

Supporting Information

Nickel(II)-Catalyzed Synthesis of Sulfinates from Aryl and Heteroaryl Boronic Acids and the Sulfur Dioxide Surrogate DABSO

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1. General Information

Reactions were performed under inert nitrogen atmosphere with anhydrous solvent unless otherwise stated. Reagents were purchased from Sigma-Aldrich, Fisher Scientific, Fluorochem, Tokyo Chemical Industry UK or Strem Chemicals and were used as supplied unless otherwise stated. Other solvents, if stated as anhydrous, were collected fresh from an in-house solvent purification system, which involves passing the solvent through anhydrous alumina columns. Glassware was oven-dried, and allowed to cool to room temperature under nitrogen. Cooling to 0 °C was achieved using ice-water bath. Reactions were monitored by HPLC analysis and/or thin layer chromatography (TLC) using pre-coated aluminum-backed silica plates (Merck Kieselgel 60 F254). Plates were visualised under ultraviolet light (254 nm) followed by staining with KMnO₄. Flash column chromatography was carried out using Geduran® Si 60, 40-63 micron silica gel; the compound to be purified was either loaded as oil or pre-absorbed onto silica. Petrol refers to the fraction of light Petroleum ether boiling in the range 40-60 °C.

¹H NMR spectra were obtained on a Brüker AVIII HD 400 (400 MHz), AVII 500 (500 MHz) or AVIII HD 500 (500 MHz) spectrometer using the residual solvent as an internal standard. ¹³C NMR spectra were obtained on a Brüker AVIII HD 400 (101 MHz), AVII 500 (126 MHz) or AVIII HD 500 (126 MHz) spectrometer using the ¹H decoupling method and the residual solvent as an internal standard. ¹⁹F NMR spectra were obtained on a Brüker AVIII HD 400 (377 MHz) spectrometer using the ¹H decoupling method. Acquisitions were carried out at room temperature unless otherwise stated. Chemical shifts (δ) are reported in parts per million (ppm) from the residual solvent peak and coupling constants (J) were given in Hertz (Hz) and rounded to the nearest 0.5 Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (p), multiplet (m), broad (br), apparent (app.).

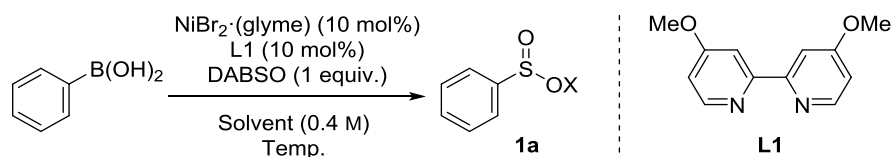
Low resolution ESI mass spectra were recorded on a Waters LCT Premier spectrometer. High resolution mass spectra were recorded either on a Brüker MicroTOF spectrometer under electrospray ionization conditions (ESI) or on a Waters LCT Premier spectrometer under the conditions of chemical ionization (CI) by the internal service at Chemistry Research Laboratory, University of Oxford. Samples for mass spectra were prepared as 1 mg/mL solution in MeOH (LRMS, HRMS-ESI) or submitted neat (HRMS-CI). Values quoted are a ratio of mass to charge in Daltons. High resolution values are calculated to four decimal places from the molecular formula, all found within a tolerance of five ppm.

Infrared spectra were recorded on a Brüker Tensor 27 FT-IR spectrometer. Melting points were determined using a Stuart Scientific Melting Point Apparatus SMP1.

Optical rotations were measured on a Schmidt Haensch UniPol L2000 polarimeter at 589 nm, 25 °C. $[\alpha]_D^{25}$ is expressed in deg cm³ g⁻¹ dm⁻¹ and c is expressed in g/100 cm³. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC in a Dionex P680 chromatograph with a Dionex UVD170U detector (Daicel Chiralpak IC column).

2. Optimization of Conditions

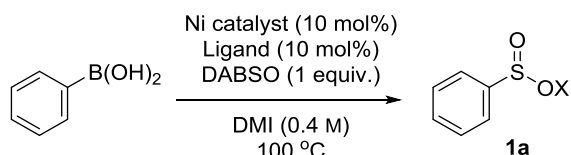
Table S1. Solvent Screening



Entry	Solvent	Temperature ($^{\circ}\text{C}$)	Yield of 1a (%)	Boronic acid conversion (%)
1	Dioxane	80	0	0
2	Dioxane	100	Trace	Trace
3	DMA	100	Trace	Trace
4	NMP	100	0	0
5	DMF	100	0	0
6	DMSO	100	Trace	Trace
7	Sulfolane	100	Trace	Trace
8	IPA	100	0	0
9	DMI	100	Trace	27
10	DMPU	100	Trace	25
11	Nitrobenzene	100	0	0
12	Benzonitrile	100	Trace	Trace
13	Nitromethane	100	0	0

Reaction conditions: Phenylboronic acid (0.20 mmol, 1.0 equiv.), DABSO (0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (0.02 mmol, 10 mol%), L1 (0.02 mmol, 10 mol%), solvent (0.5 mL, 0.4 M). Yields of **1a** and boronic acid conversion were calculated from HPLC analysis using acetophenone as an internal standard.

Table S2. Nickel Catalyst and Ligand Screening



Entry	Ni catalyst	Ligand	Yield of 1a (%)	Boronic acid conversion (%)
1	NiBr ₂ ·(glyme)	L1	Trace	27
2	NiBr ₂ ·(glyme)	L1 (20 mol%)	Trace	18
3	NiBr ₂ ·(glyme)	-	Trace	Trace
4	(TMEDA)Ni(<i>o</i> -tolyl)Cl	-	0	0
5	NiBr ₂ ·(diglyme)	L1	Trace	8
6	Ni(acac) ₂	-	0	0
7	Ni(acac) ₂	L1	0	0
8	Ni(dppe)Cl ₂	-	0	0
9	NiBr ₂ ·(glyme)	L2	Trace	Trace
10	NiBr ₂ ·(glyme)	L3	0	0
11	NiBr ₂ ·(glyme)	L4	Trace	Trace
12	NiBr ₂ ·(glyme)	L5	Trace	15
13	NiBr ₂ ·(glyme)	L6	Trace	10
14	NiBr ₂ ·(glyme)	L7	Trace	Trace
15	NiBr ₂ ·(glyme)	L8	Trace	Trace
16	NiBr ₂ ·(glyme)	L9	0	0
17	NiBr ₂ ·(glyme)	L10	Trace	18
18	NiBr₂·(glyme)	L11	Trace	37
19	NiBr ₂ ·(glyme)	L12	Trace	Trace
20	NiBr ₂ ·(glyme)	L13	Trace	27

Reaction conditions: Phenylboronic acid (0.20 mmol, 1.0 equiv.), nickel catalyst (10 mol%), ligand (10 mol%), DABSO (0.20 mmol, 1.0 equiv.), DMI (0.5 mL, 0.4 M), 100 °C. Yields of **1a** and boronic acid conversion were calculated from HPLC analysis using acetophenone as an internal standard.

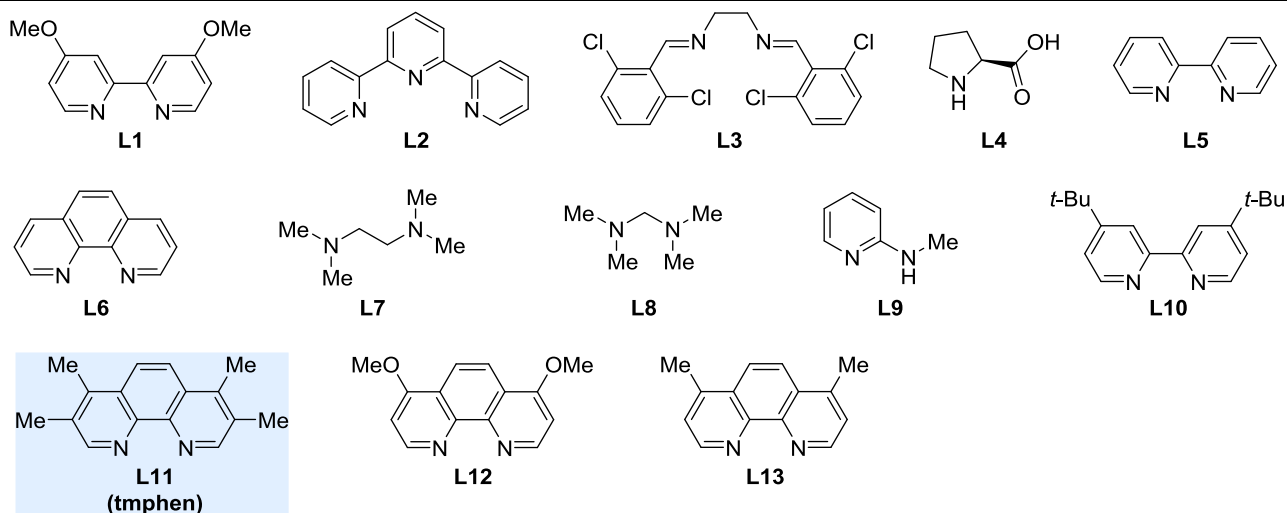
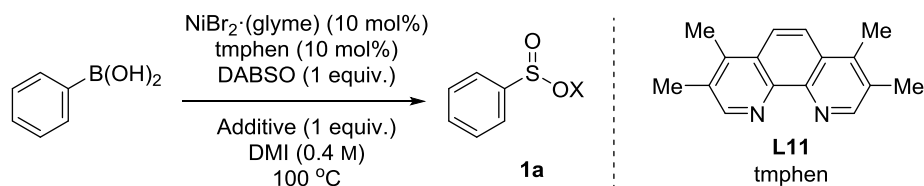
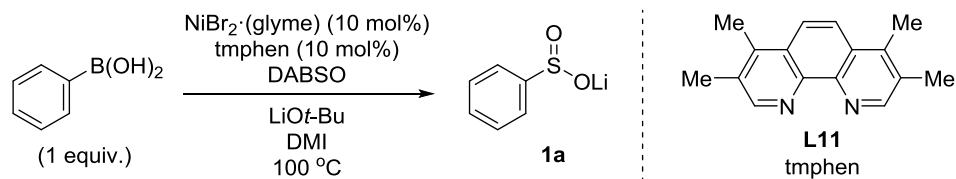


Table S3. Additive Screening

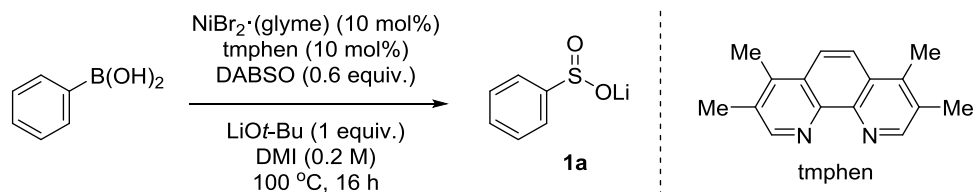
Entry	Additive	Yield of 1a (%)	Boronic acid conversion (%)
1	-	Trace	37
2	Et_3N	Trace	Trace
3	K_3PO_4	Trace	Trace
4	AcOH	0	0
5	NaBF_4	0	0
6	DBU	0	0
7	K_2CO_3	13	66
8	Li_2CO_3	33	71
9	NaOH	34	34
10	$\text{LiOH} \cdot \text{H}_2\text{O}$	54	83
11	$\text{KO}t\text{-Bu}$	64	66
12	$\text{LiO}t\text{-Bu}$	78	83
13	$\text{NaO}t\text{-Bu}$	36	39
14	LiOMe	46	70

Reaction conditions: Phenylboronic acid (0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (10 mol%), *tmphen* (10 mol%), additive (0.20 mmol, 1.0 equiv.), DABSO (0.20 mmol, 1.0 equiv.), DMI (0.5 mL, 0.4 M), 100 °C. Yields of **1a** and boronic acid conversion were calculated from HPLC analysis using acetophenone as an internal standard.

Table S4. Loading of DABSO, LiOt-Bu and Concentration Screening.

Entry	DABSO (equiv.)	LiOt-Bu (equiv.)	Concentration (M)	Yield of 1a (%)
1	1.0	1.0	0.4	78
2	2.0	1.0	0.4	0
3	1.0	2.0	0.4	67
4	1.0	1.5	0.4	68
5	1.0	0.5	0.4	39
6	1.0	1.0	1.0	Trace
7	1.0	1.0	0.2	90
8	0.6	1.0	0.2	91
9 ^a	0.6	1.0	0.2	0

^a Under air atmosphere. Yields of **1a** and boronic acid conversion were calculated from HPLC analysis using acetophenone as an internal standard.

Table S5. Variations of the optimized conditions.

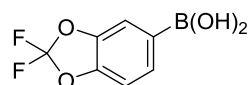
Entry	Variations	Yield of 1a (%)
1	-	91
2	No [Ni] / <i>tmphen</i>	0
3	No <i>tmphen</i>	Trace
4	No LiOt-Bu	0
5	90 °C	31
6	DMSO as solvent instead of DMI	0
7	1.0 equiv. DABSO	90
8	2.0 equiv. LiOt-Bu	68
9	20 mol% <i>tmphen</i>	28
10	0.4 M DMI	78
11	1.0 equiv. $\text{K}_2\text{S}_2\text{O}_5$ instead of DABSO	0
12	1.0 equiv. PhBF_3K instead of PhB(OH)_2	0

Reaction conditions: Phenylboronic acid (0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (10 mol%), *tmphen* (10 mol%), DABSO (0.12 mmol, 0.6 equiv.), LiOt-Bu (0.20 mmol, 1.0 equiv.), DMI (1.0 ml, 0.2 M), 100 °C, 16 h. Yields of **1a** and boronic acid conversion were calculated from HPLC analysis using acetophenone as an internal standard.

3. Experimental Procedures

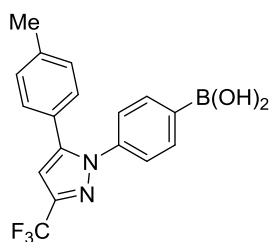
3.1 Preparation of aryl boronic acids

Preparation of (2,2-difluorobenzo[d][1,3]dioxol-5-yl)boronic acid



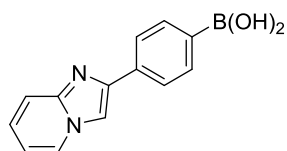
The title boronic acid was prepared using a literature method.¹

Preparation of (4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)boronic acid



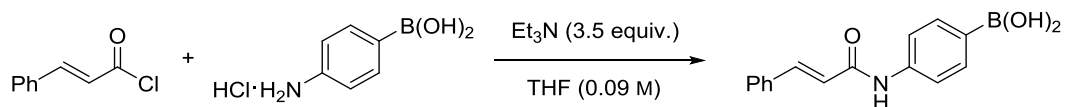
The title boronic acid was prepared using a modified literature method.² The trituration was done with pentane instead of EtOAc.

Preparation of (4-(imidazo[1,2-*a*]pyridin-2-yl)phenyl)boronic acid



The title boronic acid was prepared using a literature method.³

Synthesis of (4-cinnamamidophenyl)boronic acid



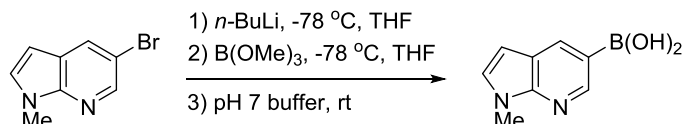
In a 50 mL round bottom flask, 4-aminophenylboronic acid hydrochloride (173 mg, 1.0 mmol, 1.0 equiv.) in THF (10 mL) was added Et₃N (0.49 mL, 3.5 mmol, 3.5 equiv.) (*note 1*). With stirring, cinnamoyl chloride (167 mg, 1.0 mmol, 1.0 equiv.) in THF (1 mL) was added dropwise to the mixture. The mixture was stirred at rt overnight. With stirring and/or sonication, the mixture was acidified to pH 2-3 with conc. HCl (ca. 11-12 drops). All volatiles were removed under reduced pressure. To the resultant solid was added CH₂Cl₂ and H₂O (ca. 10 mL each). The mixture was sonicated until the solid became free-flowing. The solid was filtered under vacuum, washed with CH₂Cl₂ and a small amount of Et₂O, and further dried under suction to afford the product as an off-white solid (84 mg, 31%) (*note 2*).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.22 (s, 1H), 7.91 (s, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.55 (m, 5H), 7.48 – 7.39 (m, 3H), 6.85 (d, *J* = 15.5 Hz, 1H); **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 163.6, 140.9, 140.3, 134.9, 134.7, 129.8, 129.0, 128.7, 127.7, 122.3, 118.0; **LRMS** (ESI⁺) *m/z* 535.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₁₅H₁₅O₃NB⁺ requires 268.1140 [M+H]⁺, found 268.1141; **IR** (thin film, ν_{max}/cm⁻¹) 3293, 2360, 1660, 1344; **m.p.** (Et₂O): 173-175 °C.

Note:

1. 4-Aminophenylboronic acid hydrochloride was purchased from Carbosynth (CAS No: 80460-73-7; Product Code: FA33740). It was quite insoluble in THF. All solvent used in this reaction was not dried.
2. The desired product is very soluble in THF, modest soluble in acetone, MeOH and EtOAc, slightly soluble in Et₂O, and almost insoluble in CH₂Cl₂.

Synthesis of (1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)boronic acid^{2, 4}

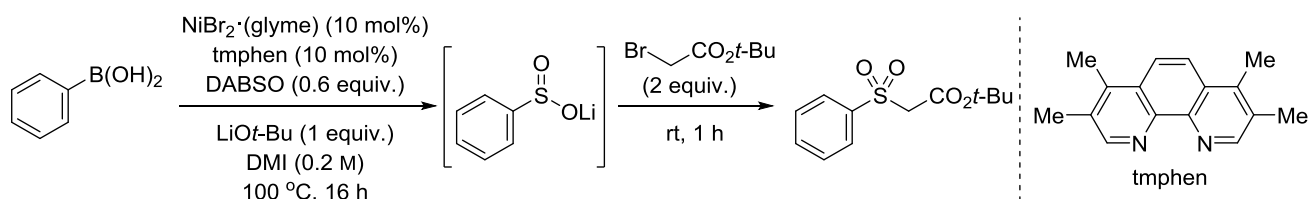


5-bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine⁵ (307 mg, 1.45 mmol, 1.0 equiv.) was dissolved in anhydrous THF (9 mL) and cooled to -78 °C. *n*-BuLi (0.73 mL of a 2.2 M solution in hexane, 1.61 mmol, 1.1 equiv.) was added dropwise. The resulting solution was stirred at -78 °C for 1.5 h. B(OMe)₃ (0.25 mL, 2.24 mmol, 1.5 equiv.) was added dropwise, before the solution was warmed to rt and stirred at this temperature for 1.5 h. pH 7 buffer solution (9 mL) was then added and the mixture was stirred at rt for 2 h. The mixture was partitioned between water and EtOAc. The aqueous phase was extracted with EtOAc (× 2). The combined organic phases were washed with water and brine, dried (Na₂SO₄) and concentrated. The resultant solid was triturated with Et₂O to afford the product as a pale yellow solid (95 mg, 37%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.63 (d, *J* = 1.5 Hz, 1H), 8.34 (d, *J* = 1.5 Hz, 1H), 8.06 (s, 2H), 7.46 (d, *J* = 3.5 Hz, 1H), 6.46 (d, *J* = 3.5 Hz, 1H), 3.81 (s, 3H); **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 148.5, 134.7, 129.7, 119.4, 119.1, 99.2, 30.81, 1 × ArC not observed; **LRMS** (ESI⁺) *m/z* 177.1 ([M+H]⁺); **HRMS** (ESI⁺) *m/z* C₈H₁₀O₂N₂B⁺ requires 177.0830 [M+H]⁺, found 177.0831; **IR** (thin film, ν_{max}/cm⁻¹) 3102, 1598, 1331, 1262, 1186, 721; **m.p.** (Et₂O): 288-289 °C.

3.2 General Procedure A: Two-step synthesis of sulfones (exemplified by the preparation of sulfone 2a)

tert-Butyl 2-(phenylsulfonyl)acetate (2a)



Phenylboronic acid (24.4 mg, 0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (6.1 mg, 0.02 mmol, 10 mol%), *tmphen* (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N_2 ($\times 4$) (*note 4*). DMI (1.0 mL) was added and the reaction mixture was heated at $100\text{ }^\circ\text{C}$ for 16 h. The solution was cooled to rt. *tert*-Butylbromoacetate (60 μL , 0.40 mmol, 2.0 equiv.) was then added and the reaction was stirred at rt for 1 h. The reaction was diluted with water (10 mL) and extracted with EtOAc ($3 \times 10\text{ mL}$). The combined organic phases were dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography (40% Et₂O in Petrol) afforded the product as a colourless oil (44.9 mg, 88%).

R_f (40% Et₂O in Petrol) = 0.23; **¹H NMR** (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0\text{ Hz}$, 2H), 7.67 (t, $J = 8.0\text{ Hz}$, 1H), 7.57 (t, $J = 8.0\text{ Hz}$, 2H), 4.03 (s, 2H), 1.34 (s, 9H); **¹³C NMR** (101 MHz, CDCl_3) δ 161.3, 139.0, 134.2, 129.2, 128.6, 83.7, 62.2, 27.8; **LRMS** (ESI⁺) m/z 279.0 ([M+Na]⁺), 535.1 ([2M+Na]⁺).

Data is consistent with the literature.⁶

Note:

1. $\text{NiBr}_2 \cdot (\text{glyme})$ was purchased from Sigma-Aldrich or Strem Chemicals. *Tmphen* was purchased from Sigma-Aldrich, Tokyo Chemical Industry UK or Alfa Aesar. DABSO was prepared using literature method.⁷ LiOt-Bu was purchased from Strem Chemicals. DMI was from a Sigma-Aldrich Sure/Seal bottle ($\geq 99.5\%$ (GC), catalog no.: 40725-100ML).

2. $\text{NiBr}_2 \cdot (\text{glyme})$ is slightly deliquescent and discolours from orange to yellow after exposure to air for prolonged time. Although we did not recognise any significant change in reactivity, we suggest the catalyst is flushed and stored under N_2 every time after used.

3. We find that anhydrous DMI gave more consistent results.

4. The reaction was evacuated ($< 5\text{ mbar}$) and filled with N_2 ($\times 4$). The first evacuation was at least 5 min. The remaining three times were at least 1 min.

5. All reaction were easily monitored by HPLC analysis for the conversion of boronic acids to sulfinates in step 1 and the conversion of sulfinates to products in step 2.

6. In step 1, protodeboronation products were generally the major and usually the only side products formed.

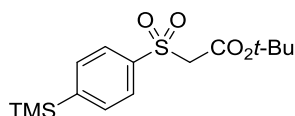
7. In some cases, the reaction mixture would become a gel in the alkylation step (step 2), especially with the less reactive boronic acids. The alkylation reaction were generally fast and all sulfonates should have converted into the desired product (observed by HPLC analysis) before the mixture turned to a gel.

8. In some cases, the aqueous and organic phases did not separate. Usually, adding more water and EtOAc would solve the problem.

9. The crude product was dry-loaded with silica gel on a pre-packed silica gel column.

10. DMI has a high boiling point (225 °C) and it dissolves in both water and EtOAc, but is only slightly soluble in Et₂O. Generally the crude products contain certain amount of DMI especially when EtOAc was used in the aqueous workup. The DMI in the crude product can be removed using flash column chromatography. More silica gel is suggested to use if > 60% EtOAc in Petrol is used as the eluting solvent because DMI could coelute with the desired product. Occasionally, DMI could be removed by washing the combined organic phases in aqueous workup with H₂O five times.

***tert*-Butyl 2-((4-(trimethylsilyl)phenyl)sulfonyl)acetate (2b)**

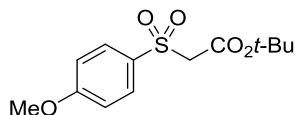


Prepared according to general procedure A using 4-(trimethylsilyl)phenylboronic acid (38.8 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (20% Et₂O in Petrol) afforded the title product as a colourless oil (58.9 mg, 90%).

R_f (20% Et₂O in Petrol) = 0.12; **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 4.02 (s, 2H), 1.34 (s, 9H), 0.29 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.4, 149.0, 139.2, 134.0, 127.4, 83.6, 62.2, 27.7, -1.3; **LRMS** (ESI⁺) *m/z* 351.1 ([M+Na]⁺), 679.2 ([2M+Na]⁺).

Data is consistent with the literature.⁸

tert-Butyl 2-((4-methoxyphenyl)sulfonyl)acetate (2c)

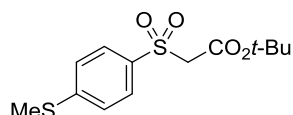


Prepared according to general procedure A using 4-methoxyphenylboronic acid (30.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% Et₂O in Petrol) afforded the title product as a colourless oil (52.3 mg, 91%).

R_f (40% Et₂O in Petrol) = 0.22; **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.99 (s, 2H), 3.87 (s, 3H), 1.37 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.2, 161.6, 130.9, 130.5, 114.4, 83.5, 62.4, 55.8, 27.8; **LRMS** (ESI⁺) *m/z* 309.1 ([M+Na]⁺), 595.1 ([2M+Na]⁺).

Data is consistent with the literature.⁶

tert-Butyl 2-((4-(methylthio)phenyl)sulfonyl)acetate (2d)

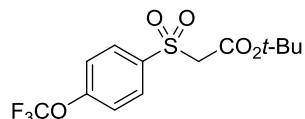


Prepared according to general procedure A using 4-(methylthio)phenylboronic acid (33.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (25% EtOAc in Petrol) afforded the title product as a yellow oil (42.7 mg, 71%).

R_f (25% EtOAc in Petrol) = 0.24; **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.00 (s, 2H), 2.51 (s, 3H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.5, 148.0, 134.6, 128.9, 125.3, 83.7, 62.3, 27.8, 14.8; **LRMS** (ESI⁺) *m/z* 325.1 ([M+Na]⁺), 627.1 ([2M+Na]⁺).

Data is consistent with the literature.⁸

tert-Butyl 2-((4-(trifluoromethoxy)phenyl)sulfonyl)acetate (2e)

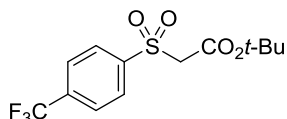


Prepared according to general procedure A using 4-(trifluoromethoxy)phenylboronic acid (41.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (10-15% EtOAc in Petrol) afforded the title product as a colourless oil (54.8 mg, 81%).

R_f (10% EtOAc in Petrol) = 0.21; **¹H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.97 (m, 2H), 7.42 – 7.36 (m, 2H), 4.05 (s, 2H), 1.36 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.1, 153.3 (q, *J* = 1.5 Hz), 137.1, 131.0, 120.8, 120.2 (q, *J* = 260.0 Hz), 83.9, 62.0, 27.7; **¹⁹F NMR** (377 MHz, CDCl₃) δ -57.7; **LRMS** (ESI⁺) *m/z* 363.0 ([M+Na]⁺).

Data is consistent with the literature.⁹

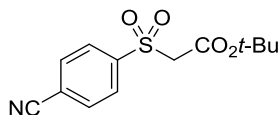
tert-Butyl 2-((4-(trifluoromethyl)phenyl)sulfonyl)acetate (2f)



Prepared according to general procedure A using 4-(trifluoromethyl)phenylboronic acid (38.0 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% Et₂O in Petrol) afforded the title product as a colourless oil which solidified to an off-white solid when left standing (53.5 mg, 82%).

R_f (40% Et₂O in Petrol) = 0.35; **¹H NMR** (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 4.07 (s, 2H), 1.37 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.1, 142.5, 135.9 (q, *J*_{CF} = 33.5 Hz), 129.4, 126.4 (q, *J*_{CF} = 4.0 Hz), 123.2 (q, *J*_{CF} = 273.0 Hz), 84.2, 61.9, 27.8; **¹⁹F NMR** (377 MHz, CDCl₃) δ -63.3; **LRMS** (ESI⁺) *m/z* 347.1 ([M+Na]⁺), 671.1 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₃H₁₅O₄F₃NaS⁺ requires 347.0535 [M+Na]⁺, found 347.0536; **IR** (thin film, ν_{max}/cm⁻¹) 1733, 1404, 1322, 1165, 1145, 1187, 1063; **m.p.** (CH₂Cl₂): 95-97 °C.

tert-Butyl 2-((4-cyanophenyl)sulfonyl)acetate (2g)

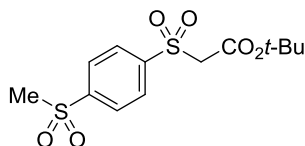


Prepared according to general procedure A using 4-cyanophenylboronic acid (29.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% Et₂O in Petrol) afforded the title product as a pale yellow solid (42.1 mg, 75%).

R_f (40% Et₂O in Petrol) = 0.19; **¹H NMR** (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 4.07 (s, 2H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.0, 143.0, 133.0, 129.5, 118.0, 117.1, 84.4, 61.7, 27.8; **LRMS** (ESI⁺) *m/z* 304.1 ([M+Na]⁺), 585.1 ([2M+Na]⁺).

Data is consistent with the literature.⁸

tert-Butyl 2-((4-(methanesulfonyl)phenyl)sulfonyl)acetate (2h)

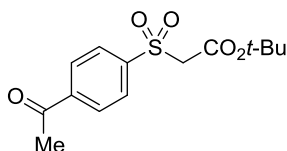


Prepared according to general procedure A using 4-(methanesulfonyl)phenylboronic acid (40.0 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (50% EtOAc in Petrol) afforded the title product as a white solid (49.9 mg, 75%).

R_f (50% EtOAc in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 8.15 (app. s, 4H), 4.09 (s, 2H), 3.09 (s, 3H), 1.37 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 160.9, 145.8, 144.0, 129.9, 128.4, 84.4, 61.8, 44.4, 27.8; **LRMS** (ESI⁺) *m/z* 357.1 ([M+Na]⁺), 691.1 ([2M+Na]⁺).

Data is consistent with the literature.⁹

tert-Butyl 2-((4-acetylphenyl)sulfonyl)acetate (2i)

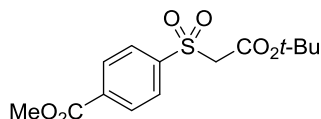


Prepared according to general procedure A using 4-acetylphenylboronic acid (32.8 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (60% Et₂O in Petrol) afforded the title product as a white solid (41.4 mg, 69%).

R_f (60% Et₂O in Petrol) = 0.22; **¹H NMR** (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 4.06 (s, 2H), 2.65 (s, 3H), 1.36 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 196.7, 161.1, 142.7, 141.2, 129.1, 128.9, 84.1, 61.9, 27.8, 27.0; **LRMS** (ESI⁺) *m/z* 321.1 ([M+Na]⁺), 619.2 ([2M+Na]⁺).

Data is consistent with the literature.⁸

Methyl 4-((2-(tert-butoxy)-2-oxoethyl)sulfonyl)benzoate (2j)

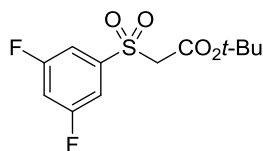


Prepared according to general procedure A using 4-methoxycarbonylphenylboronic acid (36.0 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% Et₂O in Petrol) afforded the title product as a white solid (46.0 mg, 73%).

R_f (40% Et₂O in Petrol) = 0.17; **¹H NMR** (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 4.06 (s, 2H), 3.96 (s, 3H), 1.35 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 165.5, 161.1, 142.8, 135.2, 130.3, 128.8, 84.1, 62.0, 52.9, 27.8; **LRMS** (ESI⁺) *m/z* 337.1 ([M+Na]⁺), 651.1 ([2M+Na]⁺).

Data is consistent with the literature.⁸

tert-Butyl 2-((3,5-difluorophenyl)sulfonyl)acetate (2k)

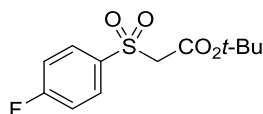


Prepared according to general procedure A using 3,5-difluorophenylboronic acid (31.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (10% EtOAc in Petrol) afforded the title product as a colourless oil (38.8 mg, 66%).

R_f (10% EtOAc in Petrol) = 0.23; **¹H NMR** (400 MHz, CDCl₃) δ 7.53 – 7.45 (m, 2H), 7.13 (tt, *J* = 8.4, 2.3 Hz, 1H), 4.05 (s, 2H), 1.40 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.9 (dd, *J* = 255.5, 11.5 Hz), 160.9, 142.2 (t, *J* = 8.5 Hz), 112.4 (m), 109.9 (t, *J* = 25.0 Hz), 84.4, 61.9, 27.8; **¹⁹F NMR** (377 MHz, CDCl₃) δ -105.0; **LRMS** (ESI⁺) *m/z* 293.0 ([M+H]⁺), 315.0 ([M+Na]⁺).

Data is consistent with the literature.⁹

tert-Butyl 2-((4-fluorophenyl)sulfonyl)acetate (2l)

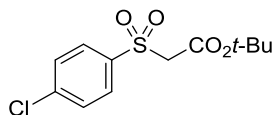


Prepared according to general procedure A using 4-fluorophenylboronic acid (28.0 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% Et₂O in Petrol) afforded the title product as a colourless oil (49.0 mg, 89%).

R_f (40% Et₂O in Petrol) = 0.29; **¹H NMR** (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.30 – 7.22 (m, 2H), 4.04 (s, 2H), 1.39 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 166.2 (d, *J*_{CF} = 257.0 Hz), 161.4, 135.1 (d, *J*_{CF} = 3.0 Hz), 131.7 (d, *J*_{CF} = 10.0 Hz), 116.6 (d, *J*_{CF} = 23.0 Hz), 83.9, 62.2, 27.8; **¹⁹F NMR** (377 MHz, CDCl₃) δ -102.7; **LRMS** (ESI⁺) *m/z* 571.1 ([2M+Na]⁺).

Data is consistent with the literature.⁶

***tert*-Butyl 2-((4-chlorophenyl)sulfonyl)acetate (2m)**



Prepared according to general procedure A using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (30% Et₂O in Petrol) afforded the title product as a colourless oil (51.1 mg, 88%).

The same procedure was followed but using NiBr₂·(glyme) (3.1 mg, 0.01 mmol, 5 mol%) and tmphen (2.4 mg, 0.02 mmol, 5 mol%) instead, affording the title product (46.1 mg, 79%).

The same procedure was followed but using NiBr₂·(glyme) (1.5 mg, 0.005 mmol, 2.5 mol%) and tmphen (1.2 mg, 0.005 mmol, 2.5 mol%) at 110 °C instead, affording the title product (40.9 mg, 70%).

The same procedure was followed but in 0.50 mmol scale using 4-chlorophenylboronic acid (76.0 mg, 0.50 mmol, 1.0 equiv.), NiBr₂·(glyme) (1.5 mg, 0.005 mmol, 1 mol%), tmphen (1.2 mg, 0.005 mmol, 1 mol%), DABSO (72.1 mg, 0.30 mmol, 0.6 equiv.) and LiOt-Bu (40.0 mg, 0.50 mmol, 1.0 equiv.), DMI (2.5 mL) at 110 °C and *tert*-butylbromoacetate (150 μL, 1.0 mmol, 2.0 equiv.), affording the title product (62.6 mg, 43%).

Gram scale reaction: the same procedure was followed but on a 7.0 mmol scale using 4-chlorophenylboronic acid (1095 mg, 7.0 mmol, 1.0 equiv.), NiBr₂·(glyme) (54 mg, 0.175 mmol, 2.5 mol%), tmphen (41 mg, 0.175 mmol, 2.5 mol%), DABSO (1009 mg, 4.2 mmol, 0.6 equiv.) and LiOt-Bu (560 mg, 7.0 mmol, 1.0 equiv.), DMI (35 mL) at 110 °C and *tert*-Butylbromoacetate (2.1 mL, 14 mmol, 2.0 equiv.). In the aqueous workup, the combined organic phases were washed with H₂O five times to remove DMI. Purification by flash column chromatography (30% Et₂O in Petrol) afforded the title product (1.45 g, 71%).

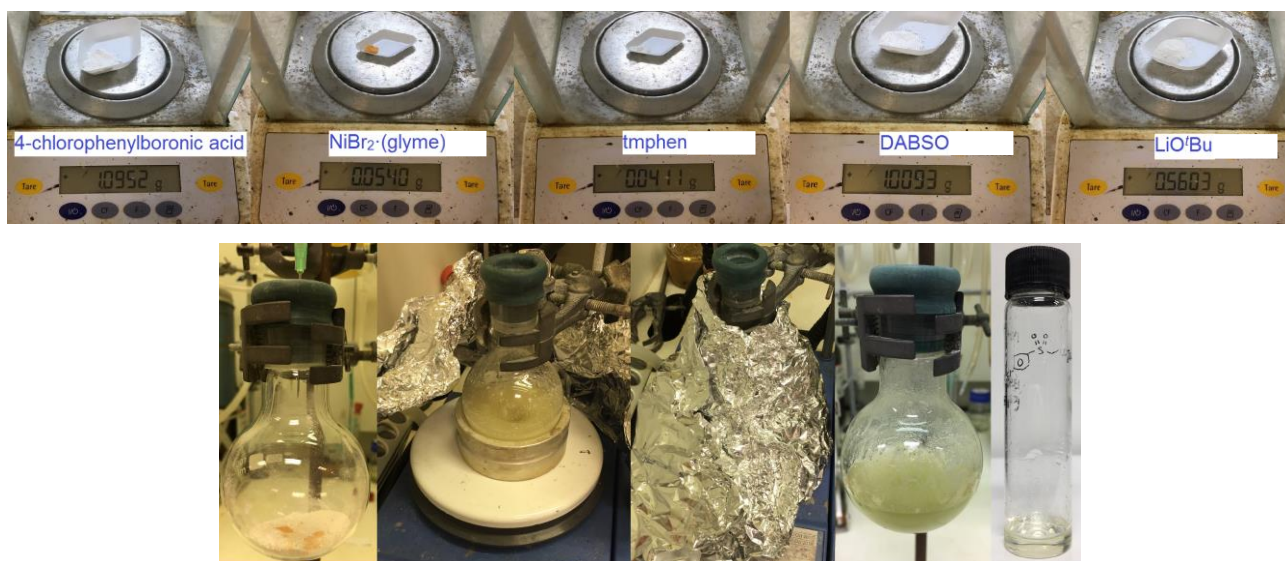
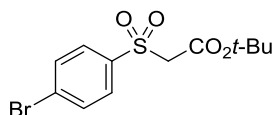


Figure S1. Gram scale reaction.

R_f (30% Et₂O in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 4.03 (s, 2H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.3, 141.1, 137.5, 130.2, 129.6, 84.0, 62.1, 27.8; **LRMS** (ESI⁺) m/z 313.0 ([M+Na]⁺), 603.0 ([2M+Na]⁺).

Data is consistent with the literature.⁸

tert-Butyl 2-((4-bromophenyl)sulfonyl)acetate (2n)

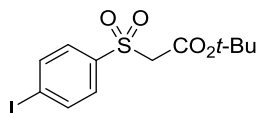


Prepared according to general procedure A using 4-bromophenylboronic acid (40.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% Et₂O in Petrol) afforded the title product as a colourless oil (51.5 mg, 77%).

R_f (40% Et₂O in Petrol) = 0.32; **¹H NMR** (400 MHz, CDCl₃) δ 7.80 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 4.02 (s, 2H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.3, 138.0, 132.6, 130.3, 129.7, 84.0, 62.1, 27.8; **LRMS** (ESI⁺) m/z 357.0 ([M+Na]⁺).

Data is consistent with the literature.⁸

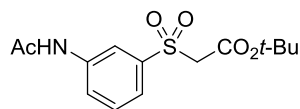
tert-Butyl 2-((4-iodophenyl)sulfonyl)acetate (2o)



Prepared according to general procedure A using 4-iodophenylboronic acid (49.6 mg, 0.20 mmol, 1.0 equiv.), NiI₂ (6.3 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (15% EtOAc in Petrol) afforded the title product as an off-white solid (57.6 mg, 75%).

R_f (15% EtOAc in Petrol) = 0.31; **¹H NMR** (400 MHz, CDCl₃) δ 7.93 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 4.02 (s, 2H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) 161.2, 138.6, 138.5, 130.0, 102.4, 84.0, 62.0, 27.8; **LRMS** (ESI⁺) m/z 405.0 ([M+Na]⁺), 786.9 ([2M+Na]⁺). **HRMS** (ESI⁻) m/z C₁₂H₁₄O₄I⁻ requires 380.9663 [M-H]⁻, found 380.9663; **IR** (thin film, ν_{max}/cm^{-1}) 1730, 1568, 1327, 1293, 1145, 1082, 1006; **m.p.** (CH₂Cl₂): 96-97 °C.

tert-Butyl 2-((3-acetamidophenyl)sulfonyl)acetate (2p)

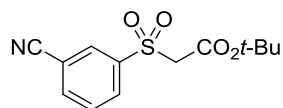


Prepared according to general procedure A using 3-acetamidophenylboronic acid (35.8 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (60% EtOAc in Petrol) afforded the title product as a colourless oil (40.8 mg, 65%).

R_f (60% EtOAc in Petrol) = 0.27; **¹H NMR** (400 MHz, CDCl₃) δ 8.49 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 4.06 (s, 2H), 2.19 (s, 3H), 1.33 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.4, 161.2, 139.6, 139.1, 130.1, 125.3, 123.2, 118.9, 84.1, 62.0, 27.8, 24.5; **LRMS** (ESI⁺) *m/z* 336.1 ([M+Na]⁺), 649.2 ([2M+Na]⁺).

Data is consistent with the literature.⁶

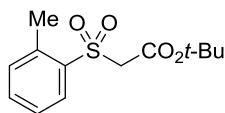
tert-Butyl 2-((3-cyanophenyl)sulfonyl)acetate (2q)



Prepared according to general procedure A using 3-cyanophenylboronic acid (29.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40-60% Et₂O in Petrol) afforded the title product as a colourless oil (41.5 mg, 74%).

R_f (60% Et₂O in Petrol) = 0.27; **¹H NMR** (400 MHz, CDCl₃) 8.25 – 8.22 (m, 1H), 8.18 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.96 (app. dt, *J* = 8.0, 1.5 Hz, 1H), 7.74 (app. td, *J* = 8.0, 0.5 Hz, 1H), 4.08 (s, 2H), 1.39 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) 161.0, 140.6, 137.3, 132.8, 132.6, 130.3, 117.0, 113.9, 84.4, 61.8, 27.8; **LRMS** (ESI⁺) *m/z* 304.1 ([M+Na]⁺), 585.1 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₃H₁₅O₄NNaS⁺ requires 304.0614 [M+Na]⁺, found 304.0615; **IR** (thin film, ν_{max}/cm⁻¹) 2980, 2360, 1731, 1473, 1335, 1142, 1087.

tert-Butyl 2-(*o*-tolylsulfonyl)acetate (2r)

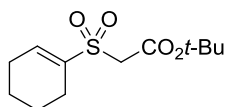


Prepared according to general procedure A using *o*-tolylboronic acid (27.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) at 120 °C. Purification by flash column chromatography (30% Et₂O in Petrol) afforded the title product as a pale yellow oil (17.0 mg, 31%).

R_f (30% Et₂O in Petrol) = 0.25; **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 (app. td, *J* = 7.5, 1.5 Hz, 1H), 7.41 – 7.33 (m, 2H), 4.08 (s, 2H), 2.71 (s, 3H), 1.29 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) 161.2, 138.3, 137.2, 134.2, 132.8, 130.9, 126.6, 83.7, 61.7, 27.7, 20.4; **HRMS** (ESI⁺) *m/z* C₁₃H₁₈O₄NaS⁺ requires 293.0818 [M+Na]⁺, found 293.0816.

Data is consistent with the literature.⁸

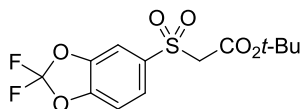
tert-Butyl 2-(cyclohex-1-en-1-ylsulfonyl)acetate (2s)



Prepared according to general procedure A using 1-cyclohexen-1-yl-boronic acid (25.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) at 110 °C. Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a white solid (23.2 mg, 45%).

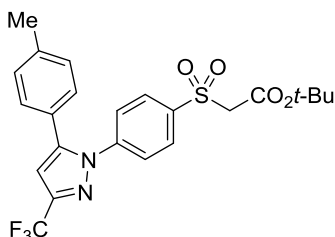
R_f (20% EtOAc in Petrol) = 0.36; **¹H NMR** (400 MHz, CDCl₃) δ 6.95 (tt, *J* = 4.0, 1.5 Hz, 1H), 3.84 (s, 2H), 2.43 – 2.33 (m, 2H), 2.33 – 2.19 (m, 2H), 1.83 – 1.70 (m, 2H), 1.71 – 1.57 (m, 2H), 1.45 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.8, 141.5, 138.1, 83.5, 58.5, 27.9, 25.7, 23.6, 22.0, 20.8; **LRMS** (ESI⁺) *m/z* 283.1 ([M+Na]⁺), 543.2 ([2M+Na]⁺).

Data is consistent with the literature.⁶

tert-Butyl 2-((2,2-difluorobenzo[d][1,3]dioxol-5-yl)sulfonyl)acetate (2t)

Prepared according to general procedure A using (2,2-difluorobenzo[d][1,3]dioxol-5-yl)boronic acid (40.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a white solid (46.5 mg, 69%).

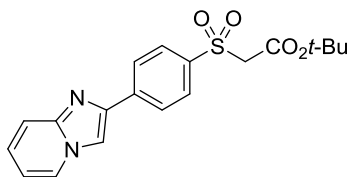
R_f (20% EtOAc in Petrol) = 0.35; **¹H NMR** (400 MHz, CDCl₃) δ 7.78 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 4.05 (s, 2H), 1.41 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.3, 147.8, 143.8, 135.1, 131.9 (t, *J*_{CF} = 259.5 Hz), 126.2, 110.5, 110.0, 84.2, 62.3, 27.9; **¹⁹F NMR** (377 MHz, CDCl₃) δ -49.3; **LRMS** (ESI⁺) *m/z* 359.0 ([M+Na]⁺), 695.0 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₃H₁₄O₆F₂NaS⁺ requires 359.0371 [M+Na]⁺, found 359.0370; **IR** (thin film, ν_{max}/cm⁻¹) 1729, 1483, 1234, 1155, 1126, 824; **m.p.** (CH₂Cl₂): 139-140 °C.

tert-butyl 2-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)acetate (2u)

Prepared according to general procedure A using (4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)boronic acid (69.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (15-30% EtOAc in Petrol) afforded the title product as a yellow oil which solidified on-standing to an off-white solid (67.7 mg, 70%).

R_f (15% EtOAc in Petrol) = 0.20; **¹H NMR** (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 4.04 (s, 2H), 2.38 (s, 3H), 1.39 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.1, 145.4, 144.3 (q, *J*_{CF} = 39.0 Hz), 143.8, 140.0, 138.2, 129.9, 129.8, 128.8, 125.8, 125.4, 121.1 (q, *J*_{CF} = 269.5 Hz), 106.7, 84.0, 62.0, 27.8, 21.4; **¹⁹F NMR** (377 MHz, CDCl₃) δ -62.5; **HRMS** (ESI⁺) *m/z* C₂₃H₂₄O₄N₂F₃S⁺ requires 481.1403 [M+H]⁺, found 481.1400; **IR** (thin film, ν_{max}/cm⁻¹) 1732, 1596, 1332, 1236, 1135, 975, 809; **m.p.** (CH₂Cl₂): 144-145 °C.

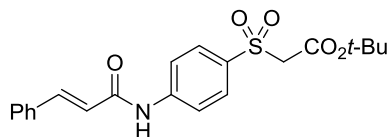
tert-Butyl 2-((4-(imidazo[1,2-a]pyridin-2-yl)phenyl)sulfonyl)acetate (2v)



Prepared according to general procedure A using (4-(imidazo[1,2-a]pyridin-2-yl)phenyl)boronic acid (47.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). The step 2 alkylation was left for 6 h instead. Purification by flash column chromatography (60-70% EtOAc in Petrol) afforded the title product as an off-white solid (35.2 mg, 47%).

R_f (60% EtOAc in Petrol) = 0.19; **¹H NMR** (400 MHz, CDCl₃) δ 8.16 – 8.10 (m, 3H), 7.99 – 7.93 (m, 3H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.24 – 7.17 (m, 1H), 6.85 – 6.78 (m, 1H), 4.07 (s, 2H), 1.35 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.4, 146.0, 143.5, 139.8, 137.6, 129.1, 126.4, 126.0, 125.7, 117.9, 113.2, 110.0, 83.8, 62.3, 27.8; **HRMS** (ESI⁺) *m/z* C₁₉H₂₁O₄N₂S⁺ requires 373.1217 [M+H]⁺, found 373.1219; **IR** (thin film, ν_{max}/cm⁻¹) 1730, 1600, 1371, 1320, 1145, 1086, 737; **m.p.** (CH₂Cl₂): 179-181 °C.

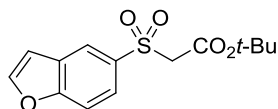
tert-Butyl 2-((4-cinnamamidophenyl)sulfonyl)acetate (2w)



Prepared according to general procedure A using (4-cinnamamidophenyl)boronic acid (53.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). The step 2 alkylation was left for 2 h instead. Purification by flash column chromatography (40% EtOAc in Petrol) afforded the title product as a colourless viscous oil which solidified on-standing to an off-white solid (59.4 mg, 74%).

R_f (40% EtOAc in Petrol) = 0.24; **¹H NMR** (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.92 – 7.83 (m, 4H), 7.76 (d, *J* = 15.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.38 – 7.31 (m, 3H), 6.67 (d, *J* = 15.5 Hz, 1H), 4.04 (s, 2H), 1.37 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.8, 161.4, 144.0, 143.8, 134.3, 133.1, 130.5, 129.9, 129.0, 128.2, 120.3, 119.6, 84.0, 62.3, 27.8; **LRMS** (ESI⁺) *m/z* 803.2 ([2M+H]⁺), 825.3 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₂₁H₂₄O₅NS⁺ requires 402.1370 [M+H]⁺, found 402.1371; **IR** (thin film, ν_{max}/cm⁻¹) 3658, 2981, 1731, 1628, 1395, 1142, 726; **m.p.** (CH₂Cl₂): 158-159 °C.

tert-Butyl 2-(benzofuran-5-ylsulfonyl)acetate (2x)

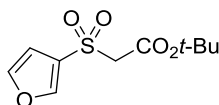


Prepared according to general procedure A using benzofuran-5-ylboronic acid (32.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a pale yellow oil (38.8 mg, 65%).

R_f (20% EtOAc in Petrol) = 0.24; **¹H NMR** (400 MHz, CDCl₃) δ 8.24 (d, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.77 (d, *J* = 2.5 Hz, 1H), 7.65 (app. dt, *J* = 8.5, 1.0 Hz, 1H), 6.90 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.07 (s, 2H), 1.34 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.5, 157.6, 147.6, 133.7, 128.0, 124.7, 123.3, 112.3, 107.3, 83.7, 62.6, 27.8; **LRMS** (ESI⁺) *m/z* 314.1 ([M+NH₄]⁺), 615.1 ([2M+Na]⁺).

Data is consistent with the literature.⁸

tert-butyl 2-(furan-3-ylsulfonyl)acetate (2y)

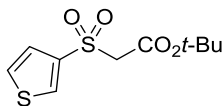


Prepared according to general procedure A using 3-furanylboronic acid (22.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). The first step of the reaction was performed in 1 h instead of 16 h, due to the instability of the corresponding sulfinate. Purification by flash column chromatography (25% EtOAc in Petrol) afforded the title product as a colourless oil (22.2 mg, 45%).

R_f (25% EtOAc in Petrol) = 0.25; **¹H NMR** (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.53 (app. t, *J* = 2.0 Hz, 1H), 6.75 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.03 (s, 2H), 1.44 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.5, 148.0, 144.8, 127.1, 109.4, 84.0, 62.4, 27.9; **LRMS** (ESI⁺) *m/z* 269.0 ([M+Na]⁺).

Data is consistent with the literature.⁶

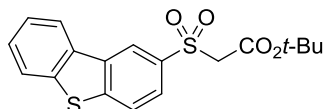
tert-Butyl 2-(thiophen-3-ylsulfonyl)acetate (2z)



Prepared according to general procedure A using 3-thienylboronic acid (25.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). The first step of the reaction was performed in 2 h instead of 16 h, due to the instability of the corresponding sulfinate. Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as an off-white solid (27.4 mg, 52%).

R_f (20% EtOAc in Petrol) = 0.32; **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.47 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.43 (dd, *J* = 5.0, 1.5 Hz, 1H), 4.04 (s, 2H), 1.40 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.4, 139.5, 133.8, 128.1, 126.6, 83.8, 62.4, 27.9; **LRMS** (ESI⁺) *m/z* 285.0 ([M+Na]⁺). Data is consistent with the literature.⁸

tert-Butyl 2-(dibenzo[*b,d*]thiophen-2-ylsulfonyl)acetate (2aa)

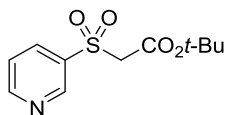


Prepared according to general procedure A using dibenzo[*b,d*]thiophen-2-ylboronic acid (45.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a pale yellow viscous oil (54.8 mg, 76%).

R_f (20% EtOAc in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.21 (app. d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.88 (app. d, *J* = 7.5 Hz, 1H), 7.58 – 7.48 (m, 2H), 4.14 (s, 2H), 1.34 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.4, 145.7, 140.0, 135.8, 135.2, 134.5, 128.1, 125.6, 125.4, 123.5, 123.1, 122.3, 122.2, 83.8, 62.6, 27.8; **LRMS** (ESI⁺) *m/z* 385.0 ([M+Na]⁺).

Data is consistent with the literature.⁹

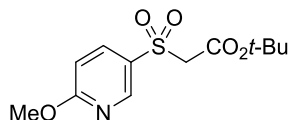
tert-Butyl 2-(pyridin-3-ylsulfonyl)acetate (2ab)



Prepared according to general procedure A using 3-pyridinylboronic acid (24.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (50% EtOAc in Petrol) afforded the title product as a colourless oil (37.7 mg, 73%).

R_f (50% EtOAc in Petrol) = 0.25; **¹H NMR** (400 MHz, CDCl₃) δ 9.13 (app. d, 1H, *J* = 2.0 Hz), 8.89 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.22 (ddd, *J* = 8.0, 2.0, 1.5 Hz, 1H), 7.53 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.08 (s, 2H), 1.36 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) 161.1, 154.6, 149.7, 136.7, 135.5, 123.8, 84.3, 62.2, 27.8; **LRMS** (ESI⁺) *m/z* 258.1 ([M+H]⁺), 280.1 ([M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₁H₁₆O₄NS⁺ requires 258.0795 [M+H]⁺, found 258.0794; **IR** (thin film, ν_{max}/cm⁻¹) 2981, 2361, 1732, 1323, 1150, 702.

tert-Butyl 2-((6-methoxypyridin-3-yl)sulfonyl)acetate (2ac)

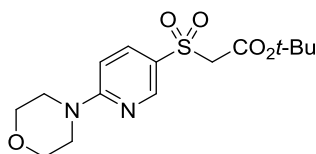


Prepared according to general procedure A using 6-methoxy-3-pyridinylboronic acid (30.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (30% Et₂O in Petrol) afforded the title product as a pale yellow oil (39.7 mg, 69%).

R_f (30% Et₂O in Petrol) = 0.16; **¹H NMR** (400 MHz, CDCl₃) δ 8.70 (dd, *J* = 2.5, 0.5 Hz, 1H), 8.01 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.85 (dd, *J* = 9.0, 0.5 Hz, 1H), 4.02 (s, 2H), 4.02 (s, 3H), 1.41 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 167.5, 161.5, 149.6, 138.7, 128.3, 111.5, 84.0, 62.6, 54.6, 27.9; **LRMS** (ESI⁺) *m/z* 288.1 ([M+H]⁺), 310.1 ([M+Na]⁺).

Data is consistent with the literature.⁸

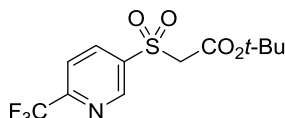
tert-Butyl 2-((6-morpholinopyridin-3-yl)sulfonyl)acetate (2ad)



Prepared according to general procedure A using 6-(morpholino)pyridine-3-boronic Acid (41.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (30-50% EtOAc in Petrol) afforded the title product as an orange oil which solidified on-standing to a yellow solid (46.0 mg, 67%).

R_f (50% EtOAc in Petrol) = 0.24; **¹H NMR** (400 MHz, CDCl₃) δ 8.60 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.85 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.61 (dd, *J* = 9.0, 0.5 Hz, 1H), 3.98 (s, 2H), 3.80 – 3.76 (m, 4H), 3.70 – 3.66 (m, 4H), 1.41 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.8, 160.8, 150.2, 137.8, 122.7, 105.0, 83.7, 66.6, 62.7, 44.9, 27.9; **LRMS** (ESI⁺) *m/z* 343.1 ([M+H]⁺); **HRMS** (ESI⁺) *m/z* C₁₅H₂₃O₅N₂S⁺ requires 343.1322 [M+H]⁺, found 343.1322; **IR** (thin film, ν_{max}/cm⁻¹) 1729, 1589, 1308, 1258, 1141, 944; **m.p.** (CH₂Cl₂): 101-103 °C.

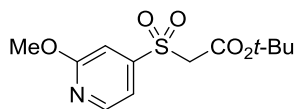
tert-Butyl 2-((6-(trifluoromethyl)pyridin-3-yl)sulfonyl)acetate (2ae)



Prepared according to general procedure A using 6-(trifluoromethyl)-3-pyridinylboronic acid (38.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (10-20% EtOAc in Petrol) afforded the title product as a white solid (38.1 mg, 59%).

R_f (20% EtOAc in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 9.23 (d, *J* = 2.5 Hz, 1H), 8.45 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.91 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.12 (s, 2H), 1.40 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 160.9, 152.6 (q, *J*_{CF} = 35.5 Hz), 150.1, 138.9, 138.2, 120.8 (q, *J*_{CF} = 275.5 Hz), 120.8 (q, *J*_{CF} = 3.1 Hz), 84.9, 62.0, 27.8; **¹⁹F NMR** (377 MHz, CDCl₃) δ -68.3; **LRMS** (ESI⁺) *m/z* 348.1 ([M+Na]⁺), 673.1 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₂H₁₄F₃NNaO₄S⁺ requires 348.0488 [M+Na]⁺, found 348.0489; **IR** (thin film, ν_{max}/cm⁻¹) 2981, 2361, 1733, 1381, 1333, 1151, 1078; **m.p.** (CH₂Cl₂): 107-109 °C.

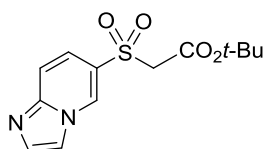
tert-Butyl 2-((2-methoxypyridin-4-yl)sulfonyl)acetate (2af)



Prepared according to general procedure A using 2-methoxypyridine-4-boronic acid (30.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a pale yellow oil (35.1 mg, 61%).

R_f (20% EtOAc in Petrol) = 0.31; **¹H NMR** (400 MHz, CDCl₃) δ 8.40 (dd, *J* = 5.5, 0.5 Hz, 1H), 7.32 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.23 (dd, *J* = 1.5, 0.5 Hz, 1H), 4.04 (s, 2H), 3.99 (s, 3H), 1.38 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.8, 160.8, 149.3, 148.9, 113.9, 110.5, 84.3, 61.5, 54.5, 27.8; **LRMS** (ESI⁺) *m/z* 310 ([M+Na]⁺), 597.2 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₂H₁₈O₅NS⁺ requires 288.0900 [M+H]⁺, found 288.0901; **IR** (thin film, ν_{max}/cm⁻¹) 2981, 1732, 1383, 1333, 1143.

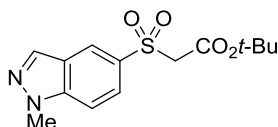
tert-Butyl 2-(imidazo[1,2-a]pyridin-6-ylsulfonyl)acetate (2ag)



Prepared according to general procedure A using (imidazo[1,2-a]pyridin-6-yl)boronic acid (32.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (100% EtOAc) afforded the title product as a yellow oil which solidified on-standing to a pale yellow solid (31.2 mg, 53%).

R_f (100% EtOAc) = 0.32; **¹H NMR** (400 MHz, CDCl₃) δ 8.88 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.84 – 7.69 (m, 3H), 7.53 (dd, *J* = 9.5, 2.0 Hz, 1H), 4.11 (s, 2H), 1.36 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.3, 145.2, 136.5, 130.7, 125.6, 121.7, 118.3, 114.5, 84.3, 62.0, 27.8; **LRMS** (ESI⁺) *m/z* 297.1 ([M+H]⁺), 593.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₁₃H₁₇O₄N₂S requires 297.0904 [M+H]⁺, found 297.0900; **IR** (thin film, ν_{max}/cm⁻¹) 1729, 1628, 1306, 1128, 729; **m.p.** (CH₂Cl₂): 122-124 °C.

tert-Butyl 2-((1-methyl-1H-indazol-5-yl)sulfonyl)acetate (2ah)

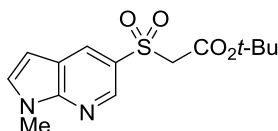


Prepared according to general procedure A using 1-methyl-1H-indazol-5-yl-5-boronic acid (35.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40-50% EtOAc in Petrol) afforded the title product as a pale yellow oil (38.7 mg, 62%).

R_f (50% EtOAc in Petrol) = 0.39; **¹H NMR** (400 MHz, CDCl₃) δ 8.39 (dd, *J* = 1.5, 1.0 Hz, 1H), 8.14 (d, *J* = 1.0 Hz, 1H), 7.87 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.53 (d, *J* = 9.0, 1H), 4.12 (s, 3H), 4.06 (s, 2H), 1.34 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) 161.6, 141.4, 134.9, 131.1, 125.3, 124.6, 123.3, 109.8, 83.7, 62.6, 36.1, 27.8; **LRMS** (ESI⁺) *m/z* 311.1 ([M+H]⁺), 643.2 ([2M+Na]⁺).

Data is consistent with the literature.⁶

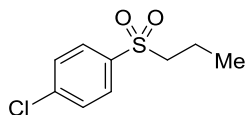
tert-Butyl 2-((1-methyl-1H-pyrrolo[2,3-*b*]pyridin-5-yl)sulfonyl)acetate (2ai)



Prepared according to general procedure A using (1-methyl-1H-pyrrolo[2,3-*b*]pyridin-5-yl)boronic acid (35.2 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (40% EtOAc in Petrol) afforded the title product as a yellow solid (40.0 mg, 64%).

R_f (40% EtOAc in Petrol) = 0.26; **¹H NMR** (400 MHz, CDCl₃) δ 8.81 (d, *J* = 2.0 Hz, 1H), 8.42 (d, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 3.5 Hz, 1H), 6.60 (d, *J* = 3.5 Hz, 1H), 4.07 (s, 2H), 3.93 (s, 3H), 1.35 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 161.6, 149.4, 143.0, 132.2, 130.2, 126.9, 119.5, 101.5, 83.7, 63.1, 31.8, 27.8; **LRMS** (ESI⁺) *m/z* 311.1 ([M+H]⁺), 621.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₁₄H₁₉O₄N₂S⁺ requires 311.1060 [M+H]⁺, found 311.1060; **IR** (thin film, ν_{max}/cm⁻¹) 1729, 1326, 1143, 1074, 730; **m.p.** (CH₂Cl₂): 110-112 °C.

1-Chloro-4-(propylsulfonyl)benzene (3a)

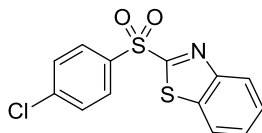


4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ (× 4). DMI (1.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. 1-Iodopropane (40 μL, 0.40 mmol, 2.0 equiv.) was then added. The reaction was stirred at 100 °C for 30 min before cooling to rt. The reaction was diluted with water (10 mL) and extracted with Et₂O (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (10-40% Et₂O in Petrol) afforded the title product as an off-white solid (33.8 mg, 77%).

R_f (40% Et₂O in Petrol) = 0.36; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 3.10 – 3.01 (m, 2H), 1.80 – 1.65 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.5, 137.7, 129.7 (overlapping of two carbons), 58.1, 16.6, 13.1; LRMS (ESI⁺) *m/z* 241.0 ([M+Na]⁺), 459.0 ([2M+Na]⁺).

Data is consistent with the literature.¹⁰

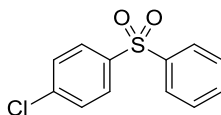
2-((4-Chlorophenyl)sulfonyl)benzo[d]thiazole (3b)



4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ (× 4). DMI (1.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. 2-Chlorobenzothiazole (50 μL, 0.40 mmol, 2.0 equiv.) was then added. The reaction was stirred at 100 °C for 1.5 h before cooling to rt. The reaction was diluted with water (10 mL) and extracted with Et₂O (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (25% Et₂O in Petrol) afforded the title product as an off-white solid (50.4 mg, 81%).

R_f (25% Et₂O in Petrol) = 0.34; ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.12 (m, 1H), 8.09 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.99 – 7.92 (m, 1H), 7.60 – 7.52 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 153.0, 141.6, 137.1, 137.0, 130.5, 130.0, 128.2, 127.8, 125.7, 122.4; LRMS (ESI⁺) *m/z* 332.0 ([M+Na]⁺); HRMS (ESI⁺) *m/z* C₁₃H₉O₂N³⁵ClS₂⁺ requires 309.9758 [M+H]⁺, found 309.9760; IR (thin film, ν_{max}/cm⁻¹) 1473, 1339, 1161, 1088, 757, 636; m.p. (CH₂Cl₂): 173-175 °C.

1-Chloro-4-(phenylsulfonyl)benzene (3c)

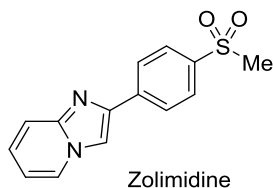


4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ (× 4). DMI (1.0 mL) was added and the reaction mixture was stirred at 100 °C for 16 h. The reaction was cooled to rt before diphenyliodonium triflate (172 mg, 0.40 mmol, 2.0 equiv.) was added. The reaction was then stirred at 100 °C for 3 h before cooling to rt and was diluted with water (10 mL) and extracted with Et₂O (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (20% Et₂O in Petrol) afforded the title product as an off-white solid (29.3 mg, 58%).

R_f (20% Et₂O in Petrol) = 0.25; **¹H NMR** (400 MHz, CDCl₃) δ 7.95 – 7.90 (m, 2H), 7.90 – 7.85 (m, 2H), 7.60 – 7.55 (m, 1H), 7.54 – 7.45 (m, 4H); **¹³C NMR** (101 MHz, CDCl₃) δ 141.3, 140.3, 140.0, 133.6, 129.7, 129.5, 129.2, 127.8; **LRMS** (ESI⁺) *m/z* 275.0 ([M+Na]⁺), 527.0 ([2M+Na]⁺).

Data is consistent with the literature.¹¹

Zolimidine (3d)

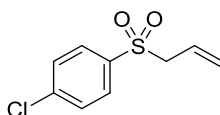


(4-(imidazo[1,2-*a*]pyridin-2-yl)phenyl)boronic acid (47.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ (× 4). DMI (1.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. The reaction was cooled to rt. Methyl iodide (40 μL, 0.6 mmol, 3.0 equiv.) was then added and the reaction was stirred at rt for 6 h. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (90% EtOAc in Petrol) afforded the title product as an off-white solid (36.6 mg, 67%).

R_f (90% EtOAc in Petrol) = 0.26; **¹H NMR** (400 MHz, CDCl₃) δ 8.17 – 8.09 (m, 3H), 8.01 – 7.92 (m, 3H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.22 (ddd, *J* = 9.0, 7.0, 1.0 Hz, 1H), 6.82 (app. td, *J* = 7.0, 1.0 Hz, 1H), 3.08 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 146.1, 143.6, 139.4, 139.3, 128.0, 126.7, 126.0, 125.7, 117.9, 113.2, 109.8, 44.7; **HRMS** (ESI⁺) *m/z* C₁₄H₁₃O₂N₂S⁺ requires 273.0692 [M+H]⁺, found 273.0691.

Data is consistent with the literature.¹²

1-(Allylsulfonyl)-4-chlorobenzene (3e)

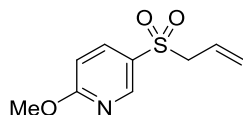


Prepared according to general procedure A using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) and allyl bromide (35 μL, 0.40 mmol, 2.0 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a yellow oil (34.0 mg, 78%).

R_f (20% EtOAc in Petrol) = 0.31; **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.52 (dt, *J* = 8.5, 2.0 Hz, 2H), 5.78 (ddt, *J* = 17.5, 10.0, 7.5 Hz, 1H), 5.34 (app. dq, *J* = 10.0, 1.0 Hz, 1H), 5.15 (app. dq, *J* = 17.0, 1.0 Hz, 1H), 3.80 (app. dt, *J* = 7.5, 1.0 Hz, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 140.7, 136.8, 130.1, 129.5, 125.2, 124.6, 61.0; **LRMS** (ESI⁺) *m/z* 239.0 ([M+Na]⁺).

Data is consistent with the literature.¹³

5-(Allylsulfonyl)-2-methoxypyridine (3f)

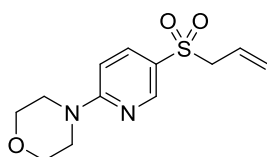


Prepared according to general procedure A using 6-methoxy-3-pyridinylboronic acid (30.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) and allyl bromide (35 μL, 0.40 mmol, 2.0 equiv.). Purification by flash column chromatography (25% EtOAc in Petrol) afforded the title product as a white solid (28.2 mg, 66%).

R_f (25% EtOAc in Petrol) = 0.29; **¹H NMR** (400 MHz, CDCl₃) δ 8.62 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.93 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.83 (dd, *J* = 9.0, 0.5 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.0, 7.5 Hz, 1H), 5.36 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.17 (dq, *J* = 17.0, 1.0 Hz, 1H), 4.01 (s, 3H), 3.80 (dt, *J* = 7.5, 1.0 Hz, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 167.3, 149.3, 138.6, 127.6, 125.2, 124.8, 111.4, 61.5, 54.5; **LRMS** (ESI⁺) *m/z* 236.0 ([M+Na]⁺), 449.0 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₉H₁₂NO₃S⁺ requires 214.0532 [M+H]⁺, found 214.0532.

Data is consistent with the literature.¹⁴

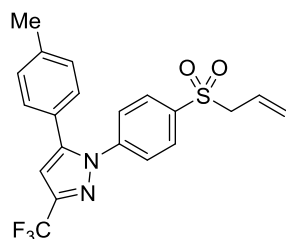
4-(5-(Allylsulfonyl)pyridin-2-yl)morpholine (3g)



Prepared according to general procedure A using 6-(morpholino)pyridine-3-boronic acid (41.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) and allyl bromide (35 μL, 0.40 mmol, 2.0 equiv.). The alkylation step was left for 24 h instead. Purification by flash column chromatography (50-60% EtOAc in Petrol) afforded the title product as a pale yellow solid (39.9 mg, 74%).

R_f (50% EtOAc in Petrol) = 0.21; **¹H NMR** (400 MHz, CDCl₃) δ 8.54 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.79 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.60 (dd, *J* = 9.0, 0.5 Hz, 1H), 5.81 (ddt, *J* = 17.5, 10.0, 7.5 Hz, 1H), 5.35 (app. dq, *J* = 10.0, 1.0 Hz, 1H), 5.18 (app. dq, *J* = 17.0, 1.5 Hz, 1H), 3.82 – 3.74 (m, 6H), 3.70 – 3.63 (m, 4H); **¹³C NMR** (101 MHz, CDCl₃) δ 160.8, 150.0, 137.7, 125.2, 124.8, 122.4, 105.1, 66.6, 61.6, 45.0; **LRMS** (ESI⁺) *m/z* 269.1 ([M+H]⁺), 537.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₁₂H₁₇O₃N₂S⁺ requires 269.0954 [M+H]⁺, found 269.0954; **IR** (thin film, ν_{max}/cm⁻¹) 1587, 1499, 1304, 1136, 1115, 942; **m.p.** (CH₂Cl₂): 148-149 °C.

1-(4-(Allylsulfonyl)phenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (3h)



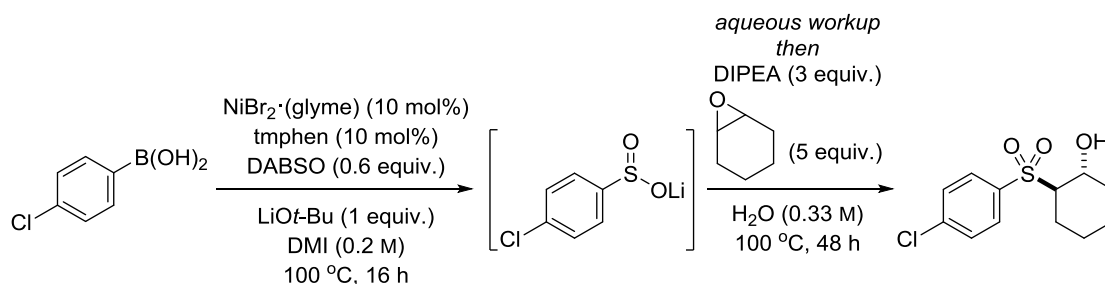
Prepared according to general procedure A using (4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)boronic acid (69.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) and allyl bromide (35 μ L, 0.40 mmol, 2.0 equiv.). Purification by flash column chromatography (15-30% EtOAc in Petrol) afforded the title product as a colourless viscous oil (64.2 mg, 79%).

R_f (15% EtOAc in Petrol) = 0.27; **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.50 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 5.77 (ddt, *J* = 17.0, 10.0, 7.5 Hz, 1H), 5.32 (app. dd, *J* = 10.0, 1.0 Hz, 1H), 5.13 (app. dq, *J* = 17.0, 1.0 Hz, 1H), 3.81 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 145.5, 144.3 (q, *J*_{CF} = 39.0 Hz), 143.5, 140.0, 137.5, 129.9, 129.7, 128.8, 125.7, 125.5, 125.2, 124.5, 121.1 (q, *J*_{CF} = 269.0 Hz), 106.5, 61.0, 21.4; **¹⁹F NMR** (377 MHz, CDCl₃) δ -62.4; **LRMS** (ESI⁺) *m/z* 407.1 ([M+H]⁺), 813.2 ([2M+H]⁺).

Data is consistent with the literature.¹⁴

3.3 General Procedure B: Two-step synthesis of β -hydroxysulfones (exemplified by the preparation of β -hydroxysulfones **3i**)

2-((4-Chlorophenyl)sulfonyl)cyclohexan-1-ol (3i**)**



4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (6.1 mg, 0.02 mmol, 10 mol%), *tmphen* (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N_2 ($\times 4$). DMI (1.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. After cooling the solution to rt, aq. H_3PO_4 (3 mL, 2 M) and brine (1 mL) were added to the mixture. The mixture was then extracted with EtOAc (3×2 mL) (*note 1*). The combined organic phases were transferred to a 10 mL round-bottom flask and was added DIPEA (0.11 mL, 0.60 mmol, 3.0 equiv.). The solution became cloudy after adding DIPEA indicating the formation of sulfinate salt from sulfinic acid. The volatiles were removed under reduced pressure (< 20 mbar for at least 1 min). H_2O (0.6 mL) and cyclohexene oxide (100 μL , 1.0 mmol, 5.0 equiv.) were added. The reaction mixture was then stirred at 100 °C for 48 h. The reaction was diluted with water (10 mL) and extracted with EtOAc (3×10 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography (30% EtOAc in Petrol) afforded the title product as a white solid (42.2 mg, 77%).

R_f (30% EtOAc in Petrol) = 0.43; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 4.07 (s, 1H), 3.88 (app. td, $J = 10.0, 5.0$ Hz, 1H), 2.97 (ddd, $J = 12.5, 9.5, 4.0$ Hz, 1H), 2.17 – 2.05 (m, 1H), 1.95 – 1.84 (m, 1H), 1.76 – 1.65 (m, 2H), 1.38 – 1.10 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.0, 135.6, 130.6, 129.7, 69.2, 68.4, 34.4, 25.8, 24.6, 23.7; HRMS (ESI $^+$) m/z $\text{C}_{12}\text{H}_{16}\text{O}_3^{35}\text{ClS}^+$ requires 275.0503 $[\text{M}+\text{H}]^+$, found 275.0506.

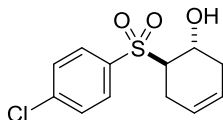
Data is consistent with the literature.¹⁵

Note:

1. Ring-opening reaction followed by elimination was observed if the aqueous workup was not performed.

(Also see the notes in general procedure A)

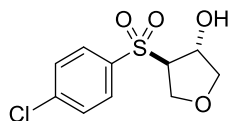
6-((4-Chlorophenyl)sulfonyl)cyclohex-3-en-1-ol (3j)



Prepared according to general procedure B using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), 7-oxabicyclo[4.1.0]hept-3-ene¹⁶ (97 mg, 1.0 mmol, 5.0 equiv.). Purification by flash column chromatography (30% EtOAc in Petrol) afforded the title product as an off-white solid (46.2 mg, 85%).

R_f (30% EtOAc in Petrol) = 0.35; **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 5.64 – 5.54 (m, 1H), 5.54 – 5.44 (m, 1H), 4.17 (td, *J* = 9.5, 6.0 Hz, 1H), 3.86 (s, 1H), 3.31 (td, *J* = 10.5, 6.5 Hz, 1H), 2.62 – 2.51 (m, 1H), 2.37 – 2.07 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 141.1, 135.9, 130.5, 129.7, 124.7, 122.7, 66.0, 65.4, 34.2, 26.1; **HRMS** (ESI⁺) *m/z* C₁₂H₁₃O₃³⁵ClNaS⁺ requires 295.0166 [M+Na]⁺, found 295.0167; **IR** (thin film, ν_{max}/cm⁻¹) 3492, 1307, 1275, 1143, 1088, 759; **m.p.** (CH₂Cl₂): 112-114 °C.

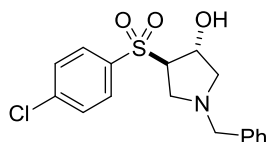
4-((4-Chlorophenyl)sulfonyl)tetrahydrofuran-3-ol (3k)



Prepared according to general procedure B using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), 3,4-epoxytetrahydrofuran (72 μL, 1 mmol, 5.0 equiv.). Purification by flash column chromatography (40–50% EtOAc in Petrol) afforded the title product as an off-white solid (37.2 mg, 71%).

R_f (50% EtOAc in Petrol) = 0.29; **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 4.94 – 4.81 (m, 1H), 4.14 – 3.94 (m, 3H), 3.77 – 3.67 (m, 2H), 3.11 – 2.96 (m, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 141.4, 136.5, 130.1, 129.9, 75.1, 72.5, 72.1, 67.2; **HRMS** (ESI⁺) *m/z* C₁₀H₁₂O₄³⁵ClS⁺ requires 263.0139 [M+Na]⁺, found 263.0140; **IR** (thin film, ν_{max}/cm⁻¹) 3388, 1311, 1146, 1084, 908; **m.p.** (CH₂Cl₂): 138-140 °C.

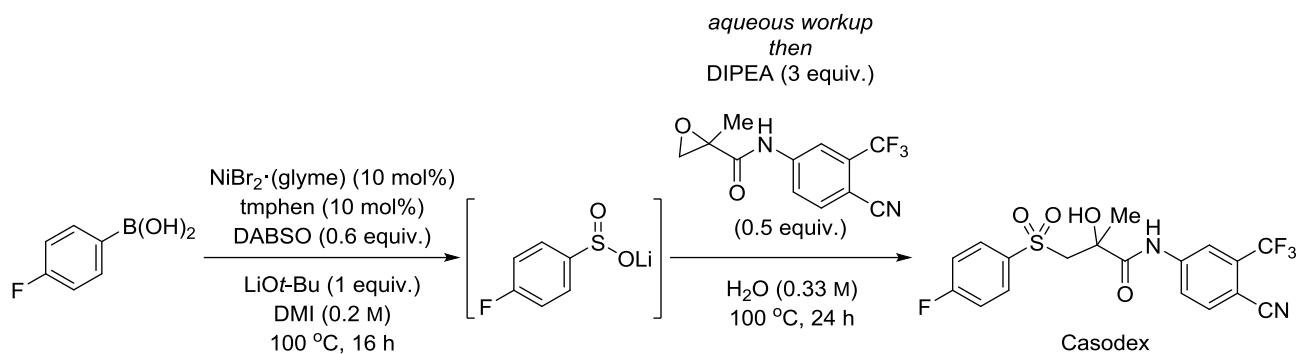
1-Benzyl-4-((4-chlorophenyl)sulfonyl)pyrrolidin-3-ol (3I)



Prepared according to general procedure B using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), 3-benzyl-6-oxa-3-azabicyclo[3.1.0]hexane¹⁷ (175 mg, 1.0 mmol, 5.0 equiv.). Purification by flash column chromatography (30–35–40% EtOAc in Petrol) afforded the title product as a pale yellow solid (34.7 mg, 49%).

R_f (40% EtOAc in Petrol) = 0.24; **¹H NMR** (400 MHz, CDCl₃) 7.79 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.22 (m, 3H), 7.22 – 7.14 (m, 2H), 4.67 (app. dt, *J* = 6.0, 3.5 Hz, 1H), 3.65 – 3.52 (m, 3H), 3.39 (br. s, 1H), 2.97 (dd, *J* = 10.5, 8.5 Hz, 1H), 2.80 – 2.66 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 140.9, 137.5, 136.7, 130.1, 129.9, 128.8, 128.5, 127.6, 71.7, 71.5, 61.5, 59.3, 52.8; **LRMS** (ESI⁺) *m/z* 352.1 ([M+H]⁺), 703.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₁₇H₁₉O₃N³⁵ClS⁺ requires 352.0769 [M+H]⁺, found 352.0764; **IR** (thin film, ν_{max}/cm⁻¹) 3383, 1311, 1148, 1089, 756, 627; **m.p.** (CH₂Cl₂): 102–104 °C.

Casodex (3m)



4-Fluorophenylboronic acid (56.0 mg, 0.40 mmol, 1.0 equiv.), NiBr₂·(glyme) (12.3 mg, 0.04 mmol, 10 mol%), tmphen (9.5 mg, 0.04 mmol, 10 mol%), DABSO (57.7 mg, 0.24 mmol, 0.6 equiv.) and LiOt-Bu (32.0 mg, 0.40 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ (× 4). DMI (2.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. After cooling the solution to rt, aq. H₃PO₄ (6 mL, 2 M), brine (2 mL) and EtOAc (4 mL) were added to the reaction mixture. The two layers were separated and the aqueous phase was further extracted with EtOAc (2 × 4 mL). The combined organic phases were transferred to a 25 mL round-bottom flask and DIPEA (0.22 mL, 1.2 mmol, 3.0 equiv.) was added. The solution became cloudy after adding DIPEA, indicating the formation of sulfinate salt from sulfinic acid. The volatiles were removed under reduced pressure (< 20 mbar for at least 1 min). H₂O (1.2 mL) and *N*-(4-cyano-3-(trifluoromethyl)phenyl)-2-methyloxirane-2-carboxamide (54.0 mg, 0.20 mmol, 0.5 equiv.) were added. The reaction mixture was then stirred at 100 °C for 24 h. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (50% EtOAc in Petrol) afforded the product as a white solid (48.2 mg, 56%). (*Product yield was calculated based on the epoxide.*)

R_f (50% EtOAc in Petrol) = 0.33; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.38 (s, 1H), 8.43 (d, *J* = 2.0 Hz, 1H), 8.22 (dd, *J* = 8.5, 2.0 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.88 (m, 2H), 7.43 – 7.32 (m, 2H), 6.41 (s, 1H), 3.95 (d, *J* = 15.0 Hz, 1H), 3.72 (d, *J* = 15.0 Hz, 1H), 1.41 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 173.7, 164.9 (d, *J*_{CF} = 252.0 Hz), 143.2, 137.1 (d, *J*_{CF} = 3.0 Hz), 136.2, 131.41 (q, *J*_{CF} = 32.0 Hz), 131.38 (d, *J*_{CF} = 10.0 Hz), 122.9, 122.5 (q, *J*_{CF} = 273.5 Hz), 117.5 (q, *J*_{CF} = 5.0 Hz), 116.1 (d, *J*_{CF} = 23.0 Hz), 115.8, 101.9 (q, *J*_{CF} = 2.0 Hz), 73.1, 63.5, 27.2; ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -61.1, -105.6; HRMS (ESI⁻) *m/z* C₁₈H₁₃O₄N₂F₄S⁻ requires 429.0538 [M-H]⁻, found 429.0538.

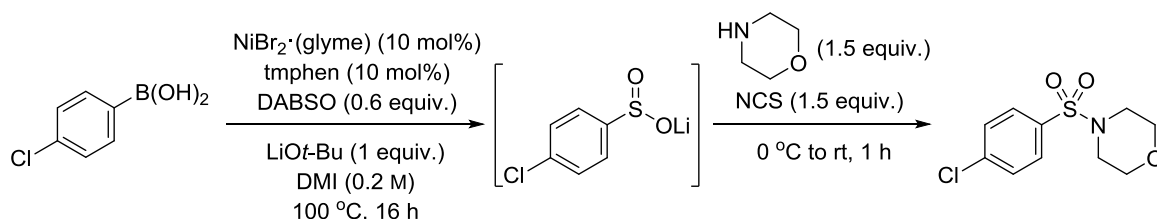
Data is consistent with the literature.¹⁸

Using the original general procedure B also gave the desired product, but with ca. 15% inseparable side product.

(See the notes in general procedure A and B)

3.4 General Procedure C: Two-step synthesis of substituted sulfonamides (exemplified by the preparation of sulfonamide **4a**)

4-((4-Chlorophenyl)sulfonyl)morpholine (4a)



4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N_2 ($\times 4$). DMI (1.0 mL) was added and the reaction mixture was heated at $100\text{ }^\circ\text{C}$ for 16 h. After cooling the solution to $0\text{ }^\circ\text{C}$, morpholine (26 μL , 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.) were added. The reaction mixture was then stirred at rt for 1 h. The reaction was diluted with water (10 mL) and extracted with EtOAc ($3 \times 10\text{ mL}$). The combined organic phases were dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a white solid (41.1 mg, 79%).

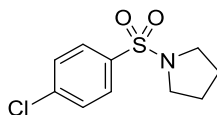
R_f (20% EtOAc in Petrol) = 0.20; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.5\text{ Hz}$, 2H), 7.52 (d, $J = 8.5\text{ Hz}$, 2H), 3.77 – 3.69 (m, 4H), 3.02 – 2.95 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 139.8, 133.8, 129.6, 129.3, 66.1, 46.0; **LRMS** (ESI^+) m/z 284.0 ($[\text{M}+\text{Na}]^+$), 545.0 ($[\text{2M}+\text{Na}]^+$).

Data is consistent with the literature.²

Note: replacing NCS with SO_2Cl_2 or aq. NaOCl also resulted the desired sulfonamide but with lower yield (50-60%).

(Also see the notes in general procedure A)

1-((4-Chlorophenyl)sulfonyl)pyrrolidine (4b)

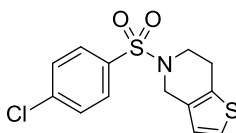


Prepared according to general procedure C using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), pyrrolidine (25 μL, 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as an off-white solid (35.2 mg, 72%).

R_f (20% EtOAc in Petrol) = 0.31; **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 3.26 – 3.20 (m, 4H), 1.80 – 1.74 (m, 4H); **¹³C NMR** (101 MHz, CDCl₃) δ 139.2, 135.7, 129.4, 129.0, 48.1, 25.4; **LRMS** (ESI⁺) *m/z* 246.0 ([M+H]⁺), 268.0 ([M+Na]⁺).

Data is consistent with the literature.¹⁹

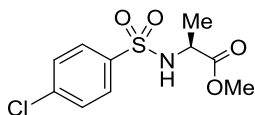
5-((4-Chlorophenyl)sulfonyl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (4c)



Prepared according to general procedure C using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), 4,5,6,7-tetrahydrothieno[3,2-c]pyridine (41.8 mg, 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (10% EtOAc in Petrol) afforded the title product as a white solid (49.4 mg, 79%).

R_f (10% EtOAc in Petrol) = 0.27; **¹H NMR** (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 5.0 Hz, 1H), 6.72 (d, *J* = 5.0 Hz, 1H), 4.23 (s, 2H), 3.45 (t, *J* = 5.5 Hz, 2H), 2.90 (t, *J* = 5.5 Hz, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 139.5, 135.5, 132.6, 130.4, 129.5, 129.0, 124.7, 123.9, 45.9, 44.0, 25.2; **LRMS** (ESI⁺) *m/z* 649.0 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₃H₁₃³⁵ClNO₂S₂⁺ requires 314.0071 [M+H]⁺, found 314.0071; **IR** (thin film, ν_{max}/cm⁻¹) 2918, 1346, 1166, 937, 763; **m.p.** (CH₂Cl₂): 180-181 °C.

Methyl ((4-chlorophenyl)sulfonyl)-L-alaninate (4d)

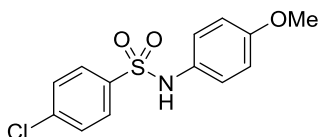


4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ (× 4). DMI (1.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. After cooling the solution at 0 °C, L-alanine methyl ester hydrochloride (41.6 mg, 0.30 mmol, 1.5 equiv.), DIPEA (70 μL, 0.40 mmol, 2.0 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.) were added. The reaction mixture was then stirred at rt for 1 h. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (30-40% EtOAc in Petrol) afforded the title product as a white solid (22.0 mg, 40%, >99% ee).

R_f (40% EtOAc in Petrol) = 0.50; **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 5.34 (d, *J* = 8.5 Hz, 1H), 4.00 (dq, *J* = 8.5, 7.0 Hz, 1H), 3.57 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 172.6, 139.5, 138.5, 129.5, 128.8, 52.8, 51.6, 20.0; **HRMS** (ESI⁺) *m/z* C₁₀H₁₂O₄N³⁵ClNaS⁺ requires 300.0068 [M+Na]⁺, found 300.0068; the **ee** was determined by HPLC using a Chiralpak IA-3 column (*n*-hexane/*i*-PrOH, 96:4); flow rate 1.0 mL/min; τ_{major} = 41.87 min, τ_{minor} = 45.65 min (>99% ee); [α]_D²⁵ +5.6° (*c* = 1.0, CHCl₃).

Data is consistent with the literature.²⁰

4-Chloro-*N*-(4-methoxyphenyl)benzenesulfonamide (4e)

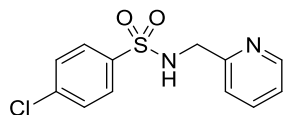


Prepared according to general procedure C using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), 4-methoxyaniline (36.9 mg, 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a brown solid (34.2 mg, 57%).

R_f (20% EtOAc in Petrol) = 0.23; **¹H NMR** (400 MHz, CDCl₃) δ 7.62 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.39 (s, 1H), 3.77 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 158.4, 139.5, 137.6, 129.4, 128.9, 128.5, 125.8, 114.7, 55.6; **HRMS** (ESI⁺) *m/z* C₁₃H₁₂O₃N³⁵ClNaS⁺ requires 320.0119 [M+Na]⁺, found 320.0120.

Data is consistent with the literature.²¹

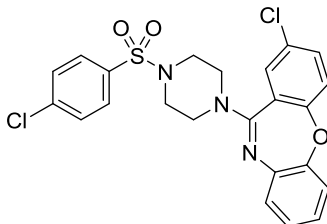
4-Chloro-*N*-(pyridin-2-ylmethyl)benzenesulfonamide (4f)



Prepared according to general procedure C using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), 2-pyridinylmethanamine (31 μL, 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (60% EtOAc in Petrol) afforded the title product as an off-white solid (32.6 mg, 58%).

R_f (60% EtOAc in Petrol) = 0.24; **¹H NMR** (400 MHz, CDCl₃) δ 8.43 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.60 (app. td, *J* = 7.5, 2.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.12 (m, 2H), 6.42 (t, *J* = 5.0 Hz, 1H), 4.26 (d, *J* = 5.0 Hz, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.7, 149.1, 139.1, 138.4, 137.0, 129.3, 128.7, 122.9, 122.2, 47.5; **HRMS** (ESI⁺) *m/z* C₁₂H₁₂O₂N₂³⁵ClS⁺ requires 283.0303 [M+H]⁺, found 283.0301; **IR** (thin film, ν_{max}/cm⁻¹) 2981, 2360, 1332, 1161, 1094, 753; **m.p.** (CH₂Cl₂): 118-119 °C.

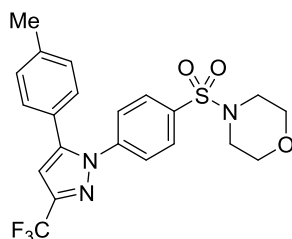
2-Chloro-11-(4-((4-chlorophenyl)sulfonyl)piperazin-1-yl)dibenzo[*b,f*][1,4]oxazepine (4g)



Prepared according to general procedure C using 4-chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), amoxapine (94.1 mg, 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (30% Et₂O in Petrol) afforded the title product as a colourless viscous oil which solidified in a freezer to an off-white solid (49.1 mg, 50%).

R_f (30% Et₂O in Petrol) = 0.26; **¹H NMR** (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.39 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.12 – 7.05 (m, 3H), 7.03 – 6.97 (m, 1H), 3.63 (s, 4H), 3.14 (s, 4H); **¹³C NMR** (101 MHz, CDCl₃) δ 159.4, 158.3, 151.7, 139.9, 139.7, 134.4, 133.0, 130.6, 129.8, 129.2, 128.8, 127.2, 126.0, 125.2, 124.6, 123.0, 120.3, 46.9, 45.7; **LRMS** (ESI⁺) *m/z* 488.1 ([M+H]⁺), 975.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₂₃H₂₀O₃N₃³⁵Cl₂S⁺ requires 488.0597 [M+H]⁺, found 488.0596; **IR** (thin film, ν_{max}/cm⁻¹) 2981, 1587, 1471, 1353, 1167, 944, 761; **m.p.** (CH₂Cl₂): 209-211 °C.

4-((4-(5-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)morpholine (4h)

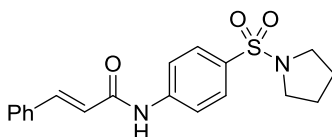


Prepared according to general procedure C using 4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenylboronic acid (69.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), morpholine (26 μL, 0.30 mmol, 1.5 equiv.) and NCS (40.1 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (20% EtOAc in Petrol) afforded the title product as a white solid (66.7 mg, 74%).

R_f (20% EtOAc in Petrol) = 0.29; **¹H NMR** (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 3.77 – 3.69 (m, 4H), 3.03 – 2.94 (m, 4H), 2.38 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 145.4, 144.3 (q, *J*_{CF} = 38.5 Hz), 143.0, 140.0, 134.8, 129.9, 128.9, 128.8, 125.69, 125.66, 121.1 (q, *J*_{CF} = 269.0 Hz), 106.5, 66.1, 46.0, 21.4; **¹⁹F NMR** (377 MHz, CDCl₃) δ -62.4; **LRMS** (ESI⁺) *m/z* 452.1 ([M+H]⁺), 903.2 ([2M+H]⁺); **HRMS** (ESI⁺) *m/z* C₂₁H₂₁F₃N₃O₃S⁺ requires 452.1250 [M+H]⁺, found 452.1244; **IR** (thin film, ν_{max}/cm⁻¹) 1472, 1353, 1236, 1163, 1113, 944, 765, 731.

Data is consistent with the literature.²

N-(4-(Pyrrolidin-1-ylsulfonyl)phenyl)cinnamamide, NP16 (4i)

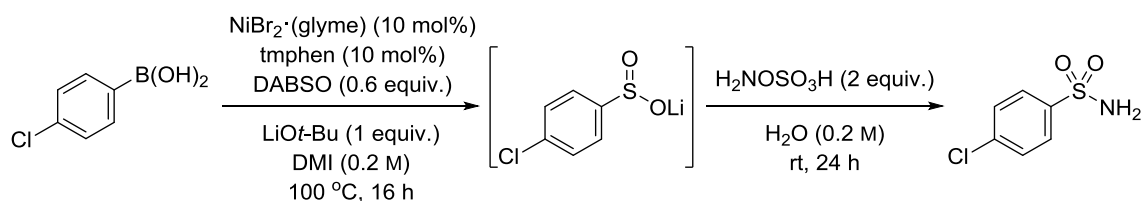


Prepared according to general procedure C using 4-cinnamamidophenylboronic acid (53.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) pyrrolidine (34 μL, 0.40 mmol, 2.0 equiv.) and NCS (53.4 mg, 0.40 mmol, 2.0 equiv.). Purification by flash column chromatography (50% EtOAc in Petrol) afforded the title product as a pale yellow viscous oil which solidified on-standing to an off-white solid. (47.2 mg, 66%).

R_f (50% EtOAc in Petrol) = 0.38; **¹H NMR** (400 MHz, CDCl₃) δ 8.59 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.80 – 7.73 (m, 3H), 7.52 – 7.47 (m, 2H), 7.38 – 7.30 (m, 3H), 6.72 (d, *J* = 15.5 Hz, 1H), 3.27 – 3.15 (m, 4H), 1.76 – 1.66 (m, 4H); **¹³C NMR** (101 MHz, CDCl₃) 164.8, 143.5, 142.7, 134.5, 131.2, 130.4, 129.0, 128.8, 128.2, 120.5, 119.7, 48.2, 25.3; **LRMS** (ESI⁺) *m/z* 713.2 ([2M+H]⁺), 735.2 ([2M+Na]⁺); **HRMS** (ESI⁺) *m/z* C₁₉H₂₁O₃N₂S⁺ requires 357.1267 [M+H]⁺, found 357.1268; **IR** (thin film, ν_{max}/cm⁻¹) 3340, 1694, 1629, 1591, 1531, 1335, 1150; **m.p.** (CH₂Cl₂): 244-245 °C.

3.5 General Procedure D: Two-step synthesis of primary sulfonamides (exemplified by the preparation of sulfonamide **4j**)

4-Chlorobenzenesulfonamide (4j)



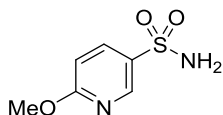
4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N_2 ($\times 4$). DMI (1.0 mL) was added and the reaction mixture was heated at $100\text{ }^\circ\text{C}$ for 16 h. After cooling the solution to rt, hydroxylamine-O-sulfonic acid (45.2 mg, 0.40 mmol, 2.0 equiv.) and H_2O (1.0 mL) were added. The reaction mixture was then stirred at rt for 24 h. The reaction was quenched with sat. NaHCO_3 (10 mL) (caution: gas formation) and extracted with EtOAc ($3 \times 10\text{ mL}$). The combined organic phases were dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography (35% EtOAc in Pentane) afforded the product as a white solid (28.7 mg, 75%).

R_f (35% EtOAc in Pentane) = 0.29; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.83 (d, $J = 8.5\text{ Hz}$, 2H), 7.65 (d, $J = 8.5\text{ Hz}$, 2H), 7.45 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 143.0, 136.5, 129.0, 127.6; **LRMS** (ESI^+) m/z 209.0 ($[\text{M}+\text{NH}_4]^+$), 405.0 ($[\text{2M}+\text{Na}]^+$).

Data is consistent with the literature.²²

(Also see the notes in general procedure A)

6-Methoxypyridine-3-sulfonamide (4k)

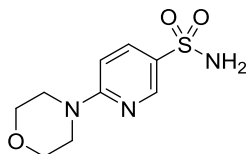


Prepared according to general procedure D using 6-methoxy-3-pyridinylboronic acid (30.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), hydroxylamine-*O*-sulfonic acid (45.2 mg, 0.40 mmol, 2.0 equiv.). Purification by flash column chromatography (50% EtOAc in Petrol) afforded the title product as an off-white solid (26.6 mg, 71%).

R_f (50% EtOAc in Petrol) = 0.31; **¹H NMR** (400 MHz, DMSO-*d*₆) δ 8.57 (dd, *J* = 2.5, 0.5 Hz, 1H), 8.06 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.44 (s, 2H), 7.00 (dd, *J* = 9.0, 0.5 Hz, 1H), 3.92 (s, 3H); **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 165.2, 145.2, 137.0, 133.9, 111.0, 54.0; **LRMS** (ESI⁺) *m/z* 189.0 ([M+H]⁺), 399.0 ([2M+Na]⁺); **HRMS** (ESI⁻) *m/z* C₆H₇N₂O₃S⁻ requires 187.0183 [M-H]⁻; found 187.0183; **IR** (thin film, ν_{max}/cm⁻¹) 3334, 3233, 2981, 2361, 1589, 1481, 1337, 1306, 1160, 741.

Data is consistent with the literature.²³

6-Morpholinopyridine-3-sulfonamide (4l)

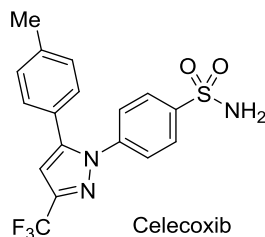


Prepared according to general procedure D using 6-(morpholino)pyridine-3-boronic acid (41.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), hydroxylamine-*O*-sulfonic acid (45.2 mg, 0.40 mmol, 2.0 equiv.). Purification by flash column chromatography (80% EtOAc in Petrol) afforded the title product as a yellow solid (33.7 mg, 69%).

R_f (80% EtOAc in Petrol) = 0.30; **¹H NMR** (400 MHz, DMSO-*d*₆) δ 8.46 (d, *J* = 2.5 Hz, 1H), 7.85 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.22 (s, 2H), 6.94 (d, *J* = 9.0 Hz, 1H), 3.71 – 3.65 (m, 4H), 3.60 – 3.55 (m, 4H); **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 159.8, 145.8, 135.3, 128.7, 106.0, 65.8, 44.7; **LRMS** (ESI⁺) *m/z* 244.1 ([M+H]⁺), 487.2 ([2M+H]⁺); **HRMS** (ESI⁻) *m/z* C₉H₁₂N₃O₃S⁻ requires 242.0605 [M-H]⁻; found 242.0607; **IR** (thin film, ν_{max}/cm⁻¹) 3252, 2361, 1591, 1309, 1148, 1112, 943, 606.

Data is consistent with the literature.²⁴

Celecoxib (4m)



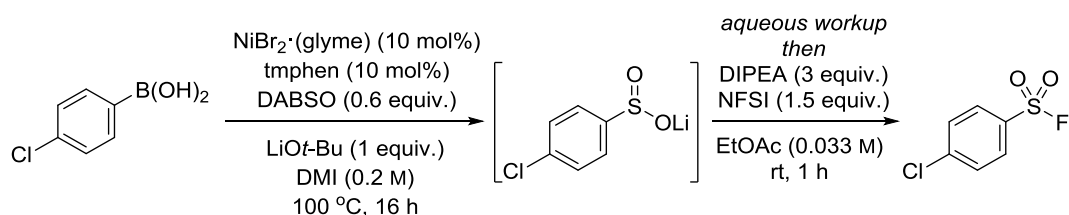
(4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)boronic acid (69.3 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N₂ four times. DMI (1.0 mL) was added and the reaction mixture was heated at 100 °C for 16 h. After cooling the solution at rt, hydroxylamine-*O*-sulfonic acid (113 mg, 1.0 mmol, 5.0 equiv) and H₂O (1.0 mL) were added. The reaction mixture was then stirred at 60 °C for 2 h. The reaction was quenched with sat. NaHCO₃ (10 mL) (caution: gas formation) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (Na₂SO₄), filtered and concentrated. Purification by flash column chromatography (25-30% EtOAc in Petrol) afforded the product as an off-white solid (42.9 mg, 56%).

R_f (30% EtOAc in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 5.11 (s, 2H), 2.37 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 145.4, 144.2 (q, *J*_{CF} = 38.5 Hz), 142.7, 141.4, 140.0, 129.9, 128.9, 127.6, 125.8, 125.6, 121.2 (q, *J*_{CF} = 269.5 Hz), 106.49, 21.47; **¹⁹F NMR** (377 MHz, CDCl₃) δ -62.4; **LRMS** (ESI⁺) *m/z* 382.1 ([M+H]⁺), 763.2 ([2M+H]⁺).

Data is consistent with the literature.²⁵

3.6 General Procedure E: Two-step synthesis of sulfonyl fluorides (exemplified by the preparation of sulfonyl fluoride **5a**)

4-Chlorobenzenesulfonyl fluoride (**5a**)



4-Chlorophenylboronic acid (31.3 mg, 0.20 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (6.1 mg, 0.02 mmol, 10 mol%), *tmphen* (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.) and LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N_2 four times. DMI (1.0 mL) was added and the reaction mixture was heated at $100\text{ }^\circ\text{C}$ for 16 h. After cooling the solution to rt, aq. H_3PO_4 (3 mL, 2 M) and brine (1 mL) were added to the mixture. The mixture was then extracted with EtOAc (3×2 mL). The combined organic phase was transferred to a 25 mL round-bottom flask and was added DIPEA (0.11 mL, 0.60 mmol, 3.0 equiv.). The solution became cloudy after adding DIPEA indicating the formation of sulfinate salt from sulfinic acid. NFSI (95 mg, 0.30 mmol, 1.5 equiv.) was added to the mixture, flushed with N_2 and sealed. The reaction mixture was then stirred at rt for 1 h. Without further workup, the reaction mixture was dry-loaded to silica gel which was then purified by flash column chromatography (10% CH_2Cl_2 in Petrol) to afford the product as a colourless oil (18.6 mg, 48%).

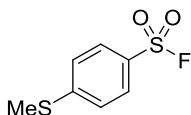
R_f (10% CH_2Cl_2 in Petrol) = 0.27; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 – 7.92 (m, 2H), 7.66 – 7.58 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.8, 131.6 (d, $J_{\text{CF}} = 26.0$ Hz), 130.3, 130.0; $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ 66.5.

Data is consistent with the literature.²⁶

Note: Fluorination without aqueous workup in step 2 resulted in much lower yields (20-30%), possibly due to the intolerance of sulfonyl fluorides with strong base such as LiOt-Bu . Hence, an aqueous workup, previously adopted by Pfizer,²⁷ is required to achieve good yields of sulfonyl fluorides.

(Also see the notes in general procedure A)

4-(Methylthio)benzenesulfonyl fluoride (5b)

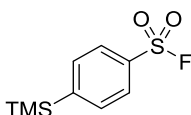


Prepared according to general procedure E using 4-(methylthio)phenylboronic acid (33.6 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), NFSI (95 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (5% EtOAc in Petrol) afforded the title product as a white solid (28.5 mg, 69%).

R_f (5% EtOAc in Petrol) = 0.29; **¹H NMR** (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.55 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 150.4, 128.7, 128.1 (d, *J*_{CF} = 24.5 Hz), 125.5, 14.8; **¹⁹F NMR** (377 MHz, CDCl₃) δ 66.9.

Data is consistent with the literature.²⁶

4-(Trimethylsilyl)benzenesulfonyl fluoride (5c)

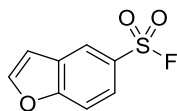


Prepared according to general procedure E using 4-(trimethylsilyl)phenylboronic acid (38.8 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), NFSI (63 mg, 0.20 mmol, 1.0 equiv.). Purification by flash column chromatography (10% CH₂Cl₂ in Petrol) afforded the title product as a pale yellow oil (27.7 mg, 60%).

R_f (10% CH₂Cl₂ in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.77 (app. dd, *J* = 8.5, 1.0 Hz, 2H), 0.33 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 151.3, 134.5, 133.2 (d, *J*_{CF} = 24.0 Hz), 127.2, -1.4; **¹⁹F NMR** (377 MHz, CDCl₃) δ 65.9.

Data is consistent with the literature.²⁶

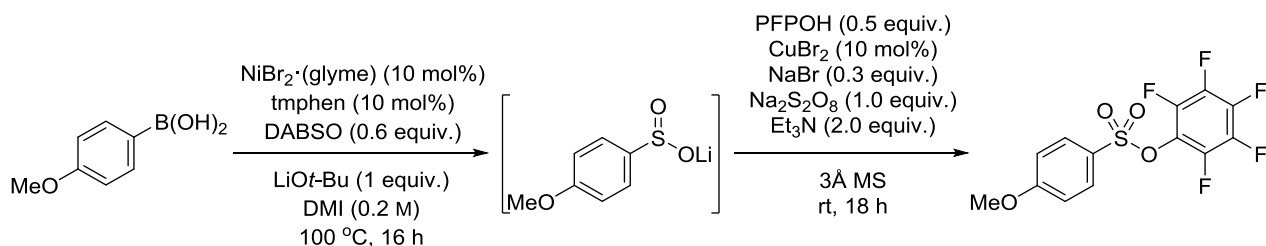
Benzofuran-5-sulfonyl fluoride (5d)



Prepared according to general procedure E using benzofuran-5-ylboronic acid (32.4 mg, 0.20 mmol, 1.0 equiv.), NiBr₂·(glyme) (6.1 mg, 0.02 mmol, 10 mol%), tmphen (4.7 mg, 0.02 mmol, 10 mol%), DABSO (28.8 mg, 0.12 mmol, 0.6 equiv.), LiOt-Bu (16.0 mg, 0.20 mmol, 1.0 equiv.), NFSI (95 mg, 0.30 mmol, 1.5 equiv.). Purification by flash column chromatography (5% EtOAc in Petrol) afforded the title product as a colourless oil (21.9 mg, 55%).

R_f (5% EtOAc in Petrol) = 0.30; **¹H NMR** (400 MHz, CDCl₃) δ 8.34 (d, *J* = 2.0 Hz, 1H), 7.96 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.72 (app. dq, *J* = 9.0, 1.0 Hz, 1H), 6.95 (dd, *J* = 2.5, 1.0 Hz, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 158.2, 148.2, 128.4, 127.6 (d, *J*_{CF} = 24.5 Hz), 124.5, 123.4, 113.0, 107.3; **¹⁹F NMR** (377 MHz, CDCl₃) δ 67.9; **HRMS** (APCI⁻) *m/z* C₈H₄O₃FS⁻ requires 198.9871 [M-H]⁻; found 198.9868; **IR** (thin film, ν_{max}/cm⁻¹) 2922, 2360, 1405, 1257, 1212, 1174, 764.

3.7 Preparation of perfluorophenyl 4-methoxybenzenesulfonate (6)



Procedure for step 2 was adopted from a publication from our group,⁴ with a slightly different workup procedure.

4-Methoxyphenylboronic acid (76.0 mg, 0.50 mmol, 1.0 equiv.), $\text{NiBr}_2 \cdot (\text{glyme})$ (15.4 mg, 0.05 mmol, 10 mol%), tmphen (11.8 mg, 0.05 mmol, 10 mol%), DABSO (72.1 mg, 0.30 mmol, 0.6 equiv.) and LiOt-Bu (40.0 mg, 0.50 mmol, 1.0 equiv.) were added to a 10 mL reaction vial. The vial was then sealed with a rubber septum, evacuated and filled with N_2 ($\times 4$). DMI (2.5 mL) was added and the reaction mixture was heated at $100\text{ }^\circ\text{C}$ for 16 h. After cooling the solution to rt , pentafluorophenol (46 mg, 0.25 mmol, 0.5 equiv.) (*note 1*), CuBr_2 (11.2 mg, 0.05 mmol, 10 mol%), $\text{Na}_2\text{S}_2\text{O}_8$ (119 mg, 0.50 mmol, 1.0 equiv.), NaBr (15.5 mg, 0.15 mmol, 0.30 equiv.), 3 Å molecular sieves (*ca.* 250 mg) (*note 2*) and Et_3N (140 μL , 1 mmol, 2.0 equiv.) were added. The reaction vial was resealed under air and was stirred at rt for 18 h. The reaction was filtered through a plug of silica and washed with Et_2O and water (*ca.* 10 mL each). The two layers were separated and the aqueous phase was extracted with Et_2O ($2 \times 10\text{ mL}$). The combined organic phases were washed with aq. Na_2CO_3 ($2 \times 15\text{ mL}$, 1M) (*note 3*), dried (Na_2SO_4), filtered and concentrated. Purification by flash column chromatography (20% Et_2O in Petrol) afforded the title product as a pale yellow oil (36.5 mg, 52%). (*Product yield was calculated based on the pentafluorophenol.*)

R_f (20% Et_2O in Petrol) = 0.29; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (d, $J = 9.0\text{ Hz}$, 2H), 7.05 (d, $J = 9.0\text{ Hz}$, 2H), 3.93 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 165.2, 142.4 (app. ddq, $J = 257.5, 12.0, 3.5\text{ Hz}$), 140.3 (app. dtt, $J = 255.5, 13.5, 4.0\text{ Hz}$), 138.0 (app. dtdd, $J = 253.5, 14.5, 5.5, 3.0\text{ Hz}$), 131.1, 125.9, 124.4 (app. tdt, $J = 14.3, 5.0, 2.0\text{ Hz}$), 114.9, 56.0; $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -150.7, -155.7, -161.2; **LRMS** (ESI^+) m/z 377.0 ($[\text{M}+\text{Na}]^+$), 731.0 ($[\text{2M}+\text{Na}]^+$).

Data is consistent with the literature.⁴

Note:

1. Pentafluorophenol (mp $34\text{--}36\text{ }^\circ\text{C}$) always melts while weighing to form a mixture of liquid and solid. Hence, it is advised to add pentafluorophenol by the following procedure: using a glass pipette to transfer a small amount of the reaction mixture from step 1 to a small vial containing pentafluorophenol (caution: a white fume formed). The solution containing pentafluorophenol was then transferred back to the mother liquid in the 10 mL reaction vial. These were done for another two times to ensure a quantitative transfer of the pentafluorophenol. (Adding warmed and melted pentafluorophenol using a syringe is not advised as it may solidify in the syringe and cause blockage.)

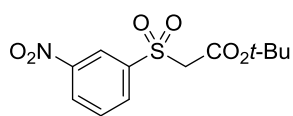
2. The molecular sieves were activated at ca. 200 °C under vacuum (< 1 mbar) overnight, crushed to powder and stored in 200 °C oven.

3. The aq. Na₂CO₃ removes any remaining pentafluorophenol which may coelute with the desired product on flash column chromatography. (pK_{aH} of CO₃²⁻: 3.7; pK_a of pentafluorophenol: 5.5)

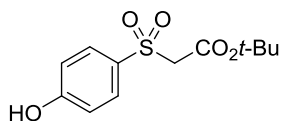
(Also see the notes in general procedure A)

3.8 Low Yielding/Unsuccessful Substrate Scope

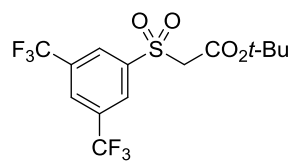
Sulfones (using general procedure A)



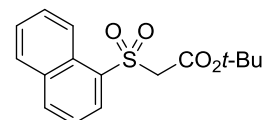
ca. 32% isolated



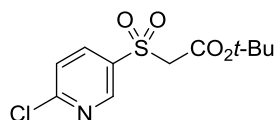
ca. 24% isolated



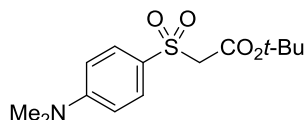
(NMR: 18% product)



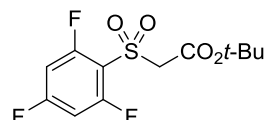
(NMR: 15-18%)



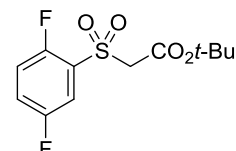
(NMR: 8% product)



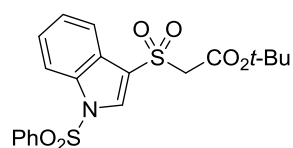
(NMR: no product)



(NMR no product)

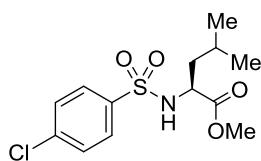


(NMR: no product)

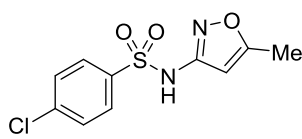


(NMR/MS: no product)

Sulfonamides (using general procedure C)

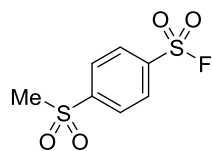


ca. 33% isolated

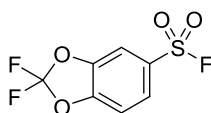


ca. 26% isolated

Sulfonyl fluorides (using general procedure E)



ca. 37% isolated



ca. 16% isolated

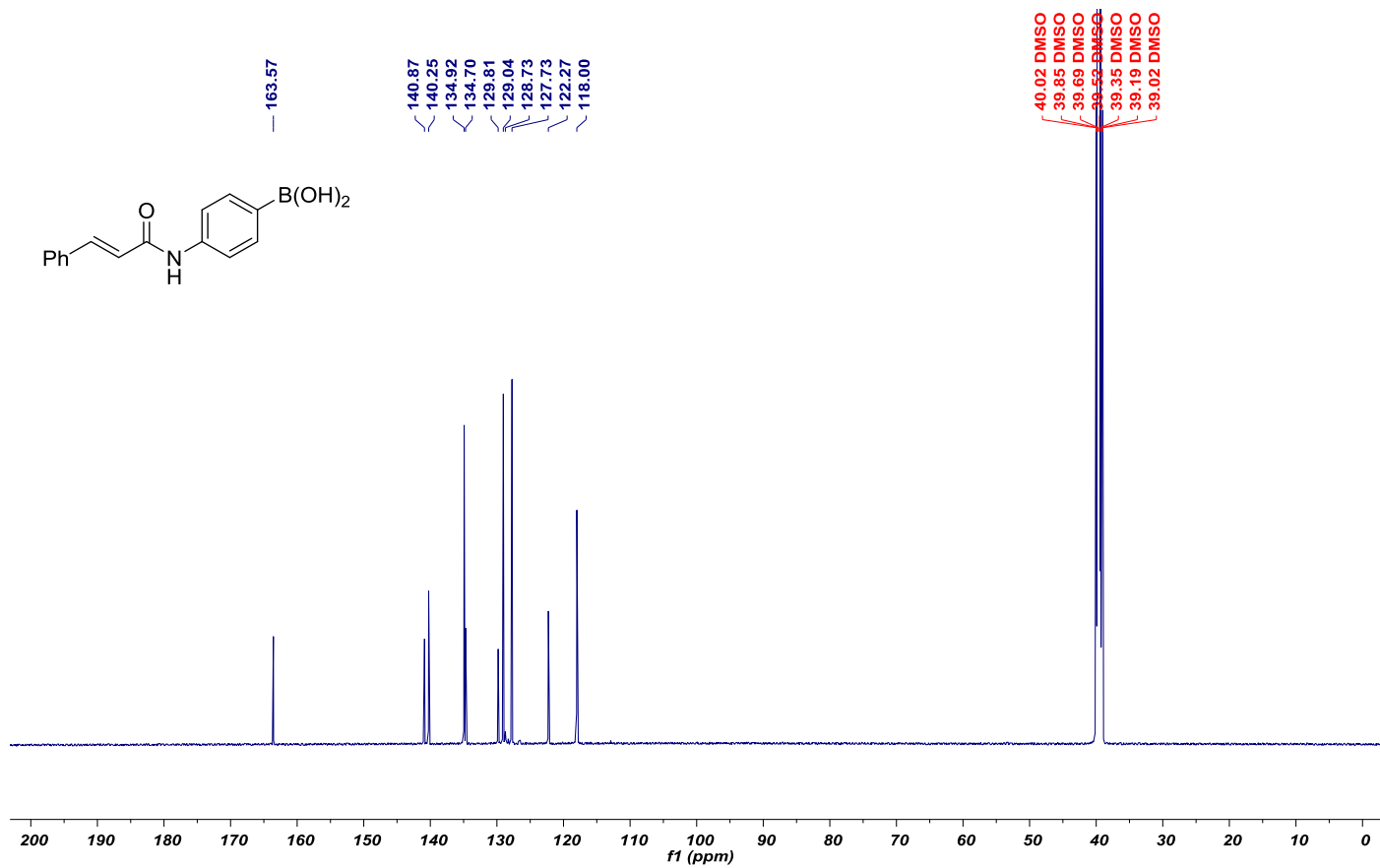
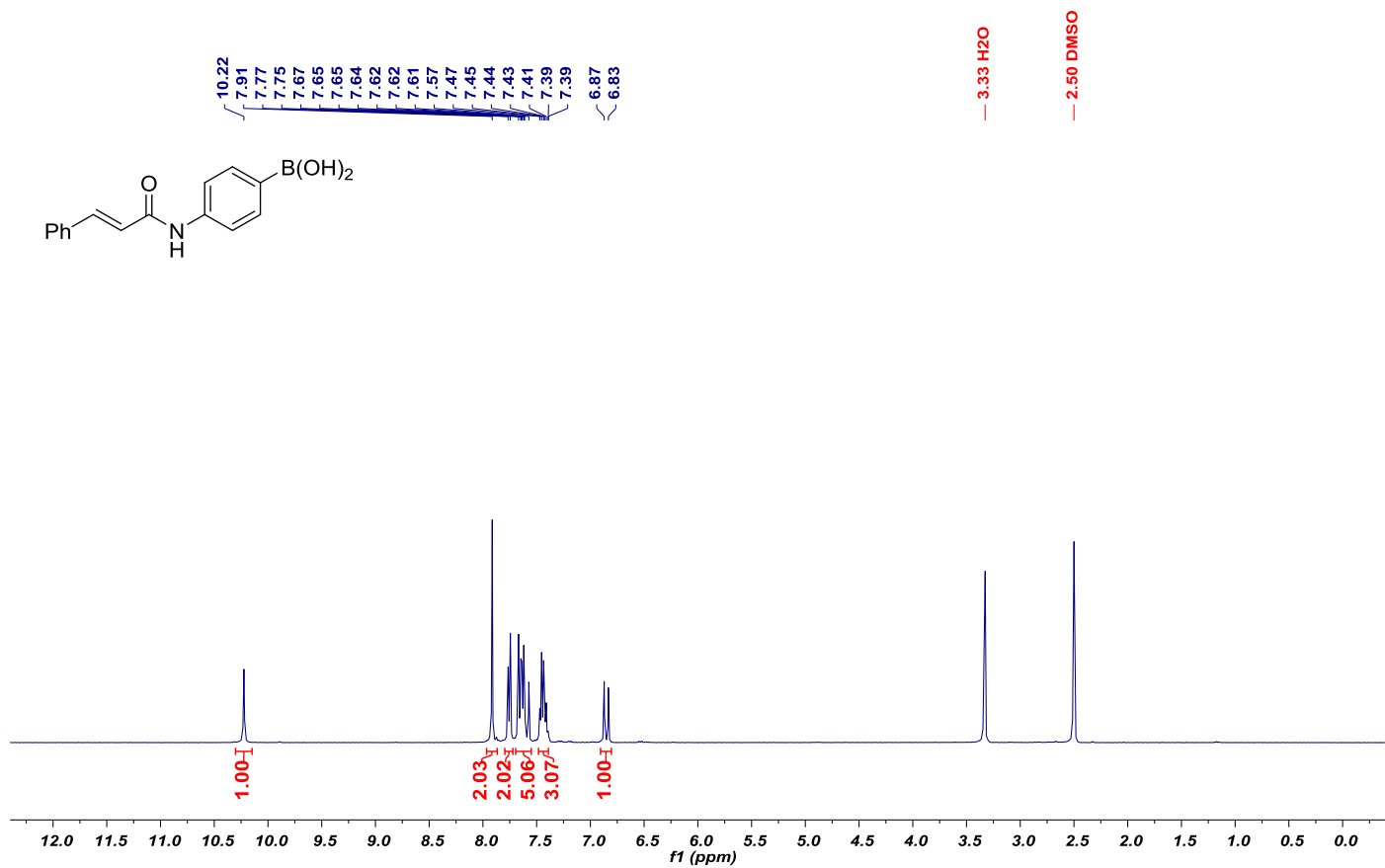
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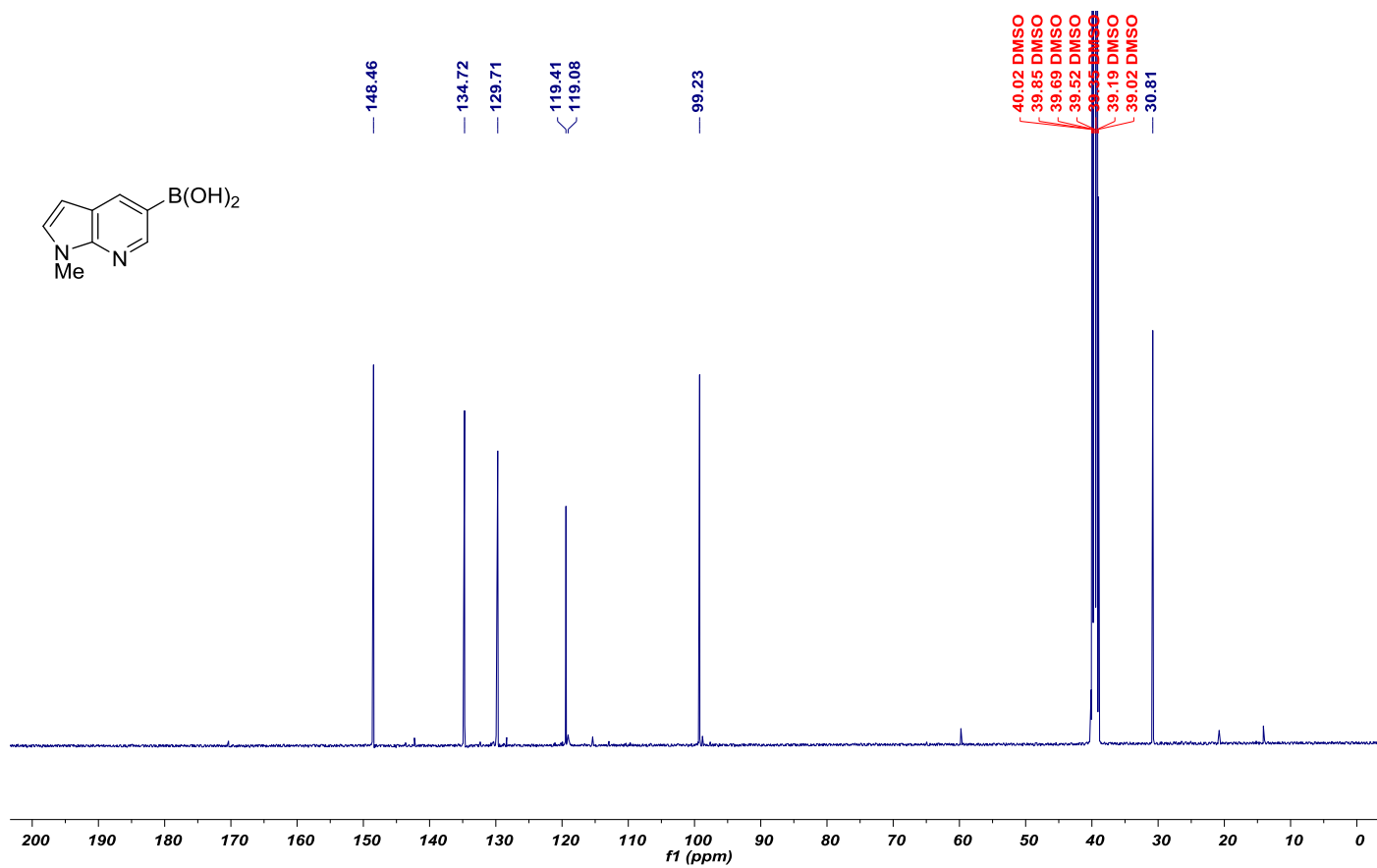
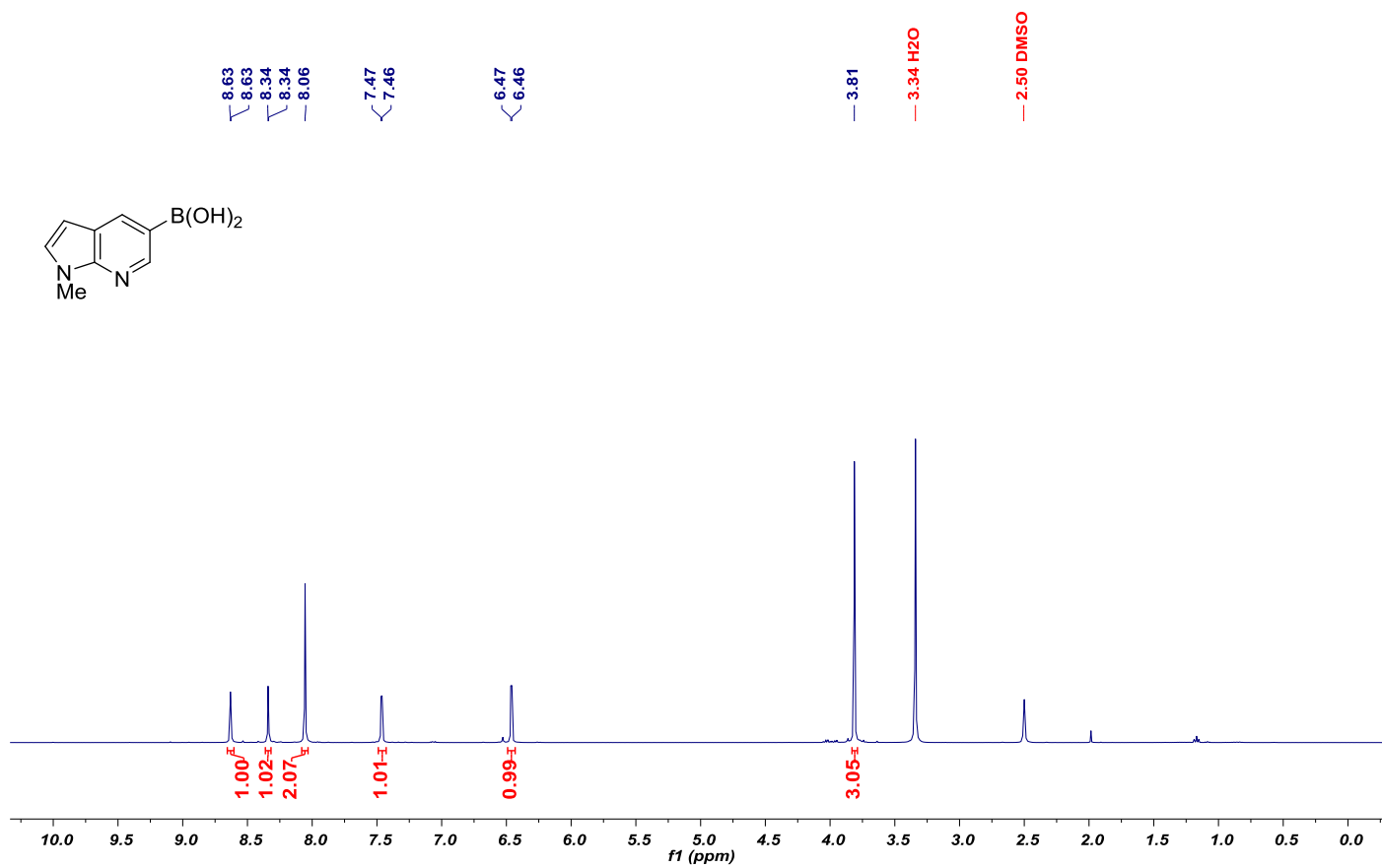
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5. NMR Spectra

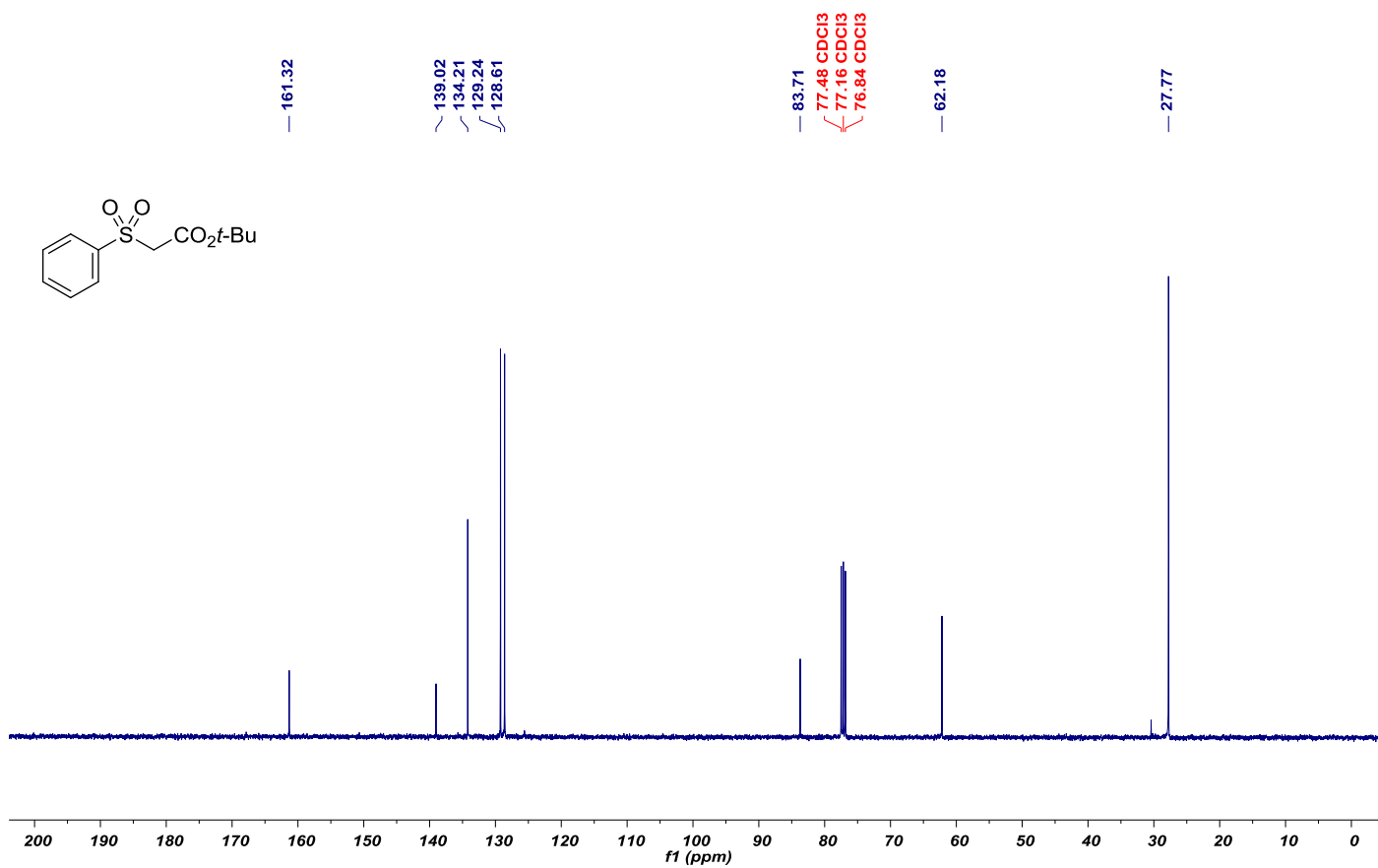
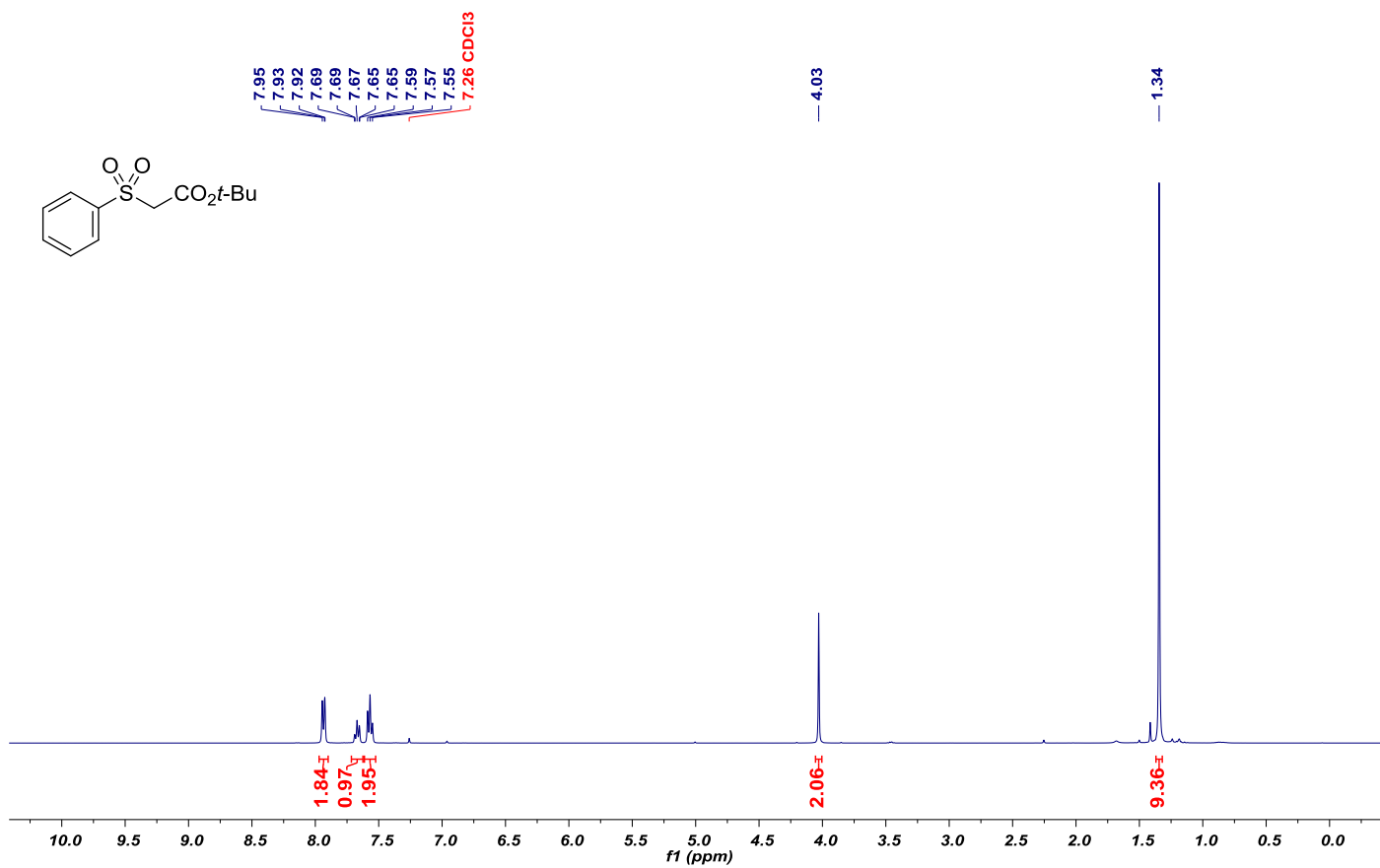
NMR spectrum of (4-cinnamamidophenyl)boronic acid



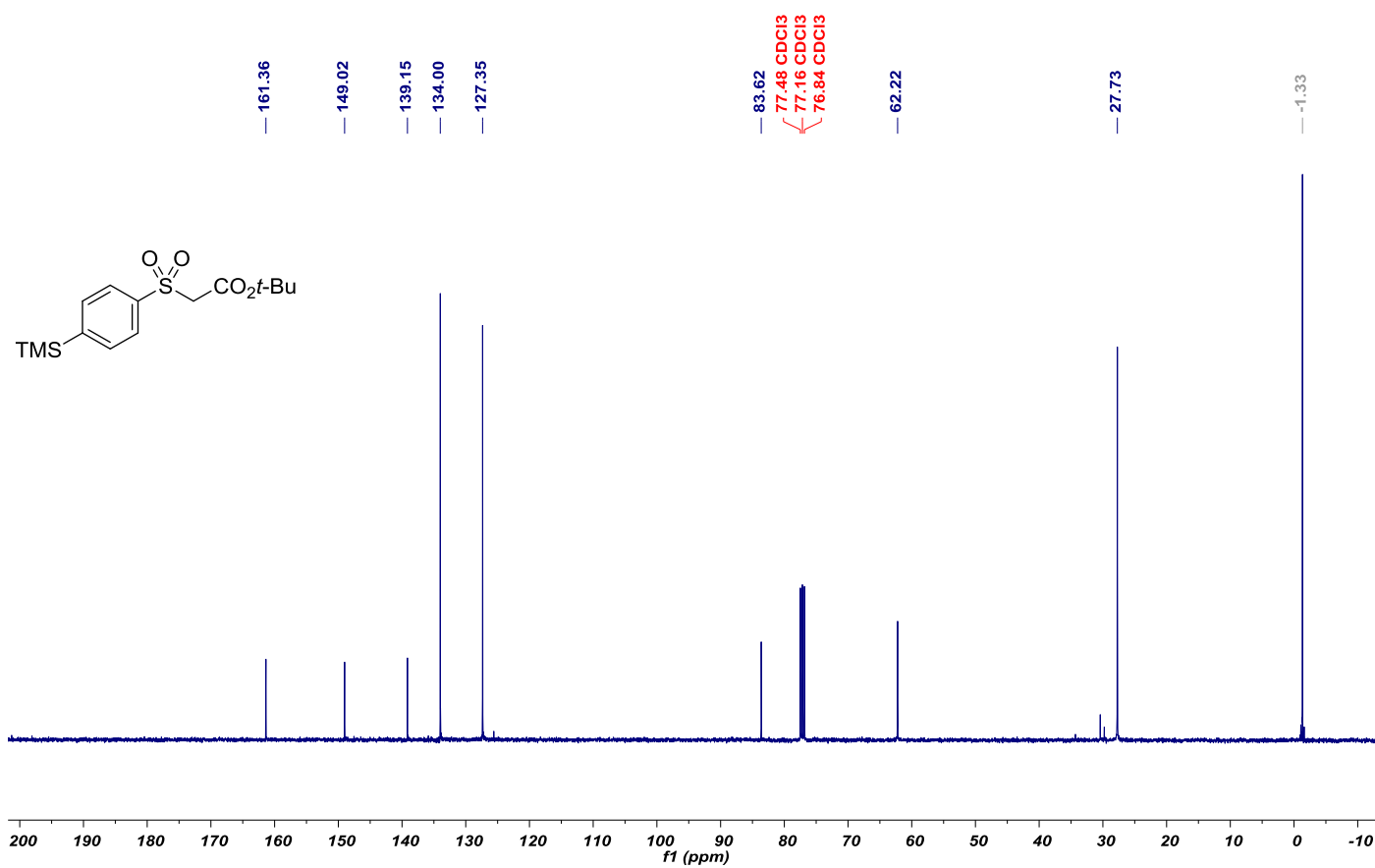
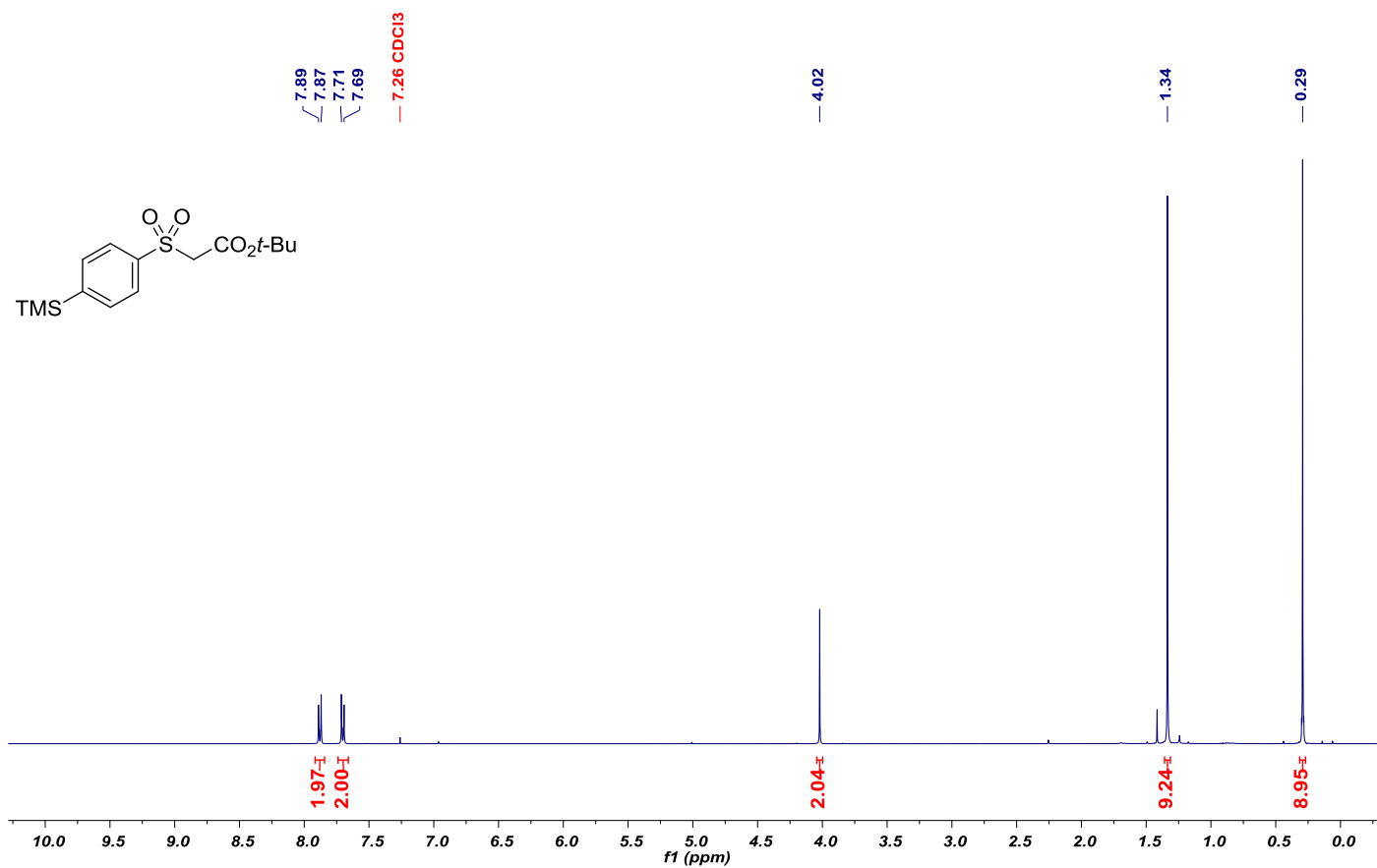
NMR spectrum of (1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)boronic acid



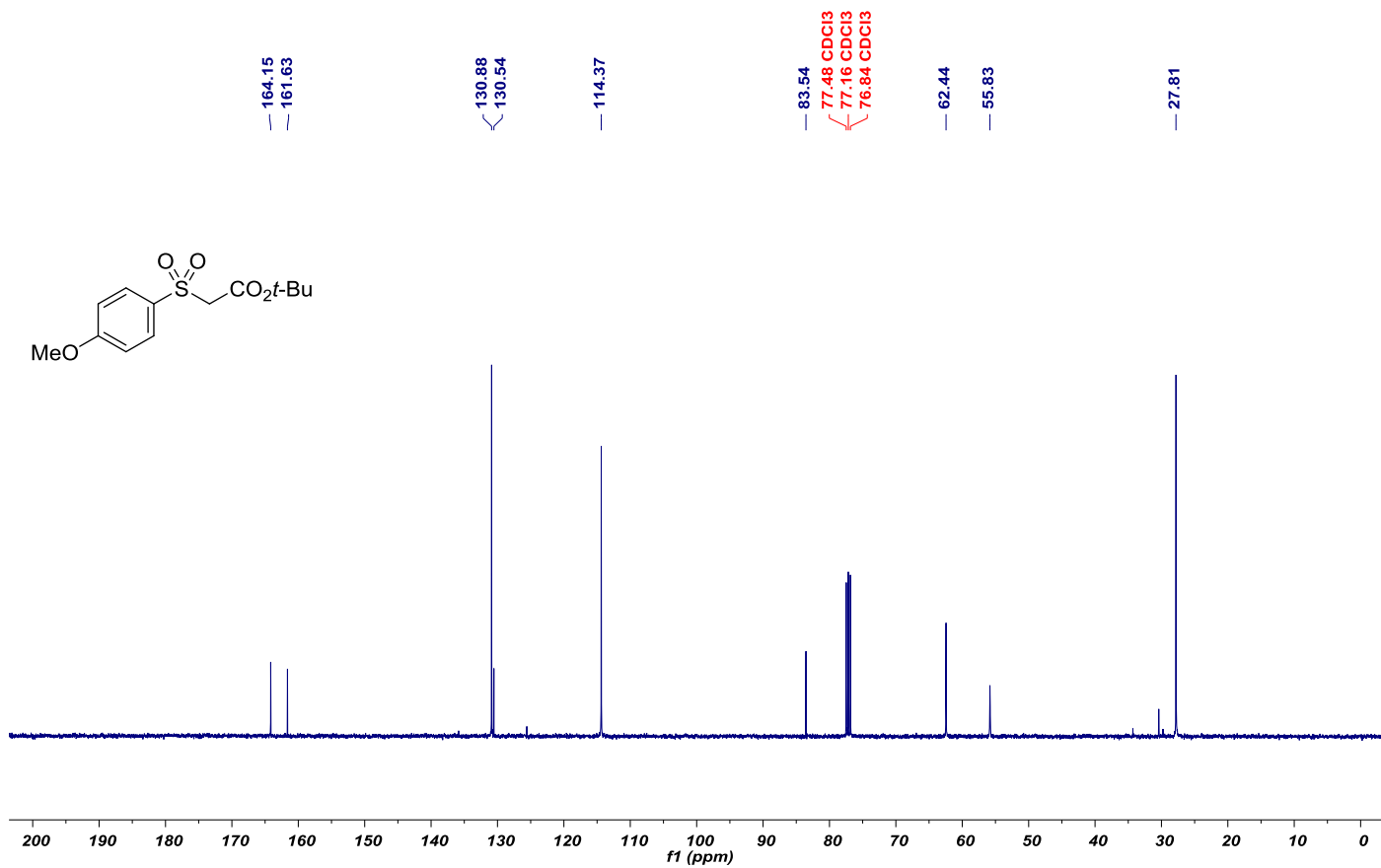
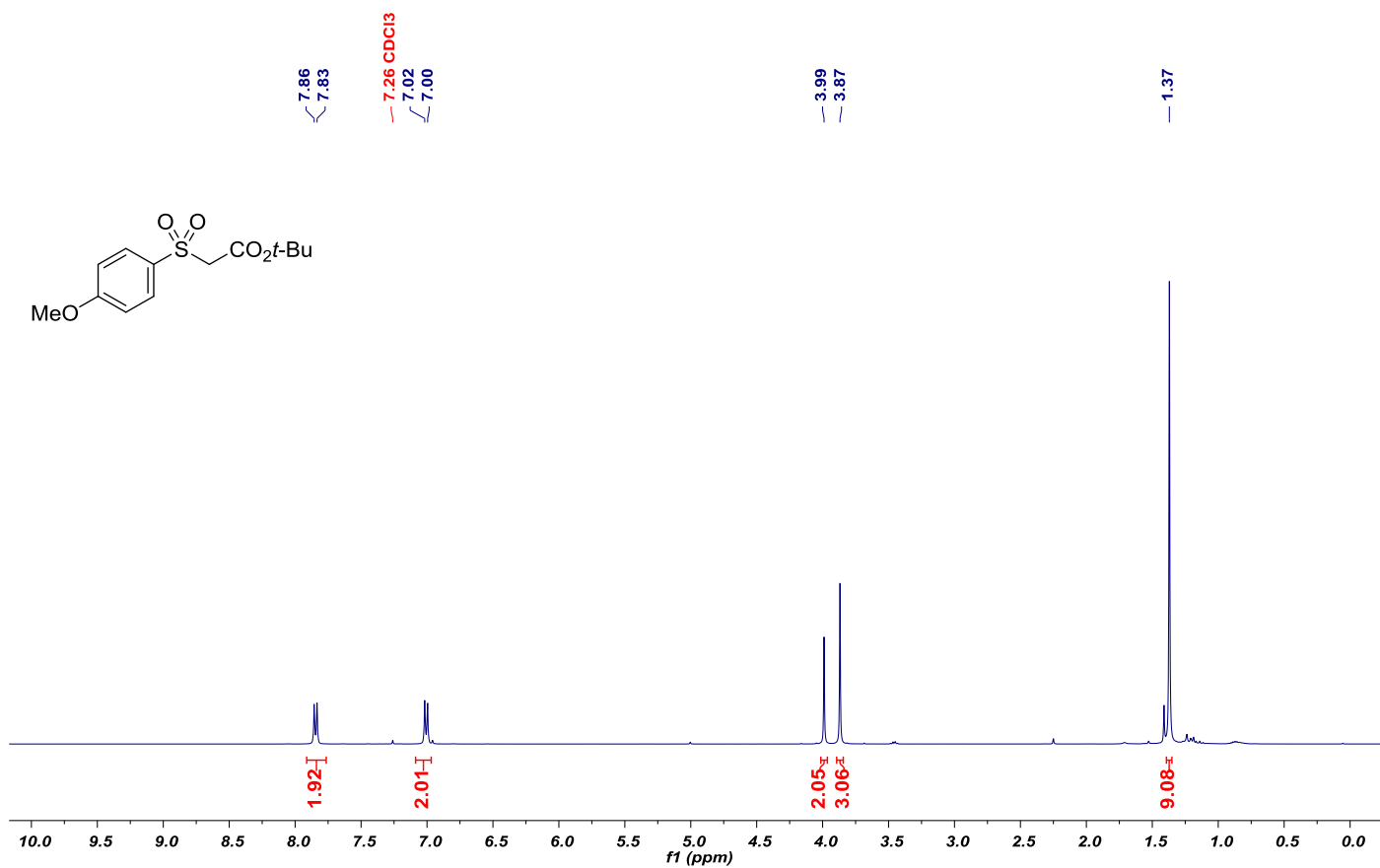
NMR spectrum of sulfone **2a**



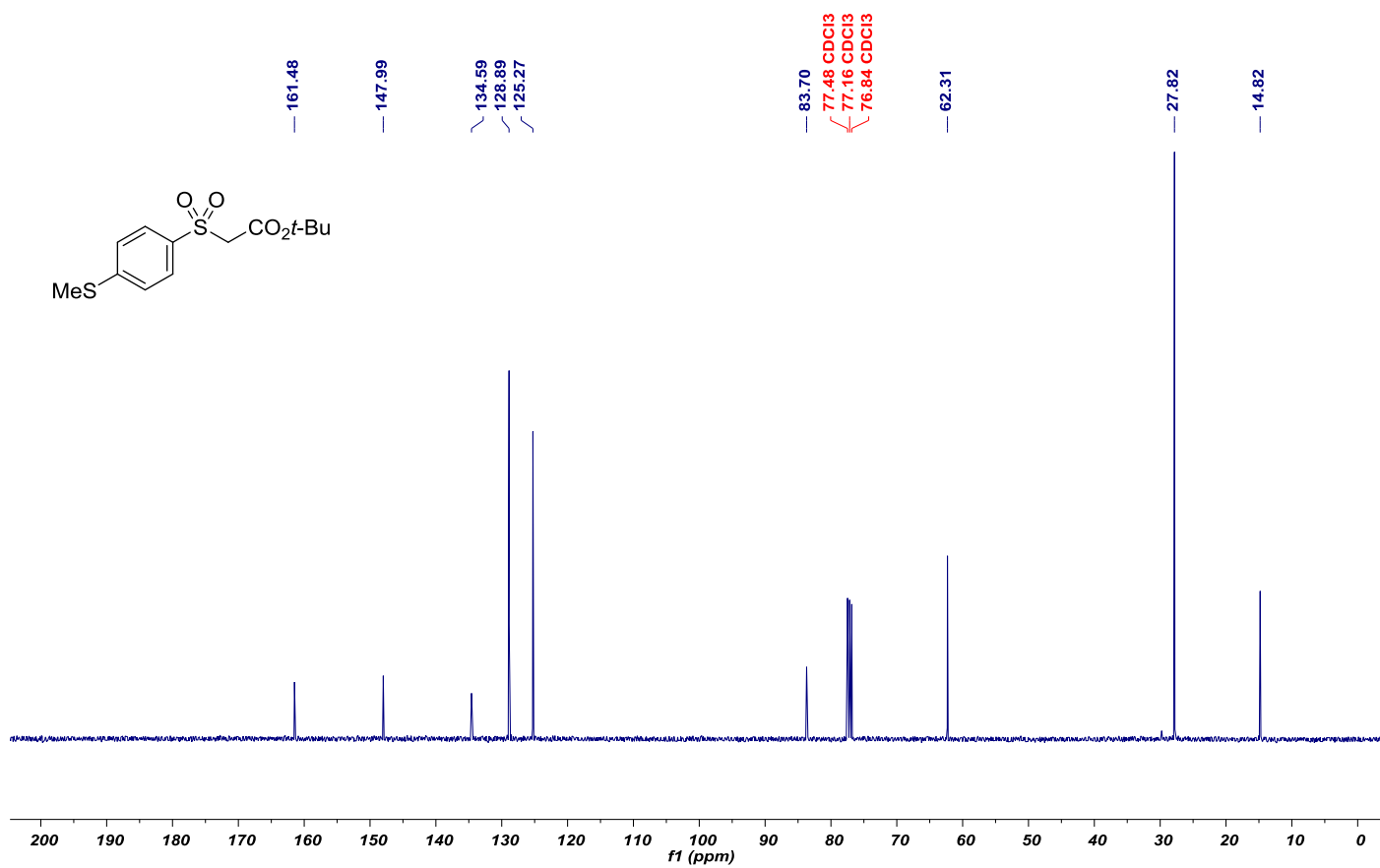
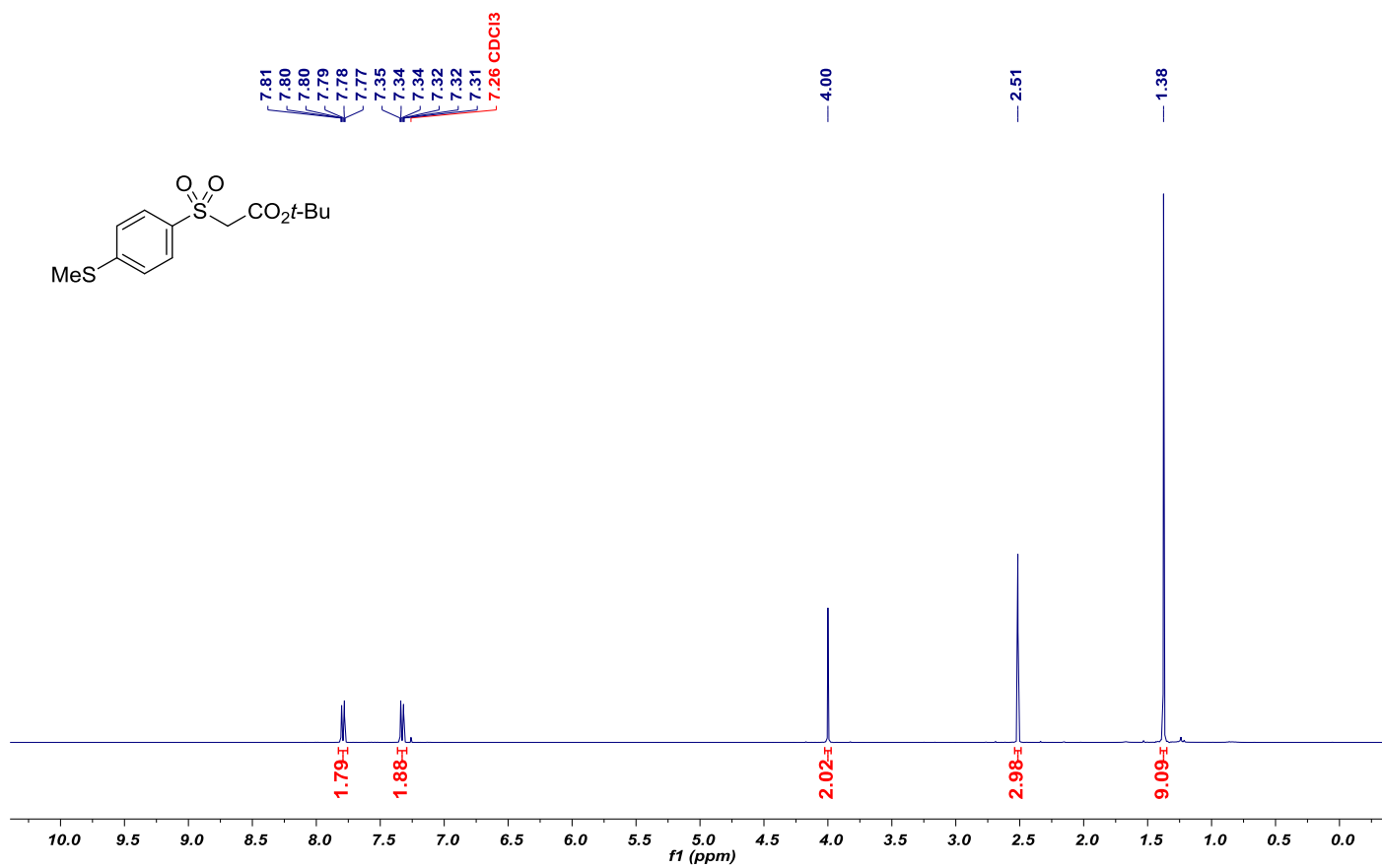
NMR spectrum of sulfone **2b**



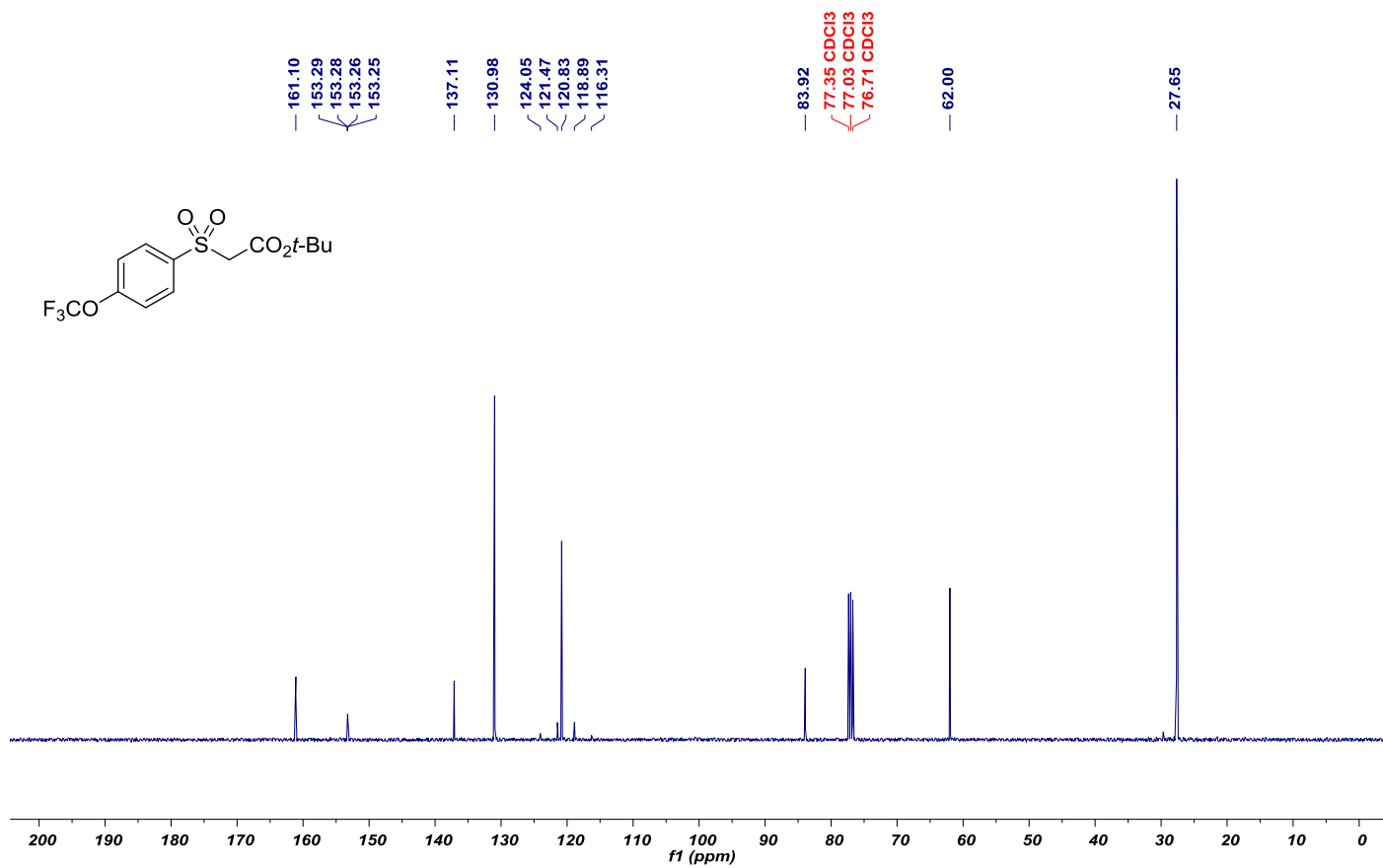
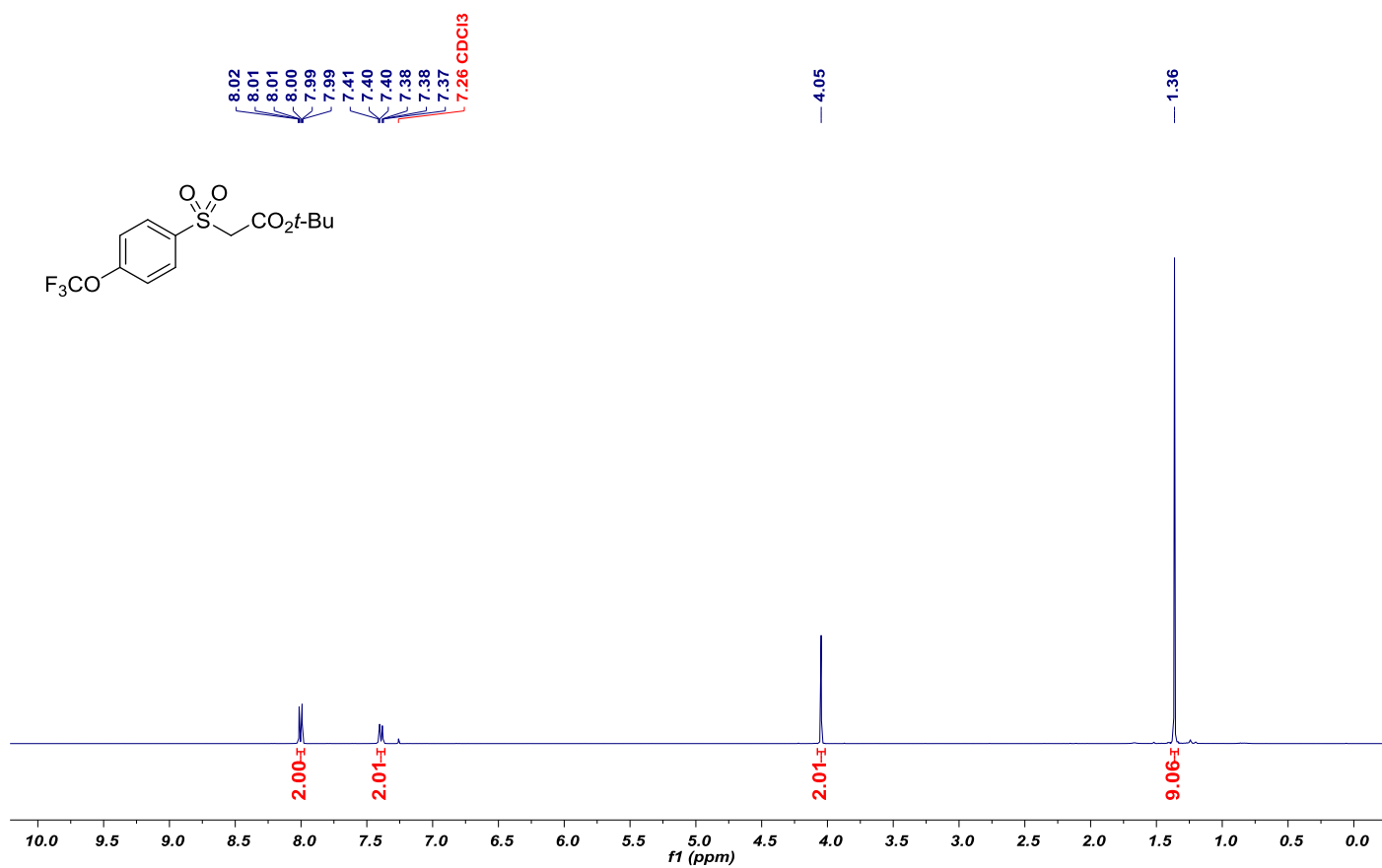
NMR spectrum of sulfone **2c**



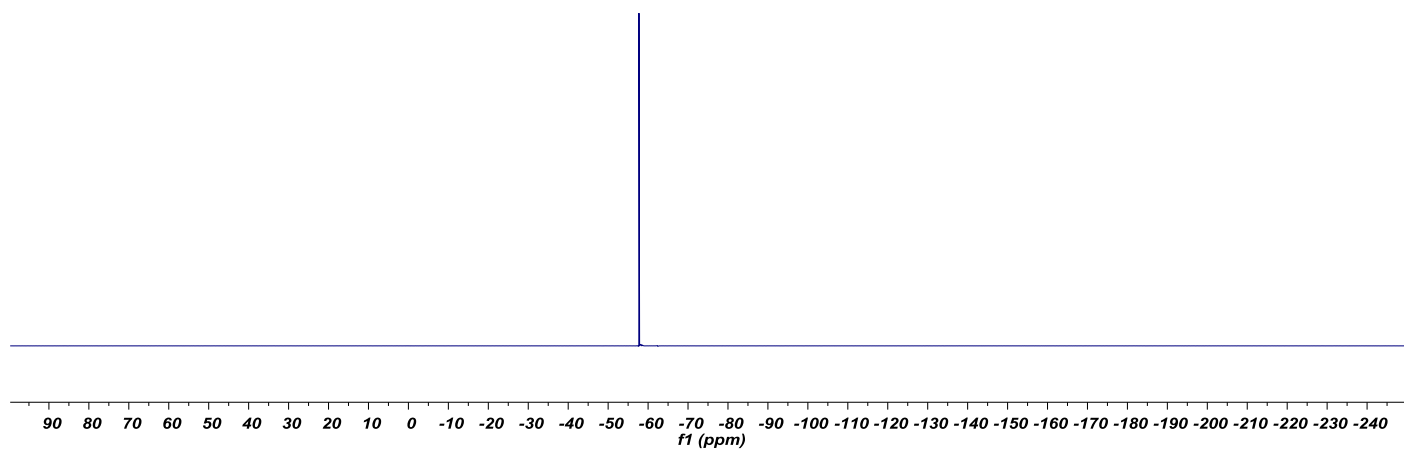
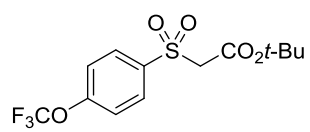
NMR spectrum of sulfone **2d**



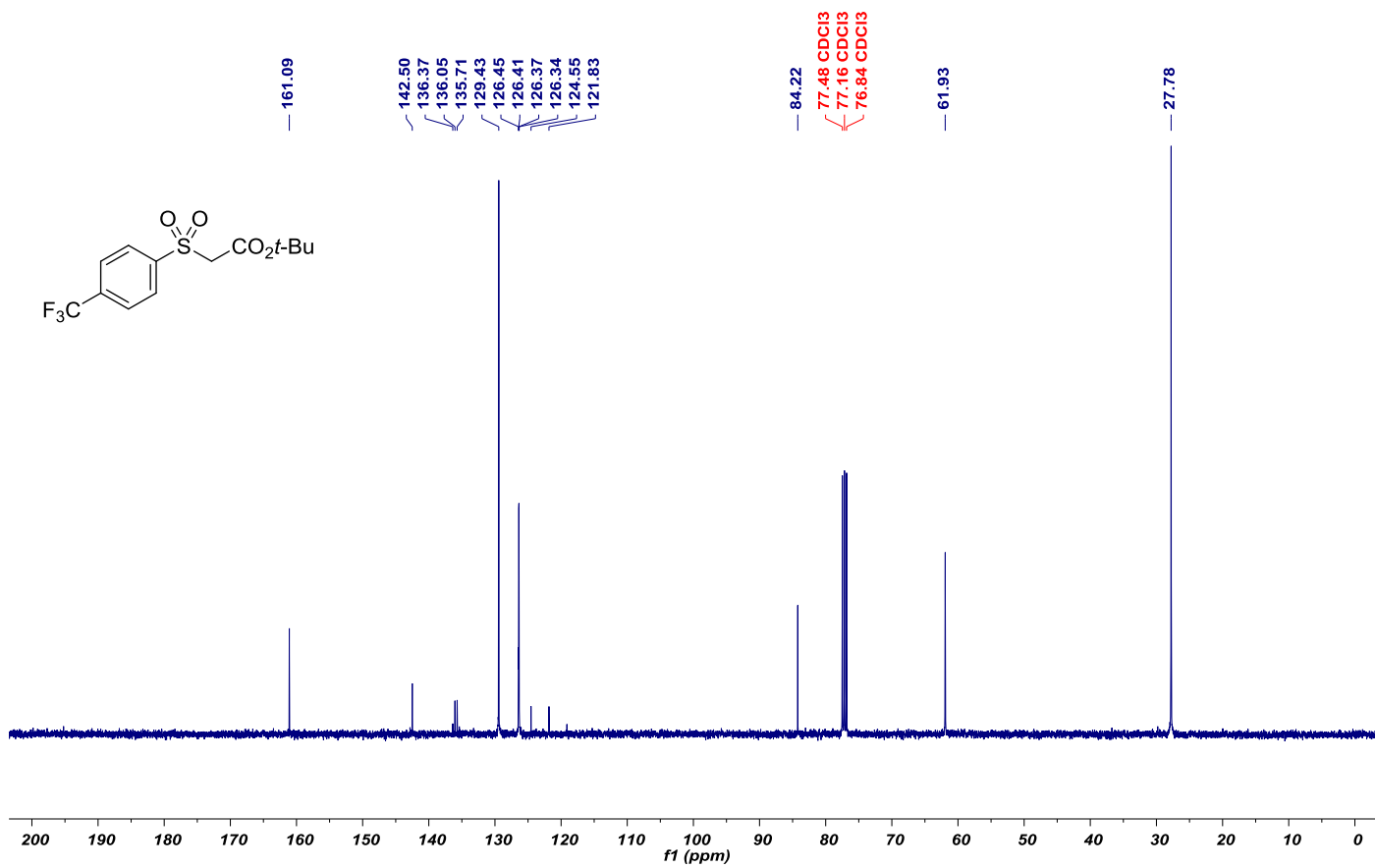
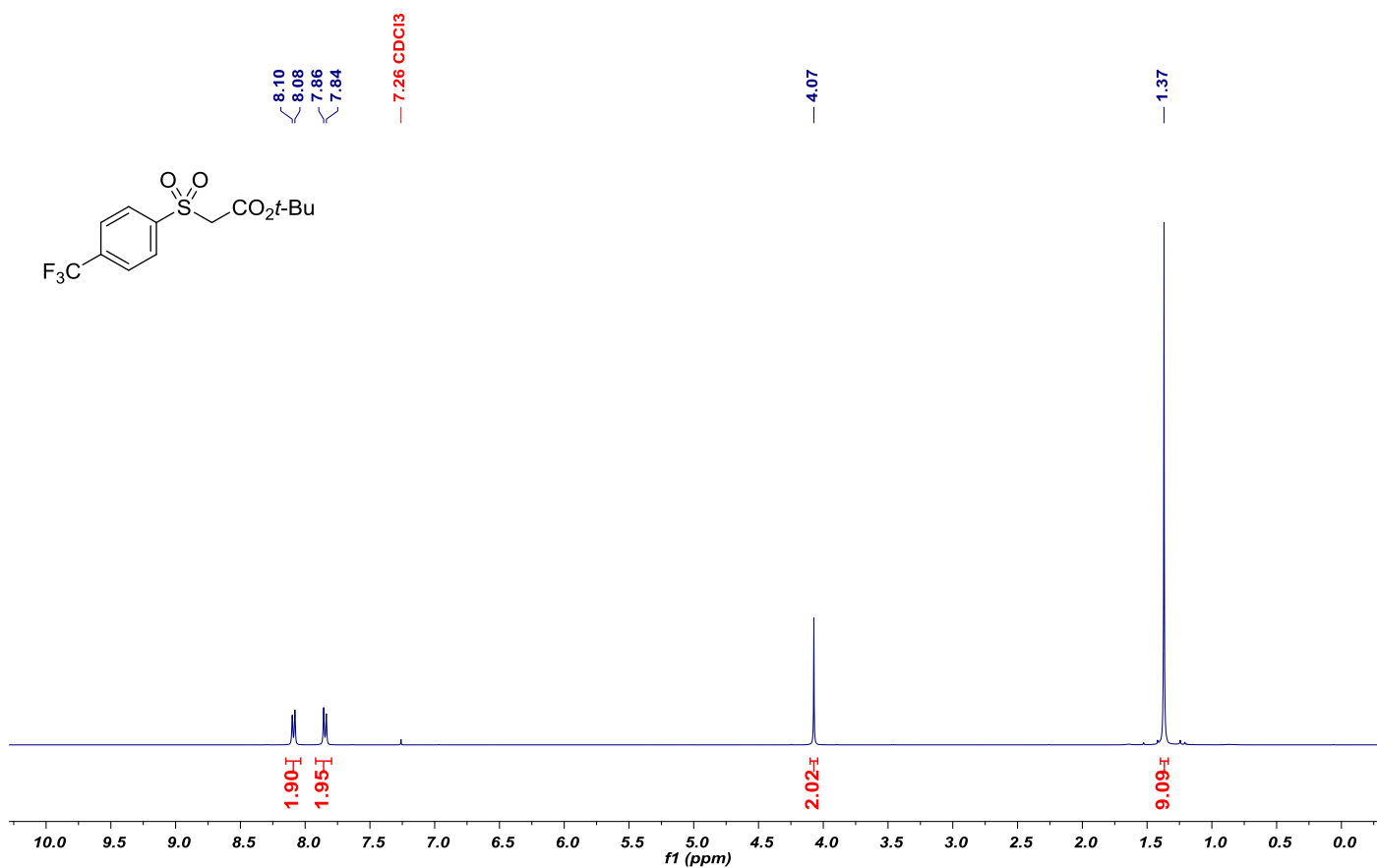
NMR spectrum of sulfone **2e**

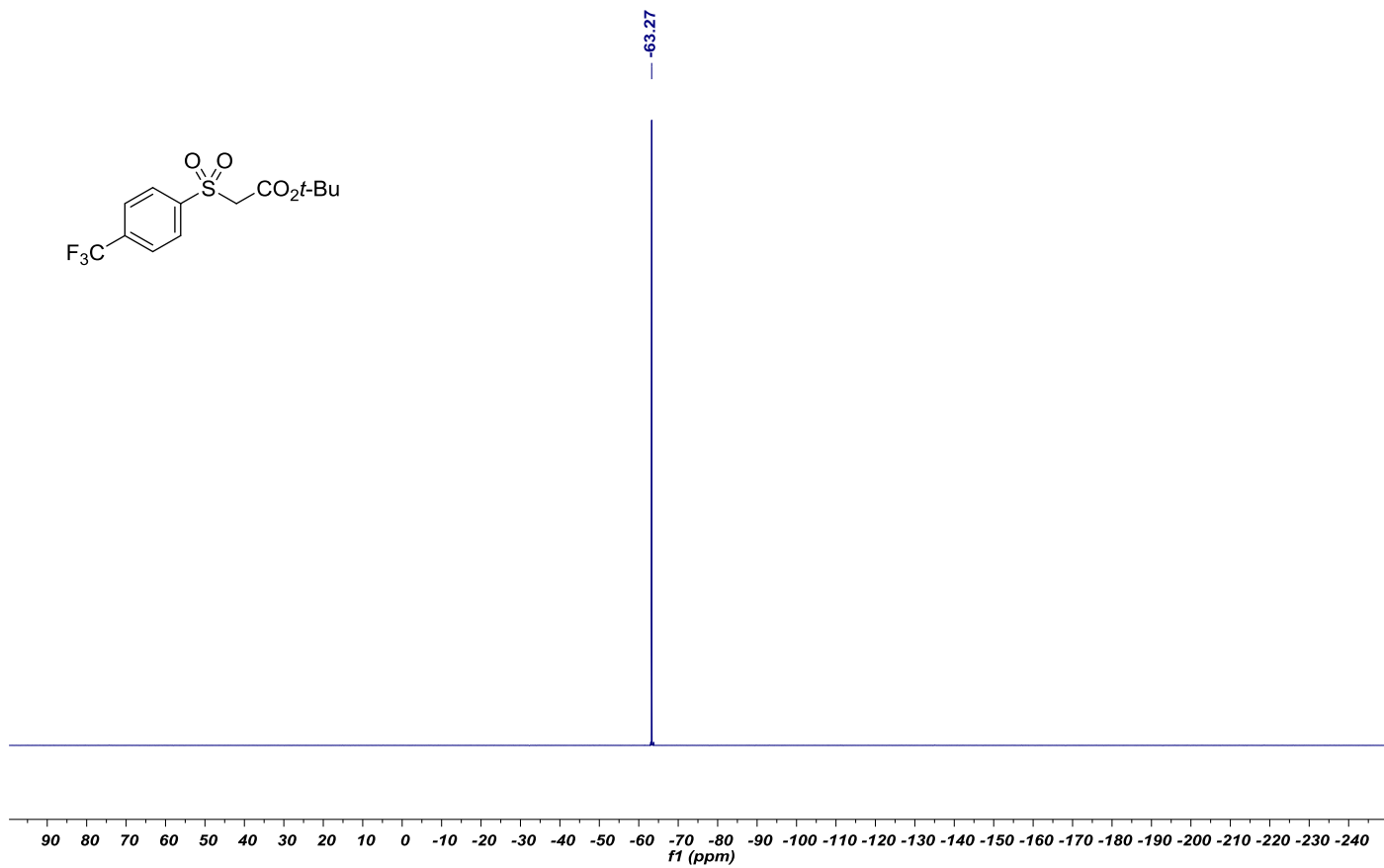
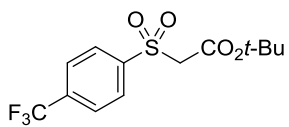


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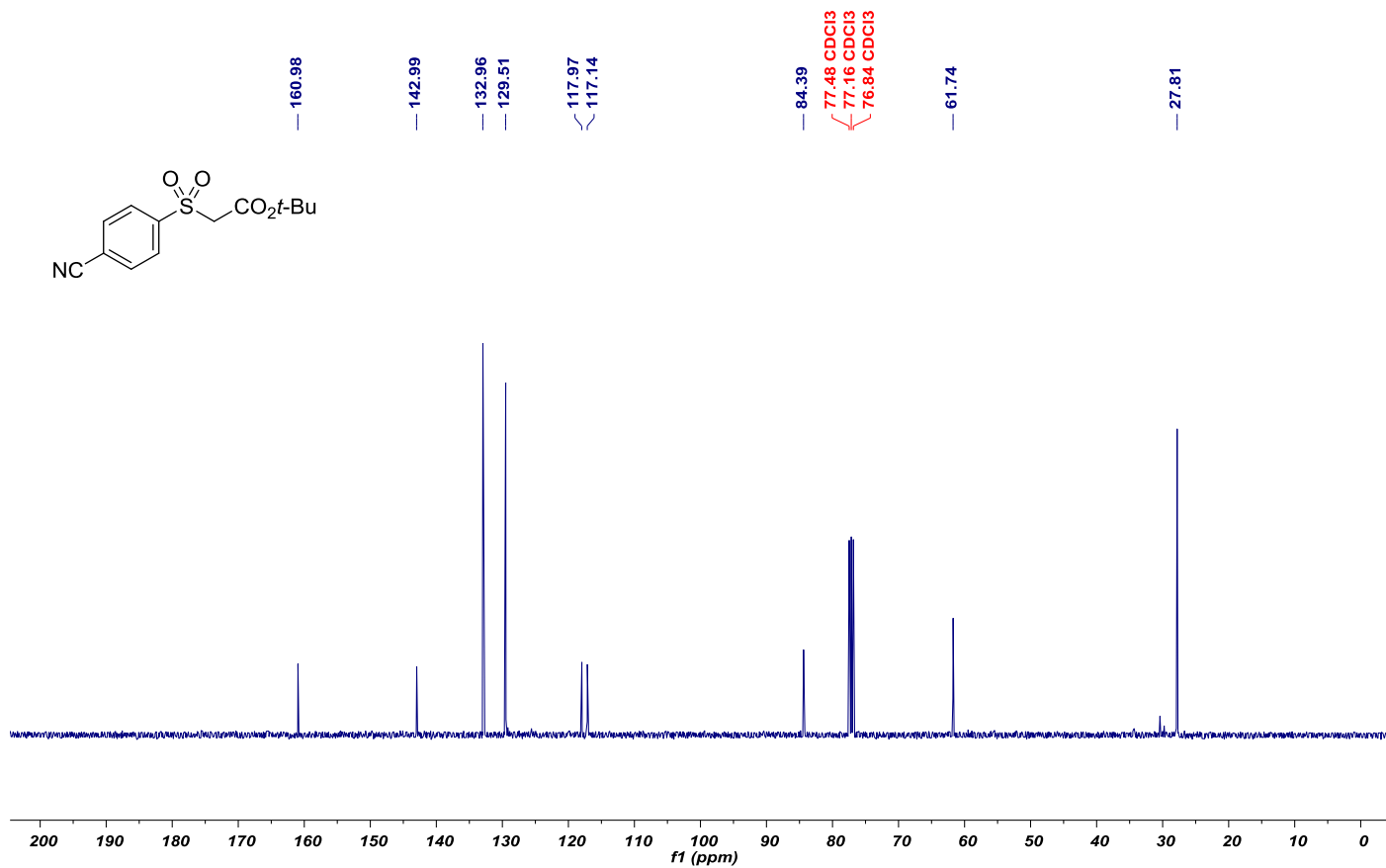
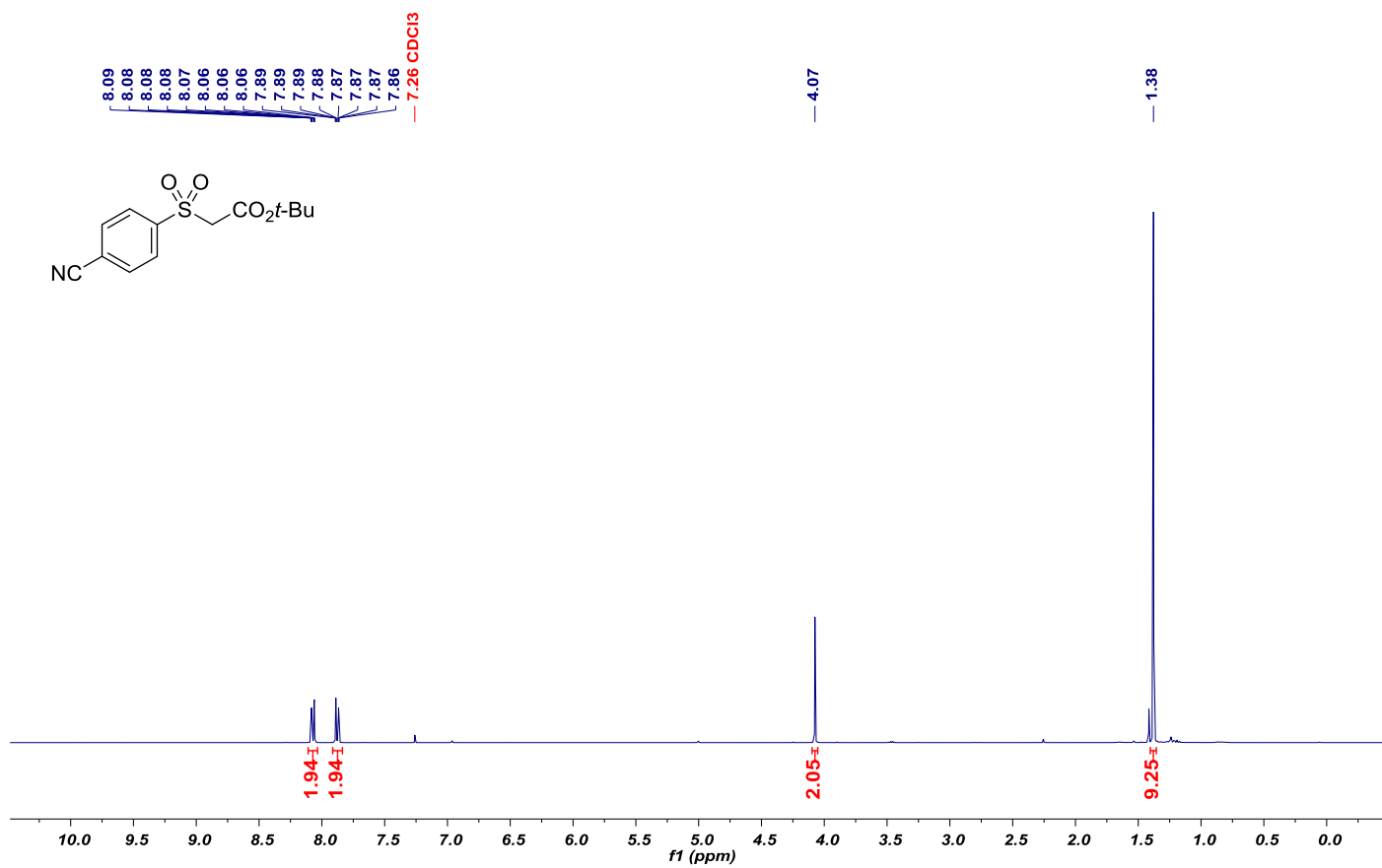


NMR spectrum of sulfone 2f

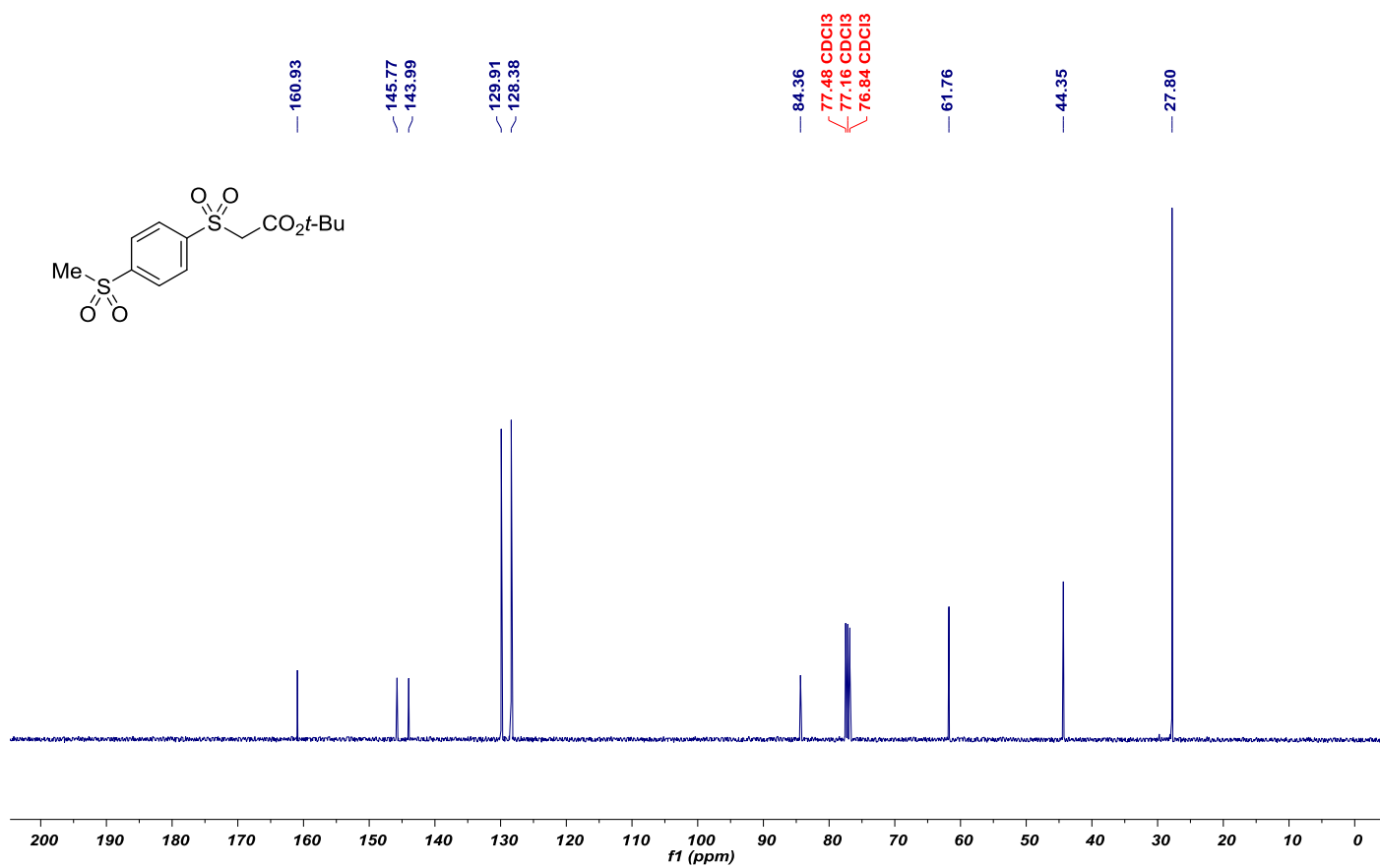
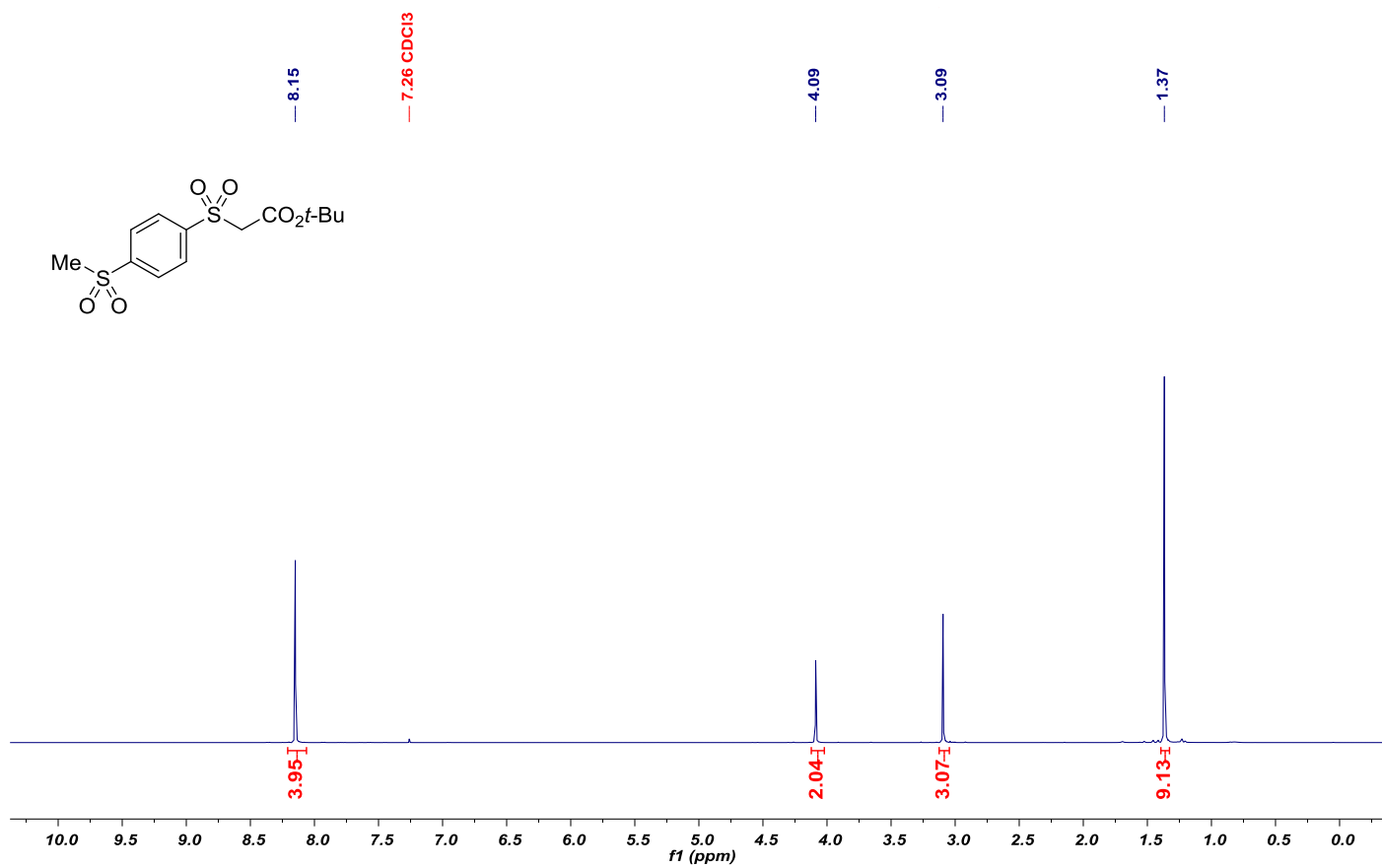




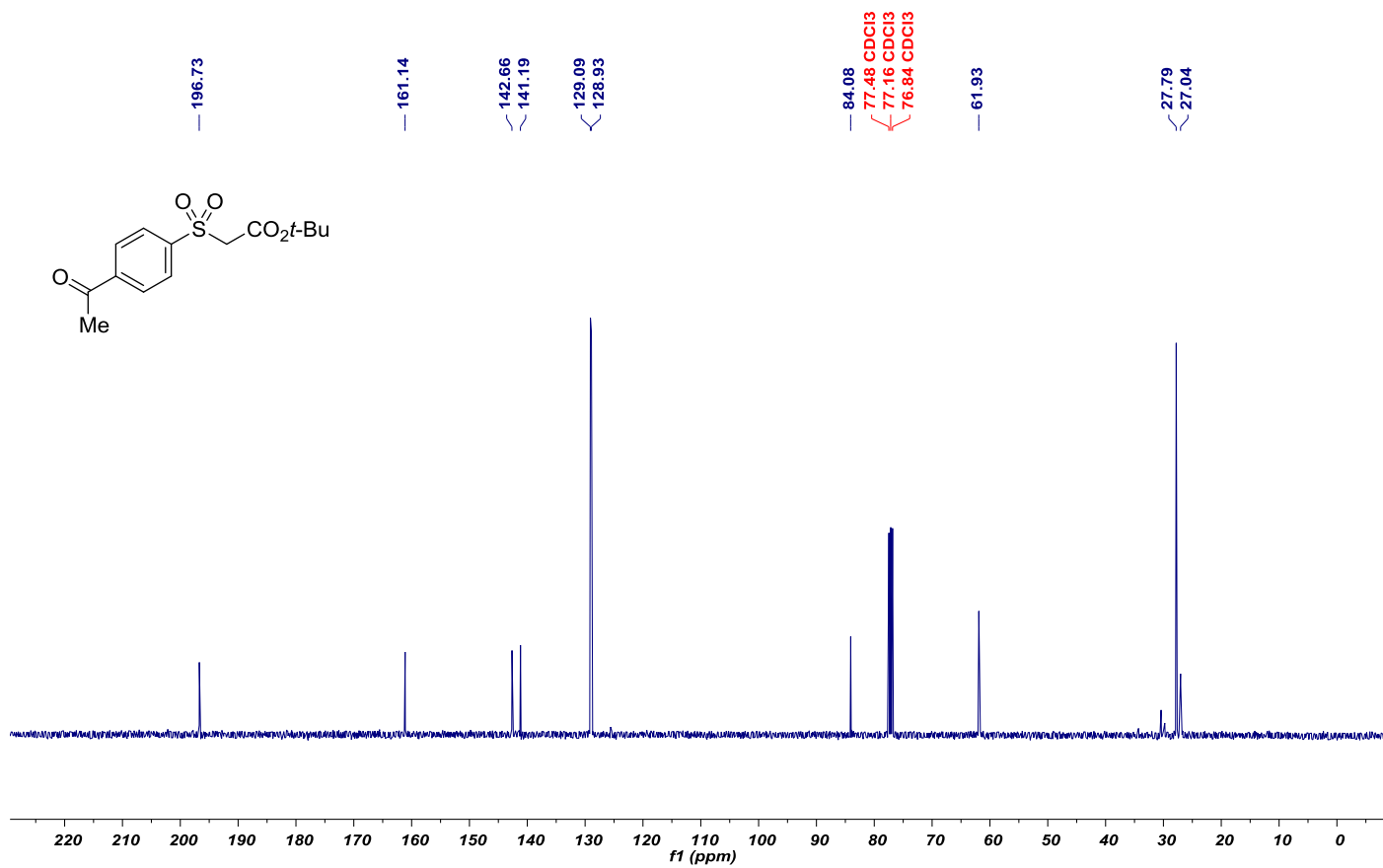
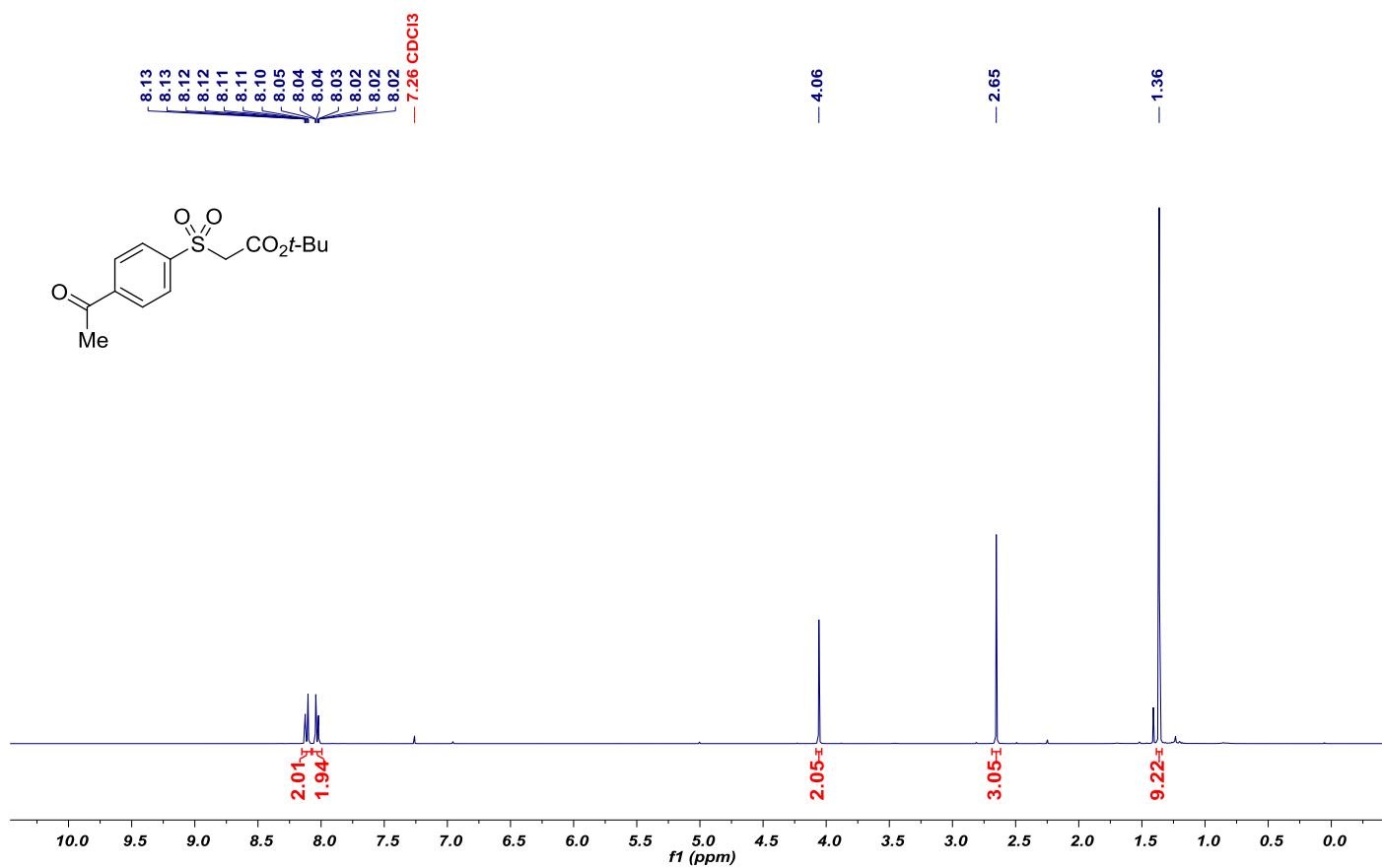
NMR spectrum of sulfone **2g**



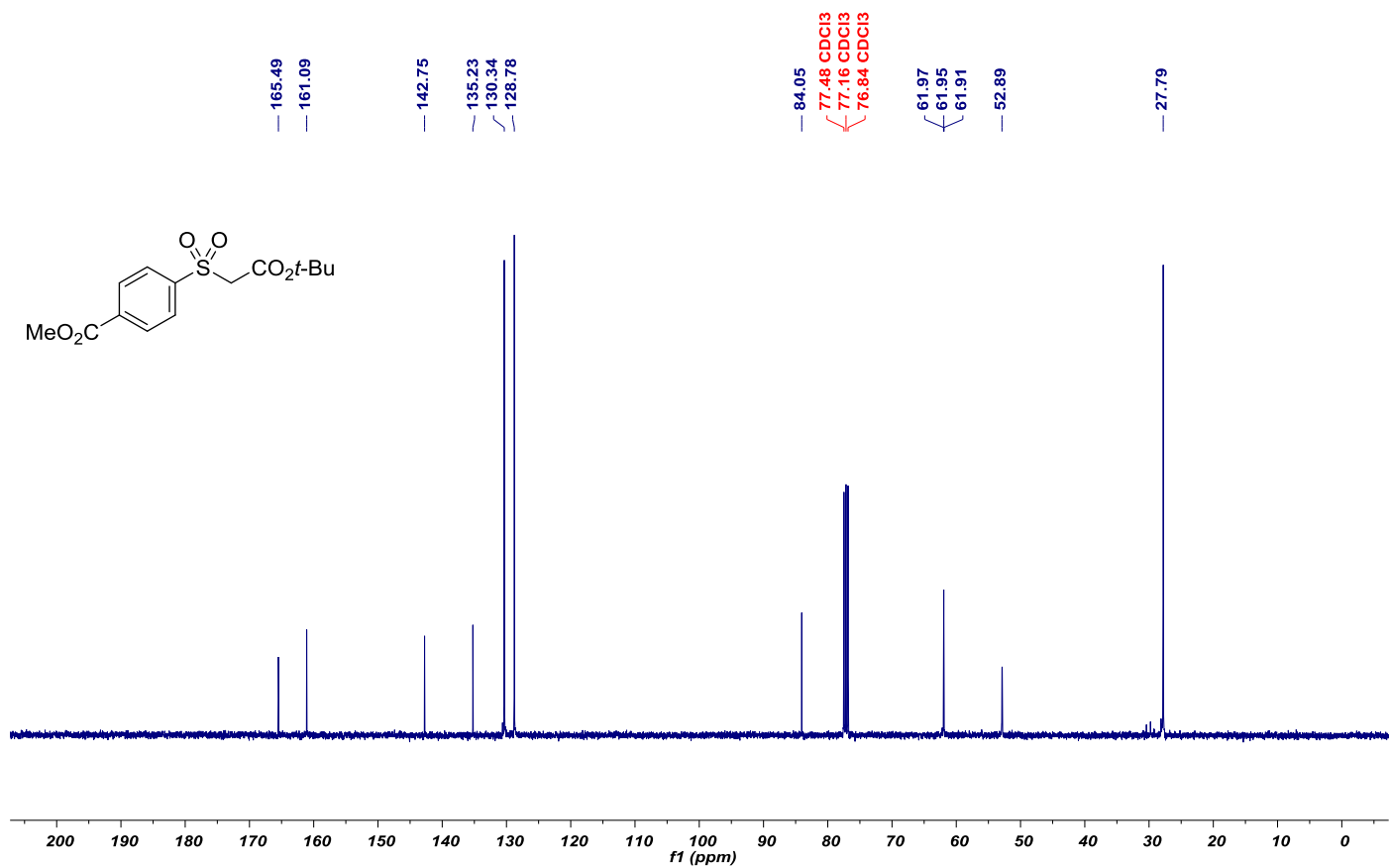
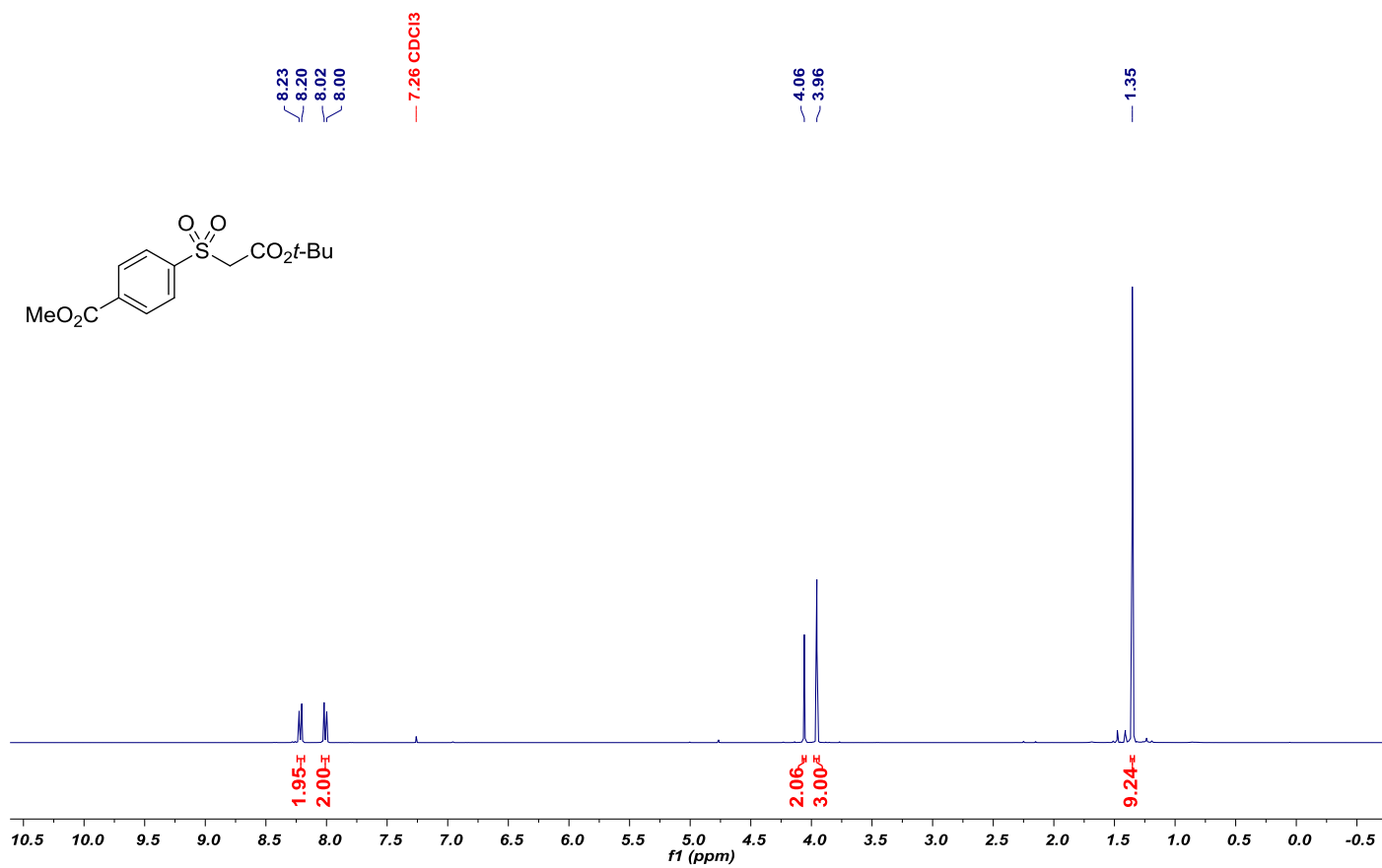
NMR spectrum of sulfone **2h**



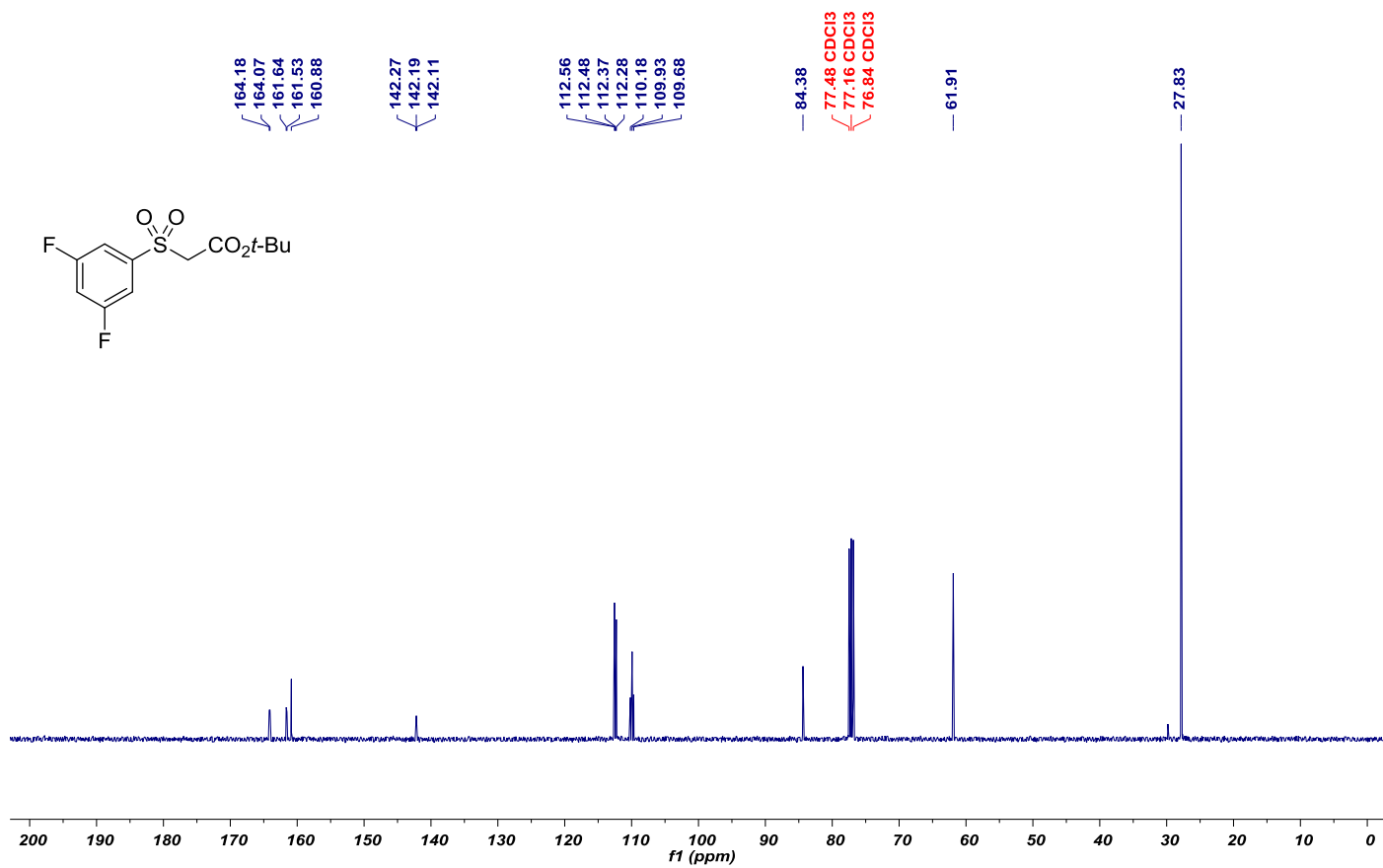
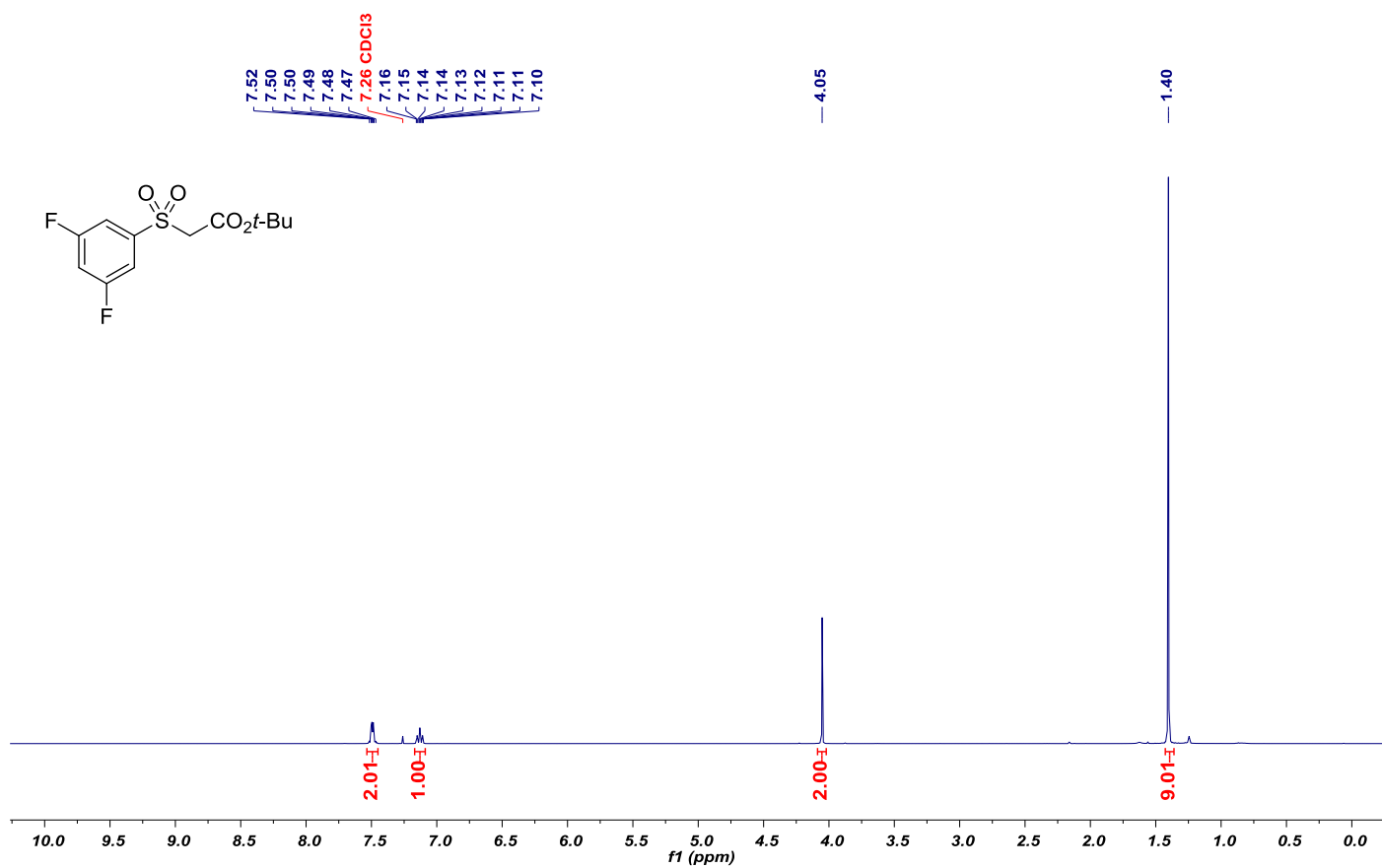
NMR spectrum of sulfone 2i

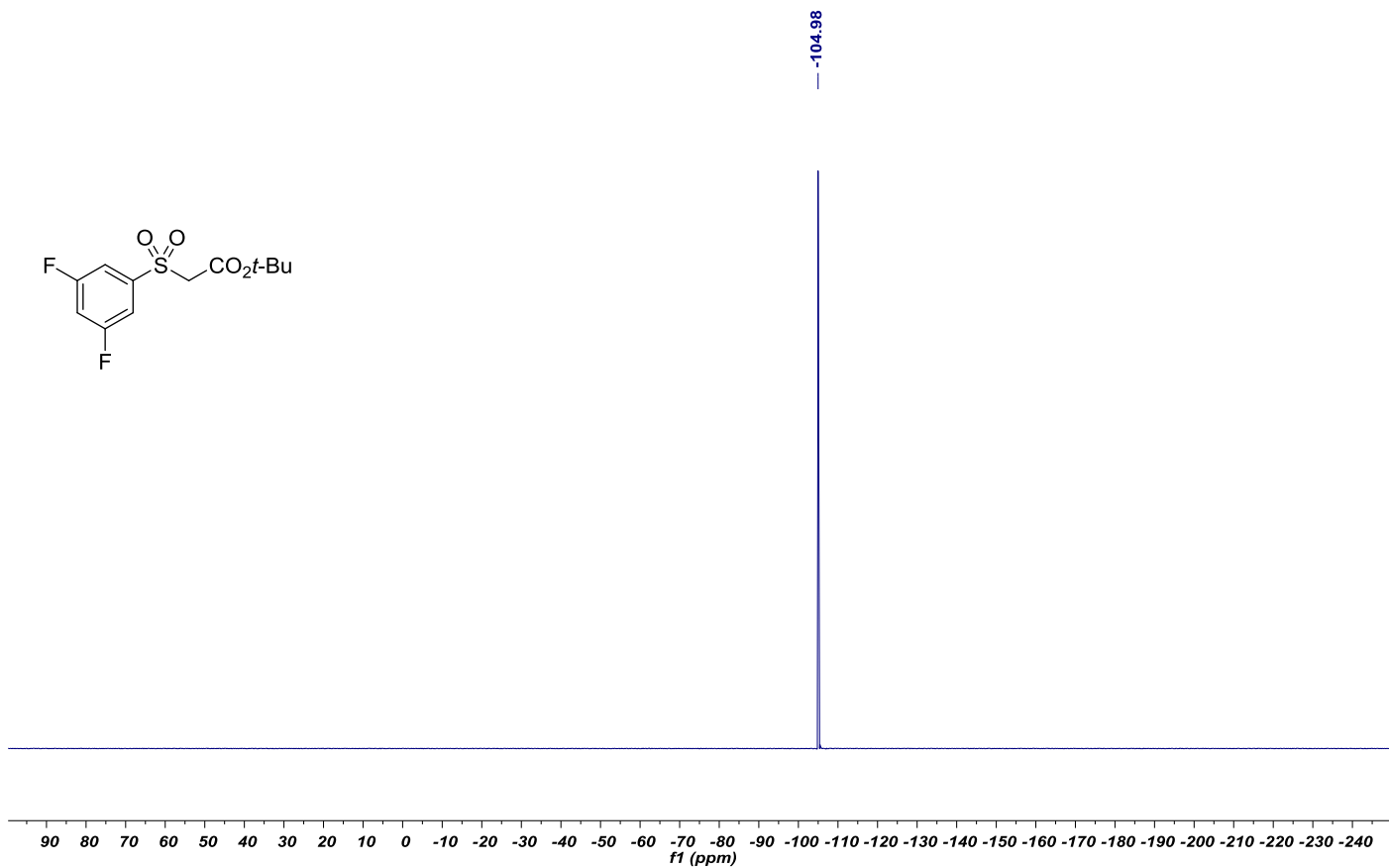
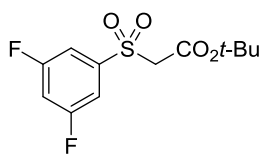


NMR spectrum of sulfone 2j

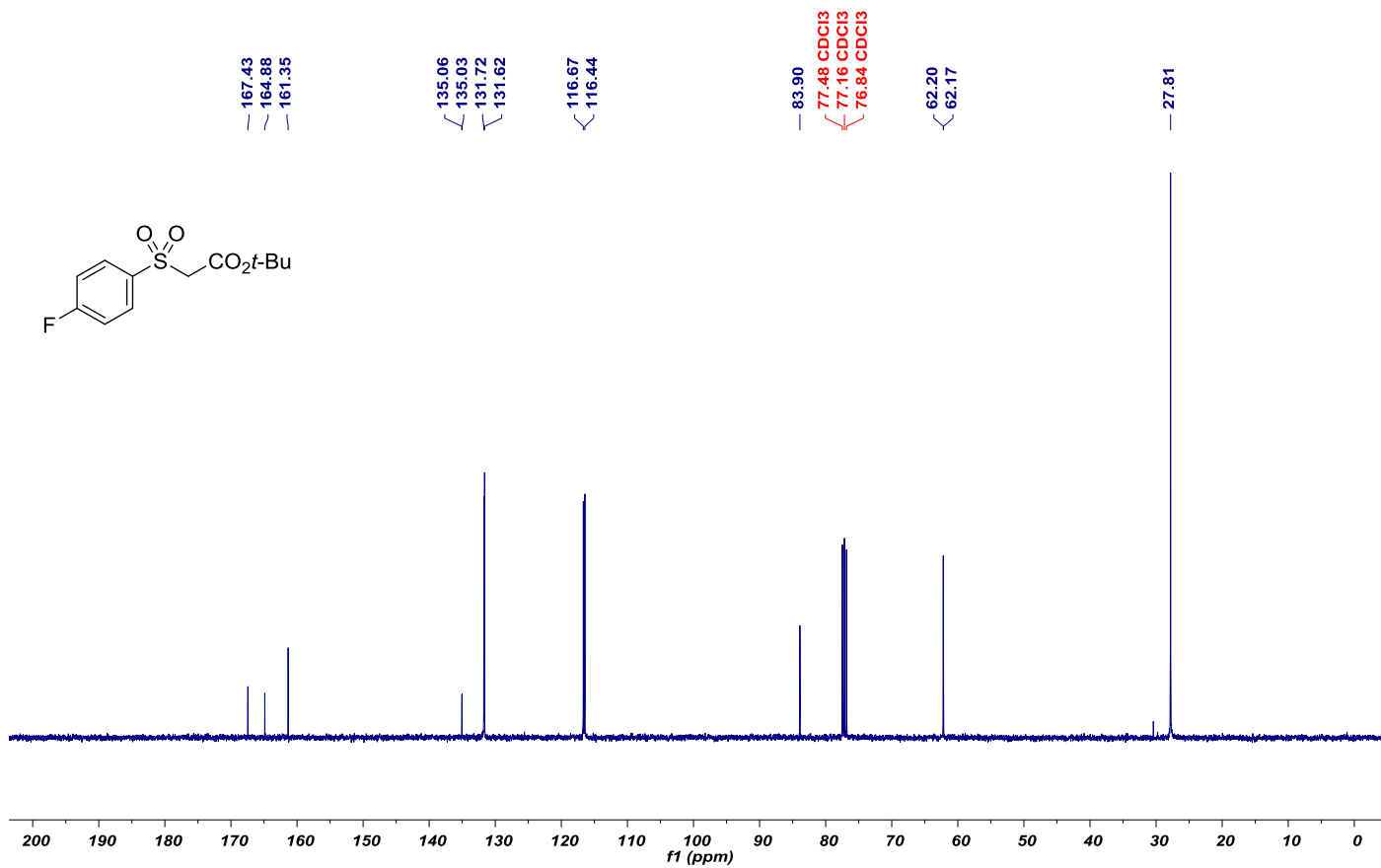
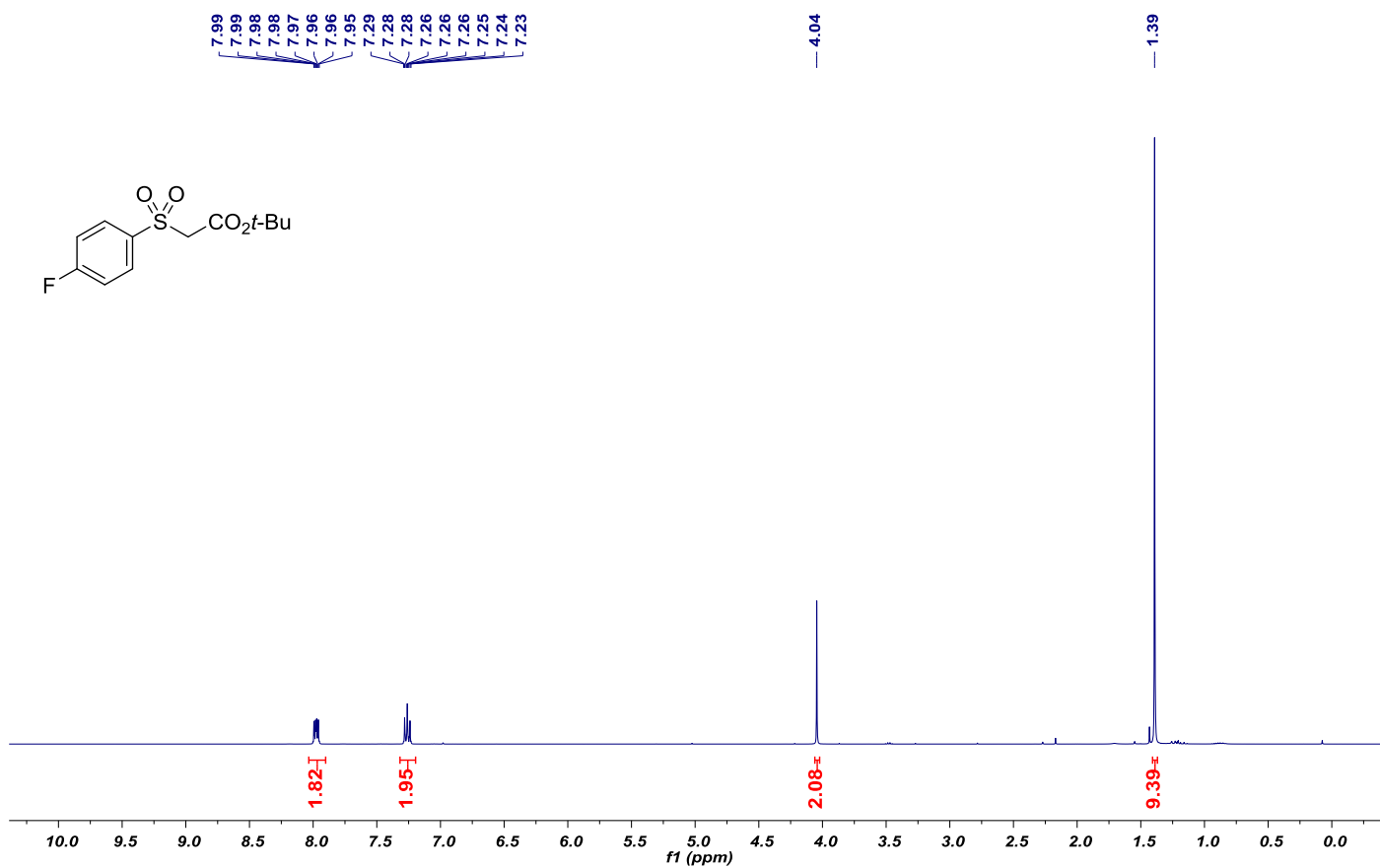


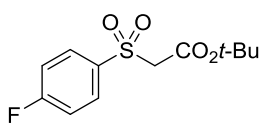
NMR spectrum of sulfone 2k



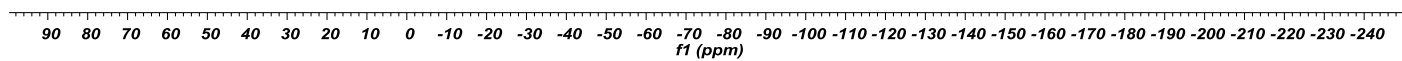


NMR spectrum of sulfone 2I

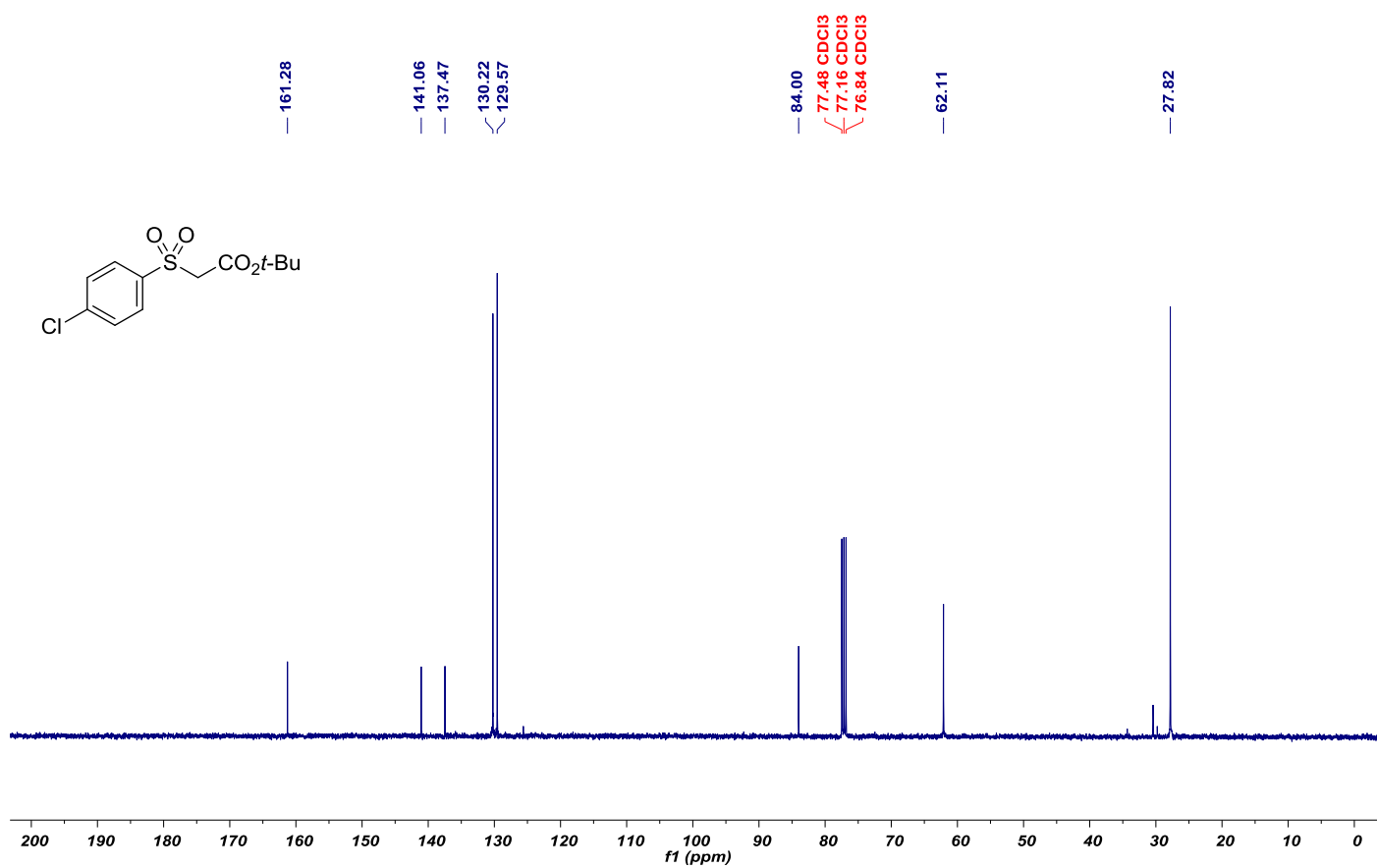
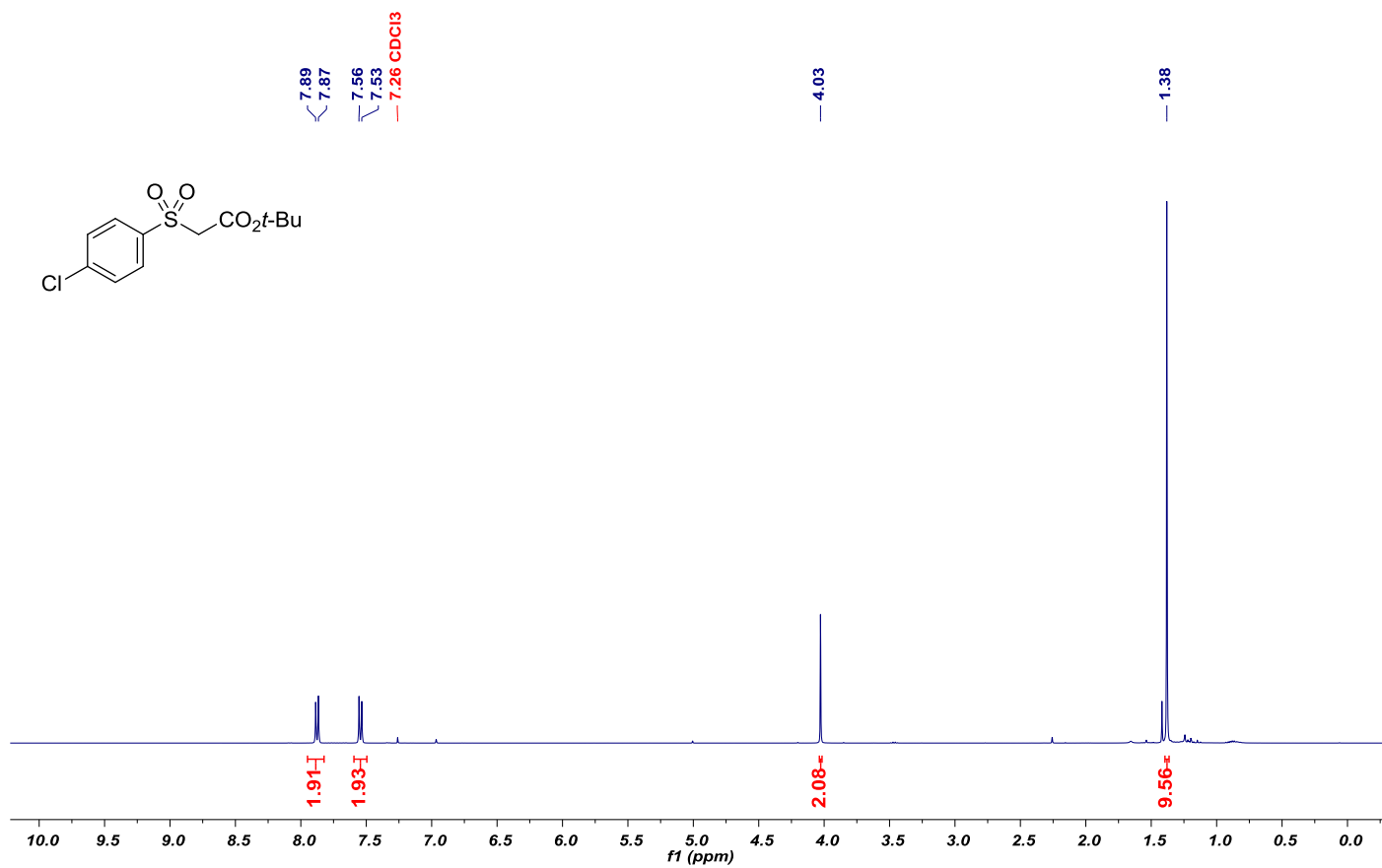




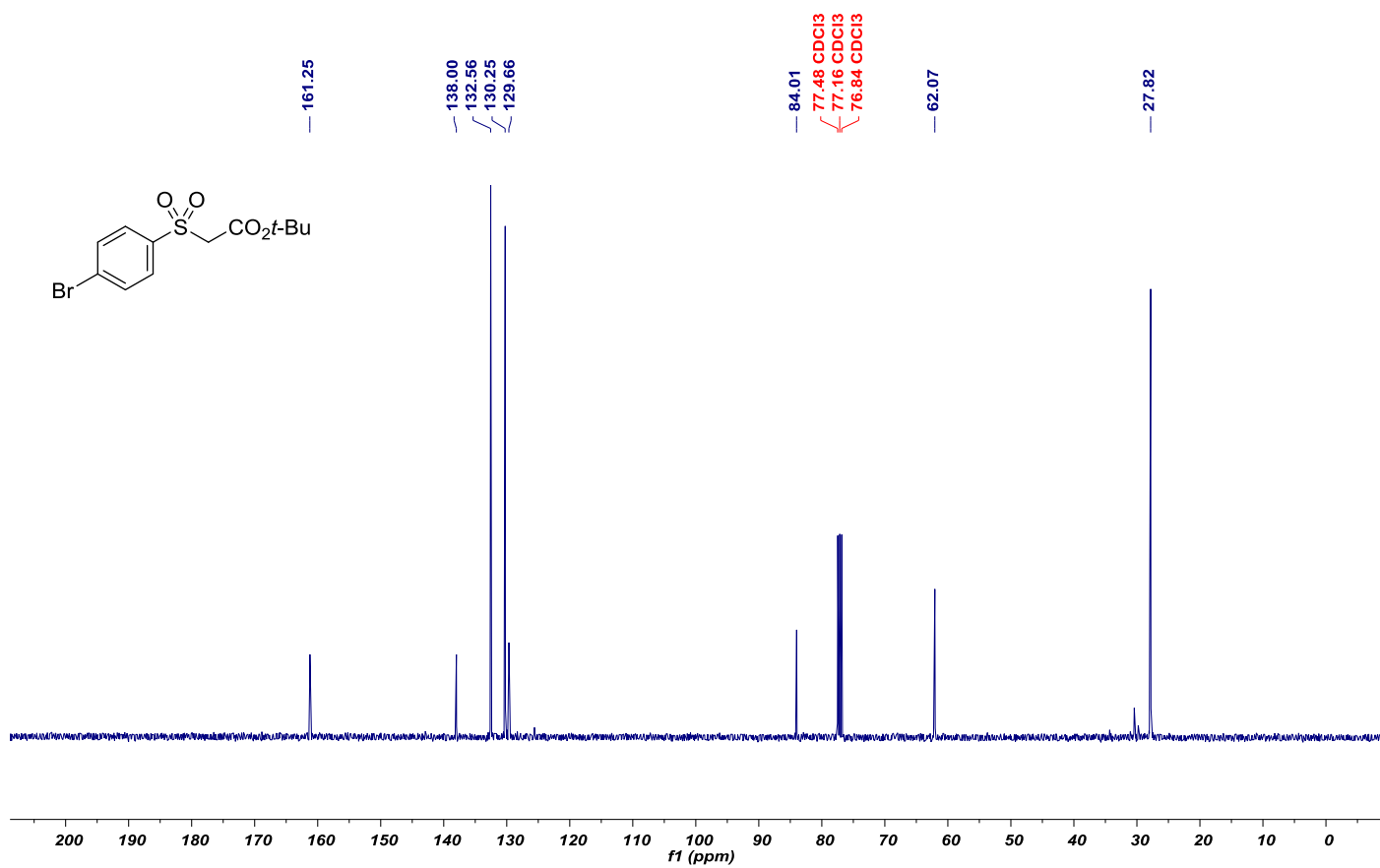
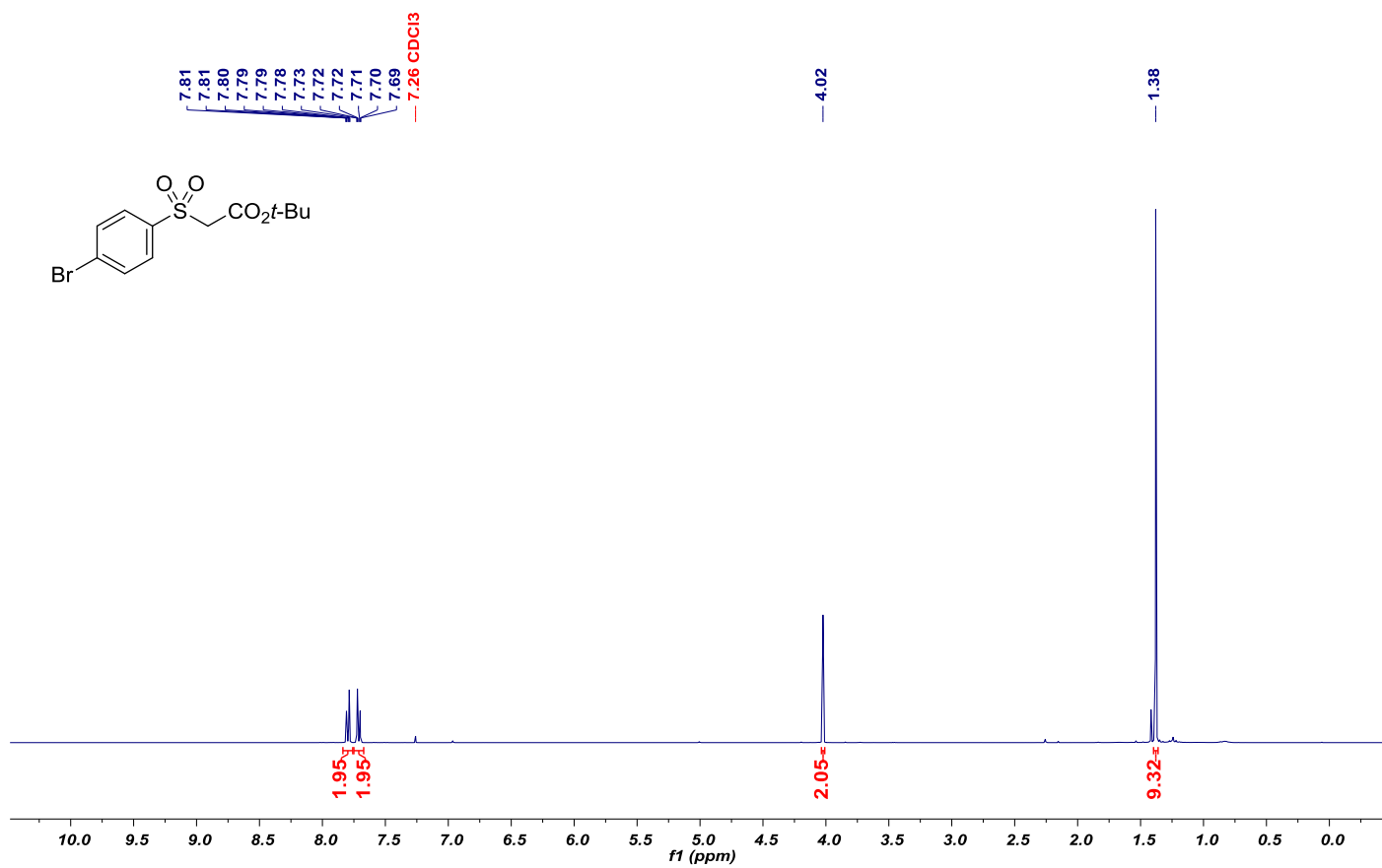
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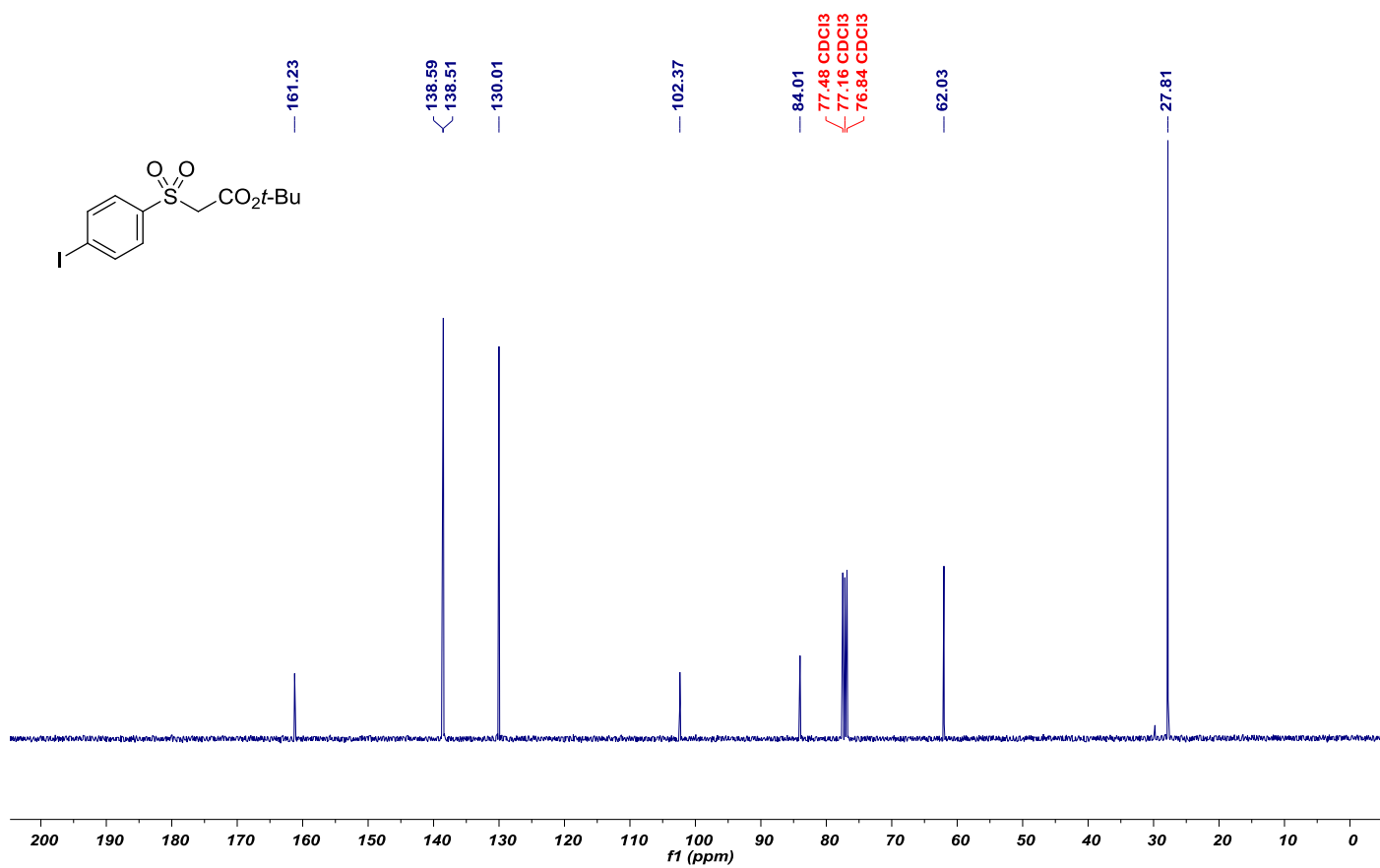
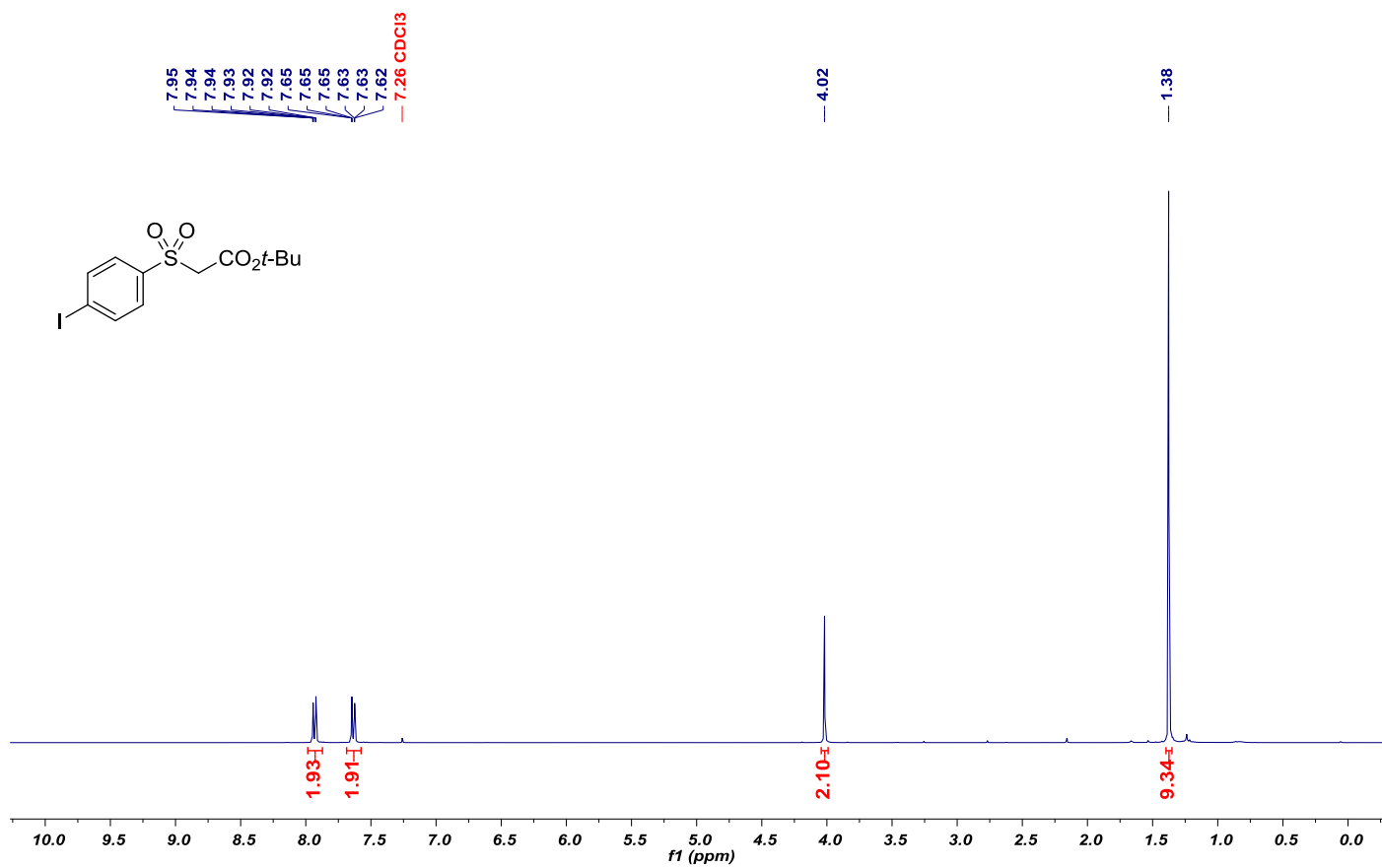
NMR spectrum of sulfone **2m**



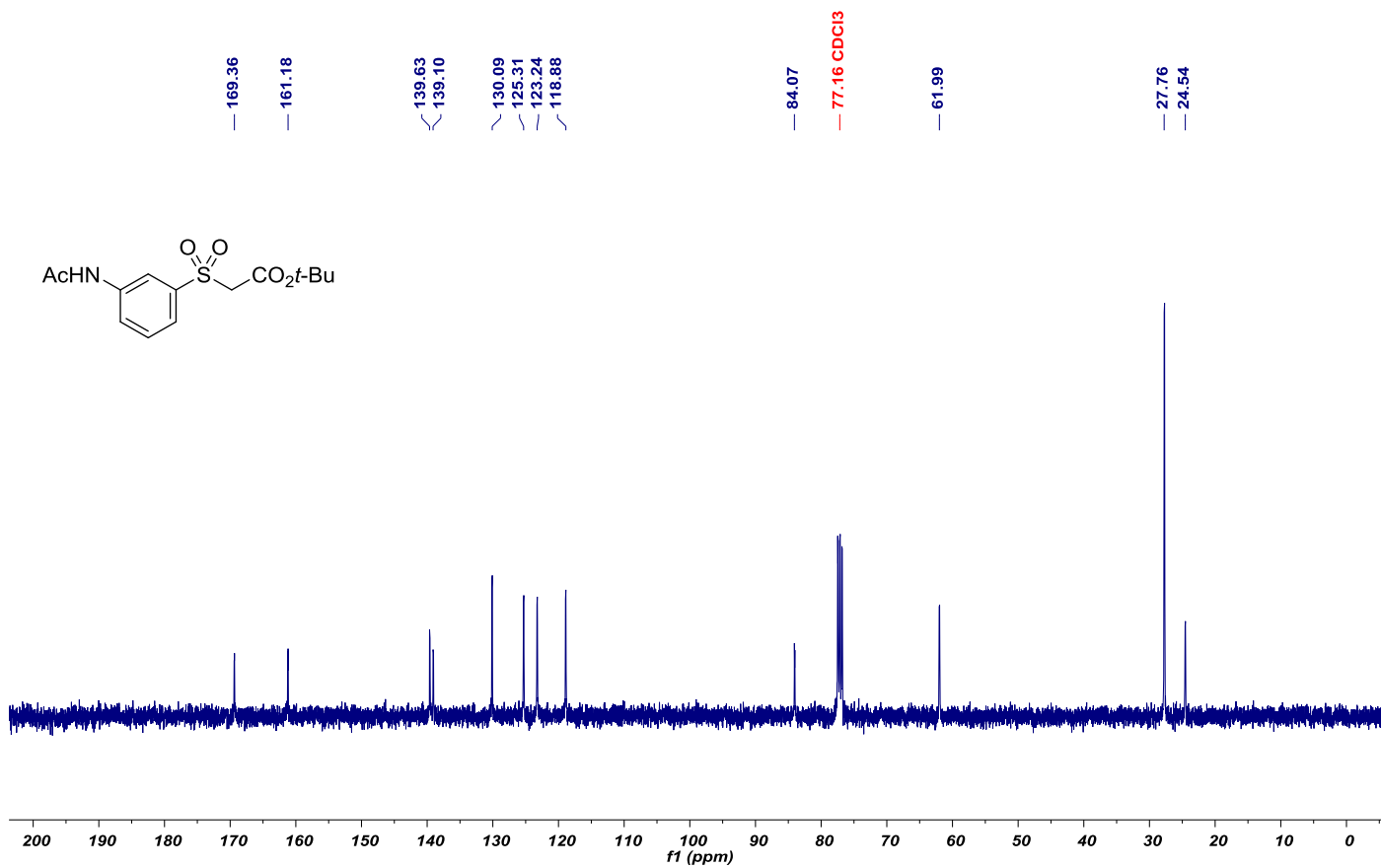
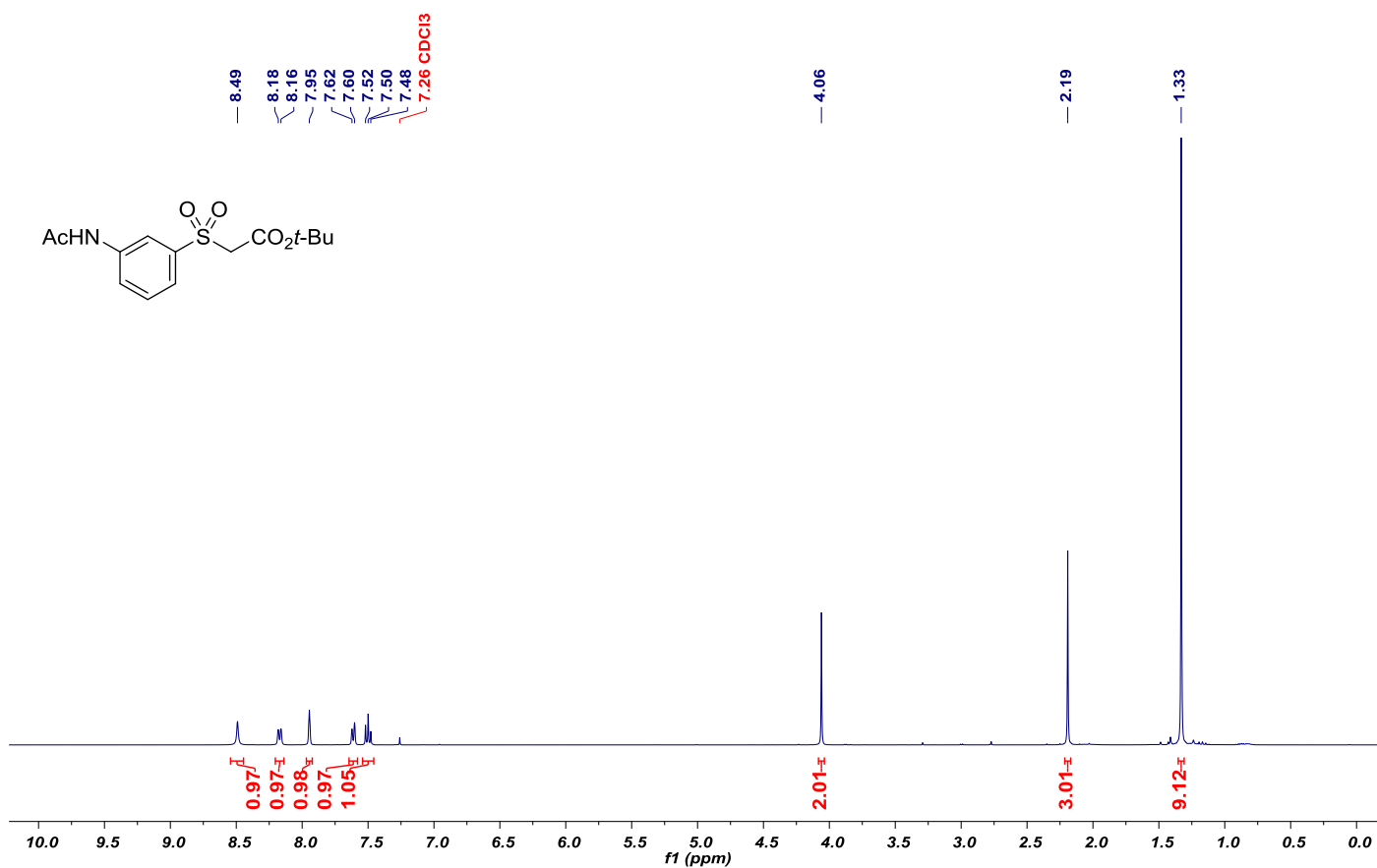
NMR spectrum of sulfone **2n**



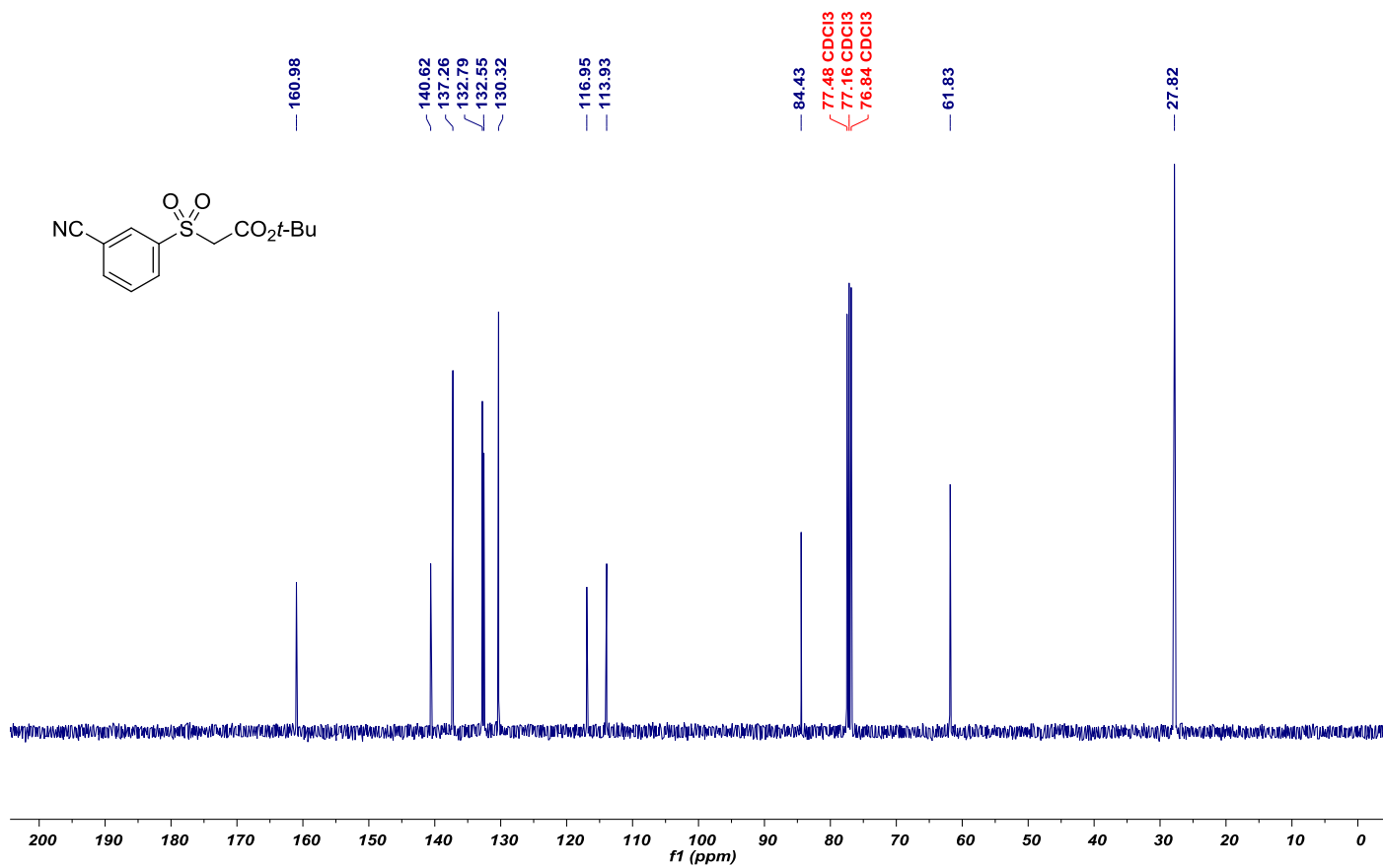
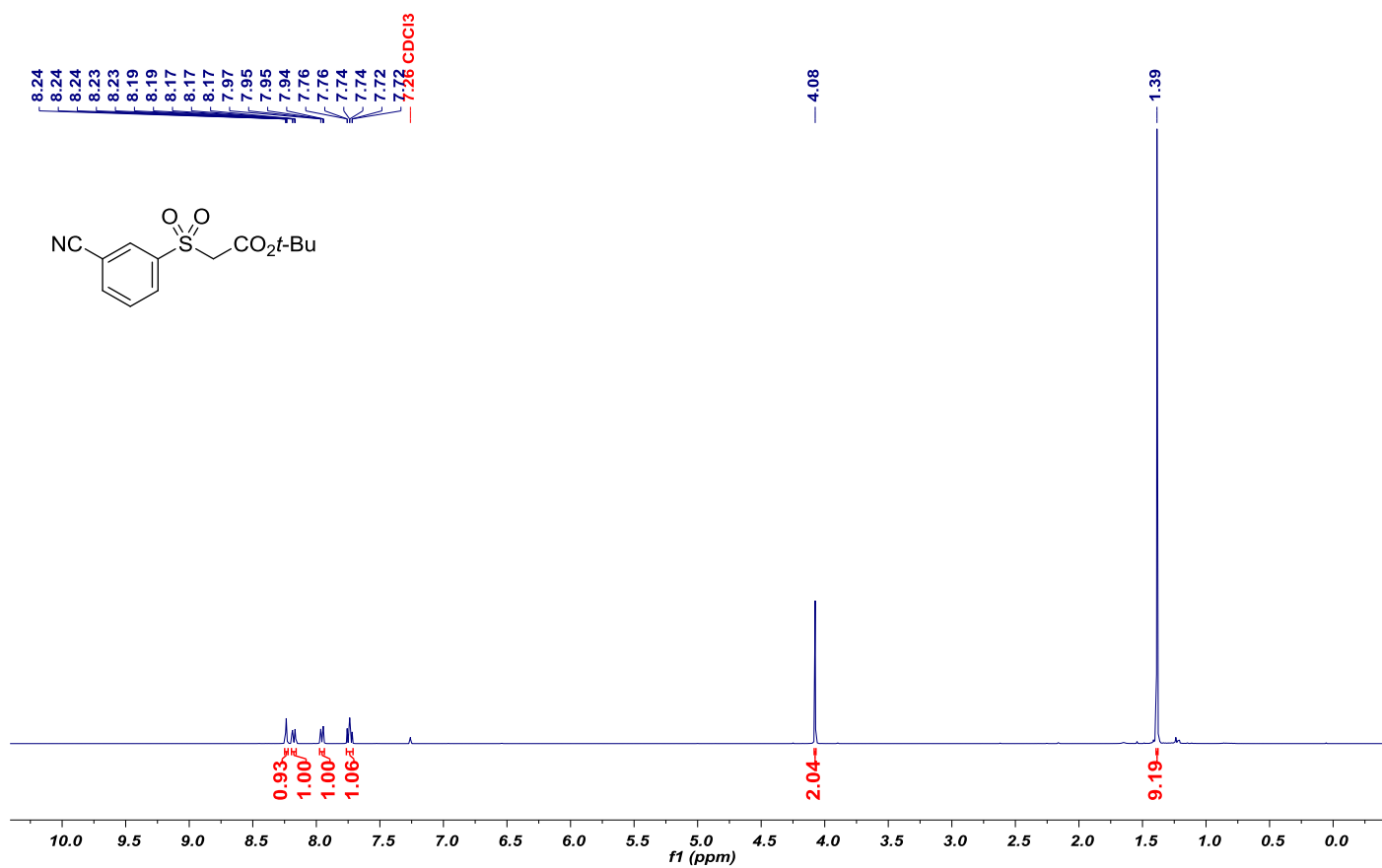
NMR spectrum of sulfone **2o**



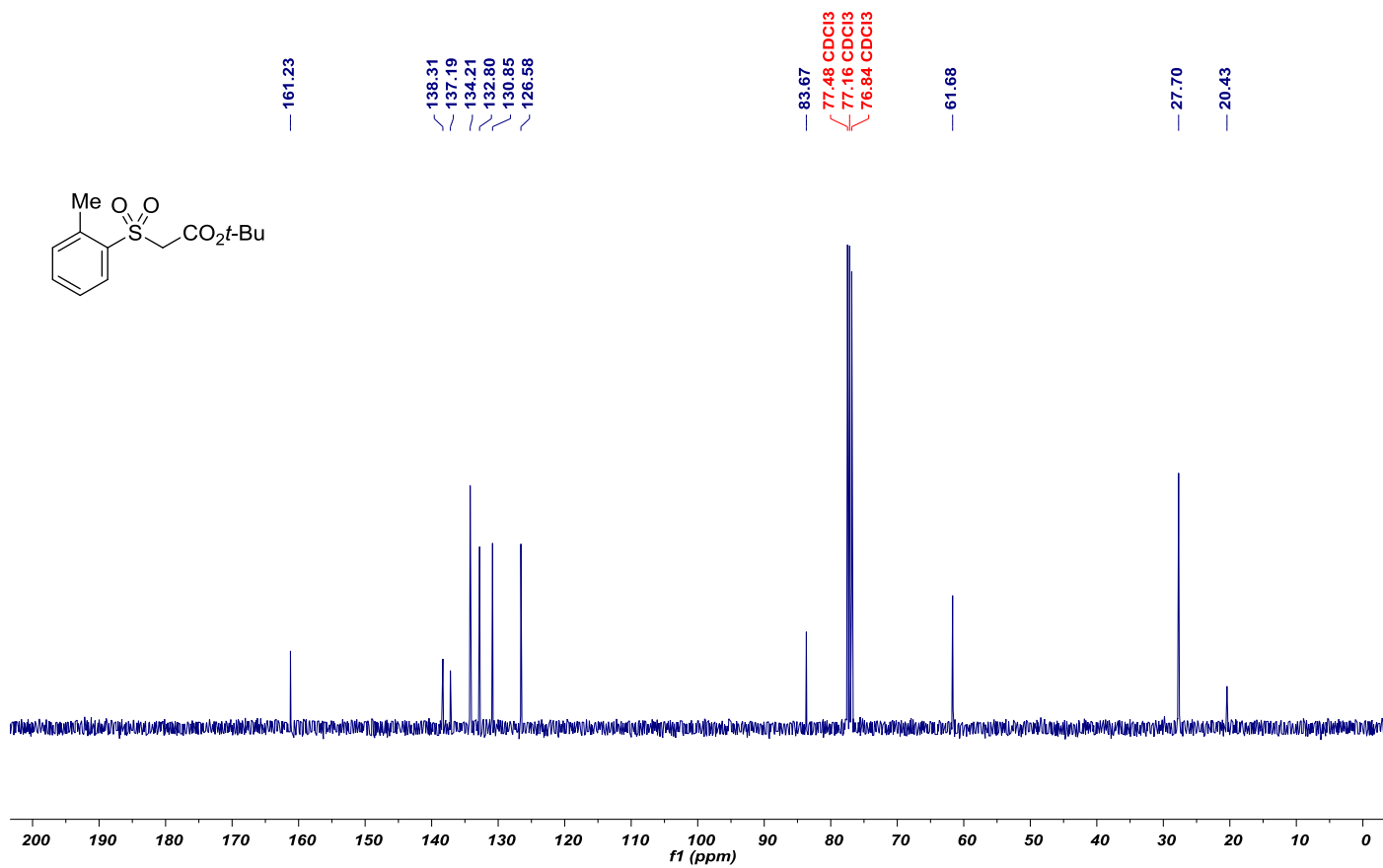
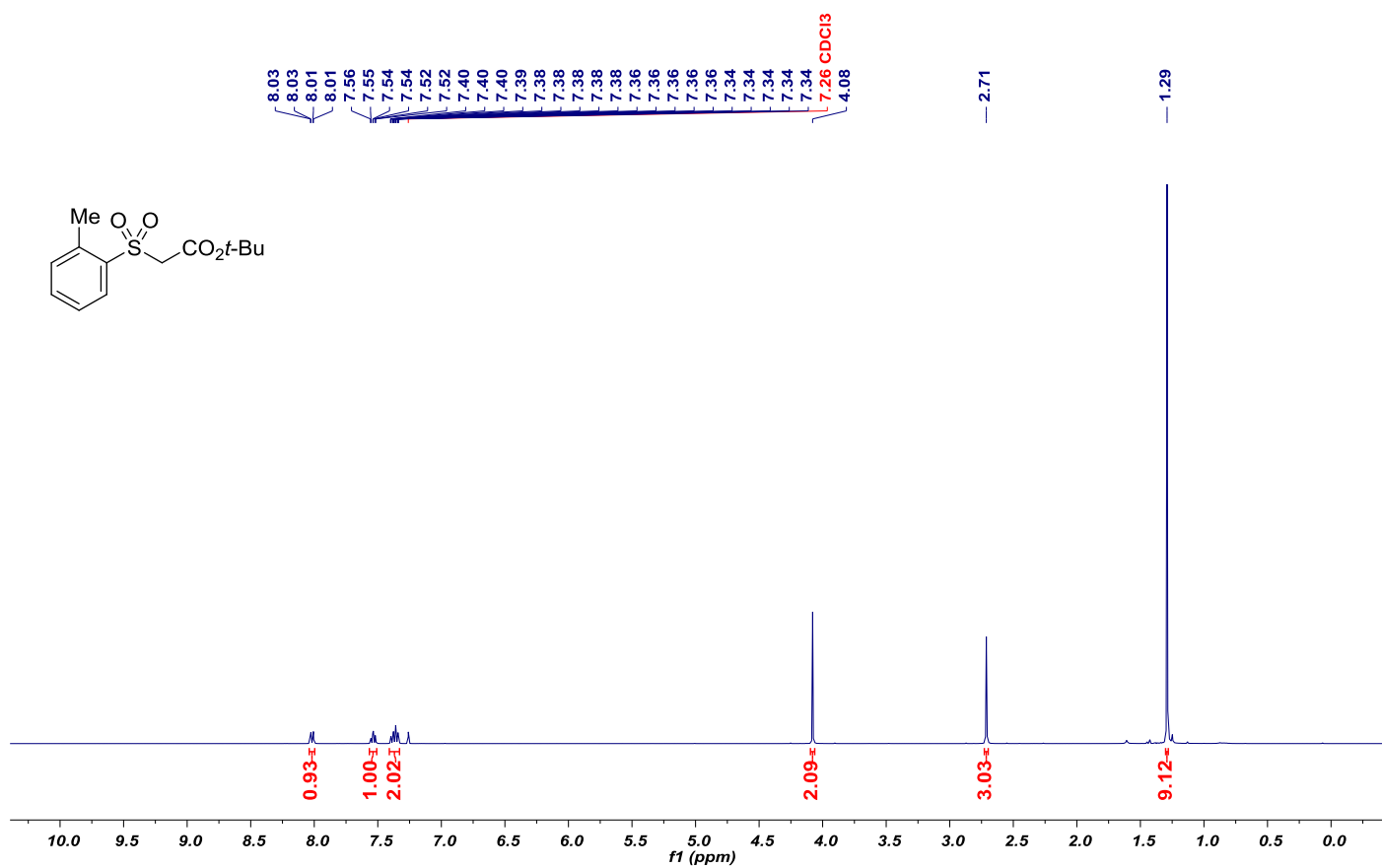
NMR spectrum of sulfone **2p**



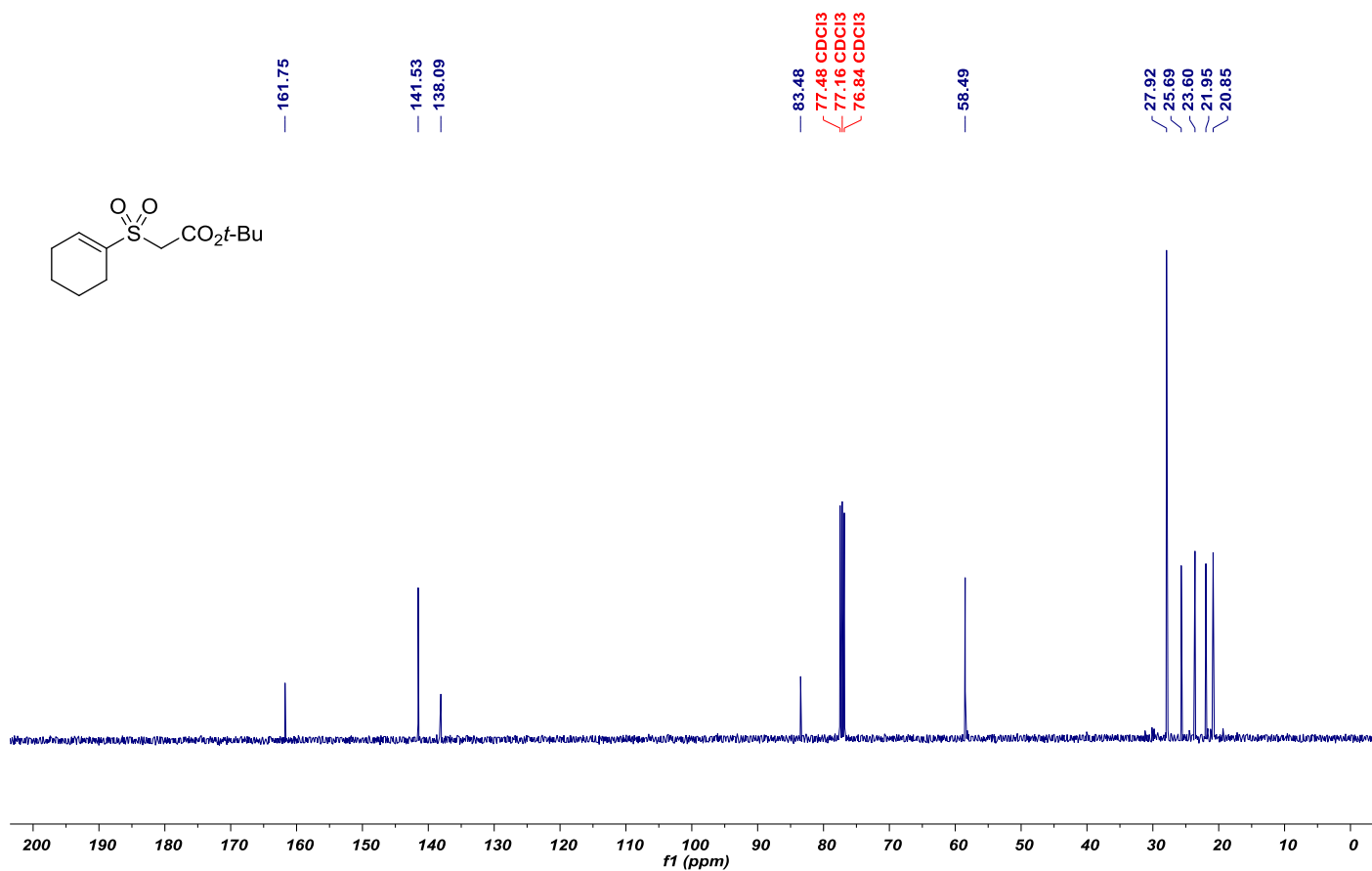
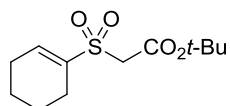
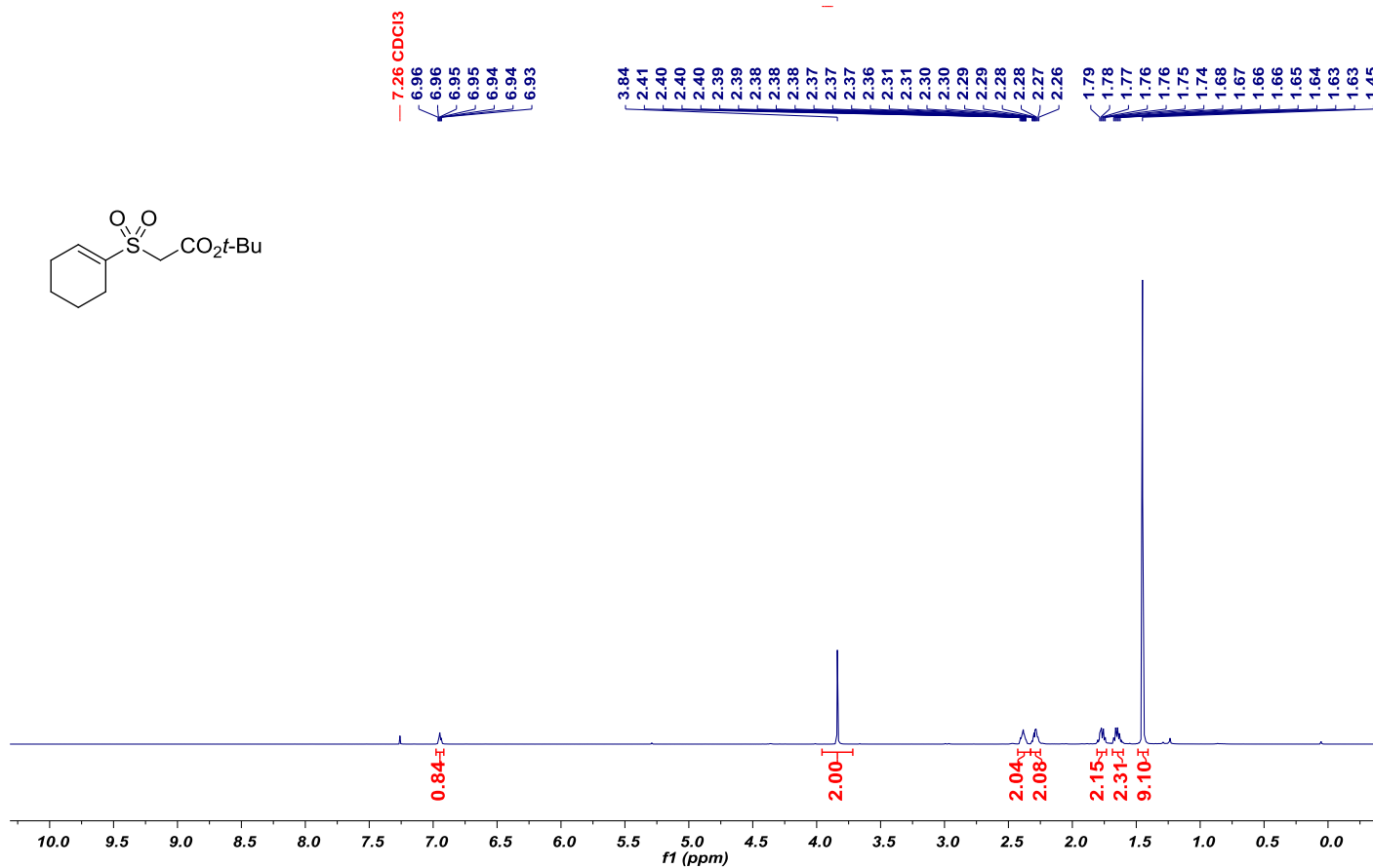
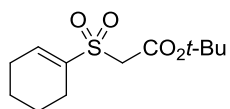
NMR spectrum of sulfone **2q**



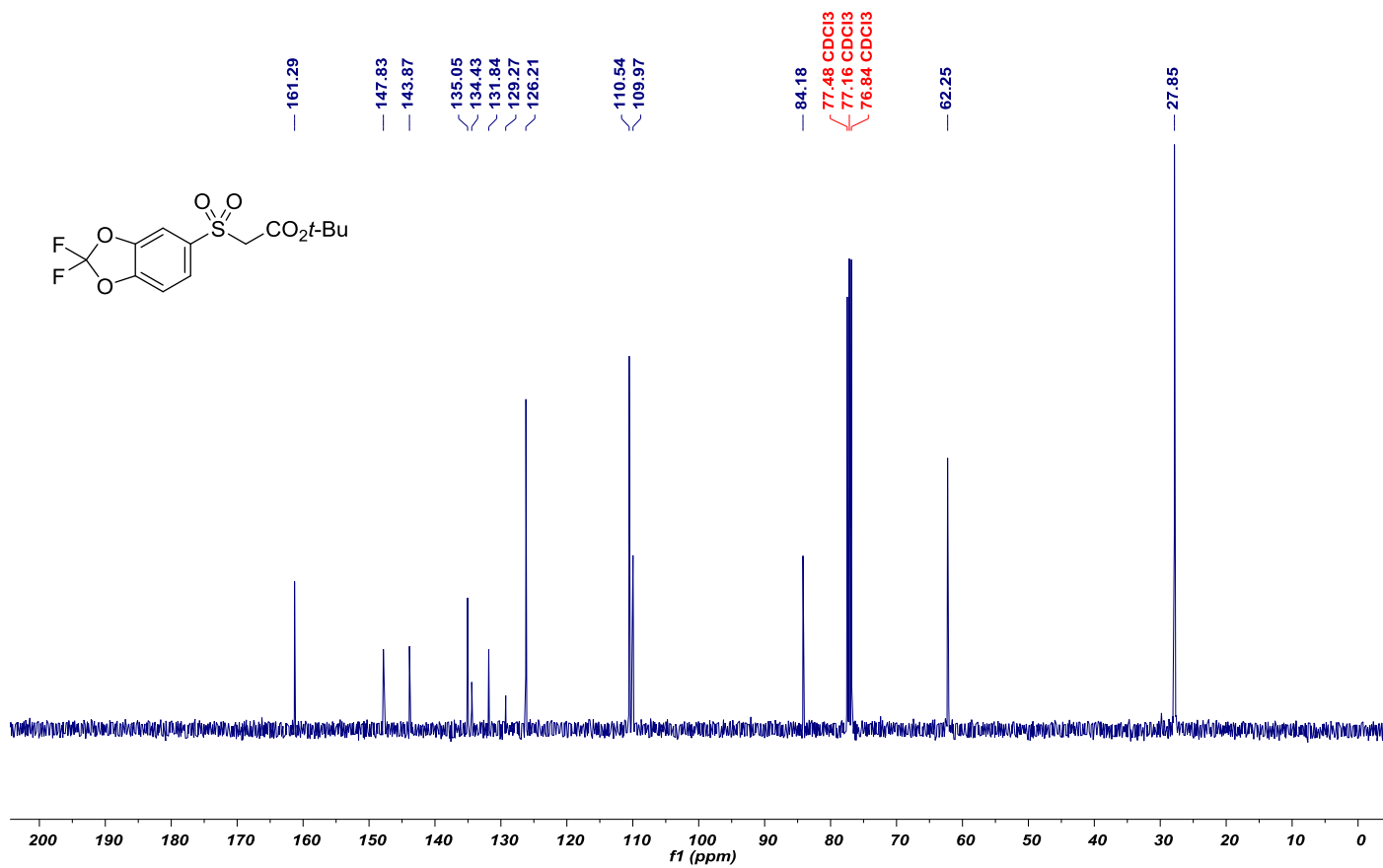
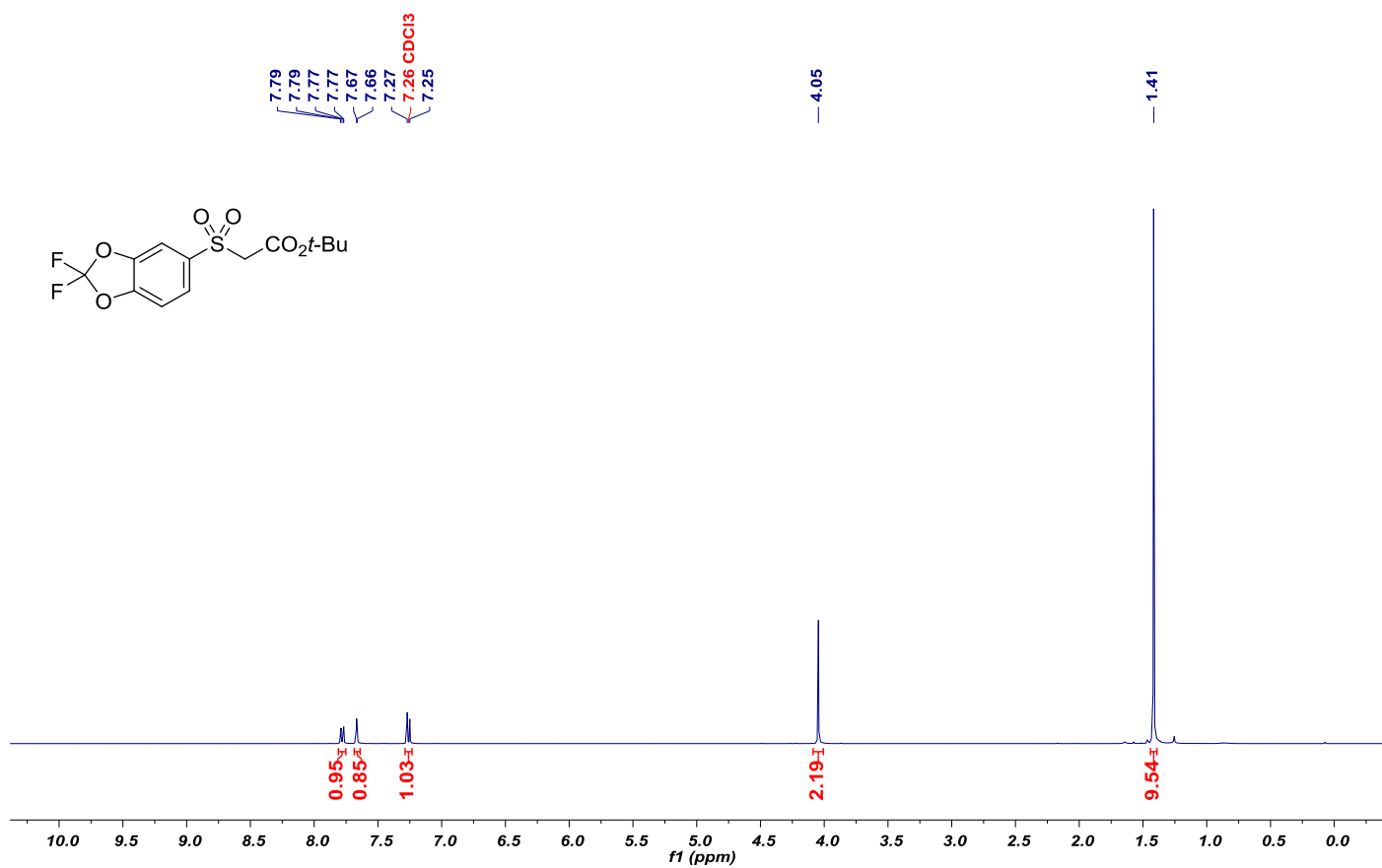
NMR spectrum of sulfone 2r

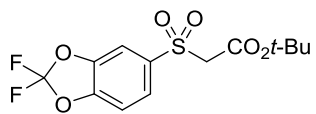


NMR spectrum of sulfone 2s

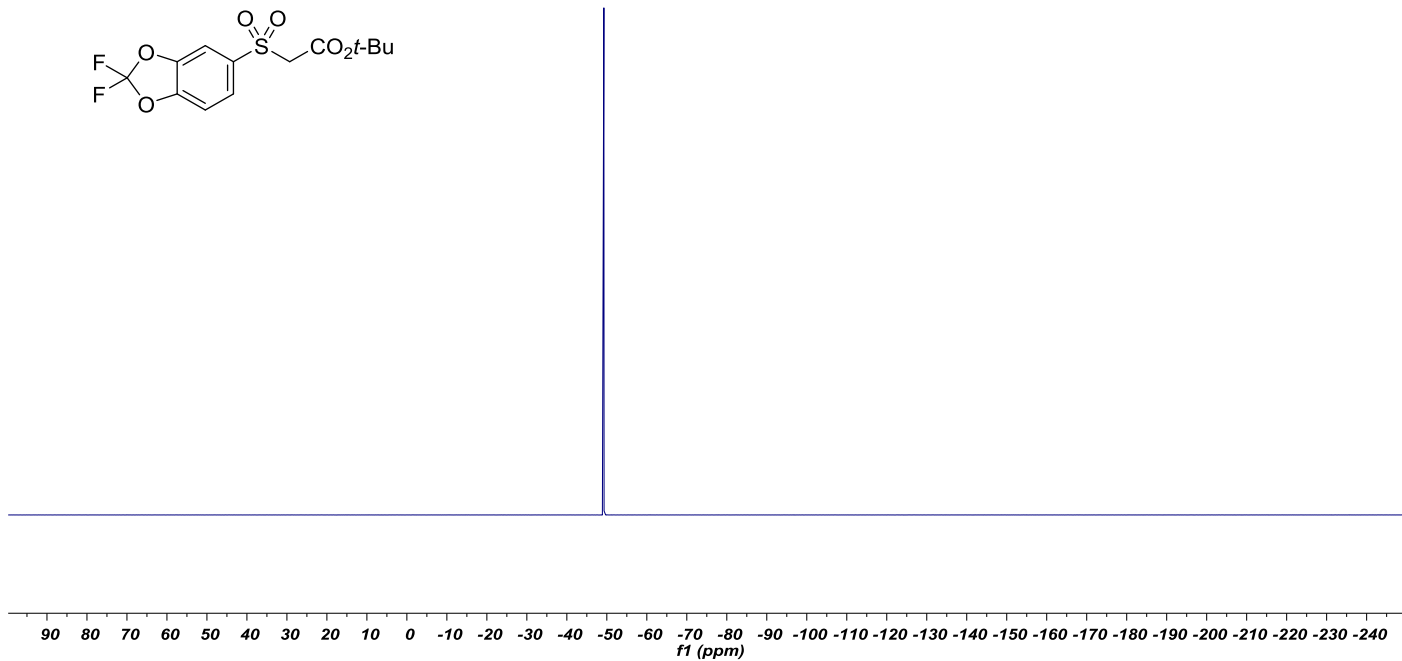


NMR spectrum of sulfone 2t

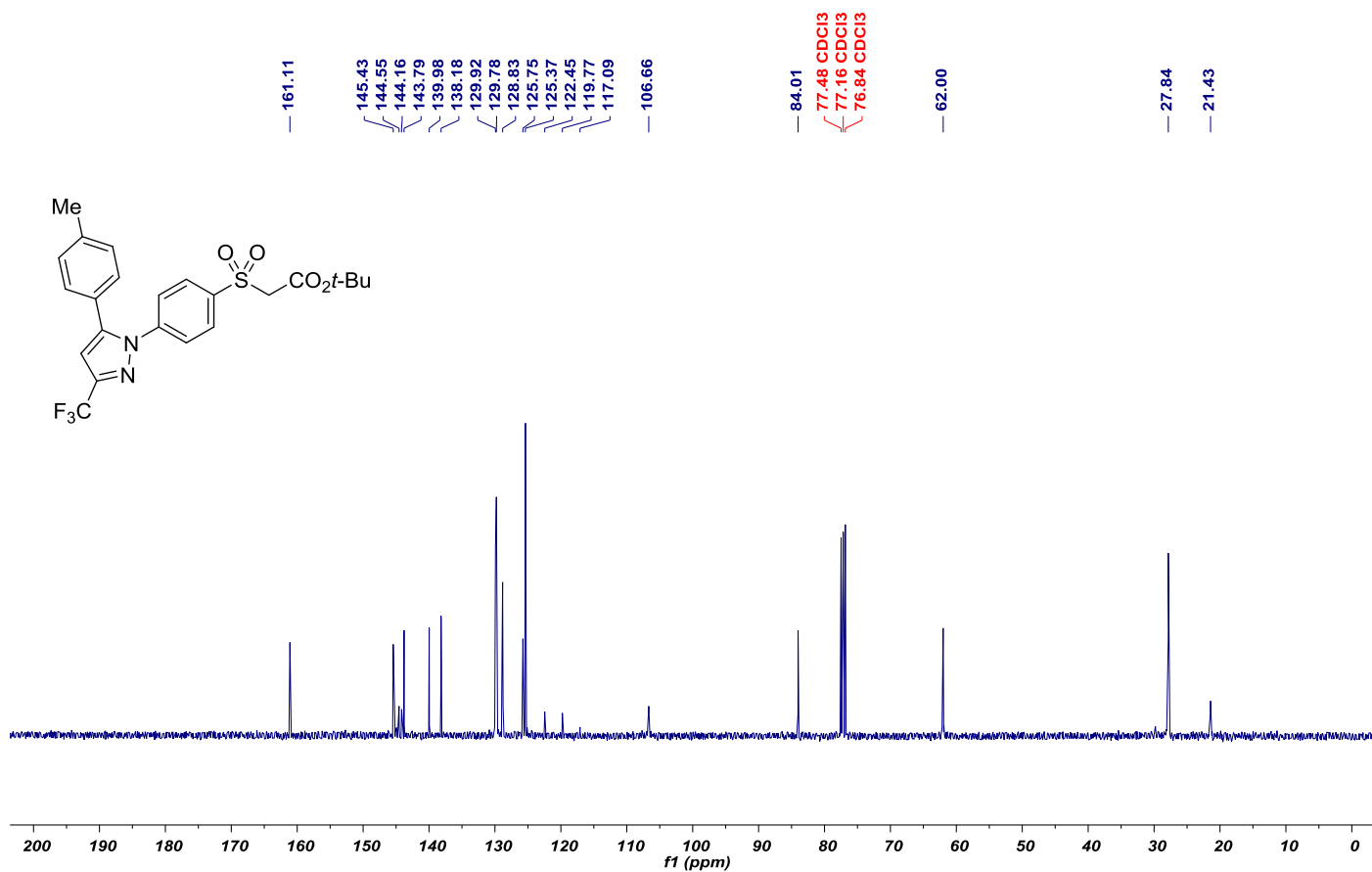
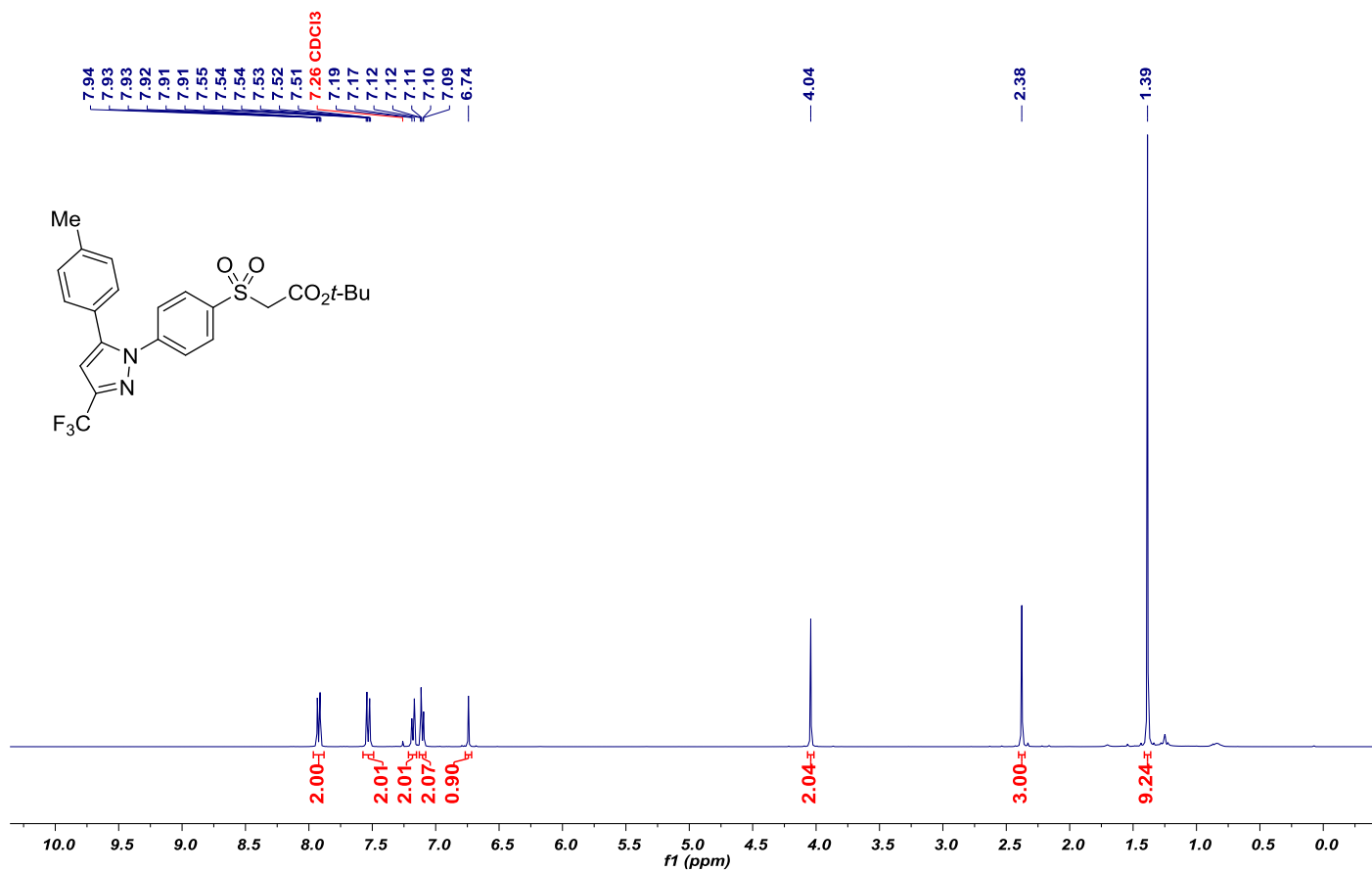


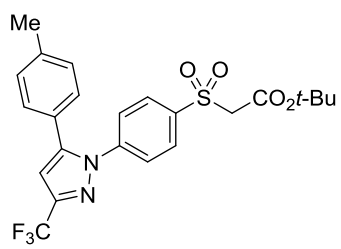


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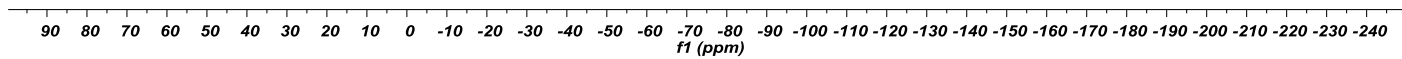


NMR spectrum of sulfone **2u**

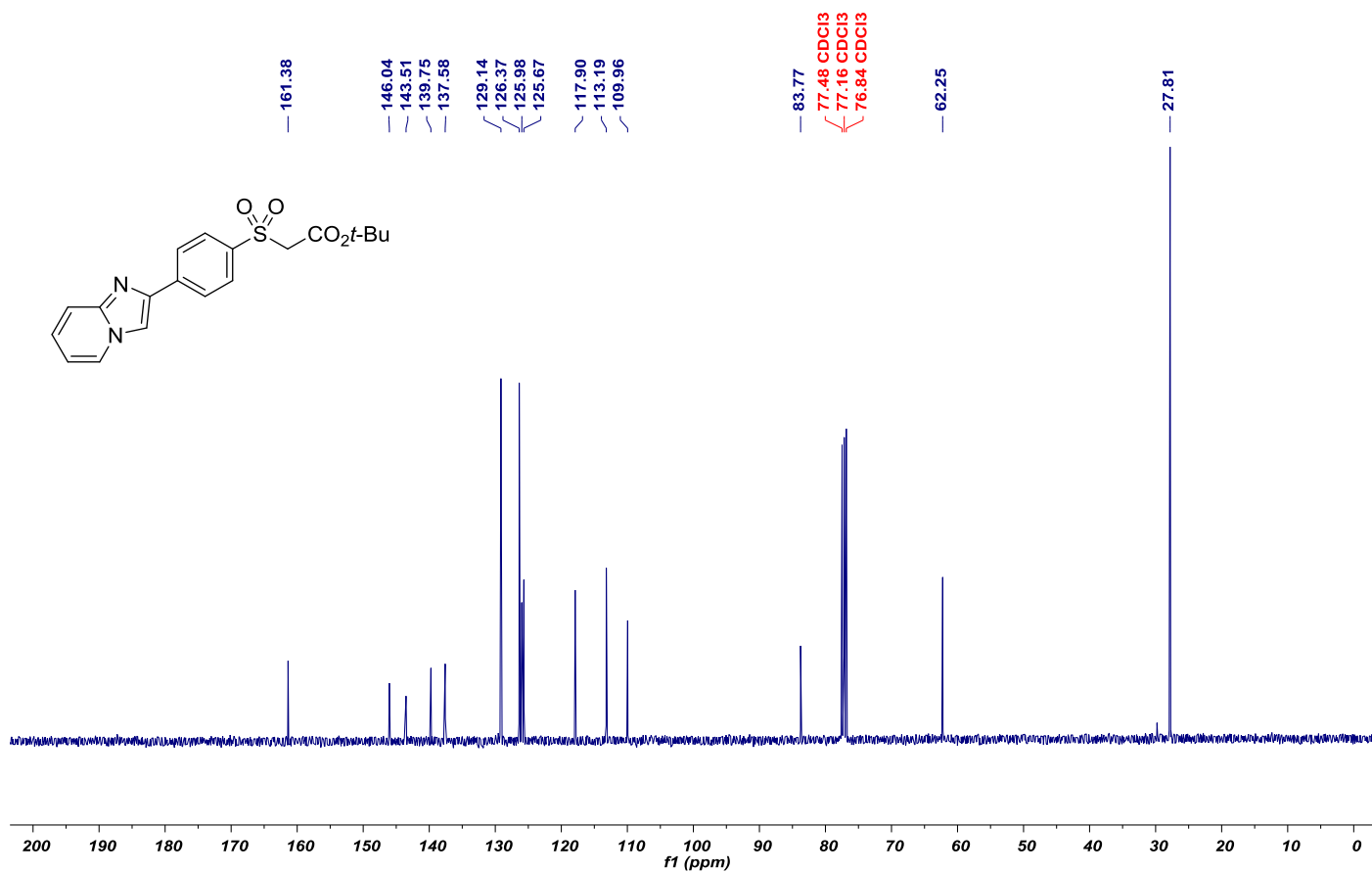
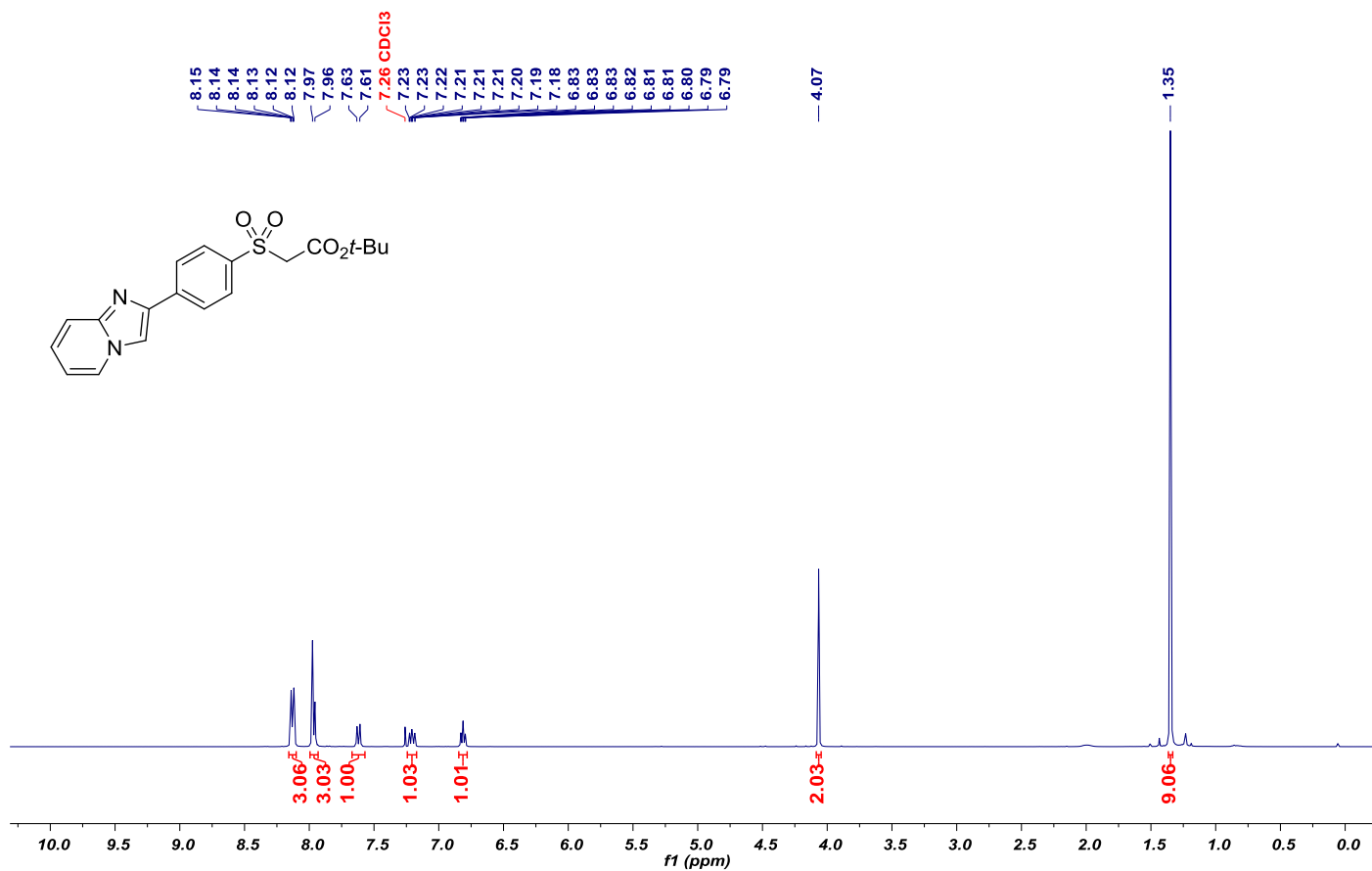




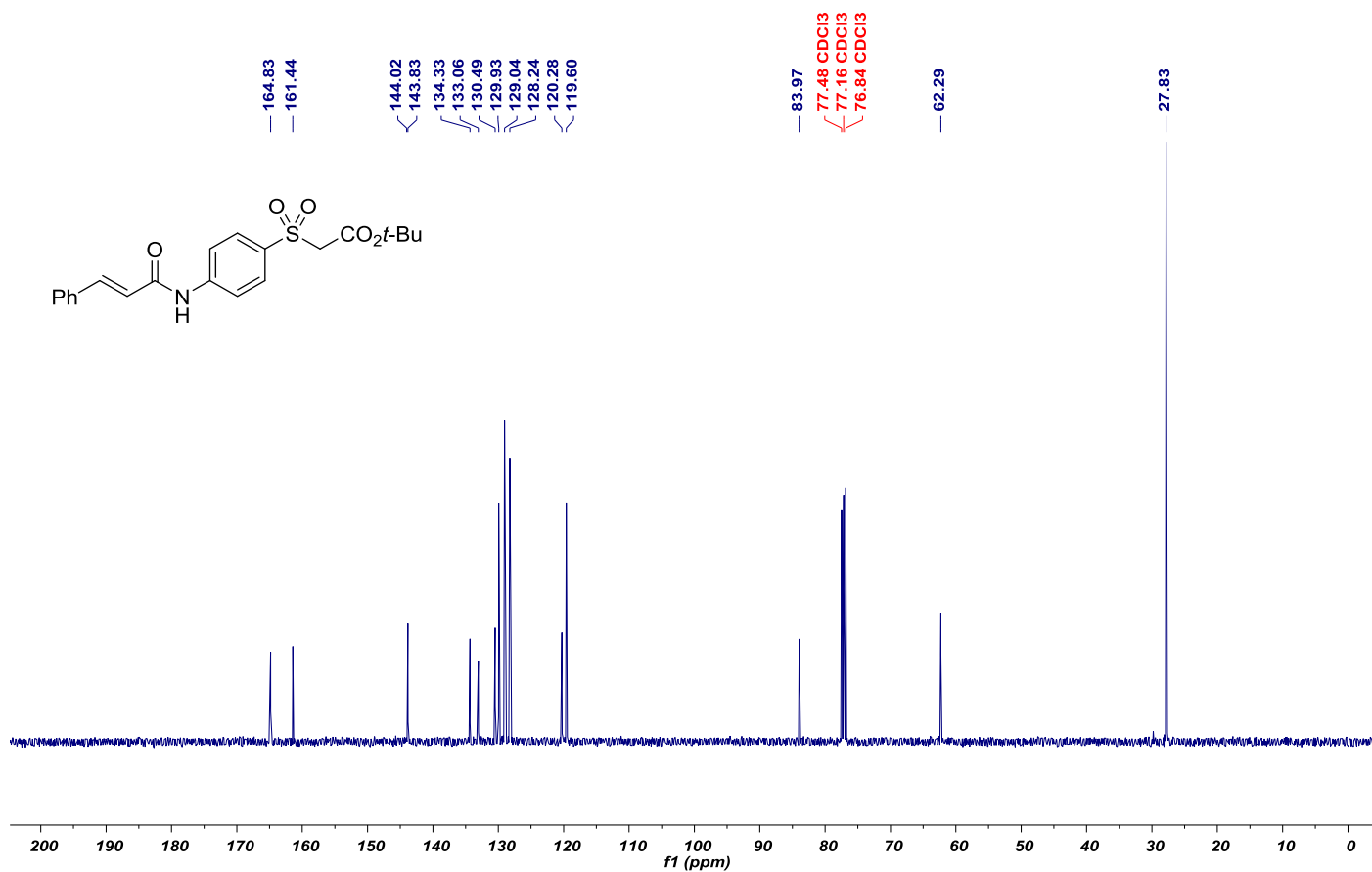
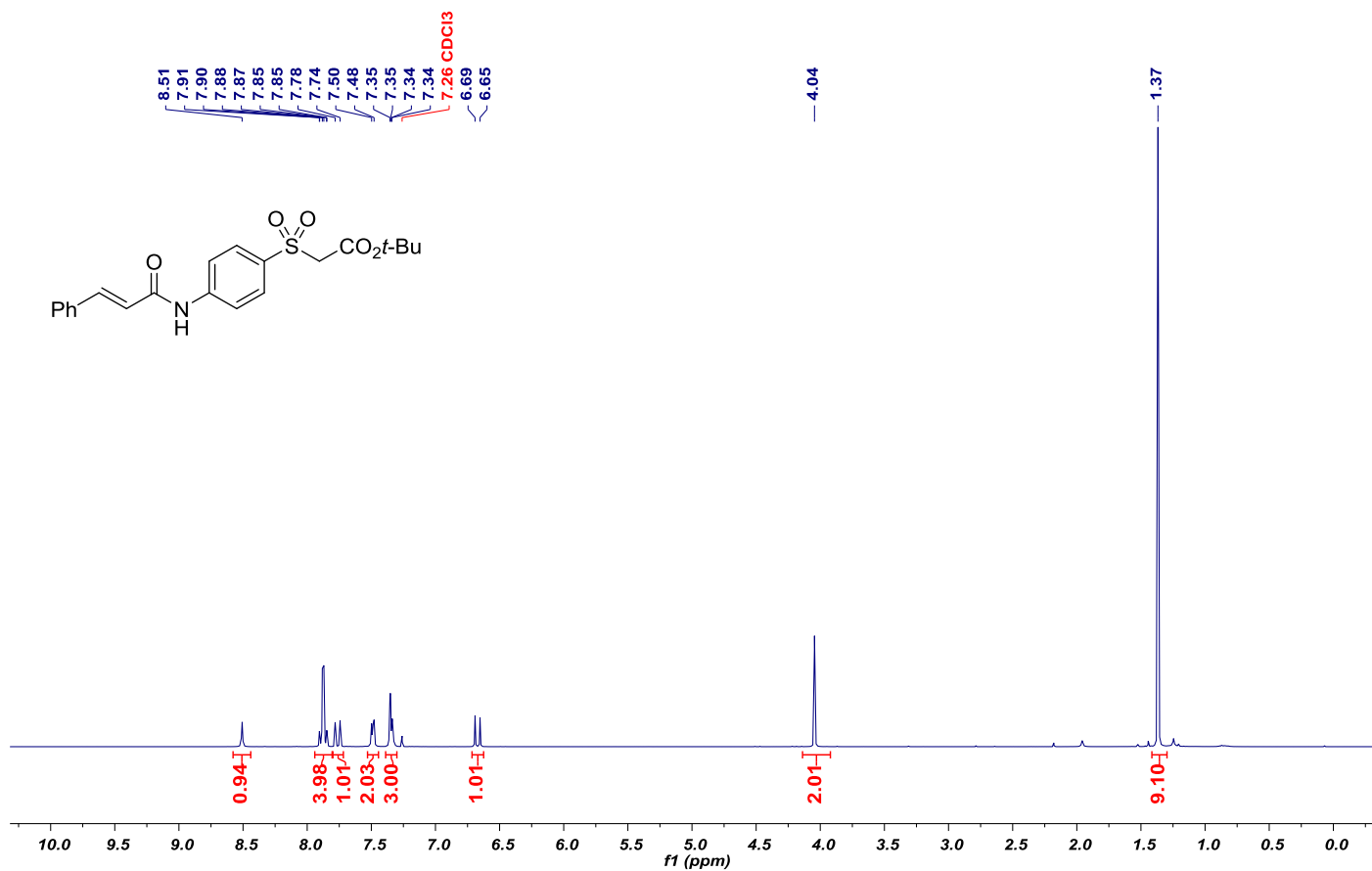
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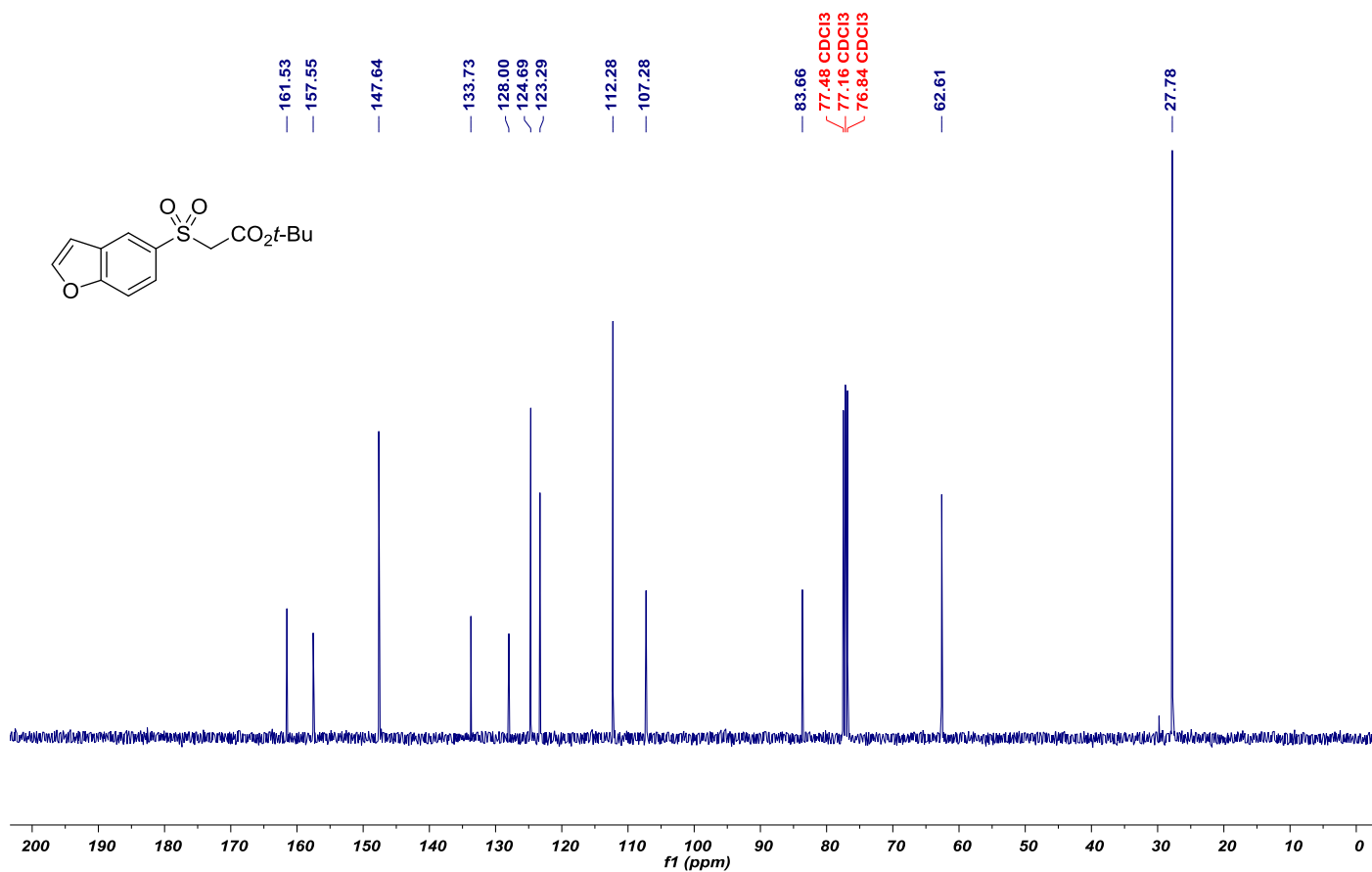
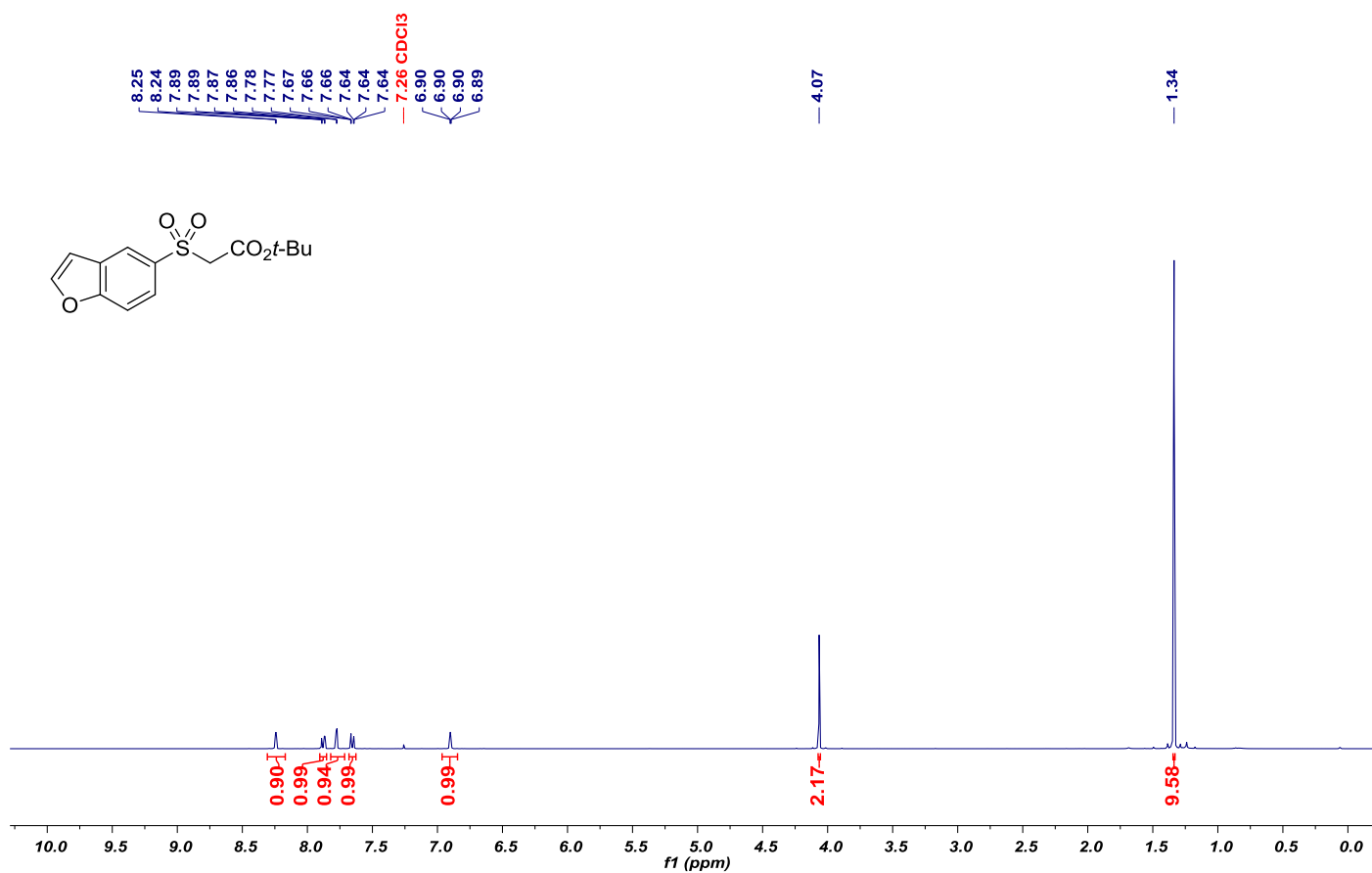
NMR spectrum of sulfone **2v**



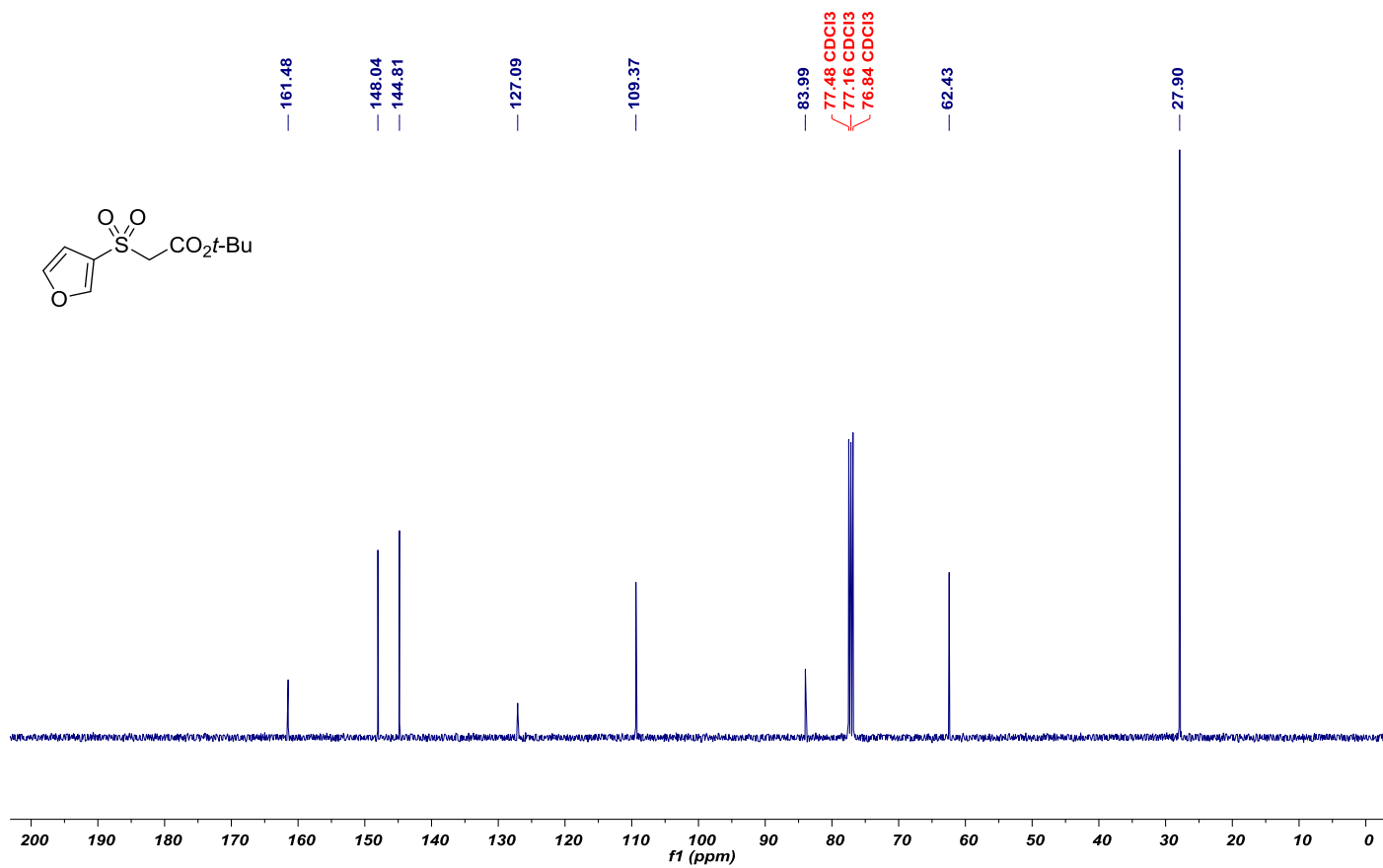
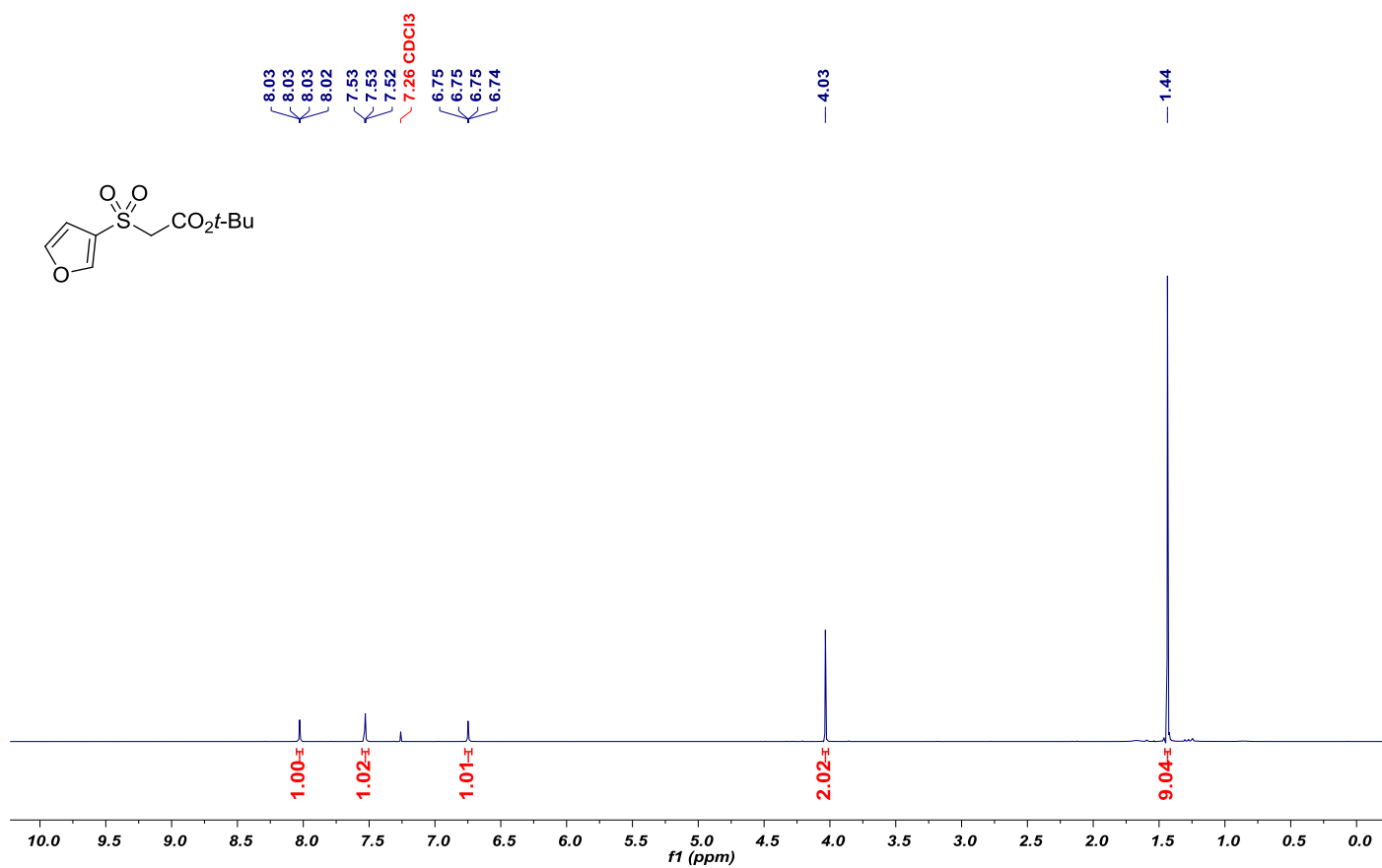
NMR spectrum of sulfone **2w**



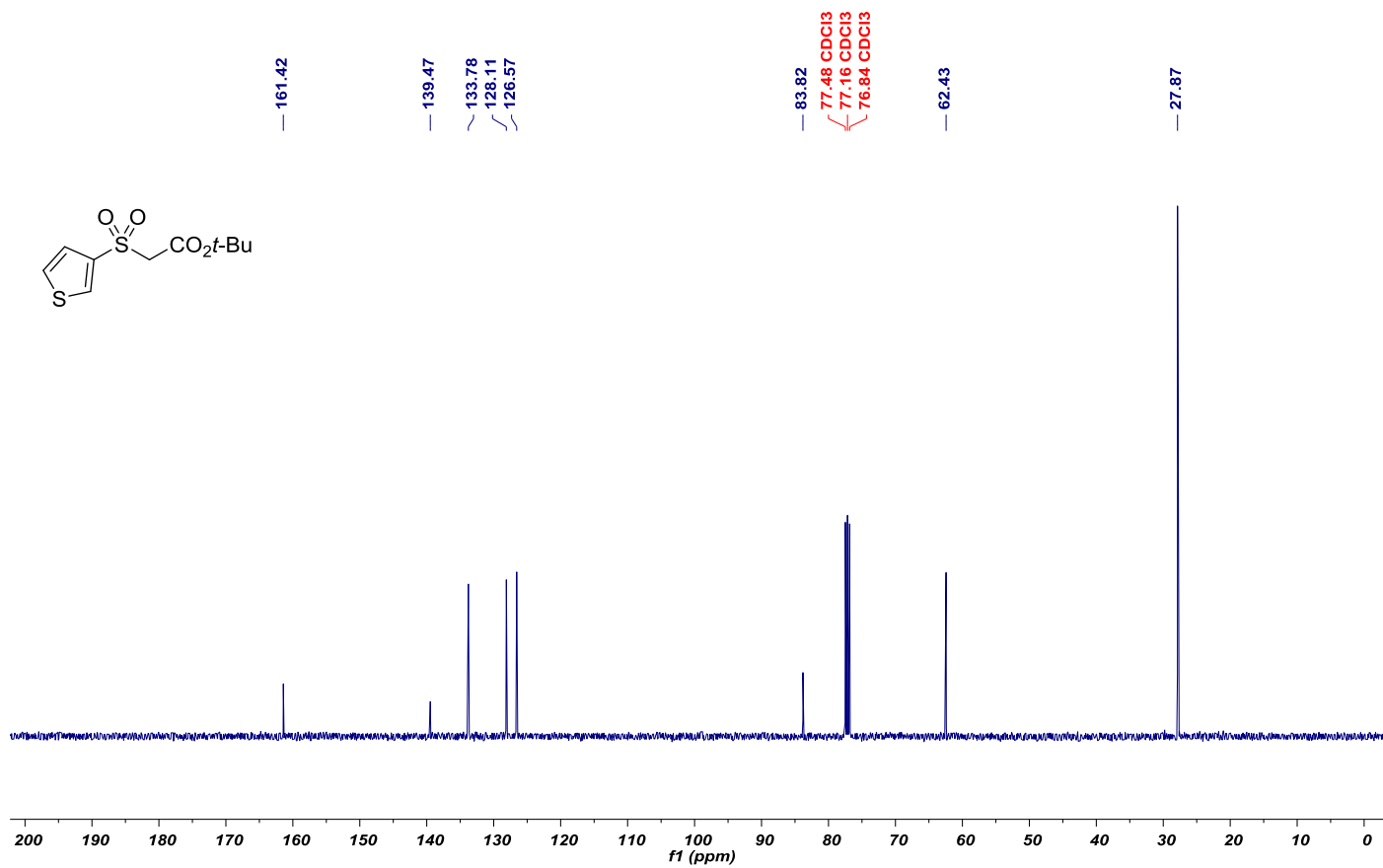
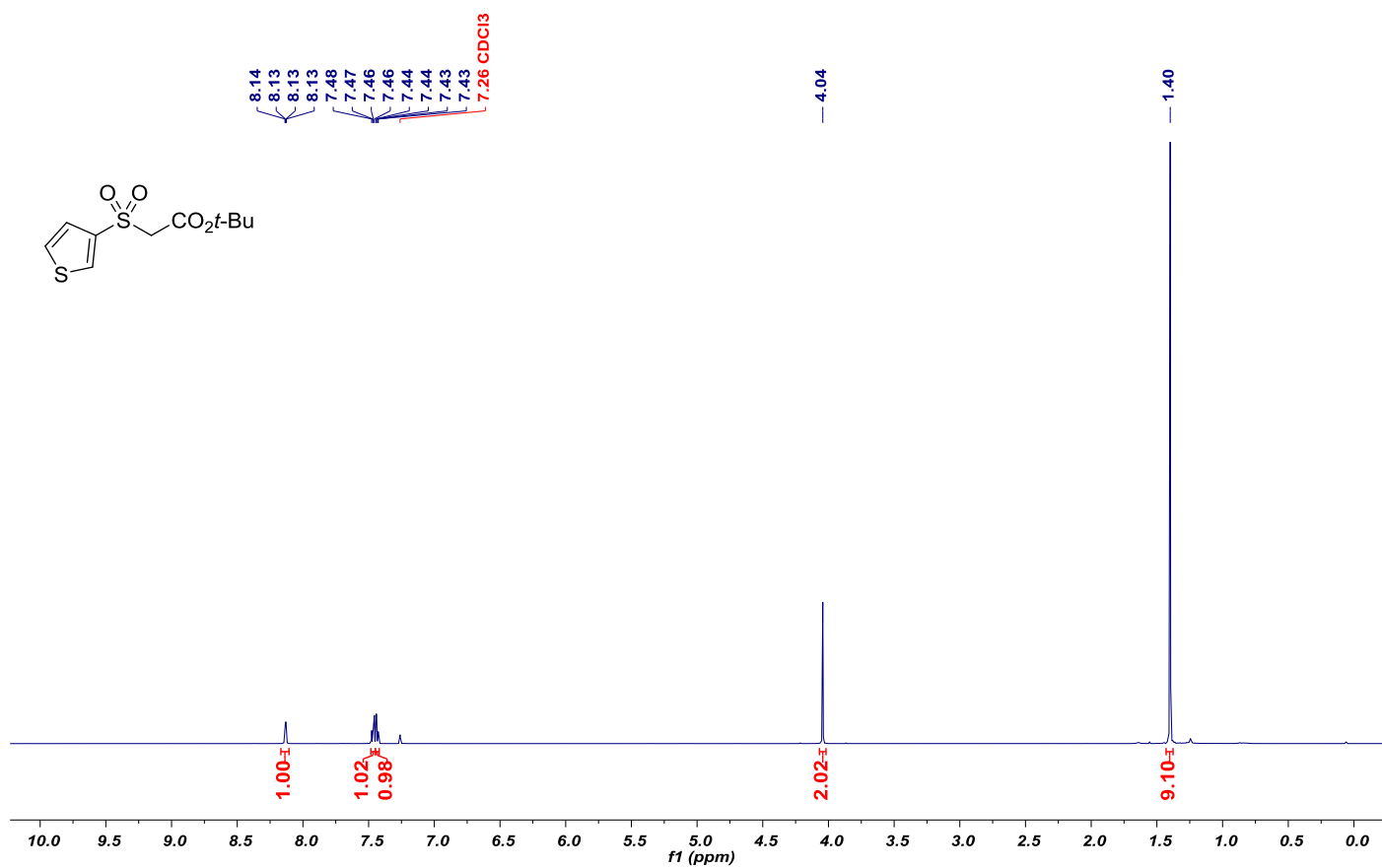
NMR spectrum of sulfone **2x**



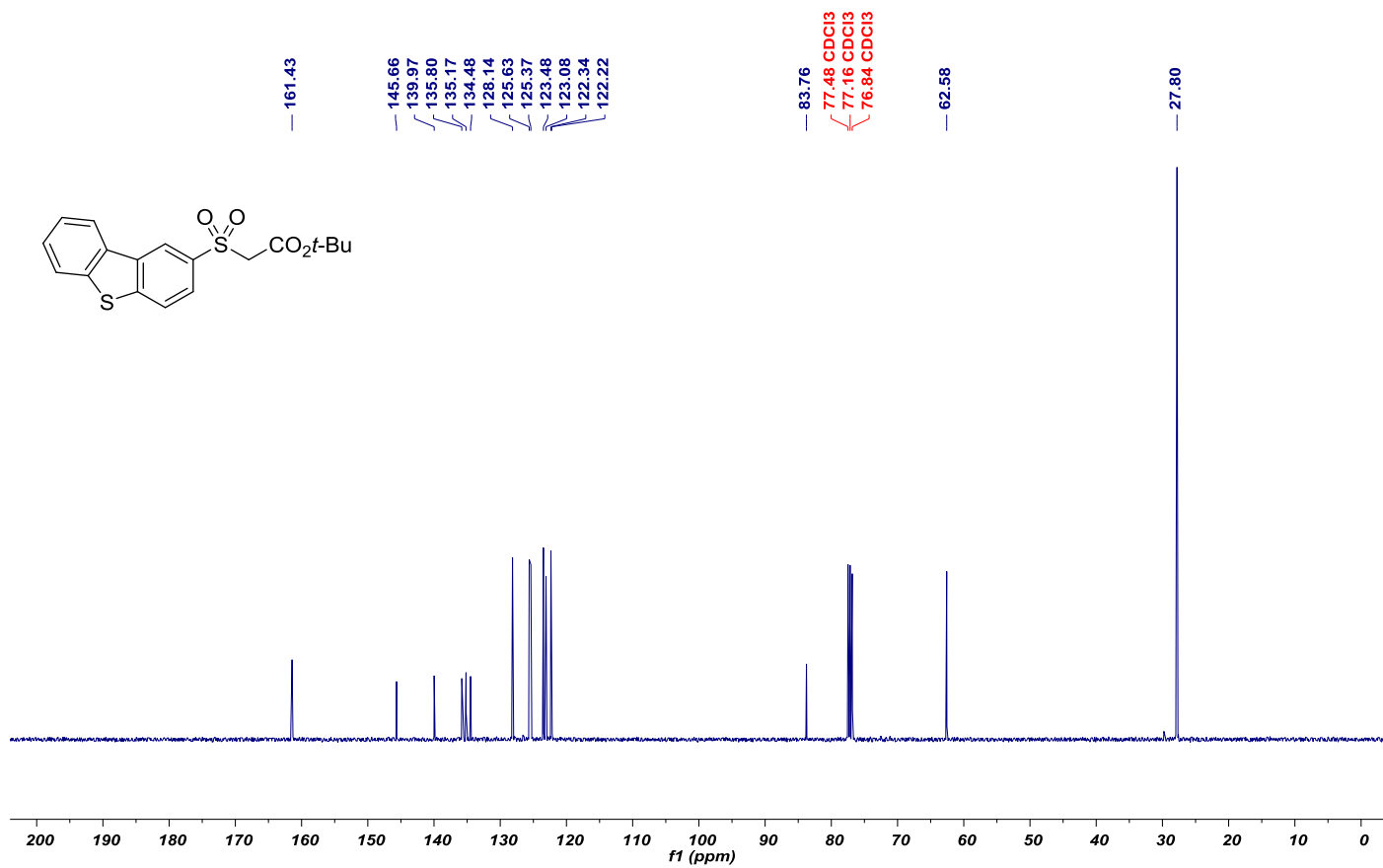
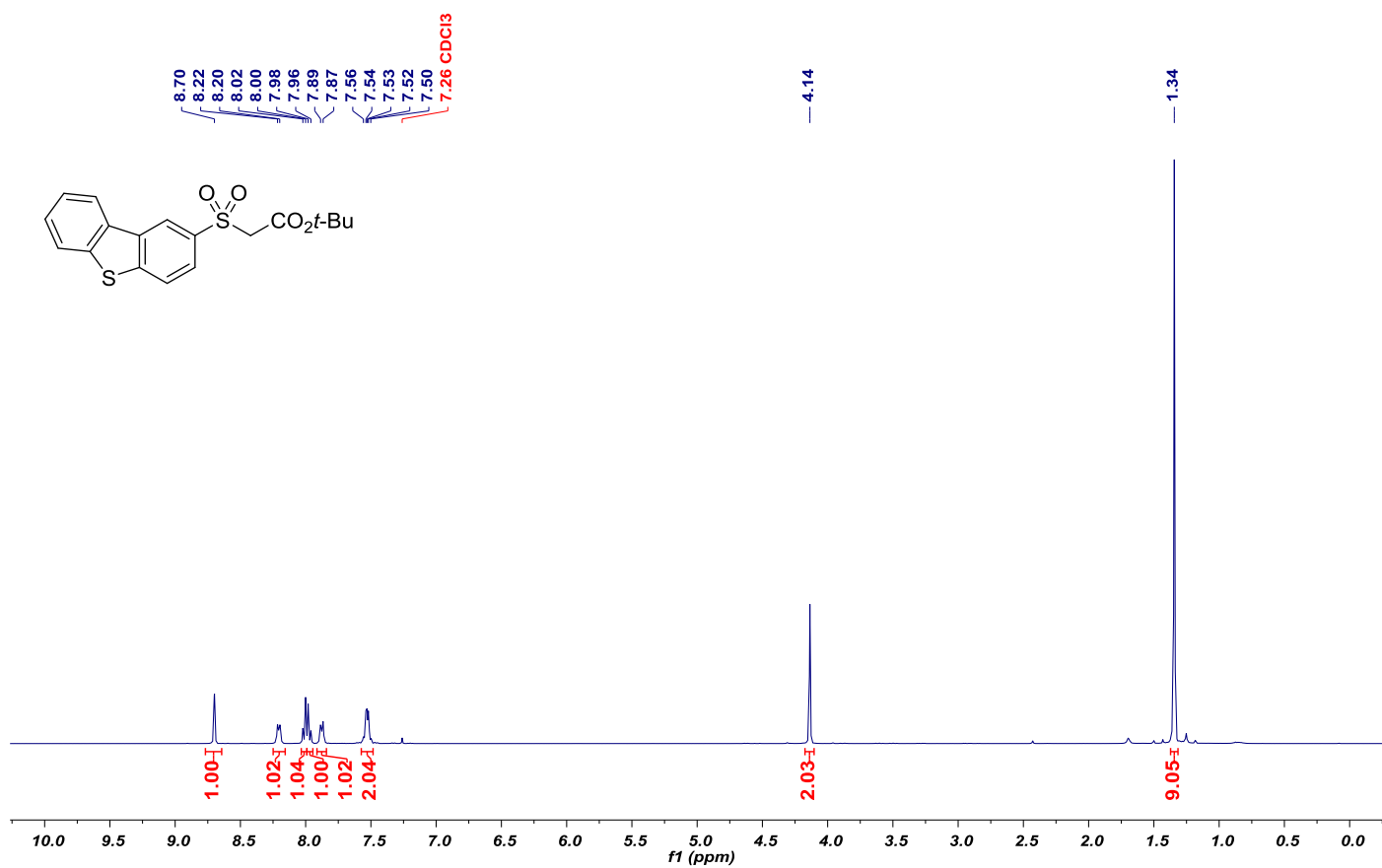
NMR spectrum of sulfone **2y**



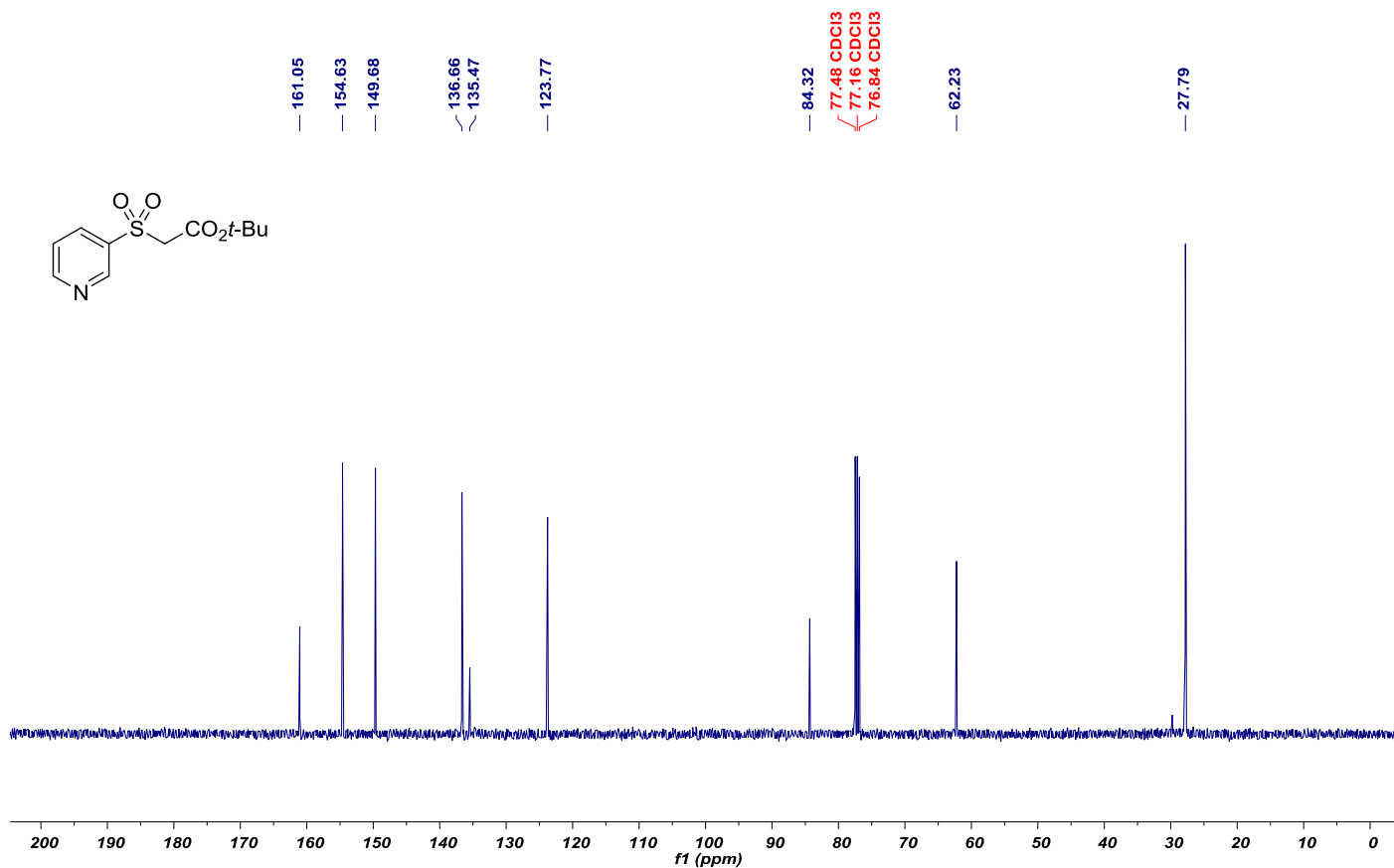
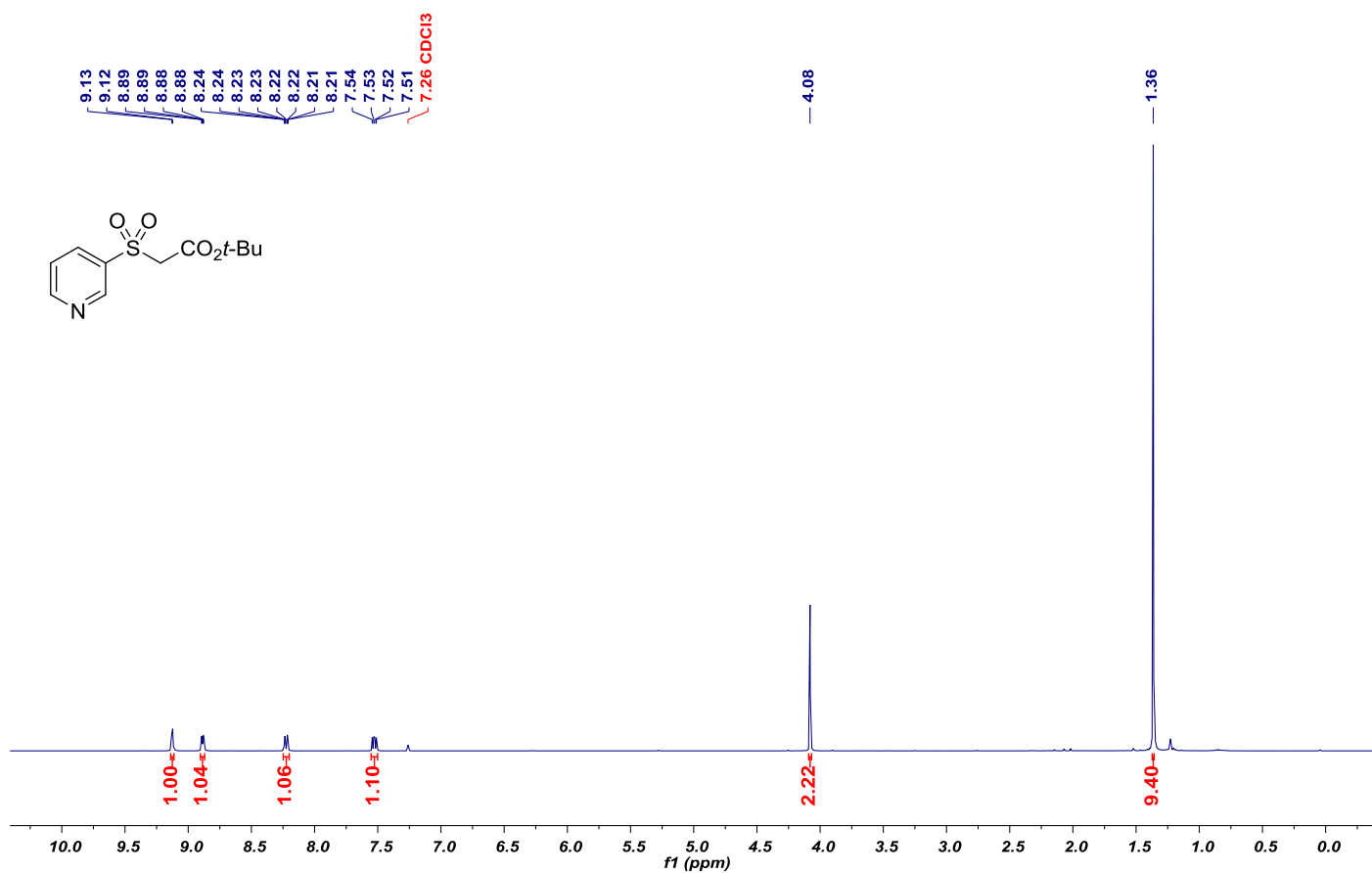
NMR spectrum of sulfone **2z**



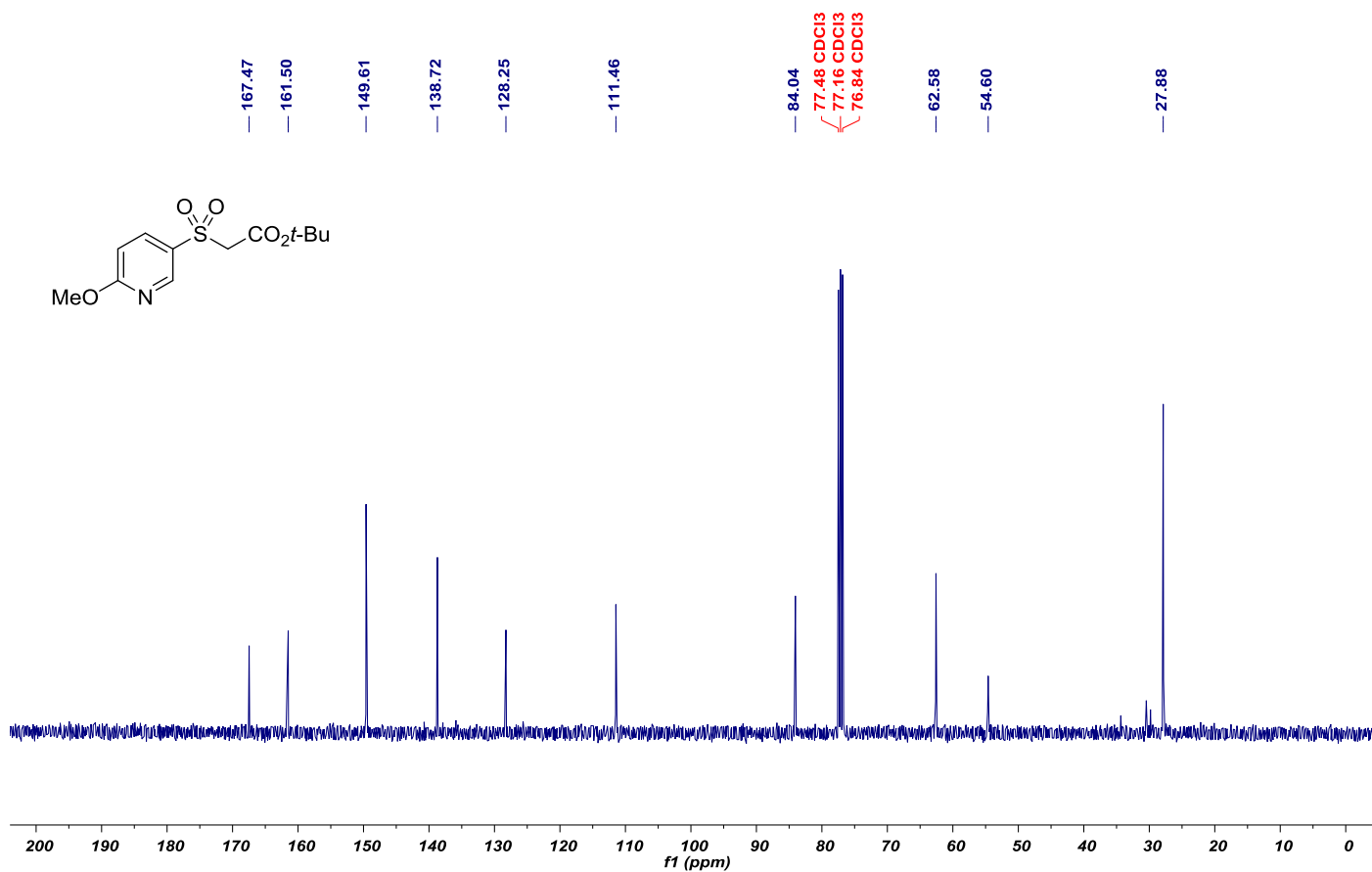
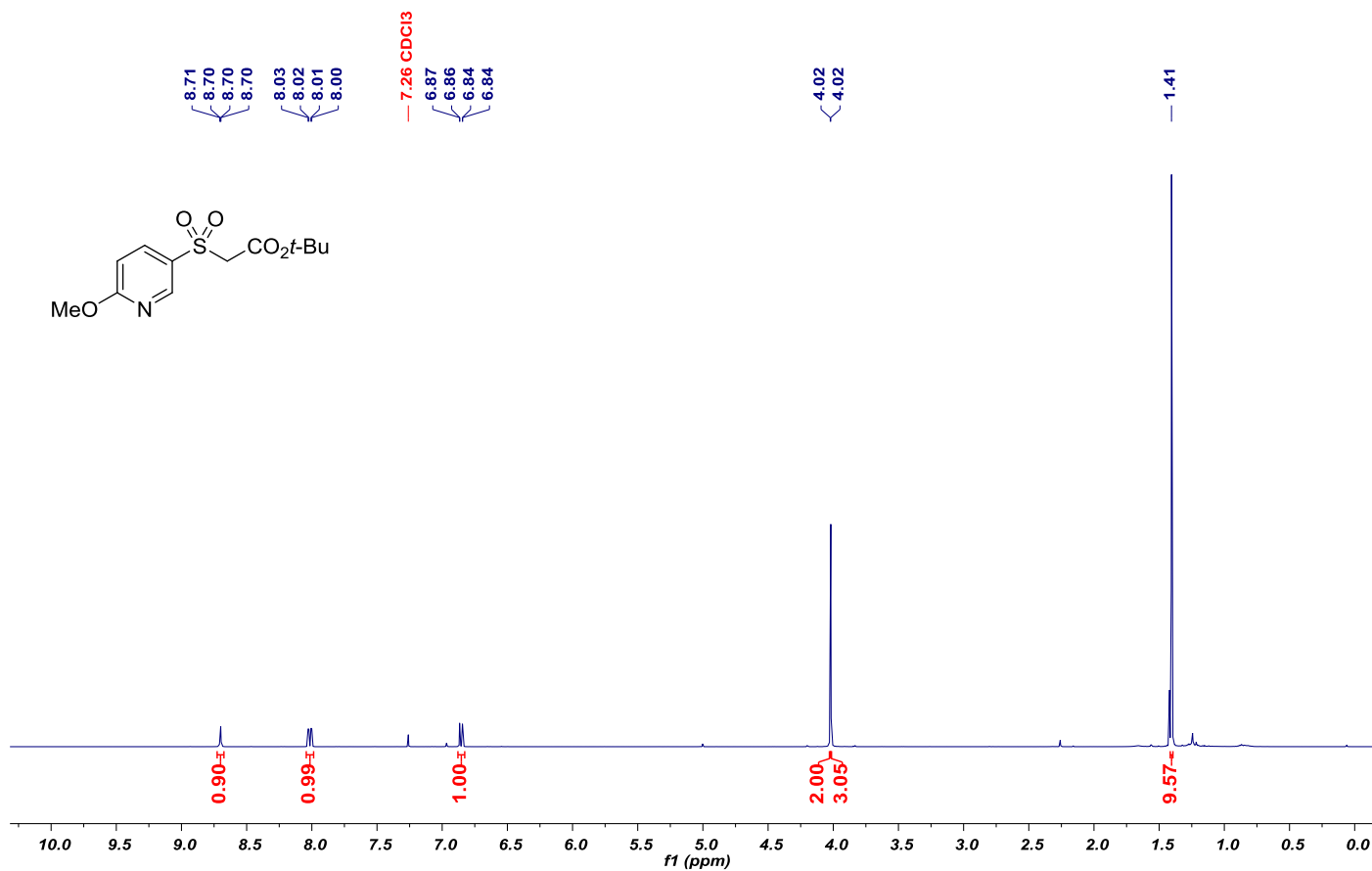
NMR spectrum of sulfone 2aa



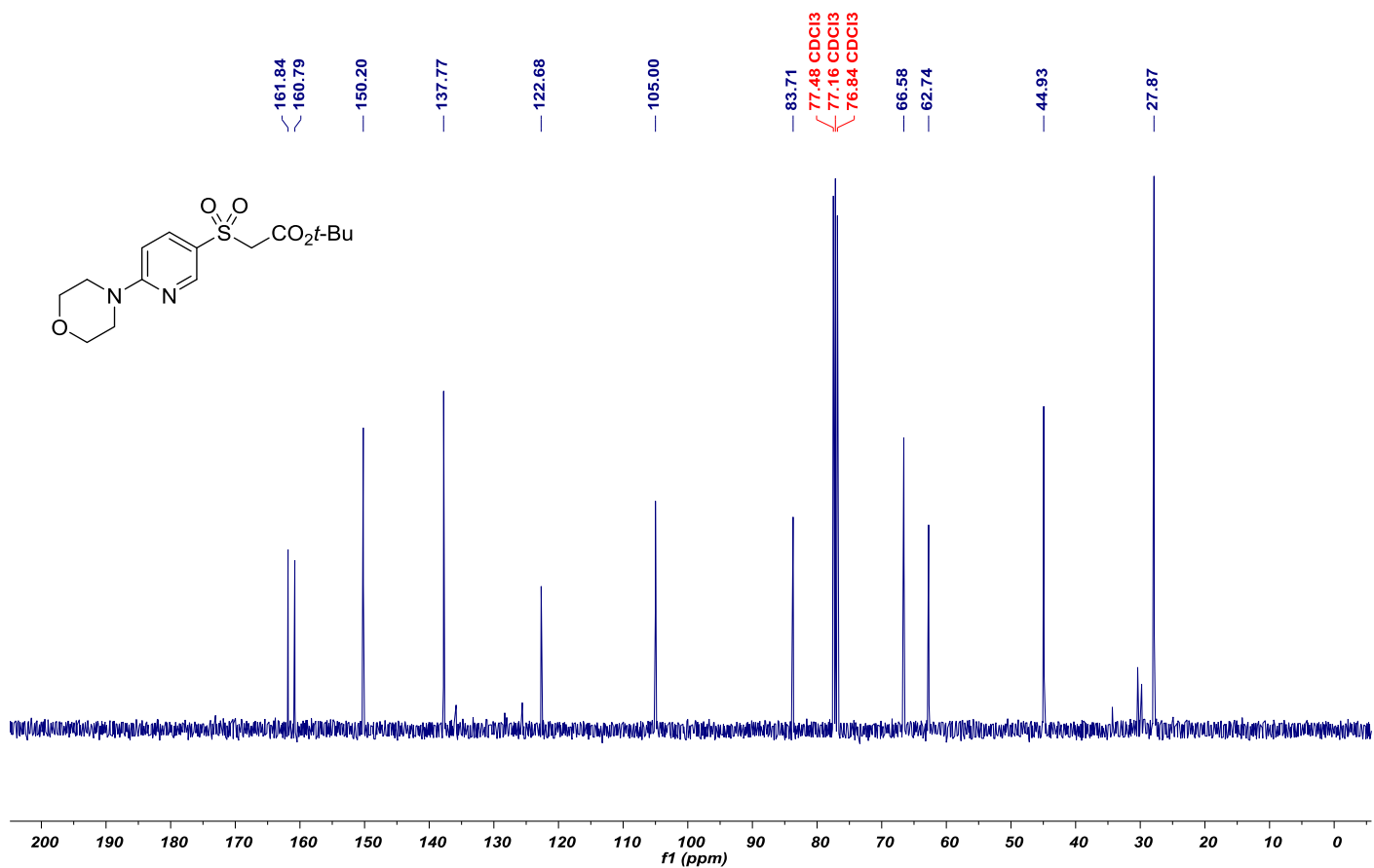
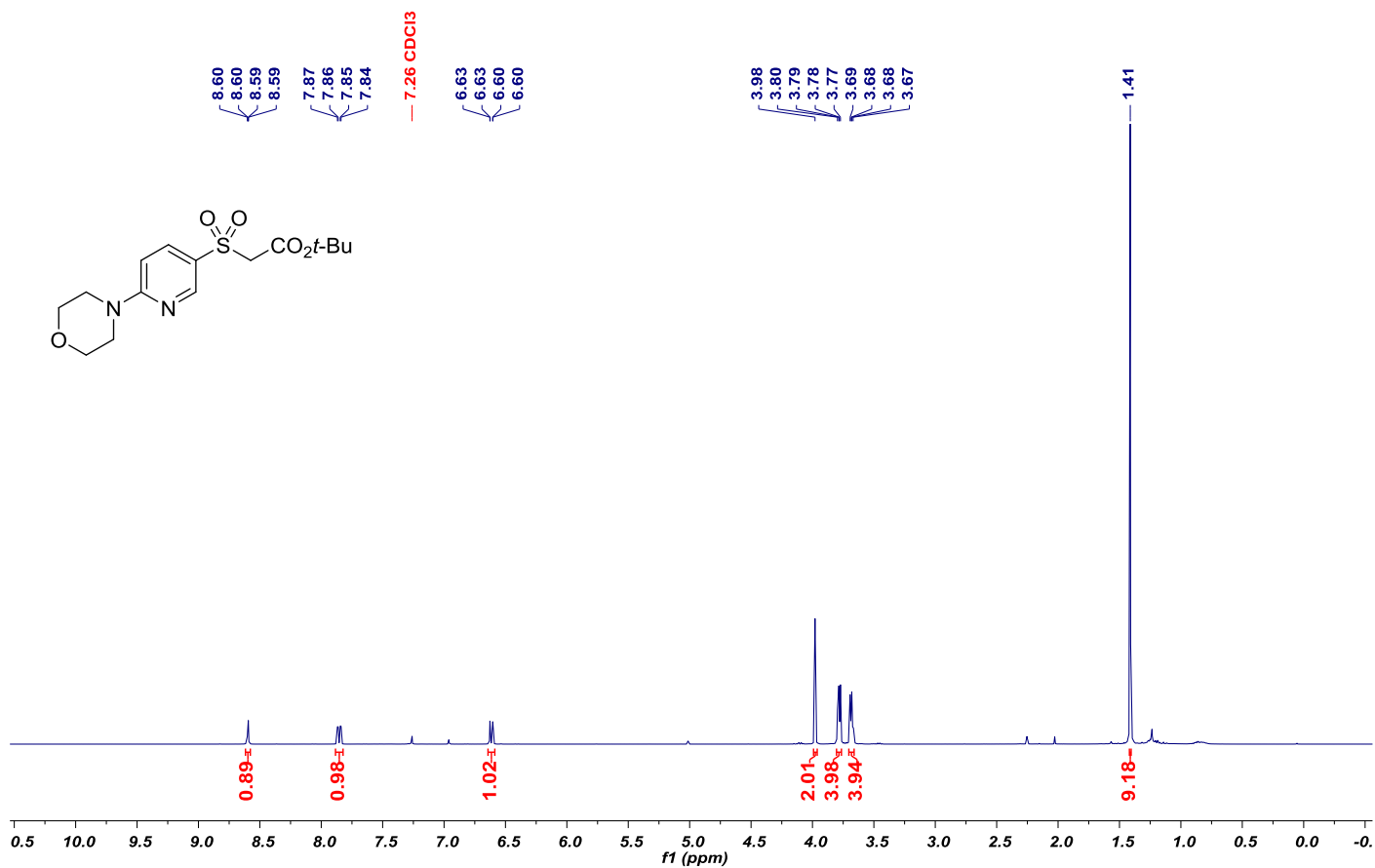
NMR spectrum of sulfone **2ab**



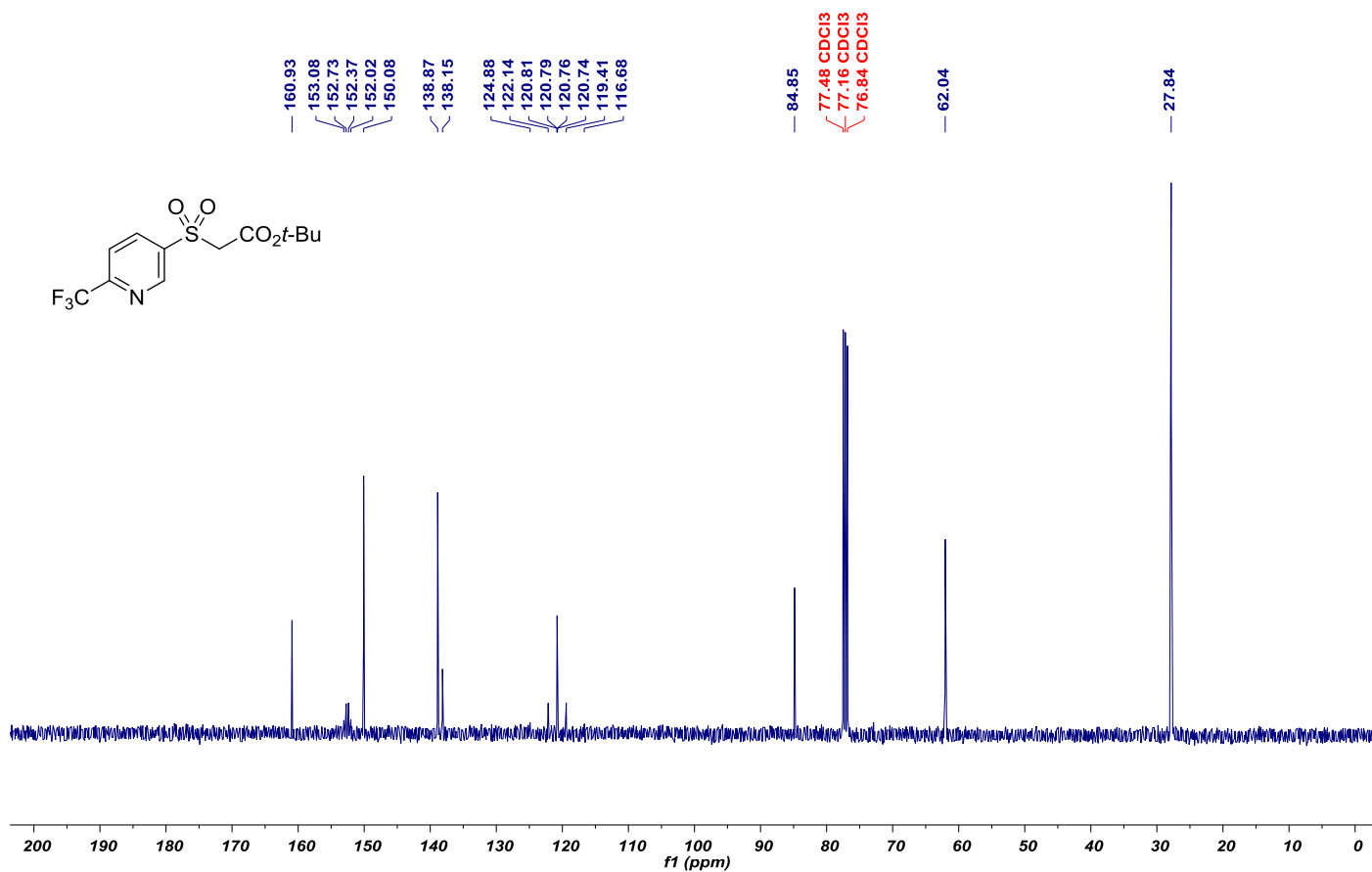
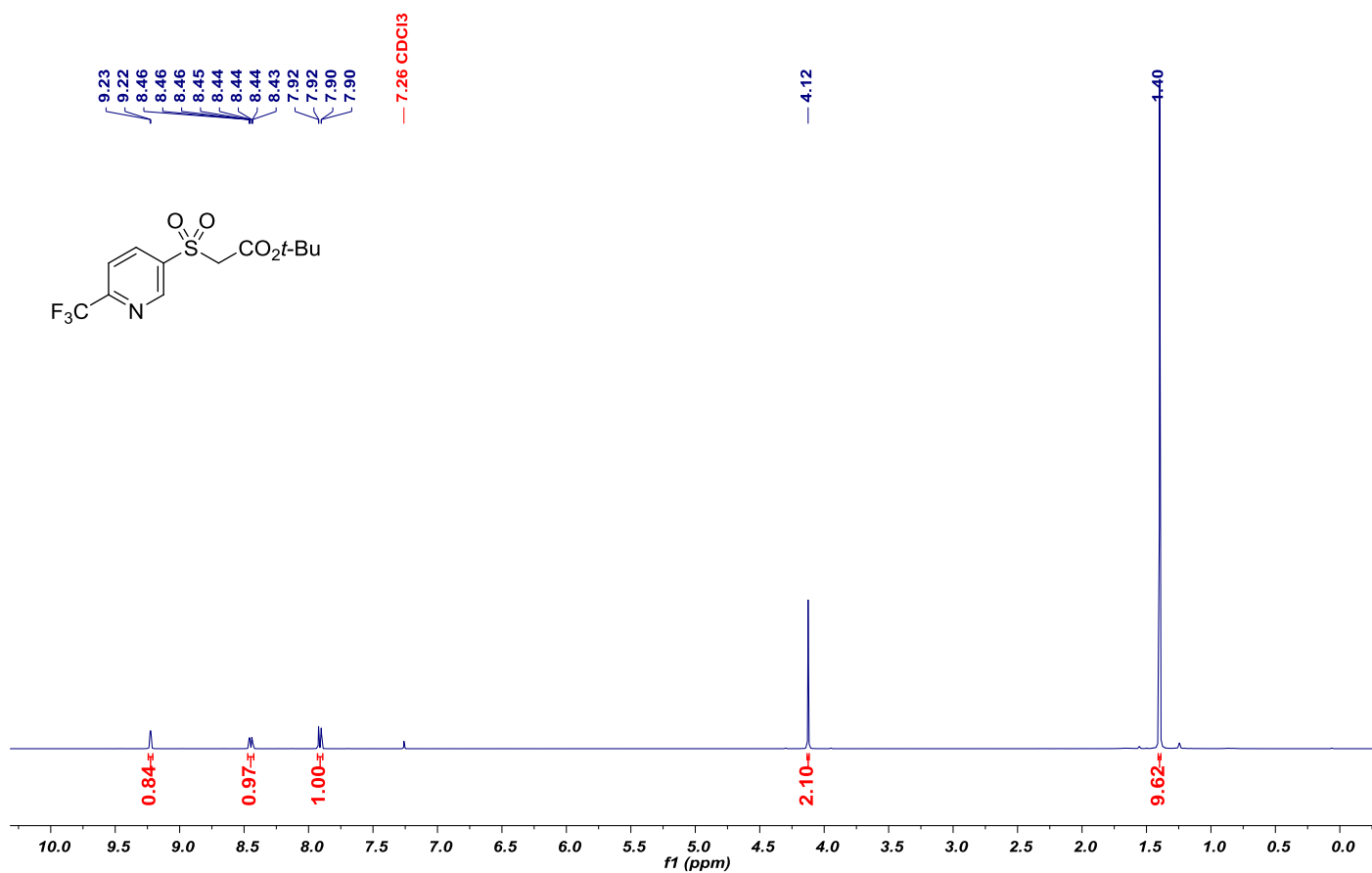
NMR spectrum of sulfone **2ac**



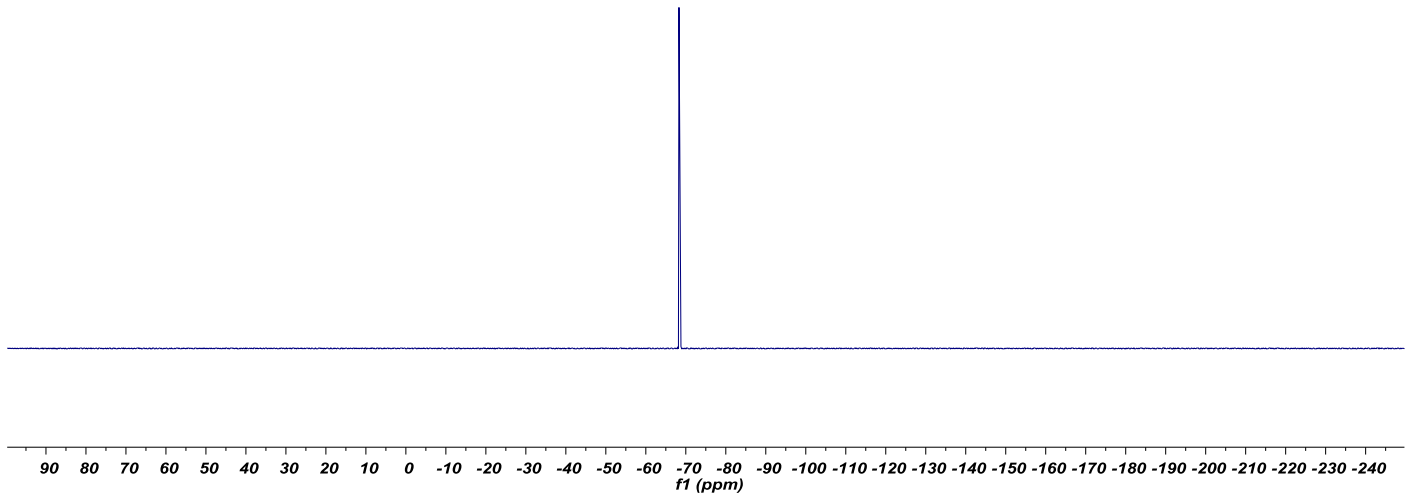
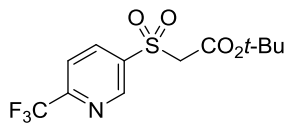
NMR spectrum of sulfone **2ad**



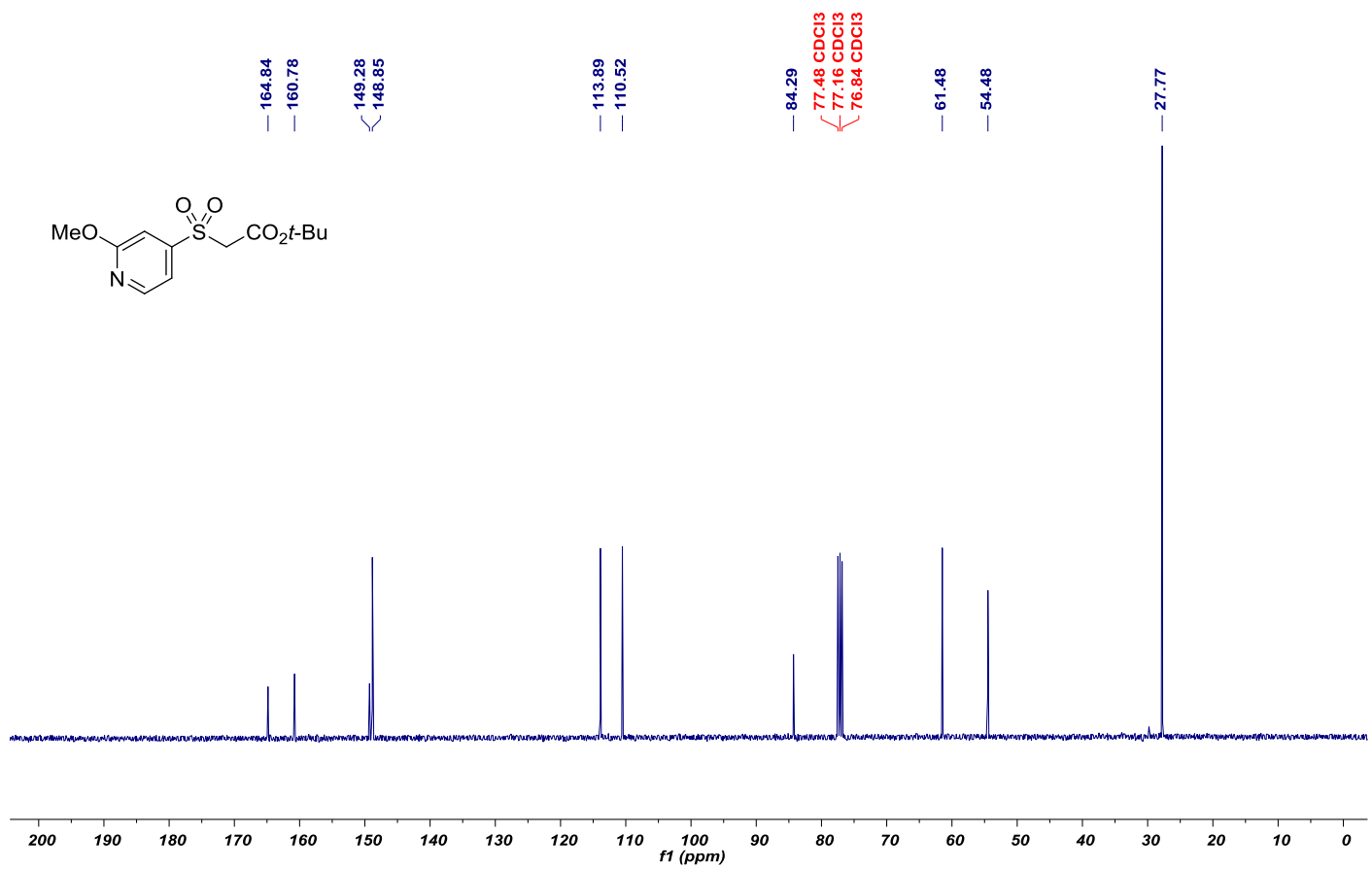
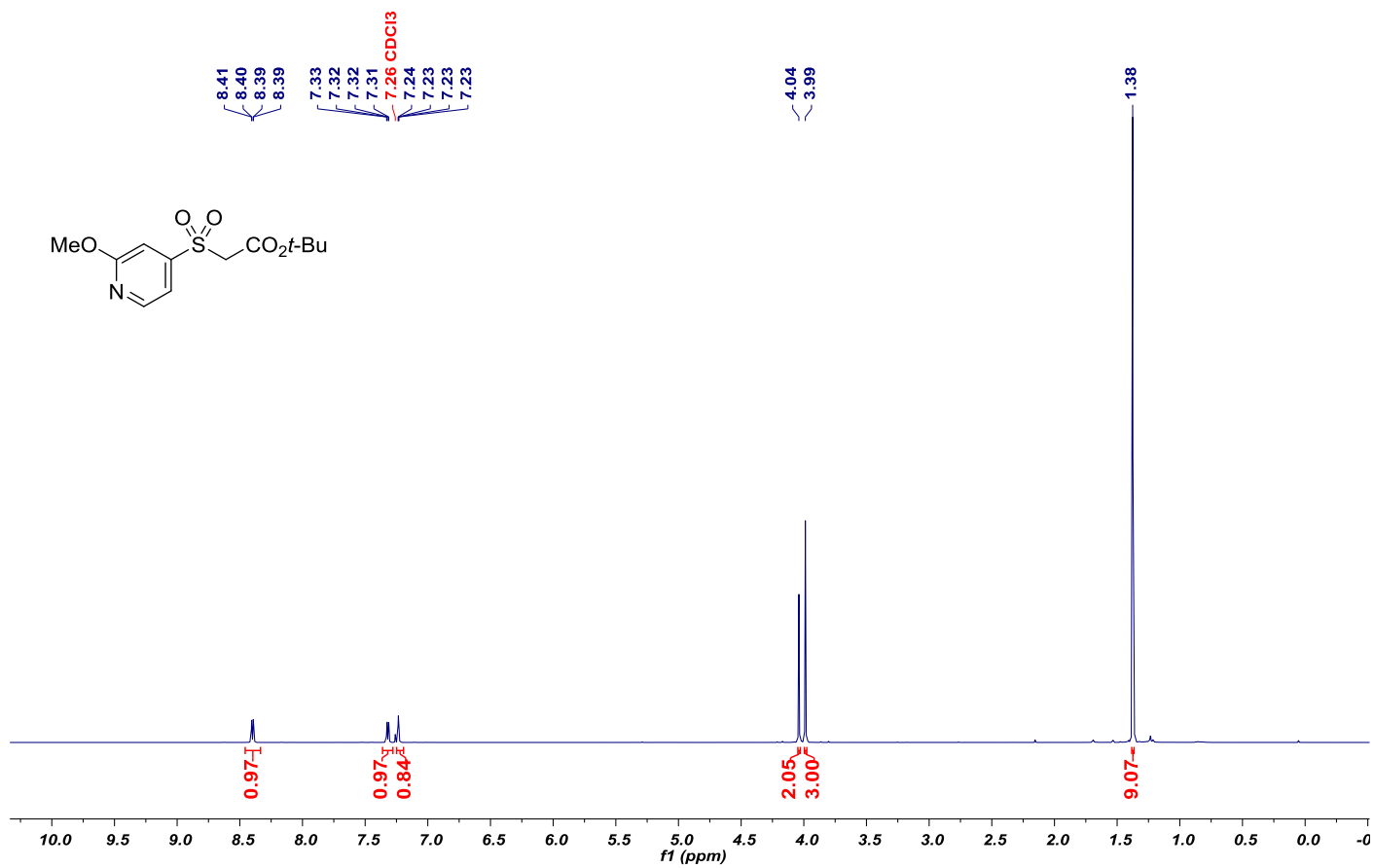
NMR spectrum of sulfone **2ae**



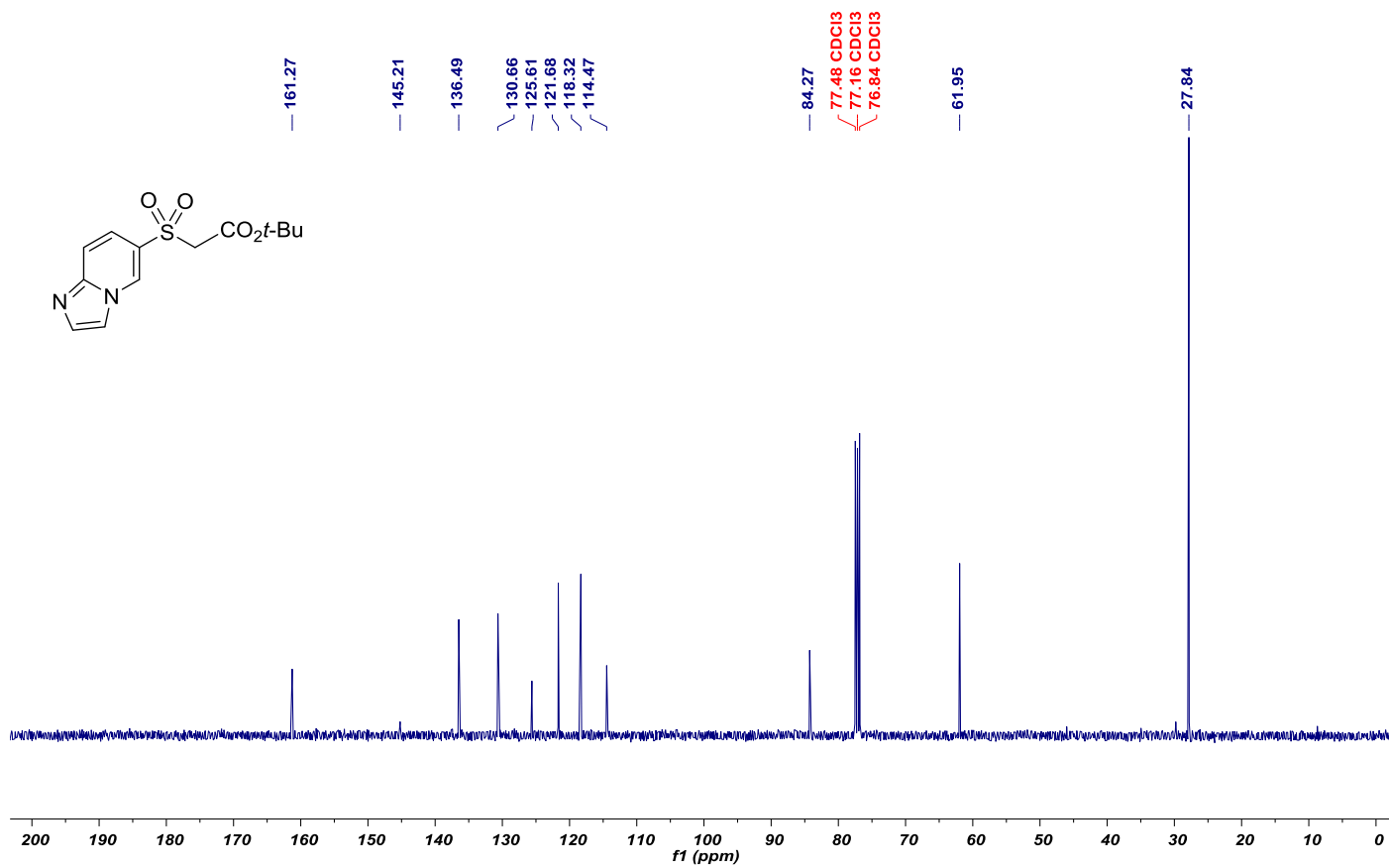
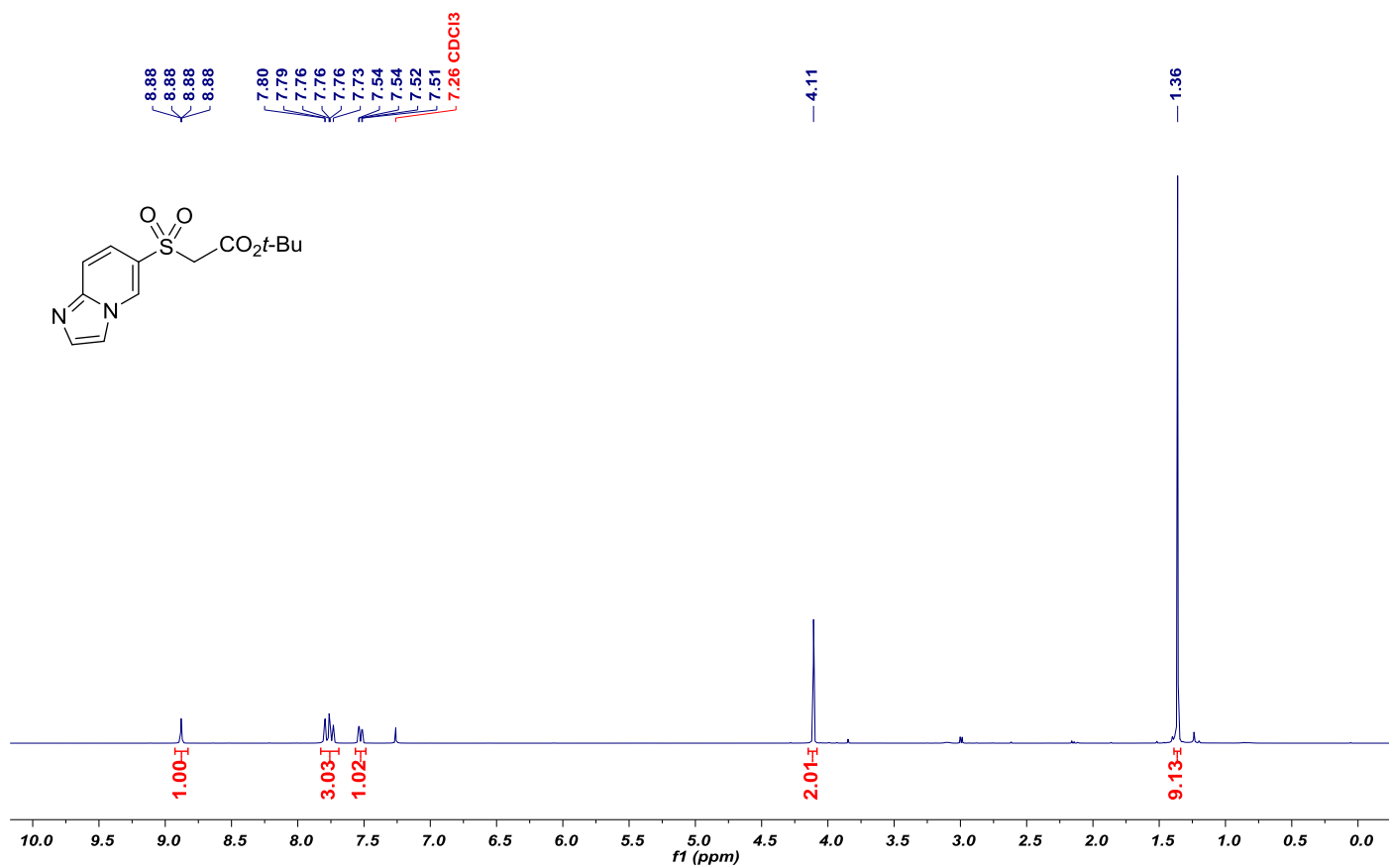
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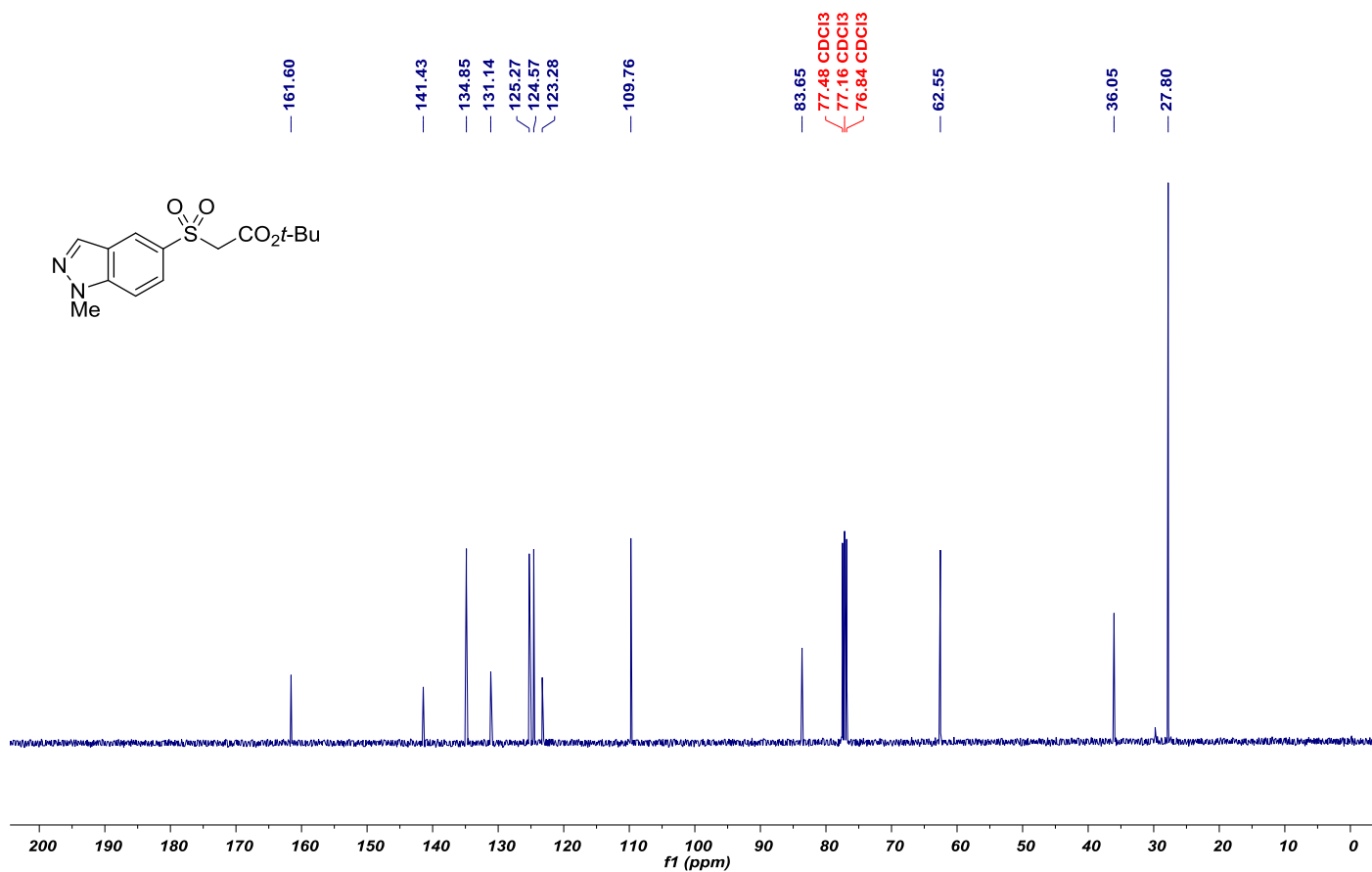
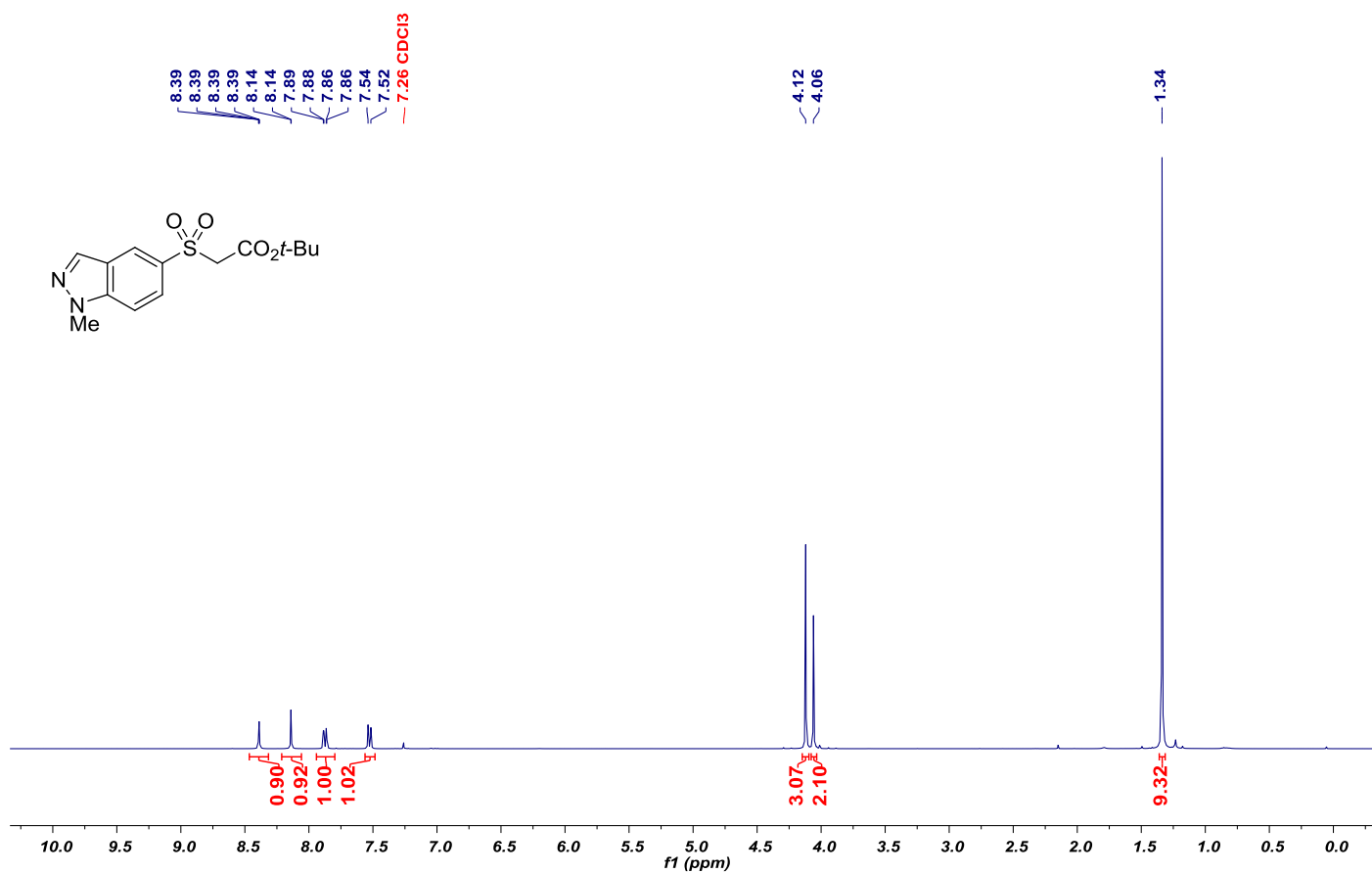
NMR spectrum of sulfone **2af**



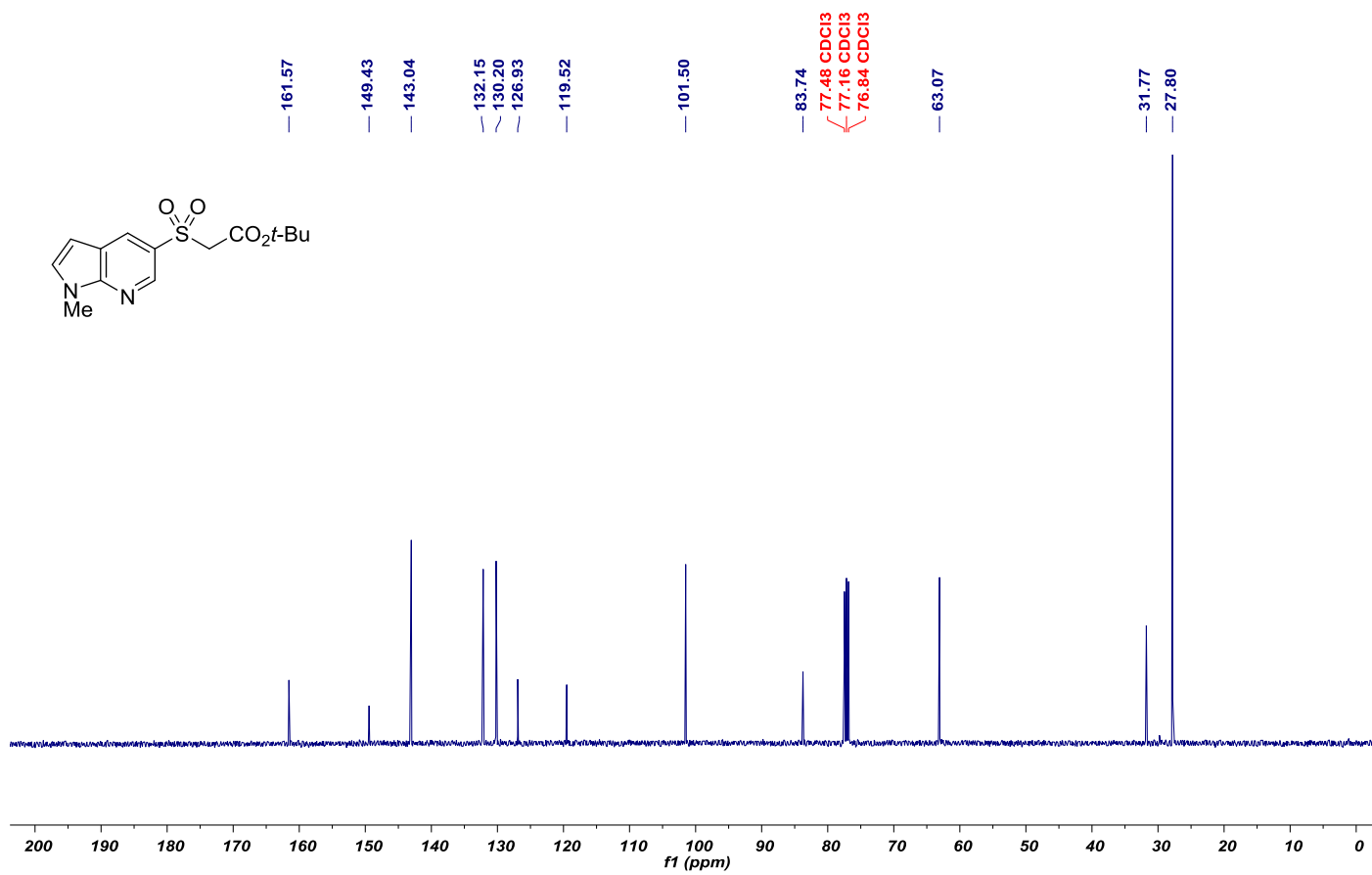
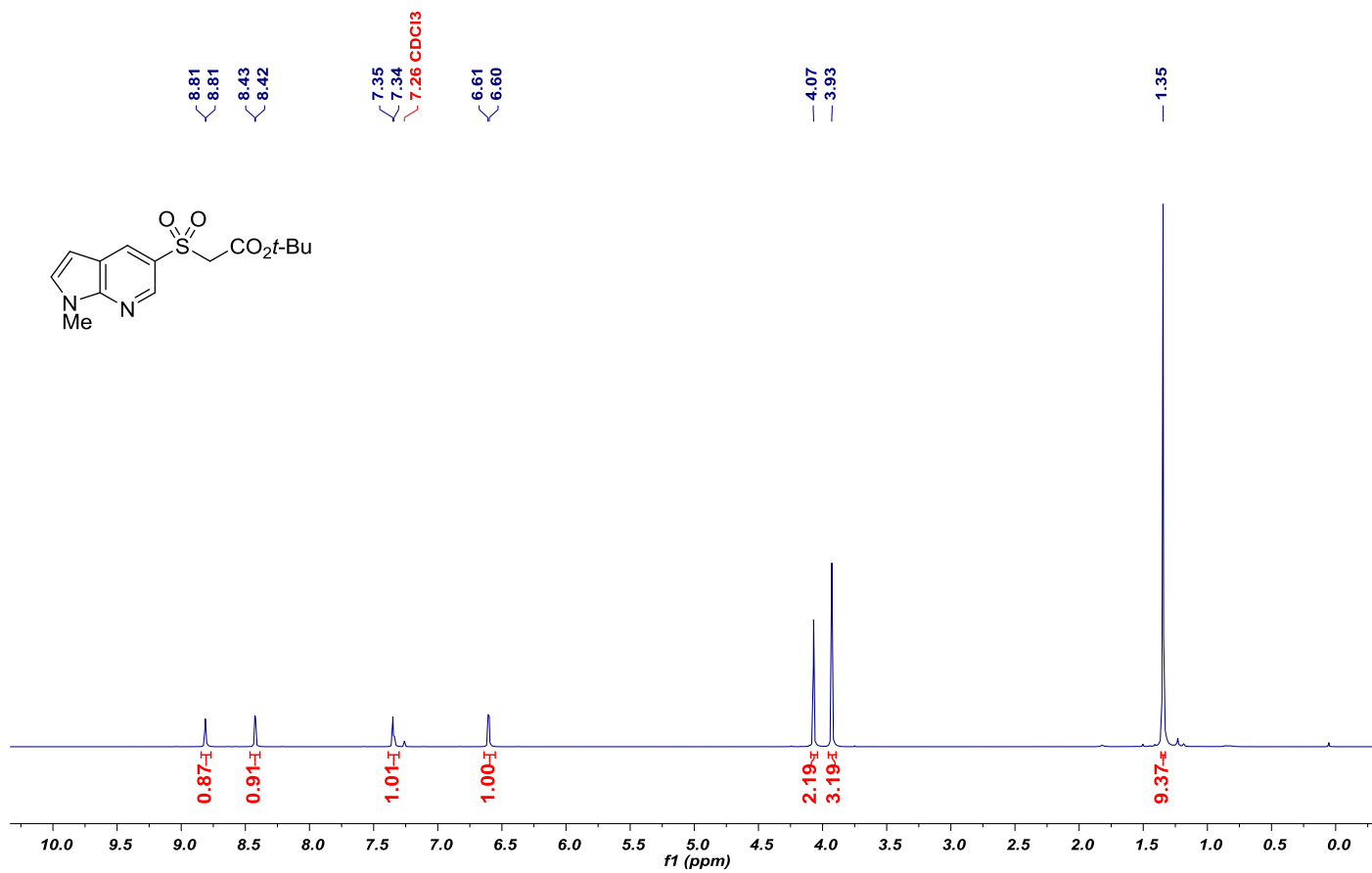
NMR spectrum of sulfone **2ag**



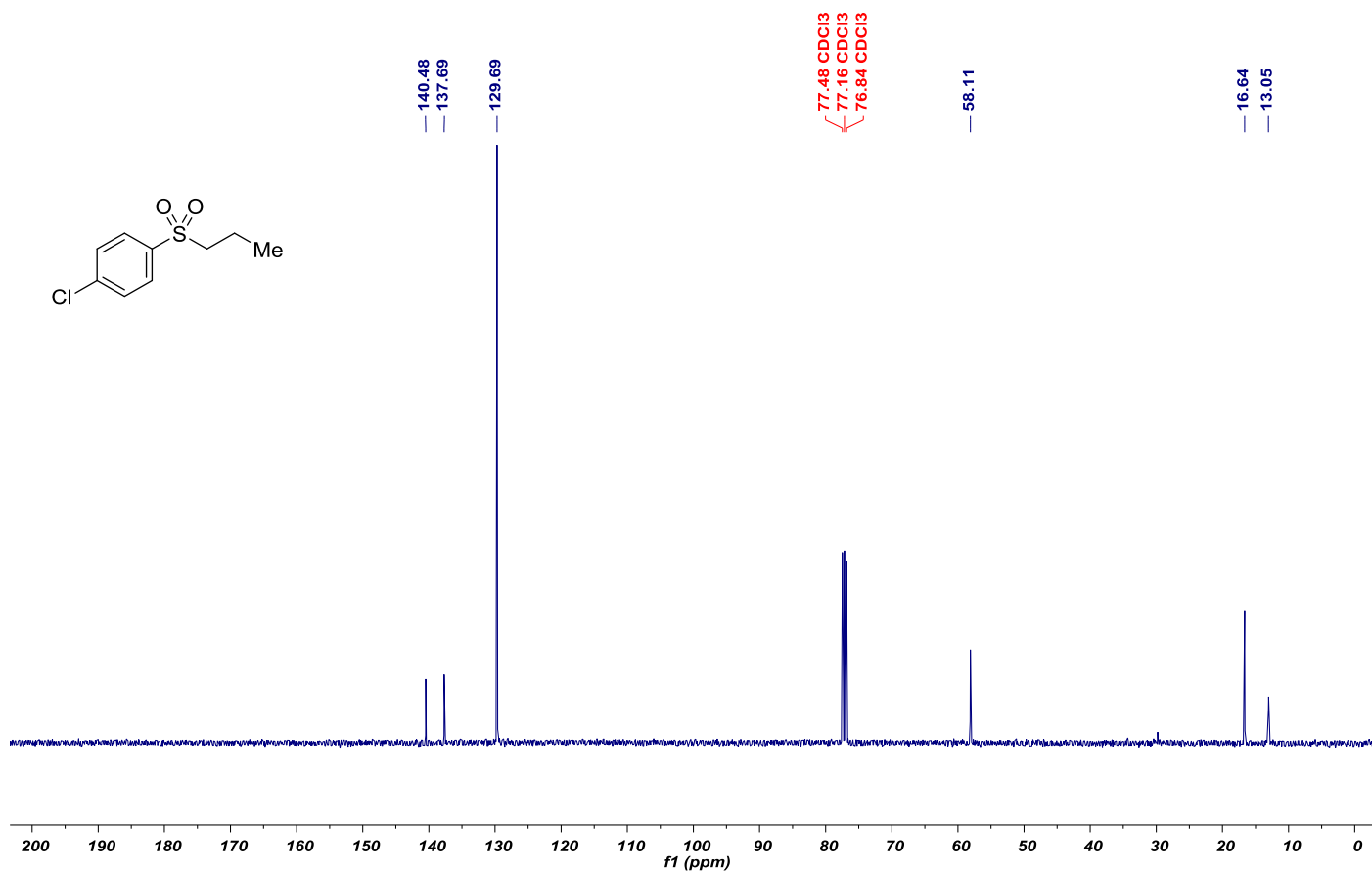
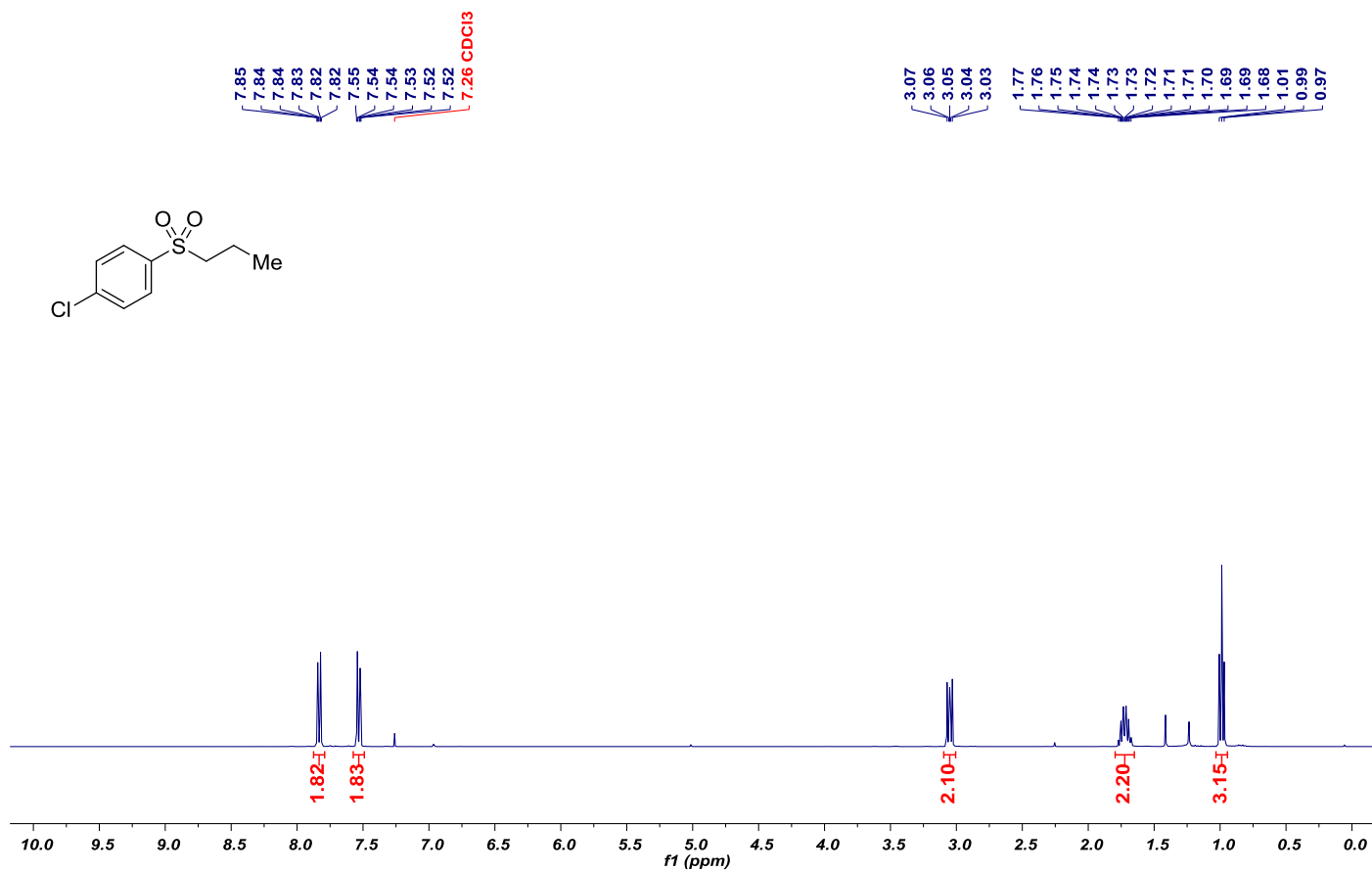
NMR spectrum of sulfone **2ah**



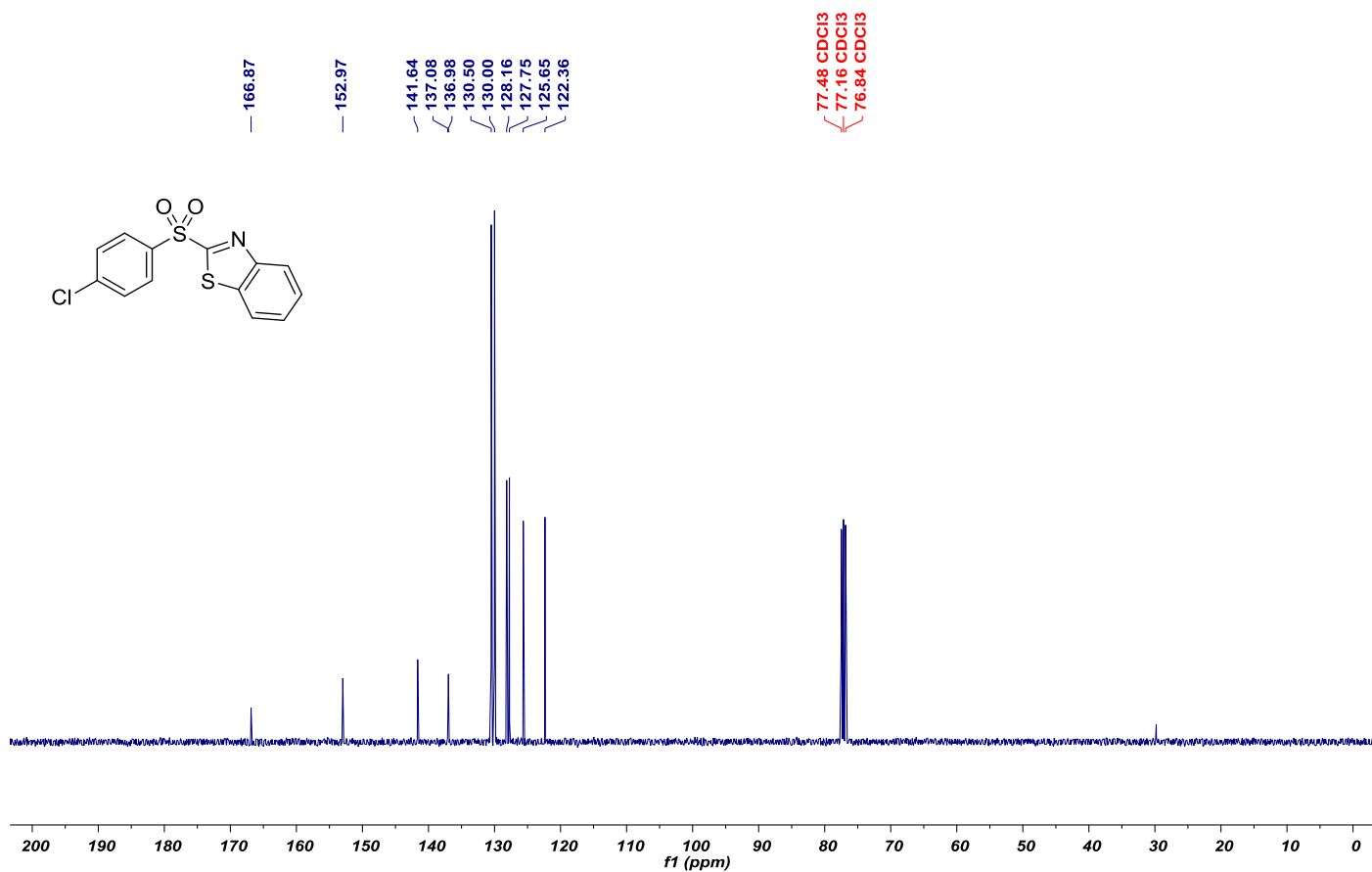
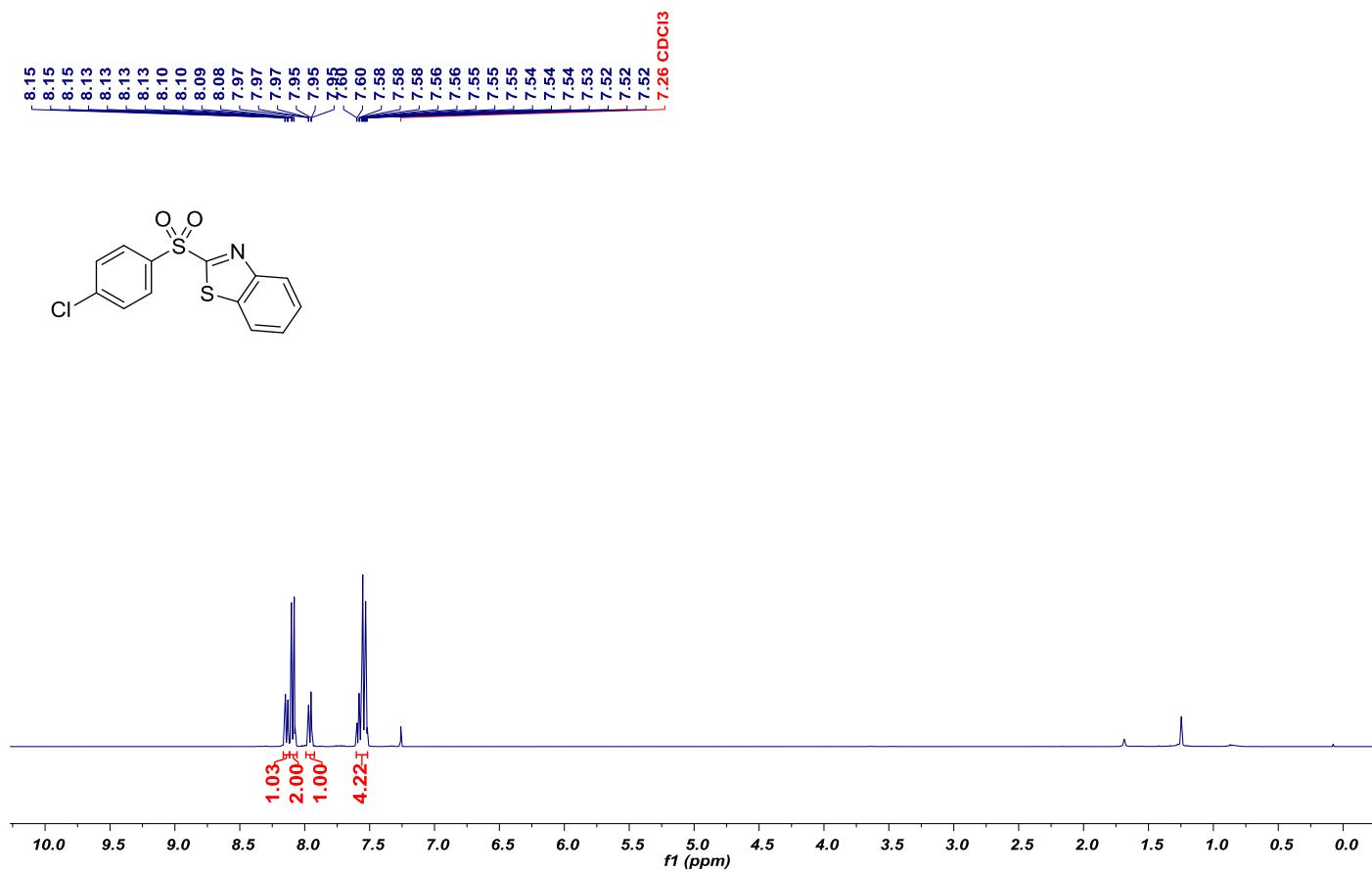
NMR spectrum of sulfone **2ai**



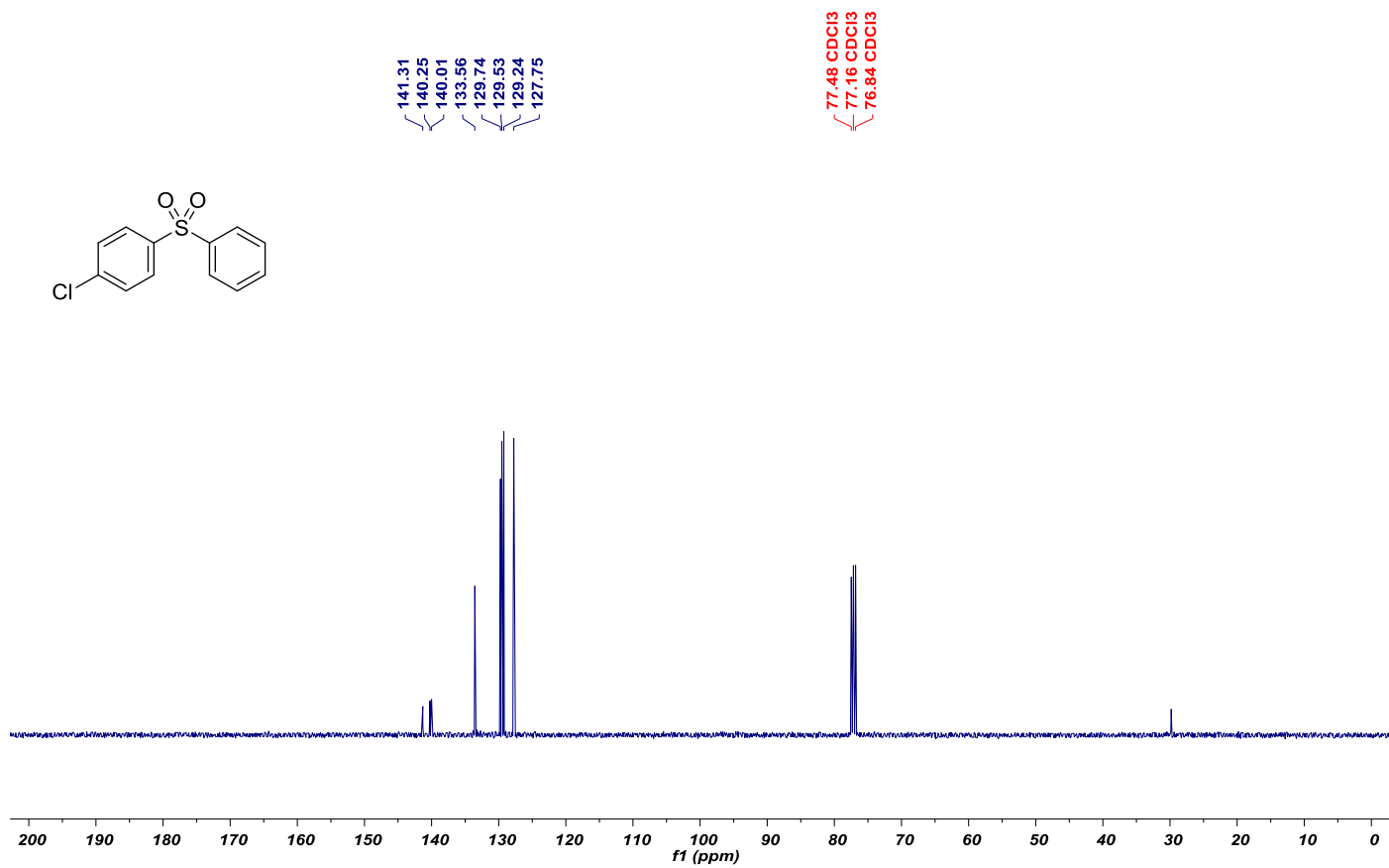
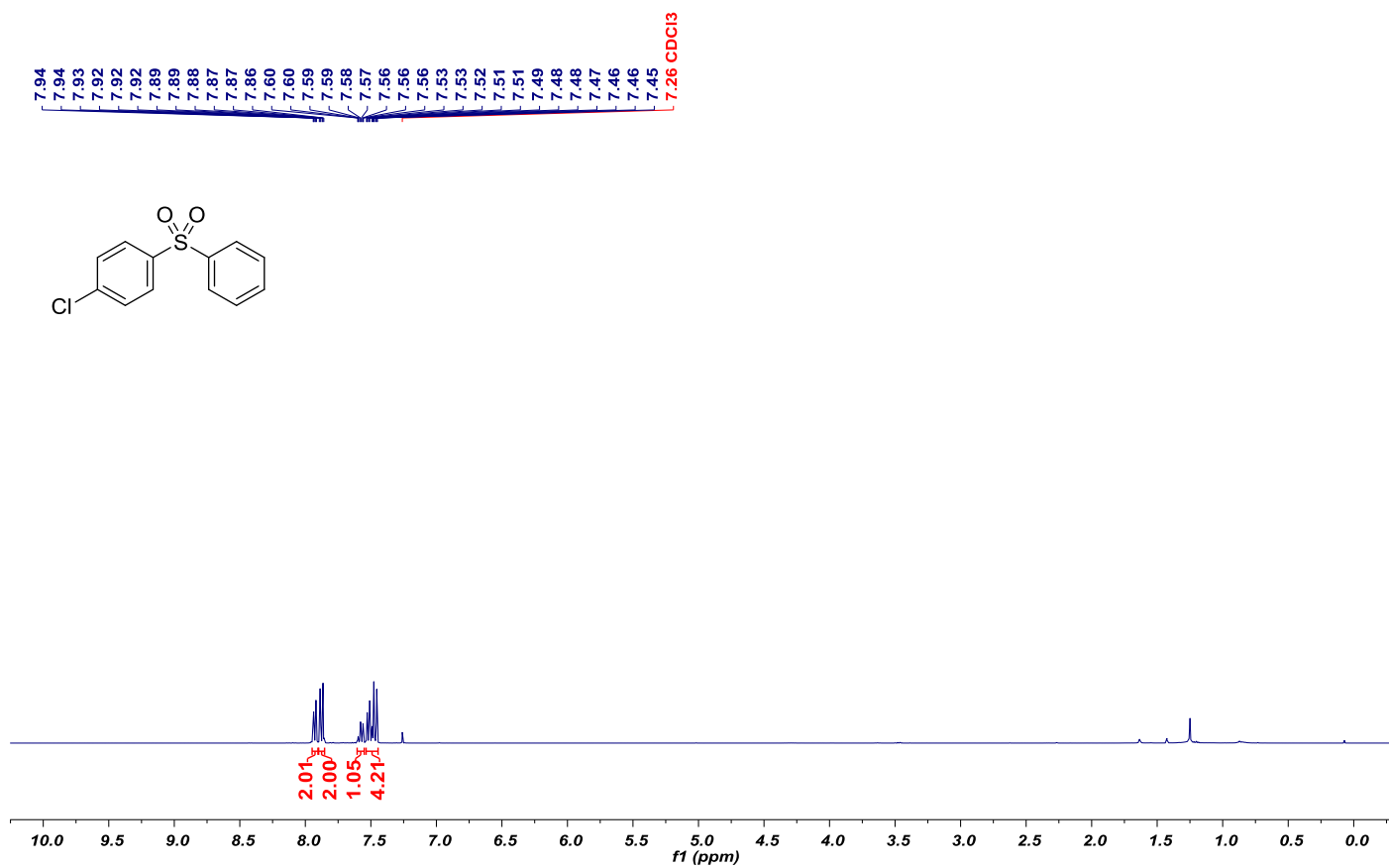
NMR spectrum of sulfone **3a**



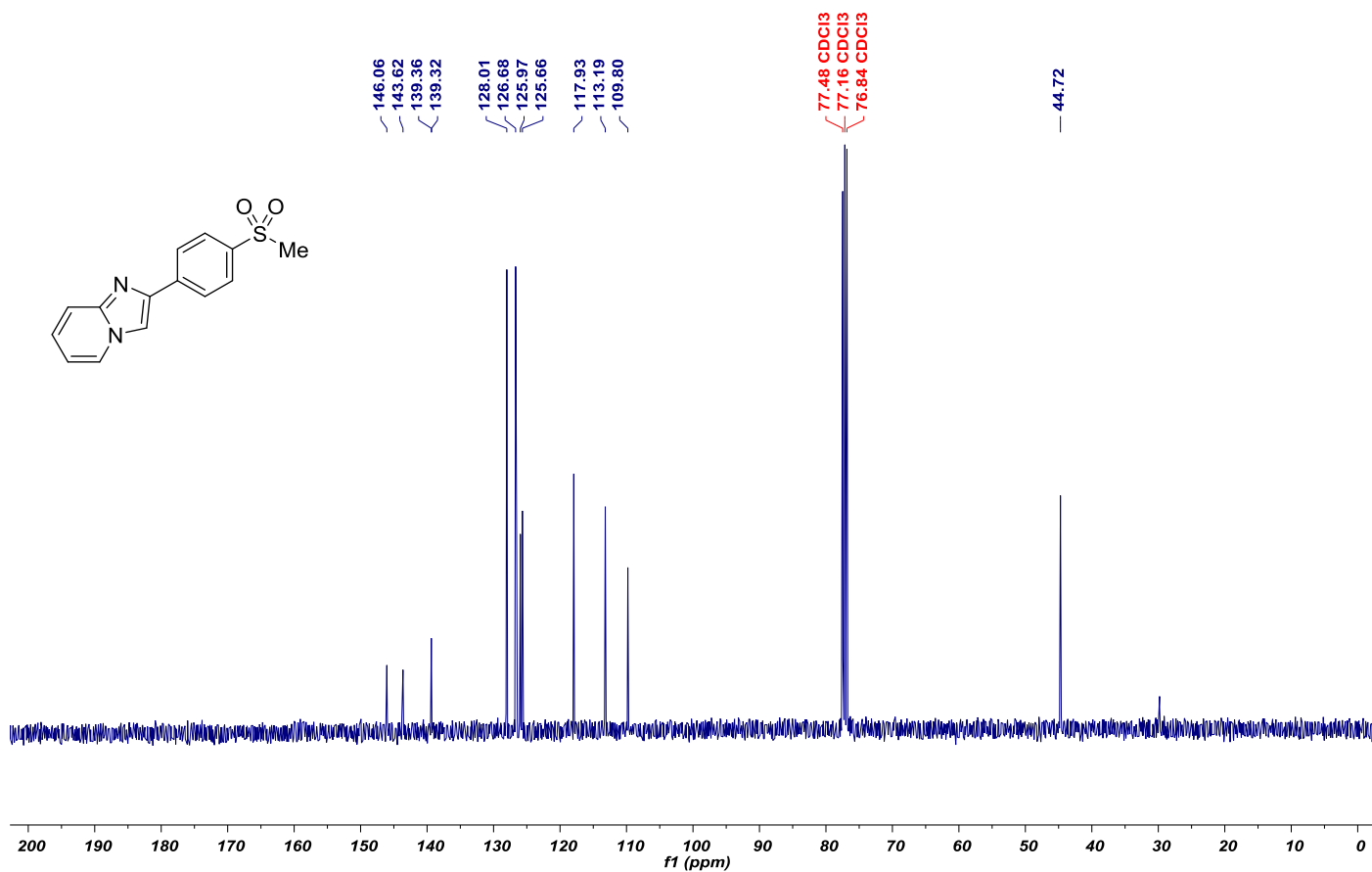
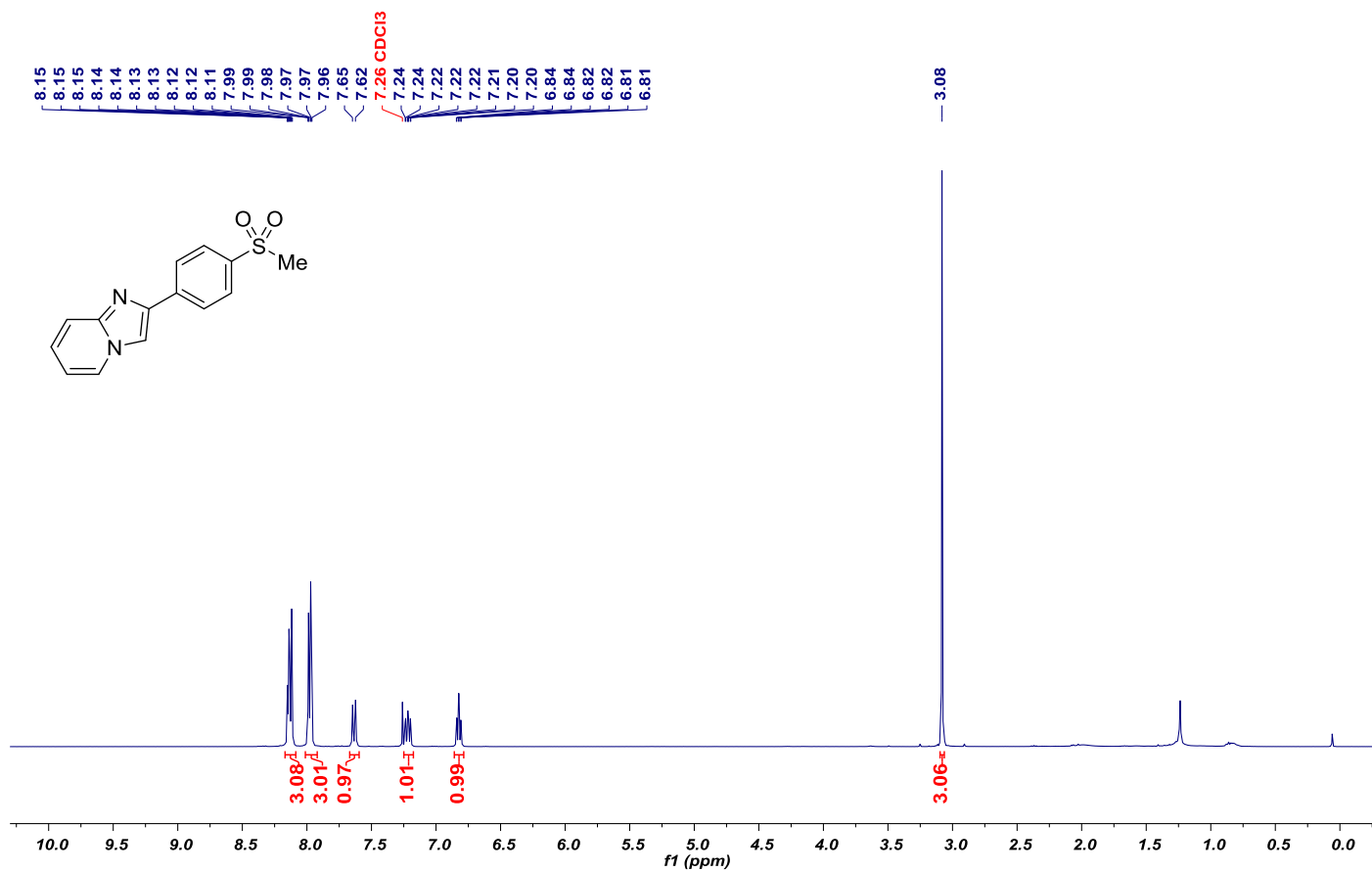
NMR spectrum of sulfone 3b



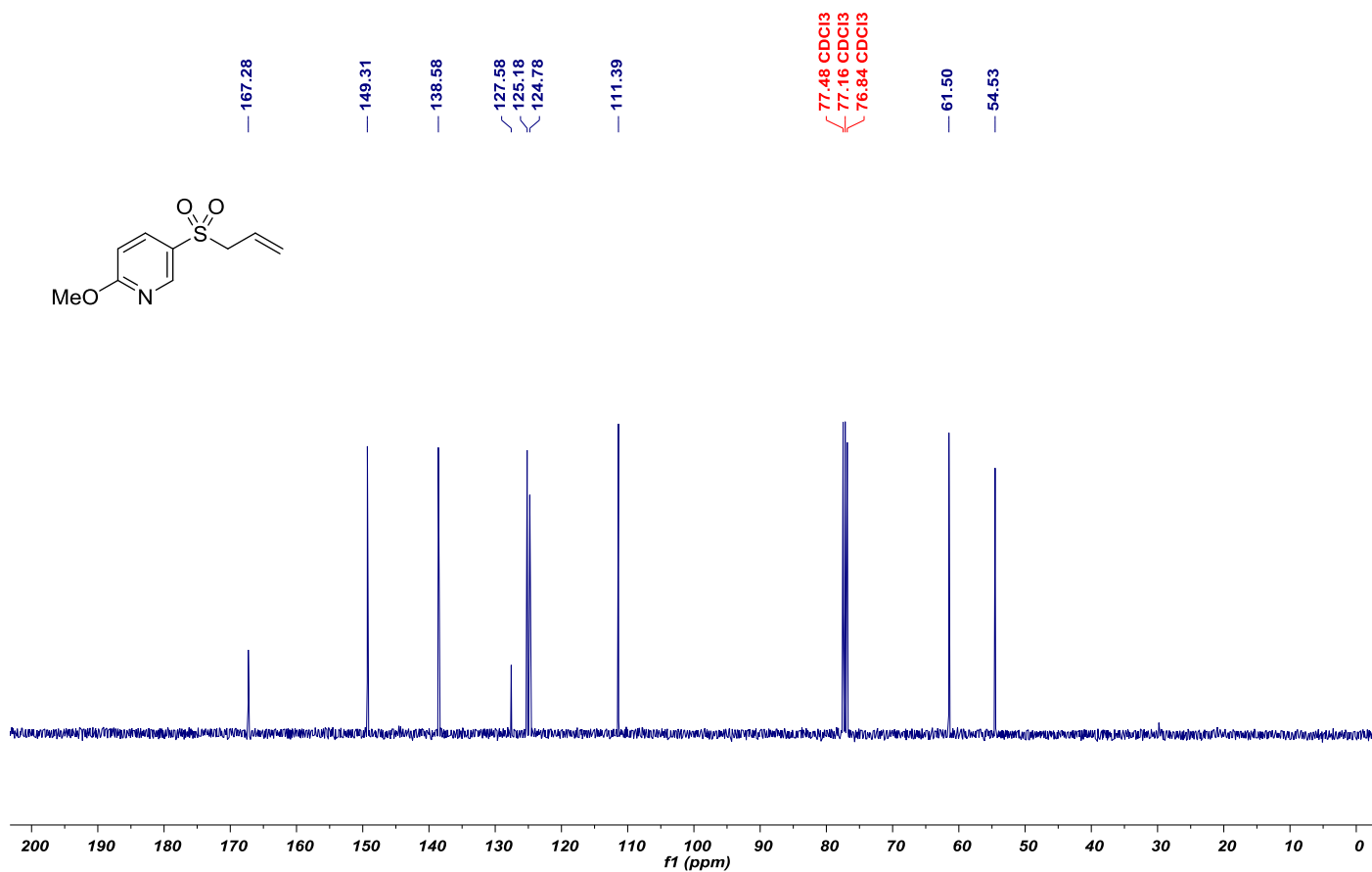
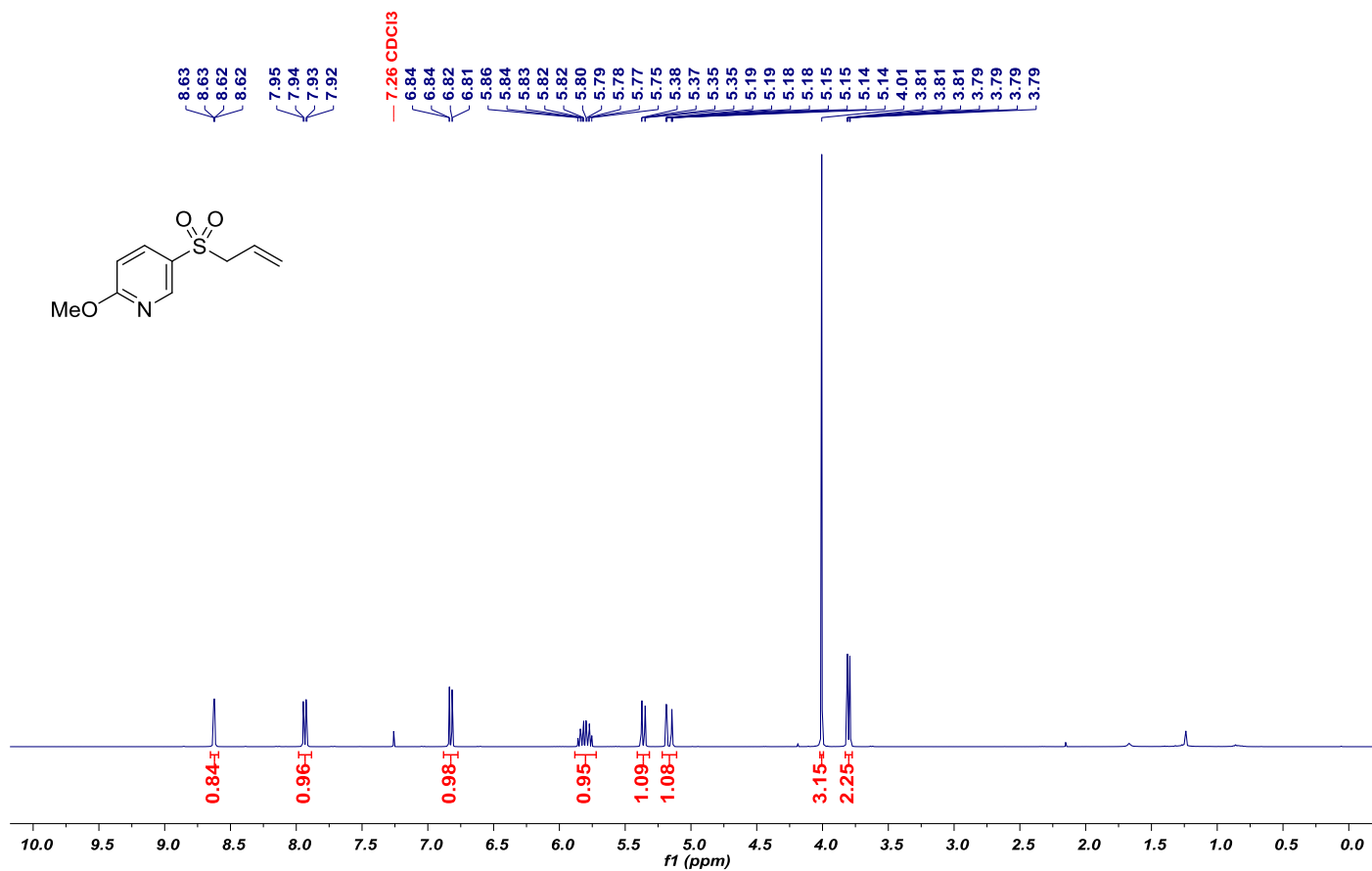
NMR spectrum of sulfone 3c



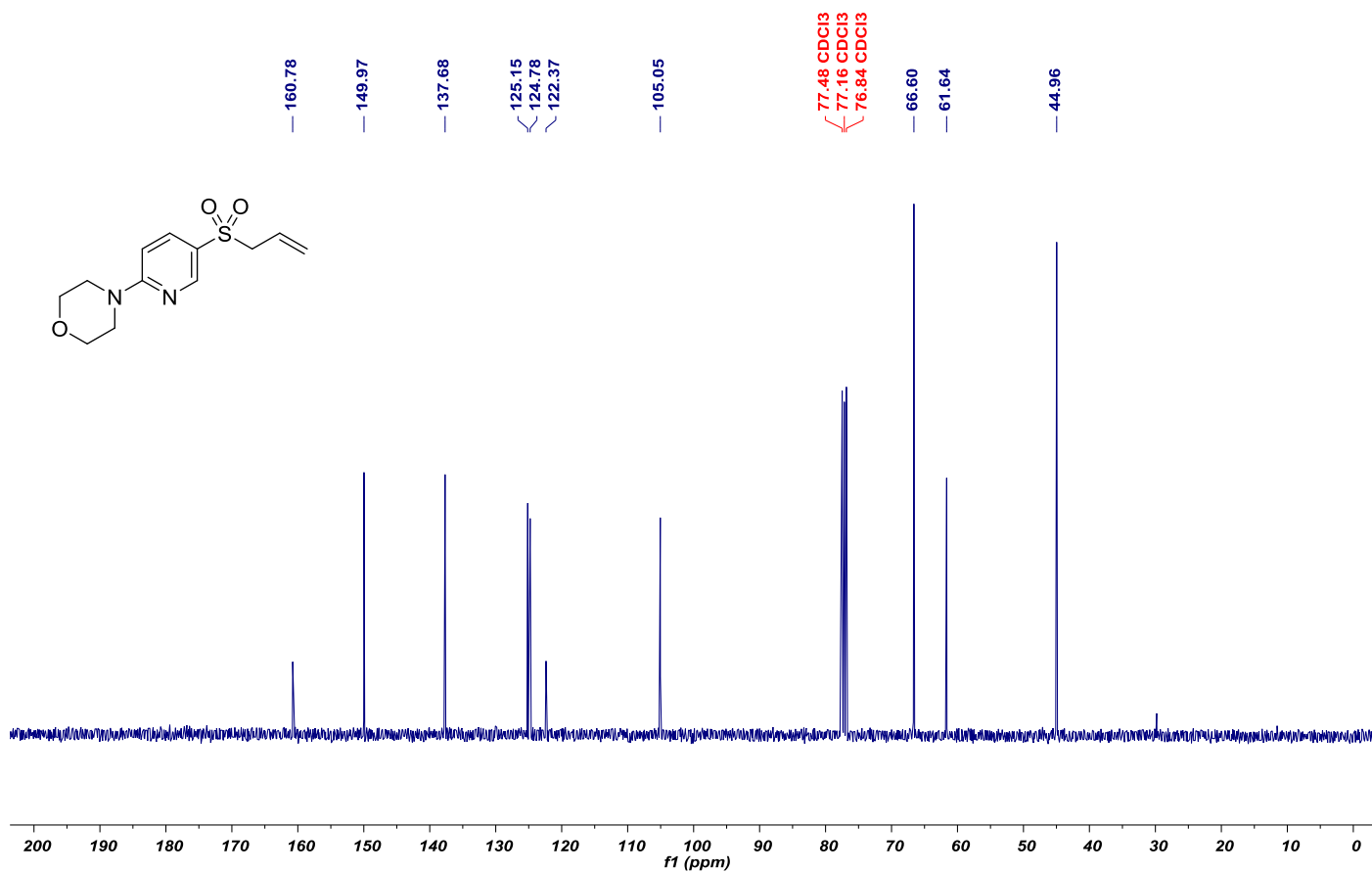
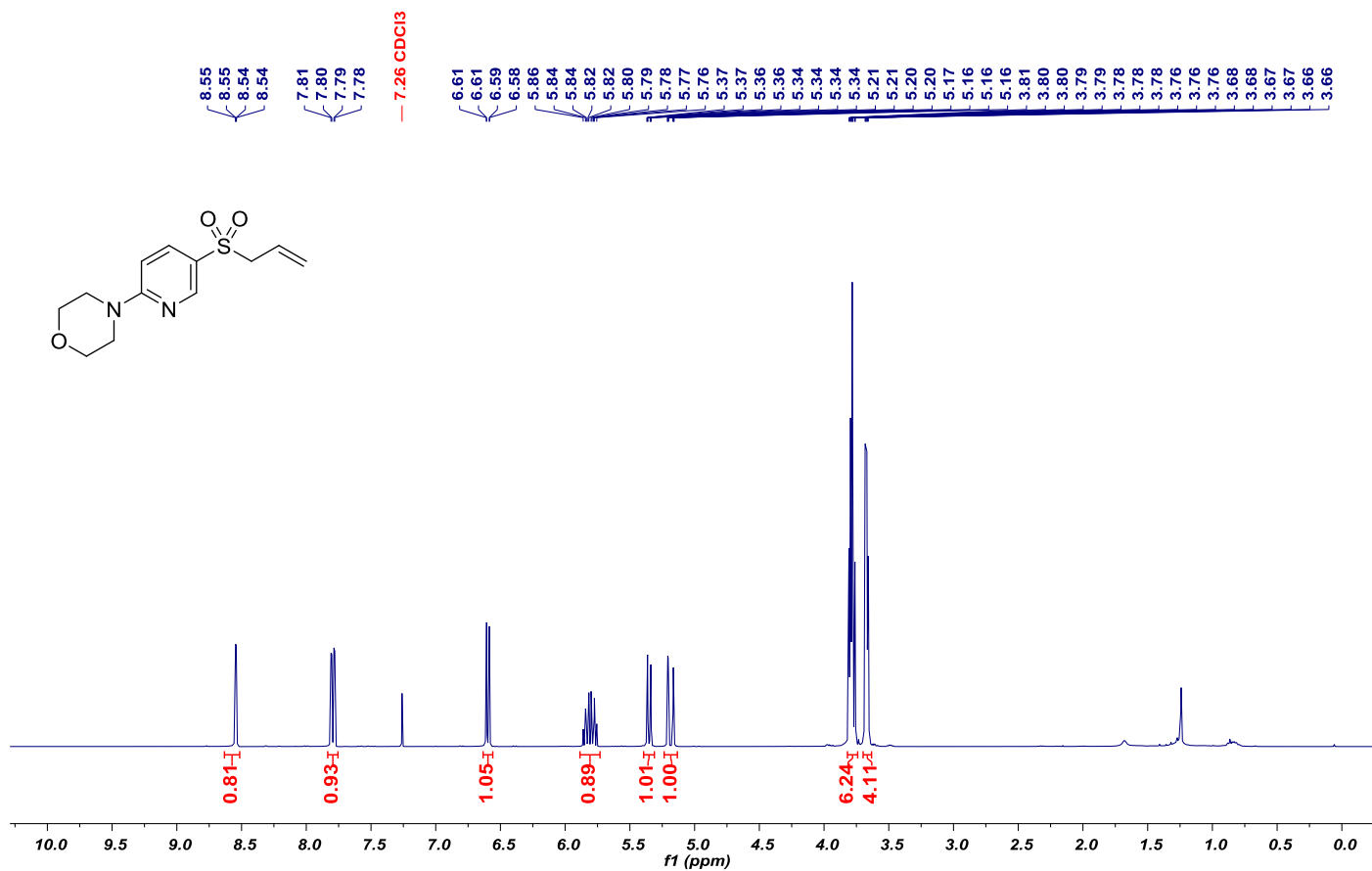
NMR spectrum of sulfone **3d**



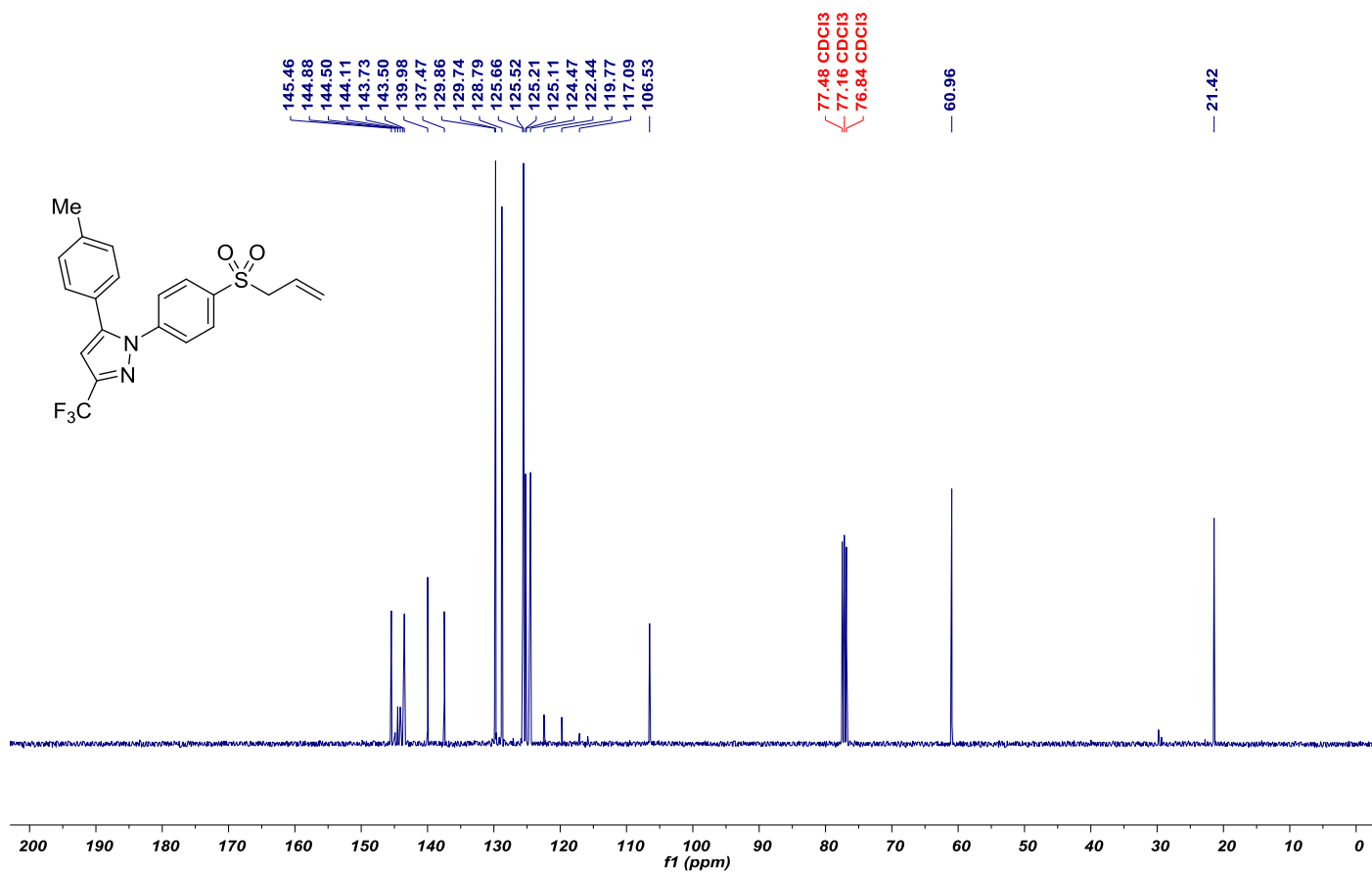
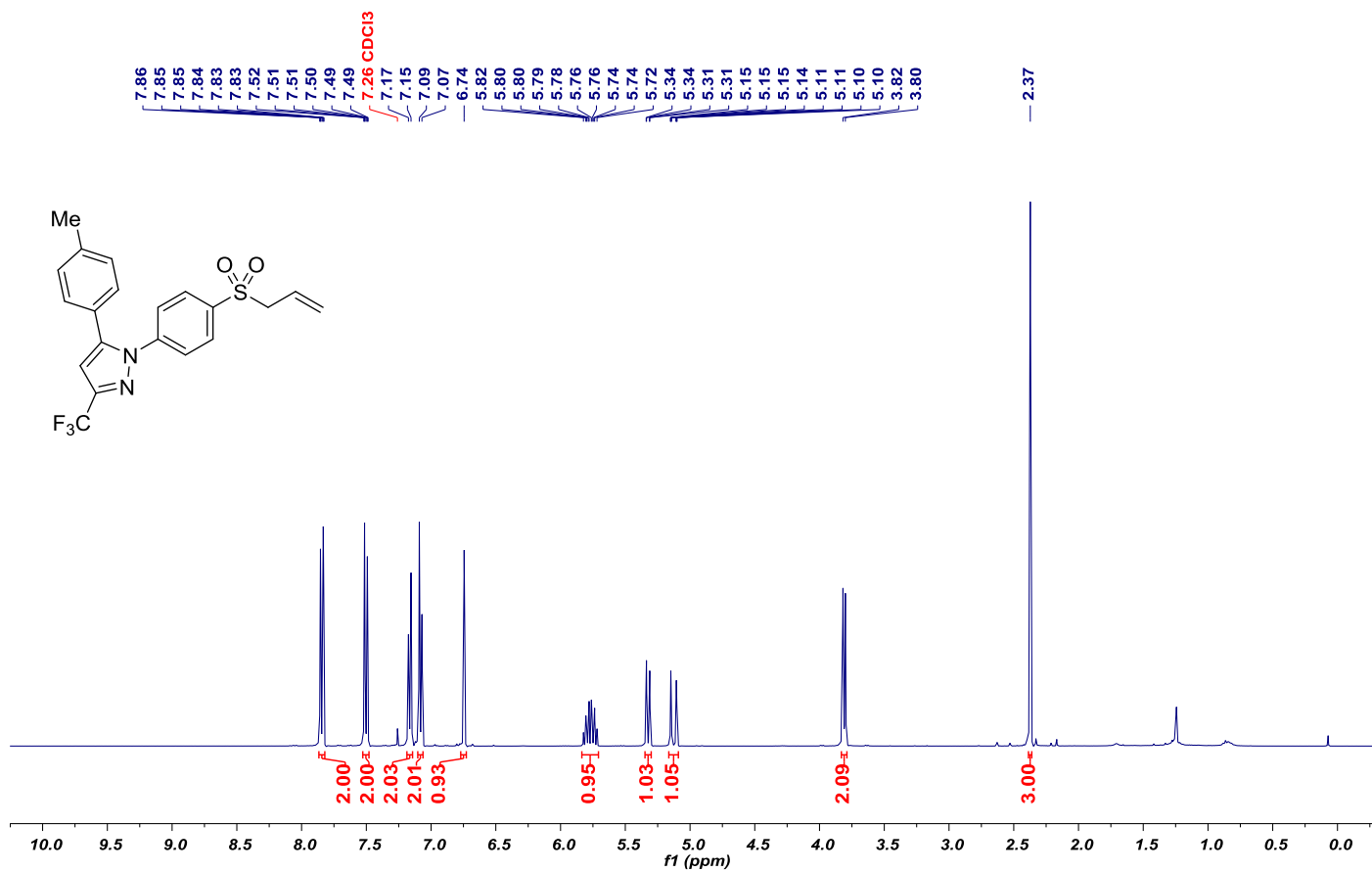
NMR spectrum of sulfone 3f

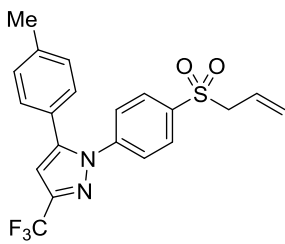


NMR spectrum of sulfone 3g

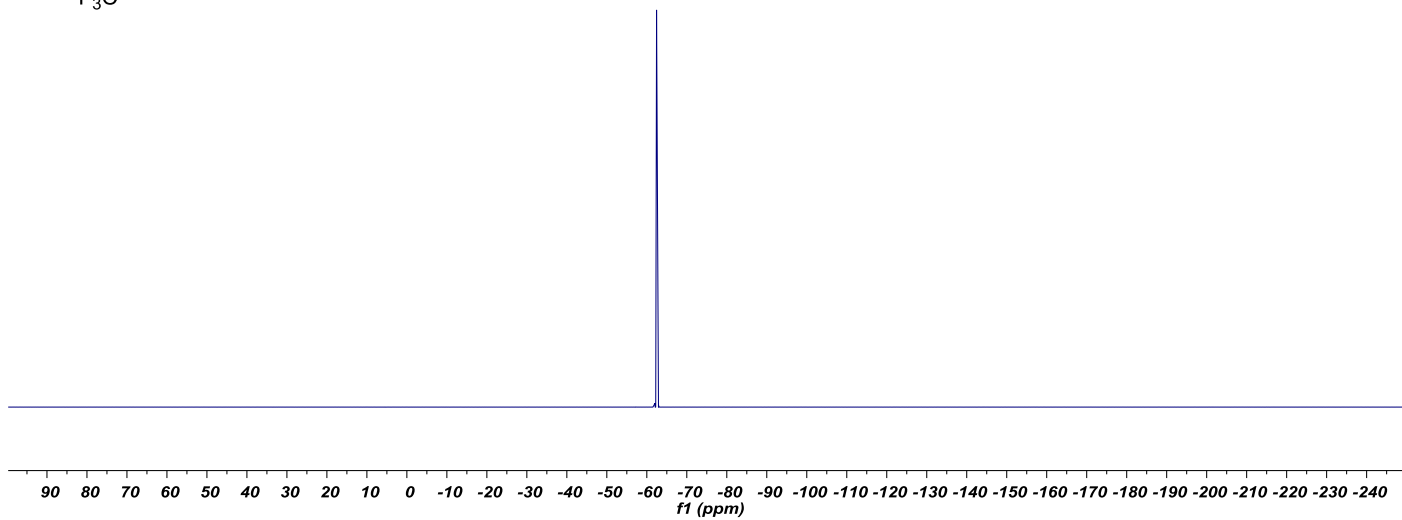


NMR spectrum of sulfone 3h

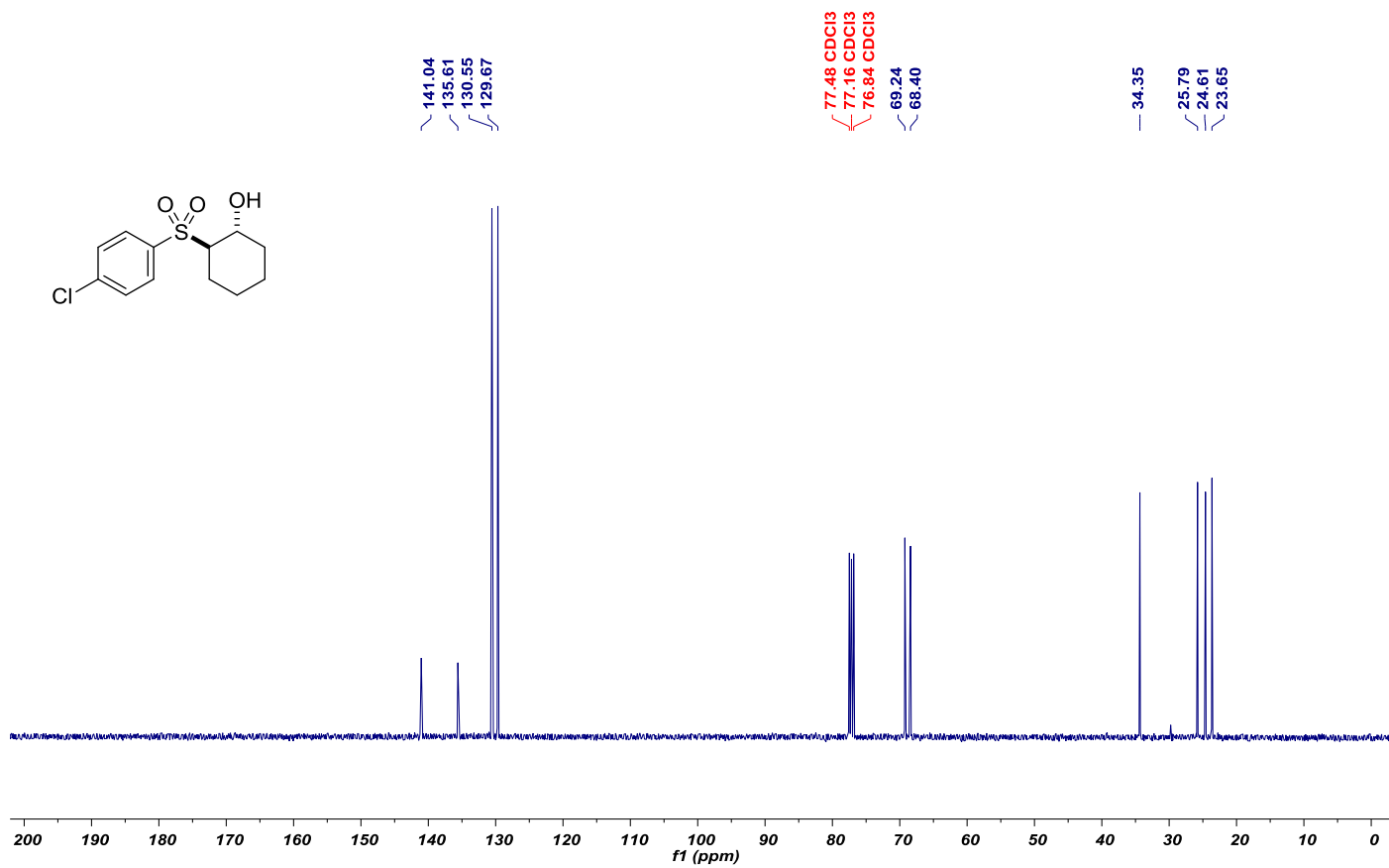
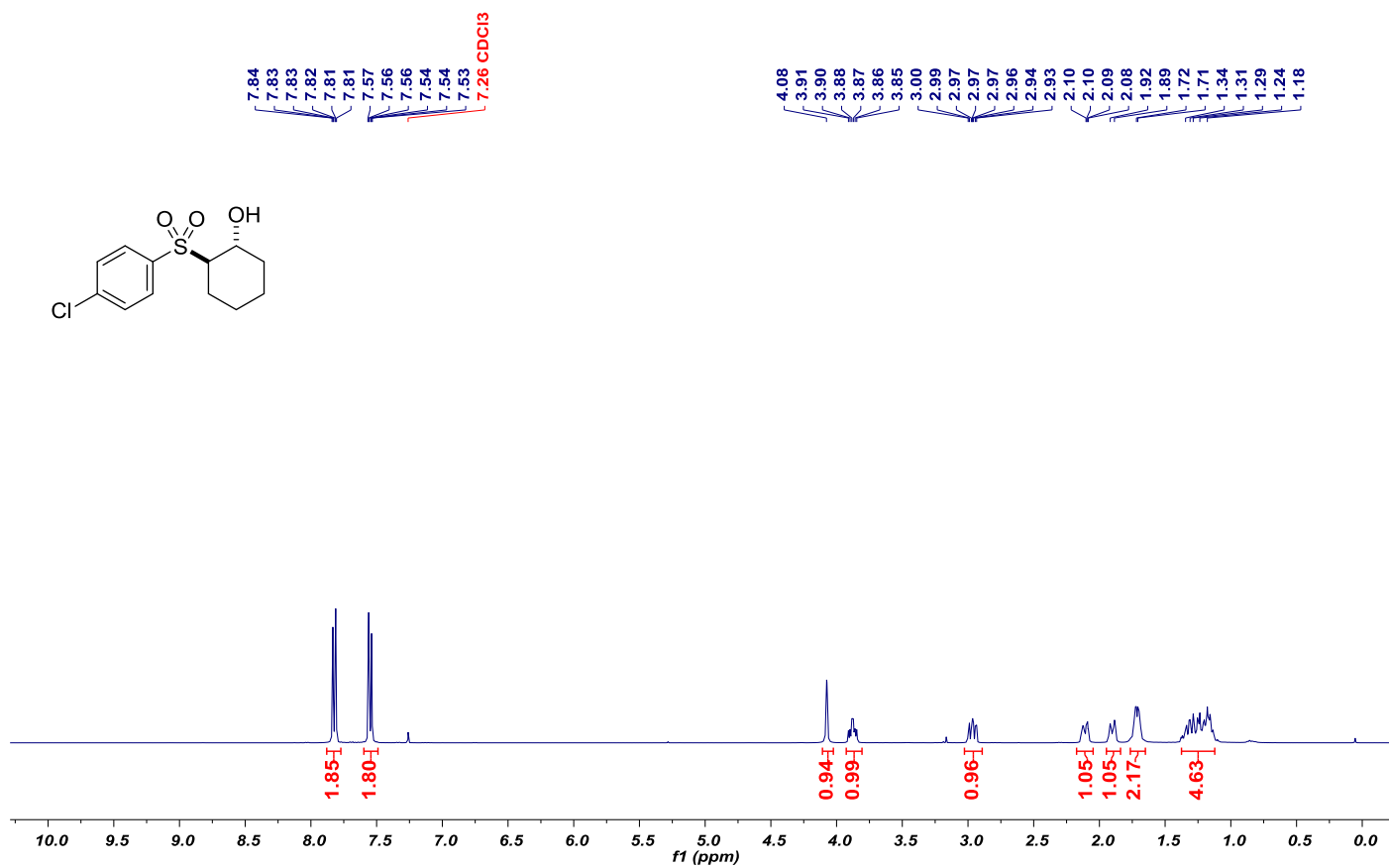
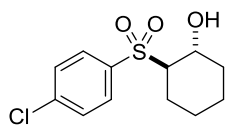




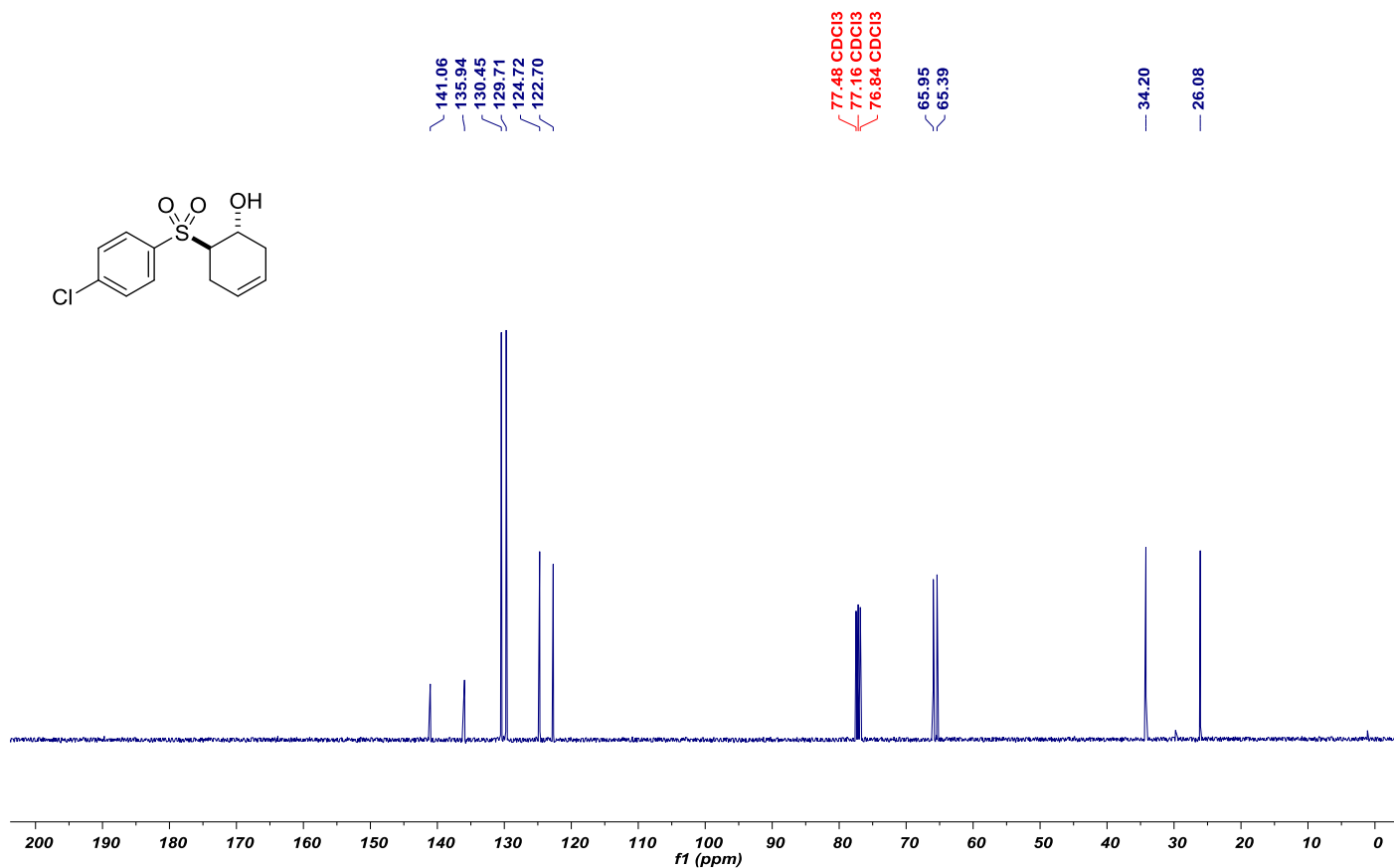
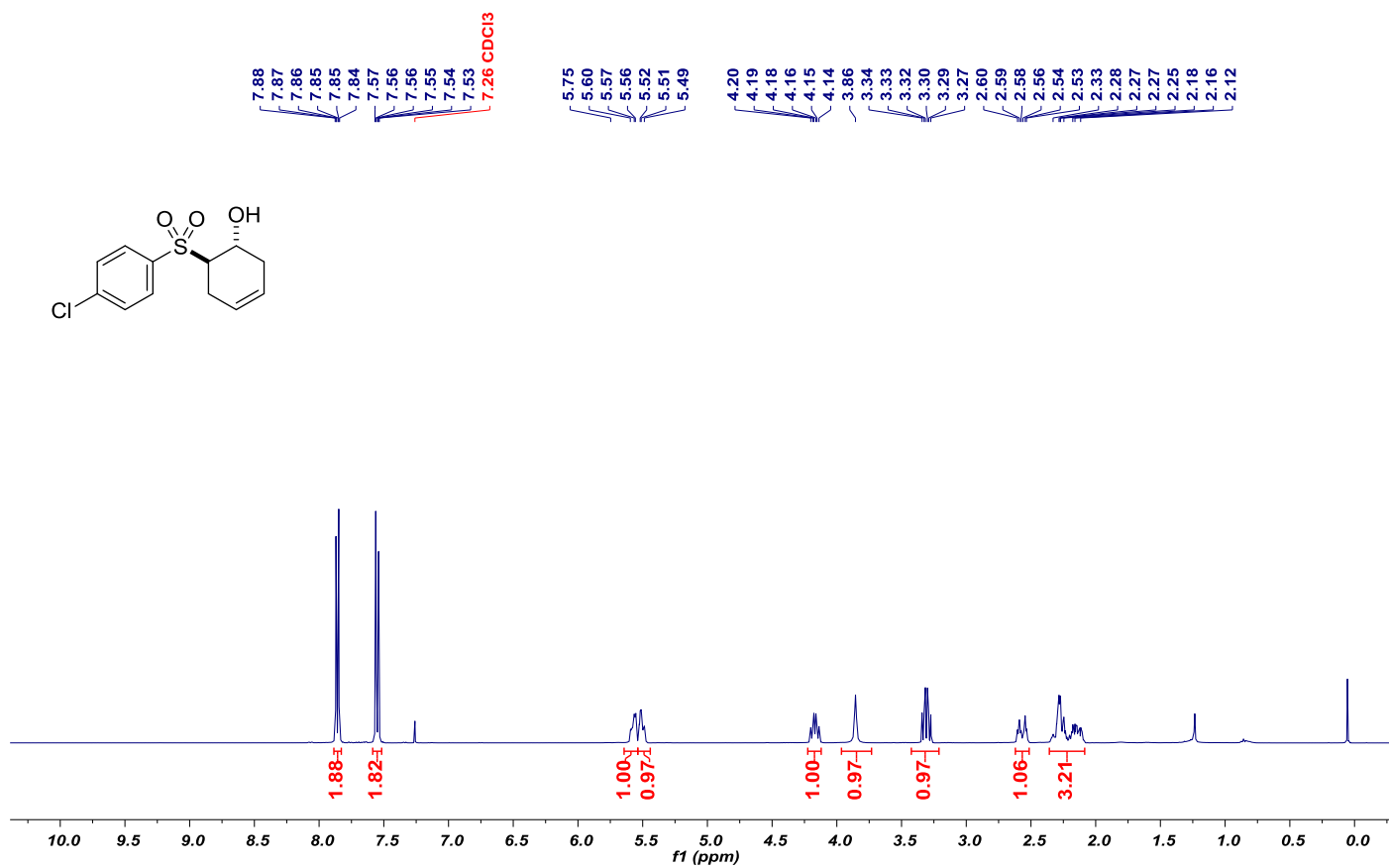
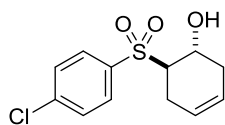
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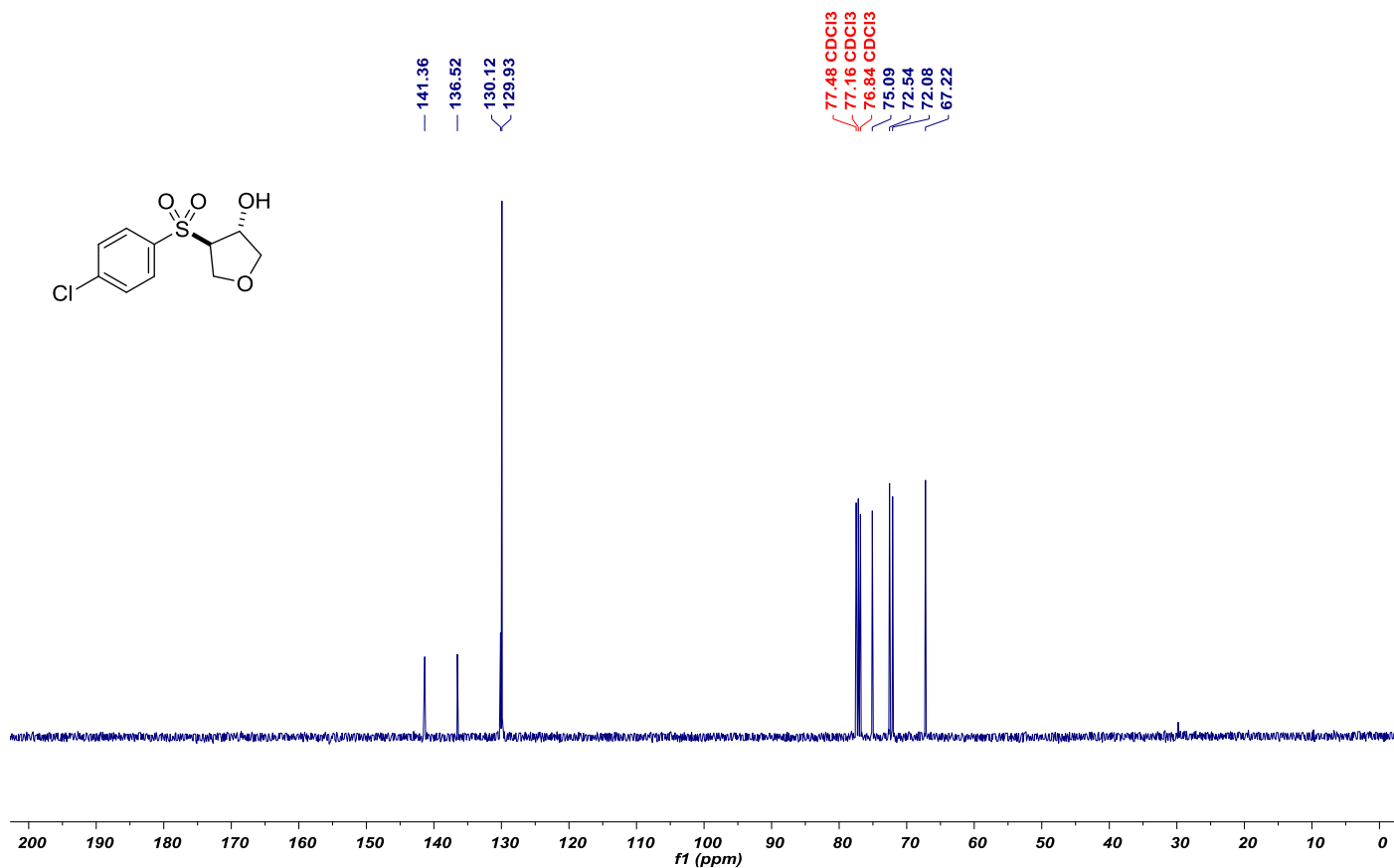
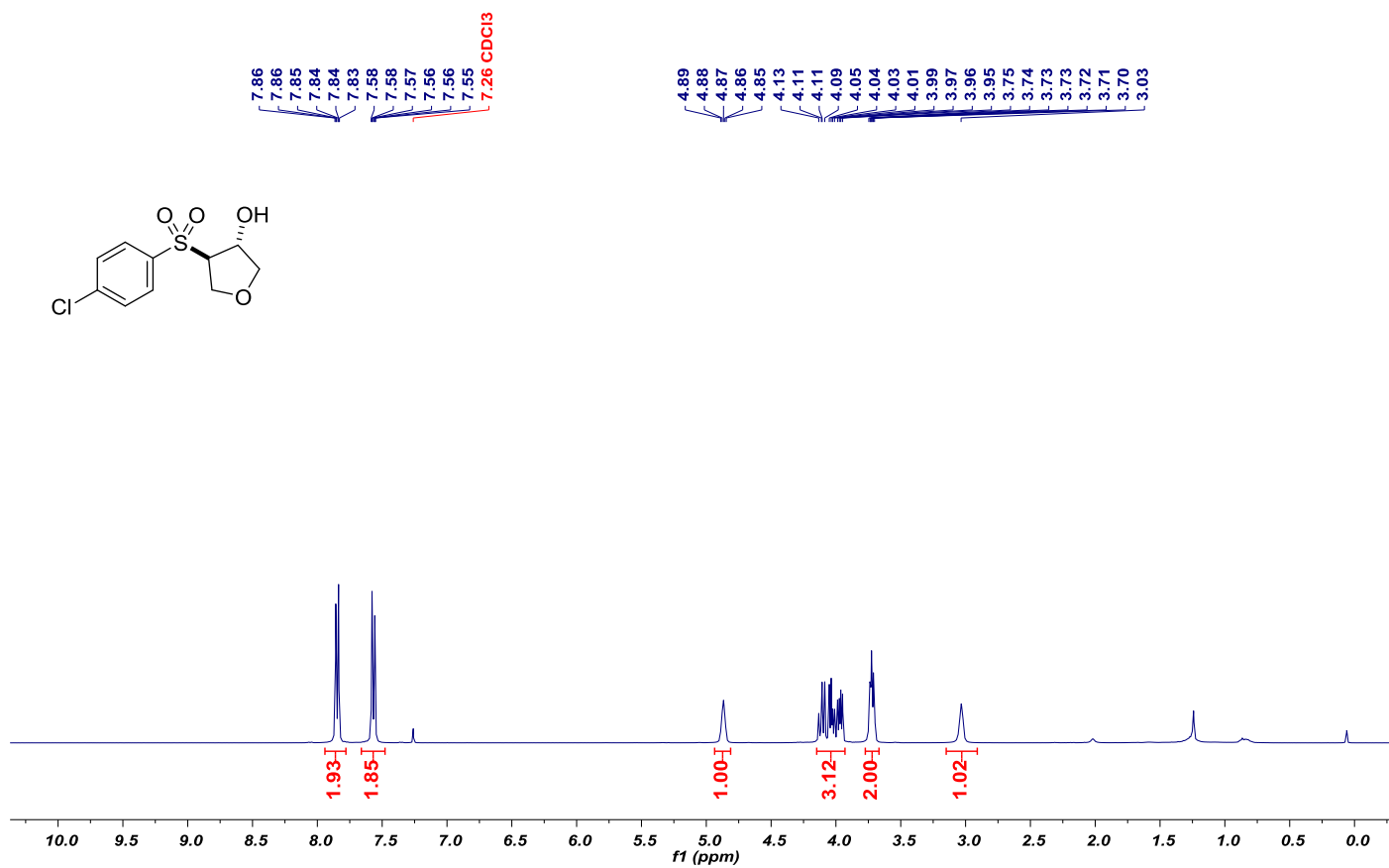
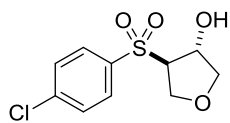
NMR spectrum of β -hydroxysulfone 3i



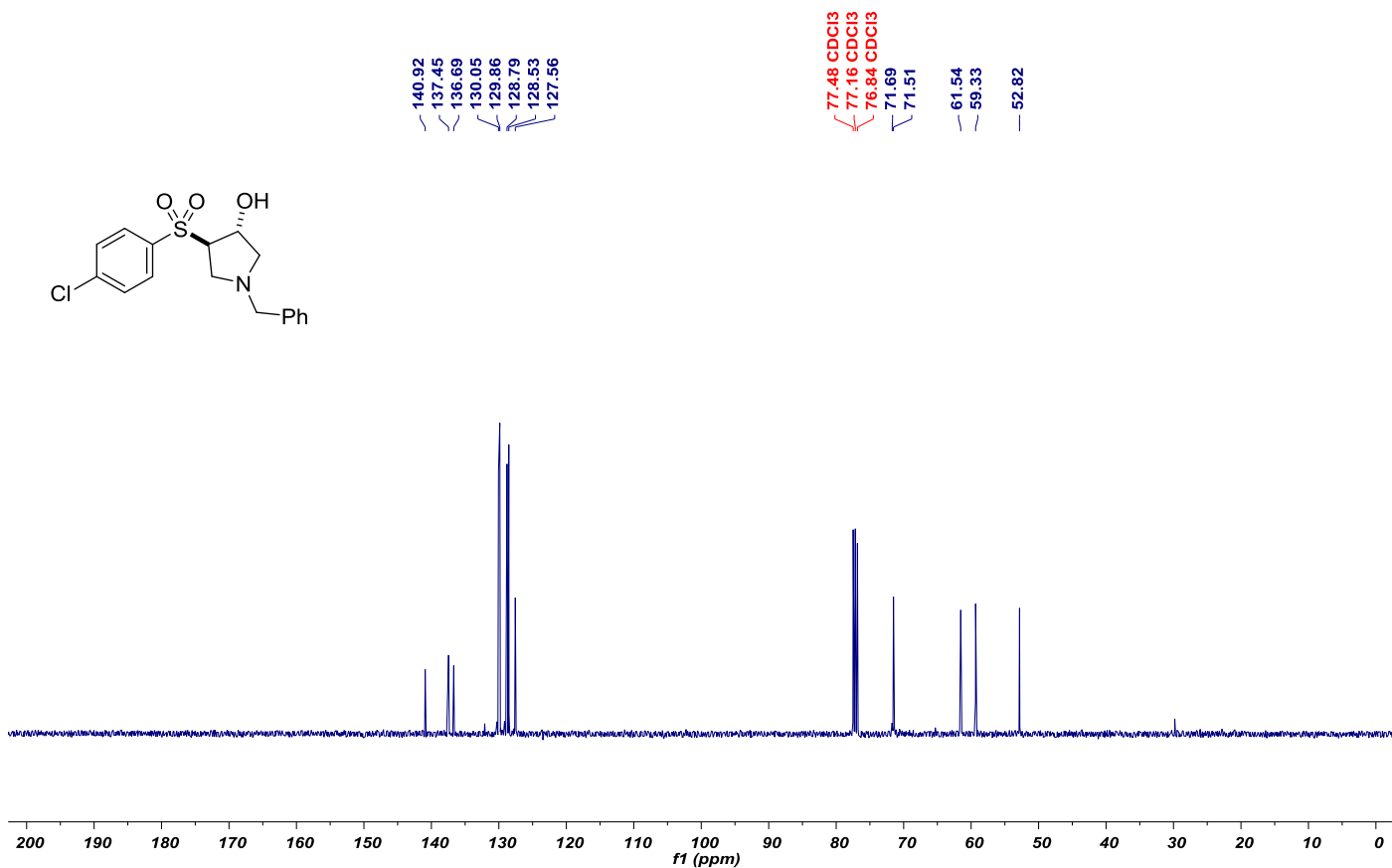
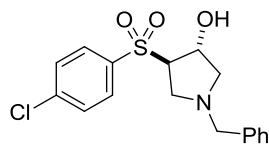
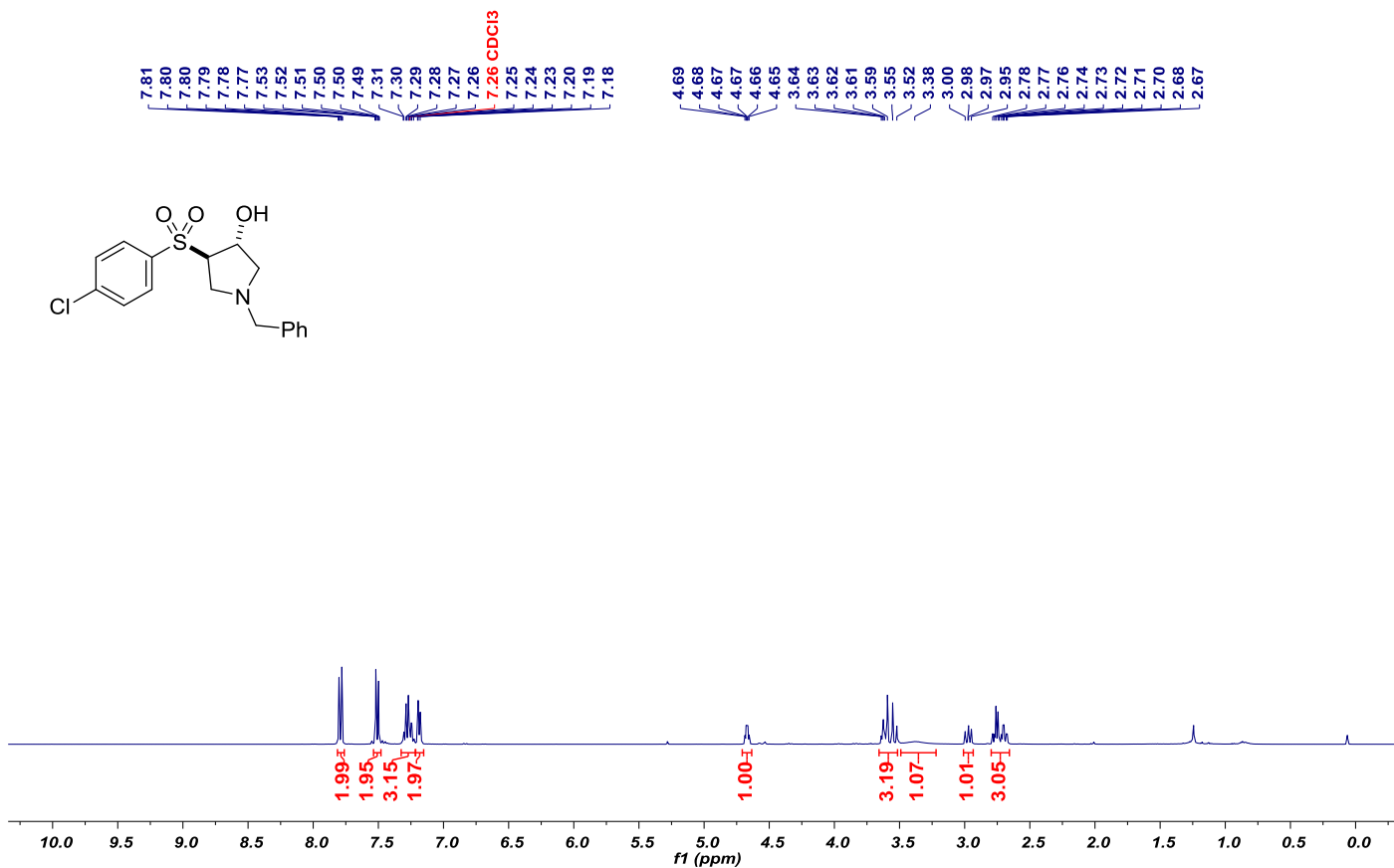
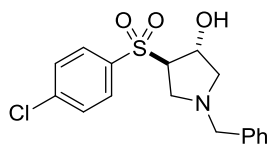
NMR spectrum of β -hydroxysulfone 3j



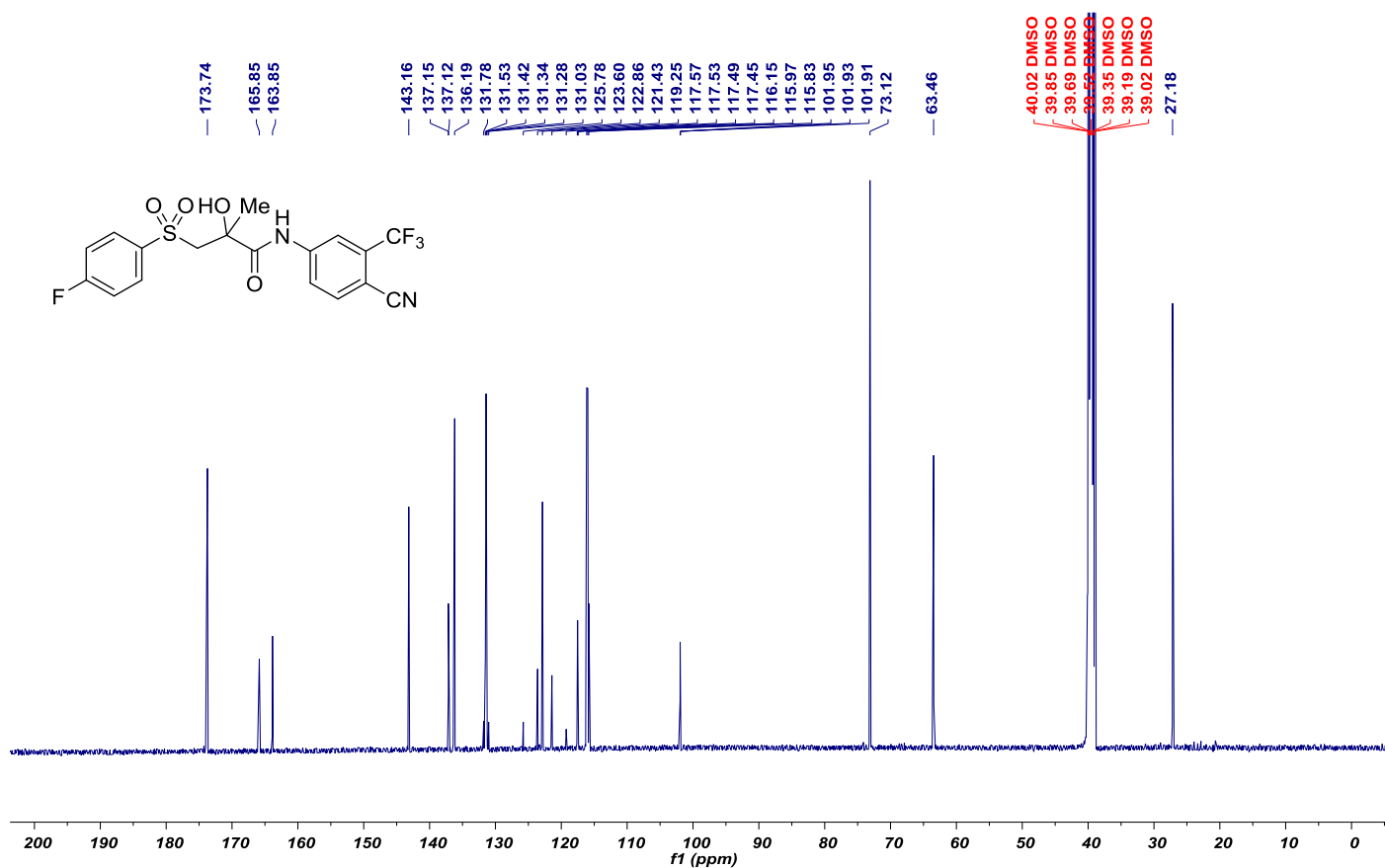
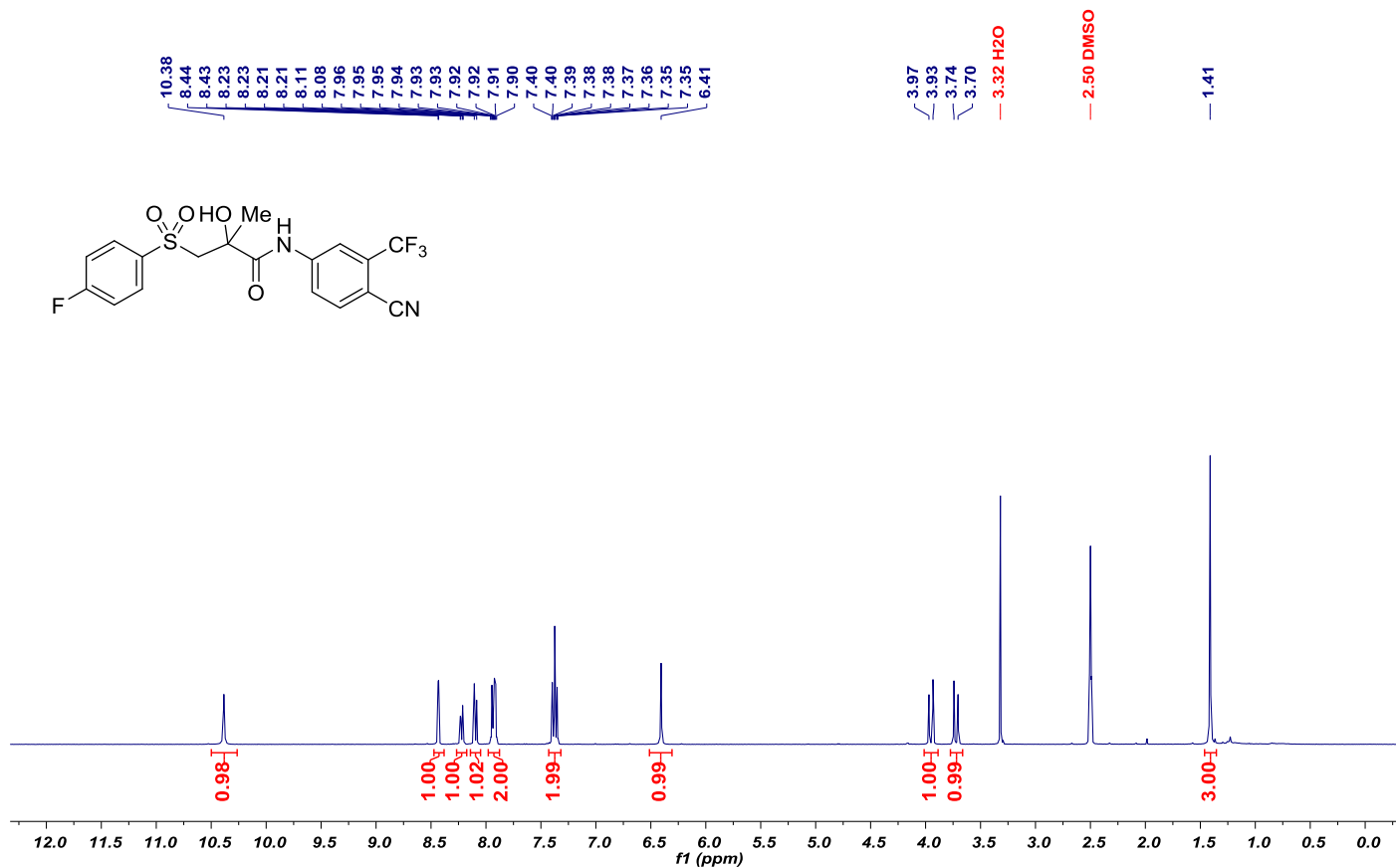
NMR spectrum of β -hydroxysulfone **3k**

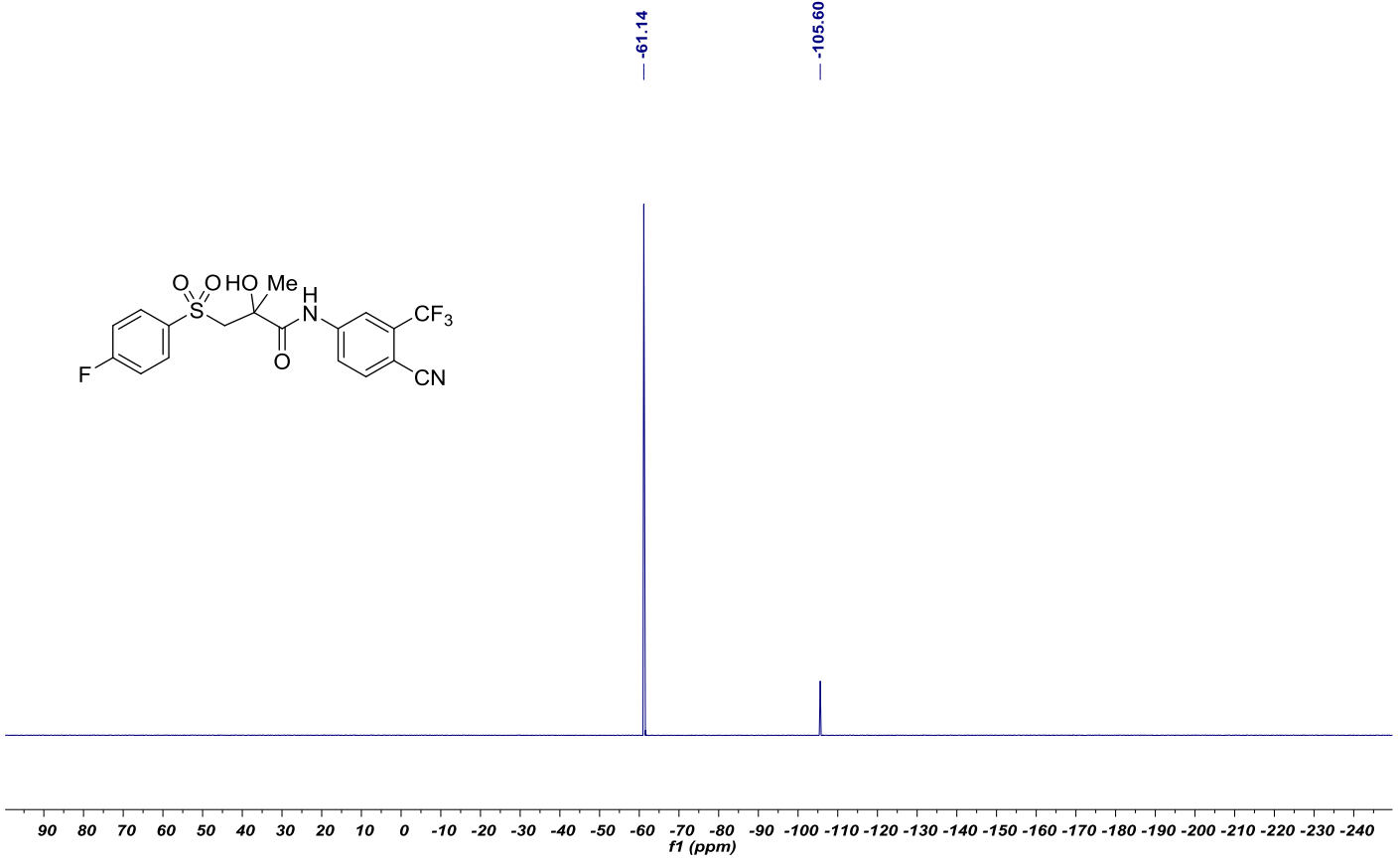
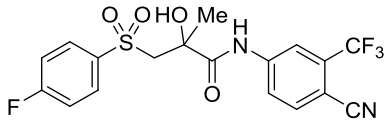


NMR spectrum of β -hydroxysulfone 3I

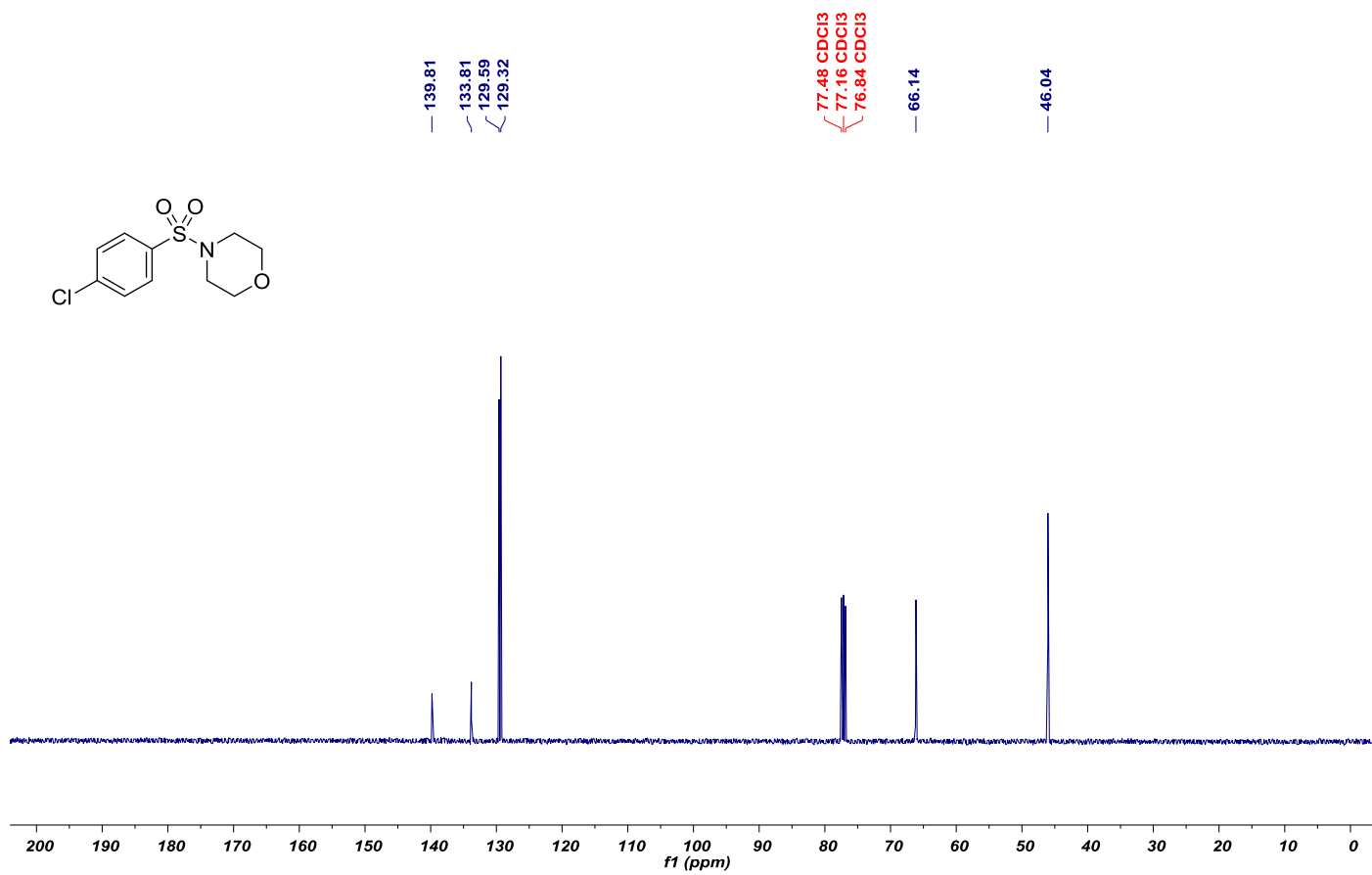
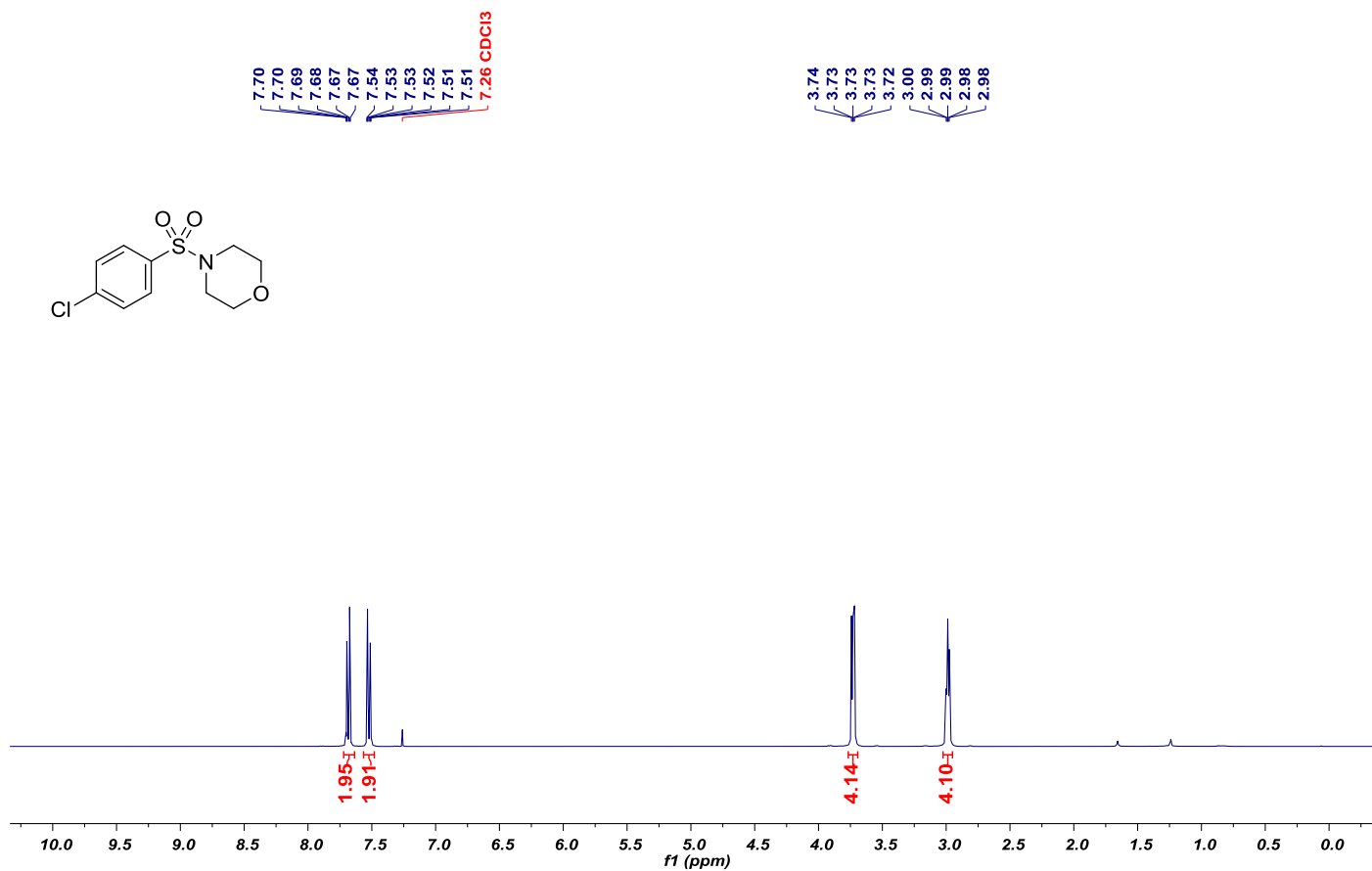


NMR spectrum of β -hydroxysulfone **3m**

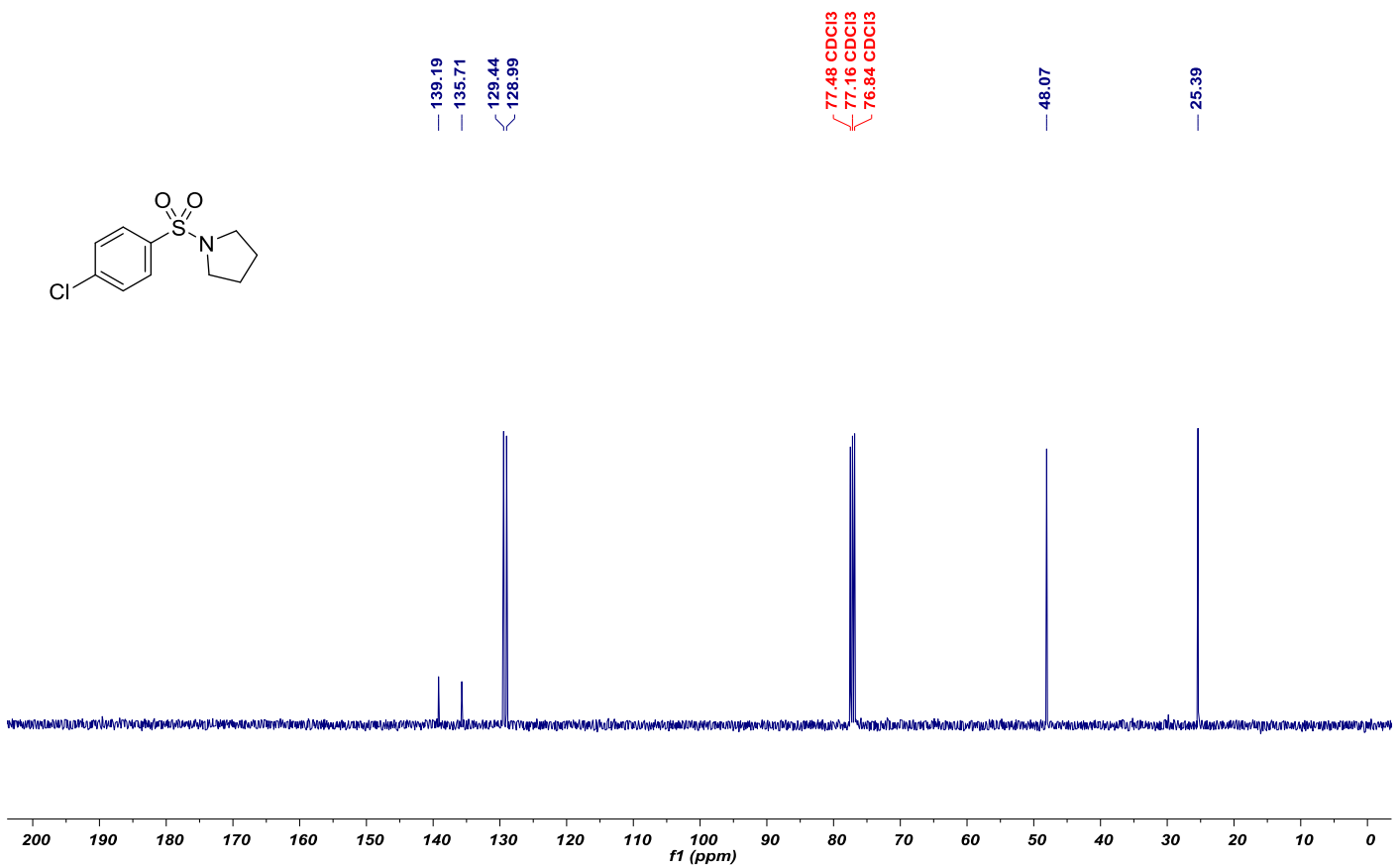
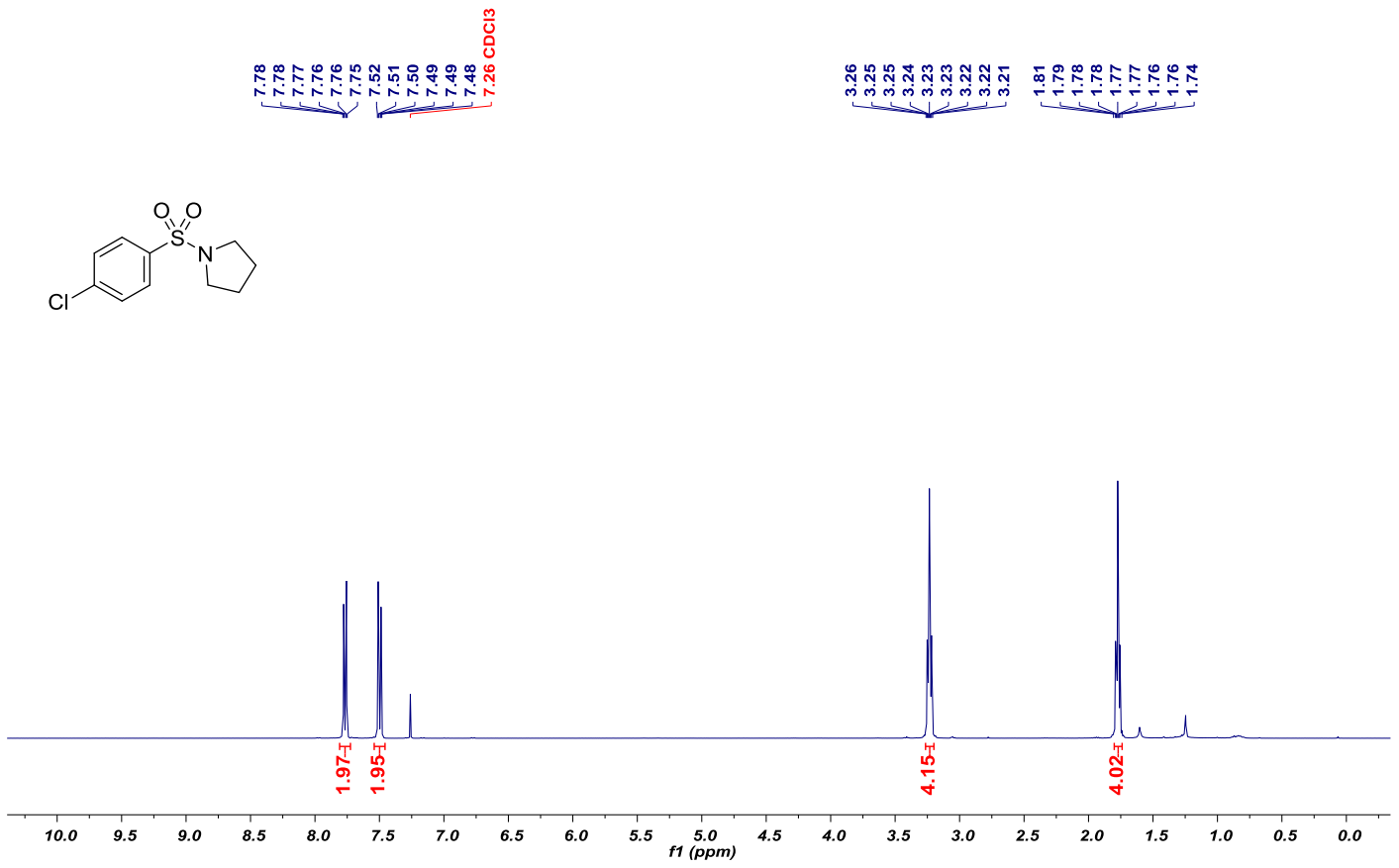




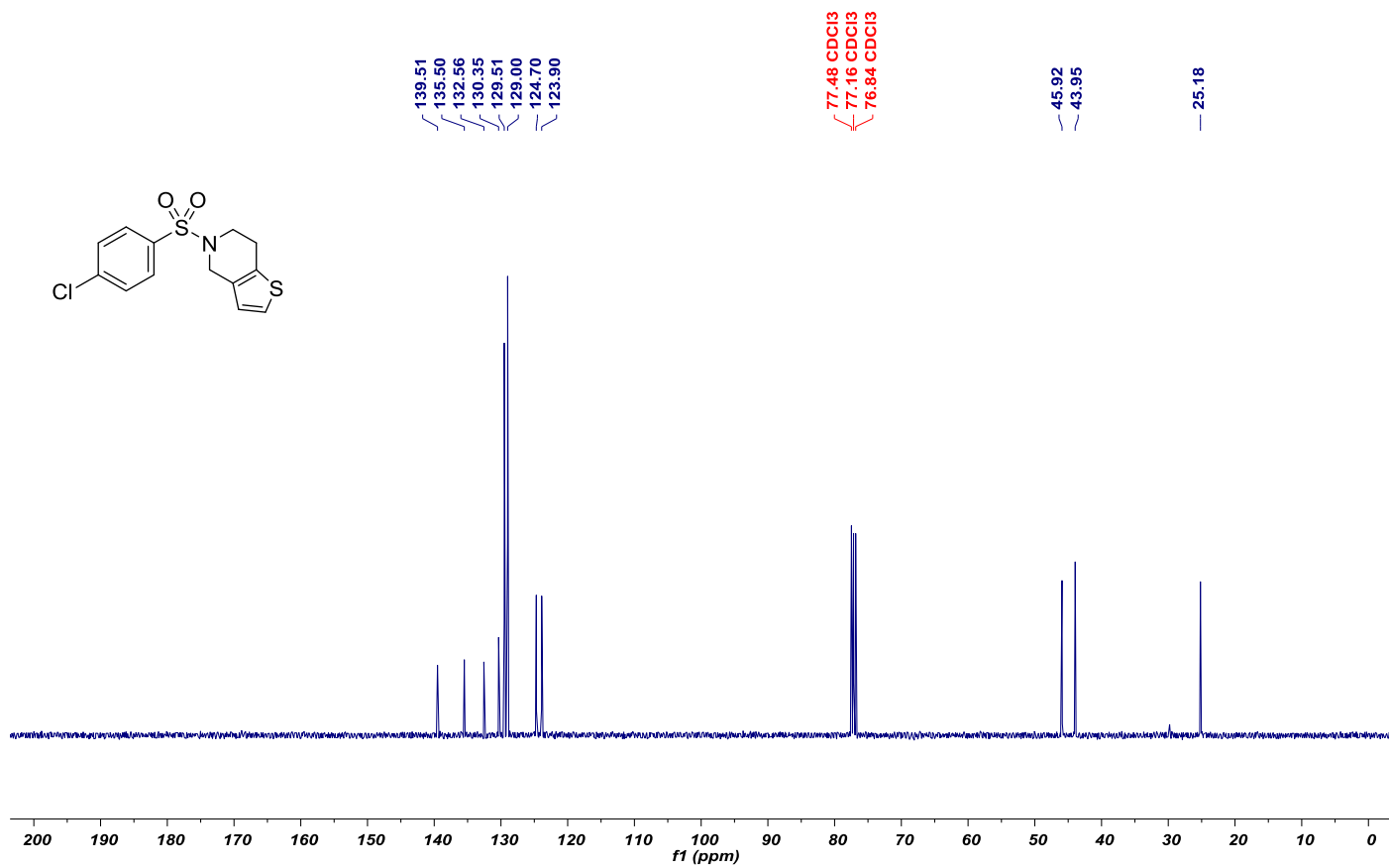
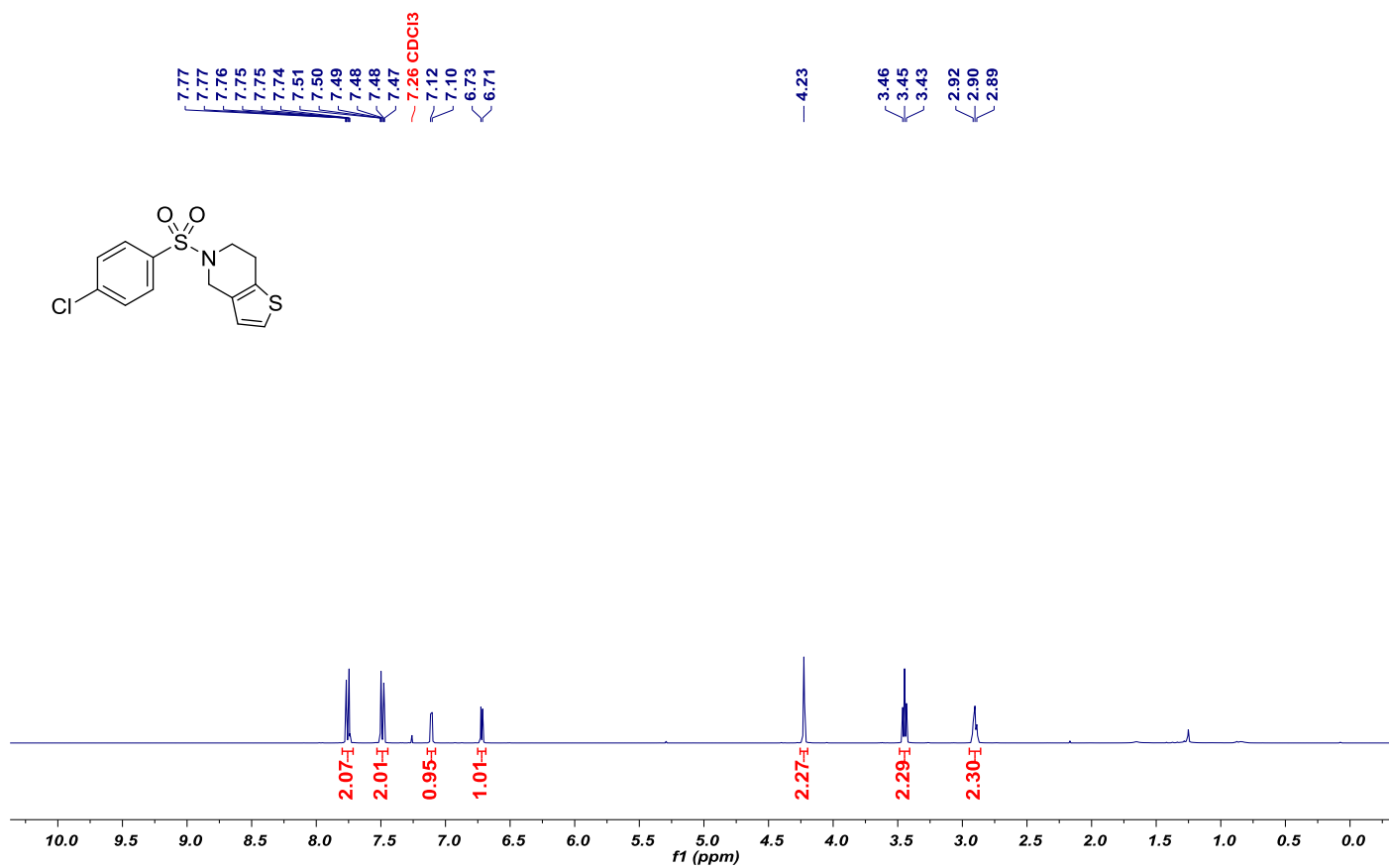
NMR spectrum of sulfonamide **4a**



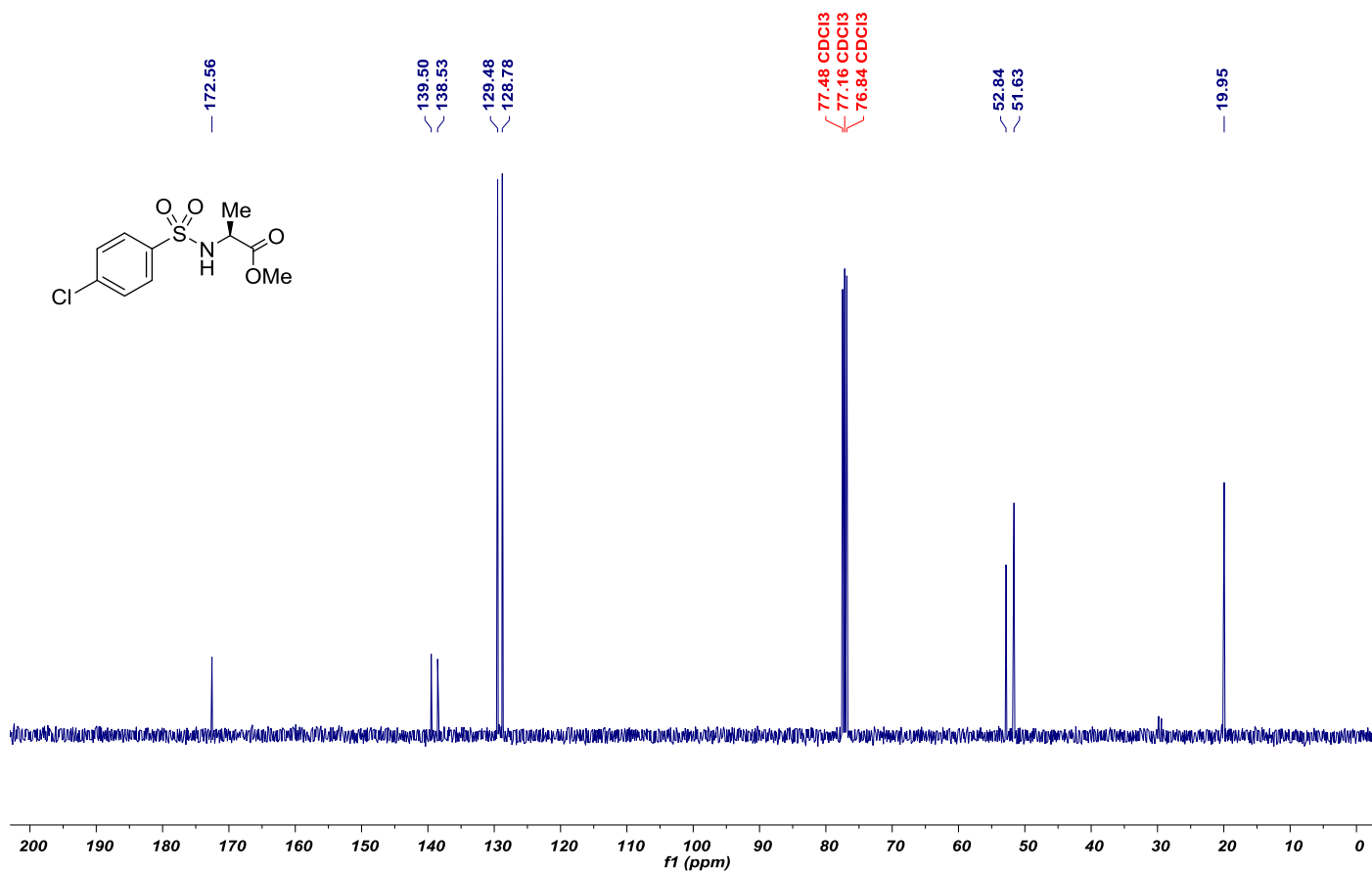
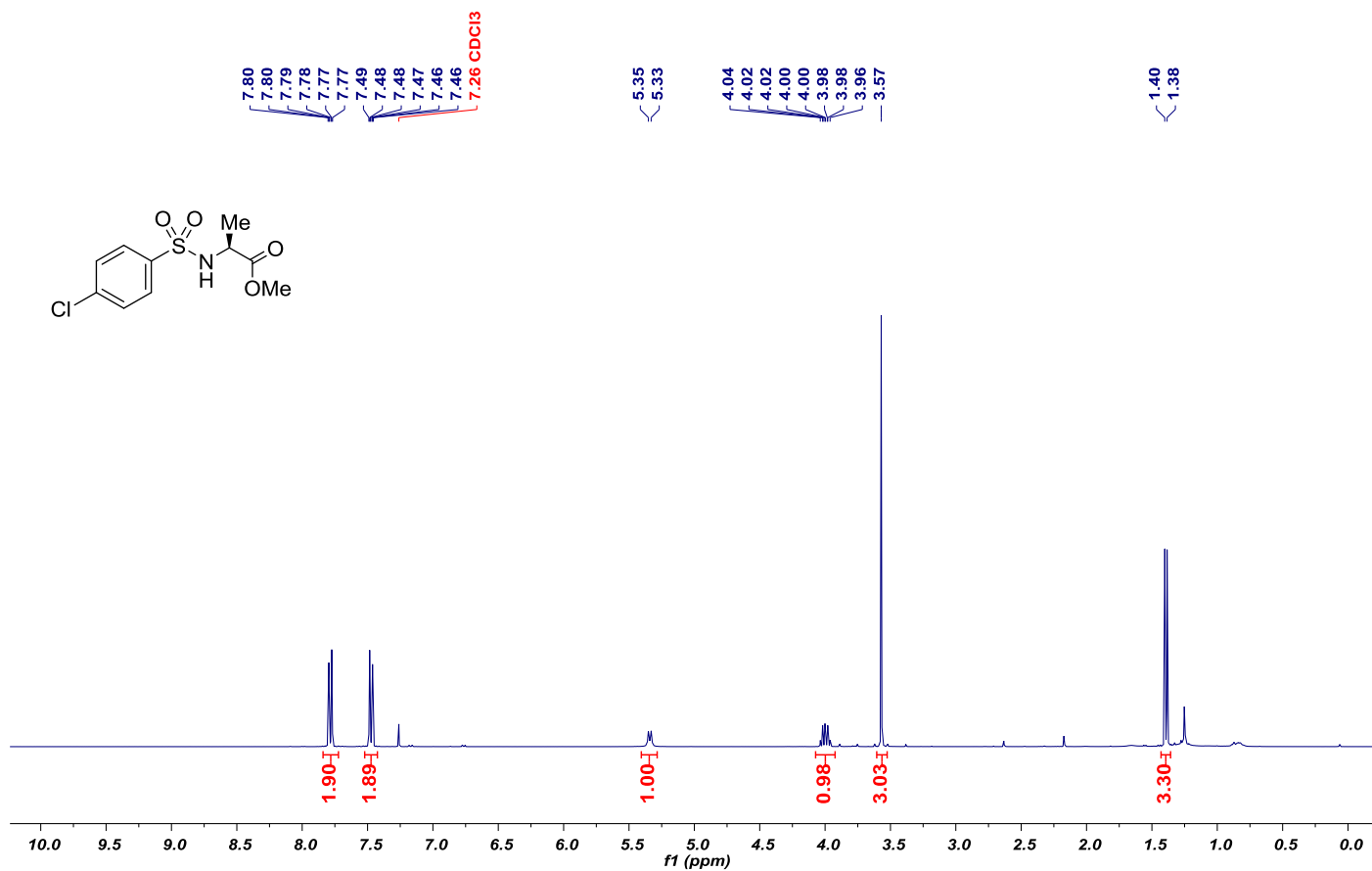
NMR spectrum of sulfonamide **4b**



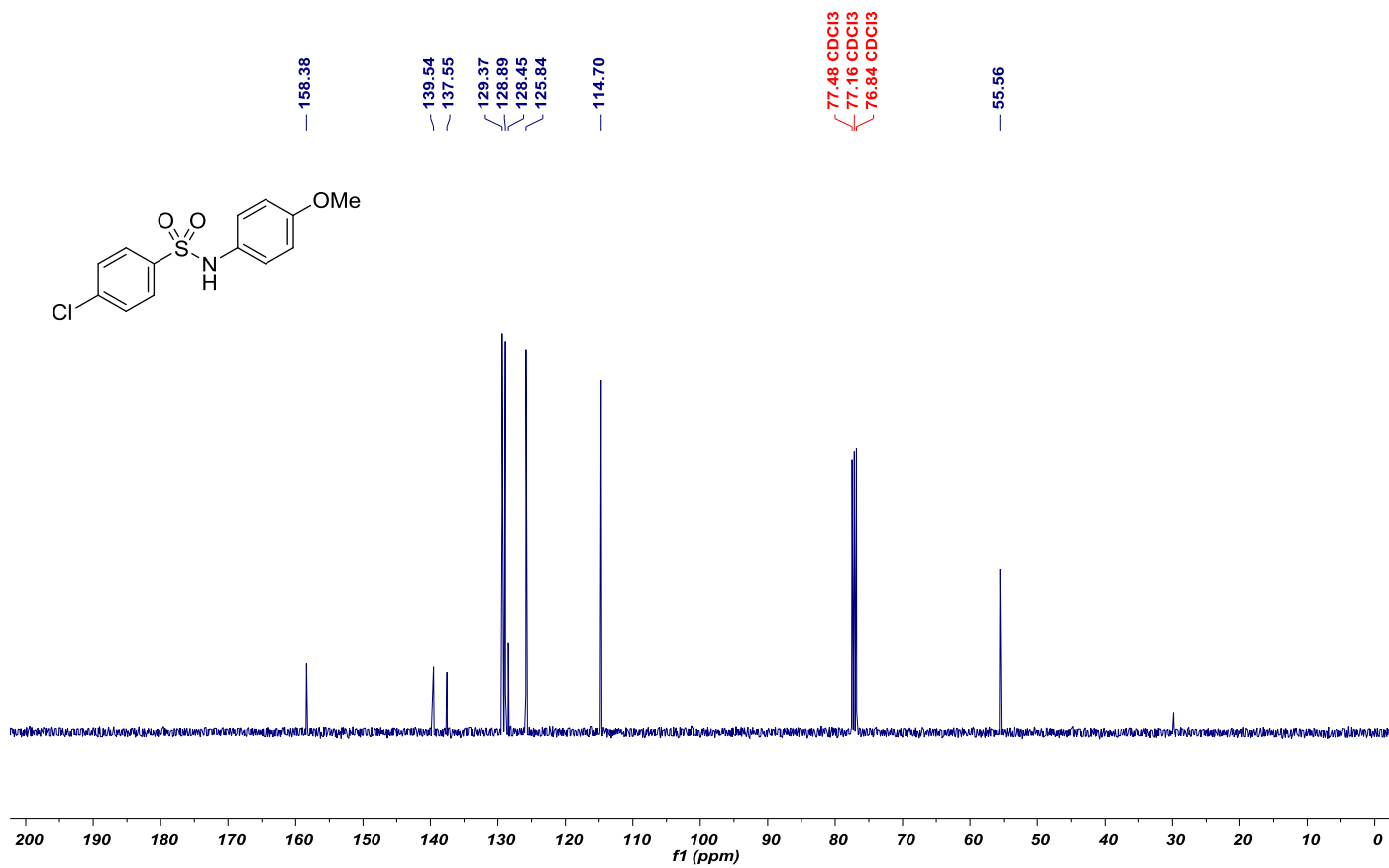
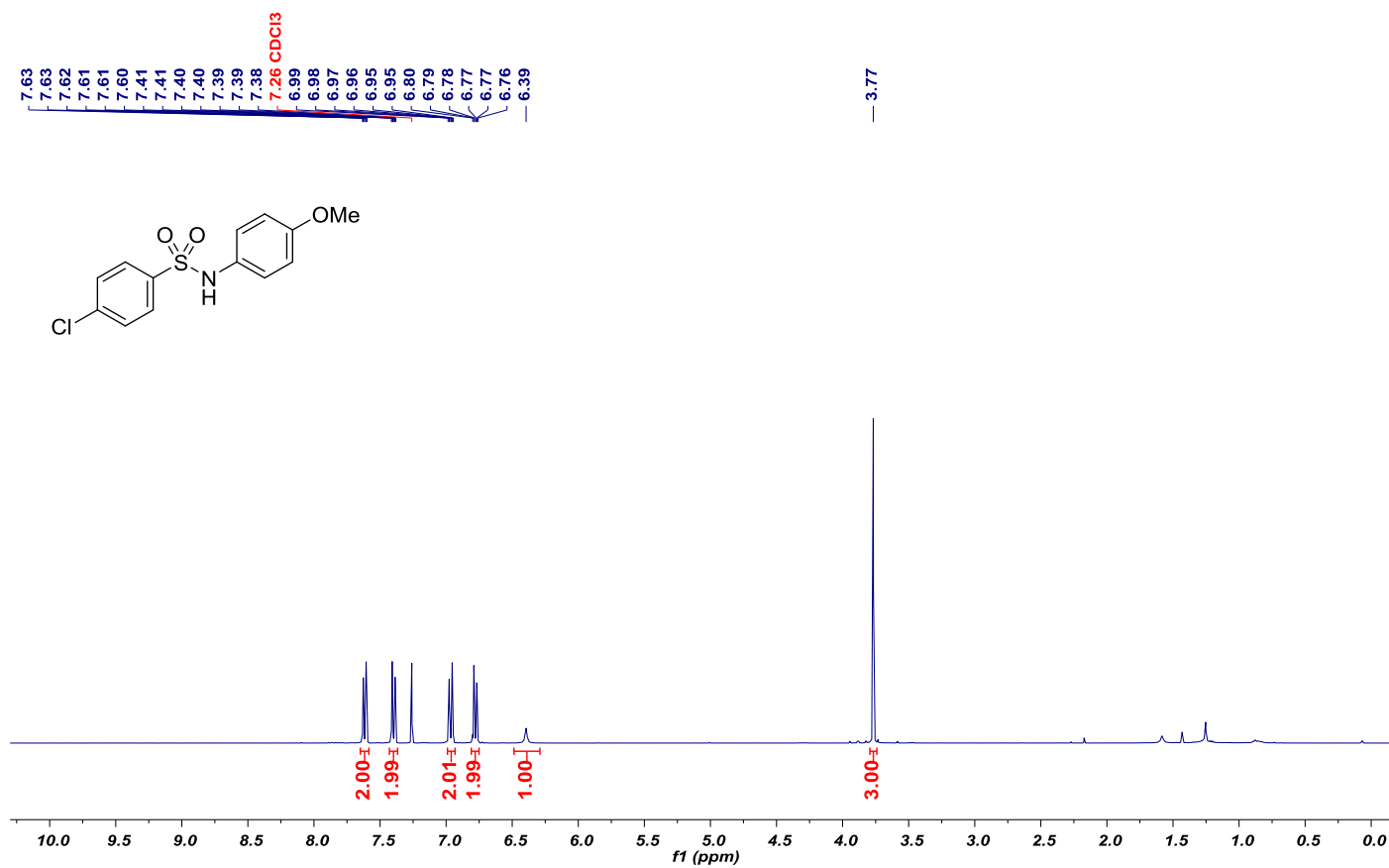
NMR spectrum of sulfonamide **4c**



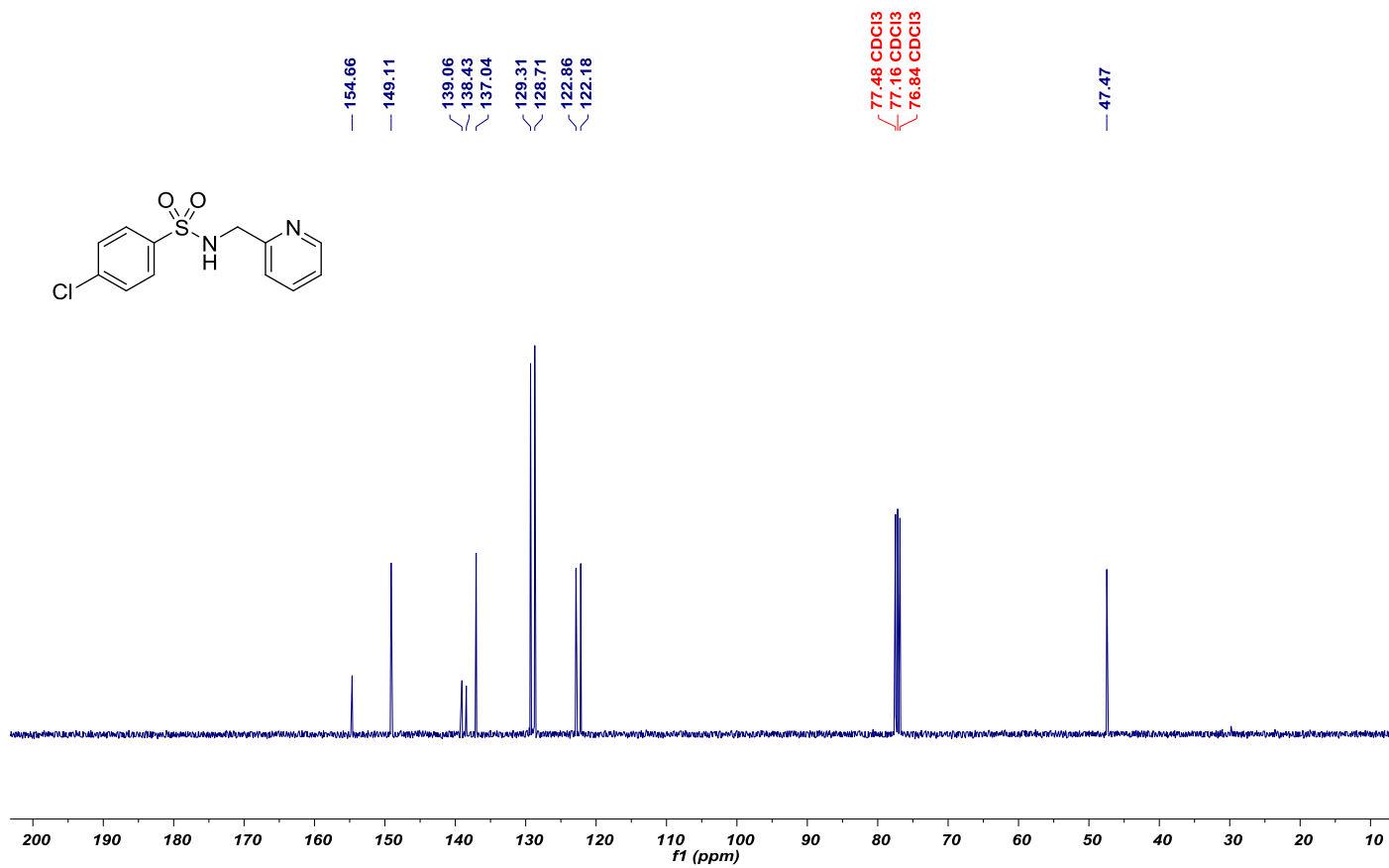
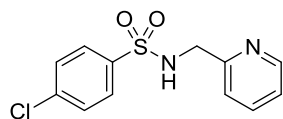
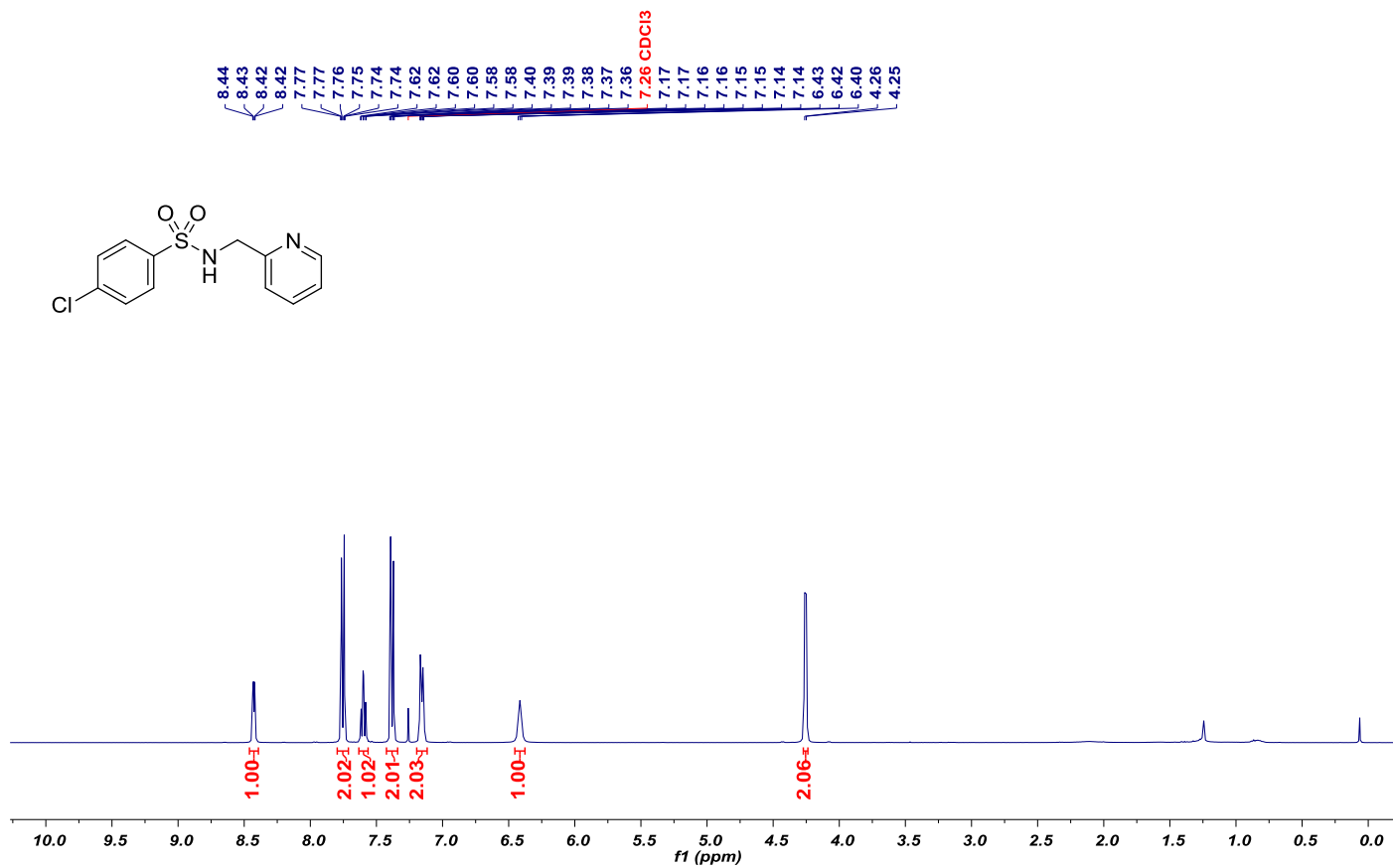
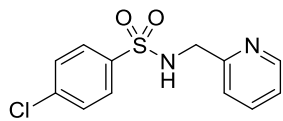
NMR spectrum of sulfonamide **4d**



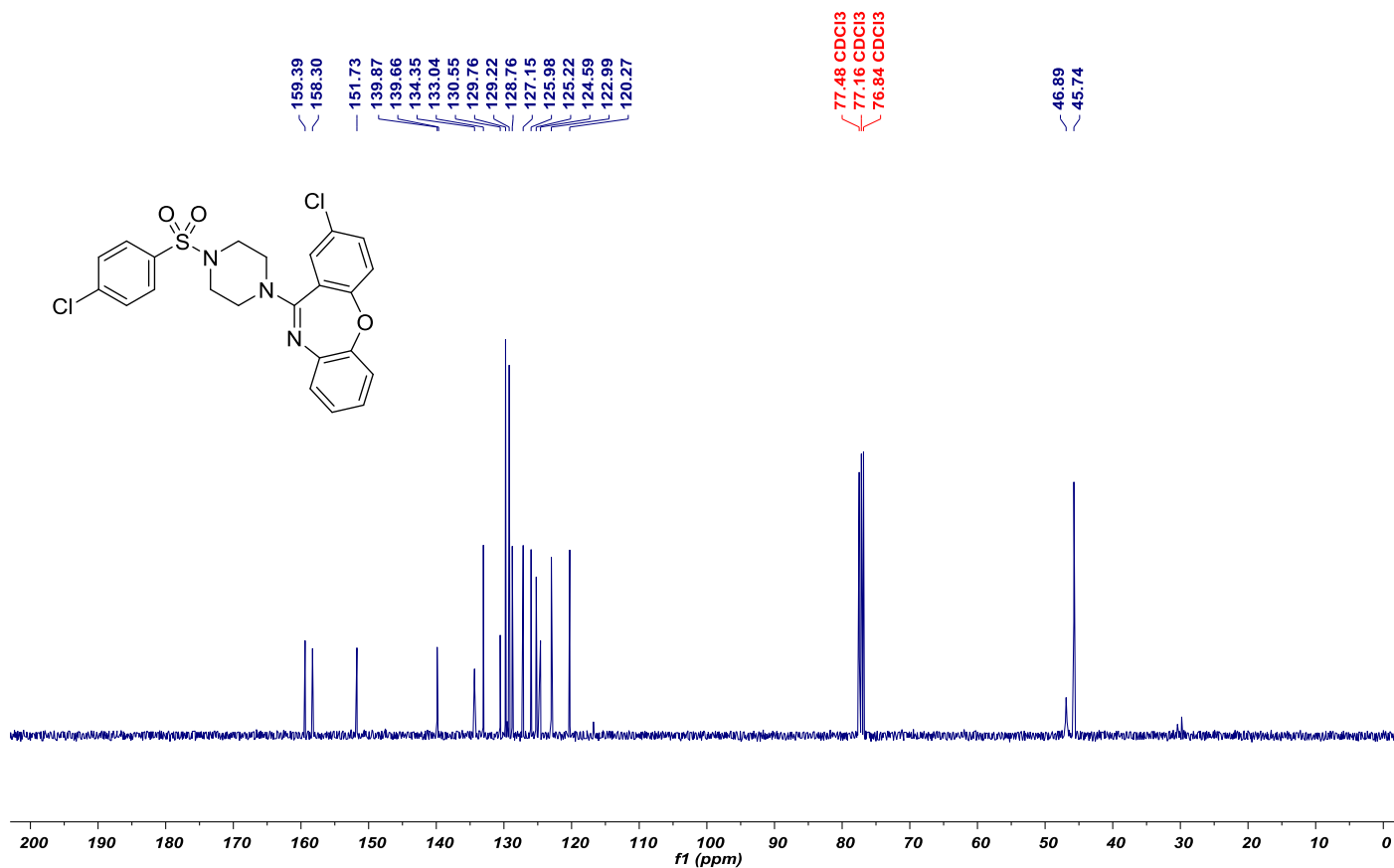
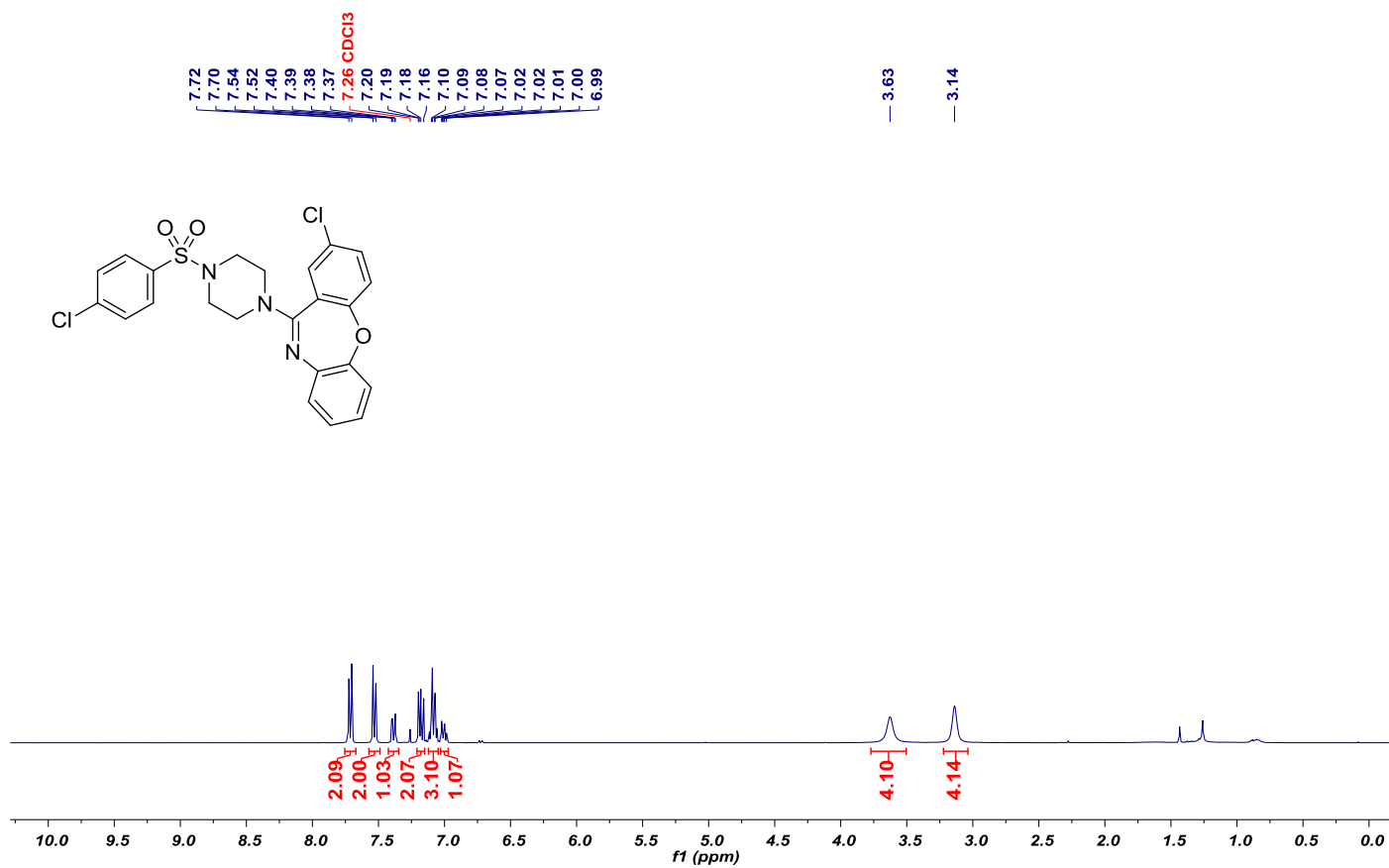
NMR spectrum of sulfonamide **4e**



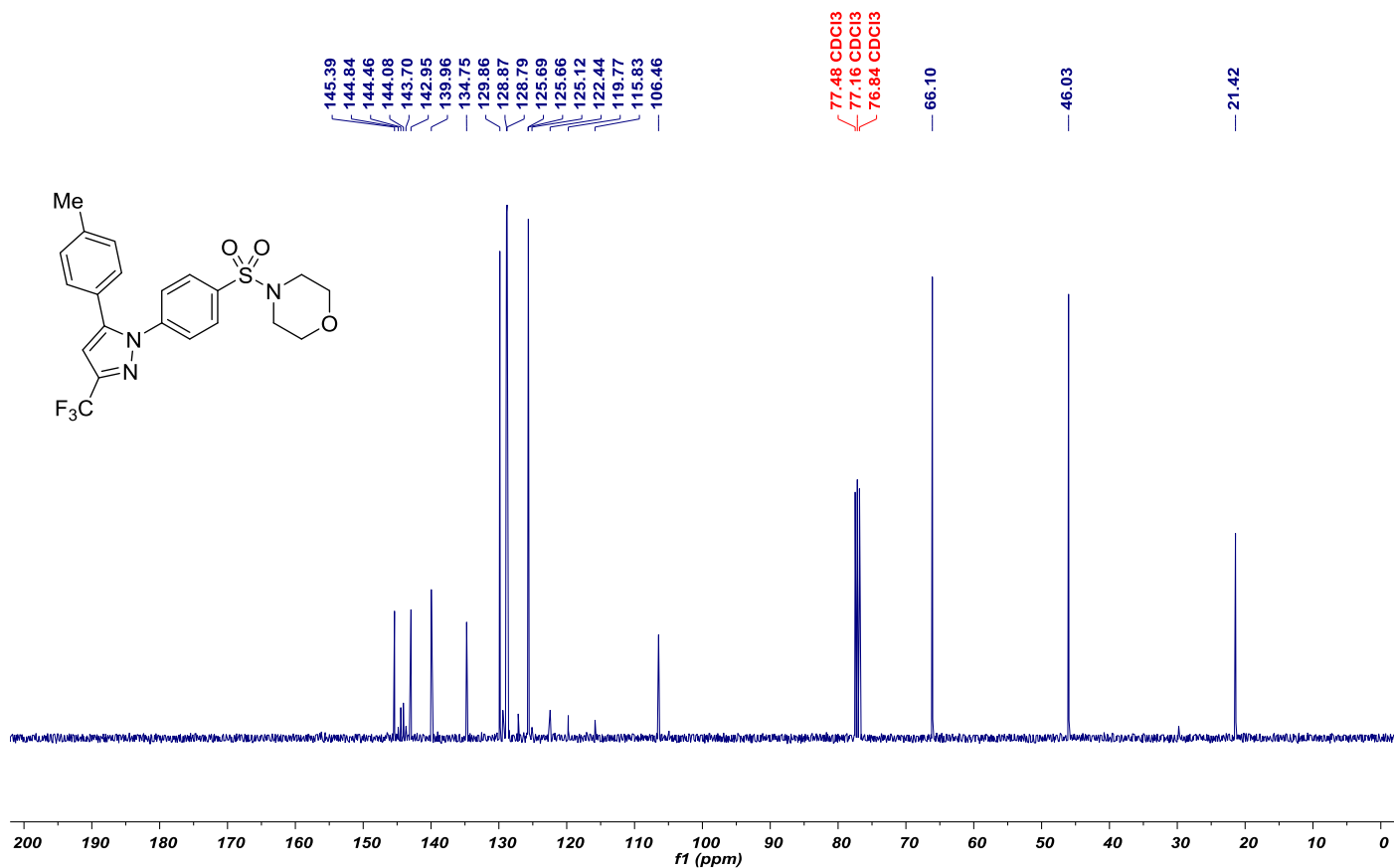
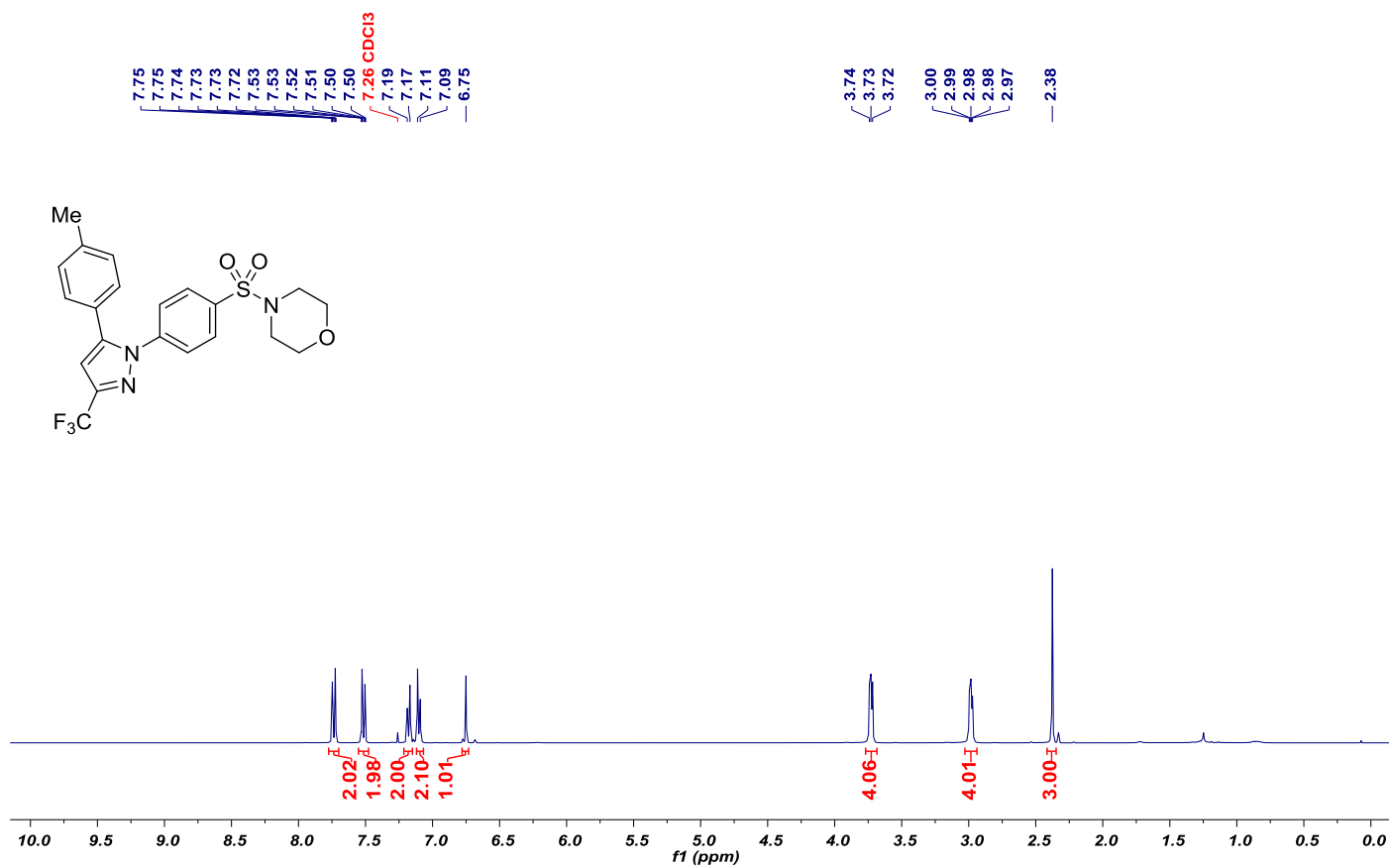
NMR spectrum of sulfonamide 4f

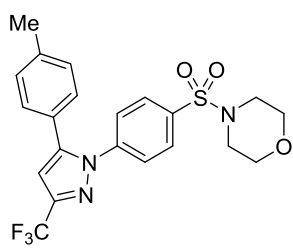


NMR spectrum of sulfonamide **4g**

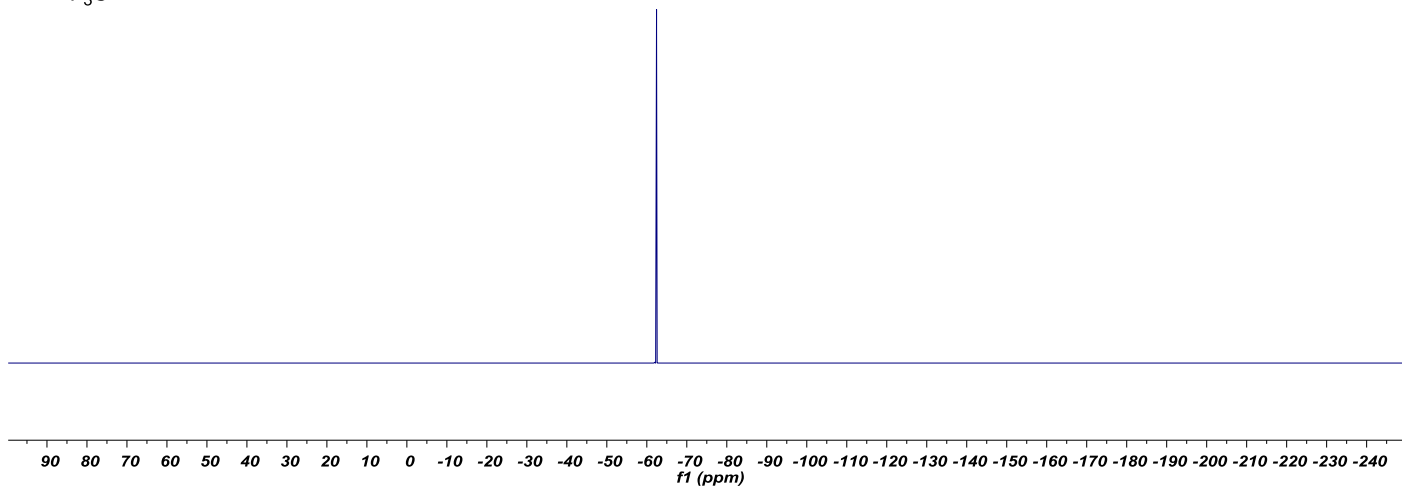


NMR spectrum of sulfonamide **4h**

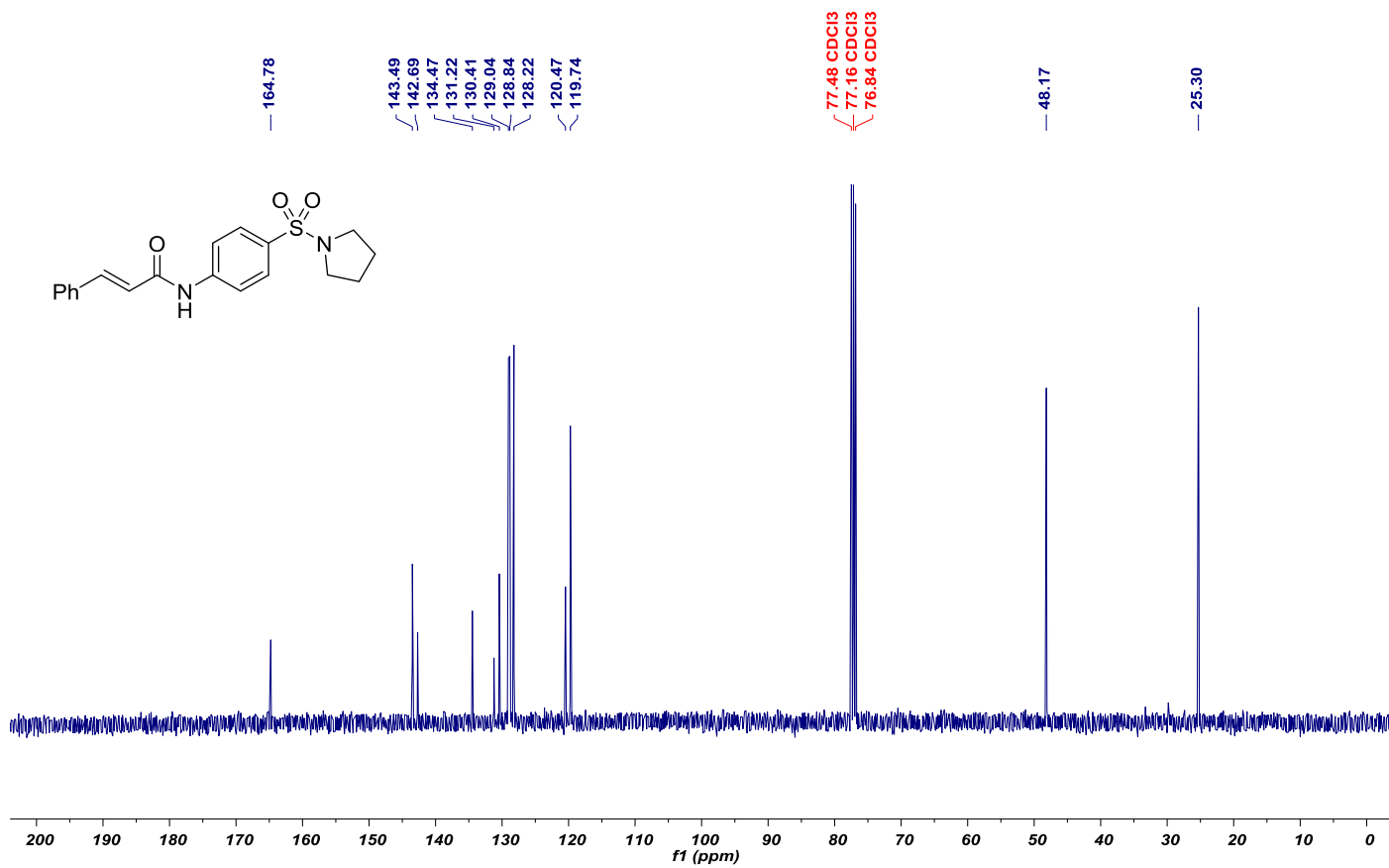
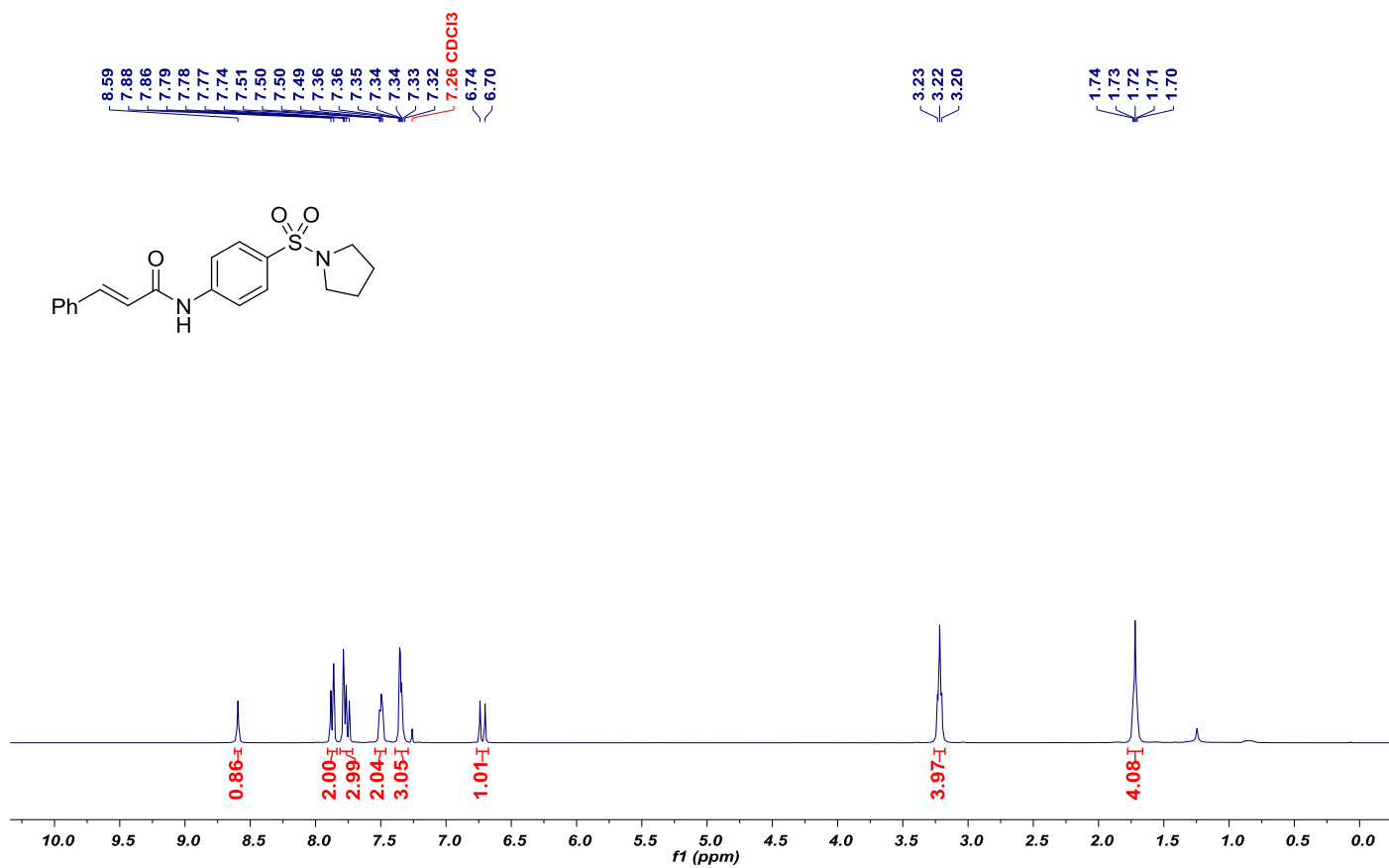




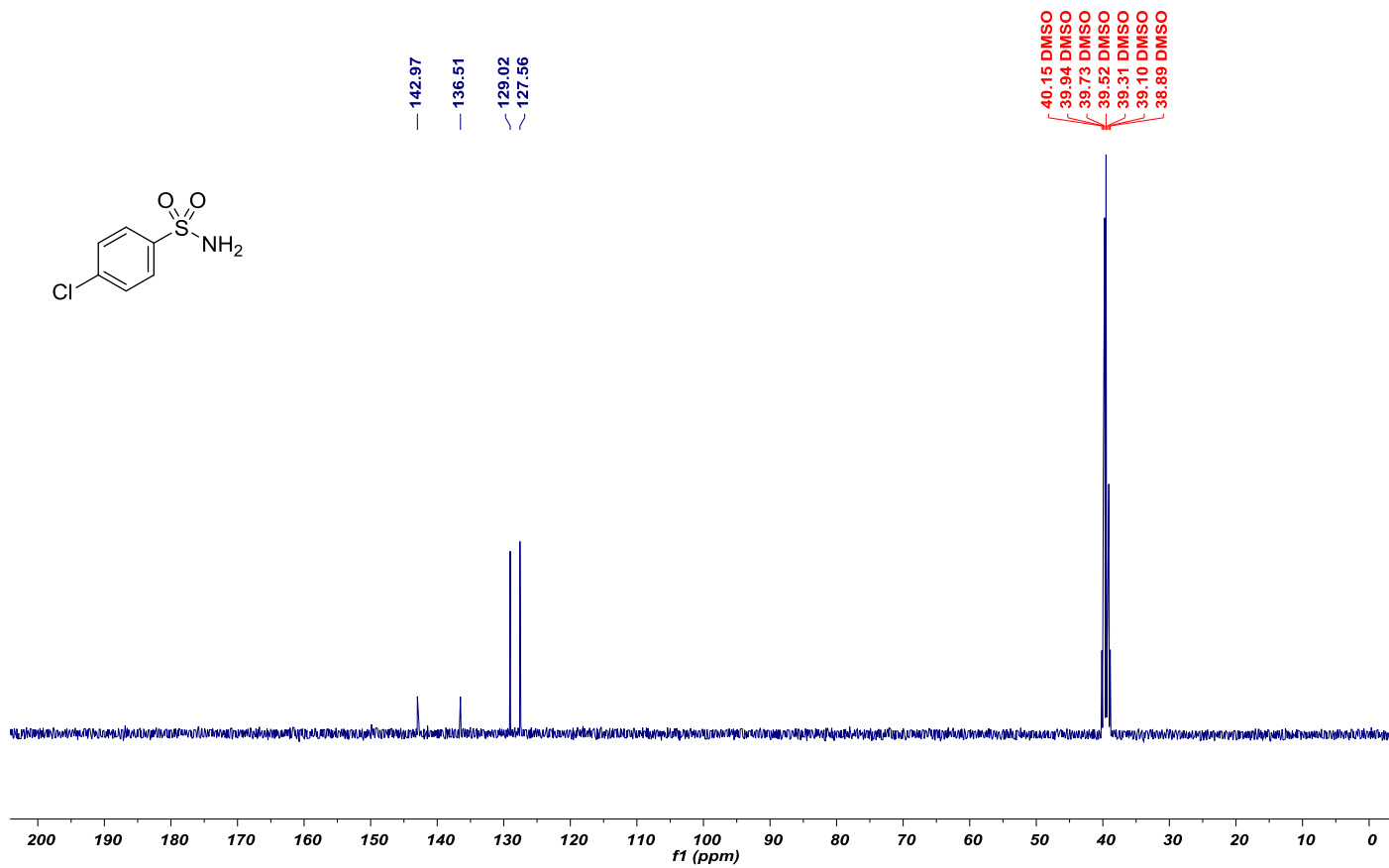
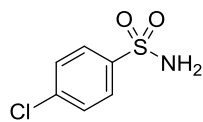
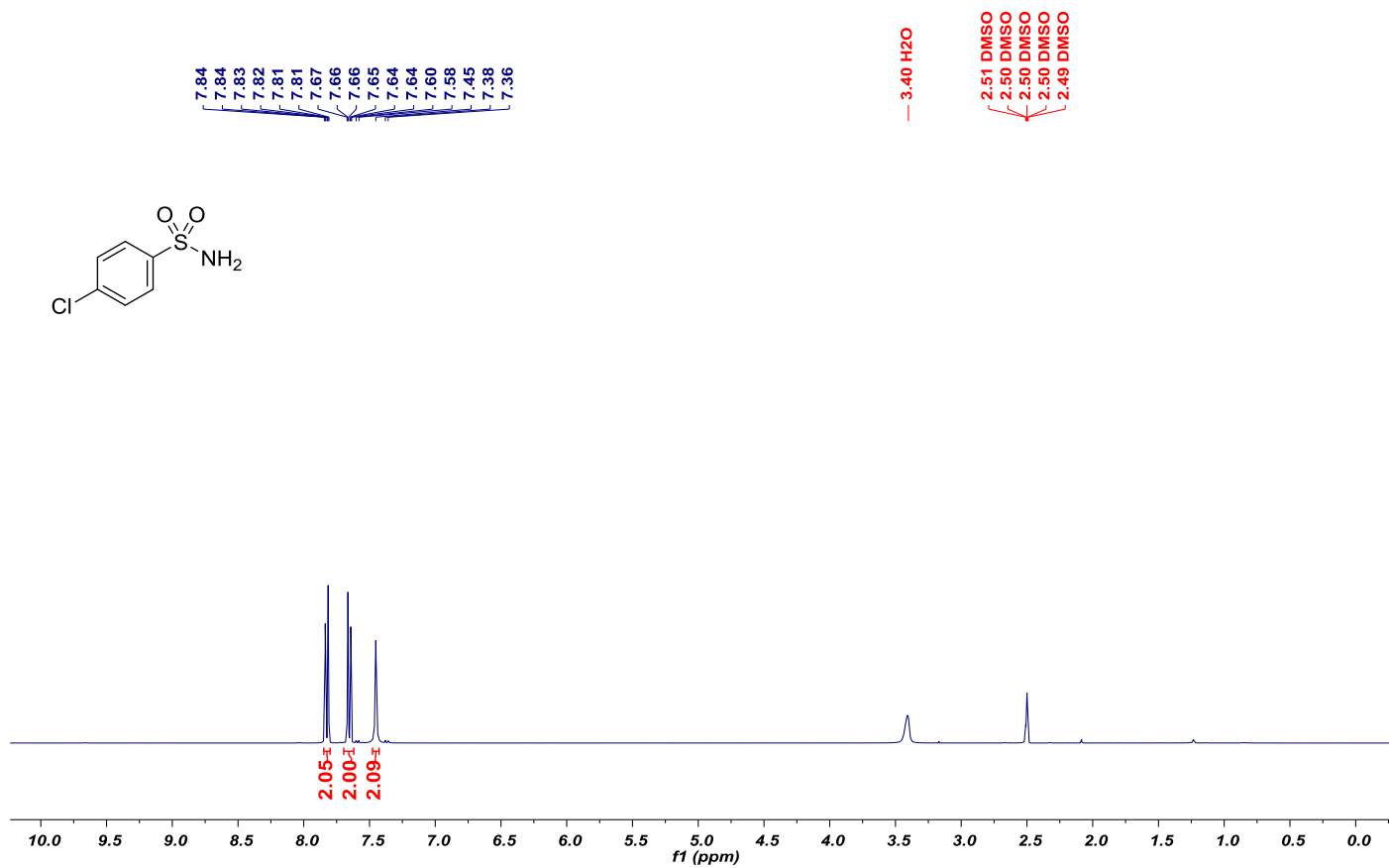
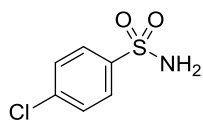
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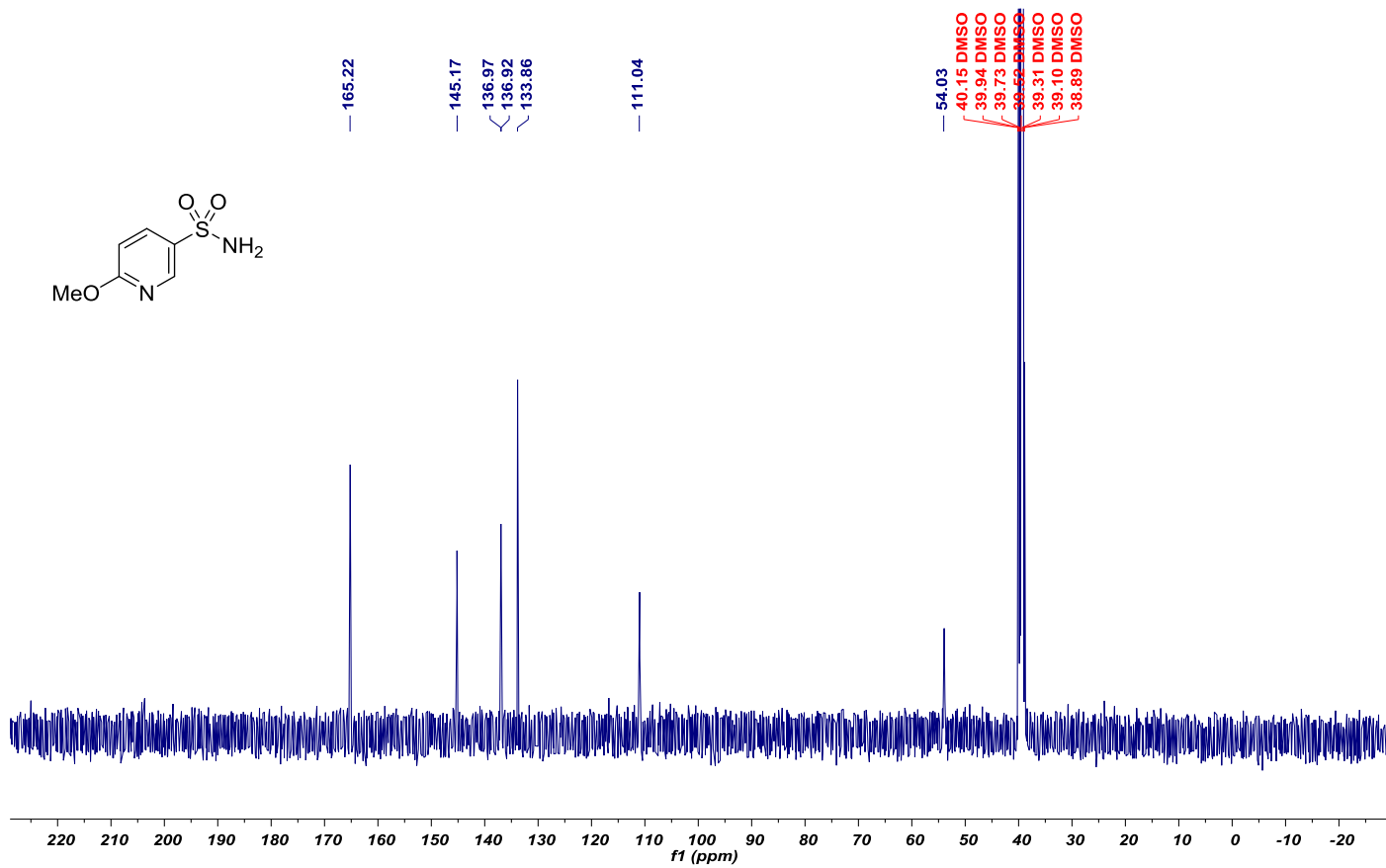
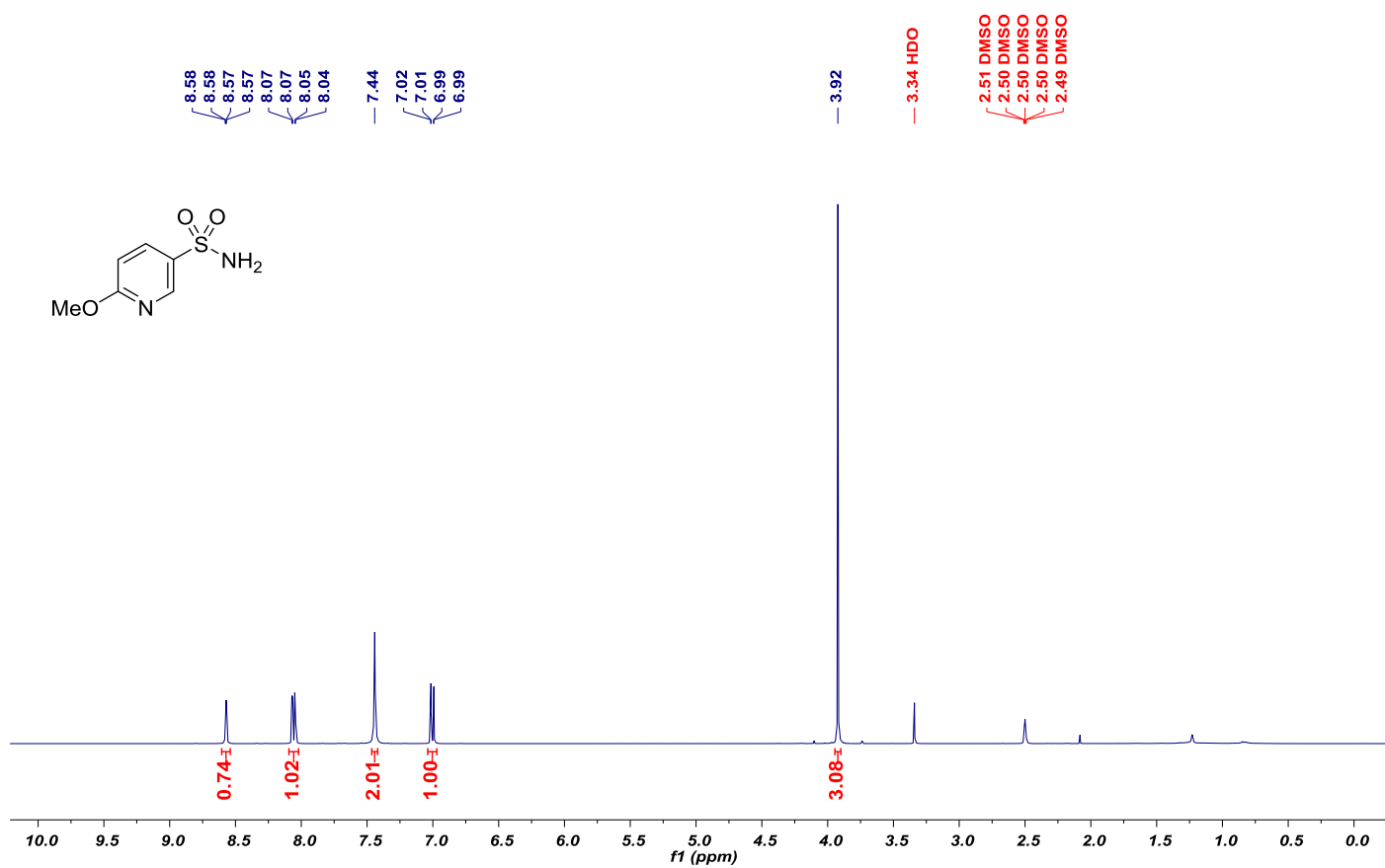
NMR spectrum of sulfonamide 4i



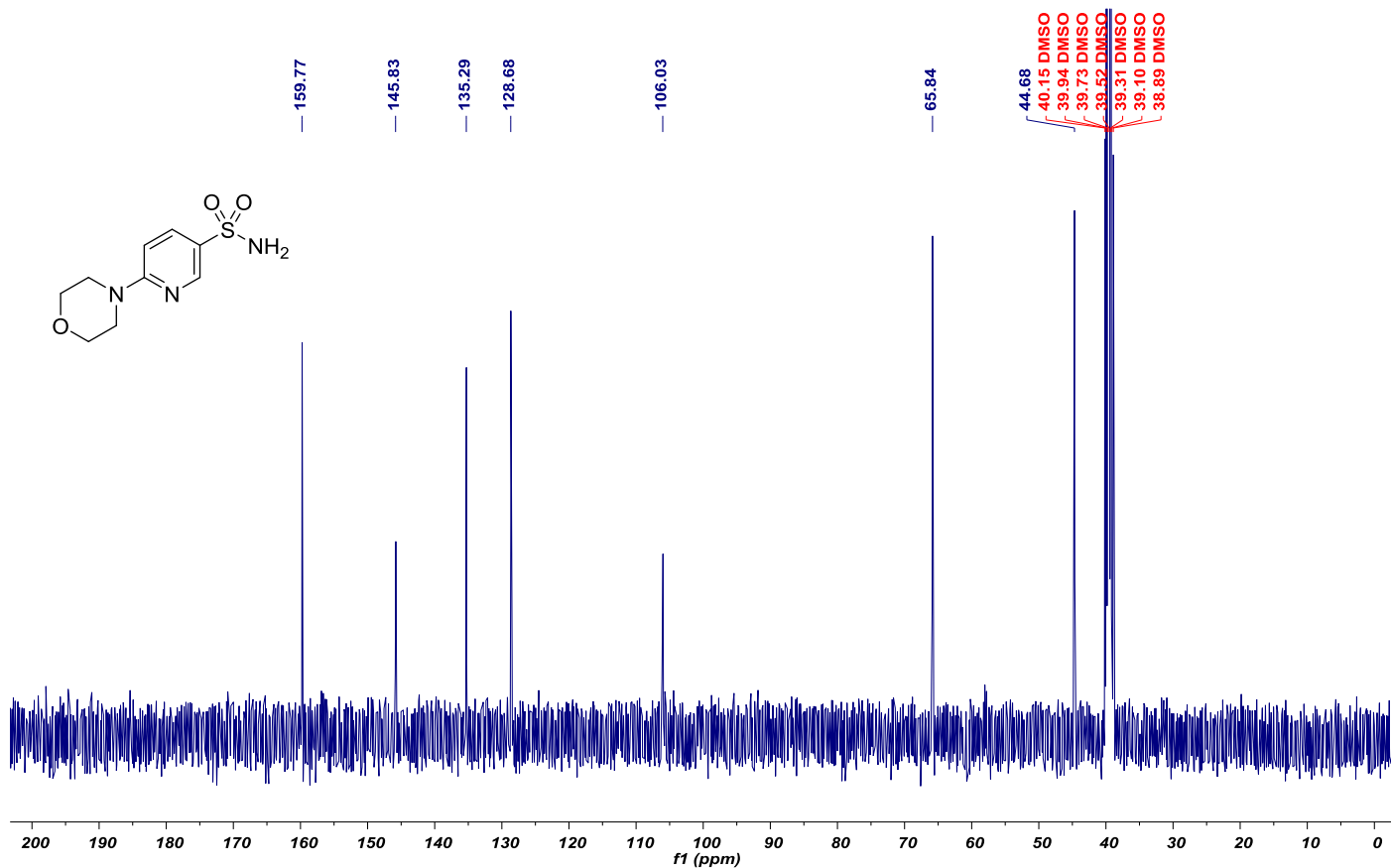
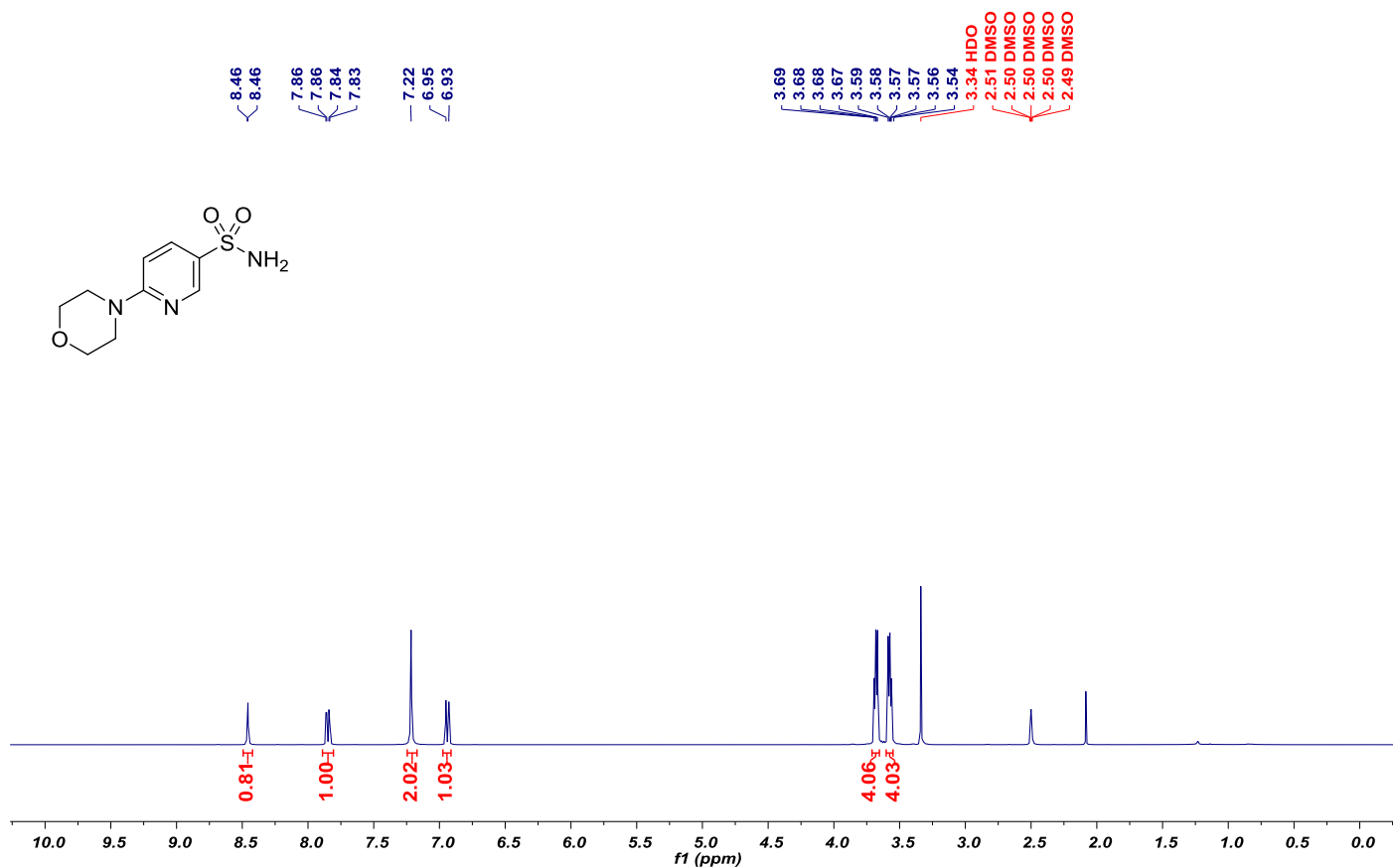
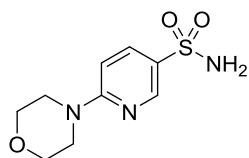
NMR spectrum of sulfonamide 4j



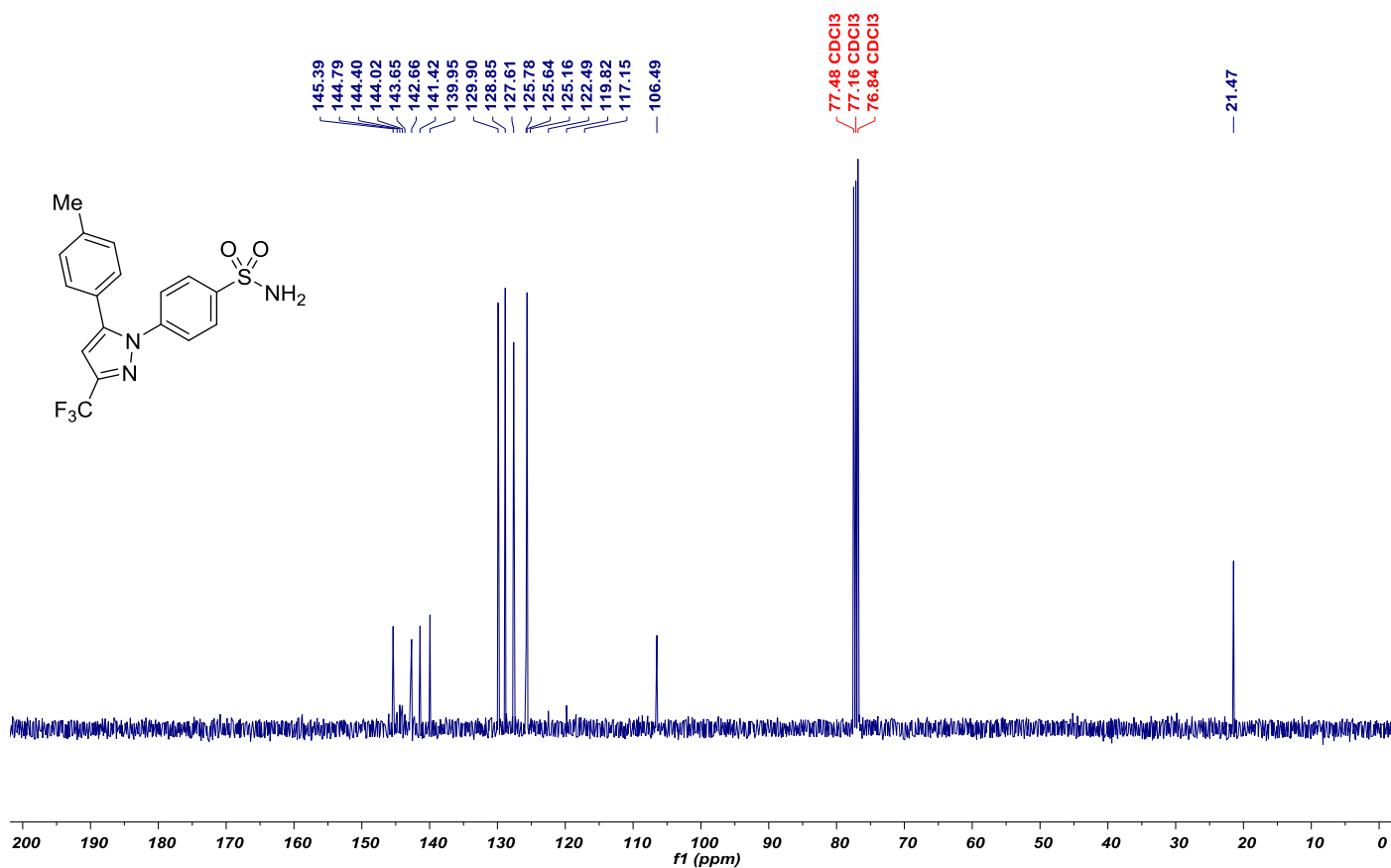
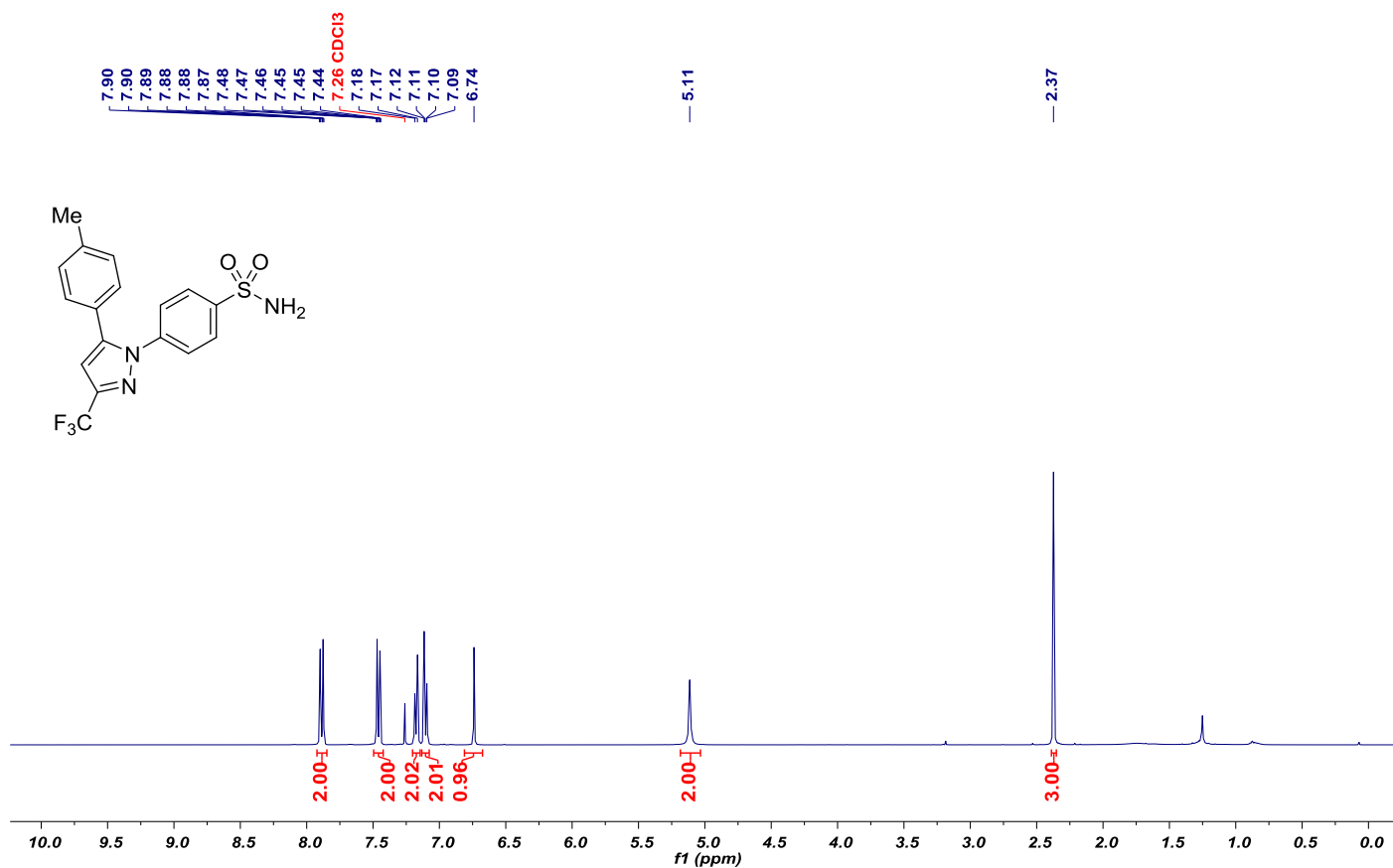
NMR spectrum of sulfonamide **4k**

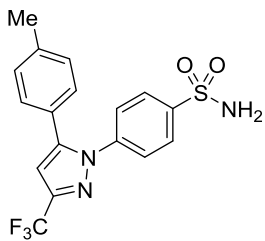


NMR spectrum of sulfonamide 4I

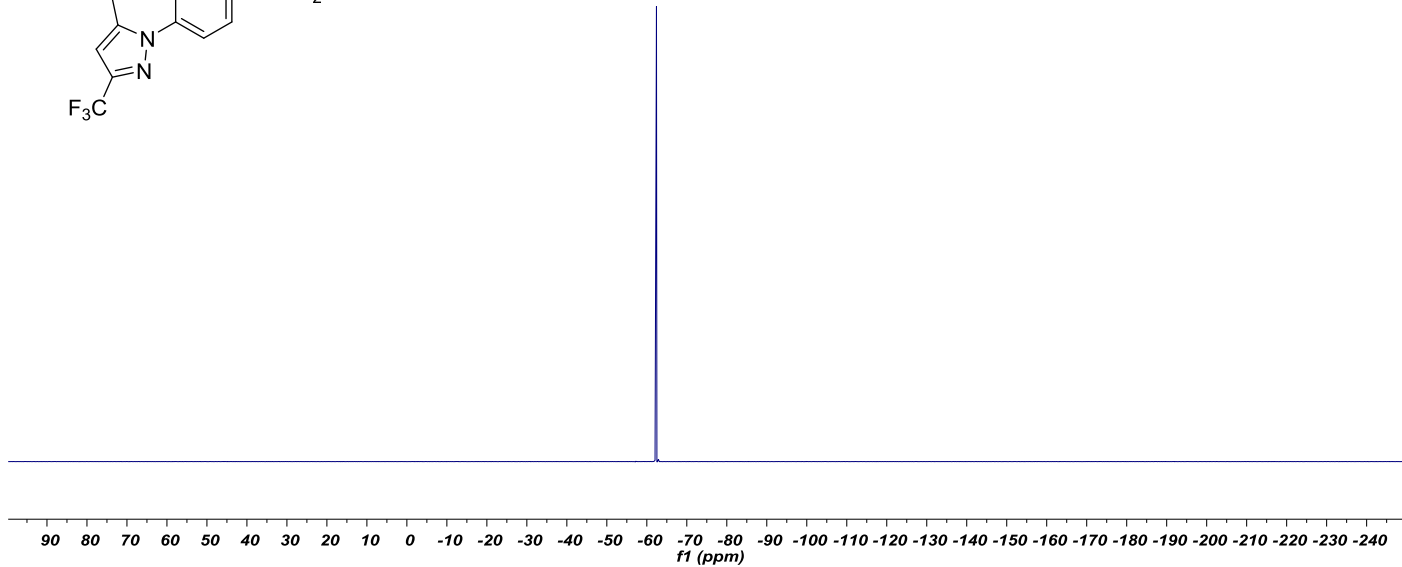


NMR spectrum of sulfonamide **4m**

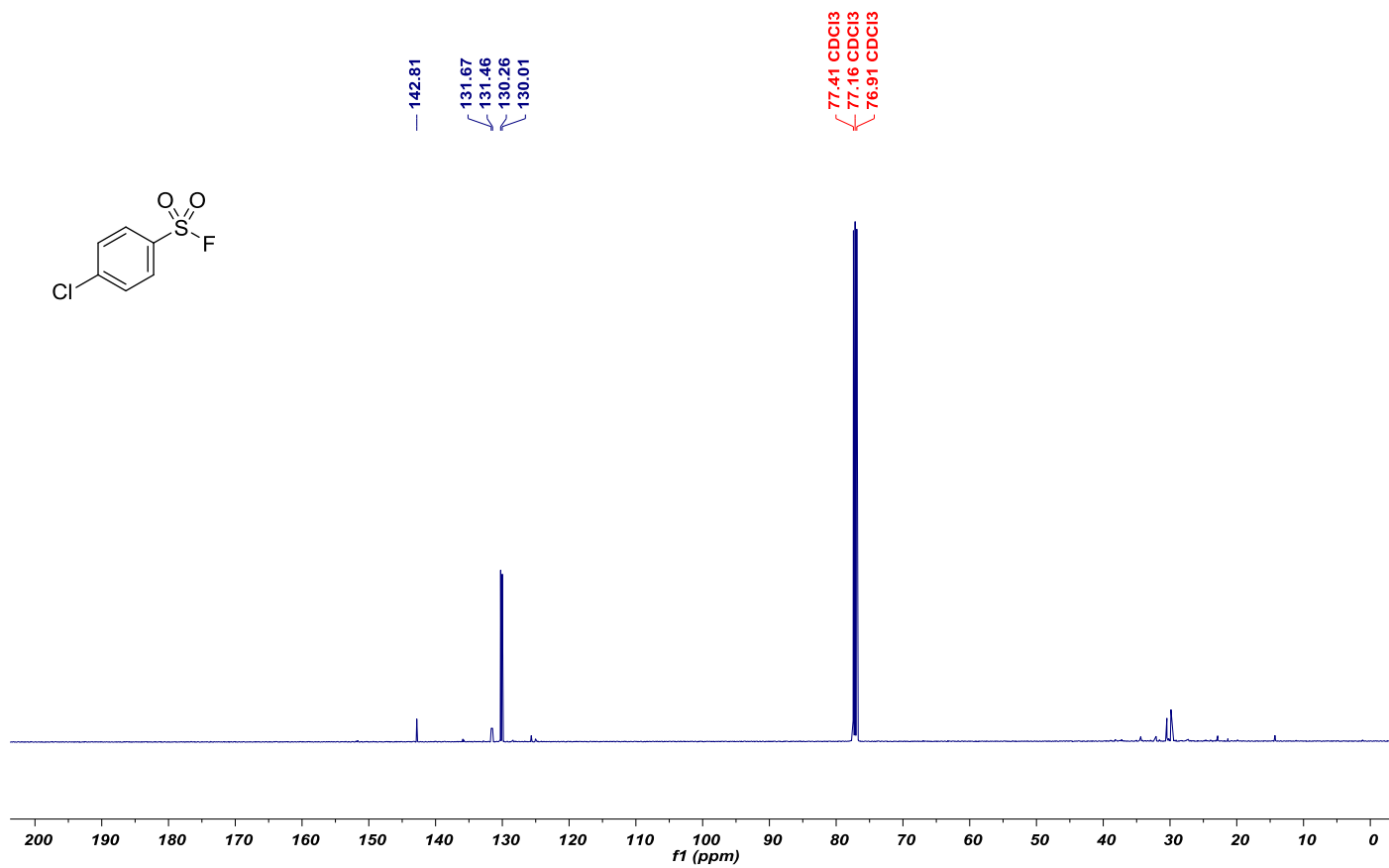
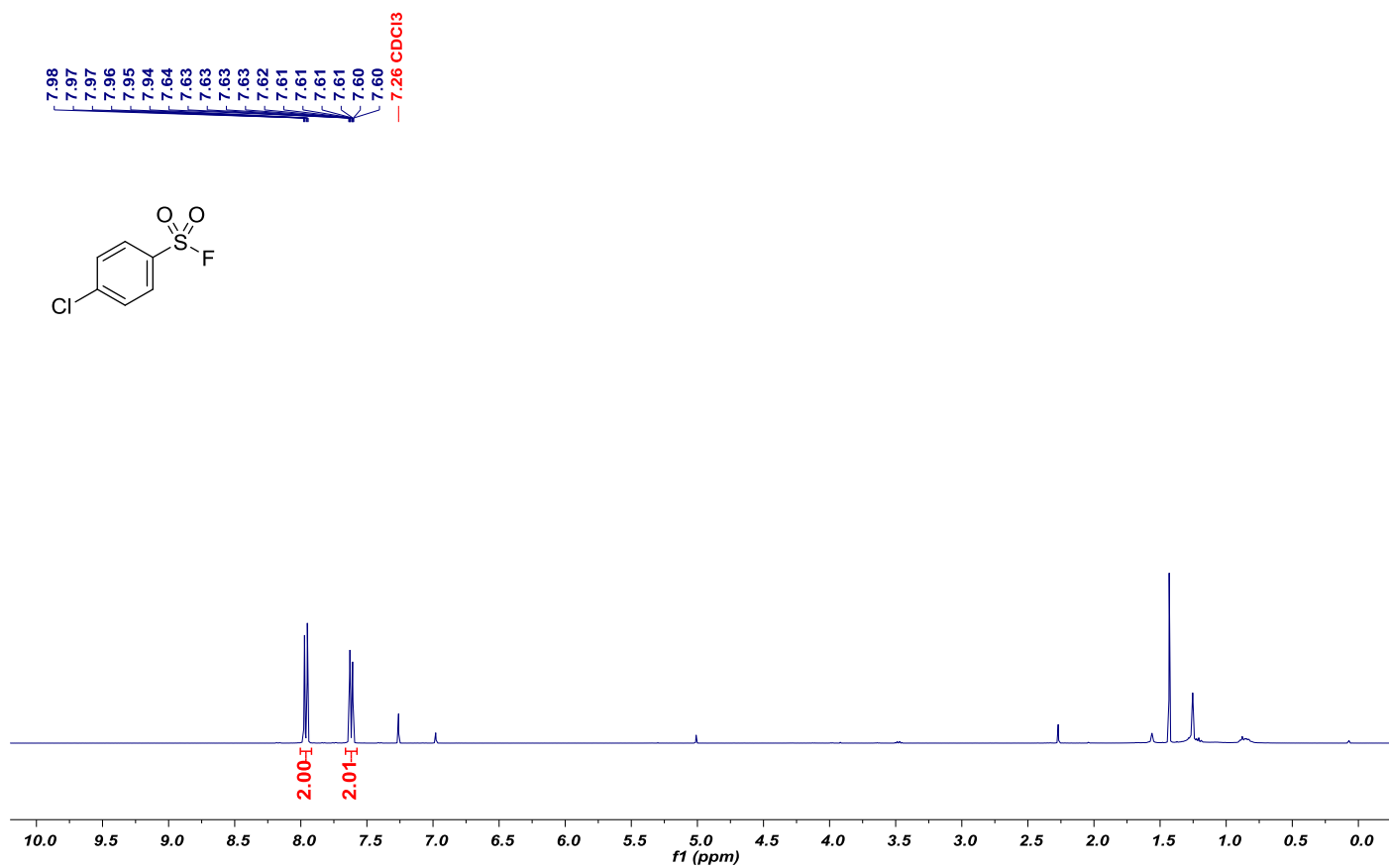




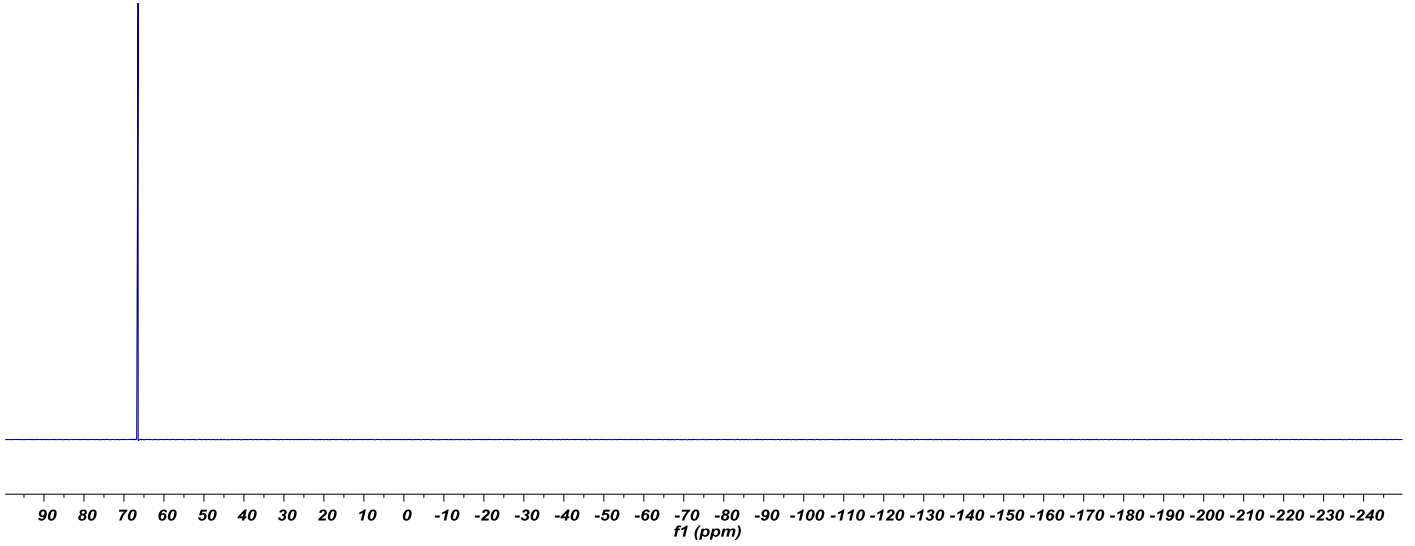
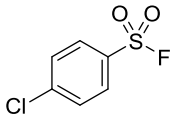
— 62.42



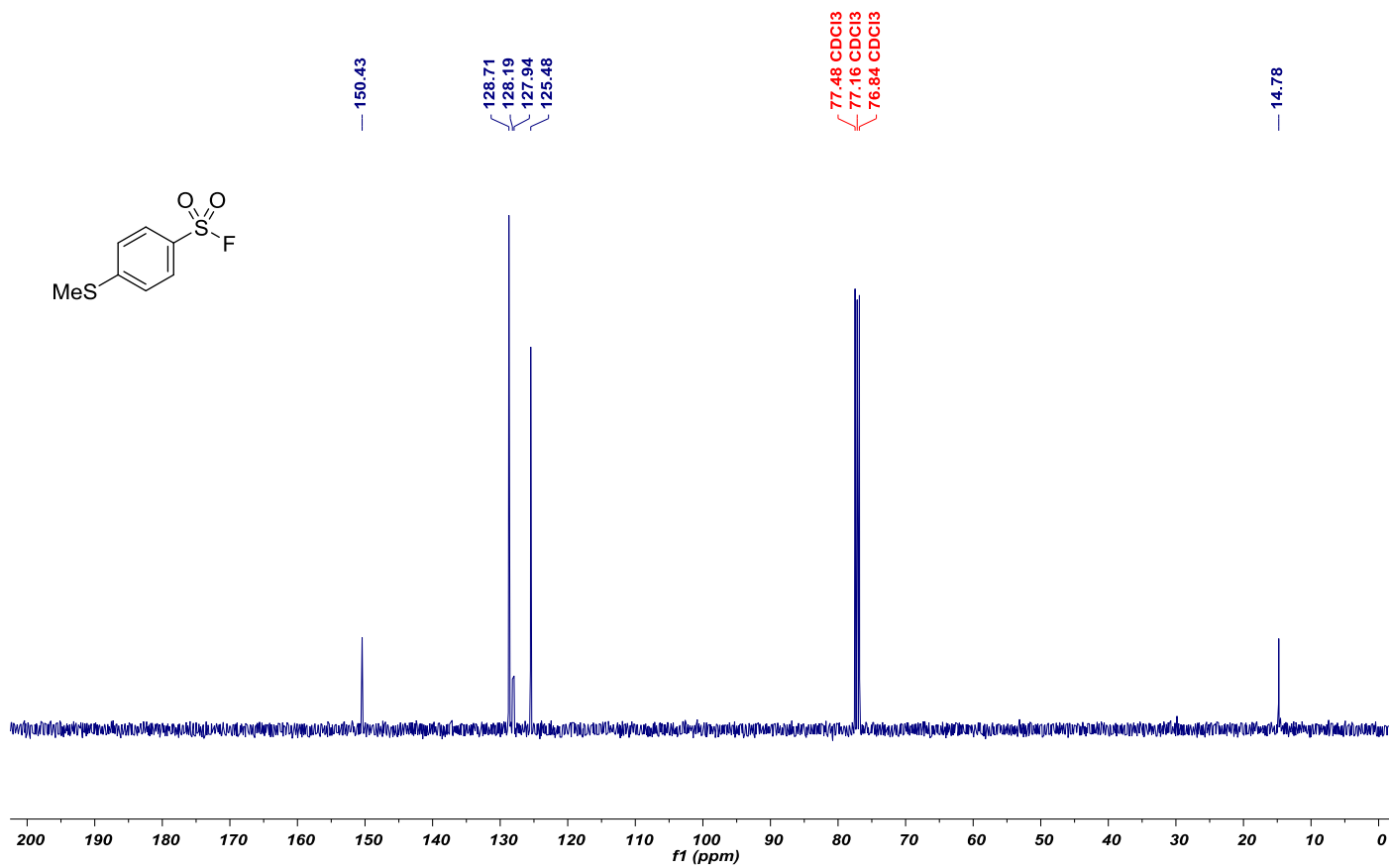
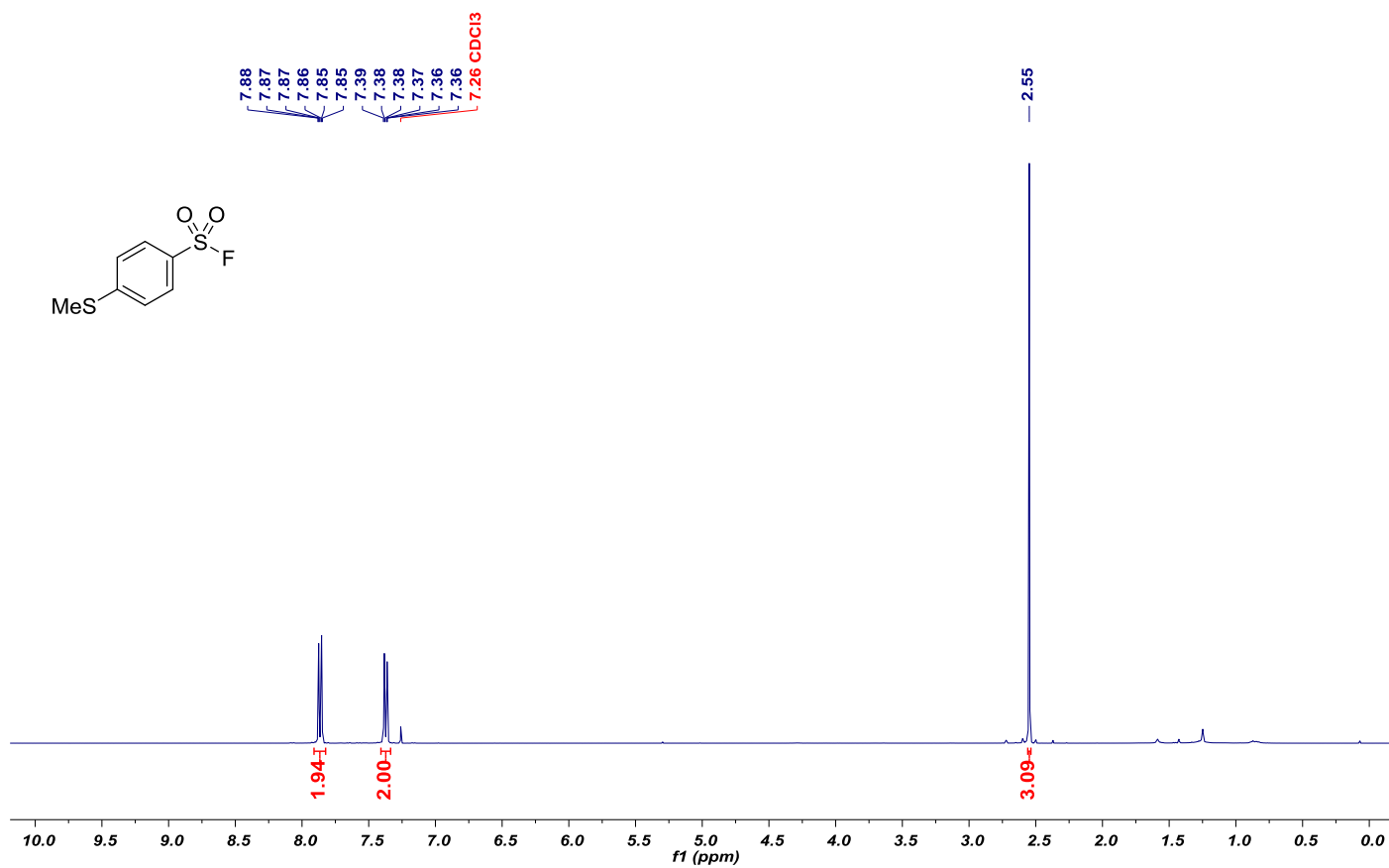
NMR spectrum of sulfonyl fluoride 5a



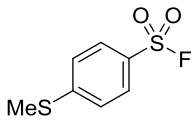
66.47



NMR spectrum of sulfonyl fluoride **5b**

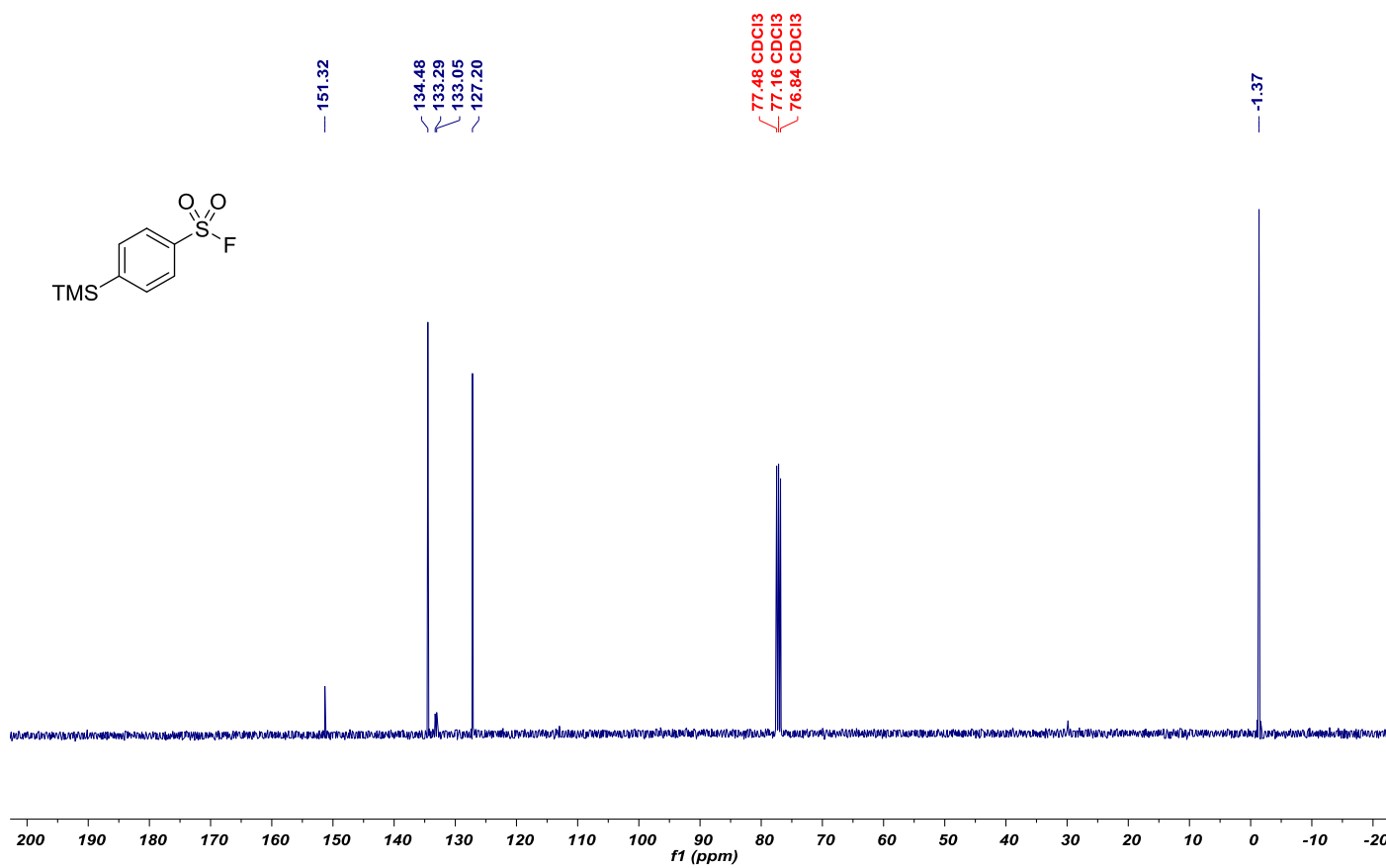
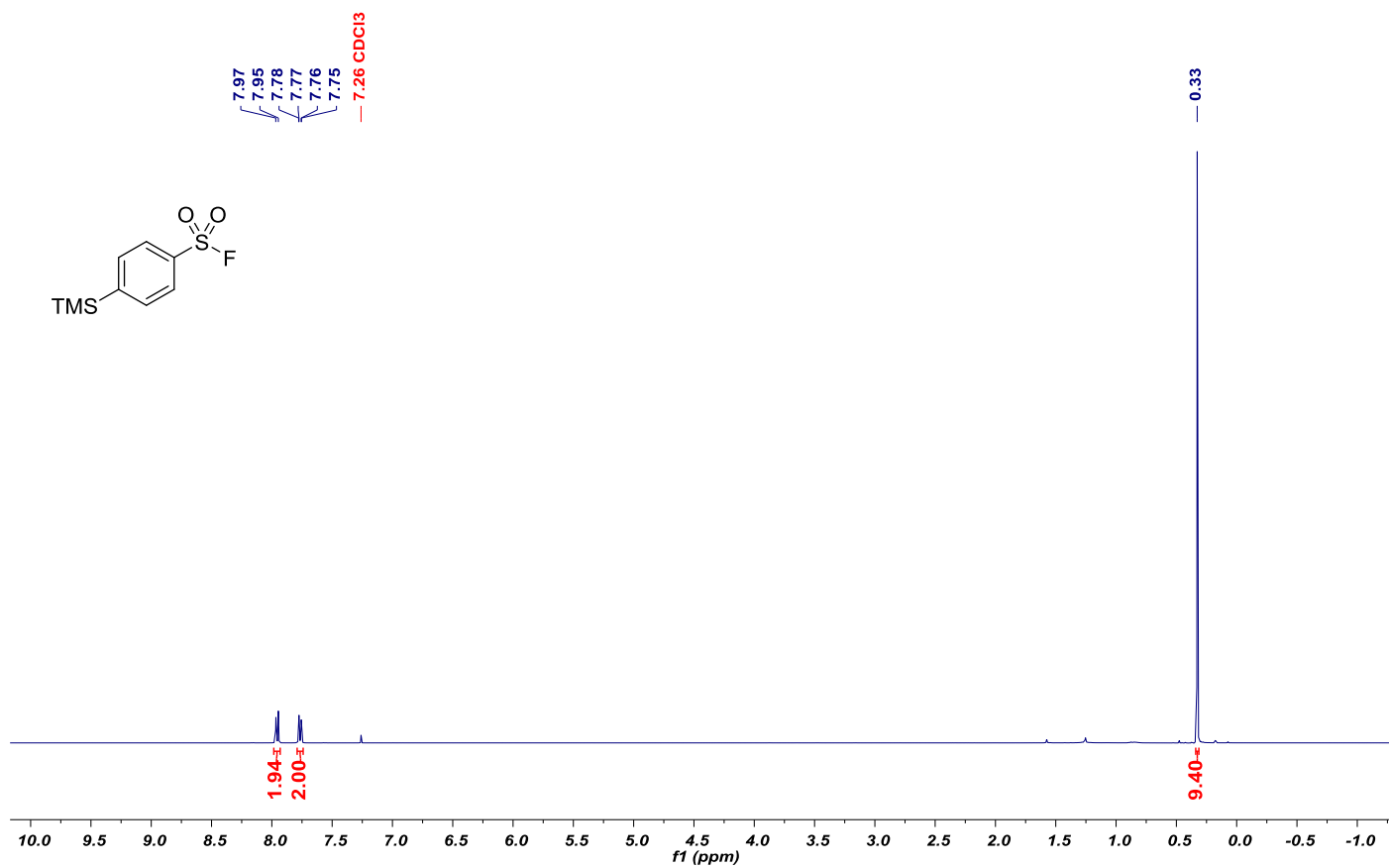


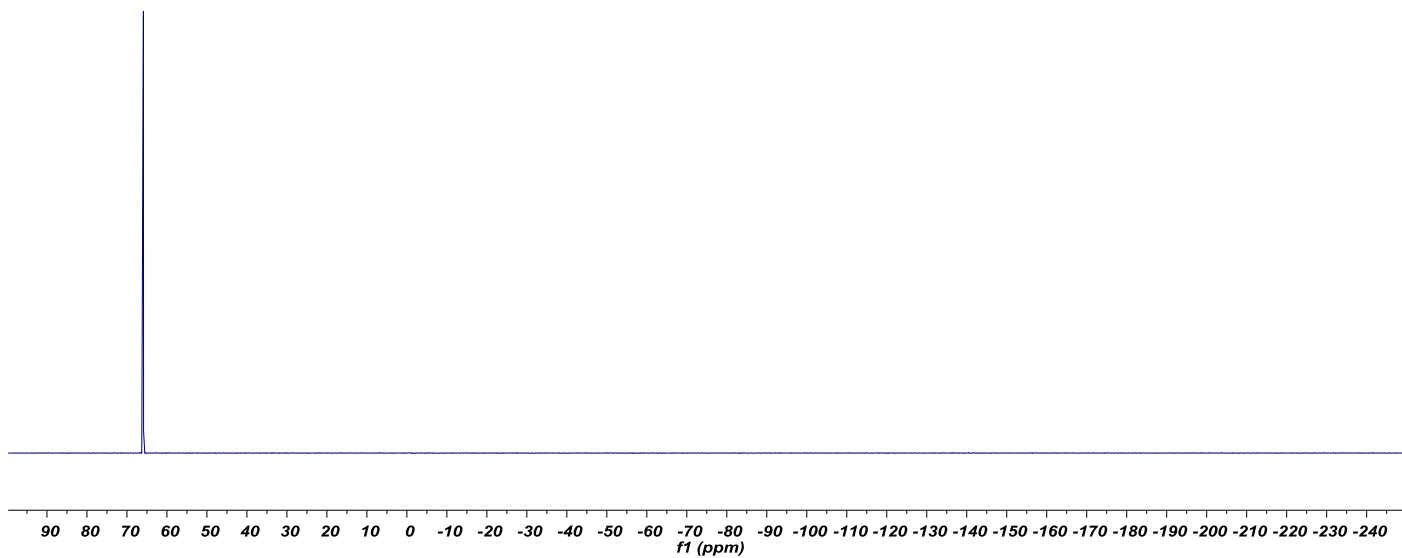
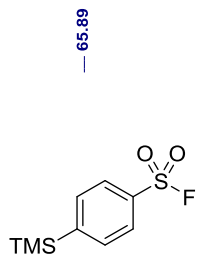
66.86



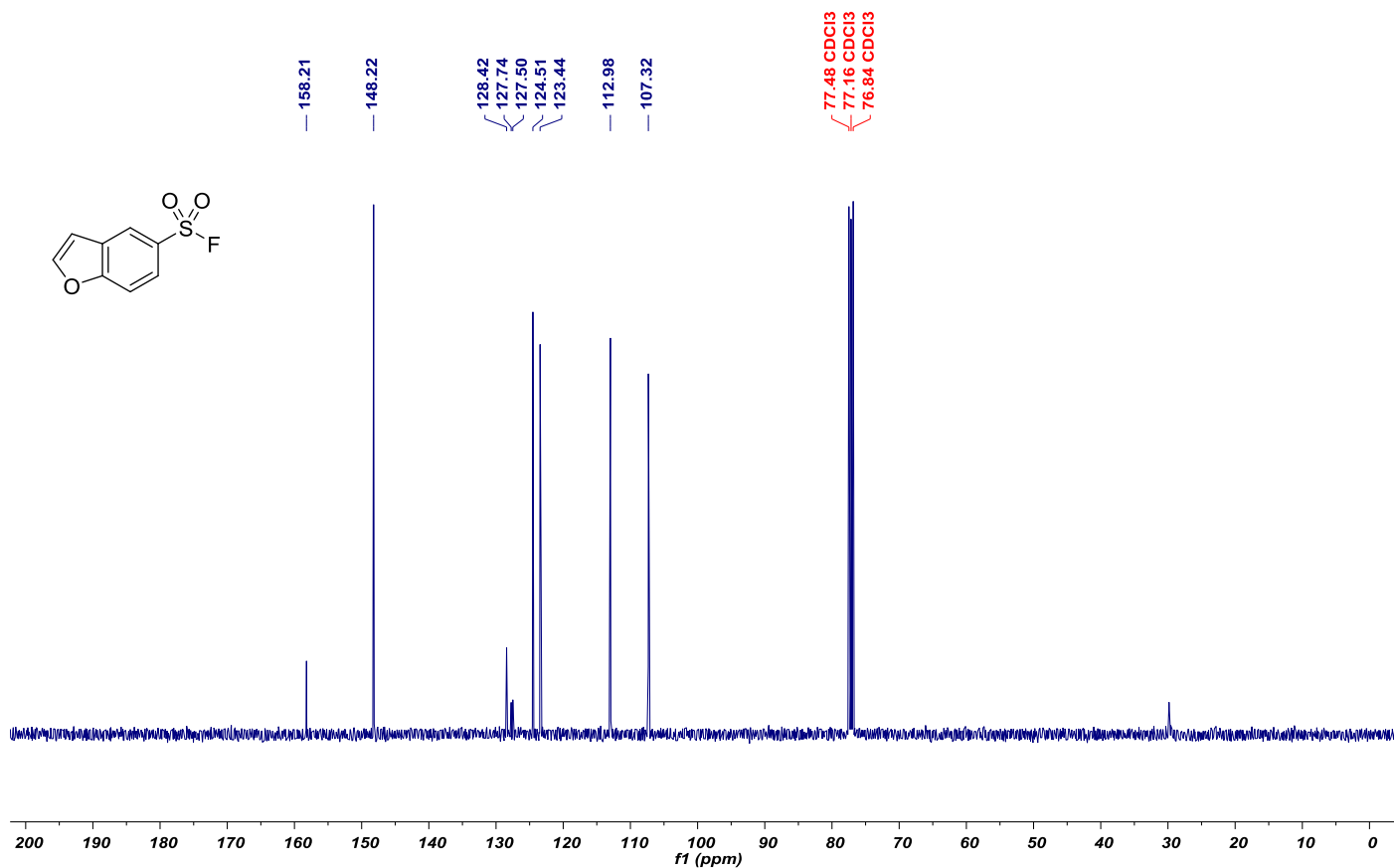
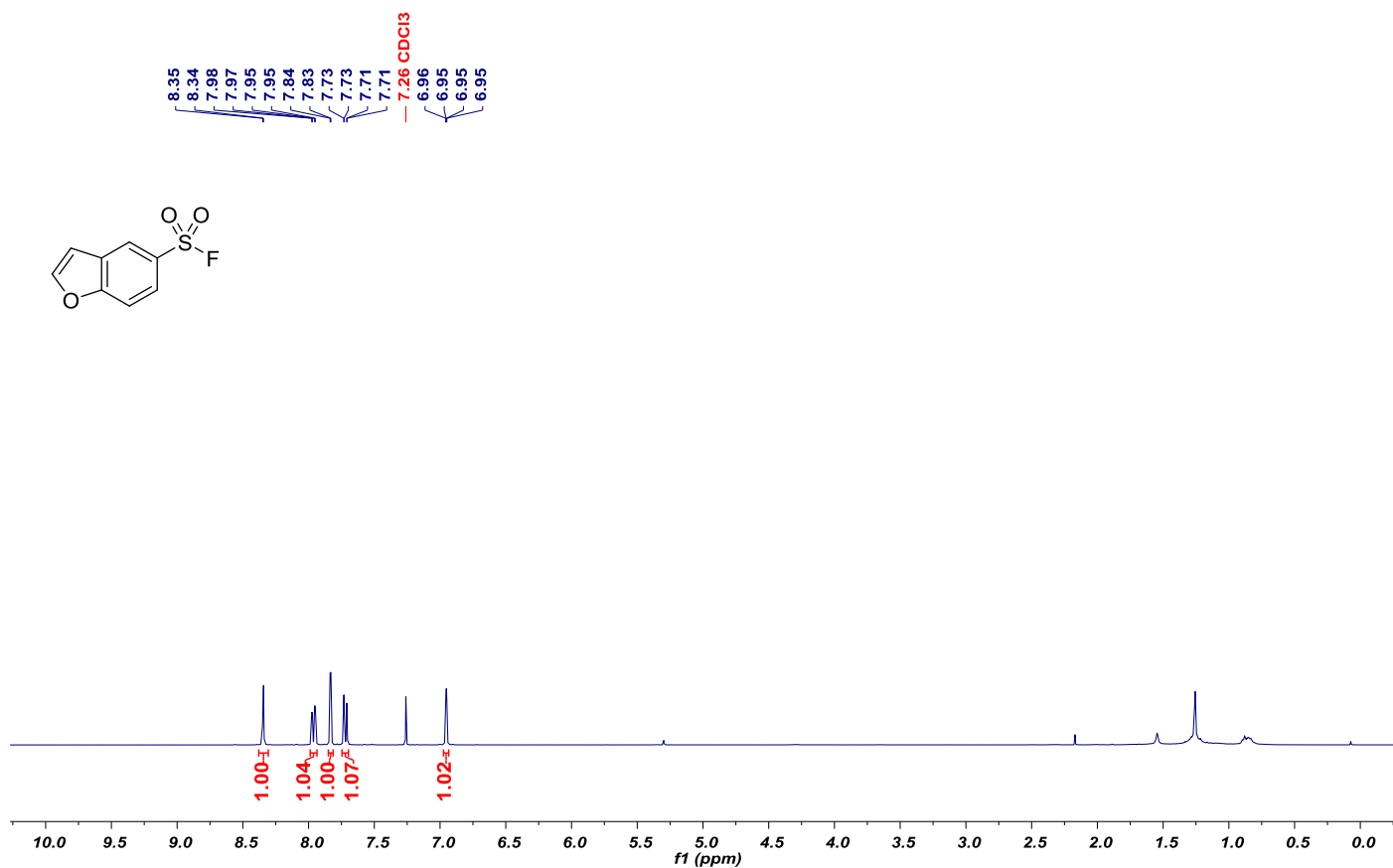
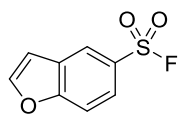
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

NMR spectrum of sulfonyl fluoride **5c**

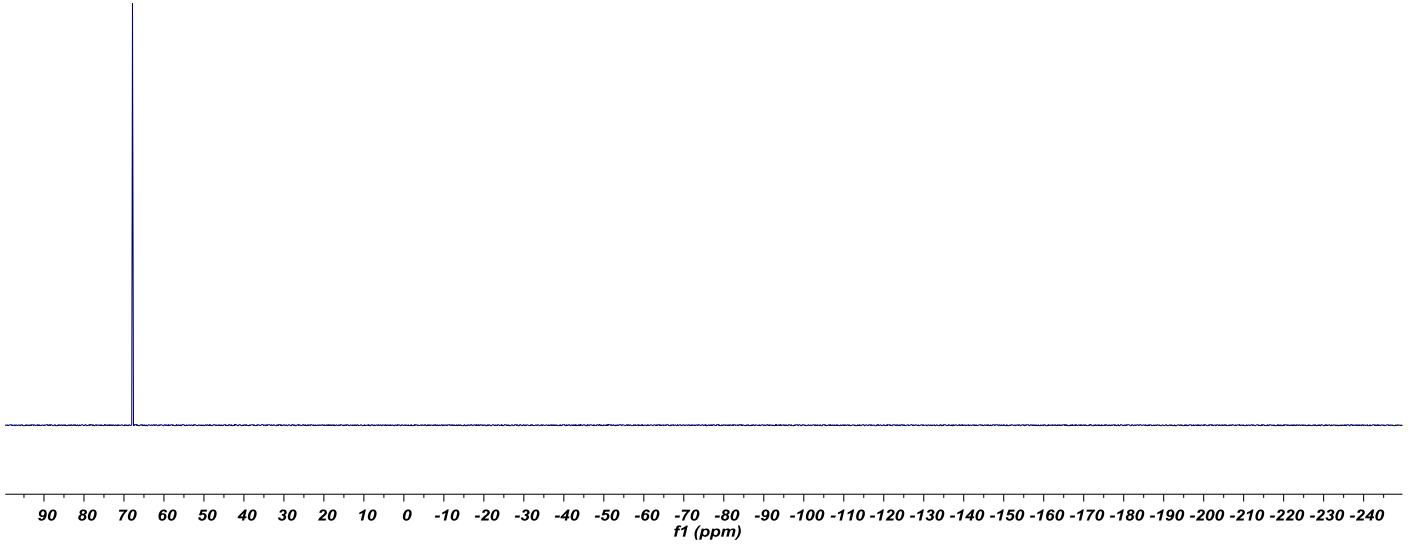
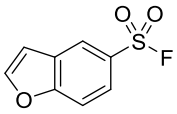




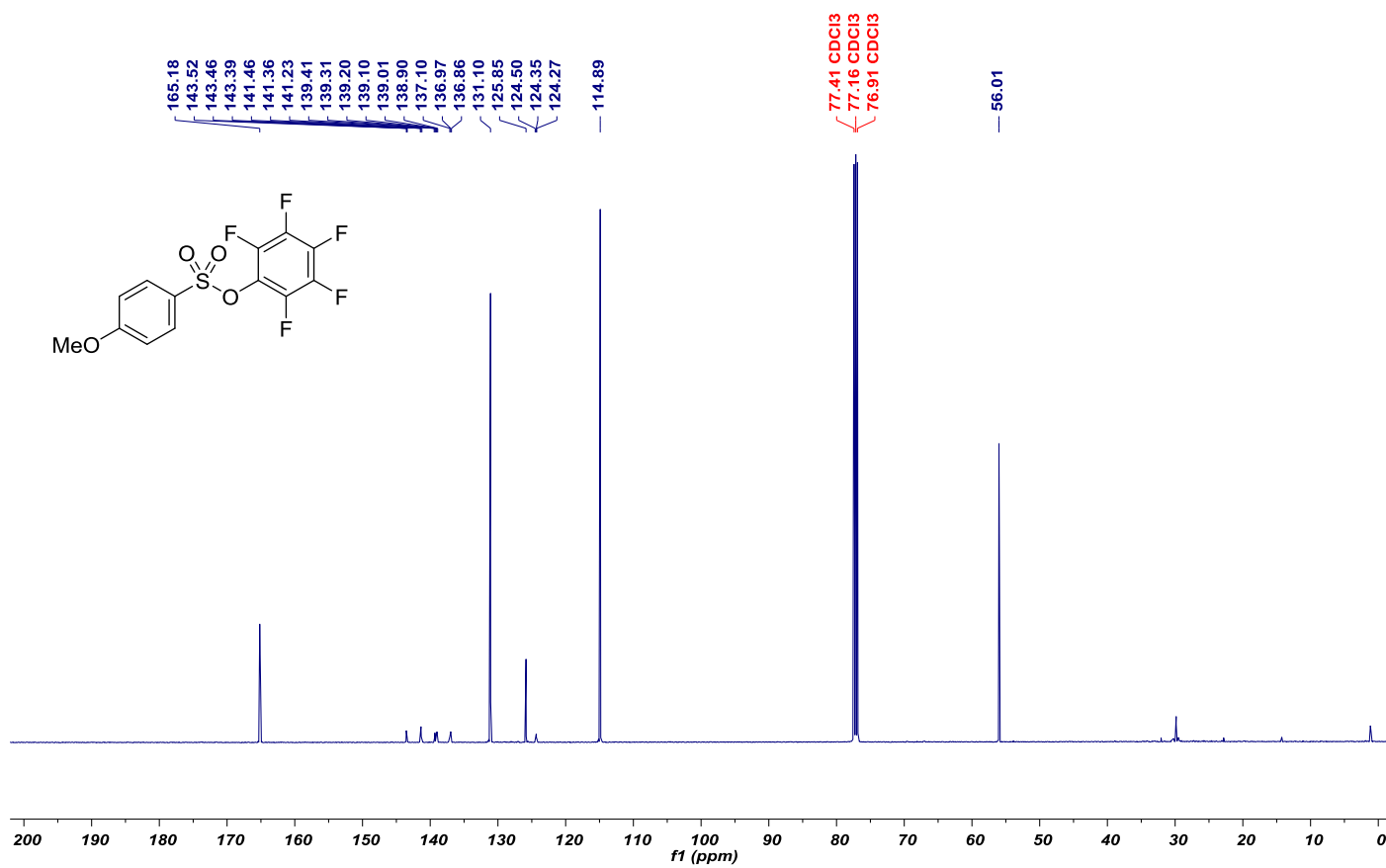
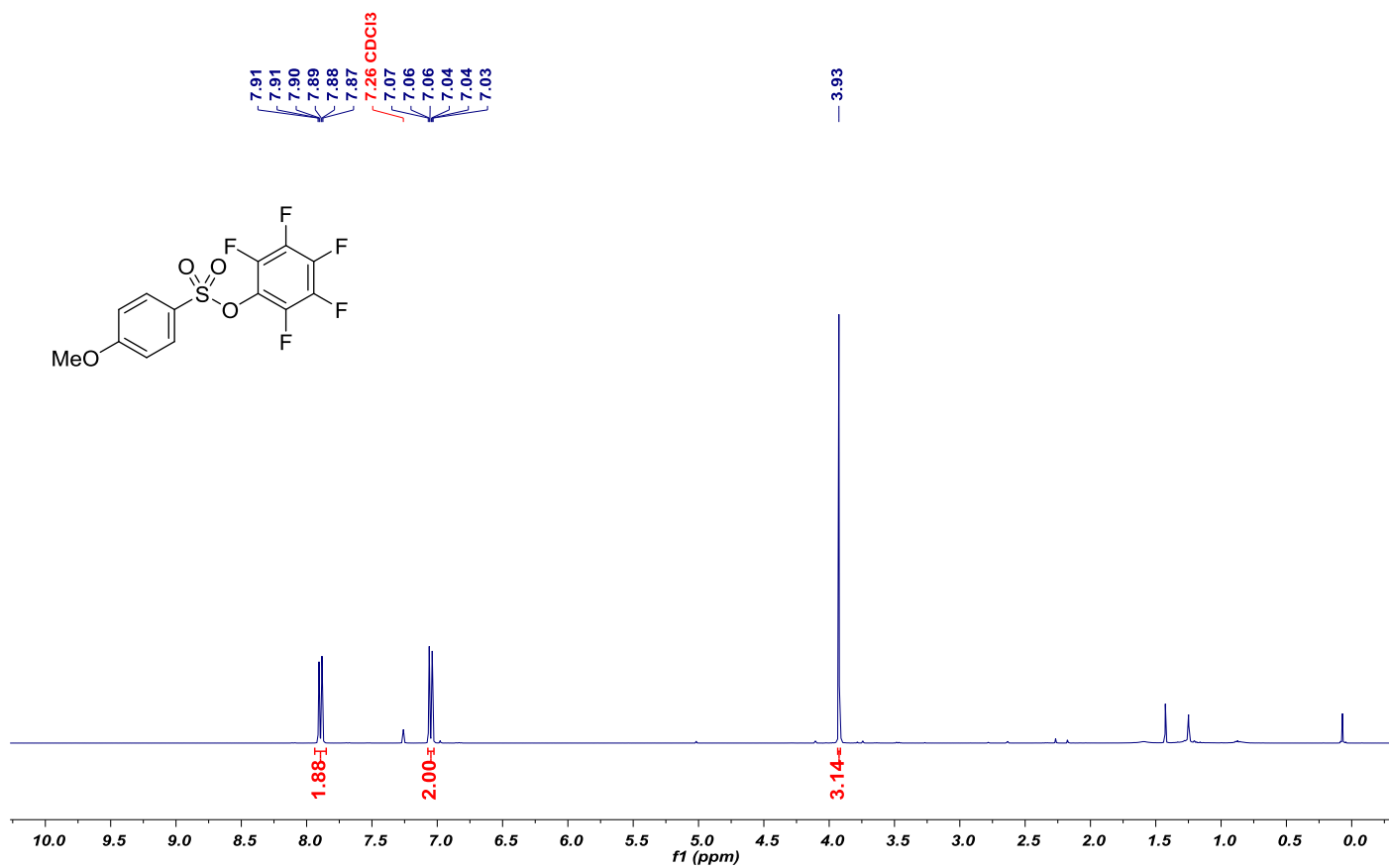
NMR spectrum of sulfonyl fluoride **5d**



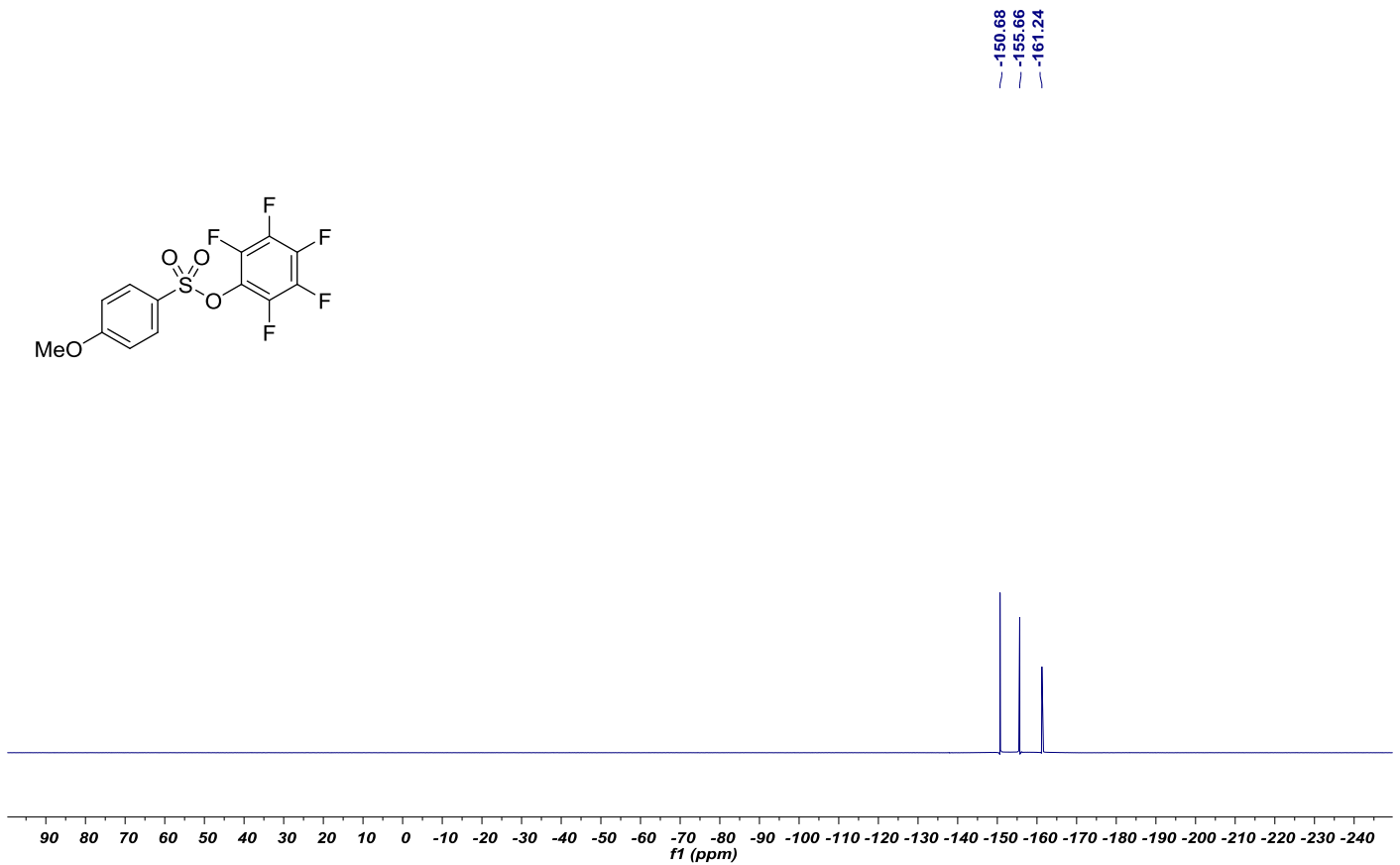
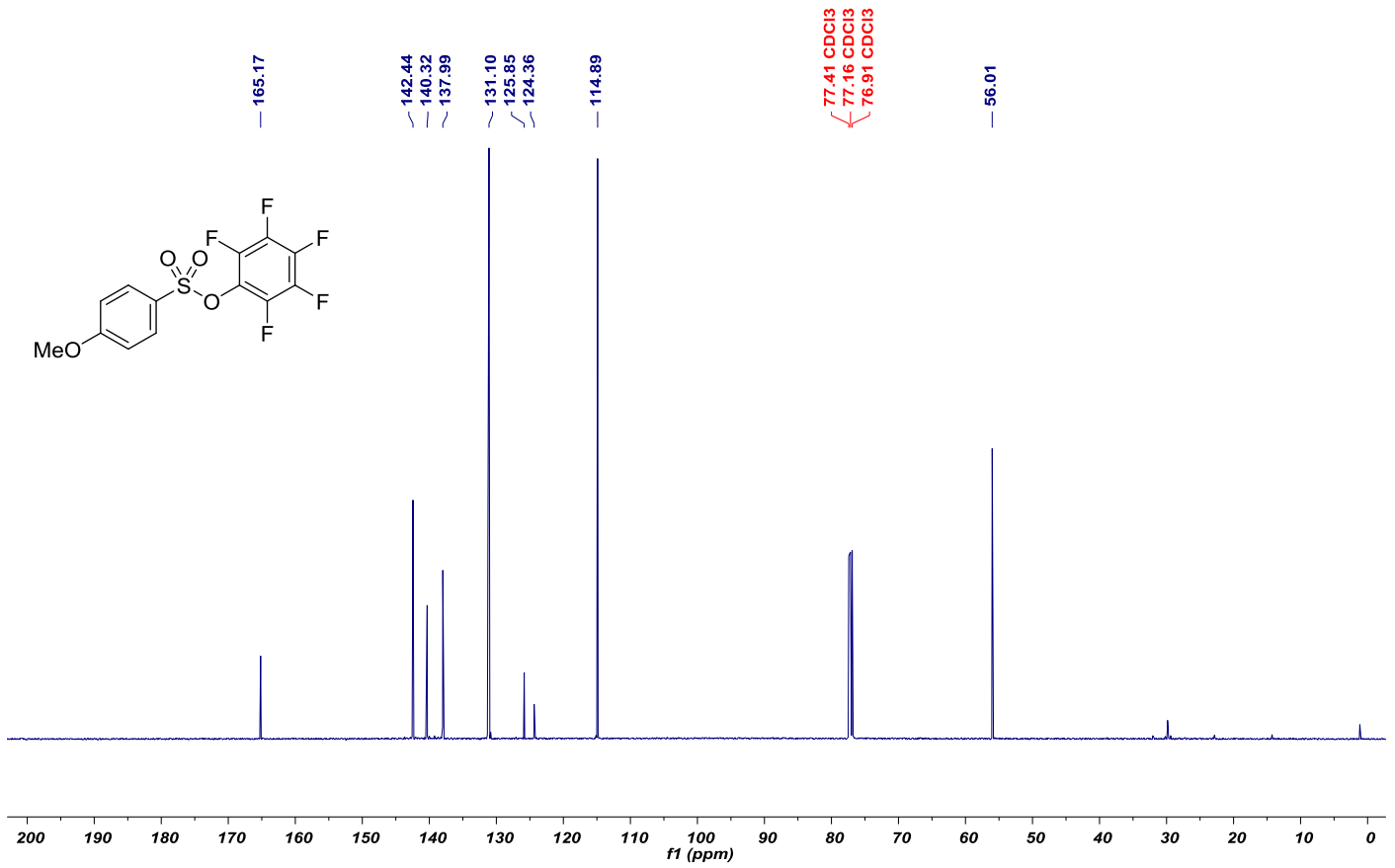
67.86



NMR spectrum of sulfonate ester **6**

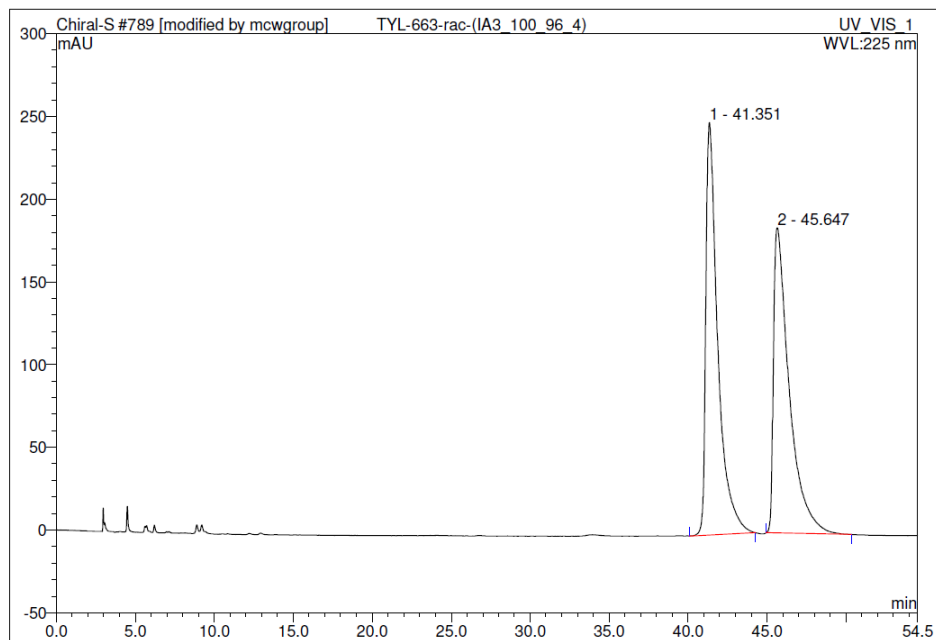
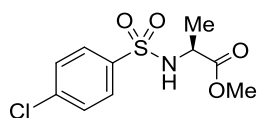


^{13}C NMR spectra using the ^1H and ^{19}F decoupling method.

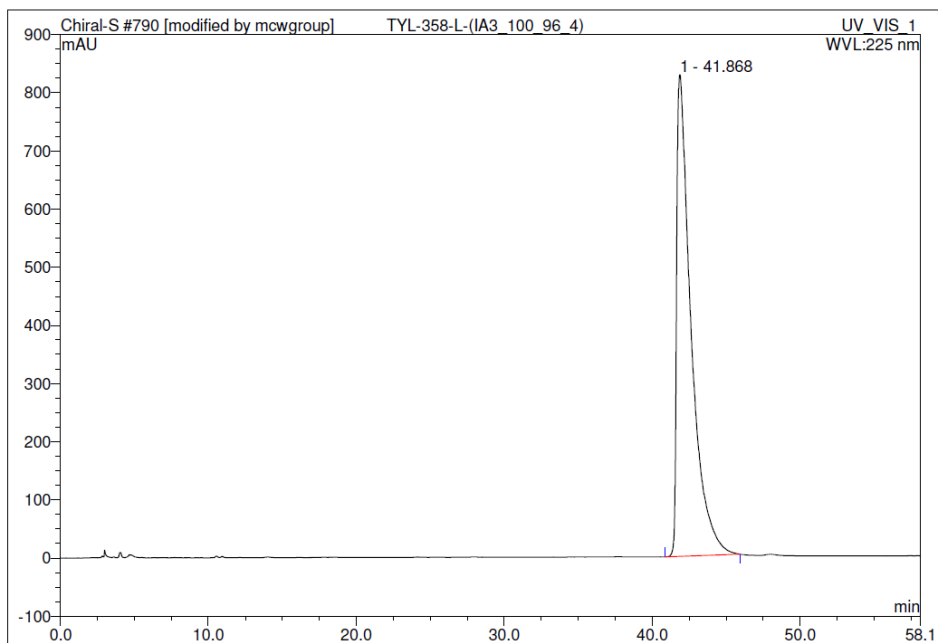


6. Chiral HPLC Traces

Methyl ((4-chlorophenyl)sulfonyl)-L-alaninate (4d)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	41.35	n.a.	249.325	218.568	50.71	n.a.	BMB*
2	45.65	n.a.	184.458	212.416	49.29	n.a.	BMB*
Total:			433.783	430.984	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	41.87	n.a.	827.696	932.640	100.00	n.a.	BMB*
Total:			827.696	932.640	100.00	0.000	