Alkyl halides via visible light mediated dehalogenation

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Supporting information

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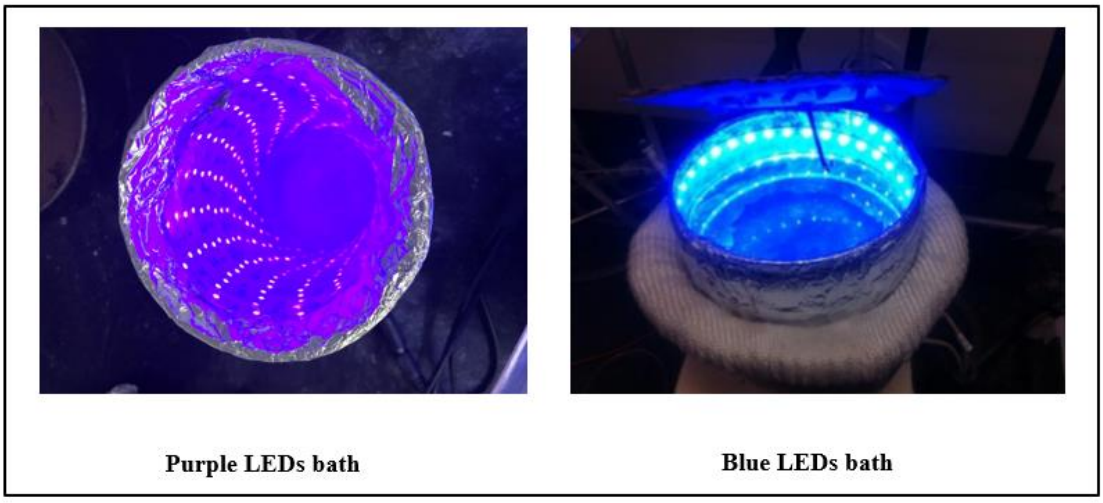
General Experimental:

All reagents were obtained from commercial suppliers (Aldrich, VWR, TCI Chemicals, and Oakwood Chemicals) and used without further purification unless otherwise noted. Acetonitrile (CH_3CN) was dried for 48 h over activated 3 A^o molecular sieves. Distilled diisopropylethylamine was stored over KOH pellets with air tight light resistant container.

Reactions were monitored by a combination of thin layer chromatography (TLC), (obtained from sorbent technologies Silica XHL TLC Plates, w/UV254, glass backed, 250 µm, 20 x 20 cm) and were visualized with ultraviolet light, potassium permanganate stain, GC-MS (QP 2010S, Shimadzu equipped with auto sampler) and 1H NMR (*vide infra*). Isolations were carried out using Teledyne Isco Combiflash Rf 200i flash chromatograph with Redisep Rf normal phase silica (4 g, 12 g, 24 g, 40 g) with product detection at 254 and 288 nm and by ELSD (evaporative light scattering detection). NMR spectra were obtained on a 400 MHz Bruker Avance III spectrometer and Neo 600 MHz. 1H and 13C NMR chemical shifts are reported in ppm relative to the residual protio solvent peak (1H, 13C). Photophysical properties were studied on Varian Cary Eclipse spectrophotometer. Mass spectra (HRMS) analysis was performed on LTQ-OrbitrapXL by Thermo Scientific ltd using a Heatedelectrospray ionization (H-ESI) source.

Reactions were set up in a light bath which consists of Blue LEDs (λ_{max} emission ~ 450 nm) or purple LEDs (λ_{max} emission ~ 410 nm) as described below. Blue LEDs (200 LEDs)/ purple LEDs (240 LEDs) were wrapped around the walls of glass crystallization dish and secured with masking tape and then wrapped with aluminum foil. A lid which rest on the top was fashioned from cardboard and holes were made such that reaction tubes were held firmly in the cardboard lid which was placed on the top of bath. Water was added to the bath such that the tubes were submerged in the water which was at 28 ^{o}C. (Temperature of the bath was maintained at 28 ^{o}C using a fan).

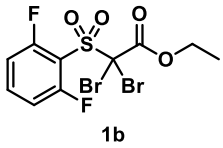


Purple LEDs bath **Blue LEDs bath**

Synthesis of alkyl bromide/chloride substrates:

Alkyl bromides and alkyl chlorides were synthesized according to the literature procedures and some procedures were modified slightly to increase the yield of alkyl bromides and chlorides.[1]

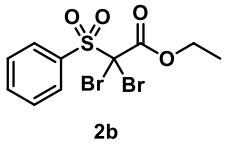
Ethyl 2,2-dibromo-2-((2,6-difluorophenyl)sulfonyl)acetate



1b

Ethyl 2-((2,6-difluorophenyl)sulfonyl)acetate (1.0 g, 3.9 mmol, 1 equiv) and triethylamine (1.2 g, 11.7 mmol, 3 equiv) in 25 mL of DCM was stirred for 20 min. Bromine (2.5 g, 15.6 mmol, 4 equiv) was added in to the reaction. The progress of the reaction was monitored by TLC. The reaction was stirred at room temperature for 15 h. After consumption of the starting material, the mixture was diluted with H_2O (15 mL) and then extracted with EtOAc (3×15 mL). The organic layers were combined and washed with brine then dried with $MgSO_4$. The crude product was concentrated *in vacuo* and purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 19% on a 40 g silica column to afford **1b** in 95% yield (3.7 mmol, 1.6 g).[1a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (tt, *J* = 8.4, 5.7 Hz, 1H), 7.11 (ap t, *J* = 8.4 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.4 – -98.5 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 161.4 – 160.5 (dd), 138.8 (qd, *J* = 9.7, 8.2, 4.6 Hz), 114.1 (d, *J* = 4.6 Hz), 113.9 (d, *J* = 5.8 Hz), 71.0, 66.6, 14.1. HRMS (ESI) calcd. for $[C_{10}H_8Br_2F_2O_4SNa]^+$ $[M+Na]^+$: m/z, 444.8355 found 444.8355.

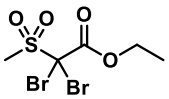
Ethyl 2,2-dibromo-2-(phenylsulfonyl)acetate



2b

Ethyl 2-(phenylsulfonyl)acetate (0.9 g, 3.9 mmol, 1 equiv) and triethylamine (1.2 g, 11.7 mmol, 3 equiv) in 25 mL of DCM was stirred for 20 min. Bromine (2.5 g, 15.6 mmol, 4 equiv) was added in to the reaction. The progress of the reaction was monitored by TLC. The reaction was stirred at room temperature for 17 h. After consumption of the starting material, the mixture was diluted with H_2O (15 mL) and then extracted with EtOAc (3×15 mL). The organic layers were combined and washed with brine then dried with $MgSO_4$. The crude product was concentrated *in vacuo* and purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 21% on a 40 g silica column to afford **2b** in 93% yield (3.6 mmol, 1.4 g).[1a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, 2H), 7.75 (t, 1H), 7.60 (t, *J* = 7.9 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 135.9, 133.1, 132.9, 129.1, 69.2, 66.0, 14.1. HRMS (ESI) calcd. for $[C_{10}H_{10}Br_2O_4SNa]^+$ $[M+Na]^+$: m/z, 408.8544 found 408.8541.

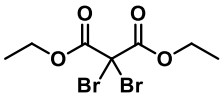
Ethyl 2,2-dibromo-2-(methylsulfonyl)acetate



3b

Ethyl 2-(methylsulfonyl)acetate (0.7 g, 3.9 mmol, 1 equiv) and triethylamine (1.2 g, 11.7 mmol, 3 equiv) in 25 mL of DCM was stirred for 20 min. Bromine (2.5 g, 15.6 mmol, 4 equiv) was added in to the reaction. The progress of the reaction was monitored by TLC. The reaction was stirred at room temperature for 20 h. After consumption of the starting material, the mixture was diluted with H_2O (15 mL) and then extracted with EtOAc (3×15 mL). The organic layers were combined and washed with brine then dried with $MgSO_4$. The crude product was concentrated *in vacuo* and purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 27% on a 40 g silica column to afford **3b** in 90% yield (3.5 mmol, 1.1 g).[1a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (q, *J* = 7.1 Hz, 2H), 3.50 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 67.1, 66.2, 37.3, 14.1. HRMS (ESI) calcd. for $[C_5H_8Br_2O_4SNa]^+$ $[M+Na]^+$: m/z, 346.8387 found 346.8385.

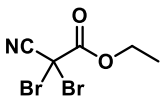
Diethyl 2,2-dibromomalonate



4b

Bromine (2 g, 12.5 mmol, 4 equiv) was added into a solution of diethyl malonate (0.5 g, 3.12 mmol, 1 equiv) in 30 mL DCM. Then, the reaction was stirred at room temperature for 20 h. The progress of the reaction was monitored by TLC. After consumption of the starting material, the mixture was diluted with H_2O (20 mL) and then extracted with EtOAc (3×15 mL). The organic layers were combined and washed with brine then dried with $MgSO_4$. The crude product was concentrated *in vacuo* and purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 7% on a 24 g silica column to afford **4b** in 96% yield (3 mmol, 0.95 g).[1g, 2]

Ethyl 2,2-dibromo-2-cyanoacetate

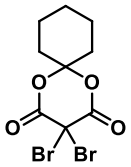


5b

Bromine (2 g, 12.5 mmol, 4 equiv) was added into a solution of ethyl 2-cyanoacetate (0.4 g, 3.1 mmol, 1 equiv) in 30 mL DCM. The progress of the reaction was monitored by TLC. The reaction was stirred at room temperature for 20 h. After consumption of the starting material, the mixture was diluted with H_2O (20 mL) and then extracted with EtOAc (3×15 mL). The organic layers were combined and washed with brine then dried with $MgSO_4$. The crude product was concentrated

in vacuo and purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 9% on a 24 g silica column to afford **5b** in 95% yield (3 mmol, 0.80 g).[1g, 3]

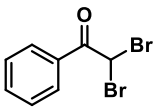
3,3-Dibromo-1,5-dioxaspiro[5.5]undecane-2,4-dione



6b

To a chilled (0 °C) 2 M solution of NaOH (5 mL), 1,5-dioxaspiro[5.5]undecane-2,4-dione (0.9 g, 5 mmol, 1 equiv) was added and stirred for 15 min to get homogeneous reaction mixture. Then, bromine (1.6 g, 10 mmol, 2 equiv) was added dropwise at 0 °C. After addition, the reaction was stirred for 45 minutes at 0 °C and solid crude was observed at the end of the reaction. Then, it was filtered and washed with distilled water and extracted with toluene (3 x 3 mL). The organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to afford **6b** in 75% yield (3.8 mmol, 1.3 g).[1b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (t, 4H), 1.77 (p, *J* = 6.3 Hz, 4H), 1.52 (p, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 108.6, 39.2, 36.8, 23.9, 22.3. HRMS (ESI) calcd. for $[C_9H_{10}Br_2O_4Na]^+$ [M+Na]$^+$: m/z, 364.8823 found 364.8822.

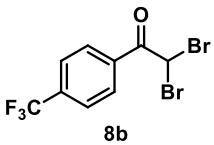
2,2-dibromo-1-phenylethan-1-one



7b

Bromine (1.4 g, 9 mmol, 2 equiv) was added dropwise over a period of 20 minutes into 3 mL of anhydrous 1,4-dioxane at room temperature under a flow of Ar. Then, the reaction mixture was stirred for another 30 minutes. A solution of acetophenone (0.5 g, 4.2 mmol, 1 equiv) in 2 mL of dioxane was added into the reaction mixture at once and stirred for another 5 h. At the end of the reaction, ice cold water (50 mL, 10 volumes with respect to the dioxane) was added to the reaction flask causing the product to precipitate which was filtered from solution. The filtrate was washed with hexane to afford **7b** in 92% yield (3.9 mmol, 1.1 g).[1c, 4]

2,2-Dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one

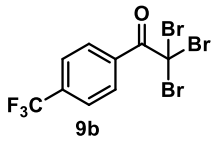


8b

Bromine (1.4 g, 9 mmol, 2 equiv) was added dropwise over a period of 20 minutes into 3 mL of anhydrous 1,4-dioxane at room temperature under a flow of Ar. Then, the reaction mixture was stirred for another 30 minutes. 1-(4-(trifluoromethyl)phenyl)ethan-1-one (0.8 g, 4.2 mmol, 1 equiv) in 2 mL of dioxane was added into the reaction mixture at once and stirred for another 5 h. At the end of the reaction, ice cold

water (50 mL, 10 volumes with respect to the dioxane) was added to the reaction flask causing the product to precipitate which was filtered from solution. The filtrate was washed with hexane to afford **8b** in 93% yield (3.9 mmol, 1.4 g).[1c, 5]

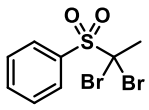
2,2,2-tribromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one



9b

To a solution of 1-(4-(trifluoromethyl)phenyl)ethan-1-one (0.5 g, 2.7 mmol, 1 equiv) in AcOH (10 mL) and 3 mL of water, Br_2 (2.1 g, 13.5 mmol, 5 equiv) was added at 0 °C. Then, the reaction mixture was brought to reflux for 60 h. The reaction mixture was diluted with water and extracted with ethylacetate (3×10 mL). The organic layers were combined and washed with water, saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via automated flash chromatography using DCM in hexanes (0% to 100%) with product eluting at 0.2% on a 40 g silica column to afford **9b** in 45% yield (1.2 mmol, 0.5 g).[6]

((1,1-Dibromoethyl)sulfonyl)benzene



10b

To (ethylsulfonyl)benzene (0.4 g, 2.2 mmol, 1 equiv) in anhydrous THF (11 mL) at -78 °C was added n-BuLi (3 mL, 4.8 mmol, 1.6 M in hexane). Before addition of n-BuLi, it should be titrated to find the exact concentration of n-BuLi (as given below). After addition, the yellow mixture was allowed to warm to room temperature and then again cooled to -78 °C. Bromine (1.1 g, 6.6 mmol, 3 equiv) was added slowly, and the mixture was then warmed to room temperature. The reaction was stirred at room temperature for 13 h. The reaction was diluted with 1 M $NaHSO_3$, the mixture was extracted with diethyl ether (3 x 10 mL) and the combined extracts were dried over $MgSO_4$ and concentrated. The collected crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 10% on a 24 g silica column to afford **10b** in 80% yield (1.8 mmol, 0.6 g).[1d, 7]

General procedure for n-BuLi titration:

An oven dried 25 ml three neck flask equipped with an argon inlet adapter, a stirring bar and two rubber septa. The flask was charged with menthol (0.64 mmol, 100 mg), 2,2'-dipyridyl (2.5 mg) and 10 mL of dry THF. To the resulting solution is added n-BuLi via 1.0 mL syringe (graduated in 0.01 mL increments) in a

dropwise fashion. During addition, it was observed that periodic quantities of a red colored complex appeared in the solution. It could be noted that in the early stage of the titration this red color dispersed rapidly. As one nears the endpoint, the red coloration required longer periods of time to disperse. At this point, it is necessary to slow the rate of addition. Eventually, the addition of a single drop of n-BuLi caused a persistent red coloration of the solution. Then, find the difference between initial and final volumes of n-BuLi to get the used volume of n-BuLi in the titration. Finally, calculate the molarity of n-BuLi.

Calculation:

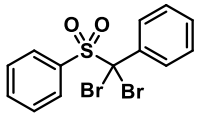
100 mg menthol = 0.64 mmol which reacts with 0.64 mmol n-BuLi.

This amount of n-BuLi is present in V ml (used volume in the titration) of the analyte.

Since molarity equals mol/L, it also equals mmol/mL. Thus:

0.64 mmol / V mL = Concentration of n-BuLi solution

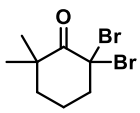
((Dibromo(phenyl)methyl)sulfonyl)benzene



11b

To (benzylsulfonyl)benzene (0.5 g, 2.2 mmol, 1 equiv) in anhydrous THF (11 mL) at -78 °C was added n-BuLi (3 mL, 4.8 mmol, 1.6 M in hexane). The yellow mixture was warmed to room temperature and then again cooled to -78 °C. Bromine (1.1 g, 6.6 mmol, 3 equiv) was added in a single portion, and the mixture was then warmed to room temperature. The reaction was stirred at room temperature for 10 h. The reaction was diluted with 1 M $NaHSO_3$, the mixture was extracted with diethyl ether (3 x 10 mL) and the combined extracts were dried over $MgSO_4$ and concentrated. The crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 4% on a 24 g silica column to afford **11b** in 65% yield (1.43 mmol, 0.55 g). [1d, 7]

2,2-Dibromo-6,6-dimethylcyclohexan-1-one

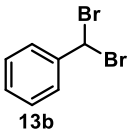


12b

A solution of 2,2-dimethylcyclohexan-1-one (0.5 g, 4 mmol, 1 equiv) in DCM (2 mL) was added dropwise to a solution of n-bromosuccinimide (1.6 g, 8.8 mmol, 2.2 equiv) and p-TsOH (0.13 g, 0.8 mmol, 0.2 equiv) in DCM (15 mL) at 0 °C. The reaction mixture was then brought to reflux for 15 h. After addition of H_2O (10 mL), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The

residue was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 0.1% on a 24 g silica column to afford **12b** in 85% yield (3.4 mmol, 1.0 g).[1e, 8]

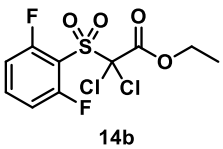
(Dibromomethyl)benzene



13b

13b was synthesized according to a modified literature procedure. Benzyl bromide (0.4 g, 2.3 mmol, 1 equiv), N-bromosuccinimide (0.5 g, 2.6 mmol, 1.1 equiv) and azobis(isobutyronitrile) (3 mg, 0.01 mmol, 0.006 equiv) in 10 mL of CCl_4 was heated for 10 h under reflux. The mixture was cooled and the precipitate (succinimide) was filtered off and washed with 5 mL of CCl_4, and the filtrate was washed in succession with a 5% solution of Na_2SO_3, a 10% solution of Na_2CO_3, and water and dried over $MgSO_4$. The solvent was removed, and the residue was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 0.1% on a 24 g silica column to afford **13b** in 70% yield (1.6 mmol, 0.4 g).[9]

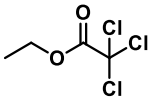
Ethyl 2,2-dichloro-2-((2,6-difluorophenyl)sulfonyl)acetate



14b

Ethyl 2-((2,6-difluorophenyl)sulfonyl)acetate (1 g, 3.9 mmol, 1 equiv) and triethylamine (1.18 g, 11.7 mmol, 3 equiv) in 25 mL of DCM was stirred for 20 min. N-chlorosuccinimide (1.6 g, 11.7 mmol, 3 equiv) was added in to the reaction. The progress of the reaction was monitored by TLC. The reaction was stirred at room temperature for 21 h. After consumption of the starting material, the mixture was diluted with H_2O (15 mL) and then extracted with EtOAc (3×10 mL). The organic layers were combined and washed with brine then dried with $MgSO_4$. The crude product was concentrated *in vacuo* and purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 30% on a 40 g silica column to afford **14b** in 80% yield (3.1 mmol, 1.01 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (tt, *J* = 8.5, 5.7 Hz, 1H), 7.11 (ap t, *J* = 16.8 Hz, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.3 (ddd, *J* = 8.9, 5.8, 2.9 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6 (dd, *J* = 266.5, 2.6 Hz), 160.4, 138.4 (t, *J* = 11.5 Hz), 113.6, 113.4 (d, *J* = 4.6 Hz), 93.6, 66.0, 13.6. HRMS (ESI) calcd. for $[C_{10}H_8Cl_2F_2O_4SNa]^+$ $[M+Na]^+$: m/z, 354.9386 found 354.9383.

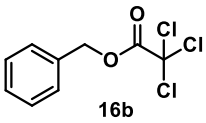
Ethyl 2,2,2-trichloroacetate



15b

A mixture of trichloroacetic acid (0.7 g, 4.3 mmol, 1 equiv), concentrated sulfuric acid (0.1 mL), and ethanol (5 mL) was refluxed for 7 h. Then the flask was cooled to room temperature, water (10 mL) was added to the content of the flask, and the crude was extracted with diethyl ether (3×10 mL). The organic layers were combined and washed with a 10% sodium carbonate solution and dried with anhydrous $MgSO_4$. The solvent was removed, and the residue was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 8% on a 24 g silica column to afford **15b** in 85% yield (3.7 mmol, 0.70 g).[1f, 10]

Benzyl 2,2,2-trichloroacetate

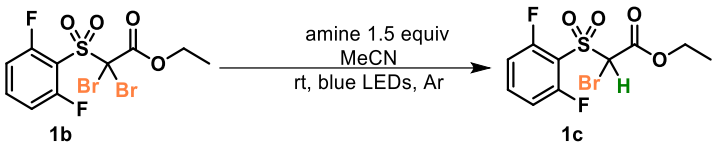


16b

A mixture of trichloroacetic acid (0.7 g, 4.3 mmol, 1 equiv), concentrated sulfuric acid (0.1 mL), and benzyl alcohol (1.4 g, 12.9 mmol, 3 equiv) in 10 mL of MeCN was refluxed for 5 h. Then the flask was cooled to room temperature, water (10 mL) was added to the content of the flask, and the crude was extracted with diethyl ether (3×10 mL). The combined organic extracts were washed with a 10% sodium carbonate solution and dried with anhydrous $MgSO_4$. The solvent was removed, and the residue was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 0.5% on a 24 g silica column to afford **16b** in 70% yield (3 mmol, 0.76 g).[1f, 11]

Optimization of hydrodebromination:

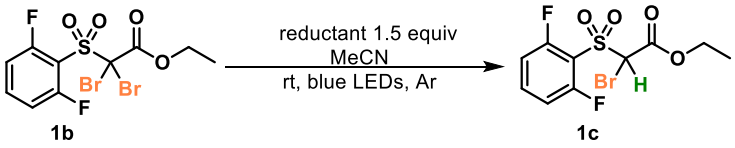
Optimization of amine structure:



entry	amine	time	conv%[a]	**1c**%[a]
1	Et_3N	90 min	78[b]	75
2	Bu_3N	90 min	98[b]	65
3	DIPEA	45 min	100	96
4	DABCO	90 min	47	2
5	DBU	90 min	94[b]	75
6	4-methoxytriphenylamine	90 min	3	3
7	2,2,6,6-tetramethylpiperidine	90 min	2	2

[a]determined by ^{19}F NMR.[b]didebrominated product is 10-15%.

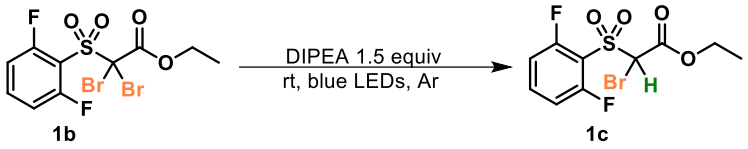
Attempted hydrodebromination with other potential reductants:



entry	reductant	time	conv%[a]	**1c**%[a]
1	Hantzsch ester	75 min	63[b]	51
2	4-fluorothiophenol	75 min	7	7
3	Sodium ascorbate	75 min	1	1
4	Sodium oxalate	75 min	0	0

[a]determined by ^{19}F NMR.[b]didebrominated product is 12%.

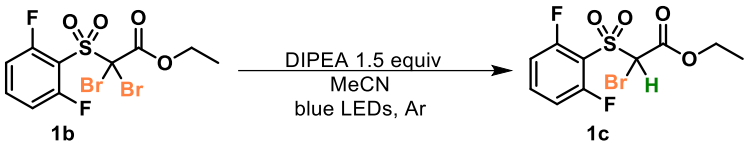
Solvent optimization:



entry	solvent	time	conv%[a]	**1c**%[a]
1	Toluene	90 min	37	37
2	THF	90 min	39	38
3	DCM	90 min	20	20
4	NMP	60 min	40	23
5	MeCN	45 min	100	96
6	DMF	60 min	100[b]	87
7	DMSO	60 min	100[b]	85
8	MeOH	60 min	100[b]	60

[a]determined by ^{19}F NMR.[b]didebrominated product is 10-15%

Temperature optimization:



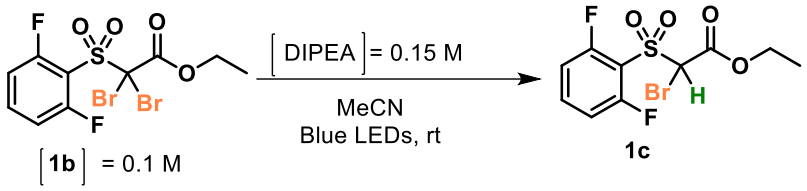
entry	temperature	time	conv%[a]	**1c**%[a]
1	0 °C	90 min	87	83
2	28 °C (rt)	45 min	100	96
3	45 °C	30 min	100	90

[a]determined by ^{19}F NMR.

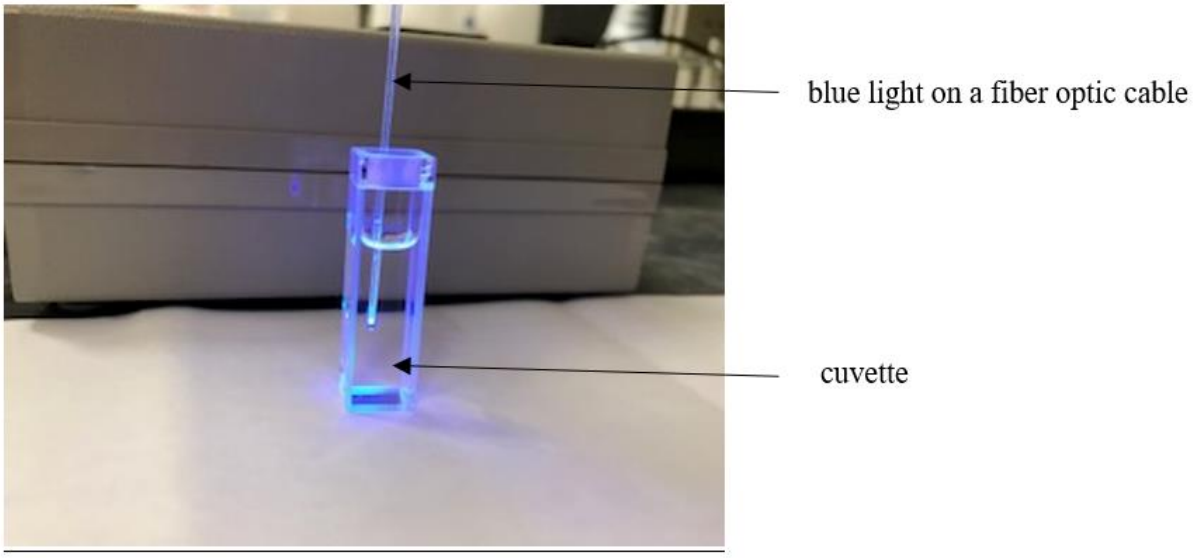
Mechanistic experiments

UV-Vis experiments:

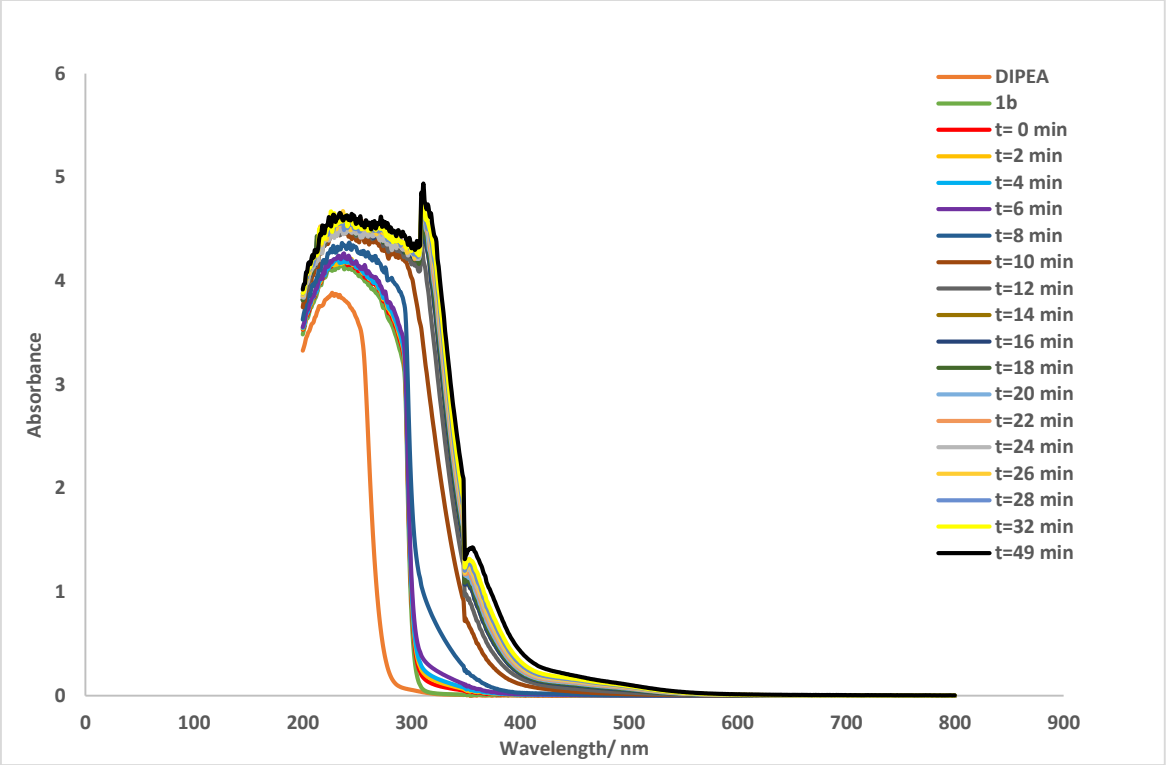
Time-dependent UV/Vis spectra of hydrodebromination reaction of **1b**:



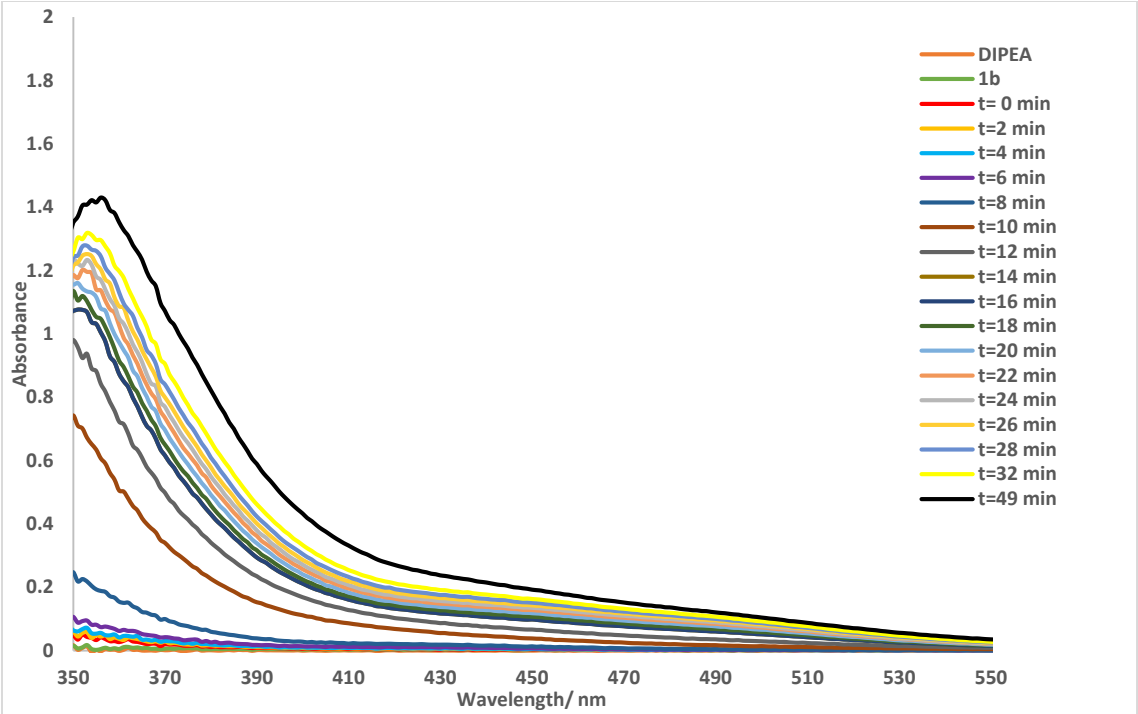
Brominated compound **1b** (101.3 mg, 0.24 mmol, 1 equiv) and *N*, *N*-diisopropylethylamine (62.8 µL, 0.36 mmol, 1.5 equiv) was added into 1 cm path quartz cuvette and total volume was adjusted to 2.4 mL by adding MeCN to the cuvette. Then, the blue light on a fiber optic cable was dipped in the cuvette and reaction was irradiated. UV-Vis spectra were recorded for the reaction at different reaction times using Varian Cary Eclipse spectrophotometer. The appearance of an absorption band in the visible region as a function of time is consistent with the formation of a streptocyanine dye as the reaction progresses.



Time-dependent UV/Vis spectra of debromination reaction of **1b**

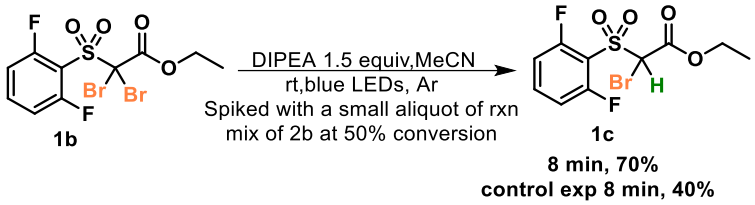


Expansion of the above spectrum:

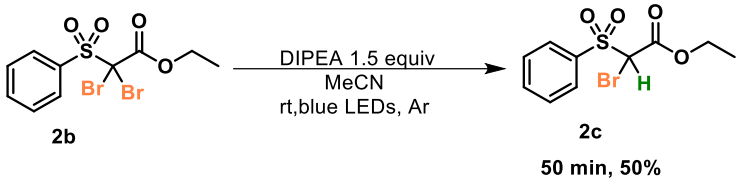


Exp 1:

Spiking experiment:

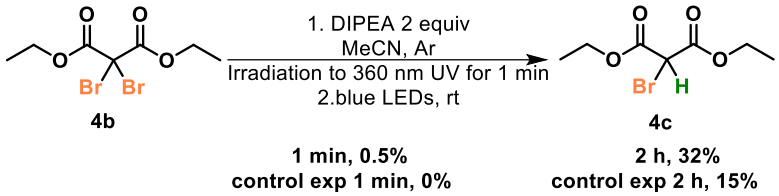


Reaction of **2b** used for above spiking:



An NMR tube fitted with a rubber septum was charged with brominated sulfone **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N*, *N*-diisopropylethylamine (31.4 µL, 0.18 mmol, 1.5 equiv) and MeCN (1.2 mL). Then the reaction mixture was spiked with a 20 µL aliquot of reaction mixture of **2b** at 50% conversion. The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then the piece of aluminum foil was removed and the tube was placed in a blue LED bath. Meanwhile, a control experiment was set up without any reaction mixture of **2b**. The reactions were monitored by 19F NMR. After 8 min, the spiked reaction showed 70% conversion while the control experiment showed only 40% conversion, indicating that a species formed during the reaction of a different substrate was capable of accelerating the formation of a different product. This is suggestive that the postulated streptocyanine dye is capable of catalyzing this hydrodebromination reaction.

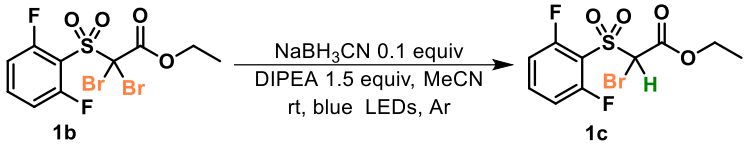
Exp 2:



An NMR tube fitted with a rubber septum was charged with brominated compound **4b** (38.15 mg, 0.12 mmol, 1 equiv), *N*, *N*-diisopropylethylamine (41.8 µL, 0.24 mmol, 2 equiv) and MeCN (01.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. The piece of aluminum foil was removed and the colorless reaction mixture was irradiated with

the long wavelength UV light (360 nm) produced by a hand held TLC lamp, for 1 min. Then, the tube was returned to a blue LED bath. Meanwhile, the control experiment was immediately placed in the same blue LED bath. The reactions were monitored by 1H NMR. After 2 h, the UV-exposed reaction mixture showed 32% conversion while the control experiment showed only 15% conversion. This experiment suggests that UV light can initiate reaction faster than blue light.

Exp 3:

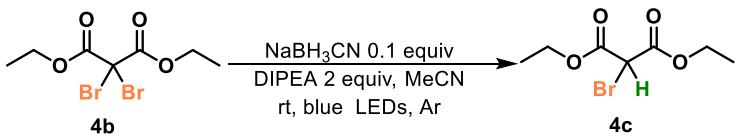


1b **1c**

9 min, 28%
control exp 9 min, 53%

An NMR tube fitted with a rubber septum was charged with brominated compound **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N, N*-diisopropylethylamine (31.4 µL, 0.18 mmol, 1.5 equiv), $NaBH_3CN$ (0.8 mg, 0.012 mmol, 0.1 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then, the piece of aluminum foil was removed and the tube was placed in a blue LED bath. Meanwhile, a control experiment was set up containing no $NaBH_3CN$. The reactions were monitored by 19F NMR. After 9 min, the reaction mixture containing $NaBH_3CN$ showed only 28% conversion, while the positive control experiment showed 53% conversion. Indicating the presence of the hydride source retarded the rate of the reaction. Importantly, a dark version of this reaction showed that the $NaBH_3CN$ did not reduce the substrate.

Exp 4:



4b **4c**

10 h, 25%
control exp 10 h, 65%

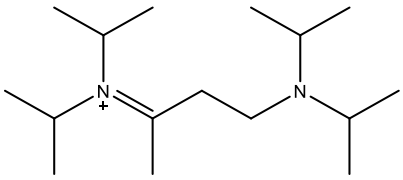
An NMR tube fitted with a rubber septum was charged with brominated compound **4b** (38.15 mg, 0.12 mmol, 1 equiv), *N, N*-diisopropylethylamine (41.8 µL, 0.24 mmol, 2 equiv), $NaBH_3CN$ (0.8 mg, 0.012 mmol, 0.1 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then, the piece of aluminum foil was removed and the tube was placed in a blue LED bath. The control experiment was set up without adding $NaBH_3CN$. The

reactions were monitored by 1H NMR. After 10 h, the reaction containing the $NaBH_3CN$ showed only 25% conversion while the positive control experiment gave 65% conversion. Again, this experiment shows that the presence of the hydride source retarded the rate of the reaction. Importantly, a dark version of this reaction showed that the $NaBH_3CN$ did not reduce the substrate. A further observation concerning experiments 3 and 4 was the slowing of the formation of colored reaction mixture. These observations are consistent with a streptocyanine based dye in which the iminium functional group would be expected to be reduced by the $NaBH_3CN$.

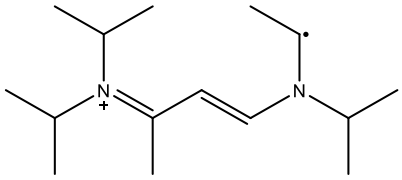
Evidence for streptocyanine dye:

A 12×75 mm borosilicate tube fitted with a rubber septum was charged with brominated compound **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N, N*-diisopropylethylamine (31.4 μL, 0.18 mmol, 1.5 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. The tube was placed in a blue LED bath which was at 28 °C. The reaction was monitored by the Expression Compact Mass Spectrometer (CMS)- Advion in the positive detection mode to detect the cyanine dyes. Mass spectrum of crude reaction when t=7 min has given below. It revealed masses of 255, 238 and 169 which could explain the following streptocyanine dye and its hydrolyzed products. Furthermore, after complete conversion of 1b, crude reaction was subjected to GCMS. It also showed hydrolyzed product of streptocyanine dye. Attempts to isolate the colored material failed as its quantity seemed to be very low.

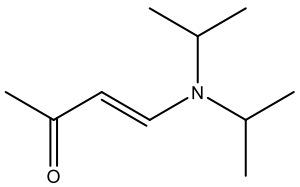
A m/z = 255



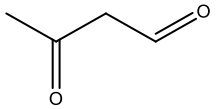
B m/z = 238



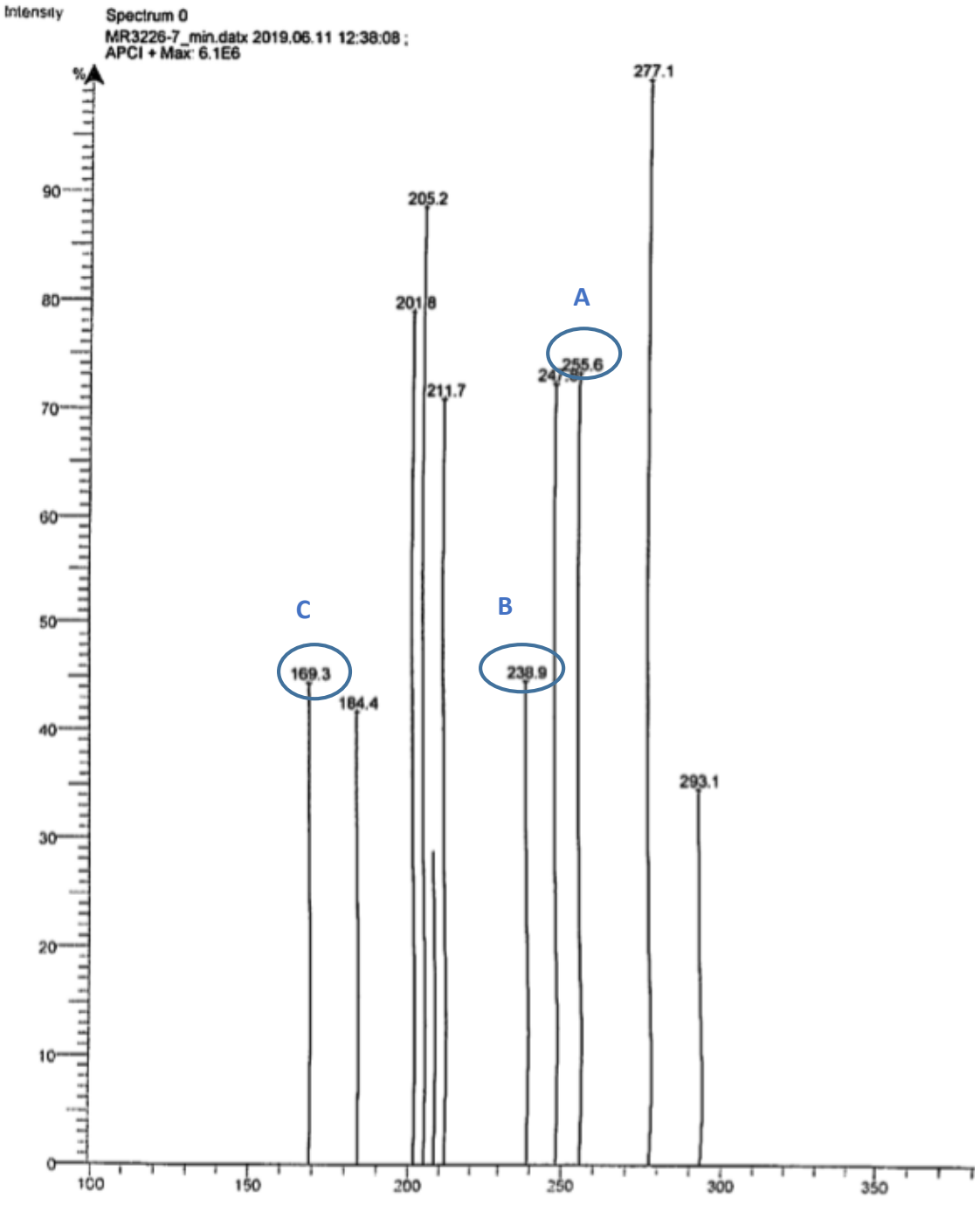
C m/z = 169



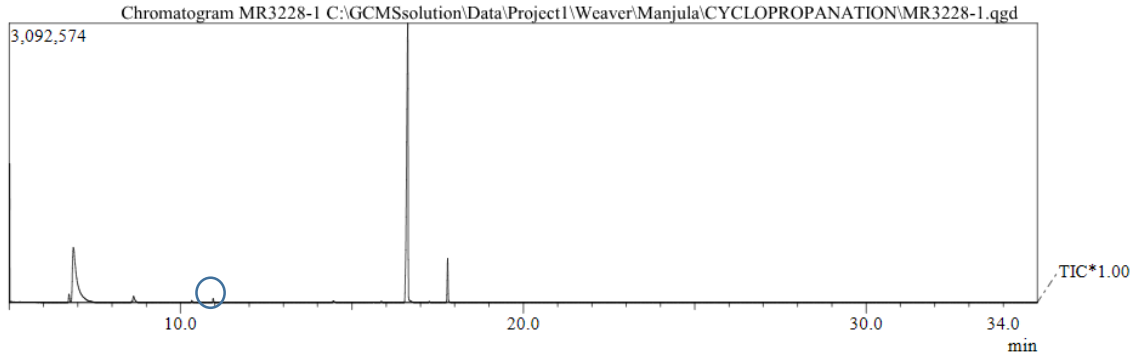
D m/z = 86

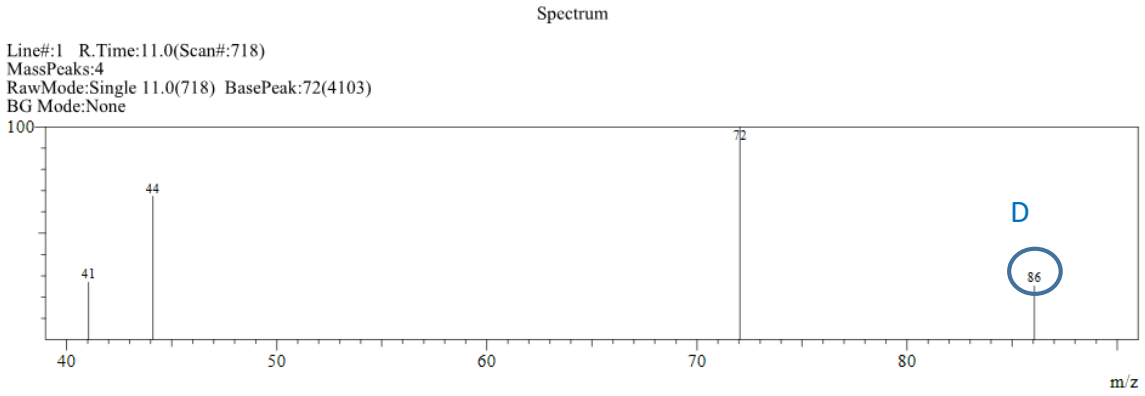


CMS- Mass spectrum of crude reaction of 1b when t= 7 min



GC- MS of crude reaction when t= 45 min

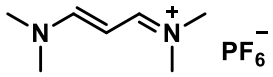




Following experiments were set up to answer the reviewers' questions:

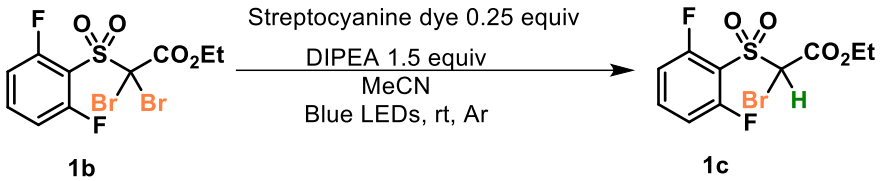
1) Experiments related to streptocyanine dye

We postulate that a streptocyanine dye formed under the reaction conditions, and that it is responsible for photoinduced electron transfer process. We have performed several experiments that are consistent with our hypothesis. While the exact dye we believe to be involved was not commercially available, we were able to purchase the following related streptocyanine dye.



Methanaminium, N-[3-(dimethylamino)-2-propen-1-ylidene]-N-methyl-, hexafluorophosphate

Following reaction was performed using a catalytic amount of this streptocyanine dye. This allowed to see if the reaction was accelerated by the presence of this dye.



1b **1c**

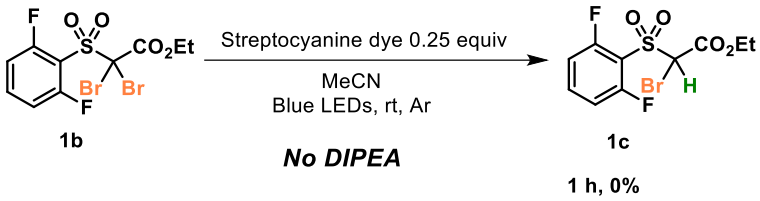
20 min, 91%

control (without streptocyanine dye): 20 min, 67%

An NMR tube fitted with a rubber septum was charged with brominated sulfone **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N, N*-diisopropylethylamine (31.4 µL, 0.18 mmol, 1.5 equiv), streptocyanine dye (8.2 mg, 0.03 mmol, 0.25 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then, the piece of aluminum foil was removed and the tube was placed in a blue LED bath. Meanwhile, a control experiment was set up without any streptocyanine dye in the reaction. The reactions were monitored by 19F NMR. After 20 min, streptocyanine dye contained reaction showed 91% conversion while the control experiment (without

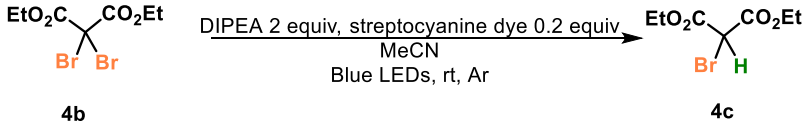
streptocyanine dye) showed only 67% conversion, indicating that having streptocyanine dye accelerates the rate of the reaction.

A control experiment showing that the streptocyanine dye itself does not serve as a stoichiometric reagent in the debromination was performed.

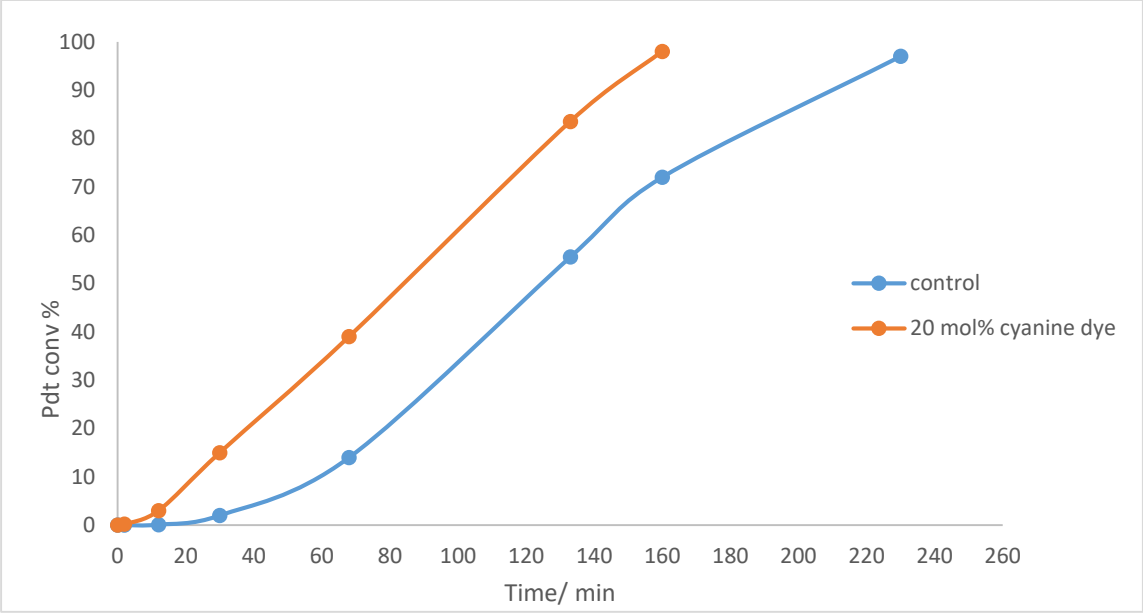


An NMR tube fitted with a rubber septum was charged with brominated sulfone **1b** (50.6 mg, 0.12 mmol, 1 equiv), streptocyanine dye (8.2 mg, 0.03 mmol, 0.25 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then, the piece of aluminum foil was removed and the tube was placed in a blue LED bath. The reaction was monitored by 19F NMR. After 1 h, reaction showed 0% conversion indicating that having DIPEA is necessary for the reaction.

A similar experiment was performed on a second substrate. Again, a similar acceleration was seen. It should be noted that the inflection in the rate profile is still observed. We believe that this explained by the formation of the dye during the course of the reaction, which may be even more active than the commercially available dye.



An NMR tube fitted with a rubber septum was charged with diethyl 2,2-dibromomalonate **4b** (19.1 mg, 0.06 mmol, 1 equiv), *N, N*-diisopropylethylamine (21 µL, 0.12 mmol, 2 equiv) streptocyanine dye (3.3 mg, 0.012 mmol, 0.2 equiv) and MeCN (0.6 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then the piece of aluminum foil was removed and the tube was placed in a blue LED bath. Meanwhile, a control experiment was set up without any streptocyanine dye in the reaction. The reactions were monitored by 1H NMR. Different time points were collected to plot a graph time vs product conversion as below. It indicates that having streptocyanine dye accelerates the rate of the reaction.



UV-Vis experiments of streptocyanine dye:

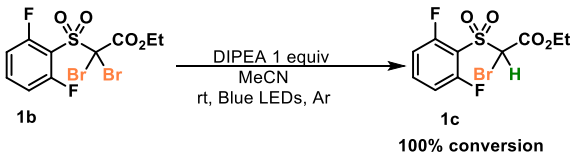
UV/Vis spectra were recorded using 1 cm path quartz cuvette and Varian Cary Eclipse spectrophotometer. MeCN was used as the solvent. UV/Vis spectra were recorded for following mixtures.

1. Streptocyanine dye (0.012 mmol of streptocyanine dye in 2.1 ml total volume of MeCN)

2. DIPEA (0.06 mmol of DIPEA in 2.1 ml total volume of MeCN)

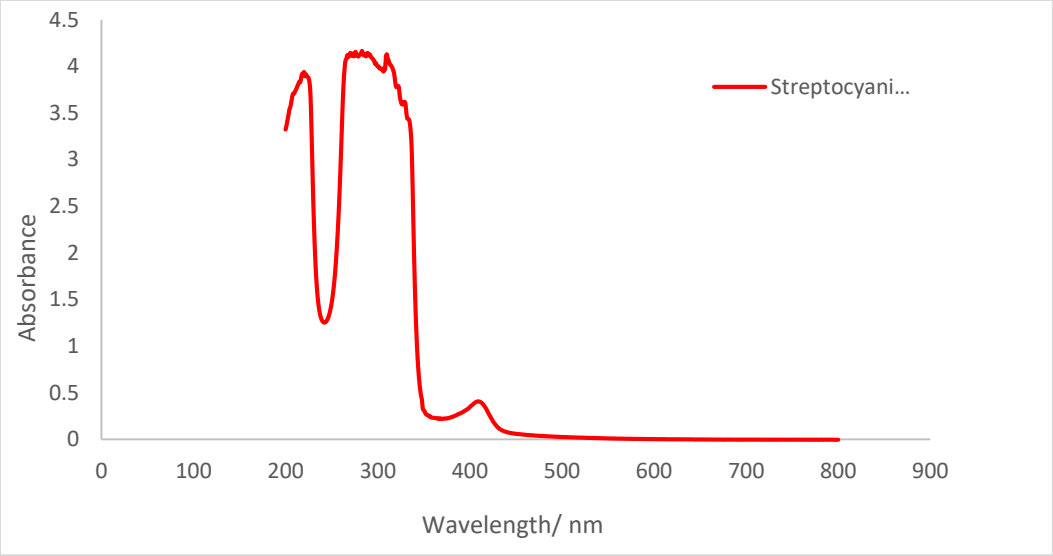
3. Streptocyanine dye and DIPEA (0.012 mmol of streptocyanine dye and 0.06 mmol of DIPEA in 2.1 ml total volume of MeCN)

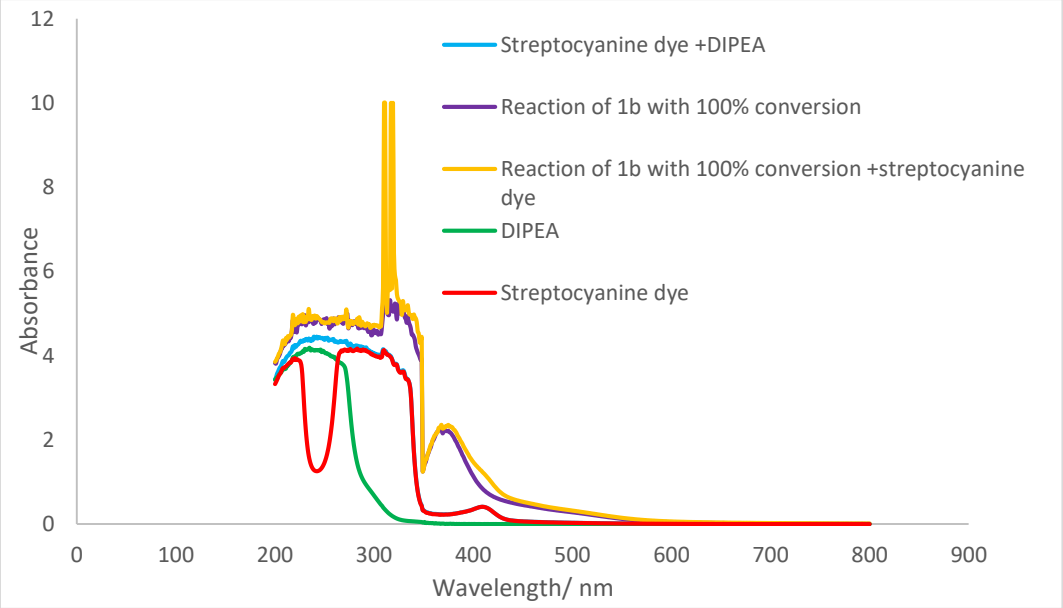
4. Reaction of **1b** with 100% conversion



(**1b** 0.12 mmol, DIPEA 0.06 mmol in total volume of 2.1 mL of MeCN)

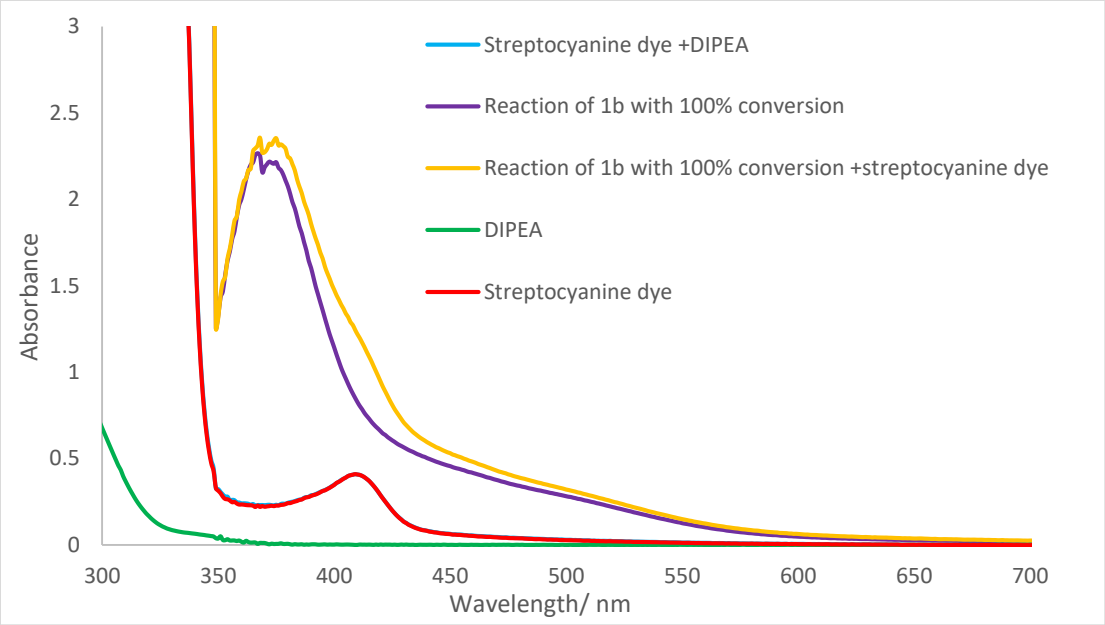
5. Reaction of **1b** with 100% conversion and streptocyanine dye (0.012 mmol)





Commercial streptocyanine dye absorbs in the visible region with λ= 413 nm. Reaction of **1b** with 100% conversion also absorbs in the same visible region.

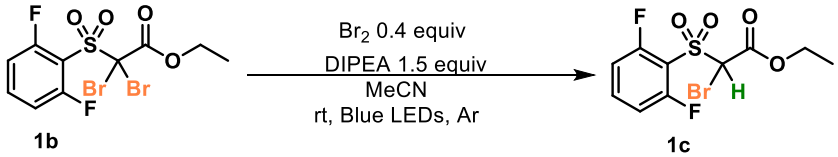
Expansion of the above spectrum:



2) Br_2 related experiments

During the debromination reactions, upon irradiation of the reaction mixture with blue LEDs, it was noted that the appearance of the reaction mixture changed from colorless to deep yellow and later to yellowish brown. It was suggested that the brownish color may result from the formation of Br_2. The following experiments probed the formation of Br_2.

Experiment 1: Addition of Br_2 to the reaction



30 min, 5%
24 h, 16%

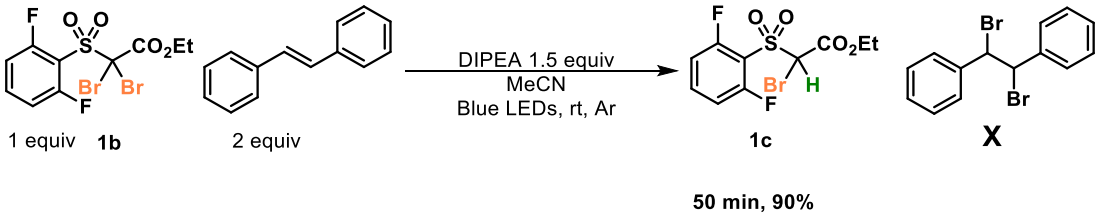
control exp (without Br_2) 30 min, 90%

An NMR tube fitted with a rubber septum was charged with brominated sulfone **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N*, *N*-diisopropylethylamine (31.4 μL, 0.18 mmol, 1.5 equiv), bromine (2.5 μL, 0.048 mmol, 0.4 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient

light and degassed via Ar bubbling for 10 min. Then the piece of aluminum foil was removed and the tube was placed in a blue LED bath. Meanwhile, a control experiment was set up without any bromine in the reaction. The reactions were monitored by 19F NMR. After 30 min, the bromine contained reaction showed only 5% conversion while the control experiment (normal conditions-no Br2) gave 90% conversion, indicating that bromine significantly retarded the rate of the reaction.

Experiment 2: Addition of bromine scavenger to the reaction

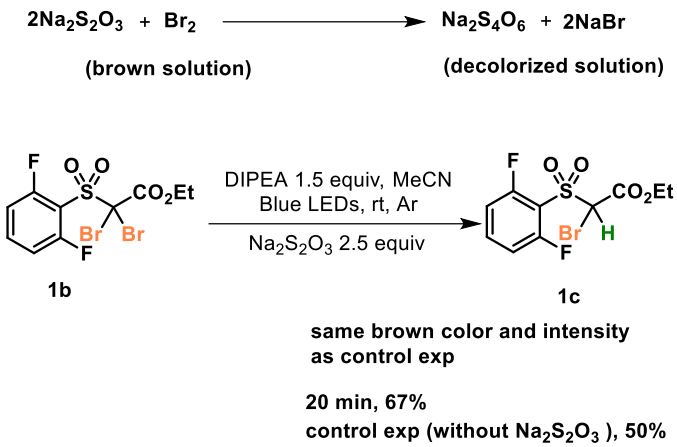
Bromination of (E)-1,2-diphenylethene is well known reaction in literature.[12] If the reaction forms bromine in the reaction, (E)-1,2-diphenylethene would react with bromine and form the di-brominated product. Therefore, following reaction was set up.



An NMR tube fitted with a rubber septum was charged with brominated sulfone **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N*, *N*-diisopropylethylamine (31.4 µL, 0.18 mmol, 1.5 equiv), (E)-1,2-diphenylethene (43.3 mg, 0.24 mmol, 2 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then the piece of aluminum foil was removed and the tube was placed in a blue LED bath. After 50 min, the reaction was monitored by 19F NMR and it showed complete conversion with 90% product. Then, the reaction was subjected to GCMS. It did not show the mass of the dibrominated stilbene product.

Experiment 3: Addition of bromine scavenger $Na_2S_2O_3$ to the reaction

$Na_2S_2O_3$ can react with bromine and which would be expect to decolorize the brownish colored solution.



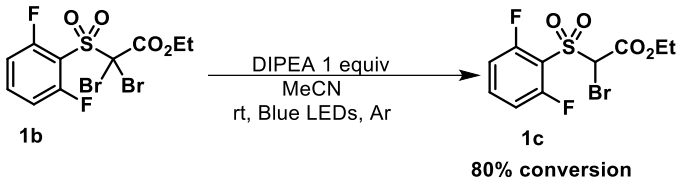
An NMR tube fitted with a rubber septum was charged with brominated sulfone **1b** (50.6 mg, 0.12 mmol, 1 equiv), *N*, *N*-diisopropylethylamine (31.4 µL, 0.18 mmol, 1.5 equiv), $Na_2S_2O_3$ (47.4 mg, 0.3 mmol, 2.5 equiv) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min. Then the piece of aluminum foil was removed and the tube was placed in a blue LED bath. After 20 min, the reaction was monitored by 19F NMR. $Na_2S_2O_3$ contained reaction showed 67% conversion while the control experiment showed 50% conversion. By visual inspection, the same brown color and intensity was observed for both the reactions.

Experiment 4: UV-Vis experiment

UV/Vis spectra were recorded using 1 cm path quartz cuvette and Varian Cary Eclipse spectrophotometer. MeCN was used as the solvent. UV/Vis spectra were recorded for following mixtures.

1. Bromine (0.06 mmol of Br_2 in 2.1 ml total volume of MeCN)
2. Bromine and DIPEA (0.06 mmol of Br_2 and 0.06 mmol of DIPEA in 2.1 ml total volume of MeCN)

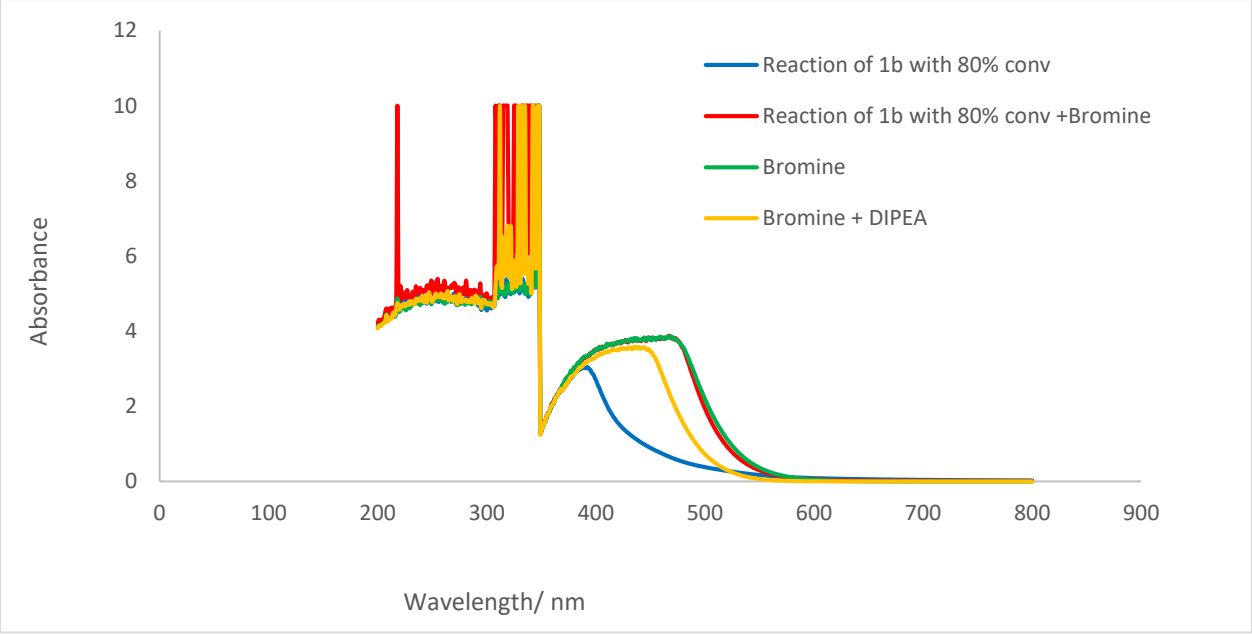
3. Reaction of **1b** at 80% conversion



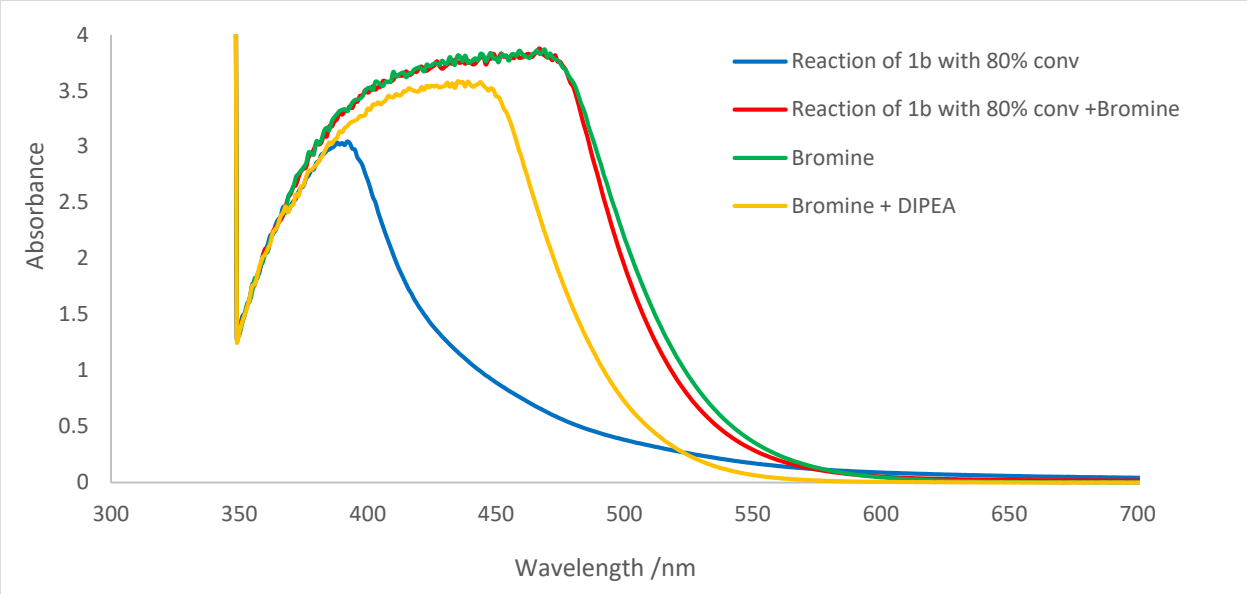
(**1b** 0.12 mmol, DIPEA 0.06 mmol in total volume of 2.1 ml of MeCN)

4. Reaction of **1b** at 80% conversion (as above) and bromine (0.06 mmol)

While bromine does absorb in the visible region with λ_{max}= 468 nm, the reaction mixture of **1b (**at 80% conversion) absorbs the visible region with λ_{max}= 393 nm. This suggests that bromine is neither present or involved in the reaction.



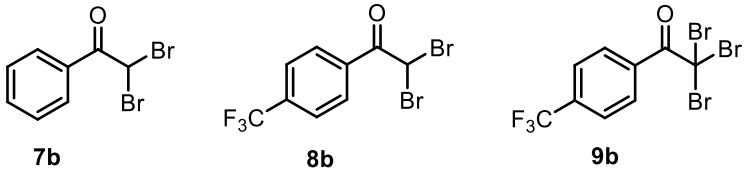
Expansion of the above spectrum:



3) For the direct EDA pathway, it is proposed that a halogen-nitrogen EDA complex results in a bathochromic shift which enables excitation and subsequent loss of a bromide anion. This is based on a UV shift observed with substrate 7b when mixed with DIPEA. The UV shift could be as a direct result of deprotonation forming a charged species leading to a UV shift and not due to the EDA complex.

To be clear, this is only possible for two substrates **7b** and **8b** which have acidic protons. Arguably, if we formed the enolate, the absorption spectrum would likely look substantially different than the EDA complex. Thus, we performed UV-Vis experiments on **8b** and **9b**, which are nearly identical except that the last acidic proton is replaced with a bromine. We observed similar spectra, and think it is likely that these two classes of substrates still proceed through an EDA complex, though we cannot completely rule out the suggested possibility.

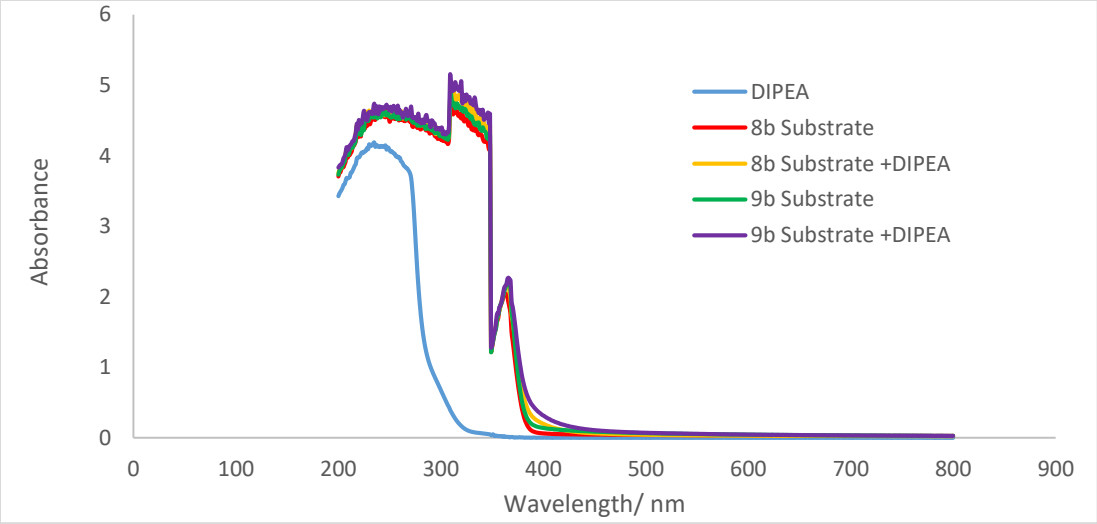
A UV-Vis experiment was performed on **9b** which could not undergo such a mechanism as that suggested by the reviewer. Like **8b**, it also displays a bathochromic shift **7b**, suggesting that these two may be undergoing the same mechanism. The following spectra were recorded.



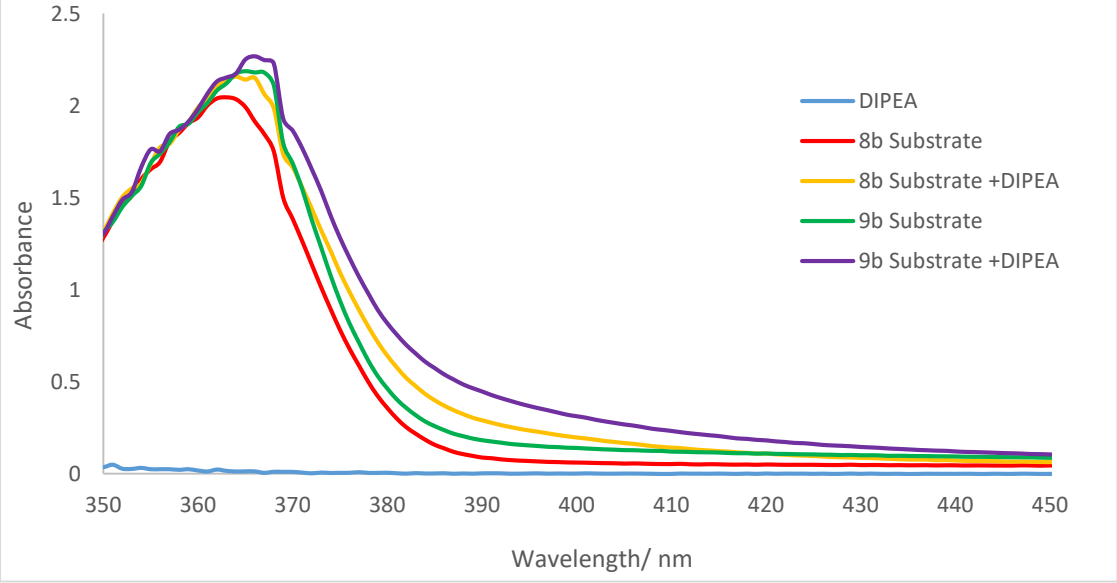
7b **8b** **9b**

1. **8b** or **9b** (0.21 mmol of **8b** or **9b** in 2.1 mL total volume of MeCN)

2. **8b** or **9b** with DIPEA (0.21 mmol of **8b** or **9b** with 0.315 mmol of DIPEA in 2.1 mL total volume of MeCN)



Expansion of the above spectrum:



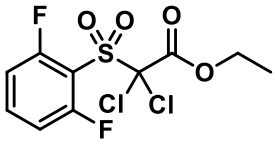
4) Purple LEDs and a vast excess of DIPEA are used in particular for dehalogenation of chlorides. This supports a hypothesis that an initial homolytic cleavage is necessary which ultimately leads to propagation in the system.

These conditions also are expected to facilitate the reaction under our proposed mechanism, unlike the proposed homolysis radical chain mechanism.

Sulfone **14b** formed an EDA complex that absorbed in the UV region (given in the below), but not in the visible (hence not visually detectable). As shown below the absorption of in MeCN approaches zero near 319 nm but a 1:4 mixture of **14b** and DIPEA showed a slight bathochromic displacement but its absorbance drops off before it reaches the visible region. This study, included in the SI, indicates that the EDA complex is likely the only species that can absorb a photon, suggesting that a radical chain mechanism that involves continual homolysis is unlikely.

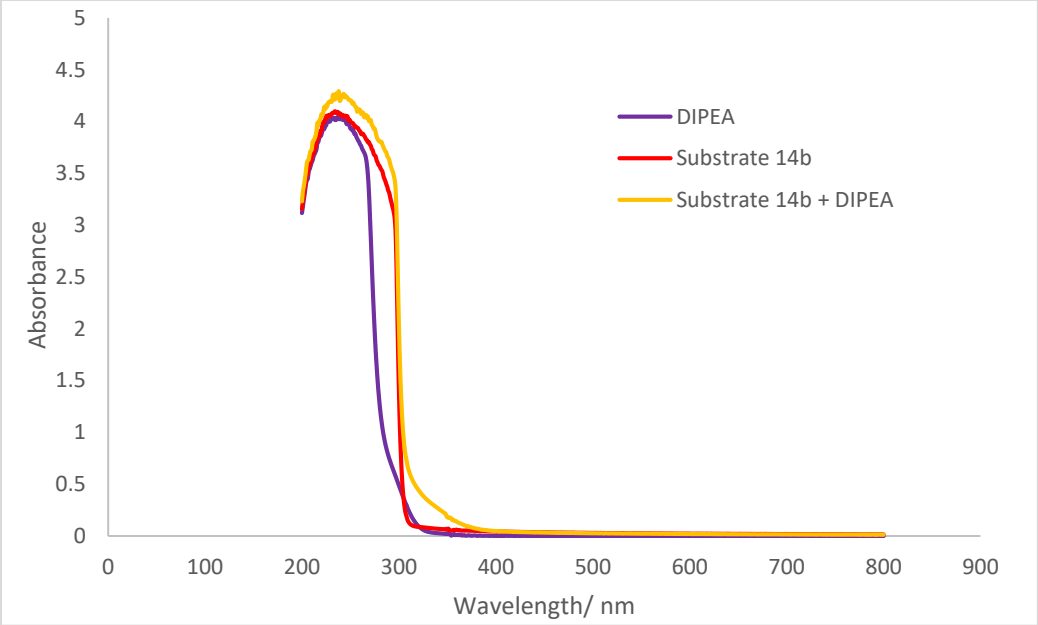
UV/Vis spectra were recorded using 1 cm path quartz cuvette and Varian Cary Eclipse spectrophotometer. MeCN was used as the solvent. UV/Vis spectra were recorded for following mixtures.

1. **14b** (0.06 mmol of **14b** in 2.1 mL total volume of MeCN)
2. DIPEA (0.24 mmol of DIPEA in 2.1 mL total volume of MeCN)
3. **14b** & DIPEA (0.06 mmol of **14b** and 0.24 mmol of DIPEA in 2.1 mL total volume of MeCN)

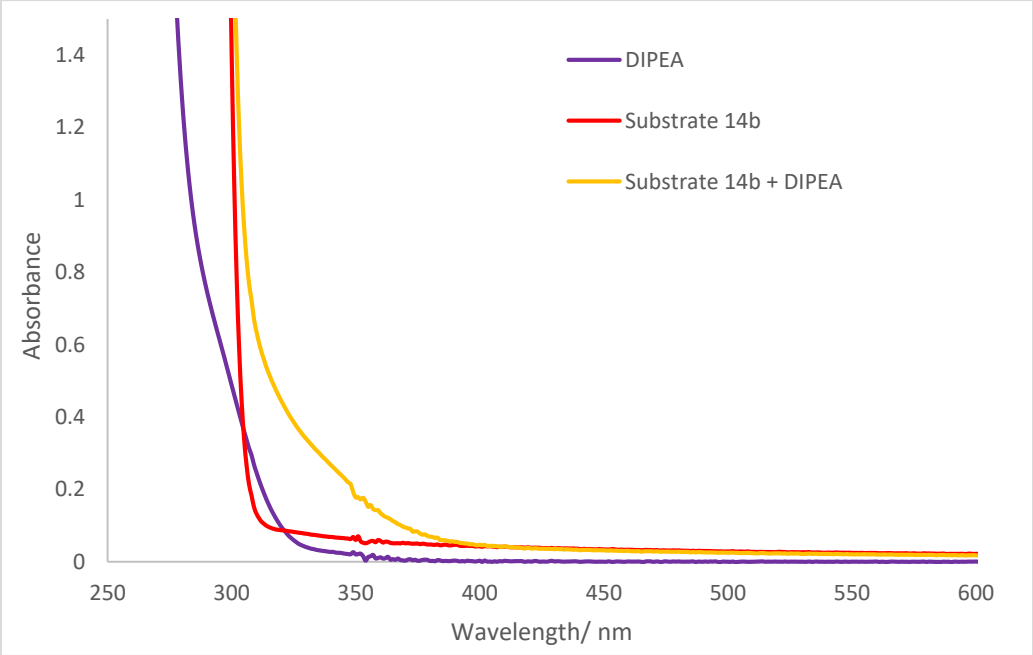


14b

sulfone 14b did not form any visually detectable EDA complex which was supported by UV-Vis experiments. As shown below the absorption of in MeCN approaches zero near 319 nm but a 1:4 mixture of 14b and DIPEA showed a slight bathochromic displacement but its absorbance too drops off before it reaches the visible region.

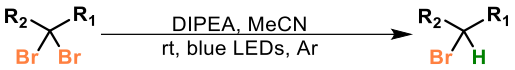


Expansion of the above spectrum:



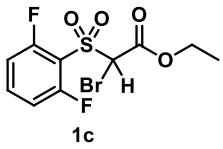
Light mediated dehalogenation

General procedure a for hydrodebromination:



A 12×75 mm borosilicate tube fitted with a rubber septum was charged with brominated compound (0.12 mmol, 1 equiv), *N, N*-diisopropylethylamine (X equivalent of amine) and MeCN (1.2 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 10 min and then left under positive Ar pressure by removing the exit needle. Then, the piece of aluminum foil was removed and the tube was placed in a blue LED bath (description above) and the lower portion of the tube was submerged under the water bath which was at 28 ^{o}C. The reaction was monitored by TLC, 1H NMR or GC-MS. After the completion of selective debromination, MeCN was removed via rotovap and the residue was treated with sat. $NaHCO_3$ solution (2 mL) and extracted with DCM (3 x 2 mL). The organic portions were combined and dried over anhydrous $MgSO_4$. The crude product was concentrated *in vacuo* and purified via normal phase chromatography.

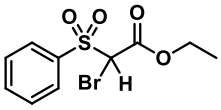
Ethyl 2-bromo-2-((2,6-difluorophenyl)sulfonyl)acetate



1c

The general procedure **A** was followed using ethyl 2,2-dibromo-2-((2,6-difluorophenyl)sulfonyl)acetate (50.6 mg, 0.12 mmol, 1 equiv) and *N, N*-diisopropylethylamine (31.4 µL, 0.18 mmol, 1.5 equiv) in 1.2 mL MeCN. After the completion of the reaction in 45 min, the crude was purified via automated flash chromatography using ether in hexanes (0% to 100%) with product eluting at 30% on a 4 g silica column to afford **1c** in 93% yield (38 mg, 0.112 mmol) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (tt, *J* = 8.5, 5.9 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 5.48 (s, 1H), 4.36 – 4.24 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.4 (dd, *J* = 8.4, 5.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (dd, *J* = 263.5, 3.0 Hz), 161.3, 137.7 (t, *J* = 11.4 Hz), 113.8 – 113.6 (m), 113.6 – 113.4 (m), 64.5, 60.4, 13.9. GC/MS (m/z, relative intensity) 263 (30), 224 (1), 154 (100). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_{10}H_8BrF_2O_4S]^-$ [M-H]$^-$ m/z, 340.9295 found 340.9301.

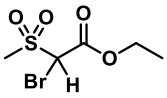
Ethyl 2-bromo-2-(phenylsulfonyl)acetate



2c

The general procedure **A** was followed using ethyl 2,2-dibromo-2-(phenylsulfonyl)acetate (46.3 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (31.4 μL, 0.18 mmol, 1.5 equiv) in 1.2 mL MeCN. After the completion of the reaction in 2 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 23% on a 4 g silica column to afford **2c** in 92% yield (33.8 mg, 0.11 mmol) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 5.24 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 134.9, 134.5, 130.4, 128.8, 63.7, 58.4, 13.6. GC/MS (m/z, relative intensity) 306 (M^+, 1), 280 (1), 141 (60). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_{10}H_{10}BrO_4S]^-$ $[M-H]^-$ m/z, 304.9483 found 304.9492.

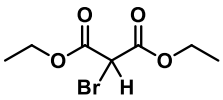
Ethyl 2-bromo-2-(methylsulfonyl)acetate



3c

The general procedure **A** was followed using ethyl 2,2-dibromo-2-(methylsulfonyl)acetate (38.9 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (31.4 μL, 0.18 mmol, 1.5 equiv) in 1.2 mL MeCN. After the completion of the reaction in 3 h, the crude was purified via automated flash chromatography using ether in hexanes (0% to 100%) with product eluting at 28% on a 4 g silica column to afford **3c** in 90% yield (26.5 mg, 0.108 mmol) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.28 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ163.2, 64.3, 55.8, 37.2, 13.9. GC/MS (m/z, relative intensity) 216 (10), 166 (10), 120 (100). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_5H_8BrO_4S]^-$ $[M-H]^-$ m/z, 242.9327 found 242.9335.

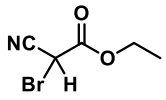
Diethyl 2-bromomalonate



4c

The general procedure **A** was followed using diethyl 2,2-dibromomalonate (38.15 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 μL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 18 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 7% on a 4 g silica column to afford **4c** in 91% yield (26.2 mg, 0.109 mmol) as an oil. NMR chemical shifts and mass spectrum details have reported in literature[13] and NMR chemical shifts match with the literature values. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 4H), 1.30 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 63.7, 42.8, 14.3.

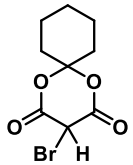
Ethyl 2-bromo-2-cyanoacetate



5c

The general procedure **A** was followed using ethyl 2,2-dibromo-2-cyanoacetate (32.5 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 μL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 19 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 12% on a 4 g silica column to afford **5c** in 89% yield (20.5 mg, 0.107 mmol) as an oil. NMR chemical shifts and mass spectrum details have reported in literature[14] and NMR chemical shifts match with the literature values. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

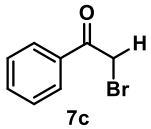
3-Bromo-1,5-dioxaspiro[5.5]undecane-2,4-dione



6c

The general procedure **A** was followed using 3,3-dibromo-1,5-dioxaspiro[5.5]undecane-2,4-dione (41 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 μL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 18 h, the crude was purified via silica plug to afford **6c** in 85% yield as a mixture of 89:11 monodebrominated to didebrominated product based on ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (s, 1H), 2.17 – 2.09 (m, 2H), 2.04 – 1.94 (m, 4H), 1.81 – 1.72 (m, 4H), 1.57 – 1.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ161.4, 108.6, 37.2, 37.0, 35.1, 24.3, 22.7, 22.6. This compound decomposed under GC conditions. HRMS (ESI) calcd. for $[C_9H_{10}BrO_4]^-$ $[M\text{-}H]^-$ m/z, 260.9762 found 260.9782.

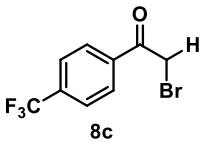
2-Bromo-1-phenylethan-1-one



7c

The general procedure **A** was followed using 2,2-dibromo-1-phenylethan-1-one (33.4 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 μL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 21 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 3% on a 4 g silica column to afford **7c** in 93% yield (22.2 mg, 0.112 mmol) as an oil. NMR chemical shifts and mass spectrum details have reported in literature[15] and NMR chemical shifts match with the literature values. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, 2H), 7.61 (tt, *J* = 6.9, 1.3 Hz, 1H), 7.55 – 7.45 (m, 2H), 4.46 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 134.1, 129.1, 129.0, 31.1.

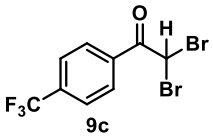
2-Bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one



8c

The general procedure **A** was followed using 2,2-dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (41.5 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 μL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 20 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 1% on a 4 g silica column to afford **8c** in 94% yield (30.1 mg, 0.113 mmol) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 4.45 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ-63.3. ^{13}C NMR (101 MHz, $CDCl_3$) δ190.5, 137.5 – 136.0 (m), 135.3 (q, *J* = 32.8 Hz), 129.5, 126.1 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.9 Hz), 30.4. GC/MS (m/z, relative intensity) 266 (M^+, 1), 173 (100), 145 (50). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_9H_5BrF_3O]^-$ [M-H]$^-$ m/z, 264.9476 found 264.9484.

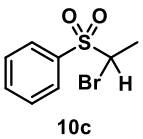
2,2-Dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one



9c

The general procedure **A** was followed using 2,2,2-tribromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (51 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (31.4 μL, 0.18 mmol, 1.5 equiv) in 1.2 mL MeCN. After the completion of the reaction in 10 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 0.1% on a 4 g silica column to afford **9c** in 88% yield (36.7 mg, 0.106 mmol) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 6.62 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ185.5, 136.0 (q, *J* = 33.0 Hz), 134.4 – 133.9 (m), 130.7, 127.81 (q, *J* = 272.9 Hz), 126.4 (q, *J* = 3.7 Hz), 39.5. GC/MS (m/z, relative intensity) 327(1), 266 (1), 173 (100). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_9H_4Br_2F_3O]^-$ [M-H]$^-$ m/z, 344.8561 found 344.8568.

((1-Bromoethyl)sulfonyl)benzene

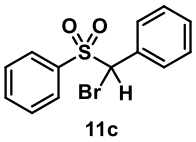


10c

The general procedure **A** was followed using ((1,1-dibromoethyl)sulfonyl)benzene (39.4 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 μL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 22 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 10% on a 4 g silica column to afford **10c** in 90% yield (27 mg, 0.108 mmol) as an oil. NMR chemical shifts and mass spectrum details

have reported in literature[7] and mass spectrum details match with the literature values. GC/MS (m/z, relative intensity) 248 (M^+, 2), 250 ($M^+ + 2$, 2), 125 (90), 77 (100).

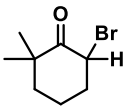
((Bromo(phenyl)methyl)sulfonyl)benzene



11c

The general procedure **A** was followed using ((dibromo(phenyl)methyl)sulfonyl)benzene (46.8 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 µL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 20 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 6% on a 4 g silica column to afford **11c** in 91% yield (34 mg, 0.109 mmol) as an oil. NMR chemical shifts and mass spectrum details have reported in literature [7] and NMR chemical shifts match with the literature values. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.50 – 7.43 (m, 2H), 7.40 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 5.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 134.6, 131.2, 130.5, 130.4, 130.2, 129.0, 128.7, 65.8.

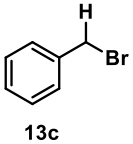
6-Bromo-2,2-dimethylcyclohexan-1-one



12c

The general procedure **A** was followed using 2,2-dibromo-6,6-dimethylcyclohexan-1-one (34.1 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (41.8 µL, 0.24 mmol, 2 equiv) in 1.2 mL MeCN. After the completion of the reaction in 25 h, the crude was purified via automated flash chromatography using diethyl ether in hexanes (0% to 100%) with product eluting at 1% on a 4 g silica column to afford **12c** in 89% yield (21.9 mg, 0.107 mmol) as an oil. NMR chemical shifts and mass spectrum details have reported in literature[16] and mass spectrum details match with the literature values. GC/MS (m/z, relative intensity) 204 (M^+, 10), 206 ($M^+ + 2$, 10), 97 (70), 69 (100).

(Bromomethyl)benzene

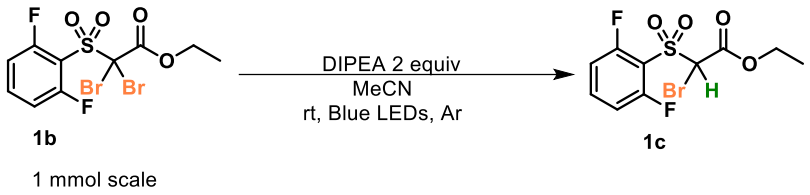


13c

The general procedure **A** was followed using (dibromomethyl)benzene (30 mg, 0.12 mmol) and *N, N*-diisopropylethylamine (83.6 µL, 0.48 mmol, 4 equiv) in 1.2 mL MeCN. After the completion of the reaction in 72 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 0.1% on a 4 g silica column to afford **13c** in 80% yield (16.4 mg, 0.096 mmol) as an oil. NMR chemical shifts match with the literature

values.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.35 (ddd, *J* = 7.4, 5.9, 1.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 4.51 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 129.5, 129.3, 128.9, 34.0.

Hydrodebromination in large scale



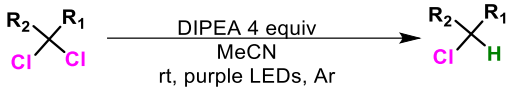
1b

1 mmol scale

1c

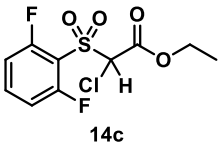
A 18×150 mm borosilicate tube fitted with a rubber septum was charged with **1b** (422 mg, 1 mmol, 1 equiv), *N*, *N*-diisopropylethylamine (349 µL, 2 mmol, 2 equiv) and MeCN (10 mL). The reaction tube was covered with piece of aluminum foil to avoid ambient light and degassed via Ar bubbling for 30 min and then left under positive Ar pressure by removing the exit needle. Then, the piece of aluminum foil was removed and the tube was placed in a blue LED bath (description above) and the lower portion of the tube was submerged under the water bath which was at 28 °C and the reaction was stirred. The reaction was monitored by 19F NMR. After the complete consumption of **1b** (6 h), crude reaction showed 80% of **1c** product according to 19F NMR. MeCN was removed via rotovap and the residue was treated with sat. $NaHCO_3$ solution (20 mL) and extracted with DCM (3 x 10 mL). The organic portions were combined and dried over anhydrous $MgSO_4$. The crude product was concentrated *in vacuo* and purified via normal phase chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 26% on a 40 g silica column to afford **1c** in 76% as a solid.

General procedure B for hydrodechlorination



This procedure is identical to general procedure **A** except that the blue LEDs were exchanged with violet LEDs and increased loading of amine was used. This procedure was used for all the hydrodechlorination reactions. Substrate (0.12 mmol, 1 equiv) and *N*, *N*-diisopropylethylamine (83.6 µL, 0.48 mmol, 4 equiv) in 1.2 mL MeCN. The tube was placed in a purple LEDs bath. The reaction was monitored by TLC, 1H NMR or GC-MS. After the completion of selective dechlorination, MeCN was removed via rotovap and the residue was treated with sat. $NaHCO_3$ solution (2 mL) and extracted with DCM (3 x 2 mL). The organic portions were combined and dried over anhydrous $MgSO_4$. The crude product was concentrated *in vacuo* and purified via normal phase chromatography.

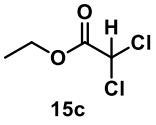
Ethyl 2-chloro-2-((2,6-difluorophenyl)sulfonyl)acetate



14c

The general procedure **B** was followed using ethyl 2,2-dichloro-2-((2,6-difluorophenyl)sulfonyl)acetate (40 mg, 0.12 mmol) and *N*, *N*-diisopropylethylamine (83.6 µL, 0.48 mmol, 4 equiv) in 1.2 mL MeCN. After the completion of the reaction in 50 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 20% on a 4 g silica column to afford **14c** in 85% yield (30.5 mg, 0.102 mmol) as an oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (tt, *J* = 8.5, 5.9 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 5.44 (s, 1H), 4.35 (qq, *J* = 6.8, 3.6 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.5 (dd, *J* = 8.5, 5.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (dd, *J* = 263.8, 3.1 Hz), 161.1, 137.8 (t, *J* = 11.3 Hz), 113.8 – 113.7 (m), 113.6 – 113.4 (m), 72.6, 64.5, 13.9. GC/MS (m/z, relative intensity) 270 (5), 177 (100), 161 (60). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_{10}H_8ClF_2O_4S]^-$ $[M-H]^-$ m/z, 296.9800 found 296.9808.

ethyl 2,2-dichloroacetate

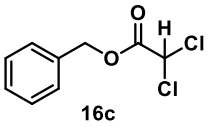


15c

The general procedure **B** was followed using ethyl 2,2,2-trichloroacetate (23 mg, 0.12 mmol) and *N*, *N*-diisopropylethylamine (83.6 µL, 0.48 mmol, 4 equiv) in 1.2 mL MeCN. After the completion of the reaction in 72 h, the crude was purified via automated flash

chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 10% on a 4 g silica column to afford **15c** in 70% yield (13.2 mg, 0.084 mmol) as an oil. NMR chemical shifts and mass spectrum details have reported in literature[18] and NMR chemical shifts match with the literature values. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (s, 1H), 4.33 (qd, *J* = 7.1, 1.5 Hz, 2H), 1.35 (td, *J* = 8.7, 6.7, 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 64.8, 64.2, 14.3.

Benzyl 2,2-dichloroacetate



16c

The general procedure **B** was followed using benzyl 2,2,2-trichloroacetate (30.4 mg, 0.12 mmol) and *N*, *N*-diisopropylethylamine (83.6 μL, 0.48 mmol, 4 equiv) in 1.2 mL MeCN. After the completion of the reaction in 60 h, the crude was purified via automated flash chromatography using EtOAc in hexanes (0% to 100%) with product eluting at 20% on a 4 g silica column to afford **16c** in 78% yield (20.5 mg, 0.094 mmol) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 5H), 5.98 (s, 1H), 5.29 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ164.8, 134.6, 129.4, 129.2, 128.9, 69.5, 64.7. GC/MS (m/z, relative intensity) 218 (M^+, 10), 107 (18), 91 (100). The compound produced thermally generated impurities under GC conditions. HRMS (ESI) calcd. for $[C_9H_7Cl_2O_2]^-$ $[M-H]^-$ m/z, 216.9823 found 216.9785.

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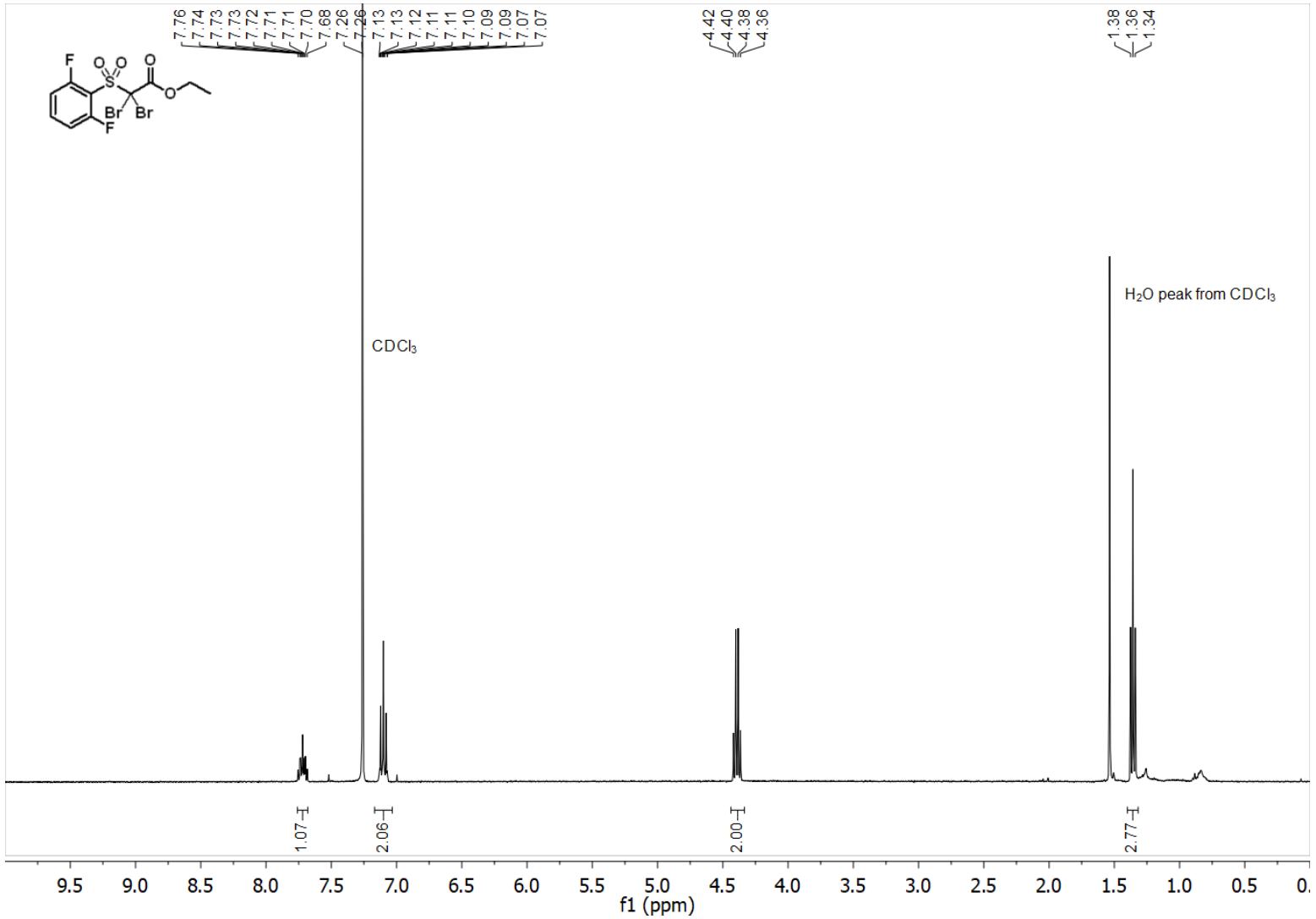
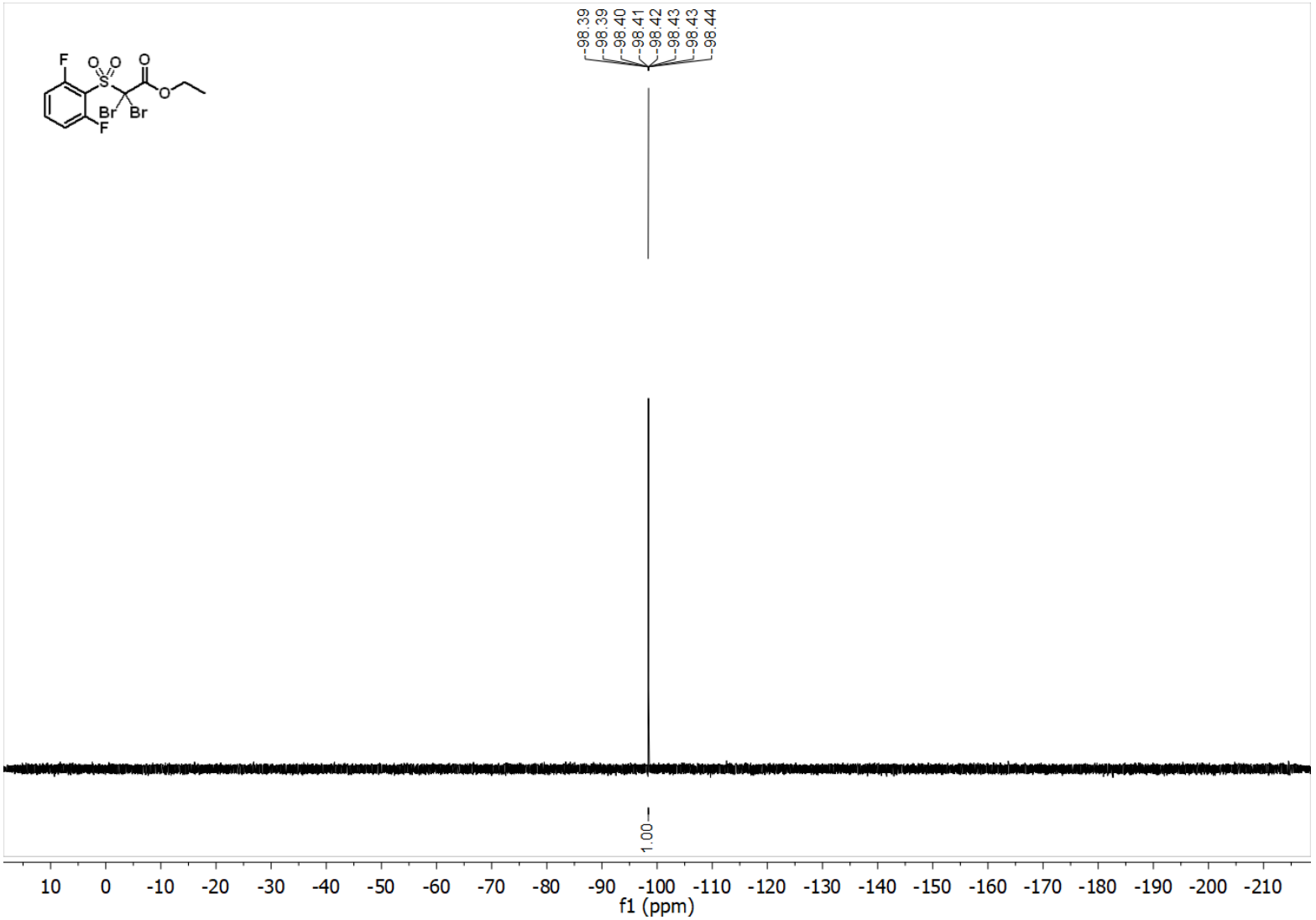
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1b Ethyl 2,2-dibromo-2-((2,6-difluorophenyl)sulfonyl)acetate



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1b Ethyl 2,2-dibromo-2-((2,6-difluorophenyl)sulfonyl)acetate



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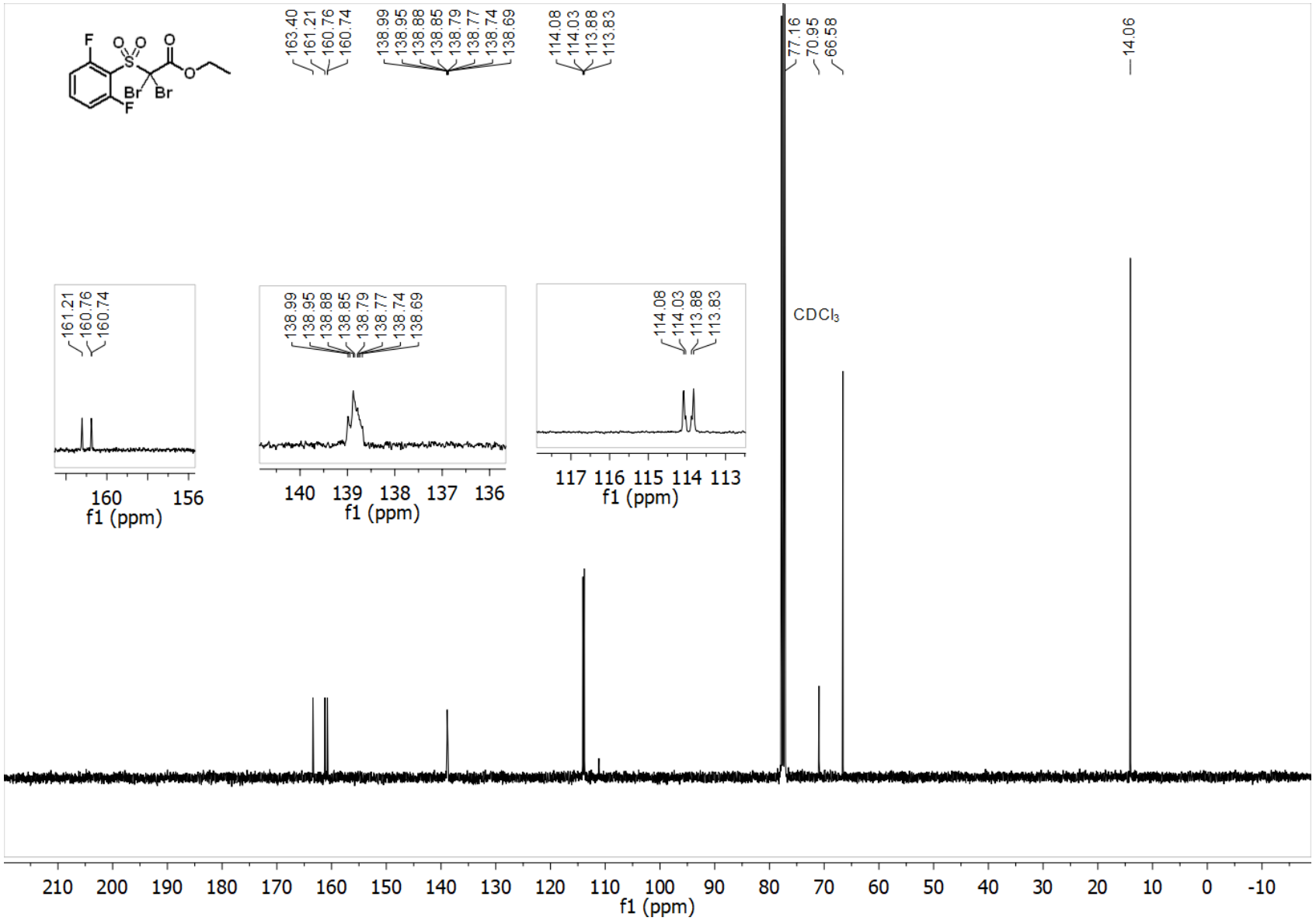

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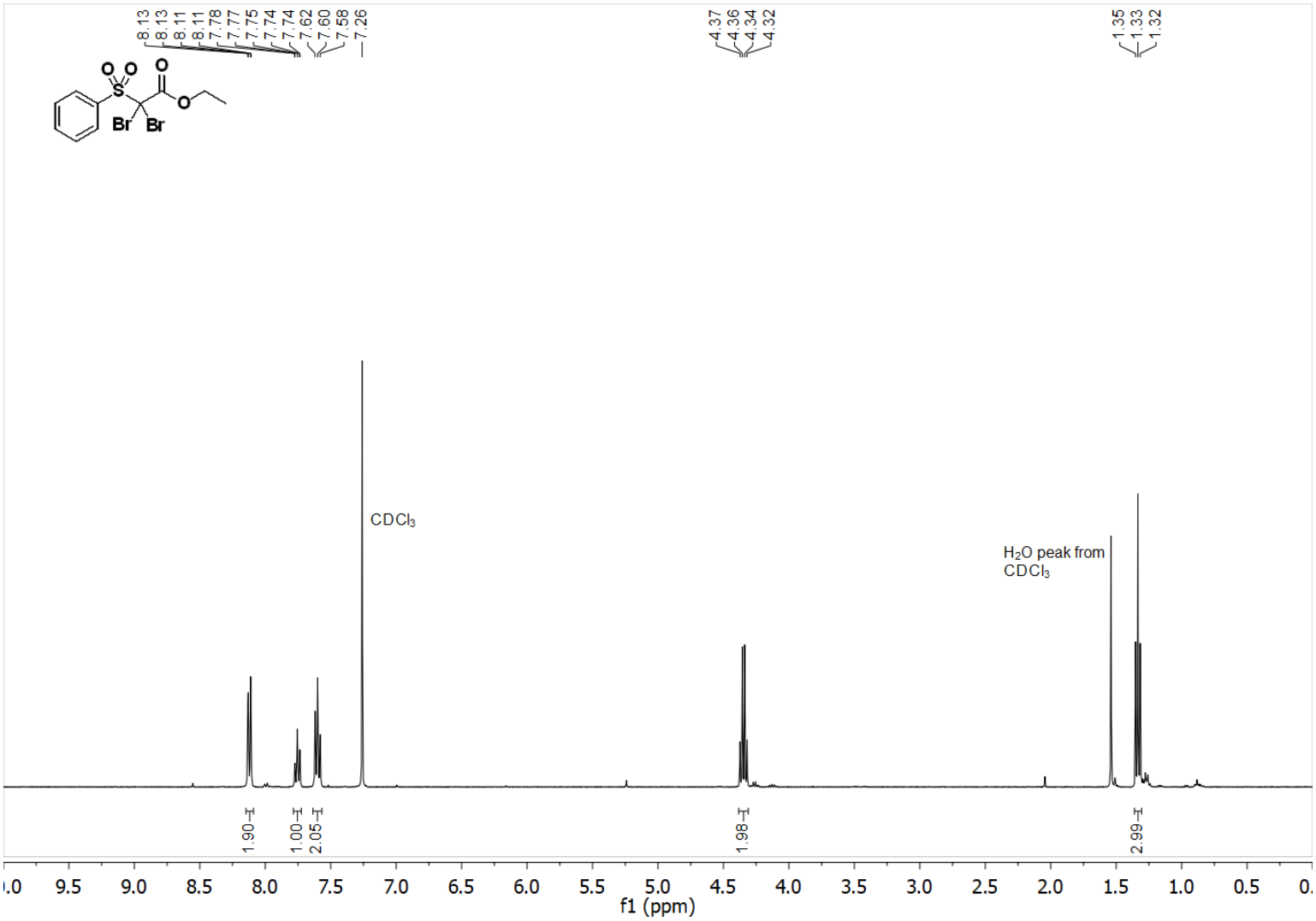

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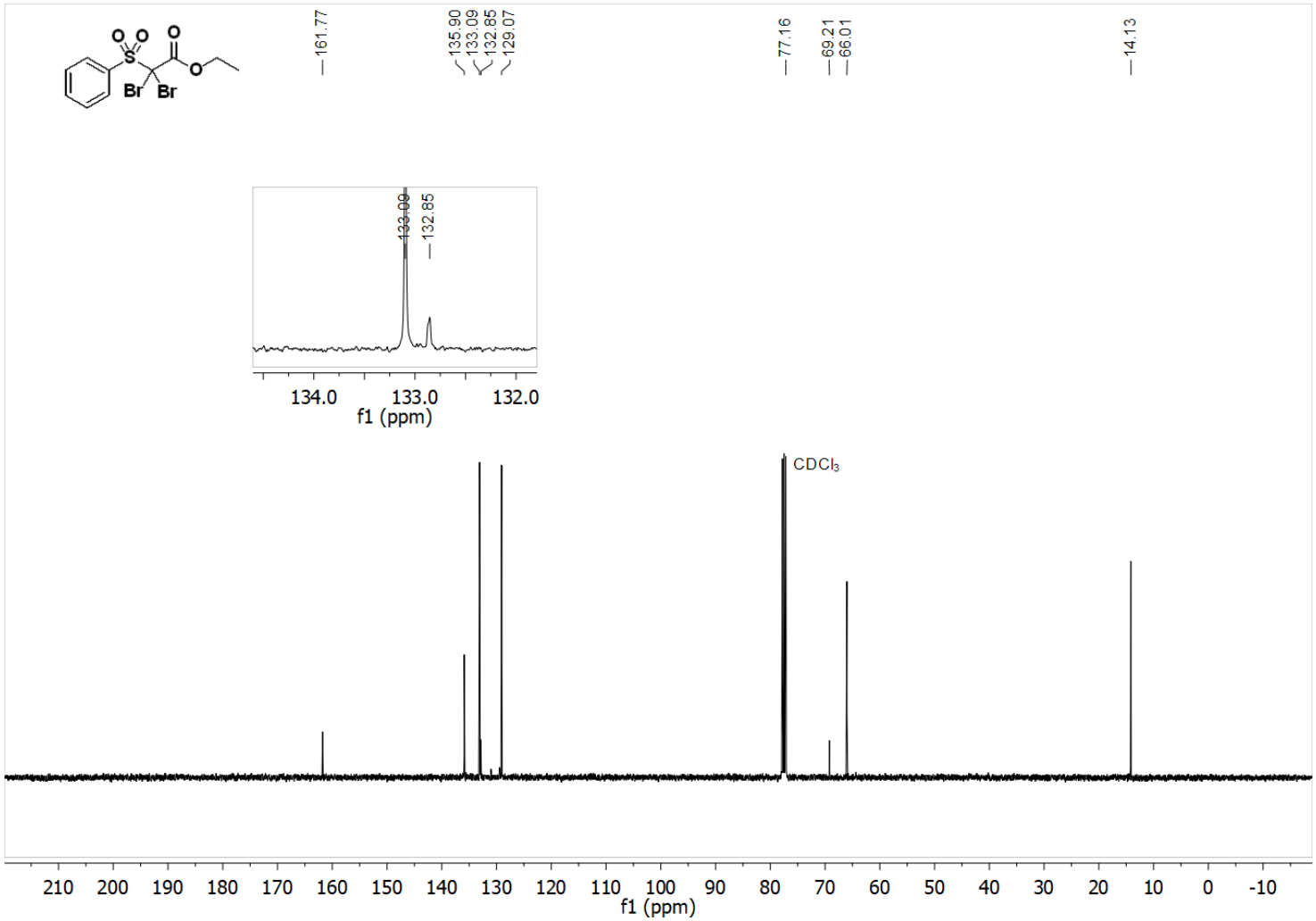

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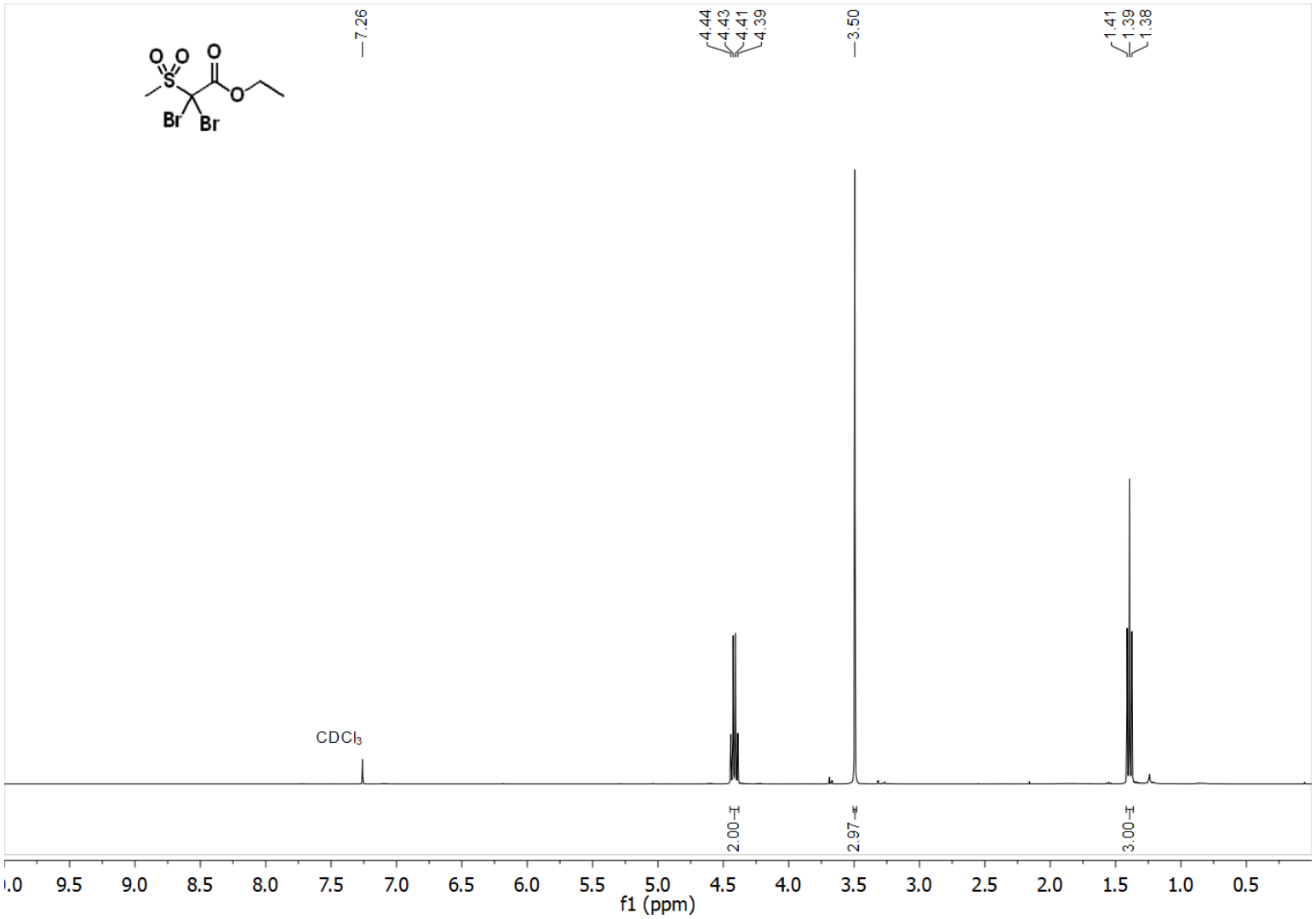

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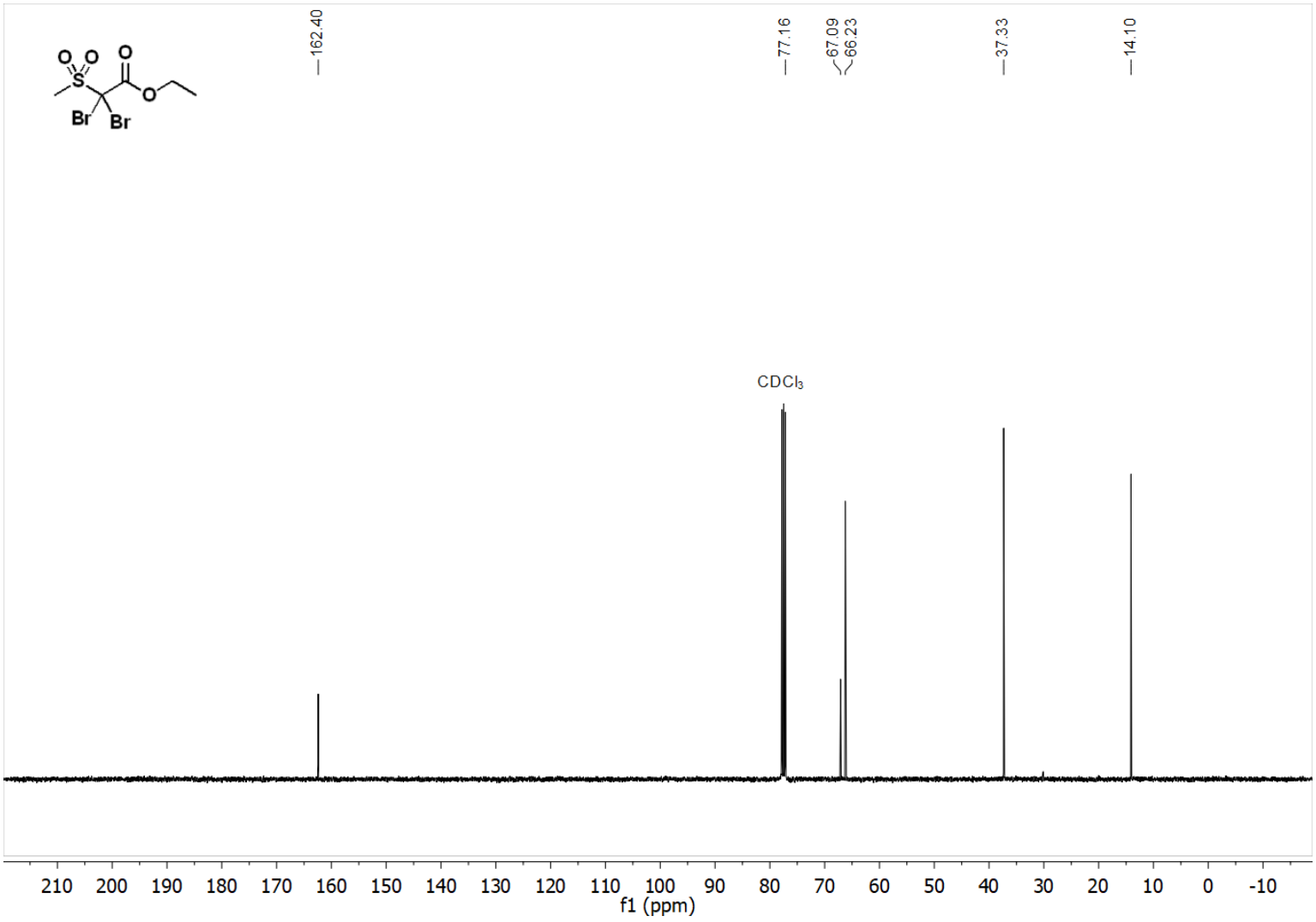

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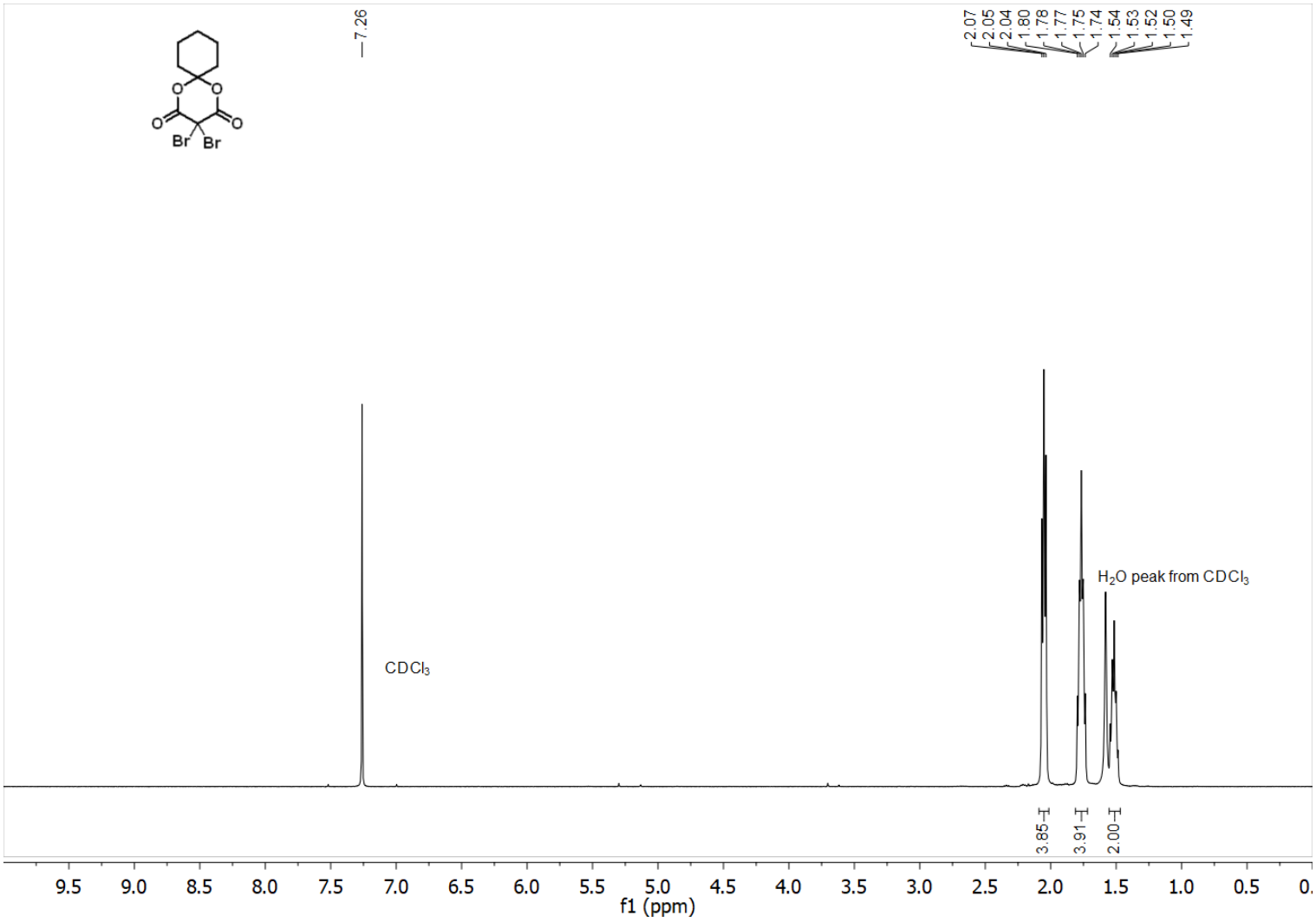

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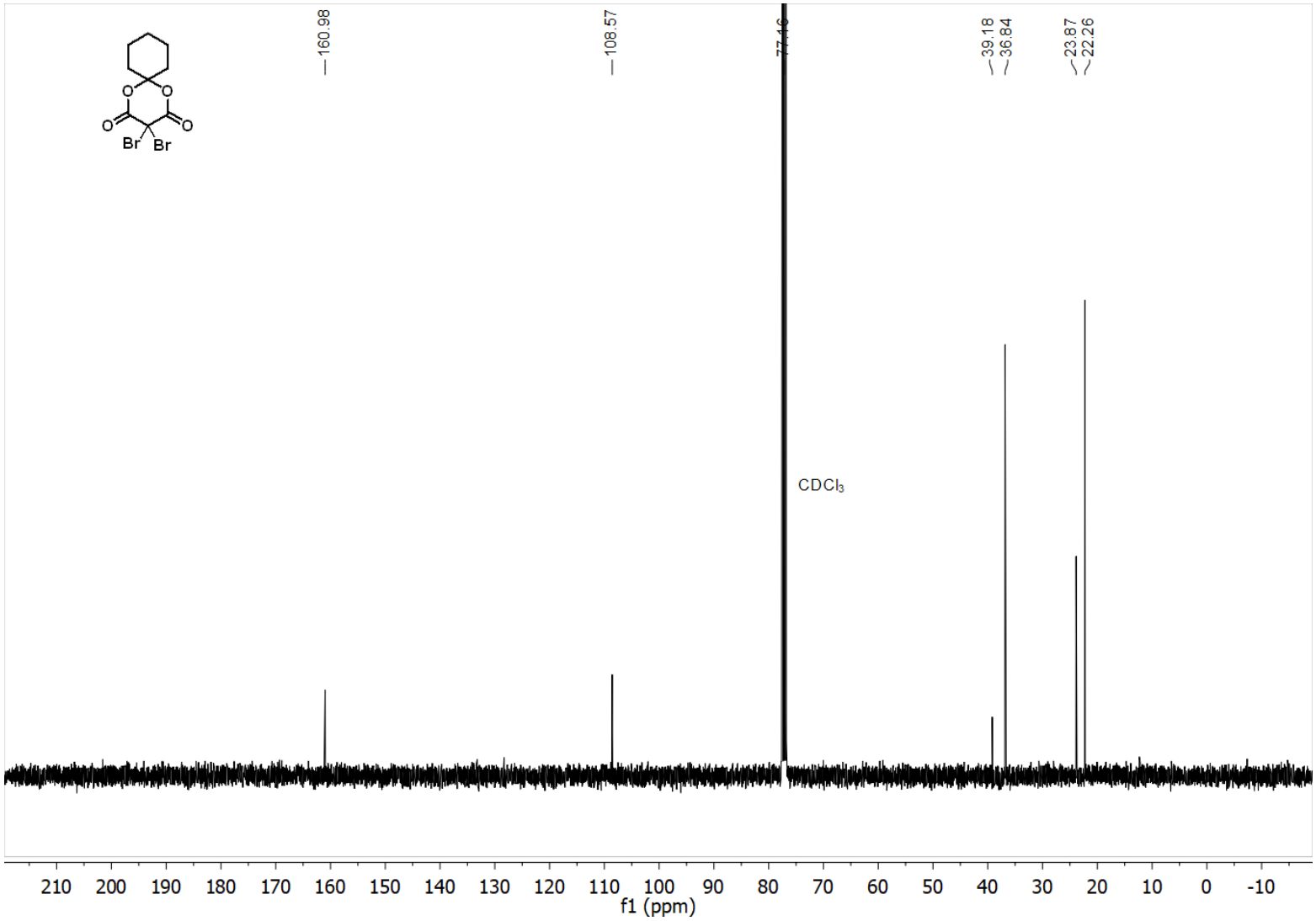

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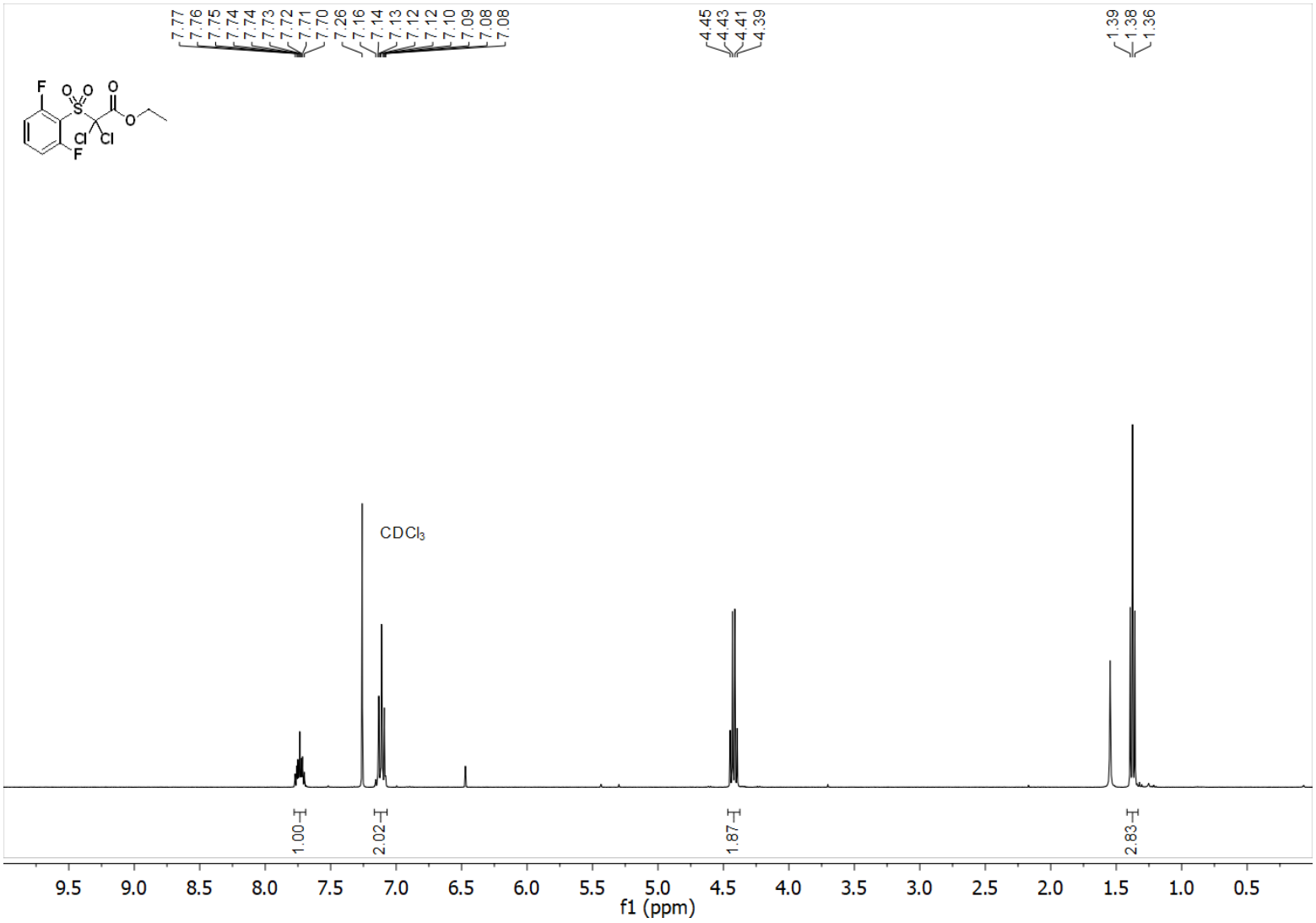

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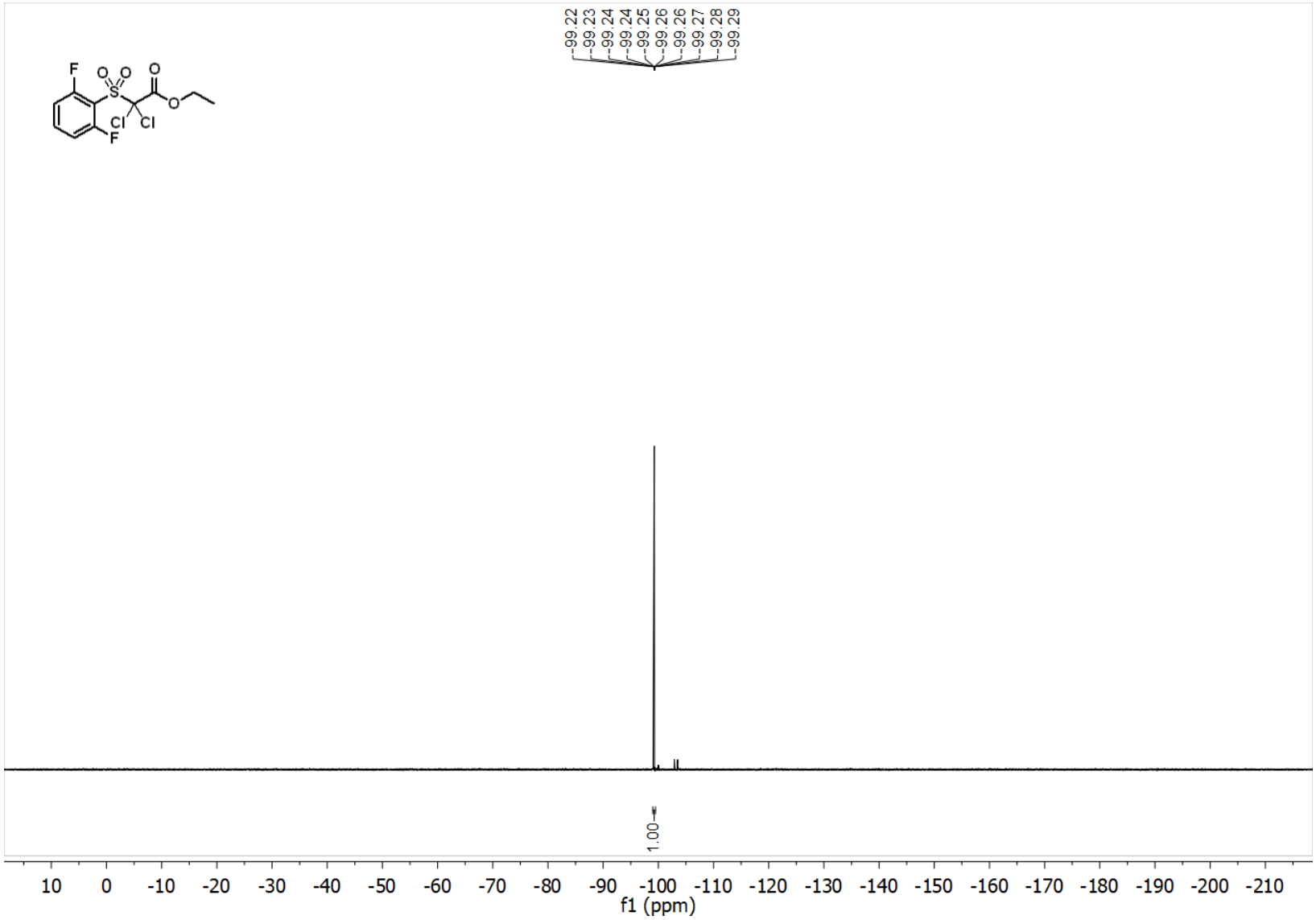

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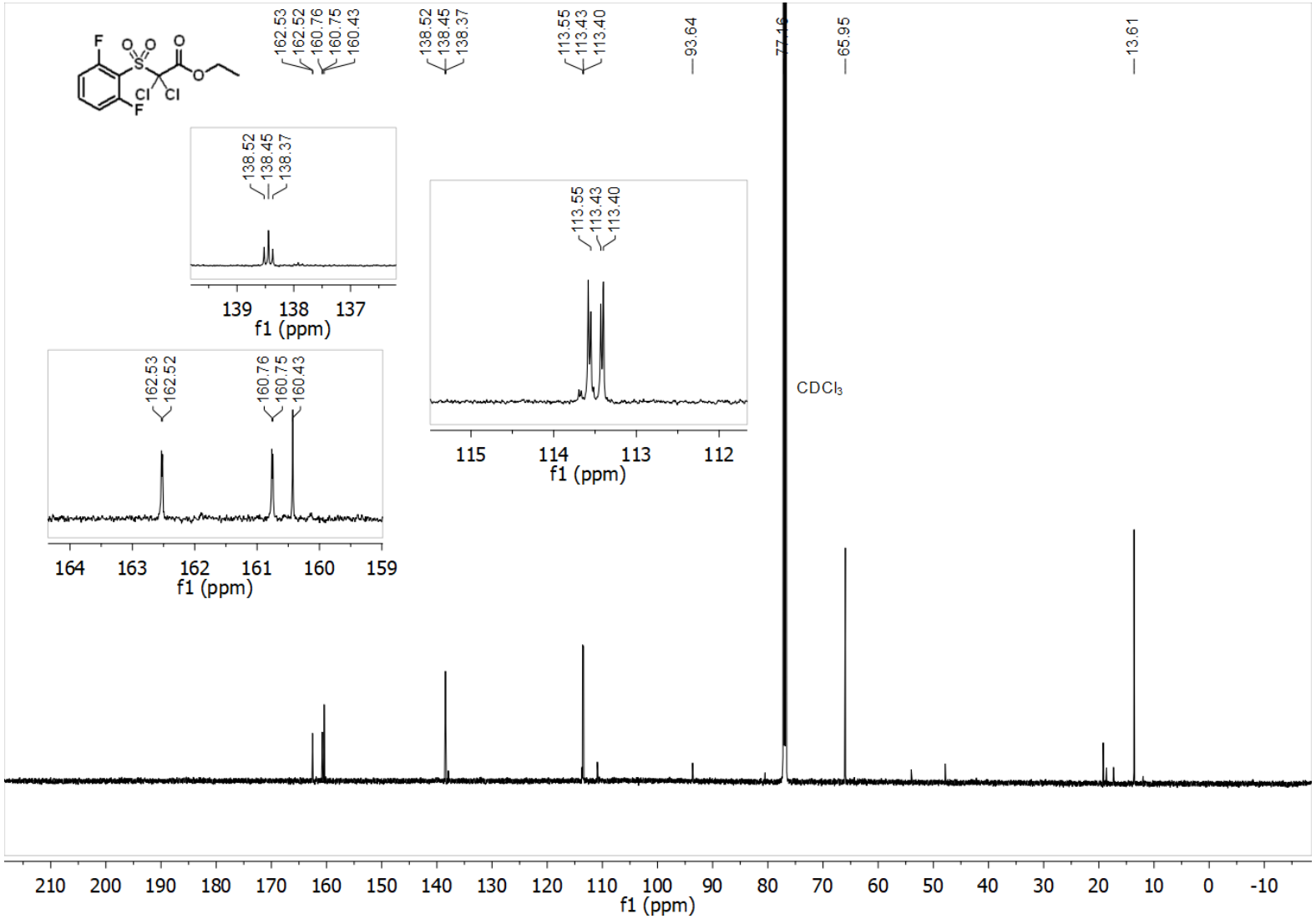

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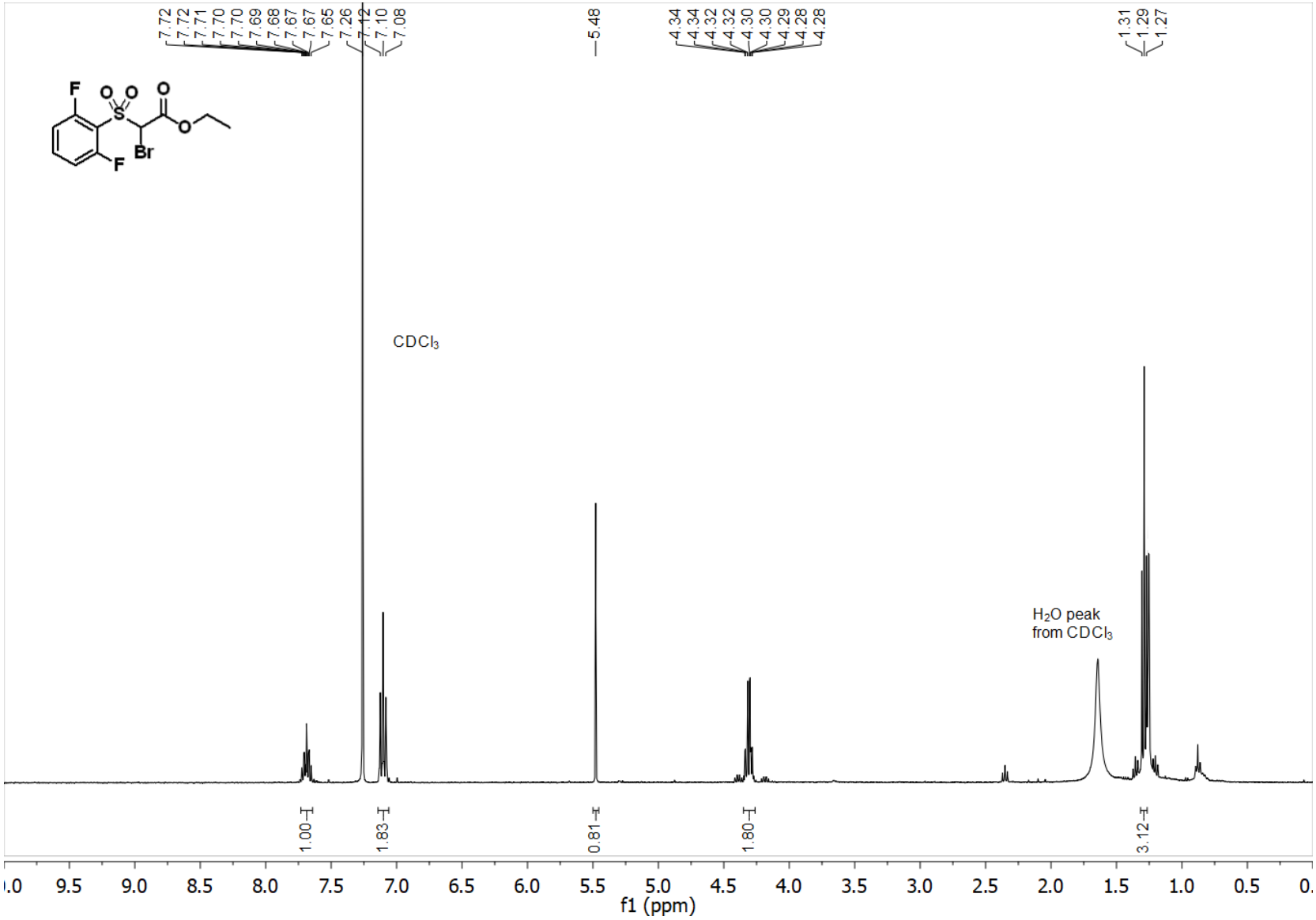
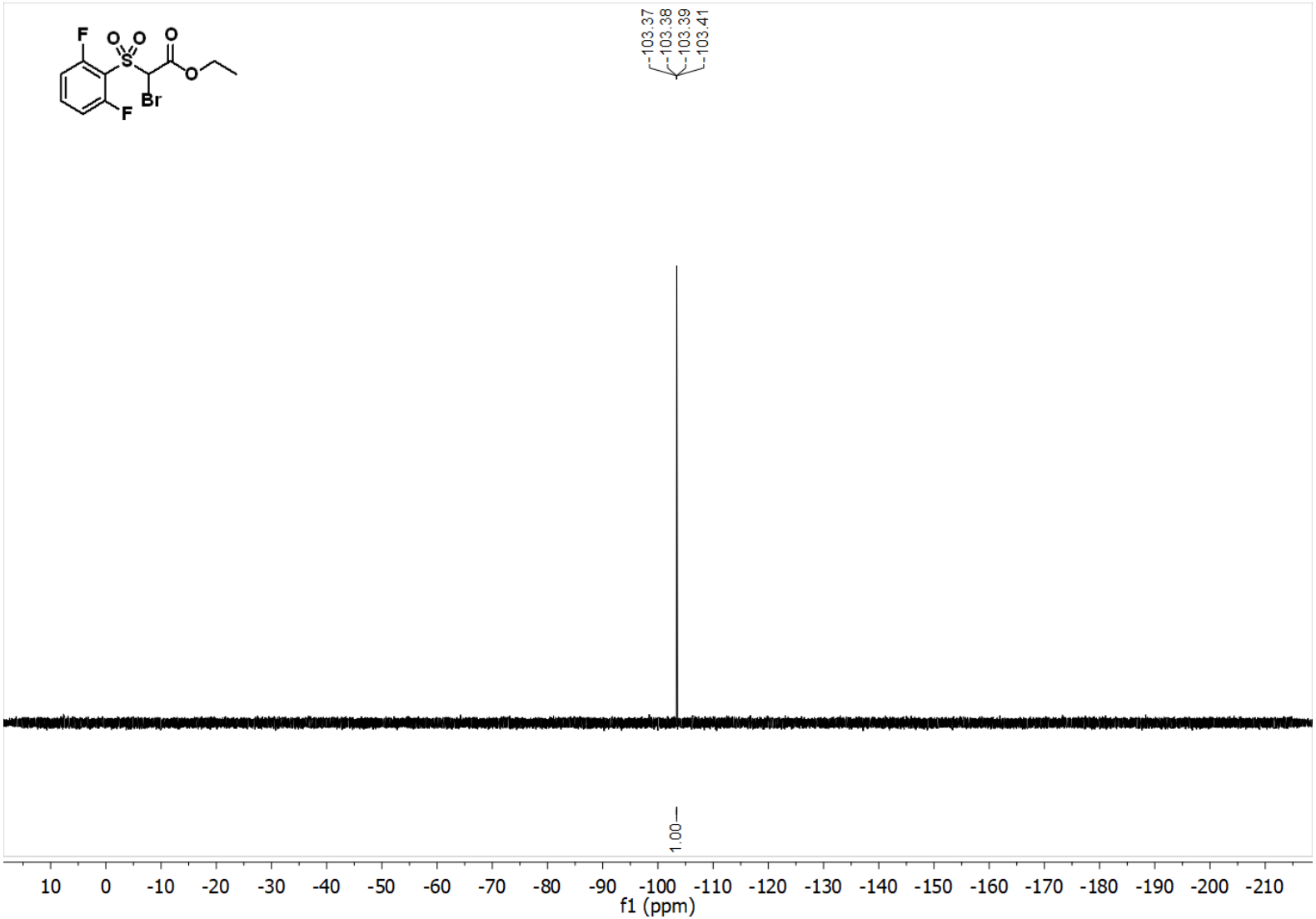
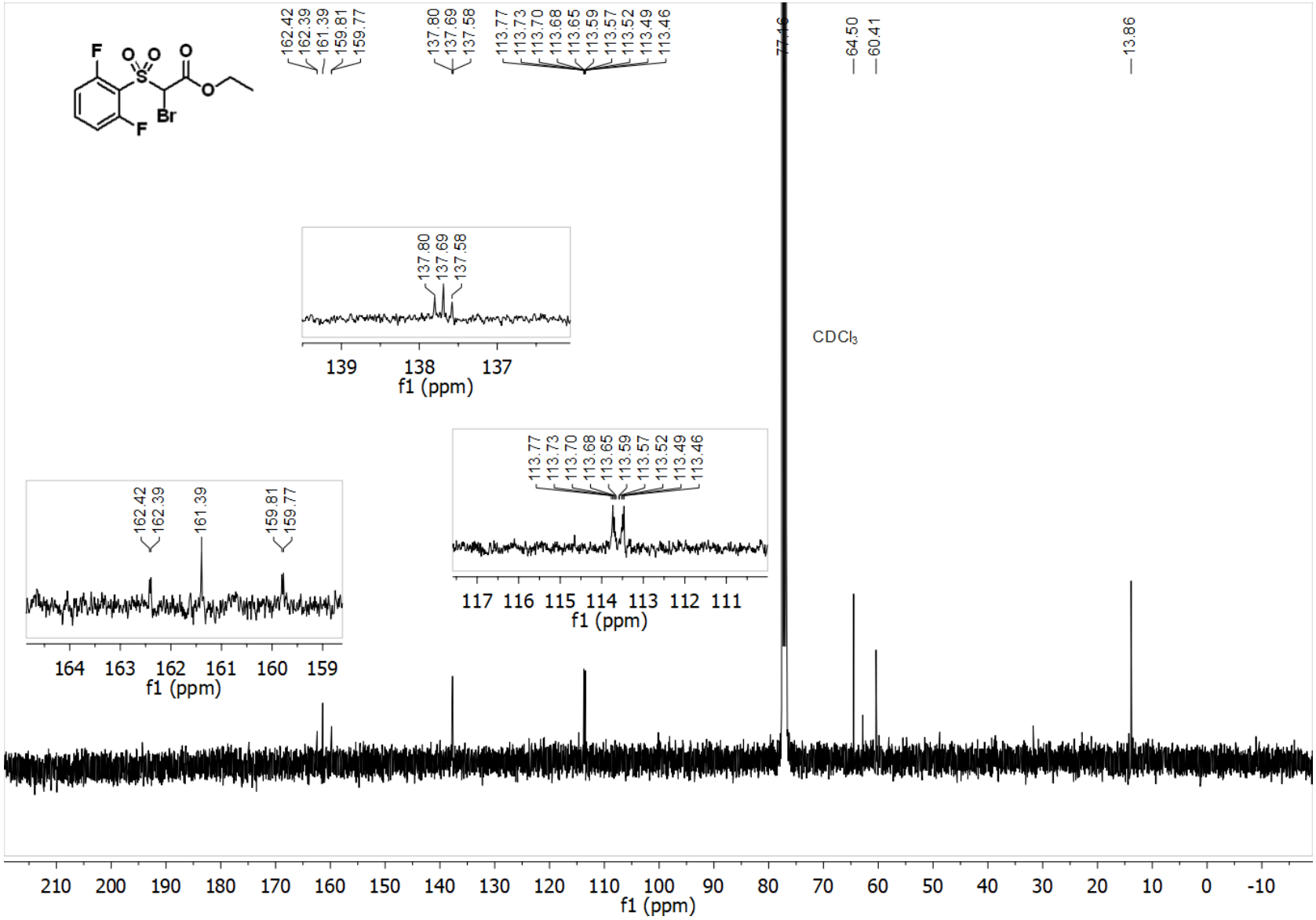


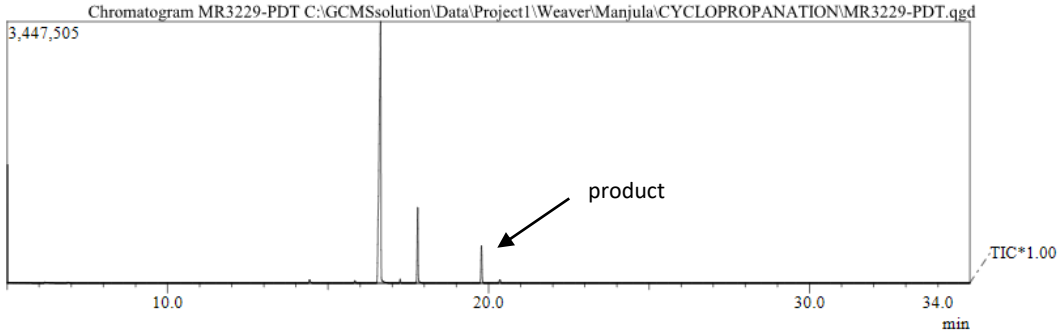
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1c ethyl 2-bromo-2-((2,6-difluorophenyl)sulfonyl)acetate

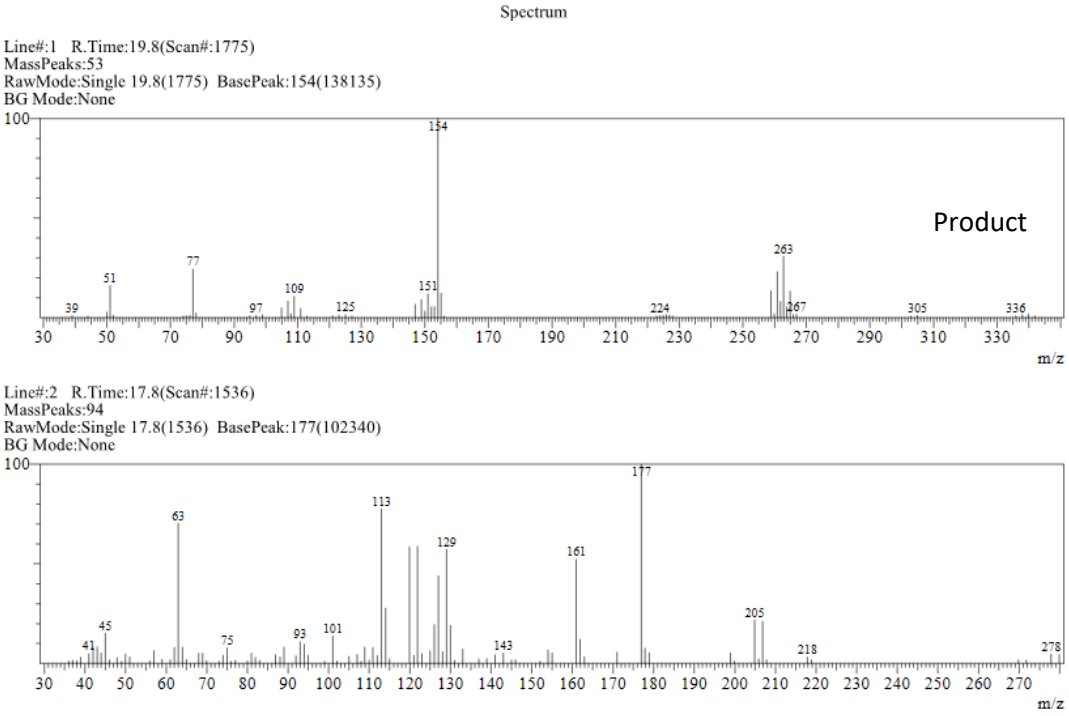


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1c ethyl 2-bromo-2-((2,6-difluorophenyl)sulfonyl)acetate

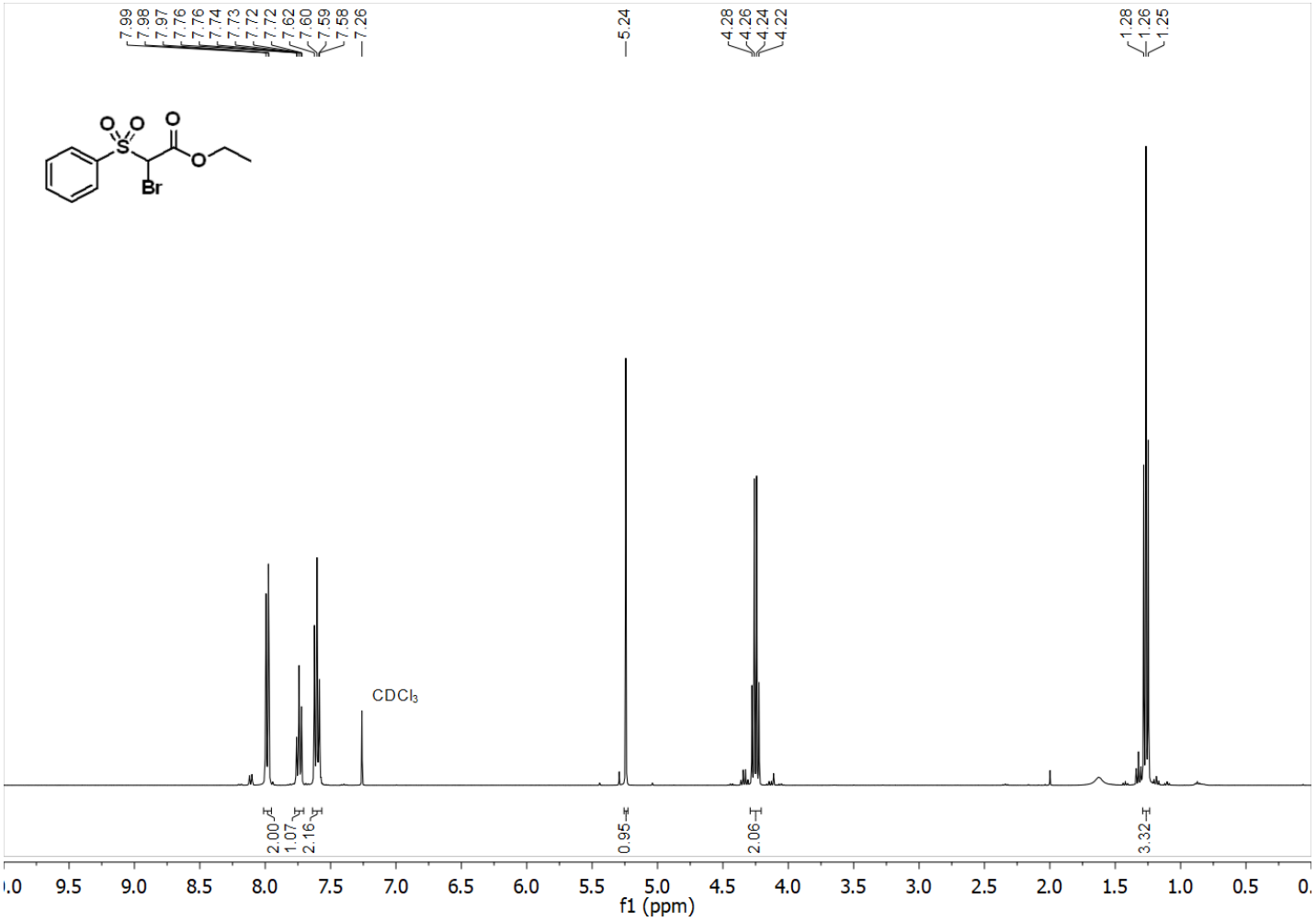


GC and MS of 1c ethyl 2-bromo-2-((2,6-difluorophenyl)sulfonyl)acetate

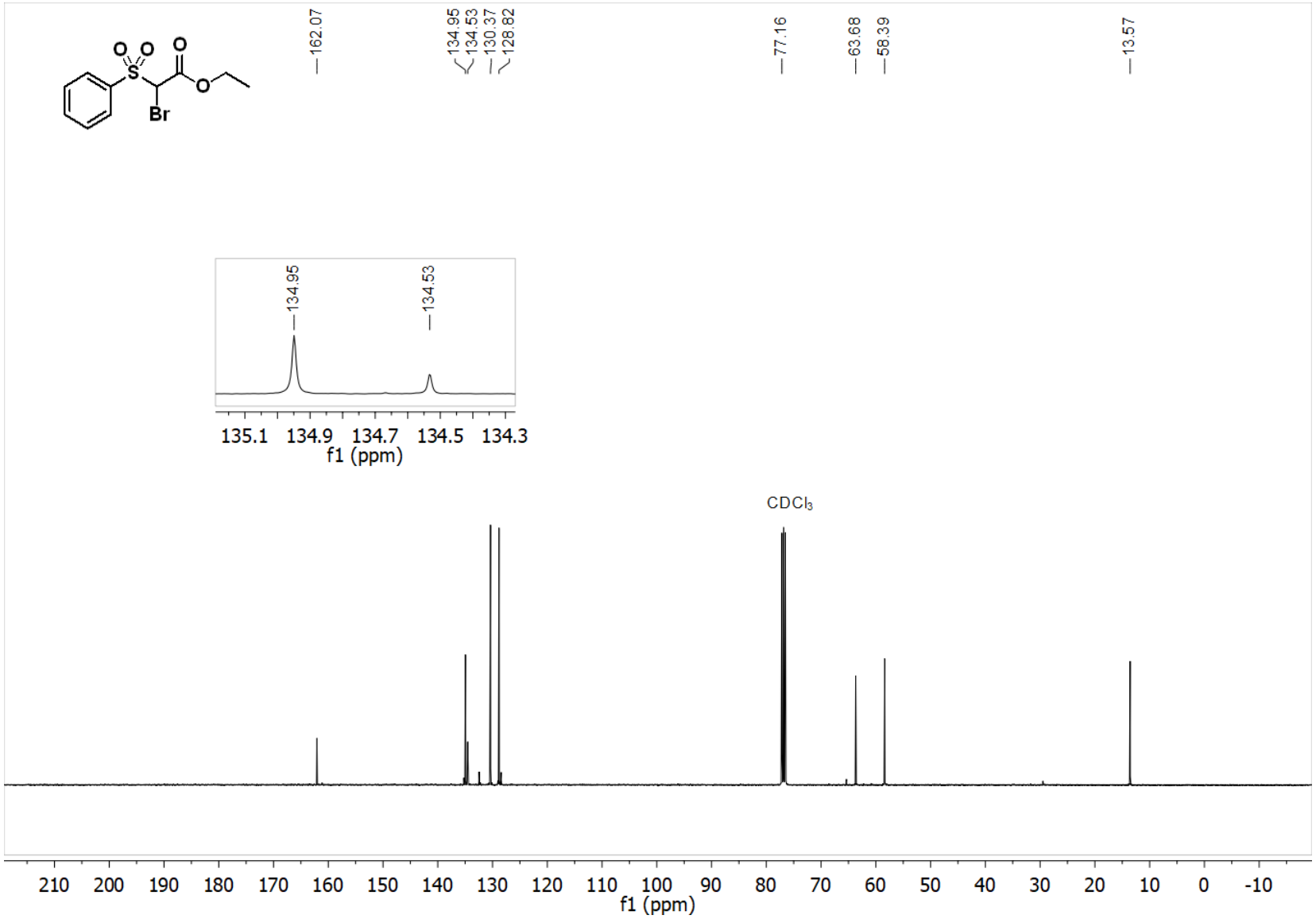




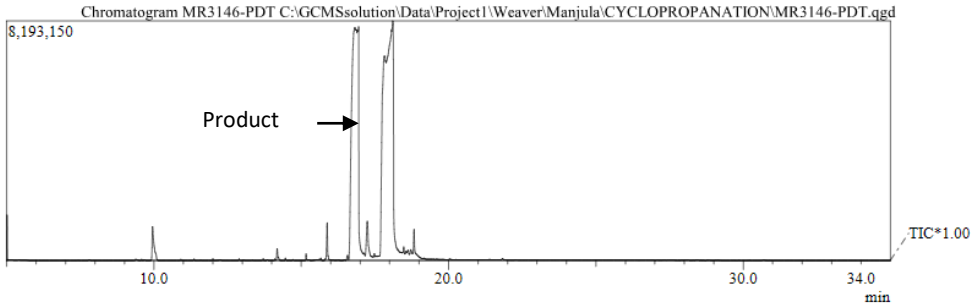
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2c ethyl 2-bromo-2-(phenylsulfonyl)acetate



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2c ethyl 2-bromo-2-(phenylsulfonyl)acetate

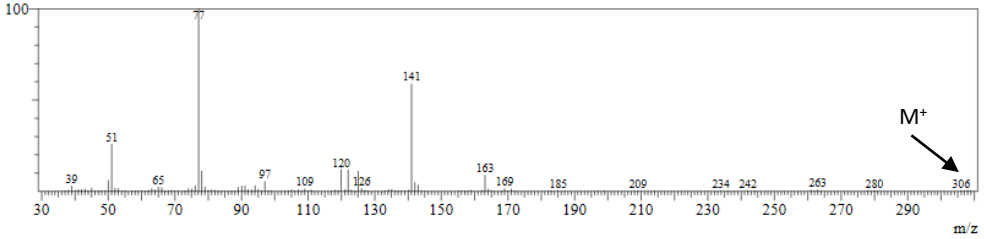


GC and MS of 2c ethyl 2-bromo-2-(phenylsulfonyl)acetate

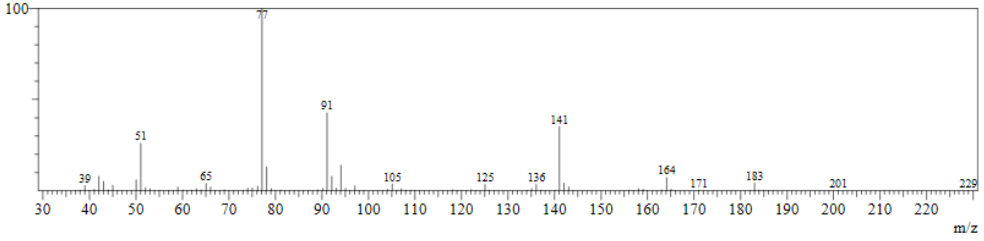


Spectrum

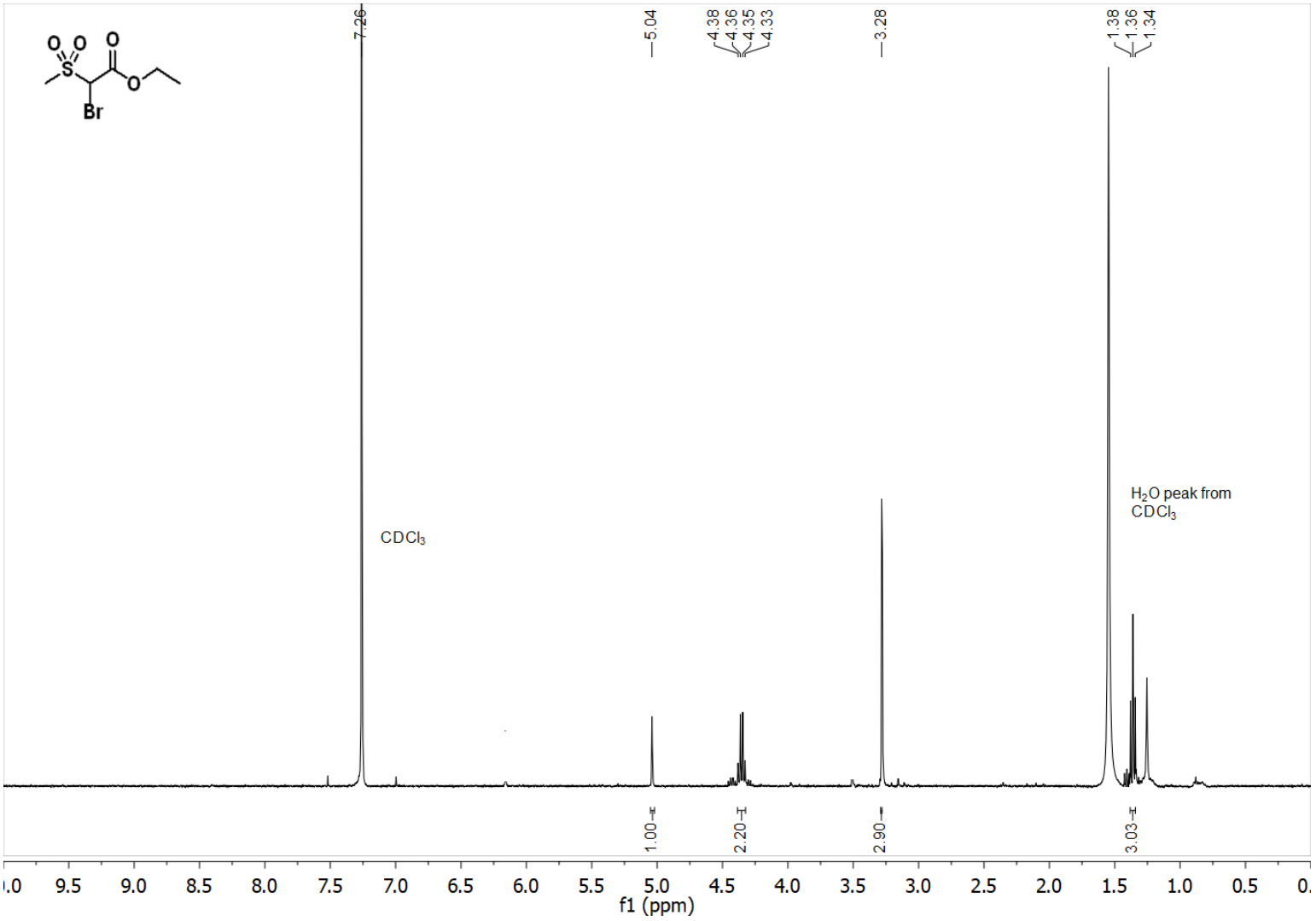
Line#:1 R.Time:17.9(Scan#:1552)
MassPeaks:134
RawMode:Single 17.9(1552) BasePeak:77(2102633)
BG Mode:None



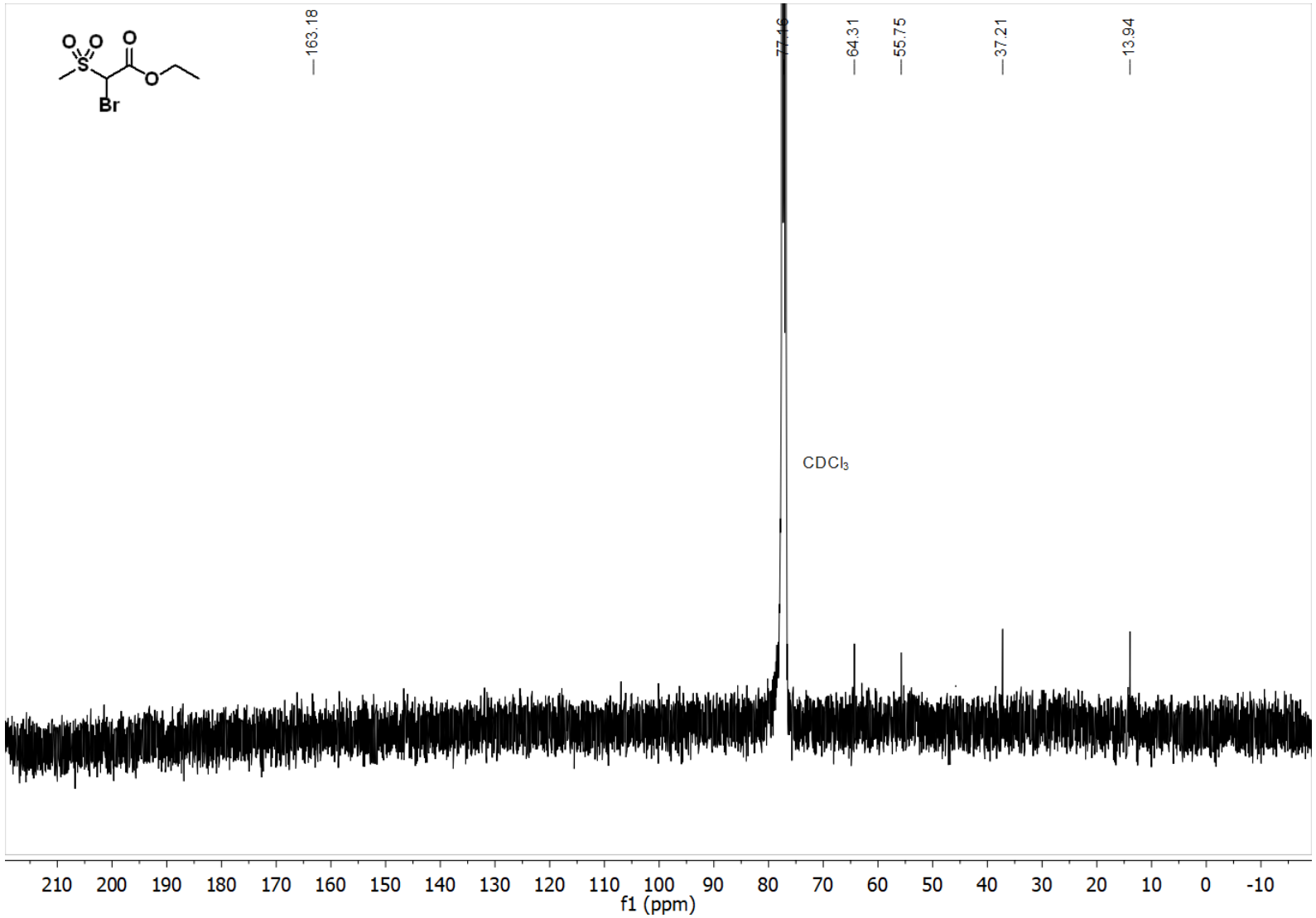
Line#:2 R.Time:16.8(Scan#:1419)
MassPeaks:107
RawMode:Single 16.8(1419) BasePeak:77(2358321)
BG Mode:None



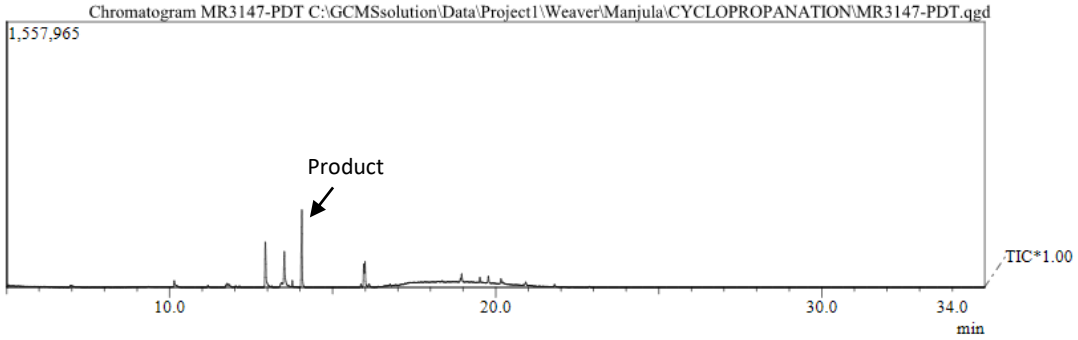
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c ethyl 2-bromo-2-(methylsulfonyl)acetate



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3c ethyl 2-bromo-2-(methylsulfonyl)acetate

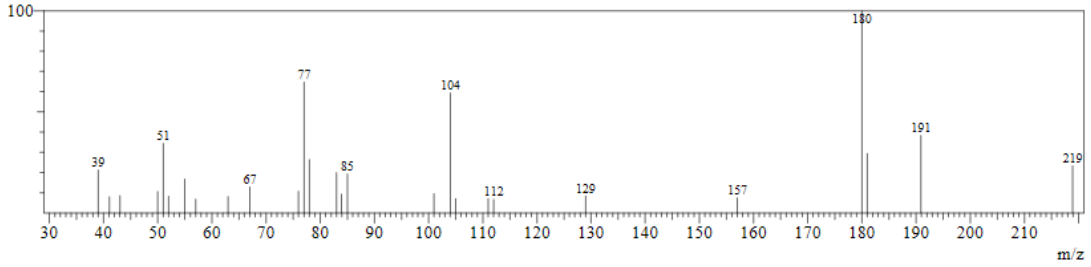


GC and MS of 3c ethyl 2-bromo-2-(methylsulfonyl)acetate

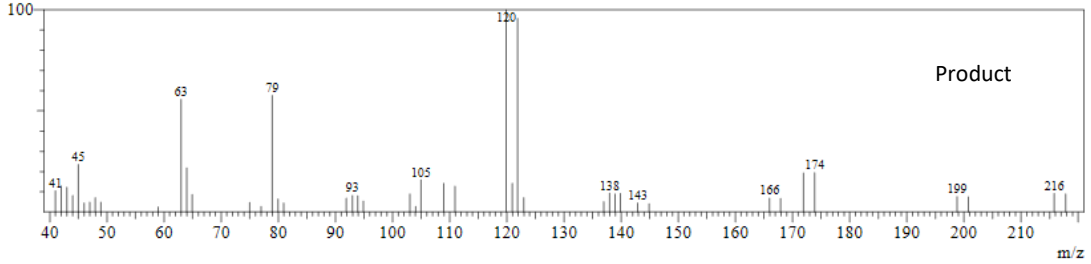


Spectrum

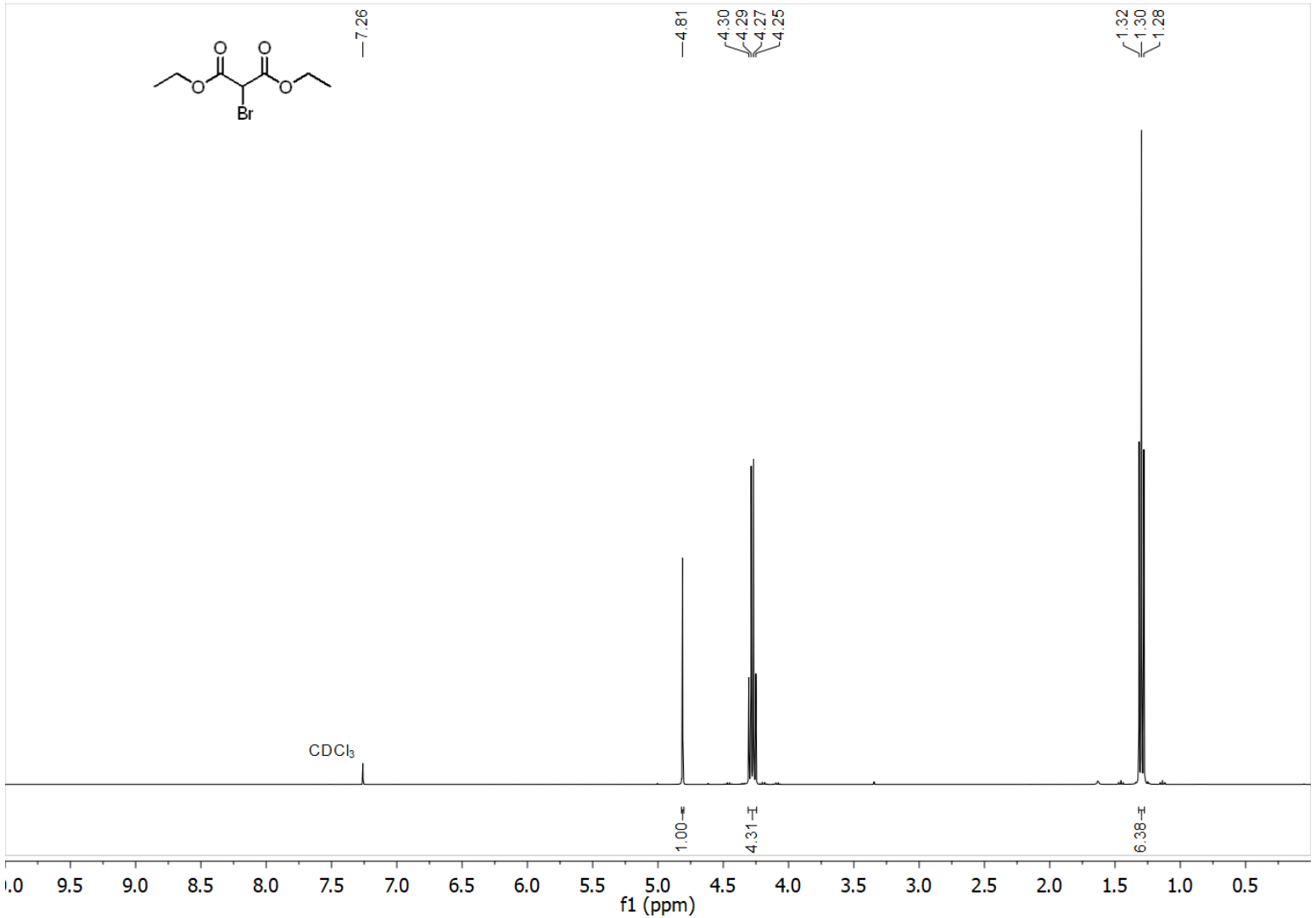
Line#:1 R.Time:16.0(Scan#:1318)
MassPeaks:27
RawMode:Single 16.0(1318) BasePeak:180(14954)
BG Mode:None



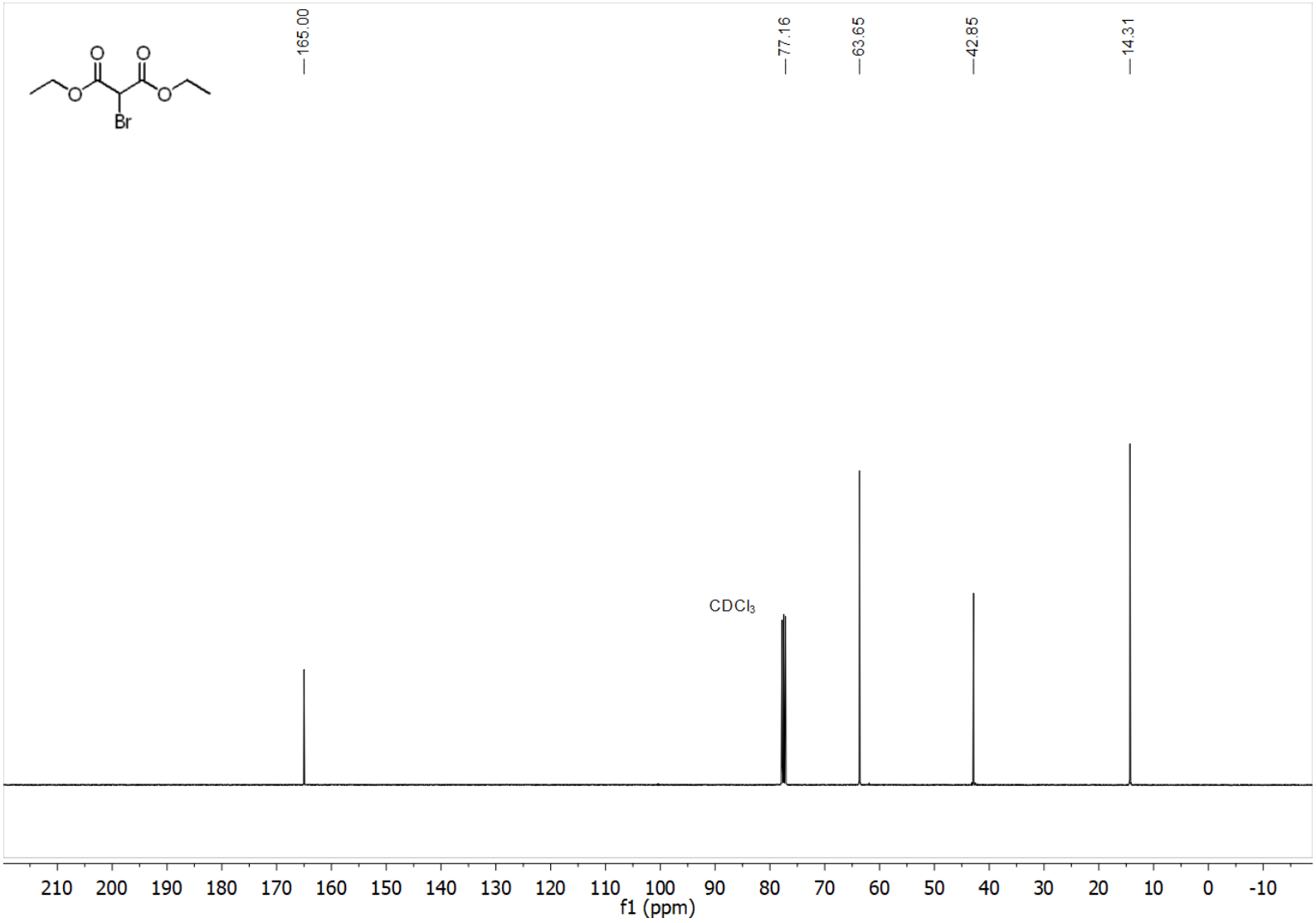
Line#:2 R.Time:14.1(Scan#:1088)
MassPeaks:45
RawMode:Single 14.1(1088) BasePeak:120(46498)
BG Mode:None



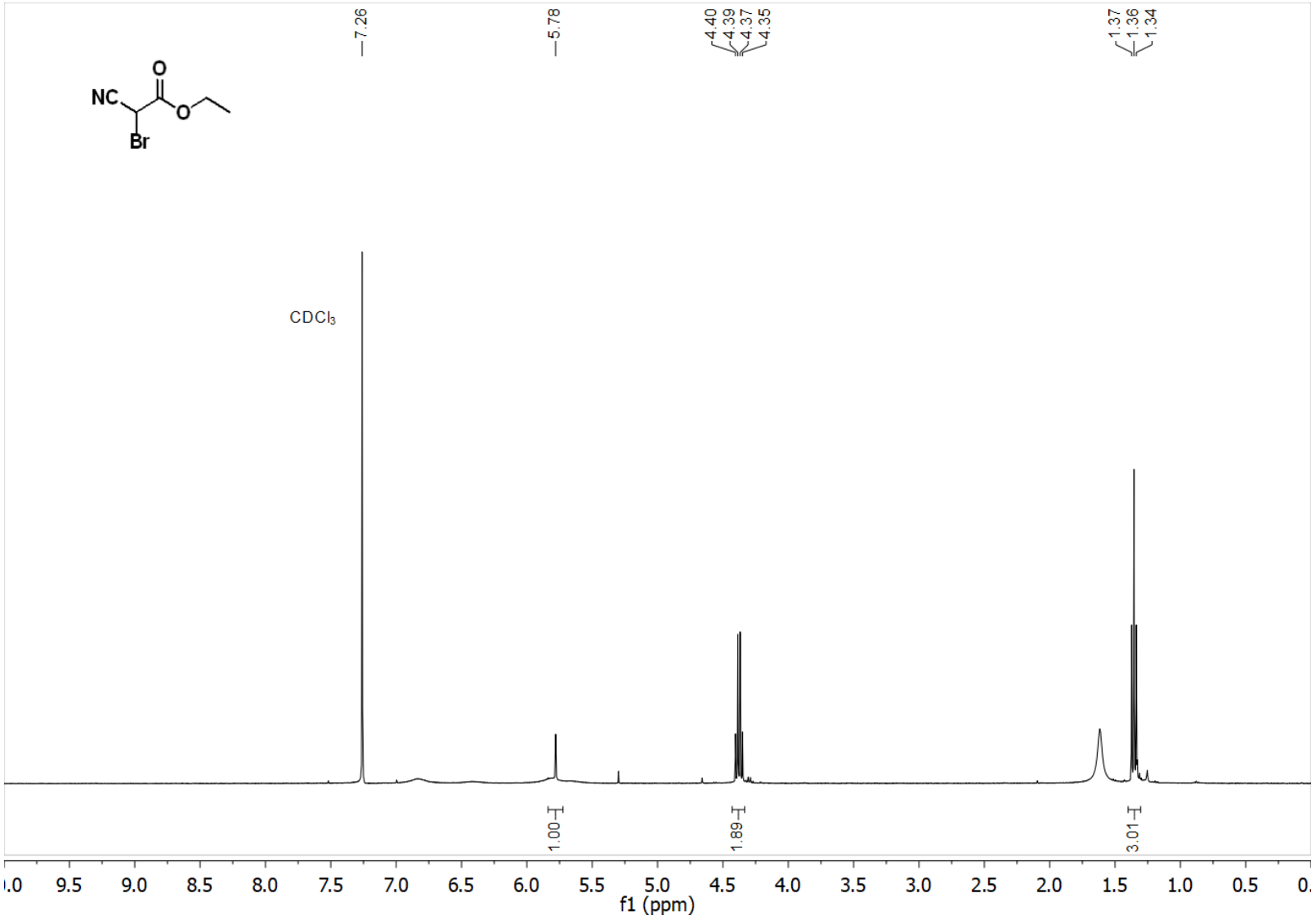
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4c diethyl 2-bromomalonate



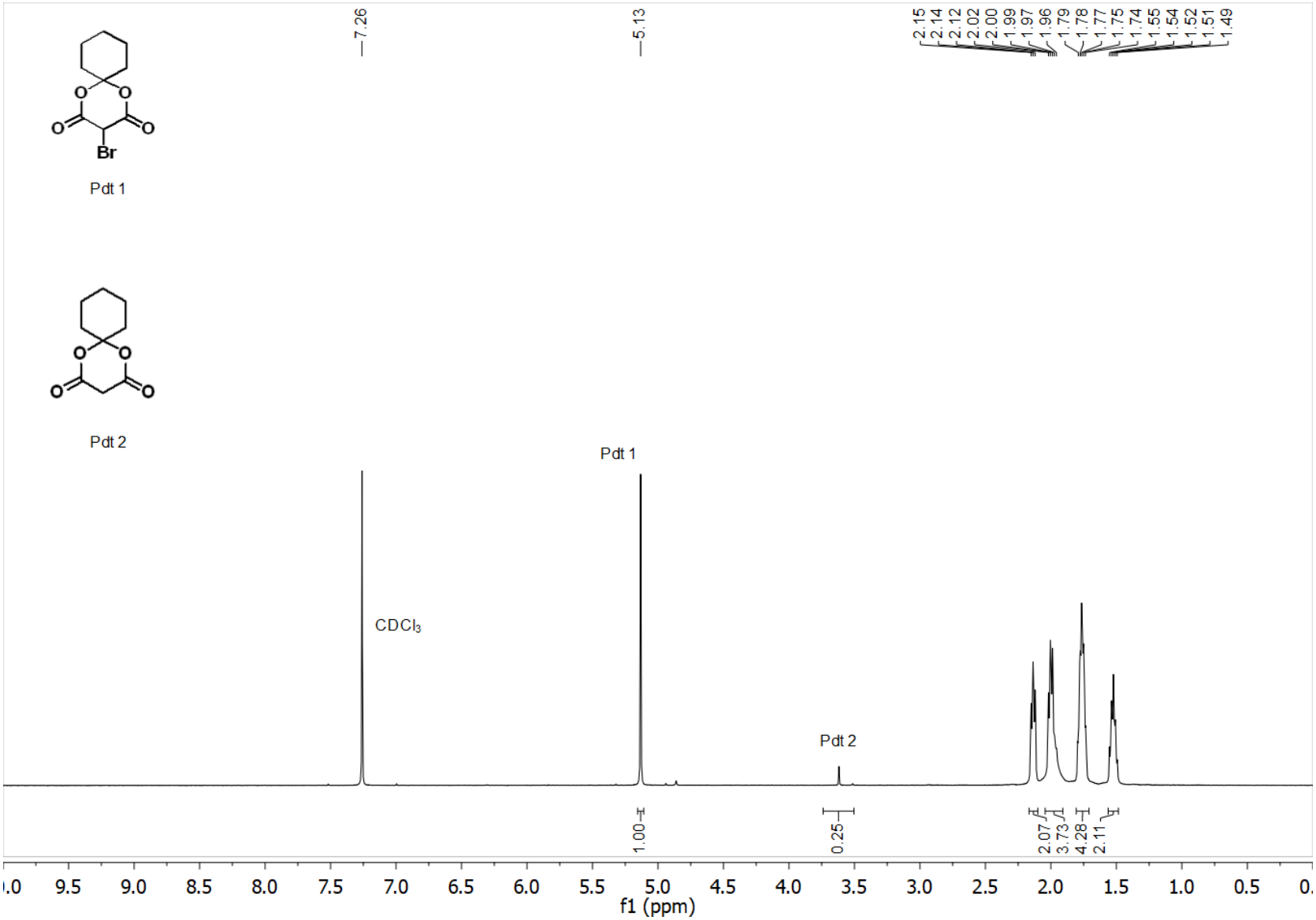
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4c diethyl 2-bromomalonate



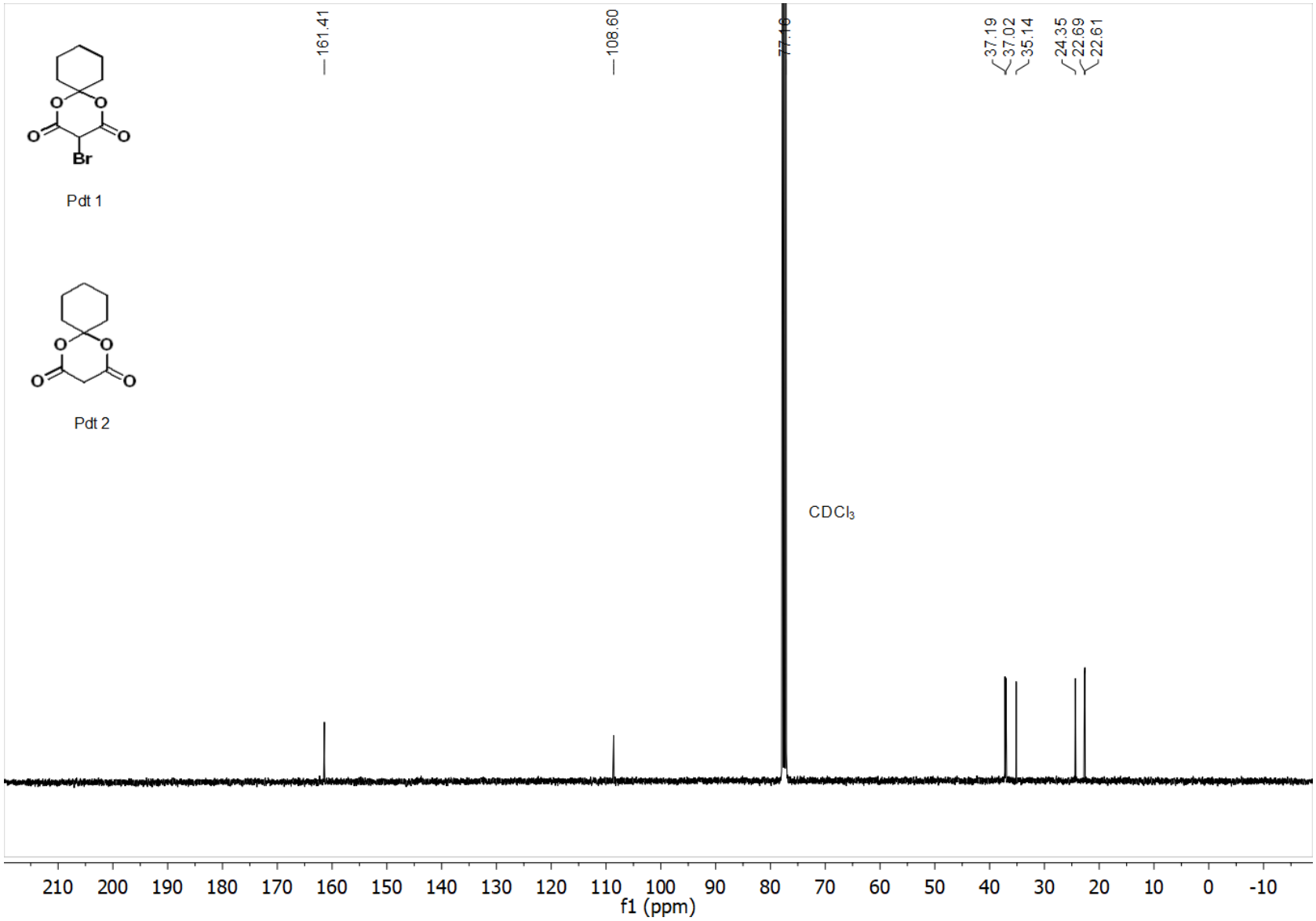
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5c ethyl 2-bromo-2-cyanoacetate



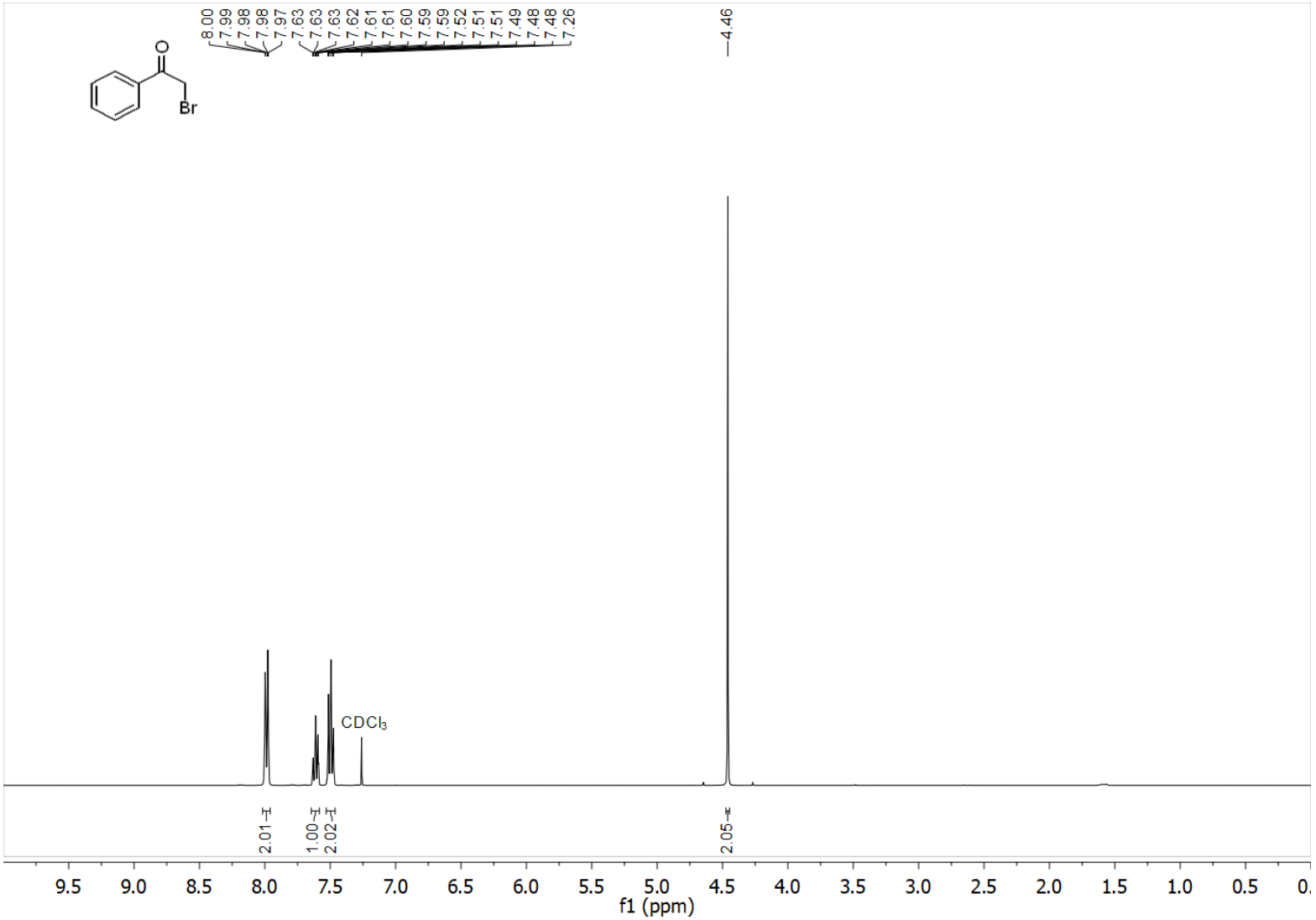
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6c 3-bromo-1,5-dioxaspiro[5.5]undecane-2,4-dione



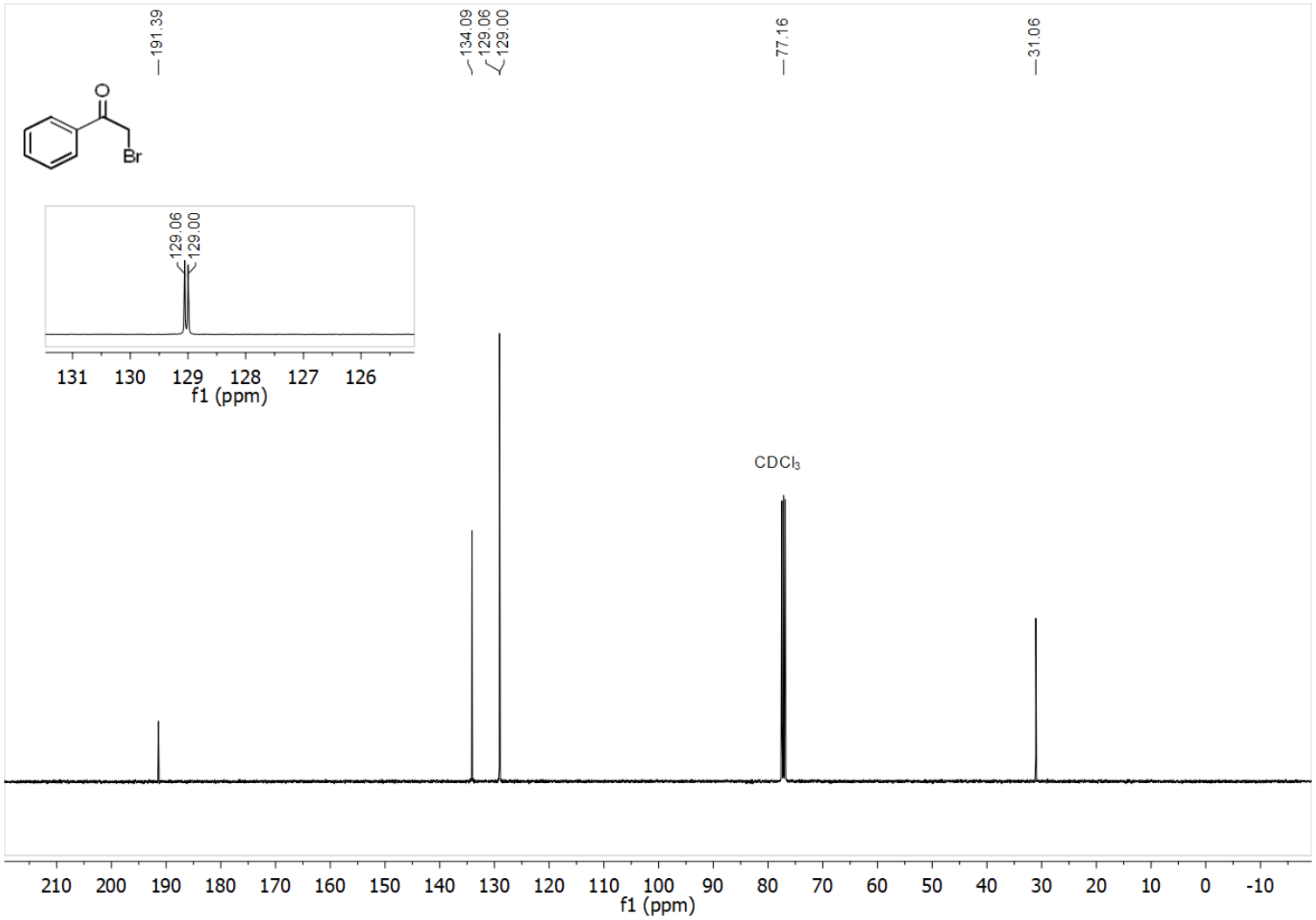
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 6c 3-bromo-1,5-dioxaspiro[5.5]undecane-2,4-dione



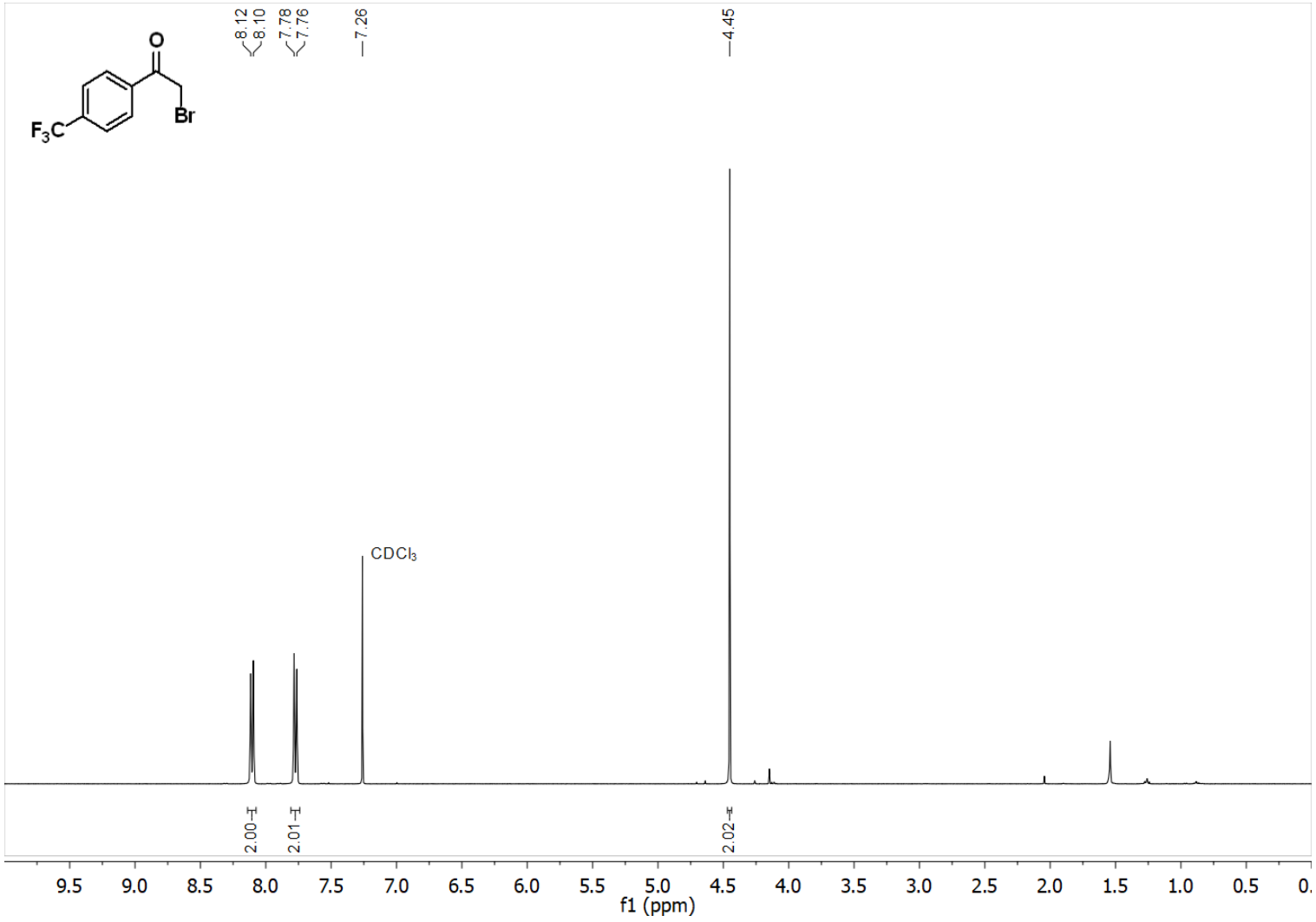
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7c 2-Bromo-1-phenylethan-1-one



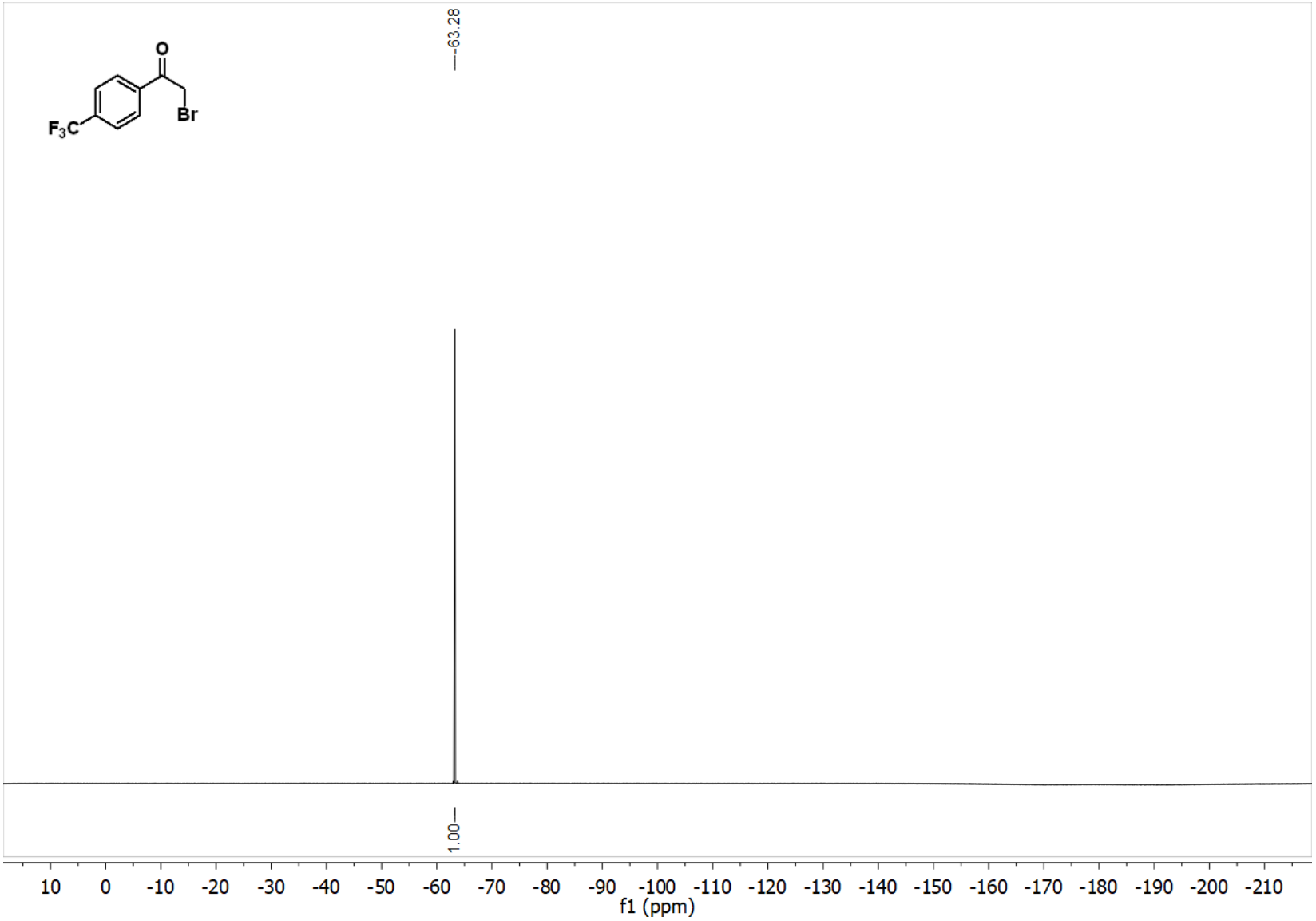
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 7c 2-Bromo-1-phenylethan-1-one



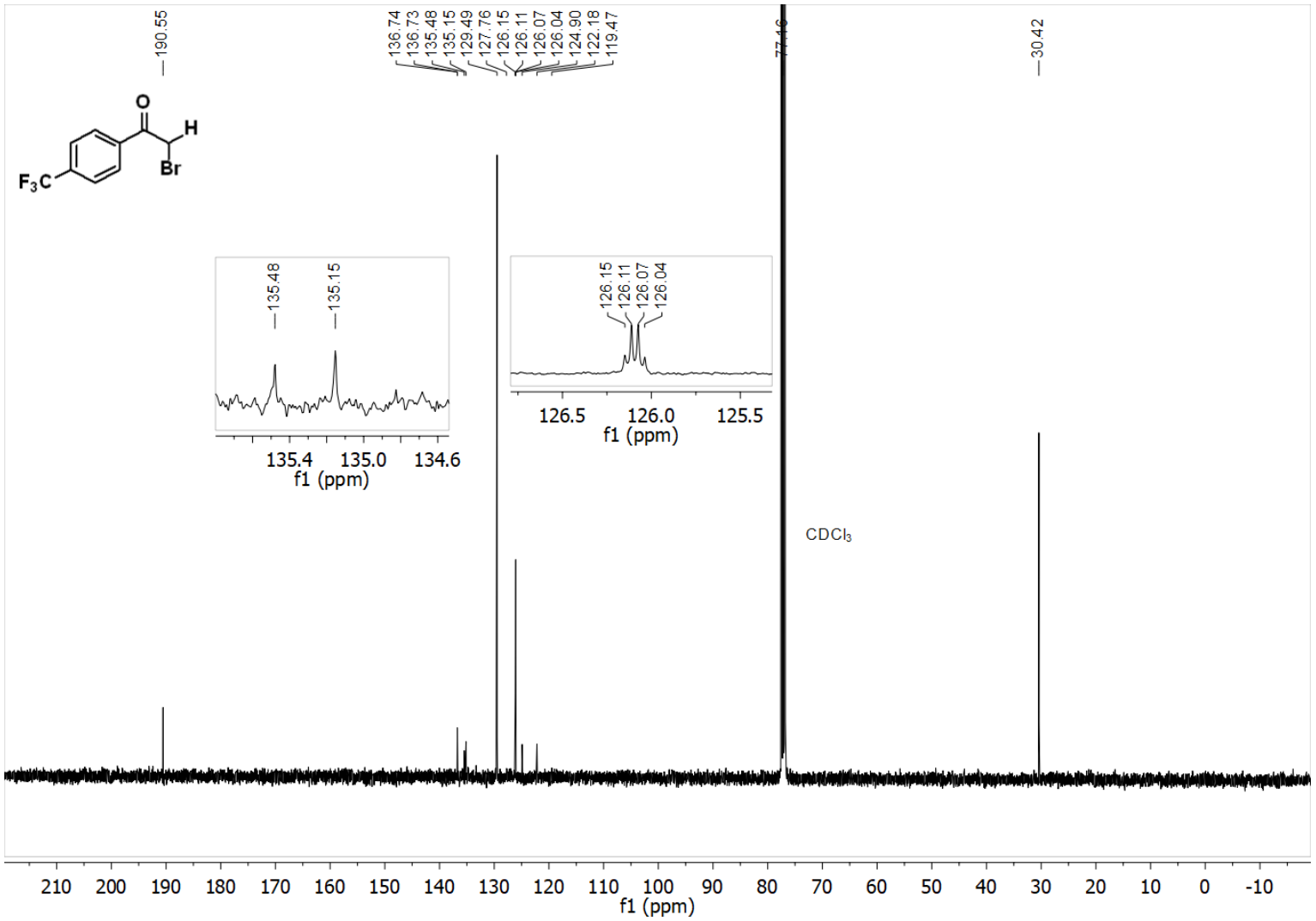
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8c 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one



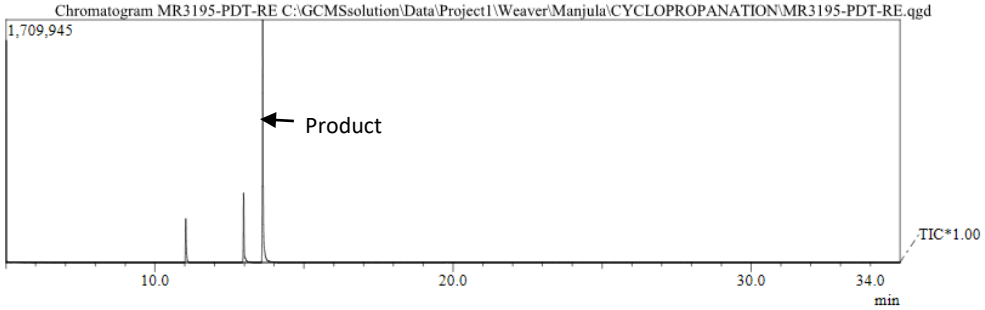
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 8c 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one

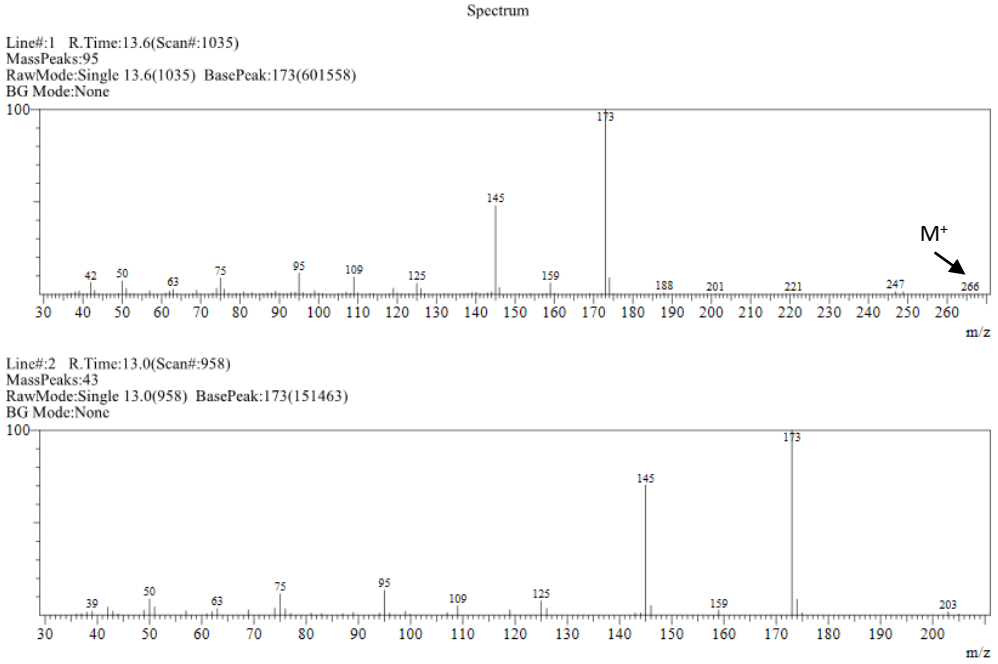


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 8c 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one

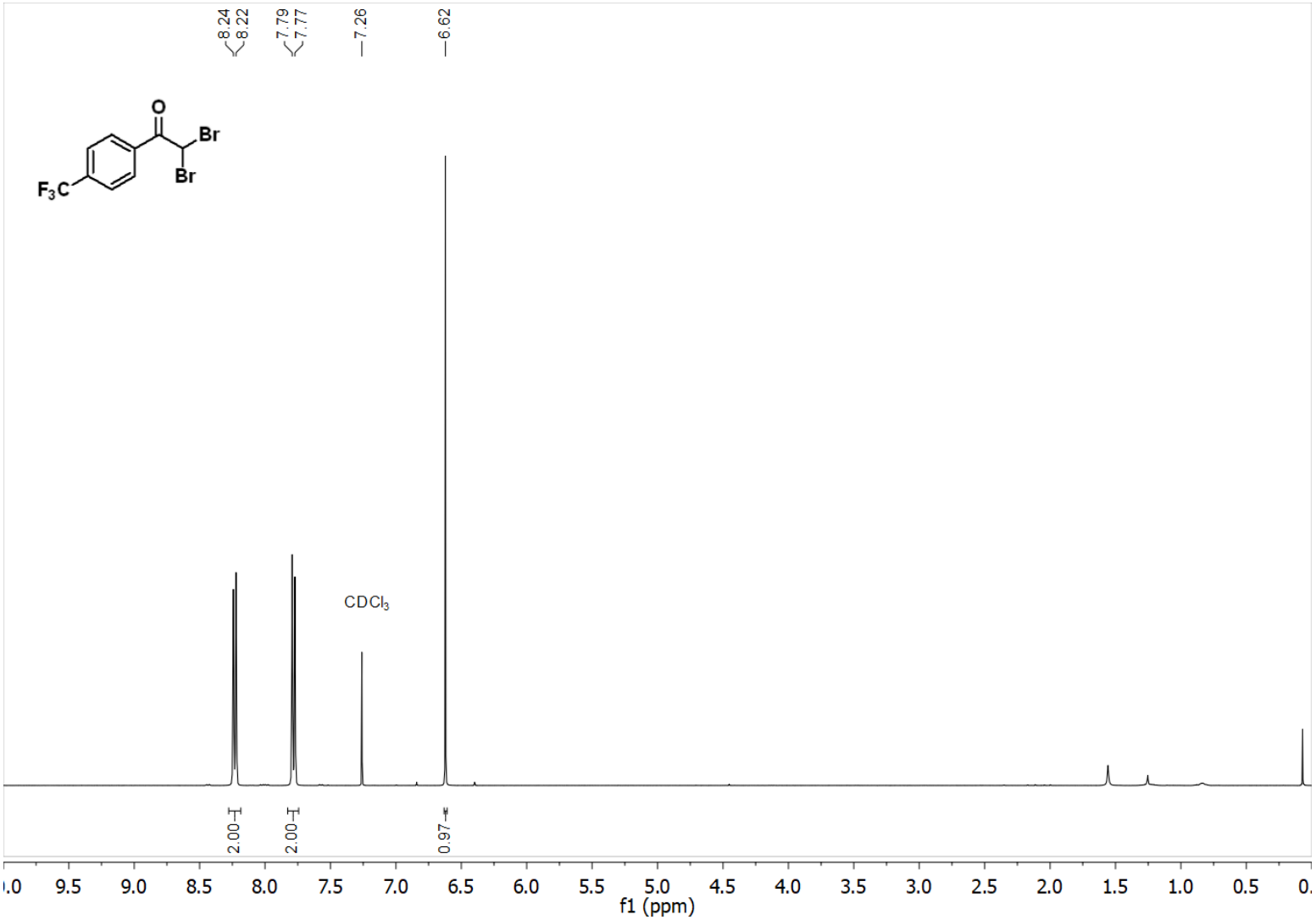


GC and MS of 8c 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one

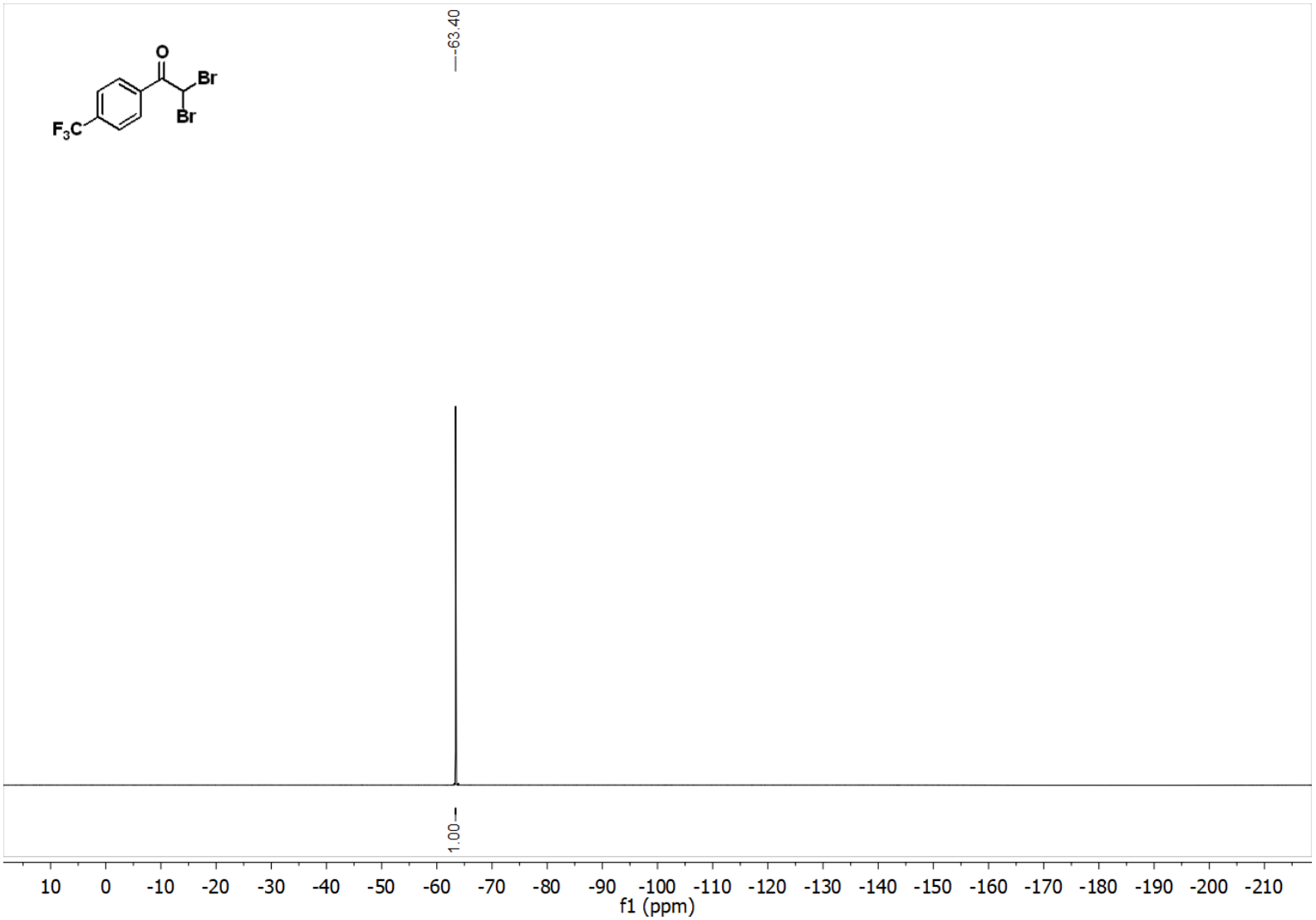




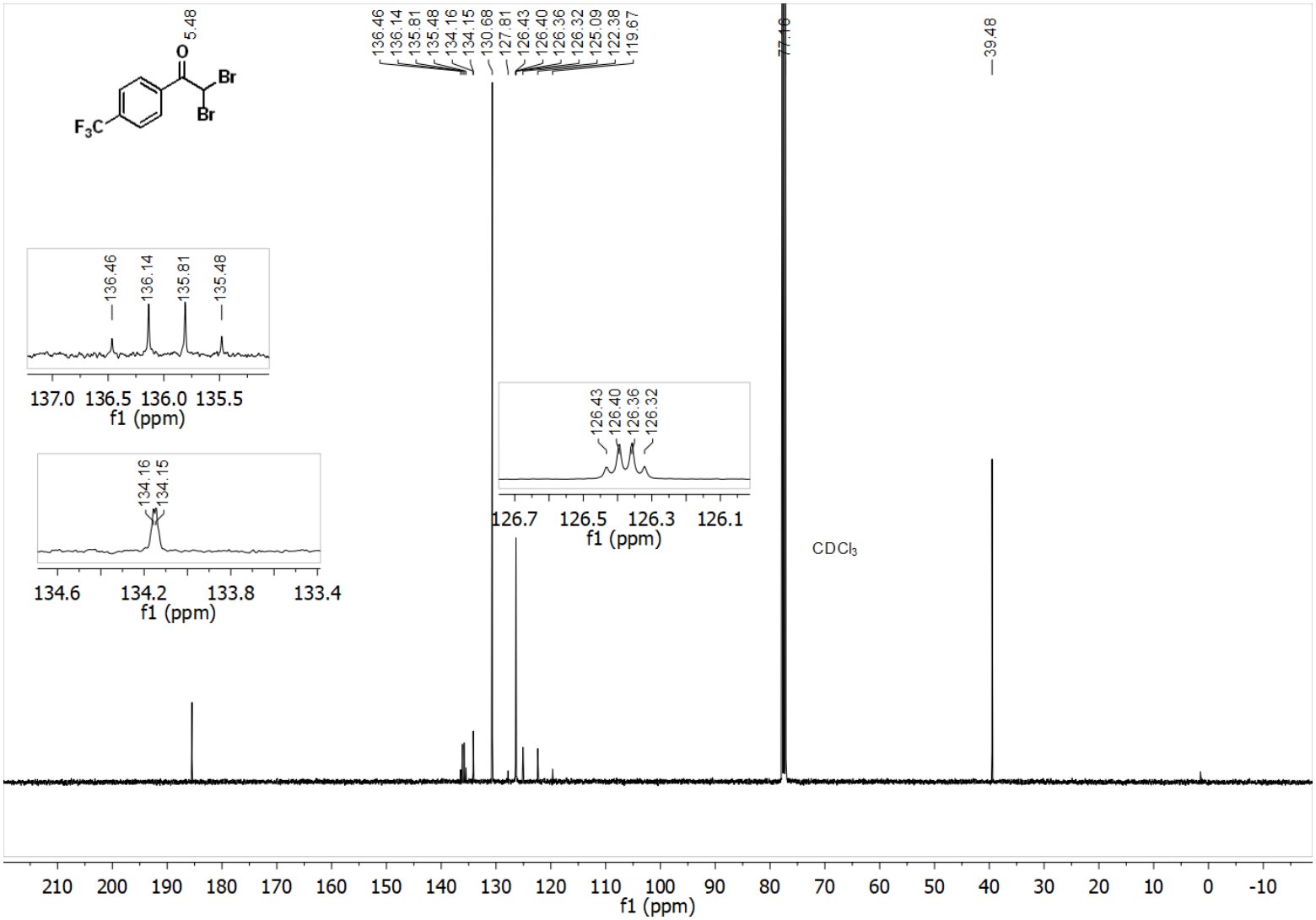
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 9c 2,2-dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one



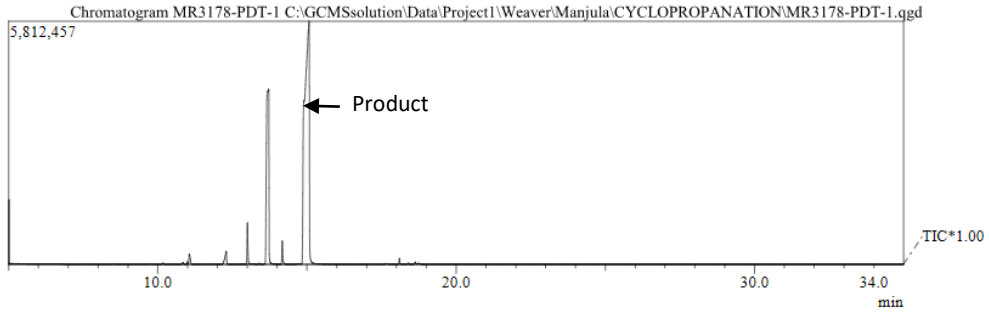
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 9c 2,2-dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one

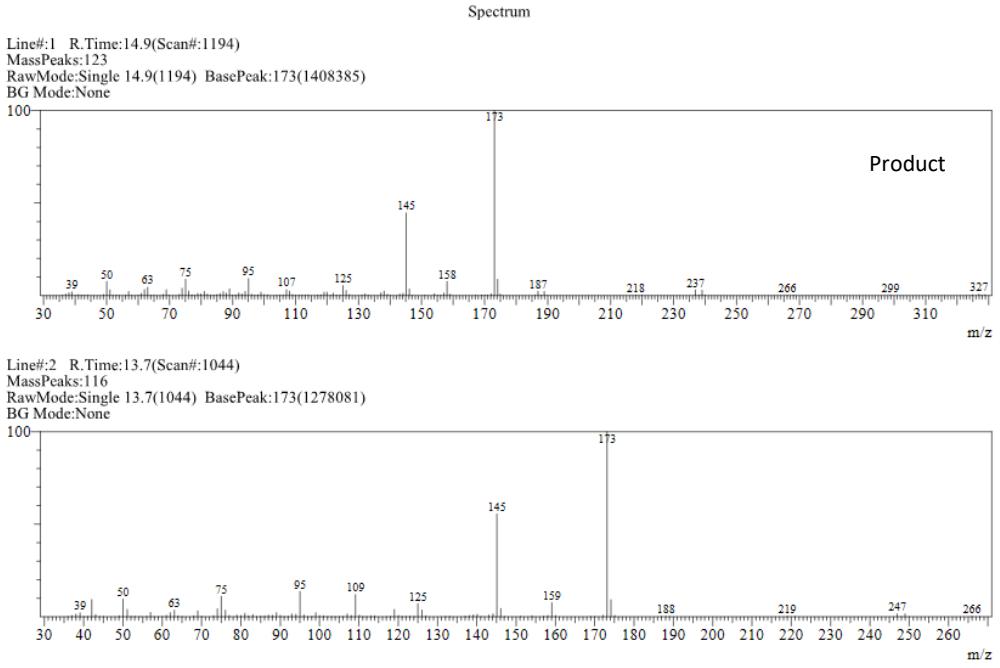


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 9c 2,2-dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one

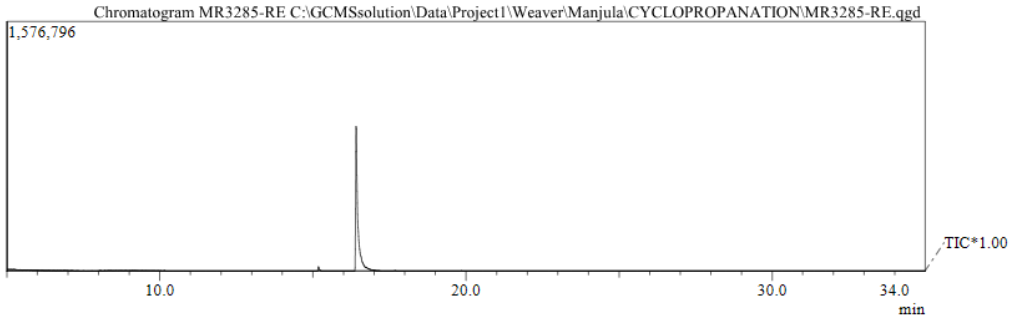


GC and MS of 9c 2,2-dibromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one



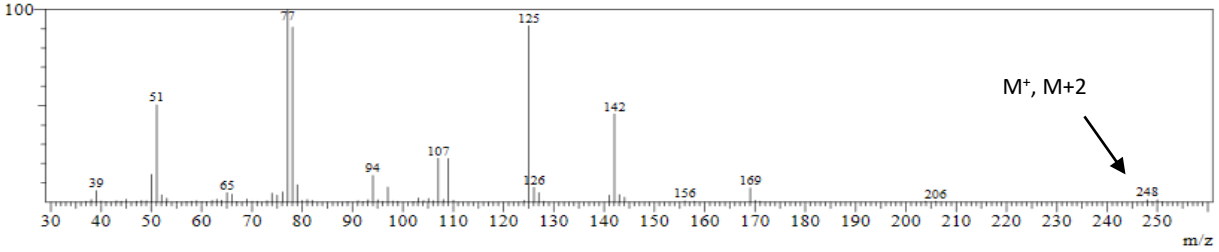


GC and MS of 10c ((1-Bromoethyl)sulfonyl)benzene

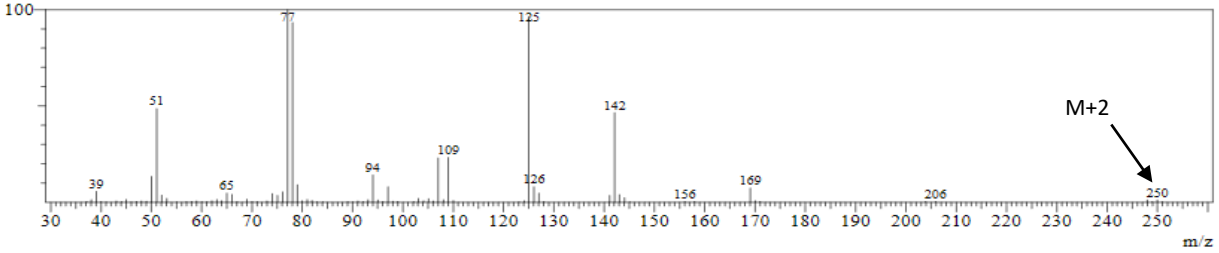


Spectrum

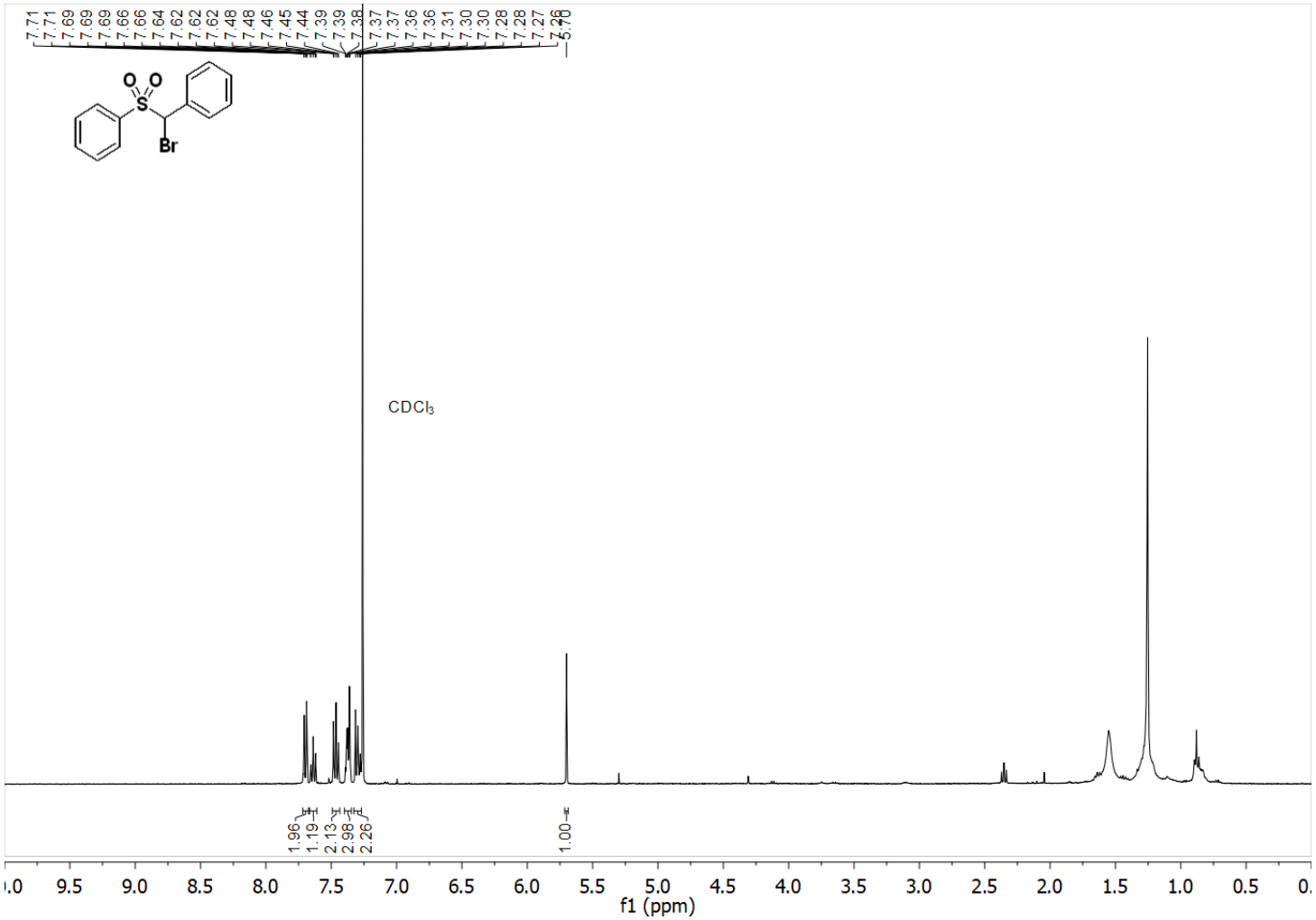
Line#:1 R.Time:16.1(Scan#:1330)
MassPeaks:79
RawMode:Single 16.1(1330) BasePeak:77(530170)
BG Mode:None



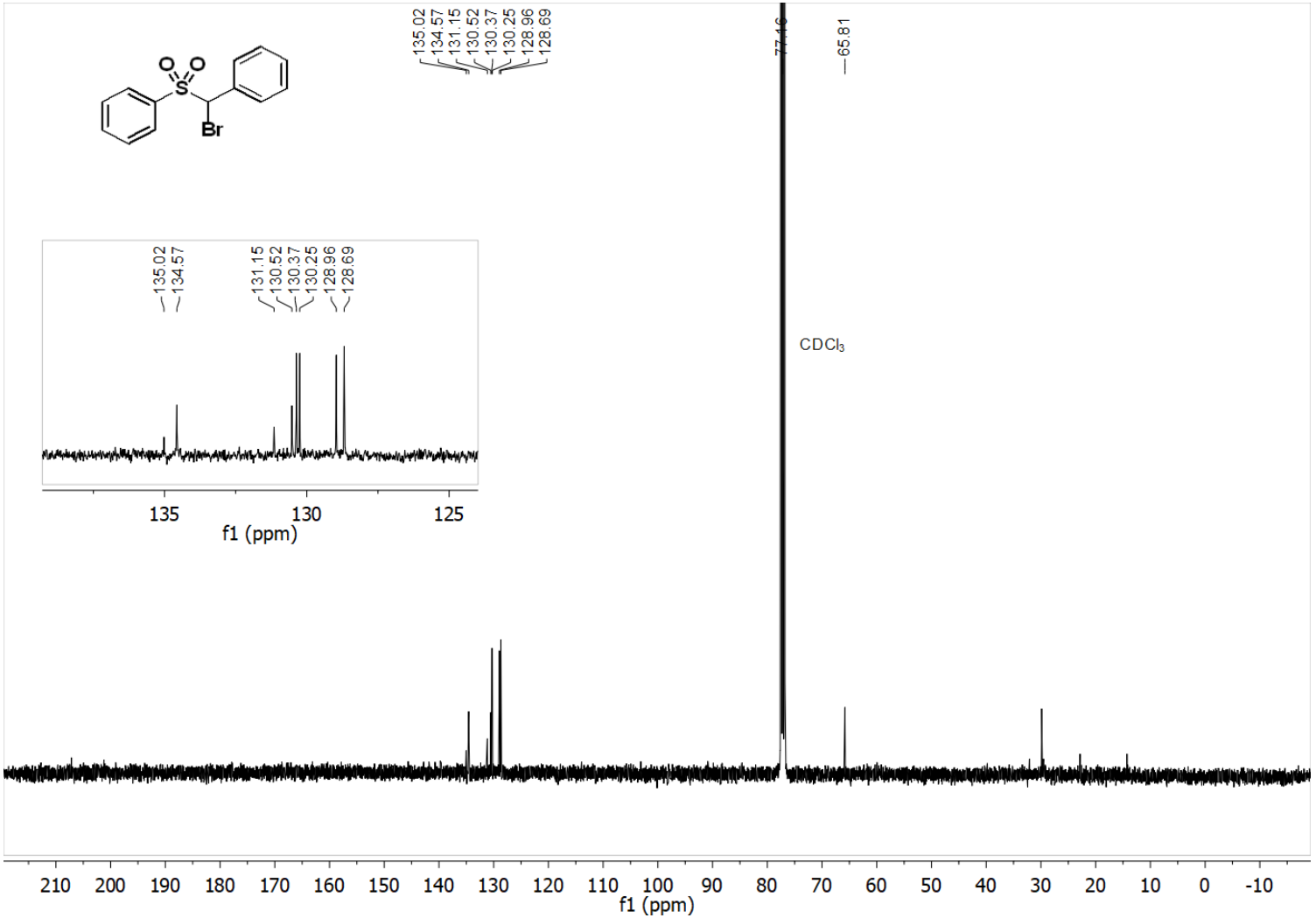
Line#:2 R.Time:16.1(Scan#:1333)
MassPeaks:85
RawMode:Single 16.1(1333) BasePeak:77(744030)
BG Mode:None



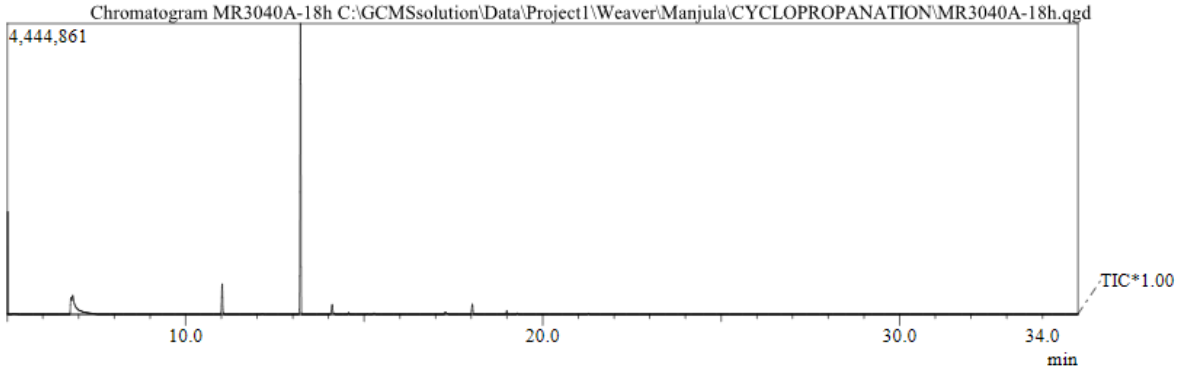
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 11c ((Bromo(phenyl)methyl)sulfonyl)benzene



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 11c ((Bromo(phenyl)methyl)sulfonyl)benzene

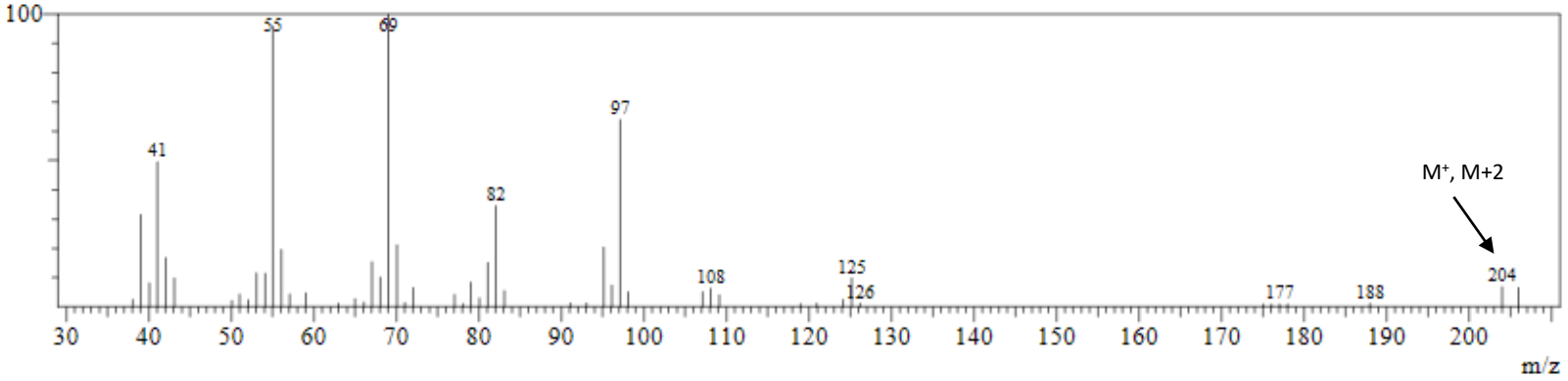


GC and MS of 12c 6-Bromo-2,2-dimethylcyclohexan-1-one

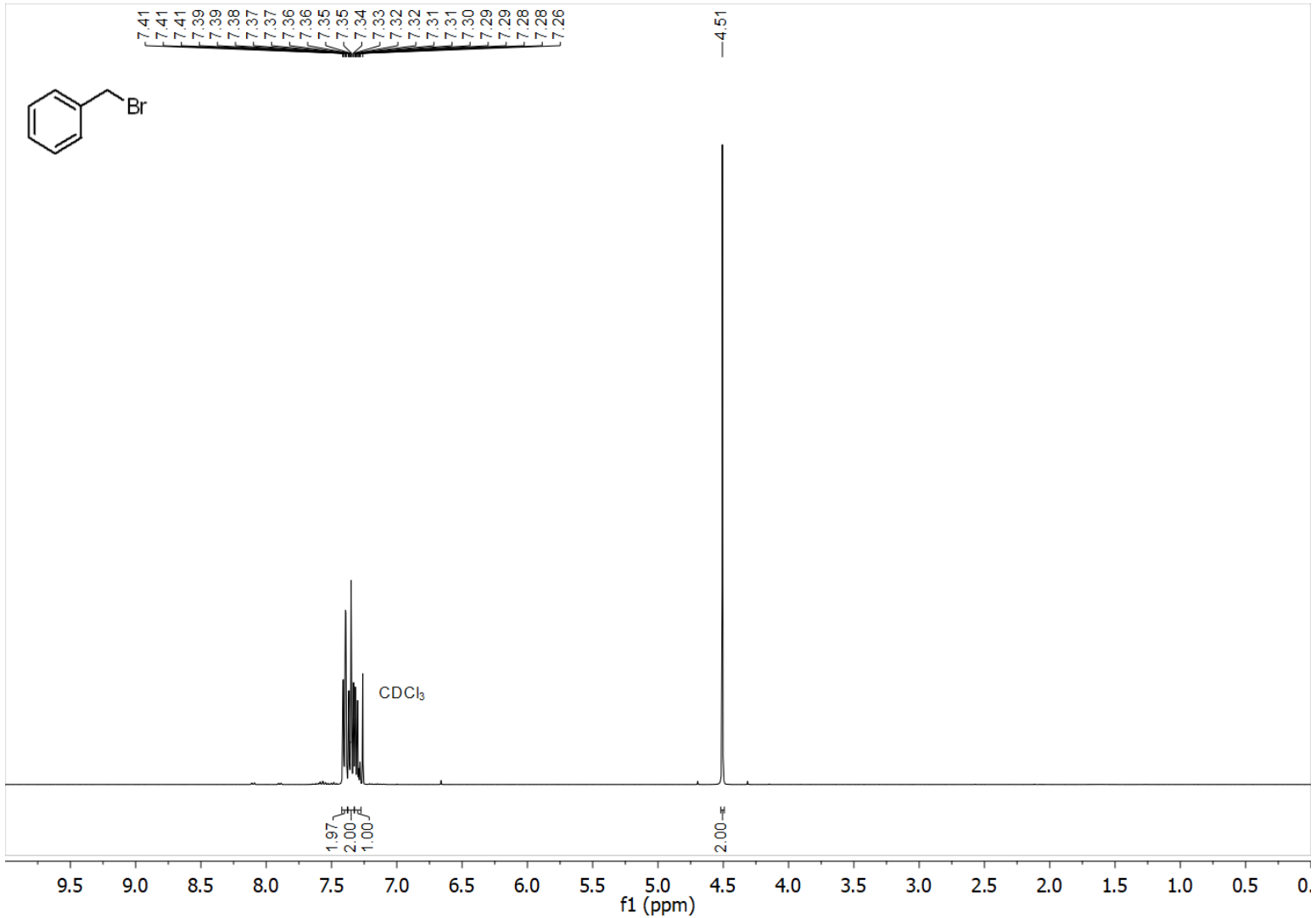


Spectrum

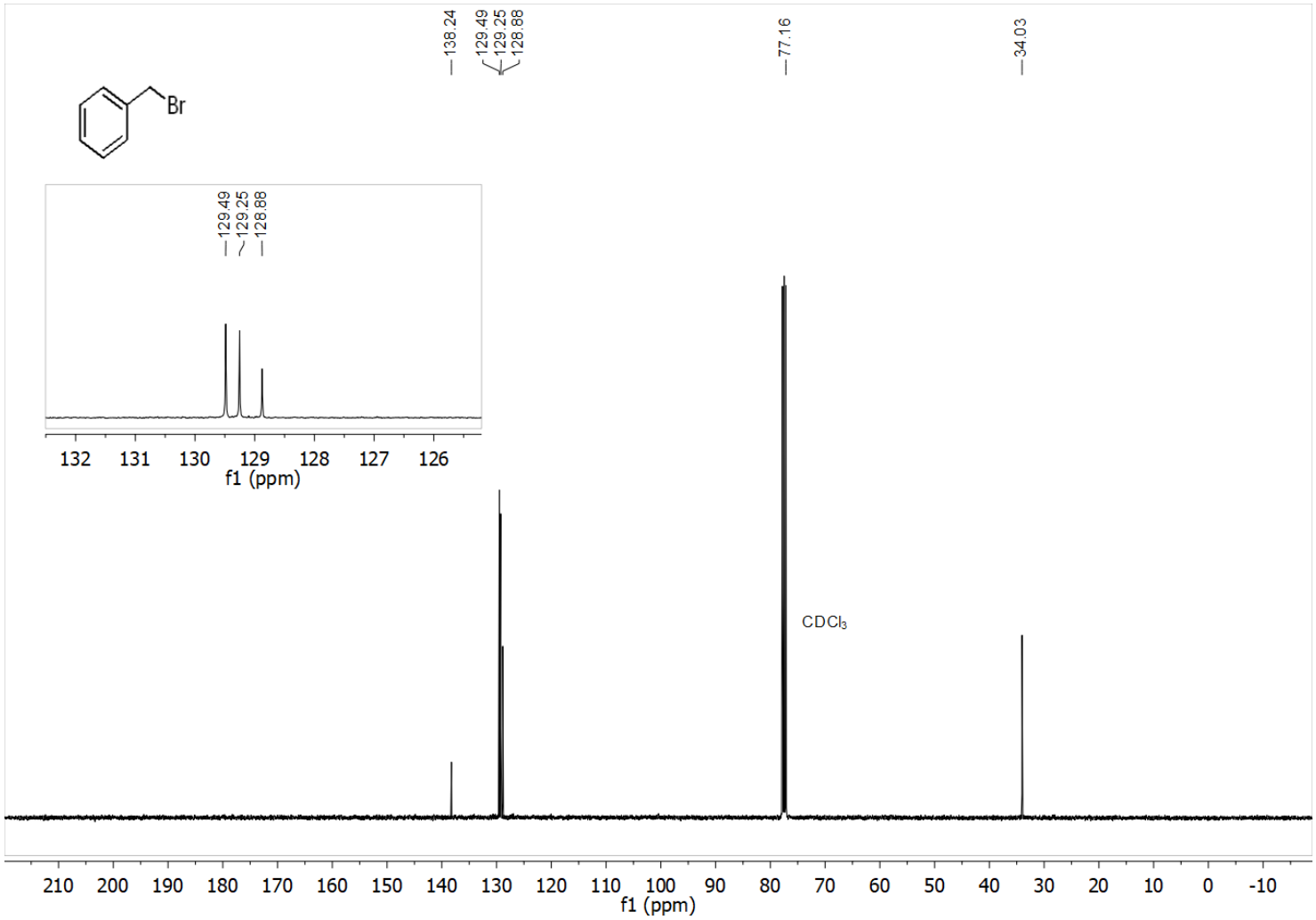
Line#:1 R.Time:13.2(Scan#:989)
MassPeaks:52
RawMode:Single 13.2(989) BasePeak:69(120745)
BG Mode:None



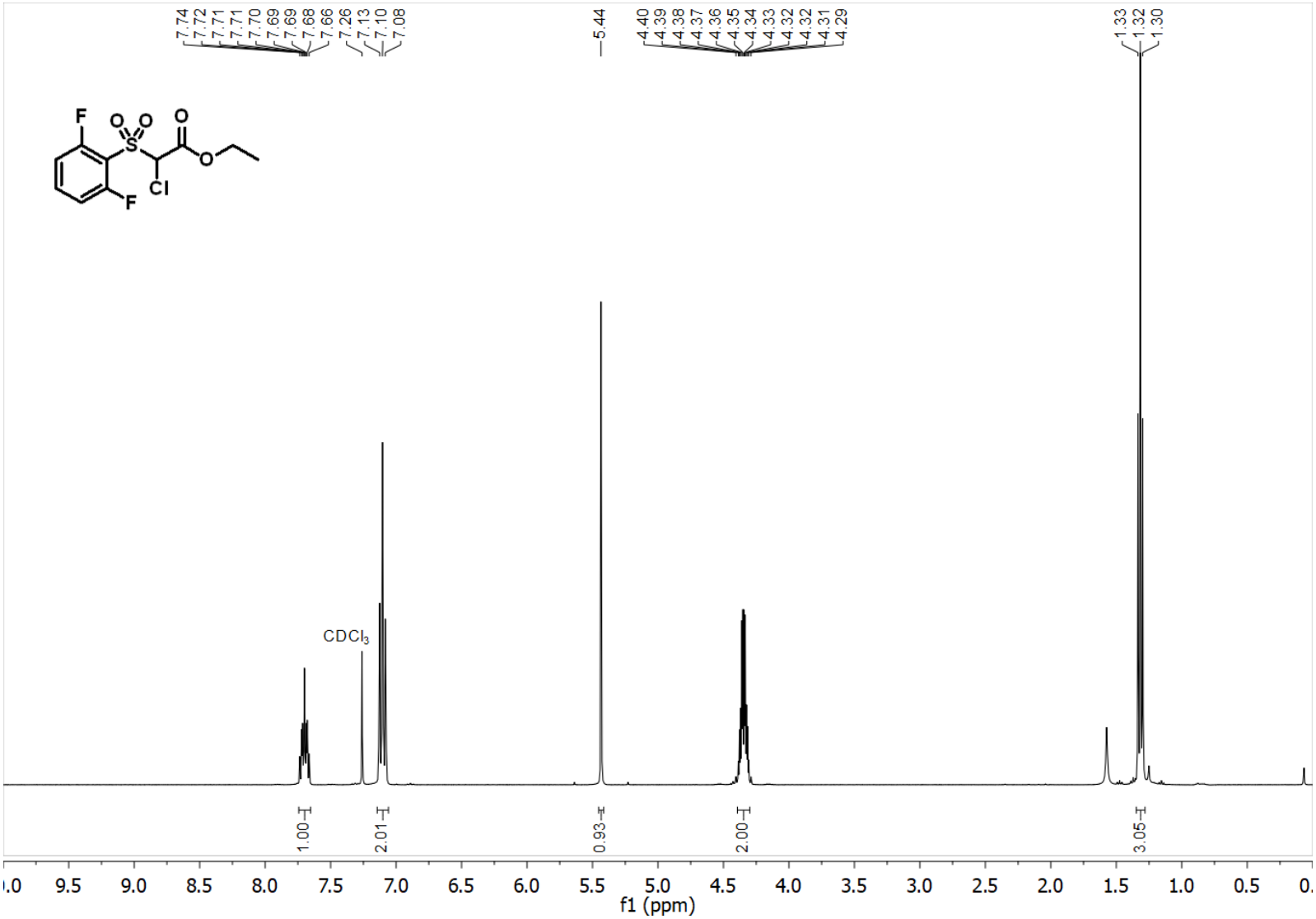
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 13c (Bromomethyl)benzene



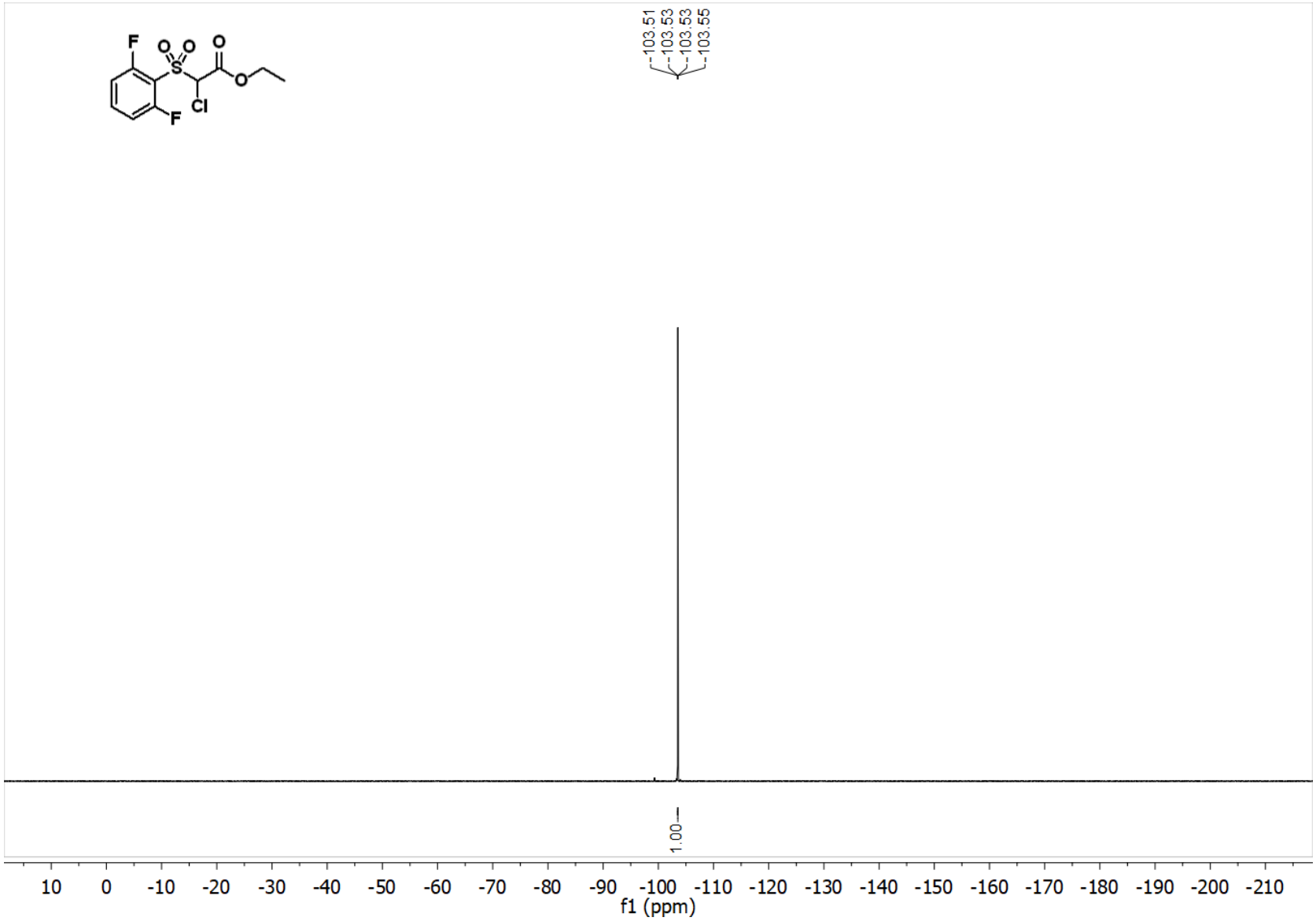
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 13c (Bromomethyl)benzene



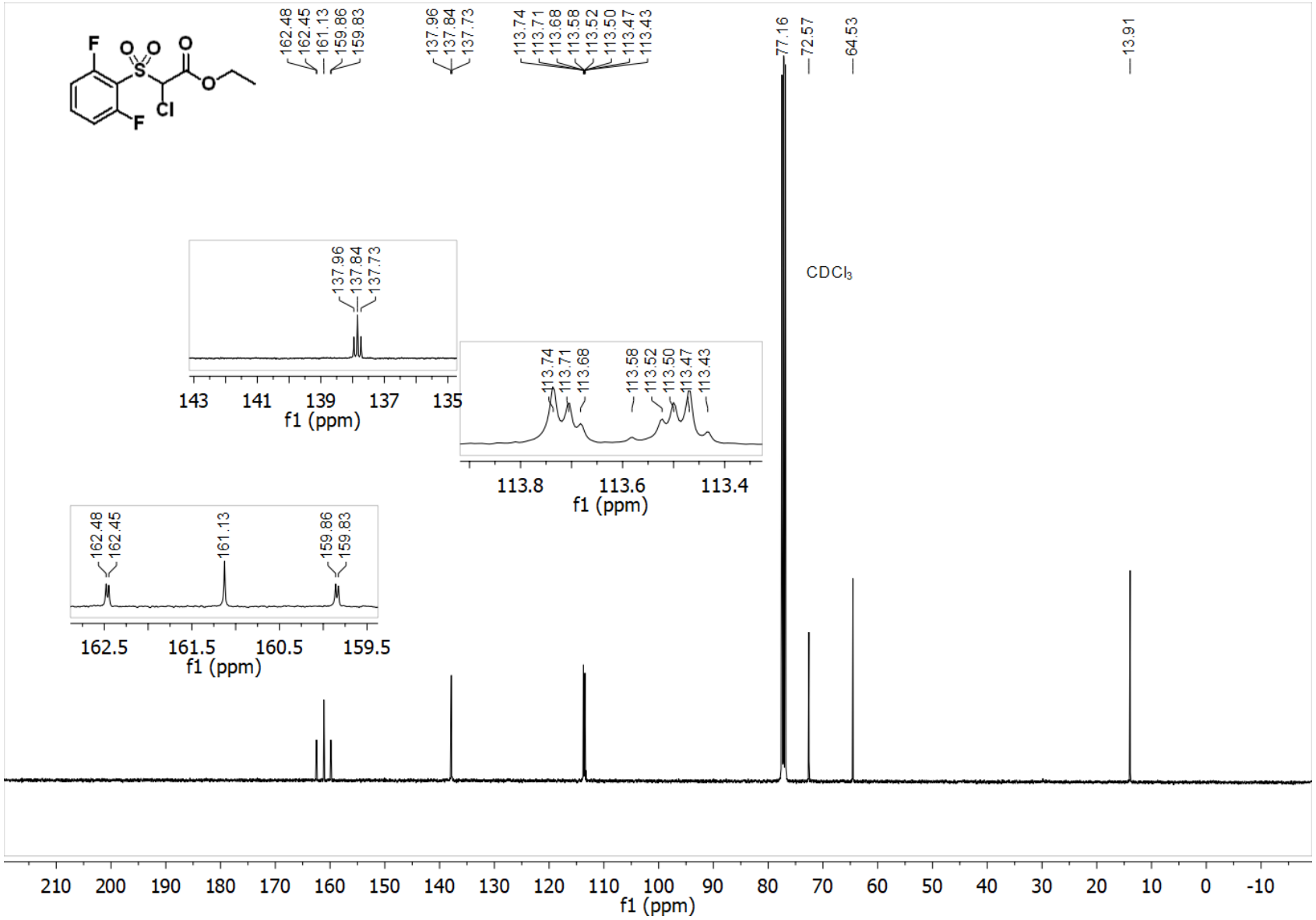
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 14c ethyl 2-chloro-2-((2,6-difluorophenyl)sulfonyl)acetate



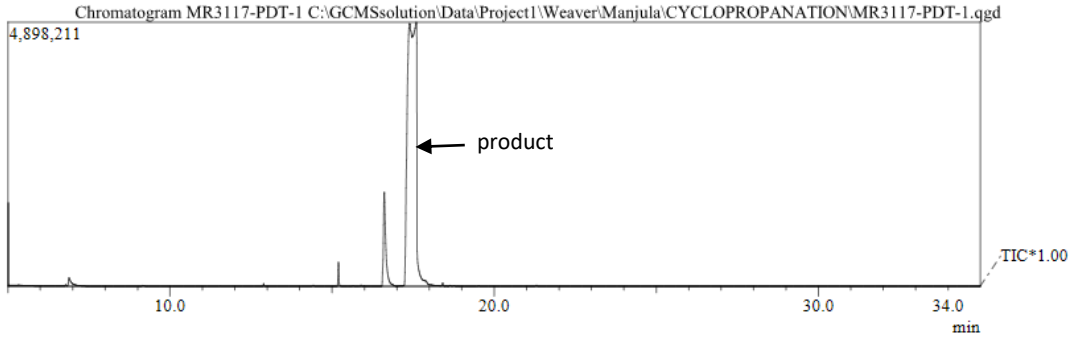
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 14c ethyl 2-chloro-2-((2,6-difluorophenyl)sulfonyl)acetate



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 14c ethyl 2-chloro-2-((2,6-difluorophenyl)sulfonyl)acetate



GC and MS of 14c ethyl 2-chloro-2-((2,6-difluorophenyl)sulfonyl)acetate



Spectrum

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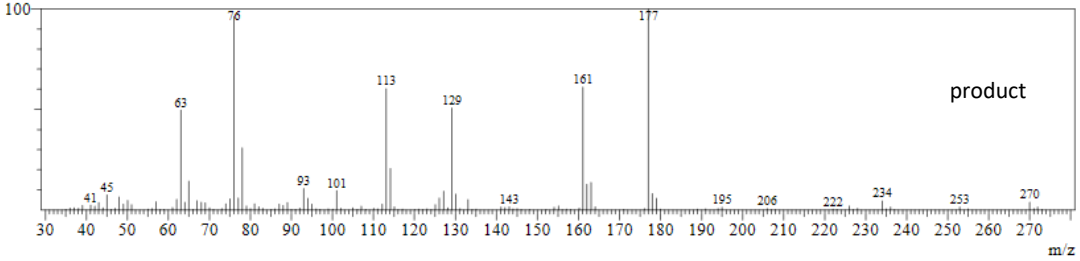
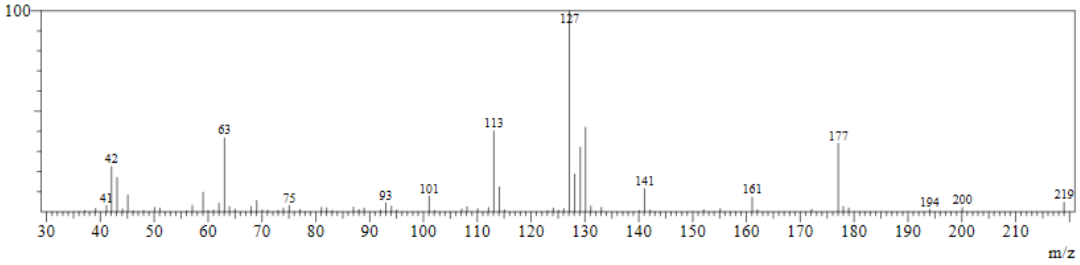
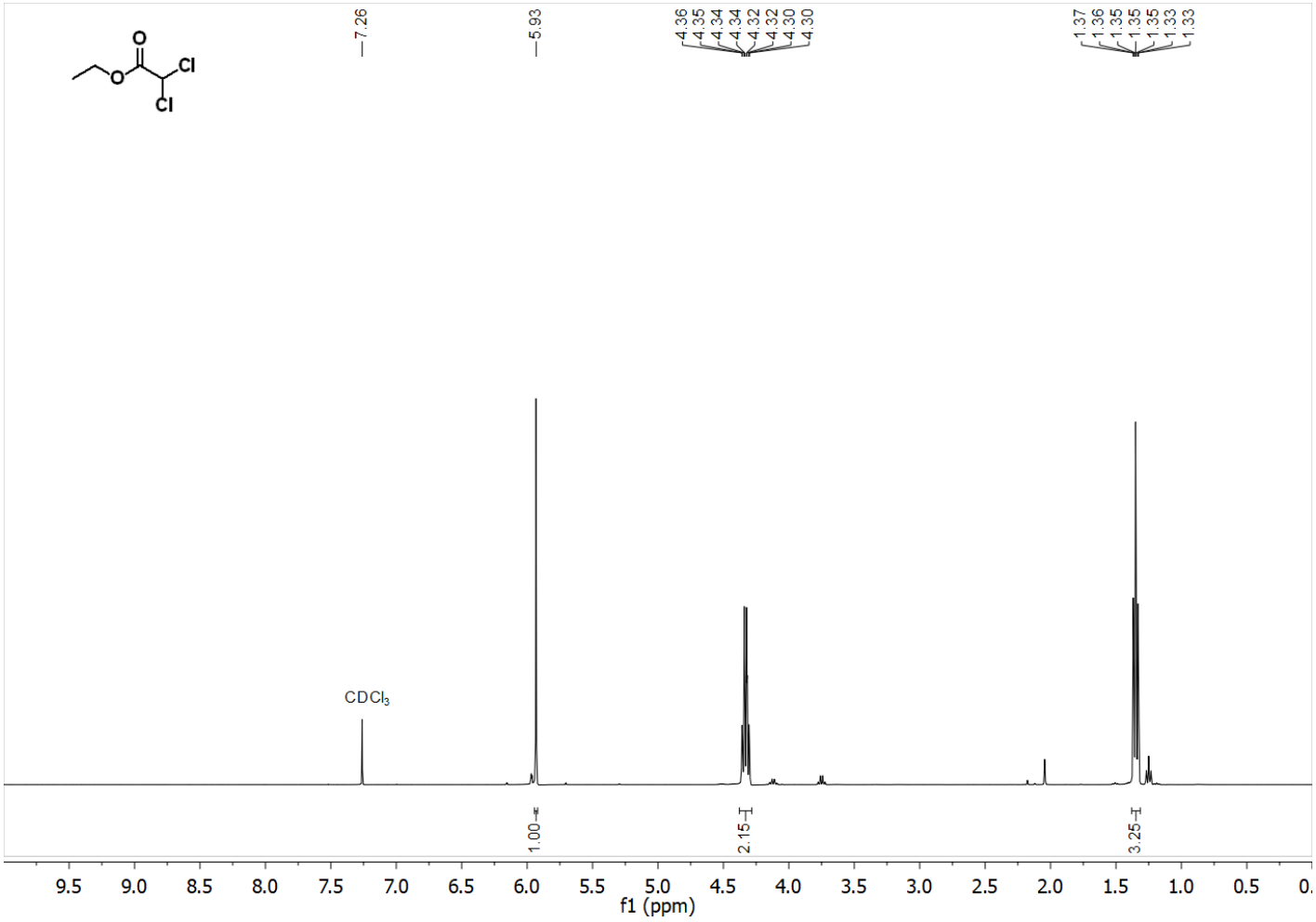
MassPeaks:133
RawMode:Single 17.5(1498) BasePeak:177(626318)
BG Mode:None



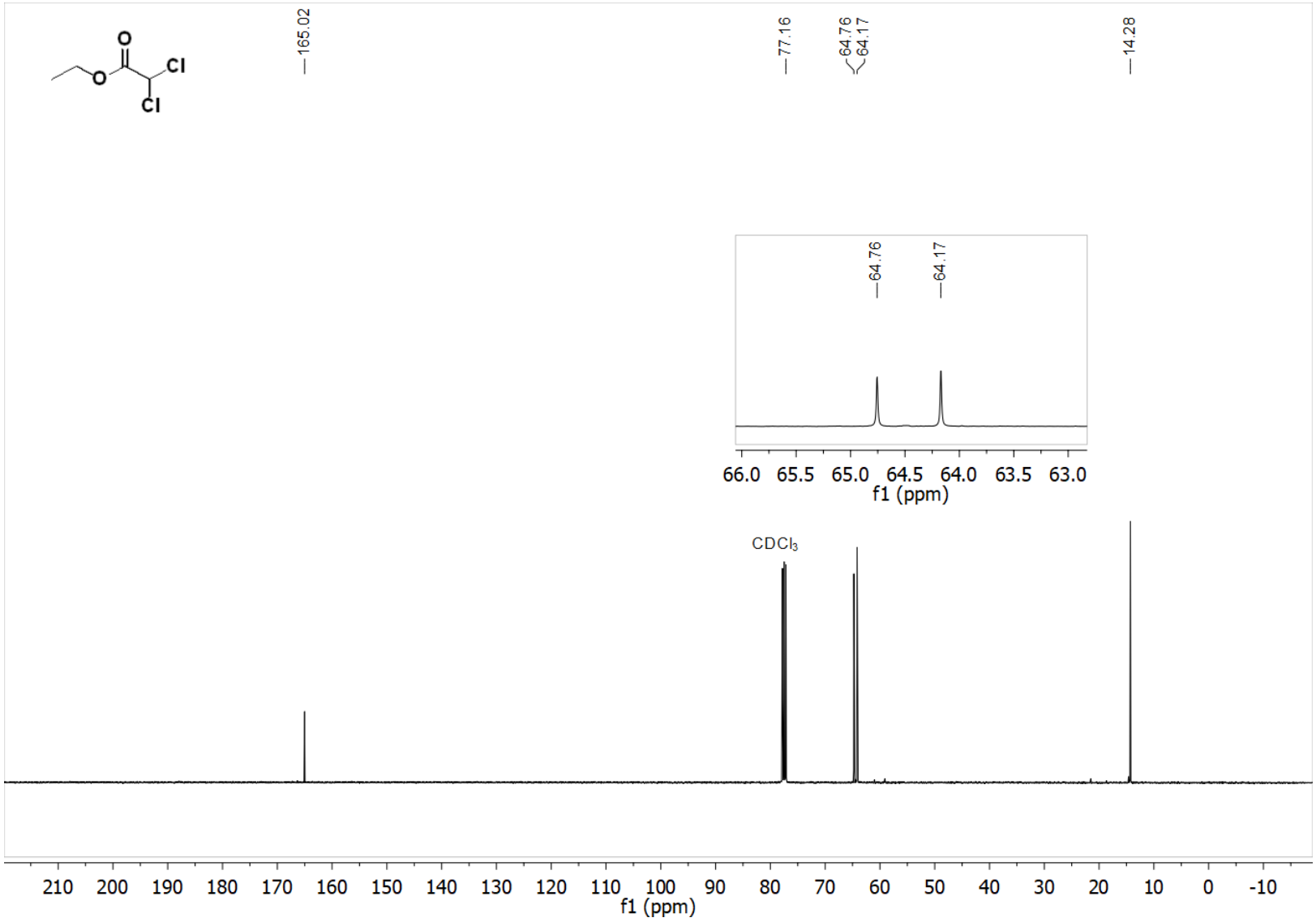
Line#:2 R.Time:16.6(Scan#:1398)
MassPeaks:71
RawMode:Single 16.6(1398) BasePeak:127(193636)
BG Mode:None



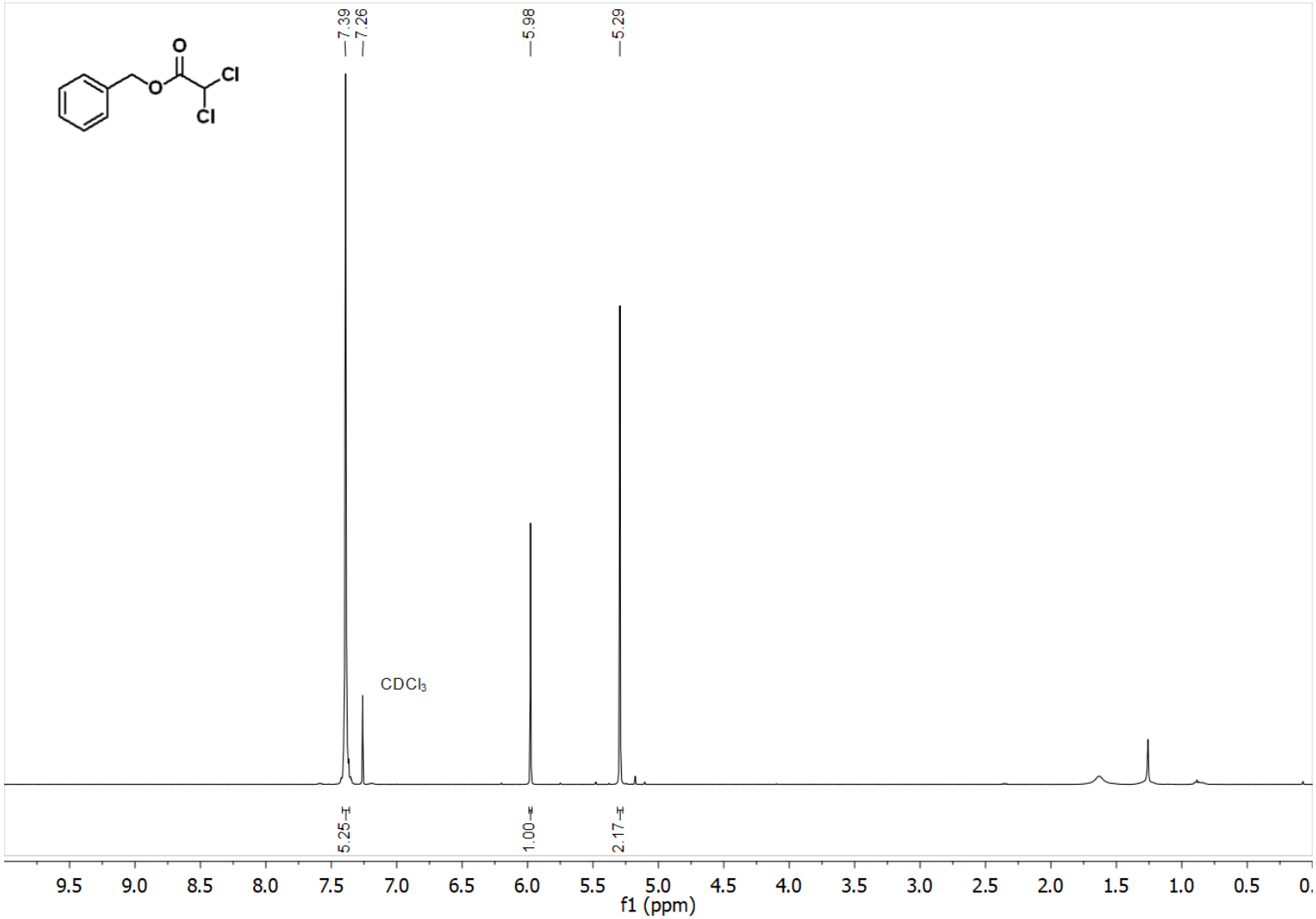
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 15c ethyl 2,2-dichloroacetate



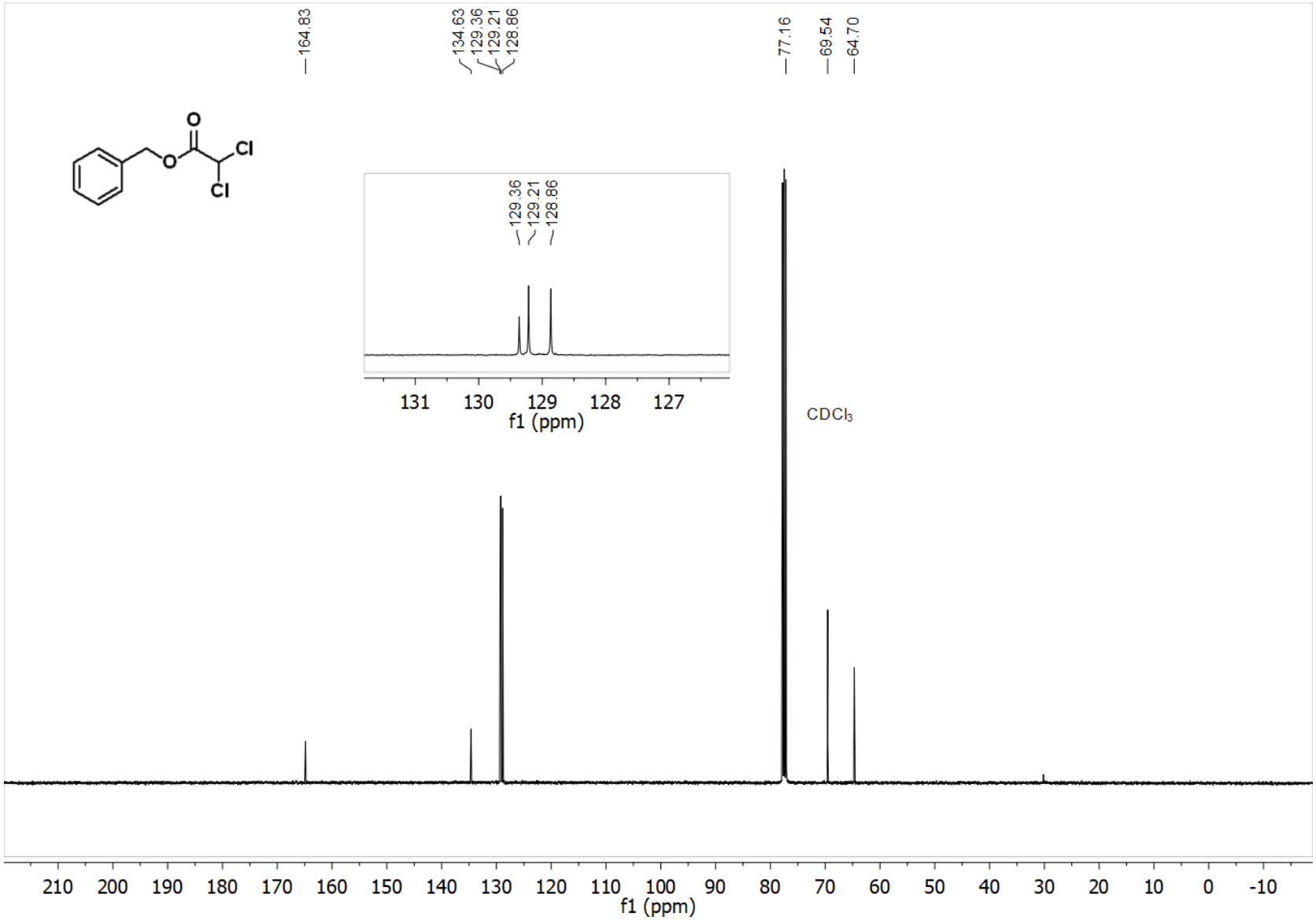
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 15c ethyl 2,2-dichloroacetate



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 16c benzyl 2,2-dichloroacetate



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 16c benzyl 2,2-dichloroacetate



GC and MS of 16c benzyl 2,2-dichloroacetate