Monofluoromethylation of Acyl Chlorides and Chloroformates employing Fluorobis(phenylsulfonyl)methane. Synthesis of Monofluoromethyl Ketones *via* Selective Zinc mediated Reductive Desulfonylation

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General Information

Unless otherwise specified, all materials were purchased from commercial sources and used without further purification. The reactions were carried out under nitrogen or argon atmosphere in flame-dried or oven-dried crimp top vials. Acetonitrile (HPLC grade) was distilled over P_2O_5. The products were purified *via* reverse phase flash column chromatography with water (HPLC grade) and acetonitrile (HPLC grade) as solvents. ^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra were recorded on 400 MHz, 500 MHz, or 600 MHz NMR spectrometers. Chemical shifts were determined relative to $CHCl_3$ (for ^{1}H spectra), $CDCl_3$ (for ^{13}C spectra), and $CFCl_3$ (for ^{19}F spectra), respectively. NMR yields were determined via ^{19}F spectral analysis of the neat reaction mixture using fluorobenzene as the internal standard. Mass spectrometric data were recorded *via* Agilent liquid chromatography mass spectrometer (LCQTOF) using electron ionization (EI) or electrospray ionization (ESI). IR data were recorded on a JASCO FT/IR spectrometer**.** Crystallographic data for the small molecules have been deposited at the Cambridge Structural Database (CSD) managed by the Cambridge Crystallographic Data Centre (CCDC). The structures can be found under the deposition number 2427870-2427890 and 2427902.

General Procedure A - Synthesis of Bis(phenylsulfonyl)methane

Benzenethiol (2.1 equiv) was added to a round bottom flask. NaOH pellets (2.53 equiv) were crushed to a fine powder and dissolved in anhydrous ethanol (60 mL). The NaOH solution was then added to the thiol solution, and the mixture was stirred for 2 hours at room temperature. Dibromomethane (20 mmol, 1 equiv) was added in one portion to the reaction mixture, and the corresponding suspension was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The obtained crude bis(phenylthio)methane was transferred to a larger round bottom flask, and dissolved in glacial acetic acid (50 mL). Hydrogen peroxide (30%, 100 mL) was slowly added at room temperature, causing the mixture to turn cloudy. The flask was then placed in a pre-heated oil bath at 100 °C, an air condenser was attached, and the mixture was stirred for approximately 2 hours at 100°C. The solution turned clear after a few minutes. A foamy precipitate, the bis(phenylsulfonyl)methane, typically formed after 15-30 minutes. The reaction was stirred until the formation of more solid stopped. The mixture was allowed to cool to room temperature and was carefully diluted with deionized water. The precipitate was thoroughly washed with deionized water until the filtrate was no longer acidic. The solid was then transferred to a flask, dissolved in dichloromethane, and precipitated with hexanes to obtain a fluffy white solid. The obtained bis(phenylsulfonyl)methane was dried in vacuo.

General Procedure B - Synthesis of Fluorobis(phenylsulfonyl)methane

Bis(phenylsulfonyl)methane (2.96g, 10 mmol, 1.3 equiv.) was added to a round bottom flask under a nitrogen atmosphere. The solid was dissolved in anhydrous THF (25 mL), and the solution was cooled to 0 °C using an ice-water bath. To this solution, NaH (7.69 mmol, 1.0 equiv.) was slowly added in small portions. The solution turned cloudy after each addition of NaH and needed to be stirred for a short period before the next portion was added. Once all the NaH had been added, the resulting suspension was stirred for 30 minutes at 0 °C. Selectfluor® (7.69 mmol, 1.0 equiv.)was crushed to a fine powder and subsequently added in one portion to the suspension, followed by a small amount of anhydrous acetonitrile. The mixture was then stirred overnight. After completion of the reaction, the reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, evaporated under reduced pressure, and purified via flash column chromatography (hexanes : ethyl acetate). The obtained solid was dissolved in dichloromethane and precipitated with hexanes. Fluorobis(phenylsulfonyl)methane was obtained as a fluffy white solid in 75% yield.

General Procedure C - Synthesis of Fluorobis(phenylsulfonyl)methyl ketones

In an argon glovebox, fluorobis(phenylsulfonyl)methane FBSM (0.20 mmol, 1.0 equiv, 62.8 mg) and Cs_2CO_3 (0.72 mmol, 3.6 equiv, 234 mg) were added to a 5 mL oven dried crimp top vial. Under N_2 atmosphere, distilled acetonitrile (2.0 mL, 0.1 M) was added to the vial. The reaction mixture was stirred for 15 minutes at room temperature. Subsequently, the corresponding acid chloride (0.4 mmol, 2.0 equiv) was added dropwise and the reaction mixture was stirred for 1 hour at room temperature (solid acyl chlorides were dissolved in 0.4-0.5 mL distilled THF). After completion of the reaction, monitored by ^{19}F-NMR, the reaction mixture was diluted with dichloromethane and the suspension was filtered. The vial was rinsed with dichloromethane (3 x 5 mL). The solvent was removed under reduced pressure and the obtained oily residue was purified via reverse phase flash column chromatography (water : acetonitrile). The fractions were combined, solid NaCl was added, shaken, and the two formed layers were separated. The acetonitrile was removed under reduced pressure and a watery-oily suspension was obtained. Distilled water was added to dissolve precipitated NaCl, followed by dichloromethane. The aqueous layer was extracted with dichloromethane (3 x 25 mL). The organic layers were combined, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The obtained oily product was triturated with hexanes. The solvent was decanted, and the obtained solidified product was dried in vacuo.

Note: If an oil is obtained after the solvent was removed, a trituration with hexanes results in the formation of a solid product.

General Procedures D - Reductive Desulfonylation

General Procedure D-1 – Partial Reduction

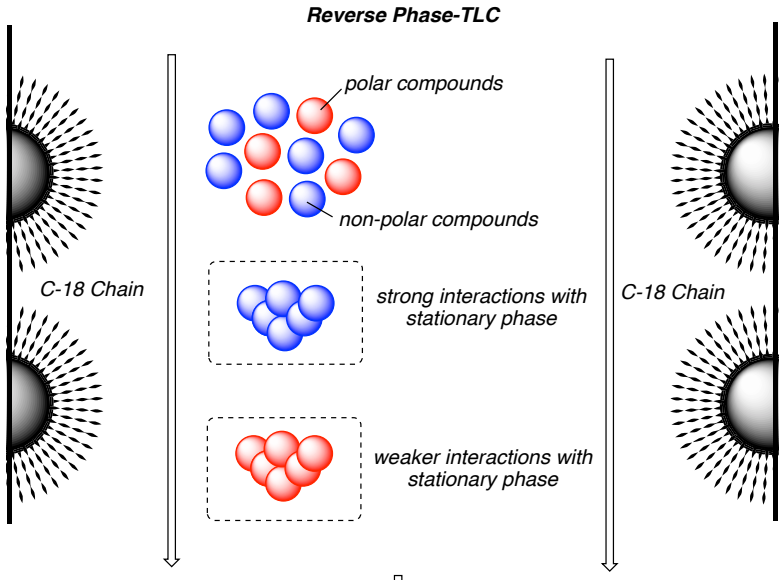
To an 8 dram vial, the substrate (0.2 mmol, 1 equiv) was added, followed by anhydrous ethanol (1 mL) and glacial acetic acid (0.5 mL). Zinc flakes (20 mesh, 13 mg) were then added to the vial, and the walls of the vial were rinsed with an additional 1 mL of anhydrous ethanol. The vial was capped and placed in a sonicator, where the mixture was sonicated for 1 hour. The reaction progress was carefully monitored by ^{19}F NMR, using fluorobenzene as an internal standard. Upon completion of the reaction, the mixture was diluted with water and extracted with dichloromethane (4 x 5 mL). The combined organic layers were washed with deionized water (2 x 5 mL) and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography using hexanes and dichloromethane (35-50% DCM in hexanes). The fractions were combined, the solvent removed under reduced pressure, and the corresponding oil triturated with hexanes to obtain the solidified product.

General Procedure D-2 – Full Reduction

To an 8 dram vial, the substrate (0.2 mmol, 1 equiv) was added, followed by anhydrous ethanol (1 mL) and glacial acetic acid (0.5 mL). Zinc flakes (20 mesh, 106 mg) were then added to the vial, and the walls of the vial were rinsed with an additional 1 mL of anhydrous ethanol. The vial was capped and placed in a sonicator, where the mixture was sonicated for 1 hour. The reaction progress was carefully monitored by ^{19}F NMR, using fluorobenzene as an internal standard. Upon completion of the reaction, the mixture was diluted with water and extracted with dichloromethane (4 x 5 mL). The combined organic layers were washed with deionized water (2 x 5 mL) and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography using hexanes and dichloromethane (15% DCM in hexanes). The fractions were combined, the solvent removed under reduced pressure, and the corresponding product was obtained as a colorless oil.

Lipophilicity Assessment *via* Reverse Phase Thin-Layer-Chromatography

Lipophilicity refers to the chemical property of a substance's ability to dissolve in fats, oils, and non-polar solvents, indicating its affinity for lipids over water. This characteristic is crucial in pharmacology and chemistry as it influences the absorption, distribution, metabolism, and excretion of compounds in biological systems.[1–4] Lipophilicity is typically determined using the shaken flask method, where a compound is dissolved in a biphasic system of water and a non-polar solvent, such as octanol. After thorough shaking and equilibration, the concentration of the compound in each phase is measured, allowing the partition coefficient (log P) to be calculated, which quantifies the compound's lipophilicity. This method is time-consuming and labour-intensive, often requiring extended periods for equilibration and precise analytical techniques, making it an expensive service frequently offered by specialized laboratories.



Most of the compounds presented in this research were purified via reverse-phase flash column chromatography, using acetonitrile and water as the eluent system and a C18 modified silica column. This method inspired the use of C18 modified thin layer chromatography (TLC) plates for assessing lipophilicity, as they replicate the interactions of water and octanol in the shaken flask method. This approach offers a faster, more efficient way to quickly evaluate lipophilicity trends for small organic molecules, streamlining the process of determining this crucial property.

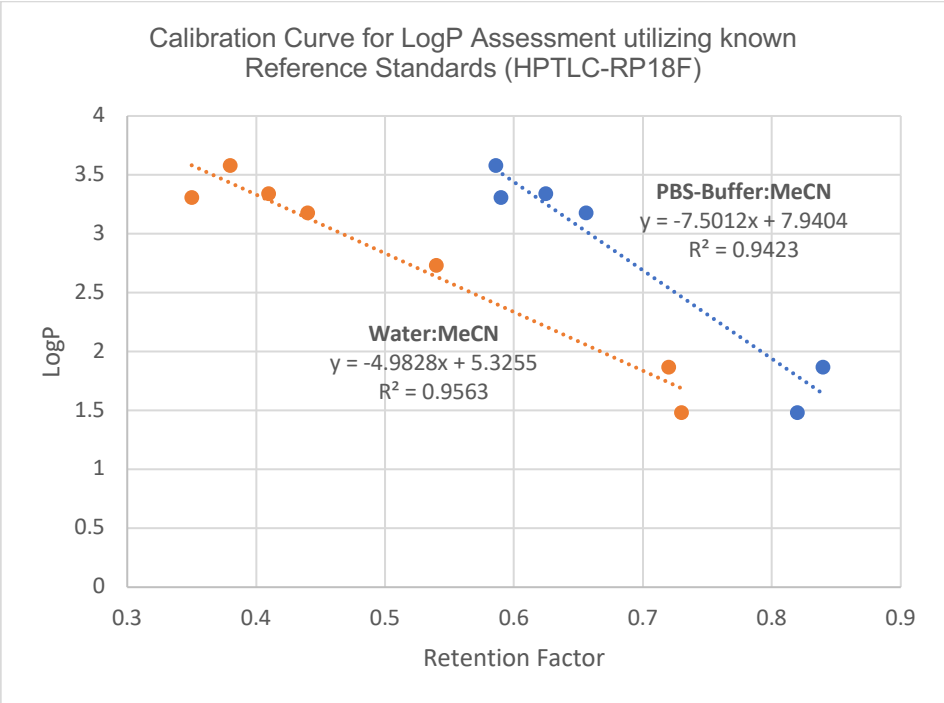
In reverse-phase thin layer chromatography (TLC), the separation principle is based on the differing affinities of compounds for the hydrophobic C18-stationary phase and the polar mobile phase (water:acetonitrile). Compounds with greater hydrophobicity will interact more strongly with the stationary phase and travel more slowly, while more hydrophilic compounds will preferentially stay in the mobile phase and move faster along the plate.

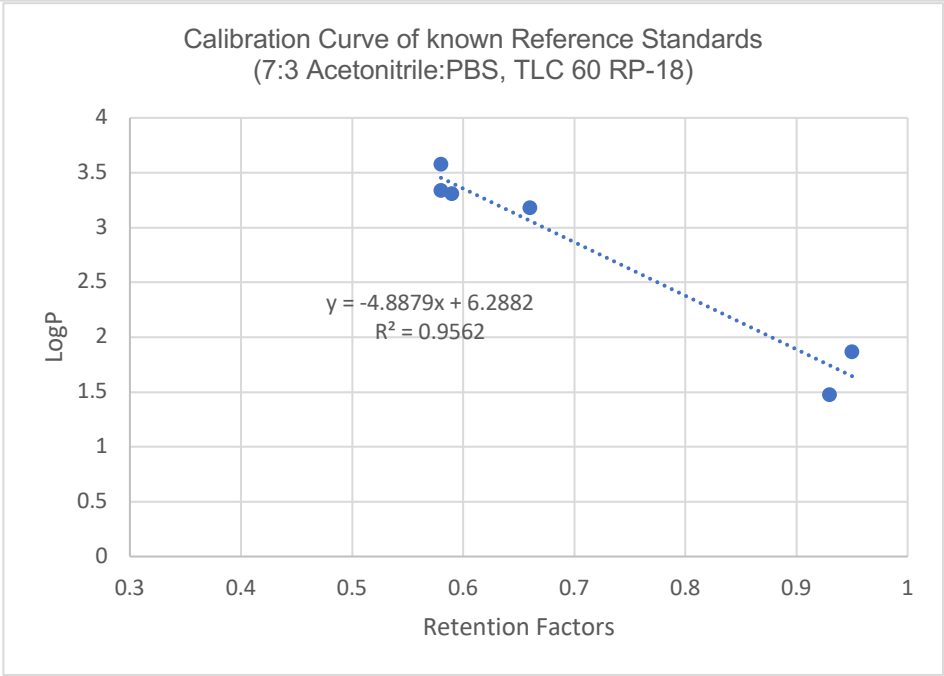
To establish reference values, it was necessary to run reference compounds with known logP values in the same reaction system to obtain a calibration curve. The retention factors obtained from these reference compounds allow for the referencing of new compounds with unknown logP values, facilitating the comparison and interpretation of their lipophilicity. This method helps visualize important trends in lipophilicity, which can be crucial for drug discovery purposes, aiding in the prediction of absorption, distribution, and overall bioavailability of potential drug candidates.

For establishing a calibration curve, several reference compounds with known theoretical logP values were used. Phenol, with a logP value of 1.46, and benzoic acid, with a logP of 1.87, served as more hydrophilic references. Toluene, with a logP of 2.73, and dibenzyl ether, with a logP of 4.35, provided moderately hydrophobic reference points. More hydrophobic compounds such as fluorenone, with a logP of 3.99, and naphthalene, with a logP of 3.30, were also included. Benzophenone, with a logP of 3.18, and cholesterol, with a logP of 7.00, represented highly hydrophobic references. These compounds collectively span a broad range of lipophilicity, making them ideal for generating a comprehensive calibration curve to assess the lipophilicity of new compounds.

The analysis of the isolated compounds during their purification via reverse-phase column chromatography revealed that a 7:3 eluent system of acetonitrile to water provided an effective separation. This eluent mixture achieved decent retention factor (Rf) values, indicating that the compounds were well-resolved on the column. To correlate these values to more biological relevant values, a commonly used phosphate buffered saline solution (PBS) of molecular biology grade was used.

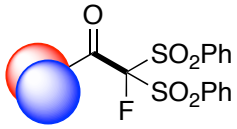
Reference Standard	LogP(reported)
Phenol	1.46
Benzoic acid	1.87
Toluene	2.73
Dibenzylether	4.35
Fluorenone	3.99
Naphthalene	3.30
Benzophenone	3.18





The analysis of the reference standards has shown that, depending on the reverse-phase TLC plate used (from different vendors), a new calibration curve needs to be measured for accurate comparison. Each calibration curve should be specific to the utilized reverse-phase TLC plate, ensuring precise logP determination of the samples. This approach accounts for potential variations in the plates' properties, allowing for consistent and reliable evaluation of compound lipophilicity.

Lipophilicity Assessment of Compound Class 1

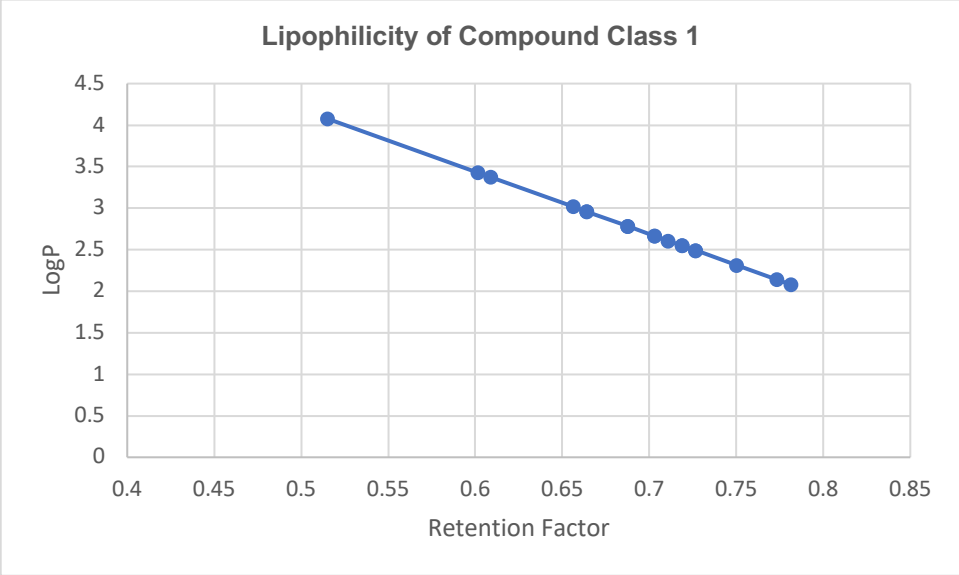


The retention factors were determined *via* reverse phase thin layer chromatography utilizing a phosphate buffered saline : acetonitrile eluent mixture (3:7 v/v). The experimental LogP value was obtained by plotting the calculated retention factor RF into the calibration curve equation

$$R_F = \frac{Distance\ traveled\ by\ compound}{Distance\ traveled\ by\ solvent}$$

$$LogP = -7.5012 * R_F + 7.9404$$

The results are shown in the graph below



The experimentally determined lipophilicity values were compared with theoretical methods

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
3c	4.08	3.61	5.52	7.50	4.05	4.37	5.01
2w	3.37	2.94	5.88	7.89	3.64	5.15	5.10
2g	3.02	3.48	5.57	7.32	3.84	4.24	4.89
3g	2.96	3.16	4.22	6.02	2.80	2.48	3.73
2i	2.96	2.76	4.55	6.63	3.69	3.81	4.29
2e	2.78	3.43	4.26	6.33	3.20	3.36	4.12
2c	2.78	2.72	4.59	6.78	3.58	3.52	4.24
2o	2.67	2.99	4.78	8.19	3.79	3.94	4.74
2t	2.67	2.65	4.53	6.68	3.47	3.49	4.16

2m	2.61	3.00	4.59	6.78	3.58	3.52	4.29
2q	2.55	2.41	4.00	6.58	3.36	3.27	3.92
2n	2.55	3.10	4.09	6.51	3.24	3.39	4.07
2j	2.49	2.50	4.00	6.58	3.36	3.27	3.94
2v	2.49	2.90	3.75	5.81	2.82	2.87	3.63
2l	2.31	3.24	3.87	6.03	2.66	2.91	3.74
2u	2.08	2.51	3.30	5.62	1.36	2.23	3.00
2p	2.56	1.63	2.48	2.57	2.25	2.91	2.37
2b	3.02	2.62	4.53	6.68	3.47	3.49	4.16
2d	2.79	2.74	4.26	6.33	3.20	3.36	3.98

Correlation of LogP and theoretical methods of compound class 1

	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Av. Log
LogP(exp)	0.50	0.77	0.50	0.70	0.75	0.71

The best correlation of the experimentally determined LogP values was obtained with XLogP3 with a correlation factor of 0.77.

The dataset correlation showed an improved when dividing the set into different subsets

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
3c	4.08	3.61	5.52	7.50	4.05	4.37	5.01
2g	3.02	3.48	5.57	7.32	3.84	4.24	4.89
2e	2.78	3.43	4.26	6.33	3.20	3.36	4.12
2l	2.31	3.24	3.87	6.03	2.66	2.91	3.74
2u	2.08	2.51	3.30	5.62	1.36	2.23	3.00
2d	2.79	2.74	4.26	6.33	3.20	3.36	3.98

	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Av. Log
LogP(exp)	0.69	0.86	0.90	0.85	0.89	0.88

The best correlation of the experimentally determined logP values was obtained with WLOGP with a correlation factor of 0.90. This has shown that separating the dataset into subsets shows direct improvement of the correlation factor. All of the theoretical methods show strong correlation with the experimental dataset and show the same trend:

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
2u	2.08	2.51	3.30	5.62	1.36	2.23	3.00
2l	2.31	3.24	3.87	6.03	2.66	2.91	3.74
2e	2.78	3.43	4.26	6.33	3.20	3.36	4.12

2d	2.79	2.74	4.26	6.33	3.20	3.36	3.98
2g	3.02	3.48	5.57	7.32	3.84	4.24	4.89
3c	4.08	3.61	5.52	7.50	4.05	4.37	5.01

An example for the halide subset results is listed below

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
2j	2.49	2.50	4.00	6.58	3.36	3.27	3.94
2q	2.55	2.41	4.00	6.58	3.36	3.27	3.92
2b	2.65	2.62	4.53	6.68	3.47	3.49	4.16
2t	2.67	2.65	4.53	6.68	3.47	3.49	4.16
2c	2.78	2.72	4.59	6.78	3.58	3.52	4.24
2h	2.92	2.98	4.55	6.63	3.69	3.81	4.33

The correlation of the halide subset is shown below

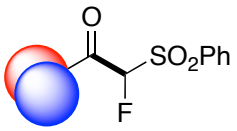
	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Av. Log
LogP(exp)	0.95	0.80	0.51	0.99	0.96	0.95

The best correlation of the experimentally determined LogP values was obtained with MLogP with a correlation factor of 0.99 (besides the average Log). The correlation with iLogP shows a very good prediction of the experimentally obtained LogP values.

Compound	LogP(exp)	iLogP
2j	2.49	2.50
2q	2.55	2.41
2b	2.65	2.62
2t	2.67	2.65
2c	2.78	2.72
2h	2.92	2.98

This has shown that separating the dataset into subsets of halide containing compounds shows direct improvement of the overall correlation factor and prediction.

Lipophilicity Assessment of Compound Class 2

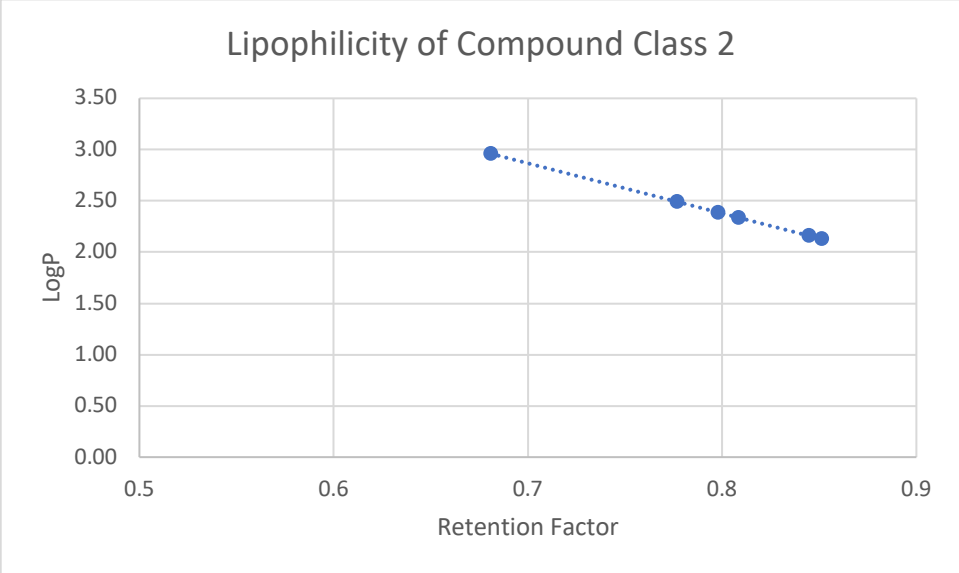


The retention factors were determined *via* reverse phase thin layer chromatography utilizing a phosphate buffered saline : acetonitrile eluent mixture (3:7 v/v). The experimental LogP value was obtained by plotting the calculated retention factor RF into the calibration curve equation

$$R_F = \frac{Distance\ traveled\ by\ compound}{Distance\ traveled\ by\ solvent}$$

$$LogP = -4.8879 * R_F + 6.2882$$

The results are shown in the graph below



The experimentally determined lipophilicity values were compared with theoretical methods

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
4a	2.39	2.09	3.67	4.79	3.03	3.31	3.38
4b	2.34	1.96	3.41	4.45	2.76	3.17	3.15
4c	2.16	1.78	3.15	4.70	2.90	3.09	3.12
4d	2.13	1.64	3.15	4.70	2.90	3.09	3.10
4e	2.49	2.08	3.74	4.90	3.15	3.35	3.44
4f	2.96	2.53	4.72	5.44	3.48	4.01	4.04

Correlation of LogP and theoretical methods of compound class 2

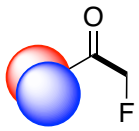
	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
LogP(exp)	0.98	0.99	0.87	0.90	0.98	0.98

The best correlation of the experimentally determined LogP values was obtained with XLogP3 with a correlation factor of 0.99. All theoretical methods presented show very strong correlations with correlation factors greater than 87%. The results, including the ordering of compounds based on their lipophilicity, are summarized in the table below. This table highlights the differences in lipophilic behavior across the series, providing a clear comparison between the least and most lipophilic compounds.

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
4d	2.13	1.64	3.15	4.70	2.90	3.09	3.10
4c	2.16	1.78	3.15	4.70	2.90	3.09	3.12
4b	2.34	1.96	3.41	4.45	2.76	3.17	3.15
4a	2.39	2.09	3.67	4.79	3.03	3.31	3.38
4e	2.49	2.08	3.74	4.90	3.15	3.35	3.44
4f	2.96	2.53	4.72	5.44	3.48	4.01	4.04

The correlations between the experimental and theoretical values presented in this series are consistently strong, indicating a high degree of reliability and accuracy in the predictive methods used. Among the compounds analyzed, **4d** (2-Fluoro) was identified as the least lipophilic, demonstrating the lowest affinity for lipid environments. In contrast, **4f** (4-*tert* butyl) emerged as the most lipophilic compound, exhibiting the highest lipid solubility. These findings highlight the variation in lipophilicity within the series and provide valuable insights for future research and application in pharmaceutical development.

Lipophilicity Assessment of Compound Class 3

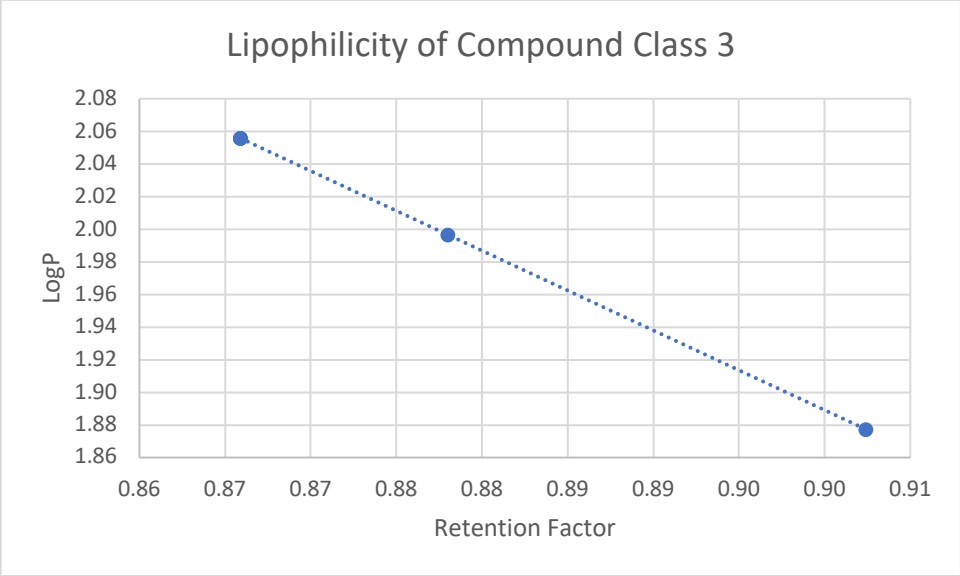


The retention factors were determined *via* reverse phase thin layer chromatography utilizing a phosphate buffered saline : acetonitrile eluent mixture (3:7 v/v). The experimental LogP value was obtained by plotting the calculated retention factor RF into the calibration curve equation

$$R_F = \frac{Distance\ traveled\ by\ compound}{Distance\ traveled\ by\ solvent}$$

$$LogP = -4.8879 * R_F + 6.2882$$

The results are shown in the graph below



The experimentally determined lipophilicity values were compared with theoretical methods

Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS IT	Average
5a	2.06	1.57	2.70	2.91	2.52	3.08	2.56
5b	2.06	1.63	2.48	2.57	2.25	2.91	2.37
5c	1.88	1.42	2.10	2.82	2.37	2.86	2.31
5d	2.00	1.18	2.08	2.82	2.37	2.86	2.26
5e	2.06	1.71	2.66	3.02	2.67	3.12	2.63

Correlation of LogP and theoretical methods of compound class 3

	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
LogP(exp)	0.52	0.79	0.04	0.31	0.65	0.61

The best correlation of the experimentally determined LogP values was obtained with XLogP3 with a correlation factor of 0.79. This dataset gives a first insight into the correlation with the current theoretical methods but needs more datapoints. It clearly shows that the existing theoretical datasets need more datapoints to cover all possible molecular interactions that influence the lipophilicity.

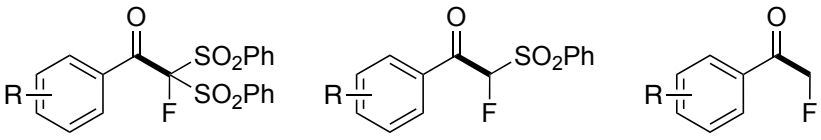
Compound	LogP(exp)	iLogP	XLogP3	WLogP	MLogP	SILICOS-IT	Average
5c	1.88	1.42	2.10	2.82	2.37	2.86	2.31
5d	2.00	1.18	2.08	2.82	2.37	2.86	2.26
5a	2.06	1.57	2.70	2.91	2.52	3.08	2.56
5e	2.06	1.71	2.66	3.02	2.67	3.12	2.63
5b	2.06	1.63	2.48	2.57	2.25	2.91	2.37

The correlations between the experimental and theoretical values presented in this series are moderately strong, indicating that more datapoints are necessary but already indicates the potential of this method to predict logp values for future drug development. Among the compounds analyzed, **5c** (4-Fluoro) was identified as the least lipophilic, demonstrating the lowest affinity for lipid environments. In contrast, **5b** (4-Methyl) emerged as the most lipophilic compound of this series, exhibiting the highest lipid solubility. These findings highlight the variation in lipophilicity within the series and provide valuable insights for future research and application in pharmaceutical development.

Conclusion

The presented method demonstrates a very good alternative to the established shaken flask method, allowing for the quick assessment of ***lipophilicity trends*** in a series of similar compounds. The comparison with existing theoretical methods revealed very strong correlations for most of the analyzed compounds. Despite the relatively small datasets, the results show promising potential for future lipophilicity assessments.

In this study, a series of various compounds were analysed, revealing that lipophilicity decreases with the partial and full removal of sulfonylphenyl groups. While the absolute values should be used with caution due to the limited dataset size, the strong correlations with theoretical methods suggest this approach as a highly effective alternative for assessing lipophilicity trends within various series of molecules throughout a drug development process, which could be of significant relevance for compounds of pharmaceutical interest.



Compound	**2b**	**4a**	**5a**
R =	4-Chloro		
LogP(exp)	2.65	2.39	2.06
Compound	**2d**	**4b**	**5b**
R =	4-Methyl		
LogP(exp)	2.79	2.34	2.06
Compound	**2j**	**4c**	**5c**
R =	4-Fluoro		
LogP(exp)	2.49	2.16	1.88
Compound	**2p**	**4d**	**5d**
R =	2-Fluoro		
LogP(exp)	2.56	2.13	2.00

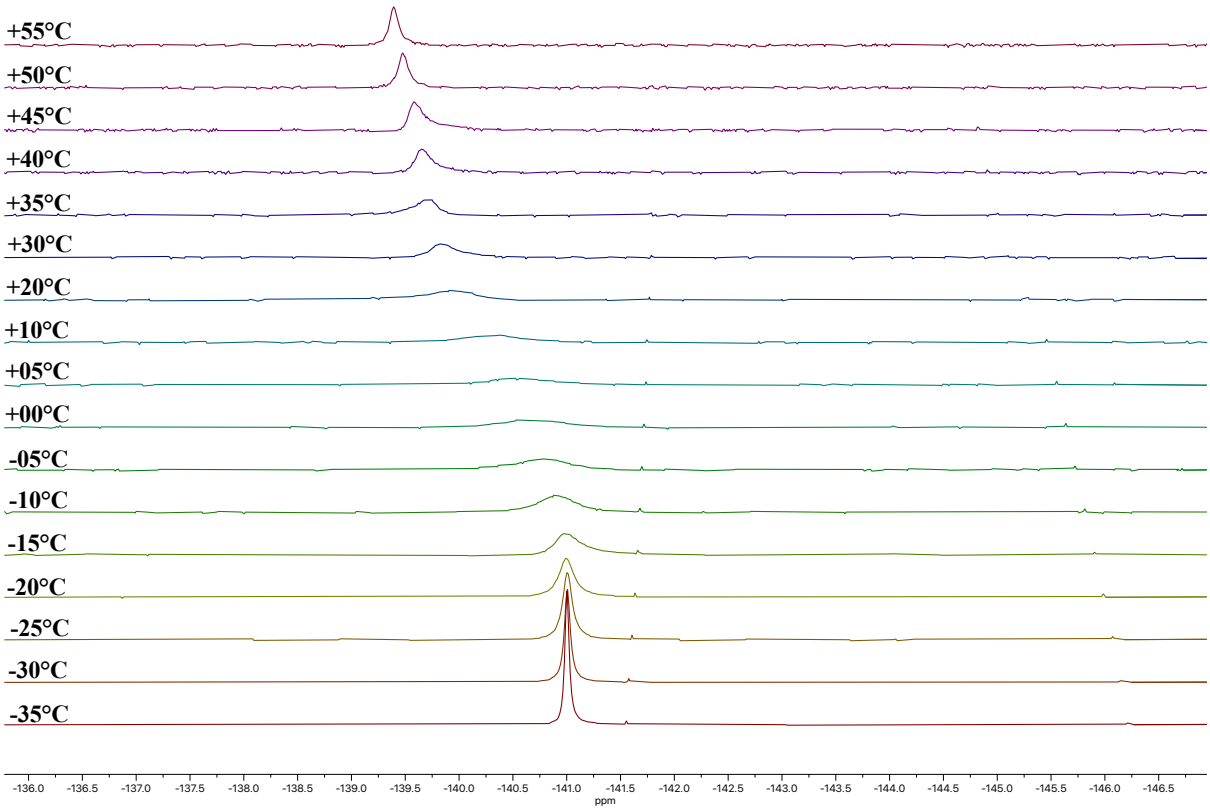
“Lipophilic” “Hydrophilic”

The 4-methyl series shows the largest difference after desulfonylation. With a difference of 0.73 units on the logarithm scale, compound **5b** is expected to be 5.37 times more hydrophilic than its bissulfonated analogue **2d**. The 2-fluoro series shows the smallest difference after desulfonylation. With a difference of 0.56 units, compound **5d** is expected to be 3.63 times more hydrophilic than its bissulfonated analogue **2p**. These examples represent the principle for utilizing this presented system for evaluating molecules in drug development.

Variable Temperature Studies

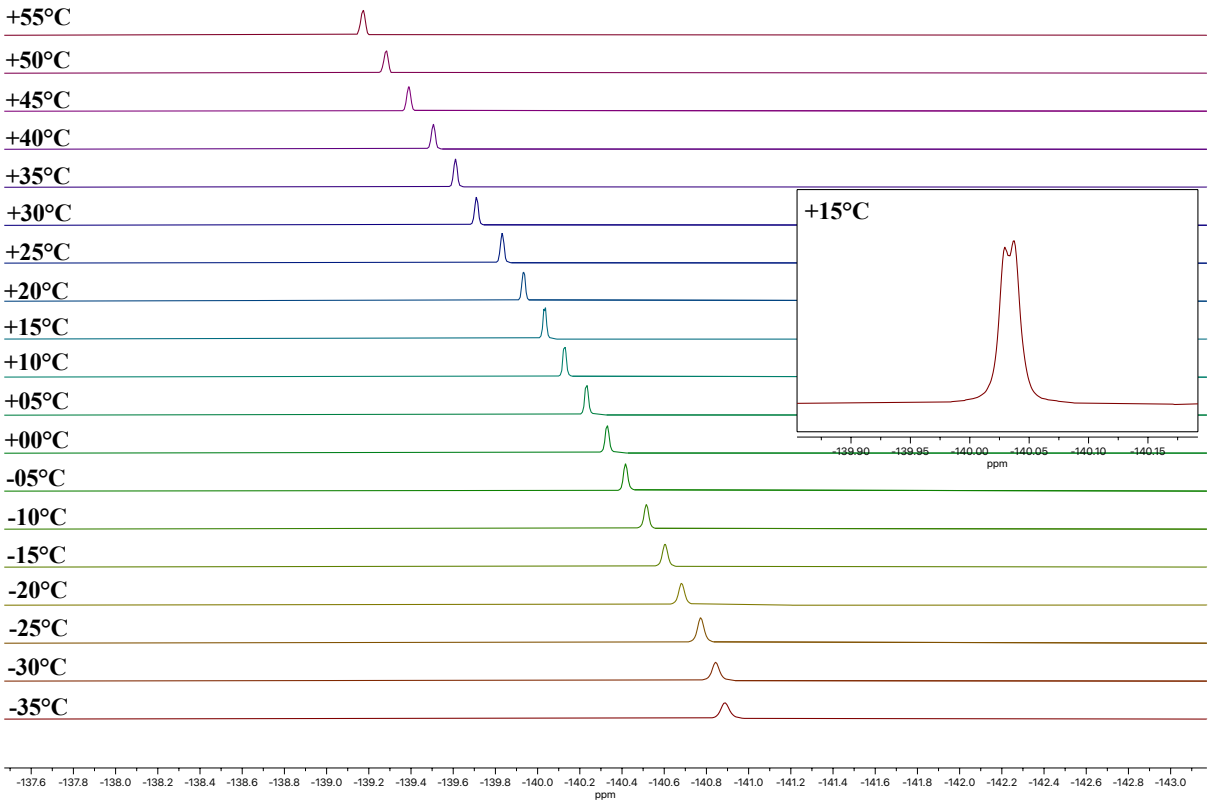
^{19}F-NMR Study of Compound 2a in $CDCl_3$

Compound 2a was dissolved in deuterated chloroform ($CDCl_3$) to prepare an NMR sample. The sample was then transferred to an NMR tube and analyzed using a 600 MHz NMR spectrometer. Spectra were recorded at various temperatures ranging from -35 to +55 °C, with temperature adjustments made incrementally. Before each measurement, the NMR sample was left at the target temperature for a few minutes to ensure thermal equilibration and a stable temperature was reached.



^{19}F-NMR Study of Compound 2m in $CDCl_3$

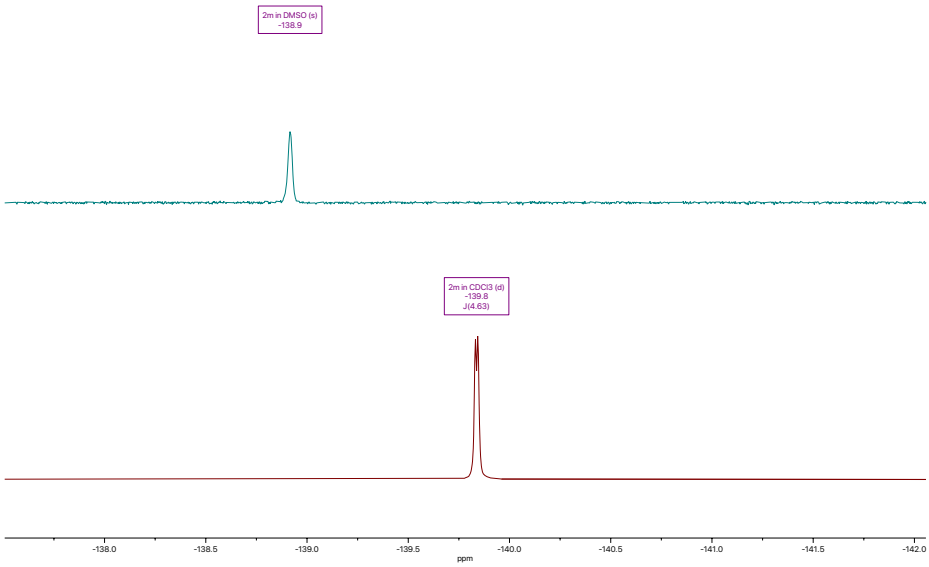
Compound 2m was dissolved in deuterated chloroform ($CDCl_3$) to prepare an NMR sample. The sample was then transferred to an NMR tube and analyzed using a 600 MHz NMR spectrometer. Spectra were recorded at various temperatures ranging from -35 to +55 °C, with temperature adjustments made incrementally. Before each measurement, the NMR sample was left at the target temperature for a few minutes to ensure thermal equilibration and a stable temperature was reached.



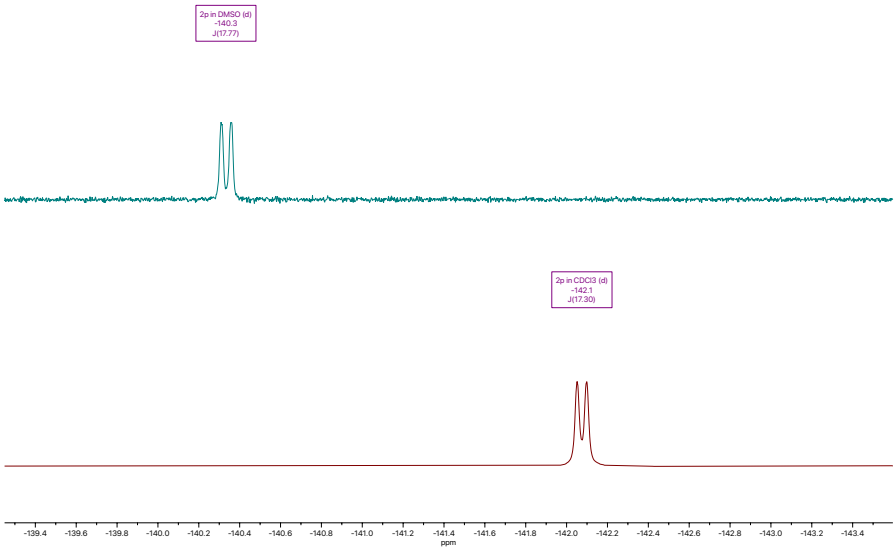
Hydrogen Interaction Studies – DMSO-D_6 vs. $CDCl_3$

DMSO, known for its strong hydrogen bond-accepting ability, was introduced to disrupt potential intramolecular hydrogen bonding interactions. Upon dissolving compound **2m** and **2p** in DMSO-D_6 and analyzing the ^{19}F NMR spectrum, a noticeable shift in the fluorine signal was observed, along with sharpening of previously broad peaks.

^{19}F-NMR spectra of substrate **2m** in DMSO-D6 (top) and $CDCl_3$ (bottom). Both spectra were referenced to $CFCl_3$.



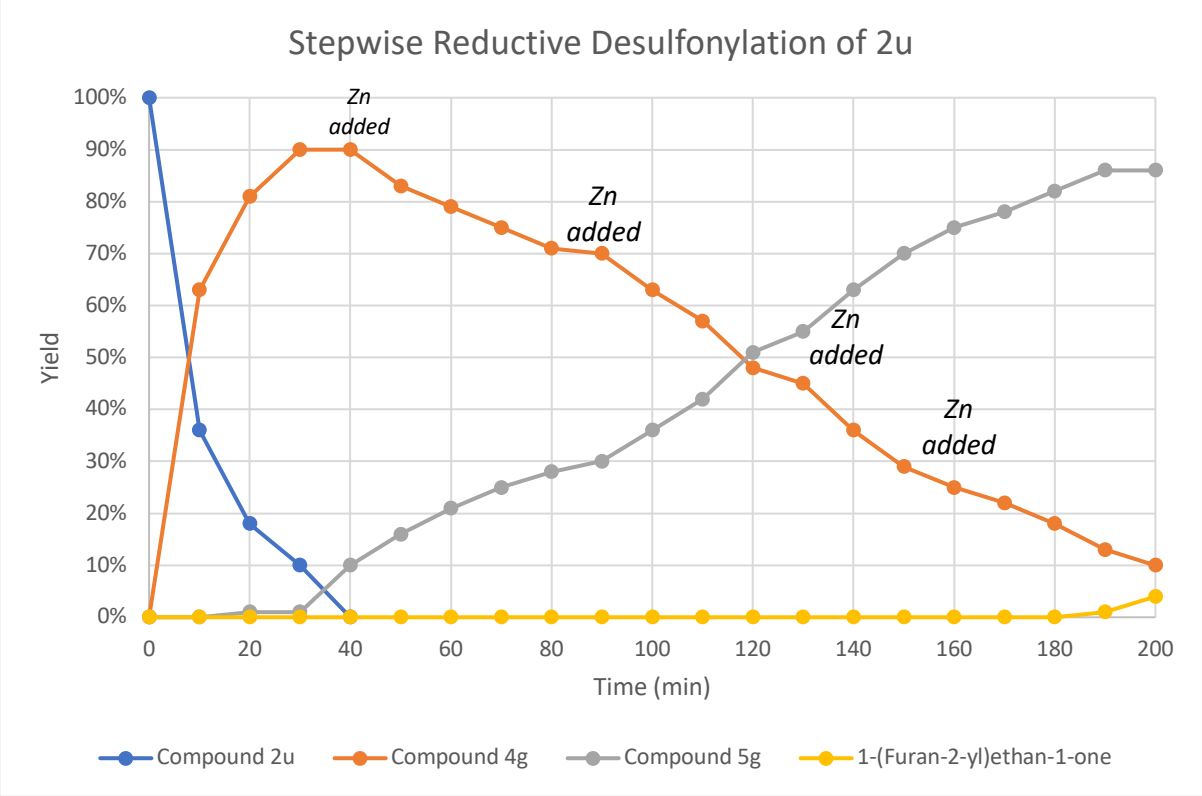
^{19}F-NMR spectra of substrate **2p** in DMSO-D6 (top) and $CDCl_3$ (bottom). Both spectra were referenced to $CFCl_3$



This behavior suggests that the through space coupling interactions were significantly reduced or disrupted by the competitive hydrogen bonding capacity of DMSO. These results provide further evidence supporting the role of van der Waals forces in influencing the fluorine environment and demonstrate the importance of solvent effects in probing such interactions.

Reductive Desulfonylation of 2u – Tracking of Reaction Progress

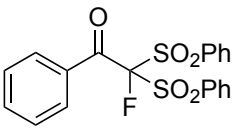
To an 8 dram vial, the **2u** (0.2 mmol, 1 equiv) was added, followed by anhydrous ethanol (1 mL) and glacial acetic acid (0.5 mL). Zinc flakes (20 mesh) were then added to the vial, and the walls of the vial were rinsed with an additional 1 mL of anhydrous ethanol. The vial was capped and placed in a sonicator, where the mixture was sonicated. The reaction progress was carefully monitored by ^{19}F NMR, using fluorobenzene as an internal reference.



Experimental Data and Characterization

Compounds 2a-2w

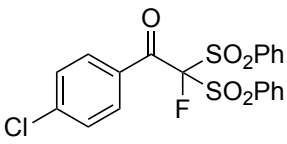
2-Fluoro-1-phenyl-2,2-bis(phenylsulfonyl)ethan-1-one (2a)



Prepared from benzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (59% water : 41% MeCN) and **2a** was obtained as a white solid (71 mg, 0.170 mmol, 85%)

Melting Point: 113-115°C, **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 0H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 135.9, 135.1, 134.5, 131.5 (d, *J* = 0.8 Hz), 129.8 (d, *J* = 6.7 Hz), 128.5, 113.2 (d, *J* = 282.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.9 (s, 1F). **IR (neat, cm^{-1}) ν :** 2917, 2363, 2353, 2012, 1682, 1592, 1476, 1446, 1348, 1314, 1242, 1183, 1171, 1154, 1117, 1077, 876, 760, 681, 649, 606. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H16FO5S2+ 419.0418; Found: 419.0411 (1.7ppm).

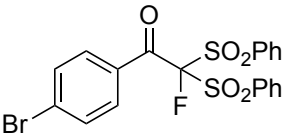
1-(4-Chlorophenyl)-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2b)



Prepared from 4-chlorobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (49% water : 51% MeCN) and **2b** was obtained as a white solid (79 mg, 0.17 mmol, 87%)

Melting Point: 117-119°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 4H), 7.74 (t, *J* = 7.4 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 4H), 7.34 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5, 141.4, 136.0, 134.9, 132.7, 131.5, 131.3 (d, *J* = 6.8 Hz), 129.4, 129.0, 113.2 (d, *J* = 280.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.8 (s, 1F). **IR (neat, cm^{-1}) ν :** 3086, 1682, 1581, 1486, 1474, 1448, 1402, 1360, 1348, 1311, 1283, 1242, 1181, 1159, 1113, 1090, 1077, 1033, 1011, 998, 929, 884, 733, 649. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15ClFO5S2+ 453.0028; Found: 453.0041 (2.9 ppm).

1-(4-Bromophenyl)-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2c)

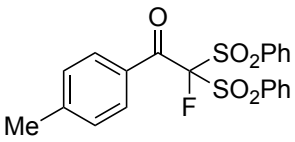


Prepared from 4-bromobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2c** was obtained as a white solid (90 mg, 0.180 mmol, 90%).

Melting Point: 141-143°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 4H), 7.74 (t, *J* = 7.4 Hz, 2H), 7.54 (dt, *J* = 22.0, 8.2 Hz, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9 (d, *J* = 22.9 Hz), 136.0, 134.9, 133.1 (d, *J* = 3.6 Hz), 132.0 (d, *J* = 1.0 Hz), 131.6 – 131.4 (m), 131.2 (d, *J* = 6.7 Hz), 130.3, 129.4, 113.2 (d, *J* = 280.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.9 (s, 1F). **IR (neat, cm^{-1}) ν:** 3097, 2360, 2262, 1922, 1678, 1577, 1560, 1481, 1448, 1395, 1350, 1313, 1242, 1184, 1157, 1114, 1074, 1006, 953, 828,

801, 720, 684. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15BrFO5S2+ 496.9523; Found: 496.9537 (2.8 ppm).

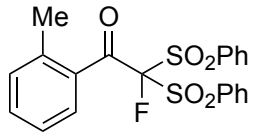
2-Fluoro-2,2-bis(phenylsulfonyl)-1-(*p*-tolyl)ethan-1-one (2d)



Prepared from *p*-toloyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (50% water : 50% MeCN) and **2d** was obtained as a white solid (78 mg, 0.180 mmol, 90%)

Melting Point: 151-152°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 4H), 7.72 (t, *J* = 7.5 Hz, 2H), 7.62 – 7.51 (m, 6H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.6 (d, *J* = 21.6 Hz), 145.9, 135.8, 135.2, 131.9, 131.5, 130.0, 129.2, 113.3 (d, *J* = 283.4 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.5 (s, 1F). **IR (neat, cm^{-1}) ν :** 3067, 2924, 1673, 1601, 1582, 1565, 1474, 1450, 1409, 1351, 1316, 1255, 1190, 1171, 1157, 1109, 1077, 1032, 1015, 997, 980, 817, 757, 683. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C21H18FO5S2+ 433.0574; Found: 433.0581 (1.6 ppm).

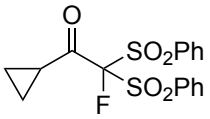
2-Fluoro-2,2-bis(phenylsulfonyl)-1-(*o*-tolyl)ethan-1-one (2e)



Prepared from *o*-toloyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2e** was obtained as a white solid (73 mg, 0.168 mmol, 84%).

Melting Point: 160-162°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 4H), 7.76 (t, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.5 (d, *J* = 22.9 Hz), 140.4, 135.9, 135.0, 133.4, 132.9, 132.1, 131.7, 129.6 (d, *J* = 11.3 Hz), 129.3, 125.2, 112.5 (d, *J* = 284.6 Hz), 20.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -138.4 (d, *J* = 5.4 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3290, 3268, 1687, 1596, 1582, 1447, 1355, 1345, 1316, 1234, 1181, 1157, 1107, 1078, 1010, 998, 937, 876, 762, 711, 653, 608. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C21H18FO5S2+ 433.0574; Found: 433.0581 (1.6 ppm).

1-Cyclopropyl-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2f)

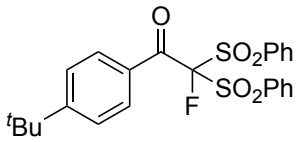


Prepared from cyclopropanecarbonyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (58% water : 42% MeCN) and **2f** was obtained as a white solid (70 mg, 0.182 mmol, 91%).

Melting Point: 135-136°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 4H), 7.75 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 4H), 2.92 – 2.81 (m, 1H), 1.25 – 1.08 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1 (d, *J* = 18.9 Hz), 136.0, 135.0, 131.1, 129.3, 112.0 (d, *J* = 273.0 Hz), 20.1, 15.7. **^{19}F NMR** (376

MHz, $CDCl_3$) δ -145.1 (s, 1F). **IR (neat, cm^{-1}) ν :** 3097, 3012, 1719, 1582, 1477, 1450, 1419, 1385, 1352, 1339, 1315, 1291, 1196, 1184, 1139, 1079, 1042, 912, 851, 759. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C17H16FO5S2+ 383.0418; Found: 383.0430 (3.1 ppm).

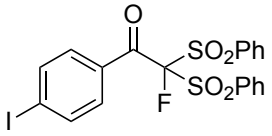
1-(4-(*tert*-Butyl)phenyl)-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2g)



Prepared from 4-*tert* butylbenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (42% water : 58% MeCN) and **2g** was obtained as a white solid (83 mg, 0.176 mmol, 88%).

Melting Point: 131-134°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 4H), 7.72 (t, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9 (d, *J* = 21.0 Hz), 158.7, 135.8, 135.1, 131.8 (d, *J* = 3.8 Hz), 131.5, 130.0 (d, *J* = 6.8 Hz), 129.2, 125.6, 113.4 (d, *J* = 282.7 Hz), 35.4, 31.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.7 (s, 1F). **IR (neat, cm^{-1}) ν :** 2951, 1692, 1600, 1582, 1448, 1407, 1349, 1313, 1240, 1198, 1172, 1155, 1113, 1078, 1034, 1009, 834, 753, 715, 679, 621, 553, 522. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C24H24FO5S2+ 475.1044; Found: 475.1052 (1.7 ppm).

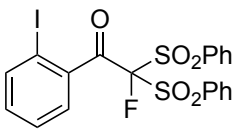
2-Fluoro-1-(4-iodophenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2h)



Prepared from 4-iodobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2h** was obtained as a white solid (86 mg, 0.158 mmol, 79%).

Melting Point: 129-132°C **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 4H), 7.73 (t, *J* = 8.2 Hz, 4H), 7.57 (t, *J* = 7.8 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.2 (d, *J* = 22.5 Hz), 138.0, 136.0, 134.9, 133.6, 131.5, 130.9 (d, *J* = 6.6 Hz), 129.4, 113.2 (d, *J* = 281.1 Hz), 103.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -140.0 (s, 1F). **IR (neat, cm^{-1}) ν :** 3100, 2952, 1678, 1576, 1475, 1392, 1361, 1340, 1314, 1242, 1181, 1158, 1077, 1059, 1023, 1002, 884, 816, 754, 679, 549. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15FIO5S2+ 544.9384; Found: 544.9401 (3.1 ppm).

2-Fluoro-1-(2-iodophenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2i)

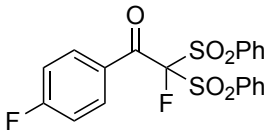


Prepared from 2-iodobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (52% water : 48% MeCN) and **2i** was obtained as a pale yellow solid (100 mg, 0.184 mmol, 92%).

Melting Point: 149-151°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 4H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 6.8 Hz, 2H), 7.68 – 7.55 (m, 5H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 6.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9 (d, *J* = 23.1 Hz), 142.5, 136.7 (d, *J* = 2.9 Hz), 136.1, 134.8, 133.8,

131.9 – 131.7 (m), 131.0 (d, *J* = 10.8 Hz), 129.4, 127.5, 112.3 (d, *J* = 283.5 Hz), 94.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.3 (d, *J* = 4.8 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3283, 3099, 1694, 1574, 1474, 1446, 1424, 1357, 1315, 1265, 1230, 1180, 1158, 1121, 1111, 1077, 1056, 1026, 1005, 937, 870, 813, 757, 651, 541. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15FIO5S2+ 544.9384; Found: 544.9399 (2.8 ppm).

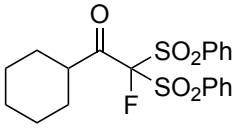
2-Fluoro-1-(4-fluorophenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2j)



Prepared from 4-fluorobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2j** was obtained as a white solid (68 mg, 0.156 mmol, 78%).

Melting Point: 123-126°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 4H), 7.96 (t, *J* = 7.5 Hz, 4H), 7.79 (t, *J* = 7.7 Hz, 4H), 7.26 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0 (d, *J* = 23.6 Hz), 166.6 (d, *J* = 258.8 Hz), 136.0, 135.0, 133.0 (dd, *J* = 9.6, 7.0 Hz), 131.5, 130.7 (t, *J* = 3.3 Hz), 130.3, 129.6, 129.3, 116.0 (d, *J* = 23.1 Hz), 113.3 (d, *J* = 281.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.8 (s, 1F), -139.5 (s, 1F). **IR (neat, cm^{-1}) ν :** 3099, 3071, 1687, 1594, 1506, 1476, 1447, 1409, 1317, 1314, 1245, 1165, 1119, 1076, 1030, 1010, 940, 882, 841, 683, 540. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15F2O5S2+ 437.0323; Found: 437.0330 (1.6 ppm).

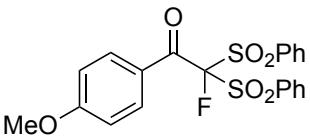
1-Cyclohexyl-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2k)



Prepared from cyclohexoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2k** was obtained as a white solid (64 mg, 0.150 mmol, 75%).

Melting Point: 114-117°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 4H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 4H), 2.69 – 2.46 (m, 1H), 1.71 – 1.63 (m, 2H), 1.60 (s, 1H), 1.50 (d, *J* = 12.0 Hz, 2H), 1.08 (d, *J* = 21.8 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.5 (d, *J* = 22.7 Hz), 135.9, 135.1, 131.5, 129.3, 111.4 (d, *J* = 278.9 Hz), 48.1, 27.9, 25.5, 25.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -147.9 (s, 1F). **IR (neat, cm^{-1}) ν :** 3066, 2963, 2854, 1720, 1582, 1476, 1449, 1351, 1314, 1292,3 1171, 1107, 1077, 997, 897, 847, 758, 682, 609. **HRMS** (TOF-MS ES+) m/z: **[M+Na]+** Calcd for C20H21FNaO5S2+ 447.0707; Found: 447.0715 (1.8 ppm).

2-Fluoro-1-(4-methoxyphenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2l)

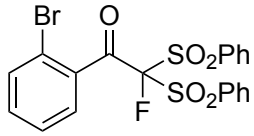


Prepared from *p*-anisoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2l** was obtained as a white solid (63 mg, 0.140 mmol, 70%).

Melting Point: 135-138°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 4H), 7.76 (d, *J* = 5.0 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 183.8 (d, *J* = 23.1 Hz), 164.9, 135.8, 135.2, 132.8, 131.5, 129.2, 127.2, 114.0, 113.5 (d, *J* = 282.3 Hz), 55.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.0 (s, 1F). **IR (neat, cm^{-1}) ν :** 3098, 3007, 1844, 1681, 1592, 1567, 1508, 1448, 1422, 1348, 1310, 1268, 1248, 1171, 1157, 1120, 1106, 1078, 1033, 1018, 929, 886, 834, 751, 678, 595. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C21H18FO6S2+ 449.0523; Found: 449.0533 (2.2 ppm).

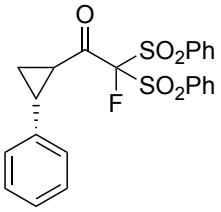
1-(2-Bromophenyl)-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2m)



Prepared from 2-bromobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (48% water : 52% MeCN) and **2m** was obtained as a white solid (84 mg, 0.168 mmol, 84%).

Melting Point: 126-128°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 4H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.65 – 7.53 (m, 5H), 7.40 – 7.30 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.3 (d, *J* = 24.1 Hz), 136.1, 135.0 (d, *J* = 13.9 Hz), 134.3 (d, *J* = 2.9 Hz), 133.7, 132.0 – 131.6 (m), 131.1 (d, *J* = 9.6 Hz), 129.4, 126.8, 121.9, 112.4 (d, *J* = 283.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.8 (d, *J* = 4.8 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3062, 2931, 1690, 1578, 1560, 1464, 1449, 1428, 1356, 1346, 1313, 1282, 1227, 1155, 1078, 1009, 997, 857, 760, 754, 722, 681, 531. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15BrFO5S2+ 496.9523; Found: 496.9538 (3.0 ppm).

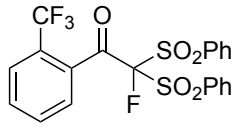
2-Fluoro-1-((1*R*,2*R*)-2-phenylcyclopropyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2n)



Prepared from (1*R*,2*R*)-2-phenylcyclopropane-1-carbonyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (42% water : 58% MeCN) and **2n** was obtained as a white solid (83 mg, 0.182 mmol, 91%).

Melting Point: °C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.73 (q, *J* = 7.7 Hz, 2H), 7.55 (q, *J* = 7.7 Hz, 4H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 6.3 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 3.15 – 3.06 (m, 1H), 2.62 – 2.52 (m, 1H), 1.76 (dt, *J* = 9.2, 4.6 Hz, 1H), 1.64 (td, *J* = 7.6, 4.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.3 (d, *J* = 19.2 Hz), 138.5, 136.0, 135.0 (d, *J* = 8.0 Hz), 131.1, 129.4, 128.8, 127.4, 112.0 (d, *J* = 273.4 Hz), 34.1, 30.4, 22.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.2 (s, 1F). **IR (neat, cm^{-1}) ν :** 3093, 3067, 3004, 1704, 1668, 1605, 1580, 1566, 1494, 1457, 1445, 1400, 1361, 1341, 1311, 1241, 1191, 1177, 1146, 1124, 1076, 1042, 1029, 997, 795, 698, 547. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C23H20FO5S2+ 459.0731; Found: 459.0740 (2.0 ppm).

2-fluoro-2,2-bis(phenylsulfonyl)-1-(2-(trifluoromethyl)phenyl)ethan-1-one (2o)

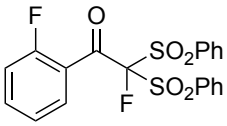


Prepared from 2-(trifluoromethyl)benzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography

(41% water : 59% MeCN) and **2o** was obtained as a white solid (87 mg, 0.178 mmol, 89%).

Melting Point: 138-141°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 4H), 8.00 – 7.93 (m, 1H), 7.78 (q, *J* = 7.0 Hz, 3H), 7.72 – 7.64 (m, 2H), 7.61 (t, *J* = 7.9 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0 (d, *J* = 23.4 Hz), 136.1, 134.8, 132.8, 132.6, 131.8, 131.3, 130.8 (d, *J* = 9.2 Hz), 130.0 (d, *J* = 33.0 Hz), 129.2, 128.0 (d, *J* = 5.4 Hz), 122.8 (d, *J* = 274.3 Hz), 113.0 (d, *J* = 283.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.3 (s, 3F), -138.9 (s, 1F). **IR (neat, cm^{-1}) ν :** 3102, 1696, 1596, 1477, 1449, 1359, 1347, 1306, 1288, 1224, 1147, 1120, 1078, 1039, 1011, 998, 767, 754, 718, 682, 643, 571, 532. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C21H15F4O5S2+ 487.0292; Found: 487.0304 (2.5 ppm).

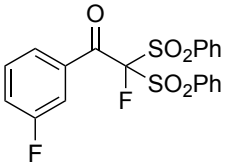
2-Fluoro-1-(2-fluorophenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2p)



Prepared from 2-fluorobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (44% water : 56% MeCN) **2p** was obtained as a white solid (68 mg, 0.156 mmol, 78%).

Melting Point: 134-135°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 4H), 7.55 – 7.43 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 9.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5 (d, *J* = 25.9 Hz), 160.4 (d, *J* = 260.4 Hz), 136.0, 135.2 (d, *J* = 8.8 Hz), 135.0, 131.6, 130.9 (d, *J* = 7.2 Hz), 129.3, 124.0 (d, *J* = 3.8 Hz), 123.4 (d, *J* = 3.1 Hz), 123.3 (d, *J* = 3.1 Hz), 116.6 (d, *J* = 21.4 Hz), 111.9 (d, *J* = 282.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.8 (ddd, *J* = 22.5, 11.2, 6.5 Hz, 1F), -142.1 (d, *J* = 17.6 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3102, 3069, 1700, 1605, 1577, 1482, 1449, 1357, 1348, 1316, 1279, 1240, 1222, 1157, 1122, 1077, 1013, 998, 938, 888, 845, 683, 549. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15F2O5S2+ 437.0323; Found: 437.0331 (1.8 ppm).

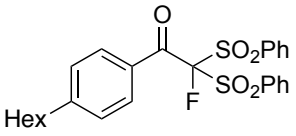
2-Fluoro-1-(3-fluorophenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2q)



Prepared from 3-fluorobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (44% water : 56% MeCN) **2q** was obtained as a white solid (48 mg, 0.110 mmol, 55%).

Melting Point: 137-139°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 4H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.35 (q, *J* = 7.9 Hz, 1H), 7.27 (q, *J* = 9.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 249.0 Hz), 136.1, 134.9, 131.5, 130.3 (d, *J* = 7.4 Hz), 129.4, 125.6, 121.6 (d, *J* = 21.3 Hz), 116.5 (dd, *J* = 23.9, 6.7 Hz), 113.1 (d, *J* = 281.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.6 (td, *J* = 8.7, 5.6 Hz, 1F), -140.4 (s, 1F). **IR (neat, cm^{-1}) ν :** 3097, 3073, 1682, 1580, 1481, 1445, 1357, 1342, 1311, 1262, 1181, 1172, 1151, 1119, 1077, 999, 939, 866, 683, 658. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15F2O5S2+ 437.0323; Found: 437.0335 (2.7 ppm).

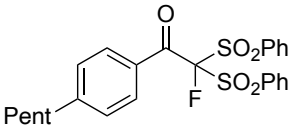
2-Fluoro-1-(4-hexylphenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2r)



Prepared from 4-hexylbenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (30% water : 70% MeCN) and **2r** was obtained as a white solid (83 mg, 0.160 mmol, 80%).

Melting Point: 110-112°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 4 H, 7.14 (d, *J* = 8.2 Hz, 2H), 2.71 – 2.44 (m, 2H), 1.62 – 1.52 (m, 2H), 1.37-1.23 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0 (d, *J* = 20.3 Hz), 150.8, 135.8, 135.1, 132.1 (d, *J* = 3.7 Hz), 131.5, 130.1 (d, *J* = 6.8 Hz), 129.2, 128.6 (d, *J* = 1.0 Hz), 113.3 (d, *J* = 282.6 Hz), 36.2, 31.7, 30.9, 29.0, 22.7, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.6 (s, 1F). **IR (neat, cm^{-1}) ν :** 3060, 2925, 2853, 1677, 1602, 1581, 1563, 1448, 1414, 1355, 1315, 1239, 1157, 1111, 1077, 998, 936, 888, 844, 823, 758, 681, 603, 536. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C26H28FO5S2+ 503.1357; Found: 503.1367 (2.0 ppm).

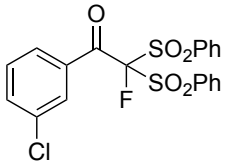
2-Fluoro-1-(4-pentylphenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2s)



Prepared from 4-pentylbenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (37% water : 63% MeCN) and **2s** was obtained as a white solid (73 mg, 0.150 mmol, 75%).

Melting Point: 105-106°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.38 – 1.22 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0 (d, *J* = 19.2 Hz), 150.8, 135.8, 135.2, 132.1, 131.5, 130.1 (d, *J* = 6.9 Hz), 129.2, 128.6, 113.3 (d, *J* = 282.7 Hz), 36.2, 31.5, 30.6, 22.6, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.6 (s, 1F). **IR (neat, cm^{-1}) ν :** 3059, 2920, 2854, 1676, 1601, 1581, 1470, 1448, 1415, 1350, 1315, 1253, 1239, 1155, 1109, 1076, 1033, 998, 936, 840, 757, 681, 655, 631, 535. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C25H26FO5S2+ 489.1200; Found: 489.1209 (1.8 ppm).

2-Fluoro-1-(3-chlorophenyl)-2,2-bis(phenylsulfonyl)ethan-1-one (2t)

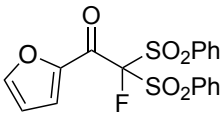


Prepared from 3-chlorobenzoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (40% water : 60% MeCN) and **2t** was obtained as a pale pink solid (36 mg, 0.08 mmol, 40%).

Melting Point: 125-128°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 5H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9 (d, *J* = 22.9 Hz), 136.1, 135.8, 134.9, 134.4, 131.5, 129.9, 127.8 (d, *J* = 6.6 Hz), 113.0 (d, *J* = 280.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -140.4 (s, 1F). **IR (neat, cm^{-1}) ν :** 3097, 2954, 1690, 1579, 1567, 1445, 1414, 1358, 1347, 1313, 1242, 1171, 1154, 1118, 997, 849, 680, 549.

HRMS (TOF-MS ES+) m/z: **[M+H]+** Calcd for C20H15ClFO5S2+ 453.0028; Found: 453.0042 (3.1 ppm).

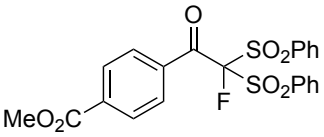
2-Fluoro-1-(furan-2-yl)-2,2-bis(phenylsulfonyl)ethan-1-one (2u)



Prepared from 2-furoyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (60% water : 40% MeCN) and **2u** was obtained as a white solid (61 mg, 0.150 mmol, 75%).

Melting Point: 143-145°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.65 (s, 1H), 7.55 (t, *J* = 7.9 Hz, 4H), 7.44 (s (broad), 1H), 6.63 – 6.42 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2 (d, *J* = 20.2 Hz), 149.8, 149.1 (d, *J* = 3.9 Hz), 136.0, 135.0, 131.4 (d, *J* = 0.9 Hz), 129.3, 125.0 (d, *J* = 12.4 Hz), 113.2 (d, *J* = 2.7 Hz), 111.9 (d, *J* = 277.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -144.8 (s, 1F). **IR (neat, cm^{-1}) ν :** 3153, 3059, 1655, 1580, 1552, 1456, 1390, 1356, 1343, 1313, 1163, 1294, 1077, 997, 915, 884, 797, 753, 711, 592. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C18H14FO6S2+ 409.0210; Found: 409.0221 (2.7 ppm).

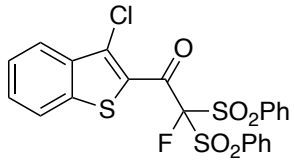
Methyl 4-(2-fluoro-2,2-bis(phenylsulfonyl)acetyl)benzoate (2v)



Prepared from methyl 4-(chlorocarbonyl)benzoate following the general procedure C. The product was purified via reverse phase flash column chromatography (46% water : 54% MeCN) **2v** was obtained as a white solid (75 mg, 0.158 mmol, 79%).

Melting Point: 150-152°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.1, 3.3 Hz, 6H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.57 (t, *J* = 7.9 Hz, 3H), 3.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9 (d, *J* = 23.2 Hz), 165.9, 137.7 (d, *J* = 3.5 Hz), 136.1, 134.9 (d, *J* = 6.8 Hz), 131.5, 129.5, 129.5, 129.4, 113.0 (d, *J* = 280.9 Hz), 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -140.5 (s, 1F). **IR (neat, cm^{-1}) ν :** 3155, 3070, 2950, 1727, 1698, 1654, 1581, 1500, 1435, 1405, 1359, 1348, 1280, 1159, 1111, 1077, 997, 754, 676, 593, 506. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C22H18FO7S2+ 477.0472; Found: 477.0482 (2.1 ppm).

1-(3-chlorobenzo[*b*]thiophen-2-yl)-2-fluoro-2,2-bis(phenylsulfonyl)ethan-1-one (2w)



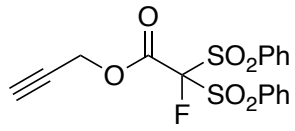
Prepared from 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (46% water : 54% MeCN) and **2w** was obtained as a yellow solid (50 mg, 0.098 mmol, 49%).

Melting Point: decomposed above 150°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 4H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 5H), 7.49 (t, *J*

= 7.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.5 (d, *J* = 22.9 Hz), 140.3 (d, *J* = 8.8 Hz), 136.0, 135.6, 135.0, 132.4, 132.1, 131.5, 129.9, 129.4, 126.2, 124.7, 122.7, 111.4 (d, *J* = 282.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -141.0 (s, 1F). **IR (neat, cm^{-1}) ν :** 3158, 3096, 3065, 2027, 1670, 1593, 1581, 1470, 1448, 1414, 1352, 1251, 1173, 1157, 1021, 998, 884, 864, 682. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C22H15ClFO5S3+ 508.9749; Found: 508.9759 (2.0 ppm).

Compounds 3a to 3h

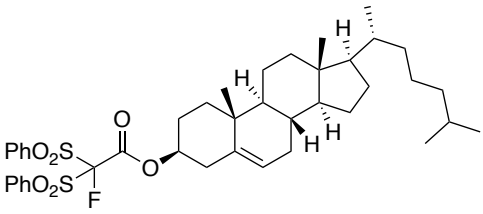
Prop-2-yn-1-yl 2-fluoro-2,2-bis(phenylsulfonyl)acetate (3a)



Prepared from propargyl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (50% water : 50% MeCN) and **2x** was obtained as a yellow oil (70 mg, 0.176 mmol, 88%).

Melting Point: 132-133°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 4H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 4H), 4.81 (d, *J* = 2.2 Hz, 2H), 2.58 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8 (d, *J* = 23.9 Hz), 136.2, 134.5, 131.2 (d, *J* = 1.2 Hz), 129.4, 109.0 (d, *J* = 274.3 Hz), 77.3, 75.3, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.9 (s, 1F). **IR (neat, cm^{-1}) ν :** 3304, 3233, 1768, 1584, 1449, 1364, 1170, 1128, 1080, 682, 649. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C17H14FO6S2+ 397.0210; Found: 397.0223 (3.3 ppm).

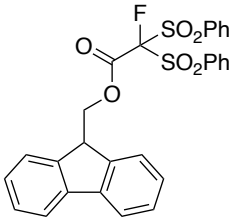
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)2,3,4,7,8,9,10,11,12,13, 14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl-2-fluoro-2,2-bis(phenylsulfonyl) acetate (3b)



Prepared from cholesteryl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (100% MeCN) and **2y** was obtained as a fluffy white solid (129 mg, 0.178 mmol, 89%).

Melting Point: 182-183°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 4H), 7.76 (t, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 4H), 5.36 (d, *J* = 5.3 Hz, 1H), 4.69 (dt, *J* = 11.7, 6.6 Hz, 1H), 2.37 (t, *J* = 11.5 Hz, 1H), 2.19 (dd, *J* = 13.1, 3.0 Hz, 1H), 2.06 – 1.93 (m, 2H), 1.82 (dd, *J* = 32.5, 14.4 Hz, 3H), 1.73 – 1.63 (m, 1H), 1.63 – 1.42 (m, 7H), 1.30 (dd, *J* = 28.4, 8.7 Hz, 5H), 1.20 – 1.03 (m, 7H), 1.01 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 4H), 0.89 – 0.80 (m, 6H), 0.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6 (d, *J* = 23.0 Hz), 138.8, 135.9, 135.0, 131.2, 129.3, 123.7, 108.9 (d, *J* = 274.8 Hz), 79.5, 56.8, 56.3, 50.1, 42.5, 39.8 (d, *J* = 16.6 Hz), 37.5, 36.9, 36.7, 36.3, 35.9, 32.0 (d, *J* = 8.9 Hz), 28.4, 28.2, 27.3, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.3 (s, 1F). **IR (neat, cm^{-1}) ν :** 3105, 2960, 2935, 2911, 2882, 2863, 2849, 1758, 1496, 1448, 1359, 1253, 1155, 1119, 1027, 991, 963, 819, 750, 682, 555. **HRMS** (TOF-MS ES+) m/z: **[M+Na]+** Calcd for C41H55FNaO6S2+ 749.3316; Found: 749.3329 (1.7 ppm).

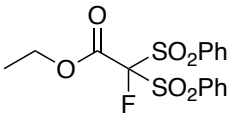
(9*H*-fluoren-9-yl)methyl 2-fluoro-2,2-bis(phenylsulfonyl)acetate (3c)



Prepared from methyl 9-fluorenylmethoxycarbonyl chloride following the general procedure C. The product was purified via reverse phase flash column chromatography (46% water : 54% MeCN) and **2z** was obtained as a white solid (79 mg, 0.148 mmol, 74%).

Melting Point: 169-173°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 4H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.74 – 7.66 (m, 4H), 7.56 (t, *J* = 7.7 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 4.37 (d, *J* = 7.6 Hz, 2H), 4.20 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6 (d, *J* = 23.4 Hz), 142.8, 141.4, 136.1, 134.8, 131.2 (d, *J* = 1.1 Hz), 129.4, 128.3, 127.6, 120.2, 109.2 (d, *J* = 274.1 Hz), 70.9, 46.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.3 (s, 1F). **IR (neat, cm^{-1}) ν :** 3097, 1747, 1581, 1449, 1363, 1349, 1314, 1259, 1161, 1117, 1077, 1002, 949, 935, 883, 848, 754, 562. **HRMS** (TOF-MS ES+) m/z: **[M+Na]+** Calcd for C28H21FNaO6S2+ 559.0656; Found: 559.0668 (2.1 ppm).

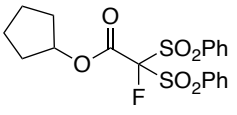
Ethyl-2-fluoro-2,2-bis(phenylsulfonyl)acetate (3d)



Prepared from ethyl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (50% water : 50% MeCN) and **2aa** was obtained as a white solid (69 mg, 0.180 mmol, 90%).

Melting Point: 85°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 4H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 4H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2 (d, *J* = 23.3 Hz), 134.8, 131.3, 131.0, 129.9, 128.8, 109.0 (d, *J* = 273.8 Hz), 65.0, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.6 (s, 1F). **IR (neat, cm^{-1}) ν :** 2355, 2021, 1763, 1582,1450, 1360, 1347, 1252, 1154, 1118, 998, 970, 899, 756, 718, 615, 554. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C16H16FO6S2+ 387.0367; Found: 387.0378 (2.8 ppm).

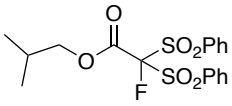
Cyclopentyl-2-fluoro-2,2-bis(phenylsulfonyl)acetate (3e)



Prepared from cyclopentyl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (45% water : 55% MeCN) and **2ab** was obtained as a colorless oil (66 mg, 0.156 mmol, 78%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 4H), 7.75 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 4H), 5.23 (p, *J* = 2.6 Hz, 1H), 1.86 – 1.66 (m, 6H), 1.66 – 1.53 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8 (d, *J* = 23.2 Hz), 135.9, 135.0, 131.1 (d, *J* = 1.3 Hz), 129.3, 108.9 (d, *J* = 273.9 Hz), 82.9, 32.5, 23.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.5 (s, 1F). **IR (neat, cm^{-1}) ν :** 2975, 2362, 1757, 1449, 1361, 1267, 1161, 1128, 1079. **HRMS** (TOF-MS ES+) m/z: **[M+Na]+** Calcd for C19H19FNaO6S2+ 449.0499; Found: 449.0510 (2.4 ppm).

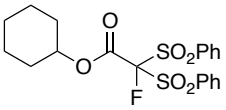
Isobutyl-2-fluoro-2,2-bis(phenylsulfonyl)acetate (3f)



Prepared from isobutyl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (45% water : 55% MeCN) and **2ab** was obtained as a colorless oil (61 mg, 0.146 mmol, 73%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 4H), 7.75 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 4H), 3.98 (d, *J* = 6.5 Hz, 2H), 1.98 (ds, *J* = 13.3, 7.1 Hz, 1H), 0.94 (d, *J* = 6.7 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3 (d, *J* = 23.3 Hz), 136.0, 134.8, 131.1 (d, *J* = 1.2 Hz), 129.3, 109.1 (d, *J* = 273.8 Hz), 74.6, 27.7, 18.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.6 (s, 1F). **IR (neat, cm^{-1}) ν :** 2961, 1760, 1449, 1362, 1339, 1314, 1160, 1128, 1078. **HRMS** (TOF-MS ES+) m/z: **[M+Na]+** Calcd for C18H19FNaO6S2+ 437.0499; Found: 437.0513 (3.2 ppm).

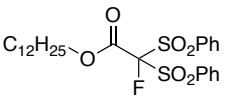
Cyclohexyl-2-fluoro-2,2-bis(phenylsulfonyl)acetate (3g)



Prepared from cyclohexyl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (45% water : 55% MeCN) and **2ab** was obtained as a white solid (68 mg, 0.154 mmol, 77%).

Melting Point: 107-108°C.**^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 4H), 4.92 (t, *J* = 8.2 Hz, 1H), 1.89 – 1.65 (m, 4H), 1.62 – 1.43 (m, 3H), 1.41 – 1.30 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6 (d, *J* = 23.1 Hz), 135.9, 134.9, 131.2, 129.3, 108.9 (d, *J* = 274.2 Hz), 78.2, 31.0, 25.2, 23.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.2 (s, 1F). **IR (neat, cm^{-1}) ν :** 2967, 2849, 1716, 1581, 1472, 1443, 1342, 1312, 1290,3 1164, 1107, 1070. **HRMS** (TOF-MS ES+) m/z: **[M+Na]+** Calcd for C20H21FNaO6S2+ 463.0656; Found: 463.0669 (2.8 ppm).

Dodecyl 2-fluoro-2,2-bis(phenylsulfonyl)acetate (3h)

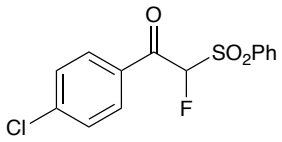


Prepared from lauryl chloroformate following the general procedure C. The product was purified via reverse phase flash column chromatography (6% water : 94% MeCN) and **2ab** was obtained as a colorless oil (53 mg, 0.100 mmol, 50%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 1H), 1.62 (p, *J* = 7.1 Hz, 1H), 1.26 (s, 3H), 0.88 (t, *J* = 6.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3 (d, *J* = 23.3 Hz), 136.0, 134.8, 131.2 (d, *J* = 0.9 Hz), 129.3, 109.0 (d, *J* = 273.9 Hz), 69.0, 32.0, 29.8, 29.7, 29.5, 29.5, 29.2, 28.3, 25.6, 22.8, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.6 (s, 1F). **IR (neat, cm^{-1}) ν :** 2968, 1751, 1440, 1345, 1335, 1314, 1152, 1124, 1073, 1069. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C26H36FO6S2+ 527.1932; Found: 527.1939 (1.3 ppm).

Compounds 4a-4f

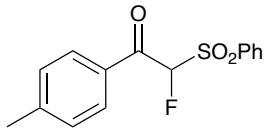
1-(4-Chlorophenyl)-2-fluoro-2-(phenylsulfonyl)ethan-1-one (4a)



Prepared following the general procedure D-1. The product was purified via flash column chromatography (hexanes:DCM) **4a** was obtained as a white solid (37 mg, 0.120 mmol, 60%).

Melting Point: 139-140°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 6.25 (d, *J* = 48.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.6 (d, *J* = 18.1 Hz), 142.0, 135.6, 134.7, 132.3, 131.4 (d, *J* = 3.2 Hz), 130.0, 129.6, 129.4, 100.8 (d, *J* = 233.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -179.4 (d, *J* = 48.1 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3107, 2974, 1690, 1590, 1569, 1491, 1445, 1327, 1312, 1247, 1157, 1111, 1015. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C14H11ClFO3S+ 313.0096; Found: 313.0104 (2.6 ppm).

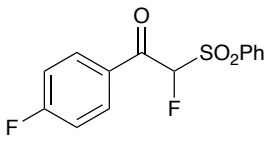
2-Fluoro-2-(phenylsulfonyl)-1-(*p*-tolyl)ethan-1-one (4b)



Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4b** was obtained as a white solid (42 mg, 0.144 mmol, 72%).

Melting Point: 141°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.33 (d, *J* = 48.0 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0 (d, *J* = 17.5 Hz), 146.6, 135.4, 134.8, 131.7, 130.0, 129.7, 129.5, 100.3 (d, *J* = 231.7 Hz), 22.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -180.2 (d, *J* = 48.0 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3095, 3064, 2984, 1670, 1604, 1584, 1569, 1452, 1320, 1254, 1150, 1099. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C15H14FO3S+ 293.0642; Found: 293.0652 (3.4 ppm).

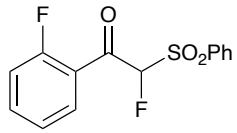
2-Fluoro-1-(4-fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (4c)



Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4c** was obtained as a white solid (487mg, 0.160 mmol, 80%).

Melting Point: 131-134°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 8.5 Hz, 2H), 6.25 (d, *J* = 48.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1 (d, *J* = 18.1 Hz), 167.0 (d, *J* = 259.0 Hz), 135.5, 134.8, 133.0 (dd, *J* = 9.9, 3.2 Hz), 130.5, 130.0, 129.6, 116.4 (d, *J* = 22.2 Hz), 100.8 (d, *J* = 233.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.9 – -119.2 (m, 1F), -179.1 (d, *J* = 48.1 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3097, 3068, 2981, 1687, 1596, 1583, 1415, 1321, 1237, 1167, 1102, 1076. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C14H11F2O3S+ 297.0391; Found: 297.0400 (3.0 ppm).

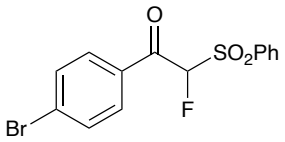
2-Fluoro-1-(2-fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (4d)



Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4d** was obtained as a white solid (44 mg, 0.150 mmol, 75%).

Melting Point: 134-135°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 3H), 7.77 – 7.64 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 16.8 Hz, 1H), 6.58 (d, *J* = 47.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6 (d, *J* = 17.9 Hz), 162.3 (d, *J* = 265.9 Hz), 136.5, 134.8, 131.7, 130.6, 129.8 (d, *J* = 91.9 Hz), 129.0, 124.7, 123.3, 117.0 (d, *J* = 189.0 Hz), 105.9 – 97.3 (m). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.5 – -116.5 (m, 1F), -181.7 (dd, *J* = 47.7, 10.7 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3102, 2982, 1607, 1595, 1509, 1454, 1415, 1321, 1253, 1237, 1180, 1101. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C14H11F2O3S+ 297.0391; Found: 297.0391 (2.4 ppm).

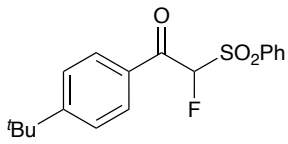
1-(4-Bromophenyl)-2-fluoro-2-(phenylsulfonyl)ethan-1-one (4e)



Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4e** was obtained as a white solid (50 mg, 0.140 mmol, 70%).

Melting Point: 150-151°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 8.01 – 7.84 (m, 4H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 6.24 (d, *J* = 48.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9 (d, *J* = 18.1 Hz), 135.6, 134.7, 132.7, 131.3 (d, *J* = 3.1 Hz), 131.0, 130.0, 129.6, 100.7 (d, *J* = 233.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -179.5 (d, *J* = 48.1 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3103, 3069, 2973, 1692, 1584, 1564, 1489, 1444, 1400, 1327, 1310, 1248, 1182, 1157. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C14H11BrFO3S+ 356.9591; Found: 356.9598 (2.0 ppm).

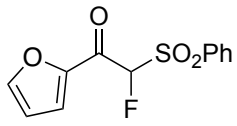
1-(4-(*tert*-Butyl)phenyl)-2-fluoro-2-(phenylsulfonyl)ethan-1-one (4f)



Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4f** was obtained as a white solid (55 mg, 0.166 mmol, 83%).

Melting Point: 134-137°C. **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 6.33 (d, *J* = 48.0 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9 (d, *J* = 17.4 Hz), 159.4, 135.4, 134.8, 131.5, 130.1, 130.0 (d, *J* = 2.6 Hz), 129.5, 126.1, 100.3 (d, *J* = 231.9 Hz), 35.6, 31.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -180.2 (d, *J* = 48.0 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2972, 2869, 1684, 1600, 1584, 1444, 1410, 1329, 1253, 1158, 1101. **HRMS** (TOF-MS ES+) m/z: **[M+H]+** Calcd for C18H20FO3S+ 335.1112; Found: 335.1123 (3.3 ppm).

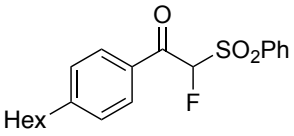
2-Fluoro-1-(furan-2-yl)-2-(phenylsulfonyl)ethan-1-one (4g)



Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4g** was obtained as a white solid (42 mg, 0.156 mmol, 78%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.75 (s, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.46 (s, 1H), 6.64 (d, *J* = 2.1 Hz, 1H), 6.13 (d, *J* = 47.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (d, *J* = 19.8 Hz), 150.2, 149.2, 135.5, 134.6, 130.1, 129.5, 122.7, 113.4, 100.1 (d, *J* = 232.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -182.8 (d, *J* = 47.7 Hz, 1F).

2-Fluoro-1-(4-hexylphenyl)-2-(phenylsulfonyl)ethan-1-one (4h)

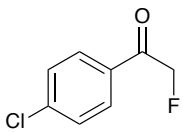


Prepared following the general procedure D-1. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **4h** was obtained as a white solid (52 mg, 0.144 mmol, 72%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.74 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 48.0 Hz, 1H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.64 (d, *J* = 7.1 Hz, 2H), 1.32 (s, 6H), 0.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0 (d, *J* = 17.6 Hz), 151.5, 135.3, 134.9, 131.9, 130.1, 130.1, 129.5, 129.1, 100.4 (d, *J* = 231.7 Hz), 36.4, 31.8, 31.0, 29.1, 22.7, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -182.1 (d, *J* = 46.7 Hz, 1F). **IR (neat, cm^{-1}) ν :** 3058, 2919, 2850, 1677, 1600, 1554, 1440, 1315, 1154, 1101, 1077.

Compounds 5a-5g

1-(4-Chlorophenyl)-2-fluoroethan-1-one (5a)

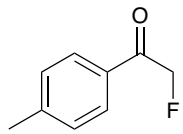


Prepared following the general procedure D-2. The product was purified via flash column chromatography (hexanes:DCM) **5a** was obtained as a colorless oil (25 mg, 0.146 mmol, 73%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 5.48 (d, *J* = 46.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.6 (d, *J* = 16.1 Hz), 140.9, 132.2, 129.6 (d, *J* = 3.1 Hz), 129.5, 83.8 (d, *J* = 183.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -230.1 (t, *J* = 46.9 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2364, 2154, 1708, 1592, 1402, 1284, 1229, 1093

The structural data of the known compound is in conformity with the literature results.[5]

2-Fluoro-1-(*p*-tolyl)ethan-1-one (5b)

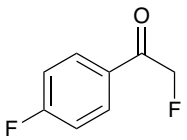


Prepared following the general procedure D-2. The product was purified via flash column chromatography (hexanes:DCM **5b** was obtained as a colorless oil (20 mg, 0.130 mmol, 65%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 5.46 (d, *J* = 47.0 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.2 (d, *J* = 15.5 Hz), 145.3, 131.4, 129.7, 128.1 (d, *J* = 2.6 Hz), 83.6 (d, *J* = 182.3 Hz), 21.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -231.2 (t, *J* = 47.0 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2360, 2154, 1706, 1654, 1608, 1324, 1184, 1096.

The structural data of the known compound is in conformity with the literature results.[5]

2-Fluoro-1-(4-fluorophenyl)ethan-1-one (5c)

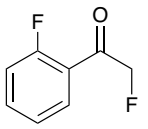


Prepared following the general procedure D-2. The product was purified via flash column chromatography (hexanes:DCM) **5c** was obtained as a colorless oil (22 mg, 0.140 mmol, 70%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 5.7 Hz, 1H), 7.18 (t, *J* = 8.5 Hz, 1H), 5.48 (d, *J* = 46.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.3 (ddd, *J* = 13.7, 8.3, 5.4 Hz, 1F), -229.8 (t, *J* = 47.0 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2951, 2353, 2161, 1707, 1682, 1239, 1105.

The structural data of the known compound is in conformity with the literature results.[6]

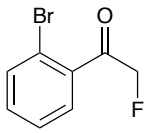
2-Fluoro-1-(2-fluorophenyl)ethan-1-one (5d)



Prepared following the general procedure D-2. The product was purified via flash column chromatography (hexanes:DCM) **5d** was obtained as a colorless oil (22 mg, 0.142 mmol, 71%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 8.04 (t, *J* = 6.9 Hz, 1H), 7.61 (q, *J* = 6.1 Hz, 1H), 7.30 (dd, *J* = 16.9, 9.4 Hz, 1H), 7.22 – 7.03 (m, 1H), 5.44 (dd, *J* = 47.0, 3.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.5 (dd, *J* = 15.6, 5.0 Hz), 162.5 (d, *J* = 253.7 Hz), 136.0 (d, *J* = 9.0 Hz), 130.8, 125.2 (d, *J* = 3.0 Hz), 121.8, 116.7 (d, *J* = 23.4 Hz), 94.7 – 81.3 (m). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.9 – -109.1 (m, 1F), -227.8 (td, *J* = 47.0, 11.0 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2362, 2167, 1768, 1704, 1610, 1453, 1279, 1090.
The structural data of the known compound is in conformity with the literature results.[7]

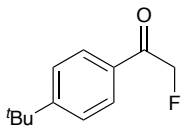
1-(2-Bromophenyl)-2-fluoroethan-1-one (5e)



Prepared following the general procedure D-2. The product was purified via flash column chromatography (hexanes:DCM) **5e** was obtained as a colorless oil (30 mg, 0.136 mmol, 68%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 1H), 7.48 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.32 (m, 1H), 5.37 (d, *J* = 47.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.0 (d, *J* = 18.8 Hz), 137.7, 134.0, 133.0, 129.7 (d, *J* = 2.0 Hz), 127.7, 119.6, 84.3 (d, *J* = 186.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -225.0 (t, *J* = 47.2 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2375, 2153, 1698, 1651, 1590, 1558, 1466, 1286, 1221.
The structural data of the known compound is in conformity with the literature results.[8]

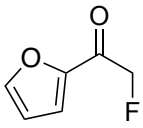
1-(4-(*tert*-Butyl)phenyl)-2-fluoroethan-1-one (5f)



Prepared following the general procedure D-2. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **5f** was obtained as a colorless oil (30 mg, 0.156 mmol, 78%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.51 (d, *J* = 47.0 Hz, 2H), 1.26 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -231.2 (t, *J* = 47.0 Hz, 1F). **IR (neat, cm^{-1}) ν :** 2364, 2015, 1737, 1606, 1368, 1249, 1221.
The structural data of the known compound is in conformity with the literature results.[9]

2-Fluoro-1-(furan-2-yl)ethan-1-one (5g)



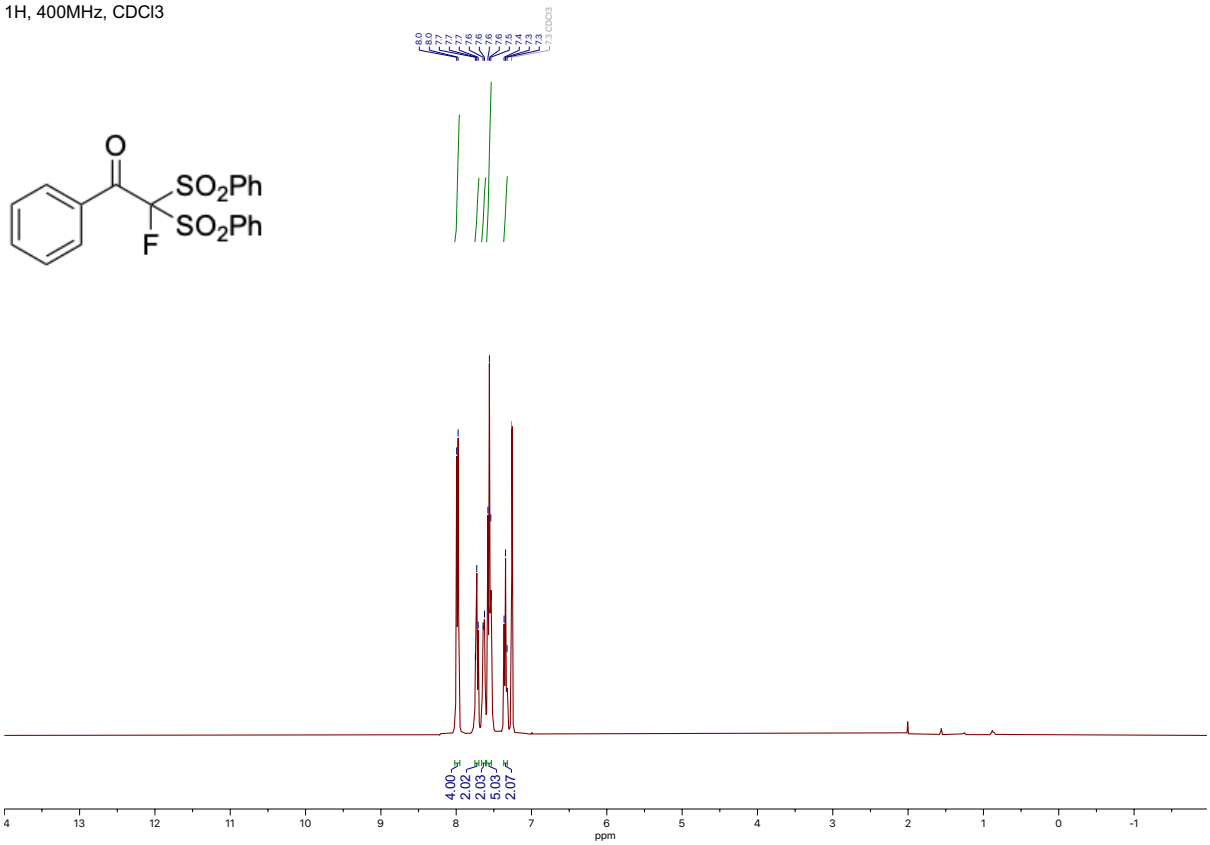
Prepared following the general procedure D-2. The product was purified via reverse phase flash column chromatography (hexanes:DCM) **5g** was obtained as a colorless oil (18 mg, 0.140 mmol, 70%).

^{1}H NMR (399 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.38 (s, 1H), 6.60 (s, 1H), 5.33 (d, *J* = 47.0 Hz, 1H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -232.7 (t, *J* = 45.4 Hz, 1F).

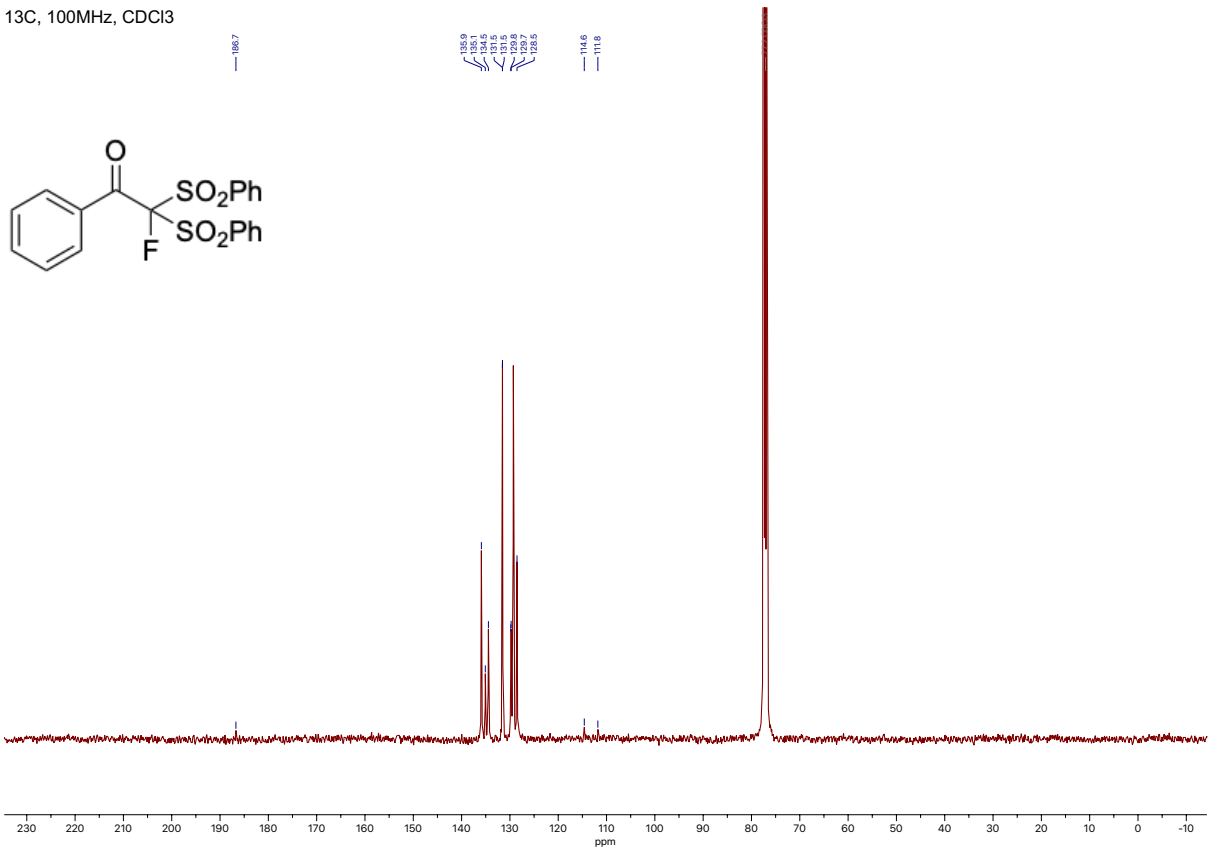
The structural data of the known compound is in conformity with the literature results.[10]

NMR Spectra of Compounds

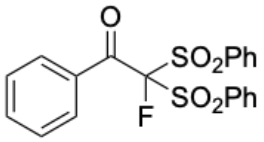
1H, 400MHz, CDCl3



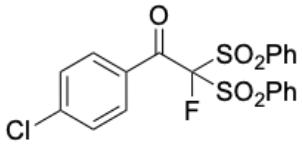
13C, 100MHz, CDCl3



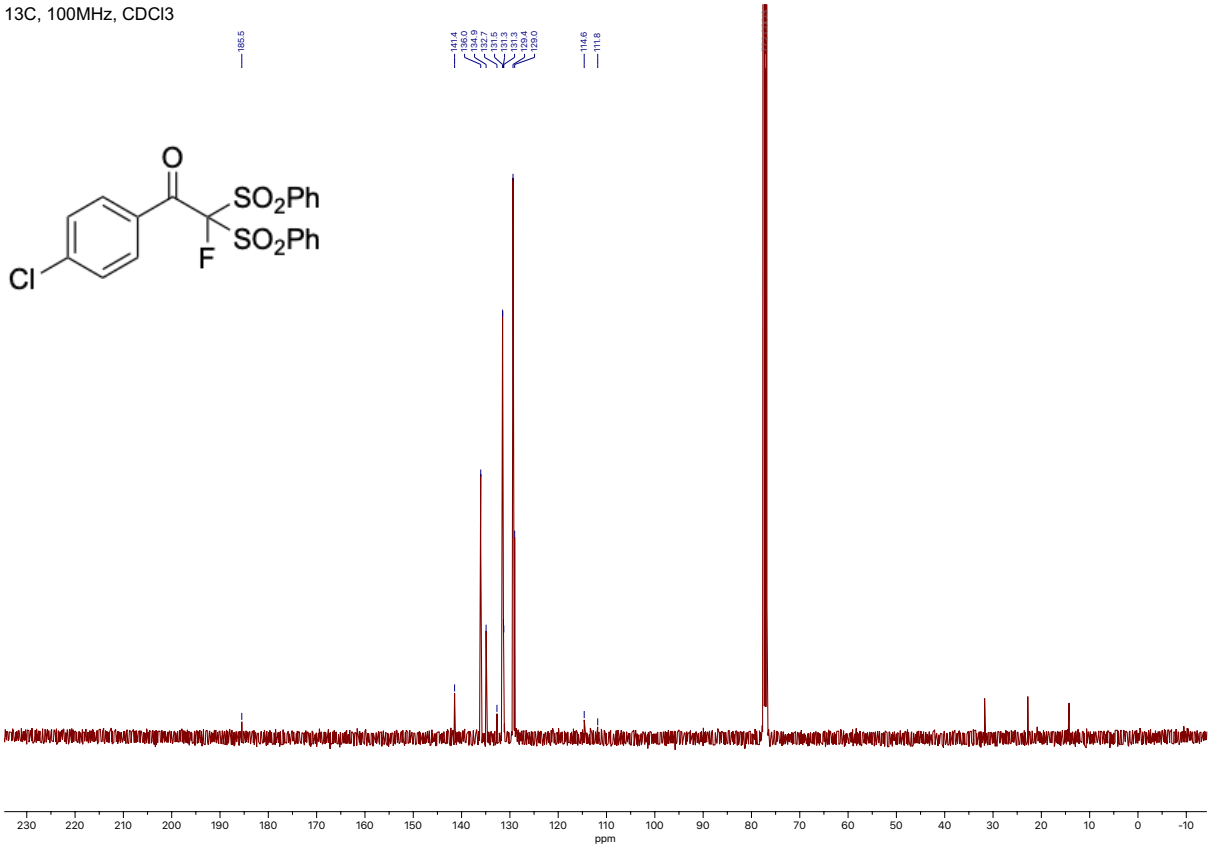
19F, 376MHz, CDCl3



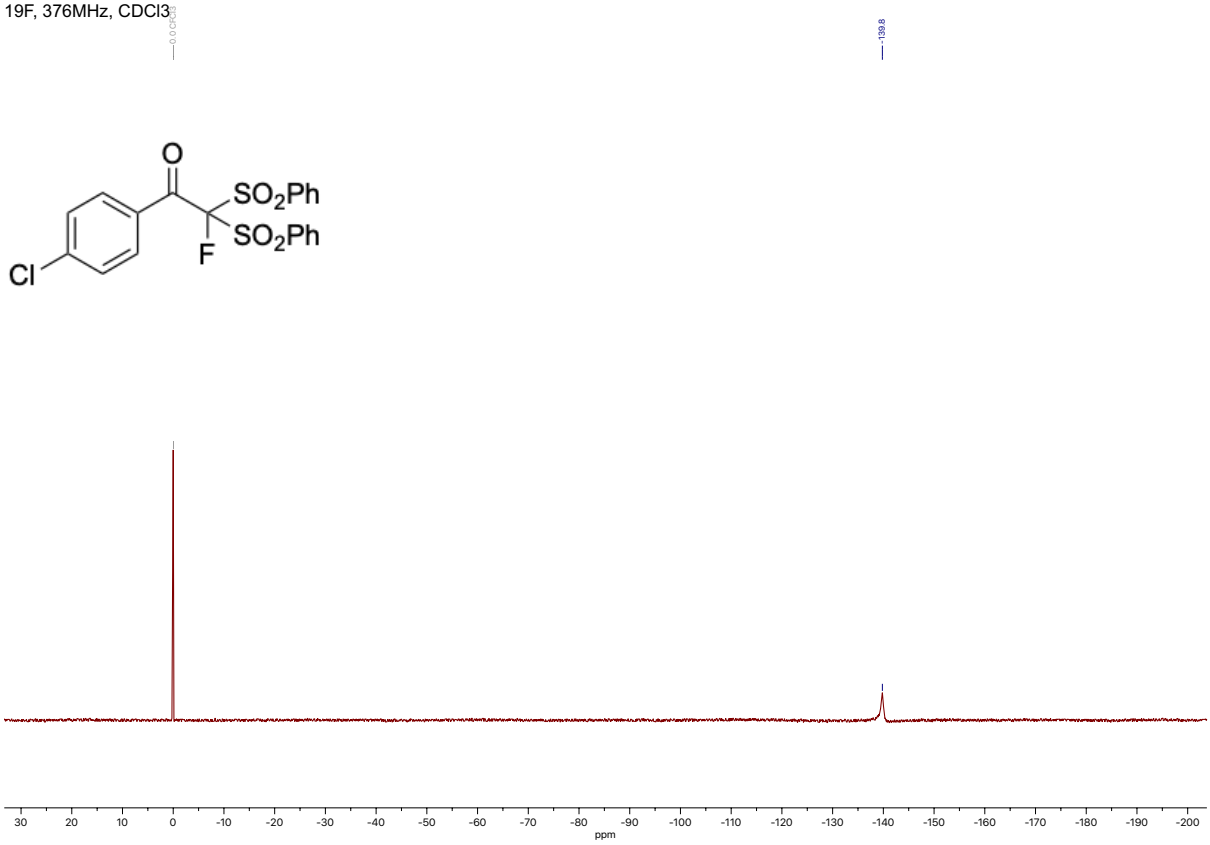
1H, 400MHz, CDCl3



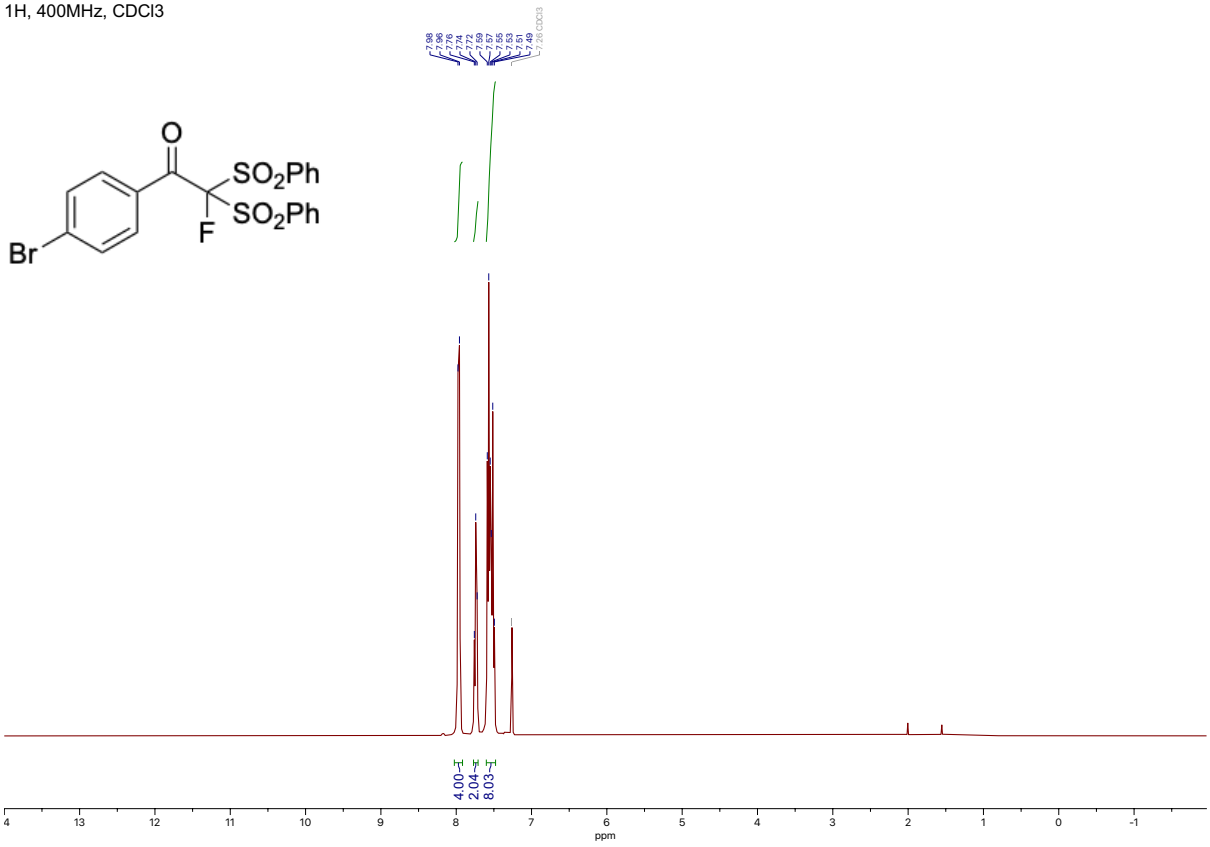
13C, 100MHz, CDCl3



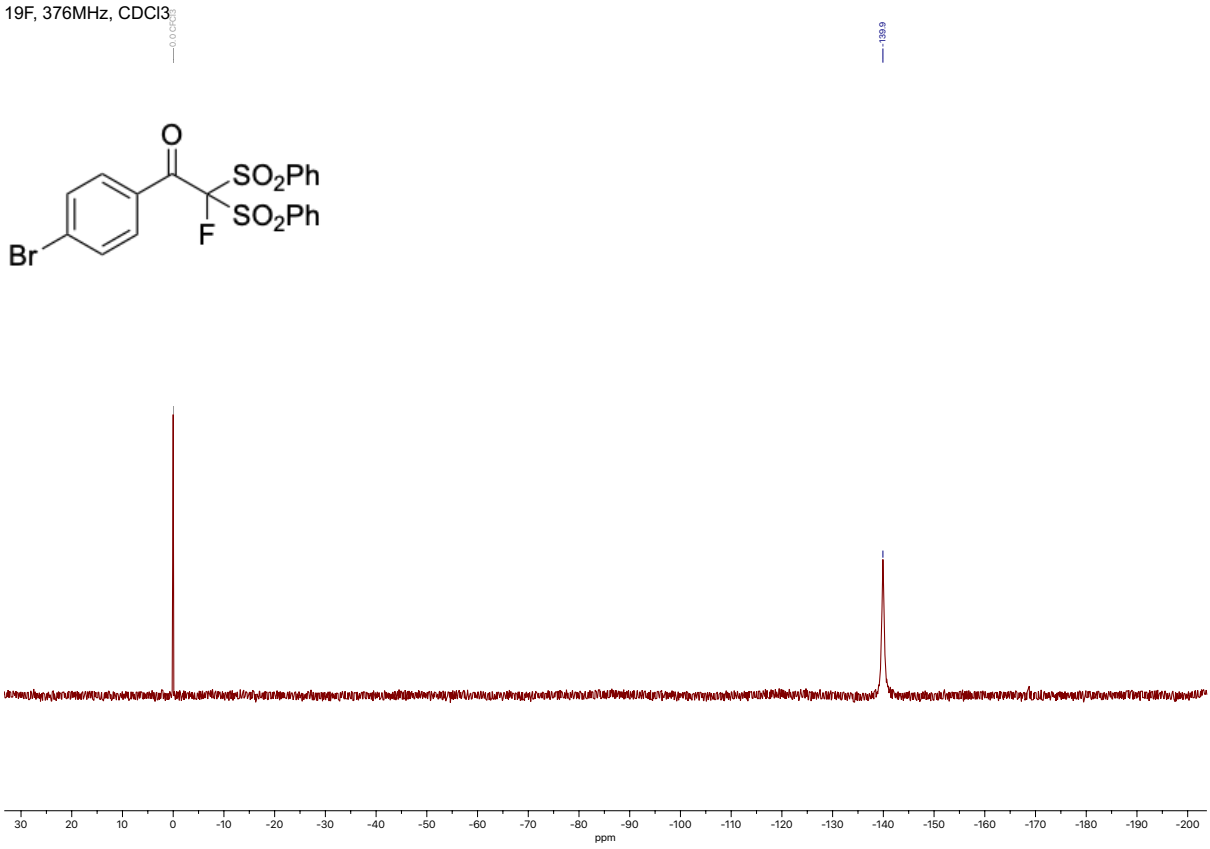
19F, 376MHz, CDCl3



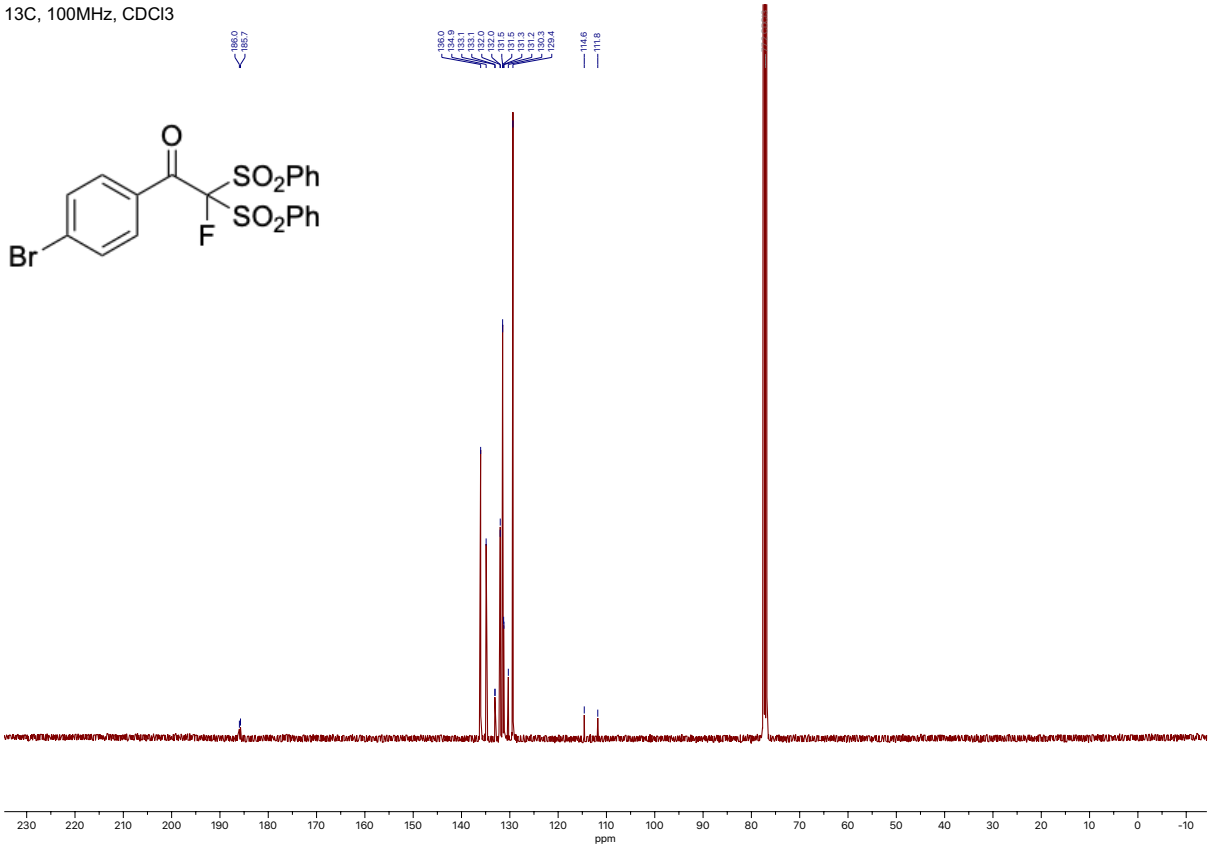
1H, 400MHz, CDCl3



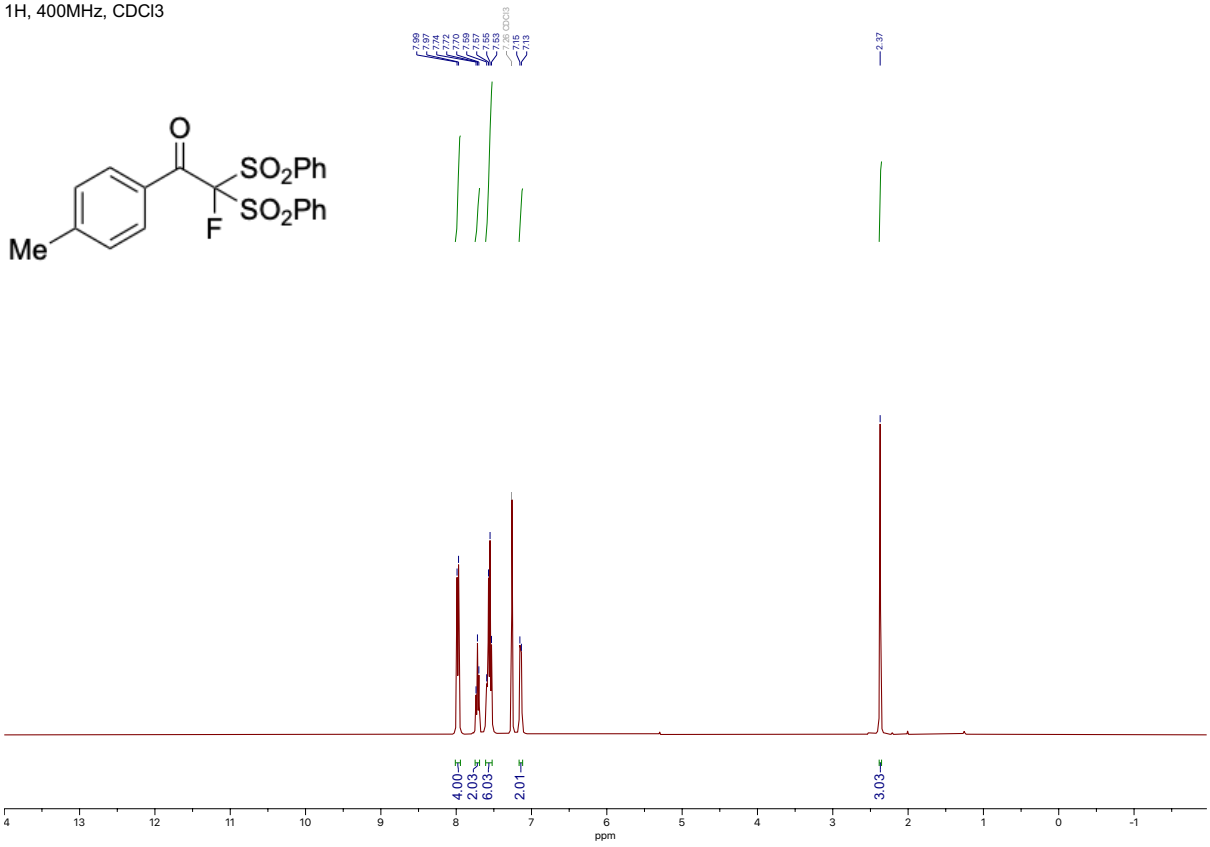
19F, 376MHz, CDCl3



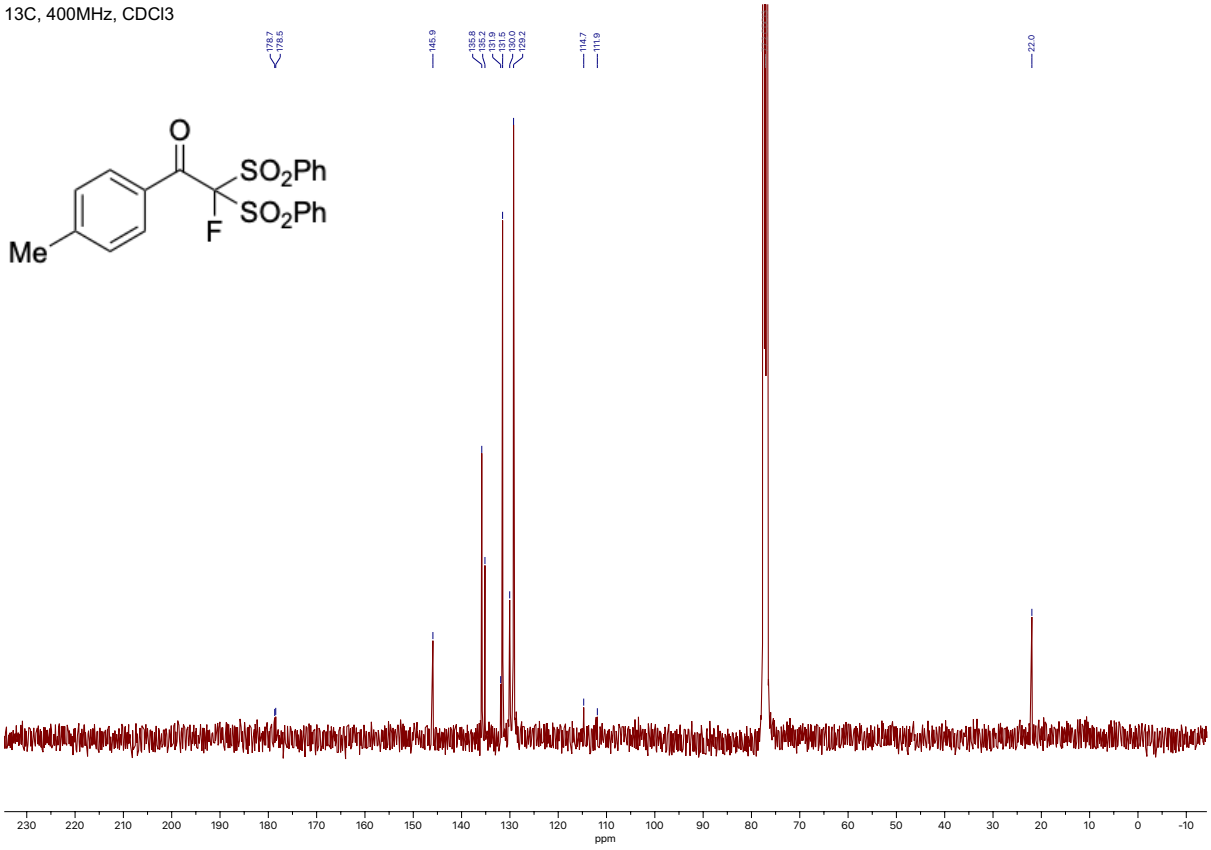
13C, 100MHz, CDCl3



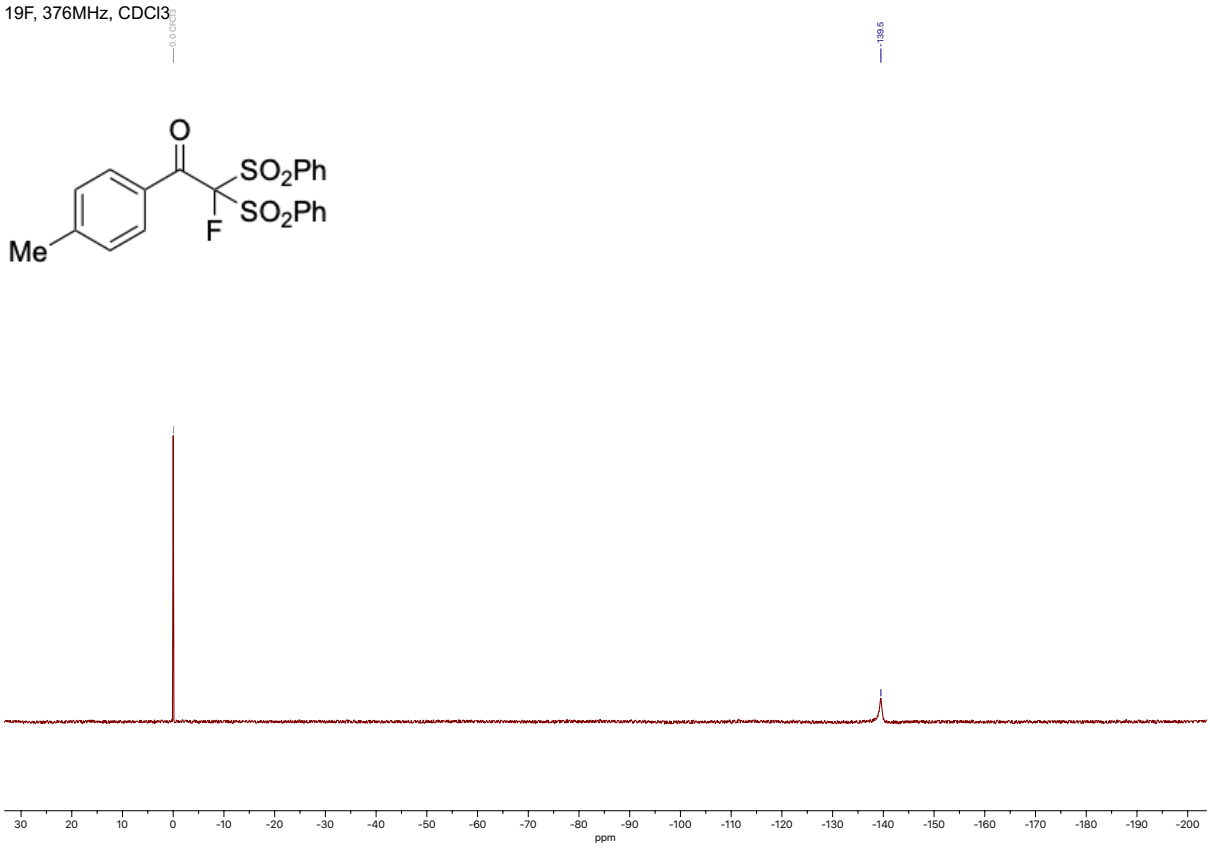
1H, 400MHz, CDCl3



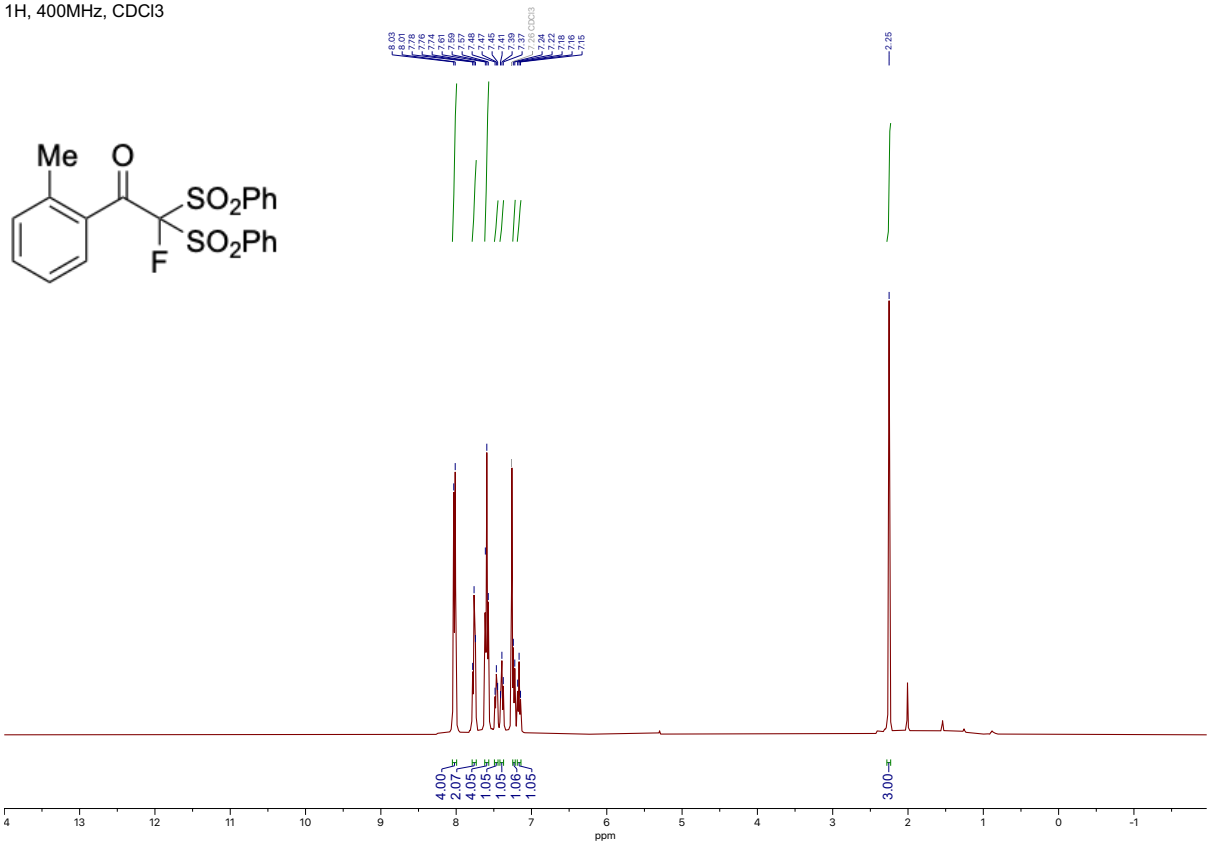
13C, 400MHz, CDCl3



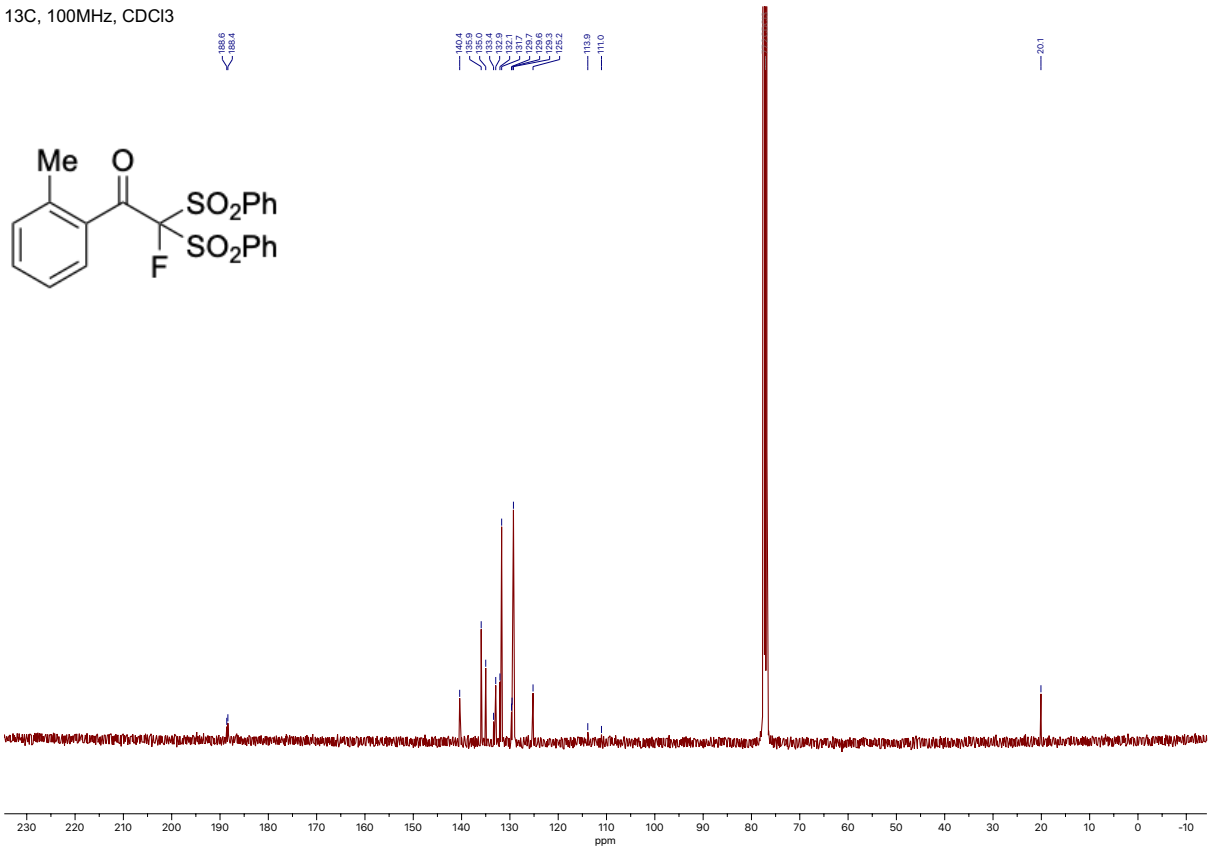
19F, 376MHz, CDCl3



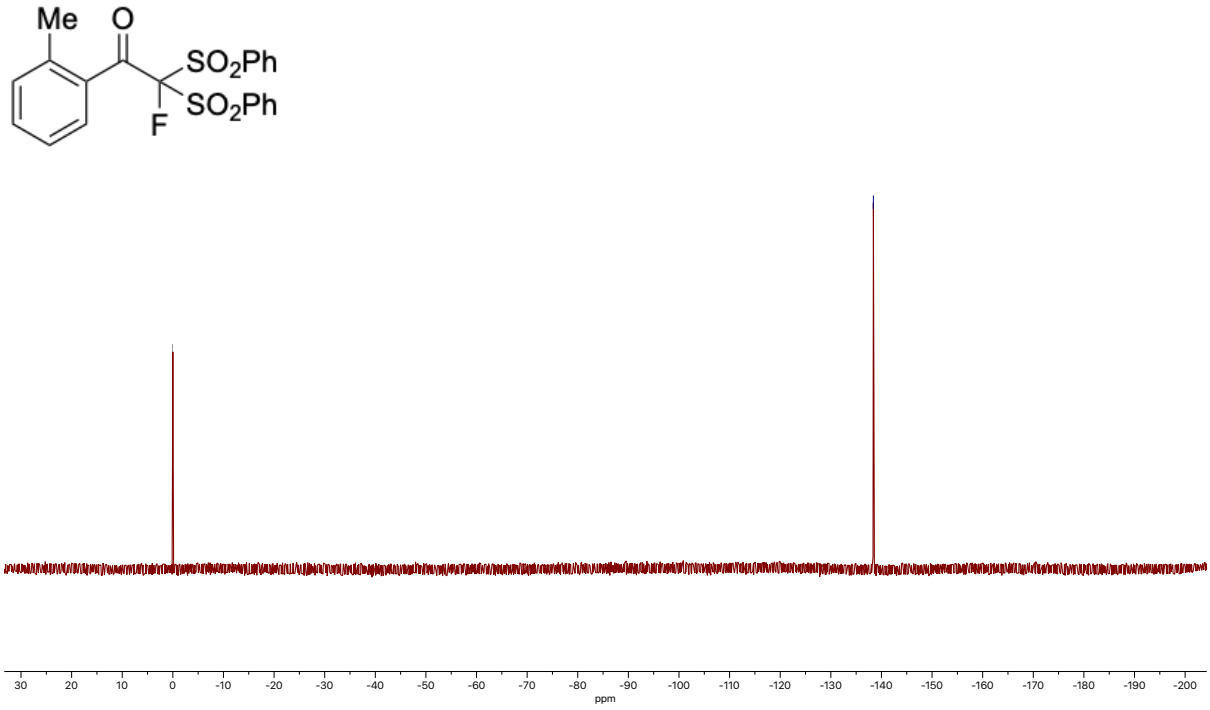
1H, 400MHz, CDCl3



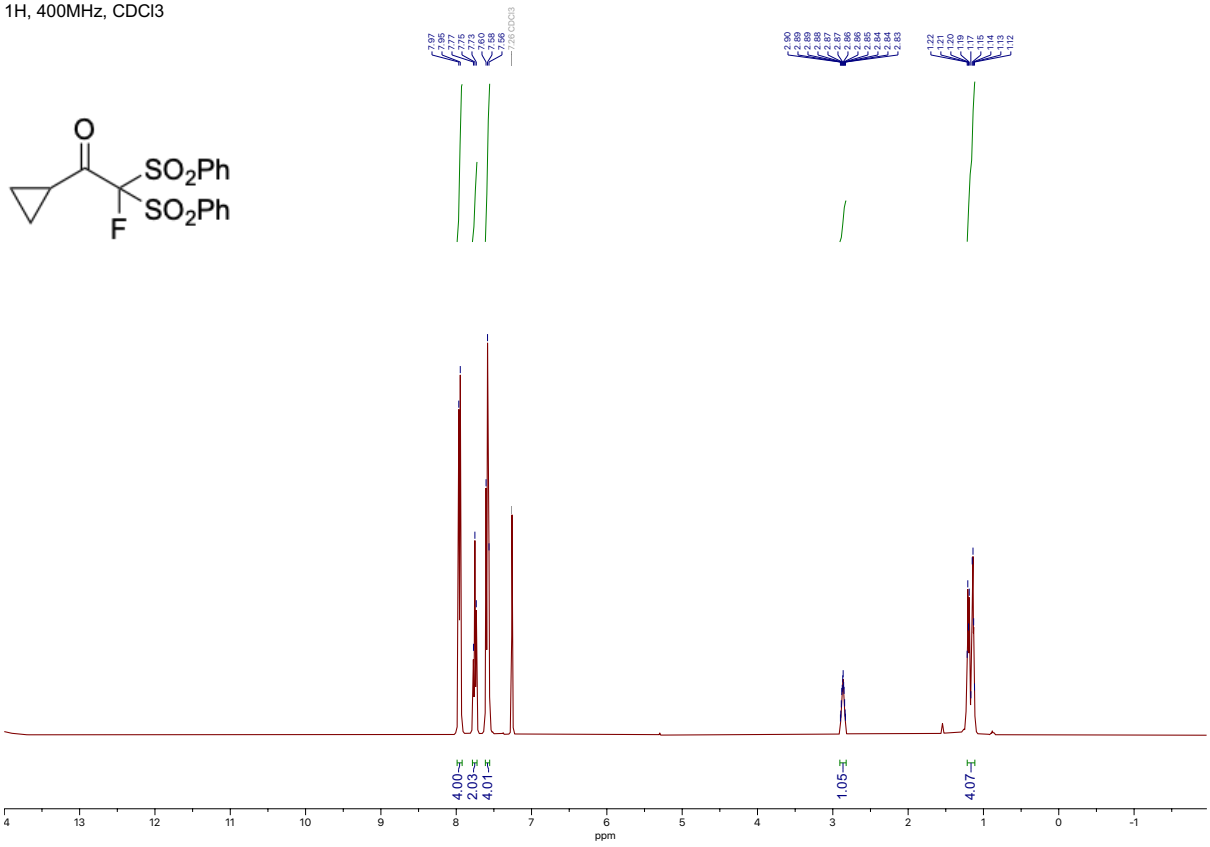
13C, 100MHz, CDCl3



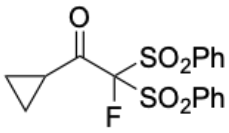
19F, 376MHz, CDCl3



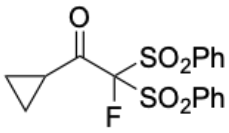
1H, 400MHz, CDCl3



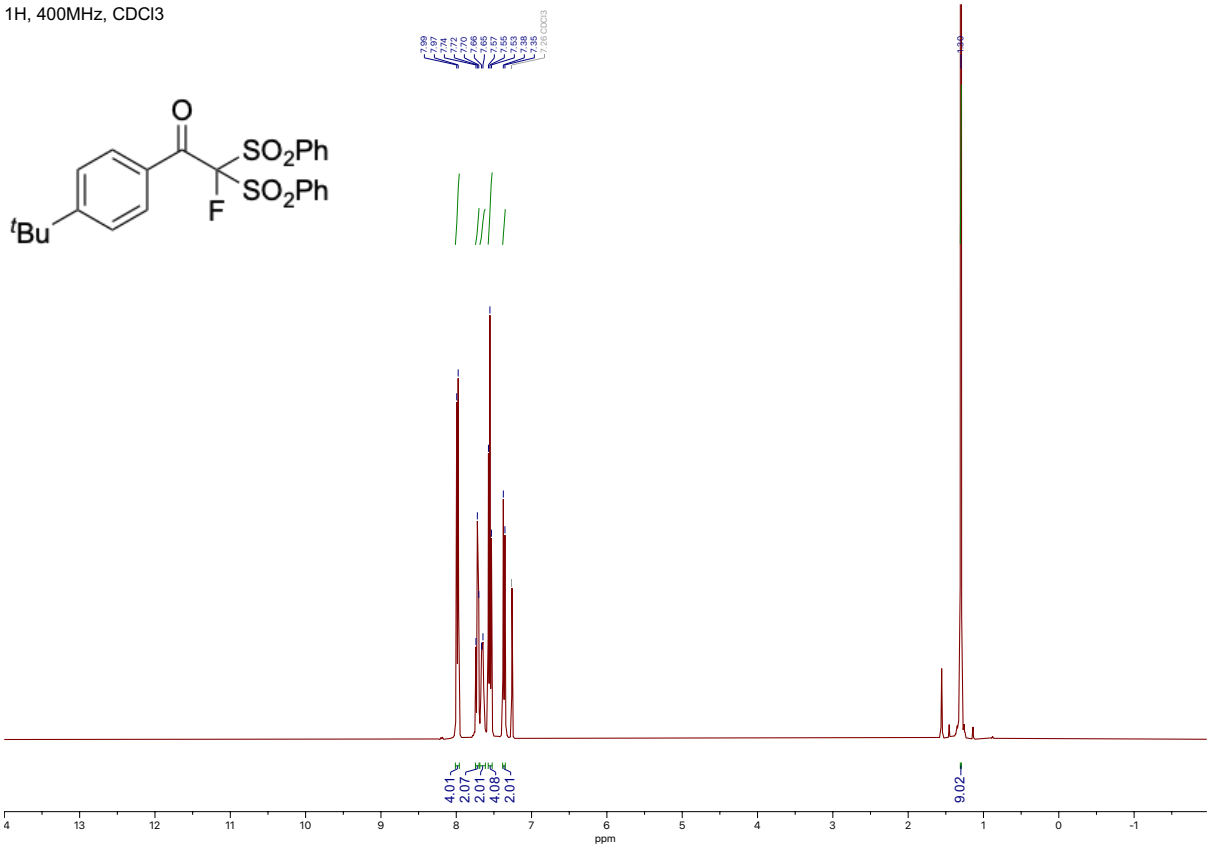
19F, 376MHz, CDCl3



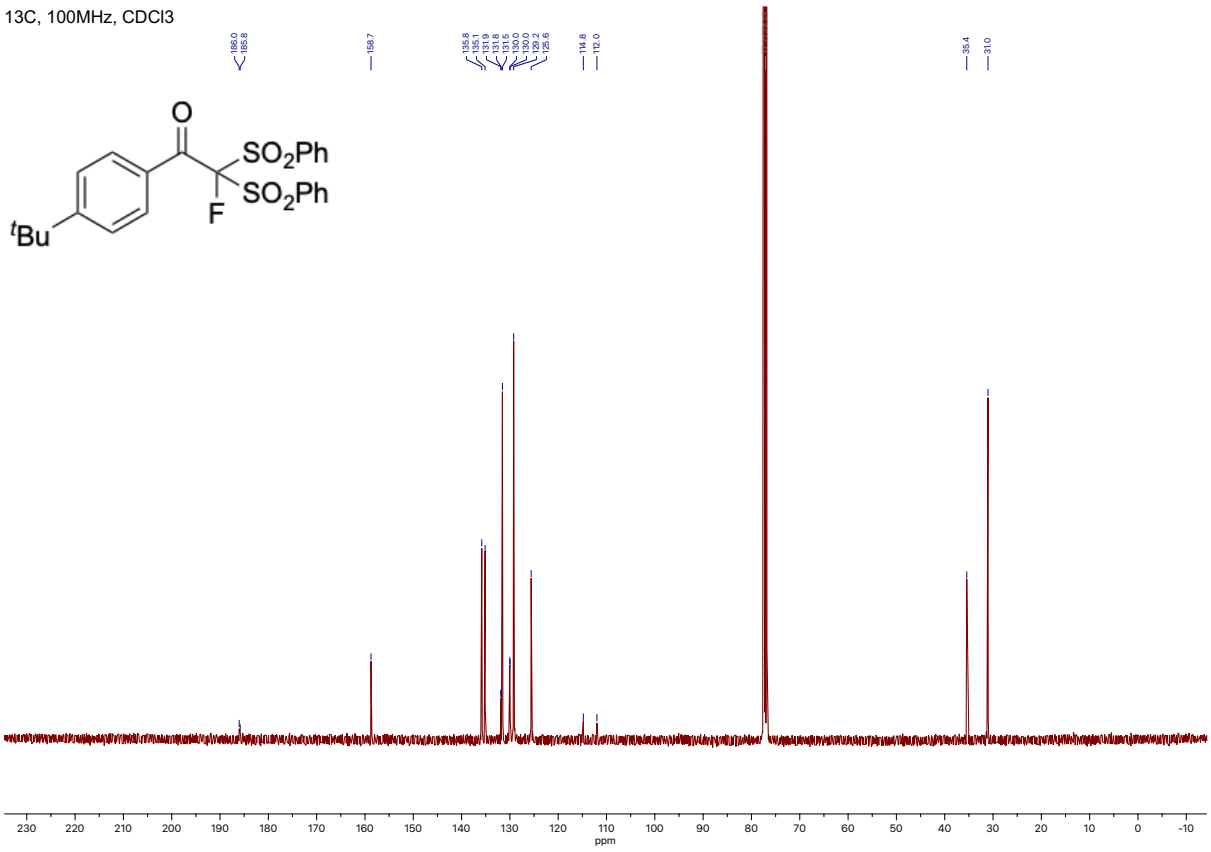
13C, 100MHz, CDCl3



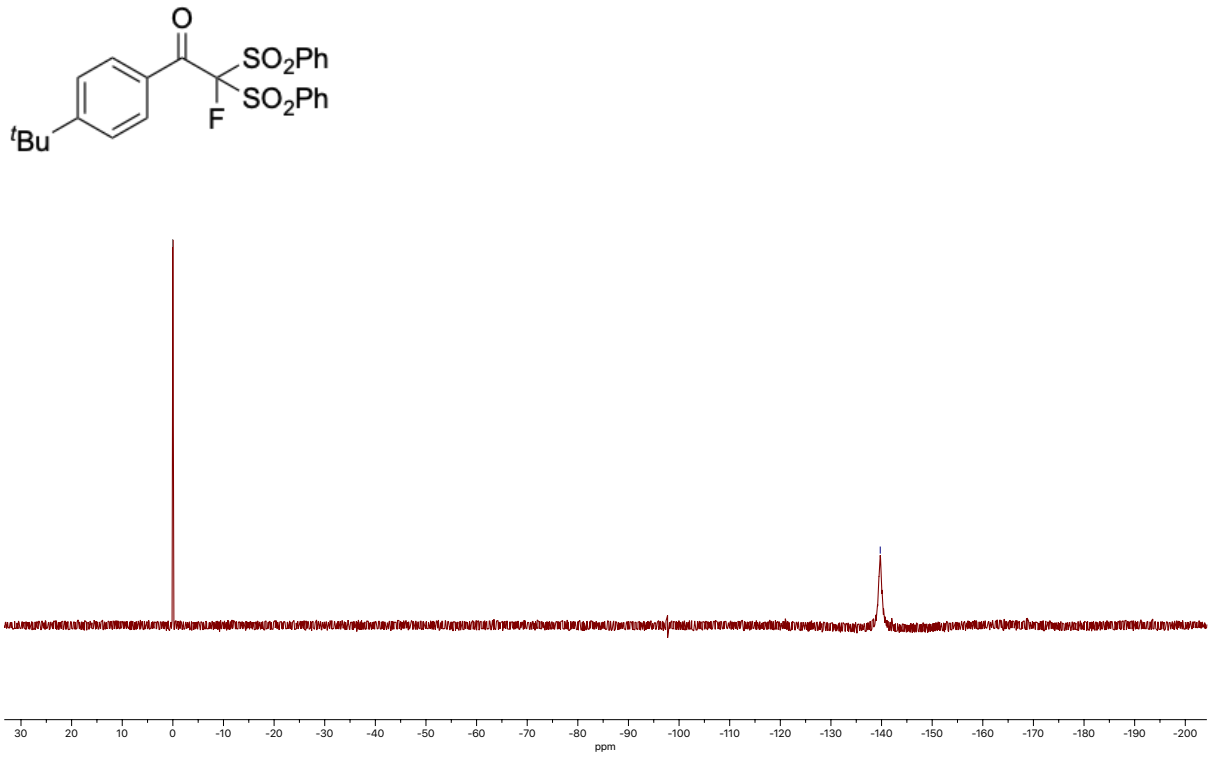
1H, 400MHz, CDCl3



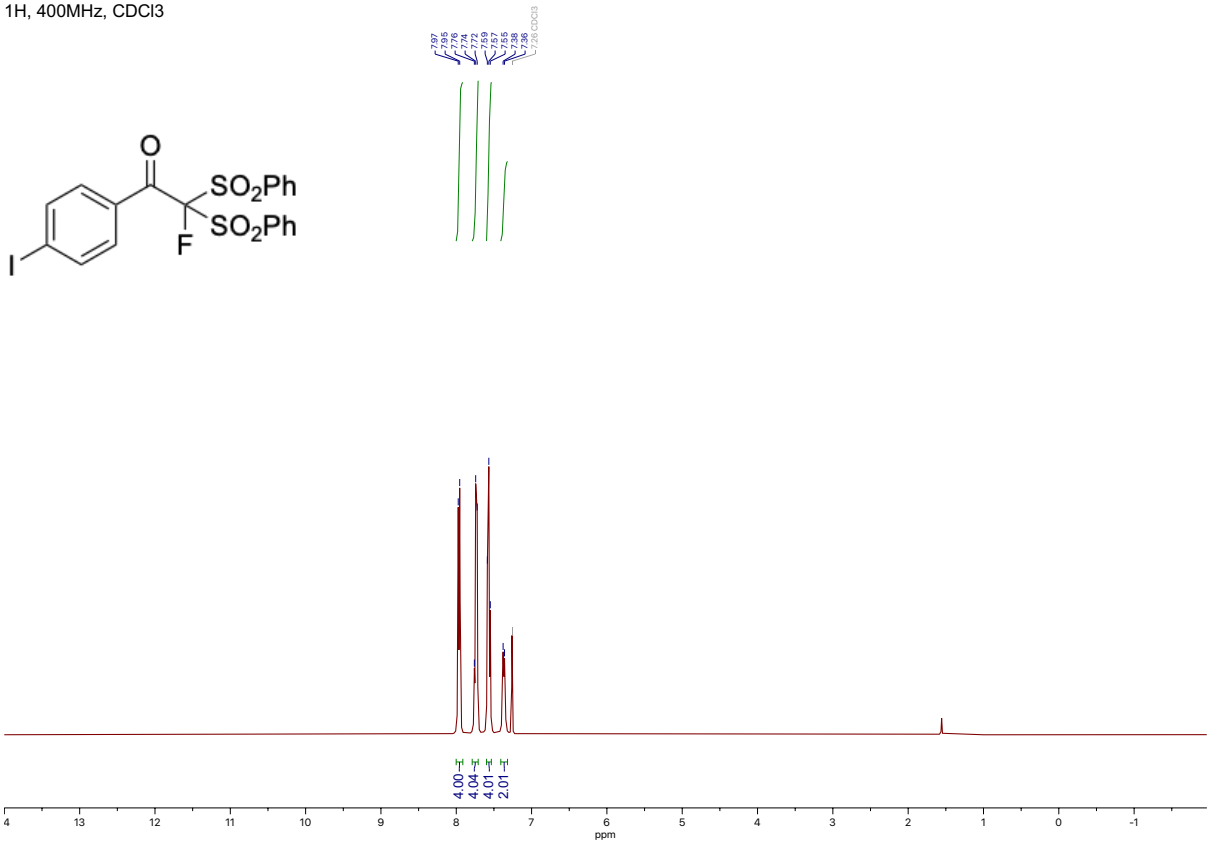
13C, 100MHz, CDCl3



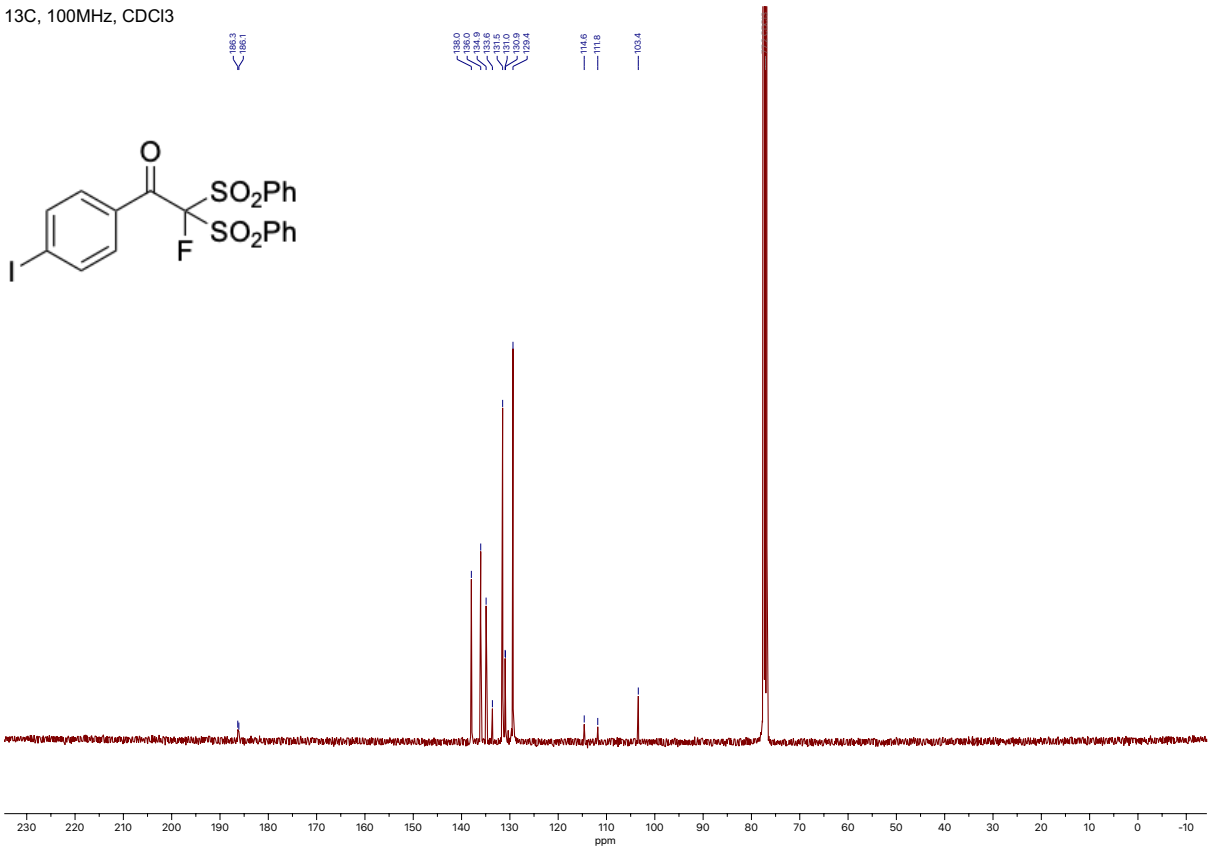
19F, 376MHz, CDCl3



1H, 400MHz, CDCl3



13C, 100MHz, CDCl3



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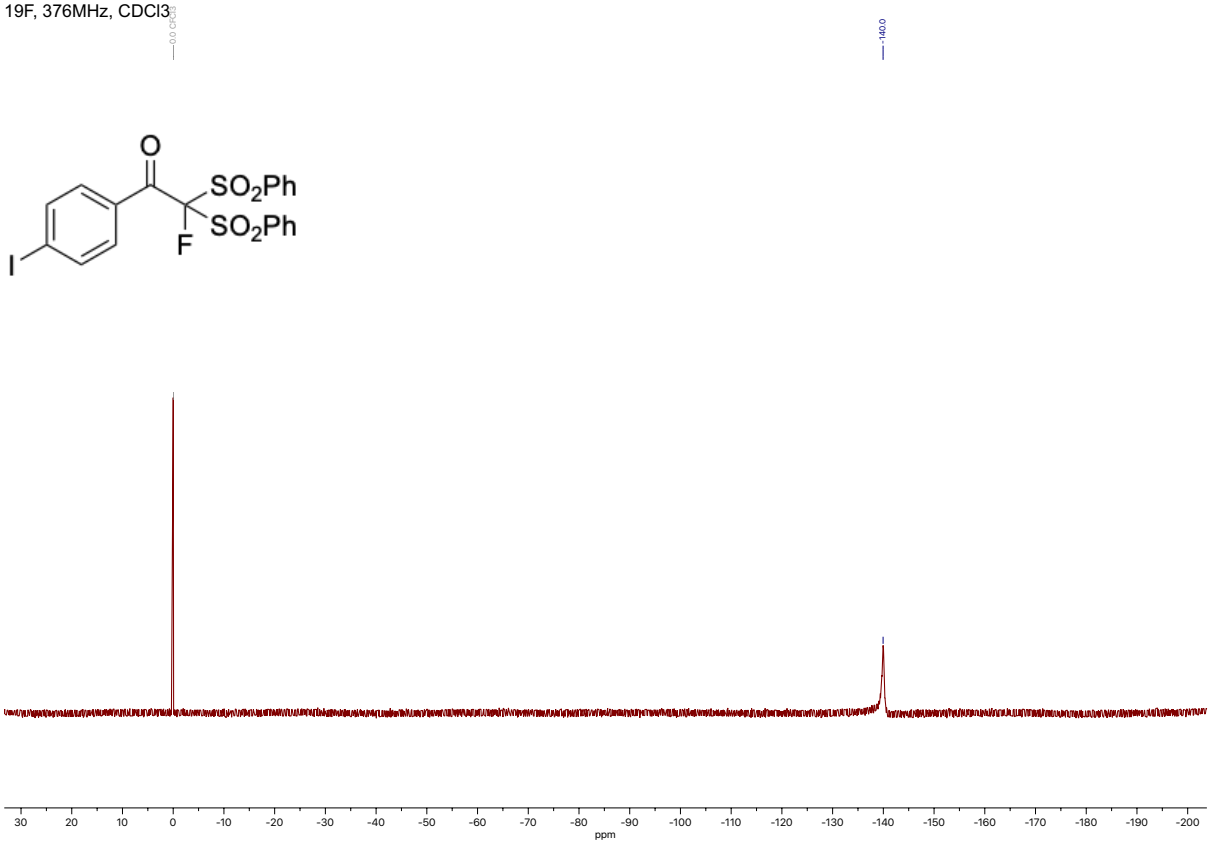

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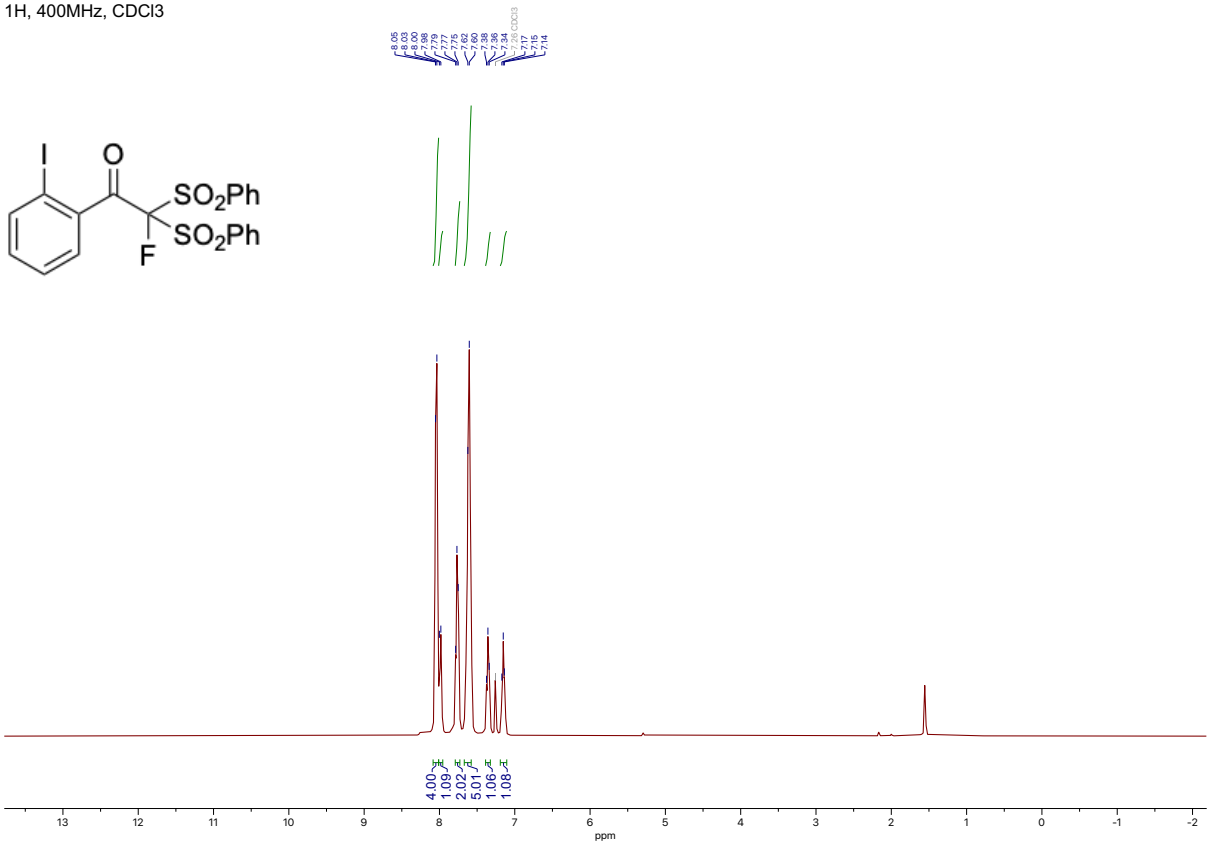

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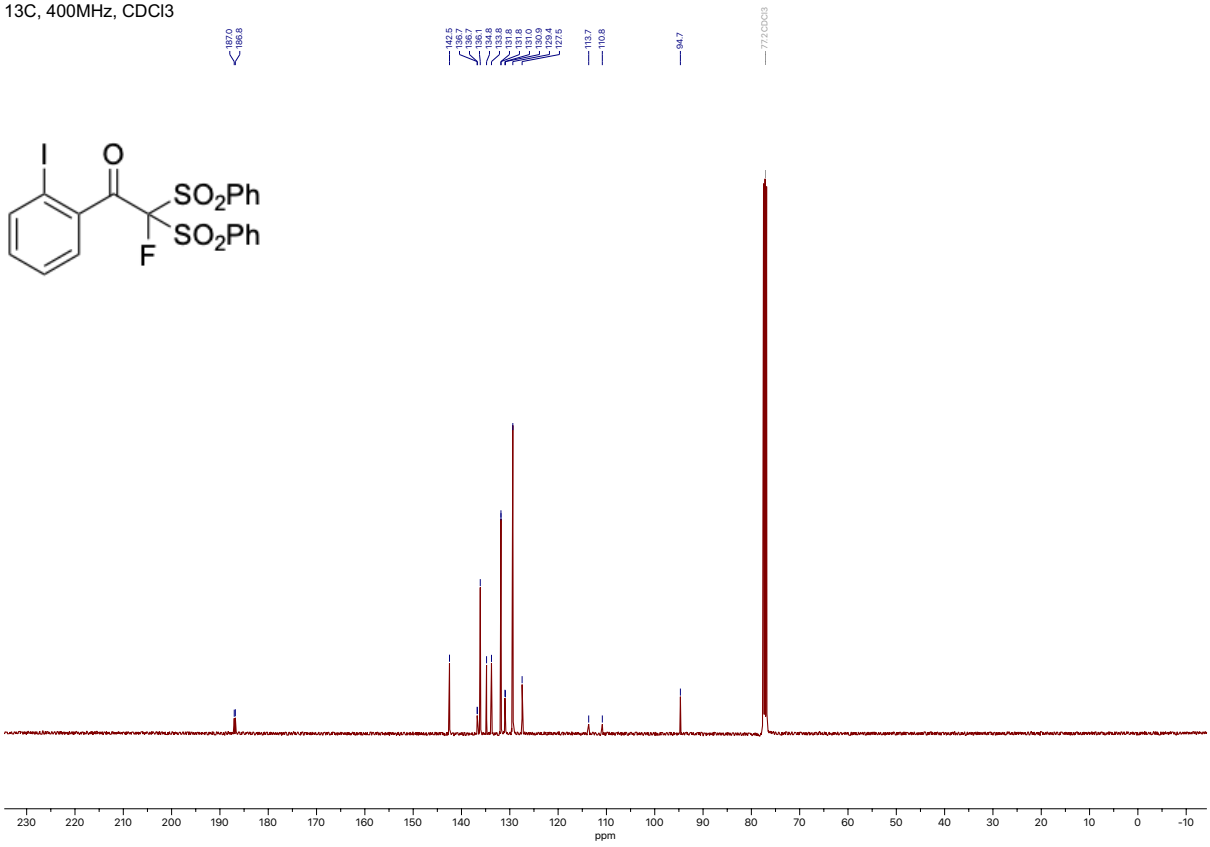

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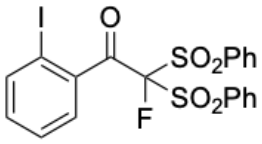

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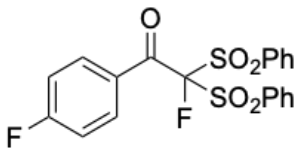

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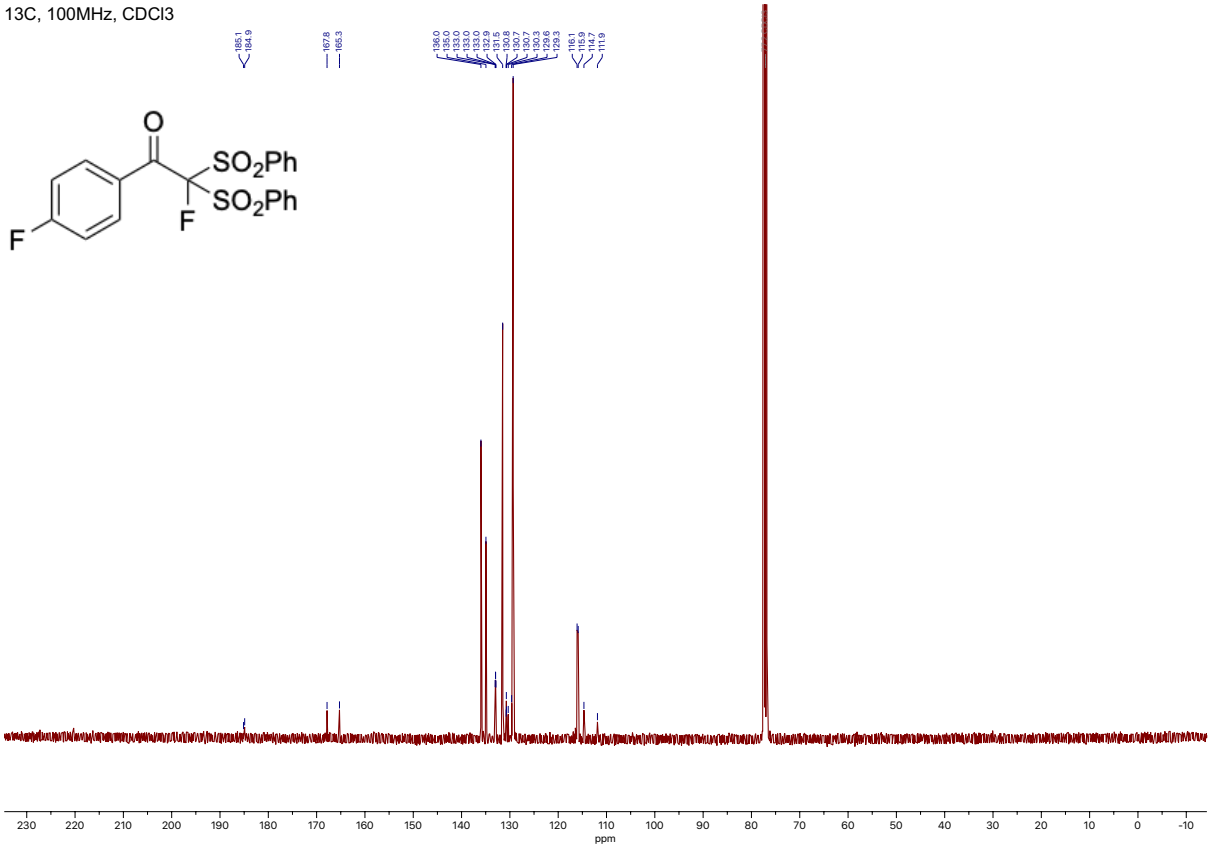

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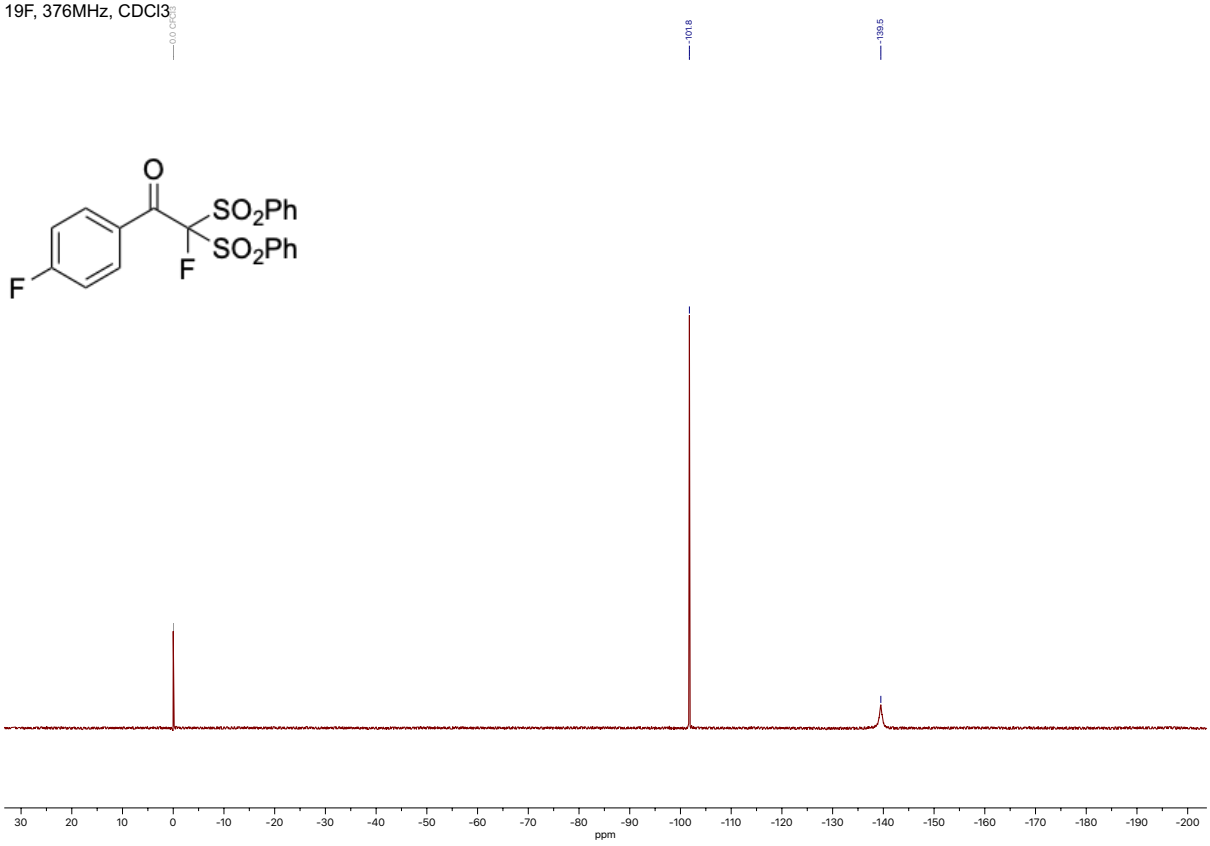

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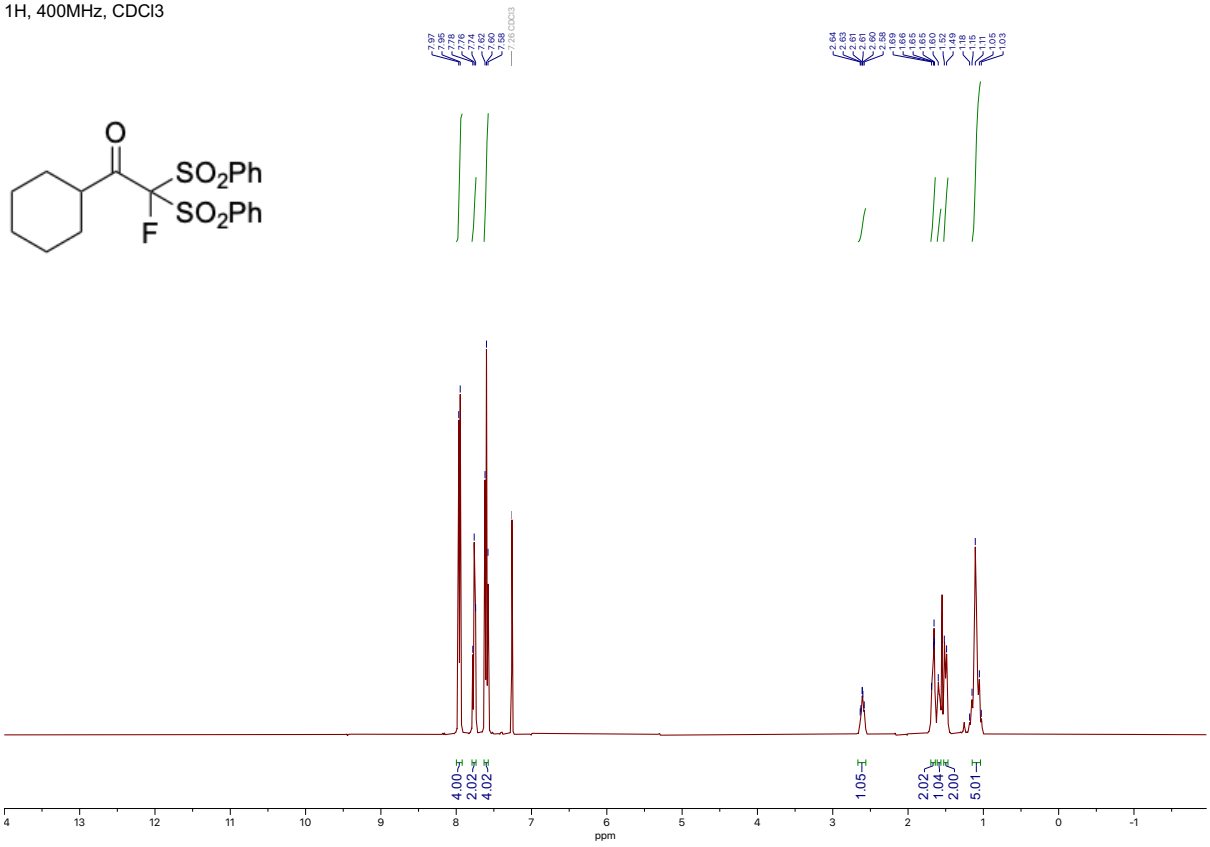

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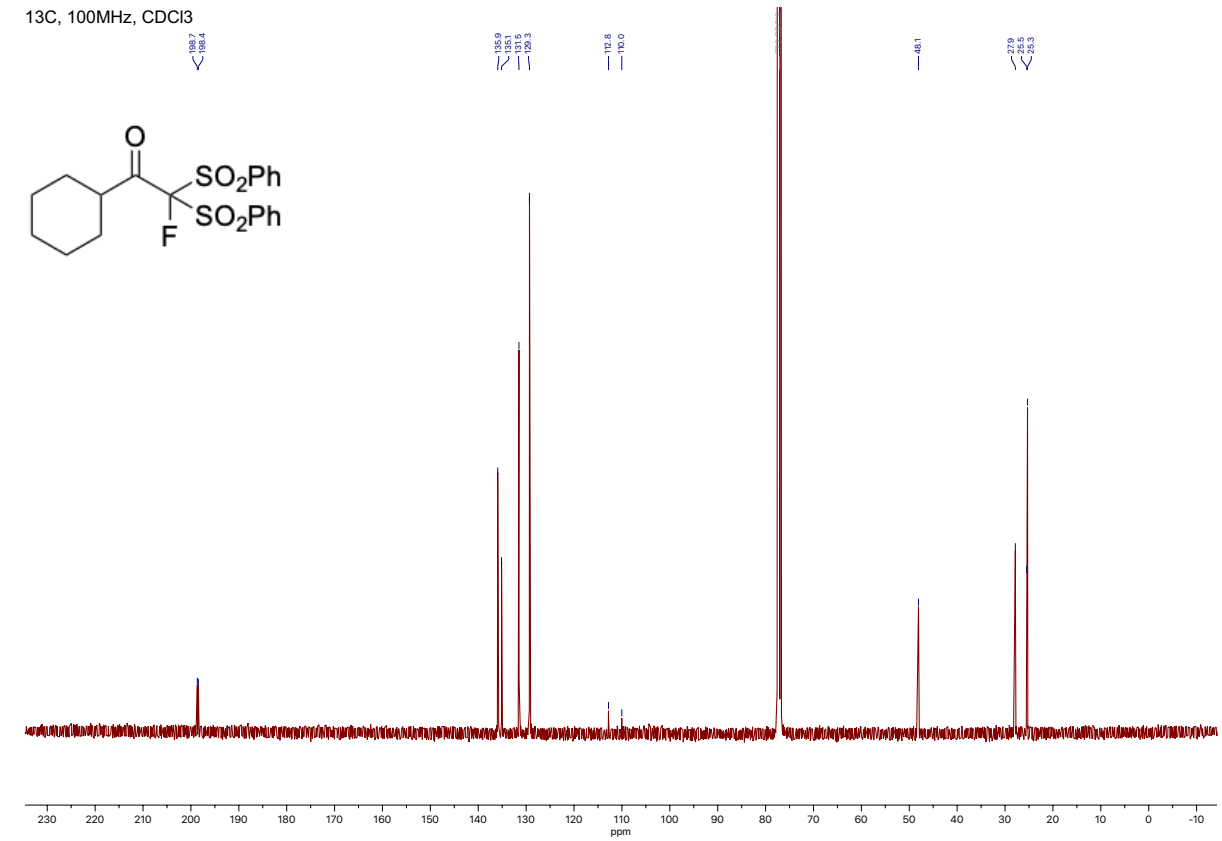

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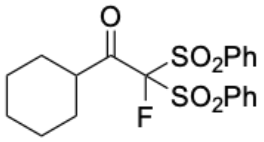

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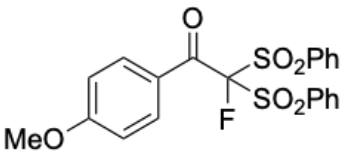

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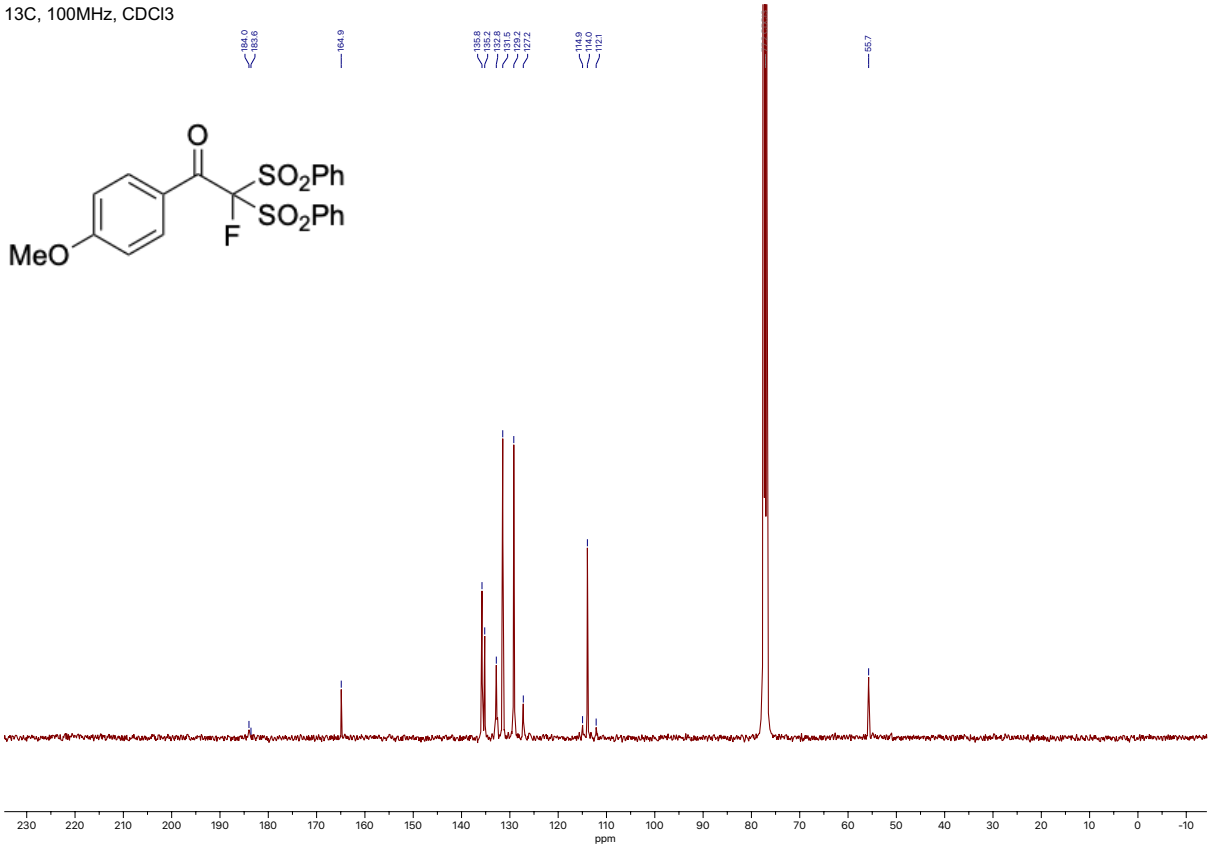

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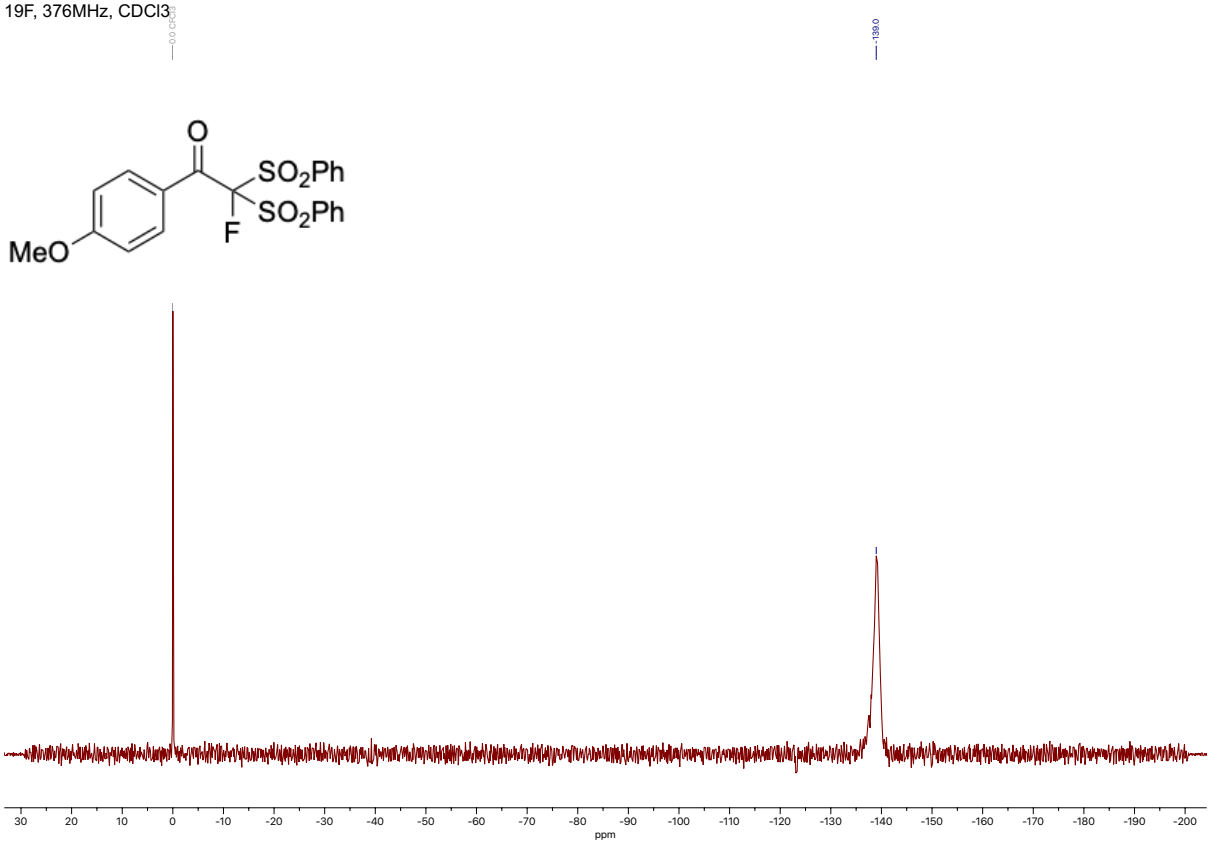

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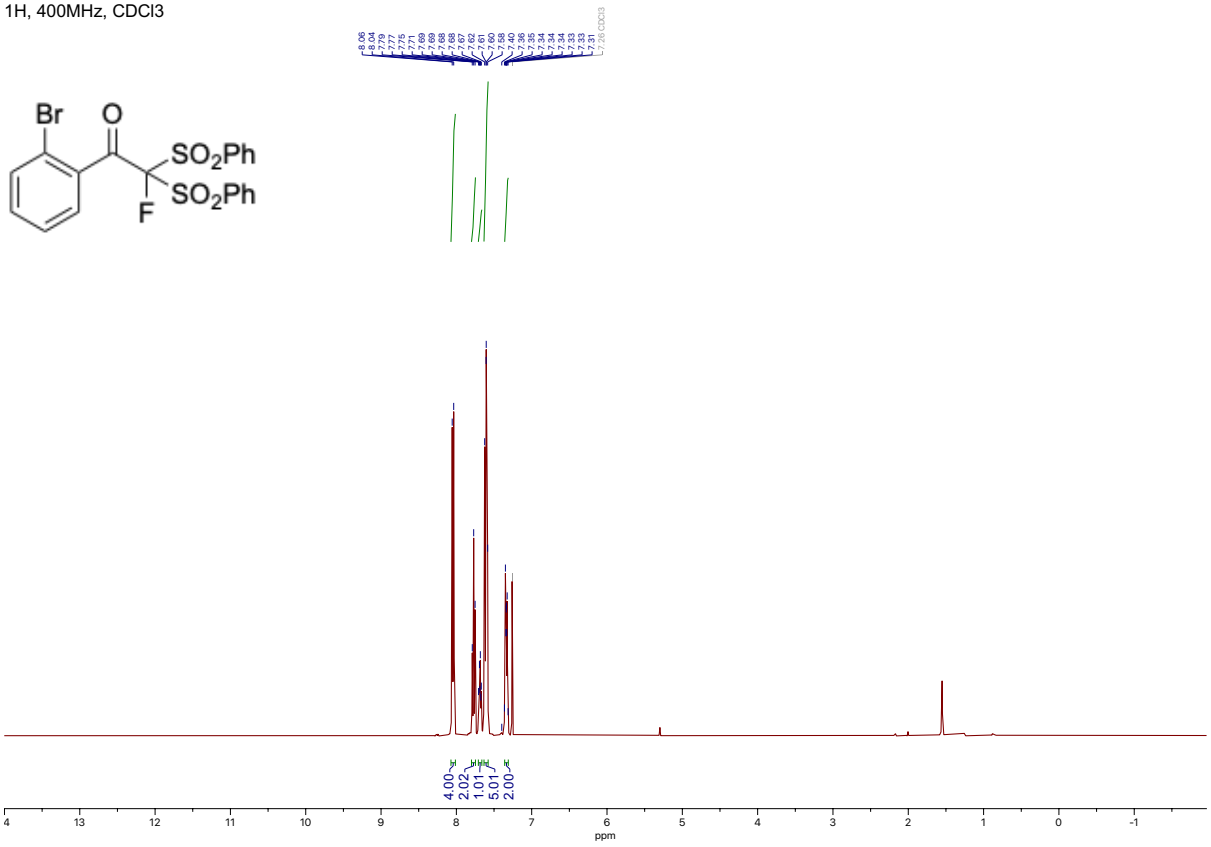

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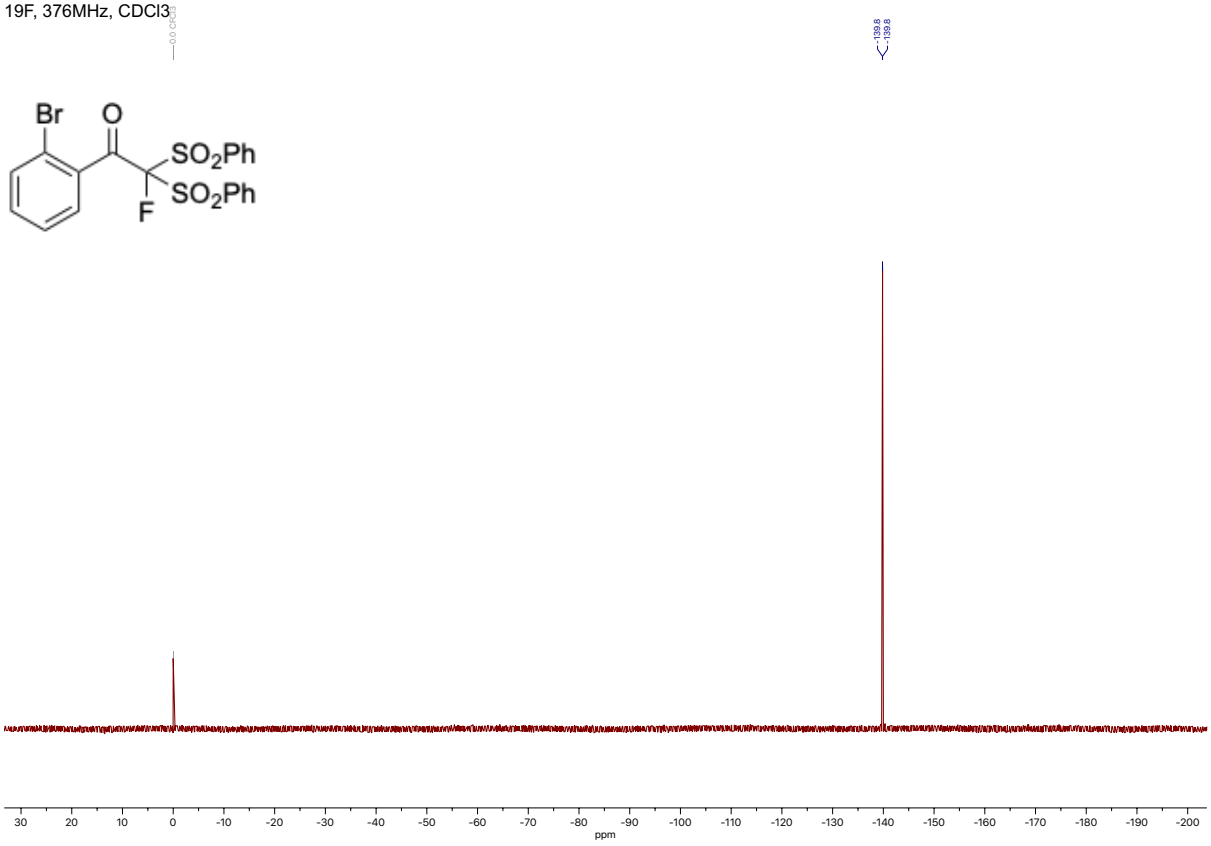

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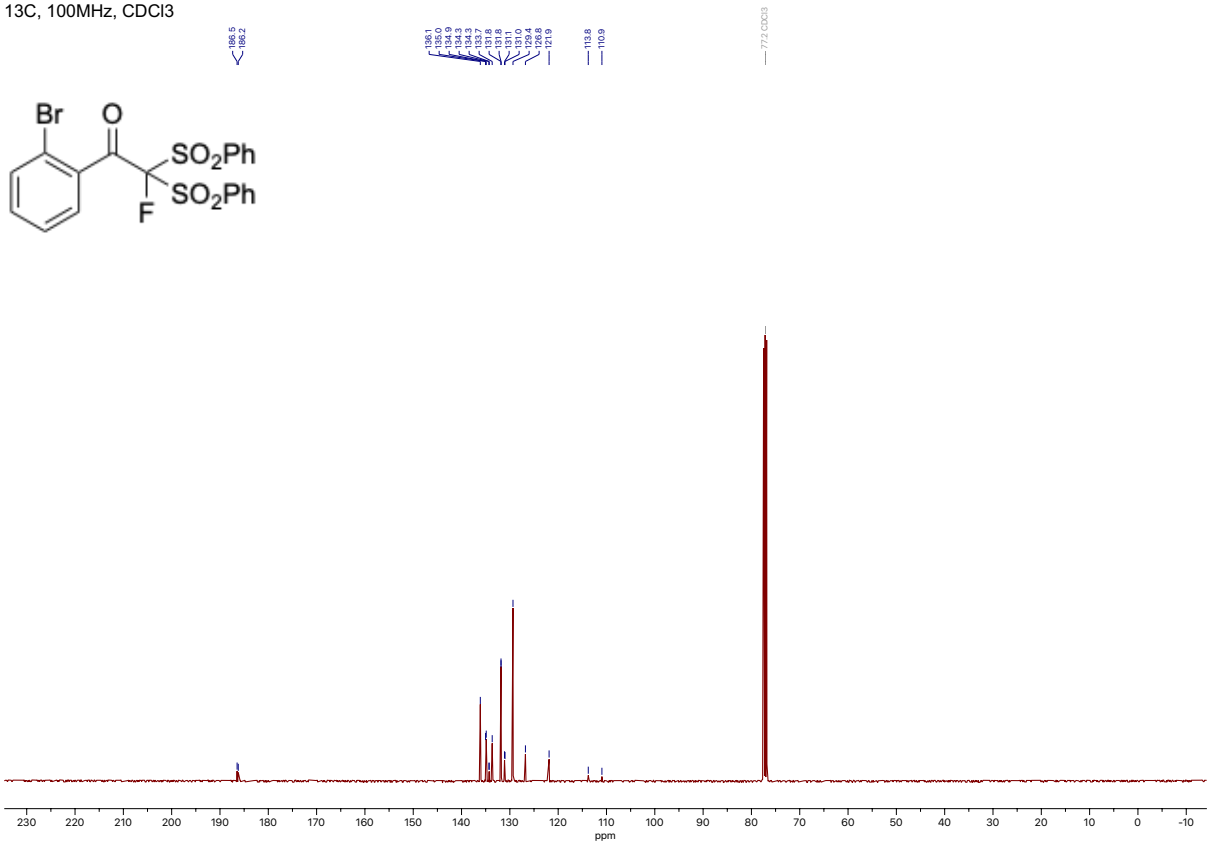

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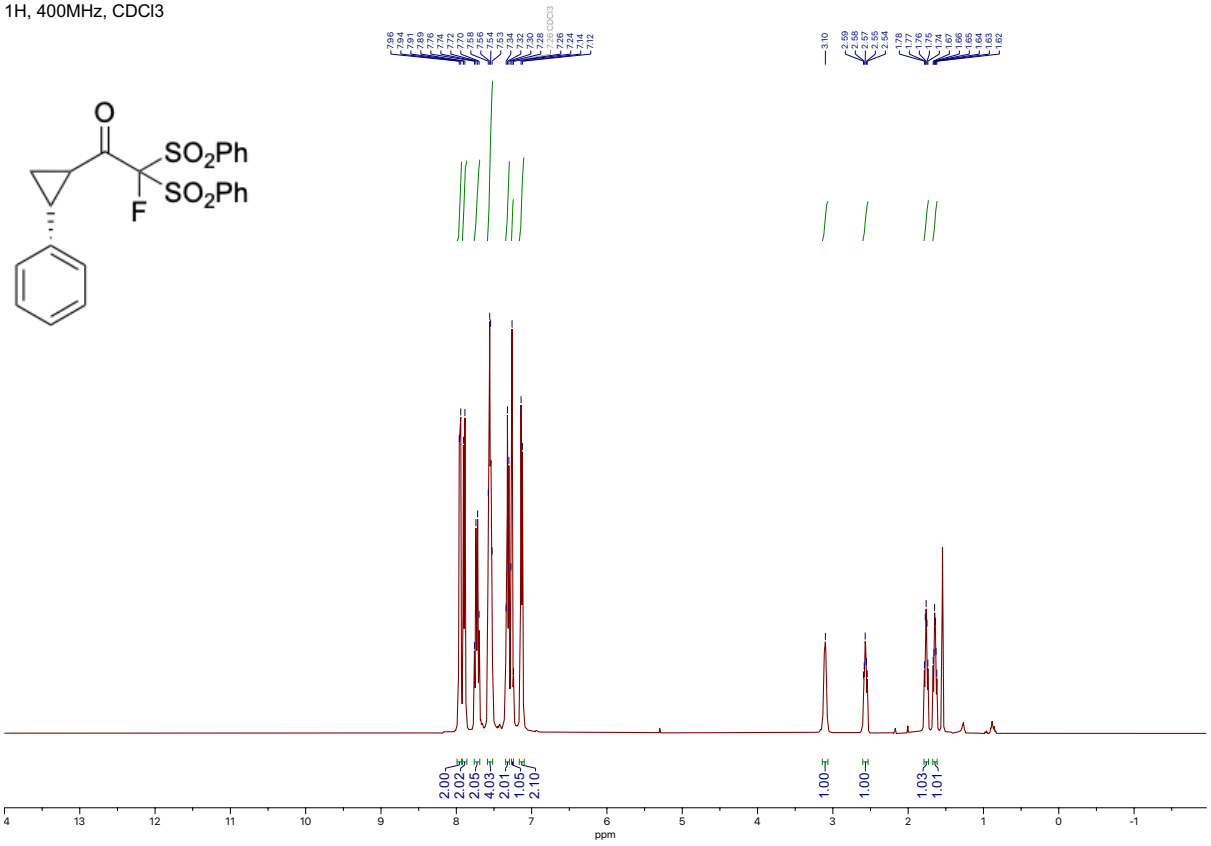

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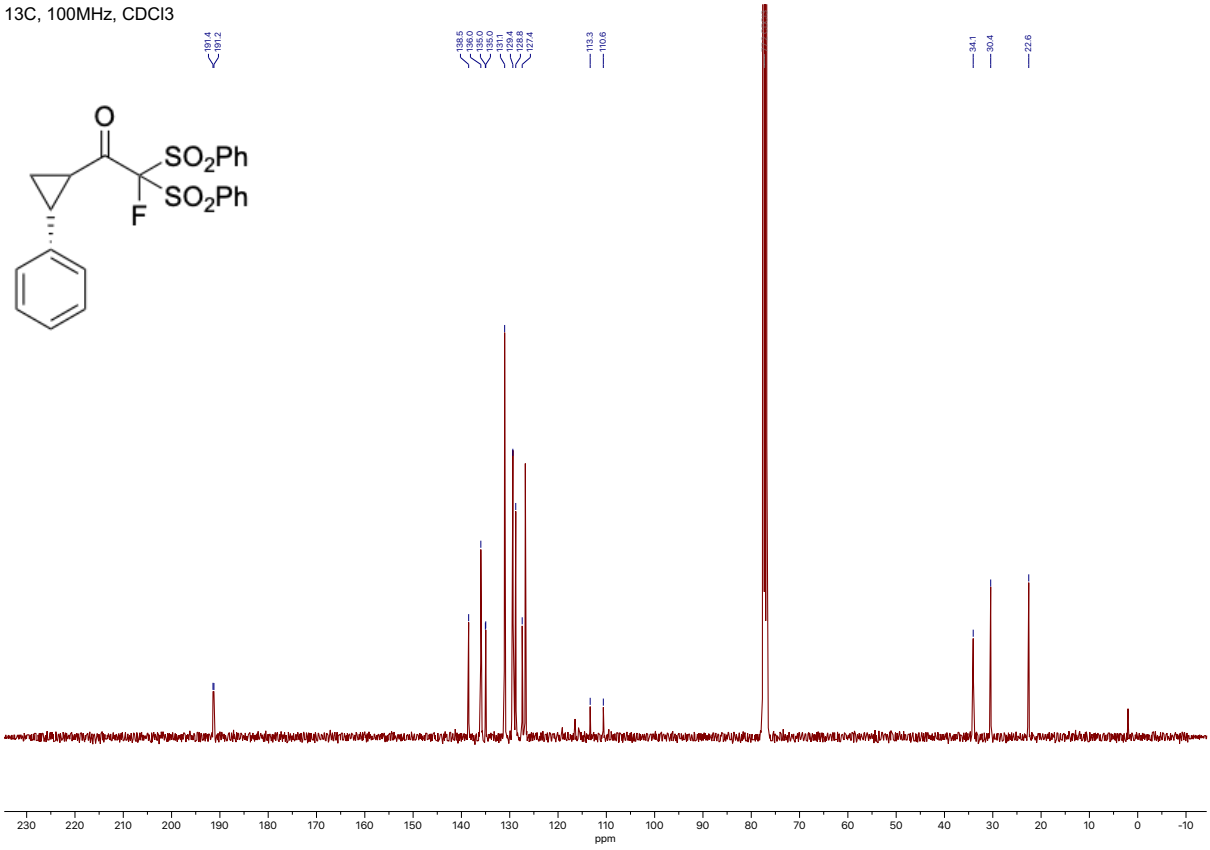

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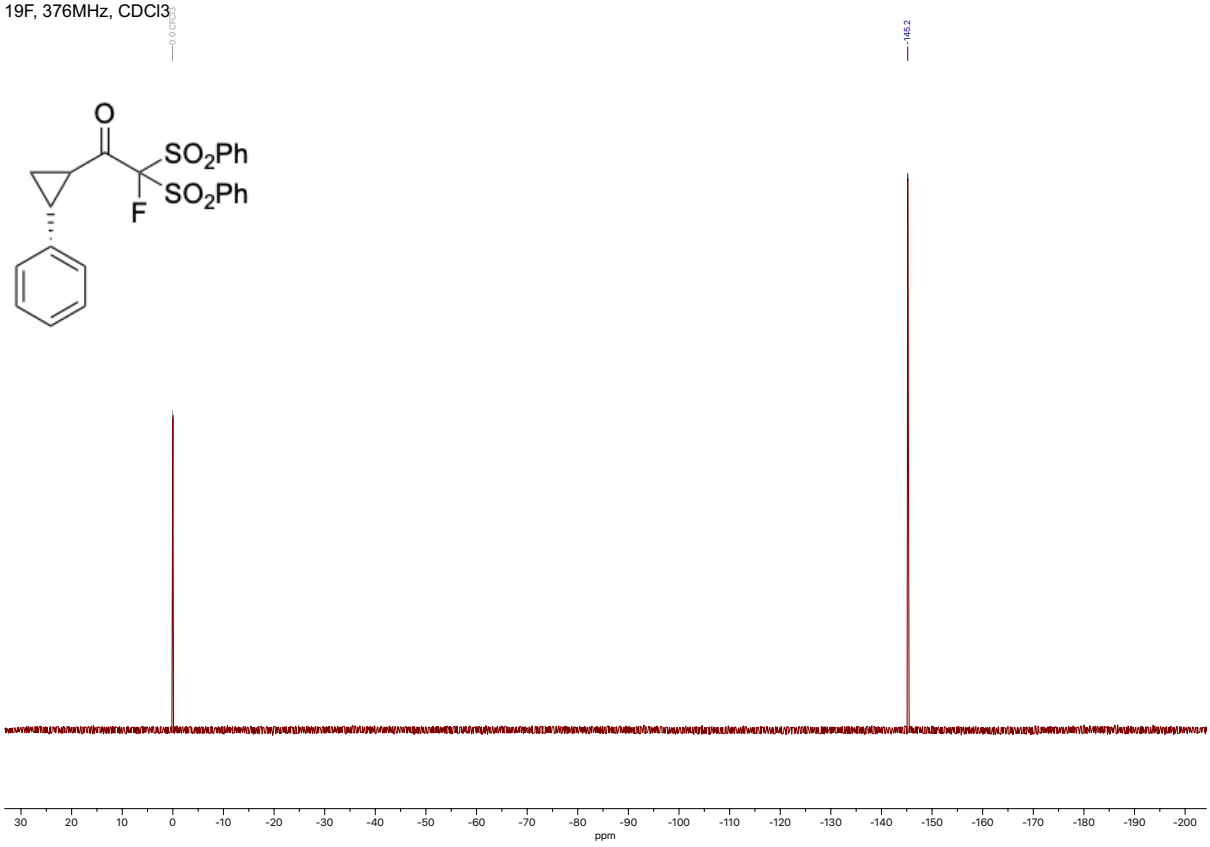

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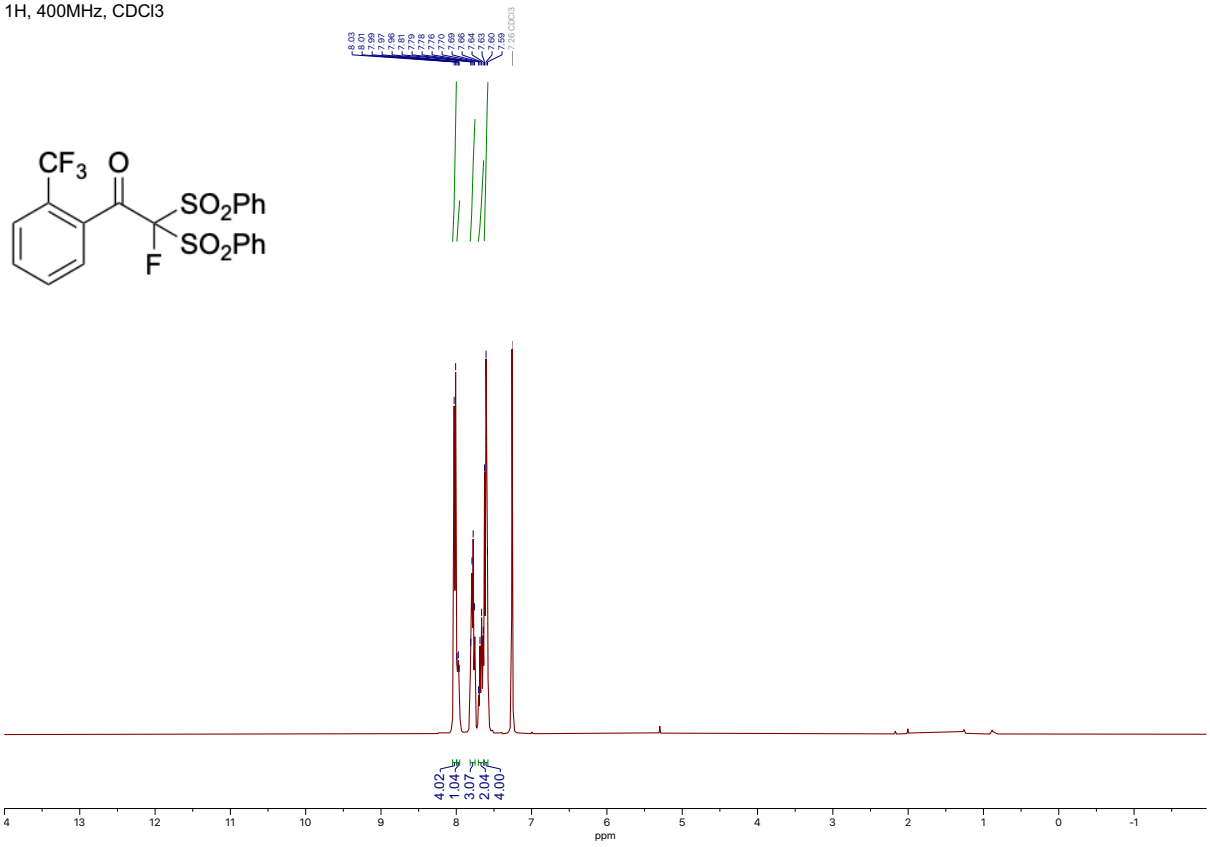

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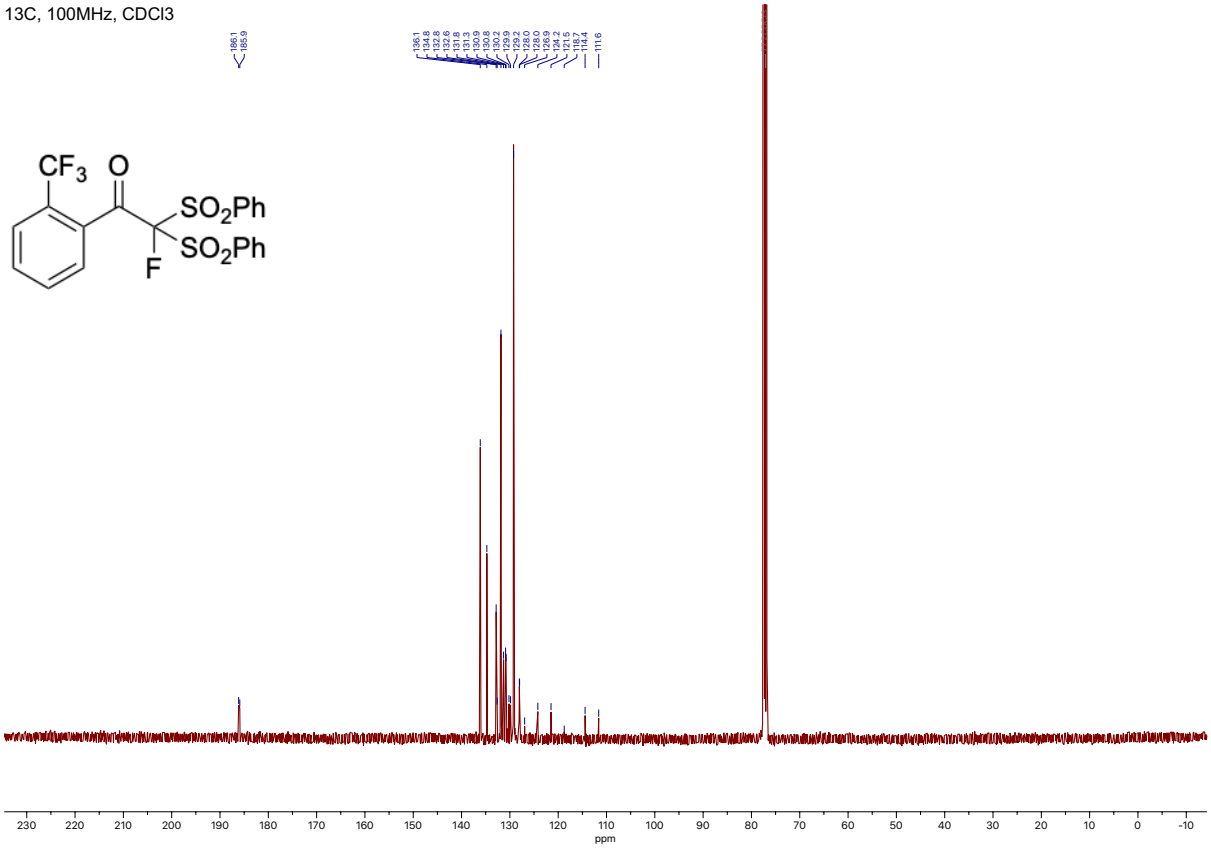

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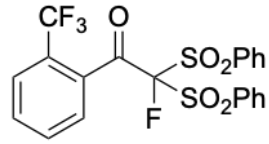

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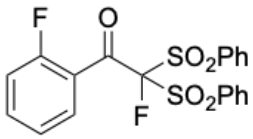

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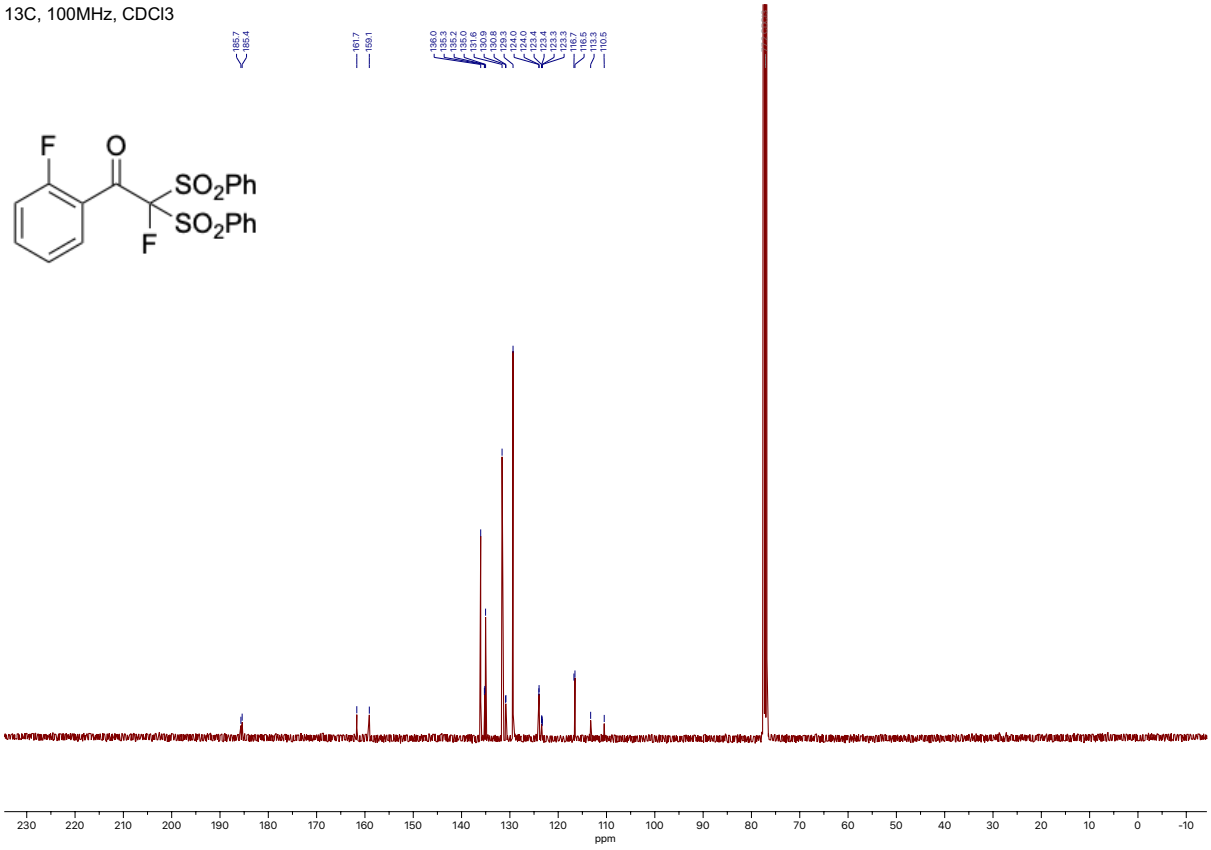

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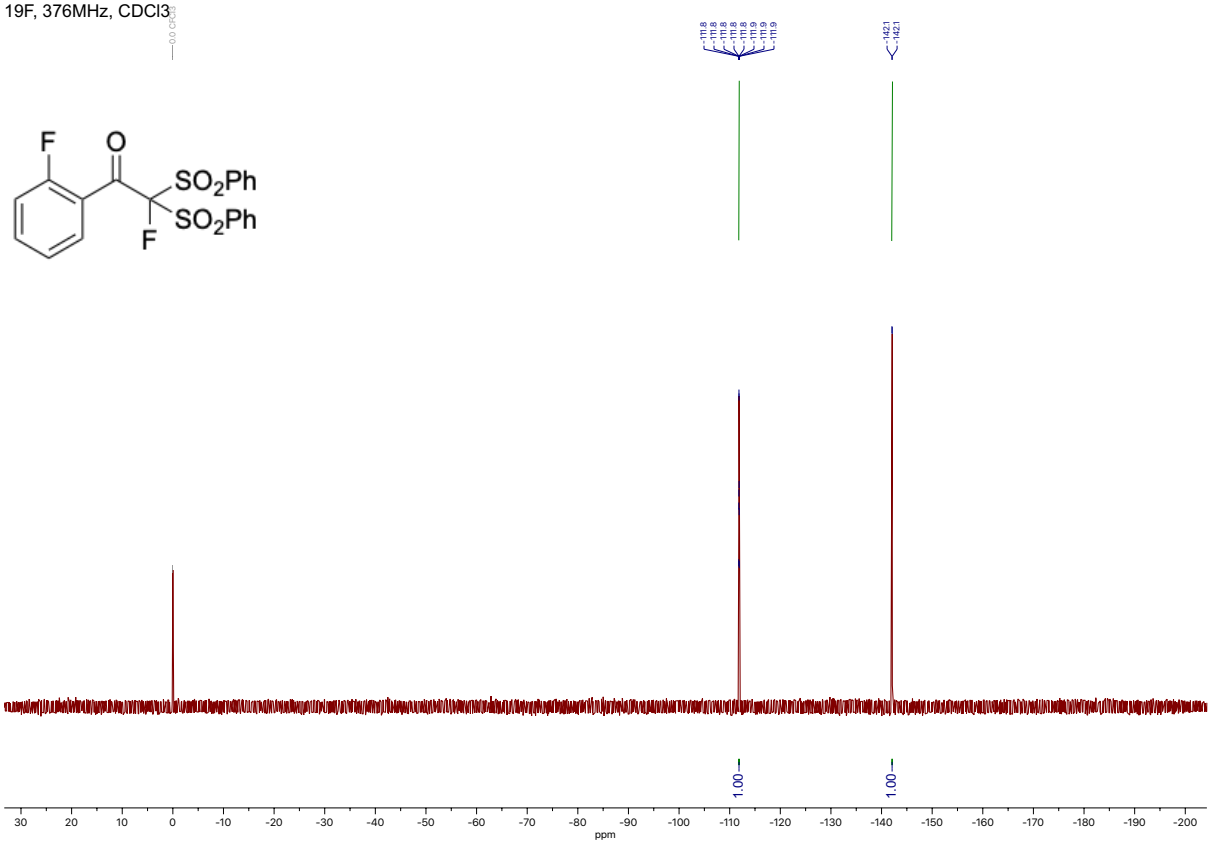

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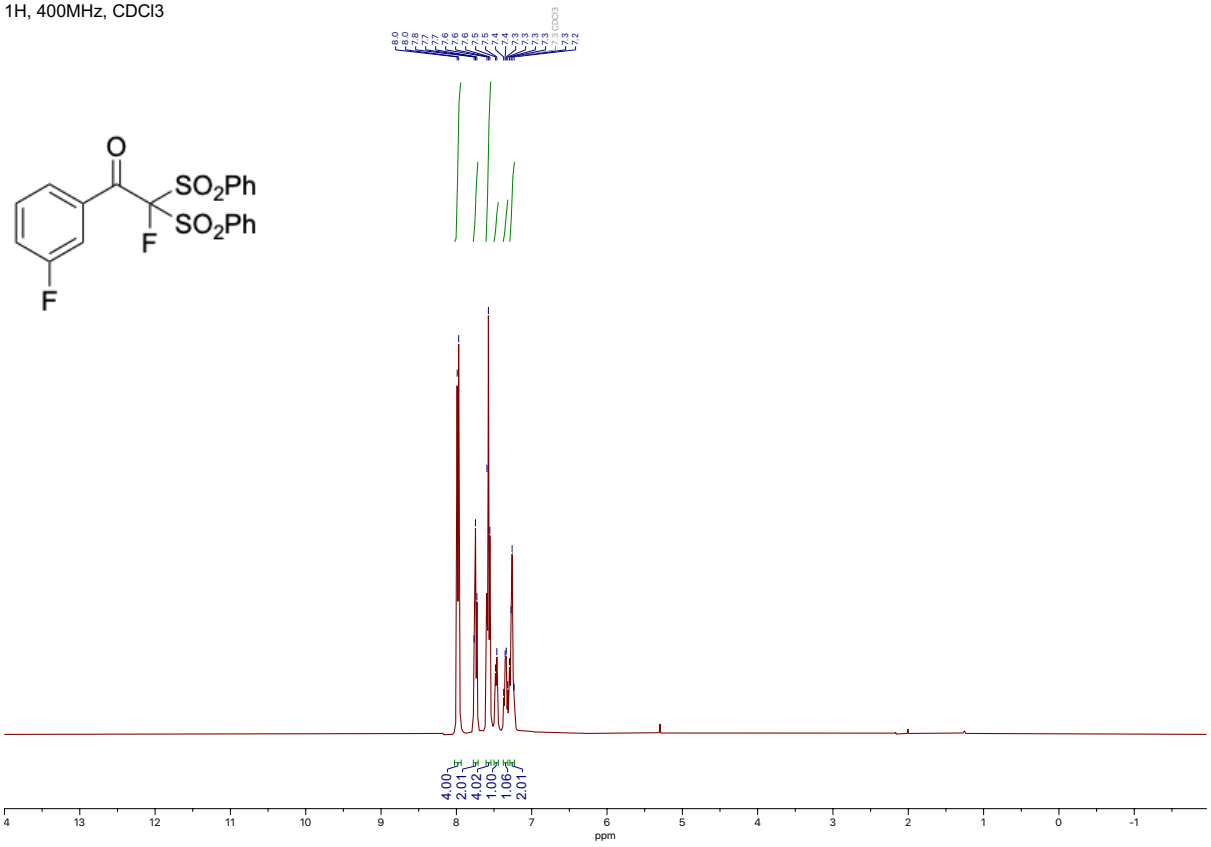

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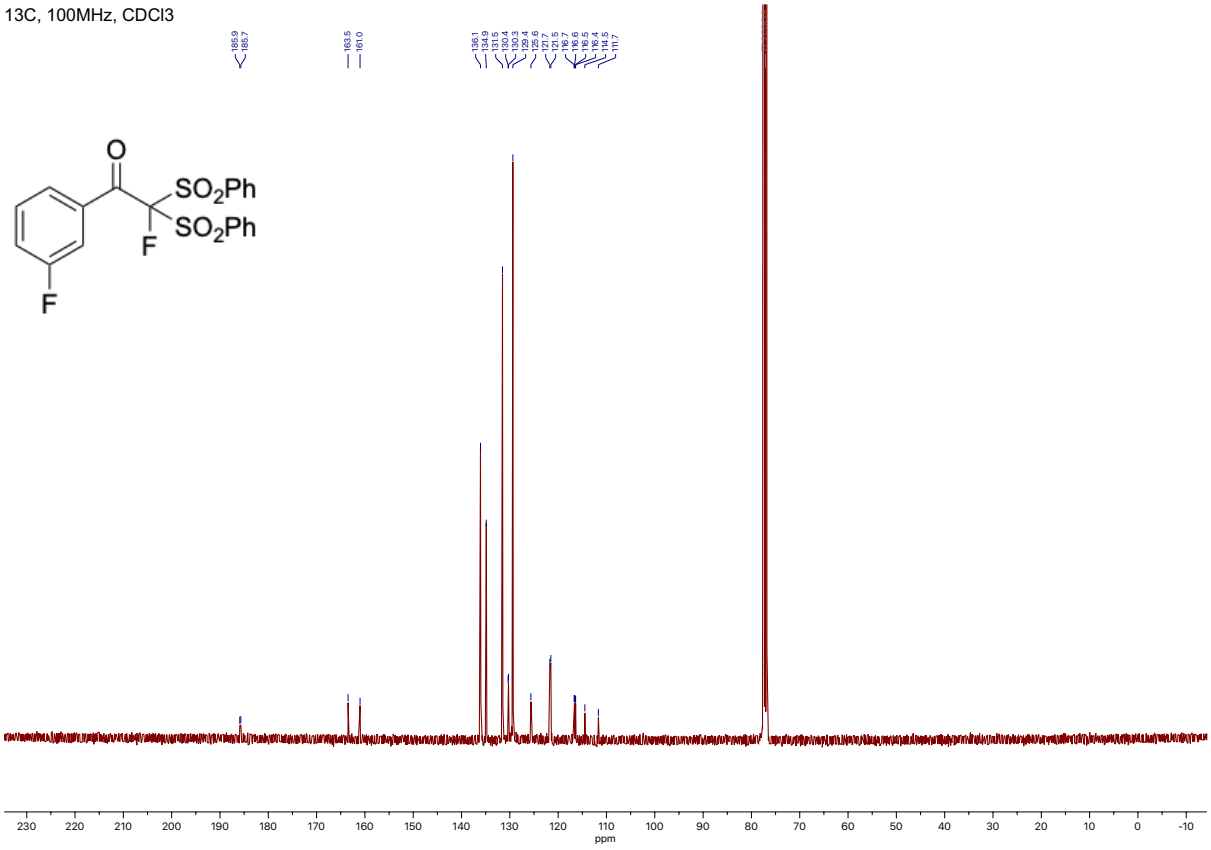

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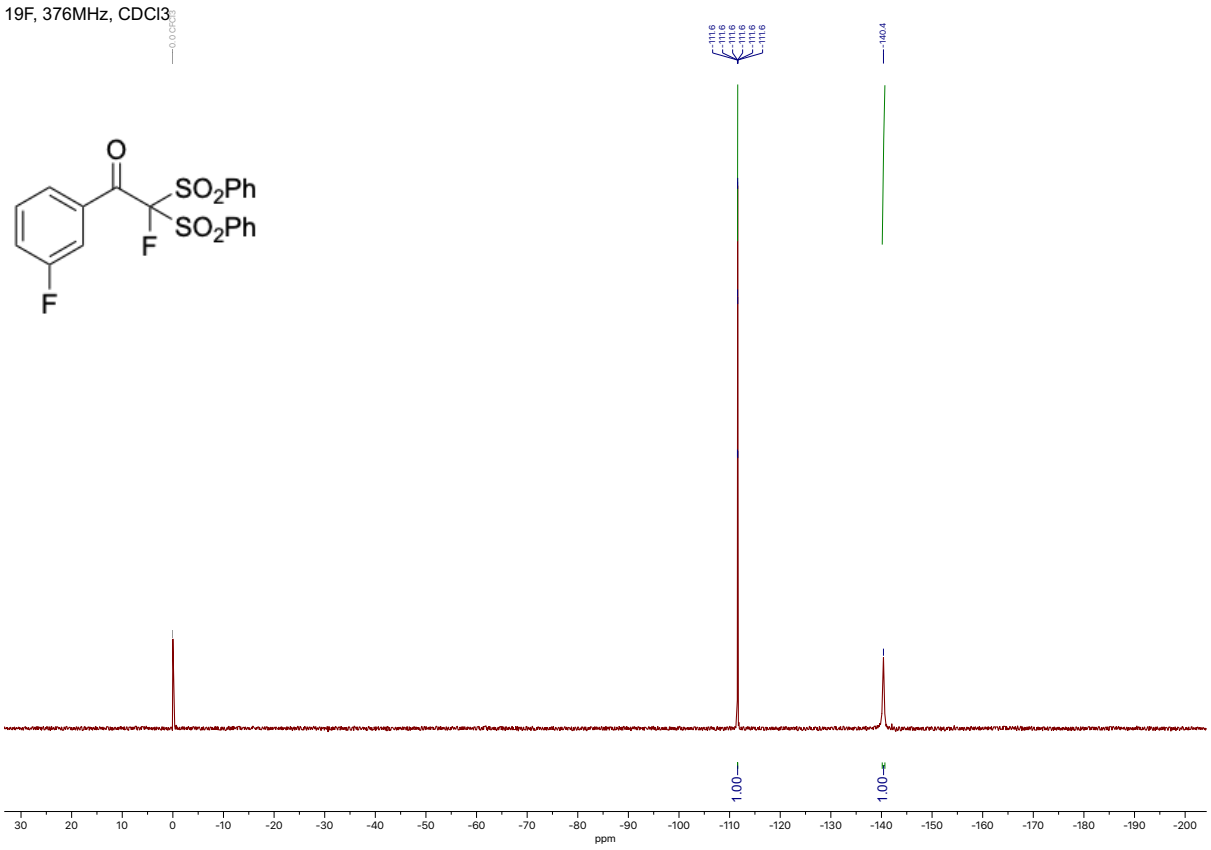

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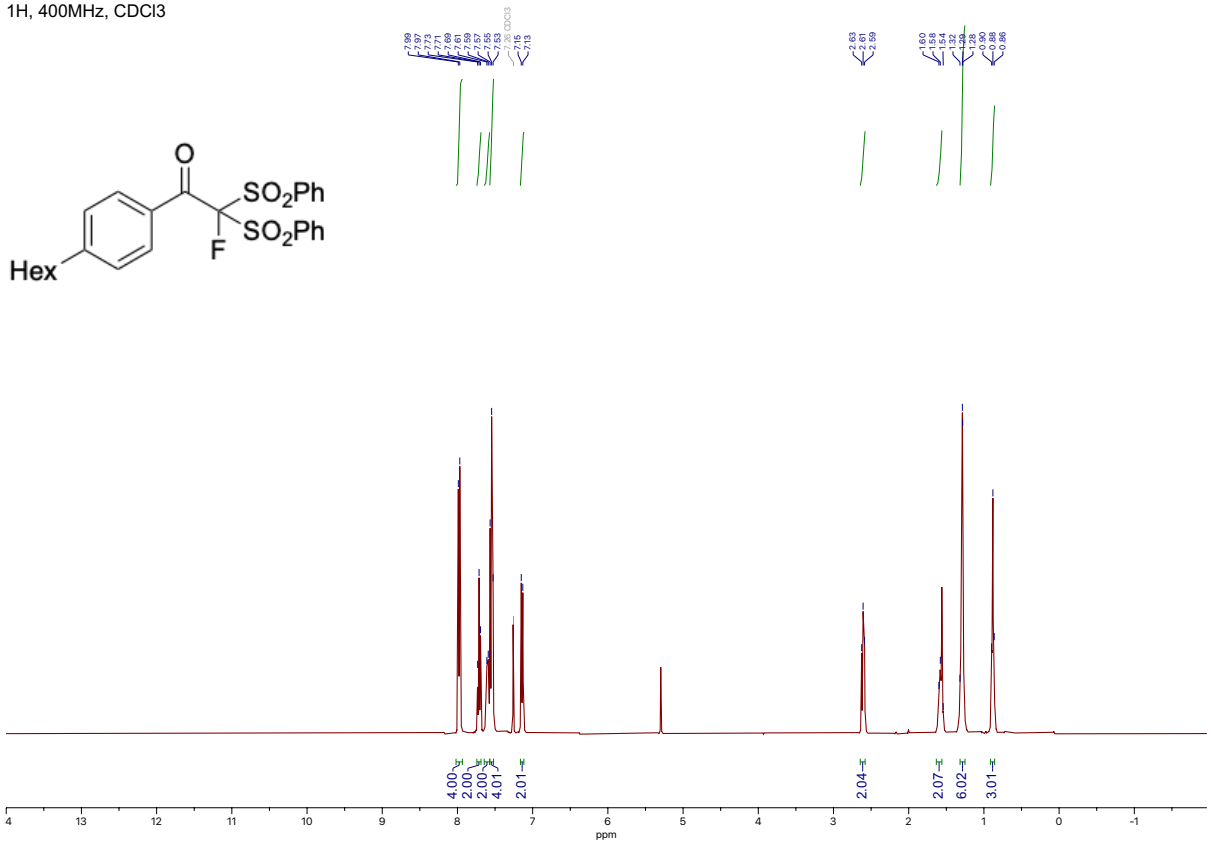

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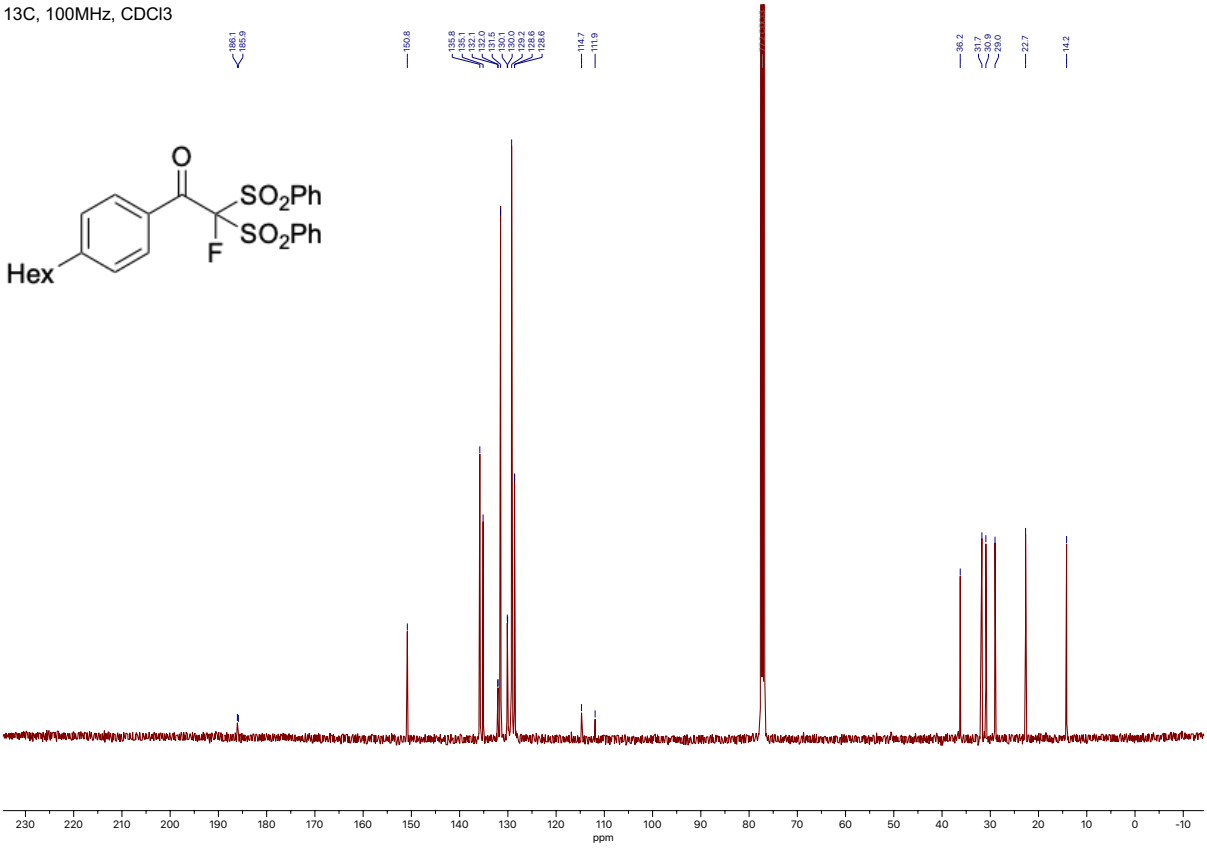

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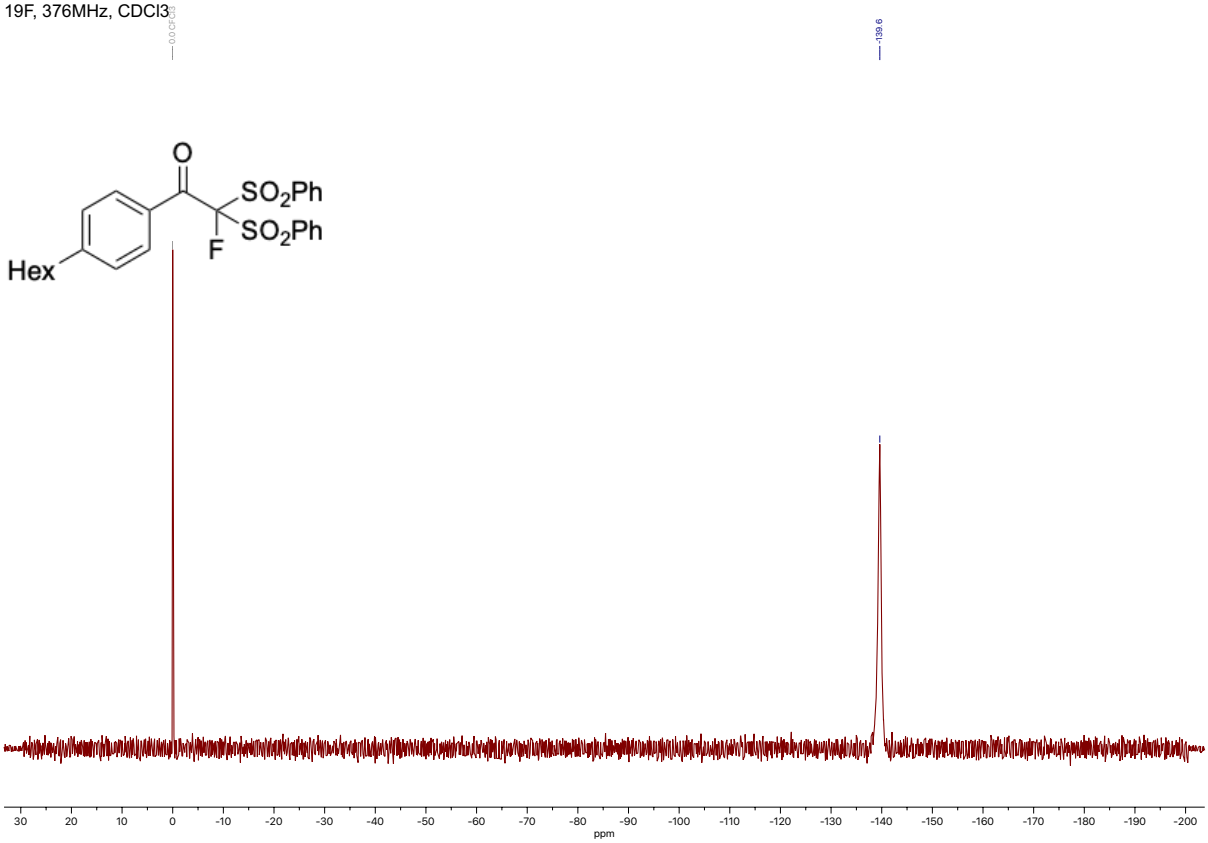

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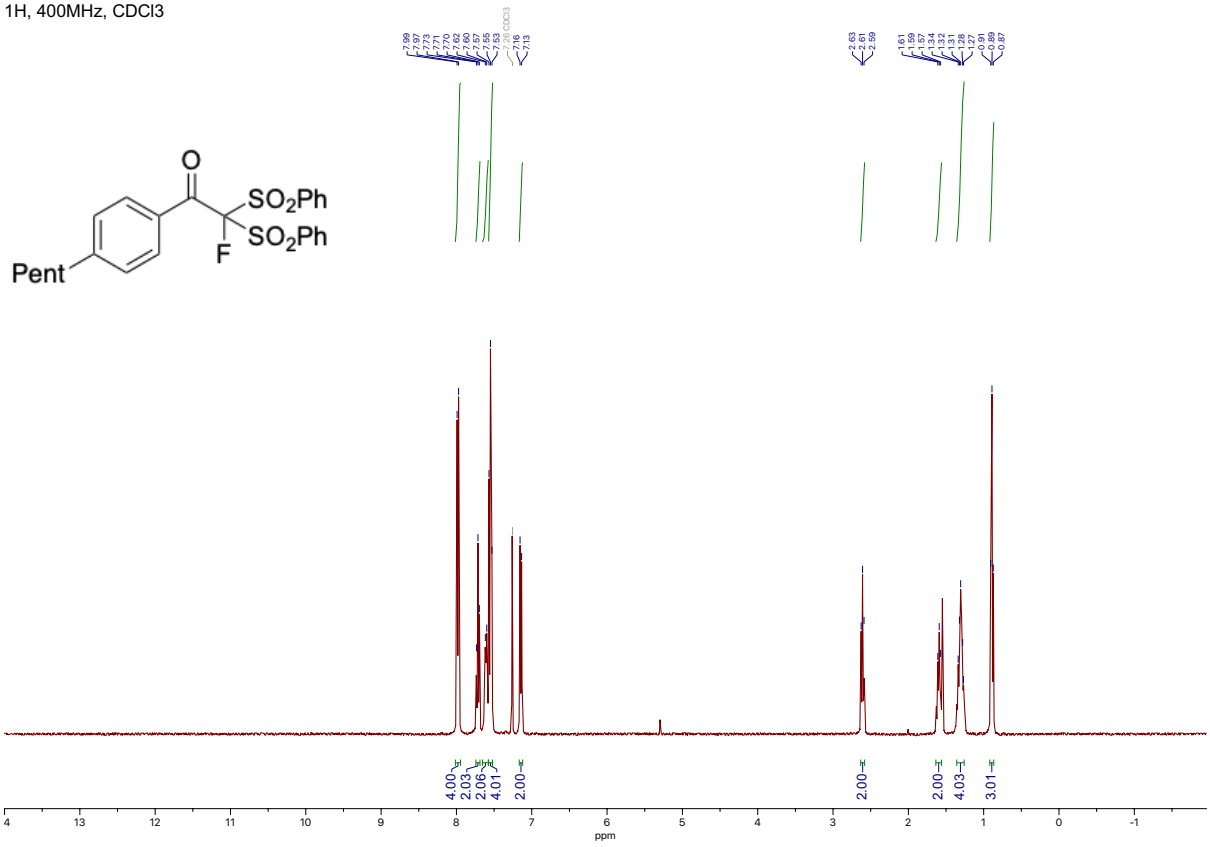

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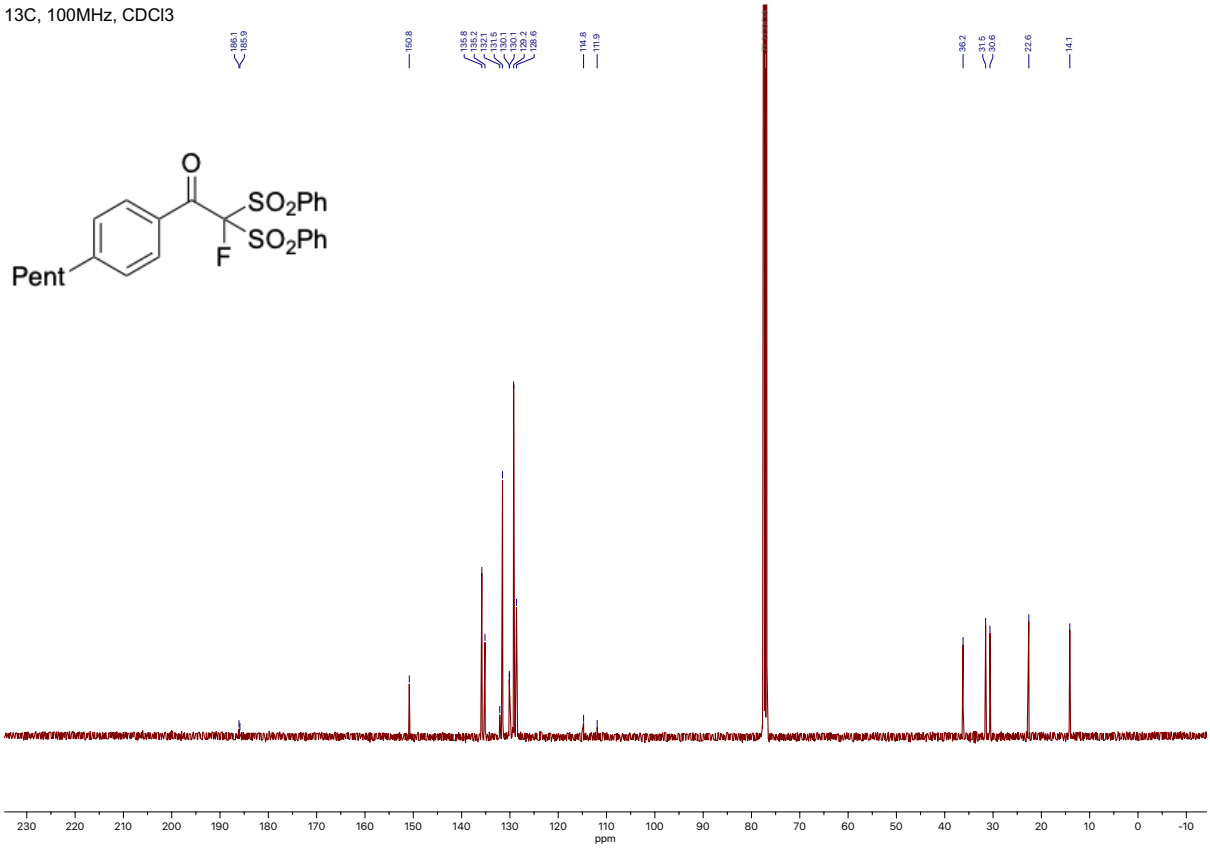

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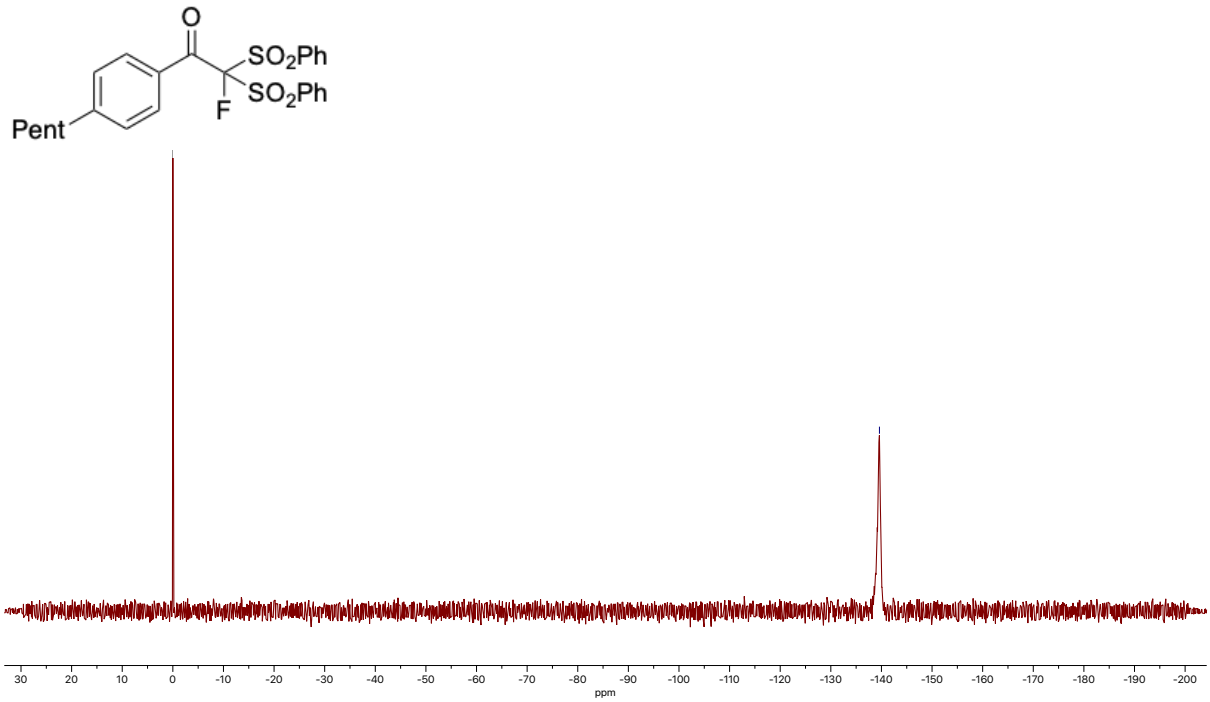

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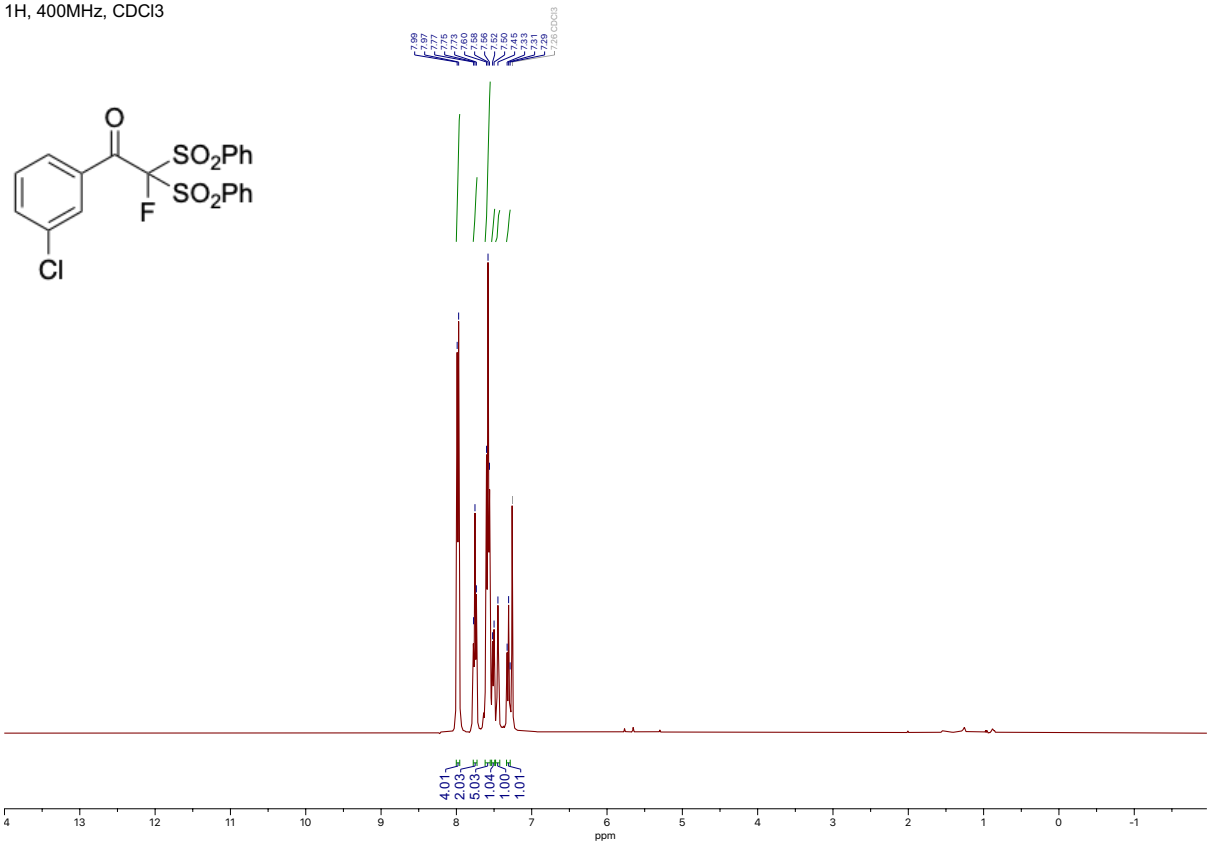

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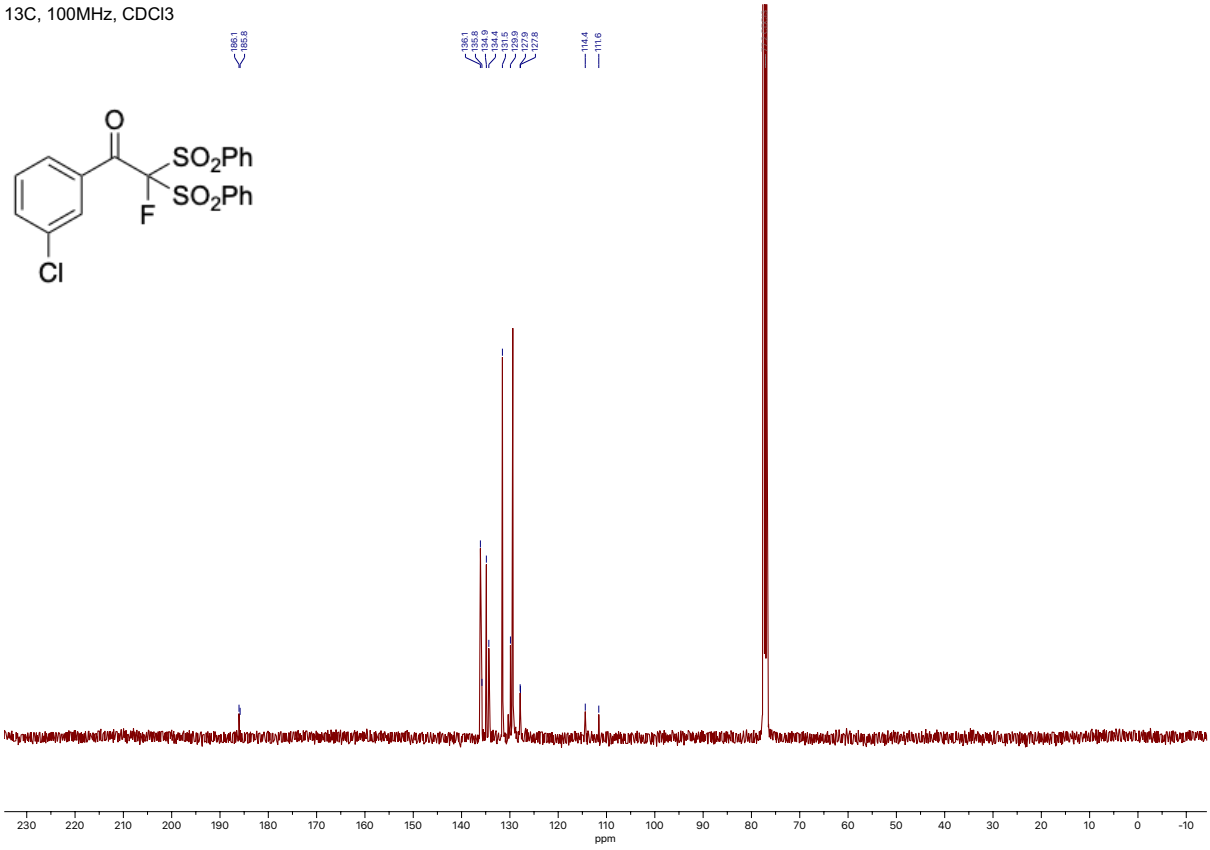

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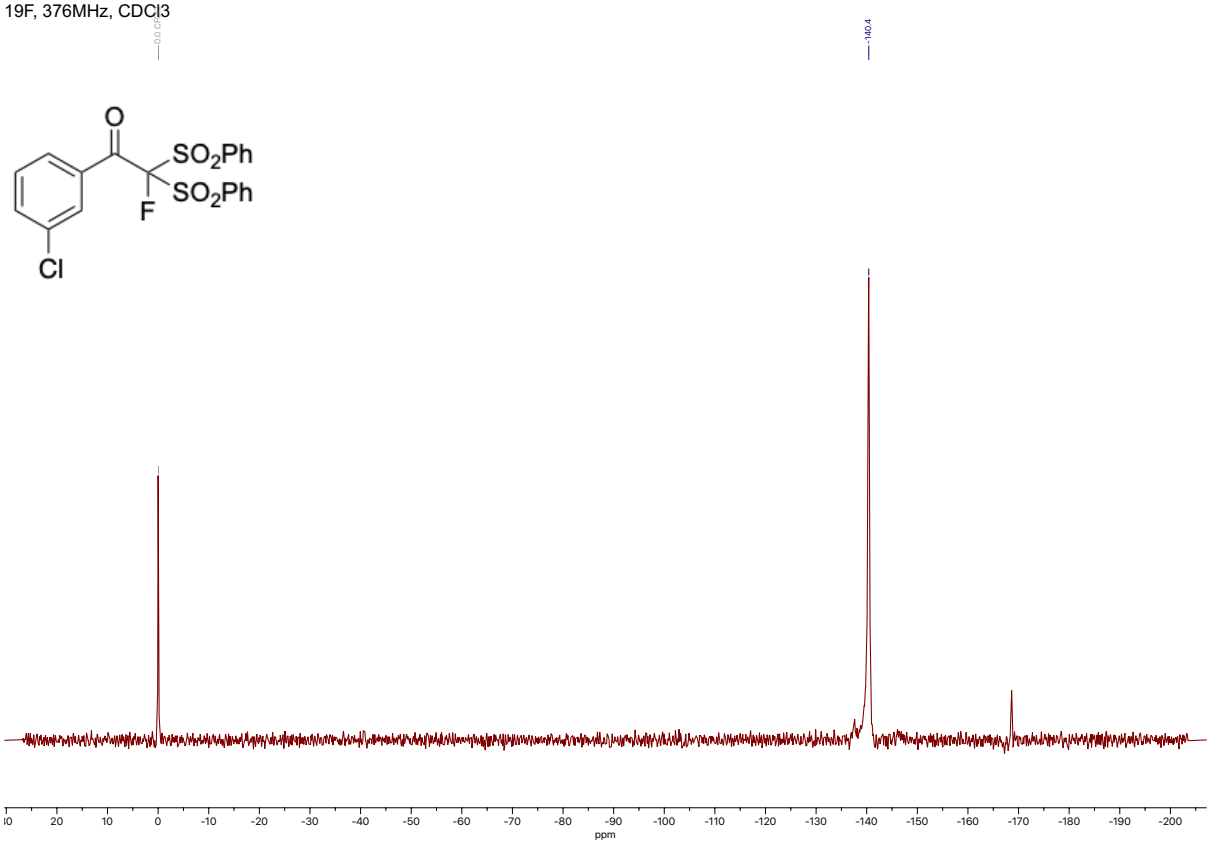

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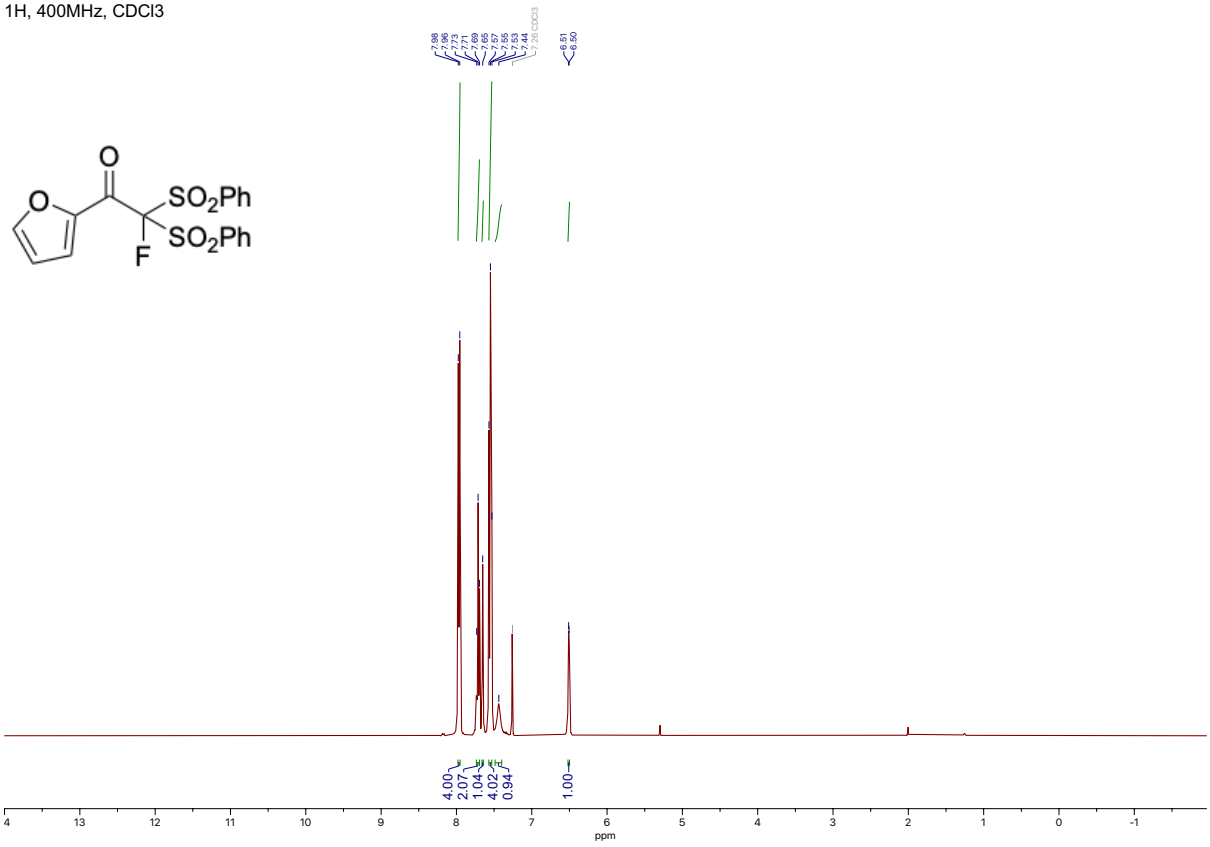

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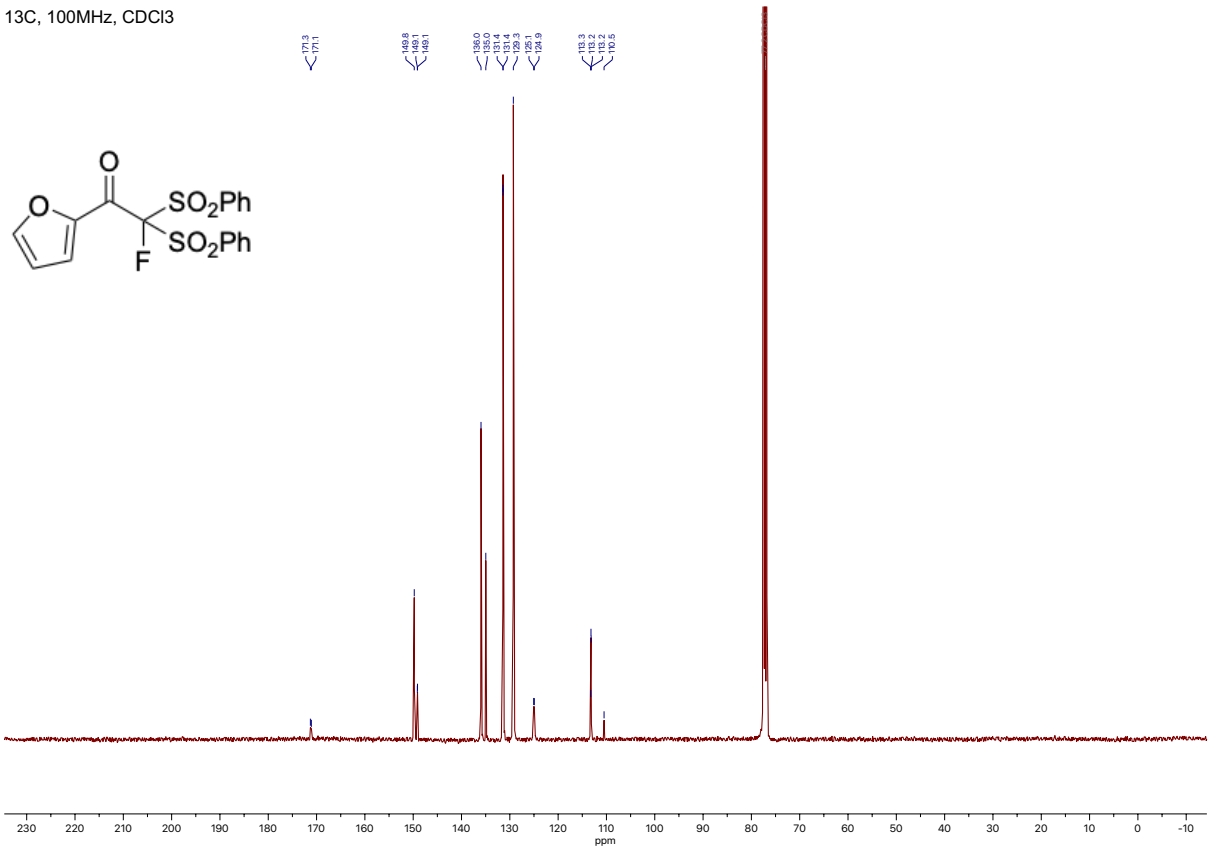

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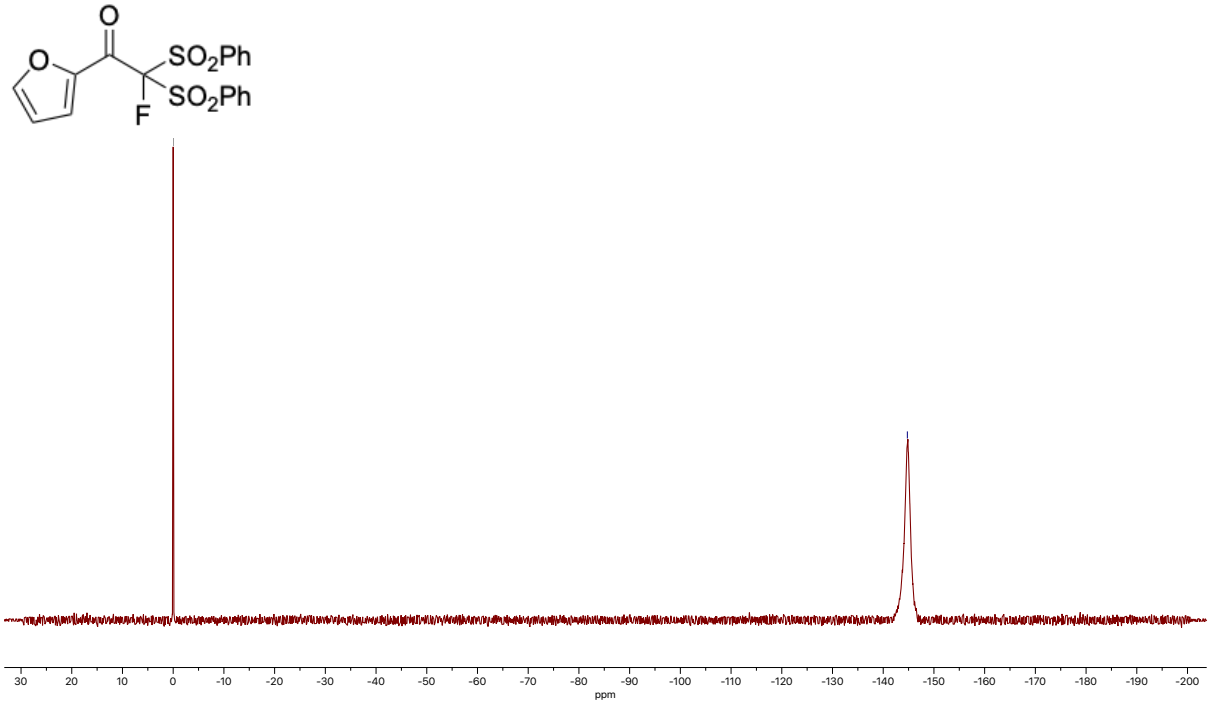

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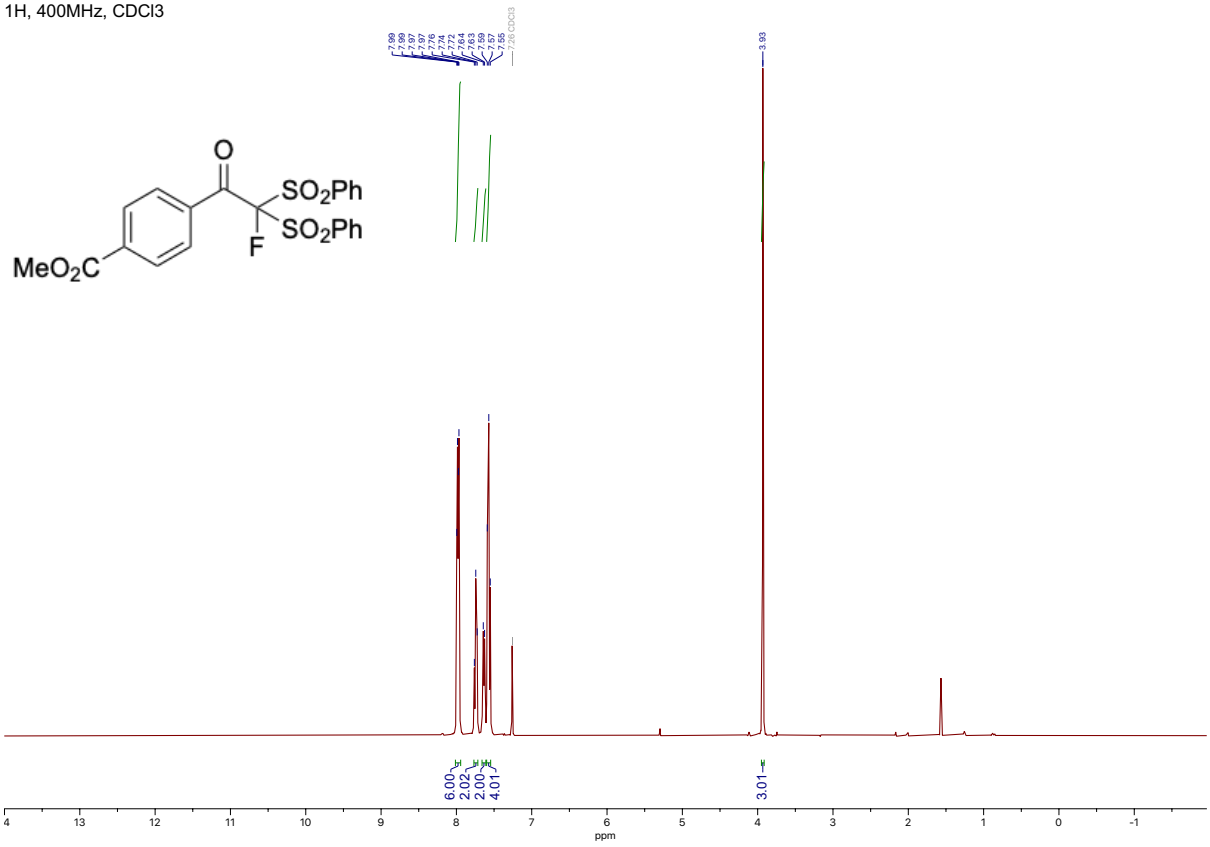

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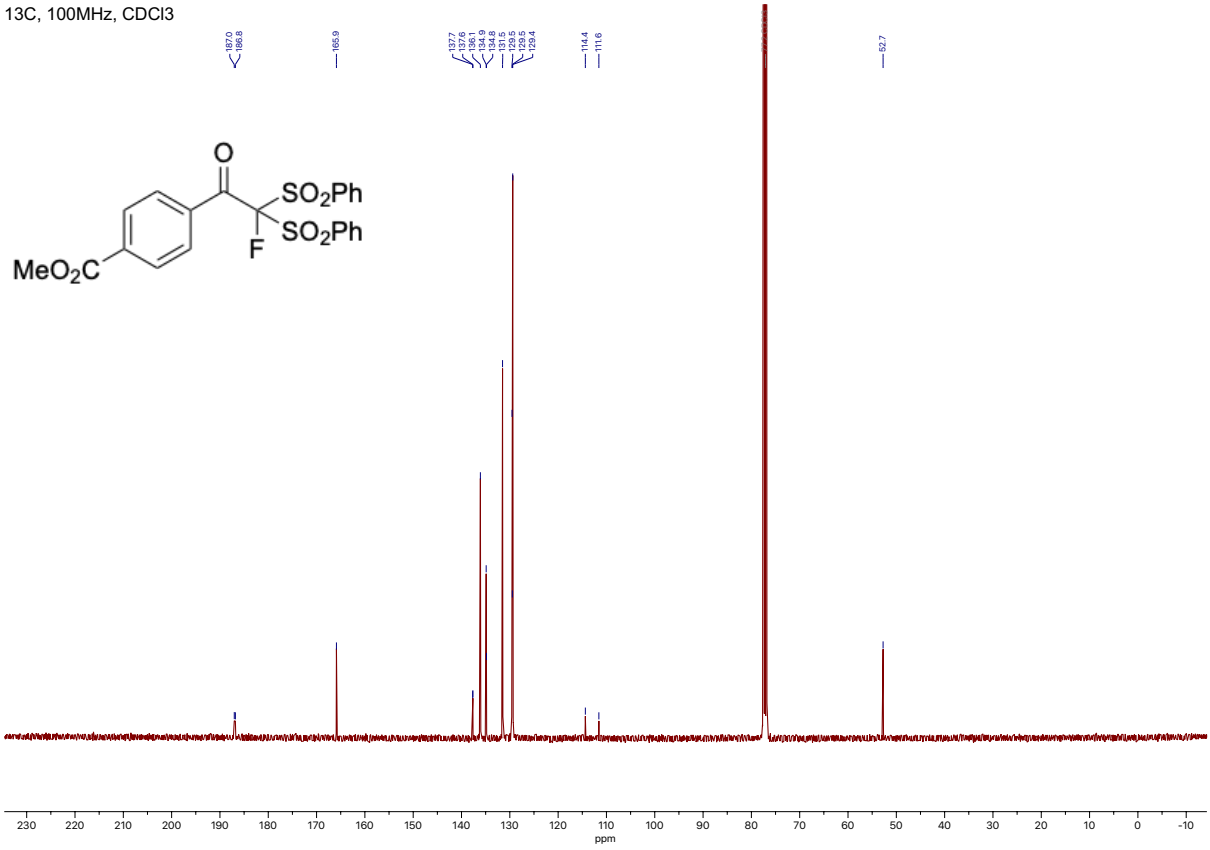

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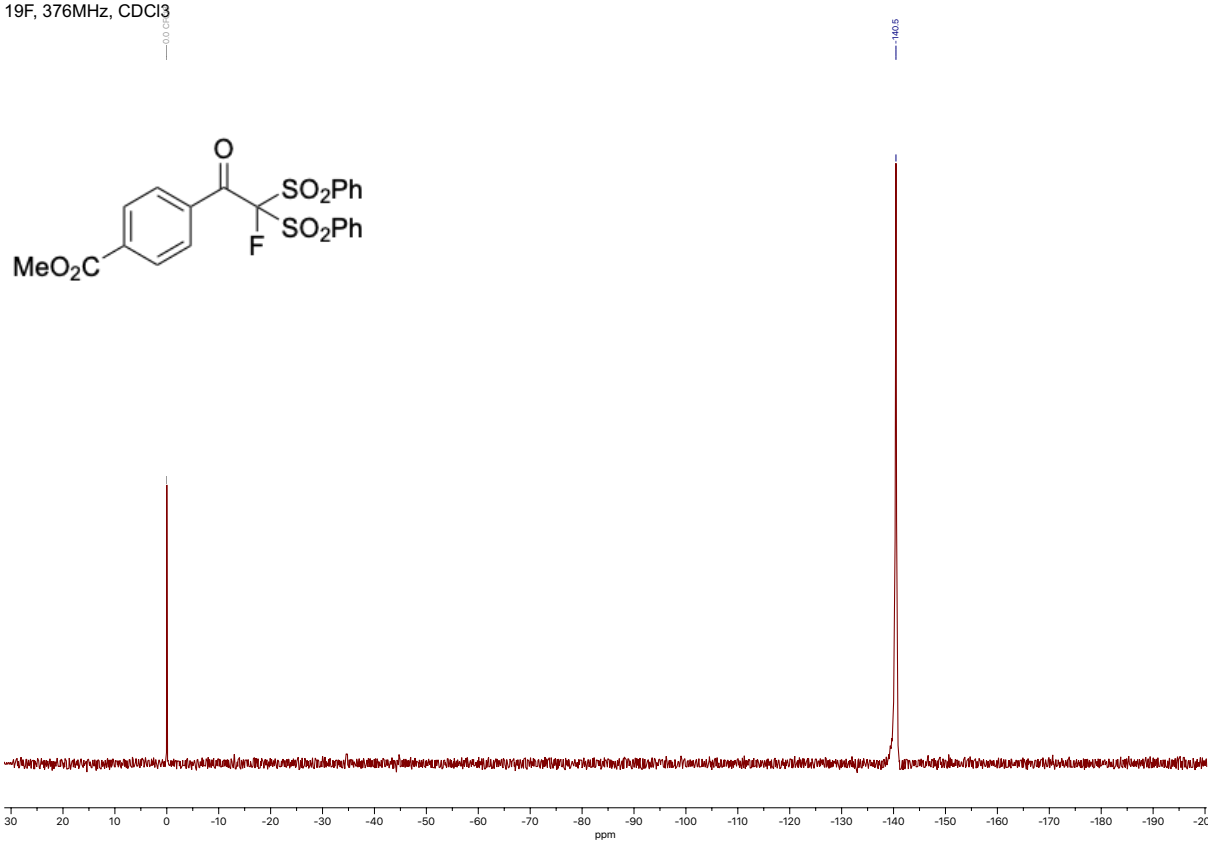

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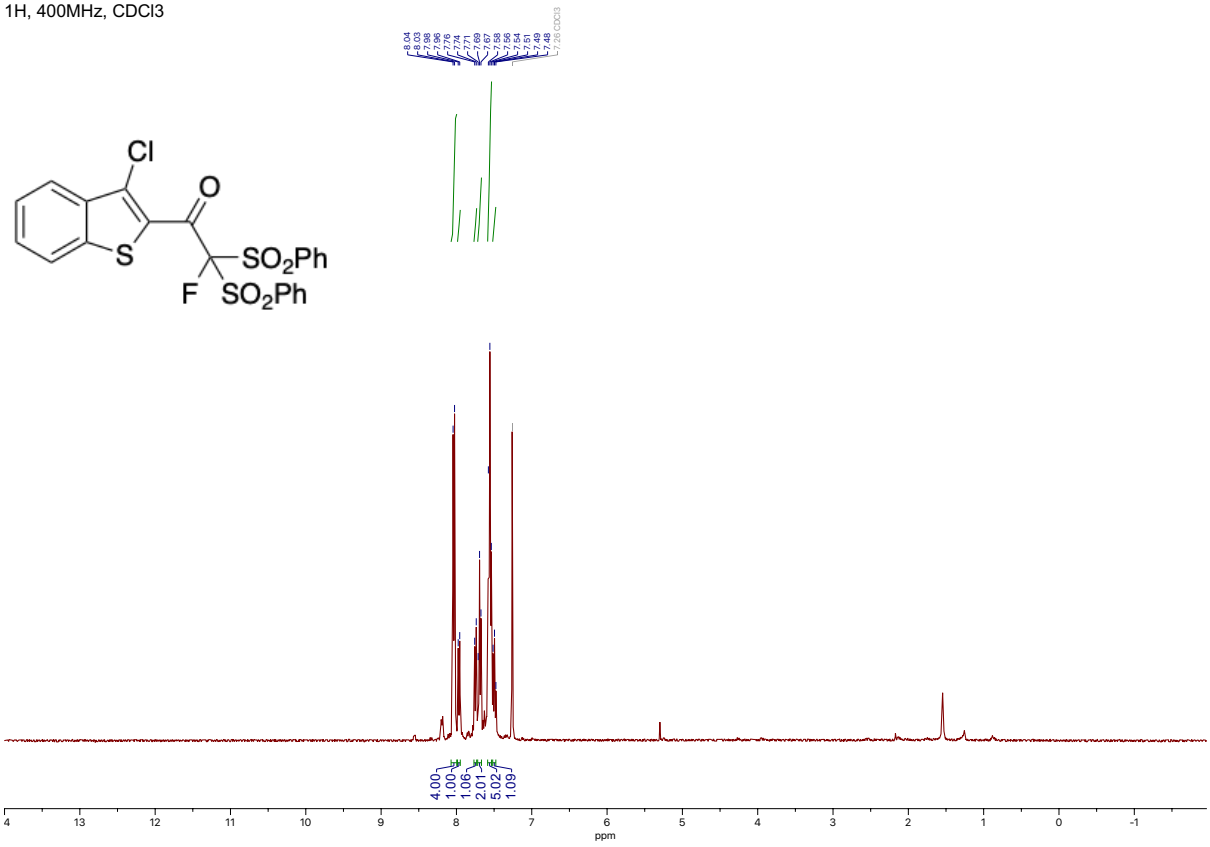

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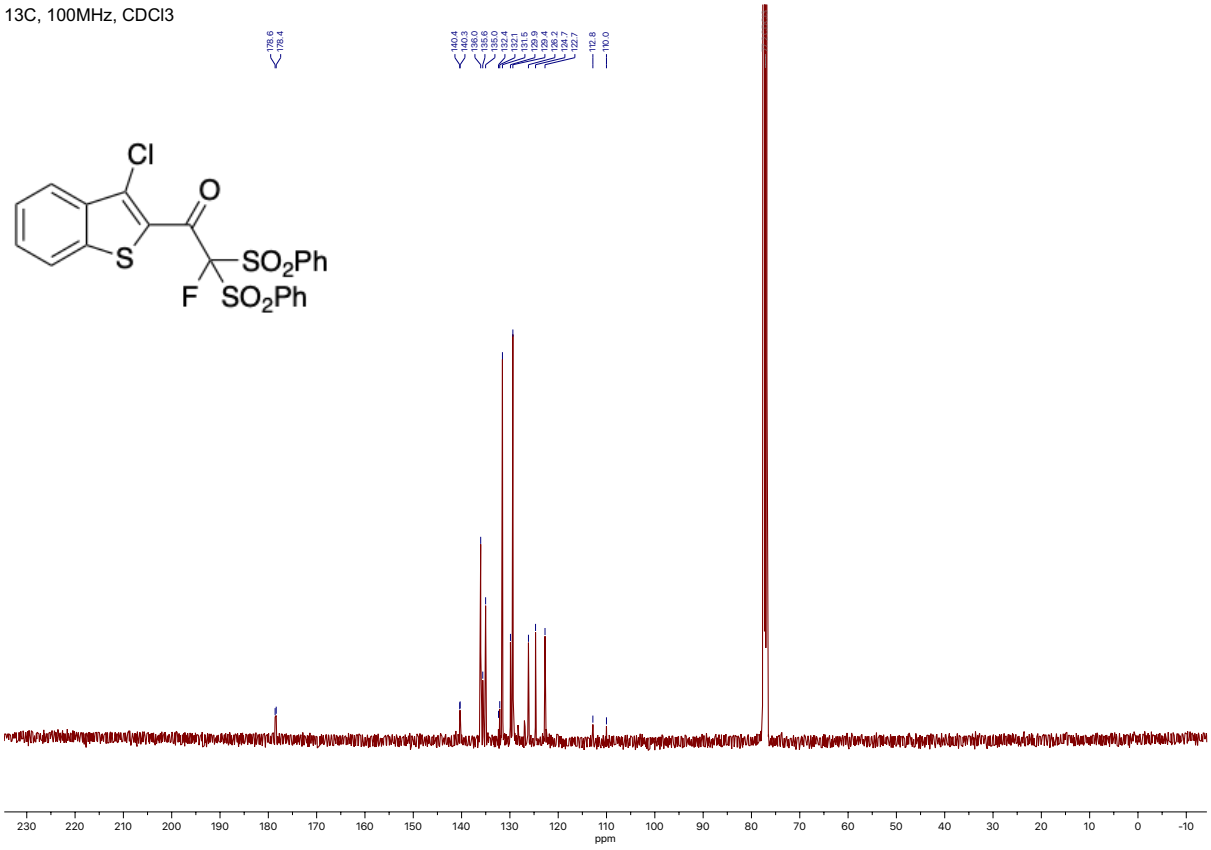

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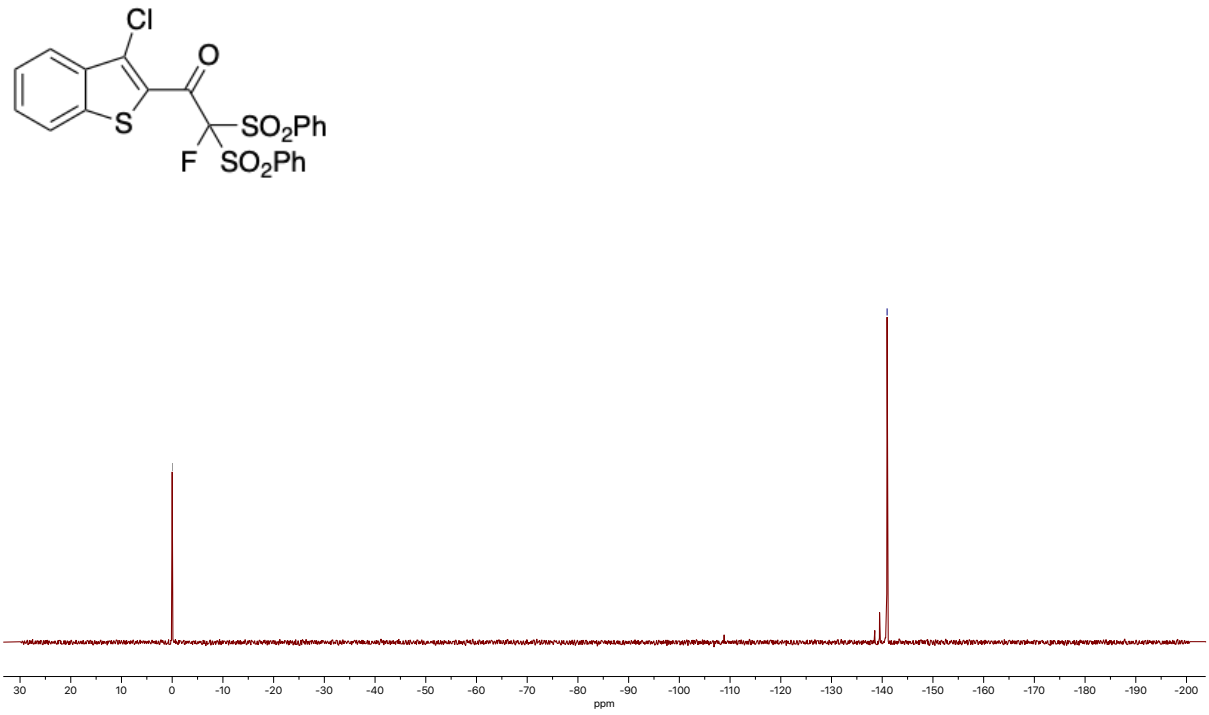

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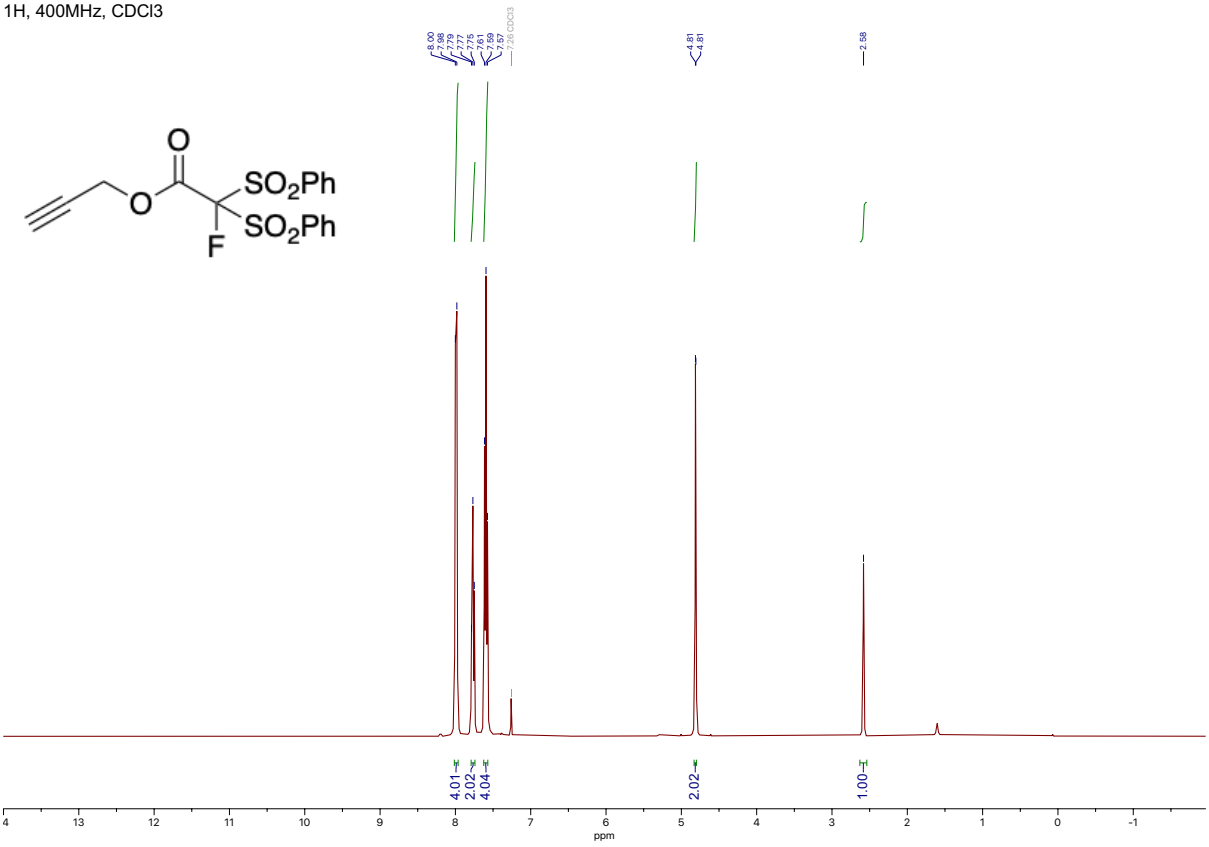

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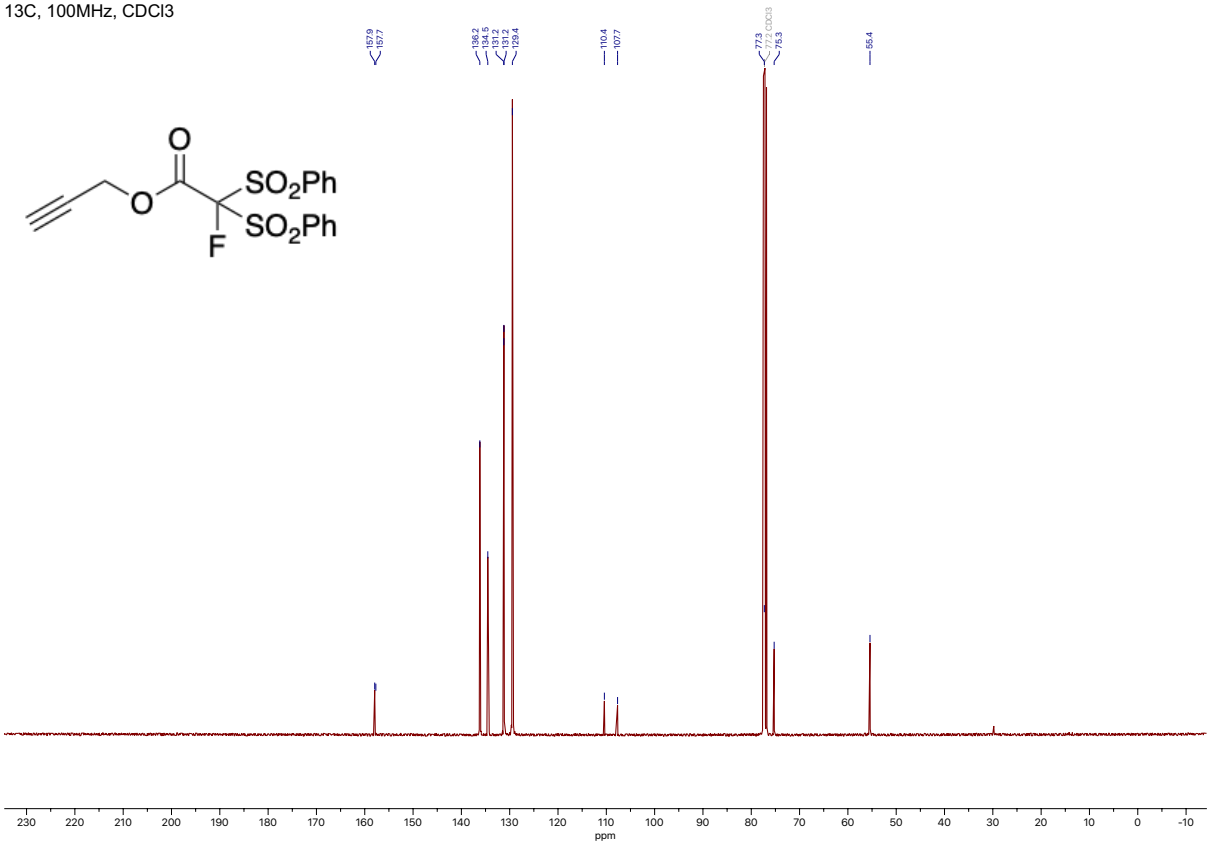

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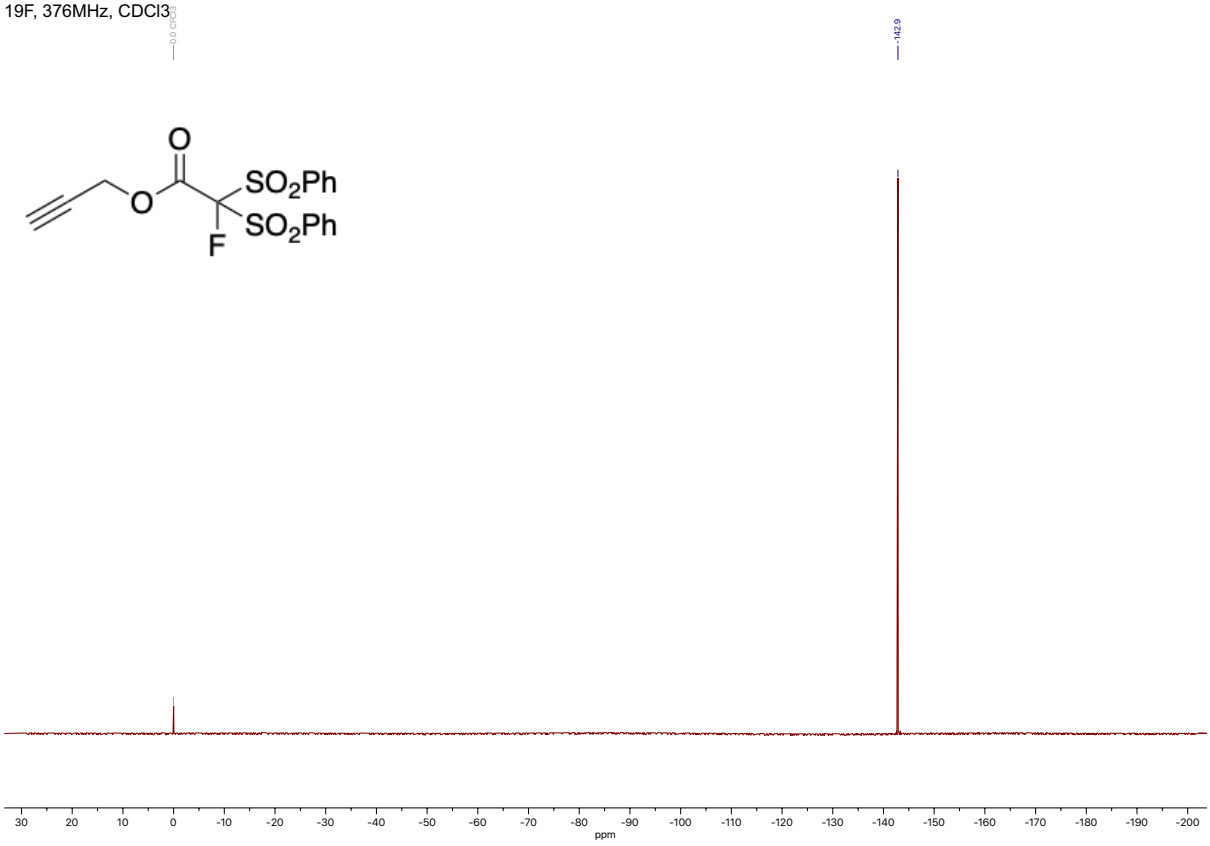

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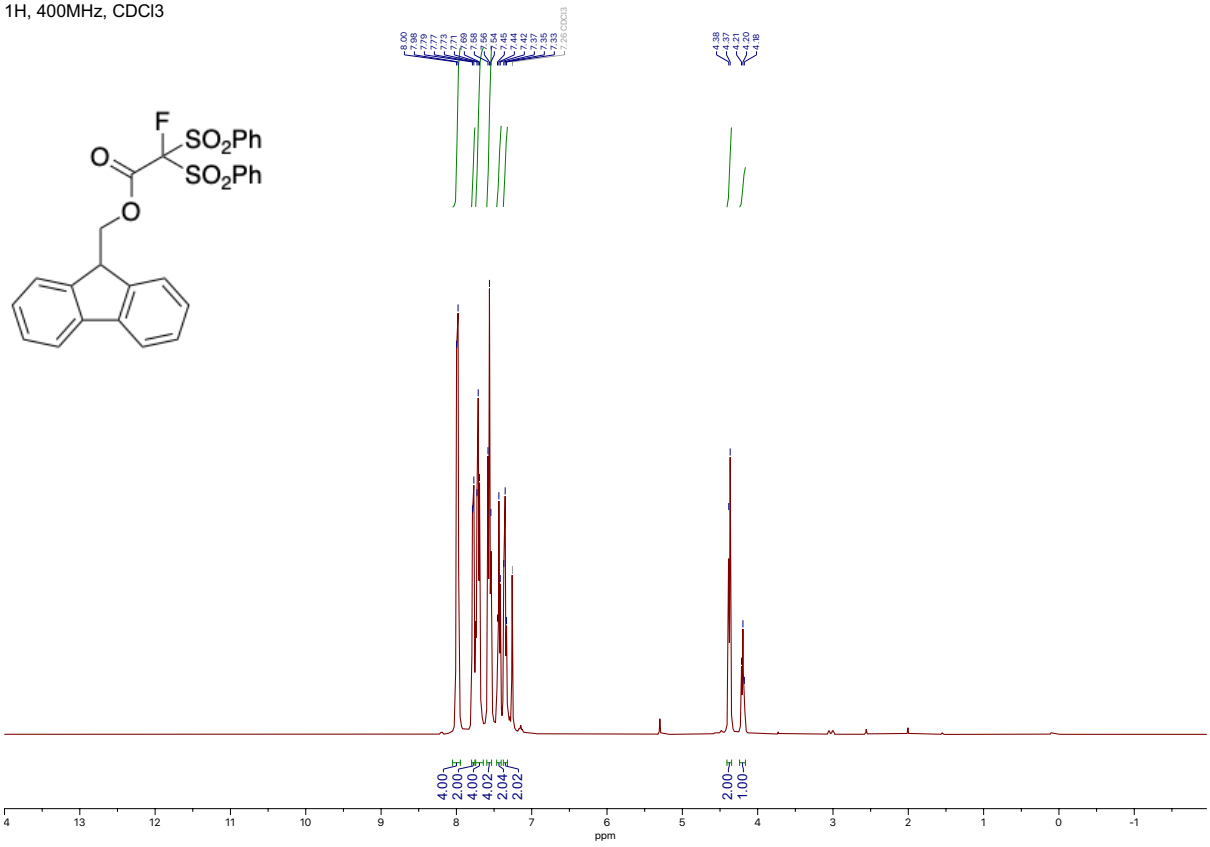

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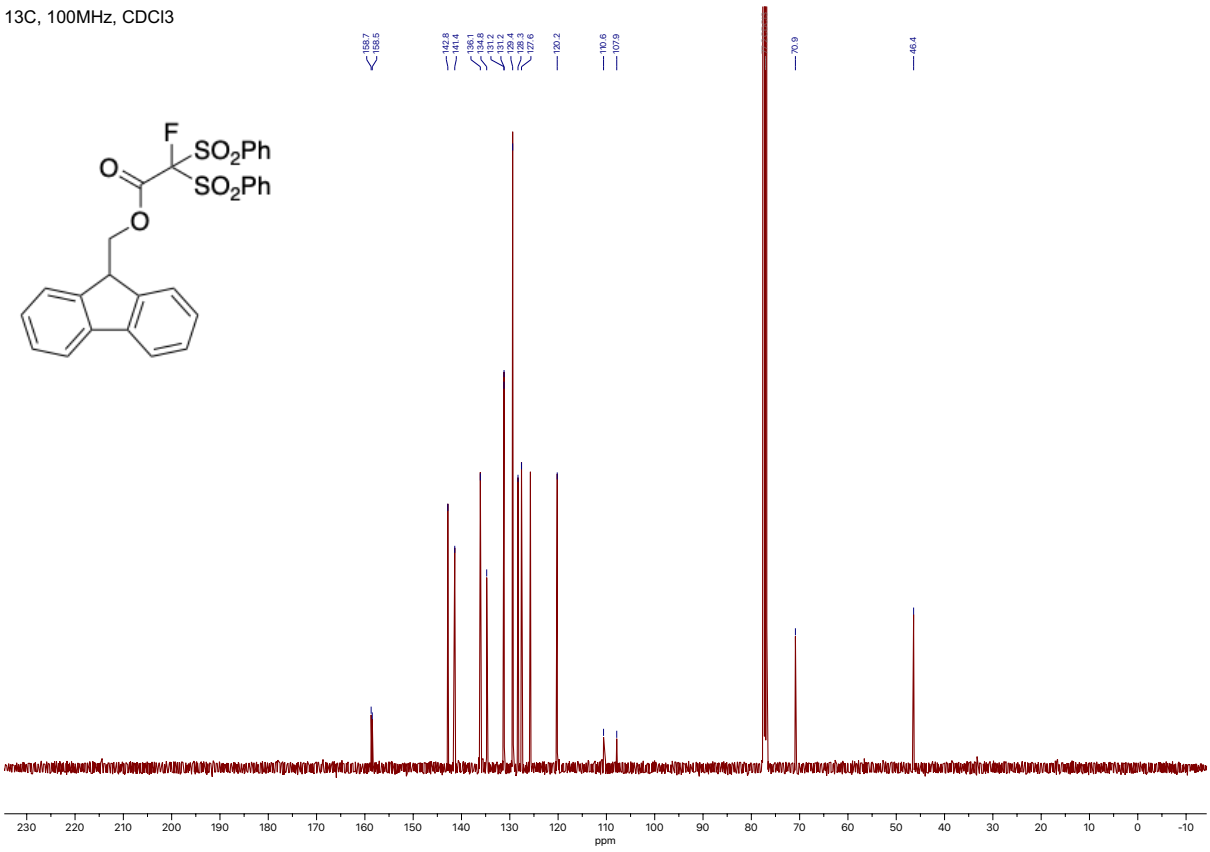

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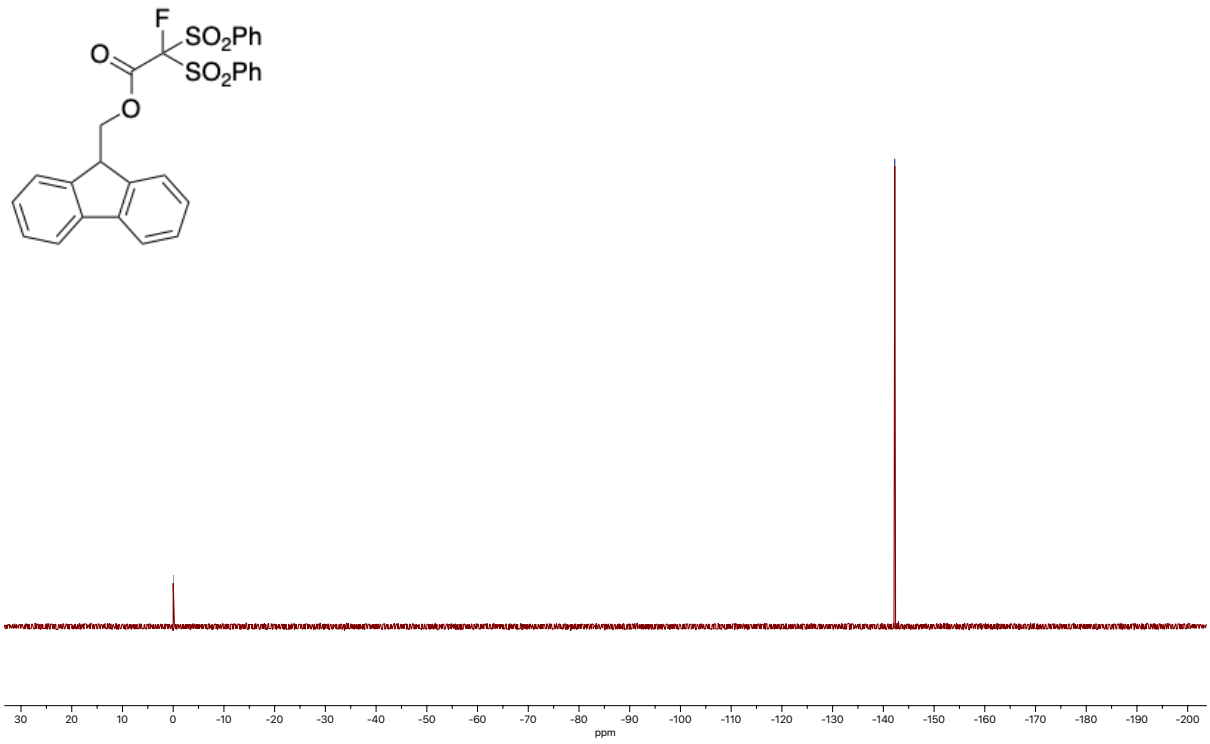

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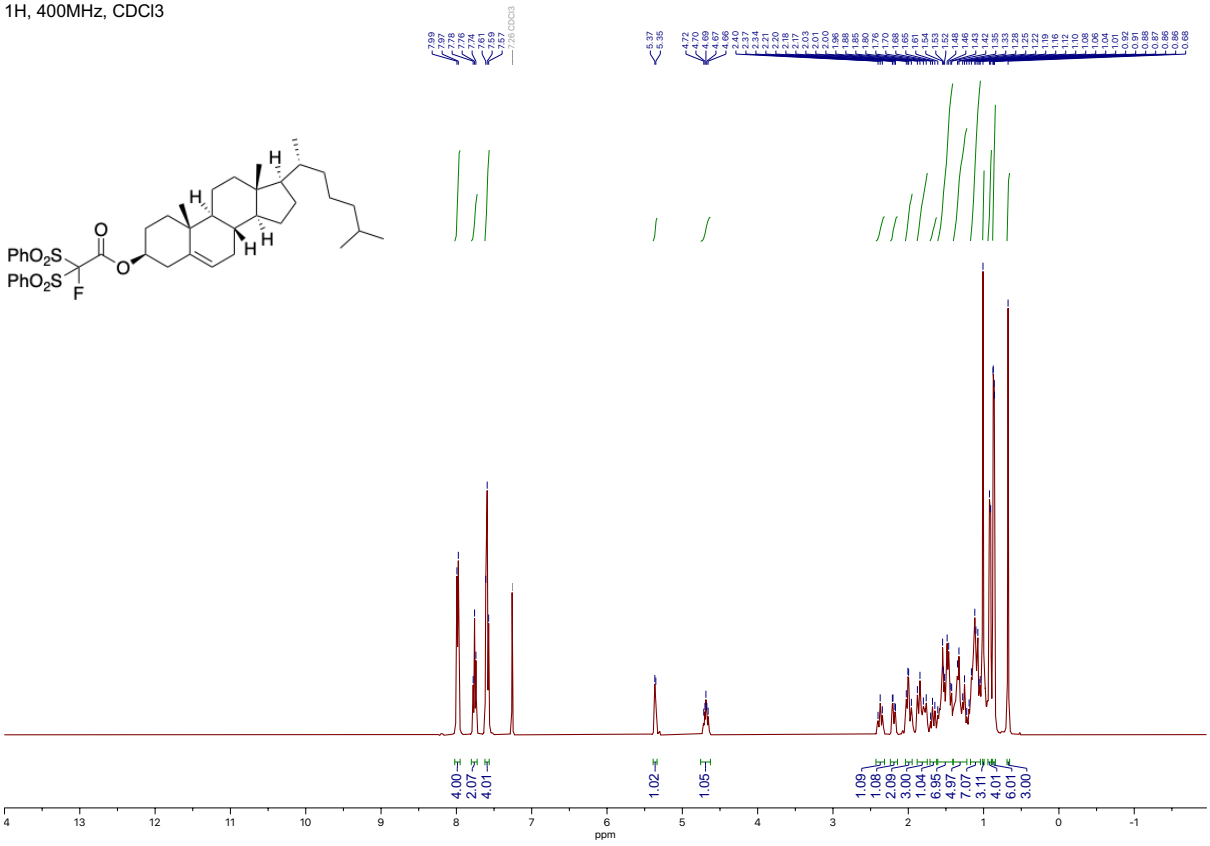
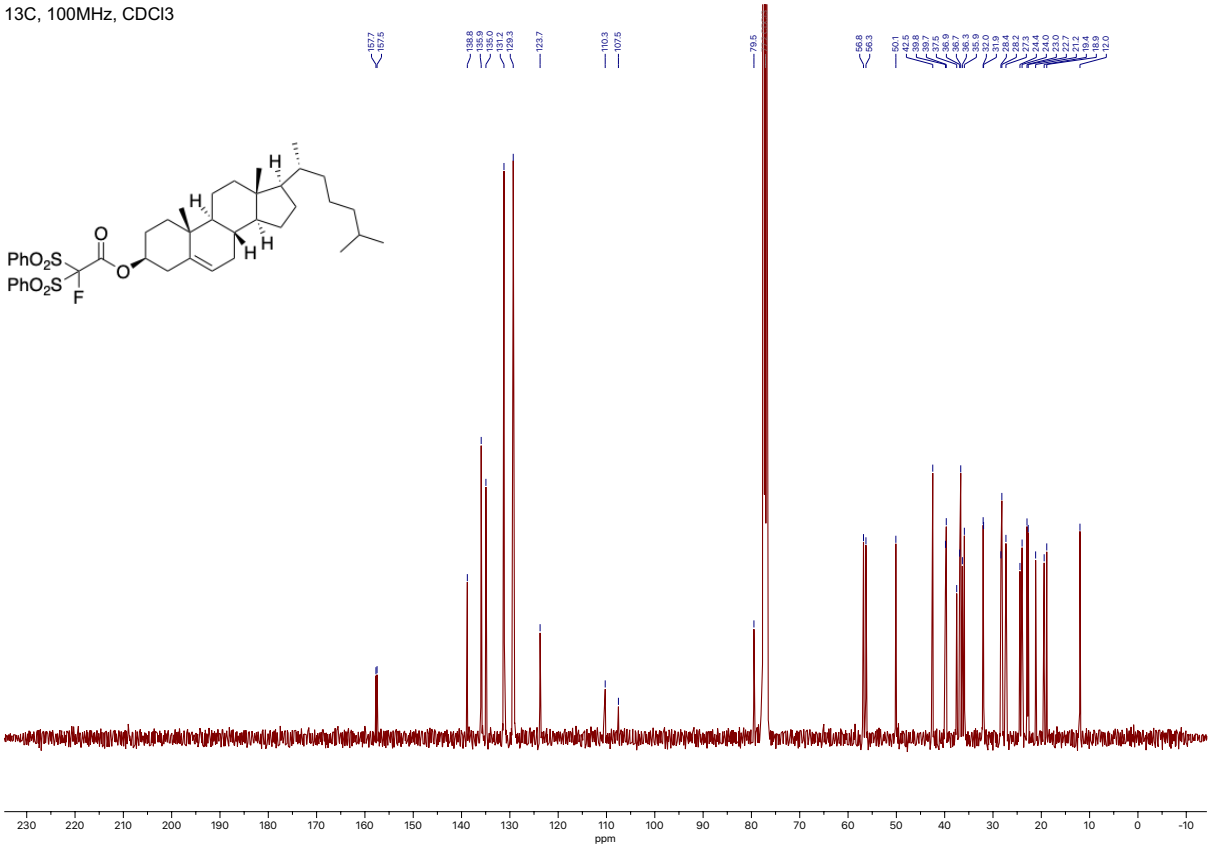
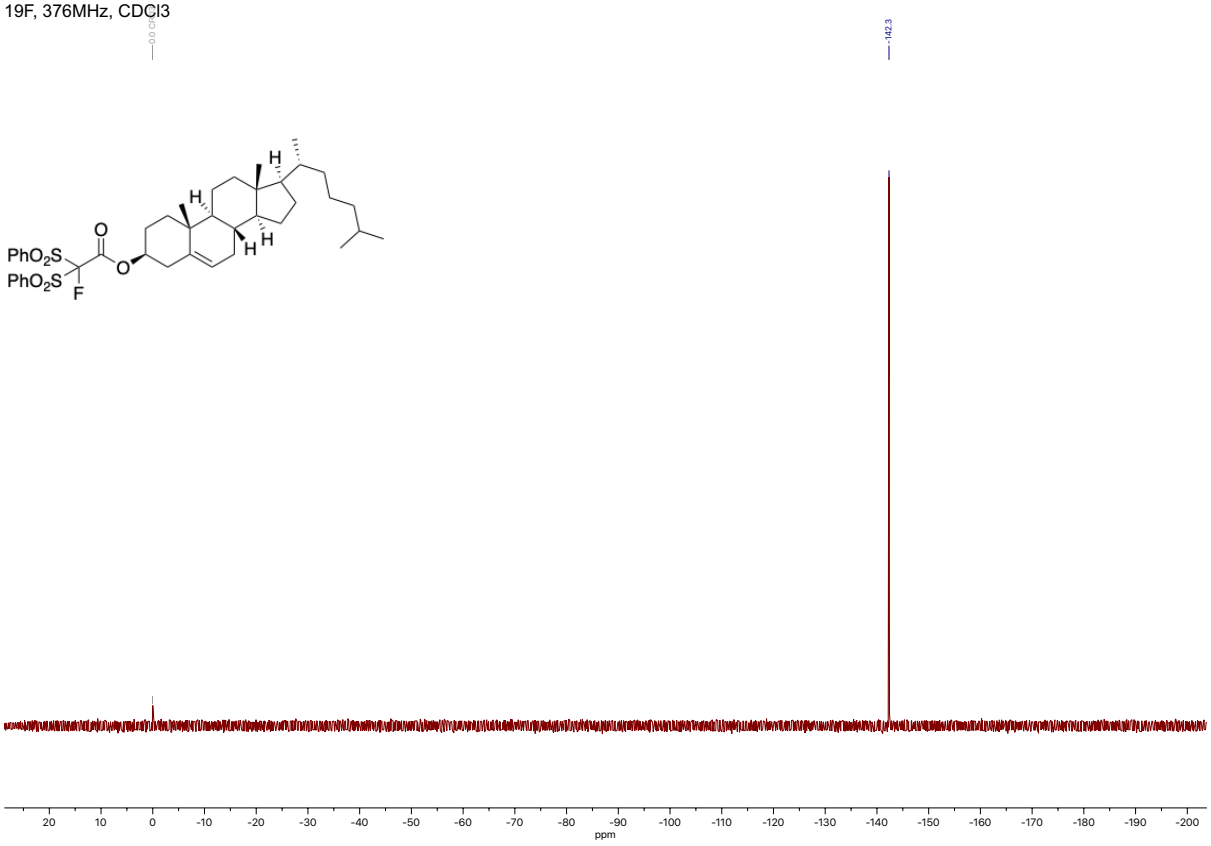


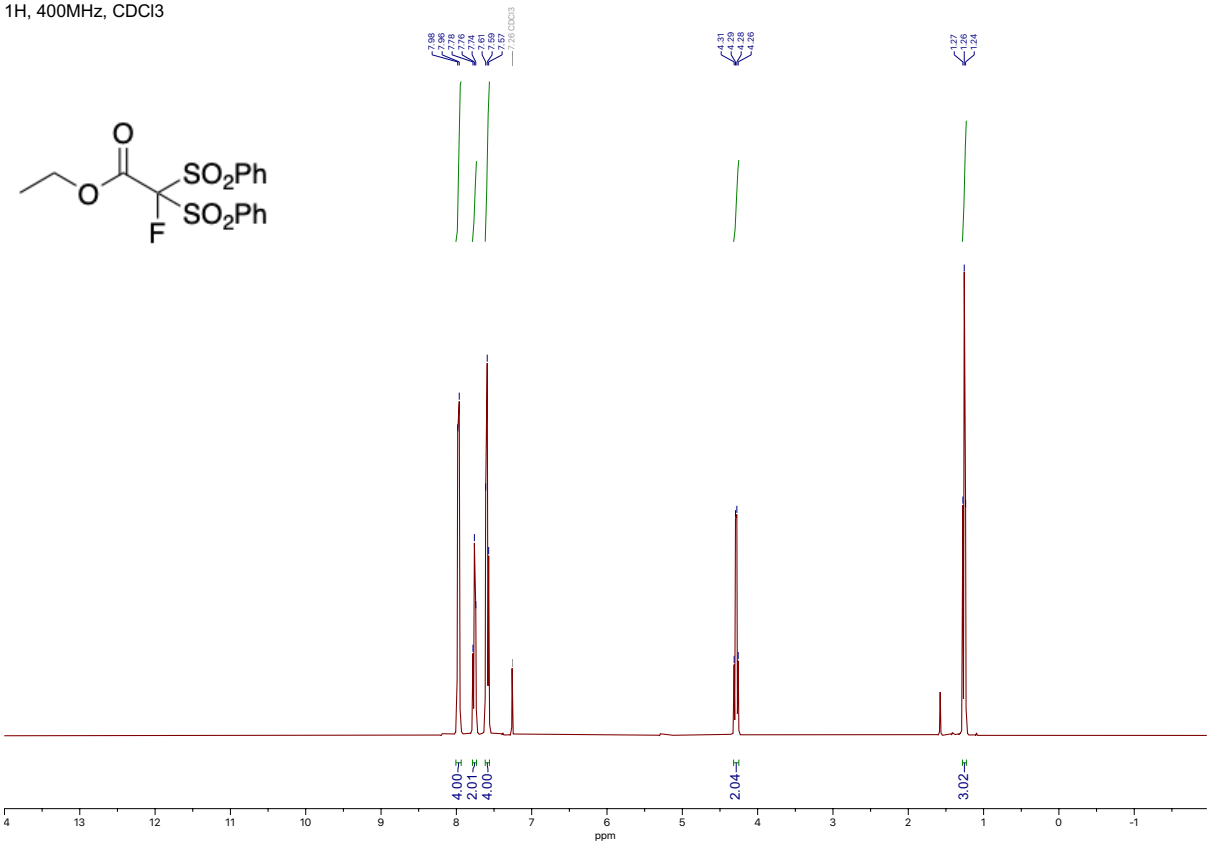
13C, 100MHz, CDCl3



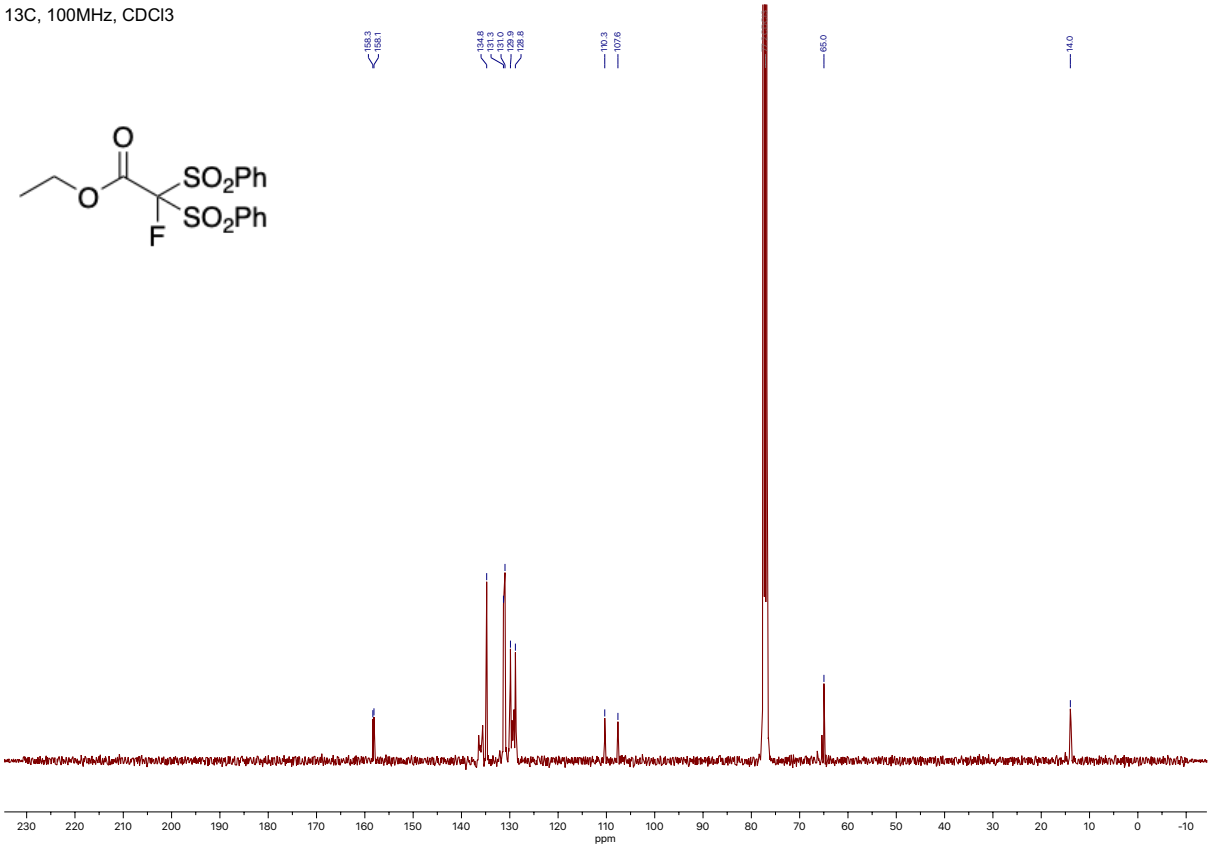
19F, 376MHz, CDCl3



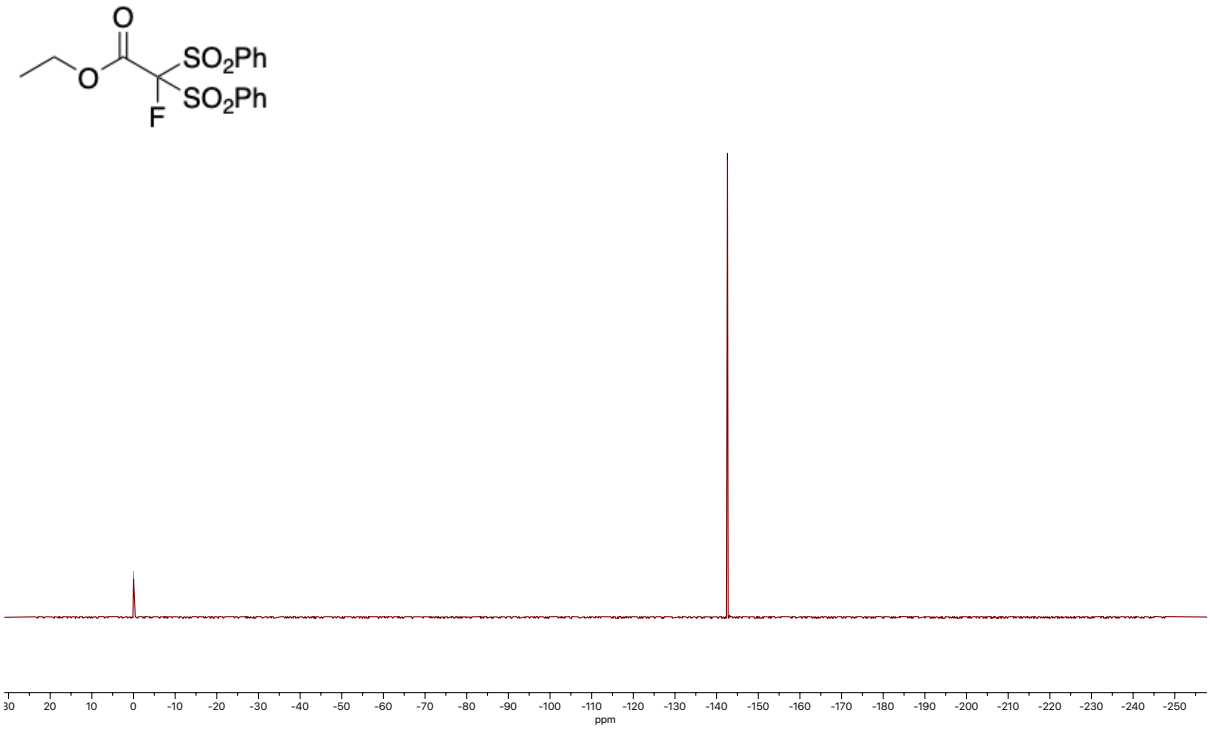
1H, 400MHz, CDCl3



13C, 100MHz, CDCl3



19F, 376MHz, CDCl3



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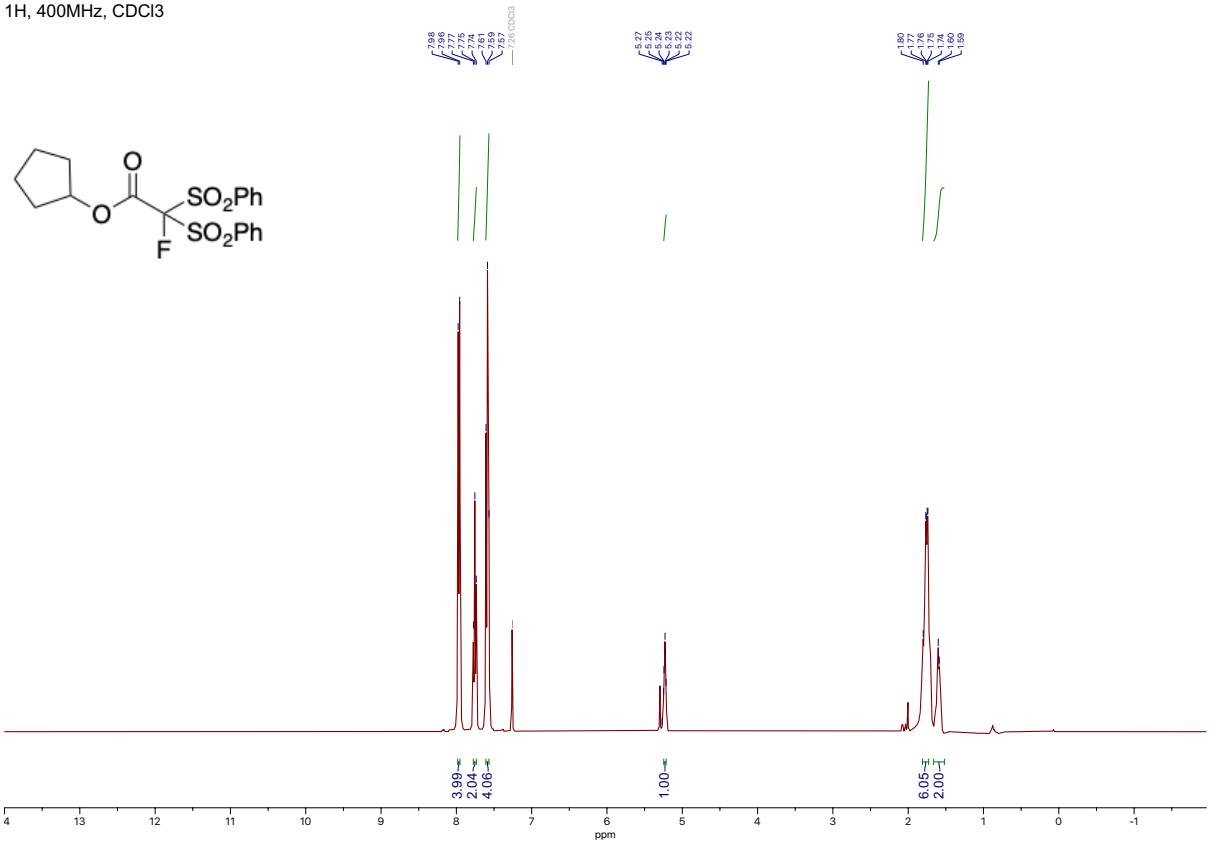

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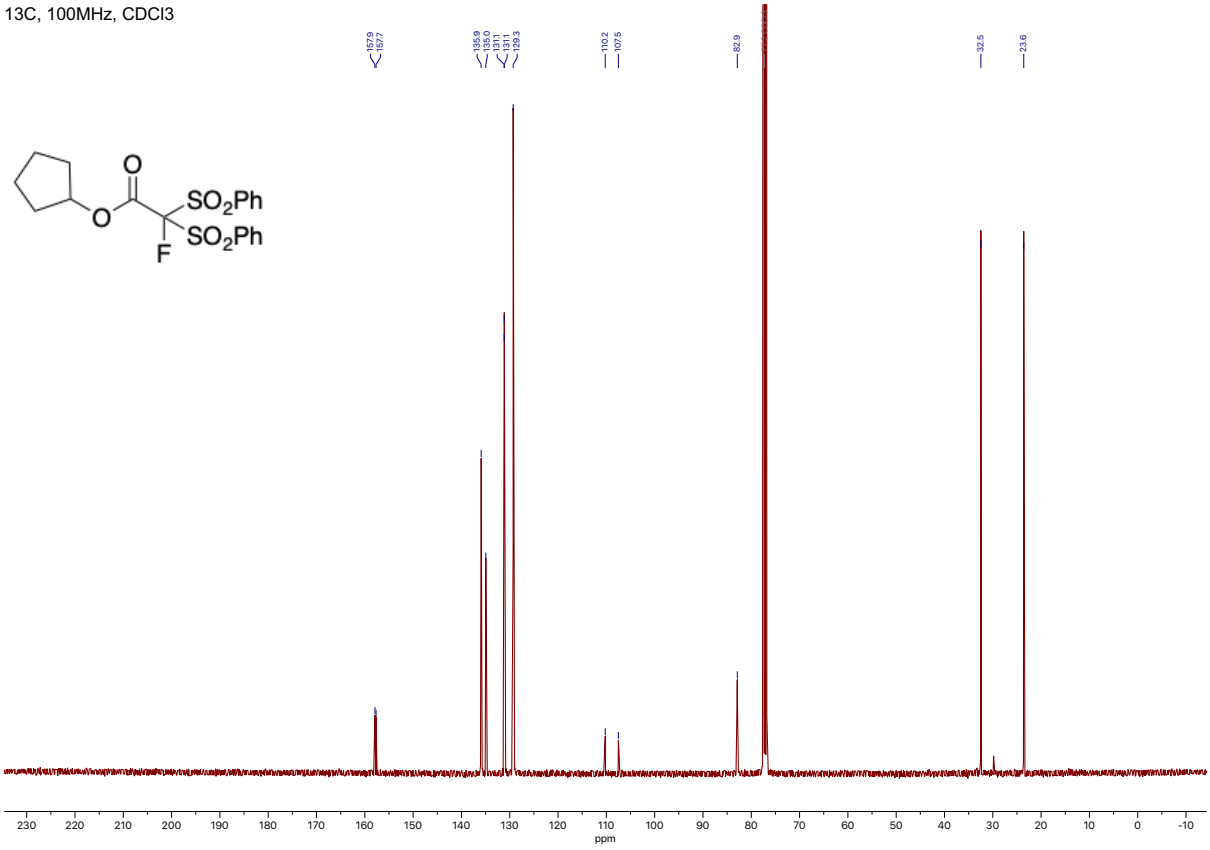

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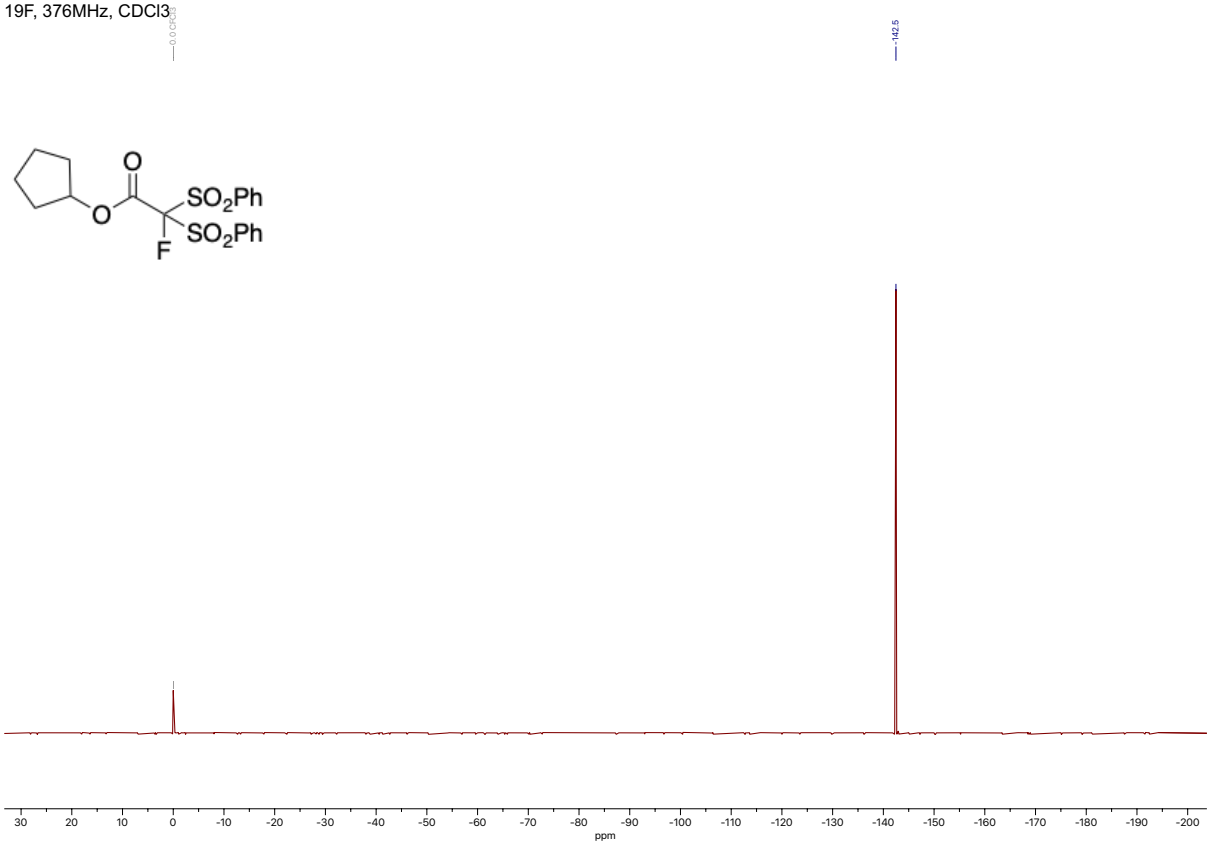

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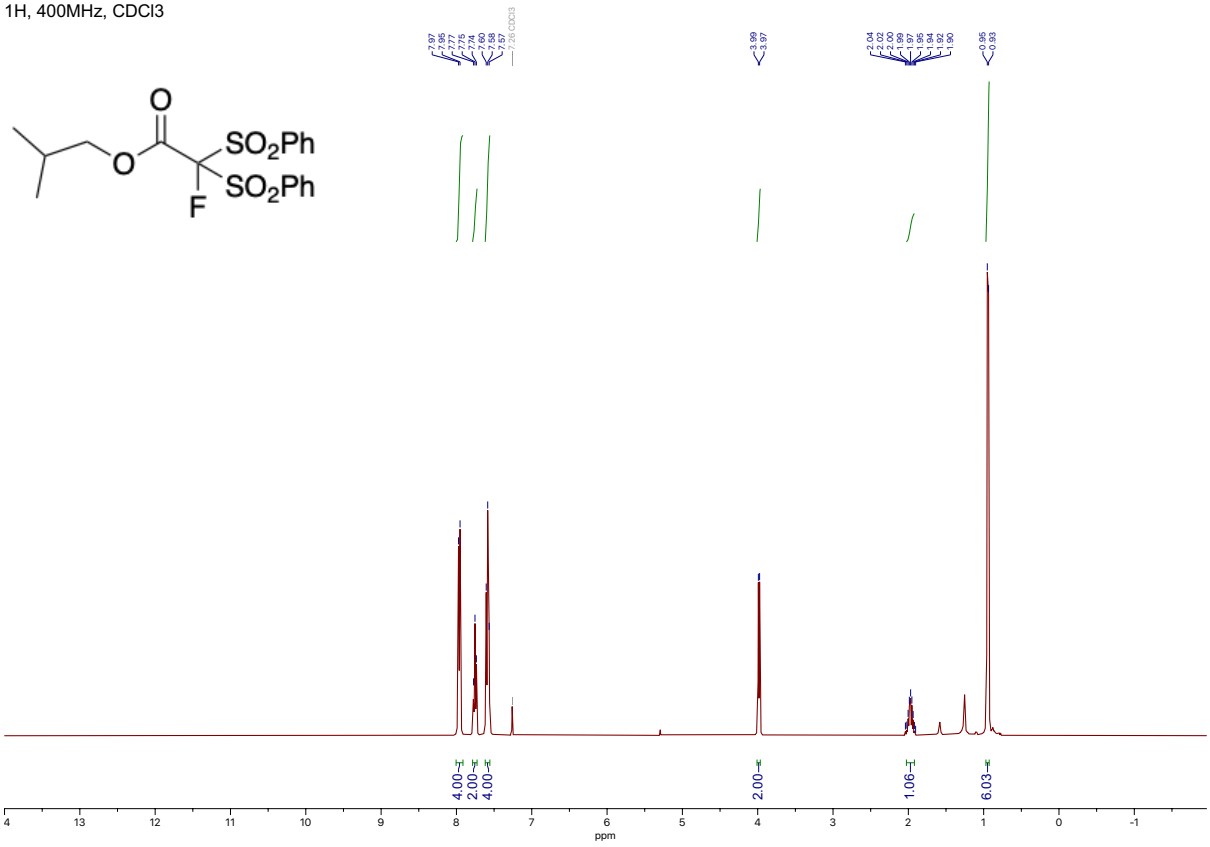

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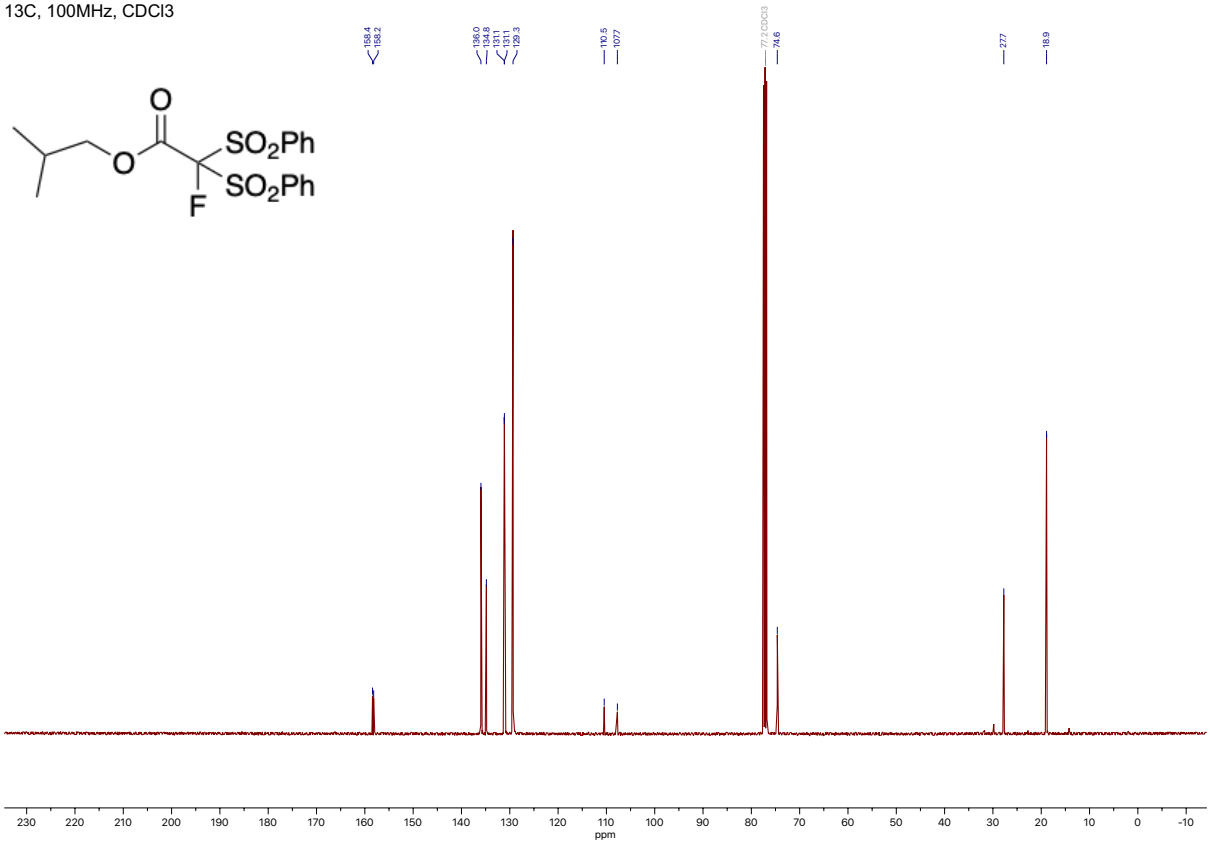

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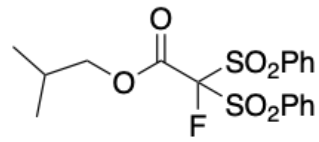

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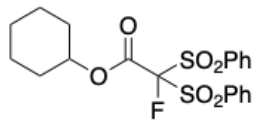

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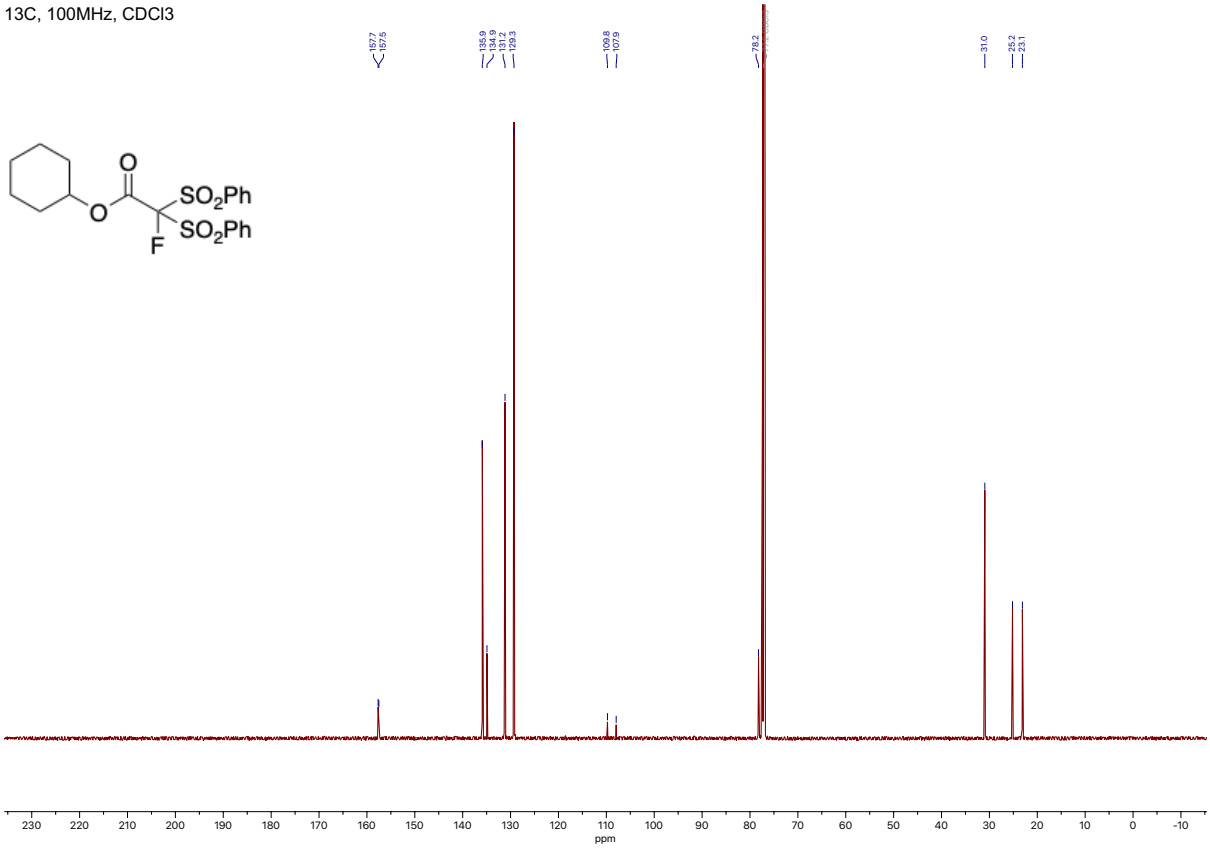

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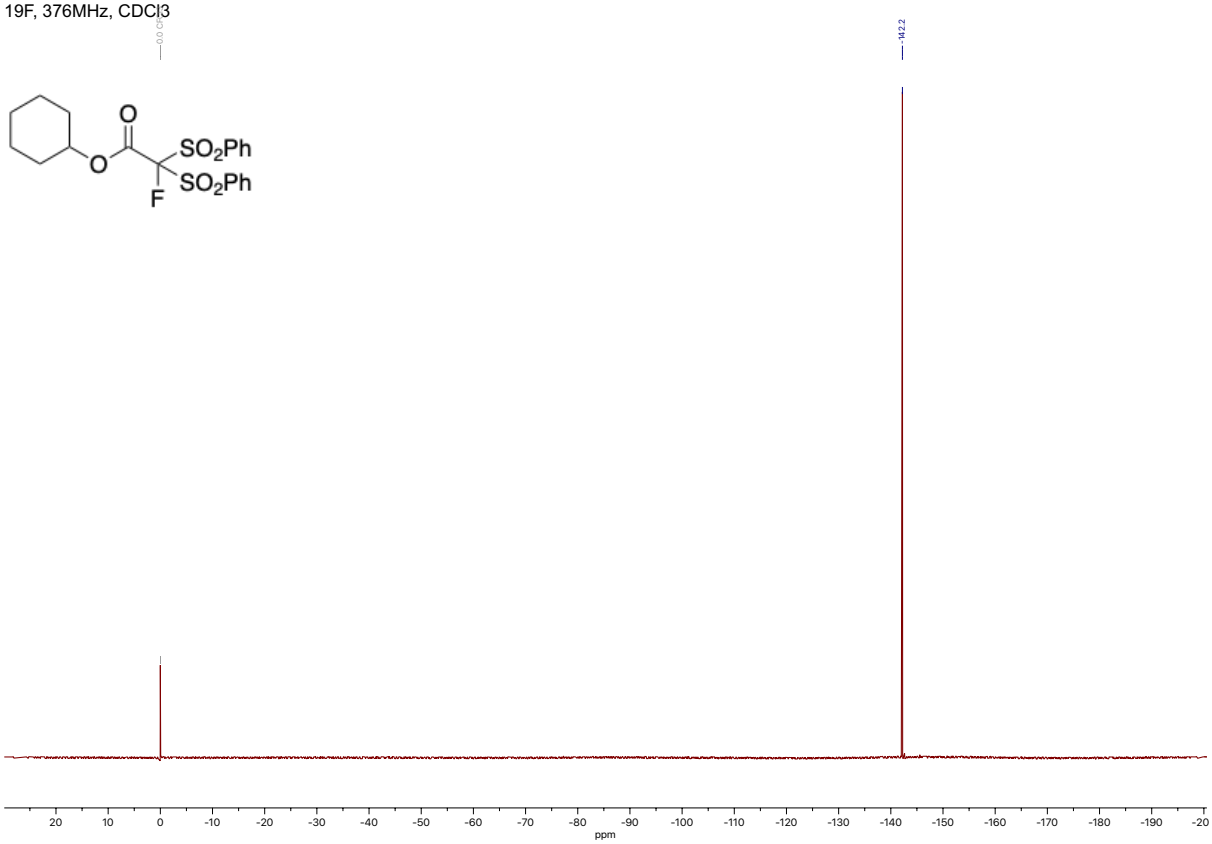

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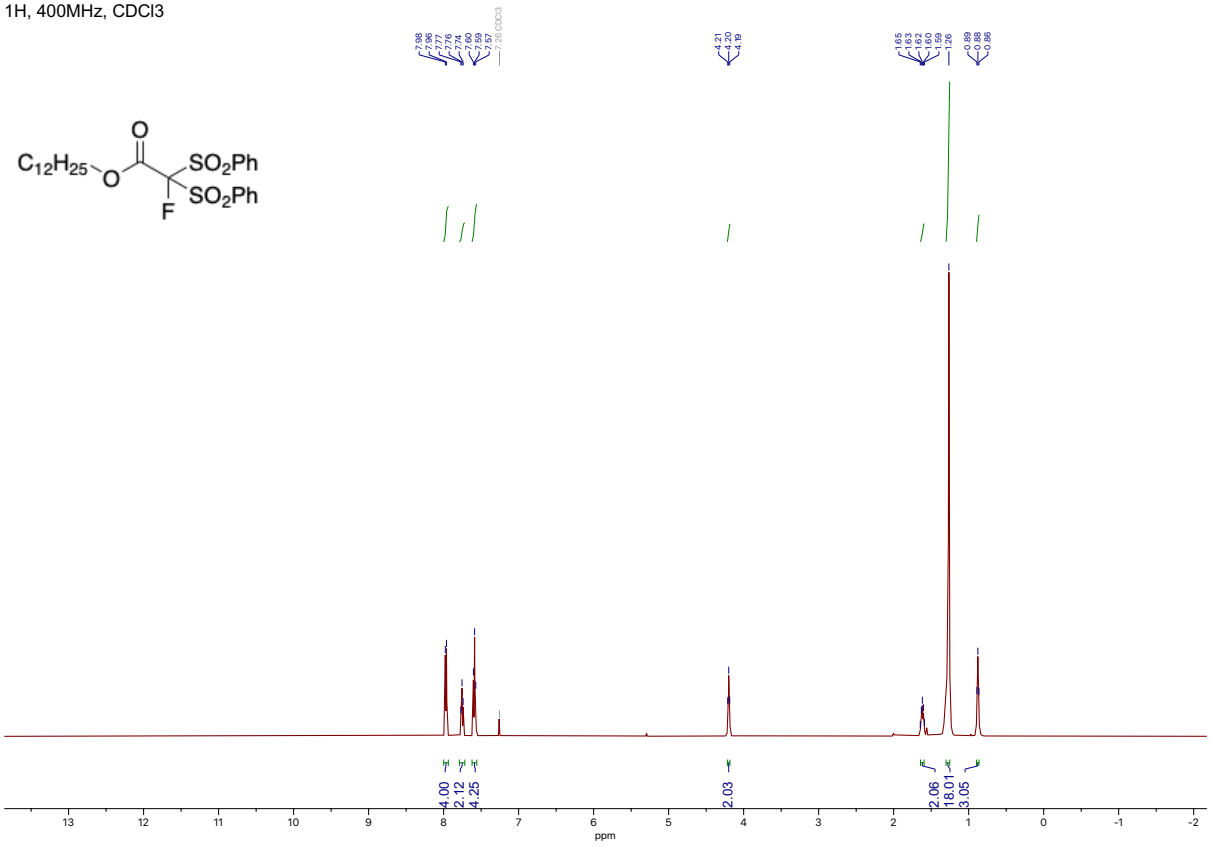
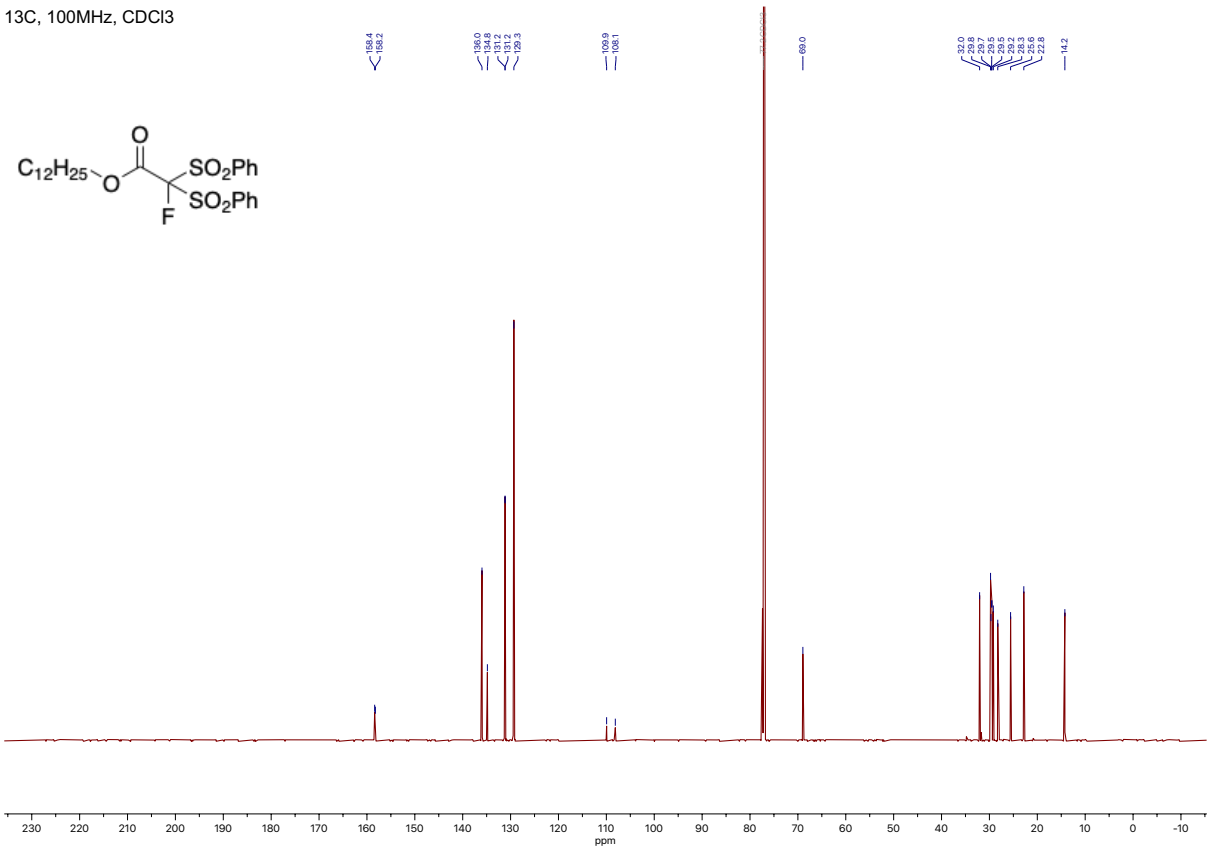


13C, 100MHz, CDCl3



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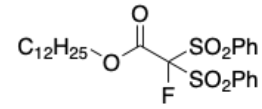

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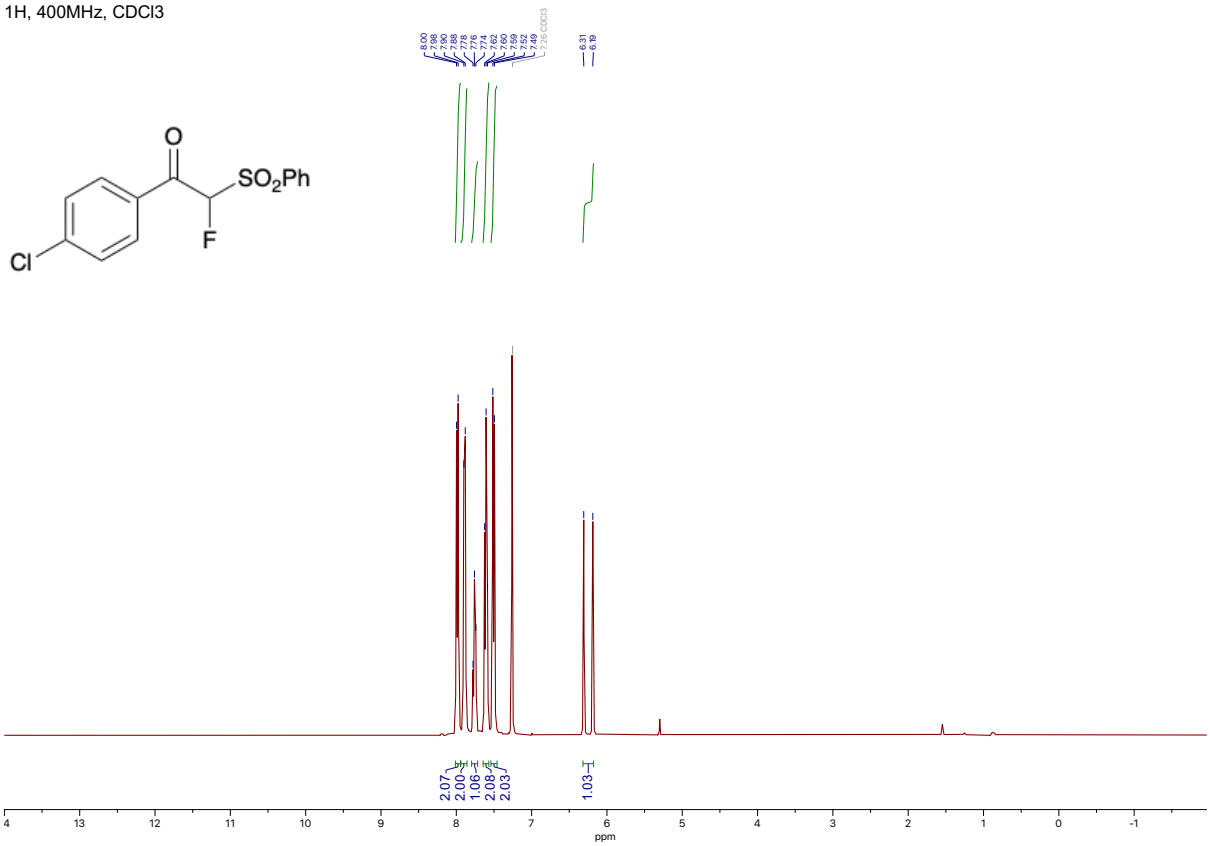

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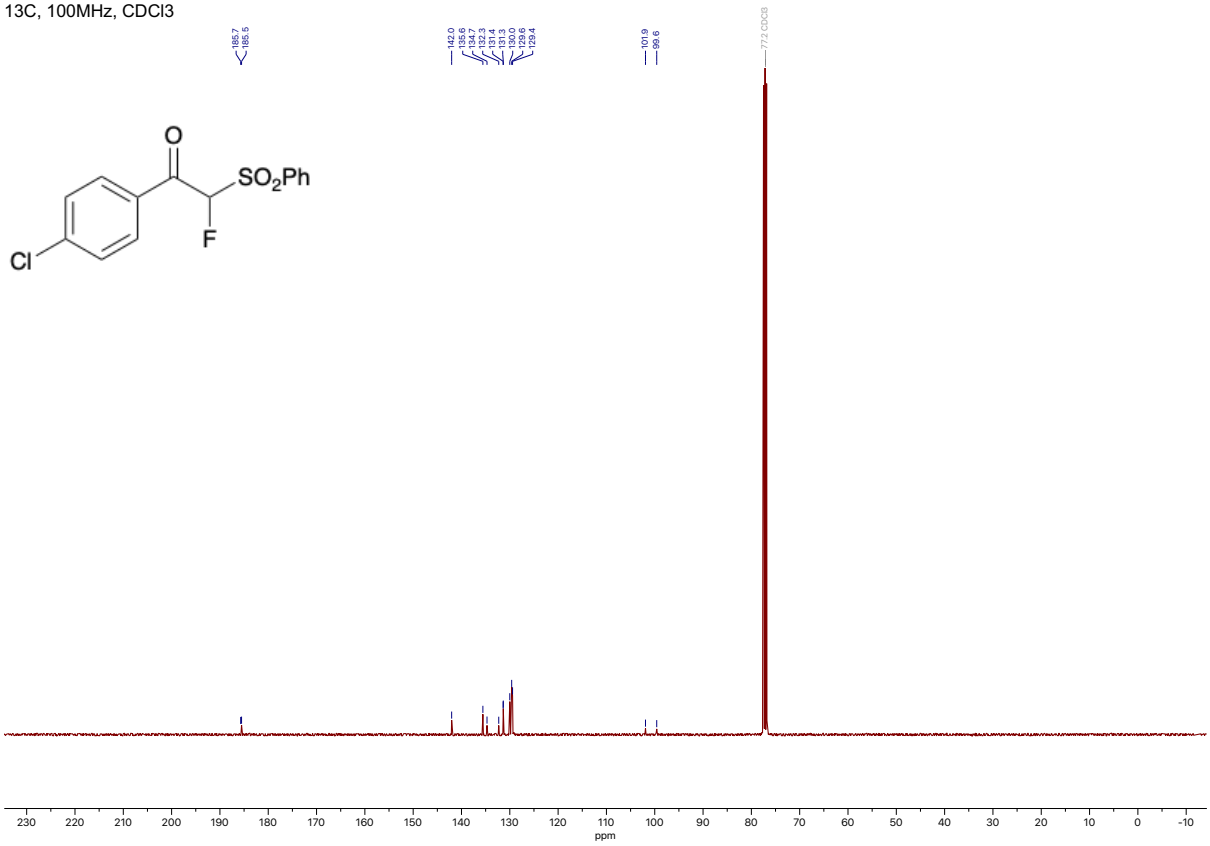

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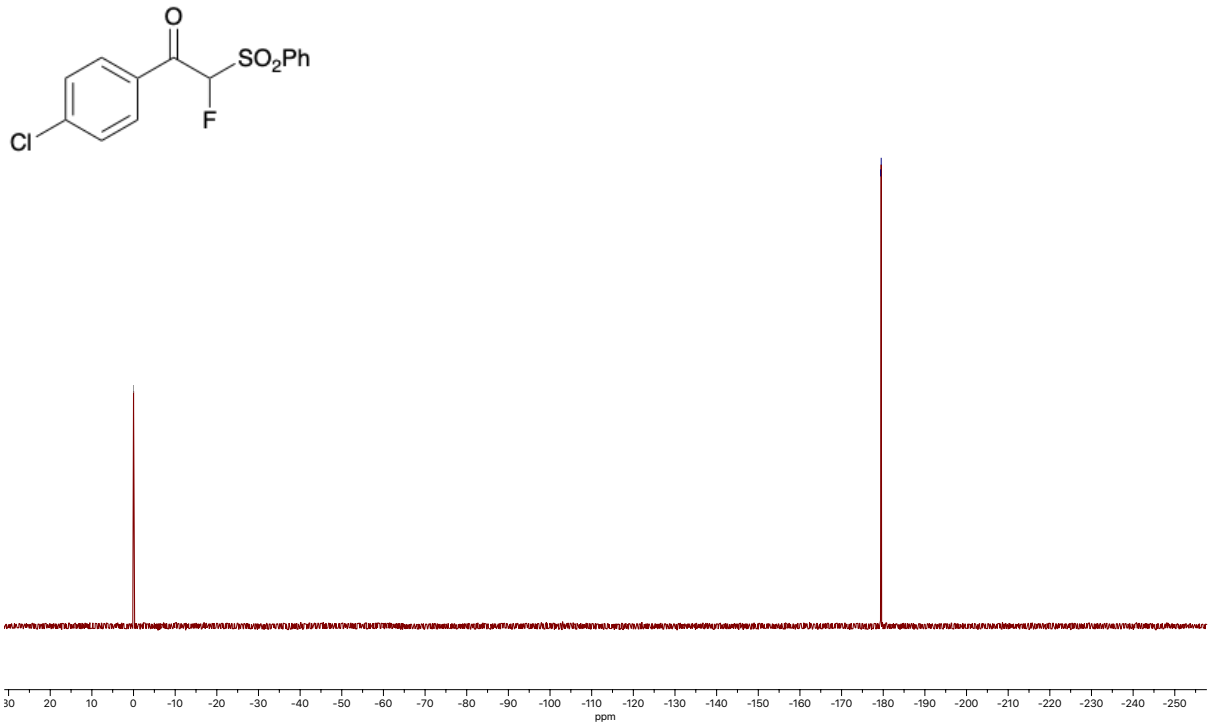

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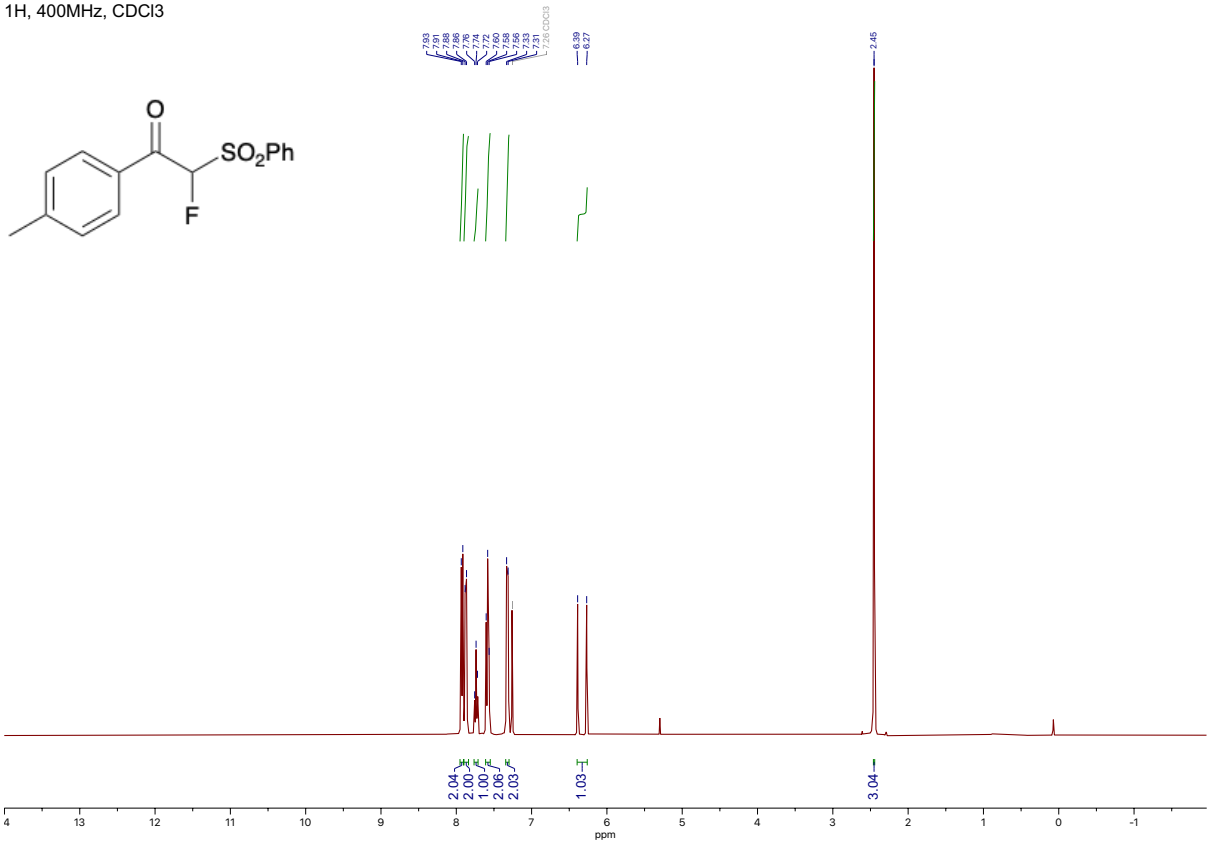

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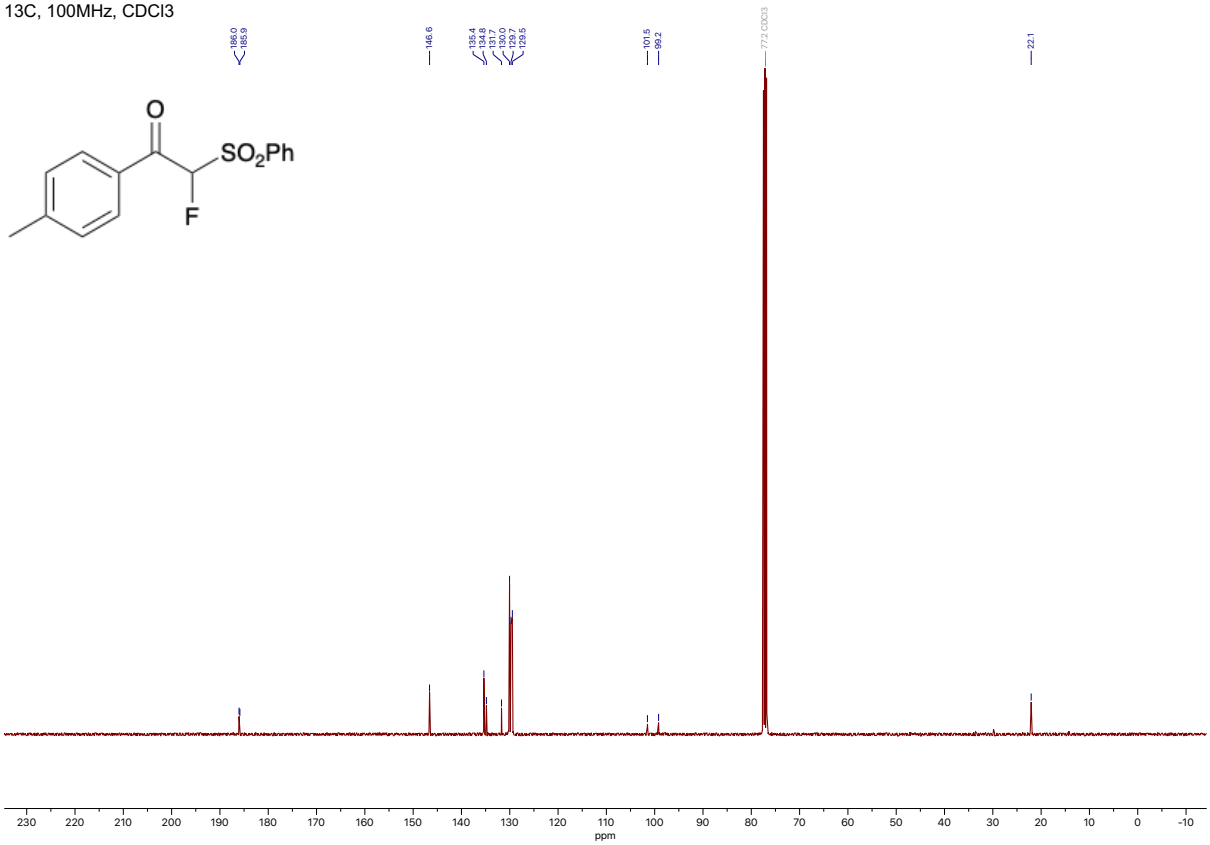

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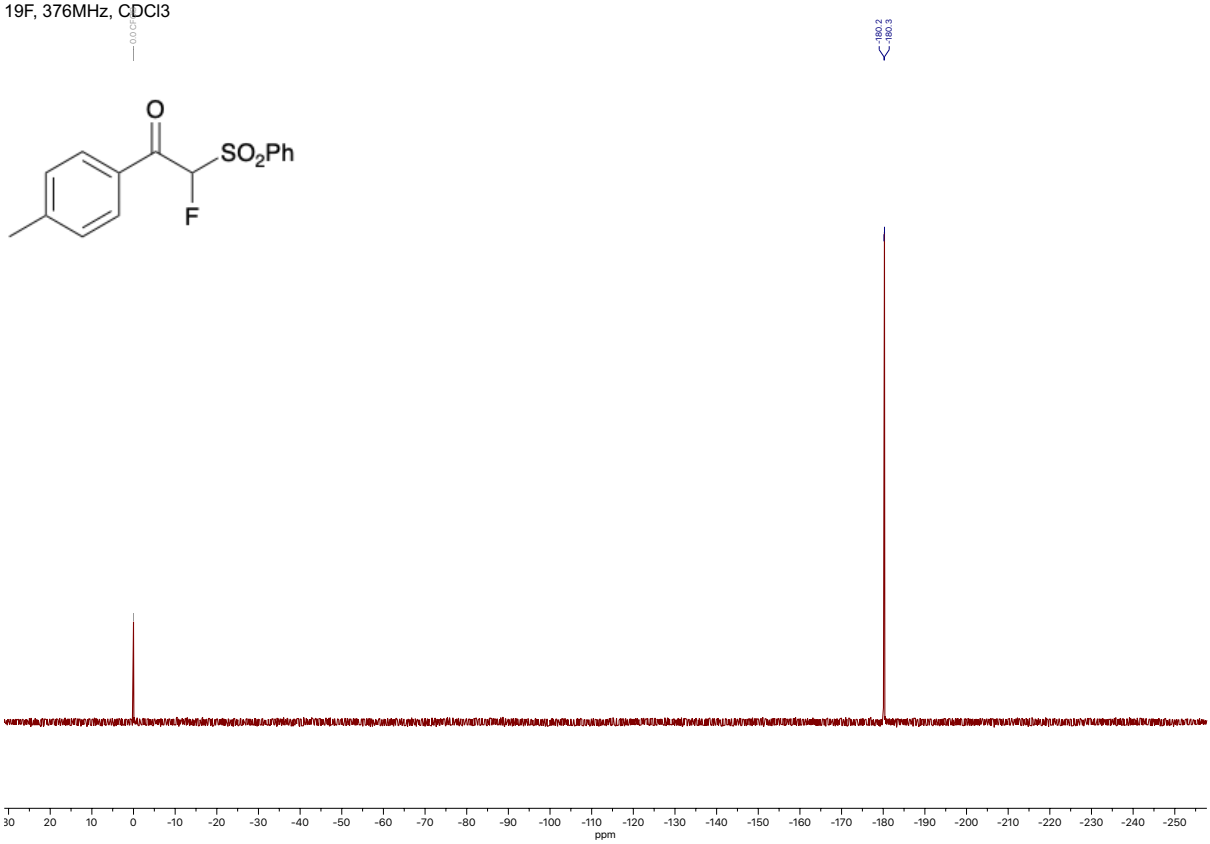

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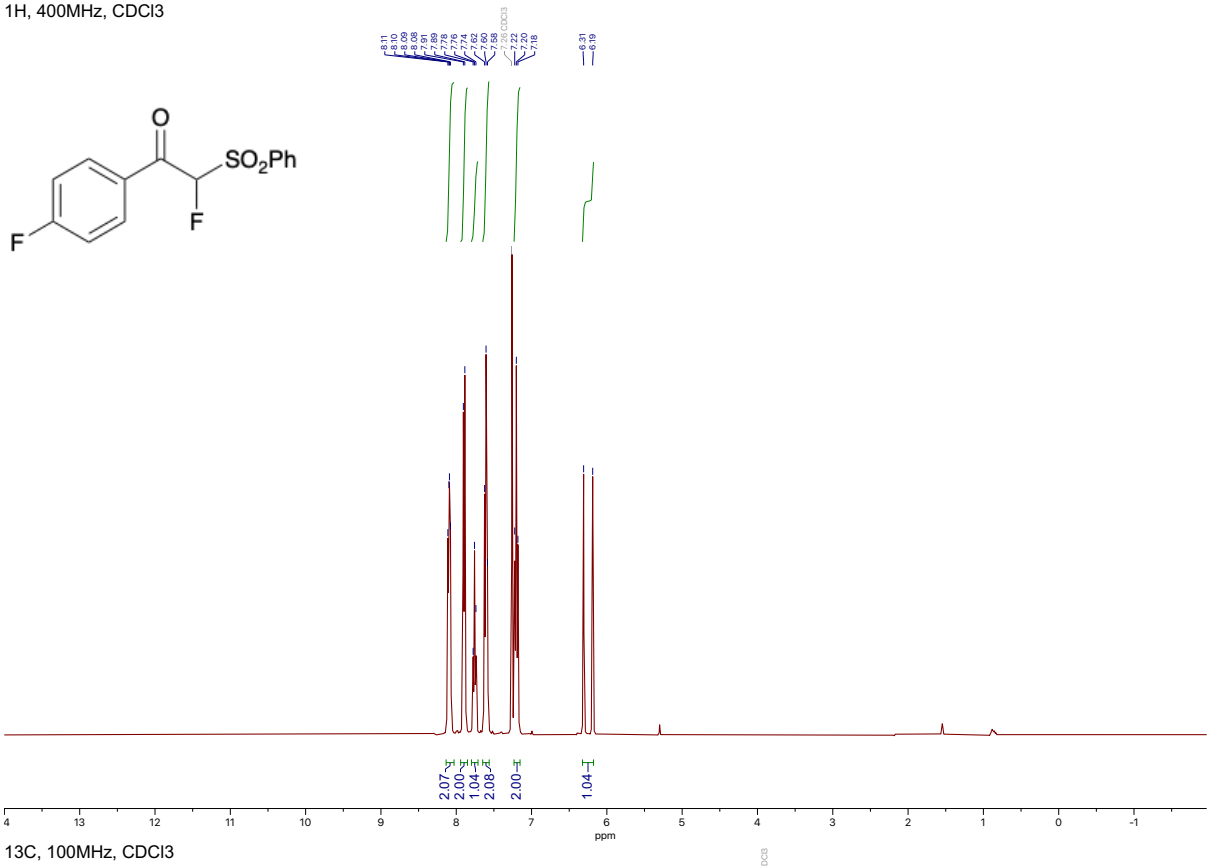

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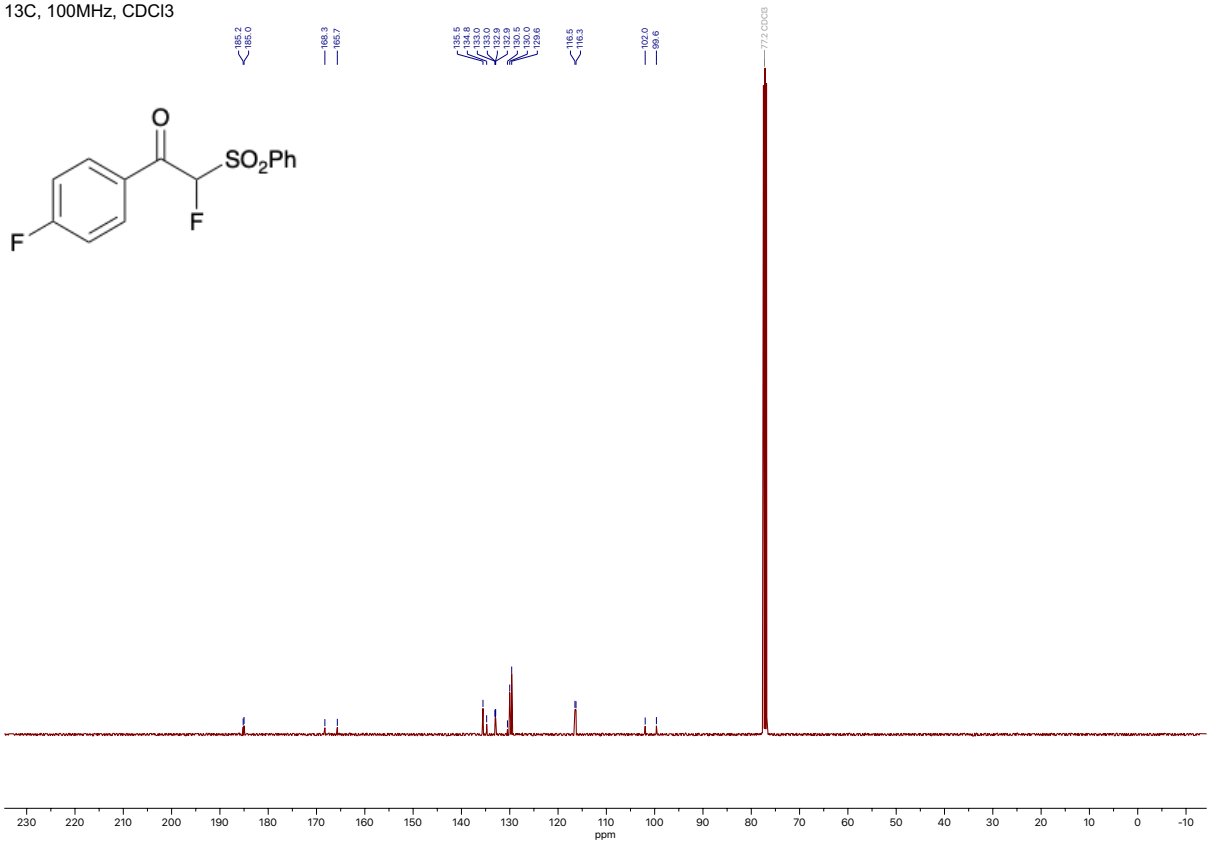

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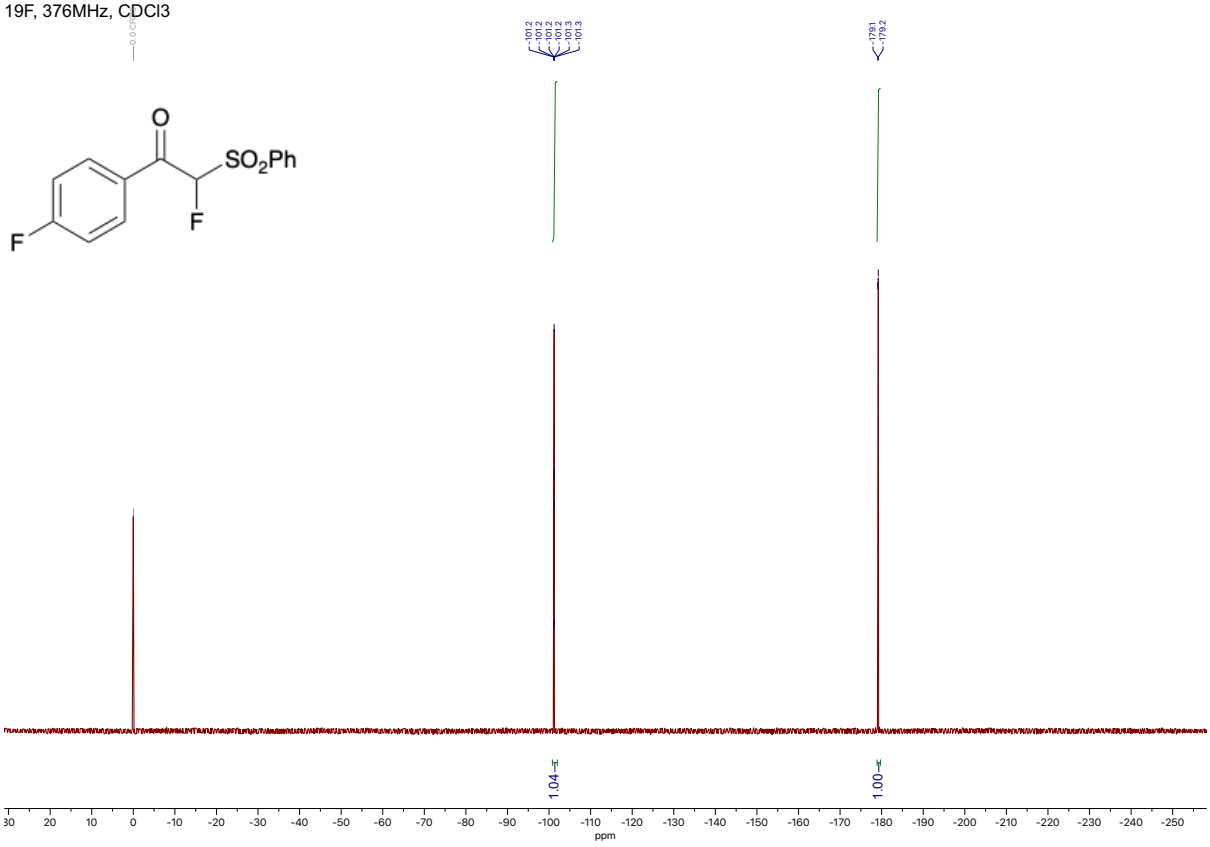

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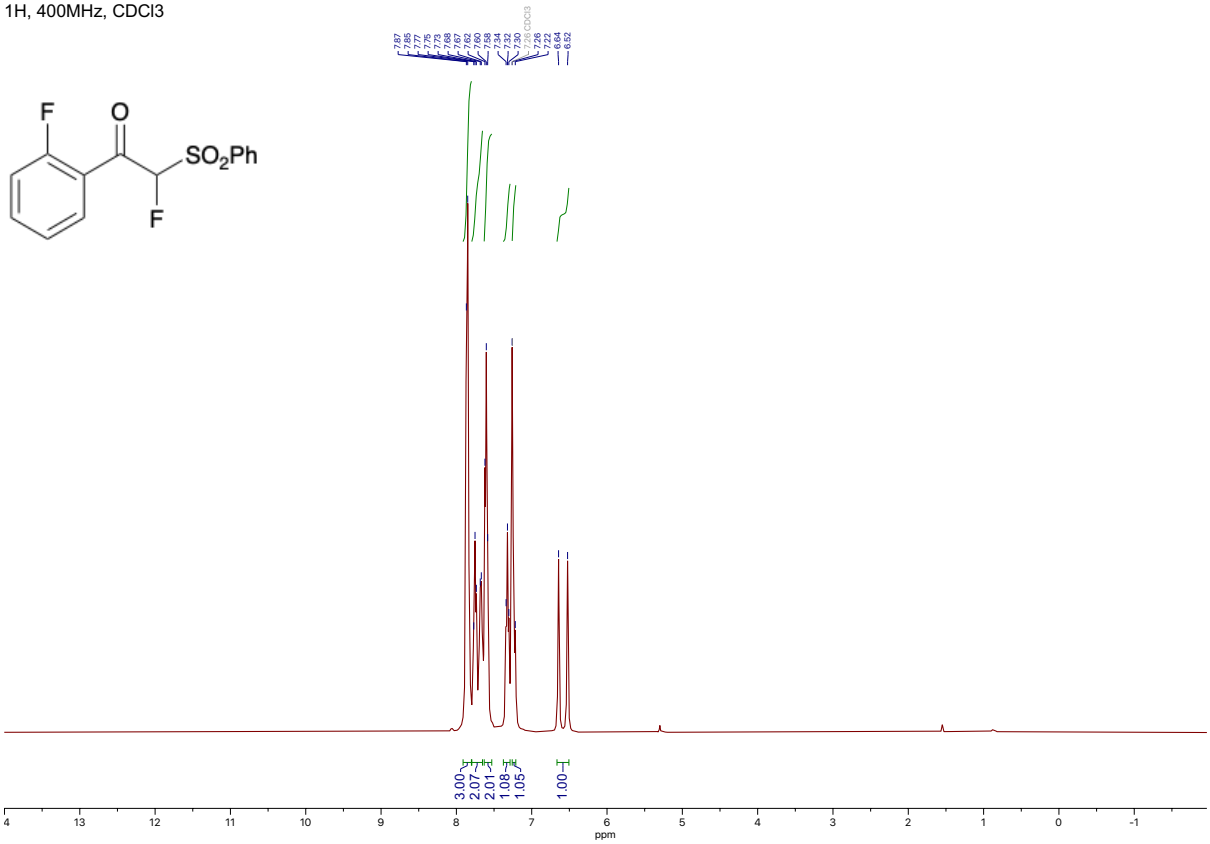

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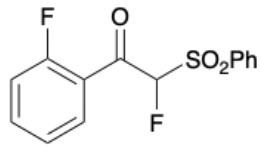

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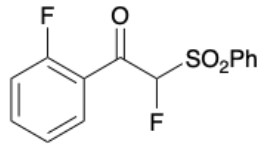

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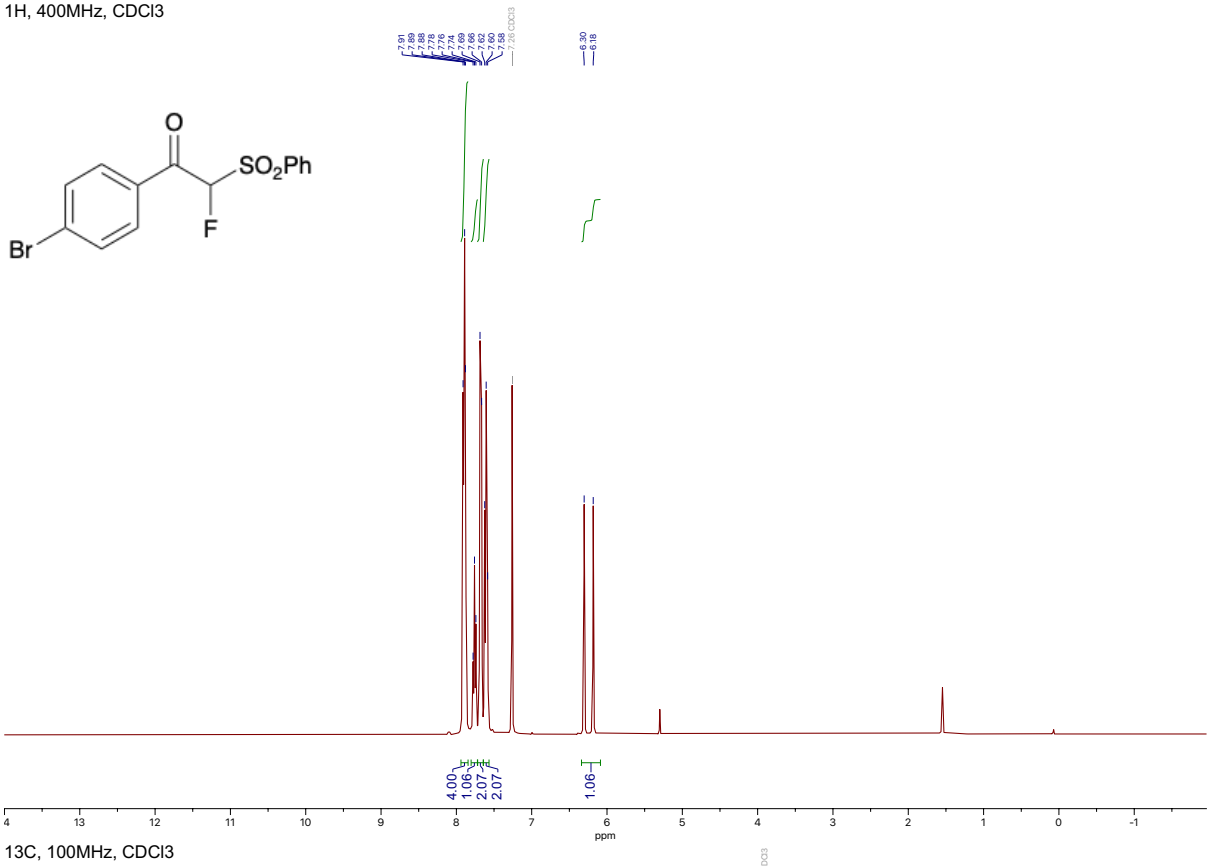
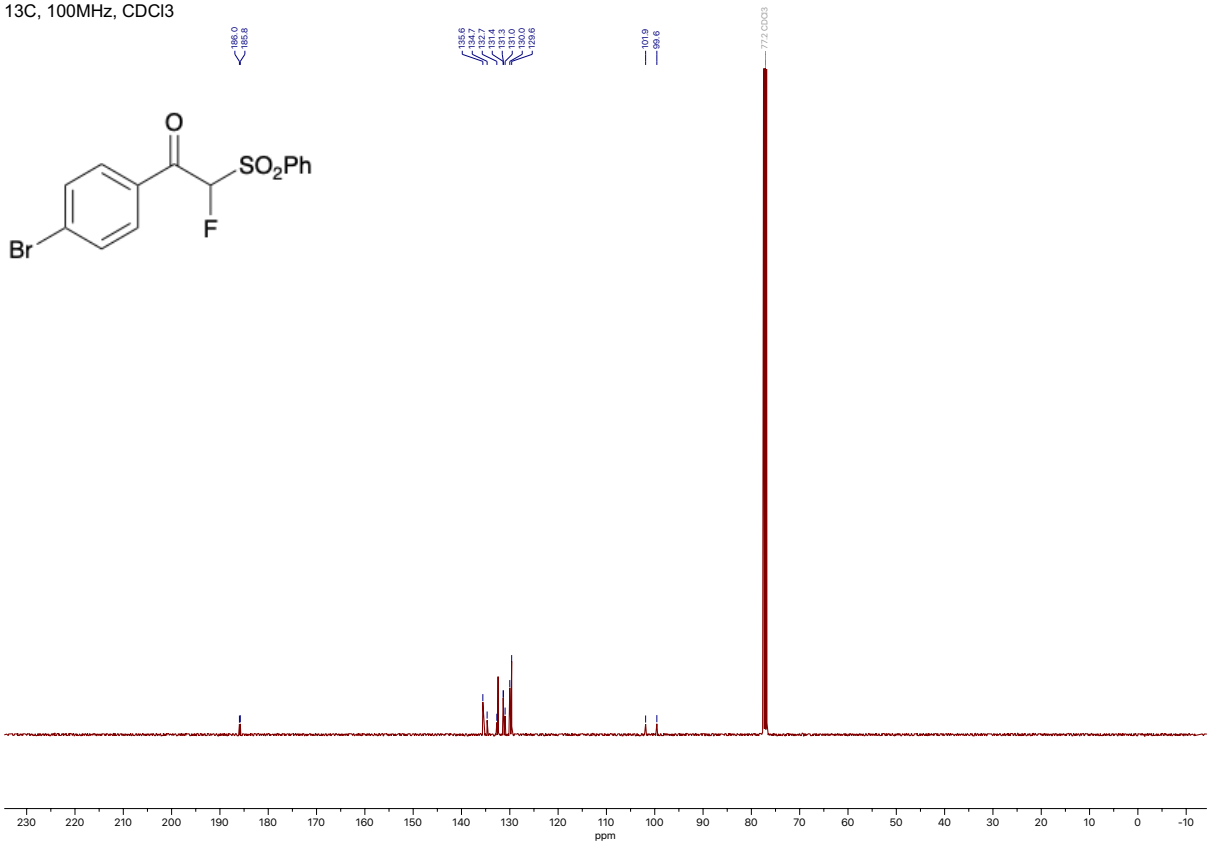
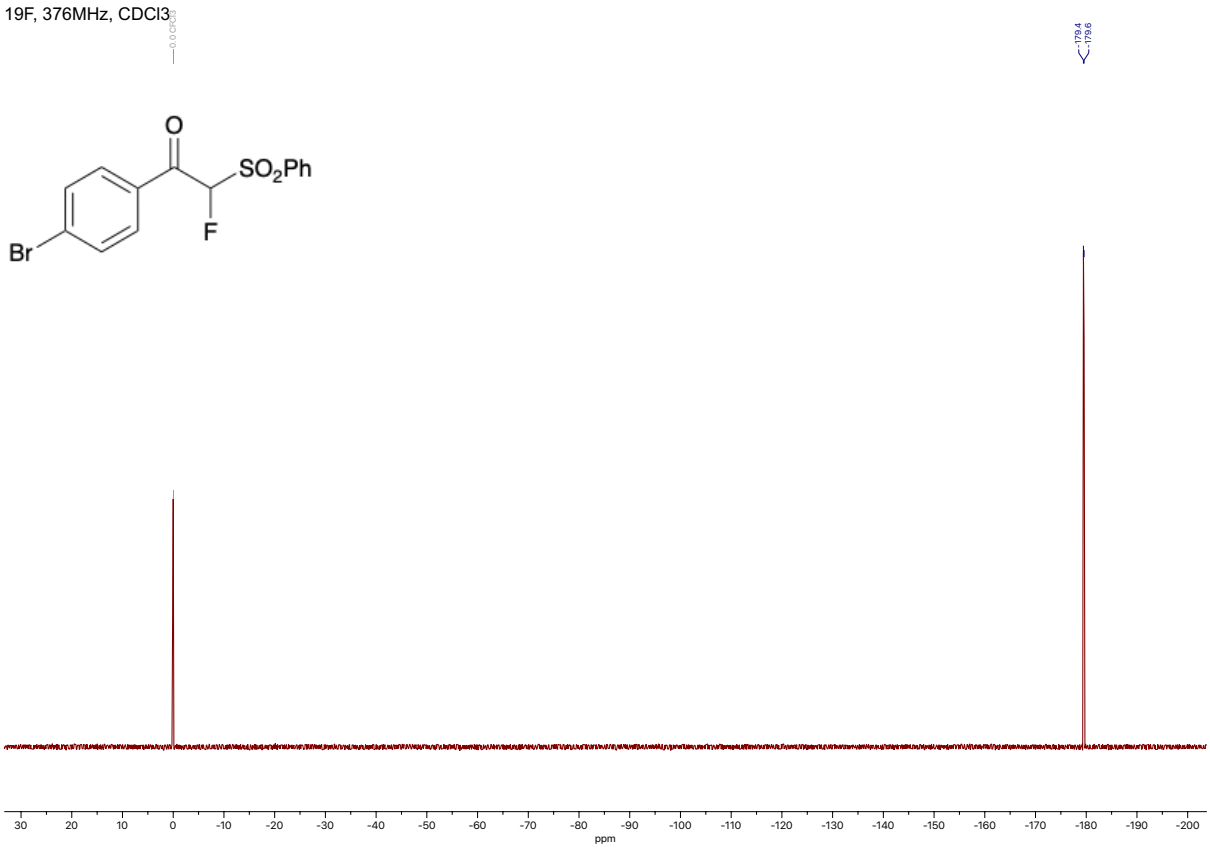


13C, 100MHz, CDCl3



19F, 376MHz, CDCl3



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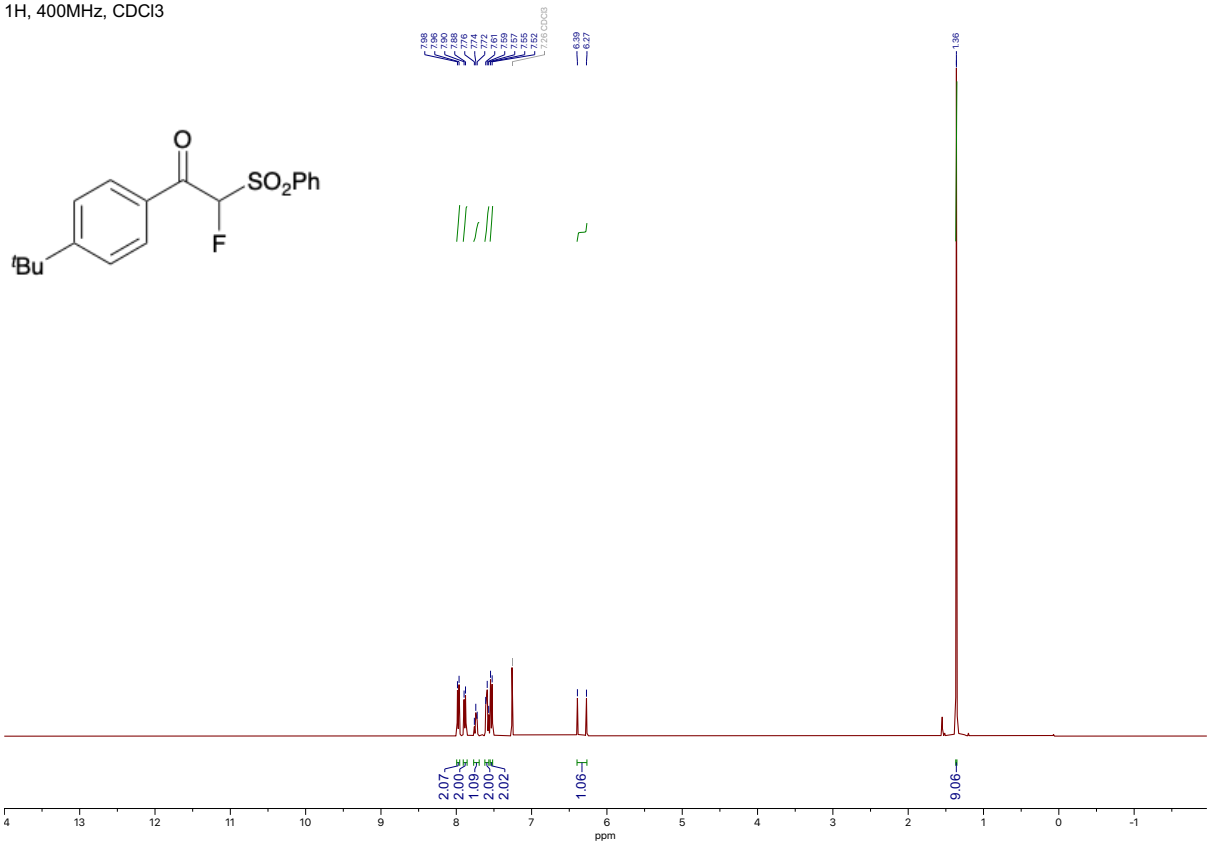

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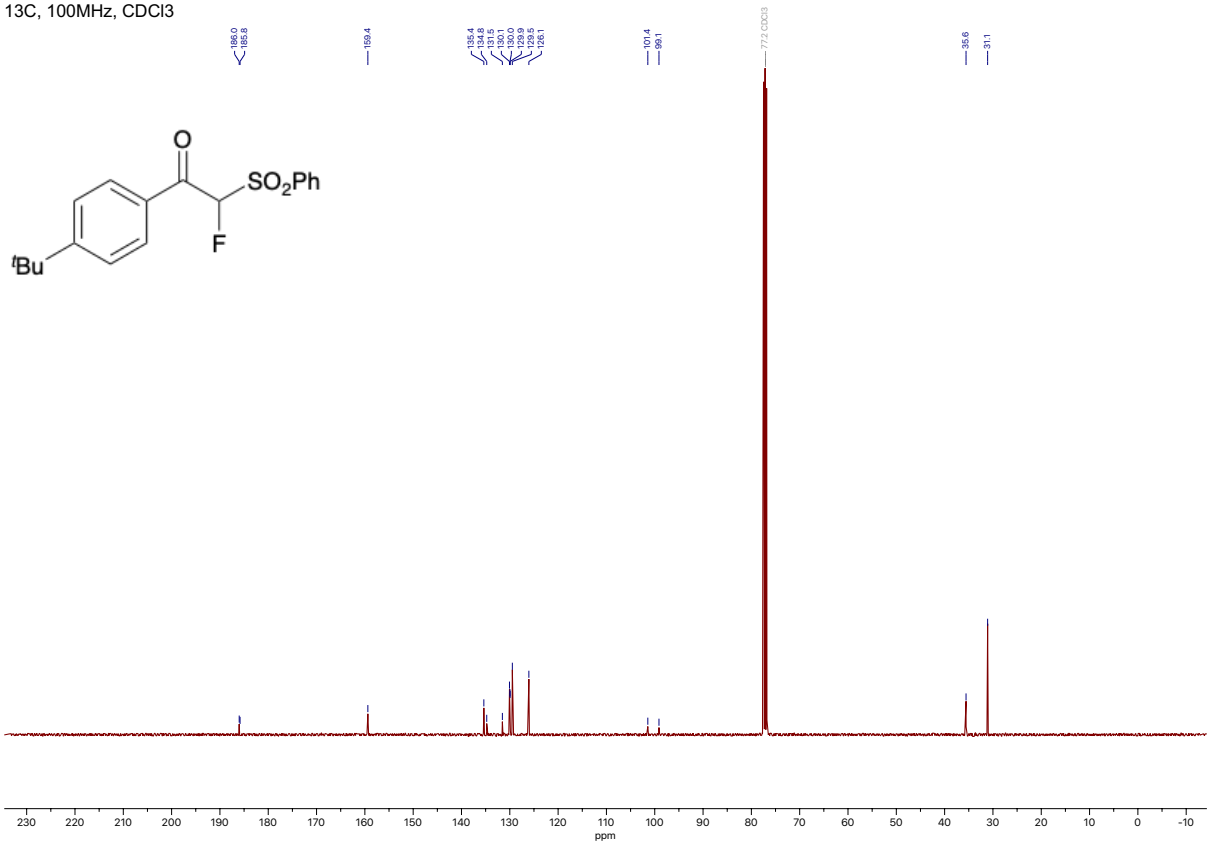

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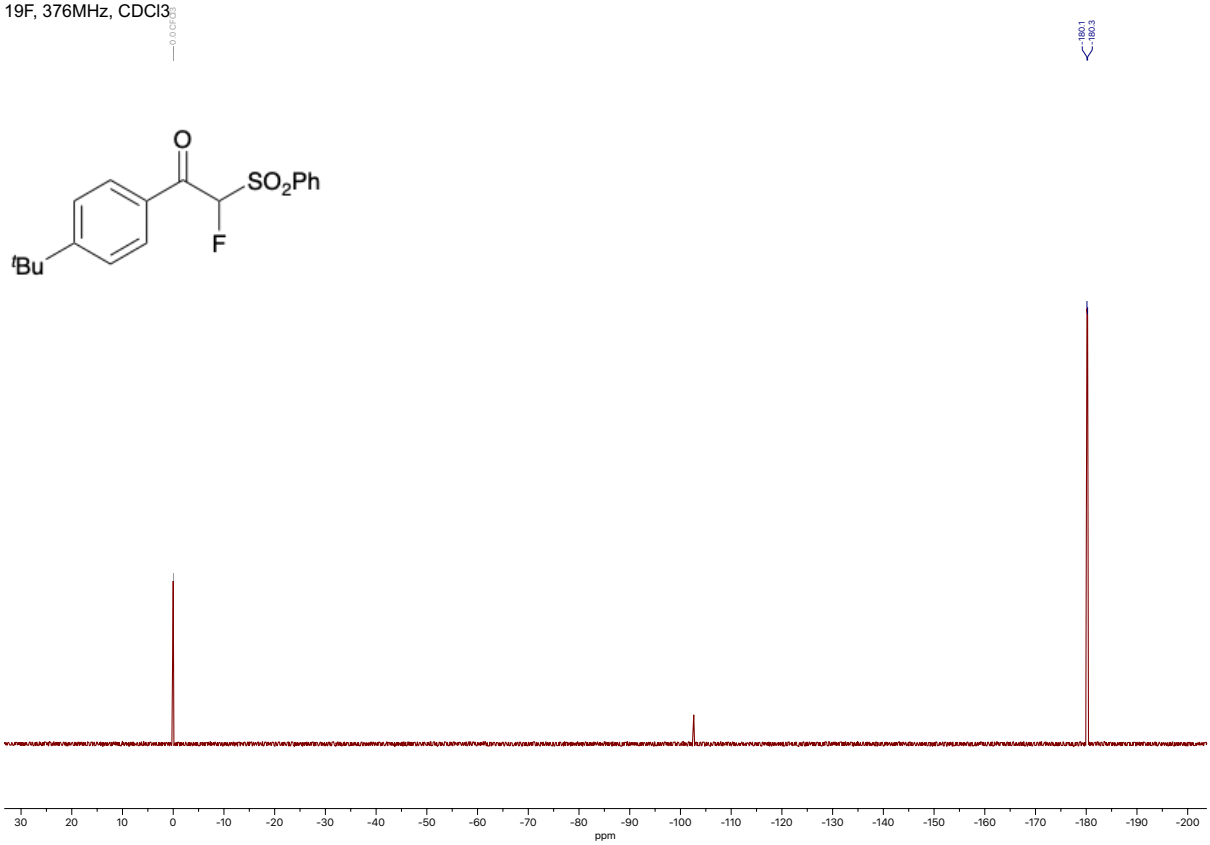

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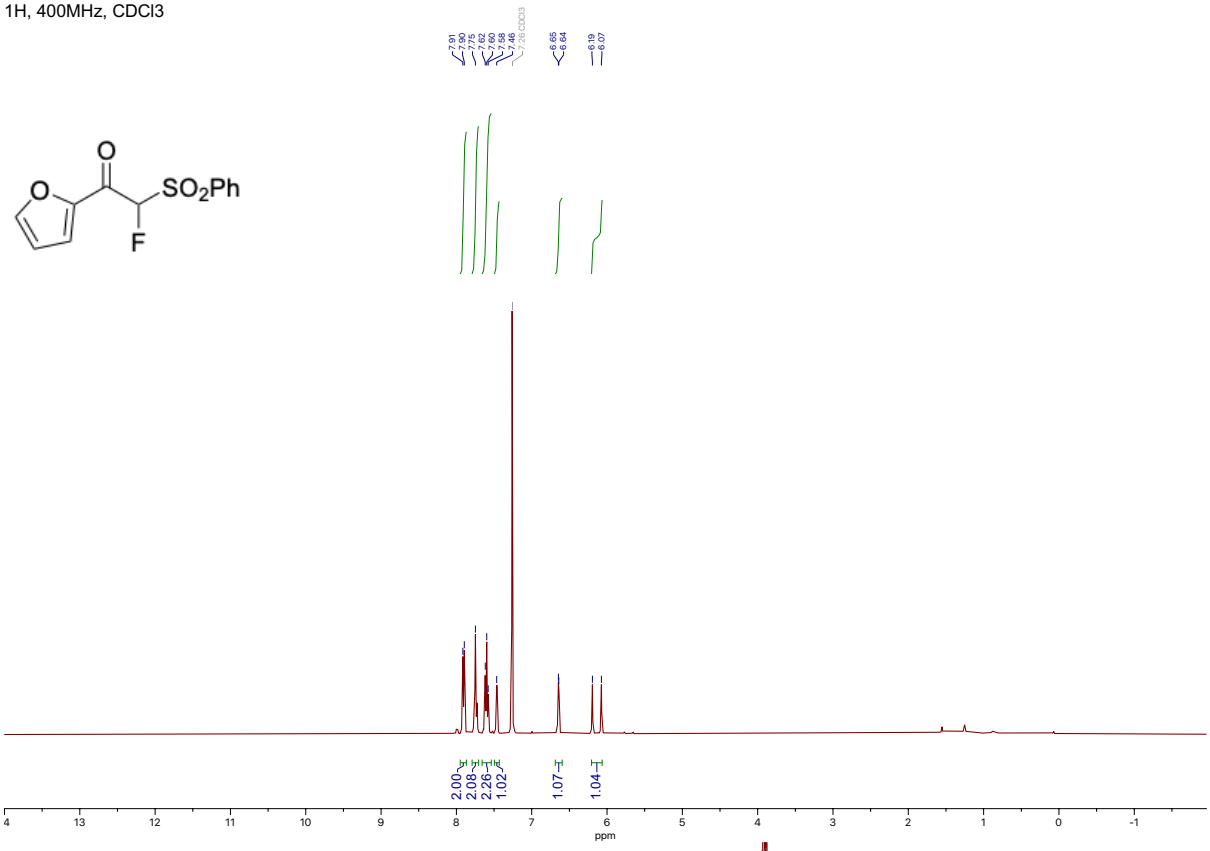
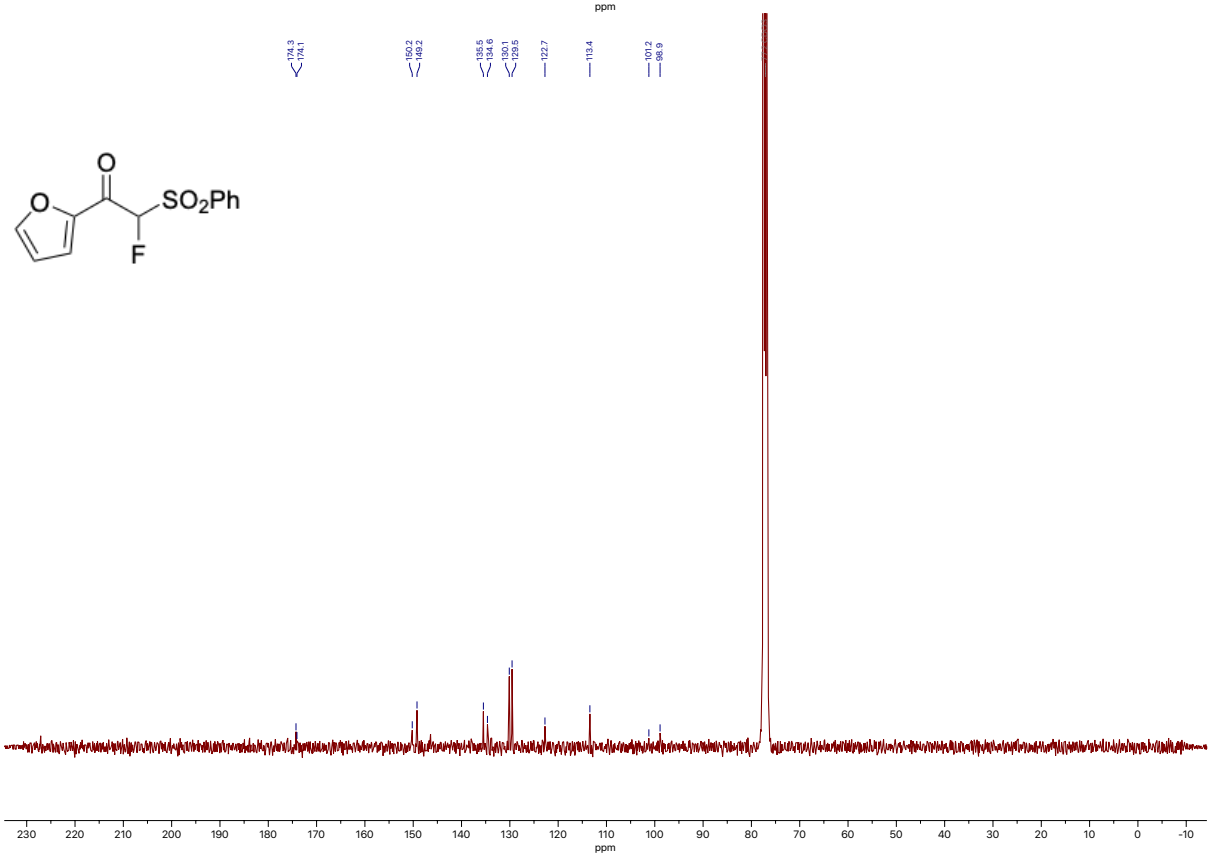
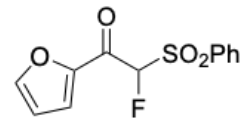
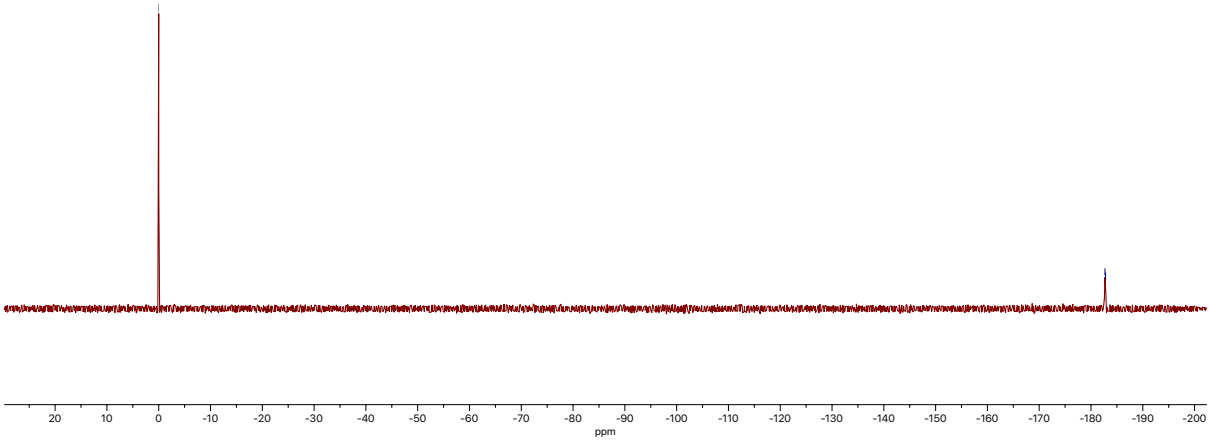


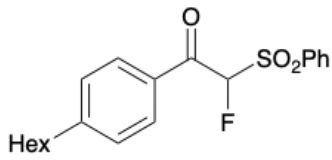


19F, 376MHz, CDCl3

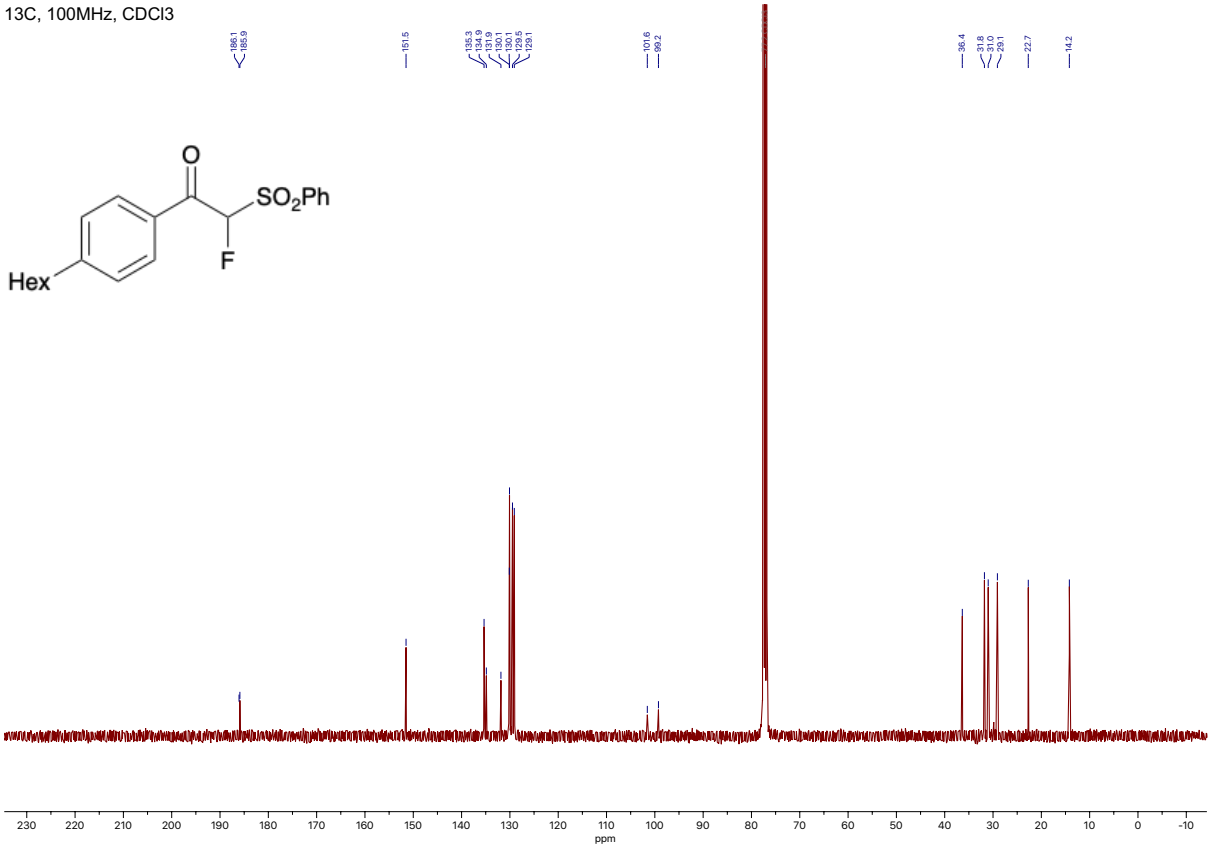




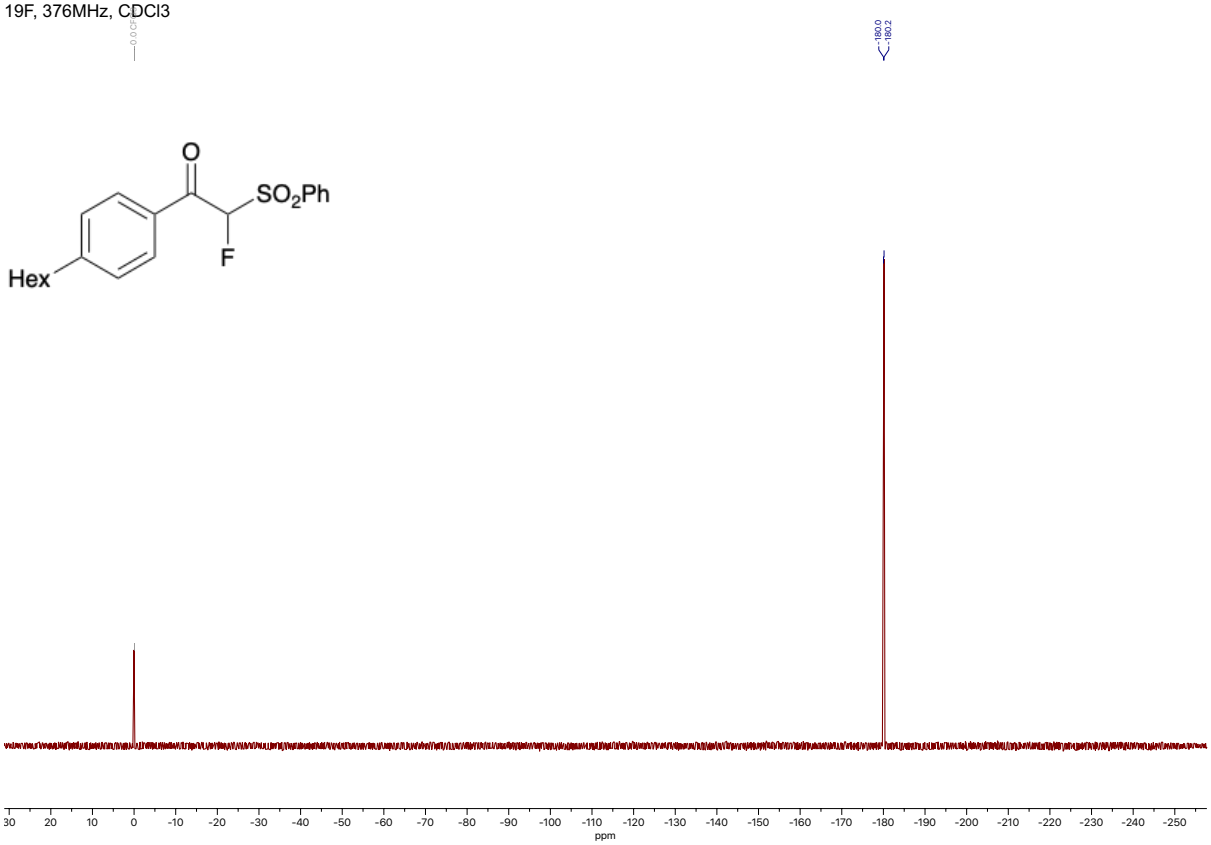
1H, 400MHz, CDCl3



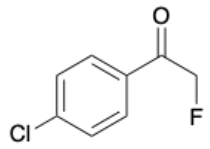
13C, 100MHz, CDCl3



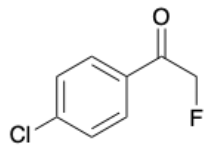
19F, 376MHz, CDCl3



1H, 400MHz, CDCl3



13C, 100MHz, CDCl3



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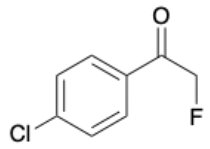

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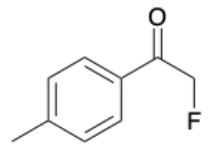
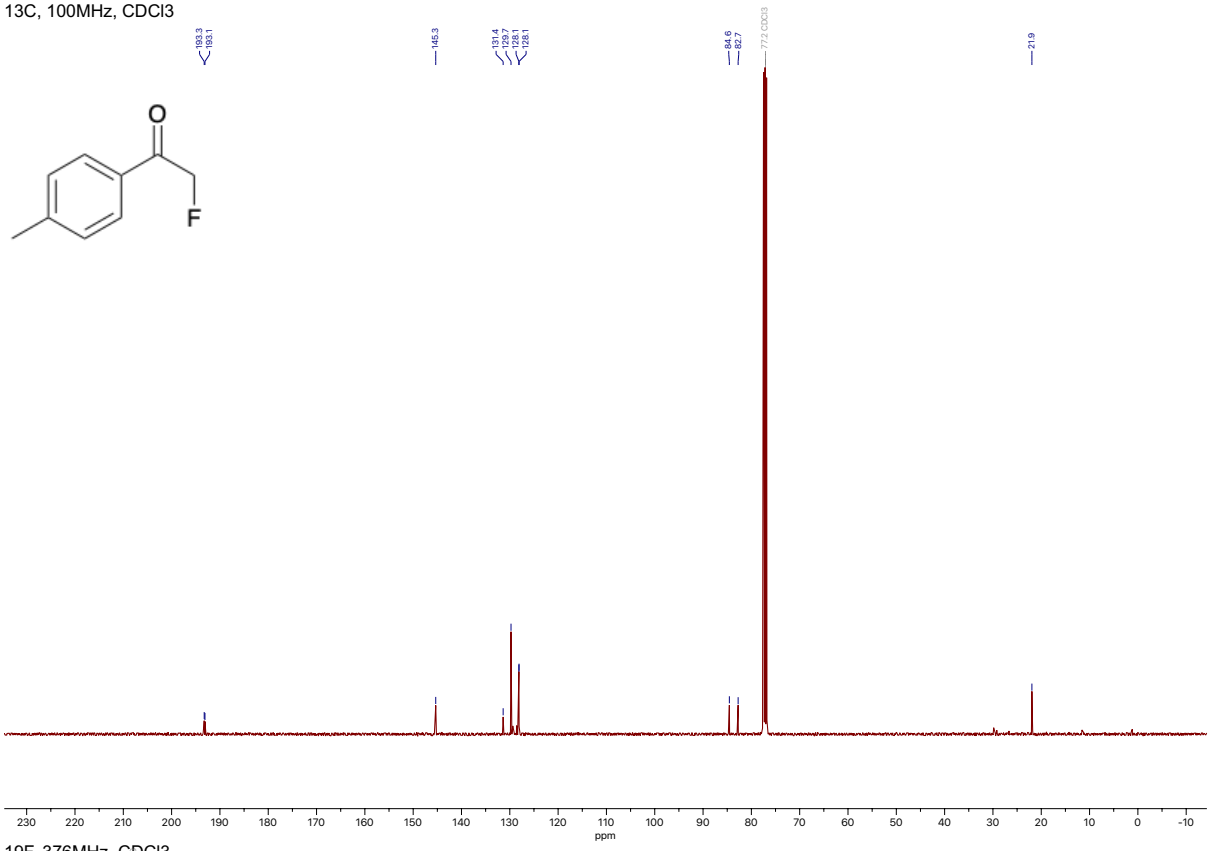
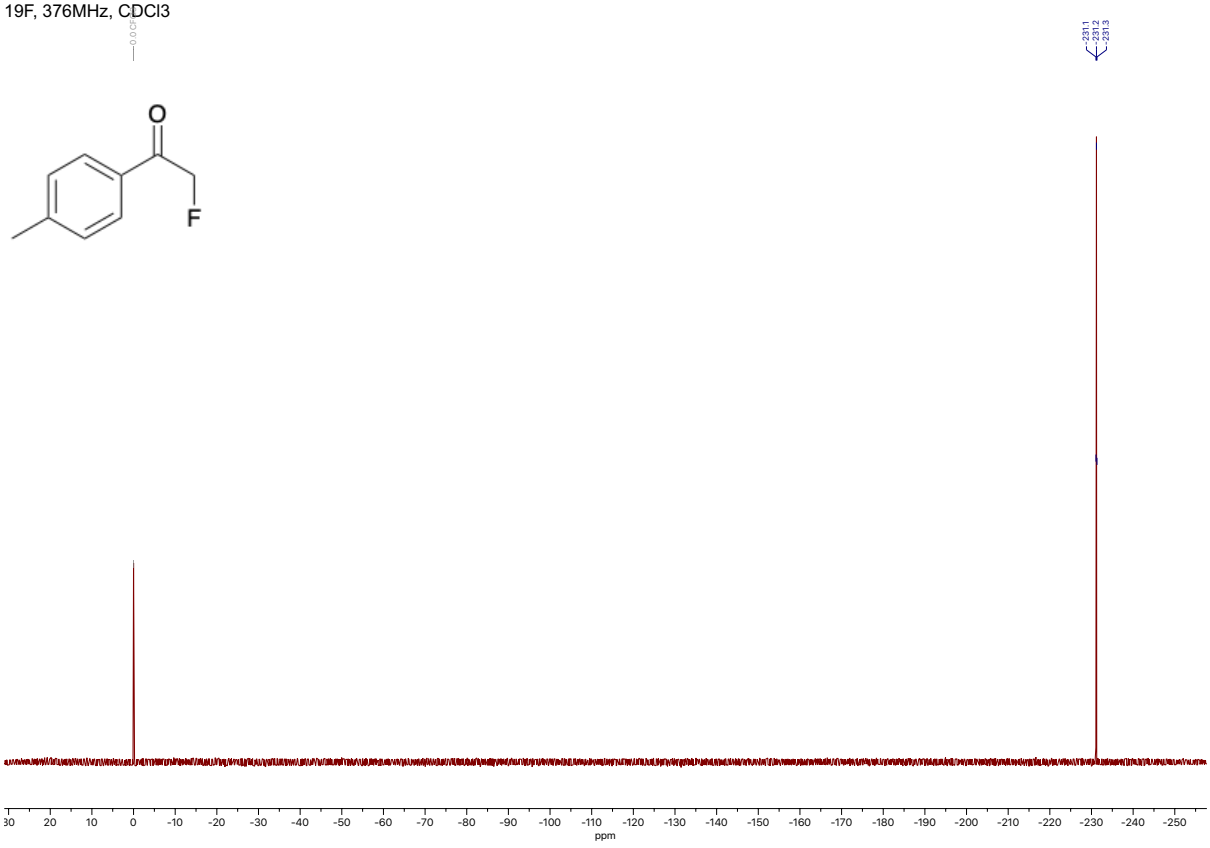


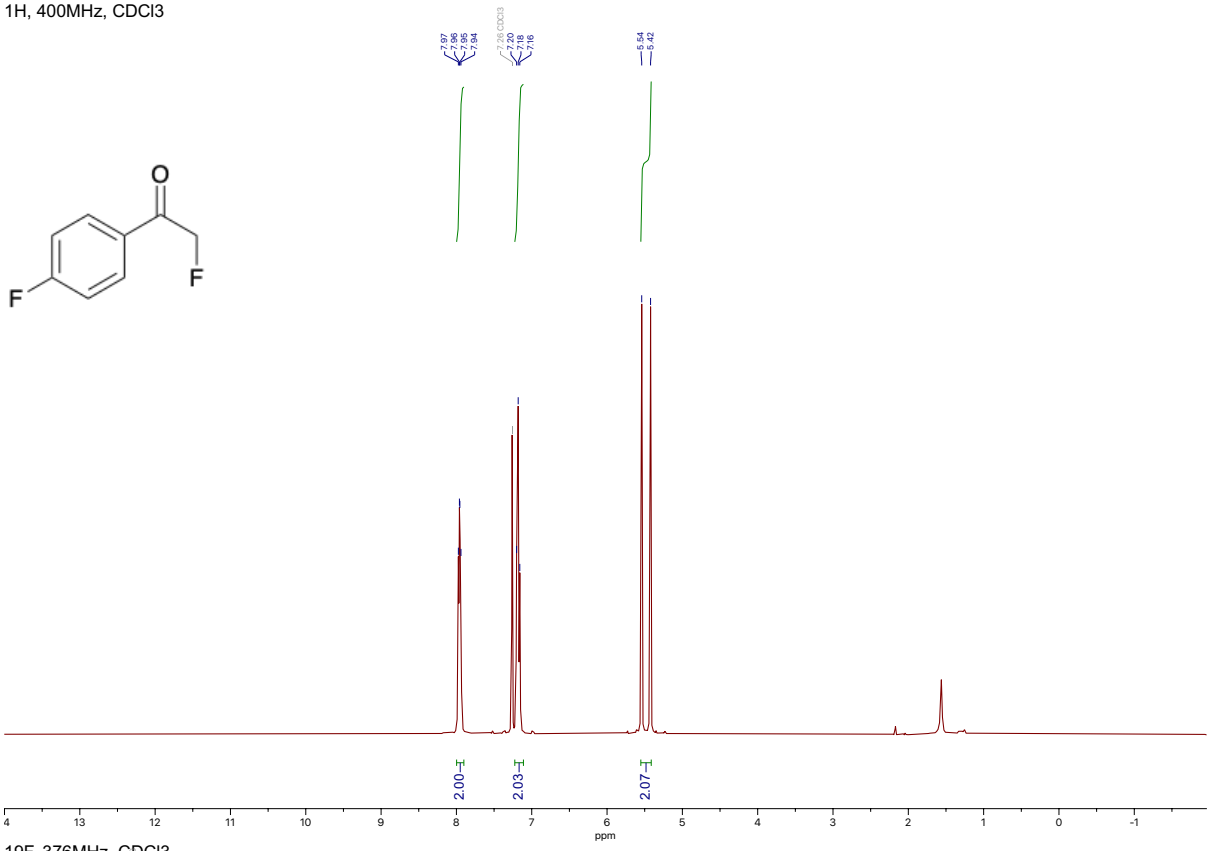
13C, 100MHz, CDCl3



19F, 376MHz, CDCl3



1H, 400MHz, CDCl3



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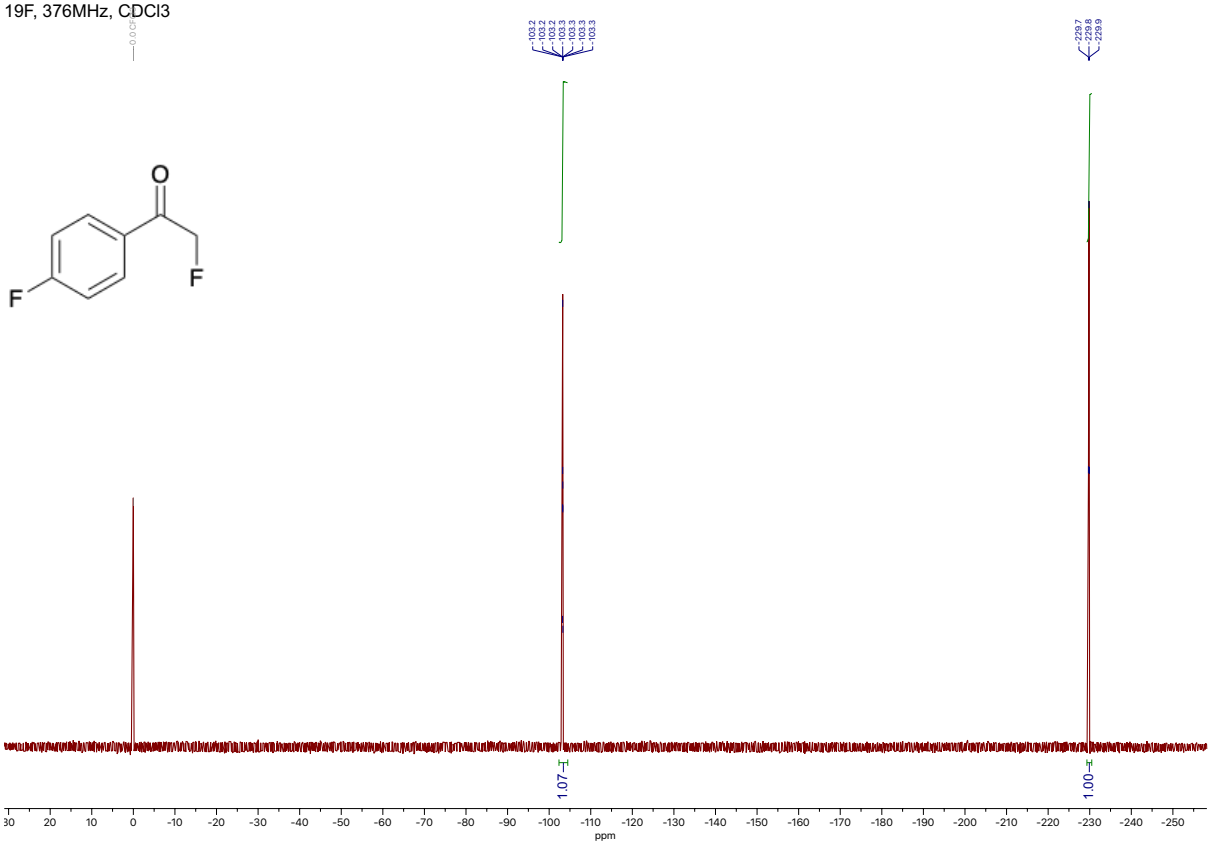

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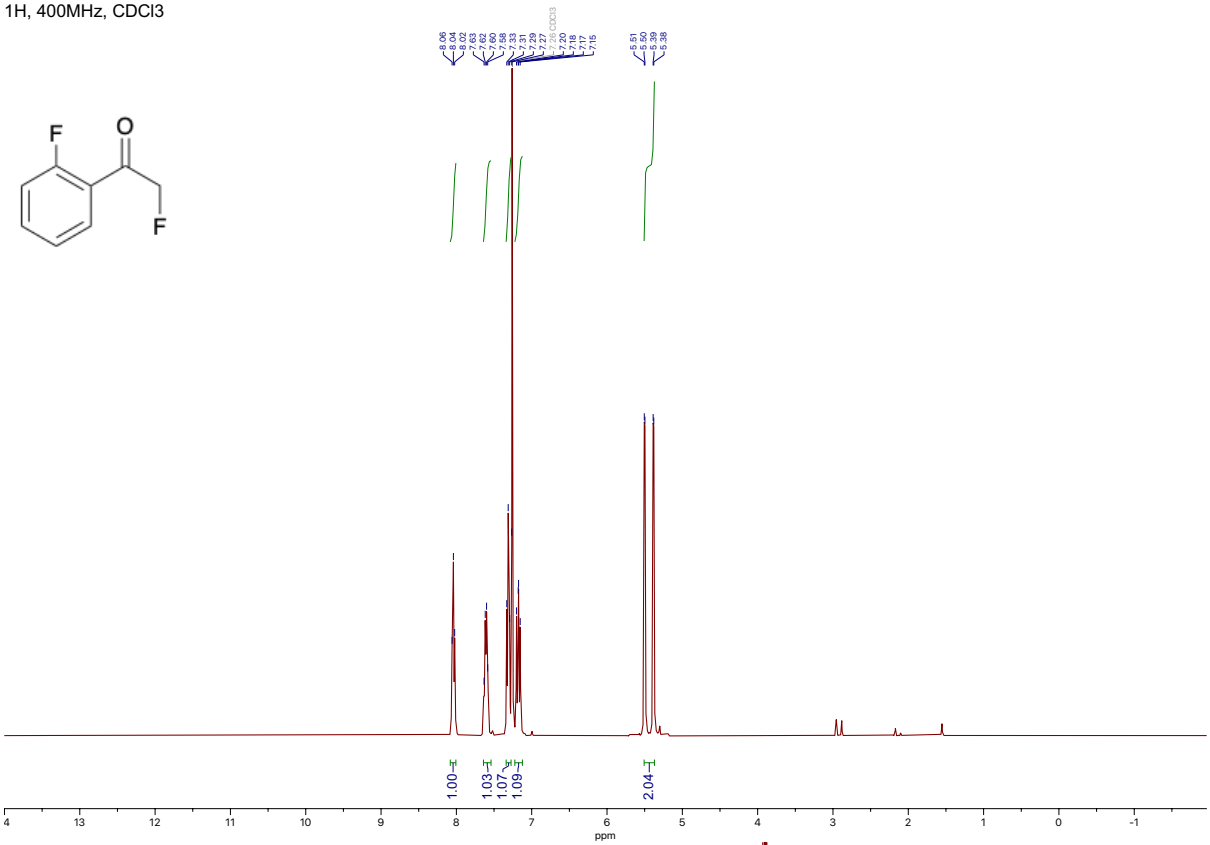
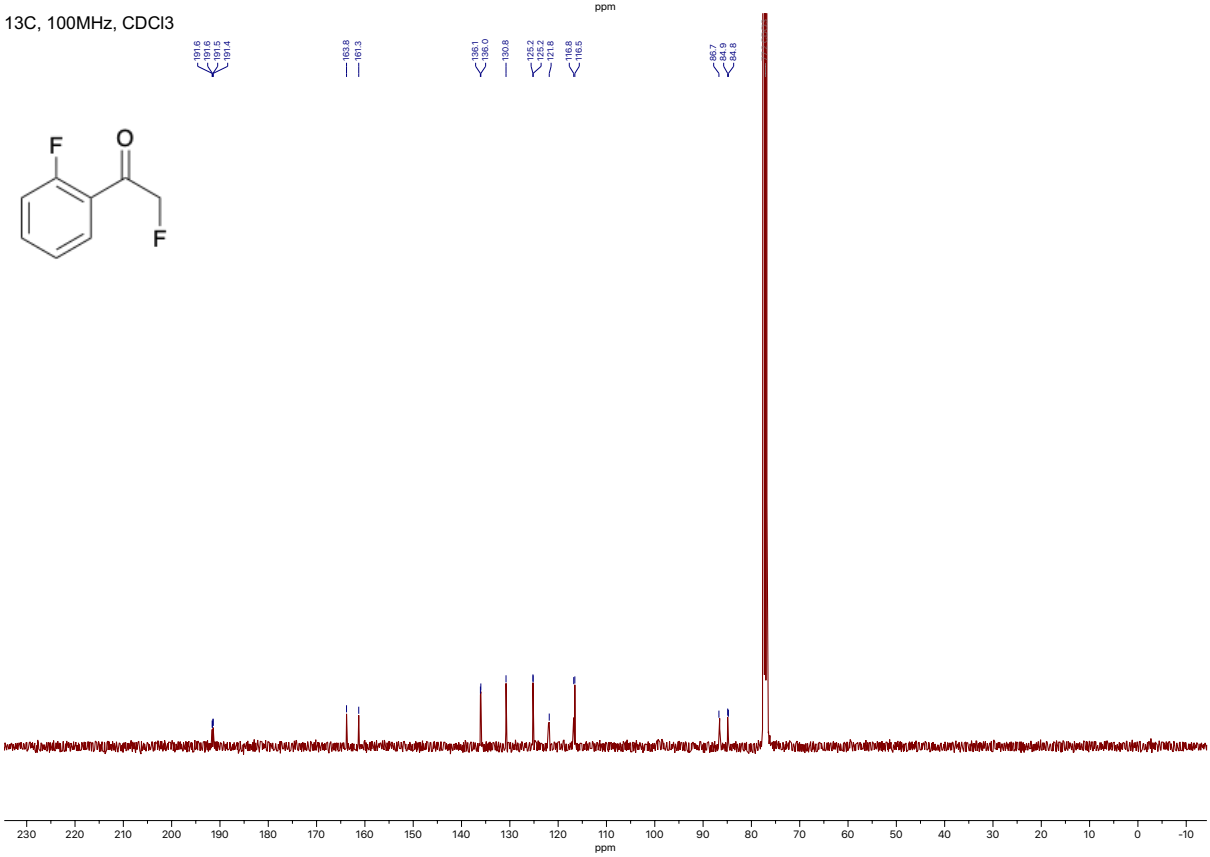
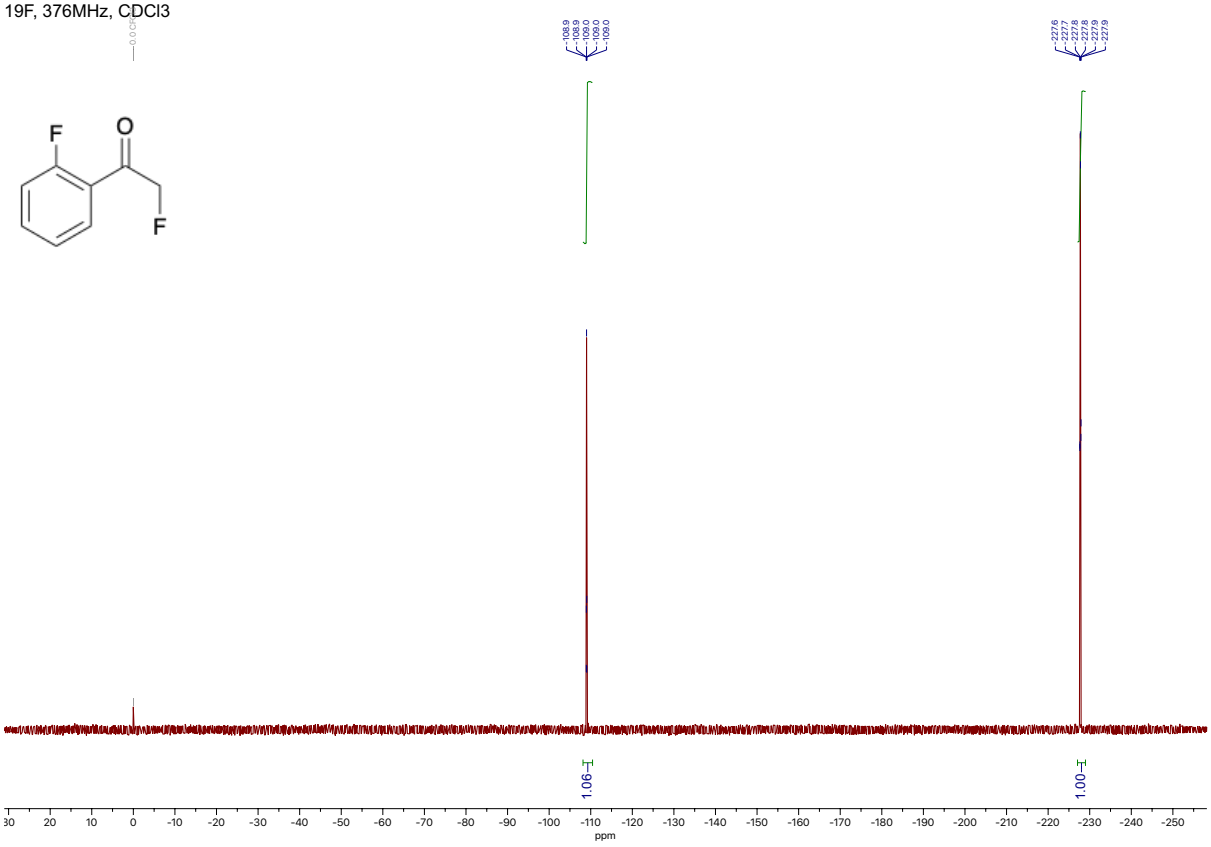


13C, 100MHz, CDCl3



19F, 376MHz, CDCl3



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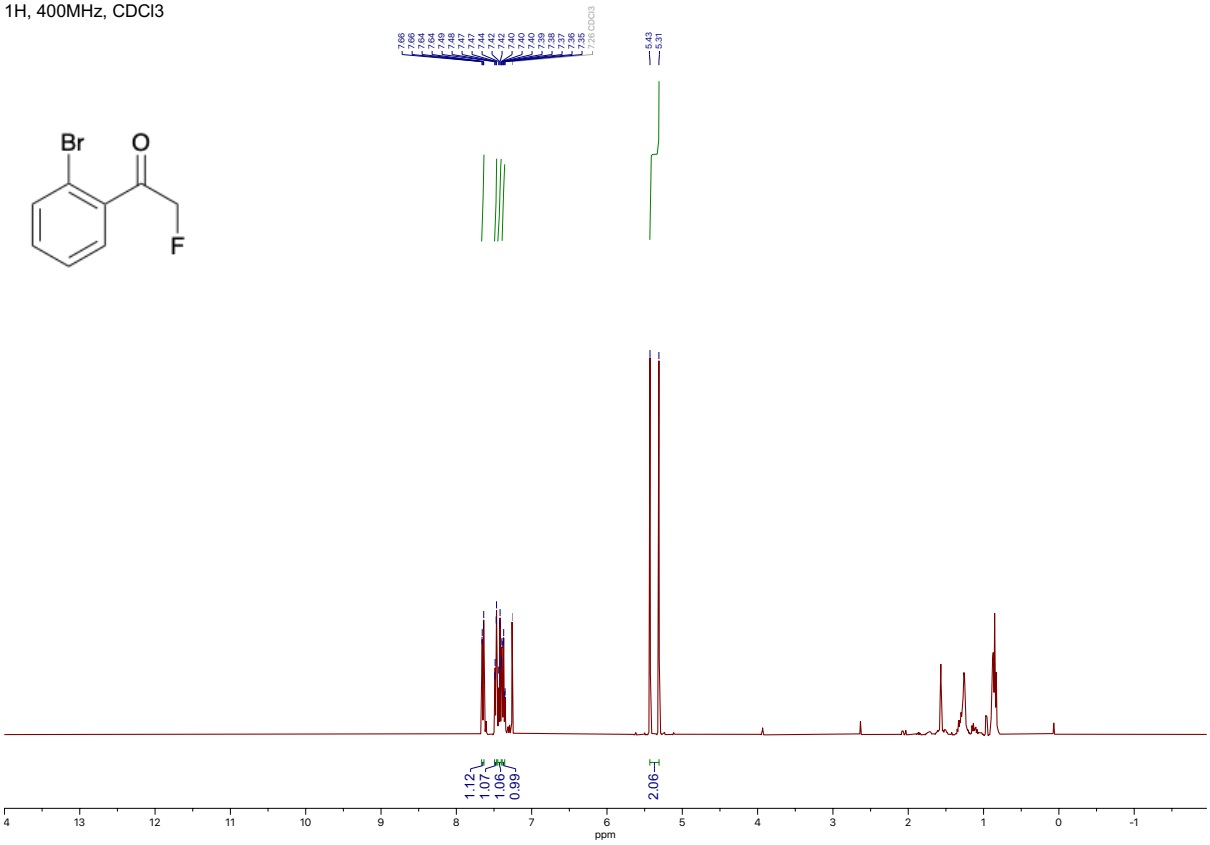
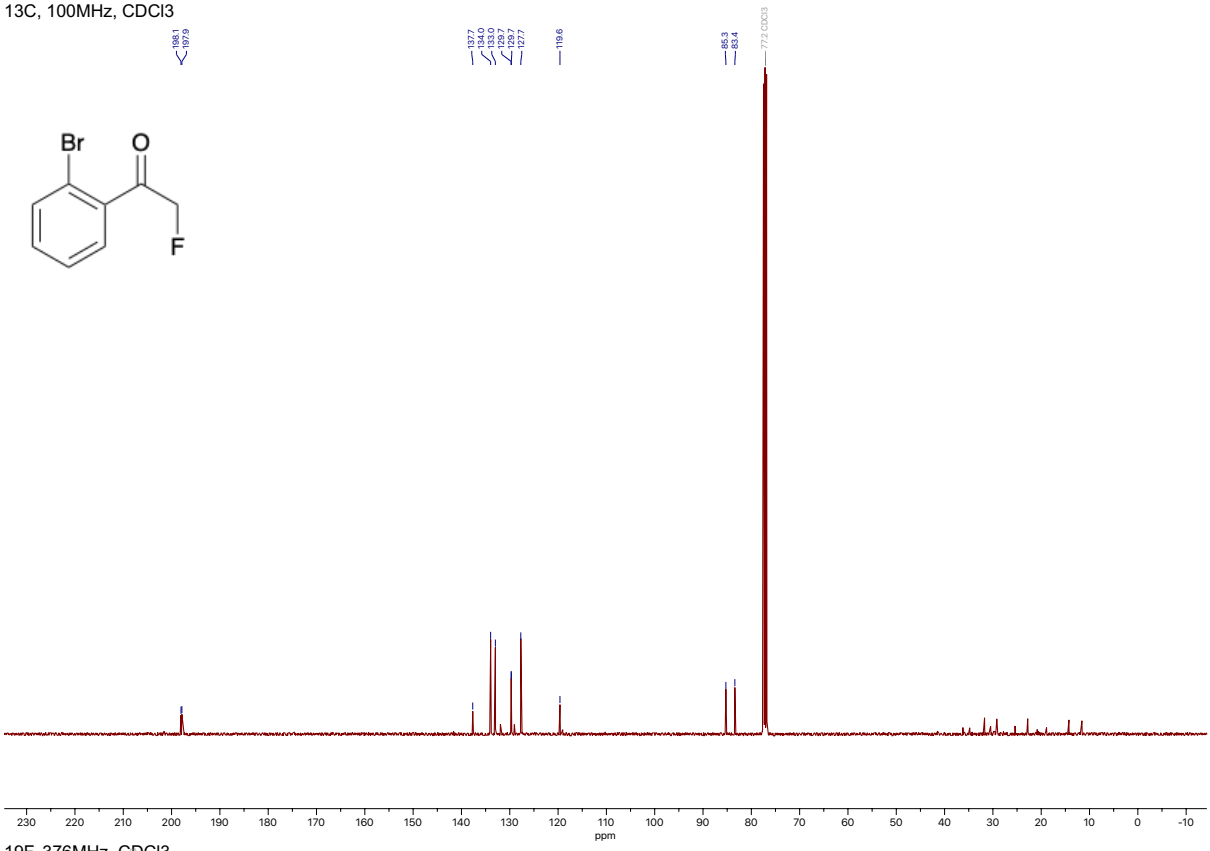


13C, 100MHz, CDCl3



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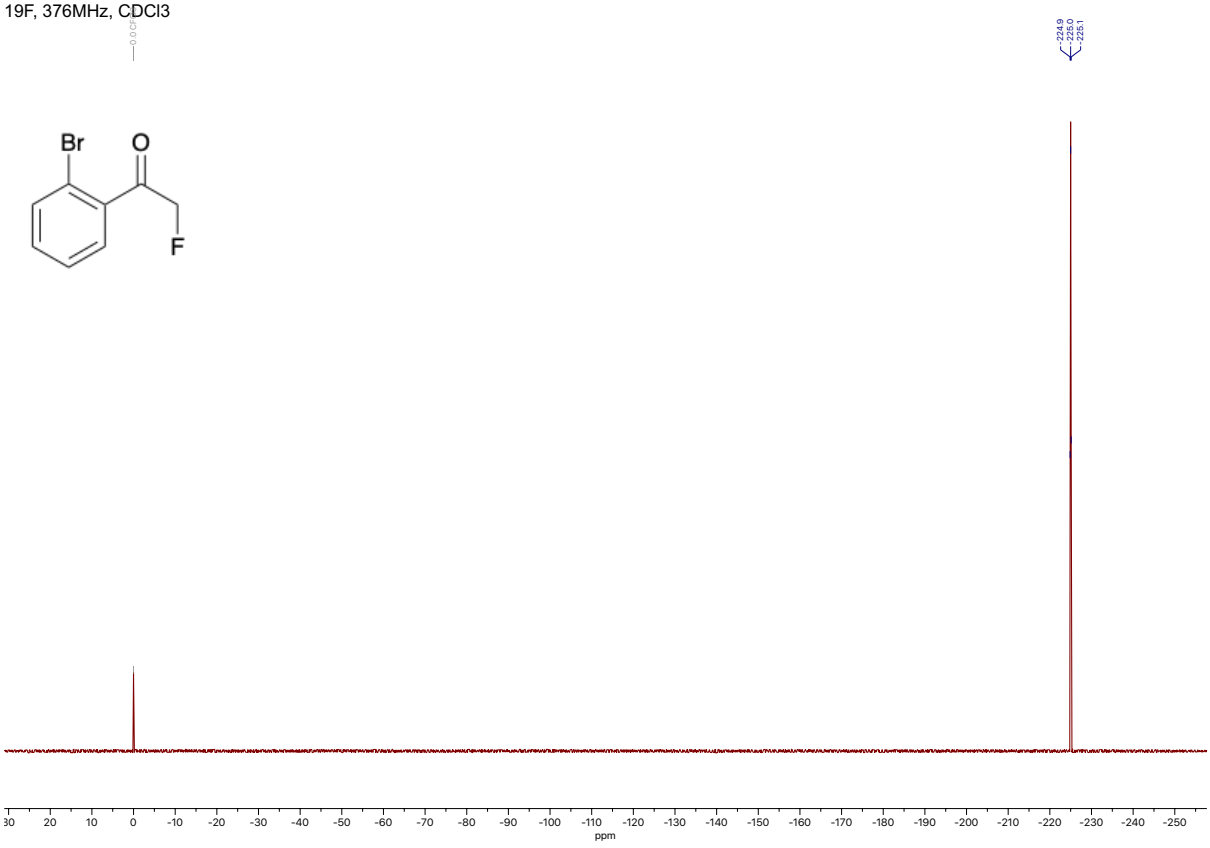
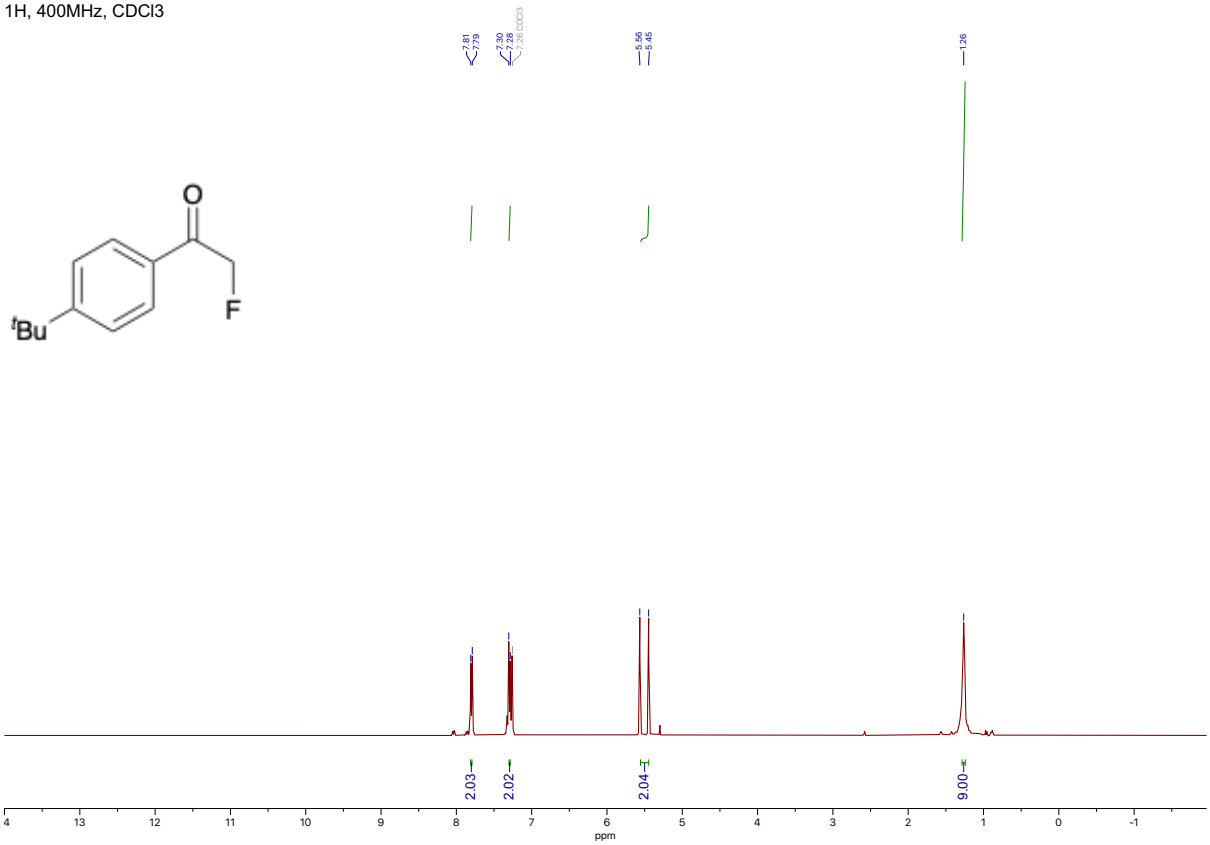
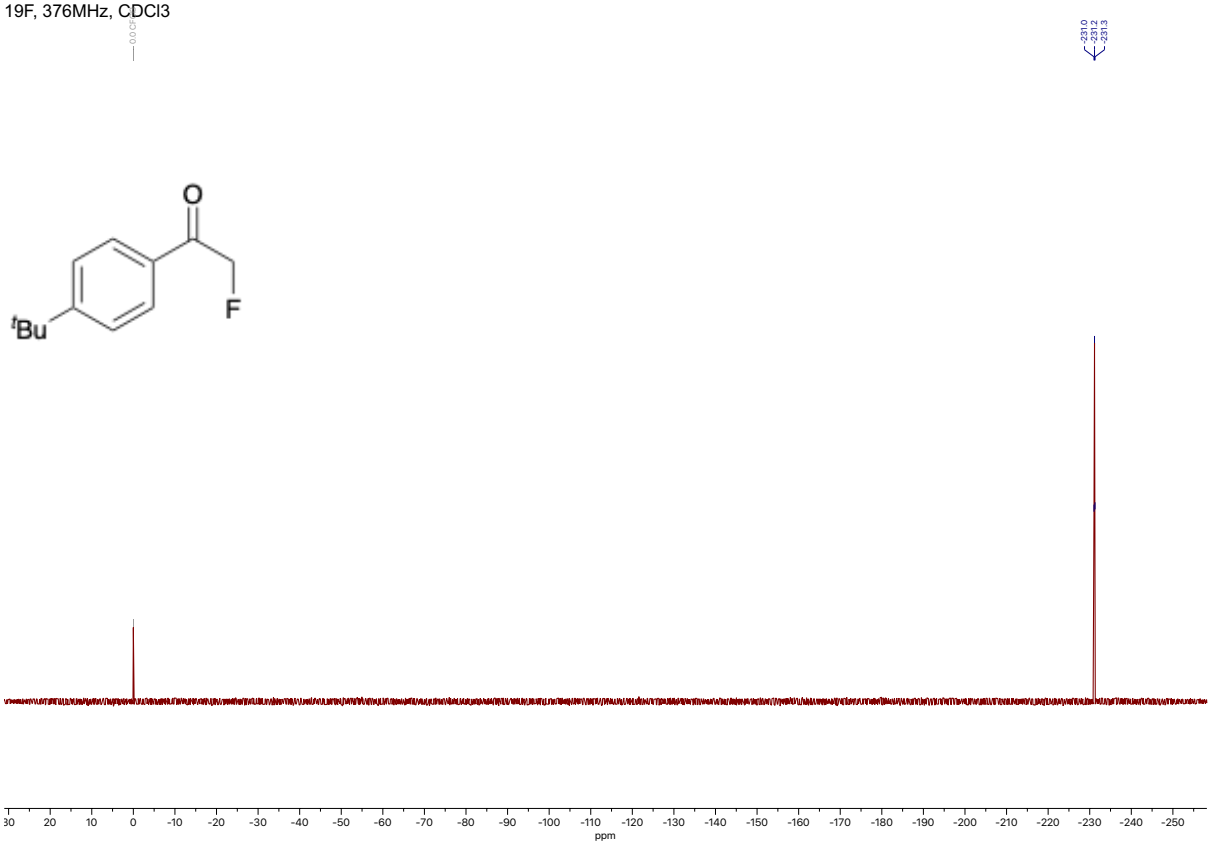


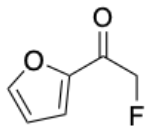
1H, 400MHz, CDCl3



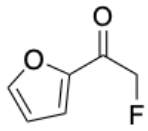
19F, 376MHz, CDCl3



1H, 400MHz, CDCl3



19F, 376MHz, CDCl3



Crystallographic Data

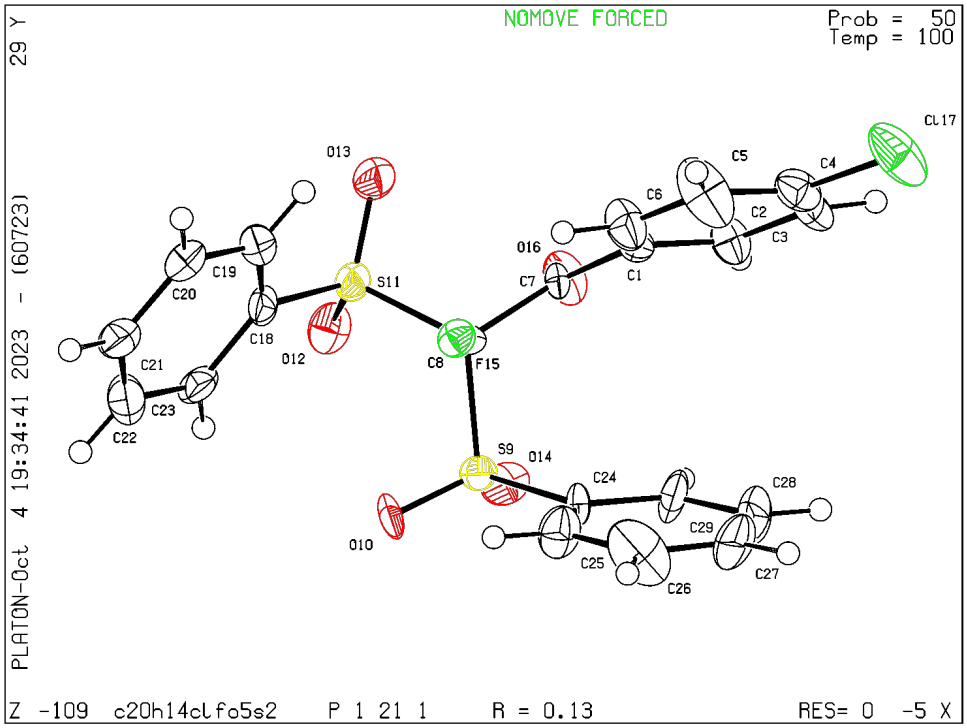
Crystallographic Data for Compound 2b #2427875

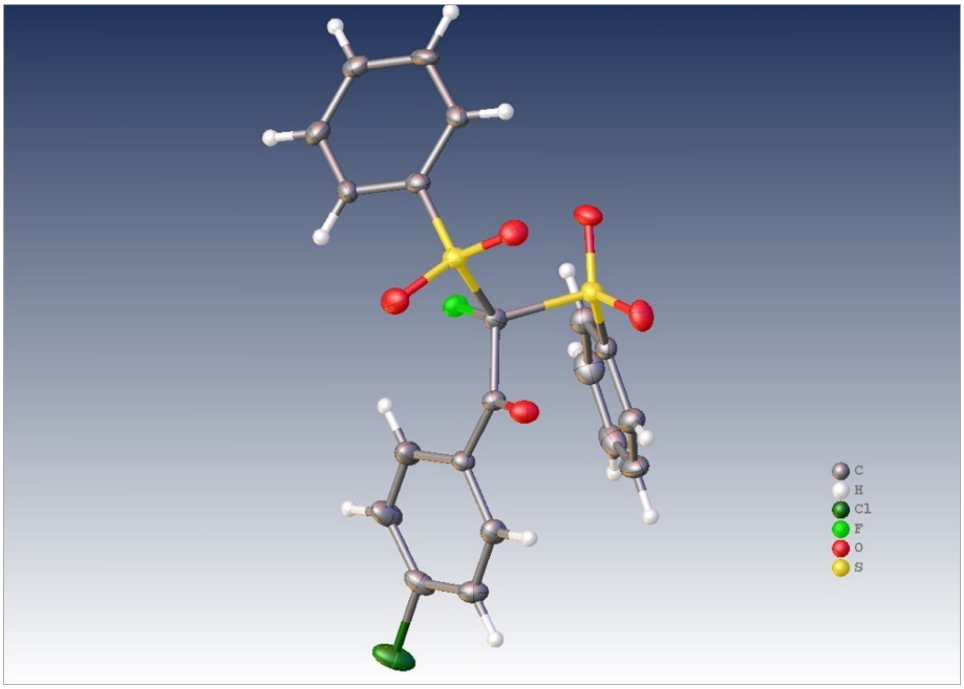
Table 1 Sample and crystal data for 4-chloro substituted compound 2b

Wavelength	1.54184	
Temperature:	100 K	
Unit Cell Dimensions	a = 7.9580(2)	$\alpha = 90$
	b = 13.8602(3)	$\beta = 93.258(2)$
	c = 8.7664(2)	$\gamma = 90$
Volume	965.37(4)	
Space group	P 1 21 1	
Hall group	P 2yb	
Moiety formula	C20 H14 Cl F O5 S2	
Density (calculated)	1.558	
Z	2	
F000	464.0	
R(reflections)	0.0316(3433)	
Theta(max)	79.915	
wR2(reflections)	0.0873(3523)	

Table 2 Data collection and structure refinement for 4-chloro substituted compound 2b

Identification code	final
Empirical formula	$C_{40}H_{48}O_{10}F_2S_4Cl_2$
Formula weight	925.92
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.9580(2)
b/Å	13.8602(3)
c/Å	8.7664(2)
α/°	90
β/°	93.258(2)
γ/°	90
Volume/Å^3	965.37(4)
Z	2
ρcalcmg/mm3	3.185
μ/mm^{-1}	8.292
F(000)	968.0
Crystal size/mm^3	0.26 × 0.16 × 0.05
2Θ range for data collection	10.106 to 159.83°
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 14, -9 ≤ l ≤ 11
Reflections collected	9383
Independent reflections	3525[R(int) = 0.0359]
Data/restraints/parameters	3525/1/262
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.1045
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1052
Largest diff. peak/hole / e Å^{-3}	0.30/-0.50
Flack parameter	-0.04(2)


NOMOVE FORCED
Prob = 50
Temp = 100
PLATON-Oct 4 19:34:41 2023 - (60723)
29 Y
Z -109 c20h14clfo5s2 P 1 21 1 R = 0.13 RES= 0 -5 X
Cl17
C5
C4
C6
C2
C3
O16
C7
C1
O13
C19
C20
S11
C18
O12
C8
F15
C21
C23
C22
S9
O14
C24
C28
C29
O10
C25
C27
C26


C
H
Cl
F
O
S

Crystallographic Data for Compound 2c #2427902

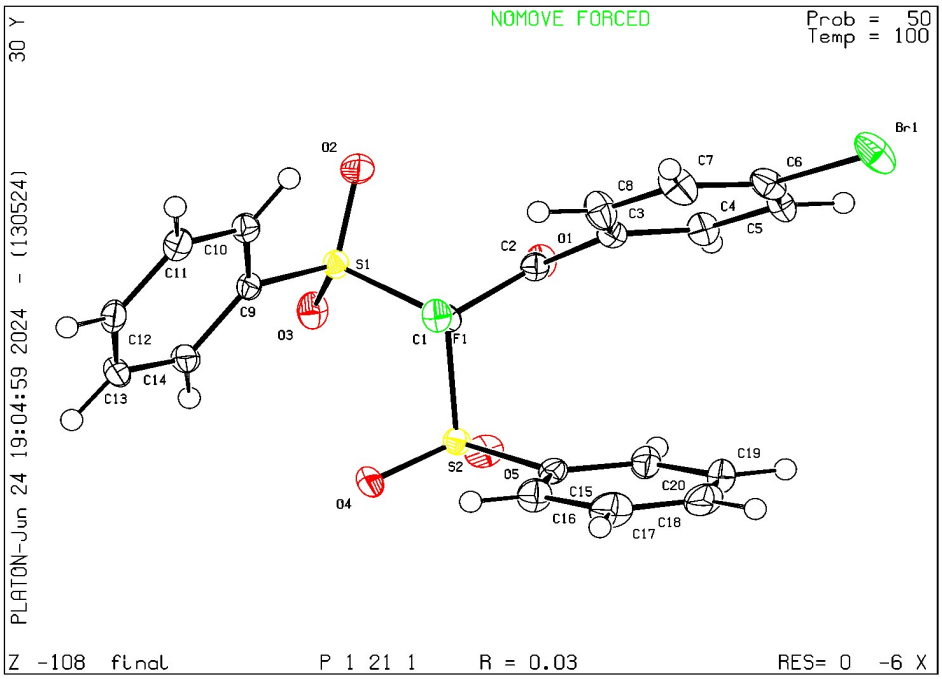
Table 3 Sample and crystal data for 4-bromo substituted compound 2c

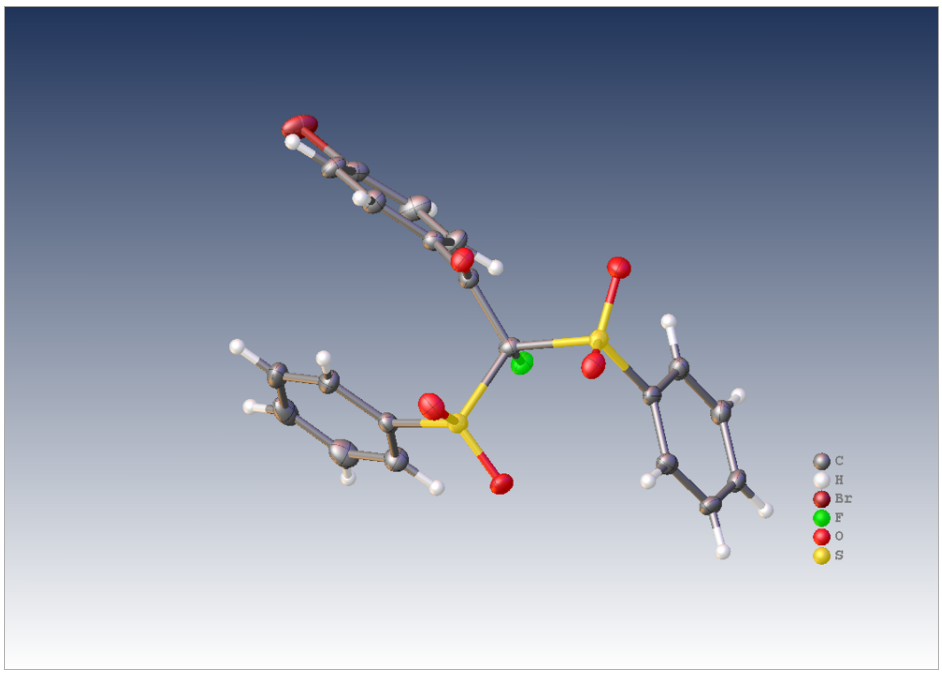
Wavelength	1.54184	
Temperature:	100 K	
Unit Cell Dimension	a = 7.9535(1)	a = 90
	b = 13.9305(2)	b = 92.192(1)
	c = 8.8111(1)	g = 90
Volume	975.52(2)	
Space group	P 1 21 1	
Hall group	P 2yb	
Moiety formula	C20 H14 Br F O5 S2	
Density (calculated)	1.693	
Z	2	
F000	500.0	
R(reflections)	0.0262 (3383)	
Theta(max)	79.922	
wR2(reflections)	0.0679 (3406)	

Table 4 Data collection and structure refinement for 4-bromo substituted compound 2c

Identification code	final
Empirical formula	C20H14BrFO5S2
Formula weight	497.34
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.95350(10)
b/Å	13.9305(2)
c/Å	8.81110(10)
α/°	90
β/°	92.1920(10)
γ/°	90
Volume/Å^3	975.52(2)
Z	2
ρcalcmg/mm3	1.693
μ/mm^{-1}	5.241
F(000)	500.0
Crystal size/mm^3	0.277 × 0.209 × 0.064
2Θ range for data collection	10.046 to 159.844°

Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 17, -11 ≤ l ≤ 7
Reflections collected	10509
Independent reflections	3406[R(int) = 0.0339]
Data/restraints/parameters	3406/1/263
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0260, wR_2 = 0.0675
Final R indexes [all data]	R_1 = 0.0261, wR_2 = 0.0676
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.55
Flack parameter	-0.002(12)





Crystallographic Data for Compound 2d #2427880

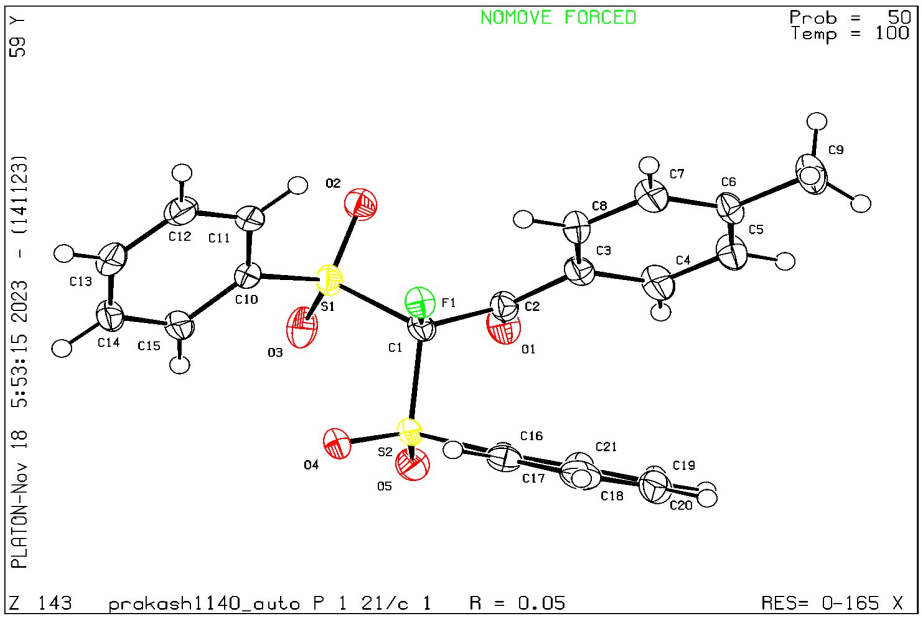
Table 5 Sample and crystal data for 4-methyl substituted compound 2d

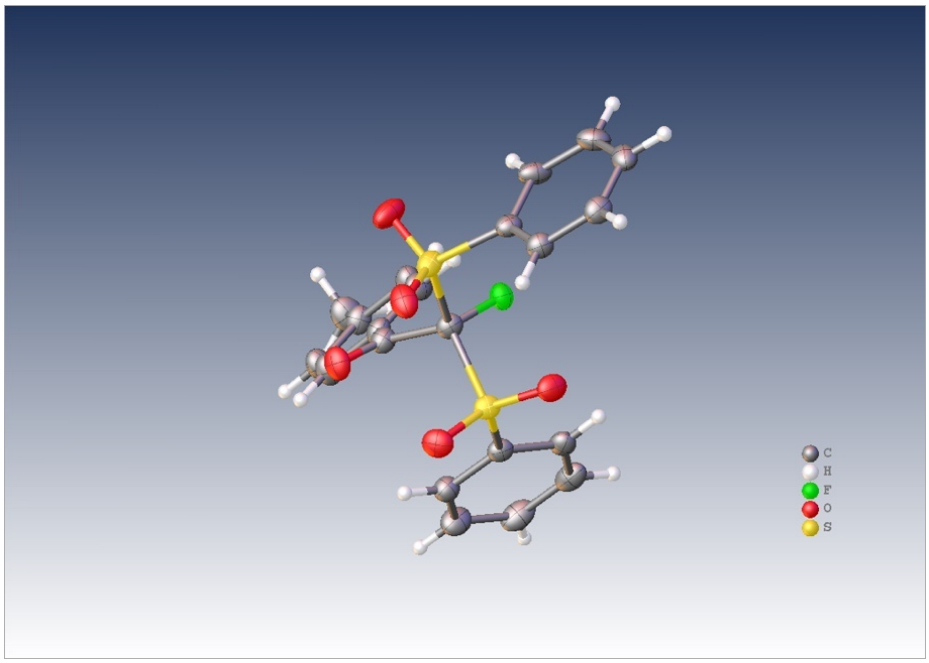
Wavelength	1.54184	
Temperature:	100 K	
Unit Cell Dimension	a = 16.6210(4)	α = 90
	b = 8.2842(2)	β = 115.877(3)
	c = 15.5276(3)	γ = 90
Volume	1923.65(9)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C21 H17 F O5 S2	
Density (calculated)	1.493	
Z	4	
F000	896.0	
R(reflections)	0.0546(3555)	
Theta(max)	80.089	
wR2(reflections)	0.1376(4082)	

Table 6 Data collection and structure refinement for 4-methyl substituted compound 2d

Identification code	Prakash1140_auto
Empirical formula	$C_{21}H_{17}FO_5S_2$
Formula weight	432.46
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.6210(4)
b/Å	8.2842(2)
c/Å	15.5276(3)
α/°	90
β/°	115.877(3)
γ/°	90
Volume/Å^3	1923.65(9)
Z	4
ρ_{calc}mg/mm3	1.493
μ/mm^{-1}	2.881
F(000)	896.0
Crystal size/mm^3	0.297 × 0.221 × 0.151
2Θ range for data collection	5.91 to 160.178°

Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 10, -19 ≤ l ≤ 15
Reflections collected	21635
Independent reflections	4082[R(int) = 0.0557]
Data/restraints/parameters	4082/0/263
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1342
Final R indexes [all data]	R_1 = 0.0621, wR_2 = 0.1376
Largest diff. peak/hole / e $Å^{-3}$	0.52/-0.49





Crystallographic Data for Compound 2e #2427890

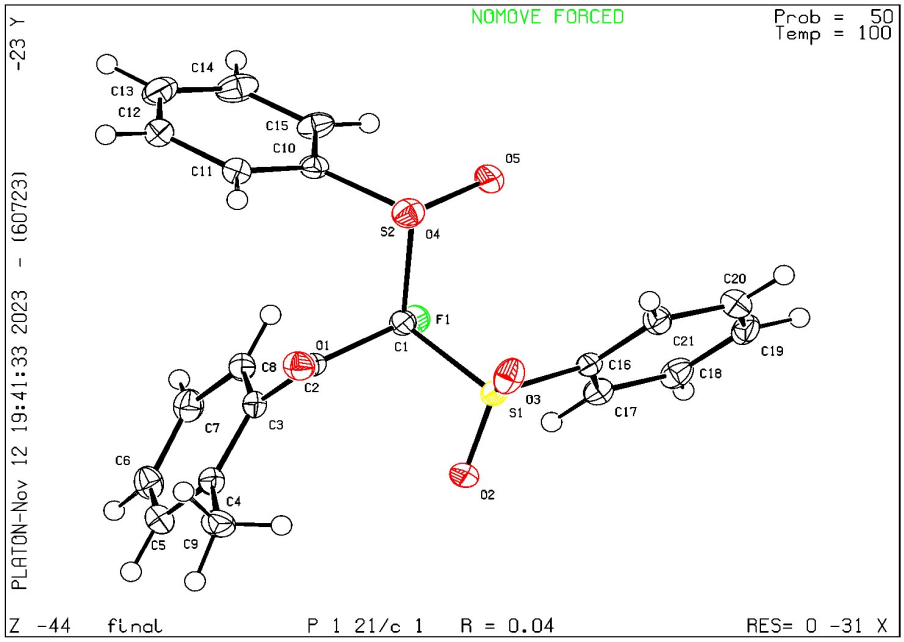
Table 7 Sample and crystal data for 2-methyl substituted compound 2e

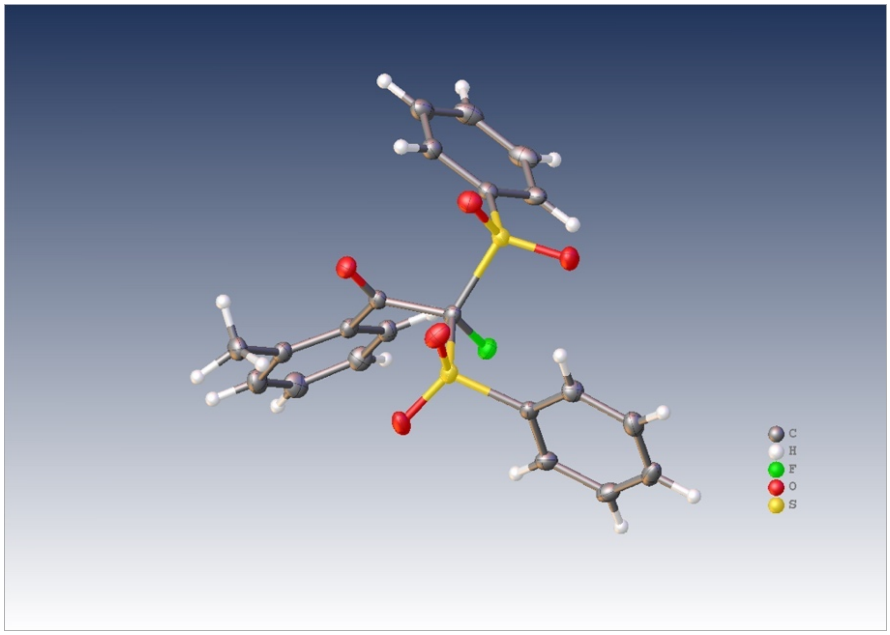
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimensions	a = 15.6629(4)	α = 90
	b = 8.1038(2)	β = 102.668(2)
	c = 15.2281(3)	γ = 90
Temperature:	100 K	
Volume	1885.84(8)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C21 H17 F O5 S2	
Dx,g cm-3	1.523	
Z	4	
F000	896.0	
R(reflections)	0.0409(3568)	
Theta(max)	79.918	
wR2(reflections)	0.1174(4025)	

Table 8 Data collection and structure refinement for 2-methyl substituted compound 2e

Identification code	final
Empirical formula	$C_{21}H_{17}FO_5S_2$
Formula weight	432.46
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.6629(4)
b/Å	8.1038(2)
c/Å	15.2281(3)
α/°	90
β/°	102.668(2)
γ/°	90

Volume/Å^3	1885.84(8)
Z	4
ρ_{calc}mg/mm^3	1.523
μ/mm^{-1}	2.939
F(000)	896.0
Crystal size/mm^3	0.144 × 0.115 × 0.04
2Θ range for data collection	5.784 to 159.836°
Index ranges	-20 ≤ h ≤ 19, -10 ≤ k ≤ 9, -18 ≤ l ≤ 19
Reflections collected	15134
Independent reflections	4025[R(int) = 0.0416]
Data/restraints/parameters	4025/0/264
Goodness-of-fit on F^2	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1110
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.1174
Largest diff. peak/hole / e Å^{-3}	0.39/-0.55

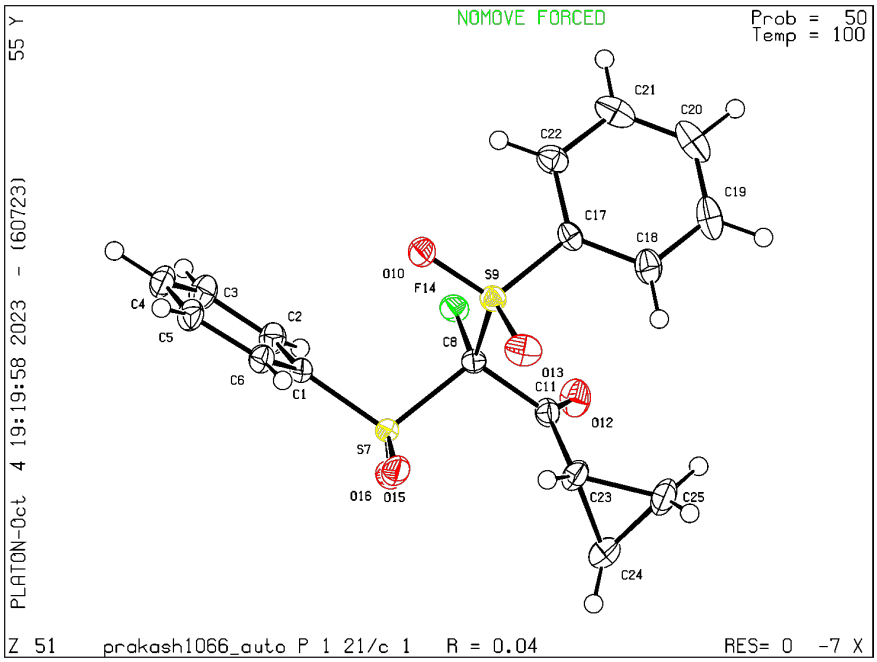



C
H
F
O
S

Crystallographic Data for Compound 2f #2427888

Table 9 Sample and crystal data for cyclopropyl substituted compound 2f

Wavelength	0.71073	
Unit Cell Dimension:	a = 10.2863(3)	α = 90
	b = 10.9184(3)	β = 99.818(2)
	c = 15.4499(4)	γ = 90
Temperature:	100 K	
Volume	1709.76(8)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C17 H15 F O5 S2	
Dx,g cm-3	1.486	
Z	4	
F000	792.0	
R(reflections)	0.0351(4129)	
Theta(max)	31.091	
wR2(reflections)	0.1013(4744)	




C
H
F
O
S

Crystallographic Data for Compound 2g #2427878

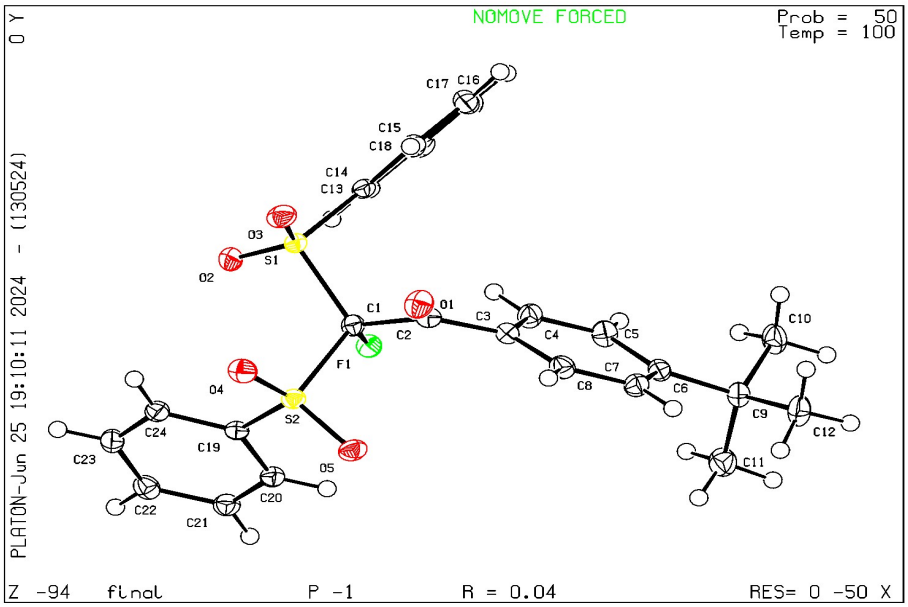
Table 10 Sample and crystal data for 4-tert butyl substituted compound 2g

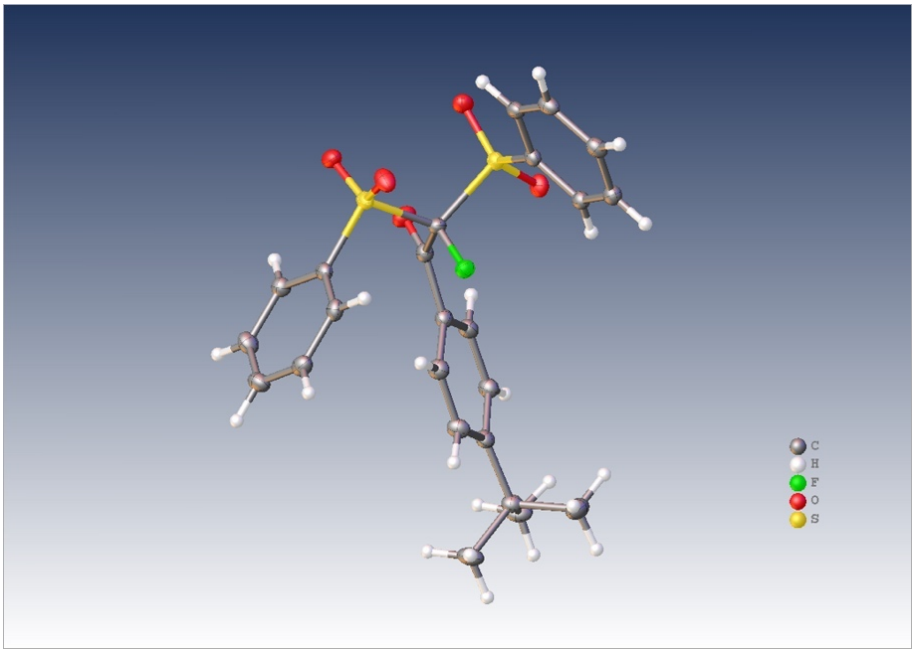
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 8.2701(3)	α = 98.003(3)
	b = 8.3246(3)	β = 101.714(3)
	c = 17.3376(7)	γ = 104.485(3)
Volume	1108.66(7)	
Space group	P -1	
Hall group	-P 1	
Moiety formula	C24 H23 F O5 S2	
Density (calculated)	1.422	
Z	2	
F000	496.0	
R(reflections)	0.0419(4204)	
Theta(max)	79.967	
wR2(reflections)	0.1091(4692)	

Table 11 Data collection and structure refinement for 4-tert butyl substituted compound 2g

Identification code	final
Empirical formula	$C_{24}H_{23}FO_5S_2$
Formula weight	474.54
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.2701(3)
b/Å	8.3246(3)
c/Å	17.3376(7)
α/°	98.003(3)
β/°	101.714(3)
γ/°	104.485(3)
Volume/Å^3	1108.66(7)
Z	2
ρ_{calc}mg/mm^3	1.422
μ/mm^{-1}	2.549
F(000)	496.0
Crystal size/mm^3	0.256 × 0.17 × 0.124
2Θ range for data collection	5.314 to 159.934°
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 8, -21 ≤ l ≤ 22

Reflections collected	16973
Independent reflections	4693[R(int) = 0.0458]
Data/restraints/parameters	4693/0/292
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0499, wR_2 = 0.1106
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.65





Crystallographic Data for Compound 2h #2427889

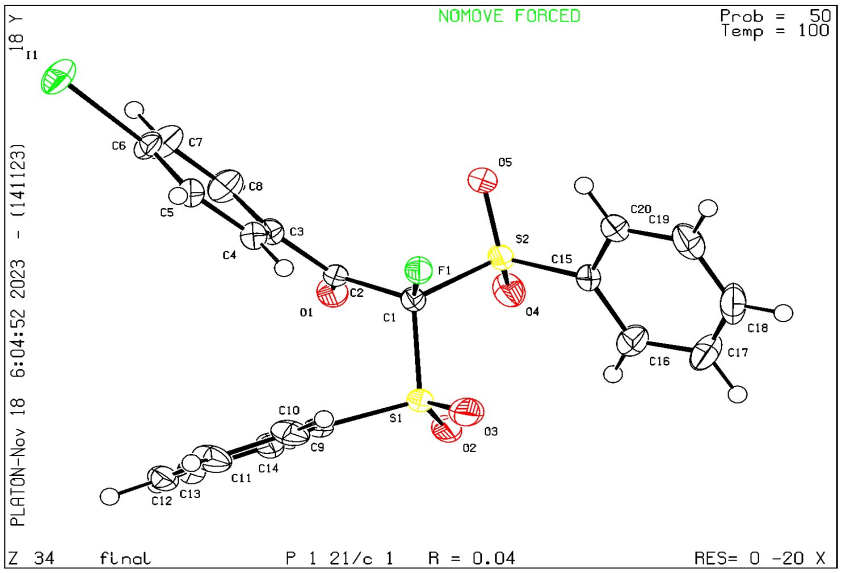
Table 12 Sample and crystal data for 4-iodo substituted compound 2h

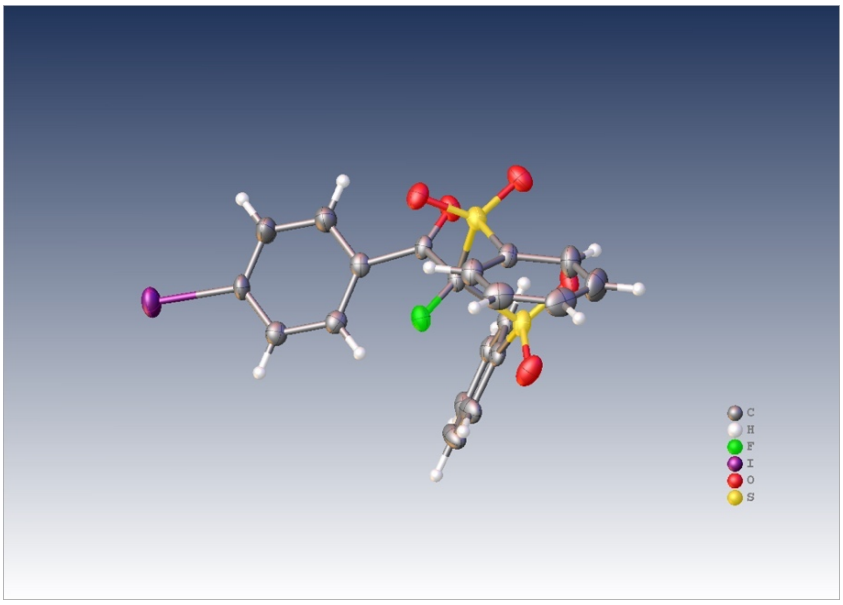
Wavelength	1.54184	
Temperature:	100 K	
Unit Cell Dimensions	a = 17.2647(3)	α = 90
	b = 8.0423(2)	β = 94.135(2)
	c = 14.3794(3)	γ = 90
Volume	1991.35(7)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C20 H14 F I O5 S2	
Density (calculated)	1.816	
Z	4	
F000	1072.0	
R(reflections)	0.0368(3781)	
Theta(max)	80.530	
wR2(reflections)	0.0953(4226)	

Table 13 Data collection and structure refinement for 4-iodo substituted compound 2h

Identification code	final
Empirical formula	$C_{20}H_{14}FIO_5S_2$
Formula weight	544.33
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.2647(3)
b/Å	8.0423(2)
c/Å	14.3794(3)
α/°	90
β/°	94.135(2)
γ/°	90
Volume/Å^3	1991.35(7)
Z	4
ρ_{calc}mg/mm3	1.816
μ/mm^{-1}	14.958
F(000)	1072.0

Crystal size/mm^3	0.147 × 0.125 × 0.093
2Θ range for data collection	5.132 to 161.06°
Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 8, -18 ≤ l ≤ 18
Reflections collected	20346
Independent reflections	4226[R(int) = 0.0463]
Data/restraints/parameters	4226/0/262
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0917
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.0953
Largest diff. peak/hole / e Å^{-3}	1.12/-0.98

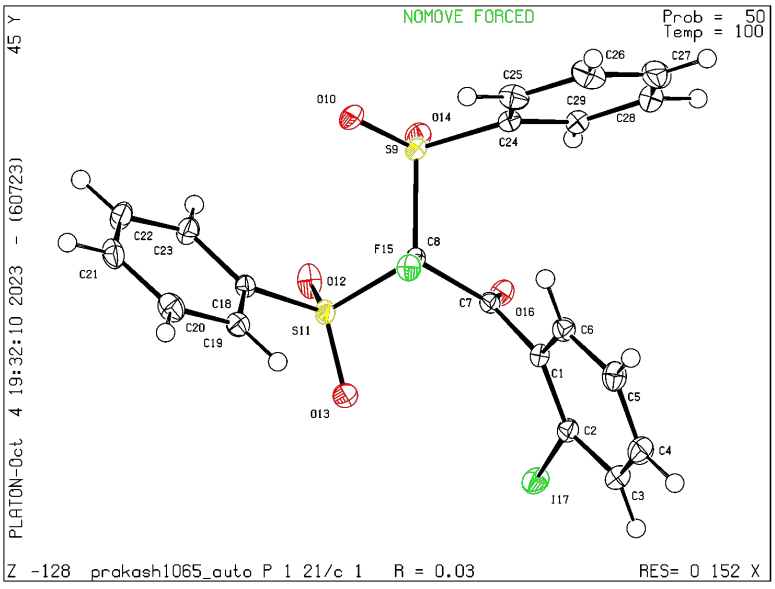


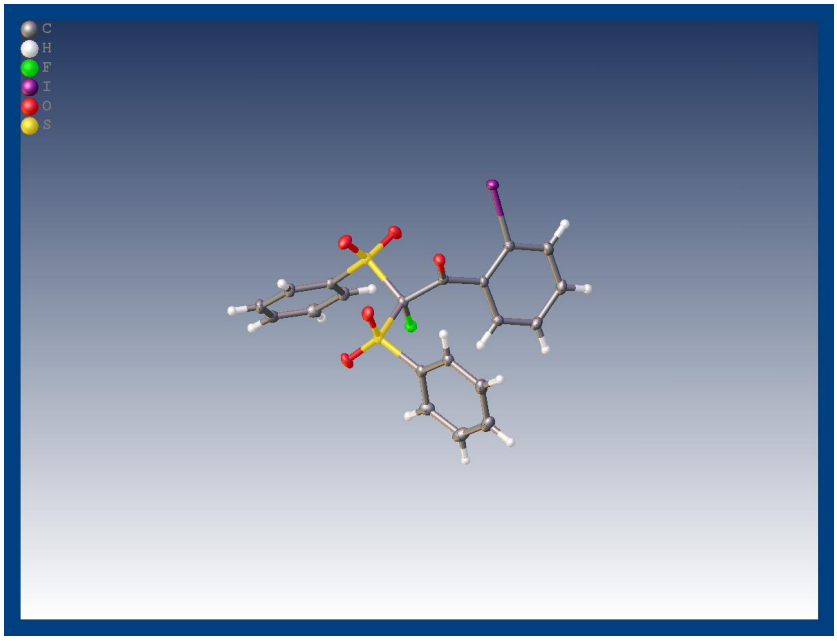


Crystallographic Data for Compound 2i #2427886

Table 14 Sample and crystal data for 2-iodo substituted compound 2i

Wavelength	0.71073	
Temperature	100 K	
United Cell Dimensions	a = 17.4250(4)	α = 90
	b = 8.06270(13)	β = 114.101(3)
	c = 15.5592(3)	γ = 90
Volume	1995.40(8)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C20 H14 F I O5 S2	
Density (calculated)	1.812	
Z	4	
F000	1072.0	
R(reflections)	0.0252(4743)	
Theta(max)	31.105	
wR2(reflections)	0.0571(5570)	




C
H
F
I
O
S

Crystallographic Data for Compound 2j #2427879

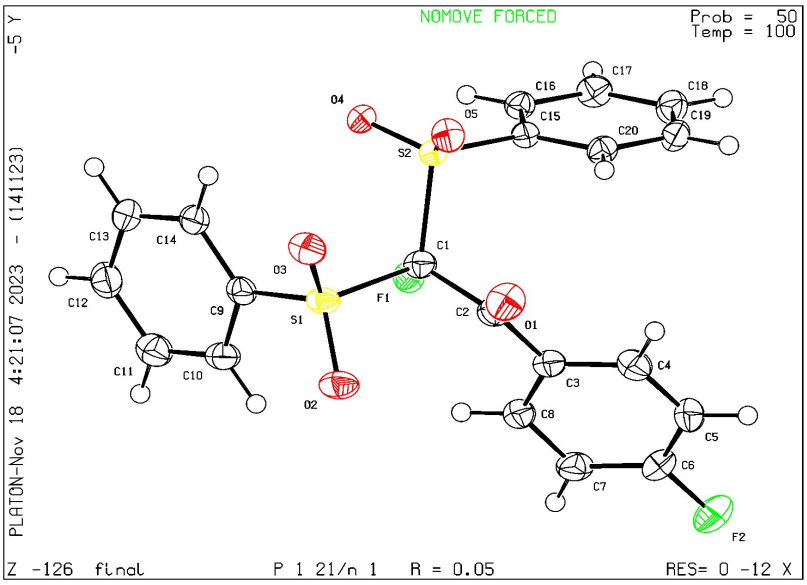
Table 15 Sample and crystal data for 4-fluoro substituted compound 2j

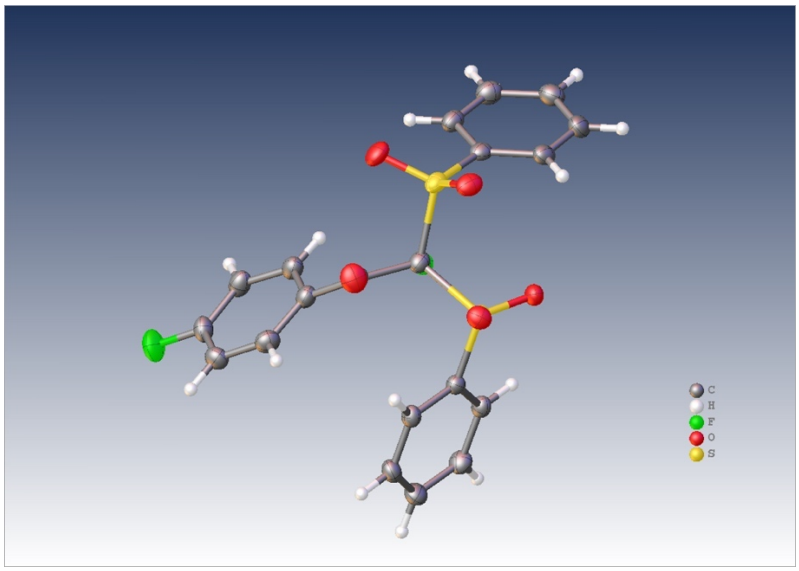
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimensions	a = 10.3372(1)	α = 90
	b = 16.7082(2)	β = 112.452(2)
	c = 11.9072(2)	γ = 90
Volume	1900.68(5)	
Space group	P 1 21/n 1	
Hall group	-P 2yn	
Moiety formula	C20 H14 F2 O5 S2	
Dx,g cm-3	1.525	
Z	4	
F000	896.0	
R(reflections)	0.0473(3813)	
Theta(max)	79.963	

Table 16 Data collection and structure refinement for 4-fluoro substituted compound 2j

Identification code	final
Empirical formula	$C_{20}H_{14}F_2O_5S_2$
Formula weight	436.43
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.33720(10)
b/Å	16.7082(2)
c/Å	11.9072(2)
α/°	90
β/°	112.452(2)
γ/°	90
Volume/Å^3	1900.68(5)
Z	4
ρ_{calc}mg/mm3	1.525
μ/mm^{-1}	3.002
F(000)	896.0
Crystal size/mm^3	0.2 × 0.13 × 0.04
2Θ range for data collection	9.624 to 159.926°
Index ranges	-13 ≤ h ≤ 12, -19 ≤ k ≤ 21, -14 ≤ l ≤ 15

Reflections collected	21344
Independent reflections	4037[R(int) = 0.0385]
Data/restraints/parameters	4037/0/262
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1131
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1147
Largest diff. peak/hole / e $Å^{-3}$	0.96/-0.48

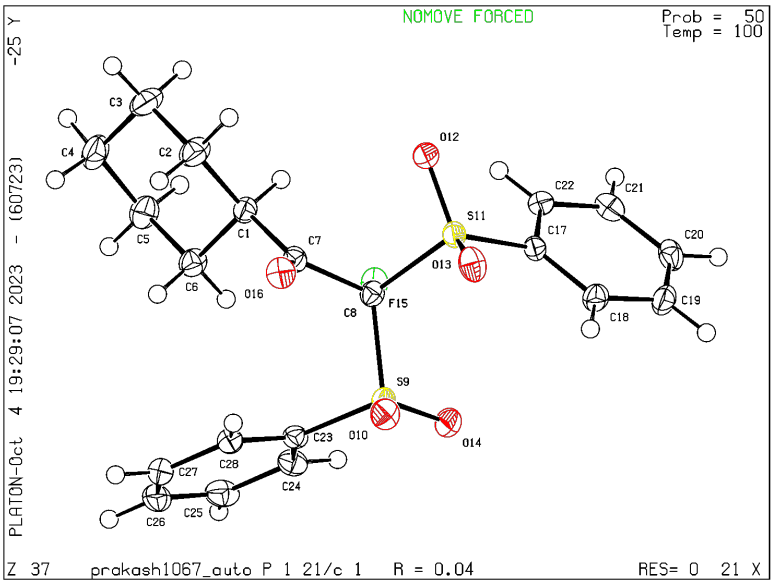


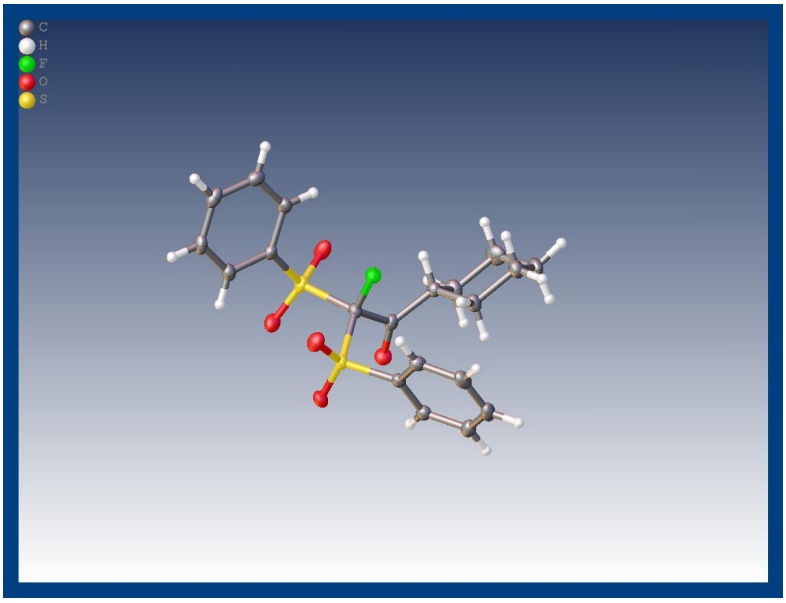


Crystallographic Data for Compound 2k #2427881

Table 17 Sample and crystal data for cyclohexyl substituted compound 2k

Wavelength	0.71073	
Temperature	100 K	
Unit Cell Dimensions	a = 15.5965(5)	α = 90
	b = 8.4659(3)	β = 94.799(3)
	c = 14.5245(5)	γ = 90
Volume	1911.07(11)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C20 H21 F O5 S2	
Density (calculated)	1.475	
Z	4	
F000	888.0	
R(reflections)	0.0439(3895)	
Theta(max)	31.089	
wR2(reflections)	0.1176(5081)	




C
H
F
O
S

Crystallographic Data for Compound 2l #2427883

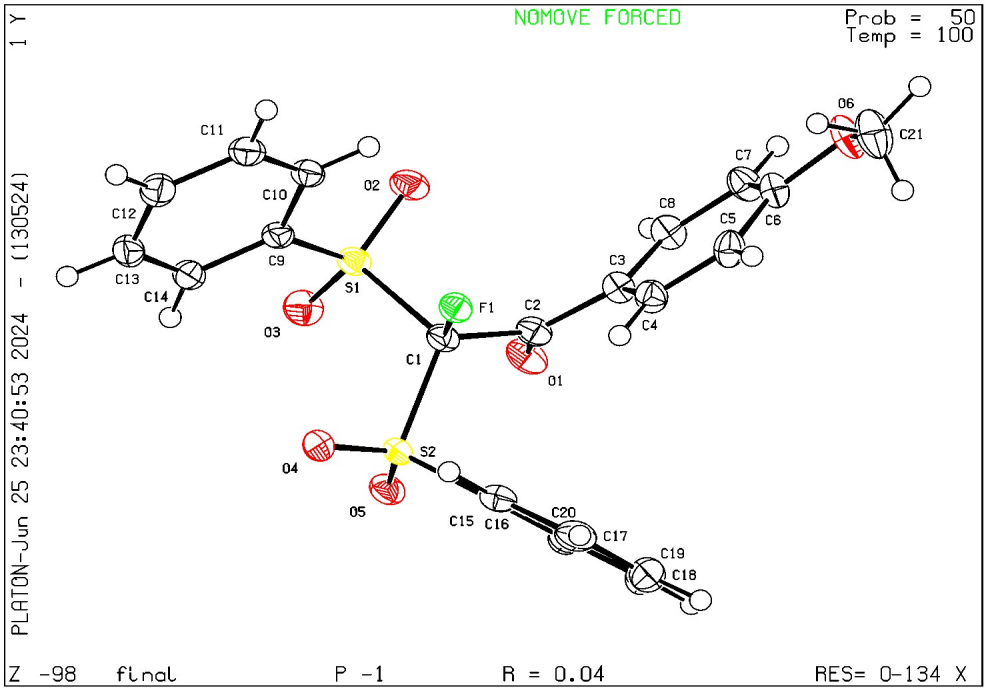
Table 18 Sample and crystal data for 4-methoxy substituted compound 2l

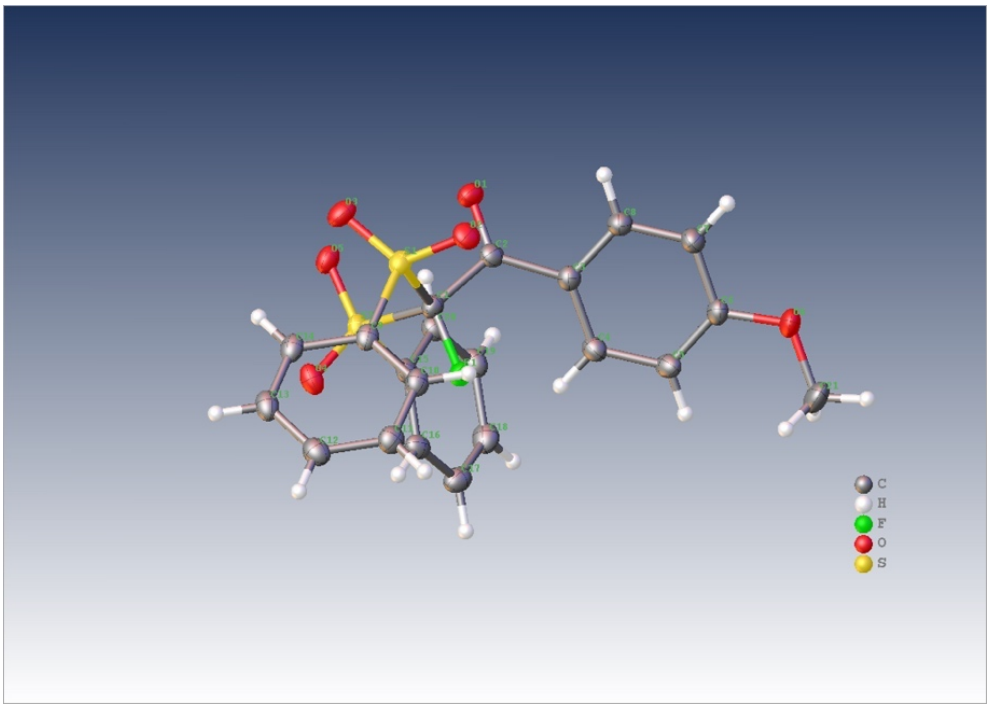
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimensions	a = 8.1330(1)	α = 103.650(1)
	b = 8.6239(1)	β = 98.883(1)
	c = 15.1497(2)	γ = 104.662(1)
Volume	972.67(2)	
Space group	P -1	
Hall group	-P 1	
Moiety formula	C21 H17 F O6 S2	
Density (calculated)	1.531	
Z	2	
F000	464.0	
R(reflections)	0.0357(3975)	
Theta(max)	80.075	
wR2(reflections)	0.0915(4119)	

Table 19 Data collection and structure refinement for 4-methoxy substituted compound 2l

Identification code	final
Empirical formula	$C_{21}H_{17}FO_6S_2$
Formula weight	448.46
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.13300(10)
b/Å	8.62390(10)
c/Å	15.1497(2)
α/°	103.6500(10)
β/°	98.8830(10)
γ/°	104.6620(10)
Volume/Å^3	972.67(2)
Z	2
ρ_{calc}mg/mm3	1.531
μ/mm^{-1}	2.912
F(000)	464.0
Crystal size/mm^3	0.236 × 0.119 × 0.108
2Θ range for data collection	6.166 to 160.15°

Index ranges	-6 ≤ h ≤ 10, -11 ≤ k ≤ 10, -19 ≤ l ≤ 19
Reflections collected	20652
Independent reflections	4119[R(int) = 0.0266]
Data/restraints/parameters	4119/0/273
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0909
Final R indexes [all data]	R_1 = 0.0365, wR_2 = 0.0915
Largest diff. peak/hole / e $Å^{-3}$	0.45/-0.41





Crystallographic Data for Compound 2m #2427873

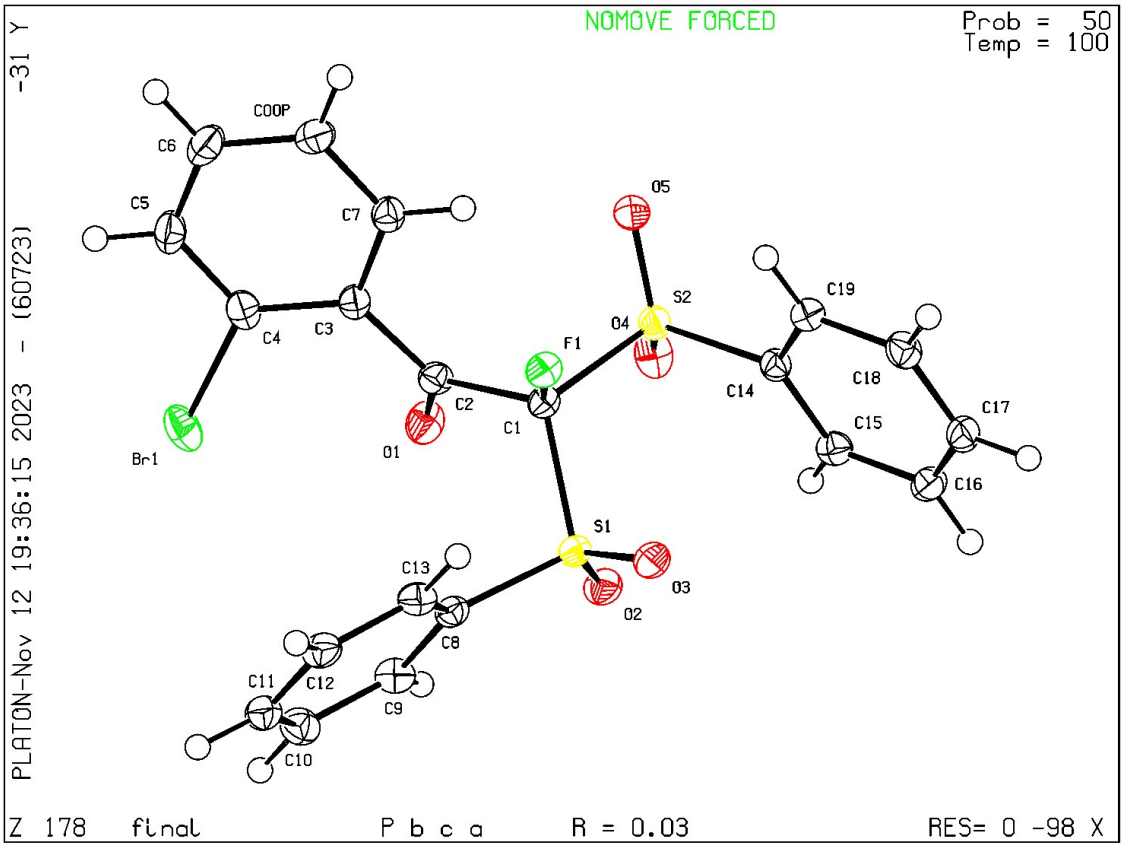
Table 20 Sample and crystal data for 4-bromo substituted compound 2m

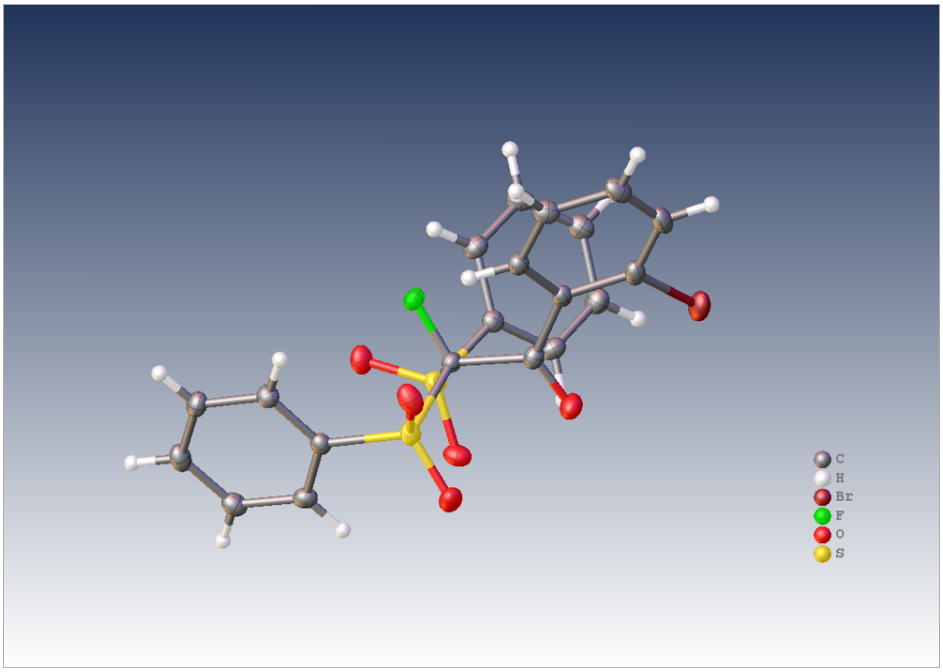
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimensions	a = 12.7777(2)	α = 90
	b = 14.0839(2)	β = 90
	c = 21.4027(3)	γ = 90
Volume	3851.63(10)	
Space group	P b c a	
Hall group	-P 2ac 2ab	
Moiety formula	C20 H14 Br F O5 S2	
Density (calculated)	1.715	
Z	8	
F000	2000.0	
R(reflections)	0.0305(3597)	
Theta(max)	79.806	
wR2(reflections)	0.0833(4077)	

Table 21 Data collection and structure refinement for 4-bromo substituted compound 2m

Identification code	final
Empirical formula	$C_{20}H_{14}O_5FS_2Br$
Formula weight	497.34
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.7777(2)
b/Å	14.0839(2)
c/Å	21.4027(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3851.63(10)
Z	8
ρ_{calc}mg/mm^3	1.715
μ/mm^{-1}	5.310
F(000)	2000.0
Crystal size/mm^3	? × ? × ?
2Θ range for data collection	8.262 to 159.612°

Index ranges	-16 ≤ h ≤ 16, -11 ≤ k ≤ 17, -27 ≤ l ≤ 25
Reflections collected	16871
Independent reflections	4077[R(int) = 0.0305]
Data/restraints/parameters	4077/0/262
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0781
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0833
Largest diff. peak/hole / e $Å^{-3}$	0.52/-0.52




C
H
Br
F
O
S

Crystallographic Data for Compound 2n #2427884

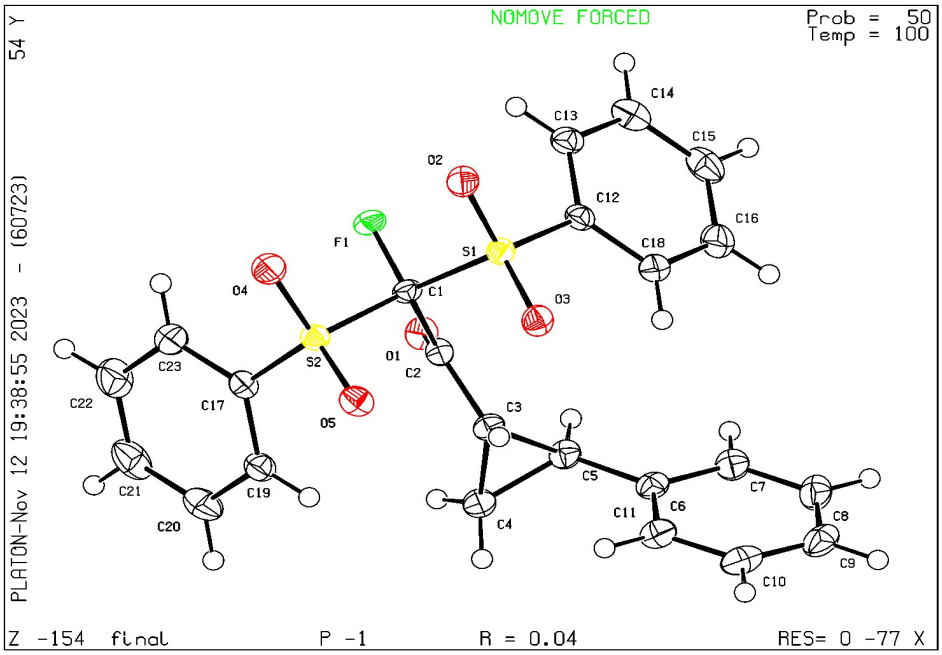
Table 22 Sample and crystal data for 2-phenylcyclopropyl substituted compound 2n

Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimensions	a = 8.2616(2)	α = 71.543(3)
	b = 10.5243(3)	β = 72.343(3)
	c = 13.3594(4)	γ = 76.521(2)
Volume	1037.77(6)	
Space group	P -1	
Hall group	-P -1	
Moiety formula	C23 H19 F O5 S2	
Density (calculated)	1.467	
Z	2	
F000	476.0	
R(reflections)	0.0350(4224)	
Theta(max)	79.784	
wR2(reflections)	0.0936(4400)	

Table 23 Data collection and structure refinement for 2-phenylcyclopropyl substituted compound 2n

Identification code	final
Empirical formula	$C_{23}H_{19}O_5FS_2$
Formula weight	458.50
Temperature/K	99.97(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.2616(2)
b/Å	10.5243(3)
c/Å	13.3594(4)
α/°	71.543(3)
β/°	72.343(3)
γ/°	76.521(2)
Volume/Å^3	1037.77(6)
Z	2
ρ_{calc}mg/mm^3	1.467
μ/mm^{-1}	2.705
F(000)	476.0
Crystal size/mm^3	0.345 × 0.286 × 0.07
2Θ range for data collection	7.202 to 159.568°

Index ranges	$-6 \le h \le 10, -13 \le k \le 13, -17 \le l \le 16$
Reflections collected	14619
Independent reflections	4400[R(int) = 0.0243]
Data/restraints/parameters	4400/0/280
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	$R_1 = 0.0350$, $wR_2 = 0.0928$
Final R indexes [all data]	$R_1 = 0.0361$, $wR_2 = 0.0936$
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.50



Crystallographic Data for Compound 2o #2427876

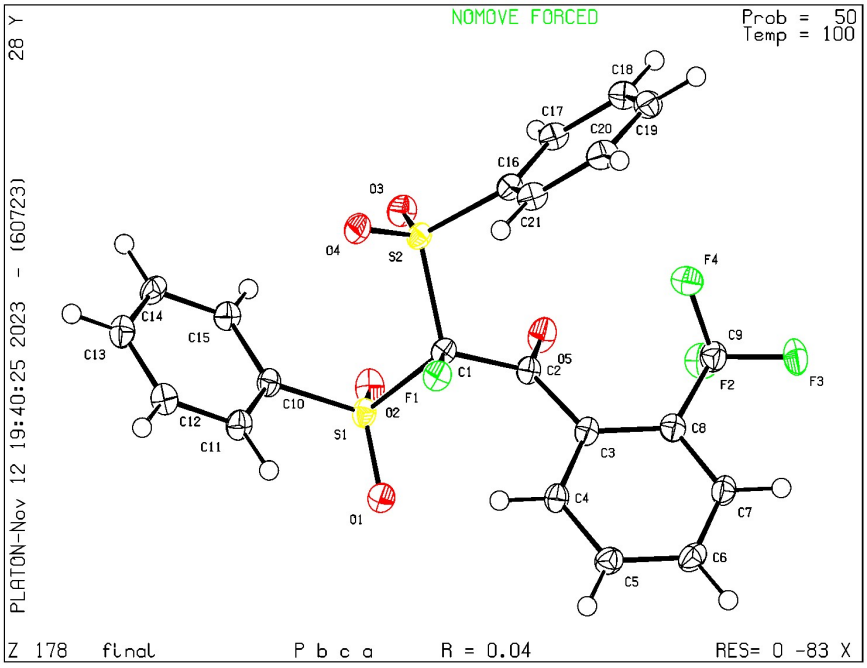
Table 24 Sample and crystal data for 2-trifluoromethyl substituted compound 2o

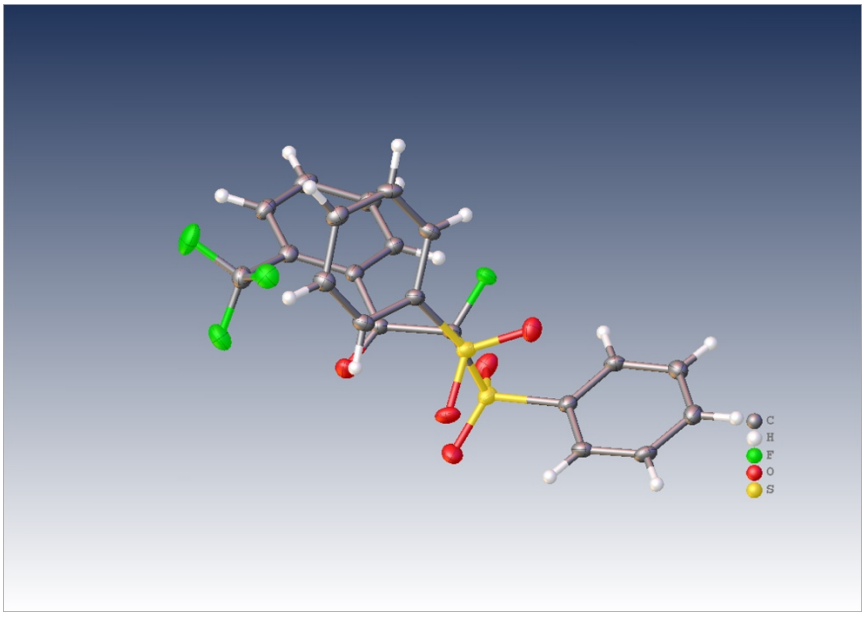
Wavelength	1.54184	
Temperature:	100 K	
Unit Cell Dimension	a = 12.8594(4)	α = 90
	b = 13.8837(3)	β = 90
	c = 21.9529(7)	γ = 90
Volume	3919.38(19)	
Space group	P b c a	
Hall group	-P 2ac 2ab	
Moiety formula	C21 H14 F4 O5 S2	
Dx,g cm-3	1.649	
Z	8	
F000	1984.0	
R(reflections)	0.0427(3662)	
Theta(max)	82.388	
wR2(reflections)	0.1213(4191)	

Table 25 Data collection and structure refinement for 2-trifluoromethyl substituted compound 2o

Identification code	final
Empirical formula	$C_{21}H_{14}O_5F_4S_2$
Formula weight	486.44
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.8594(4)
b/Å	13.8837(3)
c/Å	21.9529(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3919.38(19)
Z	8
ρ_{calc}mg/mm3	1.649
μ/mm^{-1}	3.133
F(000)	1984.0

Crystal size/mm^3	0.256 × 0.13 × 0.061
2Θ range for data collection	8.054 to 164.776°
Index ranges	-16 ≤ h ≤ 15, -17 ≤ k ≤ 10, -28 ≤ l ≤ 27
Reflections collected	17138
Independent reflections	4191[R(int) = 0.0441]
Data/restraints/parameters	4191/0/290
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0506, wR_2 = 0.1213
Largest diff. peak/hole / e Å^{-3}	0.50/-0.59





Crystallographic Data for Compound 2p #2427882

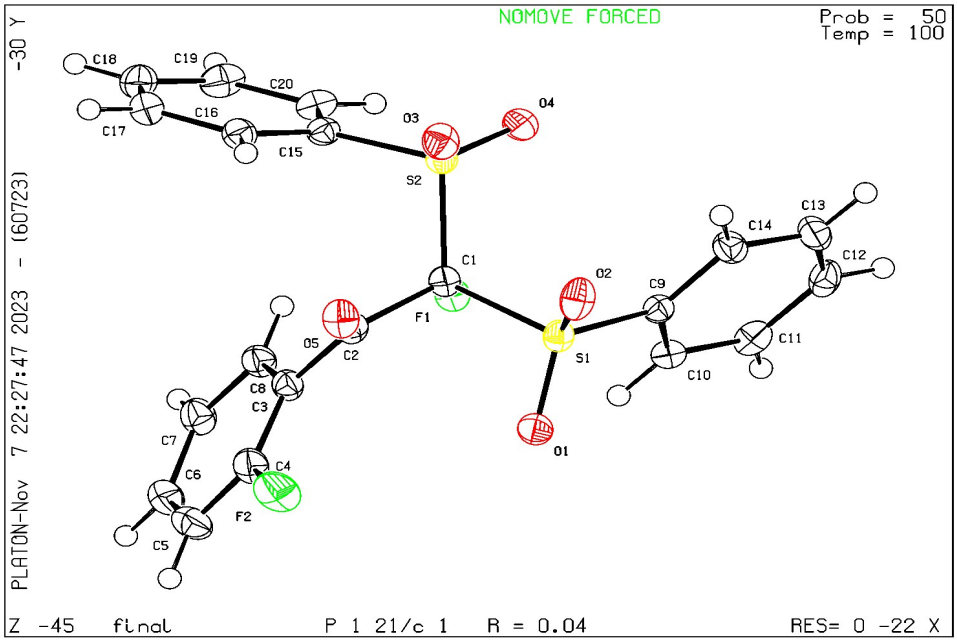
Table 26 Sample and crystal data for 2-fluoro substituted compound 2p

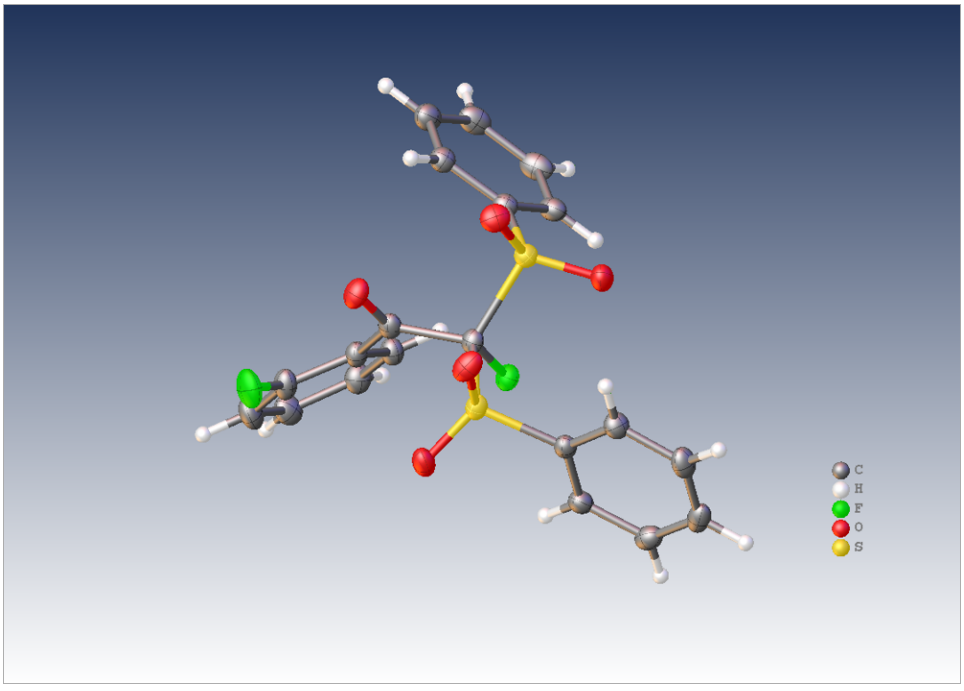
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 15.4575(3)	α = 90
	b = 8.0606(1)	β = 99.764(2)
	c = 15.0949(2)	γ = 90
Volume	1853.53(5)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C20 H14 F2 O5 S2	
Dx,g cm-3	1.564	
Z	4	
F000	896.0	
R(reflections)	0.0397(3517)	
Theta(max)	80.015	
wR2(reflections)	0.1078(3924)	

Table 27 Data collection and structure refinement for 2-fluoro substituted compound 2p

Identification code	final
Empirical formula	$C_{20}H_{14}F_2O_5S_2$
Formula weight	436.43
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.4575(3)
b/Å	8.06060(10)
c/Å	15.0949(2)
α/°	90
β/°	99.764(2)
γ/°	90
Volume/Å^3	1853.53(5)
Z	4
ρ_{calc}mg/mm3	1.564
μ/mm^{-1}	3.078
F(000)	896.0
Crystal size/mm^3	0.304 × 0.045 × 0.03

2Θ range for data collection	5.802 to 160.03°
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 10, -12 ≤ l ≤ 19
Reflections collected	15232
Independent reflections	3924[R(int) = 0.0385]
Data/restraints/parameters	3924/0/262
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.1045
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.1078
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.56





Crystallographic Data for Compound 2u #2427871

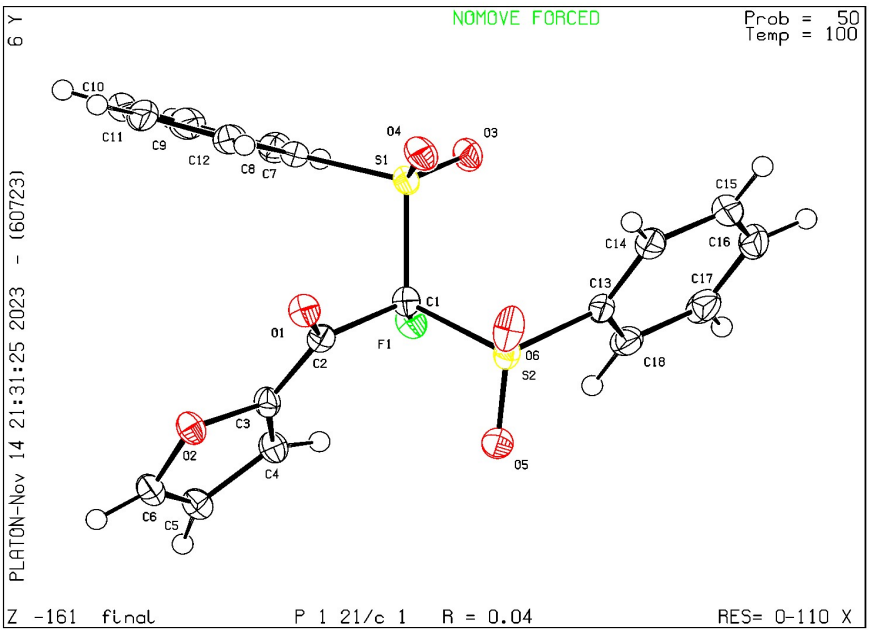
Table 28 Sample and crystal data for furyl substituted compound 2u

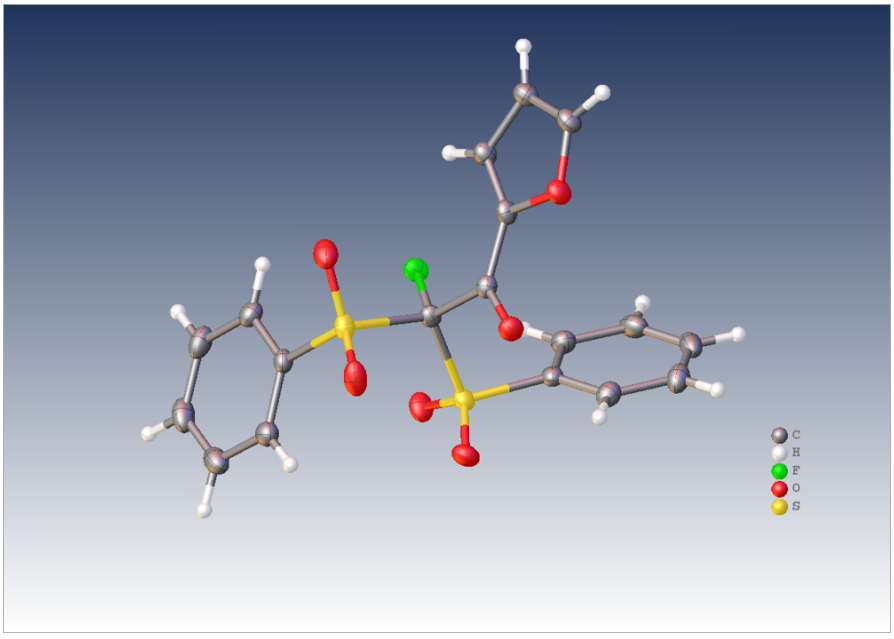
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 18.5720(4)	α = 90
	b = 6.2574(1)	β = 116.768(3)
	c = 16.8517(4)	γ = 90
Volume	1748.51(7)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C18 H13 F O6 S2	
Density (calculated)	1.551	
Z	4	
F000	840.0	
R(reflections)	0.0363(3271)	
Theta(max)	79.795	
wR2(reflections)	0.0970(3712)	

Table 29 Data collection and structure refinement for furyl substituted compound 2u

Identification code	final
Empirical formula	$C_{18}H_{13}FO_6S_2$
Formula weight	408.40
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.5720(4)
b/Å	6.25740(10)
c/Å	16.8517(4)
α/°	90
β/°	116.768(3)
γ/°	90
Volume/Å^3	1748.51(7)
Z	4
ρ_{calc}mg/mm^3	1.551
μ/mm^{-1}	3.177
F(000)	840.0
Crystal size/mm^3	0.28 × 0.204 × 0.136

2Θ range for data collection	5.33 to 159.59°
Index ranges	-23 ≤ h ≤ 23, -7 ≤ k ≤ 7, -21 ≤ l ≤ 19
Reflections collected	14237
Independent reflections	3712[R(int) = 0.0403]
Data/restraints/parameters	3712/0/244
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.0421, wR_2 = 0.0970
Largest diff. peak/hole / e $Å^{-3}$	0.45/-0.46





Crystallographic Data for Compound 2v #2427885

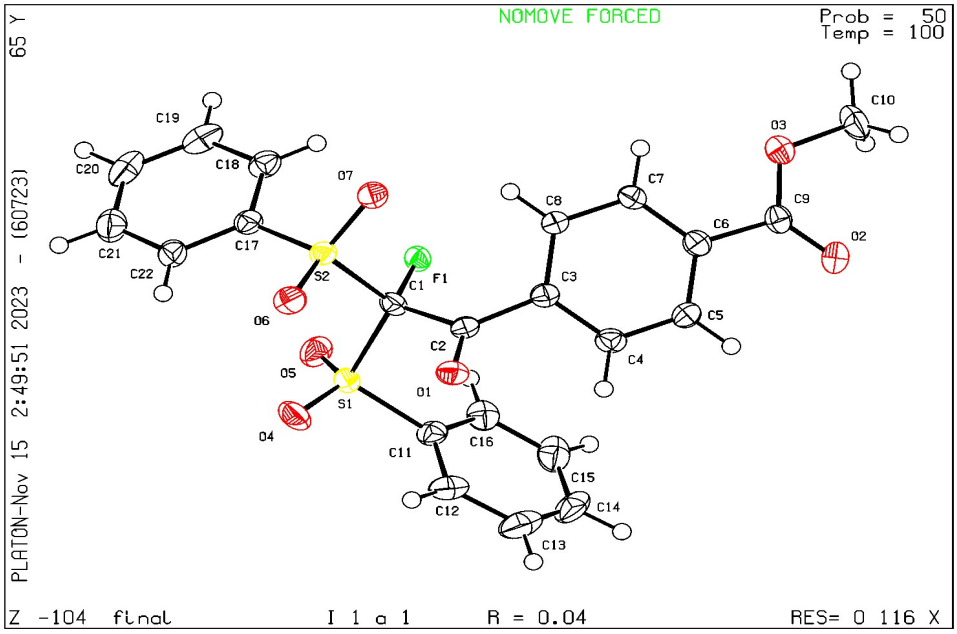
Table 30 Sample and crystal data for 4-methyl ester substituted compound 2v

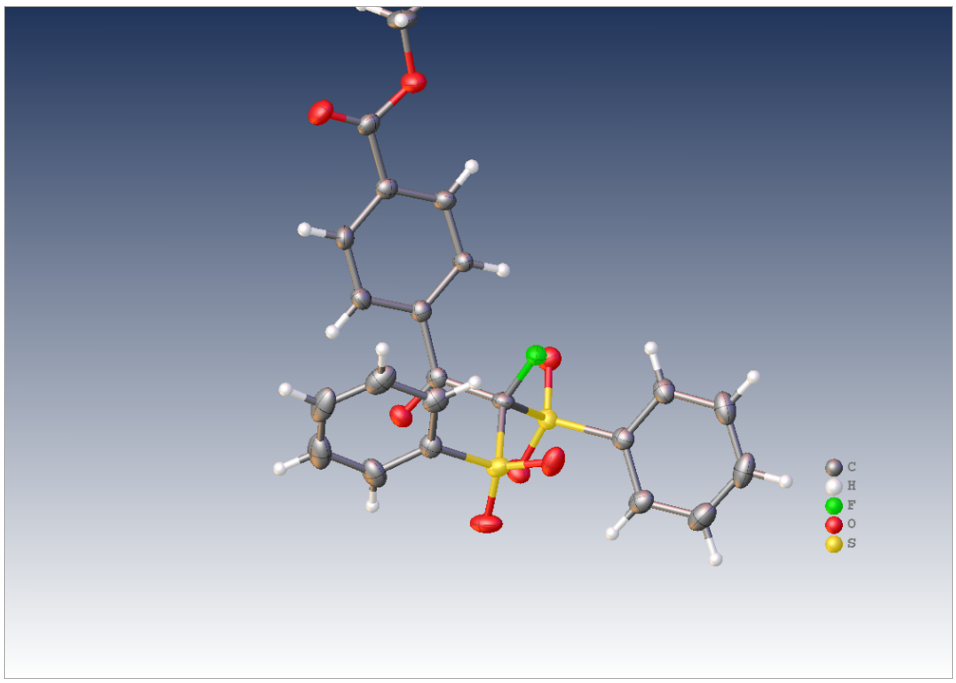
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 7.4312(1)	α = 90
	b = 19.0072(4)	β = 93.212(2)
	c = 14.7451(3)	γ = 90
Volume	2079.42(7)	
Space group	I 1 a 1	
Hall group	I -2ya	
Moiety formula	C22 H17 F O7 S2	
Density (calculated)	1.522	
Z	4	
F000	984.0	
R(reflections)	0.0388(3457)	
Theta(max)	80.208	
wR2(reflections)	0.1063(3544)	

Table 31 Data collection and structure refinement for 4-methyl ester substituted compound 2v

Identification code	final
Empirical formula	$C_{22}H_{17}FO_7S_2$
Formula weight	476.47
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	Ia
a/Å	7.43120(10)
b/Å	19.0072(4)
c/Å	14.7451(3)
α/°	90
β/°	93.212(2)
γ/°	90
Volume/Å^3	2079.42(7)
Z	4
ρ_{calc}mg/mm3	1.522
μ/mm^{-1}	2.800
F(000)	984.0
Crystal size/mm^3	0.348 × 0.203 × 0.065

2Θ range for data collection	7.596 to 160.416°
Index ranges	-8 ≤ h ≤ 9, -23 ≤ k ≤ 24, -18 ≤ l ≤ 18
Reflections collected	15835
Independent reflections	3544[R(int) = 0.0584]
Data/restraints/parameters	3544/2/290
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.1056
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1063
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.32
Flack parameter	-0.040(18)





Crystallographic Data for Compound 2w #2427874

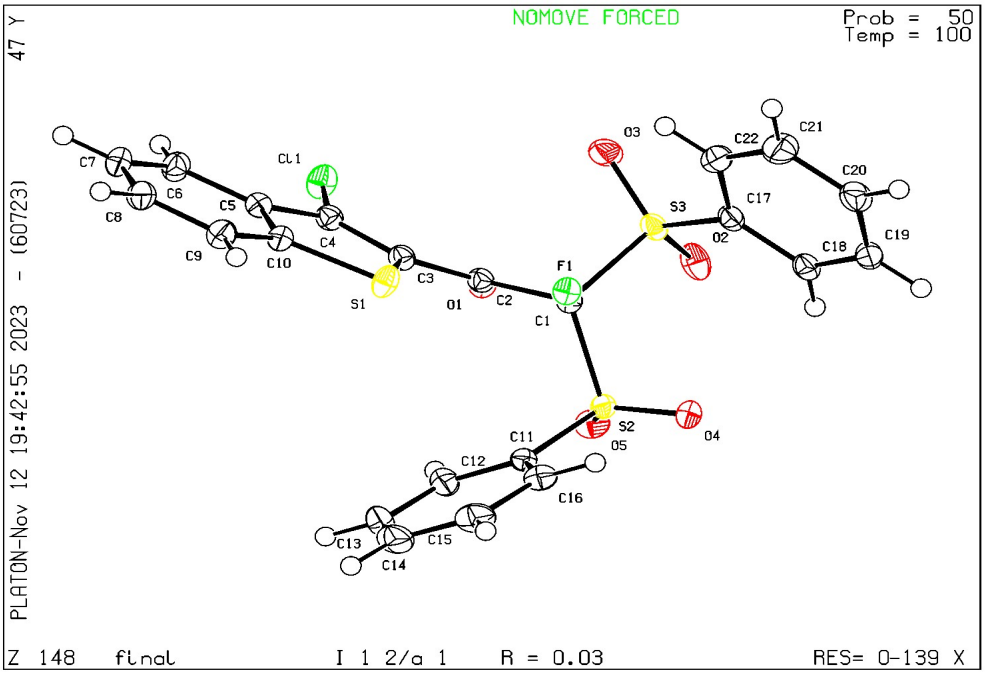
Table 32 Sample and crystal data for chlorobenzothiophene substituted compound 2w

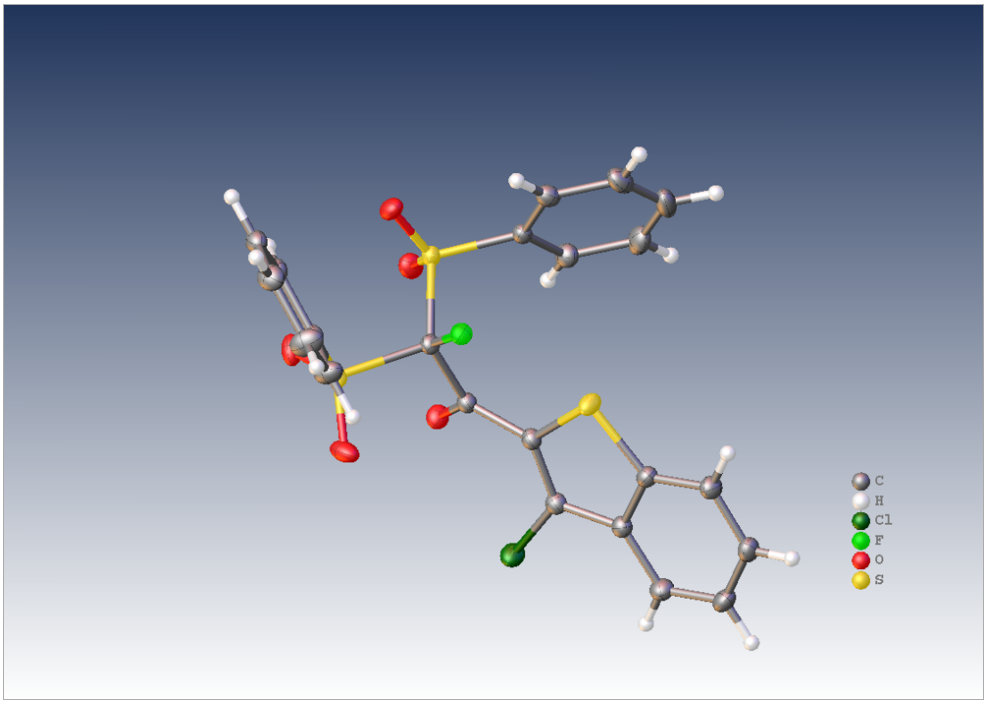
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 16.9595(2)	α = 90
	b = 7.9871(1)	β = 91.041(1)
	c = 31.2605(3)	γ = 90
Volume	4233.76(8)	
Space group	I 1 2/a 1	
Hall group	-I 2ya	
Moiety formula	C22 H14 Cl F O5 S3	
Dx,g cm-3	1.597	
Z	8	
F000	2080.0	
R(reflections	0.0298(4220)	
Theta(max)	79.989	
wR2(reflections)	0.0826(4459)	

Table 33 Data collection and structure refinement for chlorobenzothiophene substituted compound 2w

Identification code	final
Empirical formula	$C_{22}H_{14}ClFO_5S_3$
Formula weight	508.96
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	16.9595(2)
b/Å	7.98710(10)
c/Å	31.2605(3)
α/°	90
β/°	91.0410(10)
γ/°	90
Volume/Å^3	4233.76(8)
Z	8
ρ_{calc}mg/mm^3	1.597
μ/mm^{-1}	4.753
F(000)	2080.0
Crystal size/mm^3	0.389 × 0.215 × 0.072
2Θ range for data collection	5.656 to 159.978°
Index ranges	-21 ≤ h ≤ 17, -9 ≤ k ≤ 10, -39 ≤ l ≤ 38

Reflections collected	17582
Independent reflections	4459[R(int) = 0.0299]
Data/restraints/parameters	4459/0/289
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0298, wR_2 = 0.0815
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0826
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.40





Crystallographic Data for Compound 3b #2427887

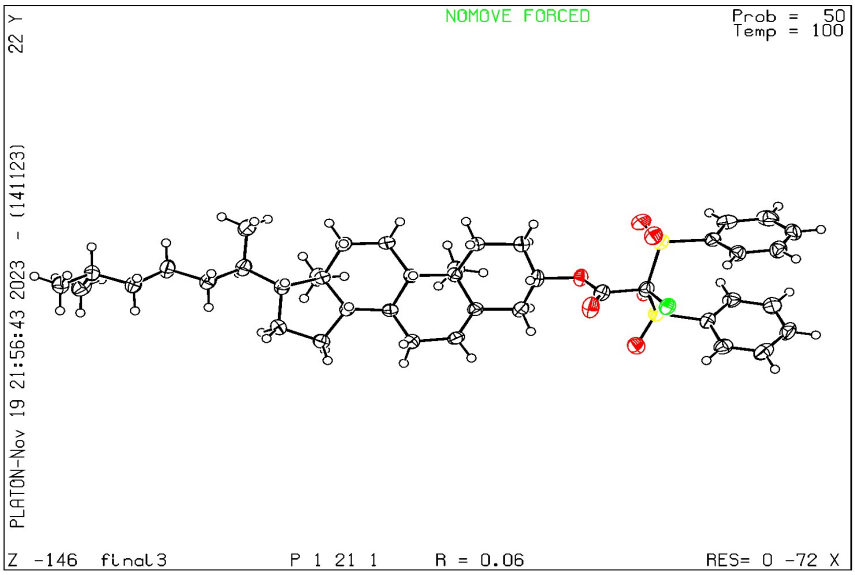
Table 34 Sample and crystal data for cholesterol substituted compound 3b

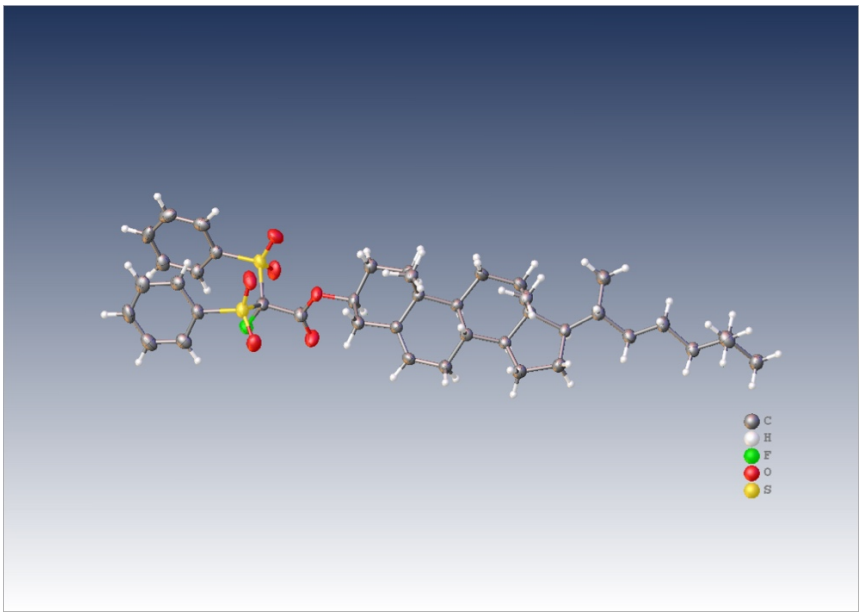
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 9.6794(5)	α = 90
	b = 11.5261(8)	β = 98.176(6)
	c = 17.4102(12)	γ = 90
Volume	1922.6(2)	
Space group	P 1 21 1	
Hall group	P 2yb	
Moiety formula	C41 H55 F O6 S2	
Density (calculated)	1.256	
Z	2	
F000	780.0	
R(reflections)	0.0600(6097)	
Theta(max)	79.824	
wR2(reflections)	0.1571(7410)	

Table 35 Data collection and structure refinement for cholesterol substituted compound 3b

Identification code	final3
Empirical formula	C41H55FO6S2
Formula weight	726.97
Temperature/K	99.98(11)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6794(5)
b/Å	11.5261(8)
c/Å	17.4102(12)
α/°	90
β/°	98.176(6)
γ/°	90
Volume/$Å^3$	1922.6(2)
Z	2
ρcalcmg/mm3	1.256
μ/mm^{-1}	1.663
F(000)	780.0
Crystal size/mm^3	0.089 × 0.066 × 0.032

2Θ range for data collection	5.128 to 159.648°
Index ranges	-9 ≤ h ≤ 12, -14 ≤ k ≤ 14, -22 ≤ l ≤ 19
Reflections collected	20087
Independent reflections	7410[R(int) = 0.0767]
Data/restraints/parameters	7410/1/456
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0600, wR_2 = 0.1476
Final R indexes [all data]	R_1 = 0.0775, wR_2 = 0.1571
Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.36
Flack parameter	-0.02(2)





Crystallographic Data for Compound 3c #2427877

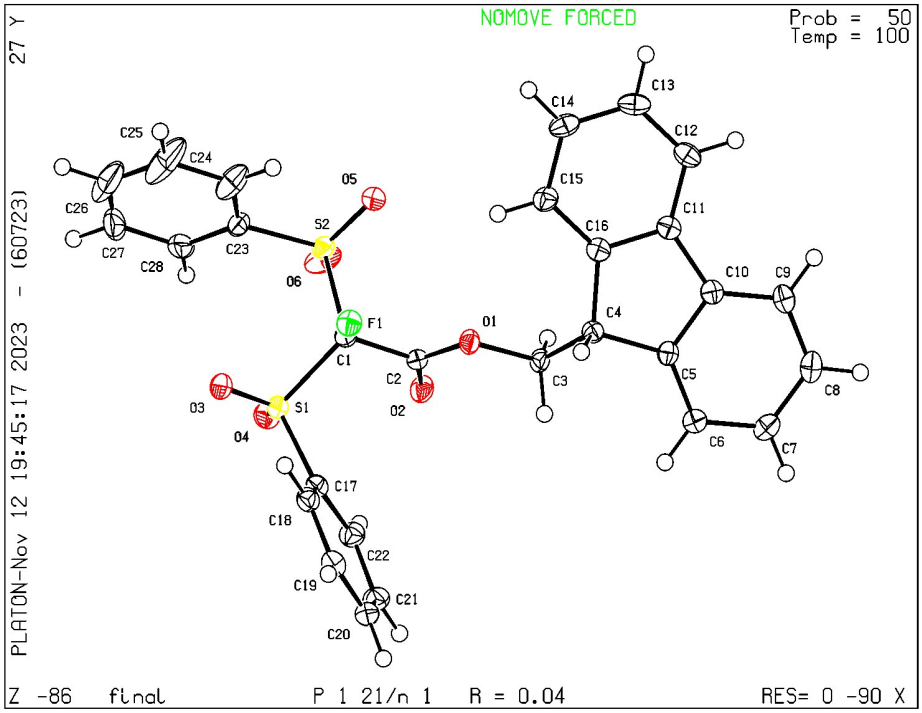
Table 36 Sample and crystal data for fmoc substituted compound 3c

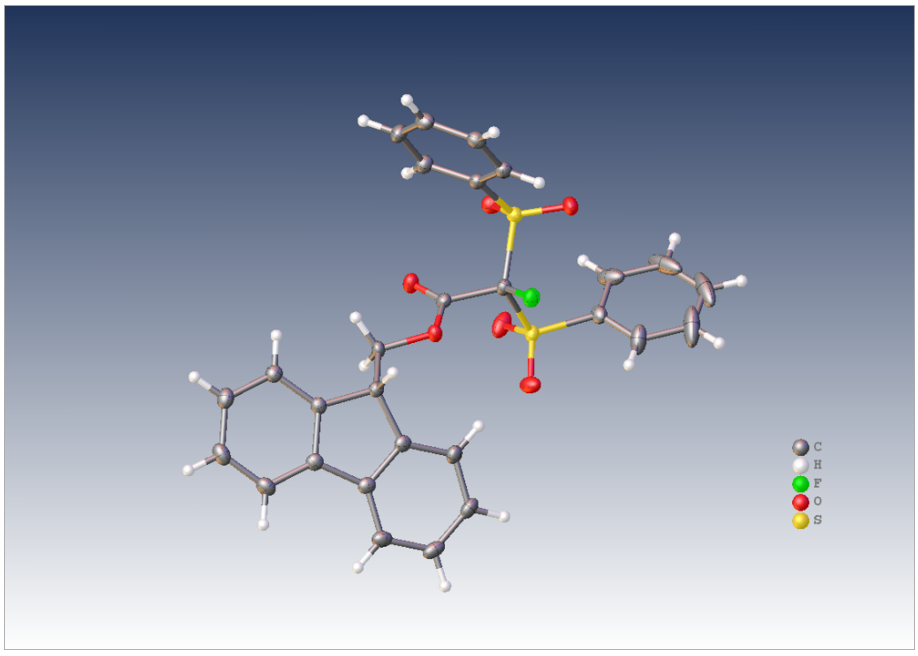
Wavelength	1.54184	
Temperature:	100 K	
Unit Cell Dimension	a = 8.1826(2)	α = 90
	b = 7.7862(2)	β = 91.370(2)
	c = 37.8984(9)	γ = 90
Volume	2413.87(10)	
Space group	P 1 21/n 1	
Hall group	-P 2yn	
Moiety formula	4(C28 H21 F O6 S2)	
Density (calculated)	1.476	
Z	1	
F000	1112.0	
R(reflections)	0.0426(4547)	
Theta(max)	80.242	
wR2(reflections)	0.1144(5165)	

Table 37 Data collection and structure refinement for fmoc substituted compound 3c

Identification code	final
Empirical formula	$C_{112}H_{84}O_{24}S_8F_4$
Formula weight	2146.27
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.1826(2)
b/Å	7.7862(2)
c/Å	37.8984(9)
α/°	90
β/°	91.370(2)
γ/°	90
Volume/Å^3	2413.87(10)
Z	1
ρcalcmg/mm3	1.476
μ/mm^{-1}	2.451
F(000)	1112.0
Crystal size/mm^3	0.208 × 0.091 × 0.07
2Θ range for data collection	4.664 to 160.484°

Index ranges	-8 ≤ h ≤ 10, -9 ≤ k ≤ 9, -48 ≤ l ≤ 47
Reflections collected	19456
Independent reflections	5165[R(int) = 0.0494]
Data/restraints/parameters	5165/18/334
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1114
Final R indexes [all data]	R_1 = 0.0486, wR_2 = 0.1144
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.48





Crystallographic Data for Compound 3d #2427872

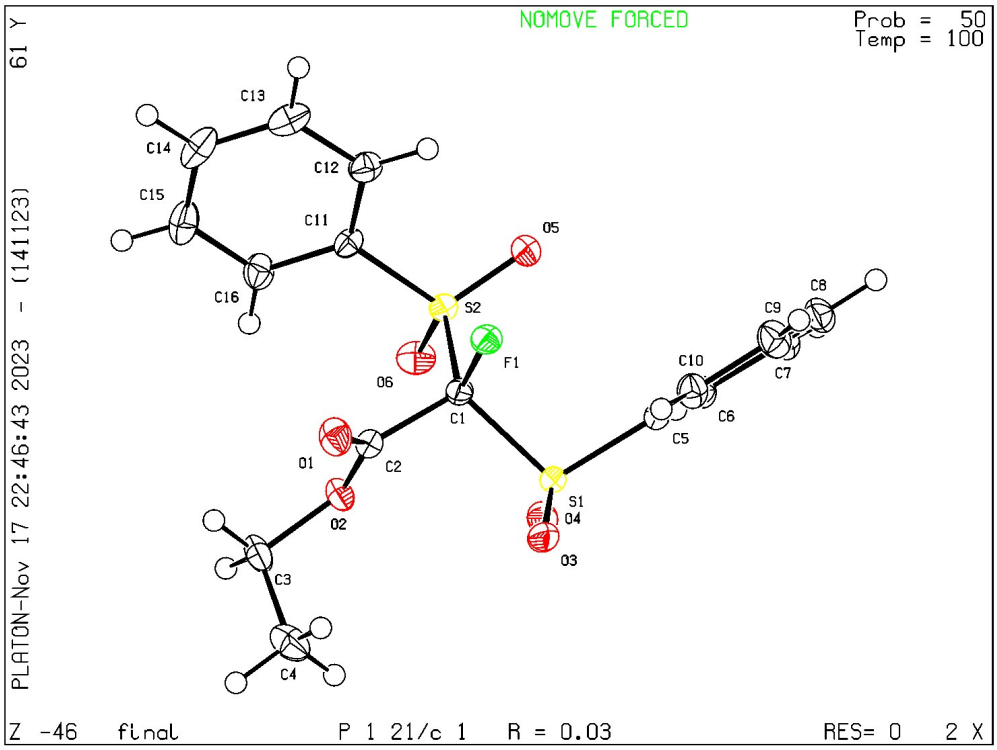
Table 38 Sample and crystal data for ethyl substituted compound 3d

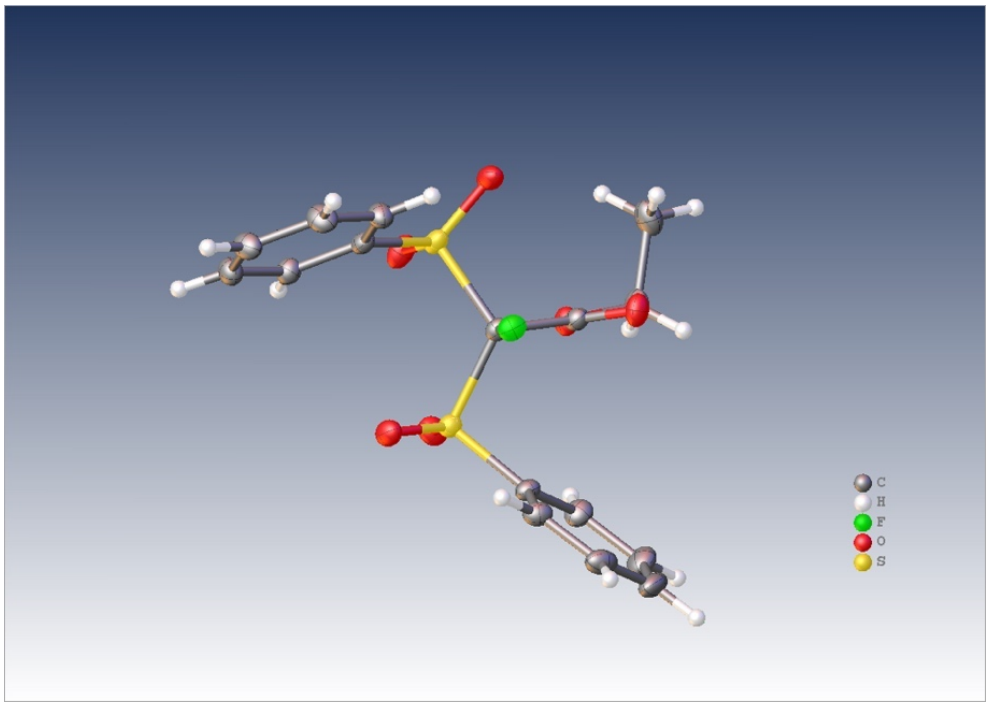
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 10.3756(1)	α = 90
	b = 10.7732(1)	β = 98.934(1)
	c = 15.8510(2)	γ = 90
Volume	1750.30(3)	
Space group	P 1 21/c 1	
Hall group	-P 2ybc	
Moiety formula	C16 H15 F O6 S2	
Density (calculated)	1.466	
Z	4	
F000	800.0	
R(reflections)	0.0301(3550)	
Theta(max)	79.846	
wR2(reflections)	0.0817(3742)	

Table 39 Data collection and structure refinement for ethyl substituted compound 3d

Identification code	final
Empirical formula	C16H15FO6S2
Formula weight	386.40
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.37560(10)
b/Å	10.77320(10)
c/Å	15.8510(2)
α/°	90
β/°	98.9340(10)
γ/°	90
Volume/$Å^3$	1750.30(3)
Z	4
ρcalcmg/mm3	1.466
μ/mm^{-1}	3.133
F(000)	800.0
Crystal size/mm^3	0.495 × 0.139 × 0.105
2Θ range for data collection	8.628 to 159.692°
Index ranges	-13 ≤ h ≤ 12, -13 ≤ k ≤ 12, -20 ≤ l ≤ 19

Reflections collected	18910
Independent reflections	3742[R(int) = 0.0321]
Data/restraints/parameters	3742/0/228
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0805
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0817
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.43





Crystallographic Data for Compound 4b #2427870

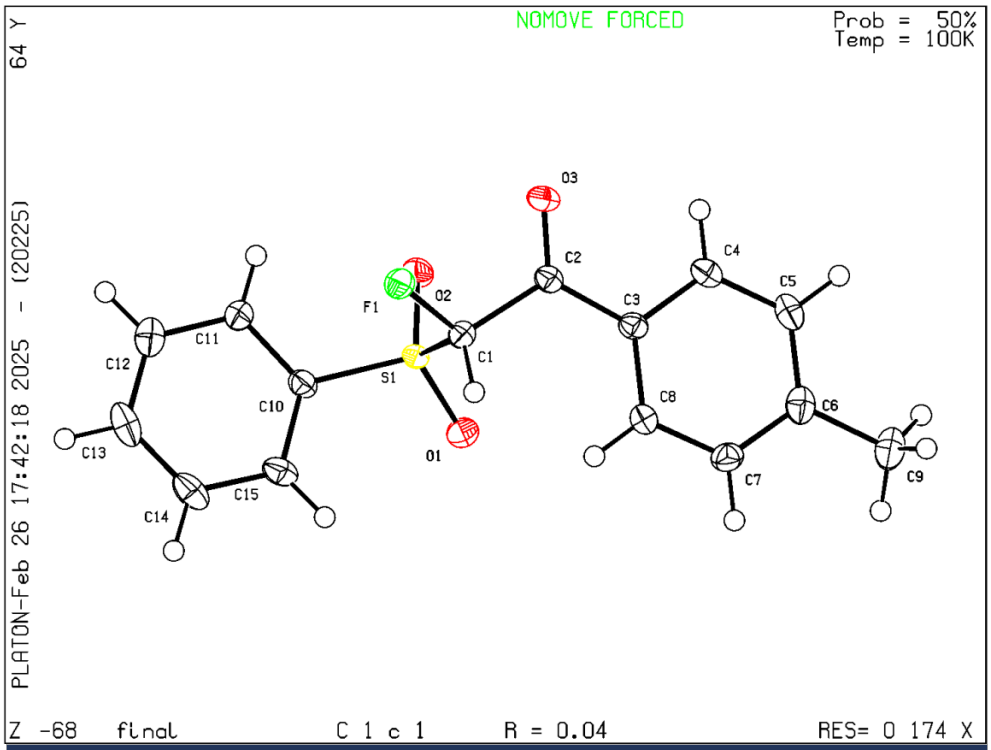
Table 40 Sample and crystal data for partially reduced 4-methyl substituted compound 4b

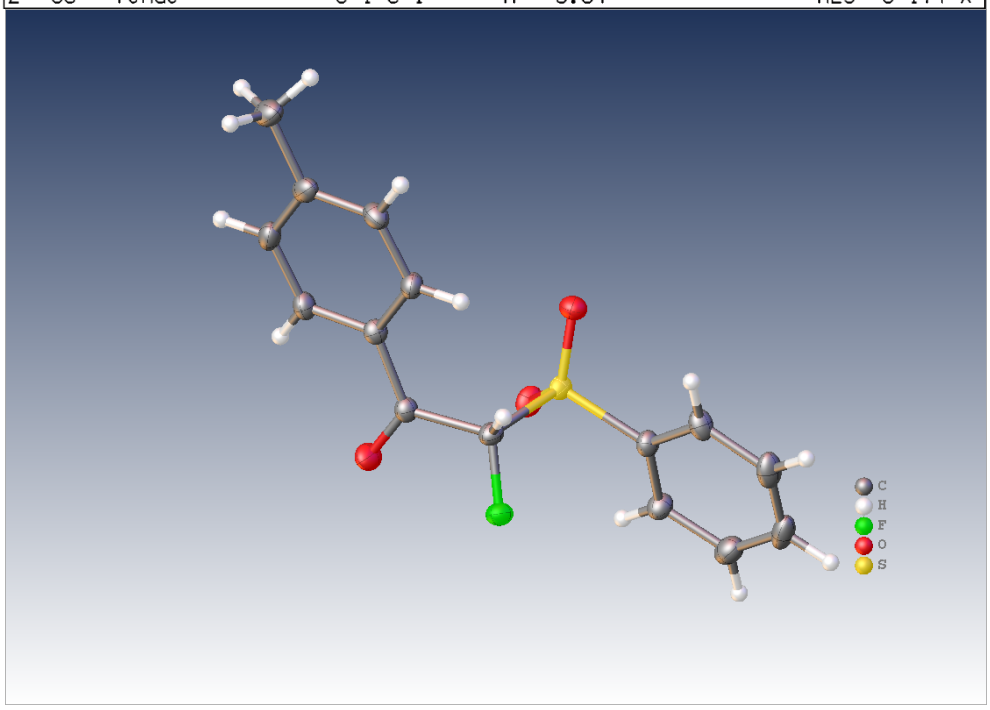
Wavelength	1.54184	
Temperature	100 K	
Unit Cell Dimension	a = 9.8930 (2)	α = 90
	b = 14.4664 (3)	β = 104.429 (2)
	c = 9.7170 (2)	γ = 90
Volume	1346.79 (5)	
Space group	C1c1	
Hall group	C -2yc	
Moiety formula	C15 H13 F O3 S	
Density (calculated)	1.442	
Z	4	
F000	608.0	
R(reflections)	0.0352 (1784)	
Theta(max)	79.697	
wR2(reflections)	0.0891 (1831)	

Table 41 Data collection and structure refinement for partially reduced 4-methyl substituted compound 4b

Identification code	final
Empirical formula	C15H13FO3S
Formula weight	292.31
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	Cc
a/Å	9.8930 (2)
b/Å	14.4664 (3)
c/Å	9.7170 (2)
α/°	90
β/°	104.429 (2)
γ/°	90
Volume/Å^3	1346.79 (5)
Z	4
ρcalcmg/mm3	1.442
μ/mm^{-1}	2.298
F(000)	800.0
Crystal size/mm^3	0.16 × 0.09 × 0.05
2Θ range for data collection	11.076 to 159.394°

Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 18, -12 ≤ l ≤ 10
Reflections collected	5113
Independent reflections	1831[R(int) = 0.0319]
Data/restraints/parameters	1831/2/182
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0887
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0891
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.38





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