Supporting Information

Synthesis of Sulfones *via* Ru(II)-Catalyzed Sulfination of Boronic Acids

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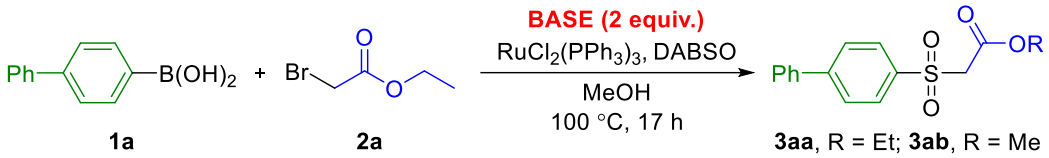
1. Reaction Optimization Data

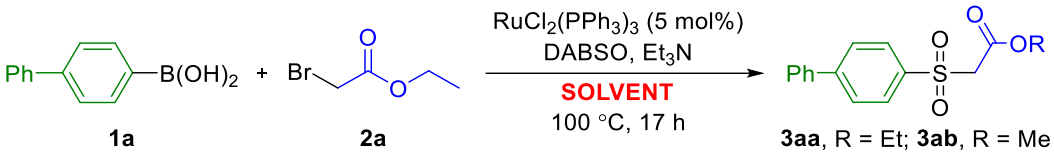
Table S1. Screening of the Base Additive[a]



entry	base	isolated yield **3aa**+**3ab**, %[b]
1	**Et_3N**	**76 (2)**
2	*i*-Pr_2NH	75 (3)
3	Cy_2NH	71 (2)
4	*t*-$BuNH_2$	65 (2)
5	DIPEA	64 (2)
6	$CyNH_2$	59 (4)
7	*N*-methyl morpholine	51 (<1)
8	DMAP	32 (3)
9	DABCO	7 (<1)
10	K_2CO_3	NR
11	K_3PO_4	NR
12	NaOAc	NR
13	Cs_2CO_3	NR
14	KF	NR

[a] Reaction conditions: **1a** (76 mg, 0.385 mmol, 1 equiv.), **2a** (3 equiv.), DABSO (1 equiv.), base (2 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) in MeOH (2 mL) at 100 °C for 17 h. [b] In parenthesis yield (%) of transesterification product **3ab** determined by ^1H NMR analysis. NR = no reaction

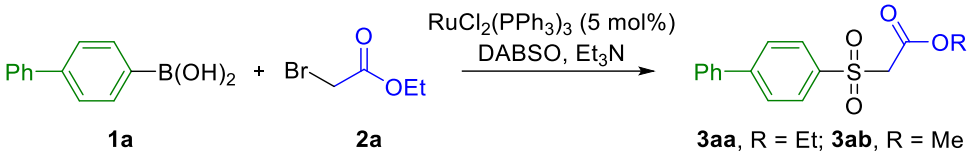
Table S2. Solvent Screening[a]



entry	solvent		isolated yield **3aa**+**3ab**, %[b]
1	**MeOH**	-	**76 (2)**
2	MeOH (N_2)	-	81 (3)
3	abs. MeOH (N_2)	-	77 (3)
4		1:1	79 (19)
5	MeOH/Tol	3:1	81 (7)
6		1:3	37 (5)
7	MeOH/DMF	1:1	70 (17)
8	MeOH/1,4-dioxane	1:1	62 (11)
9	MeOH/DCE	1:1	61 (4)
10	MeOH/THF	1:1	60 (11)
11	MeOH/acetone	1:1	49 (6)
12	MeOH/H_2O	3:1	15 (3)
13	MeOH/MeCN	1:1	9 (<1)
14	EtOH (96%)	-	23
15	abs. EtOH	-	27
16	THF	-	10
17	Tol	-	7
18	Tol/H_2O	1:1	8
19	Tol/DMF	1:1	5
20	1,4-dioxane	-	6
21	*i*-PrOH	-	<5

[a] Reaction conditions: **1a** (76 mg, 0.385 mmol, 1 equiv.), **2a** (3 equiv.), DABSO (1 equiv.), Et_3N (2 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) in solvent (2 mL) at 100 °C for 17 h. [b] In parenthesis yield (%) of transesterification product **3ab** determined by NMR analysis.

Table S3. Final Optimization of the Reaction Conditions[a]



1a **2a** **3aa**, R = Et; **3ab**, R = Me

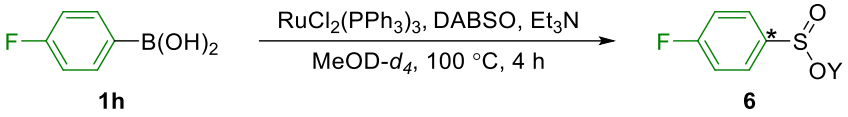
entry	solvent	variable	isolated yield **3aa**+**3ab**, %[b]
1	MeOH/Tol 1:1	-	79 (19)
2		10 mol% cat.	80 (18)
3		1 mol% cat.	54 (14)
4		at 65 °C	13 (-)
5	MeOH	-	76 (2)
6		2 equiv. **2a**	39 (2)
7		3 equiv. Et_3N	71 (15)
8		30 mol% AgOTf	67 (<1)
9		30 mol% TBAB	73 (3)
10		**8 h**	**69 (2)**
11		at 80 °C	66 (<1)
12[c]		0.6 equiv. DABSO	**3ab**, 53
13[c]		DMAP·SO_2	**3ab**, 51

[a] Initial reaction conditions: **1a** (0.385 mmol, 1 equiv.), **2a** (3 equiv.), DABSO (1 equiv.), Et_3N (2 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) in a solvent (2 mL) at 100 °C for 17 h. [b] In parenthesis yield (%) of transesterification product **3ab** determined by NMR analysis. [c] Methyl bromoacetate (**2b**) used as an electrophile.

2. Mechanistic Studies

A. Detection of sulfinate intermediate 6 (Figure S1 and Figure S2)

Formation of sulfinate intermediate **6** was proved by NMR spectroscopy, particularly, by ^{13}C NMR experiment (Figure S1). Spectra of reaction mixtures were compared with the standards of boronic acid **1h**, sulfinate **6** (Y = Na) and PPh_3 (free and coordinated). The standard reaction was performed in MeOD-d_4 and analyzed without additional treatment. When the experiment was performed in the absence of Et_3N, the reaction mixture was turbid. Therefore, it was filtered through a celite layer prior to NMR analysis.



1h **6**

Sample preparation. 4-Fluorophenylboronic acid (**1h**, 28 mg, 0.2 mmol, 1 equiv.), DABSO (1 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) were placed into a glass pressure tube (5 mL) equipped with a magnetic stirring bar. Then MeOD-d_4 (1 mL) was added followed by Et_3N (2 equiv.). The resulting mixture was stirred at 100 °C (oil bath) for 4 h. After cooling to room temperature, the reaction mixture was analyzed using NMR spectroscopy.

Conclusions: *In the presence of Et_3N, full consumption of boronic acid **1h** and formation of sulfinate salt **6** were observed (Figure S1, **III**). Without the amine only partial conversion of boronic acid **1h** was detected (Figure S1, **V**). Discrepancy of chemical shifts for the sulfur bonded carbon (*) in the sulfinate salt **6** may point to the different nature of counterion Y. Formation of corresponding mono- and dimethyl esters of aryl boronic acid under reaction conditions could lead to the changes in multiplicities detected in spectra **V** (Figure S1) for the residue of boronic acid **1h**.*

B. Detection of $B(OMe)_3$ (Figure S3 and Figure S4)

To provide complete proposal for the reaction mechanism, possible formation of $B(OMe)_3$ was investigated. Firstly, formation of $B(OMe)_3$ was detected with GC-FID by comparing chromatograms of reaction mixture and commercially available $B(OMe)_3$ sample in MeOH. Secondly, ^{11}B NMR spectrum of the reaction mixture confirmed full conversion of boronic acid into trimethyl borate.

Sample preparation. 4-Fluorophenylboronic acid (**1h**, 54 mg, 0.385 mmol, 1 equiv.), DABSO (1 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) were placed into a glass pressure tube (15 mL) equipped with a magnetic stirring bar. Then MeOH (2 mL) was added followed by Et_3N (2 equiv.) and methyl 2-bromoacetate (**2a**, 3 equiv.). The resulting mixture was stirred at 100 °C (oil bath) for 8 h. After cooling to room temperature, the reaction mixture was centrifuged and the clear supernatant was used for GC-FID analysis and ^{11}B NMR spectroscopic studies.

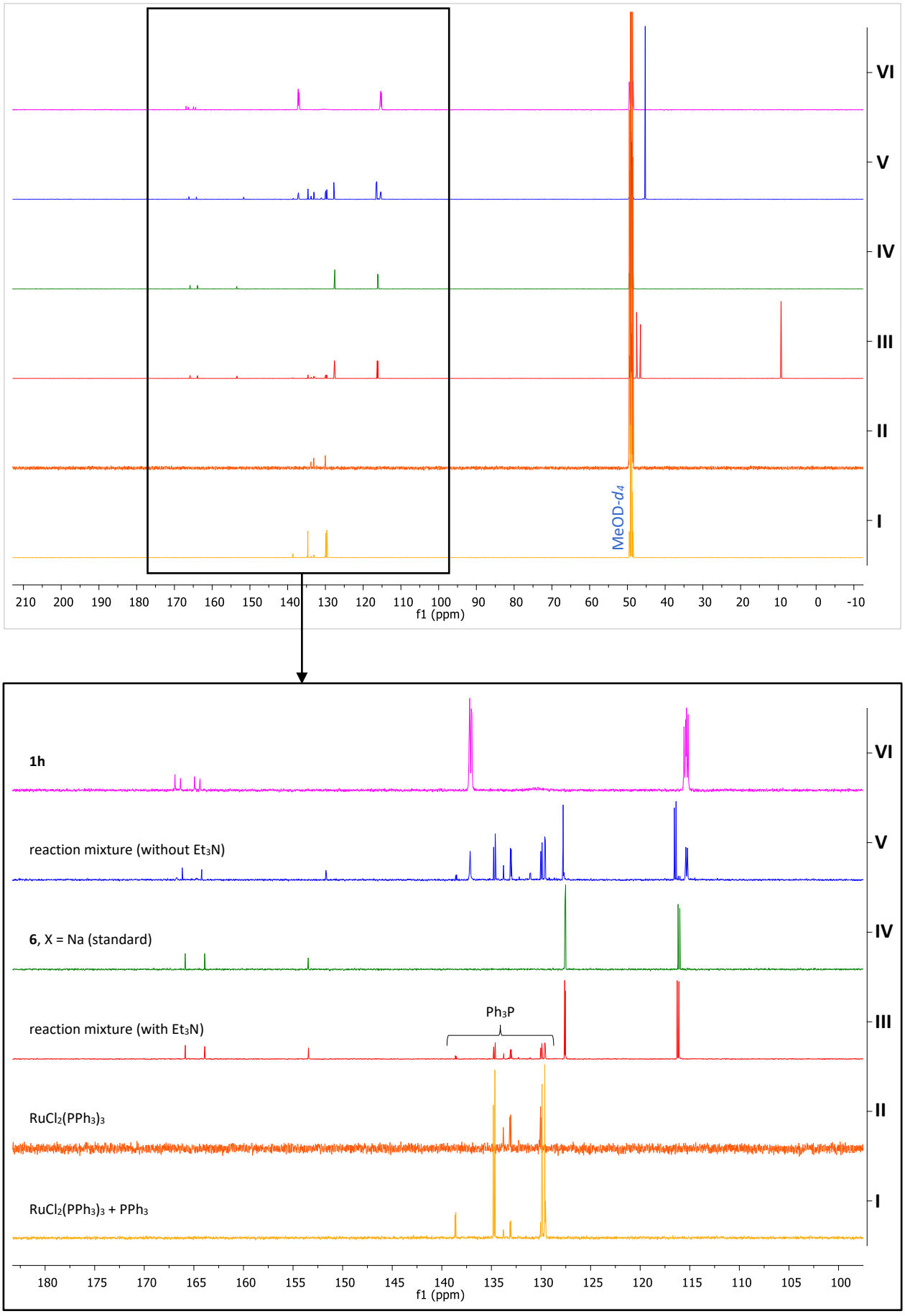


Figure S1. Detection of Sulfinate Intermediate **6**: $^{13}C\{^{1}H\}$ NMR (126 MHz, MeOD-d_4) spectra

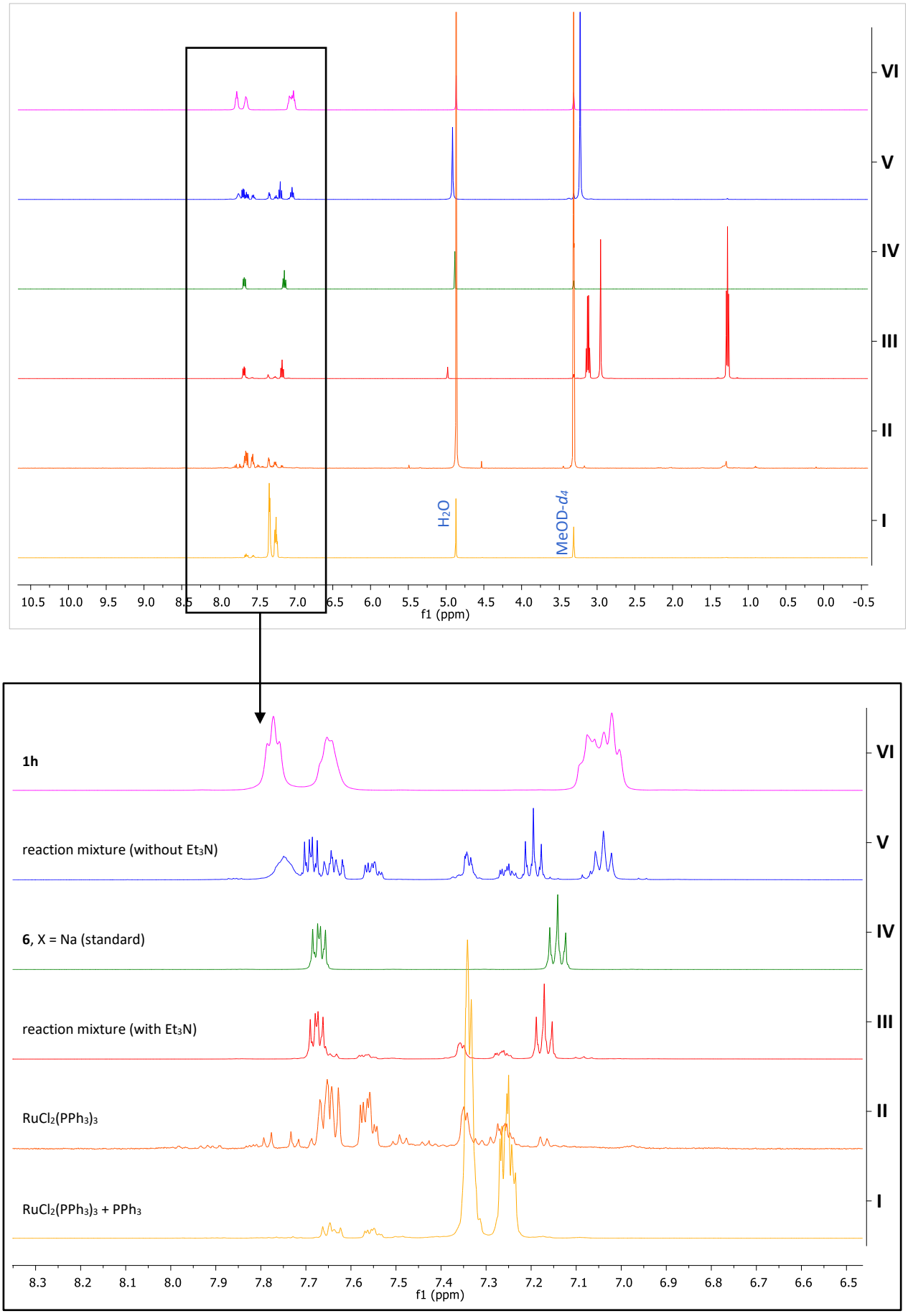


Figure S2. Detection of Sulfinate Intermediate **6**: ^{1}H NMR (500 MHz, MeOD-d_4) spectra

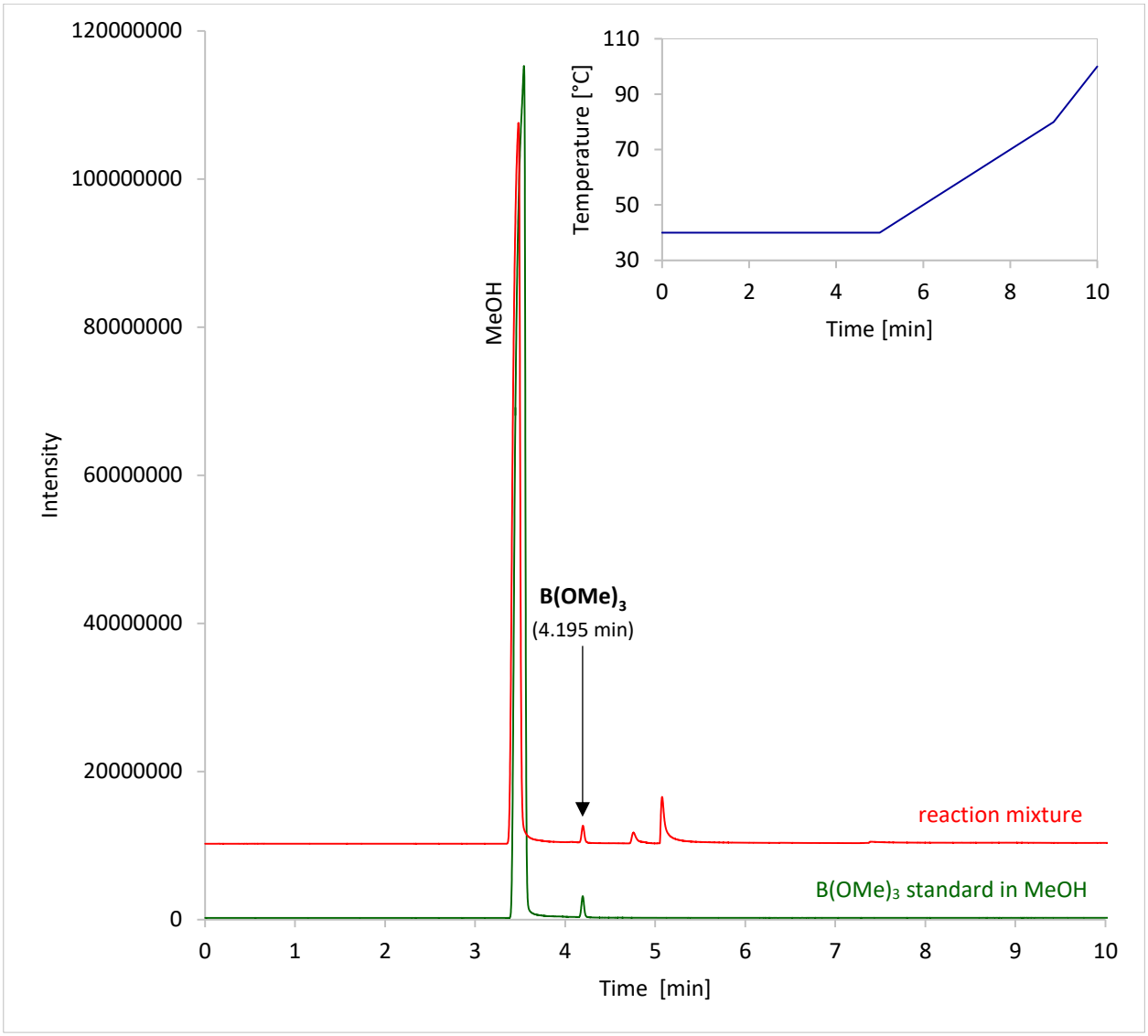


Figure S3. Detection of $B(OMe)_3$: GC-FID analysis

Table S4. Parameters for GC-FID Analysis (Figure S3)

Column	*Agilent Technologies J&W DB-1ms* capillary column, 30 m × 0.32 mmID, 0.25 µm
Column temperature	40 °C (hold for 5 min) to 80 °C @ 10 °C/min to 100 °C @ 20 °C/min (hold for 1 min at 100 °C)
Injector/Detector (FID)	250 °C/ 250 °C
Carrier gas	He @ 2 ml/min, constant flow
Injection regime	Splitless, no solvent delay
Injection volume	2 µL

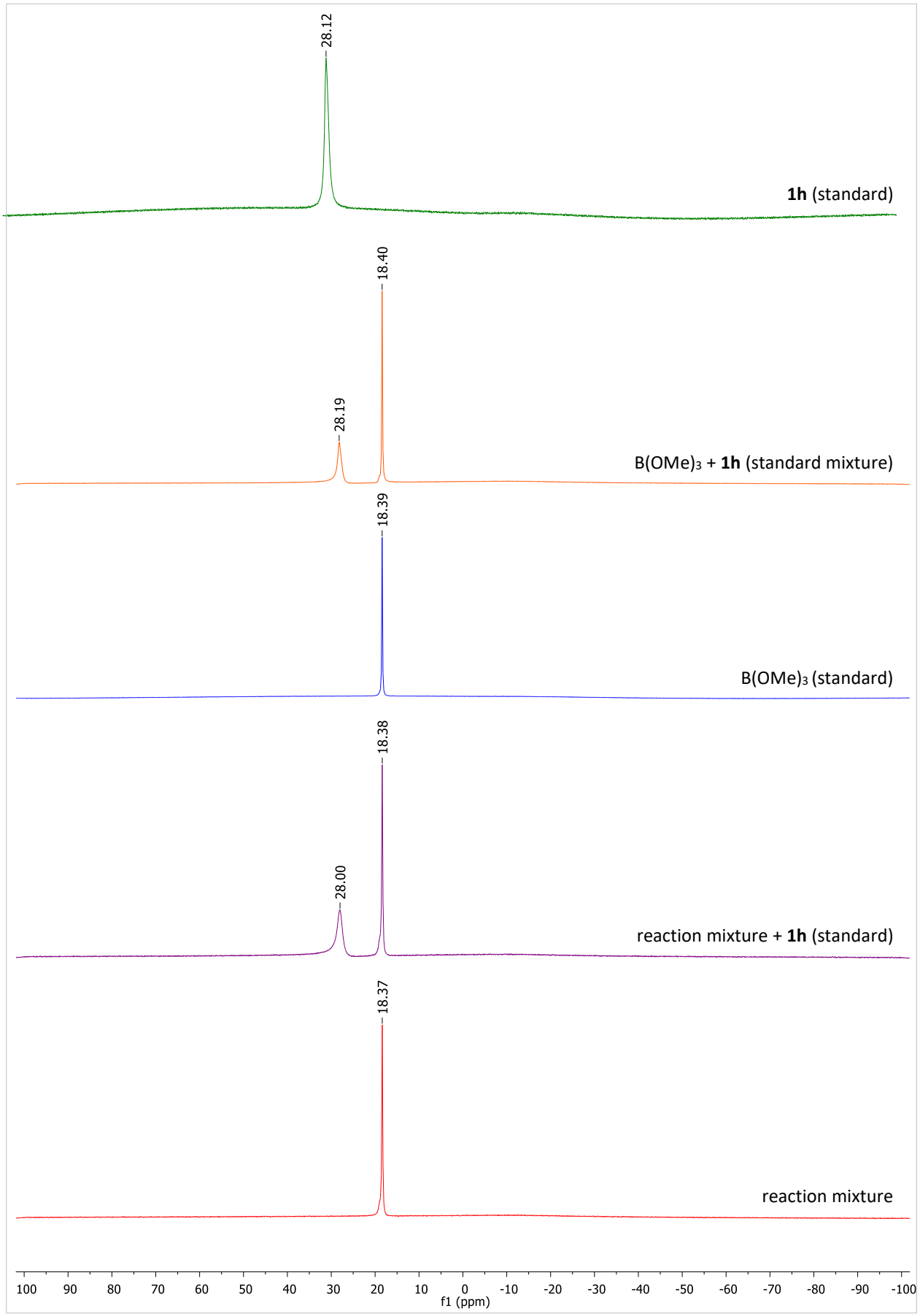
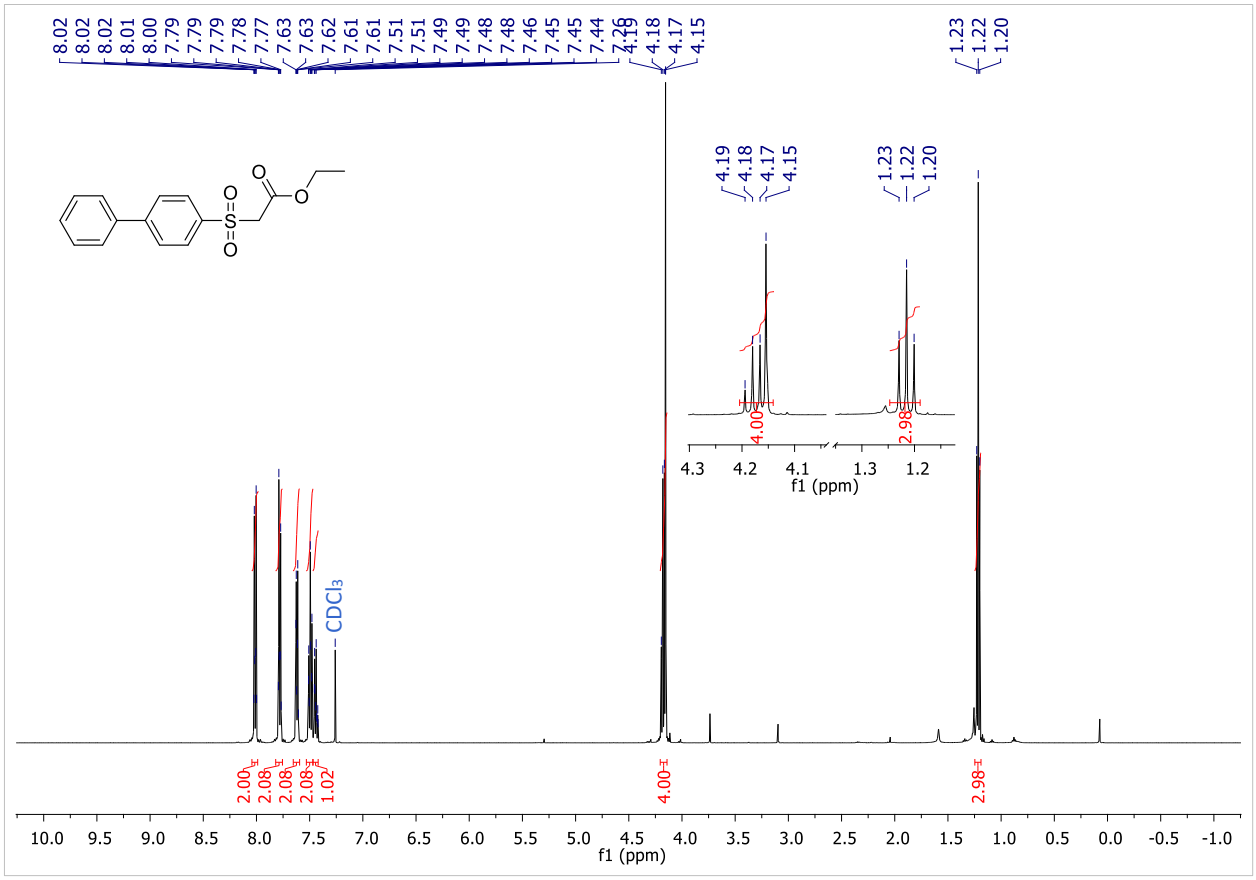


Figure S4. Detection of $B(OMe)_3$: ^{11}B NMR (160 MHz, MeOH + 10 vol% DMSO-d_6) spectra

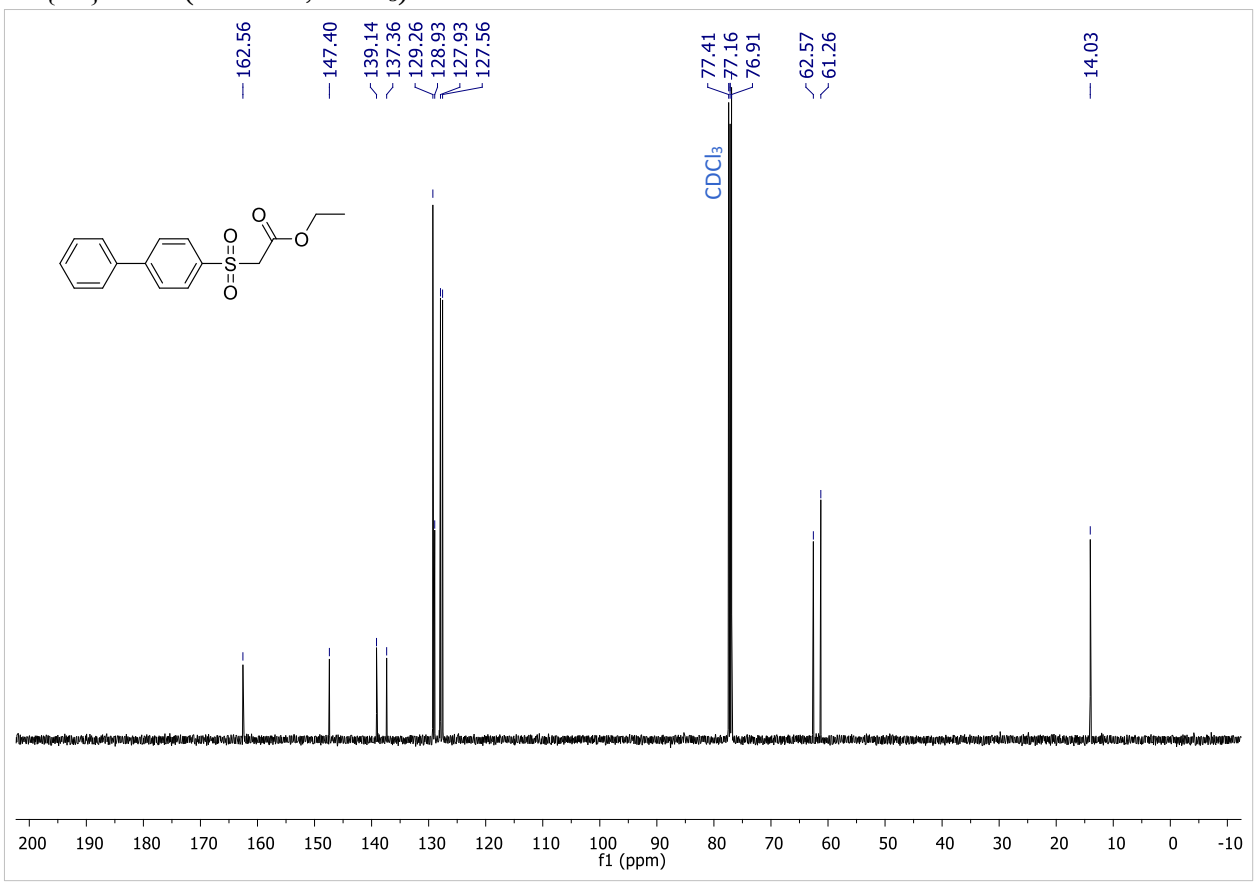
3. Copies of NMR Spectra

3aa

^{1}H NMR (500 MHz, $CDCl_3$)

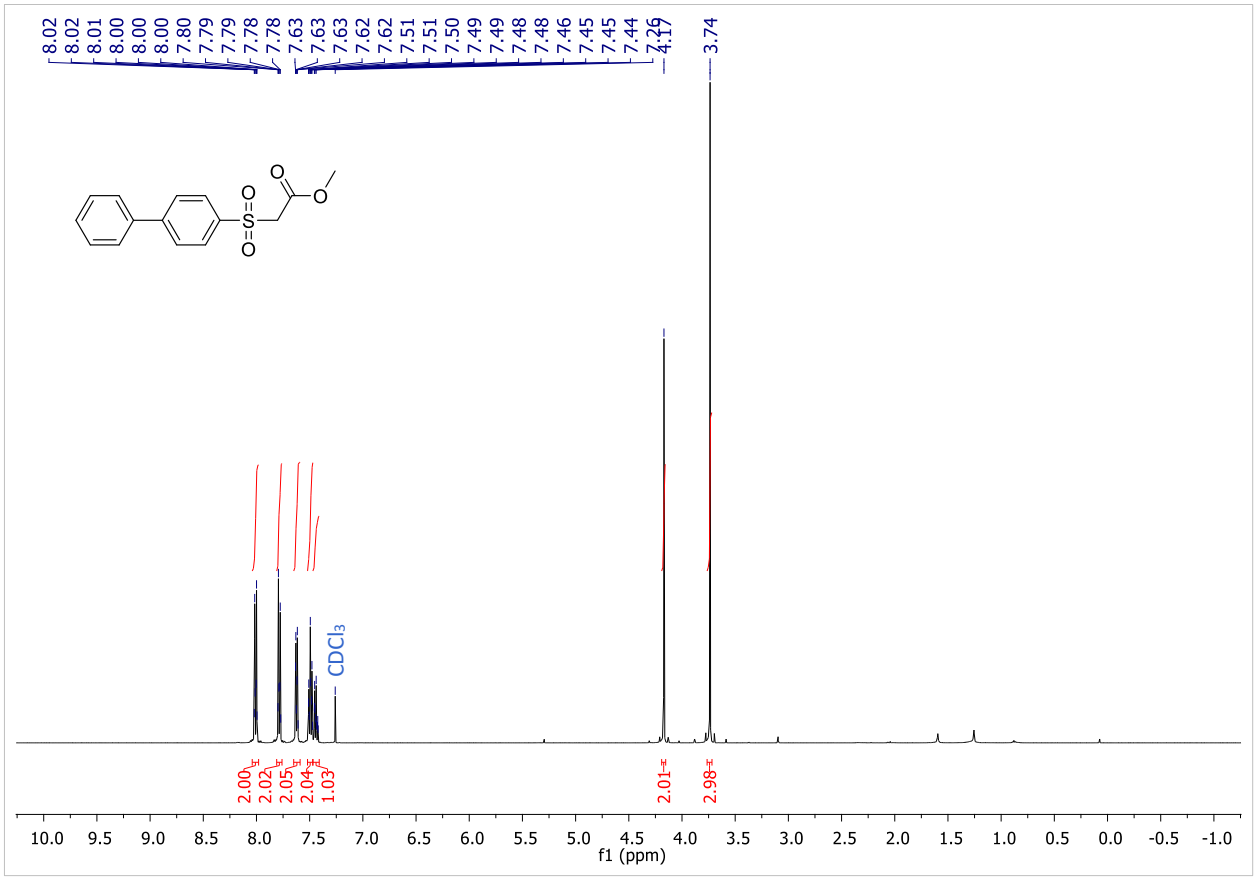


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

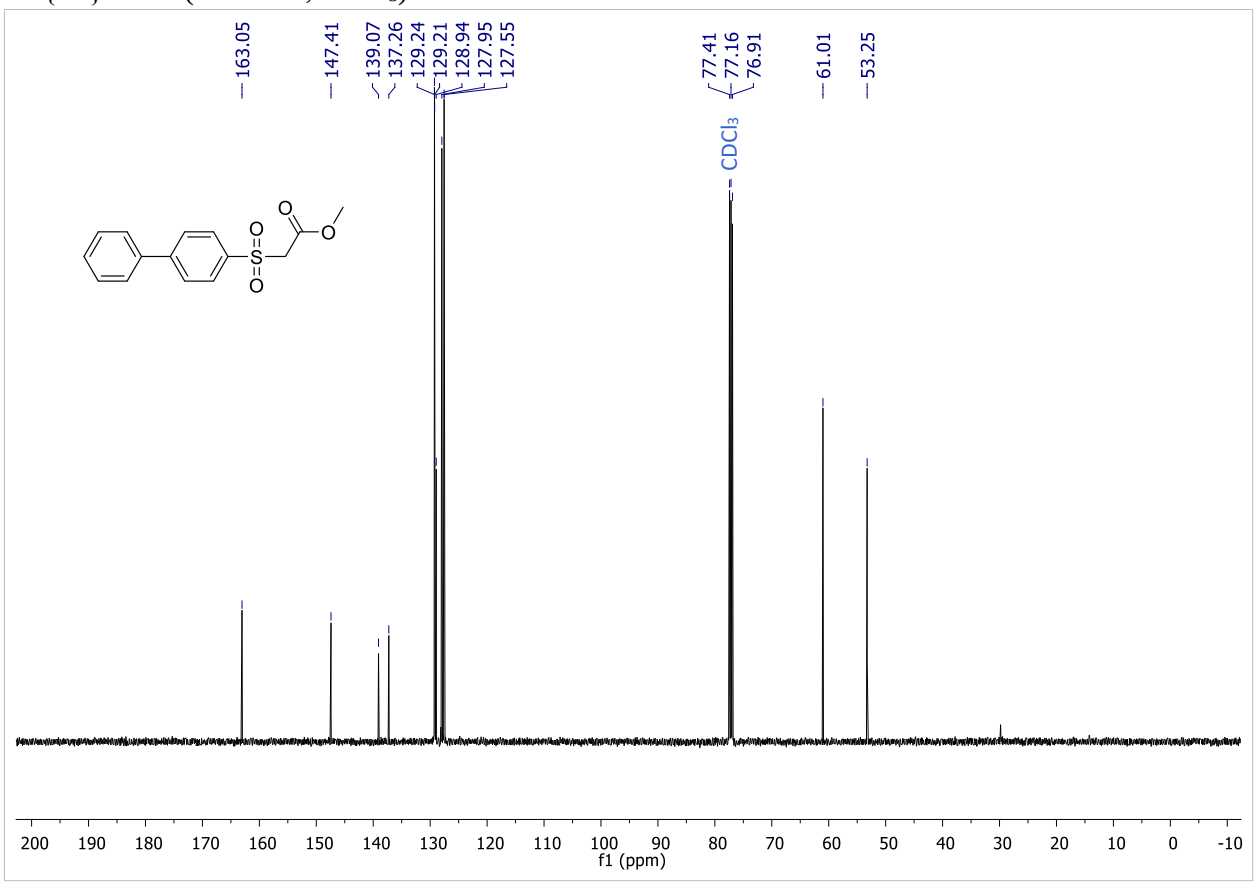


3ab

^{1}H NMR (500 MHz, $CDCl_3$)

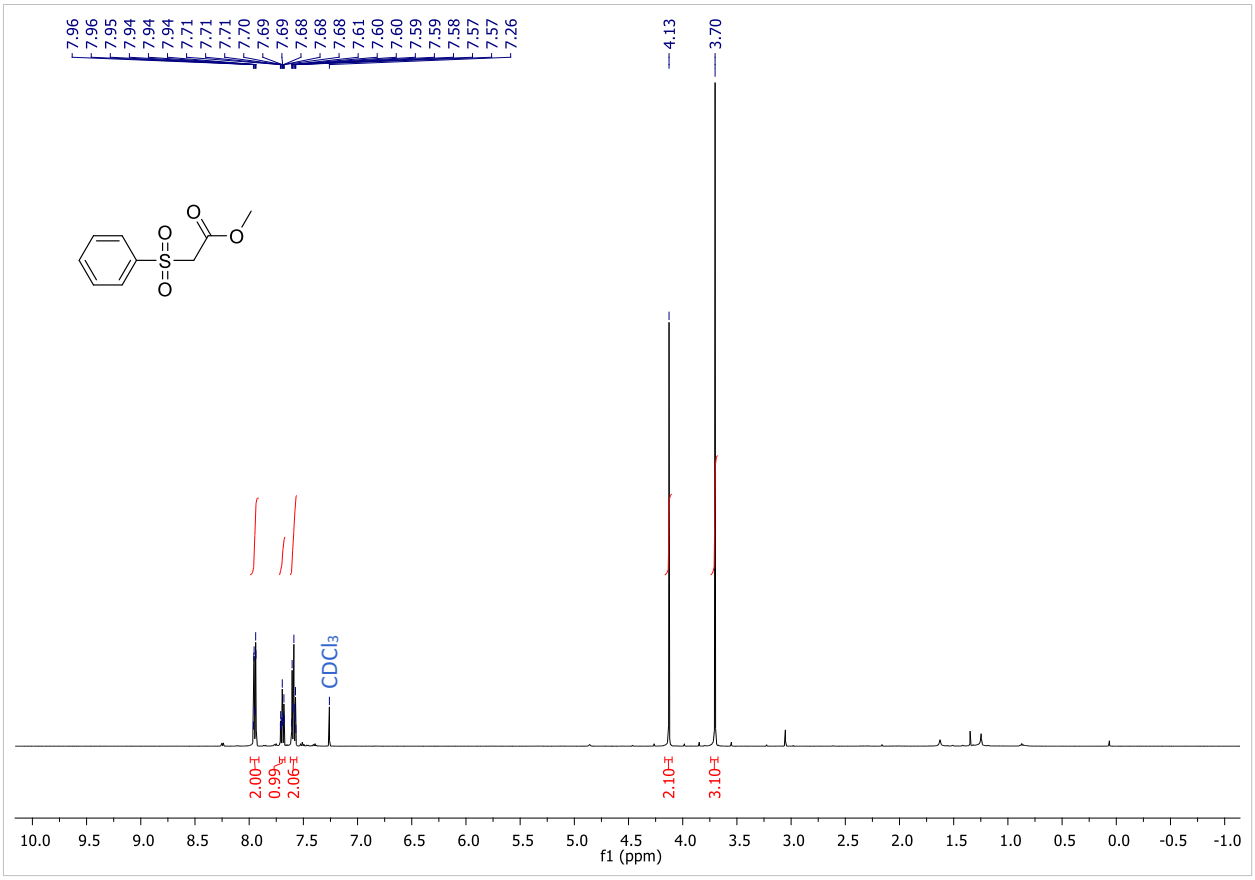


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

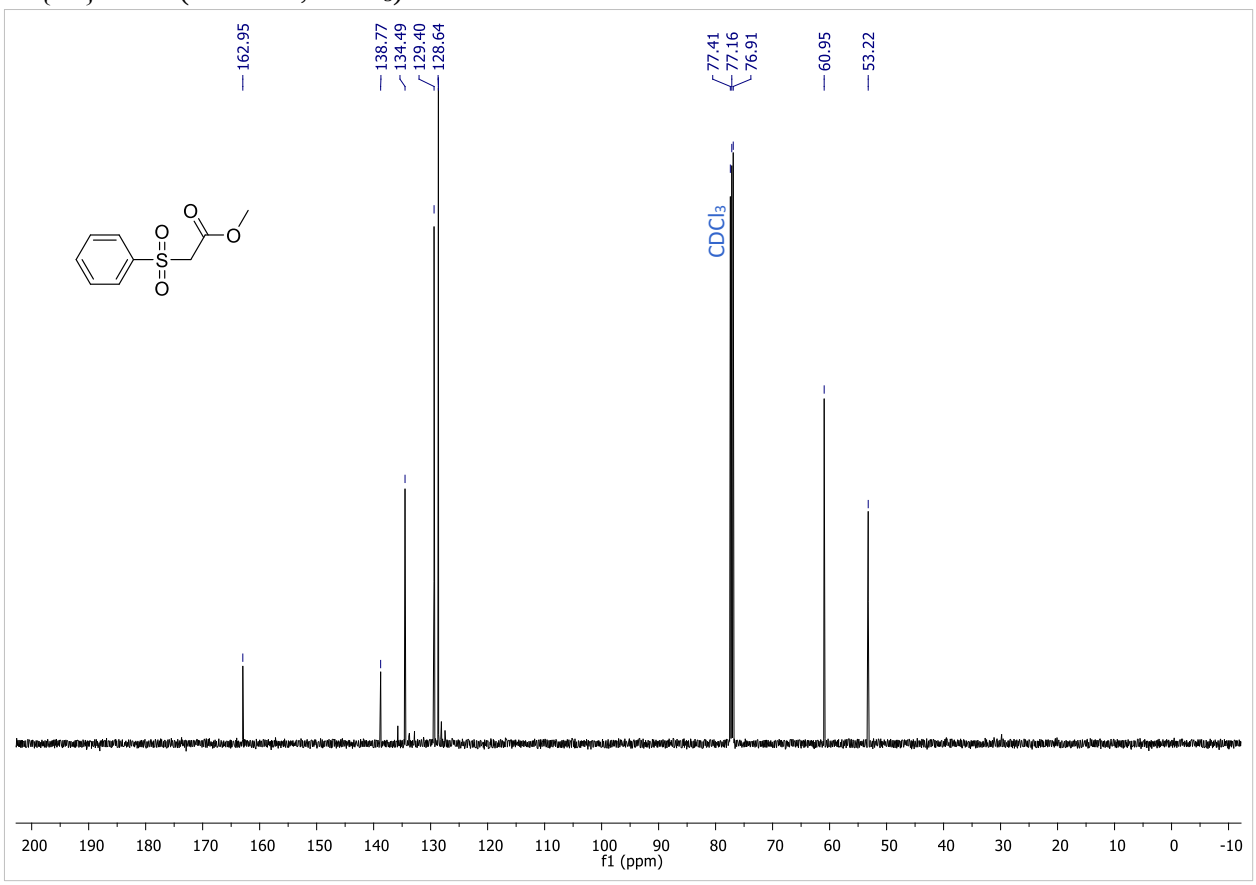


3bb

^{1}H NMR (500 MHz, $CDCl_3$)

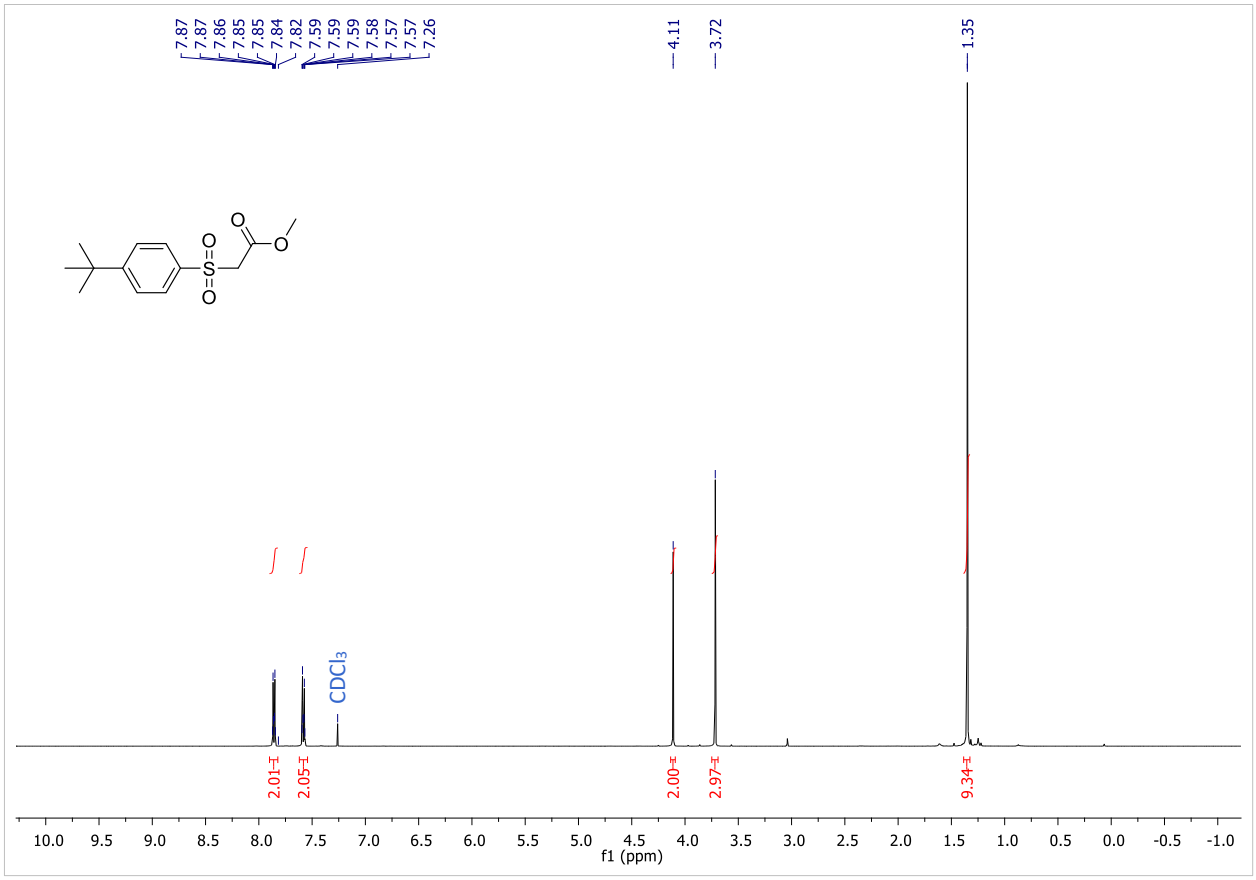


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

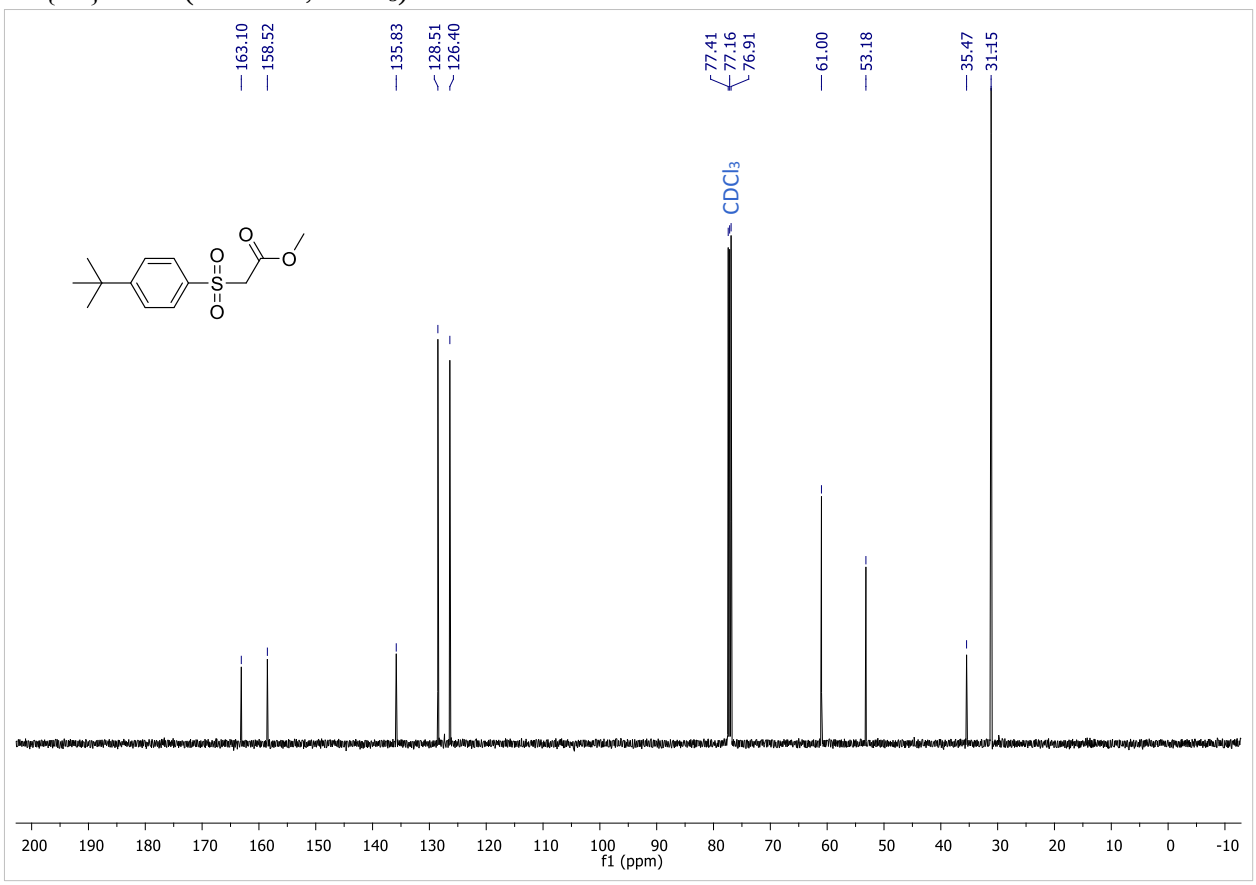


3cb

^{1}H NMR (500 MHz, $CDCl_3$)

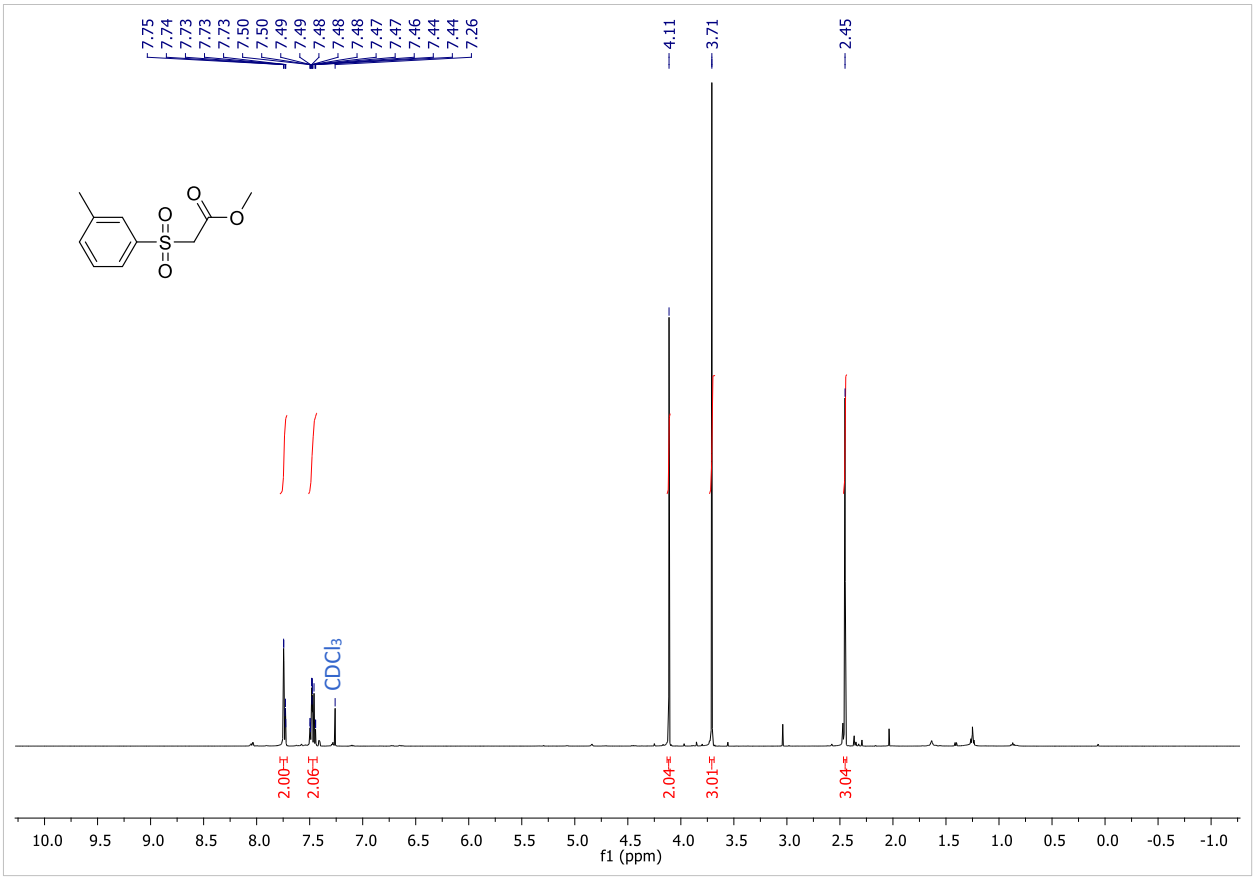


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

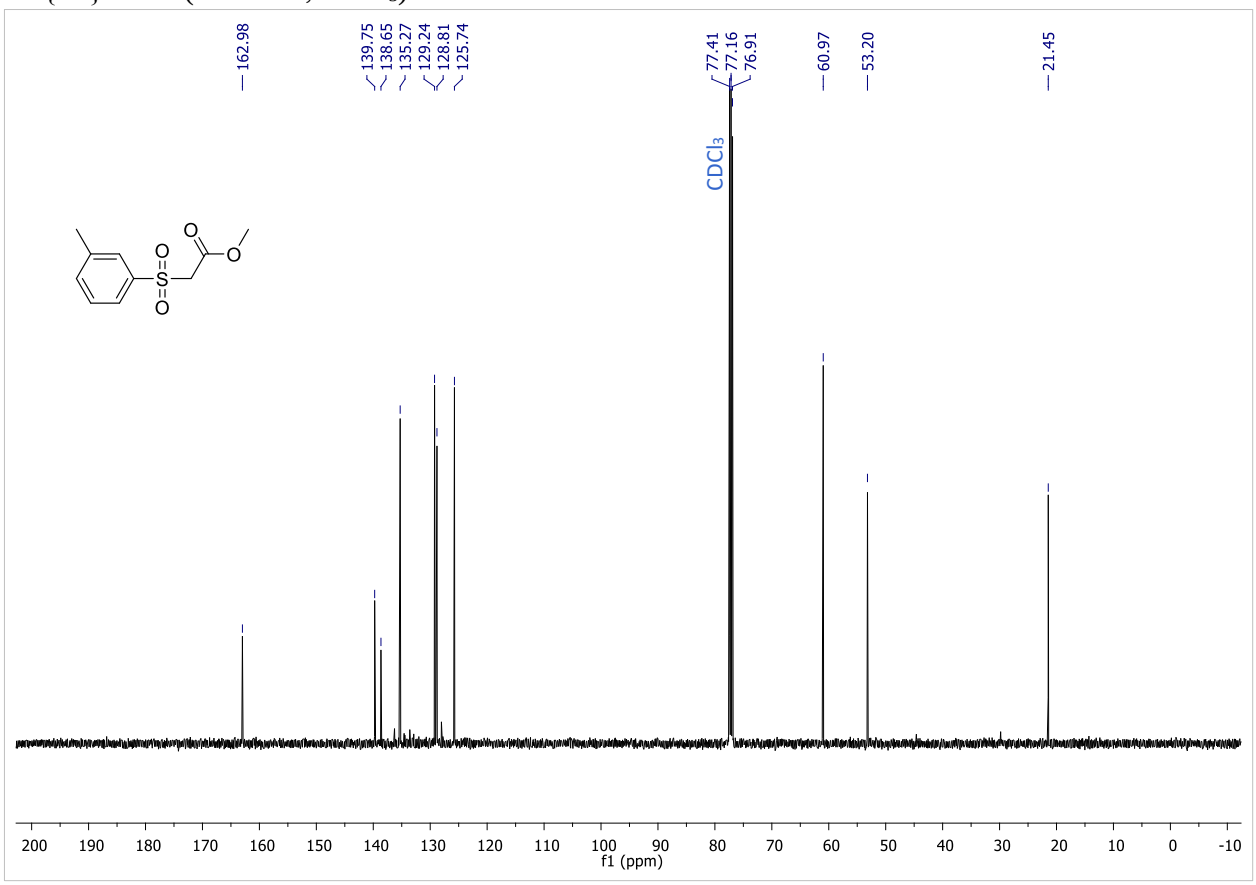


3db

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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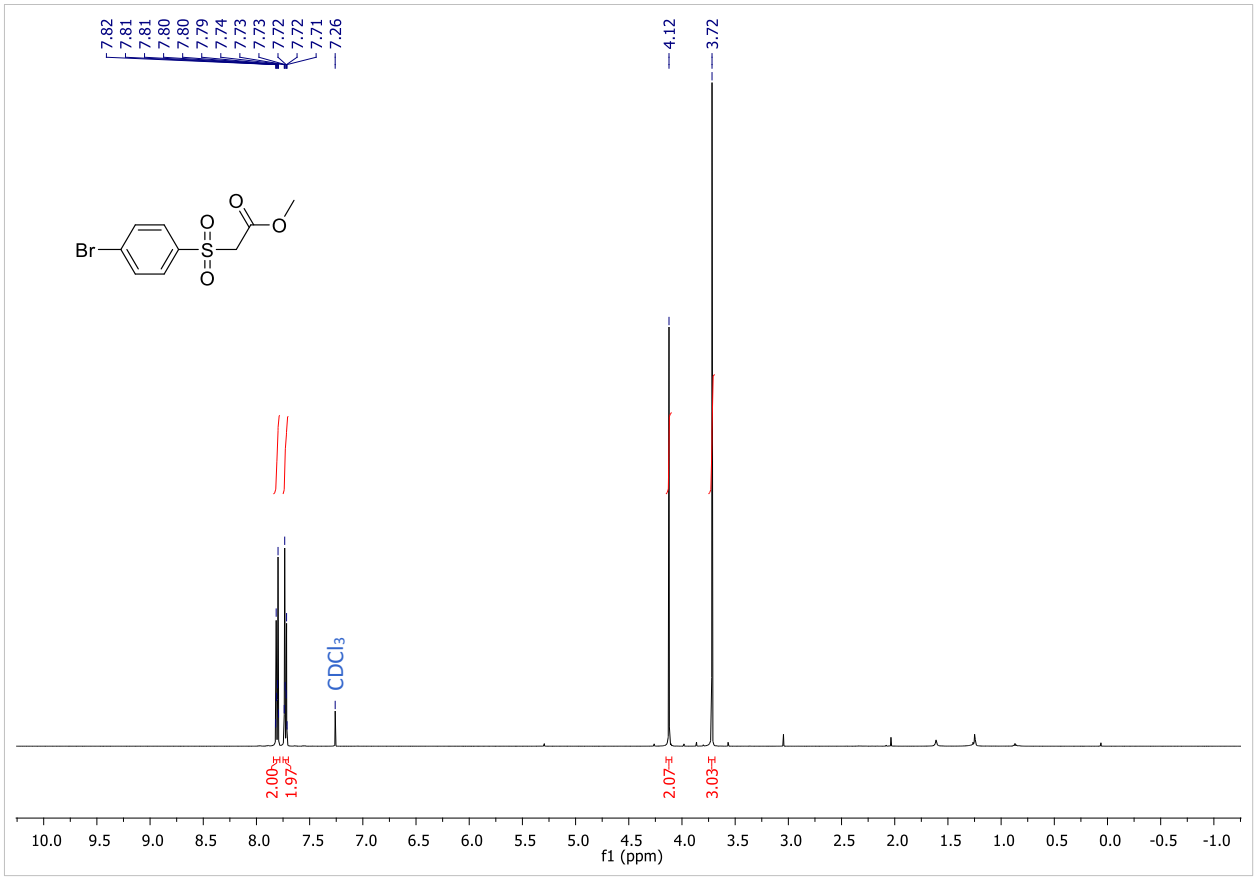
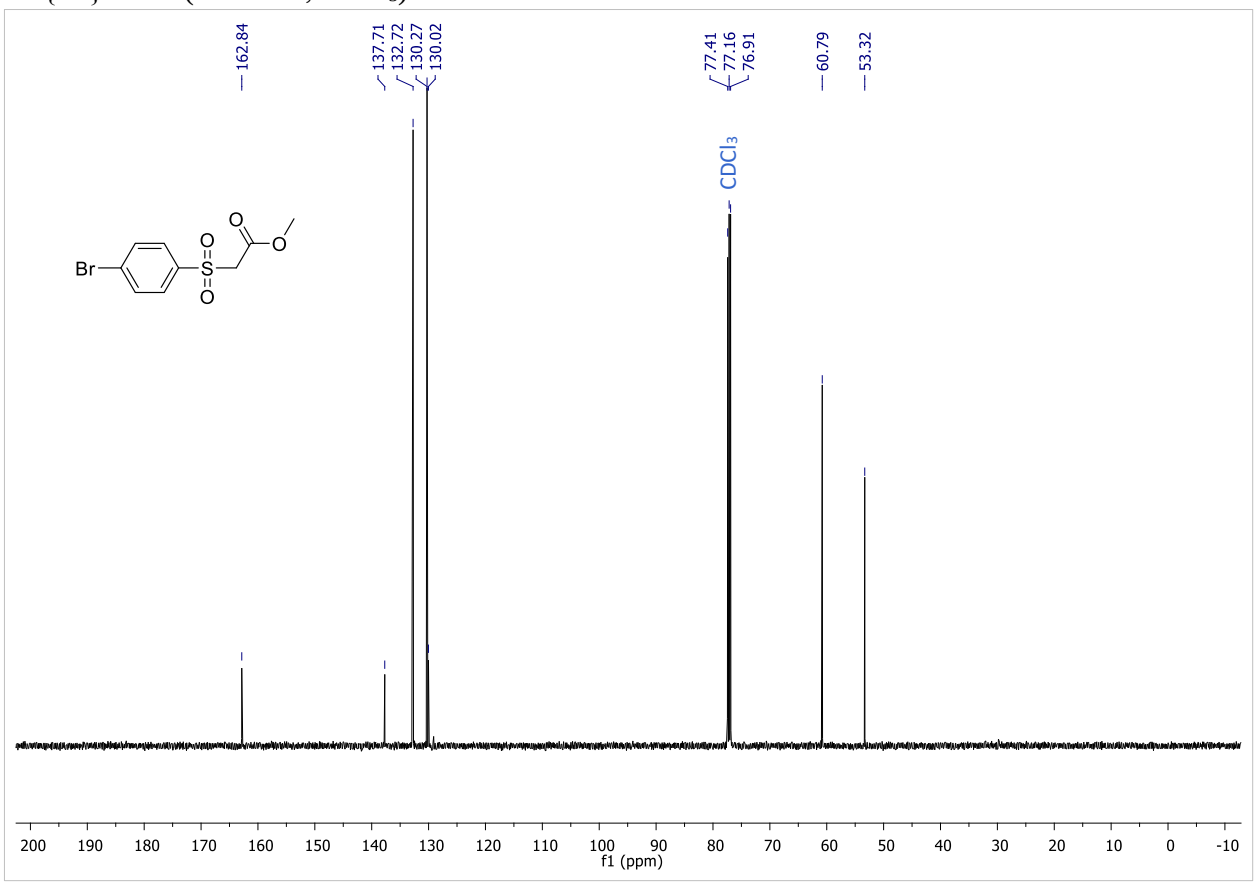
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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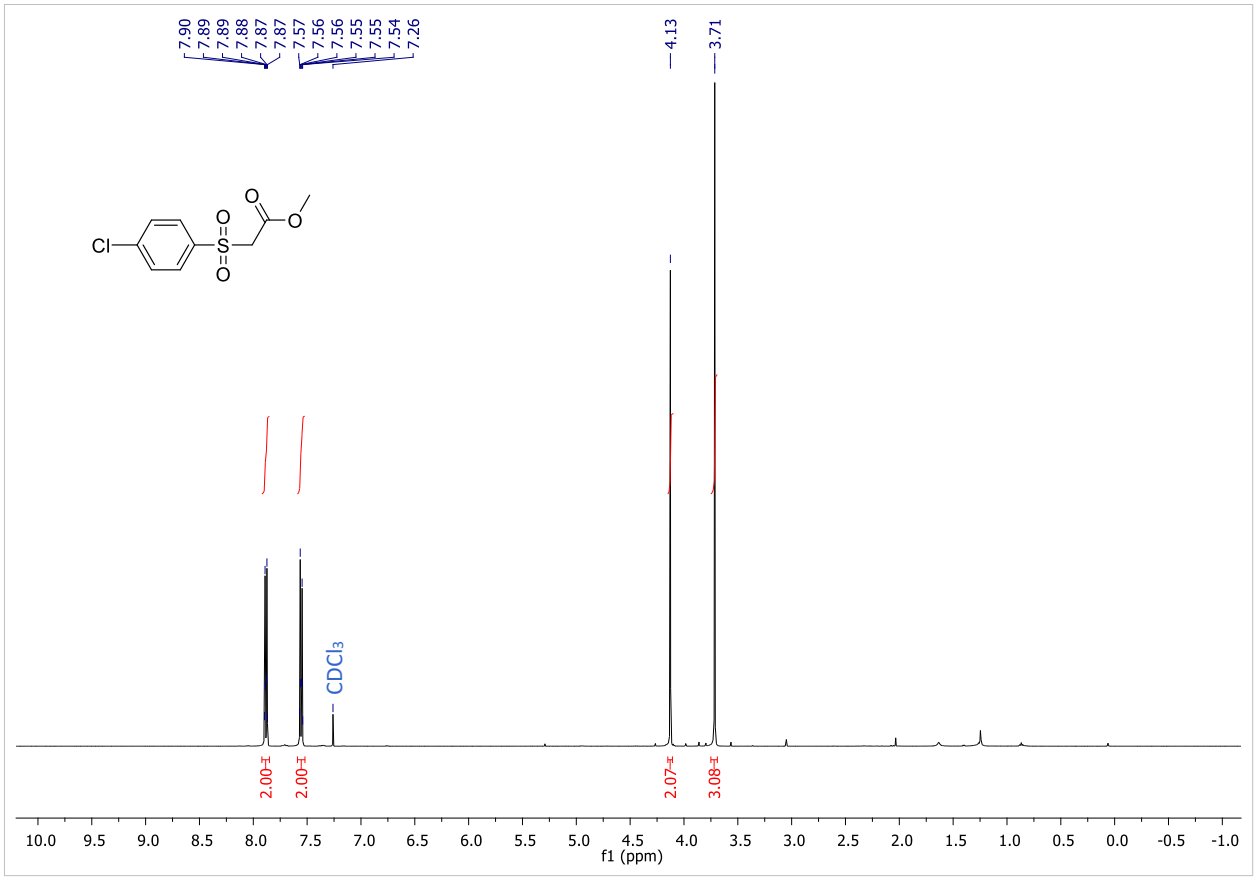

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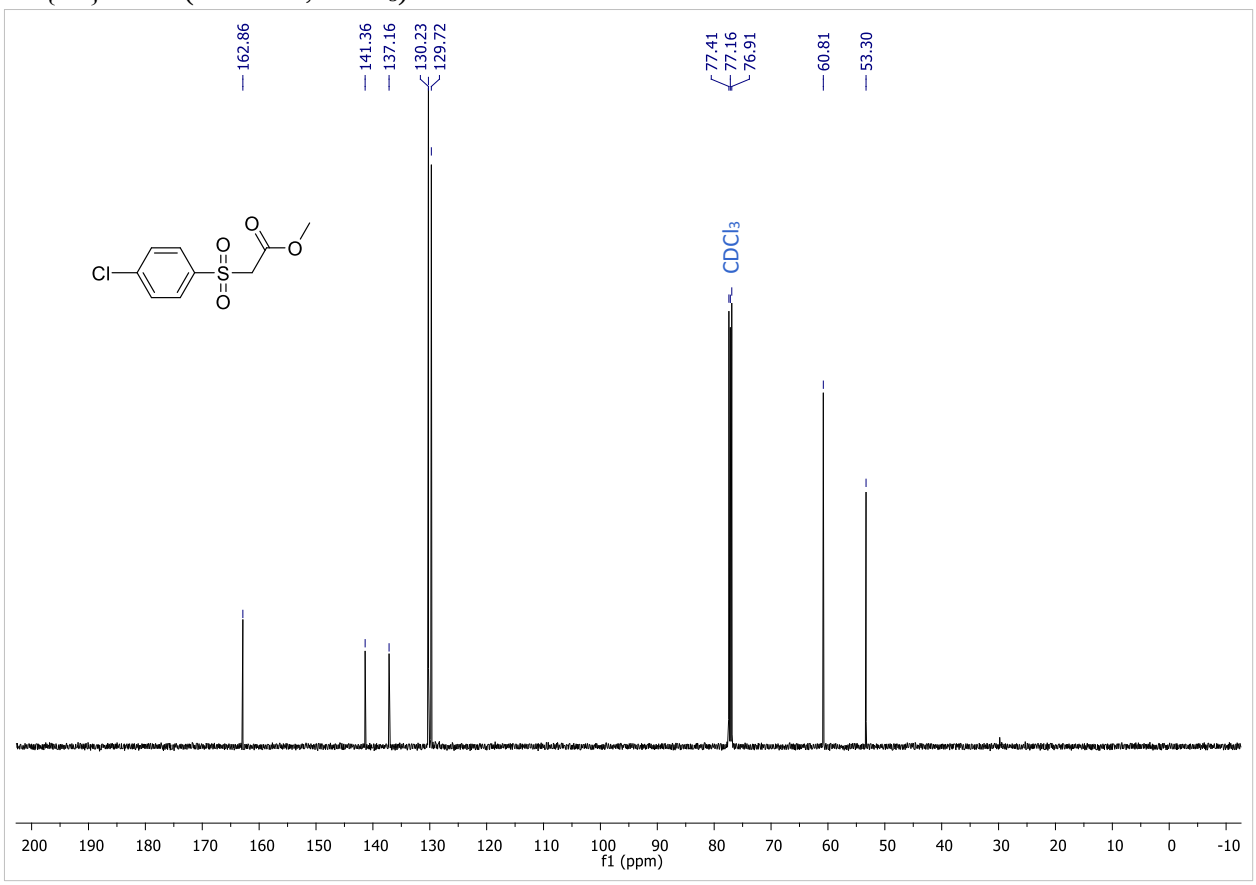

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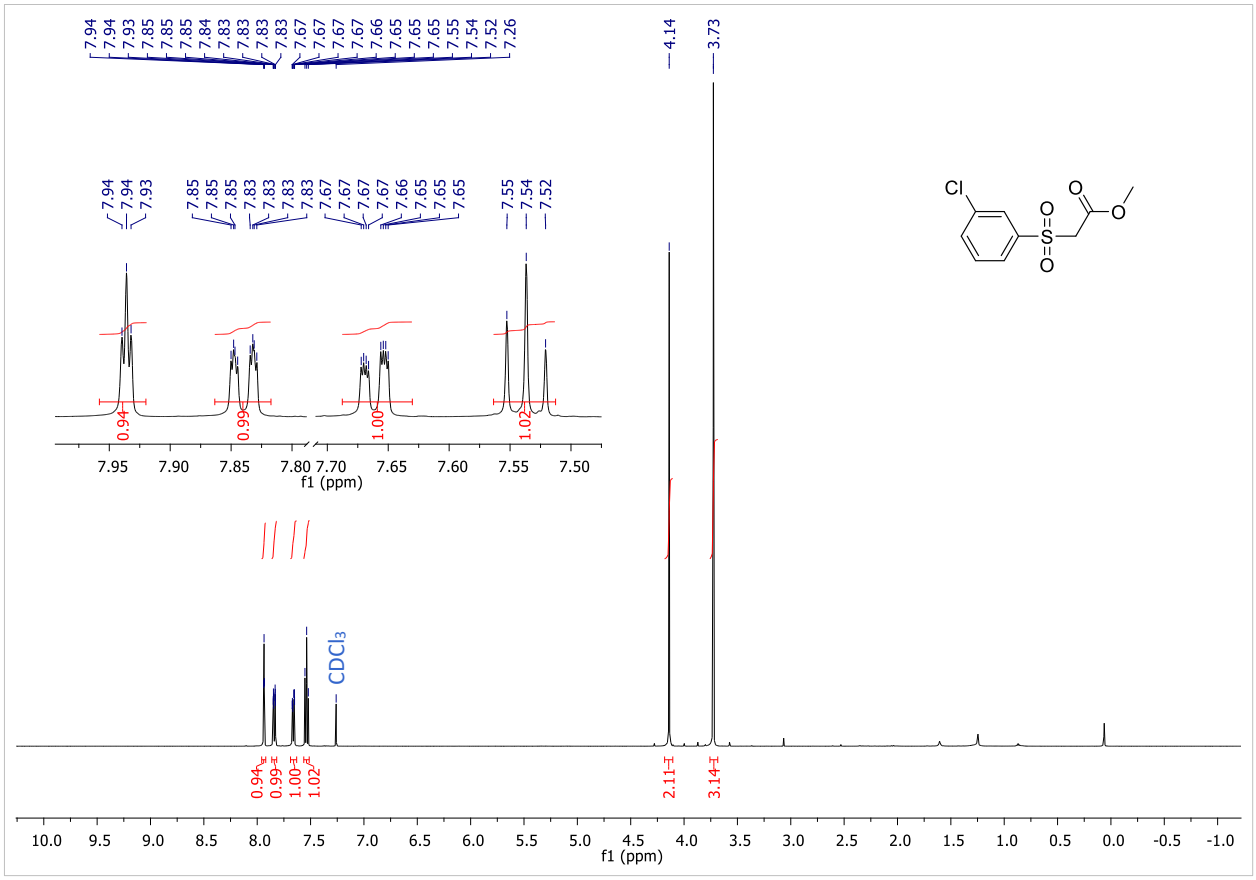
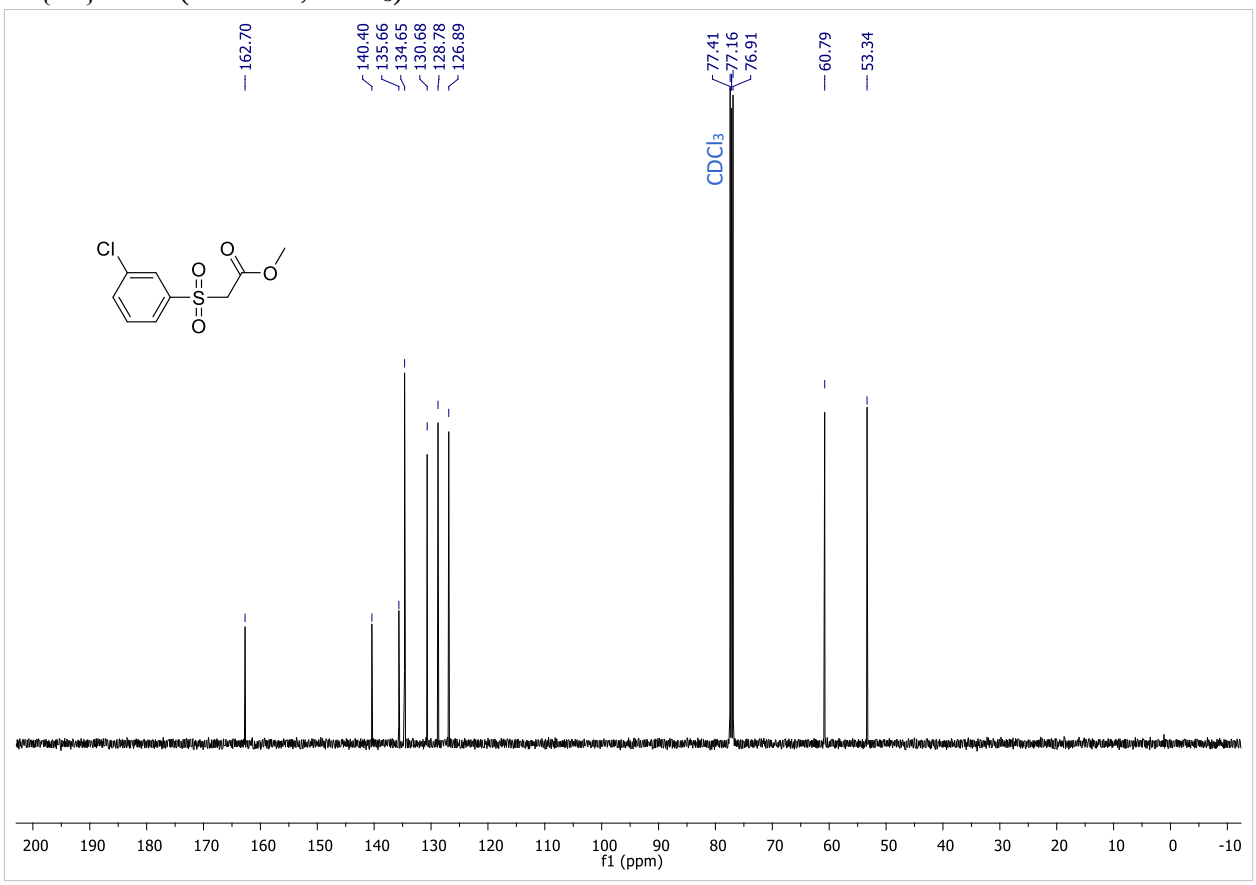


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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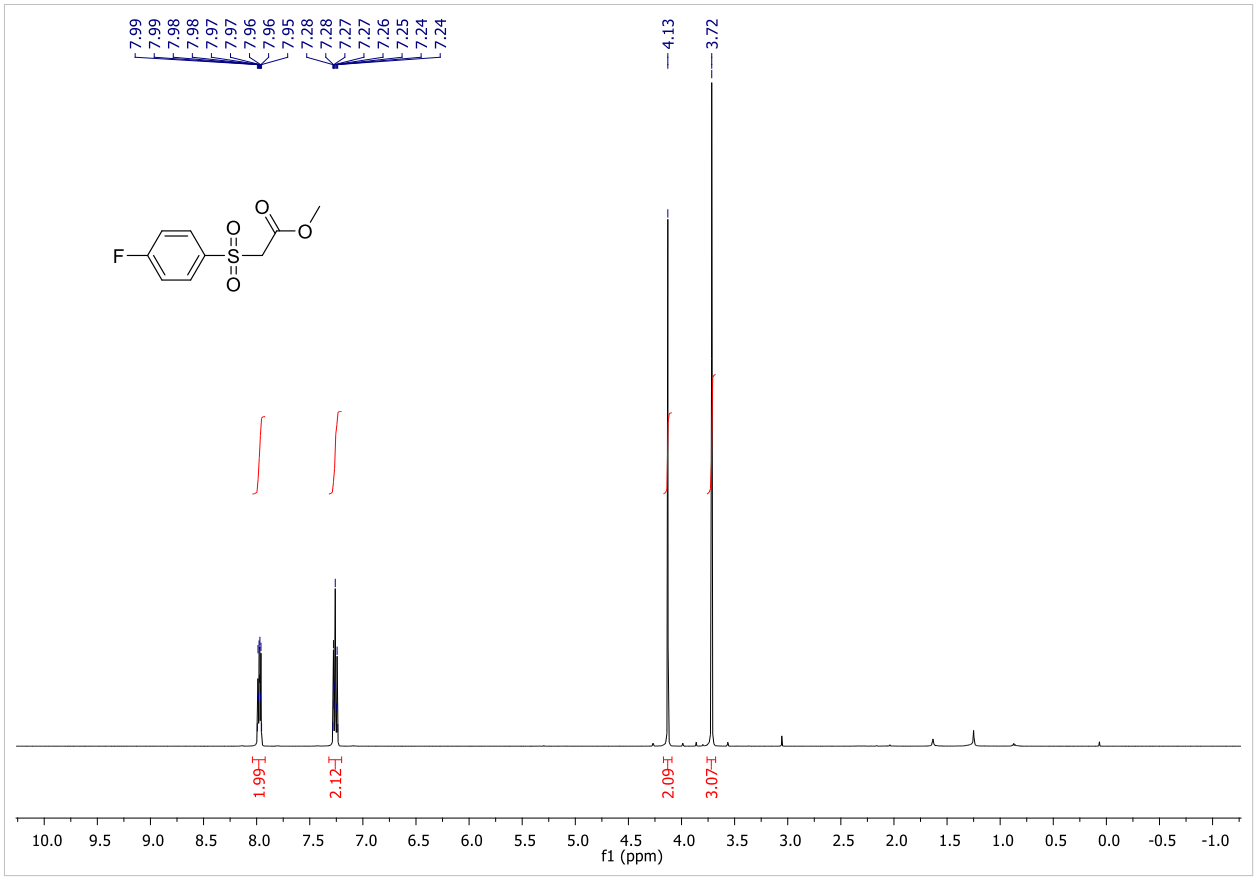

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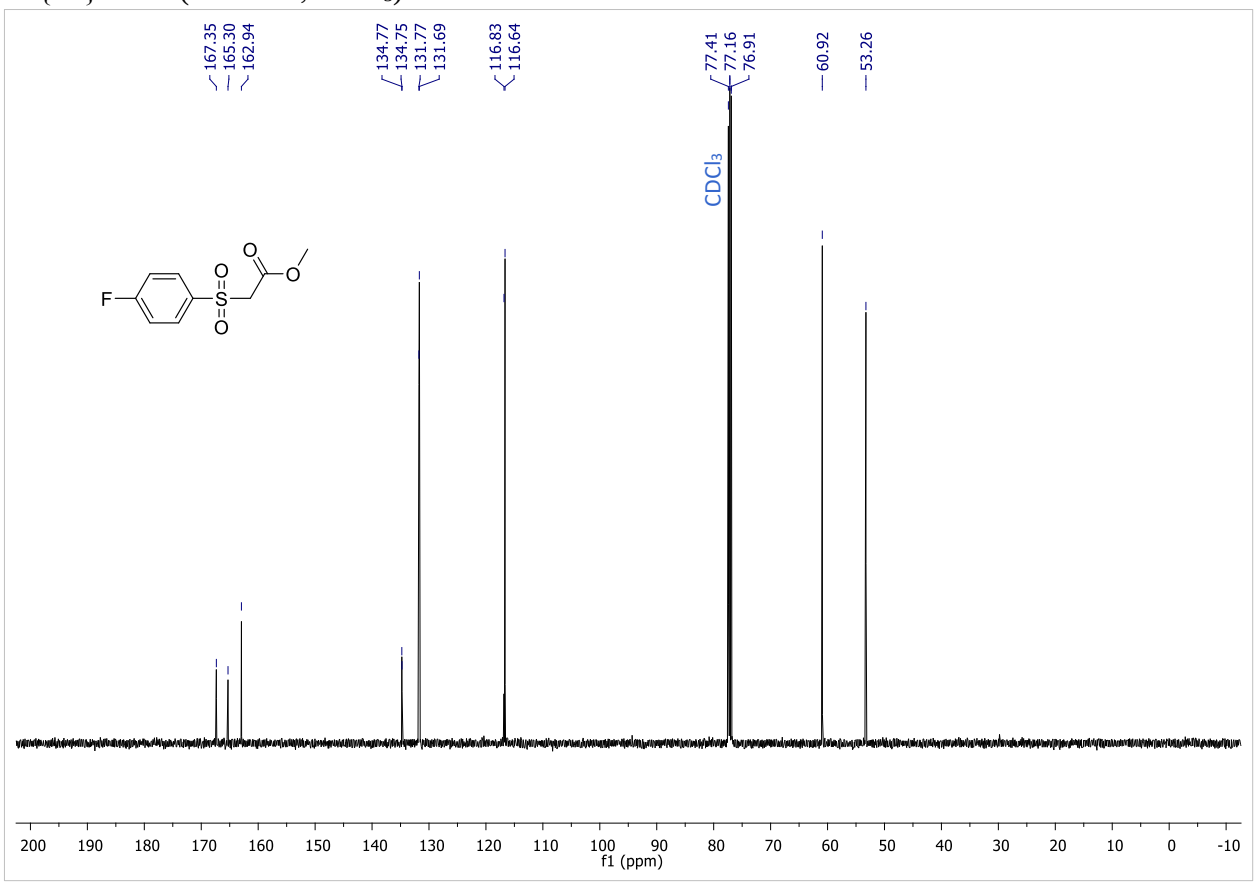

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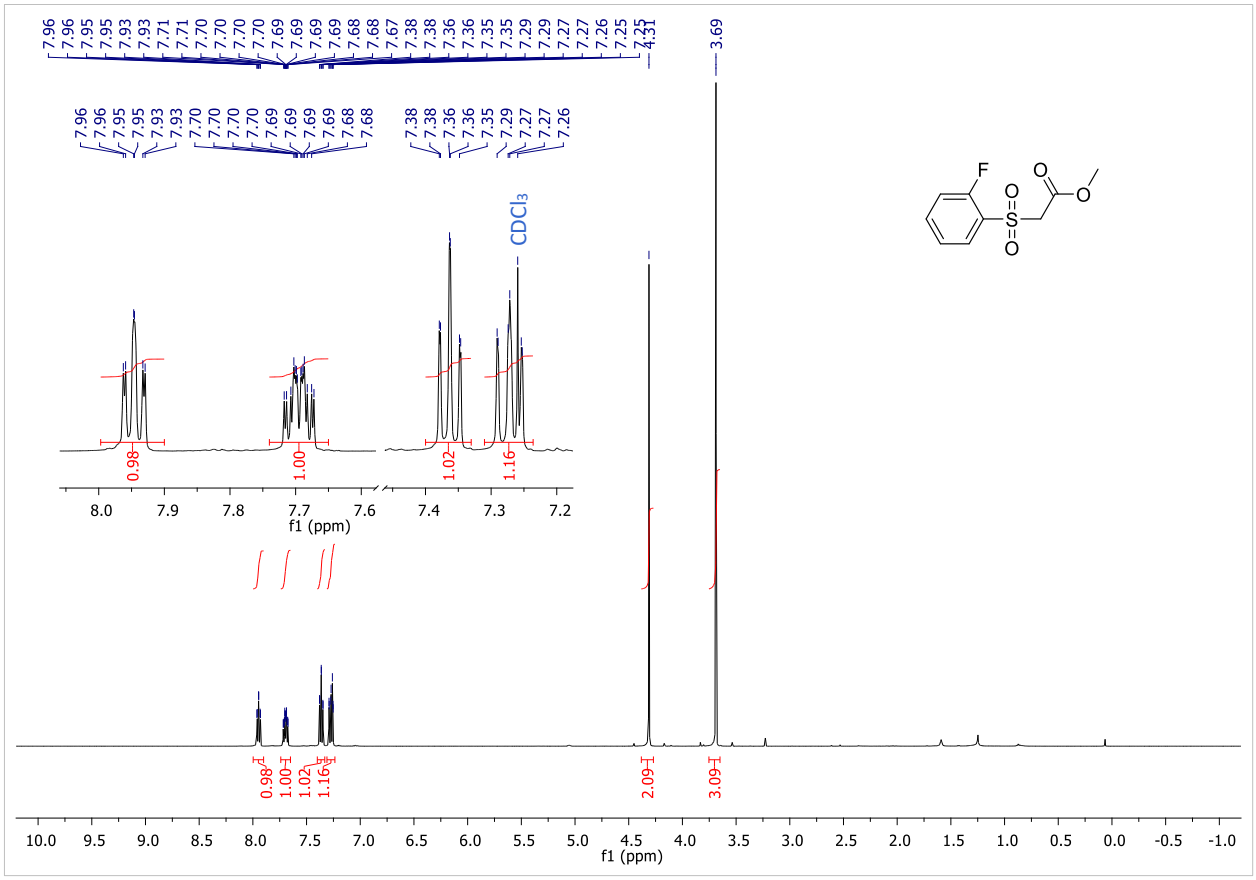
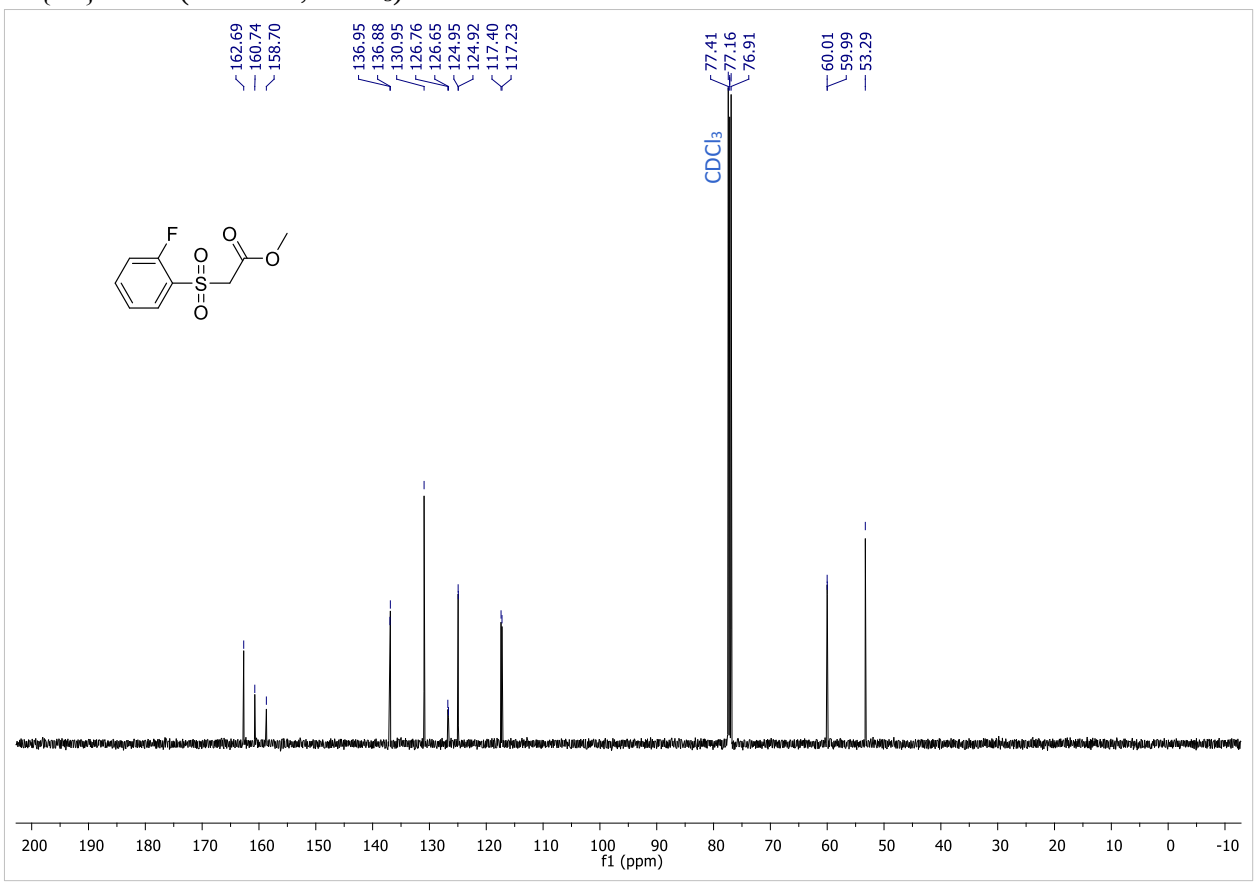


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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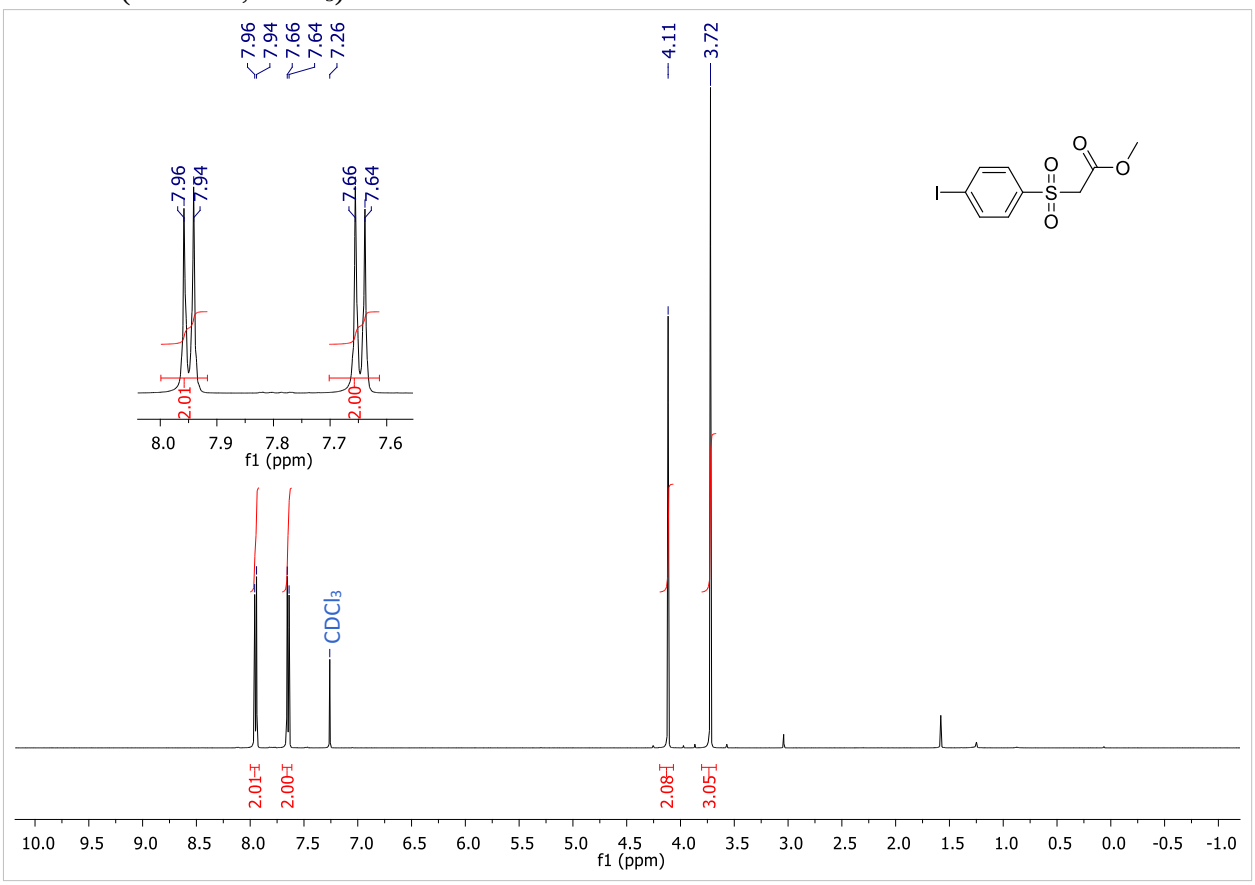
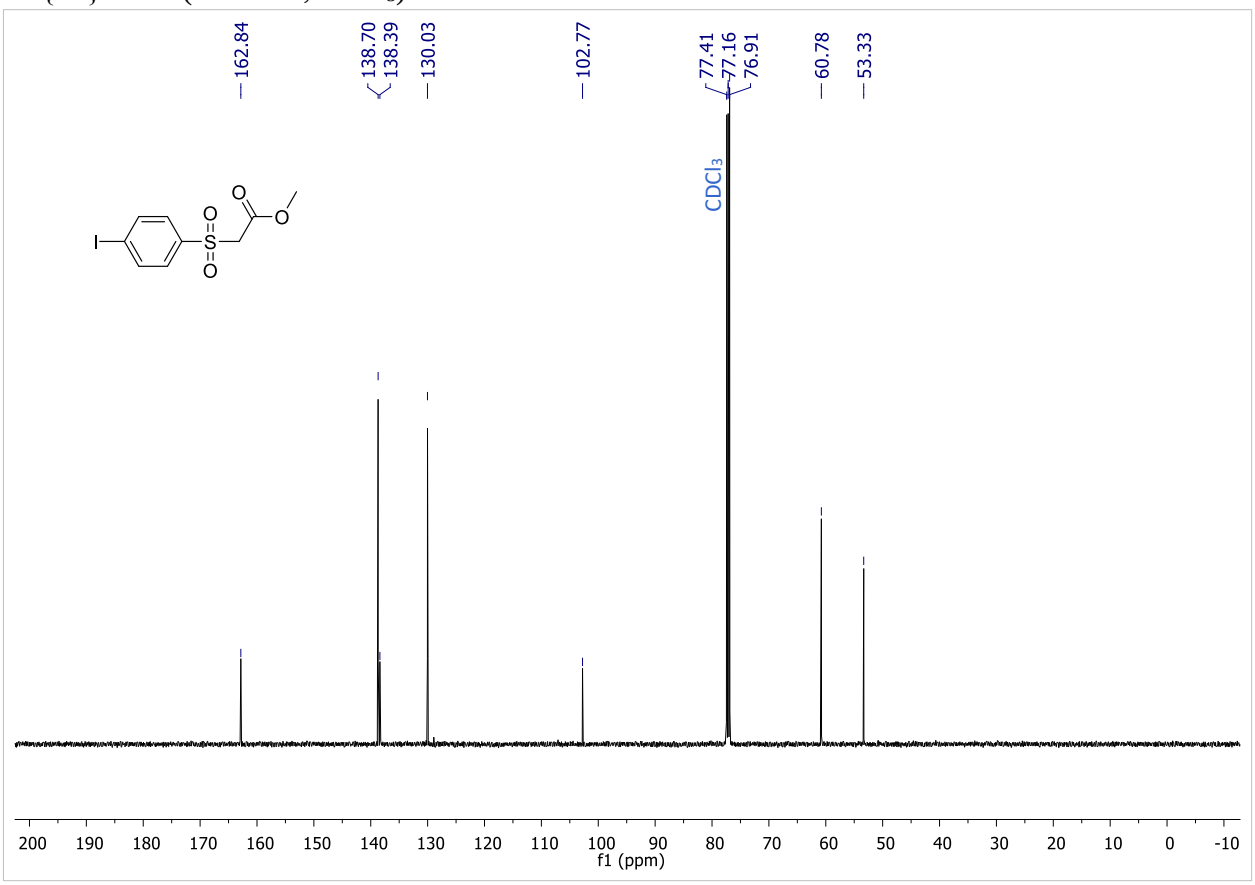


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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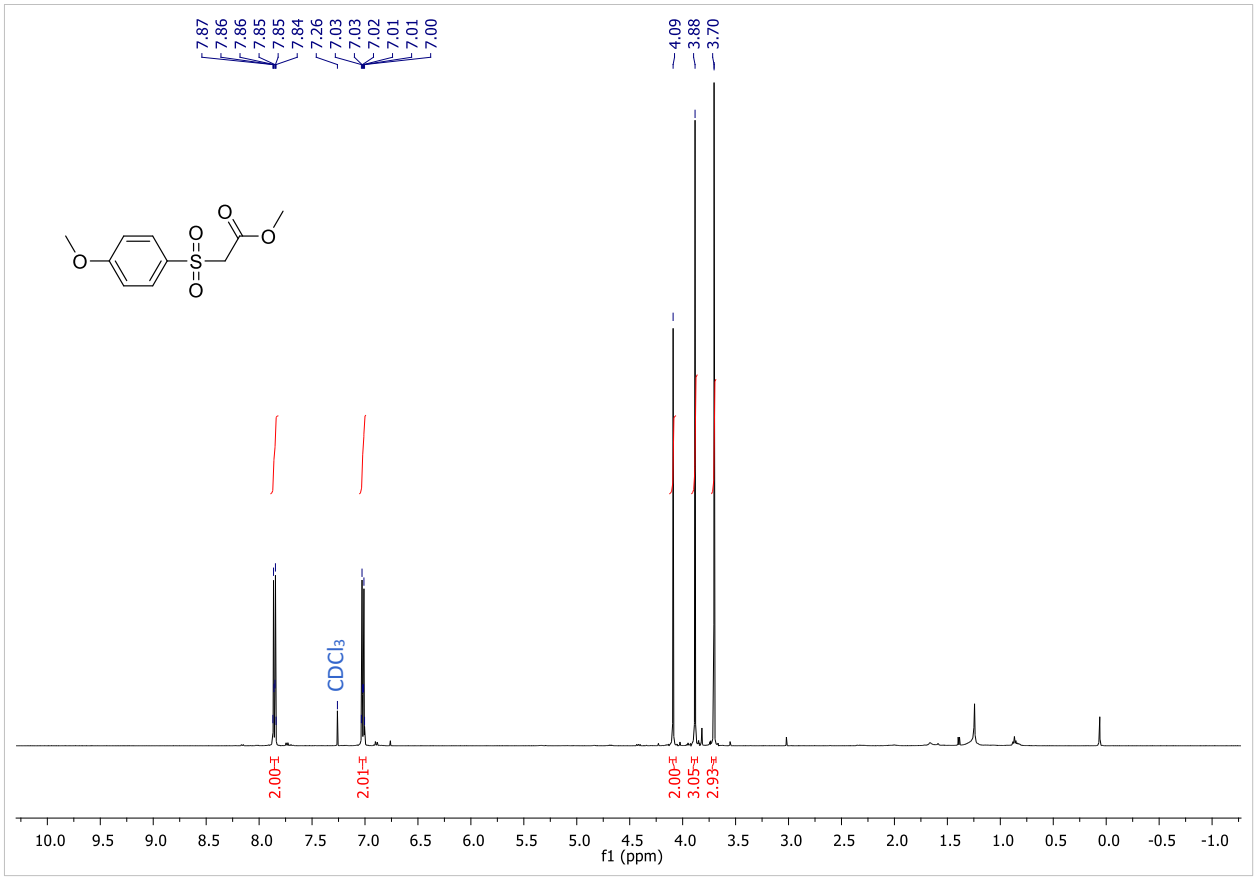
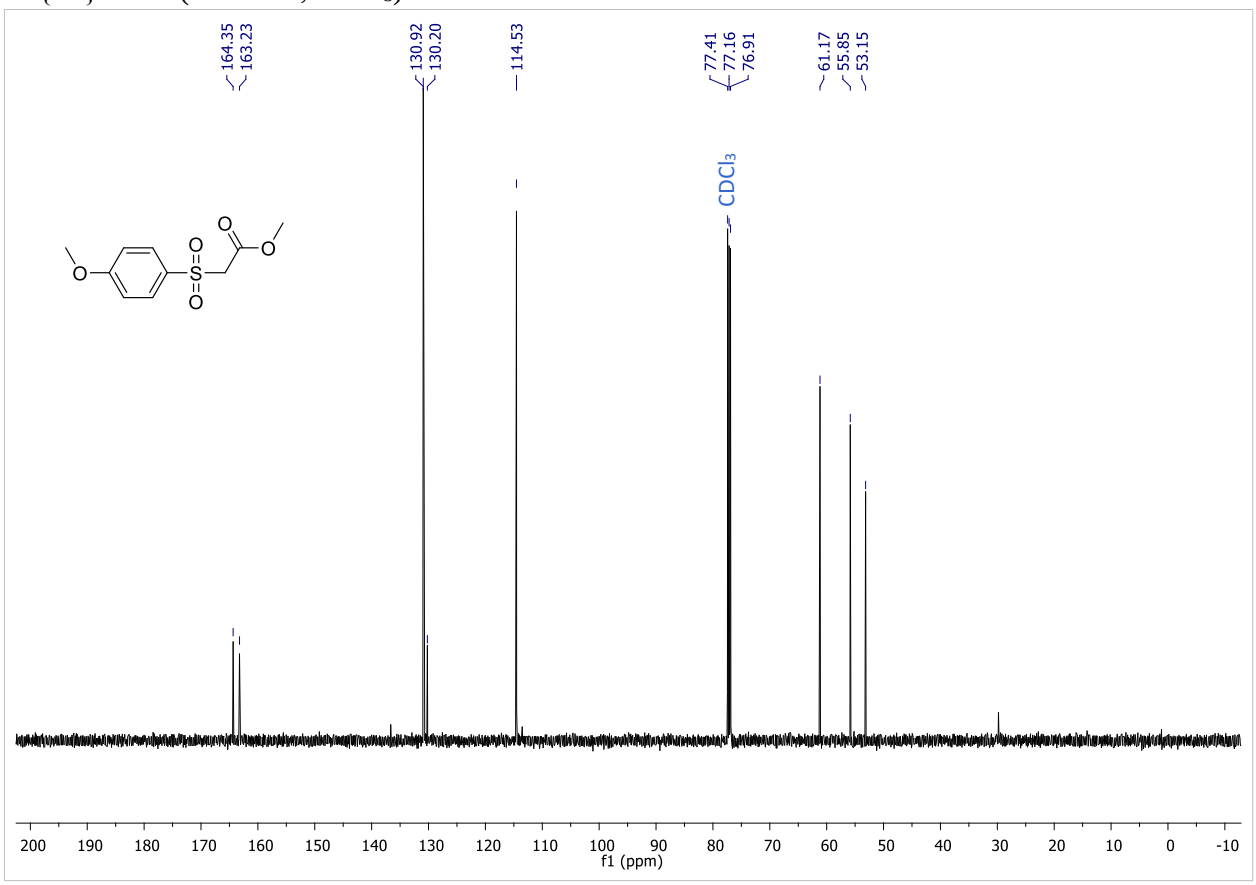


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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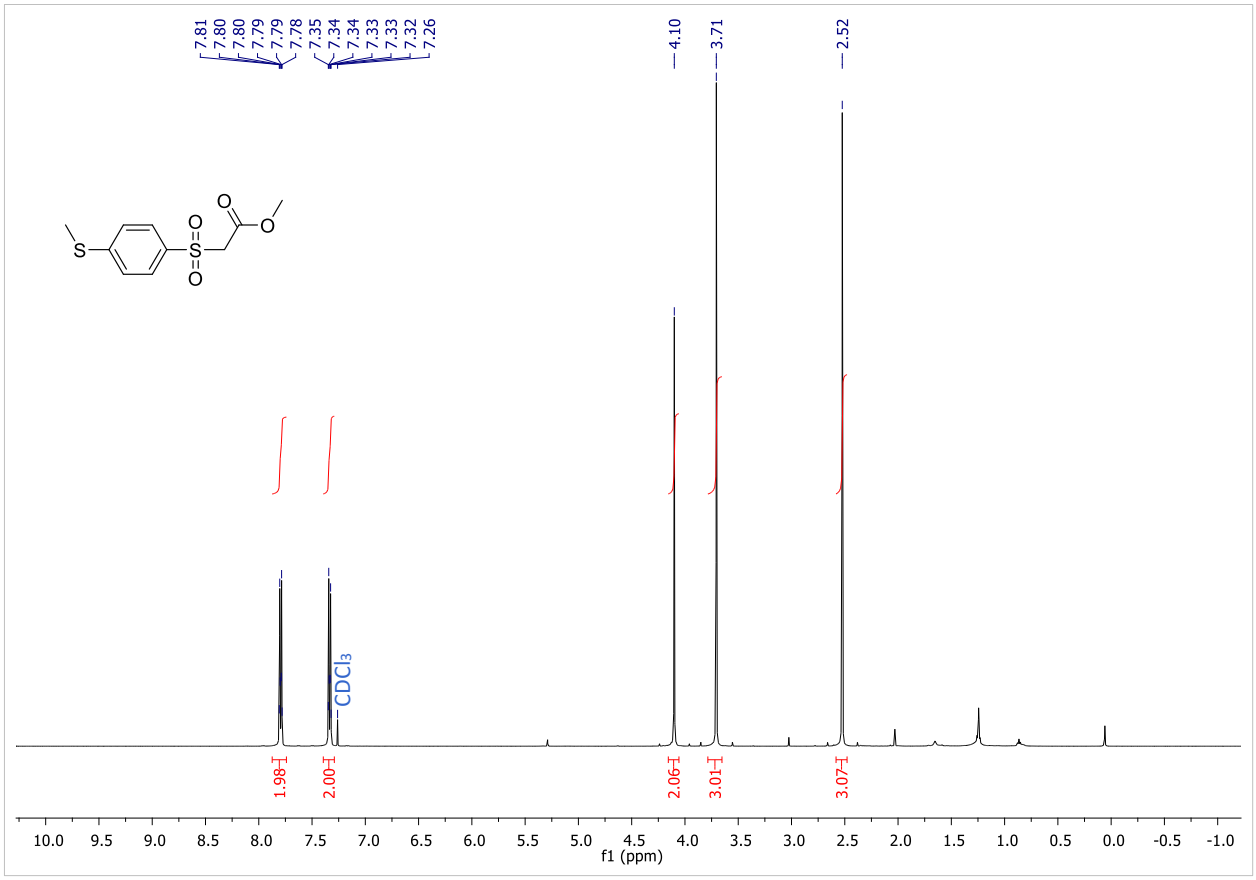
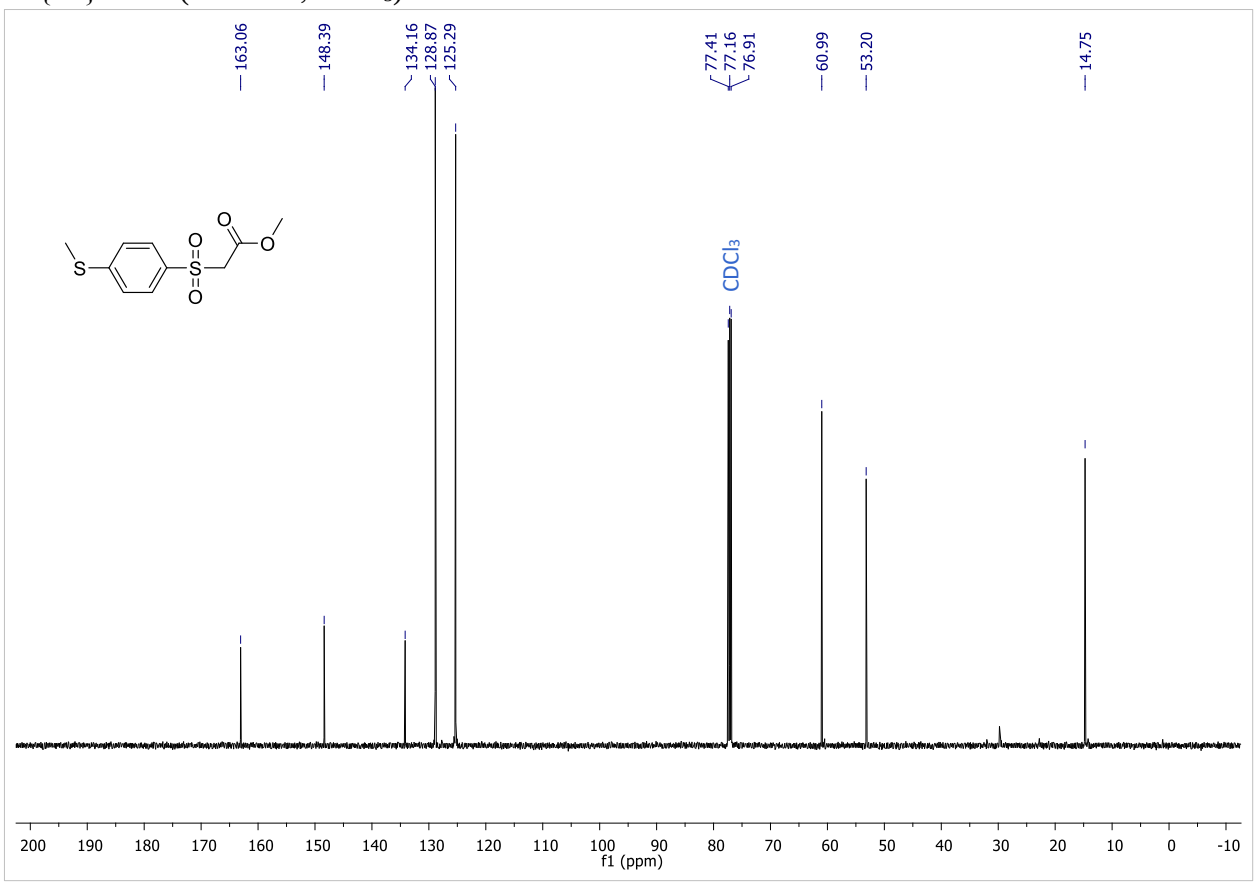
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



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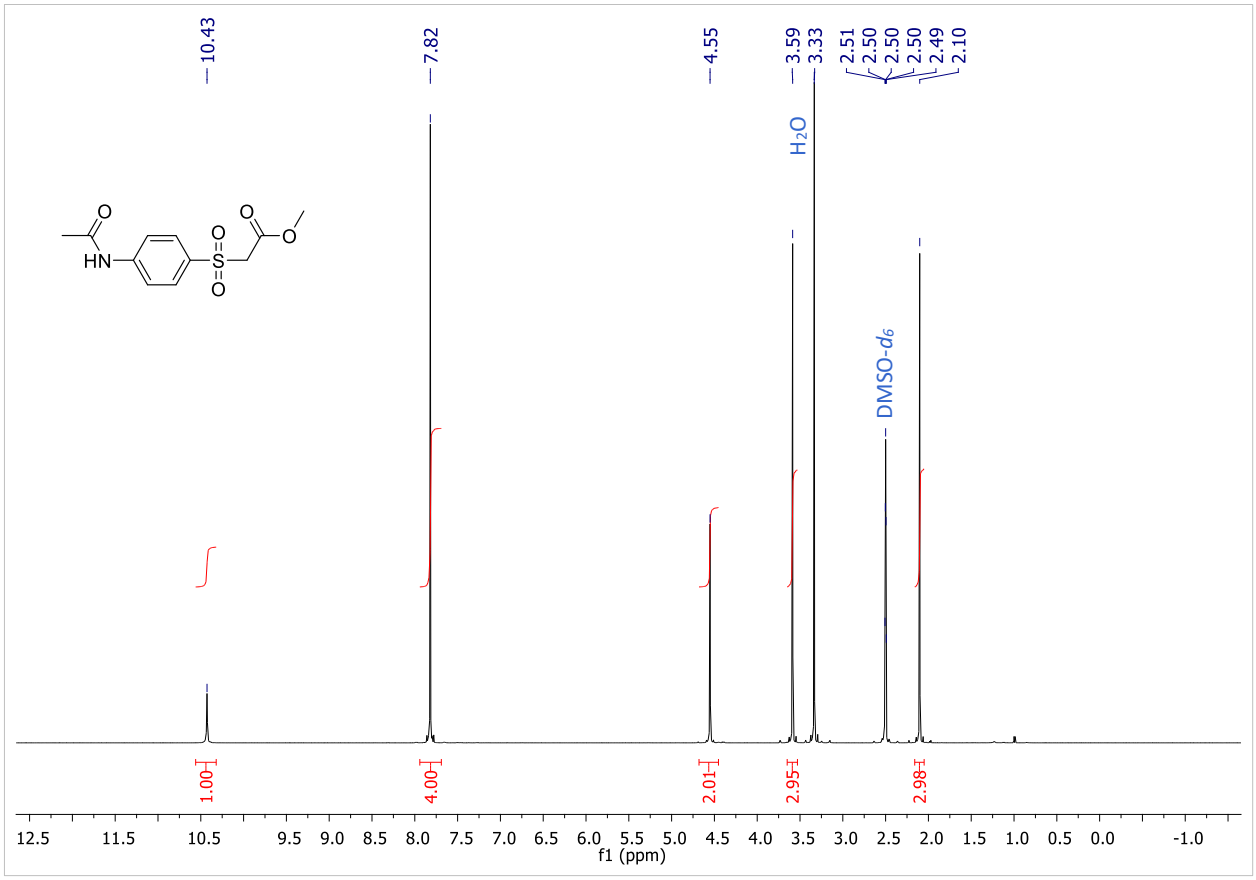
^{1}H NMR (500 MHz, DMSO-d_6)



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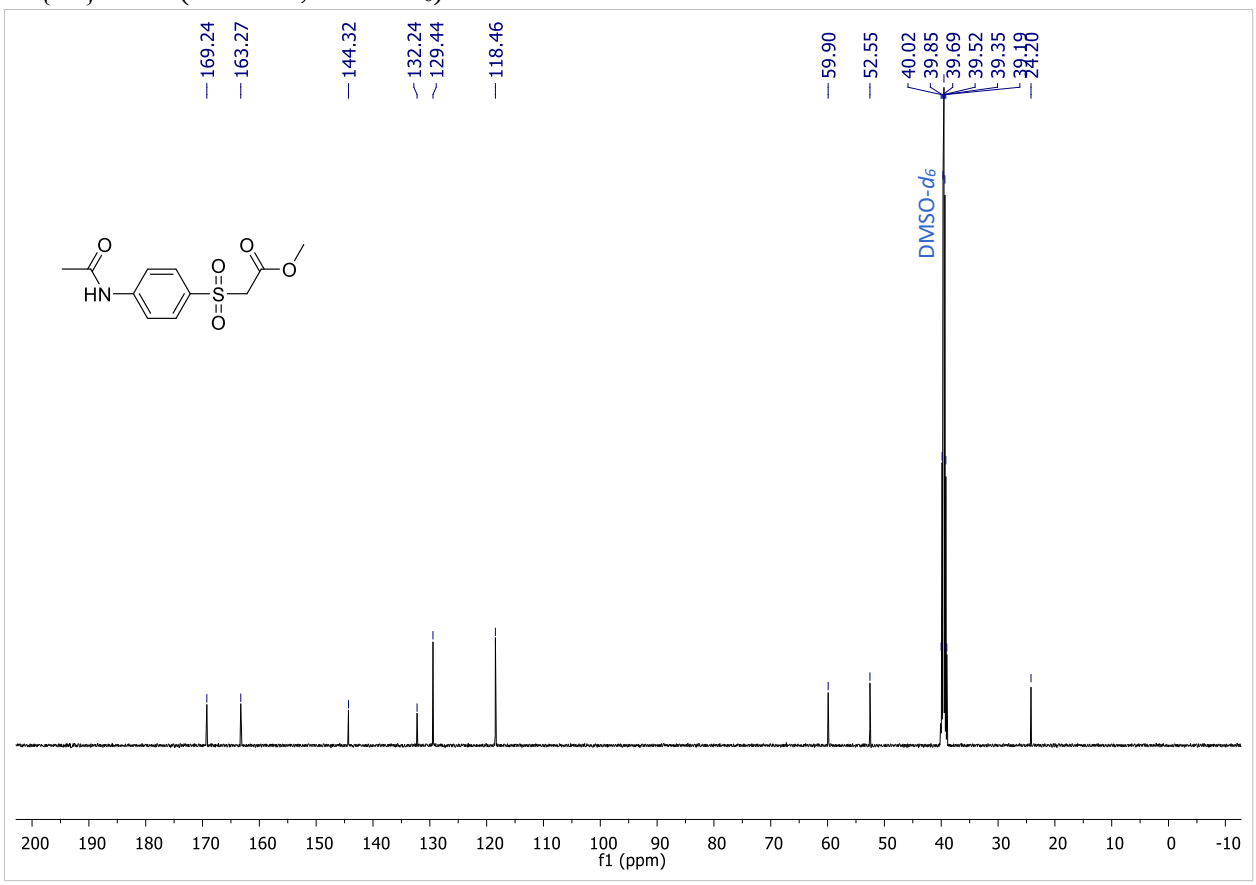

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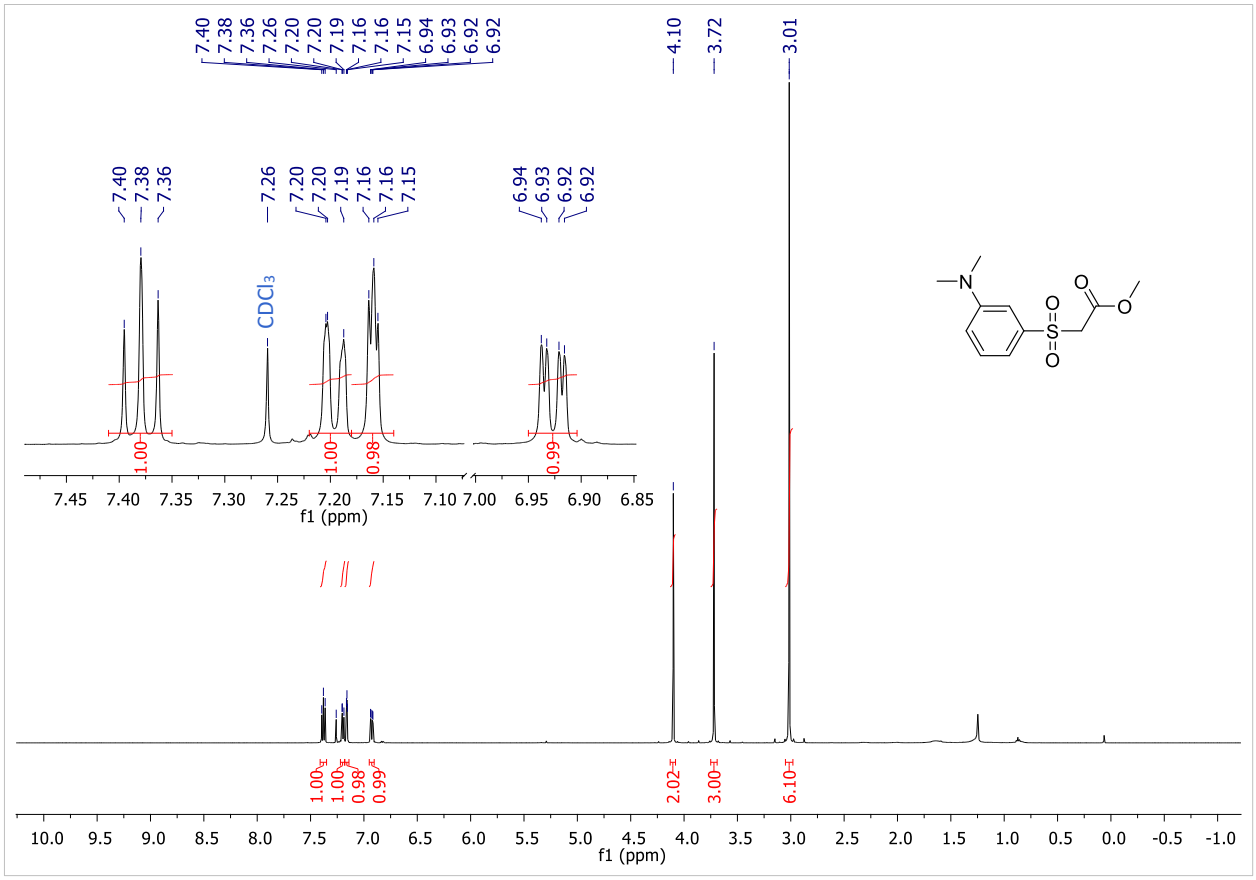
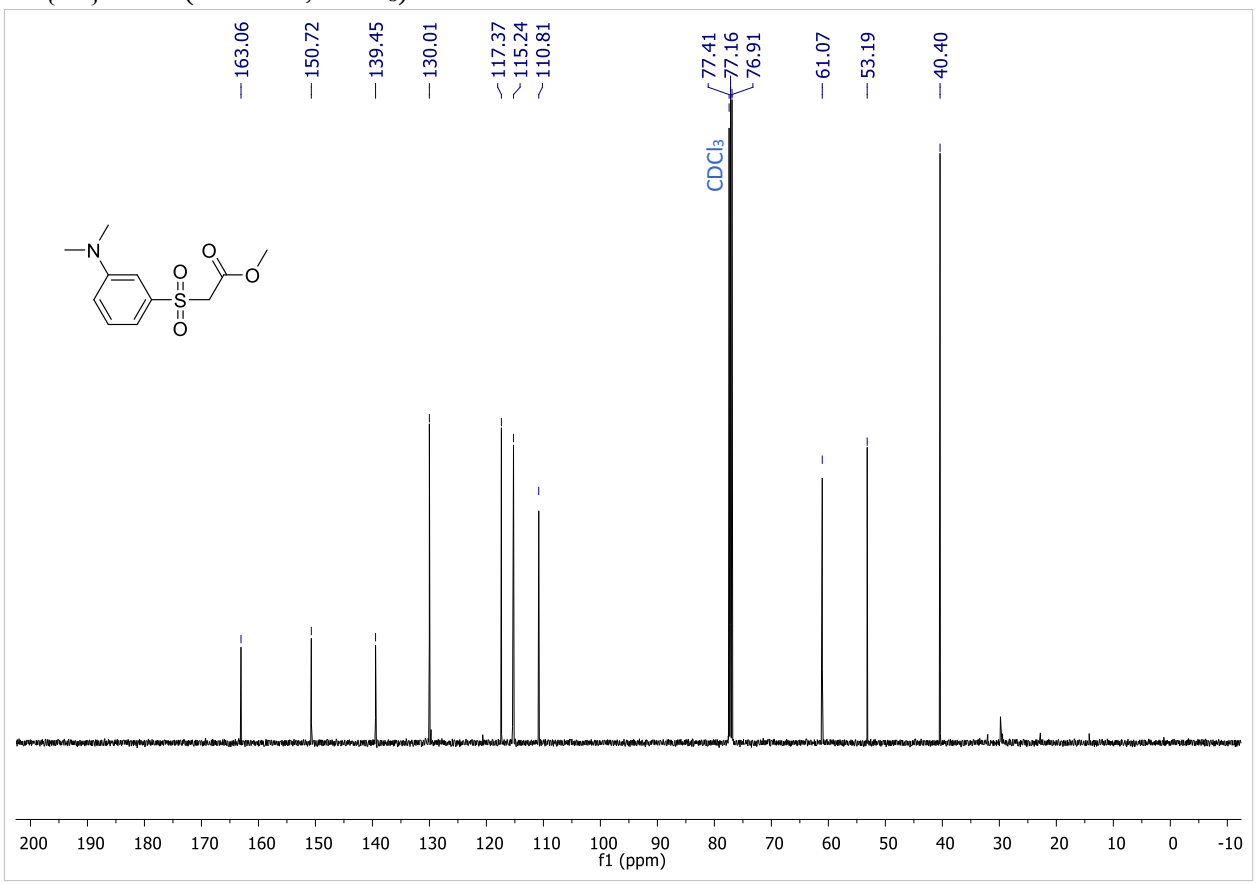
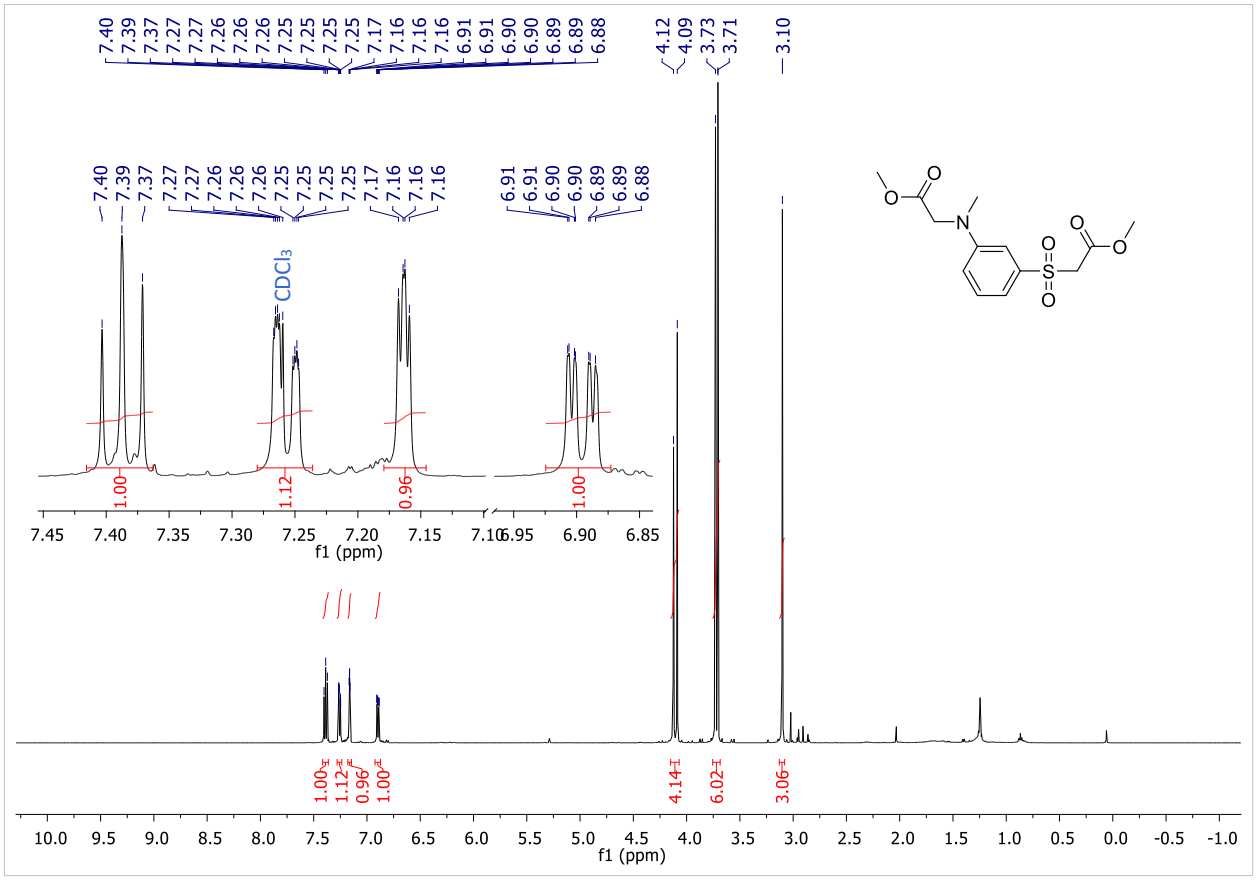


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

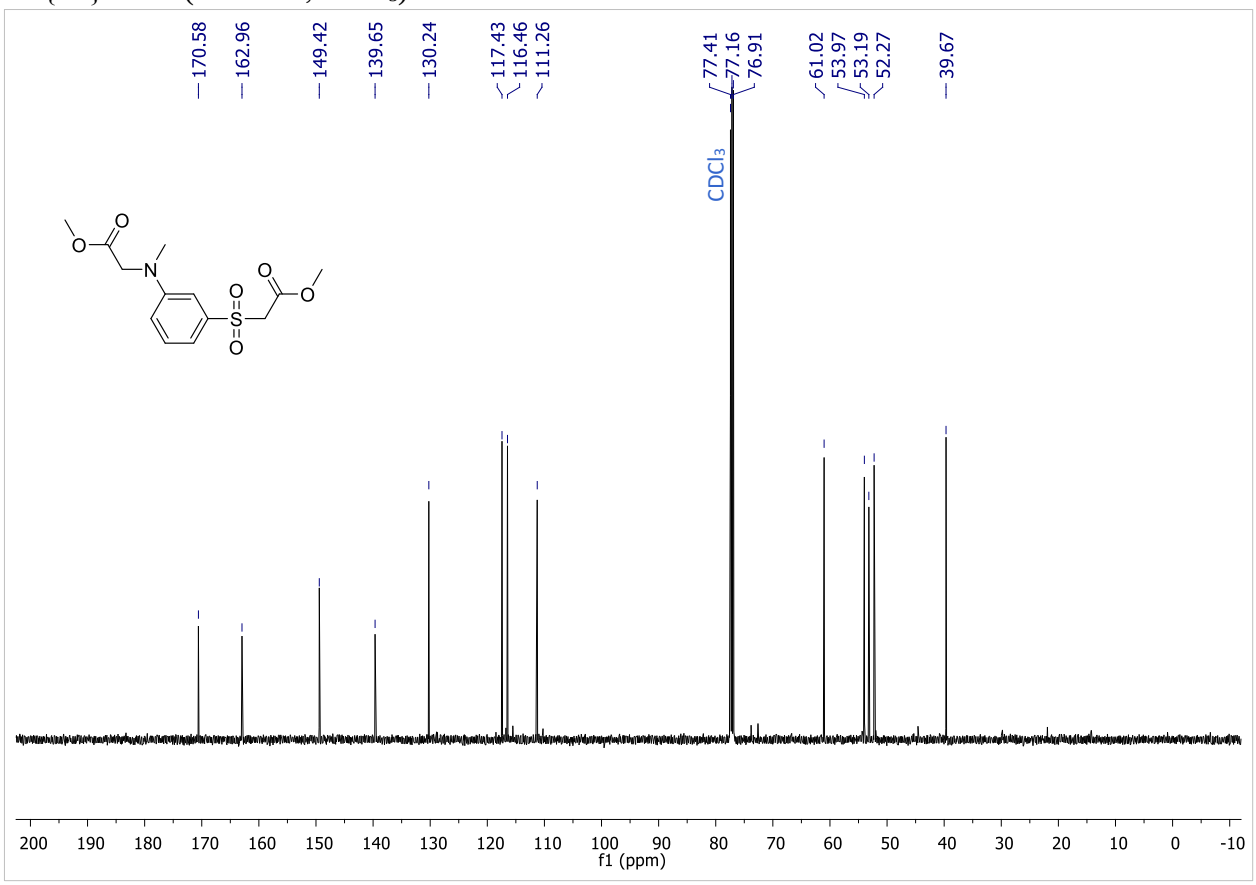


4

^{1}H NMR (500 MHz, $CDCl_3$)

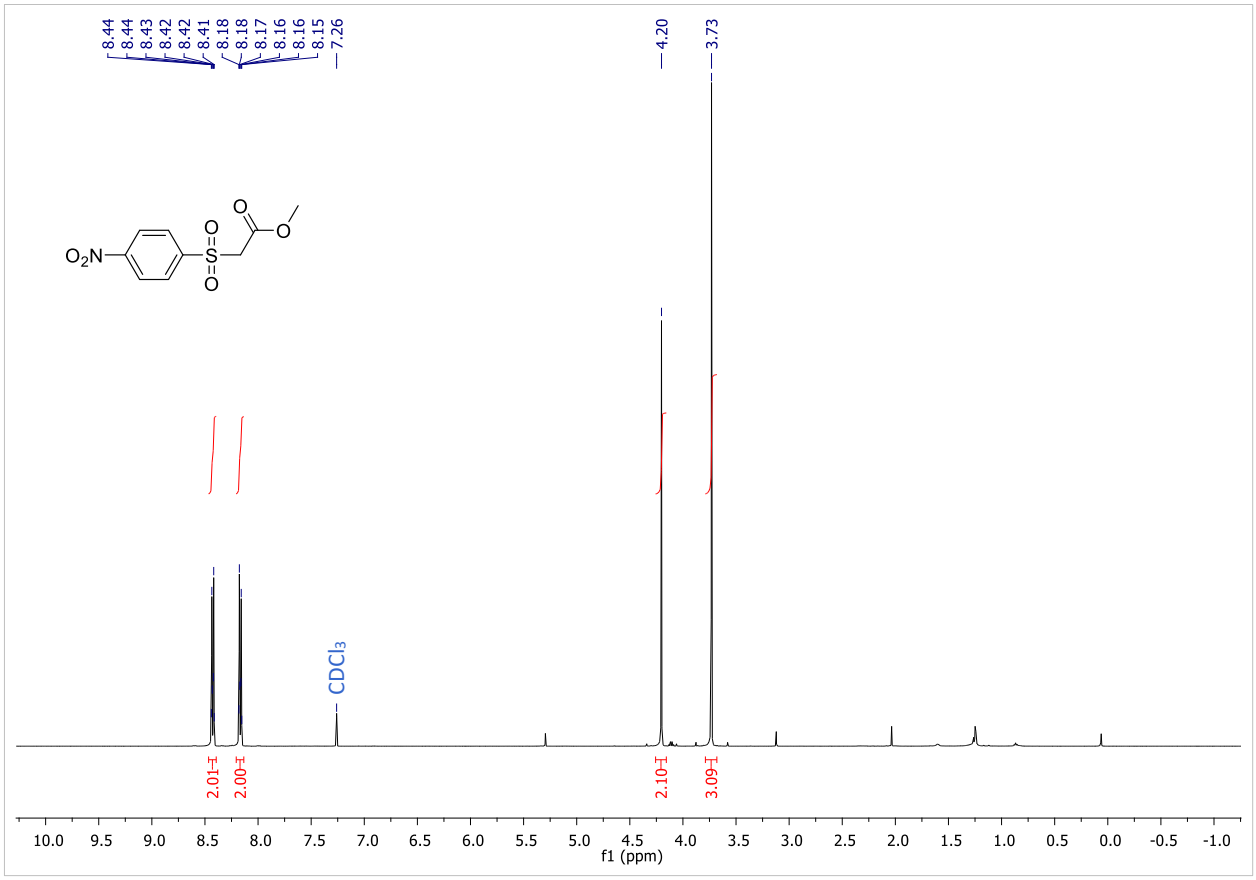


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

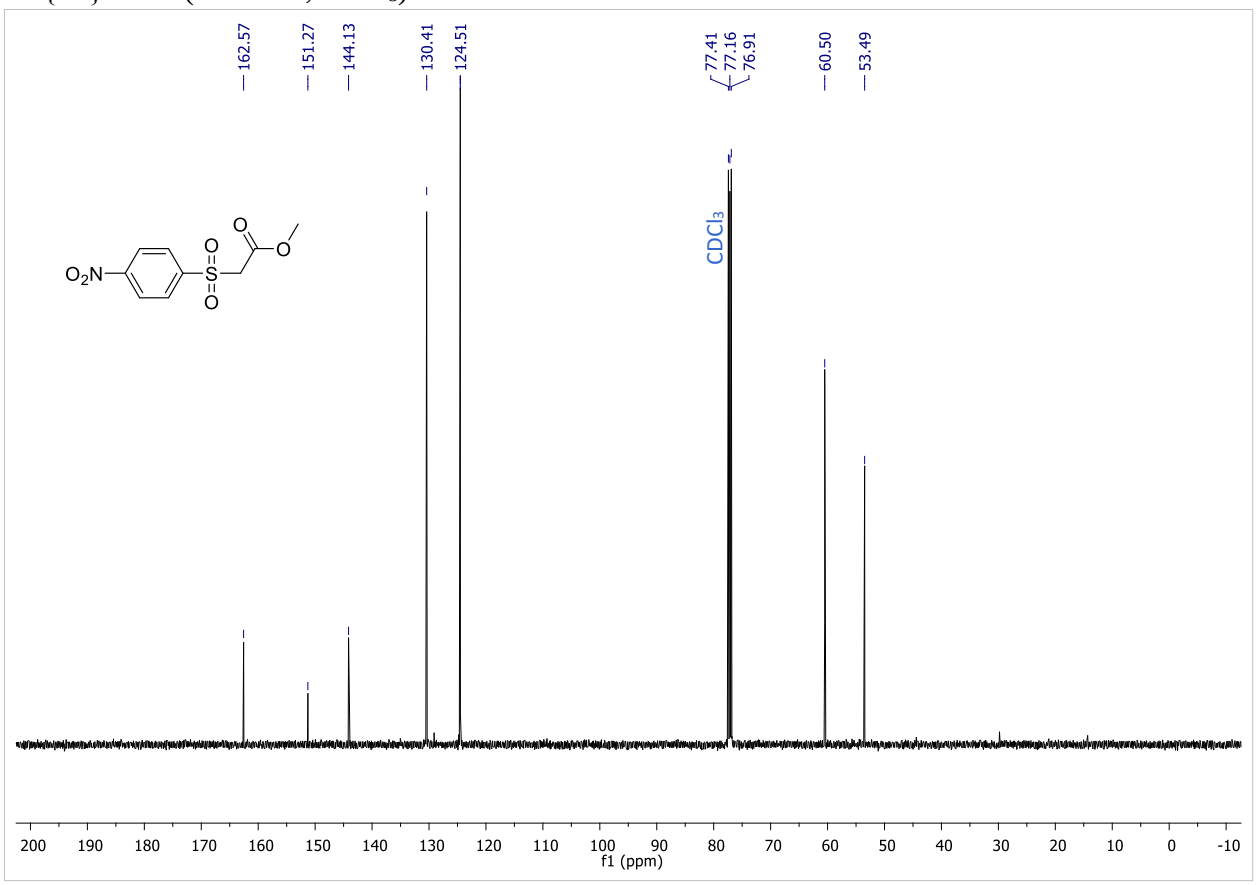


3ob

^{1}H NMR (500 MHz, $CDCl_3$)

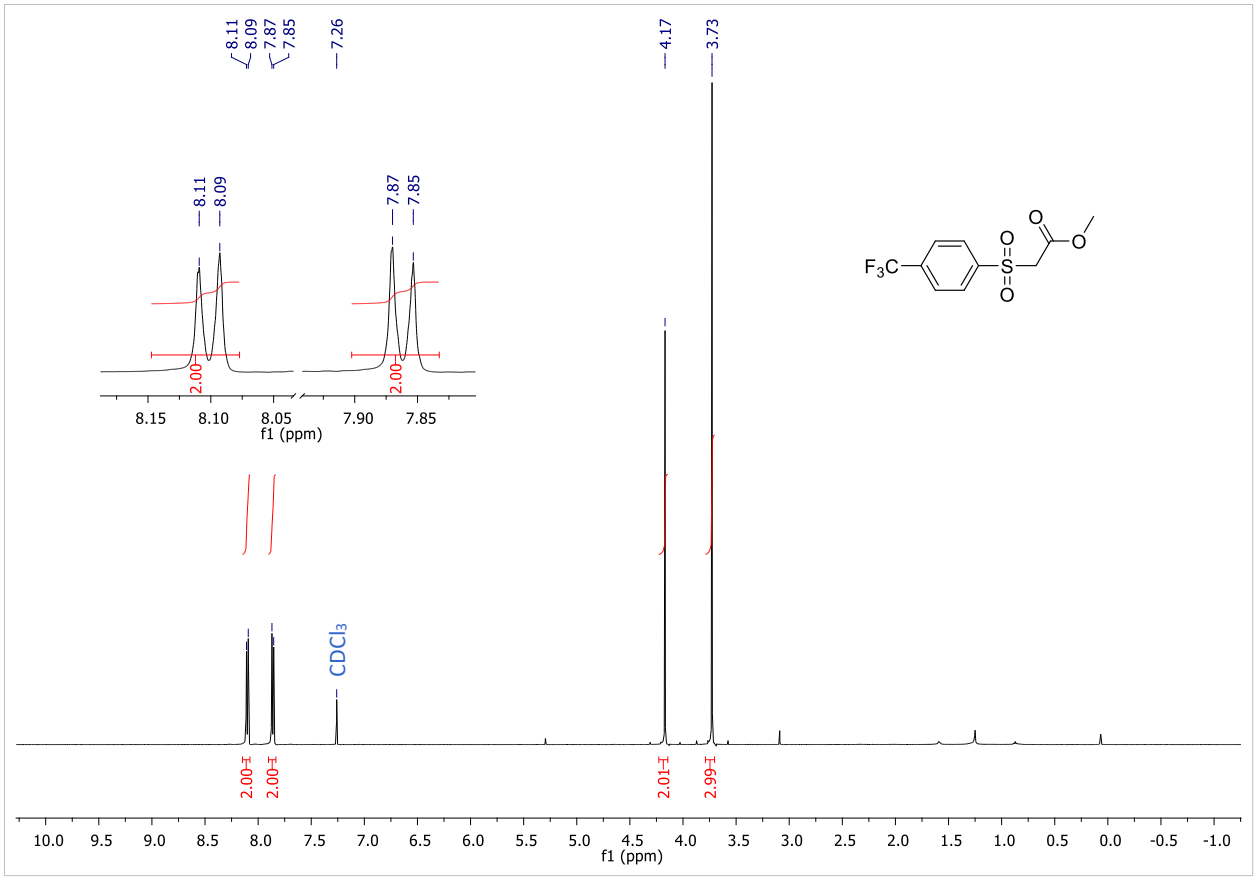


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

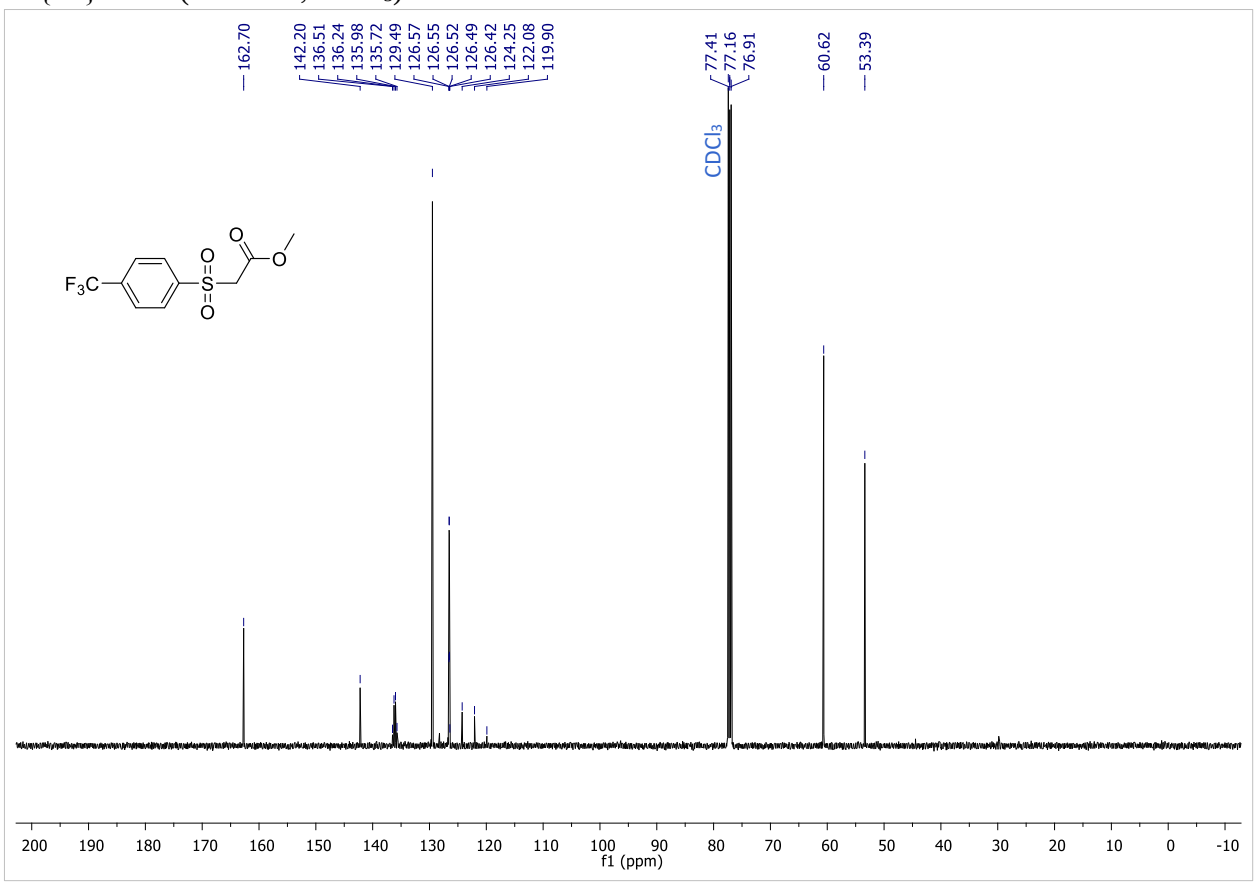


3pb

^{1}H NMR (500 MHz, $CDCl_3$)

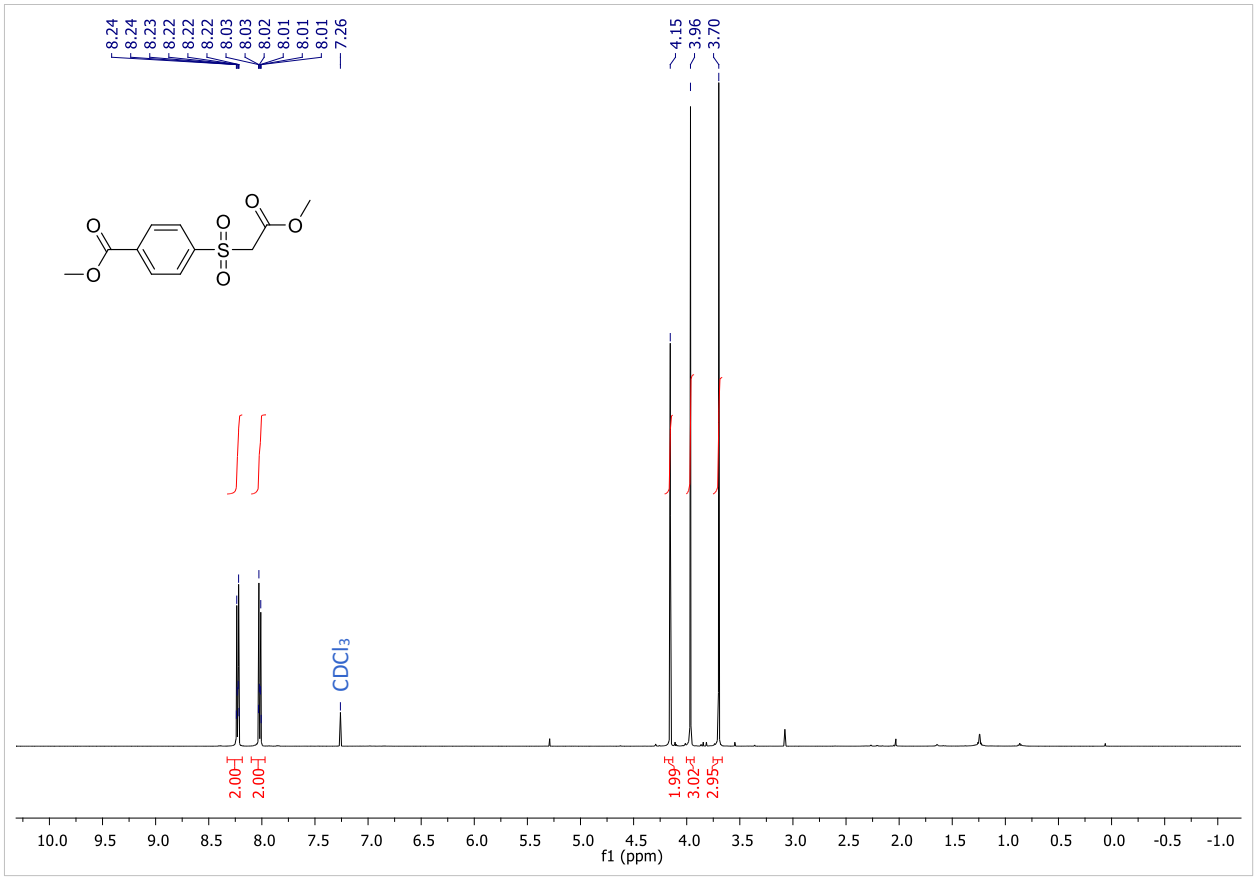


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

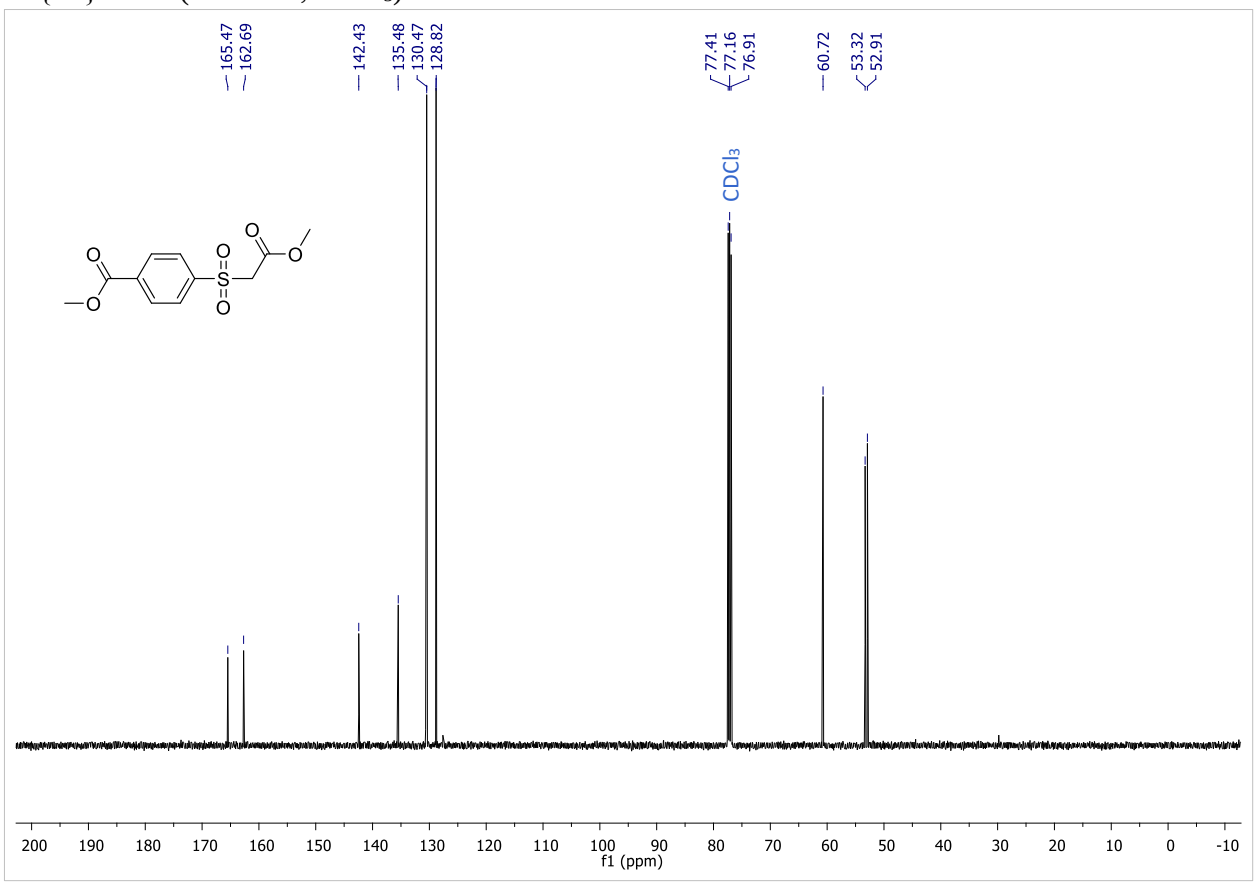


3qb

^{1}H NMR (500 MHz, $CDCl_3$)

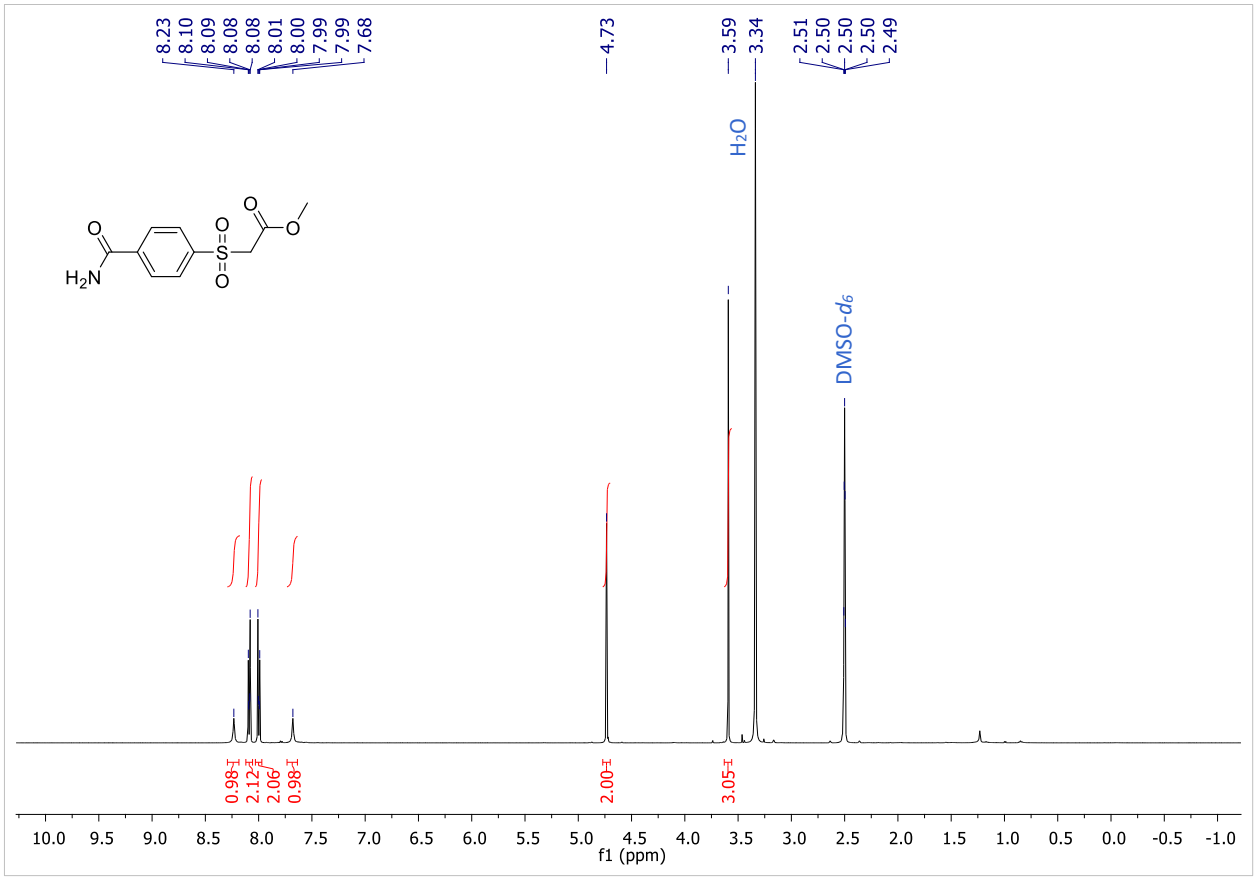


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

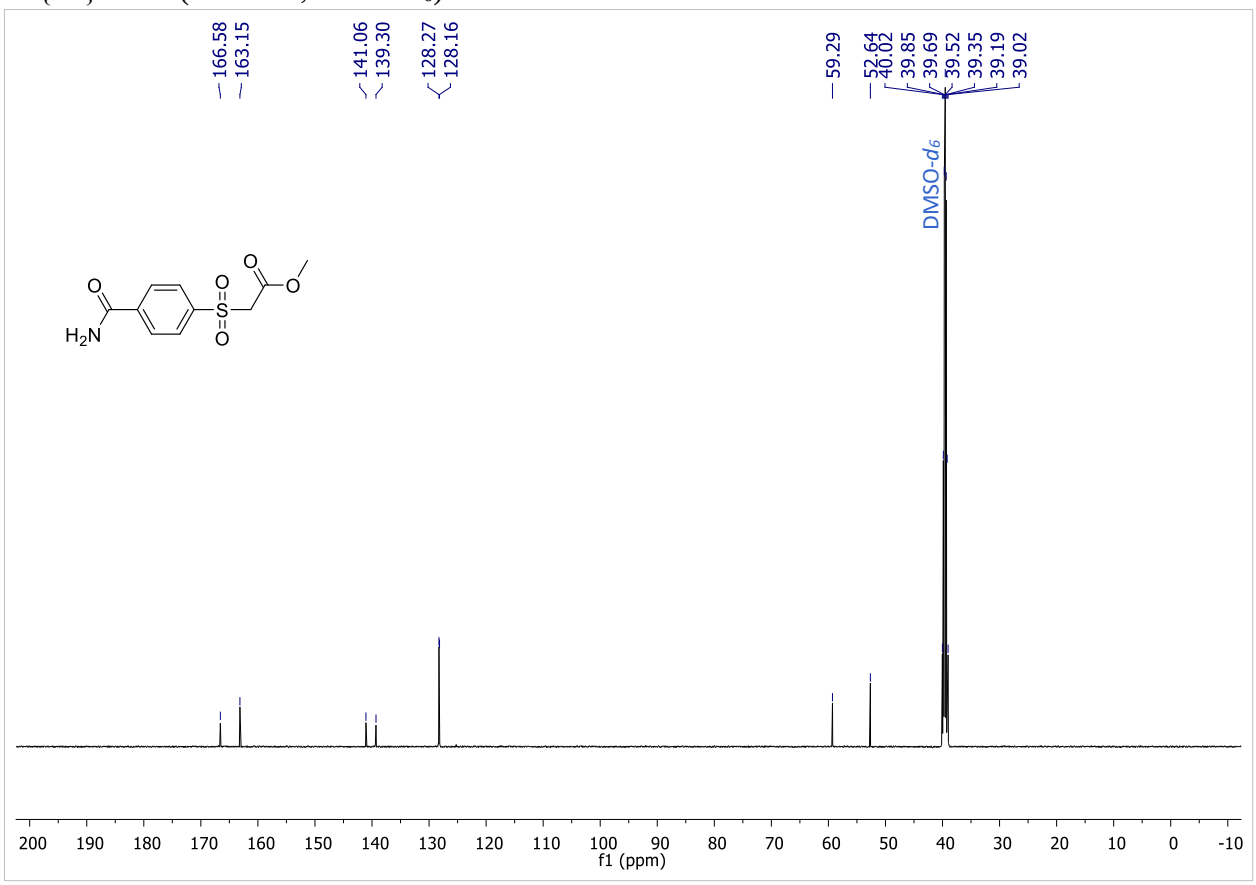


3rb

^{1}H NMR (500 MHz, DMSO-d_6)

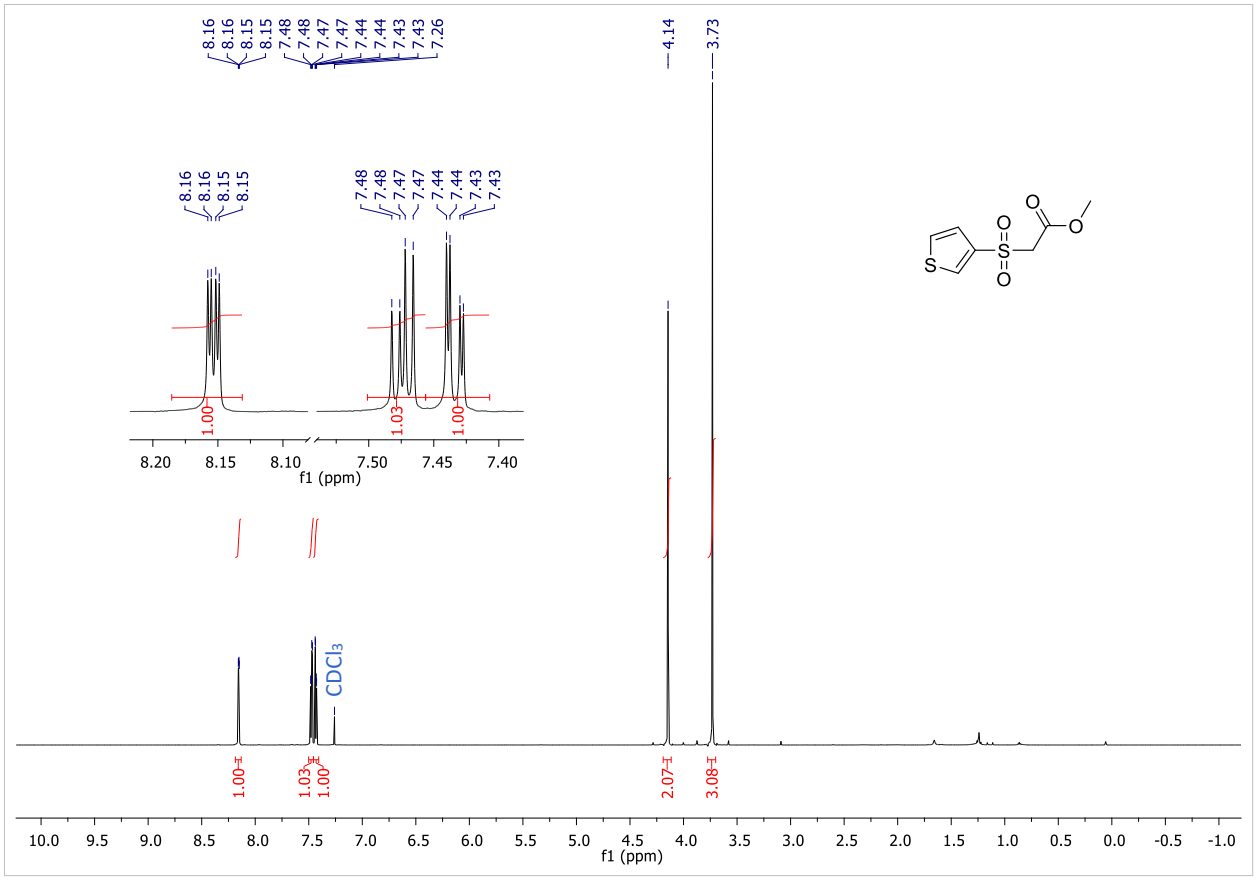


^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6)

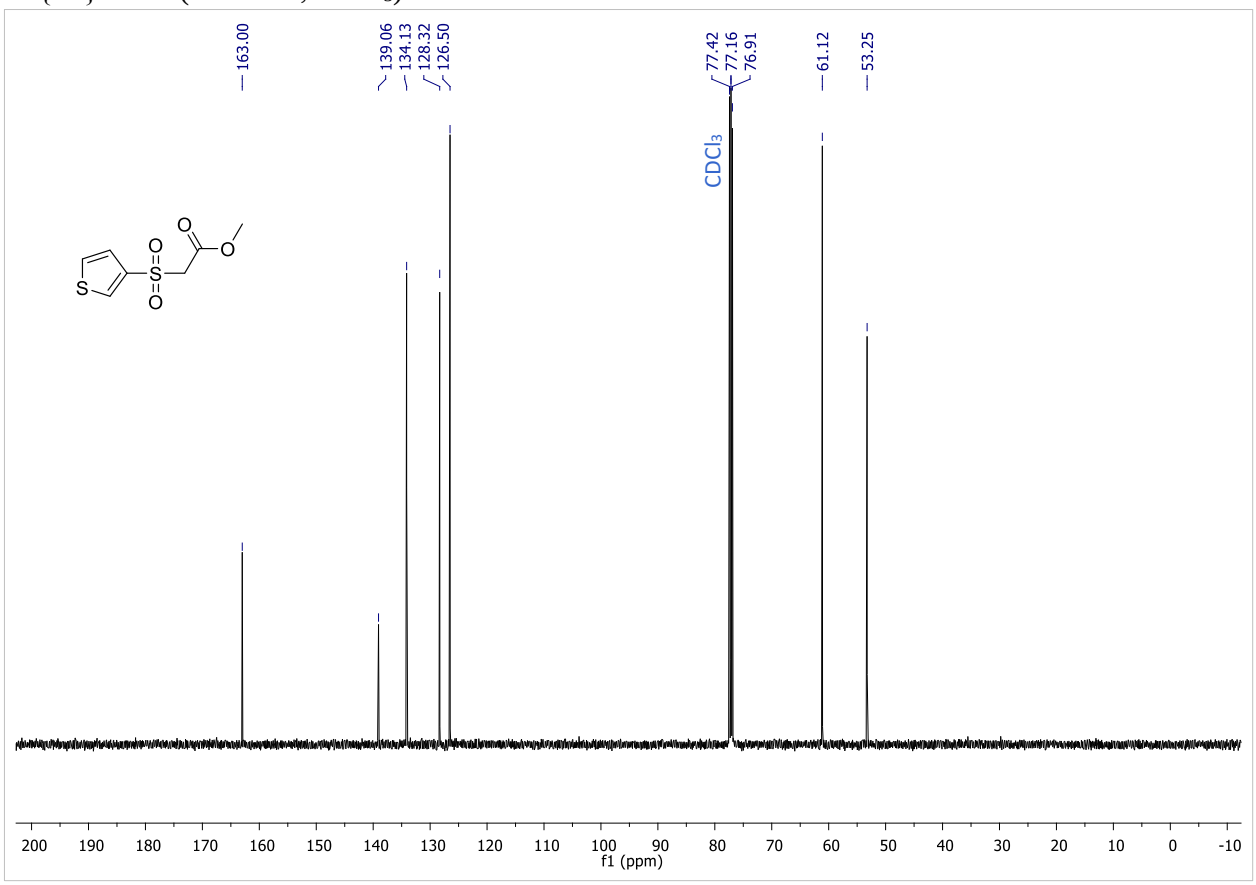


3sb

^{1}H NMR (500 MHz, $CDCl_3$)

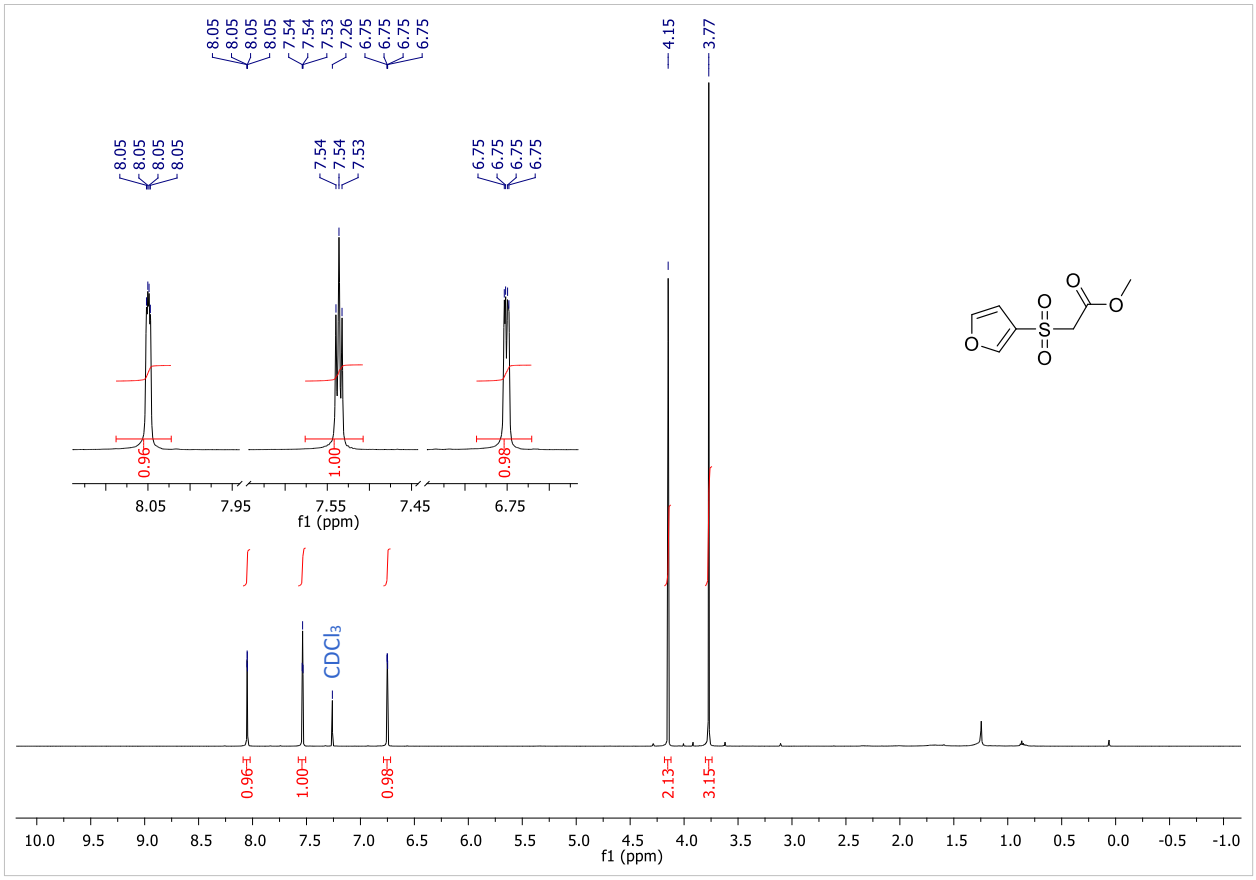


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

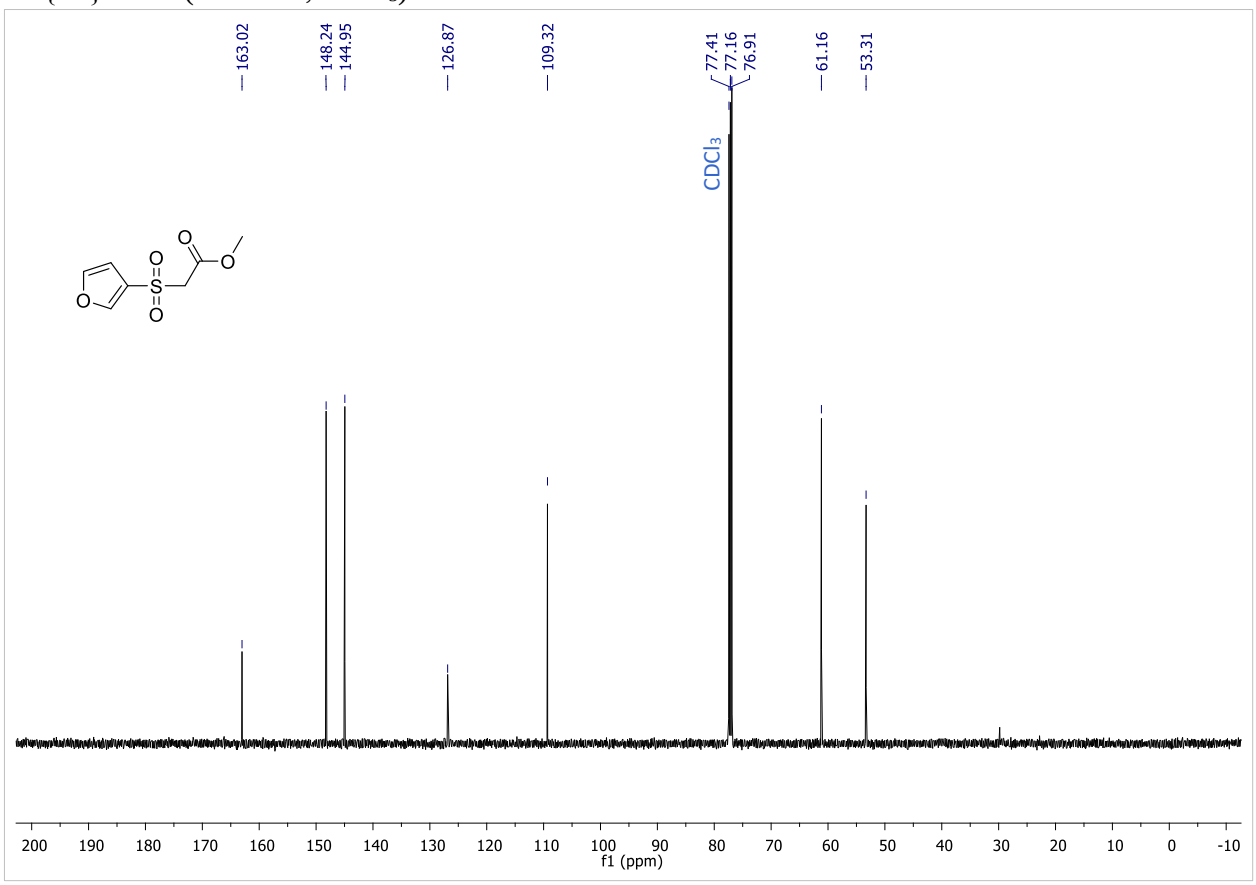


3tb

^{1}H NMR (500 MHz, $CDCl_3$)

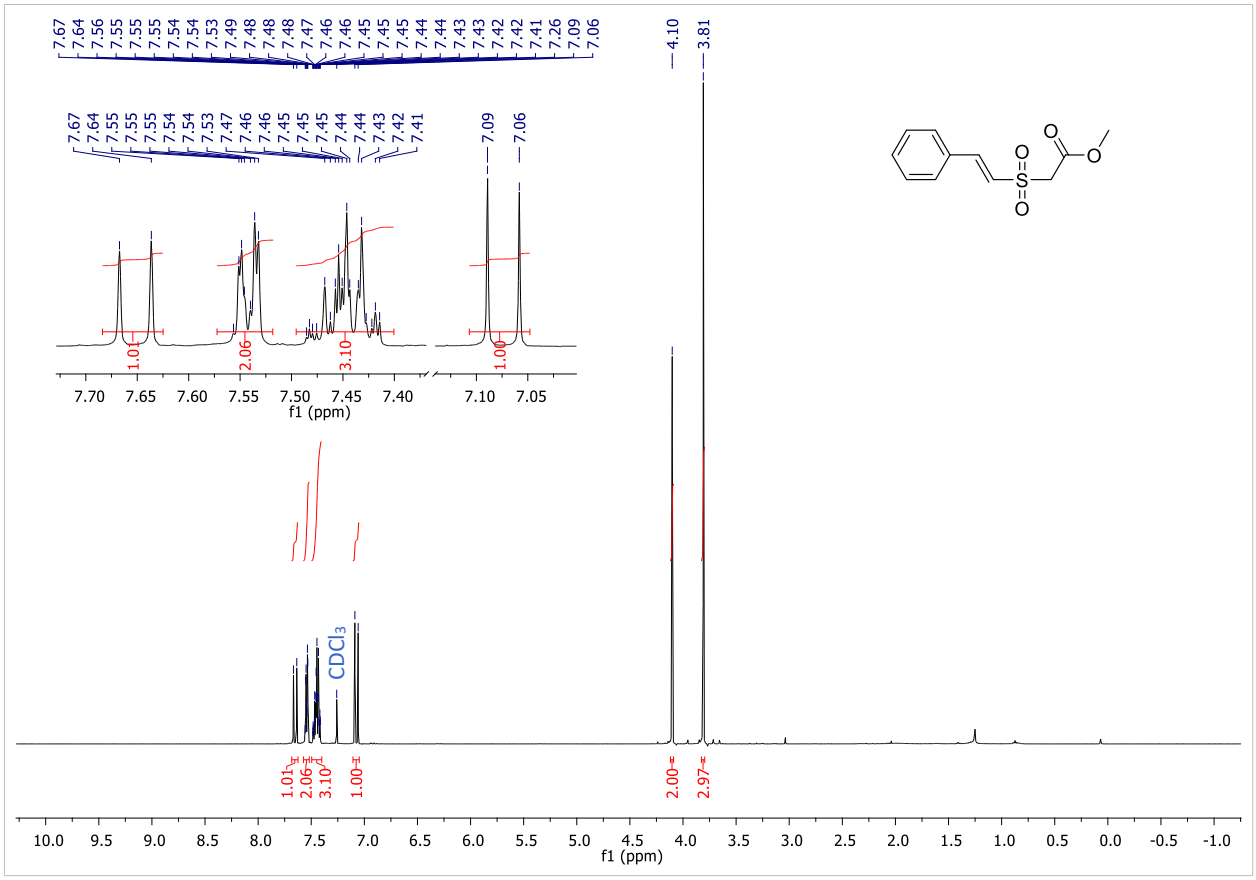


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

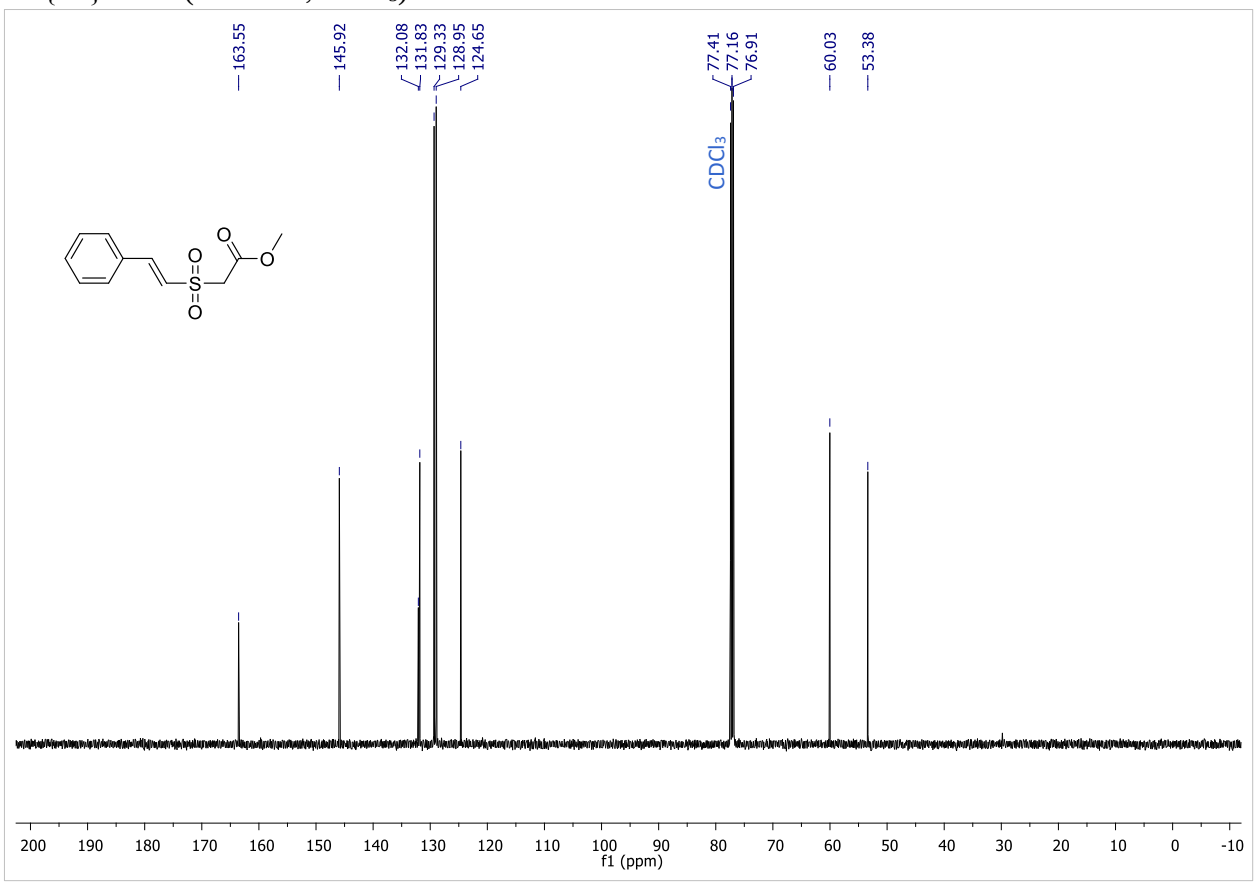


3ub

^{1}H NMR (500 MHz, $CDCl_3$)

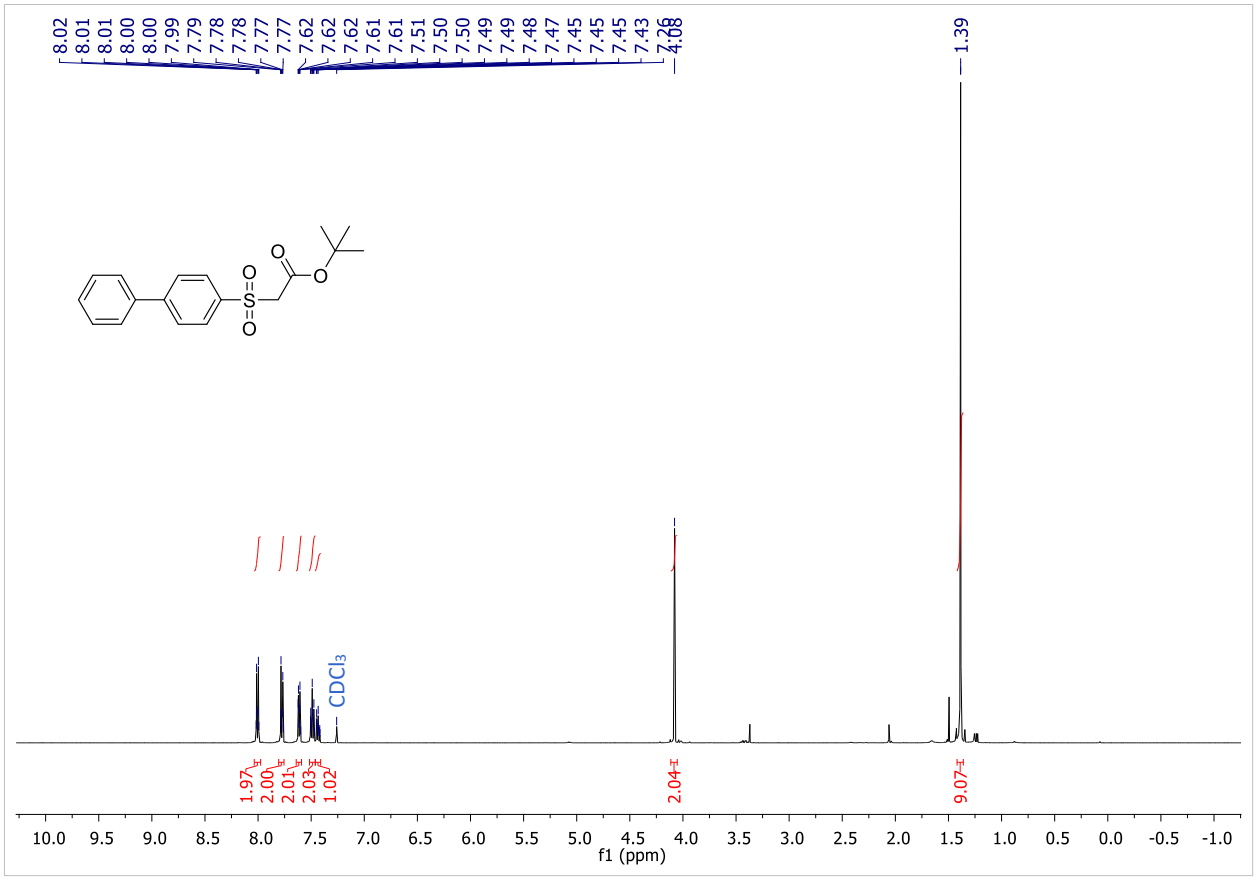


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

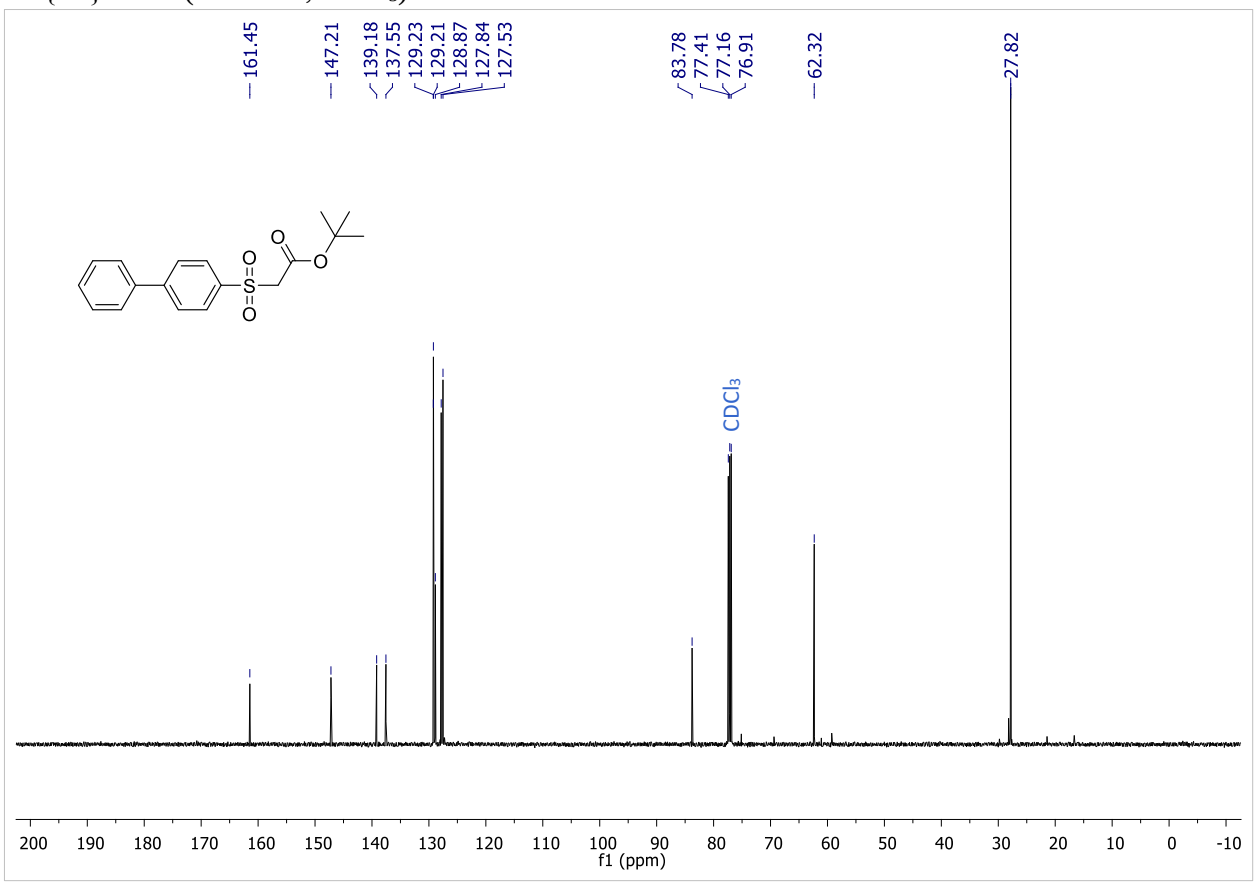


3ac

^{1}H NMR (500 MHz, $CDCl_3$)

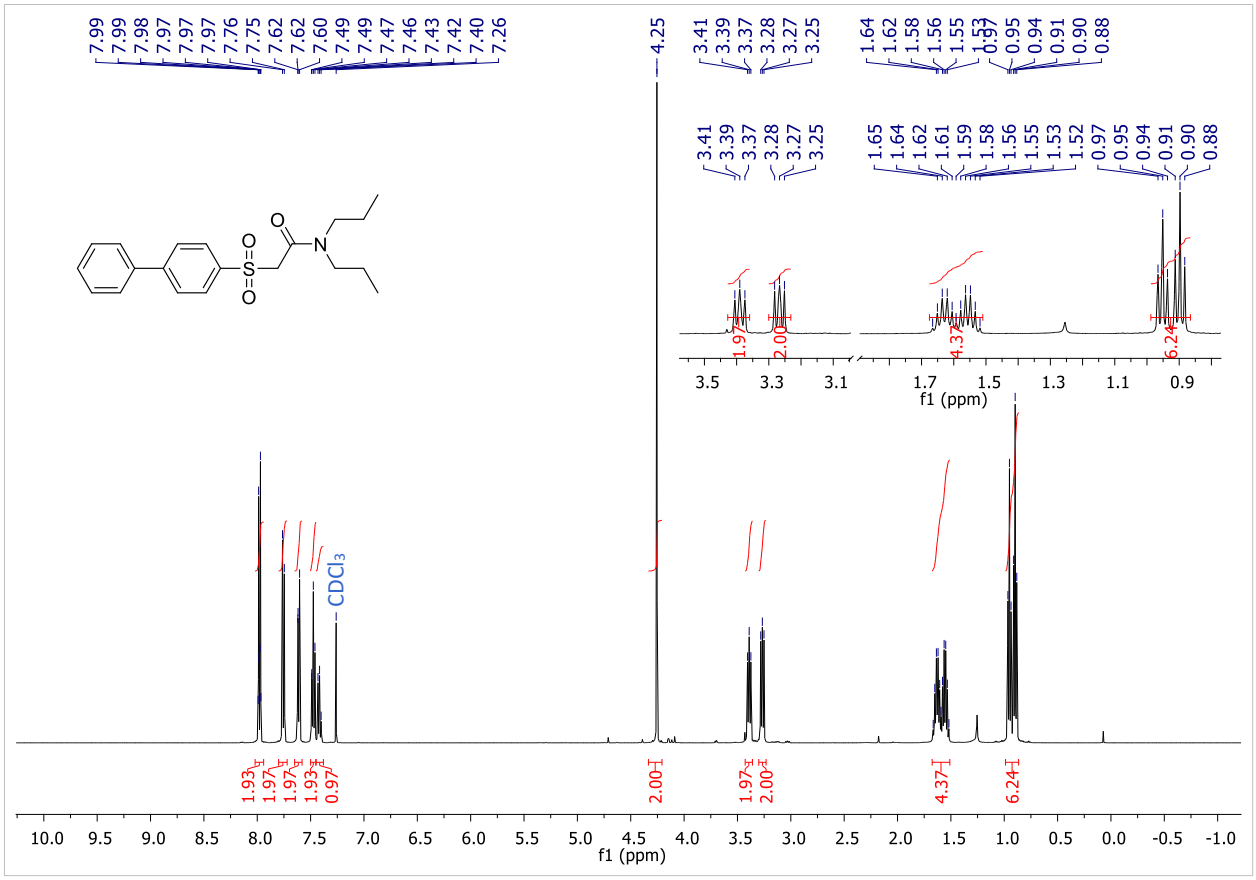


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

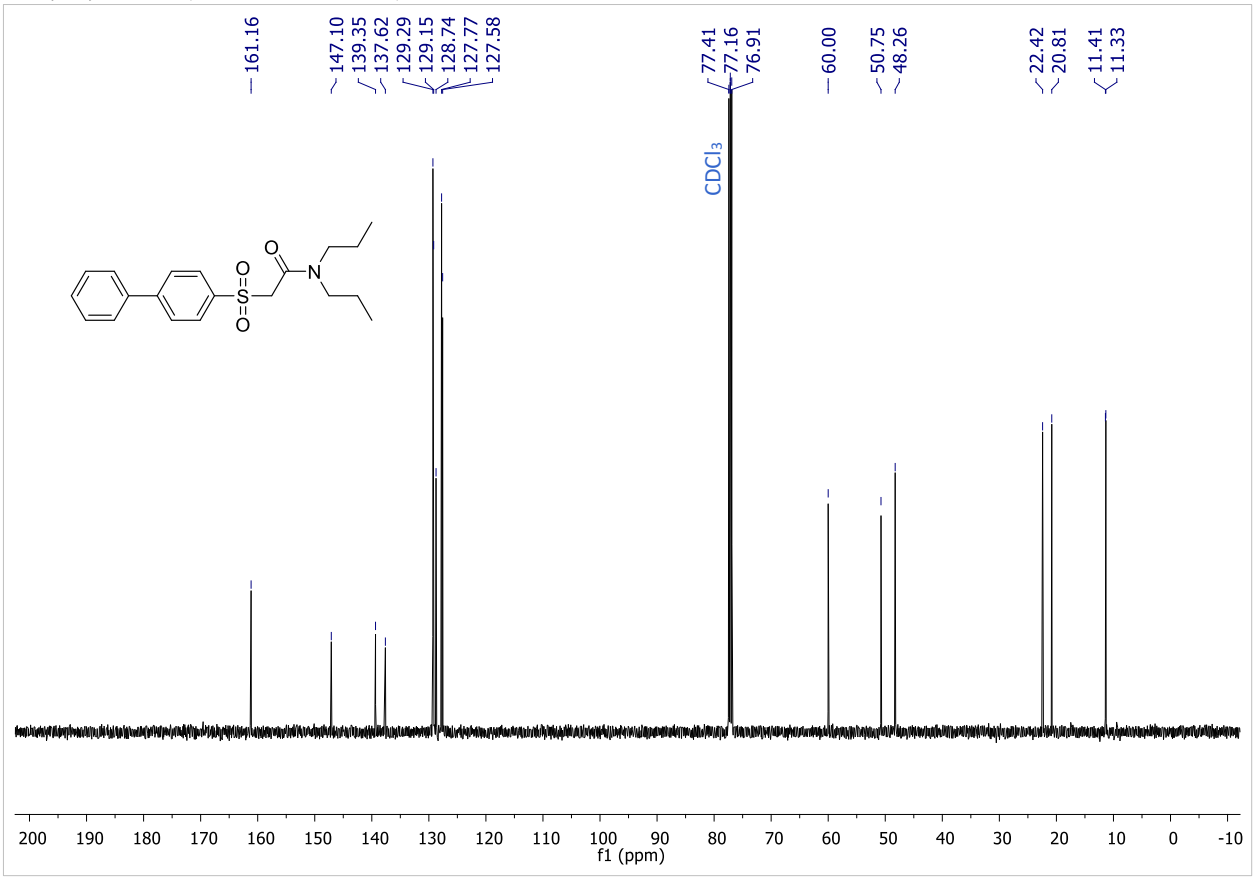


3ad

^{1}H NMR (500 MHz, $CDCl_3$)

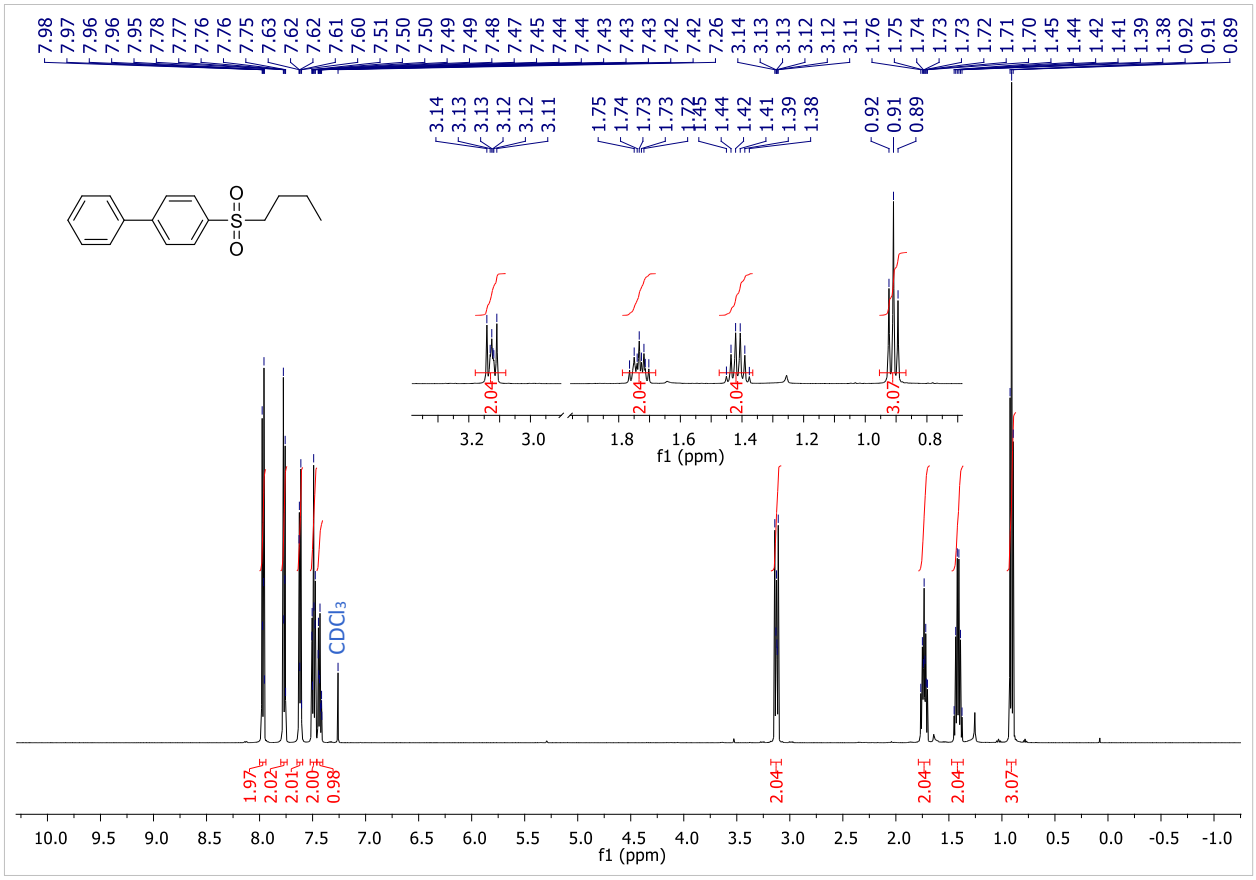


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

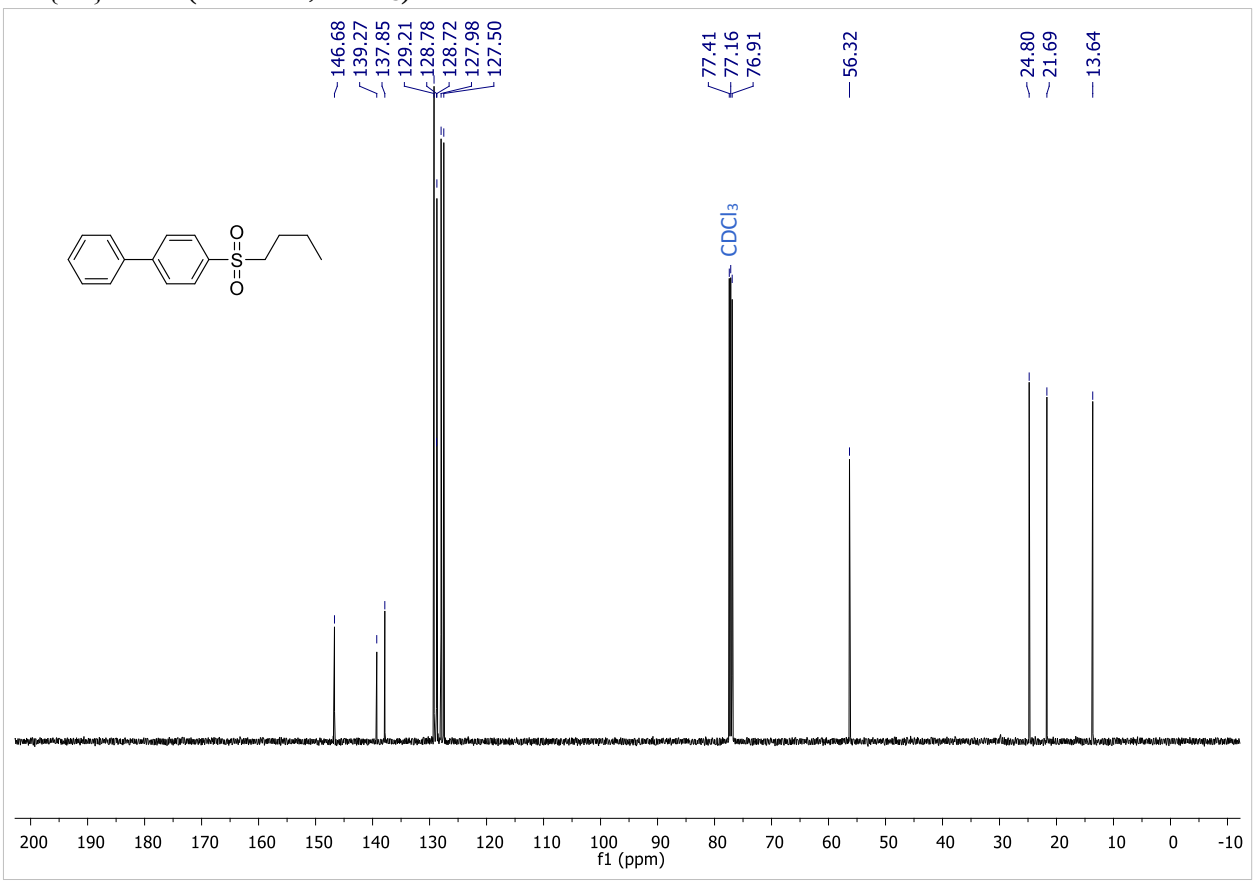


3ae

^{1}H NMR (500 MHz, $CDCl_3$)

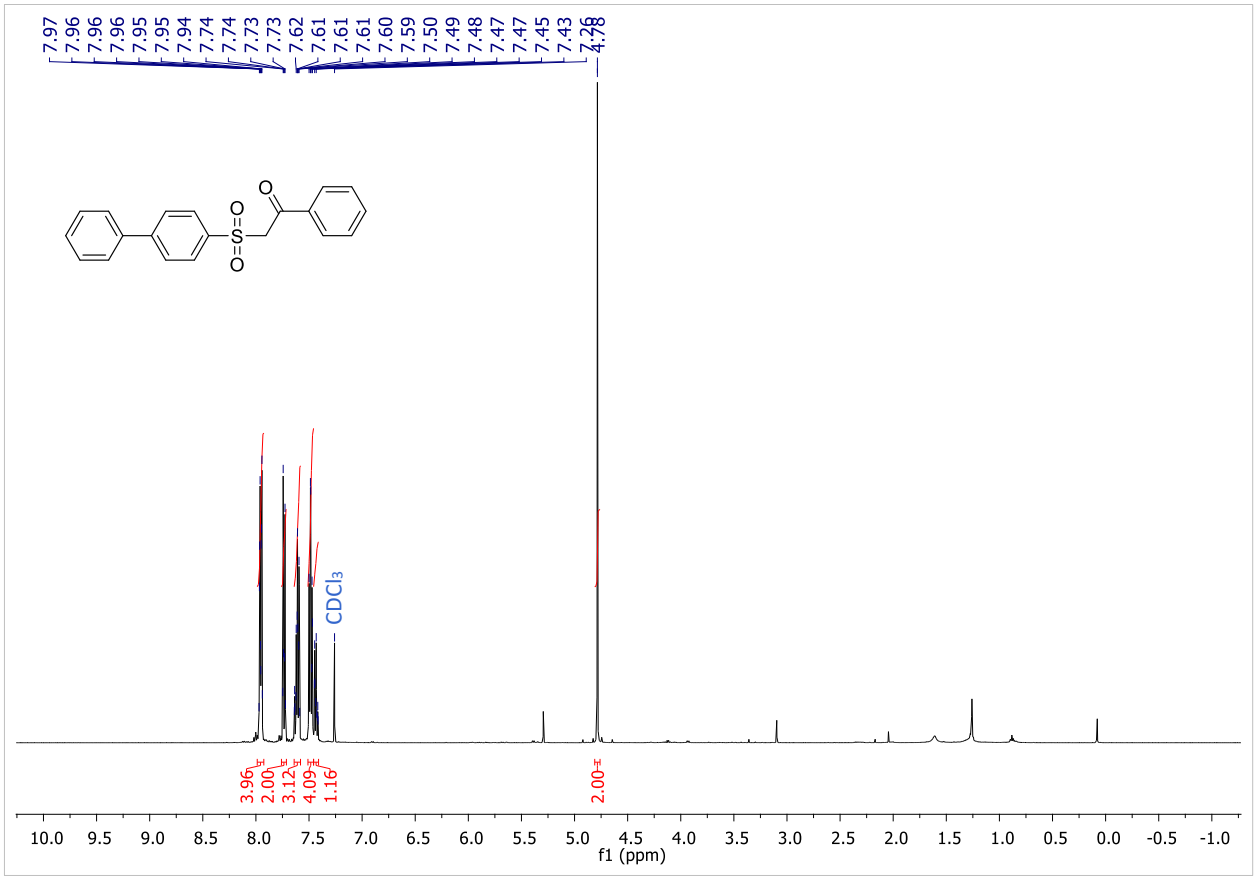


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

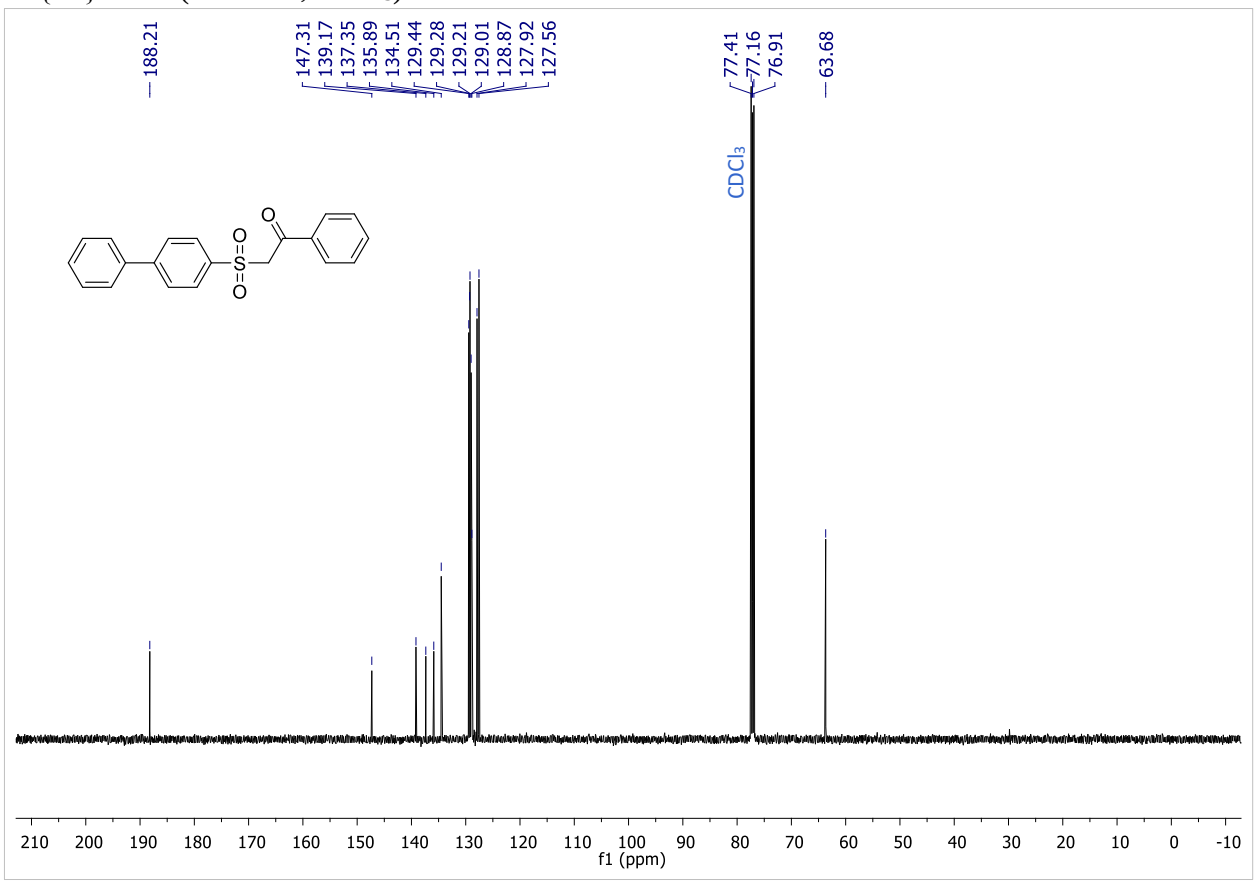


3af

^{1}H NMR (500 MHz, $CDCl_3$)

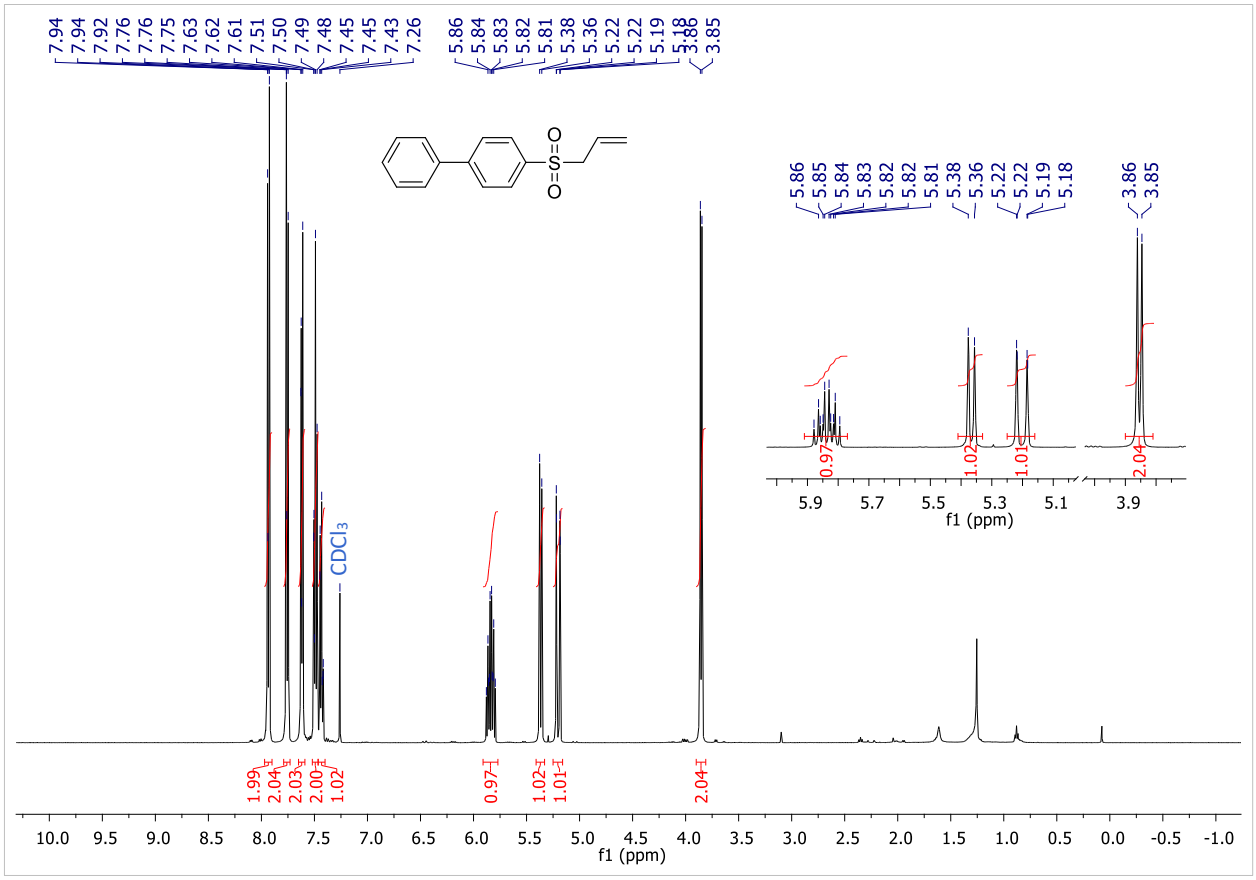


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

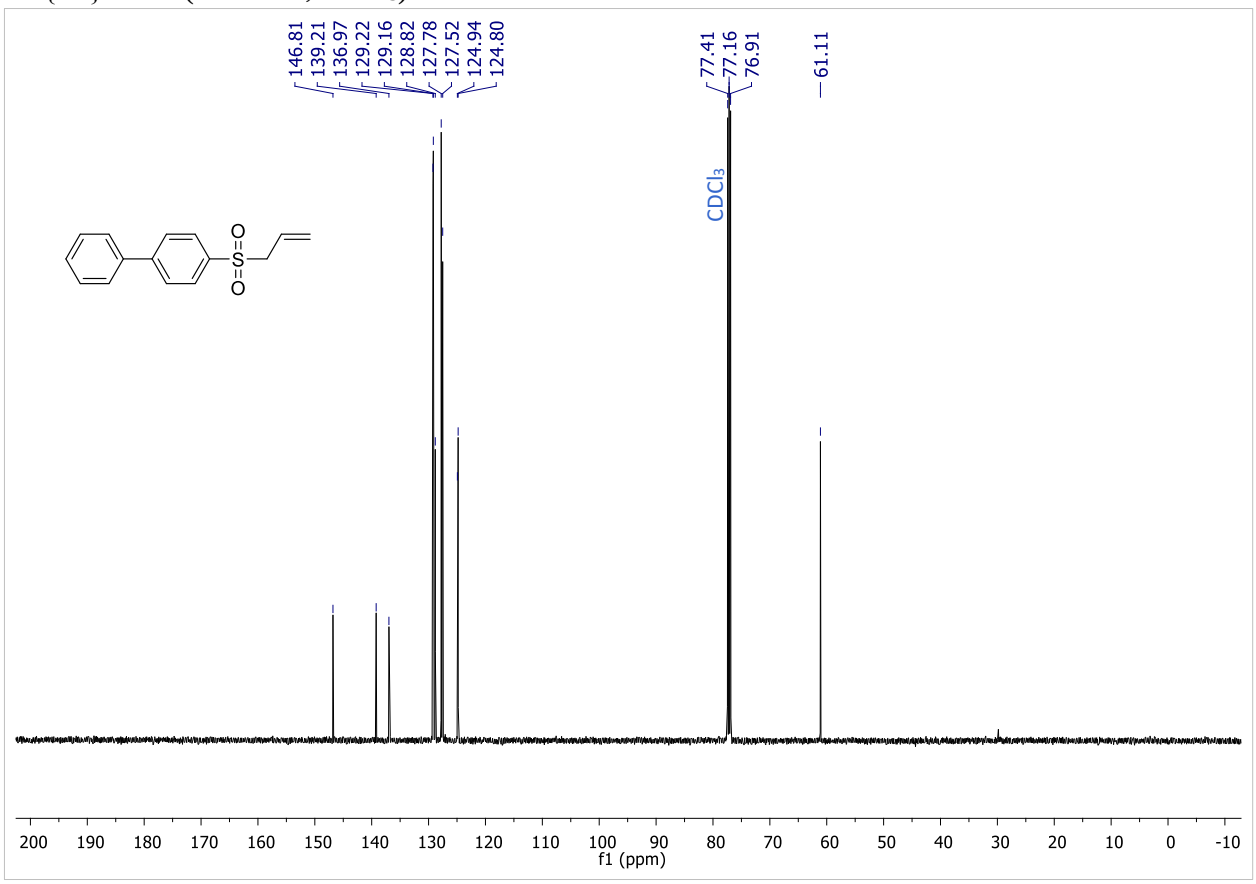


3ag

^{1}H NMR (500 MHz, $CDCl_3$)

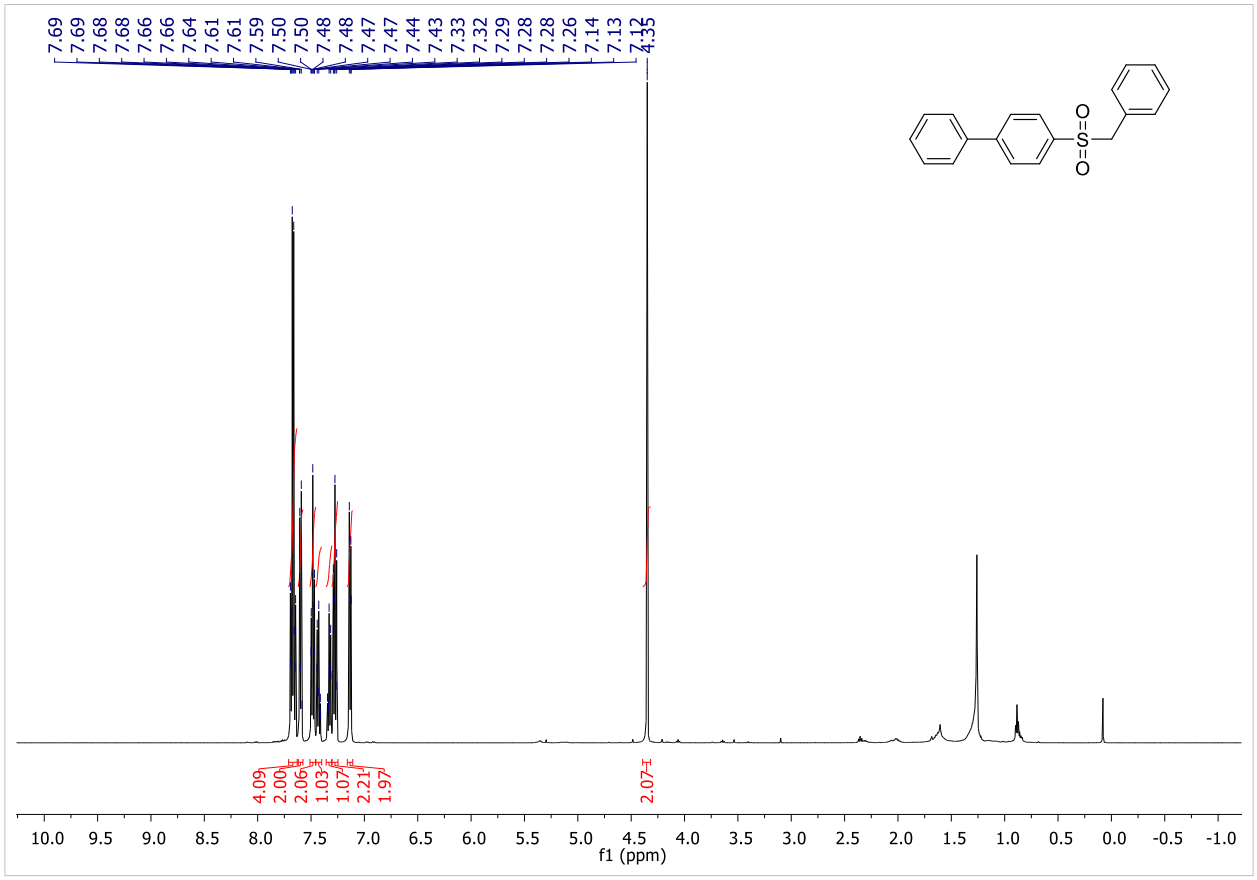


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

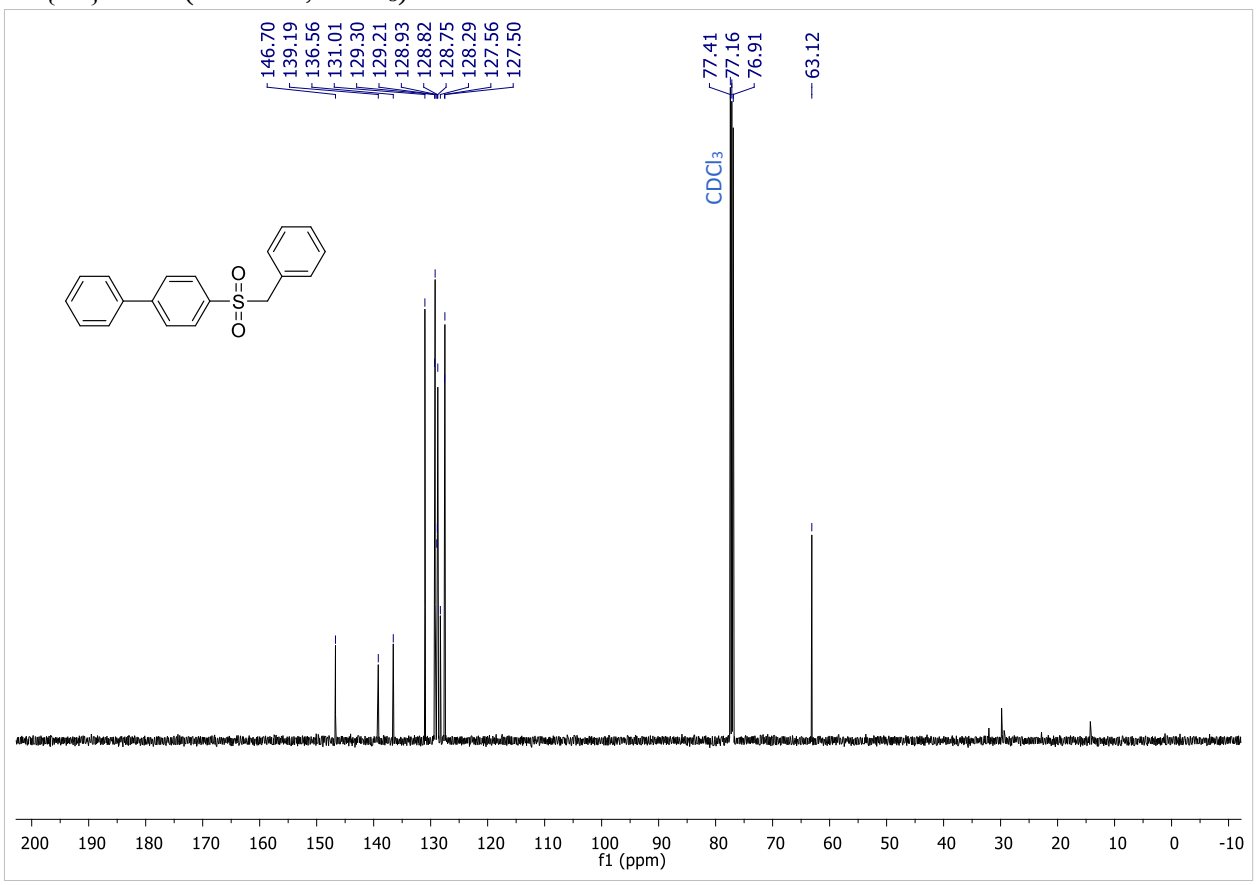


3ah

^{1}H NMR (500 MHz, $CDCl_3$)

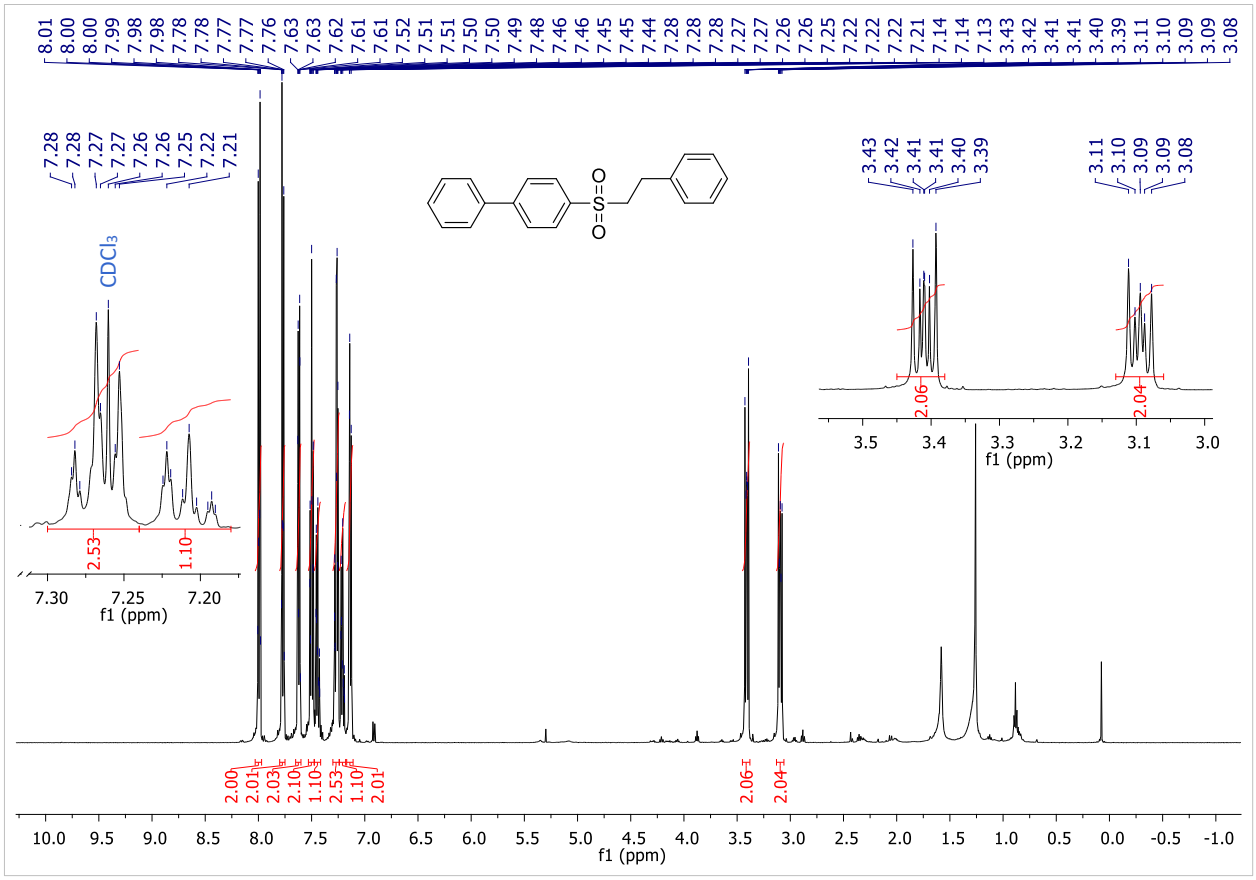


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

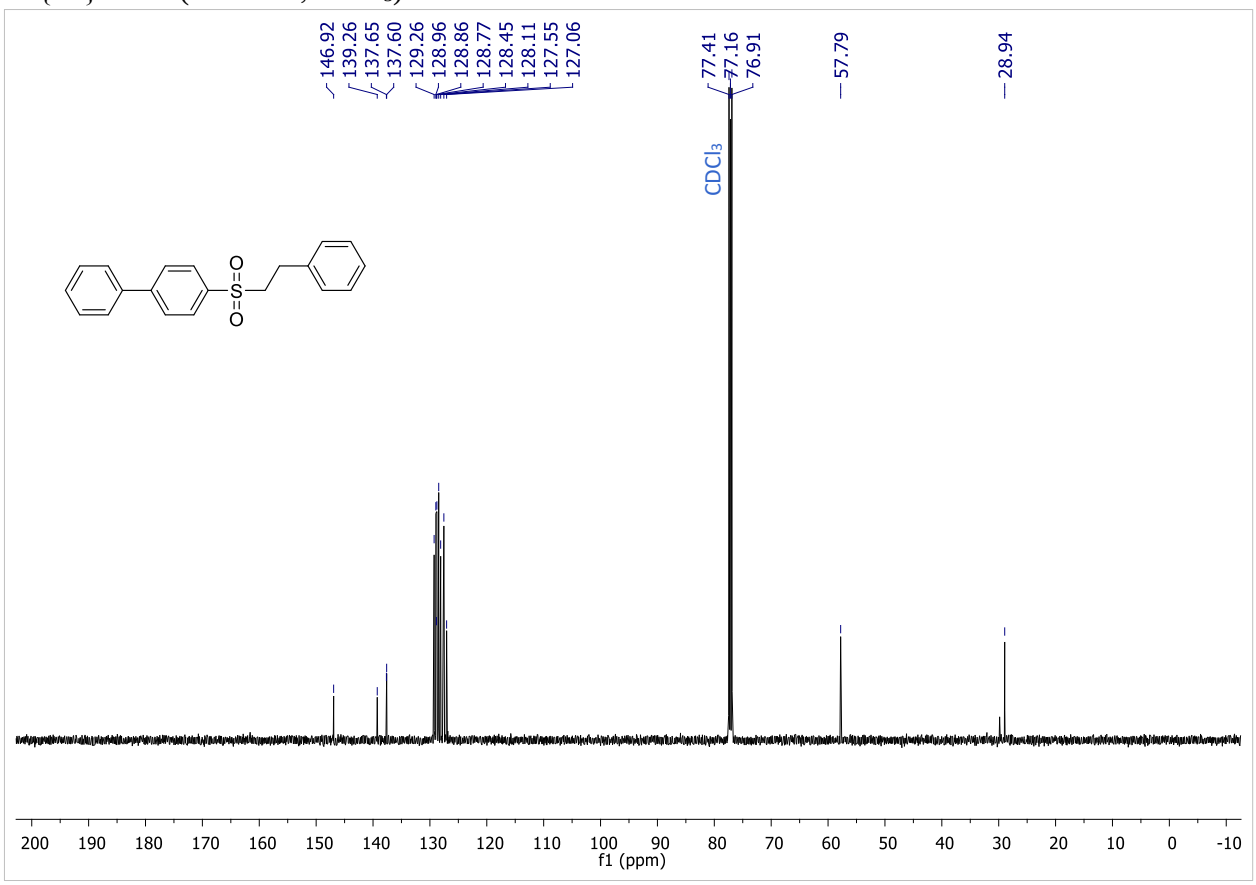


3ai

^{1}H NMR (500 MHz, $CDCl_3$)

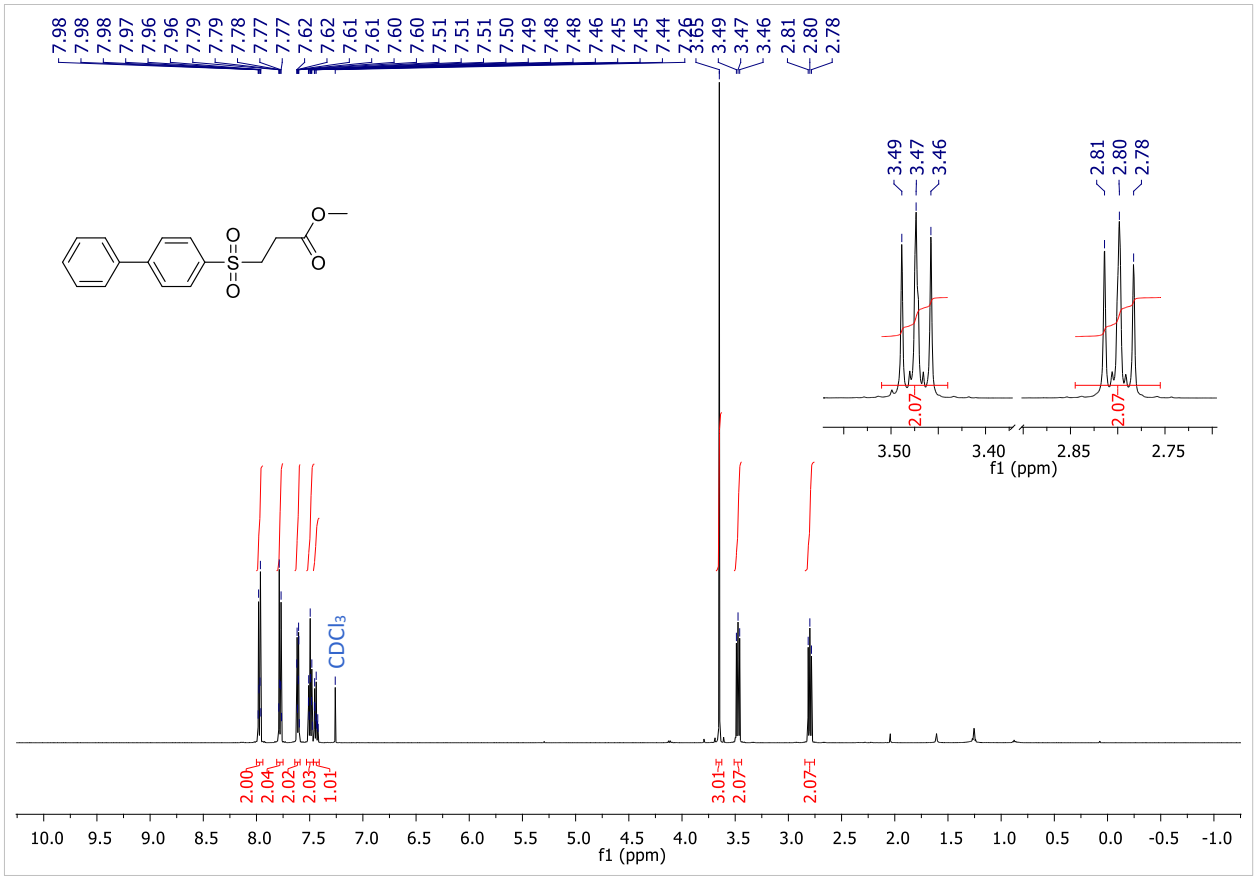


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

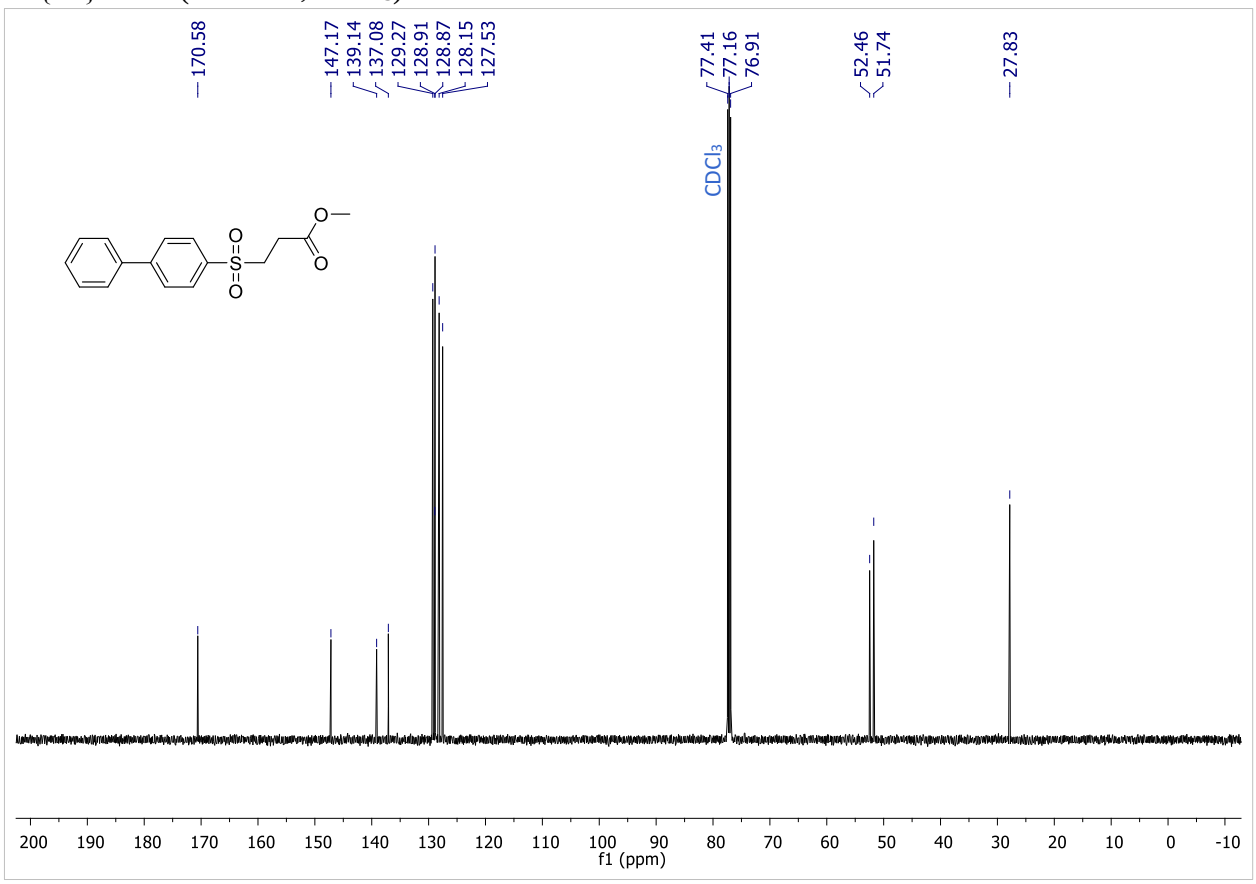


3aj

^{1}H NMR (500 MHz, $CDCl_3$)

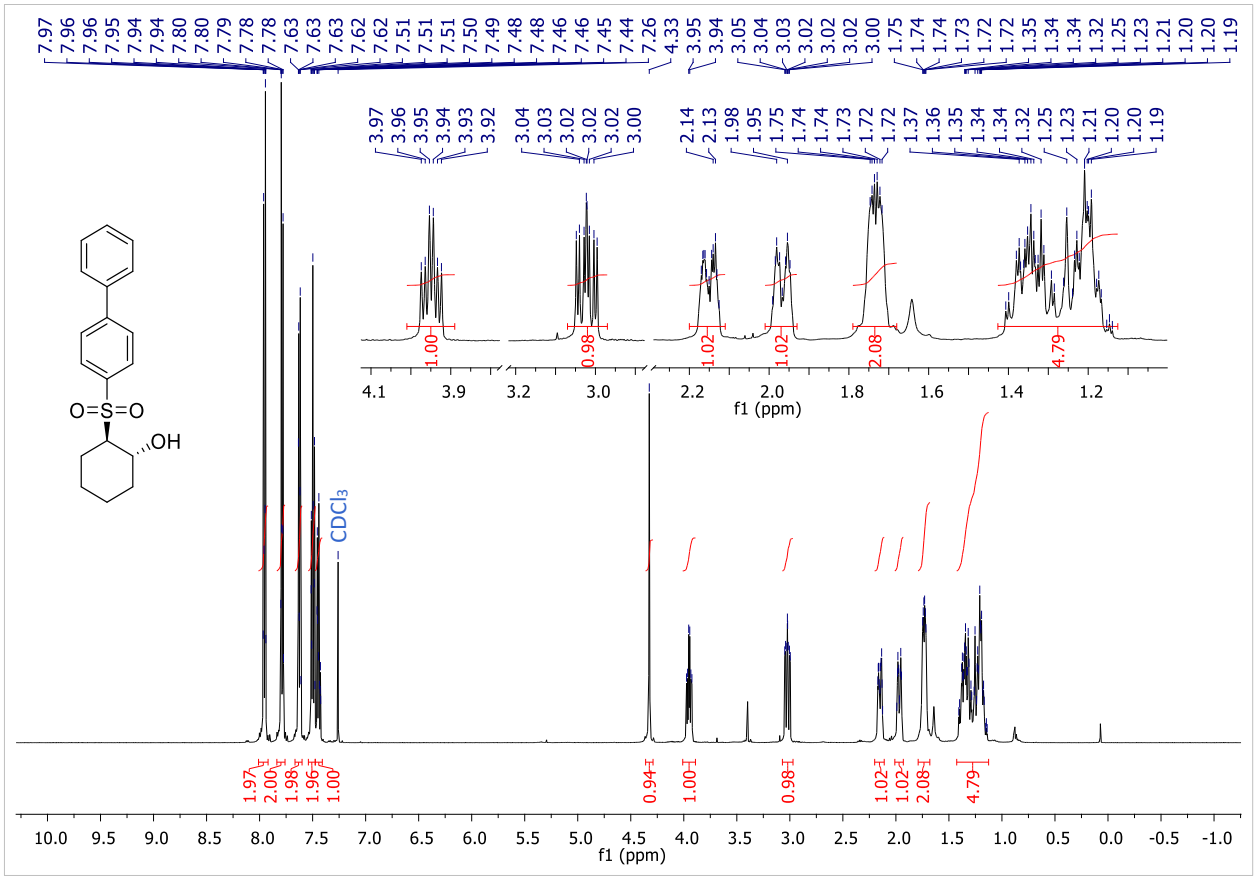


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

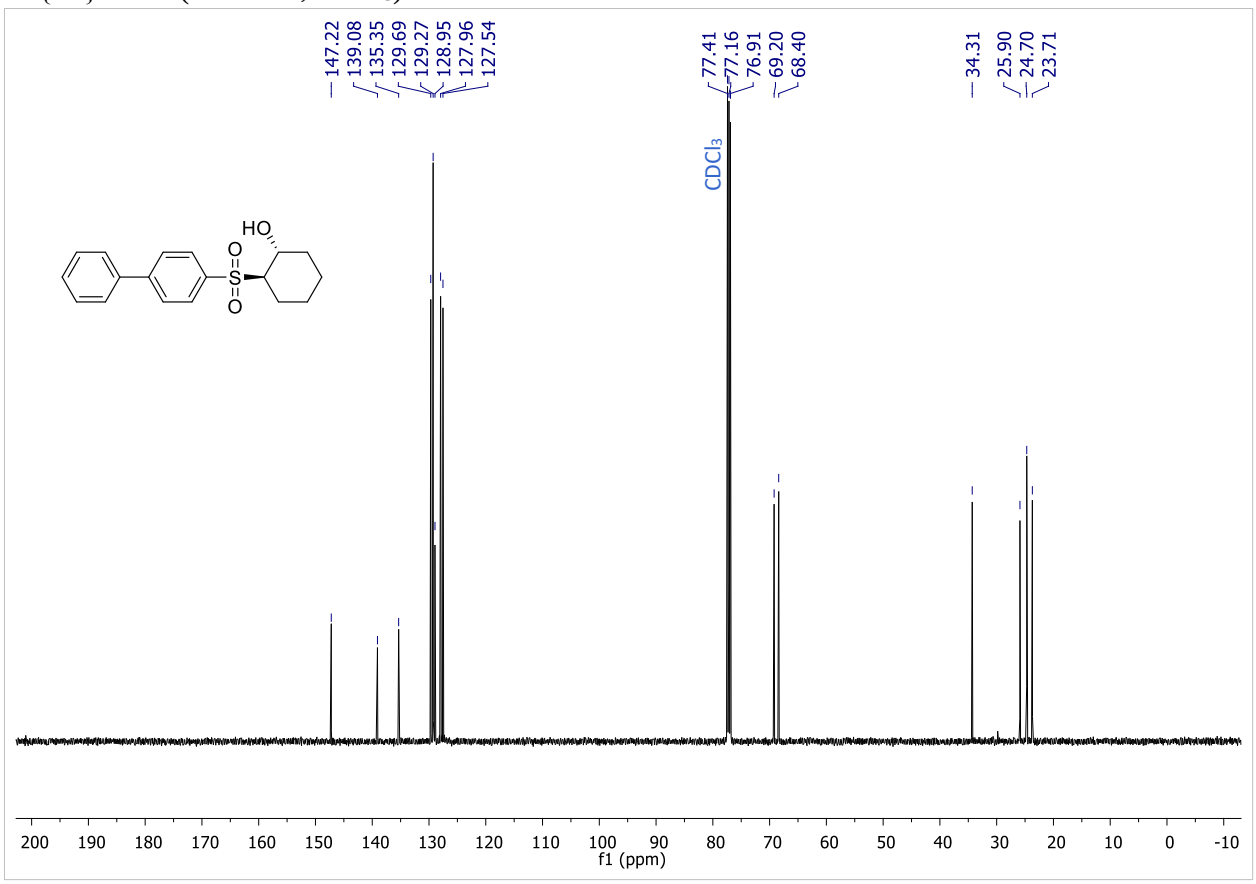


3ak

^{1}H NMR (500 MHz, $CDCl_3$)

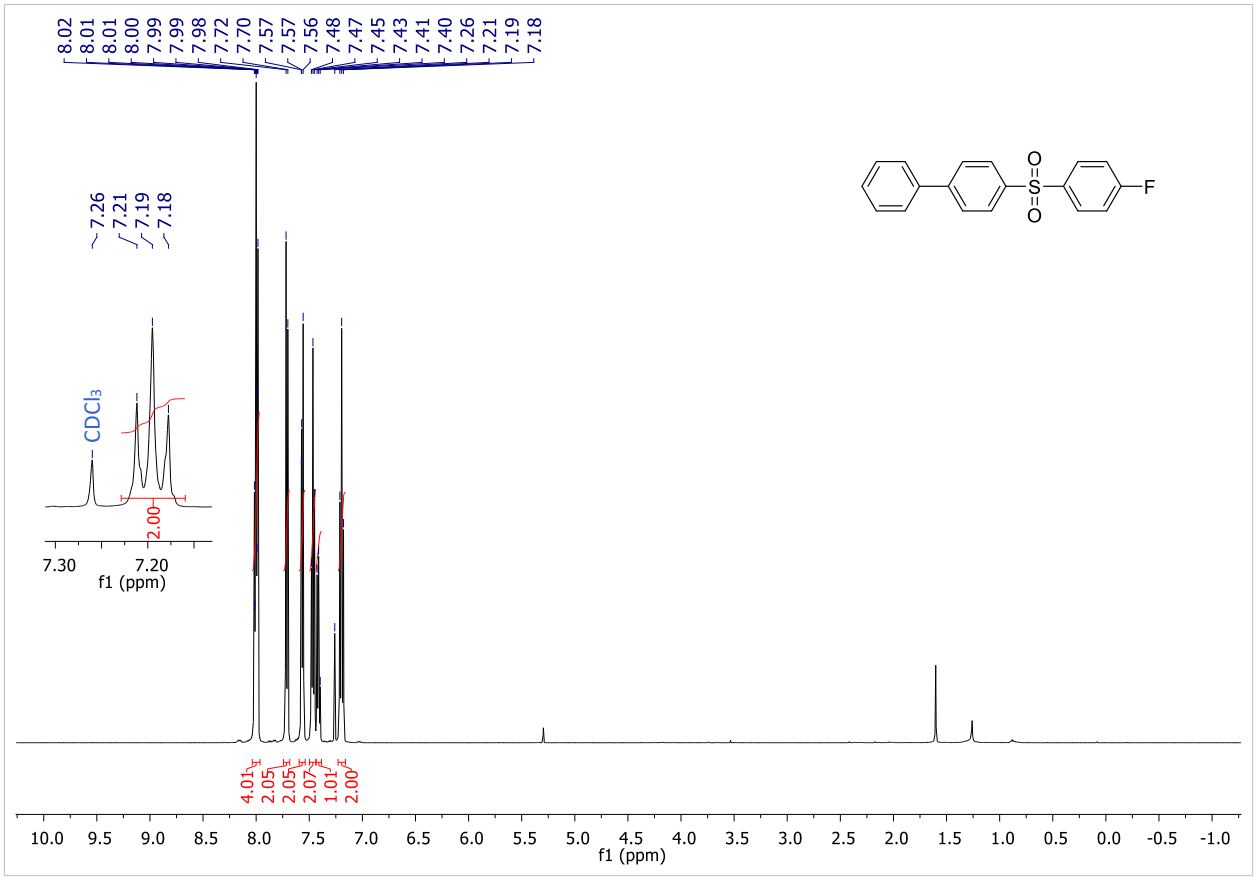


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

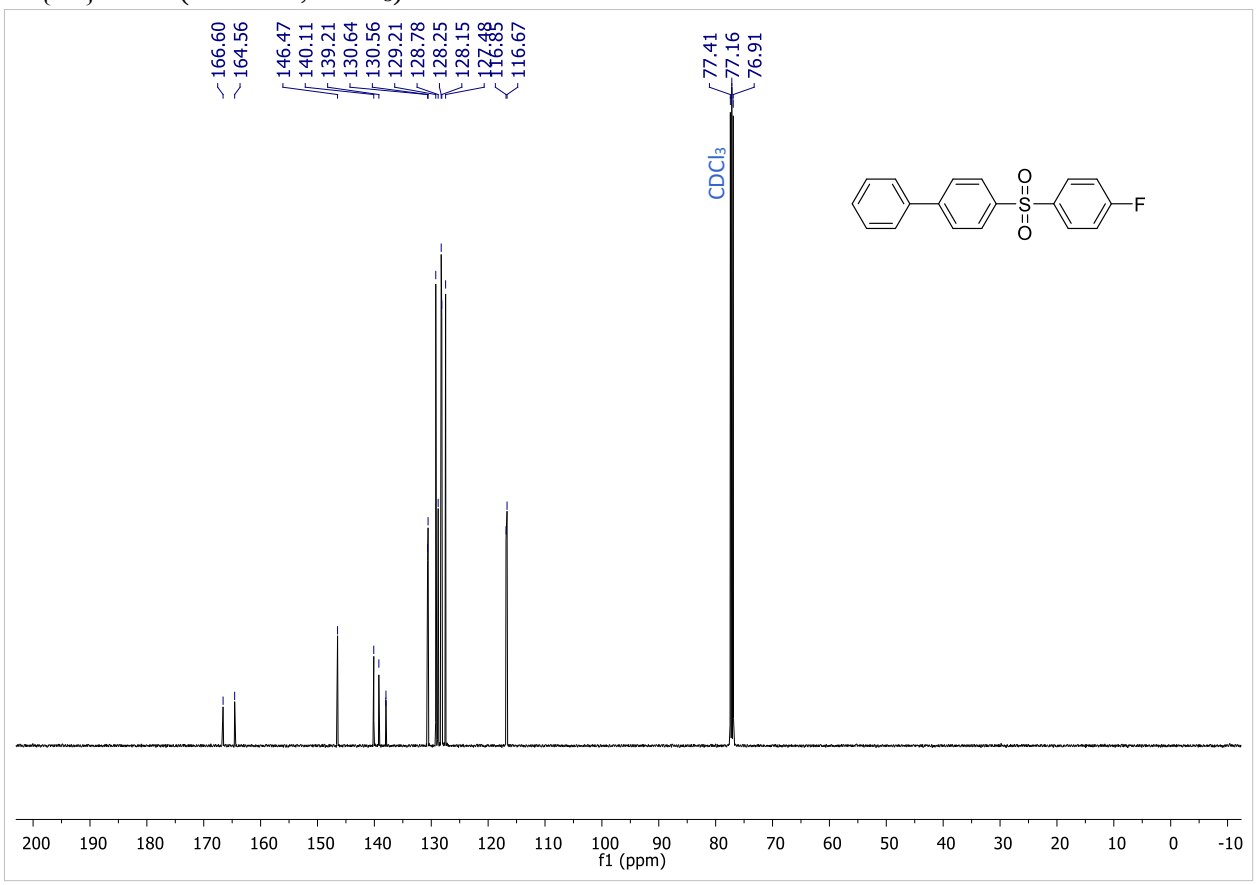


3al

^{1}H NMR (500 MHz, $CDCl_3$)

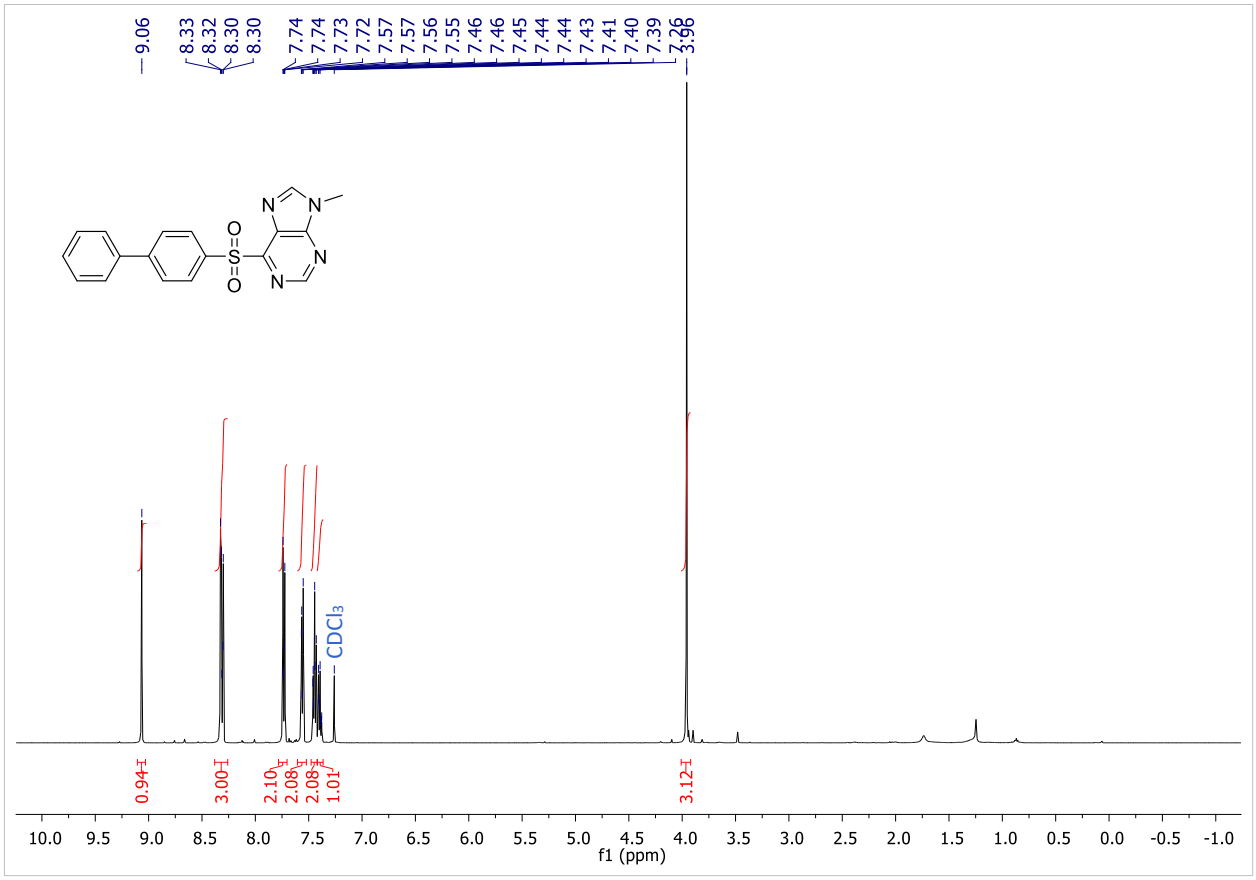


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

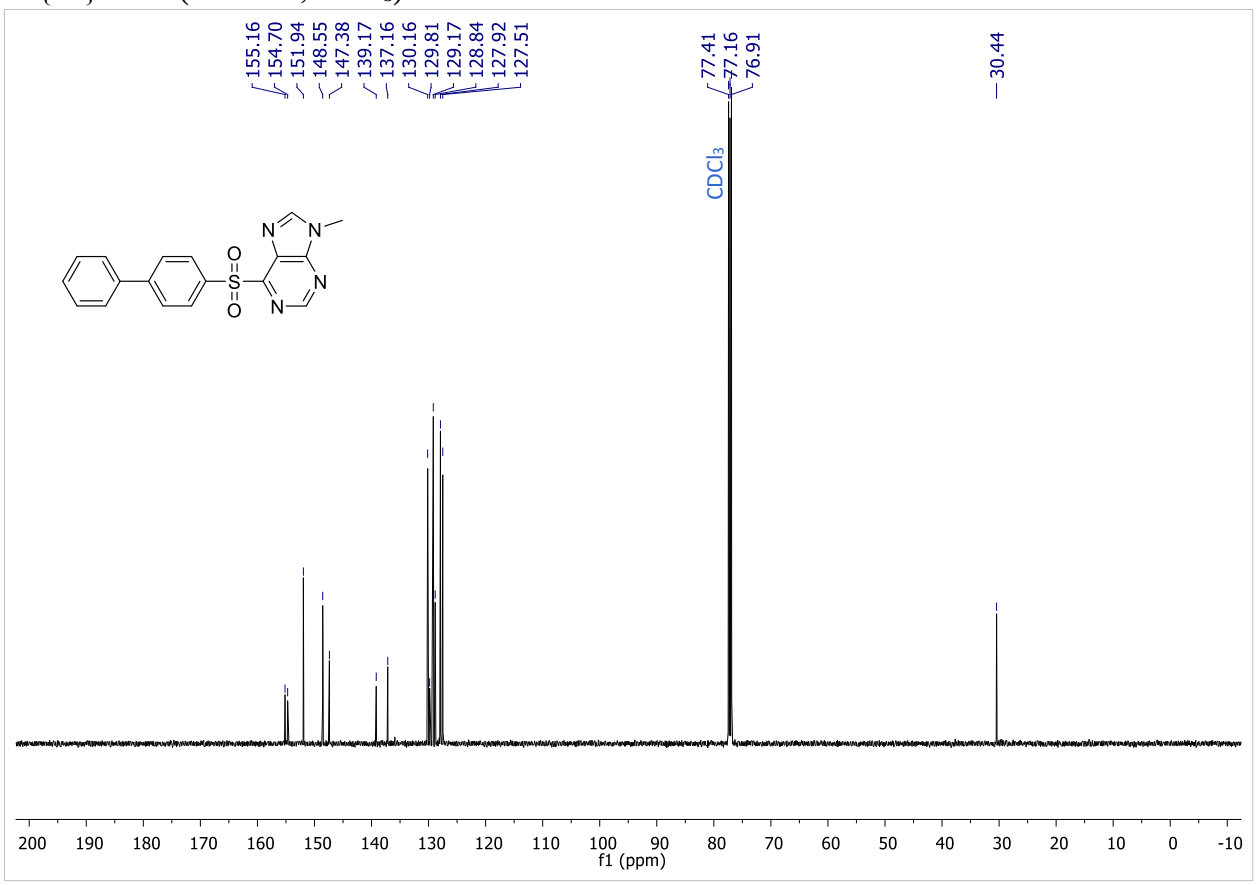


3am

^{1}H NMR (500 MHz, $CDCl_3$)

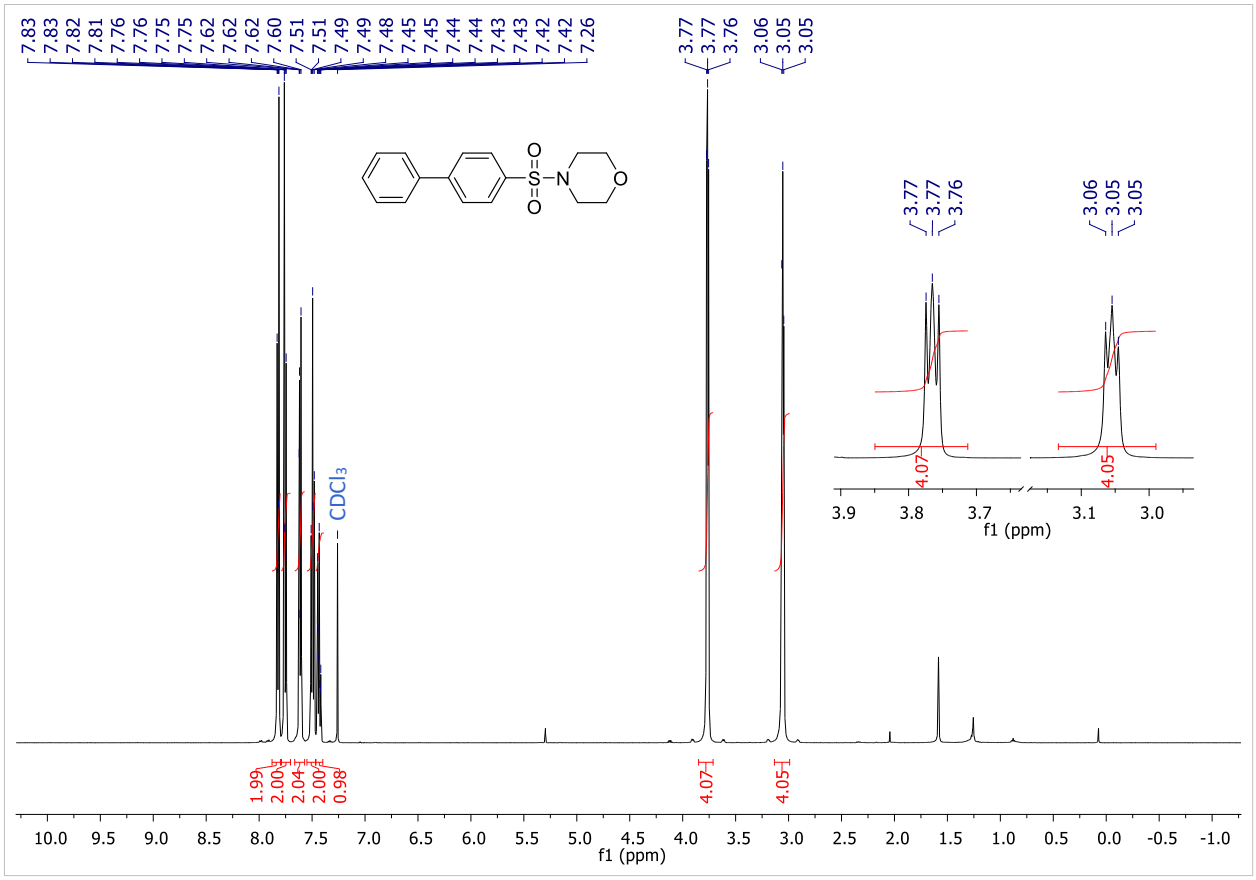


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

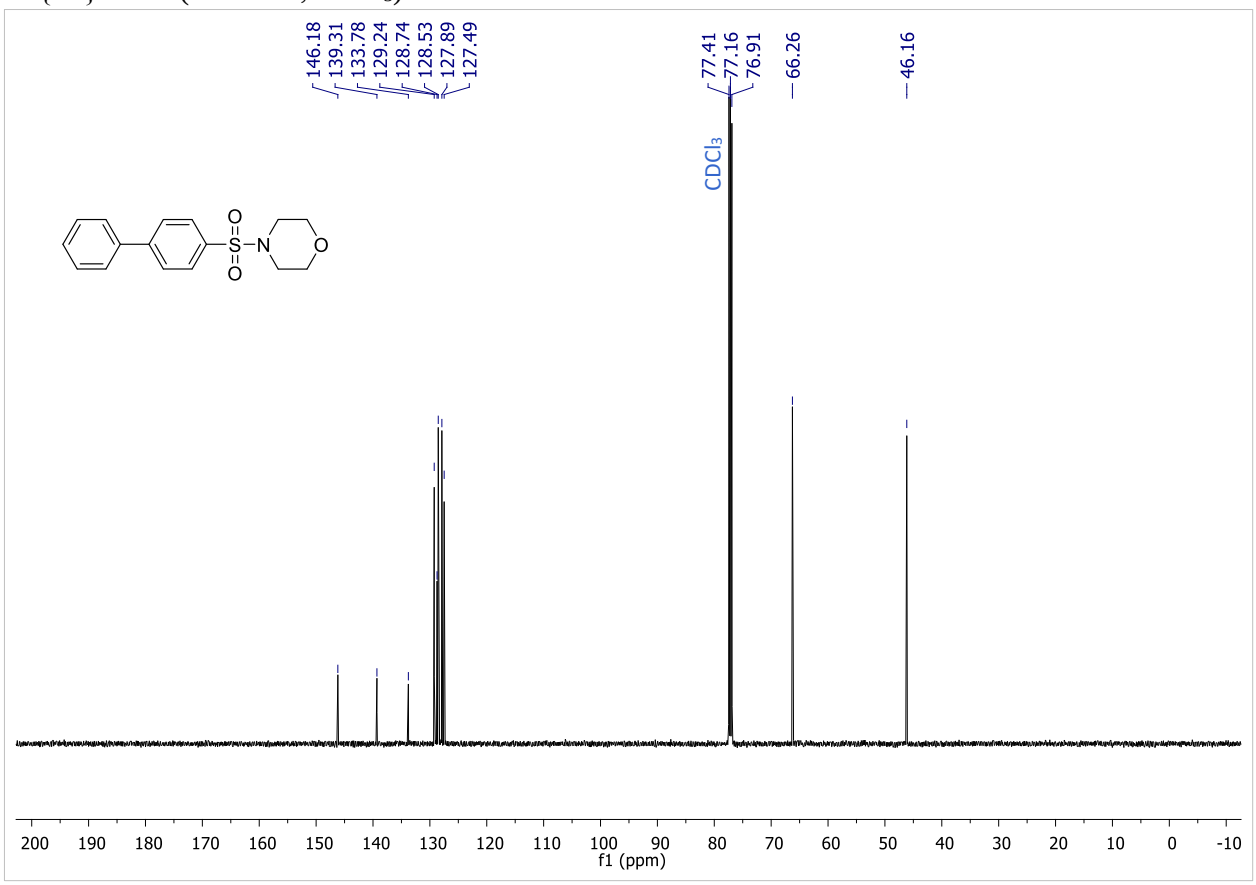


3an

^{1}H NMR (500 MHz, $CDCl_3$)

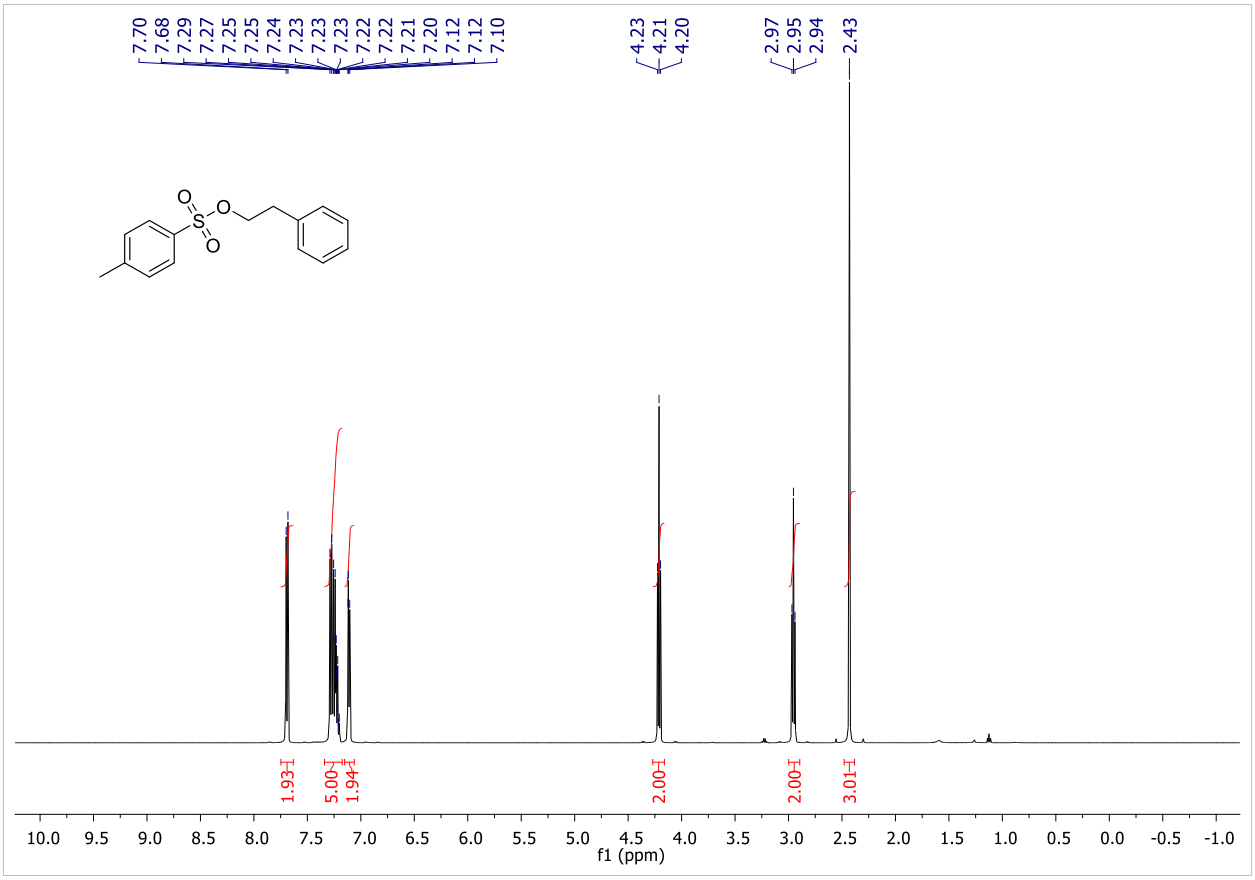


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

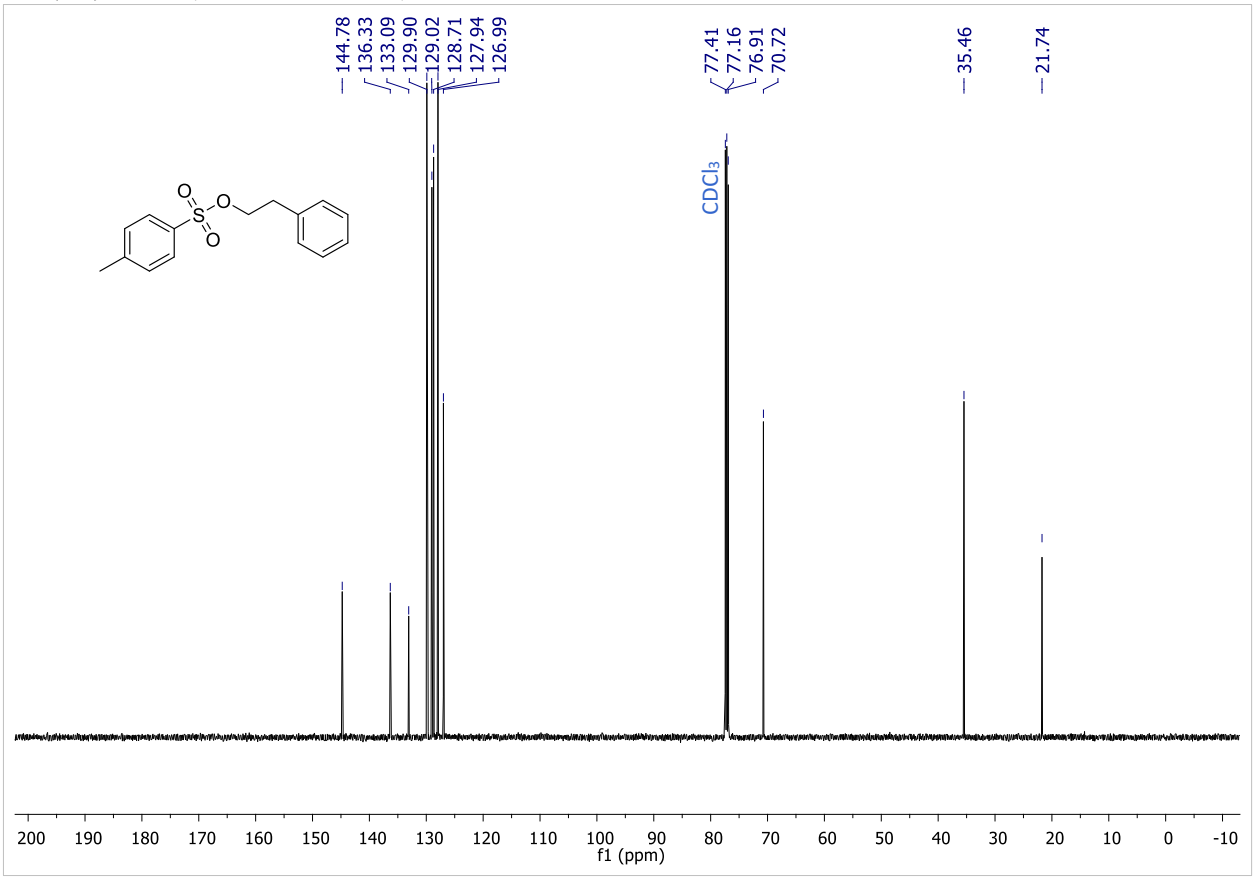


Phenethyl 4-methylbenzenesulfonate

^{1}H NMR (500 MHz, $CDCl_3$)

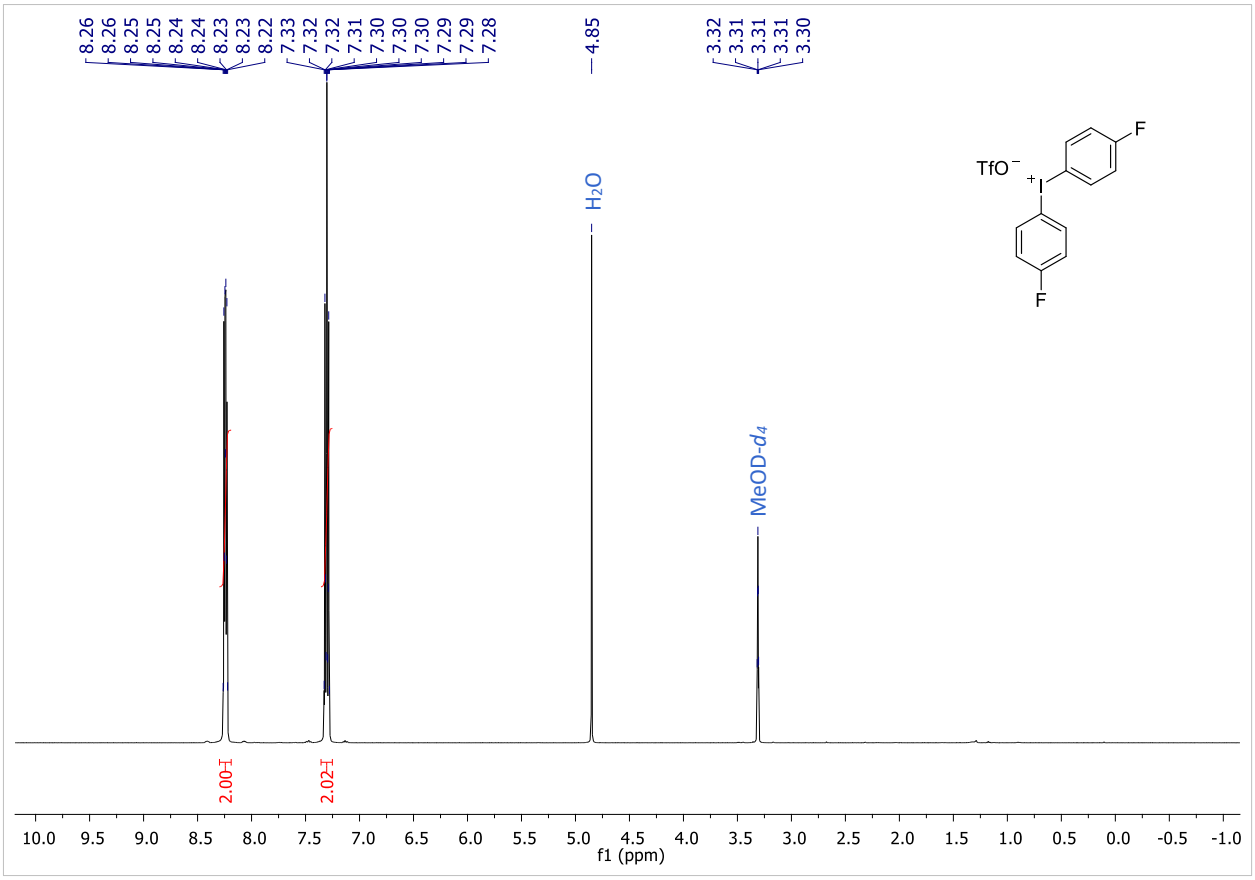


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

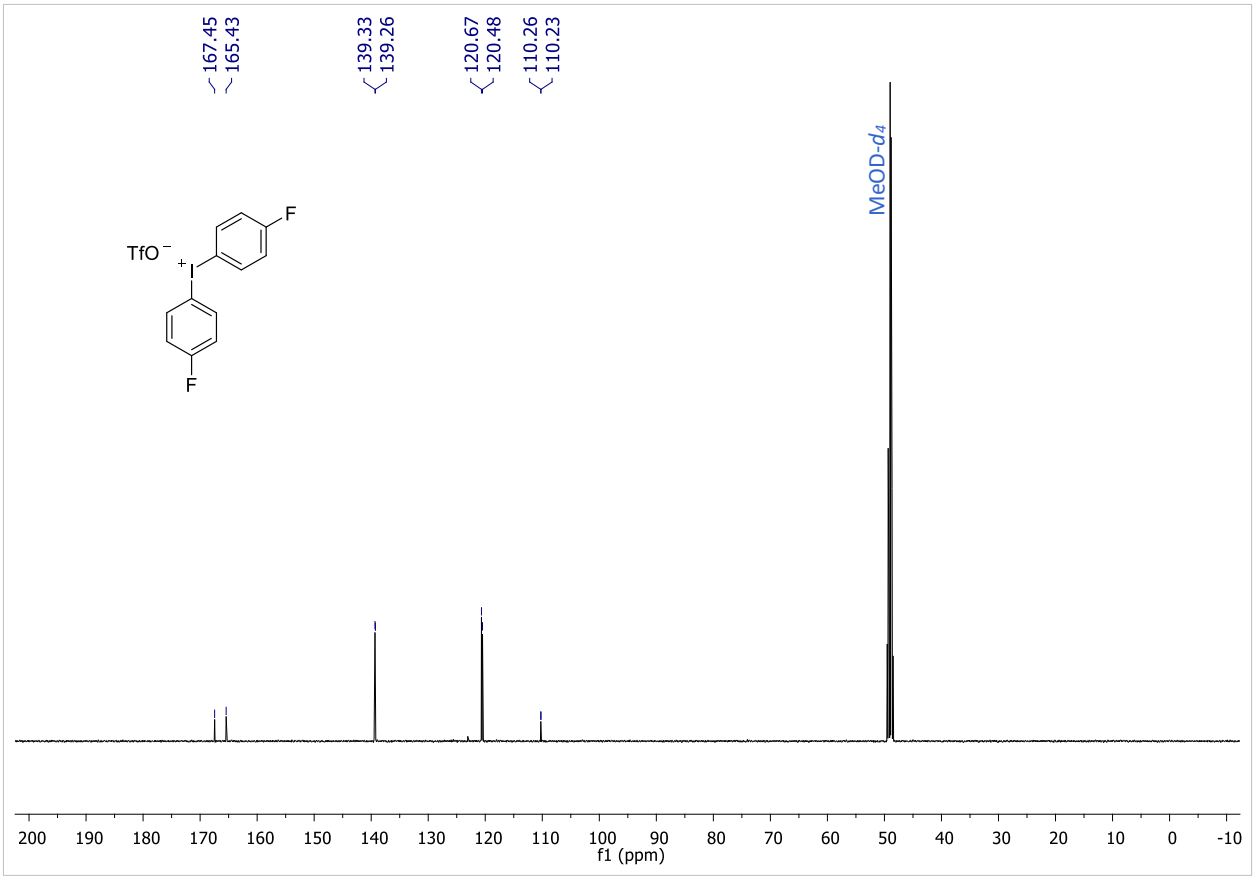


Bis(4-fluorophenyl)iodonium triflate

^{1}H NMR (500 MHz, MeOD-d_4)

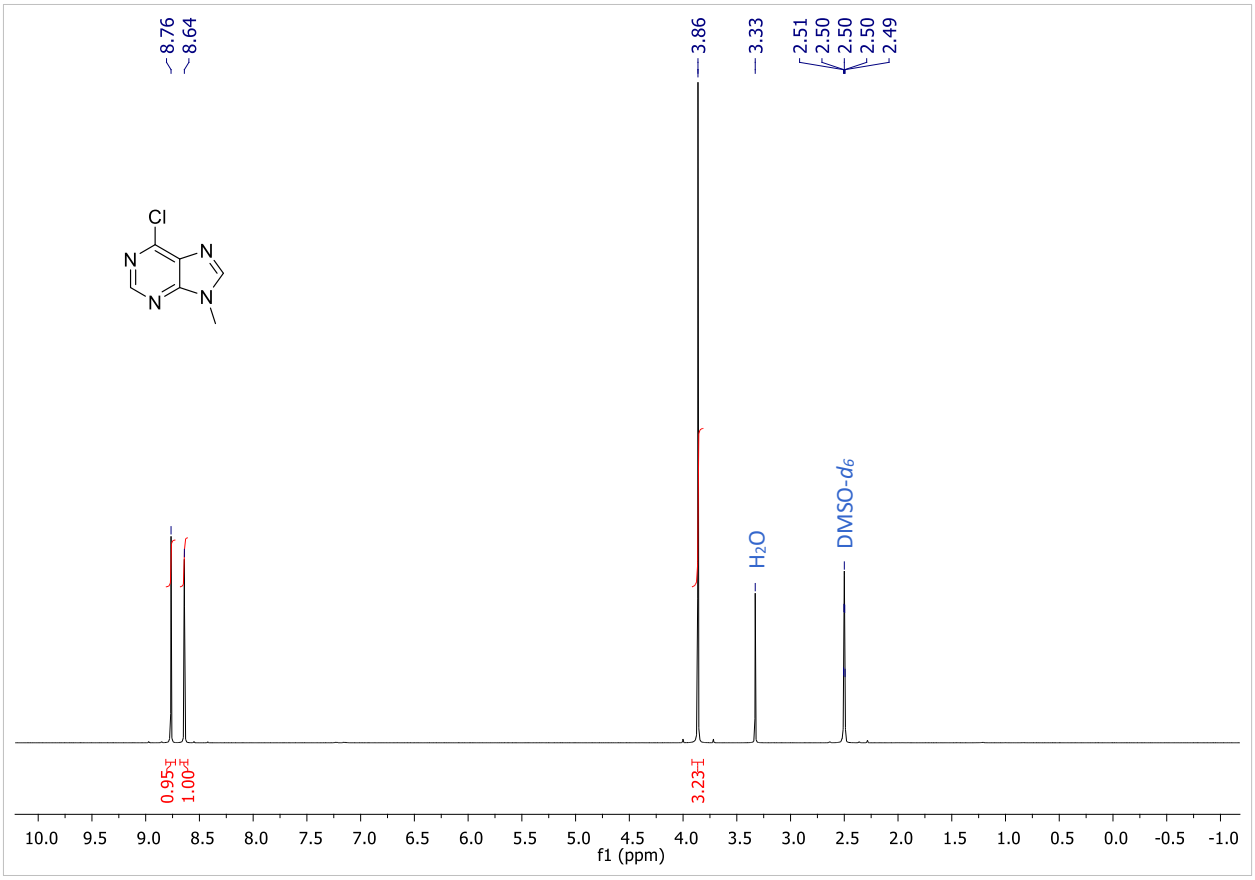


^{13}C{^{1}H} NMR (126 MHz, MeOD-d_4)



6-Chloro-9-methyl-9*H*-purine

^{1}H NMR (500 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6)