# Enabling the Cross-Coupling of Tertiary Organoboron Nucleophiles Through Radical Mediated Alkyl Transfer

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## Supplementary Material

**General considerations**

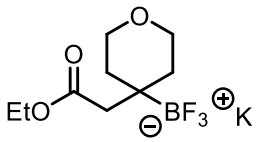
All reactions were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. DMA was purchased as 99.9%, extra dry. $K_2HPO_4$ was stored and dispensed in a dry glovebox. $IrCl_3 \cdot xH_2O$, and $Ni(TMHD)_2$ were purchased from commercial sources. All other reagents were purchased commercially and used as received. Photoredox reactions were irradiated by 1.2 W/ft. blue LED (420 nm) light strips, coiled in a circular setup approximately 38 inches in length. To accelerate the reactions, irradiation with 2–4 Kessil H150 blue LED flood lamps can also be used to complete reactions in under 24 h. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500 MHz spectrometer. $^{19}F$ NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). $^{11}B$ NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All $^{11}B$ NMR chemical shifts were referenced to an external $BF_3 \cdot OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz) and integration. The $^{13}C$ signal of the carbon bonded to boron was not observed in all cases because of quadrupolar relaxation.

**General Procedure for Conversion of Boronic Acid Derivatives to Alkyltrifluoroborate:**

To a solution of boronic acid derivative in MeOH (0.1 M) at 0 ºC was added saturated aq $KHF_2$ (4.5 M) dropwise over 30 min and then subsequently stirred for 3 h to rt. The resulting suspension was concentrated under reduced pressure. $H_2O$ was azeotropically removed by suspension in toluene (100–150 mL) followed by rotary evaporation. The remaining solid was dried under high vacuum overnight. The resultant solid was resuspended in hot acetone and filtered. The filtrate was then concentrated to minimal volume, and the trifluoroborates were precipitated by the addition of cold $Et_2O$, $CH_2Cl_2$, and/or pentanes.

**General Enone Borylation Procedure:**

Following a slightly modified literature procedure,[1] a flask was charged with CuBr (14.8 mg, 0.1 mmol), CyJohnPhos (35 mg, 0.1 mmol), bisboronic acid (537.9 mg, 6 mmol) and NaO*t*-Bu (144.2 mg, 1.5 mmol). The flask was evacuated and purged 3 times with argon. EtOH (50 mL) and enone (5.0 mmol) were added via syringe, and the mixture was stirred for 21 h. The reaction mixture was filtered through a plug of Celite and then rinsed with EtOAc (3 x 40 mL). The filtrate was concentrated, and the resultant oil was dissolved in MeOH (50 mL). This solution was cooled in an ice-bath, and then a solution of saturated $KHF_2$ (42.5 mmol, 4.5 M) was added dropwise. The mixture was warmed to rt and was stirred for 3.5 h. The suspension was then evaporated to dryness. The resultant solid was triturated and sonicated with hot acetone and filtered three times. The filtrate was then concentrated to a minimal volume, and the alkyltrifluoroborates were precipitated through dropwise addition of cold $Et_2O$ (10–50 mL). The mixture was filtered, washed with cold $Et_2O$ (5–20 mL), and dried on high vacuum overnight to yield the desired β-trifluoroboratoester or –ketone.

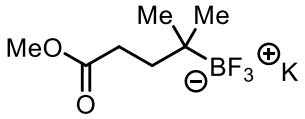



**S1**

**Potassium (4-(2-Ethoxy-2-oxoethyl)tetrahydro-2H-pyran-4-yl)trifluoroborate (S1)** prepared from ethyl 2-(tetrahydro-4H-pyran-4-ylidene)acetate (5 mmol) and obtained in 32% yield, 445 mg as a white crystalline solid, mp = 187 – 190 ºC.
$^1H$ NMR (500 MHz, acetone-$d_6$) δ 4.01 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.64 (m, 2H), 3.55 – 3.49 (m, 2H), 2.15 (s, 2H), 1.73 – 1.62 (m, 2H), 1.33 – 1.25 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).
$^{13}C$ NMR (125.8 MHz, acetone-$d_6$) δ 175.3, 64.4, 58.9, 42.2, 33.5, 13.9.
$^{19}F$ NMR (470.8 MHz, acetone-$d_6$) -146.8.
$^{11}B$ NMR (400 MHz, acetone-$d_6$) δ 5.42.
IR (ATR): ν = 1720, 1688, 1308, 1228, 1088, 1016, 999, 964, 533 $cm^{-1}$.
HRMS (ESI) m/z calc. for $C_9H_{15}BF_3O_3^-$ (M-) 238.1103, found 238.1095.

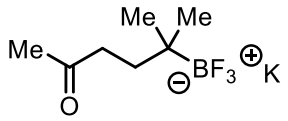
**Reductive Alkene Coupling Procedure:**

Based on a slightly modified literature procedure,[2] to a solution of 4,4,5,5-tetramethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (5.0 mmol) in 20 mL of EtOH was added anhydrous $Na_2HPO_4$ (2.12 g, 10.0 mmol), $Fe(acac)_3$ (177 mg, 10 mol %), acceptor olefin (15.0 mmol), and $PhSiH_3$ (1.62 g, 15.0 mmol). The resulting mixture was heated in an oil bath preheated to 60 °C with stirring (until GC analysis indicated the consumption of starting material boronate ester, usually 2–4 h). The reaction mixture was then cooled to rt and diluted with brine (20 mL) and EtOAc (20 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were combined, washed with brine (20 mL), dried ($Na_2SO_4$), filtered, and concentrated under reduced pressure. The resulting crude product was then purified by silica gel flash column chromatography. The pinacol boronate obtained after column chromatography was dissolved in MeOH (10–20 mL) and converted to the alkyltrifluoroborate by addition of saturated aq $KHF_2$ (12 mL, 4.5 M, 54 mmol) at 0 ºC. The mixture was then warmed to rt and stirred for 3.5 h. The suspension was then evaporated to dryness. The resultant solid was triturated and sonicated with warm acetone and filtered three times. The filtrate was then concentrated to a minimal volume, and the alkyltrifluoroborate was precipitated through dropwise addition of cold $Et_2O$ and/or pentanes (10–30 mL). The mixture was filtered, washed with cold $Et_2O$ (5–10 mL), and then dried on high vacuum overnight to yield the desired alkyltrifluoroborates.



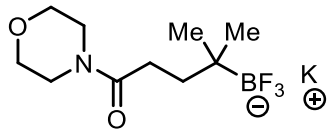

**S2**

**Potassium Trifluoro(5-methoxy-2-methyl-5-oxopentan-2-yl)borate (S2)** prepared using methyl methacrylate as the olefin acceptor and obtained in 44% yield, 522 mg as an off-white solid, mp = 129 – 131 ºC.
$^1$H NMR (500 MHz, acetone-$d_6$) δ 3.55 (s, 3H), 2.47 – 2.17 (m, 2H), 1.55 – 1.30 (m, 2H), 0.68 (s, 6H).
$^{13}$C NMR (126 MHz, acetone-$d_6$) δ 175.6, 137.0, 50.1, 36.0, 30.3, 24.1.
$^{11}$B NMR (128.4 MHz, acetone-$d_6$) δ 6.19.
$^{19}$F NMR (470.8 MHz, acetone-$d_6$) δ -150.5.
IR (ATR): : ν = 1732, 1646, 1236, 1174, 1026, 981, 937, 750, 567 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_7H_{13}BF_3O_2^-$ (M-) 196.0997, found 196.0975.




**S3**

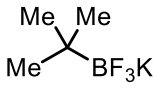
**Potassium Trifluoro(2-methyl-5-oxohexan-2-yl)borate (S3)** prepared using methyl vinyl ketone as the olefin acceptor, 45% yield, 497 mg as a colorless, viscous oil.
$^1$H NMR (500 MHz, acetone-$d_6$) δ 2.47 – 2.28 (m, 2H), 2.03 (s, 3H), 1.37 – 1.30 (m, 2H), 0.67 (s, 6H)
$^{13}$C NMR (125.8 MHz, acetone-$d_6$) δ 210.5, 40.1, 34.9, 28.6, 24.2.
$^{11}$B NMR (128.4 MHz, acetone-$d_6$) δ 6.15 (with residual $BF_4$).
$^{19}$F NMR (470.8 MHz, acetone-$d_6$) δ -149.0 (with residual $BF_4$).
IR (ATR): : ν = 1696, 1471, 1296, 1254, 1016, 749, 480 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_7H_{13}BF_3O^-$ (M-) 181.1012, found 181.1029.



**S4**

**Potassium Trifluoro(2-methyl-5-morpholino-5-oxopentan-2-yl)borate (S4)** prepared using 1-morpholinoprop-2-en-1-one as the olefin acceptor, 53% yield, 764 mg as a white crystalline solid, mp = 164 – 166 ºC.
$^{1}$H NMR (500 MHz, $CD_3CN$) δ 3.76–3.63 (m, 4H), 3.57 (s, 4H), 2.49–2.39 (m, 2H), 1.46–1.35 (m, 2H), 0.78 (s, 6H).
$^{13}$C NMR (125.8 MHz, $CD_3CN$) δ 174.2, 66.5, 46.0, 41.4, 36.8, 29.8, 24.2.
$^{11}$B NMR (128.4 MHz, $CD_3CN$) δ 6.00.
$^{19}$F NMR (470.8 MHz, $CD_3CN$) δ -149.7.
IR (ATR): ν = 1645, 1482, 1429, 1281, 1114, 1038, 1017, 963, 935, 524 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_{10}H_{18}BF_3NO_2^-$ (M-) 252.1388, found 252.1383.

**Trifluoroborates below were synthesized according to known literature procedures:**



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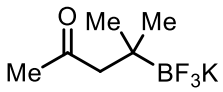
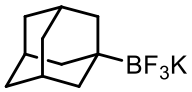
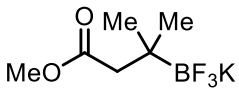


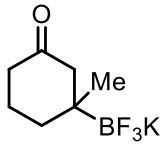
**38**



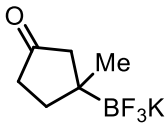
**S5**



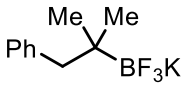
**S6**



**S7**



**S8**



**S9**

Spectral data matched that reported in the literature[1,3–5]

**Selected reaction optimization studies:**

High Throughput Experimentation was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. The screens were analyzed by UPLC with addition of an internal standard. The areas for the internal standard (IS), aryl bromide (ArBr), and product (P) from each of the screens are shown in the tables below. The ratios calculated are pertinent only to that specific screen; the ratios from one screen should not be quantitatively compared to those from a different screen. The results of the screens are illustrated in a heat map. The information conveyed in these heat maps is two-fold. First, the size of the circle corresponds to the amount of product. The larger the circle, the more product formed during the reaction. Secondly, the shade of the circle corresponds to the amount of starting material, in this case aryl bromide, remaining. The lighter the circle, the less aryl bromide remaining after 24 h. Therefore, for a reaction resulting in high conversion and product formation, the circle will be both large and light.

*Procedure for screening at 10 μmol scale:*

To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) solution of Ni source (0.1 equiv) dissolved in THF for [$Ni(COD)_2$] or DMA [for all Ni(II) sources], and 2) ligand (0.1 equiv) in DMA. After addition, the plate was sealed and the vials were allowed to stir at 60 ºC for 1 h to ensure complexation of ligand to the catalyst. Then, 100 μL of a stock solution containing potassium *tert*-butyltrifluoroborate (1.5 equiv), aryl bromide (1.0 equiv – 10 μmol), photocatalyst (0.03 equiv), and internal standard (0.1 equiv) was added to each vial. The vials were sealed and stirred over blue LED lights at rt (~24 ºC). After 24 h the reactions were opened to air and diluted with 500 μL of MeCN. After stirring, the diluted block for fifteen minutes15 min, 25 μL aliquots were then taken from the reaction vials and dosed into a 96-well UPLC block. These aliquots were further diluted by the addition of 700 μL of MeCN. The reaction mixtures were then analyzed by UPLC.

Note: If examining the effect of solid additives, these were added as slurries in THF or DCE (0.1 M) followed by solvent removal by Genovac evaporation before the following steps. If looking at the effect of liquid additives, these were added as stock solutions in DMA (1.0 M) after dosing all other ingredients.


Conditions: 3 mol % Ir cat **1**, 10 mol % Ni, 10 mol % ligand, no base, 0.05 M DMA

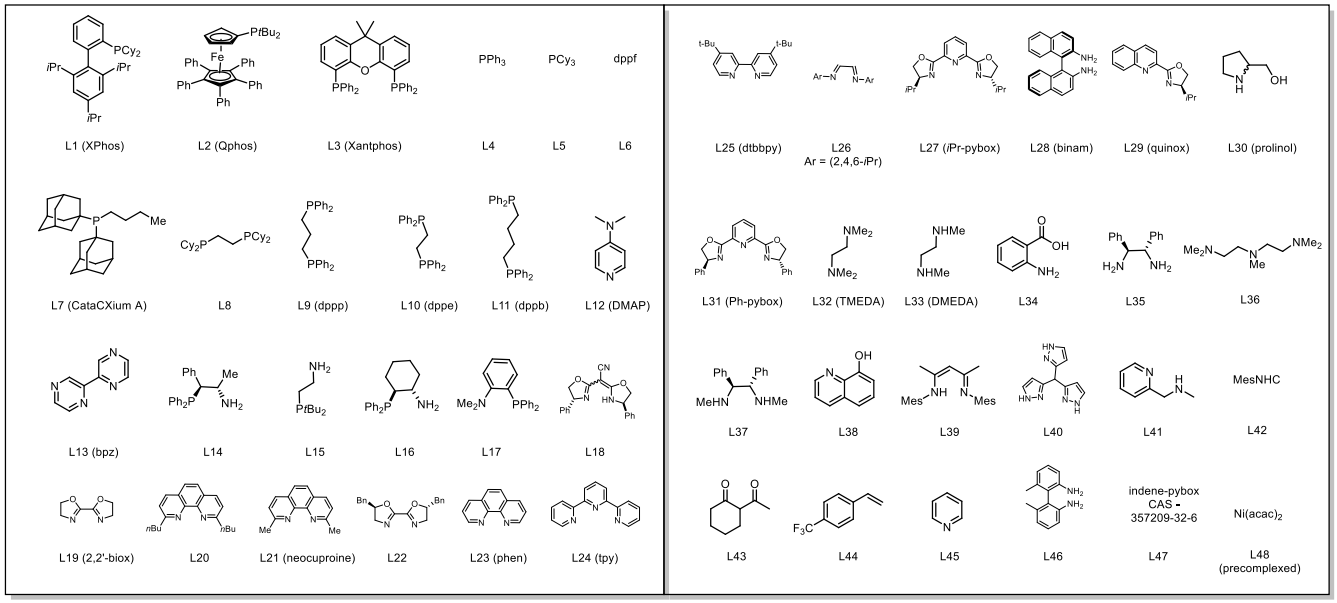
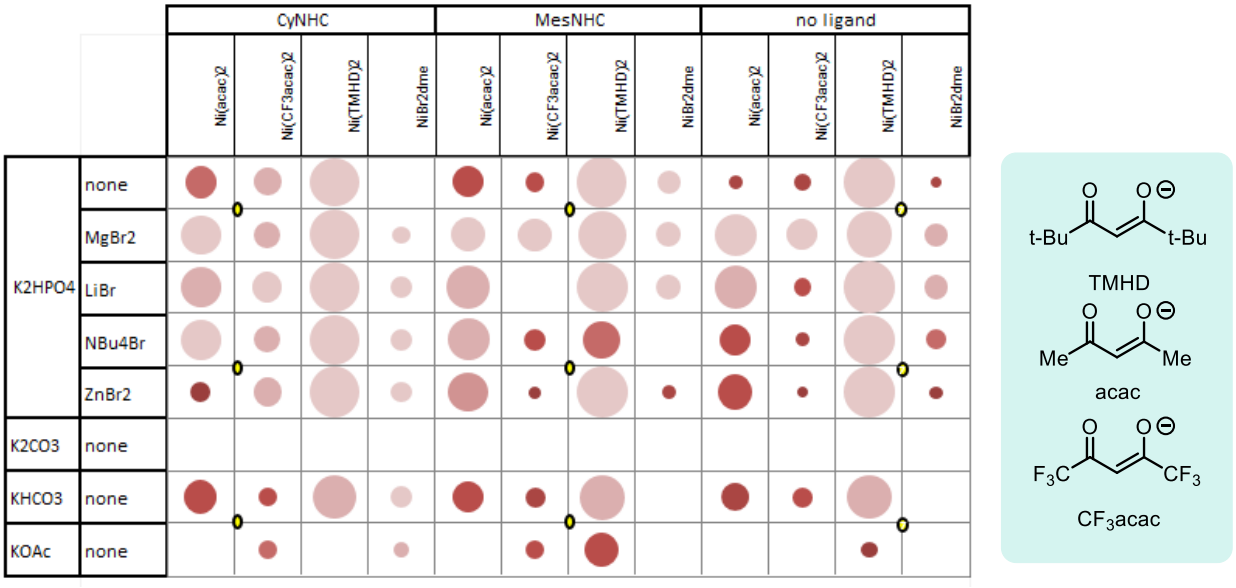



**Figure S1: Broad Ligand Screening for Baseline Conversion**

**Optimizing Precomplexed Diketonate Ligand Scaffold**




Conditions: 3 mol % Ir cat. **1**, 10 mol % Ni, 10 mol % ligand, 20 mol % additive, 1 equiv base, 0.05 M DMA

**Figure S2: Effects of ligand structure, additives, NHC additives, and bases on overall yield**

*Procedure for screening at 0.1 mmol scale:*

To a 1 dram vial containing a Teflon coated magnetic stir bar was added a stock solution of potassium *tert*-butyltrifluoroborate (2.0 equiv), aryl halide (1 equiv), photocatalyst **1** (3 mol %), and internal standard 4,4'-di-*tert*-butylbiphenyl (10 mol %) in THF. The solvent was then removed under high vacuum. To the reaction mixture was then added any additional base (1.0 equiv). The vial was then brought into a nitrogen filled glovebox and $Ni(TMHD)_2$ (10 mol %) was dosed in the reaction solvent of choice. The reactions were then monitored by GC analysis after stirring for 24 h with the product/IS ratios given below

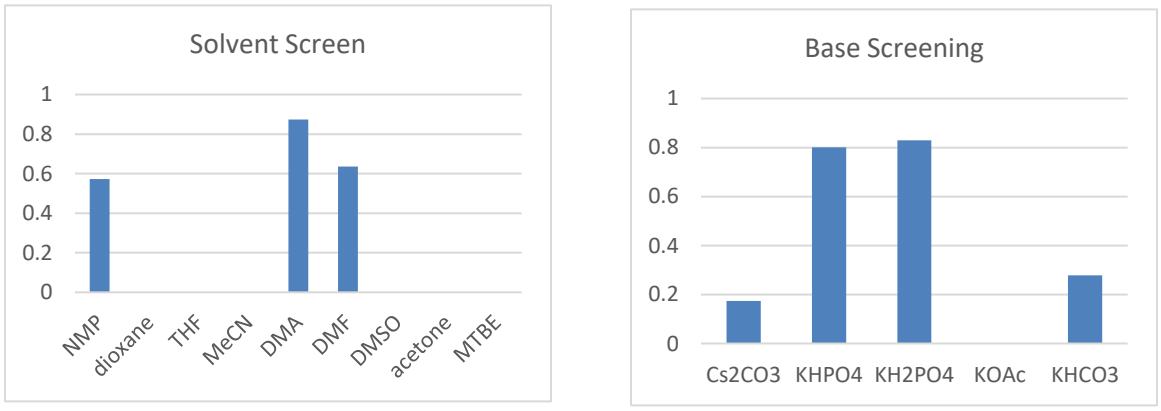



**Figure S3: Benchtop Screening of Solvents and Bases**

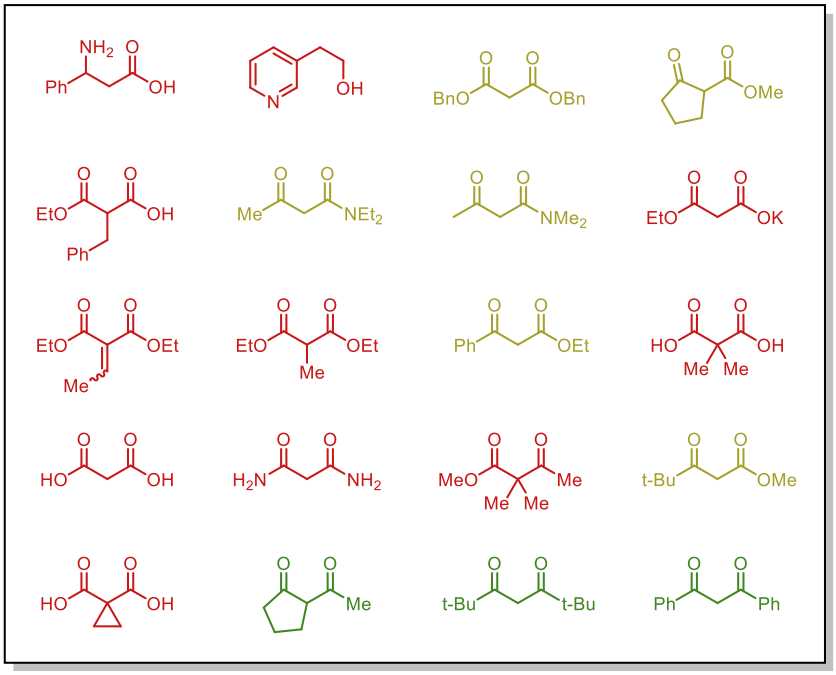


**Figure S4: Similar Structures Examined as Ligands with Relative Conversion (Red: <5%, Yellow: 5–50 %, Green: >50%)**

**Procedure for nickel complexation with above ligands:**

Based on an adapted literature procedure,[6] 2.0 equiv of ligand (0.2 mmol) were dosed into a vial $Ni(OAc)_2$ x $4H_2O$ (1.8 mg, 0.1 mmol) . To the vial was added 0.5 mL of MeOH. The vial was then capped and stirred at 50 ºC overnight to induce complexation of the ligand to the nickel center. The solvent was then removed under high vacuum to afford green to purple solids or semi-solids. The residual solid material was then dissolved in DMA and dosed as a 0.1 M stock solution.

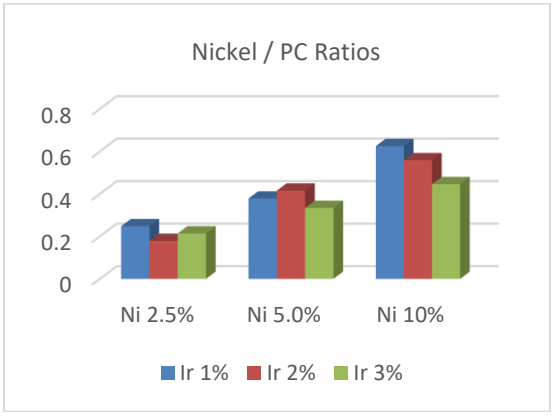



**Figure S5: Nickel to Photocatalyst Ratio Array (P/IS ratios under standard conditions after 24 h)**

| | protodehalo / IS | SM / IS | prod / IS |
|---|---|---|---|
| CzIPN (3 mol %) | 2.073079791 | 0 | 1.354213274 |
| No PC | 0.623495552 | 2.10151753 | 0.107796965 |
| No base | 1.880733945 | 0.642201835 | 1.384301733 |
| No Ni | 0.623641304 | 3.65625 | 0 |
| No light | 0.011927181 | 3.925925926 | 0.026365348 |
| Ni(COD)2 / ligand | 0.450913242 | 1.146118721 | 2.171803653 |
| Std. cond | 0.298283262 | 0 | 3.617310443 |
| No Zn | 0.448275862 | 0 | 3.065922921 |
| NiI2 / ligand | 0.108389467 | 3.259644825 | 0.309246785 |
| pyridine (20 mol %) | 1.993569132 | 0.437299035 | 0.080385852 |

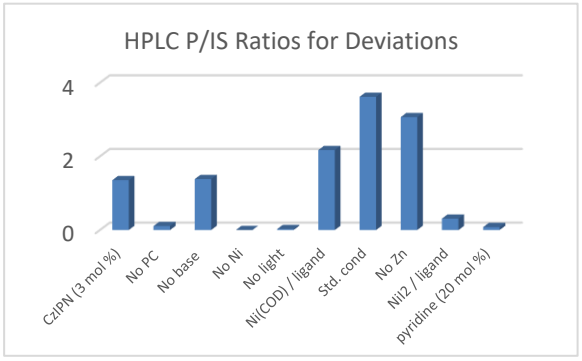
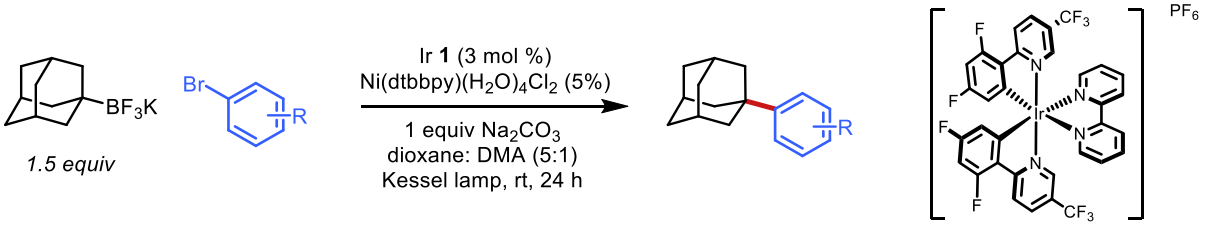


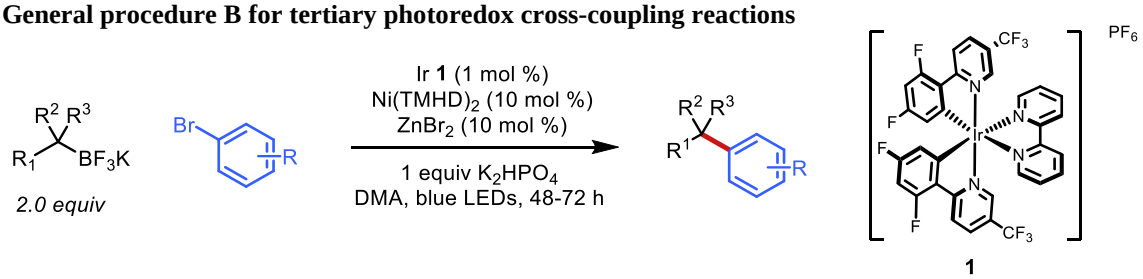

**Figure S6: Deviation from Standard Conditions (HPLC ratios after 48 h)**

**General procedure A for adamantyltrifluoroborates photoredox cross-coupling reactions:**




To a 4 dram borosilicate glass vial equipped with a Teflon-coated magnetic stir bar was added adamantyltrifluoroborate **S5** (181 mg, 0.75 mmol, 1.5 equiv), Ir[dFCF$_3$ppy]$_2$(bpy)PF$_6$ **1** (15.0 mg, 0.03 equiv), Ni(dtbbpy)(H$_2$O)$_4$Cl$_2$ (7.0 mg, 0.05 equiv), Na$_2$CO$_3$ (1.0 mmol, 2 equiv) and aryl bromide (0.5 mmol, 1 equiv) (liquid aryl bromides were added with solvent). The vial was then purged and evacuated 3x under argon atmosphere. To the vial was then added dioxane/DMA in a (6 mL in 5:1 mixture). The entire mixture was then sparged for 10 min with argon and then placed on a stir plate 4 cm away from 4 Kessil H150 blue flood lamps for 24 h. Two fans were placed above the reaction setup (shown below) to maintain an ambient temperature of 28–30 °C. After completion, the reaction mixture was diluted with an equal volume of H$_2$O and extracted with EtOAc (3 x 5 mL). The organic layer was then dried (Na$_2$SO$_4$), filtered, concentrated onto silica, and then purified by silica gel chromatography, eluting with EtOAc and hexanes to obtain the products in pure form.

**General procedure B for tertiary photoredox cross-coupling reactions**




To a 4 dram borosilicate glass vial equipped with a Teflon-coated magnetic stir bar was added tertiary alkyltrifluoroborate (1.0 mmol, 2 equiv), Ir[dFCF$_3$ppy]$_2$(bpy)PF$_6$ **1** (5.0 mg, 0.01 equiv), and aryl bromide (0.5 mmol, 1 equiv) (liquid aryl bromides were added with solvent). The vial was then transferred into a glove box where Ni(TMHD)$_2$ (21.2 mg, 0.05 mmol), ZnBr$_2$ (11.3 mg, 0.05 mmol), and anhydrous K$_2$HPO$_4$ (87 mg, 0.5 mmol) were added. The vial was then capped and removed from the glovebox. Anhydrous DMA (5 mL) was added to the vial via syringe under inert atmosphere. The vial was then sparged with argon for 10 min. The vial containing all the reagents was further sealed with parafilm and Teflon tape and stirred for 48–72 h approximately 4 cm away from a ring of blue LED lights strips (see below). A fan was blown across the reaction setup to maintain an ambient temperature around 27 °C. After completion, the crude reaction mixture was diluted with H$_2$O (10 mL) and extracted with Et$_2$O (2 X 10 mL) EtOAc (5 mL). The organic layer was then washed with saturated aq NaCl (5 mL) and dried (Na$_2$SO$_4$). The resulting organics were then concentrated, and the residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain products in pure form.

**General procedure C for tertiary photoredox cross-couplings**

Setup for these reactions remains the same as procedure B, however, the reactions are instead irradiated with 4 Kessil H150 blue flood lamps at 30 °C for 24 h. The greater light intensity in these systems significantly accelerates reaction progress and mirrors acceleration seen in other systems.[7]

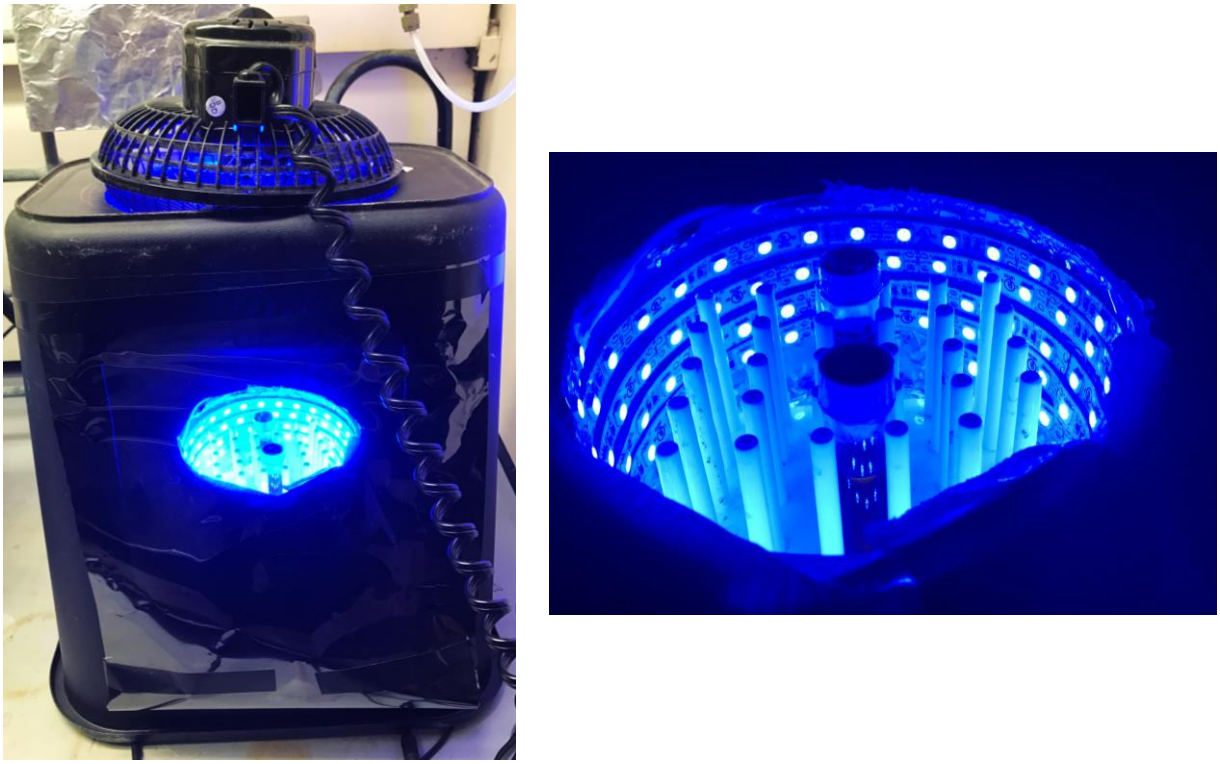


**Figure S7:** Procedure B photoredox cross-coupling reaction set-up (0.50 mmol scale)

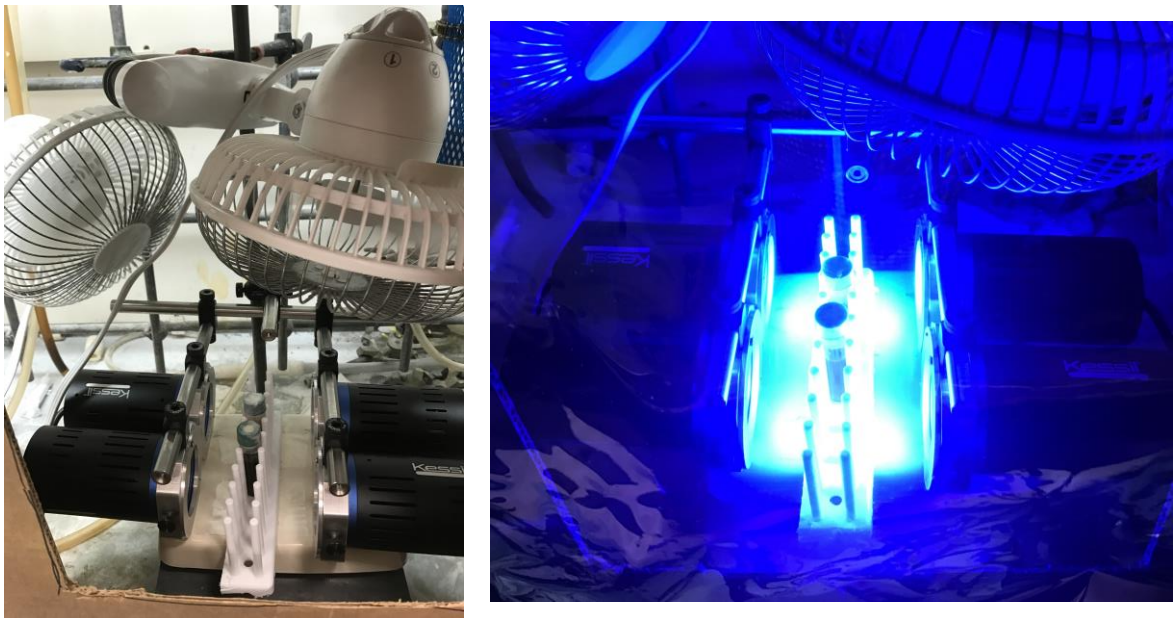


**Fig S8**: Procedure A and C Kessil lamp setup for shortened reaction times (0.25 – 0.50 mmol scale)

**Cyclic Voltammetry (CV) Data**

Electrochemical measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer (observed in 0.002 M MeCN; $[N(Bu)_4](PF_6)$ = 0.1 M; Ag/AgCl = electrode; reported in SCE based on a ferrocene internal standard).

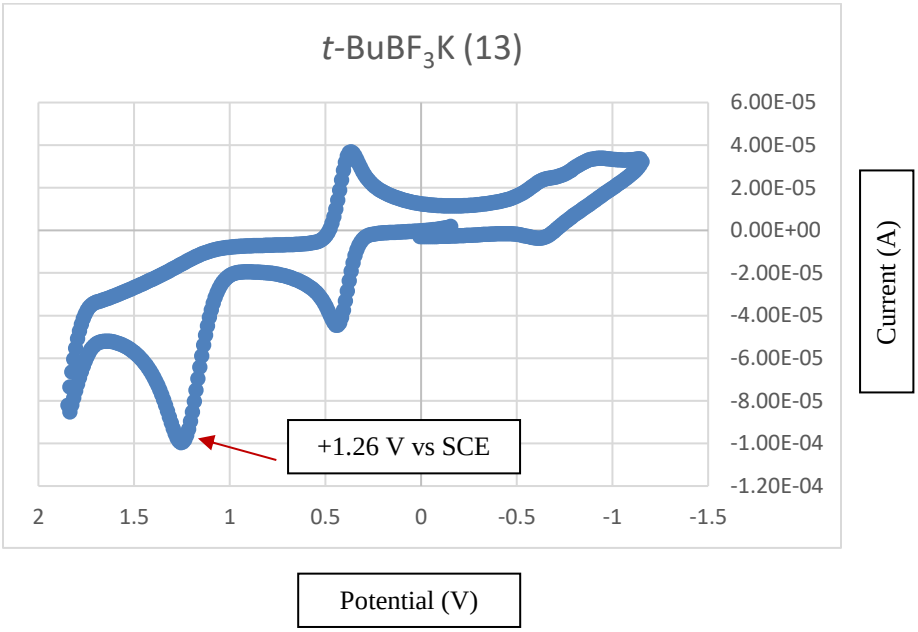



**Figure S9: Oxidation Potential of Tertiary Alkyltrifluoroborate 13**

**Alkyltrifluoroborate Oxidation Experiment**

Based on a literature procedure reported by Akita,[5] a one dram vial equipped with a Teflon coated magnetic stir bar was charged with alkyltrifluoroborate **13** (82 mg, 0.50 mmol) and $Ir[dFCF_3ppy]_2(bpy)PF_6$ **1** (10 mg, 0.01 mmol), then acetone (5.0 mL), MeOH (0.5 mL) and methyl vinyl ketone (140 mg, 2.0 mmol) were added under inert atmosphere. The vessel was degassed by Ar sparging for 10 min. The vial was then exposed to the blue LED setup in procedure B (vide supra) at rt for 24 h. The resulting mixture was extracted with $CH_2Cl_2$, and the combined organic layers were dried ($Na_2SO_4$) and filtered. The filtrate was concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel to afford **14** as a colorless oil (47 mg, 73%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 2.44-2.40 (m, 2H), 2.18 (s, 3H), 1.52-1.48 (m, 2H), 0.91 (s, 9H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$): δ 209.2, 39.1, 37.0, 29.5, 29.1, 28.8.
Spectroscopic data matches that previously reported.[8]

**Nickel oxidative addition complex synthesis:**

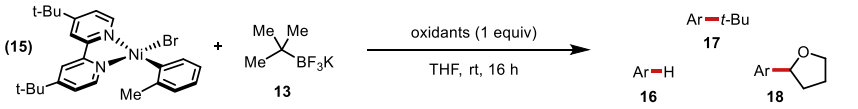
Nickel complex (**15**) was prepared according to an adapted literature procedure.[9] A dry, clean 50 mL round bottom flask was charged a Teflon coated stir bar and 536 mg of 4,4'-di-*tert*-butyl-2,2'-bipyridine (2.0 mmol), and brought into a glove box under inert atmosphere. In the glove box, 5 mL of dry, degassed, cooled toluene (~20 ºC) was added to dissolve the ligand. To the mixture was then added a solution containing 550 mg of $Ni(COD)_2$ (2.0 mmol) in 20 mL of cooled toluene (~20 ºC), followed by 3.4 mL of 2-bromotoluene (20 mmol). The mixture was then stirred to room temperature over the course of 9 h. The resultant orange mixture was filtered and then concentrated to a residue under high vacuum overnight. The residue was then extracted with ether. Evaporation of the ether afforded **15** as an orange powder (647 mg, 65%). $^1$H NMR (500 MHz, acetone-$d_6$) δ 9.27 (d, $J$ = 4.4 Hz, 1H), 8.40 (d, $J$ = 19.0 Hz, 2H), 7.68 (s, 1H), 7.57 – 7.48 (m, $J$ = 6.4 Hz, 1H), 7.33 (s, 1H), 7.07 – 6.95 (m, $J$ = 5.5 Hz, 1H), 6.77 – 6.62 (m, 3H), 3.01 (s, 3H), 1.43 (s, 9H), 1.36 (s, 9H).

**Nickel oxidative addition complex experiments:**

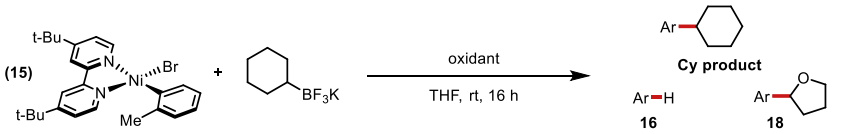
To a 1 dram vial was added **15** (12.5 mg, 0.025 mmol), oxidant (0.025 mmol), and alkyltrifluoroborate (0.025 mmol). The vial was then capped, purged and evacuated three times. Under inert atmosphere, 0.5 mL of dry, degassed THF was introduced via syringe. For the oxidant reactions, these were wrapped with tin foil and stirred vigorously overnight. For the vials containing photocatalyst, the oxidant was replaced with 2.5 mg of photocatalyst (0.0025 mmol) and the reactions were stirred vigorously in front of a blue LED light setup (see above) overnight.

After 16 hours, the reactions were quenched by addition of 1 mL of acetonitrile containing 10 mol % of 4,4'-di-*tert*-butylbiphenyl. Aliquots from the reaction were then taken and further diluted with acetonitrile before being analyzed by GCMS. Yields were determined by ratio to internal standard.

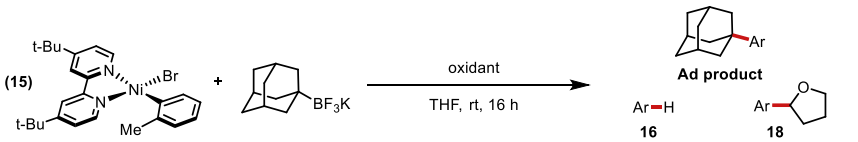
***Stoichiometric Experiments with Nickel (II) Oxidative Addition Complex***




| Oxidant | Ar-H (16) | product (17) | THF-adduct (18) |
|---|---|---|---|
| Ir cat (10 mol %) with hν (420 nm) | 3% | 0% | 10% |
| $AgNO_3$ (dark) | 15% | 0% | 0% |
| DMP (dark) | 4% | 0% | 15% |
| CAN (dark) | 6% | 0% | 17% |
| TBPA $SbCl_6$ (dark) | 9% | 0% | 20% |

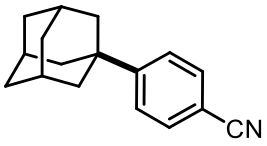



| Oxidant | Ar-H (16) | Cy product | THF-adduct (18) |
|---|---|---|---|
| Ir cat (10 mol %) with hν (420 nm) | 4% | 38% | 5% |



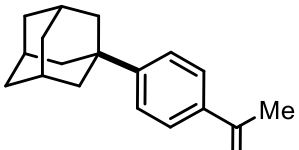

| Oxidant | Ar-H (16) | Ad product | THF-adduct (18) |
|---|---|---|---|
| Ir cat (10 mol %) with hν (420 nm) | 10% | trace | 7% |

## Compound Characterization Data



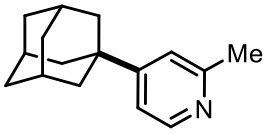

**19**

**4-(Adamantan-1-yl)benzonitrile (19):** obtained as a white amorphous solid using procedure A at 0.50 mmol scale (76 mg, 64%), mp = 125–128 ºC.
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 2.12 (s, 3H), 1.90 (s, 6H), 1.83 – 1.72 (m, 6H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.8, 132.2, 126.0, 119.4, 109.4, 42.9, 37.0, 36.7, 28.8.
IR (ATR): ν = 2916, 2898, 2847, 2233, 1506, 1343, 1101, 849, 806, 563 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{17}H_{19}N$ (M+) 237.1517, found 237.1501.



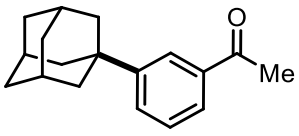

**20**

**1-(4-((3r,5r,7r)-Adamantan-1-yl)phenyl)ethan-1-one (20):** obtained as a white solid using procedure A at 0.50 mmol scale (97 mg, 76%), mp = 108–110 ºC.
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H), 2.12 (s, 3H), 1.92 (s, 6H), 1.83 – 1.72 (m, 6H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.1, 157.1, 134.8, 128.5, 125.3, 43.0, 36.8, 36.8, 28.9, 26.7.
IR (ATR): ν = 2907, 2848, 1678, 1602, 1359, 1267, 1245, 832, 804, 596 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{18}H_{22}O$ (M+) 254.1671, found 254.1675.



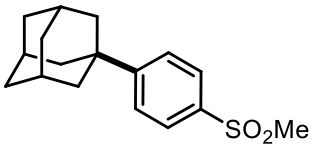

**21**

**4-((3r,5r,7r)-Adamantan-1-yl)-2-methylpyridine (21):** obtained as a pale yellow semi-solid using procedure A at 0.25 mmol scale (29 mg, 51%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 5.4 Hz, 1H), 7.11 (s, 1H), 7.06 (d, *J* = 5.4 Hz, 1H), 2.55 (s, 3H), 2.11 (s, 3H), 1.89 (s, 6H), 1.83 – 1.75 (m, 6H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 160.1, 158.0, 148.9, 119.7, 117.4, 42.3, 36.5, 36.0, 28.6, 24.5.
IR (ATR): ν = 2901, 2848, 1602, 1550, 1449, 1397, 1296, 1038, 976, 837, 806 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{16}H_{21}N$ (M+) 227.1674, found 227.1665.



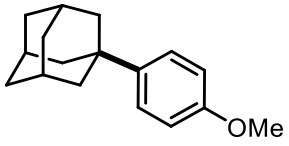

**22**

**1-(3-((3r,5r,7r)-Adamantan-1-yl)phenyl)ethan-1-one (22):** obtained as a colorless semi-solid with procedure A at 0.25 mmol scale (43 mg, 68%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.8 Hz, 1H), 2.61 (s, 3H), 2.12 (s, 3H), 1.94 (s, 6H), 1.82 – 1.75 (m, 6H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 193.8, 152.0, 137.2, 130.1, 128.5, 126.0, 124.8, 43.2, 36.8, 36.5, 29.0, 26.9.
IR (ATR): ν = 2900, 1847, 1682, 1426, 1355, 1270, 963, 789, 695, 588 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{18}H_{23}O$ (M+H) 255.1743, found 255.1748.



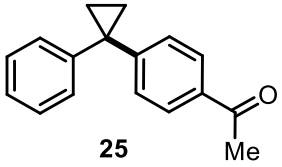

**23**

**1-(4-(Methylsulfonyl)phenyl)adamantane (23):** obtained as a white amorphous solid with procedure A at 0.25 mmol scale (66 mg, 91%), mp = 167–170 ºC.
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 3.04 (s, 3H), 2.13 (s, 3H), 1.92 (s, 6H), 1.83 – 1.72 (m, 6H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 157.8, 137.7, 127.4, 126.2, 44.7, 43.0, 37.0, 36.7, 28.8.
IR (ATR): ν = 2902, 2848, 1596, 1449, 1308, 1291, 1148, 1090, 954, 777, 558, 473 $cm^{-1}$
HRMS (EI) m/z calc. for $C_{17}H_{22}O_2S$ (M+) 290.1341, found 290.1341



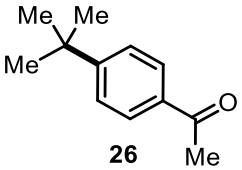

**24**

**(3r,5r,7r)-1-(4-Methoxyphenyl)adamantane (24)** obtained as a pale yellow oil using procedure A at 0.25 mmol scale (12 mg, 20%).
$^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 3H), 2.01 (s, 3H), 1.80 (s, 6H), 1.70 (s, 6H).
$^{13}$C NMR (125.8 MHz, DMSO-$d_6$) δ 157.4, 143.4, 125.9, 113.8, 55.3, 43.2, 36.6, 35.4, 28.7.
HRMS (EI) m/z calc. for $C_{17}H_{16}O$ (M+) 242.1671, found 242.1677.
Spectroscopic data matches with previously reported data.[10]



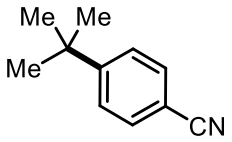

**25**

**1-(4-(1-Phenylcyclopropyl)phenyl)ethan-1-one (25):** obtained as a colorless oil with procedure A at 0.25 mmol scale (55 mg, 93% yield).
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.19 (m, 7H), 2.57 (s, 3H), 1.43 – 1.32 (m, 4H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 197.9, 151.9, 144.6, 135.0, 129.1, 128.6, 128.6, 128.0, 126.6, 30.2, 26.7, 17.2.
IR (ATR): ν = 3143, 2950, 1678, 1603, 1404, 1265, 957, 821, 760, 699, 598 $cm^{-1}$.
HRMS (EI) m/z calc. for $C_{17}H_{16}O$ (M+) 236.1201, found 236.1206.



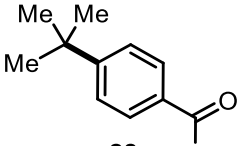

**26**

**1-(4-(*tert*-Butyl)phenyl)ethan-1-one (26)**: obtained as a colorless oil with procedure B (80 mg, 90%).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 2.58 (s, 3H), 1.36 (s, 9H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 198.0, 157.0, 134.8, 128.4, 125.7, 35.2, 31.2.
Spectroscopic data matches with previously reported data.[11]



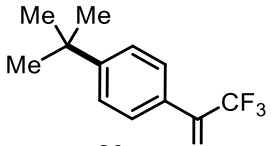

**27**

**4-(*tert*-Butyl)benzonitrile (27):** obtained as a colorless oil with procedure B (71 mg, 89%); with C (66 mg, 83%)
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 1.34 (s, 9H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 156.6, 131.9, 126.1, 119.0, 109.2, 35.2, 30.8.
HRMS (ESI) m/z calc. for $C_{11}H_{14}N$ (M+H) 160.1126, found 160.1123.
Spectroscopic data matches with previously reported data.[11]



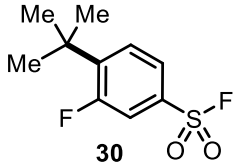

**28**

**4-(*tert*-Butyl)benzaldehyde (28):** obtained as a crystalline solid with procedure B (74 mg, 91%) (with <5% protodehalogenation).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 9.98 (s, 1H), 7.83 – 7.80 (m, 2H), 7.56 – 7.54 (m, 2H), 1.36 (s, 9H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 192.2, 158.6, 134.2, 129.8, 126.1, 125.6, 35.5, 31.2.
HRMS (ESI) m/z calc. for $C_{11}H_{15}O$ (M+H) 163.1123, found 163.1129.
Spectroscopic data matches with previously reported data.[11]



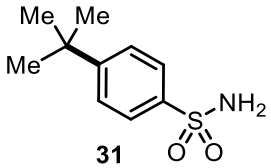

**29**

**1-(4-(*tert*-Butyl)phenyl)-2,2,2-trifluoroethan-1-one (29)**: obtained as a colorless oil with procedure B (109 mg, 96%).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.57 – 7.55 (m, 2H), 1.37 (s, 9H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 180.2 (q, *J* = 34.7 Hz), 160.0, 130.3 (q, *J* = 2.5 Hz), 127.5, 126.3, 116.9 (q, *J* = 291.4 Hz), 35.58, 31.02.
$^{19}$F NMR ($CDCl_3$, 282.4 MHz): δ -71.3.
HRMS (ESI) m/z calc. for $C_{12}H_{16}O$ (M+) 230.0918, found 230.0904.
Spectroscopic data matches with previously reported data.[12]



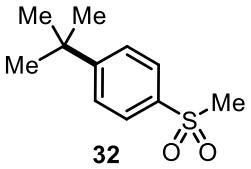

**30**

**4-(*tert*-Butyl)-3-fluorobenzenesulfonyl fluoride (30)**: obtained as a colorless oil with procedure B (69 mg, 59%).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.87 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 11.5, 1.5 Hz, 1H), 1.36 (s, 9H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 182.0, 163.8 (d, *J* = 7.5 Hz), 160.7, 130.6, 122.1 (d, *J* = 3.3 Hz), 115.0 (d, *J* = 20.6 Hz), 36.0, 30.9.
$^{19}$F NMR ($CDCl_3$, 470.8 MHz): δ 106.8(1), 106.8(3).
IR (ATR): ν = 2970, 1607, 1571, 1420, 1215, 1203, 781, 644, 535 $cm^{-1}$.
HRMS (EI) m/z calc. for $C_{10}H_{12}F_2O_2S$ (M+) 234.0526, found 234.0534.



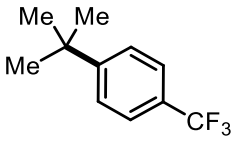

**31**

**4-(*tert*-Butyl)benzenesulfonamide** (**31)**: obtained as a colorless oil with procedure B (47 mg, 44%).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.51 (d, *J* = 7.0 Hz, 2H), 5.12 (bs, 2H), 1.34 (s, 9H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 156.7, 139.1, 126.4, 126.3, 35.3, 31.2.
HRMS (ESI) m/z calc. for $C_{10}H_{15}NO_2S$ (M+) 213.0824, found 213.0837.
Spectroscopic data matches with previously reported data.[13]



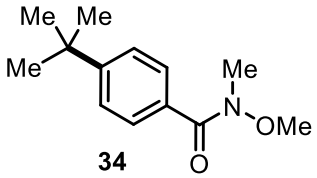

**32**

**1-(*tert*-Butyl)-4-(methylsulfonyl)benzene** (**32)**: obtained as a colorless oil with procedure B (88 mg, 83%),.
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.85 – 7.83 (m, 2H), 7.56 – 7.54 (m, 2H), 3.02 (s, 3H), 1.33 (s, 9H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 157.7, 137.8, 127.3, 126.5, 44.7, 35.4, 31.2.
HRMS (ESI) m/z calc. for $C_{11}H_{16}O_2S$ (M+) 212.0871, found 212.0863.
Spectroscopic data matches with previously reported data.[11]



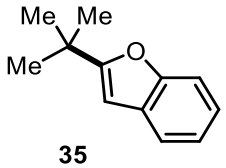

**33**

**1-(*tert*-Butyl)-4-(trifluoromethyl)benzene (33)** obtained as a pale yellow oil with procedure B (96 mg, 95%).
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 1.35 (s, 9H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 155.3, 127.9 (q, *J* = 31.4 Hz), 125.8, 125.1 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 271.8 Hz), 35.1, 31.3 (residual ligand peaks, less than 5% at 27.5, 90.9, 201.6).
$^{19}$F NMR ($CDCl_3$, 282.4 MHz): δ 62.3.
HRMS (ESI) m/z calc. for $C_{11}H_{13}F_3$ (M+) 202.0969, found 202.0958.
Spectroscopic data matches with previously reported data.[14]



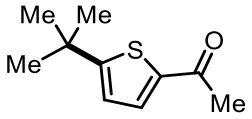

**34**

**4-(*tert*-Butyl)-N-methoxy-N-methylbenzamide** (**34**) obtained as yellow oil with procedure B (43 mg, 39%).
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 3.59 (s, 3H), 3.36 (s, 3H), 1.34 (s, 9H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 169.9, 153.9, 131.0, 128.0, 124.9, 60.9 34.8, 33.9, 31.0.
HRMS (ESI) m/z calc. for $C_{13}H_{20}NO_2$ (M+H) 222.1494, found 222.1492.
Spectroscopic data matches with previously reported data.[14]



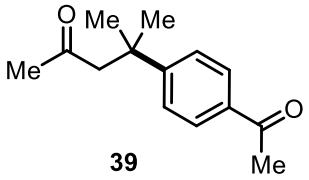

**35**

**2-(*tert*-Butyl)benzofuran (35):** obtained as a colorless oil with procedure C (46 mg, 53%).
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.14 (m, 2H), 6.37 (s, 1H), 1.40 (s, 9H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.1, 154.5, 128.8, 123.0, 122.2, 120.2, 110.7, 98.8, 32.9, 28.8.
Spectroscopic data matches with previously reported data.[15]



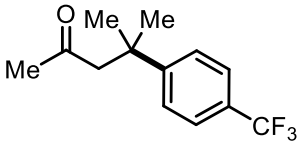

**36**

**1-(5-(*tert*-Butyl)thiophen-2-yl)ethan-1-one (36):** obtained as a yellow oil with procedure B (60 mg, 66%).
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.9 Hz, 1H), 6.88 (d, *J* = 3.9 Hz, 1H), 2.52 (s, 3H), 1.41 (s, 9H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 190.6, 167.2, 141.2, 132.5, 122.8, 35.1, 32.1, 26.4.
HRMS (ESI) m/z calc. for $C_{10}H_{15}OS$ (M+H) 183.0844, found 183.0821.
Spectroscopic data matches with previously reported data.[16]



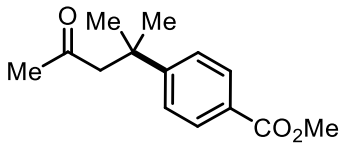

**39**

**4-(4-Acetylphenyl)-4-methylpentan-2-one** (**39)**: obtained as a colorless oil with procedure B (73 mg, 67%).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.93 – 7.91 (m, 2H), 7.47 – 7.44 (m, 2H), 2.82 (s, 2H), 2.59 (s, 3H), 1.89 (s, 3H), 1.45 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 206.9, 197.6, 153.9, 134.9, 128.3, 125.7, 56.2, 37.4, 31.6, 28.8, 26.4.
IR (ATR): ν = 2964, 1715, 1678, 1605, 1406, 1356, 1269, 1014, 958, 596 $cm^{-1}$.
HRMS (ESI) m/z calc. for $C_{14}H_{18}O_2Na$ (M+Na) 241.1204, found 241.1210.



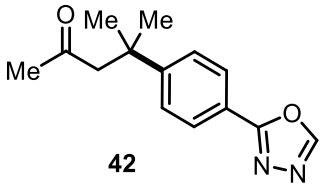

**40**

**4-Methyl-4-(4-(trifluoromethyl)phenyl)pentan-2-one** (**40)**: obtained as a clear oil, procedure B (89 mg, 73%).
$^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 2.81 (s, 2H), 1.91 (s, 3H), 1.45 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 206.8, 152.4 128.2, 125.8, 125.1 (q, *J* =3.8 Hz), 124.1 (q, *J* = 275.5 Hz) 56.1, 37.2, 31.6, 28.3.
$^{19}$F NMR ($CDCl_3$, 470.8 MHz): δ -62.4.
IR (ATR): ν = 2967, 1718, 1618, 1409, 1325, 1112, 1104, 1068, 1014, 838, 530 $cm^{-1}$.
HRMS (ESI) m/z calc. for $C_{13}H_{15}OF_3$ (M+) 244.1075, found 244.1072.



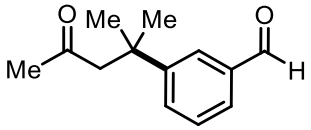

**41**

**Methyl 4-(2-Methyl-4-oxopentan-2-yl)benzoate** (**41)**: obtained as a colorless oil with procedure B (93 mg, 82%).
$^1$H NMR ($CDCl_3$, 500 MHz): δ 7.98 – 7.95 (m, 2H), 7.43 – 7.40 (m, 2H), 3.88 (s, 3H), 2.78 (s, 2H), 1.84 (s, 3H), 1.42 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 207.3, 167.1, 153.9, 129.7, 128.0, 125.7, 56.6, 52.1, 37.6, 31.8, 29.0.
HRMS (ESI) m/z calc. for $C_{14}H_{19}O_3$ (M+H) 235.1334, found 235.1340.
Spectroscopic data matches with previously reported data.[11]



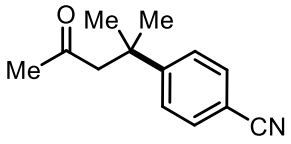

**42**

**4-(4-(1,3,4-Oxadiazol-2-yl)phenyl)-4-methylpentan-2-one** (**42)**: obtained as a yellow oil with procedure B (73 mg, 60%).
$^1$H NMR ($CDCl_3$, 500 MHz): δ 8.45 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 2.82 (s, 2H), 1.90 (s, 3H), 1.46 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 207.1, 164.8, 153.0, 152.6, 127.2, 126.5, 121.3, 56.5, 37.6, 31.8, 29.0.
IR (ATR): ν = 3250, 2965, 1714, 1616, 1494, 1380, 1097, 954, 713, 640 $cm^{-1}$.
HRMS (ESI) m/z calc. for $C_{14}H_{17}N_2O_2$ (M+H) 245.1290, found 245.1282.



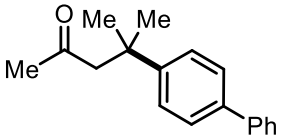

**43**

**3-(2-Methyl-4-oxopentan-2-yl)benzaldehyde** (**43)**: obtained as a colorless oil with procedure C (62 mg, 61%).
$^1$H NMR ($CDCl_3$, 500 MHz): δ 10.02 (s, 1H), 7.88 (s, 1H), 7.72 – 7.70 (m, 1H), 7.66 – 7.63 (m, 1H), 7.51 – 7.48 (m, 1H), 2.82 (s, 2H), 1.90 (s, 3H), 1.46 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 207.1, 192.7, 149.8, 136.6, 132.0, 129.1, 128.1, 126.5, 56.4, 37.4, 31.9, 29.1.
IR (ATR): ν = 2964, 1694, 1603, 1361, 1261, 1177, 1083, 801, 697 $cm^{-1}$.
HRMS (ESI) m/z calc. for $C_{13}H_{16}O_2$ (M+) 204.1150, found 204.1149.



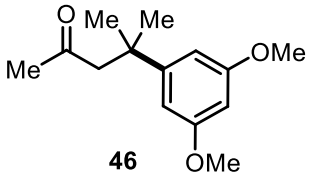

**44**

**4-(2-Methyl-4-oxopentan-2-yl)benzonitrile** (**44)**: obtained as a colorless oil with procedure C (73 mg, 73%).
$^1$H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 2.81 (s, 2H), 1.93 (s, 3H), 1.42 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 206.6, 154.2, 132.2, 126.5, 119.1, 109.9, 56.1, 37.6, 31.7, 29.0.
HRMS (ESI) m/z calc. for $C_{13}H_{16}NO$ (M+H) 202.1232, found 202.1240.
Spectroscopic data matches with previously reported data.[17]



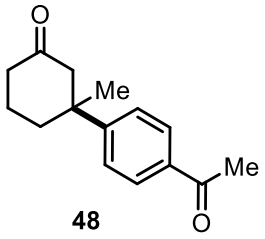

**45**

**4-([1,1'-Biphenyl]-4-yl)-4-methylpentan-2-one** (**45)**: obtained as a viscous oil with procedure C (54 mg, 43%).
$^1$H NMR ($CDCl_3$, 500 MHz): δ 7.61 – 7.53 (m, 4H), 7.45 – 7.40 (m, 4H), 7.35 – 7.31 (m, 1H), 2.79 (s, 2H), 1.86 (s, 3H), 1.47 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 208.1, 147.5, 140.9, 138.9, 128.9, 127.3, 127.1(1), 127.0(8), 126.1, 57.0, 37.3, 32.0, 29.1.
IR (ATR): ν = 2962, 2927, 1715, 1702, 1487, 1356, 1161, 765, 697 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_{18}H_{20}O$ (M+) 252.1514, found 252.1521.



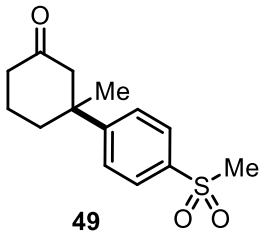

**46**

**4-(3,5-Dimethoxyphenyl)-4-methylpentan-2-one** (**46)**: obtained as a colorless oil with procedure B (40 mg, 34%).
$^1$H NMR ($CDCl_3$, 500 MHz): δ 6.52 (d, *J* = 2.0 Hz, 2H), 6.33 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 6H), 2.71 (s, 2H), 1.86 (s, 3H), 1.40 (s, 6H).
$^{13}$C NMR ($CDCl_3$, 125.8 MHz): δ 207.9, 160.6, 150.9, 104.4, 97.1, 56.7, 55.1, 37.5, 31.7, 28.8.
IR (ATR): ν = 2961, 1838, 1703, 1594, 1423, 1315, 1203, 1154, 1052, 700 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_{14}H_{20}O_3Na$ (M+Na) 259.1310, found 259.1313.




**48**

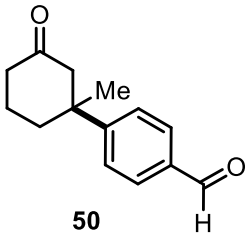
**3-(4-Acetylphenyl)-3-methylcyclohexan-1-one** (**48)**: obtained as a colorless oil with procedure C (97 mg, 75%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 2.89 (d, *J* = 14.2 Hz, 1H), 2.57 (s, 3H), 2.46 (d, *J* = 14.2 Hz, 1H), 2.37 – 2.13 (m, 3H), 2.00 – 1.83 (m, 2H), 1.63 (bs, 1H), 1.33 (s, 3H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 210.9, 197.8, 153.0, 135.4, 128.8, 126.1, 53.0, 43.4, 40.8, 37.9, 29.9, 26.7, 22.1.
HRMS (ESI) m/z calc. for $C_{15}H_{19}O_2$ (M+H) 231.1385, found 231.1372.
Spectroscopic data matches with previously reported data.[18]




**49**

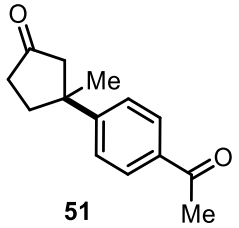
**3-Methyl-3-(4-(methylsulfonyl)phenyl)cyclohexan-1-one** (**49)**: obtained as a colorless oil with procedure C (87 mg, 65%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 3.05 (s, 3H), 2.89 (d, *J* = 14.2 Hz, 1H), 2.50 (d, *J* = 14.2 Hz, 1H), 2.38 – 2.19 (m, 3H), 1.97 (d, *J* = 12.6 Hz, 2H), 1.68 – 1.62 (m, 1H), 1.35 (s, 3H).

$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 210.2, 153.7, 138.4, 127.6, 126.7, 52.6, 44.4, 43.3, 40.6, 37.6, 29.7, 21.9.
IR (ATR): ν = 2929, 1705, 1596, 1305, 1146, 1094, 954, 727, 538 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_{14}H_{18}O_3S$ (M+) 266.0977, found 266.0987.



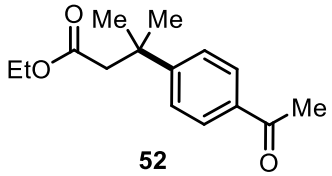
**50**

**4-(1-Methyl-3-oxocyclohexyl)benzaldehyde** (**50**): obtained as a colorless oil with procedure C (63 mg, 58%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 2.90 (d, *J* = 14.1 Hz, 1H), 2.49 (d, *J* = 14.1 Hz, 1H), 2.38 – 2.18 (m, 3H), 2.02 – 1.85 (m, 2H), 1.70 – 1.62 (m, 1H), 1.35 (s, 3H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 210.5, 191.7, 154.4, 134.6, 129.9, 126.3, 52.7, 43.4, 40.6, 37.7, 29.6, 21.9.
IR (ATR): ν = 2936, 1701, 1608, 1226, 825 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_{14}H_{16}O_2$ (M+) 216.1150, found 216.1146.



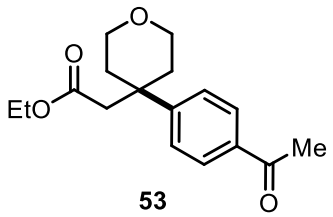
**51**

**3-(4-Acetylphenyl)-3-methylcyclopentan-1-one** (**51**): obtained as a white semi-solid with procedure C (72 mg, 67%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 2.64 (d, *J* = 17.5 Hz, 1H), 2.59 (s, 3H), 2.54 – 2.28 (m, 5H), 1.40 (s, 3H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 217.8, 197.8, 154.1, 135.5, 128.9, 125.9, 52.0, 44.2, 36.7, 35.7, 29.3, 26.7.
IR (ATR): ν = 2960, 1739, 1679, 1605, 1406, 1271, 1156, 958, 836, 601 cm$^{-1}$.
HRMS (ESI) m/z calc. for $C_{14}H_{16}O_2$ (M+) 216.1150, found 216.1165.



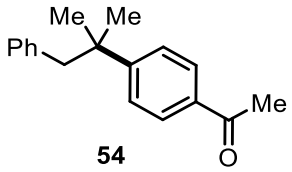
**52**

**Ethyl 3-(4-Acetylphenyl)-3-methylbutanoate (52)** obtained as a colorless oil with procedure C (62 mg, 50 %).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 6.7, 1.8 Hz, 2H), 7.46 (dd, *J* = 6.7, 1.8 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 2H), 2.58 (s, 3H), 1.47 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 3H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 198.0, 171.3, 154.0, 135.1, 128.4, 126.0, 60.2, 48.2, 37.6, 29.0, 26.7, 14.2.
IR (ATR): ν = 2971, 1730, 1682, 1606, 1406, 1366, 1270, 1034, 837 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{15}H_{20}O_3$ (M+) 248.1412, found 248.1416.



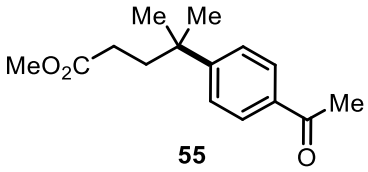

**53**

**Ethyl 2-(4-(4-Acetylphenyl)tetrahydro-2H-pyran-4-yl)acetate (53)** obtained as a colorless oil with procedure C (60 mg, 41%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 3.89 – 3.76 (m, 4H), 3.66 – 3.48 (m, 2H), 2.65 (s, 2H), 2.59 (s, 3H), 2.34 – 2.22 (m, 2H), 2.12 – 1.98 (m, 2H), 0.98 (t, *J* = 7.1 Hz, 3H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 197.9, 170.6, 150.0, 135.5, 128.6, 127.1, 64.2, 60.3, 46.9, 39.0, 36.2, 26.8, 14.1.
IR (ATR): ν = 2956, 1727, 1682, 1605, 1407, 1358, 1114, 1030, 831 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{17}H_{22}O_4$ (M+) 290.1518, found 290.1537.



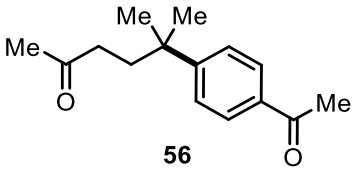

**54**

**1-(4-(2-Methyl-1-phenylpropan-2-yl)phenyl)ethan-1-one (54)** obtained as a colorless oil using procedure C (68 mg 54%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.10 (m, 3H), 6.84 – 6.72 (m, 2H), 2.89 (s, 2H), 2.60 (s, 3H), 1.35 (s, 6H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 197.9, 154.6, 138.1, 134.7, 130.2, 128.0, 127.5, 126.4, 126.0, 50.7, 39.2, 28.0, 26.5.
IR (ATR): ν = 3028, 2966, 2926, 1682, 1605, 1357, 1269, 1015, 838, 702 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{18}H_{20}O$ (M+) 252.1514, found 252.1529.




**55**

**Methyl 4-(4-Acetylphenyl)-4-methylpentanoate (55)** obtained as a colorless oil with procedure C (76 mg, 61 %).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 3.60 (s, 3H), 2.60 (s, 3H), 2.18 – 1.92 (m, 4H), 1.35 (s, 6H).
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.0, 174.3, 154.0, 135.1, 128.6, 126.2, 51.7, 38.8, 37.9, 30.0, 28.7, 26.7.
IR (ATR): ν = 2963, 1736, 1682, 1606, 1566, 1435, 1357, 1269, 1118, 958, 601 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{15}H_{20}O_3$ (M+) 248.1412, found 248.1413.




**56**

**5-(4-Acetylphenyl)-5-methylhexan-2-one (56)** obtained as a colorless oil with procedure C (40 mg, 34%).
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 2.60 (s, 3H), 2.16 (t, *J* = 8.0 Hz, 2H), 2.04 (s, 3H), 1.95 (t, *J* = 8.0 Hz, 2H), 1.34 (s, 6H).
$^{13}$C NMR (125.8 MHz, $CDCl_3$) δ 208.5, 197.7, 154.0, 134.8, 128.3, 126.0, 39.3, 37.5, 37.2, 29.8, 28.6, 26.4.
IR (ATR): ν = 2964, 1713, 1682, 1606, 1271, 838, 640, 556 cm$^{-1}$.
HRMS (EI) m/z calc. for $C_{15}H_{20}O_2$ (M+) 232.1463, found 232.1460.

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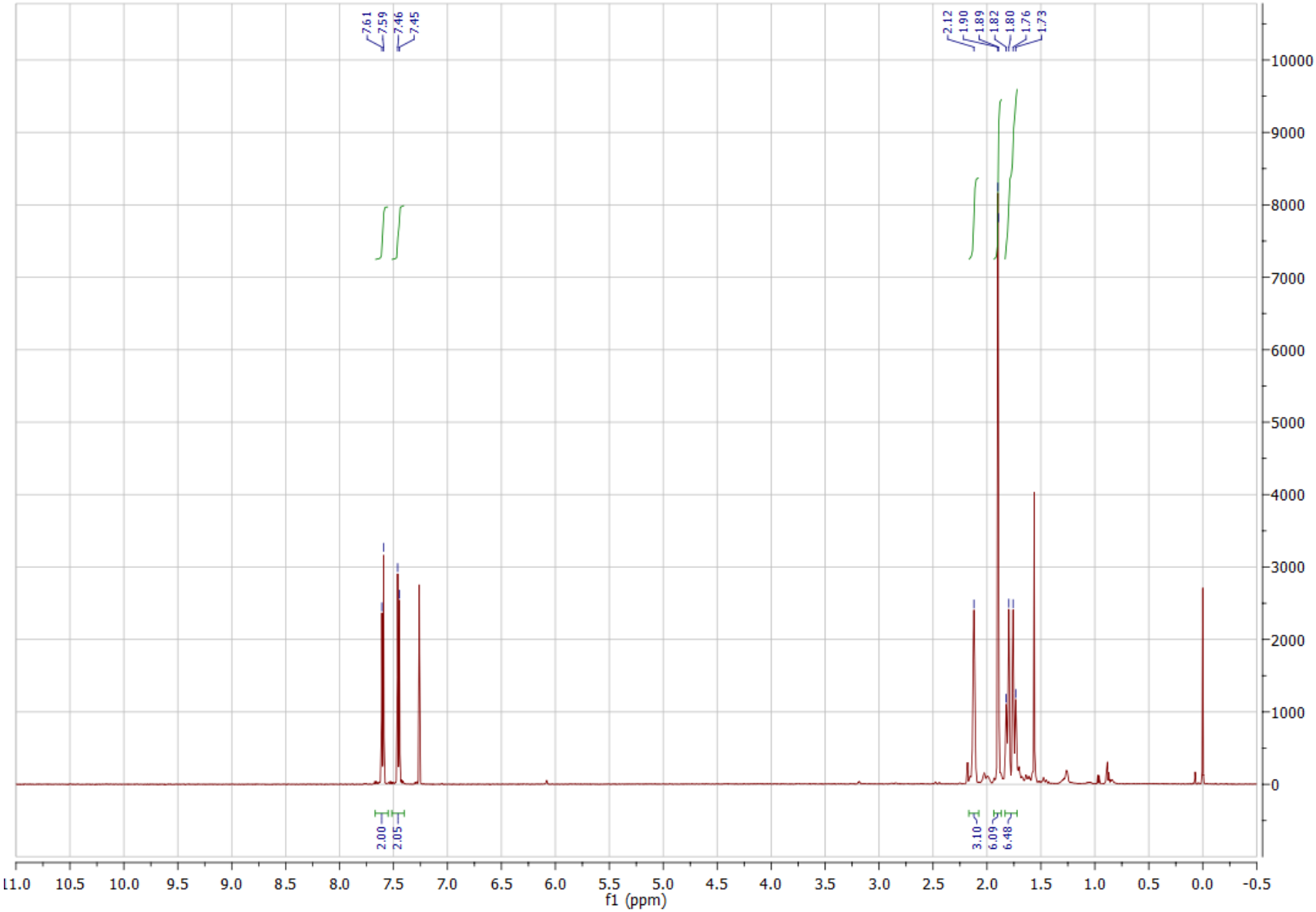
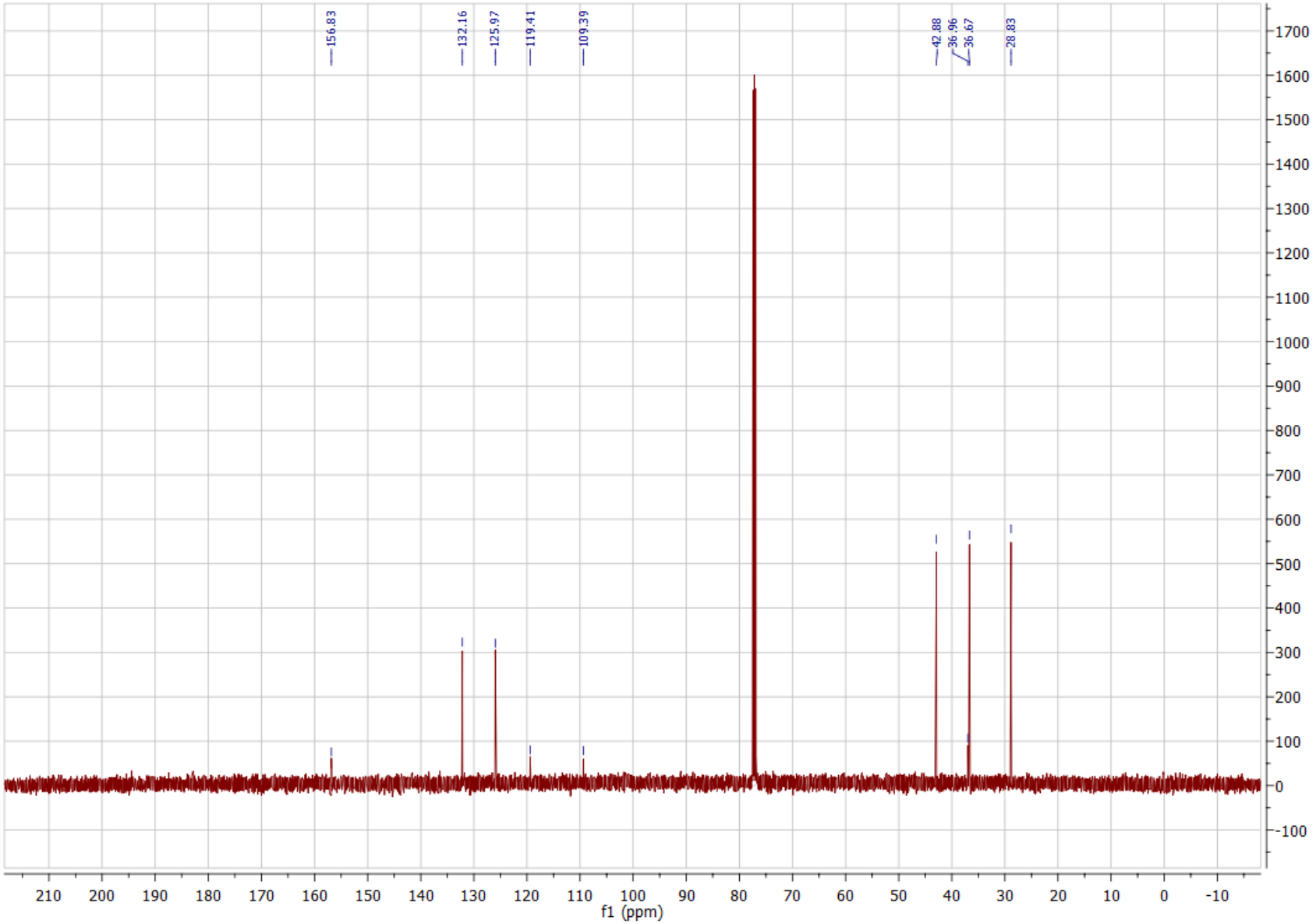
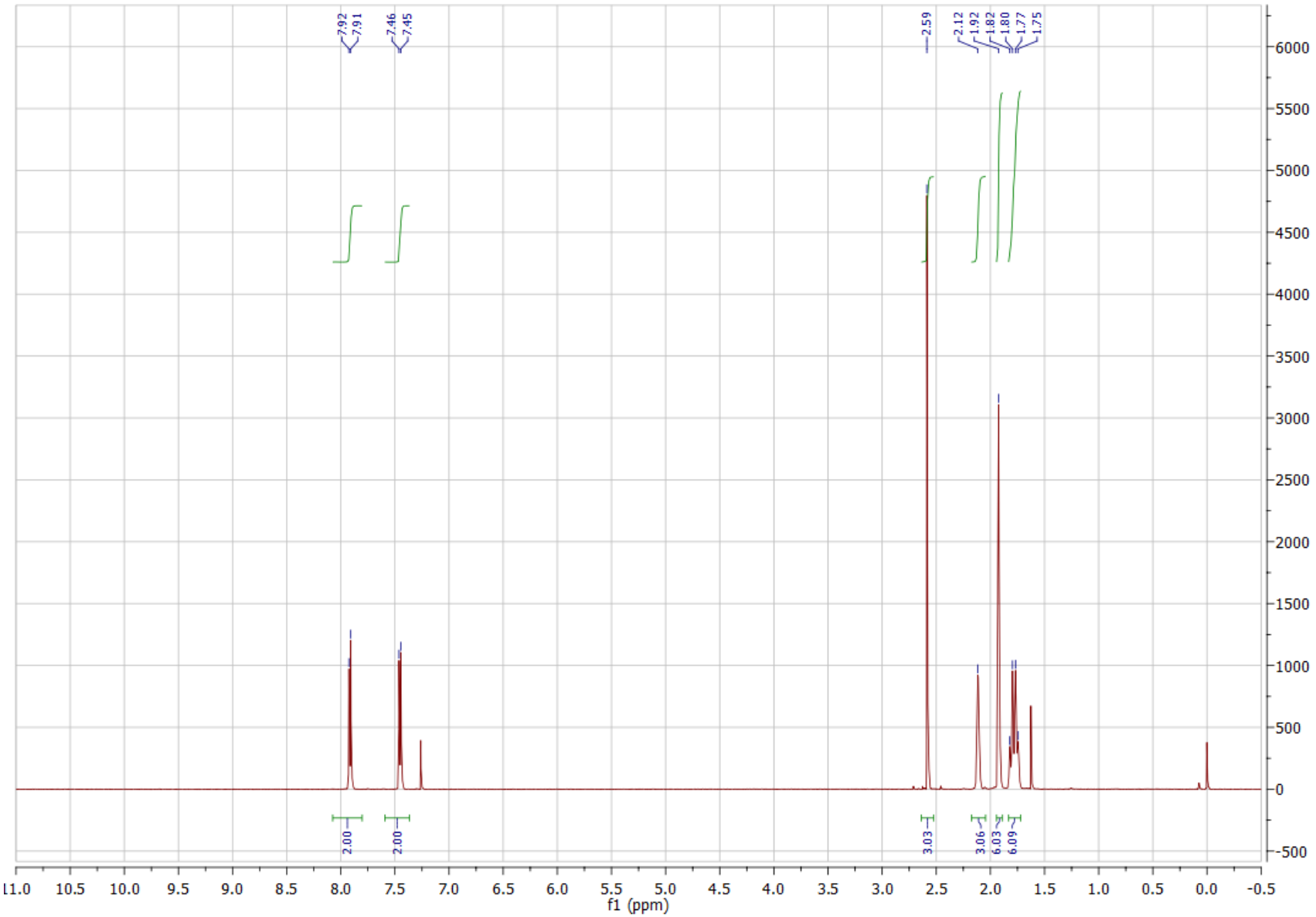
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(adamantan-1-yl)benzonitrile (**19**)



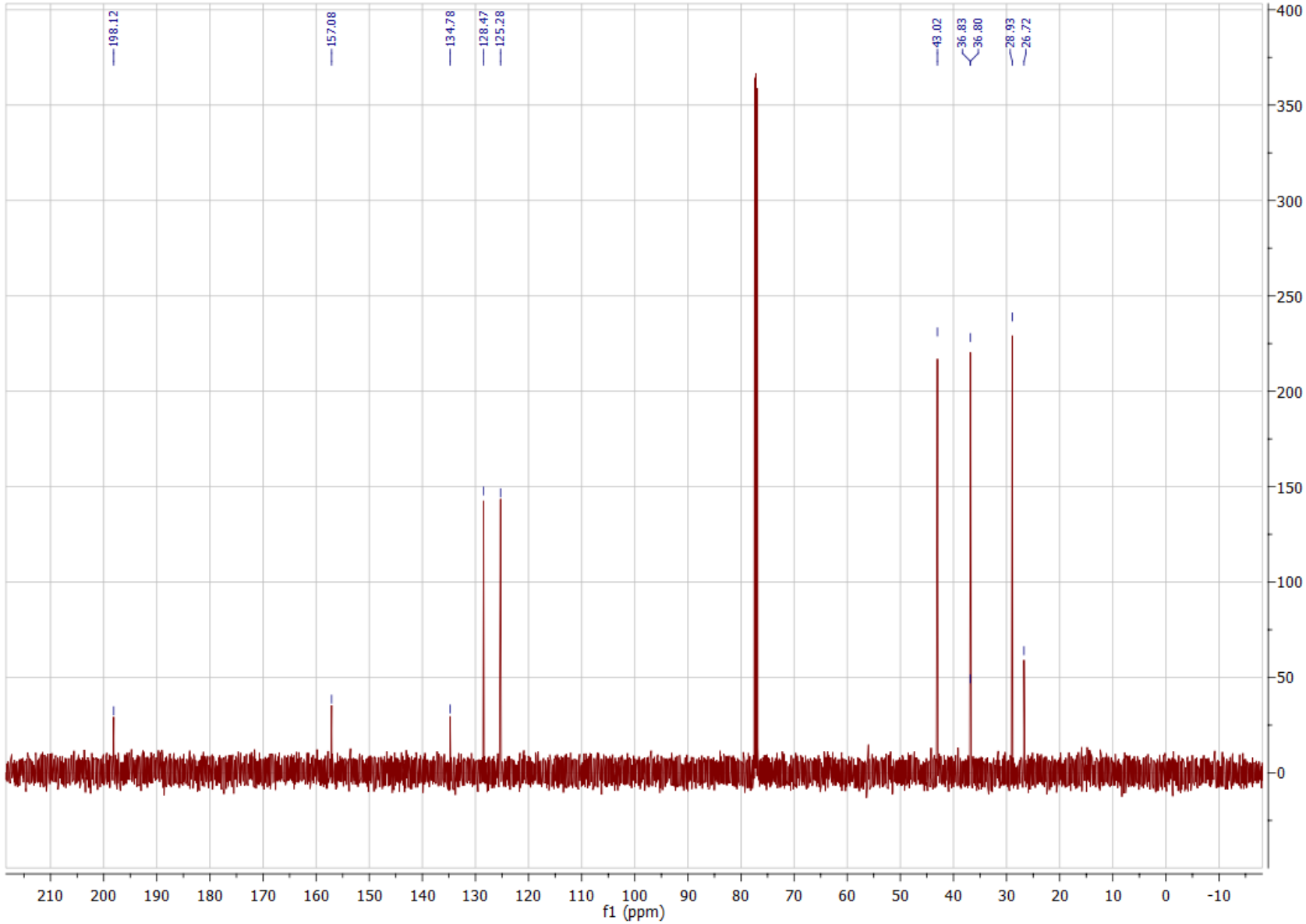
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(adamantan-1-yl)benzonitrile (**19**)



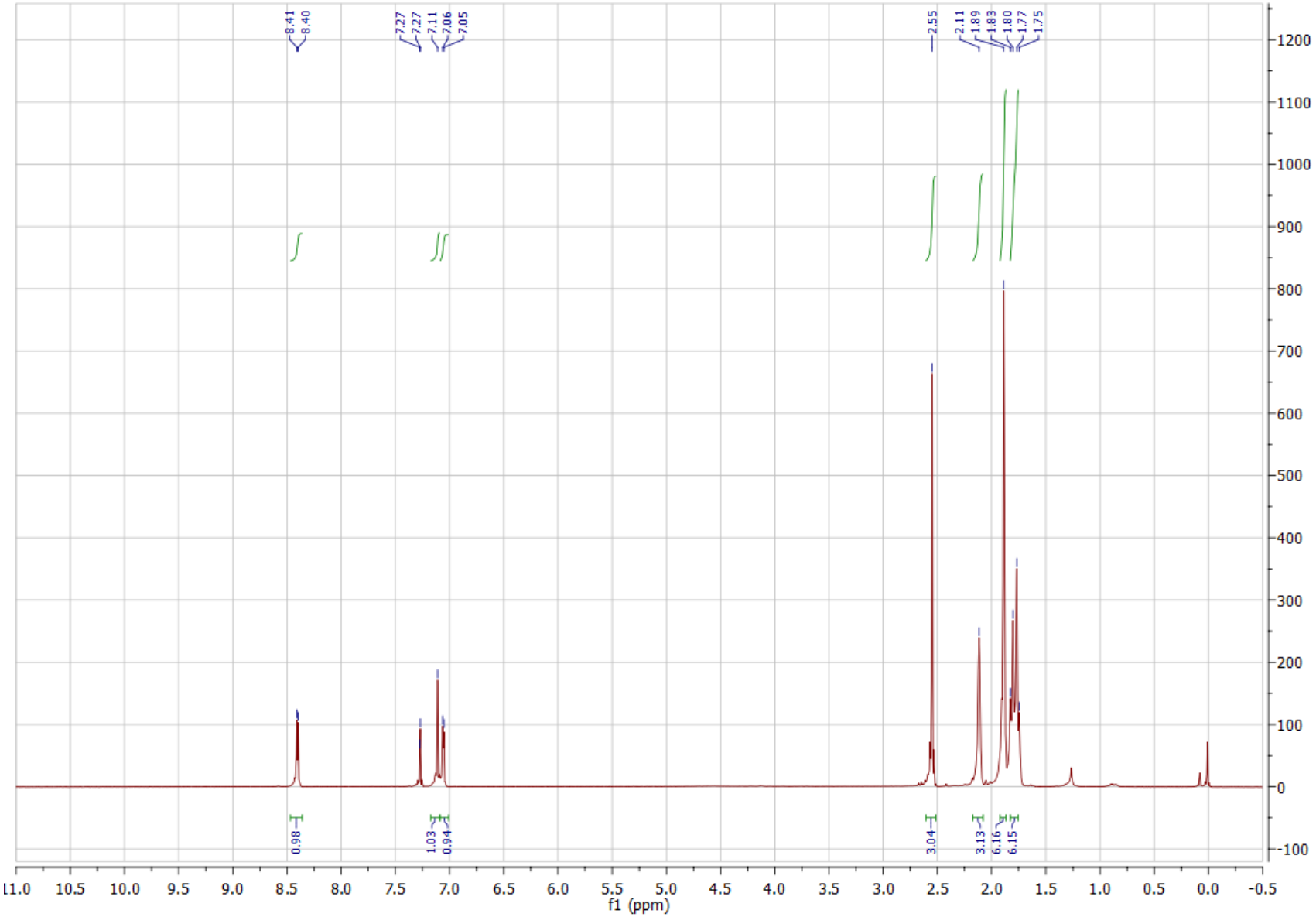
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(4-((3r,5r,7r)-Adamantan-1-yl)phenyl)ethan-1-one (**20**)



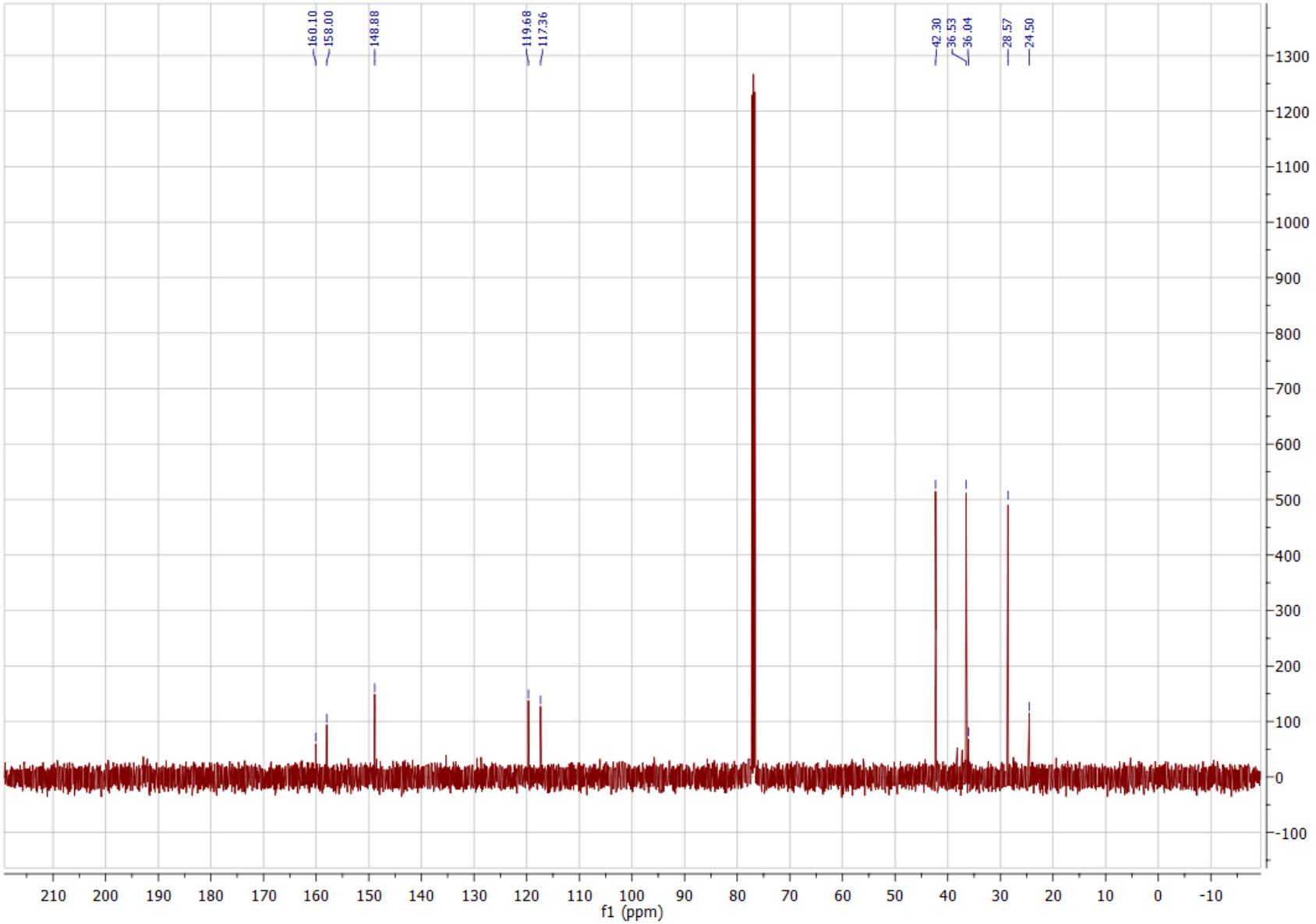
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(4-((3r,5r,7r)-Adamantan-1-yl)phenyl)ethan-1-one (**20**)



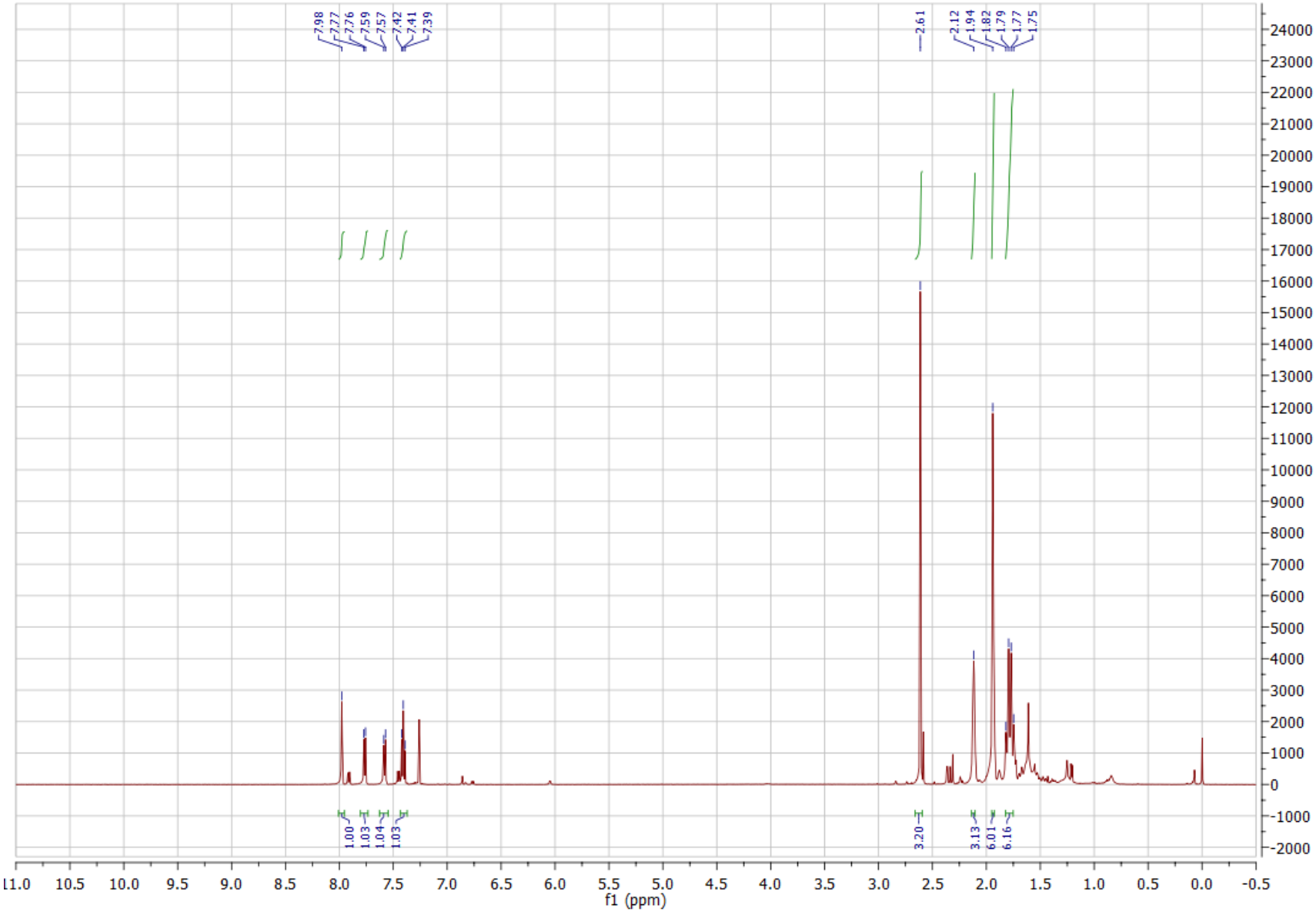
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-((3r,5r,7r)-adamantan-1-yl)-2-methylpyridine **(21):**



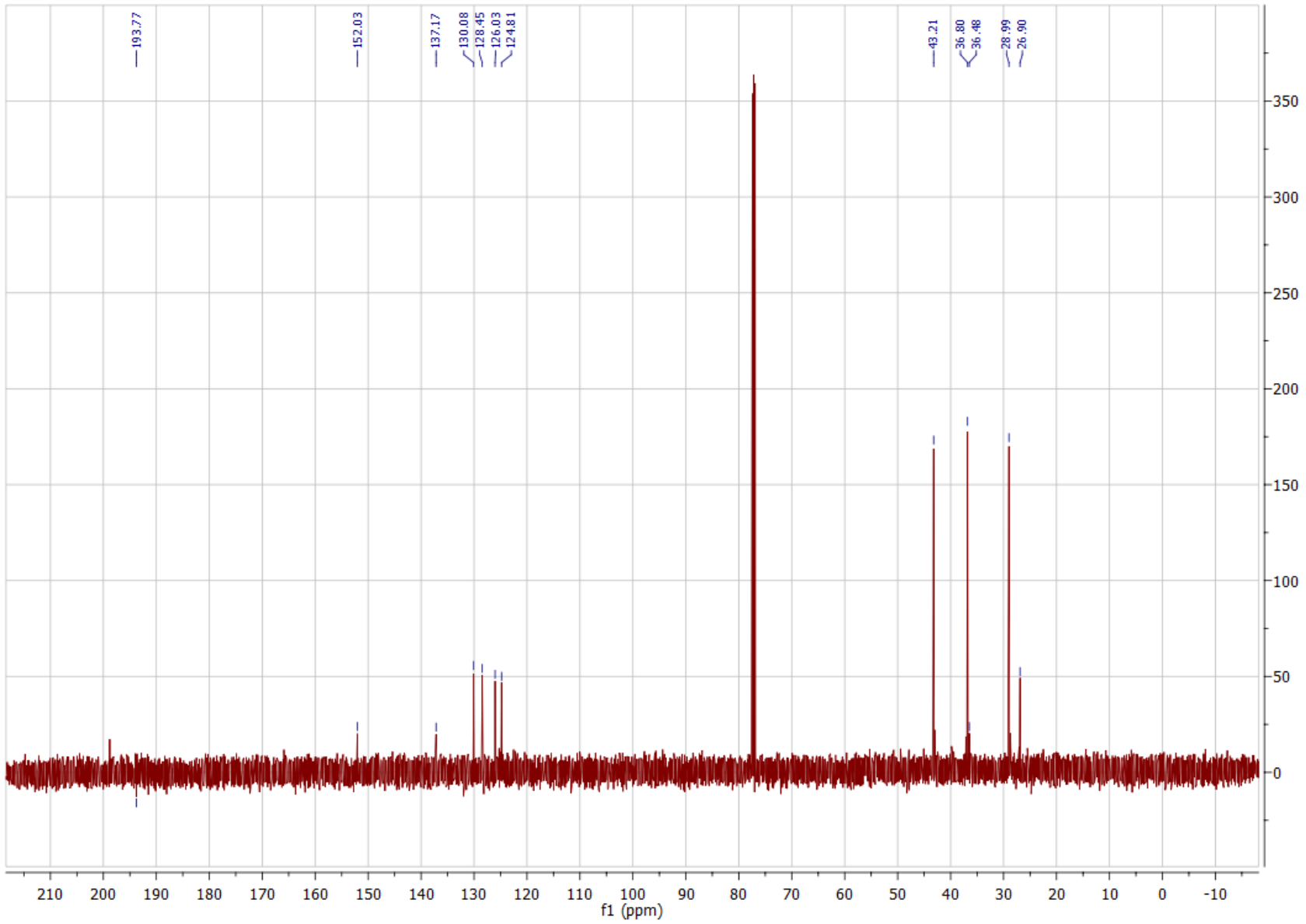
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-((3r,5r,7r)-adamantan-1-yl)-2-methylpyridine **(21):**



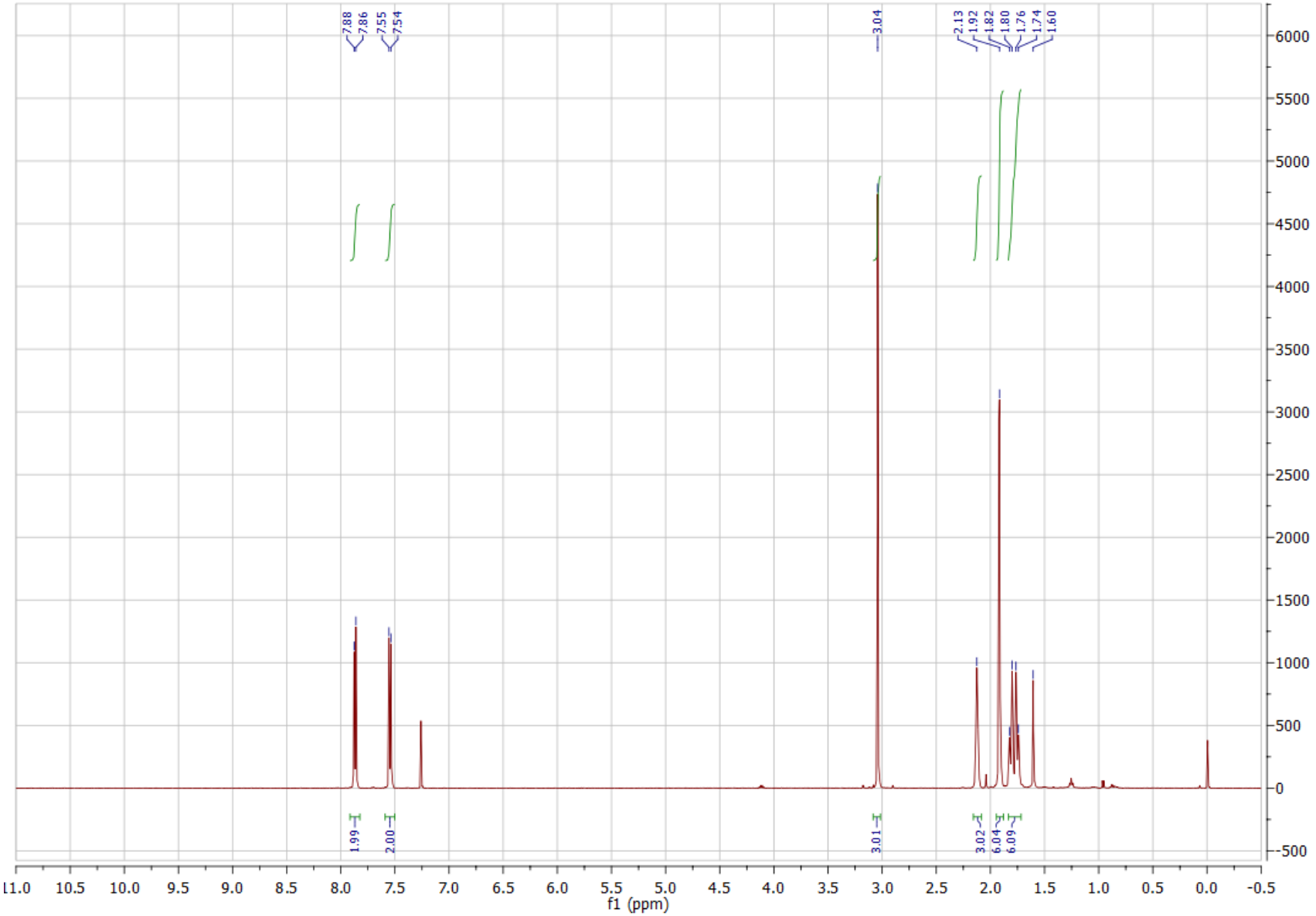
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(3-((3r,5r,7r)-Adamantan-1-yl)phenyl)ethan-1-one (**22**)



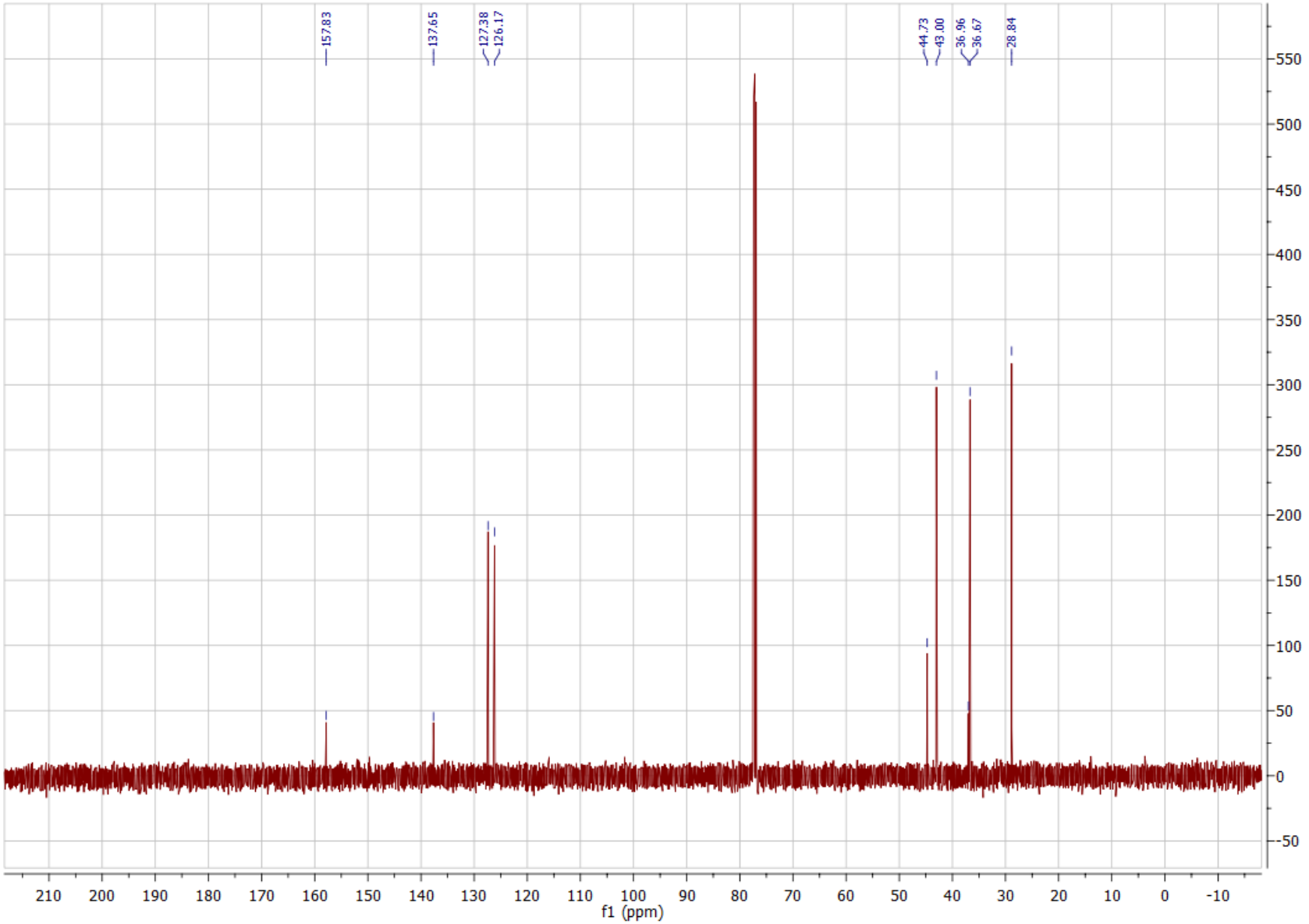
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(3-((3r,5r,7r)-Adamantan-1-yl)phenyl)ethan-1-one (**22**)



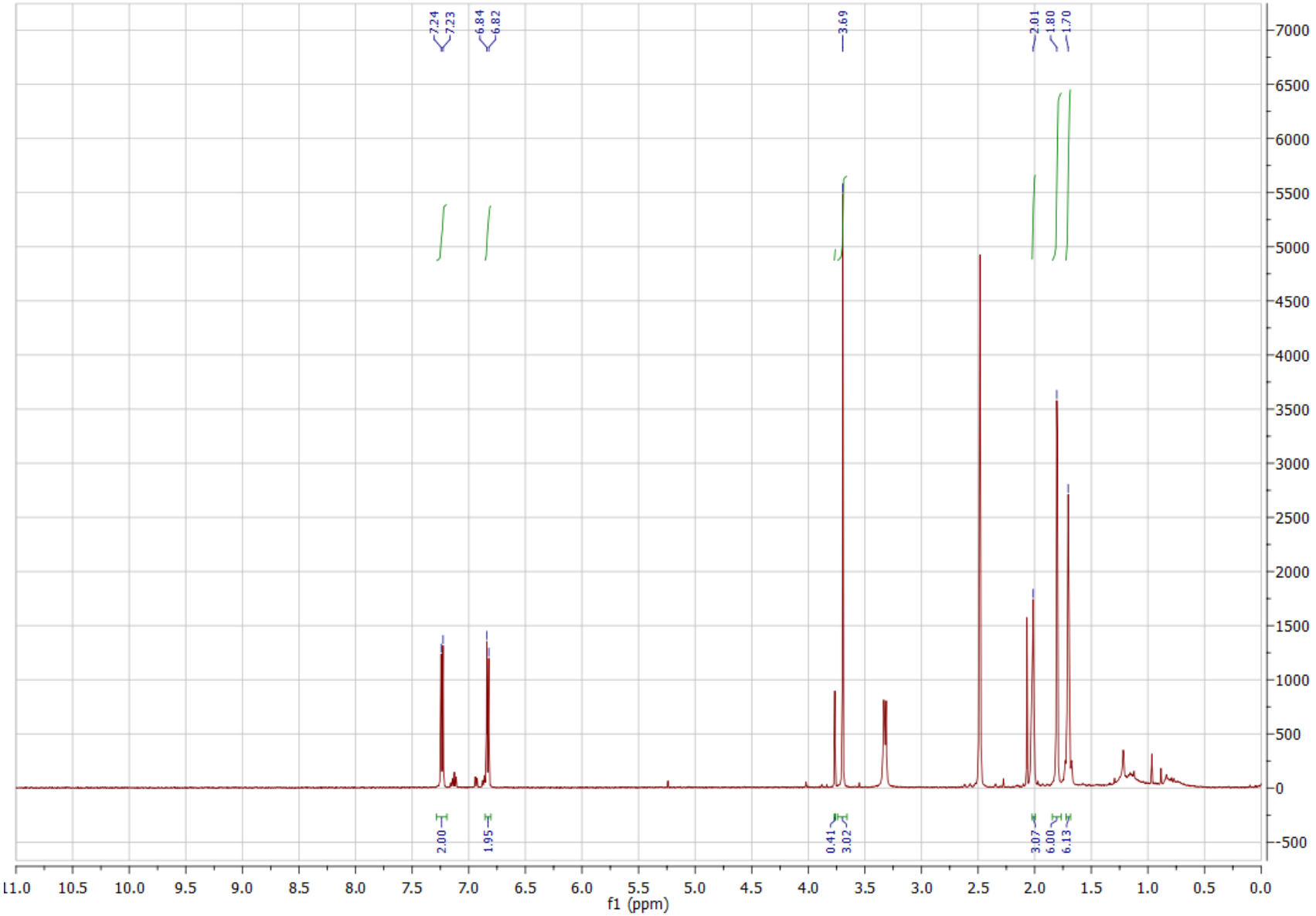
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(4-(methylsulfonyl)phenyl)adamantane (**23**)



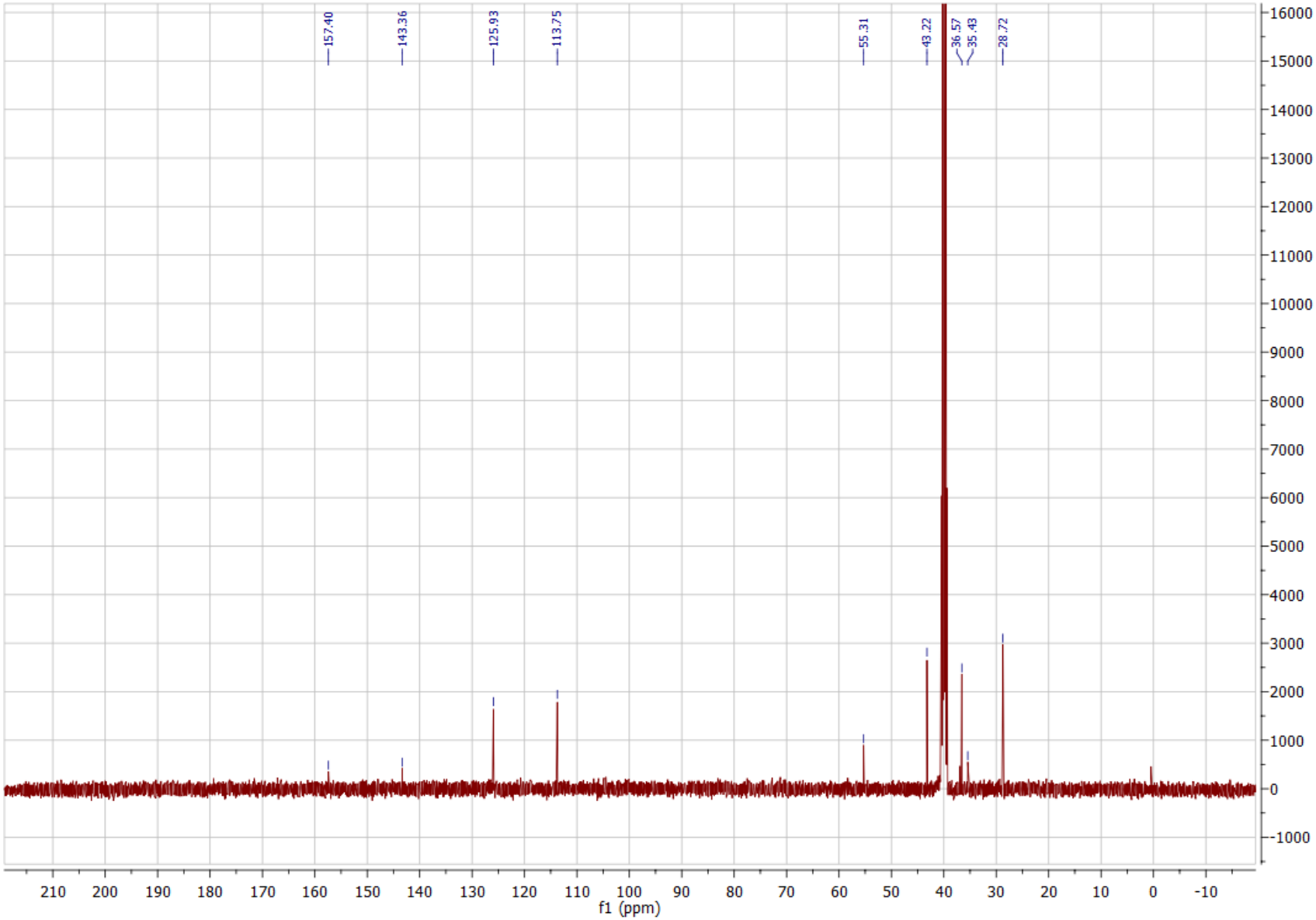
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(4-(methylsulfonyl)phenyl)adamantane (**23**)



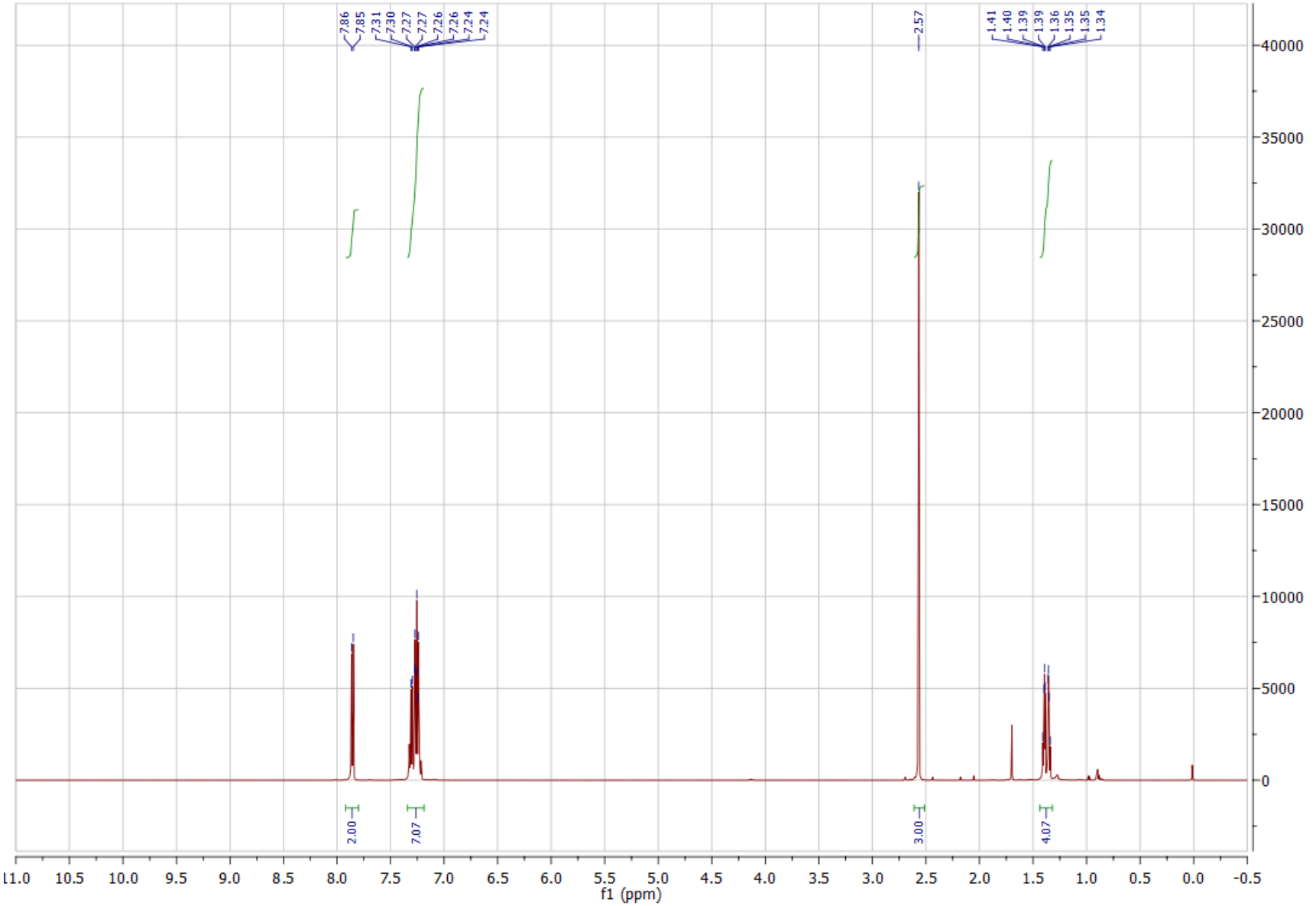
$^{1}$H NMR (DMSO-$d_6$, 500 MHz) of (3r,5r,7r)-1-(4-methoxyphenyl)adamantane (**24**): (with less than 5% anisole)



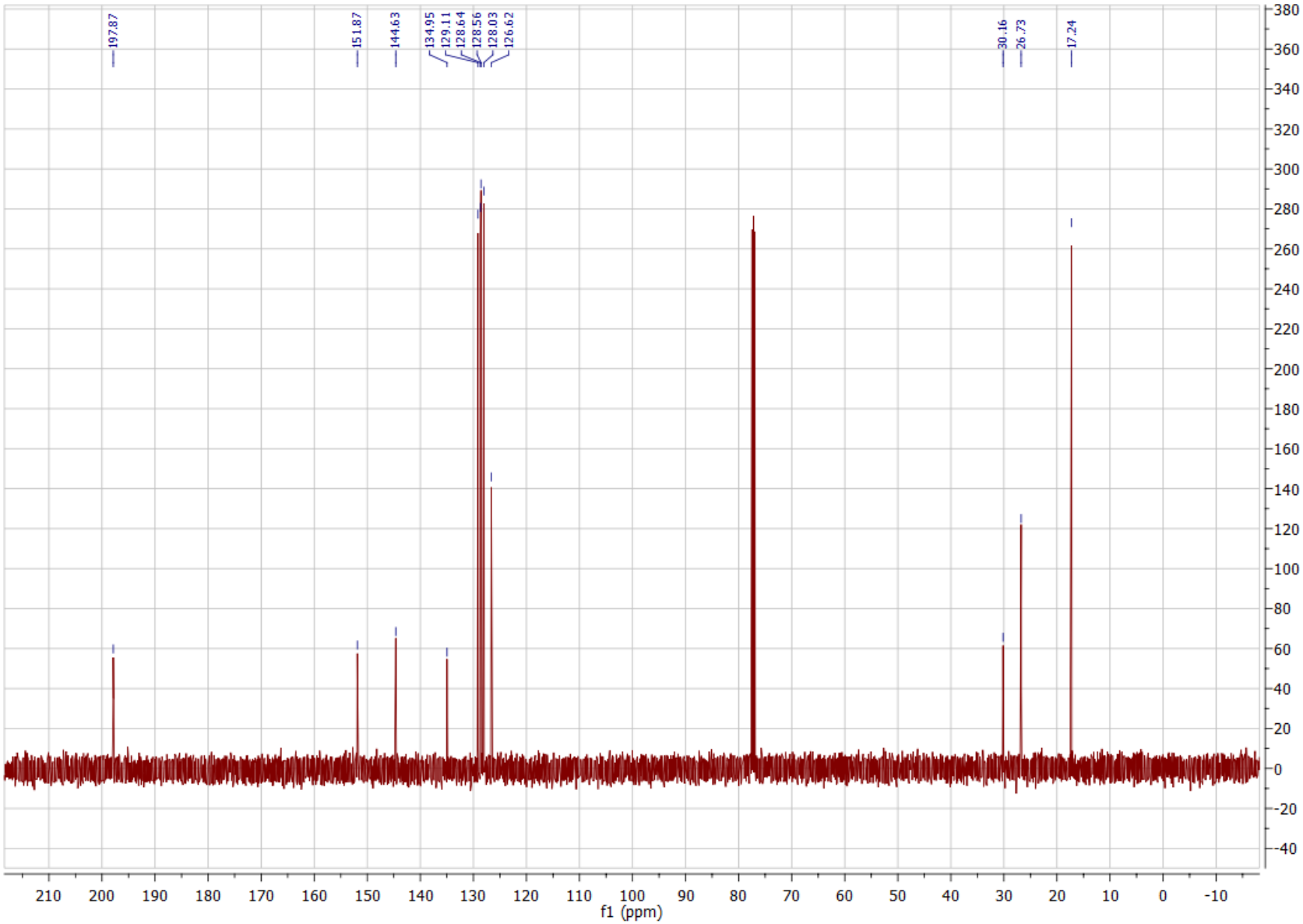
$^{13}$C NMR (DMSO-$d_6$, 125.8 MHz) of (3r,5r,7r)-1-(4-methoxyphenyl)adamantane (**24**):



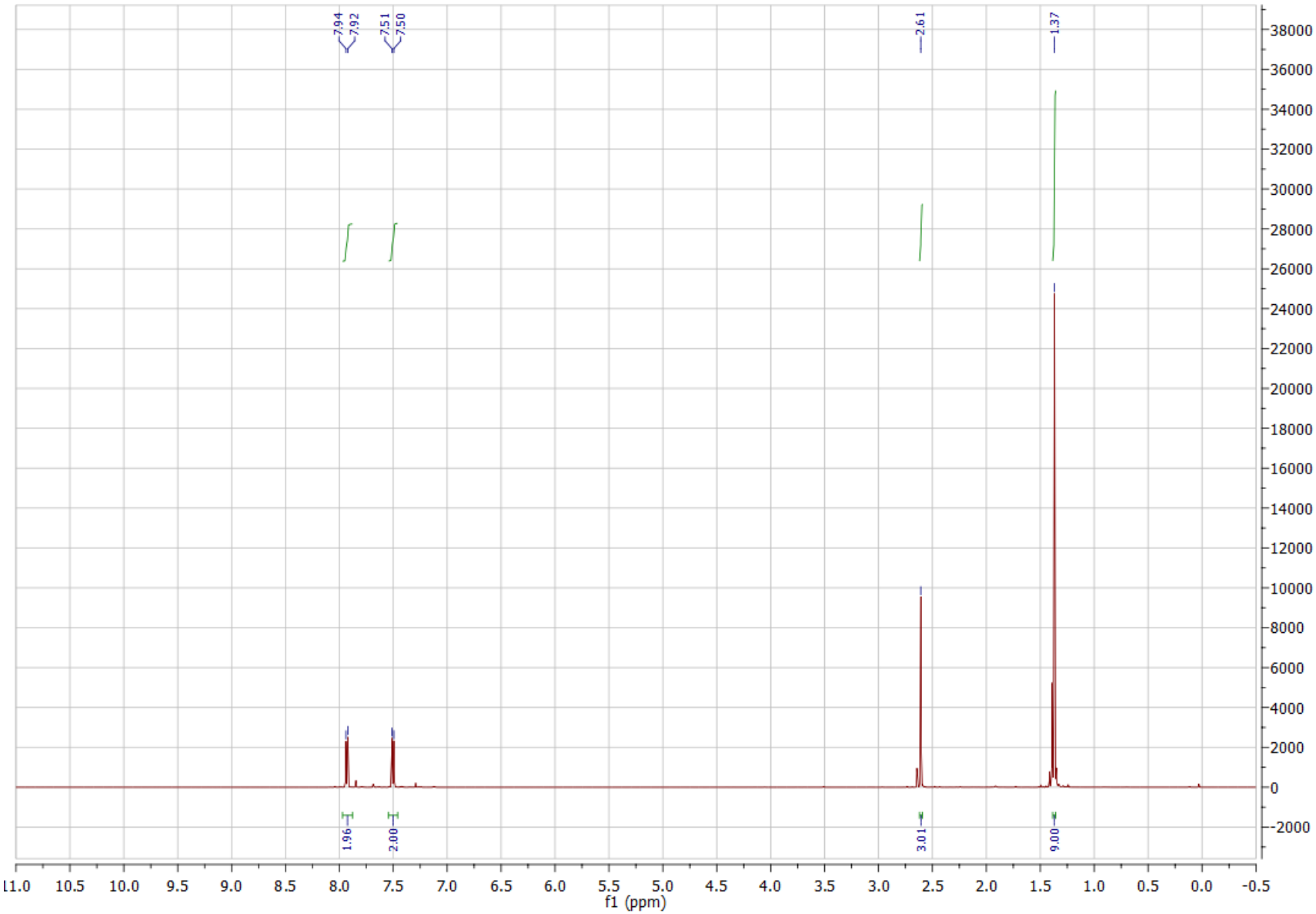
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(4-(1-phenylcyclopropyl)phenyl)ethan-1-one (**25**)



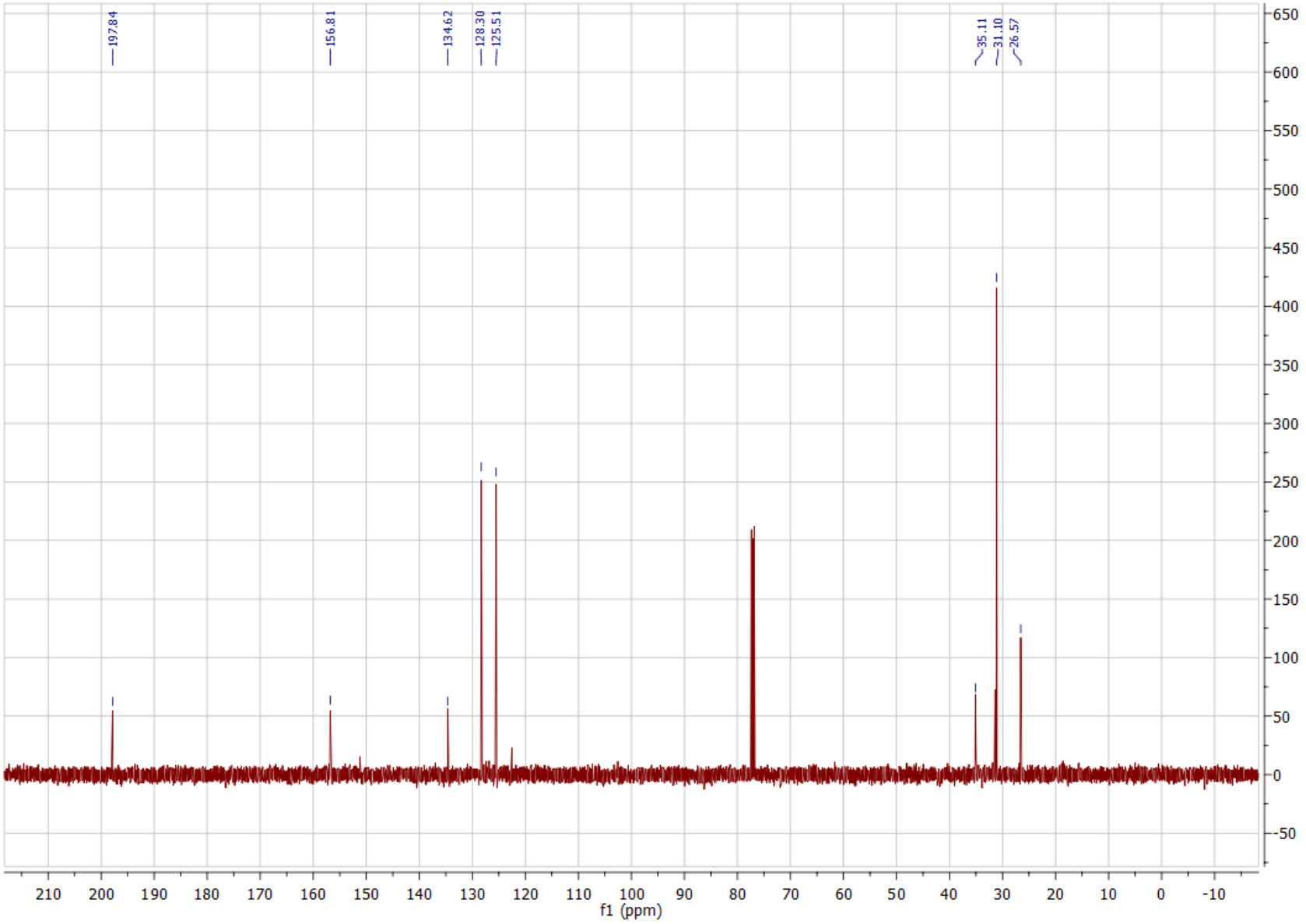
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of 1-(4-(1-phenylcyclopropyl)phenyl)ethan-1-one (**25**)



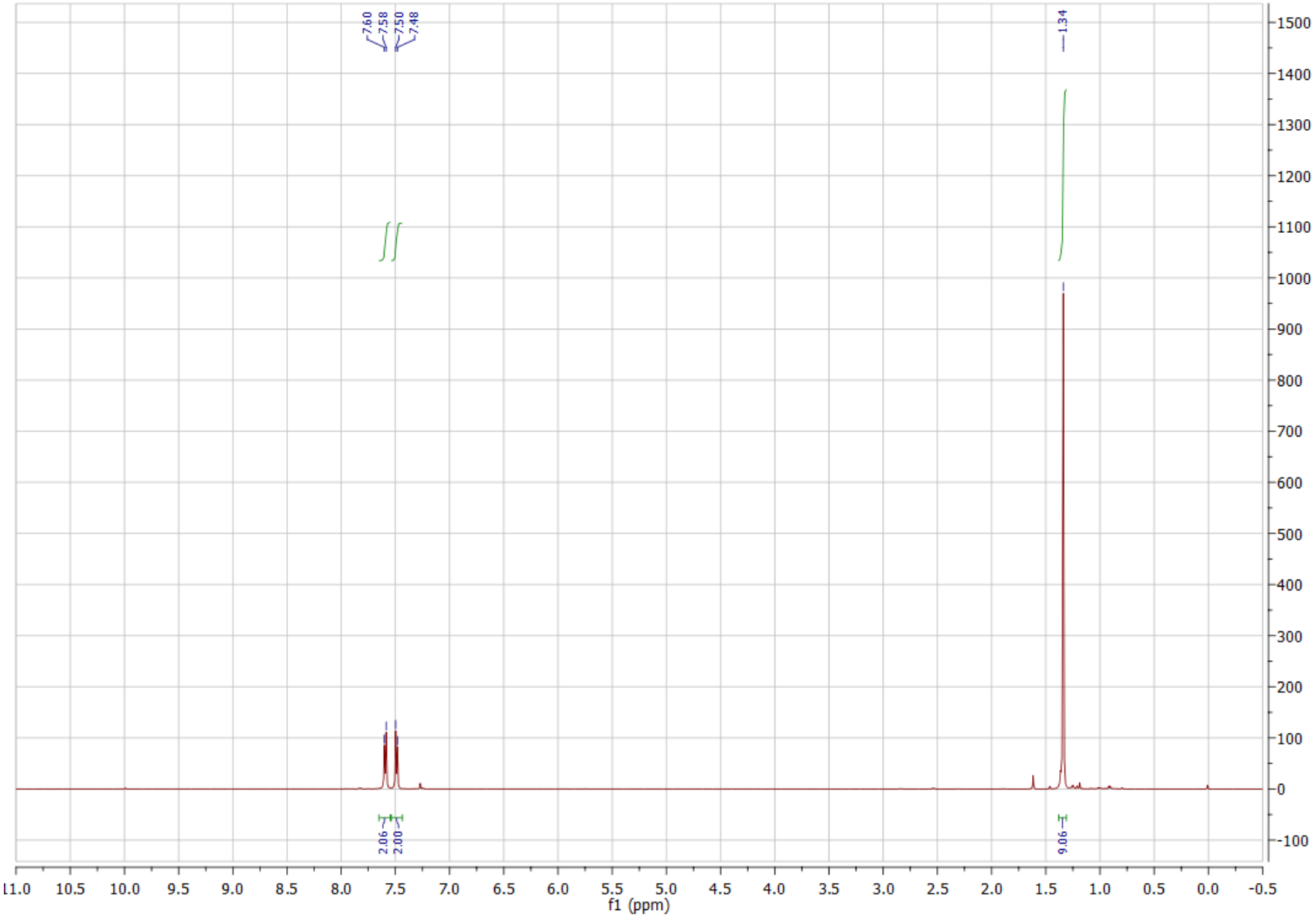
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(4-(*tert*-Butyl)phenyl)ethan-1-one (**26**)



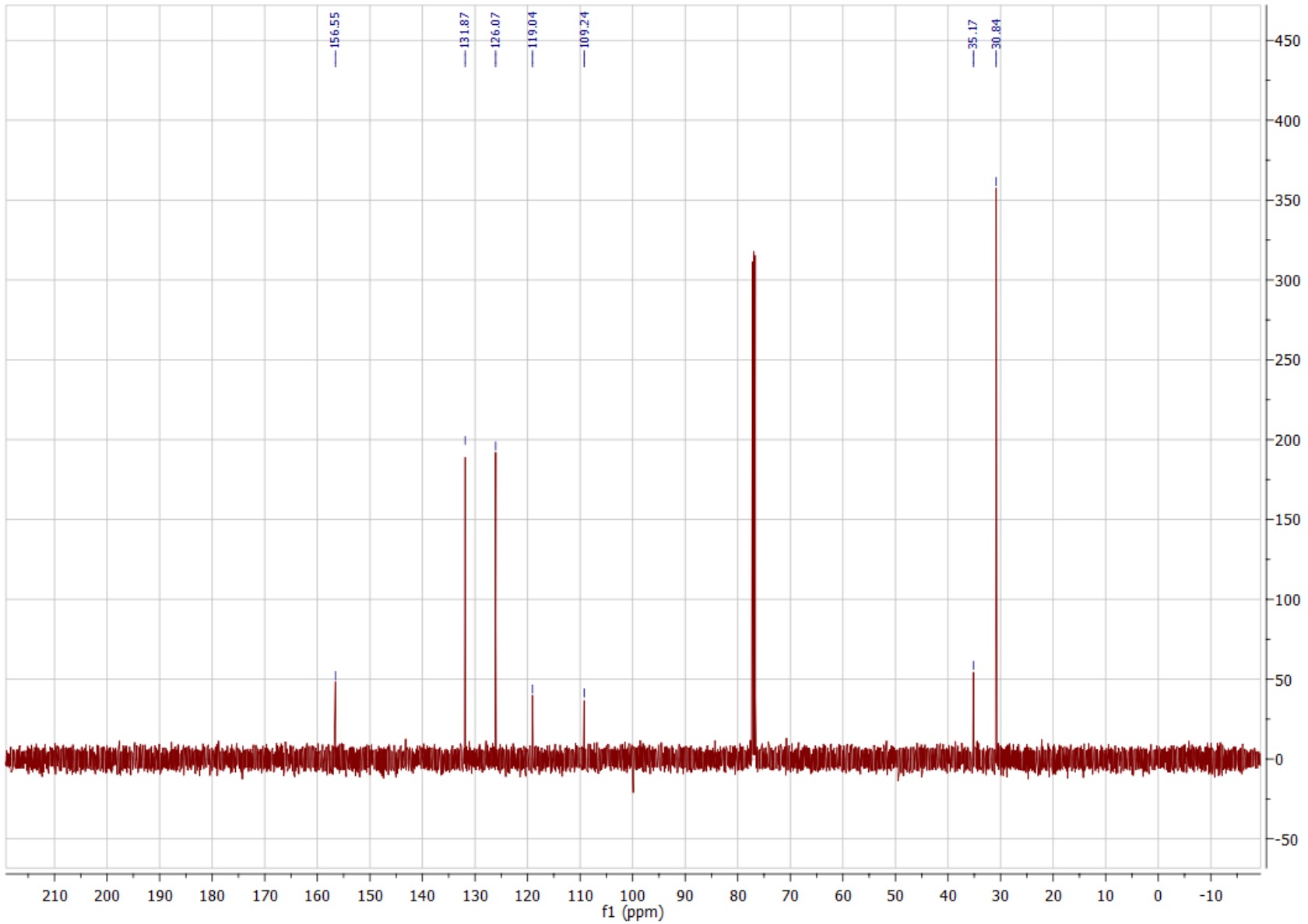
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of 1-(4-(*tert*-Butyl)phenyl)ethan-1-one (**26**)



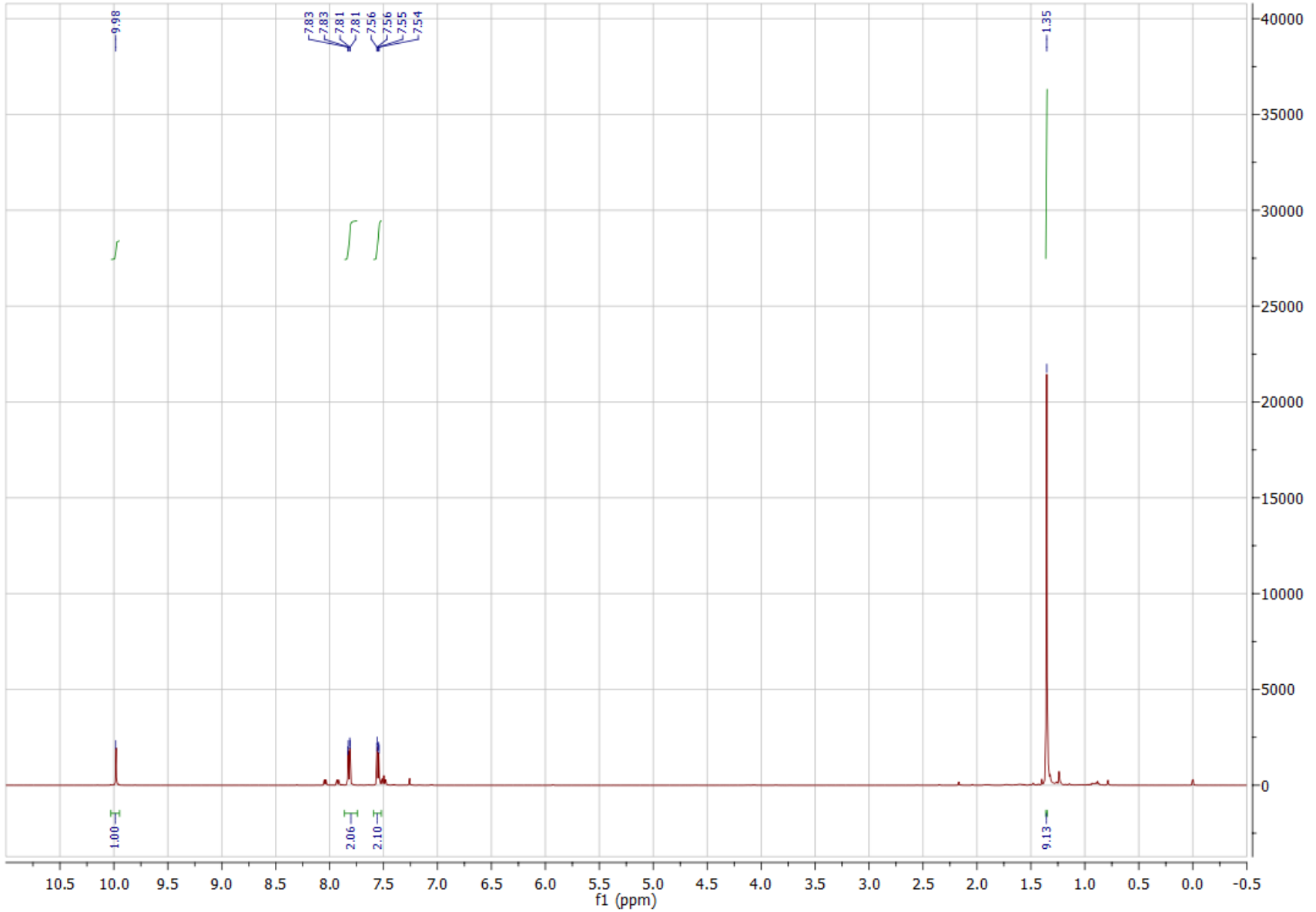
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(*tert*-Butyl)benzonitrile (**27**)



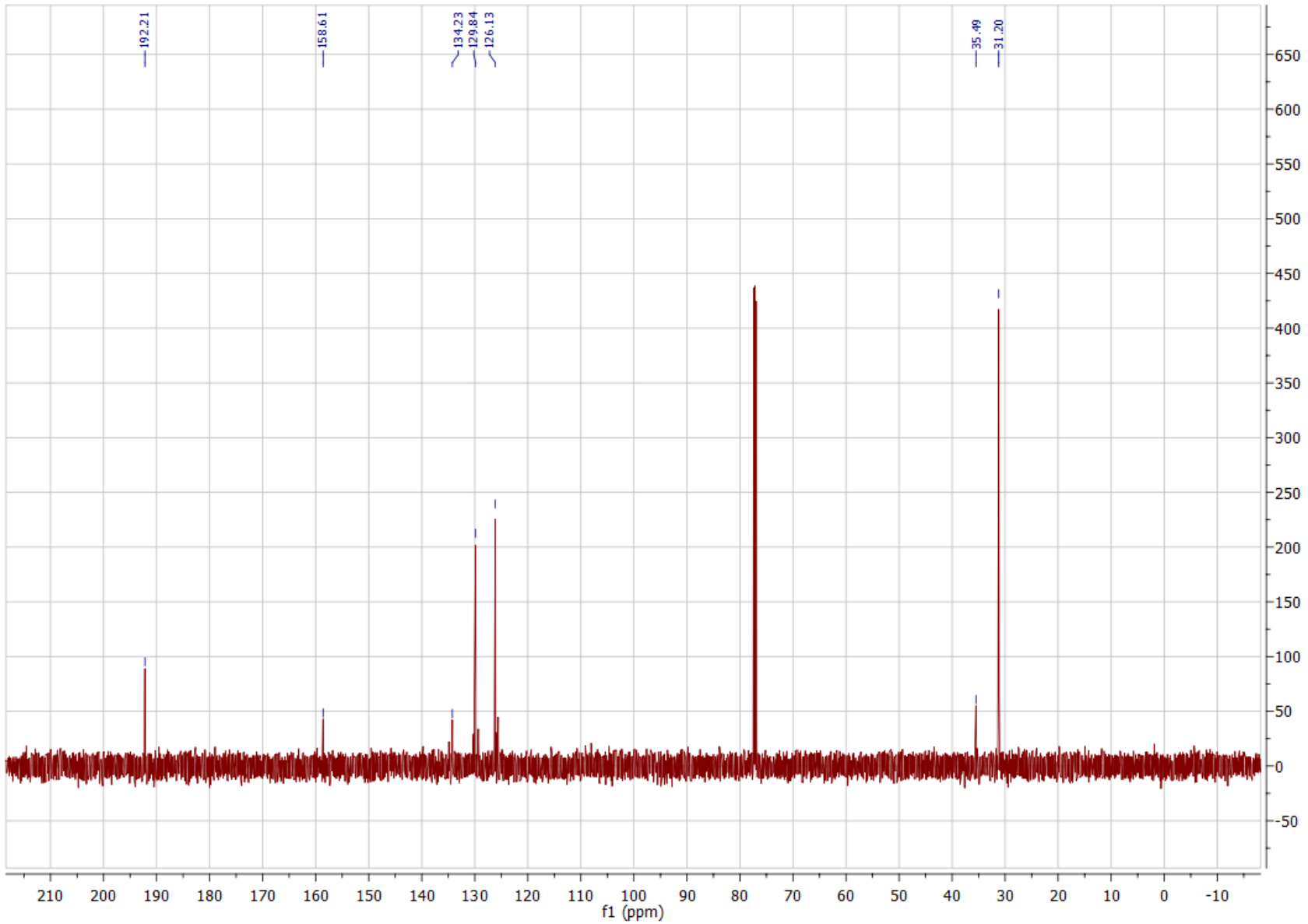
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(*tert*-Butyl)benzonitrile (**27**)



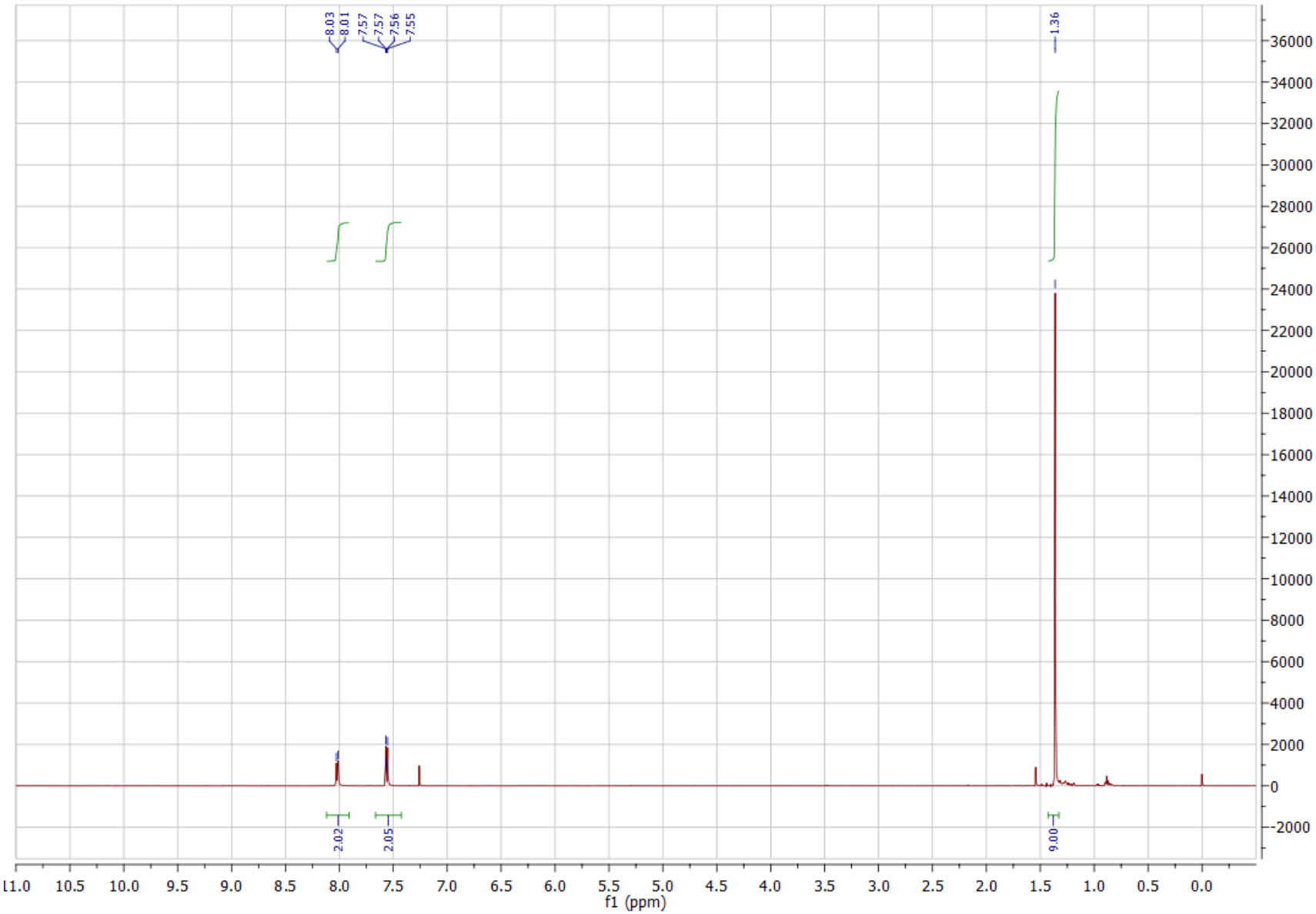
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(*tert*-Butyl)benzaldehyde (**28**)



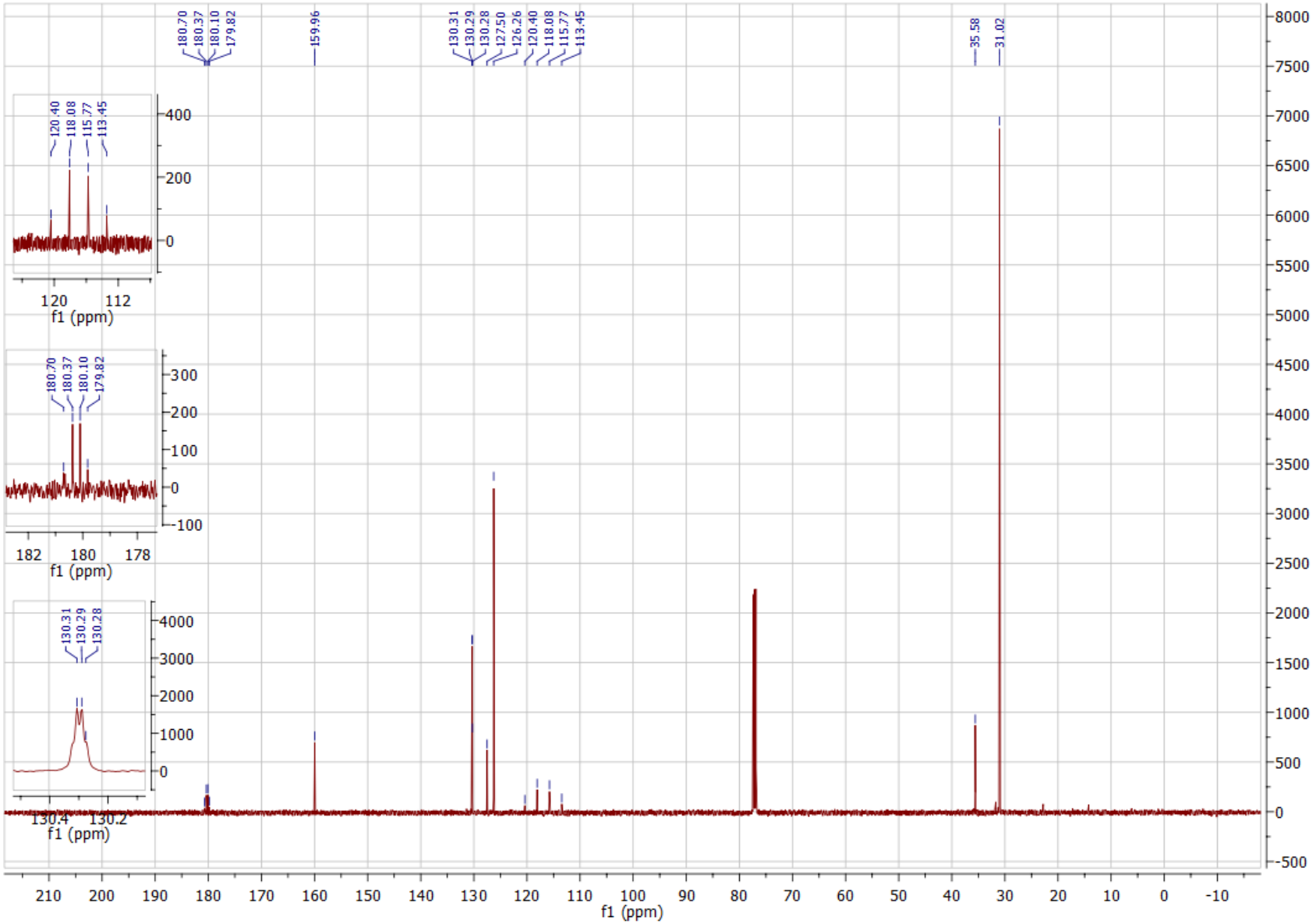
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of 4-(*tert*-Butyl)benzaldehyde (**28**)



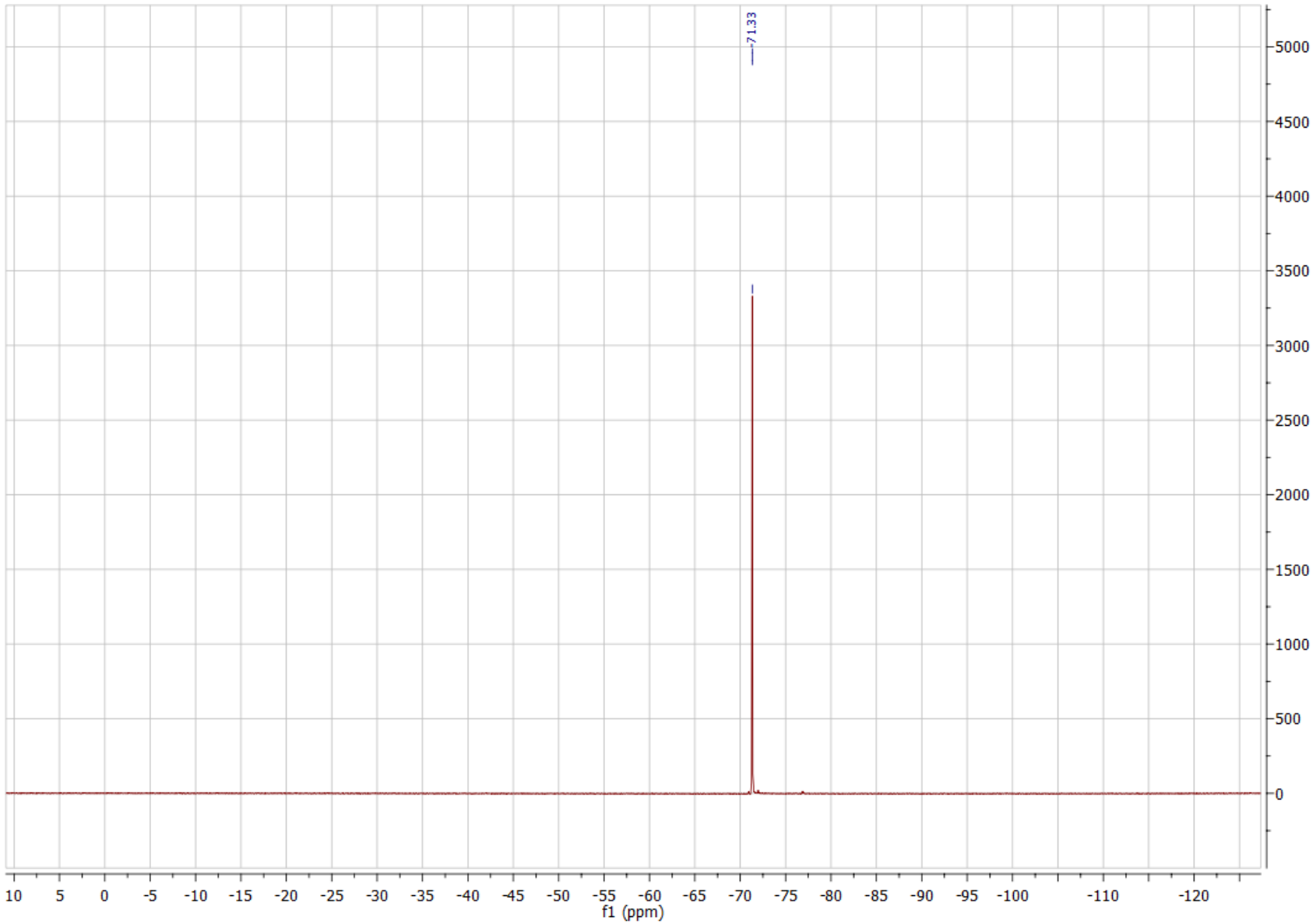
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethan-1-one (**29**)



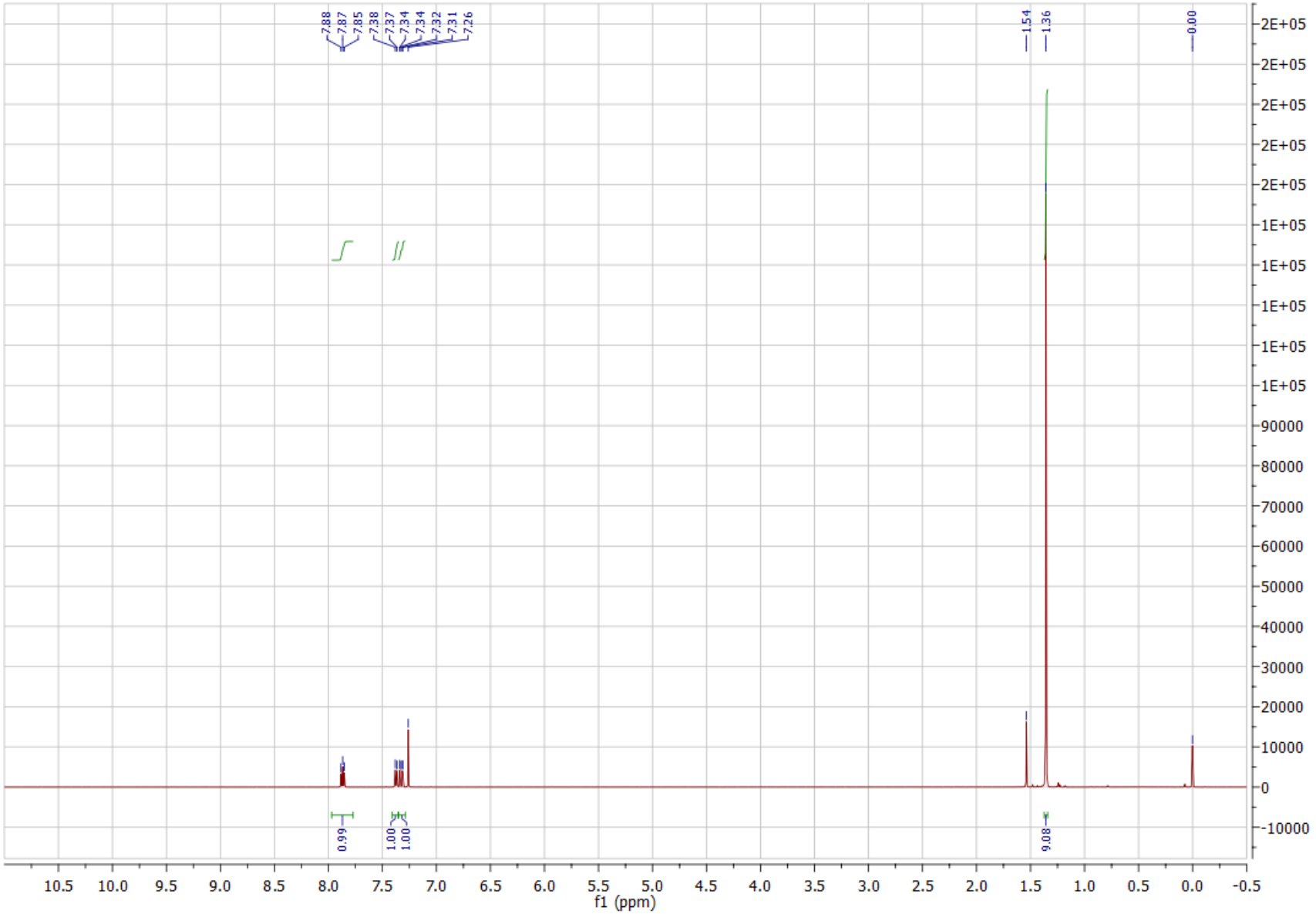
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethan-1-one (**29**)



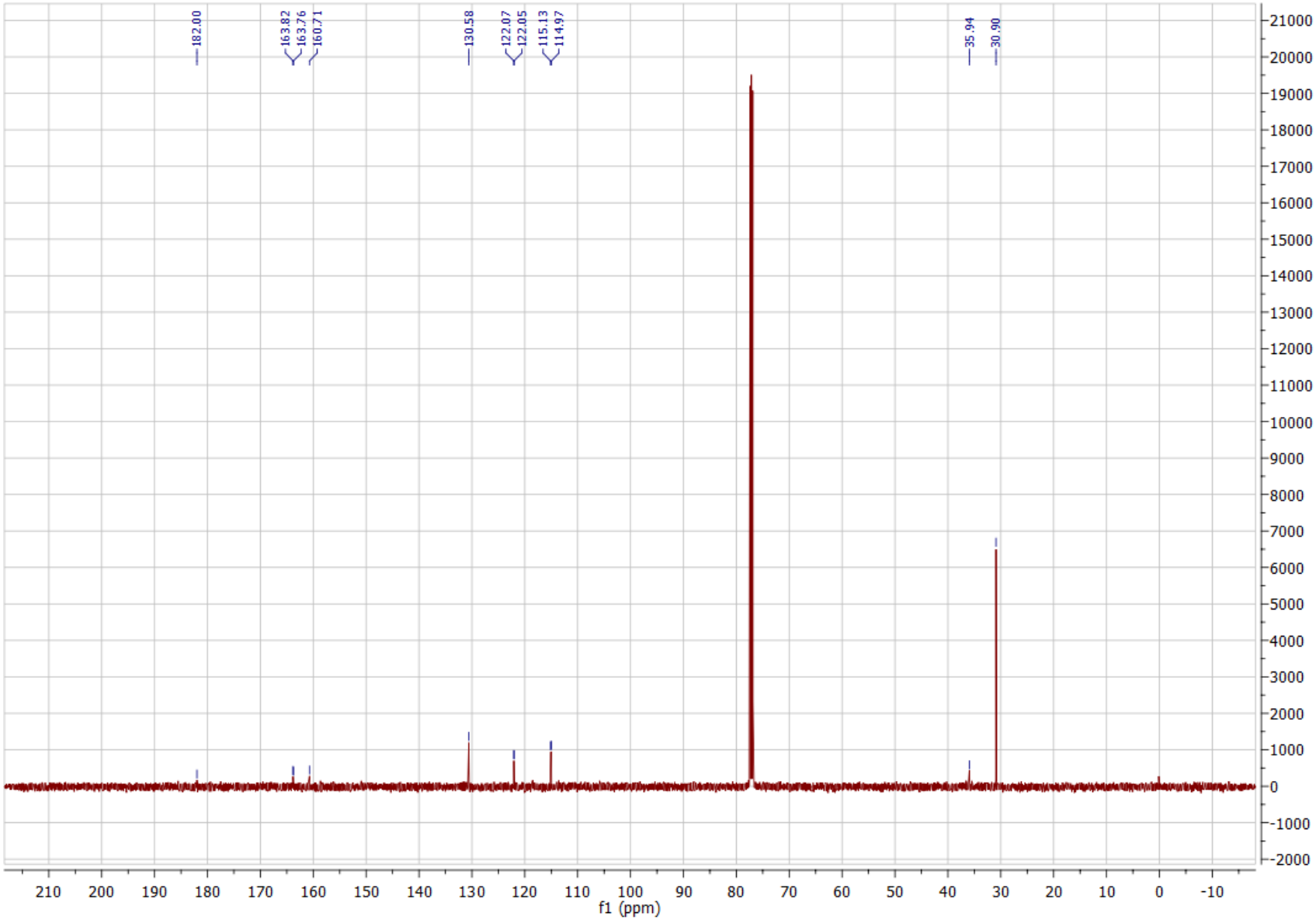
$^{19}F$ NMR ($CDCl_3$, 282.4 MHz) of 1-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethan-1-one (**29**)



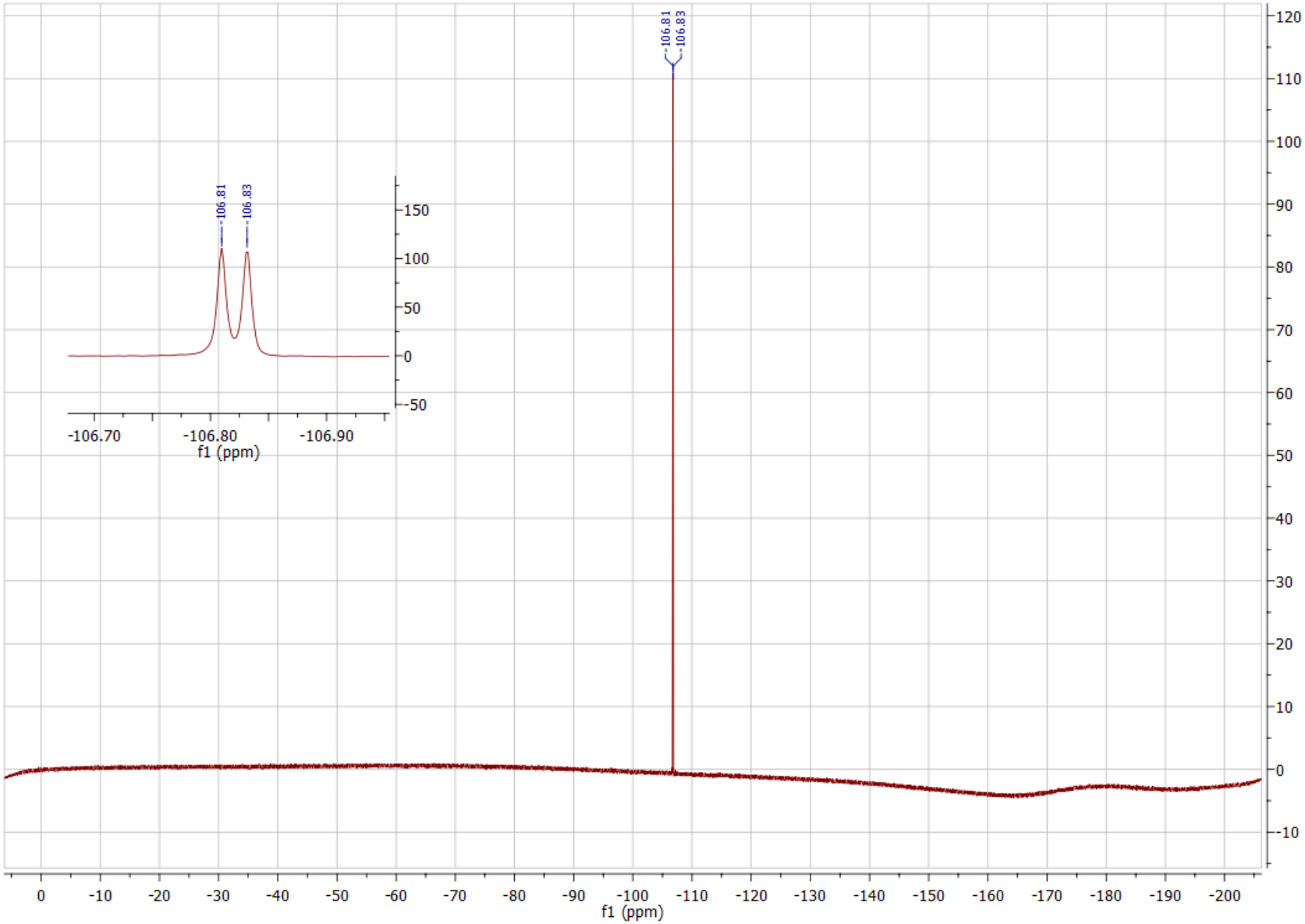
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(tert-butyl)-3-fluorobenzenesulfonyl fluoride (**30**)



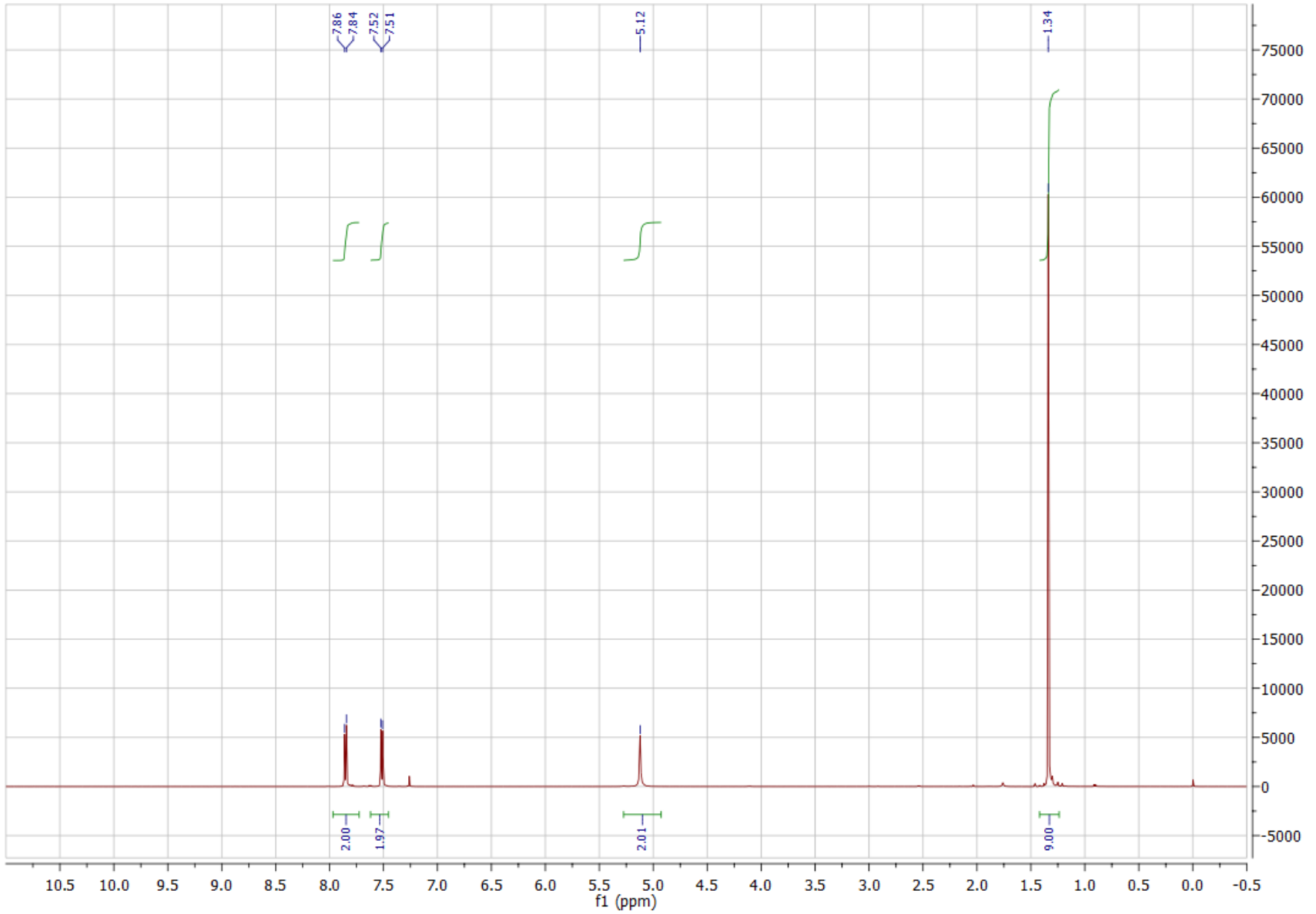
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(tert-butyl)-3-fluorobenzenesulfonyl fluoride (**30**)



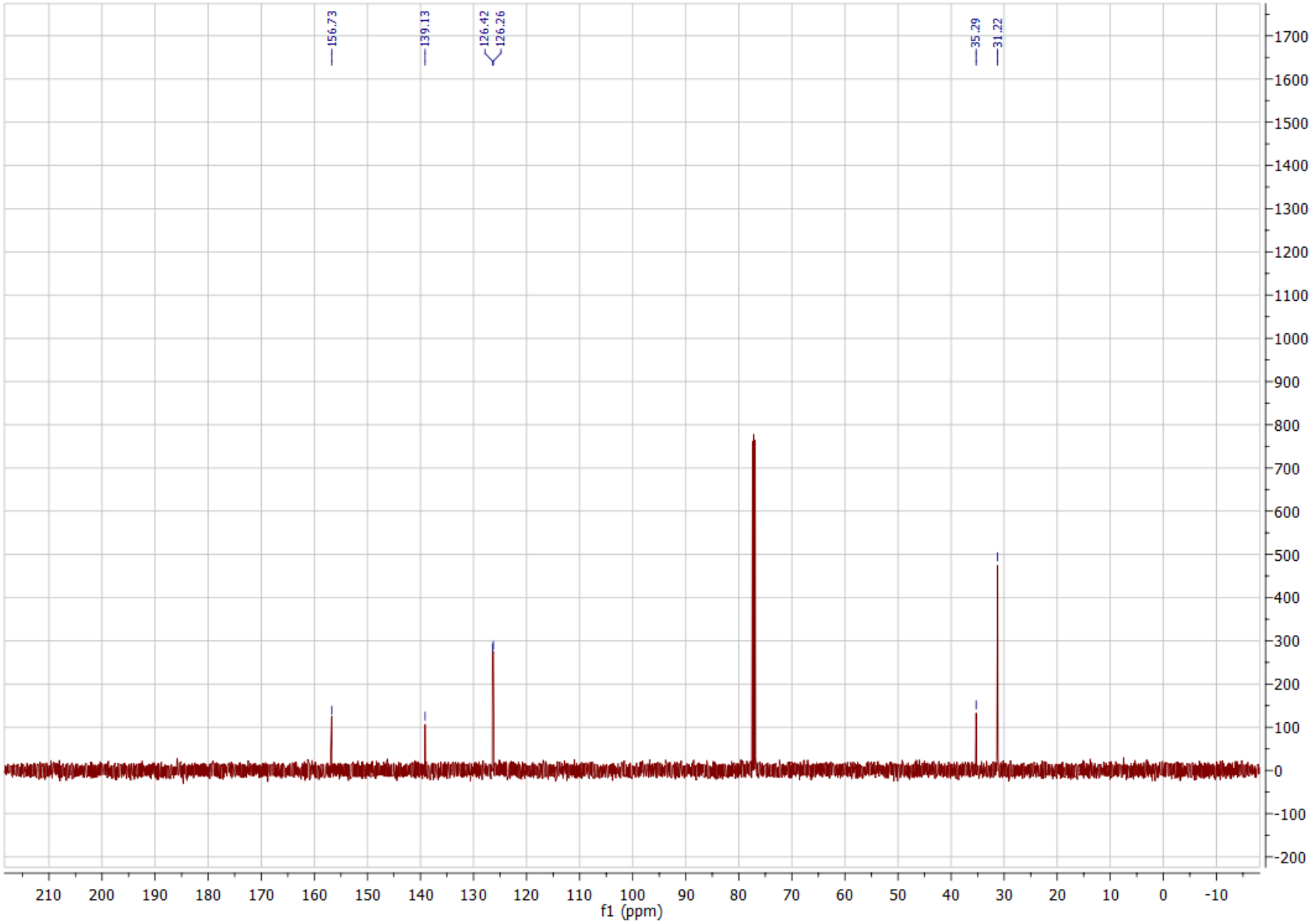
$^{19}F$ NMR ($CDCl_3$, 470.8 MHz) of 4-(tert-butyl)-3-fluorobenzenesulfonyl fluoride (**30**)



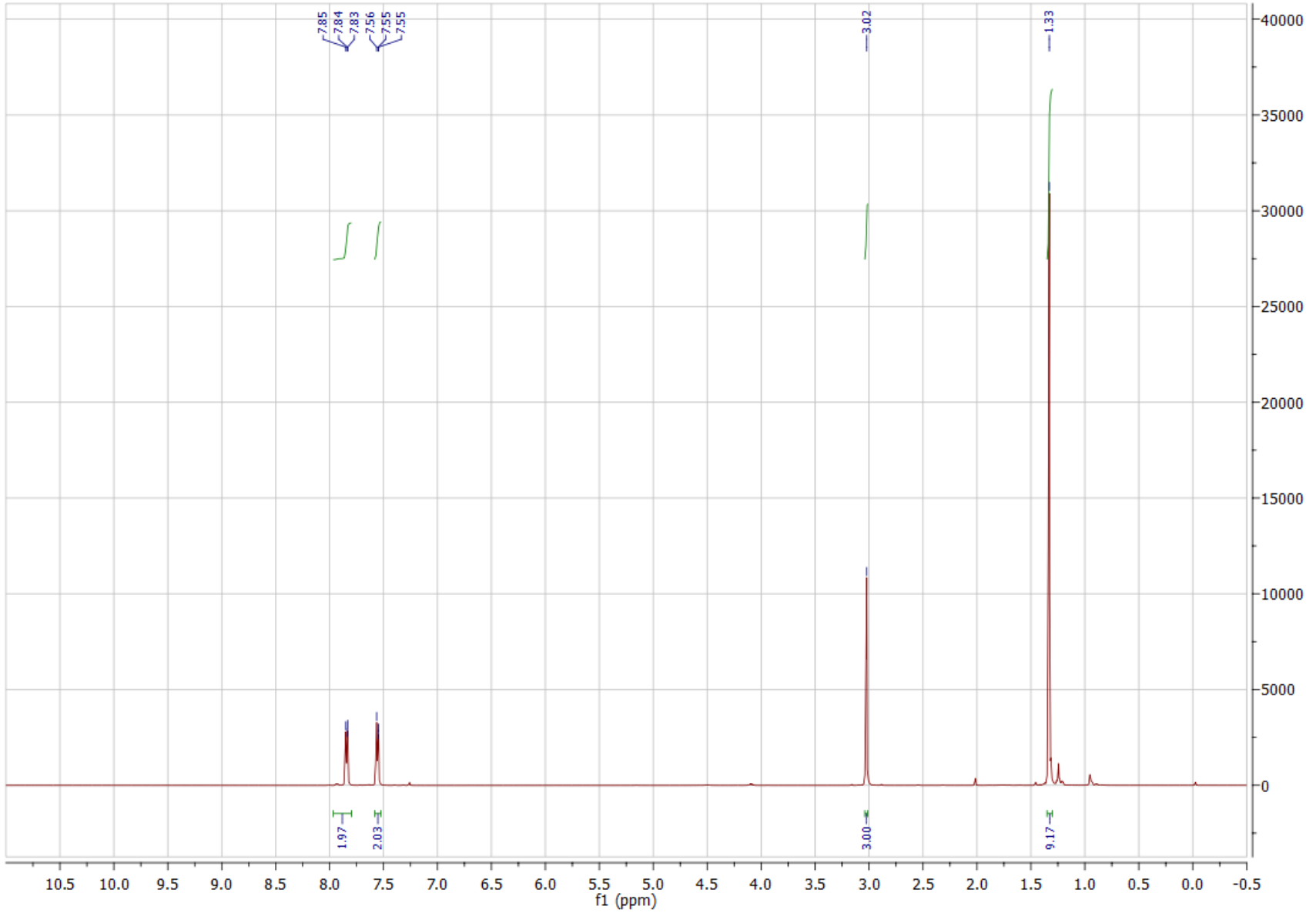
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(*tert*-Butyl)benzenesulfonamide (**31**)



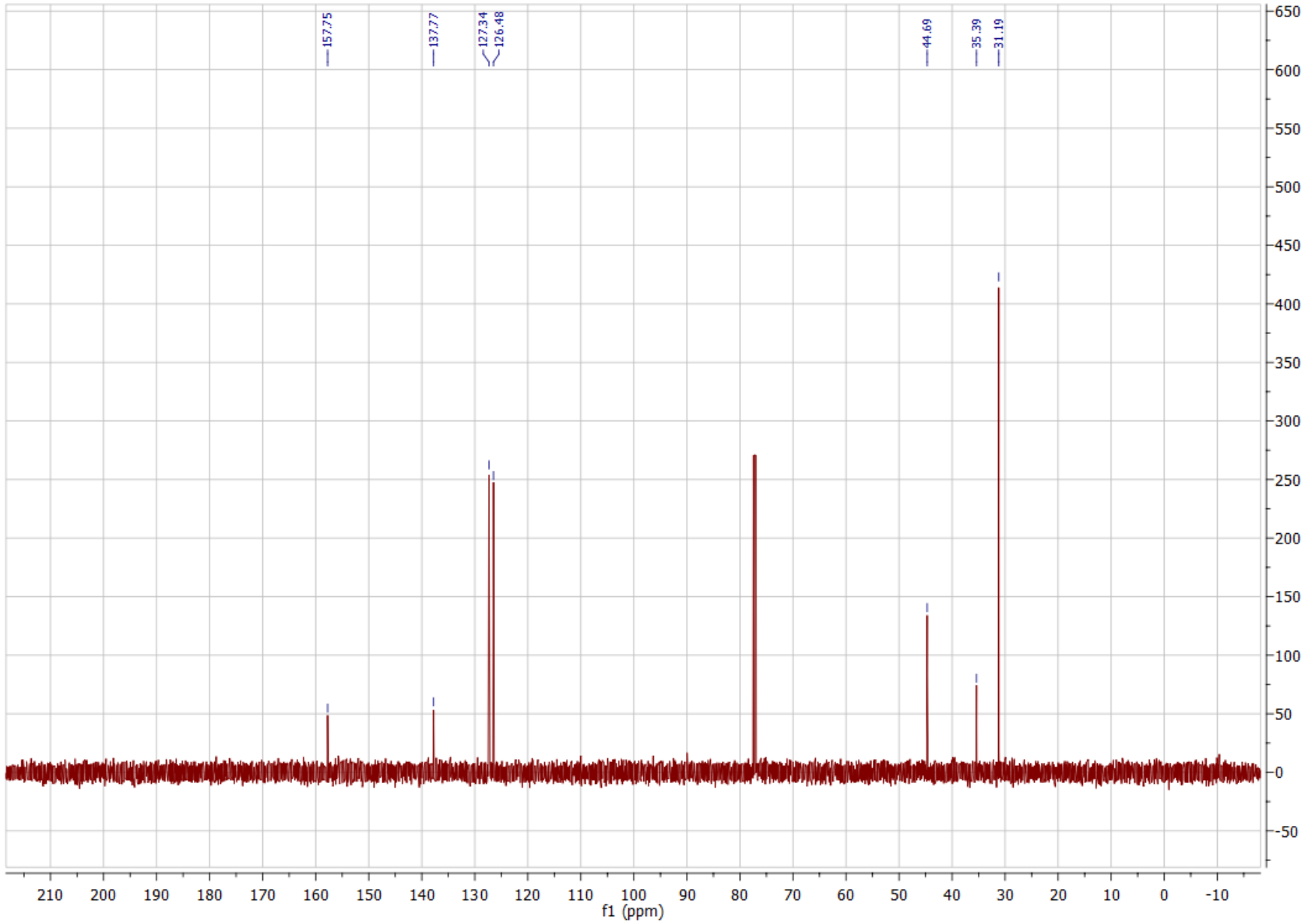
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(*tert*-Butyl)benzenesulfonamide (**31**)



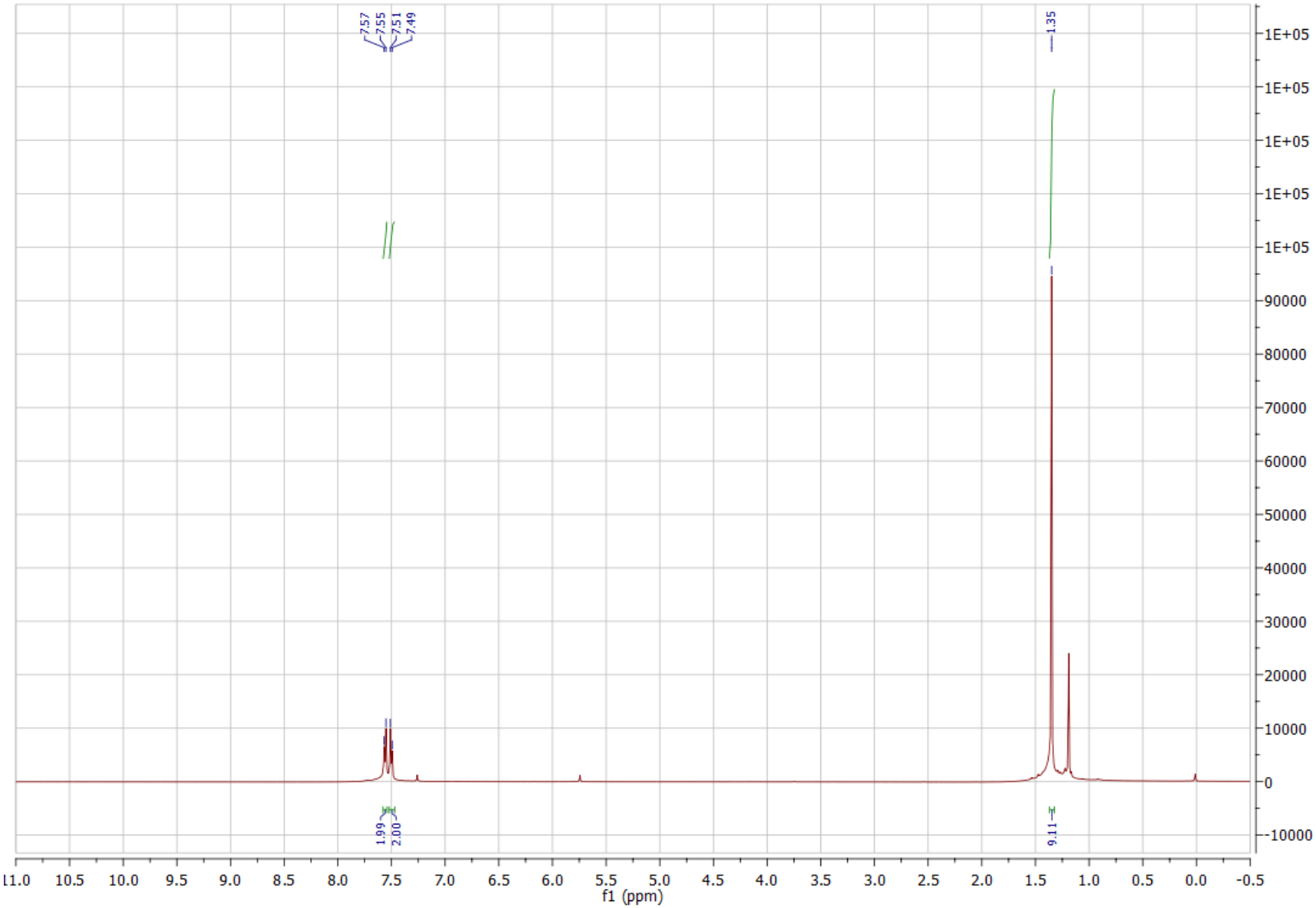
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(*tert*-Butyl)-4-(methylsulfonyl)benzene (**32**)



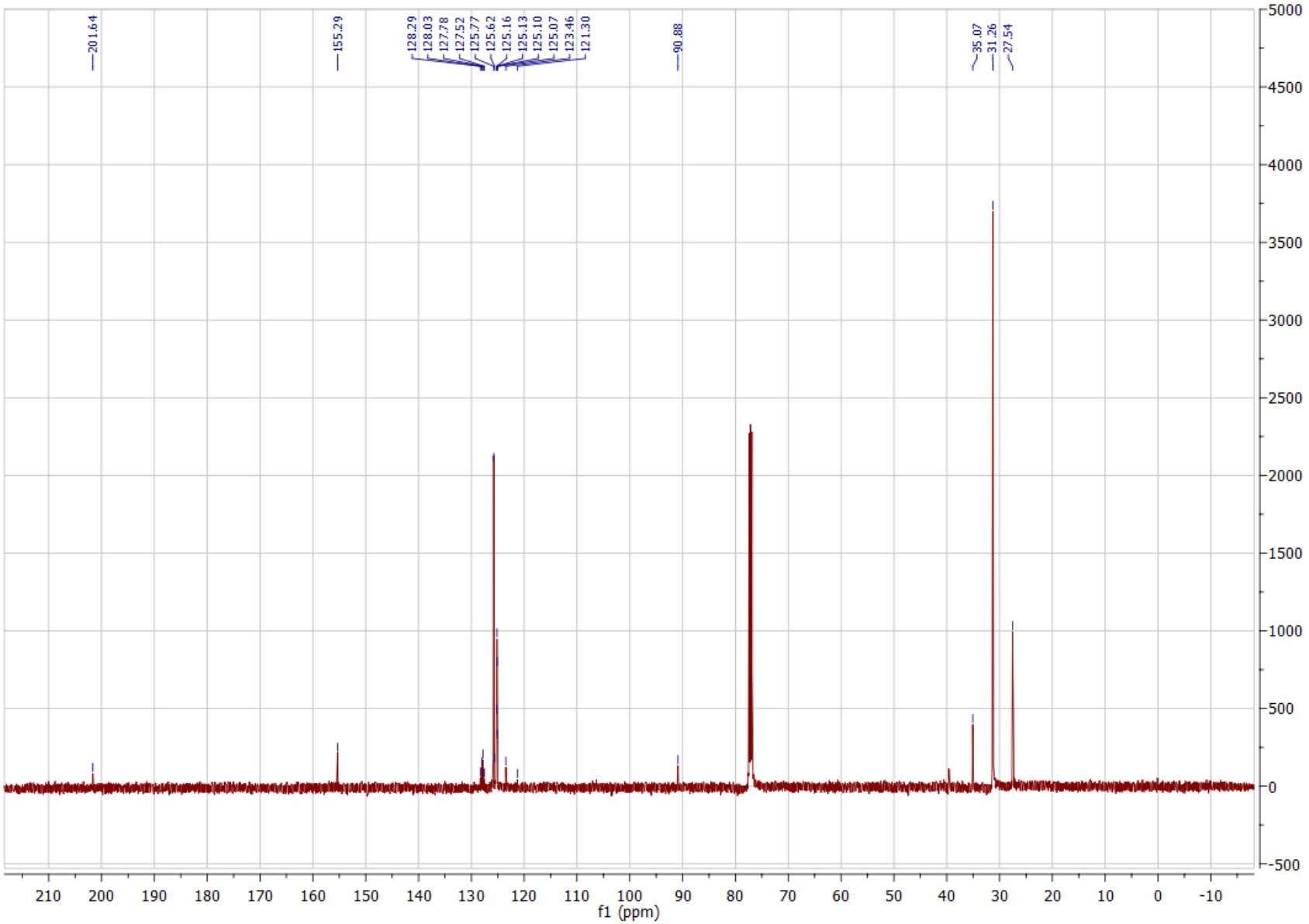
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of 1-(*tert*-Butyl)-4-(methylsulfonyl)benzene (**32**)



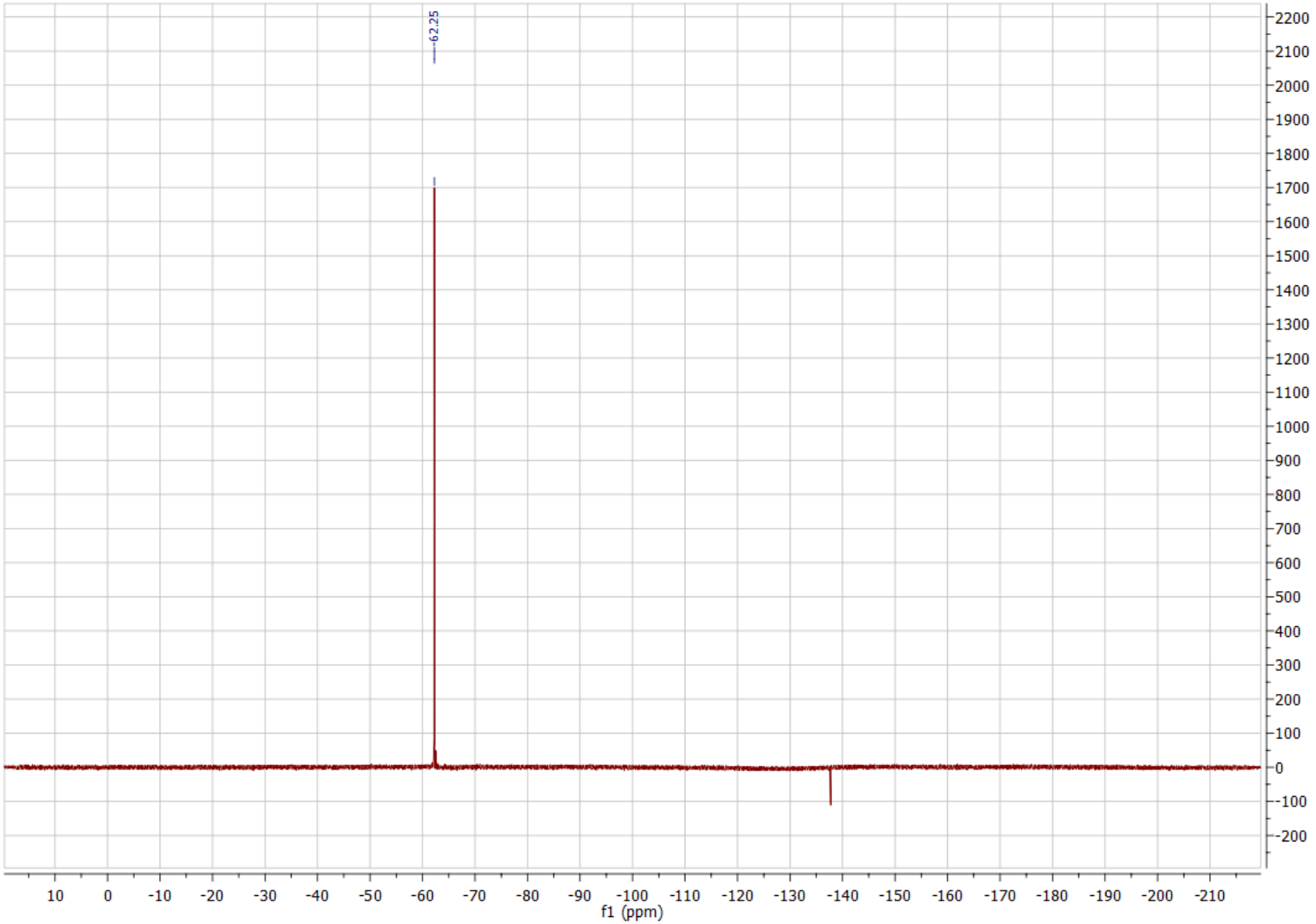
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(tert-butyl)-4-(trifluoromethyl)benzene (**33**) (with <5% ligand)



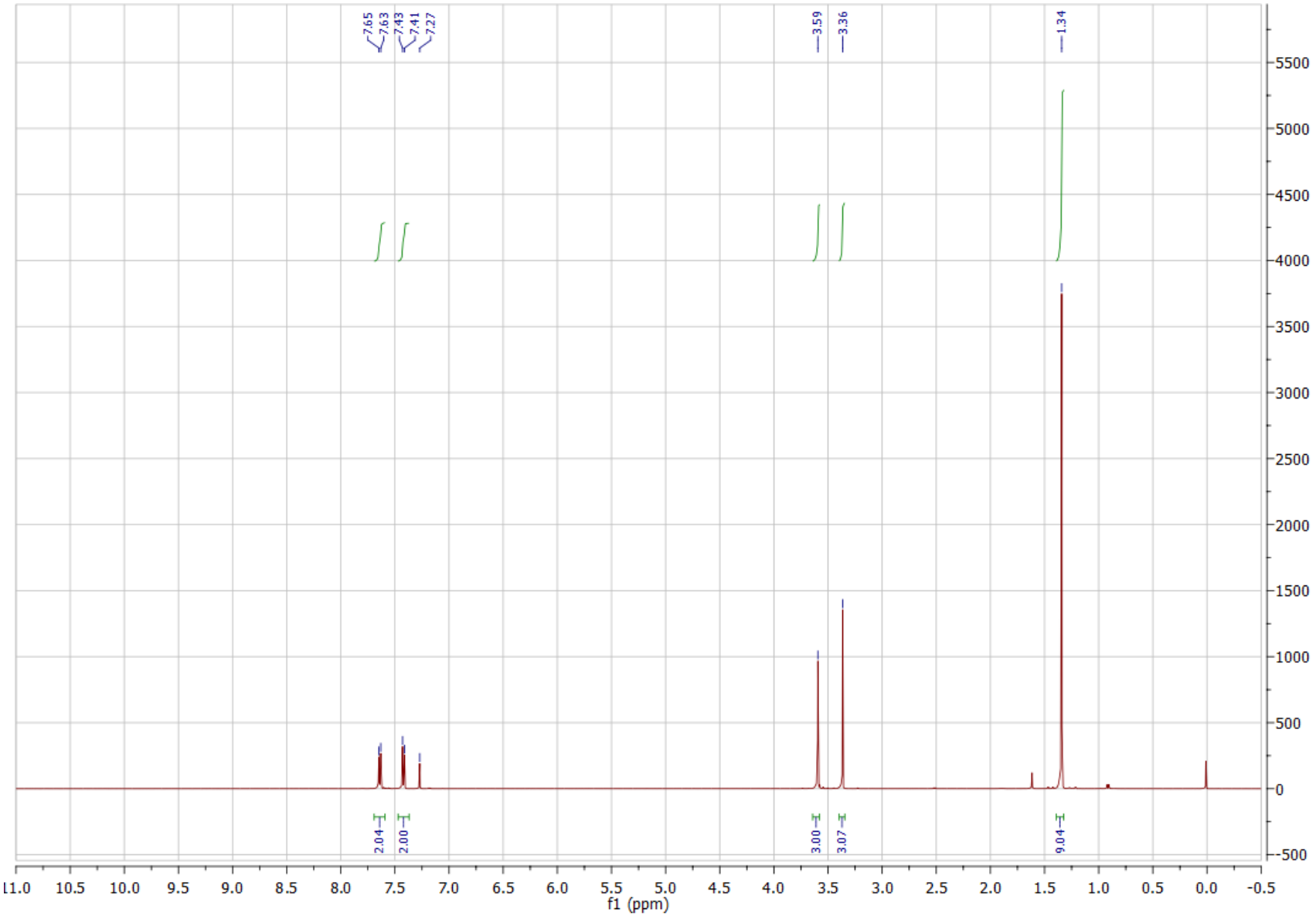
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(tert-butyl)-4-(trifluoromethyl)benzene (**33**) (with <5% ligand)



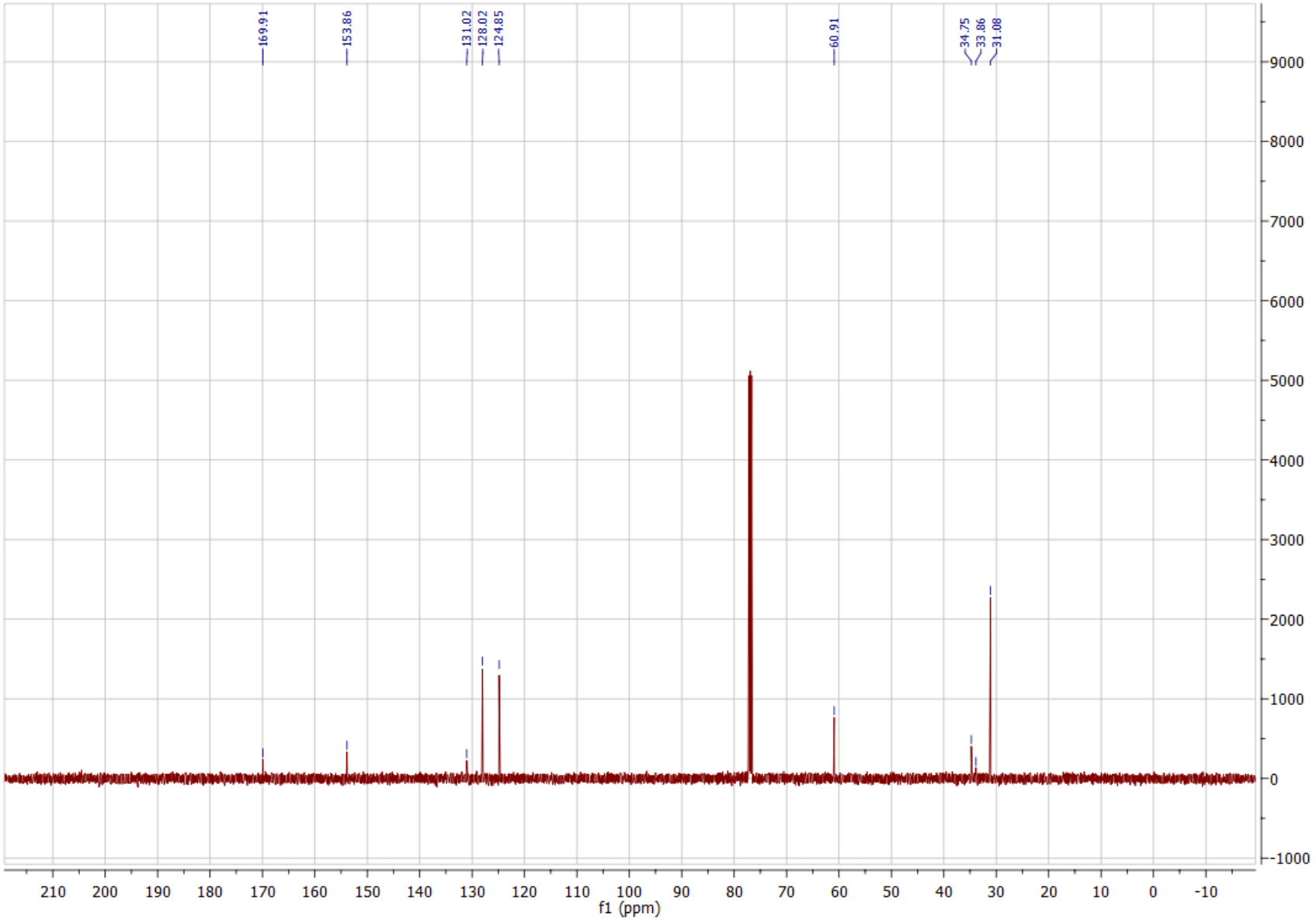
$^{19}F$ NMR ($CDCl_3$, 282.4 MHz) of 1-(tert-butyl)-4-(trifluoromethyl)benzene (**33**) (with <5% ligand)



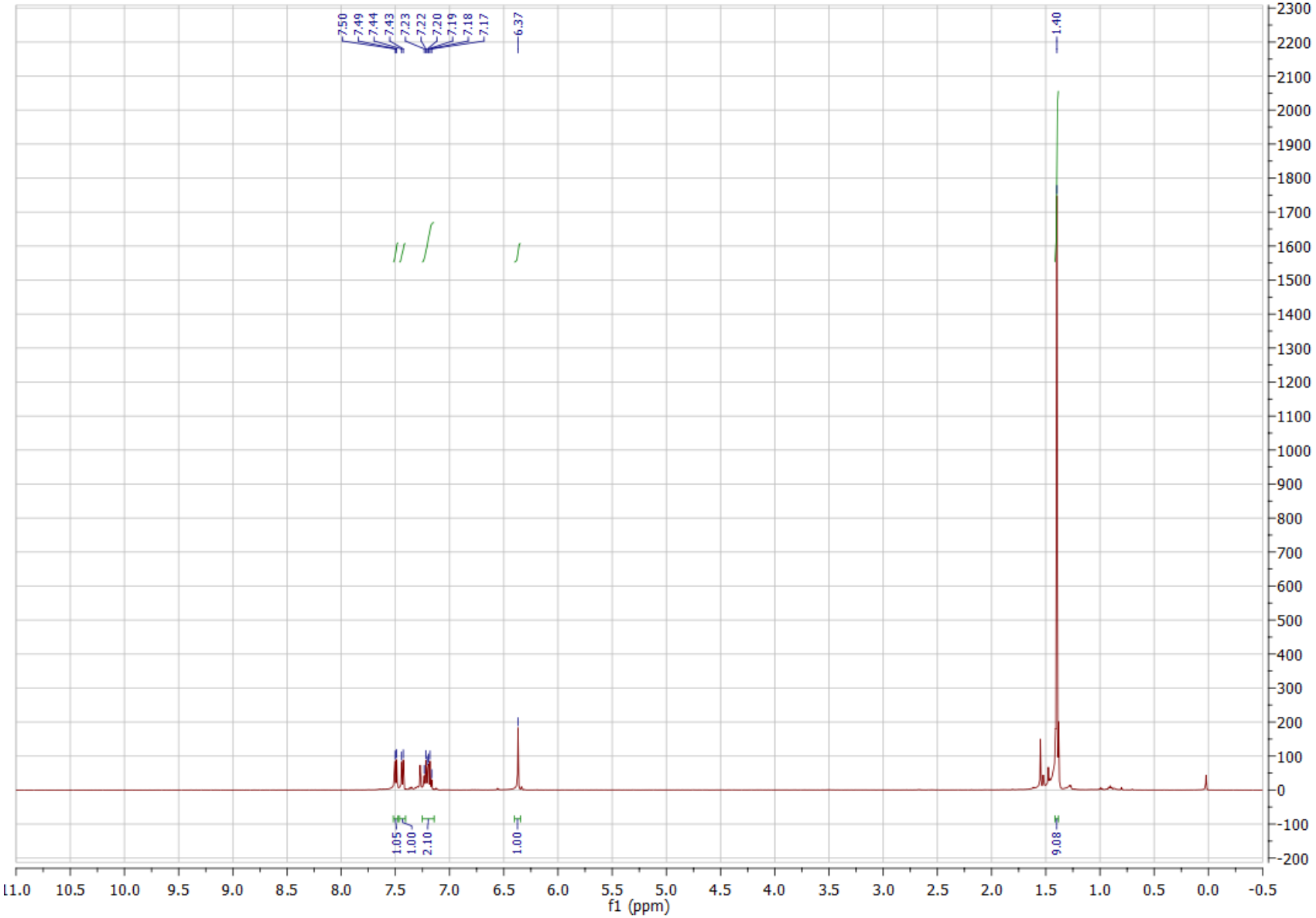
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(tert-butyl)-N-methoxy-N-methylbenzamide (**34**)



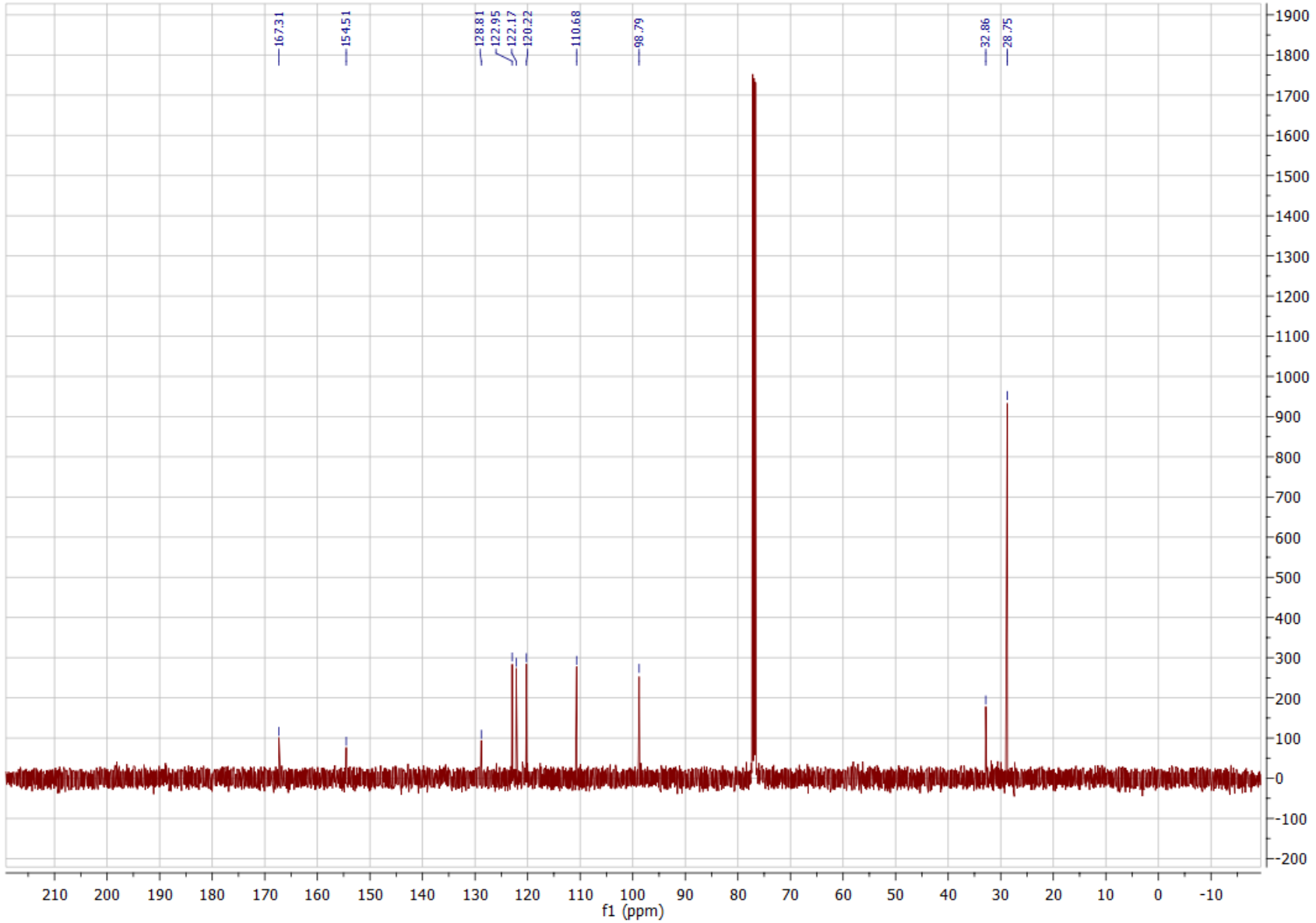
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(tert-butyl)-N-methoxy-N-methylbenzamide (**34**)



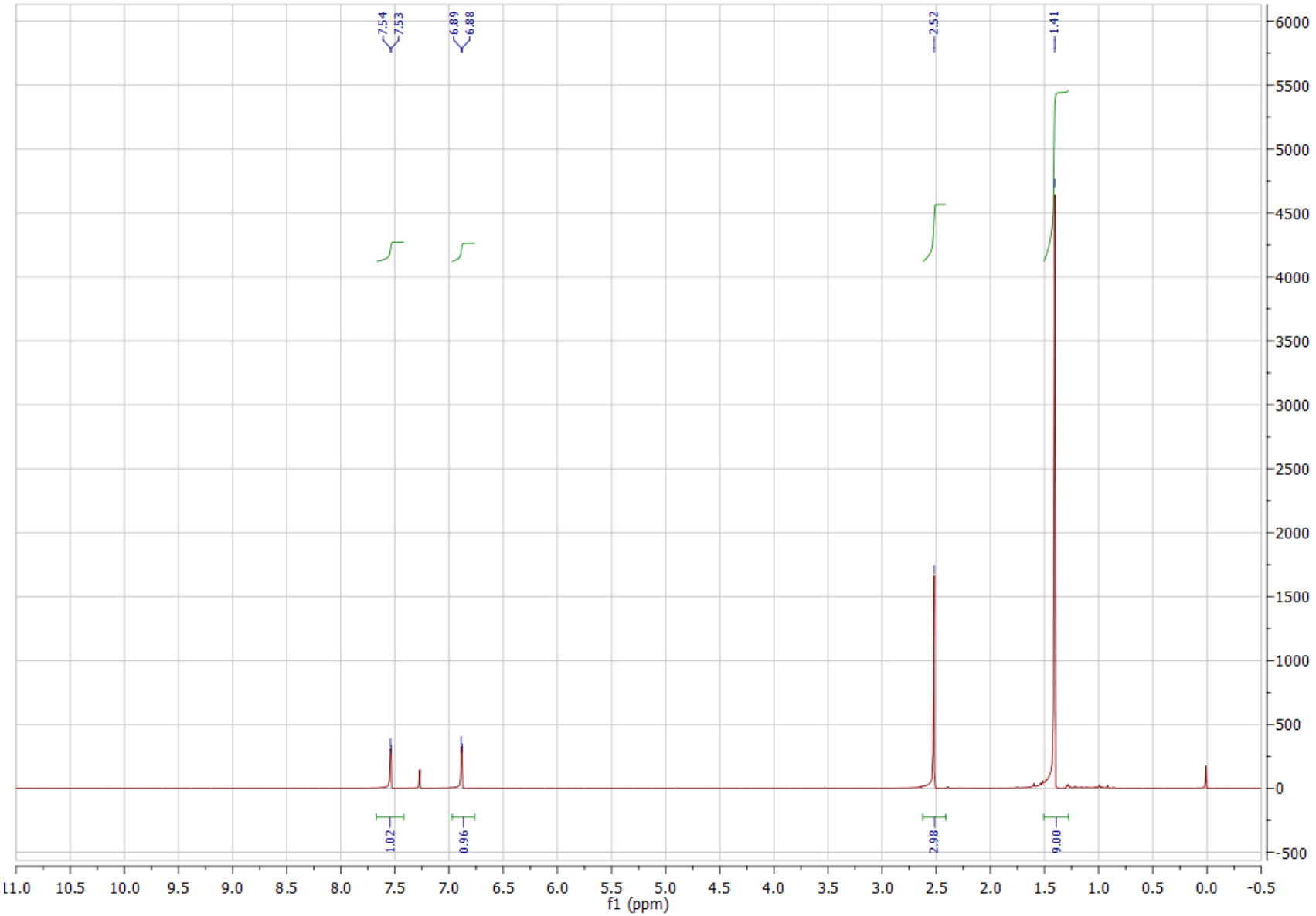
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 2-(*tert*-Butyl)benzofuran (**35**)



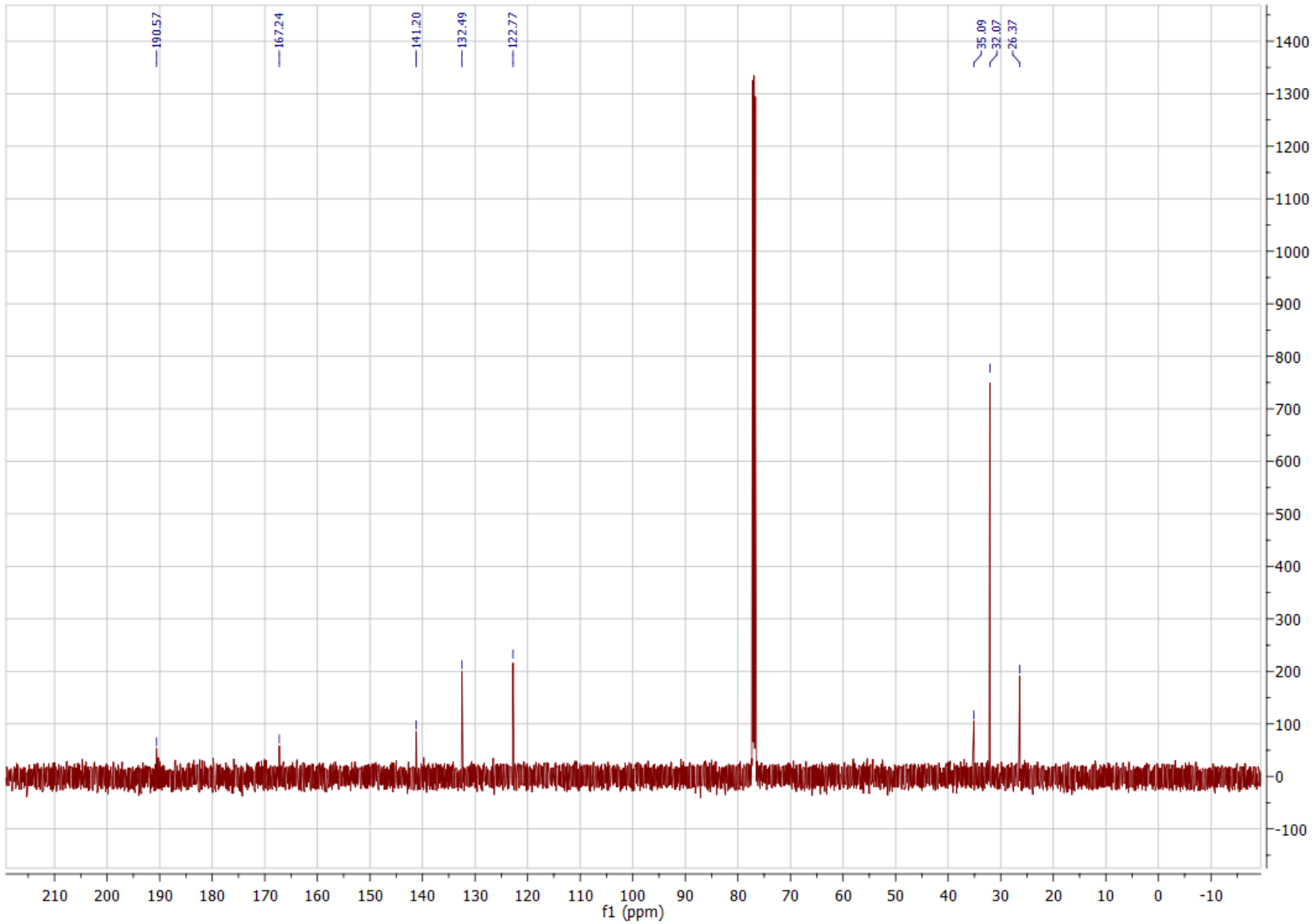
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of 2-(*tert*-Butyl)benzofuran (**35**)



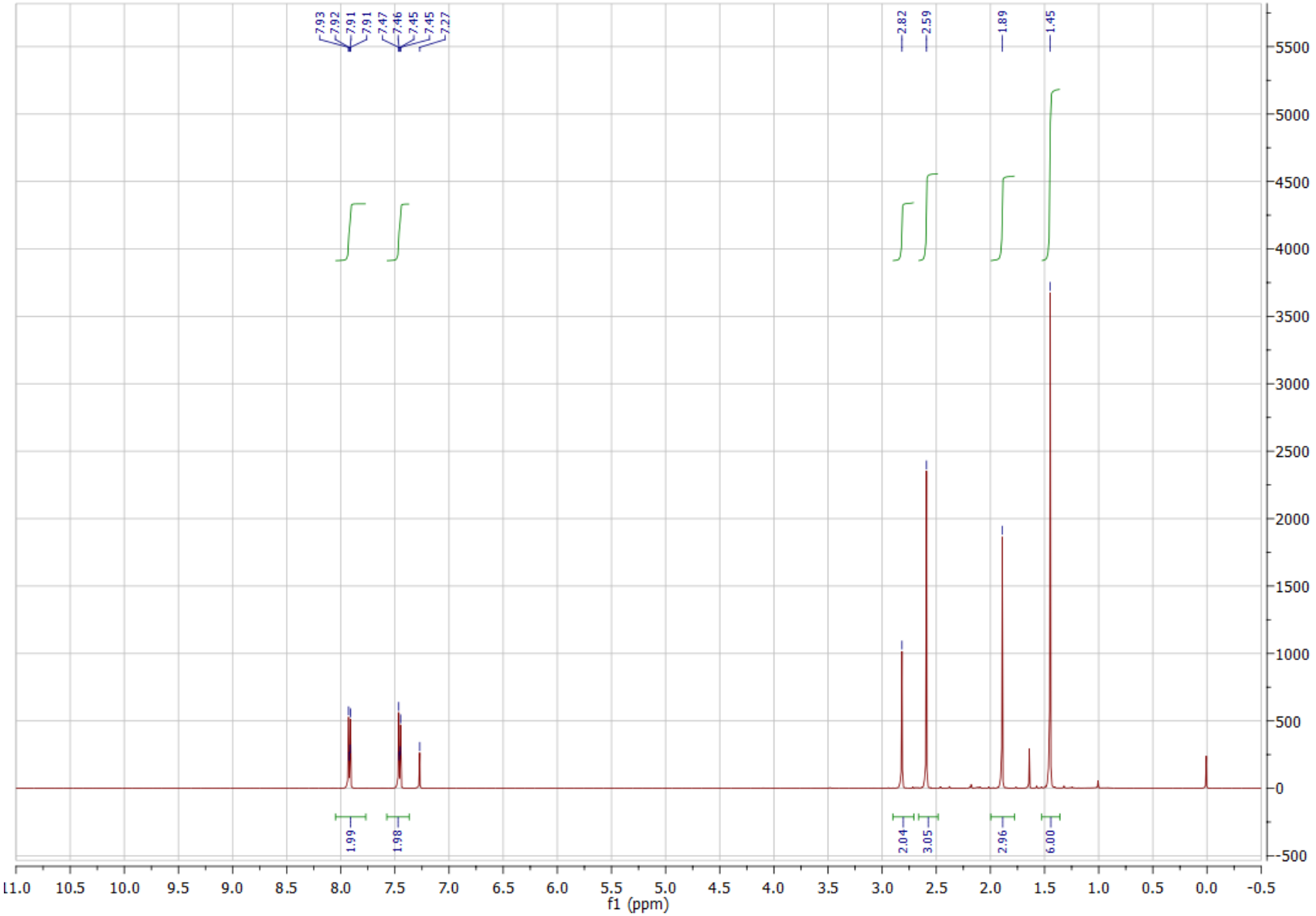
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(5-(tert-butyl)thiophen-2-yl)ethan-1-one **(36)**



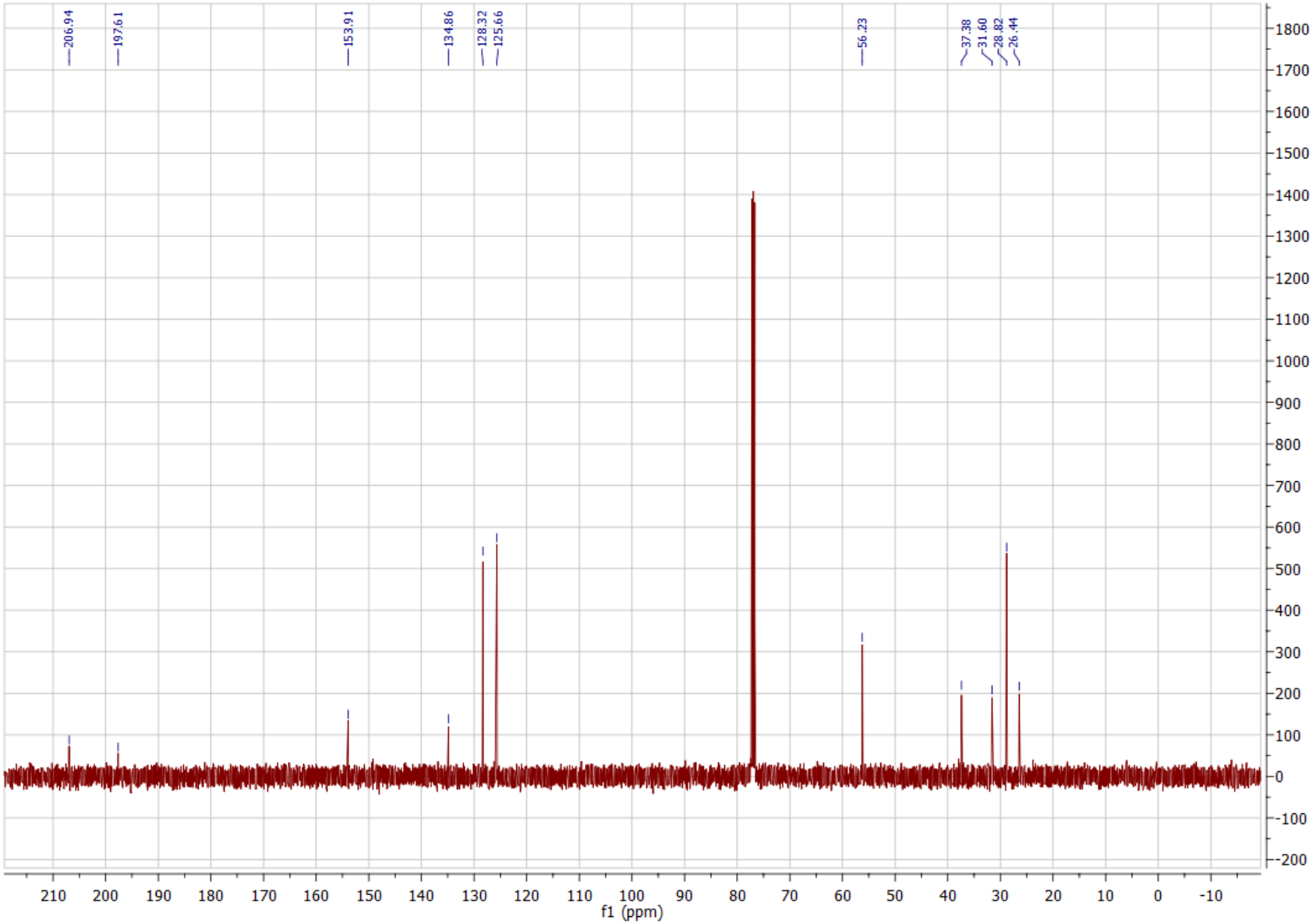
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(5-(tert-butyl)thiophen-2-yl)ethan-1-one **(36)**



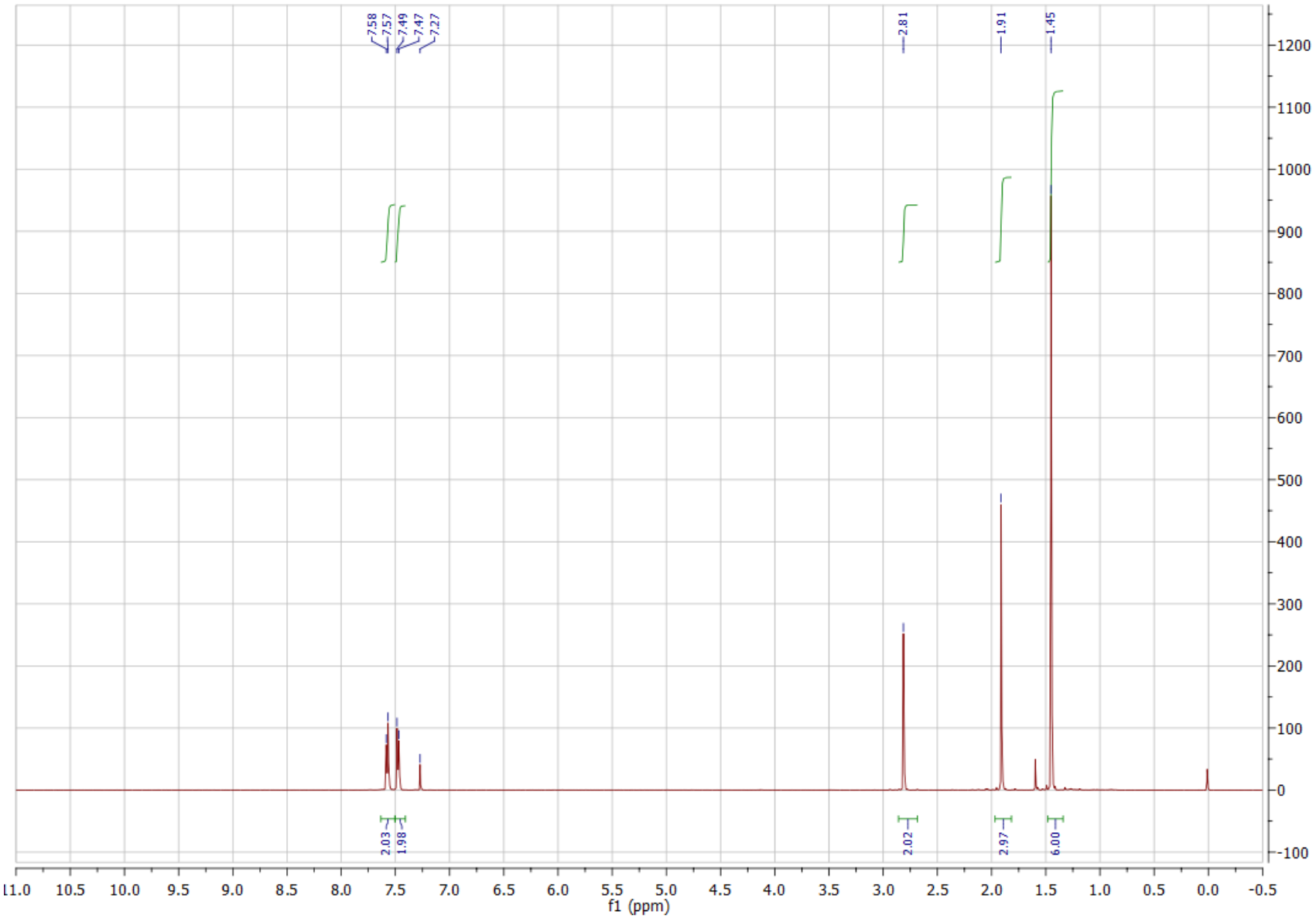
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(4-Acetylphenyl)-4-methylpentan-2-one **(39)**



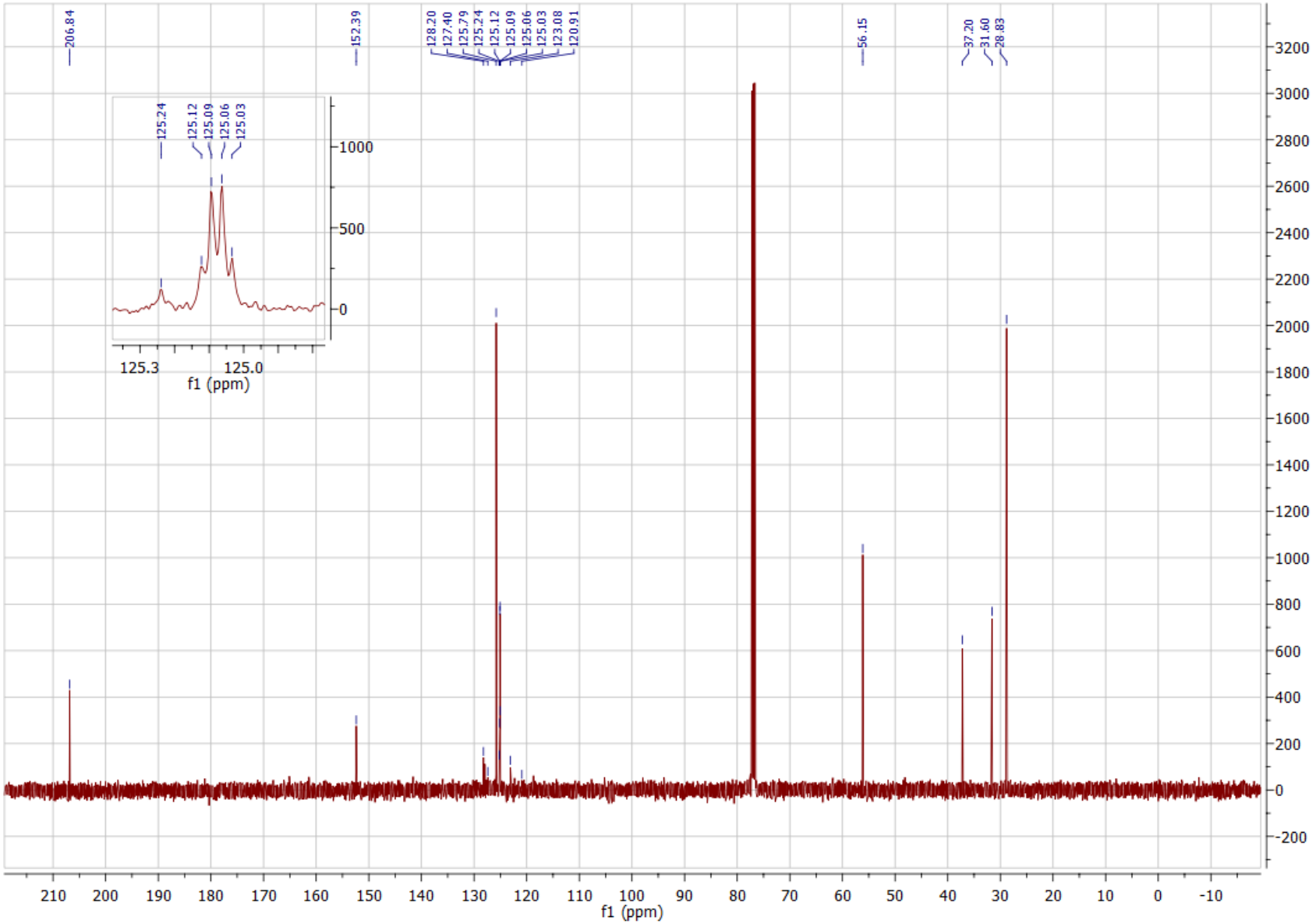
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of of 4-(4-Acetylphenyl)-4-methylpentan-2-one **(39)**



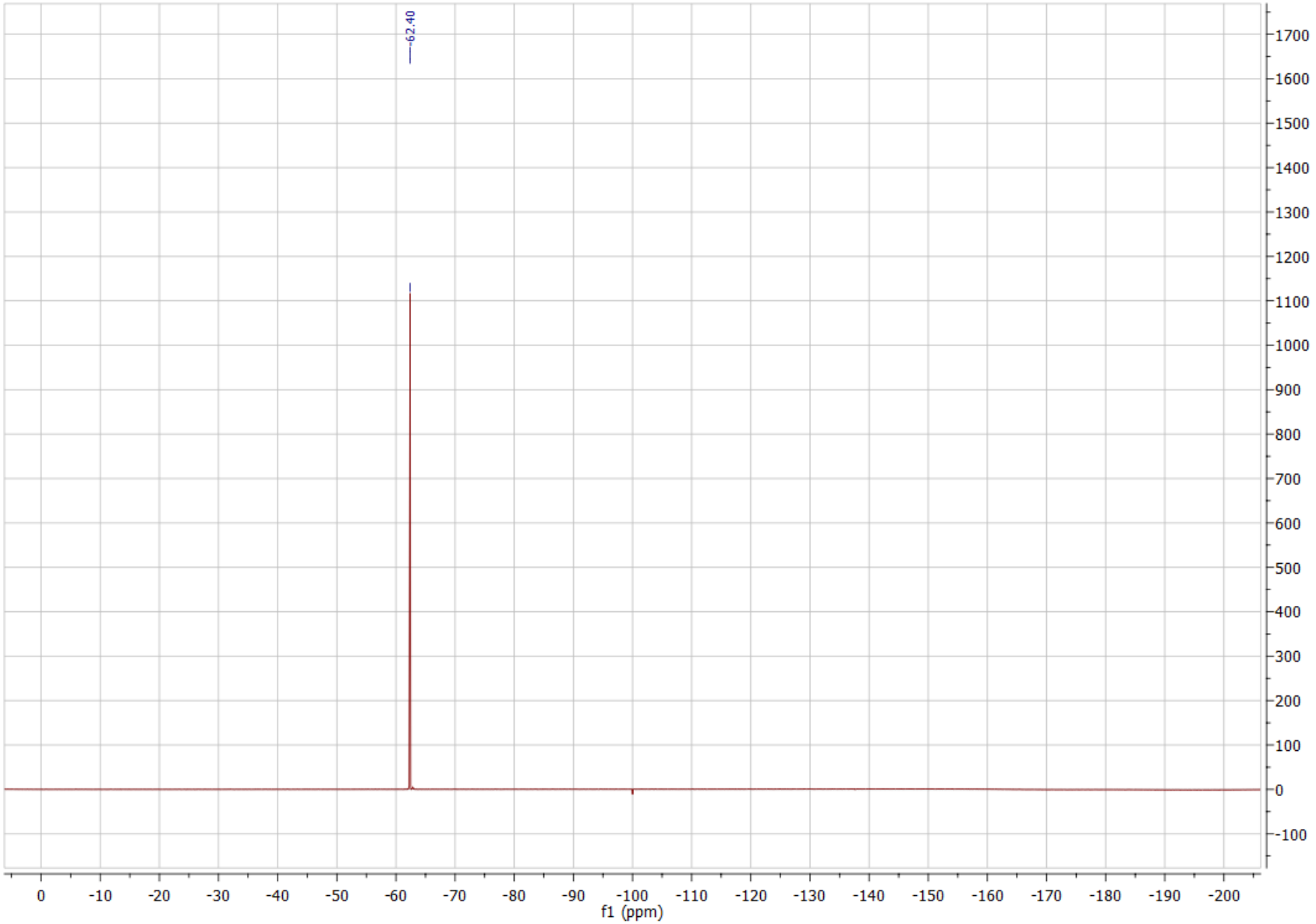
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-Methyl-4-(4-(trifluoromethyl)phenyl)pentan-2-one **(40)**



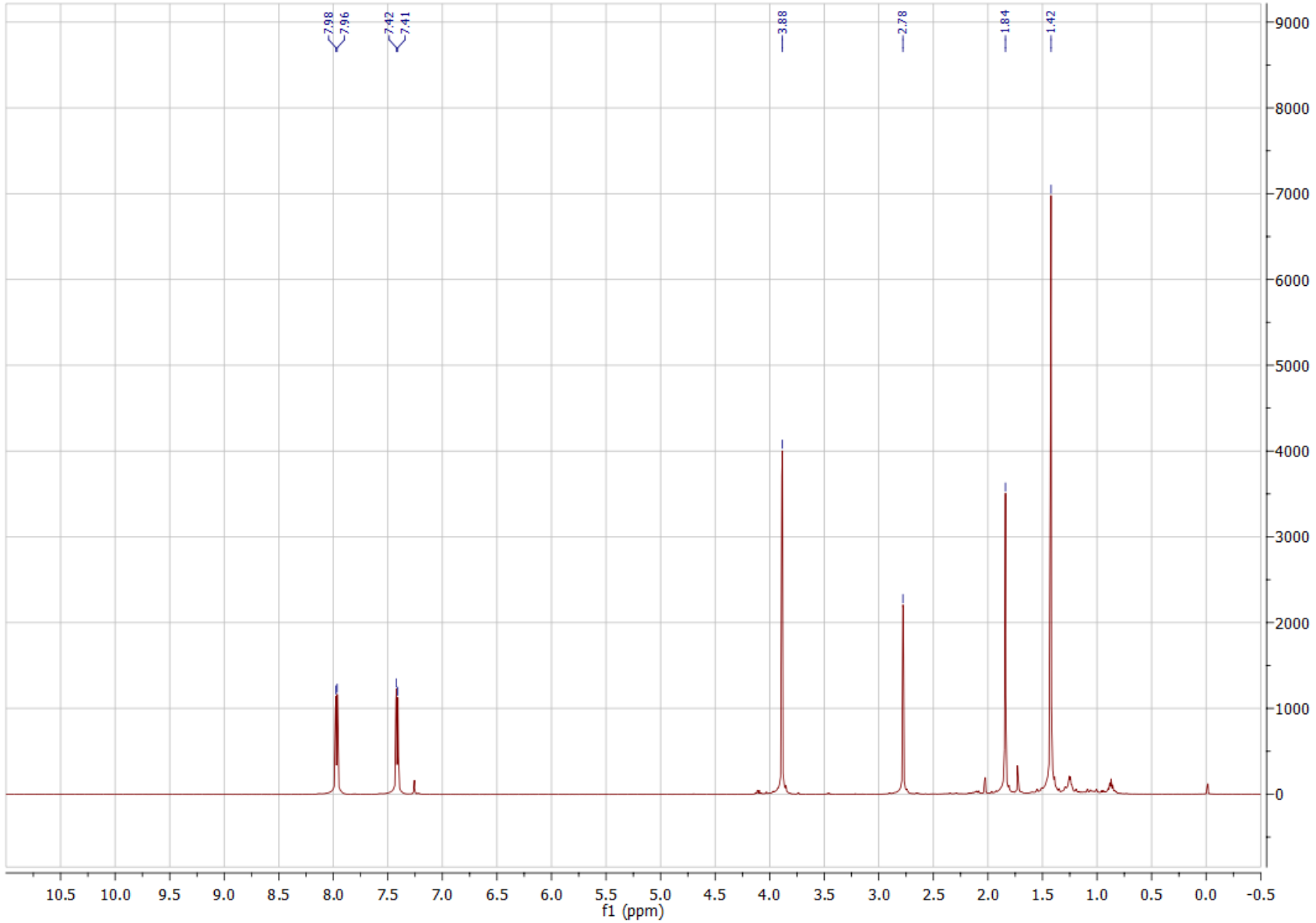
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-Methyl-4-(4-(trifluoromethyl)phenyl)pentan-2-one **(40)**



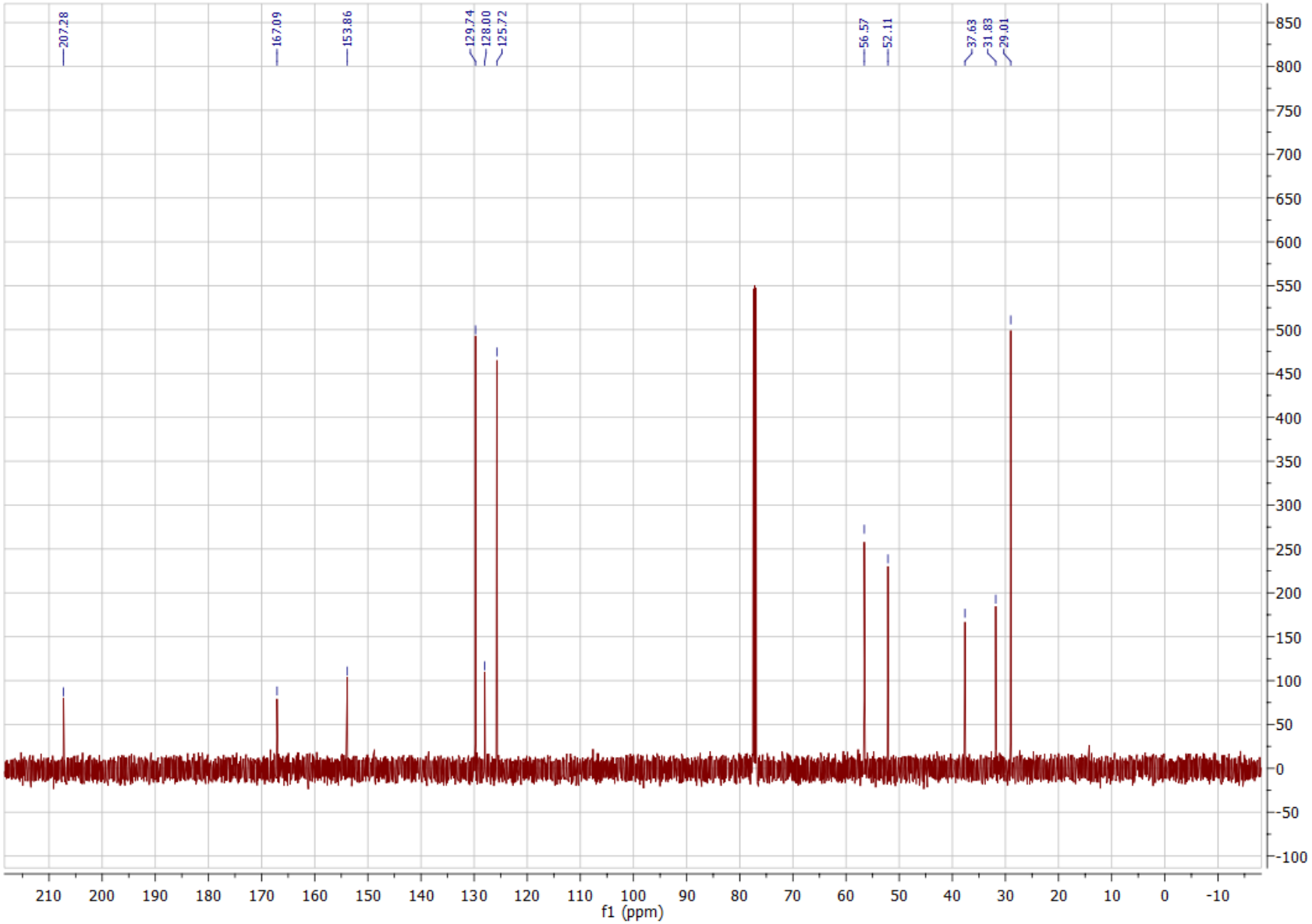
$^{19}F$ NMR ($CDCl_3$, 470.8 MHz) of 4-Methyl-4-(4-(trifluoromethyl)phenyl)pentan-2-one **(40)**



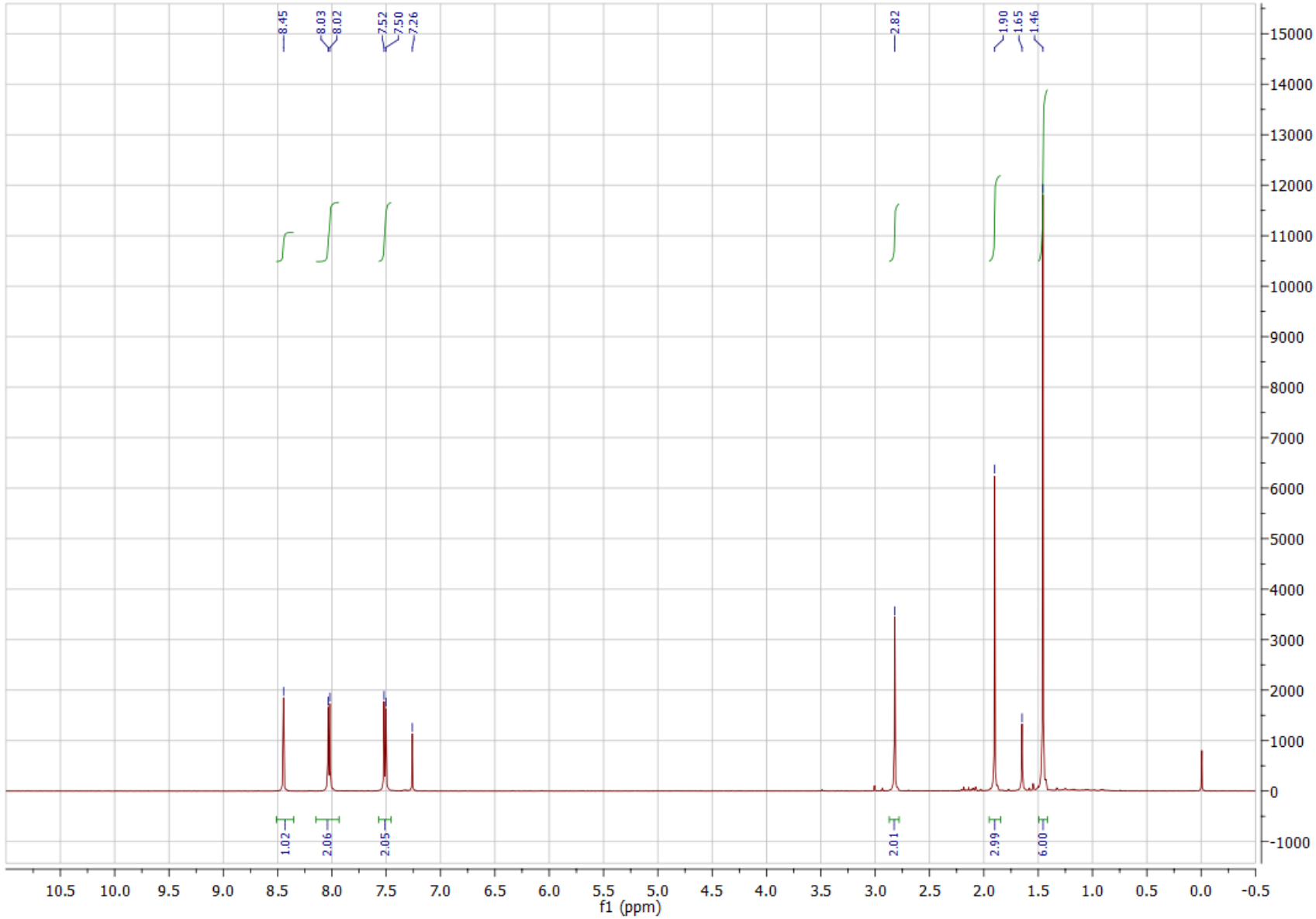
$^{1}$H NMR ($CDCl_3$, 500 MHz) of Methyl 4-(2-methyl-4-oxopentan-2-yl)benzoate **(41)**



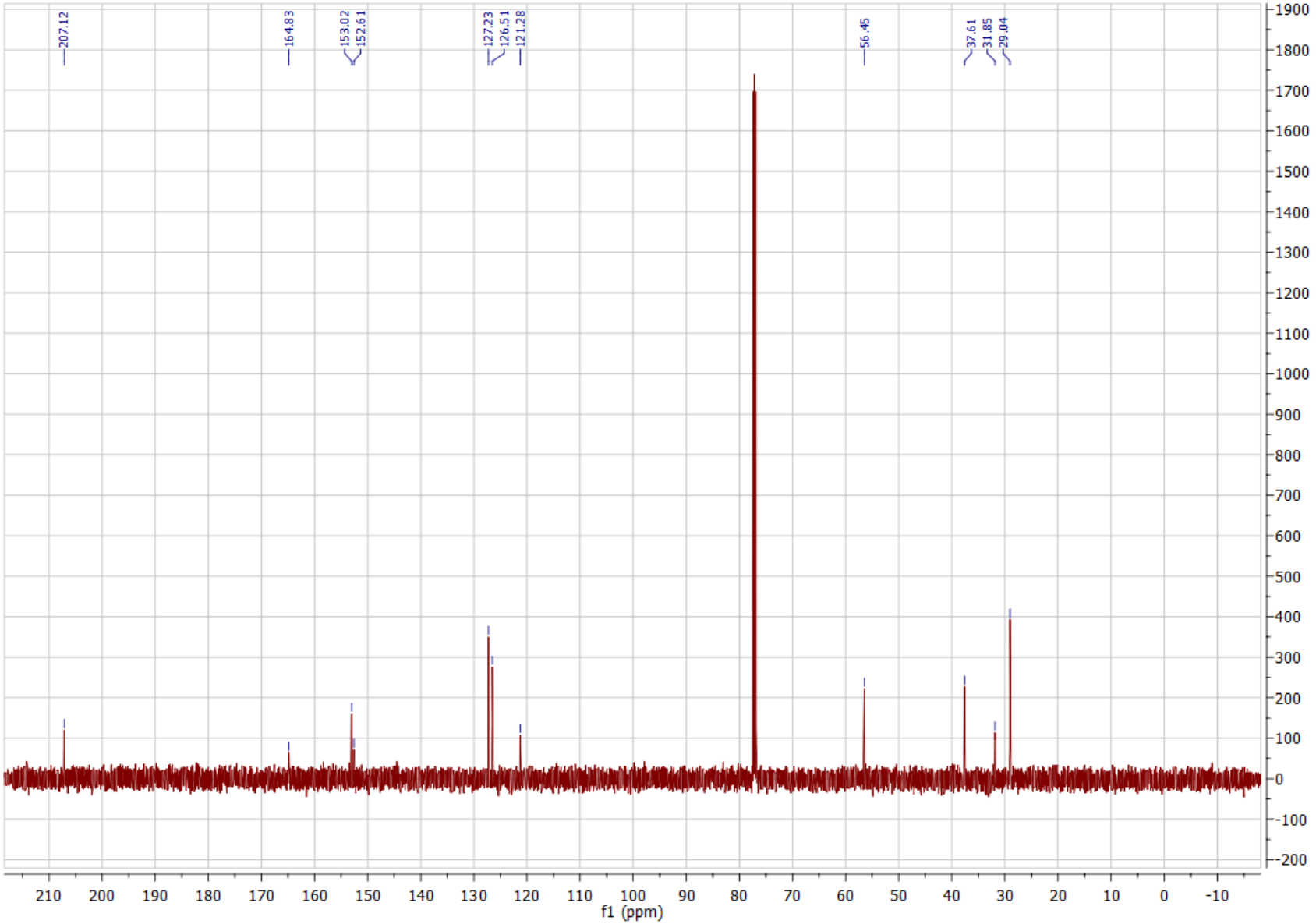
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of Methyl 4-(2-methyl-4-oxopentan-2-yl)benzoate **(41)**



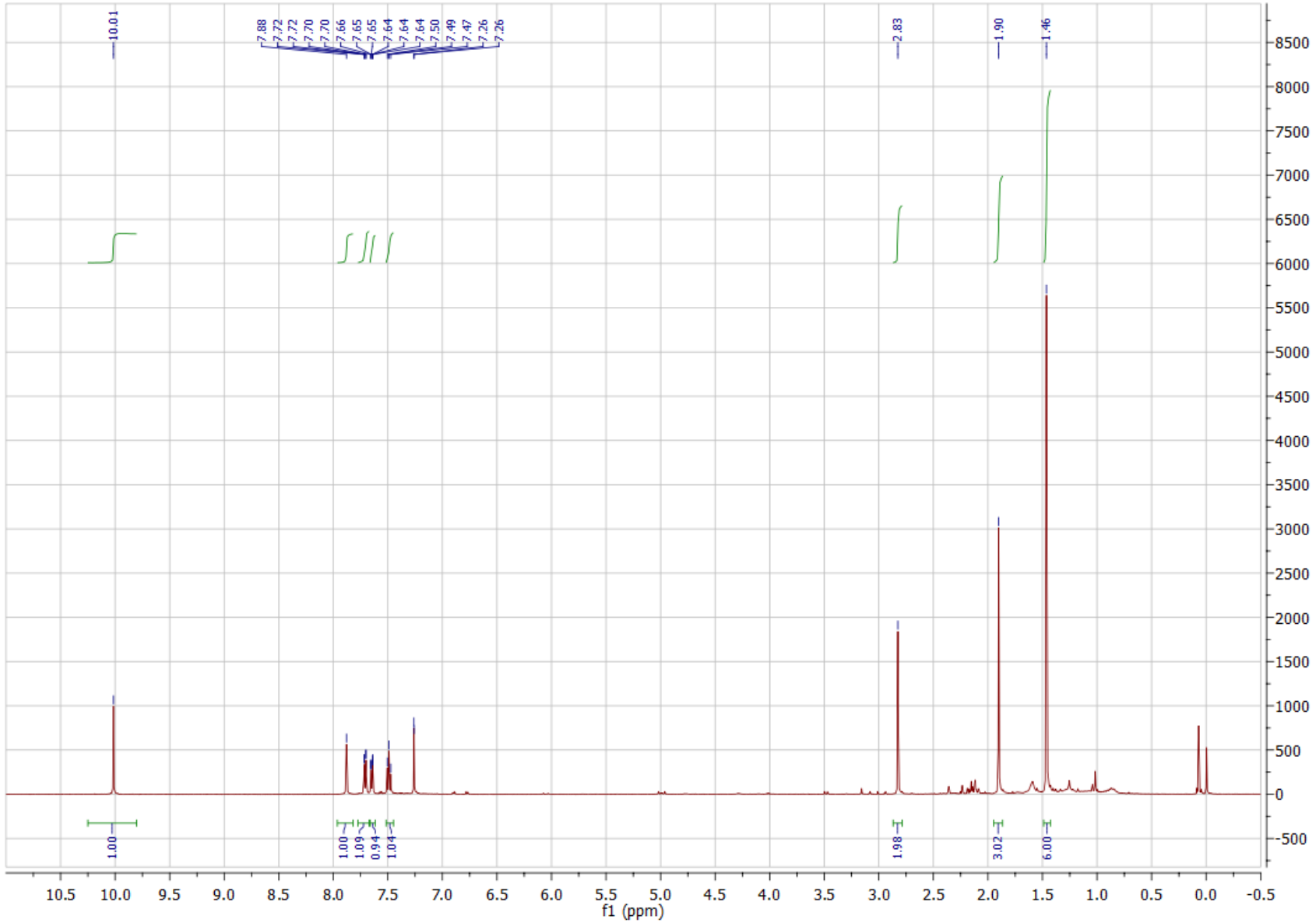
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(4-(1,3,4-Oxadiazol-2-yl)phenyl)-4-methylpentan-2-one **(42)**



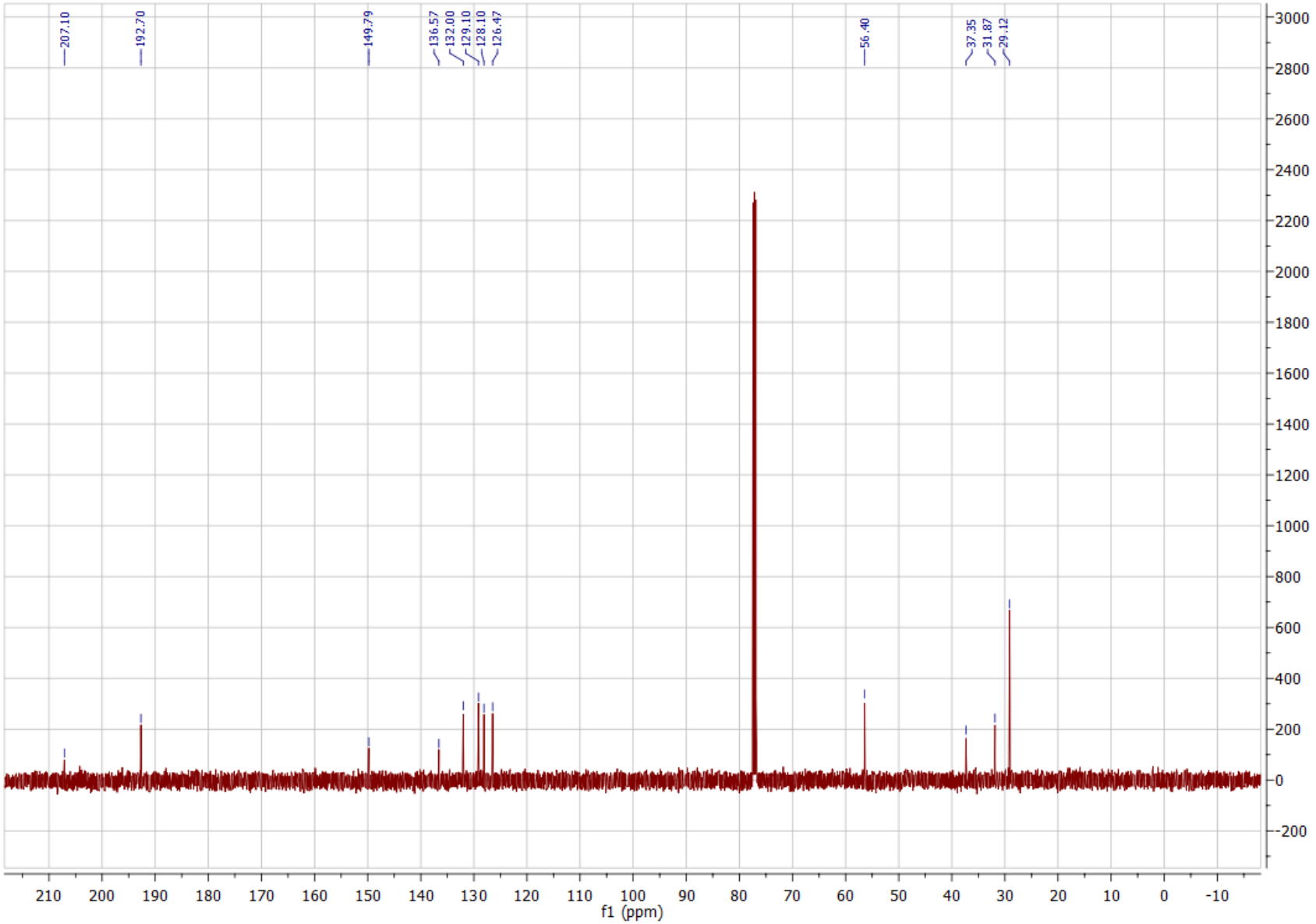
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(4-(1,3,4-Oxadiazol-2-yl)phenyl)-4-methylpentan-2-one **(42)**



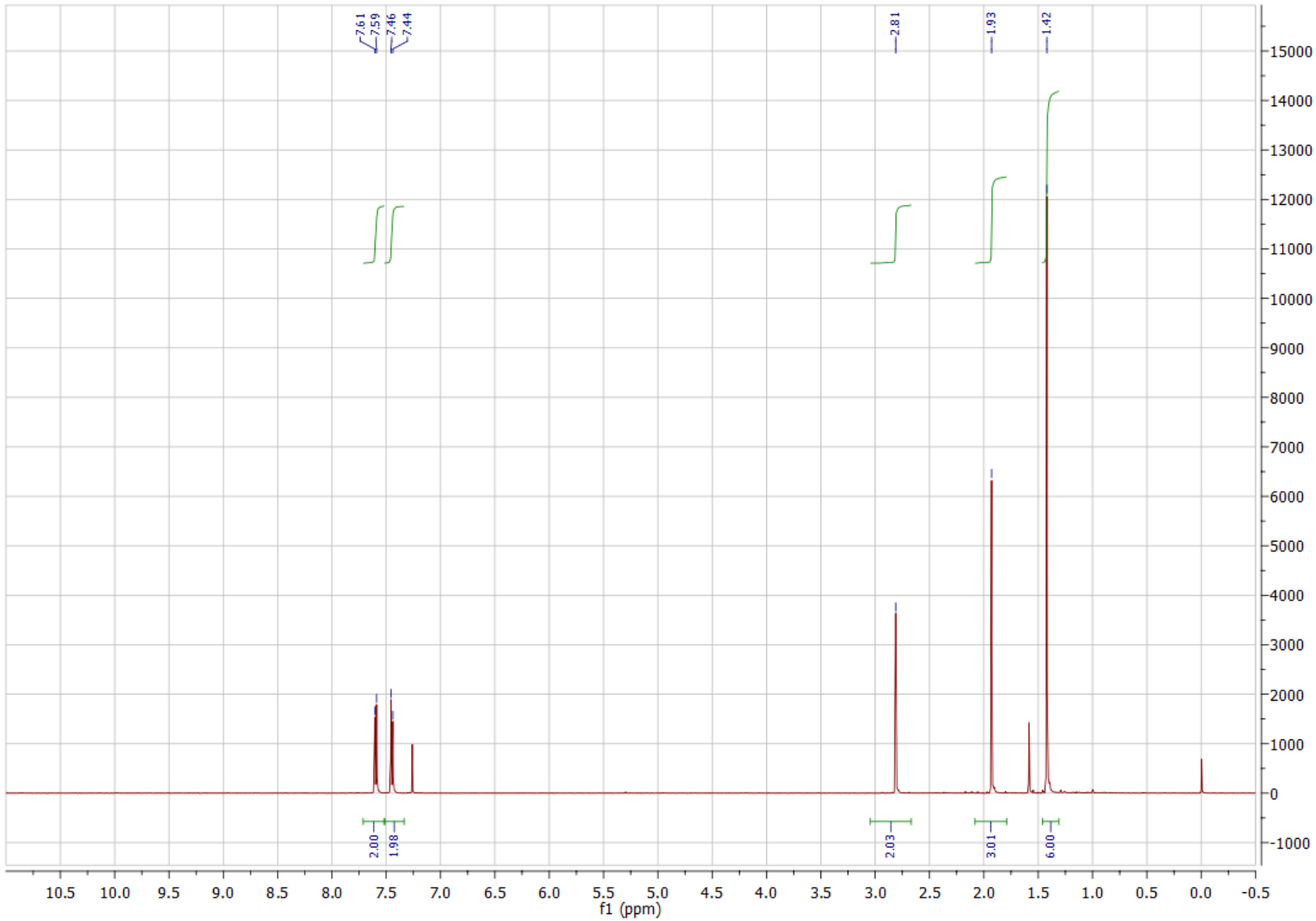
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 3-(2-Methyl-4-oxopentan-2-yl)benzaldehyde **(43)**



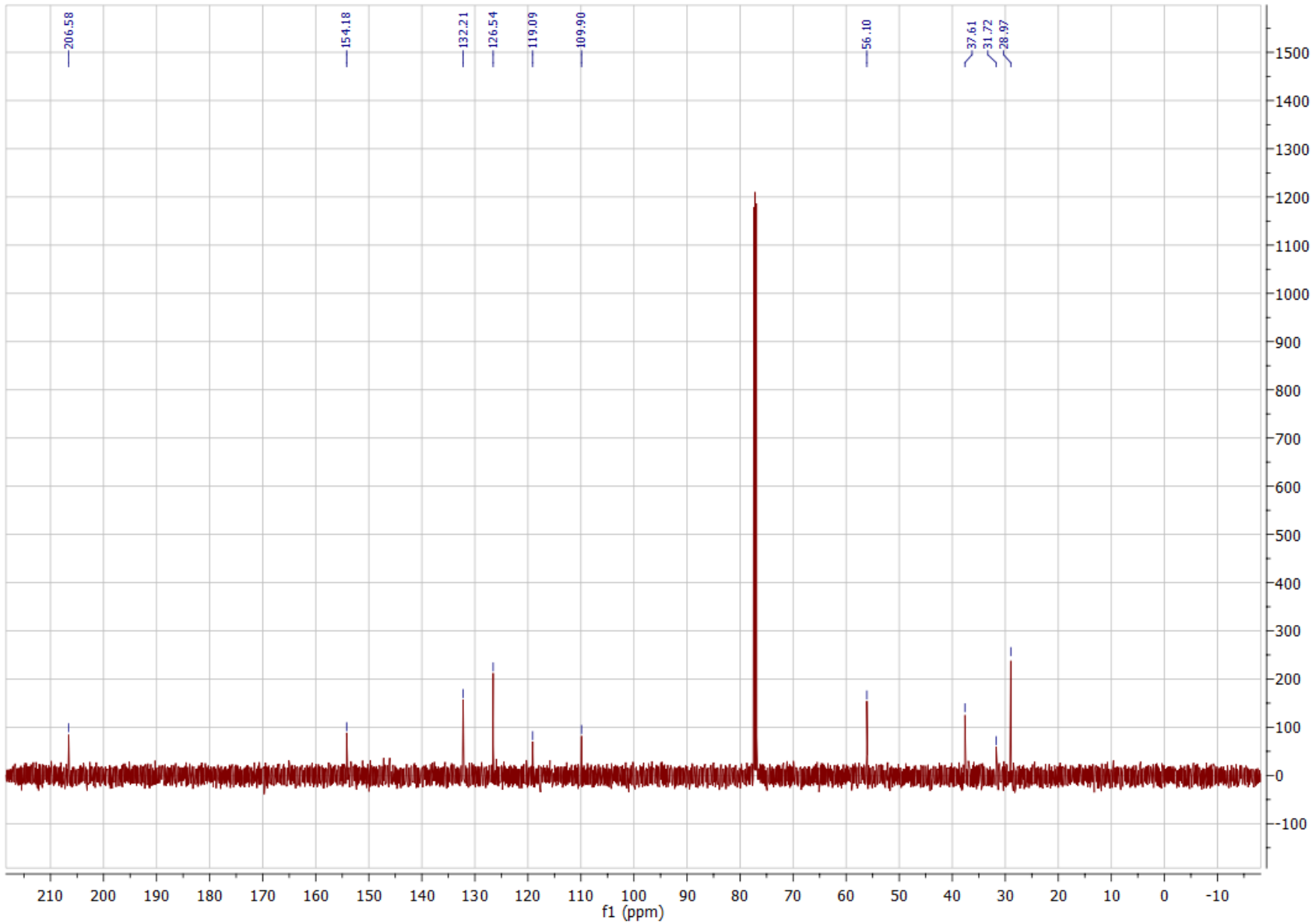
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 3-(2-Methyl-4-oxopentan-2-yl)benzaldehyde **(43)**



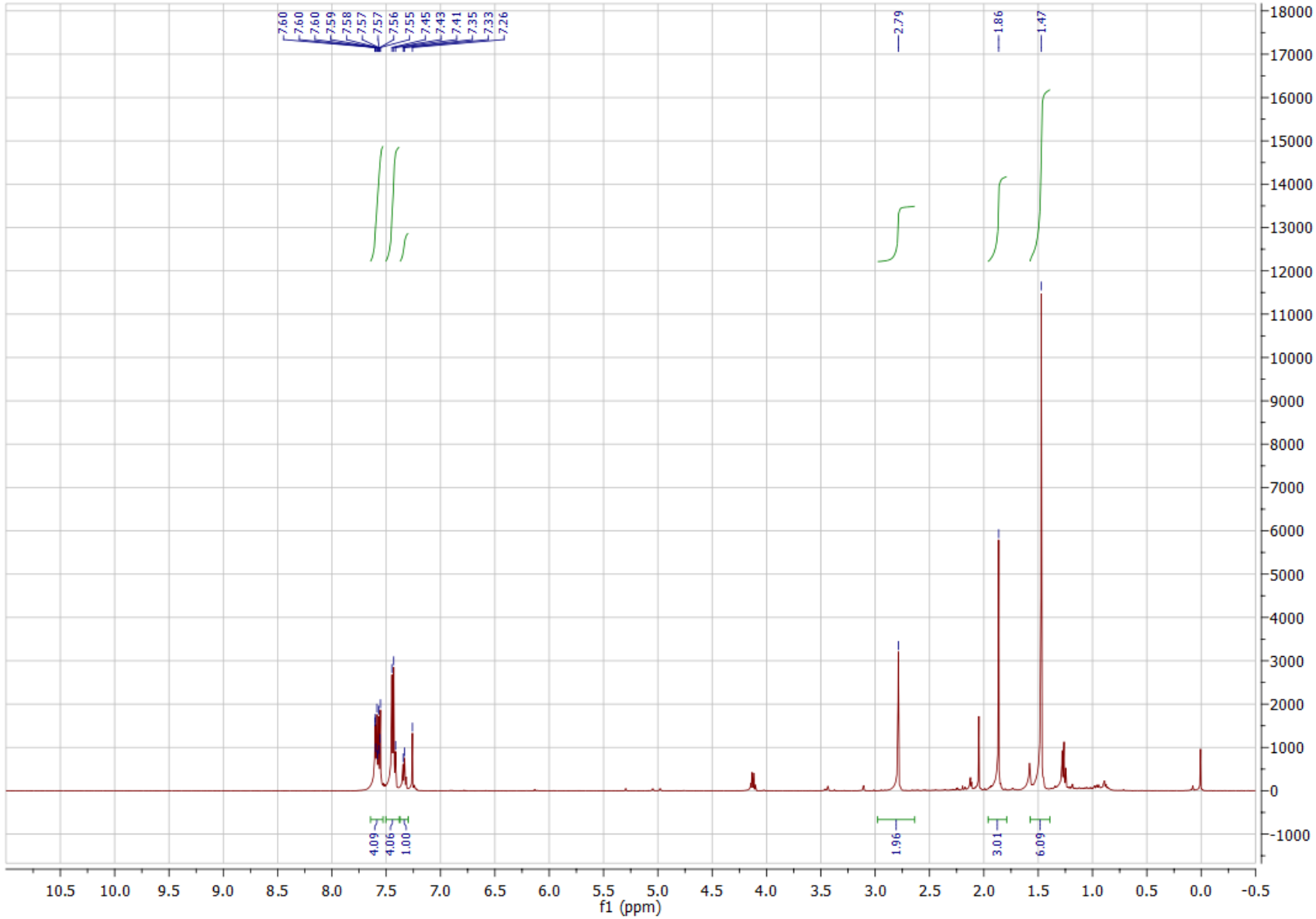
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(2-Methyl-4-oxopentan-2-yl)benzonitrile **(44)**



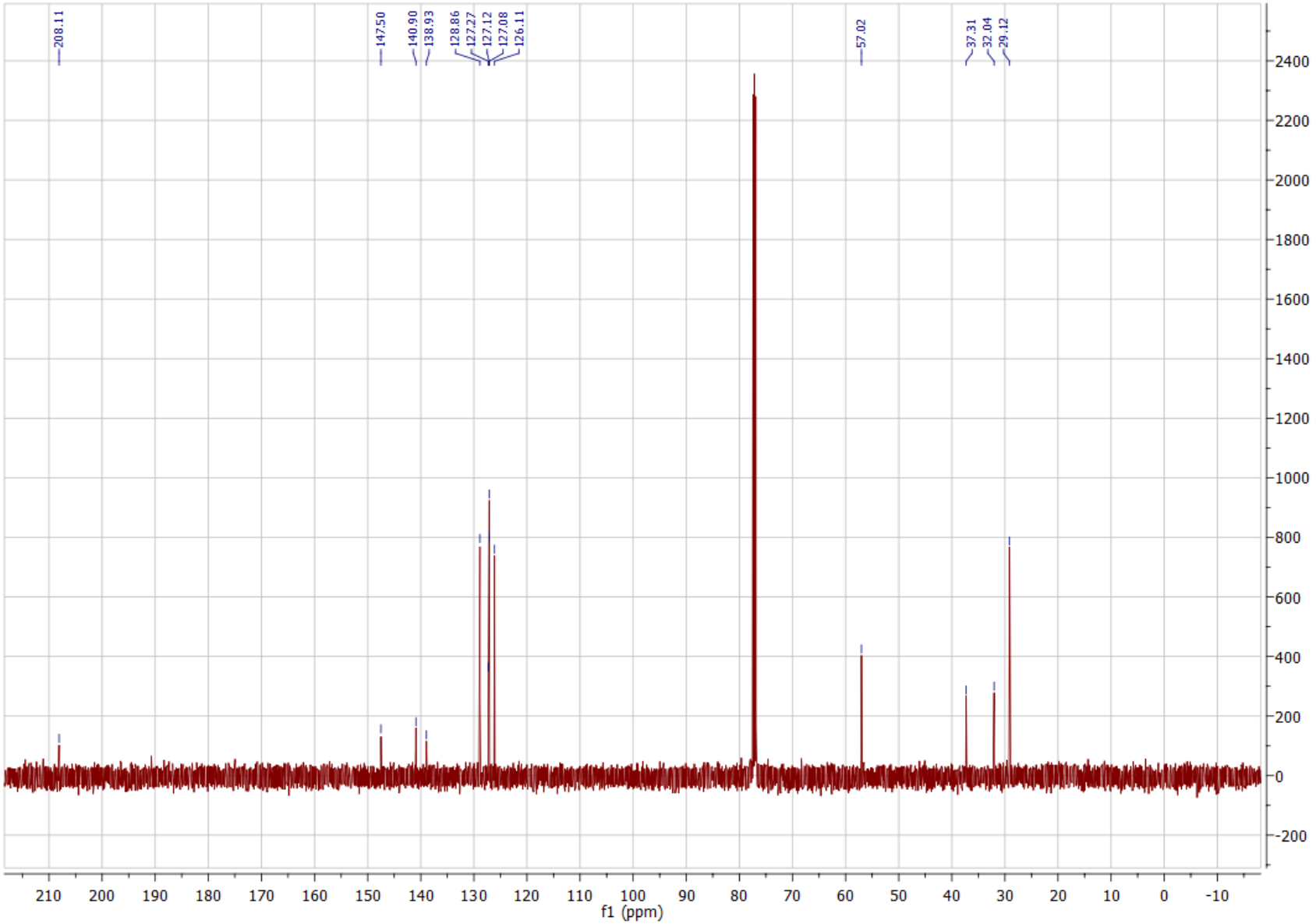
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(2-Methyl-4-oxopentan-2-yl)benzonitrile **(44)**



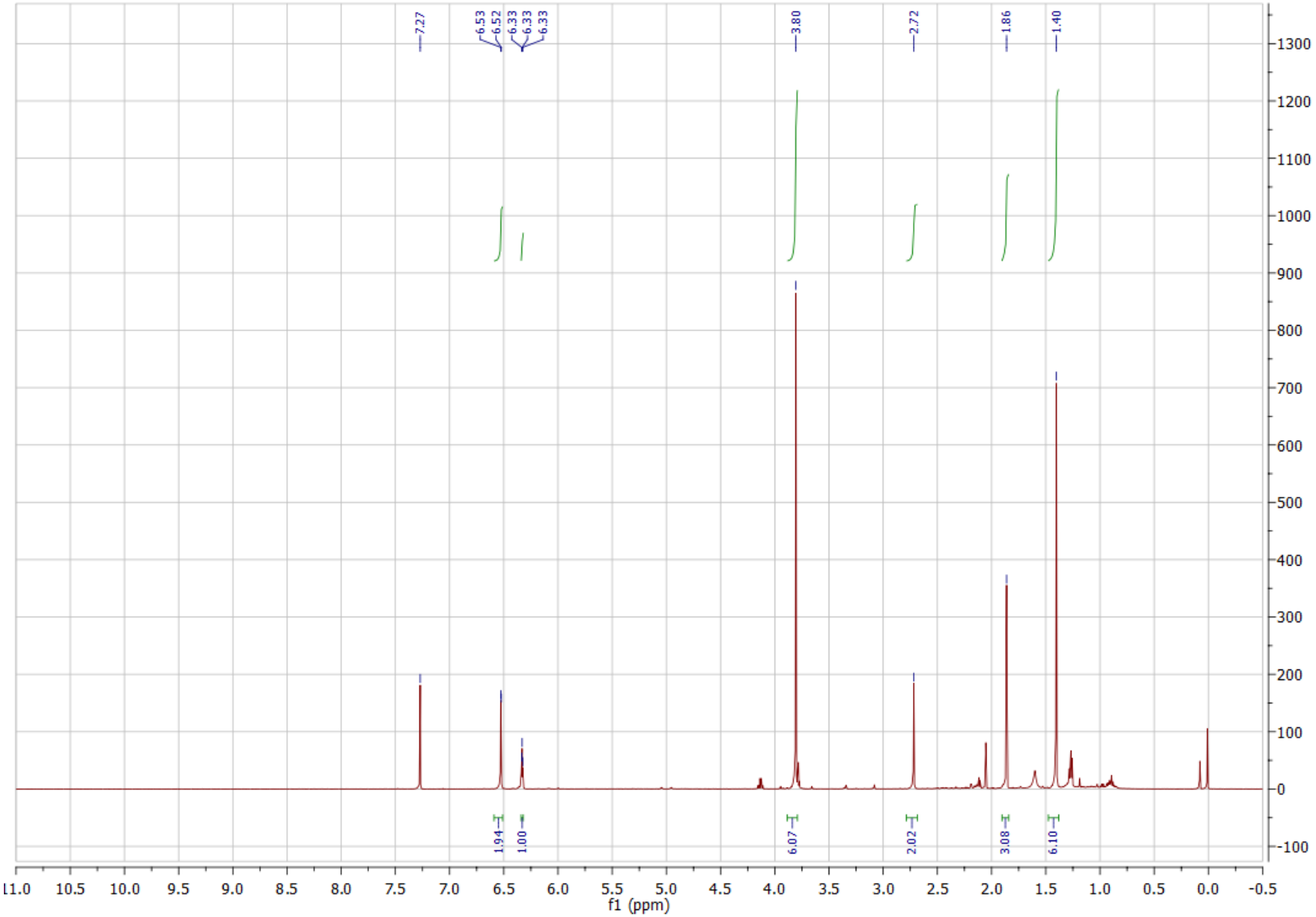
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-([1,1'-Biphenyl]-4-yl)-4-methylpentan-2-one **(45)**



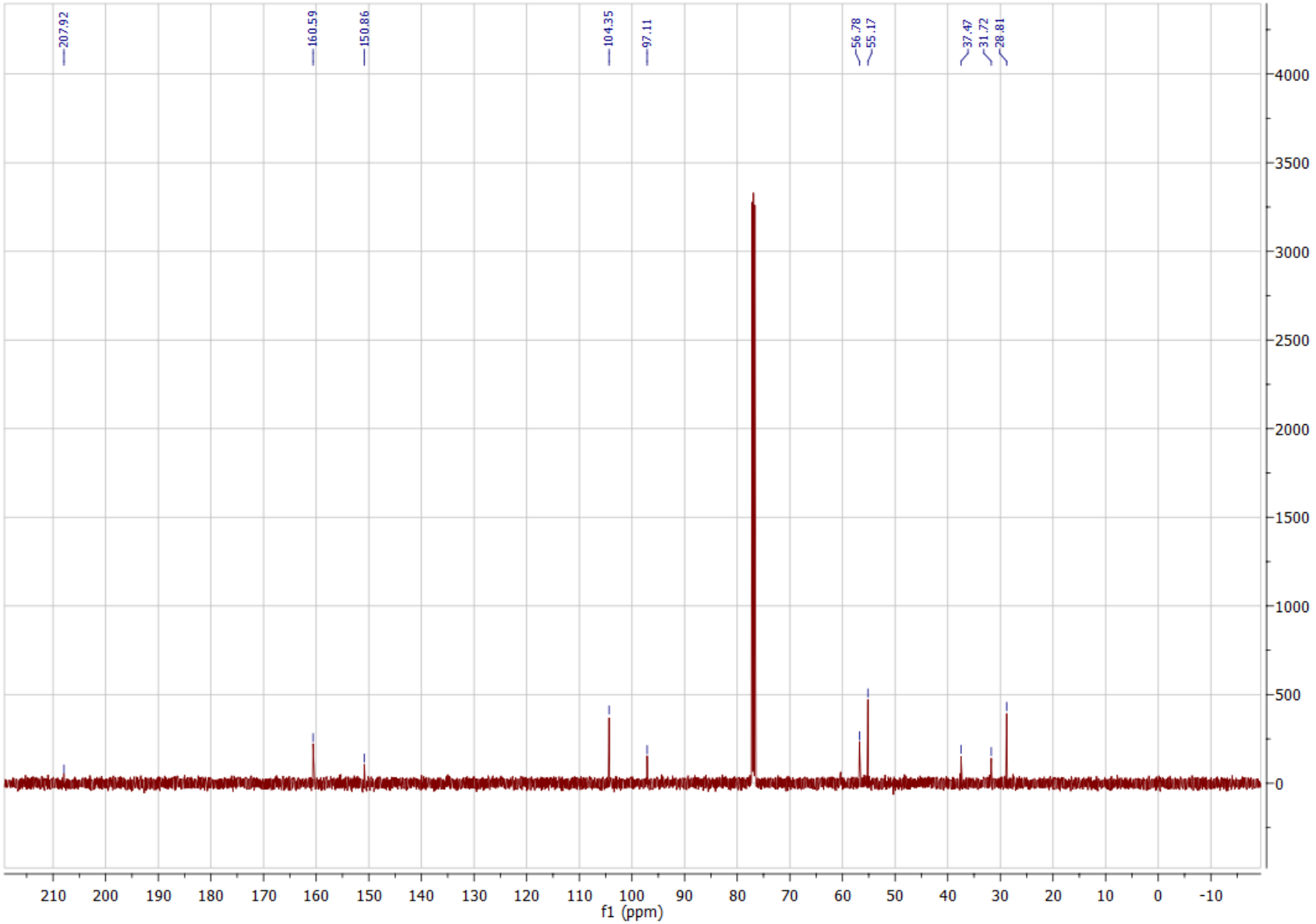
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-([1,1'-Biphenyl]-4-yl)-4-methylpentan-2-one **(45)**



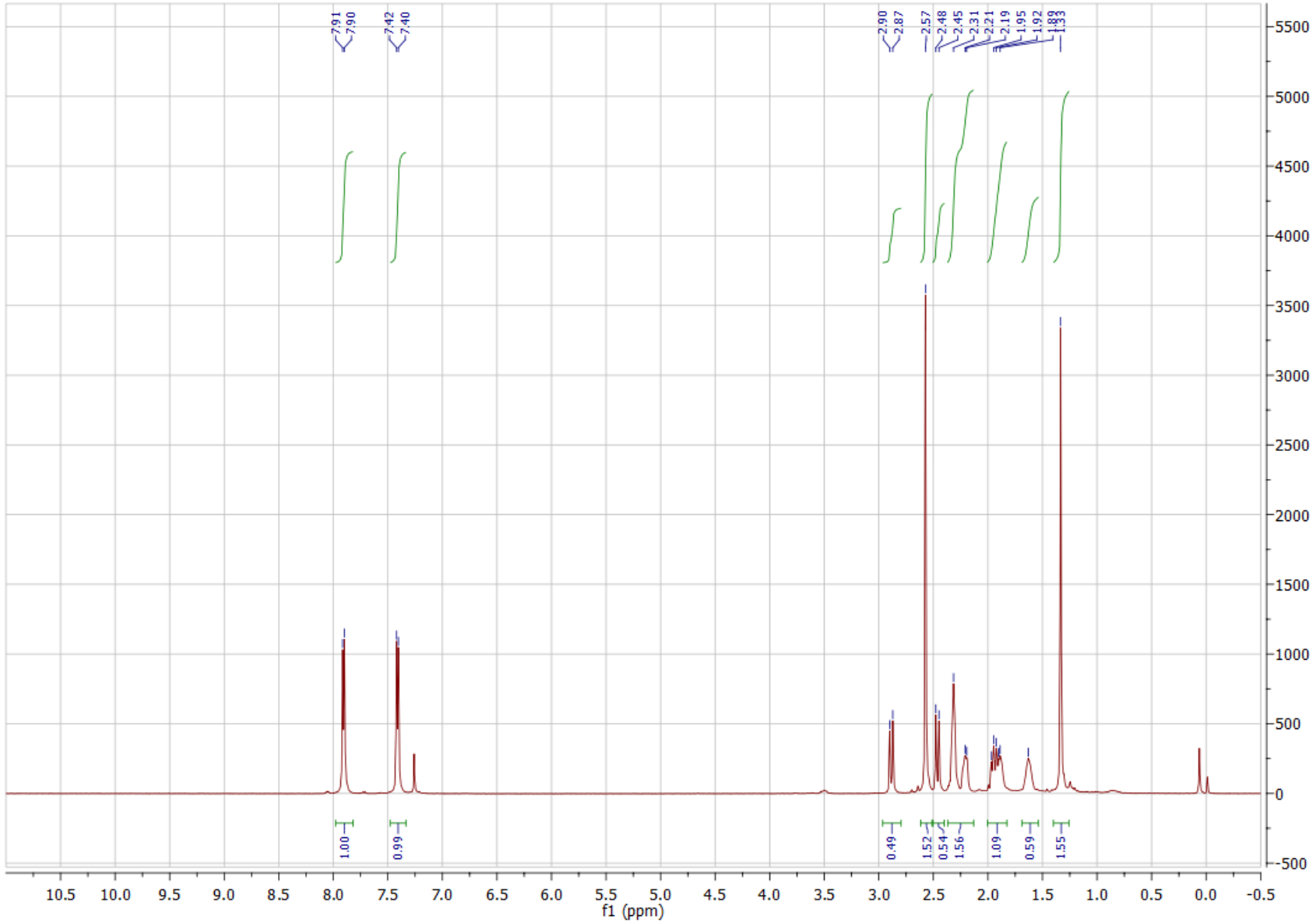
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(3,5-Dimethoxyphenyl)-4-methylpentan-2-one **(46)**



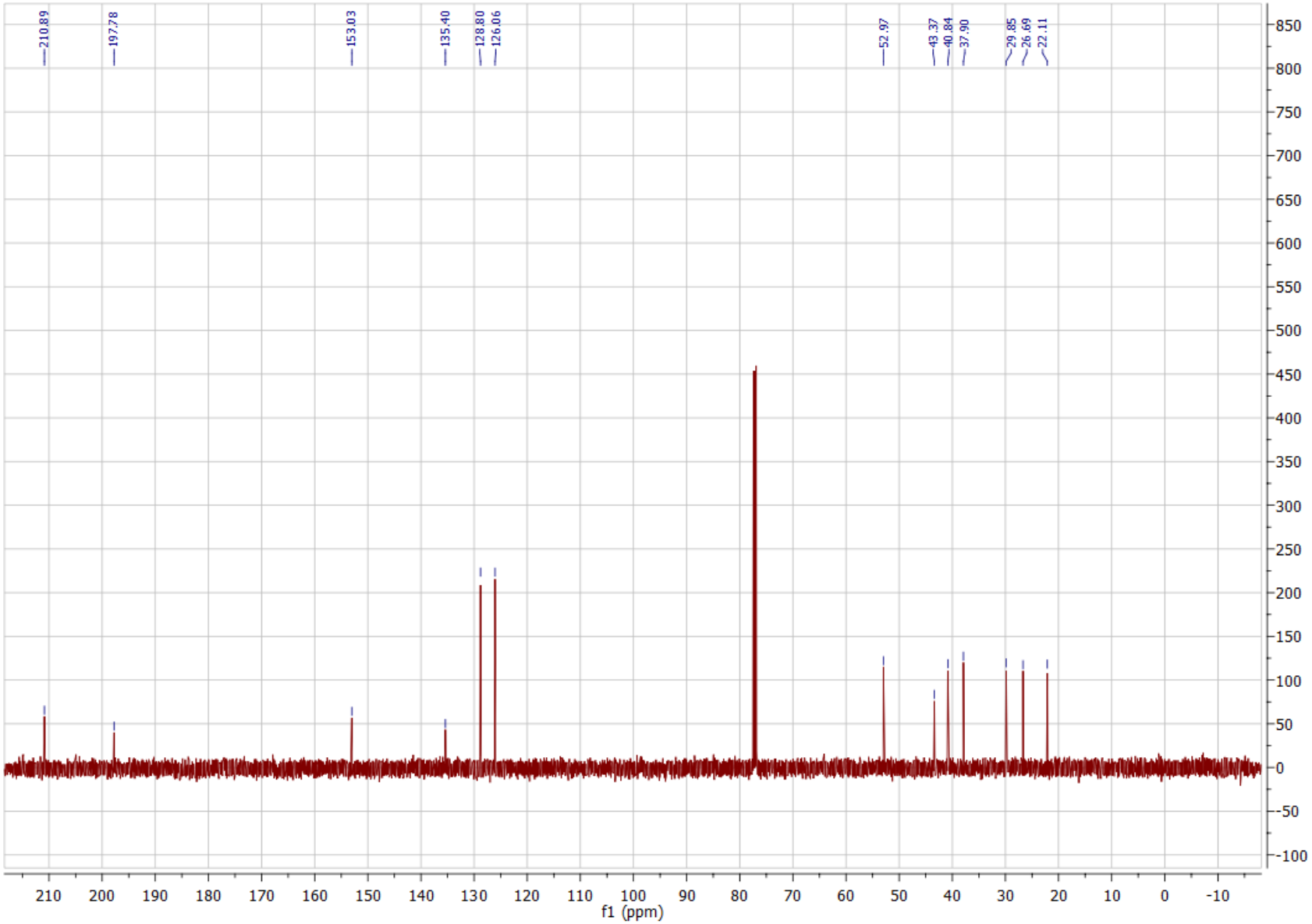
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 4-(3,5-Dimethoxyphenyl)-4-methylpentan-2-one **(46)**



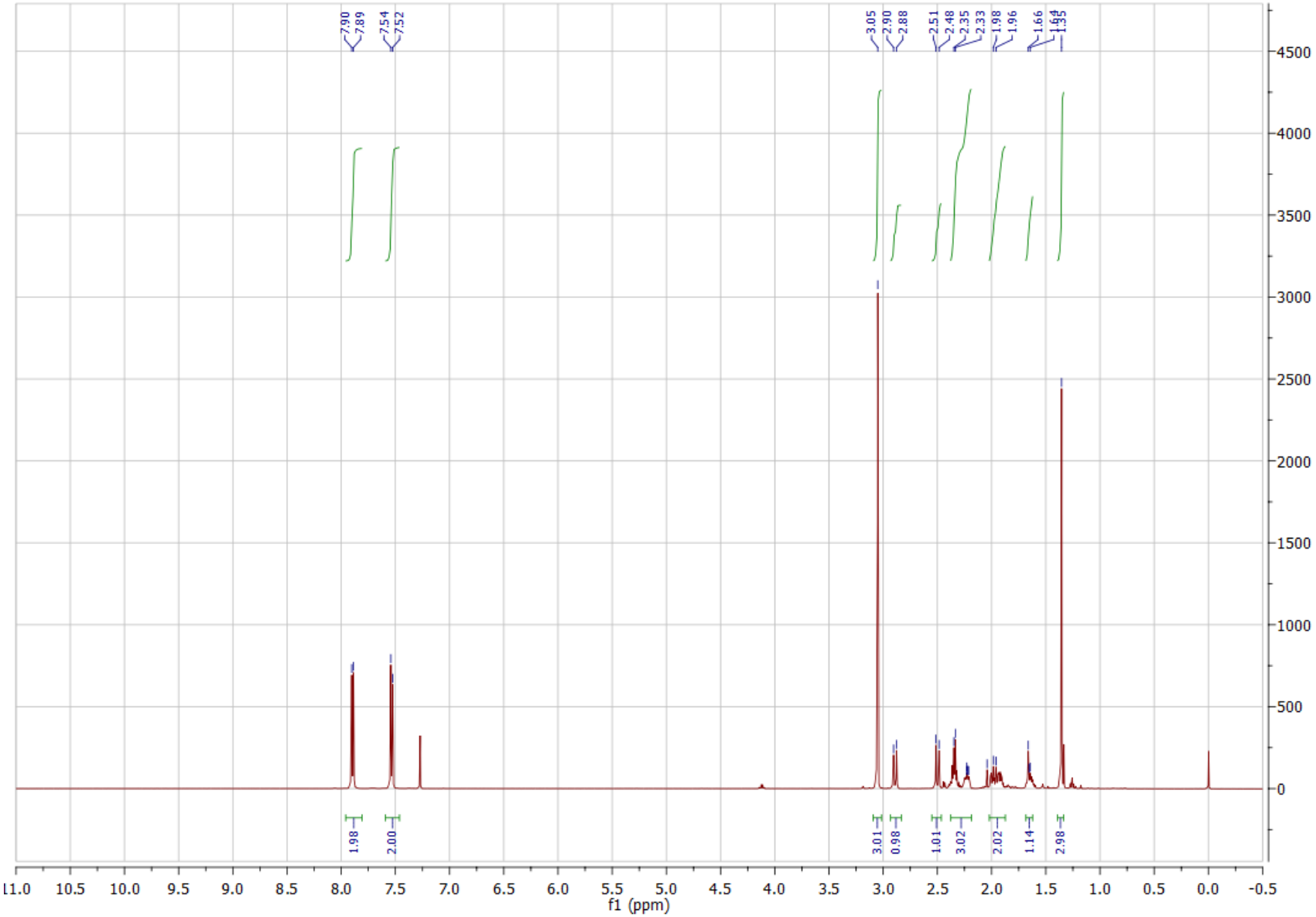
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 3-(4-acetylphenyl)-3-methylcyclohexan-1-one **(48)**



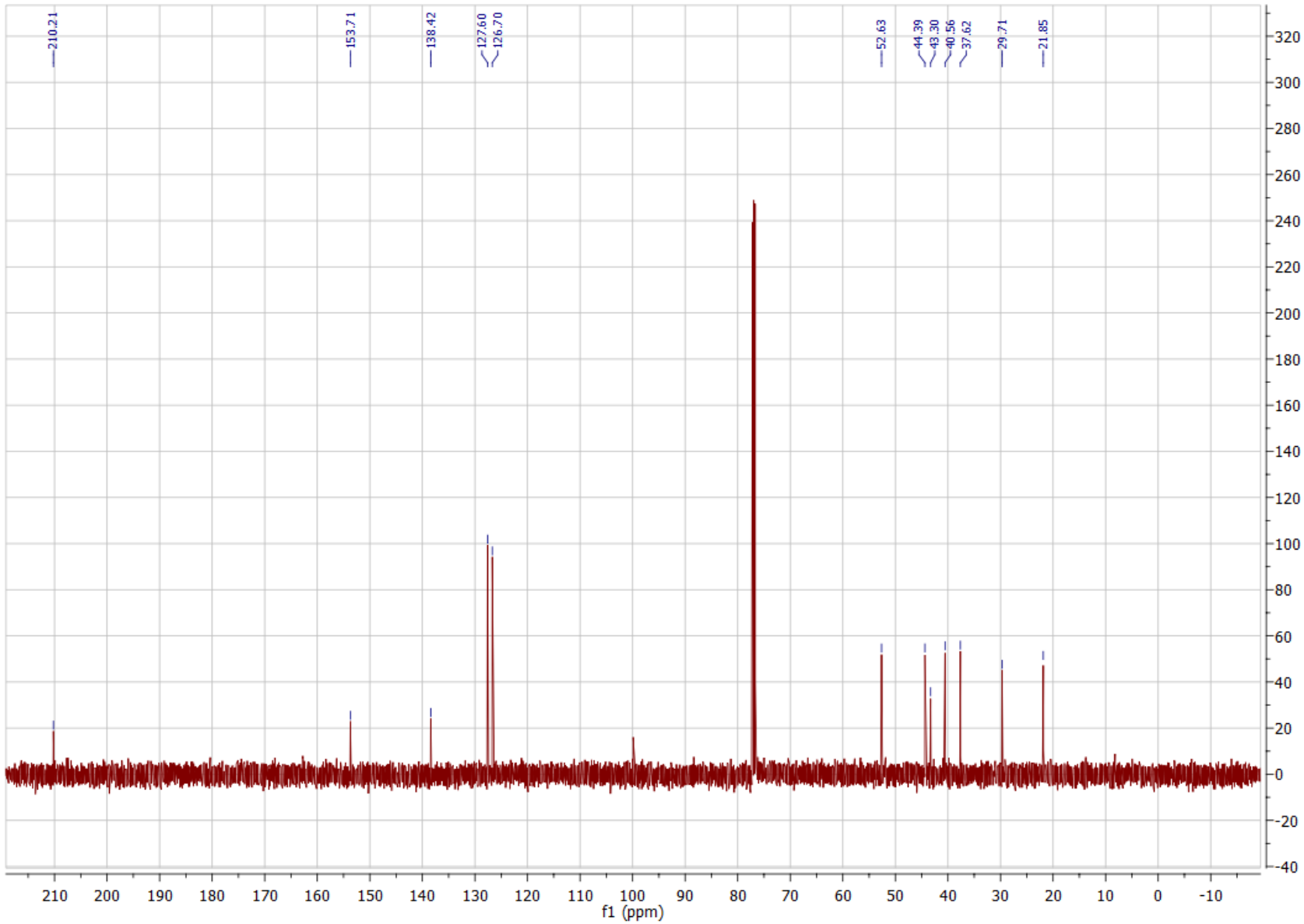
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 3-(4-acetylphenyl)-3-methylcyclohexan-1-one **(48)**



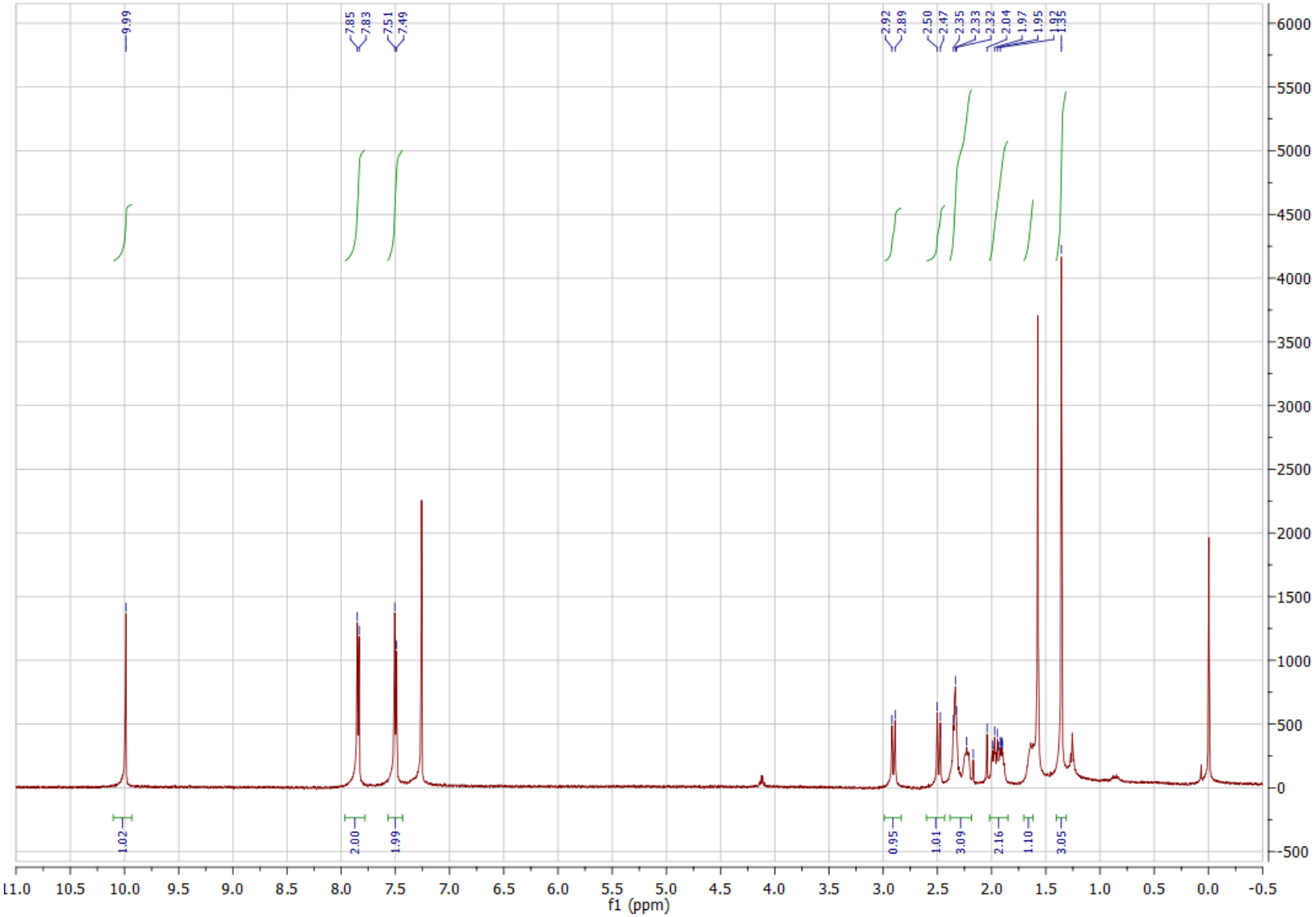
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 3-methyl-3-(4-(methylsulfonyl)phenyl)cyclohexan-1-one **(49)**



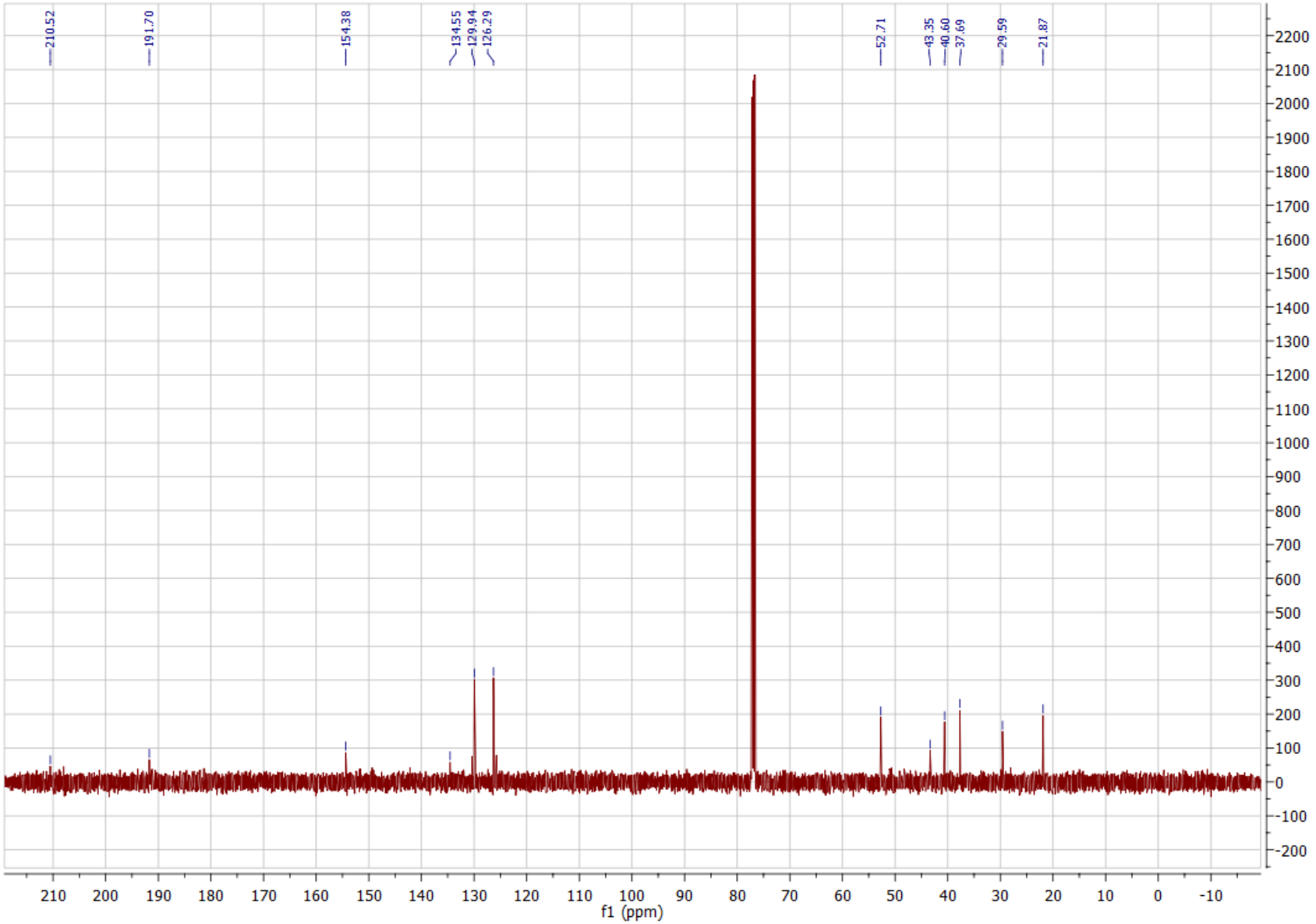
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 3-methyl-3-(4-(methylsulfonyl)phenyl)cyclohexan-1-one **(49)**



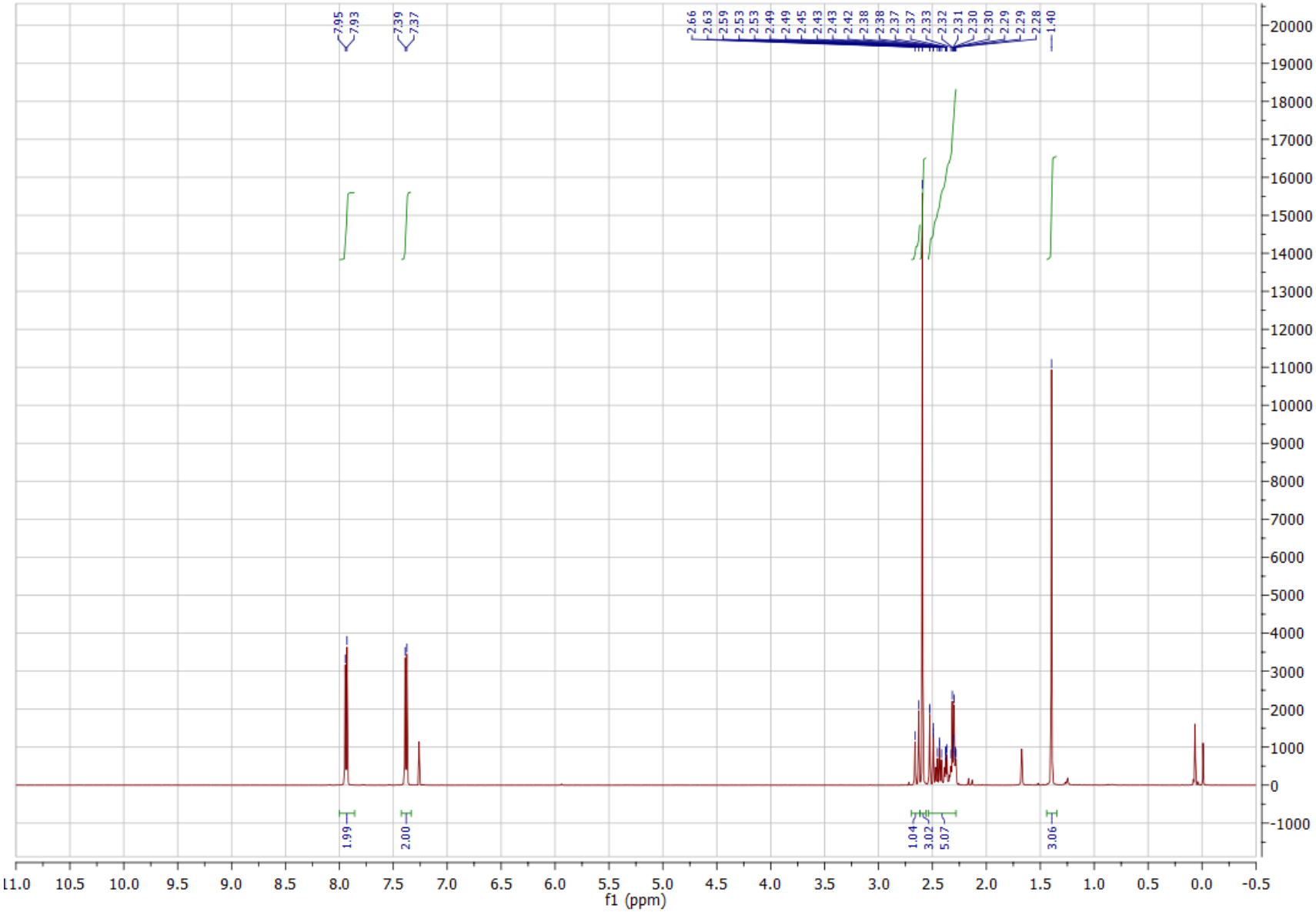
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 4-(1-Methyl-3-oxocyclohexyl)benzaldehyde (**50**)



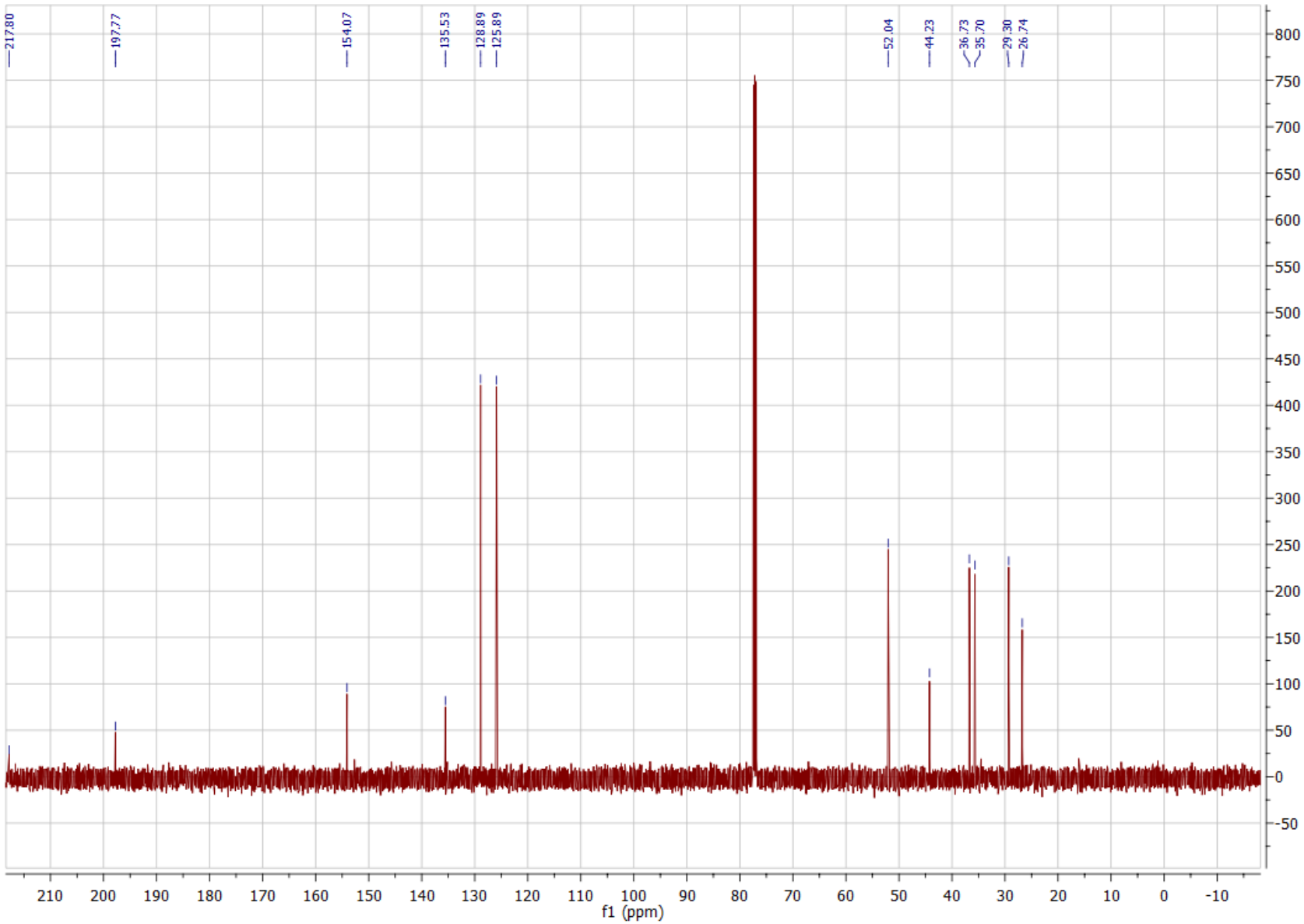
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of 4-(1-Methyl-3-oxocyclohexyl)benzaldehyde (**50**)



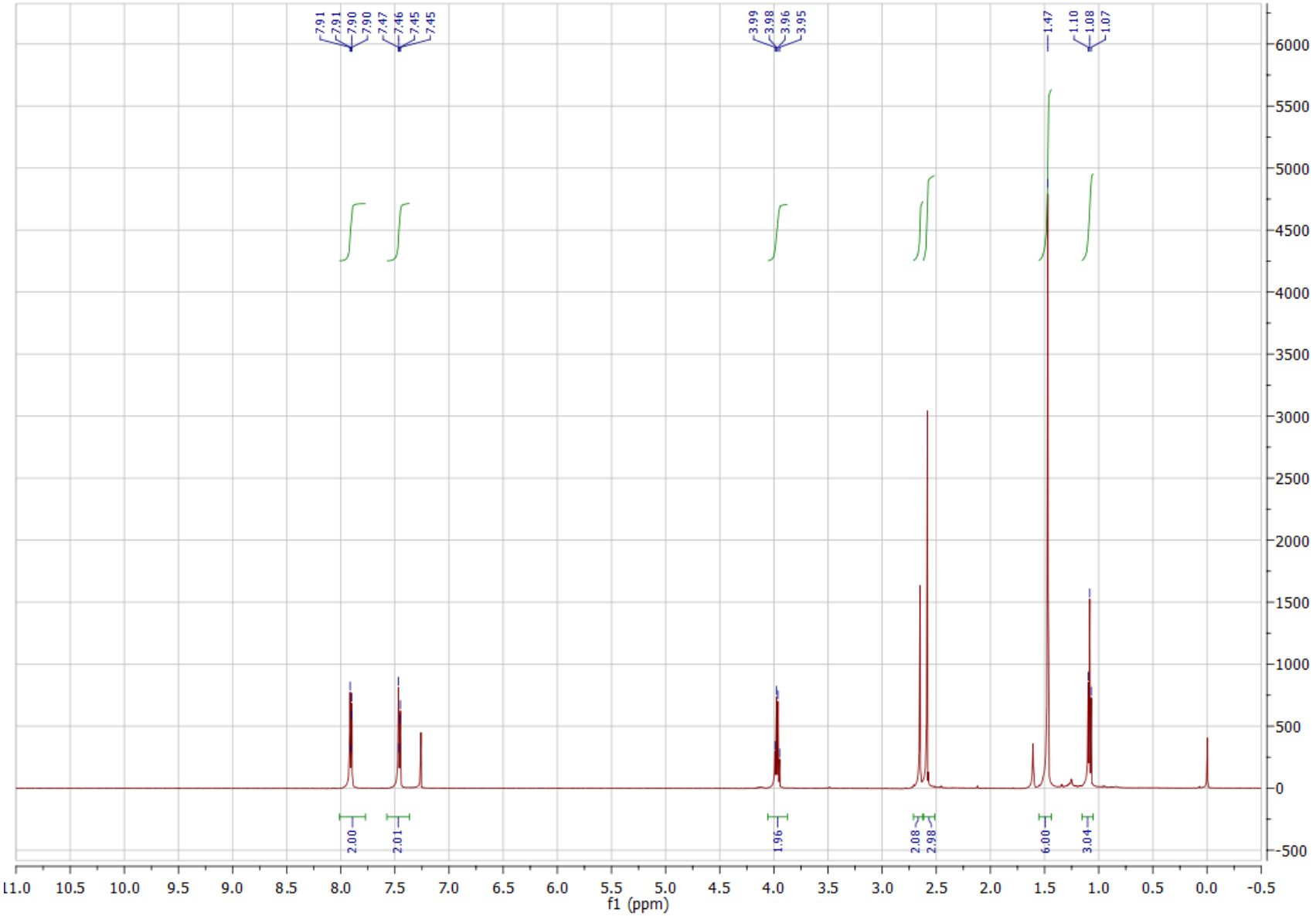
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 3-(4-Acetylphenyl)-3-methylcyclopentan-1-one **(51)**



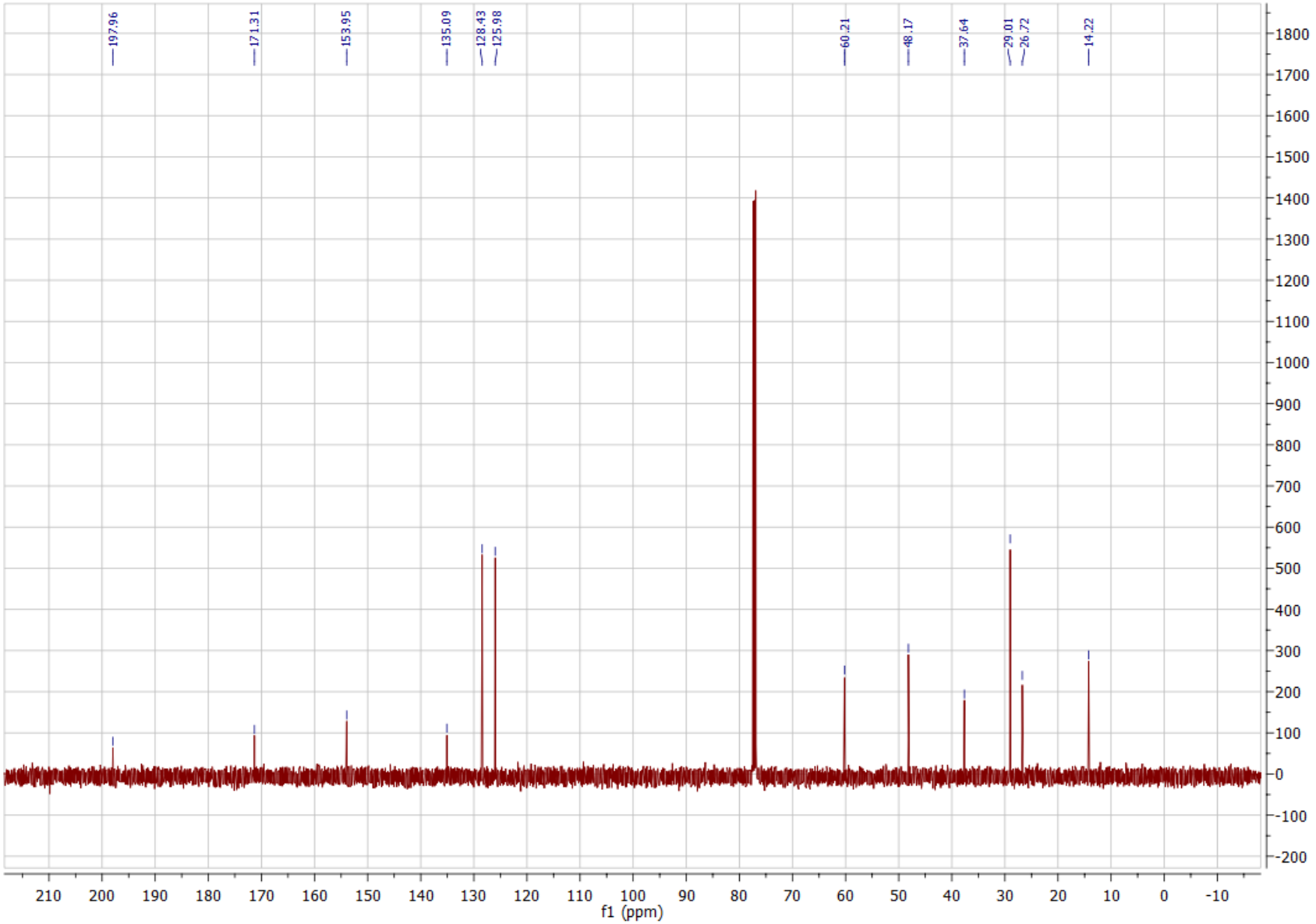
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 3-(4-Acetylphenyl)-3-methylcyclopentan-1-one **(51)**



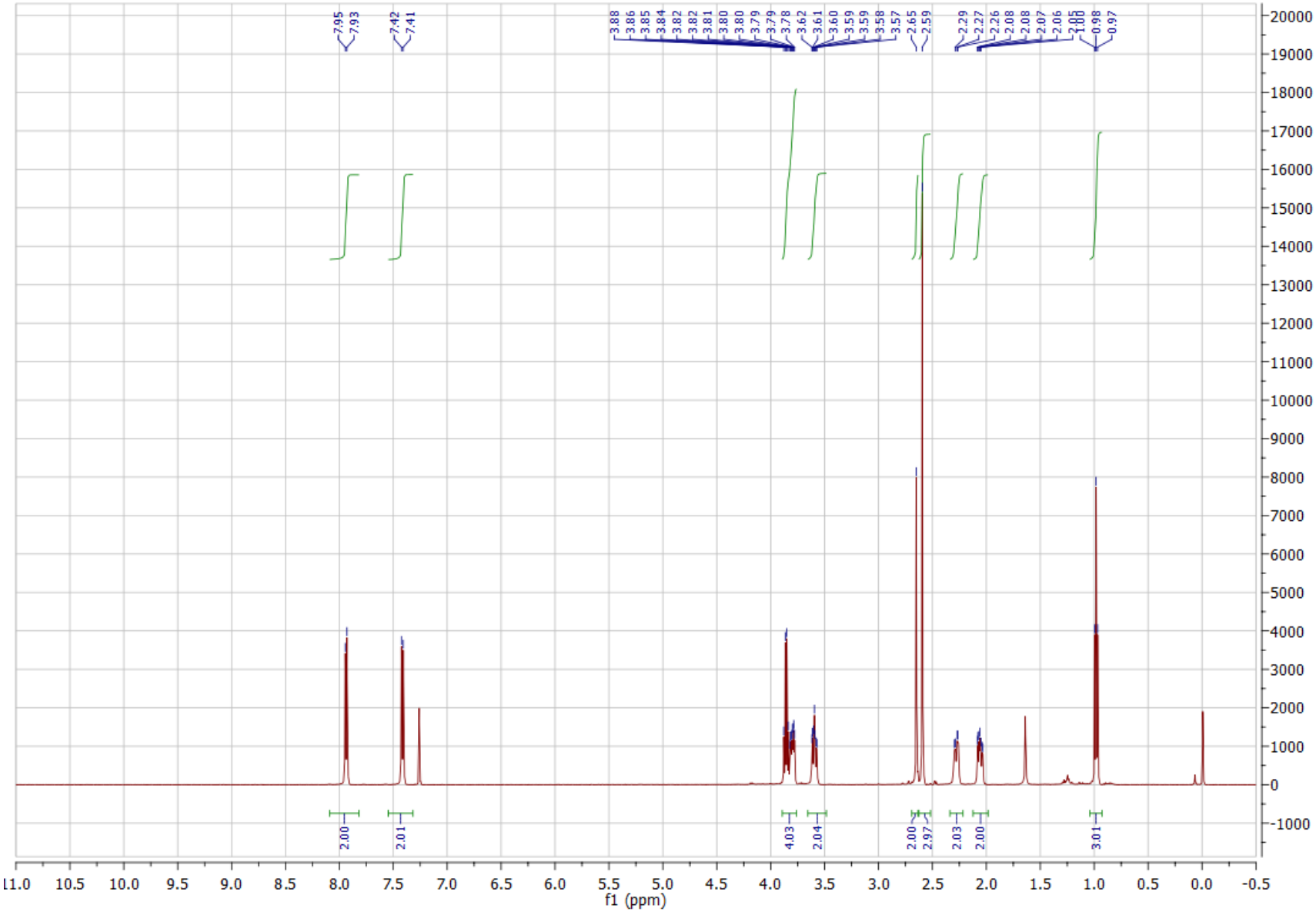
$^{1}$H NMR ($CDCl_3$, 500 MHz) of ethyl 3-(4-acetylphenyl)-3-methylbutanoate **(52)**



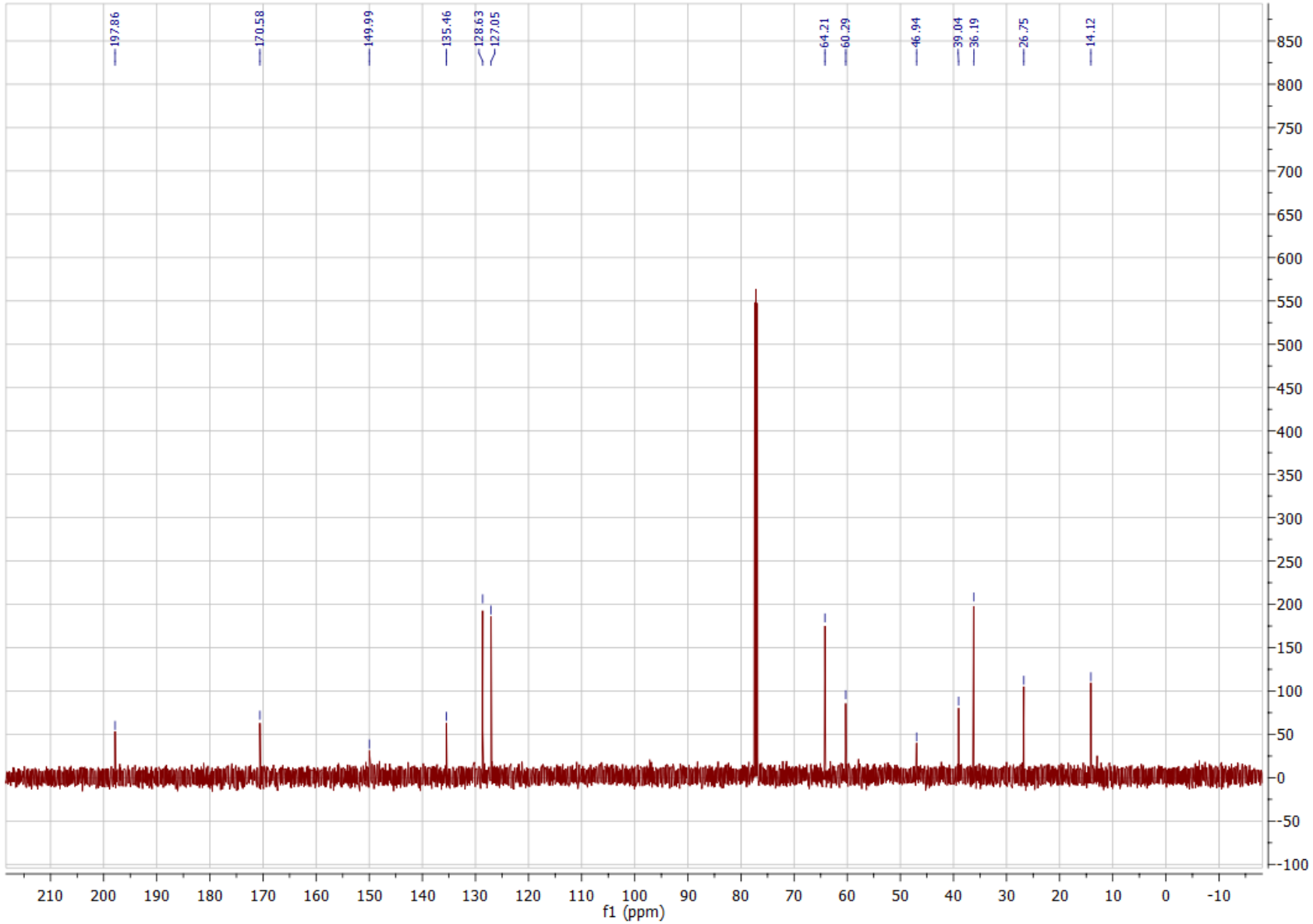
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of Ethyl 3-(4-acetylphenyl)-3-methylbutanoate **(52)**



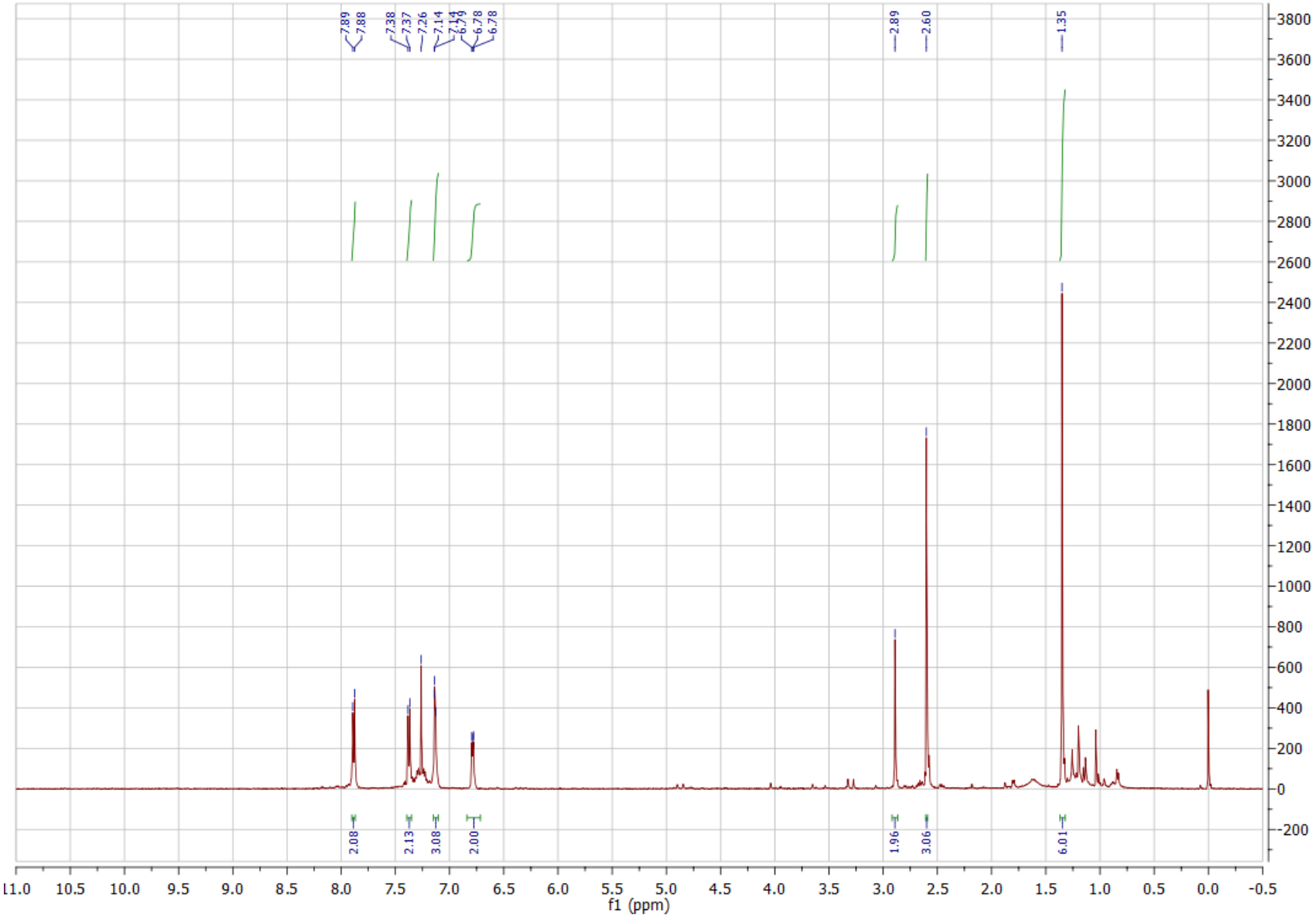
$^{1}$H NMR ($CDCl_3$, 500 MHz) of ethyl 2-(4-(4-acetylphenyl)tetrahydro-2H-pyran-4-yl)acetate **(53)**



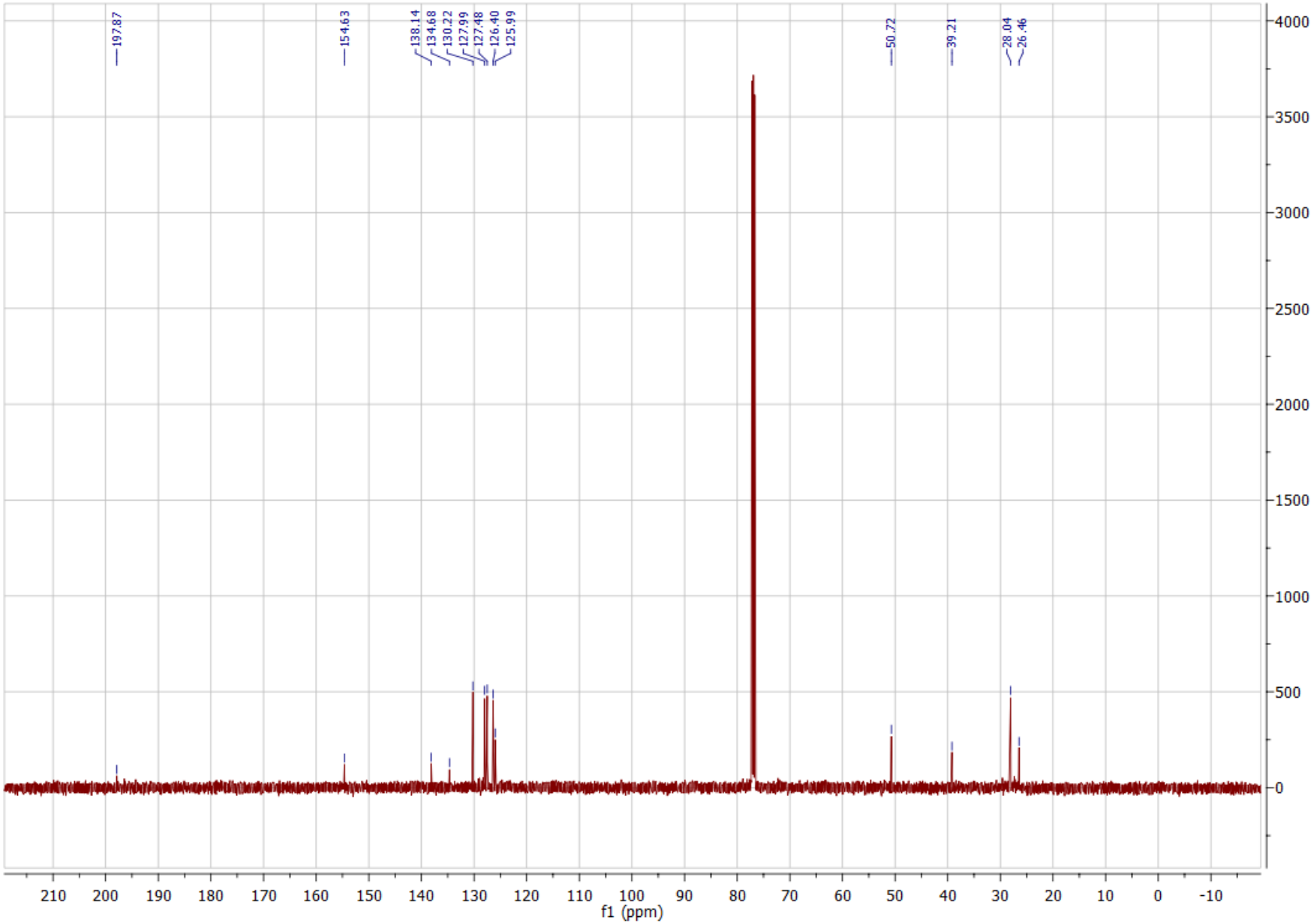
$^{13}$C NMR ($CDCl_3$, 125.8 MHz) of ethyl 2-(4-(4-acetylphenyl)tetrahydro-2H-pyran-4-yl)acetate **(53)**



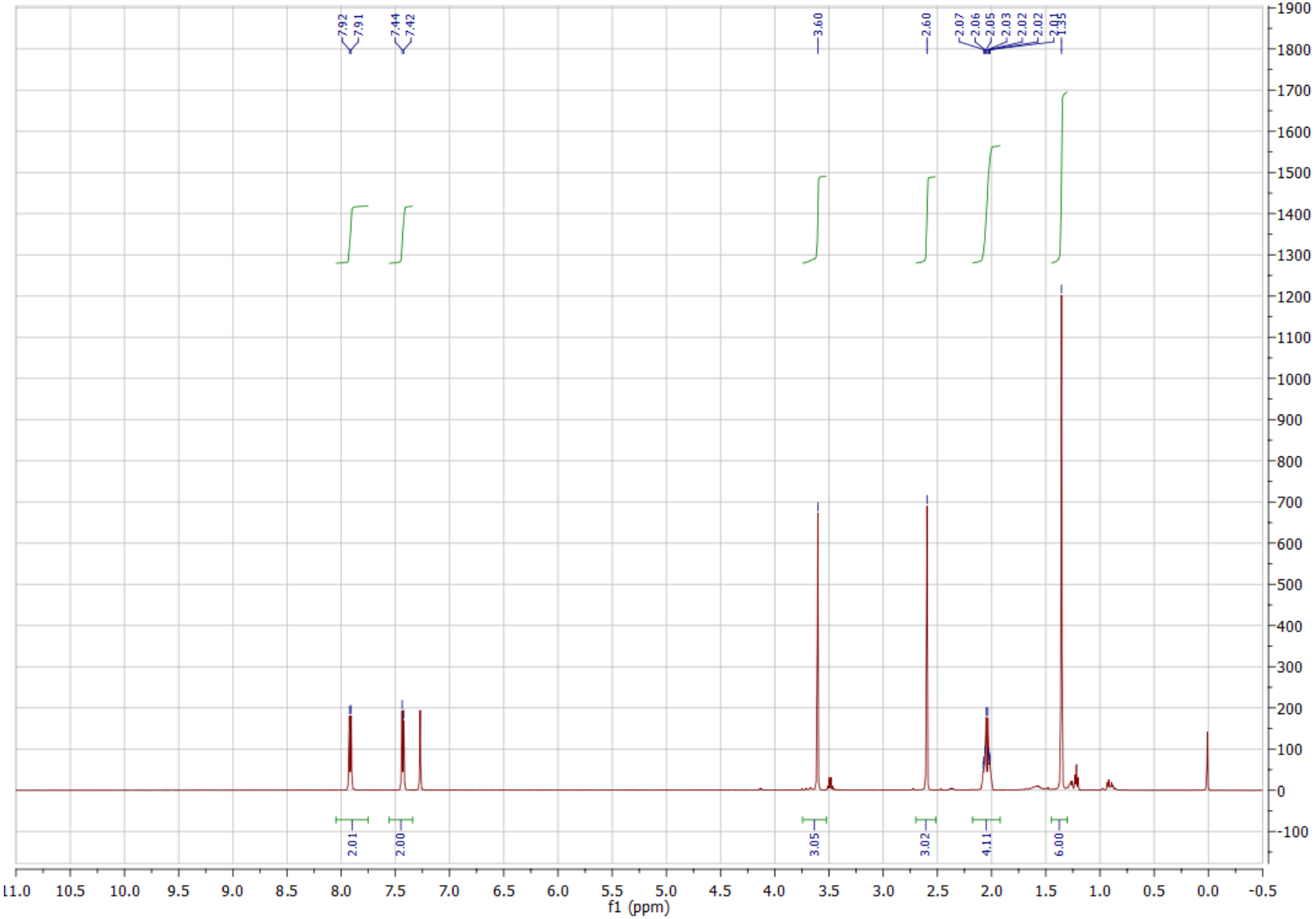
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 1-(4-(2-methyl-1-phenylpropan-2-yl)phenyl)ethan-1-one (**54**)



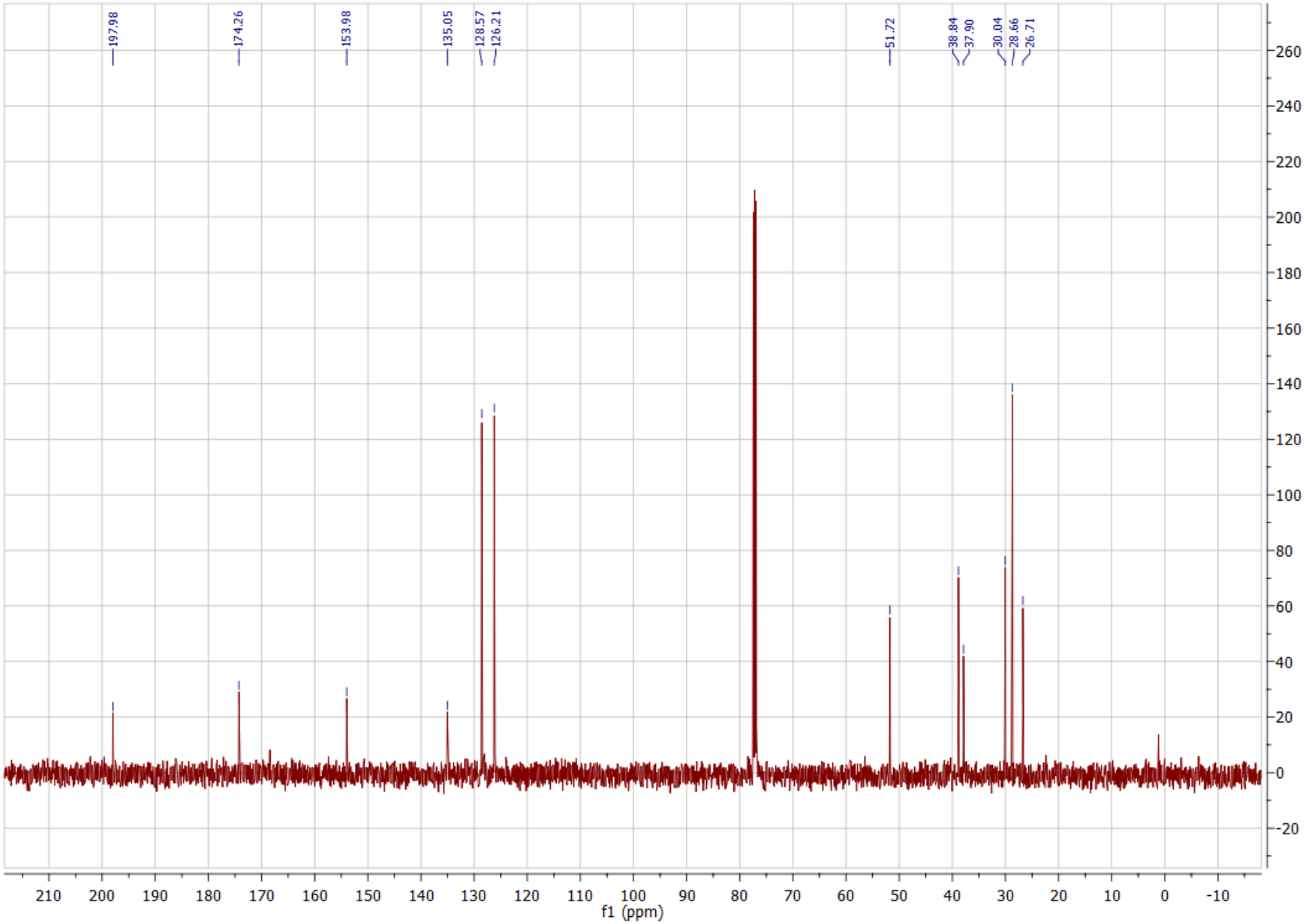
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 1-(4-(2-methyl-1-phenylpropan-2-yl)phenyl)ethan-1-one (**54**)



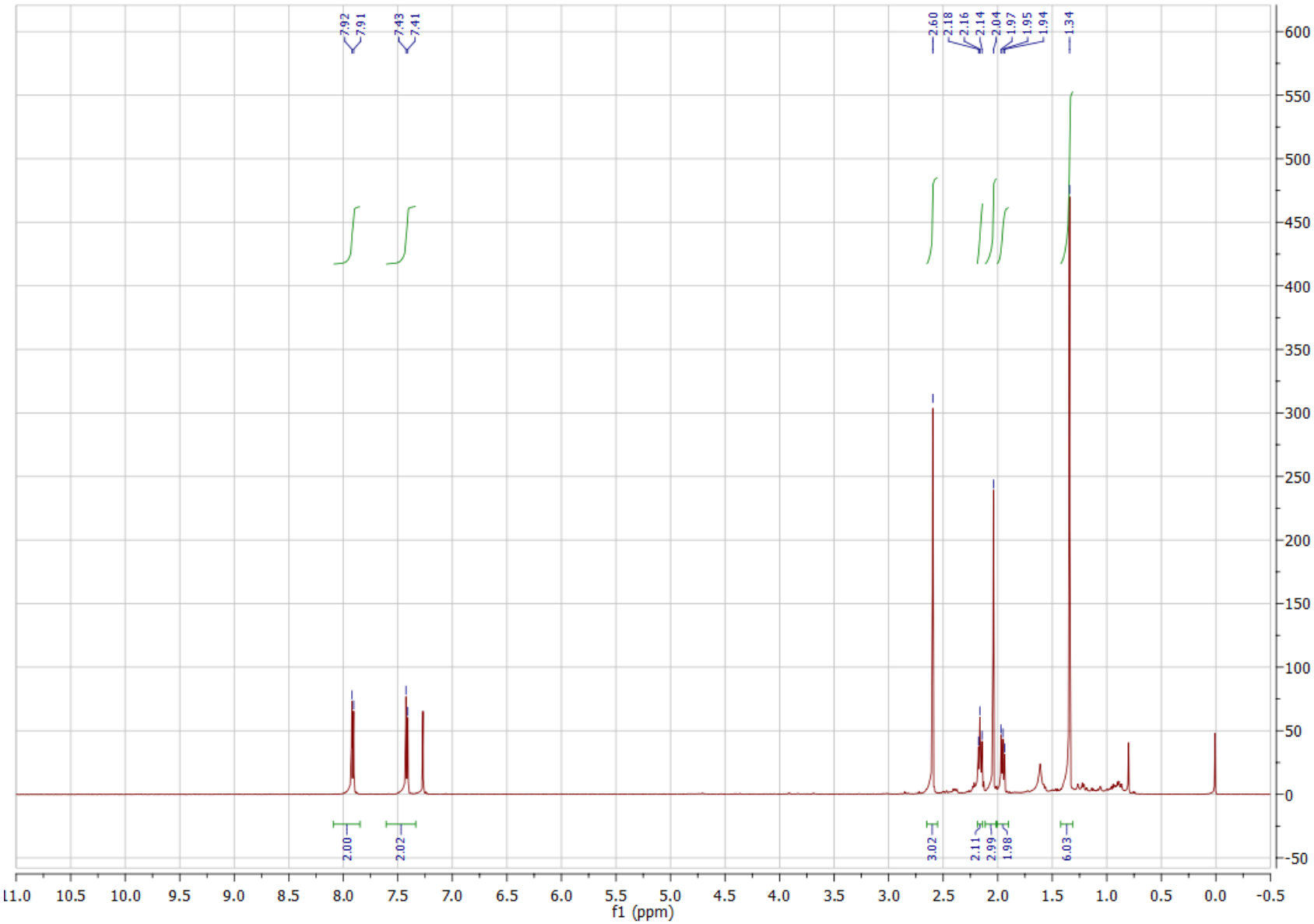
$^{1}$H NMR ($CDCl_3$, 500 MHz) of methyl 4-(4-acetylphenyl)-4-methylpentanoate (**55**)



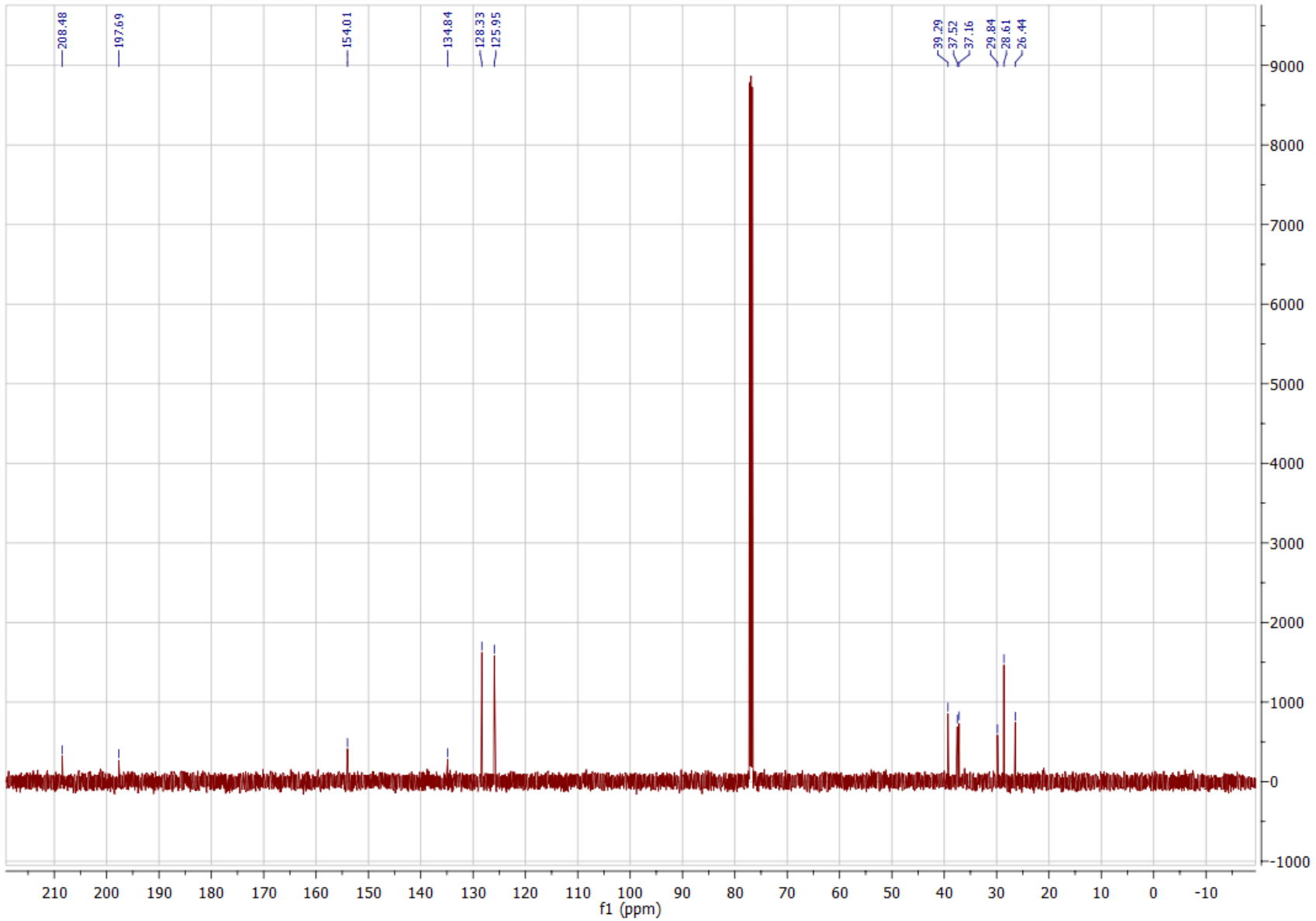
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of methyl 4-(4-acetylphenyl)-4-methylpentanoate (**55**)



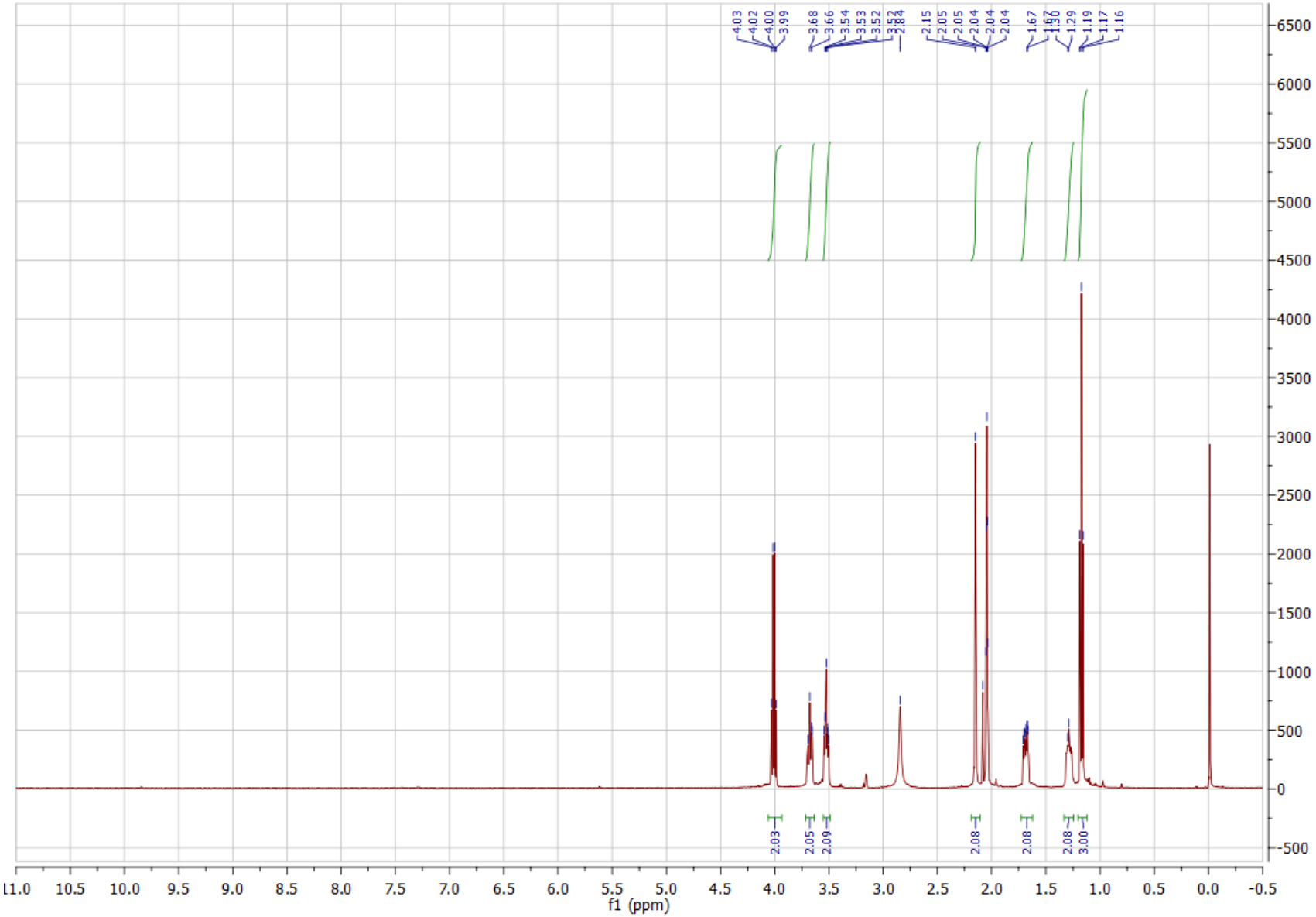
$^{1}$H NMR ($CDCl_3$, 500 MHz) of 5-(4-Acetylphenyl)-5-methylhexan-2-one (**56**)



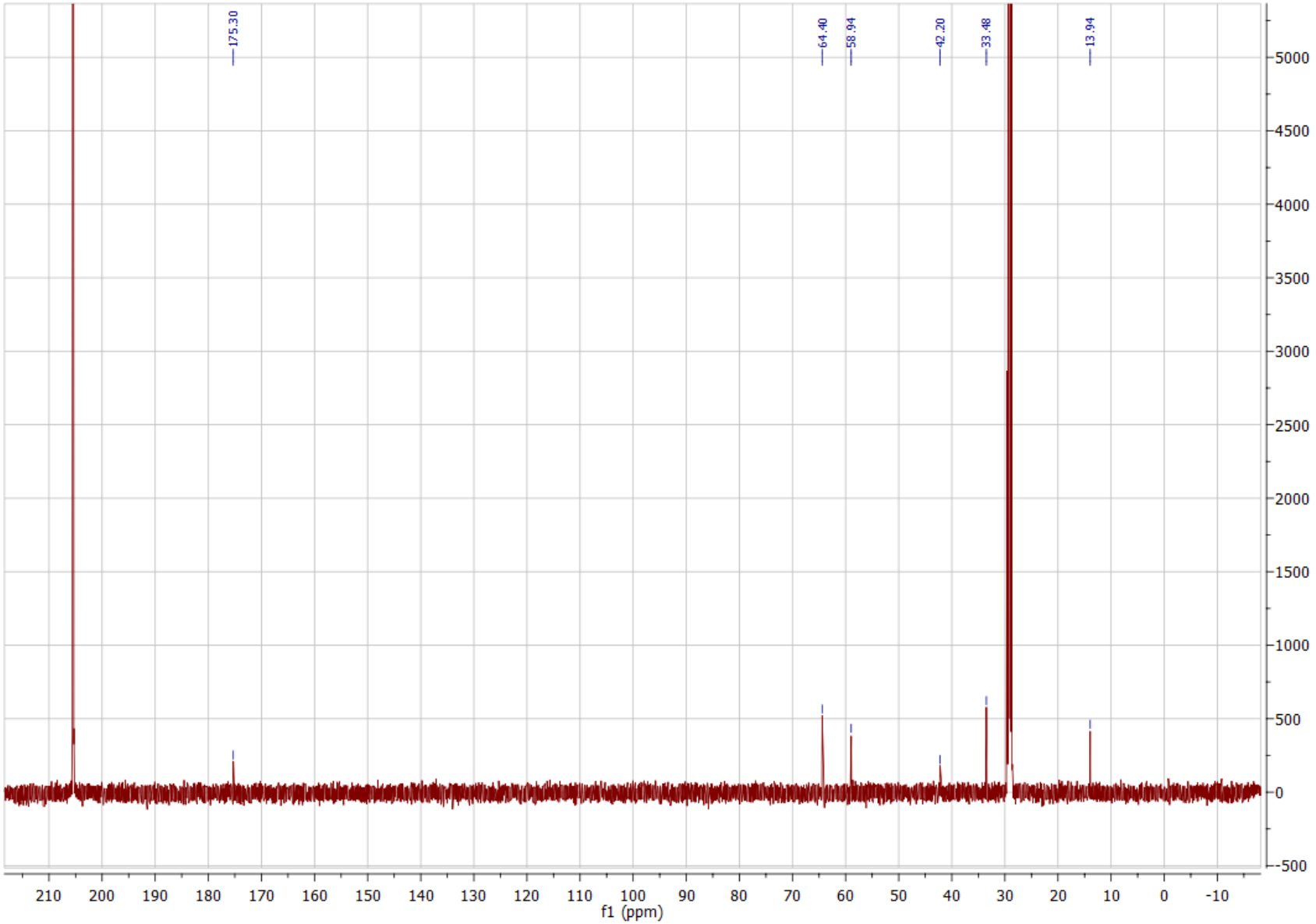
$^{13}C$ NMR ($CDCl_3$, 125.8 MHz) of 5-(4-Acetylphenyl)-5-methylhexan-2-one (**56**)



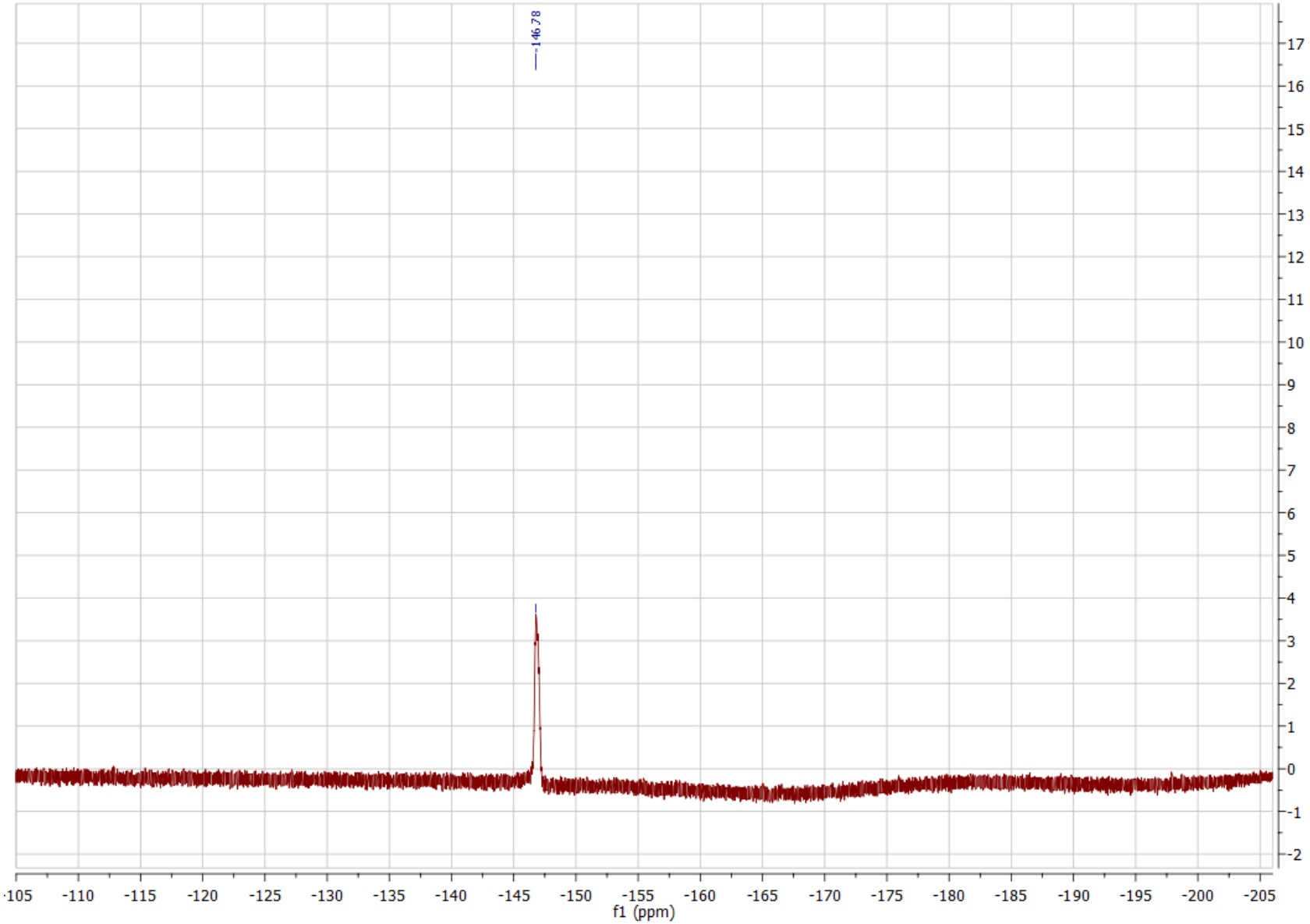
$^{1}$H NMR (acetone-$d_6$, 500 MHz) of potassium (4-(2-ethoxy-2-oxoethyl)tetrahydro-2H-pyran-4-yl)trifluoroborates (**S1**)



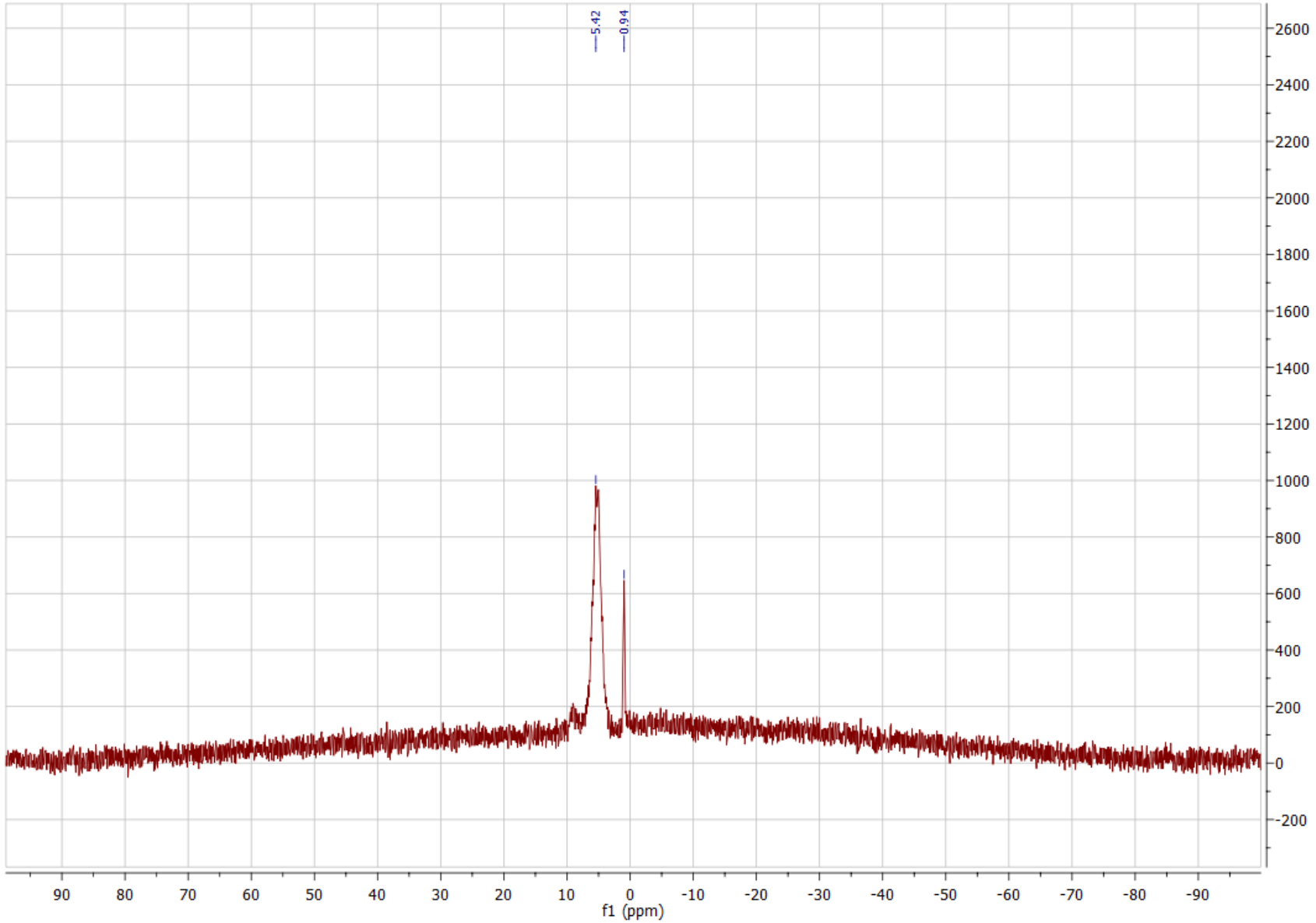
$^{13}$C NMR (acetone-$d_6$, 125.8 MHz) of potassium (4-(2-ethoxy-2-oxoethyl)tetrahydro-2H-pyran-4-yl)trifluoroborates (**S1**)



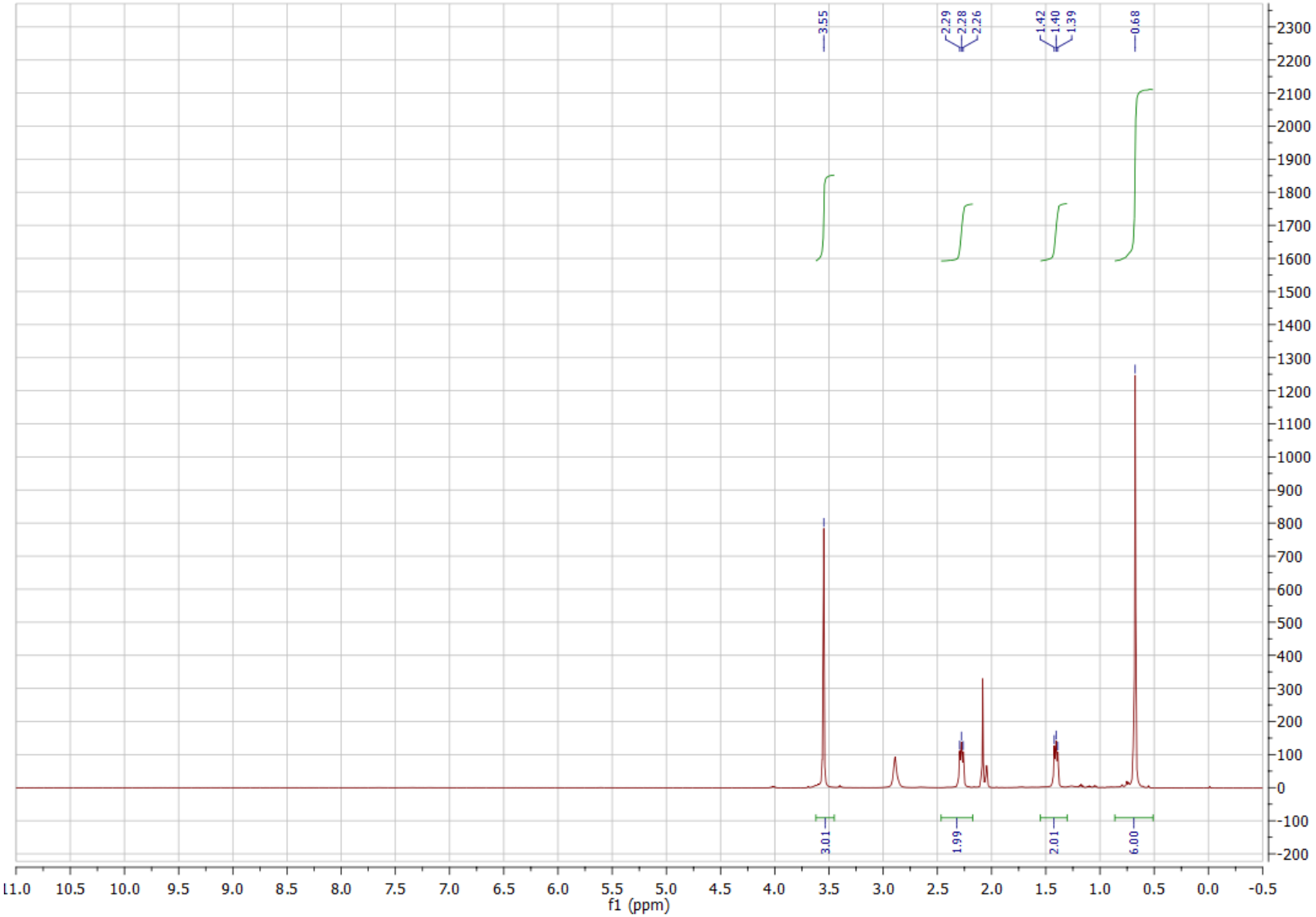
$^{19}$F NMR (acetone-$d_6$, 470.8 MHz) of potassium (4-(2-ethoxy-2-oxoethyl)tetrahydro-2H-pyran-4-yl)trifluoroborates (**S1**)



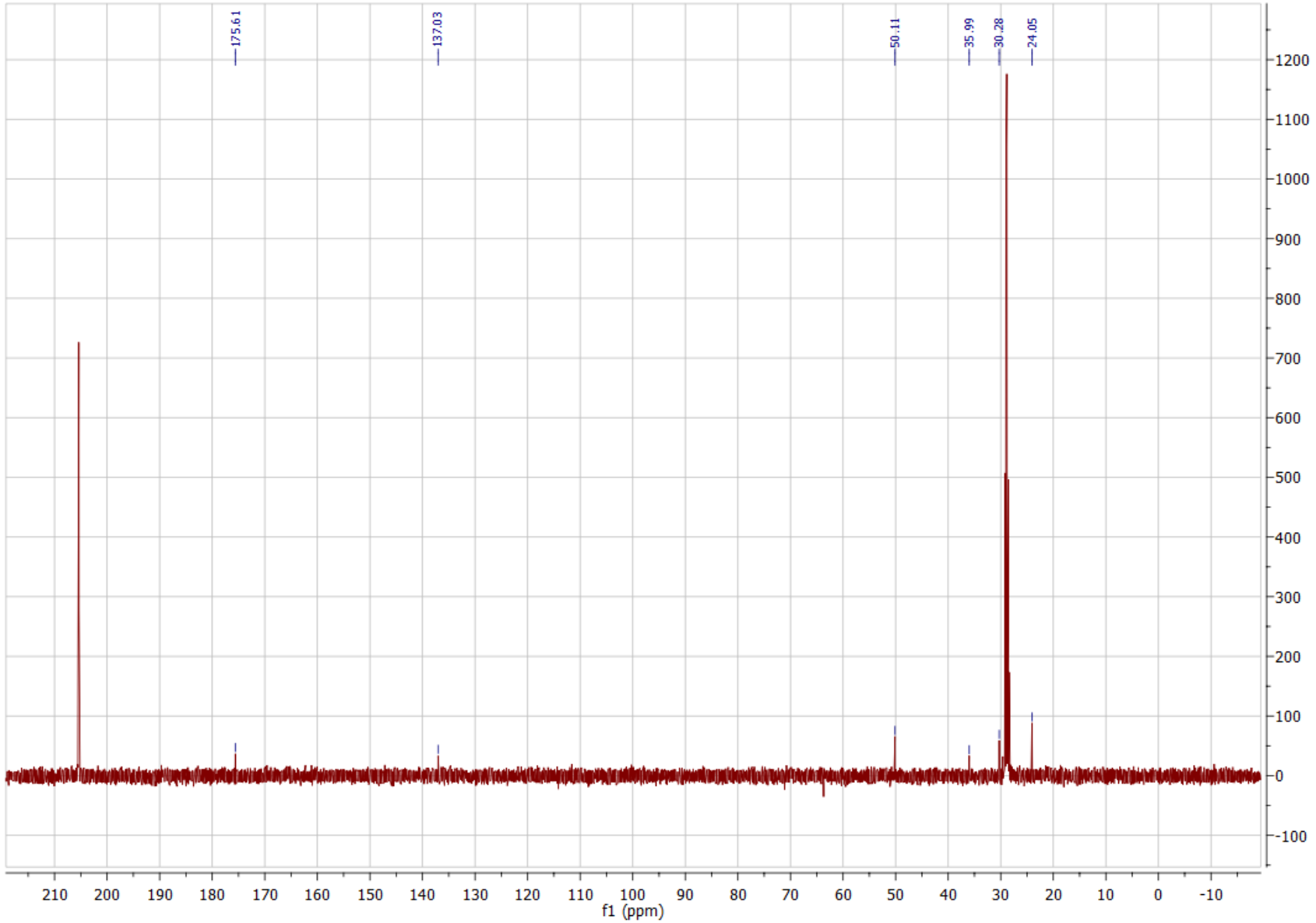
$^{11}$B NMR (acetone-$d_6$, 128.4 MHz) of potassium (4-(2-ethoxy-2-oxoethyl)tetrahydro-2H-pyran-4-yl)trifluoroborates (**S1**)



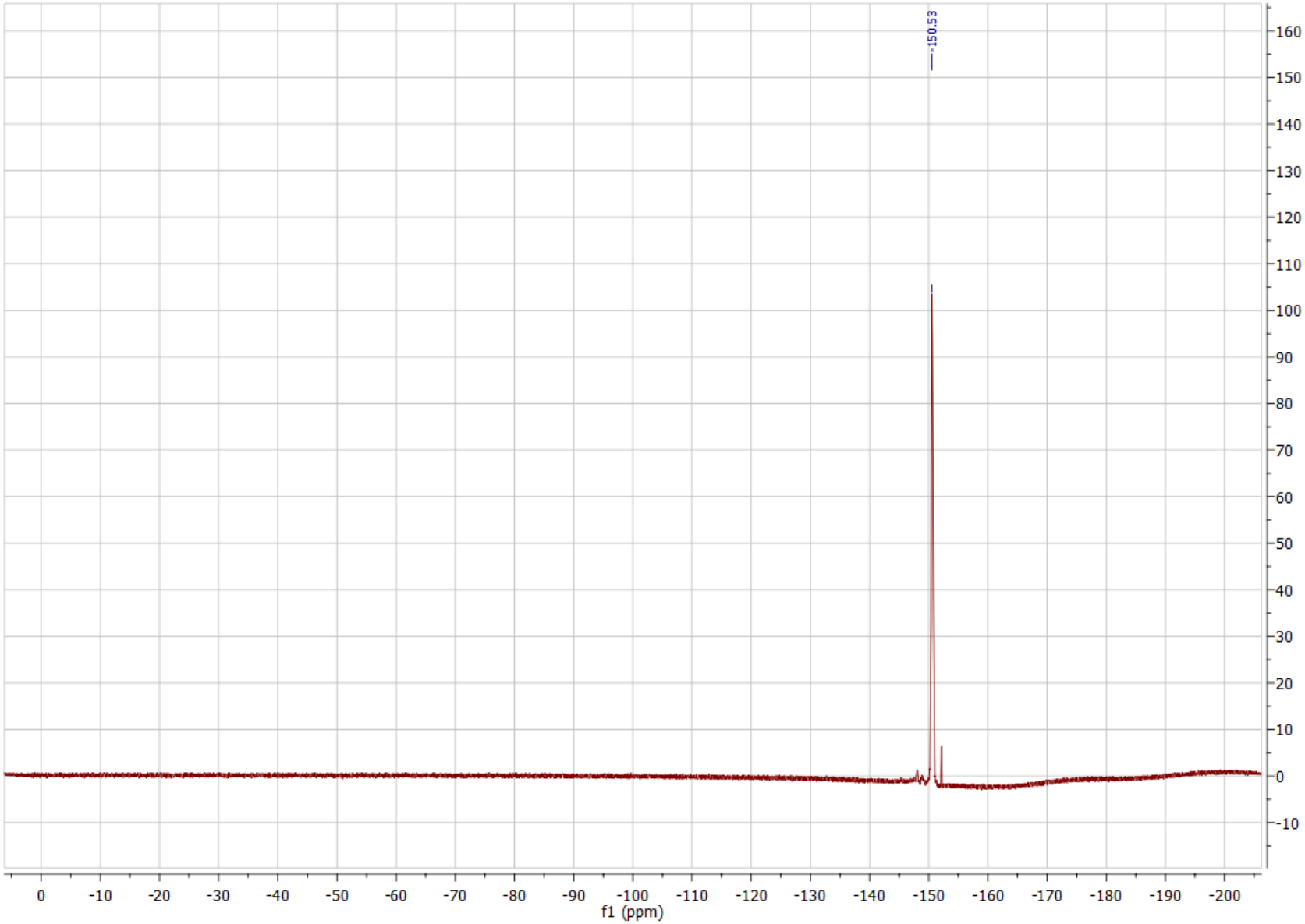
$^{1}$H NMR (acetone-$d_6$, 500 MHz) of potassium trifluoro(5-methoxy-2-methyl-5-oxopentan-2-yl)borate **(S2)**



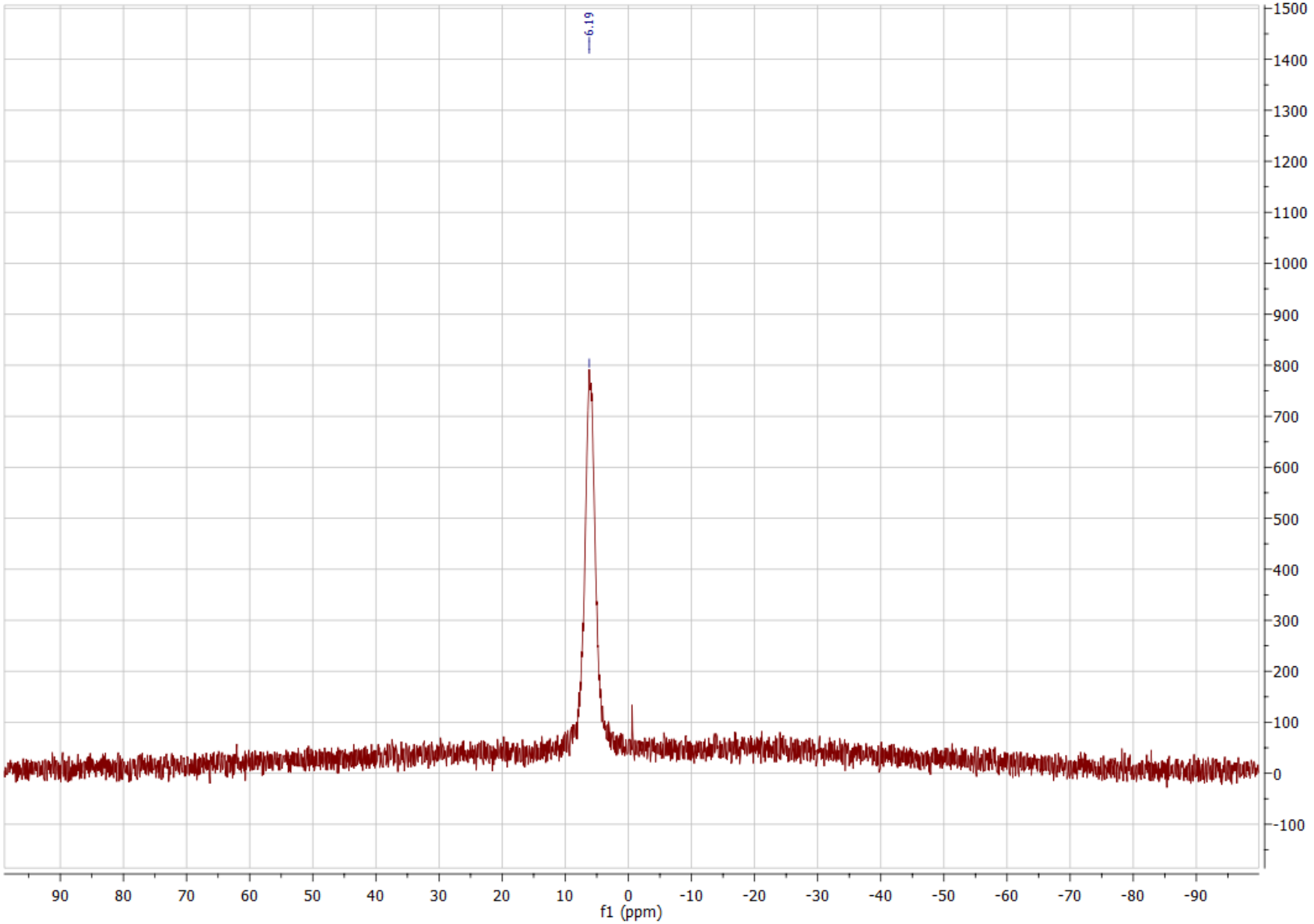
$^{13}$C NMR (acetone-$d_6$, 125.8 MHz) of potassium trifluoro(5-methoxy-2-methyl-5-oxopentan-2-yl)borate **(S2)**



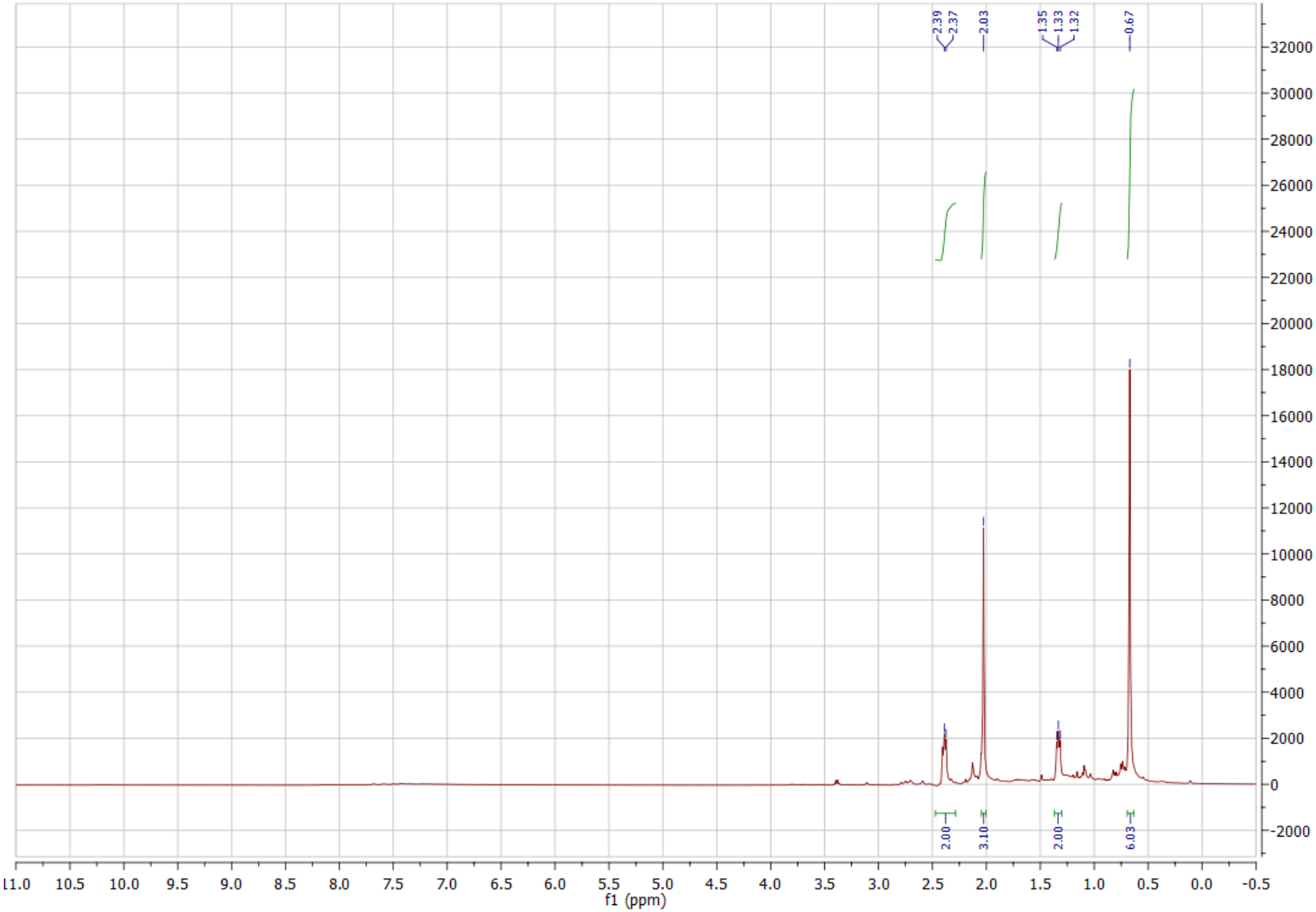
$^{19}$F NMR (acetone-$d_6$, 470.8 MHz) of potassium trifluoro(5-methoxy-2-methyl-5-oxopentan-2-yl)borate **(S2)**



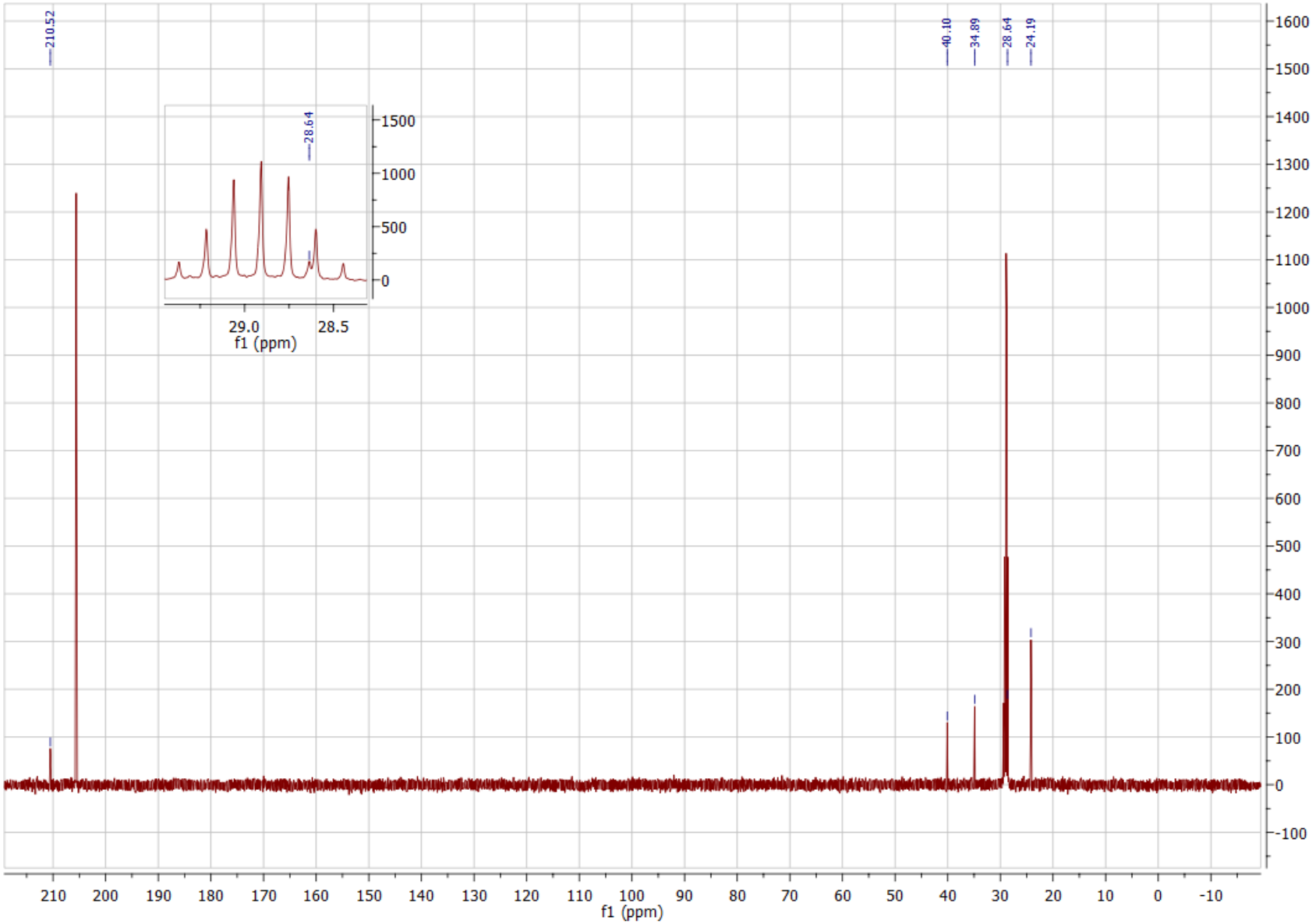
$^{11}$B NMR (acetone-$d_6$, 128.4 MHz) of potassium trifluoro(5-methoxy-2-methyl-5-oxopentan-2-yl)borate **(S2)**



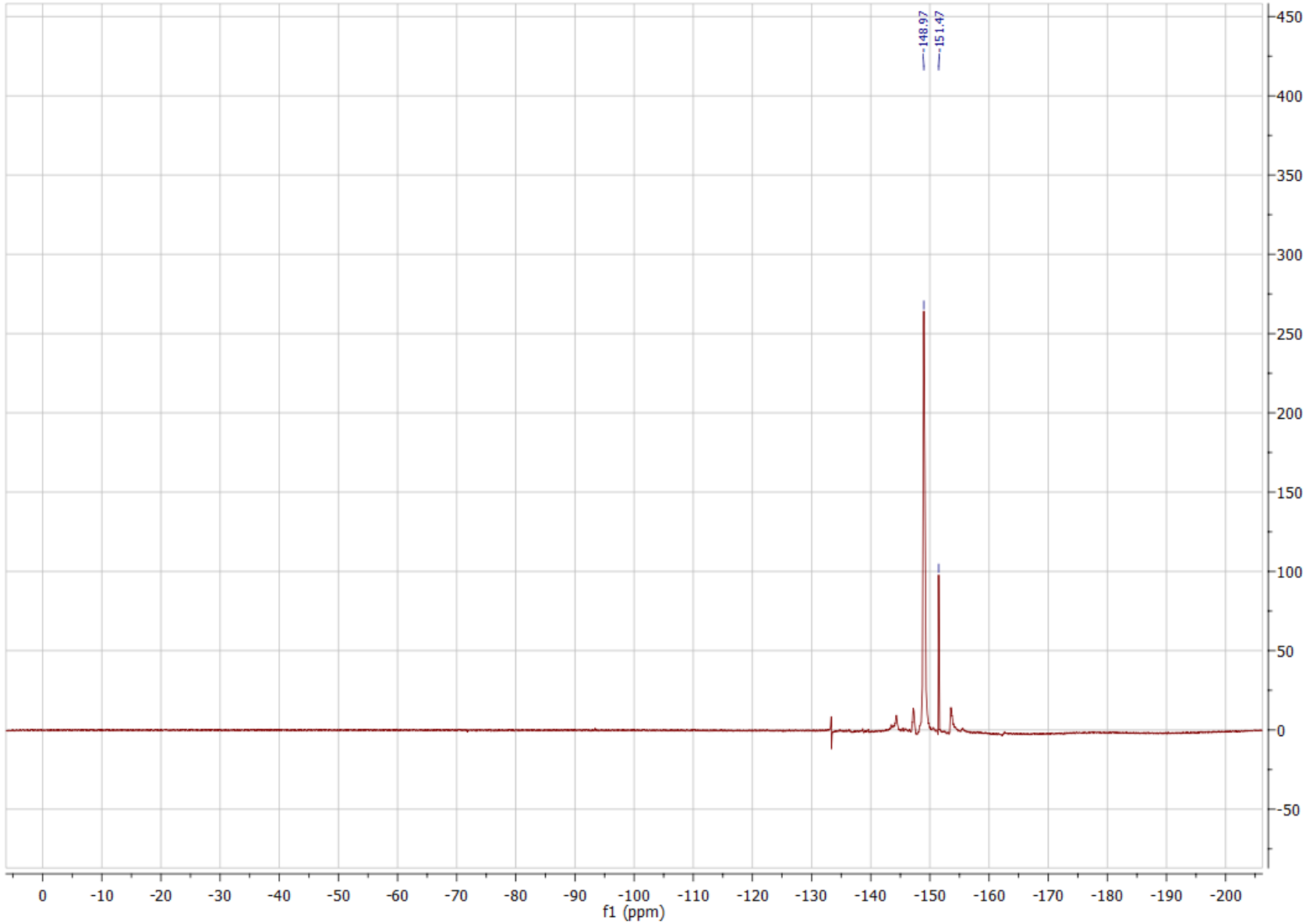
$^{1}$H NMR (acetone-$d_6$, 500 MHz) of potassium trifluoro(2-methyl-5-oxohexan-2-yl)borate (**S3**)



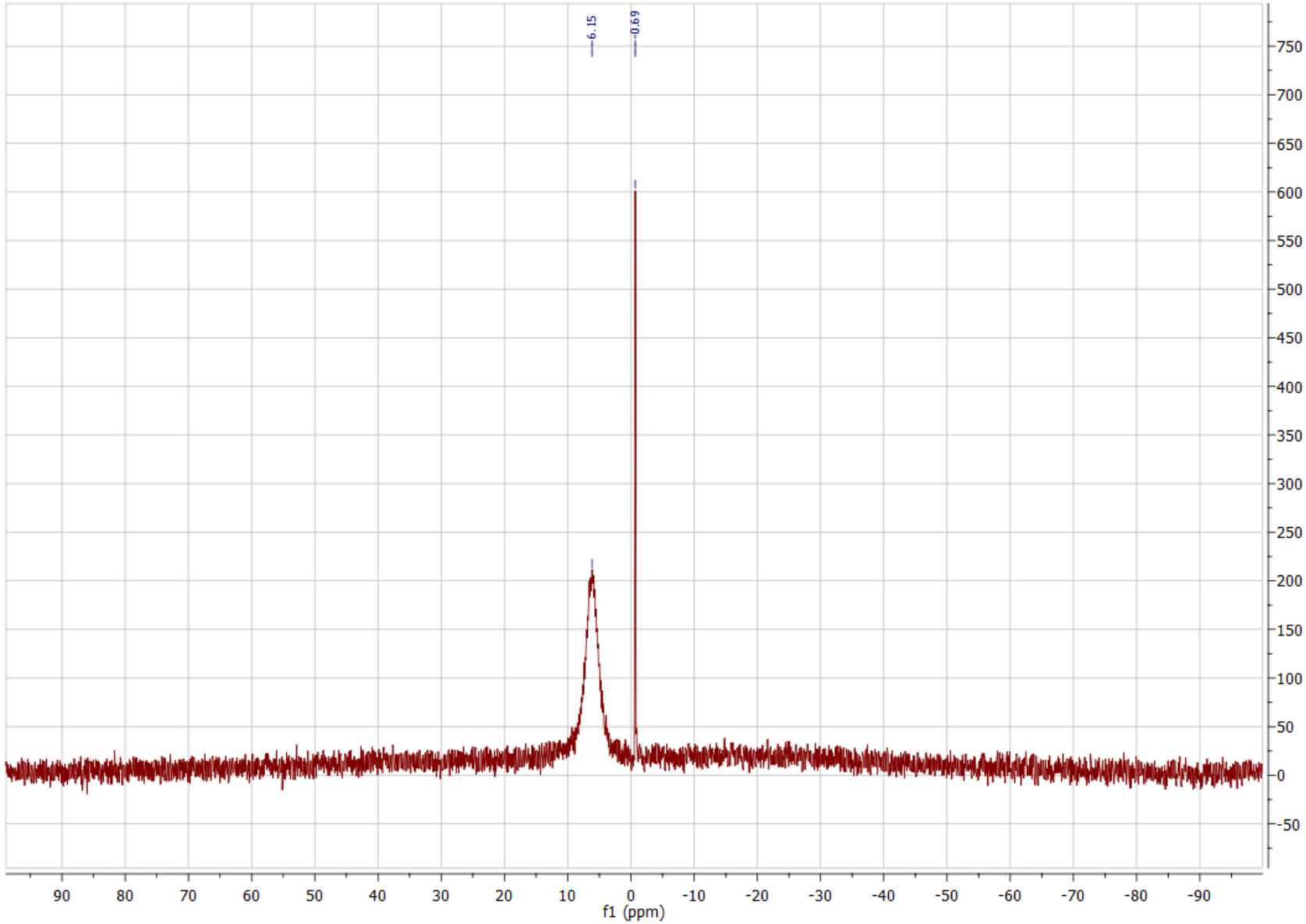
$^{13}$C NMR (acetone-$d_6$, 125.8 MHz) of potassium trifluoro(2-methyl-5-oxohexan-2-yl)borate (**S3**)



$^{19}F$ NMR (acetone-$d_6$, 470.8 MHz) of potassium trifluoro(2-methyl-5-oxohexan-2-yl)borate (**S3**) with residual $BF_4$

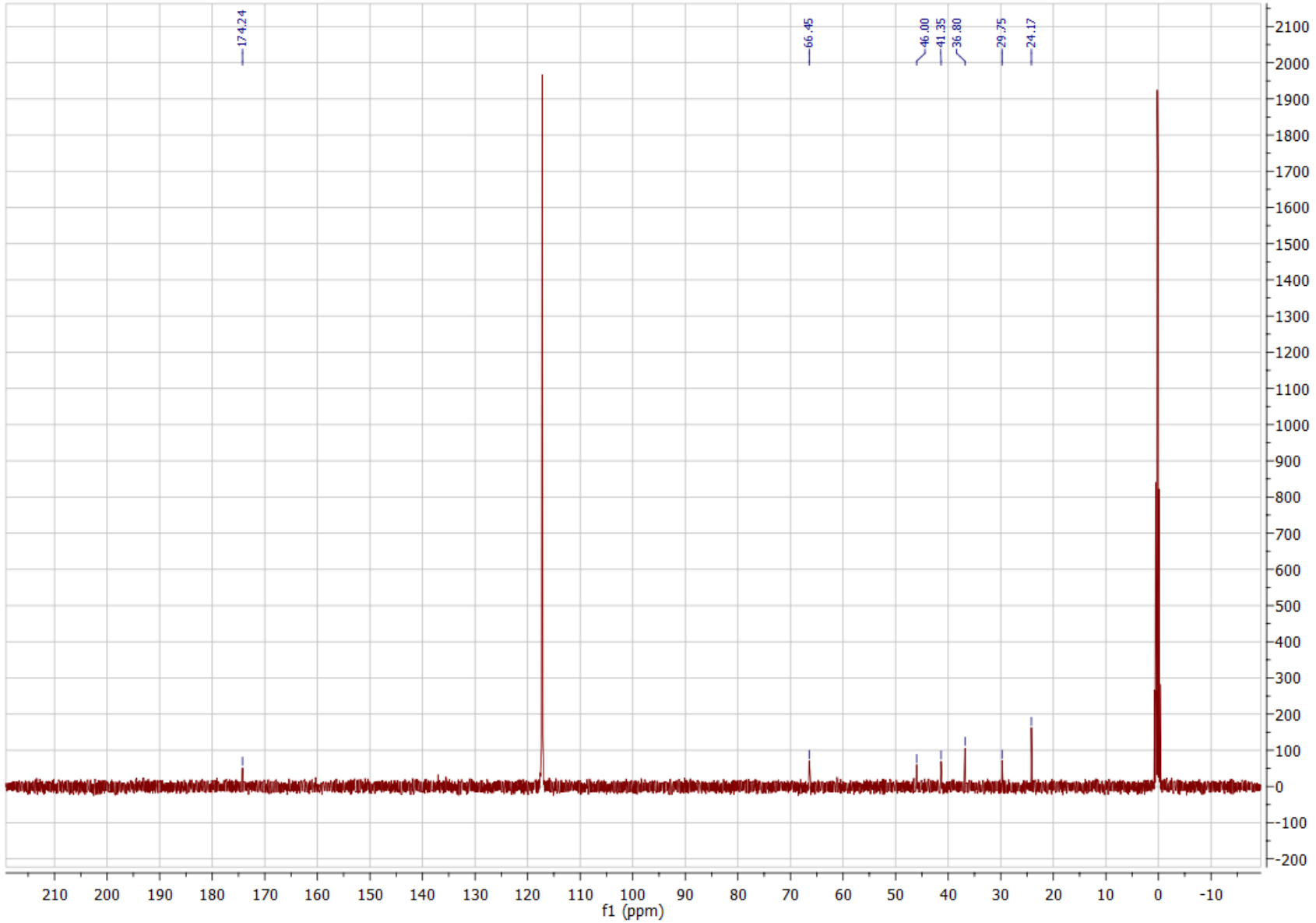


$^{11}B$ NMR ($d_6$-acetone, 128.4 MHz) of potassium trifluoro(2-methyl-5-oxohexan-2-yl)borate (**S3**) with residual $BF_4$

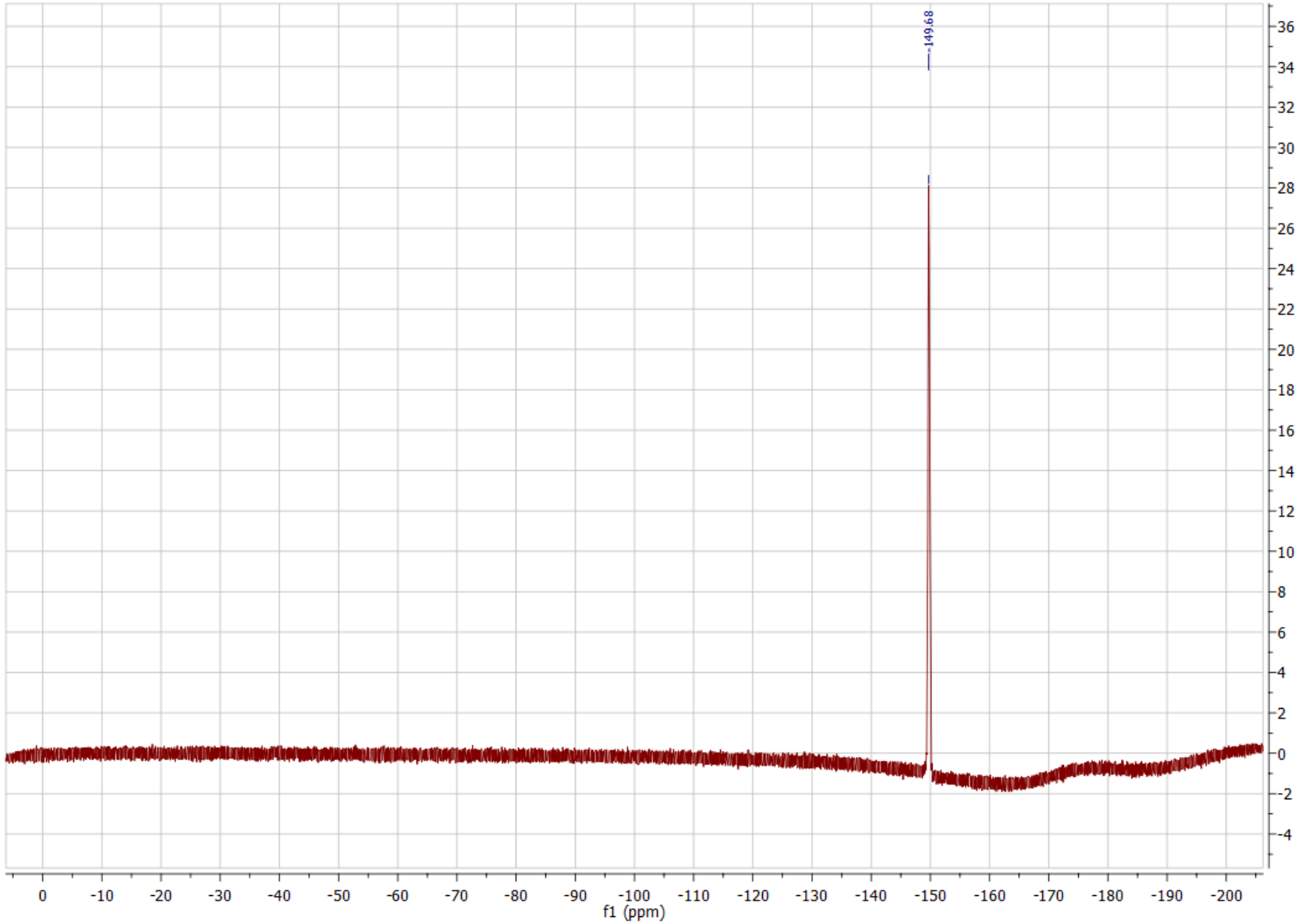


$^{1}$H NMR ($CD_3CN$, 500 MHz) of potassium trifluoro(2-methyl-5-morpholino-5-oxopentan-2-yl)borate (**S4**)

$^{13}C$ NMR ($CD_3CN$, 125.8 MHz) of potassium trifluoro(2-methyl-5-morpholino-5-oxopentan-2-yl)borate (**S4**)



$^{19}F$ NMR ($CD_3CN$, 470.8 MHz) of potassium trifluoro(2-methyl-5-morpholino-5-oxopentan-2-yl)borate (**S4**)



$^{11}$B NMR ($CD_3CN$, 128.4 MHz) of potassium trifluoro(2-methyl-5-morpholino-5-oxopentan-2-yl)borate (**S4**)