Supplementary Information

Asymmetric synthesis of unnatural α-amino acids through photoredox-mediated C–O bond activation of aliphatic alcohols

Gregory R. Alvey,[a] *Elena V. Stepanova,*[a,b] *Andrey Shatskiy,*[a] *Josefin Lantz,*[a] *Rachel Willemsen,*[a] *Alix Munoz,*[a] *Peter Dinér,*[a] *Markus D. Kärkäs**[a]

[a] Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[b] Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russia

** E-mail:* karkas@kth.se

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1. *General methods*

N-sulfinyl imine **4**,[1] reference compound **8m**[1] and 4CzIPN (**PC2**) photocatalyst[2] were synthesized according to the previously published procedures. NMR spectra were recorded in $CDCl_3$, MeOH-d_4 or DMSO-d_6 on Bruker Avance DMX 500 MHz or Bruker Ascend 400 MHz NMR spectrometers and internally calibrated against the residual undeuterated solvent peaks ($CHCl_3$: δ 7.26 for ^{1}H NMR and δ 77.16 for ^{13}C NMR; CHD_2OD: δ 3.31 for ^{1}H NMR and δ 49.00 for ^{13}C NMR; DMSO-d_5: δ 2.50 for ^{1}H NMR and δ 39.52 for ^{13}C NMR). The photocatalytic reactions were carried out in 8 mL or 12 mL vials equipped with a stirring bar and a septum. The reaction vials were placed in a 3D-printed polypropylene holder to maintain the distance between the reaction vial and the lamp at ca. 2 cm and illuminated with 440 nm LED (40 W, Kessil PR160L, set to maximum intensity) with continuous stirring at 1200 rpm and fan cooling. The isolated products were purified by column chromatography with silica gel (high-purity grade, 60 Å, 130–270 mesh, Sigma-Aldrich, Art. No. 288608-1KG) or by preparative thin-layer chromatography (1 mm silica gel layer on glass, 60 Å, Merk, Art. No. 1.13895.0001).

2. *Electrochemical, fluorescence quenching and spectroelectrochemical studies*

Electrochemical measurements were performed under Ar in a one-compartment electrochemical cell with glassy carbon as the working electrode (⌀ 3 mm), Pt coil as the auxiliary electrode, and saturated calomel electrode (SCE) as the reference electrode, using CHI750E bipotentiostat (CH Instruments). The cyclic voltammetry (CV) measurements of alkyl oxalate salts **3a-Na**, **3x-Na** and **3y-Na** were performed at 0.05 V s^{-1} scan rate on 3 mM solutions of the salts in DMF/MeCN/water 5.4/0.6/0.027 (vol.) with 0.1 M $TBAPF_6$ as the supporting electrolyte (Fig. 4B and S1).

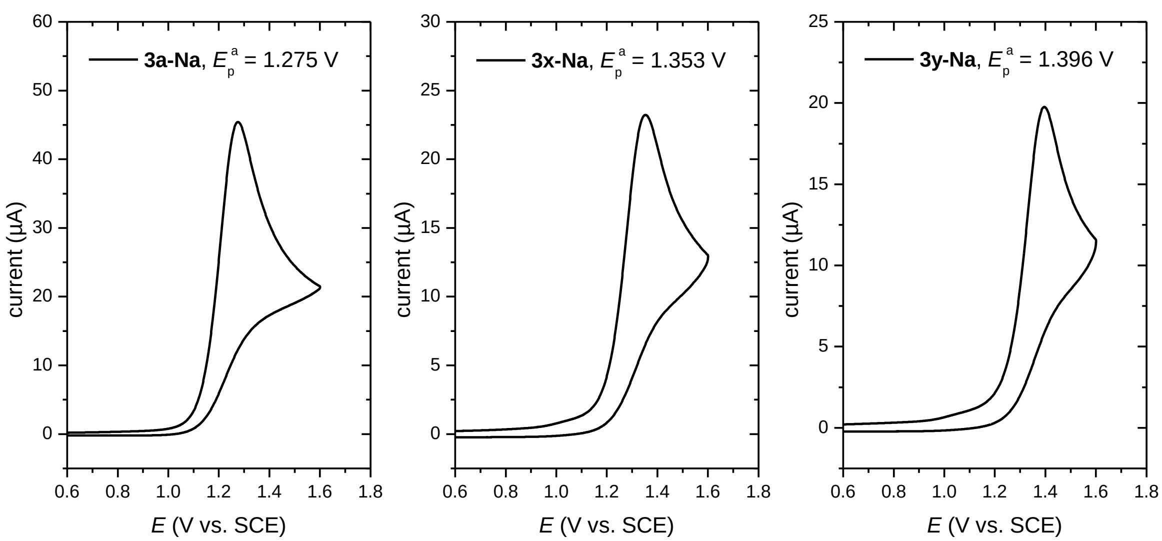


Fig. S1. Electrochemical measurements for alkyl oxalate salts **3a-Na**, **3x-Na** and **3y-Na**.

The steady-state fluorescence quenching measurements were performed under Ar on FS5 spectrofluorometer (Edinburgh Instruments) using 10 x 10 mm quartz cuvettes. The measurements were carried out on the solutions of photocatalyst **PC4** (15 µM) in DMF/MeCN/water 5.4/0.6/0.027 (vol.) with varying concentration of the oxalate salt **3y-Na** (0 mM, 5 mM, 10 mM) or imine **4**. The emission spectra were recorded at 500–1000 nm with excitation at 420 nm (Fig. 4B and S2).

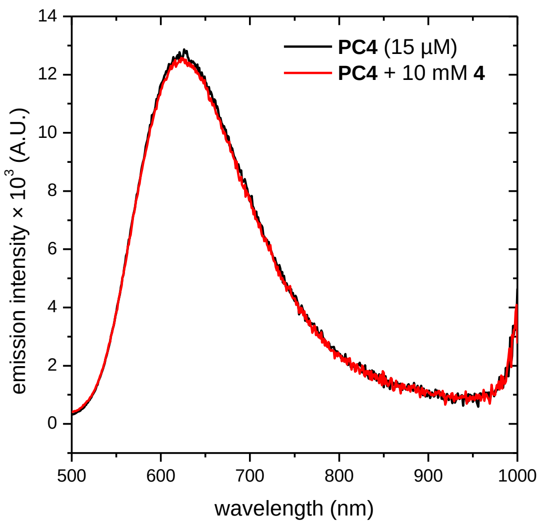


Fig. S2. Fluorescence quenching measurements for photocatalyst **PC4** and imine **4**.

Spectroelectrochemical measurements aiming at obtaining the UV-vis spectrum of unstable $\mathbf{PC4}^{\mathbf{red}}$ species were performed using CHI750E bipotentiostat (CH Instruments), Varian Cary 50 UV-vis Spectrophotometer, and SEC-C Spectroelectrochemical Cell (ALS, 1 mm optical path length, Pt mesh as the working and the auxiliary electrodes, and Ag/AgCl reference electrode, externally calibrated against SCE for conversion of the potential values). The measurements were performed on solution of **PC4** (0.2 mM) in DMF/MeCN/water 5.4/0.6/0.027 (vol.) with 0.1 M $TBAPF_6$ as the supporting electrolyte (Fig. 4B).

Photoinduced reduction of oxalate salts **3a-Na**, **3x-Na** and **3y-Na** by the **PC4** photocatalyst were performed under Ar on Varian Cary 50 UV-vis Spectrophotometer, using a quartz cuvette from the SEC-C Spectroelectrochemical Cell (ALS, 1 mm optical path length). The measurements were carried out on 1 mM solutions of **3a-Na**, **3x-Na** and **3y-Na** with 0.2 mM **PC4** in DMF/MeCN/water 5.4/0.6/0.027 (vol.). The UV-vis spectra were recorded before and after irradiation of the solutions with 440 nm LED (40 W, Kessil PR160L, set to maximum intensity) for 30 s (Fig. 4B). The LED was positioned ca. 2 cm from the UV-vis cuvette.

3. *Computational studies*

All stationary points were optimized, first at the B3LYP/6-311+G(d,p) level of theory, and further re-optimized at the B3LYP/6-311+G(d,p) level of theory,[3,4,5,6] as implemented in Gaussian 16 Rev D.01. In the optimizations, the Grimme correction for dispersion (D3) was used in combination with the Conductor-like Polarizable Continuum Model (CPCM) using the parameters for acetonitrile and the default Unified Force Field radii (UFF)[7,8] as implemented in Gaussian 16 Rev D.01.[9] All geometries were characterized as

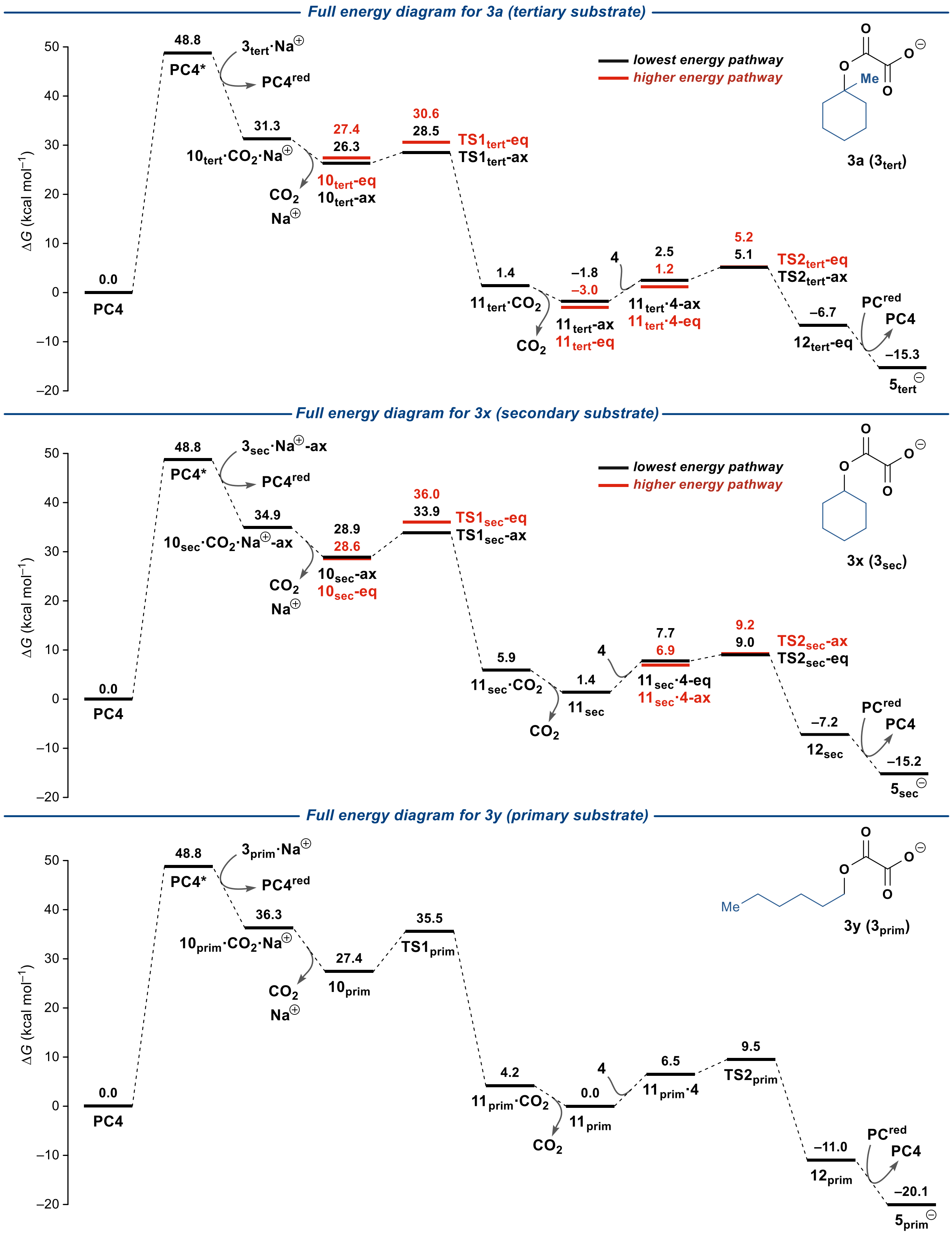


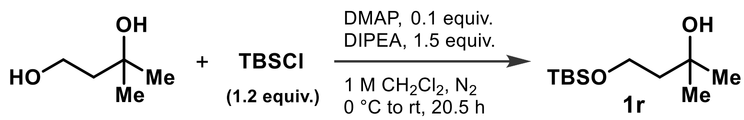
Fig. S3. Full calculated energy diagrams for substrates **3a** (**3**$_{tert}$), **3x** (**3**$_{sec}$), and **3y** (**3**$_{prim}$).

minima or saddle points on the potential-energy surface (PES) by using the sign of the eigenvalues of the force-constant matrix obtained from a frequency calculation. Transition states with one imaginary frequency were confirmed to describe the correct movement on the PES by mode analysis and by intrinsic reaction coordinate (IRC) calculations connecting the correct reactants and products (Fig. 4C and S3).

4. *Synthetic procedures*

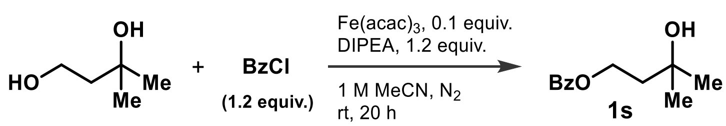
4.1 *Synthesis of starting materials*

Compound **1r** (4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-ol)



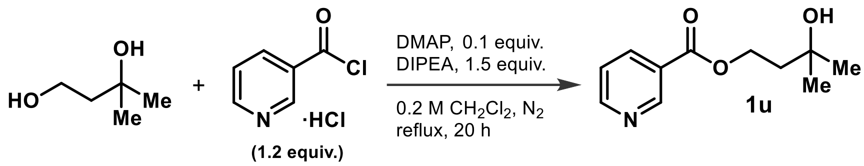
3-Methyl-1,3-butanediol (1.07 mL, 10 mmol, 1 equiv.) and DMAP (122 mg, 0.1 mmol, 0.1 equiv.) were dissolved in dry CH_2Cl_2 (10 mL) under N_2 and cooled with an ice bath. Thereafter, DIPEA (2.6 mL, 15 mmol,1.5 equiv.) and *tert*-butyldimethylsilyl chloride (1.808 g, 12 mmol, 1.2 equiv.) were added sequentially and the reaction mixture was stirred with an ice bath cooling under N_2. After 30 min the reaction mixture was allowed to warm to r.t. and stirred for 20 h. The reaction was quenched by sat. NH_4Cl (10 mL), the organic phase was separated, and the water phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo* to obtain the crude product as a brown oil. The crude product was purified by column chromatography (petroleum ether/EtOAc 20:1 → 4:1) to give 2.08 g (95%) of compound **1r**.

Compound **1s** (4-(benzoyloxy)-2-methylbutan-2-ol)



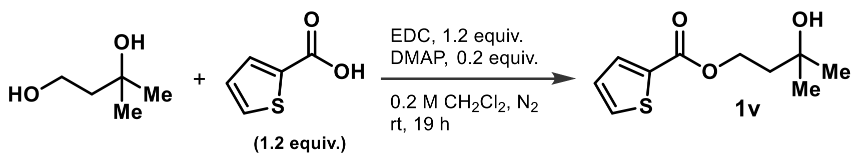
3-Methyl-1,3-butanediol (1.07 mL, 10 mmol, 1 equiv.) and $Fe(acac)_3$ (353 mg, 0.1 mmol, 0.1 equiv.) were dissolved in MeCN (10 mL) under N_2. Thereafter, DIPEA (2.09 mL, 12 mmol, 1.2 equiv.) and benzoyl chloride (1.4 mL, 12 mmol, 1.2 equiv.) were added sequentially and the reaction mixture was stirred for 20 h at r.t. The reaction mixture was concentrated *in vacuo*, the residue was dissolved in CH_2Cl_2 (20 mL) and washed with sat. aq. Na_2CO_3 (3 × 20 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo* to obtain the crude product as a brown oil. The crude product was purified by column chromatography (petroleum ether/EtOAc 10:1→2:1) to give compound **1s** as a yellow oil (1.847 g, 89% yield).

Compound **1u** (4-(benzoyloxy)-2-methylbutan-2-ol)



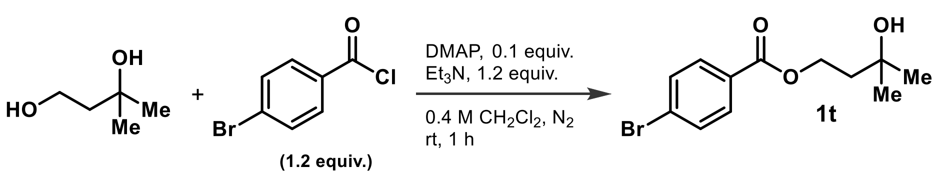
Nicotinoyl chloride hydrochloride (213.6 mg, 1.2 mmol, 1.2 equiv.) and DMAP (12.2 mg, 1.2 mmol, 0.1 equiv.) were dried *in vacuo*, then 3-methyl-1,3-butanediol (107 µL, 1 mmol, 1 equiv.) was added, dissolved in dry CH_2Cl_2 (5 mL), DIPEA (260 µL, 1.5 mmol, 1.5 equiv.) was added and the rection was refluxed for 20 h. Then it was cooled, CH_2Cl_2 (20 mL) and sat. aq. Na_2CO_3 (10 mL) were added, organic layer was separated and washed with sat.aq. Na_2CO_3 (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified on column chromatography (CH_2Cl_2/MeOH 10:1) to give compound **1u** as yellow oil (170 mg, 81% yield).

Compound **1v** (4-(2-thiophenecarboxy)-2-methylbutan-2-ol)



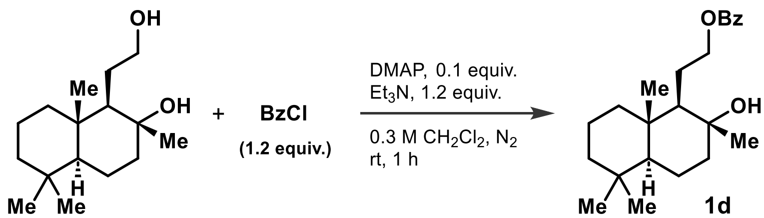
2-Thiophene-carboxylic acid (153.6 mg, 1.2 mmol, 1.2 equiv.) and DMAP (24.4 mg, 0.2 mmol, 0.2 equiv.) were dried *in vacuo*, then 3-methyl-1,3-butanediol (107 µL, 1 mmol, 1 equiv.) was added, dissolved in dry CH_2Cl_2 (5 mL), EDC (212 µL, 1.2 mmol, 1.2 equiv.) was added and the rection was stirred at r.t. for 19 h. CH_2Cl_2 (20 mL) and sat. aq. Na_2CO_3 (10 mL) were added, organic layer was separated and washed with sat. aq. Na_2CO_3 (3 × 10 mL), 5% aq. H_2SO_4 (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give compound **1v** as a yellowish oil (185 mg, 89% yield).

Compound **1t** (3-hydroxy-3-methylbutyl 4-bromobenzoate)



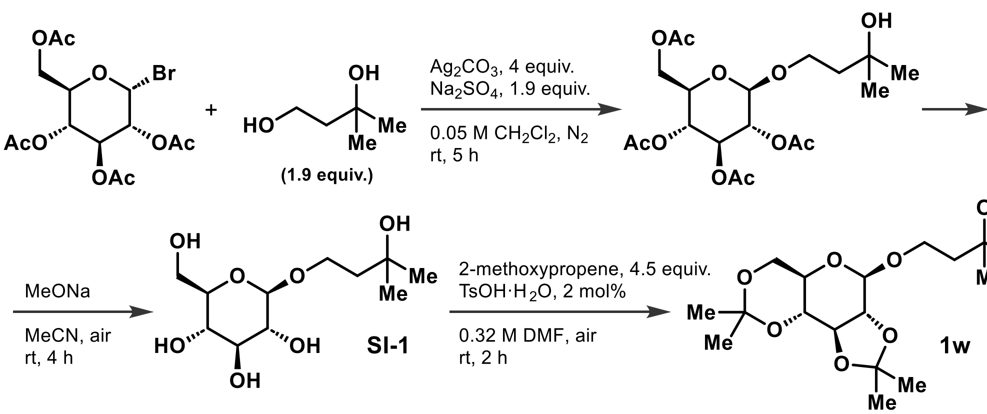
(4-bromo)benzoylchloride (526.7 mg, 2.4 mmol, 1.2 equiv.) and DMAP (22.4 mg, 0.2 mmol, 0.1 equiv.) were dried *in vacuo*, then 3-methyl-1,3-butanediol (213 µL, 2 mmol, 1 equiv.) was added, dissolved in dry CH_2Cl_2 (5 mL), Et_3N (335 µL, 2.4 mmol, 1.2 equiv.) was added and stirred for 1 h. CH_2Cl_2 (20 mL) and sat. aq. Na_2CO_3 (10 mL) were added, organic layer was separated and washed with sat. aq. Na_2CO_3 (3 × 10 mL), 5% aq. H_2SO_4 (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography CH_2Cl_2/MeOH 10:1 to give compound **1t** as a yellow oil (561 mg, 98% yield).

Compound **1d** (2-(2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl benzoate)



Sclareol glycol (381.6 mg, 1.5 mmol) and DMAP (18.3 mg, 0.15 mmol, 0.1 equiv.) were dried *in vacuo*, dissolved in dry CH_2Cl_2 (5 mL), Et_3N (251 µL, 1.8 mmol, 1.2 equiv.) and benzoyl chloride (210 µL, 1.8 mL, 1.2 equiv.) were added sequentially and the reaction mixture was stirred for 1 h at r.t. CH_2Cl_2 (20 mL) and Na_2CO_3 sat (10 mL) were added, organic layer was separated and washed with sat. aq. Na_2CO_3 (3 × 10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography petroleum ether/EtOAc 2:1 to give compound **1d** as a colorless oil (538 mg, quantitative yield).

Compound **1w** (1-(2:3,4:6-diacetone β-D-glucopyranosyloxy) 3-hydroxy-3-methylbutane)

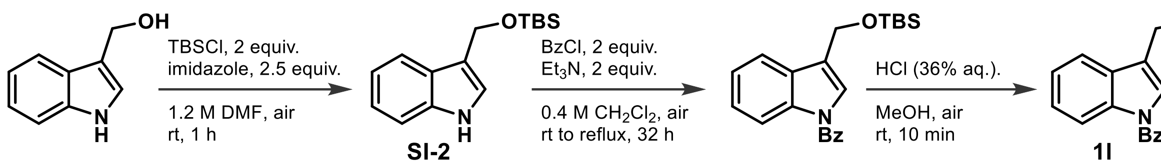


To a solution of the glucopyranosyl bromide (870 mg, 2.11 mmol, 1 equiv.) in dry CH_2Cl_2 (40 mL), anhydrous Na_2SO_4 (568 mg, 4 mmol, 1.9 equiv.) and 3-methyl-1,3-butanediol (0.426 mL, 4 mmol, 1.9 equiv.) were added and stirred at r.t. for 15 min under N_2. Ag_2CO_3 (1.103 mg, 4 equiv) was added and stirring continued for 5 h. The reaction mixture was filtered through silica gel plug, washed with CH_2Cl_2/MeOH 10:1 mixture (150 mL), filtrate was collected and concentrated *in vacuo*. The residue was purified on silica gel column chromatography petroleum ether/EtOAc 3:1 → 1:1 to give the desired glucoside as a colorless oil (580 mg) which was used directly in the next step.

The residue was dissolved in MeOH (20 mL), MeONa (10 mg) was added and stirred for 4 h at r.t. The reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel column chromatography CH_2Cl_2/MeOH 5:1 → 3:1 to give glucoside **SI-1** as a colorless oil (213 mg, 38% yield over 2 steps).

To the solution of glucoside **SI-1** (213 mg, 0.8 mmol, 1 equiv.) and 4-toluenesulphonic acid monohydrate (3 mg, 0.016 mmol, 0.02 equiv.) in DMF (2.5 mL) 2-methoxypropene (345 µL, 3.6 mmol, 4.5 equiv.) was added, and the reaction mixture was stirred at r.t. for 2 h. The reaction mixture was concentrated *in vacuo* and DMF was co-evaporated with toluene (3 × 10 mL). The residue was purified by silica gel column chromatography petroleum ether/EtOAc 5:1 → 2:1 to give diacetonide **1w** as colorless powder (159 mg, 57% yield).

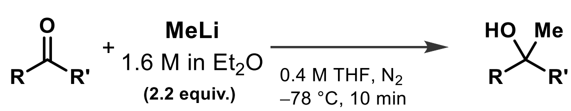
Compound **1l** ((3-(hydroxymethyl)-1H-indol-1-yl)(phenyl)methanone)



To a solution of indole-3-carbinol (883 mg, 6 mmol, 1 equiv.) and imidazole (1.021 g, 15 mmol, 2.5 equiv.) in DMF (5 mL) *tert*-butyldimethylsilyl chloride (1.808 g, 12 mmol, 2 equiv.) was added in one portion. The reaction was stirred at r.t. for 1 h, water (30 mL) was added and extracted with EtOAc (3 × 30 mL). The organic layer was washed with brine (2 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography petroleum ether/EtOAc 5:1 → 2:1 to give compound **SI-2** as a colorless solid (1.224 g, 78% yield).

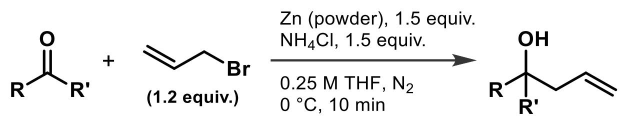
To a solution of intermediate compound **SI-2** (522 mg, 2 mmol, 1 equiv.) and Et_3N (560 µL, 4 mmol, 2 equiv.) in CH_2Cl_2 (5 mL) benzoyl chloride (465 µL, 4 mmol, 2 equiv.) was added. The reaction mixture was stirred at r.t. for 16 h and then refluxed for 16 h. Water (20 mL) was added, extracted with CH_2Cl_2 (3 × 20 mL), organic extracts were combined and washed with sat. aq. Na_2CO_3 (2 × 30 mL). The organic extract was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the desired benzoylated intermediate product. The residue was dissolved in MeOH (6.5mL) and 36% aq. HCl (450 µL) was added. The reaction mixture was stirred at r.t. for 10 min until bright pink color, then sat. aq. Na_2CO_3 (20 mL) was added. The resulted aqueous solution was extracted with EtOAc (3 × 20 mL), the organic layers were combined, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography petroleum ether/EtOAc 2:1 → 1:1 to give compound **1l** as a colorless oil (250 mg, 50% yield over two steps).

Compounds **2i**, **2j**, **2p** (*tert*-alcohols from ketones)



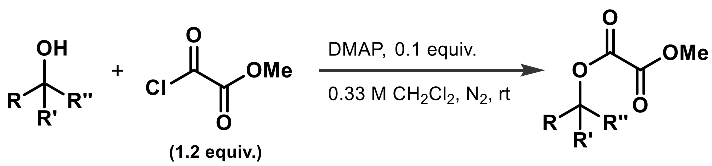
General procedure A. A ketone (4 mmol, 1.0 equiv.), was dissolved in dry THF (10 mL) and was cooled on dry CO_2-acetone bath to −78 °C. Thereafter, methyl lithium 1.6 M solution in Et_2O (2.75 mL, 4.4 mmol, 2.2 equiv.) was added dropwise and the reaction mixture was stirred until warmed to r.t. The reaction mixture was quenched by sat. aq. NH_4Cl (40 mL), the organic layer was separated, and the water layer was extracted with EtOAc (3 × 25 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo* and the residue was purified by silica gel column chromatography.

Compounds **SI-3**, **SI-4**, **SI-5** (homoallylic alcohols)



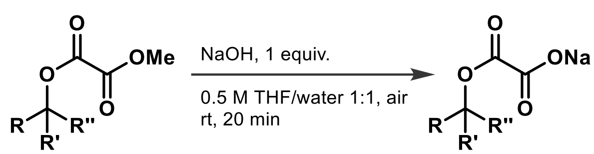
General procedure B. A suspension of ketone (2 mmol, 1.0 equiv.), zinc powder (196 mg, 3 mmol, 1.5 equiv.), and ammonium acetate (231 mg, 3 mmol, 1.5 equiv.) in dry THF (8 mL) was cooled with an ice bath. Thereafter, allyl bromide (260 µL, 3 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred for 10 min. The reaction mixture was quenched by sat. aq. $NaHCO_3$ (20 mL), ice bath was removed, and the reaction allowed to warm to r.t. Water (20 mL) was added and extracted with EtOAc (3 × 40 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated *in vacuo*.

Compounds **2a**–**2w**, **6a**–**6d** (alkyl methyl oxalates)



General procedure C. An alcohol (1 mmol) and DMAP (12.5 mg, 0.1 mmol, 0.1 equiv.) were dissolved in dry CH_2Cl_2 (3 mL) under N_2. Et_3N (0.170 mL, 1.2 equiv.) and methyl chlorooxoacetate (110 µL, 1.2 equiv.) were added sequentially and the reaction mixture was stirred at r.t. for 5 min to 4 h until full conversion of the starting material. The reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel column chromatography.

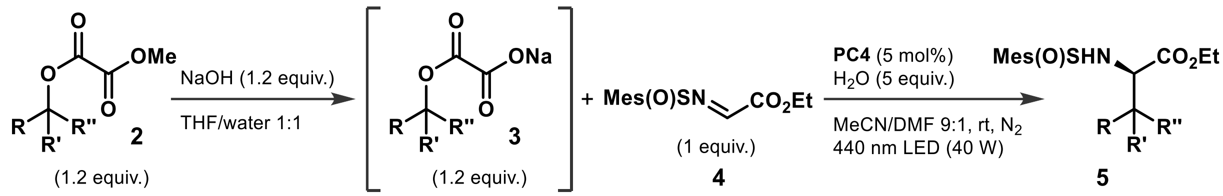
Compounds **3a-Na**, **3x-Na**, **3y-Na** (alkyl oxalate salts)



General procedure D. Methyloxalate (1.5 mmol) was dissolved in THF (1.5 mL), then aq. 1M NaOH (1.5 mL) was added dropwise. The reaction mixture was stirred for 20 min, water (20 mL) was added, extracted with EtOAc (2 × 20 mL). Water layers were combined and evaporated in vacuo to give white powder.

4.2 *General procedure for the photoredox-mediated synthesis of unnatural amino acids*

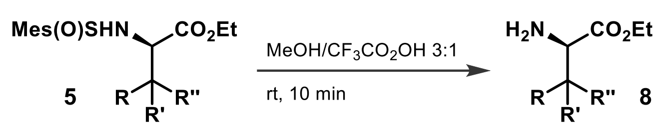
Compounds **5a**–**5w**, **7a–7d** (unnatural α-amino acids)



Methyloxalate (0.3 mmol, 1.2 equiv.) was placed in the 8 mL reaction vial, dissolved in tetrahydrofuran (0.36 mL), aq. 1M NaOH (0.36 mL, 0.36 mmol, 1.2 equiv.) was added dropwise and stirred at room temperature for 30 min. The reaction mixture was concentrated and dried *in vacuo* overnight. The *N*-sulfinyl imine **4** (80.2 mg, 0.30 mmol, 1 equiv.), [Ir(dFCF$_3$ppy)$_2$(5,5'-dCF$_3$bpy)]PF$_6$ photocatalyst (**PC4**, 10.4 mg, 3 mol%), were added to the resultant sodium salt, the reaction vial was equipped with a stirring bar and a septum, the solids were evacuated and back-filled with N_2 three times followed by addition of acetonitrile (5.4 mL), dimethylformamide (0.6 mL), and water (27 µL, 0.015 mmol, 0.05 equiv.). The vial was sealed with parafilm and sonicated for 15 min. The vial was placed in a holder ca. 2 cm from the light source (440 nm LED) and stirred (1200 rpm) under illumination with a fan cooling for 2–4 h. After the reaction was complete, it was transferred to round-bottom flask, concentrated *in vacuo* and purified by silica gel column chromatography.

4.3 *General procedure for N-sulfinyl amide deprotection*

Compounds **8a**, **8d**, **8f**, **8i** (*N*-deprotected unnatural α-amino acids)



N-sulfinyl amide **5** (0.1 mmol) was placed in a 5 mL round-bottom flask, dissolved in 1 mL MeOH and a mixture of CF_3CO_2H and MeOH (1:1 v/v, 1 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 10 min and the solvent was removed under nitrogen flow. The residue was purified by column chromatography with a gradient CH_2Cl_2/MeOH 50:1 → 10:1 as eluent and dried in vacuo overnight, resulting in the deprotected amino acid **8** or as its salt with trifluoroacetic acid.

4.4 *Unsuccessful substrates*

During investigation of the substrate scope, several alcohol substrates proved non-compatible with the disclosed protocols. For various substrates, the lack of desired reactivity was observed at the stage of methyl oxalate ester installation, methyl ester hydrolysis, or the photoreaction (Fig. S4).

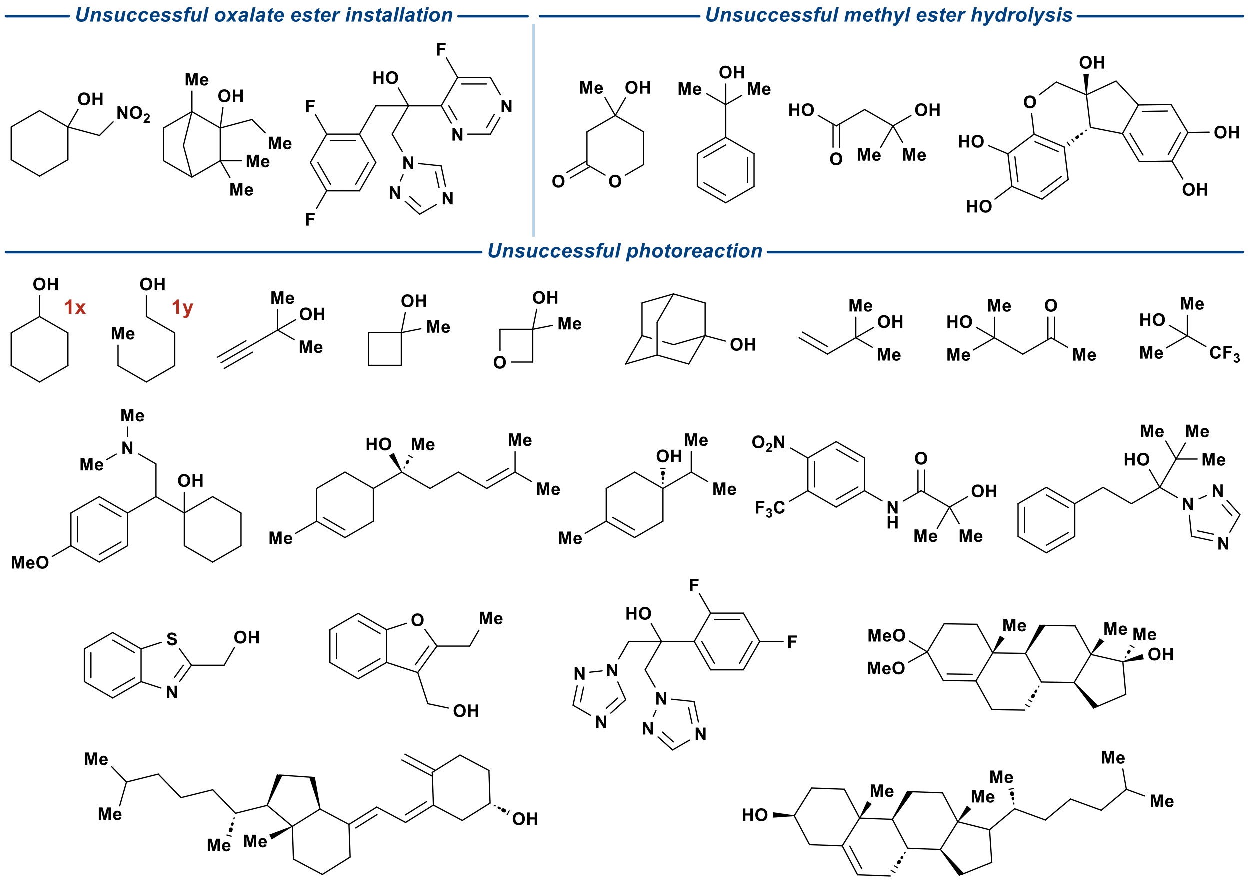
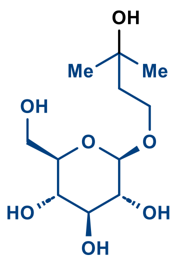


Fig. S4. Unsuccessful substrates.

5. ***Analytical data***

Compound **SI-1** (3-hydroxy-3-methylbutan-1-ol β-D-glucopyranoside)



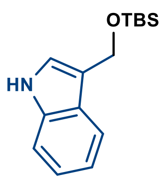
Synthesized according to the procedure described in **Section 4.1**.

^{1}H NMR (500 MHz, MeOD) δ 4.26 (d, *J* = 7.8 Hz, 1H), 4.07 (dt, *J* = 9.8, 7.1 Hz, 1H), 3.87 (d, *J* = 11.5 Hz, 1H), 3.76–3.62 (m, 2H), 3.30–3.21 (m, 2H), 3.16 (dd, *J* = 9.1, 7.8 Hz, 1H), 1.83 (td, *J* = 7.1, 2.5 Hz, 2H), 1.23 (s, 6H).

^{13}C NMR (126 MHz, MeOD) δ 104.4, 78.1, 78.0, 75.1, 71.7, 70.8, 67.5, 62.8, 43.4, 29.7, 29.6.

***R*$_f$** = 0.33 (CH_2Cl_2/MeOH 4:1, brown color upon treatment with 5% methanolic H_3PO_4 and heating)

Compound **SI-2** (3-(((*tert*-butyldimethylsilyl)oxy)methyl)-1*H*-indole)



Synthesized according to the procedure described in **Section 4.1**.

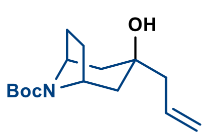
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.18–6.98 (m, 2H), 4.96 (s, 2H), 0.96 (s, 9H), 0.13 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 126.5, 122.1, 119.5, 119.3, 116.7, 111.1, 58.3, 26.1, 18.5, −5.1.

***R*$_f$** = 0.52 (petroleum ether/EtOAc 5:1)

The spectroscopic data is in agreement with the literature.[10]

Compound **SI-3** (*tert*-butyl (1*R*,3*r*,5*S*)-3-allyl-3-hydroxy-8-azabicyclo[3.2.1]octane-8-carboxylate)



Synthesized according to the **General procedure B** described in **Section 4.1** on 2 mmol scale from *N*-Boc-nortropinone. The product is a colorless oil (539 mg, **quantitative yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 17.5, 10.1, 7.5 Hz, 1H), 5.20 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.16–5.10 (dd, *J* = 17.5, 2.0 Hz, 1H), 4.24 (br.s, 1H), 2.15–2.07 (m, 4H), 2.06–1.95 (m, 1H), 1.93–1.81 (m, 3H), 1.61–1.56 (m, 2H), 1.46 (s, 9H).

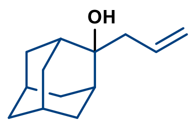
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 132.6, 120.1, 79.1, 70.5, 53.2, 52.5, 50.9, 42.7, 28.5, 28.1, 27.4.

***R*$_f$** = 0.47 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{15}H_{25}NaNO_3$ $[M + Na]^+$: 290.1726, found: 290.1727.

The spectroscopic data is in agreement with the literature.[11]

Compound **SI-4** ((1*r*,3*r*,5*r*,7*r*)-2-allyladamantan-2-ol)



Synthesized according to the **General procedure B** described in **Section 4.1** on 2 mmol scale from 2-adamantanone. The product is a colorless amorphous solid (384 mg, **quantitative yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.6, 10.2, 7.5 Hz, 1H), 5.22–5.11 (m, 2H), 2.45 (d, *J* = 7.5 Hz, 2H), 2.27–2.16 (m, 2H), 1.94–1.84 (m, 2H), 1.82 (dt, *J* = 11.6, 3.0 Hz, 2H), 1.76–1.62 (m, 7H), 1.54 (ddd, *J* = 12.6, 3.1, 1.7 Hz, 2H).

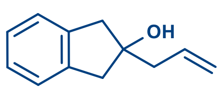
^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 118.8, 74.5, 42.7, 38.4, 37.1 (2 × CH_2), 34.4 (2 × CH_2), 32.9 (2 × CH_2), 27.4, 27.3.

***R*$_f$** = 0.43 (petroleum ether/EtOAc 10:1)

HRMS (EI): calcd for $C_{13}H_{18}$ $[M – OH]^+$: 175.1482, found: 175.1480.

The spectroscopic data is in agreement with the literature.[11]

Compound **SI-5** (2-allyl-2,3-dihydro-1*H*-inden-2-ol)



Synthesized according to the **General procedure B** described in **Section 4.1** on 2 mmol scale from 2-indenone. The crude product was purified by column chromatography using *n*-hexane/EtOAc 20:1 ⟶ 5:1 as eluent. The product is a colorless amorphous solid (263 mg, **76% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.12 (m, 4H), 6.04–5.89 (m, 1H), 5.27–5.16 (m, 2H), 3.09 (d, *J* = 16.2 Hz, 2H), 2.96 (d, *J* = 16.2 Hz, 2H), 2.52 (dt, *J* = 7.4, 1.2 Hz, 2H), 1.90 (s, 1H).

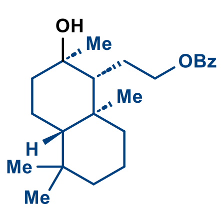
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 133.9, 126.6, 125.0, 119.1, 81.5, 46.5, 45.0.

***R*$_f$** = 0.44 (petroleum ether/EtOAc 4:1, brown color upon treatment with 5% H_3PO_4 in MeOH and heating)

HRMS (ESI): calcd for $C_{12}H_{11}$ $[M – OH]^+$: 155.0861, found: 155.0854.

The spectroscopic data is in agreement with the literature.[12]

Compound **1d** (2-((1*R*,2*R*,4a*S*,8a*S*)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl benzoate)



Synthesized according to the procedure described in **Section 4.1**.

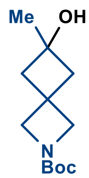
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–7.90 (m, 2H), 7.61–7.49 (m, 1H), 7.44 (dd~t, *J* = 7.8 Hz, 2H), 4.38 (qdd, *J* = 10.5, 8.5, 6.5 Hz, 2H), 1.96–1.84 (m, 2H), 1.84–1.76 (m, 1H), 1.76–1.71 (m, 1H), 1.68 (dq, *J* = 13.8, 3.3 Hz, 1H), 1.60 (dt, *J* = 13.7, 3.5 Hz, 1H), 1.49–1.34 (m, 3H), 1.35–1.22 (m, 1H), 1.22–1.18 (m, 3H), 1.20–1.07 (m, 2H), 0.96 (ddd, *J* = 14.9, 12.7, 3.2 Hz, 2H), 0.87 (s, 3H), 0.82 (s, 3H), 0.80 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 166.8, 132.8, 130.5, 129.5, 128.4, 73.7, 67.1, 58.1, 56.1, 44.5, 41.9, 39.7, 38.8, 33.4, 33.3, 24.6, 24.0, 21.5, 20.5, 18.4, 15.4.

***R*f** = 0.59 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{23}H_{34}NaO_3$ $[M + Na]^+$: 381.2400, found: 381.2401.

Compound **1i** (*tert*-butyl 6-hydroxy-6-methyl-2-azaspiro[3.3]heptane-2-carboxylate)



Synthesized according to the **General procedure A** described in **Section 4.1** on 4 mmol scale from *tert*-butyl 6-oxo-2-azaspiro[3.3]heptane-2-carboxylate. The crude product was purified by column chromatography using *n*-hexane/EtOAc 5:1 → 1:1 as eluent. The product is a white solid (662 mg, **73% yield**).

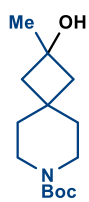
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 3.92 (s, 2H), 3.89 (s, 2H), 2.20–2.31 (m, 4H), 1.43 (s, 9H), 1.32 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 156.1, 79.3, 68.8, 48.3, 28.5, 28.4, 28.0.

***R*f** = 0.24 (hexanes/EtOAc 1:1)

HRMS (ESI): calcd for $C_{12}H_{21}NaNO_3$ $[M + Na]^+$: 250.1423, found: 250.1423.

Compound **1j** (*tert*-butyl 2-hydroxy-2-methyl-7-azaspiro[3.5]nonane-7-carboxylate)



Synthesized according to the **General procedure A** described in **Section 4.1** on 4 mmol scale from 2-oxo-7-azaspiro[3.5]nonane-7-carboxylate *tert*-butyl ester. The crude product was purified by column chromatography using *n*-hexane/EtOAc 5:1 → 2:1 as eluent. The product is a white solid (470 mg, **46% yield**).

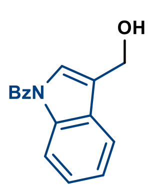
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 3.35–3.23 (m, 4H), 2.00–1.85 (m, 4H), 1.64–1.59 (m, 2H), 1.52–1.47 (m, 2H), 1.44 (s, 9H), 1.39 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 155.0, 79.3, 68.9, 46.9, 40.8, 40.6, 39.0, 37.3, 31.0, 28.5, 28.2.

***R*f** = 0.43 (hexanes/EtOAc 1:1)

HRMS (ESI): calcd for $C_{14}H_{25}NaNO_3$ $[M + Na]^+$: 278.1721, found: 278.1712.

Compound **1l** ((3-(hydroxymethyl)-1*H*-indol-1-yl)(phenyl)methanone)



Synthesized according to the procedure described in **Section 4.1**.

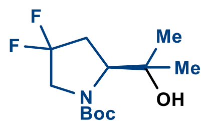
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.2 Hz, 1H), 7.78–7.71 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.62 (tt, *J* = 6.8, 1.2 Hz, 2H), 7.57–7.51 (m, 2H), 7.42 (td, *J* = 8.3, 7.8, 1.2 Hz, 1H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 (s, 1H), 4.85 (s, 2H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.6, 136.7, 134.5, 131.9, 129.5, 129.1, 128.6, 125.4, 125.2, 124.0, 121.7, 119.3, 116.7, 57.2.

R_f = 0.67 (petroleum ether/EtOAc 1:1)

HRMS (ESI): calcd for $C_{16}H_{13}NO_2$ $[M + Na]^+$: 274.0839, found: 274.0838.

Compound **1p** (*tert*-butyl (S)-4,4-difluoro-2-(2-hydroxypropan-2-yl)pyrrolidine-1-carboxylate)



Synthesized according to the **General procedure A** described in **Section 4.1**, using MeMgBr instead of MeLi, on 2 mmol scale from 1-*tert*-butyl 2-methyl (2*S*)-4,4-difluoro-1,2-pyrrolidinedicarboxylate. The crude product was purified by column chromatography using *n*-hexane/EtOAc 5:1 → 2:1 as eluent. The product is a white solid (318 mg, **60% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (t, *J* = 8.4 Hz, 1H), 4.07 – 3.92 (m, 1H), 3.49 (ddd, *J* = 24.6, 12.3, 5.9 Hz, 1H), 2.49 (dddt, *J* = 17.2, 13.9, 8.7, 2.5 Hz, 1H), 2.12 (br.s, 1H), 1.47 (s, 9H), 1.17 (s, 3H), 1.14 (s, 3H).

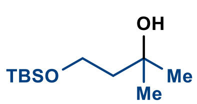
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8z, 81.8, 73.2 (br)z, 65.4 (br), 54.3 (t, *J* = 31.0 Hz), 36.9 (t, *J* = 24.7 Hz), 28.2, 27.2, 23.1 (br).

^{19}F NMR (377 MHz, $CDCl_3$) δ -97.9 (d, *J* = 230.3 Hz), -107.0 (d, *J* = 230.4 Hz).

R_f = 0.41 (hexanes/EtOAc 3:1)

HRMS (ESI): calcd for $C_{12}H_{21}NaF2NO_3$ $[M + Na]^+$: 288.1392, found: 288.1394.

Compound **1r** (4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-ol)



Synthesized according to the procedure described in **Section 4.1**.

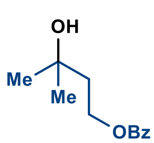
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91 (t, *J* = 5.7 Hz, 2H, OCH_2), 3.83 (s, 1H, OH), 1.70 (t, *J* = 5.7 Hz, 2H, CH_2), 1.24 (s, 6H, $C(CH_3)_2$), 0.90 (s, 9H $C(CH_3)_3$), 0.09 (s, 6H, $Si(CH_3)_2$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 70.8, 61.0, 42.9, 29.2, 25.8, 18.0, −5.6.

R_f = 0.49 (petroleum ether/EtOAc 6:1, yellow color upon treatment with $KMnO_4$ stain and heating)

The spectroscopic data is in agreement with the literature.[13]

Compound **1s** (4-(benzoyloxy)-2-methylbutan-2-ol)



Synthesized according to the procedure described in **Section 4.1**.

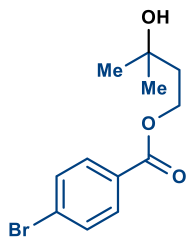
H NMR (500 MHz, $CDCl_3$) δ 8.13–8.00 (m, 2H), 7.56 (tt, *J* = 7.8, 1.3 Hz, 1H), 7.44 (dd, *J* = 8.4, 7.2 Hz, 2H), 4.51 (t, *J* = 6.8 Hz, 2H), 1.99 (t, *J* = 6.8 Hz, 2H), 1.33 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 132.9, 130.2, 129.5, 128.4, 70.1, 61.9, 41.7, 29.8.

R_f = 0.30 (petroleum ether/EtOAc 4:1)

The spectroscopic data is in agreement with the literature.[14]

Compound **1t** (3-hydroxy-3-methylbutyl 4-bromobenzoate)



Synthesized according to the procedure described in **Section 4.1**.

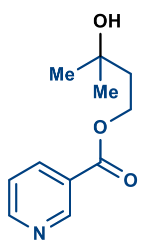
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.84 (m, 2H), 7.64–7.53 (m, 2H), 4.50 (t, *J* = 6.8 Hz, 2H), 1.98 (t, *J* = 6.8 Hz, 2H), 1.32 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 131.7, 131.0, 129.1, 128.1, 70.0, 62.2, 41.7, 29.8.

***R*$_f$** = 0.55 (CH_2Cl_2/MeOH 20:1)

The spectroscopic data is in agreement with the literature.[15]

Compound **1u** (4-(nicotynoyloxy)-2-methylbutan-2-ol)



Synthesized according to the procedure described in **Section 4.1**.

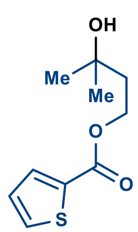
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.86–8.72 (m, 1H), 8.29 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.40 (dd, *J* = 7.8, 4.9 Hz, 1H), 4.54 (t, *J* = 6.9 Hz, 2H), 2.00 (t, *J* = 6.9 Hz, 2H), 1.33 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 153.4, 150.9, 137.0, 126.2, 123.3, 70.0, 62.3, 41.7, 29.9.

***R*$_f$** = 0.43 (CH_2Cl_2/MeOH 5:1)

HRMS (ESI): calcd for $C_{11}H_{16}NO_3$ $[M + H]^+$: 210.1125, found: 210.1124.

Compound **1v** (4-(2-thiophenecarboxy)-2-methylbutan-2-ol)



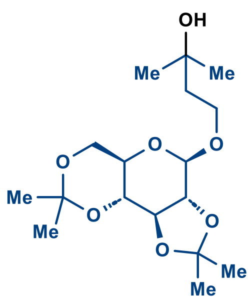
Synthesized according to the procedure described in **Section 4.1**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.48 (t, *J* = 6.7 Hz, 2H), 1.96 (t, *J* = 6.7 Hz, 2H), 1.32 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 133.8, 133.4, 132.3, 127.8, 70.1, 62.1, 41.7, 29.8.

***R*$_f$** = 0.49 (CH_2Cl_2/MeOH 5:1)

Compound **1w** (1-(2:3,4:6-diacetone β-D-glucopyranosyloxy) 3-hydroxy-3-methylbutane)



Synthesized according to the procedure described in **Section 4.1**.

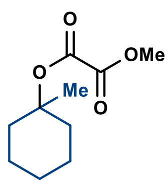
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (d, J = 7.9 Hz, 1H), 4.11 (ddd, J = 9.7, 7.3, 6.1 Hz, 1H), 3.96 (dd, J = 10.8, 5.3 Hz, 1H), 3.94–3.85 (m, 2H), 3.82 (dt, J = 9.8, 6.3 Hz, 1H), 3.64 (t, J = 9.3 Hz, 1H), 3.38 (dd, J = 9.0, 7.9 Hz, 1H), 3.27 (ddd, J = 10.2, 8.8, 5.3 Hz, 1H), 1.99–1.74 (m, 2H), 1.54 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.44 (s, 3H), 1.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 112.2, 102.2, 99.8, 77.8, 77.5, 72.7, 70.2, 69.8, 66.9, 62.2, 41.8, 29.7, 29.4, 28.9, 26.7, 26.4, 19.1.

***R*$_f$** = 0.38 (petroleum ether/EtOAc 4:1)

HRMS (ESI): calcd for $C_{17}H_{30}NaO_7$ $[M + Na]^+$: 369.1884, found: 369.1894.

Compound **2a** (methyl (1-methylcyclohexyl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 5 mmol scale from 1-methyl-cyclohexan-1-ol with 5 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 5:1 as eluent. The product is a colorless oil (940 mg, **94% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 1H), 2.24–2.08 (m, 2H), 1.52 (s, 3H), 1.60–1.39 (m, 7H), 1.33–1.19 (m, 1H).

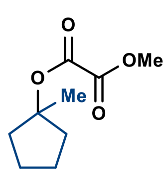
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 156.6, 86.7, 53.1, 36.2, 25.1, 24.9, 21.9.

***R*$_f$** = 0.50 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{10}H_{16}NaO_4$ $[M + Na]^+$: 223.0941, found: 223.0943.

The spectroscopic data is in agreement with the literature.[16]

Compound **2b** (methyl (1-methylcyclopentyl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 2 mmol scale from 1-methyl-cyclopentan-1-ol with 2 h reaction time. The crude product was purified by column chromatography using hexane/EtOAc 7:1 as eluent. The product is a colorless oil (542 mg, **97% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 6H), 2.28–2.12 (m, 2H), 1.85–1.71 (m, 4H), 1.70–1.64 (m, 2H), 1.63 (s, 3H).

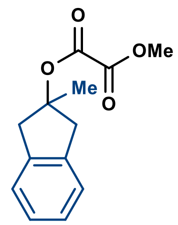
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 157.0, 94.3, 53.3, 38.8, 23.9, 23.7.

***R*$_f$** = 0.55 (hexane/EtOAc 7:1)

HRMS (ESI): calcd for $C_9H_{14}NaO_4$ $[M + Na]^+$: 209.0784, found: 209.0784.

The spectroscopic data is in agreement with the literature.[16]

Compound **2c** (methyl (2-methyl-2,3-dihydro-1*H*-inden-2-yl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 2.1 mmol scale from 2-methyl-2,3-dihydro-1*H*-inden-2-ol with 20 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 6:1 as eluent. The product is a white solid (446 mg, **91% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.16 (m, 4H), 3.87 (s, 3H), 3.51 (d, J = 16.6 Hz, 2H), 3.25 (d, J = 16.5 Hz, 2H), 1.74 (s, 3H).

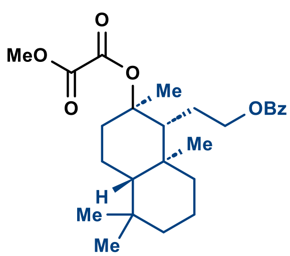
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 157.0, 139.7, 126.9, 124.6, 92.1, 53.4, 45.7, 24.1.

***R*$_f$** = 0.49 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_9H_{16}NaO_4$ $[M + Na]^+$: 257.0784, found: 257.0785.

The spectroscopic data is in agreement with the literature.[17]

Compound **2d** ((1*R*,2*R*,4a*S*,8a*S*)-1-(2-(benzoyloxy)ethyl)-2,5,5,8a-tetramethyldecahydronaphthalen-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.4 mmol scale from benzoylated sclareol glycol **1d** with 2 h reaction time. The product is a colorless oil (444 mg, **70% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18–7.94 (m, 2H), 7.63–7.49 (m, 1H), 7.44 (dd~t, J = 7.7 Hz, 2H), 4.51 (dt, J = 10.4, 7.7 Hz, 1H), 4.38 (dt, J = 10.4, 8.1 Hz, 1H), 3.83 (s, 3H), 2.84 (dt, J = 12.3, 3.9 Hz, 1H), 1.88 (td, J = 8.1, 4.4 Hz, 2H), 1.81 (d, J = 12.8 Hz, 1H), 1.73 (td, J = 13.1, 12.4, 4.4 Hz, 2H), 1.64 (s, 3H), 1.67–1.56 (m, 2H), 1.46 (dt, J = 14.4, 3.7 Hz, 1H), 1.39 (d, J = 13.3 Hz, 1H), 1.37–1.23 (m, 1H), 1.16 (td, J = 13.5, 4.3 Hz, 1H), 1.07–0.96 (m, 2H), 0.88 (s, 3H), 0.87 (s, 3H), 0.80 (s, 3H).

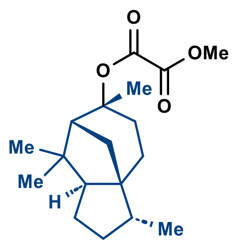
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 158.8, 155.9, 132.8, 130.5, 129.5, 128.3, 92.2, 66.1, 55.6, 55.3, 53.3, 41.7, 39.4, 39.2, 38.7, 33.3, 33.2, 25.0, 21.4, 19.90, 19.92, 18.3, 15.6.

***R*$_f$** = 0.54 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{26}H_{36}NaO_6$ $[M + Na]^+$: 467.2404, found: 467.2405.

The spectroscopic data is in agreement with the literature.[18]

Compound **2e** (methyl ((3*R*,3a*S*,6*R*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 5 mmol scale from cedrol with 1 h reaction time. The product is a white solid (1.411 g, **96% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 2.51–2.42 (m, 1H), 2.20–2.13 (m, 1H), 2.07 (td, *J* = 13.0, 6.8 Hz, 1H), 1.88 (dq, *J* = 12.1, 6.0 Hz, 1H), 1.83 (t, *J* = 8.0 Hz, 1H), 1.75–1.65 (m, 2H), 1.62 (d, *J* = 1.0 Hz, 3H), 1.56 (s, 3H), 1.56–1.51 (m, 1H), 1.51–1.47 (m, 1H), 1.46–1.34 (m, 3H), 1.33–1.24 (m, 1H), 1.17 (s, 3H), 0.99 (s, 3H), 0.84 (d, *J* = 7.1 Hz, 3H).

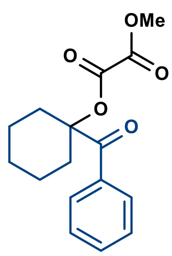
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 156.5, 91.1, 56.7, 56.6, 53.8, 53.1, 43.4, 41.1, 41.0, 36.8, 32.8, 31.2, 28.3, 26.9, 25.3, 25.2, 15.4.

***R*$_f$** = 0.74 (petroleum ether/EtOAc 3:1)

HRMS (ESI): calcd for $C_{18}H_{28}NaO_4$ $[M + Na]^+$: 331.1880, found: 331.1879.

The spectroscopic data is in agreement with the literature.[19]

Compound **2f** (1-benzoylcyclohexyl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.5 mmol scale from (1-hydroxycyclohexyl)(phenyl)methanone with 1 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 5:1 as eluent. The product is a colorless oil (433 mg, **99% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.54–7.46 (m, 1H), 7.40 (dd, *J* = 8.4, 7.2 Hz, 2H), 3.85 (s, 3H), 2.48–2.43 (m, 2H), 2.02 (ddd, *J* = 15.3, 9.1, 3.0 Hz, 2H), 1.83–1.62 (m, 5H), 1.45–1.31 (m, 1H).

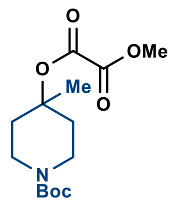
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 157.8, 156.2, 134.1, 132.8, 128.6, 128.5, 89.5, 53.5, 32.3, 24.9, 21.2.

***R*$_f$** = 0.46 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{16}H_{18}NaO_5$ $[M + Na]^+$: 313.1046, found: 313.1050.

The spectroscopic data is in agreement with the literature.[18]

Compound **2g** (1-(*tert*-butoxycarbonyl)-4-methylpiperidin-4-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 2.45 mmol scale from tert-butyl 4-hydroxy-4-methylpiperidine-1-carboxylate with 1.5 h reaction time. The crude product was purified by column chromatography using hexane/EtOAc 3:1 as eluent. The product is a white solid (451 mg, **77% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.80 (br. s, 1H), 3.09 (t, *J* = 12.4 Hz, 2H), 2.41–2.20 (m, 2H), 1.70–1.55 (m, 3H), 1.58 (s, 3H), 1.45 (s, 9H).

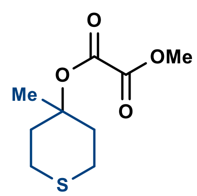
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 156.6, 154.7, 84.0, 79.7, 53.4, 35.5, 28.4, 24.7.

***R*$_f$** = 0.39 (hexane/EtOAc 3:1)

HRMS (ESI): calcd for $C_{14}H_{23}NaNO_6$ $[M + Na]^+$: 324.1418, found: 324.1418.

The spectroscopic data is in agreement with the literature.[20]

Compound **2h** (methyl (4-methyltetrahydro-2*H*-thiopyran-4-yl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 2 mmol scale from 4-methyltetrahydro-2*H*-thiopyran-4-ol with 15 min reaction time. The crude product was purified by column chromatography using hexanes/EtOAc 5:1 → 3:1 as eluent. The product is a colorless oil (432 mg, **99% yield**).

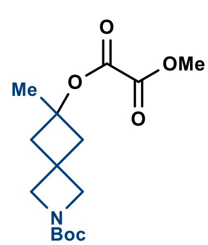
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 2.87 (t, *J* = 12.5 Hz, 2H), 2.58 (dt, *J* = 15.5, 3.2 Hz, 2H), 2.50–2.40 (m, 2H), 1.78 (ddd, *J* = 14.9, 12.0, 3.6 Hz, 2H), 1.57 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 156.4, 84.3, 53.4, 37.1, 25.9, 23.8.

***R*$_f$** = 0.50 (hexane/EtOAc 4:1)

HRMS (ESI): calcd for $C_9H_{14}NaO_4S$ $[M + Na]^+$: 241.0525, found: 241.0525.

Compound **2i** (2-(*tert*-butoxycarbonyl)-6-methyl-2-azaspiro[3.3]heptan-6-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 4 mmol scale from *tert*-butyl 6-hydroxy-6-methyl-2-azaspiro[3.3]heptane-2-carboxylate **1i** with 1 h reaction time. The crude product was purified by column chromatography using hexanes/EtOAc 3:1 → 2:1 as eluent. The product is a colorless oil (1.0 g, **99% yield**).

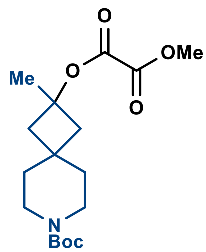
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (s, 2H), 3.93 (s, 2H), 3.88 (s, 3H), 2.63 – 2.54 (m, 2H), 2.53 – 2.44 (m, 2H), 1.55 (s, 3H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 156.2, 156.1, 80.1, 78.7, 61.4, 60.1, 53.9, 53.5, 46.0, 30.3, 28.4, 23.6.

R_f = 0.45 (hexane/EtOAc 2:1)

HRMS (ESI): calcd for $C_{15}H_{23}NaNO_6$ $[M + Na]^+$: 336.1426, found: 336.1425.

Compound **2j** (2-(*tert*-butoxycarbonyl)-6-methyl-2-azaspiro[3.3]heptan-6-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.5 mmol scale from *tert*-butyl 2-hydroxy-2-methyl-7-azaspiro[3.5]nonane-7-carboxylate **1j** with 1 h reaction time. The crude product was purified by column chromatography using hexanes/EtOAc 3:1 → 2:1 as eluent. The product is a colorless oil (395 mg, **78% yield**).

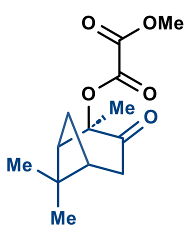
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 3H), 3.31 (ddd, *J* = 11.5, 5.6, 3.5 Hz, 4H), 2.36–2.24 (m, 2H), 2.22–2.12 (m, 2H), 1.64 (s, 3H), 1.61–1.52 (m, 4H), 1.44 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 156.3, 154.8, 80.4, 79.4, 53.5, 44.7, 40.7, 40.5, 38.9, 36.8, 30.2, 28.4, 26.1.

R_f = 0.59 (hexane/EtOAc 2:1)

HRMS (ESI): calcd for $C_{17}H_{27}NaNO_6$ $[M + Na]^+$: 364.1741, found: 364.1749.

Compound **2k** ((1*R*,2*R*,5*R*)-(+)-2-hydroxy-3-pinanone methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.5 mmol scale from (1*R*,2*R*,5*R*)-(+)-2-hydroxy-3-pinanone with 20 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 4:1 → 3:1 as eluent. The product is a colorless oil (380 mg, **99% yield**).

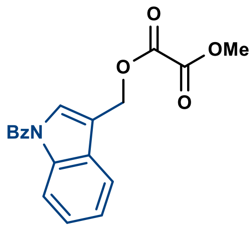
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.01 (dd~t, *J* = 6.1 Hz, 1H), 2.81 (dd, *J* = 19.2, 2.5 Hz, 1H), 2.70 (dt, *J* = 19.2, 3.2 Hz, 1H), 2.47 (dtd, *J* = 11.3, 6.1, 2.9 Hz, 1H), 2.17 (tt, *J* = 6.1, 2.9 Hz, 1H), 1.69 (s, 3H), 1.63–1.50 (m, 1H), 1.39 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.7, 158.2, 156.1, 89.7, 53.4, 48.4, 43.2, 39.4, 38.1, 27.8, 27.3, 22.5, 20.8.

R_f = 0.73 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{13}H_{18}NaO_5$ $[M + Na]^+$: 277.1046, found: 277.1050.

Compound **2l** ((1-benzoyl-1*H*-indol-3-yl)methyl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1 mmol scale from alcohol **1l** with 30 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:1 as eluent. The product is a white solid (337 mg, **quantitative yield**).

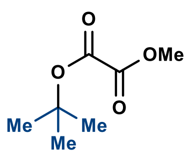
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.2 Hz, 1H), 7.76–7.70 (m, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.64 (tt, *J* = 6.8, 1.1 Hz, 1H), 7.59–7.51 (m, 2H), 7.46 (s, 1H), 7.44 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H), 5.46 (s, 3H), 3.87 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 157.8, 157.5, 136.4, 134.0, 132.2, 129.2, 129.2, 128.7, 128.4, 125.7, 124.3, 119.1, 116.6, 115.0, 60.2, 53.6.

***R*$_f$** = 0.73 (petroleum ether/EtOAc 5:1, brown color upon treatment with 5% H_3PO_4 in MeOH and heating)

HRMS (ESI): calcd for $C_{19}H_{15}NaNO_5$ $[M + Na]^+$: 360.0842, found: 360.0843.

Compound **2m** (*tert*-butyl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 3 mmol scale from *tert*-butanol with 3 h reaction time. The crude product was purified by column chromatography using hexane/EtOAc 3:1 as eluent. The product is a colorless oil (501 mg, **69% yield**).

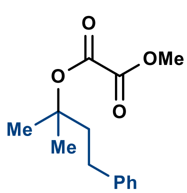
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 156.7, 84.9, 53.1, 27.6.

***R*$_f$** = 0.36 (petroleum ether/EtOAc 3:1).

The spectroscopic data is in agreement with the literature.[16]

Compound **2n** (methyl (2-methyl-4-phenylbutan-2-yl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 2 mmol scale from 2-methyl-4-phenylbutan-2-ol with 1 h reaction time. The crude product was purified by column chromatography using hexane/EtOAc 4:1 as eluent. The product is a colorless oil (725 mg, **97% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.22–7.16 (m, 3H), 3.87 (s, 3H), 2.78–2.64 (m, 2H), 2.22–2.11 (m, 2H), 1.61 (s, 6H).

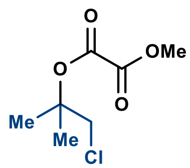
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 156.7, 141.5, 128.4, 128.3, 125.9, 86.8, 53.3, 42.4, 30.2, 25.7.

***R*$_f$** = 0.58 (petroleum ether/EtOAc 3:1)

HRMS (ESI): calcd for $C_{14}H_{18}NaO_4$ $[M + Na]^+$: 273.1098, found: 273.1095.

The spectroscopic data is in agreement with the literature.[21]

Compound **2o** (1-chloro-2-methylpropan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1 mmol scale from 1-chloro-2-methyl-2-propanol with 1 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 5:1 as eluent. The product is a colorless oil (151 mg, **78% yield**).

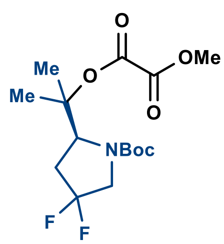
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.84 (s, 2H), 1.63 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 156.3, 84.4, 53.5, 49.8, 24.0.

***R*$_f$** = 0.43 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_7H_{11}ClNaO_4$ $[M + Na]^+$: 217.0238, found: 217.0241.

Compound **2p** ((*S*)-2-(1-(*tert*-butoxycarbonyl)-4,4-difluoropyrrolidin-2-yl)propan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1 mmol scale from *tert*-butyl (*S*)-4,4-difluoro-2-(2-hydroxypropan-2-yl)pyrrolidine-1-carboxylate **1p** with 1 h reaction time. The crude product was purified by column chromatography using hexanes/EtOAc 5:1 → 2:1 as eluent. The product is a colorless oil (395 mg, **78% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 – 4.00 (m, 1H), 3.87 (s, 3H), 3.73 – 3.58 (m, 1H), 2.70 – 2.28 (m, 2H), 1.63 (s, 3H), 1.55 (s, 3H), 1.47 (s, 9H).

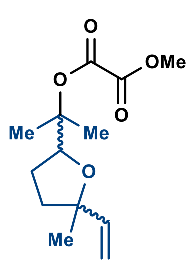
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 155.9, 155.4, 128.1 (t, J = 250.6 Hz), 88.7, 81.0, 62.6, 54.3 (t, J = 32.1 Hz), 53.4, 35.6 (t, J = 23.8 Hz), 28.2, 22.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -93.7 (d, *J* = 228.2 Hz), -104.8 (d, *J* = 228.3 Hz).

***R*$_f$** = 0.52 (hexane/EtOAc 3:1)

HRMS (ESI): calcd for $C_{15}H_{23}NaF_2NO_6$ $[M + Na]^+$: 374.1397, found: 374.1411.

Compound **2q** (methyl (2-(5-methyl-5-vinyltetrahydrofuran-2-yl)propan-2-yl) oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.5 mmol scale from linalool oxide (45:55 mixture of *cis*/*trans*-diastereomers) with 1 h reaction time. The crude product was purified by column chromatography using petroleum PhMe/EtOAc 10:1 as eluent. The product is a colorless oil (385 mg, **99% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (dd, *J* = 17.4, 10.8 Hz, 1H, *cis*), 5.79 (dd, *J* = 17.2, 10.6 Hz, 1H, *trans*), 5.14 (dd, *J* = 17.4, 1.3 Hz, 1H, *cis*), 5.12 (dd, *J* = 17.2, 1.5 Hz, 1H, *trans*), 4.94 (dd, *J* = 7.0, 1.4 Hz, 1H, *trans*), 4.92 (dd, *J* = 7.2, 1.4 Hz, 1H, *cis*), 4.09–4.02 (m, 1H, *cis*), 4.00 (dd, *J* = 7.4, 6.2 Hz, 1H, *trans*), 3.79 (s, 3H, OMe, *trans*), 3.79 (s, 3H, OMe, *cis*), 2.02–1.63 (m, 8H, *cis* + *trans*), 1.524 (s, 3H, *trans*), 1.517 (s, 3H, *cis*), 1.493 (s, 3H, *cis*), 1.487 (s, 3H, *trans*), 1.28 (s, 3H, *trans*), 1.25 (s, 3H, *cis*).

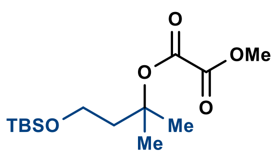
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 158.75 (*trans*), 158.73 (*cis*), 156.65 (*cis*), 156.58 (*trans*), 143.93 (*cis*), 143.50 (*trans*), 111.53 (*cis*), 111.43 (*trans*), 87.36 (*trans*), 87.30 (*cis*), 83.78 (*trans*), 83.75 (*cis*), 83.66 (*trans*), 83.43 (*cis*), 53.25 (*trans*), 53.22 (*cis*), 37.58 (*cis*), 36.89 (*trans*), 26.71 (*cis*), 26.47 (*trans*), 26.43 (*trans*), 25.62 (*cis*), 22.41 (*cis*), 22.27 (*trans*), 21.47 (*trans*), 21.33 (*cis*).

$\boldsymbol{R_f}$ = 0.57, 0.64 (PhMe/EtOAc 10:1)

HRMS (ESI): calcd for $C_{13}H_{20}NaO_5$ $[M + Na]^+$: 279.1203, found: 279.1204.

The spectroscopic data is in agreement with the literature.[16]

Compound **2r** (4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 5.8 mmol scale from alcohol **1r** with 1 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 1:1 as eluent. The product is a colorless oil (1.77 g, **quantitative yield**).

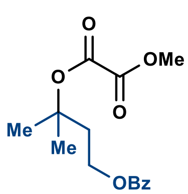
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.75 (t, *J* = 6.7 Hz, 2H), 2.10 (t, *J* = 6.7 Hz, 2H), 1.57 (s, 3H), 1.56 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 158.9, 156.7, 86.5, 58.9, 53.2, 42.8, 26.2, 25.9, 18.2, −5.5.

$\boldsymbol{R_f}$ = 0.66 (petroleum ether/EtOAc 5:1, visualized by treatment with basic $KMnO_4$ and heating)

HRMS (ESI): calcd for $C_{14}H_{28}NaO_5Si$ $[M + Na]^+$: 327.1598, found: 327.16025.

Compound **2s** (4-(benzoyloxy)-2-methylbutan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 7.54 mmol scale from alcohol **1s** with 1 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 1:1 as eluent. The product is a yellowish oil (2.19 g, **99% yield**).

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.08–7.92 (m, 2H), 7.63–7.50 (m, 1H), 7.44 (dd~t, *J* = 7.8 Hz, 2H), 4.48 (t, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 2.36 (t, *J* = 6.6 Hz, 2H), 1.65 (s, 6H).

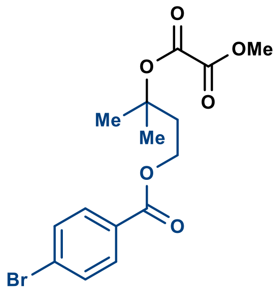
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 166.4, 158.6, 156.6, 133.0, 130.1, 129.5, 128.4, 85.4, 60.8, 53.2, 38.9, 26.1.

$\boldsymbol{R_f}$ = 0.32 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{15}H_{18}NaO_6$ $[M + Na]^+$: 317.0996, found: 317.0998.

The spectroscopic data is in agreement with the literature.[22]

Compound **2t** (4-(4-bromobenzoyloxy)-2-methylbutan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.5 mmol scale from alcohol **1t** with 30 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 3:1 as eluent. The product is a colorless oil (545 mg, **97% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.80 (m, 2H), 7.65–7.49 (m, 2H), 4.46 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 2.35 (t, *J* = 6.6 Hz, 2H), 1.64 (s, 6H).

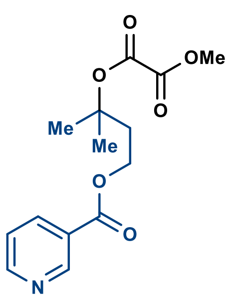
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 158.6, 156.6, 131.7, 131.1, 128.9, 128.1, 85.3, 61.0, 53.3, 38.8, 26.1.

***R*$_f$** = 0.65 (petroleum ether/EtOAc 3:1)

HRMS (ESI): calcd for $C_{15}H_{17}BrNaO_6$ $[M + Na]^+$: 395.0101, found: 395.0102.

The spectroscopic data is in agreement with the literature.[23]

Compound **2u** (4-(nicotinoyloxy)-2-methylbutan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.4 mmol scale from alcohol **1u** with 2 h reaction time. The crude product was purified by column chromatography using CH_2Cl_2/MeOH 20:1 → 5:1 as eluent. The product is a yellowish oil (410 mg, **99% yield**).

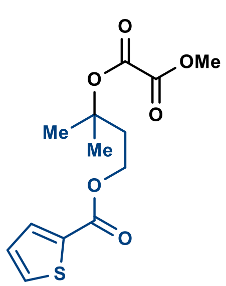
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.65 (d, *J* = 3.9 Hz, 1H), 8.14 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.26 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.38 (t, *J* = 6.7 Hz, 2H), 3.68 (s, 3H), 2.24 (t, *J* = 6.7 Hz, 2H), 1.52 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 158.6, 156.6, 153.5, 150.9, 137.0, 125.9, 123.3, 85.2, 61.2, 53.3, 38.9, 26.1.

***R*$_f$** = 0.36 (petroleum ether/EtOAc 1:1); 0.49 (CH_2Cl_2/MeOH 10:1)

HRMS (ESI): calcd for $C_{14}H_{17}NaNO_6$ $[M + Na]^+$: 318.0948, found: 318.0953.

Compound **2v** (4-(2-thiophenecarboxy)-2-methylbutan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 0.79 mmol scale from alcohol **1v** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:1 as eluent. The product is a yellowish oil (235 mg, **quantitative yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.50 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.38 (t, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 2.27 (t, *J* = 6.6 Hz, 2H), 1.58 (s, 6H).

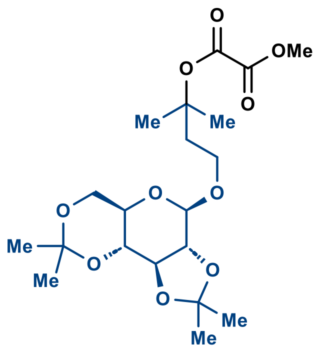
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 158.6, 156.6, 133.6, 133.5, 132.5, 127.8, 85.4, 60.9, 53.3, 39.0, 26.0.

***R*$_f$** = 0.67 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{13}H_{16}NaO_6S$ $[M + Na]^+$: 323.0560, found: 323.0563.

The spectroscopic data is in agreement with the literature.[23]

Compound **2w** (2:3,4:5-diacetylidene-β-D-glucopyranosyloxy)-2-methylbutan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 0.43 mmol scale from alcohol **1w** with 1 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:1 as eluent. The product is a white solid (186 mg, **quantitative yield**).

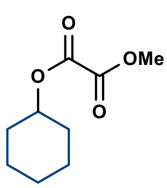
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (d, J = 7.7 Hz, 1H), 4.03 (dt, J = 10.0, 6.7 Hz, 1H), 3.87 (s, 3H), 3.91–3.86 (m, 2H, overlapping with CH_3 peak) 3.68 (dt, J = 10.0, 6.7 Hz, 1H), 3.60 (dd~t, J = 9.0 Hz, 1H), 3.54 (dd~t, J = 9.0 Hz, 1H), 3.40–3.28 (m, 2H), 2.27 (dt, J = 14.0, 6.8 Hz, 1H), 2.16 (dt, J = 14.0, 6.8 Hz, 1H), 1.57 (s, 6H), 1.56 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 156.7, 102.9 (C-1), 85.7 (2 × C), 76.3, 75.4, 73.4, 69.7, 65.8, 61.7, 53.5 (2 × CH_3), 39.2, 26.3 (2 × CH_3), 26.1 (2 × CH_3).

***R*$_f$** = 0.64 (petroleum ether/EtOAc 4:1)

HRMS (ESI): calcd for $C_{20}H_{32}NaO_{10}$ $[M + Na]^+$: 455.1887, found: 455.1894.

Compound **2x** (cyclohexyl methyl oxalate)



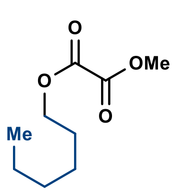
Synthesized according to the **General procedure C** described in **Section 4.1** on 2 mmol scale from cyclohexanol with 5 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 5:1 as eluent. The product is a colorless oil (341 mg, **92% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94 (td, J = 9.5, 4.7 Hz, 1H), 3.90 (s, 3H), 1.97–1.90 (m, 2H), 1.83–1.73 (m, 2H), 1.62–1.50 (m, 4H), 1.44–1.34 (m, 2H), 1.28 (tdd, J = 12.8, 9.0, 3.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 157.1, 76.4, 53.4, 31.2, 25.1, 23.6.

***R*$_f$** = 0.64 (petroleum ether/EtOAc 5:1)

Compound **2y** (*n*-hexyl methyl oxalate)



Synthesized according to the **General procedure B** described in **Section 4.1** on 2 mmol scale from *n*-hexanol with 20 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 20:1 as eluent. The product is a colorless oil (377 mg, **99% yield**).

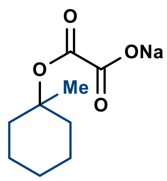
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 1.73 (p, J = 7.0 Hz, 2H), 1.45–1.24 (m, 6H), 0.97–0.70 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 157.7, 67.3, 53.5, 31.3, 28.2, 25.3, 22.5, 14.0.

R_f = 0.50 (petroleum ether/EtOAc 10:1)

HRMS (ESI): calcd for $C_9H_{16}NaO_4$ [M + Na]$^+$: 211.0941, found: 211.0942.

Compound **3a-Na** (sodium 2-(1-methyl-cyclohexyloxy)-2-oxoacetate)



Synthesized according to the **General procedure D** described in **Section 4.1** on 0.72 mmol scale from methyl oxalate **2a** with 10 min reaction time. The product is a white solid (135.2 mg, **90% yield**).

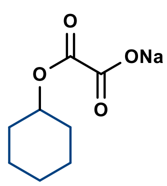
^{1}H NMR (400 MHz, DMSO) δ 2.08–1.91 (m, 2H), 1.54–1.29 (m, 7H), 1.38 (s, 3H), 1.20 (tdd, *J* = 13.8, 9.7, 5.7 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 167.1, 163.7, 79.9, 36.1, 25.3, 24.9, 21.5.

R_f = 0.00 (petroleum ether/EtOAc 10:1)

HRMS (ESI): calcd for $C_9H_{13}O_4$ [M − Na]$^-$: 185.0819, found: 185.0817.

Compound **3x-Na** (sodium 2-(cyclohexyloxy)-2-oxoacetate)



Synthesized according to the **General procedure D** described in **Section 4.1** on 1.5 mmol scale from methyl oxalate **2x** with 20 min reaction time. The product is a white solid (280 mg, **93% yield**).

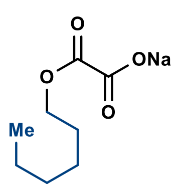
^{1}H NMR (500 MHz, DMSO) δ 4.56 (dp, *J* = 9.1, 3.9 Hz, 1H), 1.76 (dt, *J* = 8.3, 3.8 Hz, 2H), 1.66 (dq, *J* = 12.4, 4.1 Hz, 2H), 1.50 (ddd, *J* = 12.4, 6.0, 3.1 Hz, 1H), 1.41–1.26 (m, 4H), 1.21 (td, *J* = 13.4, 6.4 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 166.7, 163.0, 70.7, 50.1, 31.3, 24.9, 23.4.

R_f = 0.00 (petroleum ether/EtOAc 10:1)

HRMS (ESI): calcd for $C_8H_{11}O_4$ [M − Na]$^-$: 171.0663, found: 171.0659.

Compound **3y-Na** (sodium 2-(hexyloxy)-2-oxoacetate)



Synthesized according to the **General procedure D** described in **Section 4.1** on 1 mmol scale from methyl oxalate **2y** with 20 min reaction time. The product is a white solid (110 mg, **56% yield**).

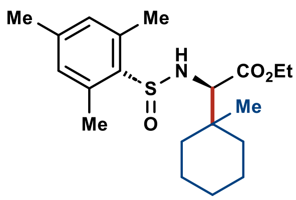
^{1}H NMR (500 MHz, DMSO) δ 3.92 (t, *J* = 6.7 Hz, 2H), 1.60–1.49 (m, 2H), 1.35–1.20 (m, 6H), 0.91–0.82 (m, 3H).

^{13}C NMR (126 MHz, DMSO) δ 166.97, 162.61, 62.62, 50.01, 30.92, 28.21, 25.11, 22.02, 13.89.

R_f = 0.00 (petroleum ether/EtOAc 10:1)

HRMS (ESI): calcd for $C_8H_{13}O_4$ [M − Na]$^-$: 173.0819, found: 173.0817.

Compound **5a** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(1-methylcyclohexyl)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2a** with 2 h reaction time. The crude product was purified by column chromatography using hexane/EtOAc/CH_2Cl_2 8:1:1 as eluent. The product is a brownish oil (98.7 mg, **90% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.55–4.01 (m, 2H), 3.83 (d, *J* = 10.1 Hz, 0H), 2.57 (s, 6H), 2.29 (s, 3H), 1.68–1.38 (m, 7H), 1.38–1.22 (m, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 3H).

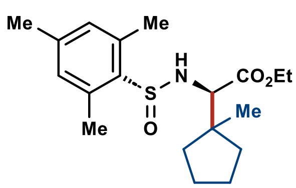
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 140.8, 138.2, 136.7, 130.7, 61.2, 37.6, 34.8, 34.7, 25.9, 21.6, 21.5, 21.0, 20.6, 19.3, 14.2.

***R*$_f$** = 0.25 (hexane/EtOAc/CH_2Cl_2 8:1:1)

HRMS (ESI): calcd for $C_{20}H_{31}NaNO_3S$ $[M + Na]^+$: 388.1917, found: 388.1923.

The spectroscopic data is in agreement with the literature.[1]

Compound **5b** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(1-methylcyclopentyl)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2b** with 2 h reaction time. The crude product was purified by column chromatography using hexane/CH_2Cl_2/EtOAc 8:1:1 as eluent. The product is a brownish oil (65 mg, **62% yield**).

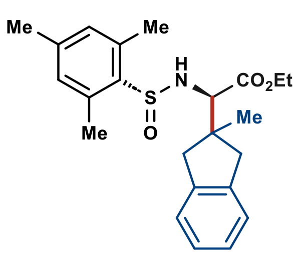
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.16 (d, *J* = 9.6 Hz, 1H), 4.44–3.93 (m, 2H), 3.74 (d, *J* = 9.6 Hz, 1H), 2.58 (s, 6H), 2.29 (s, 3H), 1.79 (dt, *J* = 12.5, 7.9 Hz, 1H), 1.73–1.57 (m, 5H), 1.42–1.31 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 140.8, 138.1, 136.8, 130.7, 65.2, 61.3, 46.6, 37.3, 36.9, 24.4, 23.8, 22.3, 21.0, 19.3, 14.2.

***R*$_f$** = 0.13 (hexane/CH_2Cl_2/EtOAc 8:1:1)

HRMS (ESI): calcd for $C_{19}H_{29}NaNO_3S$ $[M + Na]^+$: 374.1760, found: 374.1772.

Compound **5c** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(2-methyl-2,3-dihydro-1*H*-inden-2-yl)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.45 mmol scale from methyl oxalate **2b** (1.5 equiv.) with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 4:1 → 1:1 as eluent. The product is a brownish oil (31.2 mg, **21% yield**).

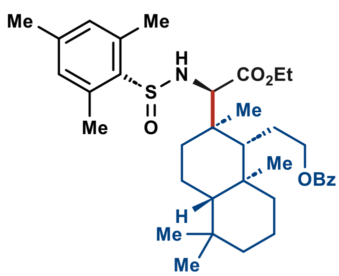
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.09 (m, 4H), 6.88 (s, 2H), 5.26 (d, *J* = 9.5 Hz, 1H), 4.19 (qd, *J* = 7.1, 1.2 Hz, 2H), 3.97 (d, *J* = 9.5 Hz, 1H), 3.24 (d, *J* = 15.8 Hz, 1H), 3.13 (d, *J* = 15.8 Hz, 1H), 2.66 (d, *J* = 15.8 Hz, 1H), 2.60 (d, *J* = 15.8 Hz, 2H), 2.60 (s, 6H), 2.30 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 141.9, 141.4, 141.0, 137.9, 136.8, 130.8, 126.4, 126.4, 124.8, 124.7, 64.7, 61.7, 47.4, 44.1, 43.5, 22.8, 21.0, 19.4, 14.2.

***R*$_f$** = 0.20 (petroleum ether/EtOAc 1:1)

HRMS (ESI): calcd for $C_{23}H_{29}NaNO_3S$ $[M + Na]^+$: 422.1760, found: 422.1760.

Compound **5d** (2-((1*R*,2*R*,4a*S*,8a*S*)-2-((*R*)-2-ethoxy-1-(((*R*)-mesitylsulfinyl)amino)-2-oxoethyl)-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl benzoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2d** with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 4:1 → 1:1 as eluent. The product is a brownish oil (87 mg, **48% yield**).

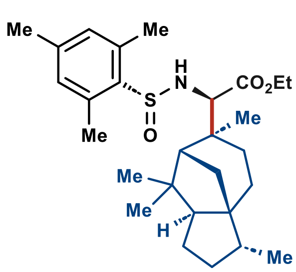
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17–8.04 (m, 2H), 7.61–7.52 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 6.86 (s, 2H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.48 (td, *J* = 10.8, 6.1 Hz, 1H), 4.41 (td, *J* = 10.7, 5.8 Hz, 1H), 4.36–4.22 (m, 2H), 3.83 (d, *J* = 10.1 Hz, 1H), 2.57 (s, 6H), 2.28 (s, 3H), 1.88–1.73 (m, 3H), 1.64–1.52 (m, 2H), 1.49–1.39 (m, 2H), 1.37 (d, *J* = 7.1 Hz, 4H), 1.31–1.18 (m, 2H), 1.17–1.07 (m, 2H), 1.04 (s, 3H), 0.94 (s, 3H), 0.91–0.85 (m, 1H), 0.83 (s, 4H), 0.78 (s, 3H), 0.70 (dd, *J* = 12.1, 2.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 166.6, 141.0, 138.1, 136.7, 132.8, 130.8, 130.5, 129.6, 128.3, 66.2, 65.6, 61.8, 56.0, 51.5, 43.2, 41.7, 40.8, 39.6, 34.1, 33.2, 33.2, 25.9, 21.6, 21.1, 19.3, 18.4, 18.3, 17.9, 16.5, 14.2.

***R*$_f$** = 0.39 (petroleum ether/EtOAc 4:1)

HRMS (ESI): calcd for $C_{36}H_{51}NaNO_5S$ $[M + Na]^+$: 632.3380, found: 632.3372.

Compound **5e** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-((3*R*,3a*S*,6*S*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2e** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 4:1 as eluent. The product is a brownish oil (30 mg, **21% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.04 (d, *J* = 9.7 Hz, 1H), 4.33 (d, *J* = 9.7 Hz, 1H), 4.28 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.15 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.58 (s, 6H), 2.29 (s, 3H), 1.98–1.86 (m, 3H), 1.75 (dd~t, *J* = 8.4 Hz, 1H), 1.71 (q, *J* = 7.1 Hz, 1H), 1.64 (ddd, *J* = 13.1, 4.8, 2.6 Hz, 1H), 1.56–1.46 (m, 2H), 1.45–1.35 (m, 3H), 1.35–1.30 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 3H), 1.01 (s, 3H), 0.89 (s, 3H), 0.88 (d, *J* = 7.1 Hz, 3H).

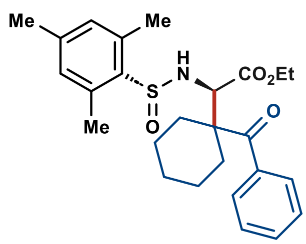
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 140.8, 138.2, 136.7, 130.8, 61.2, 61.1, 57.8, 56.8, 53.5, 45.0, 43.1, 41.7, 40.2, 37.0, 30.0, 29.9, 29.5, 29.3, 25.4, 21.0, 20.2, 19.3, 15.5, 14.1.

R_f = 0.50 (petroleum ether/EtOAc 3:1)

HRMS (ESI): calcd for $C_{28}H_{43}NaNO_3S$ $[M + Na]^+$: 469.2856, found: 496.2853.

The spectroscopic data is in agreement with the literature.[24]

Compound **5f** (ethyl (*R*)-2-(1-benzoylcyclohexyl)-2-(((*R*)-mesitylsulfinyl)amino)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2f** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 3:1 → 2:1 as eluent. The product is a brownish oil (60 mg, **44% yield**).

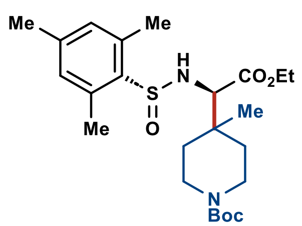
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66–7.59 (m, 2H), 7.49–7.42 (m, 1H), 7.37 (dd~t, *J* = 7.7 Hz, 2H), 6.86 (s, 1H), 5.37 (d, *J* = 9.5 Hz, 0H), 4.49 (d, *J* = 9.5 Hz, 0H), 4.20 (ABqq, *J* = 7.2, 4.1 Hz, 1H), 2.51 (s, 6H), 2.29 (s, 3H), 2.27–2.11 (m, 2H), 1.75–1.65 (m, 1H), 1.61–1.44 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.20–1.11 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.3, 171.2, 141.1, 139.7, 137.8, 136.7, 130.8, 128.1, 127.4, 62.5, 62.0, 56.4, 31.1, 30.5, 25.4, 22.5, 22.4, 21.0, 19.2, 13.9.

R_f = 0.18 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{26}H_{33}NaNO_4S$ $[M + Na]^+$: 478.2022, found: 478.2025.

Compound **5g** (*tert*-butyl 4-((*R*)-2-ethoxy-1-(((*R*)-mesitylsulfinyl)amino)-2-oxoethyl)-4-methylpiperidine-1-carboxylate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2g** with 2 h reaction time. The crude product was purified by column chromatography using hexane/CH_2Cl_2/EtOAc 8:1:1 as eluent. The product is a brownish oil (64 mg, **46% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.04 (d, *J* = 10.0 Hz, 1H), 4.31–4.12 (m, 2H), 3.77 (d, *J* = 10.0 Hz, 1H), 3.70 (br.s, 2H), 3.19–3.07 (m, 2H), 2.56 (s, 6H), 2.28 (s, 3H), 1.67 (ddd, *J* = 14.0, 10.0, 4.3 Hz, 1H), 1.55 (ddd, *J* = 14.0, 9.9, 4.8 Hz, 1H), 1.44 (s, 9H), 1.43–1.37 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.33–1.23 (m, 1H), 0.91 (s, 3H).

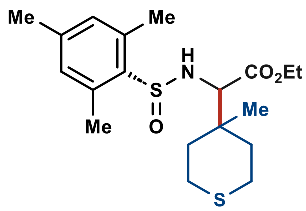
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 154.8, 141.0, 137.7, 136.7, 130.8, 79.5, 64.7, 61.5, 36.3, 33.9, 33.8, 28.4, 21.0, 19.3, 18.8, 14.1.

R_f = 0.11 (hexane/CH_2Cl_2/EtOAc 8:1:1)

HRMS (ESI): calcd for $C_{24}H_{38}NaN_2O_5S$ $[M + Na]^+$: 489.2394, found: 489.2394.

The spectroscopic data is in agreement with the literature.[1]

Compound **5h** (ethyl (2*R*,3*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3-(tetrahydro-2*H*-thiopyran-4-yl)butanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2h** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 3:1 as eluent. The product is a brownish oil (72 mg, **76% yield**).

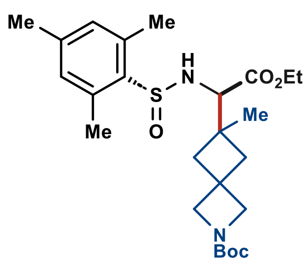
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 2H), 5.00 (d, *J* = 10.2 Hz, 1H), 4.42 – 4.15 (m, 2H), 3.81 (d, *J* = 10.2 Hz, 1H), 2.80 – 2.57 (m, 4H), 2.54 (s, 6H), 2.27 (s, 3H), 1.94 – 1.77 (m, 2H), 1.72 – 1.55 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 141.0, 137.7, 136.6, 130.8, 64.1, 61.5, 36.6, 35.3, 35.1, 23.2, 23.2, 21.0, 20.3, 19.2, 14.1.

***R*$_f$** = 0.40 (hexanes/EtOAc 3:1)

HRMS (ESI): calcd for $C_{19}H_{29}NaNO_3S_2$ $[M + Na]^+$: 406.1495, found: 406.1508.

Compound **5i** (*tert*-butyl 6-((*R*)-2-ethoxy-1-(((*R*)-mesitylsulfinyl)amino)-2-oxoethyl)-6-methyl-2-azaspiro[3.3]heptane-2-carboxylate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2i** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 3:1 as eluent. The product is a brownish oil (38 mg, **27% yield**).

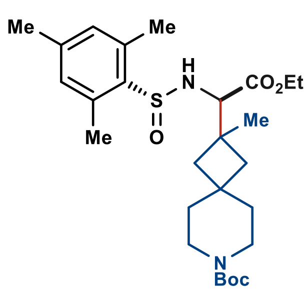
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.14 (d, *J* = 8.4 Hz, 1H), 4.31 – 4.12 (m, 2H), 3.87 (d, *J* = 8.4 Hz, 1H), 2.57 (s, 6H), 2.51 – 2.43 (m, 1H), 2.29 (s, 4H, CH_3 overlapped with CH_2), 2.01 – 1.90 (m, 2H), 1.42 (s, 9H), 1.28 (t, J = 7.2 Hz, 3H), 0.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 156.0, 141.0, 137.8, 136.7, 131.8, 130.8, 79.3, 64.6, 61.7, 43.1, 43.0, 37.0, 31.6, 28.4, 28.4, 21.7, 21.0, 19.4, 14.2.

***R*$_f$** = 0.56 (hexanes/EtOAc 2:1)

HRMS (ESI): calcd for $C_{25}H_{38}NaN_2O_5S$ $[M + Na]^+$: 501.2409, found: 501.2412.

Compound **5j** (*tert*-butyl 2-((*R*)-2-ethoxy-1-(((*R*)-mesitylsulfinyl)amino)-2-oxoethyl)-2-methyl-7-azaspiro[3.5]nonane-7-carboxylate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2j** with 3 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:1 as eluent. The product is a brownish oil 39 mg, **26% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.14 (d, *J* = 8.7 Hz, 1H), 4.30 – 4.12 (m, 2H), 3.87 (d, *J* = 8.7 Hz, 1H), 3.47 – 3.20 (m, 4H), 2.58 (s, 6H), 2.28 (s, 3H), 2.18

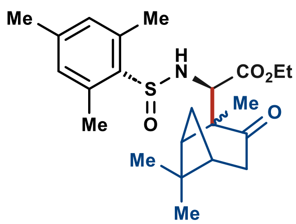
(d, J = 12.6 Hz, 1H), 1.95 (d, J = 12.6 Hz, 1H), 1.69 – 1.53 (m, 4H), 1.50 – 1.45 (m, 2H), 1.44 (s, 9H), 1.27 (t, J = 7.1 Hz, 3H), 1.05 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 154.9, 140.9, 137.9, 136.7, 131.8, 130.8, 79.3, 65.6, 61.5, 41.6 (br), 41.5, 40.2 (br), 38.7 (br), 35.2, 29.9, 28.4, 24.6 (br), 21.0, 19.4, 14.2.

***R*$_f$** = 0.55 (hexanes/EtOAc 2:1)

HRMS (ESI): calcd for $C_{27}H_{42}NaN_2O_5S$ $[M + Na]^+$: 529.2721, found: 529.2726.

Compound **5k** (ethyl (2*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2k** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 4:1 → 1:1 as eluent. Two β-diastereomers of **5k** were isolated (**5k-1** and **5k-2**) as brownish oils (**5k-1**: 47 mg, **37% yield**; **5k-2**: 50 mg, 40% yield, for **5k-2;** in total for **5k**: 97 mg, 77%).

^{1}H NMR for β-diastereomer **5k-1** (500 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.13 (d, J = 8.5 Hz, 1H), 4.28 (d, J = 8.5 Hz, 1H), 4.16–4.08 (m, 2H), 2.72–2.58 (m, 2H), 2.57 (s, 6H), 2.55–2.46 (m, 2H), 2.28 (s, 3H), 2.09 (tq, J = 6.0, 2.6 Hz, 1H), 1.92 (t, J = 6.2 Hz, 1H), 1.73 (d, J = 11.6 Hz, 1H), 1.32 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.16 (s, 3H), 0.91 (s, 3H).

^{13}C NMR for β-diastereomer **5k-1** (126 MHz, $CDCl_3$) δ 211.6, 170.8, 140.9, 137.2, 130.8, 61.6, 59.6, 54.7, 48.8, 45.1, 40.6, 38.7, 30.1, 27.5, 23.1, 21.0, 19.3, 19.0, 14.0.

***R*$_f$** for β-diastereomer **5k-1** = 0.44 (petroleum ether/EtOAc 2:1)

HRMS (ESI) for β-diastereomer **5k-1**: calcd for $C_{23}H_{33}NaNO_4S$ $[M + Na]^+$: 442.2022, found: 442.2029.

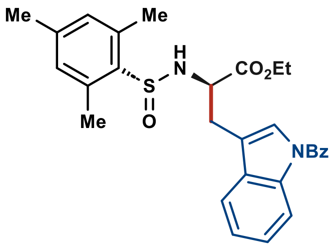
^{1}H NMR for β-diastereomer **5k-2** (500 MHz, $CDCl_3$) δ 6.86 (s, 2H), 6.76 (dt, J = 6.0, 1.7 Hz, 1H), 5.03 (d, J = 10.3 Hz, 1H), 4.45–4.13 (m, 2H), 3.86 (d, J = 10.3 Hz, 1H), 2.59–2.56 (m, 1H), 2.53 (s, 6H), 2.47 (dd, J = 16.0, 6.0 Hz, 1H), 2.28 (s, 3H), 2.25–2.10 (m, 3H), 1.77 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H), 0.91 (s, 3H), 0.88 (s, 3H).

^{13}C NMR for β-diastereomer **5k-2** (126 MHz, $CDCl_3$) δ 199.6, 172.3, 144.9, 141.1, 137.8, 136.8, 135.3, 130.8, 63.0, 61.6, 41.1, 39.7, 39.6, 27.2, 21.0, 20.4, 20.0, 19.2, 15.5, 14.1.

***R*$_f$** for β-diastereomer **5k-2** = 0.38 (petroleum ether/EtOAc 2:1)

HRMS (ESI) for β-diastereomer **5k-2**: calcd for $C_{23}H_{33}NaNO_4S$ $[M + Na]^+$: 442.2022, found: 442.2031.

Compound **5l** (ethyl 1-benzoyl-N^{α}-((*R*)-mesitylsulfinyl)-*D*-tryptophanate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2l** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 1:1 as eluent. The product is a brownish oil (50 mg, **33% yield**).

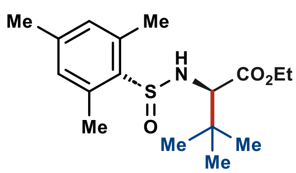
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1H), 7.67–7.61 (m, 2H), 7.62–7.55 (m, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 8.2, 7.3 Hz, 2H), 7.38 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 6.79 (s, 2H), 5.12 (d, *J* = 8.3 Hz, 1H), 4.32 (ddd, *J* = 8.3, 7.8, 5.0 Hz, 1H), 4.20–4.08 (m, 2H), 3.23 (dd, *J* = 14.8, 5.0 Hz, 1H), 3.03 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.36 (s, 6H), 2.27 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 168.3, 140.9, 137.6, 136.6, 136.2, 134.5, 131.8, 130.8, 130.6, 129.0, 128.6, 125.9, 125.3, 123.9, 118.9, 116.8, 116.5, 62.0, 57.2, 29.8, 21.0, 19.1, 14.0.

R_f = 0.23 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{29}H_{30}NaN_2O_4S$ $[M + Na]^+$: 525.1819, found: 525.1816.

Compound **5m** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethylbutanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2m** with 2 h reaction time. The crude product was purified by column chromatography using hexane/CH_2Cl_2/EtOAc 8:1:1 as eluent. The product is a brownish oil (65 mg, **67% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.05 (d, *J* = 10.0 Hz, 1H), 4.47–4.10 (m, 2H), 3.60 (d, *J* = 10.0 Hz, 1H), 2.57 (s, 6H), 2.29 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 9H).

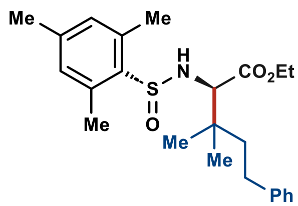
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 140.8, 138.1, 136.7, 130.8, 66.5, 61.3, 35.0, 26.5, 21.0, 19.3, 14.2

R_f = 0.32 (hexane/EtOAc 4:1)

HRMS (ESI): calcd for $C_{17}H_{27}NaNO_3S$ $[M + Na]^+$: 348.1604, found: 348.1609.

The spectroscopic data is in agreement with the literature.[1]

Compound **5n** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethyl-5-phenylpentanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2n** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 20:1 → 5:1 as eluent. The product is a brownish oil (117 mg, **94% yield**).

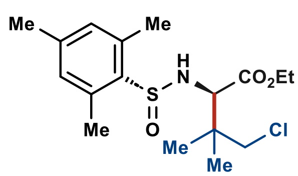
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.21–7.10 (m, 3H), 6.87 (s, 2H), 5.08 (d, *J* = 10.1 Hz, 1H), 4.32–4.19 (m, 2H), 3.81 (d, *J* = 10.1 Hz, 1H), 2.71–2.57 (m, 2H), 2.56 (s, 6H), 2.29 (s, 3H), 1.66 (ddd, *J* = 13.6, 12.3, 5.3 Hz, 1H), 1.63–1.48 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.00 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 142.5, 141.0, 138.0, 136.8, 130.8, 128.4, 128.3, 125.8, 64.7, 61.5, 41.5, 37.7, 30.3, 23.9, 23.7, 21.0, 19.3, 14.2.

***R*$_f$** = 0.32 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{24}H_{33}NaNO_3S$ $[M + Na]^+$: 438.2073, found: 438.2073.

Compound **5o** (ethyl (*R*)-4-chloro-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethylbutanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2o** with 2 h reaction time. The crude product was purified by preparative TLC using hexane/EtOAc 9:1 as eluent. The product is a brownish oil (24 mg, **22% yield**).

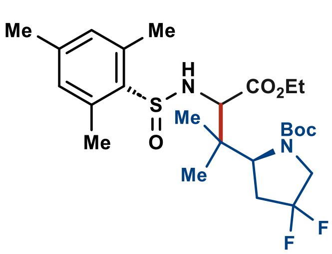
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 2H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.42–4.13 (m, 2H), 4.04 (d, *J* = 10.2 Hz, 1H), 3.61 (d, *J* = 10.8 Hz, 2H), 3.30 (d, *J* = 10.8 Hz, 2H), 2.58 (s, 6H), 2.30 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 3H), 1.09 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 141.1, 137.9, 136.8, 130.8, 61.9, 61.8, 52.8, 39.6, 29.7, 22.7, 21.2, 21.0, 19.2, 14.1.

***R*$_f$** = 0.36 (hexane/EtOAc 9:1)

HRMS (ESI): calcd for $C_{17}H_{26}ClNaNO_3S$ $[M + Na]^+$: 382.1214, found: 382.1219.

Compound **5p** (*tert*-butyl (*S*)-2-((*R*)-4-ethoxy-3-(((*R*)-mesitylsulfinyl)amino)-2-methyl-4-oxobutan-2-yl)-4,4-difluoropyrrolidine-1-carboxylate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2p** with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:1 as eluent. The product is a brownish oil 50.0 mg, **32% yield**).

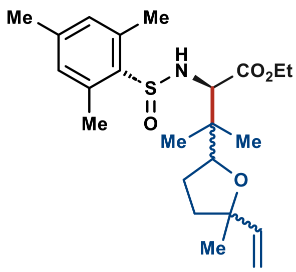
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 2H), 5.11 (d, *J* = 9.9 Hz, 1H), 4.37 – 4.19 (m, 3H), 4.13 (t, *J* = 8.9 Hz, 1H), 3.66 (br.s, 1H), 3.50 (ddd, J = 25.3, 12.8, 6.1 Hz, 1H), 3.36 (ddd, J = 24.9, 13.3, 6.1 Hz, 1H), 2.59 (s, 6H), 2.29 (s, 3H), 1.48 (s, 6H), 1.43 (s, 9H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 171.7, 141.1, 136.8, 131.9, 130.8, 81.8, 65.3, 62.8, 61.8, 54.3, 43.7, 28.2, 28.2, 21.0, 19.3, 14.1.

***R*$_f$** = 0.50 (hexanes/EtOAc 2:1)

HRMS (ESI): calcd for $C_{25}H_{38}NaF_2N_2O_5S$ $[M + Na]^+$: 539.2378, found: 539.2387.

Compound **5q** (ethyl (2*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3-methyl-3-(5-methyl-5-vinyltetrahydrofuran-2-yl)butanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2q** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 3:1 as eluent. The product is a brownish oil (58 mg, **46% yield**).

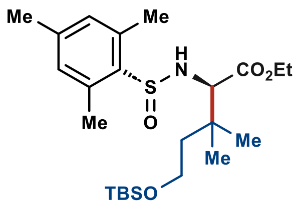
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H, CH, Mes), 6.84 (s, 2H, CH, Mes), 5.84 (dd, *J* = 17.2, 10.7 Hz, 1H, H-6), 5.80 (dd, *J* = 17.2, 10.7 Hz, 1H, H-6), 5.40 (d, *J* = 10.4 Hz, 1H, NH), 5.24 (dd, *J* = 17.2, 1.5 Hz, 1H, H-7b), 5.20 (d, *J* = 9.8 Hz, 1H, NH), 5.20 (dd, *J* = 17.2, 1.7 Hz, 1H, H-7b), 4.96 (dd, *J* = 8.2, 1.5 Hz, 1H, H-7a), 4.94 (dd, *J* = 8.1, 1.7 Hz, 1H, H-7a), 4.25–4.14 (m, 4H, H-10), 3.99 (d, *J* = 10.2 Hz, 1H, H-8), 3.97 (dd, *J* = 9.2, 7.3 Hz, 1H, H-2), 3.93 (d, *J* = 9.6 Hz, 1H, H-8), 3.83 (t, *J* = 7.2 Hz, 1H, H-2), 2.571 (s, 6H, 2 × CH_3, Mes), 2.573 (s, 6H, 2 × CH_3, Mes), 2.29 (s, 3H, CH_3, Mes), 2.27 (s, 3H, CH_3, Mes), 1.87–1.58 (m, 8H, H-3, H-4), 1.30 (t, *J* = 7.2 Hz, 6H, H-11), 1.27 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.82 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 172.6 (C-9), 143.9, 143.8 (C-6), 140.8, 140.5 (C, Mes), 138.4, 138.1 (C, Mes), 136.8, 136.7 (2 × C, Mes), 130.8, 130.7 (2 × CH, Mes), 111.2, 111.1 (C-7), 82.8, 82.7 (C-5), 81.8, 81.5 (C-2), 64.2, 63.6 (C-8), 61.4, 61.1 (C-10), 41.1, 40.2 (C-1), 37.2, 37.1 (C-3 or C-4), 26.96, 27.01 (CH_3), 26.4, 26.2 (C-3 or C-4), 21.0, 21.0 (CH_3, Mes), 20.2, 20.0 (CH_3), 19.4, 19.3 (2 × CH_3, Mes), 19.1, 18.5 (CH_3), 14.1 (C-11).

***R*$_f$** = 0.49, 0.47 (petroleum ether/EtOAc 5:1)

HRMS (ESI): calcd for $C_{23}H_{35}NaNO_4S$ $[M + Na]^+$: 444.2179, found: 444.2181.

Compound **5r** (ethyl (*R*)-5-((tert-butyldimethylsilyl)oxy)-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethylpentanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2r** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 20:1 → 10:1 as eluent. The product is a brownish oil (124 mg, **88% yield**).

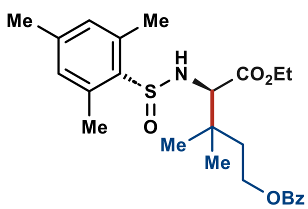
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.31–4.11 (m, 2H), 3.74 (d, *J* = 10.1 Hz, 1H), 3.71 (ddd, *J* = 7.6, 6.6, 1.3 Hz, 2H), 2.57 (s, 6H), 2.29 (s, 3H), 1.63 (dt, *J* = 14.3, 7.1 Hz, 1H), 1.57–1.50 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.97 (s, 3H), 0.94 (s, 3H), 0.89 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 140.9, 138.0, 136.8, 130.8, 65.4, 61.3, 59.5, 41.2, 36.9, 25.9, 24.1, 23.8, 21.0, 19.3, 18.2, 14.1, −5.35, −5.38.

***R*$_f$** = 0.23 (petroleum ether/EtOAc 10:1)

HRMS (ESI): calcd for $C_{24}H_{43}NaNO_4SSi$ $[M + Na]^+$: 492.2574, found: 492.2575.

Compound **5s** ((*R*)-5-ethoxy-4-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethyl-5-oxopentyl benzoate)



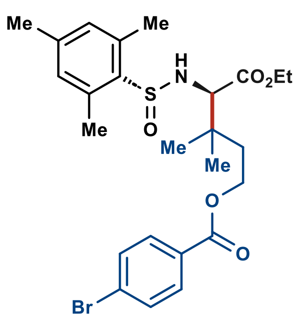
Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **2s** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 20:1 → 5:1 as eluent. The product is a brownish oil (106 mg, **77% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–7.96 (m, 2H), 7.64–7.51 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 6.87 (s, 2H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.42 (qt, *J* = 11.1, 7.0 Hz, 2H), 4.34–4.15 (m, 2H), 3.76 (d, *J* = 10.0 Hz, 1H), 2.57 (s, 6H), 2.29 (s, 3H), 1.84 (td, *J* = 7.2, 2.5 Hz, 2H), 1.38–1.28 (m, 3H), 1.06 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 166.5, 141.0, 137.8, 136.8, 132.9, 130.8, 130.2, 129.5, 128.4, 65.5, 61.6, 37.1, 37.0, 24.1, 23.7, 21.0, 19.3, 14.1.

HRMS (ESI): calcd for $C_{25}H_{33}NaNO_5S$ $[M + Na]^+$: 482.1972, found: 482.1972.

Compound **5t** ((*R*)-5-ethoxy-4-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethyl-5-oxopentyl 4-bromobenzoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.17 mmol scale from methyl oxalate **2t** (1.5 equiv.) with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 3:1 as eluent. The product is a brownish oil (46.2 mg, **58% yield**).

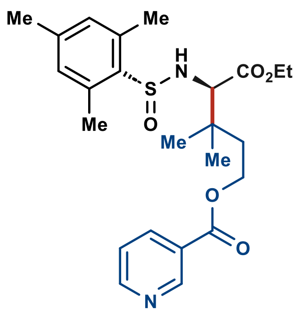
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92–7.82 (m, 2H), 7.64–7.53 (m, 2H), 6.87 (s, 2H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.47–4.35 (m, 2H), 4.34–4.18 (m, 2H), 3.75 (d, *J* = 10.0 Hz, 1H), 2.56 (s, 6H), 2.29 (s, 3H), 1.83 (td, *J* = 7.2, 3.3 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 7.2 Hz, 6H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.3, 165.8, 141.1, 137.8, 136.8, 131.7, 131.1, 130.9, 129.1, 128.1, 65.4, 61.9, 61.6, 37.0, 37.0, 24.1, 23.7, 21.1, 19.3, 14.2.

***R*$_f$** = 0.48 (petroleum ether/EtOAc 3:1)

HRMS (ESI): calcd for $C_{25}H_{32}BrNaNO_5S$ $[M + Na]^+$: 560.1077, found: 560.1078.

Compound **5u** ((*R*)-5-ethoxy-4-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethyl-5-oxopentyl nicotinate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2u** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 3:1 as eluent. The product is a brownish oil (98 mg, **71% yield**).

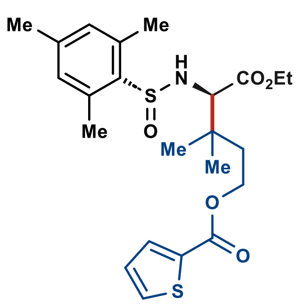
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.78 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.28 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.40 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.87 (s, 2H), 5.11 (d, *J* = 10.0 Hz, 1H), 4.51–4.39 (m, 2H), 4.34–4.17 (m, 2H), 3.74 (d, *J* = 10.0 Hz, 1H), 2.57 (s, 6H), 2.29 (s, 3H), 1.90–1.80 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 3H), 1.05 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.3, 165.1, 153.4, 150.8, 141.1, 137.8, 137.1, 136.8, 130.9, 126.1, 123.3, 65.4, 62.1, 61.7, 37.0, 37.0, 24.1, 23.7, 21.0, 19.3, 14.2.

***R*$_f$** = 0.32 (petroleum ether/EtOAc 1:1)

HRMS (ESI): calcd for $C_{24}H_{32}NaN_2O_5S$ $[M + Na]^+$: 483.1924, found: 483.1924.

Compound **5v** ((*R*)-5-ethoxy-4-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethyl-5-oxopentyl thiophene-2-carboxylate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2v** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 3:1 as eluent. The product is a brownish oil (81 mg, **58% yield**).

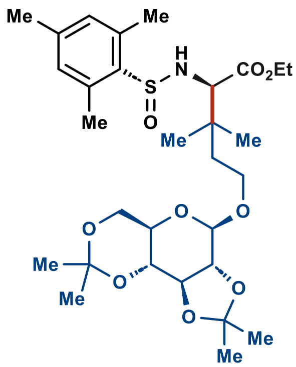
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.89 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.44 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.21 (s, 2H), 5.44 (d, *J* = 10.0 Hz, 1H), 4.79–4.66 (m, 2H), 4.68–4.51 (m, 2H), 4.09 (d, *J* = 10.0 Hz, 1H), 2.91 (s, 6H), 2.63 (s, 3H), 2.22–2.07 (m, 2H), 1.91 (s, 6H), 1.65 (t, *J* = 7.1 Hz, 3H), 1.39 (s, 3H), 1.37 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 172.3, 162.1, 141.0, 137.9, 136.8, 133.8, 133.4, 132.4, 130.8, 127.8, 65.4, 61.8, 61.6, 37.0, 37.0, 24.1, 23.8, 23.7, 21.0, 19.3, 14.1.

***R*$_f$** = 0.60 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{23}H_{31}NaNO_5S_2$ $[M + Na]^+$: 488.1536, found: 488.1535.

Compound **5w** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethyl-5-(((3a*R*,4*R*,5a*R*,9a*R*,9b*S*)-2,2,8,8-tetramethylhexahydro-[1,3]dioxolo[4',5':4,5]pyrano[3,2-*d*][1,3]dioxin-4-yl)oxy)pentanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **2w** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 3:1 → 2:1 as eluent. The product is a brownish oil (132 mg, **74% yield**).

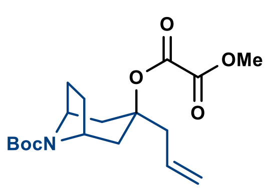
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.04 (d, *J* = 10.2 Hz, 1H), 4.67 (d, *J* = 7.9 Hz, 1H), 4.23 (ABqq, *J* = 10.8, 7.1 Hz, 2H), 4.01–3.92 (m, 2H), 3.93–3.84 (m, 2H), 3.70 (d, *J* = 10.2 Hz, 1H), 3.70–3.64 (m, 1H), 3.63 (dd~t, *J* = 9.0 Hz, 1H), 3.38 (dd, *J* = 9.0, 7.9 Hz, 1H), 3.26 (ddd, *J* = 10.3, 8.8, 5.2 Hz, 1H), 2.56 (s, 6H), 2.29 (s, 3H), 1.75 (ddd, *J* = 13.7, 9.1, 6.2 Hz, 1H), 1.67 (ddd, *J* = 13.7, 9.1, 5.7 Hz, 1H), 1.54 (s, 3H), 1.46 (s, 6H), 1.44 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.97 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 140.9, 137.9, 136.7, 130.8, 112.1, 102.3 (C-1), 99.7, 77.8, 77.6, 72.7, 69.7, 66.1, 65.2, 62.2, 61.5, 37.8, 36.8, 29.0, 26.7, 26.4, 24.1, 23.8, 21.0, 19.3, 19.1, 14.1.

***R*$_f$** = 0.47 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{30}H_{47}NaNO_9S$ $[M + Na]^+$: 620.2864, found: 620.2861.

Compound **6a** ((1*R*,3*r*,5*S*)-3-allyl-8-(*tert*-butoxycarbonyl)-8-azabicyclo[3.2.1]octan-3-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1 mmol scale from alcohol **SI-3** with 2 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 4:1 as eluent. The product is a colorless oil (140 mg, **40% yield**).

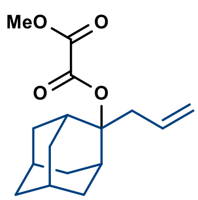
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (ddt, *J* = 17.5, 10.2, 7.4 Hz, 1H), 5.18–5.03 (m, 2H), 4.26 (br.s, 1H), 4.16 (br.s, 1H), 3.88 (s, 3H), 2.67 (dd, *J* = 12.8, 7.1 Hz, 2H), 2.38 (dd~t, *J* = 15.3 Hz, 2H), 2.07–1.82 (m, 6H), 1.46 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 156.4, 153.3, 131.0, 119.9, 87.1, 79.5, 53.4, 52.7 (br), 52.0 (br), 43.9, 38.8 (br), 38.2 (br), 28.5, 27.9 (br), 27.1 (br).

***R*$_f$** = 0.40 (petroleum ether/EtOAc 5:1)

The spectroscopic data is in agreement with the literature.[11]

Compound **6b** ((1*r*,3*r*,5*r*,7*r*)-2-allyladamantan-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.8 mmol scale from alcohol **SI-4** with 10 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 10:1 → 4:1 as eluent. The product is a colorless oil (330 mg, **66% yield**).

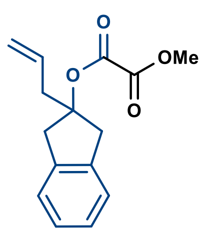
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81–5.68 (m, 1H), 5.12–5.05 (m, 2H), 3.87 (s, 3H), 2.97 (d, *J* = 7.3 Hz, 2H), 2.45 (s, 2H), 2.11–1.98 (m, 2H), 1.95–1.82 (m, 4H), 1.82–1.71 (m, 4H), 1.66–1.59 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 156.2, 131.9, 118.5, 93.2, 53.2, 38.1, 36.8, 34.2, 33.9, 32.9, 27.0, 26.7.

***R*$_f$** = 0.50 (petroleum ether/EtOAc 10:1)

HRMS (ESI): calcd for $C_{16}H_{22}NaO_4$ $[M + Na]^+$: 301.1410, found: 301.1410.

Compound **6c** (2-allyl-2,3-dihydro-1*H*-inden-2-yl methyl oxalate)



Synthesized according to the **General procedure C** described in **Section 4.1** on 1.4 mmol scale from alcohol **SI-5** with 10 min reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 20:1 → 10:1 as eluent. The product is a colorless amorphous solid (354 mg, **97% yield**).

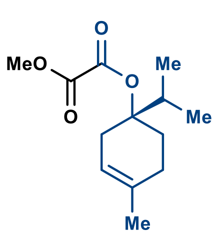
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.15 (m, 4H), 5.86–5.73 (m, 1H), 5.20–5.08 (m, 2H), 3.85 (s, 3H), 3.49 (d, *J* = 16.9 Hz, 2H), 3.33 (d, *J* = 16.9 Hz, 2H), 2.90 (dt, *J* = 7.3, 1.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 156.8, 139.5, 131.9, 126.9, 124.5, 119.3, 93.8, 53.3, 43.7, 40.7.

***R*$_f$** = 0.29 (petroleum ether/EtOAc 20:1, brown color upon treatment with 5% H_3PO_4 in MeOH)

HRMS (ESI): calcd for $C_{15}H_{16}NaO_4$ $[M + Na]^+$: 283.0941, found: 283.0942.

Compound **6d** ((*R*)-1-isopropyl-4-methylcyclohex-3-en-1-yl methyl oxalate, (−)-terpineolyl methyloxalate)



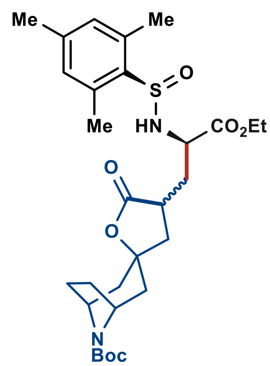
Synthesized according to the **General procedure C** described in **Section 4.1** on 1 mmol scale from (−)-terpinen-4-ol with 1 h reaction time. The crude product was purified by filtration through silica gel washing with CH_2Cl_2. The product is a yellowish oil (240 mg, **quantitative yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.22 (br.s, 1H), 3.82 (s, 3H), 2.68 (hept, *J* = 6.9 Hz, 1H), 2.52–2.40 (m, 2H), 2.28–2.15 (m, 1H), 2.05–1.95 (m, 1H), 1.90 (dd, *J* = 17.8, 5.9 Hz, 1H), 1.70 (ddd, *J* = 13.4, 11.5, 6.1 Hz, 1H), 1.63 (br.s, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 157.1, 133.7, 117.0, 91.2, 53.2, 32.6, 29.7, 27.7, 27.1, 23.1, 17.6, 17.0.

R_f = 0.71 (petroleum ether/EtOAc 5:1)

Compound **7a** (*tert*-butyl 4'-((*R*)-3-ethoxy-2-(((*R*)-mesitylsulfinyl)amino)-3-oxopropyl)-5'-oxodihydro-3'*H*-8-azaspiro[bicyclo[3.2.1]octane-3,2'-furan]-8-carboxylate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **6a** with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 1:1 as eluent. The product is a brownish oil (43 mg, **28% yield**). The product is a mixture of two γ-diastereomers (1:1).

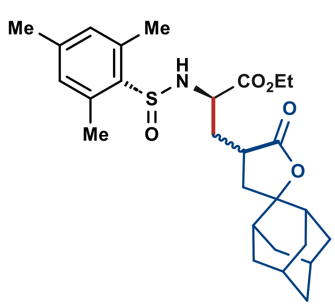
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 2H), 6.87 (s, 2H), 5.13 (d, *J* = 8.9 Hz, 0.5H), 5.11 (d, *J* = 8.5 Hz, 0.5H), 4.32–4.25 (m, 1.5H), 4.24–4.16 (m, 3H), 3.92–3.84 (m, 0.5H), 2.97–2.75 (m, 1H), 2.58 (s, 6H), 2.57–2.50 (m, 1H), 2.38 (d, *J* = 13.8 Hz, 0.5H), 2.29 (s, 1.5H), 2.29 (s, 1.5H), 2.26–2.16 (m, 1H), 2.17–2.00 (m, 3.5H), 1.97–1.89 (m, 3H), 1.89–1.82 (m, 3H), 1.81–1.70 (m, 1.5H), 1.67–1.57 (m, 1.5H), 1.48 (s, 4.5H), 1.46 (s, 4.5H), 1.32–1.25 (m, 3H). *Mixture of two γ-diastereomers is reported.*

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 177.5, 172.7, 172.4, 153.3, 153.2, 141.3, 141.2, 137.3 (d, *J* = 21.5 Hz), 136.8, 136.6, 131.0, 130.9, 82.5, 82.3, 79.7, 79.6, 62.2, 62.0, 55.3, 55.1, 43.7, 43.4, 36.2, 35.7, 34.6, 28.5, 28.5, 21.0, 19.3, 14.1, 14.1. *Mixture of two γ-diastereomers is reported.*

R_f = 0.45 (petroleum ether/EtOAc 1:1)

HRMS (ESI): calcd for $C_{29}H_{42}NaN_2O_7S$ $[M + Na]^+$: 585.2605, found: 585.2603.

Compound **7b** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3-((1*R*,3*R*)-5'-oxodihydro-3'*H*-spiro[adamantane-2,2'-furan]-4'-yl)propanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **6b** with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:3 as eluent. The product is a brownish oil (35 mg, **24% yield**). The product is a mixture of two γ-diastereomers (1:1).

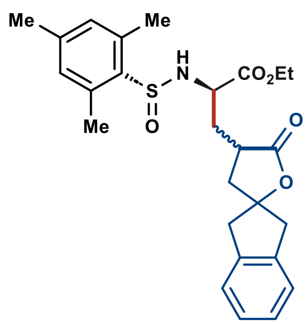
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.15 (d, *J* = 8.9 Hz, 0.5H), 5.13 (d, *J* = 8.4 Hz, 0.5H), 4.32 (td, *J* = 7.9, 5.5 Hz, 0.5H), 4.28–4.17 (m, 2H), 2.98 (tdd, *J* = 11.7, 8.8, 3.8 Hz, 0.5H), 2.88 (dtd, *J* = 11.6, 8.5, 5.9 Hz, 0.5H), 2.75 (dd, *J* = 12.6, 8.9 Hz, 0.5H), 2.69–2.61 (m, 0.5H), 2.58 (s, 3H), 2.58 (s, 3H), 2.39 (dt, *J* = 14.2, 5.8 Hz, 0.5H), 2.29 (s, 3H), 2.26–2.18 (m, 1.5H), 2.18–2.11 (m, 1H), 1.92–1.69 (m, 11H), 1.68–1.58 (m, 5H), 1.29 (t, *J* = 7.1, Hz, 1.5H), 1.27 (t, *J* = 7.1, Hz, 1.5H). *Mixture of two γ-diastereomers is reported.*

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.60, 177.52, 172.90, 172.60, 141.27, 141.10, 137.38, 136.81, 136.52, 130.97, 130.87, 88.70, 88.49, 62.13, 61.95, 55.43, 55.31, 39.28, 39.26, 38.28, 37.87, 37.35, 37.01, 36.48, 35.56, 35.49, 35.38, 35.28, 35.16, 33.76, 33.63, 33.60, 32.72, 32.70, 26.69, 26.67, 26.60, 21.03, 19.31, 19.24, 14.10, 14.08. *Mixture of two γ-diastereomers is reported.*

R_f = 0.48 (petroleum ether/EtOAc 2:1)

HRMS (ESI): calcd for $C_{27}H_{37}NaNO_5S$ $[M + Na]^+$: 510.2285, found: 510.2284.

Compound **7c** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3-(5-oxo-1',3',4,5-tetrahydro-3*H*-spiro[furan-2,2'-inden]-4-yl)propanoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.36 mmol scale from methyl oxalate **6c** with 4 h reaction time. The crude product was purified by column chromatography using petroleum ether/EtOAc 5:1 → 2:3 as eluent. The product is a brownish oil (40 mg, **29% yield**). The product is a mixture of two γ-diastereomers (1:1).

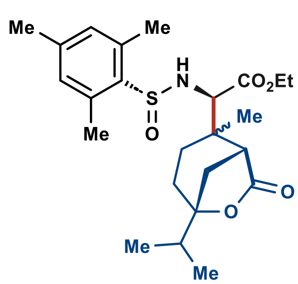
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.15 (m, 4H), 6.89 (s, 1H), 6.88 (s, 1H), 5.16 (d, *J* = 9.2 Hz, 0.5H), 5.14 (d, *J* = 8.1 Hz, 0.5H), 4.39–4.30 (m, 1H), 4.22 (qd, *J* = 7.2, 4.3 Hz, 2H), 3.94 (ddd, *J* = 10.9, 9.1, 4.1 Hz, 0.5H), 3.40 (dd, *J* = 16.6, 14.3 Hz, 1H), 3.29–3.18 (m, 1H), 3.15 (d, *J* = 15.4 Hz, 0.5H), 3.13–3.05 (m, 1.5H), 3.05–2.97 (m, 0.5H), 2.69–2.62 (m, 0.5H), 2.60 (s, 3H), 2.59 (s, 3H), 2.58–2.49 (m, 1H), 2.49–2.42 (m, 1H), 2.30 (s, 1.5H), 2.29 (s, 1.5H), 2.28–2.23 (m, 1H), 2.13 (t, *J* = 12.3 Hz, 0.5H), 2.08–2.01 (m, 0.5H), 1.96 (ddd, *J* = 14.4, 10.6, 4.1 Hz, 0.5H), 1.87 (dt, *J* = 14.2, 8.0 Hz, 0.5H), 1.29 (d, *J* = 7.1, 4.5 Hz, 1.5H), 1.26 (d, *J* = 7.1, 4.5 Hz, 1.5H). *Mixture of two γ-diastereomers is reported.*

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.33, 177.33, 172.76, 172.48, 141.32, 141.16, 139.51, 139.49, 139.36, 139.28, 137.44, 137.24, 136.81, 136.60, 131.00, 130.94, 130.91, 127.23, 127.16, 127.11, 124.62, 124.60, 124.47, 124.42, 91.29, 91.17, 62.15, 62.02, 55.34, 55.15, 45.35, 44.88, 44.79, 39.95, 39.59, 37.86, 37.27, 34.75, 34.50, 21.03, 19.30, 14.08, 14.06. *Mixture of two γ-diastereomers is reported.*

R_f = 0.51 (petroleum ether/EtOAc 1:1)

HRMS (ESI): calcd for $C_{26}H_{31}NaNO_5S$ $[M + Na]^+$: 492.1815, found: 492.1815.

Compound **7d** (ethyl (2*R*)-2-((1*S*,2*R*)-5-isopropyl-2-methyl-7-oxo-6-oxabicyclo[3.2.1]octan-2-yl)-2-(((*R*)-mesitylsulfinyl)amino)acetate)



Synthesized according to the general procedure described in **Section 4.2** on 0.3 mmol scale from methyl oxalate **6d** with 2 h reaction time. The crude product was purified by column chromatography using hexane/EtOAc 9:1 as eluent. The product is a brown solid (17.5 mg, **13% yield**). The product is a mixture of two β-diastereomers (1:3.5).

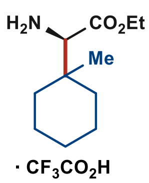
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.12 (d, *J* = 10.1 Hz, 1H), 4.34–4.20 (m, 2H), 4.18 (d, *J* = 10.1 Hz, 1H), 2.64 (dd, *J* = 5.6, 1.8 Hz, 1H), 2.53 (s, 6H), 2.28 (s, 3H), 2.16–2.05 (m, 2H), 2.01–1.92 (m, 2H), 1.83–1.74 (m, 2H), 1.43 (dt, *J* = 15.1, 9.7 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 1H). *Mixture of two β-diastereomers is reported.*

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 171.6, 141.5, 137.2, 136.7, 131.0, 89.1, 62.17, 62.03, 59.1, 48.8, 38.5, 38.1, 35.1, 35.1, 34.9, 34.2, 29.3, 26.0, 21.1, 20.0, 19.28, 19.17, 17.1, 16.8, 14.2, 14.1. *Mixture of two β-diastereomers is reported.*

***R*f** = 0.19 (hexane/EtOAc 9:1)

HRMS (ESI): calcd for $C_{24}H_{35}NaNO_5S$ $[M + Na]^+$: 472.2128, found: 472.2127.

Compound **8a** (ethyl (*R*)-2-amino-2-(1-methylcyclohexyl)acetate, trifluoroacetate salt)



Synthesized according to the general procedure described in **Section 4.2** on 0.1 mmol scale from *N*-sulfinyl amide **5a**. The product is a colorless solid (31 mg, **99% yield**).

^{1}H NMR (500 MHz, MeOD) δ 4.30 (ABqq, *J* = 16.0, 7.1, Hz, 2H), 3.88 (s, 1H), 1.70–1.40 (m, 10H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 3H).

^{13}C NMR (126 MHz, MeOD) δ 169.6, 63.4, 62.2, 37.1, 36.0, 35.2, 26.6, 22.4, 22.3, 19.9, 14.4.

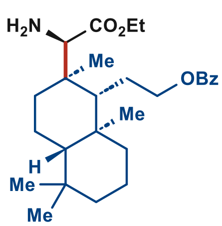
^{19}F NMR (377 MHz, MeOD) δ -77.0.

***R*f** = 0.80 (CH_2Cl_2/MeOH 10:1, red color upon treatment with ninhydrin stain)

$[\alpha]^{25}_{D}$ = −12.8 (*c* 3.4, MeOH)

HRMS (ESI): calcd for $C_{11}H_{22}NO_2$ $[M-CF_3CO_2H+H]^+$: 200.1645, found: 200.1644.

Compound **8d** (2-((1*R*,2*R*,4a*S*,8a*S*)-2-((*R*)-1-amino-2-ethoxy-2-oxoethyl)-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl benzoate)



Synthesized according to the general procedure described in **Section 4.2** on 0.1 mmol scale from *N*-sulfinyl amide **5d**. The product is a colorless solid (44 mg, **99% yield**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.97 (m, 2H), 7.59–7.51 (m, 1H), 7.42 (dd~t, *J* = 7.6 Hz, 2H), 4.52 (td, *J* = 11.0, 5.4 Hz, 1H), 4.38–4.27 (m, 1H), 4.30–4.17 (m, 2H), 4.15 (s, 1H), 1.84 (tt, *J* = 9.6, 4.8 Hz, 1H), 1.81–1.74 (m, 2H), 1.74–1.63 (m, 1H), 1.60 (dt, *J* = 13.4, 6.7 Hz, 2H), 1.54–1.41 (m, 2H), 1.39 (dd, *J* = 13.4, 3.4 Hz, 1H), 1.34 (m, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.21 (dd~t, *J* = 12.6 Hz, 1H), 1.15 (s, 3H), 1.11 (dd, *J* = 13.6, 4.2 Hz, 1H), 0.95 (s, 3H), 0.89 (ddd, *J* = 12.8, 9.0, 3.7 Hz, 1H), 0.84 (s, 3H), 0.79 (s, 3H), 0.73 (d, *J* = 11.5 Hz, 1H).

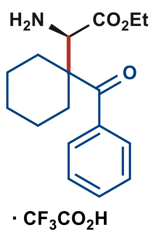
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 167.3, 133.2, 129.9, 129.5, 128.4, 65.9, 63.3, 61.3, 56.1, 50.1, 41.7, 41.6, 40.6, 39.6, 35.1, 33.1, 33.1, 25.5, 21.5, 18.1, 17.7, 17.6, 16.5, 13.8.

***R*f** = 0.80 (CH_2Cl_2/MeOH 10:1, red color upon treatment with ninhydrin stain)

$[\alpha]^{25}_{D}$ = −0.8 (*c* 4.0, MeOH)

HRMS (ESI): calcd for $C_{27}H_{42}NO_4$ $[M + H]^+$: 444.3108, found: 444.3109.

Compound **8f** (ethyl (*R*)-2-amino-2-(1-benzoylcyclohexyl)acetate, trifluoroacetate salt)



Synthesized according to the general procedure described in **Section 4.2** on 0.07 mmol scale from *N*-sulfinyl amide **5f**. The product is a colorless solid (28 mg, **99% yield**).

^{1}H NMR (500 MHz, MeOD) δ 7.76–7.64 (m, 2H), 7.65–7.52 (m, 1H), 7.49 (dd~t, *J* = 7.6 Hz, 2H), 4.65 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.42–2.29 (m, 1H), 2.29–2.13 (m, 1H), 1.93 (ddd, *J* = 13.5, 9.6, 3.4 Hz, 1H), 1.67 (ddd, *J* = 13.3, 9.0, 3.7 Hz, 1H), 1.64–1.27 (m, 6H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, MeOD) δ 207.0, 169.0, 139.8, 132.7, 129.5, 128.8, 64.0, 58.0, 55.3, 32.7, 31.2, 26.1, 23.1, 23.0, 14.1.

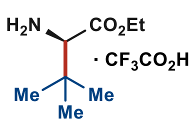
^{19}F NMR (377 MHz, MeOD) δ -77.0.

***R*$_f$** = 0.80 (CH_2Cl_2/MeOH 10:1, red color upon treatment with ninhydrin stain)

[α]^{25}$_D$ = −20.1 (*c* 3.4, MeOH)

HRMS (ESI): calcd for $C_{17}H_{24}NO_3$ [M − CF_3CO_2H + H]$^+$: 290.1751, found: 290.1752.

Compound **8m** (ethyl (*R*)-2-amino-3,3-dimethylbutanoate, trifluoroacetate salt)



Synthesized according to the general procedure described in **Section 4.2** on 0.1 mmol scale from *N*-sulfinyl amide **5m**. The product is a colorless solid (27 mg, **99% yield**).

^{1}H NMR (500 MHz, MeOD) δ 5.87 (ABqq, *J* = 16.0, 7.2 Hz, 2H), 5.33 (s, 1H), 2.89 (t, *J* = 7.2 Hz, 3H), 2.67 (s, 9H).

^{13}C NMR (126 MHz, MeOD) δ 169.7, 63.4, 62.9, 34.3, 26.7, 14.4.

^{19}F NMR (377 MHz, MeOD) δ -77.04.

***R*$_f$** = 0.70 (CH_2Cl_2/MeOH 10:1, red color upon treatment with ninhydrin stain)

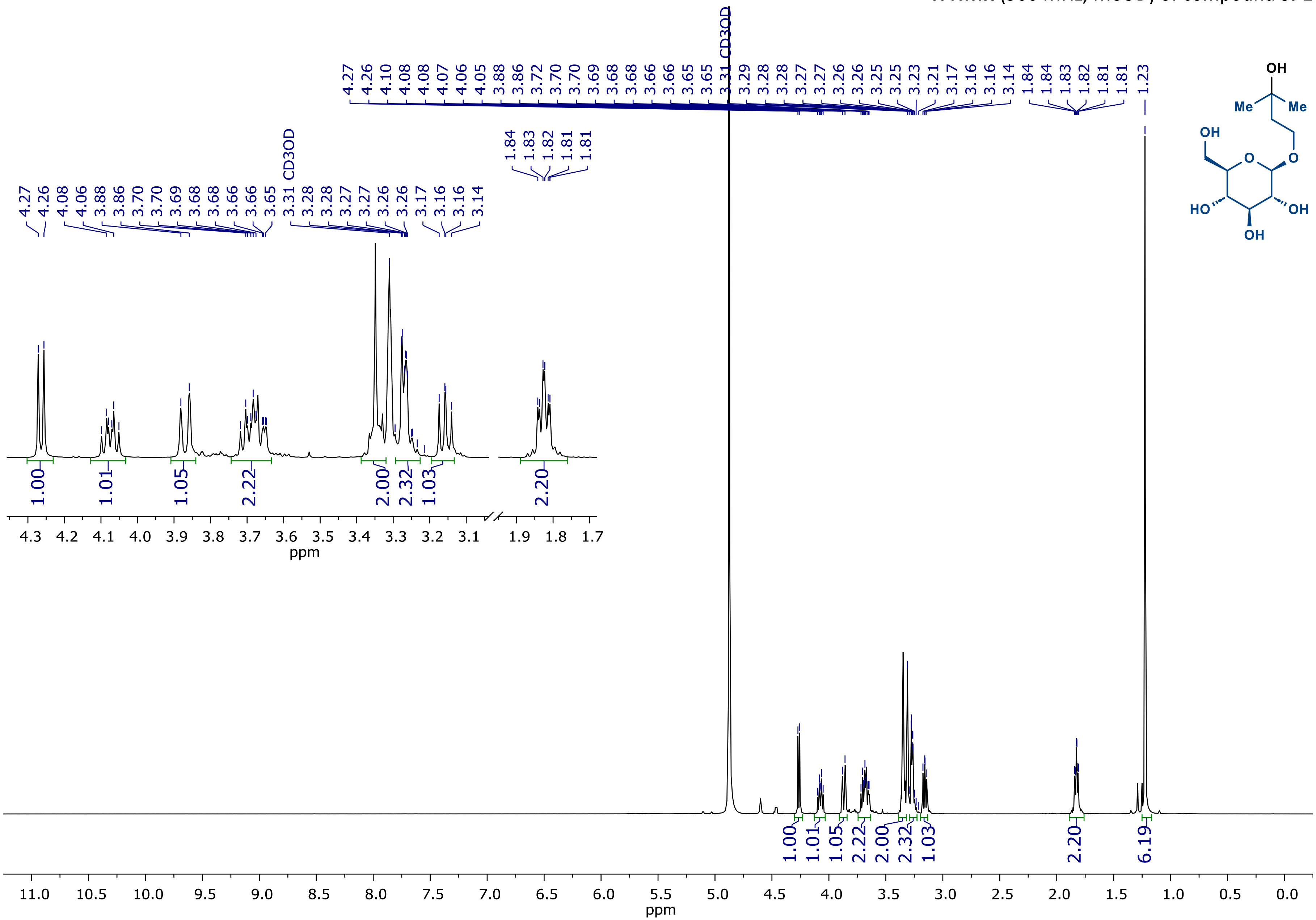
[α]^{25}$_D$ = −5.9 (*c* 4.0, MeOH)

HRMS (ESI): calcd for $C_8H_{18}NO_2$ [M − CF_3CO_2H + H]$^+$: 160.1332, found: 160.1331.

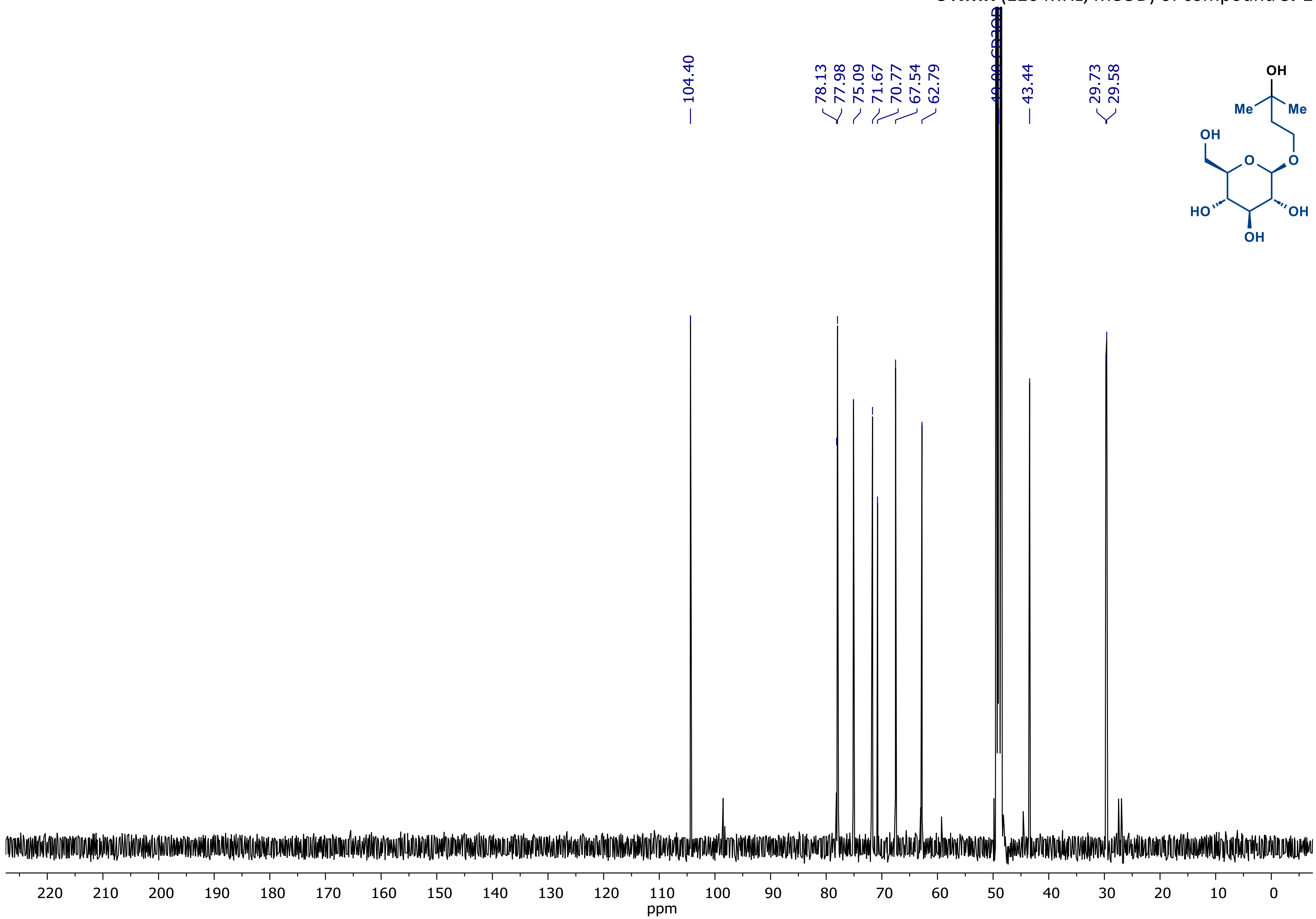
The spectroscopic data is in agreement with the literature.[1]

6. *NMR spectra*

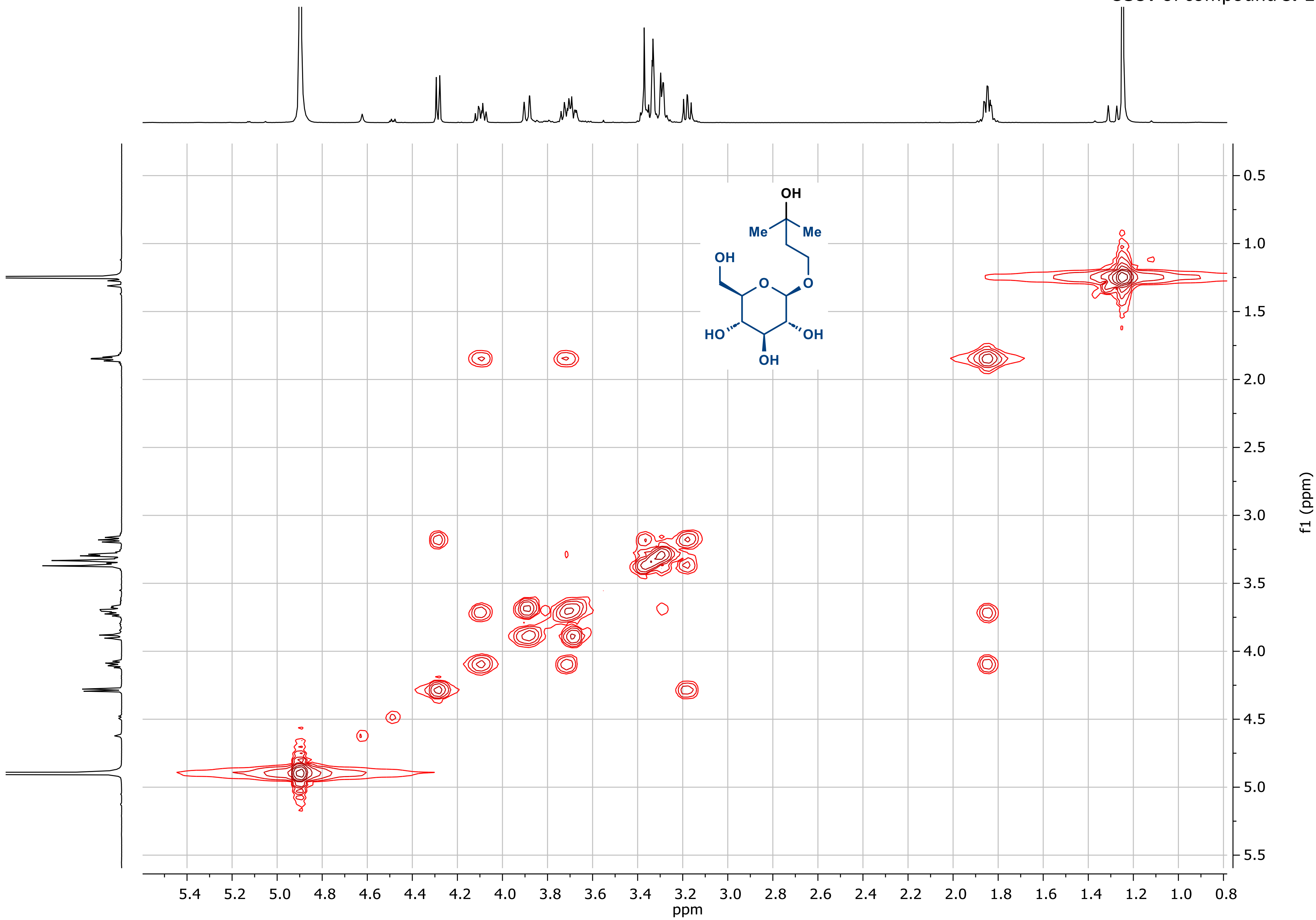
^{1}**H NMR** (500 MHz, MeOD) of compound **SI-1**



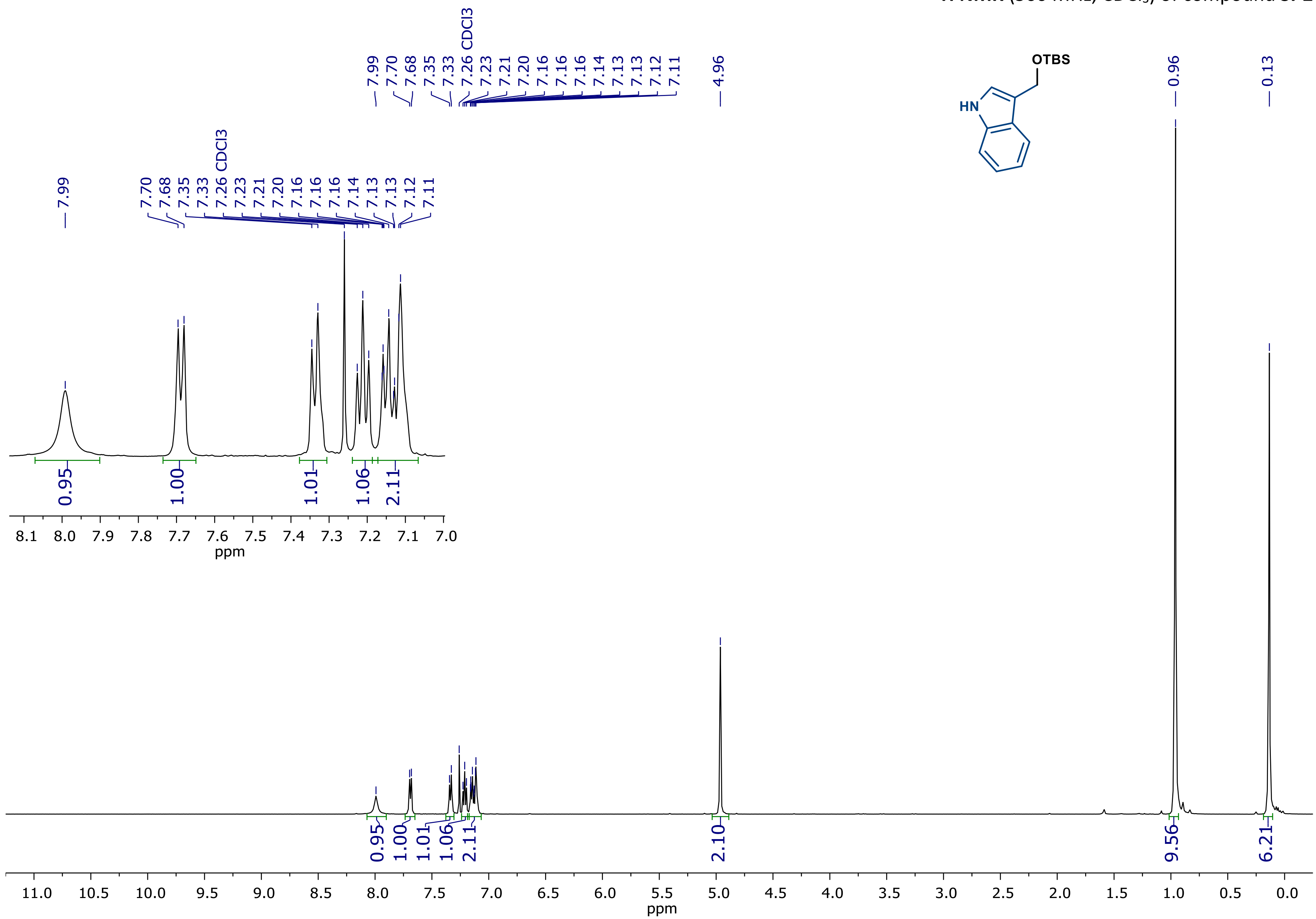
[13]C NMR (126 MHz, MeOD) of compound **SI-1**



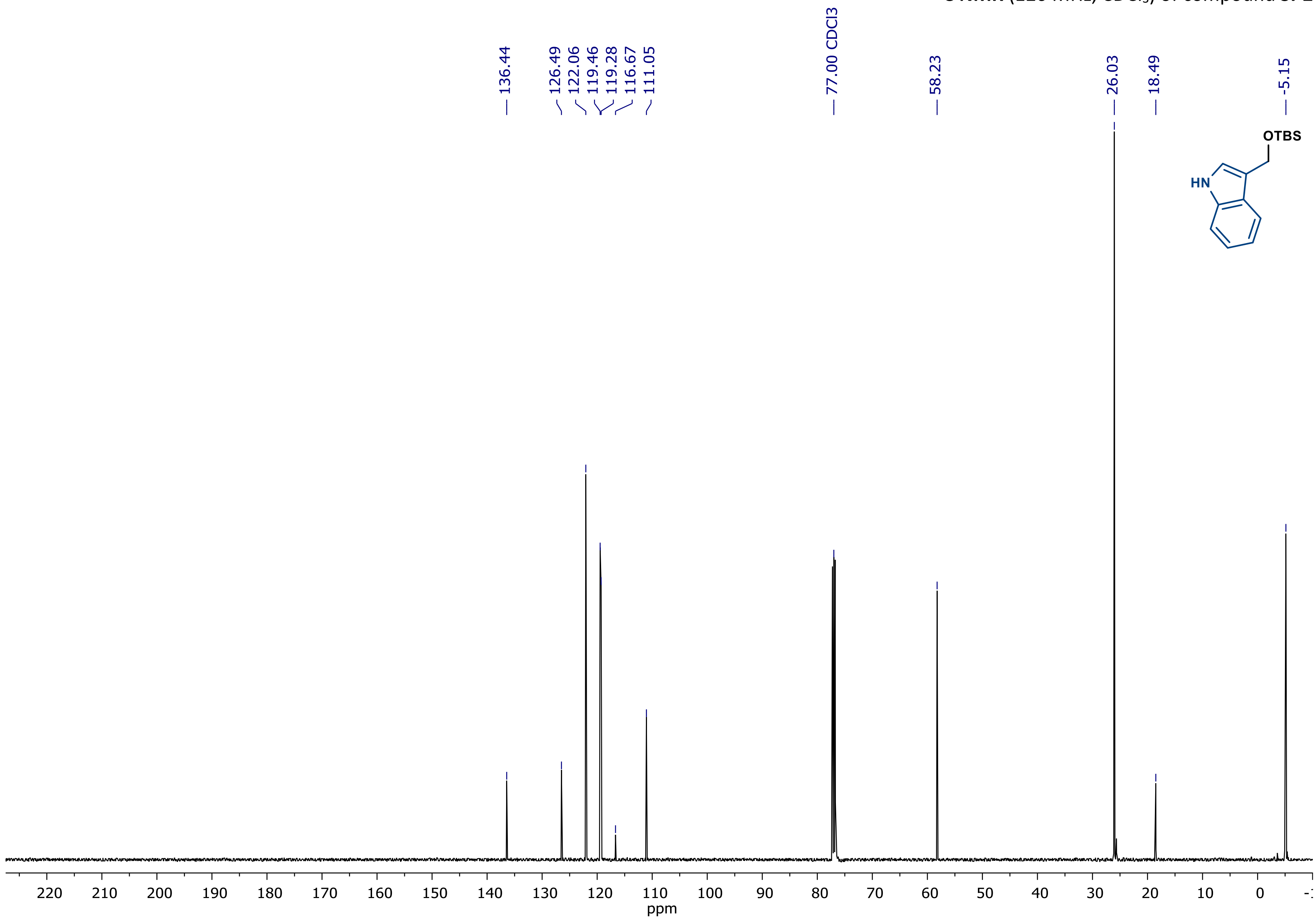
COSY of compound **SI-1**



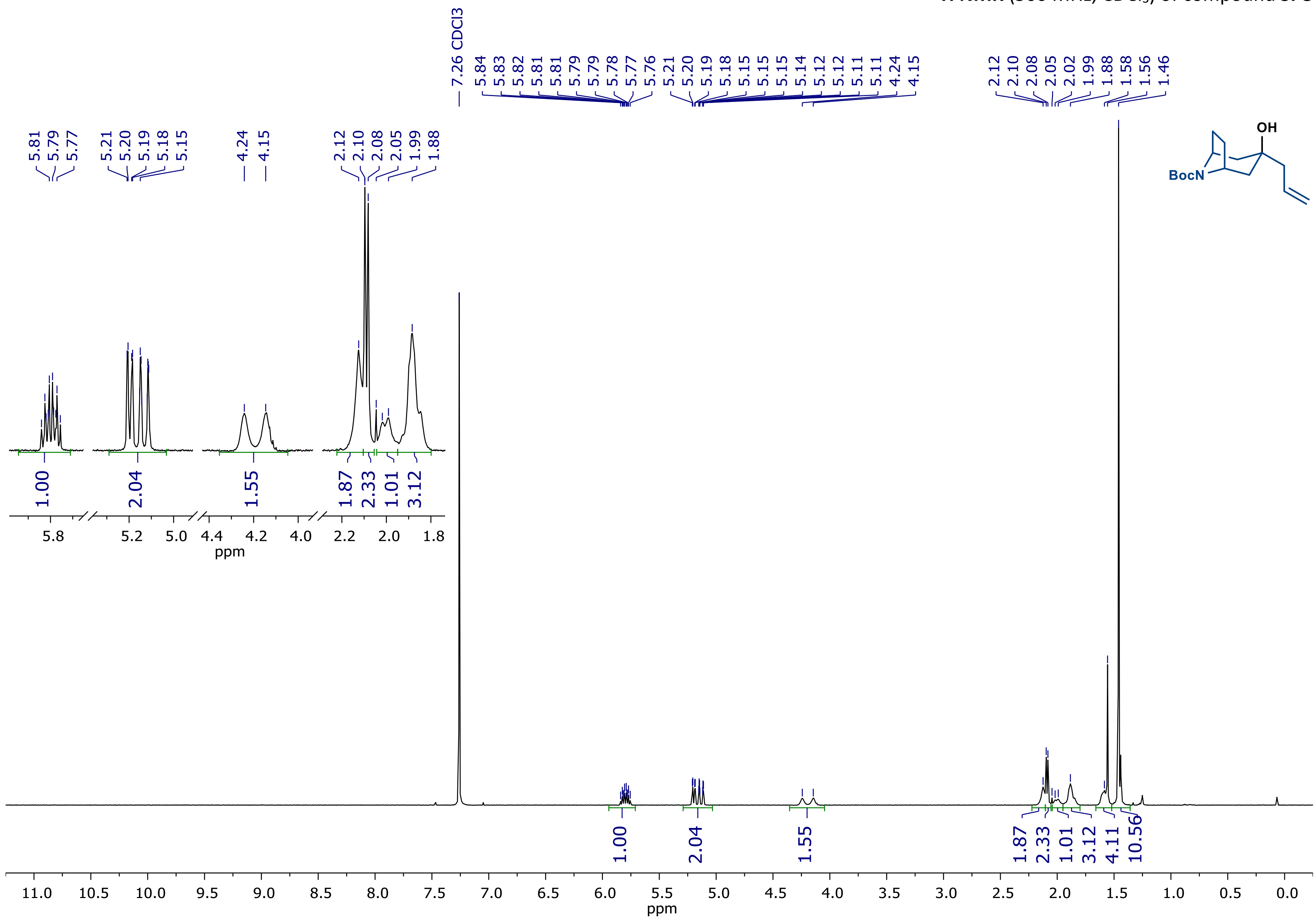
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **SI-2**



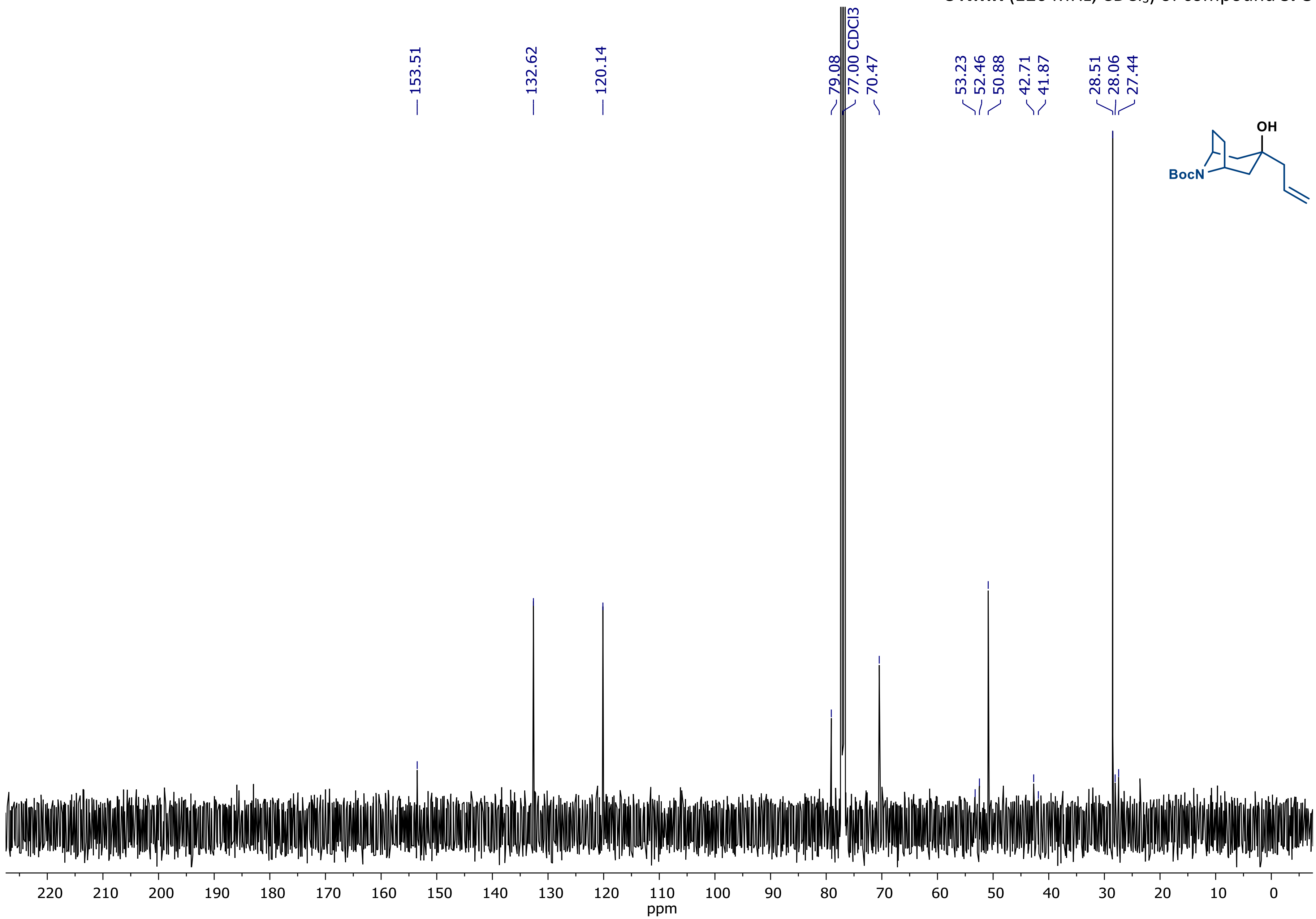
^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-2**



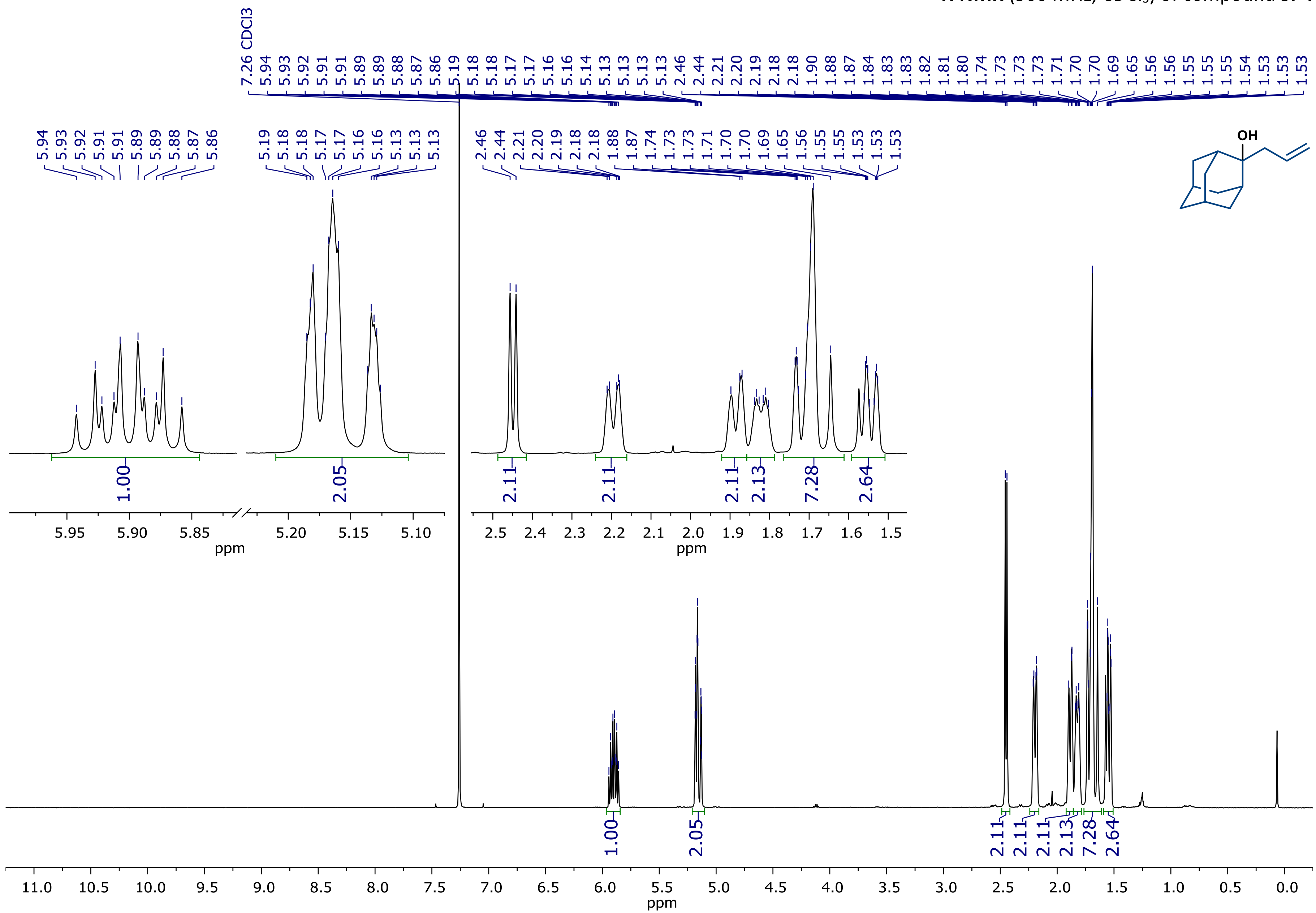
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **SI-3**



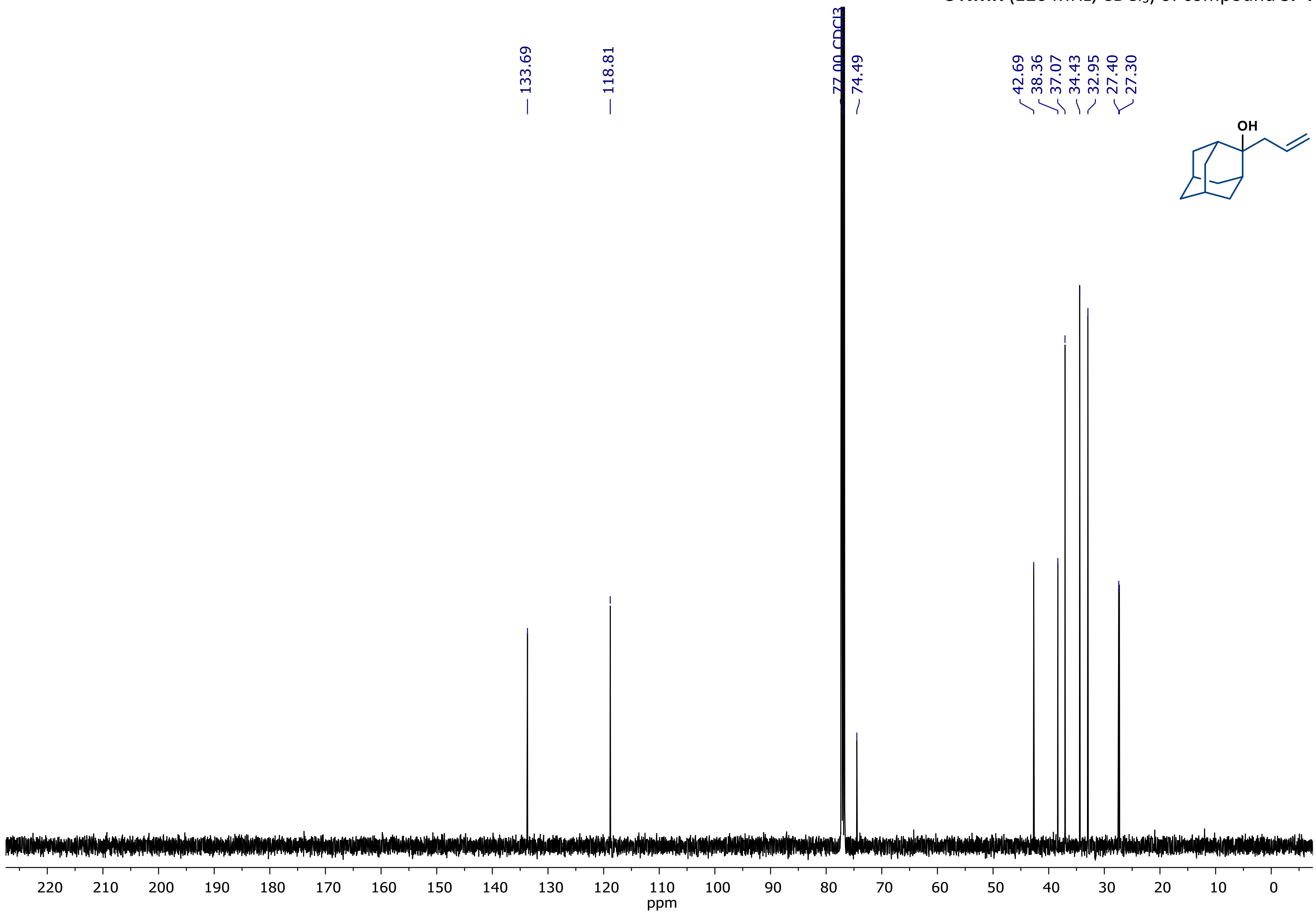
[13]C NMR (126 MHz, $CDCl_3$) of compound **SI-3**



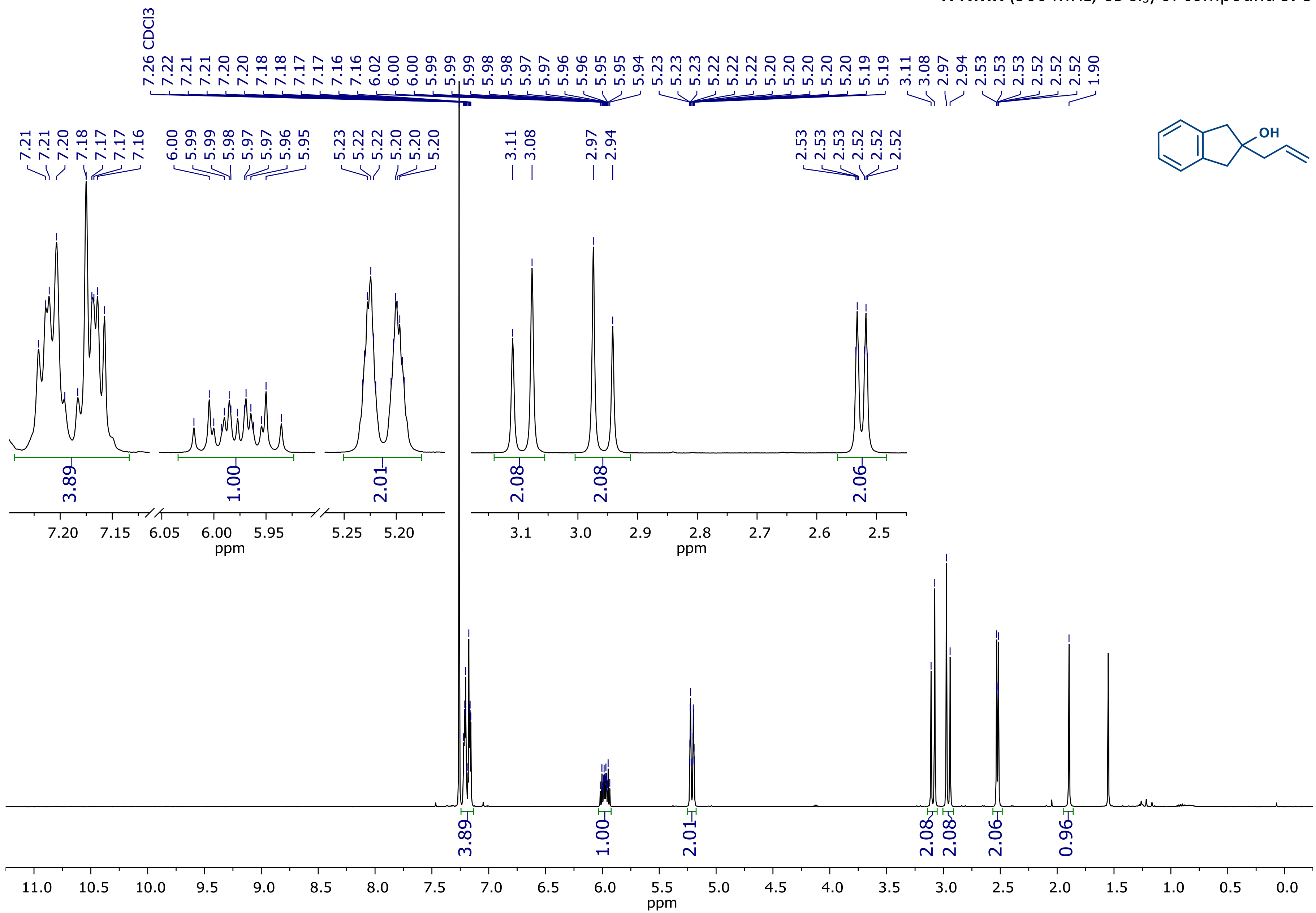
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-4**



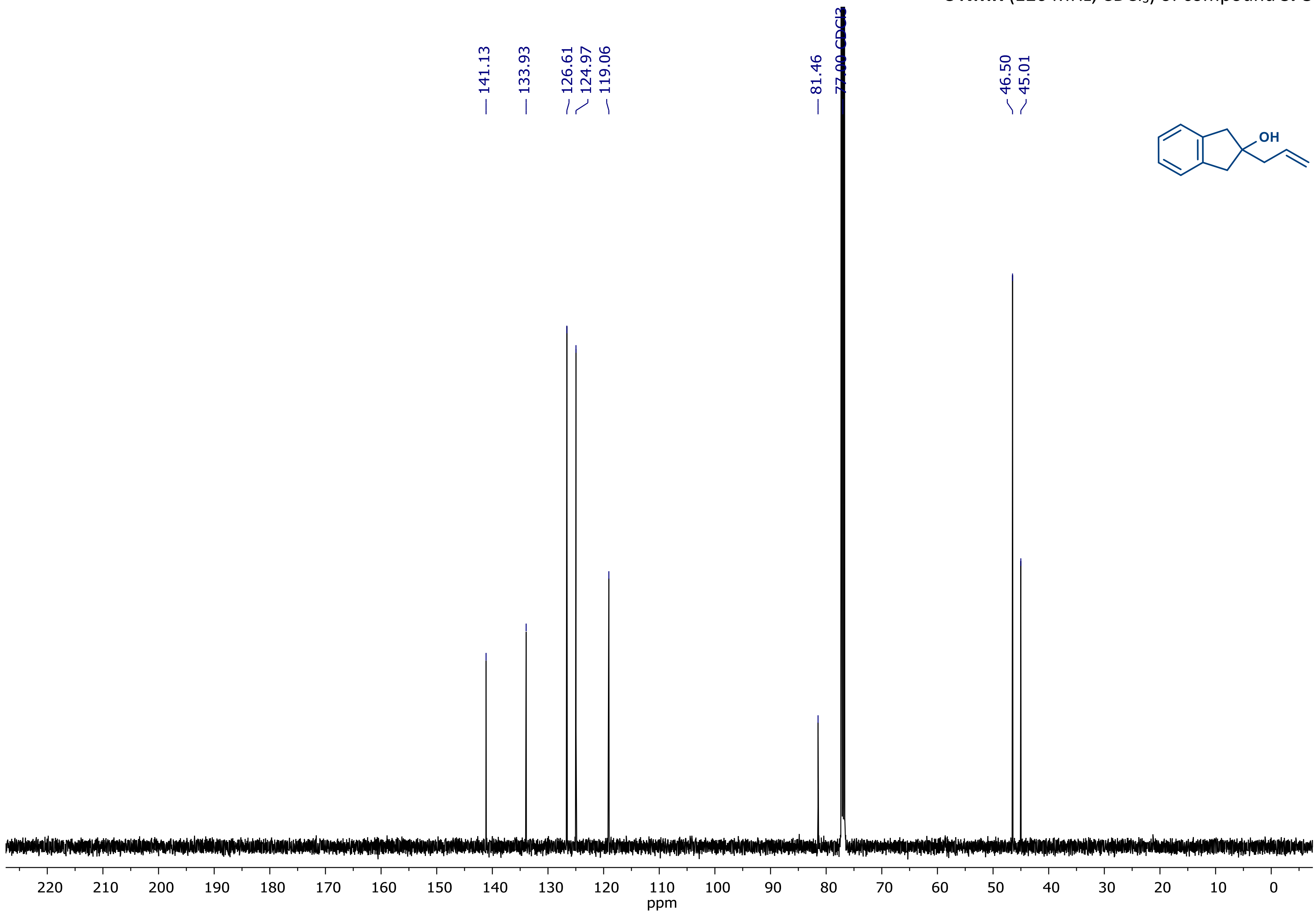
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **SI-4**



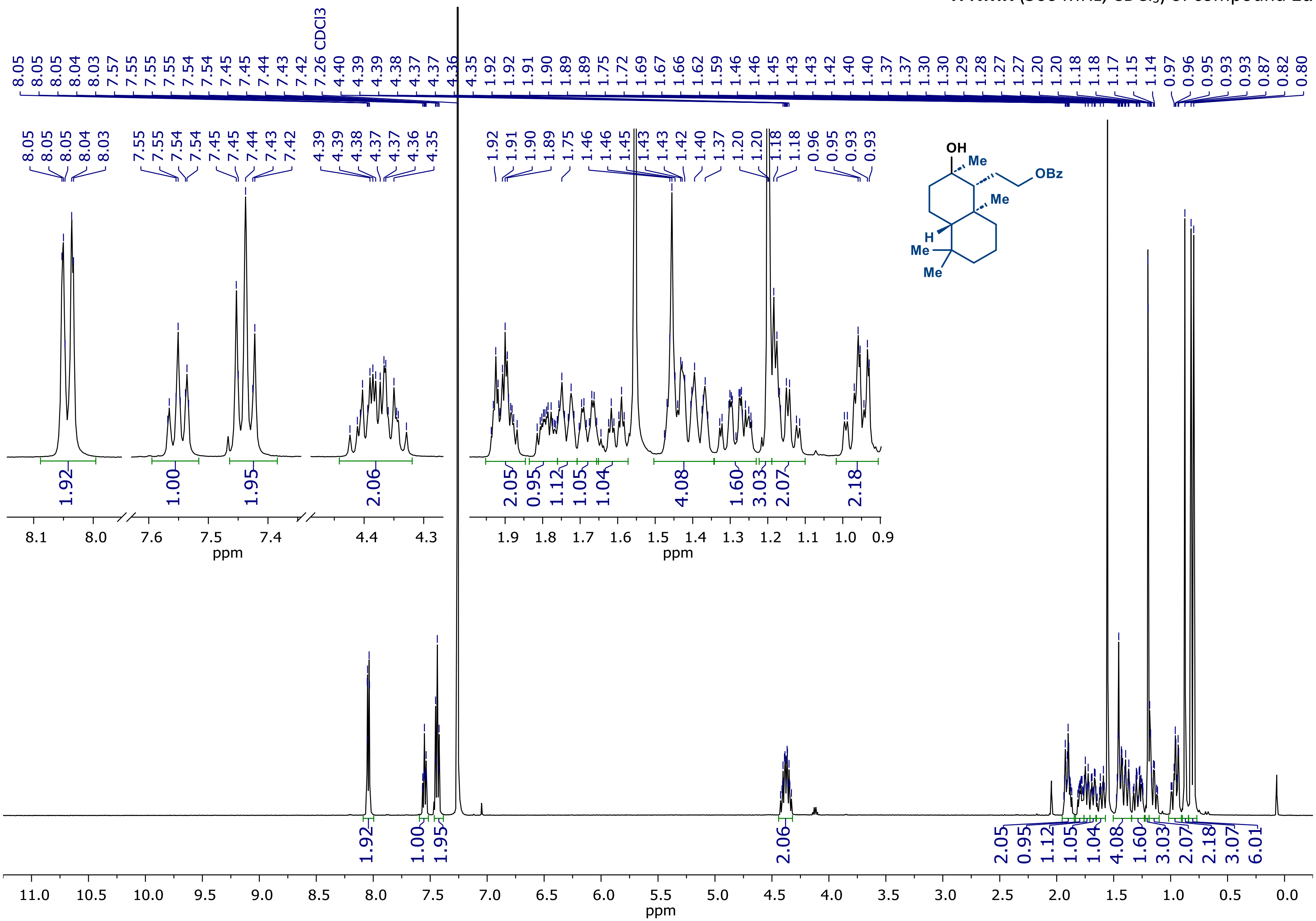
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **SI-5**



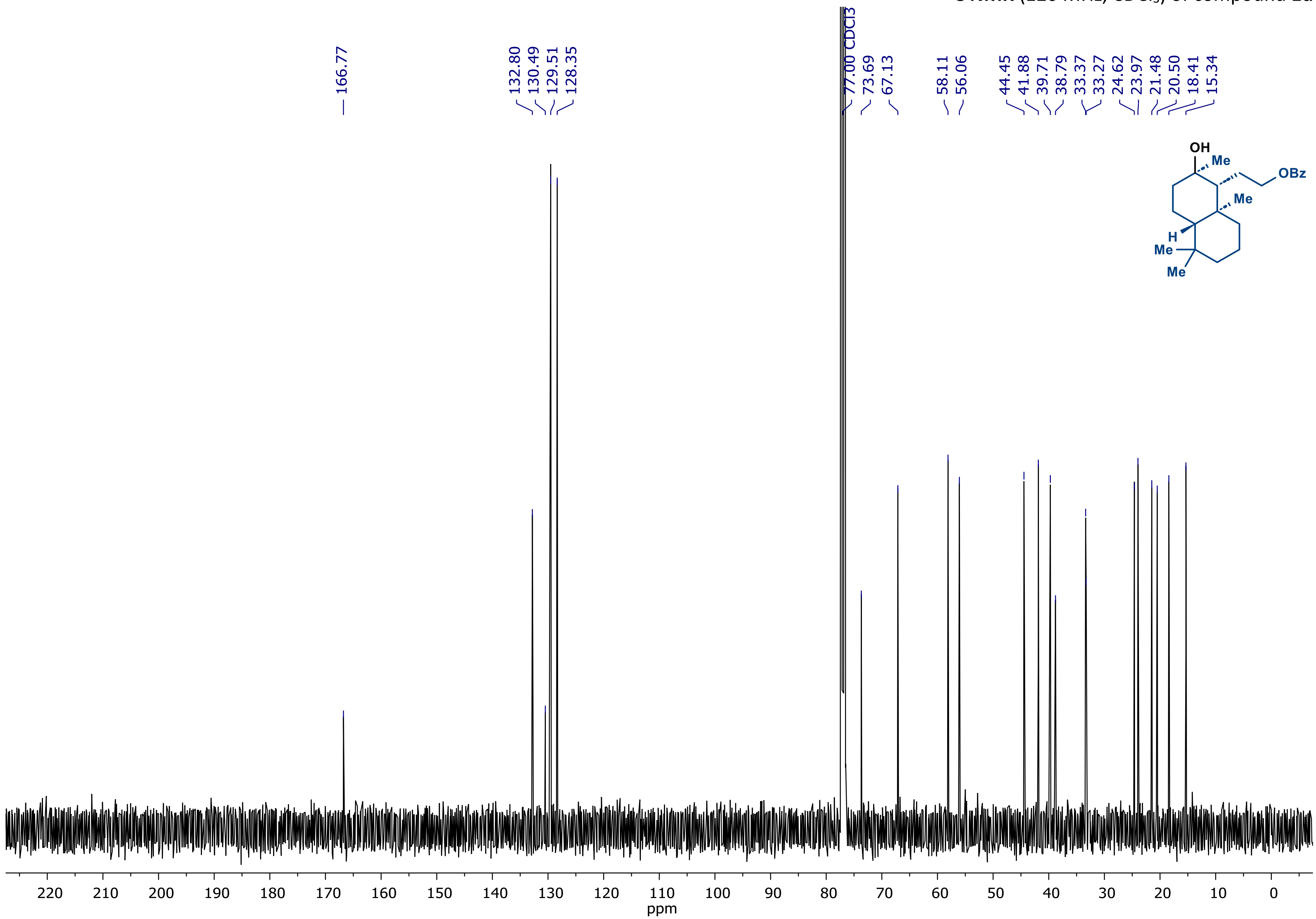
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **SI-5**



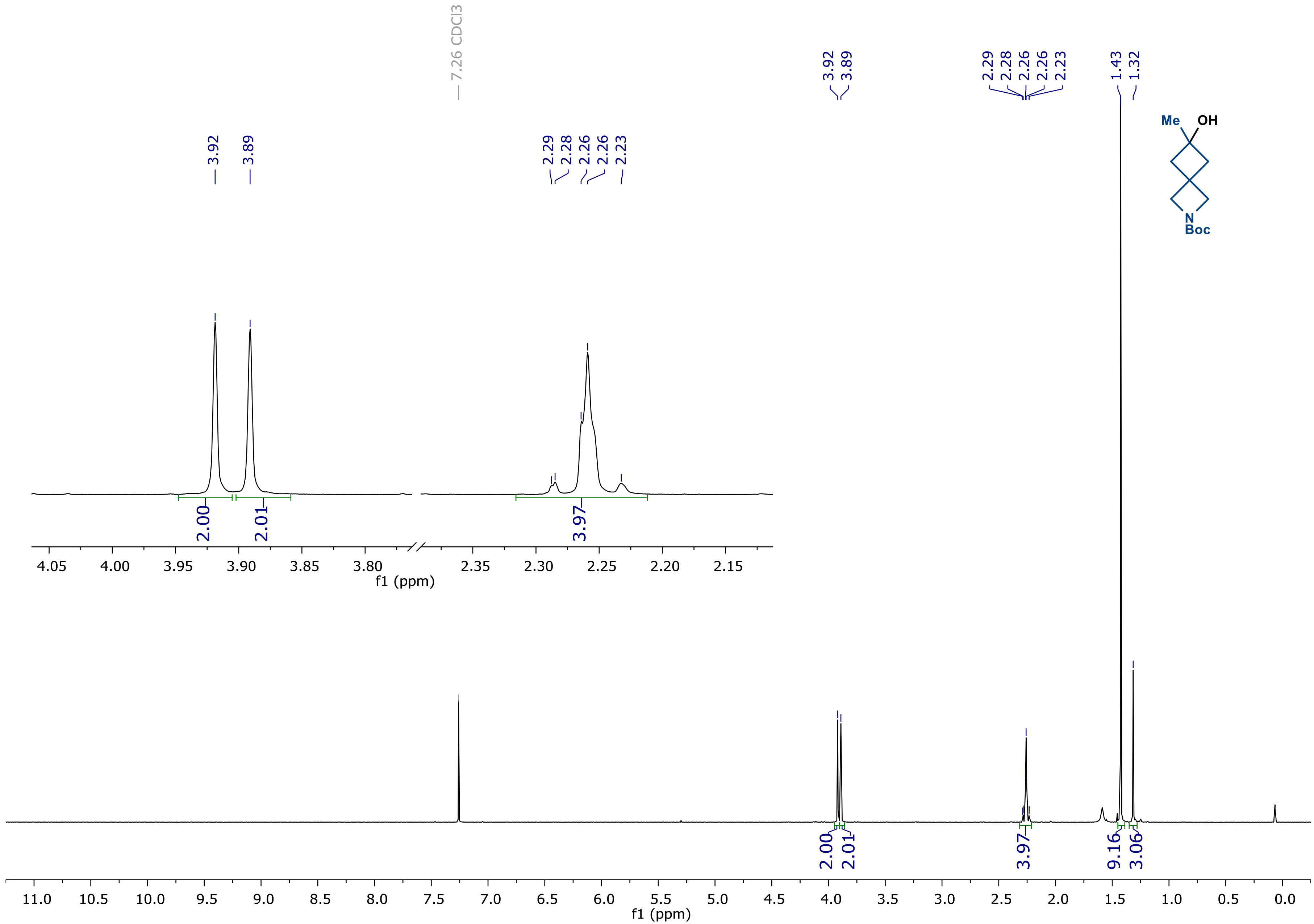
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1d**



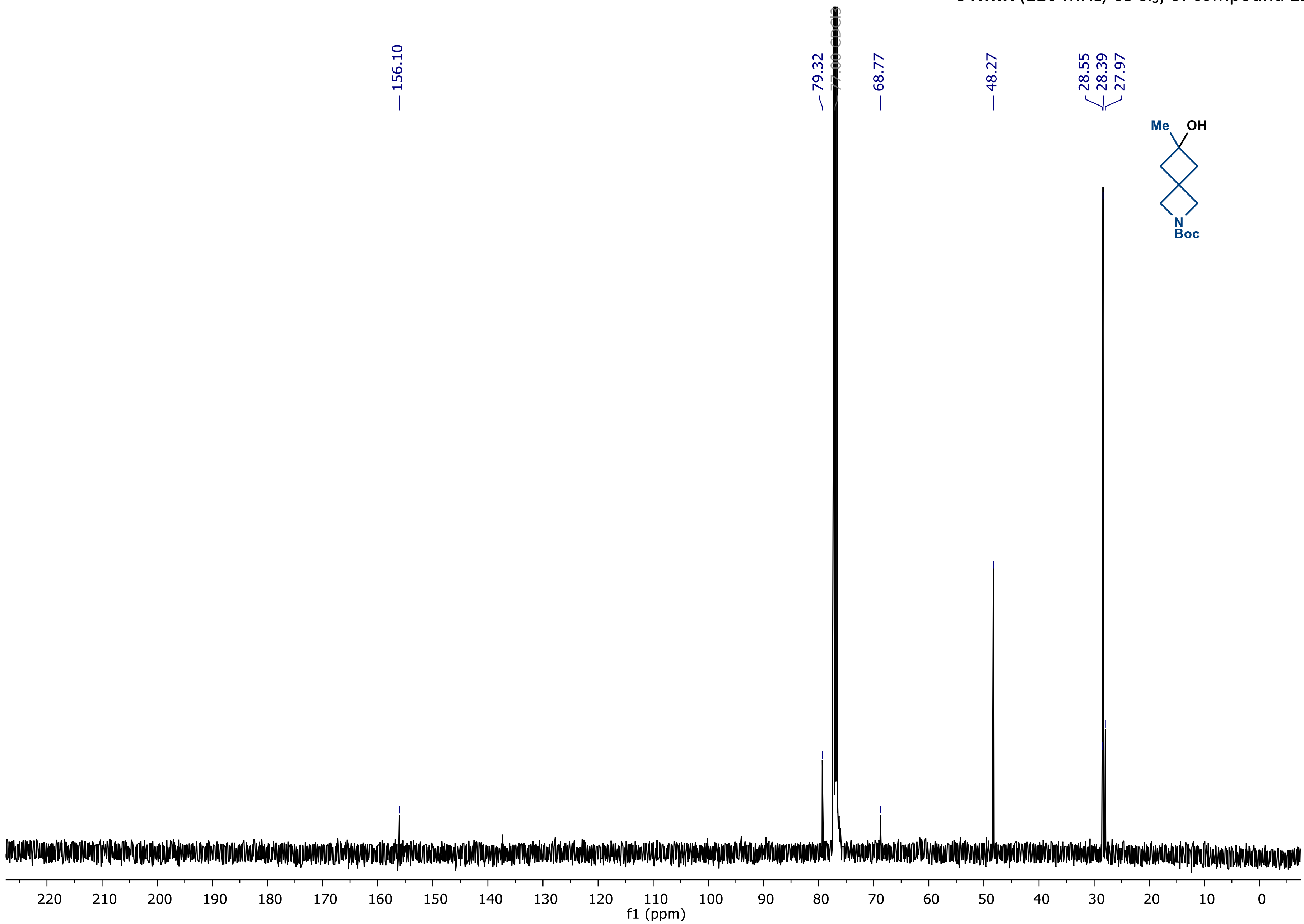
^{13}C NMR (126 MHz, $CDCl_3$) of compound **1d**



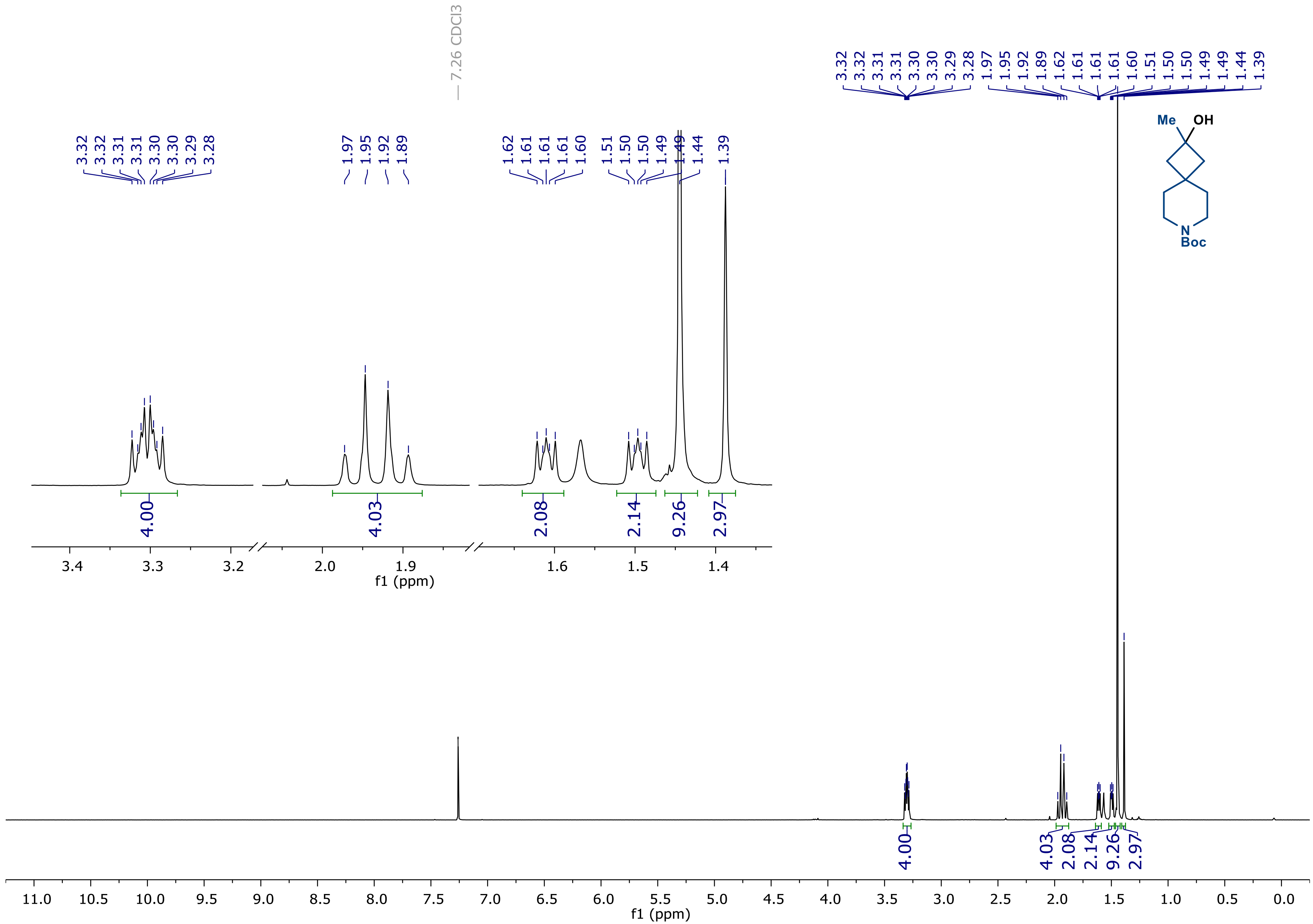
[1]H NMR (500 MHz, $CDCl_3$) of compound **1i**



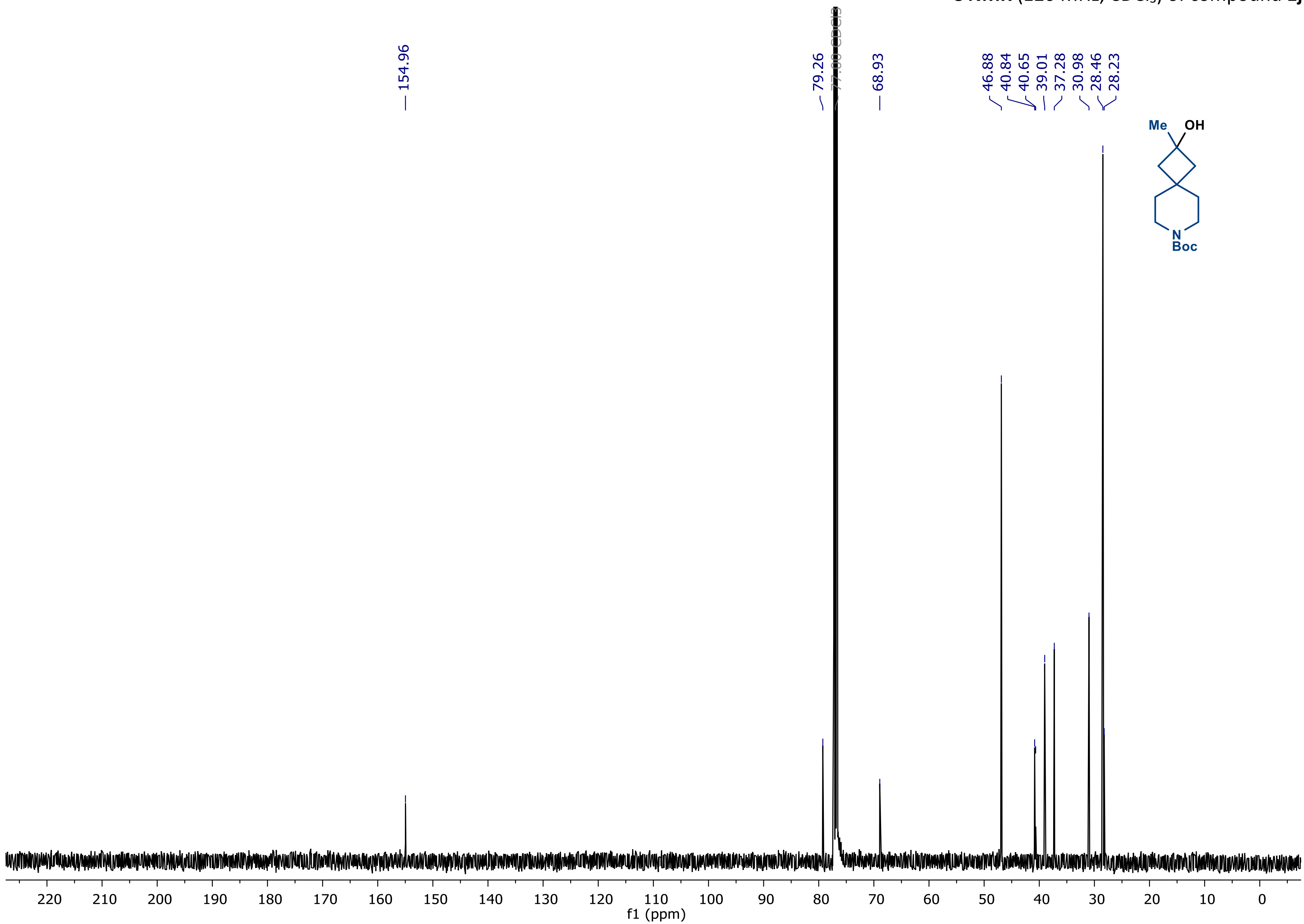
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **1i**



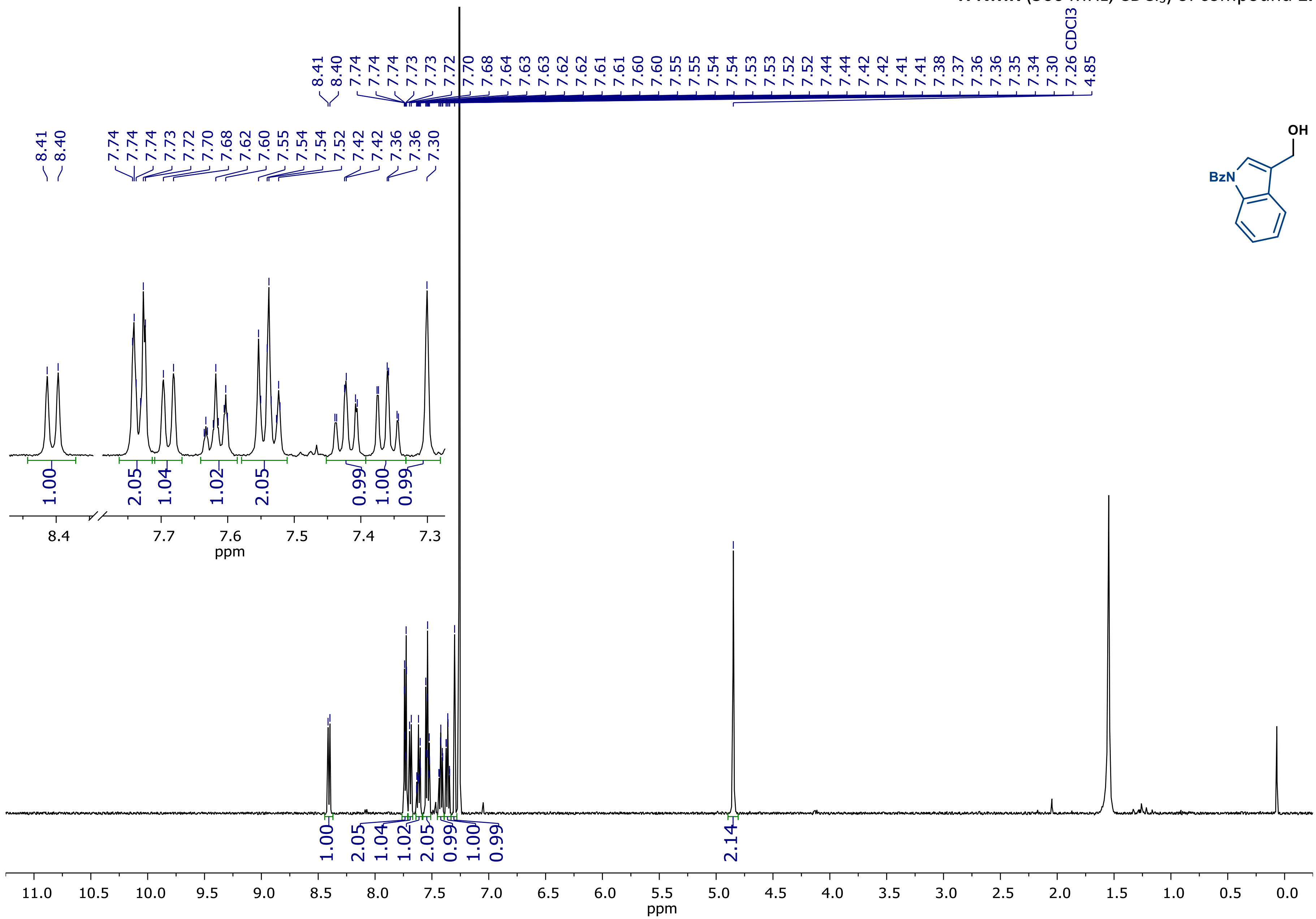
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **1j**



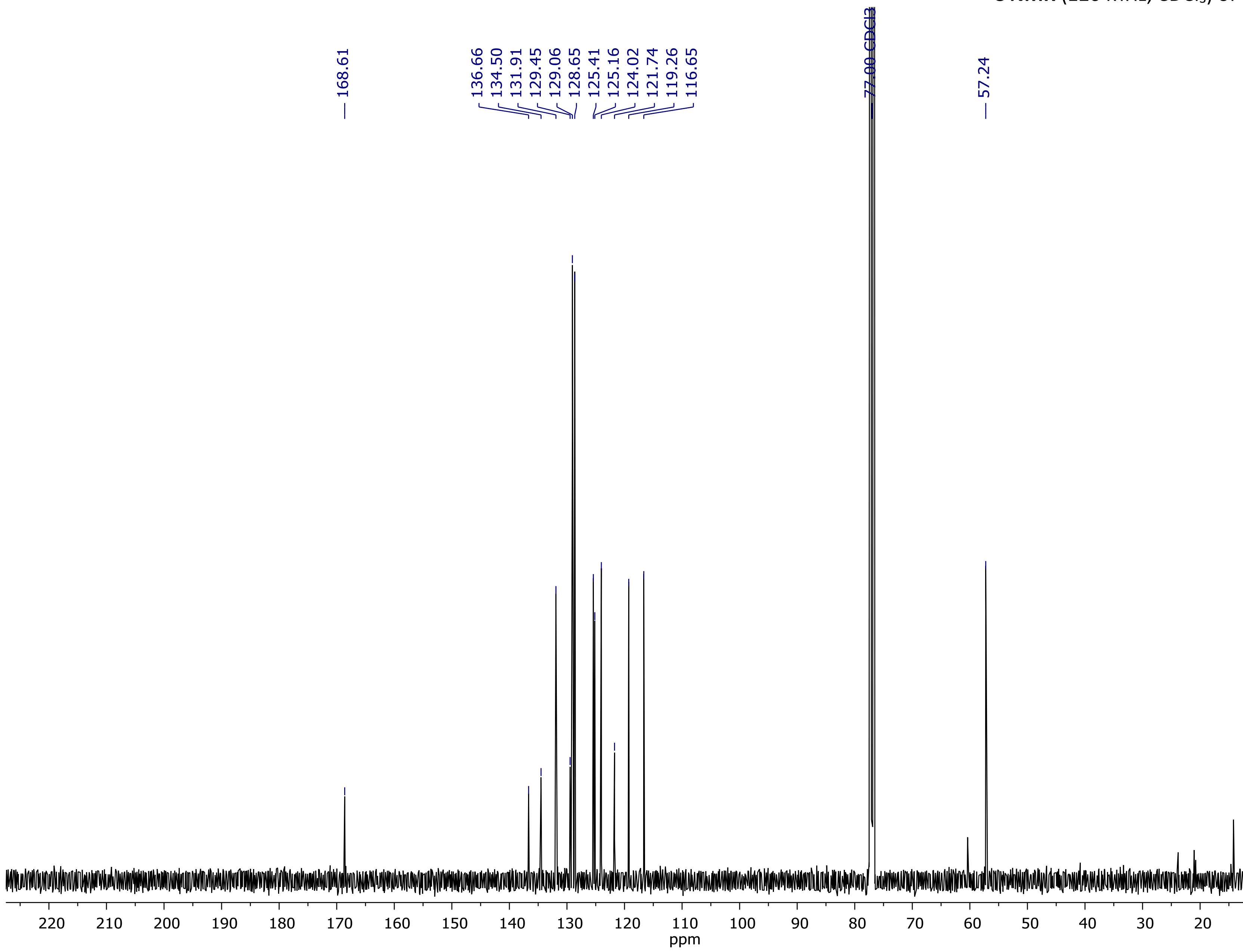
^{13}C NMR (126 MHz, $CDCl_3$) of compound **1j**

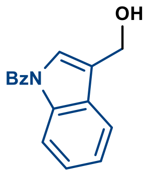


^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **1l**

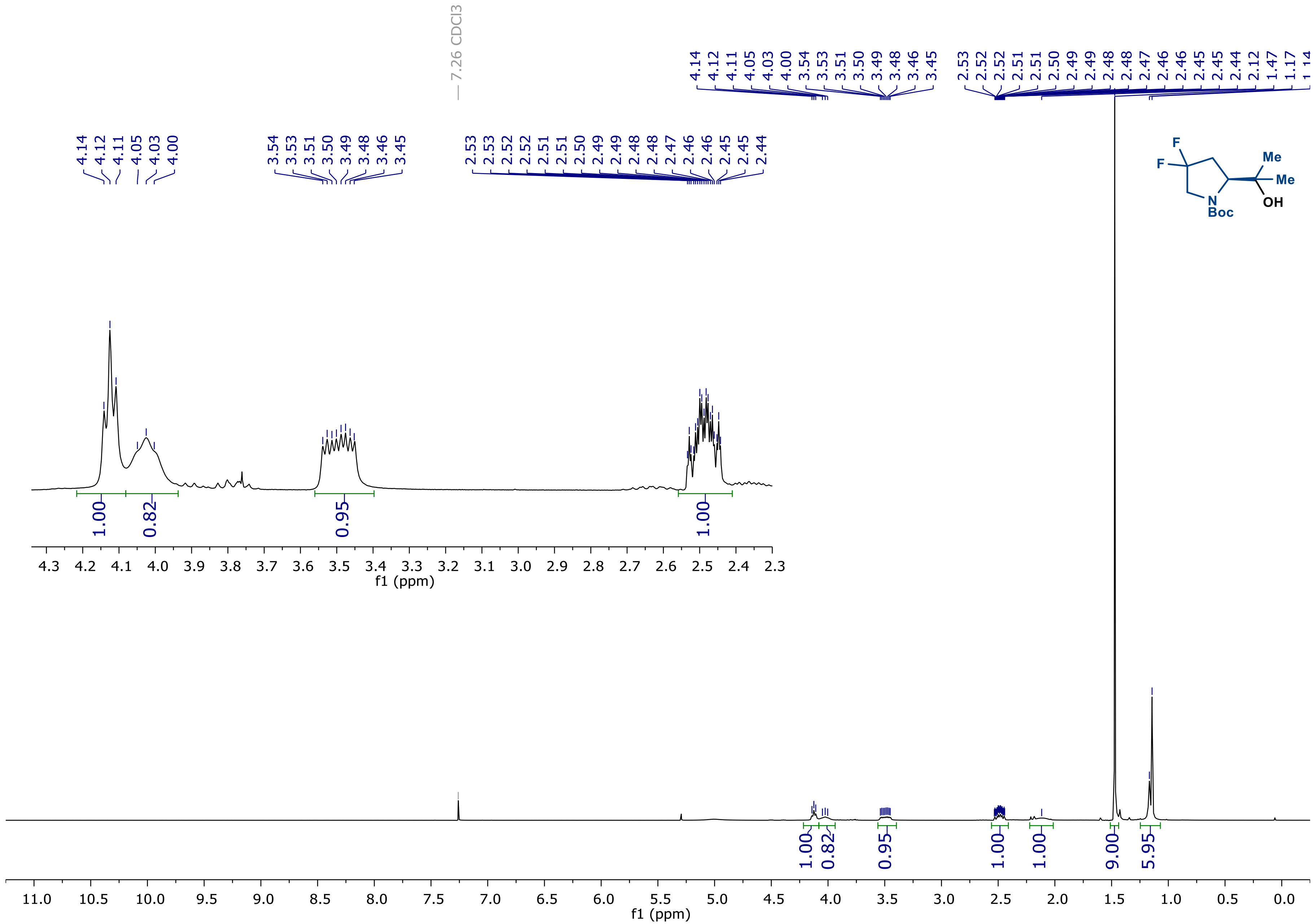


^{13}C NMR (126 MHz, $CDCl_3$) of compound **1l**

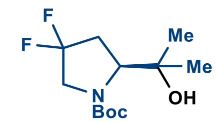


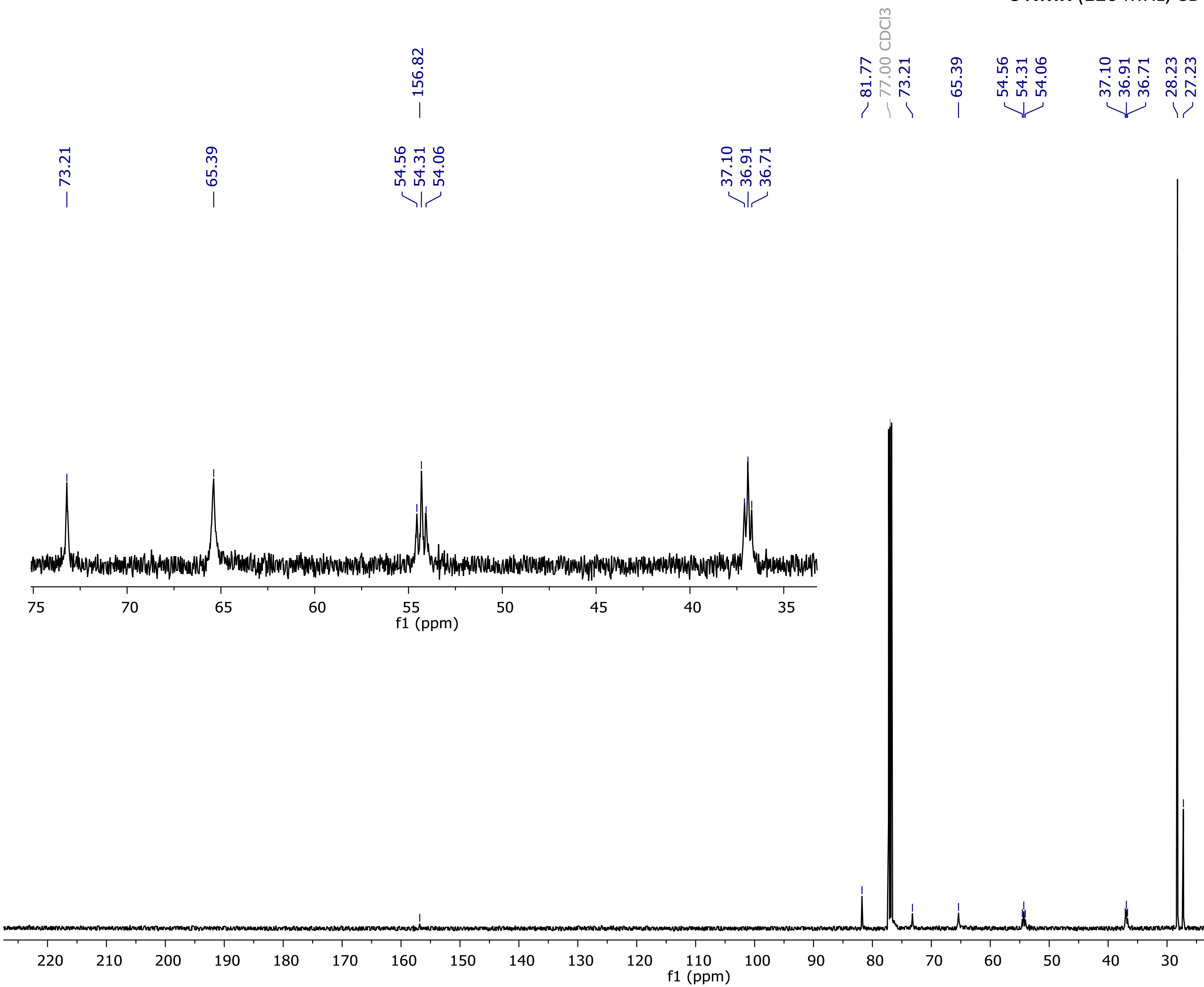


^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **1p**

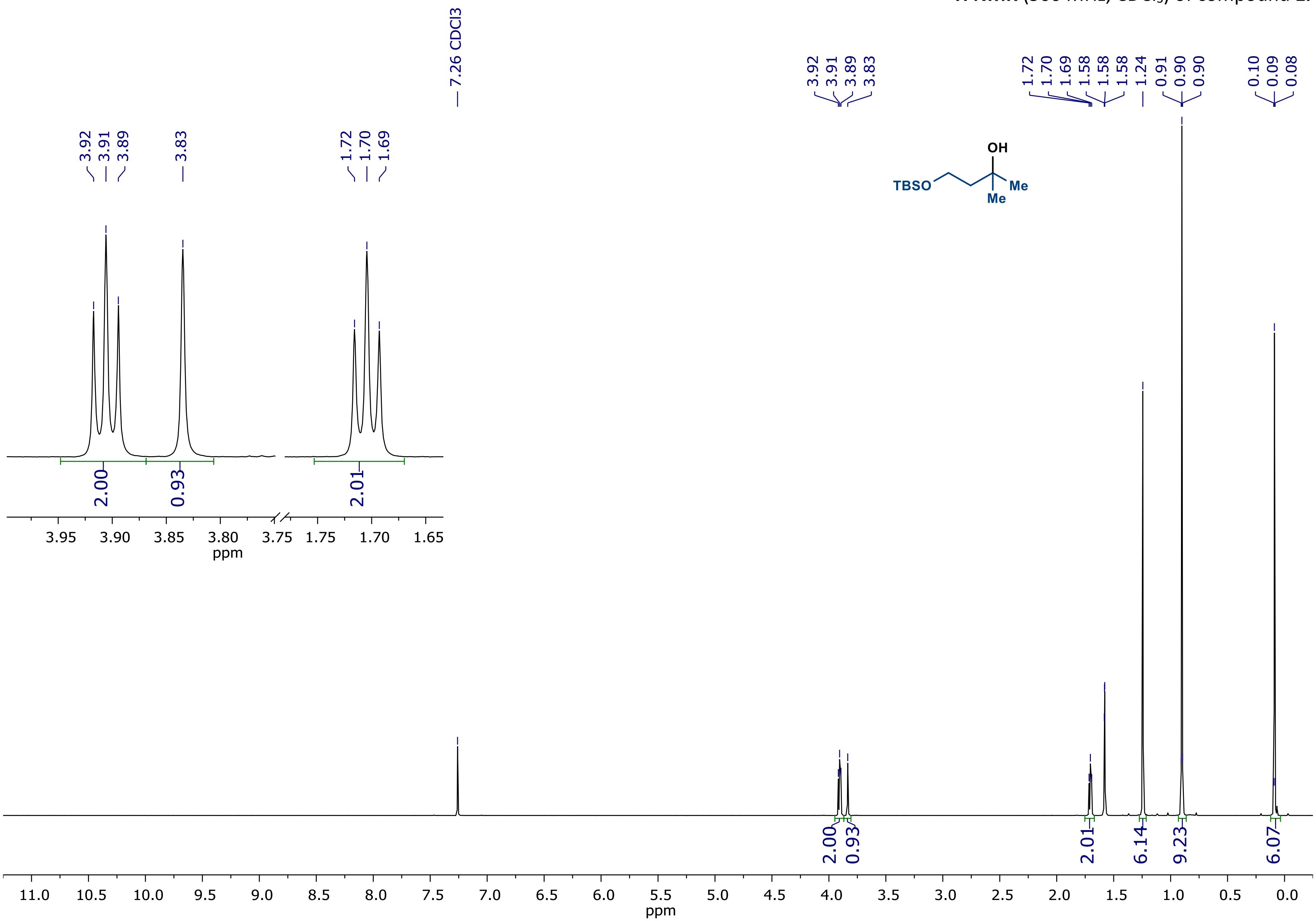


^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **1p**

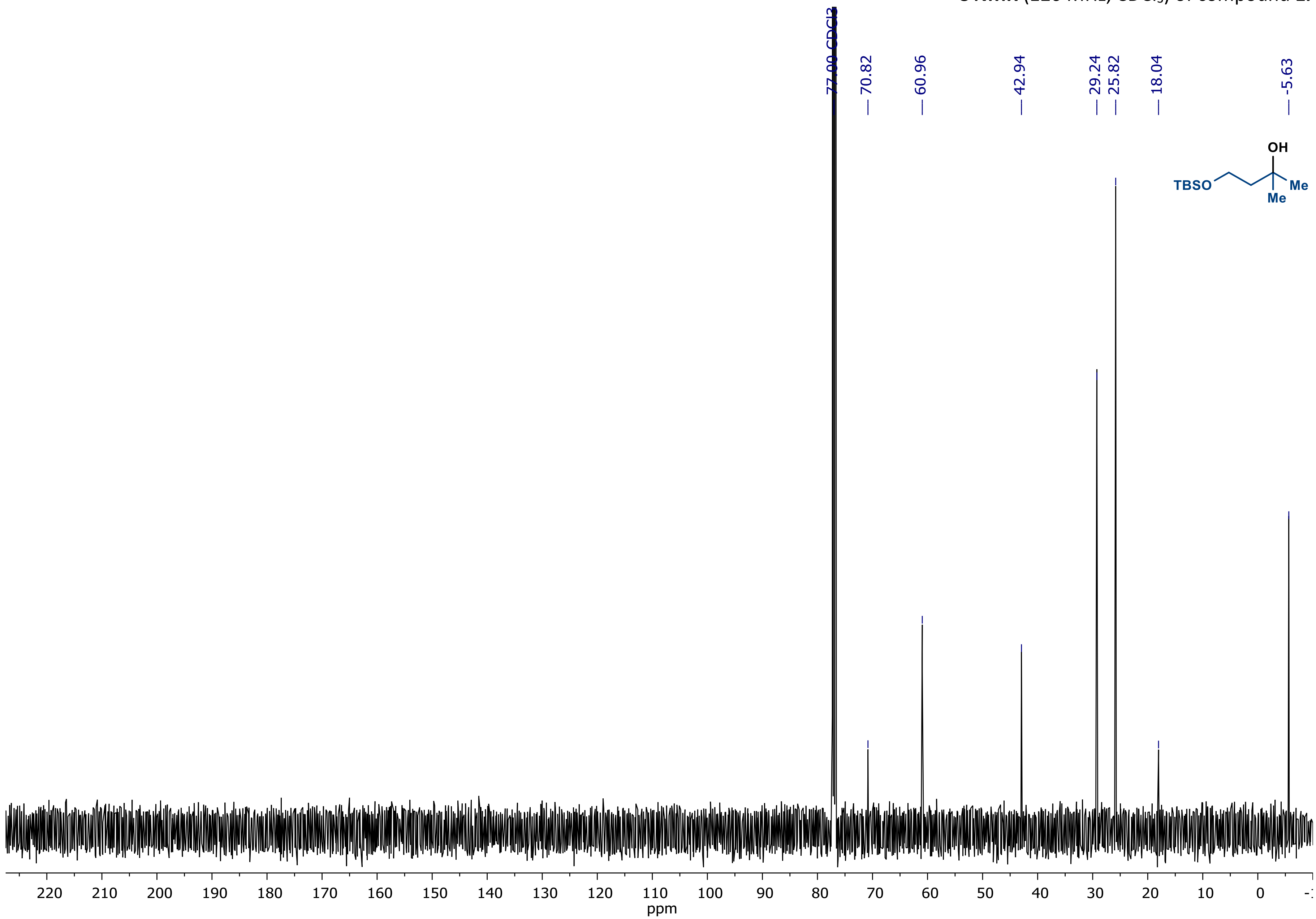




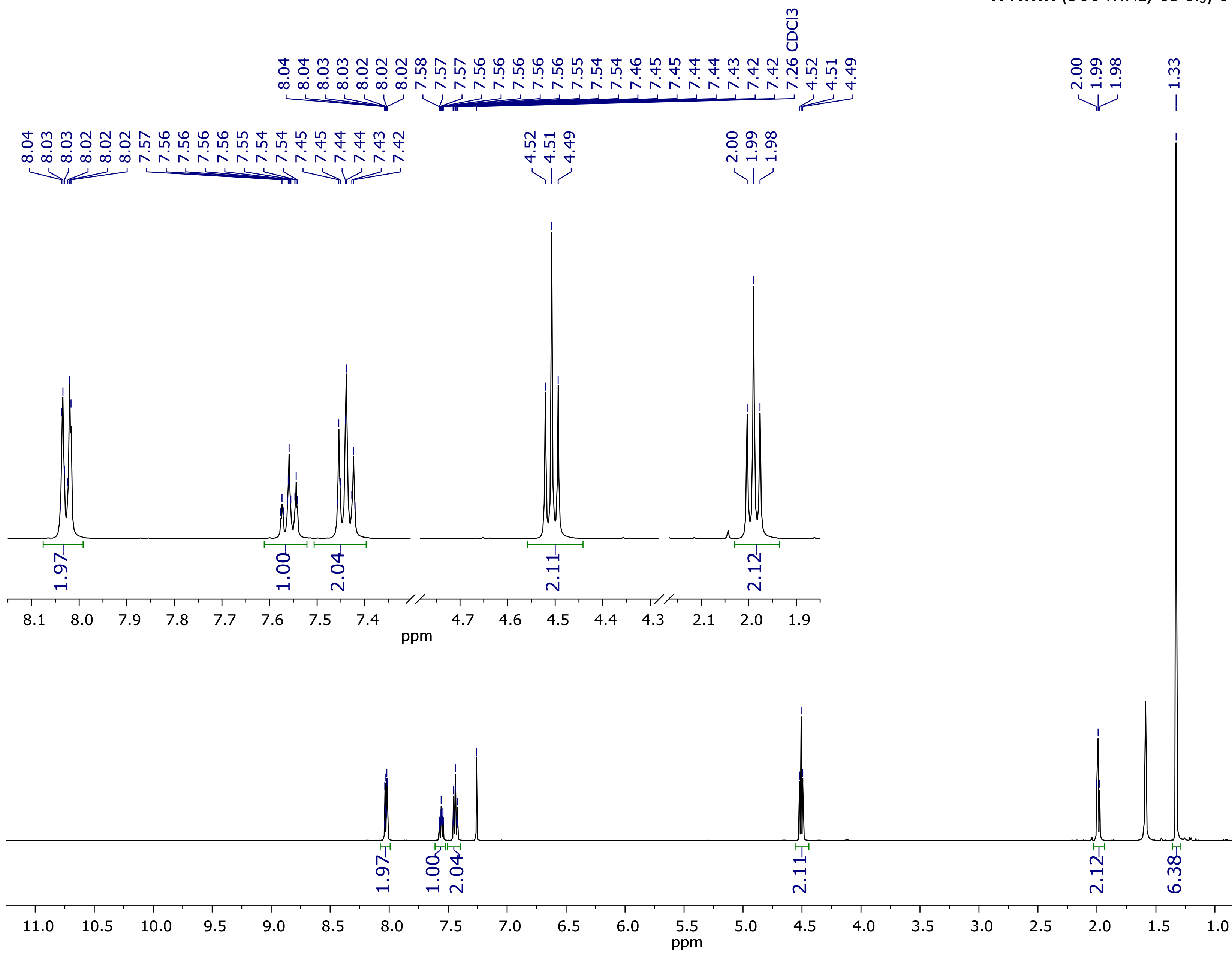
[1]**H NMR** (500 MHz, $CDCl_3$) of compound **1r**

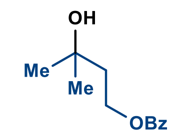


^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **1r**

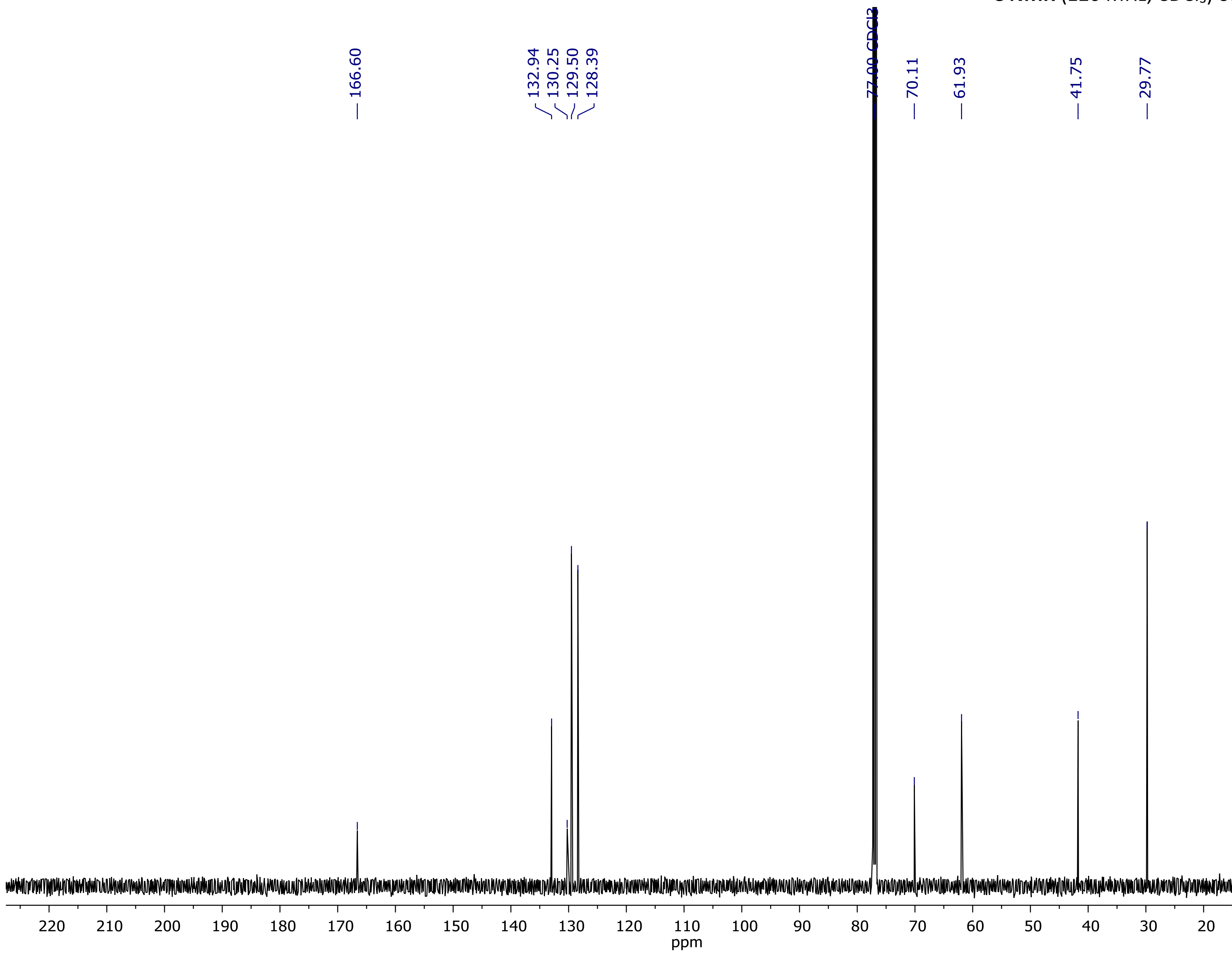


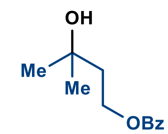
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1s**



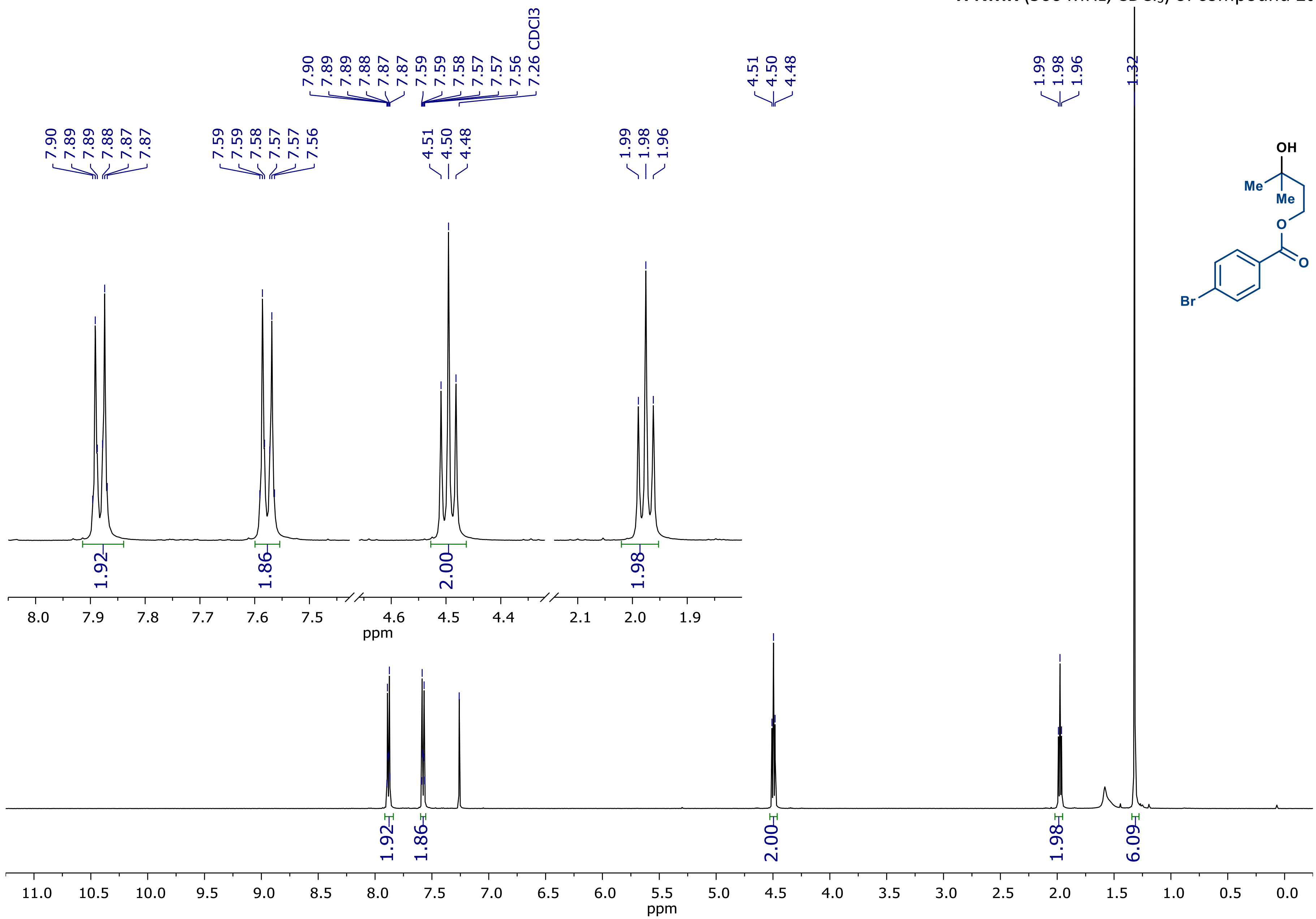


^{13}C NMR (126 MHz, $CDCl_3$) of compound **1s**

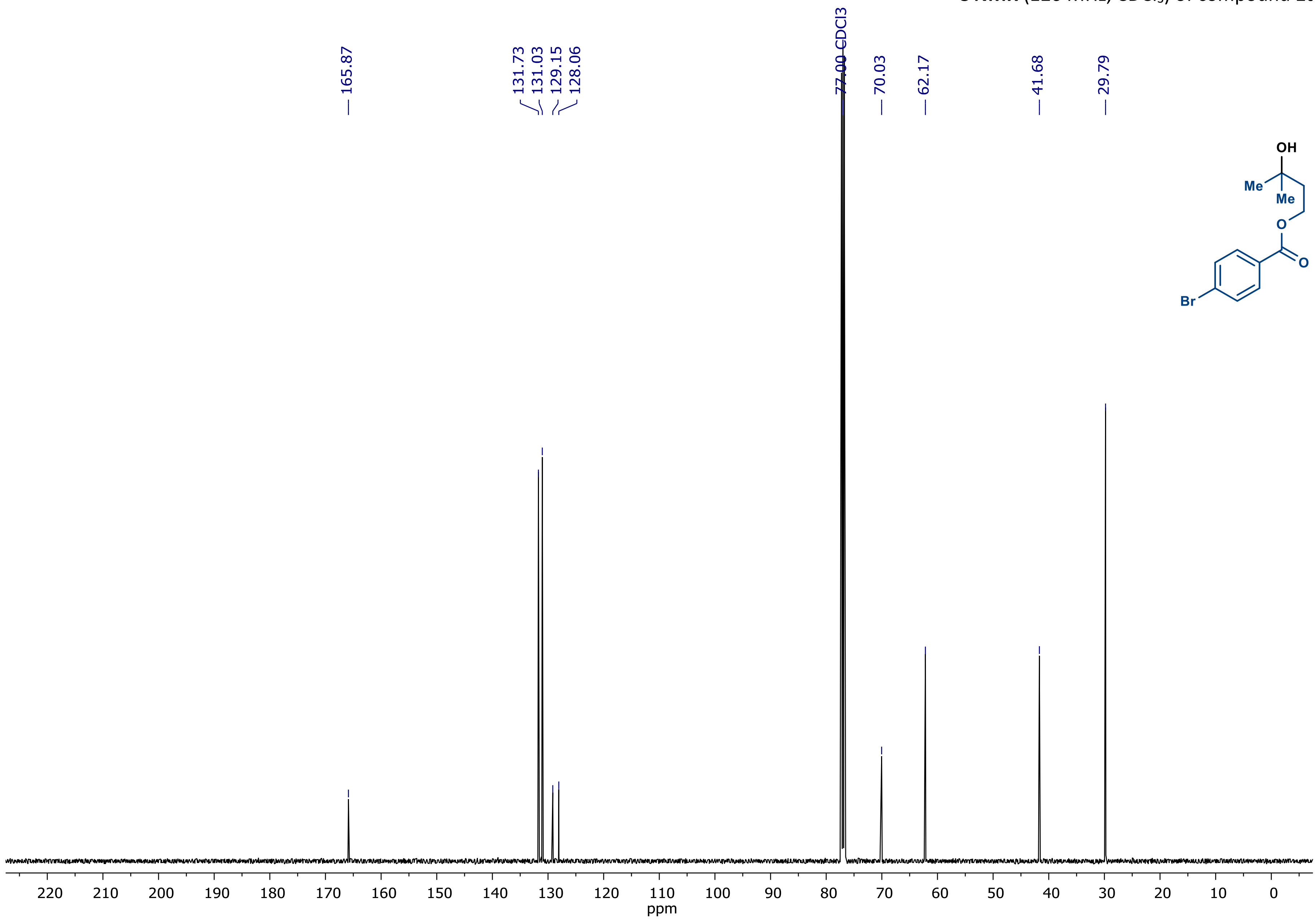




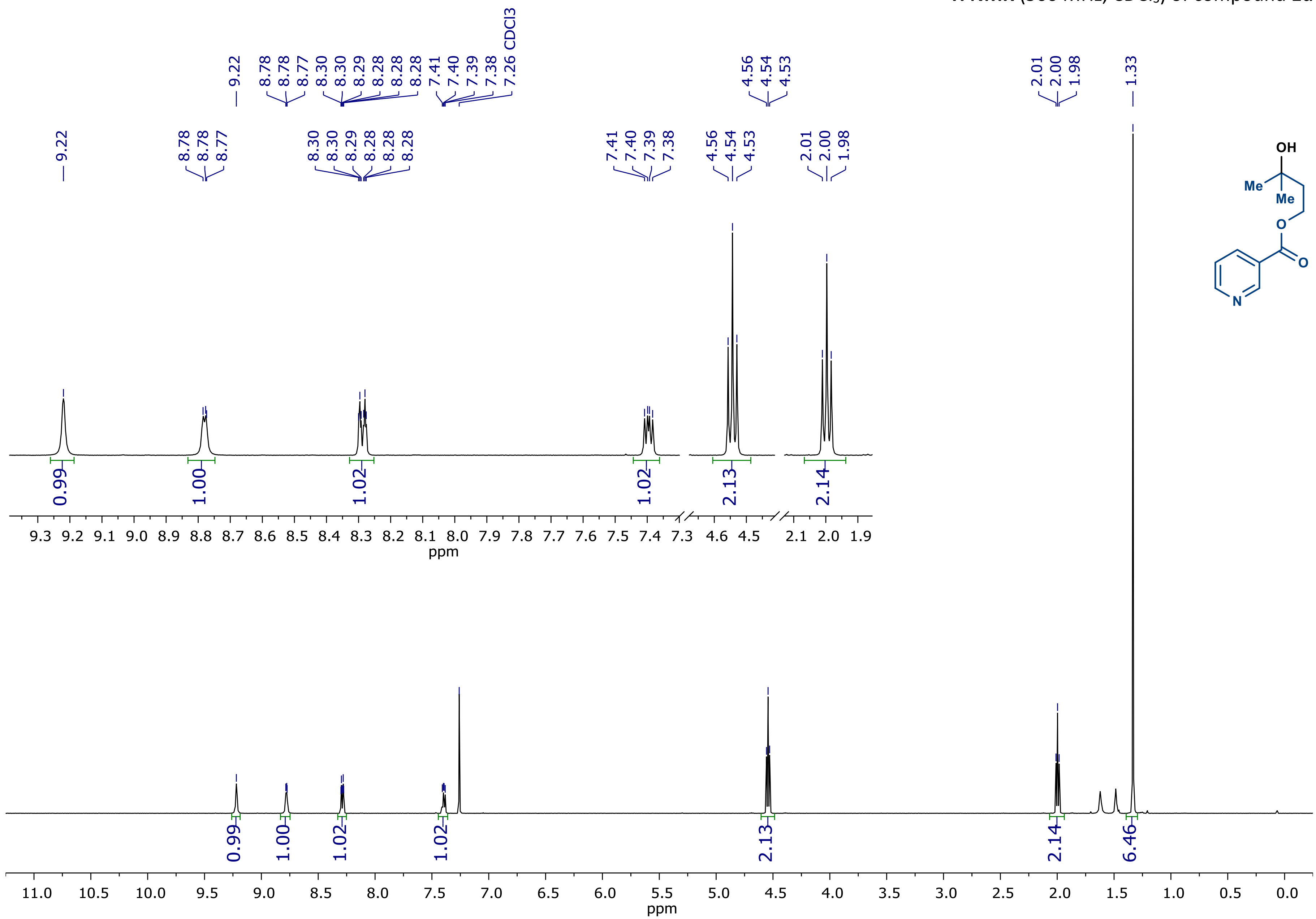
[1]H NMR (500 MHz, $CDCl_3$) of compound **1t**



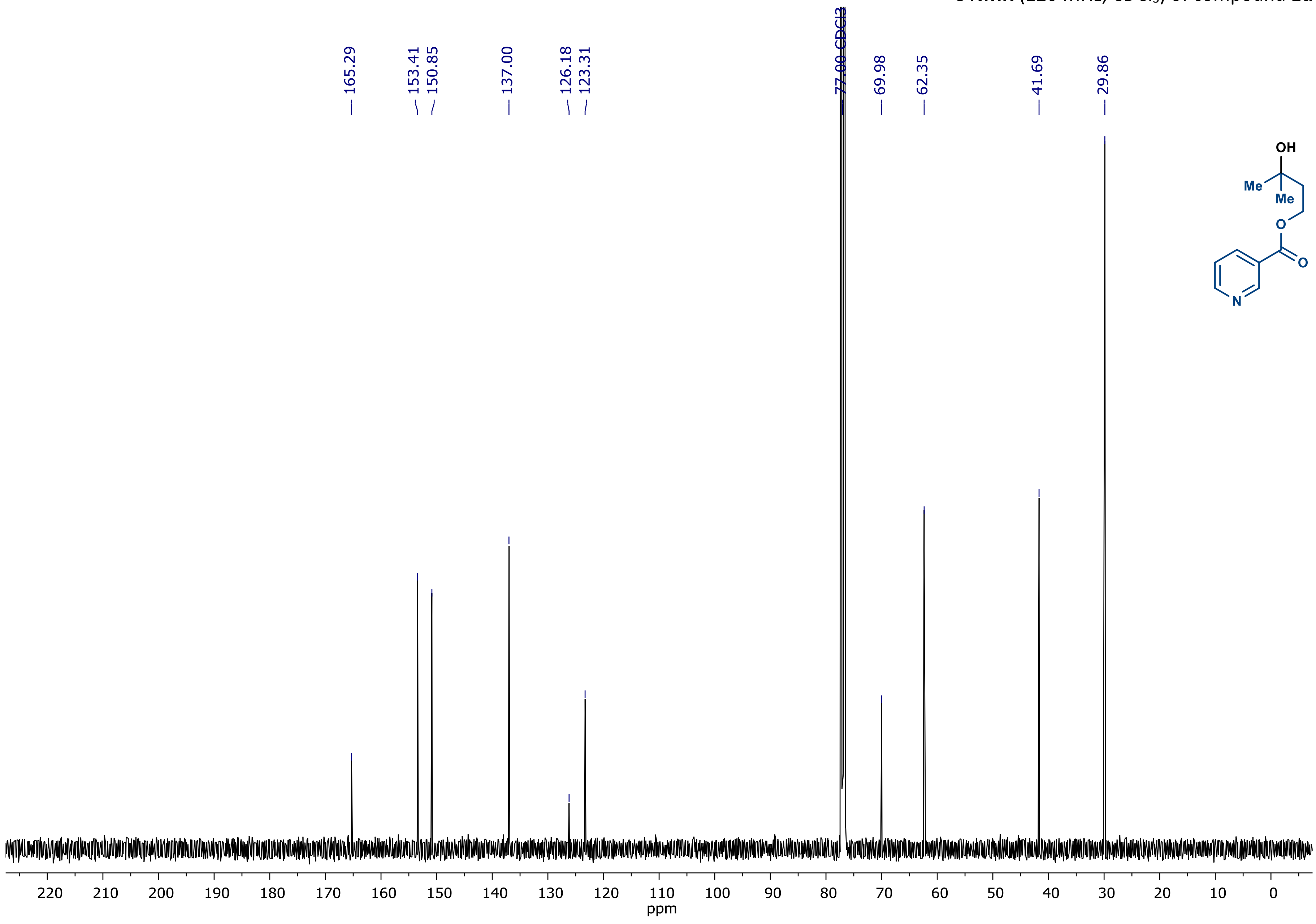
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **1t**



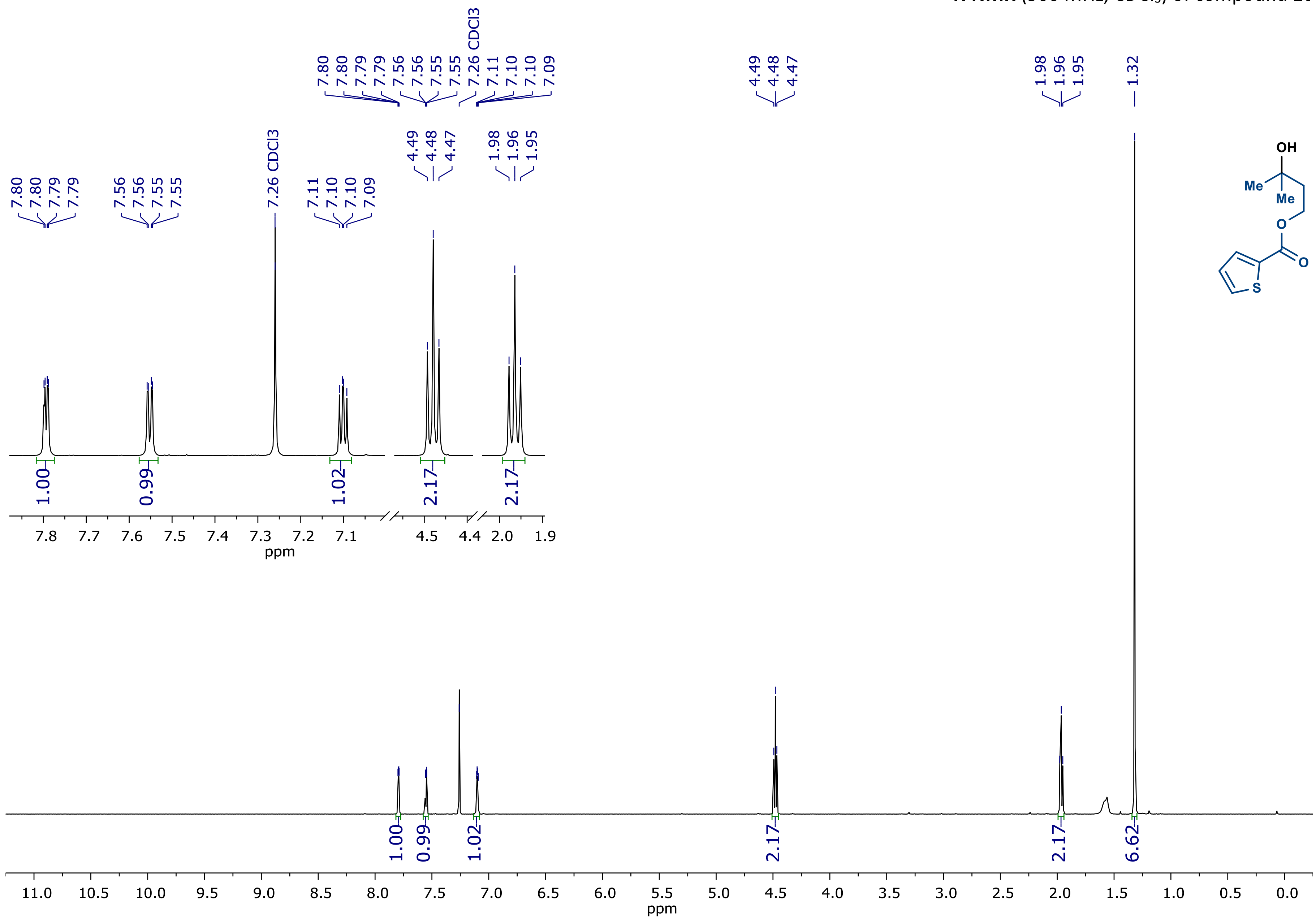
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1u**



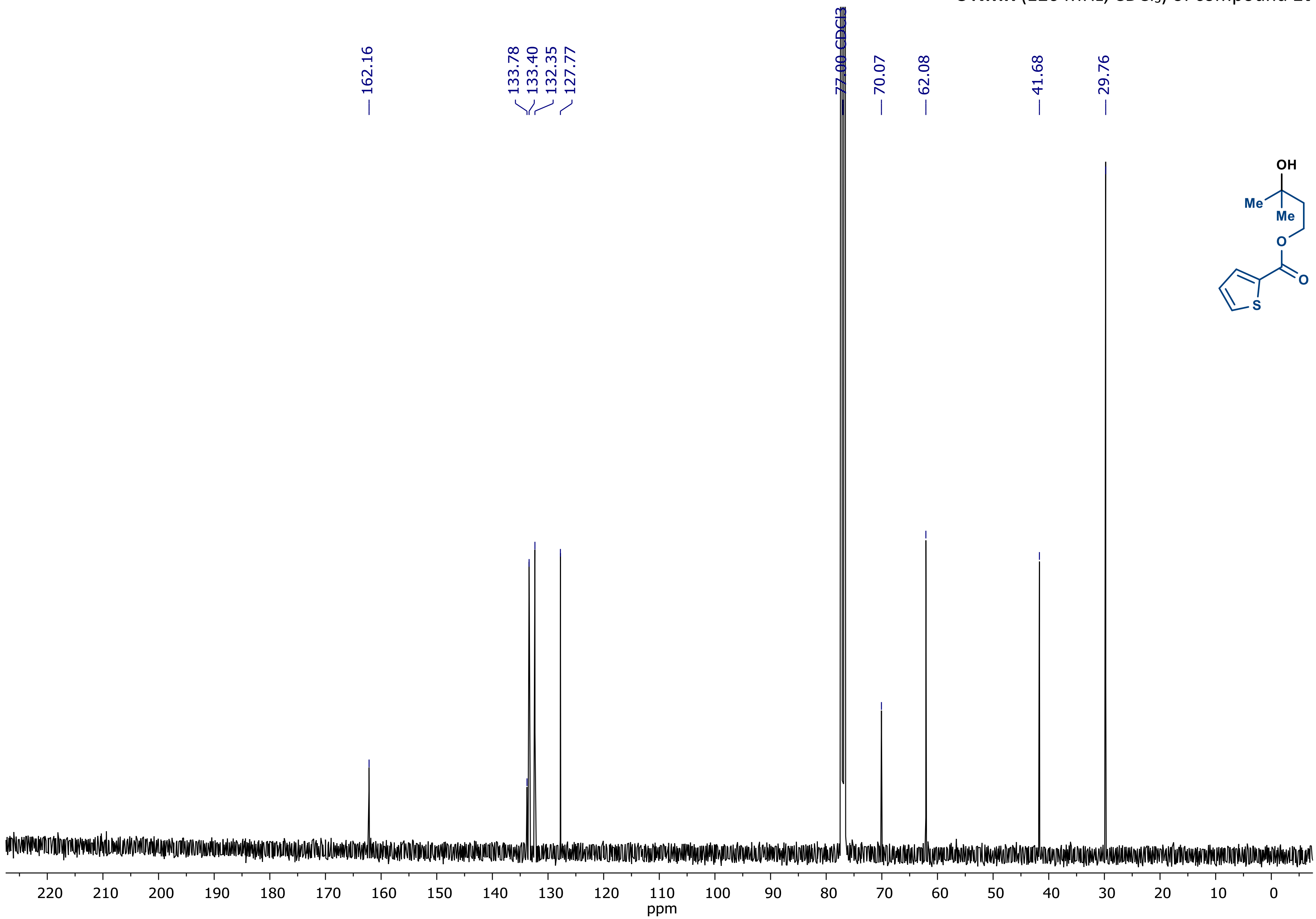
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **1u**



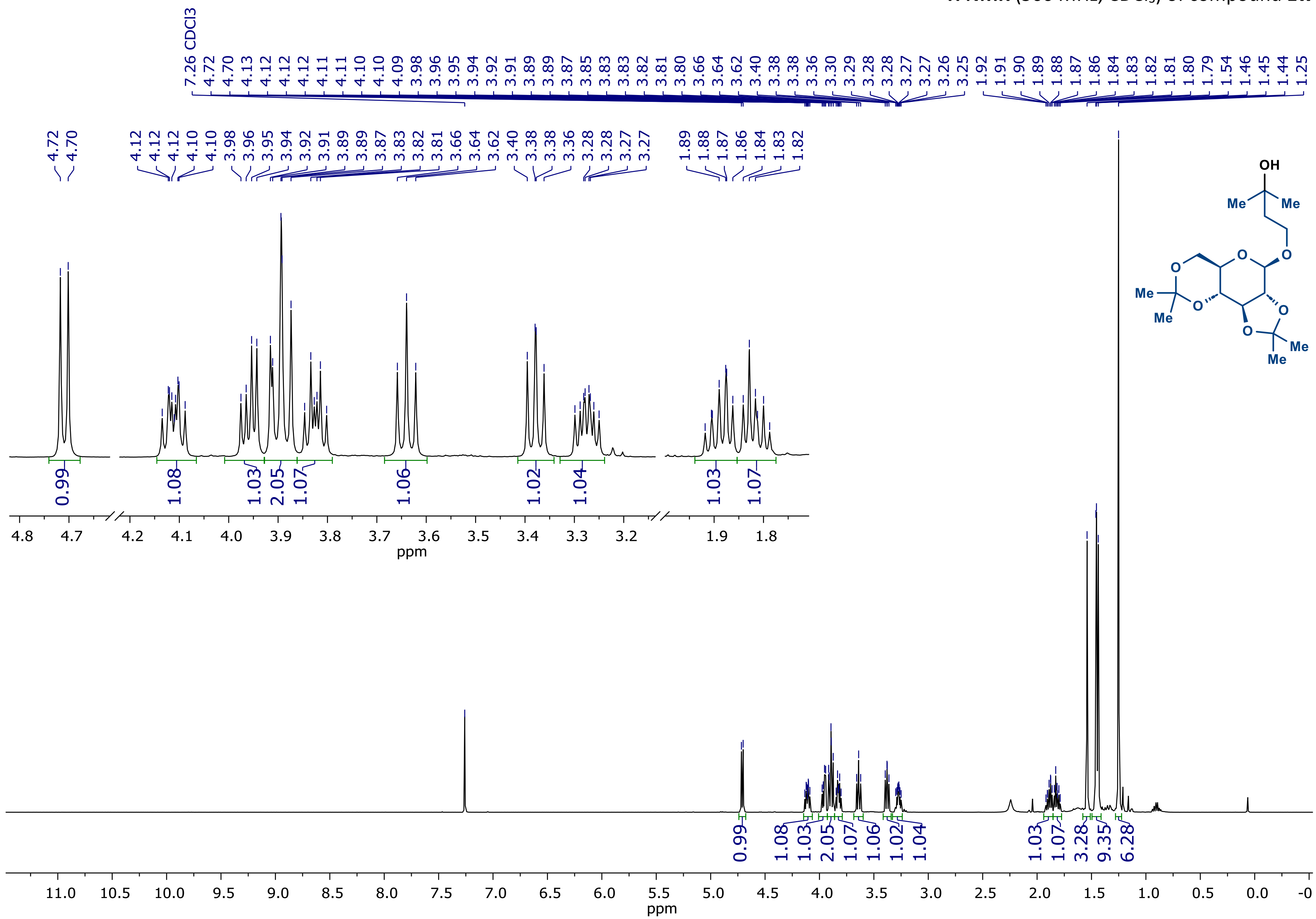
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **1v**



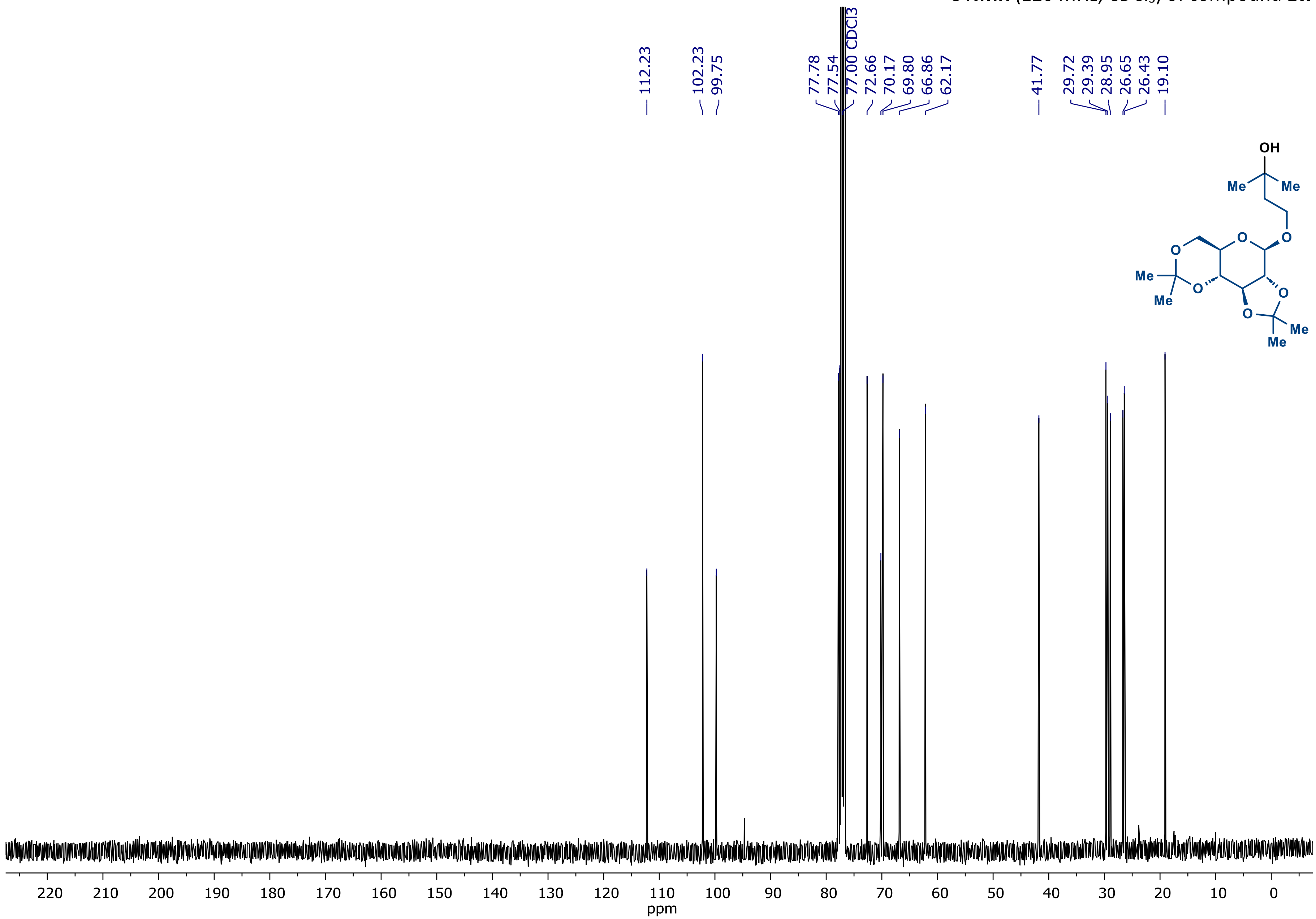
^{13}C NMR (126 MHz, $CDCl_3$) of compound **1v**



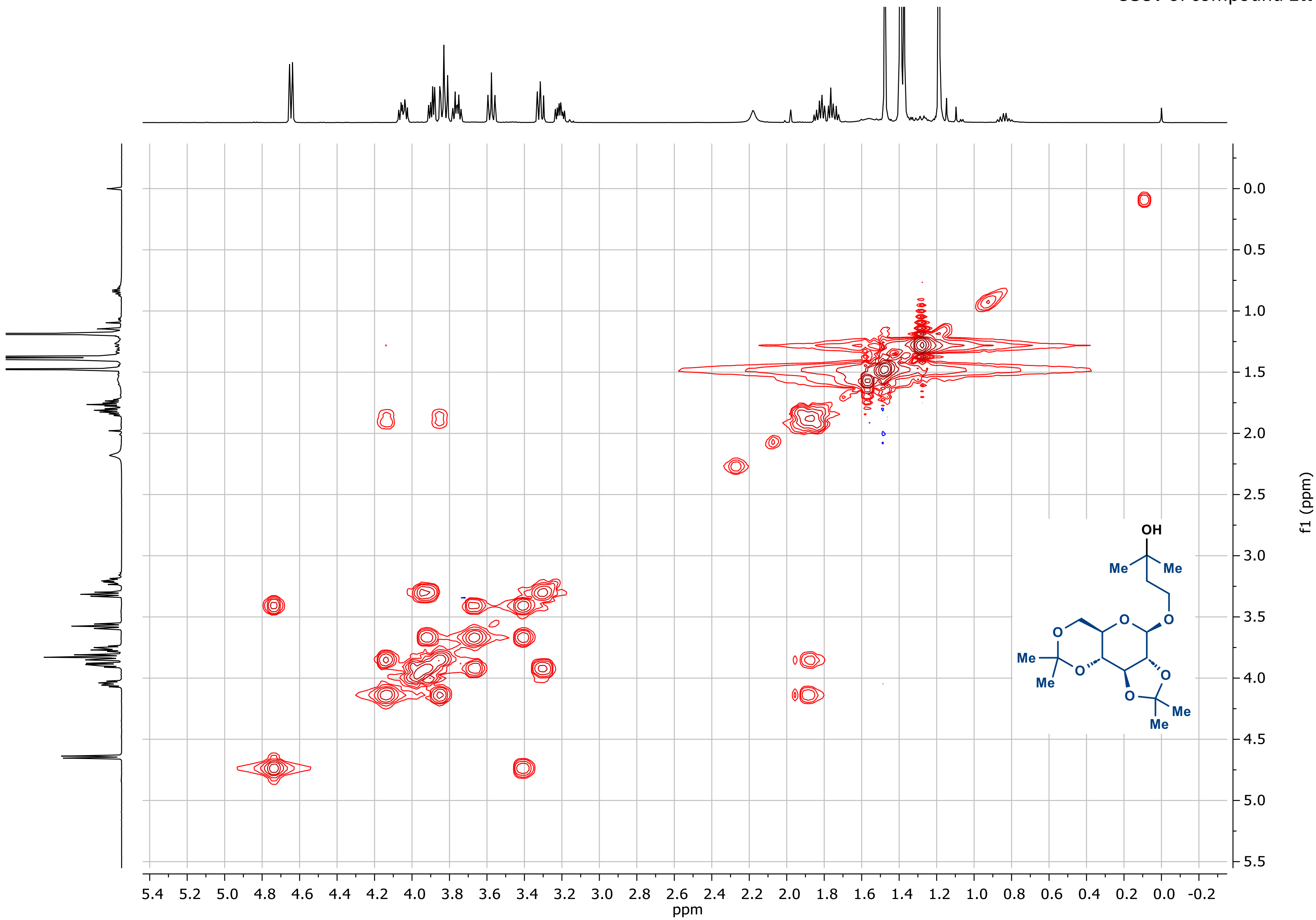
[1]H NMR (500 MHz, $CDCl_3$) of compound **1w**



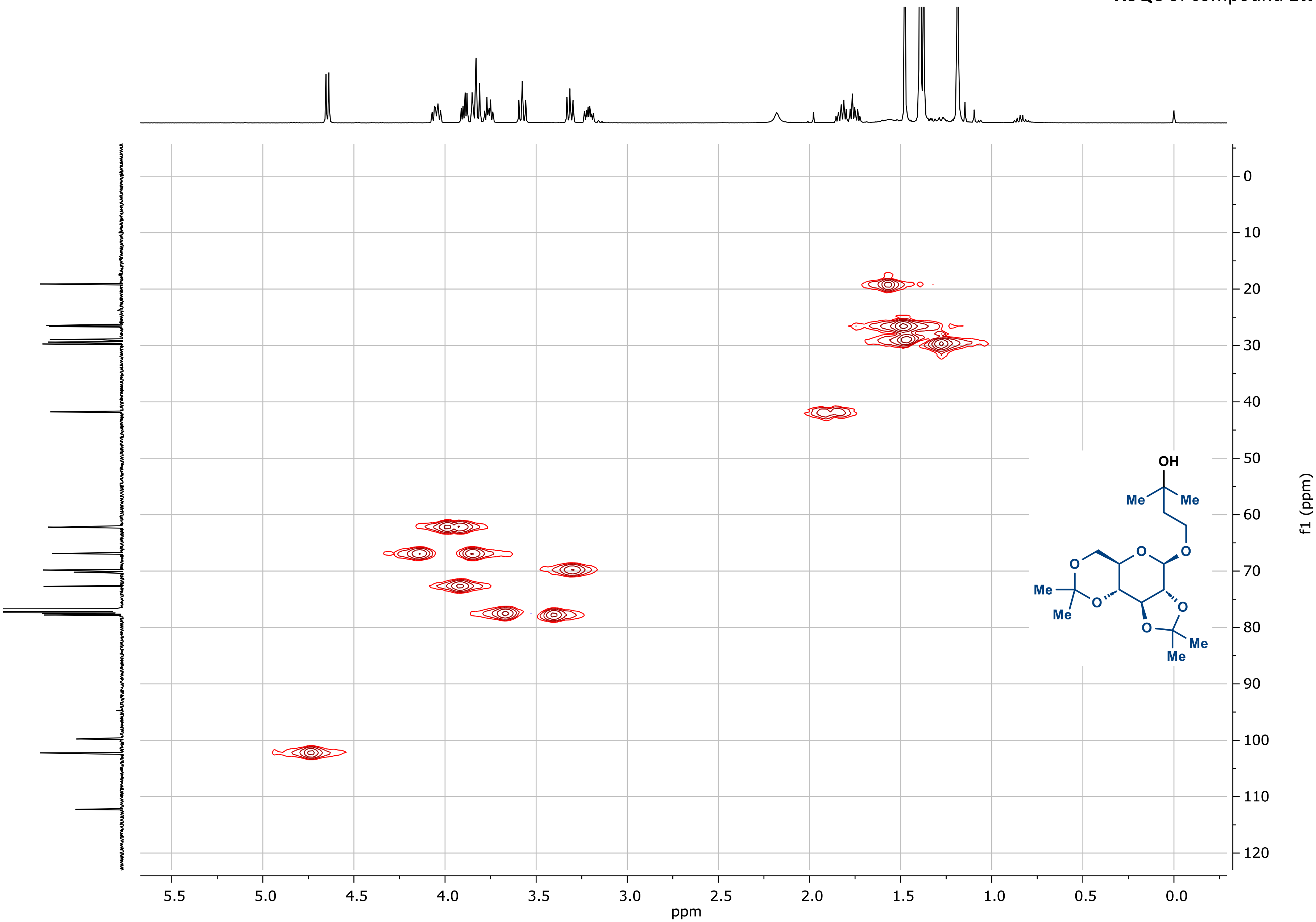
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **1w**



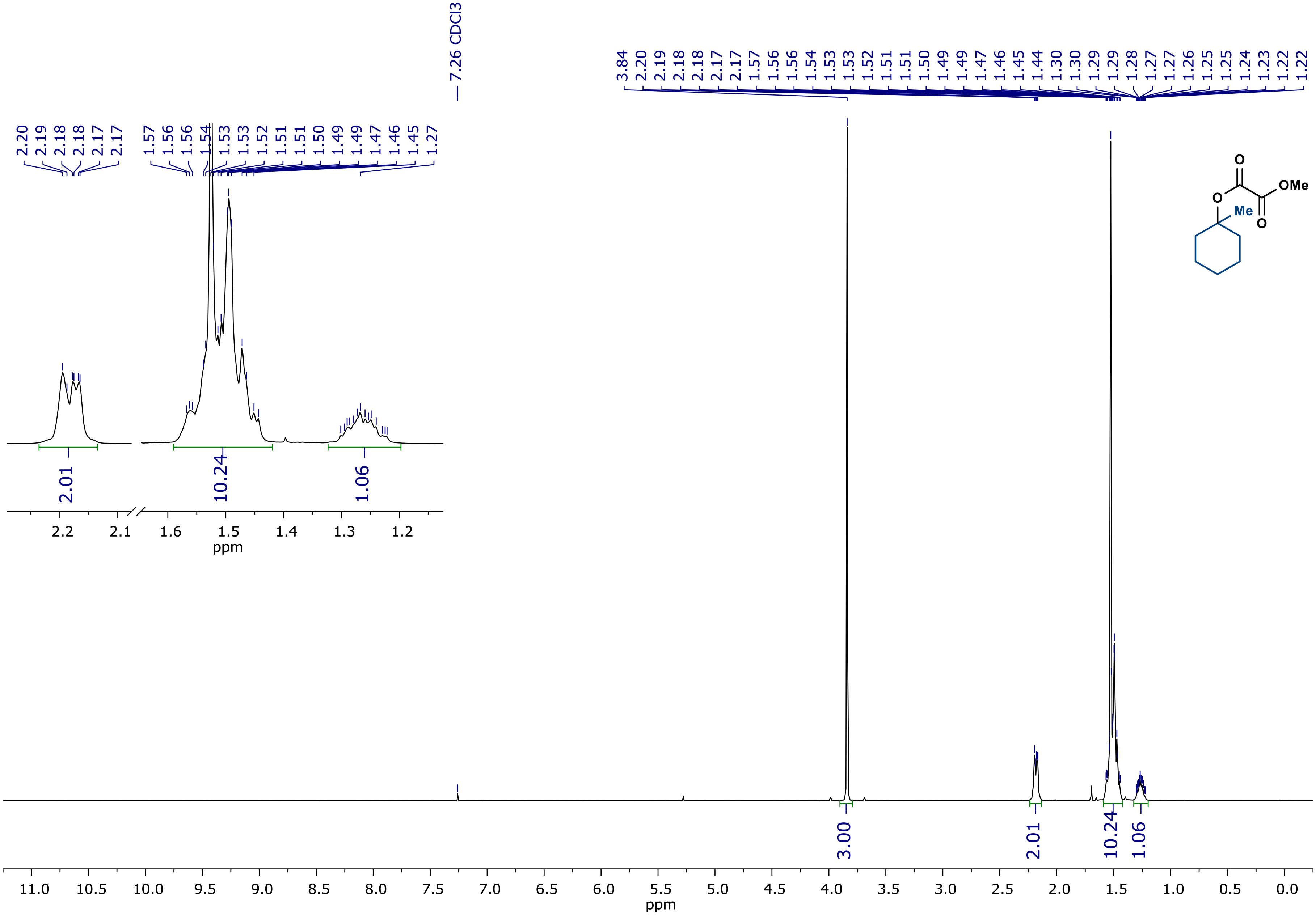
COSY of compound **1w**



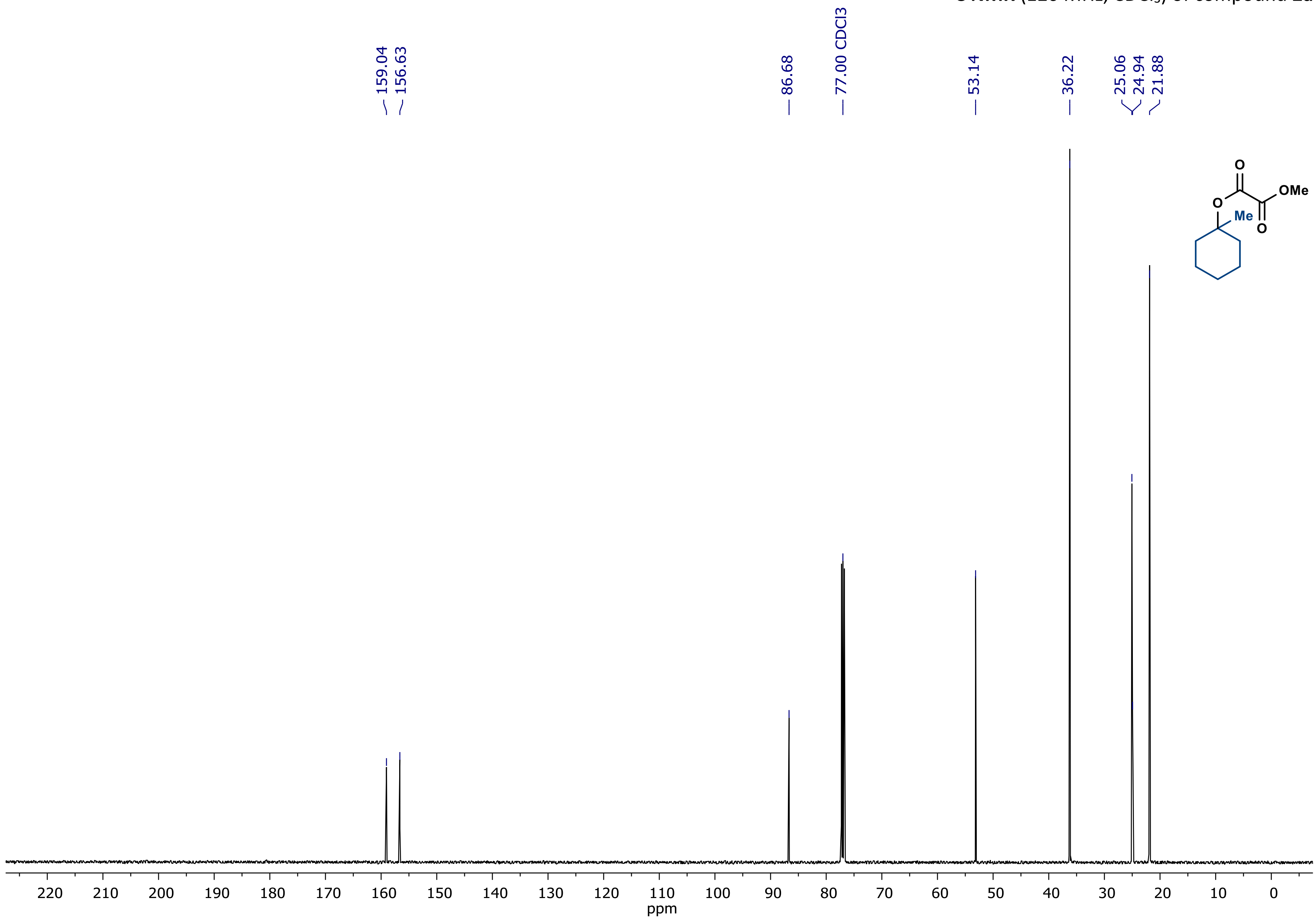
HSQC of compound **1w**



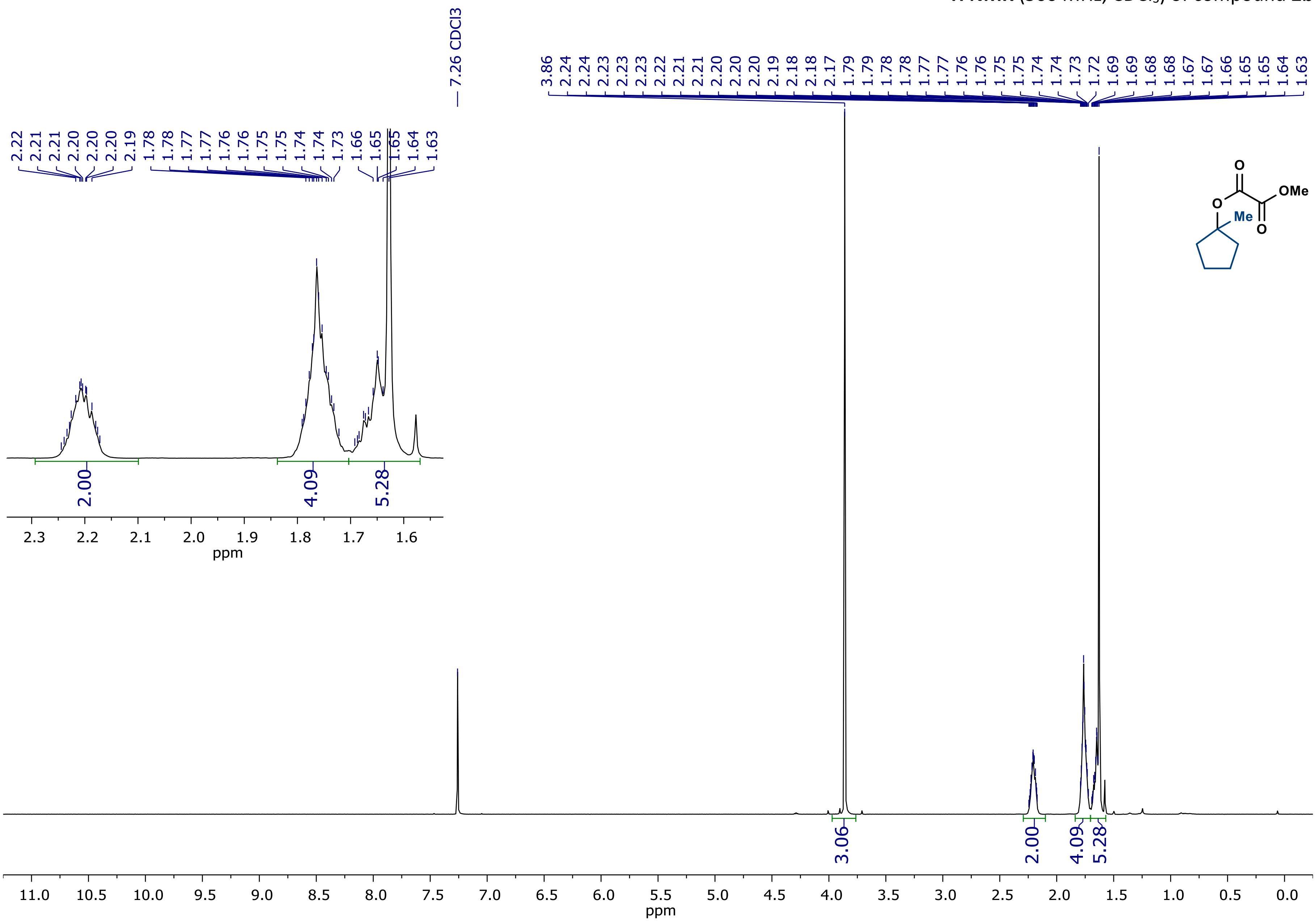
¹H NMR (500 MHz, $CDCl_3$) of compound **2a**



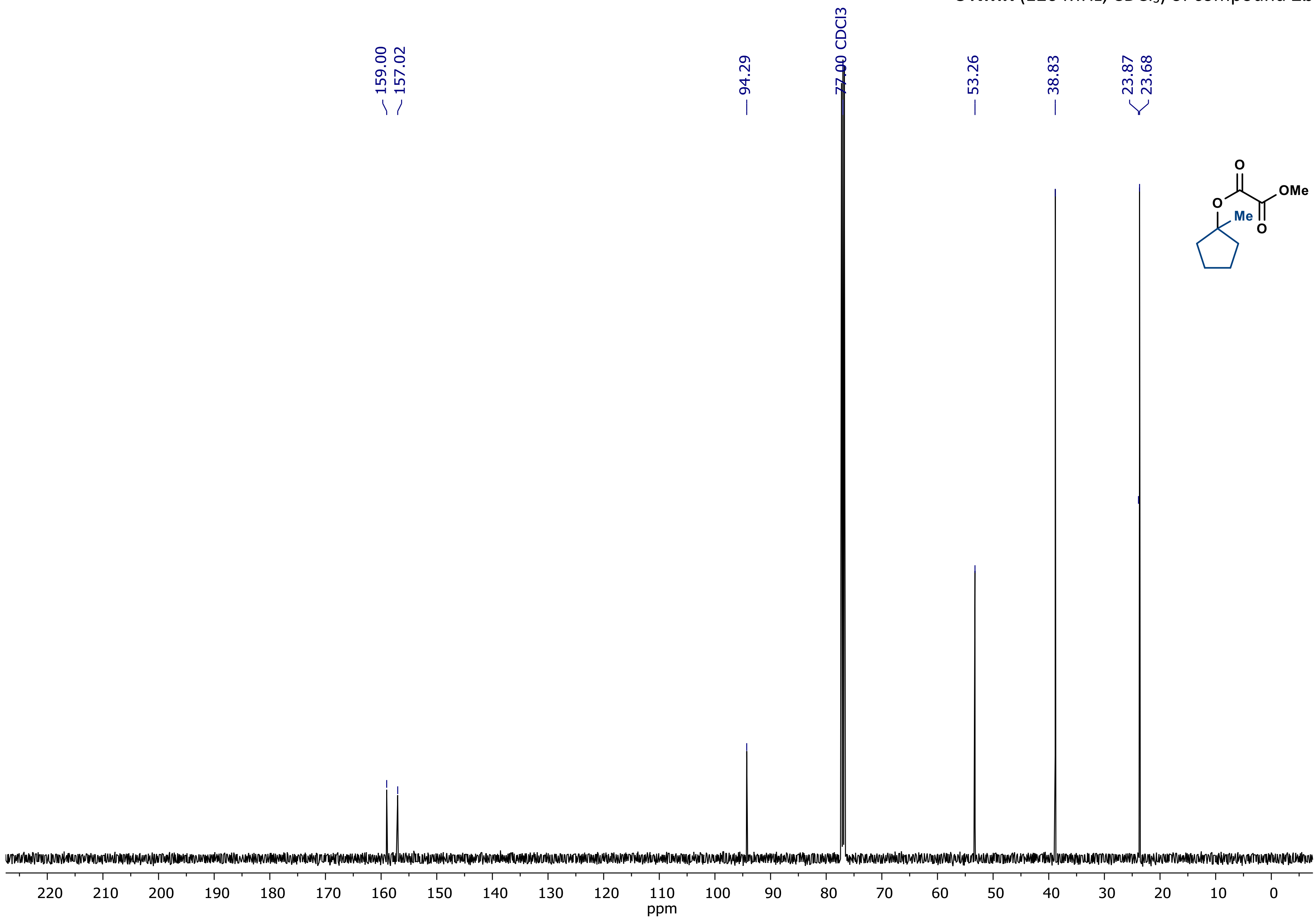
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2a**



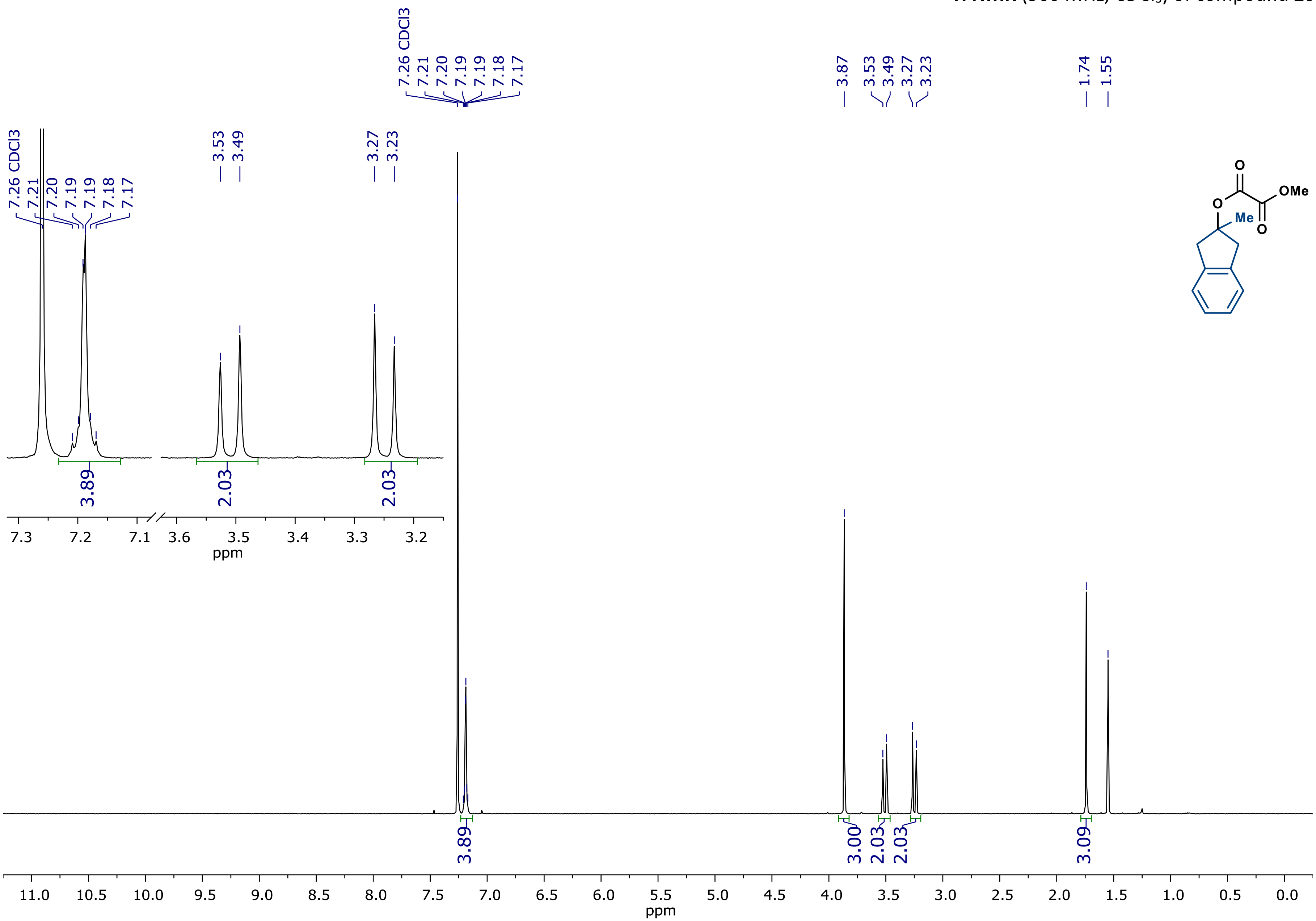
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**



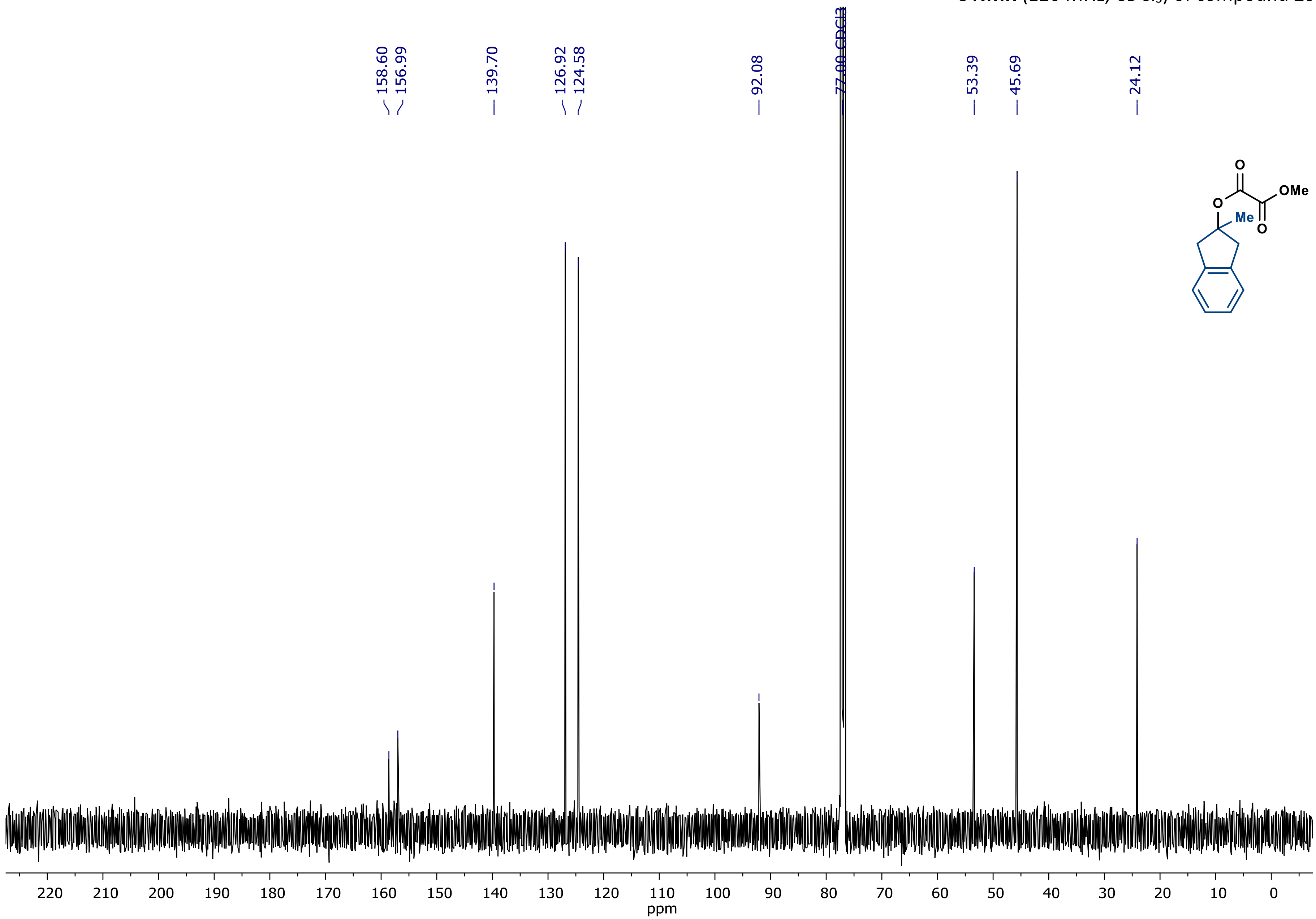
[13]C NMR (126 MHz, $CDCl_3$) of compound **2b**



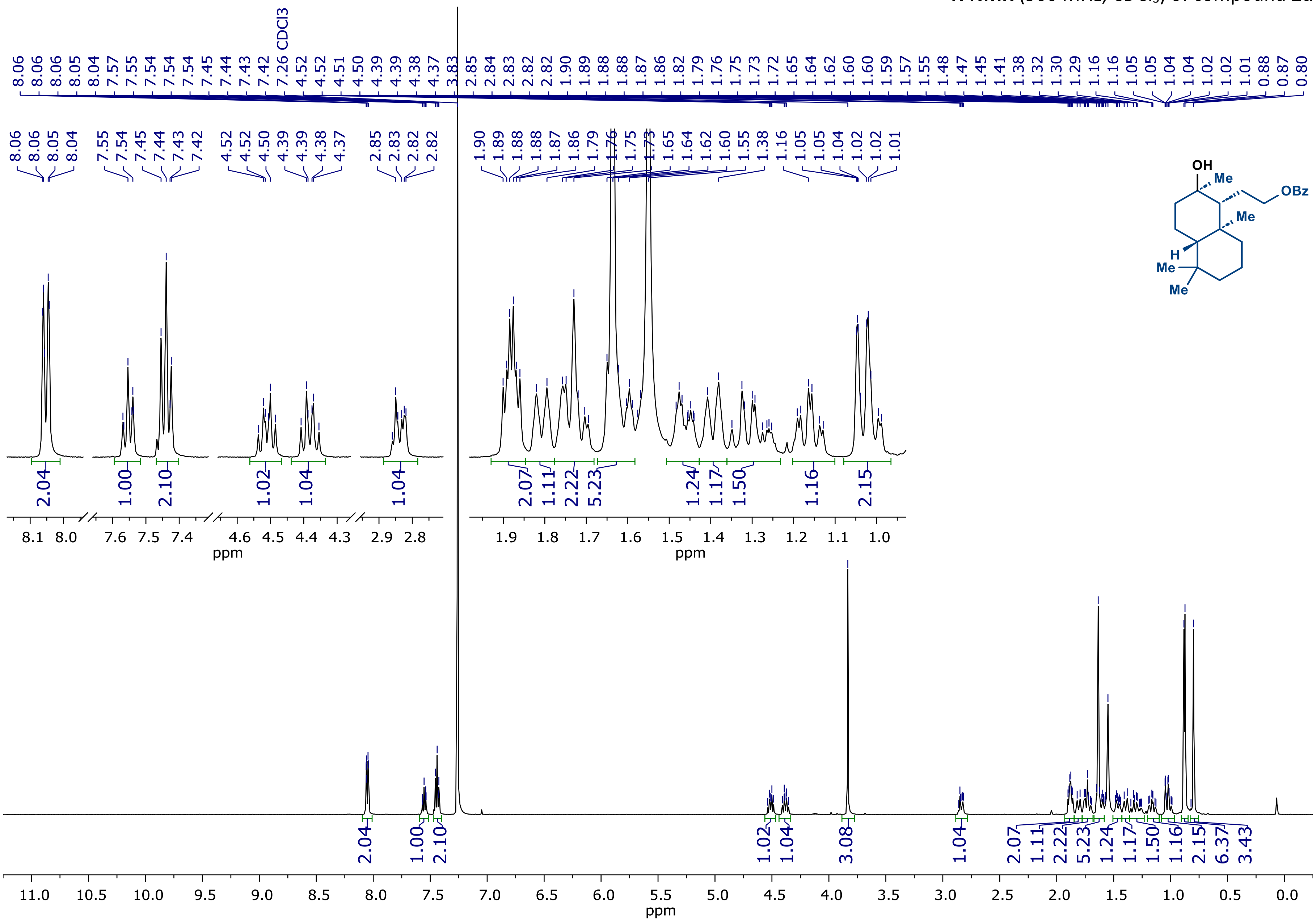
[1]H NMR (500 MHz, $CDCl_3$) of compound **2c**



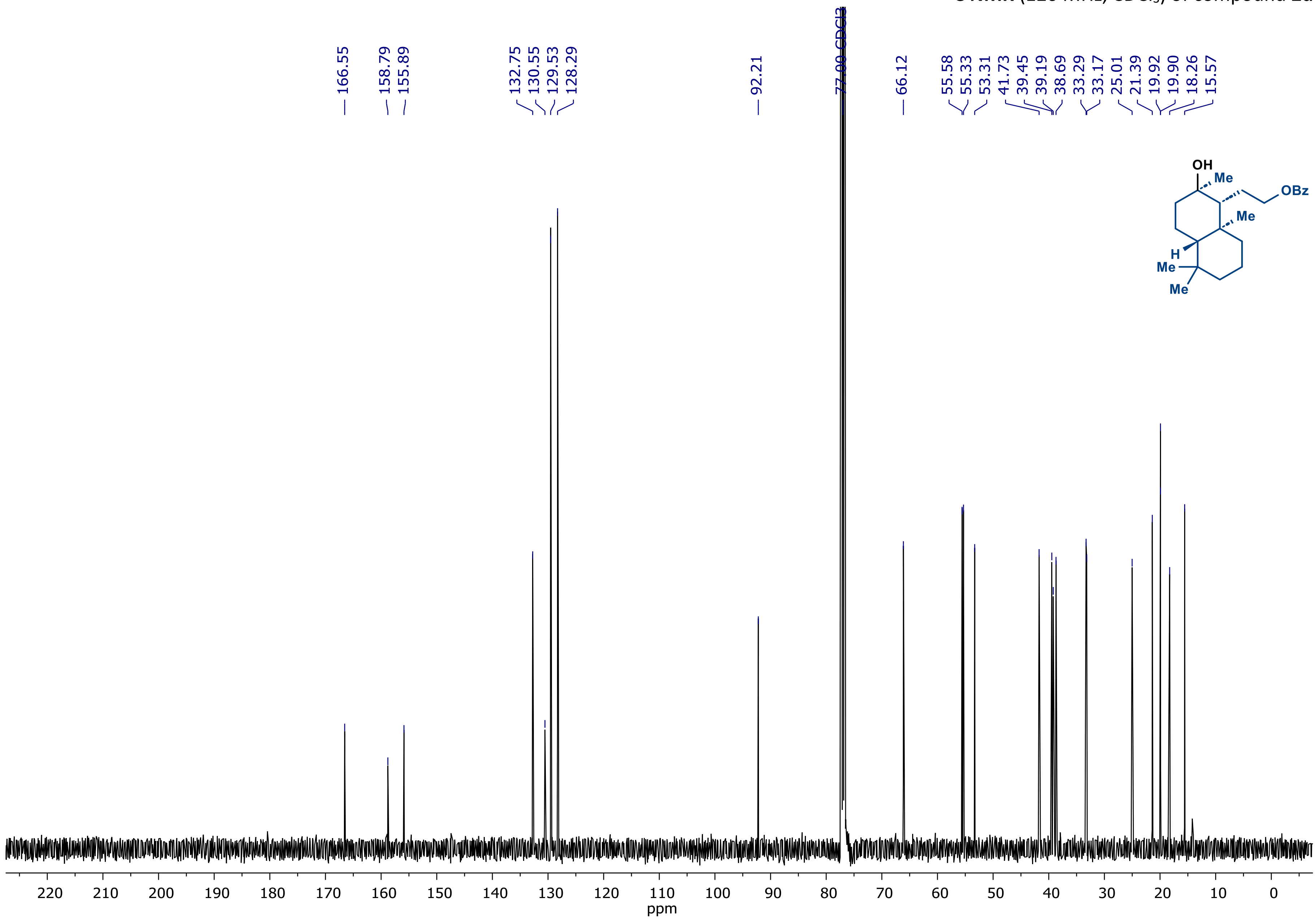
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2c**



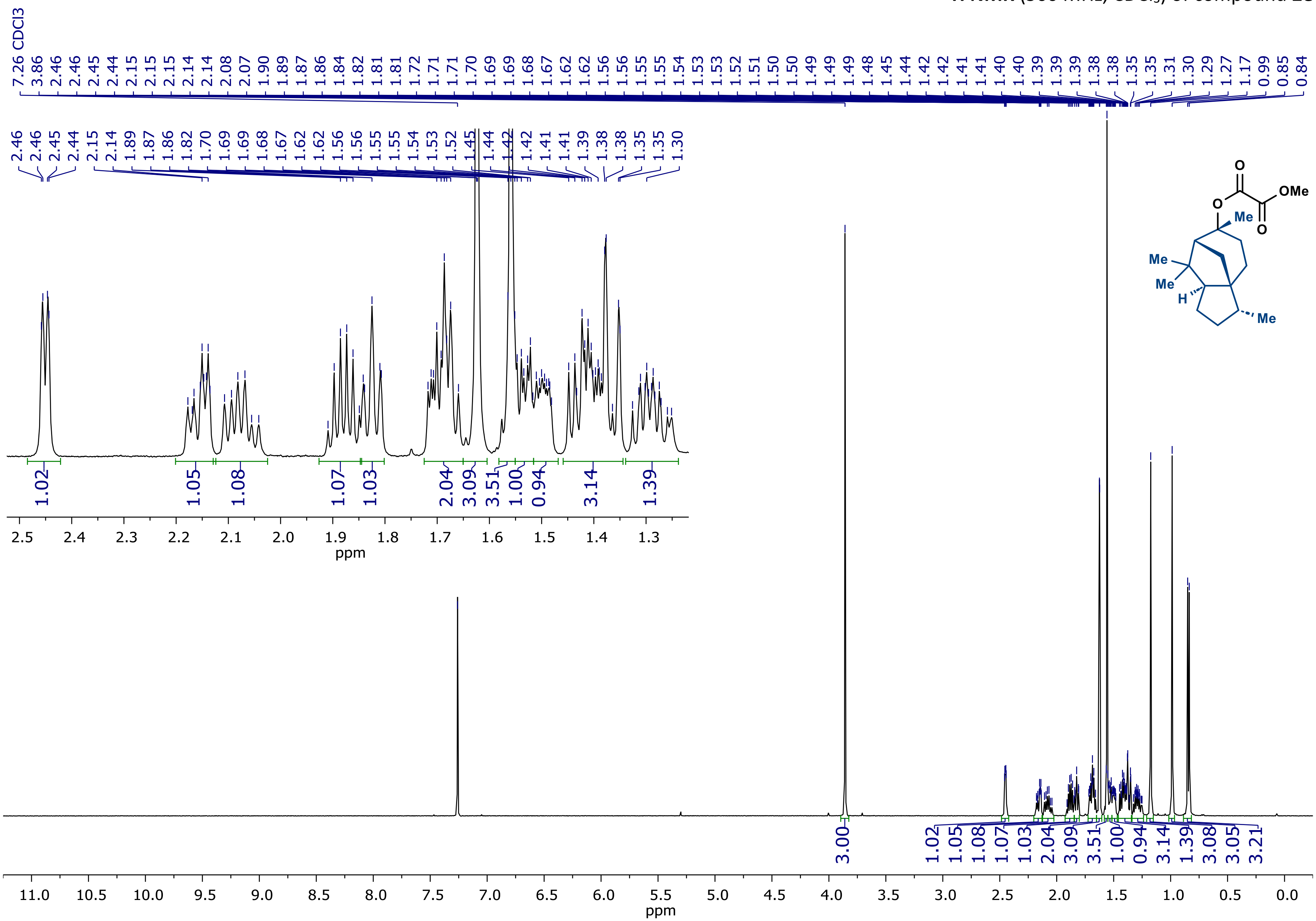
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**



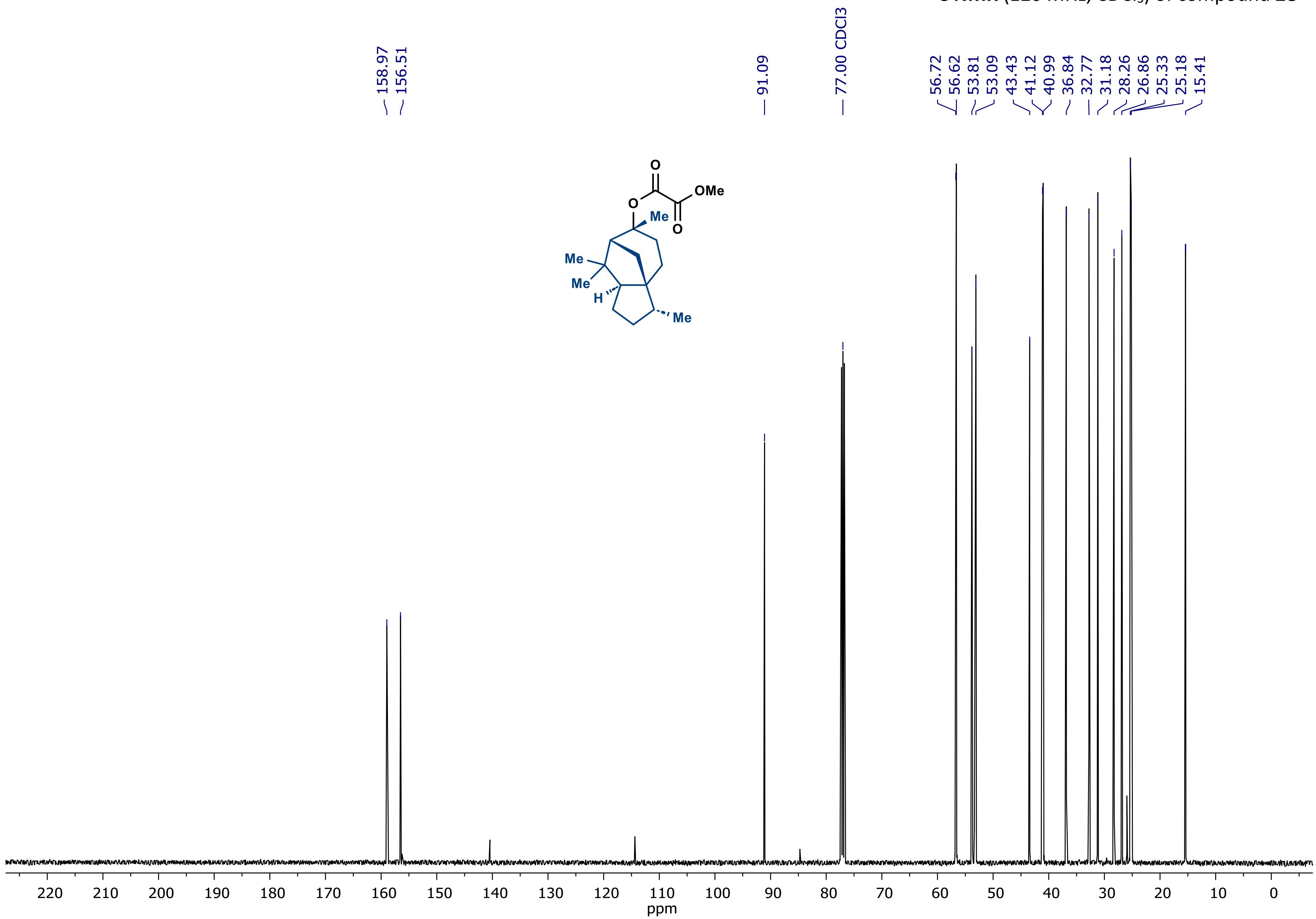
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2d**



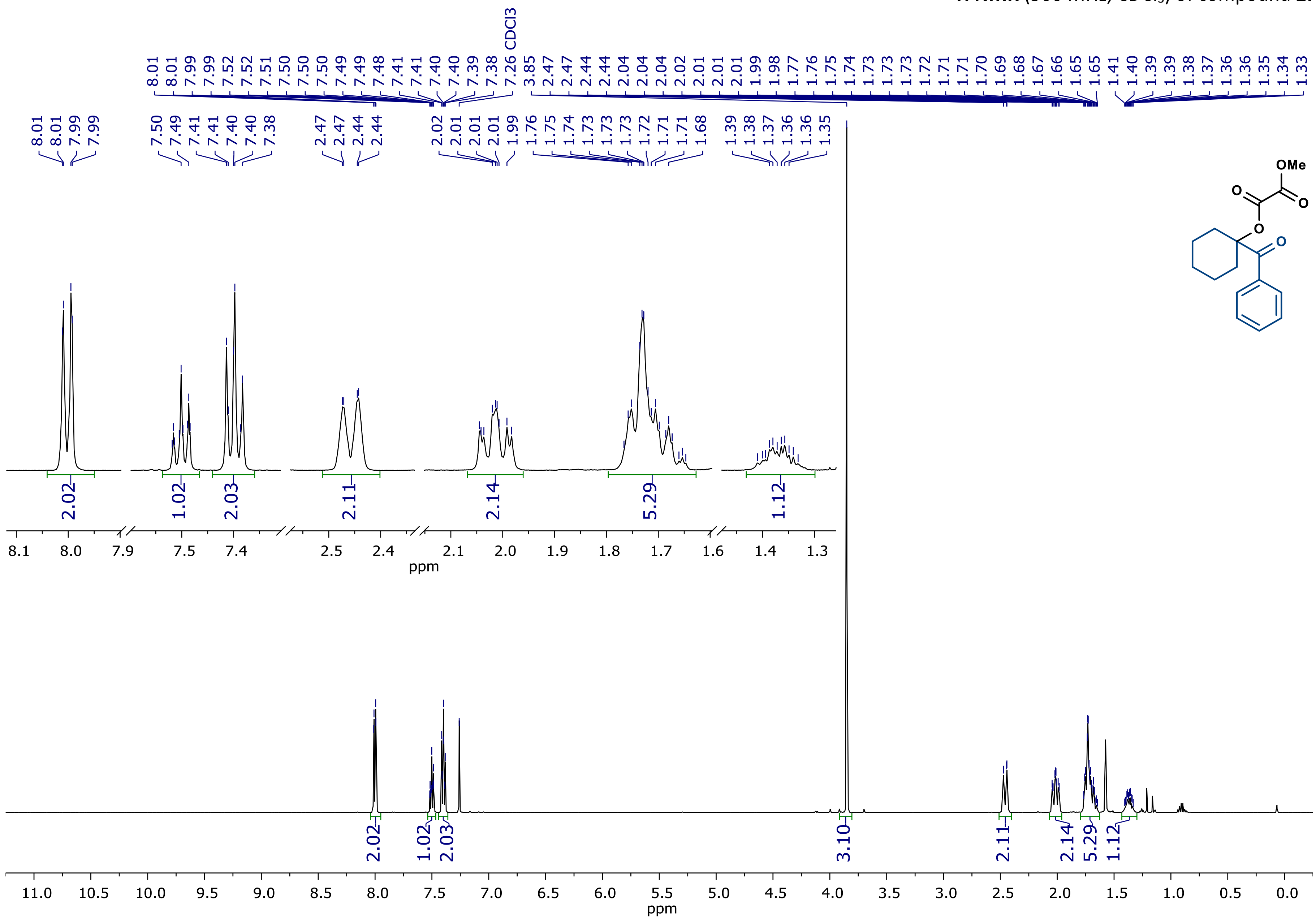
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2e**



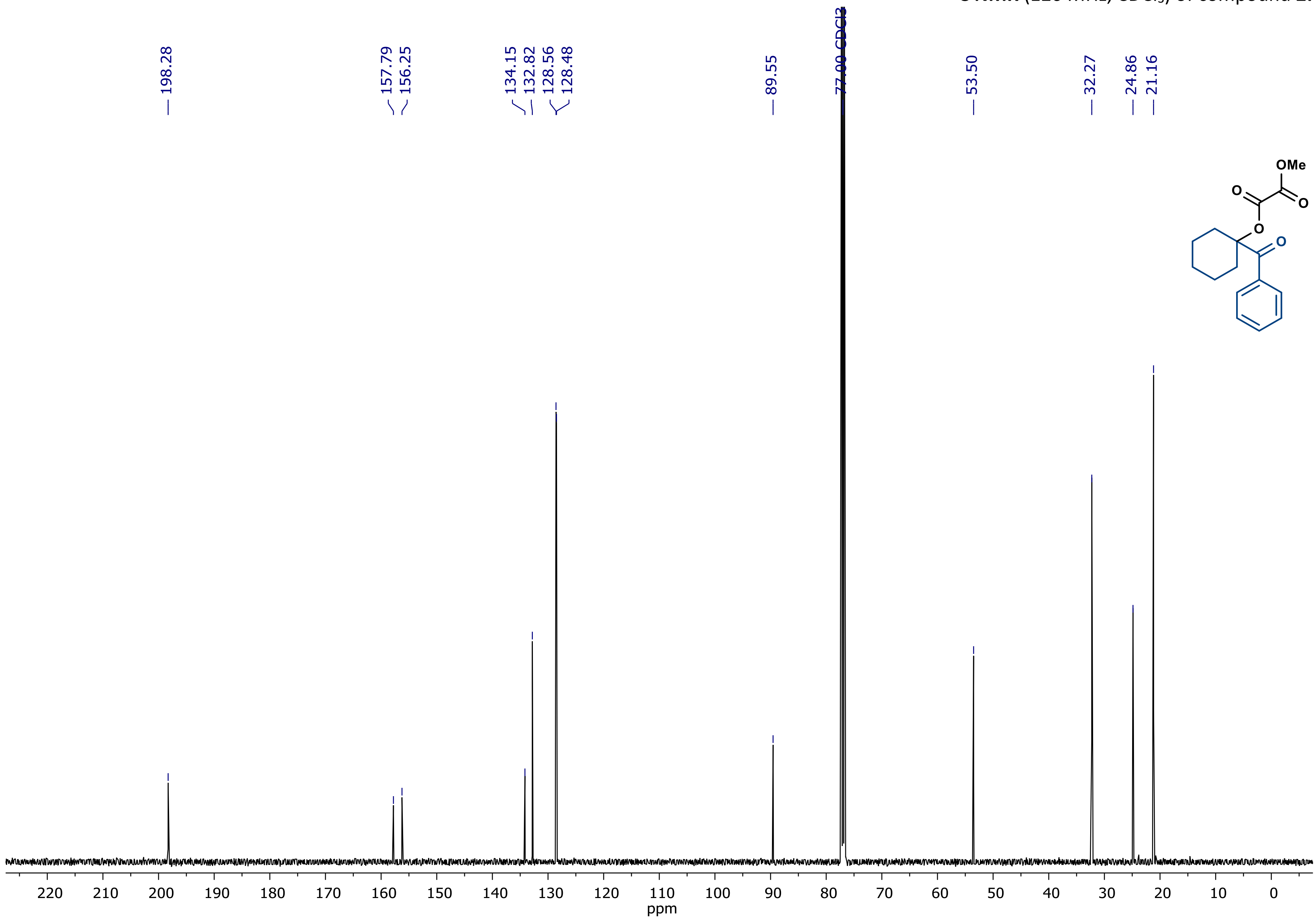
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2e**



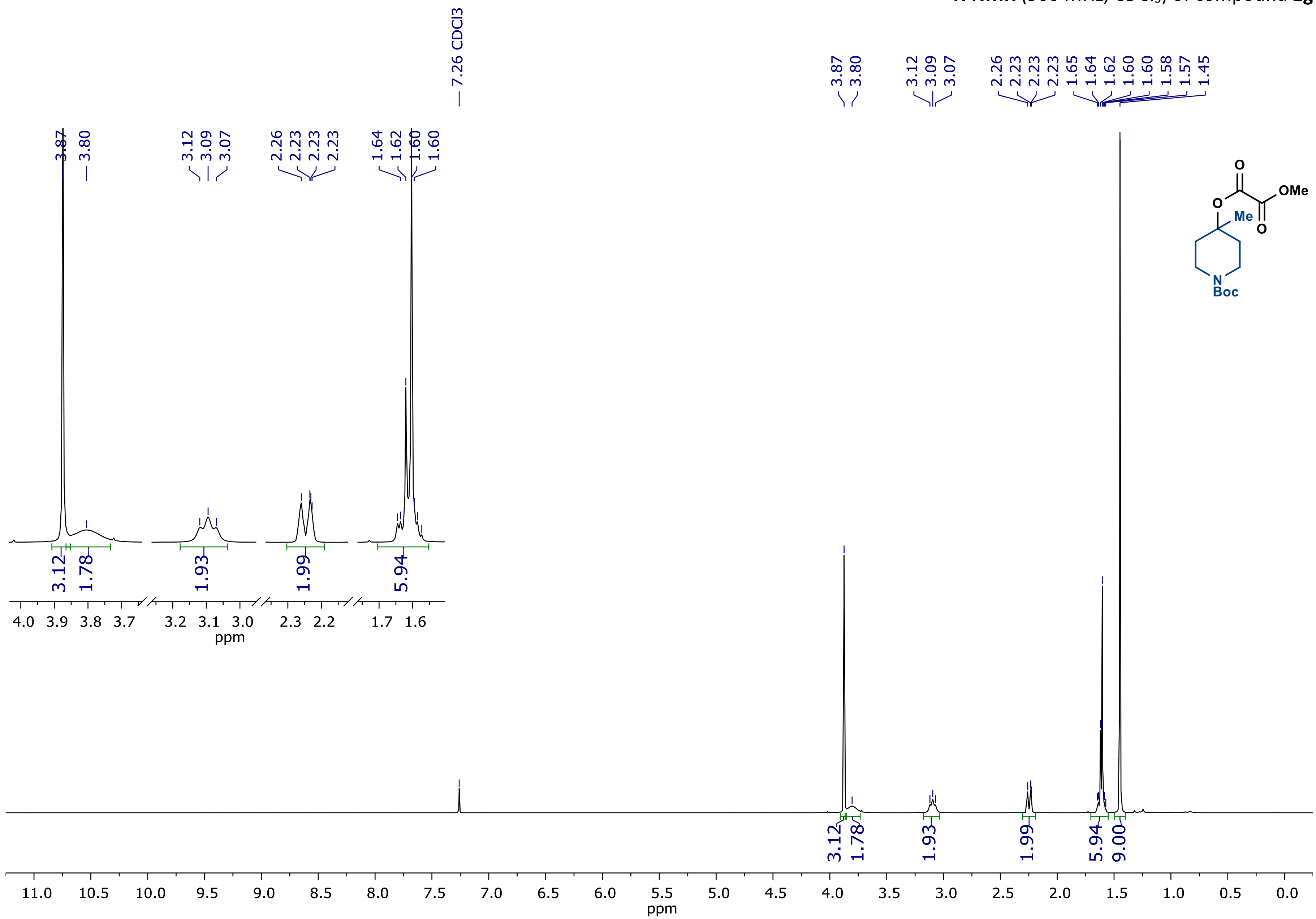
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2f**



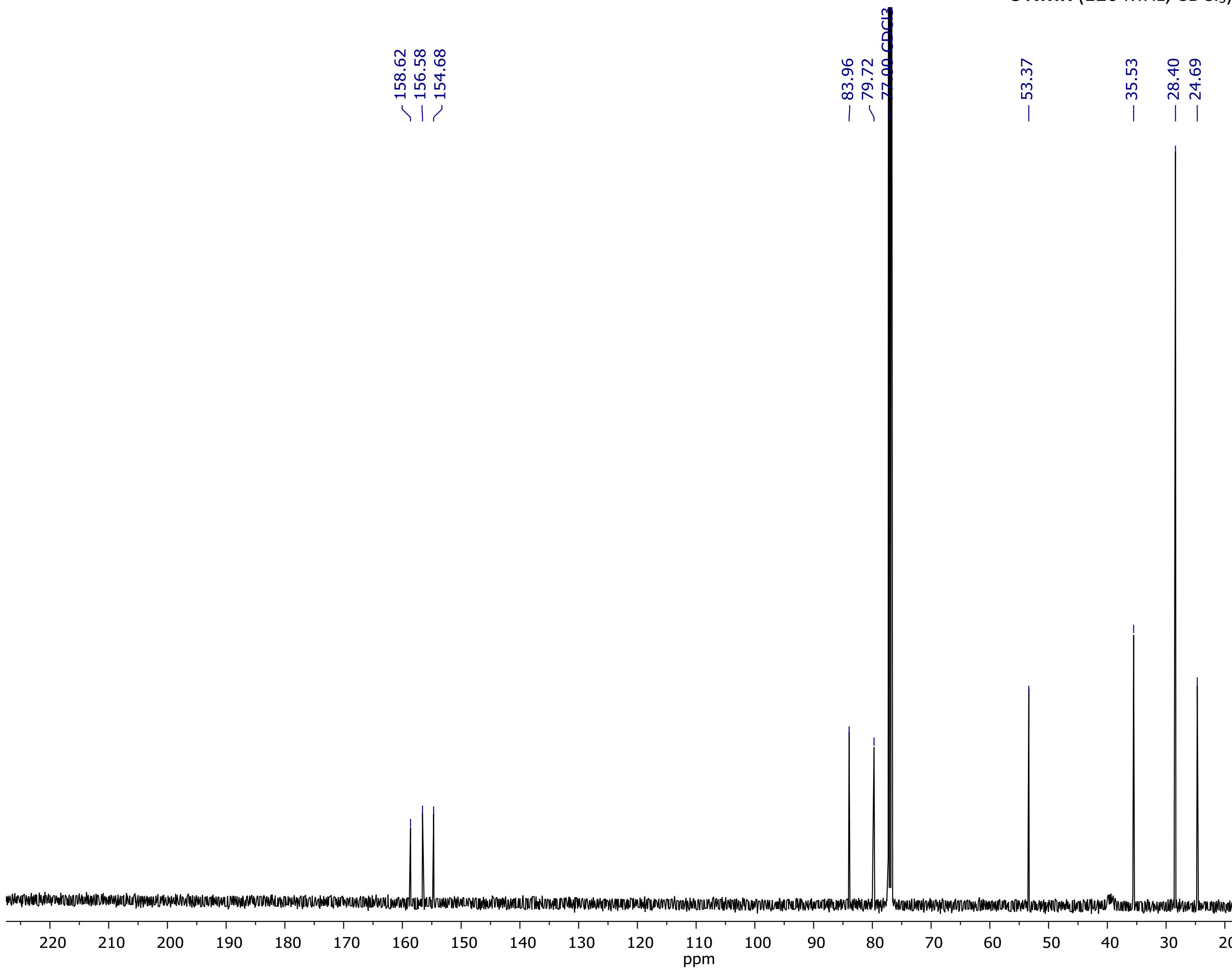
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2f**

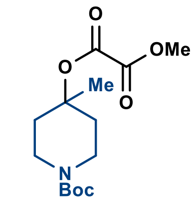


^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**

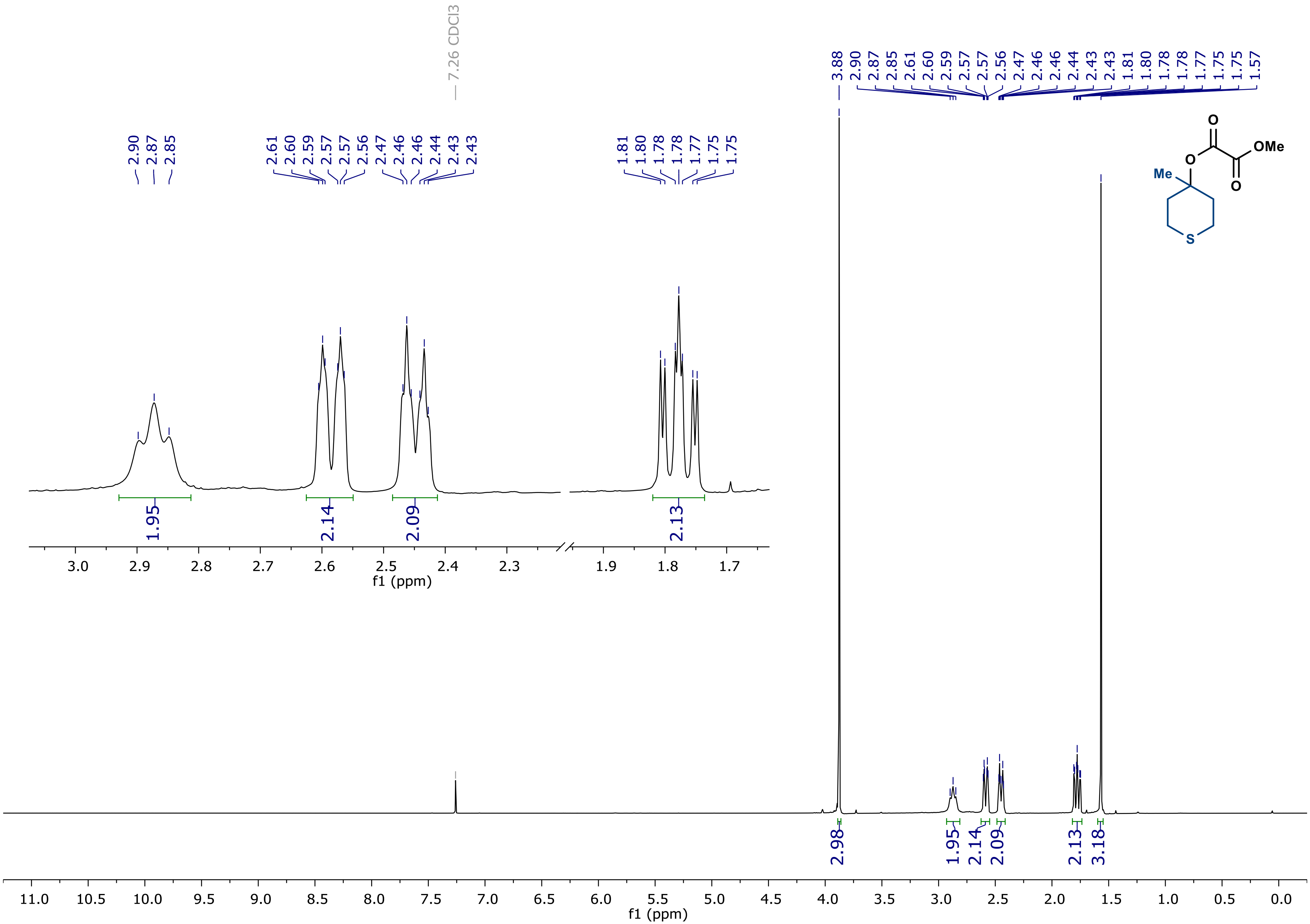


^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2g**

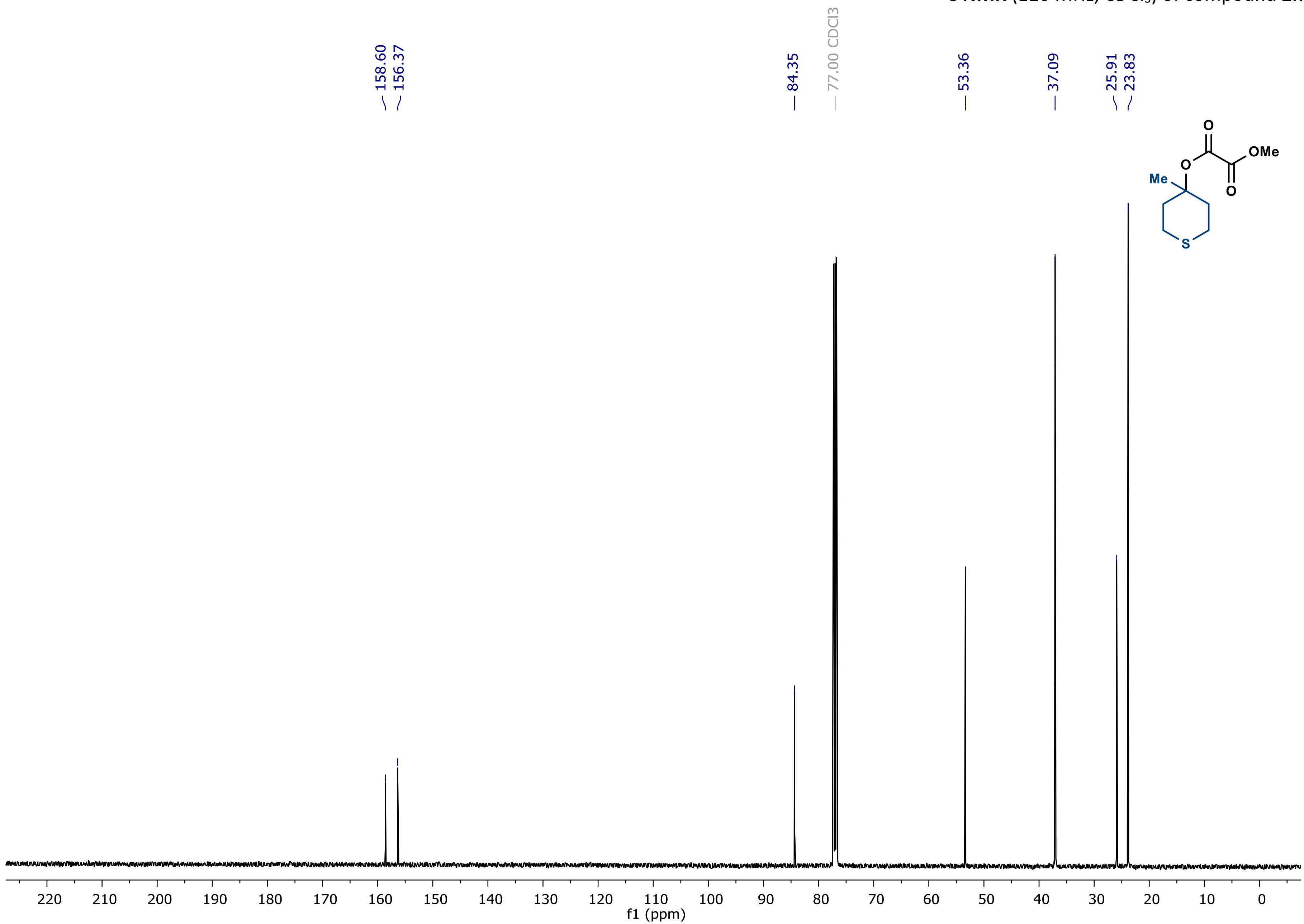




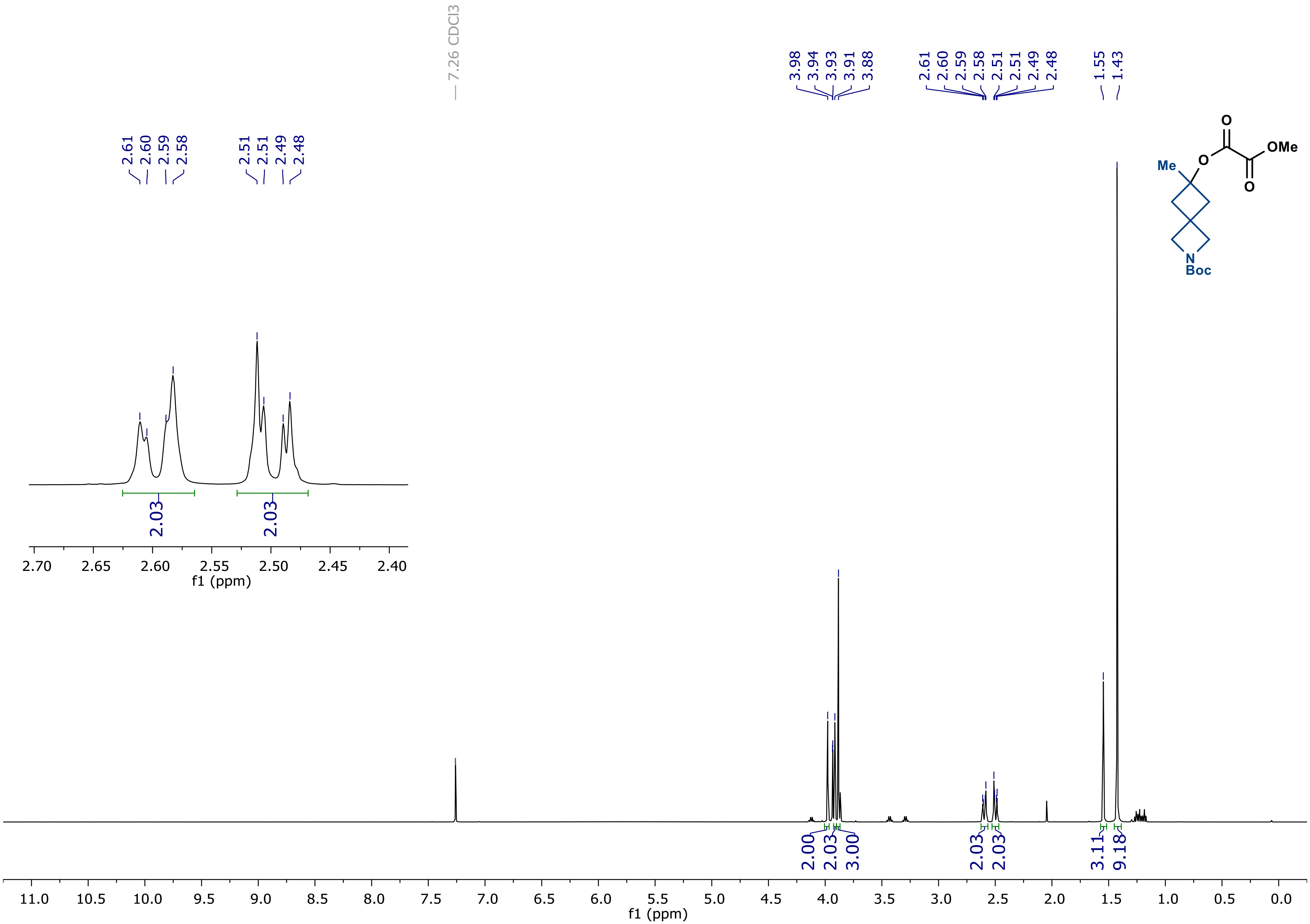
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**



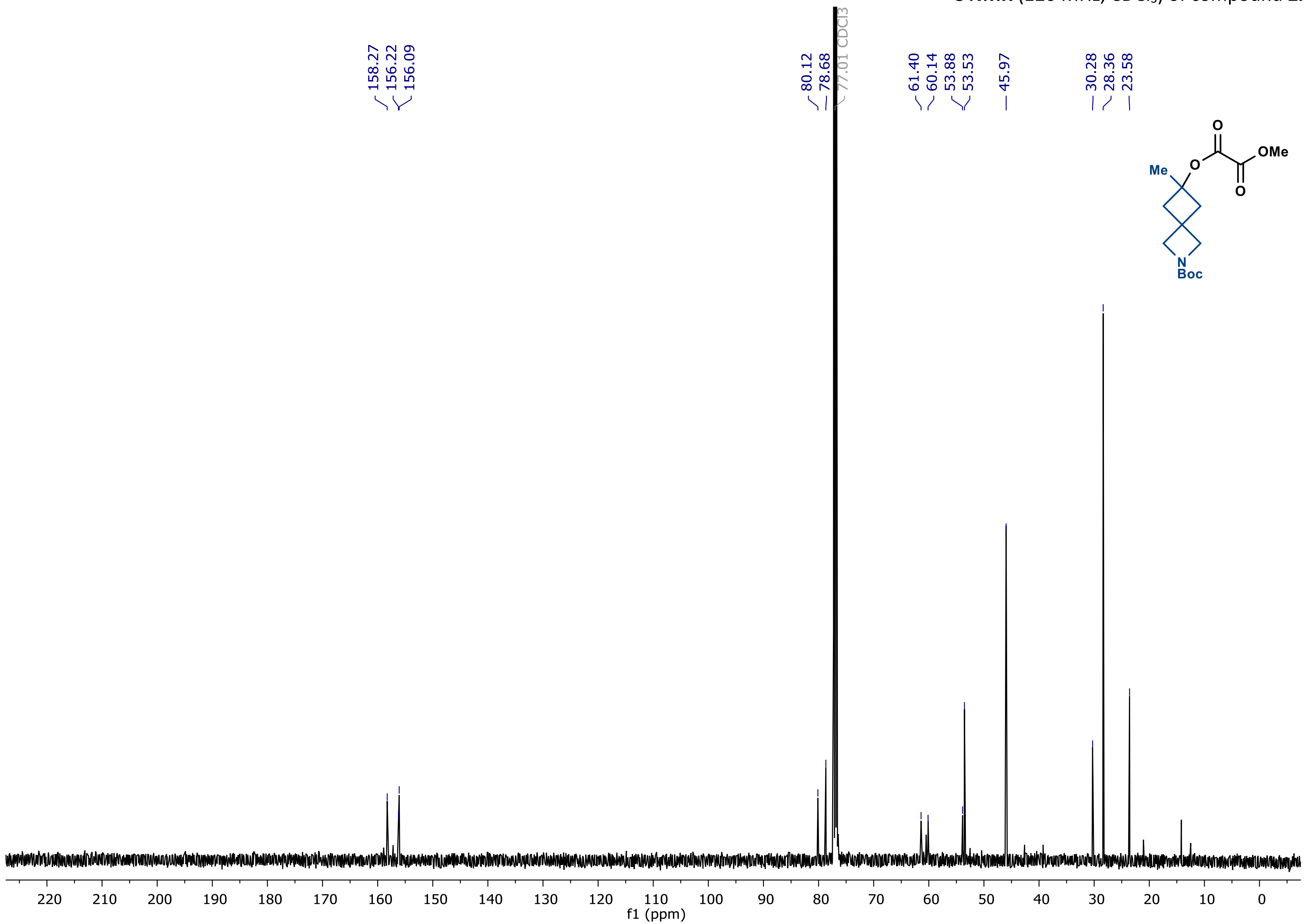
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2h**



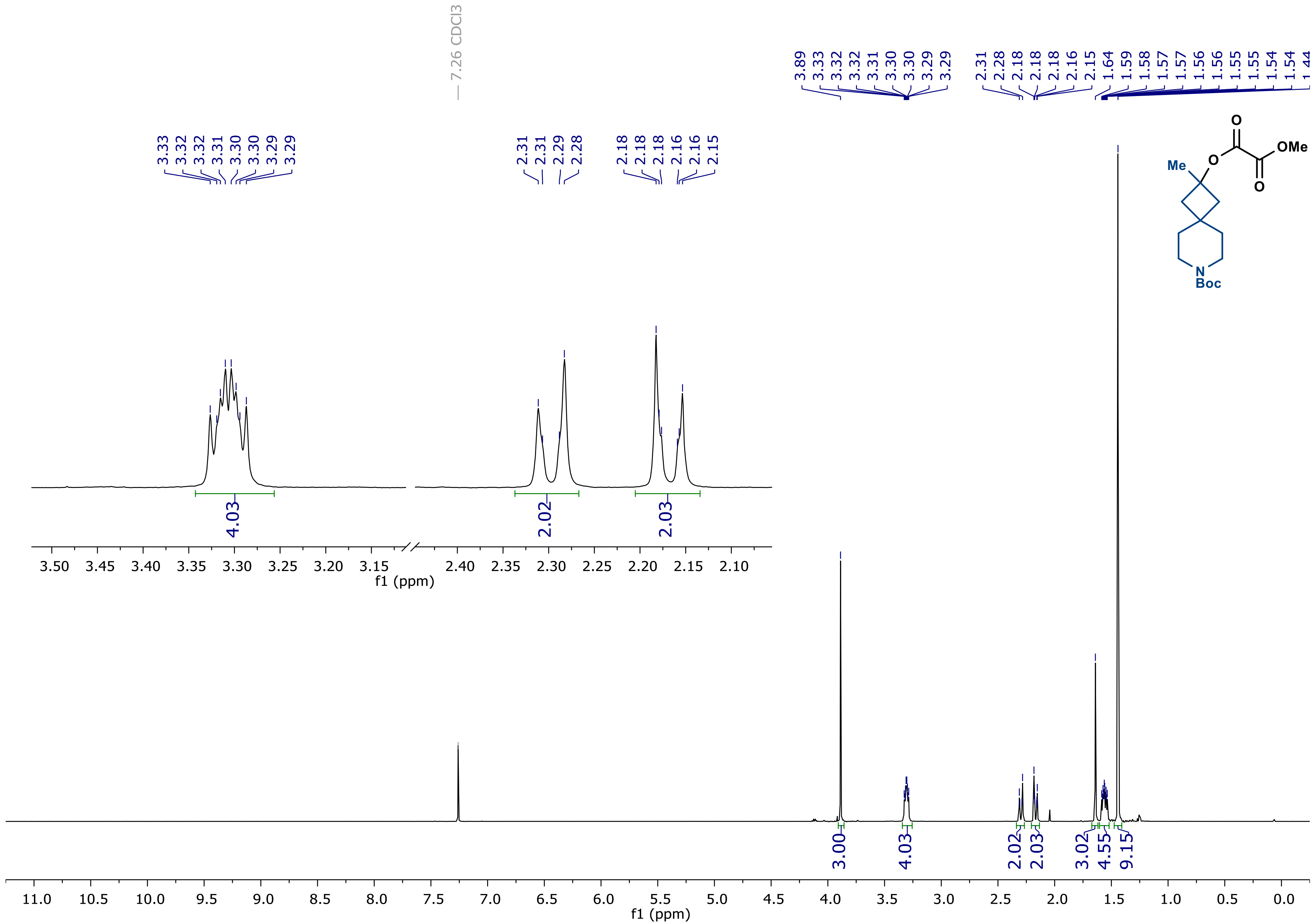
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2i**



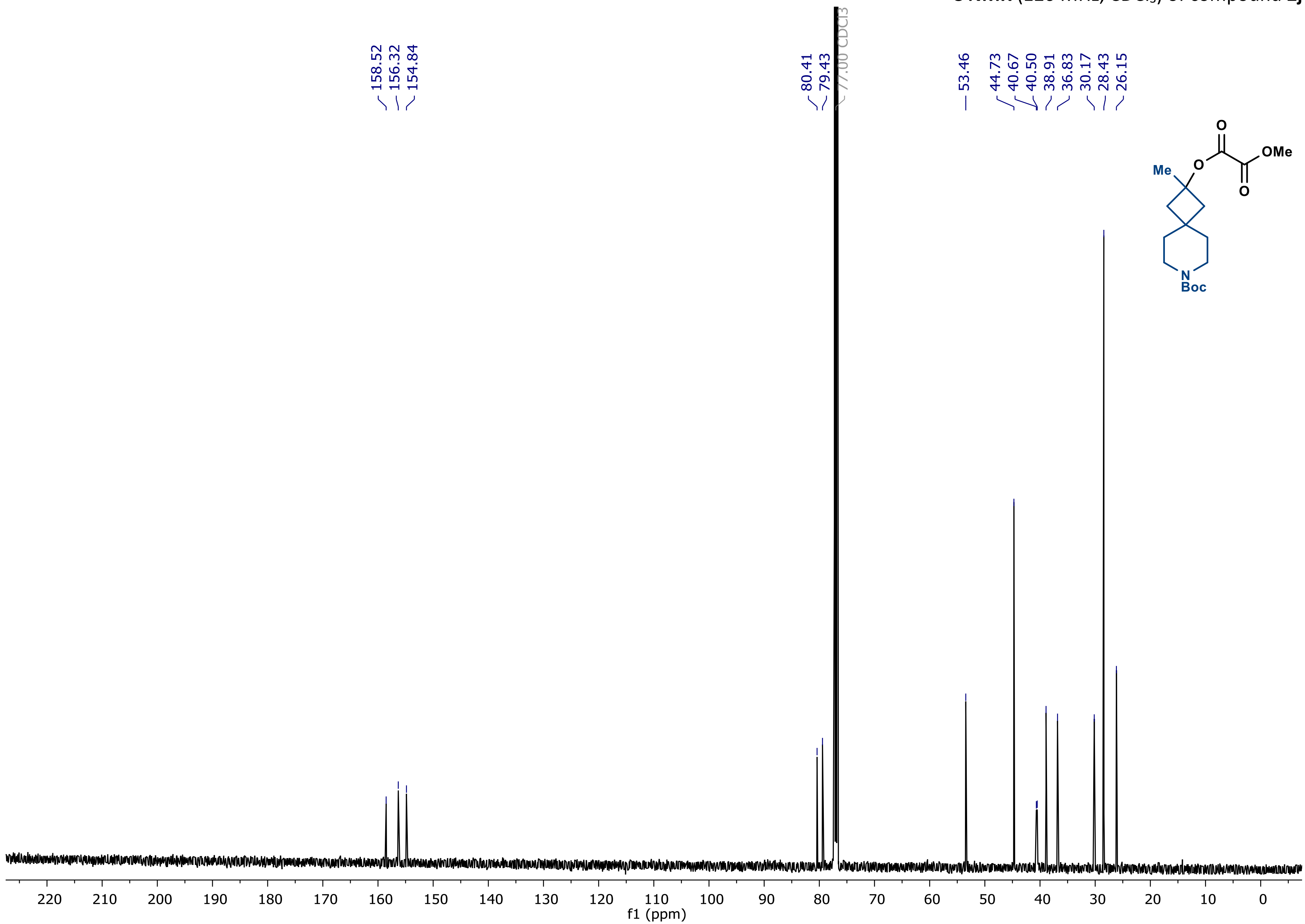
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2i**



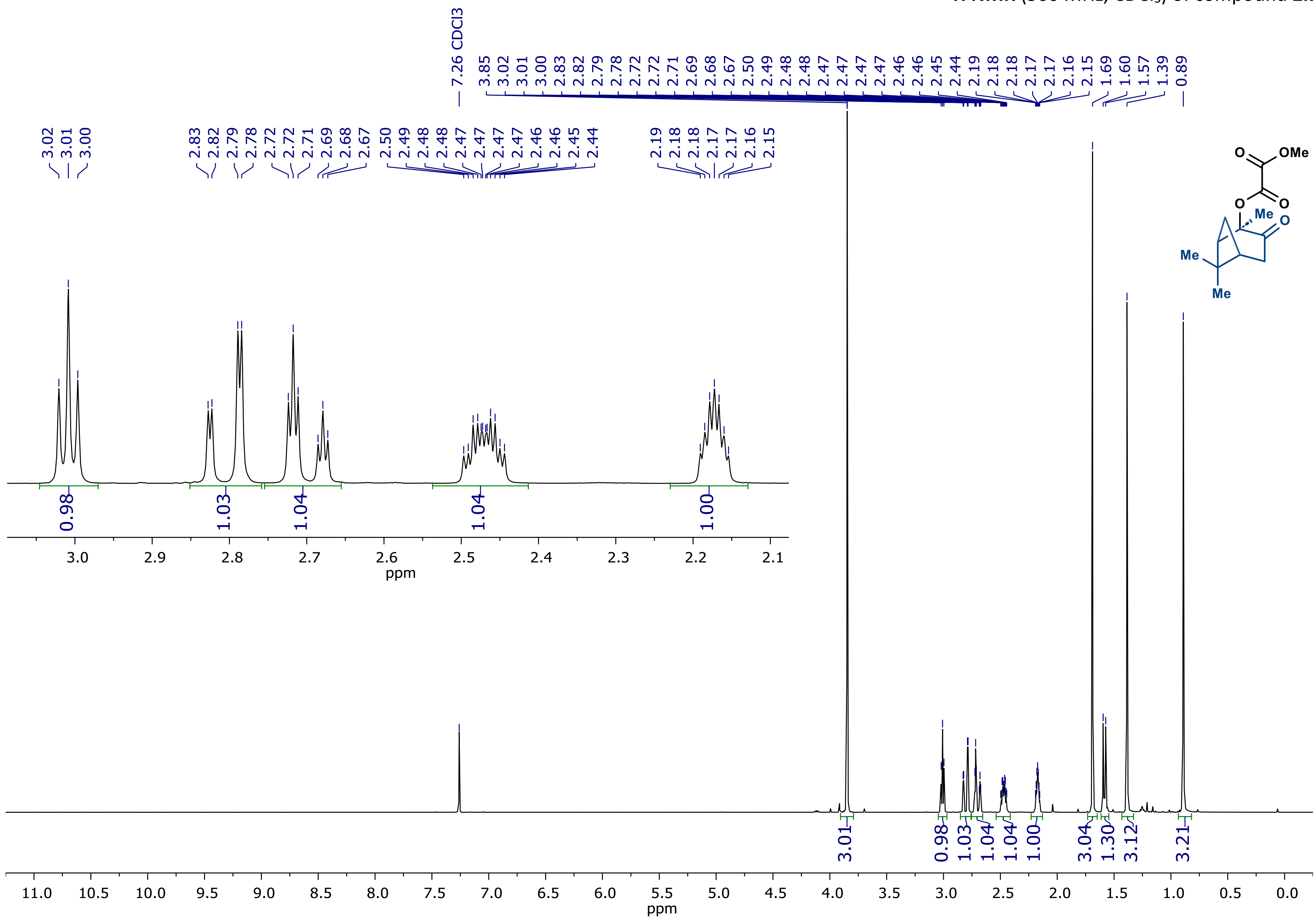
[1]H NMR (500 MHz, $CDCl_3$) of compound **2j**



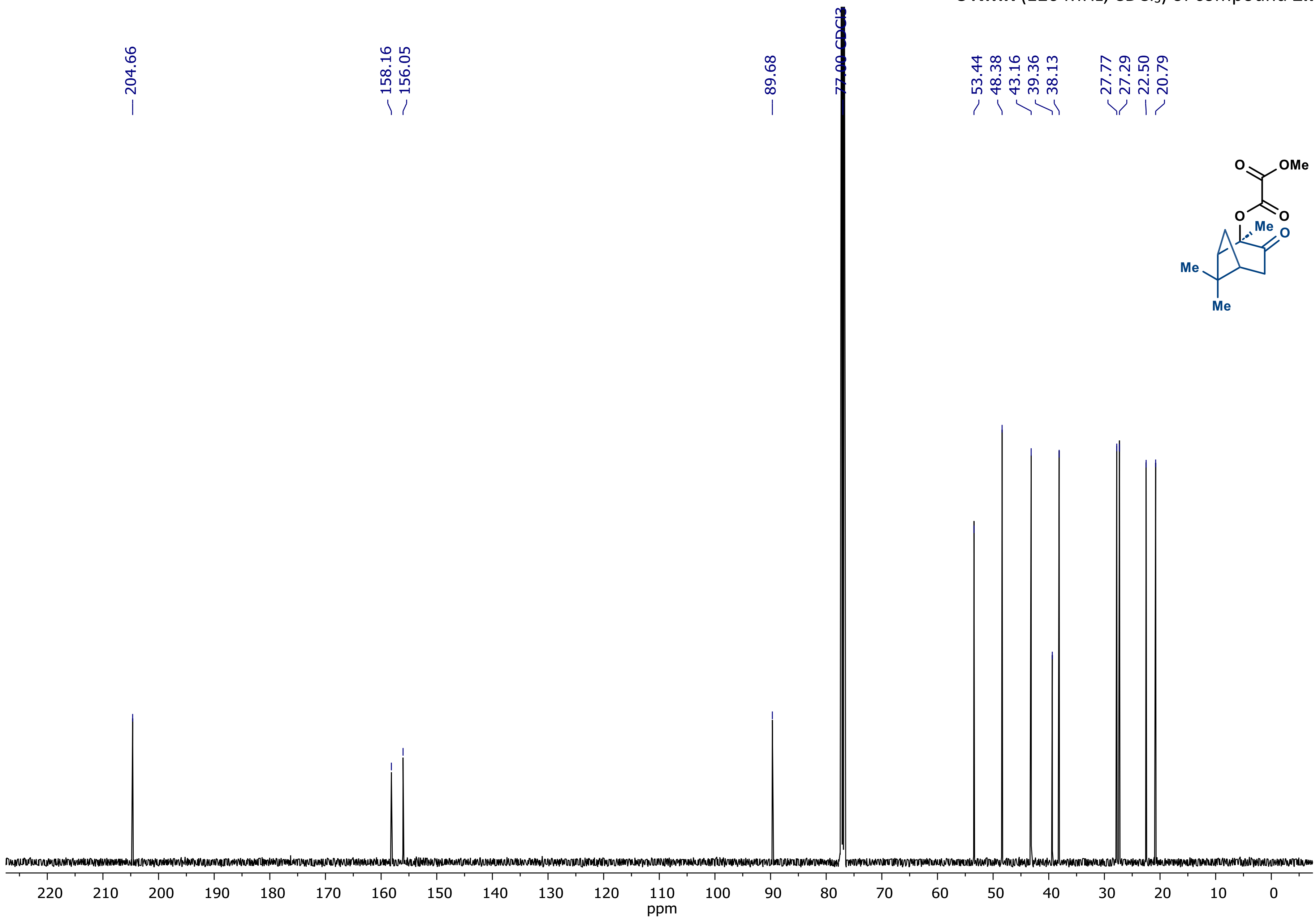
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2j**



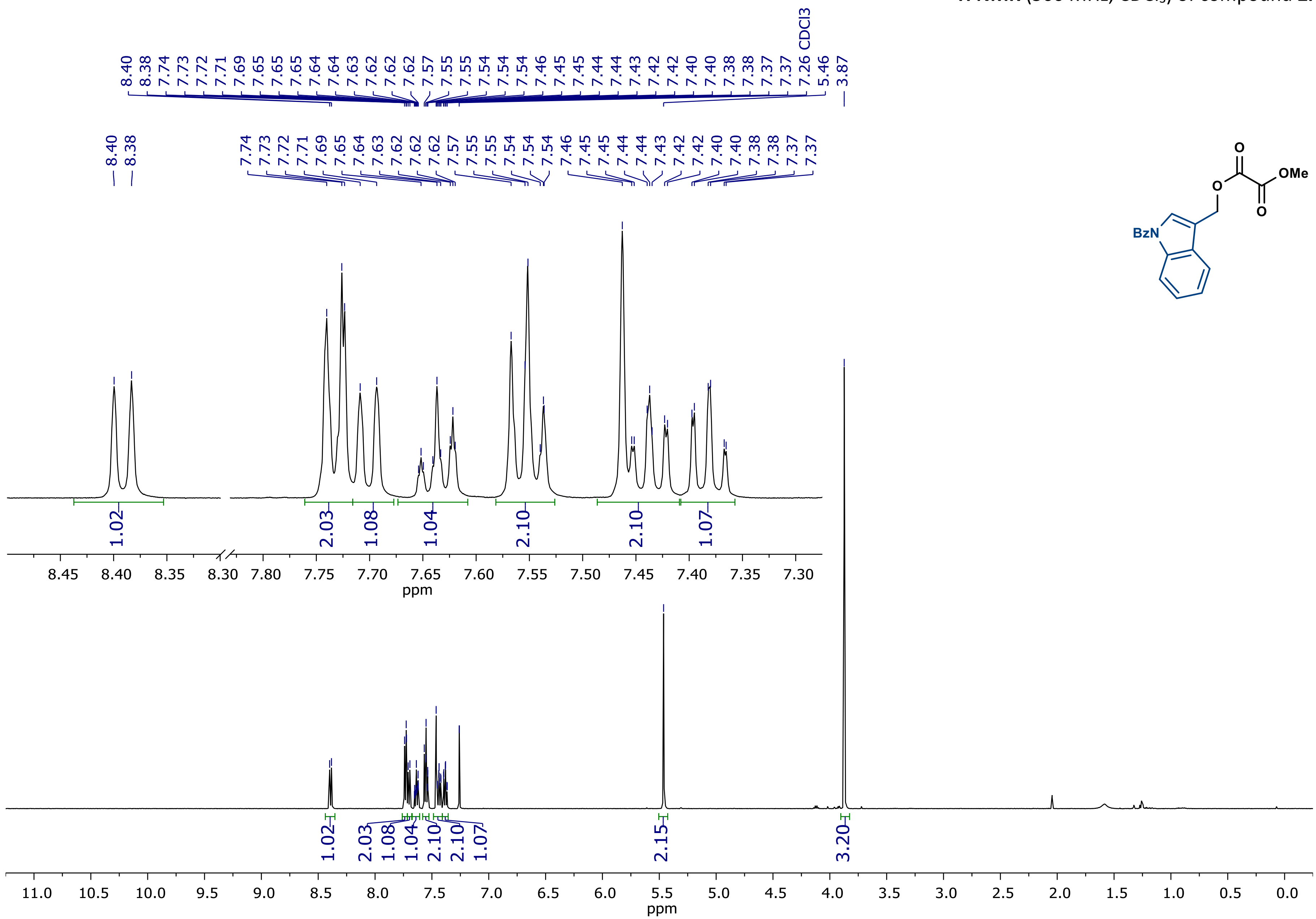
[1]H NMR (500 MHz, $CDCl_3$) of compound **2k**



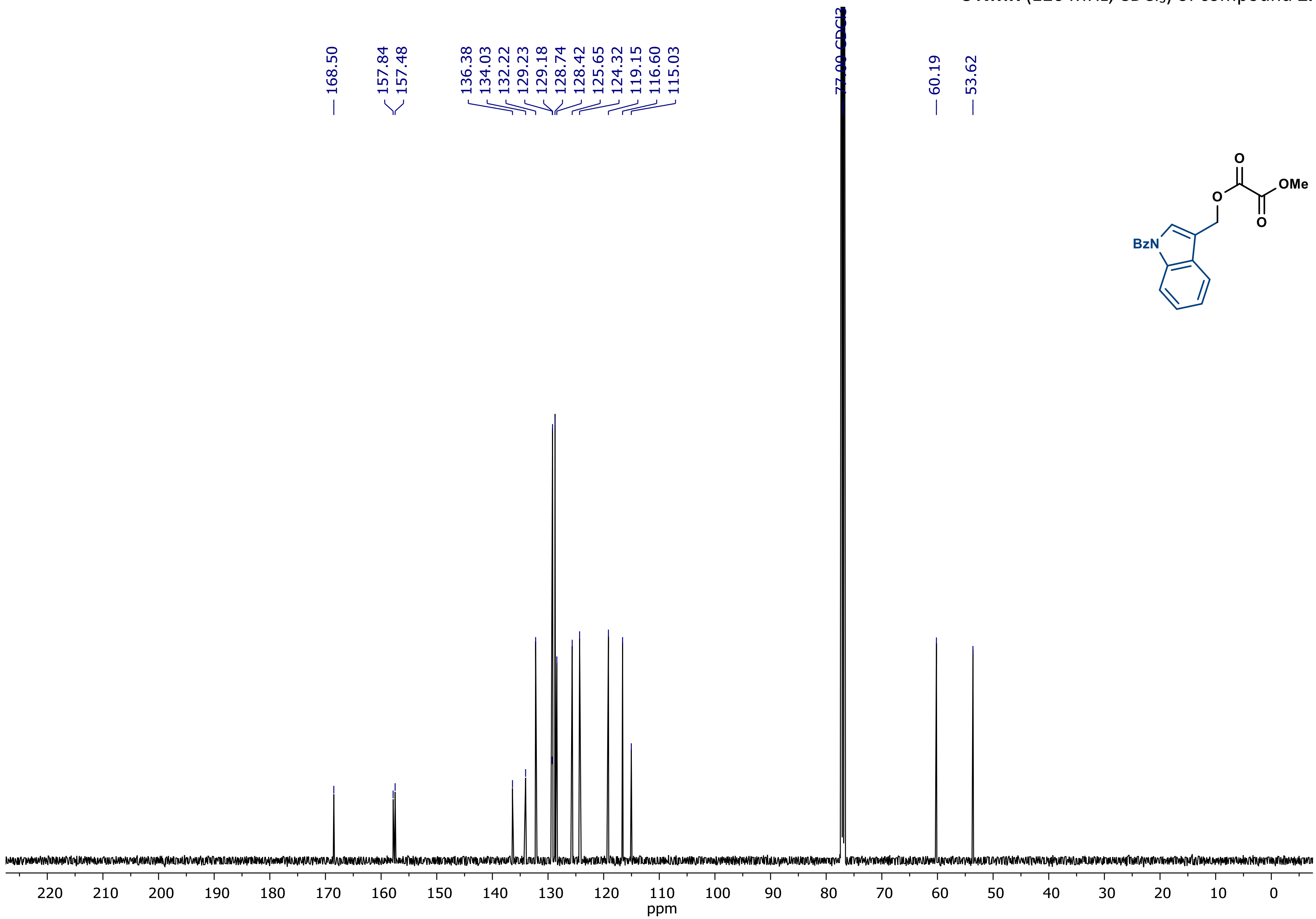
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2k**



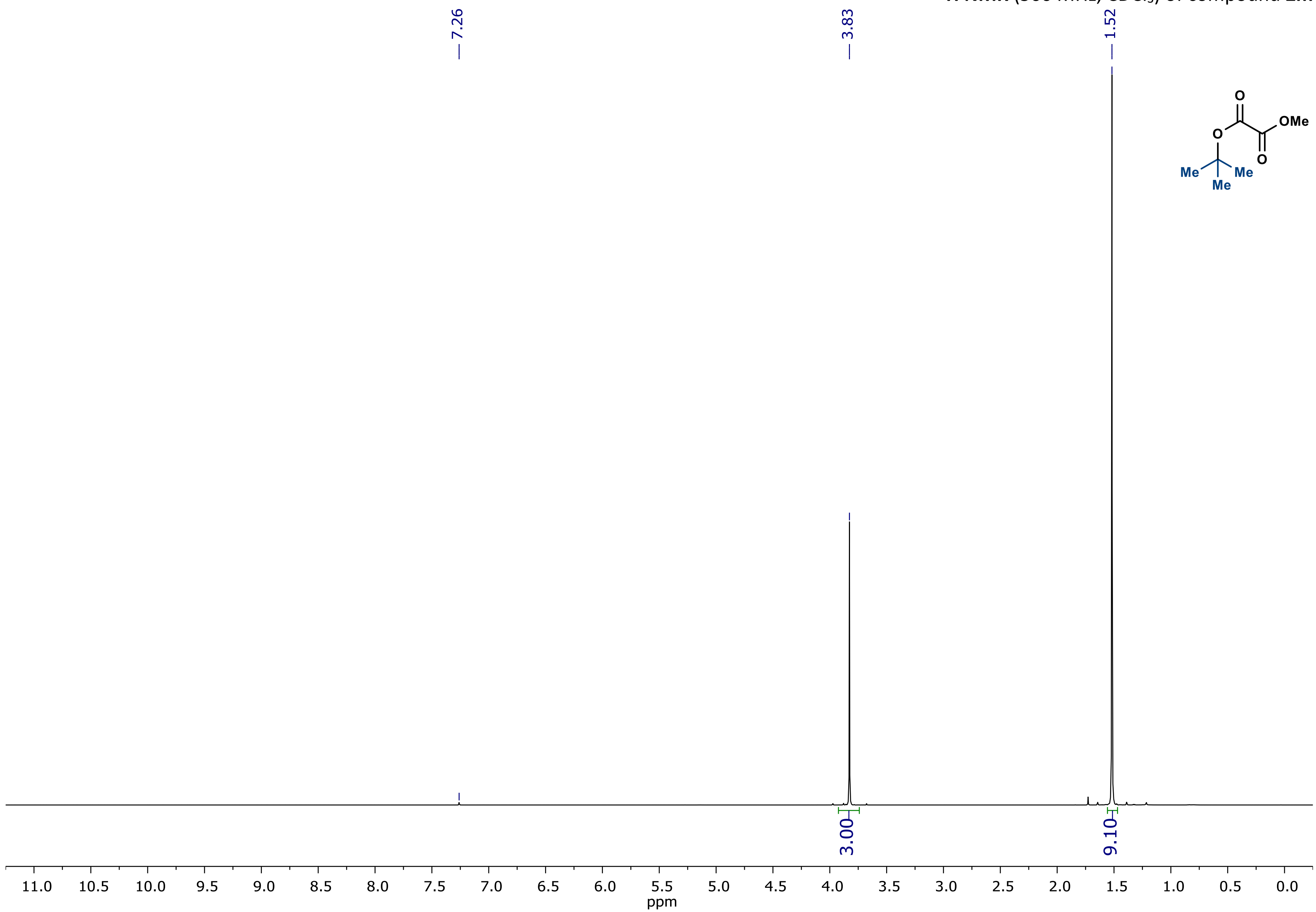
[1]H NMR (500 MHz, $CDCl_3$) of compound **2l**



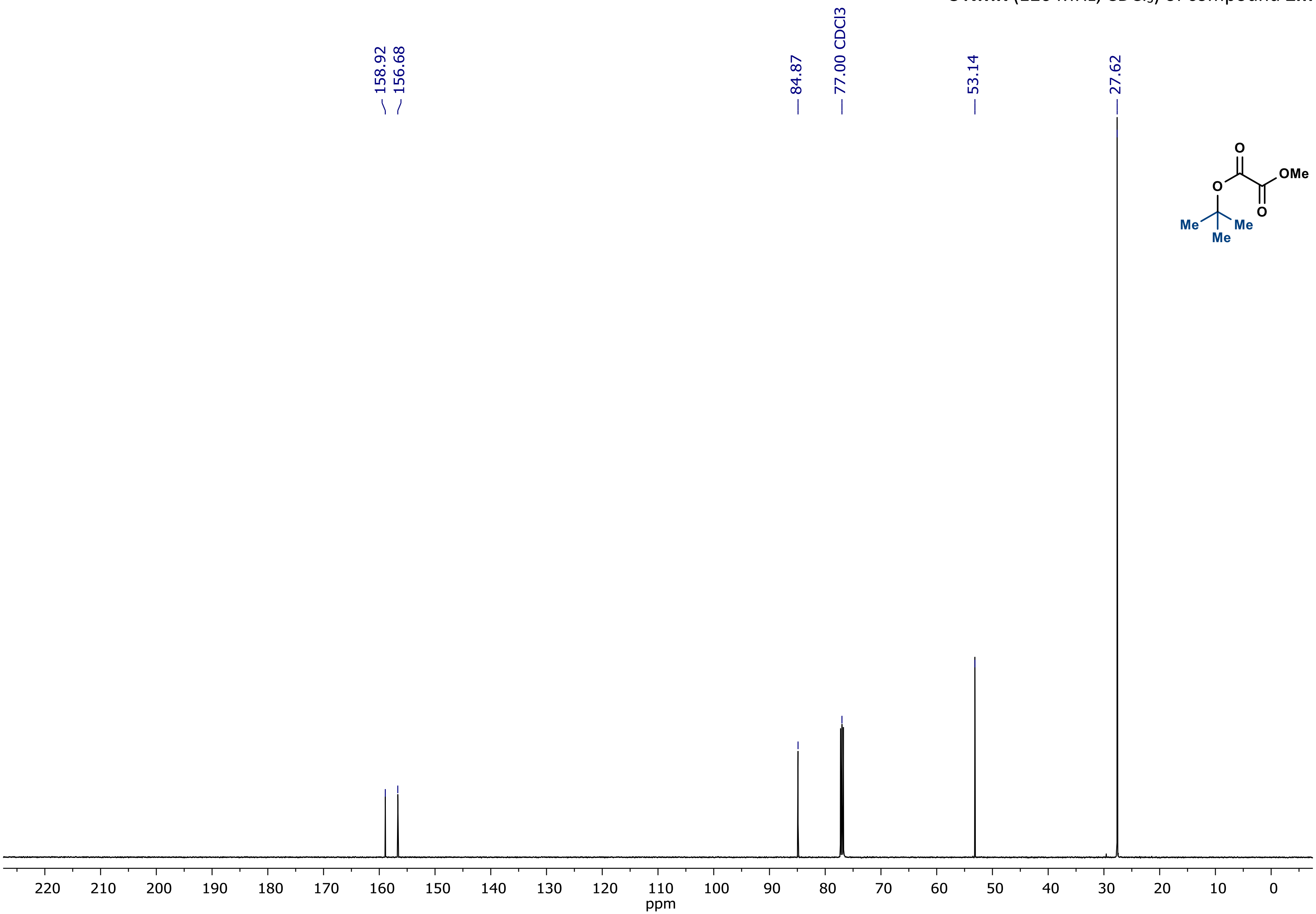
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2l**



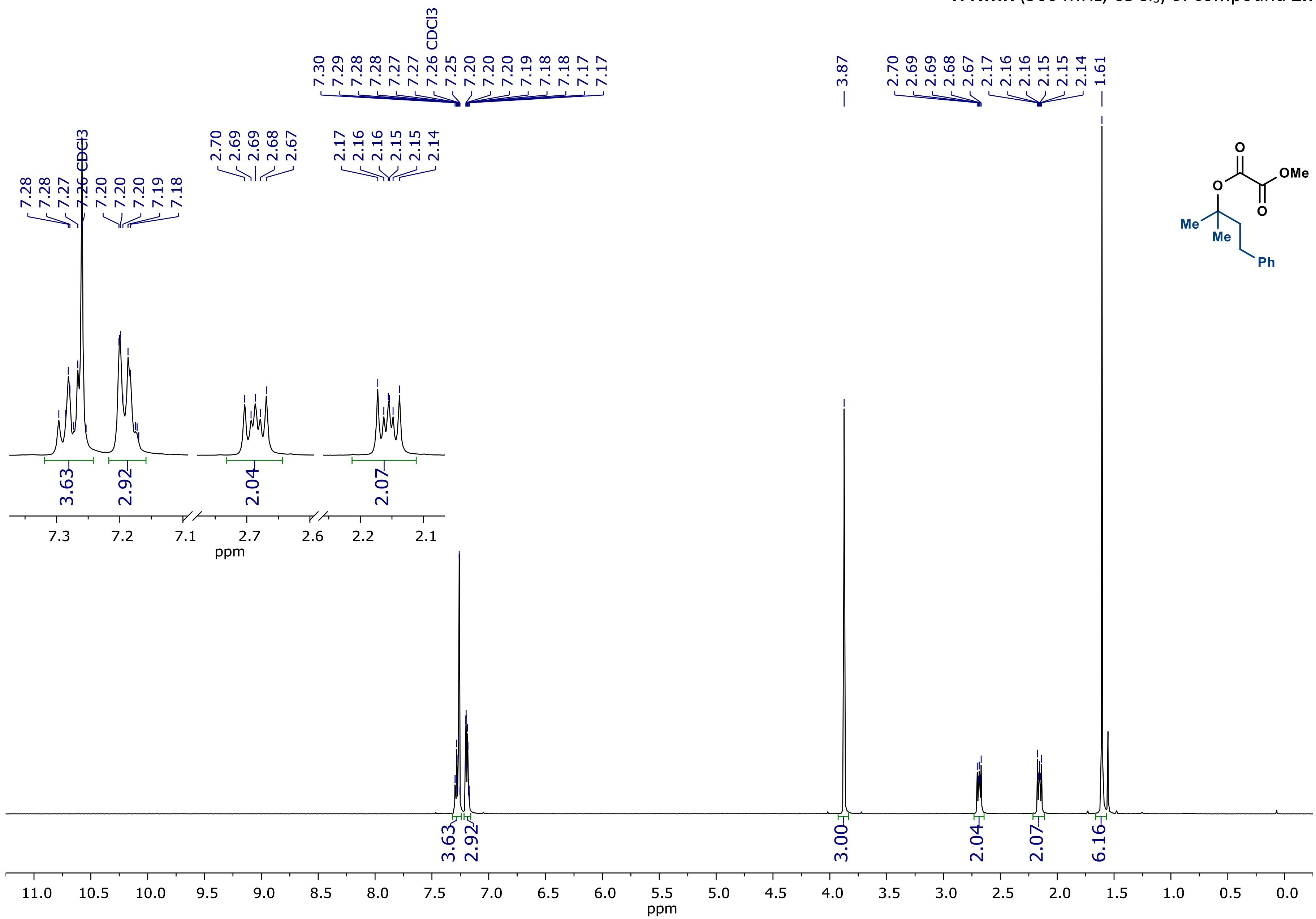
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2m**



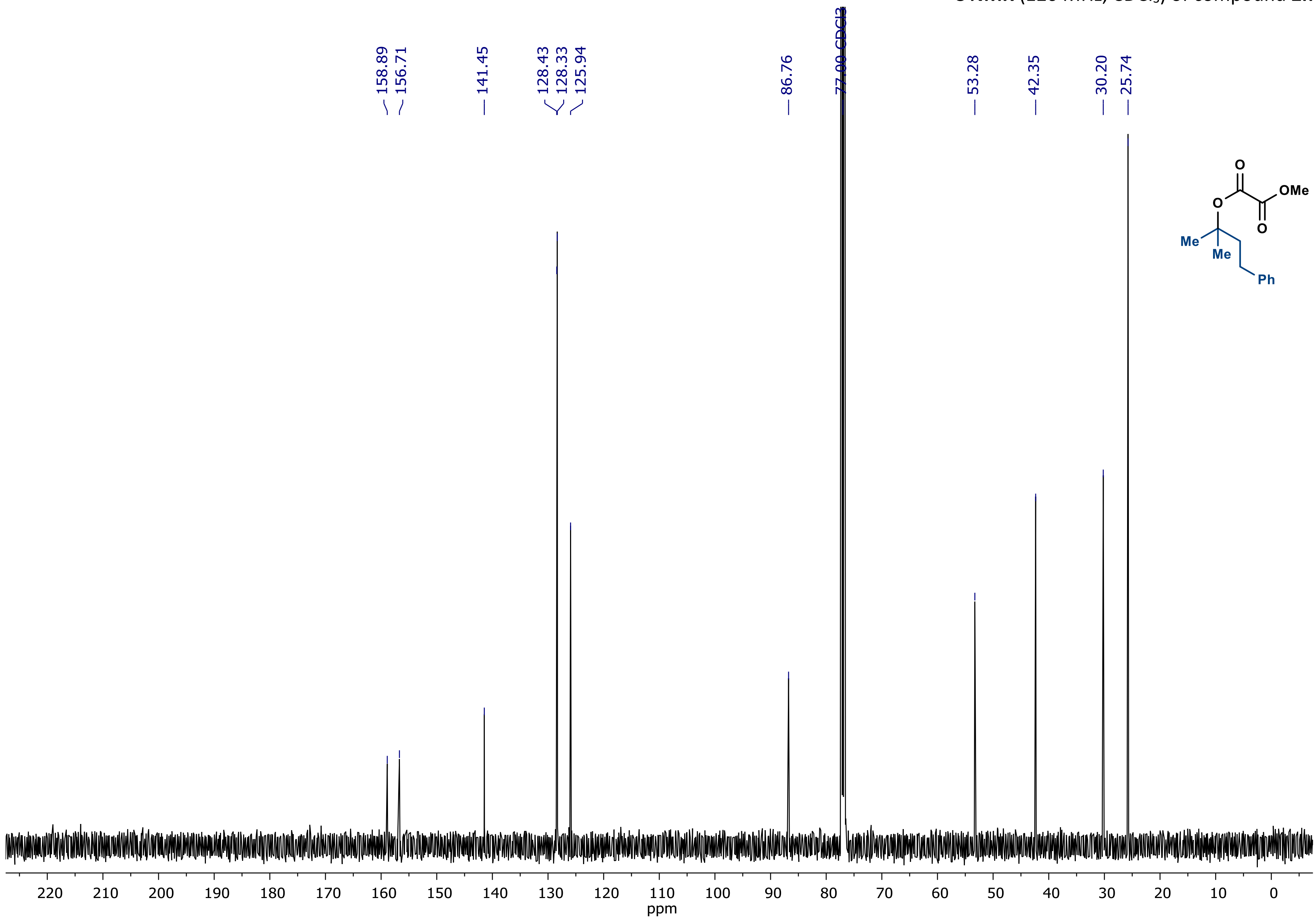
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2m**



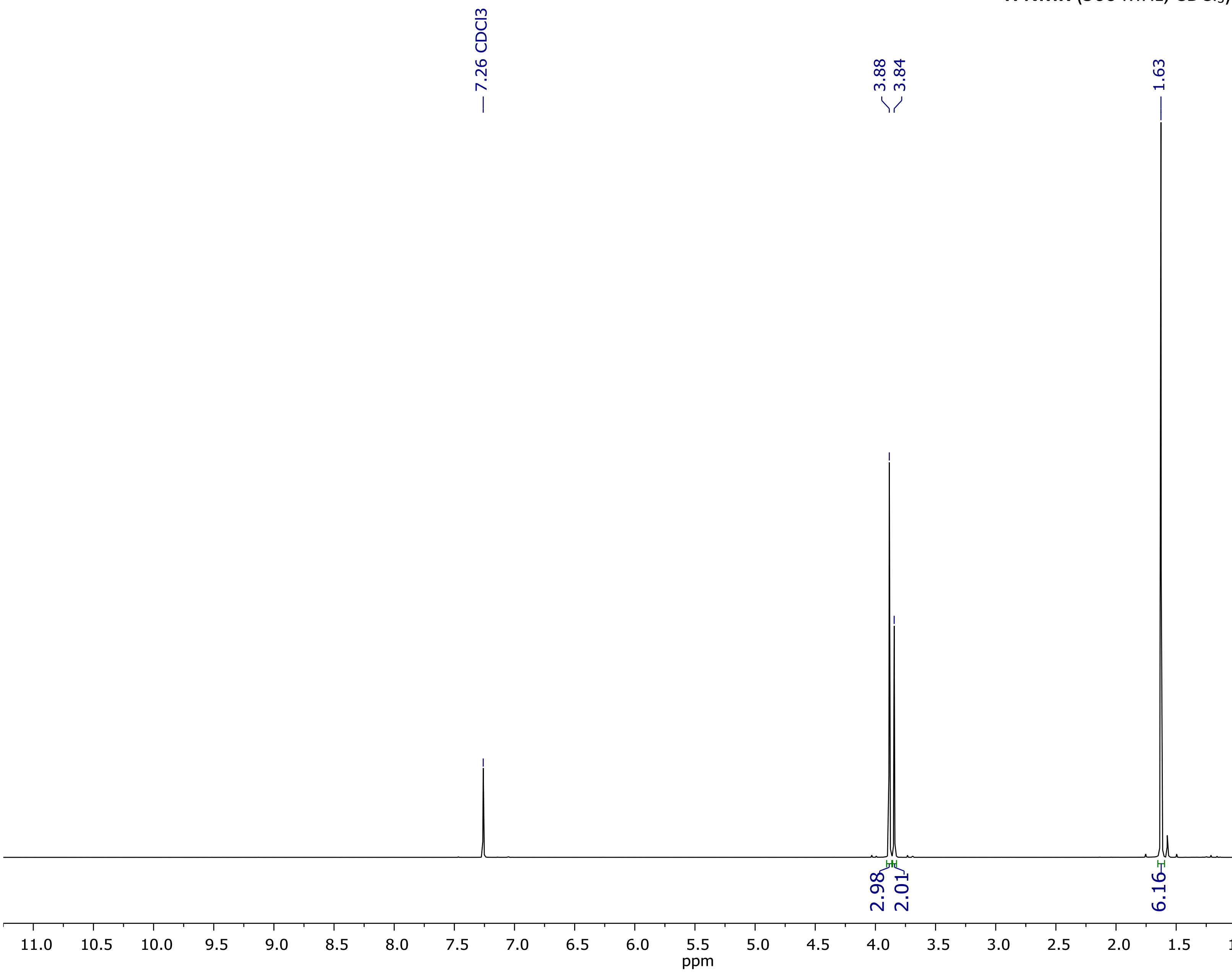
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2n**

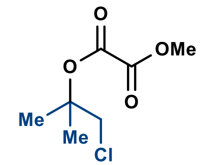


[13]C NMR (126 MHz, $CDCl_3$) of compound **2n**

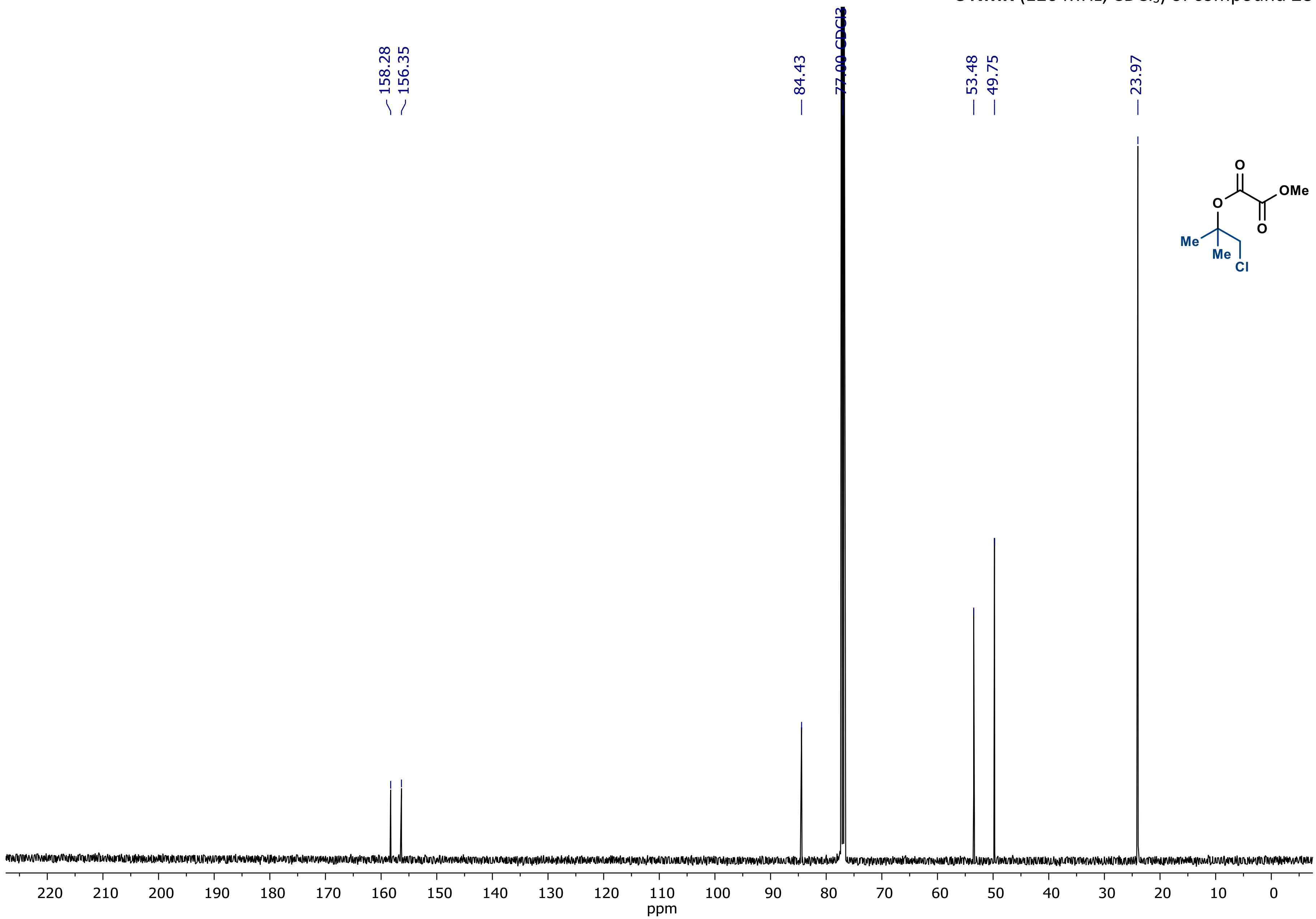


^{1}H NMR (500 MHz, $CDCl_3$) of compound **2o**

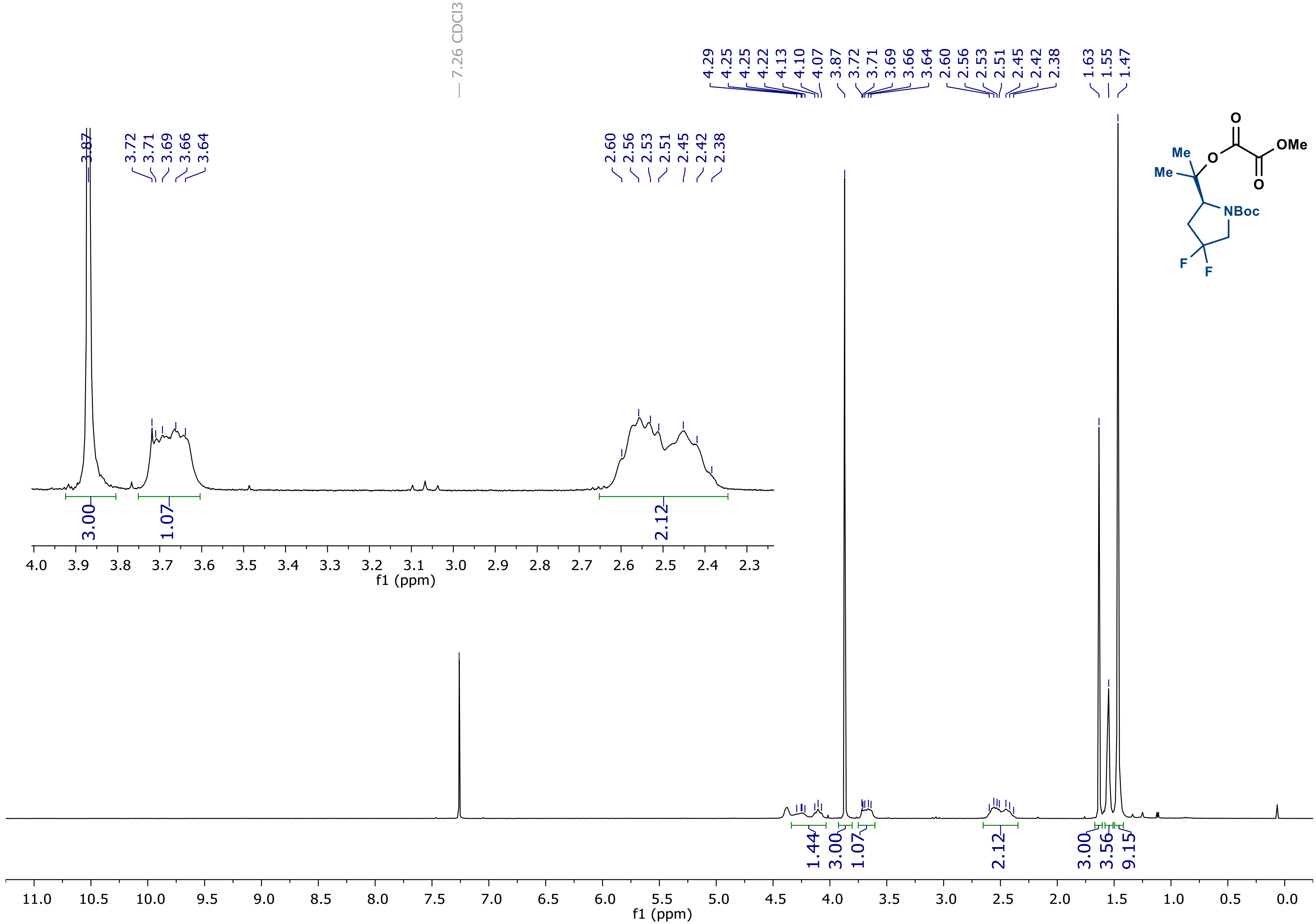




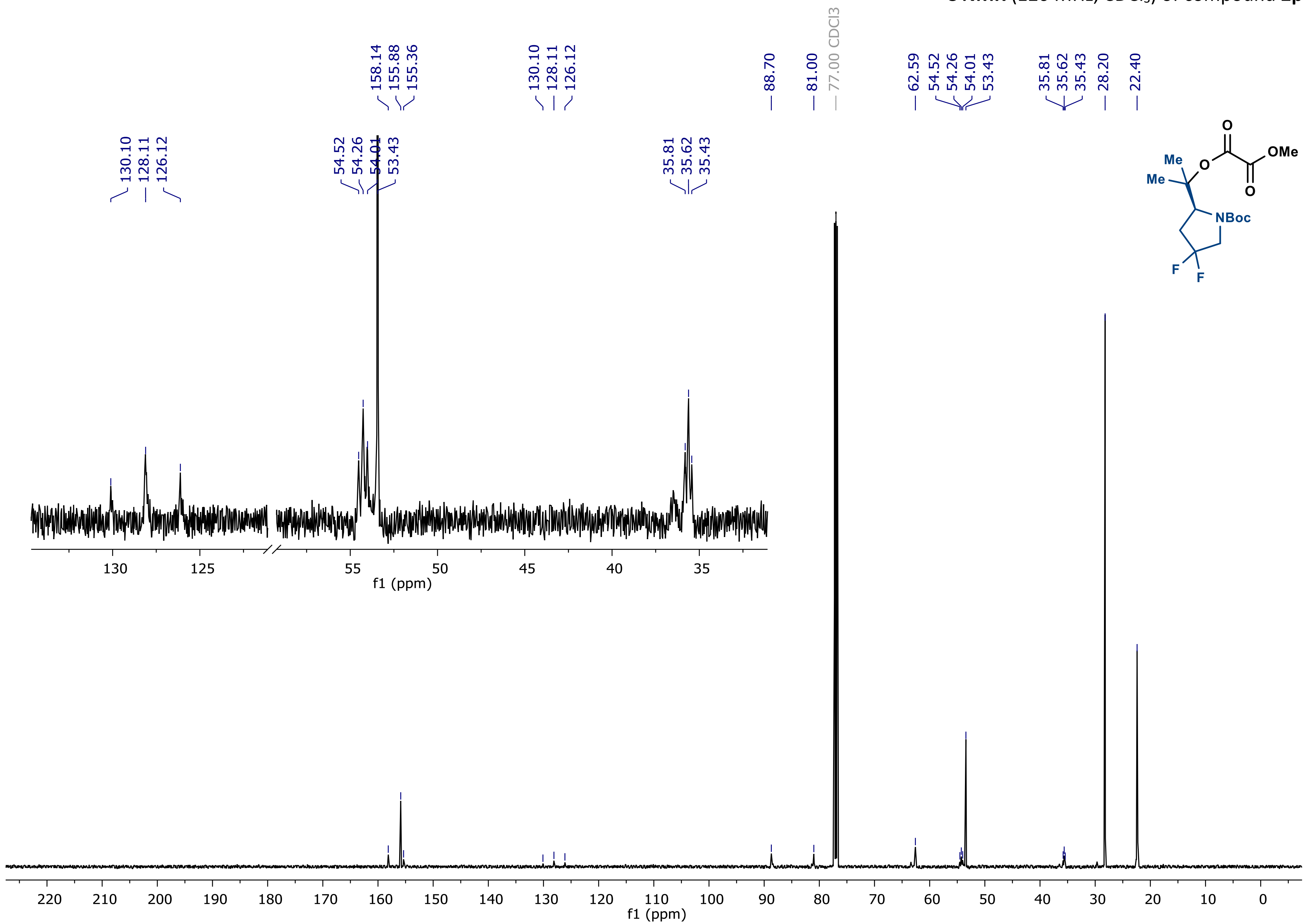
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2o**



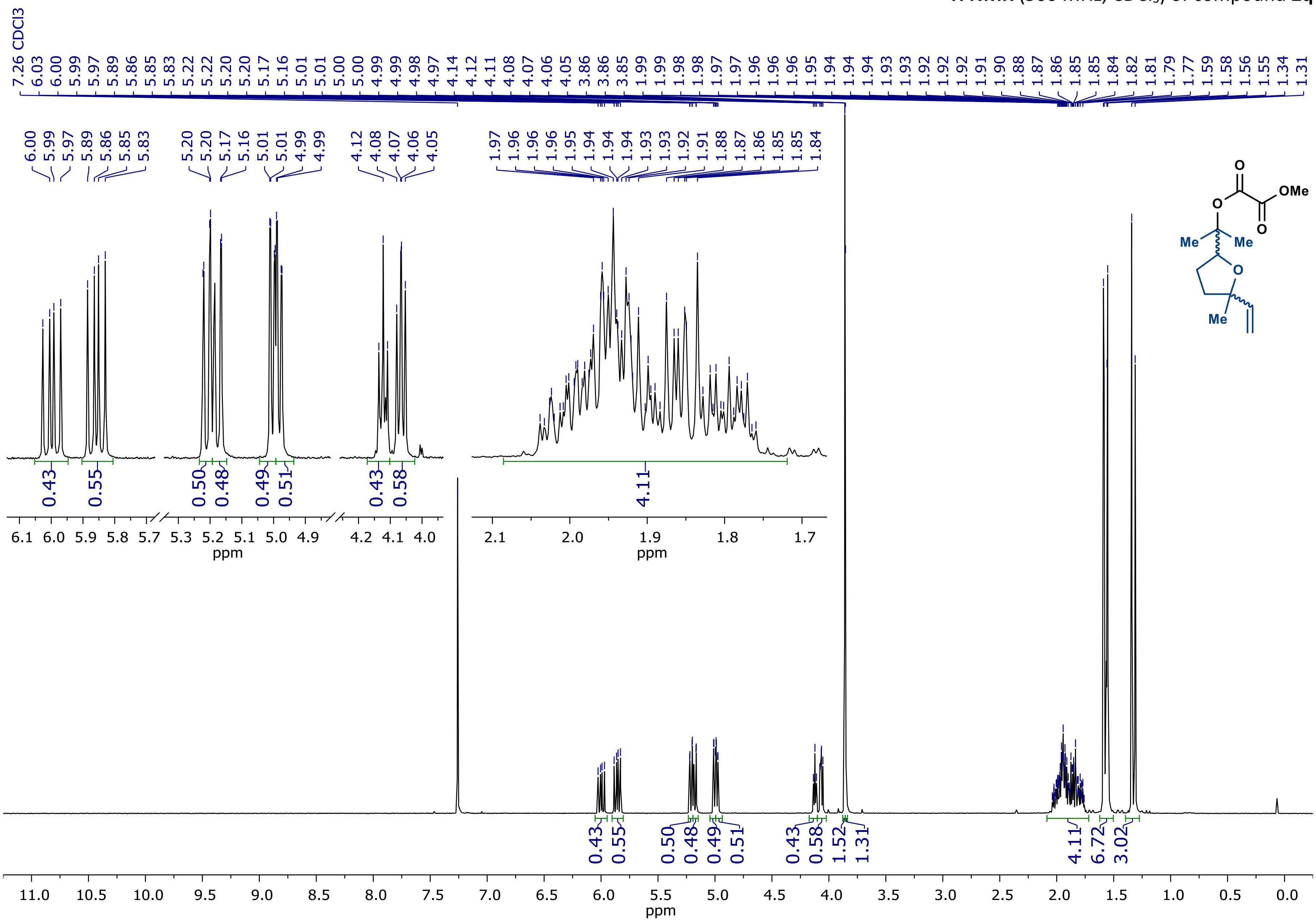
[1]H NMR (500 MHz, $CDCl_3$) of compound **2p**



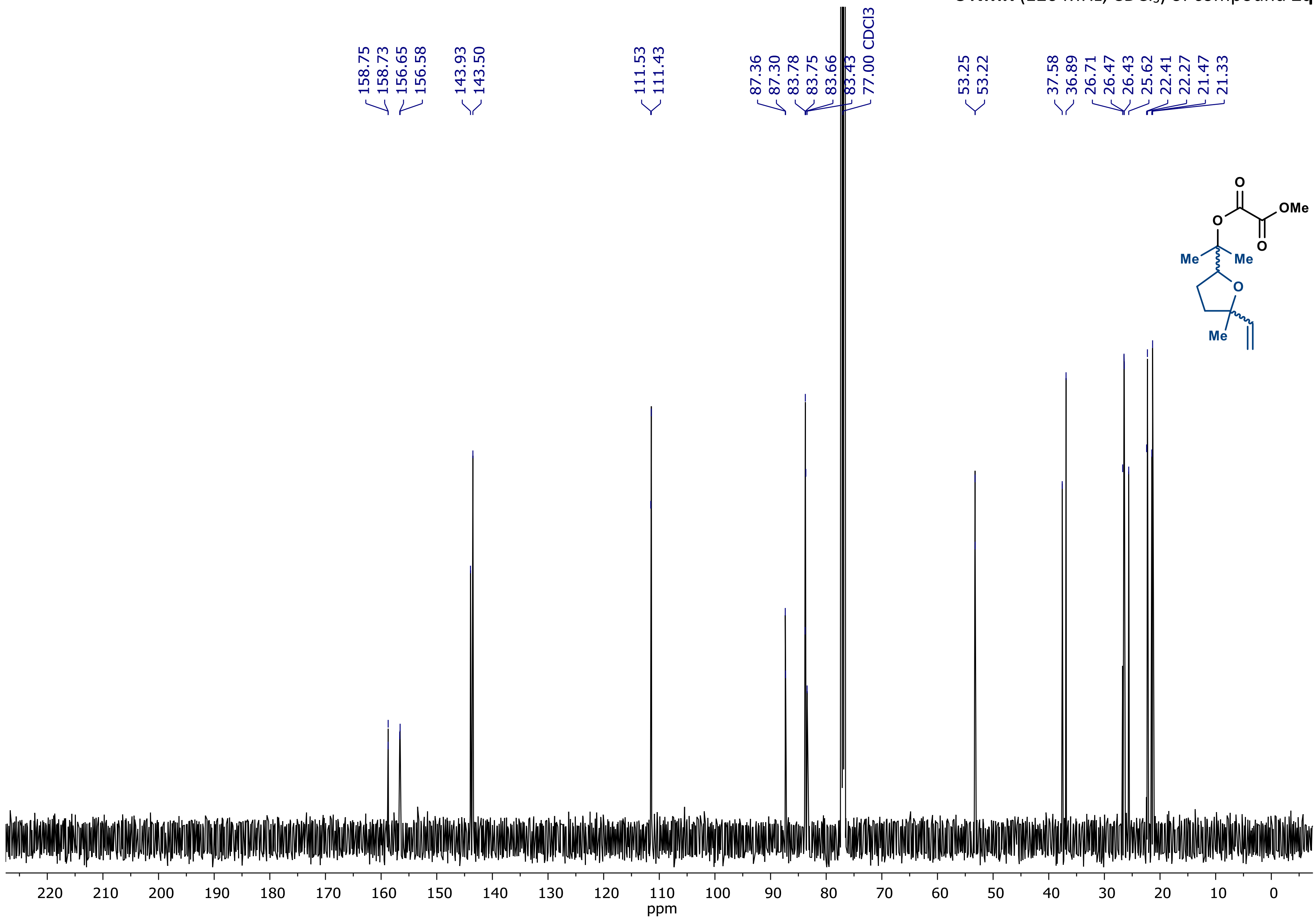
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2p**



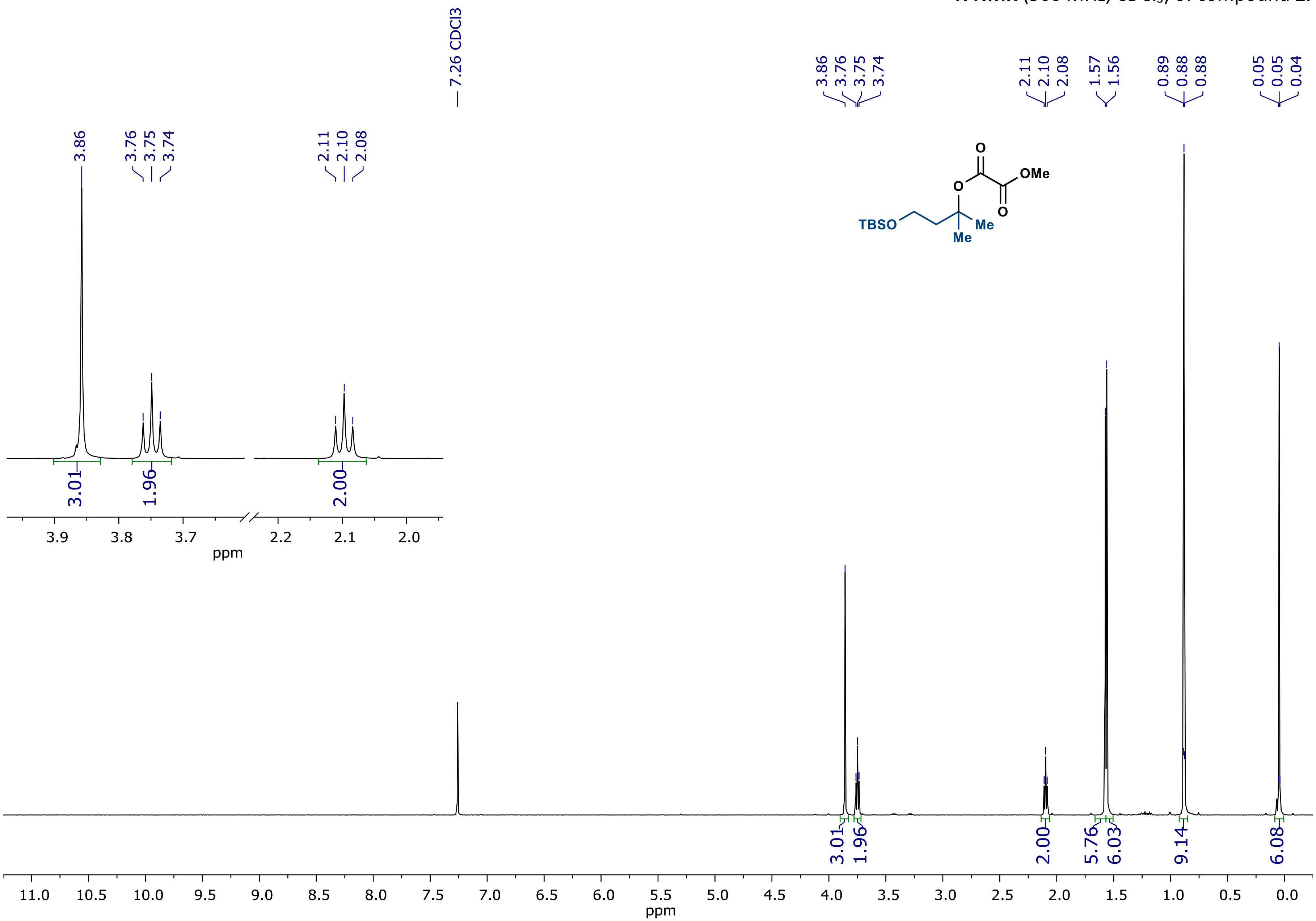
[1]H NMR (500 MHz, $CDCl_3$) of compound **2q**



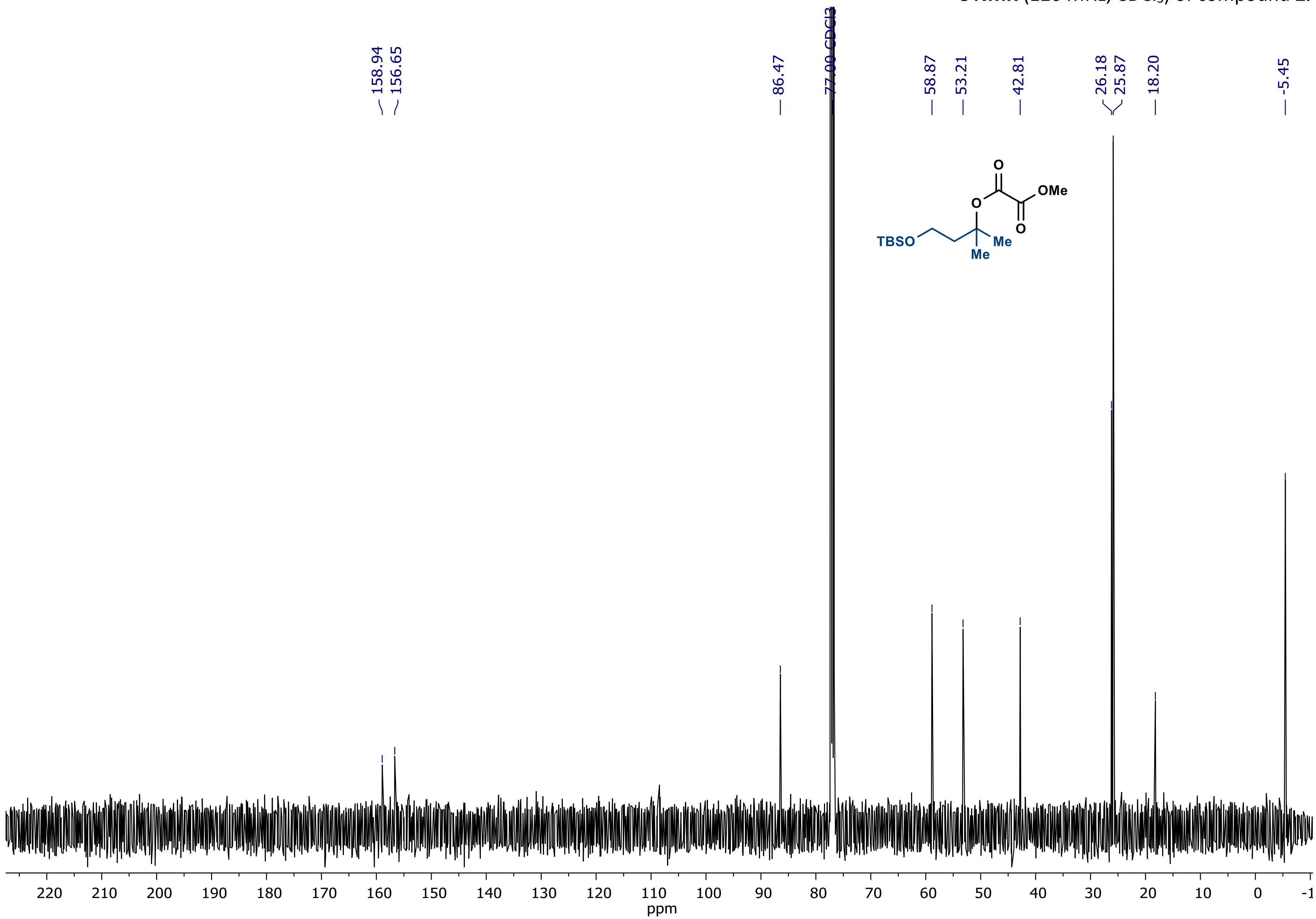
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2q**



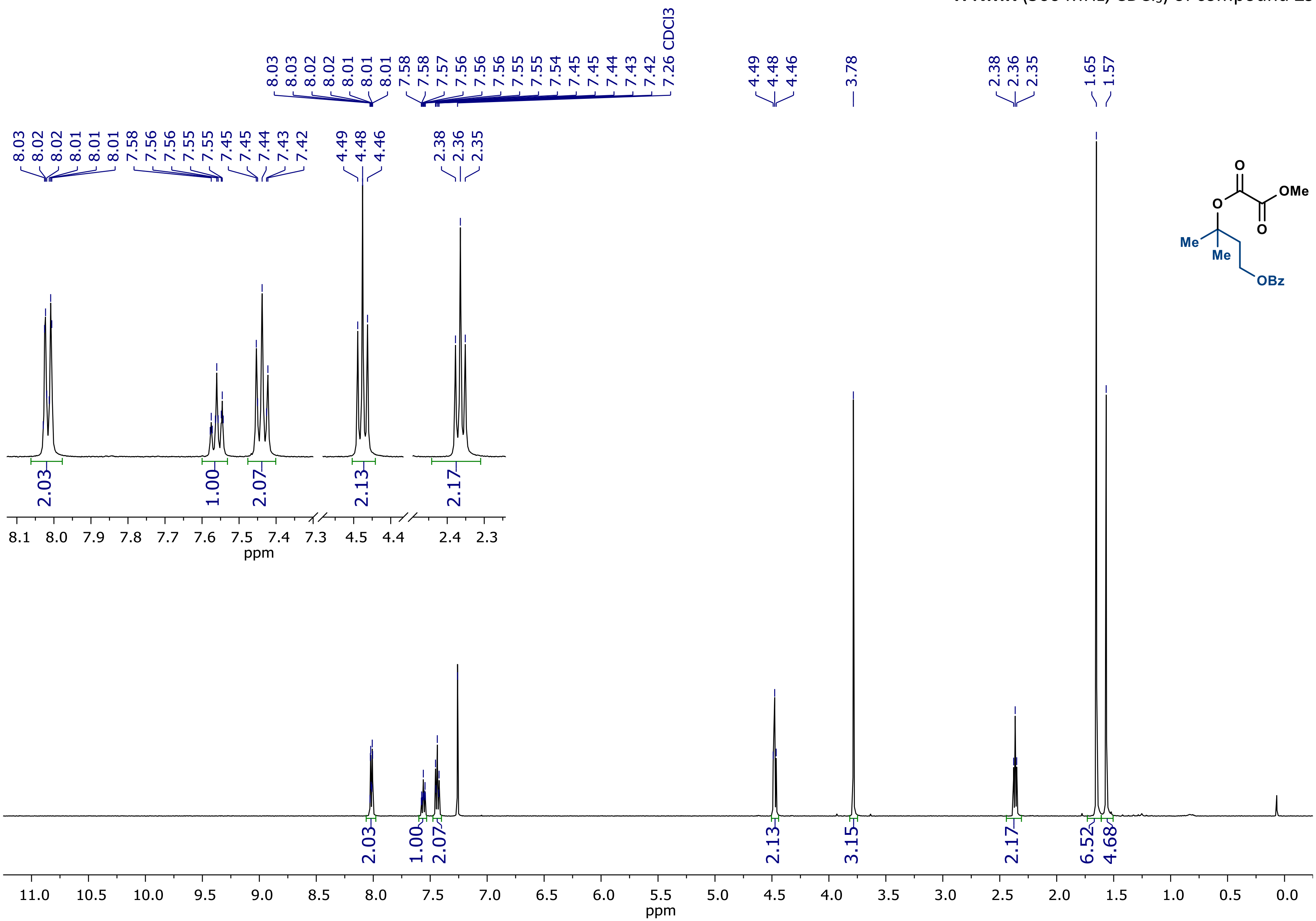
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2r**



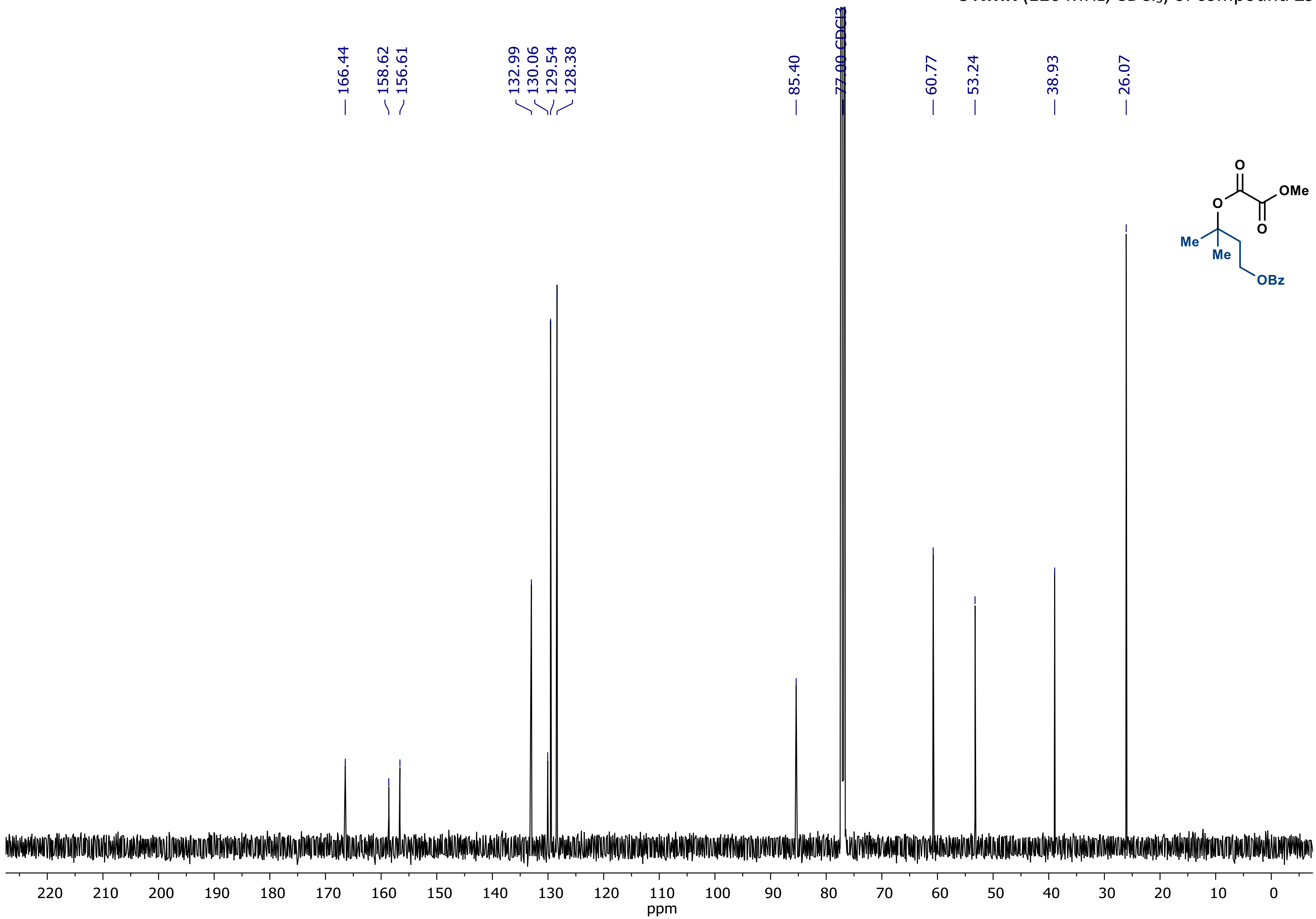
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2r**



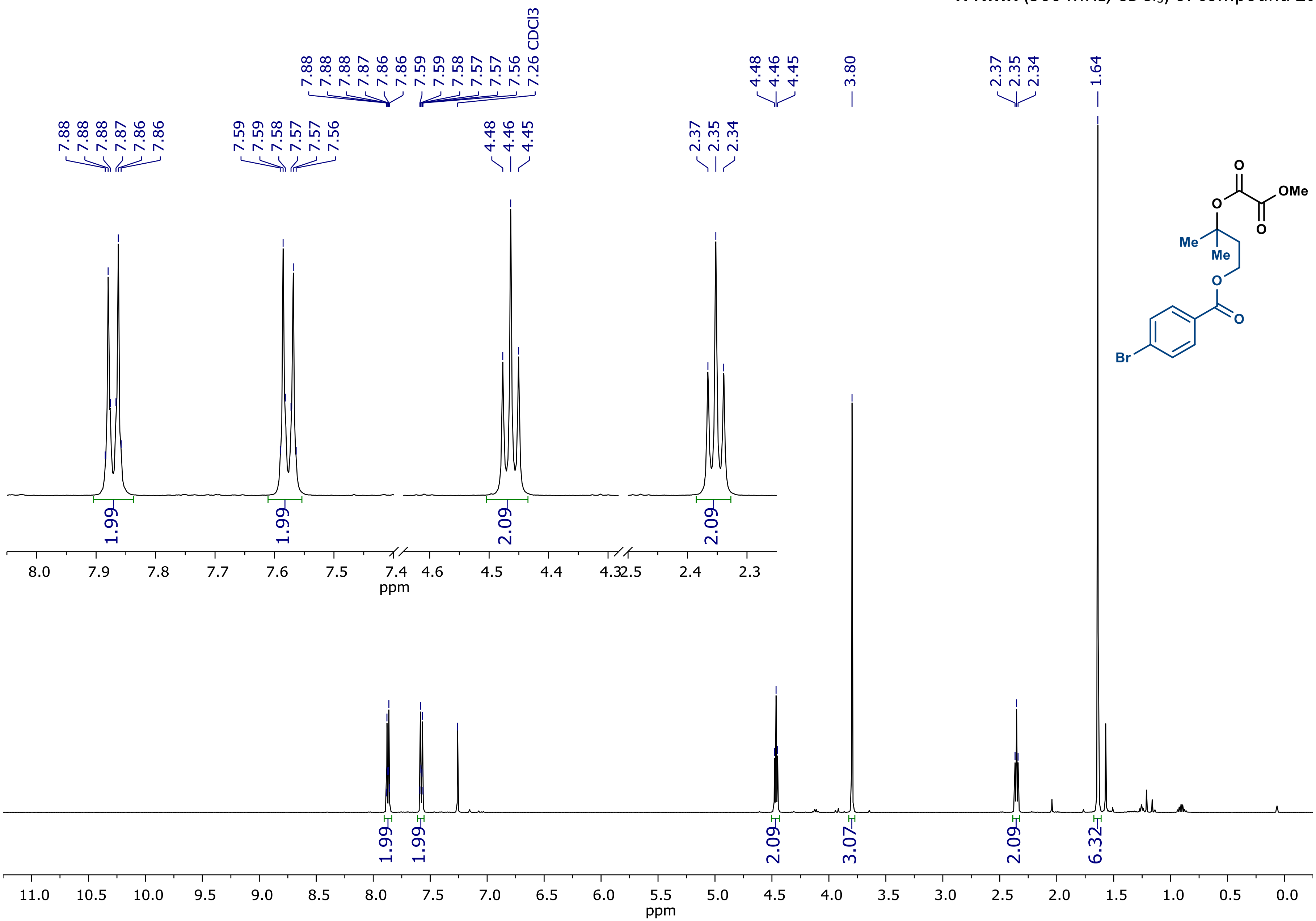
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2s**



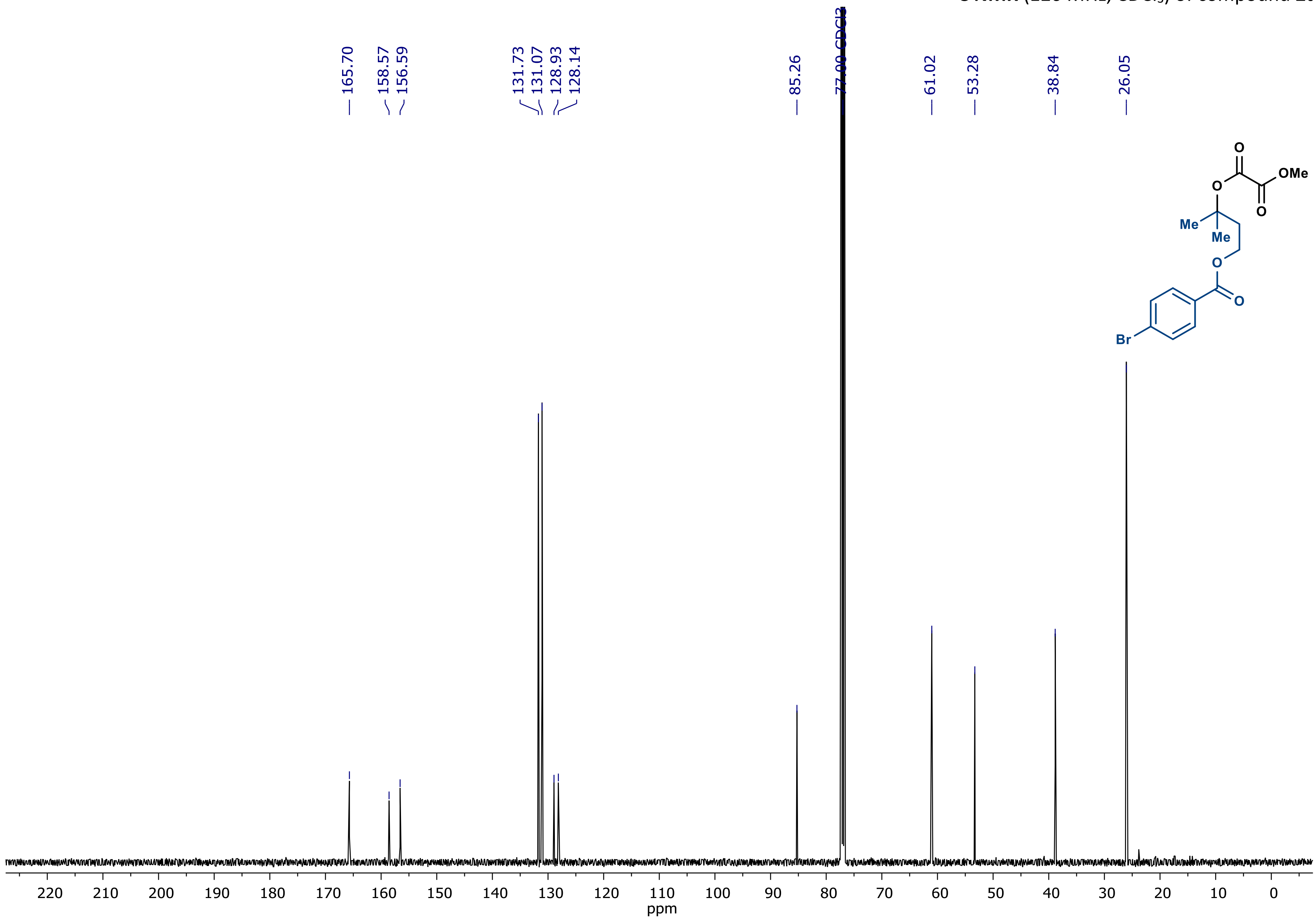
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2s**



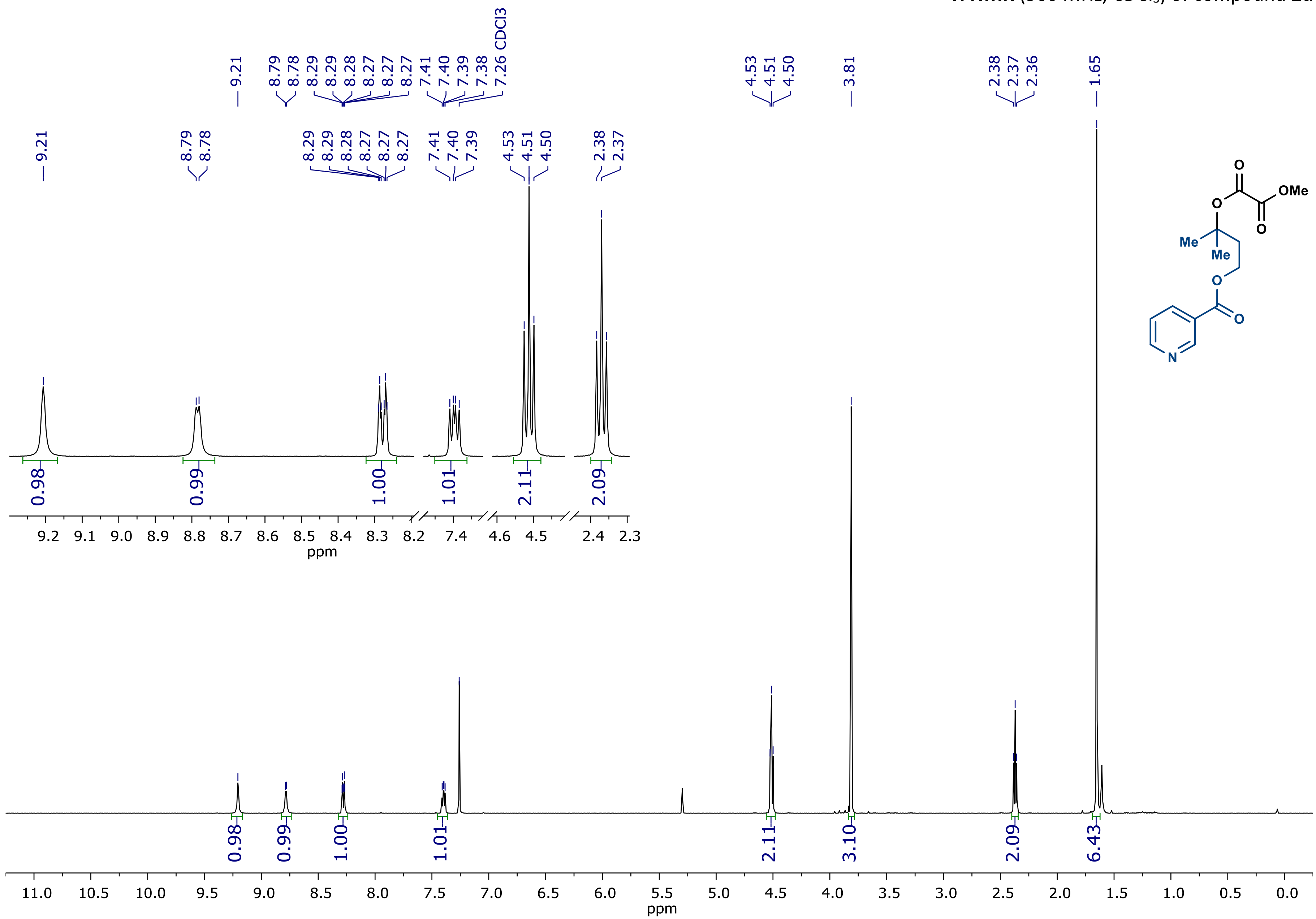
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2t**



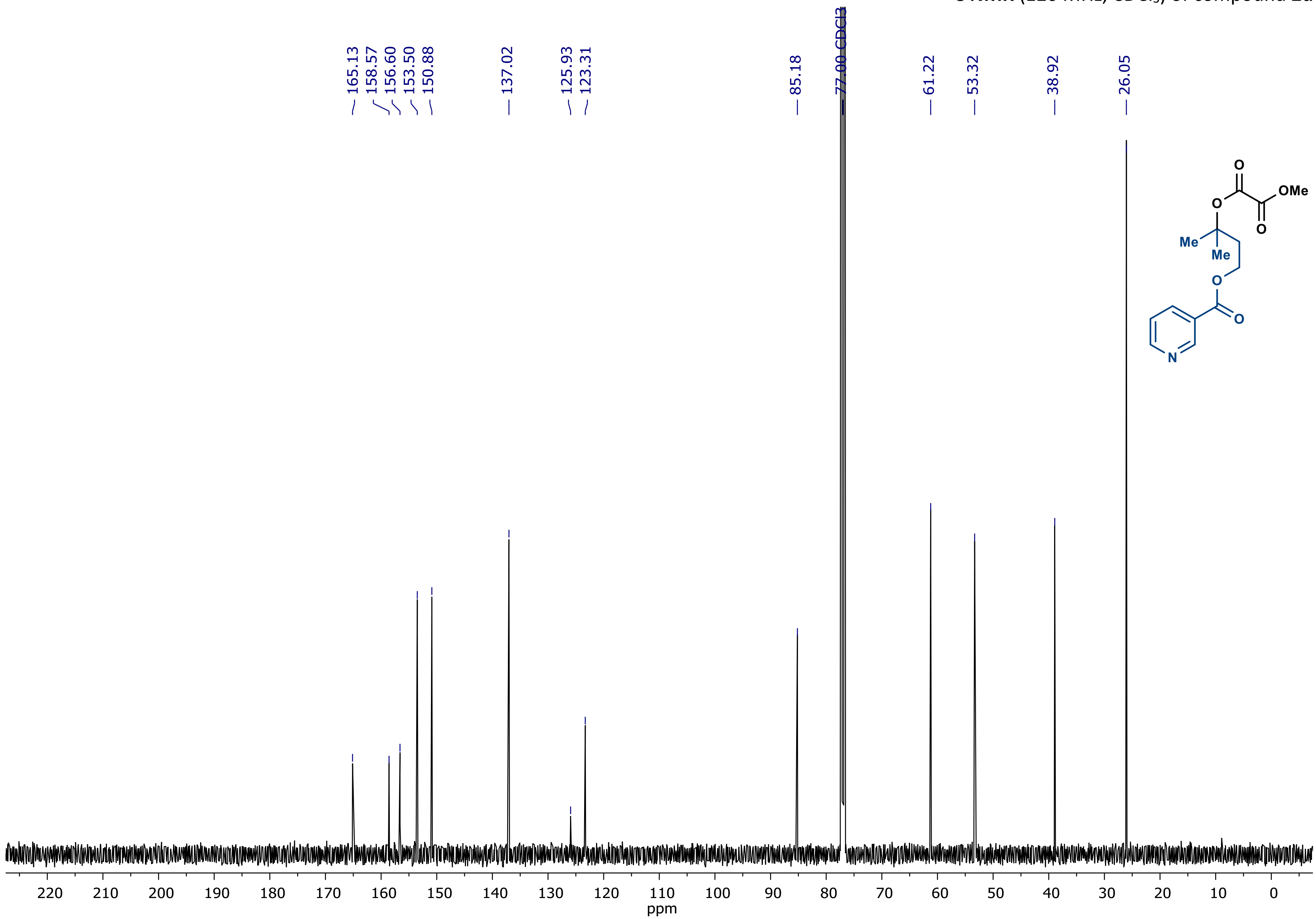
[13]C NMR (126 MHz, $CDCl_3$) of compound **2t**



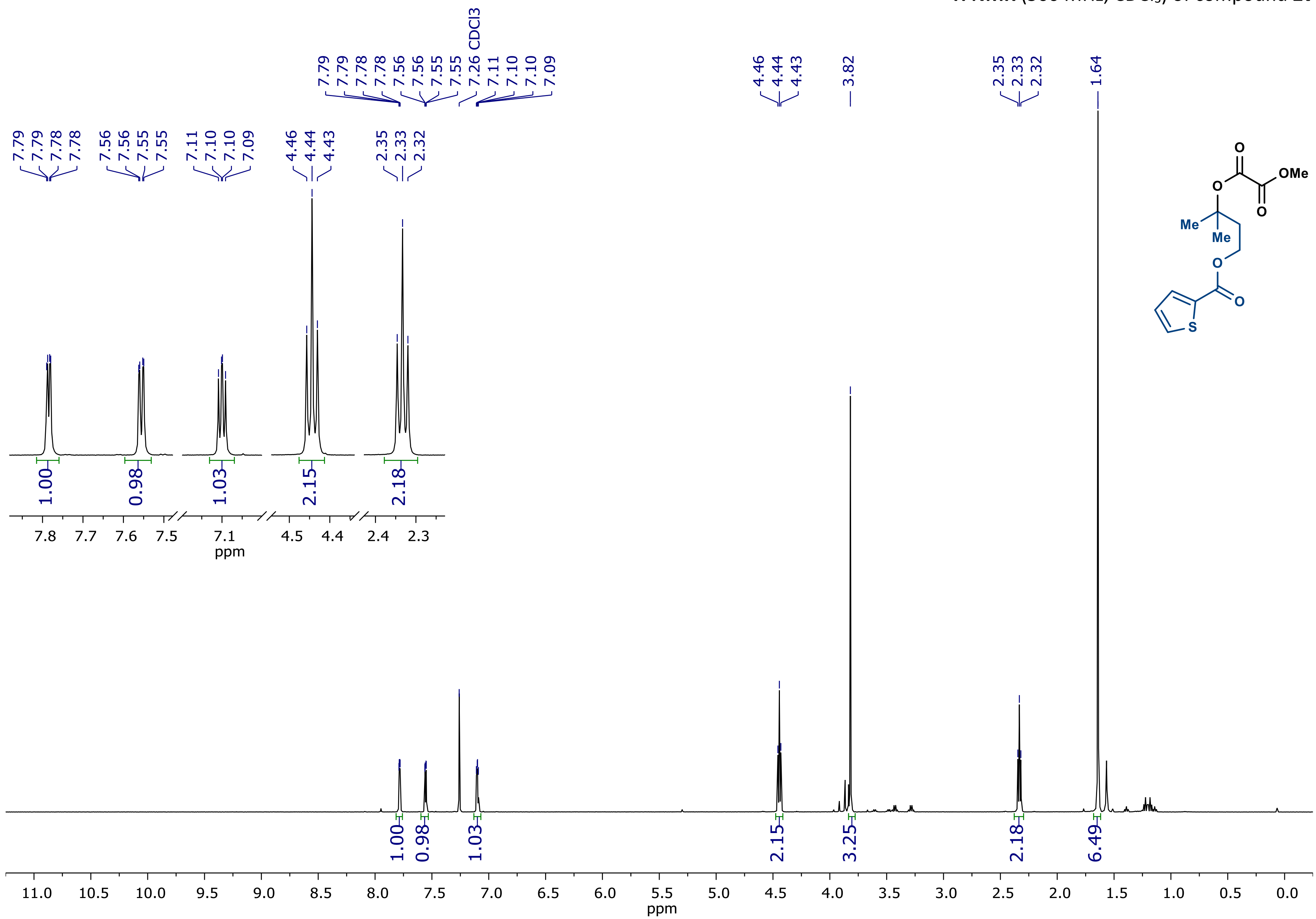
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2u**



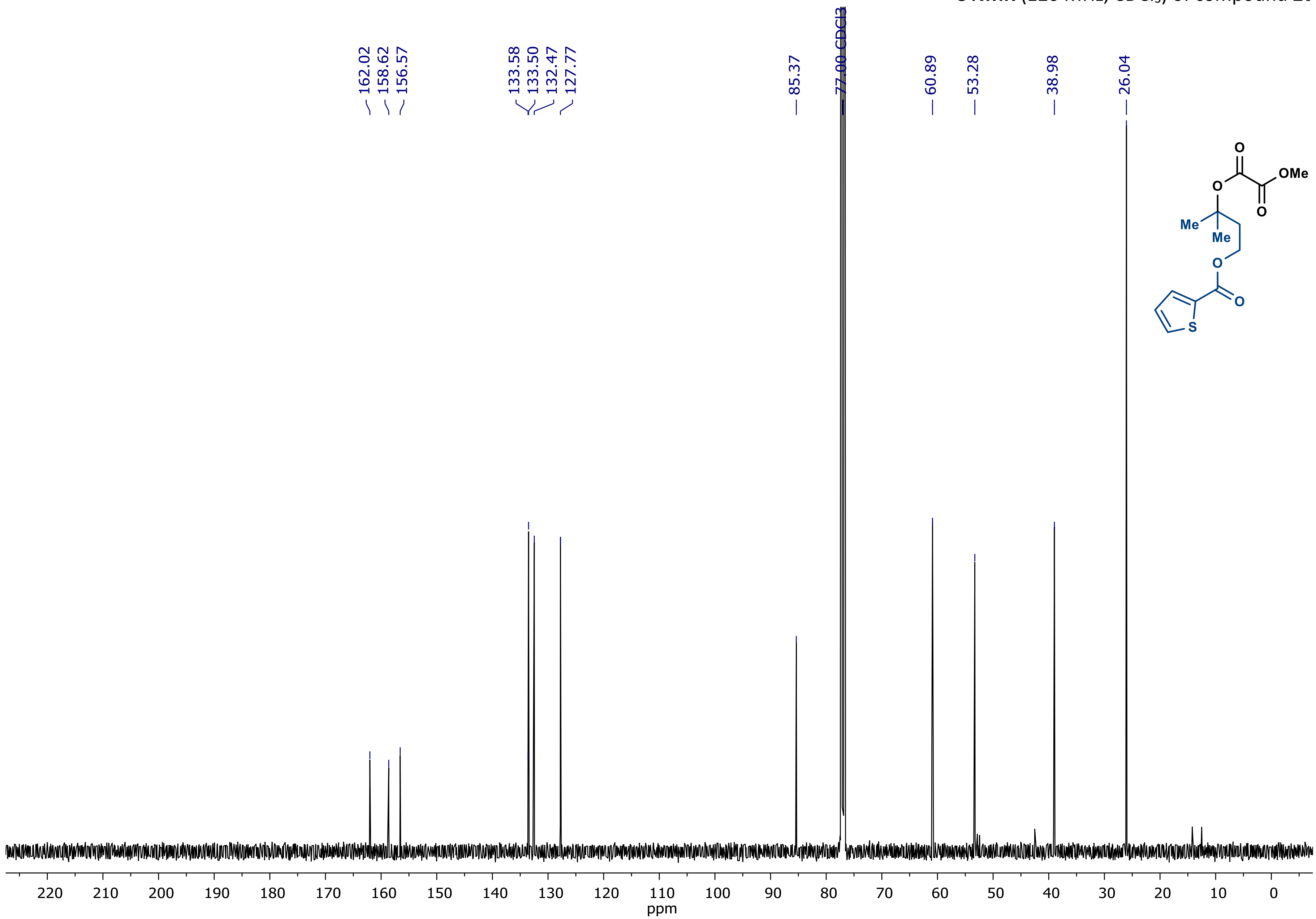
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2u**



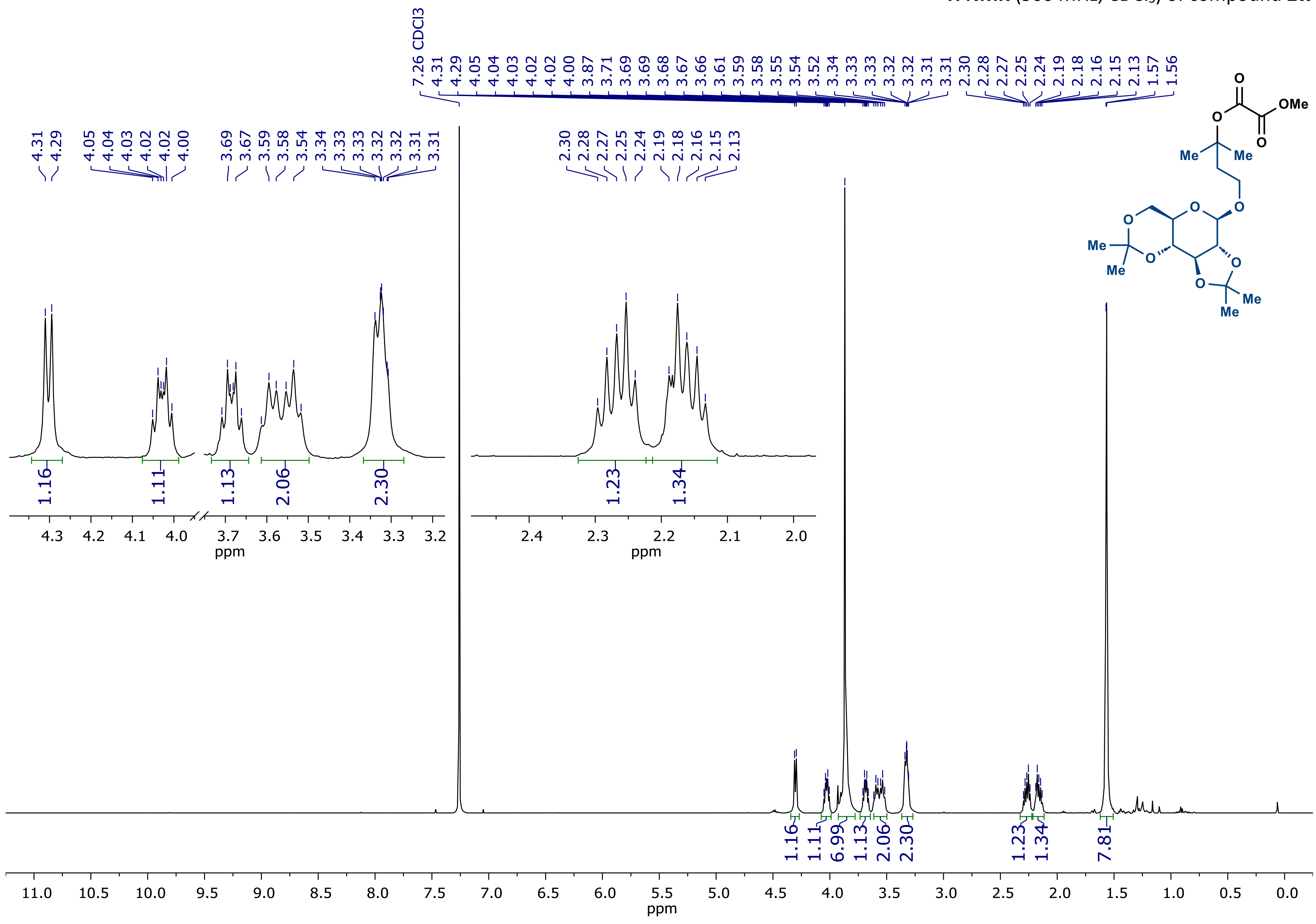
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2v**



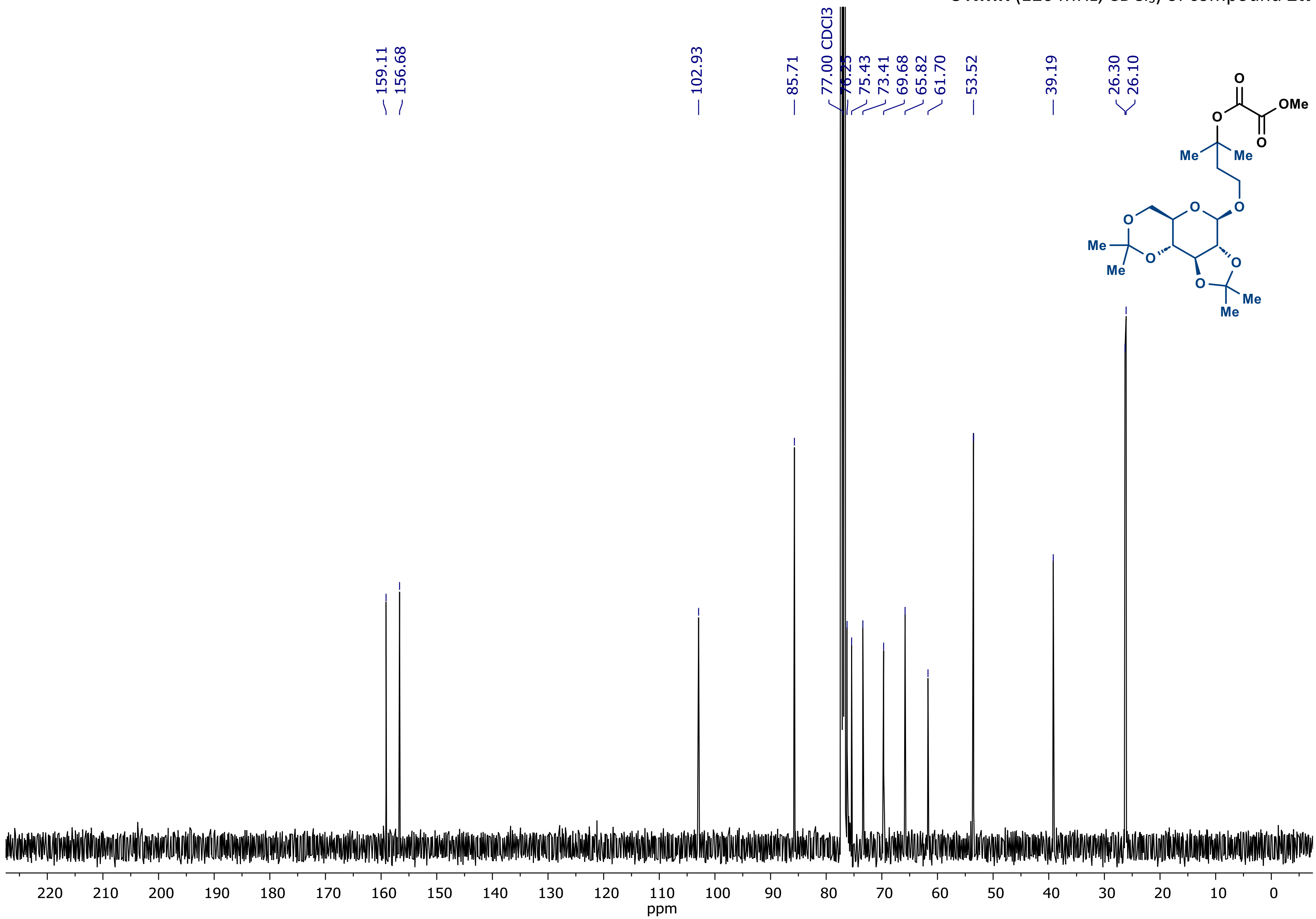
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **2v**



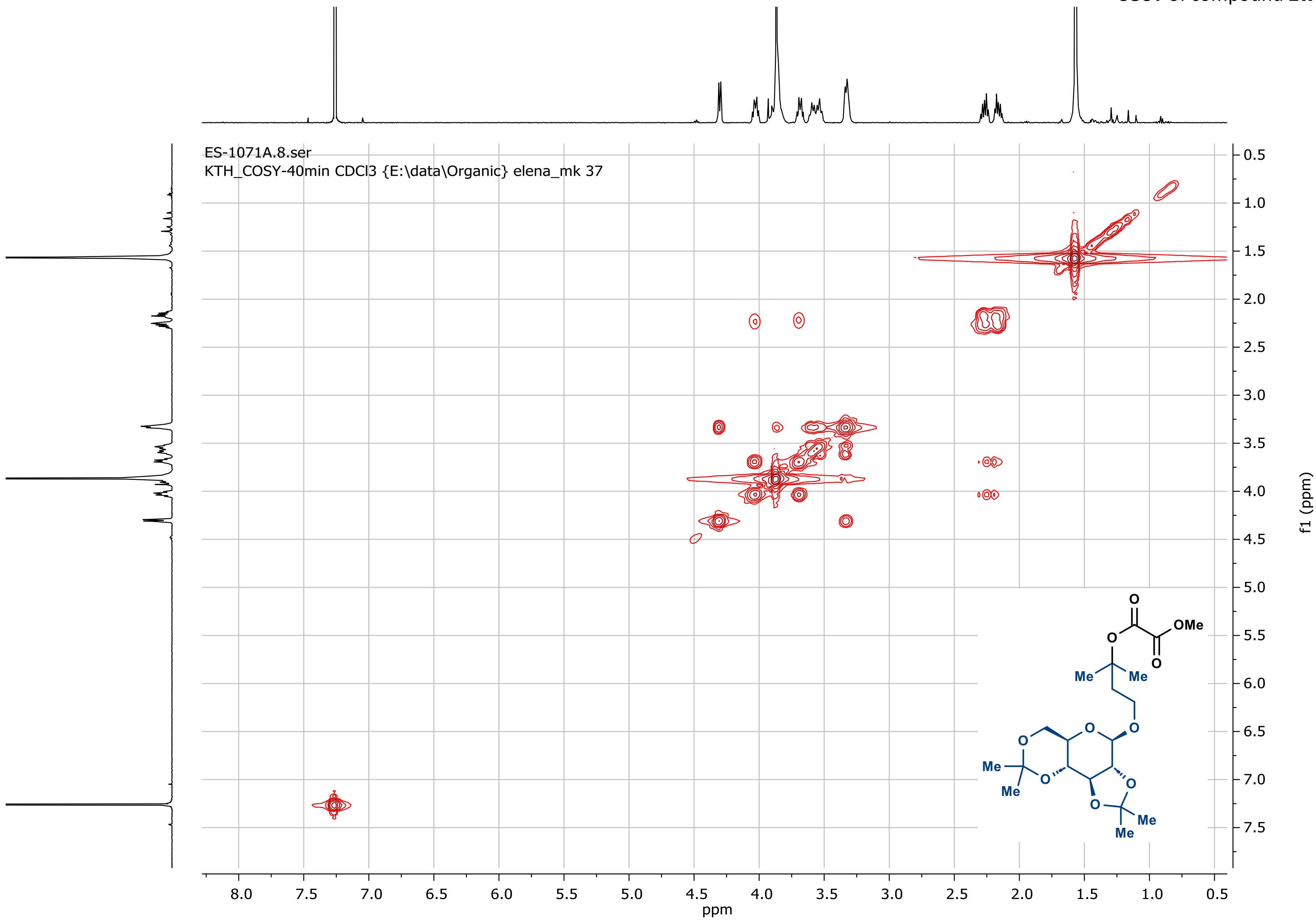
[1]H NMR (500 MHz, $CDCl_3$) of compound **2w**



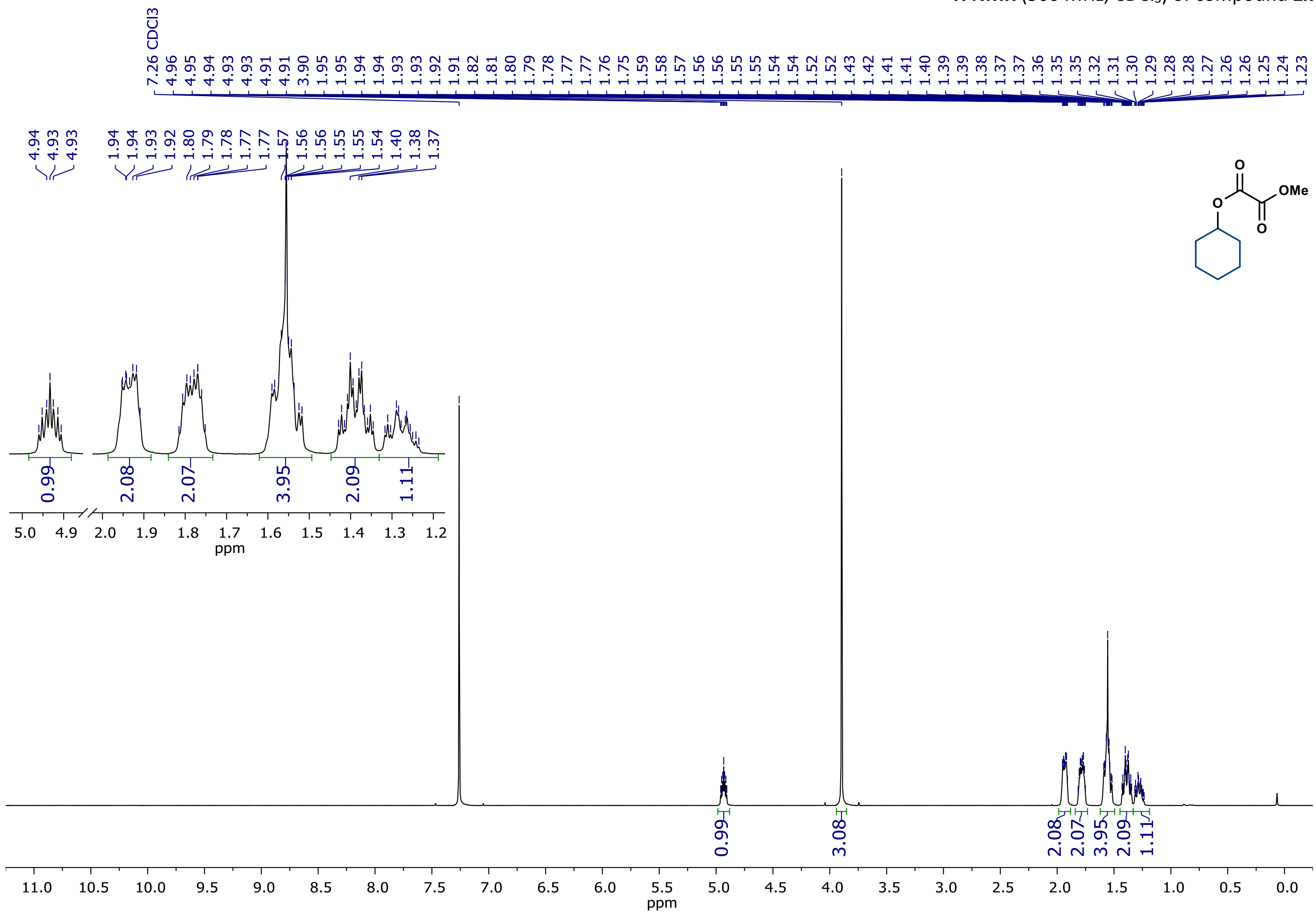
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2w**



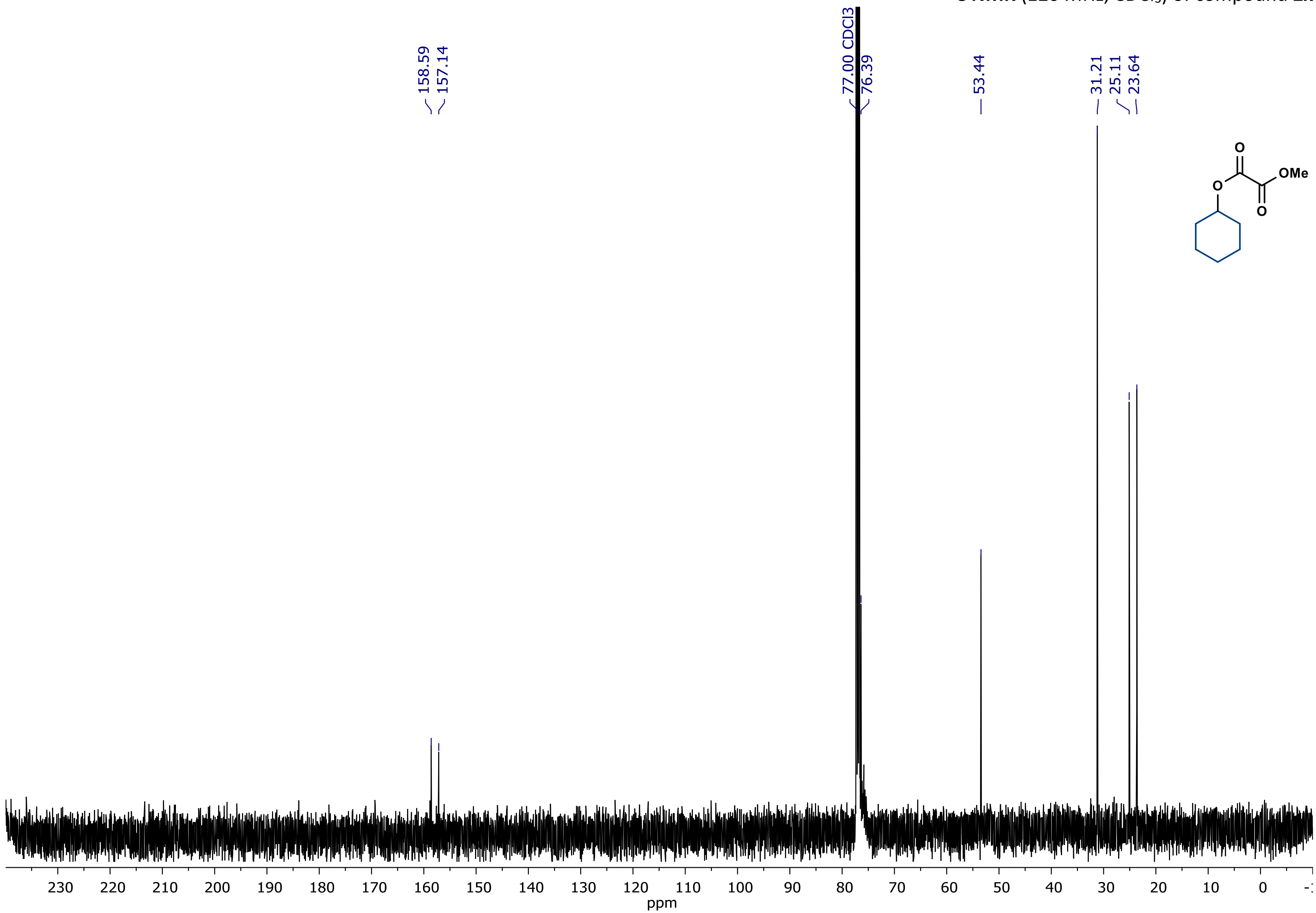
COSY of compound **2w**



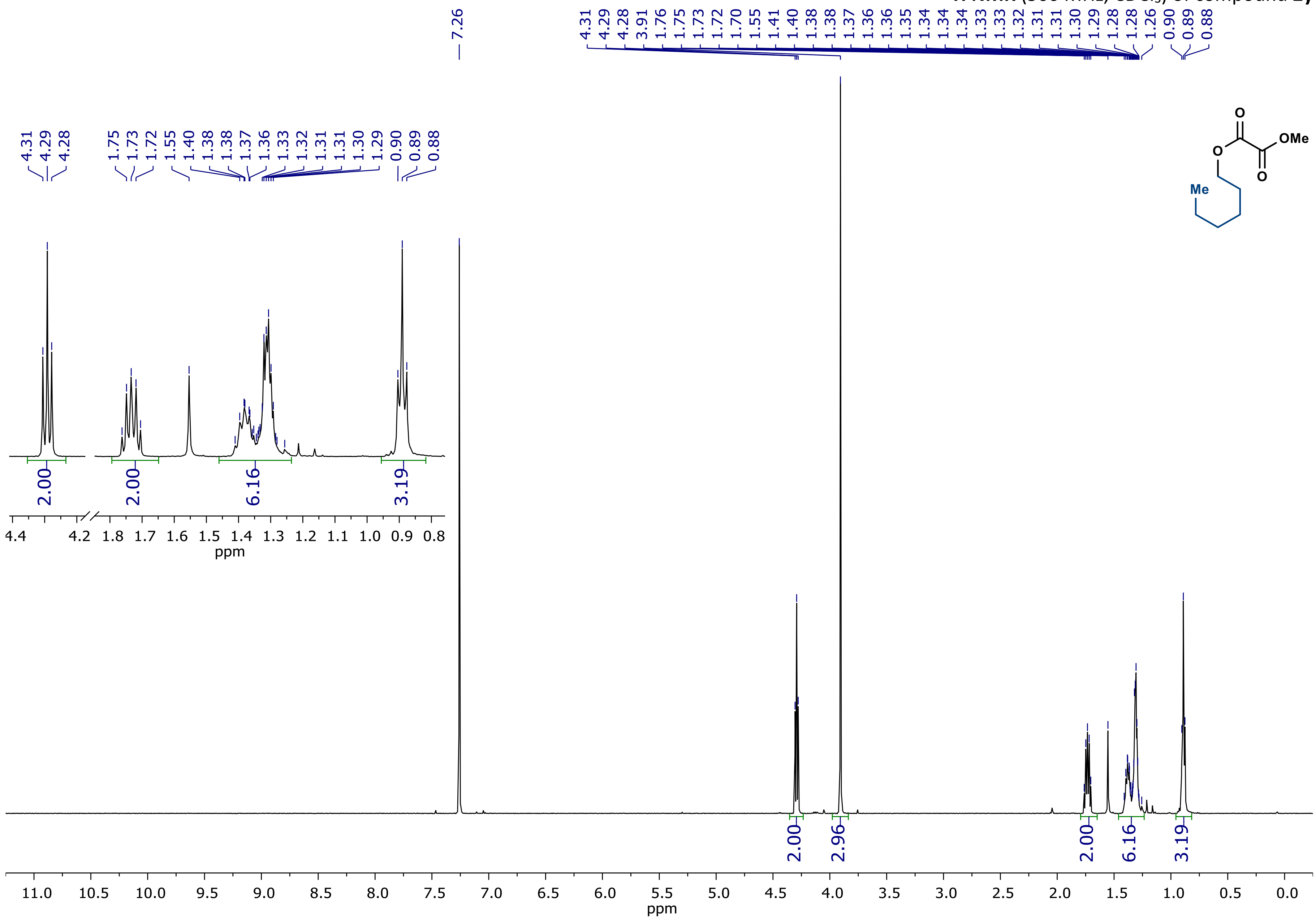
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2x**



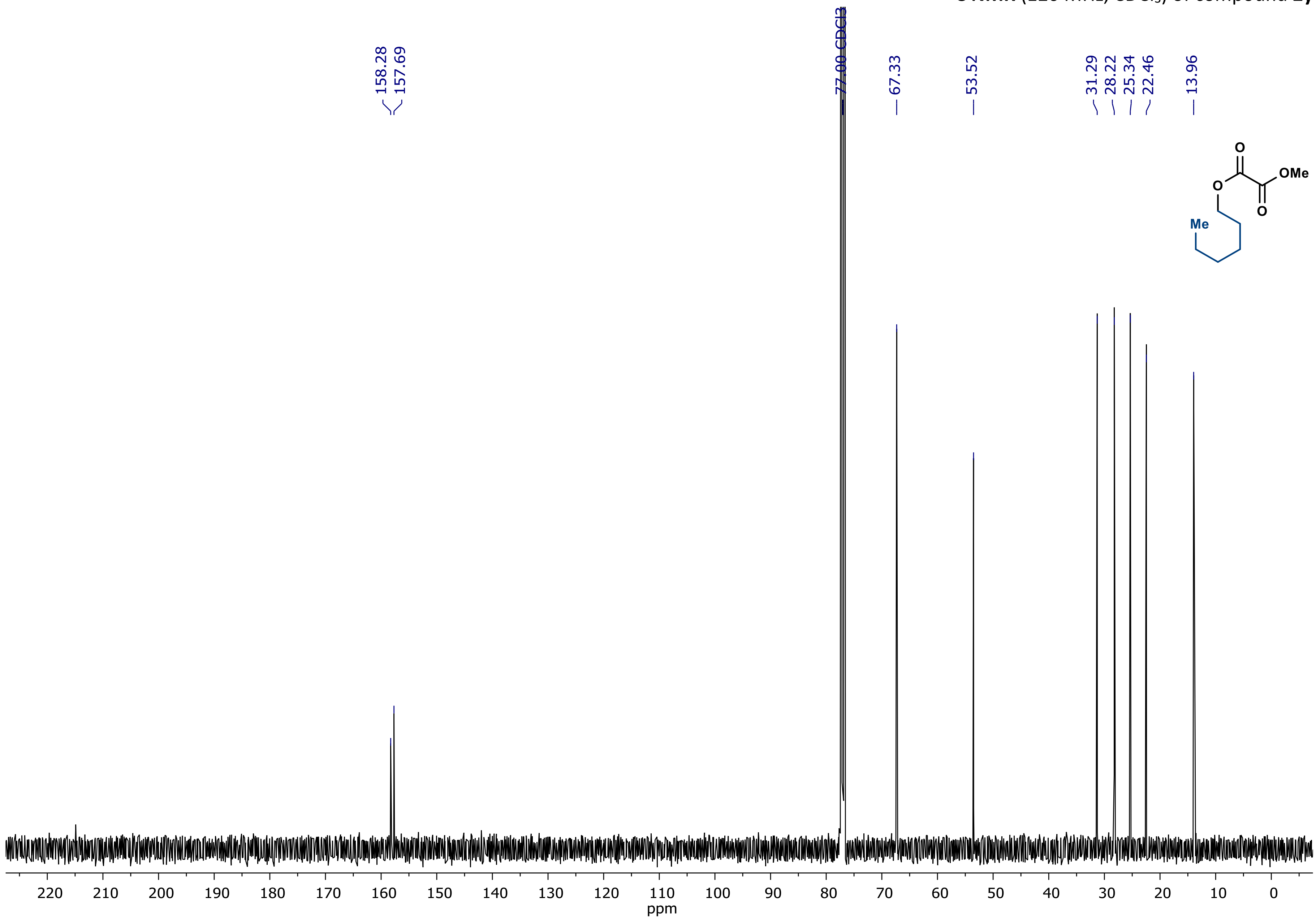
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2x**



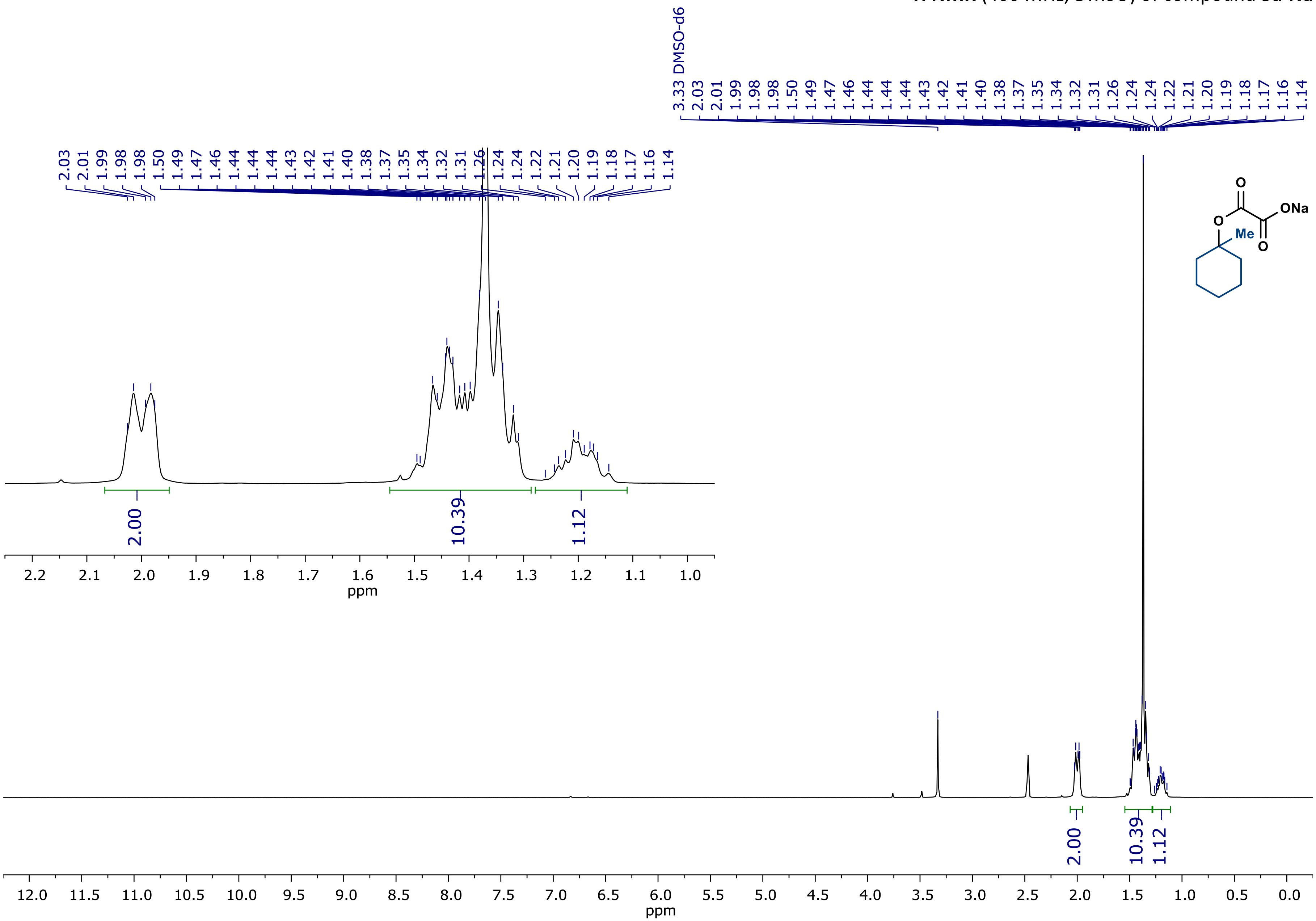
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **2y**



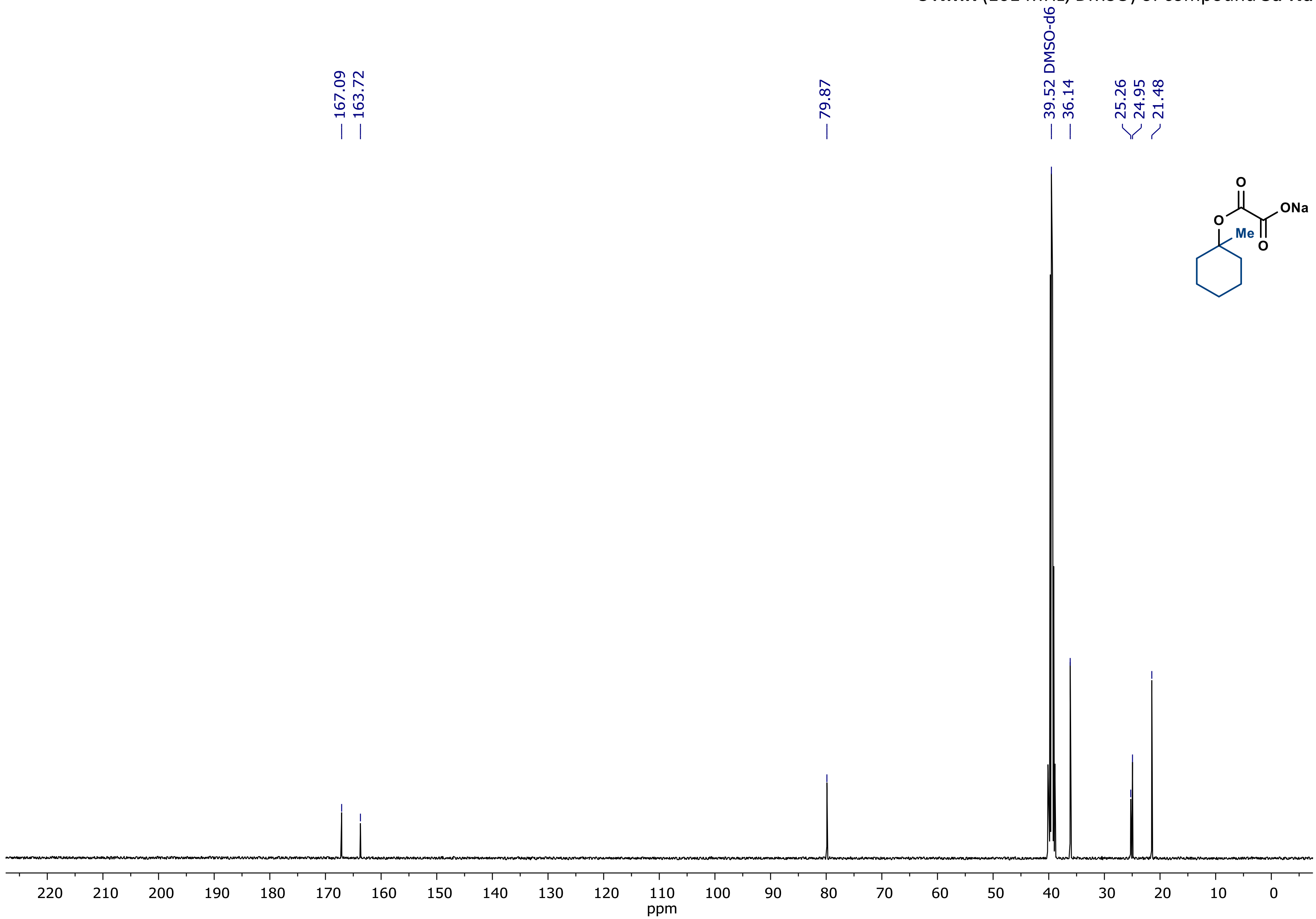
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2y**



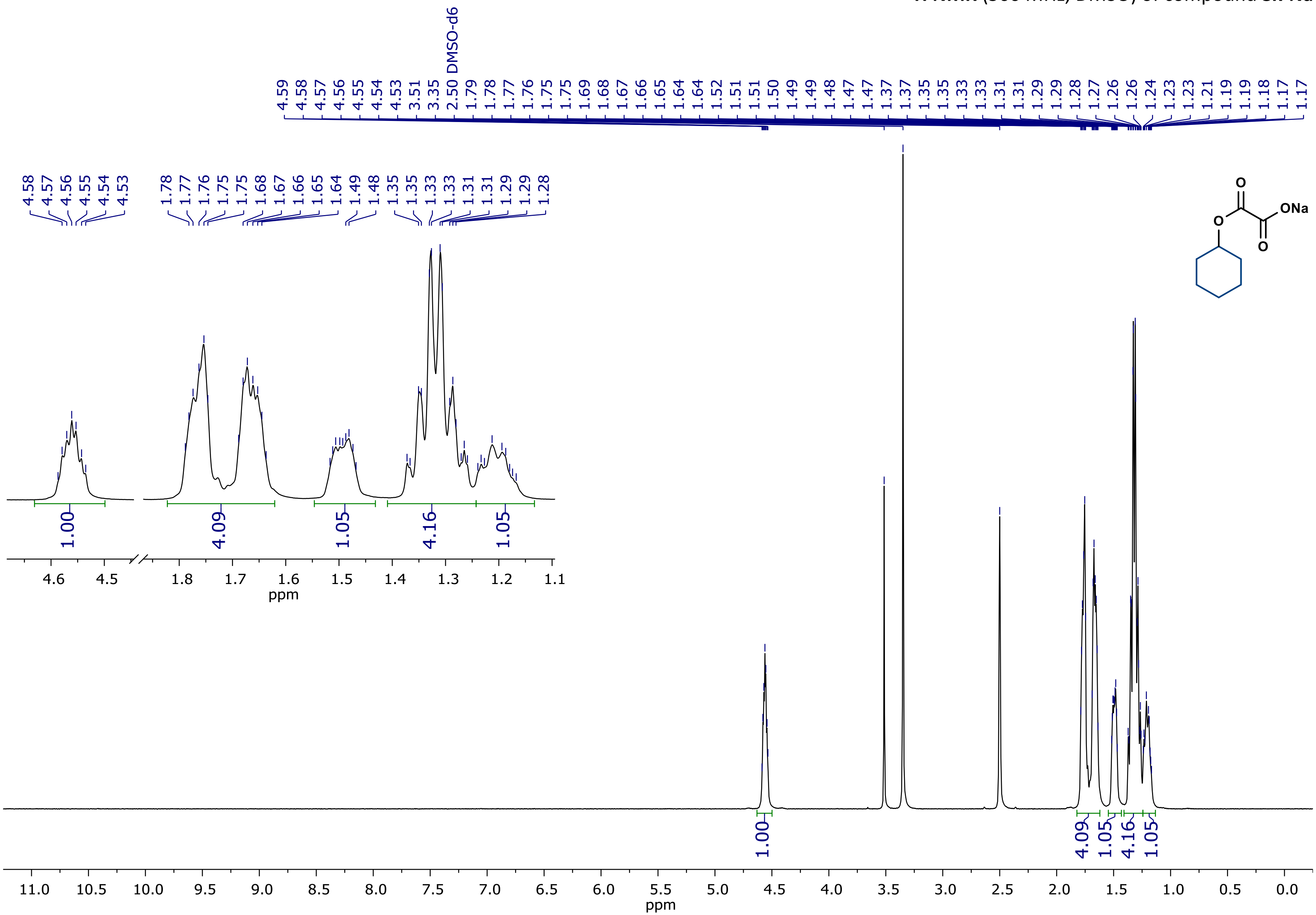
[1]H NMR (400 MHz, DMSO) of compound **3a-Na**



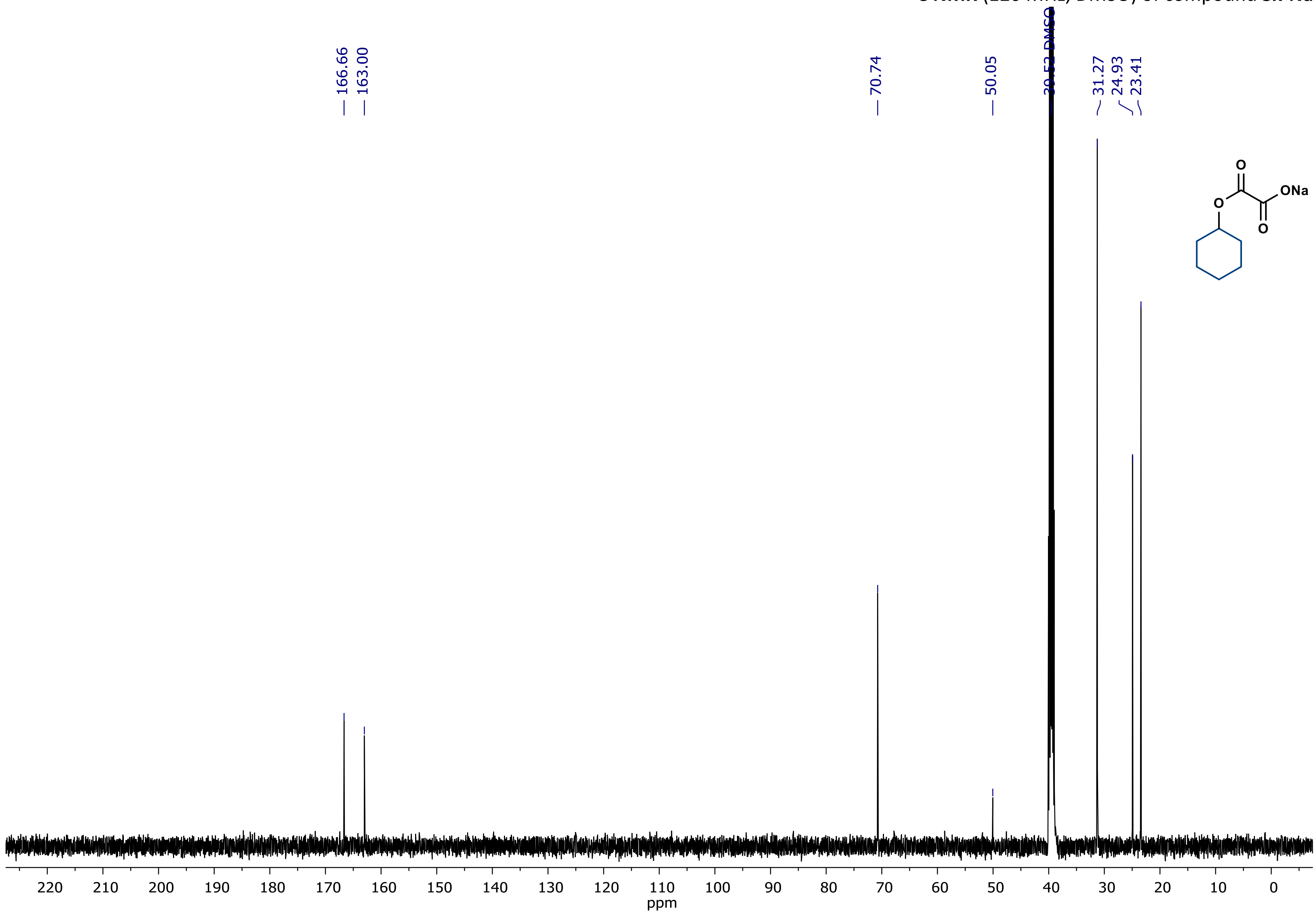
^{13}C NMR (101 MHz, DMSO) of compound **3a-Na**



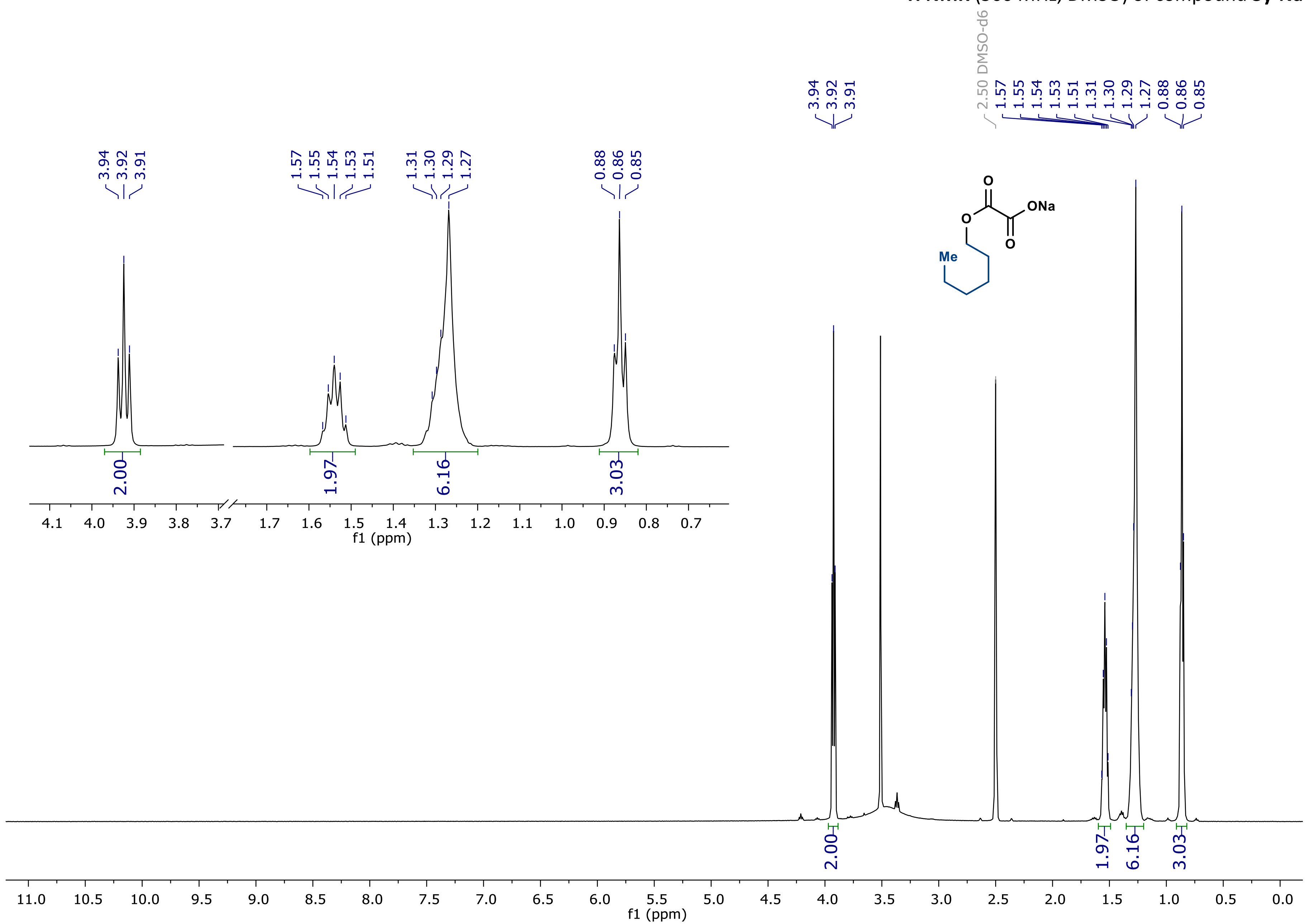
[1]H NMR (500 MHz, DMSO) of compound **3x-Na**



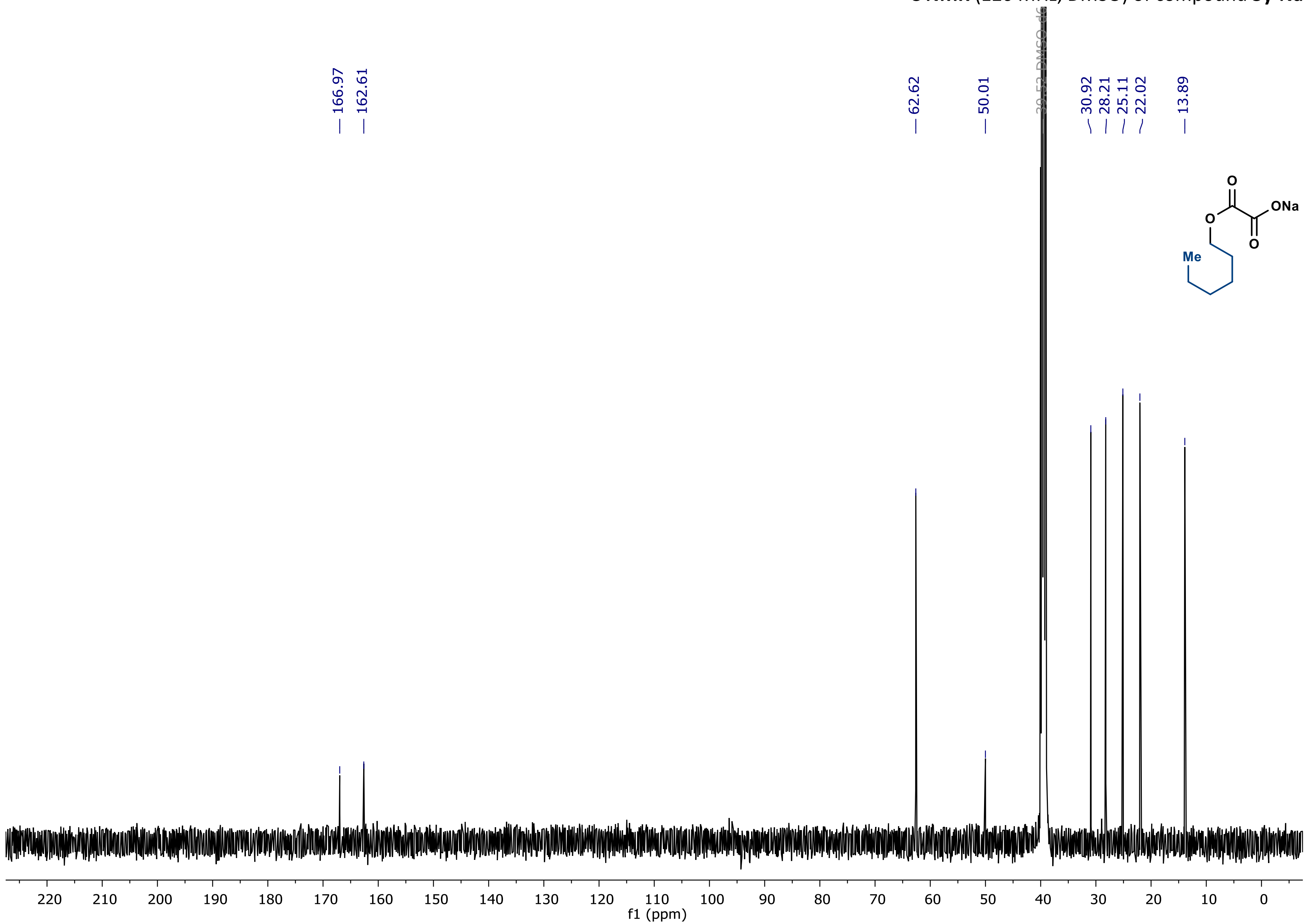
^{13}C NMR (126 MHz, DMSO) of compound **3x-Na**



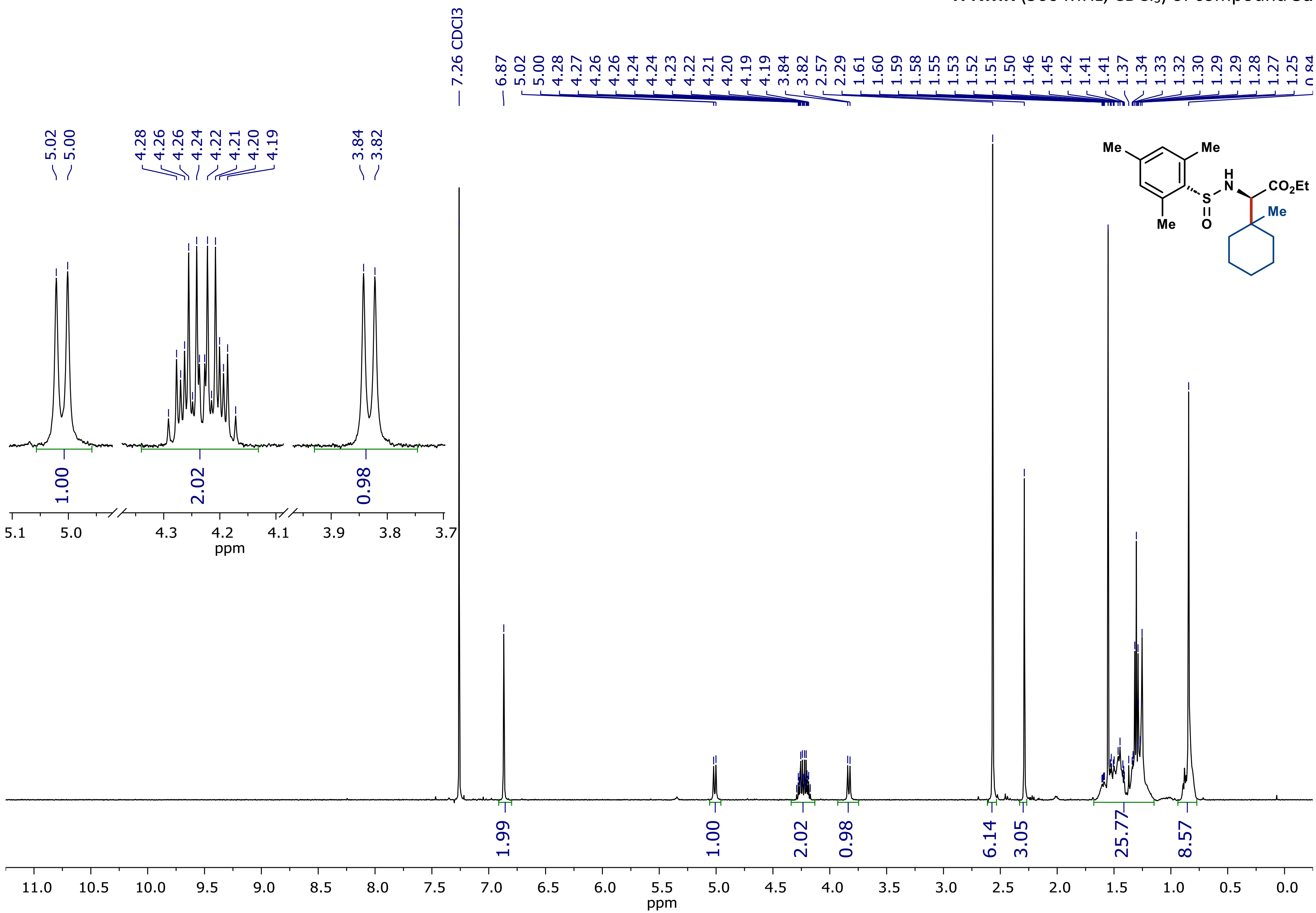
^{1}H NMR (500 MHz, DMSO) of compound **3y-Na**



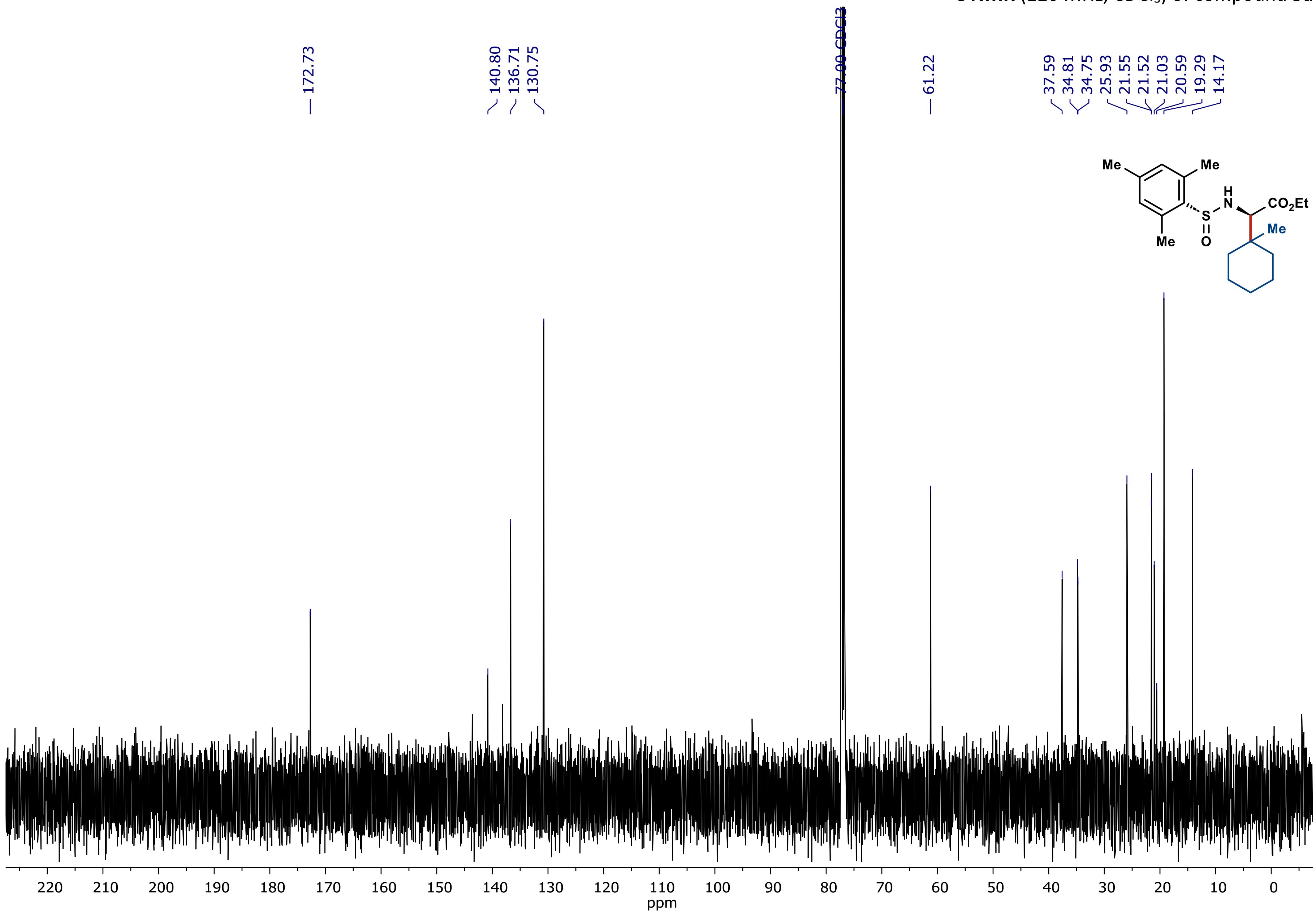
^{13}C NMR (126 MHz, DMSO) of compound **3y-Na**



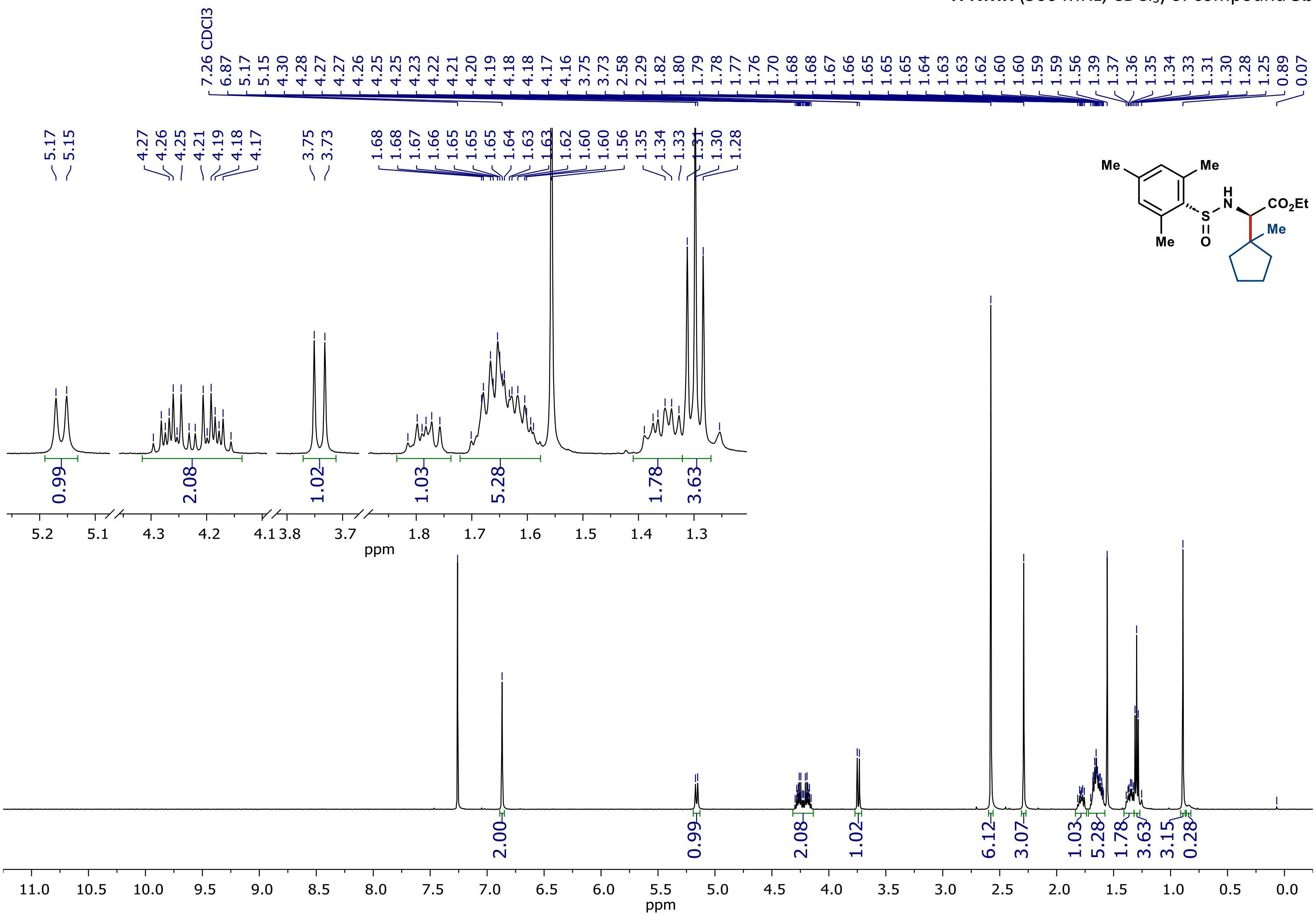
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5a**



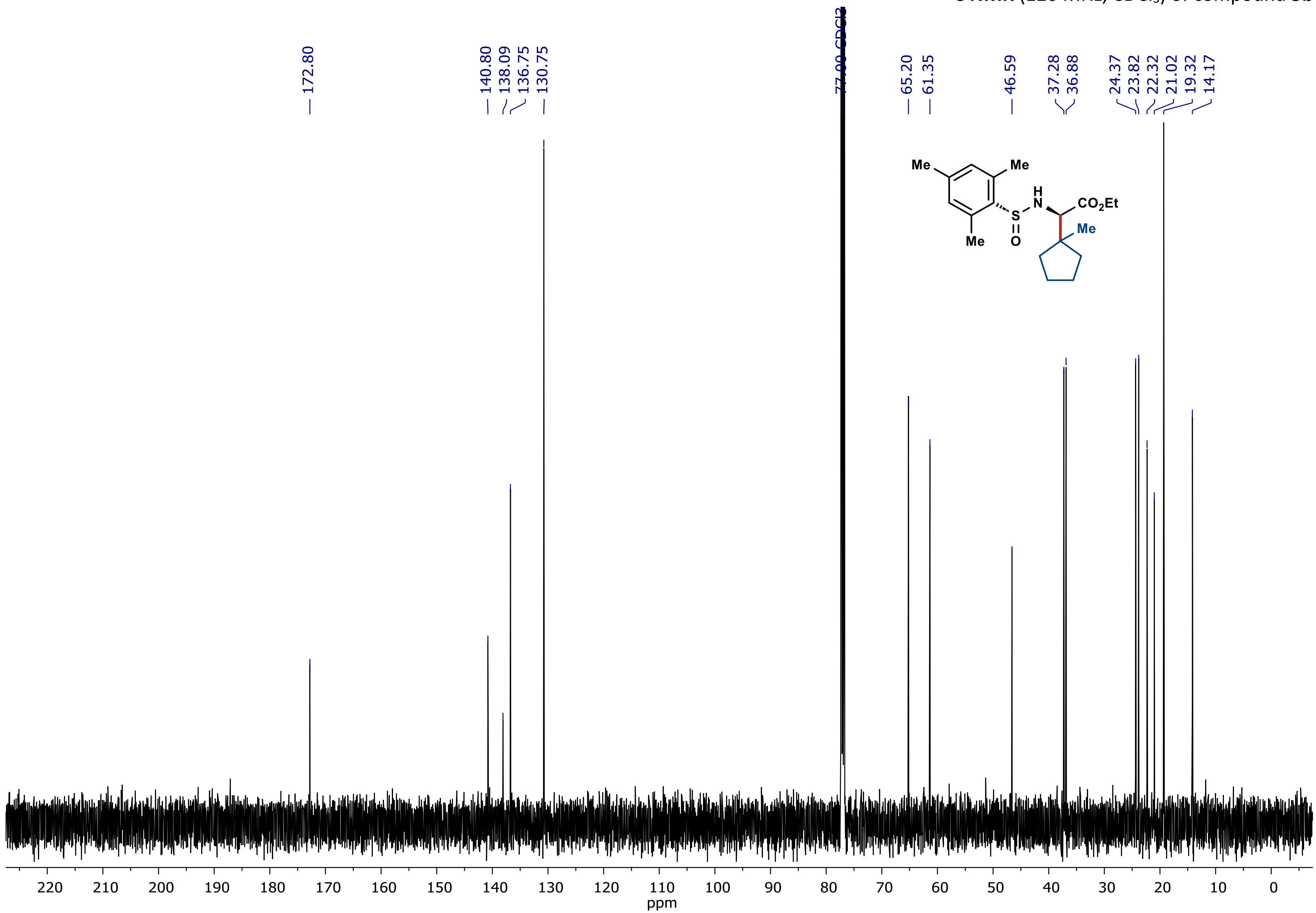
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5a**



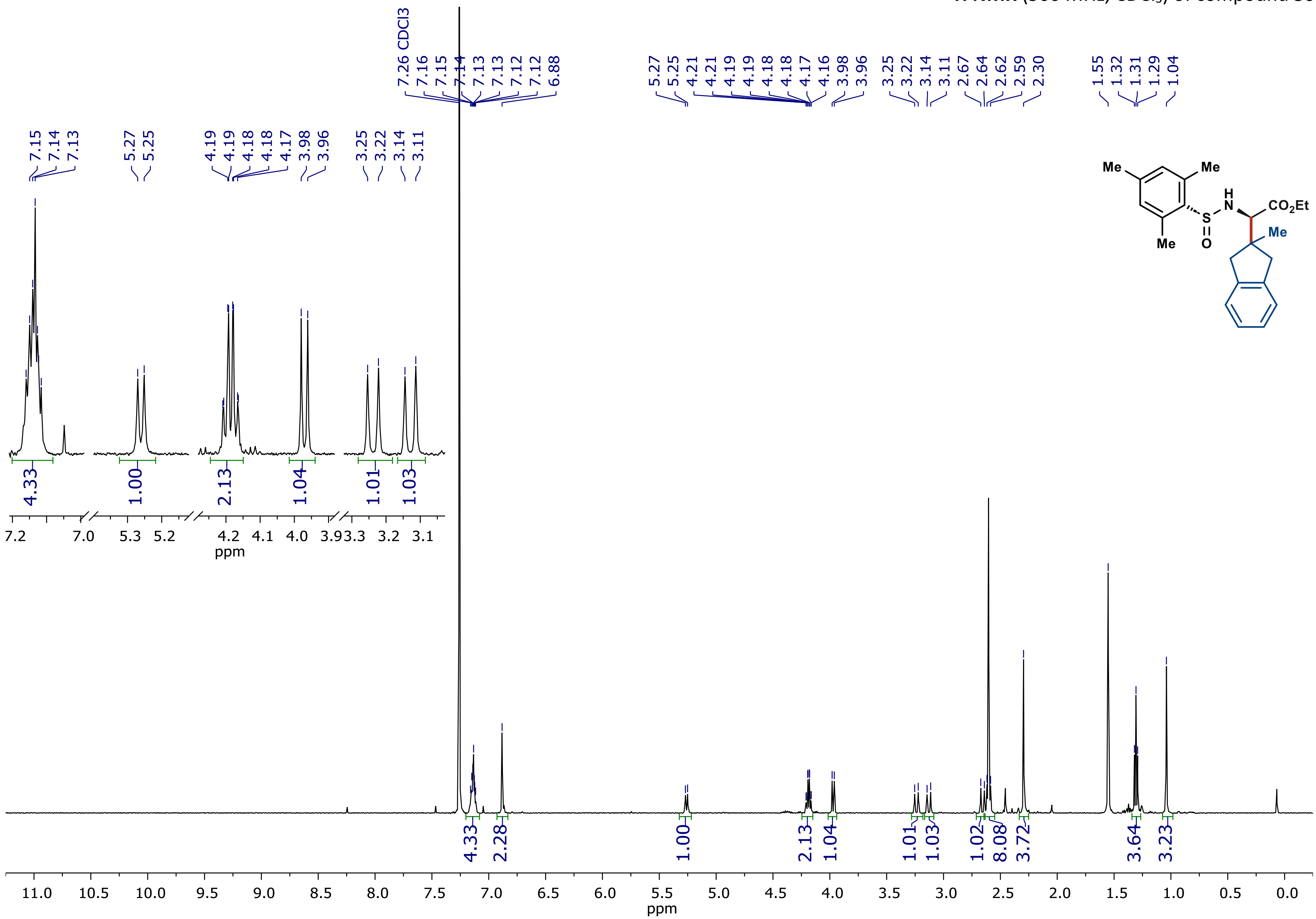
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5b**



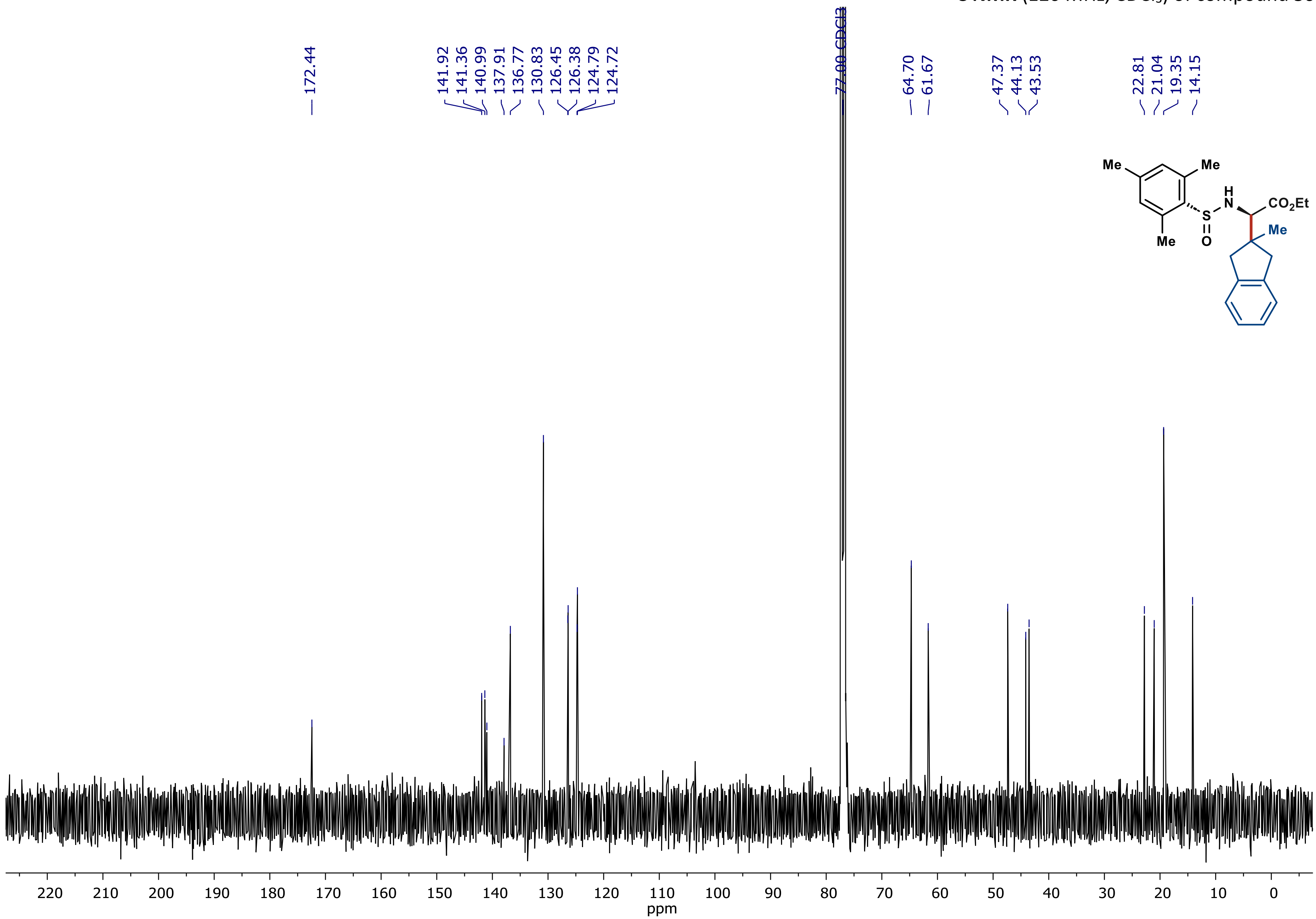
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5b**



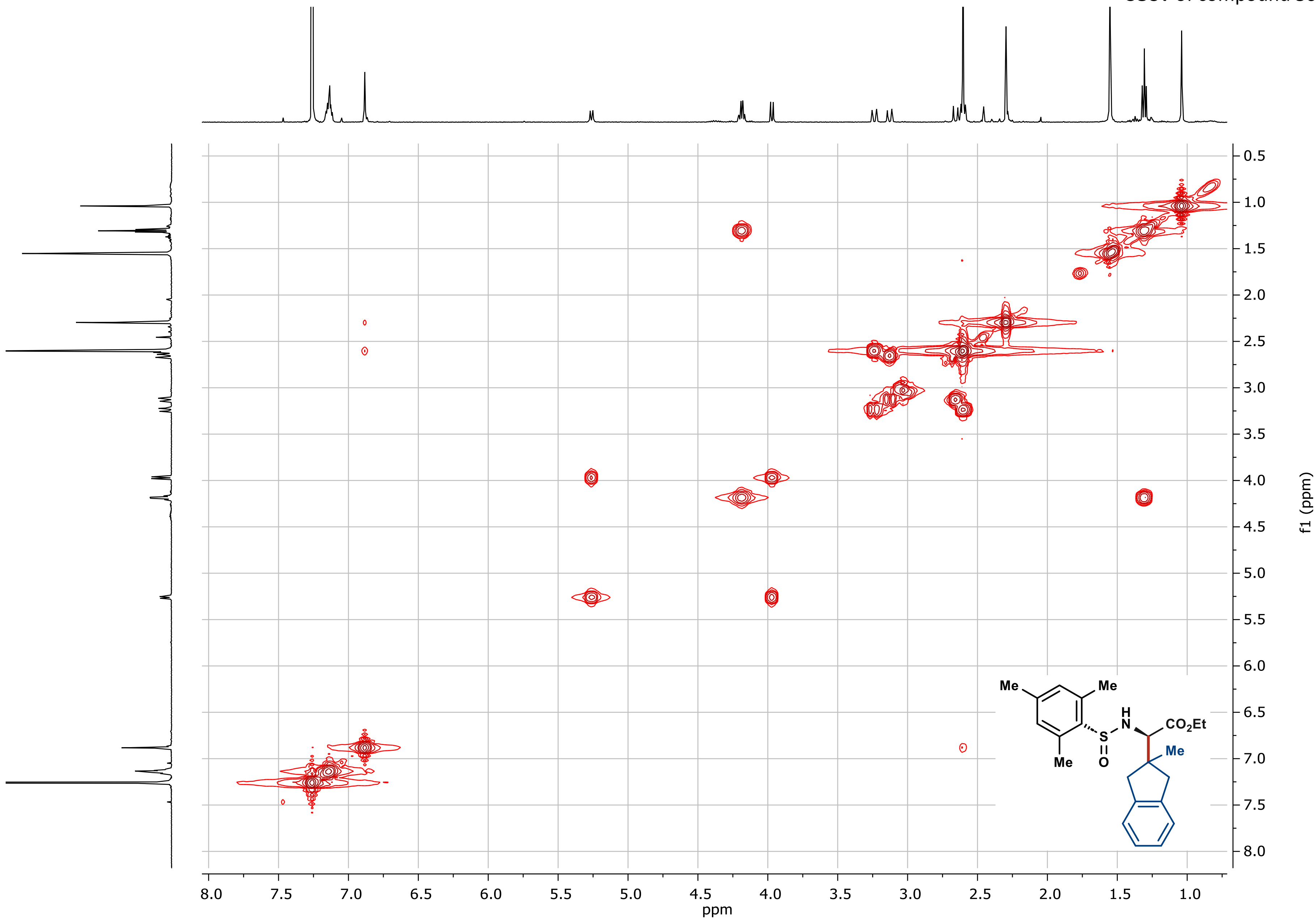
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5c**



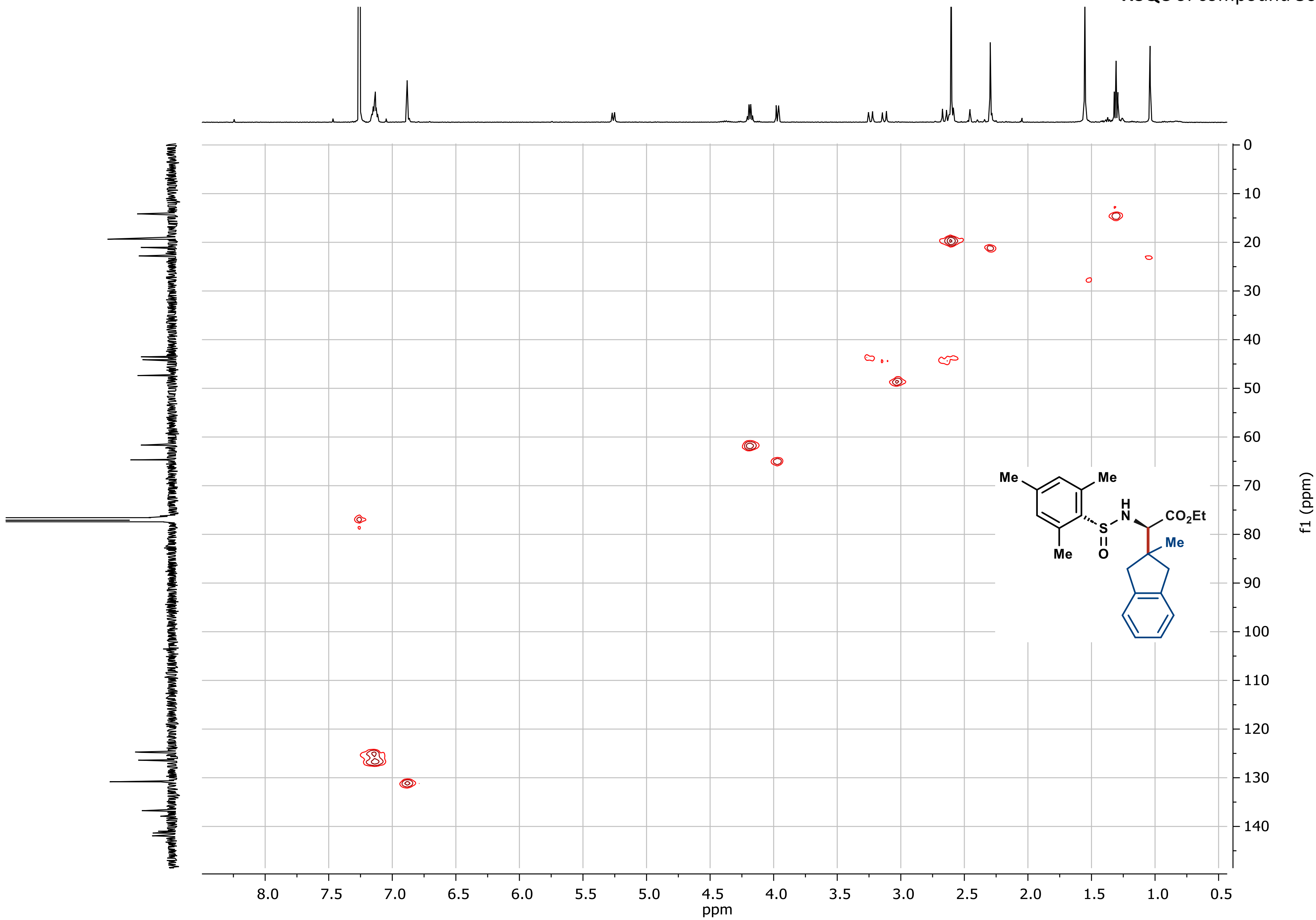
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5c**



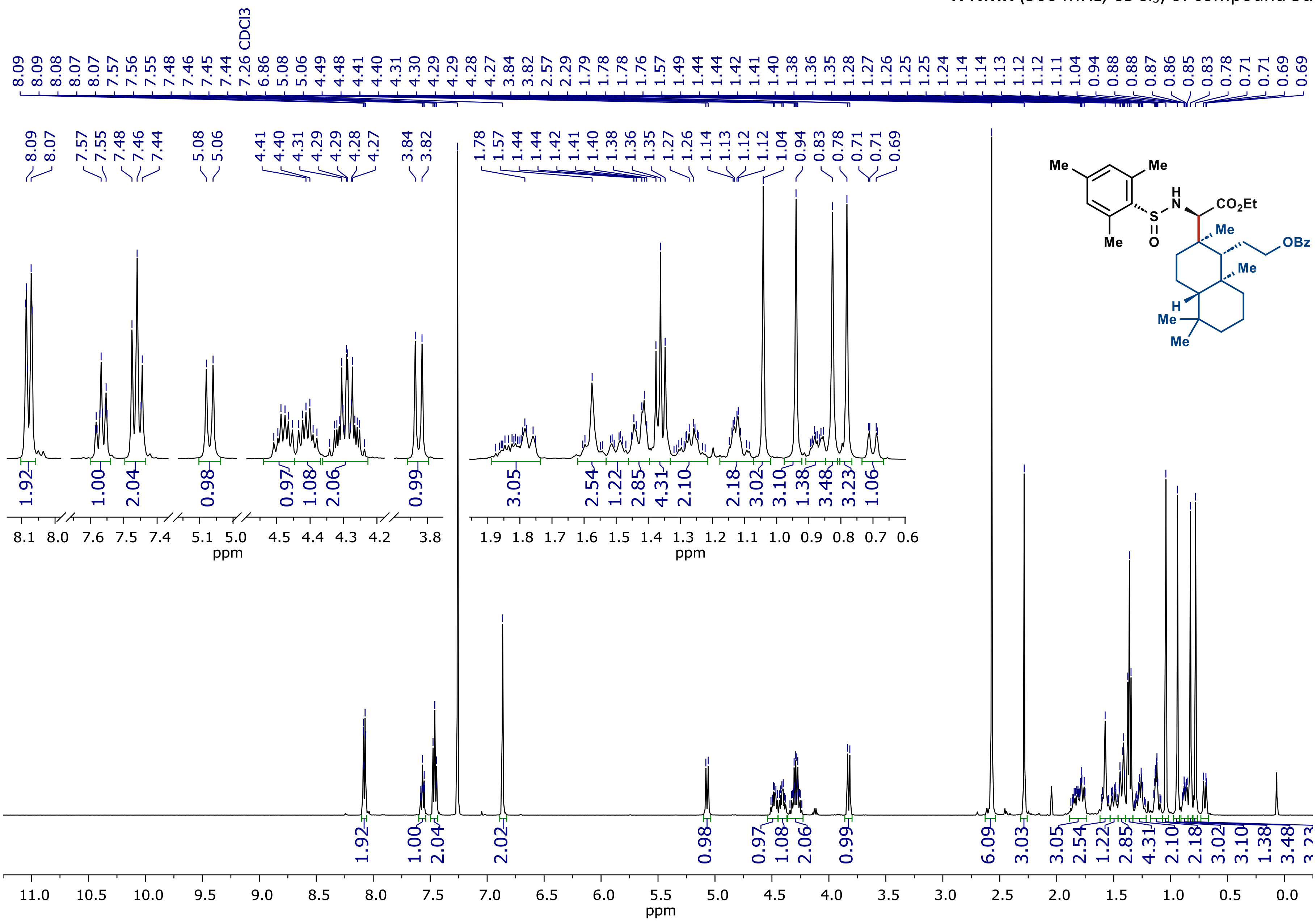
COSY of compound **5c**



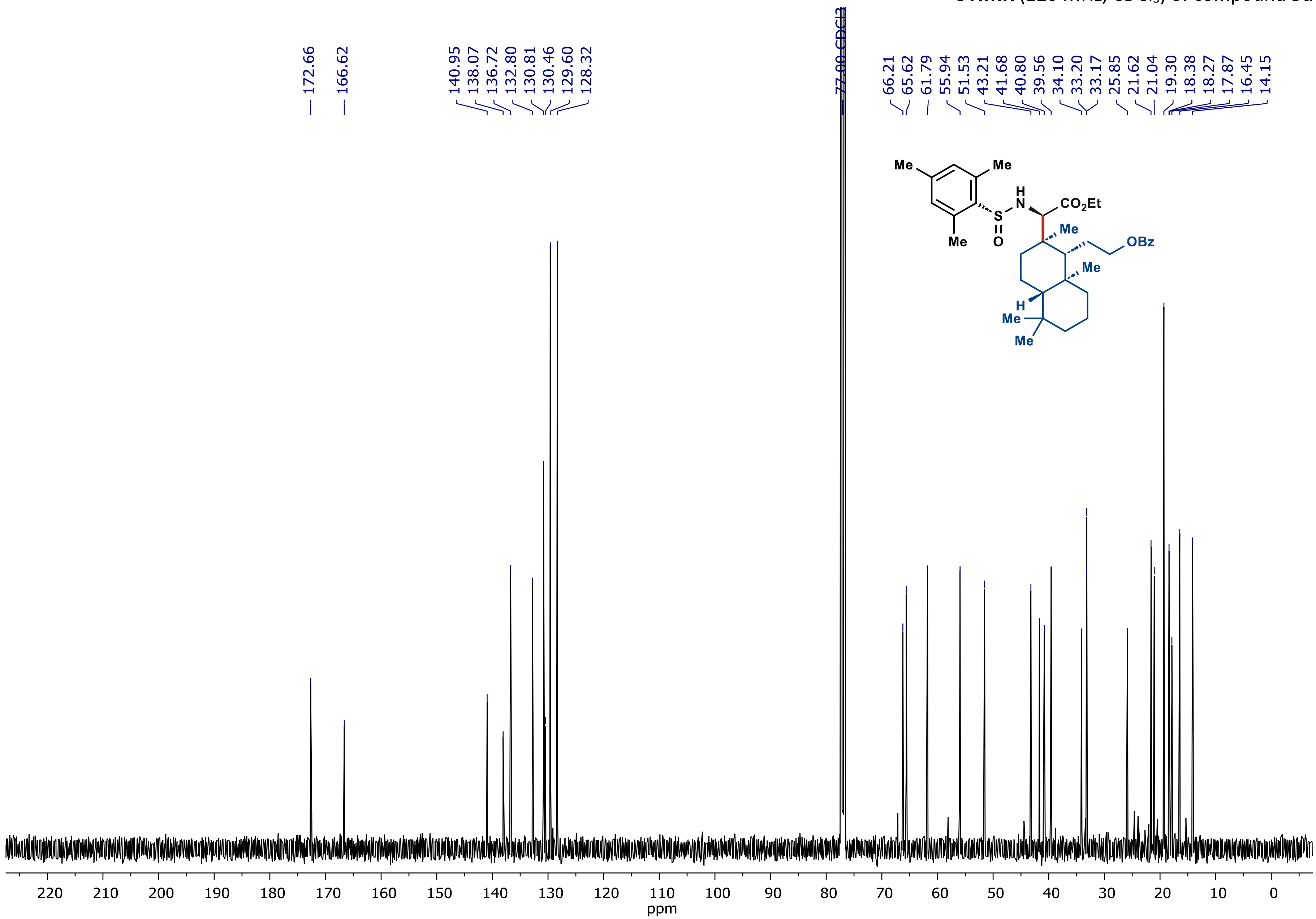
HSQC of compound **5c**



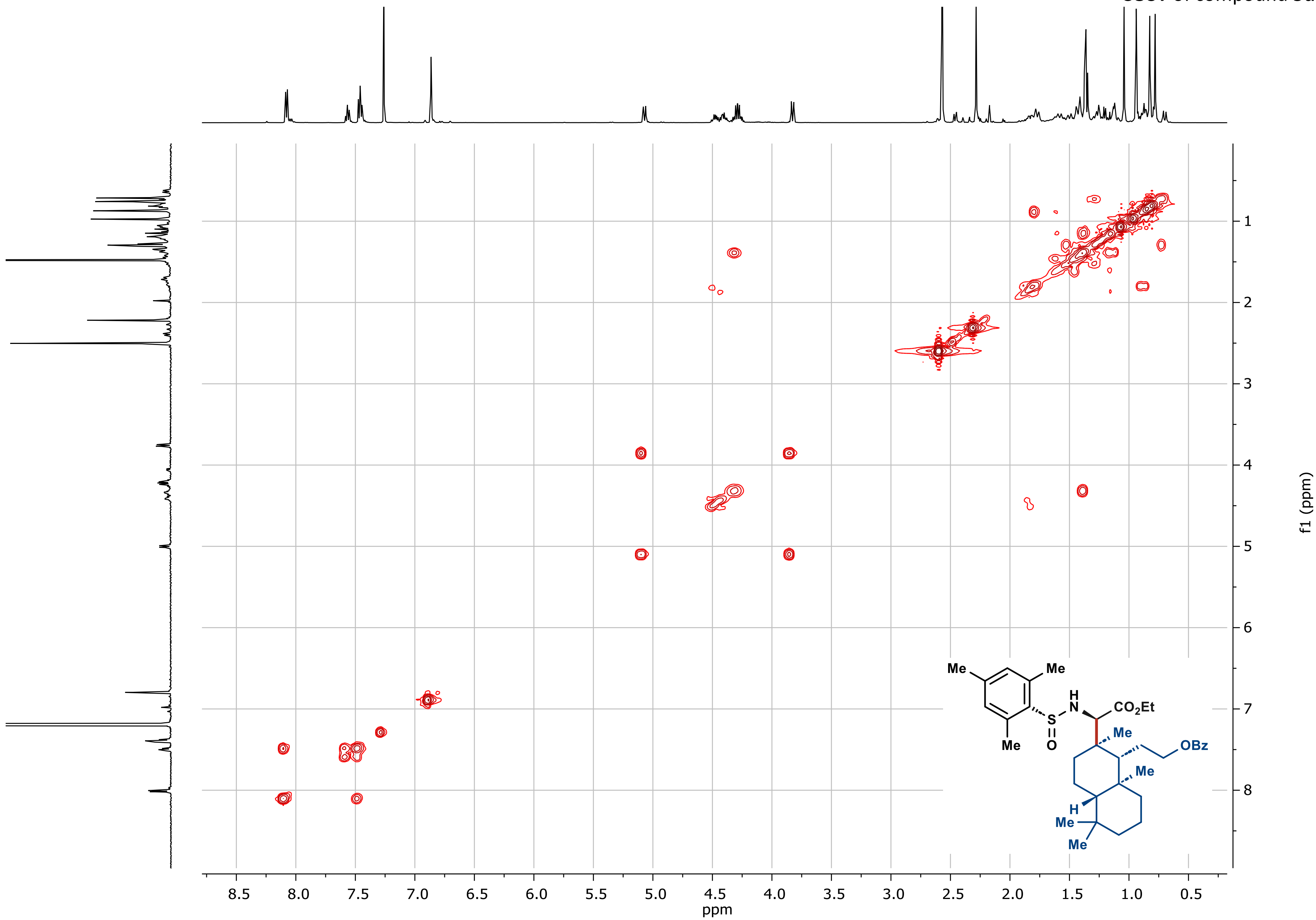
[1]H NMR (500 MHz, $CDCl_3$) of compound **5d**



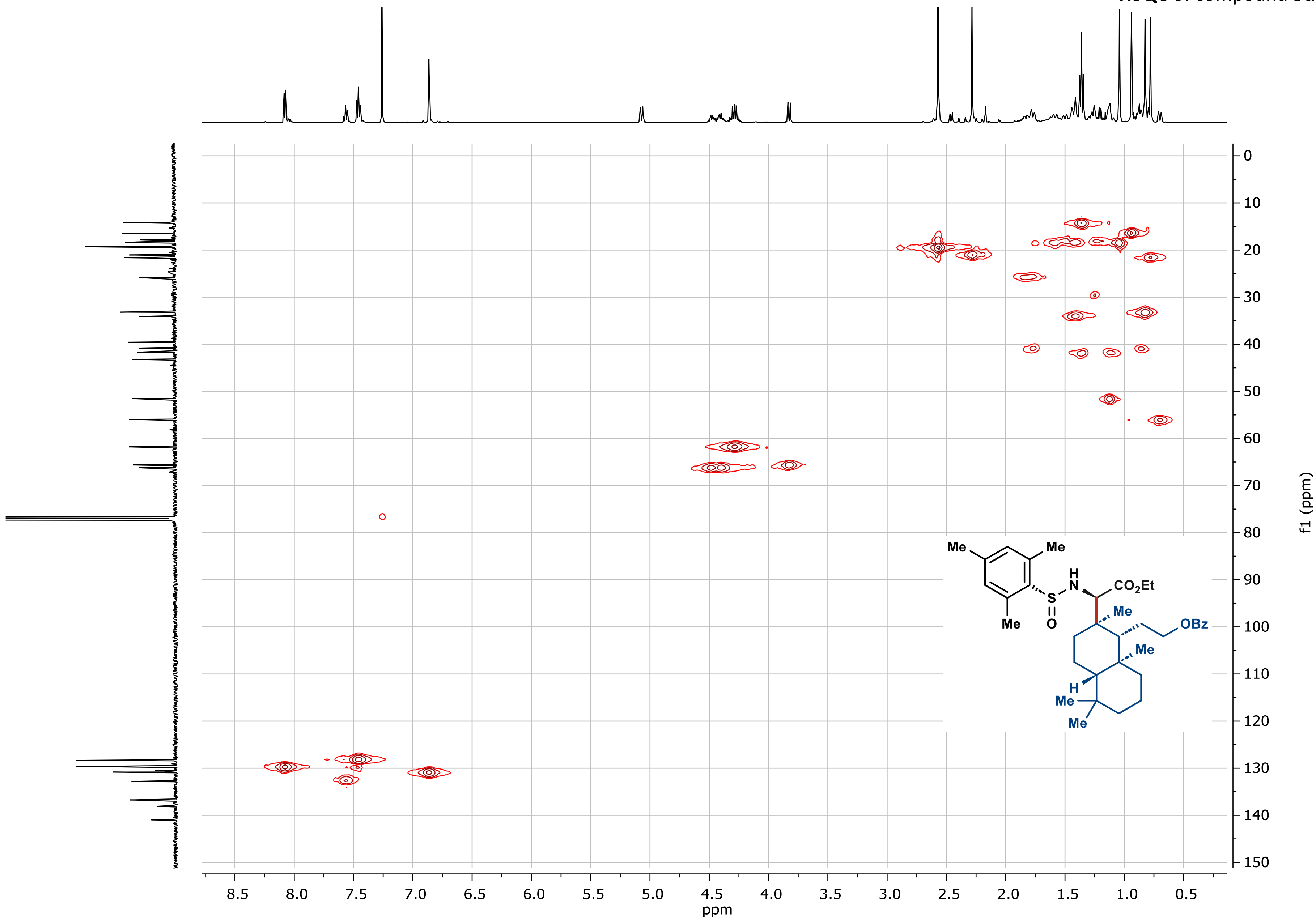
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5d**



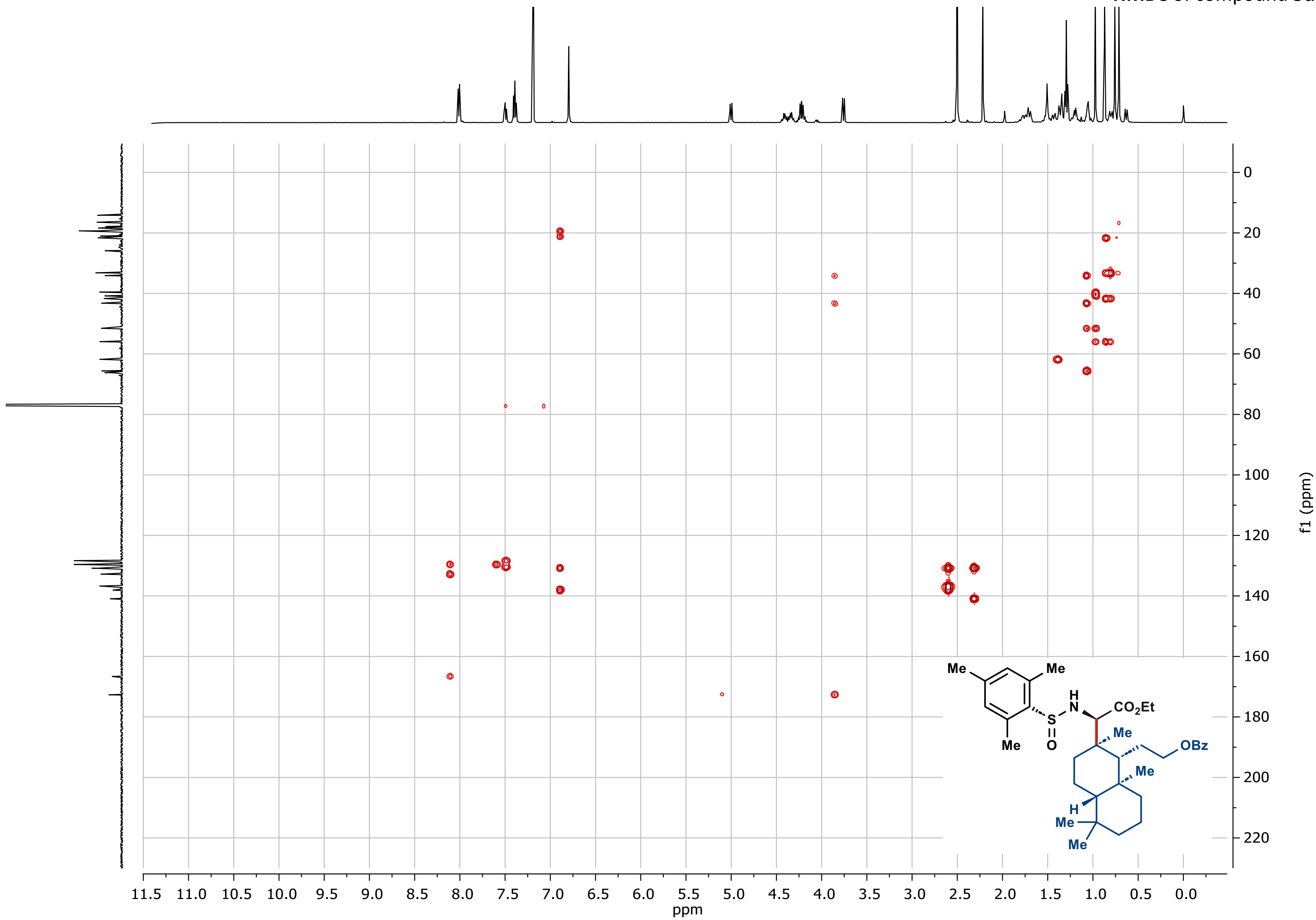
COSY of compound **5d**



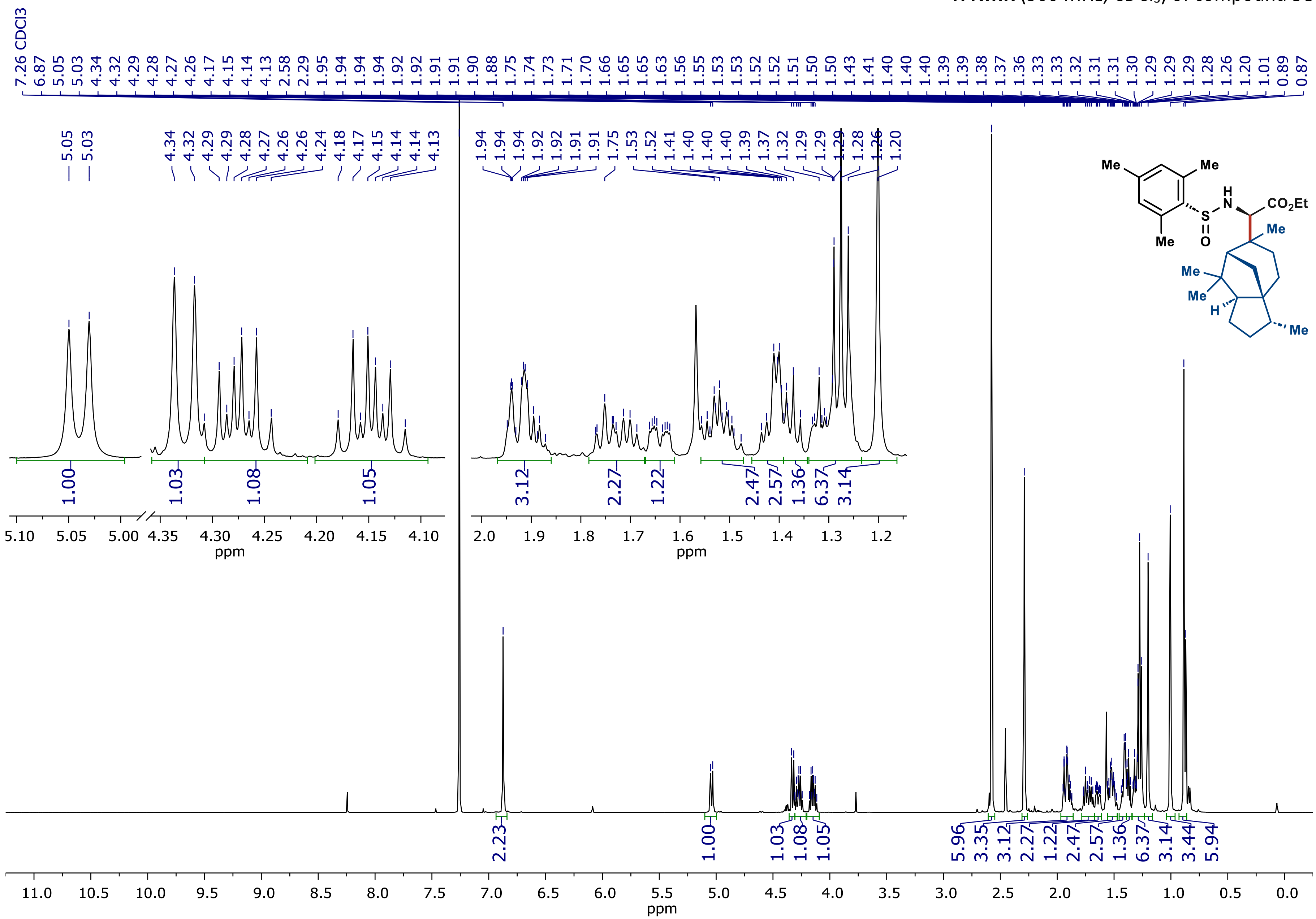
HSQC of compound **5d**



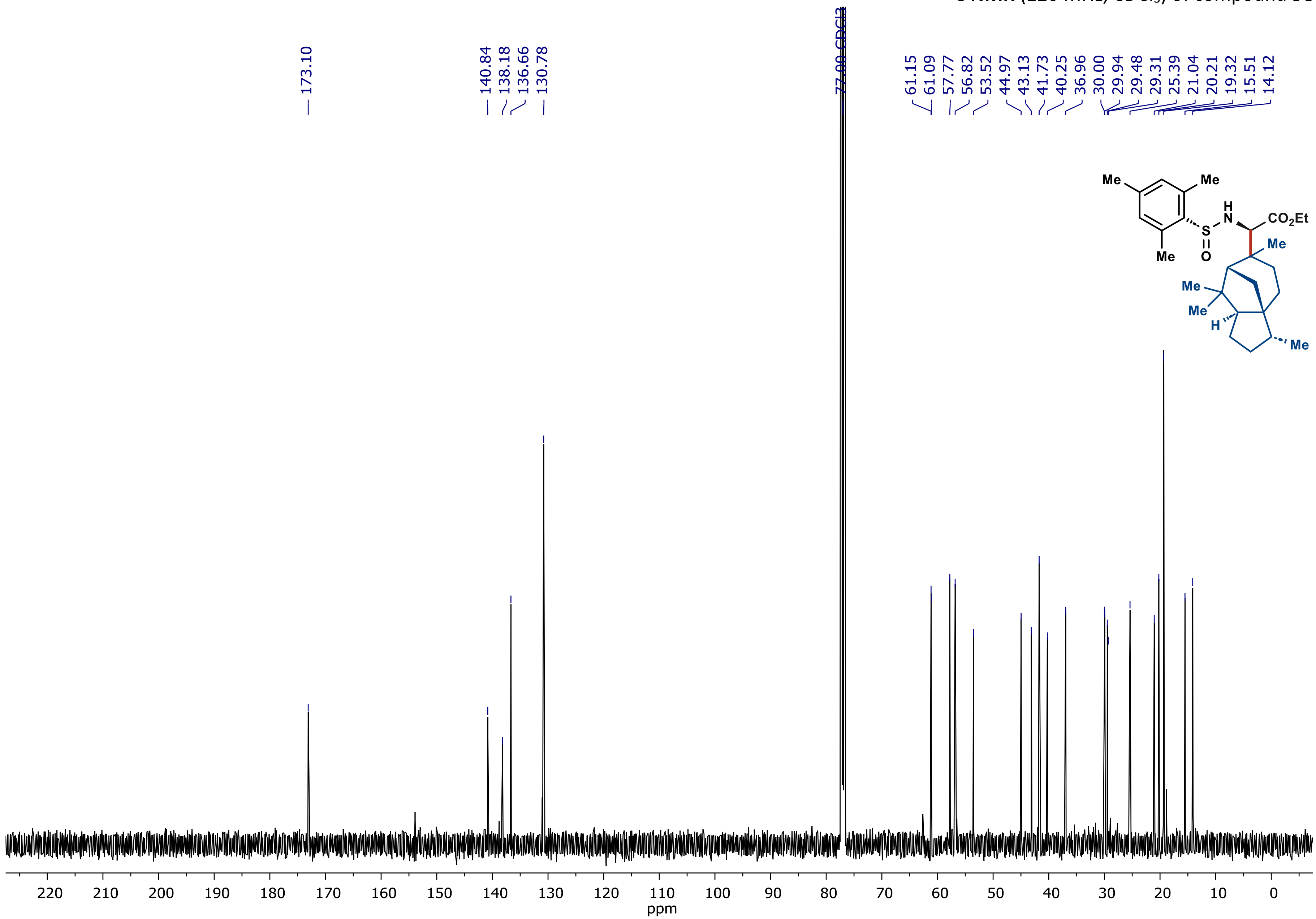
HMBC of compound **5d**



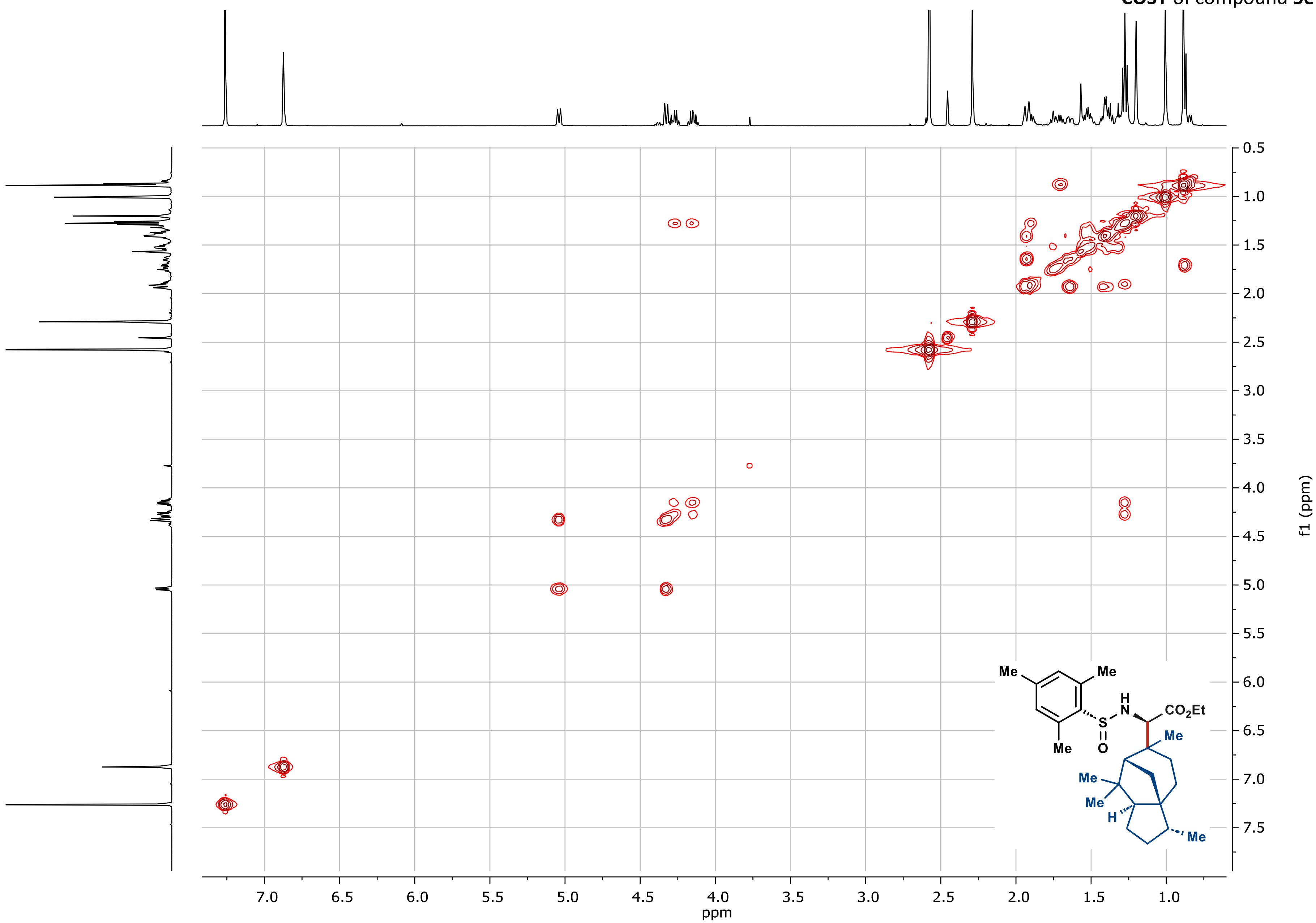
[1]H NMR (500 MHz, $CDCl_3$) of compound **5e**



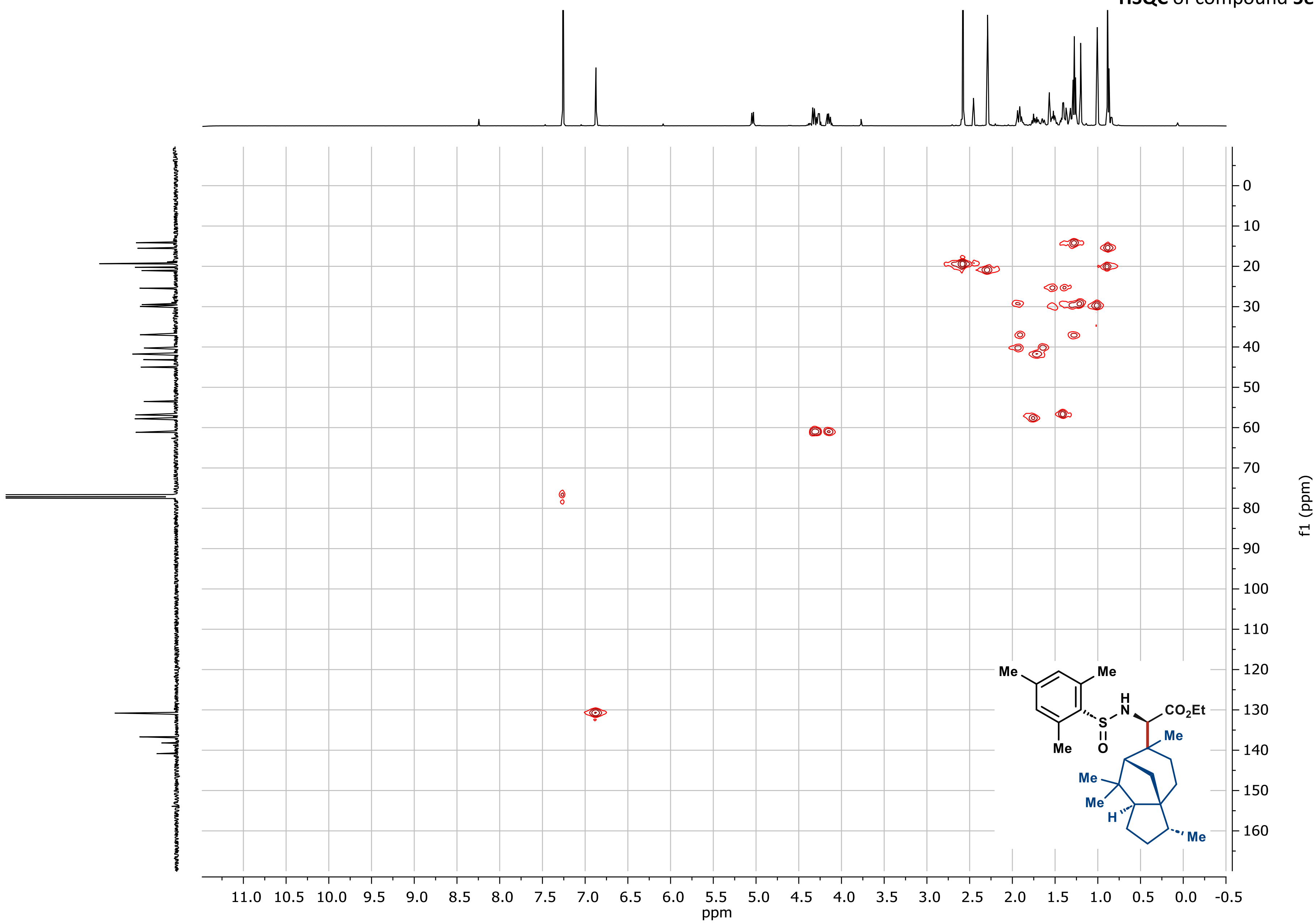
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5e**



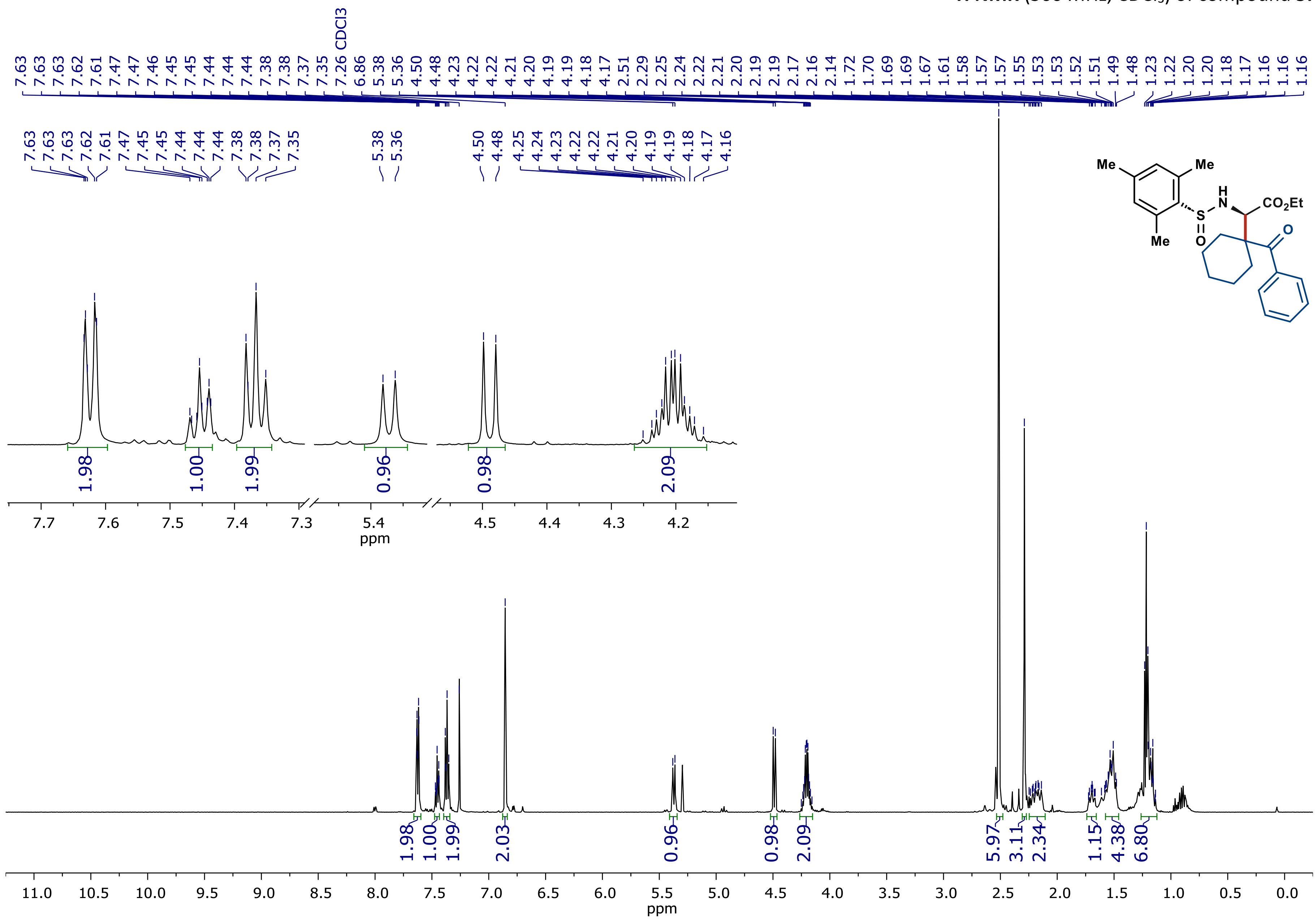
COSY of compound **5e**



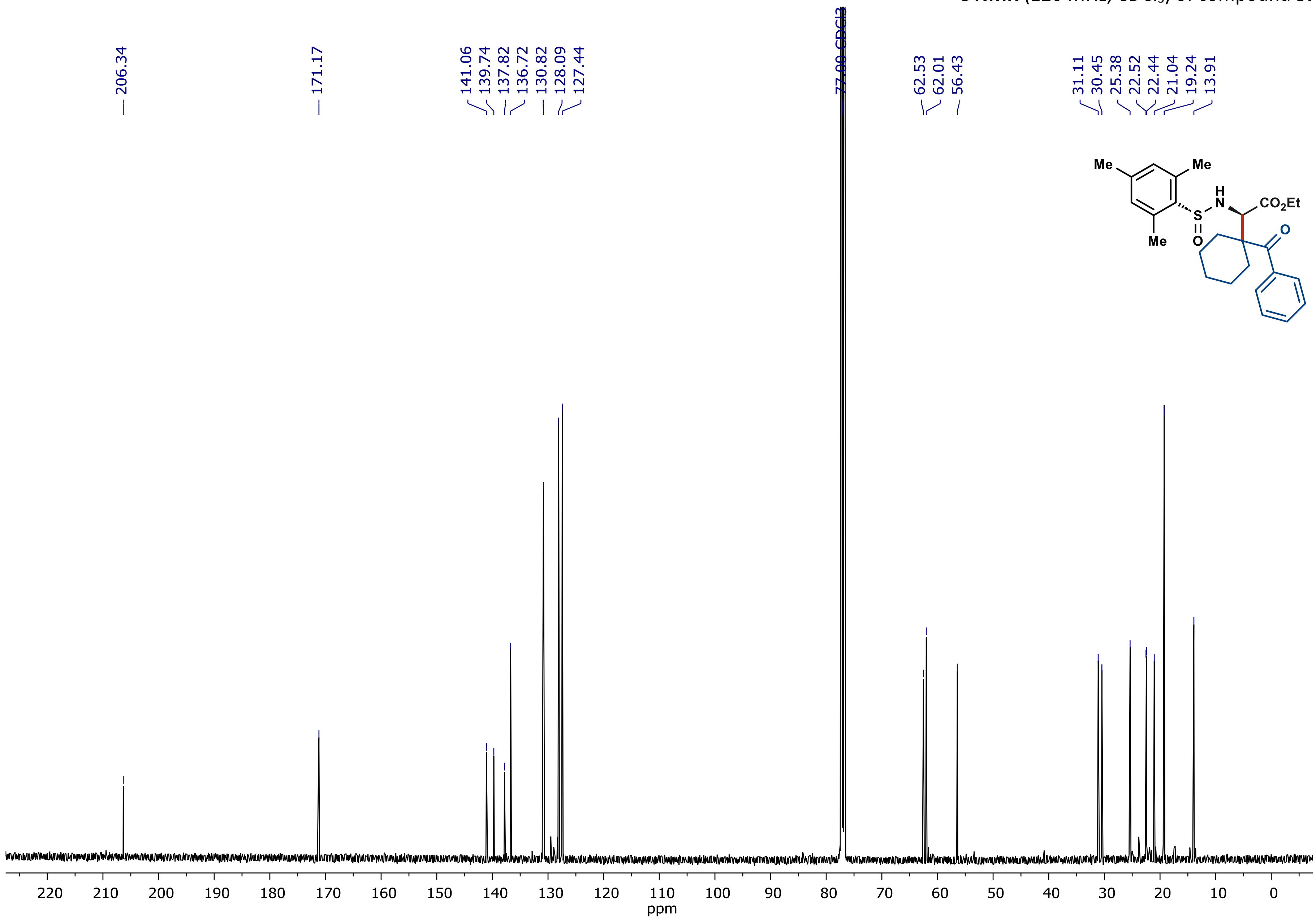
HSQC of compound **5e**



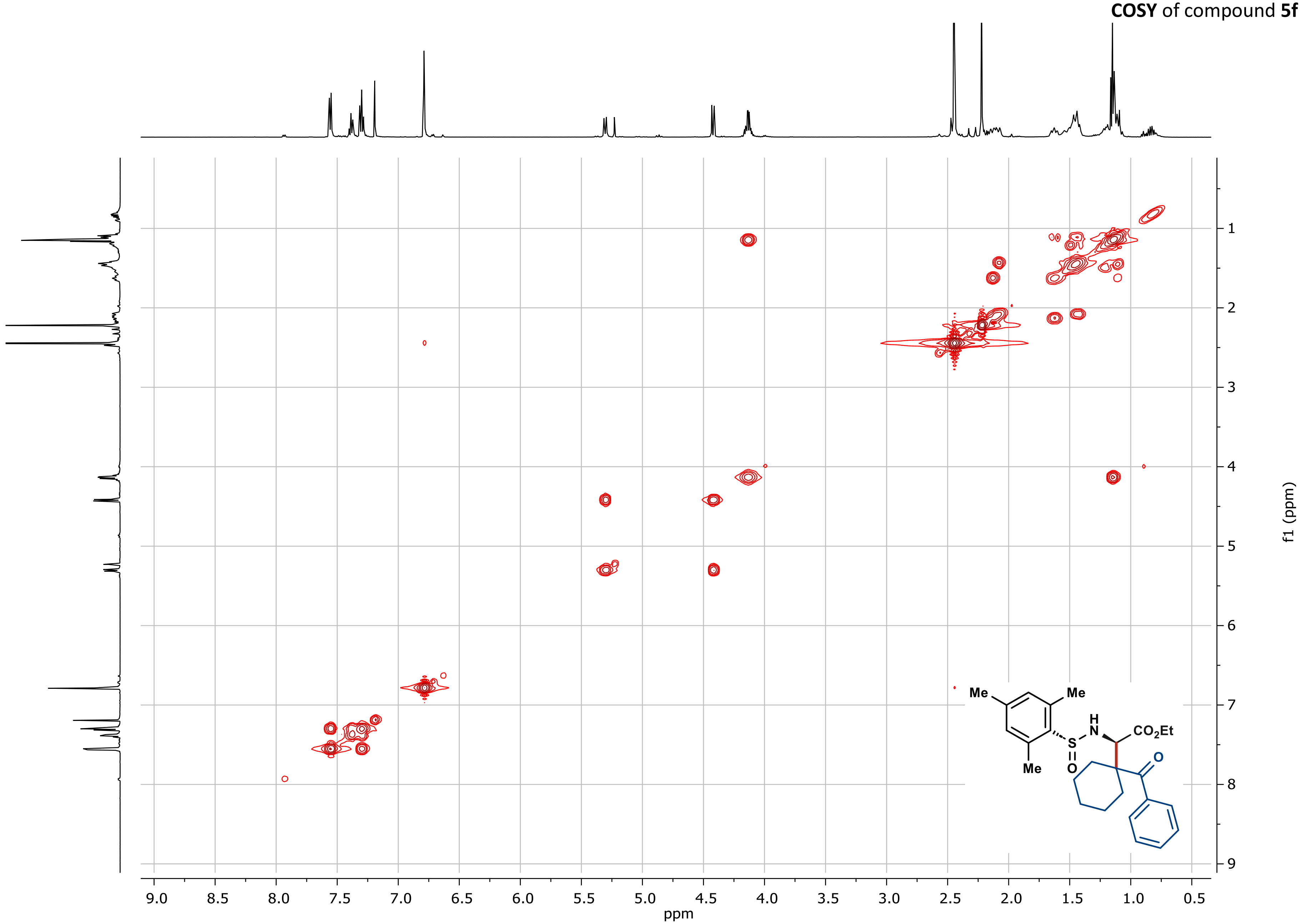
[1]**H NMR** (500 MHz, $CDCl_3$) of compound **5f**



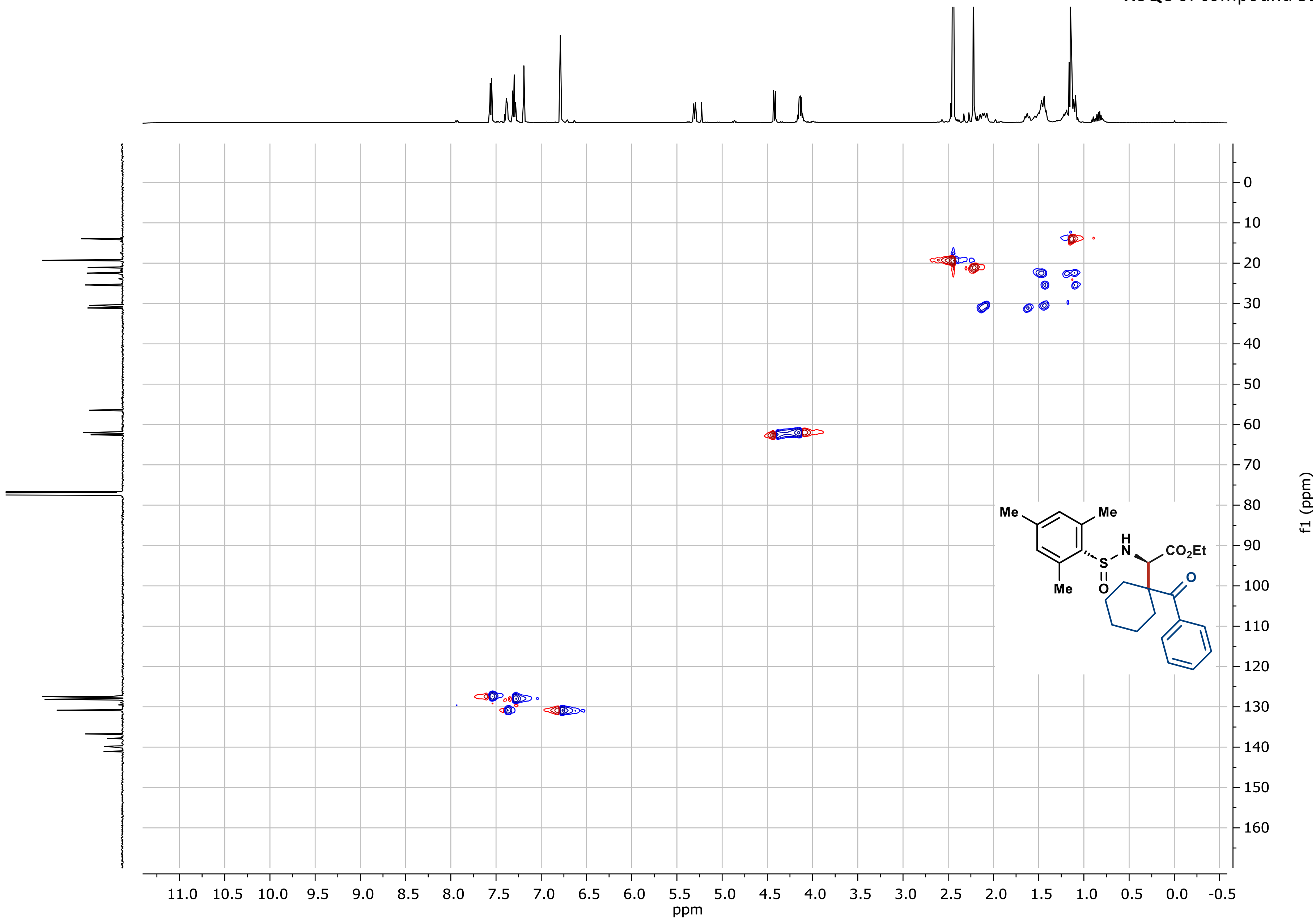
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5f**



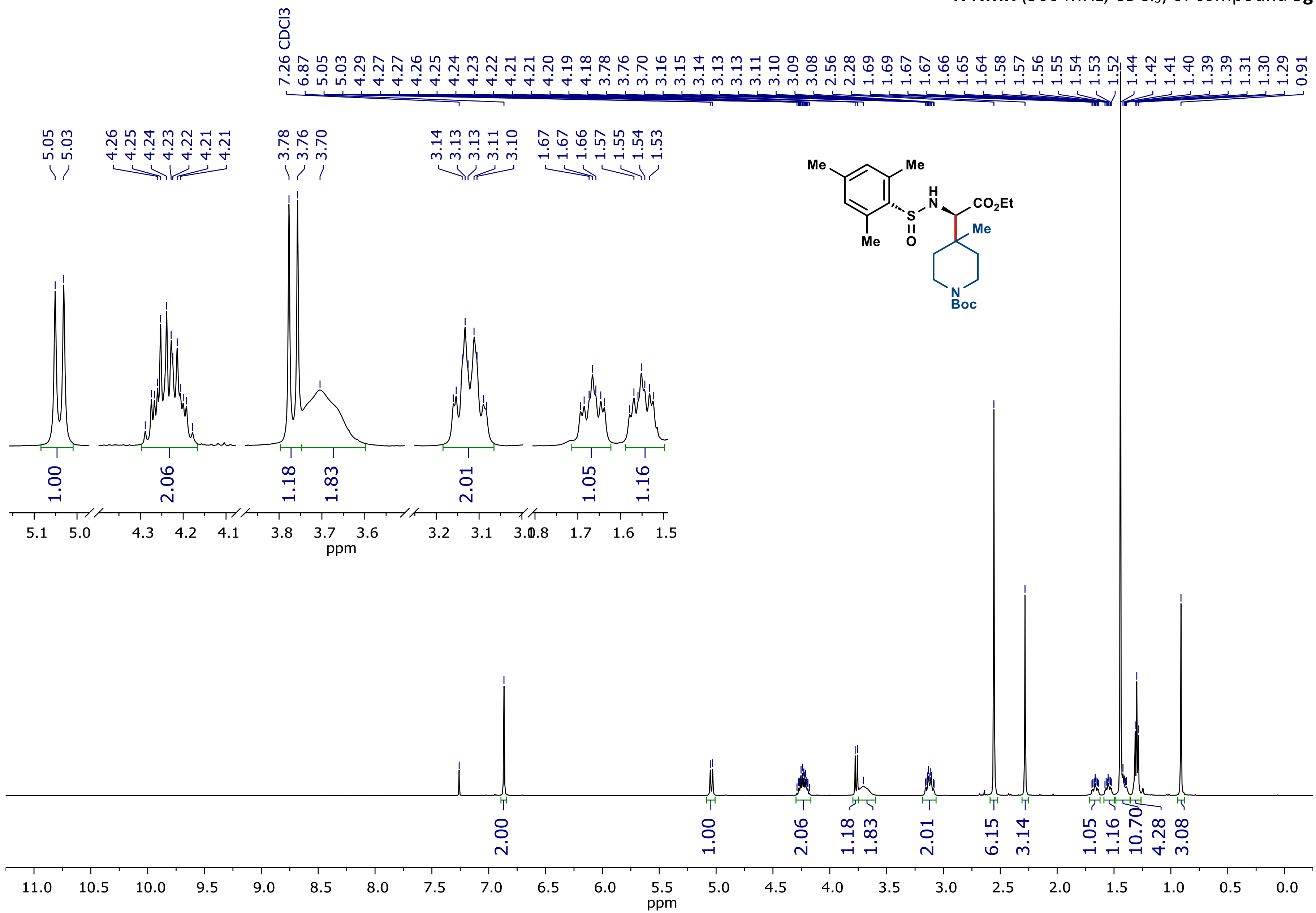
COSY of compound **5f**



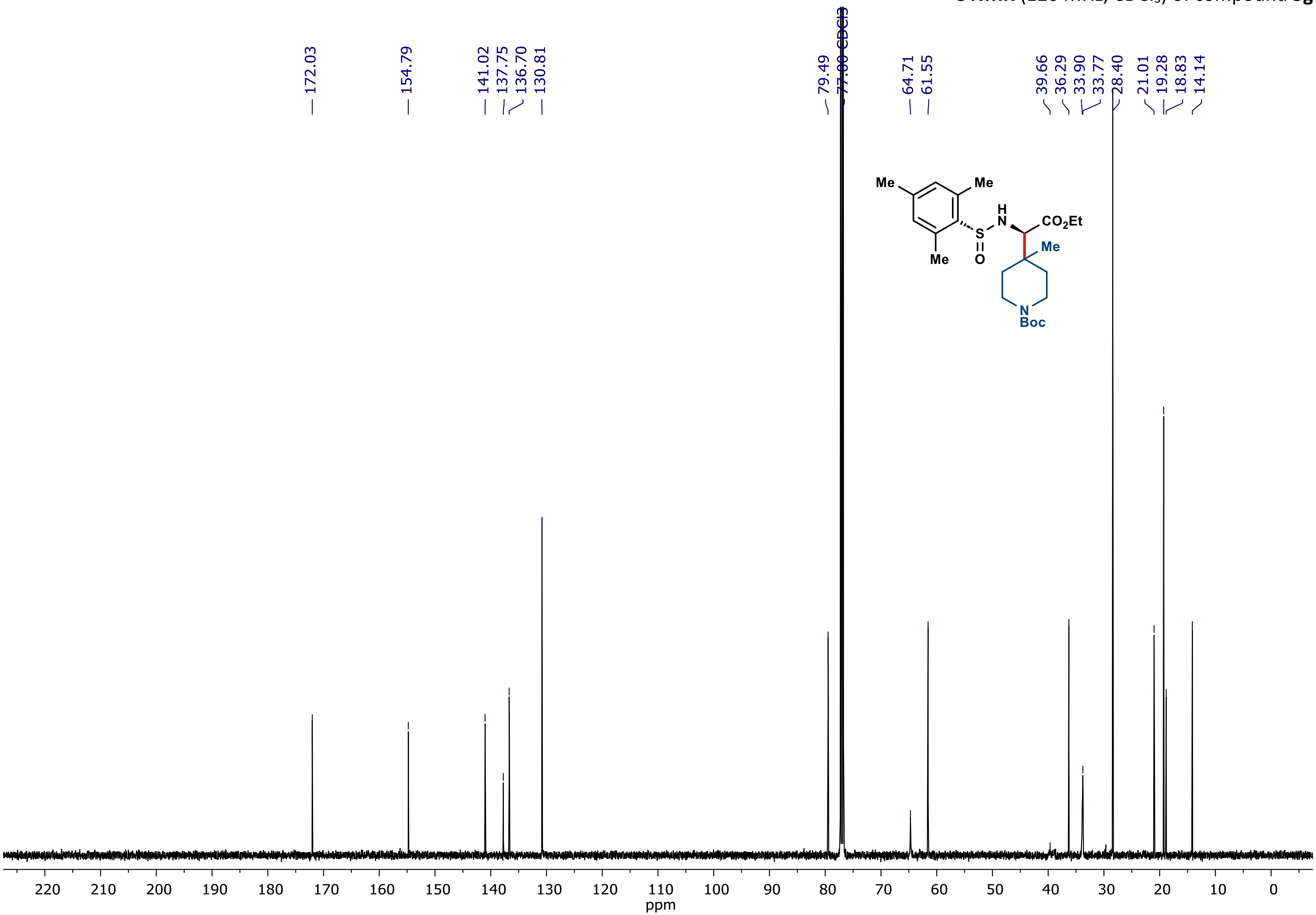
HSQC of compound 5f



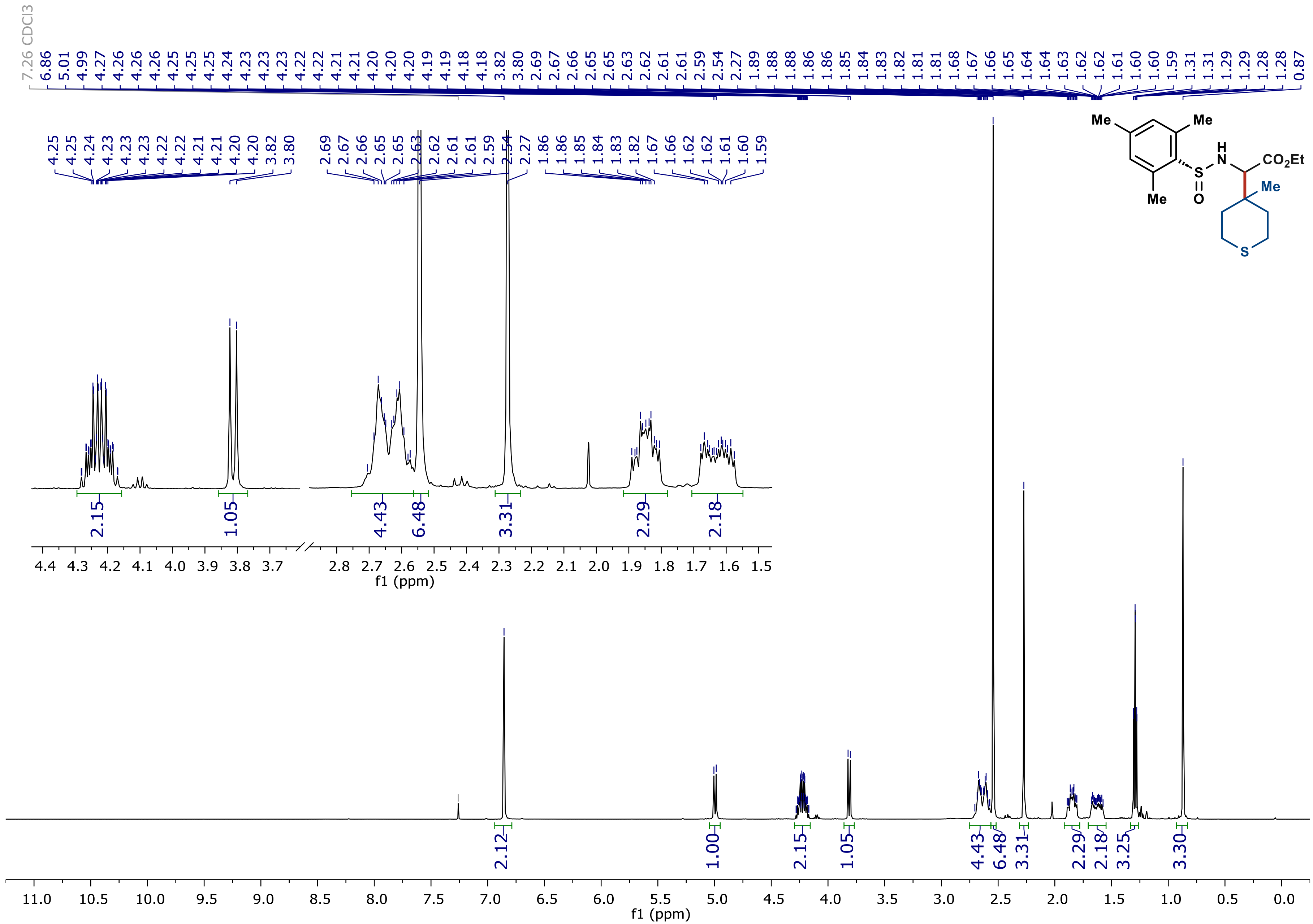
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5g**



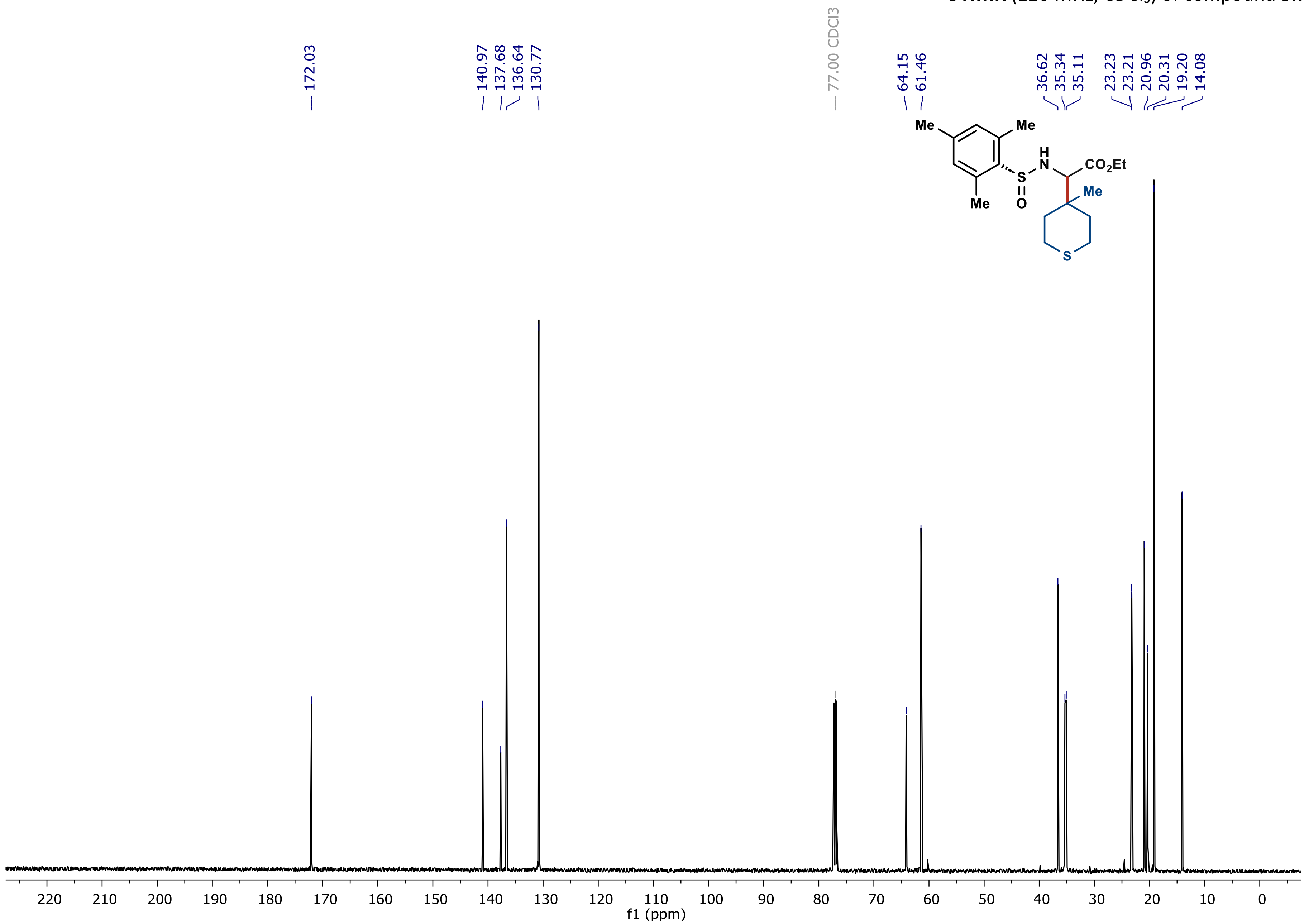
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5g**



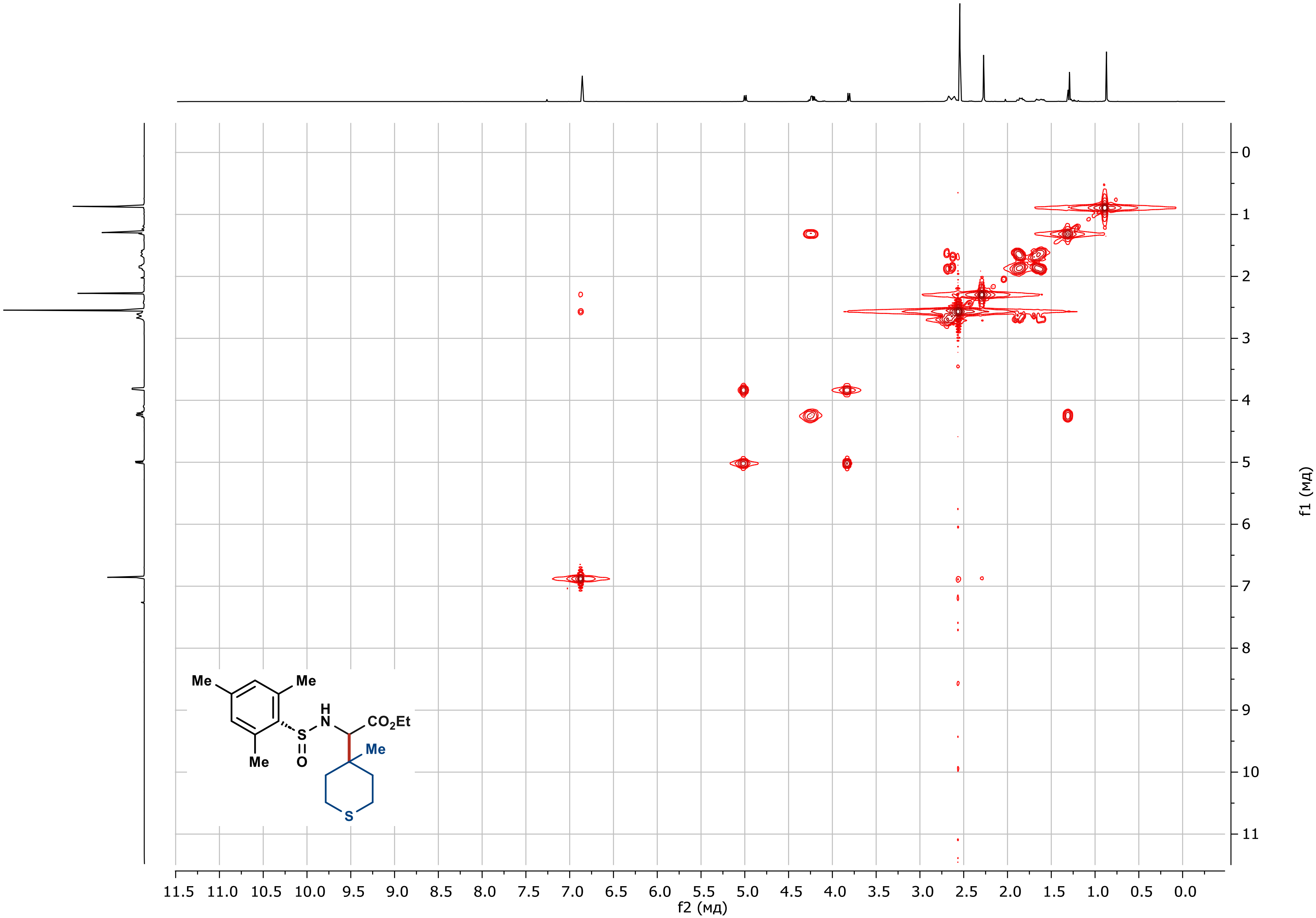
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5h**



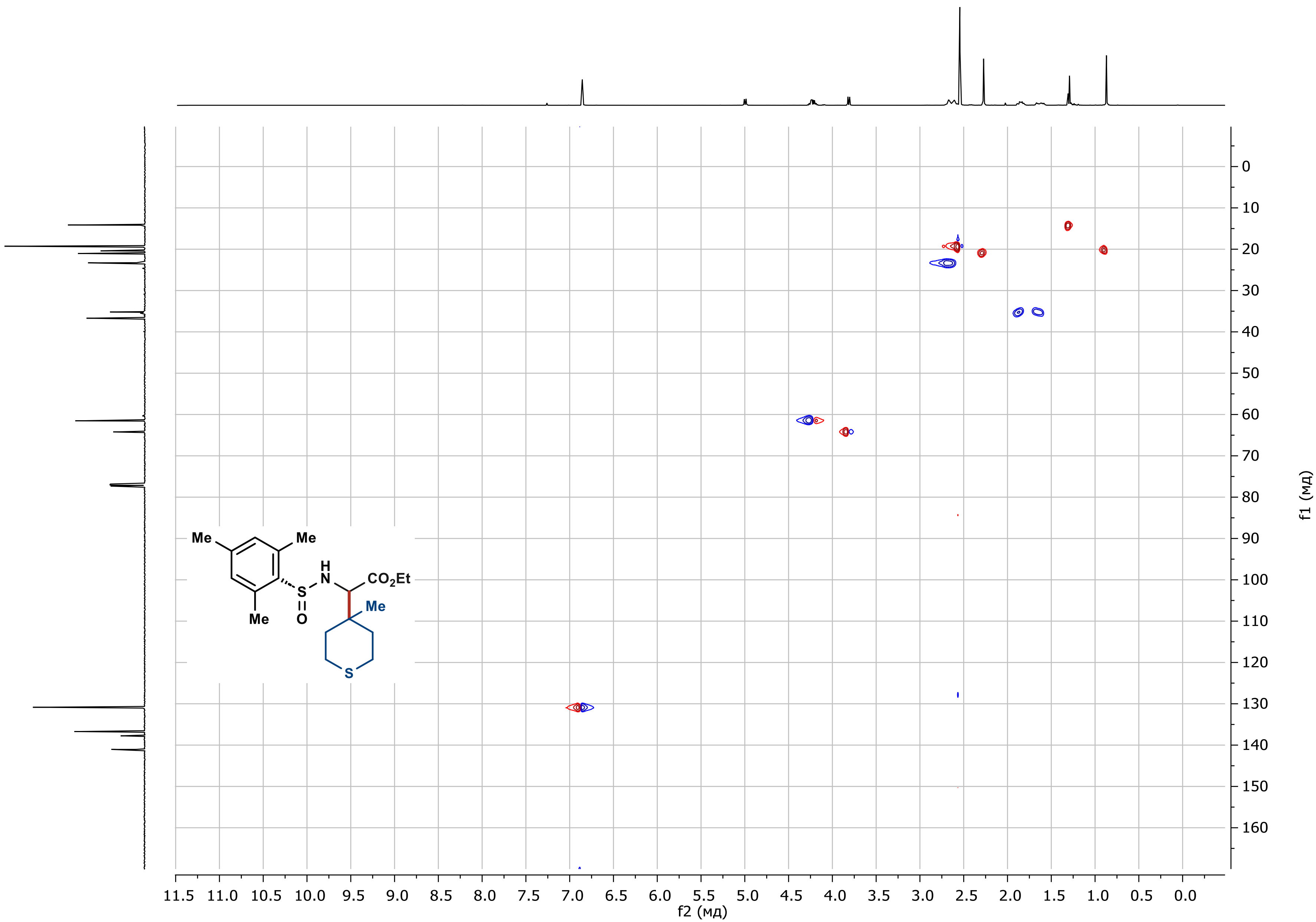
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5h**



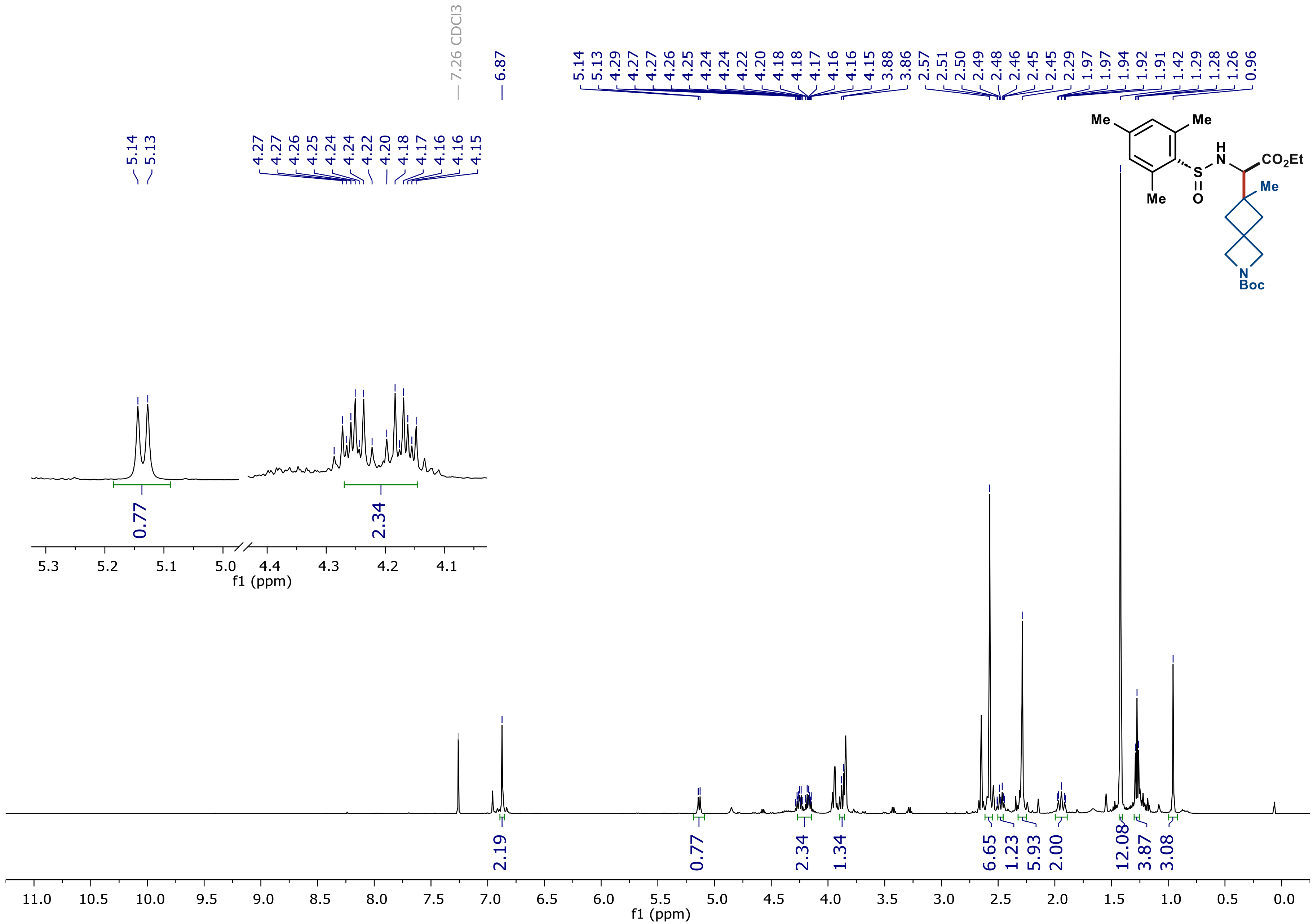
COSY of compound **5h**



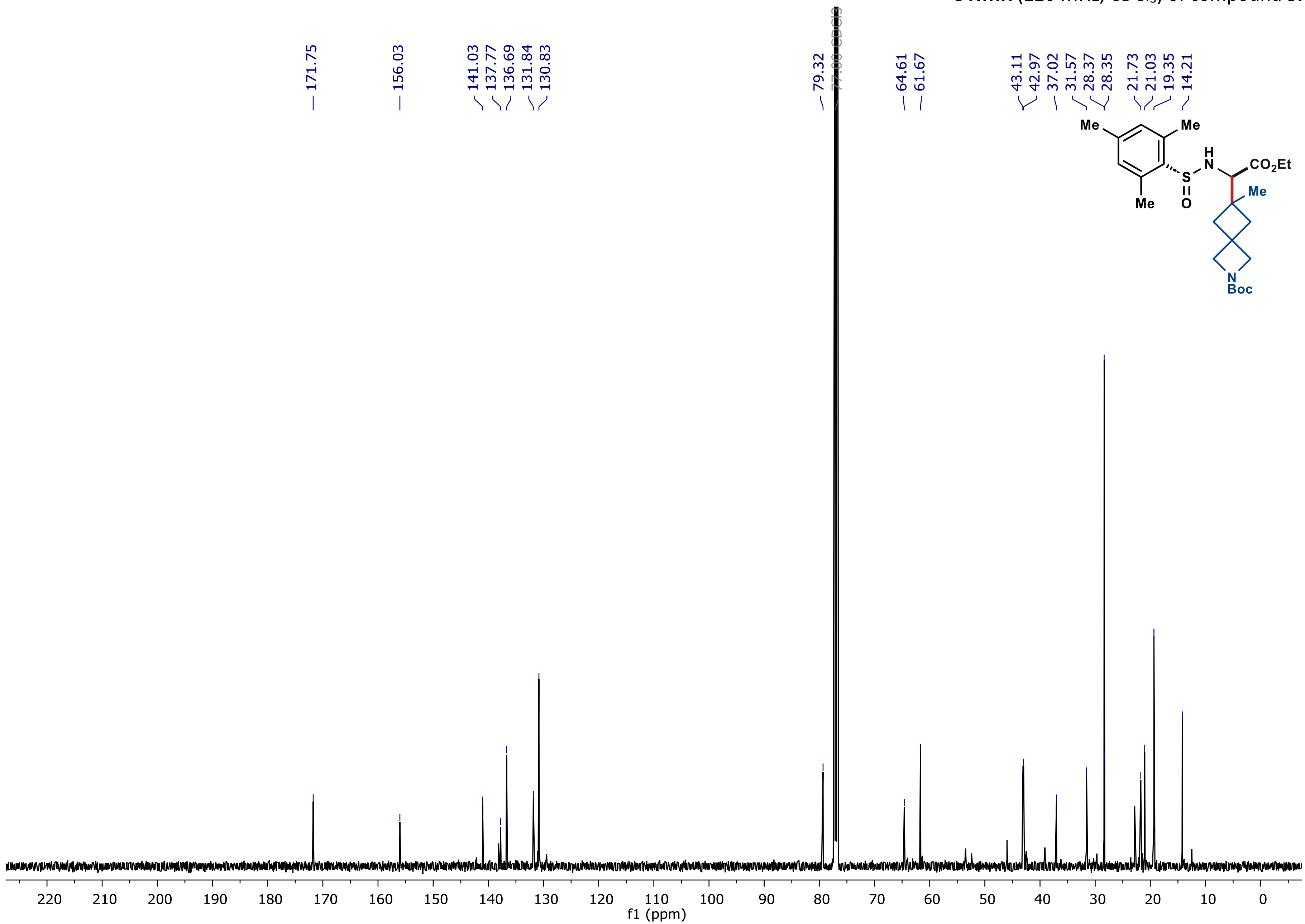
HSQC of compound **5h**



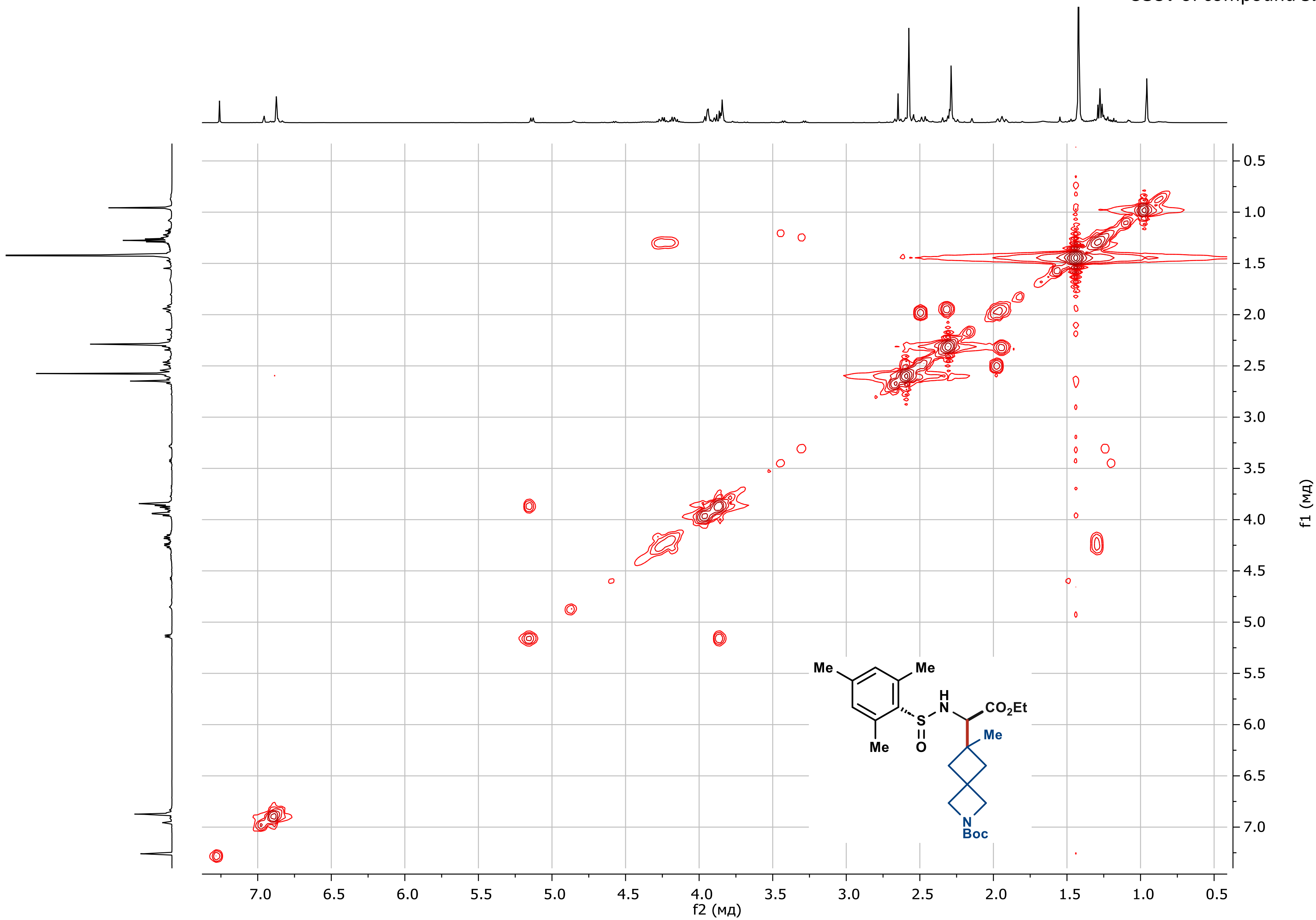
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5i**



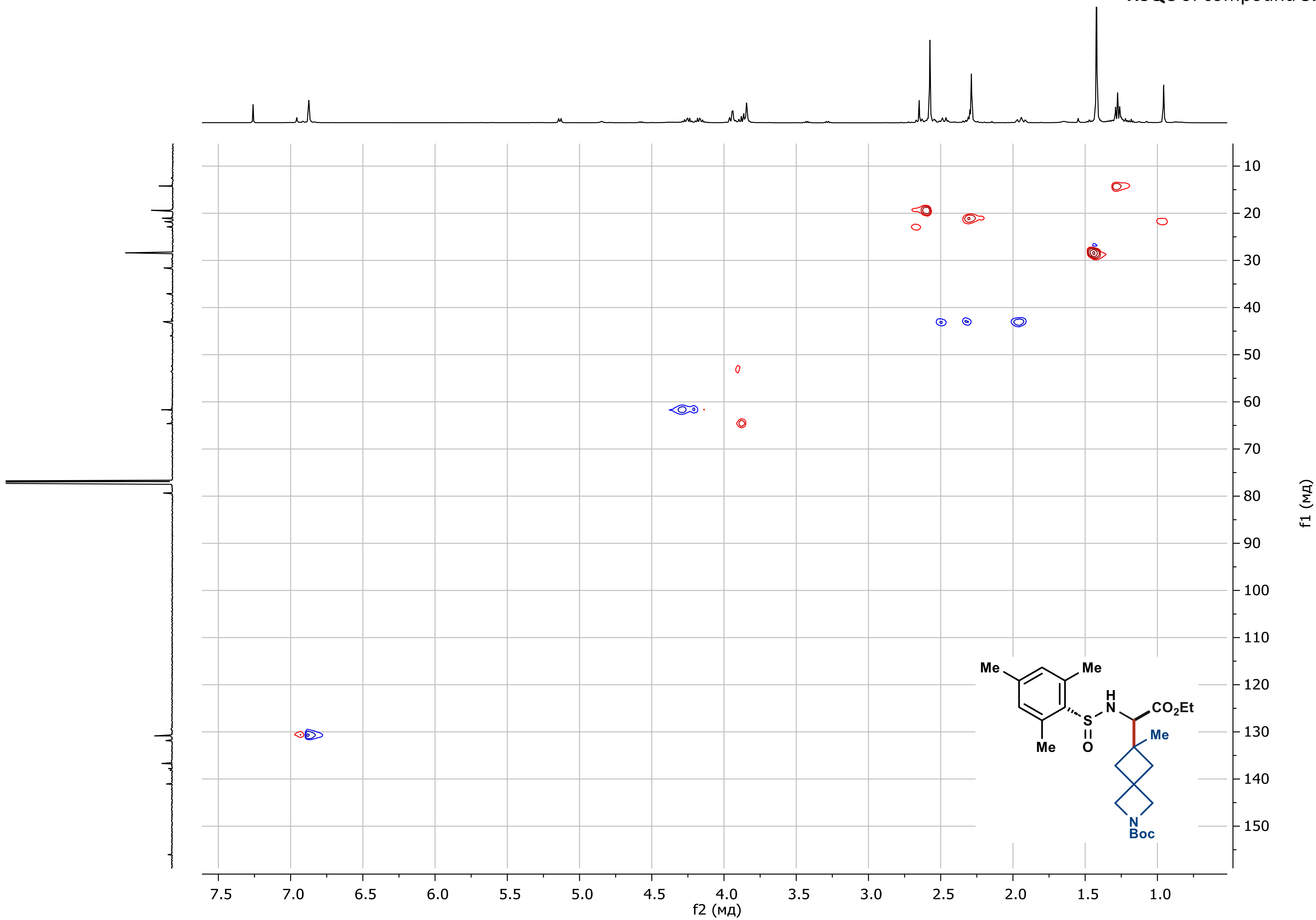
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5i**



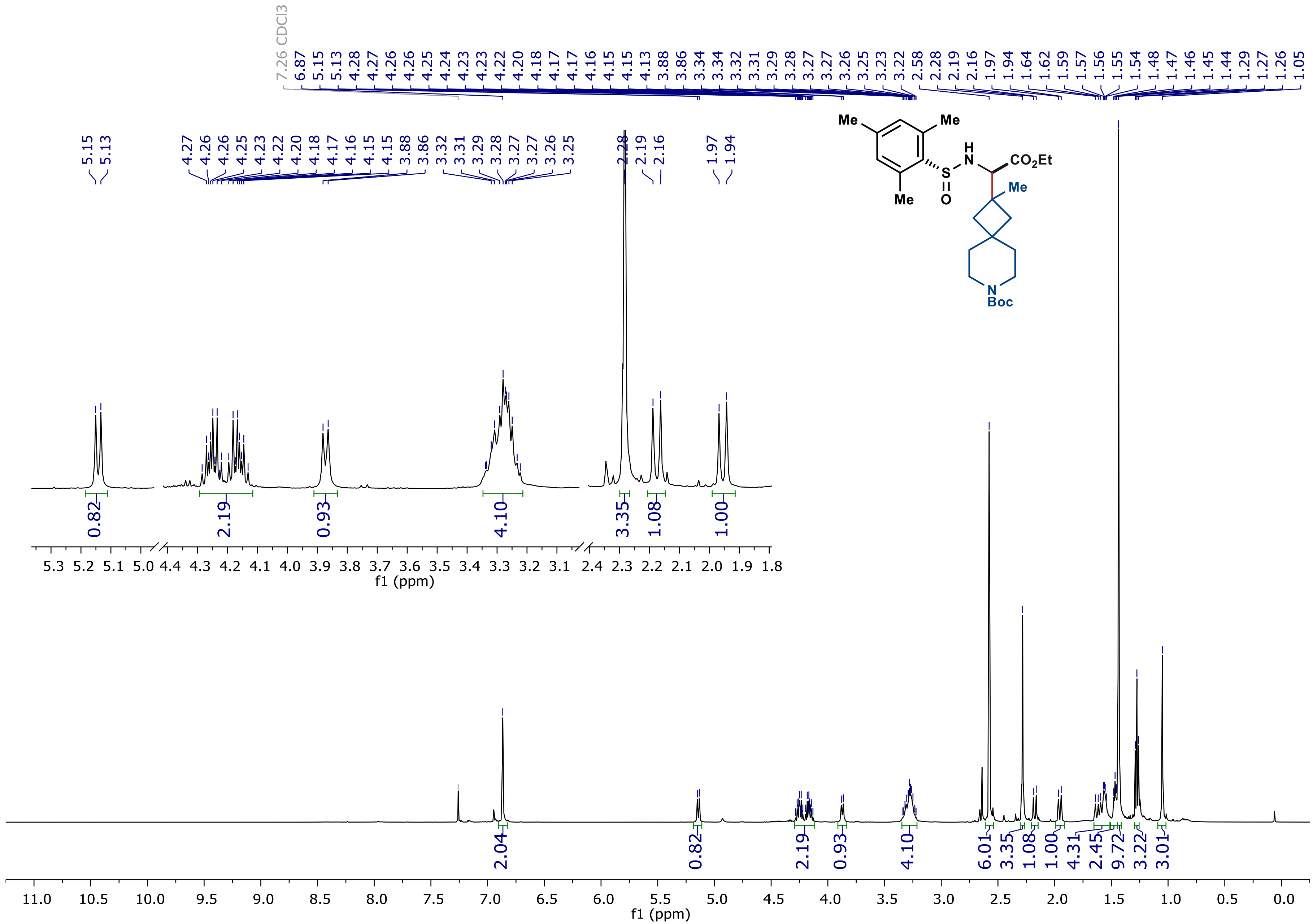
COSY of compound **5i**



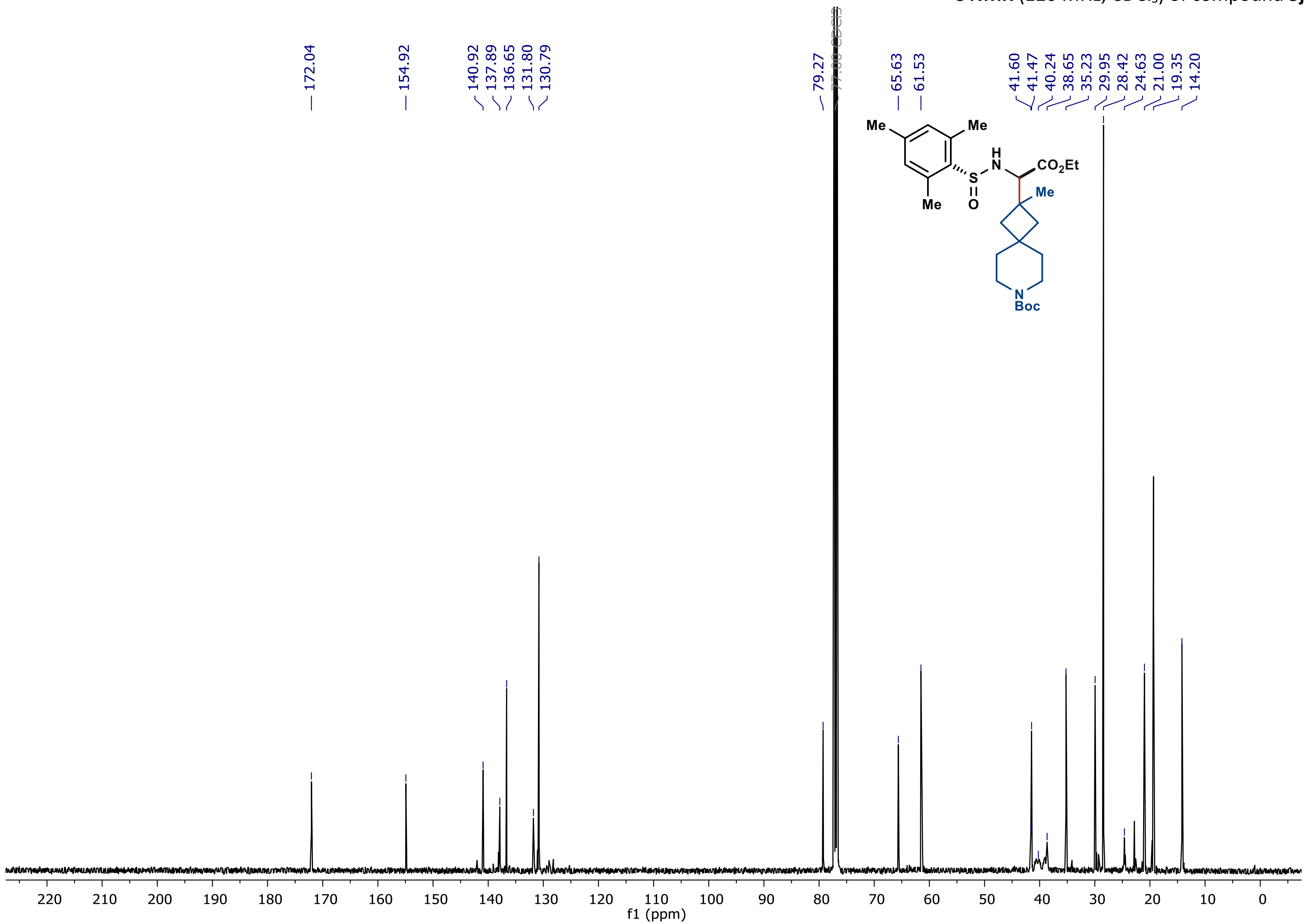
HSQC of compound **5i**



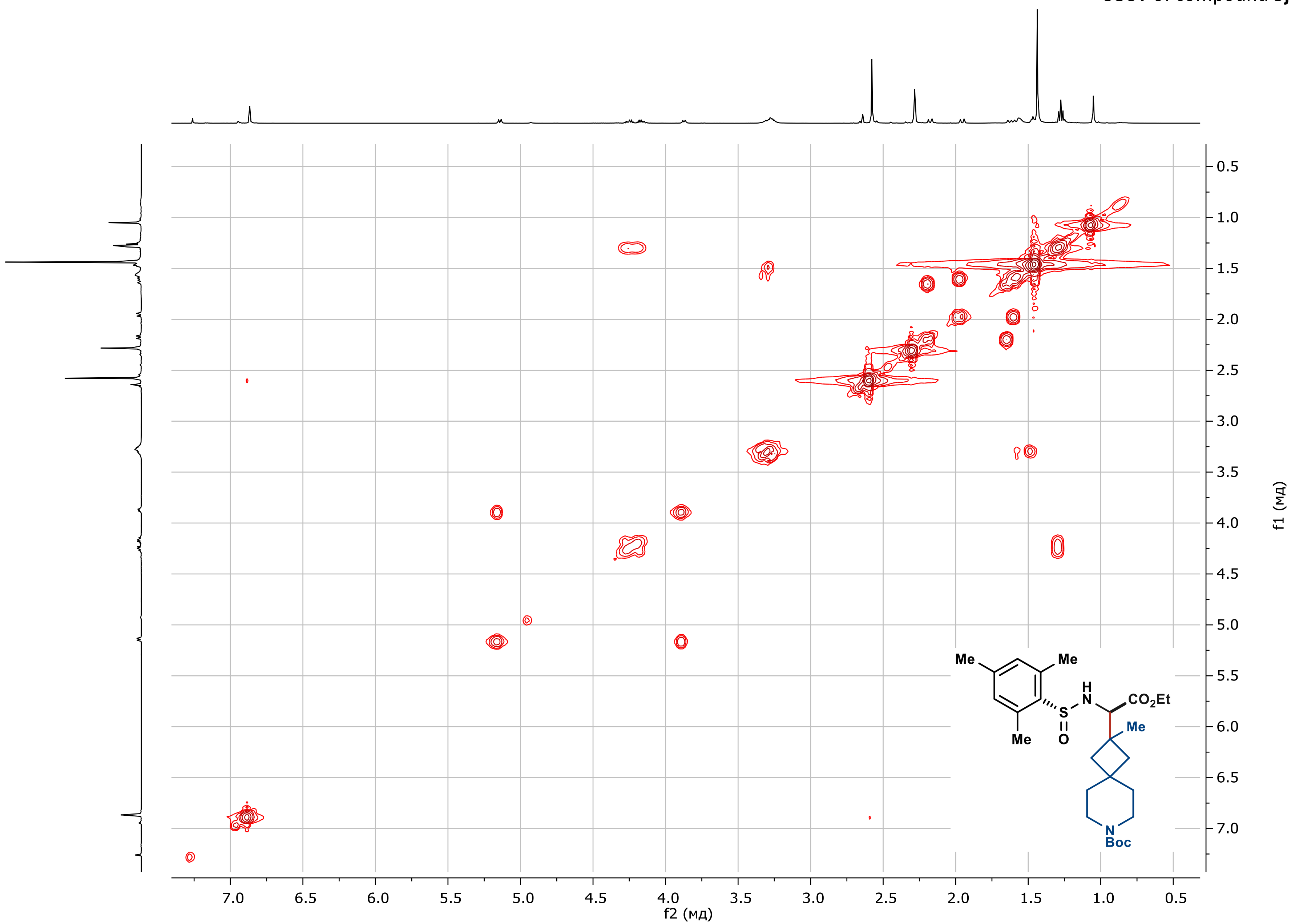
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5j**



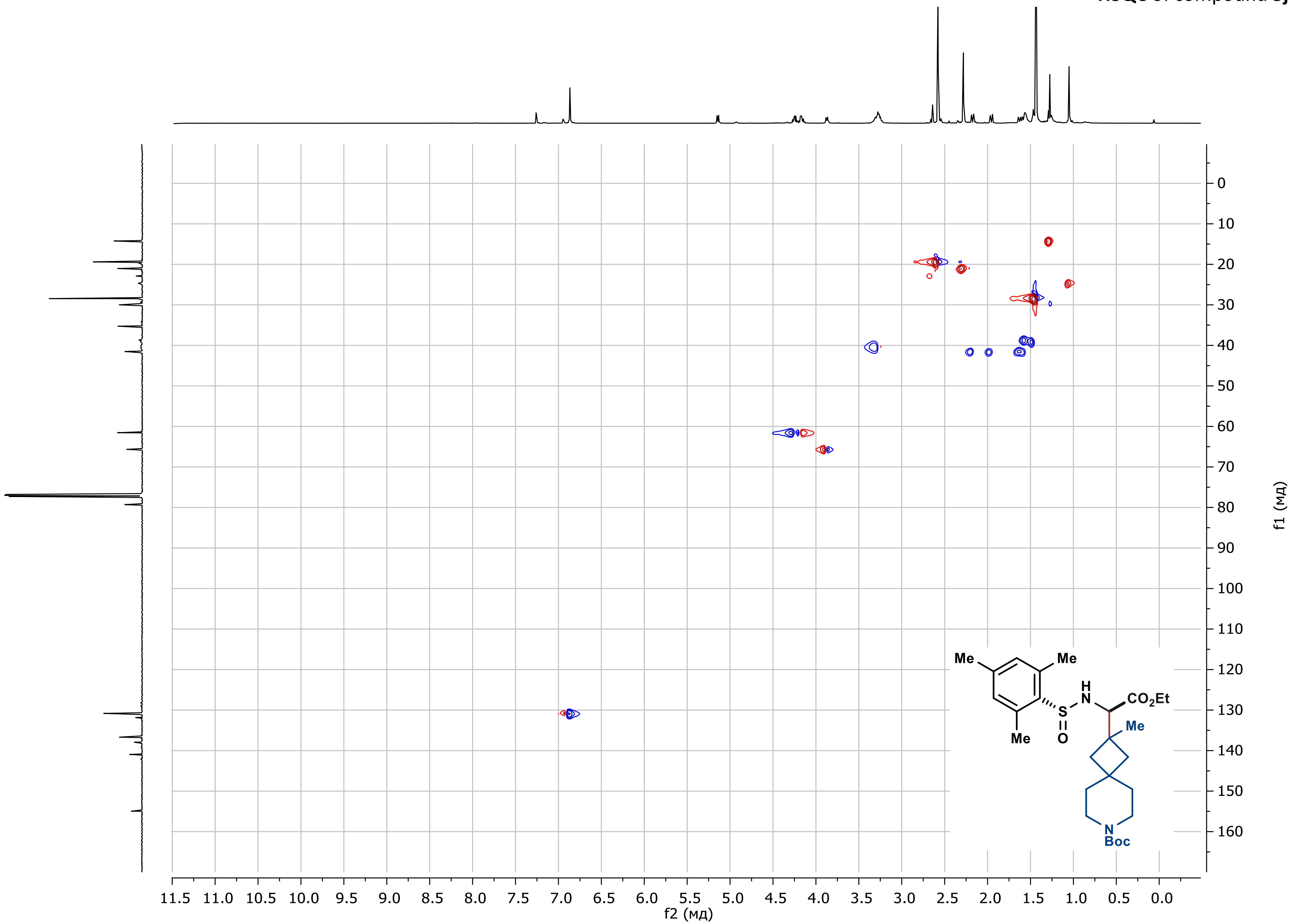
^{13}C NMR (126 MHz, CDCl$_3$) of compound **5j**



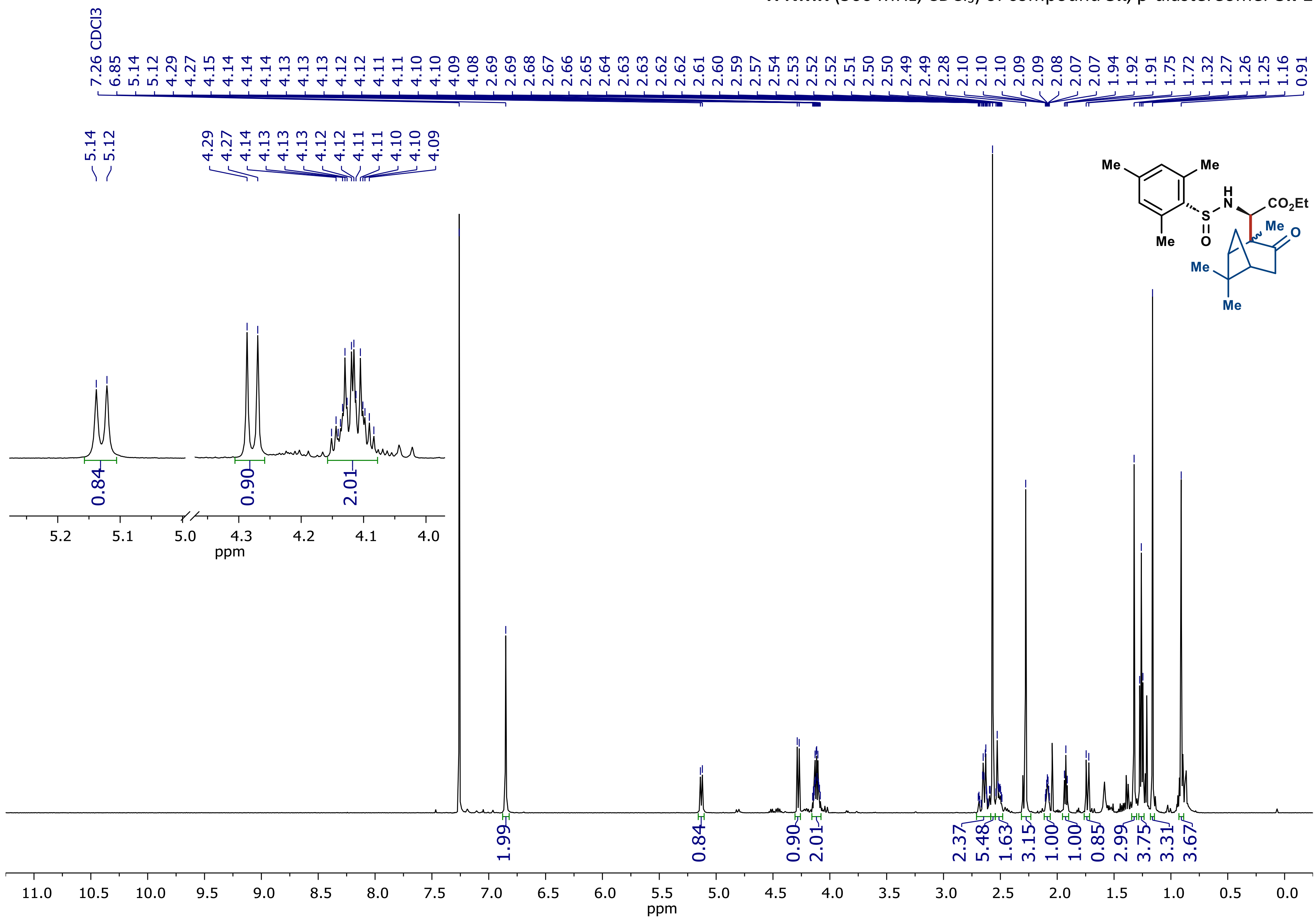
COSY of compound **5j**



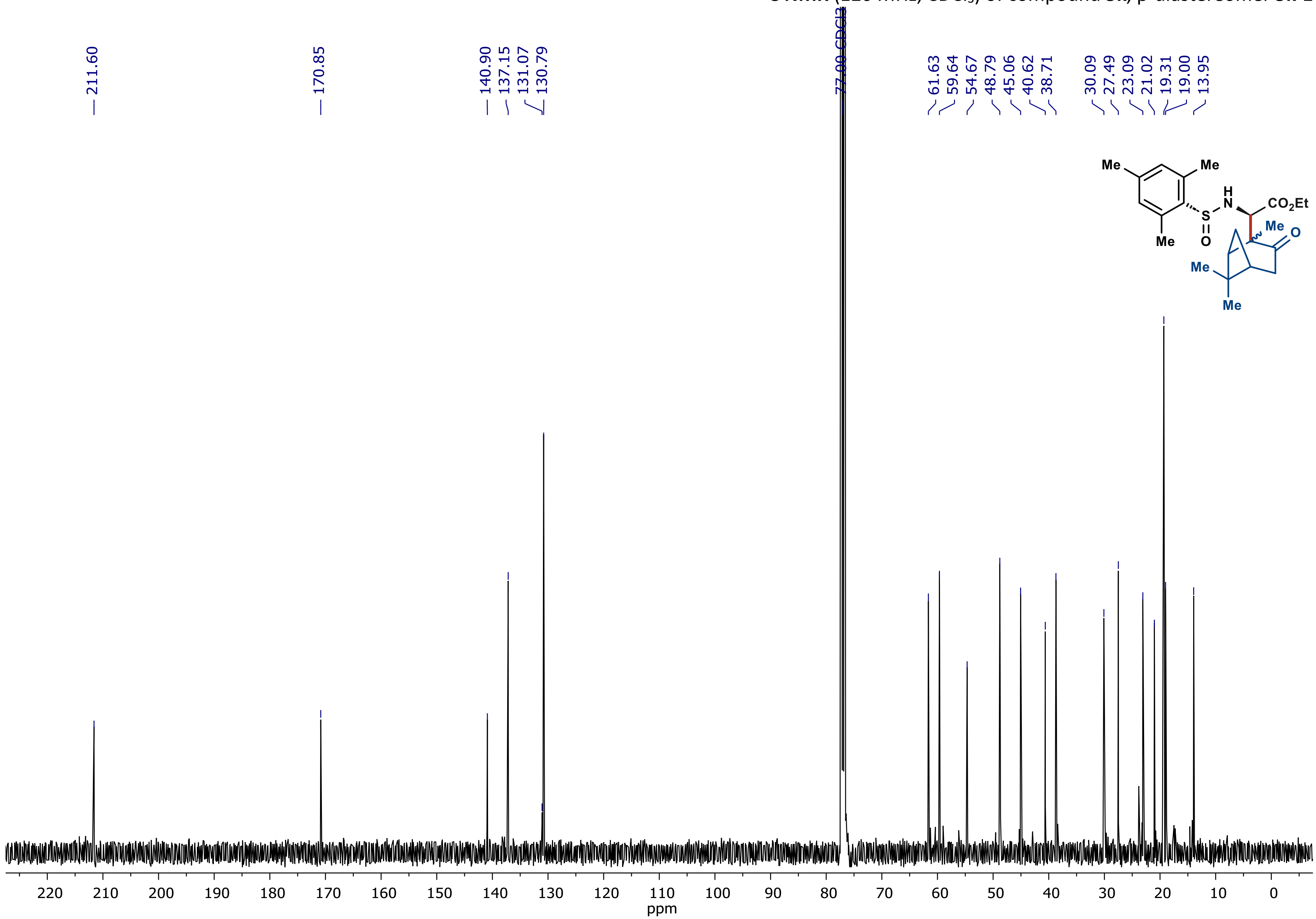
HSQC of compound **5j**



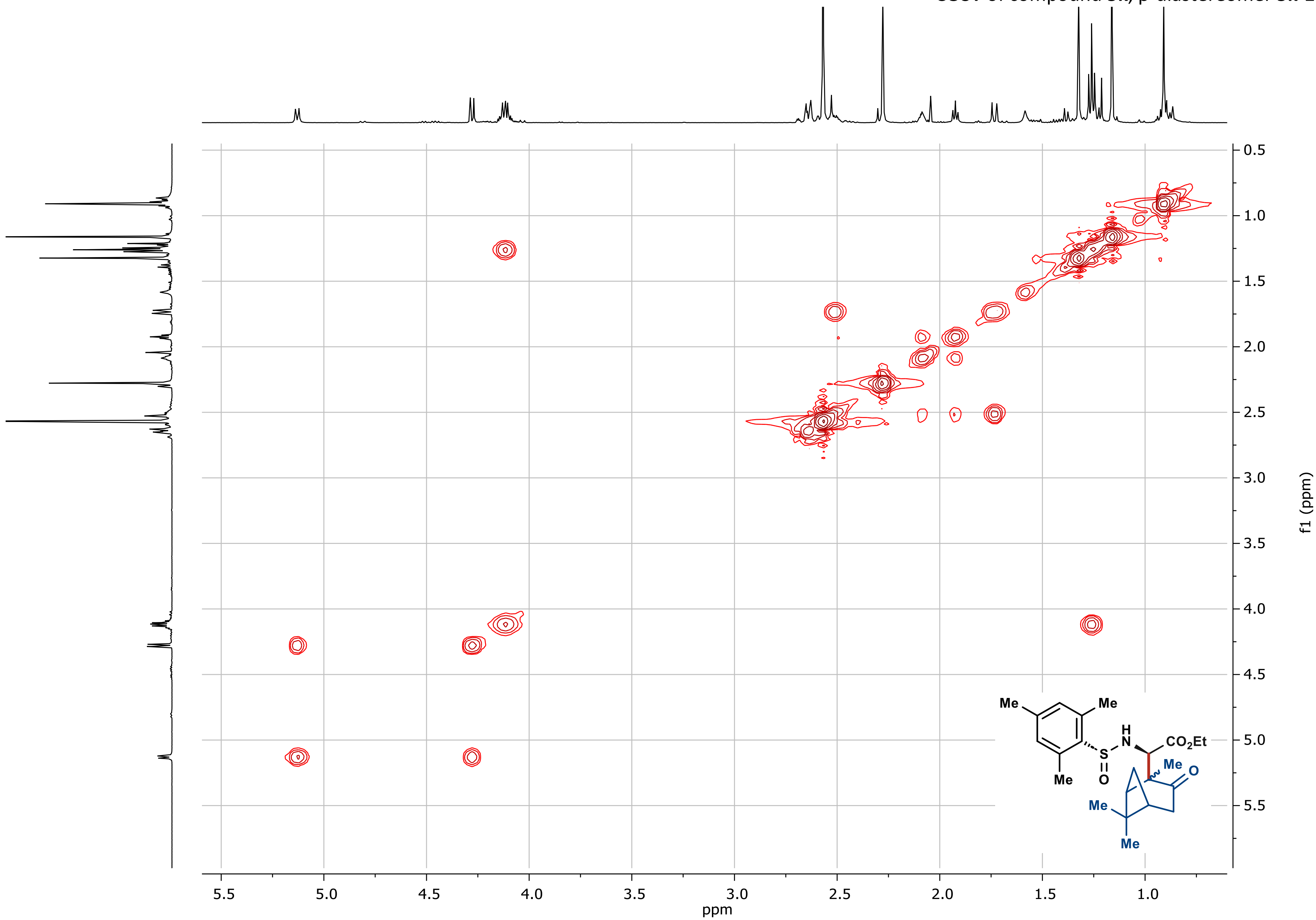
[1]**H NMR** (500 MHz, CDCl$_3$) of compound **5k**, β-diastereomer **5k-1**



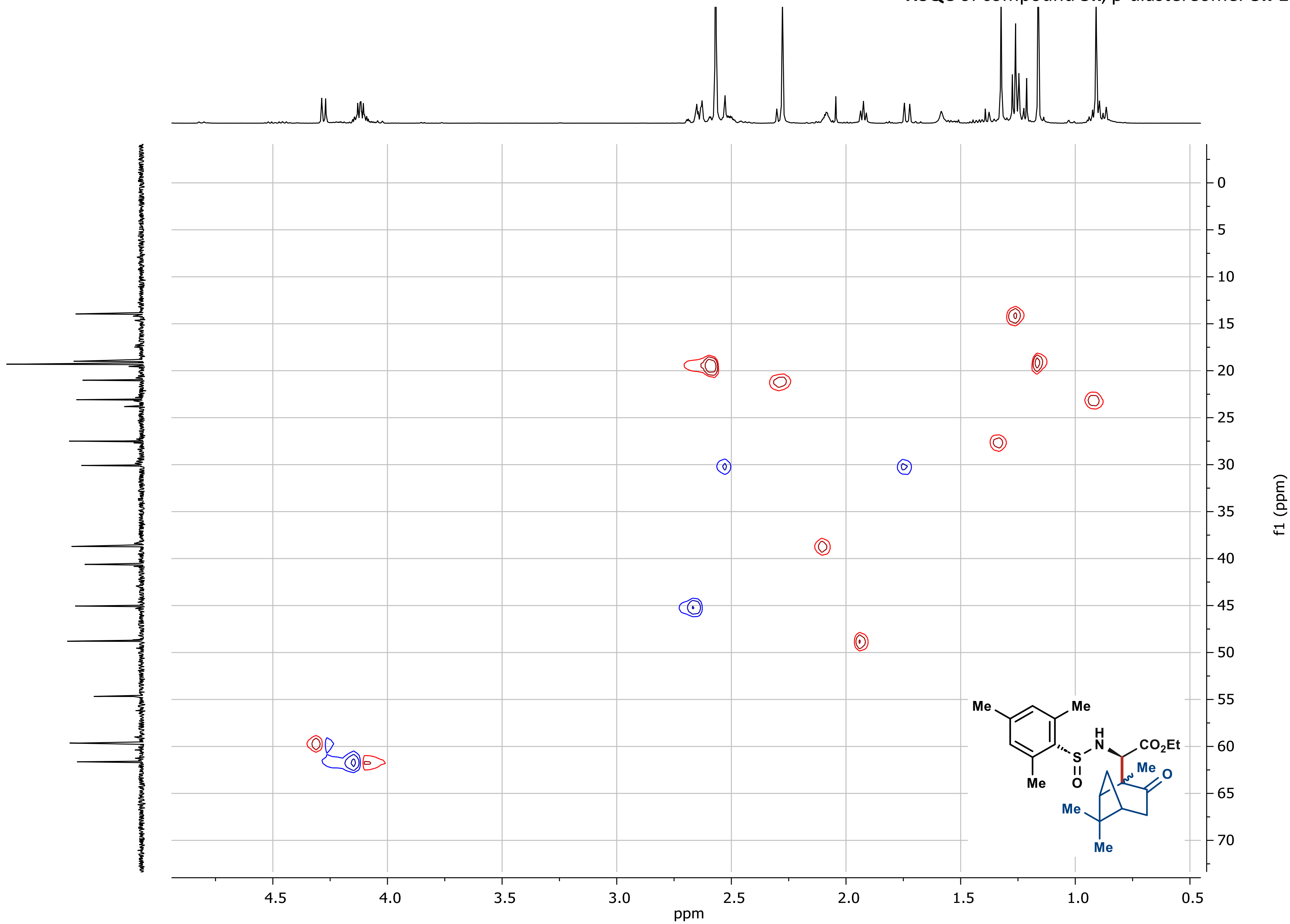
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5k**, β-diastereomer **5k-1**



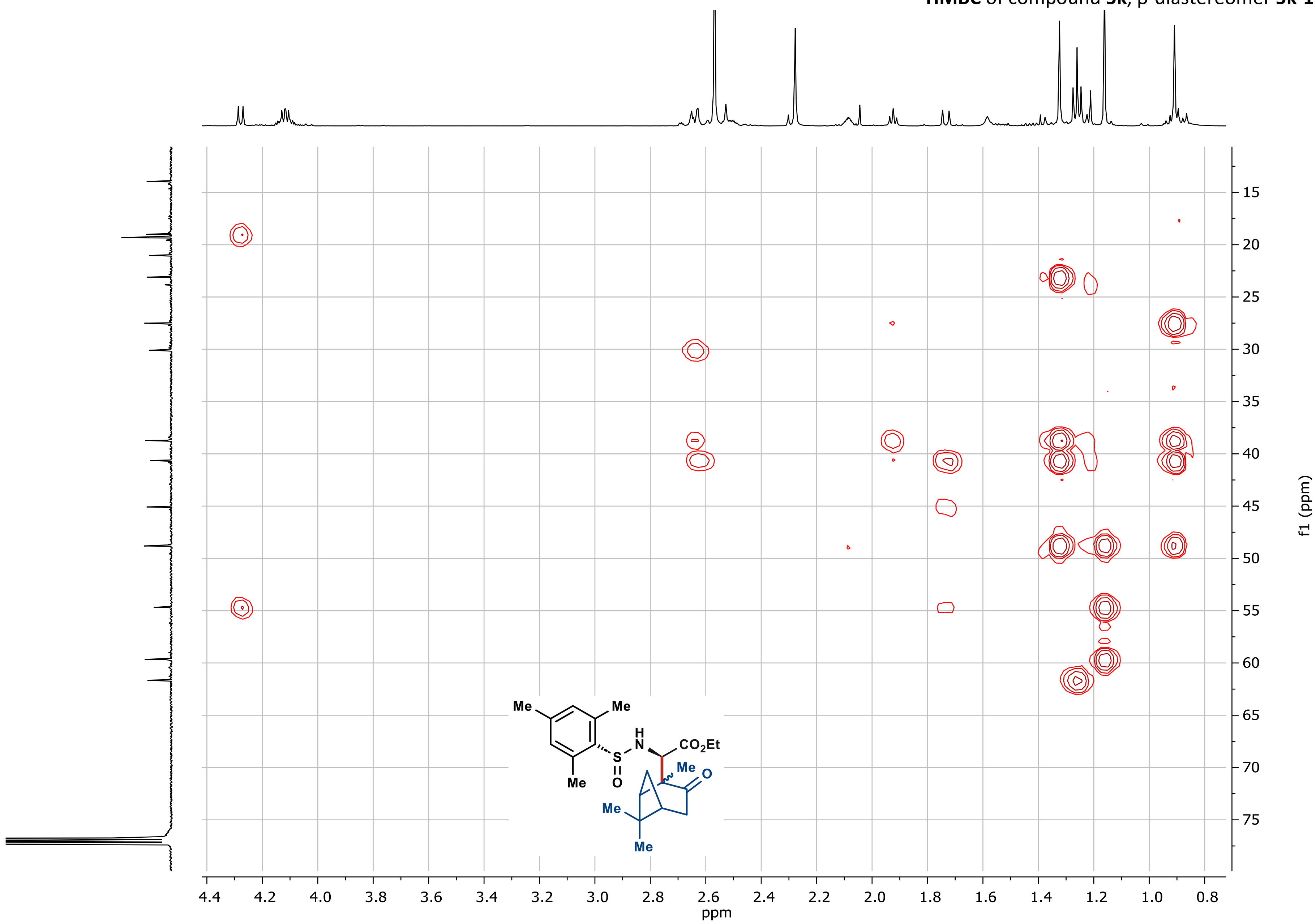
COSY of compound **5k**, β-diastereomer **5k-1**



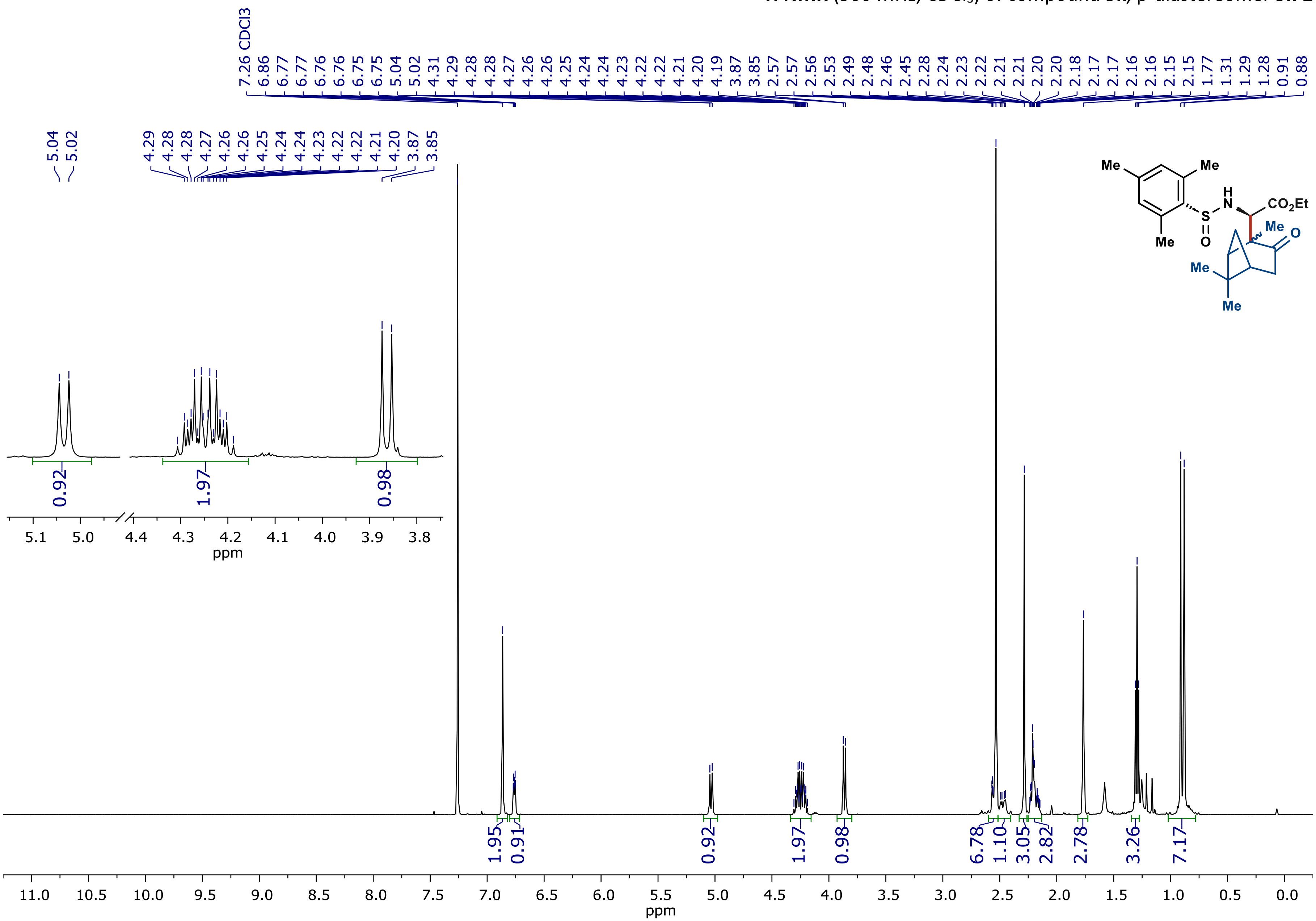
HSQC of compound **5k**, β-diastereomer **5k-1**



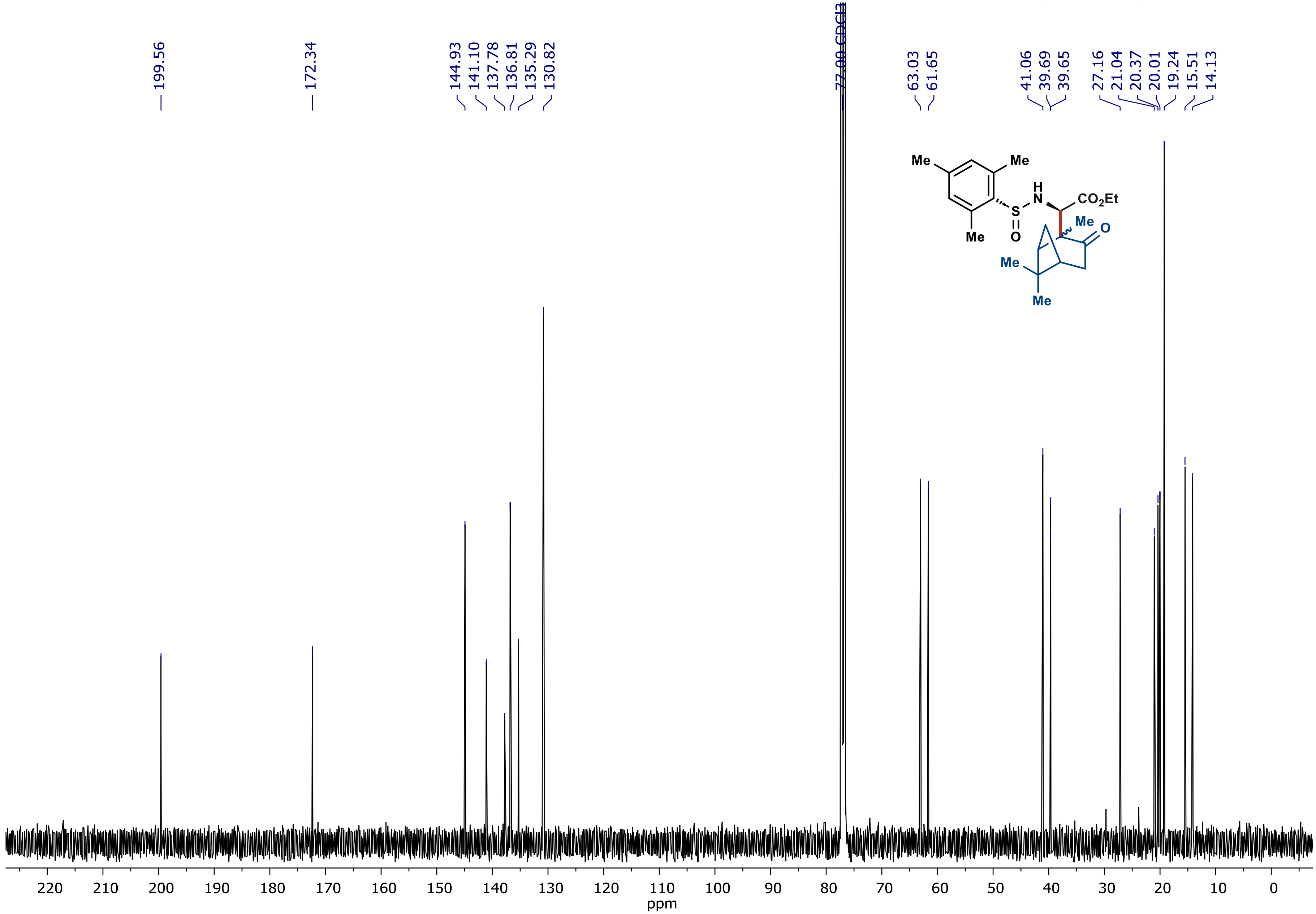
HMBC of compound **5k**, β-diastereomer **5k-1**



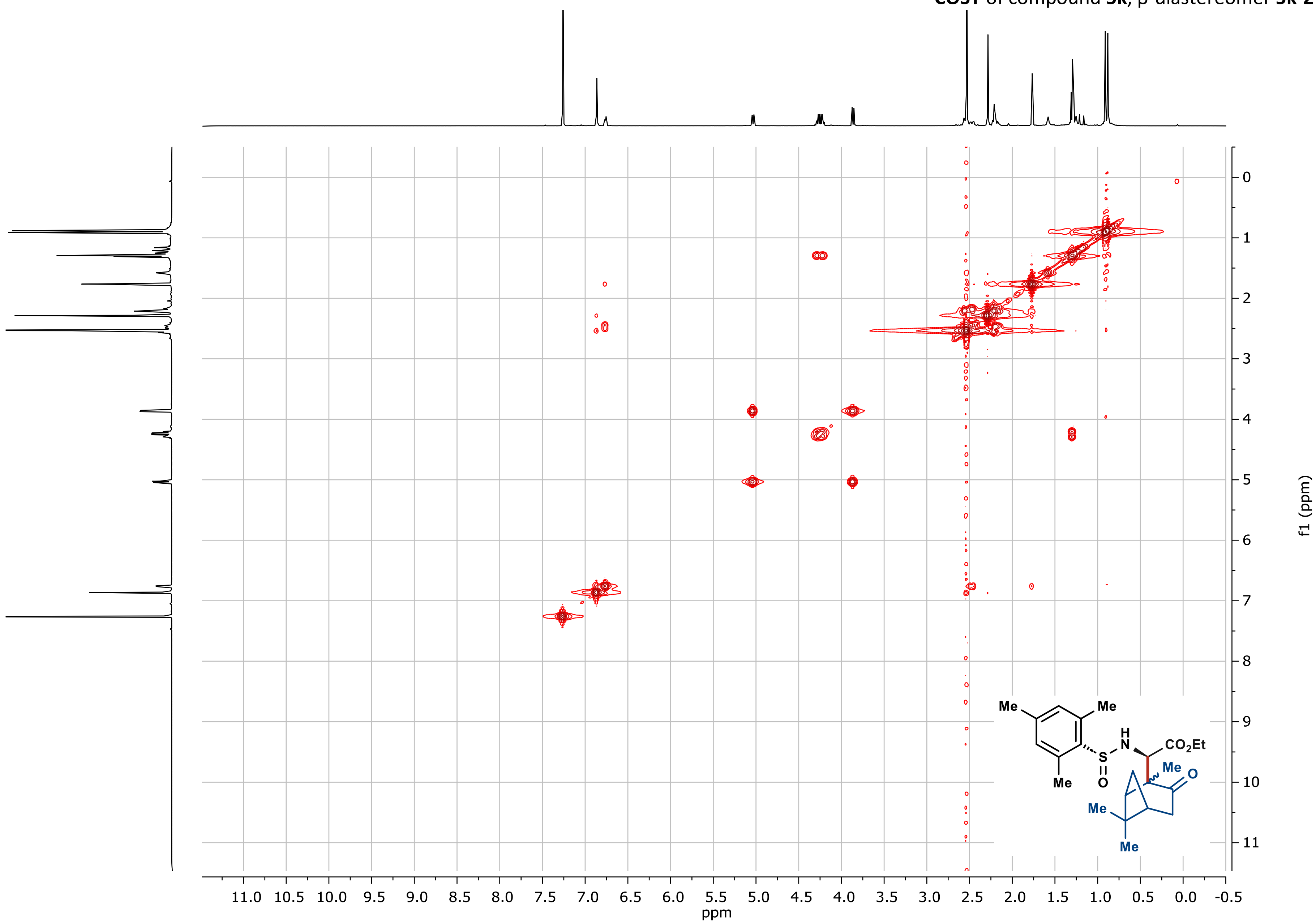
[1]H NMR (500 MHz, $CDCl_3$) of compound **5k**, β-diastereomer **5k-2**



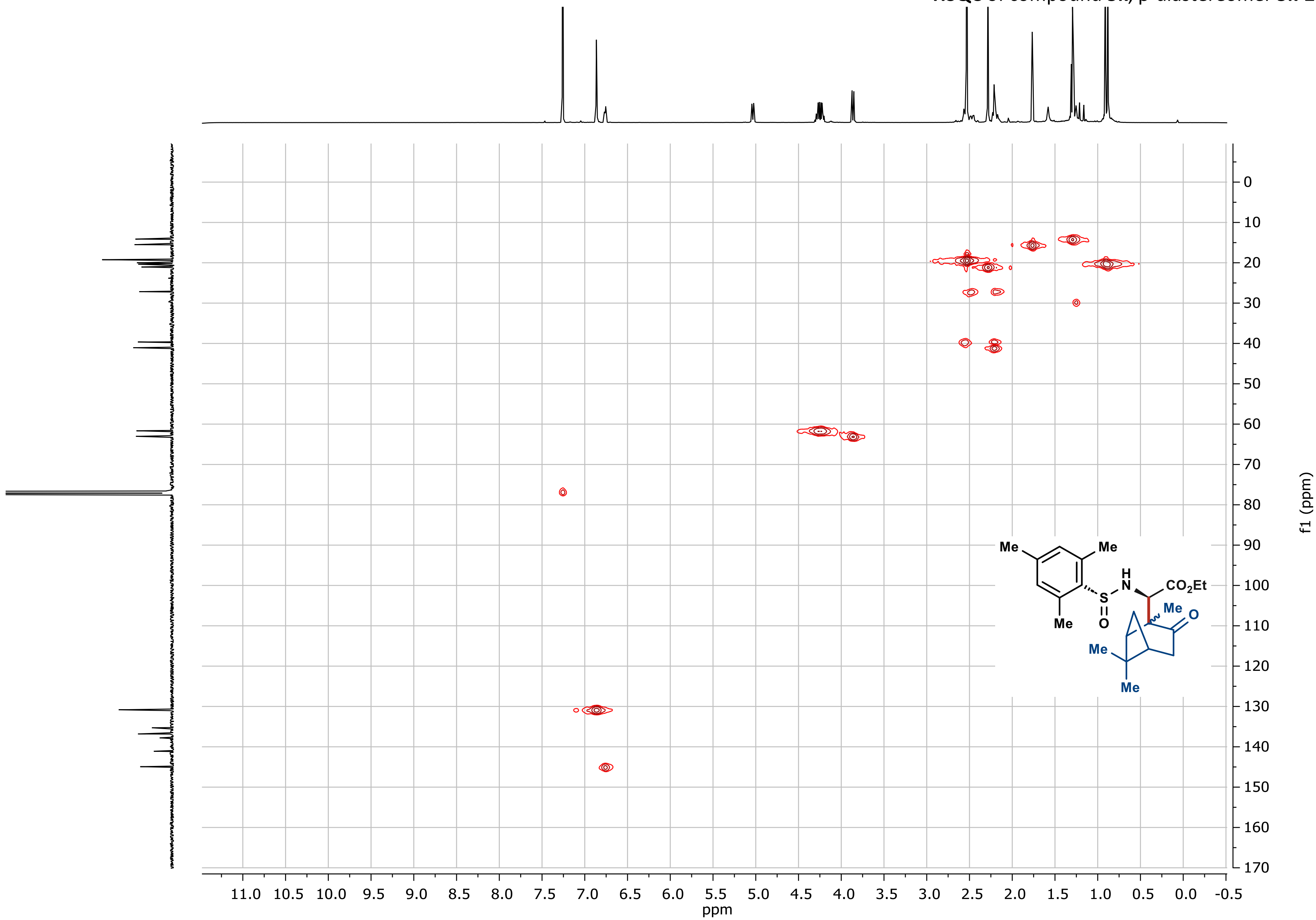
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5k**, β-diastereomer **5k-2**



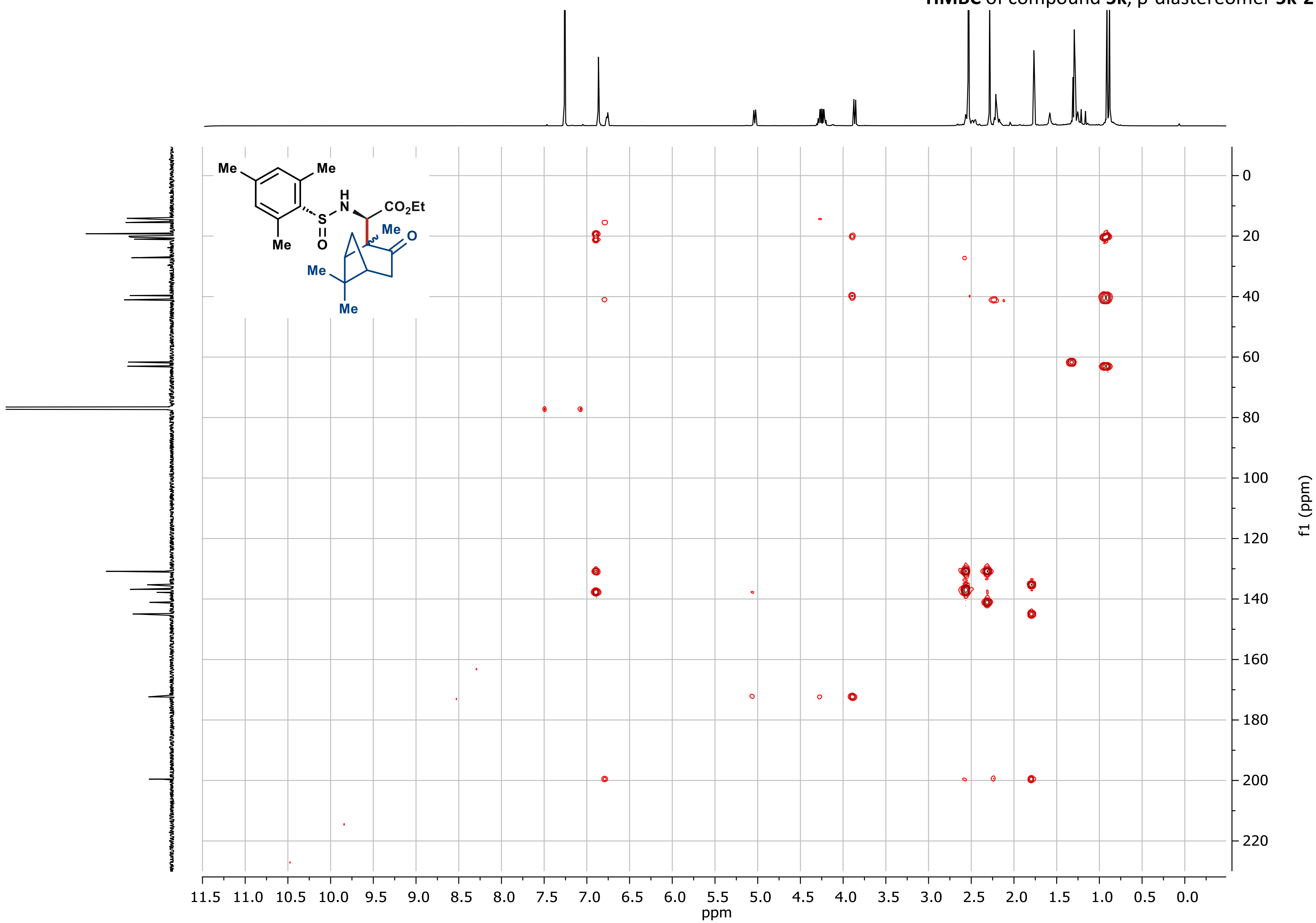
COSY of compound **5k**, β-diastereomer **5k-2**



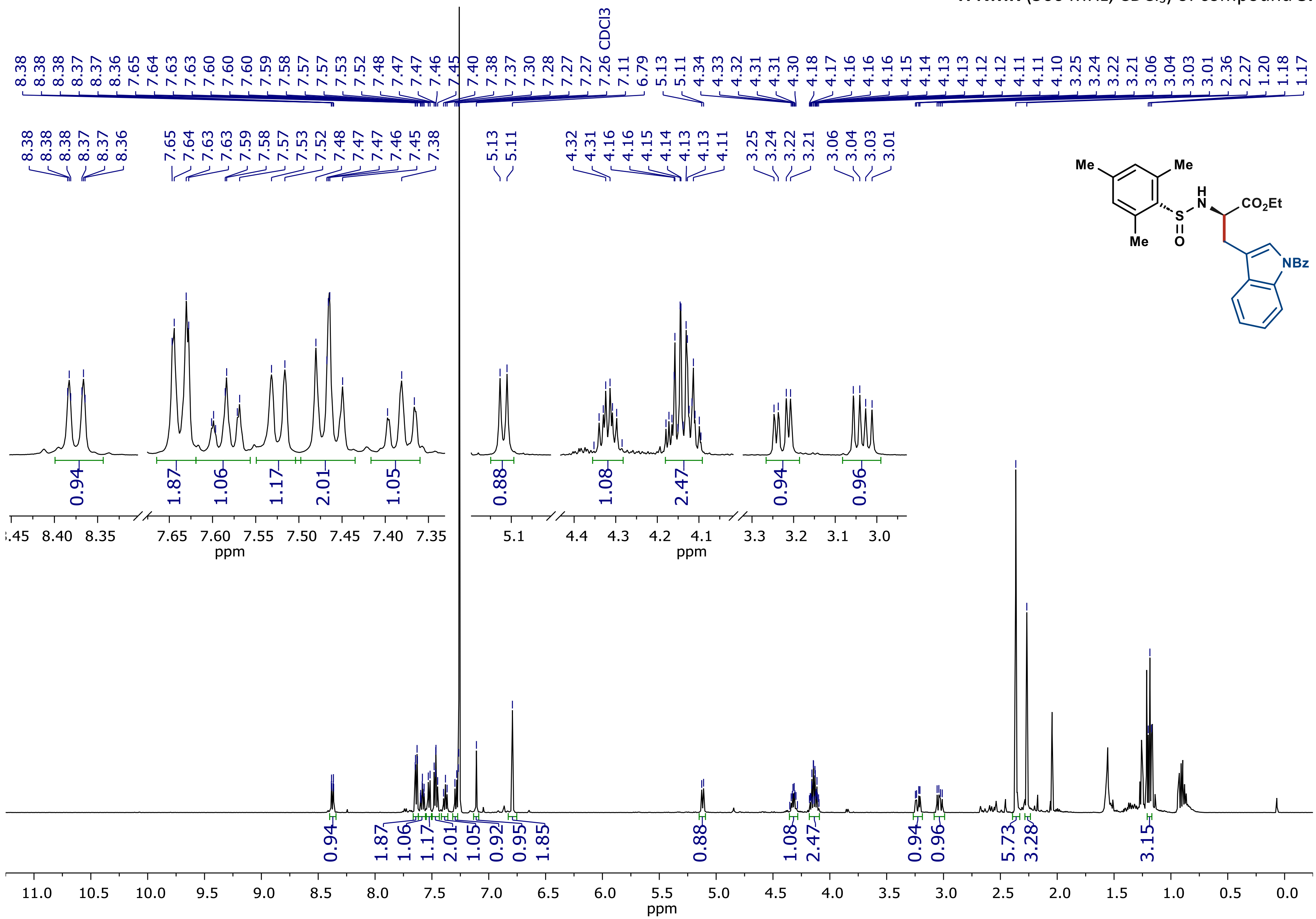
HSQC of compound **5k**, β-diastereomer **5k-2**



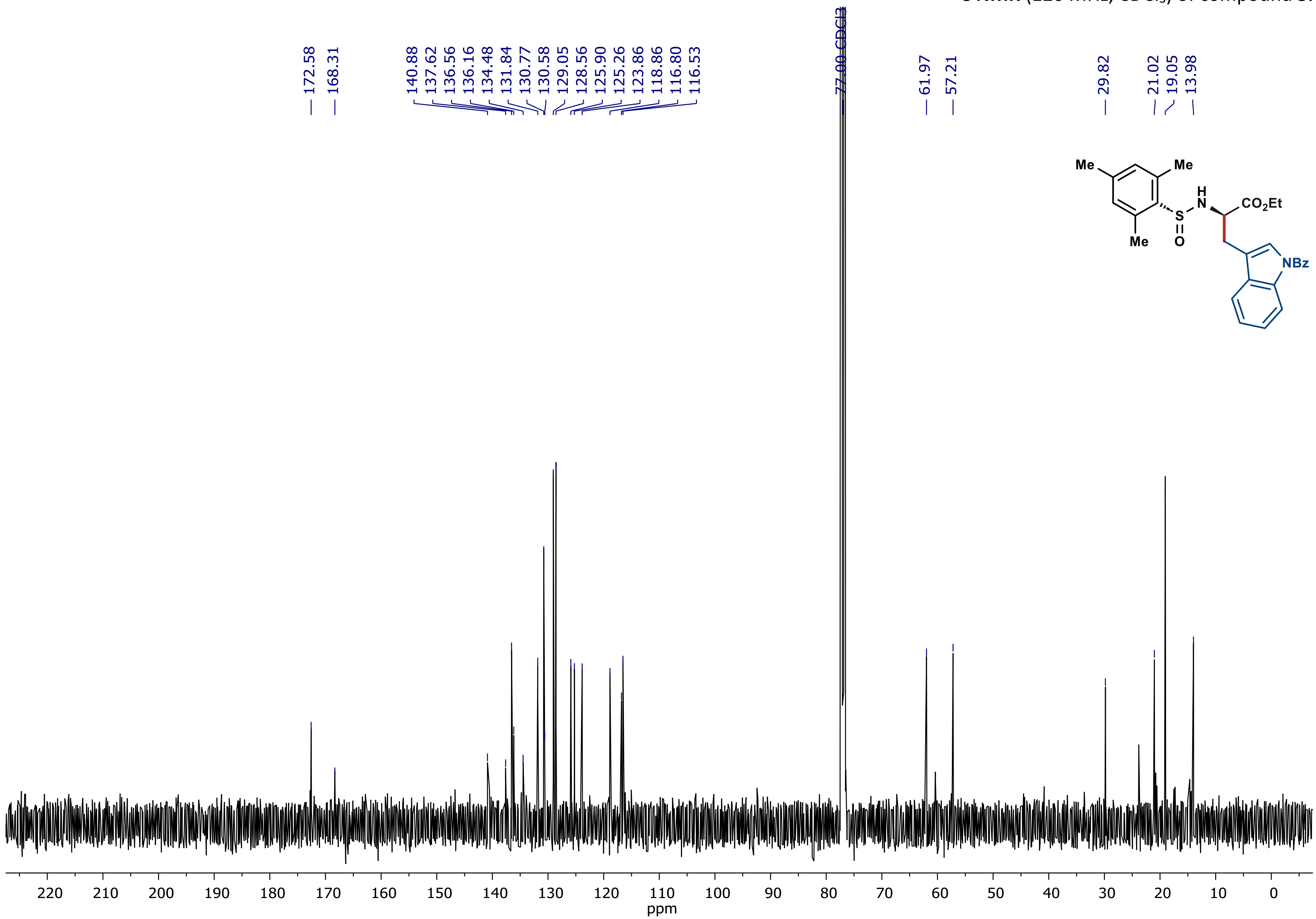
HMBC of compound **5k**, β-diastereomer **5k-2**



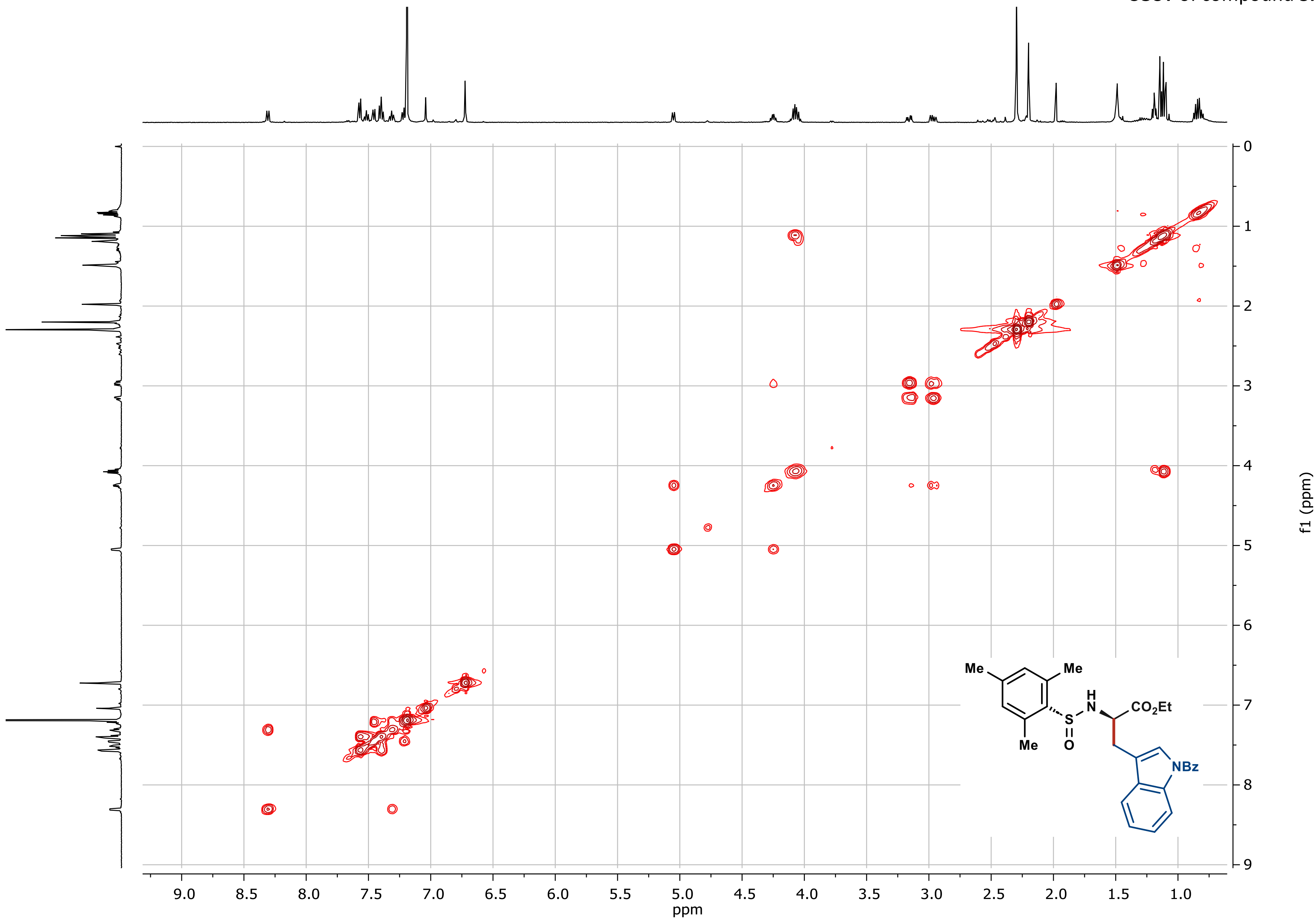
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5l**



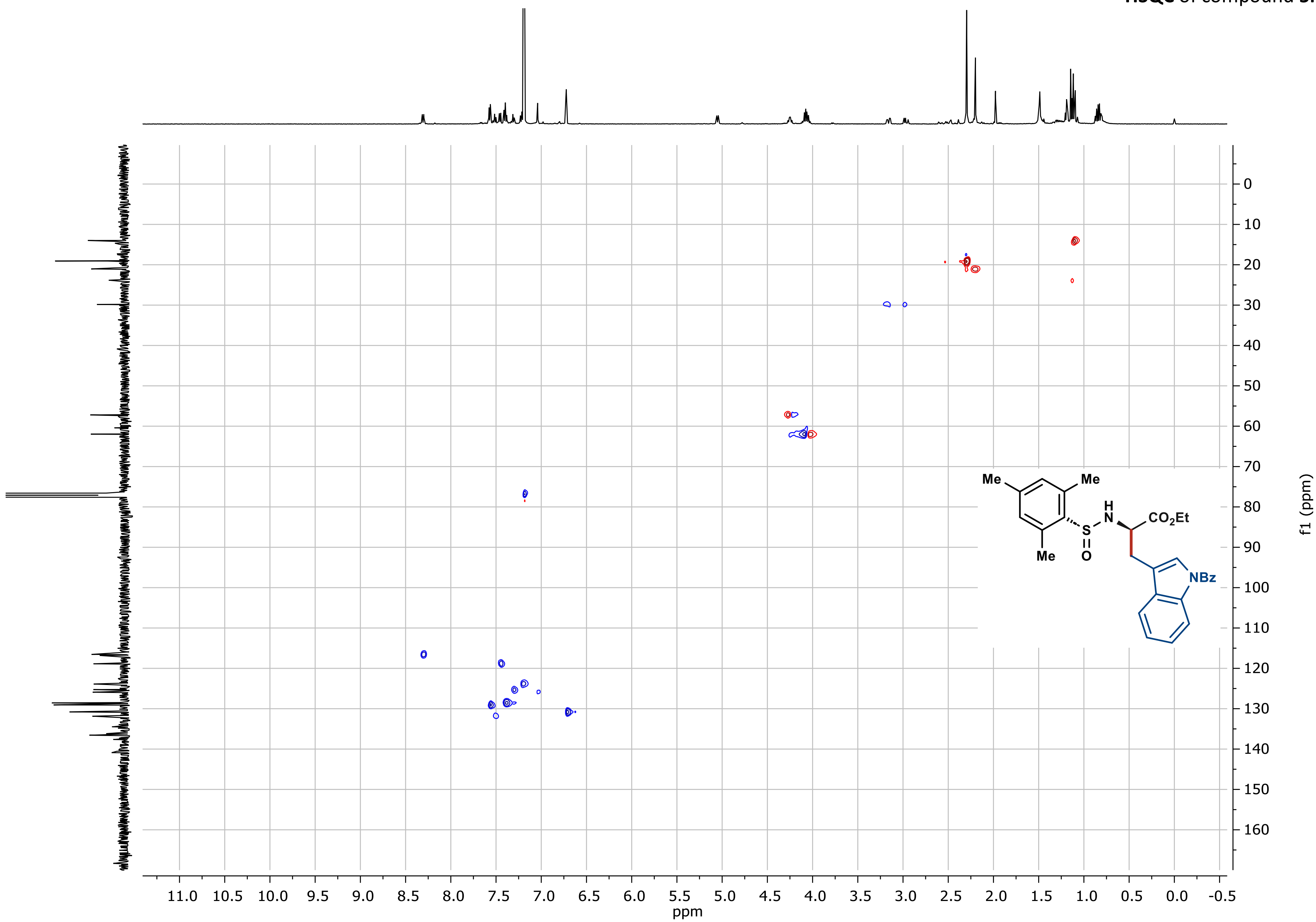
13C NMR (126 MHz, $CDCl_3$) of compound **5l**



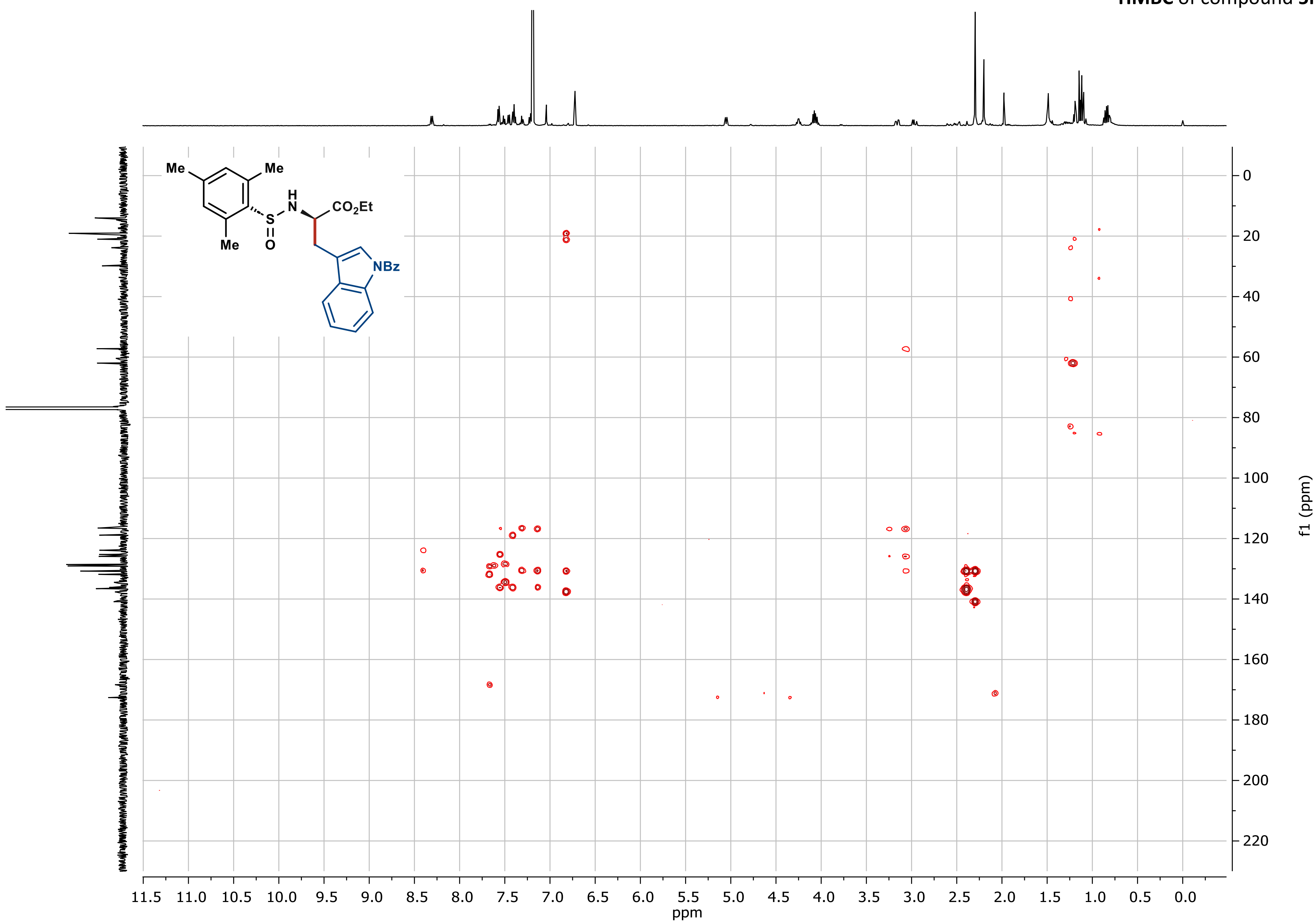
COSY of compound **5l**



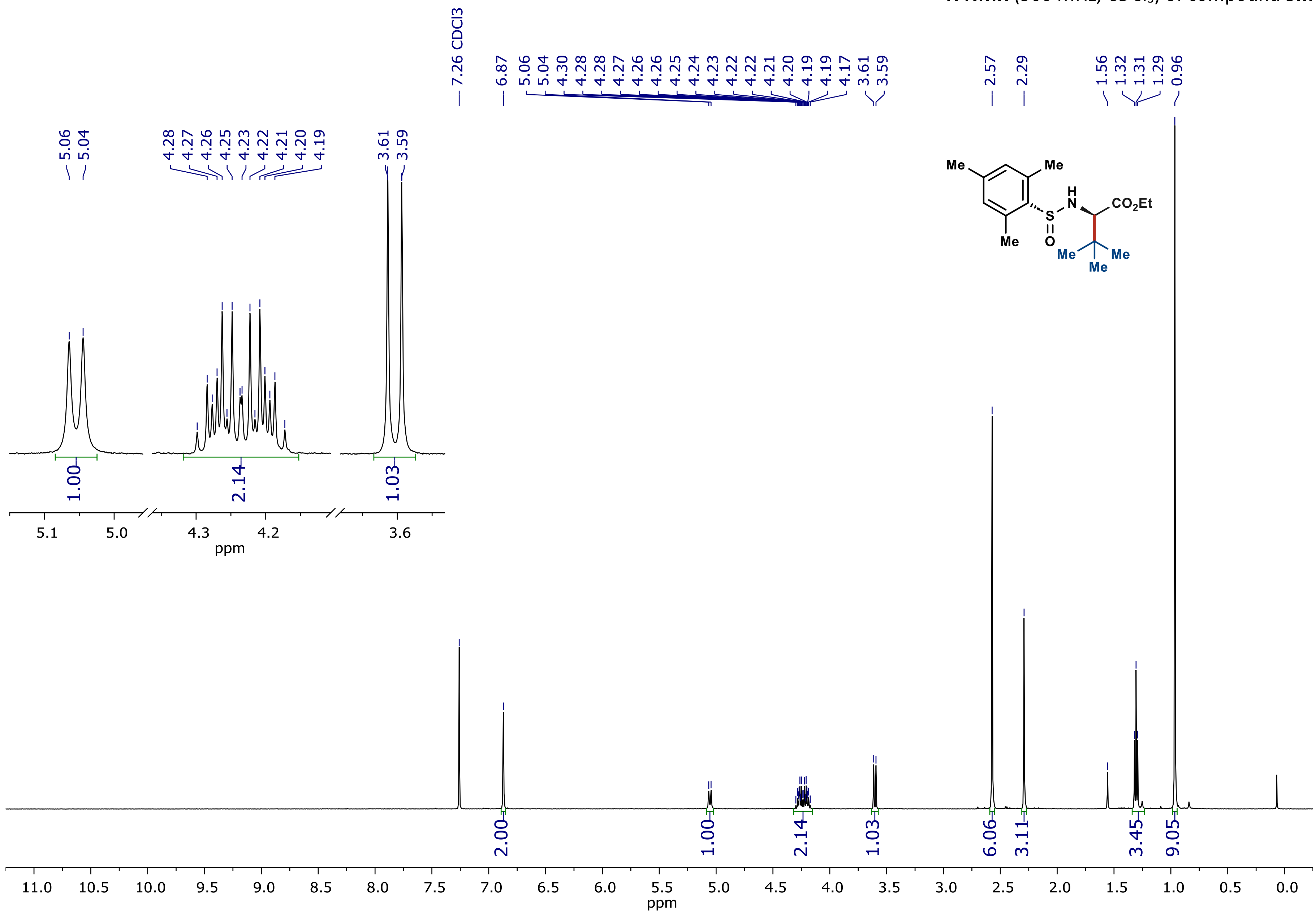
HSQC of compound **5l**



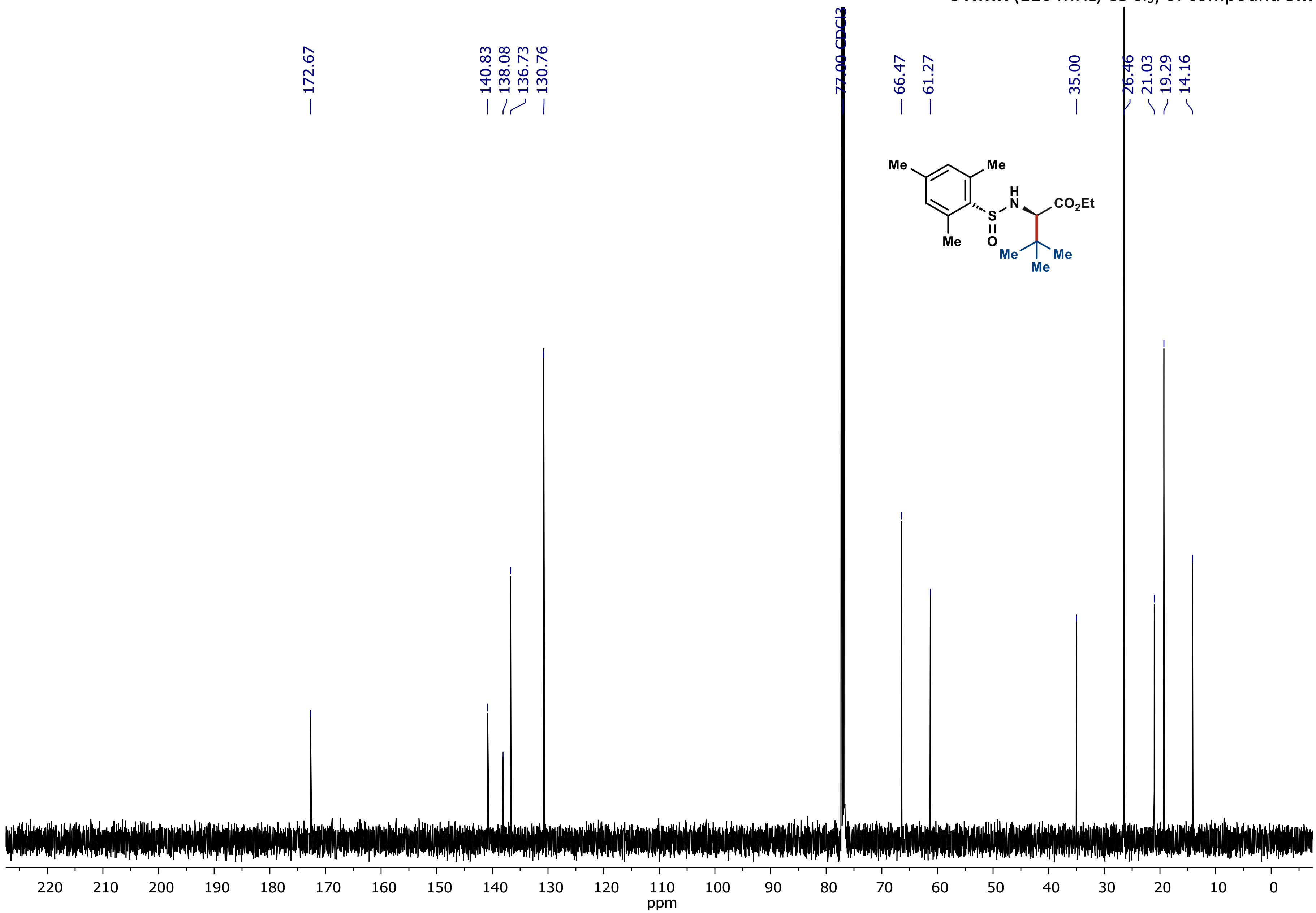
HMBC of compound **5l**



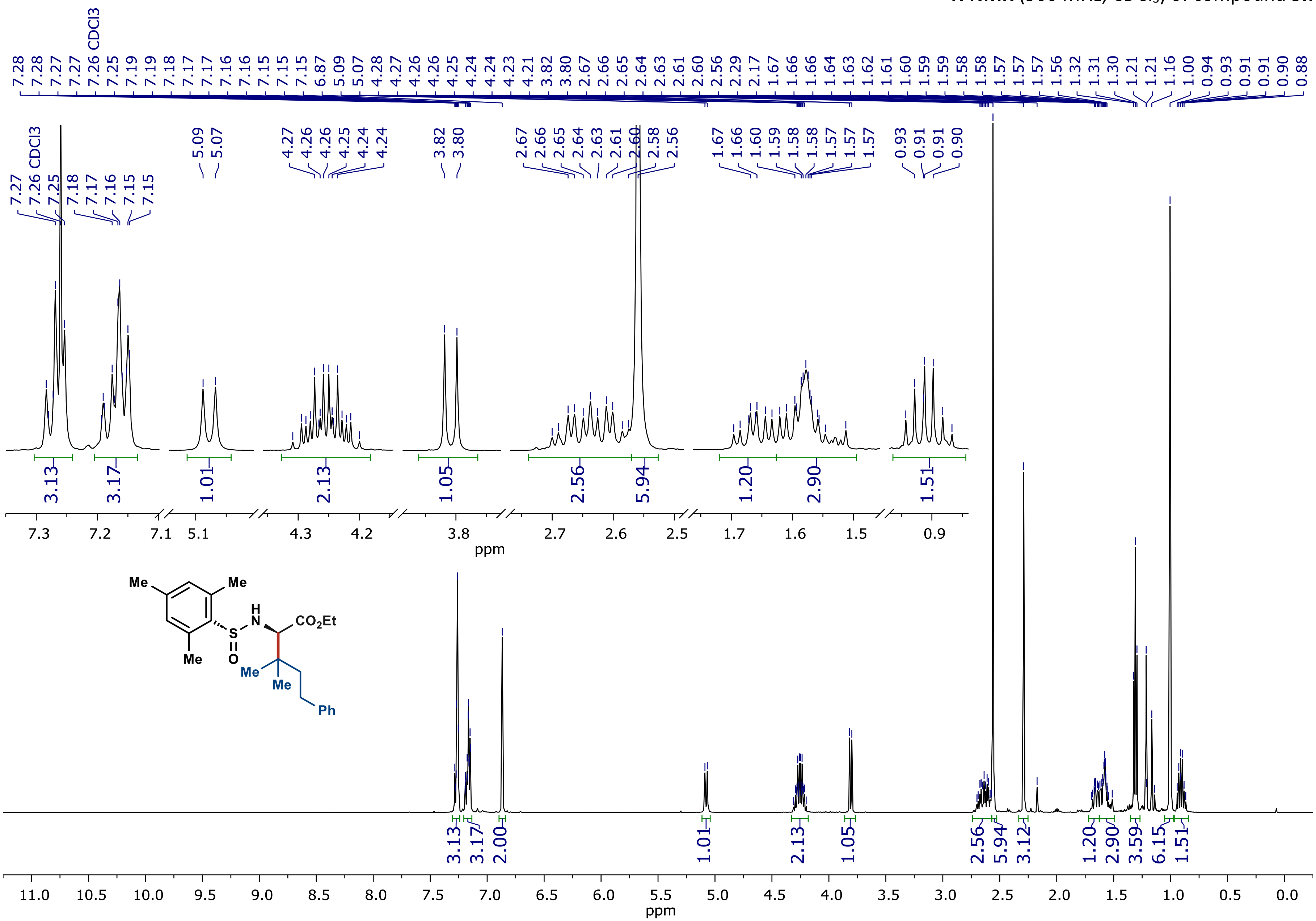
[1]H NMR (500 MHz, $CDCl_3$) of compound **5m**



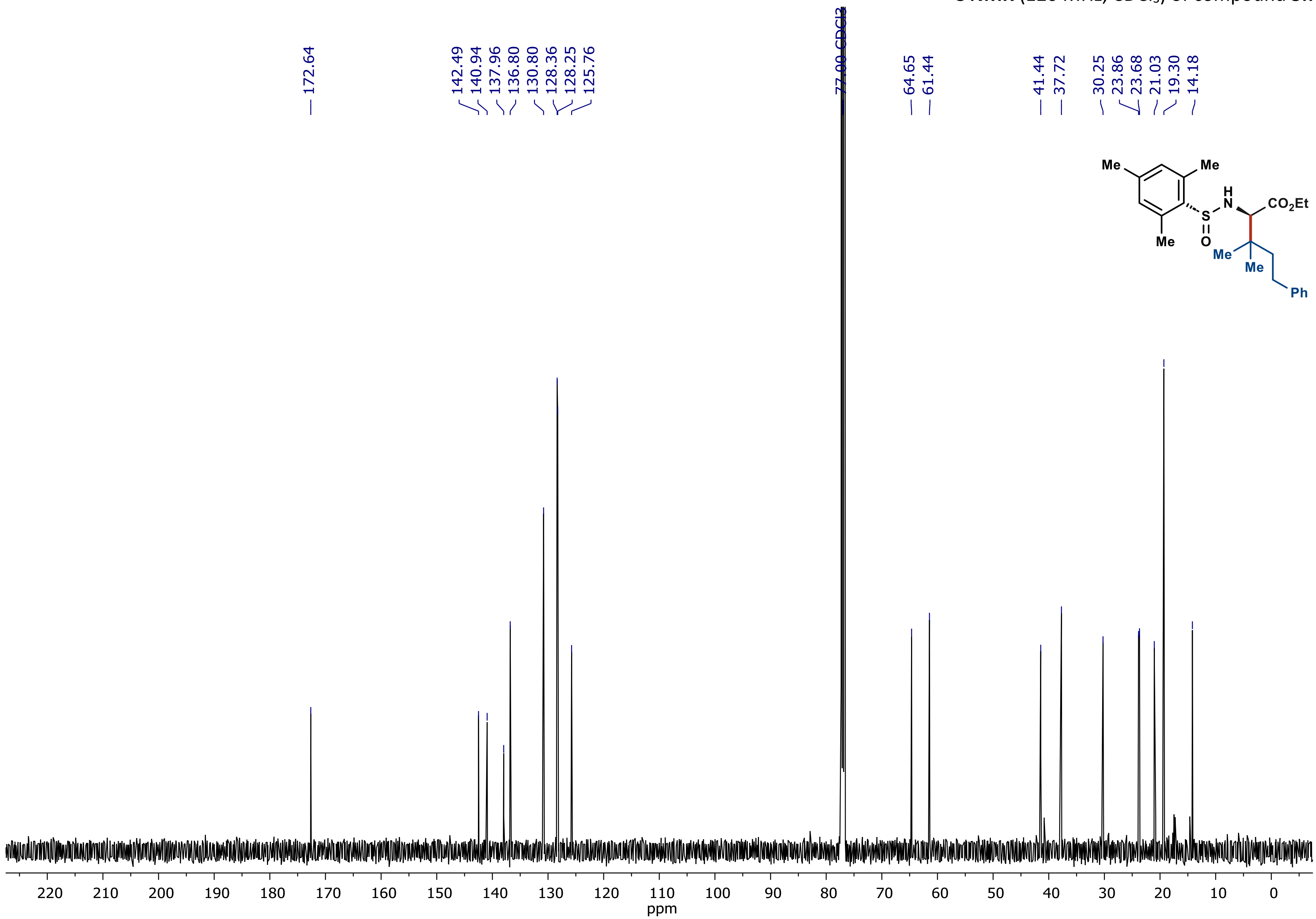
[13]C NMR (126 MHz, CDCl$_3$) of compound **5m**



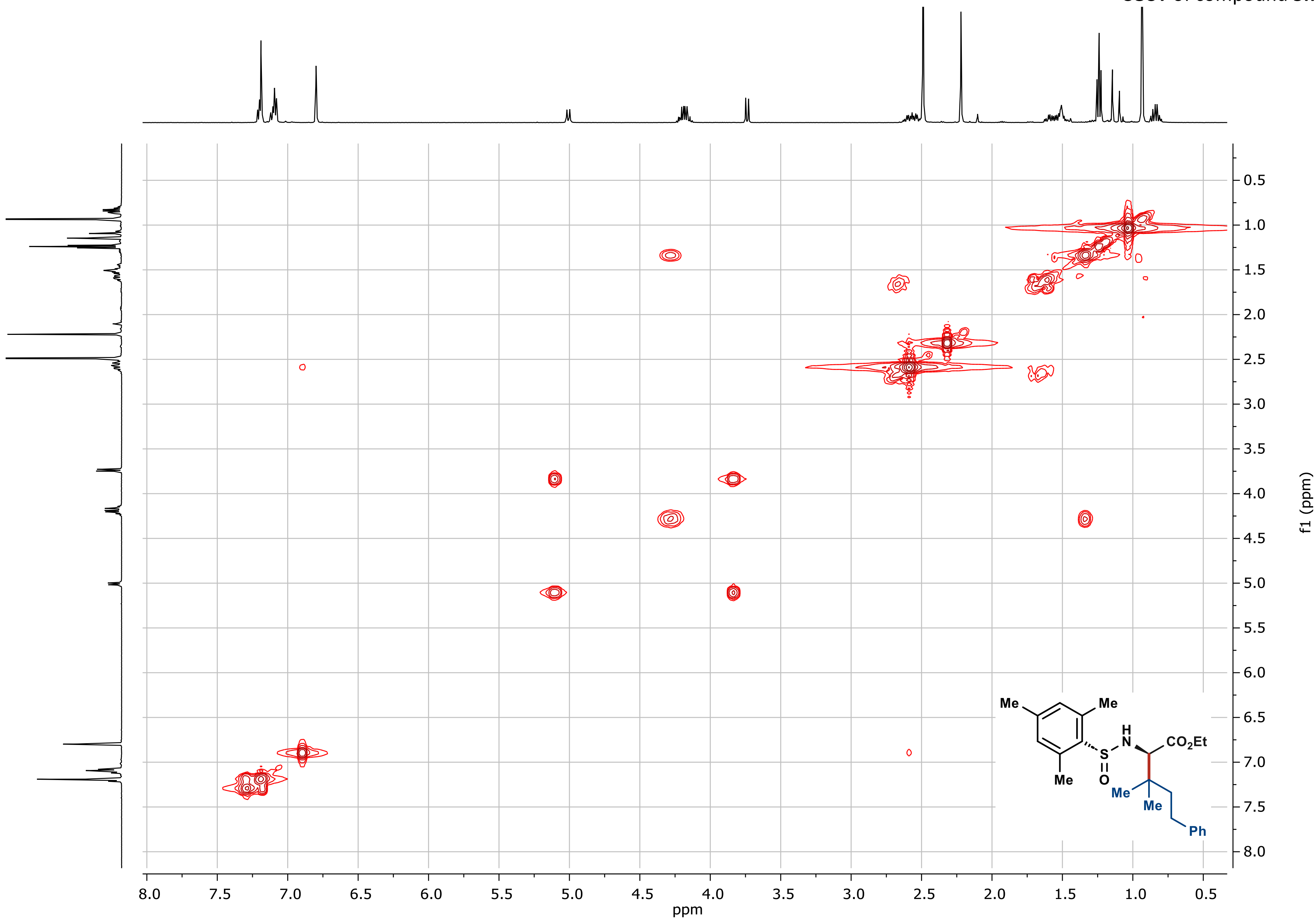
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5n**



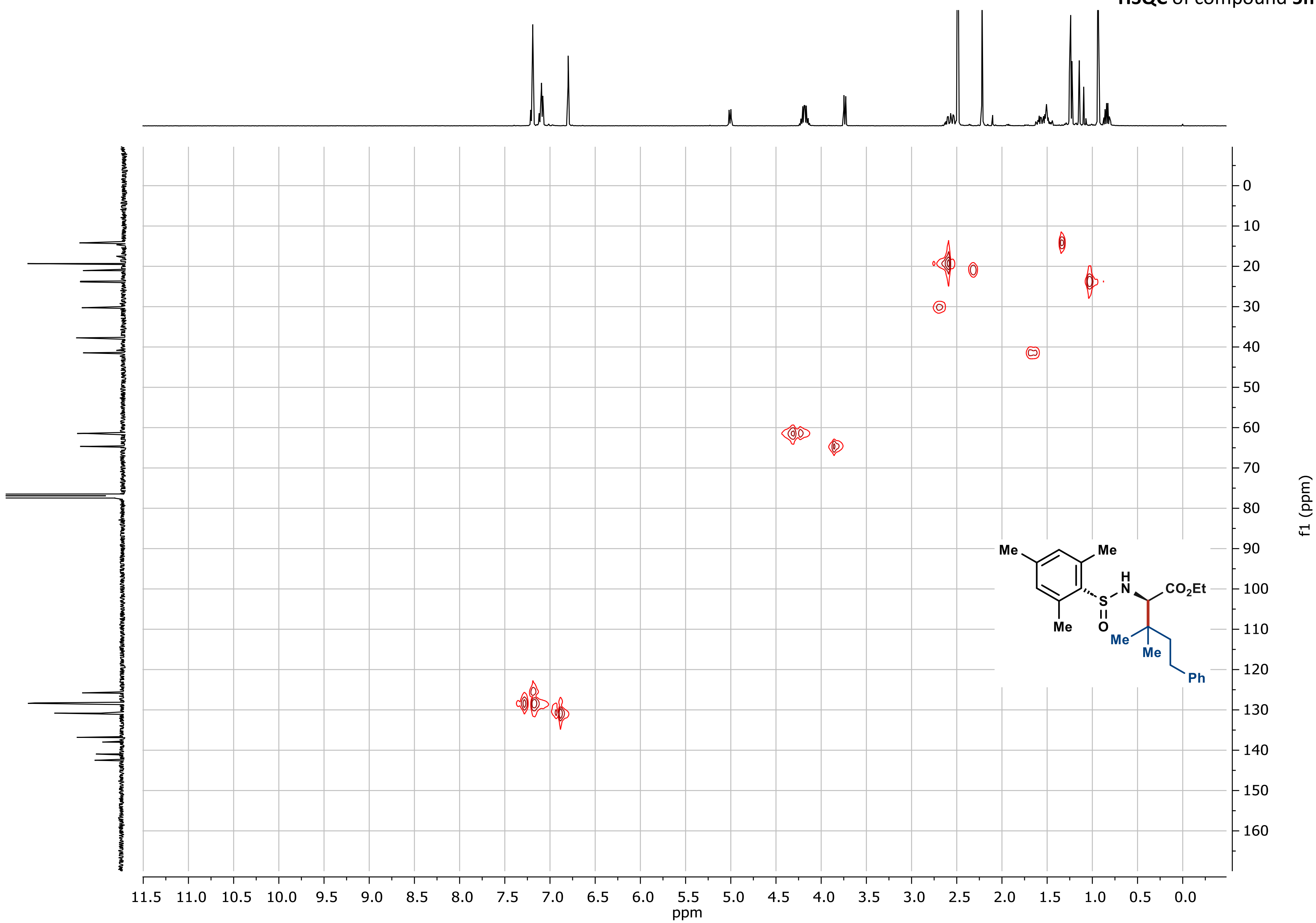
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5n**



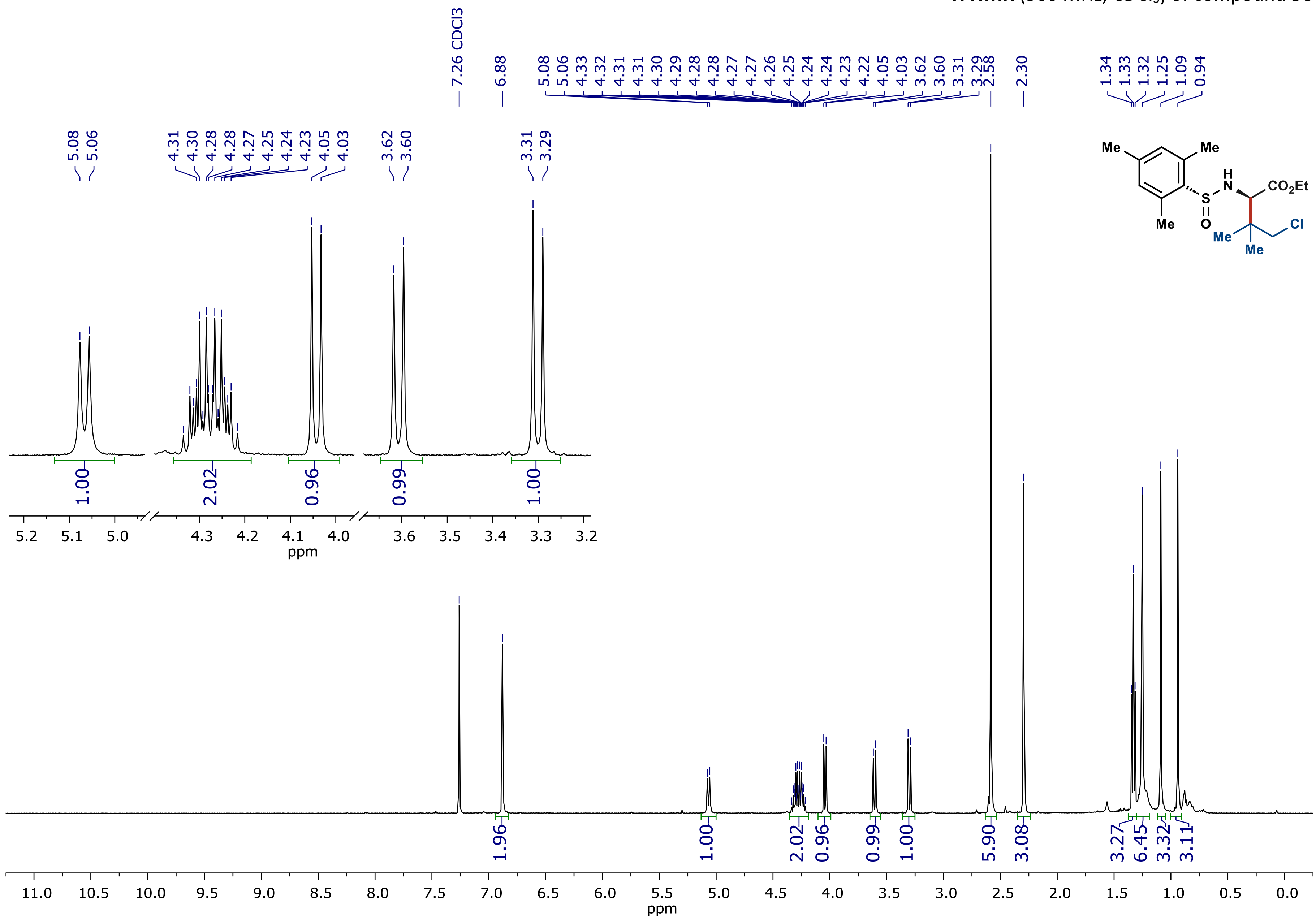
COSY of compound **5n**



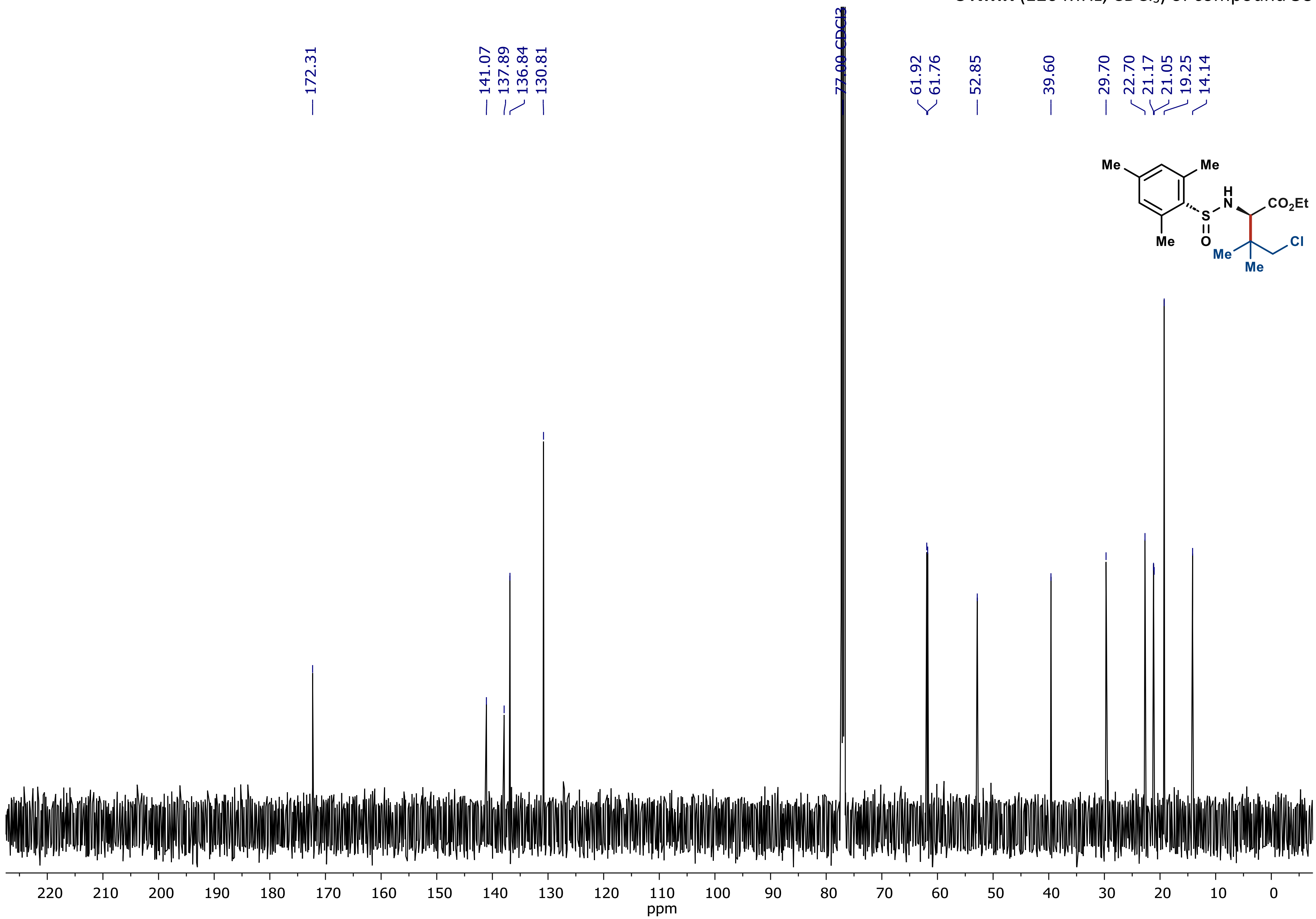
HSQC of compound **5n**



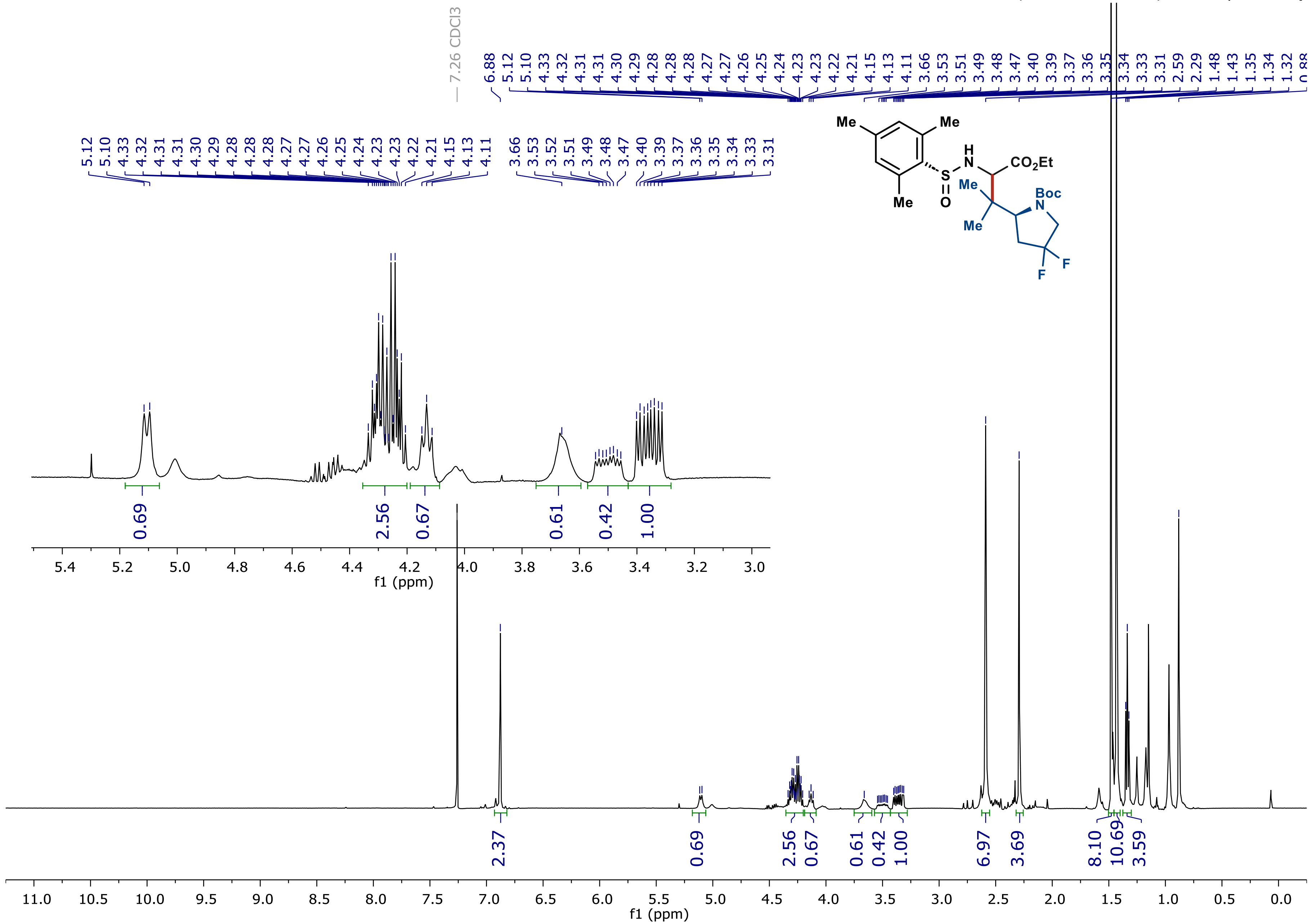
[1]H NMR (500 MHz, $CDCl_3$) of compound **5o**



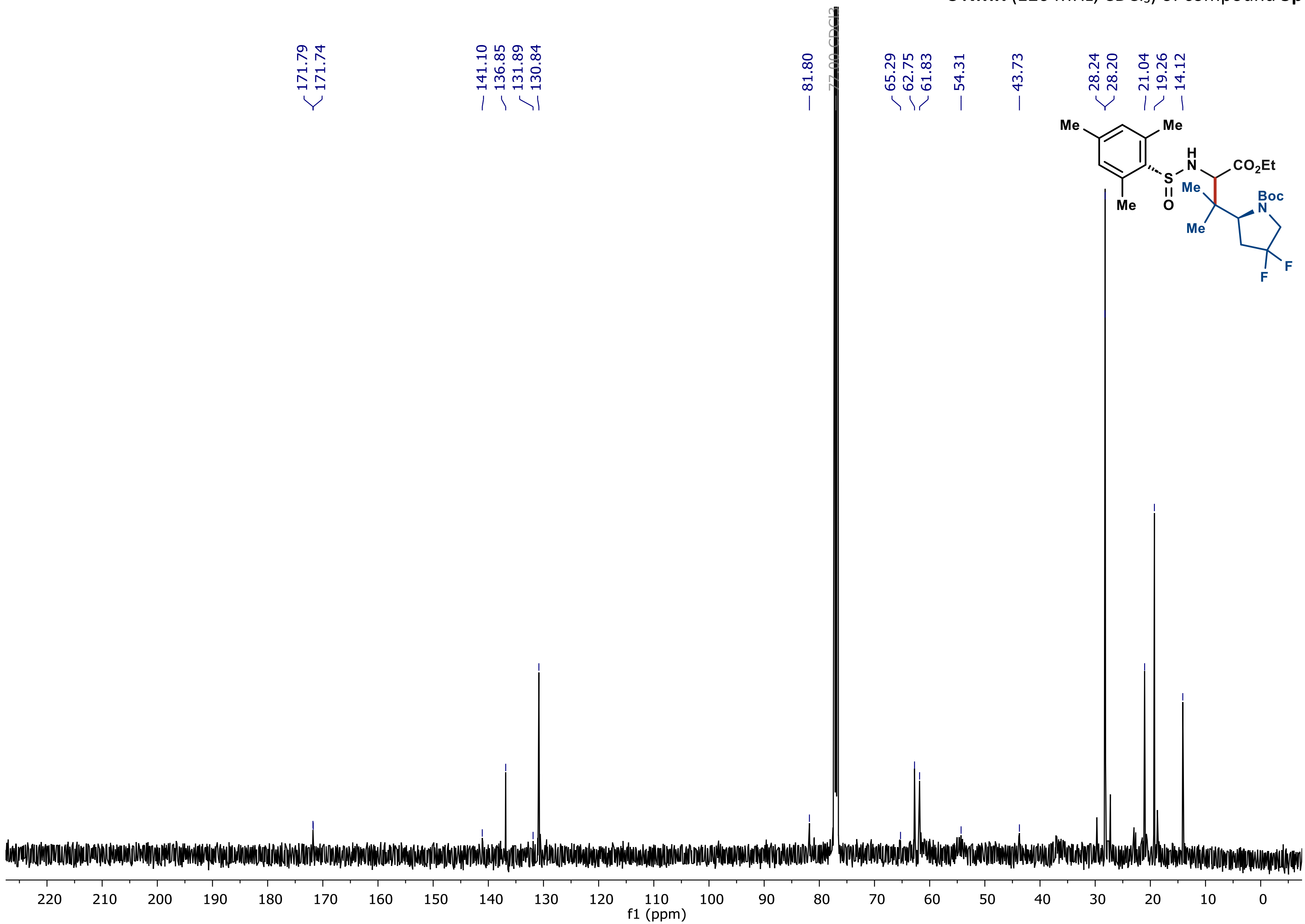
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5o**



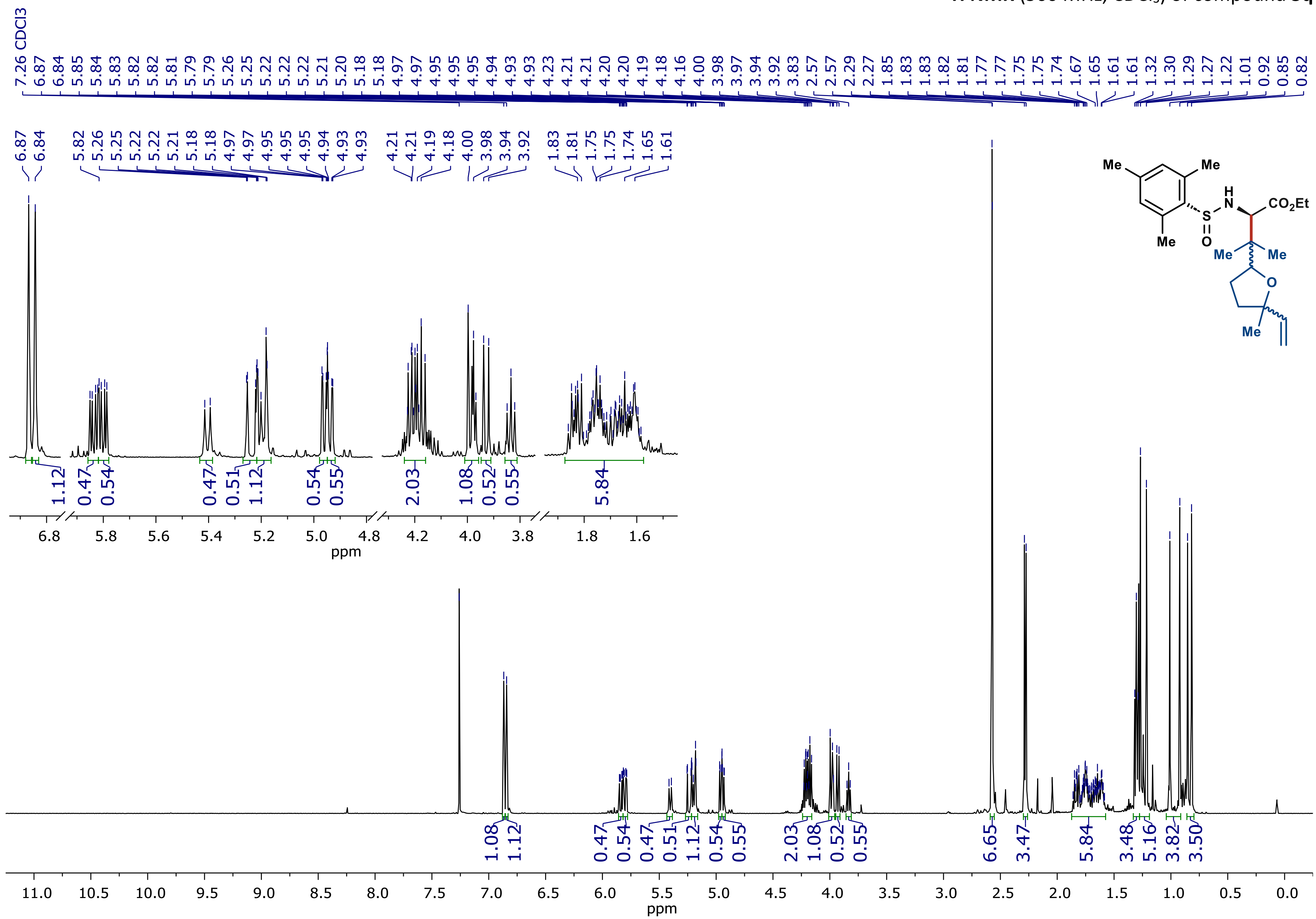
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5p**



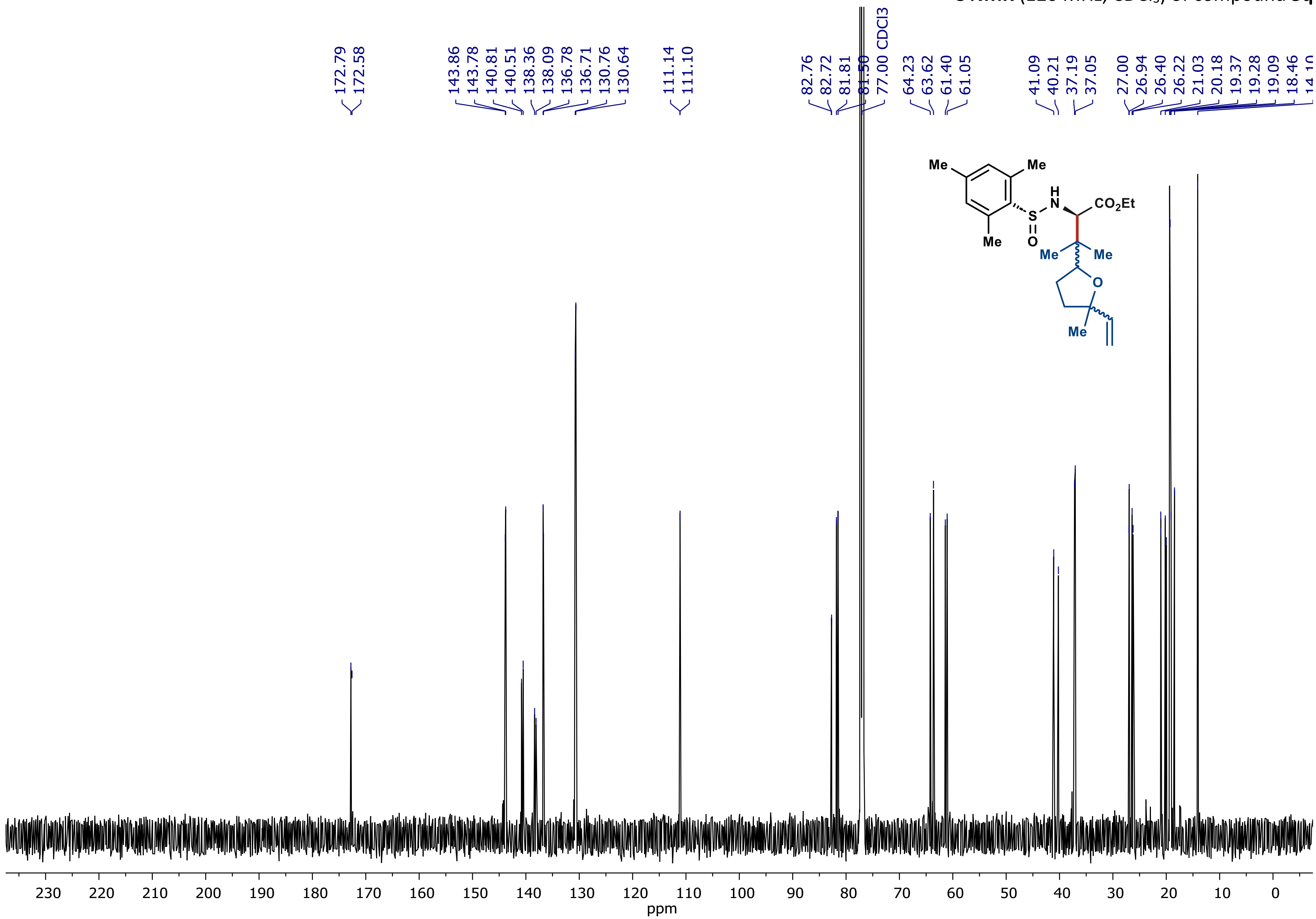
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5p**



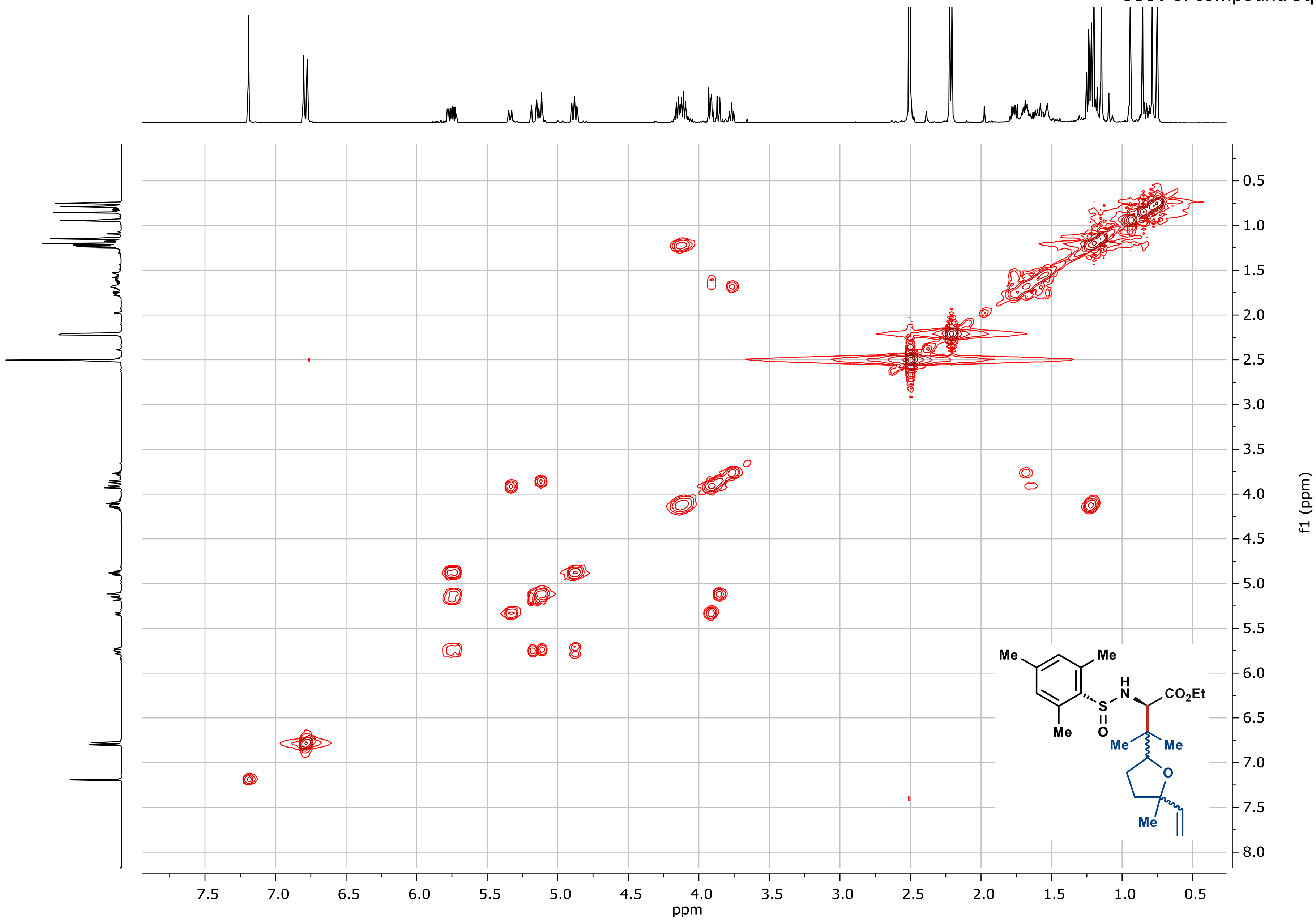
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5q**



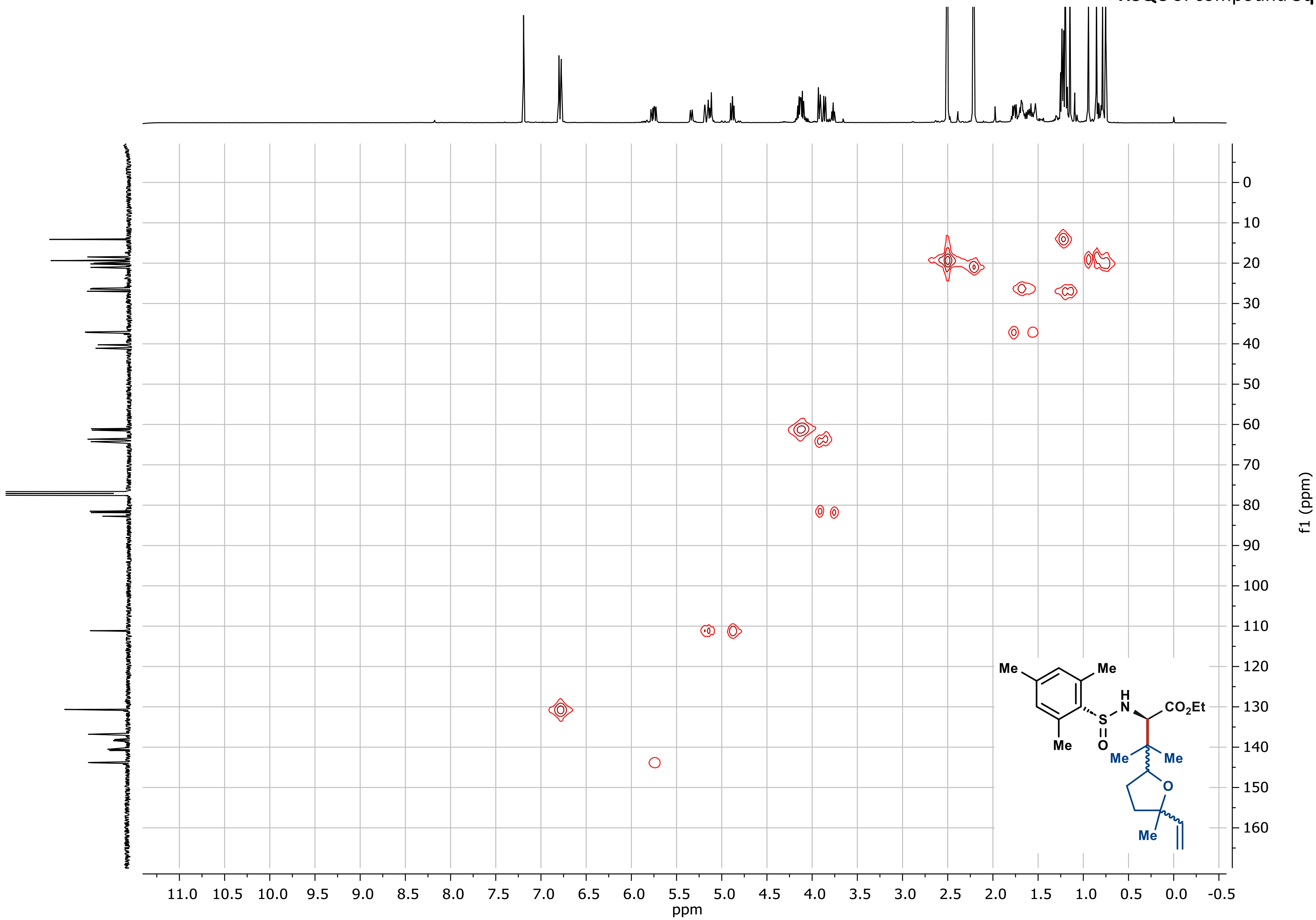
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5q**



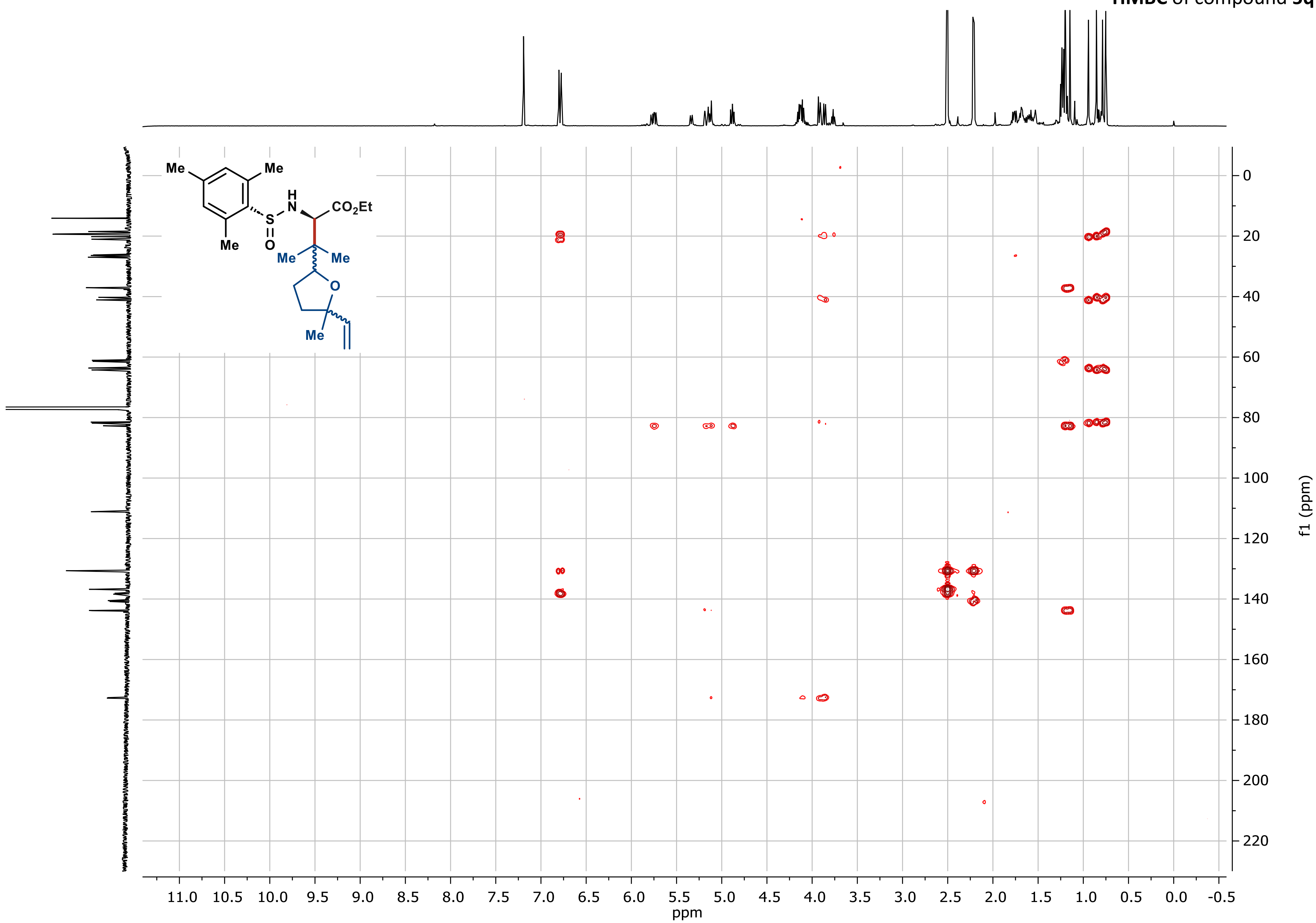
COSY of compound 5q



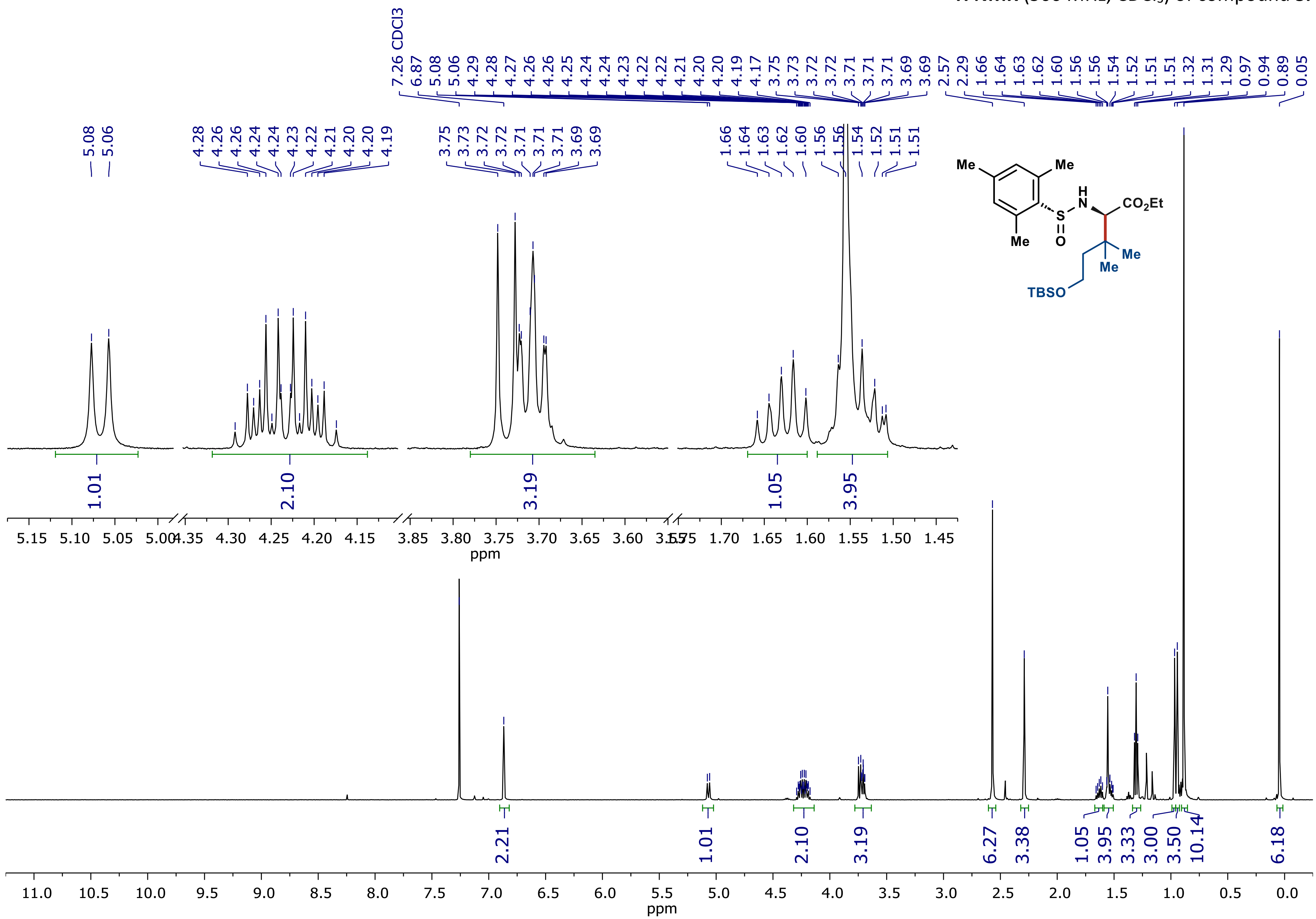
HSQC of compound **5q**



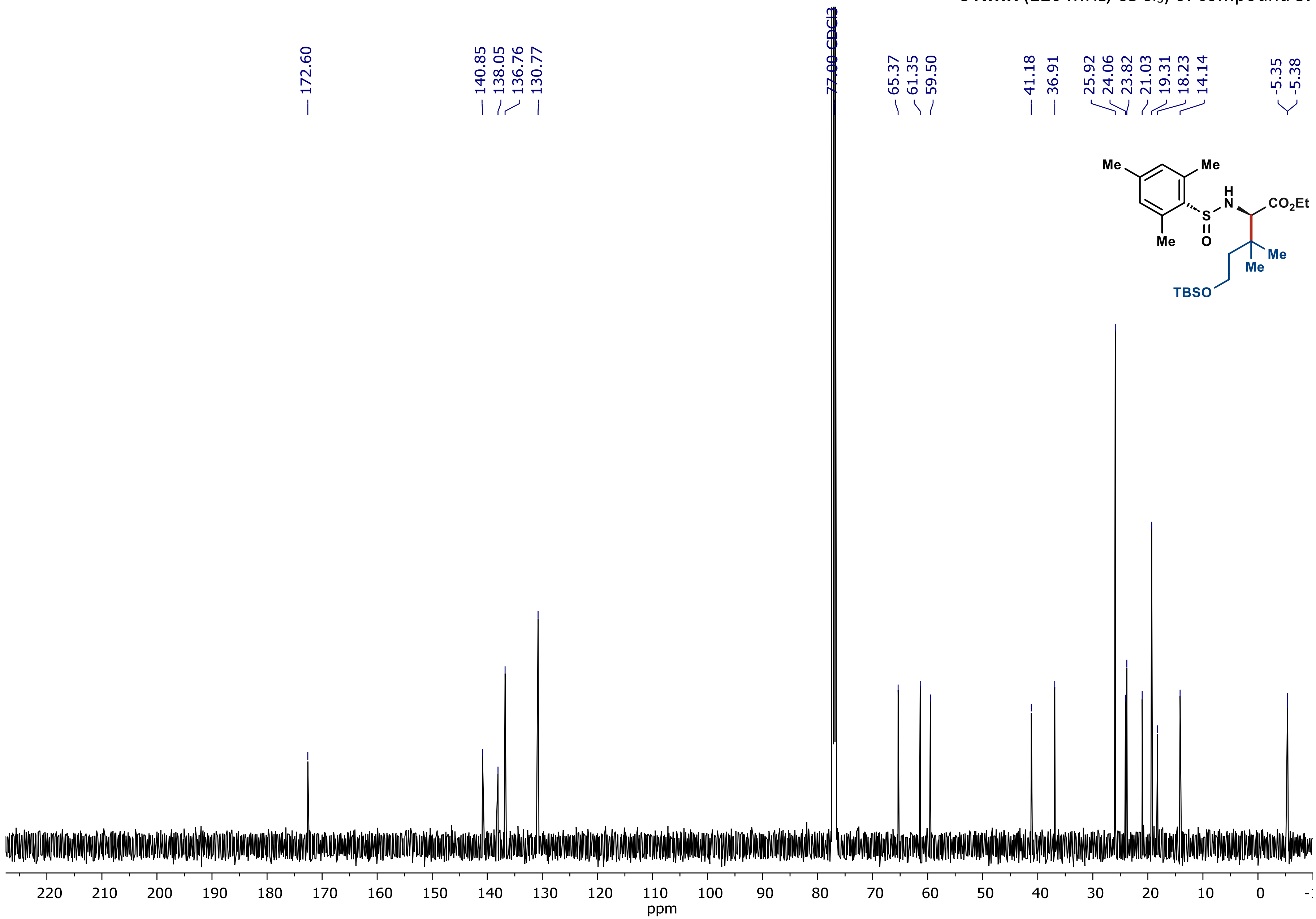
HMBC of compound **5q**



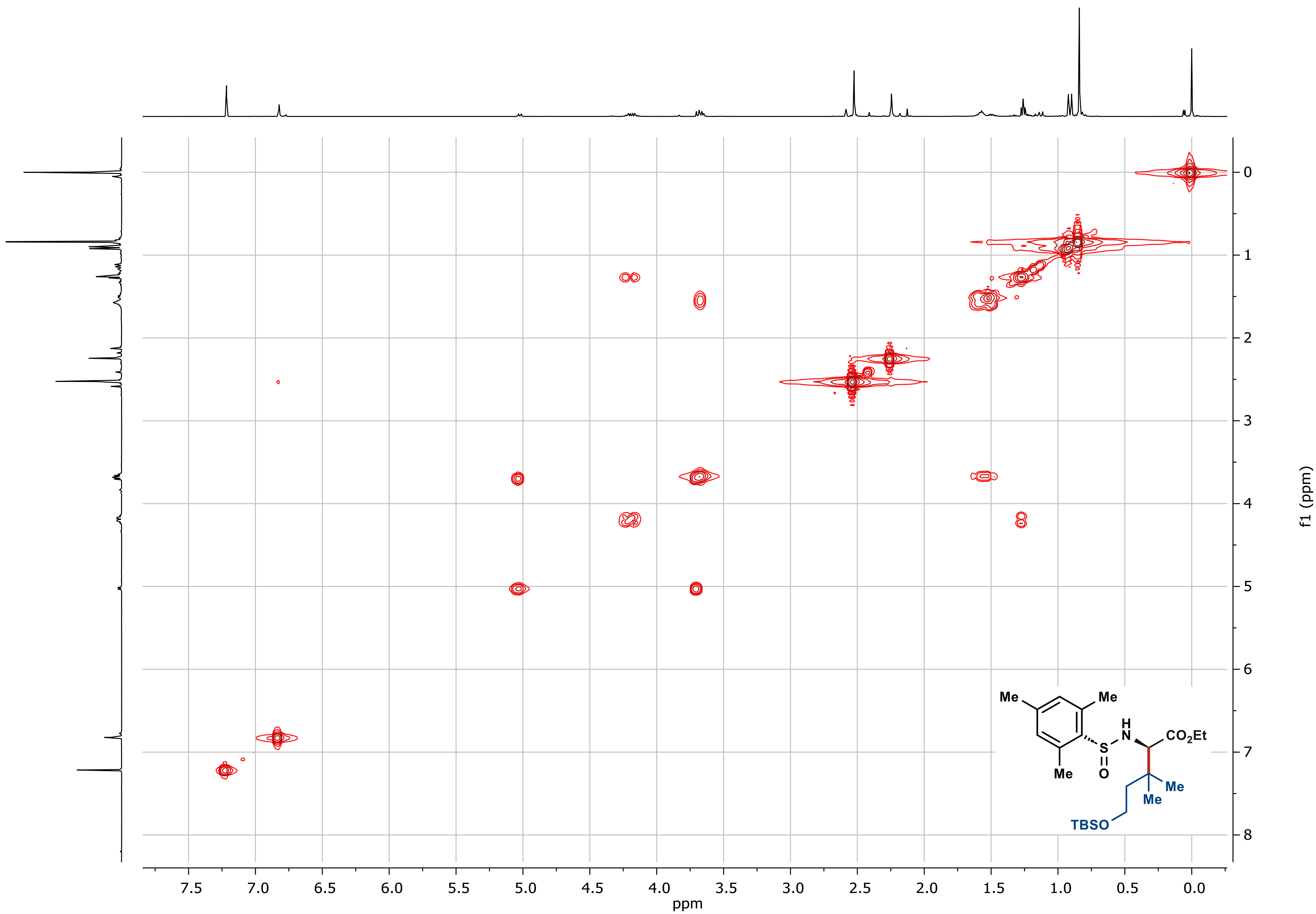
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5r**



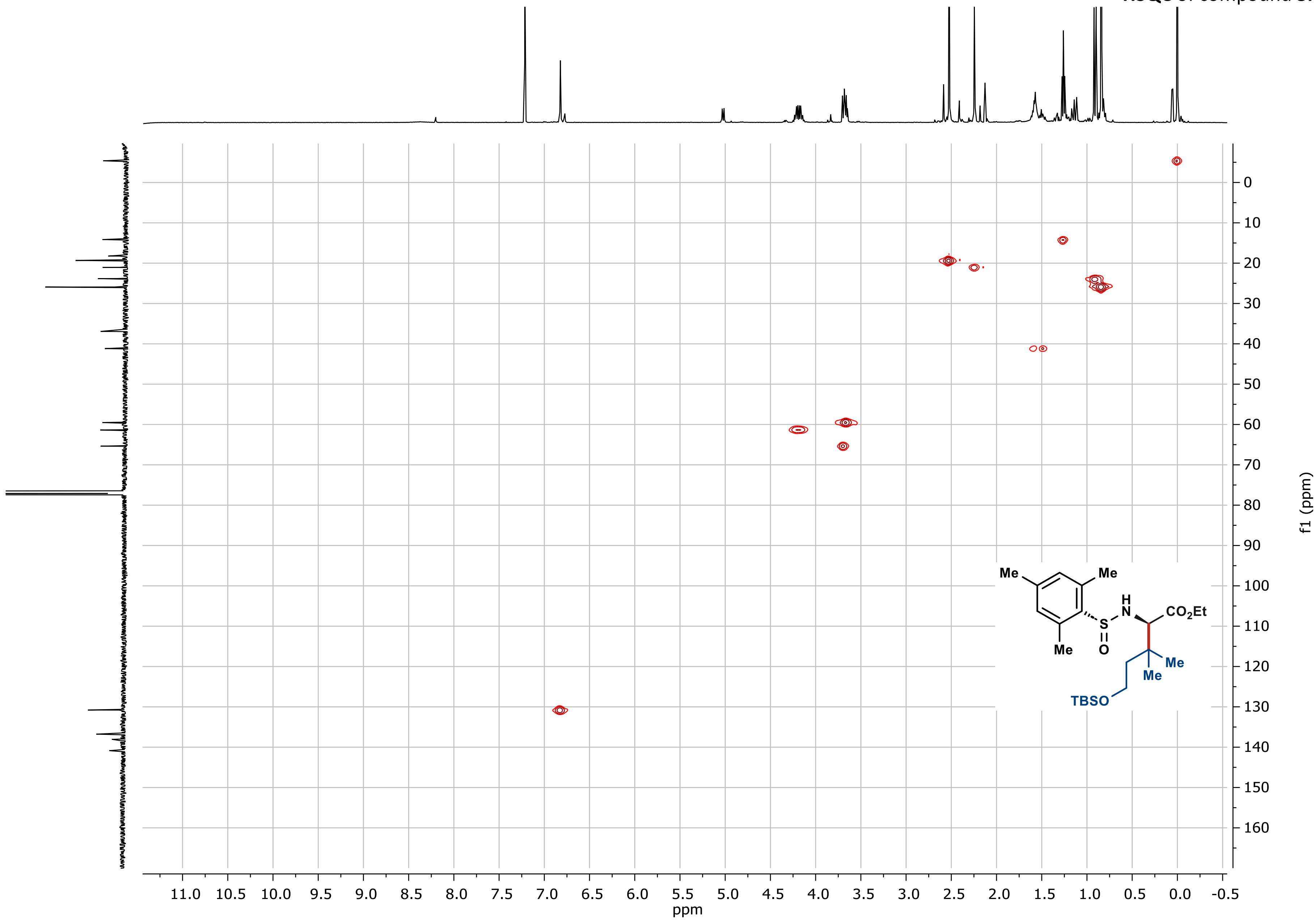
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5r**



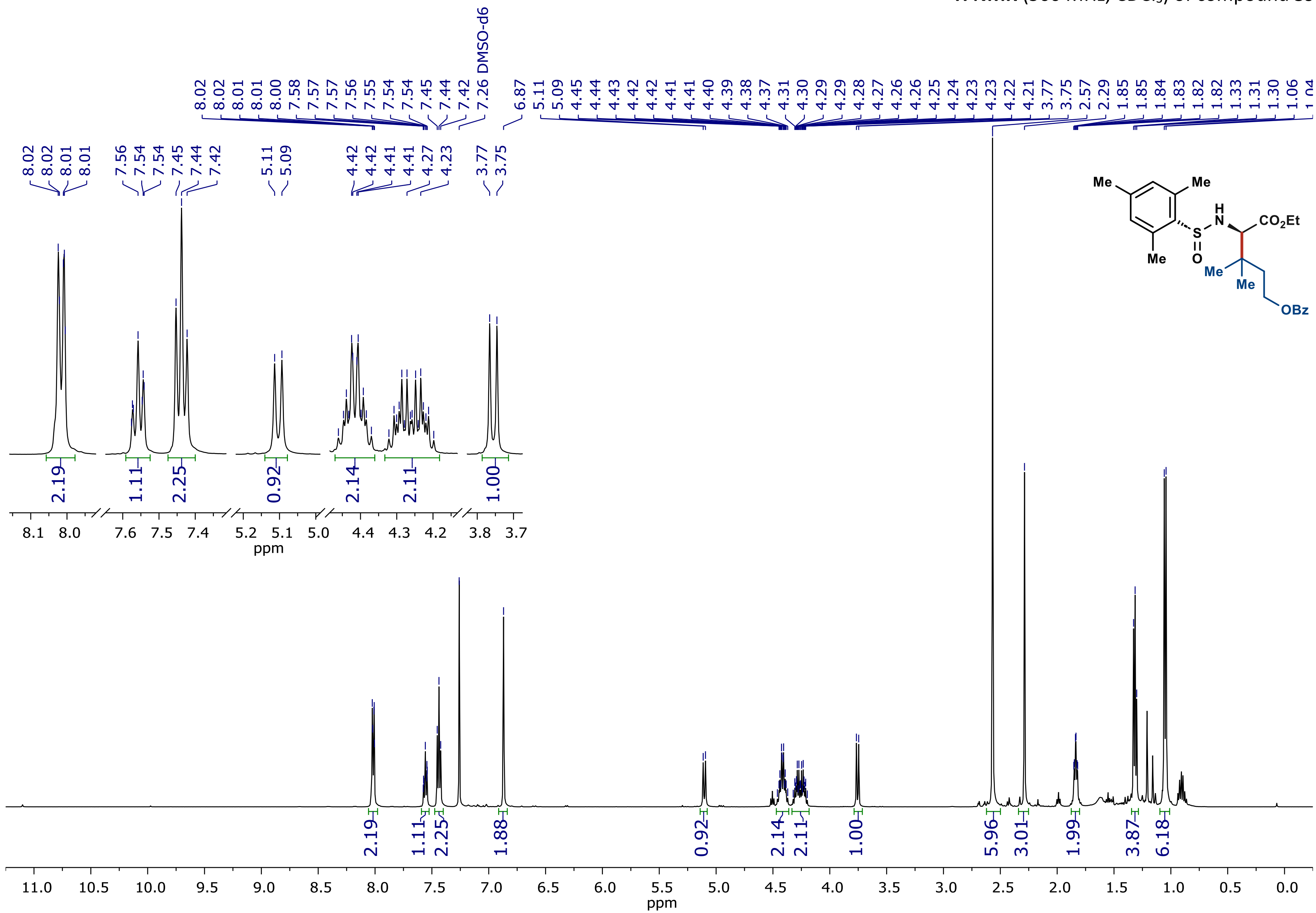
COSY of compound **5r**



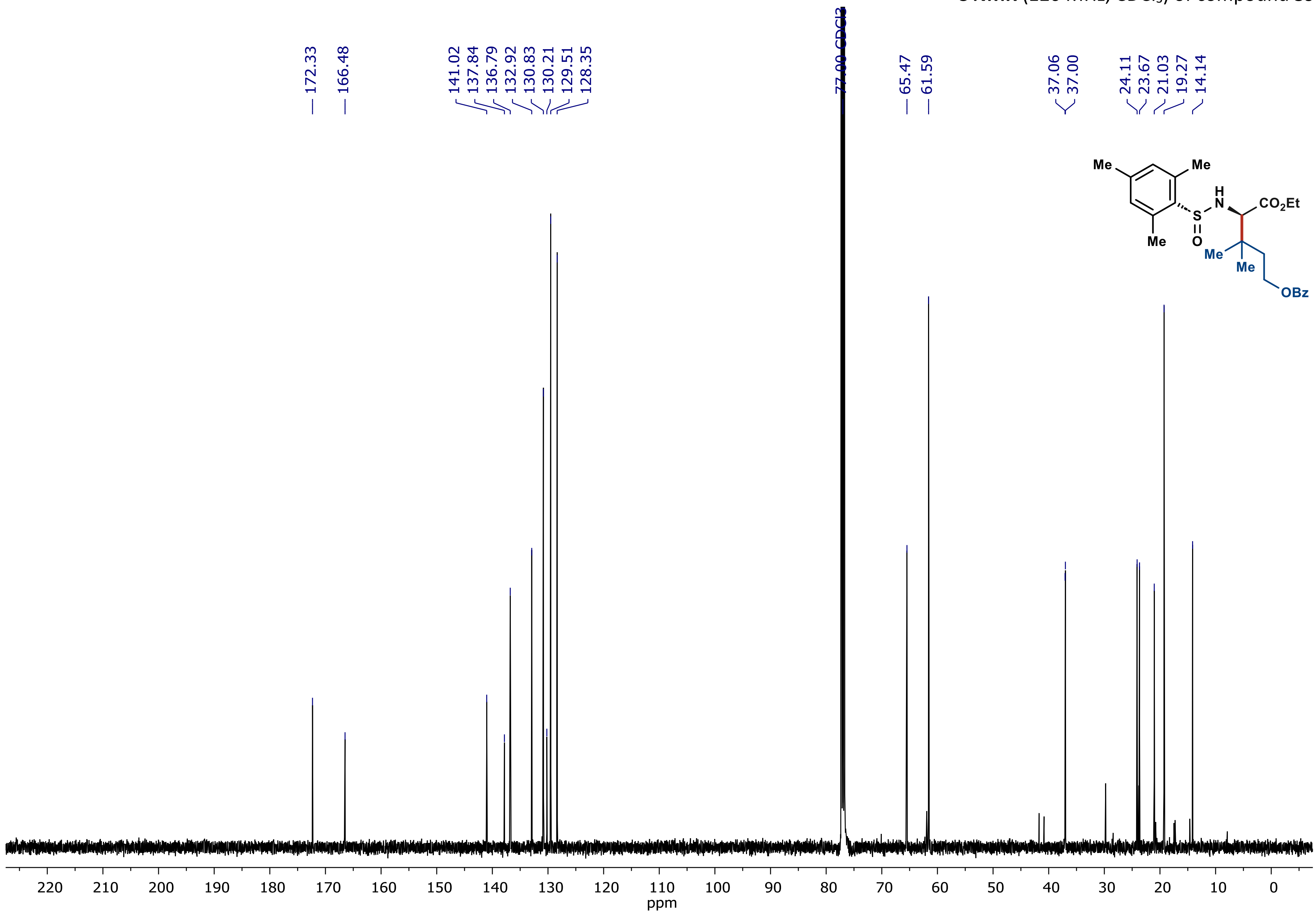
HSQC of compound **5r**



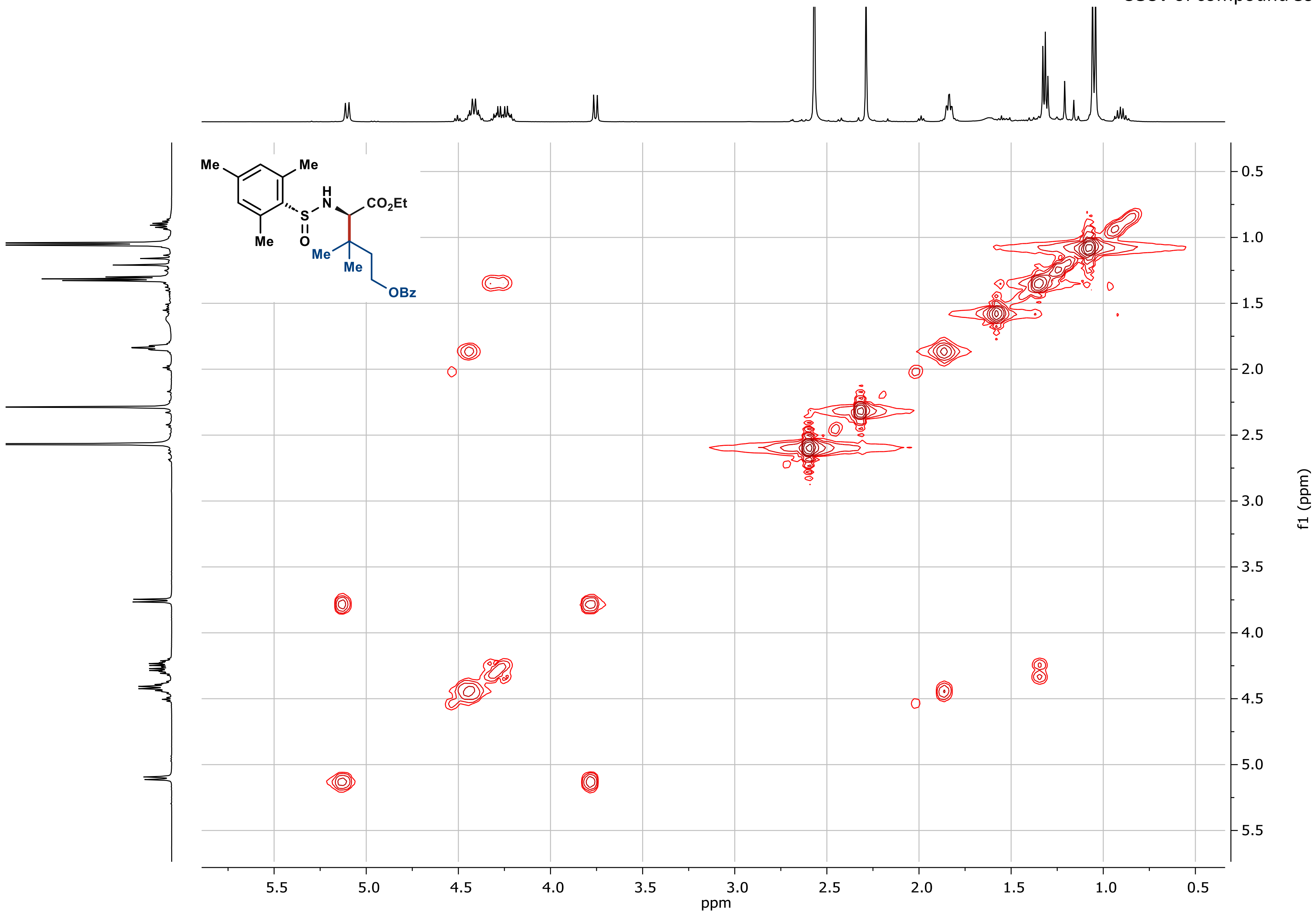
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5s**



^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5s**

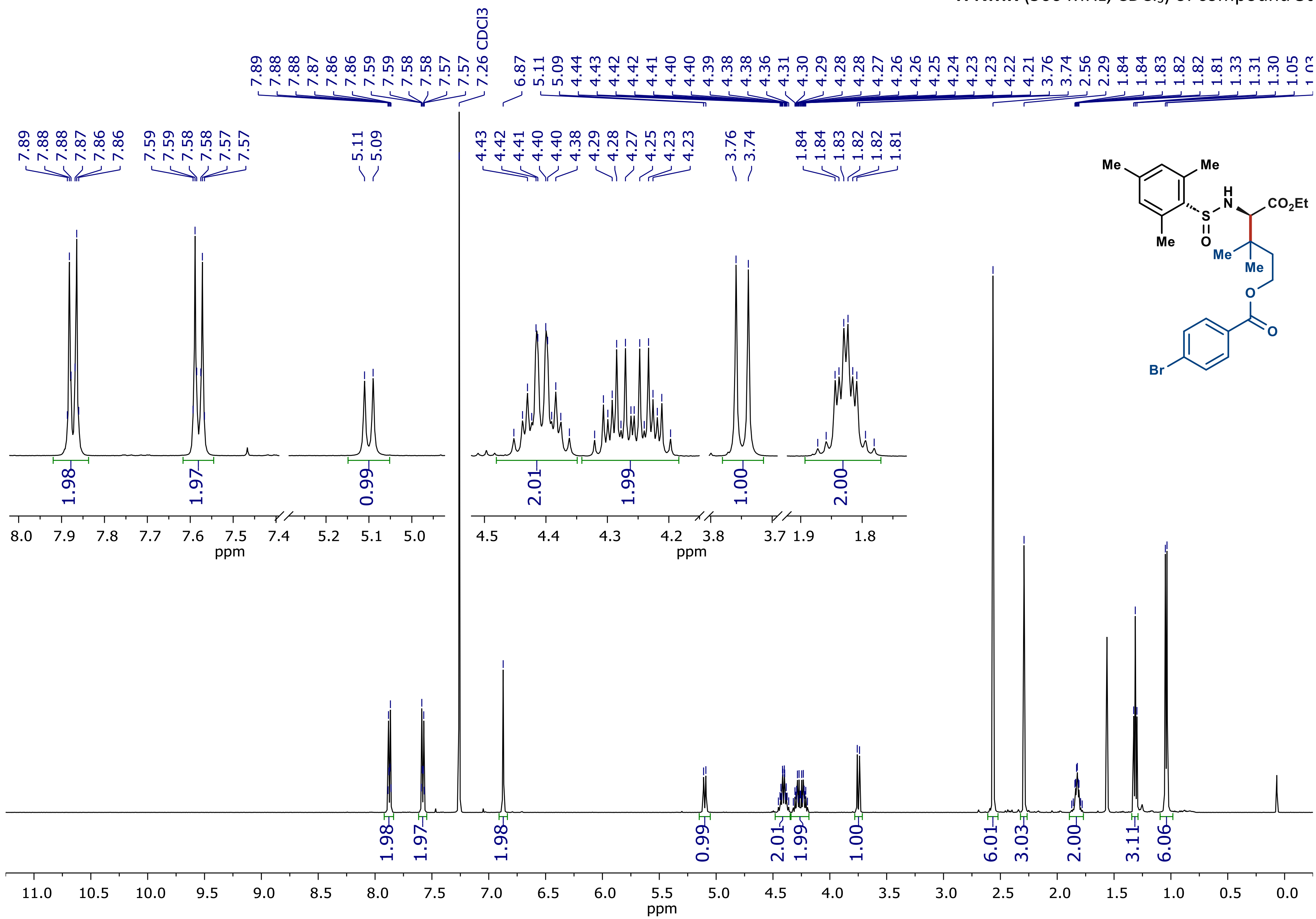


COSY of compound **5s**

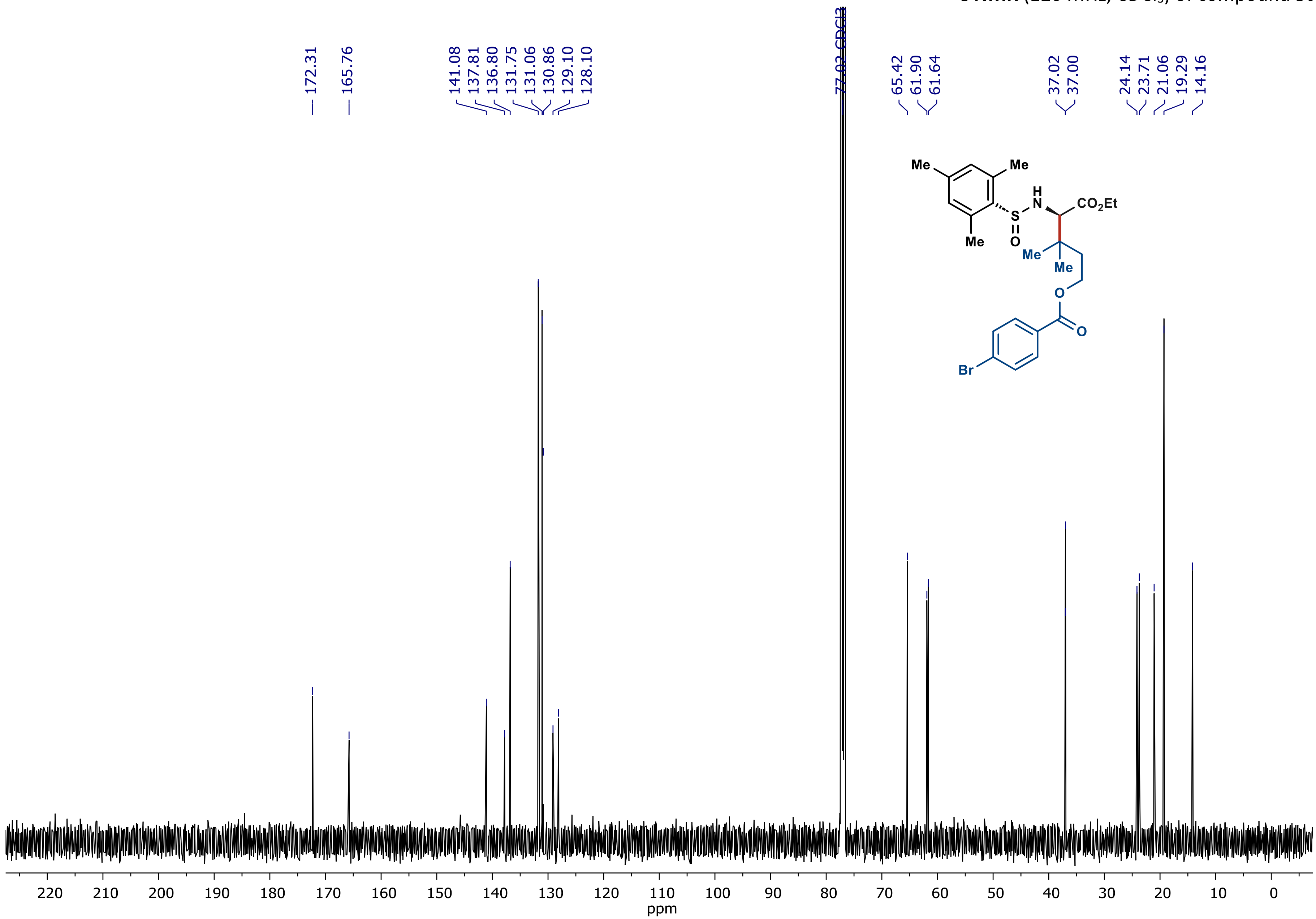


HSQC of compound **5s**

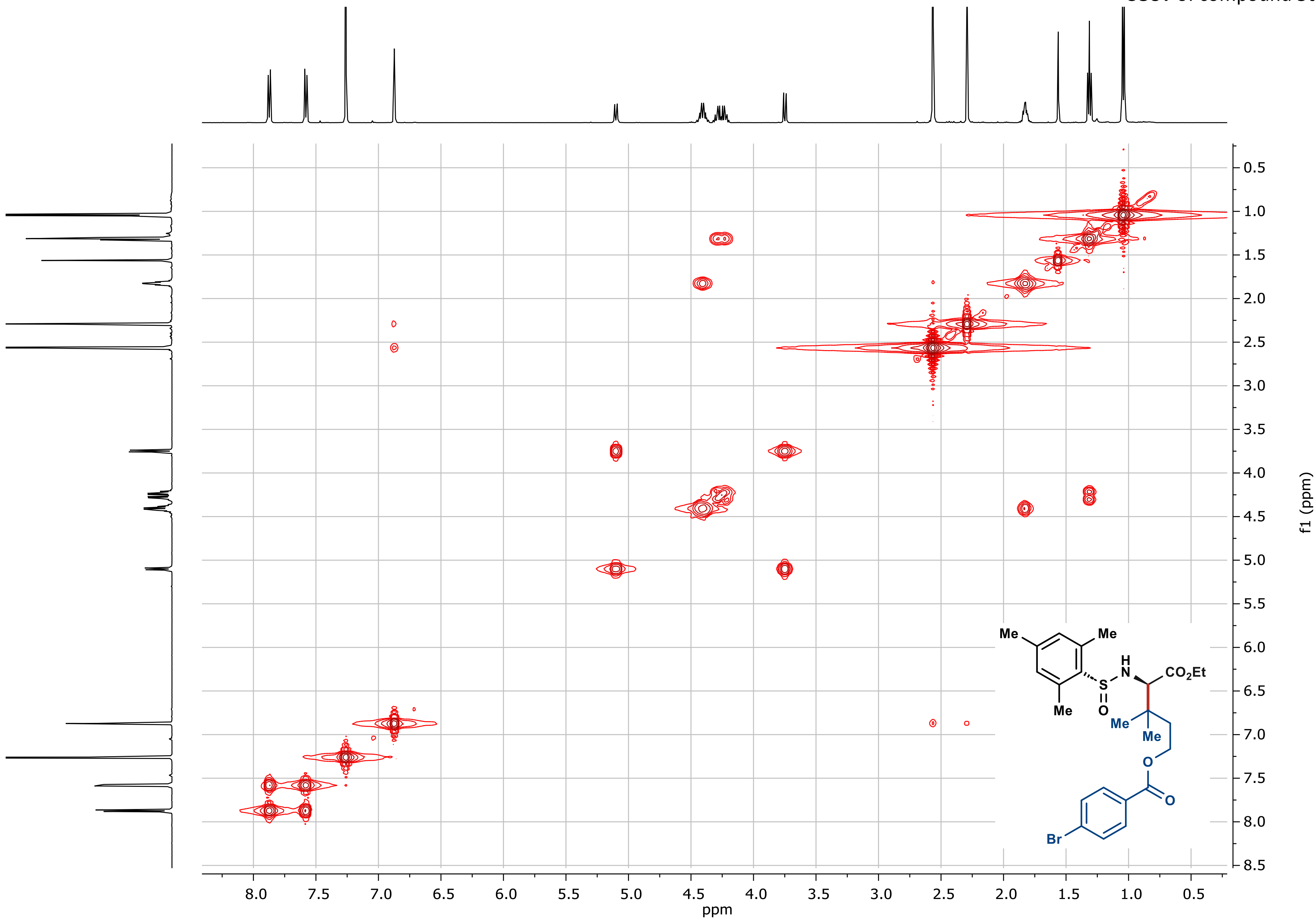
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5t**



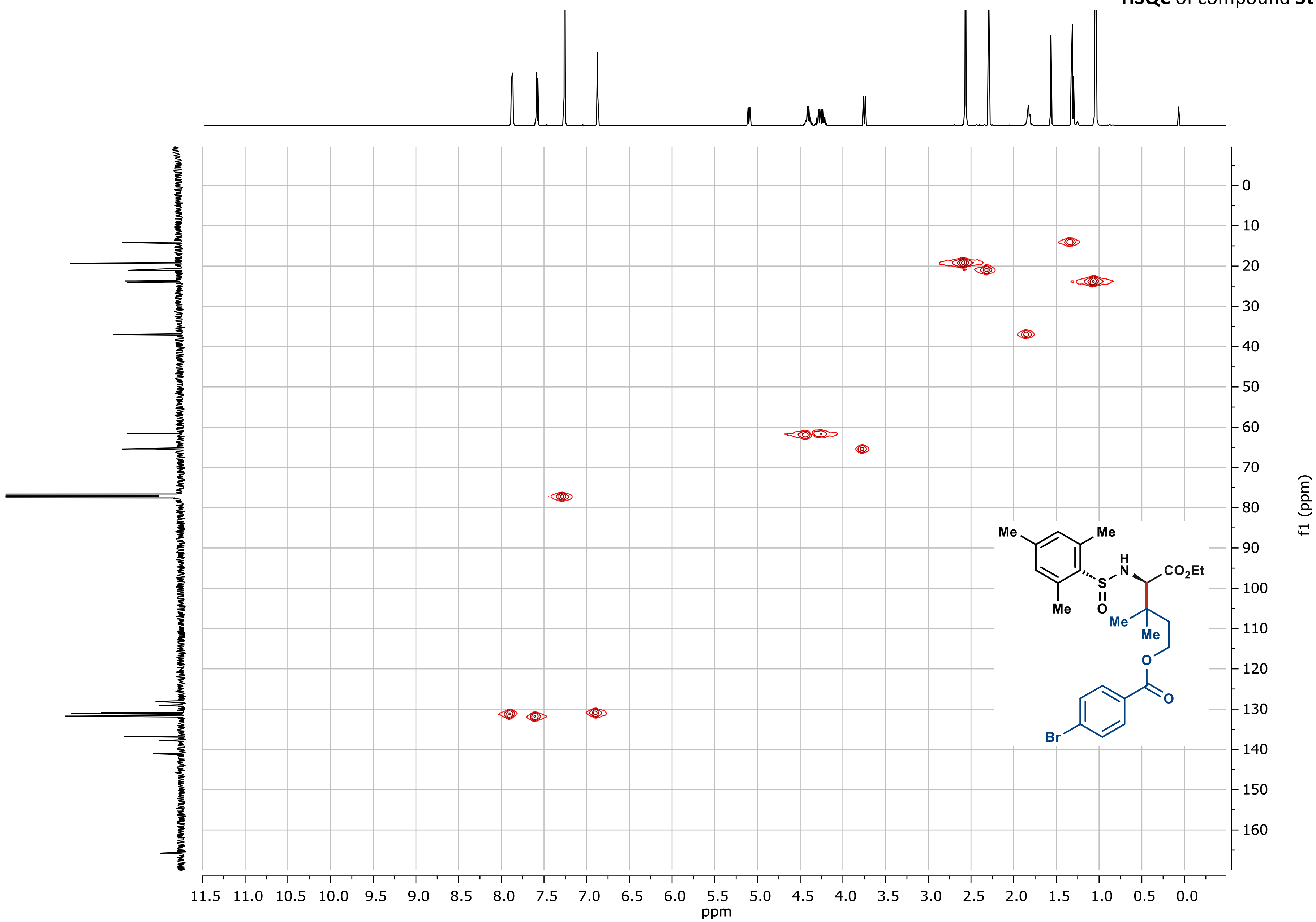
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5t**



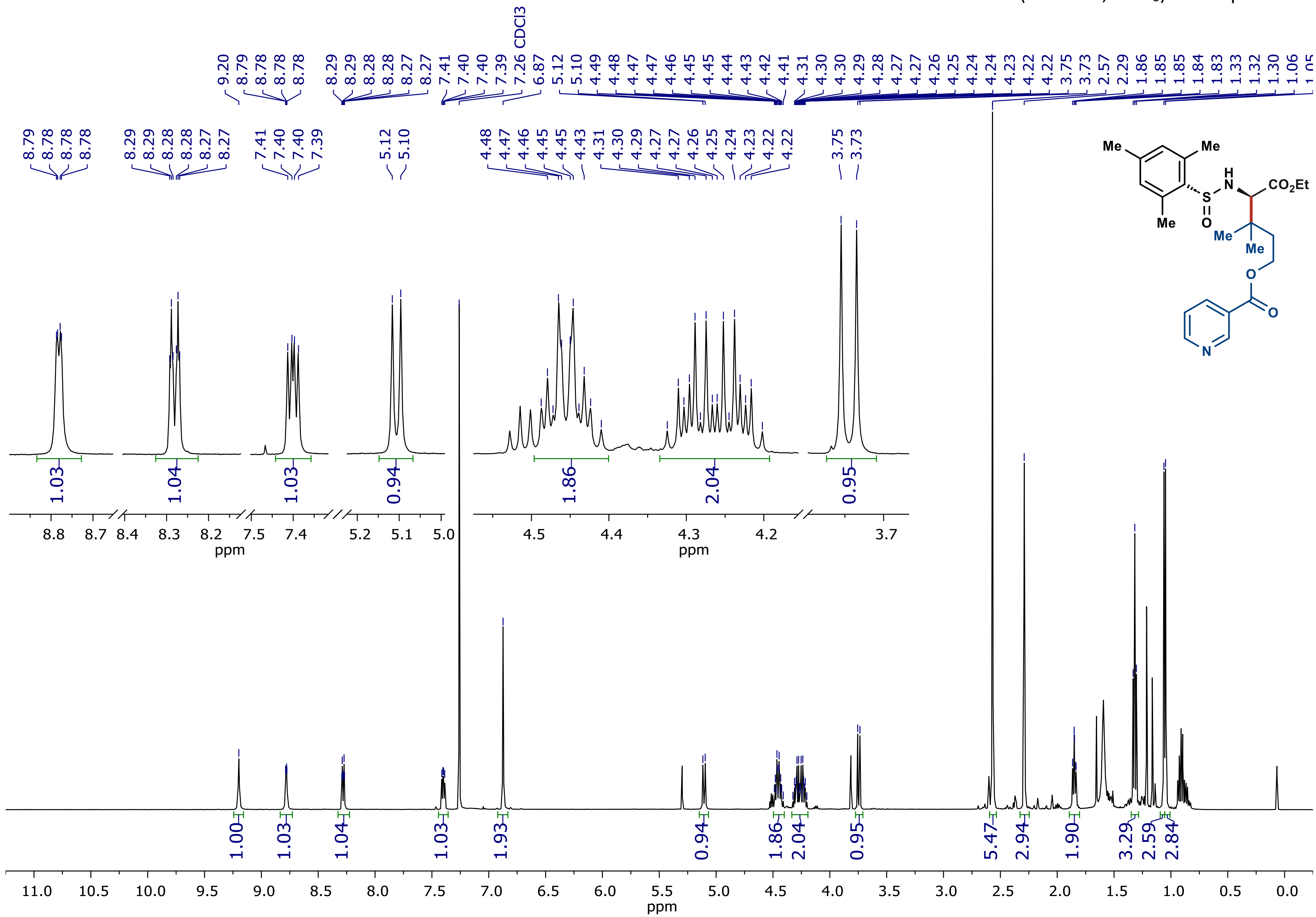
COSY of compound **5t**



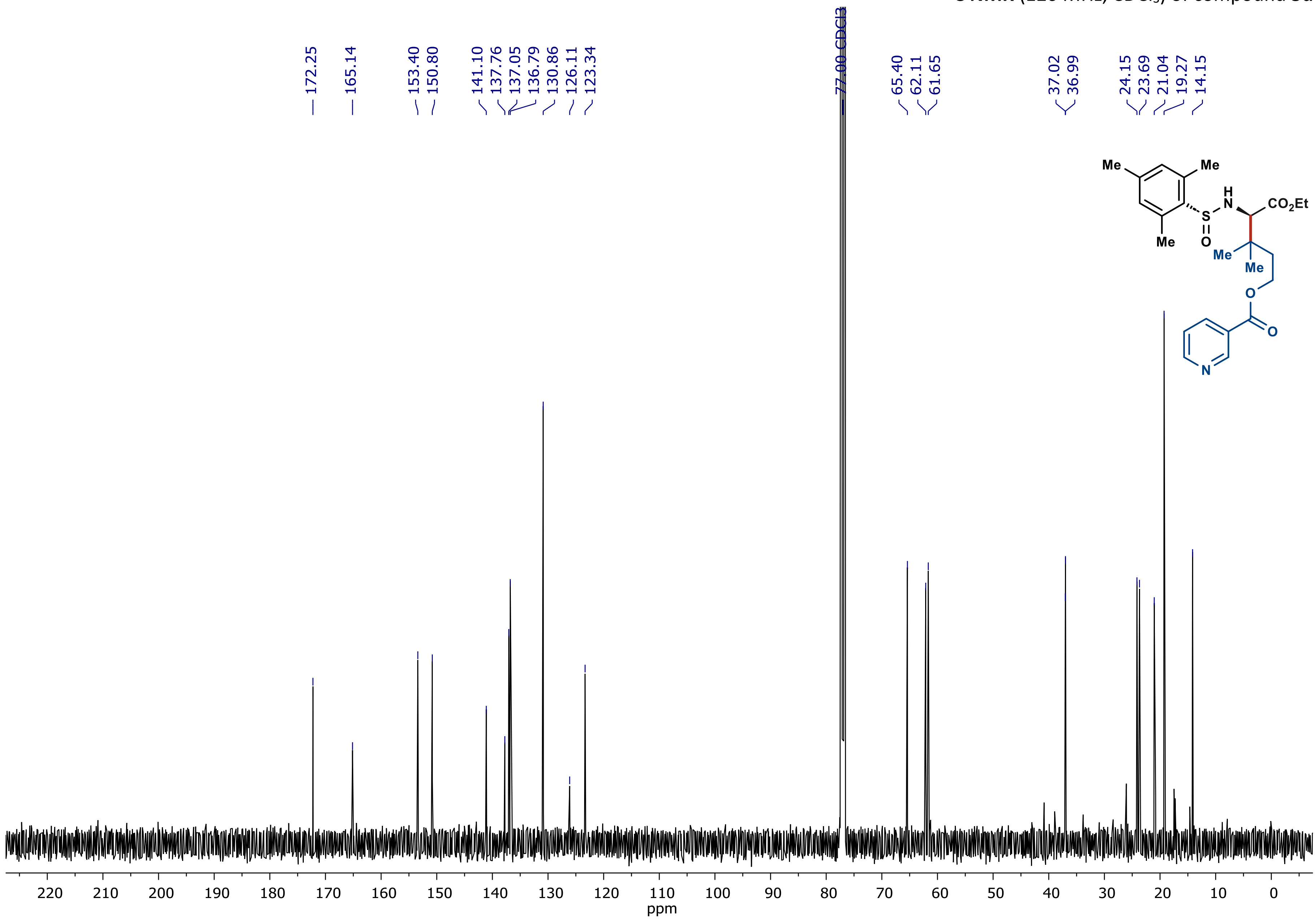
HSQC of compound **5t**



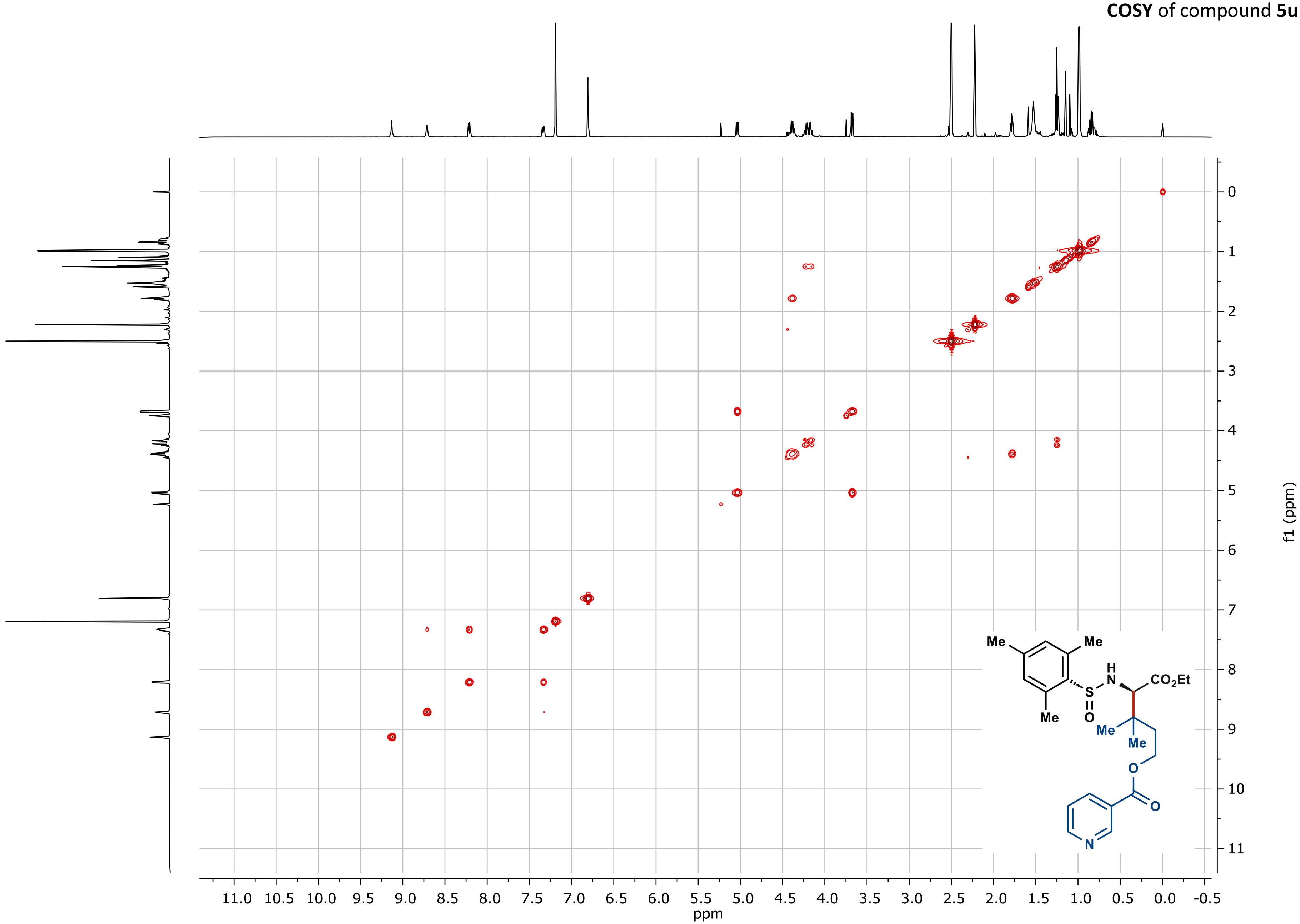
[1]H NMR (500 MHz, $CDCl_3$) of compound **5u**



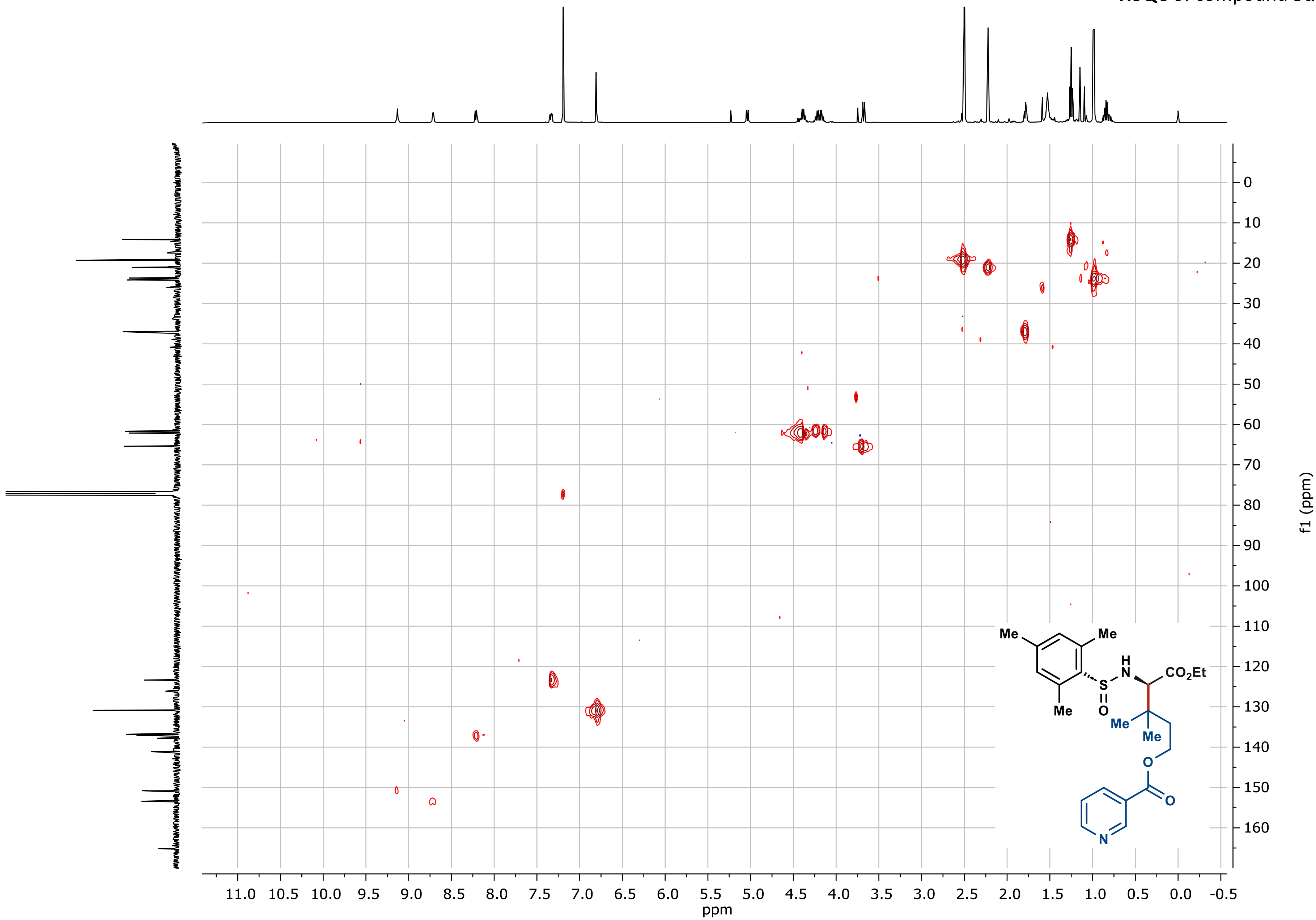
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5u**



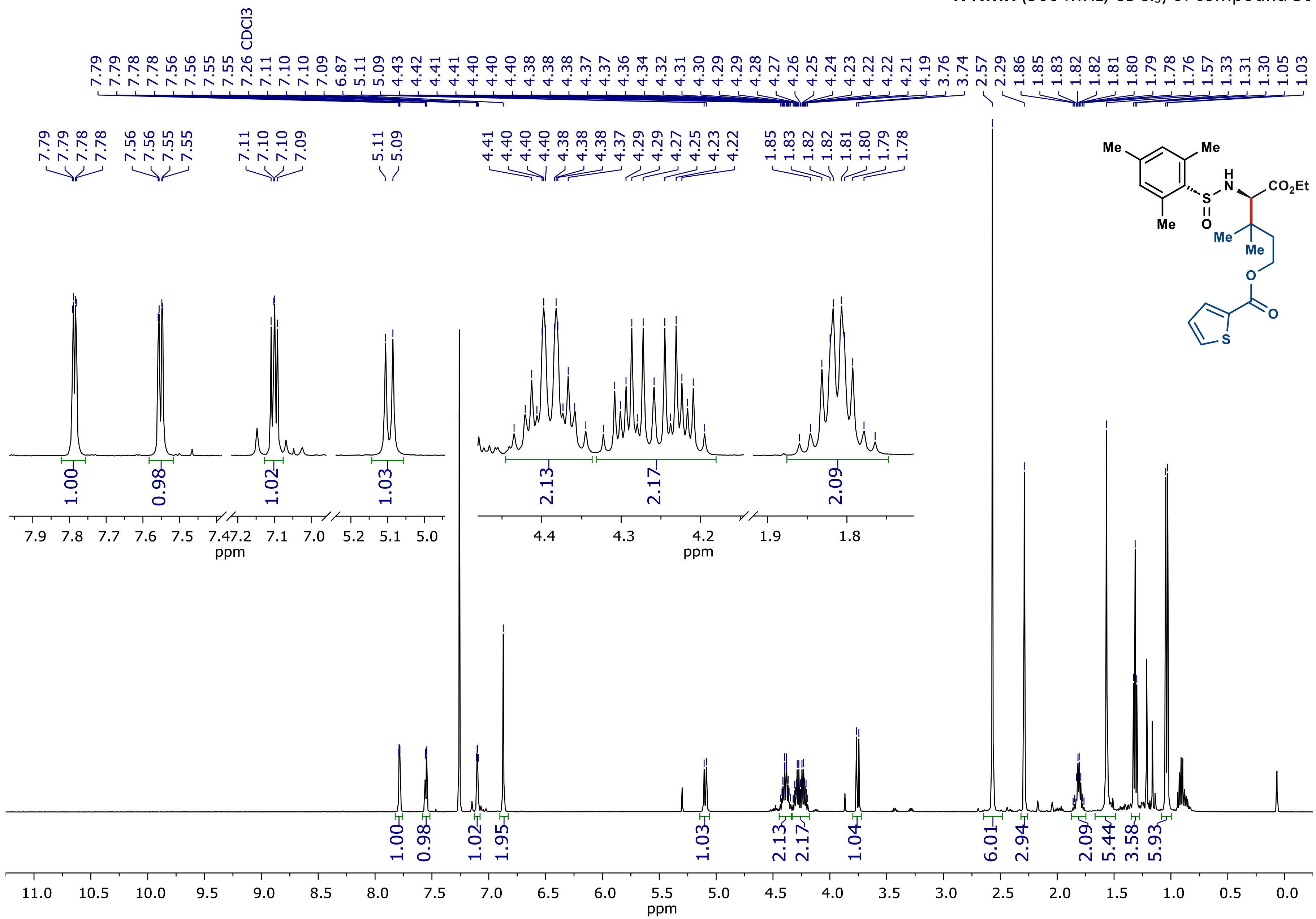
COSY of compound 5u



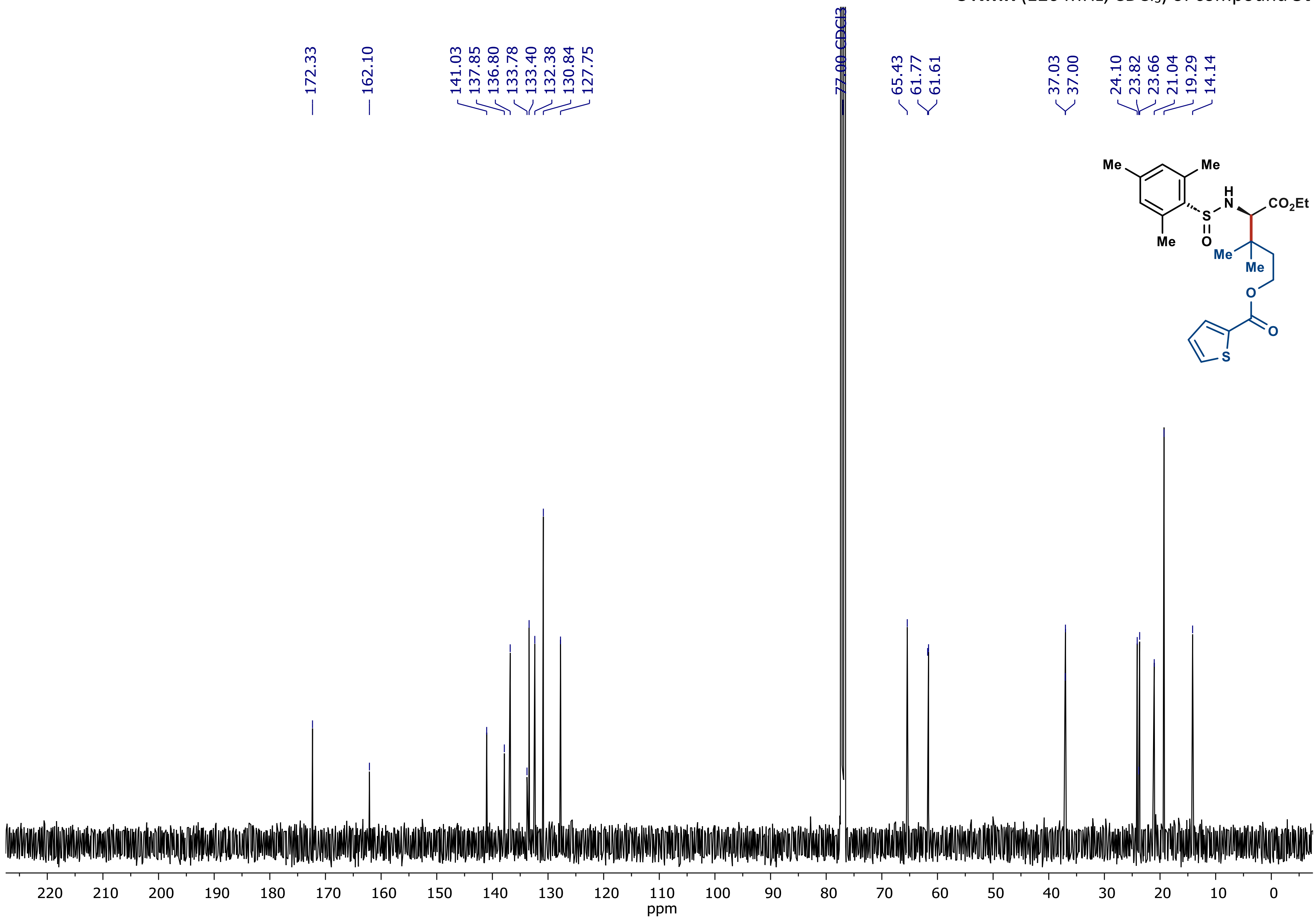
HSQC of compound **5u**



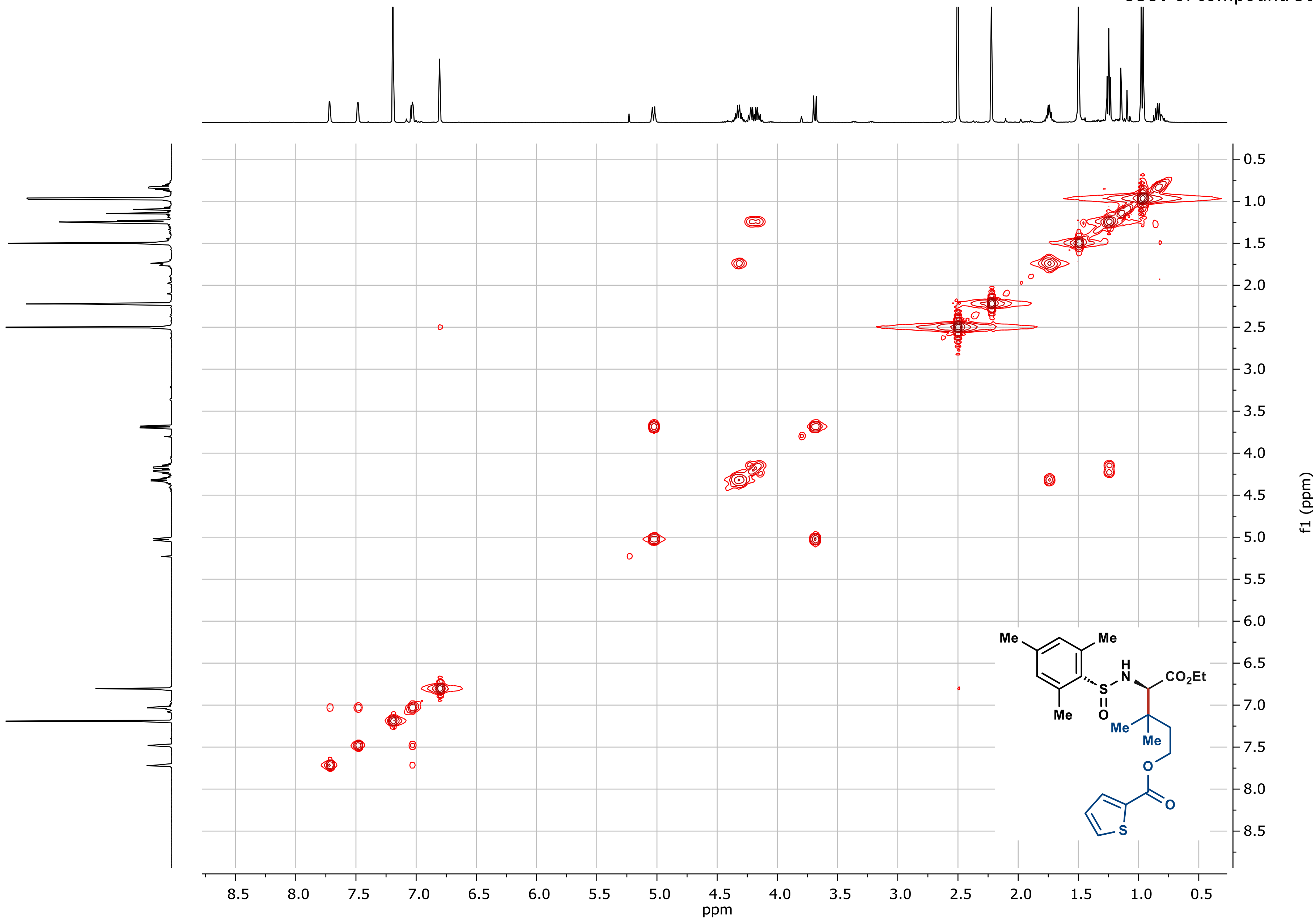
^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5v**



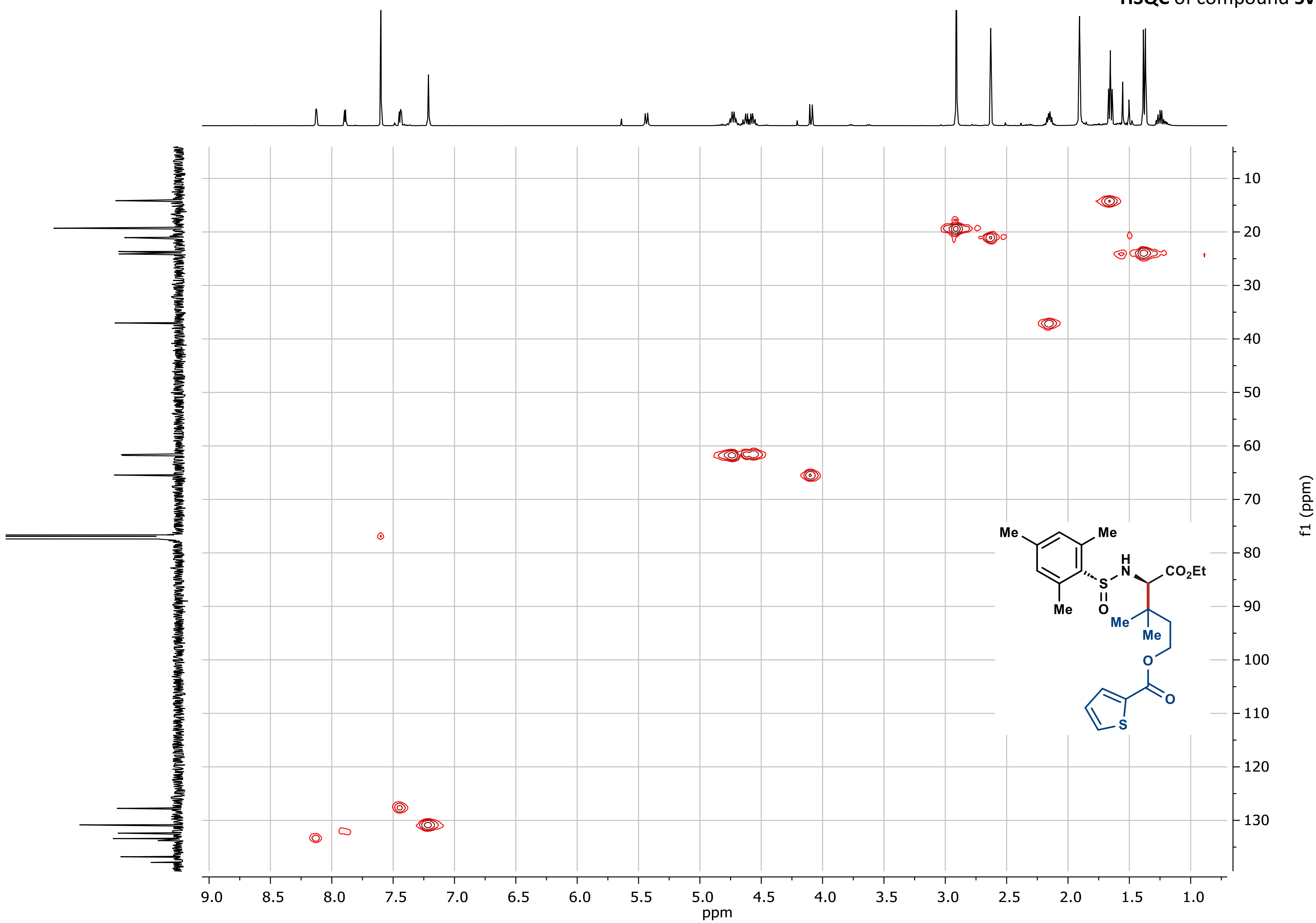
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **5v**



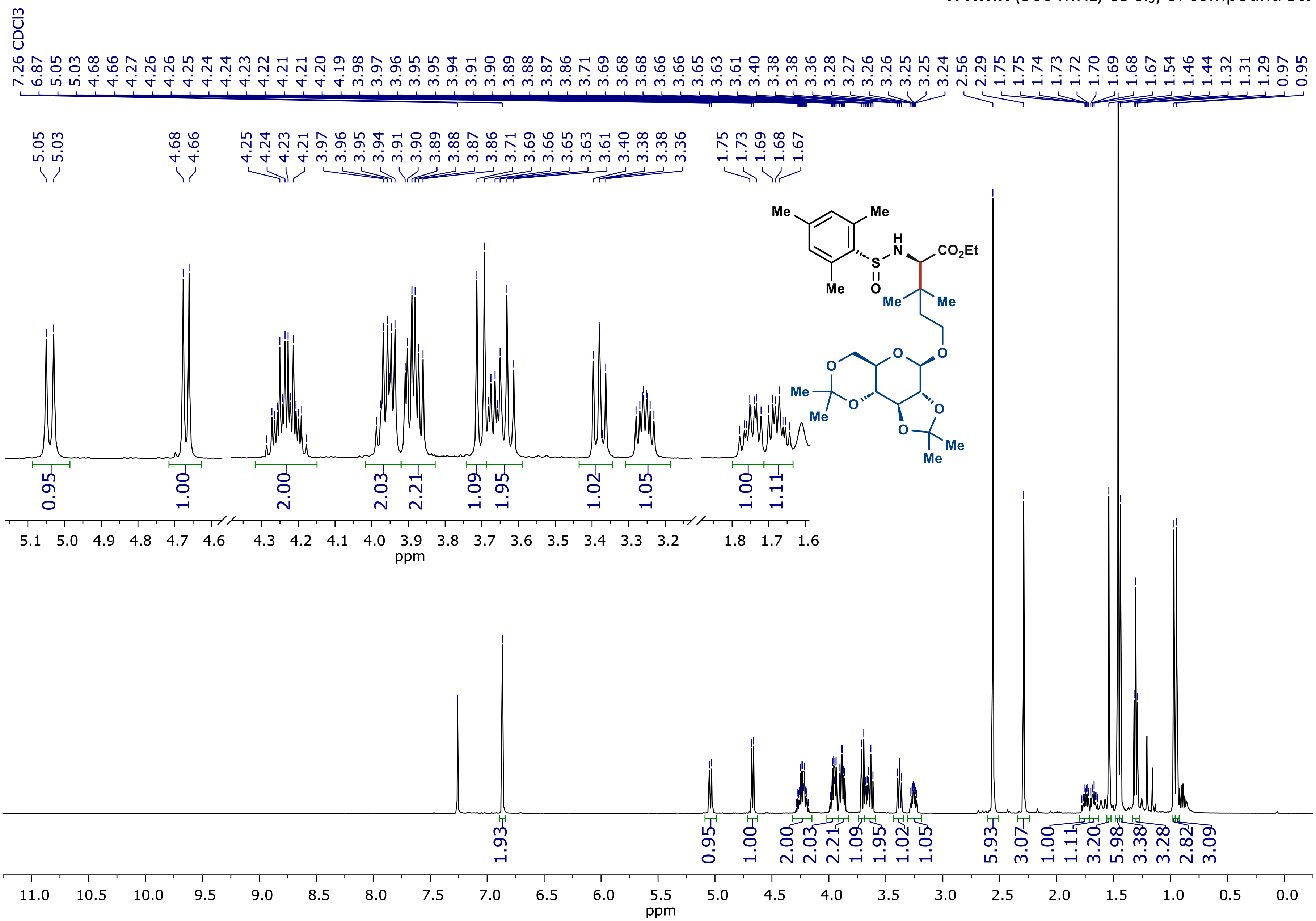
COSY of compound **5v**



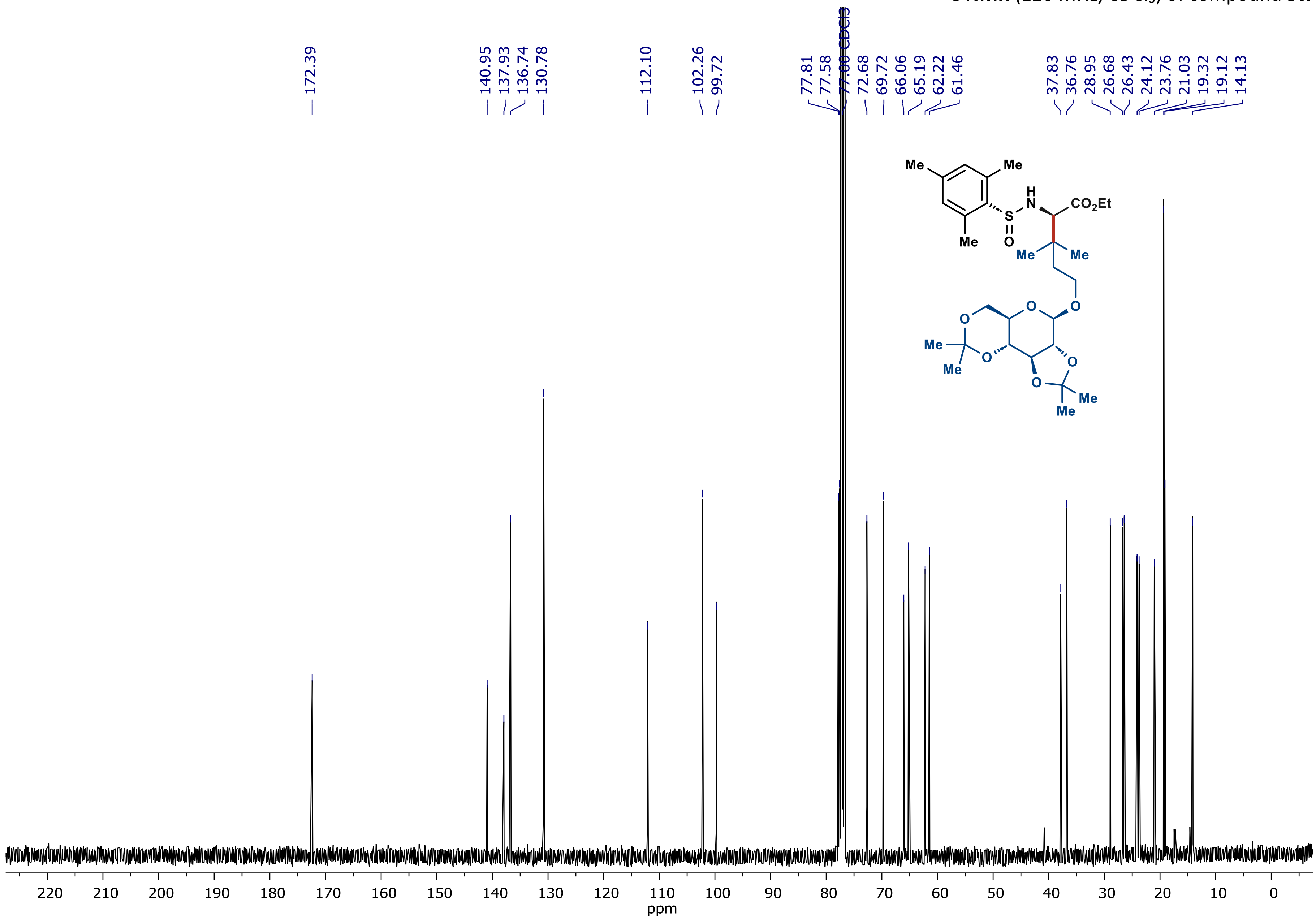
HSQC of compound 5v

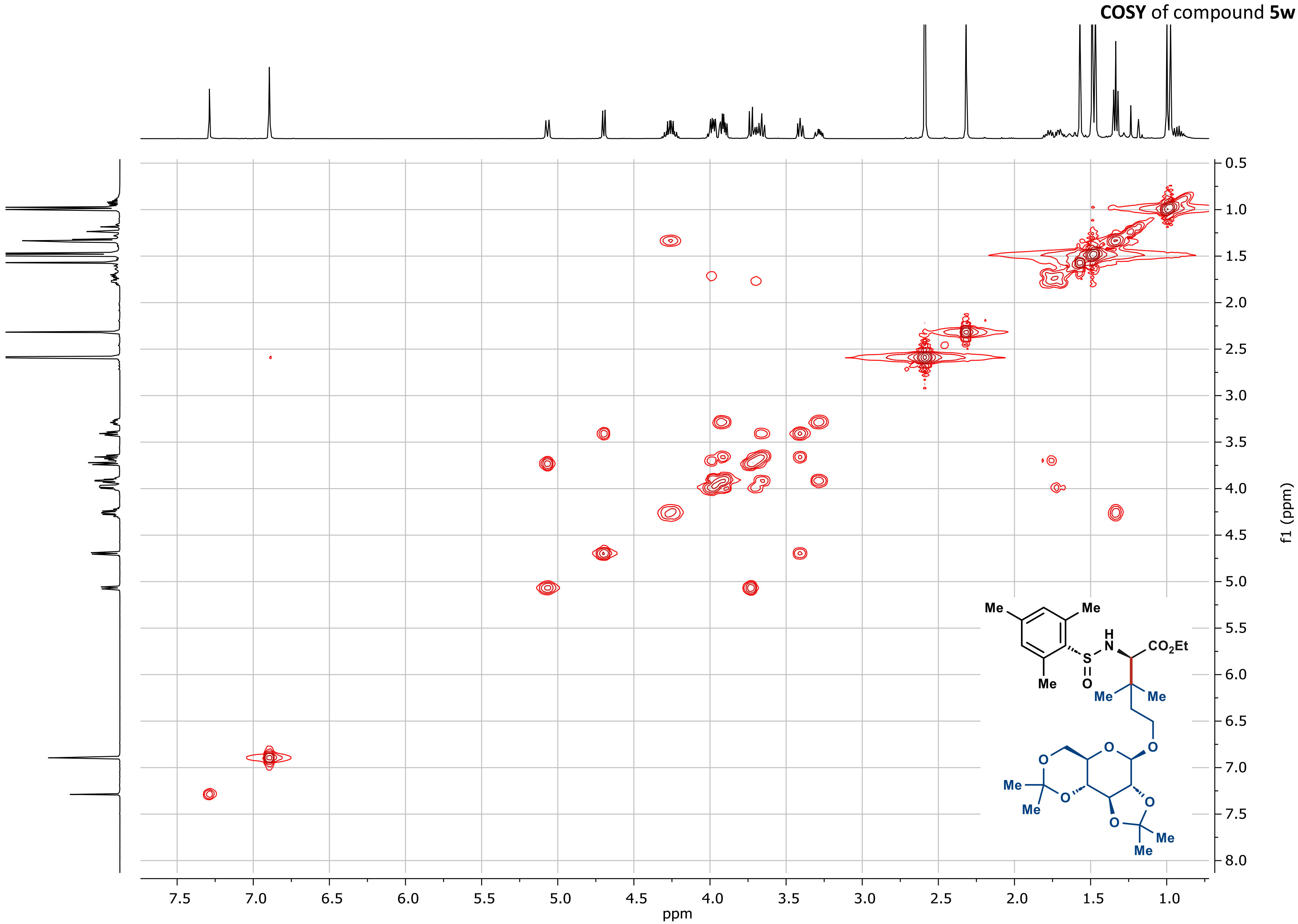


^{1}**H NMR** (500 MHz, $CDCl_3$) of compound **5w**



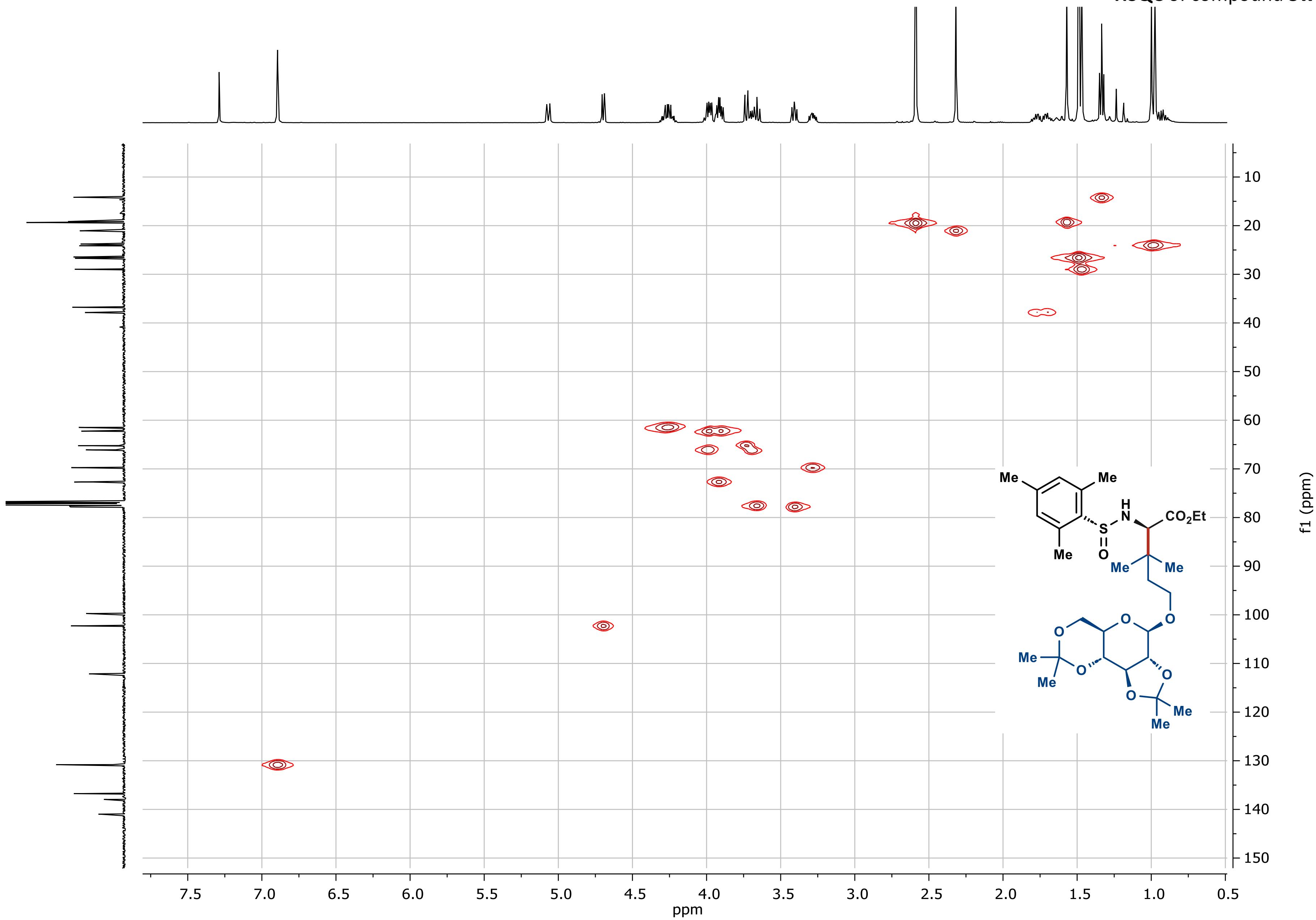
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5w**



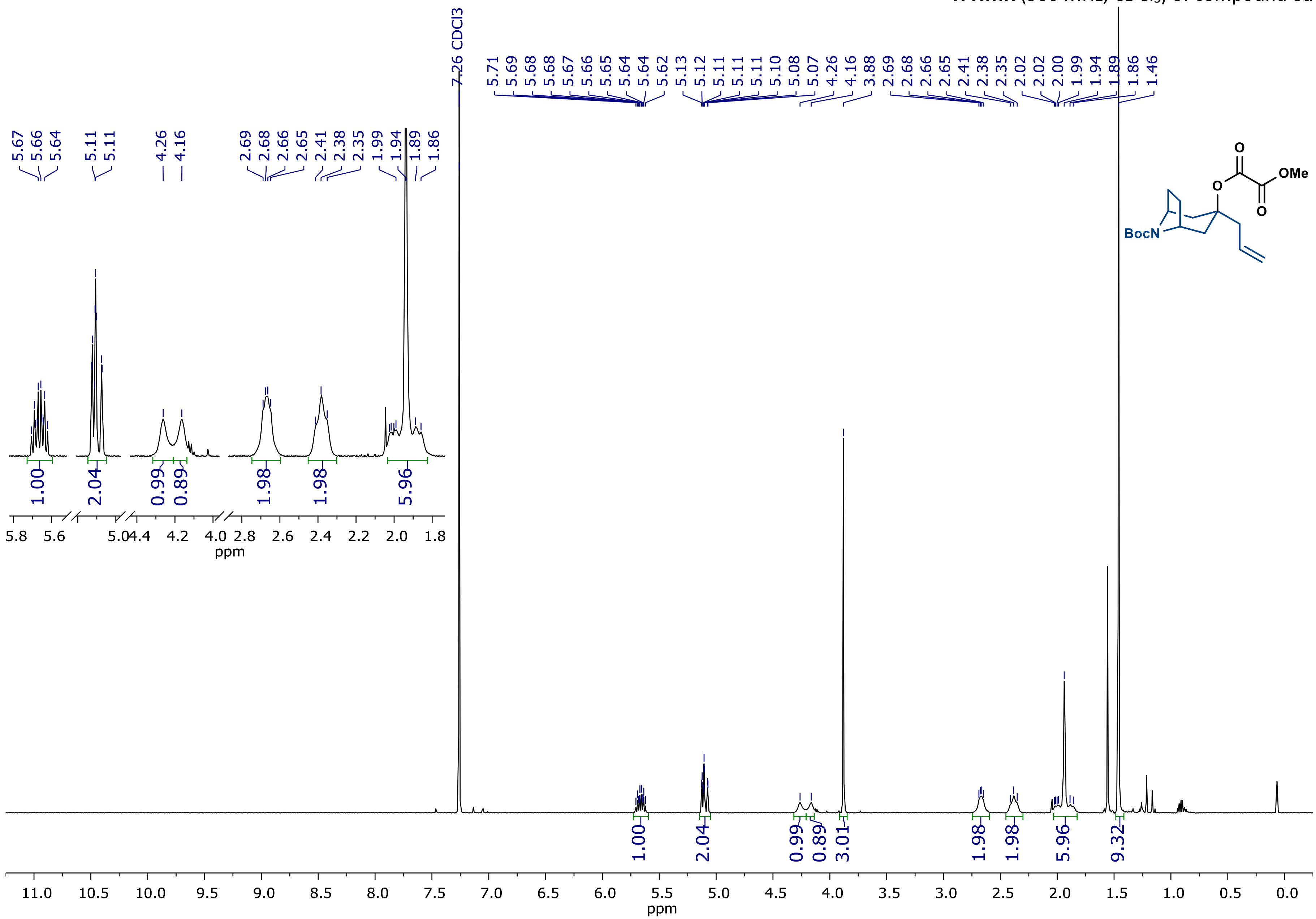


COSY of compound 5w
f1 (ppm)
ppm
Me
Me
Me
H
N
S
O
CO2Et
Me
Me
O
O
O
O
O
O
Me
Me
Me
Me

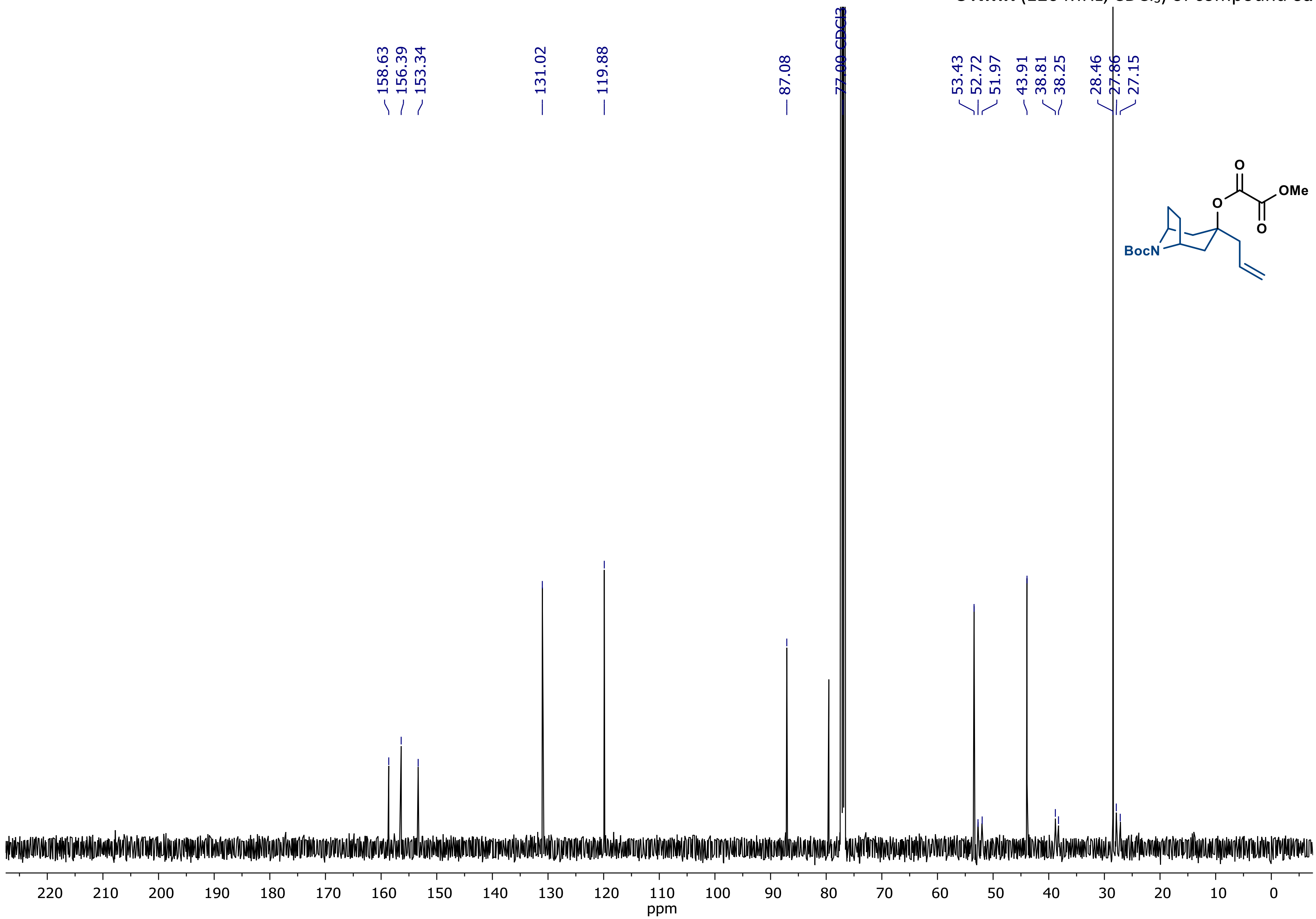
HSQC of compound **5w**



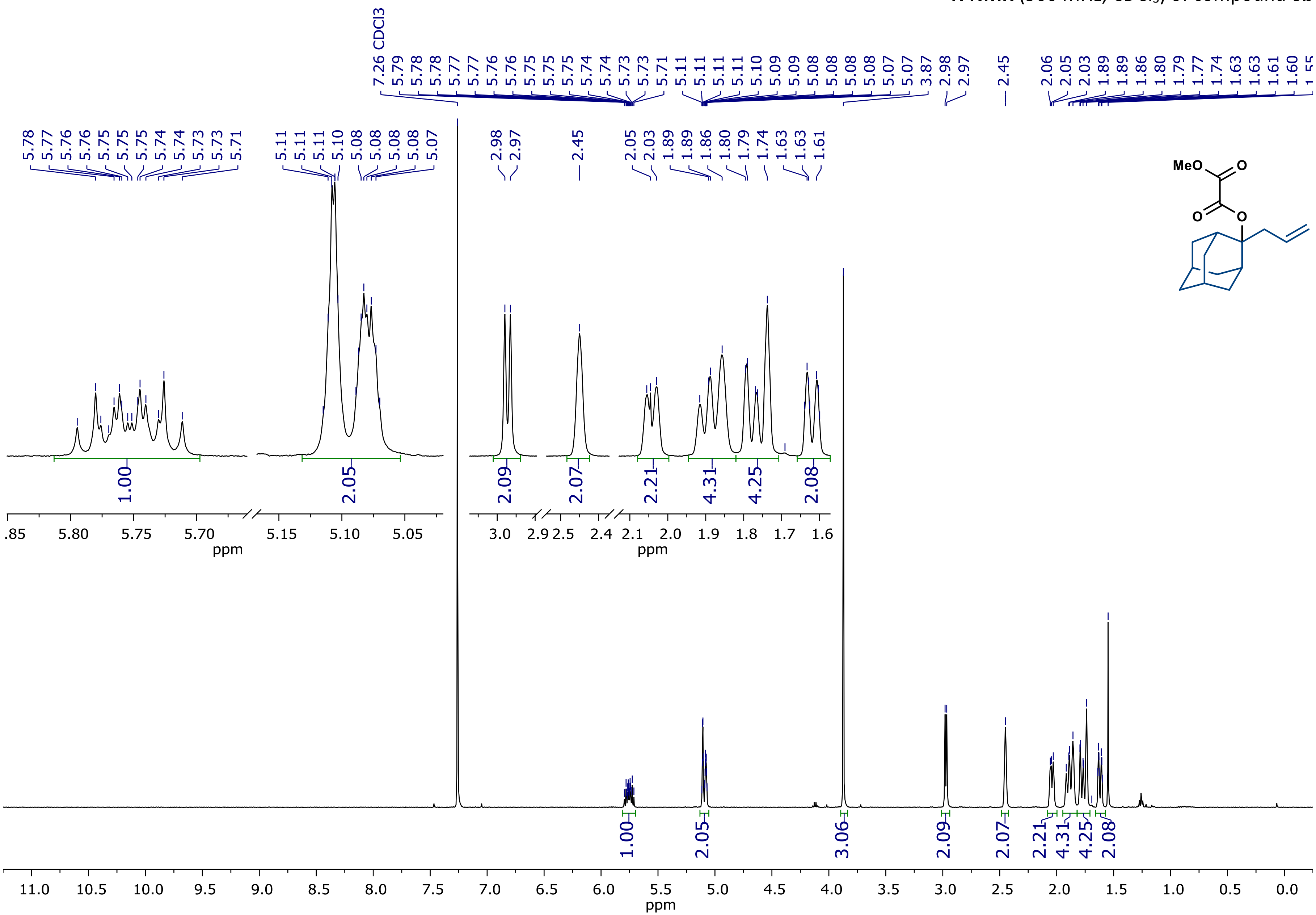
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6a**



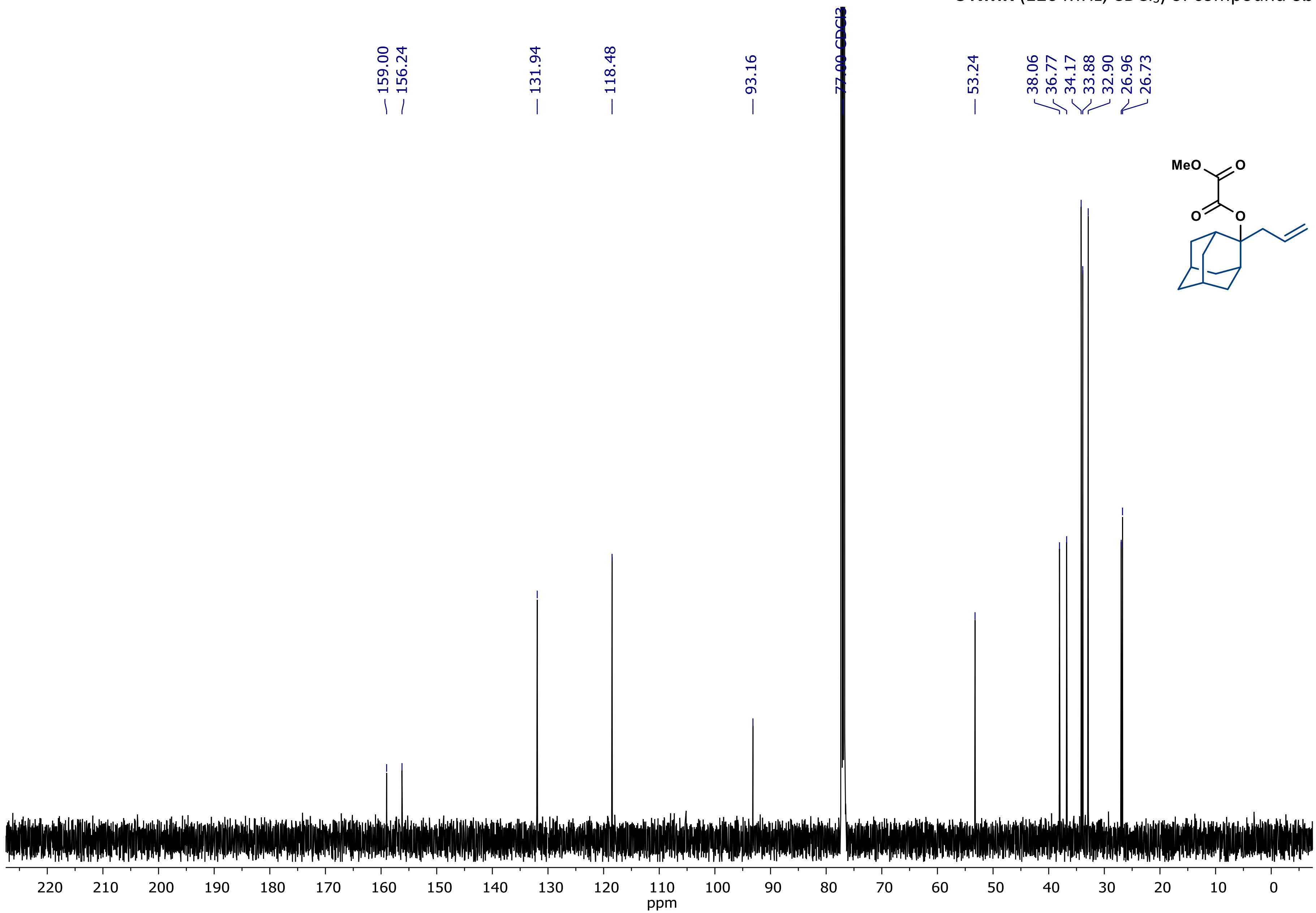
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6a**



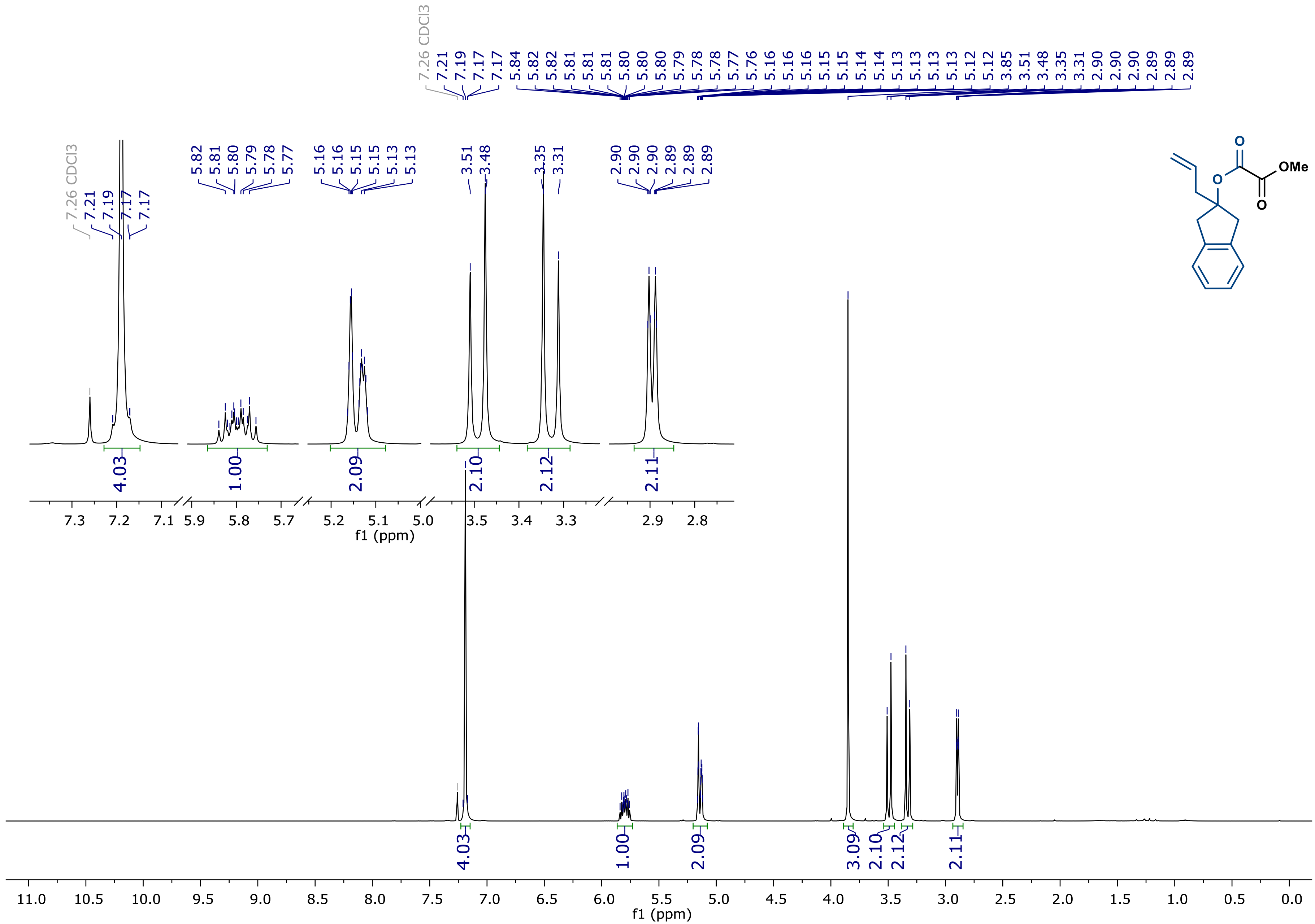
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6b**



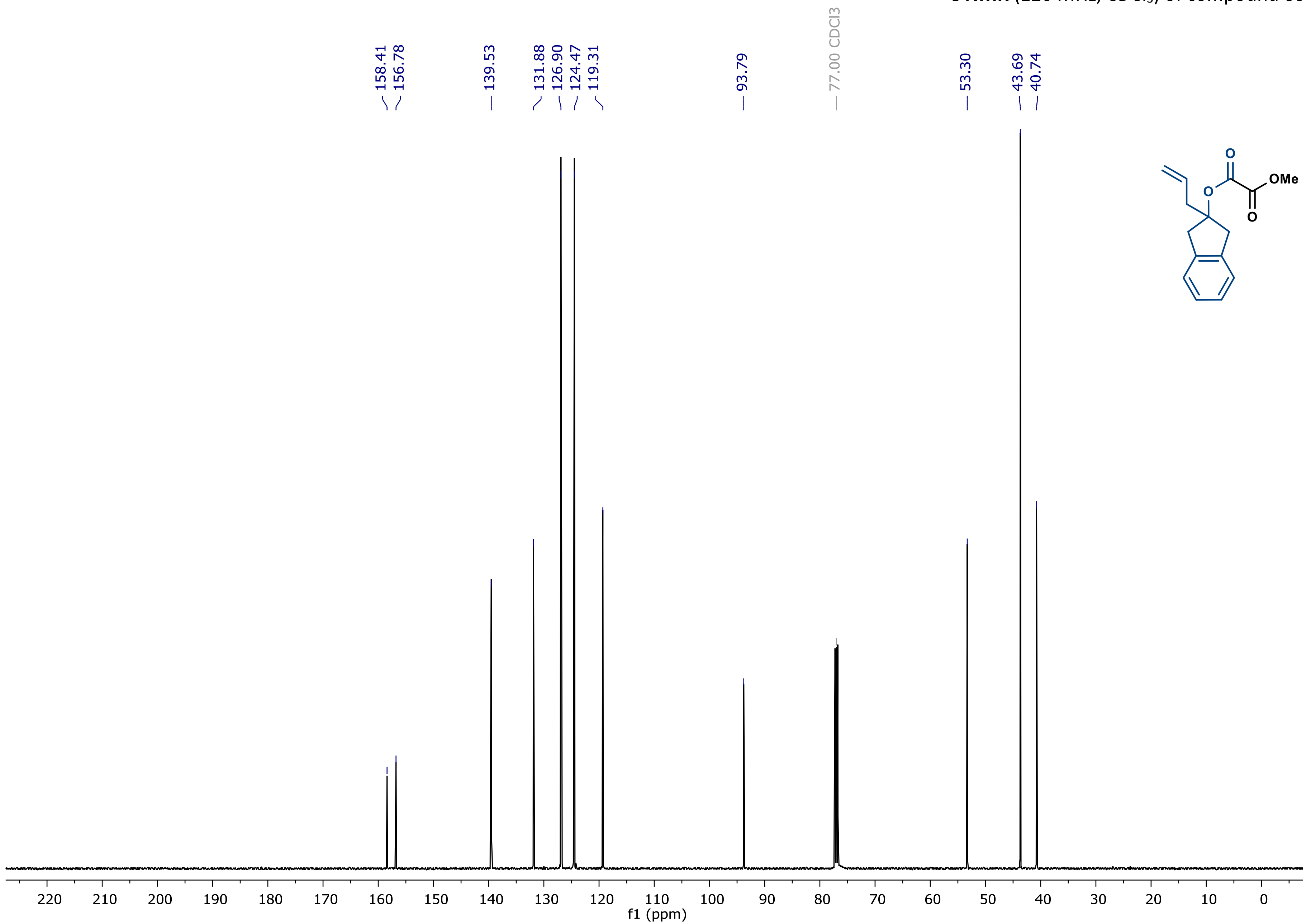
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6b**



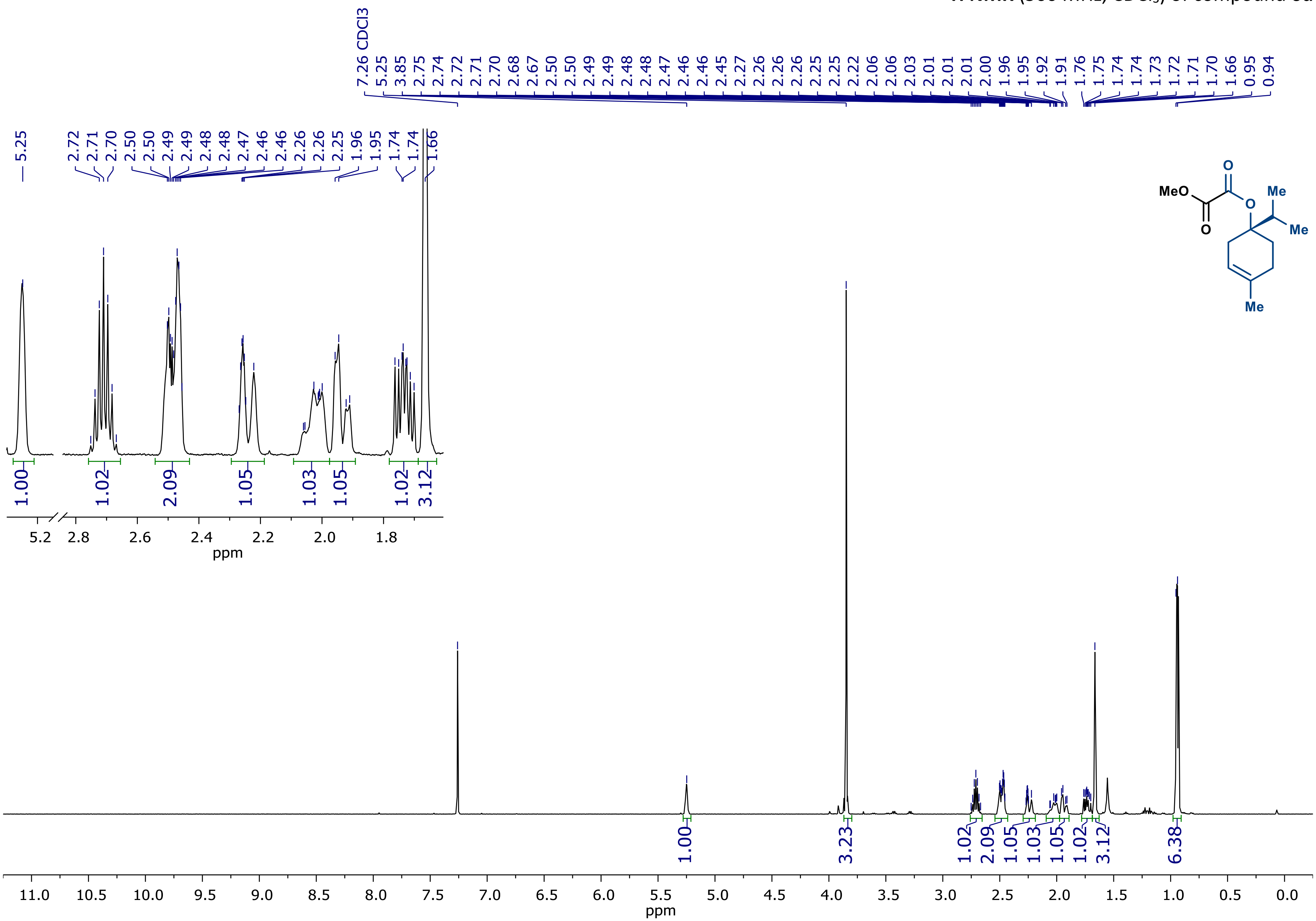
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6c**



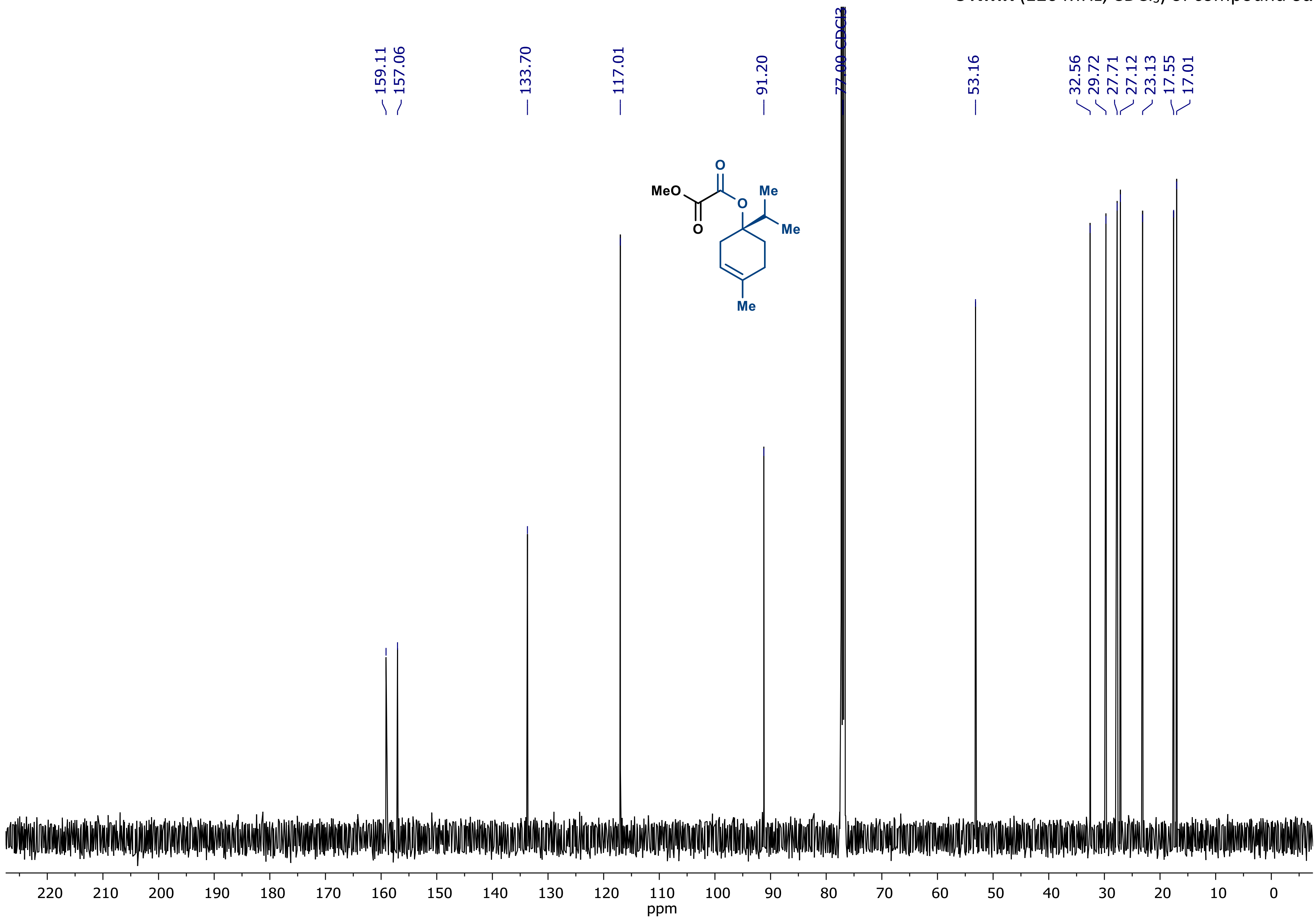
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6c**

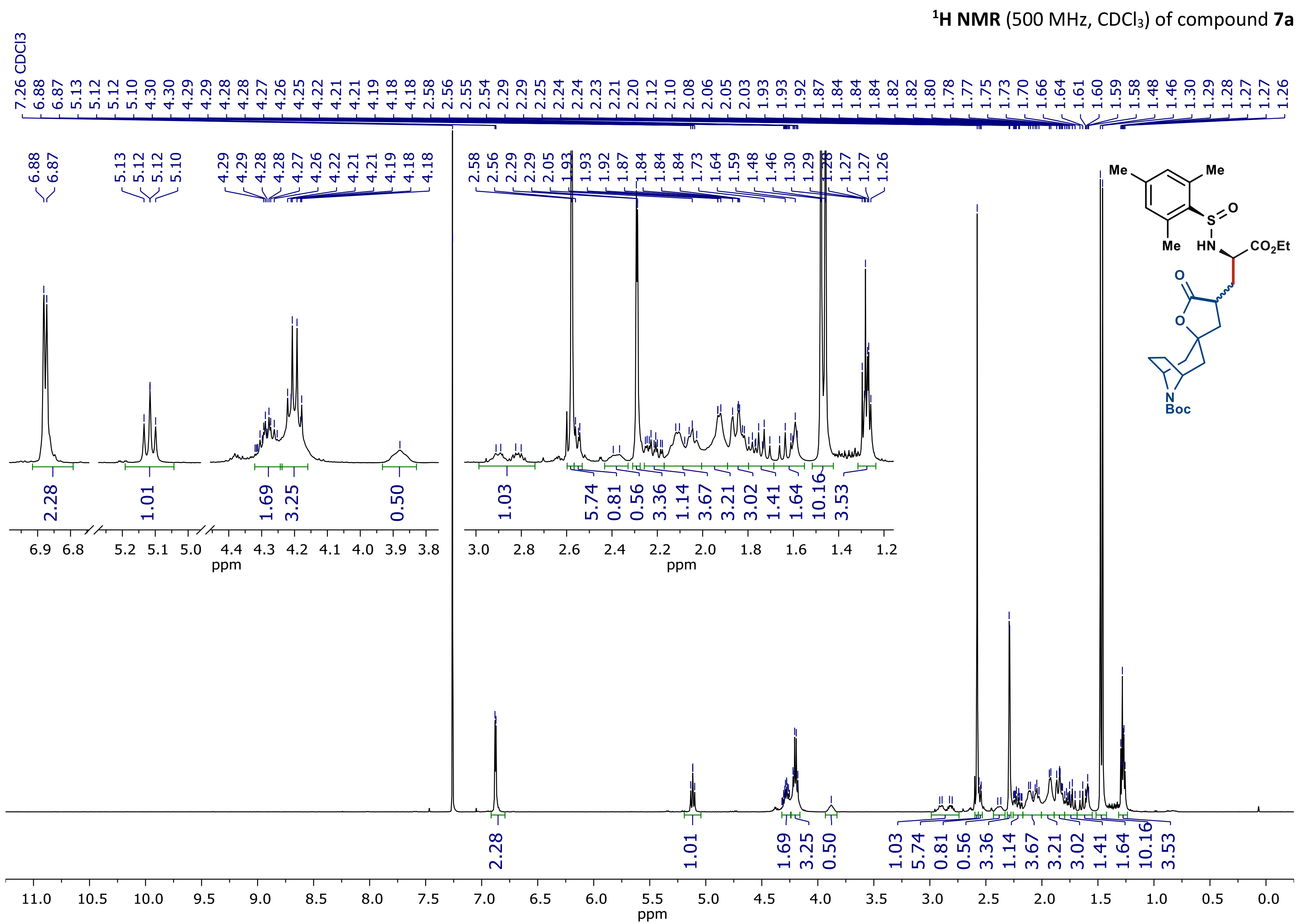


^{1}H NMR (500 MHz, $CDCl_3$) of compound **6d**



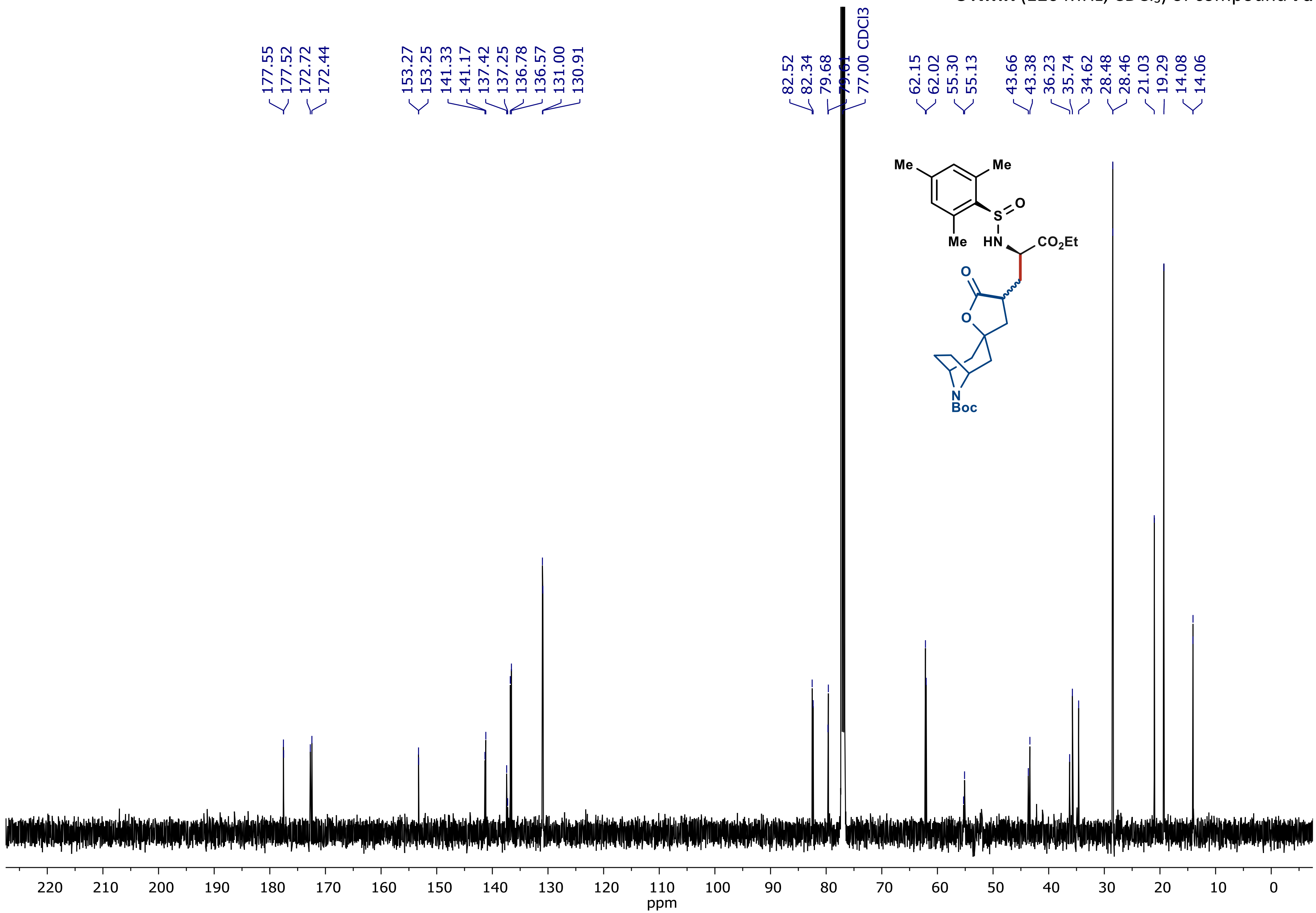
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6d**



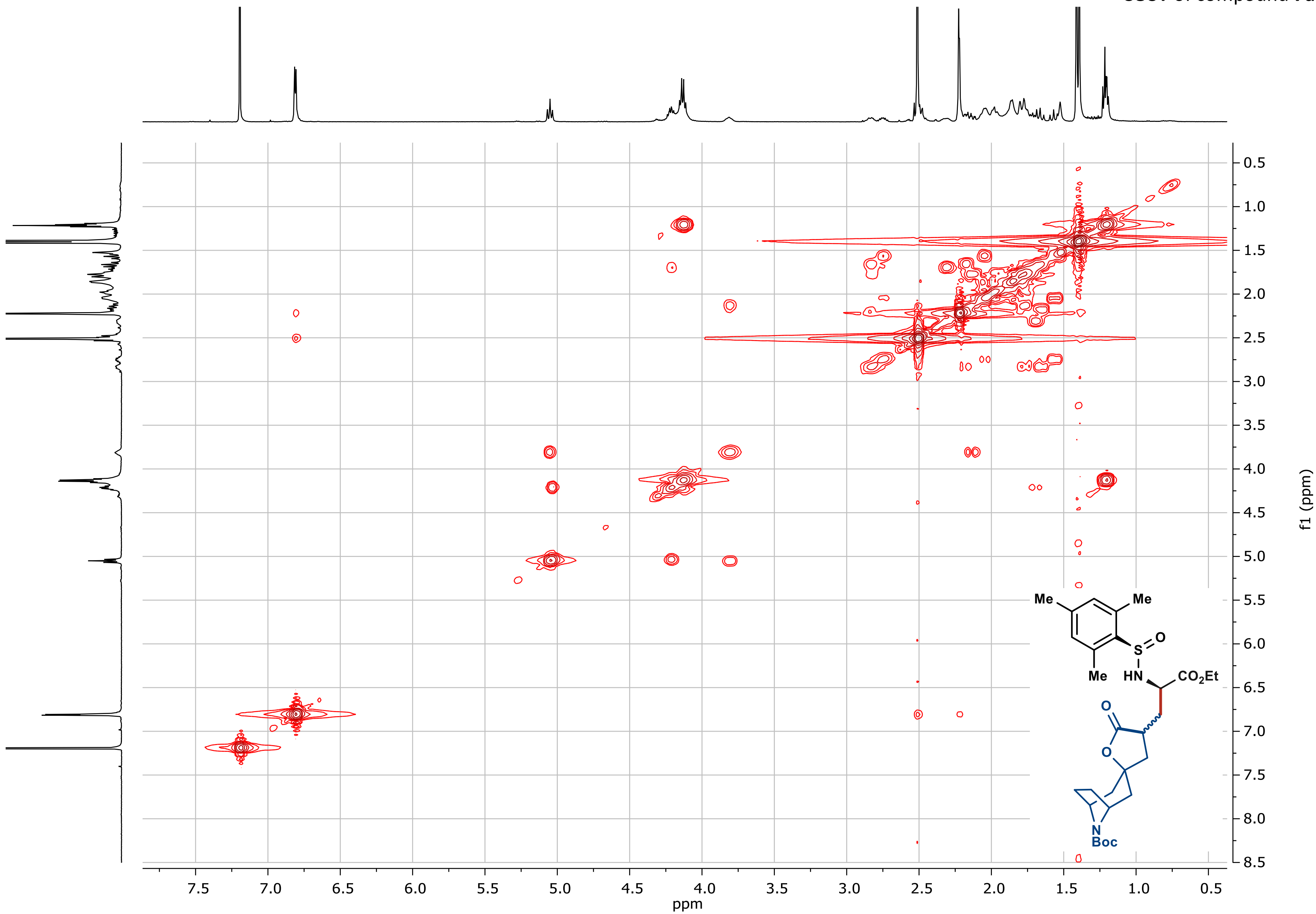


^{1}H NMR (500 MHz, $CDCl_3$) of compound 7a

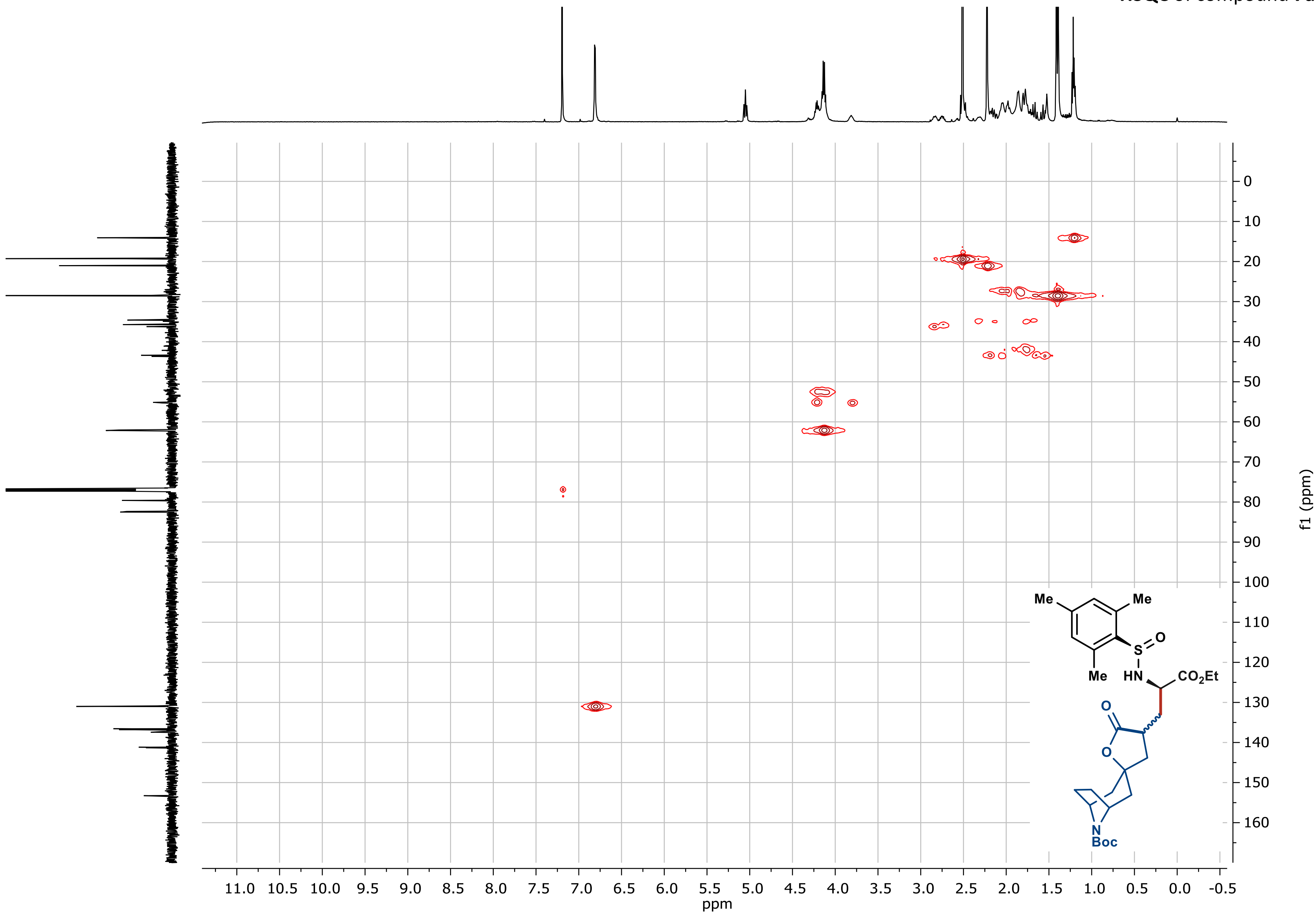
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7a**



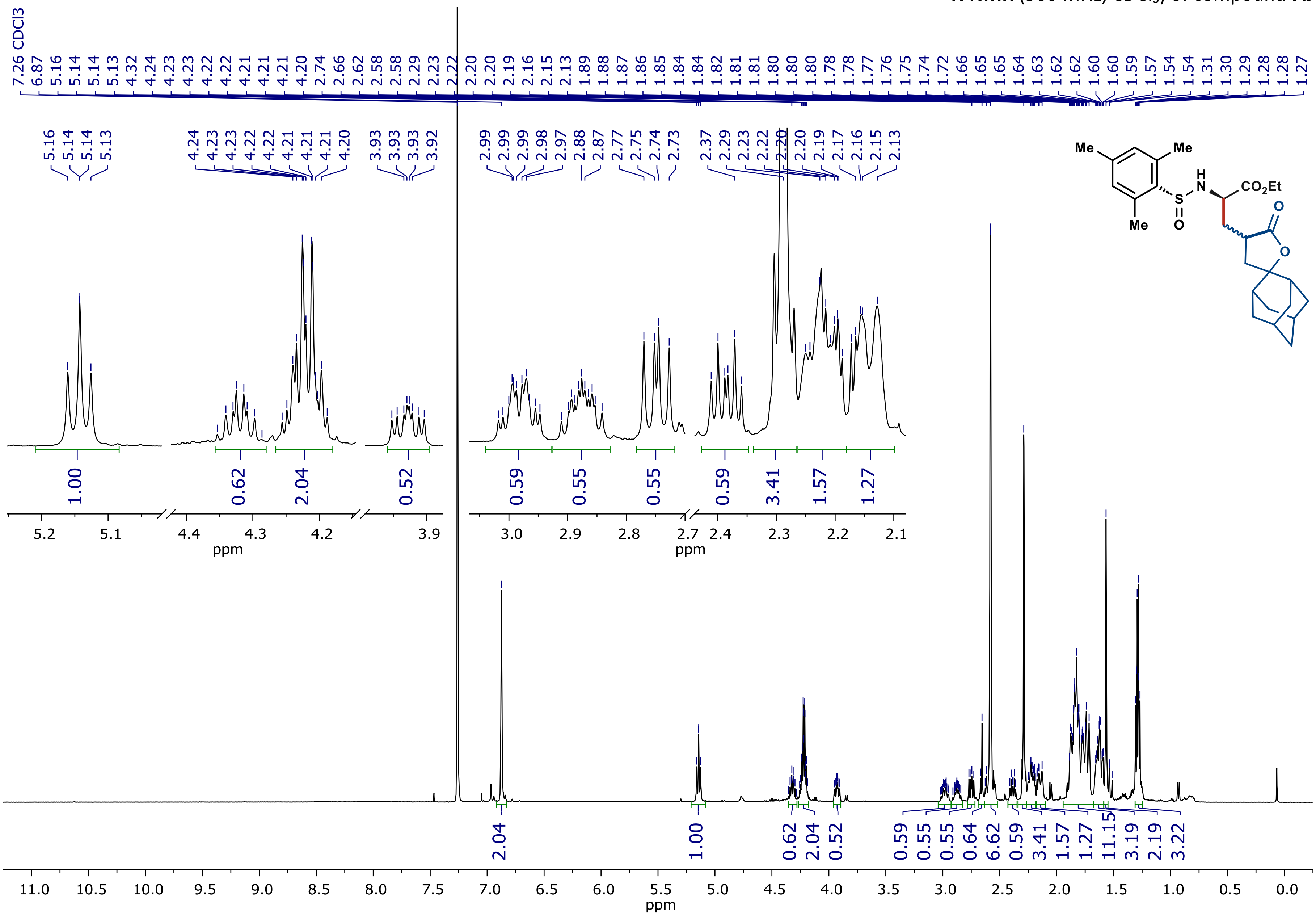
COSY of compound **7a**



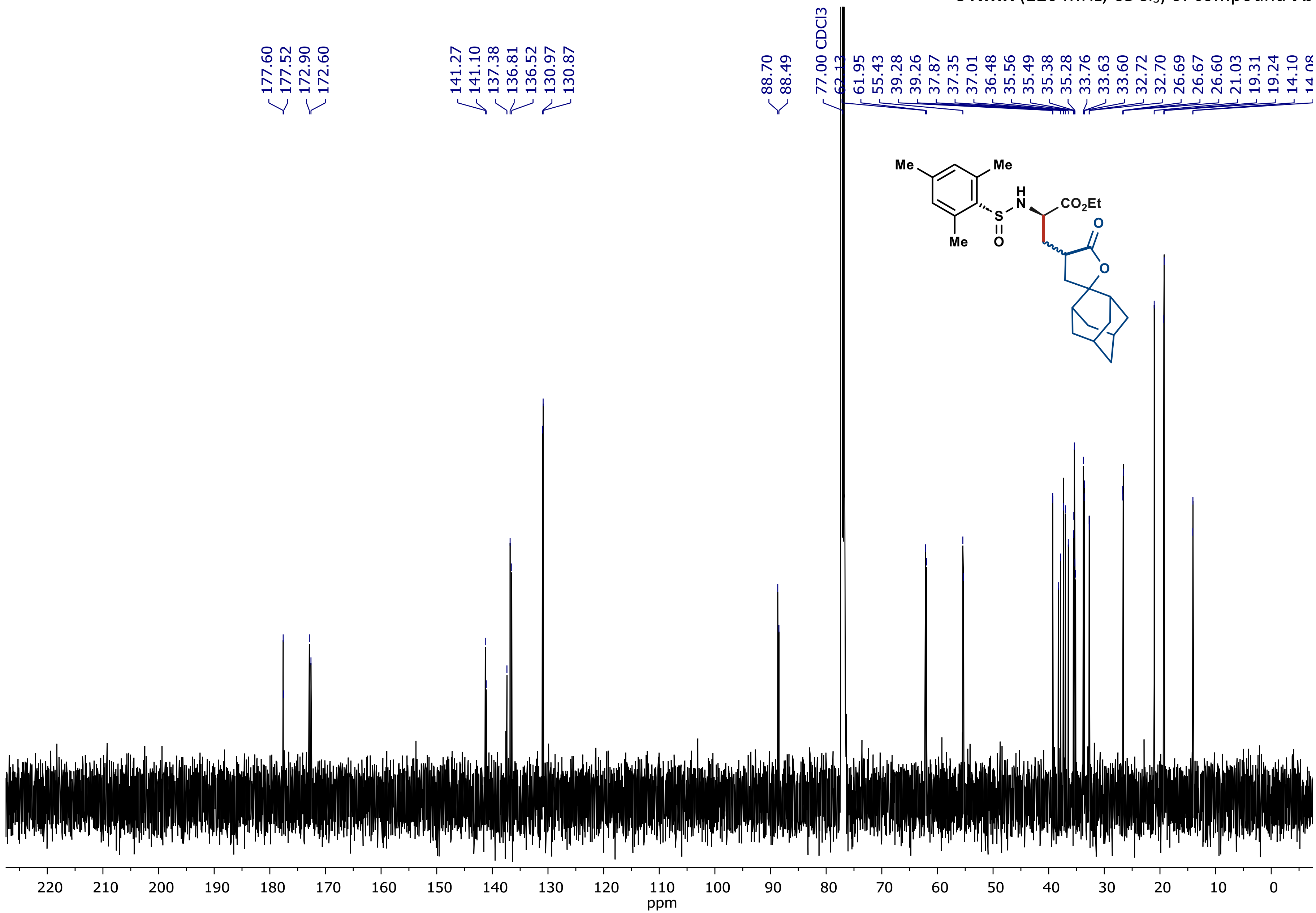
HSQC of compound **7a**



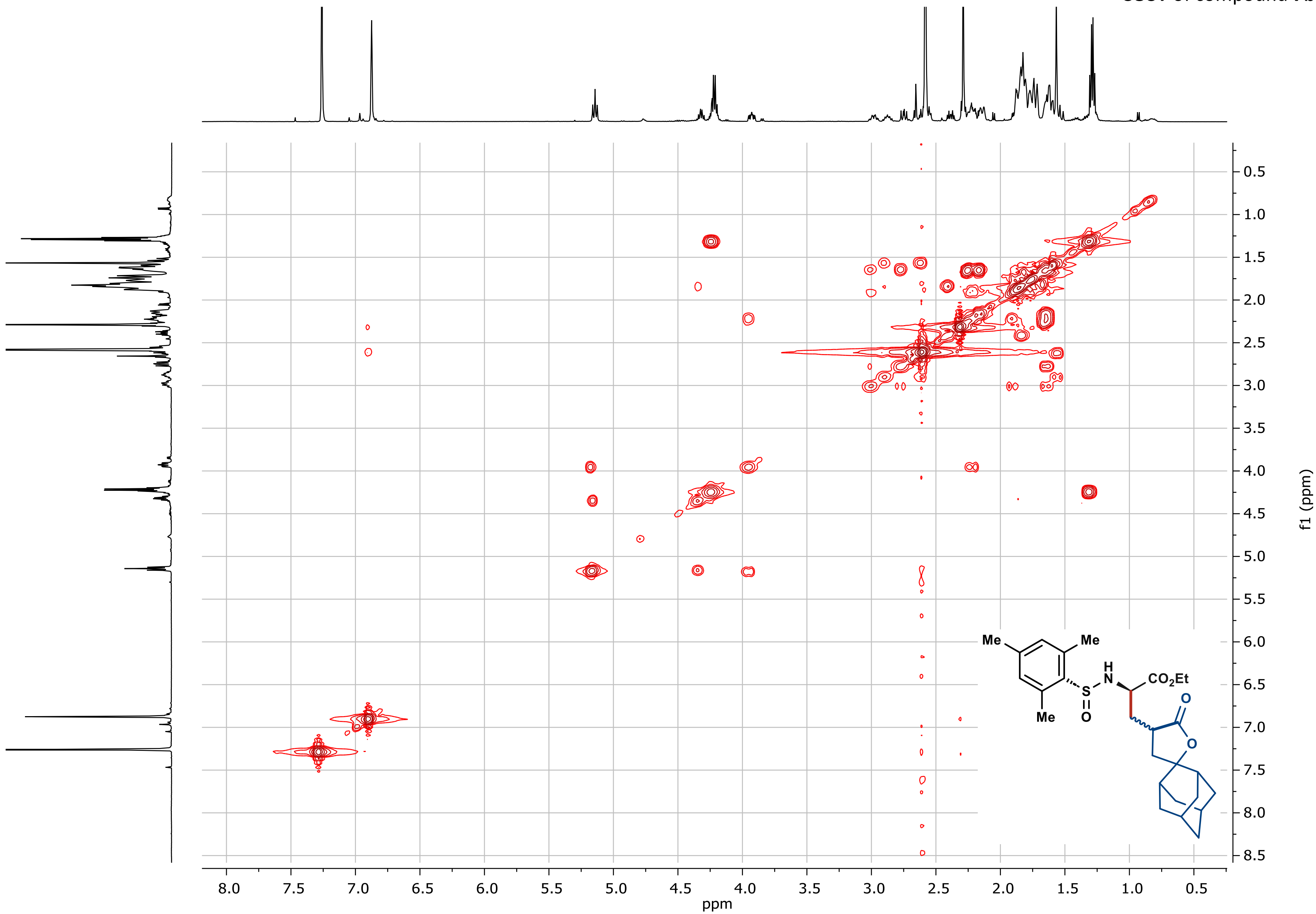
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7b**



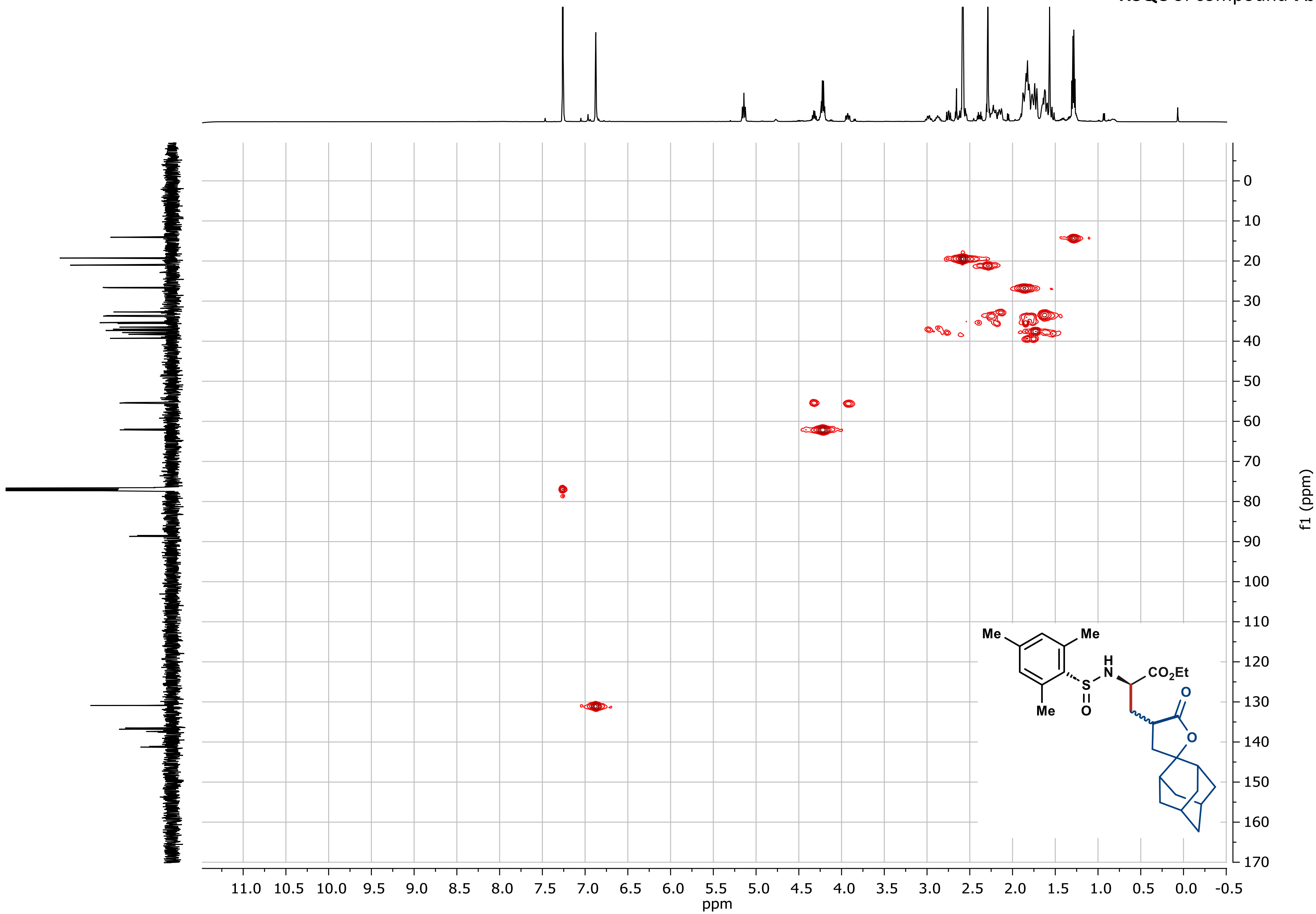
^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **7b**



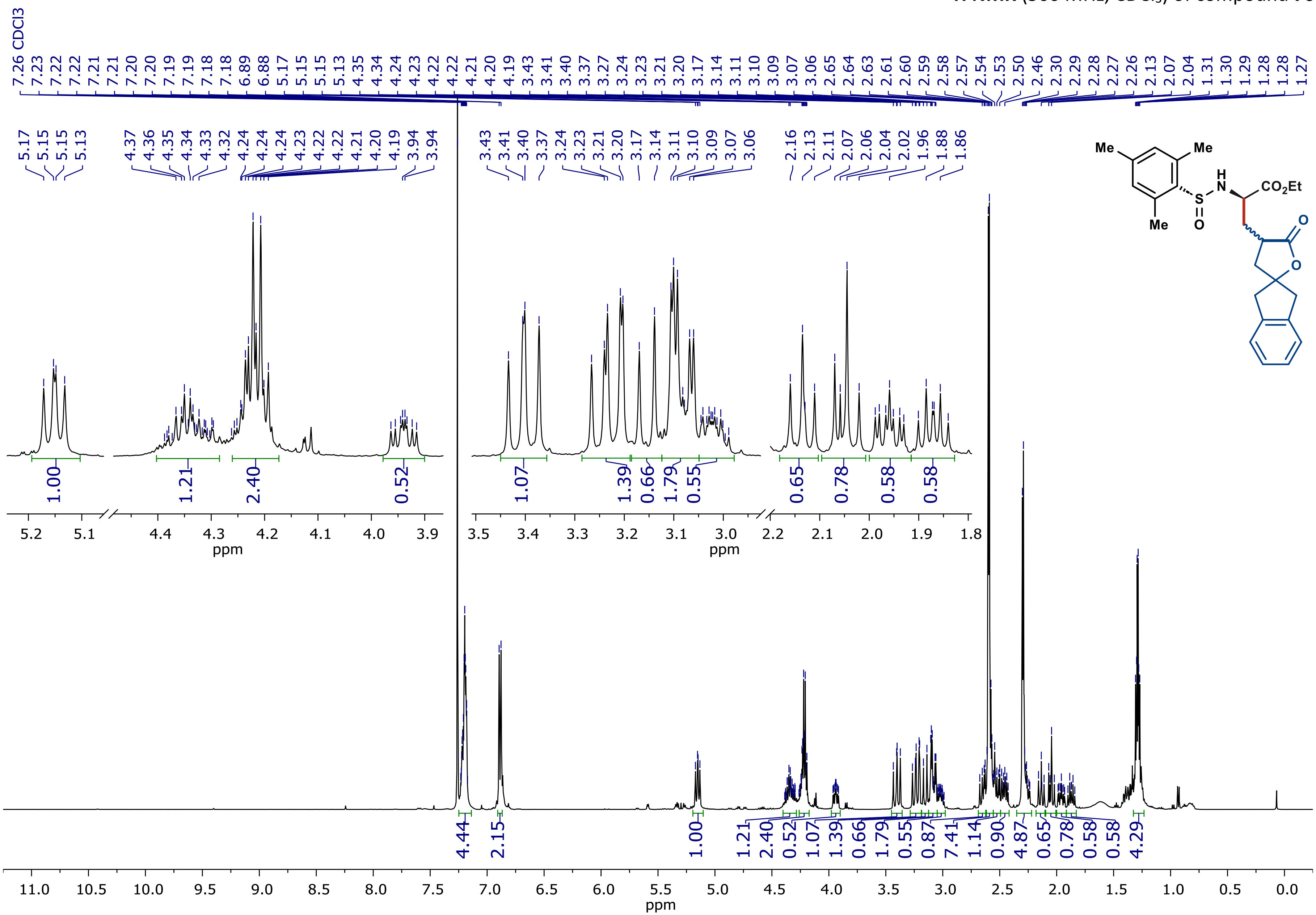
COSY of compound **7b**



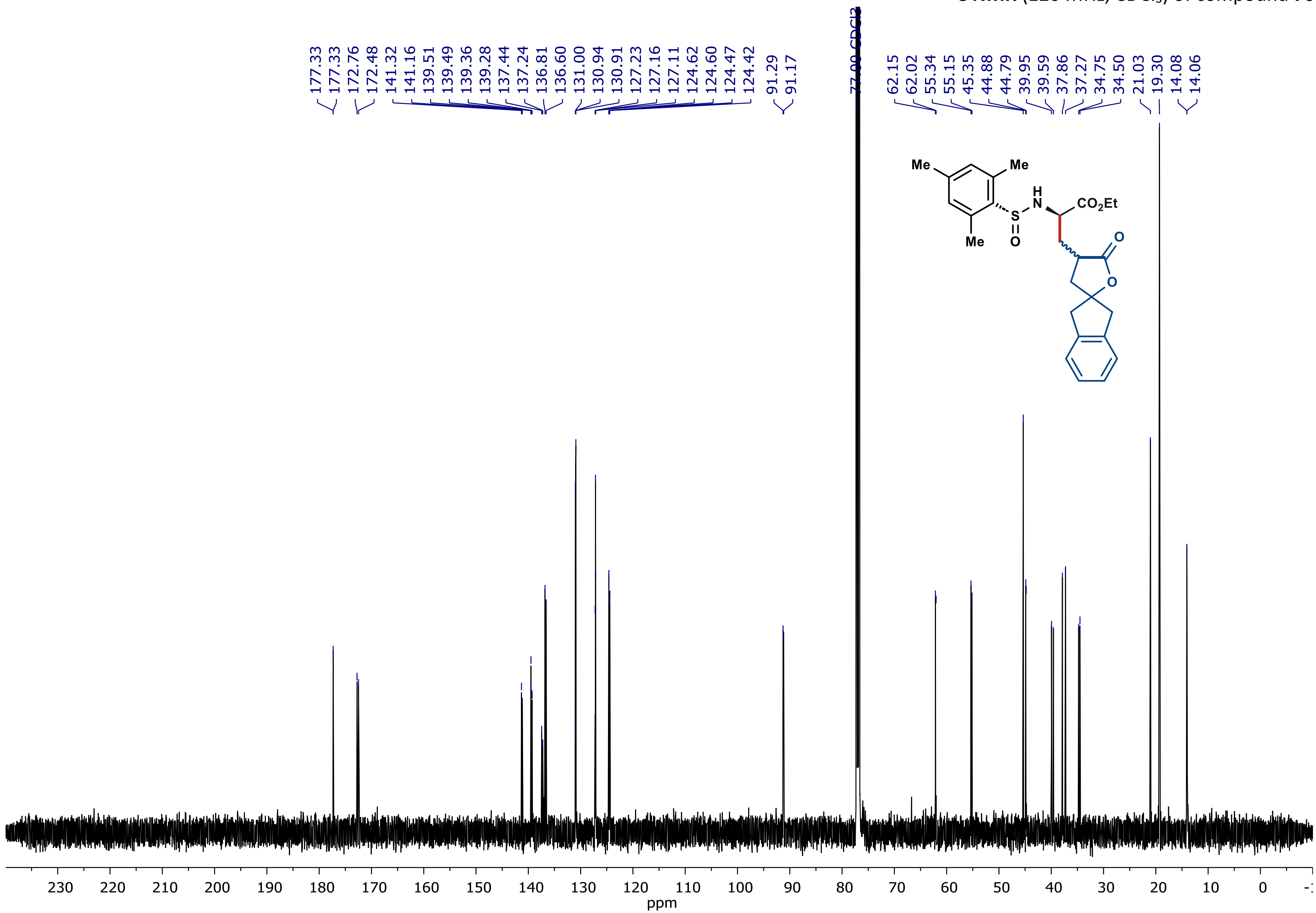
HSQC of compound **7b**



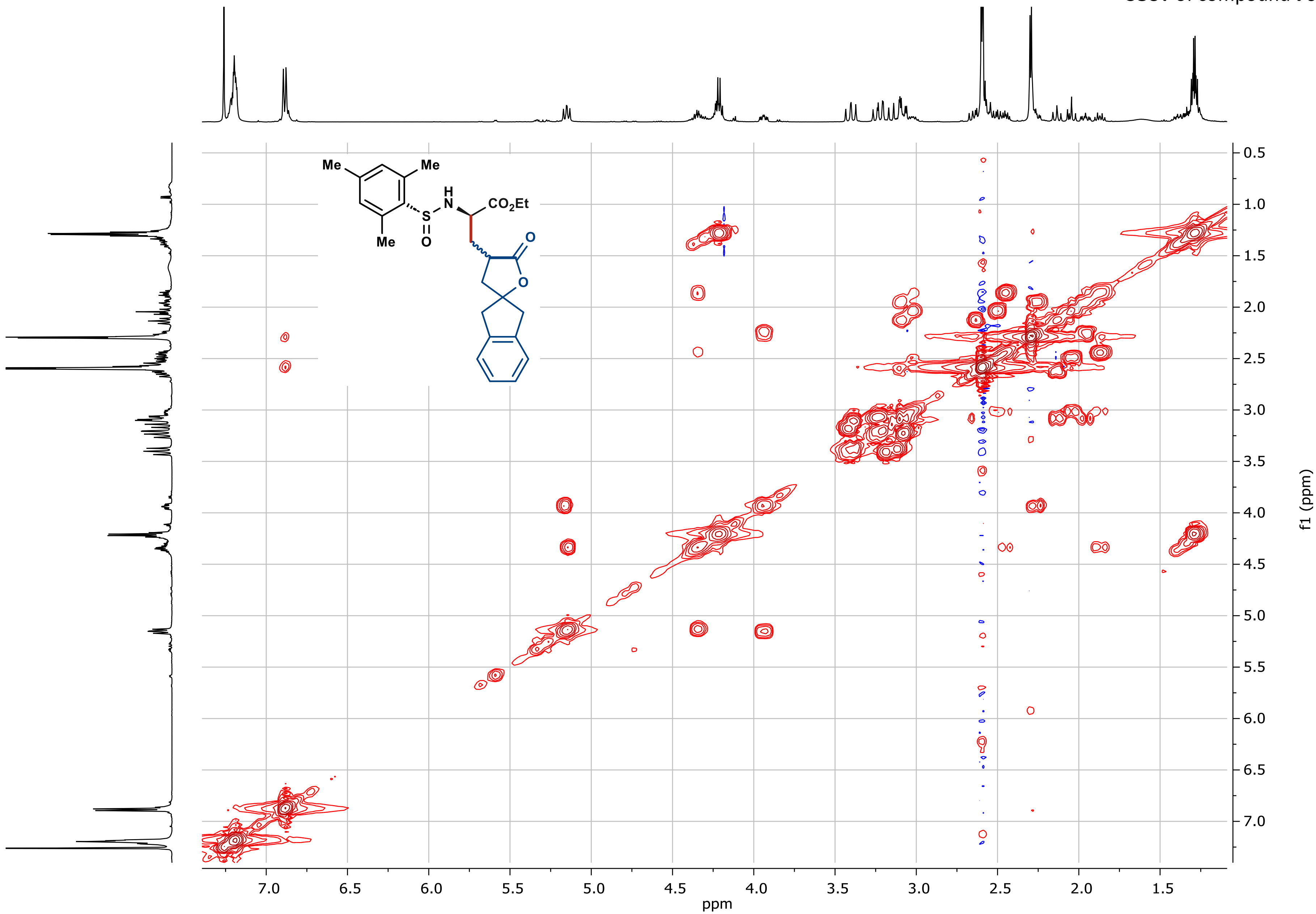
[1]H NMR (500 MHz, $CDCl_3$) of compound **7c**



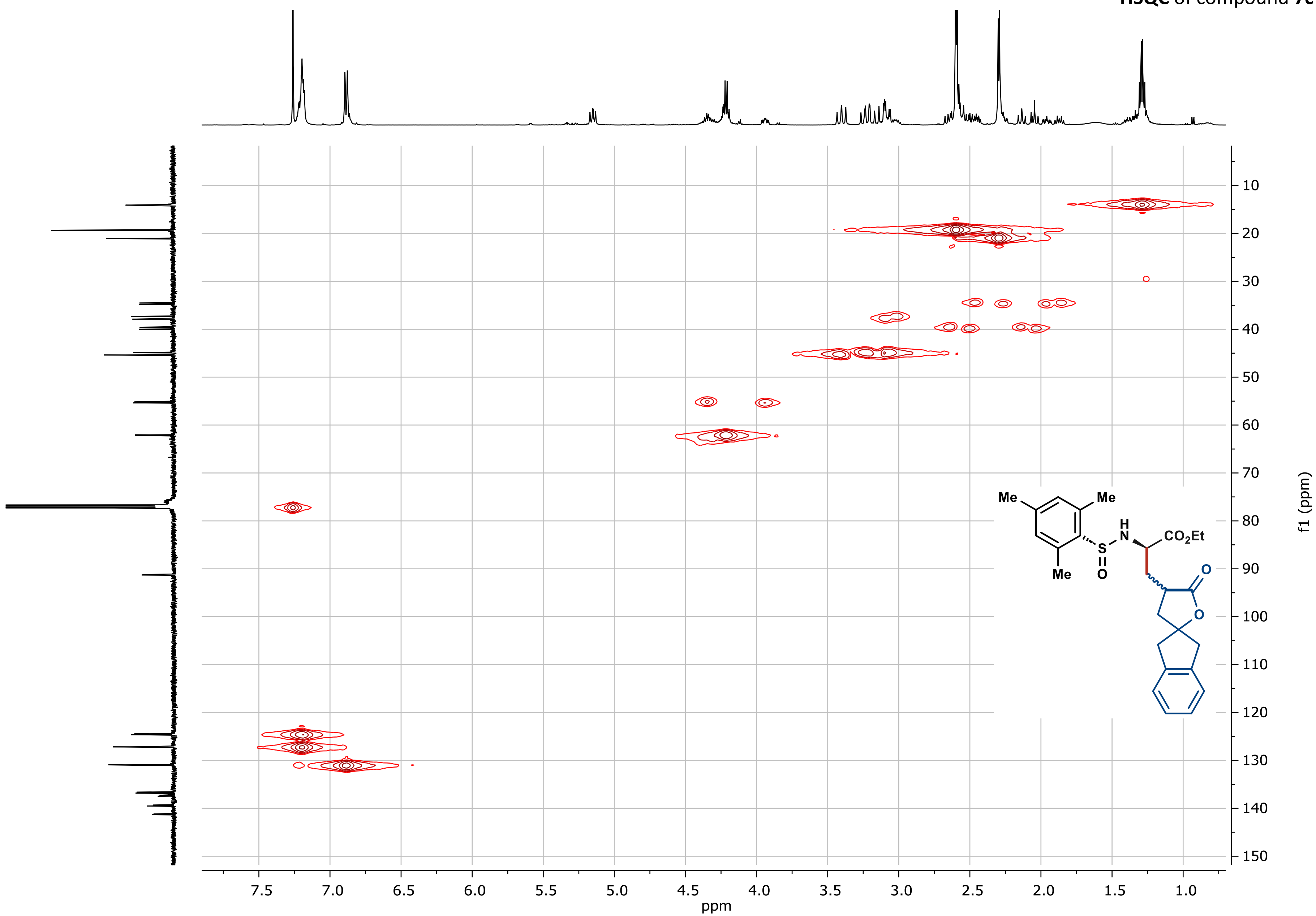
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7c**



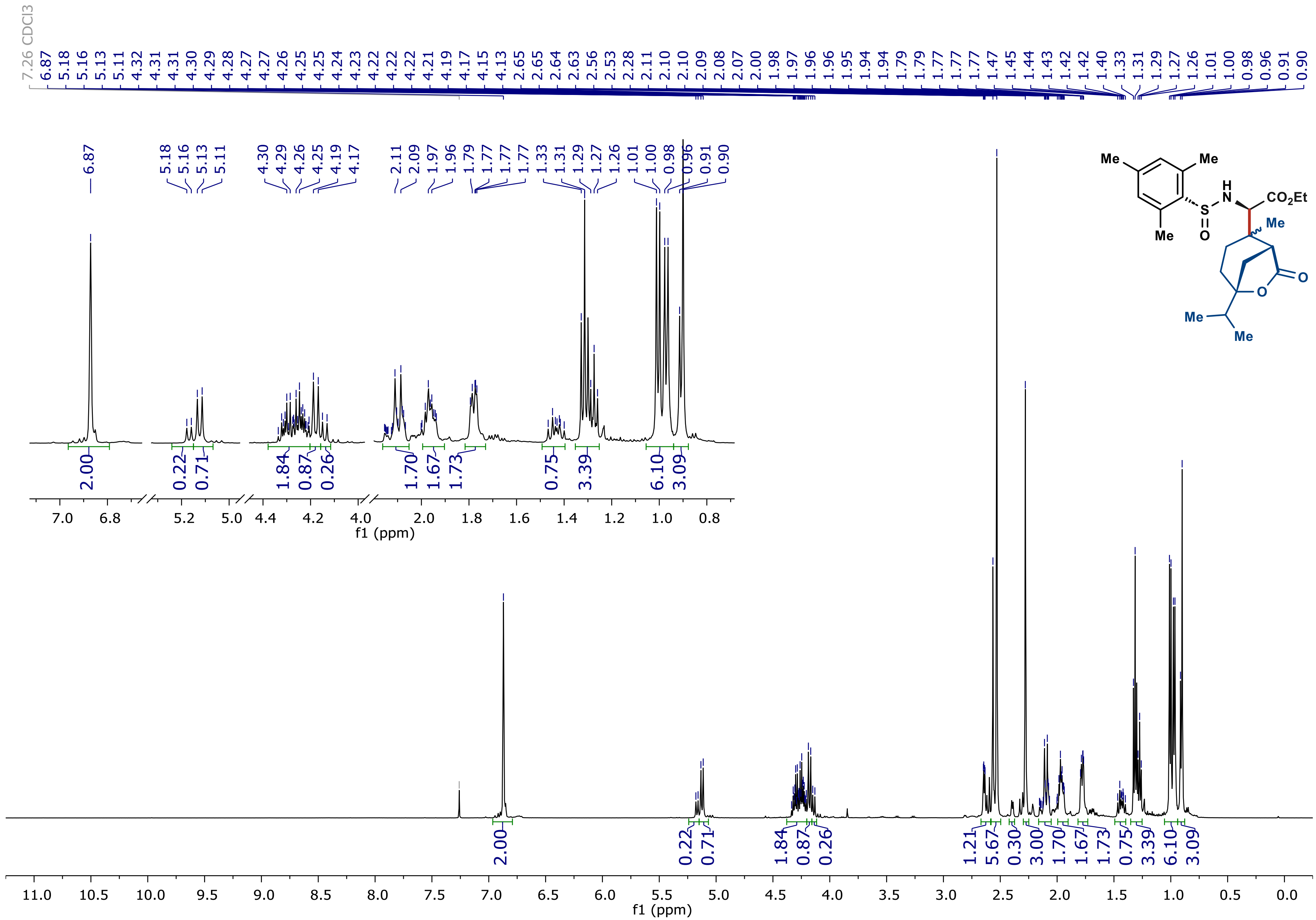
COSY of compound **7c**



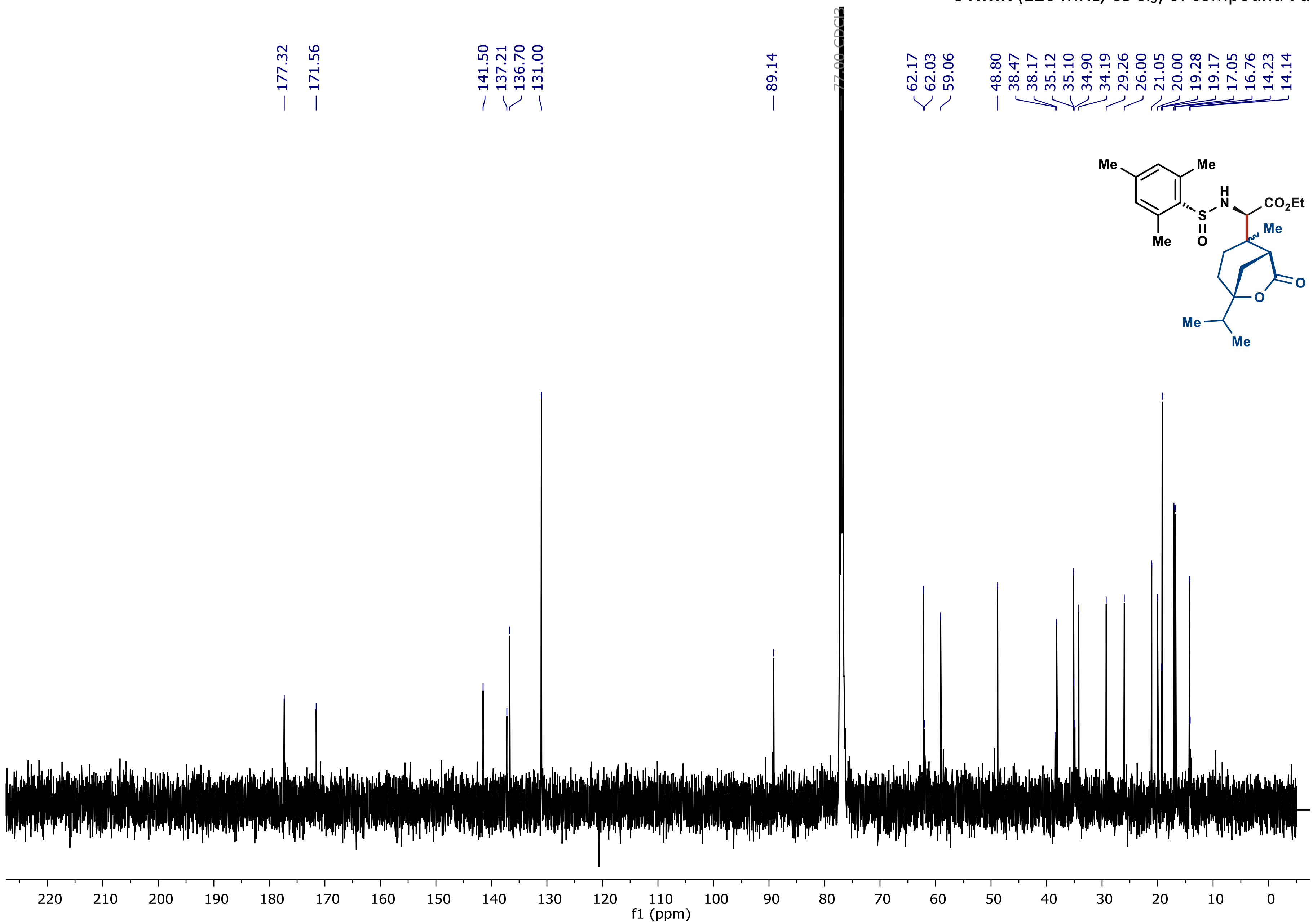
HSQC of compound **7c**



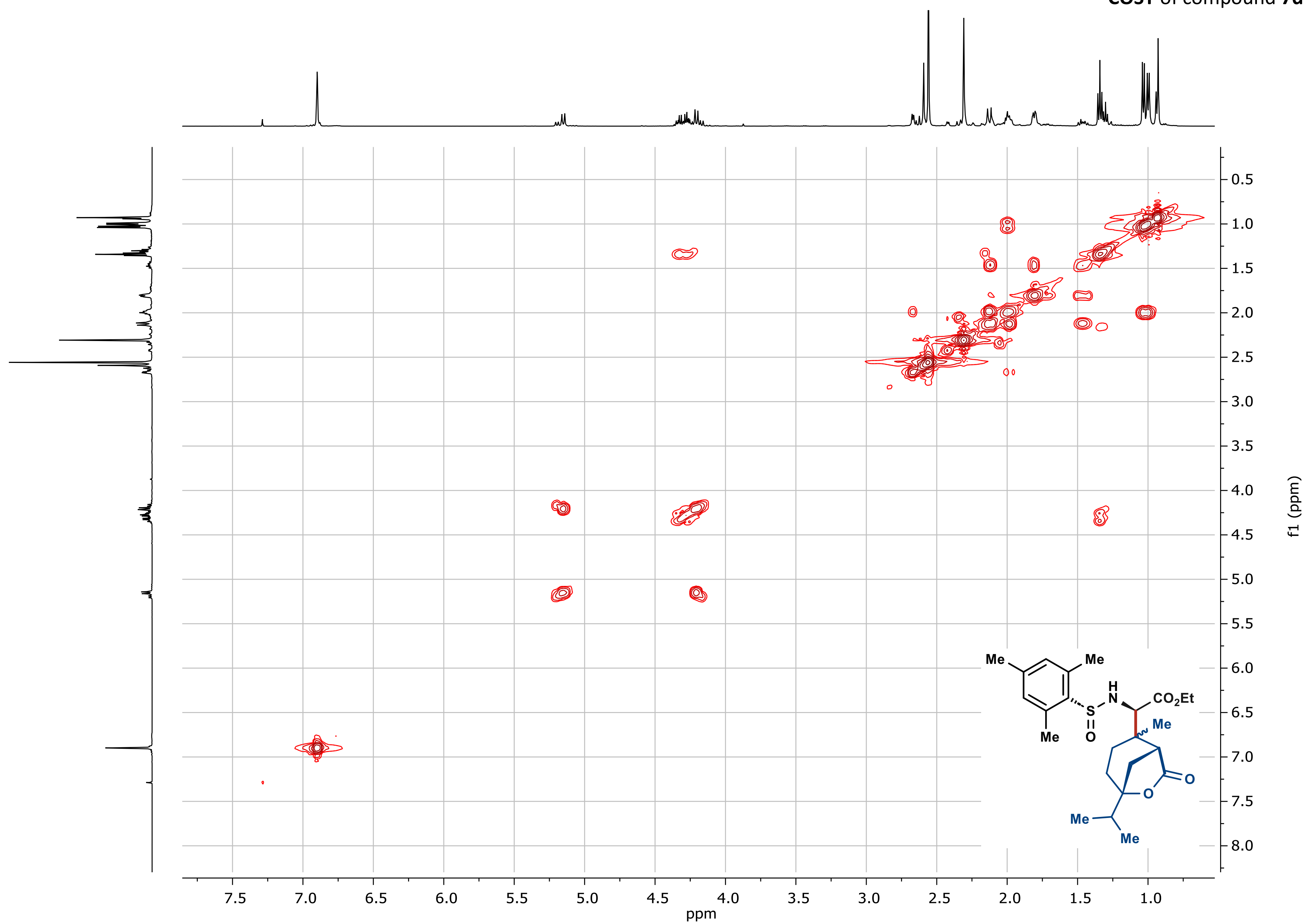
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7d**



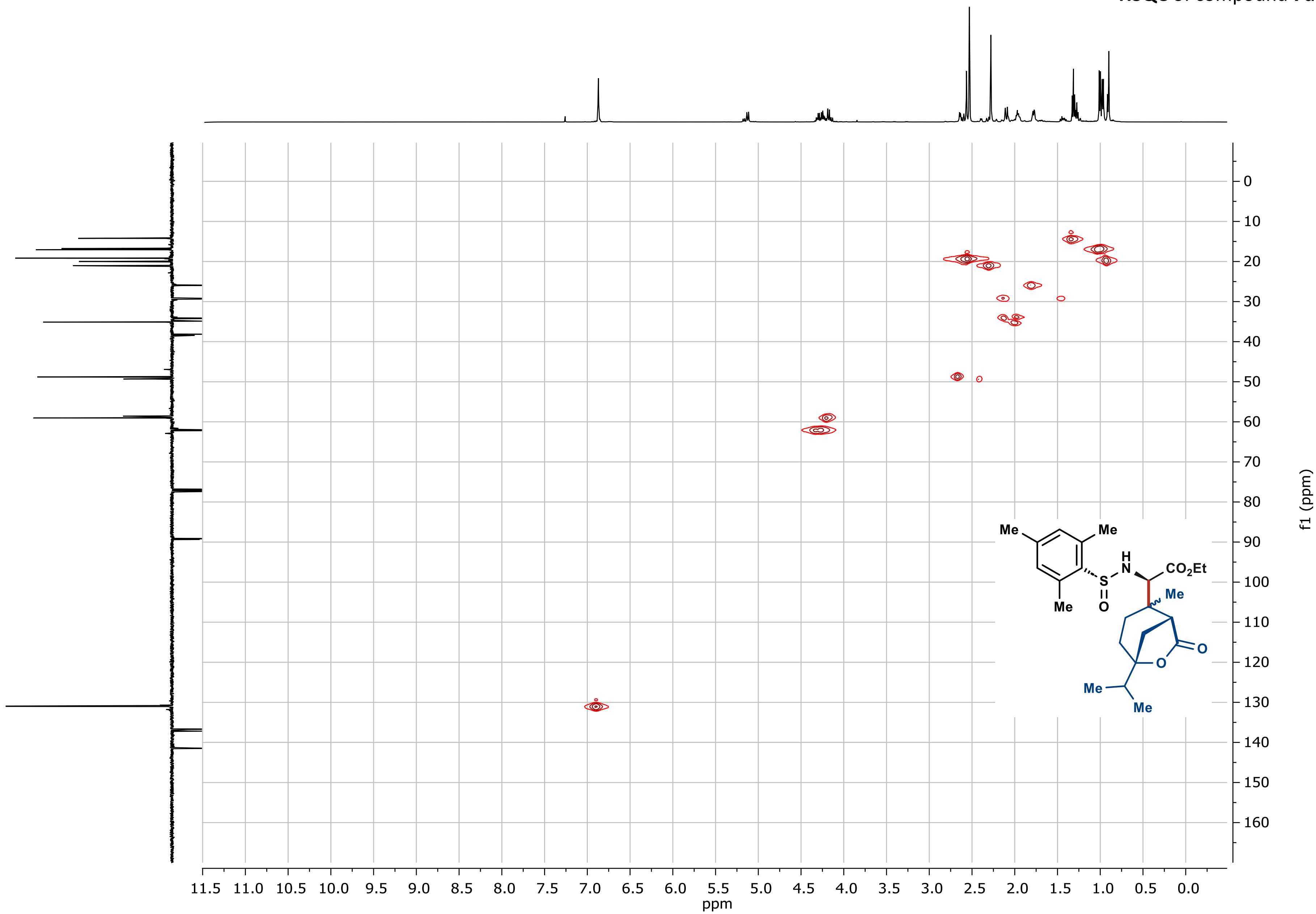
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7d**



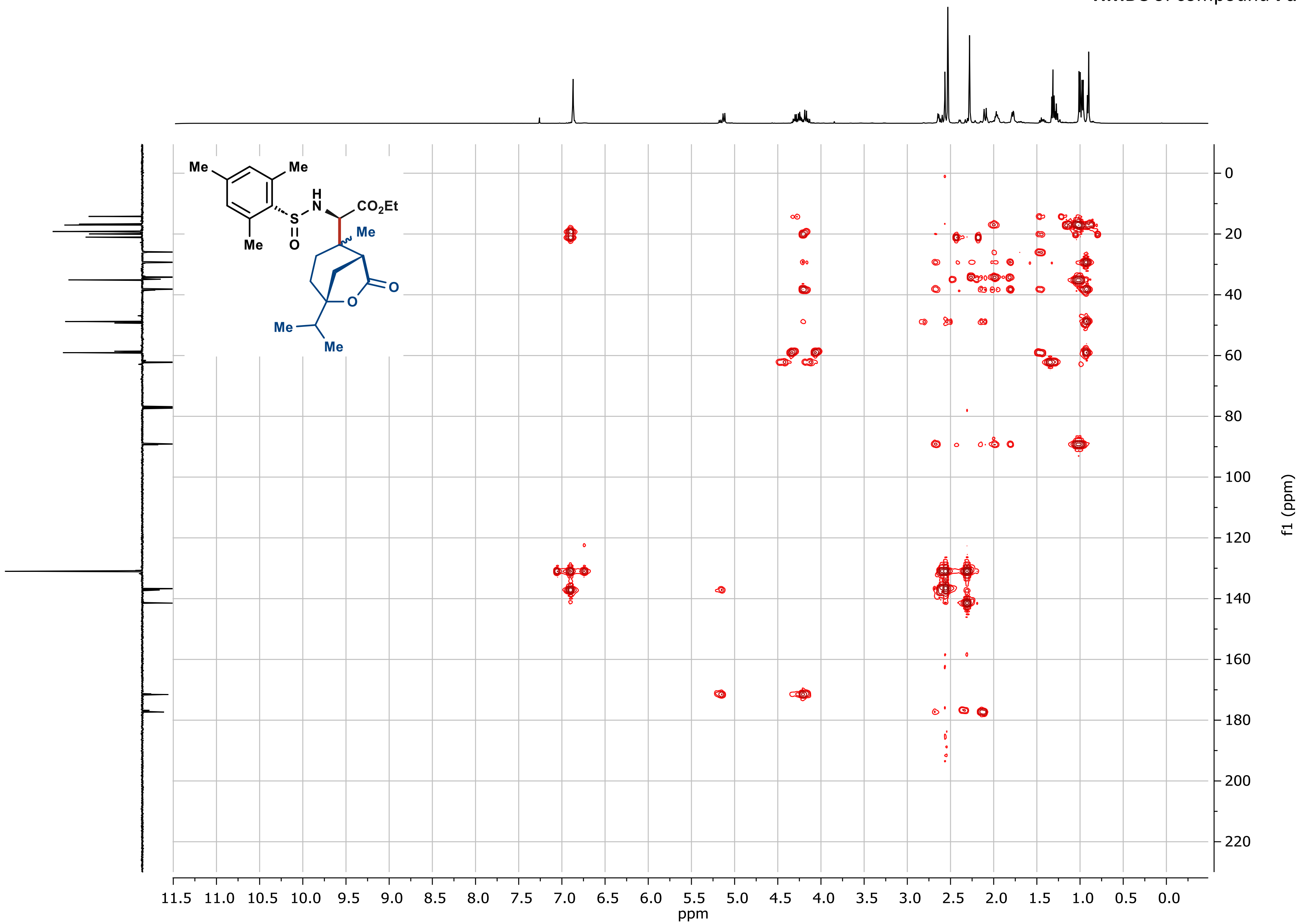
COSY of compound **7d**



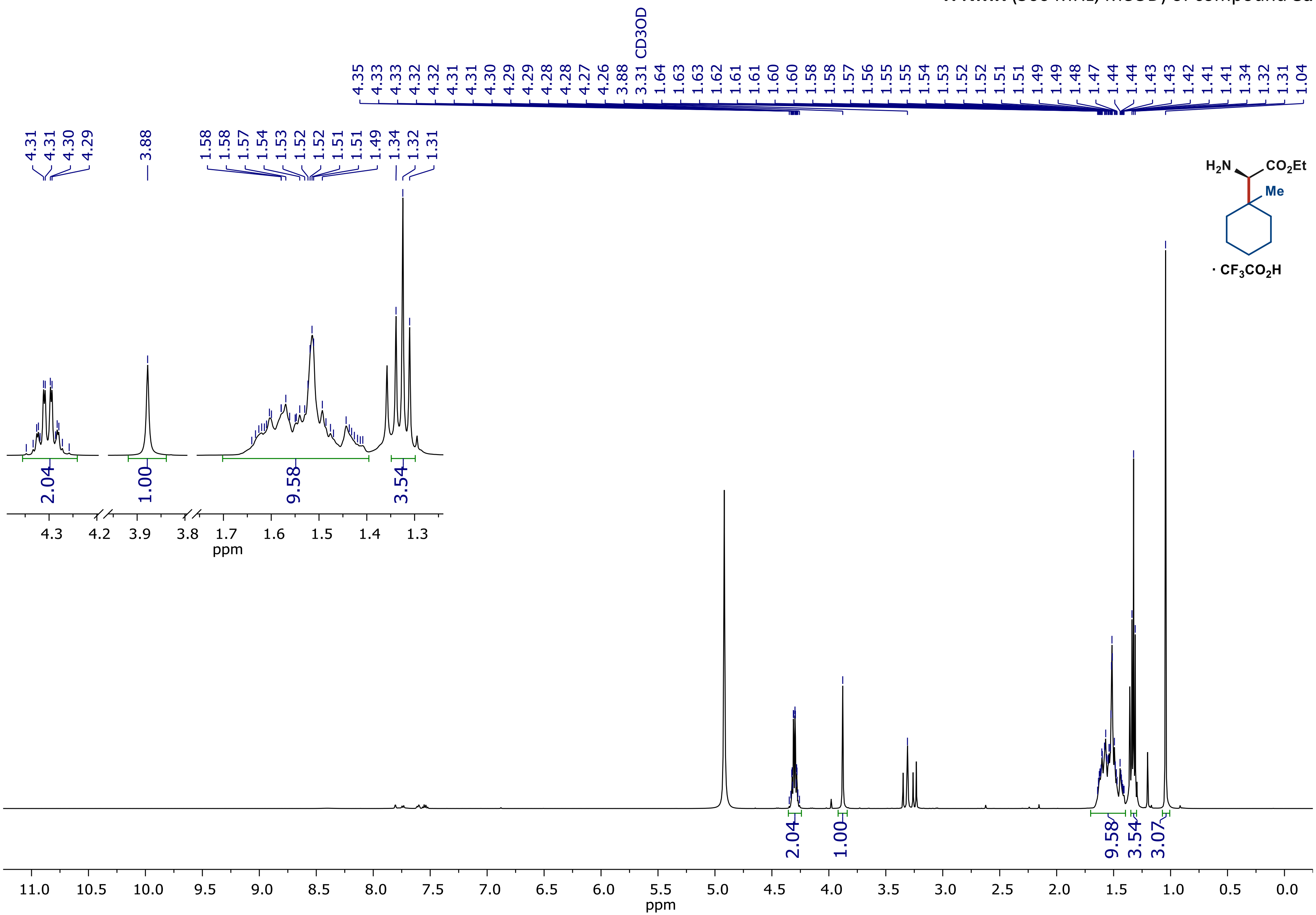
HSQC of compound **7d**



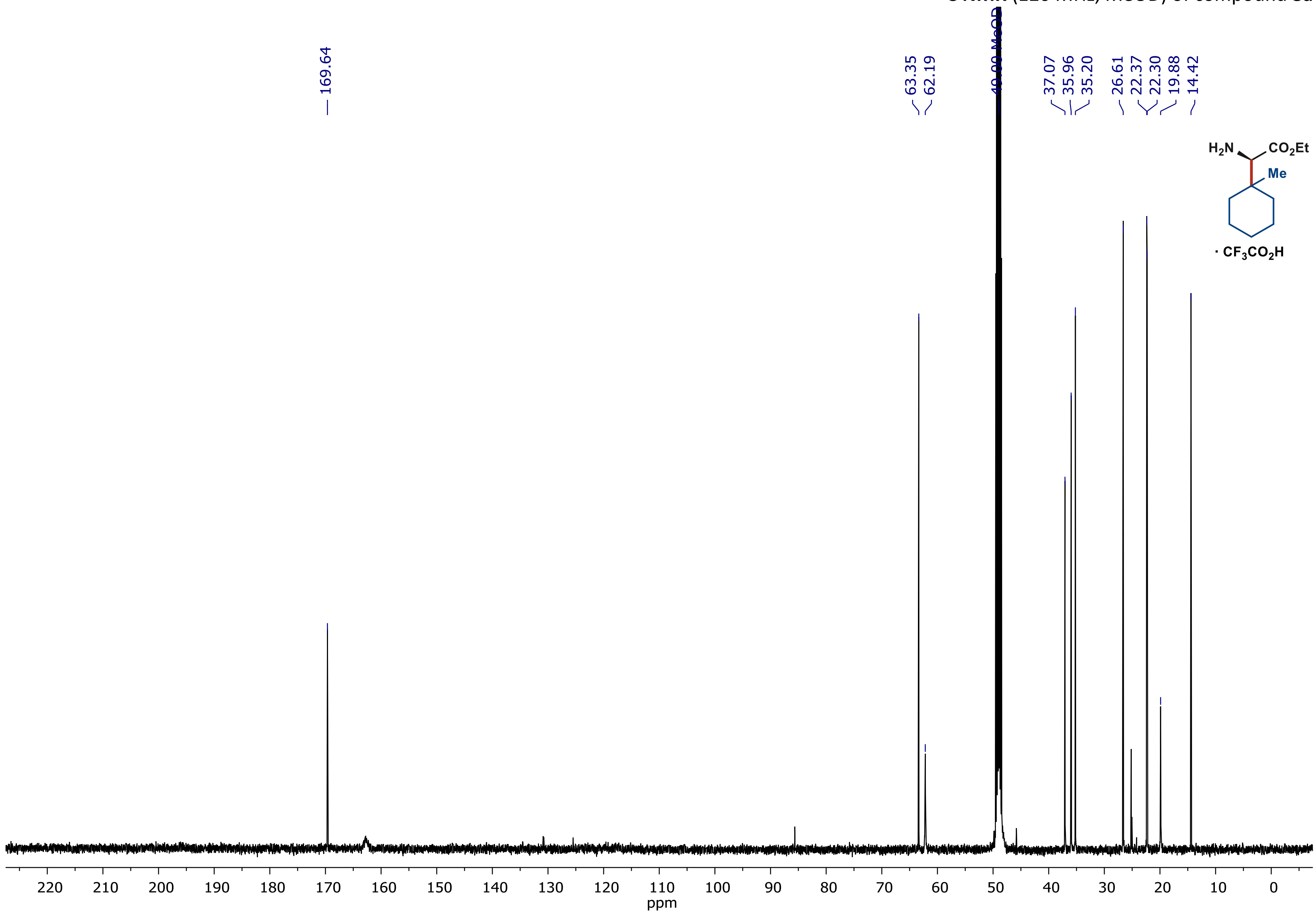
HMBC of compound **7d**



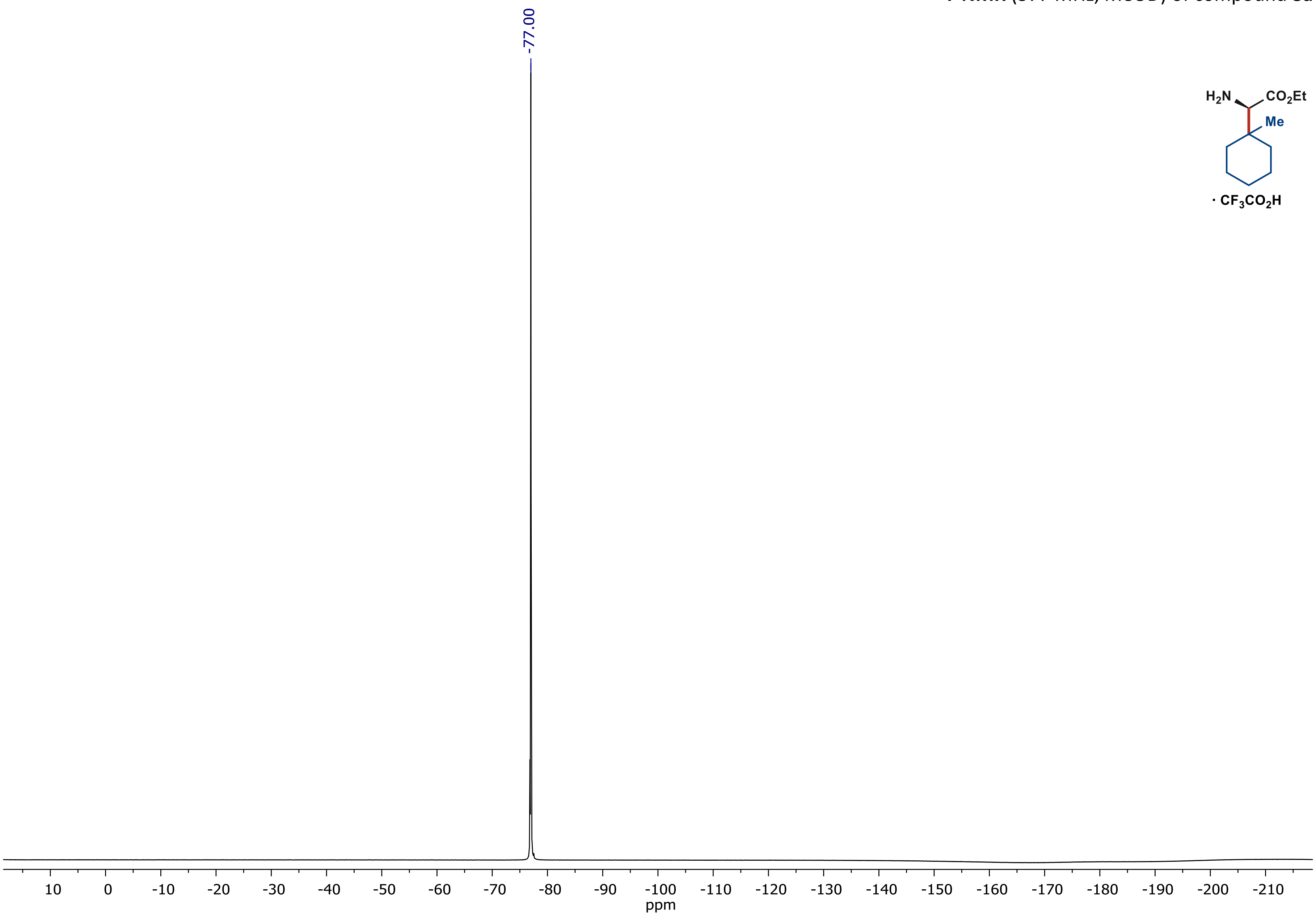
^{1}H NMR (500 MHz, MeOD) of compound **8a**



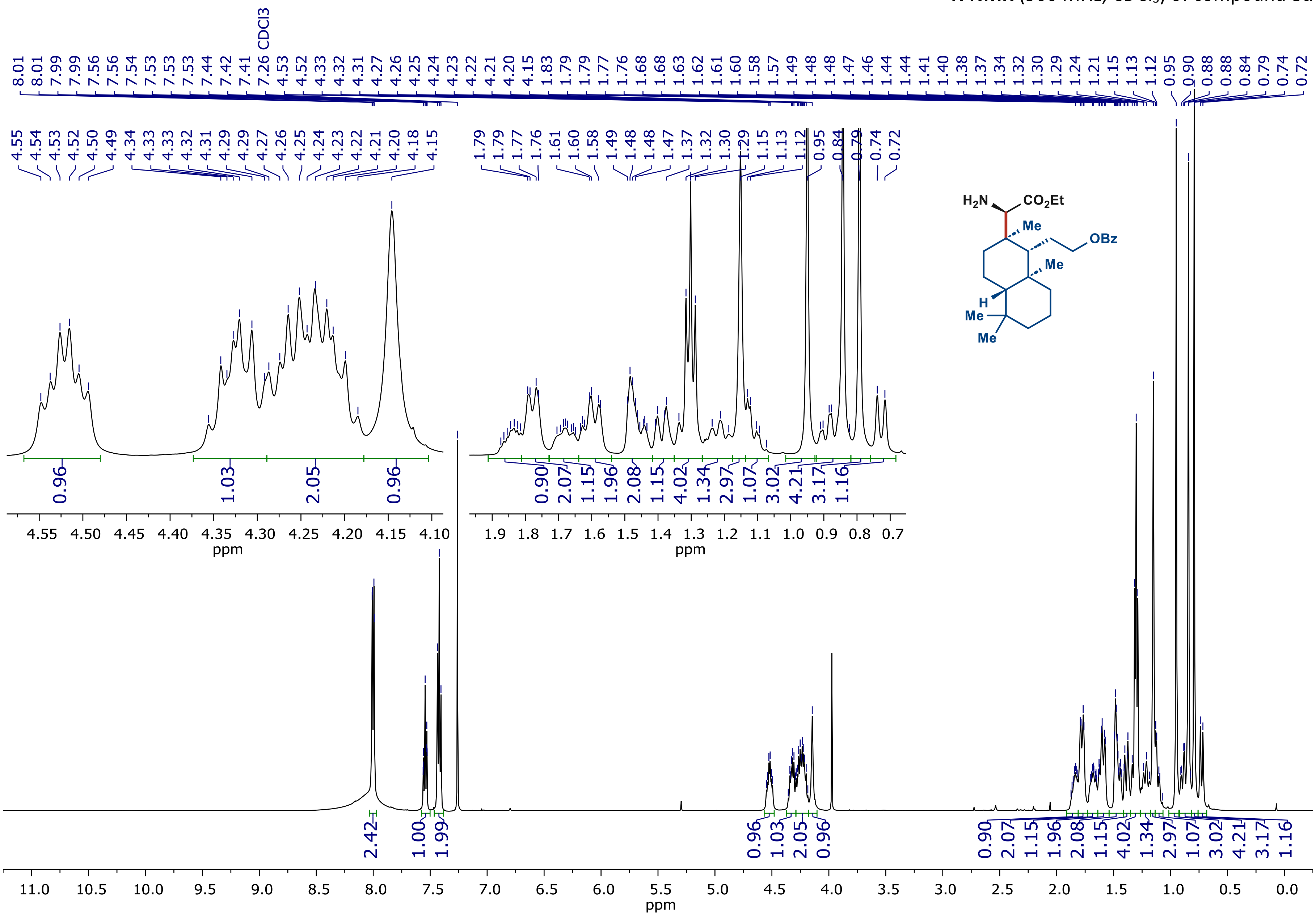
^{13}C NMR (126 MHz, MeOD) of compound **8a**



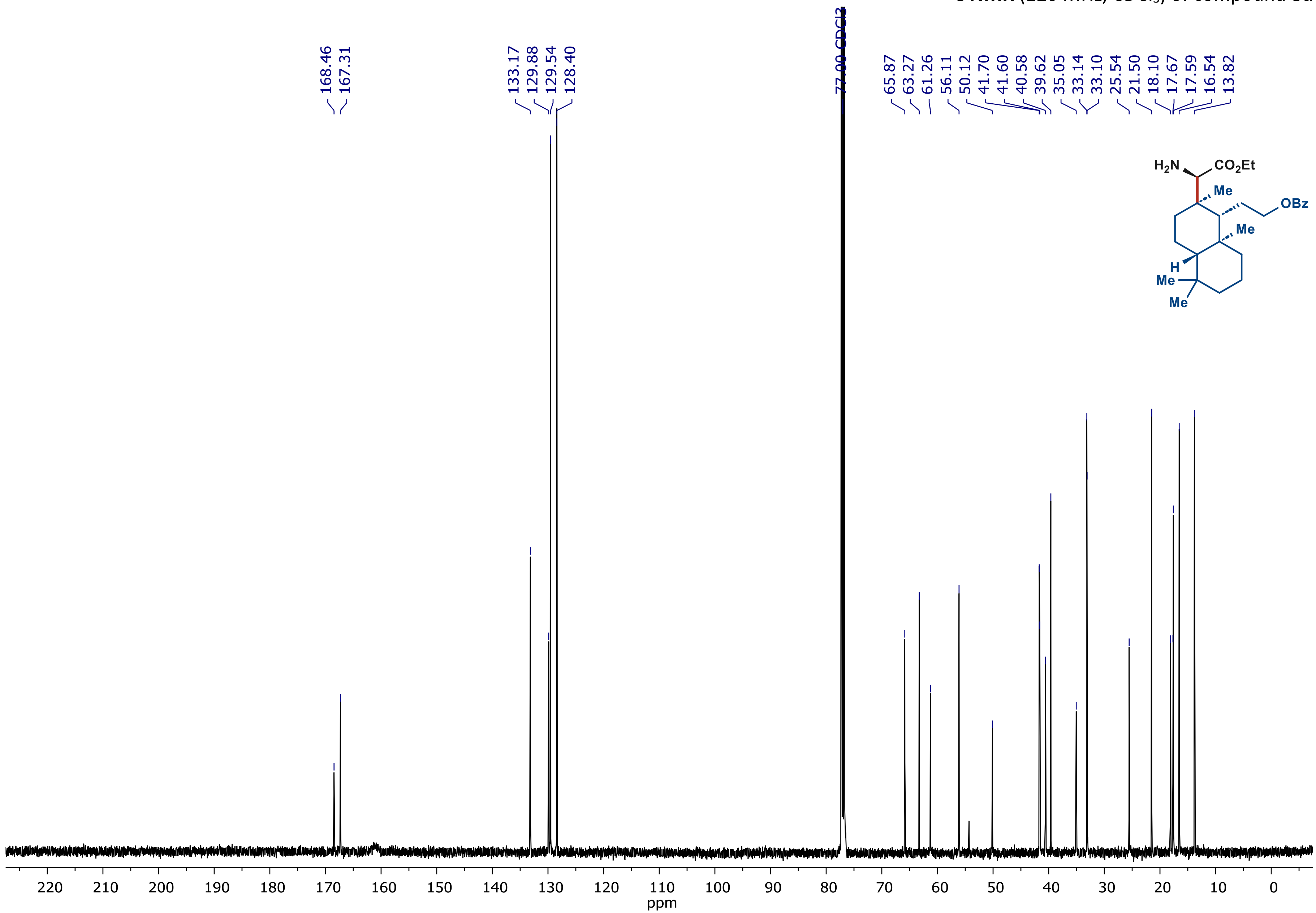
[19]F NMR (377 MHz, MeOD) of compound **8a**



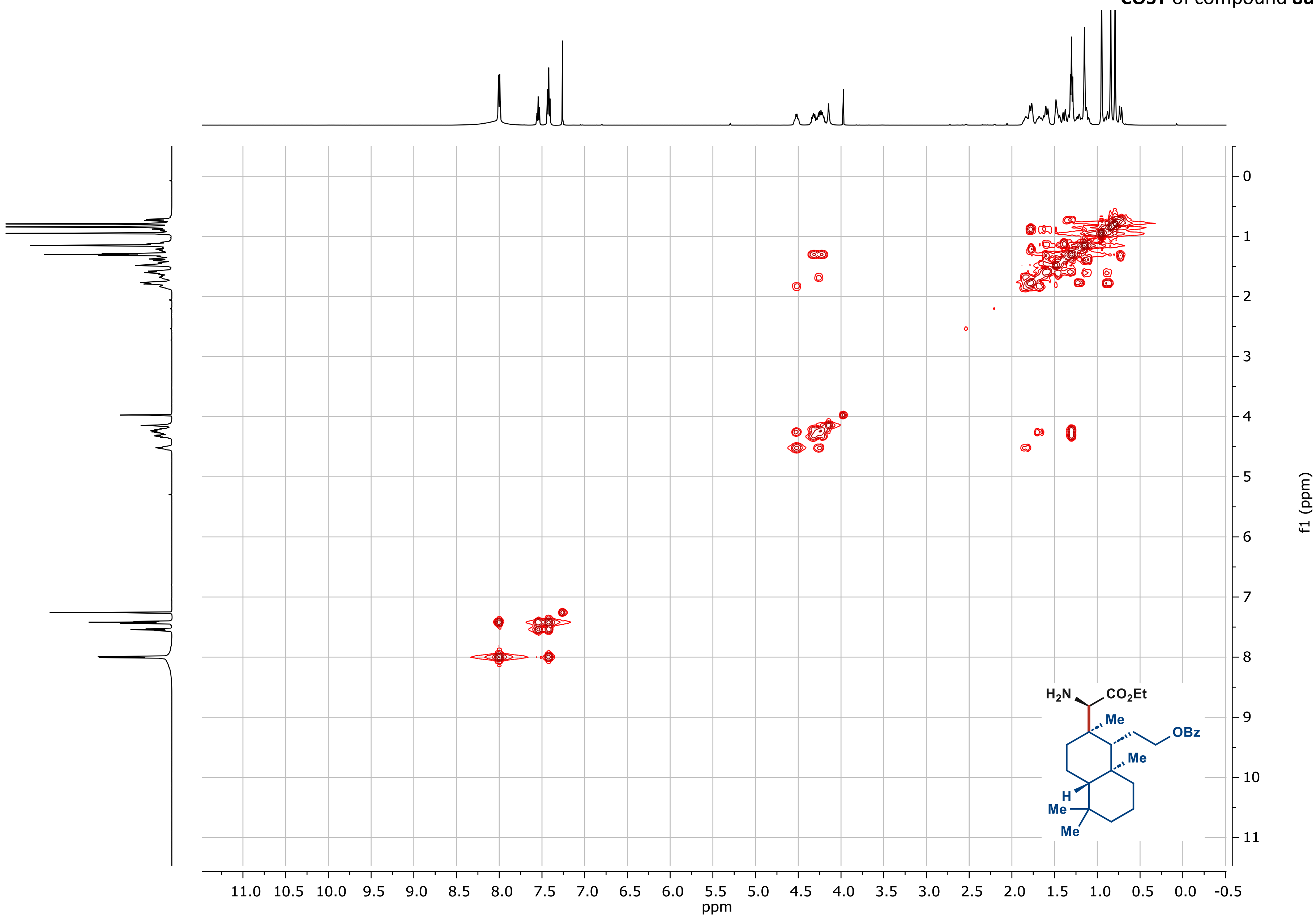
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8d**



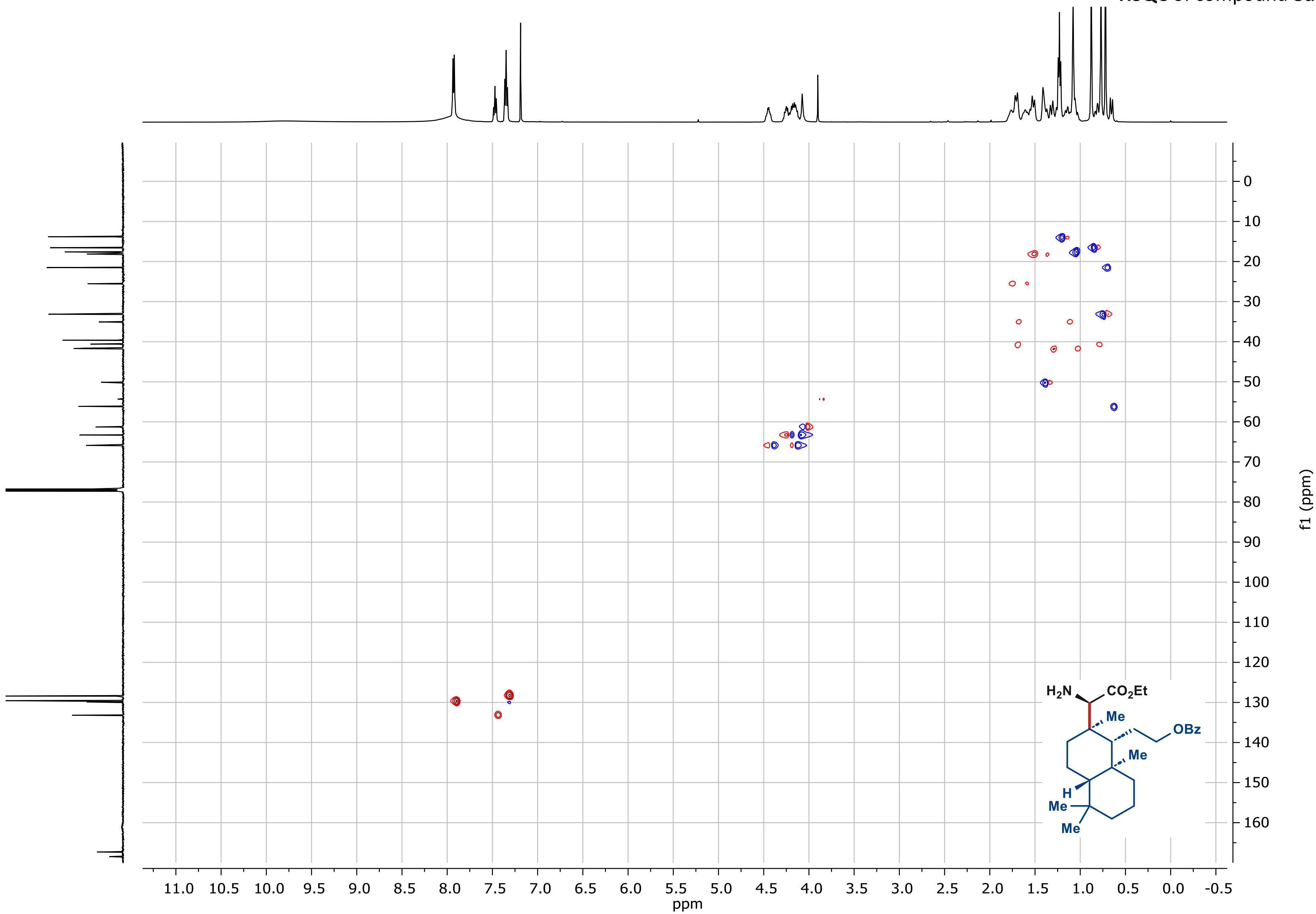
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8d**



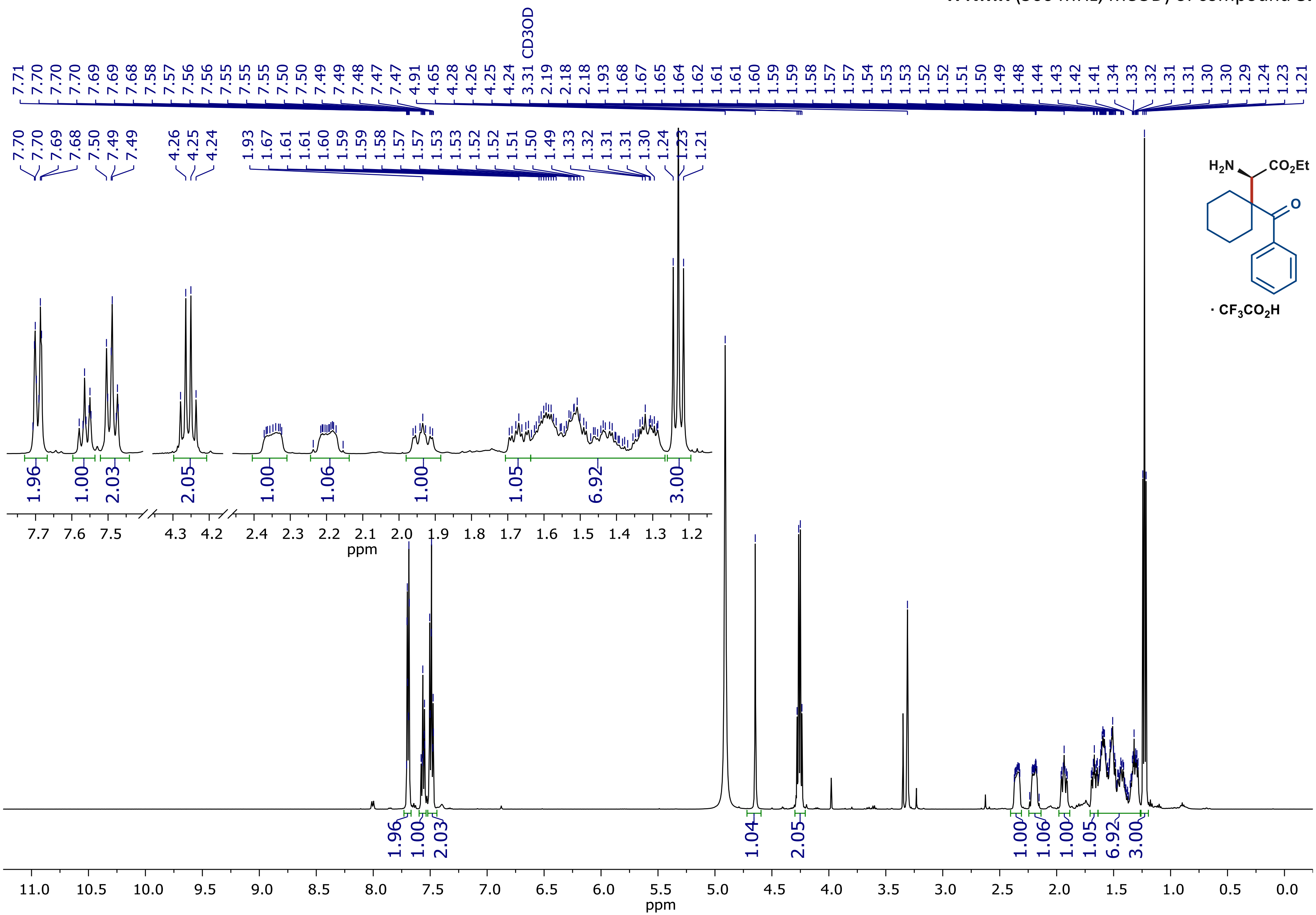
COSY of compound **8d**



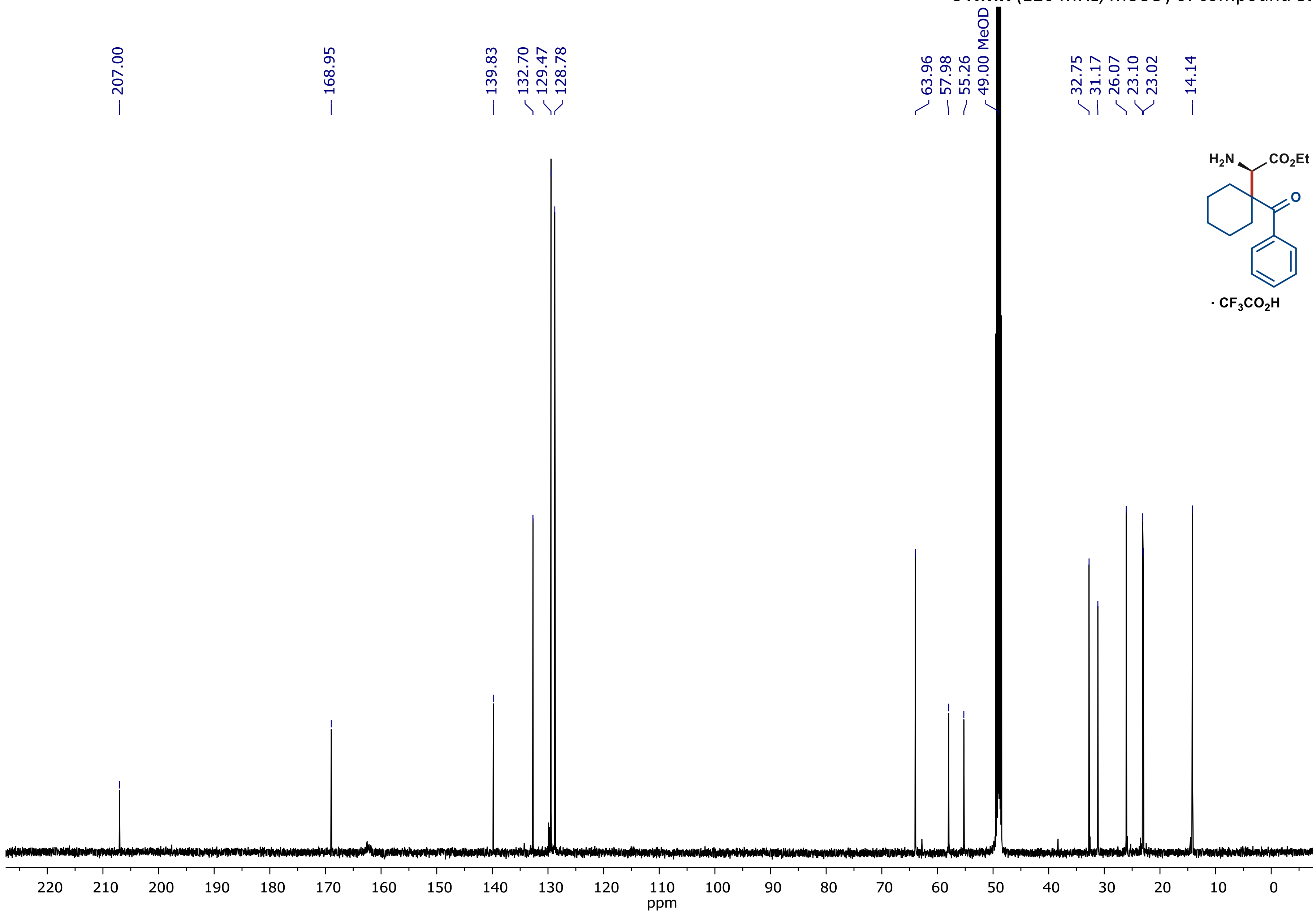
HSQC of compound **8d**



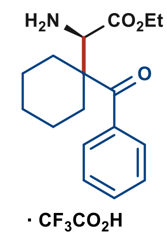
^{1}**H NMR** (500 MHz, MeOD) of compound **8f**

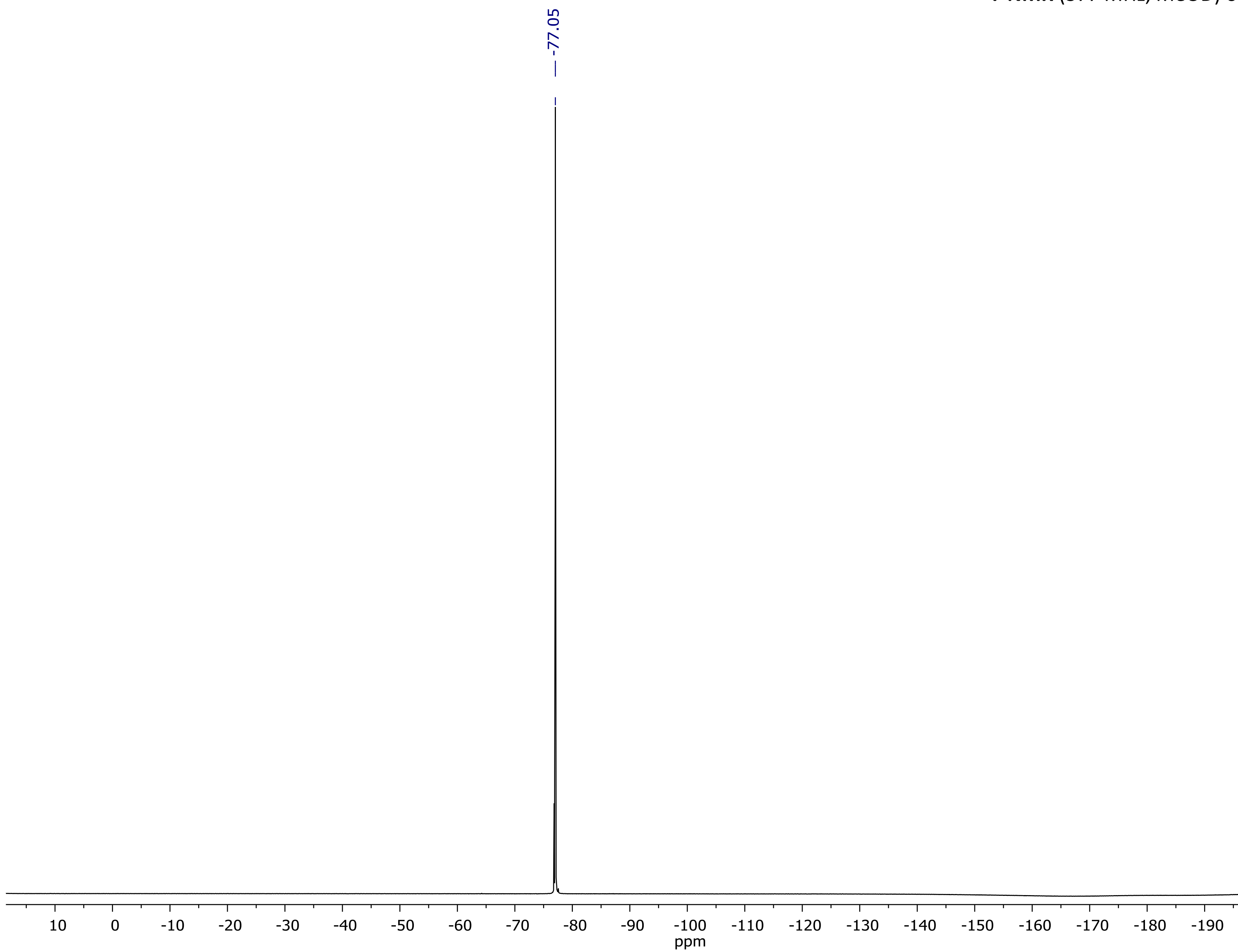


^{13}**C NMR** (126 MHz, MeOD) of compound **8f**

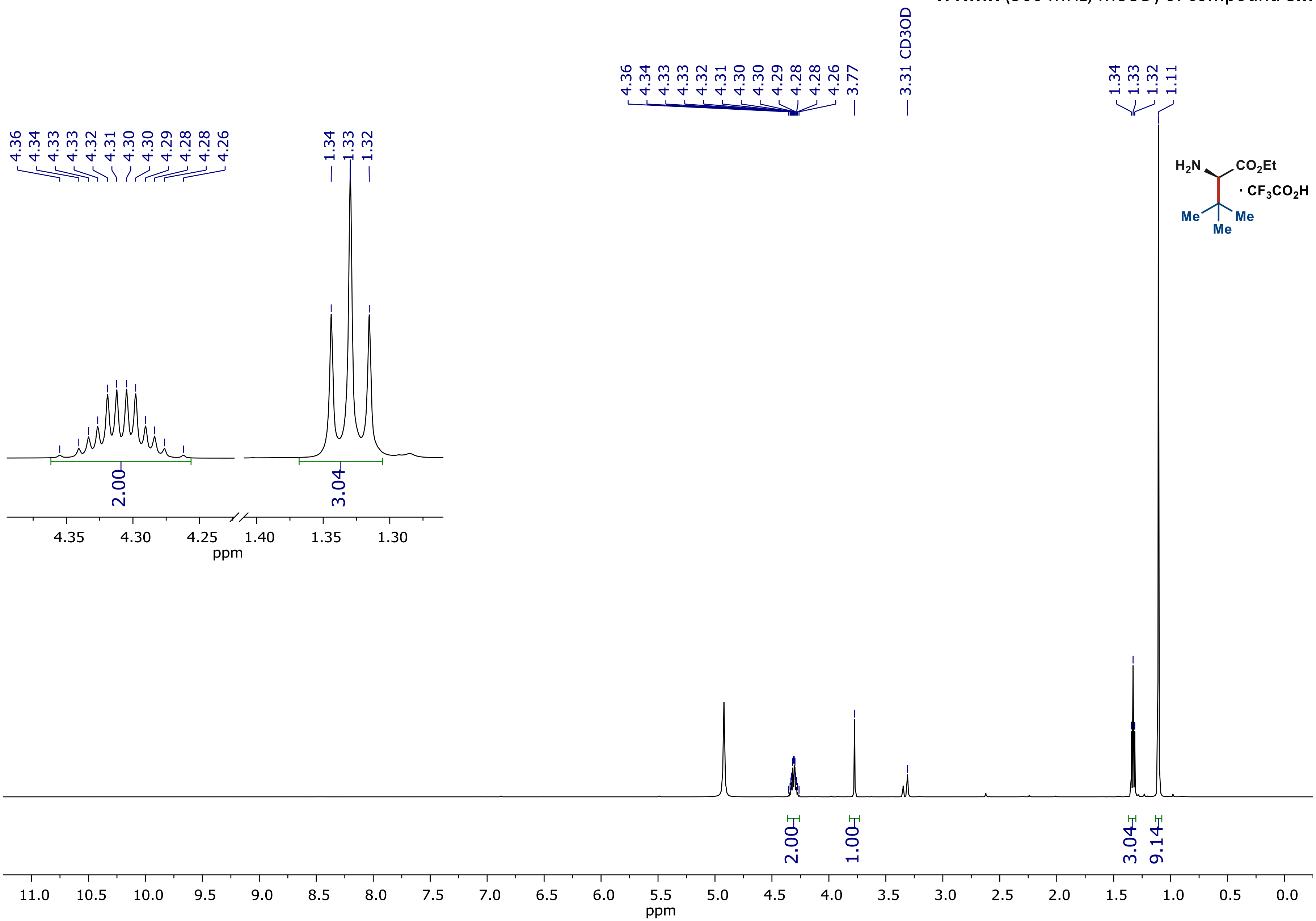


^{19}**F NMR** (377 MHz, MeOD) of compound **8f**

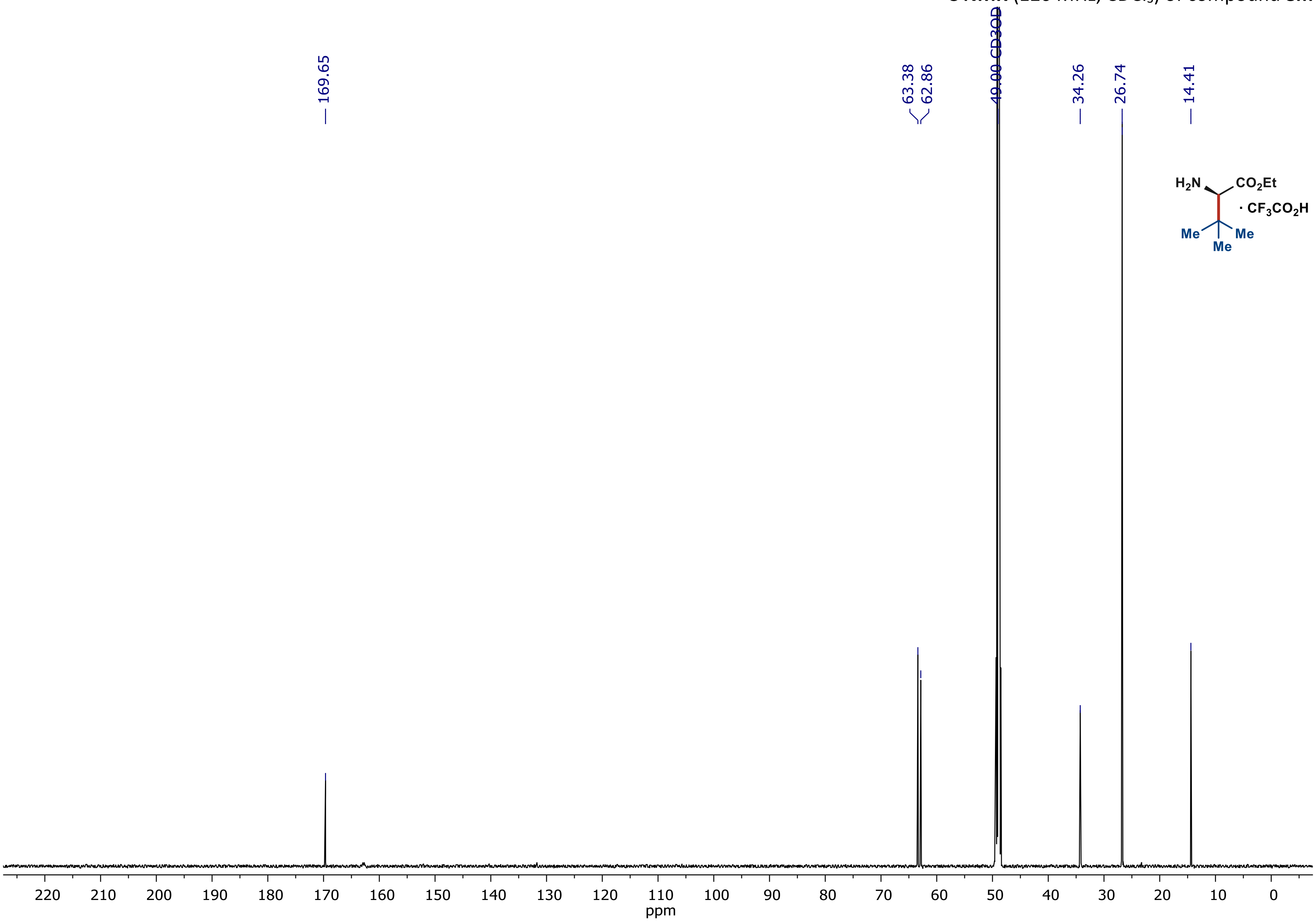




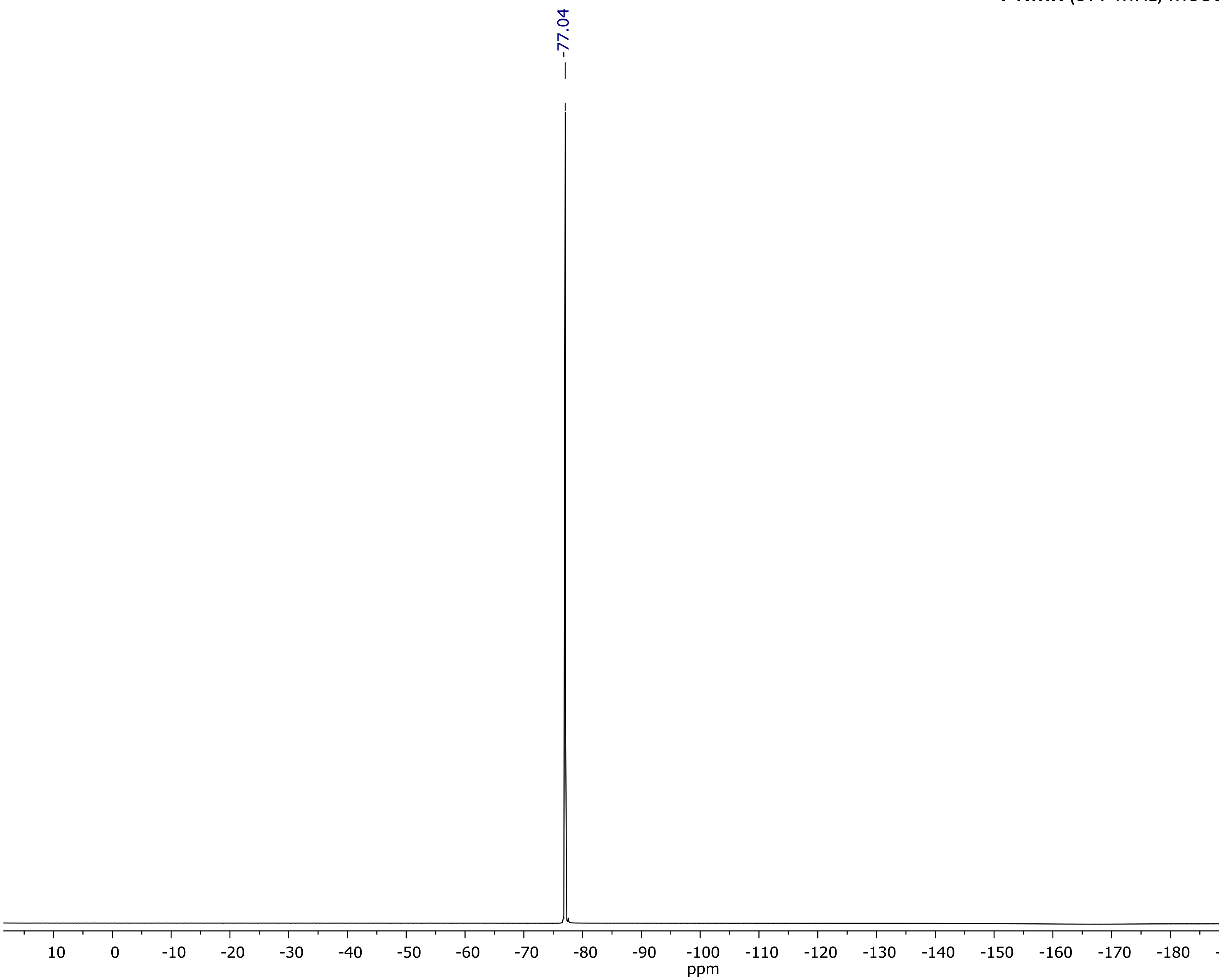
[1]**H NMR** (500 MHz, MeOD) of compound **8m**

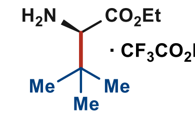


^{13}**C NMR** (126 MHz, $CDCl_3$) of compound **8m**



[19]F NMR (377 MHz, MeOD) of compound **8m**





7. *Cartesian coordinates and energies*

PC4

Charge: 1

Multiplicity: 1

E = −3303.375752

H = −3302.863402

G = −3303.002736

Cartesian coordinates:

Ir	-0.002752	0.001445	0.379864
C	0.597885	0.430411	-2.570519
C	2.141203	1.590581	-1.263331
C	1.189801	0.912904	-3.737561
C	2.767064	2.102684	-2.391234
H	2.482263	1.833363	-0.266327
C	2.287291	1.757398	-3.650698
H	0.802725	0.644607	-4.709071
C	-2.145032	-1.594981	-1.258612
C	-0.580220	-0.467195	-2.568771
C	-2.757997	-2.127590	-2.383743
H	-2.500473	-1.815019	-0.261492
C	-1.157696	-0.972726	-3.733561
C	-2.258473	-1.812023	-3.643676
H	-0.756816	-0.725771	-4.705120
C	1.094015	0.896587	1.823186
C	2.191991	0.345639	2.487730
C	0.690475	2.229076	2.125660
C	2.869442	1.111018	3.421902
H	2.532118	-0.662458	2.293176
C	1.425543	2.942013	3.082012
C	2.515581	2.413071	3.744806
H	3.061848	2.991292	4.476483
C	-1.101709	-0.887634	1.825445
C	-2.199938	-0.333605	2.487001
C	-0.699532	-2.219375	2.132954
C	-2.878404	-1.094885	3.423827
H	-2.539422	0.673904	2.288301
C	-1.435378	-2.927952	3.091827
C	-2.525372	-2.395764	3.752160
H	-3.072091	-2.970699	4.486088
C	2.030394	-2.157434	-0.255935
C	0.454159	-2.725091	1.396101
C	2.647063	-3.391180	-0.155010
H	2.387736	-1.409165	-0.946820
C	1.051953	-3.986634	1.529764
C	2.148555	-4.322429	0.756697
H	0.654497	-4.696198	2.236070
H	2.607804	-5.297613	0.857377
C	-2.039482	2.155166	-0.263680
C	-0.464195	2.730095	1.387245
C	-2.663949	3.383946	-0.159049
H	-2.395524	1.403551	-0.951486
C	-1.068754	3.988716	1.522827
C	-2.168764	4.317946	0.752863
H	-0.676367	4.698484	2.231745
H	-2.638084	5.287643	0.862061
F	-3.944466	-0.549712	4.058867
F	-1.093724	-4.201615	3.412576
F	1.083578	4.216985	3.397131
F	3.935452	0.569027	4.059682
C	3.856350	-3.701883	-0.988132
C	-3.848089	3.717116	-1.018742
F	-4.896876	4.148881	-0.277887
F	-4.276236	2.661807	-1.742495
F	-3.564768	4.712409	-1.896325
F	5.003640	-3.591430	-0.270704
F	3.822977	-4.967009	-1.465647
F	3.977042	-2.873194	-2.047726
N	1.085451	0.773693	-1.351368
N	-1.083938	-0.784842	-1.349592
N	0.968052	-1.831232	0.494339
N	-0.974785	1.834019	0.486589
C	-3.972659	-3.005506	-2.236346
C	3.975457	2.988547	-2.239930
F	4.035250	3.920829	-3.213826
F	3.984575	3.634715	-1.055535
F	5.124601	2.273452	-2.308972

F	-4.050772	-3.564365	-1.011196
F	-5.115734	-2.302953	-2.425369
F	-3.974930	-4.006758	-3.142219
H	2.752465	2.144694	-4.547685
H	-2.712230	-2.217158	-4.538723

PC4*

Charge: 1

Multiplicity: 3

E = −3303.293702

H = −3302.784

G = −3302.925035

Cartesian coordinates:

Ir	0.000009	-0.000037	0.461912
C	0.645940	0.294743	-2.503990
C	2.429226	1.126378	-1.190903
C	1.372979	0.635171	-3.677686
C	3.157915	1.476293	-2.307079
H	2.823667	1.299945	-0.200243
C	2.607784	1.215356	-3.591855
H	0.944161	0.436787	-4.649495
C	-2.429290	-1.126208	-1.190949
C	-0.646050	-0.294422	-2.504002
C	-3.158032	-1.475963	-2.307140
H	-2.823691	-1.299903	-0.200296
C	-1.373141	-0.634689	-3.677711
C	-2.607950	-1.214869	-3.591906
H	-0.944361	-0.436185	-4.649513
C	1.312923	0.689296	1.806070
C	2.315588	-0.060832	2.437017
C	1.190904	2.093089	2.067900
C	3.160206	0.572433	3.327755
H	2.441699	-1.117908	2.249394
C	2.077527	2.660912	2.982772
C	3.066159	1.928559	3.621830
H	3.739155	2.403226	4.322628
C	-1.312871	-0.689559	1.806010
C	-2.315534	0.060480	2.437064
C	-1.190828	-2.093381	2.067665
C	-3.160122	-0.572903	3.327748
H	-2.441667	1.117576	2.249566
C	-2.077418	-2.661324	2.982495
C	-3.066045	-1.929062	3.621664
H	-3.739015	-2.403819	4.322425
C	1.582545	-2.490438	-0.233933
C	-0.136783	-2.798883	1.342254
C	1.908537	-3.835964	-0.196815
H	2.111158	-1.795199	-0.868949
C	0.161061	-4.163980	1.410661
C	1.188054	-4.685325	0.640031
H	-0.409076	-4.809740	2.057521
H	1.418881	-5.741951	0.686493
C	-1.582532	2.490463	-0.233568
C	0.136845	2.798693	1.342607
C	-1.908506	3.835987	-0.196277
H	-2.111175	1.795308	-0.868654
C	-0.160983	4.163785	1.411191
C	-1.187989	4.685237	0.640653
H	0.409180	4.809457	2.058115
H	-1.418799	5.741862	0.687251
F	-4.119726	0.140877	3.946263
F	-2.006149	-3.973785	3.284076
F	2.006287	3.973339	3.284508
F	4.119812	-0.141435	3.946167
C	3.047415	-4.360066	-1.027934
C	-3.047391	4.360213	-1.027308
F	-4.152653	4.577869	-0.273464
F	-3.400121	3.503792	-2.007813
F	-2.734919	5.539156	-1.608480
F	4.152743	-4.577651	-0.274166
F	2.735008	-5.539014	-1.609126
F	3.400012	-3.503579	-2.008430
N	1.220014	0.546014	-1.262835
N	-1.220072	-0.545854	-1.262855
N	0.594437	-1.990123	0.517241

N	-0.594409	1.990043	0.517516
C	-4.500992	-2.101358	-2.180164
C	4.500874	2.101685	-2.180077
F	-4.568068	-3.311387	-2.805622
F	-4.871512	-2.305792	-0.895604
F	-5.480646	-1.344487	-2.753920
F	4.567923	3.311775	-2.805419
F	5.480519	1.344878	-2.753933
F	4.871427	2.305996	-0.895507
H	-3.157137	-1.472467	-4.488630
H	3.156931	1.473077	-4.488569

PC4 ^{red}

Charge: 1

Multiplicity: 2

E = −3303.514387

H = −3303.005126

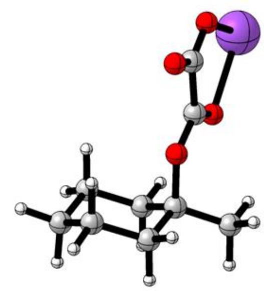
G = −3303.144879

Cartesian coordinates:

Ir	-0.000002	0.000054	0.400714
C	-0.589870	-0.398946	-2.539740
C	-2.217464	-1.500355	-1.228081
C	-1.251199	-0.853351	-3.715566
C	-2.886042	-1.965795	-2.346707
H	-2.570298	-1.732352	-0.231947
C	-2.379621	-1.622385	-3.629592
H	-0.859256	-0.592466	-4.688617
C	2.217565	1.500242	-1.228145
C	0.590116	0.398559	-2.539757
C	2.886255	1.965467	-2.346792
H	2.570291	1.732439	-0.232019
C	1.251569	0.852732	-3.715603
C	2.379975	1.621793	-3.629663
H	0.859733	0.591647	-4.688643
C	-1.108854	-0.892433	1.841098
C	-2.196331	-0.336314	2.522874
C	-0.722263	-2.234668	2.130746
C	-2.875531	-1.100577	3.454859
H	-2.524262	0.678240	2.337787
C	-1.458053	-2.946336	3.086816
C	-2.536094	-2.410703	3.764040
H	-3.083218	-2.988234	4.495617
C	1.108760	0.892724	1.841053
C	2.196213	0.336698	2.522943
C	0.722134	2.234985	2.130529
C	2.875360	1.101080	3.454870
H	2.524166	-0.677873	2.337987
C	1.457871	2.946775	3.086549
C	2.535891	2.411237	3.763883
H	3.082974	2.988862	4.495415
C	-1.992097	2.169266	-0.276030
C	-0.419646	2.744857	1.377078
C	-2.587608	3.416177	-0.206628
H	-2.348975	1.409087	-0.954733
C	-0.997020	4.019538	1.479548
C	-2.081460	4.358041	0.690506
H	-0.592042	4.737316	2.173292
H	-2.524284	5.343087	0.766413
C	1.992107	-2.169261	-0.275670
C	0.419543	-2.744645	1.377404
C	2.587562	-3.416187	-0.206131
H	2.349057	-1.409151	-0.954410
C	0.996864	-4.019342	1.480016
C	2.081323	-4.357957	0.691054
H	0.591824	-4.737043	2.173804
H	2.524096	-5.343020	0.767068
F	3.931514	0.552292	4.108841
F	1.128681	4.230606	3.390545
F	-1.128894	-4.230134	3.390980
F	-3.931705	-0.551697	4.108718
C	-3.782002	3.730094	-1.057498
C	3.781931	-3.730311	-1.056957
F	4.940864	-3.648480	-0.351805
F	3.904857	-2.887215	-2.105236
F	3.727495	-4.987906	-1.555157

F	-4.941020	3.647202	-0.352602
F	-3.728198	4.987977	-1.555013
F	-3.904258	2.887476	-2.106246
N	-1.119280	-0.741924	-1.299983
N	1.119397	0.741783	-1.300012
N	-0.943261	1.840833	0.491092
N	0.943237	-1.840722	0.491367
C	4.106417	2.799041	-2.222515
C	-4.106231	-2.799324	-2.222393
F	3.974312	4.015803	-2.831947
F	4.454359	3.047401	-0.938385
F	5.196776	2.224802	-2.815732
F	-3.974096	-4.016193	-2.831607
F	-5.196527	-2.225167	-2.815802
F	-4.454290	-3.047459	-0.938251
H	2.878677	1.964906	-4.527714
H	-2.878228	-1.965676	-4.527628

Sodium 1-methylcyclohexyloxalate (3_{tert}·Na^+)



Charge: 0

Multiplicity: 0

E = -814.360512714

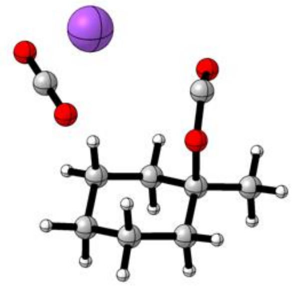
H = -814.130602

G = -814.188234

Cartesian coordinates:

C	-0.787966	-1.952466	0.968853
H	-0.057543	-1.787257	0.172929
H	-1.785603	-1.957969	0.523374
O	0.888378	-3.356482	2.091573
O	0.788572	-1.664265	3.581225
C	1.398500	-2.548693	3.001531
C	2.928495	-2.834577	3.292553
O	3.401454	-2.108938	4.204273
O	3.492216	-3.710559	2.618700
Na	2.094360	-0.483830	5.211855
H	-0.729014	-1.131562	1.682481
C	-0.535499	-3.295026	1.646667
C	-1.475716	-3.548277	2.834781
C	-0.620514	-4.453891	0.644038
C	-1.239258	-4.911849	3.496594
H	-2.495071	-3.510872	2.433217
H	-1.384895	-2.737632	3.557584
C	-0.390802	-5.824830	1.294683
H	-1.619126	-4.420969	0.194597
H	0.100944	-4.279418	-0.159685
C	-1.343828	-6.052804	2.475527
H	-1.963040	-5.053535	4.304799
H	-0.245266	-4.925538	3.958603
H	-0.518447	-6.609849	0.543141
H	0.644332	-5.885139	1.646210
H	-1.128913	-7.012888	2.955095
H	-2.375290	-6.107348	2.10349

1-Methylcyclohexyl oxyacyl radical — CO_2 — sodium complex ($10_{tert}·CO_2·Na$)



Charge: 1

Multiplicity: 2

E = -814.161127388

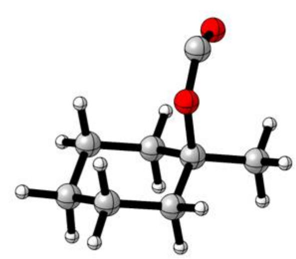
H = -813.931619

G = -813.996267

Cartesian coordinates:

C	-1.553007	-1.993989	0.630533
H	-1.118531	-1.835774	-0.358645
H	-2.596308	-2.294225	0.504696
O	0.689572	-2.688509	1.408892
O	0.558061	-0.789529	2.681632
C	1.101730	-1.635319	2.029322
C	3.141839	-4.607004	4.220726
O	3.111792	-4.173666	5.297980
O	3.166857	-5.038765	3.144515
Na	1.055237	-1.753577	5.720571
H	-1.532859	-1.055729	1.186330
C	-0.811822	-3.093197	1.370559
C	-1.300771	-3.299477	2.803751
C	-0.769007	-4.406072	0.591364
C	-0.549939	-4.416430	3.537594
H	-2.362159	-3.562966	2.724962
H	-1.253279	-2.358042	3.353985
C	-0.028899	-5.528020	1.332440
H	-1.810689	-4.700626	0.419944
H	-0.322735	-4.222966	-0.389919
C	-0.585475	-5.730092	2.747772
H	-0.975597	-4.547568	4.536079
H	0.492624	-4.114029	3.674637
H	-0.106401	-6.453198	0.754284
H	1.034865	-5.278962	1.395386
H	-0.012522	-6.500831	3.271911
H	-1.621119	-6.087902	2.687394

1-Methylcyclohexyl oxyacyl radical (axial) (10_{tert}-ax)



Charge: 0

Multiplicity: 2

E = -463.250066377

H = -463.040389

G = -463.086175

Cartesian coordinates:

C	-0.944456	-2.001374	0.876174
H	-0.233751	-1.845407	0.061891
H	-1.953687	-2.004412	0.456747
O	0.791552	-3.345142	2.017291
O	0.752458	-1.622913	3.526854
C	1.245497	-2.511251	2.893770
H	-0.870646	-1.172402	1.581038
C	-0.691872	-3.334504	1.558446
C	-1.583556	-3.573312	2.777002
C	-0.734693	-4.511909	0.586235
C	-1.329562	-4.925622	3.455187
H	-2.615001	-3.538368	2.406116
H	-1.477479	-2.748296	3.483899
C	-0.487378	-5.866148	1.264552

H	-1.731250	-4.504421	0.129865	H	-0.607804	-6.665450	0.527606
H	-0.013424	-4.337065	-0.216879	H	0.549225	-5.909324	1.614369
C	-1.435120	-6.081378	2.451661	H	-1.212460	-7.032331	2.944923
H	-2.044851	-5.058705	4.271786	H	-2.467643	-6.147230	2.085155
H	-0.331564	-4.924974	3.907783				

1-Methylcyclohexyl oxyacyl radical (equatorial) (10_{tert}-eq)

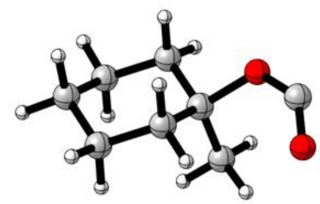
Charge: 0

Multiplicity: 2

E = -463.248612971

H = -463.038714

G = -463.084422



Cartesian coordinates:

C	0.754276	-2.992575	2.007687	H	-1.596612	-2.677619	3.374267
H	1.178482	-3.831345	2.562337	C	-0.476716	-5.862665	1.312306
H	1.398728	-2.793209	1.149263	H	-1.678744	-4.537252	0.101681
O	-1.136293	-2.180648	0.640757	H	0.051463	-4.385279	-0.206064
O	-1.121530	-0.473112	2.168225	C	-1.486707	-6.040642	2.453214
C	-1.284576	-0.977946	1.095507	H	-2.216728	-4.953150	4.188100
H	0.750360	-2.122969	2.665199	H	-0.484556	-4.831103	3.942428
C	-0.651908	-3.341488	1.543857	H	-0.564817	-6.679835	0.591002
C	-1.662875	-3.515908	2.678627	H	0.542583	-5.909358	1.711216
C	-0.694344	-4.527314	0.580578	H	-1.287010	-6.970951	2.993278
C	-1.446709	-4.849576	3.418624	H	-2.495517	-6.127691	2.030636
H	-2.667321	-3.507263	2.242472				

CO_2

Charge: 0

Multiplicity: 1

E = −188.6499252

H = −188.634783

G = −188.659051

Cartesian coordinates:

C	-2.707242	-0.060464	0.062454	O	-2.401194	-0.567040	1.060950
O	-3.013289	0.446113	-0.936041				

TS for CO_2 elimination from 1-methylcyclohexyl oxyacyl radical (axial) ($TS1_{tert}$-ax)

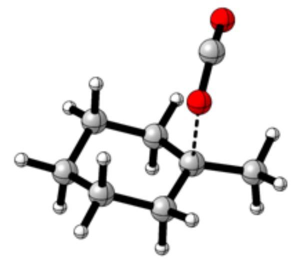
Charge: 0

Multiplicity: 2

E = -463.241405180

H = -463.034740

G = -463.082648



Cartesian coordinates:

C	-1.919926	-0.954166	-0.002623
C	-0.888150	0.135694	-0.026082
C	-0.749794	0.909499	-1.299163
H	0.127969	1.557742	-1.286794
H	-1.834452	-1.563557	-0.906322
H	-0.701693	0.248175	-2.165962
O	0.714713	-1.028422	-0.142871
O	2.490356	0.383059	0.292802
C	1.846735	-0.590500	0.029755
H	-1.635325	1.549925	-1.416801
H	-2.896054	-0.445830	-0.065134
C	-0.690417	0.890382	1.258494
H	-1.552729	1.574910	1.330065
H	0.196352	1.524198	1.193475
C	-1.881251	-1.824041	1.262608
H	-2.749889	-2.488382	1.269915
H	-0.990519	-2.458783	1.227866
C	-0.658286	0.001525	2.509433
H	0.277540	-0.567482	2.522362
H	-0.657760	0.634738	3.400919
C	-1.845672	-0.968635	2.534929
H	-1.787863	-1.611271	3.418459
H	-2.779221	-0.397418	2.618047

TS for CO_2 elimination from 1-methylcyclohexyl oxyacyl radical (equatorial) ($TS1_{tert}$-eq)

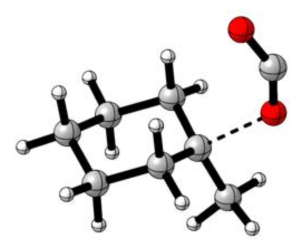
Charge: 0

Multiplicity: 2

E = -463.238581975

H = -463.031537

G = -463.079351



Cartesian coordinates:

C	-1.966074	-0.791303	-0.005817
C	-0.665494	-0.042570	0.082983
C	0.565755	-0.735812	-0.407050
H	0.833154	-1.541004	0.289803
H	-2.015028	-1.384734	-0.921413
H	0.402800	-1.187466	-1.387172
O	-0.782904	1.273960	-1.401073
O	-2.653994	2.543498	-0.920604
C	-1.675353	2.111154	-1.455511
H	1.412708	-0.049483	-0.459832
H	-2.800899	-0.084891	-0.012779
C	-0.537105	0.817887	1.309043
H	-1.342263	1.557711	1.328691
H	0.415610	1.351898	1.315186
C	-2.107521	-1.699912	1.245438
H	-3.073680	-2.210419	1.203612
H	-1.335736	-2.477105	1.220922
C	-0.670622	-0.080713	2.568409

H	0.182248	-0.766494	2.619117
H	-0.623323	0.551274	3.459580
C	-1.979703	-0.880597	2.536551
H	-2.035560	-1.541827	3.406540
H	-2.827094	-0.187682	2.608856

1-Methylcyclohexyl radical — CO_2 complex (11_{tert}·CO_2)

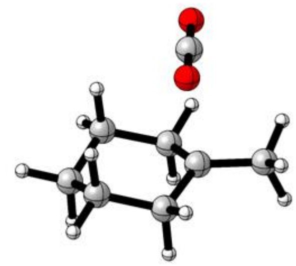
Charge: 0

Multiplicity: 2

E = -463.279840345

H = -463.072085

G = -463.125917



Cartesian coordinates:

C	0.952948	1.975127	0.822783
H	1.301018	2.497780	-0.074041
H	0.511591	2.742227	1.483739
O	1.720397	0.061099	-2.142438
O	2.409034	-1.131404	-0.272336
C	2.049288	-0.525970	-1.195849
H	1.822968	1.570742	1.350104
C	-0.041325	0.909568	0.493490
C	-0.342086	-0.138460	1.522644
C	-1.098030	1.201496	-0.529325
C	-1.029450	-1.384935	0.936978
H	-1.011794	0.298965	2.288489
H	0.572999	-0.420612	2.054593
C	-1.773918	-0.065709	-1.083017
H	-1.877675	1.834321	-0.062346
H	-0.679770	1.799936	-1.345995
C	-2.218442	-1.001499	0.047633
H	-1.352508	-2.045472	1.747832
H	-0.302123	-1.948021	0.339754
H	-2.626967	0.212947	-1.709780
H	-1.064901	-0.596561	-1.729614
H	-2.686838	-1.900169	-0.366642
H	-2.980999	-0.498466	0.657255

1-Methylcyclohexyl radical (equatorial) (11_{tert}-eq)

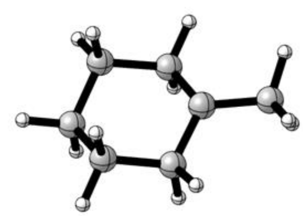
Charge: 0

Multiplicity: 2

E = -274.624469948

H = -274.433392

G = -274.473826



Cartesian coordinates:

C	-1.004721	-1.996141	0.836455
H	-0.225041	-1.910360	0.072528
H	-1.956919	-1.722460	0.346490
H	-0.821199	-1.239592	1.606330
C	-1.068211	-3.372404	1.413486
C	-1.805063	-3.583558	2.702575
C	-0.951611	-4.549519	0.491490
C	-1.429668	-4.901740	3.404192

H	-2.892801	-3.602625	2.492762	H	-2.090029	-5.067564	4.261481
H	-1.648999	-2.733175	3.375838	H	-0.409195	-4.820203	3.798223
C	-0.587387	-5.855282	1.221635	H	-0.648863	-6.699140	0.526909
H	-1.923112	-4.699970	-0.019483	H	0.453715	-5.797197	1.562211
H	-0.228252	-4.341247	-0.304860	H	-1.216173	-7.013628	2.947149
C	-1.497422	-6.088077	2.434248	H	-2.532771	-6.217678	2.091316

1-Methylcyclohexyl radical (axial) (11_{tert}-ax)

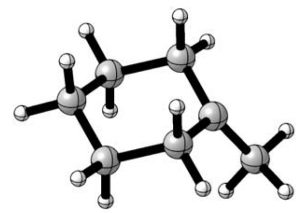
Charge: 0

Multiplicity: 2

E = -274.622668692

H = -274.431303

G = -274.471864



Cartesian coordinates:

C	-0.631635	-3.555096	1.662666	H	-2.308661	-5.161393	4.221196
C	-1.614200	-3.661965	2.792439	H	-0.570604	-5.189924	3.931336
C	-0.775413	-4.613969	0.608466	H	-0.871556	-6.792493	0.479296
C	-1.544730	-5.070192	3.441462	H	0.309556	-6.188906	1.639616
H	-2.637507	-3.519814	2.413637	H	-1.633780	-7.156962	2.847843
H	-1.439343	-2.888803	3.547109	H	-2.735289	-6.105252	1.966359
C	-0.701071	-6.027736	1.244784	C	0.695080	-2.903449	1.888209
H	-1.754974	-4.521466	0.115756	H	1.190567	-2.656372	0.943617
H	-0.012172	-4.508620	-0.168865	H	0.600529	-1.986618	2.479222
C	-1.721329	-6.169013	2.383573	H	1.386880	-3.563465	2.44191

s-cis conformer of N-sulfinyl imine (4)

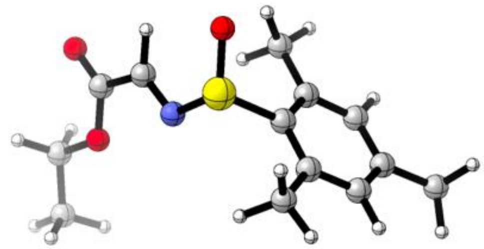
Charge: 0

Multiplicity: 1

E = −1184.479051

H = −1184.17913

G = −1184.251809

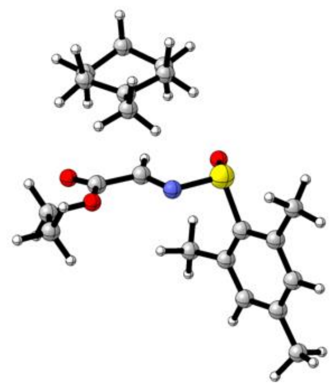


Cartesian coordinates:

C	-2.352725	0.385213	1.305839	C	-2.744721	0.479366	-1.464839
C	-3.344444	1.193599	0.745057	C	-1.730833	-0.341414	-0.966591
C	-3.560310	1.249518	-0.632491	C	-1.555487	-0.375344	0.430393

H	-3.964870	1.790755	1.405123
H	-2.895652	0.520038	-2.538959
C	-2.172726	0.373855	2.808818
H	-2.311545	-0.626874	3.226350
H	-1.175071	0.712371	3.099522
H	-2.900905	1.035466	3.278879
H	-1.315179	-1.092673	-2.933285
H	0.123848	-0.655975	-2.013861
H	-0.730786	-2.145080	-1.630006
C	-0.868557	-1.109790	-1.938631
C	-4.665658	2.097258	-1.209288
H	-4.393477	2.490965	-2.191020
H	-5.575774	1.501356	-1.336107
H	-4.909357	2.935516	-0.553564
S	-0.329747	-1.461086	1.234508
O	-0.358936	-2.831844	0.593994
N	1.071504	-0.547472	0.688340
C	1.942558	-1.204640	0.042040
H	1.835658	-2.258639	-0.226083
C	3.216753	-0.567508	-0.441089
O	4.023603	-1.203454	-1.086997
H	5.410642	0.866580	-0.123054
H	4.597387	1.343057	-1.624300
O	3.338604	0.707437	-0.097757
C	4.550257	1.397552	-0.535002
C	4.459690	2.821491	-0.034026
H	5.352322	3.370017	-0.344054
H	3.584055	3.325416	-0.448660
H	4.399864	2.848193	1.056058

1-Methylcyclohexyl radical (equatorial) — N-sulfinyl imine 4 re-precomplex (11_{tert}·4-eq)



Charge: 0

Multiplicity: 2

E = -1459.11875175

H = -1458.625110

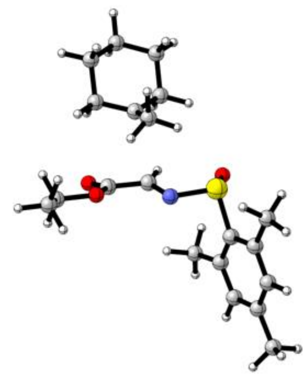
G = -1458.719000

Cartesian coordinates:

C	-3.460447	-0.707483	1.157327
C	-4.767234	-0.243537	0.984261
C	-5.204279	0.297056	-0.225738
C	-4.294816	0.381833	-1.282830
C	-2.974263	-0.057388	-1.168593
C	-2.578136	-0.604761	0.066680
H	-5.459358	-0.311197	1.817283
H	-4.618765	0.807603	-2.227390
C	-3.052723	-1.282591	2.497202
H	-2.717802	-2.319409	2.408000
H	-2.235443	-0.714948	2.949194
H	-3.896890	-1.262300	3.187239
H	-2.610859	0.330576	-3.248806
H	-1.353187	0.939719	-2.171965
H	-1.440874	-0.783525	-2.515096
C	-2.042461	0.108396	-2.344856
C	-6.631471	0.751404	-0.400734
H	-6.697568	1.598959	-1.086493
H	-7.240361	-0.056938	-0.819525
H	-7.078305	1.040230	0.552721
S	-0.909043	-1.289870	0.336705
O	-0.535709	-2.184975	-0.830067
N	-0.072454	0.236784	0.247792
C	0.908547	0.288693	-0.572114
H	1.158690	-0.512550	-1.266764
C	1.687763	1.547246	-0.779532
O	2.442151	1.677740	-1.724147
H	3.238943	3.527103	-0.014689
H	1.896782	4.187890	-0.962669
O	1.448366	2.482599	0.136776
C	2.168488	3.742339	-0.003555
C	1.773226	4.615068	1.167186
H	2.293563	5.573280	1.097223
H	0.697809	4.805444	1.165269
H	2.045565	4.142713	2.113493
C	3.128317	-0.586045	0.969770
C	2.779218	0.283902	2.130356
H	3.042169	1.329395	1.959165

H	1.711208	0.228148	2.364087
H	3.321286	-0.052055	3.029494
C	4.344171	-0.258253	0.159258
H	4.391281	0.816969	-0.040636
H	5.229076	-0.482472	0.784920
C	2.703079	-2.022226	1.043747
H	1.677210	-2.096322	1.421080
H	3.328120	-2.500565	1.821515
C	2.866936	-2.811016	-0.264816
H	2.726975	-3.877540	-0.063469
H	2.074340	-2.522772	-0.961996
C	4.452429	-1.059086	-1.148171
H	3.699643	-0.690366	-1.852846
H	5.430024	-0.879611	-1.605864
C	4.236136	-2.557201	-0.905330
H	5.026622	-2.937383	-0.244655
H	4.318632	-3.108663	-1.847232

1-Methylcyclohexyl radical (axial) — N-sulfinyl imine 4 re-precomplex (11_{tert}·4-ax)



Charge: 0

Multiplicity: 2

E = -1459.11686737

H = -1458.622707

G = -1458.716876

Cartesian coordinates:

C	-3.588743	-0.855803	1.162337
C	-4.910108	-0.402634	1.118895
C	-5.432036	0.243954	-0.002003
C	-4.594140	0.449534	-1.101056
C	-3.263092	0.028074	-1.113977
C	-2.780558	-0.630063	0.033508
H	-5.545493	-0.563986	1.983634
H	-4.984554	0.958999	-1.976523
C	-3.087176	-1.549397	2.411226
H	-2.745198	-2.566100	2.200542
H	-2.249809	-1.012065	2.863647
H	-3.884953	-1.612033	3.152055
H	-3.037487	0.638288	-3.160239
H	-1.710770	1.136978	-2.109057
H	-1.822209	-0.540005	-2.627613
C	-2.410928	0.324996	-2.324331
C	-6.873404	0.685459	-0.041060
H	-6.992665	1.601872	-0.623405
H	-7.495442	-0.083949	-0.510769
H	-7.265404	0.858423	0.963193
S	-1.089905	-1.307458	0.125925
O	-0.791182	-2.086359	-1.142256
N	-0.267644	0.228104	0.132296
C	0.659194	0.363136	-0.741439
H	0.839181	-0.353081	-1.543400
C	1.456103	1.620048	-0.844404
O	2.054544	1.911858	-1.862698
H	3.210694	3.381866	-0.062299
H	1.741713	4.265149	-0.508364
O	1.428655	2.362070	0.261944
C	2.186444	3.606681	0.240868
C	2.119004	4.193410	1.633588
H	2.674735	5.133819	1.658899
H	1.085319	4.395587	1.922392
H	2.561340	3.510916	2.362637
C	2.954618	-0.667813	0.375060
C	2.897721	-1.953626	-0.393347
H	2.021646	-2.546323	-0.118611
H	2.829332	-1.744285	-1.468964
C	2.377671	-0.596573	1.748863
H	2.162762	0.436998	2.034164
H	1.461292	-1.183481	1.841545
H	3.093701	-0.993618	2.486275
C	4.128807	0.201682	0.043010
H	4.092004	0.496472	-1.012962
H	4.127062	1.116767	0.641580
C	4.203184	-2.760986	-0.153755
C	5.444909	-0.589841	0.278373

C	5.436047	-1.914137	-0.496879
H	6.350183	-2.478215	-0.285754
H	5.436839	-1.700864	-1.573613
H	4.247486	-3.068306	0.897546
H	4.181484	-3.675303	-0.754923
H	5.553850	-0.792620	1.350154
H	6.298114	0.027545	-0.019432

re-TS for 1-methylcyclohexyl radical (equatorial) addition to N-sulfinyl imine 4 (TS2$_{tert}$-eq)

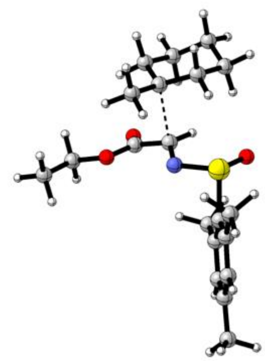
Charge: 0

Multiplicity: 2

E = -1459.11655137

H = -1458.623267

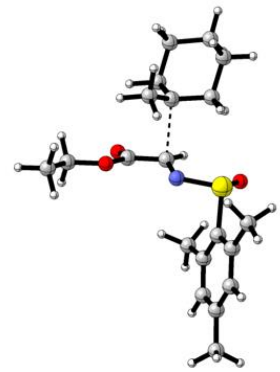
G = -1458.712555



Cartesian coordinates:

C	-3.428852	-0.897323	1.034540
C	-4.724118	-0.400818	0.860693
C	-5.087641	0.332637	-0.269322
C	-4.115826	0.579823	-1.242645
C	-2.804265	0.117153	-1.120534
C	-2.482378	-0.624357	0.031725
H	-5.465716	-0.597791	1.628075
H	-4.383270	1.153962	-2.124377
C	-3.102501	-1.690043	2.282348
H	-2.752362	-2.697324	2.041944
H	-2.320888	-1.207629	2.874596
H	-3.989131	-1.785445	2.910205
H	-2.312362	0.783493	-3.102515
H	-1.155273	1.278675	-1.864483
H	-1.158684	-0.386741	-2.436224
C	-1.800577	0.460043	-2.195061
C	-6.502291	0.821584	-0.454307
H	-6.526168	1.779956	-0.977919
H	-7.077925	0.107547	-1.052945
H	-7.013747	0.936498	0.503467
S	-0.828423	-1.358419	0.274268
O	-0.465169	-2.166917	-0.962497
N	0.033948	0.122018	0.343312
C	1.131073	0.198067	-0.380779
H	1.336946	-0.516386	-1.175508
C	1.721878	1.545514	-0.637552
O	2.376226	1.779116	-1.636094
H	3.063749	3.722225	0.019674
H	1.573270	4.185046	-0.817865
O	1.450158	2.443958	0.309339
C	1.978006	3.788106	0.115348
C	1.559797	4.608671	1.315788
H	1.936361	5.628711	1.207770
H	0.471550	4.649630	1.399206
H	1.967584	4.185949	2.236630
C	2.865049	-0.592825	0.908187
C	2.566780	0.118000	2.193806
H	2.698592	1.196969	2.108428
H	1.551207	-0.086214	2.538156
H	3.261679	-0.247097	2.963335
C	4.125341	-0.185422	0.191965
H	4.176381	0.899663	0.073270
H	4.949075	-0.444271	0.880268
C	2.570692	-2.071194	0.903295
H	1.556342	-2.264023	1.263628
H	3.232997	-2.498042	1.676430
C	2.842140	-2.791511	-0.424516
H	2.771388	-3.871308	-0.263184
H	2.057289	-2.537192	-1.142158
C	4.357644	-0.902738	-1.145081
H	3.637353	-0.533416	-1.881165
H	5.351473	-0.644896	-1.522503
C	4.216772	-2.422078	-0.994144
H	5.002387	-2.794129	-0.323683
H	4.366967	-2.912839	-1.960550

re-TS for 1-methylcyclohexyl radical (axial) addition to N-sulfinyl imine 4 (TS2$_{tert}$-ax)



Charge: 0

Multiplicity: 2

E = -1459.11580089

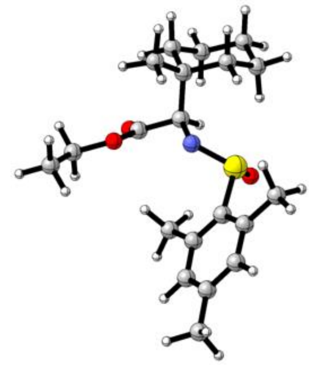
H = -1458.622207

G = -1458.712723

Cartesian coordinates:

C	-3.393794	-1.176344	0.990206
C	-4.725392	-0.750406	0.977596
C	-5.223939	0.082969	-0.024145
C	-4.352897	0.505280	-1.032023
C	-3.011513	0.119880	-1.067959
C	-2.551675	-0.728014	-0.042414
H	-5.387311	-1.083391	1.770468
H	-4.725683	1.159294	-1.814368
C	-2.920045	-2.083827	2.105770
H	-2.542429	-3.034923	1.721243
H	-2.114742	-1.625554	2.685215
H	-3.742512	-2.302140	2.787903
H	-2.728936	1.053113	-2.981722
H	-1.494322	1.462219	-1.788281
H	-1.463594	-0.117480	-2.564468
C	-2.124045	0.652452	-2.167185
C	-6.674421	0.495685	-0.039904
H	-6.793849	1.512353	-0.421350
H	-7.253333	-0.167618	-0.691380
H	-7.115056	0.445395	0.957762
S	-0.843097	-1.371327	-0.011361
O	-0.523875	-1.975458	-1.371021
N	-0.069151	0.150591	0.207455
C	0.930623	0.414172	-0.597594
H	1.113921	-0.167733	-1.500665
C	1.456891	1.809320	-0.671979
O	2.044822	2.222516	-1.653788
H	2.774496	3.891452	0.249581
H	1.226468	4.442214	-0.411433
O	1.207333	2.536943	0.417341
C	1.695627	3.909242	0.418154
C	1.337904	4.509727	1.760100
H	1.687807	5.544100	1.800487
H	0.256444	4.505268	1.912934
H	1.810337	3.953440	2.572691
C	2.864720	-0.476837	0.321916
C	2.498805	-1.936537	0.271742
H	1.730571	-2.173616	1.012076
H	2.102821	-2.197133	-0.714395
C	2.875705	0.161089	1.677122
H	3.123563	1.222162	1.635425
H	1.910315	0.040659	2.174575
H	3.630340	-0.332294	2.305903
C	3.934821	-0.086652	-0.658172
H	3.593998	-0.281334	-1.681242
H	4.171992	0.976405	-0.587876
C	3.763738	-2.797938	0.531633
C	5.206707	-0.939801	-0.400014
C	4.884274	-2.437574	-0.450521
H	5.781775	-3.023181	-0.228078
H	4.573292	-2.705862	-1.468031
H	4.108322	-2.639338	1.559544
H	3.495099	-3.854822	0.445734
H	5.620508	-0.683079	0.581654
H	5.964518	-0.678799	-1.144548

(R)-configured adduct of 4 with 1-methylcyclohexyl radical (equatorial) (12_{tert}-eq)



Charge: 0

Multiplicity: 2

E = -1459.13999376

H = -1458.643184

G = -1458.731493

Cartesian coordinates:

C	-3.135864	-1.570564	0.630270
C	-4.465819	-1.144582	0.684176
C	-4.909709	-0.019257	-0.013061
C	-3.987219	0.701737	-0.776388
C	-2.643812	0.331786	-0.862150
C	-2.248171	-0.811095	-0.147391
H	-5.170437	-1.711250	1.283774
H	-4.318453	1.581753	-1.318517
C	-2.709201	-2.800083	1.399861
H	-2.298311	-3.567195	0.737654
H	-1.941957	-2.563476	2.141425
H	-3.561570	-3.233560	1.923830
H	-2.226058	1.804267	-2.370926
H	-1.122731	1.832669	-0.993331
H	-0.970643	0.567750	-2.218588
C	-1.684886	1.176600	-1.661977
C	-6.359184	0.394375	0.030001
H	-6.464677	1.479749	-0.031306
H	-6.903310	-0.035940	-0.817469
H	-6.845950	0.048931	0.944137
S	-0.535229	-1.428507	-0.265274
O	-0.200466	-1.737550	-1.711522
N	0.262665	-0.162856	0.408607
C	1.565076	0.168280	-0.140519
H	1.739393	-0.323517	-1.099025
C	1.609103	1.665724	-0.468671
O	2.239590	2.103738	-1.405887
H	1.926954	4.218483	0.218738
H	0.545115	4.036611	-0.875031
O	0.904156	2.415925	0.375849
C	0.900079	3.856084	0.141621
C	-0.007457	4.471790	1.183560
H	-0.039180	5.554900	1.043297
H	-1.023634	4.081956	1.092359
H	0.359925	4.264439	2.190888
C	2.734605	-0.235964	0.855001
C	2.568490	0.494755	2.195588
H	2.667635	1.576578	2.081700
H	1.592160	0.288638	2.638495
H	3.340309	0.158336	2.892855
C	4.109774	0.114125	0.235484
H	4.166148	1.182210	0.011029
H	4.858949	-0.077760	1.013305
C	2.683228	-1.765232	1.093256
H	1.710111	-2.048380	1.504628
H	3.419499	-1.988251	1.874484
C	3.020975	-2.605526	-0.146872
H	3.008734	-3.665970	0.124070
H	2.252124	-2.478911	-0.916826
C	4.472602	-0.713767	-1.006146
H	3.805260	-0.459132	-1.836545
H	5.482167	-0.445783	-1.333450
C	4.391339	-2.219341	-0.719805
H	5.169899	-2.487233	0.006241
H	4.597610	-2.790771	-1.630312

(R)-configured adduct of 4 with 1-methylcyclohexyl radical (axial) (12_{tert}-ax)

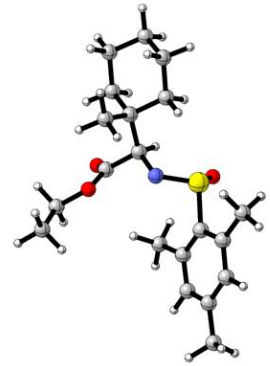
Charge: 0

Multiplicity: 2

E = -1459.13909630

H = -1458.642388

G = -1458.731350



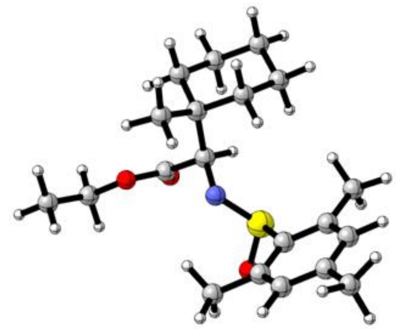
Cartesian coordinates:

C	-3.170409	-1.701420	0.565014
C	-4.495012	-1.309897	0.779012
C	-5.011899	-0.129259	0.242397
C	-4.169180	0.684023	-0.520626
C	-2.834871	0.351885	-0.761035
C	-2.364205	-0.849931	-0.205858
H	-5.136923	-1.948001	1.377301
H	-4.557458	1.607673	-0.938032
C	-2.663054	-2.992848	1.165705
H	-2.297846	-3.679177	0.396781
H	-1.839983	-2.814925	1.862502
H	-3.462133	-3.496823	1.710119
H	-2.569918	1.977298	-2.142105
H	-1.351339	1.892300	-0.868641
H	-1.290280	0.759799	-2.225664
C	-1.960670	1.293430	-1.550008
C	-6.455971	0.249616	0.454264
H	-6.573937	1.332240	0.538580
H	-7.064853	-0.080588	-0.394046
H	-6.863099	-0.215588	1.354036
S	-0.662111	-1.420358	-0.538859
O	-0.465080	-1.590603	-2.032476
N	0.177147	-0.198985	0.167302
C	1.400005	0.232150	-0.481109
H	1.475229	-0.133358	-1.509915
C	1.384250	1.761548	-0.609053
O	1.853019	2.336159	-1.566819
H	1.799427	4.206116	0.377039
H	0.273008	4.139124	-0.519966
O	0.821116	2.373386	0.430774
C	0.774252	3.831376	0.399864
C	0.025792	4.276652	1.636699
H	-0.032833	5.367585	1.653093
H	-0.990320	3.876121	1.639668
H	0.537939	3.944531	2.542290
C	2.688786	-0.277452	0.290844
C	2.656156	-1.826553	0.244342
H	1.823035	-2.193313	0.850577
H	2.463030	-2.141187	-0.789088
C	2.678863	0.224668	1.743801
H	2.747108	1.313425	1.789227
H	1.761010	-0.079509	2.250184
H	3.522744	-0.183522	2.300751
C	3.939688	0.228008	-0.468860
H	3.814546	0.011751	-1.536714
H	4.016313	1.314932	-0.378711
C	3.963118	-2.482739	0.712913
C	5.244301	-0.426426	0.010741
C	5.168588	-1.955009	-0.072786
H	6.094032	-2.404478	0.300830
H	5.071845	-2.253642	-1.124826
H	4.114087	-2.296804	1.782064
H	3.876690	-3.567797	0.598212
H	5.457341	-0.126456	1.042877
H	6.073681	-0.051578	-0.597195

Reduced (R)-configured adduct of 4 with 1-methylcyclohexyl radical (5_{tert}^{-})

Charge: −1

Multiplicity: 1



E = -1459.29514860

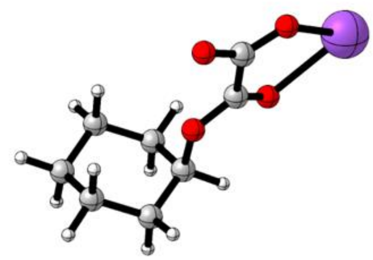
H = -1458.799478

G = -1458.887306

Cartesian coordinates:

C	-3.099684	-0.951175	-0.524884
C	-4.348668	-0.995210	0.106983
C	-4.898639	0.123283	0.732106
C	-4.158773	1.309032	0.724117
C	-2.906711	1.405331	0.110190
C	-2.383410	0.258960	-0.520584
H	-4.901187	-1.930415	0.109156
H	-4.564997	2.188253	1.216816
C	-2.563894	-2.211449	-1.171313
H	-2.392084	-2.075351	-2.242314
H	-1.609413	-2.512620	-0.733524
H	-3.270083	-3.034105	-1.043158
H	-2.740953	3.468043	0.704766
H	-1.197670	2.578429	0.668284
H	-1.931831	3.074872	-0.836275
C	-2.158524	2.715577	0.168889
C	-6.263491	0.066796	1.375407
H	-6.313570	0.706451	2.260208
H	-7.036195	0.412836	0.680009
H	-6.522932	-0.951799	1.673109
S	-0.760644	0.262696	-1.375535
O	-0.839741	1.490524	-2.335513
N	0.199154	0.495440	-0.076451
C	1.496764	-0.160710	-0.239651
H	1.496663	-0.847665	-1.095701
C	2.549671	0.869731	-0.648771
O	3.121877	0.864912	-1.725977
H	4.662969	2.443335	-0.298027
H	3.330196	3.386519	-0.979058
O	2.760991	1.826693	0.268672
C	3.689160	2.886532	-0.076198
C	3.752742	3.830237	1.106755
H	4.441834	4.649651	0.887107
H	2.768601	4.254780	1.318312
H	4.108164	3.310768	1.999690
C	1.894766	-1.008654	1.020739
C	1.767145	-0.192519	2.317162
H	2.470700	0.640690	2.336434
H	0.757948	0.211281	2.416232
H	1.971223	-0.834909	3.180220
C	3.346841	-1.532605	0.892873
H	4.038540	-0.691334	0.767815
H	3.615308	-2.004415	1.846934
C	0.933129	-2.220580	1.109215
H	-0.095764	-1.849519	1.110777
H	1.098764	-2.708232	2.078290
C	1.126467	-3.267871	0.002635
H	0.458435	-4.116767	0.184682
H	0.832000	-2.851199	-0.967166
C	3.548360	-2.562360	-0.228852
H	3.393645	-2.089722	-1.204968
H	4.584671	-2.916733	-0.217903
C	2.583002	-3.745458	-0.071792
H	2.829883	-4.286057	0.851868
H	2.710808	-4.454656	-0.896509

Sodium cyclohexyloxalate (axial) (3_{sec}·Na^+-ax)



Charge: 0

Multiplicity: 1

E = -775.031095063

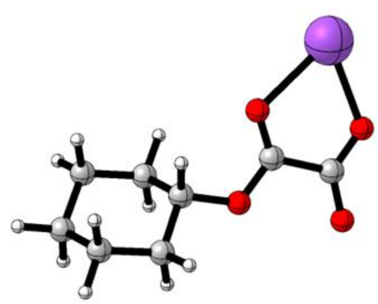
H = -774.830005

G = -774.887304

Cartesian coordinates:

O	0.883375	-3.945626	2.625943	H	-1.349074	-3.544996	4.047418
O	0.943800	-2.073563	3.868485	C	-0.616354	-5.862104	0.928183
C	1.449478	-3.117280	3.488507	H	-1.480552	-3.985868	0.274059
C	2.865399	-3.602410	3.990770	H	0.271814	-4.043485	0.111441
O	3.461229	-2.746659	4.693345	C	-1.729041	-6.273801	1.902923
O	3.231775	-4.740633	3.661117	H	-2.384712	-5.838326	3.931226
Na	2.427619	-0.767321	5.278450	H	-0.639106	-5.907475	3.732935
C	-0.447184	-3.606377	2.090463	H	-0.766039	-6.335751	-0.046609
C	-1.519489	-4.043039	3.090067	H	0.347843	-6.216090	1.309076
C	-0.561082	-4.337019	0.756416	H	-1.728602	-7.359673	2.039648
C	-1.566295	-5.568538	3.257195	H	-2.703731	-6.008590	1.472691
H	-2.481684	-3.682109	2.708239	H	-0.472655	-2.525264	1.947882

Sodium cyclohexyloxalate (equatorial) (3_{sec}·Na^+-eq)



Charge: 0

Multiplicity: 1

E = -775.031660733

H = -774.830536

G = -774.885745

Cartesian coordinates:

O	-0.952339	-2.128458	1.219159	C	-1.581559	-5.249061	3.304591
O	-0.008410	-1.092114	2.976704	H	-2.748869	-3.742080	2.268330
C	-0.583842	-1.053976	1.901798	H	-1.793612	-3.100617	3.609348
C	-0.959483	0.306404	1.193222	C	-0.401432	-5.860429	1.148146
O	-0.635887	1.318039	1.865395	H	-1.541337	-4.368573	0.061306
O	-1.517066	0.242693	0.087222	H	0.205588	-4.135887	-0.042165
Na	0.421786	1.088128	3.916644	C	-1.497080	-6.255730	2.148658
C	-0.681695	-3.450775	1.794941	H	-2.397889	-5.511141	3.983765
C	-1.784806	-3.817005	2.784613	H	-0.656256	-5.292828	3.892559
C	-0.606157	-4.427820	0.629864	H	-0.383046	-6.555884	0.304247

H	0.578204	-5.932322	1.637077
H	-1.308755	-7.261493	2.536559
H	-2.463438	-6.290604	1.629939
H	0.280782	-3.397062	2.309824

Cyclohexyl oxyacyl radical (axial) – CO_2 – sodium complex (10_{sec}·CO_2·Na^+-ax)

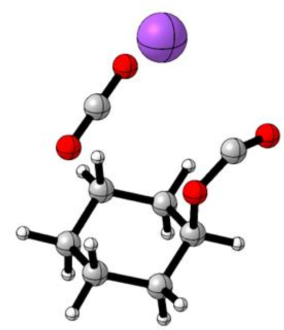
Charge: 1

Multiplicity: 2

E = -774.829121888

H = -774.628269

G = -774.689503



Cartesian coordinates:

O	0.902691	-2.820189	1.792075
O	0.560132	-0.687473	2.527123
C	1.218636	-1.632908	2.207618
C	3.169418	-4.184028	3.665597
O	3.228412	-3.206233	4.289454
O	3.113214	-5.162922	3.046381
Na	0.809887	-1.876200	5.849445
C	-0.570387	-3.137582	1.551687
C	-1.267398	-3.354162	2.887303
C	-0.571220	-4.374205	0.669392
C	-0.740515	-4.592224	3.624251
H	-2.331694	-3.487819	2.658578
H	-1.196014	-2.451927	3.496825
C	-0.063927	-5.621739	1.408435
H	-1.608280	-4.527444	0.348310
H	0.016710	-4.180695	-0.231376
C	-0.813055	-5.839428	2.731641
H	-1.311726	-4.740430	4.544726
H	0.298788	-4.423330	3.925704
H	-0.173404	-6.495791	0.760268
H	1.005028	-5.509523	1.612206
H	-0.399586	-6.704412	3.258707
H	-1.865406	-6.068738	2.520973
H	-0.965841	-2.265045	1.030443

Cyclohexyl oxyacyl radical (axial) (10_{sec}-ax)

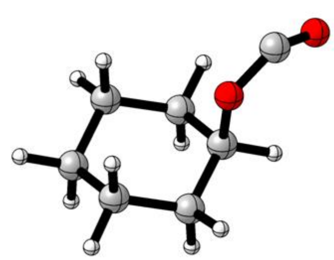
Charge: 0

Multiplicity: 2

E = -423.918307204

H = -423.737403

G = -423.781080



Cartesian coordinates:

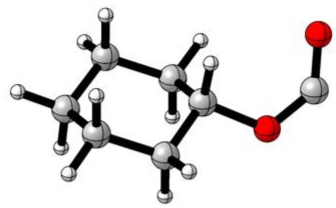
O	0.800730	-3.364889	2.191273
O	0.736394	-1.207635	2.929917
C	1.242986	-2.272435	2.730857
C	-0.635017	-3.388200	1.687085
C	-1.563583	-3.633280	2.869368
C	-0.677814	-4.492049	0.643835
C	-1.382403	-5.032603	3.474303
H	-2.586628	-3.521951	2.490136
H	-1.421080	-2.852078	3.620248
C	-0.503648	-5.888412	1.259338
H	-1.656379	-4.423028	0.153986
H	0.077139	-4.298207	-0.122431

C	-1.502444	-6.124147	2.401276
H	-2.123680	-5.185896	4.263612
H	-0.396778	-5.096396	3.948680
H	-0.624626	-6.646511	0.480407
H	0.517338	-5.988243	1.643658
H	-1.339721	-7.110158	2.846751
H	-2.522826	-6.122998	1.996639
H	-0.801403	-2.405529	1.244239

Cyclohexyl oxyacyl radical (equatorial) (10_{sec}-eq)

Charge: 0

Multiplicity: 2



E = -423.918785154

H = -423.737782

G = -423.781655

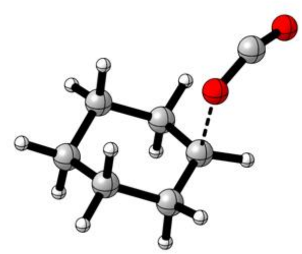
Cartesian coordinates:

O	-1.210559	-2.143192	0.690232
O	-0.209807	-0.605635	2.047243
C	-0.847126	-0.966481	1.102682
C	-0.804648	-3.346308	1.510197
C	-1.800218	-3.536596	2.643631
C	-0.769714	-4.519940	0.549601
C	-1.473429	-4.829841	3.412635
H	-2.806388	-3.603828	2.215601
H	-1.778474	-2.672748	3.312498
C	-0.445336	-5.814182	1.317646
H	-1.750872	-4.610078	0.070438
H	-0.032041	-4.335832	-0.235445
C	-1.431813	-6.041628	2.471462
H	-2.215853	-4.978494	4.201413
H	-0.501761	-4.720643	3.909536
H	-0.461284	-6.659201	0.623959
H	0.574195	-5.752376	1.717225
H	-1.156675	-6.941785	3.029153
H	-2.434383	-6.215076	2.061143
H	0.192158	-3.122890	1.897996

TS for CO_2 elimination from cyclohexyl oxyacyl radical (axial) ($TS1_{sec}$-ax)

Charge: 0

Multiplicity: 2



E = -423.905169774

H = -423.727627

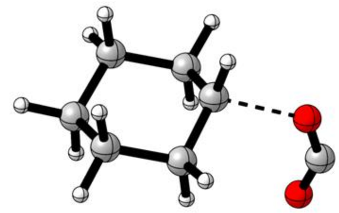
G = -423.773202

Cartesian coordinates:

O	0.928723	-3.351707	2.195931
O	1.022420	-1.302779	3.255659
C	1.317534	-2.369912	2.811540
C	-0.933718	-3.396647	1.558954
C	-1.733964	-3.627084	2.801791
C	-0.839162	-4.510652	0.567786
C	-1.479029	-5.004436	3.433642
H	-2.792197	-3.561054	2.496637
H	-1.576000	-2.817781	3.518422
C	-0.598588	-5.879280	1.226370

H	-1.802820	-4.529887	0.032192	H	-0.692327	-6.666328	0.473087
H	-0.077391	-4.286138	-0.182885	H	0.428855	-5.914637	1.602489
C	-1.572569	-6.123736	2.387311	H	-1.364471	-7.091375	2.853567
H	-2.195513	-5.171599	4.242505	H	-2.598020	-6.172989	1.998879
H	-0.480218	-5.009655	3.882871	H	-0.941131	-2.387746	1.157594

TS for CO_2 elimination from cyclohexyl oxyacyl radical (equatorial) ($TS1_{sec}$-eq)



Charge: 0

Multiplicity: 2

E = -423.902449587

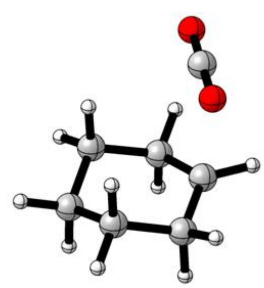
H = -423.724539

G = -423.769742

Cartesian coordinates:

C	-2.011489	-0.773970	0.008461	C	-2.101339	-1.707685	1.247638
C	-0.736882	0.002424	0.105665	H	-3.054254	-2.243959	1.219143
H	-2.054792	-1.354818	-0.914934	H	-1.307196	-2.460783	1.190076
O	-0.724274	1.236669	-1.418598	C	-0.663746	-0.088342	2.570767
O	-2.572118	2.579687	-1.054511	H	0.199169	-0.763973	2.576500
C	-1.590728	2.093357	-1.525632	H	-0.600455	0.520064	3.477566
H	-2.867673	-0.091985	0.024965	C	-1.961137	-0.908171	2.550282
C	-0.574604	0.844578	1.330941	H	-1.987782	-1.586013	3.408826
H	-1.384068	1.579188	1.390444	H	-2.818101	-0.231112	2.652746
H	0.375347	1.382562	1.321717	H	0.157032	-0.507135	-0.241944

Cyclohexyl radical — CO_2 complex (11_{sec}·CO_2)



Charge: 0

Multiplicity: 2

E = -423.945113006

H = -423.766817

G = -423.817706

Cartesian coordinates:

O	1.717265	0.081765	-2.128994	C	-0.386246	-0.121339	1.557480
O	2.413380	-1.098909	-0.254368	C	-1.145681	1.225342	-0.504159
C	2.053440	-0.500040	-1.181891	C	-1.034993	-1.380610	0.946569
C	-0.106823	0.925619	0.527895	H	-1.084919	0.288088	2.310951

H	0.525329	-0.383175	2.103016	H	-0.283309	-1.921473	0.359357
C	-1.780263	-0.057283	-1.080400	H	-2.631868	0.203492	-1.716647
H	-1.952600	1.825448	-0.043464	H	-1.046828	-0.561749	-1.720569
H	-0.730543	1.843879	-1.305569	H	-2.654326	-1.921277	-0.393433
C	-2.215954	-1.015042	0.036939	H	-3.001871	-0.537798	0.637477
H	-1.359738	-2.055116	1.745094	H	0.701419	1.631725	0.691535

Cycloxehyl radical (11_{sec})

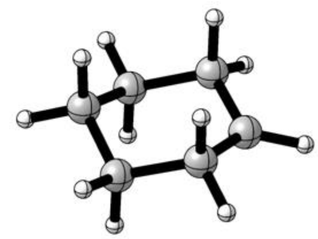
Charge: 0

Multiplicity: 2

E = -235.290758250

H = -235.129144

G = -235.165865



Cartesian coordinates:

C	-1.030131	-3.392864	1.437102	C	-1.503137	-6.085261	2.430798
C	-1.785464	-3.576131	2.714228	H	-2.096991	-5.071733	4.262041
C	-0.927865	-4.546903	0.492167	H	-0.409881	-4.838065	3.812316
C	-1.428456	-4.906290	3.411065	H	-0.654833	-6.704205	0.525375
H	-2.870532	-3.590018	2.498476	H	0.456863	-5.819188	1.566563
H	-1.624159	-2.730694	3.390153	H	-1.236765	-7.016888	2.940613
C	-0.583570	-5.862670	1.221946	H	-2.538105	-6.200537	2.081717
H	-1.899460	-4.689238	-0.017595	H	-0.787063	-2.392537	1.093891
H	-0.200220	-4.342541	-0.299305				

Cyclohexyl radical (axial) — N-sulfinyl imine 4 re-precomplex (11_{sec}·4-ax)

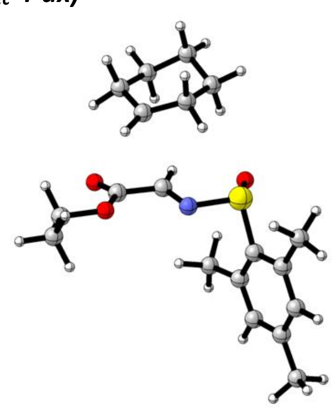
Charge: 0

Multiplicity: 2

E = -1419.78229489

H = -1419.318052

G = -1419.408936

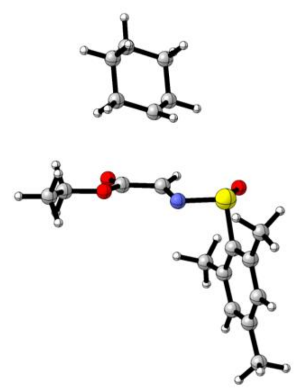


Cartesian coordinates:

C	-3.280278	-0.877590	1.078920	C	-2.840314	0.115364	-1.132907
C	-4.596059	-0.414726	0.993619	C	-2.416770	-0.599987	0.003634
C	-5.059829	0.290306	-0.117693	H	-5.273840	-0.615698	1.816814
C	-4.168721	0.544051	-1.163419	H	-4.514219	1.097600	-2.030904

C	-2.843975	-1.637728	2.313449
H	-2.489527	-2.642004	2.066874
H	-2.032718	-1.126416	2.837828
H	-3.679660	-1.739218	3.006608
H	-2.517786	0.801133	-3.141616
H	-1.253978	1.277171	-2.006590
H	-1.316546	-0.381943	-2.589884
C	-1.930741	0.464845	-2.286173
C	-6.495759	0.742382	-0.204683
H	-6.583833	1.682492	-0.753760
H	-7.098904	-0.003375	-0.733461
H	-6.932816	0.876669	0.786810
S	-0.736315	-1.291222	0.146202
O	-0.381189	-2.015445	-1.139206
N	0.084006	0.246462	0.241398
C	1.057986	0.409077	-0.570006
H	1.318290	-0.305120	-1.352493
C	1.822917	1.693547	-0.634642
O	2.553101	1.945616	-1.573337
H	3.379834	3.569380	0.350538
H	2.026488	4.332899	-0.500923
O	1.595095	2.507299	0.393808
C	2.309096	3.778920	0.396461
C	1.922788	4.506390	1.665181
H	2.440176	5.468063	1.703071
H	0.846973	4.692127	1.695730
H	2.205837	3.927398	2.546937
C	3.360121	-0.321068	0.848814
C	4.483887	-0.383842	-0.130488
H	4.566049	0.560061	-0.677768
H	5.426665	-0.483215	0.438698
C	2.804700	-1.574113	1.438297
H	1.820688	-1.384027	1.880698
H	3.452468	-1.863504	2.286109
C	2.749512	-2.747180	0.442644
H	2.530690	-3.673482	0.982220
H	1.925266	-2.590311	-0.260375
C	4.371756	-1.575164	-1.098064
H	3.572393	-1.376748	-1.822027
H	5.298757	-1.672122	-1.670733
C	4.058220	-2.876109	-0.347663
H	4.882916	-3.107694	0.339279
H	3.989588	-3.710723	-1.052354
H	3.216468	0.600909	1.403841

Cyclohexyl radical (equatorial) — N-sulfinyl imine 4 re-precomplex (11_{sec}·4-eq)



Charge: 0

Multiplicity: 2

E = -1419.77974483

H = -1419.315239

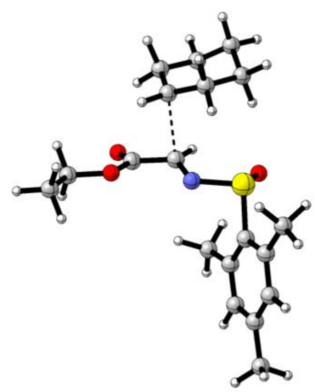
G = -1419.407580

Cartesian coordinates:

C	-3.600894	-0.730433	1.259921
C	-4.901750	-0.234768	1.138925
C	-5.373210	0.318143	-0.052387
C	-4.504530	0.382740	-1.144585
C	-3.191081	-0.087176	-1.082955
C	-2.759382	-0.645151	0.135747
H	-5.561933	-0.287726	1.998475
H	-4.855549	0.817028	-2.075442
C	-3.156076	-1.319414	2.581777
H	-2.844978	-2.362101	2.476302
H	-2.312297	-0.769681	3.006298
H	-3.974250	-1.286177	3.301928
H	-2.902833	0.302415	-3.174368
H	-1.579824	0.860502	-2.149968
H	-1.742561	-0.856511	-2.497566
C	-2.304561	0.054787	-2.296764
C	-6.794805	0.807030	-0.169897
H	-6.869149	1.651809	-0.858169
H	-7.440817	0.011549	-0.556456
H	-7.193175	1.112567	0.799701
S	-1.098678	-1.371070	0.338637
O	-0.793612	-2.271165	-0.843751
N	-0.221712	0.135190	0.223423
C	0.715737	0.159061	-0.643266

H	0.888058	-0.637510	-1.367994	H	3.453623	-1.244384	-1.599877
C	1.572326	1.370057	-0.842809	C	4.062590	0.129551	0.802426
O	2.233104	1.516211	-1.852468	H	4.203844	0.809253	-0.050082
H	3.350091	3.161301	-0.155774	H	3.758308	0.733417	1.660170
H	1.946251	4.012691	-0.821624	C	4.737303	-2.506603	-0.407681
O	1.516275	2.236140	0.164858	C	5.429278	-0.559821	1.071685
C	2.315560	3.449767	0.038103	C	5.823486	-1.465689	-0.103086
C	2.170309	4.217483	1.333131	H	6.771861	-1.967828	0.113597
H	2.754272	5.139149	1.275300	H	5.989282	-0.846734	-0.994301
H	1.126367	4.481356	1.515590	H	4.638205	-3.191125	0.442783
H	2.537854	3.628183	2.176023	H	5.013627	-3.111076	-1.277430
C	3.037769	-0.898669	0.457771	H	5.355753	-1.157557	1.987568
C	3.366890	-1.821577	-0.667546	H	6.194098	0.203890	1.245248
H	2.585141	-2.570235	-0.816469	H	2.325669	-1.211068	1.21420

re-TS for cyclohexyl radical (axial) addition to N-sulfinyl imine 4 (TS2$_{sec}$-ax)



Charge: 0

Multiplicity: 2

E = -1419.78131868

H = -1419.317569

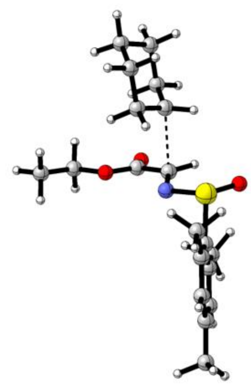
G = -1419.405182

Cartesian coordinates:

C	-3.200540	-1.023054	0.986626	H	-6.863763	0.718409	0.760787
C	-4.518739	-0.564839	0.907338	S	-0.620906	-1.312072	0.094658
C	-4.955144	0.249762	-0.138153	O	-0.259289	-1.962979	-1.232040
C	-4.034388	0.619191	-1.122141	N	0.185804	0.199266	0.293361
C	-2.703138	0.199412	-1.092896	C	1.230643	0.398208	-0.461121
C	-2.307218	-0.627390	-0.024572	H	1.471773	-0.246935	-1.305692
H	-5.220008	-0.856614	1.682382	C	1.826084	1.764808	-0.554816
H	-4.358648	1.258065	-1.937758	O	2.495723	2.105760	-1.511461
C	-2.794583	-1.907002	2.146799	H	3.178506	3.825044	0.382577
H	-2.424280	-2.877487	1.806143	H	1.712530	4.407765	-0.423781
H	-2.003124	-1.449730	2.745817	O	1.543295	2.547274	0.486754
H	-3.649365	-2.086149	2.799928	C	2.091897	3.897512	0.463810
H	-2.320541	1.068637	-3.019214	C	1.658870	4.578216	1.743633
H	-1.121808	1.478452	-1.789960	H	2.052162	5.597511	1.763360
H	-1.105893	-0.123292	-2.520151	H	0.569758	4.627582	1.809220
C	-1.759120	0.675475	-2.170655	H	2.040509	4.044330	2.616709
C	-6.392844	0.696835	-0.224052	C	3.155235	-0.299289	0.729323
H	-6.474069	1.690666	-0.669969	C	4.252208	-0.400873	-0.282703
H	-6.969670	0.008687	-0.851182	H	4.291808	0.498762	-0.902572

H	5.198248	-0.408499	0.287263	C	4.183324	-1.672434	-1.142257
C	2.701911	-1.537789	1.433323	H	3.356456	-1.585915	-1.856880
H	1.735012	-1.369973	1.917835	H	5.099414	-1.760913	-1.732917
H	3.415353	-1.696049	2.260900	C	3.971501	-2.920537	-0.276053
C	2.683472	-2.794317	0.547677	H	4.830130	-3.047316	0.396107
H	2.537880	-3.676959	1.176975	H	3.927283	-3.814036	-0.906021
H	1.832400	-2.749837	-0.137960	H	3.121392	0.612281	1.319327

re-TS for cyclohexyl radical (equatorial) addition to N-sulfinyl imine 4 (TS2$_{sec}$-eq)



Charge: 0

Multiplicity: 2

E = -1419.78024846

H = -1419.316370

G = -1419.405507

Cartesian coordinates:

C	-3.360671	-1.187116	0.903746	O	2.225736	2.222901	-1.635572
C	-4.645991	-0.702034	1.162751	H	3.595818	2.995391	0.462115
C	-5.206437	0.336612	0.418889	H	2.166044	4.037107	0.366422
C	-4.449295	0.900270	-0.611806	O	1.770477	2.006838	0.565021
C	-3.157536	0.464717	-0.911956	C	2.597307	3.168497	0.868300
C	-2.630862	-0.586456	-0.137069	C	2.612327	3.324124	2.373020
H	-5.222957	-1.155001	1.962368	H	3.222617	4.189472	2.642448
H	-4.875028	1.705870	-1.201951	H	1.602648	3.480537	2.758868
C	-2.815987	-2.320490	1.746917	H	3.038562	2.438965	2.850245
H	-2.566444	-3.194154	1.138989	C	2.720353	-1.062890	-0.541590
H	-1.909131	-2.026679	2.281389	C	3.964807	-0.532062	-1.171621
H	-3.556411	-2.628309	2.486068	H	3.880509	-0.487031	-2.259591
H	-3.058350	1.760391	-2.621875	H	4.173196	0.482553	-0.812033
H	-1.619770	1.802455	-1.599556	C	2.726695	-1.186393	0.945234
H	-1.887546	0.428188	-2.665090	H	2.860233	-0.197607	1.399045
C	-2.388766	1.147128	-2.017555	H	1.784890	-1.595736	1.316747
C	-6.585803	0.859697	0.732006	C	5.159032	-1.437493	-0.751146
H	-7.117327	1.146785	-0.178217	C	3.921505	-2.085522	1.368809
H	-7.184003	0.117091	1.263552	C	5.237317	-1.563255	0.776200
H	-6.521531	1.749859	1.366792	H	6.062109	-2.227189	1.053860
S	-0.991368	-1.309363	-0.476309	H	5.462150	-0.579745	1.207868
O	-0.886972	-1.634317	-1.957917	H	5.031811	-2.430755	-1.196398
N	-0.062417	0.090194	-0.065703	H	6.085313	-1.018516	-1.156188
C	0.832118	0.437670	-0.935114	H	3.743258	-3.109431	1.020596
H	0.842164	0.065532	-1.959228	H	3.974054	-2.121690	2.461343
C	1.679525	1.647223	-0.714245	H	2.160174	-1.806638	-1.10260

(R)-configured adduct of 4 with cycloxehyl radical (12_{sec})

Charge: 0

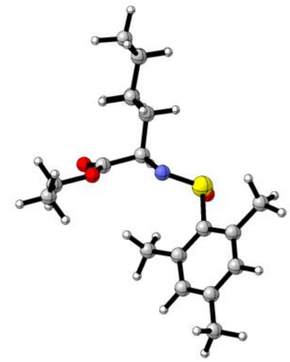
Multiplicity: 2

E = -1419.81171359

H = -1419.344208

G = -1419.431395

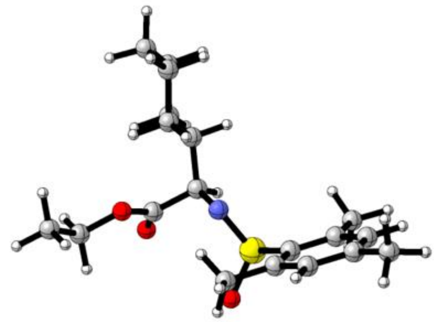
Cartesian coordinates:



C	-3.243099	-1.548452	0.633444	O	2.350200	1.996761	-1.606454
C	-4.517740	-1.034232	0.887018	H	2.513559	3.713555	0.451150
C	-4.938024	0.189429	0.362582	H	1.068086	4.018710	-0.527474
C	-4.051657	0.913227	-0.440323	O	1.184792	2.121534	0.313483
C	-2.763172	0.456580	-0.722475	C	1.434723	3.556963	0.391324
C	-2.386436	-0.779111	-0.168838	C	0.710992	4.067472	1.617667
H	-5.198623	-1.610526	1.504624	H	0.872944	5.143822	1.713369
H	-4.369876	1.861967	-0.860599	H	-0.363021	3.885658	1.537880
C	-2.842291	-2.883702	1.218554	H	1.084543	3.580458	2.521034
H	-2.569792	-3.600151	0.438617	C	2.626383	-0.825604	-0.118398
H	-1.983978	-2.786846	1.888227	C	3.864148	-0.765526	-1.026835
H	-3.667793	-3.310277	1.789070	H	3.603412	-1.095200	-2.037712
H	-2.401268	2.048239	-2.120574	H	4.207134	0.270942	-1.109308
H	-1.123645	1.824840	-0.921646	C	2.973464	-0.402216	1.316512
H	-1.271624	0.696734	-2.275035	H	3.291691	0.647647	1.317291
C	-1.837199	1.300044	-1.562430	H	2.085795	-0.464652	1.950579
C	-6.308894	0.734508	0.674665	C	4.996778	-1.634380	-0.458061
H	-6.711132	1.303108	-0.166646	C	4.106943	-1.268864	1.883791
H	-7.010350	-0.064920	0.921152	C	5.346876	-1.229502	0.980388
H	-6.262719	1.411020	1.534706	H	6.128511	-1.884249	1.378735
S	-0.758739	-1.507608	-0.557589	H	5.757110	-0.211331	0.977580
O	-0.656504	-1.760750	-2.049785	H	4.686231	-2.686892	-0.472032
N	0.206794	-0.312258	0.030741	H	5.878528	-1.557326	-1.101933
C	1.413276	-0.030407	-0.720020	H	3.757172	-2.305324	1.973594
H	1.322601	-0.317573	-1.773180	H	4.359553	-0.932998	2.894371
C	1.697722	1.473246	-0.729337	H	2.284559	-1.868103	-0.092928

Reduced (R)-configured adduct of 4 with cycloxehyl radical (5_{sec}^{-})

Charge: –1



Multiplicity: 1

E = -1419.96650123

H = -1419.499996

G = -1419.586283

Cartesian coordinates:

C	-3.327597	-0.820168	-0.955847
C	-4.501723	-1.201745	-0.294840
C	-4.910746	-0.592845	0.890900
C	-4.109220	0.424292	1.416854
C	-2.927697	0.841673	0.797520
C	-2.544096	0.206328	-0.400442
H	-5.108375	-1.995004	-0.721859
H	-4.410854	0.909339	2.341238
C	-2.941024	-1.537336	-2.232234
H	-2.888657	-0.851618	-3.081982
H	-1.958424	-2.008803	-2.144714
H	-3.670092	-2.315018	-2.467717
H	-2.540009	2.225517	2.399896
H	-1.080612	1.618399	1.574998
H	-2.073464	2.815735	0.782955
C	-2.113151	1.941633	1.435591
C	-6.163805	-1.036846	1.606920
H	-6.689400	-0.188180	2.052246
H	-6.851071	-1.548748	0.929622
H	-5.922547	-1.731359	2.419100
S	-1.043473	0.701933	-1.327893
O	-1.154571	2.254071	-1.443136
N	0.069374	0.179589	-0.248099
C	1.354202	-0.089517	-0.892950
H	1.243496	-0.315381	-1.967656
C	2.253884	1.151384	-0.896869
O	2.672734	1.688796	-1.907889
H	4.288684	2.647347	-0.058833
H	2.816472	3.626776	-0.122873
O	2.523629	1.621384	0.330807
C	3.324344	2.827572	0.422241
C	3.477939	3.153951	1.893231
H	4.076000	4.061493	2.008185
H	2.503452	3.322104	2.357556
H	3.980681	2.340377	2.421285
C	2.047089	-1.328560	-0.269210
C	3.419230	-1.606306	-0.909008
H	3.325649	-1.641269	-2.000261
H	4.101875	-0.776951	-0.678672
C	2.166874	-1.310461	1.262832
H	2.805453	-0.474849	1.566279
H	1.181578	-1.133291	1.699938
C	4.033796	-2.912970	-0.386906
C	2.766575	-2.624110	1.785803
C	4.131543	-2.911893	1.144999
H	4.528937	-3.868467	1.501078
H	4.844126	-2.137143	1.457913
H	3.407033	-3.755821	-0.706472
H	5.022137	-3.069302	-0.832104
H	2.081762	-3.452241	1.558591
H	2.860947	-2.585825	2.876530
H	1.382316	-2.164322	-0.531051

Sodium n-hexyloxalate (3_{prim}·Na^+)

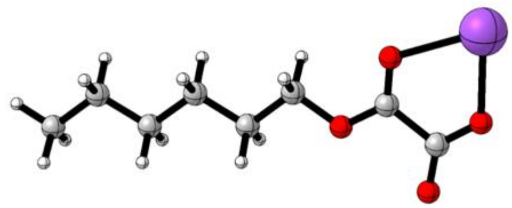
Charge: 0

Multiplicity: 1

E = -776.234782022

H = -776.011915

G = -776.074672



Cartesian coordinates:

O	0.822524	-3.999957	2.704431
O	1.011024	-2.025772	3.751212
C	1.460318	-3.123392	3.467305
C	2.866048	-3.627770	3.979231
O	3.479129	-2.768570	4.661174
O	3.209426	-4.778194	3.669191
Na	2.535780	-0.704078	5.088485
C	-0.482085	-3.608650	2.183426
H	-0.362181	-2.685920	1.610733
H	-1.143634	-3.405144	3.028960
C	-0.992288	-4.748212	1.323550
H	-0.268764	-4.943155	0.524874
H	-1.052498	-5.656371	1.932609
C	-2.364753	-4.434860	0.717472
H	-2.300101	-3.516137	0.121311
H	-3.082539	-4.231914	1.521957
C	-2.897931	-5.570501	-0.161394
H	-2.961907	-6.490104	0.434325
H	-2.178590	-5.774293	-0.964945
C	-4.268888	-5.270425	-0.775635
H	-4.203946	-4.349819	-1.368313
H	-4.987026	-5.068034	0.028286
C	-4.791219	-6.410320	-1.654958
H	-5.770102	-6.172026	-2.080614
H	-4.105591	-6.611170	-2.484577
H	-4.893374	-7.335289	-1.078179

n-Hexyl oxoacyl radical – CO_2 – sodium complex (10_{prim}·CO_2·Na^+)

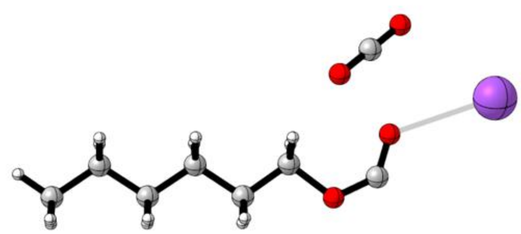
Charge: 0

Multiplicity: 2

E = -776.028670875

H = -775.806094

G = -775.874700



Cartesian coordinates:

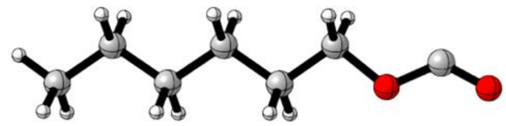
O	1.383253	-3.186368	1.129348
O	1.931170	-2.180285	3.096321
C	2.139327	-2.575450	1.986182
C	1.132030	-3.777398	5.473588
O	1.396534	-2.895638	6.180754
O	0.865684	-4.666058	4.776402
Na	4.149978	-1.552572	5.056662
C	-0.027058	-3.486377	1.545967
H	-0.503771	-2.528418	1.758995
H	0.032235	-4.079432	2.458485
C	-0.686293	-4.228753	0.408007
H	-0.664925	-3.605570	-0.491585
H	-0.112949	-5.135976	0.192397
C	-2.135226	-4.598506	0.754671
H	-2.701056	-3.687093	0.982615
H	-2.147923	-5.208793	1.665819

C	-2.835764	-5.360699	-0.374488
H	-2.265796	-6.269470	-0.605885
H	-2.825060	-4.749408	-1.285773
C	-4.280840	-5.742292	-0.037897
H	-4.848497	-4.833103	0.194429
H	-4.288885	-6.351121	0.874321
C	-4.975109	-6.505376	-1.169681
H	-6.003433	-6.766535	-0.904287
H	-5.007761	-5.905468	-2.084899
H	-4.443027	-7.433919	-1.400549

***n*-Hexyl oxyacyl radical (10$_{prim}$)**

Charge: 0

Multiplicity: 2



E = -425.121330071

H = -424.918536

G = -424.970868

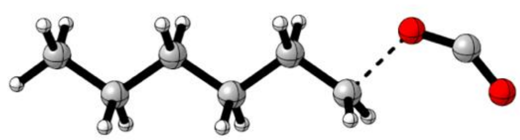
Cartesian coordinates:

C	-0.285774	-0.321248	-0.035113
C	-1.518103	0.558122	-0.048817
H	-0.323092	-0.973691	0.843331
H	-0.296491	-0.965808	-0.920109
O	-2.692383	-0.335440	-0.070479
O	-4.939053	-0.314001	0.033754
C	-3.877060	0.223162	0.036579
H	-1.562135	1.186837	-0.939622
H	-1.584722	1.182565	0.843350
C	1.000779	0.512885	-0.012003
H	0.999044	1.163753	0.870839
H	1.023738	1.174915	-0.886191
C	2.264581	-0.352678	0.000273
H	2.265635	-1.004588	-0.882568
H	2.240162	-1.016886	0.873581
C	3.558659	0.466859	0.024865
H	3.555252	1.118463	0.907078
H	3.580709	1.131060	-0.847617
C	4.816983	-0.405953	0.036900
H	4.859339	-1.045157	-0.850941
H	5.725923	0.202006	0.054741
H	4.833364	-1.058187	0.916084

TS for CO_2 elimination from *n*-hexyl oxyacyl radical (TS1$_{prim}$)

Charge: 0

Multiplicity: 2



E = -425.104396975

H = -424.905031

G = -424.957884

Cartesian coordinates:

C	-0.673518	0.198141	0.447314
O	0.903059	0.649729	-0.547725
O	2.425295	-0.935310	0.166143
C	1.913603	-0.018859	-0.391703
C	-1.645830	1.223776	-0.019700
H	-1.262187	2.225239	0.198581

H	-1.774969	1.146131	-1.103698
H	-0.275801	0.293682	1.452256
H	-0.806369	-0.822802	0.104906
C	-3.019567	1.047165	0.667561
H	-3.404483	0.042639	0.458327
H	-2.894277	1.116354	1.754081
C	-4.038458	2.093260	0.201914
H	-4.156152	2.024449	-0.886871
H	-3.646395	3.097228	0.407761
C	-5.408051	1.937089	0.870595
H	-5.796603	0.932321	0.665274
H	-5.287381	2.003981	1.958552
C	-6.421908	2.984901	0.401538
H	-6.582846	2.918522	-0.679326
H	-7.390140	2.852415	0.892557
H	-6.070060	3.997684	0.623005

n-Hexyl radical — CO_2 complex (11_{prim}·CO_2)

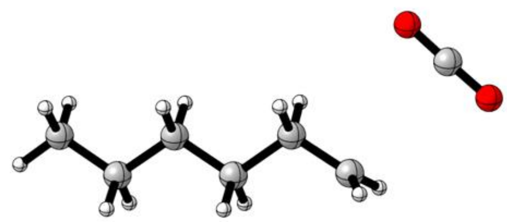
Charge: 0

Multiplicity: 2

E = -425.147232466

H = -424.947708

G = -425.007897



Cartesian coordinates:

C	-1.623656	-0.213090	0.816775
O	1.070177	0.723659	-1.019164
O	1.616191	-1.116233	0.287812
C	1.331698	-0.196400	-0.361251
C	-2.189736	0.948396	0.076733
H	-1.608365	1.852418	0.293562
H	-2.120523	0.776137	-1.003913
H	-1.220152	-0.091693	1.815891
H	-1.759022	-1.224555	0.450160
C	-3.673330	1.233544	0.425827
H	-4.270410	0.339902	0.209404
H	-3.759460	1.413599	1.503834
C	-4.241544	2.430557	-0.342773
H	-4.146042	2.247334	-1.420908
H	-3.635511	3.320185	-0.127475
C	-5.707503	2.725151	-0.008499
H	-6.311597	1.835260	-0.223329
H	-5.801508	2.907167	1.069008
C	-6.267267	3.923315	-0.781356
H	-6.212737	3.753107	-1.861539
H	-7.313691	4.112262	-0.525067
H	-5.699042	4.832634	-0.560003

n-Hexyl radical (11_{prim})

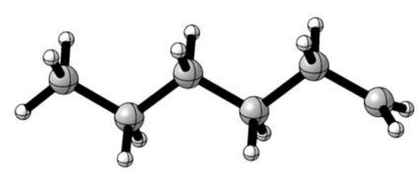
Charge: 0

Multiplicity: 2

E = -236.494728406

H = -236.311832

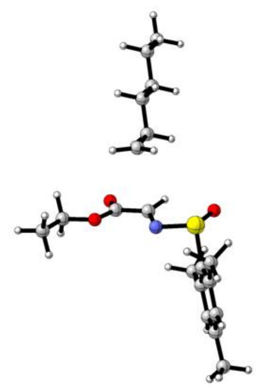
G = -236.355504



Cartesian coordinates:

C	2.254252	-1.492371	-0.001601
C	1.764772	-0.085519	-0.000026
H	1.876692	-2.025297	0.879557
H	1.876566	-2.023366	-0.883871
H	1.665010	0.468151	-0.927025
H	1.665154	0.466123	0.928198
C	3.801693	-1.603837	-0.001834
H	4.197345	-1.080380	-0.880305
H	4.197470	-1.082304	0.877726
C	4.291450	-3.055140	-0.003457
H	3.885939	-3.573485	-0.882257
H	3.886064	-3.575408	0.874263
C	5.818602	-3.180123	-0.003703
H	6.222376	-2.659339	-0.880652
H	6.222501	-2.661260	0.874327
C	6.299675	-4.634418	-0.005329
H	5.934464	-5.167004	-0.889672
H	7.391975	-4.695737	-0.005474
H	5.934590	-5.168938	0.877898

n-Hexyl radical — N-sulfinyl imine 4 re-precomplex (11_{prim}·4)



Charge: 0

Multiplicity: 2

E = -1420.98086882

H = -1420.495624

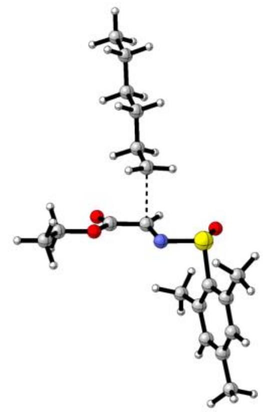
G = -1420.596941

Cartesian coordinates:

C	-3.950272	-0.973997	1.185307
C	-5.281810	-0.824135	0.789142
C	-5.637222	-0.625568	-0.545495
C	-4.620920	-0.565178	-1.502184
C	-3.271893	-0.698681	-1.167975
C	-2.958771	-0.905519	0.189408
H	-6.058762	-0.868502	1.545280
H	-4.882608	-0.404390	-2.543352
C	-3.636838	-1.189037	2.650722
H	-3.109628	-2.131959	2.818187
H	-3.009199	-0.389503	3.052232
H	-4.559237	-1.214570	3.231736
H	-2.704664	-0.655496	-3.237733
H	-1.726800	0.385069	-2.203036
H	-1.469699	-1.355836	-2.174689
C	-2.232838	-0.583044	-2.257200
C	-7.084321	-0.509126	-0.952704
H	-7.205293	0.169982	-1.799583
H	-7.474087	-1.485990	-1.258195
H	-7.703366	-0.150401	-0.128025
S	-1.249706	-1.177410	0.763328
O	-0.562652	-2.178951	-0.143656
N	-0.687315	0.449098	0.436954
C	0.353745	0.530147	-0.291432
H	0.812488	-0.325037	-0.790551
C	0.977410	1.851837	-0.633506
O	1.771931	1.951086	-1.546469
H	2.216804	4.097398	-0.042595
H	0.891002	4.438728	-1.168163
O	0.563050	2.853010	0.134724
C	1.131380	4.169738	-0.137753
C	0.530995	5.132658	0.862092
H	0.934968	6.132827	0.687891
H	-0.555166	5.176479	0.757049
H	0.775197	4.835272	1.884156
C	2.688846	0.192708	1.317533
C	3.552548	-0.431613	0.281060
H	3.122826	-1.385406	-0.044606
H	3.601331	0.219716	-0.600344
H	2.807269	1.241272	1.568714
H	2.088769	-0.412998	1.986371
C	5.001194	-0.686046	0.771404
H	5.439596	0.263734	1.099182
H	4.974011	-1.339452	1.650922

C	5.883967	-1.315049	-0.310881
H	5.433693	-2.259763	-0.641932
H	5.902417	-0.658133	-1.190058
C	7.319694	-1.575908	0.156101
H	7.298926	-2.231353	1.035253
H	7.767817	-0.631310	0.487566
C	8.195616	-2.205042	-0.931628
H	9.214052	-2.381300	-0.573710
H	7.784765	-3.165758	-1.258678
H	8.257388	-1.554473	-1.810073

re-TS for n-hexyl radical addition to N-sulfinyl imine 4 (TS2$_{prim}$)



Charge: 0

Multiplicity: 2

E = -1420.98010710

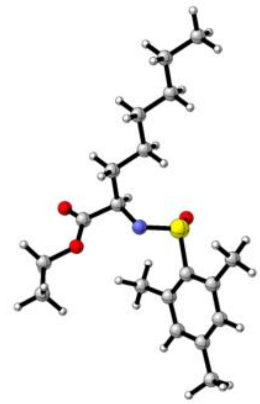
H = -1420.495207

G = -1420.592202

Cartesian coordinates:

C	-3.002715	-0.854302	0.104340
C	-3.919806	-1.072546	1.147919
C	-5.264896	-0.781039	0.904194
C	-5.704263	-0.300702	-0.329889
C	-4.759263	-0.097785	-1.339050
C	-3.401089	-0.361619	-1.153137
C	-3.512703	-1.592044	2.510384
C	-7.166846	-0.033864	-0.582106
C	-2.436855	-0.077478	-2.279485
S	-1.275845	-1.324550	0.455574
N	-0.610202	0.273168	0.359132
C	0.428630	0.395447	-0.400736
C	1.064304	1.734894	-0.614253
O	0.792577	2.613915	0.346739
C	1.382575	3.941148	0.211579
C	0.956607	4.745212	1.419989
O	-0.759856	-2.207988	-0.667122
O	1.754329	1.960539	-1.588537
C	2.340806	-0.335905	0.879730
C	3.469678	-0.488718	-0.076015
H	1.805752	-1.218935	1.212200
H	-5.985016	-0.938519	1.700480
H	-5.085902	0.282857	-2.301763
H	-3.034874	-2.573015	2.444195
H	-2.807497	-0.919379	3.005125
H	-4.388933	-1.690280	3.152064
H	-2.979342	0.067506	-3.214489
H	-1.871705	0.836372	-2.076425
H	-1.717178	-0.884754	-2.411115
H	-7.305483	0.816819	-1.253180
H	-7.637194	-0.902860	-1.054468
H	-7.702560	0.166390	0.347897
H	0.727377	-0.363335	-1.124586
H	2.467031	3.828320	0.151718
H	1.028192	4.380074	-0.723164
H	1.380591	5.750100	1.354058
H	-0.131092	4.832265	1.466305
H	1.312718	4.280438	2.341949
H	3.216665	-1.226051	-0.845489
H	3.666010	0.460755	-0.584587
H	2.325967	0.510417	1.558434
C	4.770207	-0.942865	0.635897
H	4.590058	-1.895855	1.145757
H	5.028159	-0.213534	1.412067
C	5.942182	-1.093127	-0.339669
H	5.675067	-1.819108	-1.118011
H	6.110490	-0.137906	-0.852990
C	7.240141	-1.536849	0.343098
H	7.069261	-2.490740	0.856523
H	7.503549	-0.811134	1.122003
C	8.407918	-1.683806	-0.637092
H	9.321488	-2.001241	-0.126384
H	8.180737	-2.426110	-1.409058
H	8.618533	-0.734972	-1.141024

(R)-configured adduct of 4 with n-hexyl radical (12_{prim})



Charge: 0

Multiplicity: 2

E = -1421.01932445

H = -1420.530232

G = -1420.624796

Cartesian coordinates:

C	2.263646	-2.463363	-0.501033	H	0.435384	4.930667	-1.072701
C	3.610467	-2.728297	-0.764611	H	1.648267	4.581595	0.171854
C	4.630278	-1.889509	-0.311354	O	0.640560	2.923132	-0.573157
C	4.284051	-0.749266	0.419525	C	1.230539	4.243239	-0.778159
C	2.956921	-0.426258	0.707471	C	2.288994	4.093922	-1.848545
C	1.967975	-1.304286	0.232408	H	2.757586	5.063615	-2.032898
H	3.865080	-3.615051	-1.335585	H	3.063201	3.390855	-1.533489
H	5.067878	-0.087369	0.773817	H	1.850455	3.739205	-2.783738
C	1.198786	-3.408815	-1.008933	C	-2.287546	1.402717	-0.078275
H	0.600449	-3.818013	-0.190134	C	-3.055021	0.105846	0.180727
H	0.512635	-2.908785	-1.697186	H	-2.538762	-0.734320	-0.296495
H	1.656241	-4.245338	-1.537962	H	-3.064473	-0.101175	1.257637
H	3.530183	1.219320	1.965269	H	-2.211463	1.592534	-1.153500
H	2.284819	1.607961	0.774368	H	-2.819863	2.245663	0.372092
H	1.865082	0.677175	2.216313	C	-4.494372	0.164708	-0.340738
C	2.639499	0.838550	1.464213	H	-5.020913	0.998731	0.139910
C	6.077575	-2.220263	-0.575467	H	-4.481201	0.386049	-1.415420
H	6.673812	-1.315047	-0.709776	C	-5.271968	-1.132662	-0.099842
H	6.503103	-2.769940	0.270832	H	-4.744236	-1.965974	-0.581659
H	6.188668	-2.844772	-1.463996	H	-5.280513	-1.355651	0.974989
S	0.208897	-1.017695	0.630963	C	-6.713595	-1.082976	-0.615990
O	0.020807	-1.007466	2.134814	H	-7.239950	-0.250352	-0.133553
N	-0.011267	0.420873	-0.131655	H	-6.703715	-0.858766	-1.689637
C	-0.854868	1.398351	0.526286	C	-7.481329	-2.385358	-0.371304
H	-0.935595	1.222257	1.605276	H	-8.506197	-2.323887	-0.748358
C	-0.276149	2.810117	0.383187	H	-6.991654	-3.228517	-0.869355
O	-0.658814	3.724571	1.080095	H	-7.531497	-2.615921	0.697850

Reduced (R)-configured adduct of 4 with n-hexyl radical (5_{prim}^{-})

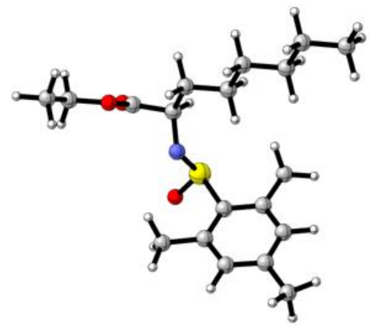
Charge: –1

Multiplicity: 1

E = -1421.17690774

H = -1420.688804

G = -1420.781411



Cartesian coordinates:

C	-2.334696	-1.423736	0.849424	H	5.845226	0.615001	-0.183116
C	-3.506160	-1.780473	0.169967	H	5.294293	-1.001644	-0.644836
C	-3.490720	-2.649123	-0.920571	O	3.816349	0.456411	-0.605626
C	-2.257358	-3.159663	-1.335356	C	5.190114	0.064220	-0.862019
C	-1.059196	-2.834029	-0.693489	C	5.486892	0.377986	-2.313487
C	-1.110760	-1.958289	0.409322	H	6.516660	0.095753	-2.546912
H	-4.452095	-1.364457	0.504414	H	4.818941	-0.177193	-2.976170
H	-2.223770	-3.828770	-2.190895	H	5.369198	1.445761	-2.512637
C	-2.432338	-0.469349	2.021318	C	1.468490	1.893293	0.064526
H	-2.078530	-0.930706	2.947210	C	0.022602	2.291819	0.362656
H	-1.828559	0.426977	1.861522	H	-0.639033	1.485198	0.031804
H	-3.467838	-0.158202	2.172266	H	-0.112329	2.374940	1.449649
H	0.054019	-4.016499	-2.106595	H	1.612734	1.783372	-1.014959
H	0.936683	-2.612169	-1.459437	H	2.147976	2.689119	0.397543
H	0.720469	-4.020789	-0.451503	C	-0.400563	3.606220	-0.297753
C	0.234832	-3.411365	-1.215711	H	0.265375	4.414374	0.032388
C	-4.767556	-3.049038	-1.620246	H	-0.268119	3.525436	-1.384688
H	-4.616346	-3.147647	-2.698311	C	-1.851398	3.991266	0.007547
H	-5.126301	-4.016876	-1.253073	H	-2.517145	3.184194	-0.325700
H	-5.561652	-2.318344	-1.450671	H	-1.983918	4.065836	1.095070
S	0.388916	-1.462643	1.341476	C	-2.288853	5.307182	-0.643424
O	1.111536	-2.810025	1.642779	H	-1.621793	6.112039	-0.310782
N	1.110014	-0.557911	0.186004	H	-2.159371	5.231568	-1.730099
C	1.853325	0.574159	0.753650	C	-3.739795	5.680050	-0.324756
H	1.679854	0.691647	1.835892	H	-4.027016	6.622253	-0.800495
C	3.338084	0.252698	0.634390	H	-4.429456	4.904839	-0.674486
O	4.024227	-0.194141	1.536796	H	-3.887482	5.791707	0.754446

2-Allyladamantan-2-yl oxyacyl radical (10’)

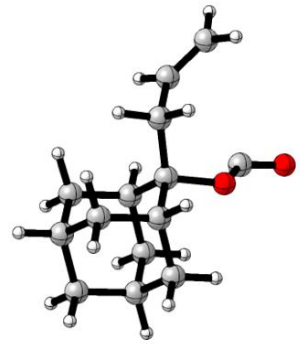
Charge: 0

Multiplicity: 2

E = -695.557897876

H = -695.238011

G = -695.292585



Cartesian coordinates:

C	-1.949149	-0.320647	-0.644725
C	-2.658261	-0.615717	-1.980639
C	-1.606094	-0.683069	-3.102825
C	-0.848440	0.659837	-3.197354
C	-1.199041	1.026670	-0.735223
C	-3.666354	0.507815	-2.291883
C	-1.866815	1.783230	-3.503416
C	-2.923143	1.855199	-2.382568
C	-2.225666	2.141969	-1.038663
C	3.145294	2.273782	-2.628444
C	1.841457	2.241498	-2.904522
C	1.585060	-0.666431	-2.338472
O	0.755271	-0.154754	-1.457855
C	-0.141320	0.976677	-1.860528
C	0.756172	2.231502	-1.865706
O	2.384249	-1.534537	-2.153098
H	-4.181233	0.298949	-3.236407
H	-4.430760	0.554681	-1.508239
H	-0.913252	-1.509354	-2.922054
H	-2.089558	-0.880154	-4.065159
H	-3.181773	-1.574551	-1.912821
H	-1.254860	-1.127247	-0.397493
H	-2.681487	-0.262393	0.167203
H	-0.687751	1.233785	0.209873
H	-3.634070	2.657223	-2.603849
H	-1.751065	3.126498	-1.054245
H	-2.963161	2.164535	-0.230056
H	-1.365075	2.747840	-3.620676
H	-2.349578	1.562360	-4.460639
H	1.193379	2.324065	-0.867312
H	1.521812	2.246337	-3.943620
H	0.120445	3.106311	-2.015188
H	3.891435	2.298410	-3.414946
H	3.508158	2.272414	-1.604685
H	-0.105982	0.604384	-3.997019

TS for CO_2 elimination from 2-allyladamantan-2-yl oxyacyl radical (TS3)

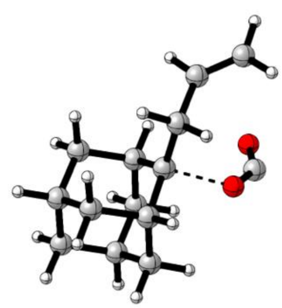
Charge: 0

Multiplicity: 2

E = -695.548151204

H = -695.230749

G = -695.285962



Cartesian coordinates:

C	1.684189	0.661460	1.380828
C	2.230952	1.058304	-0.003045
C	1.048857	1.295008	-0.958961
C	0.195227	0.013374	-1.074835
C	0.842549	-0.627955	1.262550
C	3.118846	-0.072749	-0.557218

C	1.101892	-1.132084	-1.633205
C	2.289061	-1.366255	-0.678844
C	1.759426	-1.764771	0.711354
C	-3.810202	-1.138199	-0.155898
C	-2.558183	-1.317296	-0.570166
C	-1.944043	1.823502	0.485579
O	-1.272376	0.996049	1.104482
C	-0.289853	-0.464836	0.273710
C	-1.385428	-1.504617	0.351141
O	-2.254143	2.193409	-0.609714
H	3.518178	0.209815	-1.537546
H	3.974193	-0.239785	0.106607
H	0.435986	2.128549	-0.610470
H	1.414433	1.561089	-1.956140
H	2.817332	1.978103	0.086517
H	1.074122	1.466939	1.794680
H	2.509434	0.481150	2.077369
H	0.443545	-0.916433	2.238613
H	2.915265	-2.172652	-1.073268
H	1.215635	-2.711969	0.660649
H	2.588513	-1.909161	1.411245
H	0.523506	-2.051596	-1.762021
H	1.457731	-0.833827	-2.624285
H	-1.721996	-1.570276	1.389125
H	-2.350591	-1.349466	-1.636734
H	-0.917441	-2.473091	0.121582
H	-4.628439	-1.020412	-0.857733
H	-4.058366	-1.100333	0.900934
H	-0.642615	0.181873	-1.751694

2-Allyladamantan-2-yl radical — CO_2 complex (11·CO_2)

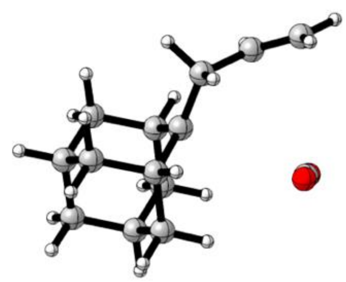
Charge: 0

Multiplicity: 2

E = -695.588167042

H = -695.269738

G = -695.330835



Cartesian coordinates:

C	1.418292	0.896817	1.141583
C	2.085138	1.163643	-0.221462
C	1.032999	1.035728	-1.340406
C	0.425081	-0.386224	-1.323679
C	0.803609	-0.522608	1.153494
C	3.207330	0.130745	-0.450096
C	1.565755	-1.422532	-1.558100
C	2.614515	-1.293194	-0.435083
C	1.947532	-1.558424	0.930127
C	-3.773498	-1.138164	0.046055
C	-2.581919	-1.231827	-0.542839
C	-2.159557	1.658550	0.974077
O	-2.137071	1.178835	2.031100
C	-0.183476	-0.675692	0.025564
C	-1.311767	-1.664868	0.147036
O	-2.190874	2.170662	-0.067527
H	3.700945	0.319923	-1.410294
H	3.970063	0.226790	0.331244
H	0.240949	1.777941	-1.202418
H	1.497000	1.226243	-2.315053
H	2.507755	2.174056	-0.230497
H	0.642897	1.644612	1.336094
H	2.157949	0.983767	1.945873
H	0.318731	-0.711844	2.116239
H	3.413101	-2.025157	-0.597555
H	1.541411	-2.575176	0.963071
H	2.684773	-1.474658	1.737405
H	1.151876	-2.436569	-1.575435
H	2.030104	-1.244169	-2.535126
H	-1.520152	-1.867131	1.202278
H	-2.492535	-0.976787	-1.596544
H	-0.996839	-2.628547	-0.295772
H	-4.653637	-0.817729	-0.501242
H	-3.908041	-1.377177	1.097209
H	-0.317012	-0.480240	-2.121869

TS for intramolecular cyclization of 2-allyladamantan-2-yl oxyacyl radical (TS4)

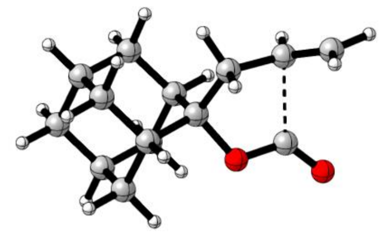
Charge: 0

Multiplicity: 2

E = -695.553022764

H = -695.234797

G = -695.286598



Cartesian coordinates:

C	-1.976436	-0.338181	-0.661594	H	-1.025656	-1.511977	-2.975483
C	-2.731093	-0.599099	-1.979271	H	-2.231580	-0.861414	-4.082300
C	-1.714351	-0.678334	-3.134765	H	-3.276306	-1.545570	-1.907453
C	-0.935299	0.651141	-3.240305	H	-1.296488	-1.165086	-0.442921
C	-1.191886	0.987849	-0.761848	H	-2.683614	-0.268764	0.171731
C	-3.720542	0.553767	-2.239791	H	-0.643585	1.168661	0.167917
C	-1.939054	1.795779	-3.505755	H	-3.645570	2.705520	-2.527342
C	-2.947140	1.883317	-2.343129	H	-1.673187	3.104697	-1.062406
C	-2.187988	2.140225	-1.025659	H	-2.892788	2.191730	-0.189681
C	3.235790	2.278846	-2.446118	H	-1.423617	2.750908	-3.638794
C	1.981879	1.912433	-2.827351	H	-2.464008	1.590263	-4.444201
C	1.810030	-0.294696	-2.321018	H	1.088745	2.355591	-0.934754
O	0.690248	-0.249593	-1.623358	H	1.798365	1.737700	-3.883573
C	-0.178641	0.924697	-1.919716	H	0.225056	3.010492	-2.317593
C	0.768972	2.135943	-1.957716	H	4.069764	2.233371	-3.136481
O	2.629331	-1.164194	-2.296643	H	3.451913	2.561484	-1.420896
H	-4.275151	0.371276	-3.167178	H	-0.213004	0.589285	-4.060081
H	-4.454261	0.609053	-1.427726				

Intramolecular cyclization product from 2-allyladamantan-2-yl oxyacyl radical (11')

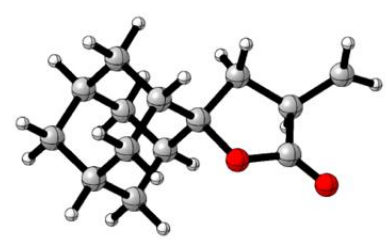
Charge: 0

Multiplicity: 2

E = -695.590987928

H = -695.271356

G = -695.323992



Cartesian coordinates:

C	-1.946908	-0.363265	-0.695332	C	-1.023988	0.670183	-3.302608
C	-2.759441	-0.602163	-1.982486	C	-1.169446	0.964117	-0.808781
C	-1.794405	-0.662323	-3.183768	C	-3.758924	0.555200	-2.176385

C	-2.038340	1.817974	-3.503956
C	-2.991205	1.886692	-2.295104
C	-2.166555	2.126137	-1.013998
C	3.311848	2.193093	-2.290252
C	2.050840	1.508019	-2.670575
C	1.957885	0.049773	-2.185700
O	0.701643	-0.229490	-1.809893
C	-0.213152	0.921572	-2.010910
C	0.760465	2.111344	-2.094392
O	2.840733	-0.773922	-2.135472
H	-4.357625	0.388453	-3.079046
H	-4.452995	0.596386	-1.329227
H	-1.094765	-1.493599	-3.064971
H	-2.353083	-0.835603	-4.109588
H	-3.301658	-1.549791	-1.902745
H	-1.254209	-1.191116	-0.523788
H	-2.616057	-0.312513	0.170329
H	-0.576814	1.130126	0.096442
H	-3.697568	2.711268	-2.433237
H	-1.637920	3.082956	-1.076797
H	-2.827995	2.184366	-0.143641
H	-1.528854	2.776095	-3.640023
H	-2.605050	1.630621	-4.421839
H	0.951900	2.497748	-1.088956
H	1.981180	1.439345	-3.763268
H	0.380054	2.929548	-2.701022
H	4.165942	2.198388	-2.953856
H	3.427988	2.583306	-1.286041
H	-0.334674	0.628193	-4.152369

8. ***References***

(1) A. Shatskiy, A. Axelsson, E. V. Stepanova, J.-Q. Liu, A. Z. Temerdashev, B. P. Kore, B. Blomkvist, J. M. Gardner, P. Dinér and M. D. Kärkäs, *Chem. Sci*., 2021, **12**, 5430–5437. https://doi.org/10.1039/D1SC00658D

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