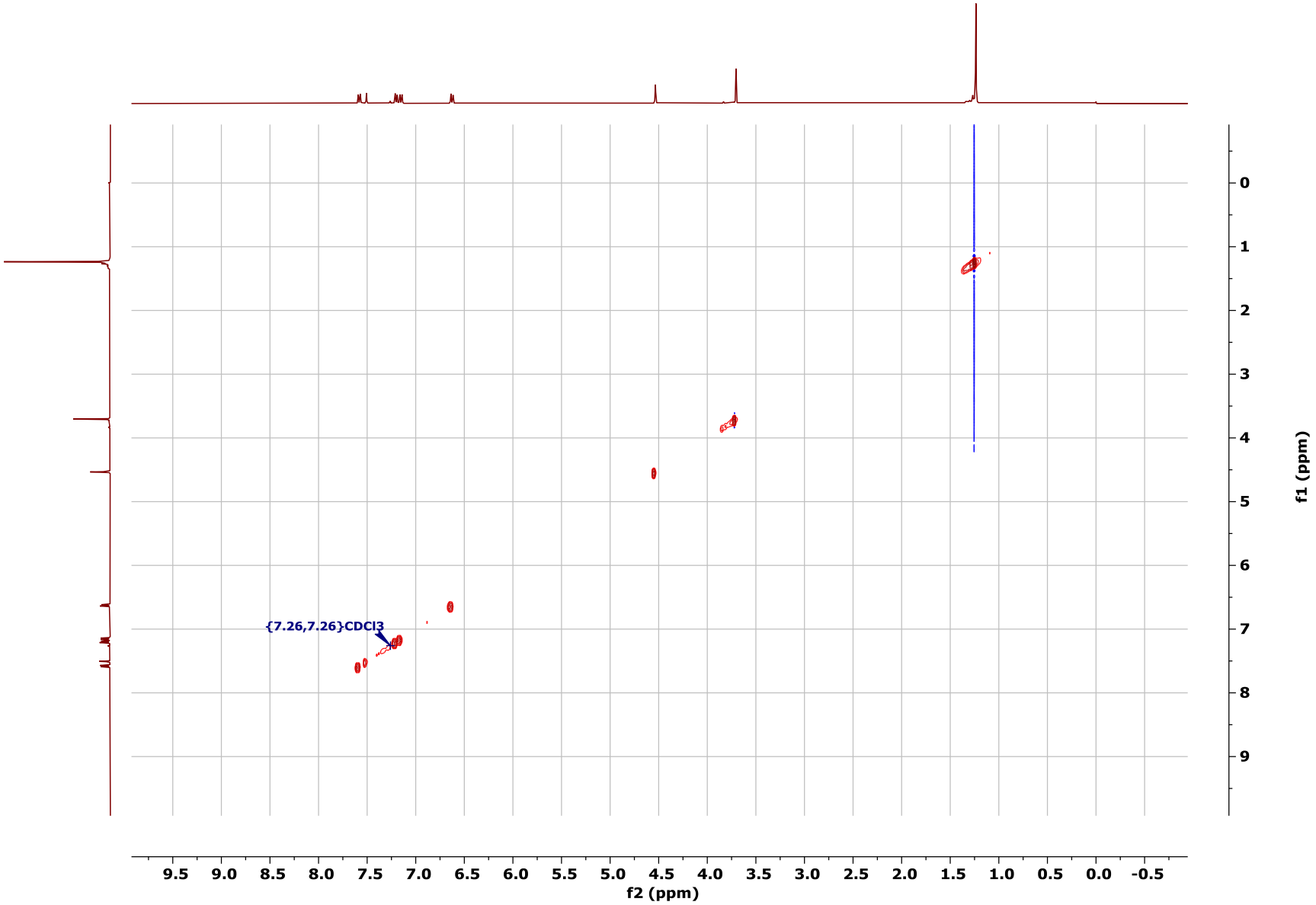
HMBC NMR spectrum of (2-(4-(tert-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



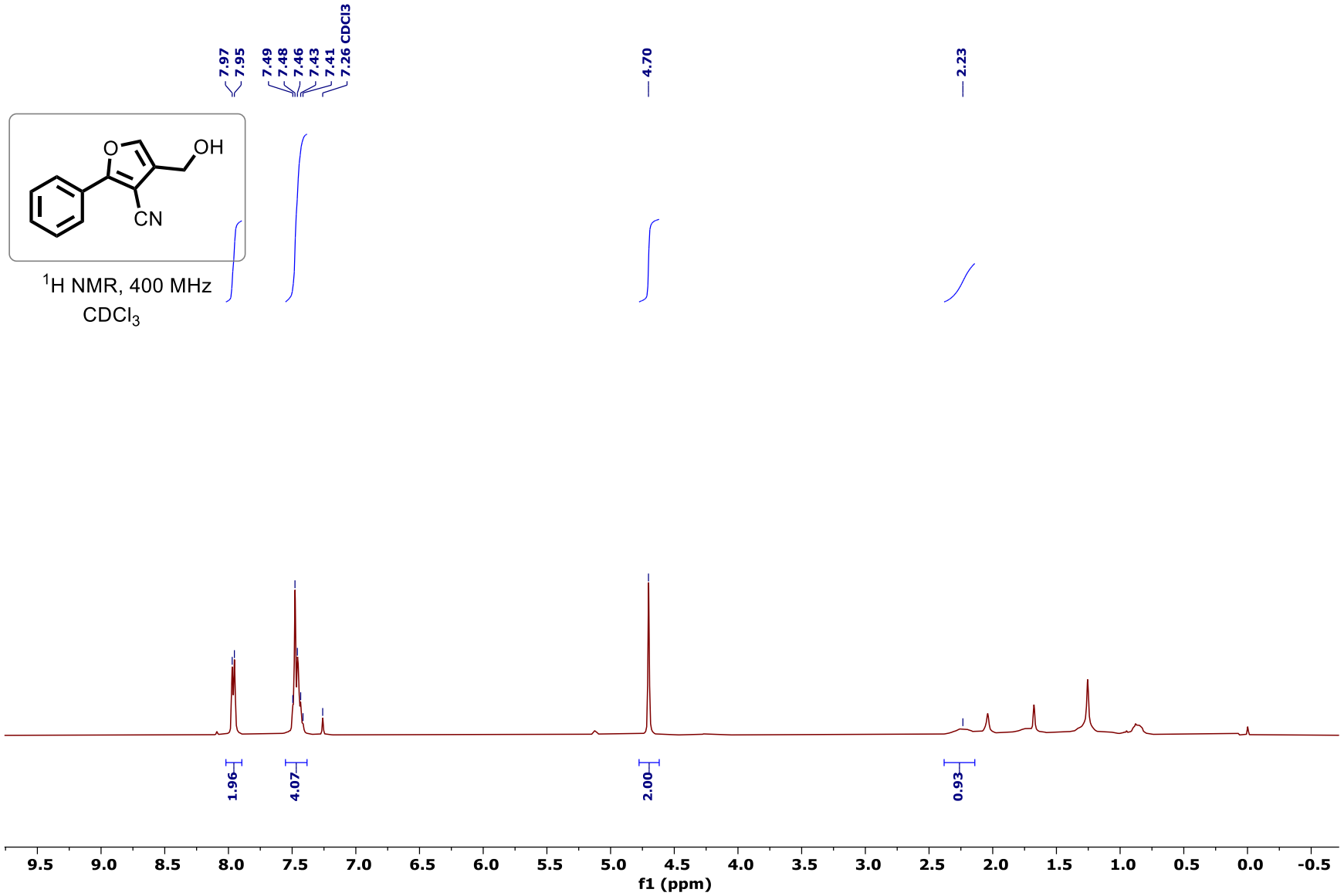
COSY NMR spectrum of (2-(4-(tert-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



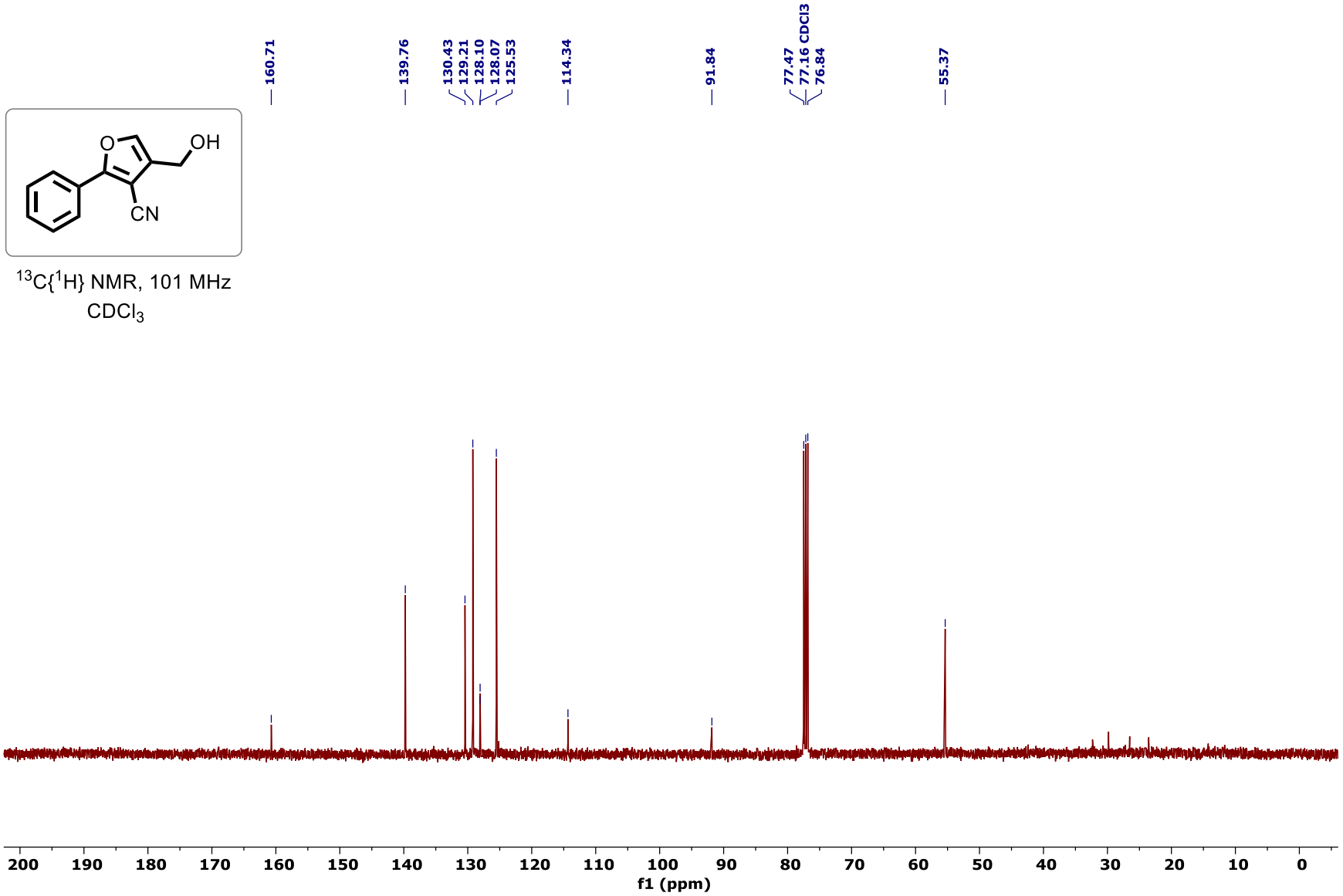
NOESY NMR spectrum of (2-(4-(tert-butyl)phenyl)-4-(hydroxymethyl)furan-3-yl)(4-methoxyphenyl)methanone (5′n):



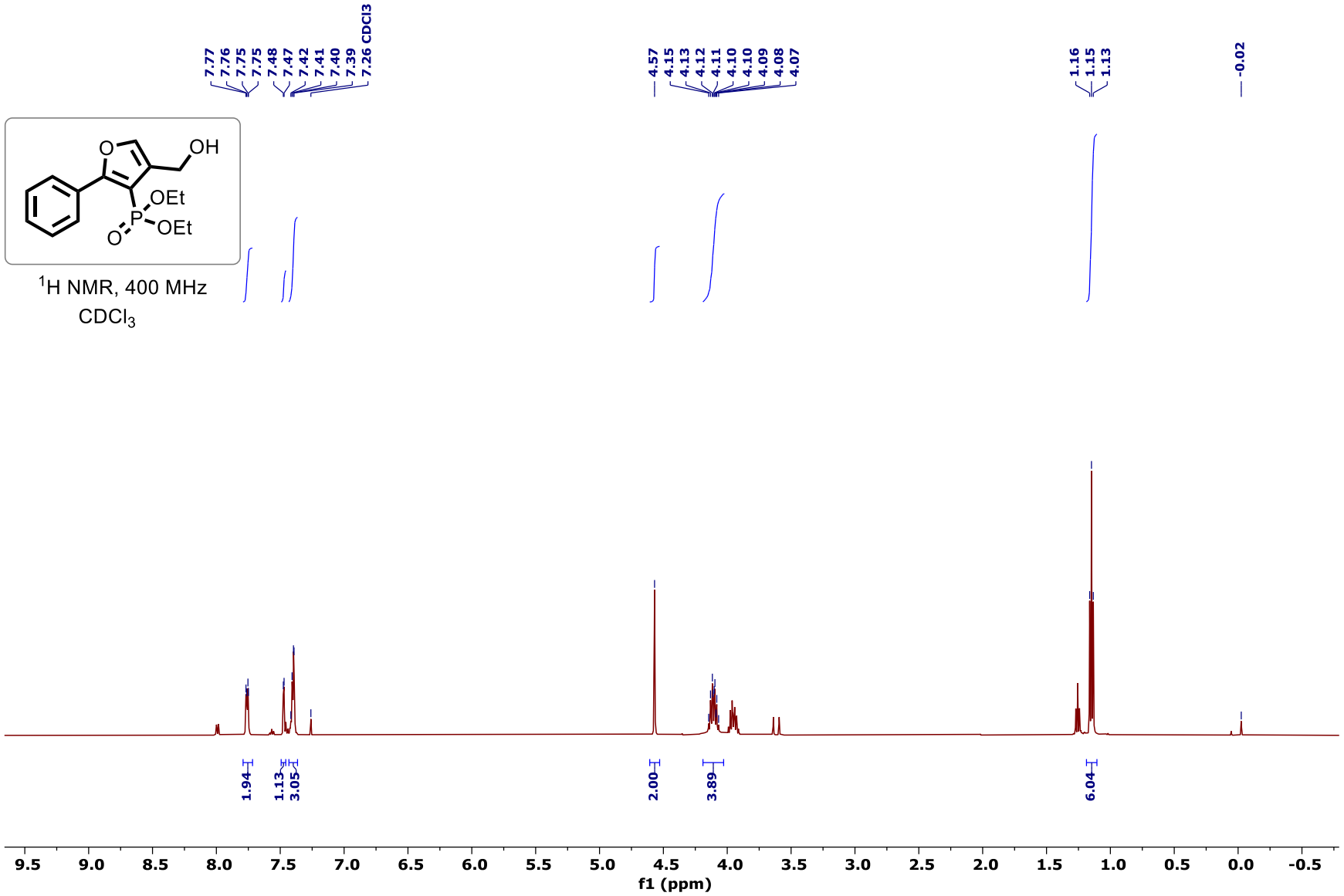
^{1}H NMR spectrum of 4-(Hydroxymethyl)-2-phenylfuran-3-carbonitrile (7):



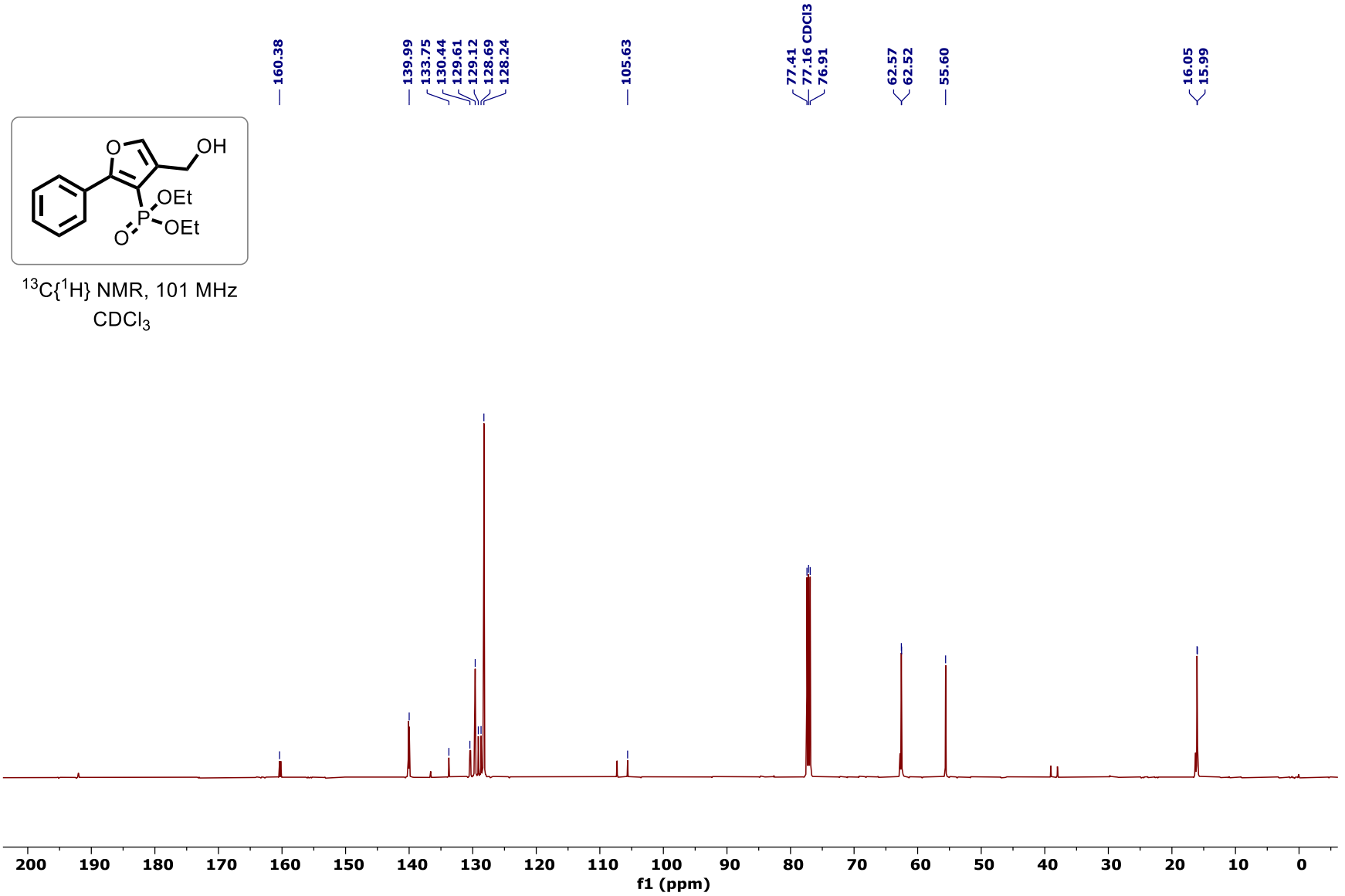
$^{13}C\{^{1}H\}$ NMR spectrum of 4-(Hydroxymethyl)-2-phenylfuran-3-carbonitrile (7):



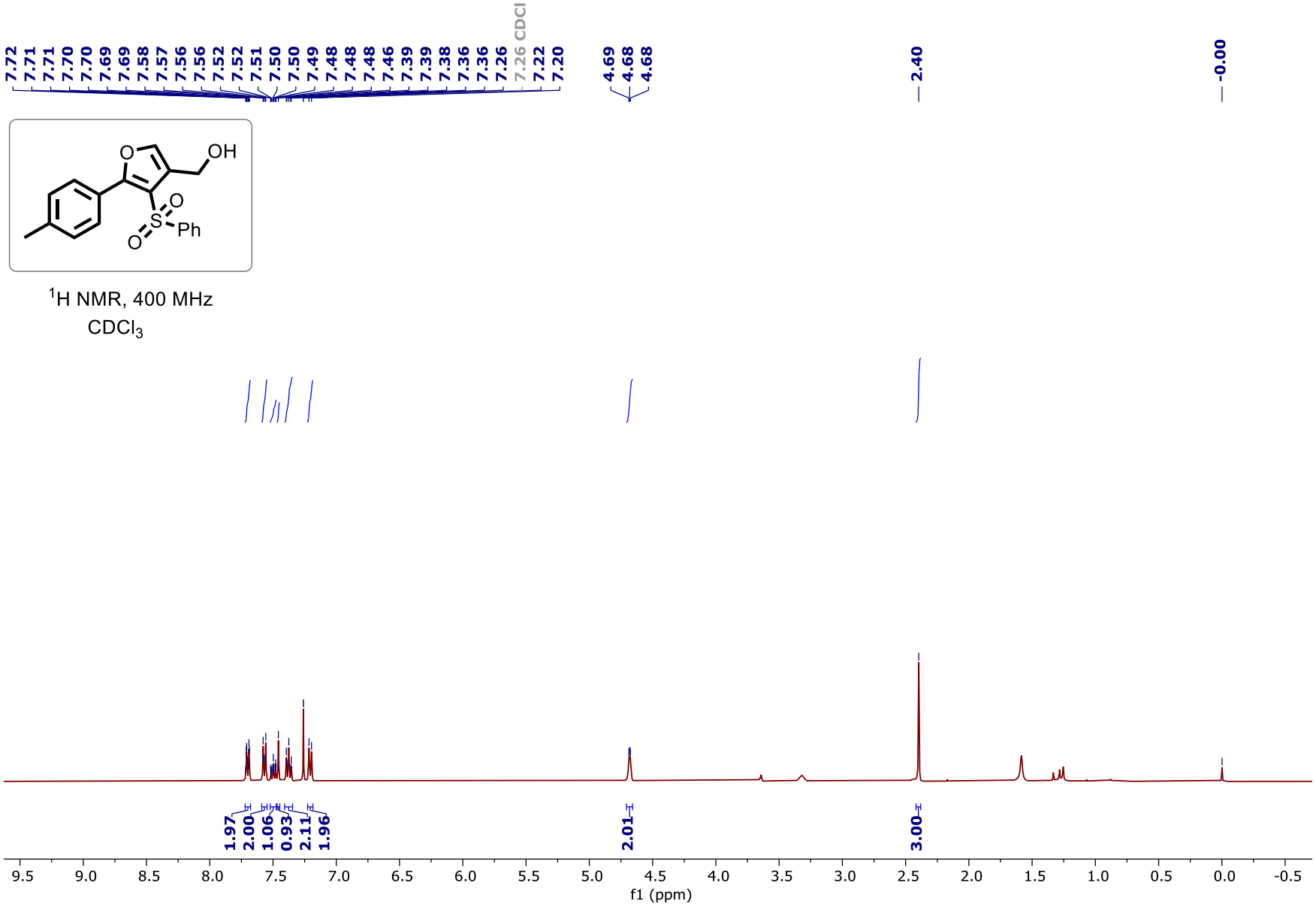
^{1}H NMR spectrum of Diethyl (4-(hydroxymethyl)-2-phenylfuran-3-yl)phosphonate (9):



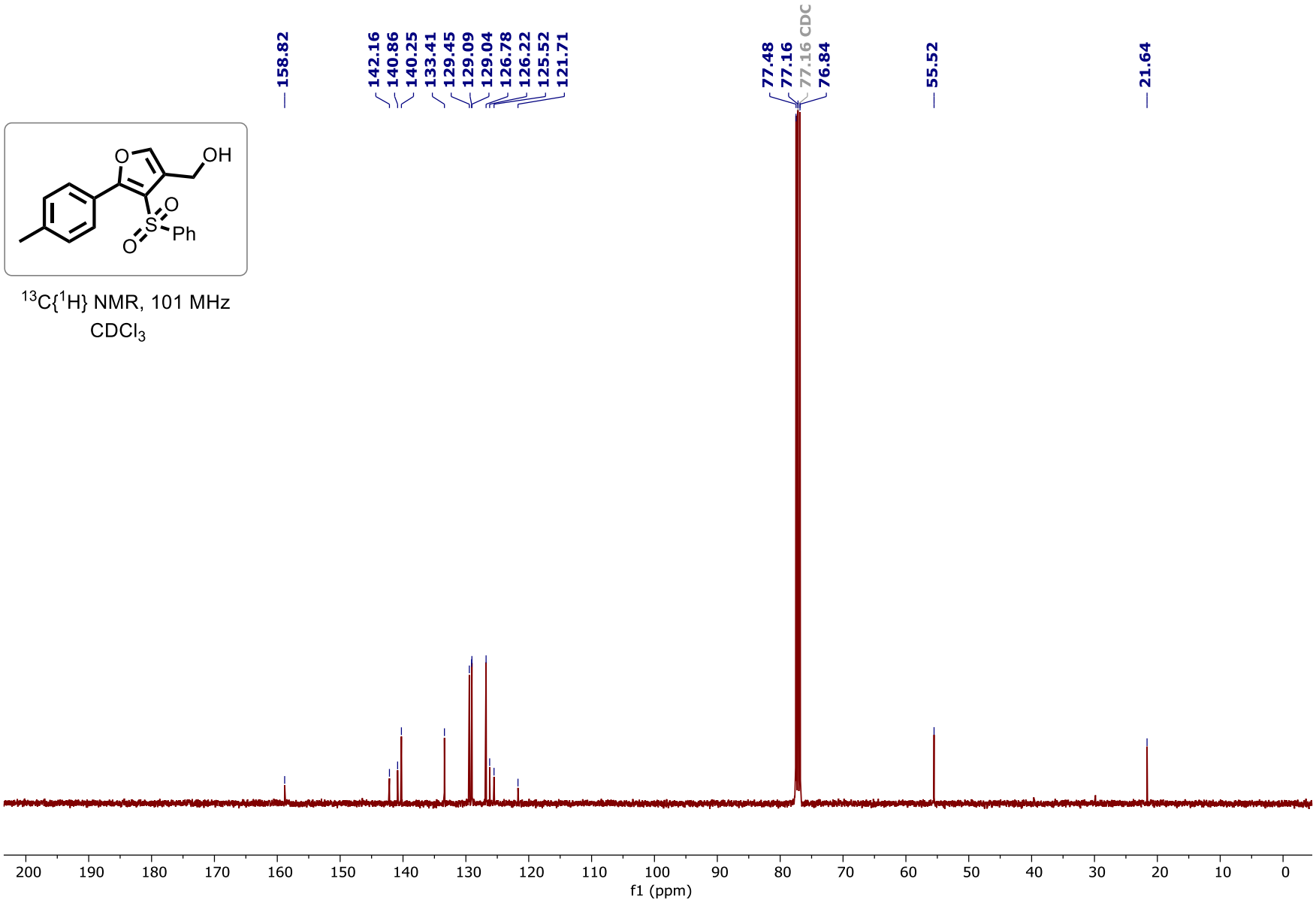
$^{13}C\{^{1}H\}$ NMR spectrum of Diethyl (4-(hydroxymethyl)-2-phenylfuran-3-yl)phosphonate (9):



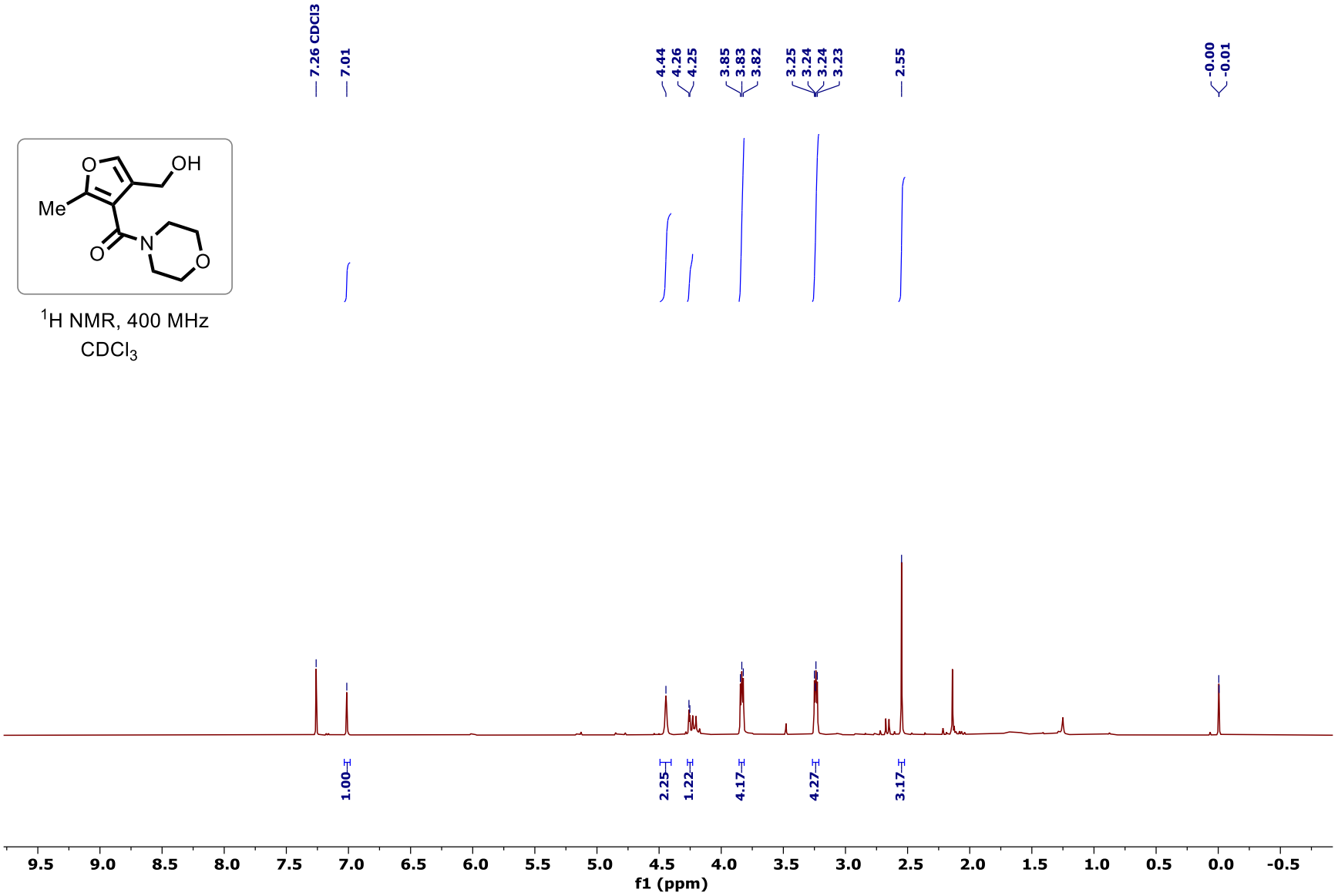
^{1}H NMR spectrum of (4-(Phenylsulfonyl)-5-(p-tolyl)furan-3-yl)methanol (11):



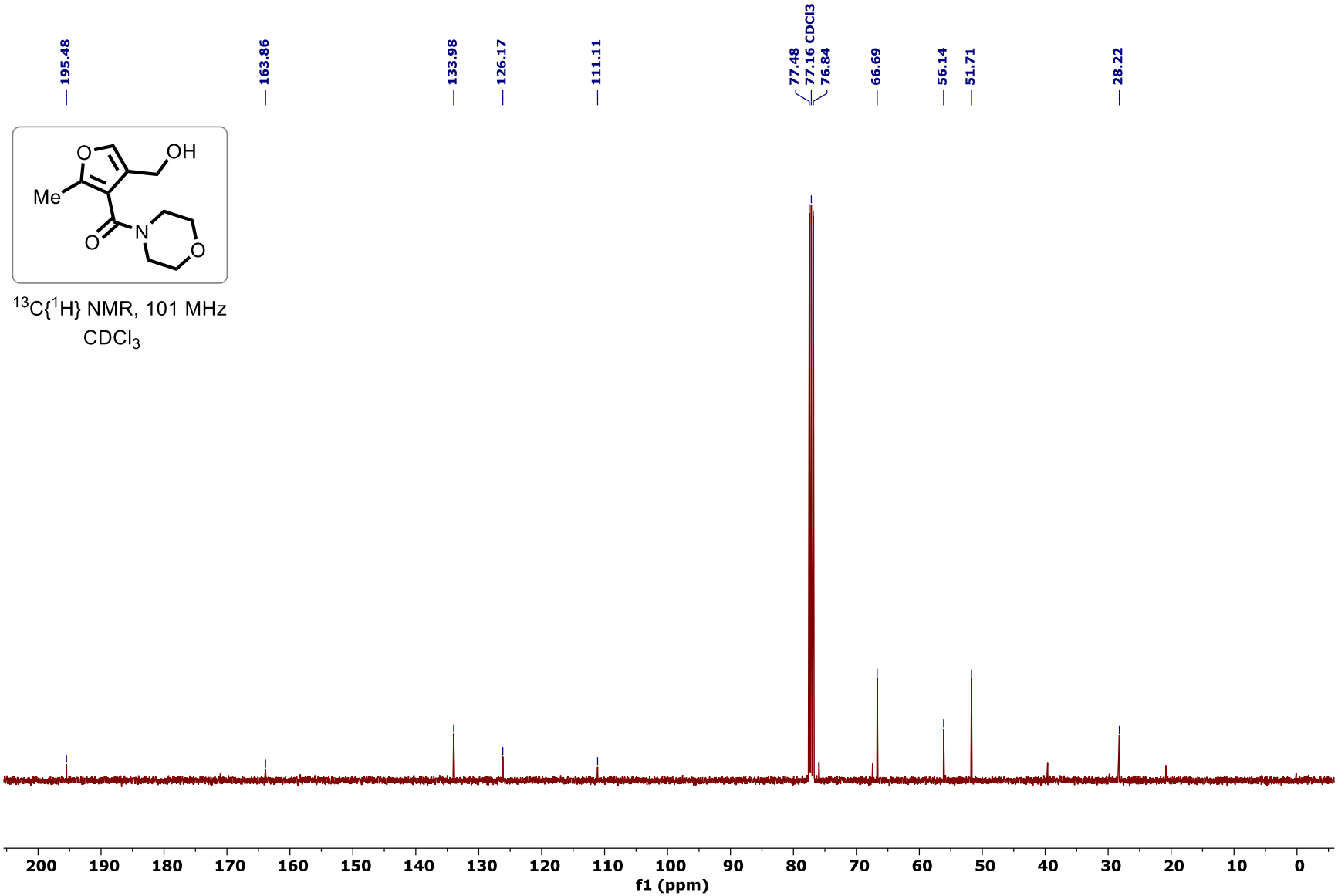
$^{13}C\{^{1}H\}$ NMR spectrum of (4-(Phenylsulfonyl)-5-(p-tolyl)furan-3-yl)methanol (11):



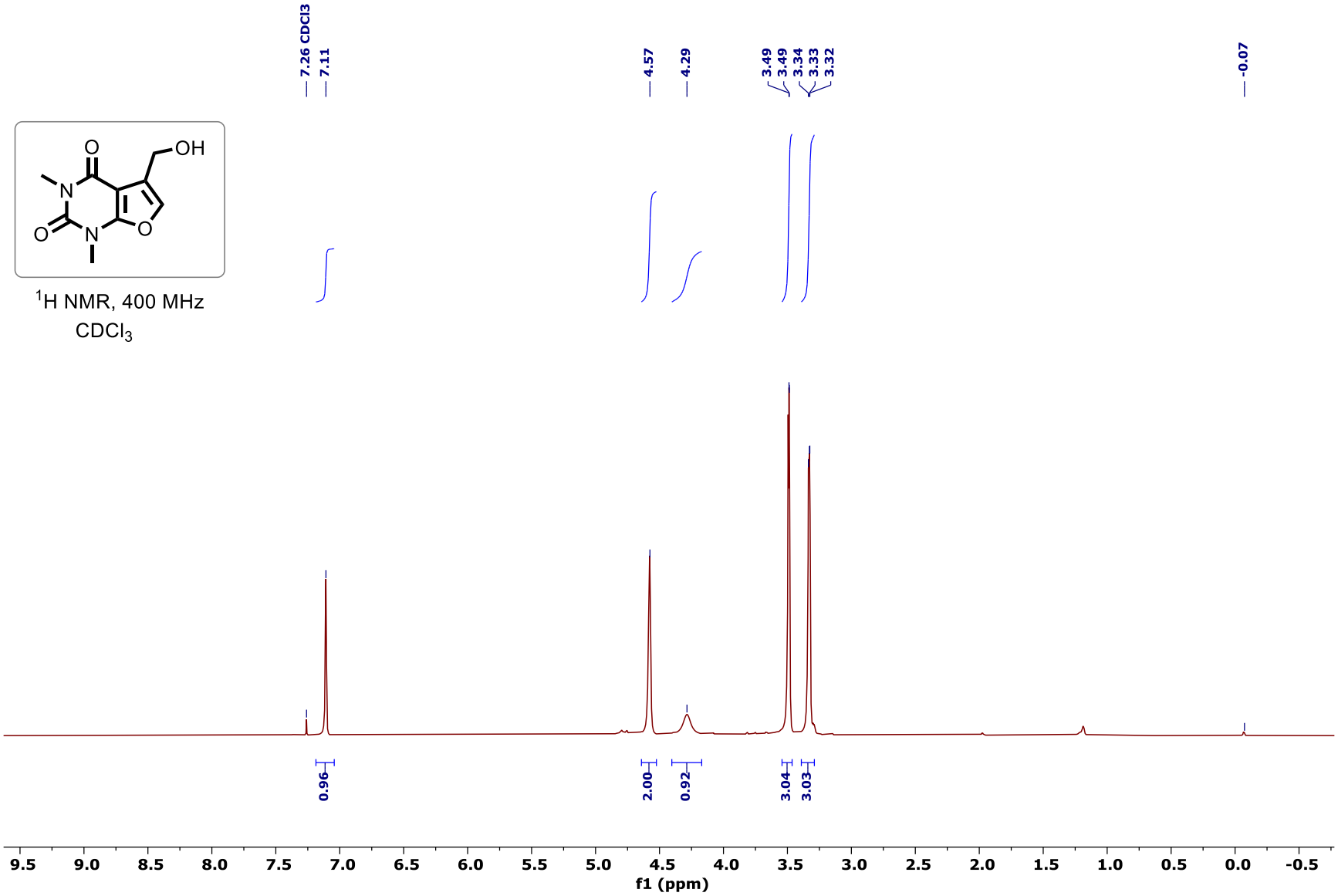
^{1}H NMR spectrum of (4-(Hydroxymethyl)-2-methylfuran-3-yl)(morpholino)methanone (13):



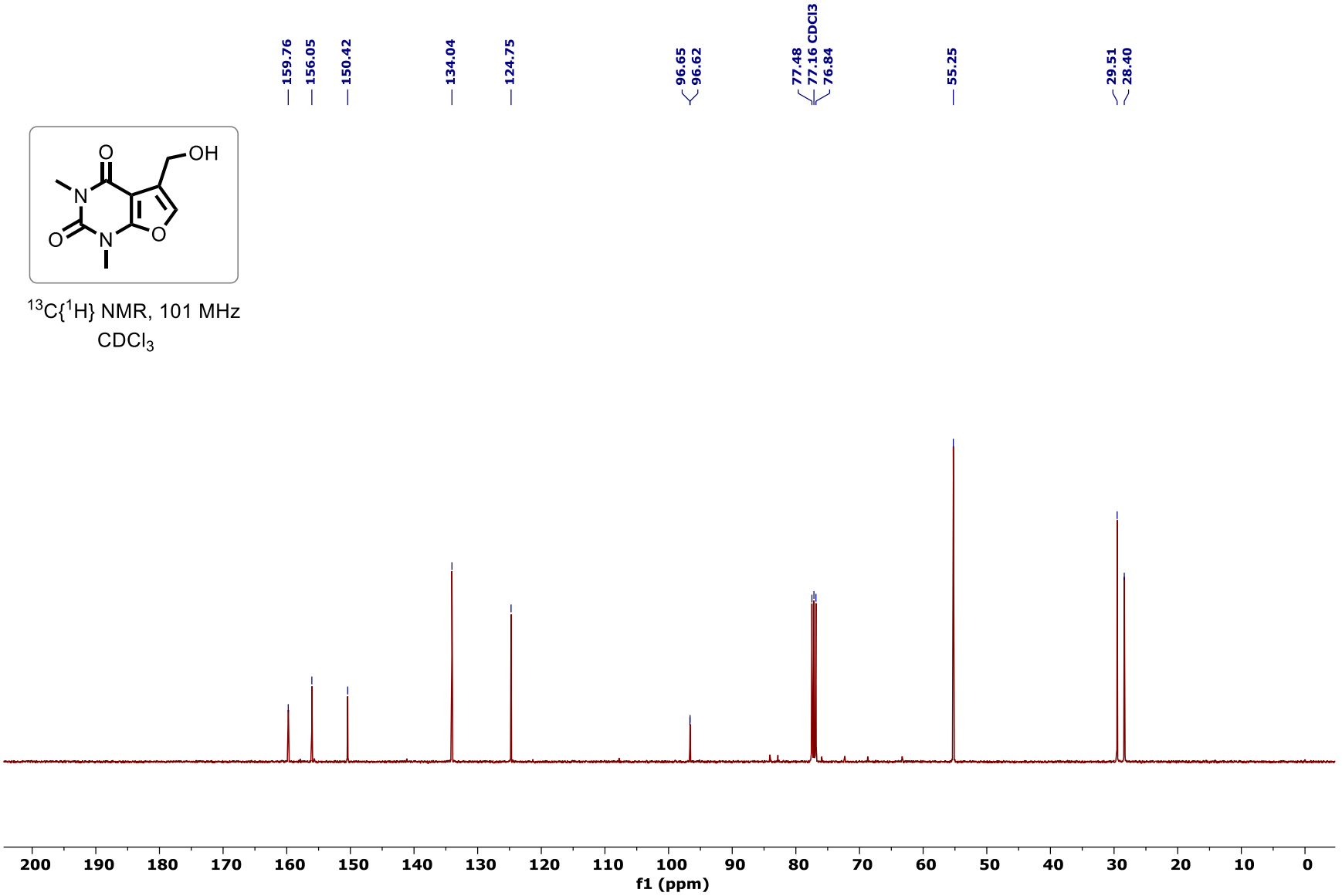
$^{13}C\{^{1}H\}$ NMR spectrum of (4-(Hydroxymethyl)-2-methylfuran-3-yl)(morpholino)methanone (13):



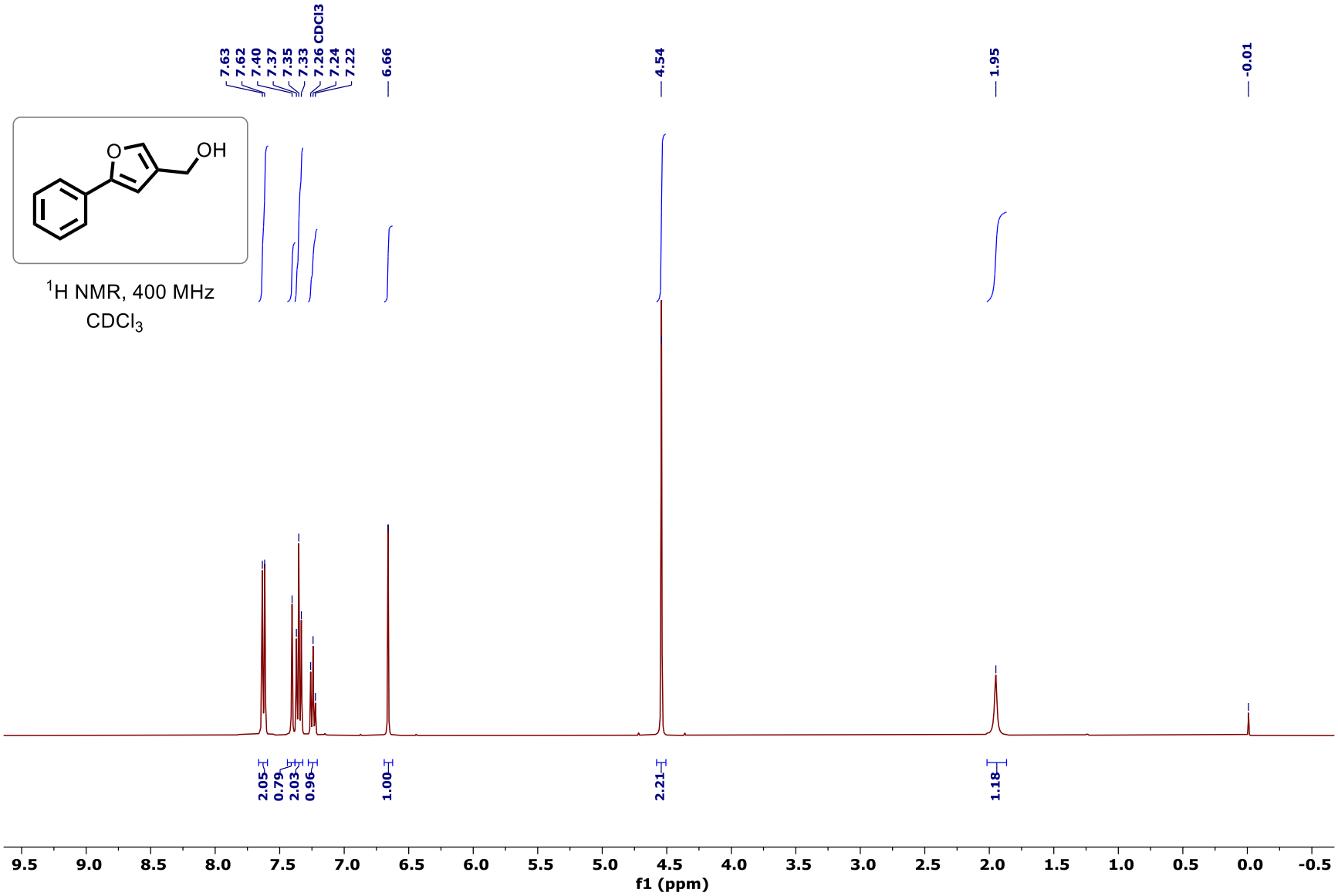
^{1}H NMR spectrum of 5-(Hydroxymethyl)-1,3-dimethylfuro[2,3-d]pyrimidine-2,4(1*H*,3*H*)-dione (15):



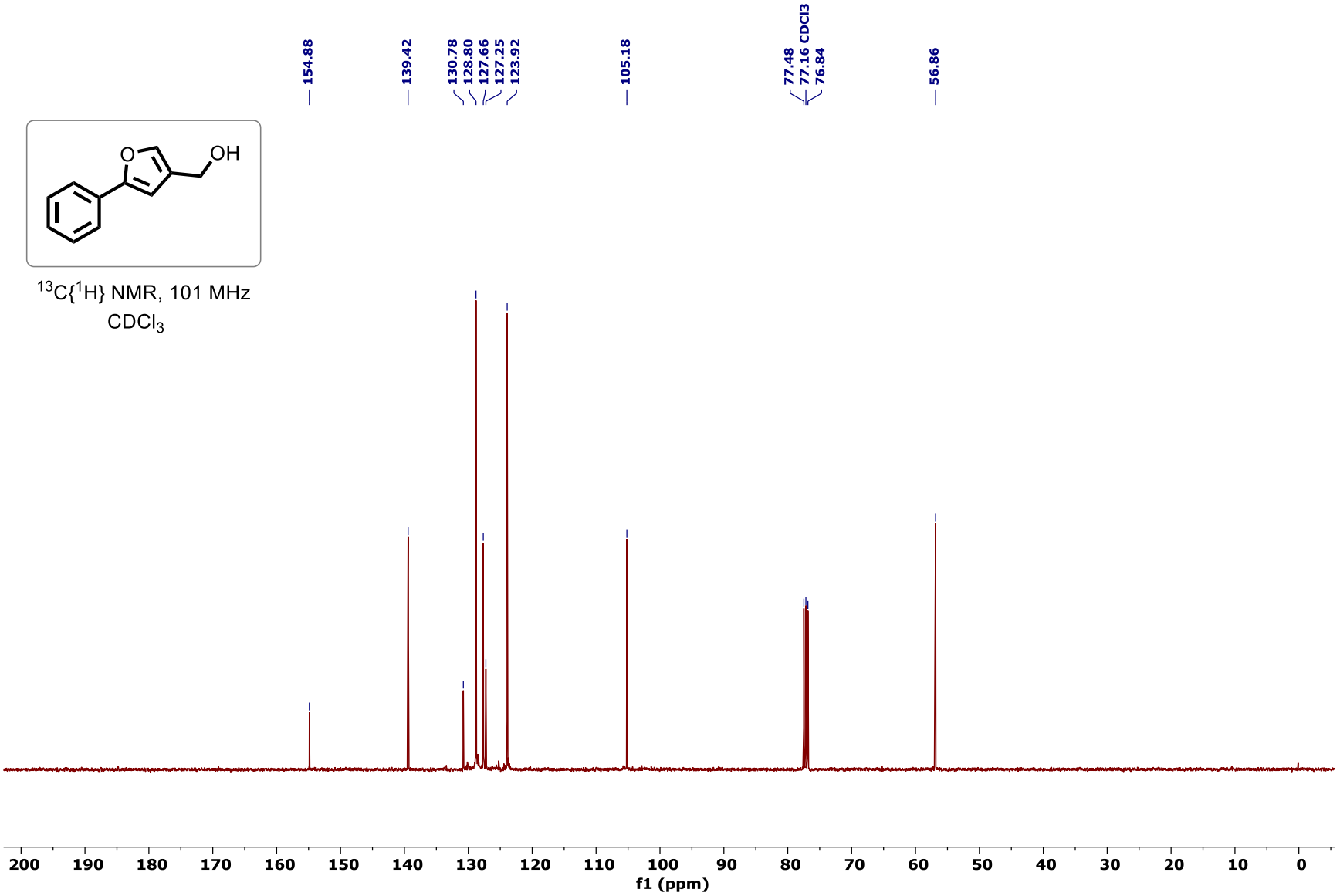
$^{13}C\{^{1}H\}$ NMR spectrum of 5-(Hydroxymethyl)-1,3-dimethylfuro[2,3-d]pyrimidine-2,4(1*H*,3*H*)-dione (15):



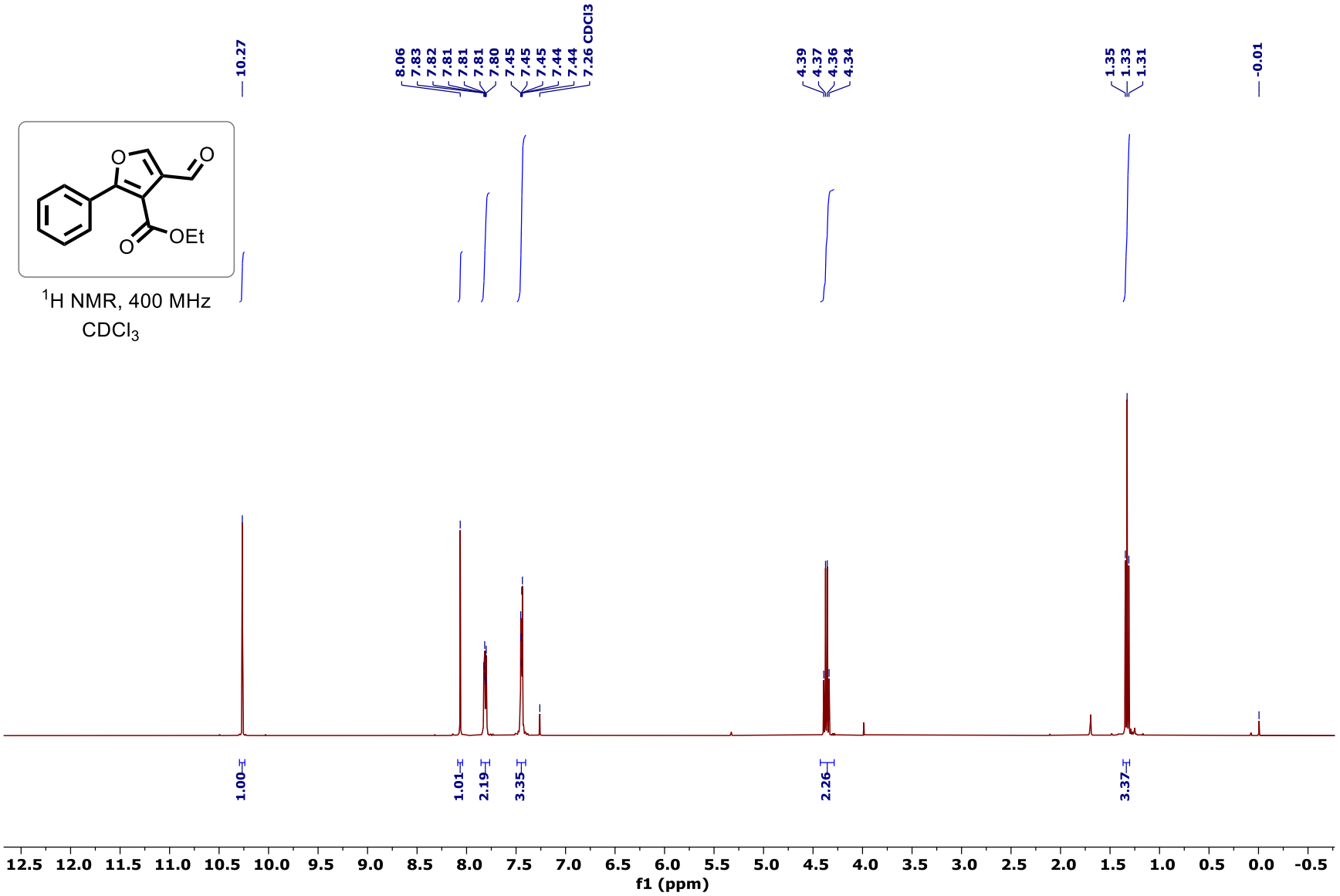
^{1}H NMR spectrum of (5-Phenylfuran-3-yl)methanol (16):



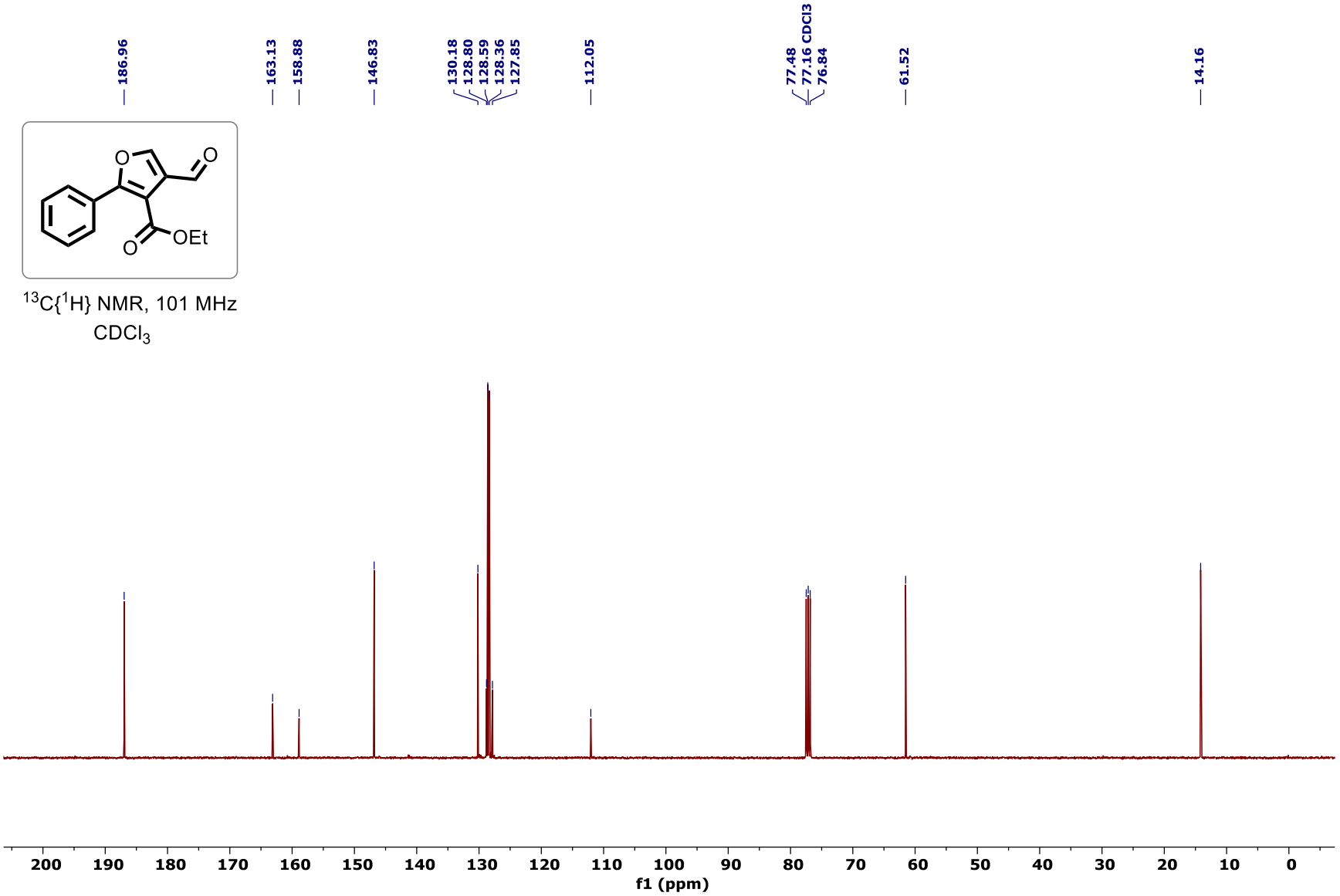
$^{13}C\{^{1}H\}$ NMR spectrum of (5-Phenylfuran-3-yl)methanol (16):



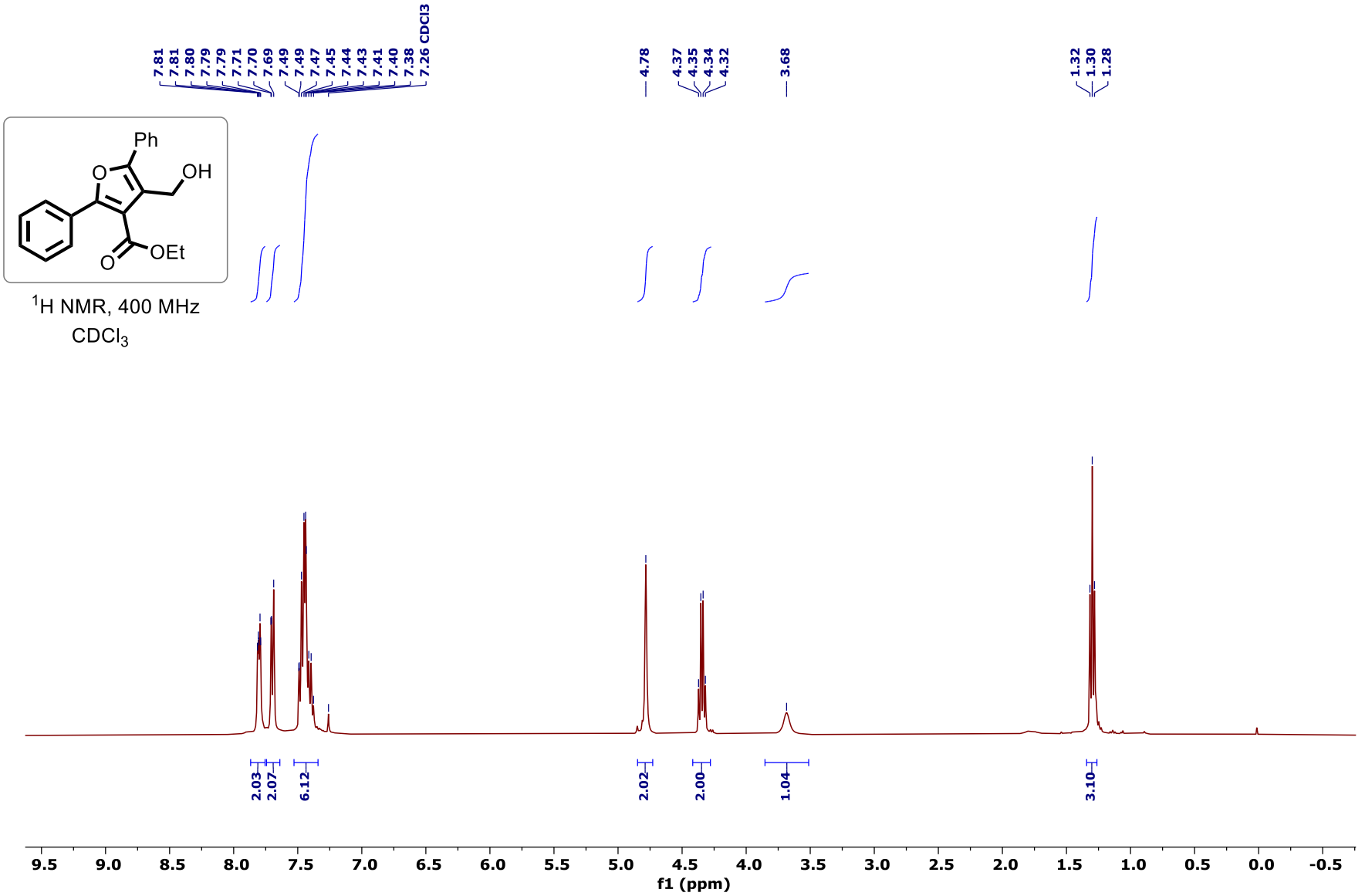
^{1}H NMR spectrum of Ethyl 4-formyl-2-phenylfuran-3-carboxylate (17):



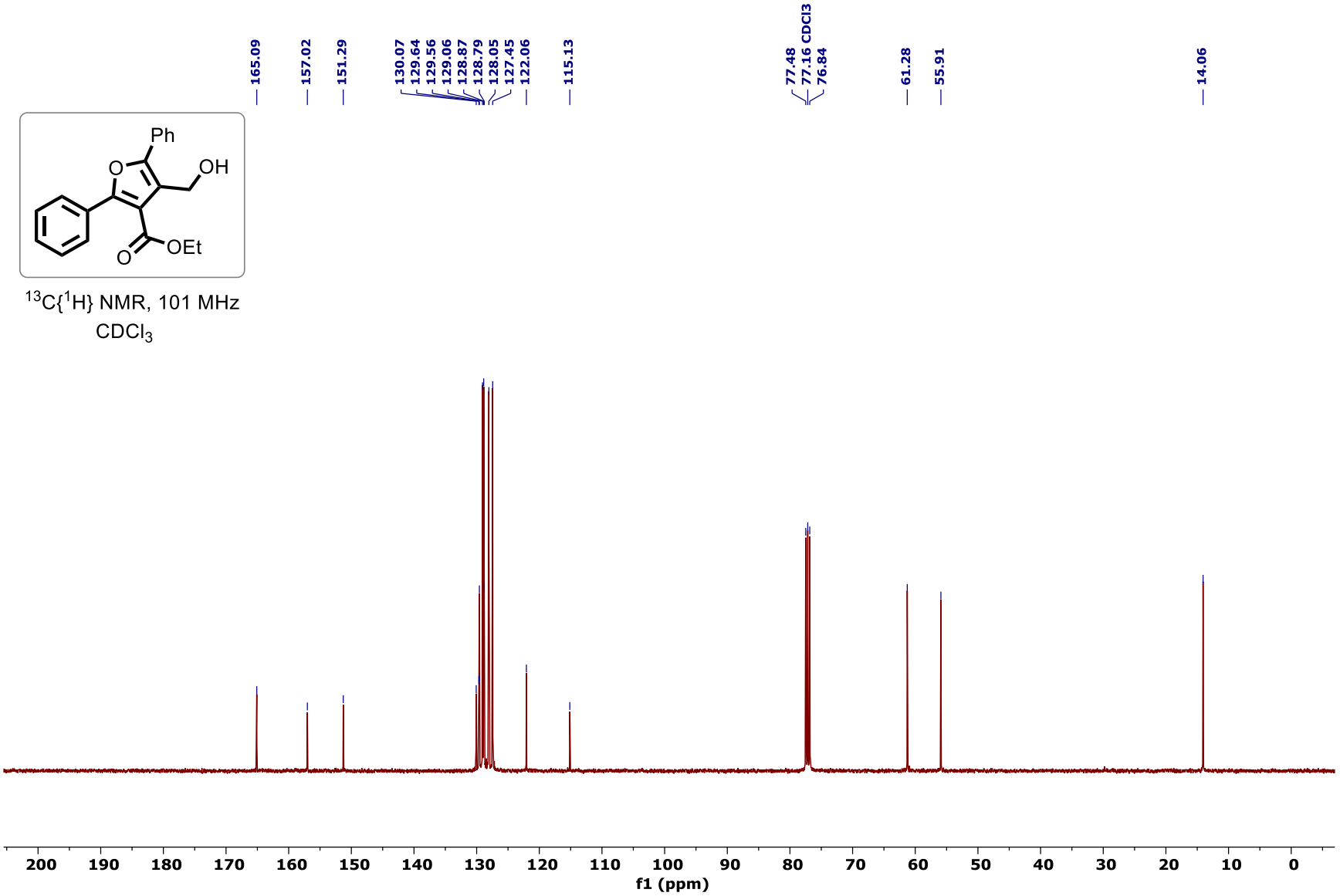
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-formyl-2-phenylfuran-3-carboxylate (17):



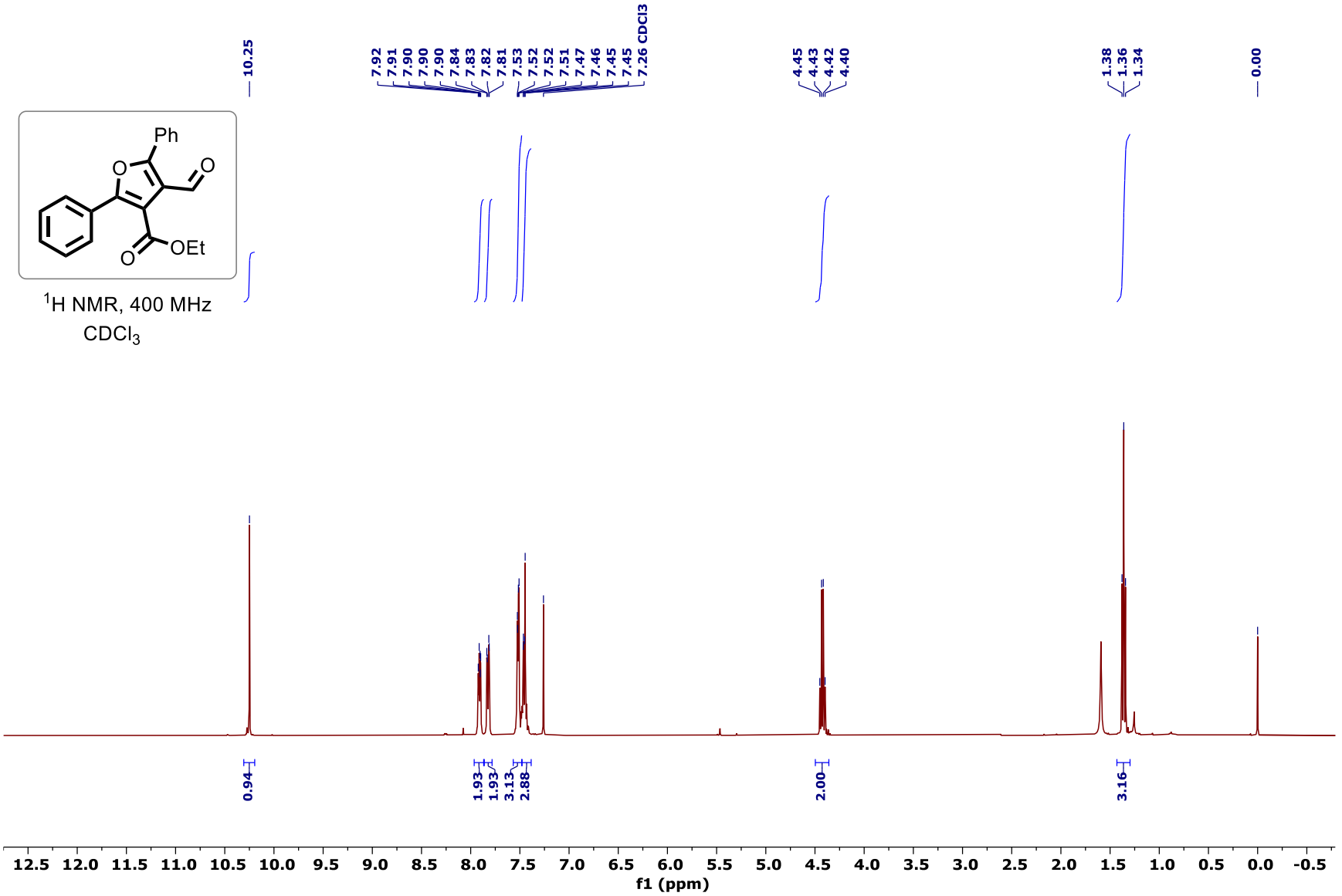
^{1}H NMR spectrum of Ethyl 4-(hydroxymethyl)-2,5-diphenylfuran-3-carboxylate (18):



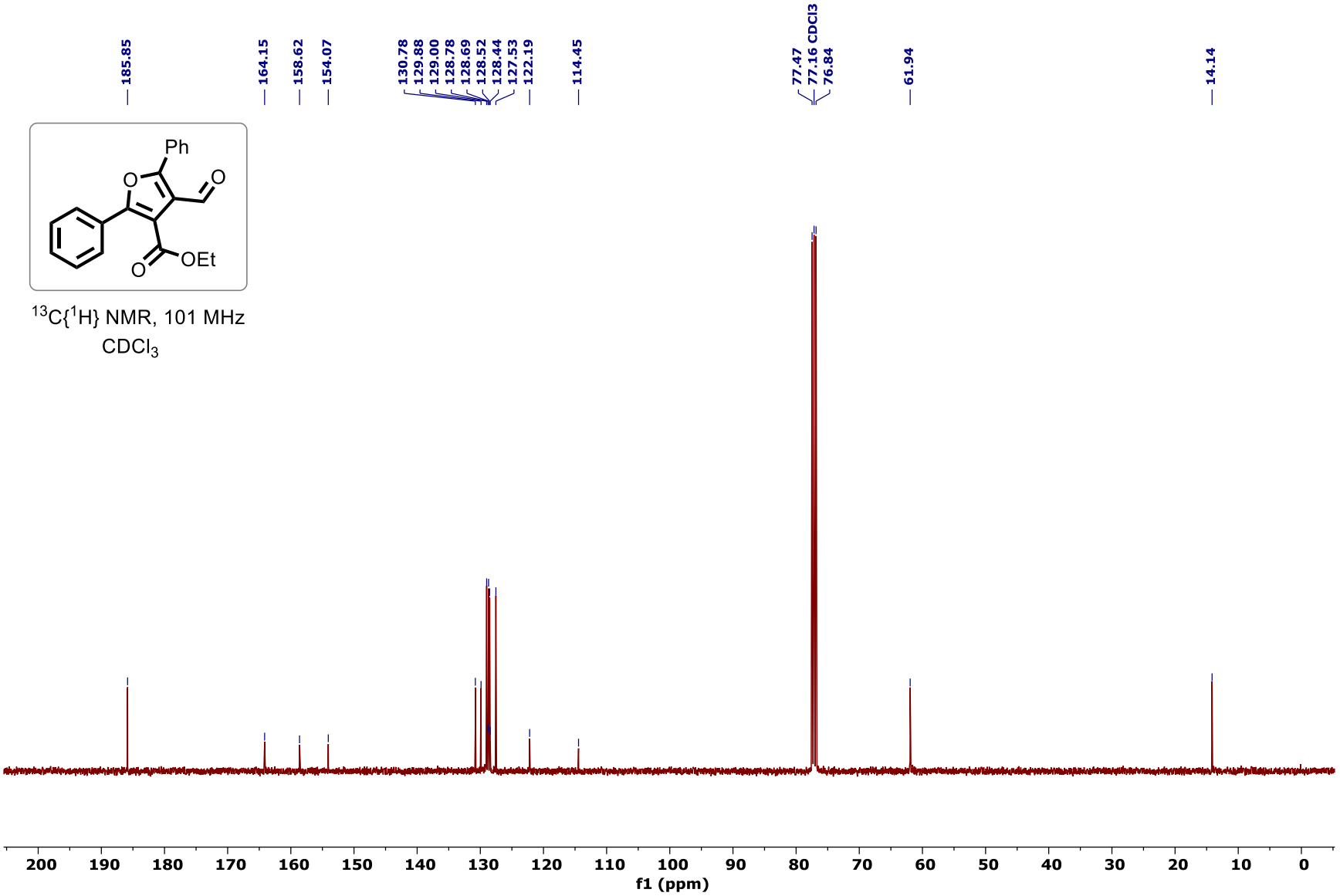
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-(hydroxymethyl)-2,5-diphenylfuran-3-carboxylate (18):



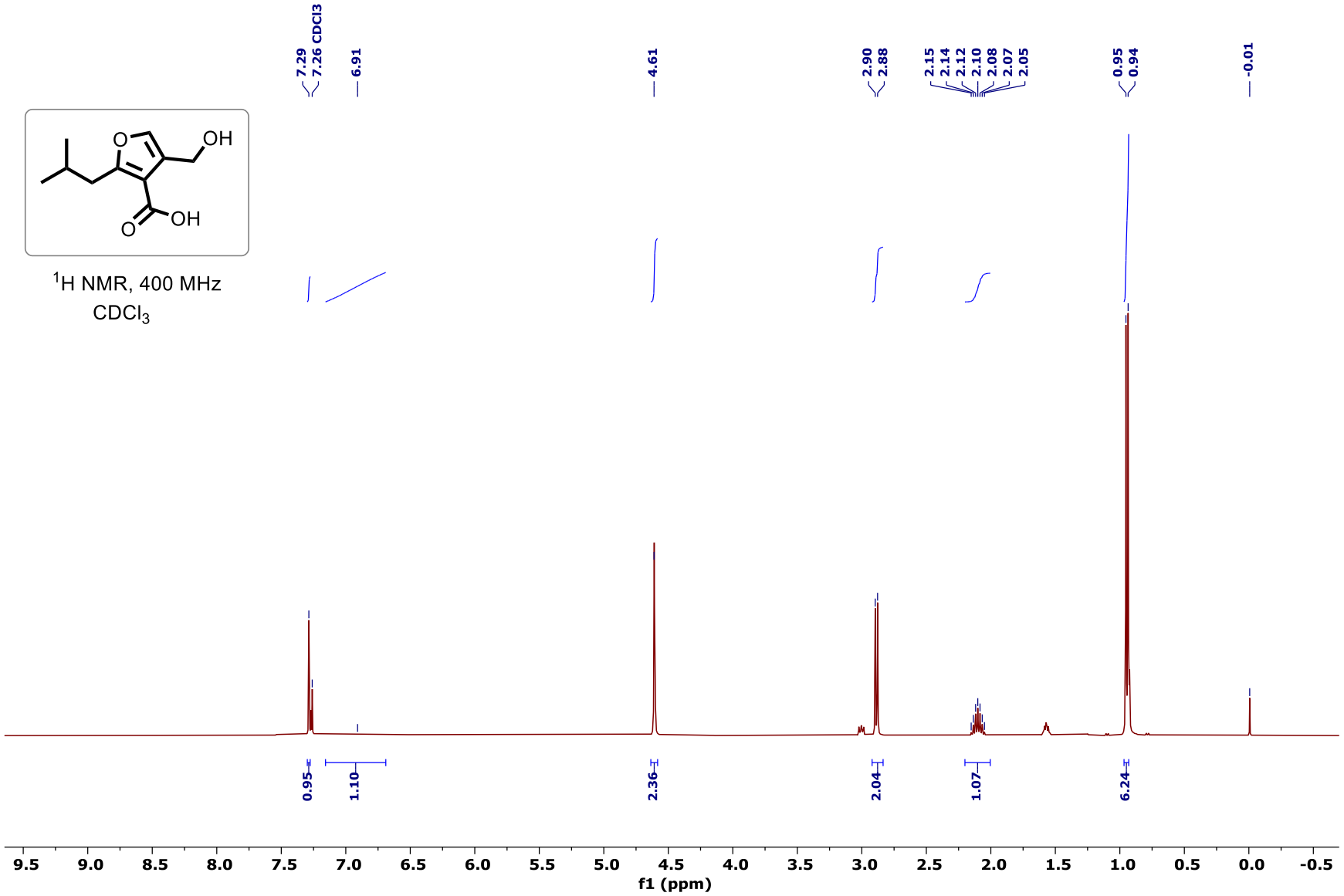
^{1}H NMR spectrum of Ethyl 4-formyl-2,5-diphenylfuran-3-carboxylate (19):



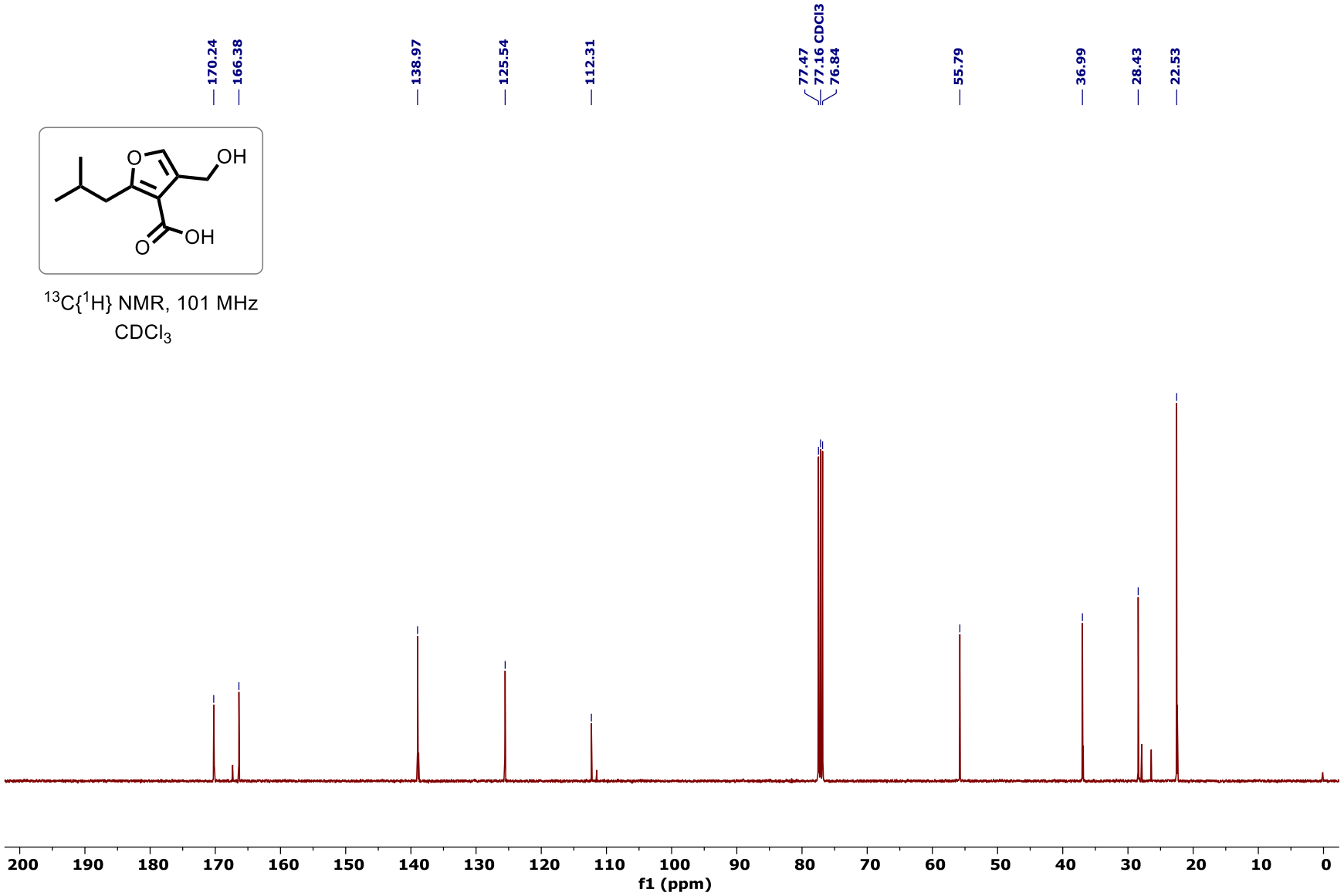
$^{13}C\{^{1}H\}$ NMR spectrum of Ethyl 4-formyl-2,5-diphenylfuran-3-carboxylate (19):



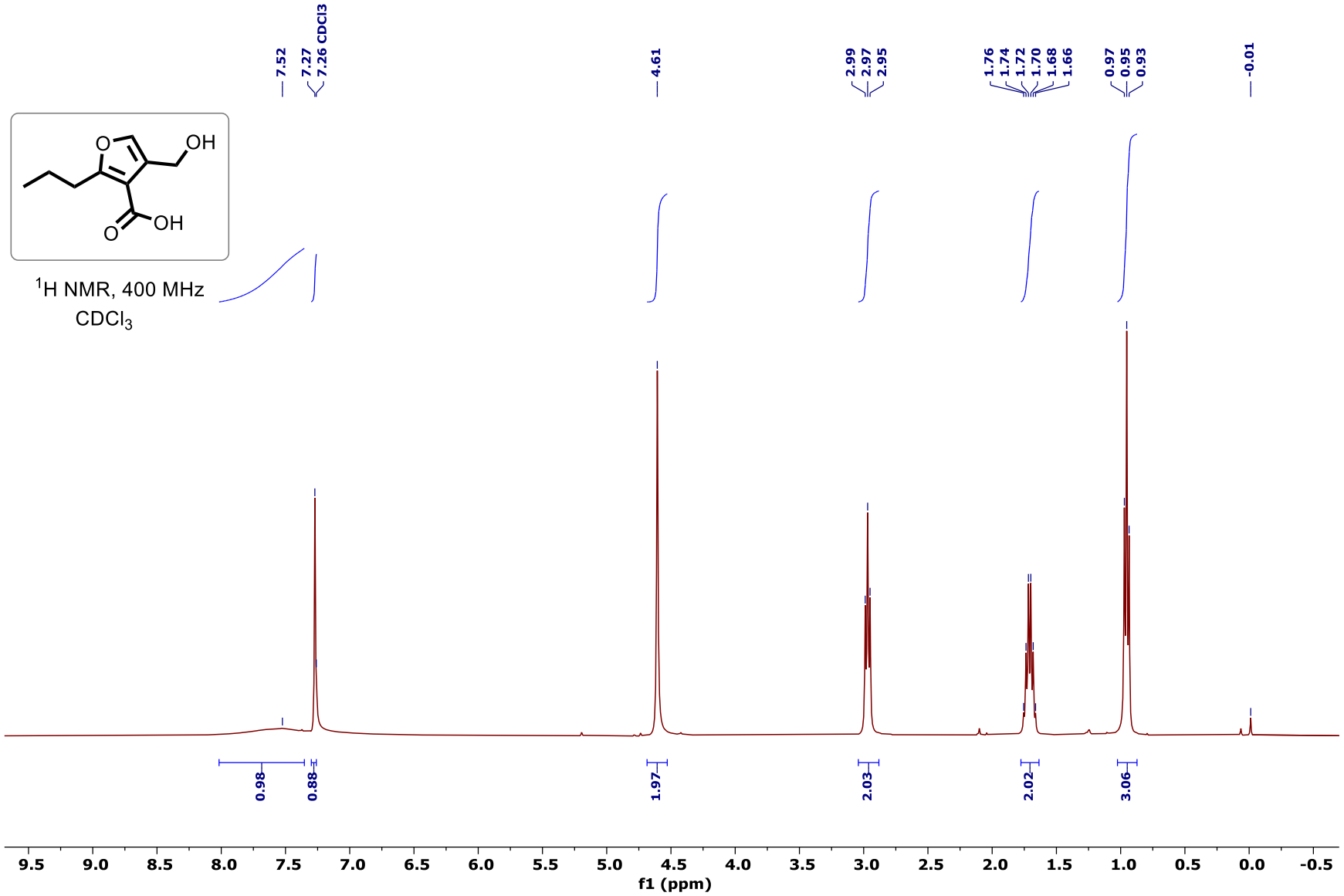
^{1}H NMR spectrum of Methylenomycin furan 1 (MMF1) (20l):



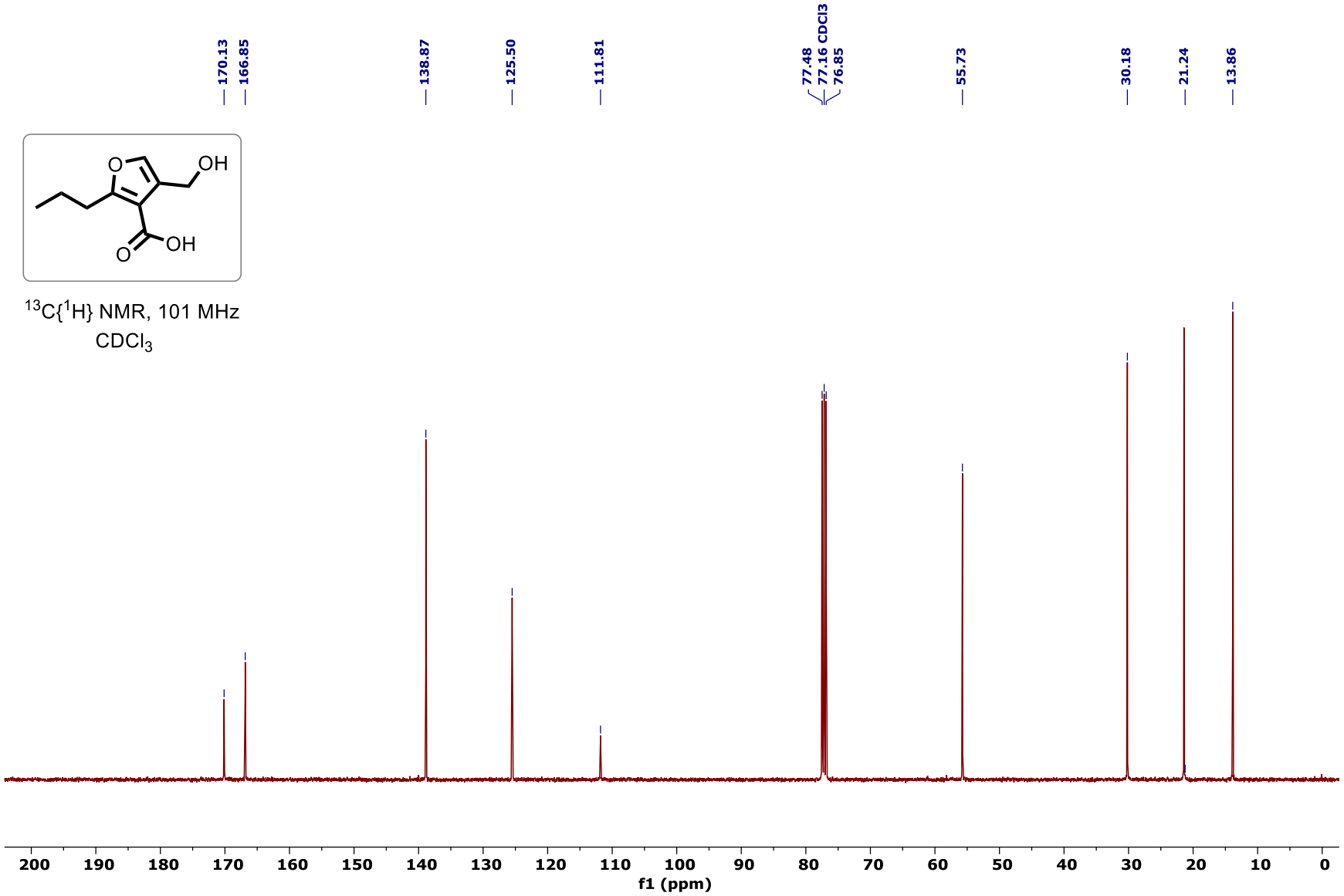
$^{13}C\{^{1}H\}$ NMR spectrum of Methylenomycin furan 1 (MMF1) (20l):



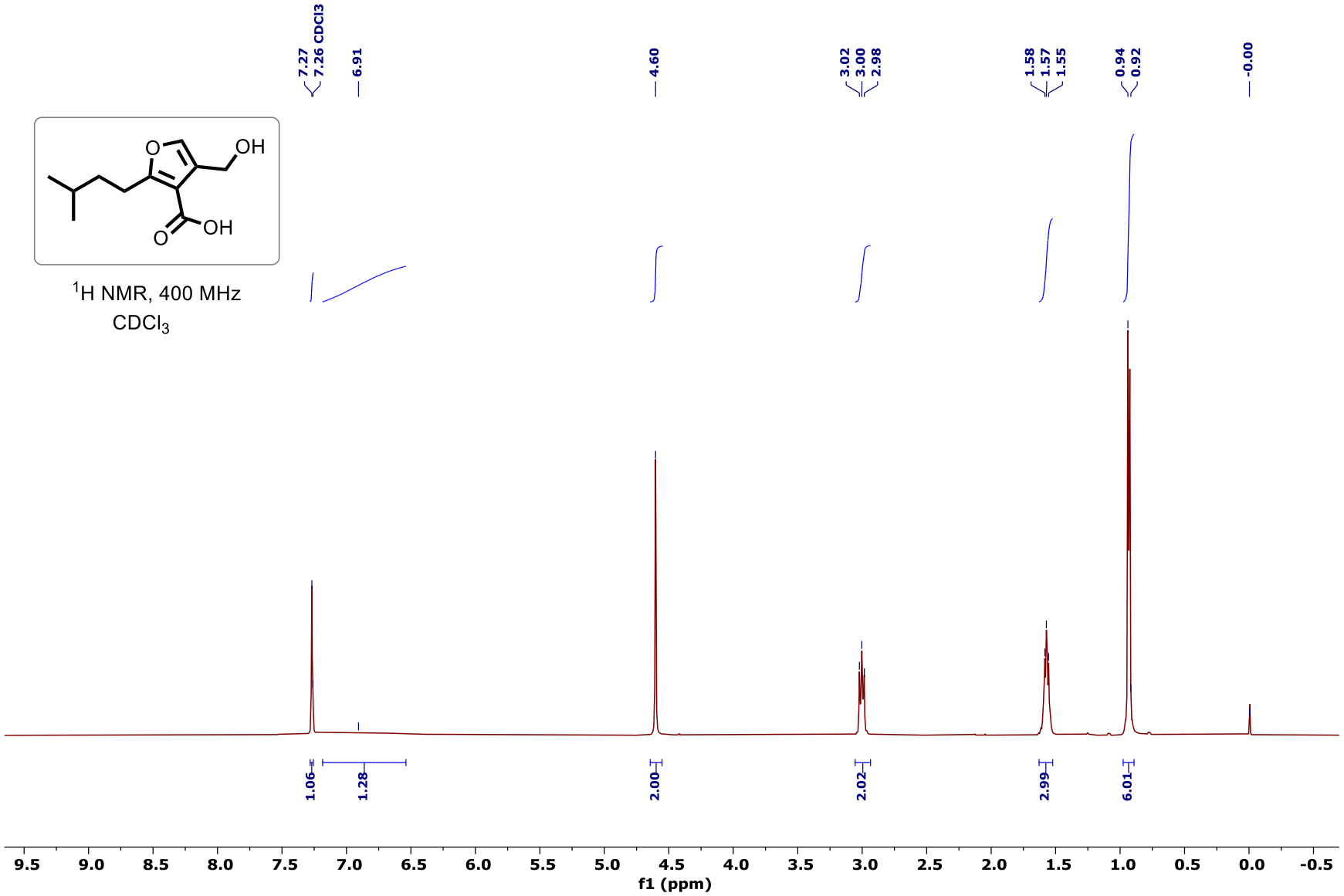
^{1}H NMR spectrum of Methylenomycin furan 2 (MMF2) (20m):



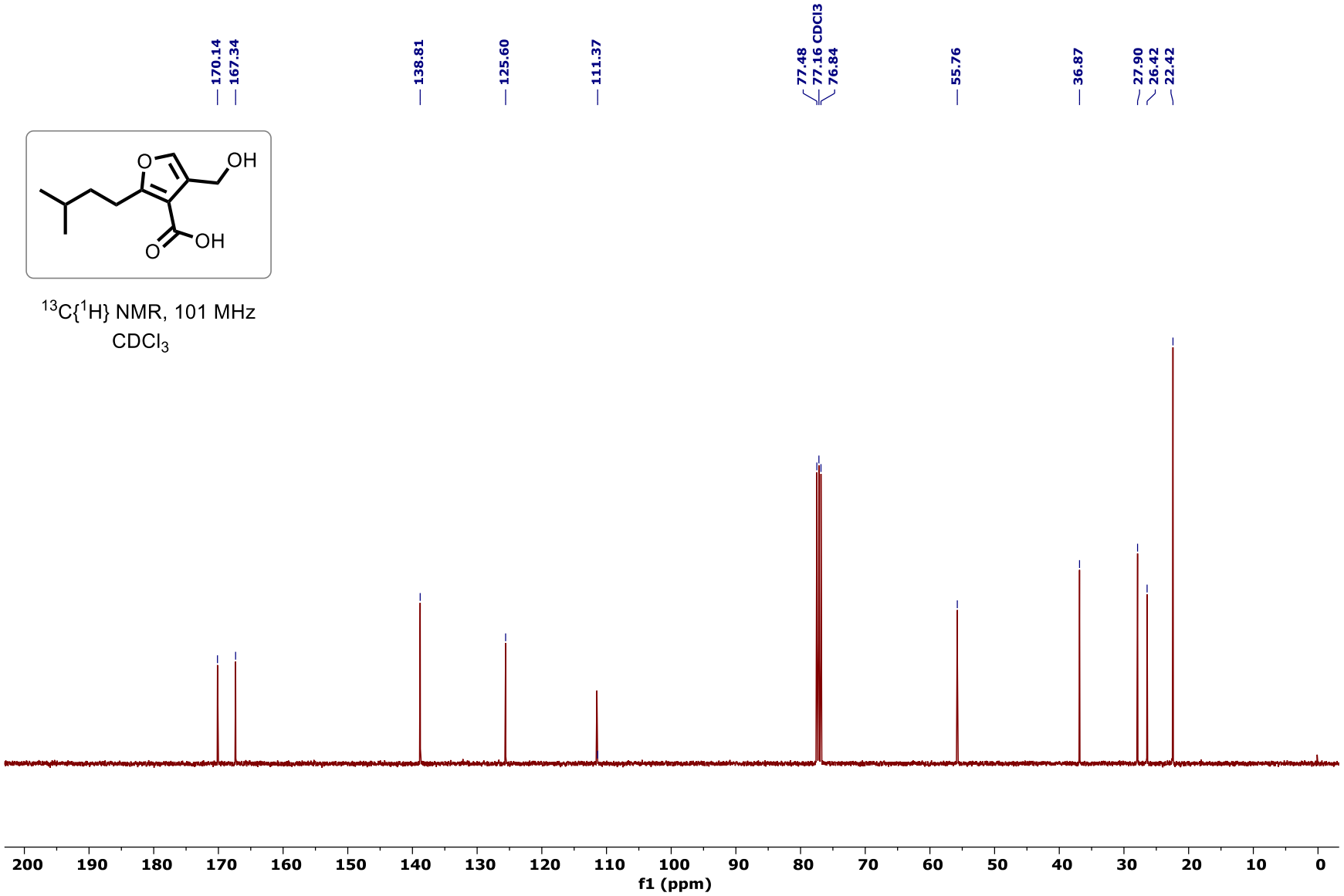
$^{13}C\{^{1}H\}$ NMR spectrum of Methylenomycin furan 2 (MMF2) (20m):



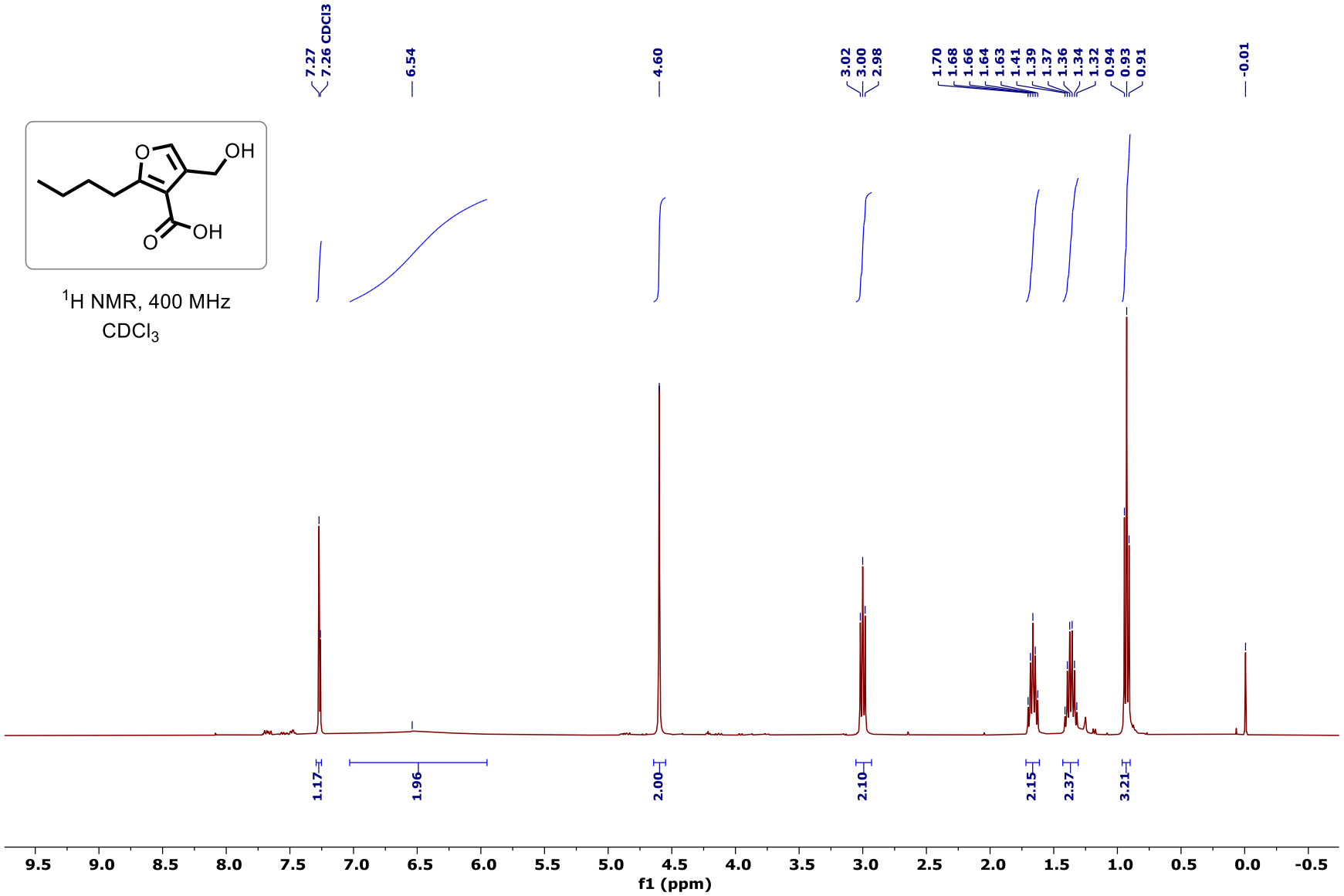
^{1}H NMR spectrum of Methylenomycin furan 3 (MMF3) (20n):



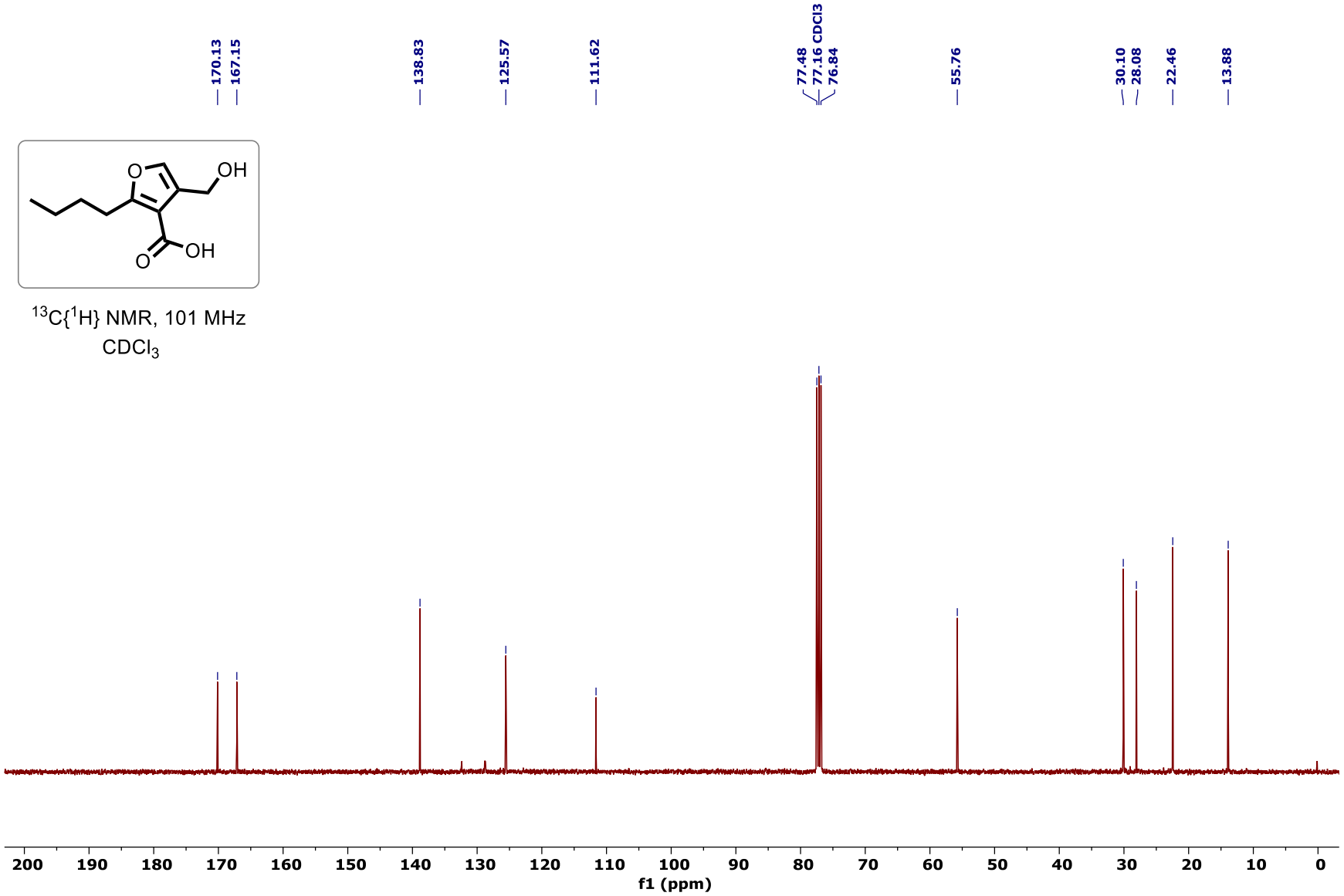
$^{13}C\{^{1}H\}$ NMR spectrum of Methylenomycin furan 3 (MMF3) (20n):



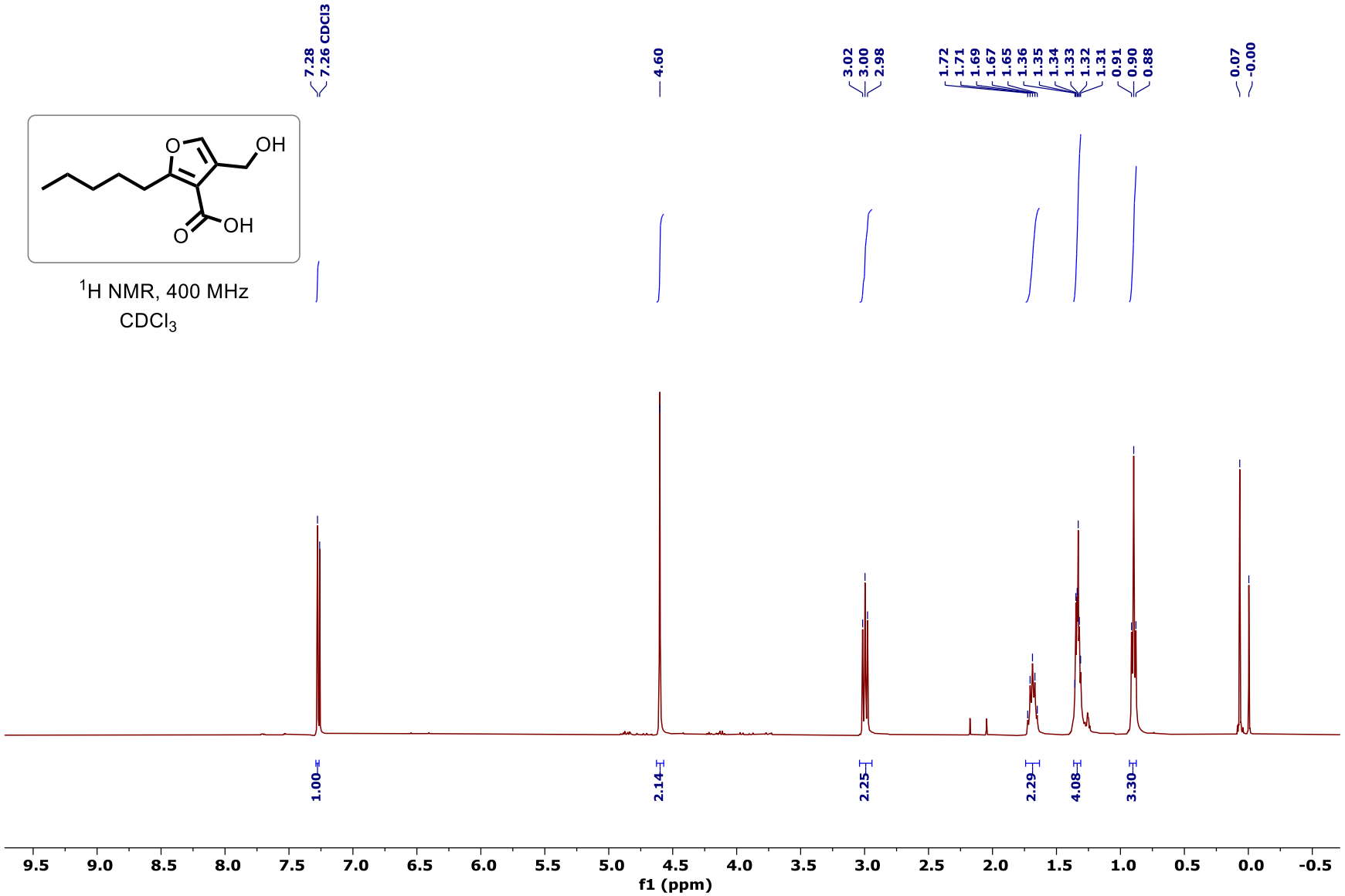
^{1}H NMR spectrum of Methylenomycin furan 4 (MMF4) (20o):



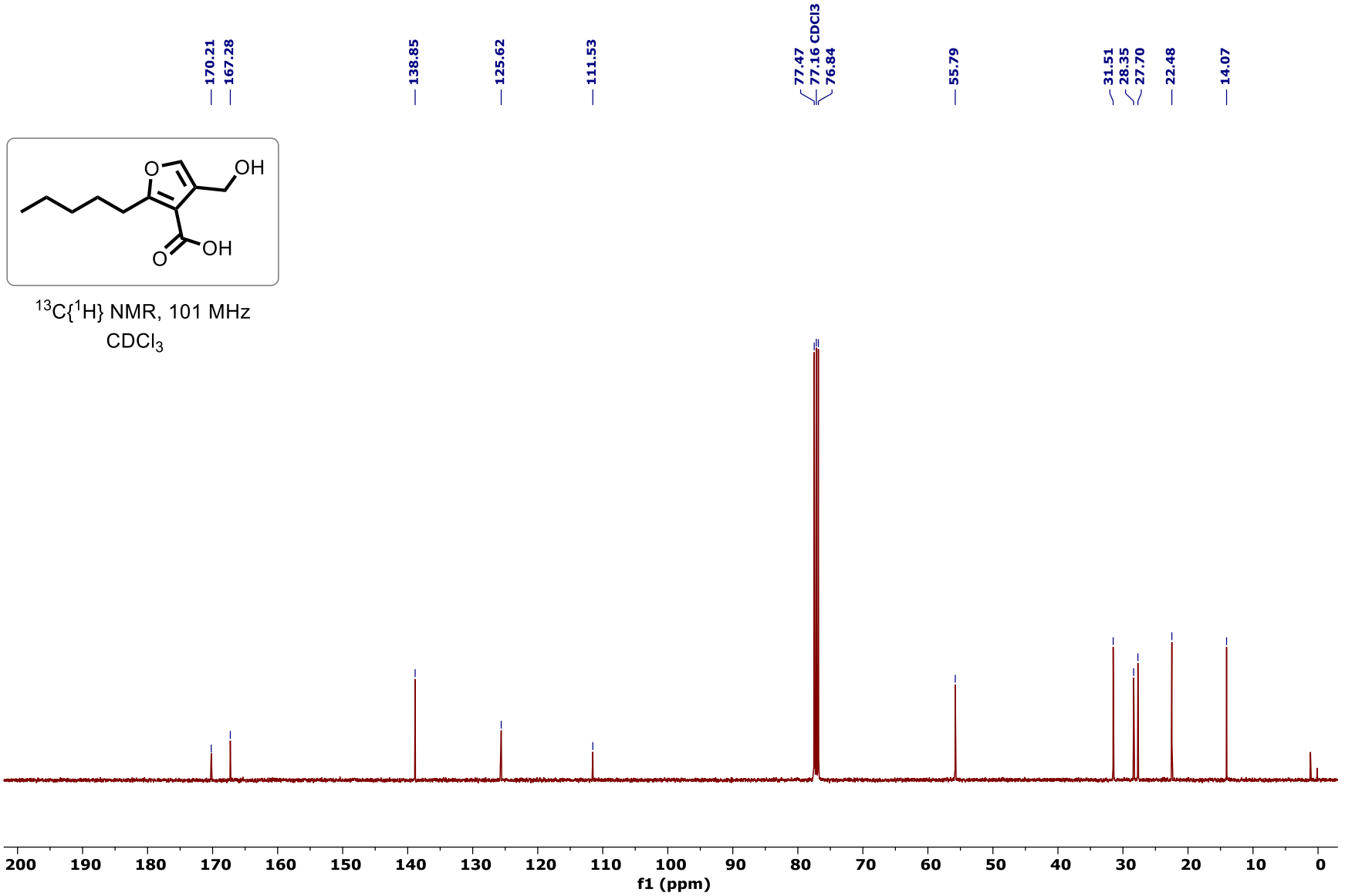
$^{13}C\{^{1}H\}$ NMR spectrum of Methylenomycin furan 4 (MMF4) (20o):



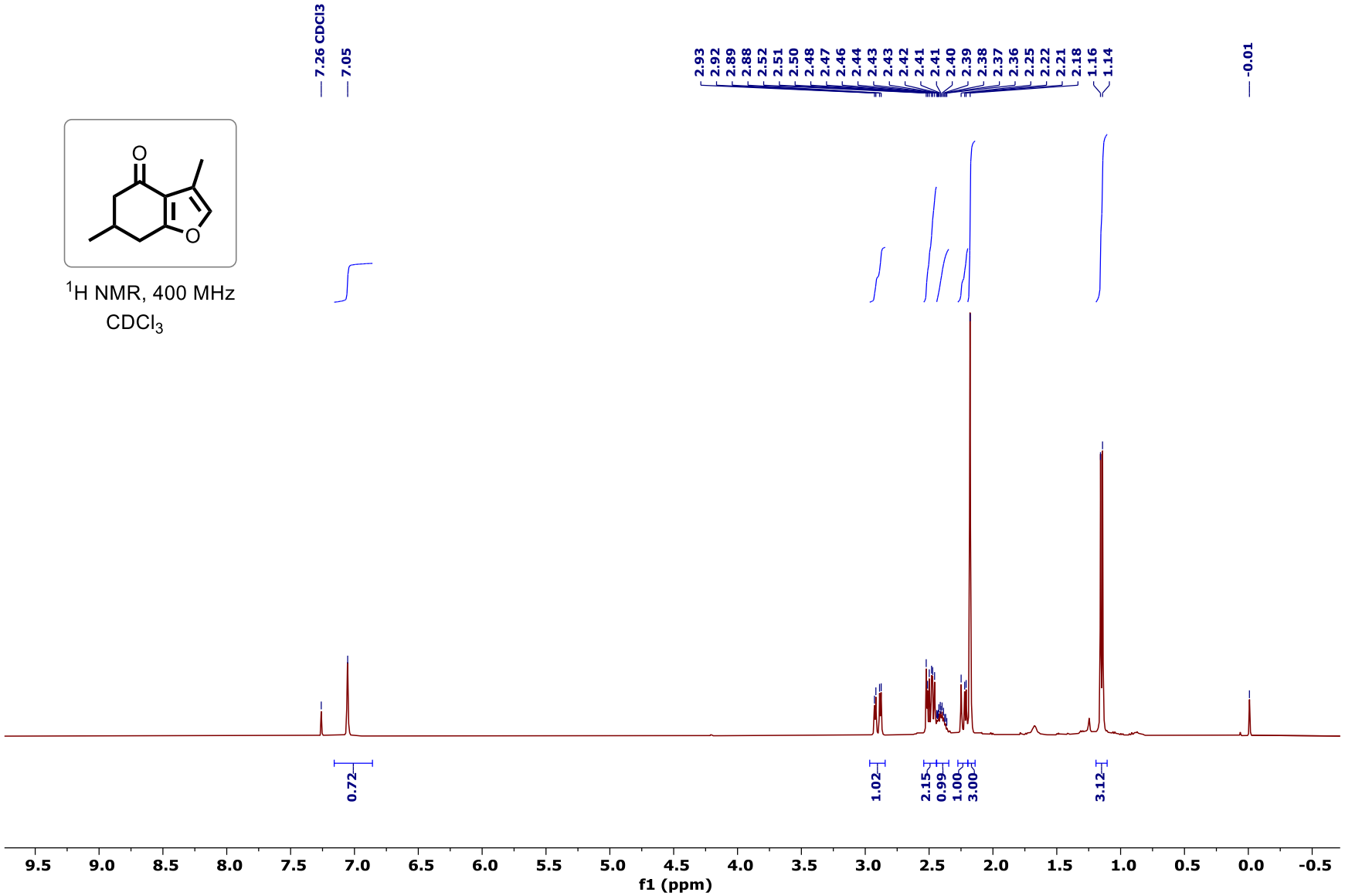
^{1}H NMR spectrum of Methylenomycin furan 5 (MMF5) (20p):



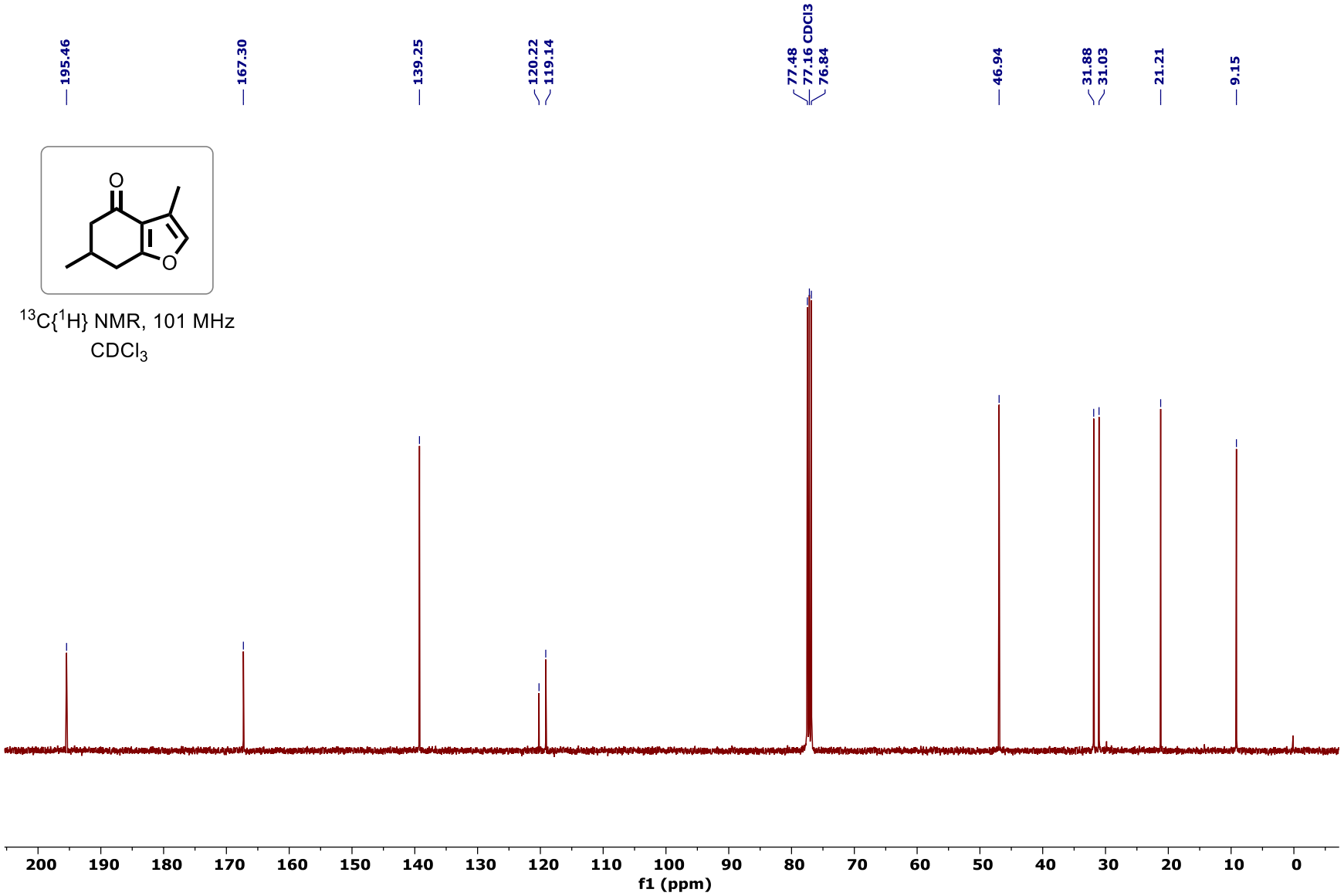
$^{13}C\{^{1}H\}$ NMR spectrum of Methylenomycin furan 5 (MMF5) (20p):



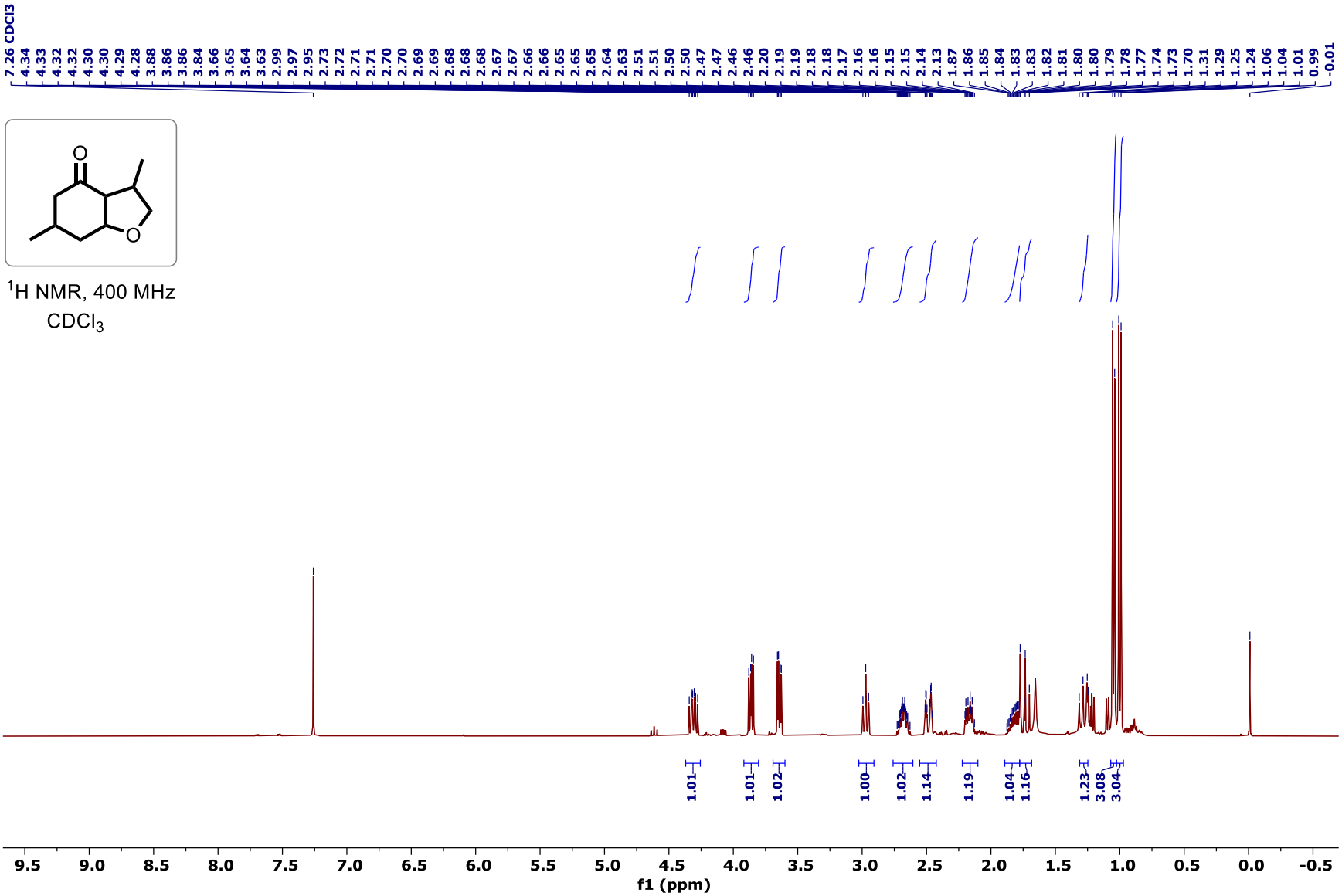
^{1}H NMR spectrum of (±)-Evodone (21):



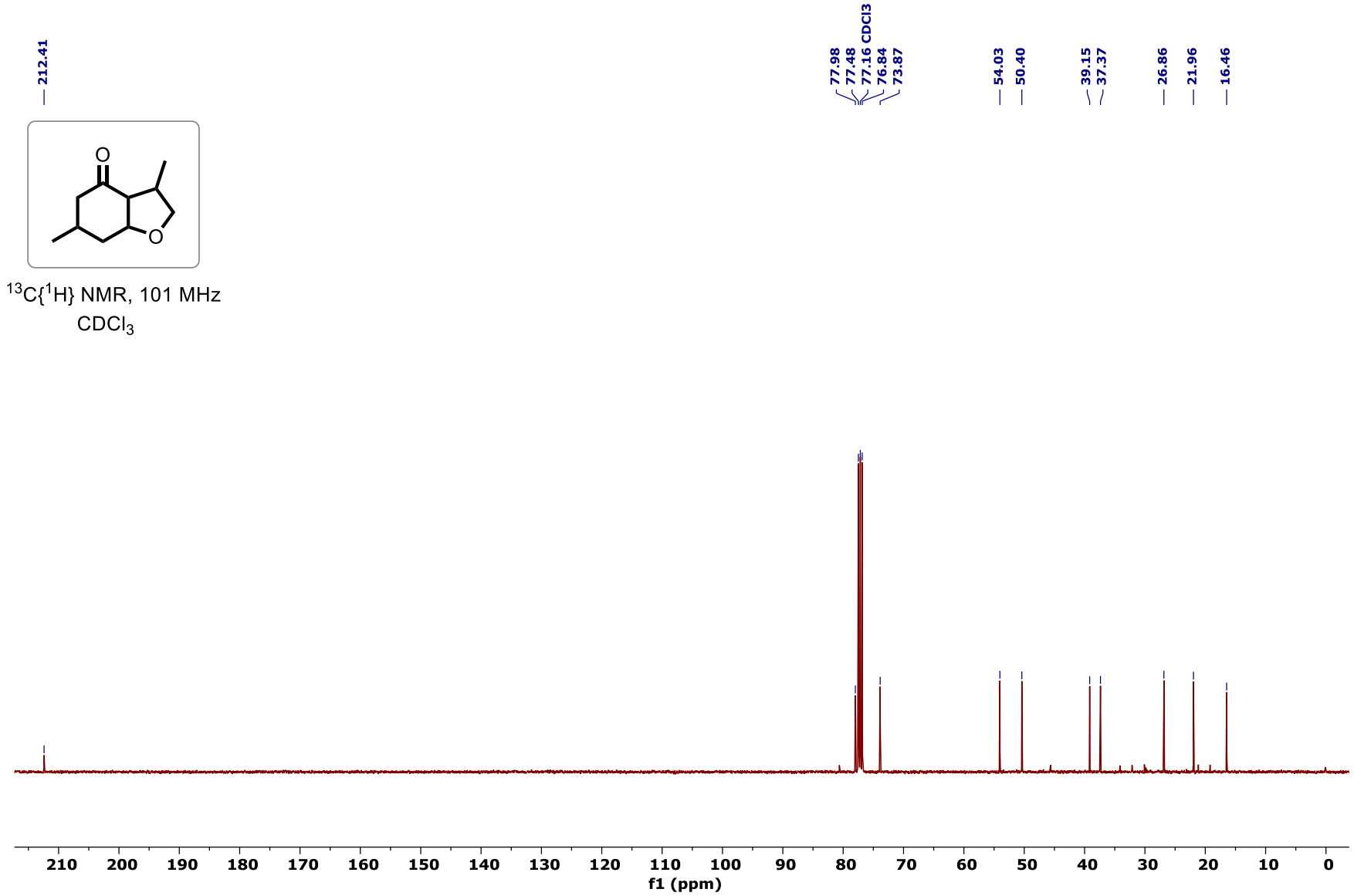
$^{13}C\{^{1}H\}$ NMR spectrum of (±)-Evodone (21):



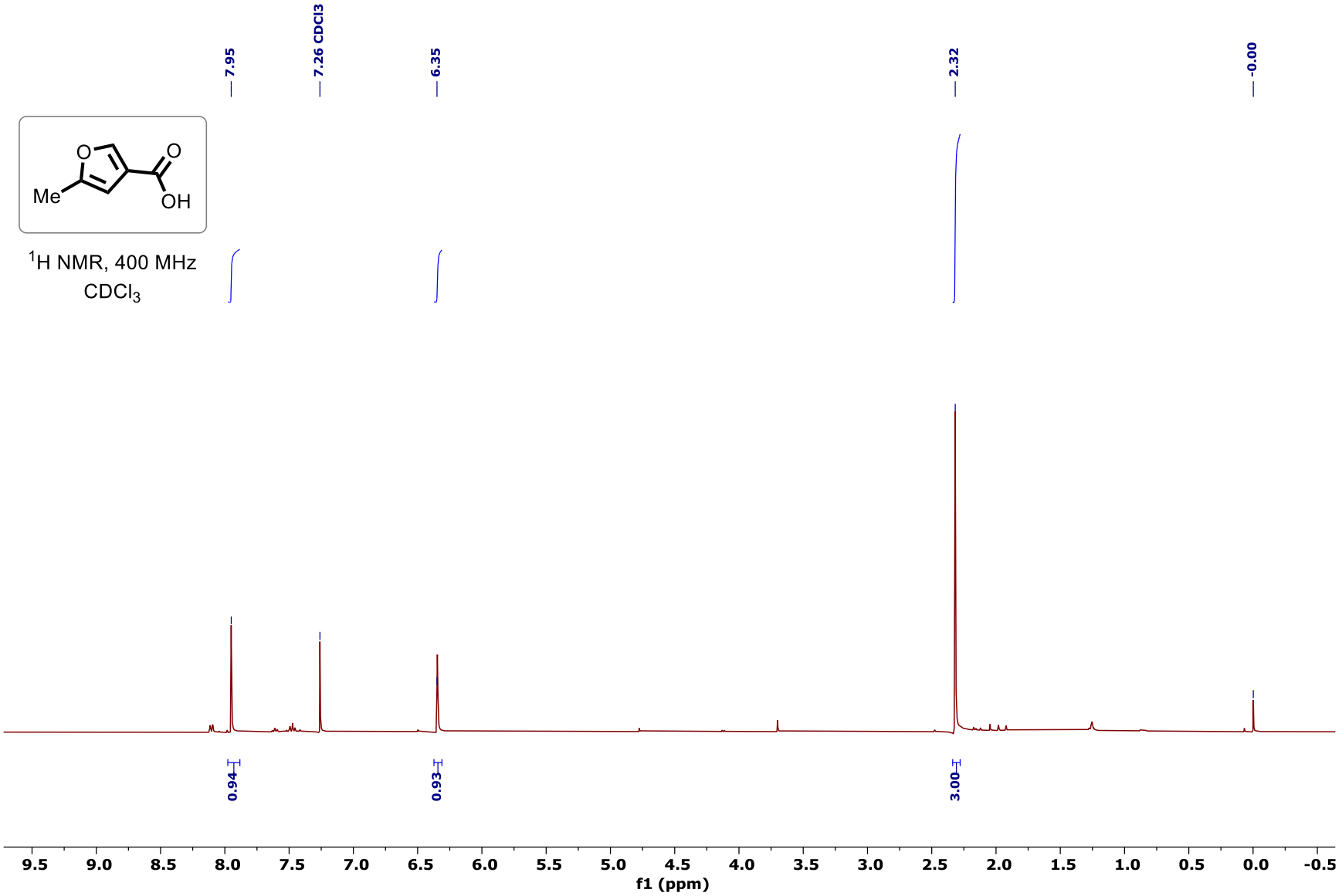
^{1}H NMR spectrum of 3,6-Dimethylhexahydrobenzofuran-4(2H)-one (21′):



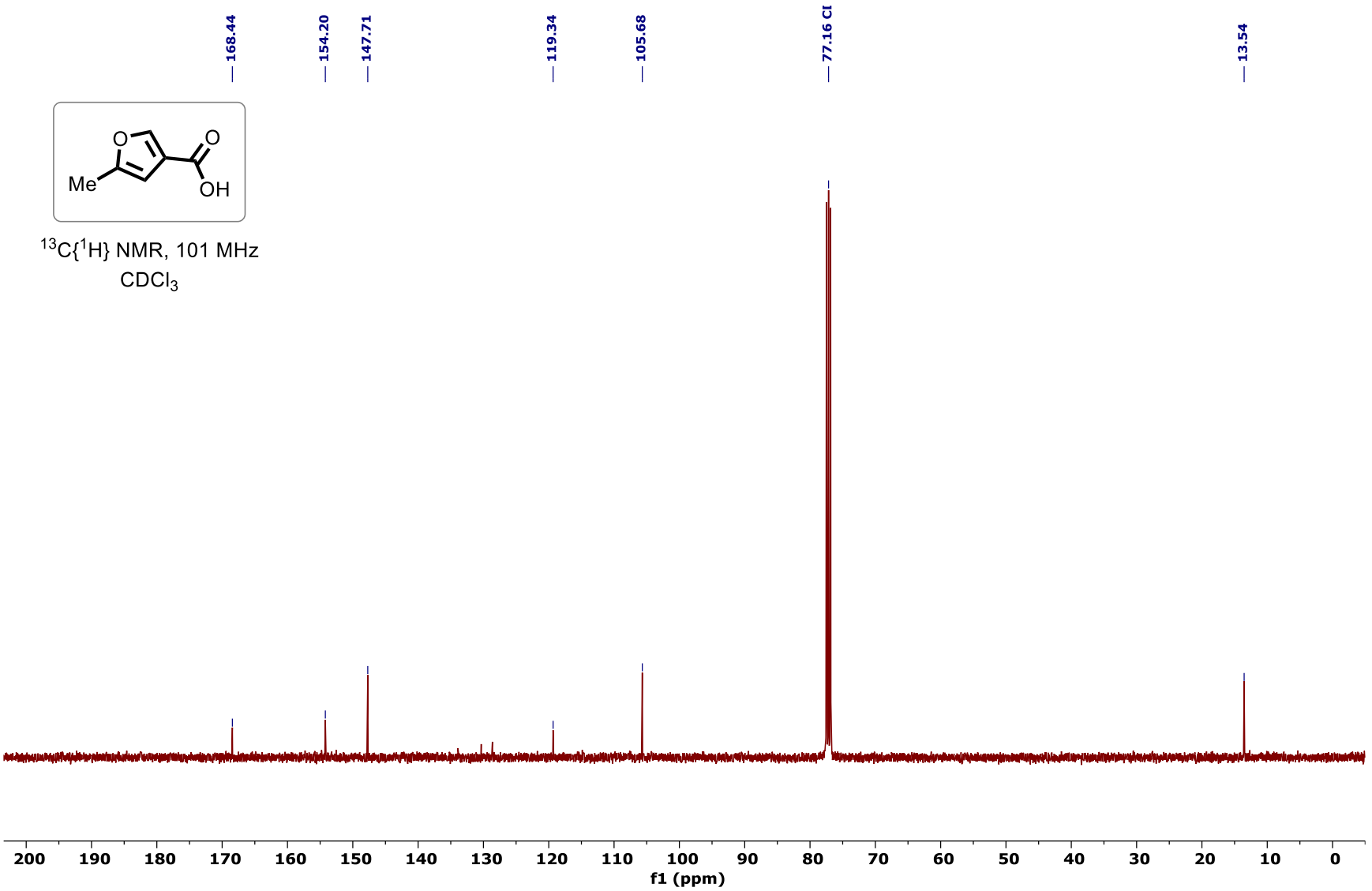
$^{13}C\{^{1}H\}$ NMR spectrum of 3,6-Dimethylhexahydrobenzofuran-4(2H)-one (21′):



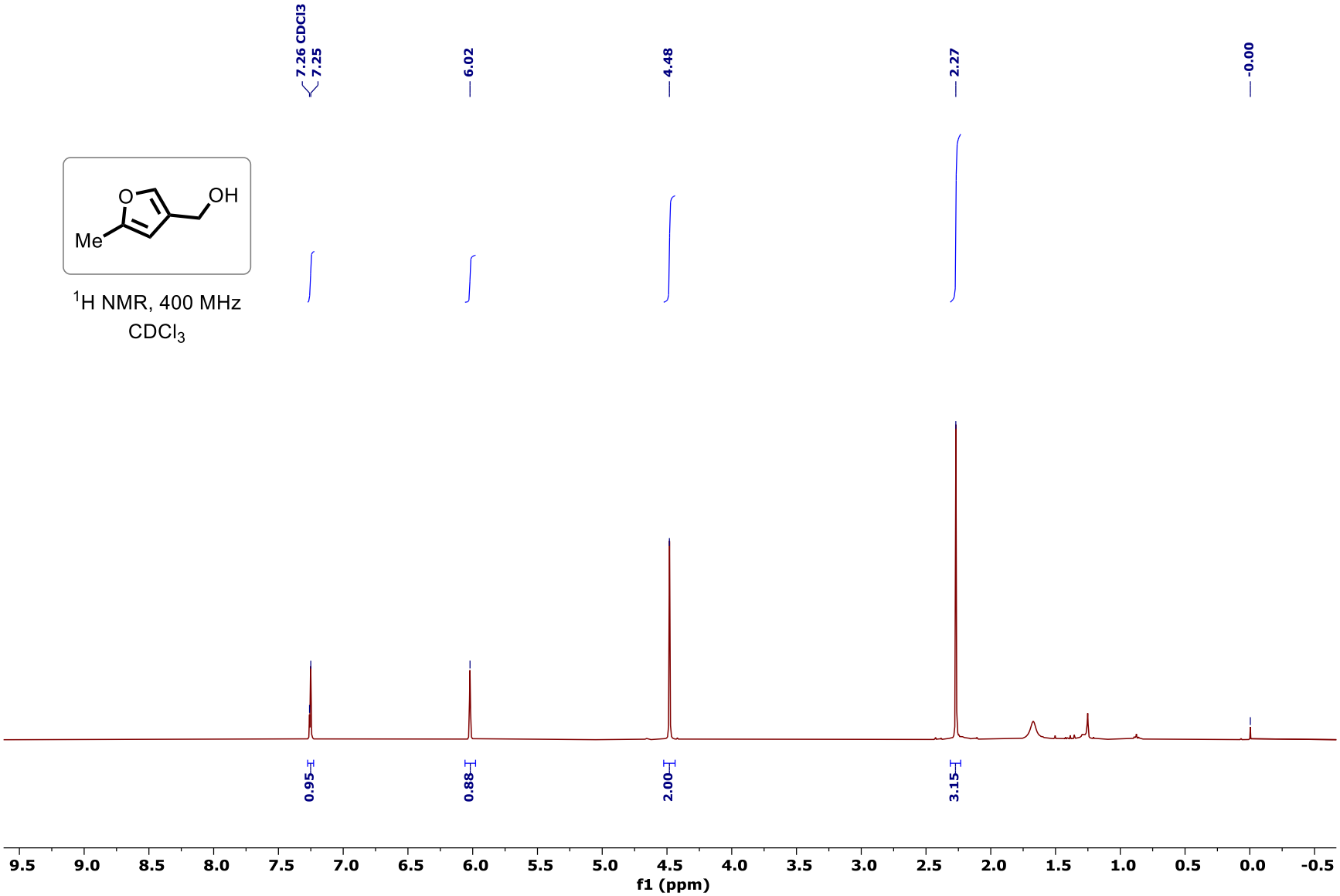
^{1}H NMR spectrum of Methylfuroic acid (27):



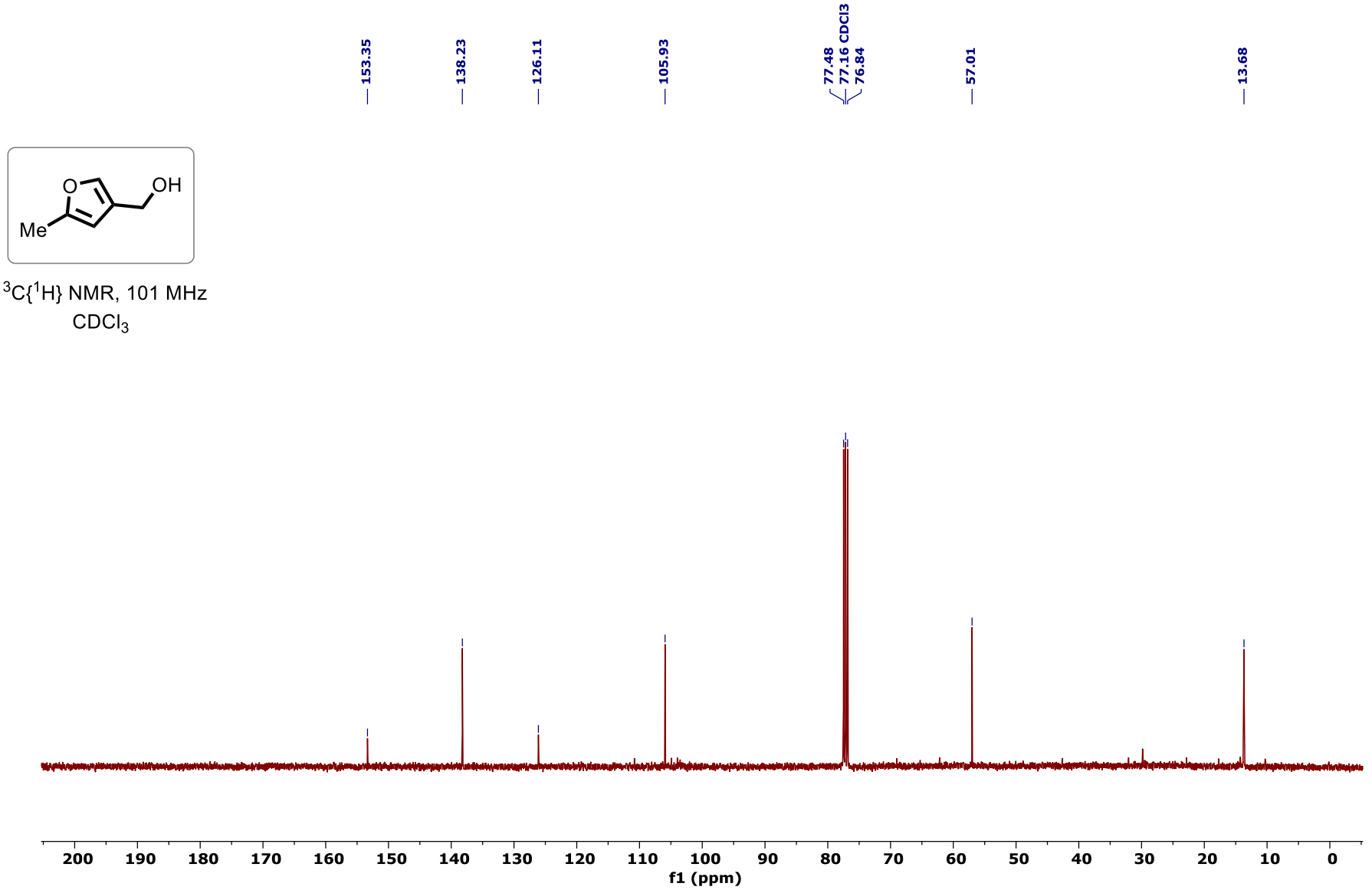
$^{13}C\{^{1}H\}$ NMR spectrum of Methylfuroic acid (27):



^{1}H NMR spectrum of (5-methylfuran-3-yl)methanol (S-27):



^{13}C NMR spectrum of (5-methylfuran-3-yl)methanol (S-27):



$^{13}C\{^{1}H\}$ NMR, 101 MHz
$CDCl_3$