

Supporting Information

Stereoselective Synthesis of Unnatural α -Amino Acids through Photoredox Catalysis

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1. Experimental

Commercial anhydrous α,α,α -trifluorotoluene (Sigma-Aldrich, Art. No. 547948-100ML) was used without further purification. When needed, CH_2Cl_2 , MeCN, and Et_3N were dried by refluxing over CaH_2 for several hours followed by distillation, and the dried solvents were used immediately after preparation. 2,2,2-Trifluoroethanol (TFE) and PhF were dried over activated 3 Å molecular sieves. The 4CzIPN photocatalyst was synthesized according to the previously published procedure.¹

The radical addition reactions were carried out in 4 mL vials (VWR, Screw neck vials N13, Art. No. MANA702962) equipped with a stirring bar (VWR, Art. No. 442-0401) and a septum (VWR, Art. No. 217-0183). The reaction vials were placed in a holder (distance between the reaction vial and the lamp is ca. 2 cm, Figure S1) and illuminated with 440 nm LED (Kessil PR160, set to maximum intensity) with continuous stirring at 1000 rpm. The isolated radical addition products were purified by column chromatography (15–20 cm height, 2 cm inner diameter) with silica gel (high-purity grade, 60 Å, 130–270 mesh, Sigma-Aldrich, Art. No. 288608-1KG) or by preparative TLC (PLC Silica gel 60 F₂₅₄, 1 mm, 20 x 20 cm, Merck, Art. No. 1.13895).

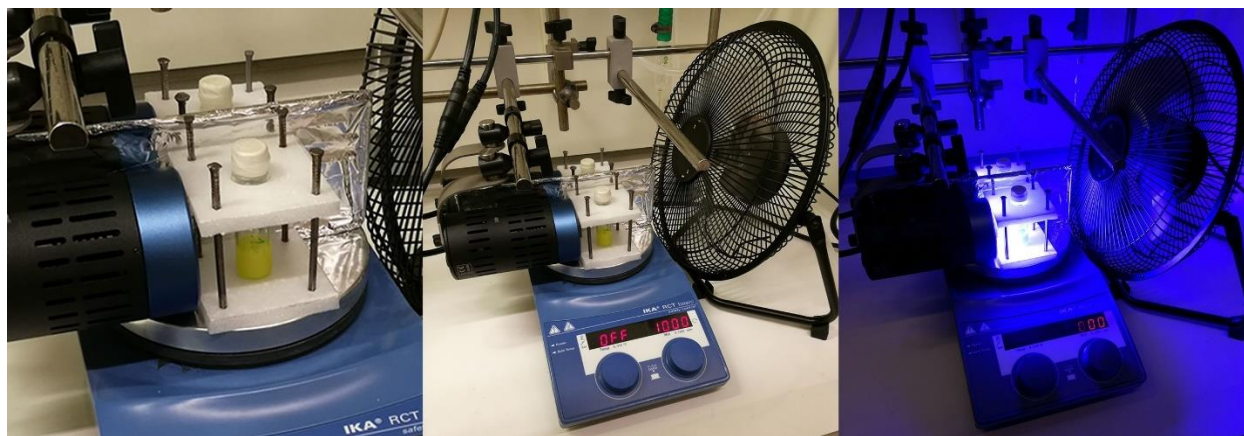


Figure S1. The reaction setup for optimization of the reaction conditions and substrate scope evaluation.

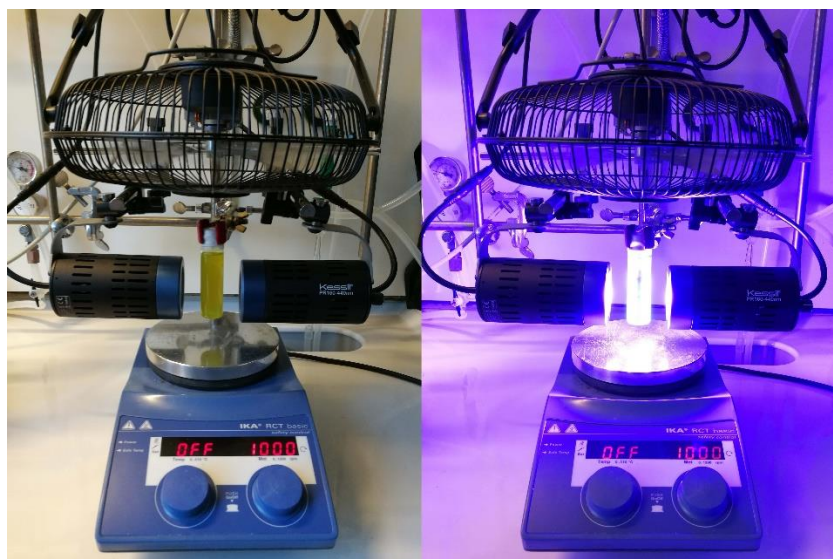
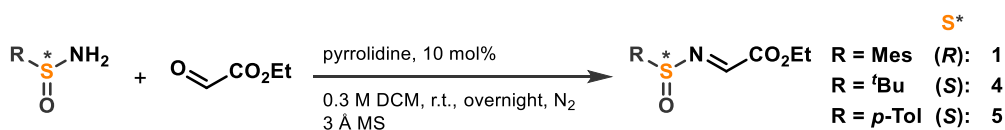


Figure S2. The reaction setup for 1 mmol scale synthesis.

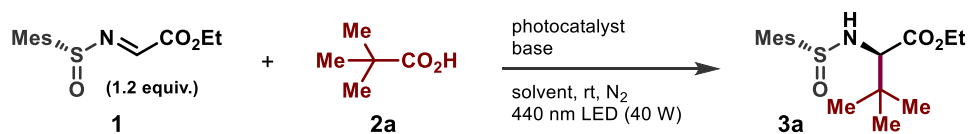
NMR spectra were recorded in CDCl₃ on Bruker Avance DMX 500 MHz or Bruker Ascend 400 MHz NMR spectrometers and internally calibrated against the residual undeuterated solvent peaks (CHCl₃: δ 7.26 for ¹H NMR and δ 77.16 for ¹³C NMR). The chemical shifts are reported in ppm and the peak multiplicities are designated as: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), td (triplet of doublets), m (multiplet).

2. General procedure for the synthesis of sulfinyl imines



Sulfinyl imines **1**, **4**, and **5** were synthesized according to a procedure adapted from reference [2]. Sulfinyl amide (1 equiv.) and 4 Å activated molecular sieves (2 g per 1 mmol of sulfinyl amide) were placed in a dry 25 mL round-bottom flask equipped with a stirring bar and a septum and evacuated and back-filled with N₂ three times. Anhydrous DCM (0.03 M), ethyl glyoxalate (1 equiv., 50% solution in toluene), and pyrrolidine (10 mol%) were added and the reaction mixture was stirred at room temperature under N₂ balloon. After 19 h the reaction mixture was filtered through celite washing with DCM, and concentrated on rotary evaporator resulting in a crude product as a yellow oil. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) and the fractions containing the desired product were combined, concentrated on rotary evaporator, and dried under vacuo overnight, resulting in the desired product.

3. Optimization of the reaction conditions



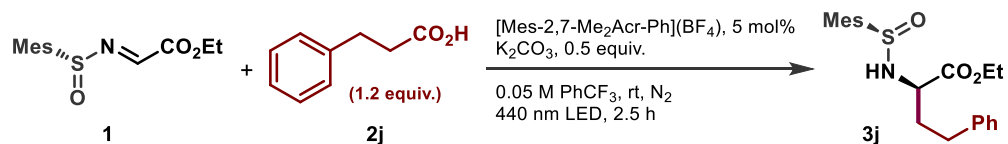
The reactions were typically performed on 0.1 mmol scale (relative to the limiting starting material). The sulfinyl imine **1**, photocatalyst, and the base were placed in the reaction vial equipped with a stirring bar and a septum. The solids were evacuated and back-filled with N₂ three times, followed by addition of a stock solution of pivalic acid **2a** in deaerated anhydrous PhCF₃ and short sonication. Thereafter, the reaction mixture was placed ca. 2 cm from the light source (440 nm LED, see Figure S1) and stirred with a fan cooling. The reactions were monitored by ¹H NMR with 1,3,5-trimethoxybenzene as an internal standard. Typically, 0.5 mL of the reaction mixture was taken at a time, filtered through a silica plug eluting with hexane/ethyl acetate 1:1, concentrated on rotary evaporator, dissolved in a stock solution of the internal standard in CDCl₃, and analyzed by ¹H NMR (500 MHz). Note, when performing the reactions with small amounts of the photocatalysts (Table S1, entries 1–8), both photocatalyst and the acid were added as stock solutions.

Table S1. Optimization of the reaction conditions with pivalic acid **2a** as the radical precursor.

<i>entry</i>	<i>photocatalyst</i>	<i>base</i>	<i>solvent</i>	<i>time</i>	<i>yield</i> ^a	<i>dr</i> ^a
1	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆), 1 mol%	Cs ₂ CO ₃ , 0.2 equiv.	DMSO, 0.1 M	20 min	< 5%	—
2	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆), 1 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	65%	4 : 1
3	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆), 1 mol%	2,6-lutidine, 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
4	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆), 1 mol%	DIPEA, 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
5	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆), 1 mol%	K ₃ PO ₄ , 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
6	[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)](PF ₆), 1 mol%	Bu ₄ NH ₂ PO ₄ , 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
7	4CzIPN, 1 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
8	[Mes-Acr-Me](BF ₄), 1 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	27%	> 95 : 5
9	[Mes-Acr-Me](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	48%	> 95 : 5
				60 min	66%	> 95 : 5
10	[Mes-Acr-Me](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	MeCN, 0.05 M	20 min	15%	> 95 : 5
11	[Mes-Acr-Me](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	CH ₂ Cl ₂ , 0.05 M	20 min	24%	> 95 : 5
12	[Mes-Acr-Ph](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	60 min	73%	> 95 : 5
13	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	60 min	78%	> 95 : 5
14	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	PhF, 0.05 M	20 min	10%	> 95 : 5
15	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	Cs ₂ CO ₃ , 0.2 equiv.	TFE, 0.05 M	20 min	< 5%	—
16	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	2,6-lutidine, 0.2 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
17	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	Li ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	60 min	< 5%	—
18	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₃ PO ₄ , 0.2 equiv.	PhCF ₃ , 0.05 M	60 min	80%	> 95 : 5
19	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₂ CO ₃ , 0.2 equiv.	PhCF ₃ , 0.05 M	60 min	84%	> 95 : 5
20	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₂ CO ₃ , 0.05 equiv.	PhCF ₃ , 0.05 M	20 min	< 5%	—
21	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₂ CO ₃ , 0.5 equiv.	PhCF ₃ , 0.05 M	60 min	85%	> 95 : 5
22	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₂ CO ₃ , 0.5 equiv.	PhCF ₃ , 0.1 M	60 min	77%	> 95 : 5
23^b	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₂ CO ₃ , 0.5 equiv.	PhCF ₃ , 0.05 M	60 min	91%	> 95 : 5
24^c	[Mes-2,7-Me ₂ Acr-Ph](BF ₄), 5 mol%	K ₂ CO ₃ , 0.5 equiv.	PhCF ₃ , 0.05 M	60 min	95%	> 95 : 5

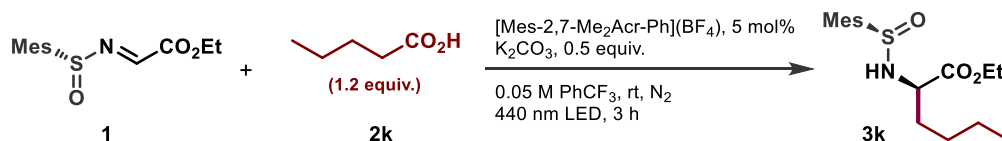
^a Determined by ¹H NMR of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard. ^b 1.0 equiv. of sulfinyl imine **1** and 1.2 equiv. of pivalic acid **2a**. ^c 1.0 equiv. of sulfinyl imine **1** and 1.5 equiv. of pivalic acid **2a**.

Table S2. Optimization of the reaction conditions with hydrocinnamic acid **2j** as the radical precursor.



entry	deviations from standard conditions	time	remaining imine ^a	yield ^a
1	none	60 min	0.67 equiv.	19%
		150 min	0.45 equiv.	22%
2	solvent: PhCF ₃ /TFE 19:1, 0.05 M	60 min	0.47 equiv.	< 5%
3	solvent: PhCF ₃ /HFIP 19:1, 0.05 M	60 min	0.46 equiv.	12%
4	solvent: PhCF ₃ /toluene 1:1, 0.05 M	20 min	0.82 equiv.	7%
5	base: Bu ₄ NOAc, 0.5 equiv.	20 min	0.74 equiv.	11%
		60 min	0.54 equiv.	20%
6	base: Bu ₄ NOBz, 0.5 equiv.	20 min	0.70 equiv.	9%
		60 min	0.49 equiv.	16%
7	base: Bu ₄ NOP(O)(OBu) ₂ , 0.5 equiv.	60 min	0.75 equiv.	9%
		270 min	0.35 equiv.	15%
8	base: CsF, 0.5 equiv.	60 min	0.65 equiv.	15%
9	light: two LEDs (double intensity)	60 min	0.55 equiv.	20%
10	additive: Bu ₄ NPF ₆ , 0.5 equiv.	60 min	0.62 equiv.	13%
11	additive: Bu ₄ NOTf, 0.5 equiv.	60 min	0.66 equiv.	11%

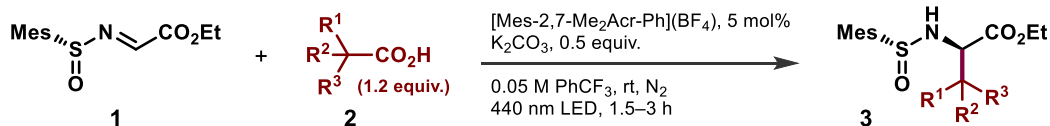
^a Determined by ¹H NMR of the crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Optimization of the reaction conditions with valeric acid **2k** as the radical precursor.

entry	deviations from standard conditions	time	remaining imine ^a	yield ^a
1	none	60 min	0.49 equiv.	32%
		180 min	0.34 equiv.	41%
2	solvent: PhCF ₃ , 0.025 M	60 min	0.62 equiv.	20%
		180 min	0.52 equiv.	21%
3	acid: 2.0 equiv.	60 min	0.18 equiv.	38%
		180 min	0 equiv.	38%
4	light: half intensity	180 min	0.37 equiv.	39%
		360 min	0.22 equiv.	45%
5	photocatalyst: 1 mol%	60 min	0.56 equiv.	21%
6	temperature: -20 °C	180 min	0.80 equiv.	11%
7	temperature: 70 °C	60 min	0.41 equiv.	21%

^a Determined by ¹H NMR of a crude reaction mixture with 1,3,5-trimethoxybenzene as an internal standard.

4. General procedure for the decarboxylative addition to sulfanyl imine **1**



The sulfanyl imine **1** (1 equiv.), [Mes-2,7-Me₂Acr-Ph](BF₄) photocatalyst (5 mol%), K₂CO₃ (0.5 equiv.), and acid **2** (1.2 equiv.) were placed in the reaction vial equipped with a stirring bar and a septum. The solids were evacuated and back-filled with N₂ three times, followed by addition of deaerated anhydrous PhCF₃ (0.05 M relative to sulfanyl imine **1**) and short sonication to obtain a fine suspension (acids that are liquid at room temperature were added as solutions in PhCF₃). Thereafter, the reaction mixture was placed ca. 2 cm from the light source (440 nm LED) and stirred under illumination with a fan cooling (see Figure S1). After the reaction was complete the mixture was filtered through a silica plug eluting with hexane/ethyl acetate 1:1, concentrated on rotary evaporator (40 °C), and the crude product **3** was purified by column chromatography or preparative TLC.

Important! Products **3** slowly epimerize in chloroform. When used, chloroform should be removed from the samples directly after column chromatography or NMR experiments to avoid epimerization.

5. Procedure for the 1 mmol scale synthesis of compound **3a**

The sulfinyl imine **1** (267.4 mg, 1 mmol, 1 equiv.), [Mes-2,7-Me₂Acr-Ph](BF₄) photocatalyst (24.5 mg, 0.05 mmol, 5 mol%), K₂CO₃ (69.1 mg, 0.5 mmol, 0.5 equiv.), and pivalic acid (122.6 mg, 1.2 mmol, 1.2 equiv.) were placed in the reaction vial (VWR, 24.0 mL sample vial, Art. No. 218-2226) equipped with a stirring bar and a septum. The solids were evacuated and back-filled with N₂ three times, followed by addition of deaerated anhydrous PhCF₃ (20 mL, 0.05 M) and short sonication to obtain a fine suspension. Thereafter, the reaction mixture was placed between **two** 440 nm LED lamps and stirred under illumination with a fan cooling (see Figure S2). After 2.5 h the reaction mixture was filtered through silica eluting with hexane/ethyl acetate 1:1, concentrated on rotary evaporator (40 °C), and the crude product was purified by column chromatography with chloroform/ethyl acetate 35:1 as eluent. The purified product was dried in vacuo overnight, resulting in **3a** as white solid (247.2 mg, 76% yield, >95:5 α dr).

6. Computational studies

Synthesis of product **3a** from the sulfinyl imine **1** and pivalic acid **2a** was selected as the model reaction for the computational studies. All calculations were performed on the M062X-D3/6-311+G(d,p)³ level of theory using Gaussian 16 package, revision B.01.⁴ The effect of the solvent (chlorobenzene) was modeled implicitly using the Solvation Model based on Density (SMD) method.⁵ Vibrational analysis confirmed that all reported structures either represents true minima (no imaginary frequencies), or the true first order saddle points (for transition states, one imaginary frequency) on the potential energy surface. Free energies were obtained by adding the thermal correction term from the frequency analysis to the electronic energy. To account for the change in the standard state (1 atm \rightarrow 1 M) an entropic correction term of 1.89 kcal/mol ($-RT\ln Q$) was added to all considered species.

6.1. Conformation analysis for sulfinyl imine **1**

Previously, Alemán and co-workers suggested that the *s-cis* conformer of sulfinyl imine **1** should be more stable compared to the *s-trans* conformer due to the hydrogen bonding between the imine hydrogen and sulfoxide oxygen.⁶ To confirm this, we performed a relaxed scan for the O–S–N–C dihedral angle with 30° increment on the M062X-3D/631+G(d)/SMD(chlorobenzene) level of theory (Figure S3). The identified minimum ($D = 0^\circ$) indeed corresponded to the *s-cis* conformation, which was then re-optimized on the M062X-D3/6-311+G(d,p)/SMD(chlorobenzene) level of theory. For comparison, the *s-trans* conformer ($D = 150^\circ$) was also re-calculated at same level of theory. The structures of the two conformers, their HOMO-3 orbitals and the relative free energies are presented in Figures 3 and S3. The *s-cis* conformer was found to be favored by 3.8 kcal/mol compared to the *s-trans* conformer, an energy difference representing a >99.8:0.2 ratio considering a 1:1 Boltzmann distribution at room temperature (298.15 K). This result is in good agreement with the previous report investigating *N-t*-Bu-sulfinyl imines, where the *s-cis* conformer was calculated to be 4.0 kcal/mol more stable than the *s-trans* conformer.⁷ However, sulfinyl imine from the previous report did not include an additional potential hydrogen bond acceptor, i.e. the carbonyl oxygen present in sulfinyl imine **1**. The hydrogen bond interaction can be

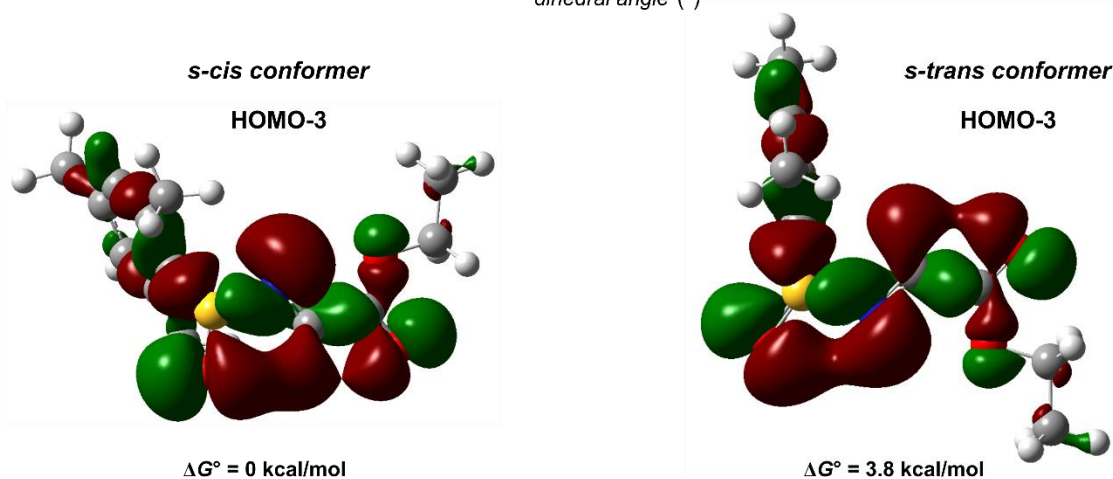
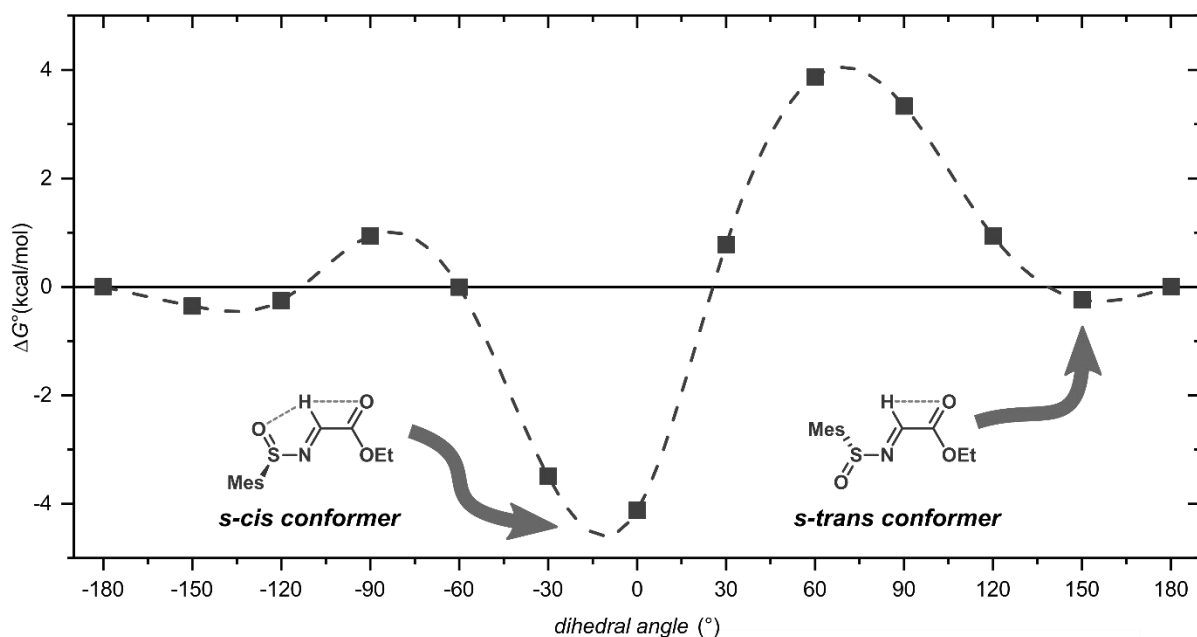


Figure S3. *Top:* Potential energy curve as derived from a relaxed scan of the O-S-N-C dihedral angle. Calculations performed on the M062X-3D/631+G(d)/SMD(chlorobenzene) level of theory. *Bottom:* HOMO-3 orbitals and the relative free energies (kcal/mol) of the *s-cis* and the *s-trans* conformations of the *N*-sulfinyl imine **1**.

visualized for the HOMO-3 orbitals of the two conformers. For the *s-cis* conformer, a constructive overlap between the imine hydrogen and the sulfoxide oxygen was observed, while for the *s-trans* conformer a constructive overlap was instead found between the imine hydrogen and the carbonyl oxygen.

To estimate the strength of the intramolecular hydrogen bonding, the relative stabilities of the corresponding conformers of *N*-sulfinyl imidoyl fluoride were evaluated at the M062X-D3/6-311+G(d,p)/SMD(chlorobenzene) level of theory (Figure S4). The comparison demonstrated that the *s-trans* conformer is 0.6 kcal/mol more stable compared to the *s-cis* conformer, indicating that the intramolecular hydrogen bond in the *N*-sulfinyl imine **1** is worth approximately 4.4 kcal/mol.

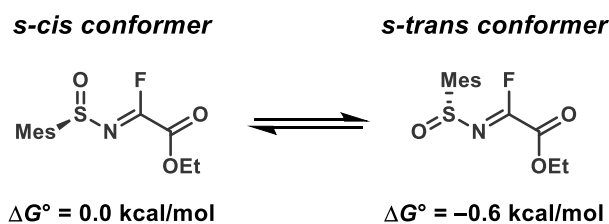


Figure S4. The relative free energies of the *s-cis* and *s-trans* conformers of the *N*-sulfinyl imidoyl fluoride.

6.2. Addition of the *tert*-butyl radical to sulfinyl imine **1**

Next, the stereodetermining radical addition of the *tert*-butyl radical derived from **2a** to the *N*-sulfinyl imine **1** was investigated. The computed free energy surface of the reaction is presented in Figure 3. The activation barriers for the *re*- and *si*-additions were found to be 6.4 and 10.2 kcal/mol, respectively. In both cases, addition of the *tert*-butyl radical to the imine is exergonic, presumably due to the formation of a more stable radical. However, the formation of the experimentally observed *R,R*-diastereomer is 2.5 kcal/mol more favored compared to the *R,S*-diastereomer. Hence, the formation of the *R,R*-diastereomer is favored both kinetically and thermodynamically.

The structure, selected distances and relative free energies of both *re*-TS and *si*-TS can be seen in Figure 3. The C–C distance and the incoming angle is similar for both transition states, *re*-TS having a slightly longer C–C distance (2.27 Å vs. 2.22 Å) and a slightly wider incoming angle ($\angle \text{NCC}$, 109.7° vs. 108.6°). The geometries agree qualitatively with a transition state for the addition of an isopropyl radical to glyoxylate oxime methyl ether reported previously by Jørgensen and co-workers.⁸ In Jørgensen's work a lower energy barrier of 1.6 kcal/mol was predicted, presumably a result of smaller stability of the isopropyl radical as compared to the *tert*-butyl radical.

Two reasons for the energetic ordering of the located transition states can be seen reasoned. Firstly, the distance between the imine hydrogen and the sulfoxide oxygen is significantly longer in the *si*-TS compared to the *re*-TS (2.53 Å vs. 2.35 Å), indicating a weaker hydrogen bond. The weaker hydrogen bond interaction can also be seen in the HOMO-3 of the two transition states (Figure S5). For the *re*-TS, a constructive overlap between the imine hydrogen and the sulfoxide oxygen can be observed, while this interaction is absent in the *si*-TS. It should be noted, however, that there is a constructive overlap between the imine hydrogen and the sulfoxide oxygen in HOMO-4 for both structures, indicating that the hydrogen bond is present in both structures but that the interaction is stronger in the *re*-TS. Secondly, there is significant steric crowding between one of the methyl groups of the mesityl substituent in the *si*-TS, which is not present in the *re*-TS. This is an effect of a rotation of the mesityl group in *si*-TS, which occurs to make room for the incoming *tert*-butyl radical. The O–S–C–C dihedral angle then becomes -50° in the *re*-TS and -2° in the *si*-TS, making the methyl group and the sulfoxide oxygen in *si*-TS almost completely coplanar.

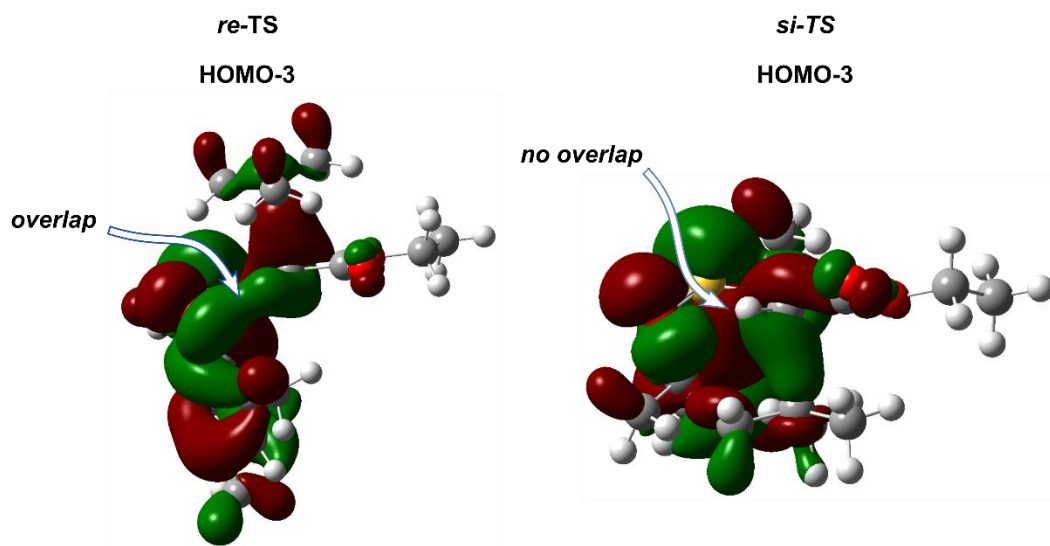


Figure S5. Plot of the HOMO-3 orbitals of the *re*-TS and *si*-TS.

6.3. Evaluation of different functionals

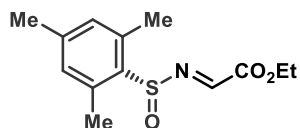
To evaluate the accuracy of the M062X-D3 functional, the single point energies of the *re*-TS and *si*-TS were recalculated using B3LYP-D3⁹ and wB97XD functionals (Table S4).¹⁰ It is worth noting that the wB97XD-functional is using the D2 version of Grimme's empirical dispersion,¹¹ instead of the D3 version that is used for the other two. As seen in Table S4, the three functionals are in excellent agreement with each other. The largest difference is between the M062X-D3 and the wB97XD functional (0.4 kcal/mol), which is to be expected since they are using different models for the empirical dispersion. Nonetheless, the tested functionals all predict that the *re*-TS is favored by 3.4–3.8 kcal/mol compared to the *si*-TS.

Table S4. Relative free energy of activation for the *re*-TS and *si*-TS computed with different functionals for the single point electronic energy.

<i>structure</i>	M062X-D3 $\Delta\Delta G^\ddagger$	B3LYP-D3 $\Delta\Delta G^\ddagger$	wB97XD $\Delta\Delta G^\ddagger$
<i>re</i> -TS	0.0 kcal/mol	0.0 kcal/mol	0.0 kcal/mol
<i>si</i> -TS	3.8 kcal/mol	3.7 kcal/mol	3.4 kcal/mol

7. Analytical data

Compound 1 (ethyl (*R,E*)-2-((mesitylsulfinyl)imino)acetate)



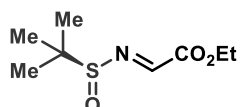
Synthesized according to the general procedure described in **Section 2** on 2.73 mmol scale. The product is a white solid (0.621 g, **85% yield**). The NMR spectra agree with the previously reported data.²

¹H NMR (500 MHz, CDCl₃) δ 8.24 (s, 1H), 6.86 (s, 3H), 4.45–4.30 (m, 2H), 2.45 (s, 9H), 2.28 (s, 4H), 1.37 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 161.53, 154.05, 142.63, 138.93, 133.17, 131.19, 62.76, 21.26, 19.02, 14.21.

R_f = 0.53 (hexane/ethyl acetate 4:1).

Compound 4 (ethyl (*S,E*)-2-((*tert*-butylsulfinyl)imino)acetate)



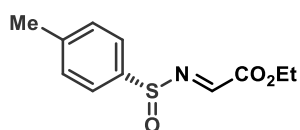
Synthesized according to the general procedure described in **Section 2** on 4.13 mmol scale. The product is a yellow oil (0.629 g, **74% yield**). The NMR spectra agree with the previously reported data.¹²

¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 4.38 (q, *J* = 6.6 Hz, 2H), 1.38 (t, *J* = 6.6 Hz, 3H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 161.26, 155.74, 62.59, 59.05, 22.87, 14.20.

R_f = 0.43 (hexane/ethyl acetate 4:1).

Compound 5 (ethyl (*R,E*)-2-((*p*-tolylsulfinyl)imino)acetate)



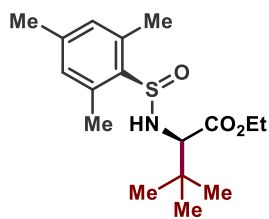
Synthesized according to the general procedure described in **Section 2** on 3.22 mmol scale. The product is a colorless oil (0.327 g, **42% yield**). The NMR spectra agree with the previously reported data.¹³

¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 1H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 4.43–4.26 (m, 2H), 2.41 (s, 3H), 1.35 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.39, 153.22, 142.69, 139.33, 62.75, 21.61, 14.17.

R_f = 0.39 (hexane/ethyl acetate 4:1).

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



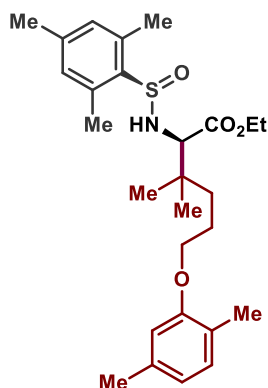
Synthesized according to the general procedure described in **Section 3** on 0.3 mmol scale and 1.5 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/ethyl acetate 9:1 as eluent. The product is a white solid (79.1 mg, **81% yield**, >95:5 α dr). The NMR spectra agree with the previously reported data.¹³

¹H NMR (500 MHz, CDCl₃) δ 6.87 (s, 2H), 5.05 (d, J = 10.0 Hz, 1H), 4.34–4.14 (m, 2H), 3.60 (d, J = 10.1 Hz, 1H), 2.57 (s, 6H), 2.29 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H), 0.97 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 172.84, 140.99, 138.24, 136.90, 130.92, 66.63, 61.44, 35.16, 26.62, 21.19, 19.45, 14.32.

R_f = 0.33 (hexane/ethyl acetate 4:1)

Compound **3b** (ethyl (*R*)-6-(2,5-dimethylphenoxy)-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethylhexanoate)



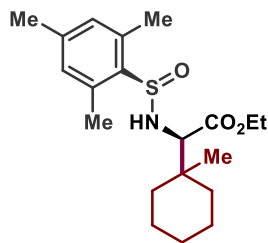
Synthesized according to the general procedure described in **Section 3** on 0.15 mmol scale and 2 h reaction time (2 h reaction time for NMR yield). The crude product (after filtration through silica plug and removal of the solvent) was dissolved in 20 mL of ethyl acetate and washed with 0.1 M aq. NaOH (5 x 10 mL) and water (10 mL), dried over anhydrous Na₂SO₄, concentrated, and purified by column chromatography using petroleum ether/CH₂Cl₂/ethyl acetate 8:1:1 as eluent. The product is a pale-yellow oil (31.3 mg, **44% yield**, >95:5 α dr).

¹H NMR (500 MHz, CDCl₃) δ 7.00 (d, J = 7.4 Hz, 1H), 6.87 (s, 2H), 6.66 (d, J = 7.4 Hz, 1H), 6.61 (s, 1H), 5.07 (d, J = 10.1 Hz, 1H), 4.31–4.18 (m, 2H), 3.90 (t, J = 6.4 Hz, 2H), 3.74 (d, J = 10.1 Hz, 1H), 2.57 (s, 6H), 2.30 (d, J = 8.4 Hz, 6H), 2.14 (s, 3H), 1.91–1.70 (m, 2H), 1.57–1.41 (m, 2H), 1.31 (t, J = 7.2 Hz, 3H), 0.97 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 172.79, 157.09, 141.07, 138.17, 136.92, 136.61, 130.95, 130.45, 123.73, 120.88, 112.17, 68.41, 65.20, 61.54, 37.60, 35.80, 24.15, 23.87, 23.70, 21.55, 21.19, 19.43, 15.88, 14.32.

R_f = 0.24 (petroleum ether/CH₂Cl₂/ethyl acetate 8:1:1)

Compound **3c** ((*R*)-*N*-((*R*)-2-(ethylperoxy)-1-(1-methylcyclohexyl)-2 λ^2 -ethyl)-2,4,6-trimethylbenzenesulfinamide)



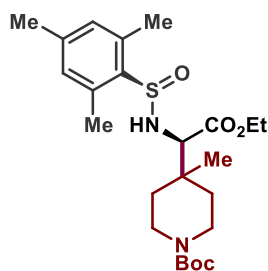
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 1.5 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography using chloroform/ethyl acetate 30:1 as eluent. The product is a pale-yellow oil (63.7 mg, **87% yield**, >95:5 α dr). The NMR spectra agree with the previously reported data.¹³

¹H NMR (500 MHz, CDCl₃) δ 6.86 (s, 2H), 5.01 (d, J = 10.1 Hz, 1H), 4.32–4.14 (m, 2H), 3.83 (d, J = 10.1 Hz, 1H), 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).

¹³C NMR (126 MHz, CDCl₃) δ 172.87, 140.94, 138.29, 136.86, 130.90, 64.85, 61.36, 37.73, 34.96, 34.89, 26.08, 21.70, 21.66, 21.17, 20.73, 19.43, 14.32.

R_f = 0.20 (chloroform/ethyl acetate 30 :1)

Compound **3d** (*tert*-butyl 4-((*R*)-2-(ethylperoxy)-1-(((*R*)-mesitylsulfinyl)amino)-2 λ^2 -ethyl)-4-methylpiperidine-1-carboxylate)



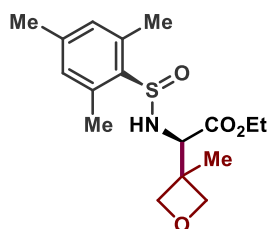
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 2 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/CH₂Cl₂/ethyl acetate 6:1:1 as eluent. The product is a pale-yellow oil (30.6 mg, **33% yield**, >95:5 α dr).

¹H NMR (500 MHz, CDCl₃) δ 6.87 (s, 2H), 5.04 (d, J = 10.0 Hz, 1H), 4.31–4.15 (m, 2H), 3.77 (d, J = 9.9 Hz, 1H), 3.80–3.60 (m, 2H), 3.20–3.06 (m, 2H), 2.56 (s, 6H), 2.29 (s, 3H), 1.72–1.61 (m, 1H), 1.60–1.51 (m, 1H), 1.45 (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).

¹³C NMR (126 MHz, CDCl₃) δ 172.20, 154.98, 141.20, 137.95, 136.88, 130.99, 79.67, 64.89, 61.72, 36.47, 34.07, 33.96, 31.73, 28.58, 22.79, 21.18, 19.45, 19.02, 14.31, 14.26.

R_f = 0.16 (hexane/CH₂Cl₂/ethyl acetate 4:1:1)

Compound **3e** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(3-methyloxetan-3-yl)acetate)



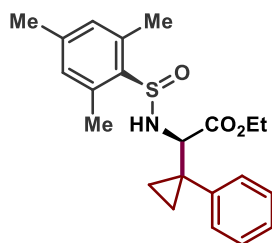
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 3 h reaction time (2 h reaction time for NMR yield). The crude product was purified by column chromatography using petroleum ether/CH₂Cl₂/ethyl acetate 2:1:1 as eluent. The product is a pale-orange oil (36.7 mg, **54% yield**, >95:5 α dr). The NMR spectra agree with the previously reported data.²

¹H NMR (500 MHz, CDCl₃) δ 6.88 (s, 2H), 5.21 (d, *J* = 8.2 Hz, 1H), 4.84 (d, *J* = 6.3 Hz, 1H), 4.74 (d, *J* = 6.1 Hz, 1H), 4.44 (d, *J* = 8.1 Hz, 1H), 4.31 (d, *J* = 6.3 Hz, 1H), 4.28–4.23 (m, 2H), 4.23–4.15 (m, 1H), 2.58 (s, 6H), 2.29 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 171.48, 141.33, 137.73, 136.88, 131.03, 80.37, 80.32, 62.21, 62.18, 42.90, 21.17, 19.45, 19.31, 14.28.

R_f = 0.28 (petroleum ether/CH₂Cl₂/ethyl acetate 2:1:1)

Compound **3f** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(1-phenylcyclopropyl)acetate)



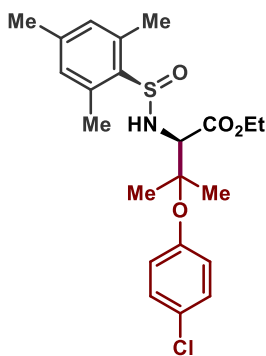
Synthesized according to the general procedure described in **Section 3** on 0.15 mmol scale and 3 h reaction time (3 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/CH₂Cl₂/ethyl acetate 8:1:1 as eluent. The product is a pale-red oil (30.0 mg, **52% yield**, 9:1 α dr). The NMR spectra agree with the previously reported data.²

¹H NMR (500 MHz, CDCl₃) δ 7.25–7.15 (m, 5H), 6.86 (s, 2H), 6.81 (s, 2H, *minor diastereomer*), 5.09 (d, *J* = 7.8 Hz, 1H), 4.71 (d, *J* = 10.1 Hz, 1H, *minor diastereomer*), 4.24–4.06 (m, 2H), 3.77 (d, *J* = 7.7 Hz, 1H), 3.54 (d, *J* = 10.1 Hz, 1H, *minor diastereomer*), 2.55 (s, 6H), 2.29 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.27–1.17 (m, 1H), 1.07–1.00 (m, 1H), 1.00–0.93 (m, 1H), 0.93–0.86 (m, 1H). *Mixture of two diastereomers is reported.*

¹³C NMR (126 MHz, CDCl₃) δ 171.63, 140.95, 140.78, 140.76, 140.10, 137.96, 137.42, 137.18, 136.85, 131.08, 131.02, 130.94, 130.62, 128.24, 128.20, 127.49, 127.34, 65.10, 64.27, 61.74, 61.45, 29.83, 29.63, 21.18, 21.11, 19.67, 19.43, 14.31, 14.23, 12.77, 12.35, 11.67, 11.51. *Mixture of two diastereomers is reported.*

R_f = 0.38 (hexane/CH₂Cl₂/ethyl acetate 8:1:1)

Compound **3g** (ethyl (*R*)-3-(4-chlorophenoxy)-2-(((*R*)-mesitylsulfinyl)amino)-3-methylbutanoate)



Synthesized according to the general procedure described in **Section 3** on 0.15 mmol scale and 1.5 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography with neutralized silica (prior to loading of the crude product the column was washed with the eluent containing 2% Et₃N, followed by pristine eluent) using petroleum ether/CH₂Cl₂/ethyl acetate 8:1:1 as eluent. The product is a pale-yellow oil (59.3 mg, **90% yield**, >95:5 α dr). The NMR spectra agree with the previously reported data.²

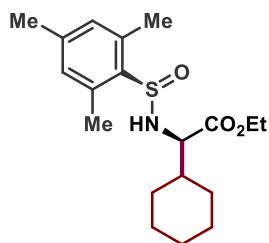
¹H NMR (500 MHz, CDCl₃) δ 7.23–7.17 (m, 2H), 6.90–6.84 (m, 4H), 5.33 (d, *J* =

9.9 Hz, 1H), 4.37–4.19 (m, 2H), 4.01 (d, $J = 9.8$ Hz, 1H), 2.58 (s, 6H), 2.29 (s, 3H), 1.36–1.25 (m, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 171.43, 152.97, 141.18, 137.89, 136.98, 131.00, 129.43, 129.19, 125.52, 81.87, 65.58, 61.89, 24.29, 23.85, 21.18, 19.46, 14.29.

$R_f = 0.16$ (petroleum ether/ CH_2Cl_2 /ethyl acetate 8:1:1)

Compound **3h** (ethyl (*R*)-2-cyclohexyl-2-(((*R*)-mesitylsulfinyl)amino)acetate)



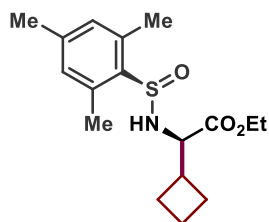
Synthesized according to the general procedure described in **Section 3** on 0.15 mmol scale and 3 h reaction time (2 h reaction time for NMR yield). The crude product was purified by preparative TLC using chloroform/ethyl acetate 12:1 as eluent. The product is a pale-yellow oil (38.7 mg, **73% yield**, >95:5 α dr).

^1H NMR (500 MHz, CDCl_3) δ 6.87 (s, 2H), 5.01 (d, $J = 9.3$ Hz, 1H), 4.31–4.15 (m, 2H), 3.76 (dd, $J = 9.3, 5.4$ Hz, 1H), 2.59 (s, 6H), 2.29 (s, 3H), 1.79–1.55 (m, 5H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.26–0.95 (m, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 173.26, 140.94, 138.32, 136.82, 130.91, 62.74, 61.61, 41.83, 29.73, 27.99, 26.13, 25.99, 21.17, 19.51, 14.32.

$R_f = 0.39$ (CHCl_3 /ethyl acetate 10:1)

Compound **3i** (ethyl (*R*)-2-cyclobutyl-2-(((*R*)-mesitylsulfinyl)amino)acetate)



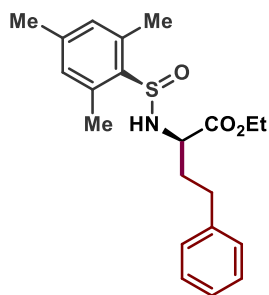
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 3 h reaction time (2.5 h reaction time for NMR yield). The crude product was purified by column chromatography using chloroform/ethyl acetate 35:1 as eluent. The product is a pale-pink oil (19.1 mg, **30% yield**, >95:5 α dr).

^1H NMR (500 MHz, CDCl_3) δ 6.87 (s, 2H), 5.04 (d, $J = 8.9$ Hz, 1H), 4.29–4.09 (m, 2H), 3.86 (dd, $J = 8.9, 7.7$ Hz, 1H), 2.66–2.53 (m, 1H), 2.59 (s, 6H), 2.28 (s, 3H), 2.07–1.91 (m, 3H), 1.91–1.72 (m, 3H), 1.27 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.88, 140.98, 138.18, 136.87, 130.93, 61.61, 61.31, 38.99, 24.94, 24.91, 21.16, 19.49, 18.02, 14.31.

$R_f = 0.20$ (chloroform/ethyl acetate 35:1)

Compound **3j** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-4-phenylbutanoate)



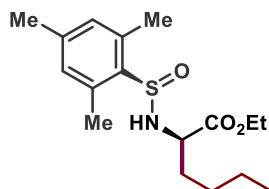
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 3 h reaction time (2.5 h reaction time for NMR yield). The crude product was purified by column chromatography using chloroform/ethyl acetate 35:1 as eluent. The product is a pale-orange oil (14.8 mg, **20% yield**, >95:5 α dr).

¹H NMR (500 MHz, CDCl₃) δ 7.32–7.26 (m, 2H), 7.23–7.13 (m, 3H), 6.89 (s, 2H), 5.15 (d, J = 8.4 Hz, 1H), 4.26–4.13 (m, 2H), 4.04–3.96 (m, 1H), 2.79–2.67 (m, 2H), 2.62 (s, 6H), 2.30 (s, 3H), 2.19–2.07 (m, 1H), 2.00–1.89 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.45, 141.14, 140.86, 138.05, 136.89, 131.01, 128.67, 128.59, 126.34, 61.90, 56.85, 35.79, 31.75, 21.19, 19.51, 14.28.

R_f = 0.22 (chloroform/ethyl acetate 35:1)

Compound **3k** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)hexanoate)



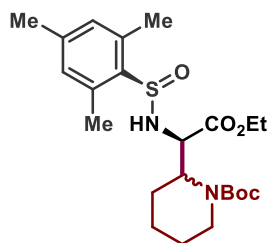
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 3 h reaction time (3 h reaction time for NMR yield). The crude product was purified by column chromatography using chloroform/ethyl acetate 35:1 as eluent. The product is a pale-orange oil (25.2 mg, **39% yield**, >95:5 α dr).

¹H NMR (500 MHz, CDCl₃) δ 6.87 (s, 2H), 5.04 (d, J = 8.5 Hz, 1H), 4.29–4.13 (m, 2H), 3.95 (td, J = 8.3, 4.8 Hz, 1H), 2.59 (s, 6H), 2.28 (s, 3H), 1.85–1.75 (m, 1H), 1.68–1.57 (m, 1H), 1.43–1.30 (m, 4H), 1.29 (t, J = 7.2 Hz, 3H), 0.92–0.85 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.75, 140.99, 138.10, 136.82, 131.05, 130.94, 61.72, 57.39, 33.84, 27.59, 22.31, 21.16, 19.44, 14.27, 14.01.

R_f = 0.24 (chloroform/ethyl acetate 30:1)

Compound **3l** (*tert*-butyl (*R*)-2-((*R*)-2-ethoxy-1-(((*R*)-mesitylsulfinyl)amino)-2-oxoethyl)piperidine-1-carboxylate)



Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 1.5 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/CH₂Cl₂/ethyl acetate 6:1:1 as eluent. The product is a pale-yellow oil (48.3 mg, **53% yield**, >95:5 α dr; 1:1 β dr).

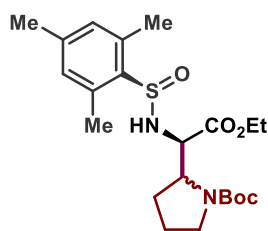
¹H NMR (500 MHz, CDCl₃) δ 6.88–6.72 (m, 4H), 5.20 (d, J = 10.8 Hz, 1H), 4.85 (d, J = 9.0 Hz, 1H), 4.46 (d, J = 10.7 Hz, 1H), 4.35–4.00 (m, 8H), 3.91 (d, J = 13.7 Hz,

1H), 2.79 (t, $J = 13.3$ Hz, 1H), 2.70–2.59 (m, 1H), 2.53 (s, 12H), 2.23 (s, 6H), 1.75–1.50 (m, 12H), 1.29 (dt, $J = 29.6, 7.0$ Hz, 6H), 1.22–0.97 (m, 18H). Mixture of two diastereomers is reported.

^{13}C NMR (126 MHz, CDCl_3) δ 173.07, 172.27, 156.32, 155.16, 141.02, 140.73, 139.33, 138.70, 137.68, 137.18, 136.76, 130.80, 130.67, 81.47, 79.76, 62.78, 61.84, 61.57, 57.73, 57.50, 52.98, 51.53, 39.98, 38.64, 29.79, 28.54, 28.26, 28.23, 28.13, 28.08, 27.93, 25.76, 25.62, 25.44, 25.07, 24.94, 23.09, 21.04, 21.02, 20.84, 19.41, 19.23, 19.14, 14.14, 13.88. Mixture of two diastereomers is reported.

$R_f = 0.28$ (hexane/ CH_2Cl_2 /ethyl acetate 4:1:1)

Compound **3m** (*tert*-butyl (*R,S*)-2-((*R*)-2-ethoxy-1-(((*R*)-mesitylsulfinyl)amino)-2-oxoethyl)pyrrolidine-1-carboxylate)



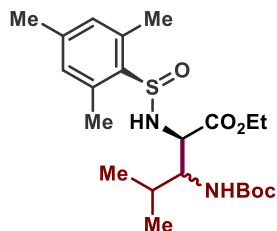
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 1.5 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/ethyl acetate 7:1 as eluent. The product is a colorless oil (0.0758 g, **86% yield**, >95:5 α dr, 1:1 β dr). Two rotamers for each diastereomer at β -position (1:1) were observed by NMR. The NMR spectra agree with the previously reported data.²

^1H NMR (500 MHz, CDCl_3) δ 6.85 (d, $J = 14.0$ Hz, 4H), 5.48 (d, $J = 8.4$ Hz, 1H), 5.39 (d, $J = 7.6$ Hz, 1H), 5.27 (d, $J = 7.0$ Hz, 1H), 5.11 (d, $J = 8.7$ Hz, 1H), 4.82 (dd, $J = 7.6, 4.0$ Hz, 1H), 4.73 (dd, $J = 7.0, 3.8$ Hz, 1H), 4.36 (s, 1H), 4.31–4.15 (m, 4H), 4.15–4.07 (m, 2H), 4.07–3.98 (m, 1H), 3.63–3.30 (m, 2H), 3.30–3.18 (m, 1H), 3.18–3.07 (m, 1H), 2.67–2.47 (m, 12H), 2.36–2.18 (m, 6H), 2.01–1.90 (m, 1H), 1.90–1.75 (m, 4H), 1.75–1.59 (m, 3H), 1.59–1.34 (m, 18H), 1.34–1.18 (m, 6H). Mixture of two rotamers for each of two diastereomers is reported.

^{13}C NMR (126 MHz, CDCl_3) δ 172.19, 171.99, 171.77, 155.30, 154.39, 154.06, 153.89, 140.97, 140.74, 138.62, 138.29, 137.72, 136.92, 136.64, 136.47, 130.84, 80.46, 80.22, 79.74, 62.12, 62.01, 61.66, 60.09, 59.43, 59.16, 58.75, 57.79, 57.32, 47.55, 47.37, 47.17, 46.69, 28.56, 28.49, 28.38, 27.71, 26.82, 26.07, 24.25, 23.78, 23.67, 22.76, 21.09, 21.05, 20.89, 19.45, 19.31, 14.20, 14.05. Mixture of two rotamers for each of two diastereomer is reported.

$R_f = 0.26$ (hexane/ethyl acetate 7:1)

Compound **3n** (ethyl (2*R*,3*S*)-3-((*tert*-butoxycarbonyl)amino)-2-(((*R*)-mesitylsulfinyl)amino)-4-methylpentanoate)



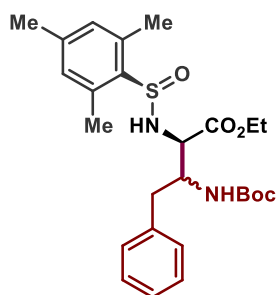
Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 1 h reaction time (0.5 h reaction time for NMR yield). The crude product was purified by column chromatography using chloroform/ethyl acetate 20:1 as eluent. The product is pale-orange oil (87.4 mg, **99% yield**, >95:5 α dr, 1.5:1 β dr).

¹H NMR (500 MHz, CDCl₃) δ 6.94–6.80 (m, 4H), 5.31 (d, J = 7.4 Hz, 1H), 5.11 (d, J = 9.6 Hz, 1H, *minor diastereomer*), 4.69 (d, J = 10.3 Hz, 1H, *minor diastereomer*), 4.39 (d, J = 10.5 Hz, 1H), 4.30–4.13 (m, 5H), 4.03 (dd, J = 9.6, 6.6 Hz, 1H, *minor diastereomer*), 3.85–3.74 (m, 2H), 2.63–2.54 (m, 12H), 2.32–2.26 (m, 6H), 1.90–1.81 (m, 1H, *minor diastereomer*), 1.81–1.70 (m, 1H), 1.42–1.33 (m, 18H), 1.29 (td, J = 7.1, 2.9 Hz, 6H), 1.11 (d, J = 6.7 Hz, 4H), 0.97 (d, J = 6.7 Hz, 4H), 0.93 (d, J = 6.8 Hz, 2H), 0.88 (d, J = 6.8 Hz, 2H). *Mixture of two diastereomers is reported.*

¹³C NMR (126 MHz, CDCl₃) δ 172.30, 172.02, 155.69, 155.42, 141.39, 141.17, 138.03, 137.73, 137.57, 136.95, 136.92, 131.08, 131.04, 131.01, 79.68, 79.50, 62.46, 62.00, 61.80, 59.55, 58.97, 57.84, 57.33, 30.51, 30.07, 29.37, 28.43, 28.41, 28.38, 28.35, 21.20, 21.17, 21.14, 20.17, 19.99, 19.70, 19.58, 19.55, 19.48, 19.43, 19.30, 18.74, 17.49, 14.24, 14.19, 14.16, 14.11. *Mixture of two diastereomers is reported.*

R_f = 0.26 & 0.40 for two diastereomers at β -position (chloroform/ethyl acetate 20:1)

Compound **3o** (ethyl (2*R*)-3-((*tert*-butoxycarbonyl)amino)-2-(((*R*)-mesitylsulfinyl)amino)-4-phenylbutanoate)



Synthesized according to the general procedure described in **Section 3** on 0.2 mmol scale and 3 h reaction time (1 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/CH₂Cl₂/ethyl acetate 6:1:1 as eluent. Two sets of fractions were combined and concentrated, resulting in pure β -diastereomer **3o-1** (20.5 mg, >95:5 α dr, >95:5 β dr) and a mixture of β -diastereomers **3o-1** and **3o-2** (78.6 mg, >95:5 α dr, 1:1 β dr). The products are pale-yellow oils (in total 99.1 mg, **>99% yield**, >95:5 α dr, 1.5:1 β dr).

¹H NMR for diastereomer **3o-1** (500 MHz, CDCl₃) δ 7.37–7.28 (m, 2H), 7.28–7.17 (m, 3H), 6.93 (s, 2H), 5.40 (d, J = 7.3 Hz, 1H), 4.58–4.41 (m, 2H), 4.28–4.12 (m, 2H), 4.04 (dd, J = 7.4, 2.3 Hz, 1H), 2.95–2.88 (m, 1H), 2.88–2.79 (m, 1H), 2.67 (s, 6H), 2.33 (s, 3H), 1.35–1.21 (m, 12H).

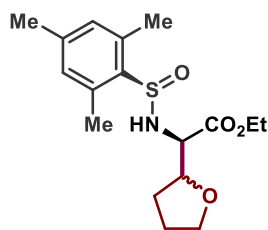
¹³C NMR for diastereomer **3o-1** (126 MHz, CDCl₃) δ 171.83, 154.92, 141.50, 138.05, 137.11, 137.02, 131.13, 129.55, 129.43, 128.83, 128.64, 126.95, 79.73, 62.52, 58.00, 54.25, 39.12, 28.38, 28.29, 21.22, 19.64, 19.61, 14.10.

¹H NMR for a mixture of diastereomers **3o-1** and **3o-2** (500 MHz, CDCl₃) δ 7.35–7.29 (m, 2H), 7.29–7.23 (m, 4H), 7.23–7.17 (m, 2H, *diastereomer 3o-2*), 7.14 (d, *J* = 7.5 Hz, 2H, *diastereomer 3o-2*), 6.93 (s, 2H), 6.89 (s, 2H, *diastereomer 3o-2*), 5.40 (d, *J* = 7.3 Hz, 1H), 5.28 (d, *J* = 8.7 Hz, 1H, *diastereomer 3o-2*), 4.77 (d, *J* = 9.1 Hz, 1H, *diastereomer 3o-2*), 4.57–4.42 (m, 2H), 4.36–4.30 (m, 1H, *diastereomer 3o-2*), 4.30–4.07 (m, 7H), 4.04 (dd, *J* = 7.6, 2.2 Hz, 1H), 2.95–2.88 (m, 1H), 2.88–2.79 (m, 1H), 2.67 (s, 6H), 2.61 (s, 6H, *diastereomer 3o-2*), 2.32 (s, 3H), 2.30 (s, 3H, *diastereomer 3o-2*), 1.38 (s, 9H, *diastereomer 3o-2*), 1.32–1.21 (m, 15H).

¹³C NMR for a mixture of diastereomers **3o-1** and **3o-2** (126 MHz, CDCl₃) δ 171.82, 171.44, 155.06, 154.91, 141.49, 141.27, 138.04, 137.65, 137.10, 137.00, 136.90, 131.12, 131.08, 130.92, 129.54, 129.48, 129.42, 129.39, 128.82, 128.71, 128.63, 128.59, 128.52, 126.94, 126.84, 126.73, 79.89, 79.72, 62.51, 62.22, 62.06, 59.65, 57.99, 54.24, 53.68, 39.10, 36.36, 31.72, 28.42, 28.28, 23.20, 22.79, 21.20, 21.18, 19.63, 19.60, 19.58, 19.52, 14.25, 14.22, 14.09.

R_f = 0.23 & 0.19 for diastereomers **3o-1** & **3o-2**, respectively (hexane/CH₂Cl₂/ethyl acetate 6:1:1)

Compound **3p** (ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-((*R*)-tetrahydrofuran-2-yl)acetate)



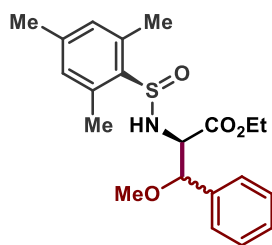
Synthesized according to the general procedure described in **Section 3** on 2 mmol scale and 3 h reaction time (2 h reaction time for NMR yield). The crude product was purified by column chromatography using hexane/CH₂Cl₂/ethyl acetate 5:2:2 as eluent. The product is a pale-yellow oil (30.4 mg, **45% yield**, >95:5 α dr, 1.3:1 β dr).

¹H NMR (500 MHz, CDCl₃) δ 6.86 (s, 4H), 5.20 (d, *J* = 9.0 Hz, 1H), 5.14 (d, *J* = 8.6 Hz, 1H, *minor diastereomer*), 4.33–4.26 (m, 1H), 4.26–4.18 (m, 4H), 4.18–4.11 (m, 1H), 4.11–4.01 (m, 1H), 4.00–3.90 (m, 1H), 3.89–3.80 (m, 1H), 3.80–3.71 (m, 2H), 3.71–3.63 (m, 1H), 2.64–2.54 (m, 12H), 2.28 (s, 6H), 2.05–1.96 (m, 1H), 1.96–1.88 (m, 2H), 1.88–1.75 (m, 5H), 1.33–1.23 (m, 6H). *Mixture of two diastereomers is reported.*

¹³C NMR (126 MHz, CDCl₃) δ 171.66, 171.59, 141.03, 141.00, 140.97, 138.14, 137.89, 137.35, 137.30, 136.93, 136.86, 131.04, 130.99, 130.94, 130.93, 80.11, 79.44, 69.40, 69.04, 68.93, 62.00, 61.96, 61.82, 61.62, 60.56, 60.03, 60.01, 59.89, 28.30, 28.26, 28.04, 27.70, 26.22, 26.12, 25.75, 25.46, 21.16, 19.57, 19.53, 19.39, 14.29, 14.27, 14.25, 14.22. *Mixture of two diastereomers is reported.*

$R_f = 0.27$ (hexane/ CH_2Cl_2 /ethyl acetate 5:2:2)

Compound **3q** (ethyl (2*R*,3*S*)-2-(((*R*)-mesitylsulfinyl)amino)-3-methoxy-3-phenylpropanoate)



Synthesized according to the general procedure described in **Section 3** on 0.15 mmol scale and 3 h reaction time (2 h reaction time for NMR yield). The crude product was purified by preparative TLC using chloroform/ethyl acetate 5:1 as eluent. The product is a colorless oil (35.1 mg, **60% yield**, >95:5 α dr, 1.4:1 β dr).

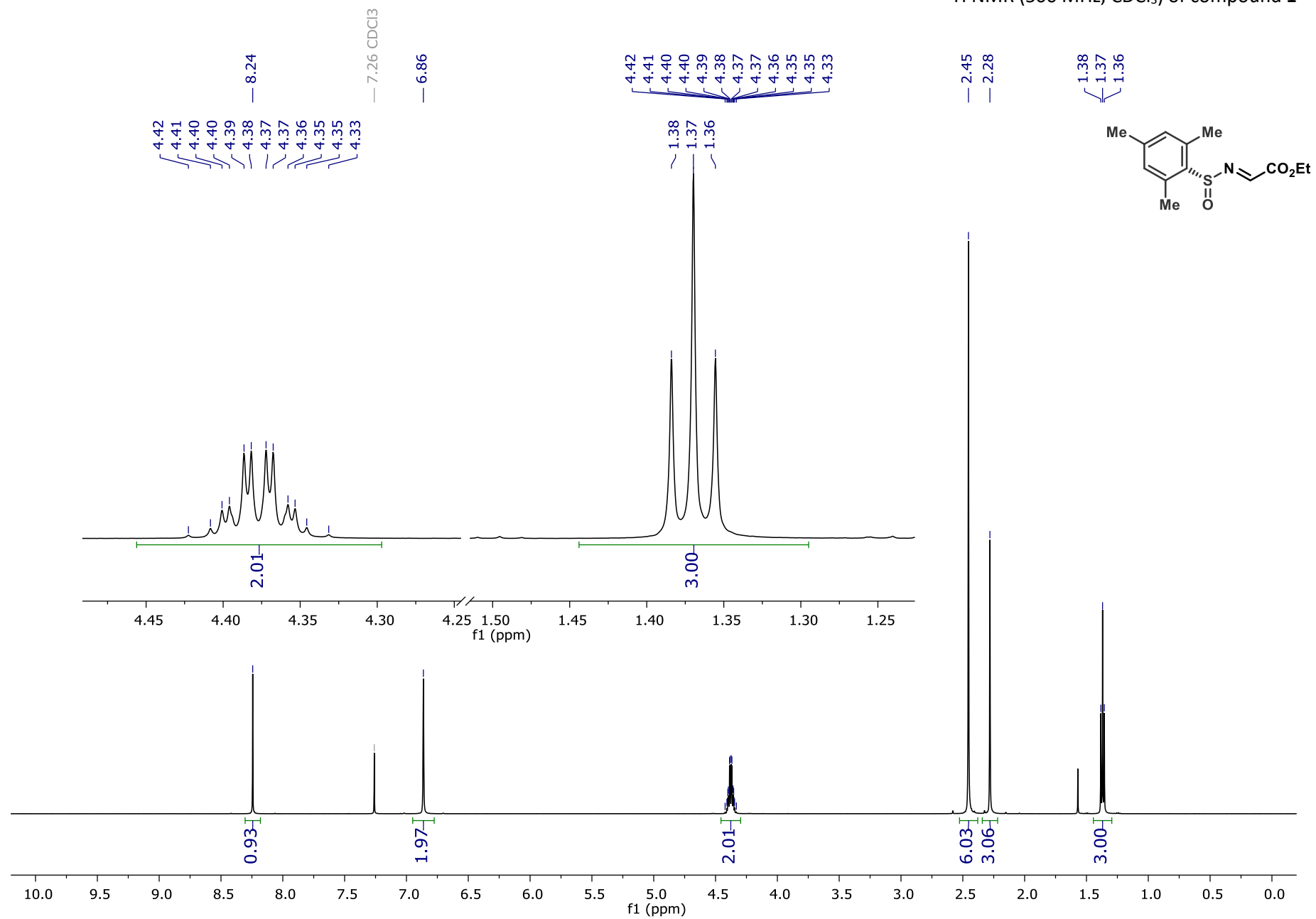
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39–7.24 (m, 4H), 7.24–7.18 (m, 1H), 6.80 (s, 2H), 5.26 (d, $J = 8.8$ Hz, 1H, *minor diastereomer*), 4.95 (d, $J = 9.4$ Hz, 1H), 4.72 (d, $J = 3.4$ Hz, 1H, *minor diastereomer*), 4.37 (d, $J = 6.8$ Hz, 1H), 4.34–4.26 (m, 1H, *minor diastereomer*), 4.26–4.16 (m, 2H), 4.16–4.08 (m, 1H), 3.24 (s, 3H), 3.23 (s, 3H, *minor diastereomer*), 2.36 (s, 3H), 2.33 (s, 3H), 2.26 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H, *minor diastereomer*), 1.25 (t, $J = 7.1$ Hz, 3H). *Mixture of two diastereomers is reported.*

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.62, 171.03, 140.84, 140.79, 138.19, 137.90, 137.50, 137.43, 137.34, 136.87, 136.82, 131.02, 130.97, 130.92, 130.77, 130.68, 128.48, 128.42, 128.39, 128.37, 128.20, 128.13, 127.75, 127.38, 127.25, 127.09, 84.77, 84.03, 63.40, 62.62, 62.04, 61.83, 57.74, 57.29, 21.14, 19.40, 19.19, 19.15, 14.28, 14.17. *Mixture of two diastereomers is reported.*

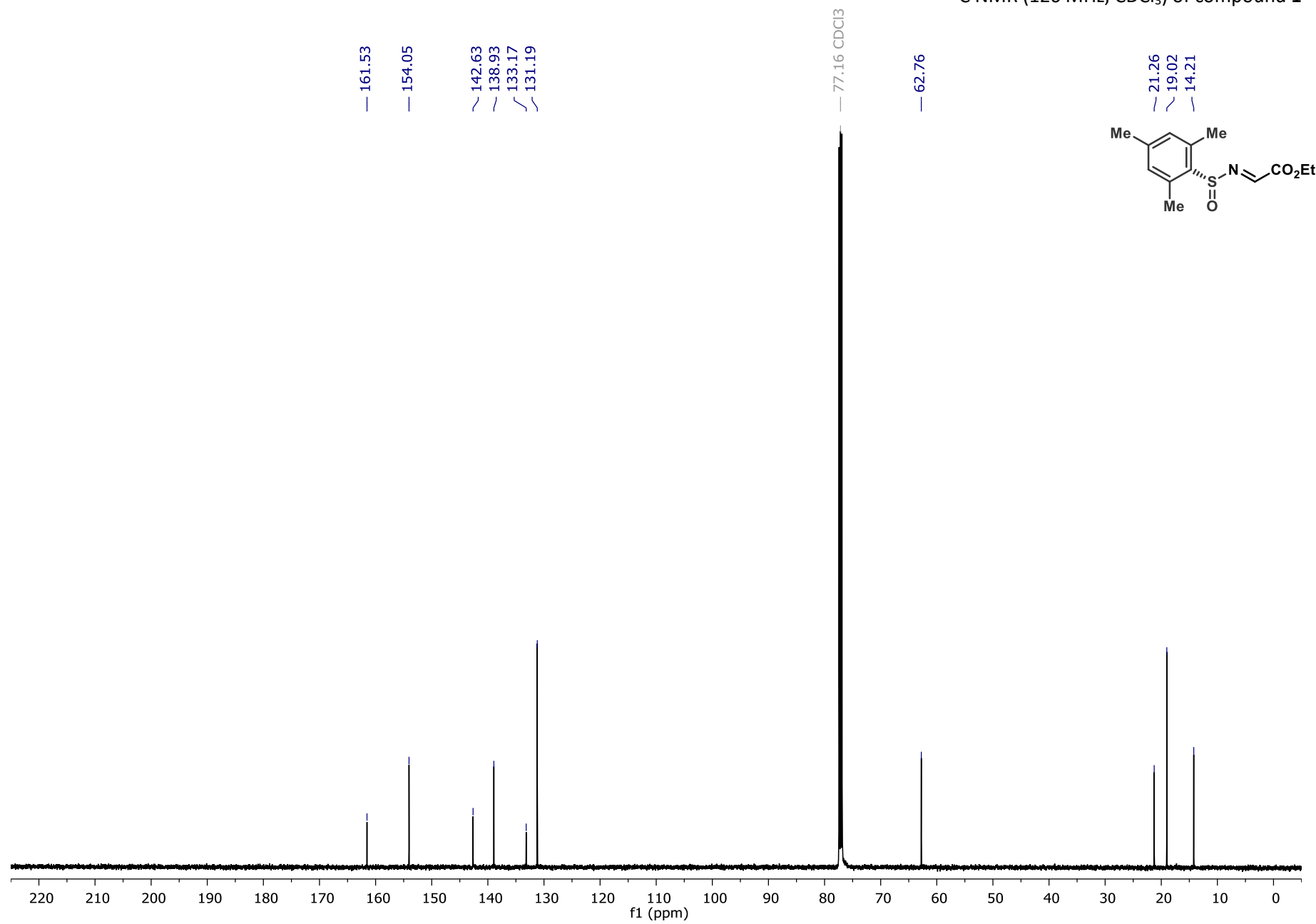
$R_f = 0.45$ & 0.61 for two diastereomers at β -position (chloroform/ethyl acetate 5:1)

8. NMR spectra

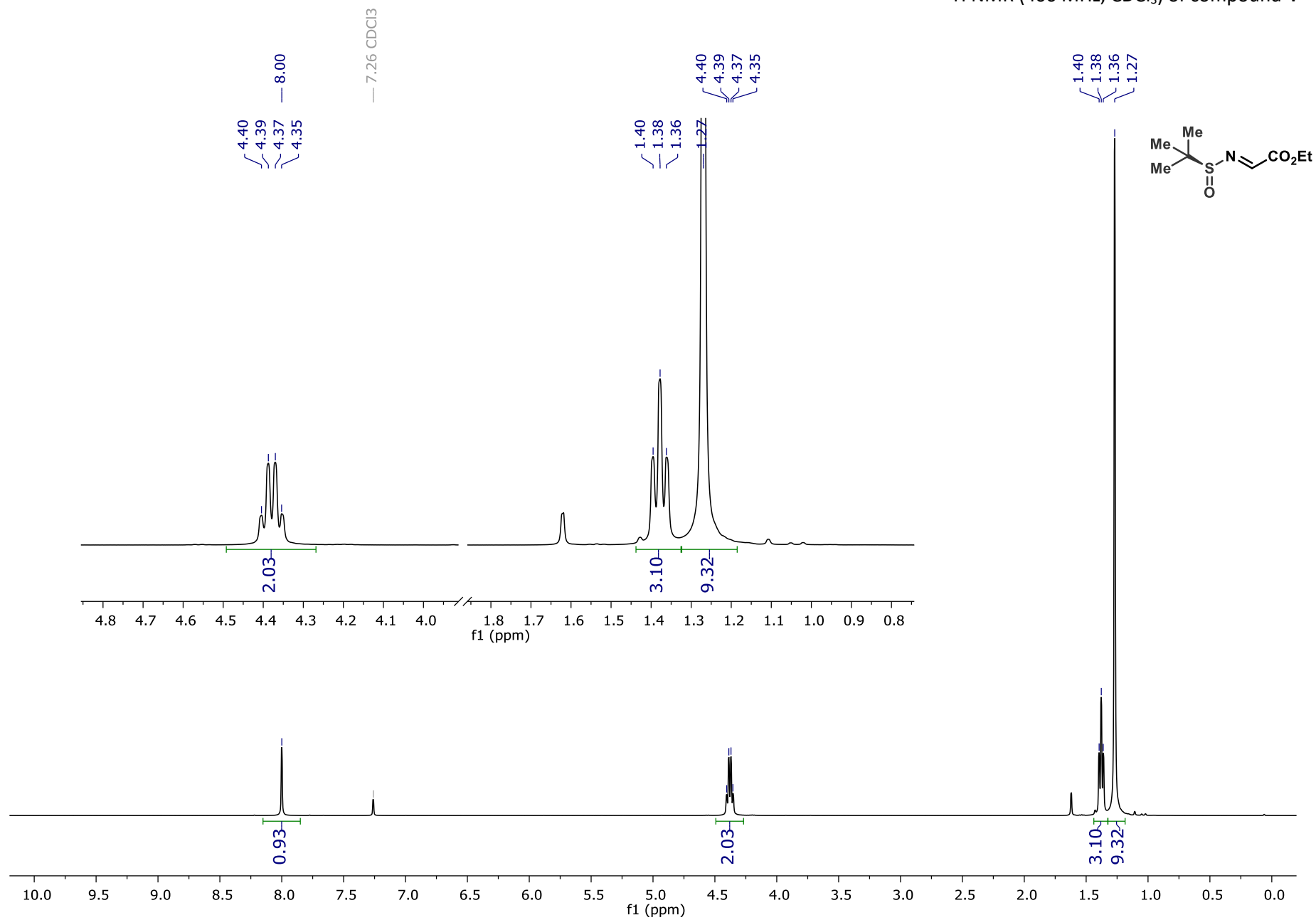
^1H NMR (500 MHz, CDCl_3) of compound **1**



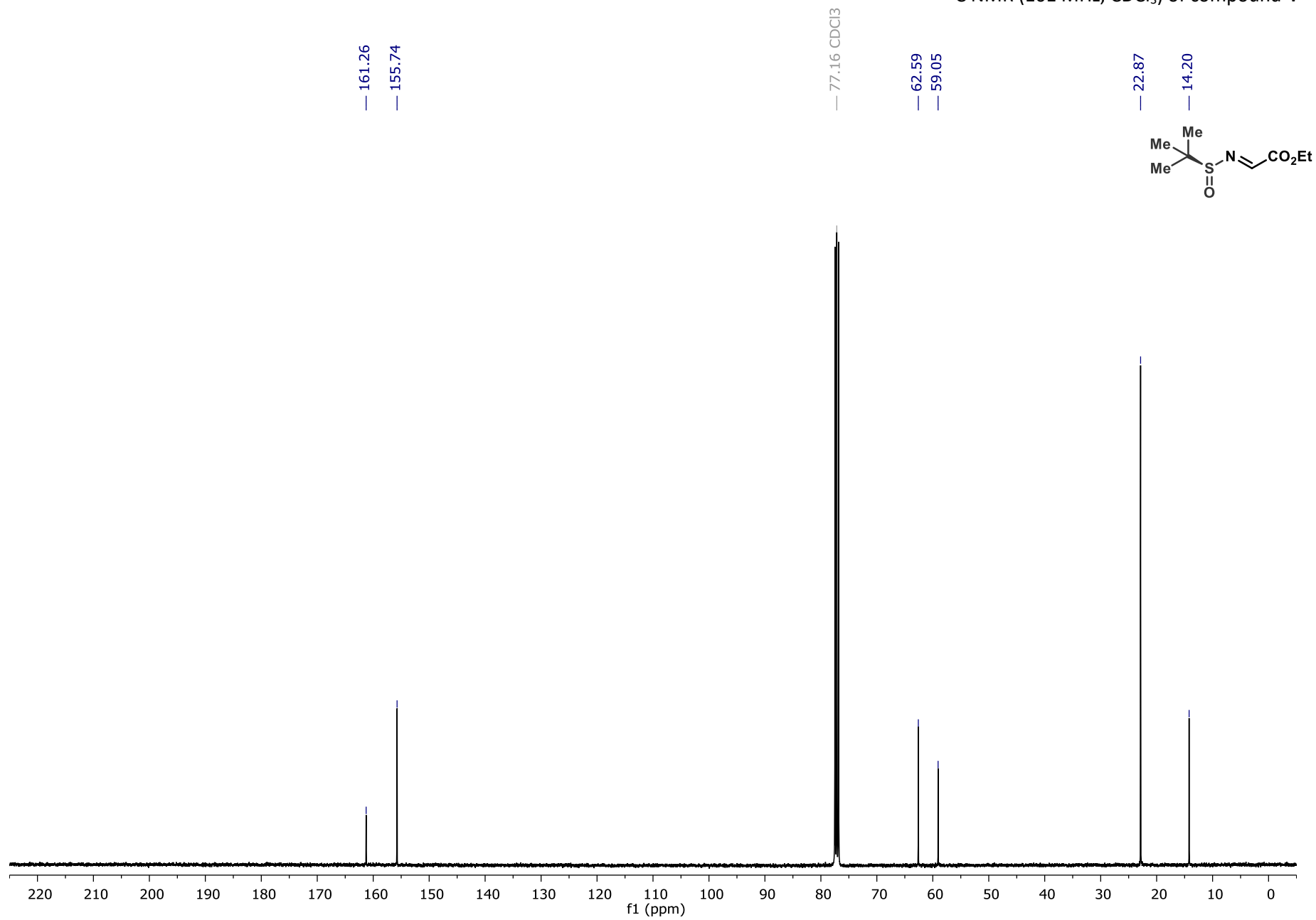
¹³C NMR (126 MHz, CDCl₃) of compound **1**



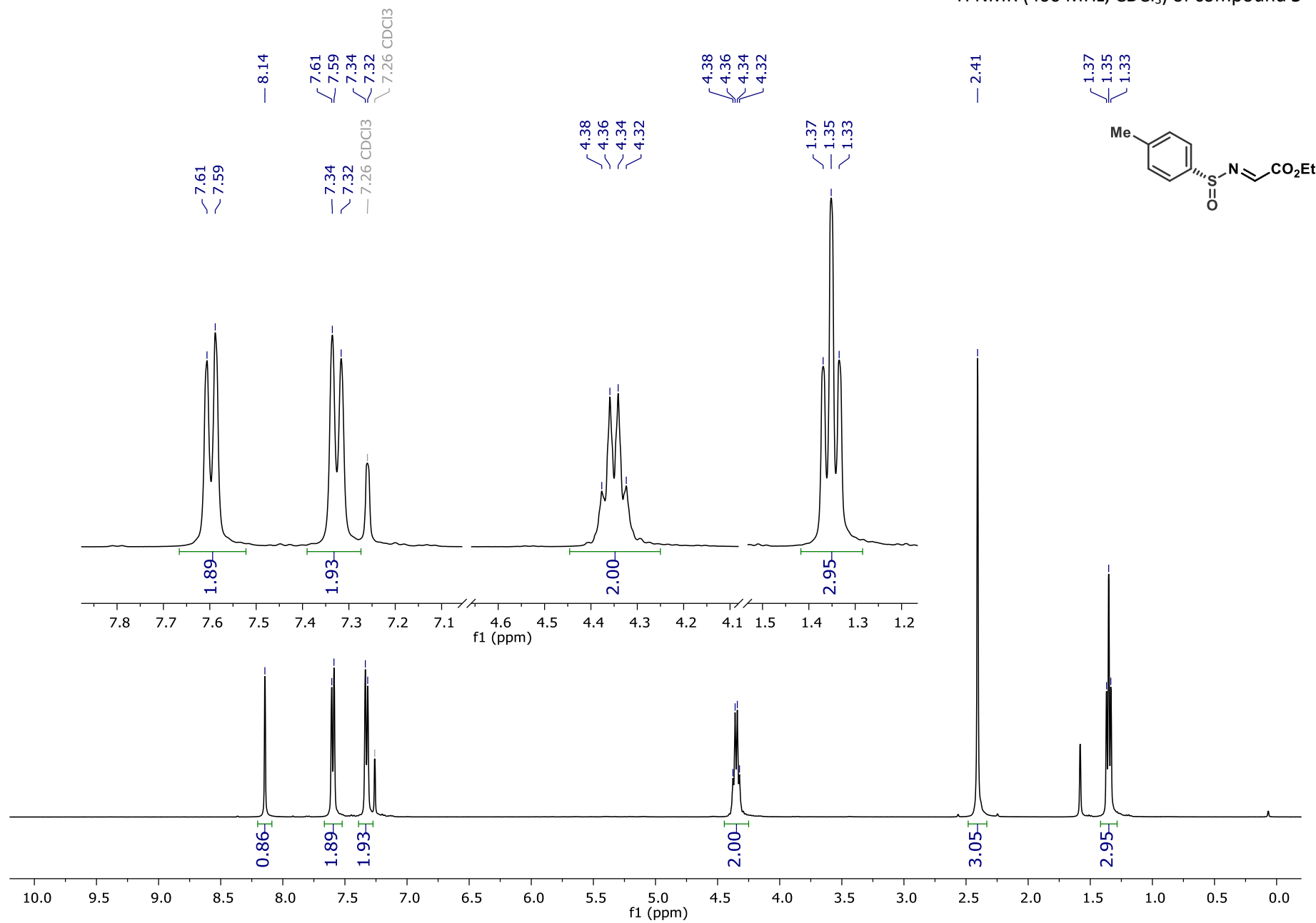
¹H NMR (400 MHz, CDCl₃) of compound 4



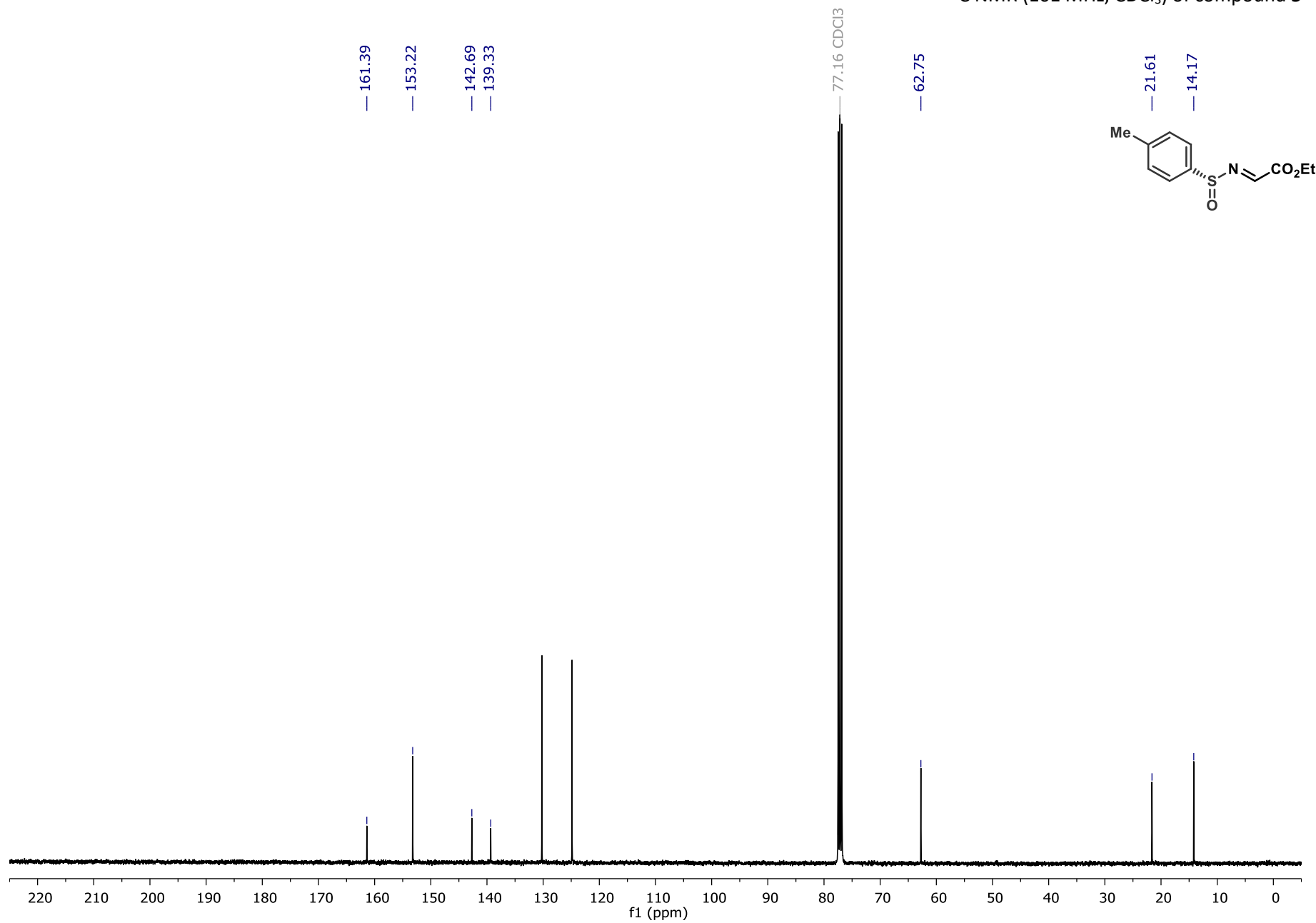
¹³C NMR (101 MHz, CDCl₃) of compound 4



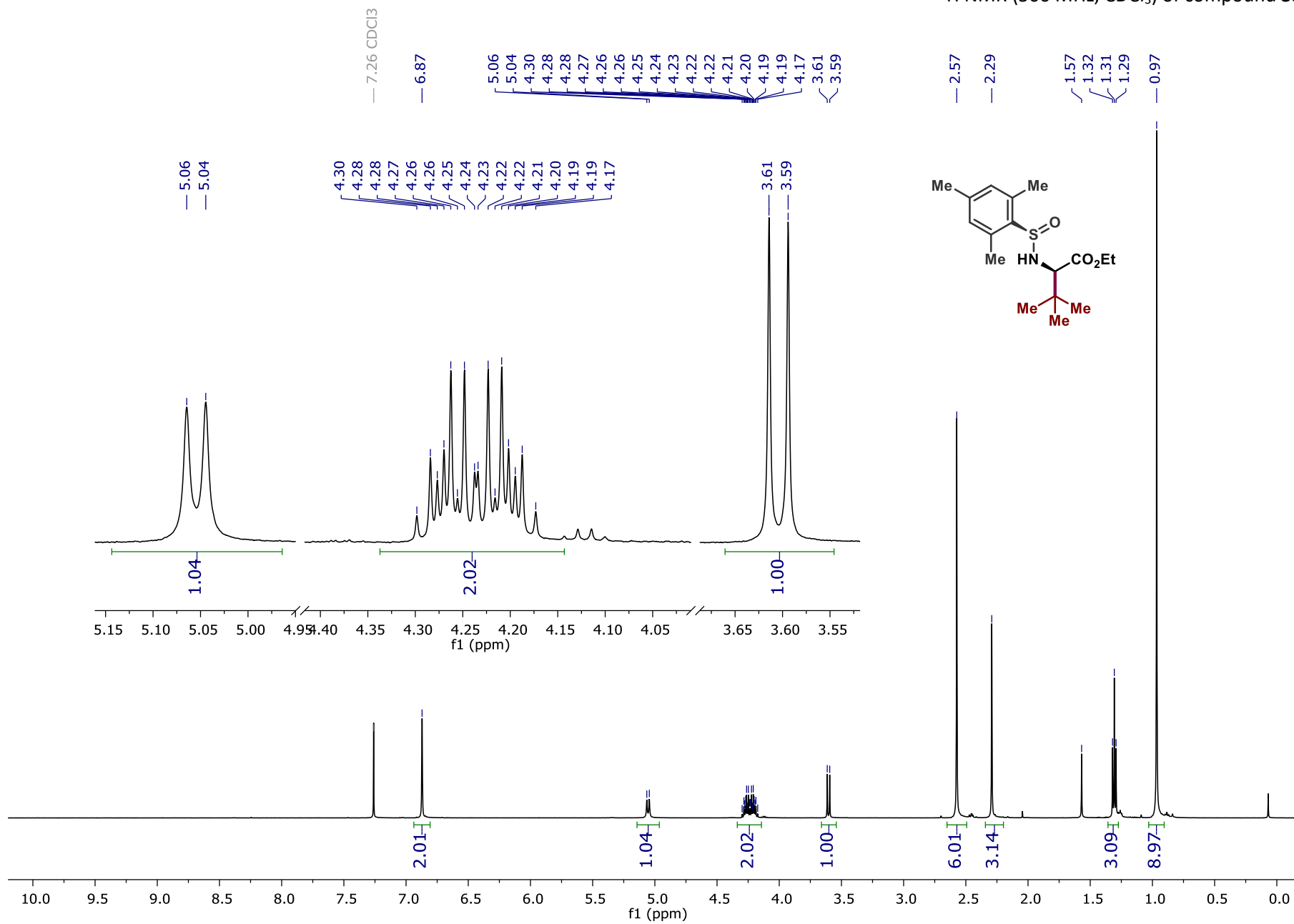
¹H NMR (400 MHz, CDCl₃) of compound 5



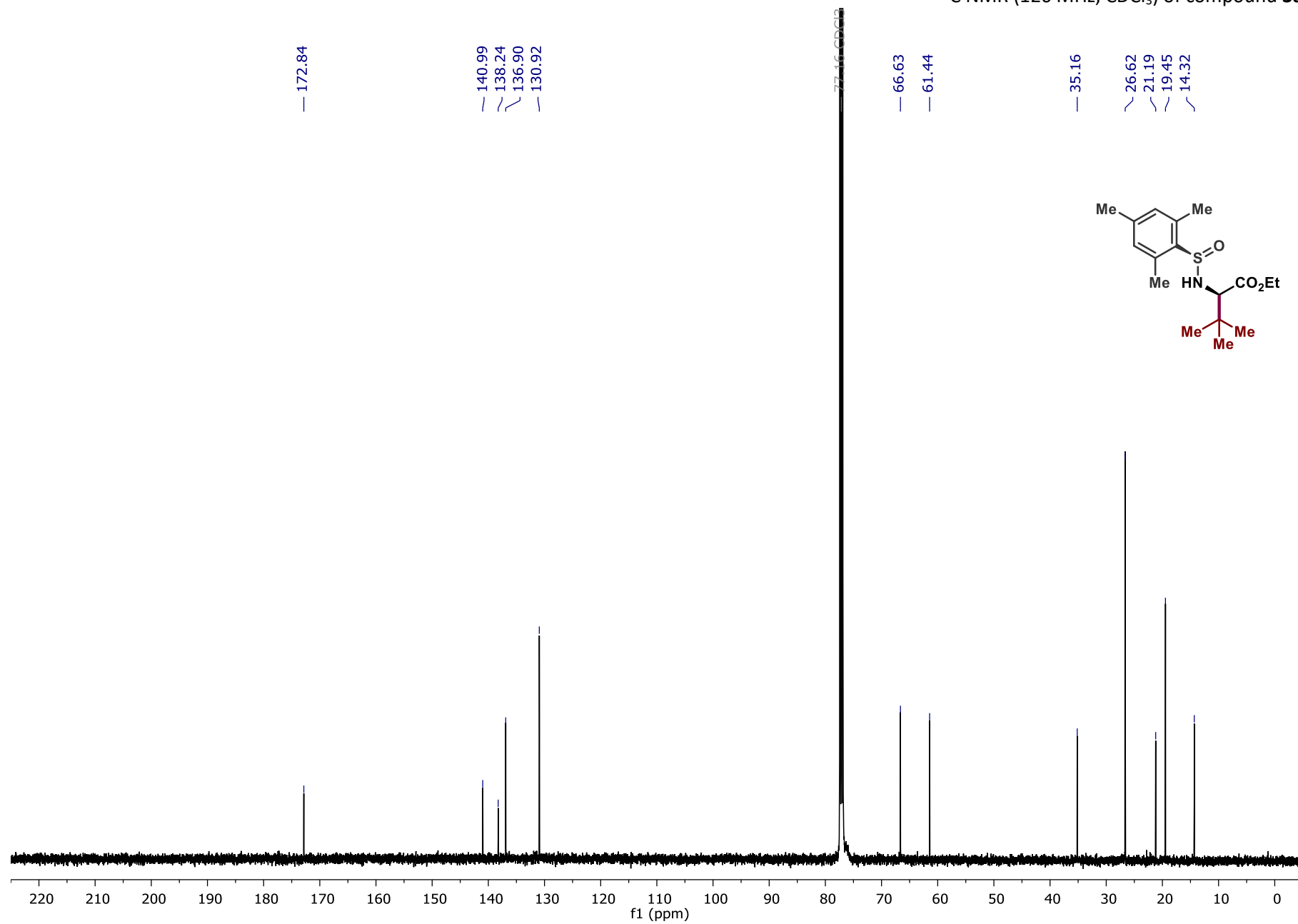
¹³C NMR (101 MHz, CDCl₃) of compound 5



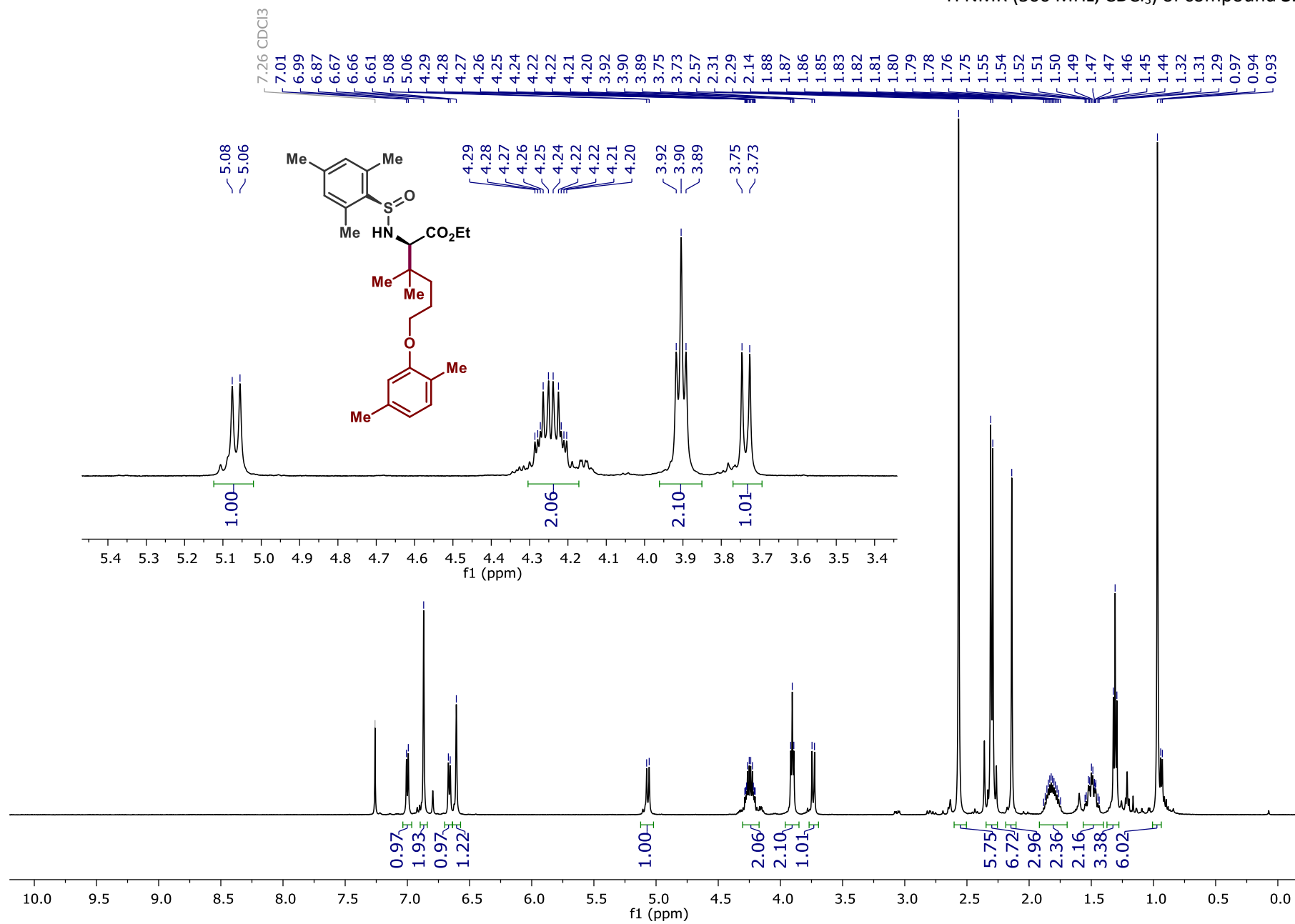
¹H NMR (500 MHz, CDCl₃) of compound **3a**



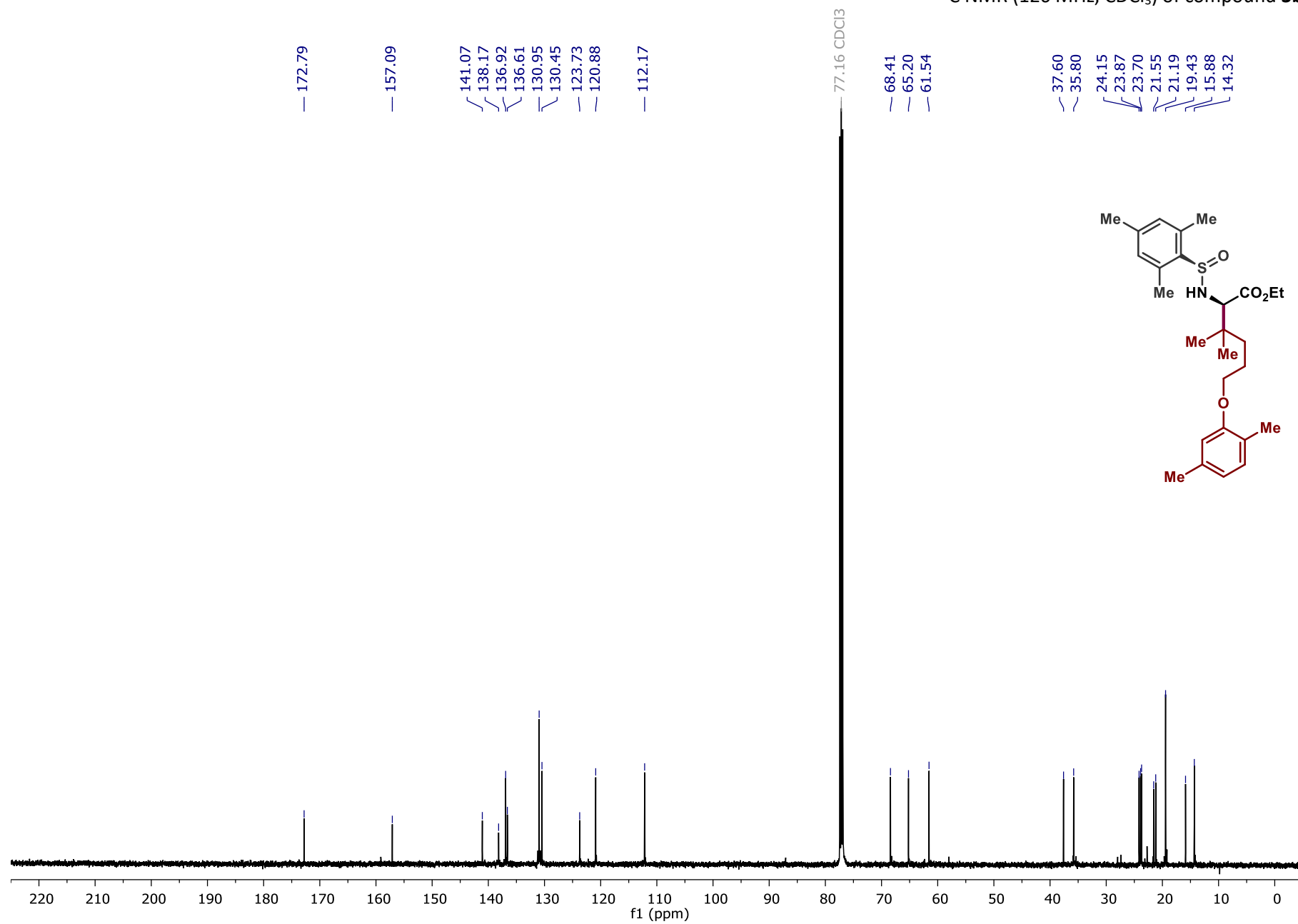
¹³C NMR (126 MHz, CDCl₃) of compound **3a**



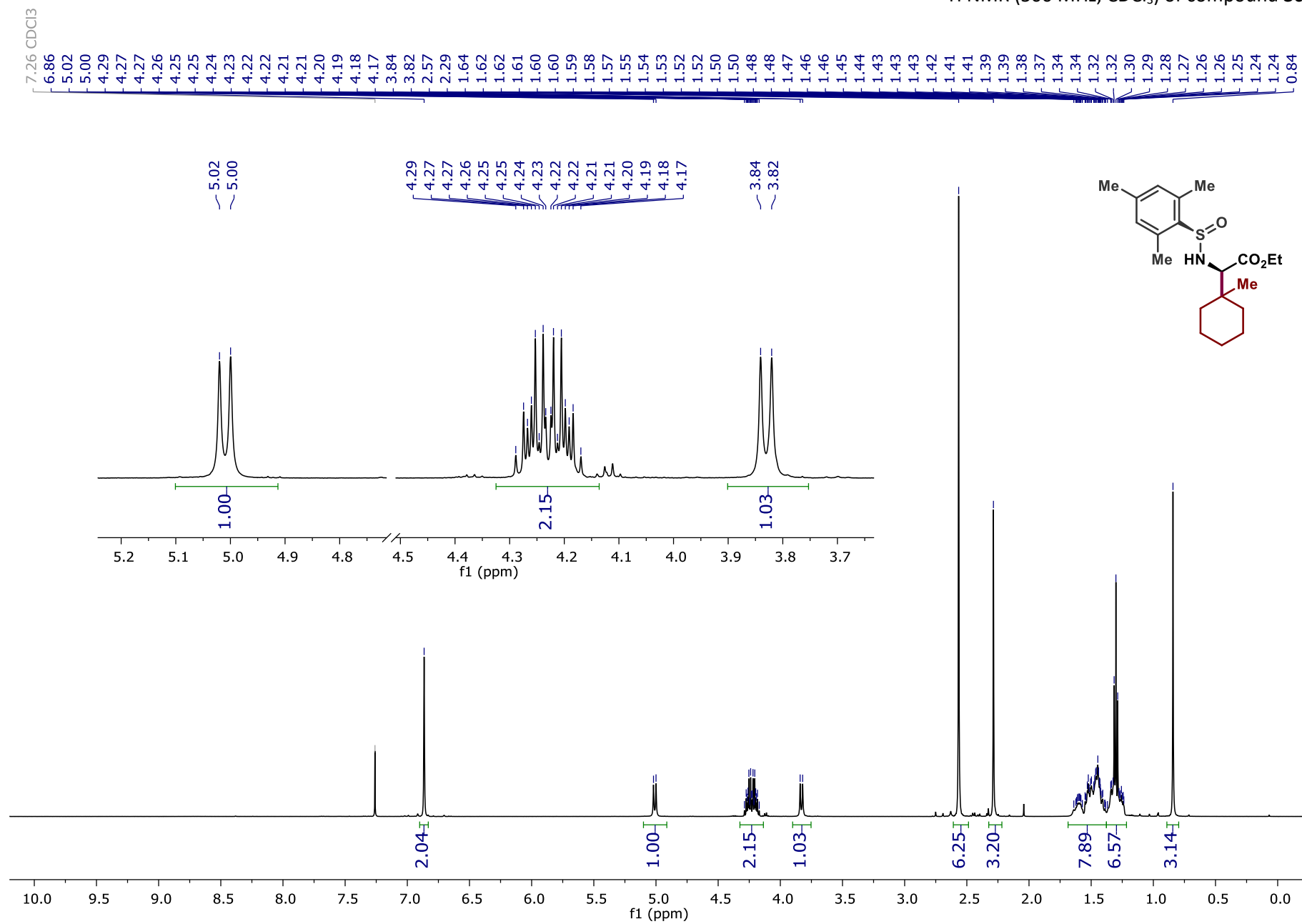
¹H NMR (500 MHz, CDCl₃) of compound **3b**



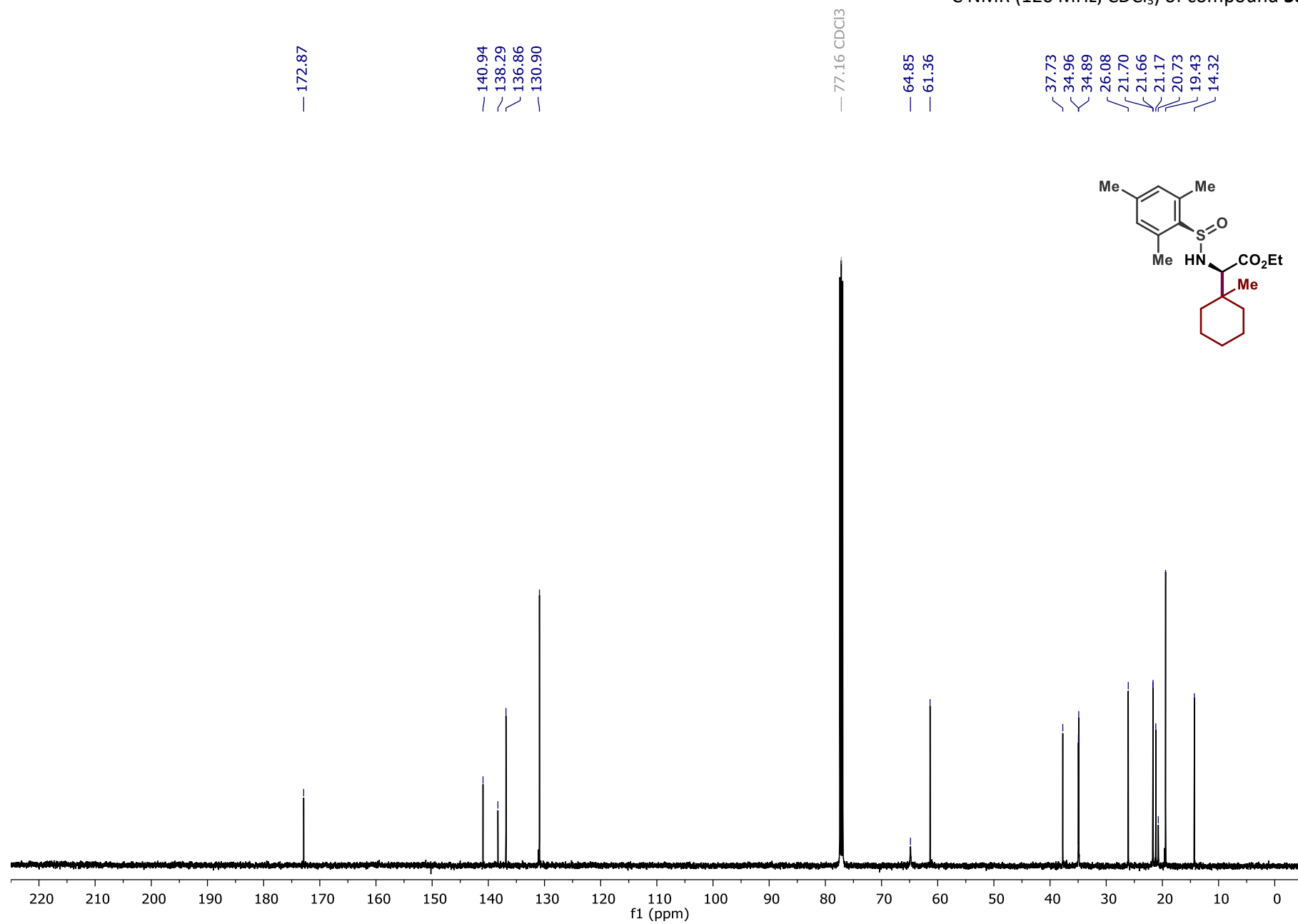
¹³C NMR (126 MHz, CDCl₃) of compound **3b**



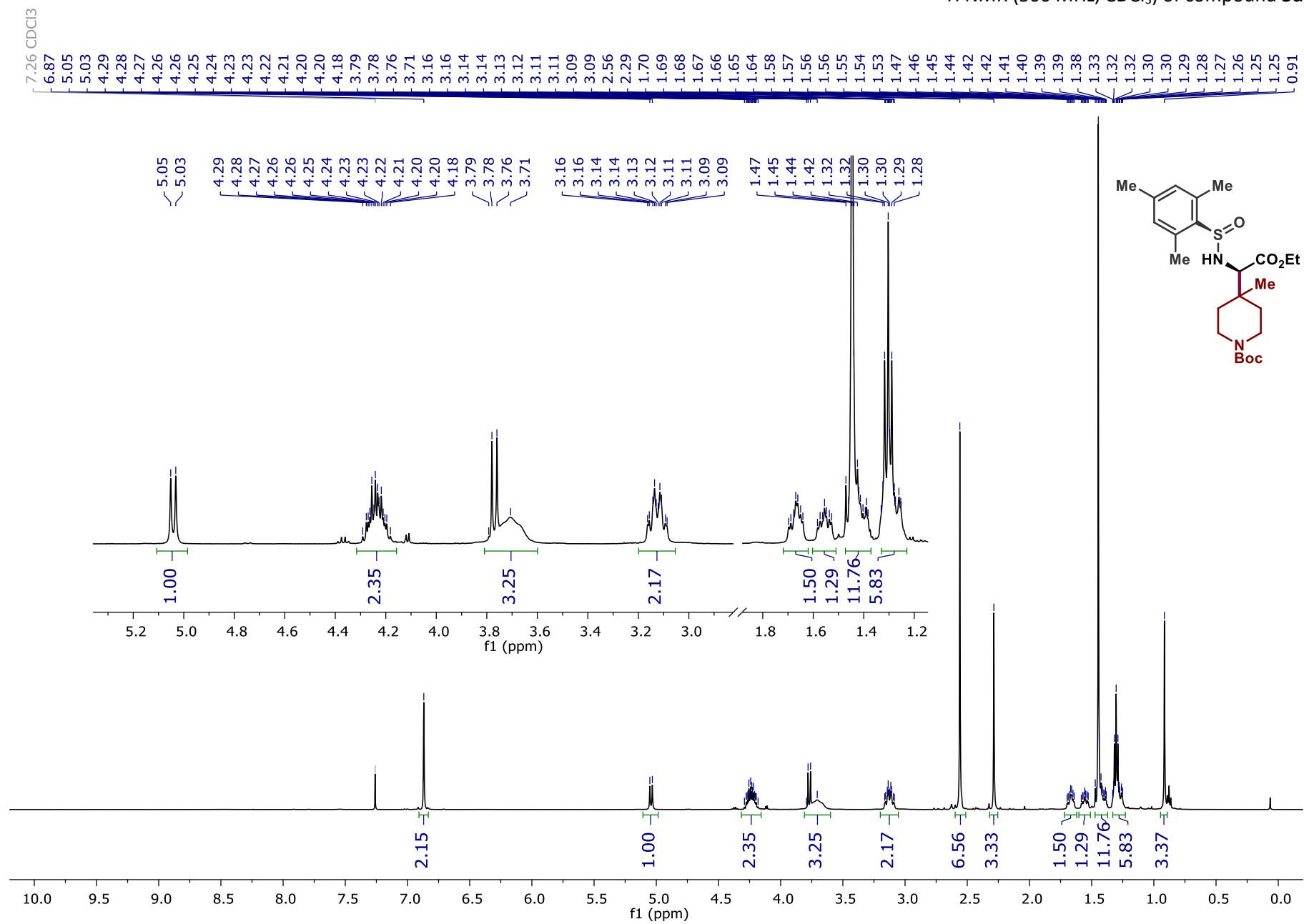
¹H NMR (500 MHz, CDCl₃) of compound **3c**



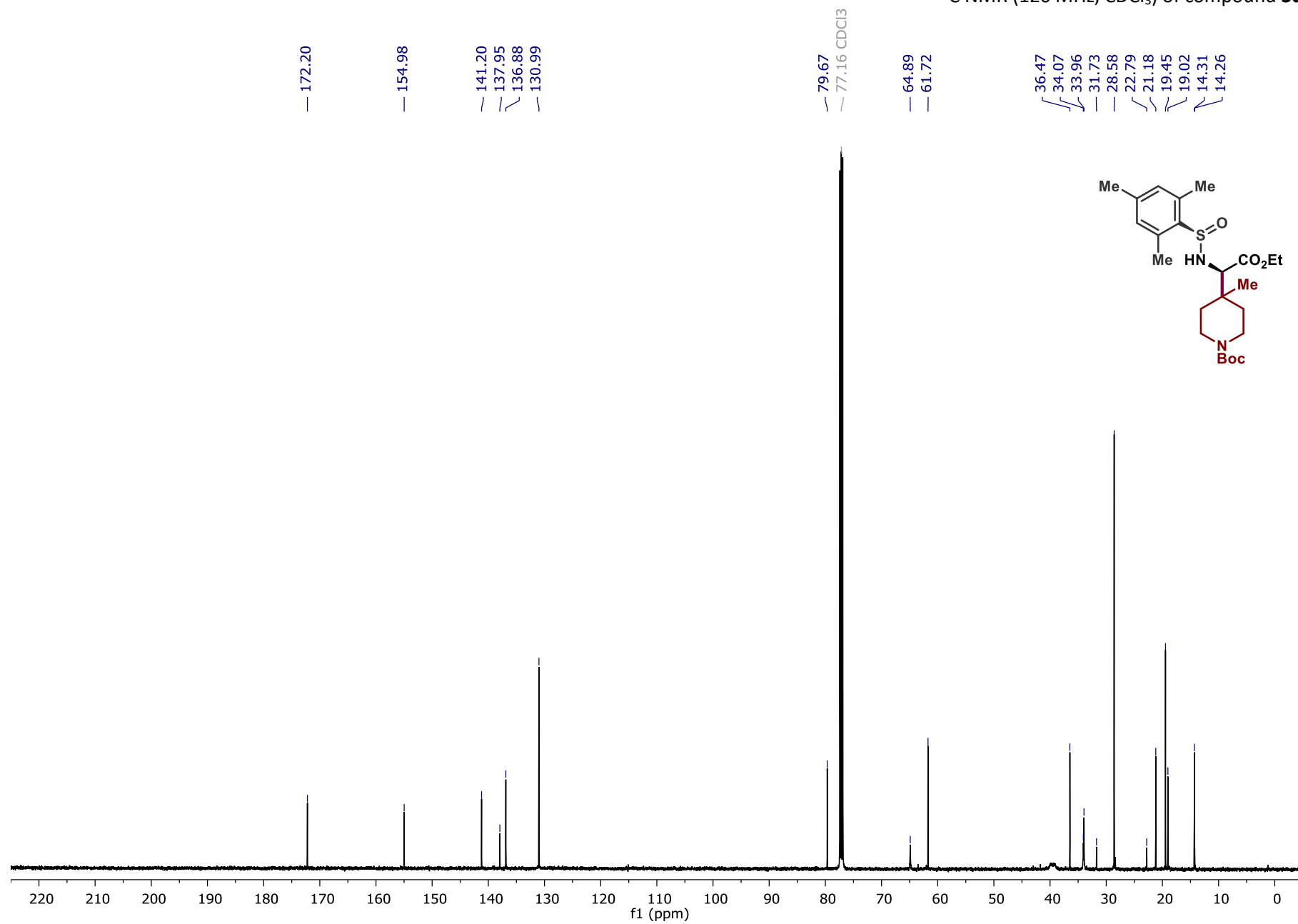
¹³C NMR (126 MHz, CDCl₃) of compound **3c**



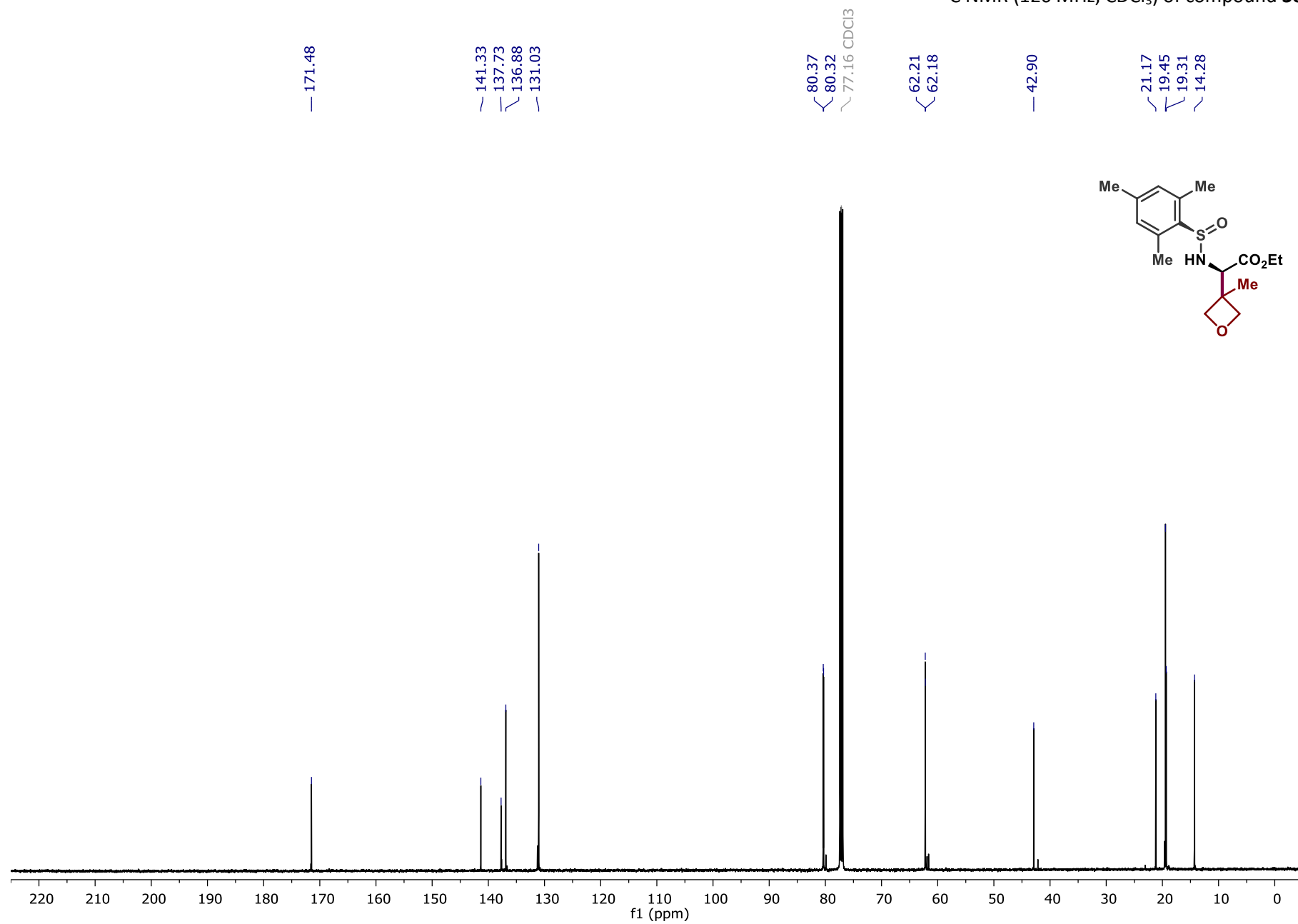
¹H NMR (500 MHz, CDCl₃) of compound **3d**



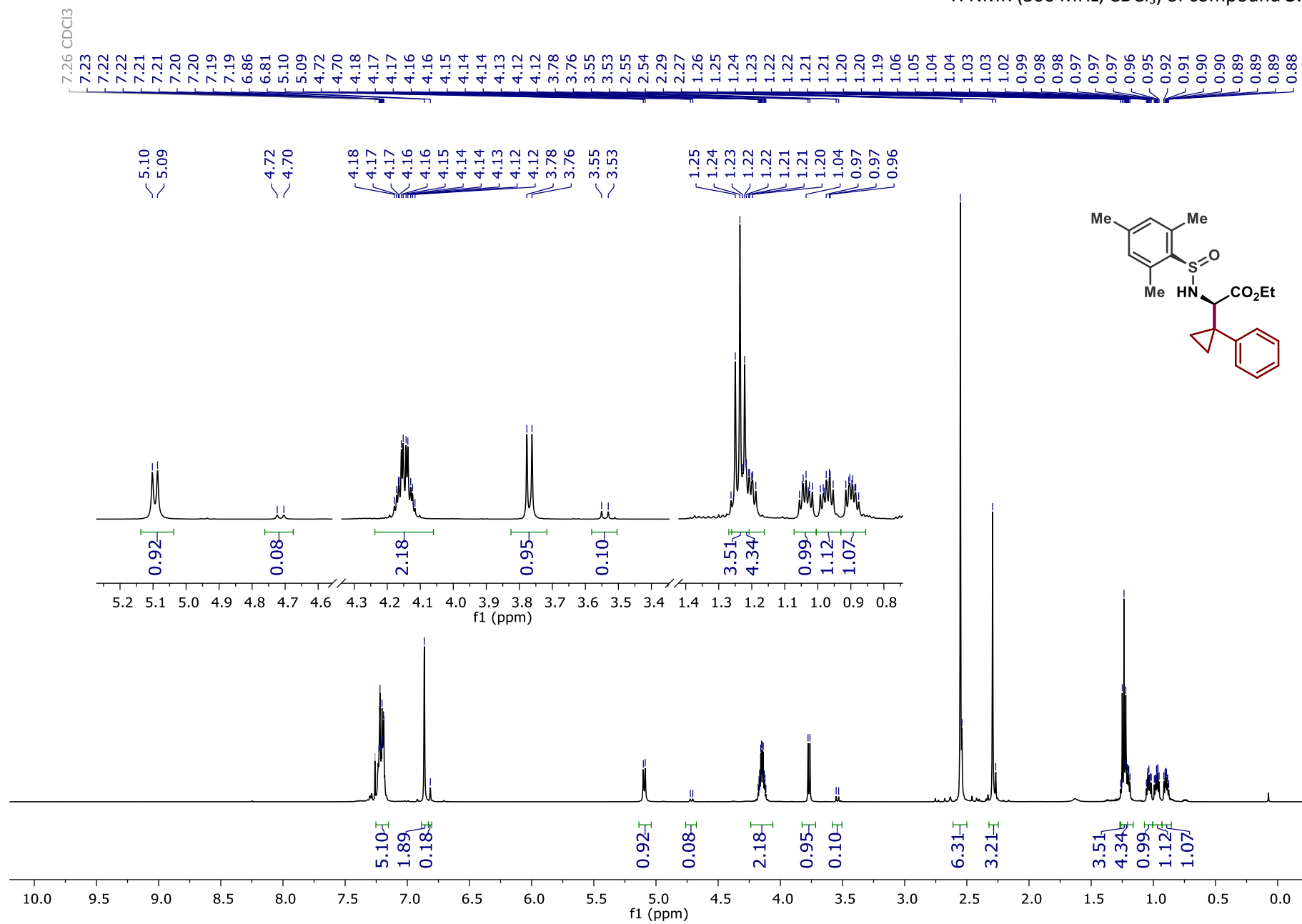
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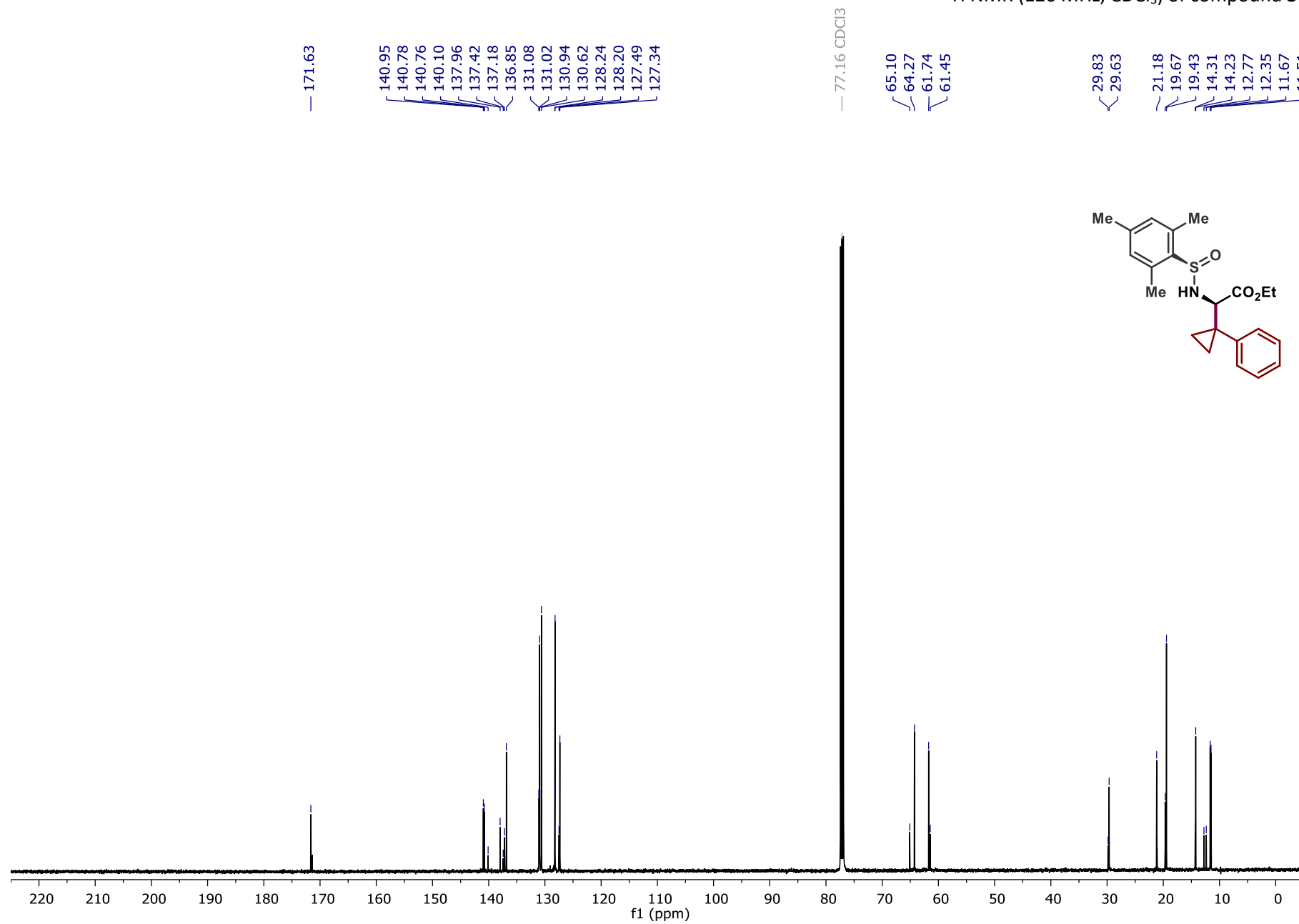
¹³C NMR (126 MHz, CDCl₃) of compound **3e**



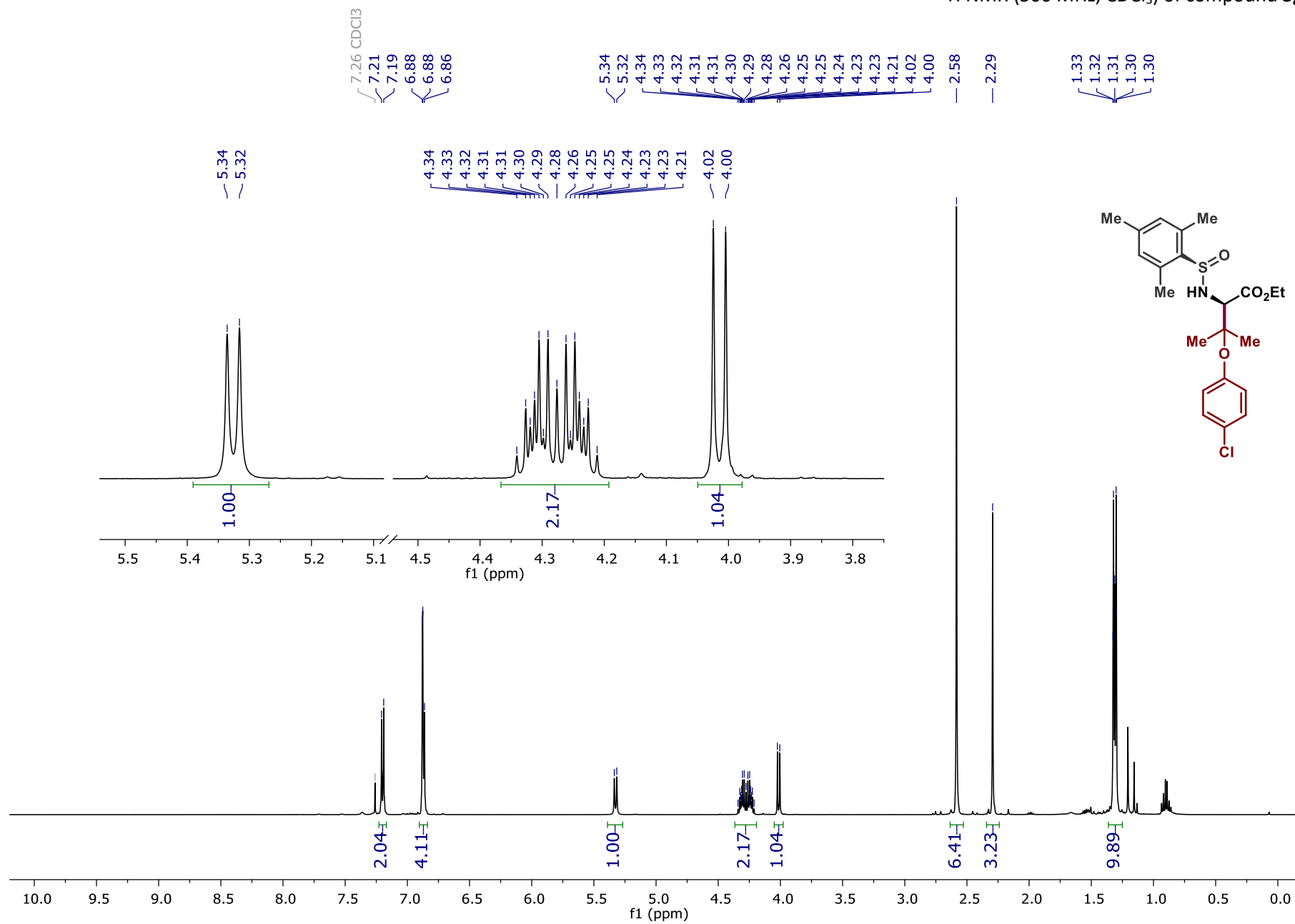
¹H NMR (500 MHz, CDCl₃) of compound **3f**



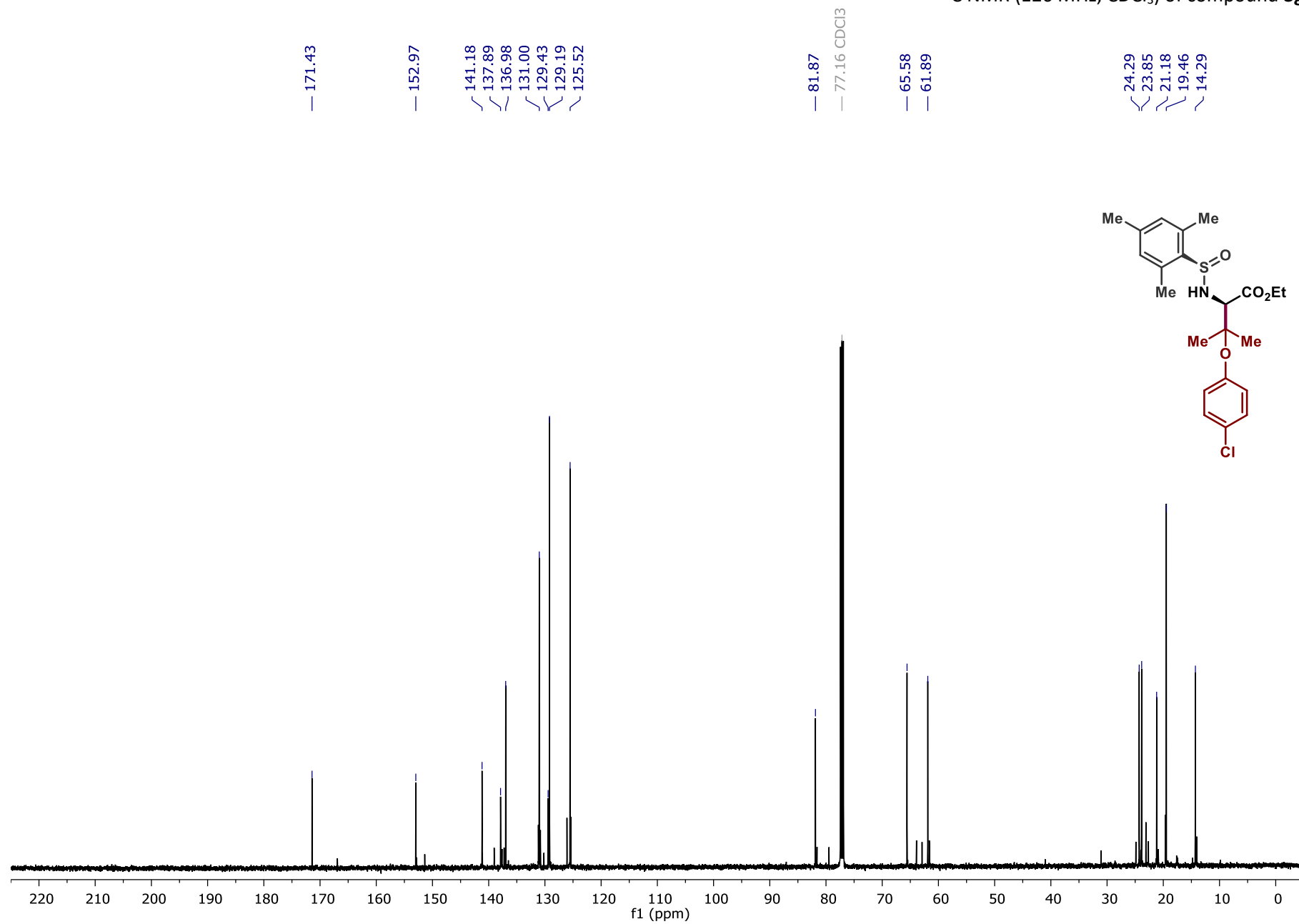
¹H NMR (126 MHz, CDCl₃) of compound **3f**



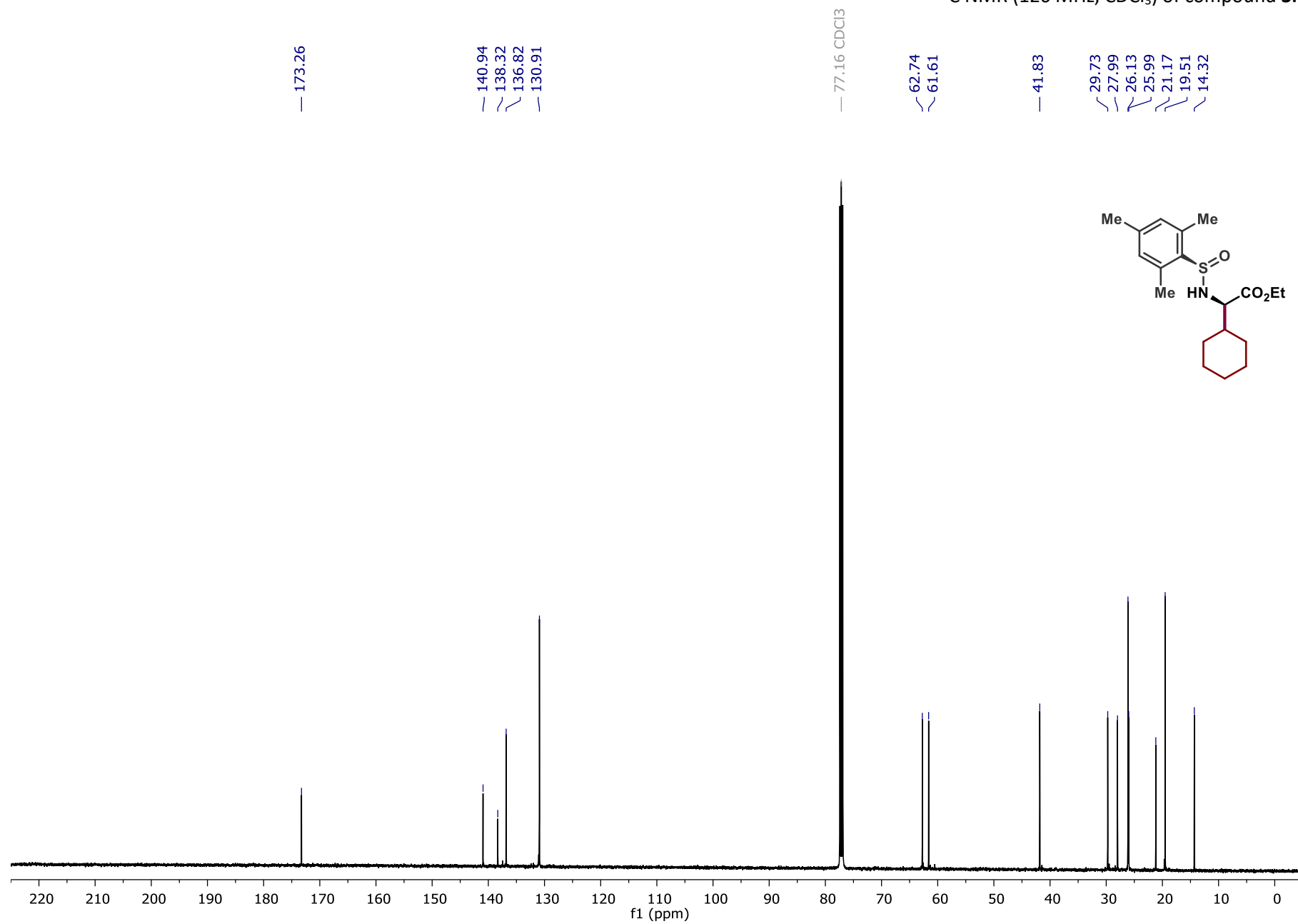
¹H NMR (500 MHz, CDCl₃) of compound **3g**



¹³C NMR (126 MHz, CDCl₃) of compound **3g**



¹³C NMR (126 MHz, CDCl₃) of compound **3h**



— 173.26

— 140.94
— 138.32
— 136.82
— 130.91

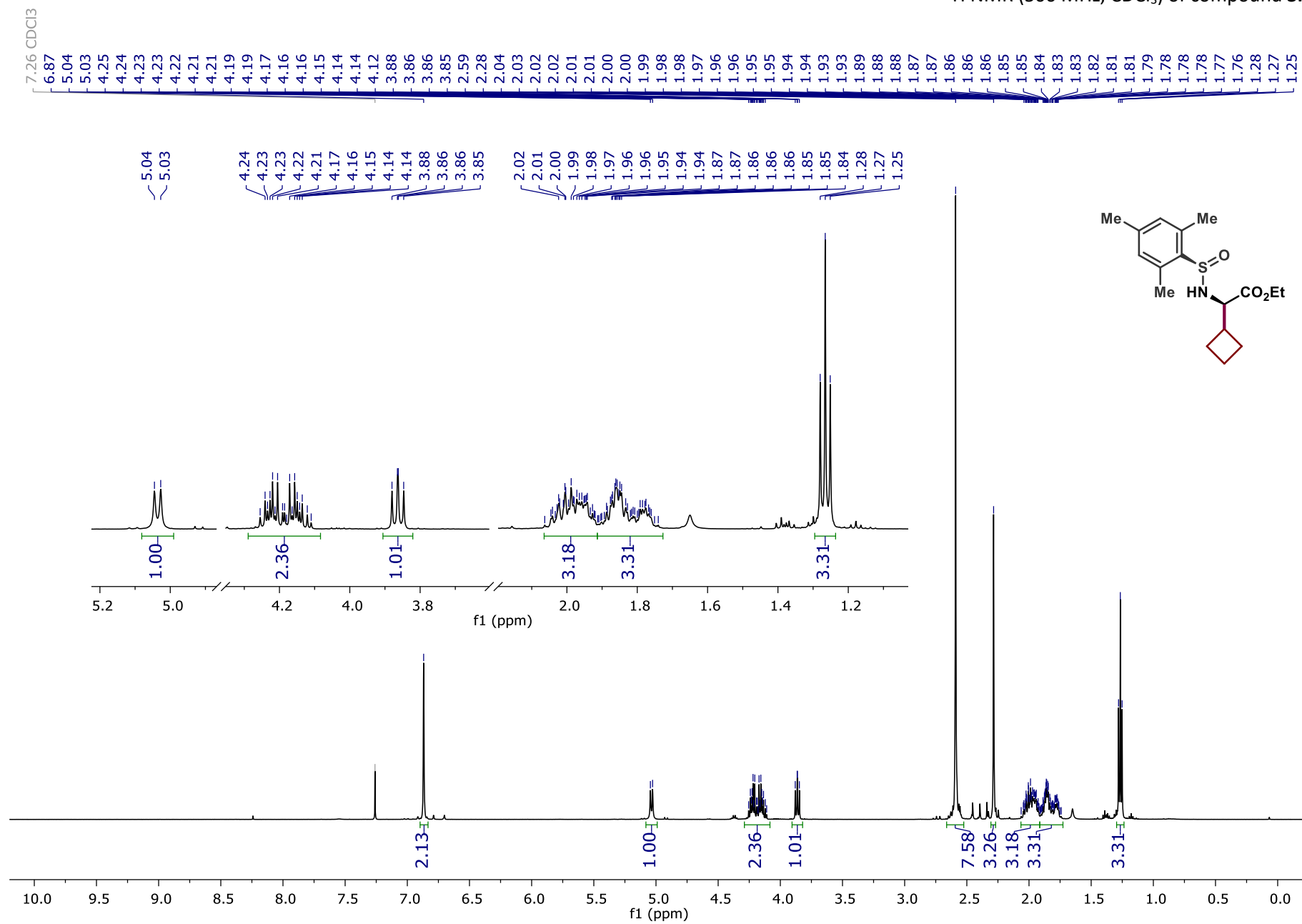
— 77.16 CDCl₃

— 62.74
— 61.61

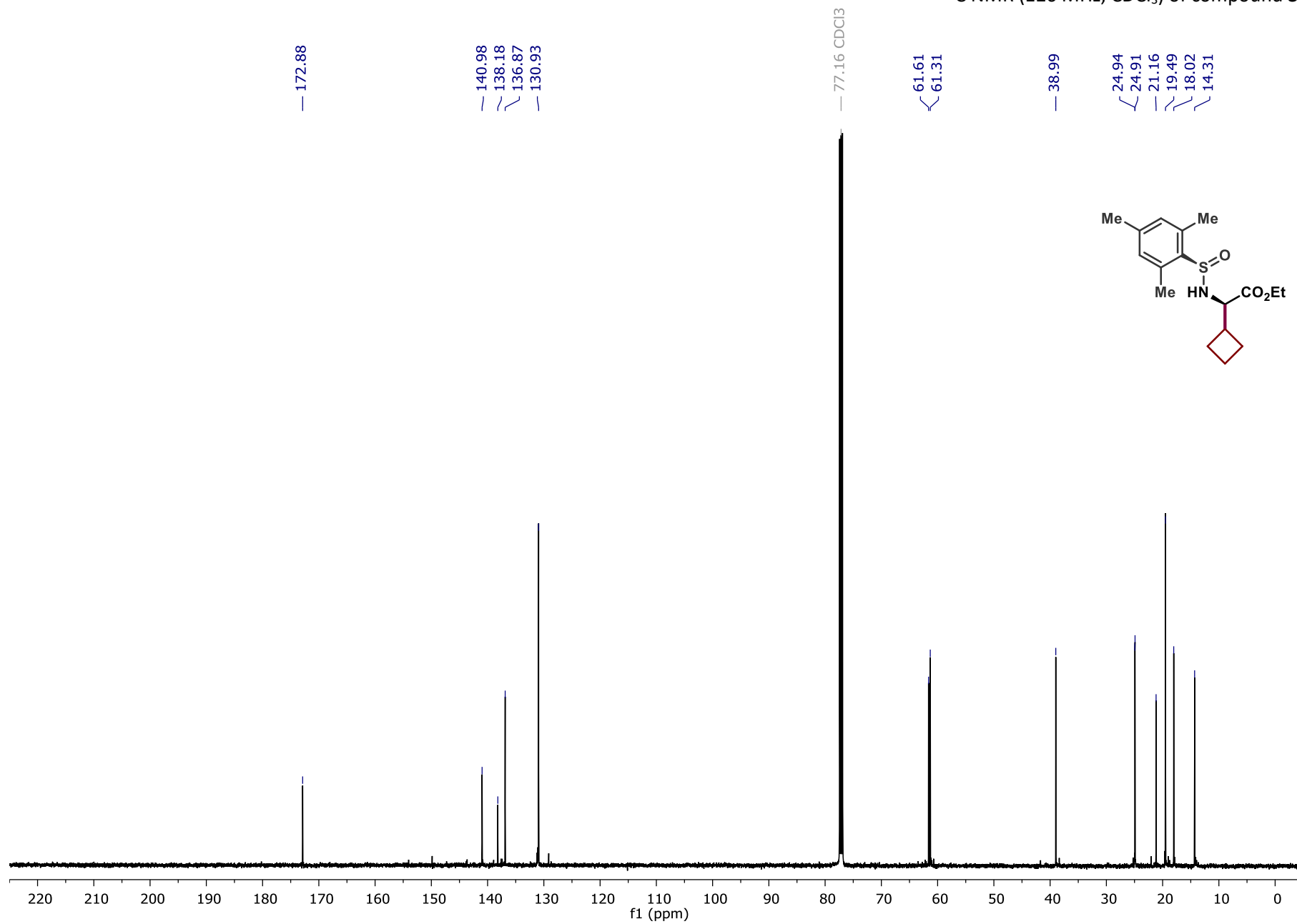
— 41.83

— 29.73
— 27.99
— 26.13
— 25.99
— 21.17
— 19.51
— 14.32

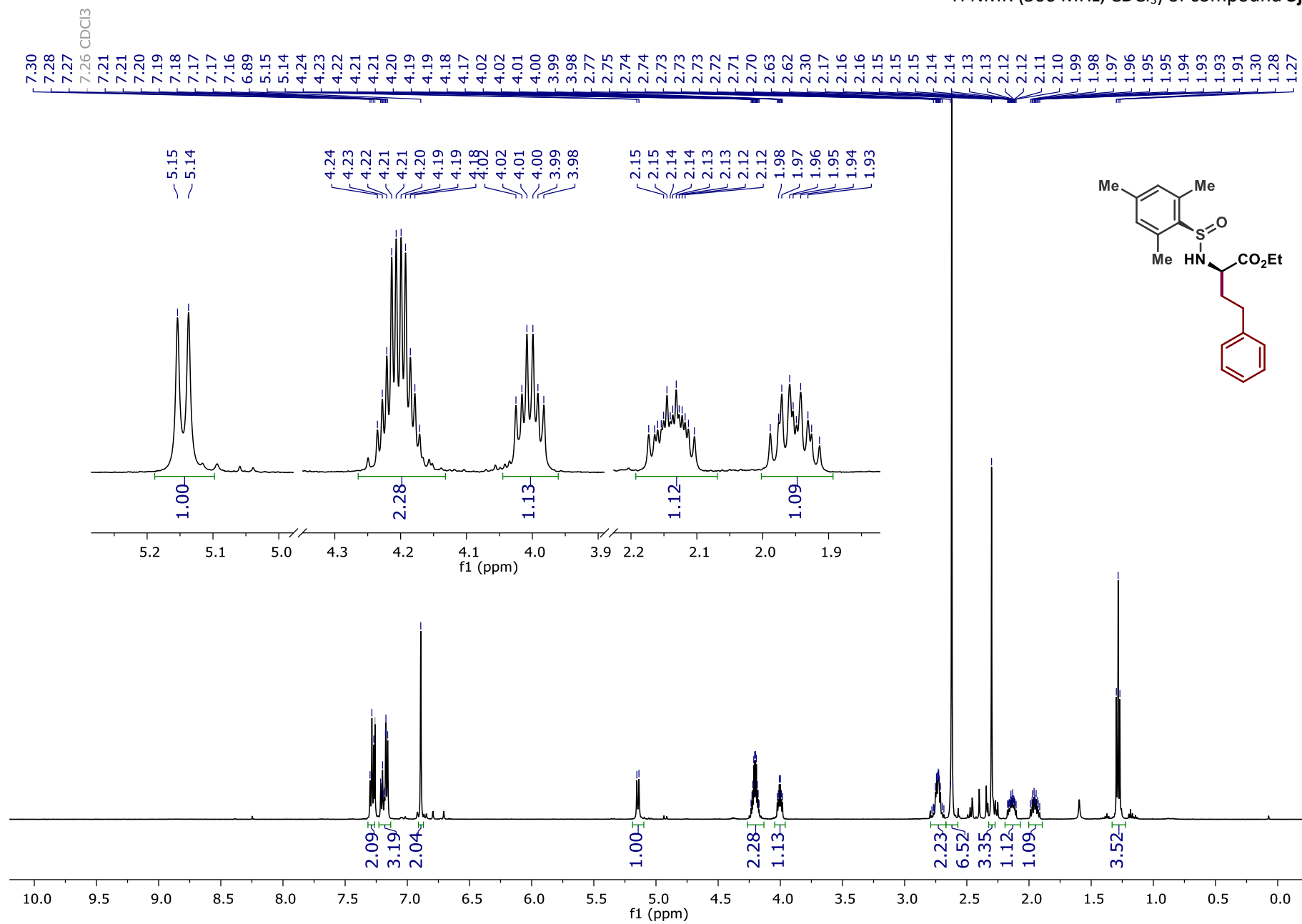
¹H NMR (500 MHz, CDCl₃) of compound **3i**



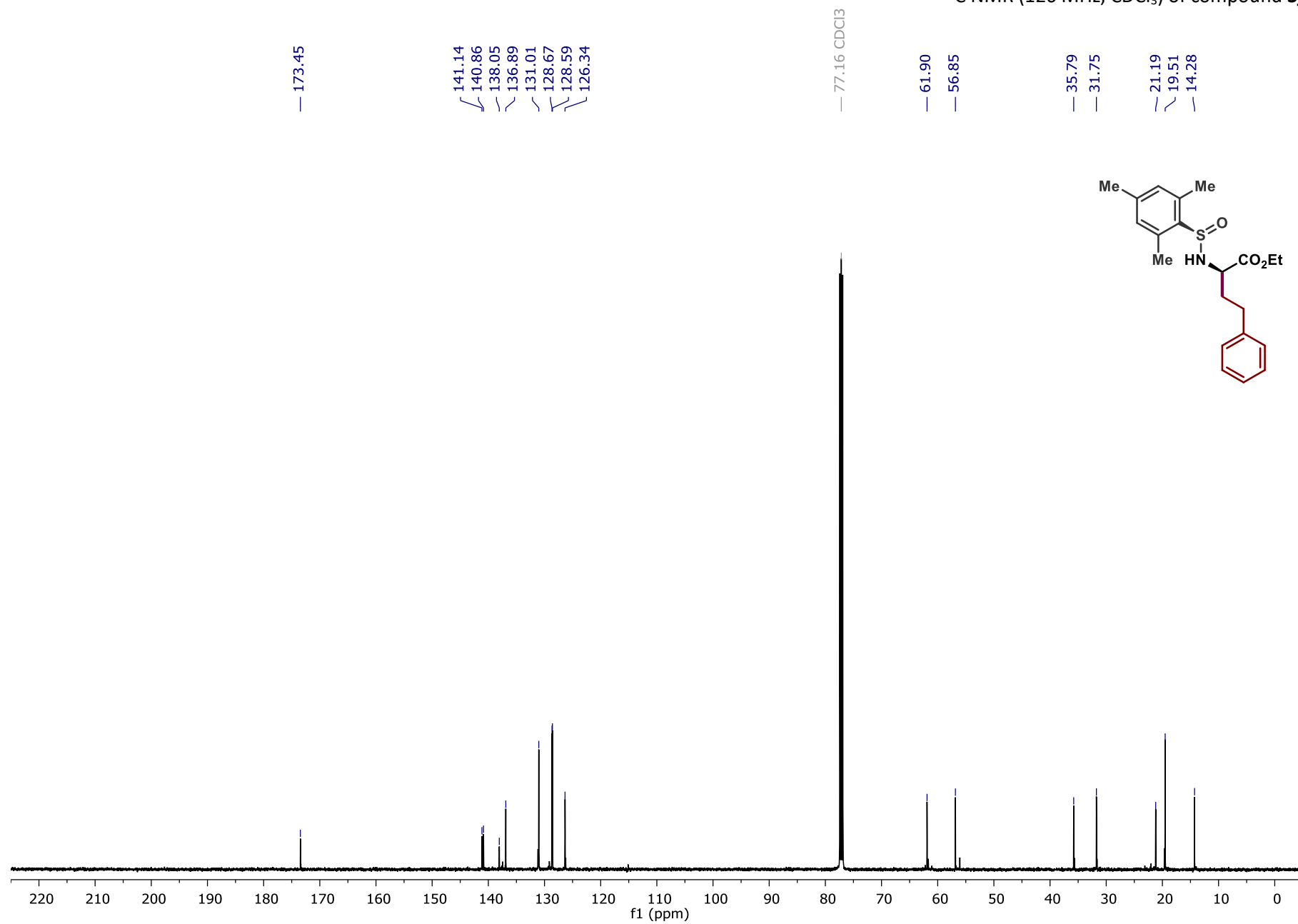
¹³C NMR (126 MHz, CDCl₃) of compound **3i**



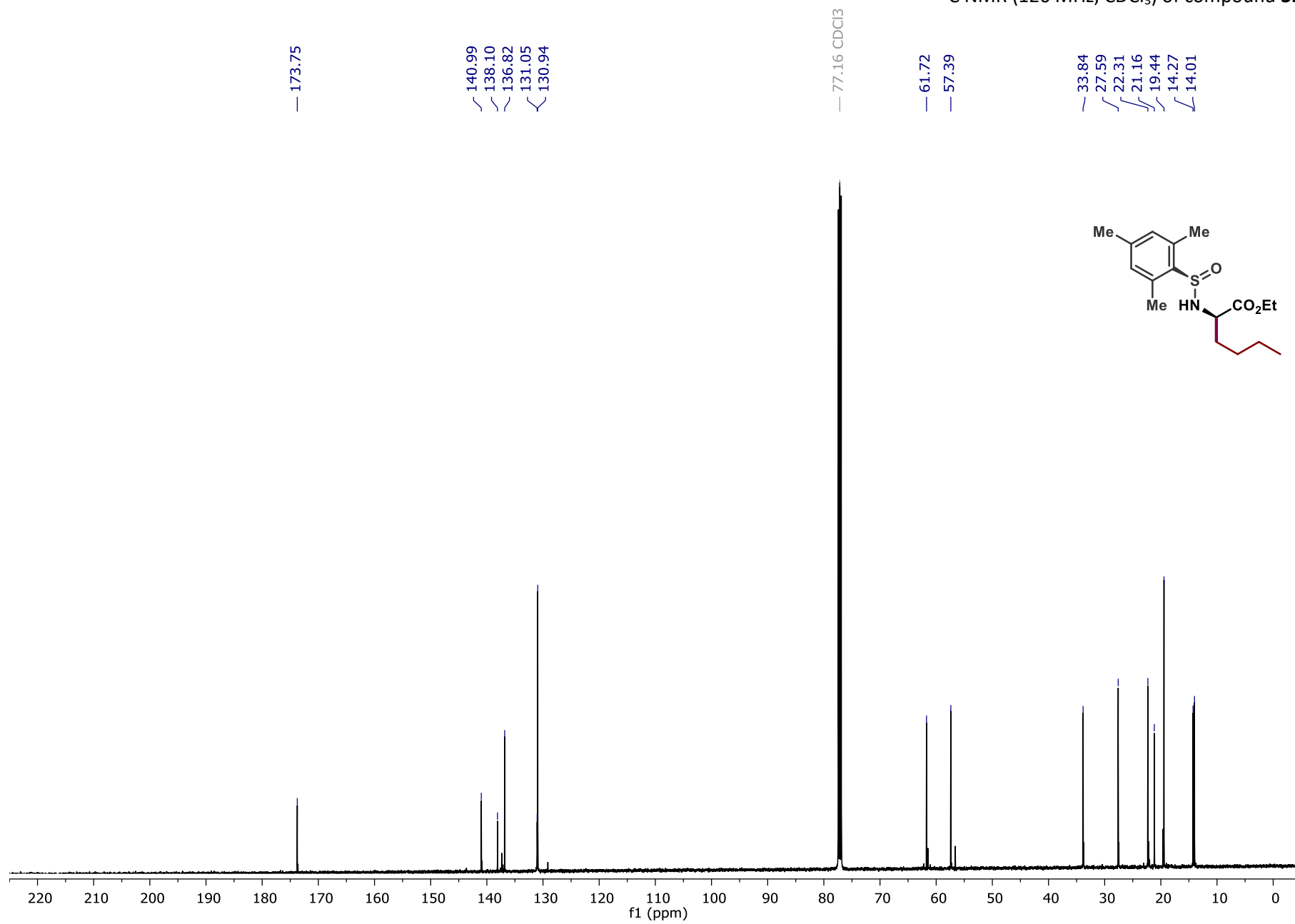
¹H NMR (500 MHz, CDCl₃) of compound **3j**



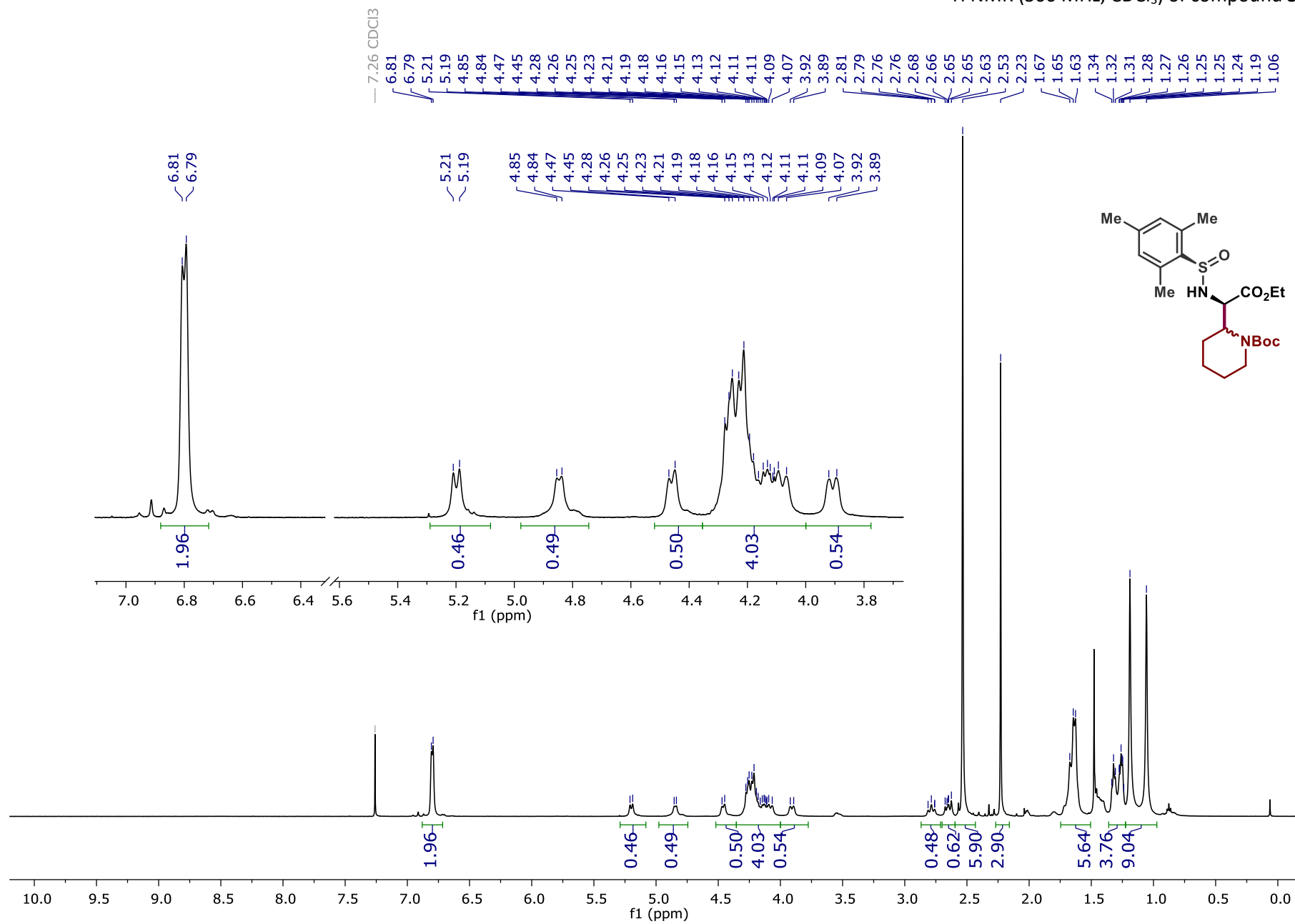
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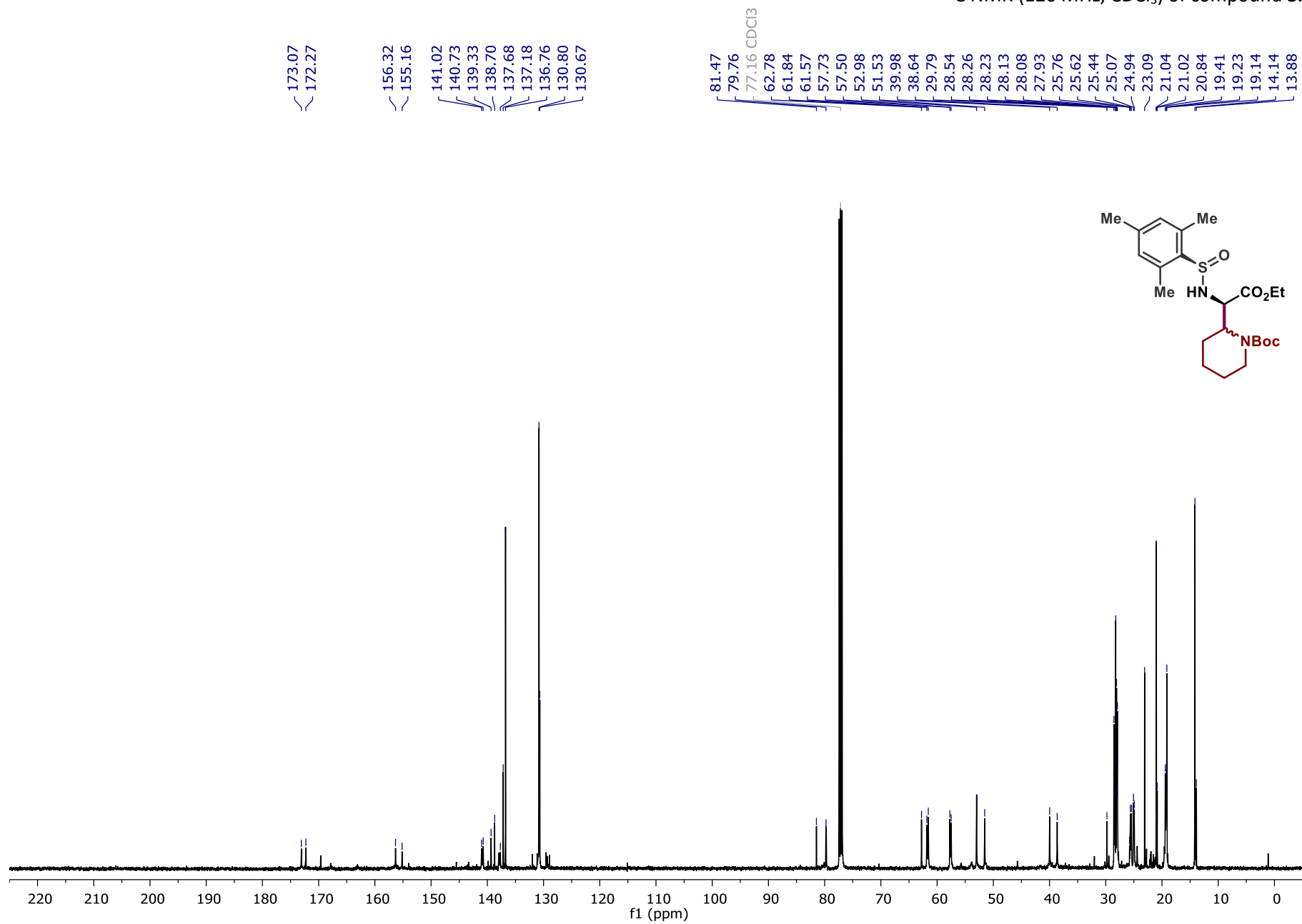
¹³C NMR (126 MHz, CDCl₃) of compound **3k**



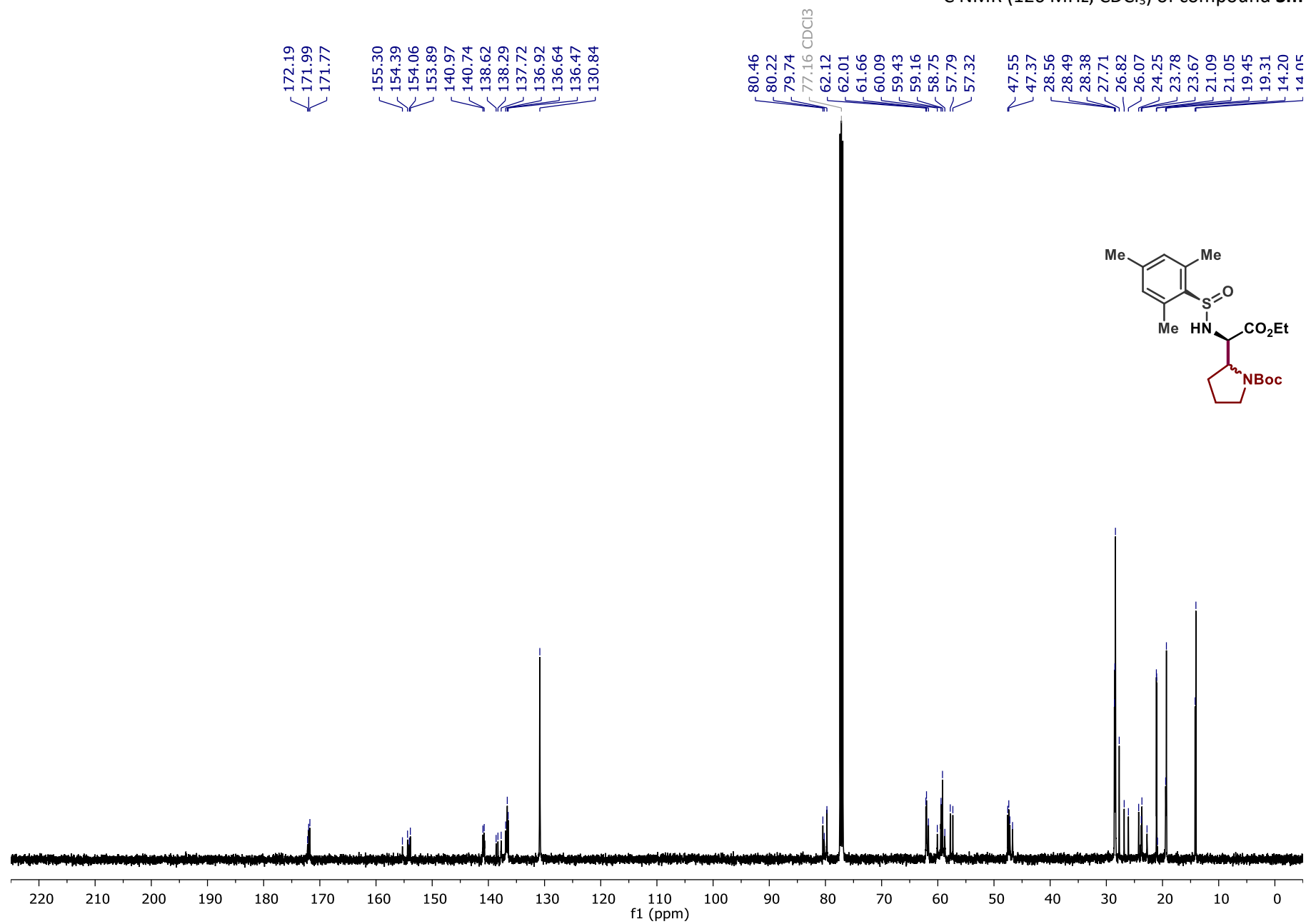
¹H NMR (500 MHz, CDCl₃) of compound **3I**



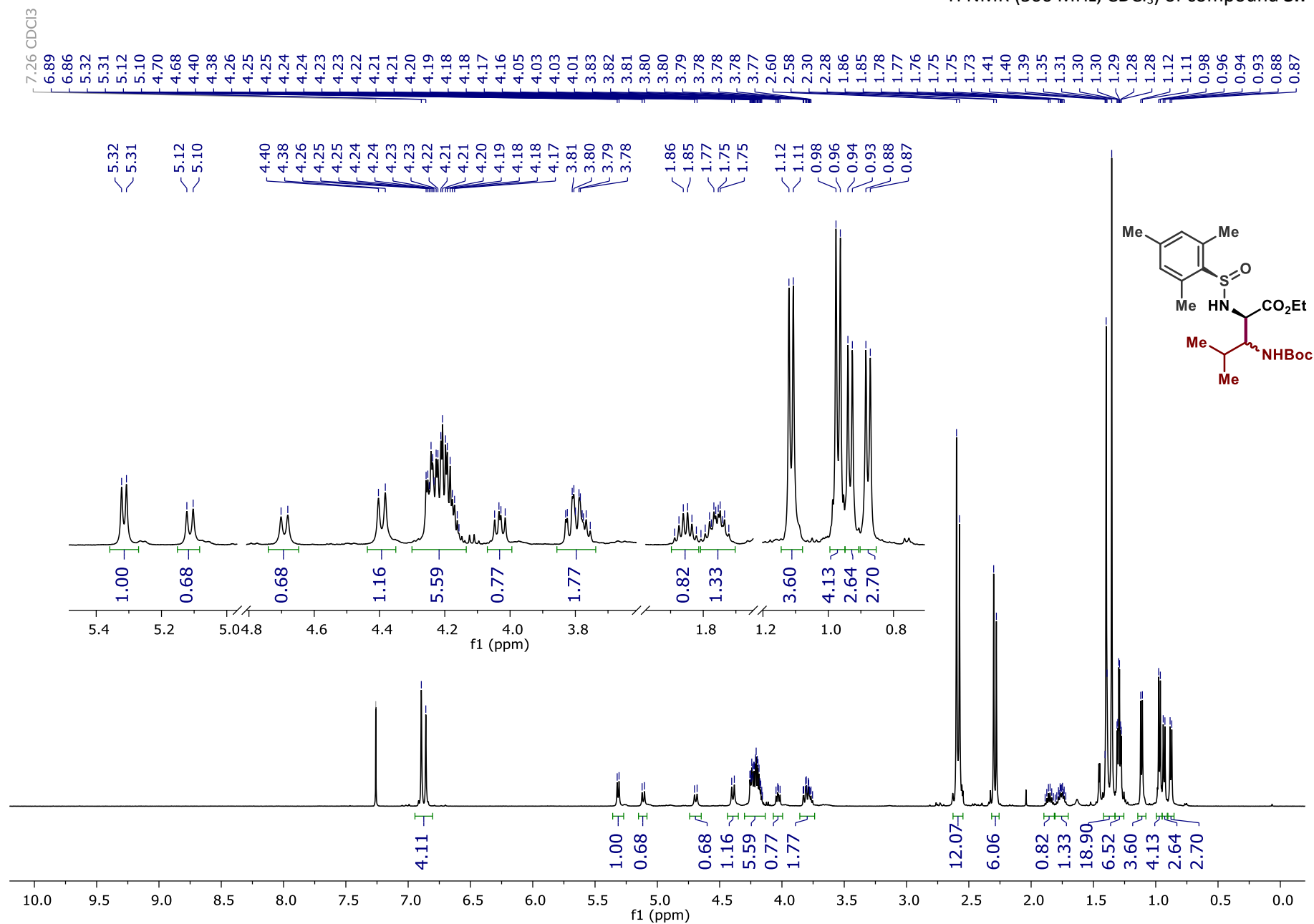
¹³C NMR (126 MHz, CDCl₃) of compound **3I**



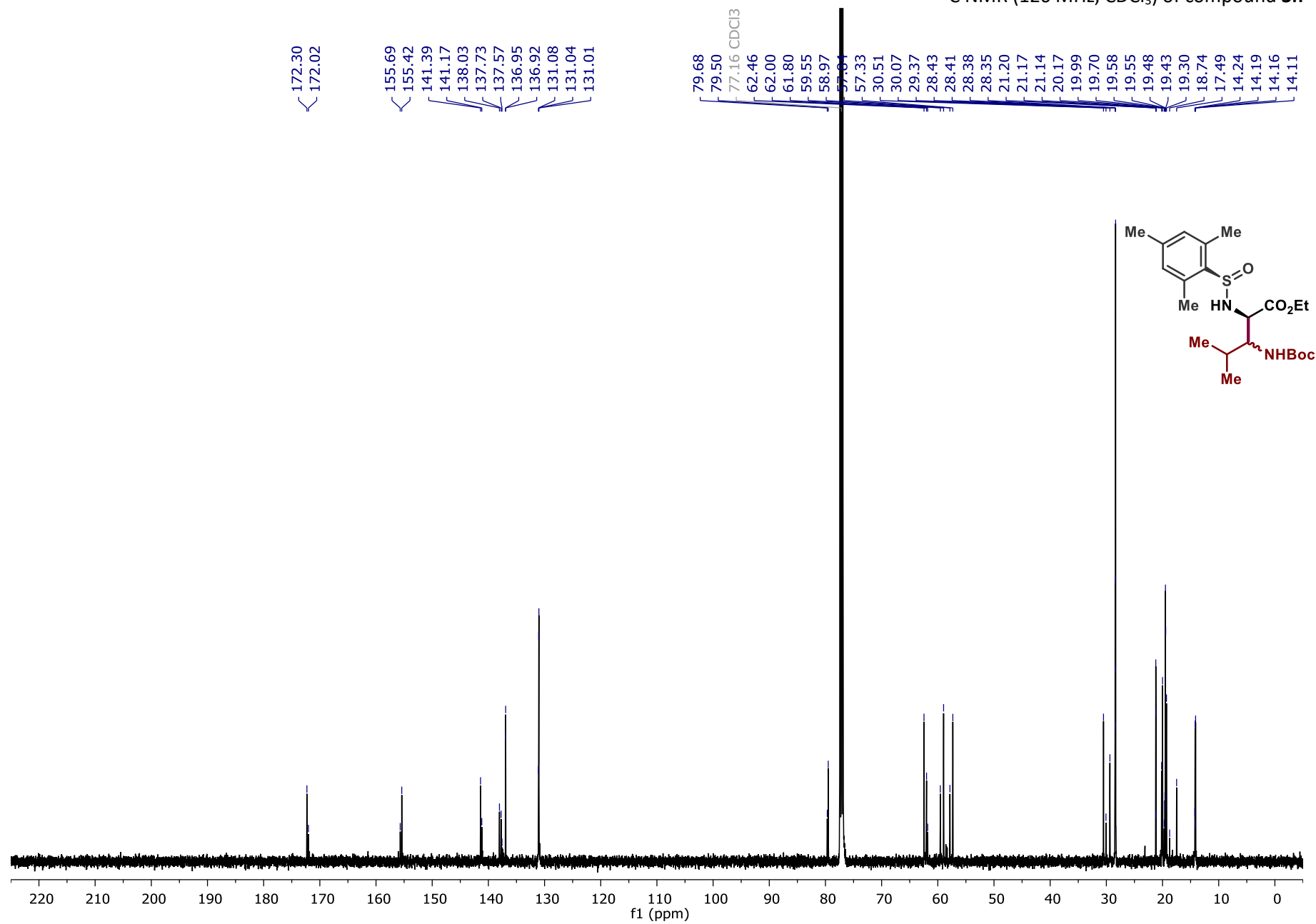
¹³C NMR (126 MHz, CDCl₃) of compound **3m**



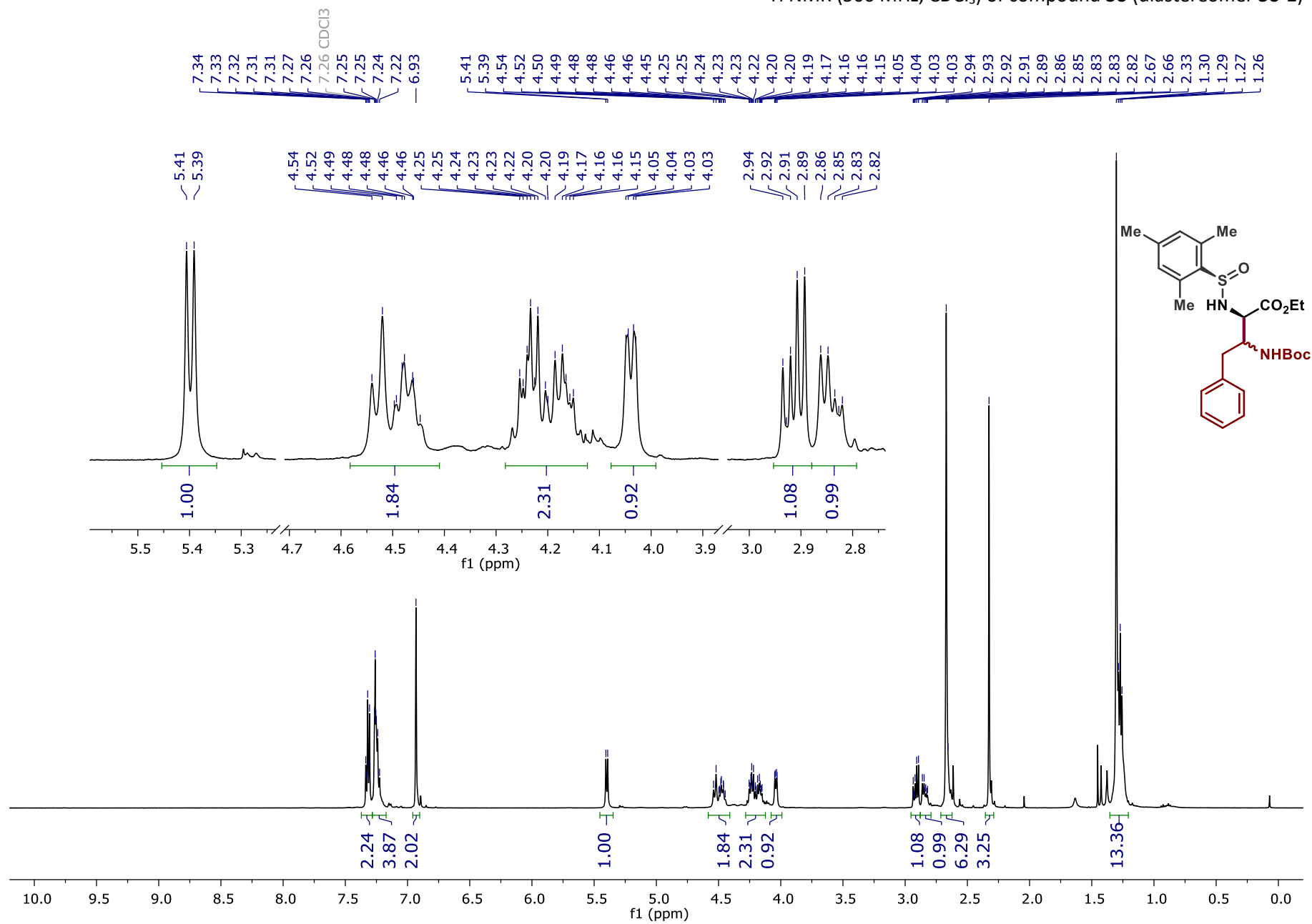
¹H NMR (500 MHz, CDCl₃) of compound **3n**



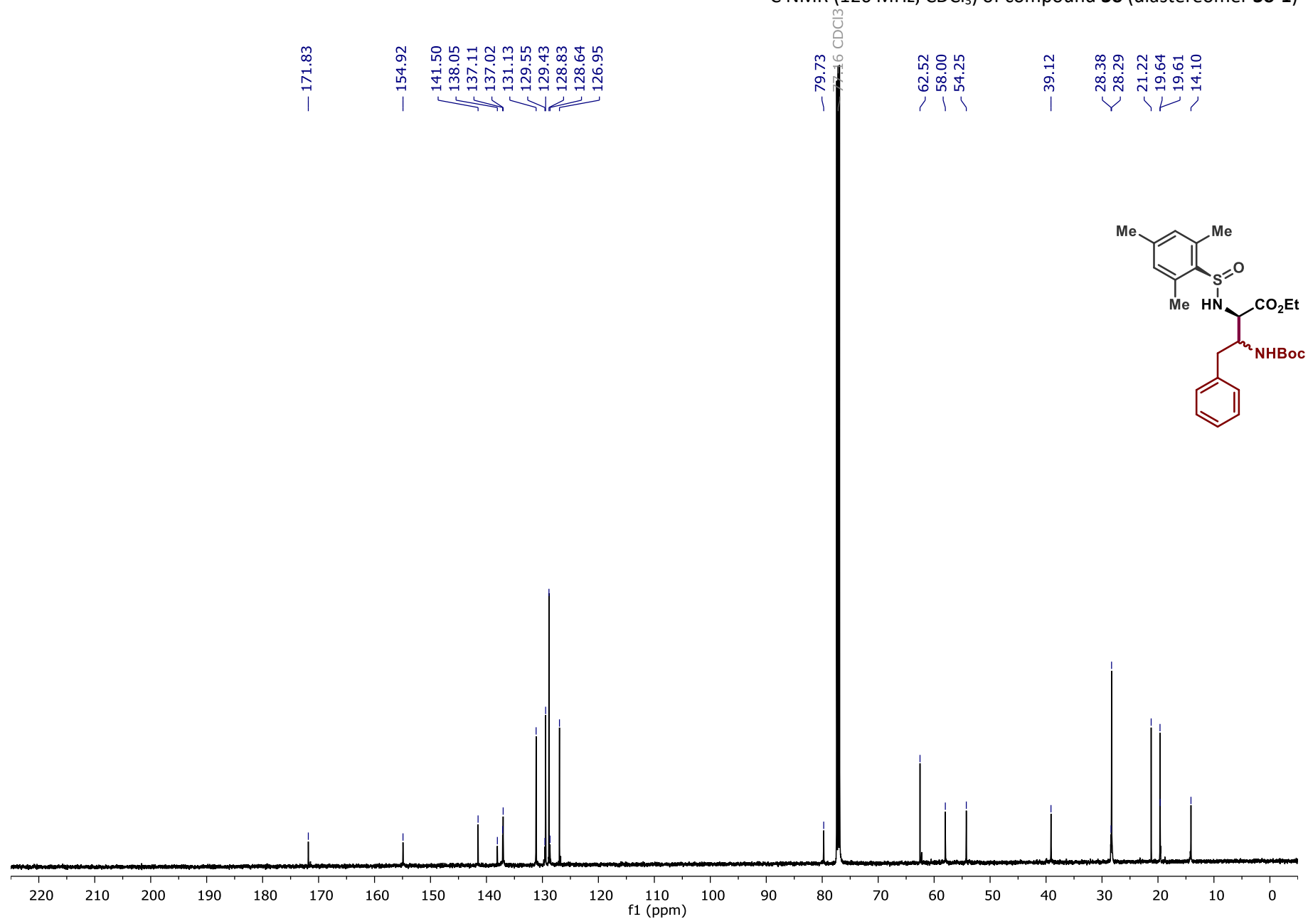
¹³C NMR (126 MHz, CDCl₃) of compound **3n**



¹H NMR (500 MHz, CDCl₃) of compound **3o** (diastereomer **3o-1**)

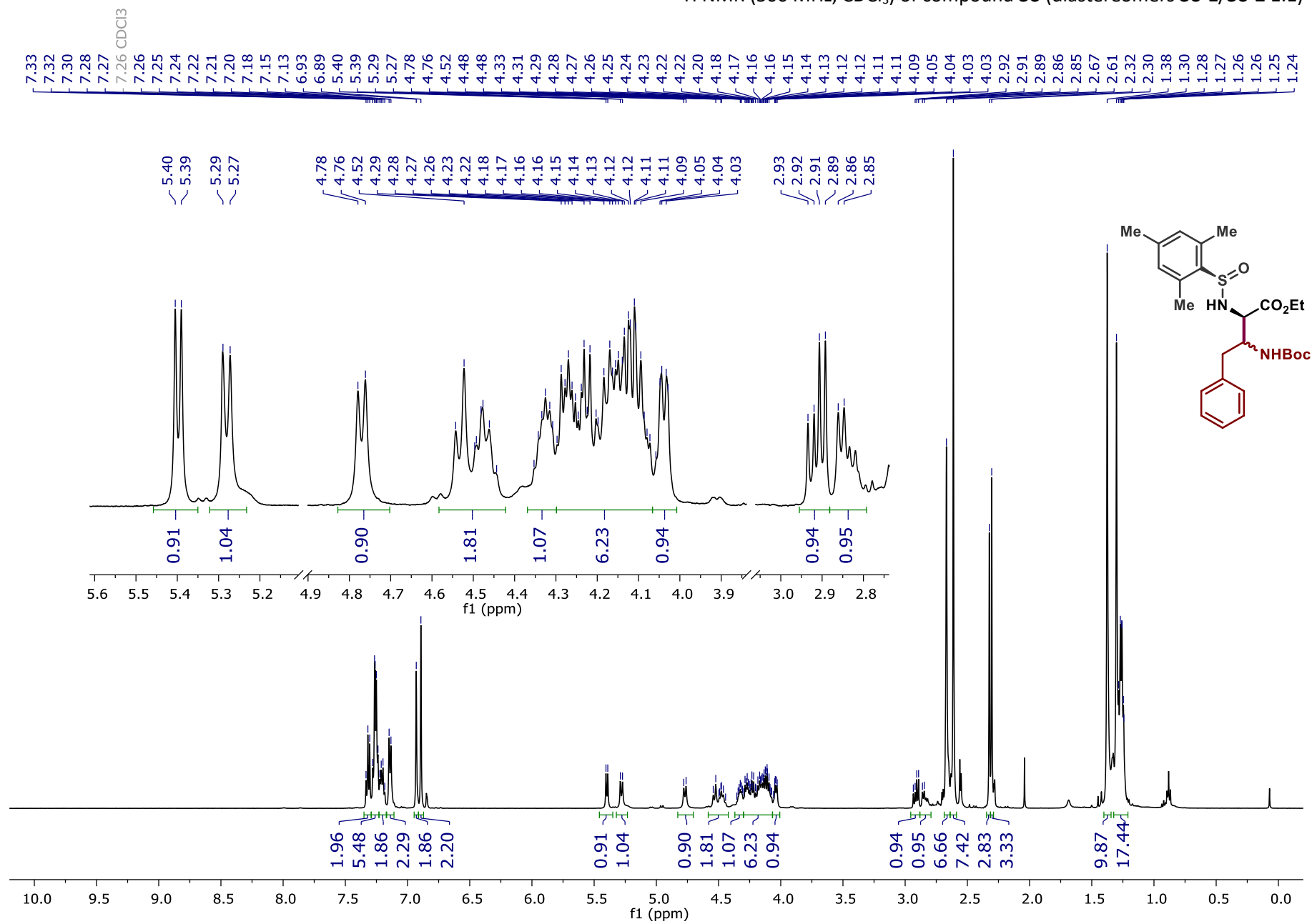


¹³C NMR (126 MHz, CDCl₃) of compound **3o** (diastereomer **3o-1**)

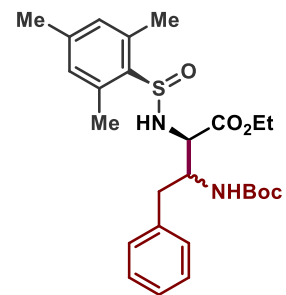
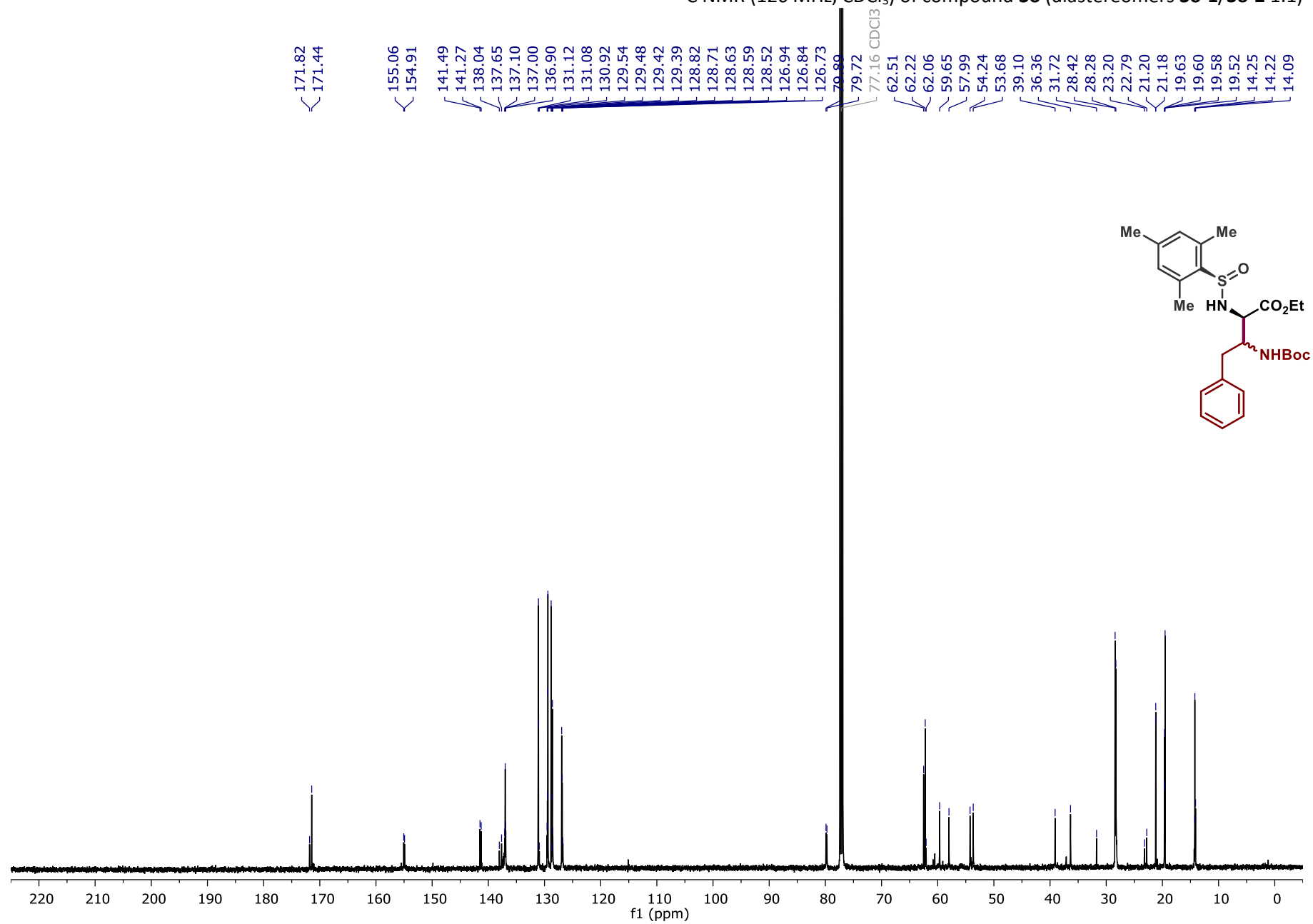


- 171.83
- 154.92
- 141.50
- 138.05
- 137.11
- 137.02
- 131.13
- 129.55
- 129.43
- 128.83
- 128.64
- 126.95
- 79.73
- 77.16 CDCl₃
- 62.52
- 58.00
- 54.25
- 39.12
- 28.38
- 28.29
- 21.22
- 19.64
- 19.61
- 14.10

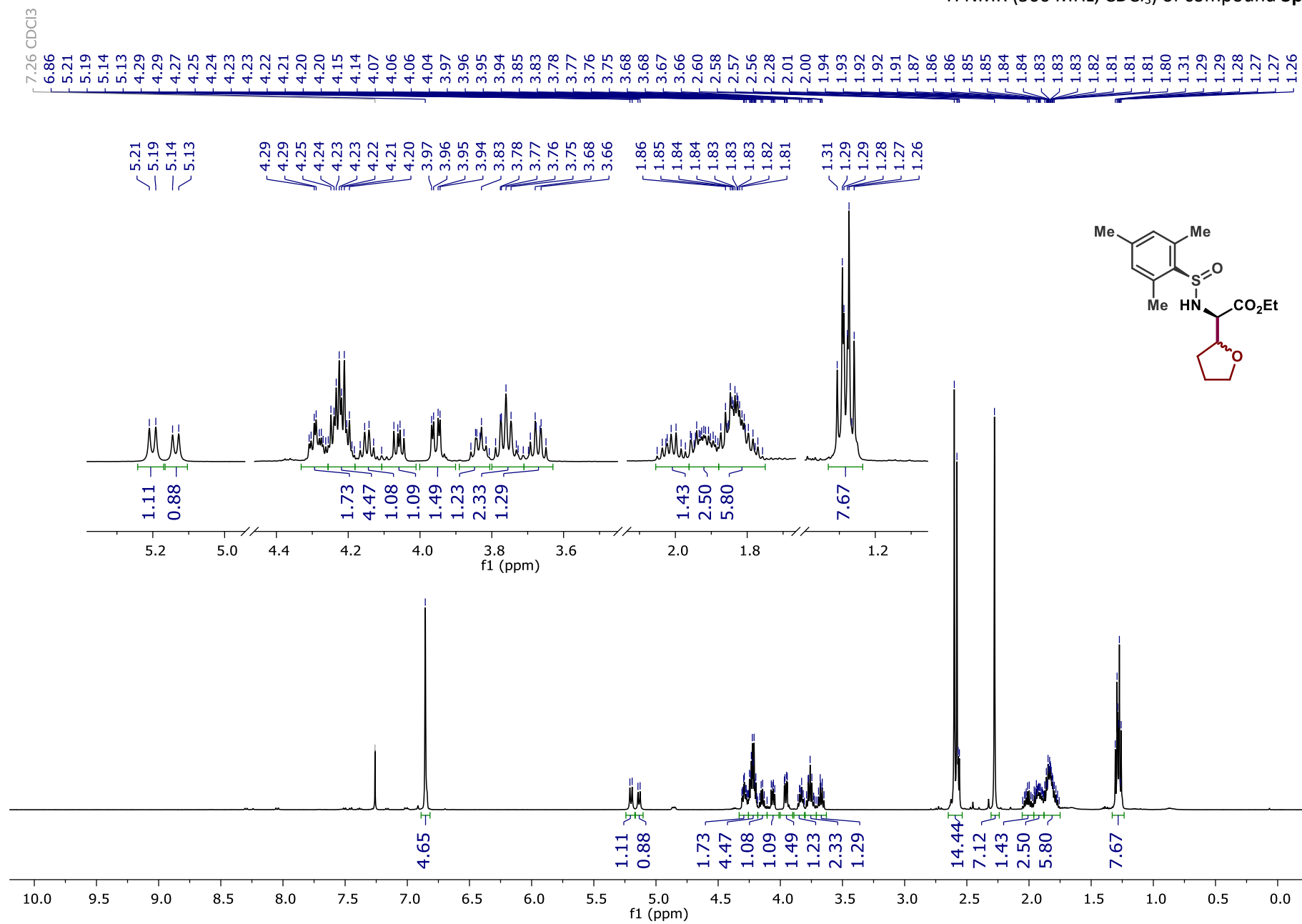
¹H NMR (500 MHz, CDCl₃) of compound **3o** (diastereomers **3o-1/3o-2** 1:1)



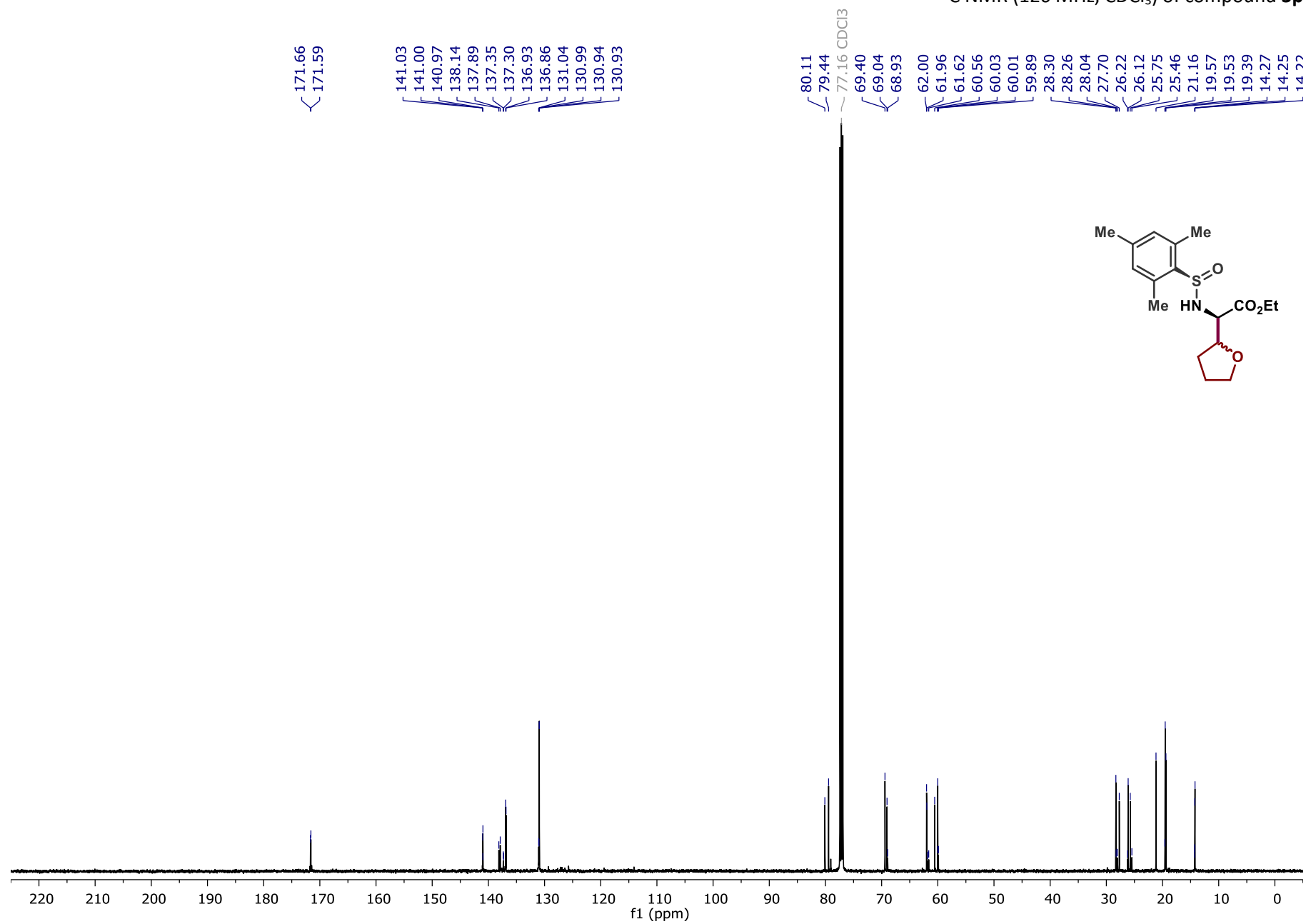
¹³C NMR (126 MHz, CDCl₃) of compound **3o** (diastereomers **3o-1/3o-2** 1:1)



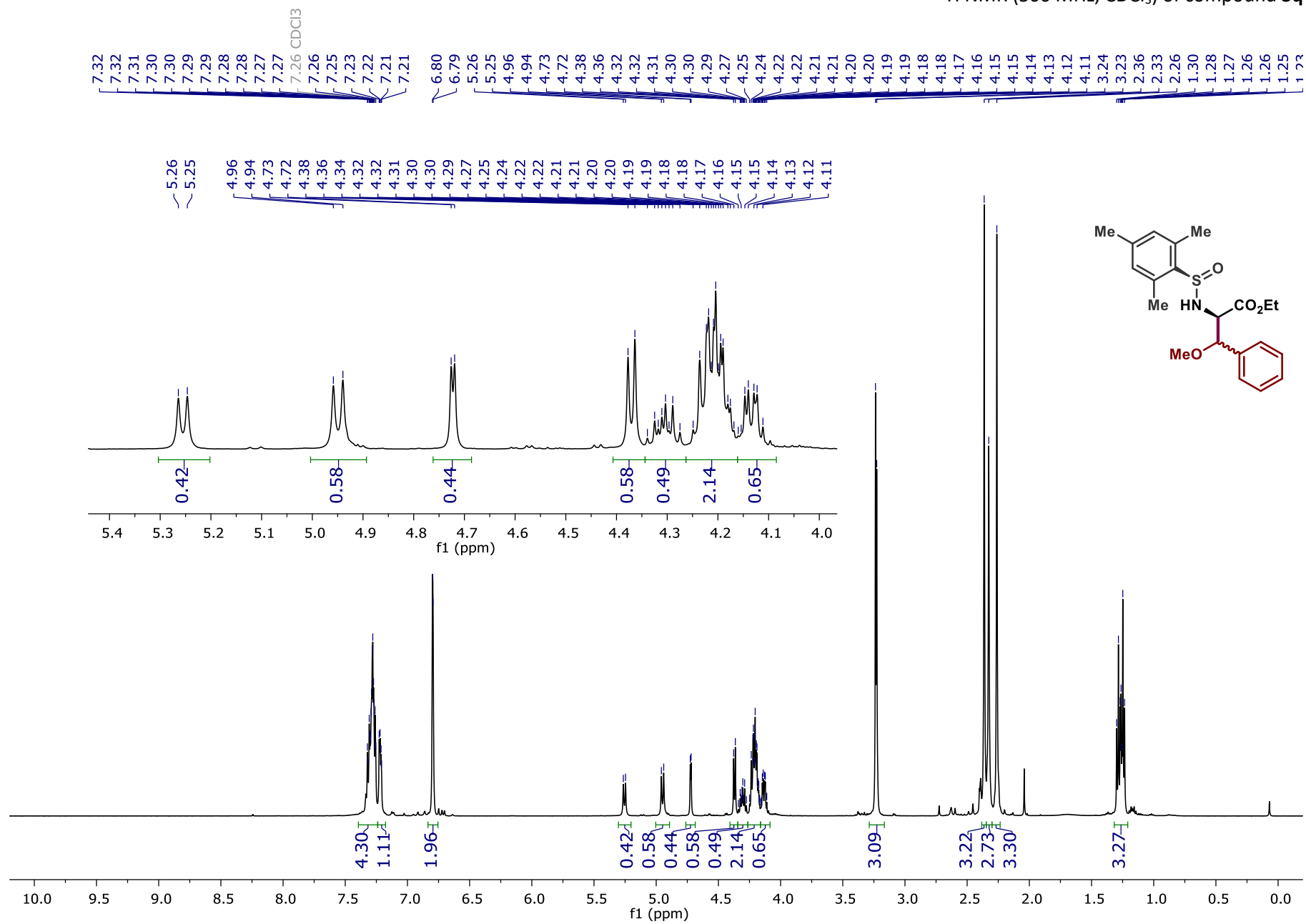
¹H NMR (500 MHz, CDCl₃) of compound **3p**



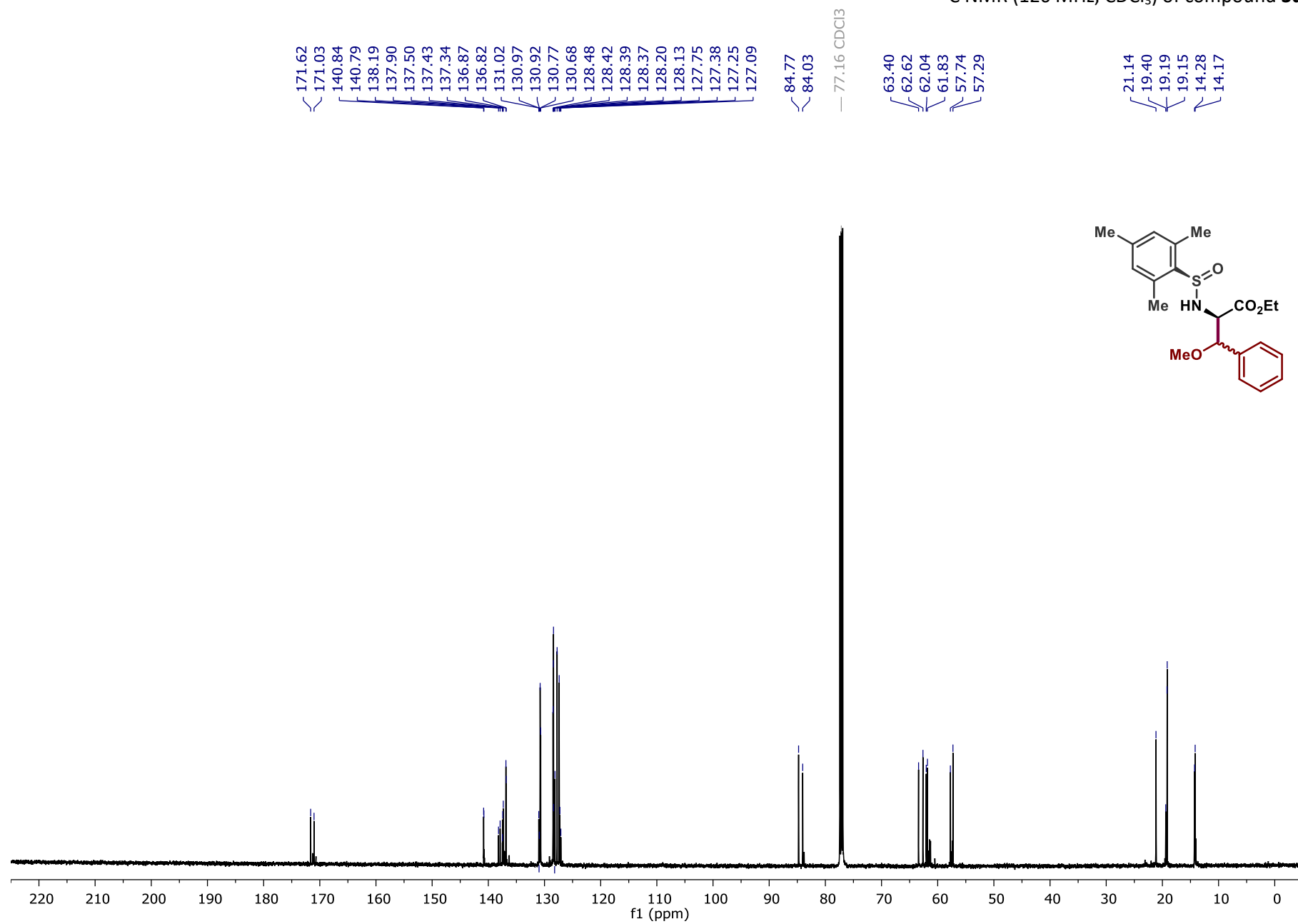
¹³C NMR (126 MHz, CDCl₃) of compound **3p**



¹H NMR (500 MHz, CDCl₃) of compound **3q**



¹³C NMR (126 MHz, CDCl₃) of compound **3q**



9. Cartesian coordinates and energies

The electronic energies (E) and the thermal correction to Gibbs free energy (ΔG_{corr}) were calculated at the M062X-D3/6-311+G(d,p)/SMD(chlorobenzene) level of theory. For *re*-TS and *si*-TS the single point electronic energies were also recalculated using the B3LYP-D3 functional (EB3LYP-D3) and the wB97XD (EwB97XD) level of theory including SMD solvation (chlorobenzene). The standard Gibbs free energy (ΔG°) is obtained by the following $\Delta G^\circ = E + \Delta G_{\text{corr}} + 0.0003027843$, where 0.003027843 is an entropic term to account for the change in standard state (1 atm \rightarrow 1 M). All energies are given in Hartree.

Tert-butyl radical

Charge: 0

Multiplicity: 2

$E = -157.749516456$

$\Delta G_{\text{corr}} = 0.088724$

$\Delta G^\circ = -157.6577646$

Cartesian coordinates:

C	0.0000000000	0.0000000000	-0.2013590000
C	0.0000000000	1.4774920000	0.0205060000
H	0.0000000000	1.7165170000	1.0971560000
H	0.8874690000	1.9509610000	-0.4087350000
H	-0.8874690000	1.9509610000	-0.4087350000
C	-1.2795450000	-0.7387460000	0.0205060000
H	-2.1333170000	-0.2069090000	-0.4087350000
H	-1.2458470000	-1.7440520000	-0.4087350000
H	-1.4865470000	-0.8582580000	1.0971560000
C	1.2795450000	-0.7387460000	0.0205060000
H	1.2458470000	-1.7440520000	-0.4087350000
H	2.1333170000	-0.2069090000	-0.4087350000
H	1.4865470000	-0.8582580000	1.0971560000

There are no imaginary frequencies

s-cis N-sulfinyl imine

Charge: 0

Multiplicity: 1

$E = -1184.08398538$

$\Delta G_{\text{corr}} = 0.232274$

$\Delta G^\circ = -1183.848684$

Cartesian coordinates

C	-2.1624280000	0.4487600000	1.2067980000
C	-3.1403390000	1.2882390000	0.6775820000
C	-3.5058870000	1.2296320000	-0.6657980000
C	-2.8525560000	0.3197290000	-1.4950850000
C	-1.8609550000	-0.5413120000	-1.0241760000
C	-1.5445580000	-0.4641320000	0.3398570000
H	-3.6242070000	2.0054480000	1.3332360000
H	-3.1130850000	0.2793320000	-2.5484920000
C	-1.7826680000	0.5675390000	2.6626210000
H	-1.9671630000	-0.3632410000	3.2048550000
H	-0.7243590000	0.8151750000	2.7797170000
H	-2.3682610000	1.3559950000	3.1353330000
H	-1.5151010000	-1.2455580000	-3.0079390000
H	-0.0977380000	-1.3741910000	-1.9586200000
H	-1.4135220000	-2.5163230000	-1.7694390000
C	-1.1843370000	-1.4745950000	-1.9945570000
C	-4.5941670000	2.1163370000	-1.2066300000
H	-4.4314810000	2.3396350000	-2.2622490000
H	-5.5654330000	1.6205480000	-1.1173480000
H	-4.6489580000	3.0554520000	-0.6537810000
S	-0.3304240000	-1.5639840000	1.1082310000
O	-0.2899470000	-2.8681730000	0.3761870000
N	1.0330460000	-0.5817560000	0.6538180000
C	1.9134400000	-1.1667450000	-0.0376430000

H	1.8337190000	-2.2039050000	-0.3749060000
C	3.1589300000	-0.4432200000	-0.4766270000
O	3.9528110000	-0.9673000000	-1.2157720000
H	5.3222680000	0.9588800000	-0.0668240000
H	4.4415610000	1.6141440000	-1.4576050000
O	3.2640330000	0.7748850000	0.0205100000
C	4.4382480000	1.5232970000	-0.3697830000
C	4.3612390000	2.8667060000	0.3118220000
H	5.2351970000	3.4605790000	0.0371670000
H	3.4643670000	3.4069120000	0.0039150000
H	4.3487030000	2.7504350000	1.3968860000

There are no imaginary frequencies

s-trans N-sulfinyl imine

Charge: 0

Multiplicity: 1

$E = -1184.07751$

$\Delta G_{\text{corr}} = 0.231867$

$\Delta G^\circ = -1183.842615$

Cartesian coordinates:

C	-2.2975130000	0.2486640000	-1.1277980000
C	-3.2860240000	-0.7122190000	-0.9061460000
C	-3.4953520000	-1.2675770000	0.3525860000
C	-2.6846620000	-0.8534980000	1.4122610000
C	-1.6845250000	0.1005550000	1.2512830000
C	-1.5121520000	0.6395760000	-0.0357530000
H	-3.9025450000	-1.0313800000	-1.7404910000
H	-2.8349530000	-1.2888420000	2.3960280000
C	-2.1043890000	0.8129290000	-2.5151800000
H	-2.2782290000	1.8915090000	-2.5377710000
H	-1.0932110000	0.6349910000	-2.8903090000

H	-2.8048860000	0.3442540000	-3.2061990000
H	-0.9746170000	-0.2202520000	3.2401920000
H	0.2125040000	0.5727830000	2.1888280000
H	-1.1474010000	1.4914850000	2.7982310000
C	-0.8482140000	0.5061110000	2.4367180000
C	-4.5696450000	-2.2952730000	0.5815800000
H	-4.1479020000	-3.2050680000	1.0157220000
H	-5.3190470000	-1.9161830000	1.2814250000
H	-5.0720070000	-2.5570000000	-0.3501770000
S	-0.2779050000	1.9145510000	-0.3460810000
O	-0.2760750000	2.8675760000	0.8028920000
N	1.1901250000	0.9778140000	-0.1616170000
C	1.2469590000	-0.1745110000	-0.6727210000
H	0.4184210000	-0.6959940000	-1.1616690000
C	2.5243860000	-0.9758450000	-0.6350610000
O	2.5786710000	-2.0710070000	-1.1347060000
H	4.5878660000	-2.0321770000	0.5676050000
H	5.0951750000	-1.3039640000	-0.9662830000
O	3.5156960000	-0.3638570000	-0.0186210000
C	4.7666990000	-1.0868180000	0.0519270000
C	5.7488440000	-0.2128590000	0.7912020000
H	6.7076940000	-0.7299430000	0.8628980000
H	5.9019020000	0.7302170000	0.2638560000
H	5.3940410000	0.0009370000	1.8008090000

There are no imaginary frequencies

s-cis N-sulfinyl imidoyl flouride

Charge: 0

Multiplicity: 1

$E = -1283.321846$

$\Delta G_{\text{corr}} = 0.221763$

$\Delta G^\circ = -1283.097055$

Cartesian coordinates:

C	-2.2426380000	0.4898420000	1.2051090000
C	-3.2410640000	1.2967790000	0.6618580000
C	-3.6095850000	1.2020790000	-0.6785580000
C	-2.9413600000	0.2878940000	-1.4922640000
C	-1.9333680000	-0.5435740000	-1.0055830000
C	-1.6132650000	-0.4277900000	0.3542420000
H	-3.7374750000	2.0178230000	1.3038270000
H	-3.2043010000	0.2212570000	-2.5438040000
C	-1.8577790000	0.6458770000	2.6558690000
H	-2.0300360000	-0.2742880000	3.2199110000
H	-0.8017510000	0.9071800000	2.7623990000
H	-2.4501450000	1.4379480000	3.1136700000
H	-1.5089410000	-1.2425840000	-2.9771630000
H	-0.1576260000	-1.4478630000	-1.8545110000
H	-1.5339430000	-2.5259510000	-1.7487630000
C	-1.2440730000	-1.4938240000	-1.9497710000
C	-4.7165900000	2.0549350000	-1.2358180000
H	-4.5365400000	2.2963930000	-2.2847280000
H	-5.6704790000	1.5222570000	-1.1772030000
H	-4.8195110000	2.9847270000	-0.6744470000
S	-0.3805400000	-1.5055690000	1.1230570000
O	-0.4600090000	-2.8501540000	0.4876570000
N	0.9542270000	-0.5527240000	0.5747190000
C	1.9645650000	-1.0006760000	-0.0050260000
C	3.1627160000	-0.1436830000	-0.3795620000
O	4.1059400000	-0.6016150000	-0.9614910000
H	5.0020230000	1.6234840000	0.1707900000
H	4.2413270000	2.0011960000	-1.3864020000
O	3.0071290000	1.1020630000	0.0089830000
C	4.0968150000	2.0054670000	-0.3046140000
C	3.7106470000	3.3674920000	0.2140060000
H	4.5127010000	4.0746560000	-0.0057750000

H	2.7963050000	3.7200200000	-0.2660120000
H	3.5572640000	3.3424950000	1.2941190000
F	2.1461760000	-2.2608690000	-0.3842660000

There are no imaginary frequencies

s-trans N-sulfinyl imidoyl fluoride

Charge: 0

Multiplicity: 1

$E = -1283.324329$

$\Delta G_{\text{corr}} = 0.223275$

$\Delta G^\circ = -1283.098026$

Cartesian coordinates:

C	-2.4220750000	0.8177370000	-0.5396040000
C	-3.3395300000	-0.0973460000	-1.0601150000
C	-3.4151280000	-1.4048340000	-0.5911640000
C	-2.5522350000	-1.8012560000	0.4335140000
C	-1.6172790000	-0.9355020000	0.9920220000
C	-1.5616090000	0.3694290000	0.4707480000
H	-4.0102450000	0.2278040000	-1.8489680000
H	-2.6109620000	-2.8175330000	0.8124440000
C	-2.4047500000	2.2317800000	-1.0676150000
H	-2.6174250000	2.9547270000	-0.2760250000
H	-1.4399020000	2.4933700000	-1.5060720000
H	-3.1673000000	2.3456180000	-1.8379380000
H	-0.8219090000	-2.5034410000	2.2046560000
H	0.3034320000	-1.1528880000	1.9753180000
H	-1.0579820000	-0.9688070000	3.0641860000
C	-0.7438920000	-1.4192640000	2.1207090000
C	-4.4098910000	-2.3797250000	-1.1591140000
H	-3.9048350000	-3.2765700000	-1.5261960000
H	-5.1193210000	-2.6959670000	-0.3898660000

H	-4.9709860000	-1.9373640000	-1.9827580000
S	-0.4108980000	1.5872510000	1.1372760000
O	-0.4258390000	1.5048040000	2.6226100000
N	1.0619980000	0.7502600000	0.6674210000
C	1.3984840000	0.7508830000	-0.5329990000
C	2.6774140000	0.1401740000	-1.0748850000
O	2.9466230000	0.1768860000	-2.2425940000
H	4.4080330000	-1.8020510000	-1.2488090000
H	5.2513000000	-0.2594880000	-1.0102530000
O	3.3913640000	-0.4020870000	-0.1156250000
C	4.6389470000	-1.0202890000	-0.5230870000
C	5.2916970000	-1.5692750000	0.7200170000
H	6.2362020000	-2.0441450000	0.4478090000
H	5.4981630000	-0.7709840000	1.4346860000
H	4.6534850000	-2.3153330000	1.1962820000
F	0.6636140000	1.2825900000	-1.5136160000

There are no imaginary frequencies

re-TS

Charge: 0

Multiplicity: 2

E = -1341.84503847

EB3LYP-D3: -1342.351768

EwB97XD: -1341.967714

ΔG_{corr} = 0.345723

ΔG° = -1341.496288

Cartesian coordinates:

C	-3.0526770000	-0.7656440000	0.9979450000
C	-4.2429540000	-0.0362660000	0.9545970000
C	-4.4986750000	0.8874680000	-0.0536800000

C	-3.5283870000	1.0871730000	-1.0372640000
C	-2.3208570000	0.3946730000	-1.0391360000
C	-2.1057440000	-0.5346360000	-0.0075360000
H	-4.9865890000	-0.2030280000	1.7275690000
H	-3.7163750000	1.8067900000	-1.8292220000
C	-2.8362690000	-1.7585090000	2.1153970000
H	-2.6962880000	-2.7722580000	1.7326450000
H	-1.9563630000	-1.5066030000	2.7115980000
H	-3.7030230000	-1.7650710000	2.7765090000
H	-1.7941460000	1.1802640000	-2.9574580000
H	-0.5439520000	1.3838210000	-1.7277320000
H	-0.8027970000	-0.2037860000	-2.4608830000
C	-1.3051470000	0.6972610000	-2.1107310000
C	-5.7919500000	1.6555050000	-0.0993650000
H	-5.6028530000	2.7316630000	-0.1170480000
H	-6.3543230000	1.4073060000	-1.0034220000
H	-6.4171140000	1.4294220000	0.7651650000
S	-0.6163530000	-1.5610560000	0.0611310000
O	-0.4154320000	-2.2116260000	-1.2834130000
N	0.4870910000	-0.2724880000	0.2811660000
C	1.4668080000	-0.2257530000	-0.5754920000
H	1.4658300000	-0.8229700000	-1.4891210000
C	2.3015120000	1.0154180000	-0.6458480000
O	2.9949820000	1.2719880000	-1.6018410000
H	4.0342890000	2.7079490000	0.2986520000
H	2.6900010000	3.6124130000	-0.4143980000
O	2.1846730000	1.7908880000	0.4232020000
C	2.9868250000	2.9886130000	0.4311700000
C	2.7508670000	3.6764830000	1.7536540000
H	3.3403190000	4.5945040000	1.7962920000
H	1.6972180000	3.9348540000	1.8729960000
H	3.0508950000	3.0328690000	2.5828720000
C	3.1946490000	-1.5027530000	0.1660110000

C	2.4001080000	-2.6271690000	0.7480830000
H	1.7885530000	-2.2949150000	1.5905080000
H	1.7673600000	-3.1097590000	-0.0009600000
H	3.0965830000	-3.3871560000	1.1295930000
C	3.9028310000	-0.6326880000	1.1574370000
H	4.4359200000	0.1928990000	0.6792410000
H	3.2159060000	-0.2363640000	1.9092300000
H	4.6512770000	-1.2430680000	1.6829880000
C	3.9054270000	-1.7832990000	-1.1193810000
H	3.2775420000	-2.3449270000	-1.8148970000
H	4.2509380000	-0.8677440000	-1.6035130000
H	4.7912030000	-2.3980510000	-0.9022160000

1 imaginary frequency: -280.15 cm^{-1}

si-TS

Charge: 0

Multiplicity: 2

$E = -1341.83971014$

EB3LYP-D3: -1342.346615

EwB97XD: -1341.963109

$\Delta G_{\text{corr}} = 0.346454$

$\Delta G^\circ = -1341.490228$

Cartesian coordinates:

C	2.2592250000	1.2987110000	-0.7795730000
C	3.2973770000	1.8187320000	-0.0124400000
C	4.0587860000	1.0147330000	0.8341920000
C	3.7657560000	-0.3430560000	0.8910750000
C	2.7337290000	-0.9269700000	0.1472110000
C	1.9773250000	-0.0762380000	-0.6723240000
H	3.5200810000	2.8792570000	-0.0860950000

H	4.3602470000	-0.9842270000	1.5346900000
C	1.4852700000	2.2261730000	-1.6840060000
H	1.4097880000	1.8318540000	-2.7008110000
H	0.4676920000	2.3724510000	-1.3170250000
H	1.9832770000	3.1946130000	-1.7327460000
H	3.2726980000	-2.8115070000	0.9836250000
H	1.5339420000	-2.6386790000	0.7121860000
H	2.5896190000	-2.9370540000	-0.6505110000
C	2.5193910000	-2.4140340000	0.3025280000
C	5.1645250000	1.6103350000	1.6631620000
H	5.8051310000	2.2529850000	1.0550910000
H	4.7514400000	2.2258430000	2.4672990000
H	5.7821010000	0.8330520000	2.1148810000
S	0.6534450000	-0.6723080000	-1.7719670000
O	0.5579600000	-2.1695120000	-1.7012620000
N	-0.6377580000	0.0763370000	-0.9521590000
C	-1.7374320000	-0.6243640000	-0.8176570000
H	-1.8661930000	-1.6070460000	-1.2727160000
C	-3.0146480000	0.1336630000	-0.6255800000
O	-4.0795870000	-0.2883460000	-1.0057760000
H	-4.4695940000	2.3456730000	-0.7342570000
H	-4.7599230000	1.4513010000	0.7653330000
O	-2.8454890000	1.2950590000	-0.0040000000
C	-4.0373450000	2.0717370000	0.2303230000
C	-3.6296460000	3.2829820000	1.0333040000
H	-4.5072710000	3.9014190000	1.2314350000
H	-3.1940380000	2.9833700000	1.9887220000
H	-2.8989390000	3.8822070000	0.4871140000
C	-1.7677080000	-1.5152720000	1.2206260000
C	-0.6998640000	-0.6914510000	1.8684250000
H	-0.9646790000	0.3683290000	1.8802800000
H	-0.5875900000	-1.0256350000	2.9092370000
H	0.2655090000	-0.8048380000	1.3733420000

C	-1.4120760000	-2.9258480000	0.8589220000
H	-1.1830160000	-3.4753820000	1.7834820000
H	-2.2463400000	-3.4346590000	0.3696180000
H	-0.5392200000	-2.9726700000	0.2058340000
C	-3.1457800000	-1.3361180000	1.7849040000
H	-3.3837590000	-0.2883070000	1.9822170000
H	-3.9160370000	-1.7747520000	1.1478590000
H	-3.1801030000	-1.8649320000	2.7482530000

1 imaginary frequency: -359.06 cm^{-1}

R,R-radical adduct

Charge: 0

Multiplicity: 2

$E = -1341.87530755$

$\Delta G_{\text{corr}} = 0.350074$

$\Delta G^\circ = -1341.522206$

Cartesian coordinates:

C	-2.9584870000	-1.1819600000	0.6447990000
C	-4.1476940000	-0.4578970000	0.7313810000
C	-4.3178000000	0.7546330000	0.0661930000
C	-3.2628710000	1.2553540000	-0.6976790000
C	-2.0495730000	0.5806500000	-0.8119170000
C	-1.9277610000	-0.6352890000	-0.1271610000
H	-4.9607700000	-0.8568720000	1.3297540000
H	-3.3840260000	2.2006520000	-1.2184740000
C	-2.8215840000	-2.4969100000	1.3708410000
H	-2.5910320000	-3.3130030000	0.6812900000
H	-2.0256400000	-2.4589000000	2.1182740000
H	-3.7539110000	-2.7407240000	1.8798820000
H	-1.3288190000	1.8828410000	-2.3514210000
H	-0.2708900000	1.7575130000	-0.9429110000

H	-0.3346960000	0.4374660000	-2.1305120000
C	-0.9282780000	1.1913650000	-1.6092720000
C	-5.6228870000	1.4991180000	0.1436820000
H	-5.4593190000	2.5781930000	0.1514100000
H	-6.2442830000	1.2649970000	-0.7258340000
H	-6.1820920000	1.2228780000	1.0386280000
S	-0.4253270000	-1.6302360000	-0.2927490000
O	-0.2304730000	-2.0037580000	-1.7325620000
N	0.6595340000	-0.5459660000	0.2953050000
C	1.9164390000	-0.4485570000	-0.4135060000
H	1.8513370000	-0.8503370000	-1.4310890000
C	2.2869480000	1.0256300000	-0.5663990000
O	2.9117350000	1.4408090000	-1.5090090000
H	3.2819770000	3.2917390000	0.3703750000
H	1.8188500000	3.5800970000	-0.5839250000
O	1.8680080000	1.7836280000	0.4399240000
C	2.1948770000	3.1870000000	0.3630540000
C	1.5514700000	3.8607220000	1.5504970000
H	1.7734630000	4.9294260000	1.5267150000
H	0.4677930000	3.7305540000	1.5271280000
H	1.9342840000	3.4476330000	2.4854470000
C	3.0606870000	-1.2356960000	0.3293420000
C	2.6030200000	-2.6880990000	0.4946740000
H	1.7814990000	-2.7719310000	1.2105720000
H	2.2828250000	-3.1155420000	-0.4608870000
H	3.4336060000	-3.2900480000	0.8719550000
C	3.3492900000	-0.6251300000	1.7017830000
H	3.7936200000	0.3700810000	1.6154630000
H	2.4380070000	-0.5439010000	2.2985580000
H	4.0581340000	-1.2620360000	2.2382790000
C	4.3209210000	-1.2058510000	-0.5389550000
H	4.1321540000	-1.6416420000	-1.5241030000
H	4.6973750000	-0.1911980000	-0.6811690000

H 5.1045820000 -1.7923290000 -0.0515210000

There are no imaginary frequencies

R,S-radical adduct

Charge: 0

Multiplicity: 2

$E = -1341.87038932$

$\Delta G_{\text{corr}} = 0.348572$

$\Delta G^\circ = -1341.518789$

Cartesian coordinates:

C	-2.7116400000	1.1329250000	0.7767620000
C	-3.9289100000	1.3931340000	0.1444600000
C	-4.4945370000	0.4938880000	-0.7546320000
C	-3.8141660000	-0.6932990000	-1.0357990000
C	-2.5944380000	-1.0021390000	-0.4423170000
C	-2.0699330000	-0.0686110000	0.4628800000
H	-4.4448910000	2.3213010000	0.3682600000
H	-4.2430110000	-1.3991080000	-1.7410850000
C	-2.1369050000	2.1361260000	1.7448150000
H	-2.0328190000	1.7123150000	2.7470010000
H	-1.1497360000	2.4776810000	1.4240090000
H	-2.7917010000	3.0047150000	1.8123320000
H	-2.5028970000	-2.8987730000	-1.4309800000
H	-0.9607850000	-2.0352950000	-1.3596670000
H	-1.5862640000	-2.8323590000	0.0881910000
C	-1.8722900000	-2.2698700000	-0.8026120000
C	-5.8124690000	0.7837530000	-1.4197570000
H	-5.7001330000	0.7977400000	-2.5068140000
H	-6.5443840000	0.0093430000	-1.1765940000
H	-6.2122810000	1.7472460000	-1.1021660000
S	-0.5357760000	-0.4040270000	1.3384410000

O	-0.6021150000	-1.7243700000	2.0419110000
N	0.5576240000	-0.2059760000	0.1840630000
C	1.9234330000	-0.5950510000	0.5183410000
H	2.0013740000	-1.0694190000	1.5021960000
C	2.7760370000	0.6701600000	0.6149110000
O	3.4767210000	0.9147920000	1.5645750000
H	3.1773890000	3.2539900000	0.4317570000
H	4.5134560000	2.3875560000	-0.3425480000
O	2.6707180000	1.4545110000	-0.4512930000
C	3.4608650000	2.6617590000	-0.4405120000
C	3.1839510000	3.3904070000	-1.7329360000
H	3.7624970000	4.3159770000	-1.7594260000
H	3.4694160000	2.7799360000	-2.5917430000
H	2.1249250000	3.6409960000	-1.8163780000
C	2.4966170000	-1.6162680000	-0.5177400000
C	2.1625790000	-1.2245620000	-1.9588760000
H	2.5682240000	-0.2449970000	-2.2162460000
H	2.5932340000	-1.9653960000	-2.6385260000
H	1.0831620000	-1.1973060000	-2.1224040000
C	1.8803890000	-2.9812990000	-0.1960710000
H	2.2143800000	-3.7216250000	-0.9282810000
H	2.1821740000	-3.3219030000	0.7983670000
H	0.7895690000	-2.9418870000	-0.2215800000
C	4.0158060000	-1.6949270000	-0.3380250000
H	4.5101850000	-0.7675870000	-0.6441890000
H	4.2849210000	-1.9006700000	0.7020190000
H	4.4141110000	-2.5024090000	-0.9579050000

There are no imaginary frequencies

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