Supporting Information

Sustainable synthesis of 1-thiol-3-alkyl bicyclo[1.1.1]pentanes *via* electron donor-acceptor complex photoactivation: a metal- and additive-free strategy for bioisostere design

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General Information

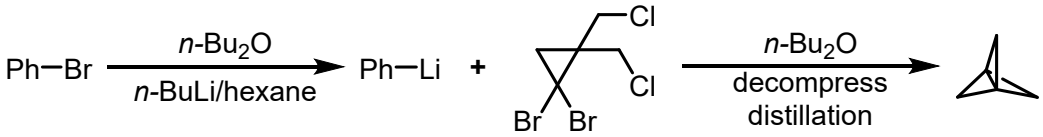
All reagents and deuterated solvents were procured commercially and used without additional purification. The products were purified via silica gel column chromatography (200-300 mesh) using a gradient elution system composed of petroleum ether (PE) (60-90°C) and ethyl acetate (EA). The nuclear magnetic resonance (NMR) spectra, including ^{1}H, ^{13}C and ^{19}F, were acquired on a Bruker Advance 500 spectrometer at room temperature, employing $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal reference standard. Melting points were measured using an X-5 Data microscopic melting point apparatus. Analytical thin-layer chromatography (TLC) was conducted on Merk precoated TLC plates (silica gel 60 F254). High-resolution mass spectrometry (HRMS) analysis was performed in positive mode electrospray ionization (ESI) using an Agilent 6530 QTOF mass spectrometer.

1. Photoreactor

Figure S1. Photograph of the photoreactor used for the reaction (distance from light source to the reaction tube: 2.0 cm; power: 10 W).

2. Experimental Section

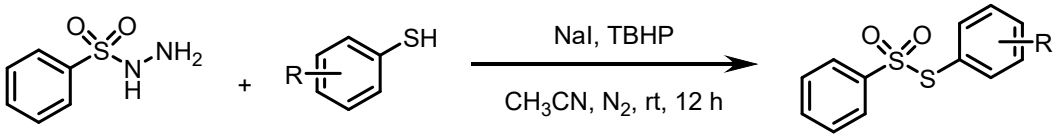
2.1 Preparation of the solution of [1.1.1]propellane in hexane



In a 150 mL three-neck round-bottom flask equipped with a magnetic stirring bar, bromobenzene (100 mmol, 1.0 equiv.) was dissolved in *n*-Bu_2O (20 mL). The reaction mixture was subsequently cooled to -30 °C. n-Butyllithium (*n*-BuLi, 100 mmol, 1.0 equiv., 2.5 M in hexane) was then added dropwise to the cooled mixture. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature, and stirred for an additional 1 h. The resulting solution of phenyllithium (PhLi) was used directly in the subsequent reaction.

In a separate reaction setup, a suspension of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (45.0 mmol) was prepared in anhydrous *n*-Bu_2O (20 mL) and cooled to -20 °C. The previously prepared PhLi solution in *n*-Bu_2O/hexane (65 mL) was added dropwise to this suspension. After the addition was completed, the reaction mixture was allowed to warm to 0 °C and stirred for 2 h. The reaction mixture was then transferred to a distillation setup. The addition funnel was replaced with a distillation head connected to a 100 mL round-bottom flask immersed in a liquid nitrogen bath. A vacuum was gradually applied to the system, and the distillate was collected while maintaining the reaction/distillation flask below 0 °C. Approximately 30 mL of distillate was obtained. The concentration of [1.1.1]propellane in the distillate was measured to be 0.4-0.6 M by ^{1}H NMR spectroscopy, using dichloromethane as an internal standard.

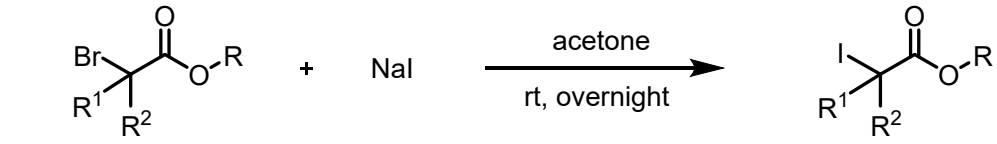
2.2 Procedures for the synthesis of thiosulfonates



All thiol compounds employed in this study are known compounds.[1] A reaction mixture was prepared by dissolving benzenesulfonyl hydrazide (516.0 mg, 3.0 mmol, 1.5 equiv) and the thiol compounds (2.0 mmol, 1.0 equiv) in acetonitrile (MeCN, 12.5 mL), followed by the addition of sodium iodide (NaI, 150.0 mg, 1 mmol, 0.5 equiv). Subsequently, *tert*-butyl hydroperoxide (TBHP, 450.5 mg, 5.0 mmol, 2.5 equiv) was introduced at room temperature. The reaction progress was

monitored by TLC, and upon completion, the reaction mixture was treated as follows: The mixture was washed with water to remove any water-soluble by-products, followed by extraction with ethyl acetate to isolate the organic components. The combined organic layers were dried over anhydrous sodium sulfate (Na_2SO_4) to remove residual moisture and then filtered to remove the drying agent. The filtrate was concentrated under reduced pressure to yield a crude residue. This residue was purified by silica gel column chromatography, using a gradient elution system consisting of petroleum ether or a mixture of petroleum ether and ethyl acetate (typically 50:1) to selectively elute the desired thiosulfonate products. The purified thiosulfonates were obtained as the final products.

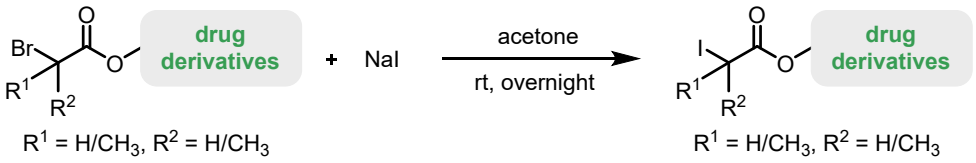
2.3 Procedures for the synthesis of iodoethyl acetate derivatives

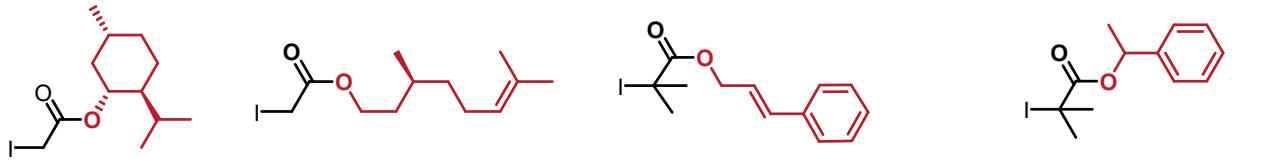


R^1 = H/CH_3, R^2 = H/CH_3 R^1 = H/CH_3, R^2 = H/CH_3

All thiol compounds used in this study are known compounds.[2,3] In a typical synthesis procedure, NaI (0.495 g, 3.3 mmol) was dissovled in acetone (5 mL) under stirring at room temperature. Ethyl 2-bromoacetate (3.0 mmol) was then added to the solution. The resulting suspension was stirred at room temperature overnight in the dark. After then, the suspension was filtrated, and the filtrate was evaporated under reduced pressure. The residue was subsequently diluted with water (1.5 mL) and extracted with pentane (3 portions of 1.5 mL each). The combined organic layers were washed with a 5% sodium thiosulfate solution (1.5 mL) followed by water (1.5 mL). The organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The final product, ethyl 2-iodoacetate, was obtained as a slightly yellow and clear liquid with a yield of 63.4 g (99%).

2.4 Preparation of the starting material drug derivatives

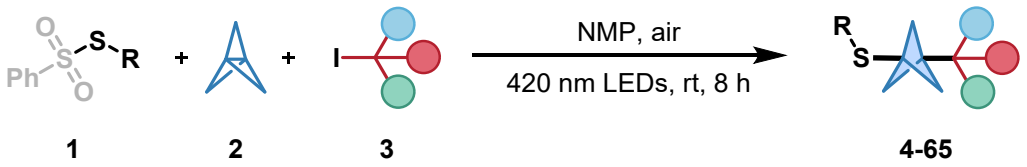




from menthol *from citronellol* *from cinnamyl alcohol* *from DL-1-Phenethylalcohol*

The general synthesis procedures were described as follows: To a stirred solution of sodium iodide (0.495 g, 3.3 mmol) in acetone (5.0 mL) was added ethyl brominated compounds containing drug molecule fragments (3.0 mmol) at room temperature. The formed suspension was stirred at room temperature overnight in the dark. The suspension was filtrated and the filtrate evaporated under reduced pressure. The residue was diluted with water (1.5 mL) and extracted with pentane (3/1.5 mL). The organic layers were washed with a sodium thiosulfate solution (5% in H_2O, 1.5 mL) and water (1.5 mL). The organic layers were dried over Na_2SO_4, filtrated, and concentrated to yield iodinated compound.

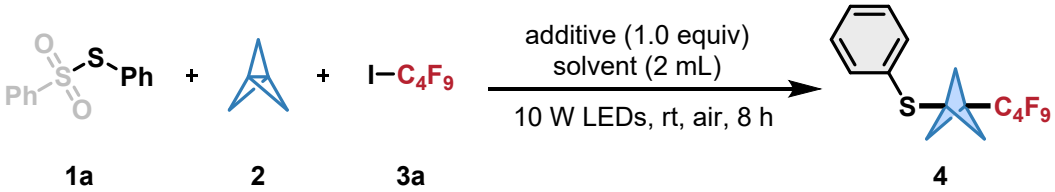
2.5 General procedure for the multicomponent reaction



A reaction mixture comprising *S*-phenyl benzenethiosulfonate (**1**, 0.2 mmol), [1.1.1]propellane (**2**, 0.4 mmol), iodohydrocarbon (**3**, 0.3 mmol) and *N*-methylpyrrolidone (NMP, 2.0 mL) was prepared in a 25 mL Schlenk tube. The mixture was vigorously stirred under an air atmosphere at room temperature while being irradiated with 420 nm LEDs (10 W) for 8 h. Upon completion of the reaction, the mixture was subjected to extraction using EtOAc,. The resulting organic layer was subsequently washed with brine, and then dried with Na_2SO_4. The solvent was then removed under reduced pressure. The crude product was further purified via silica gel column chromatography using 200-300 mesh silica gel.

2.6 Optimization of reaction conditions

Table S1. Screening of Reaction Conditions.



1a **2** **3a** **4**

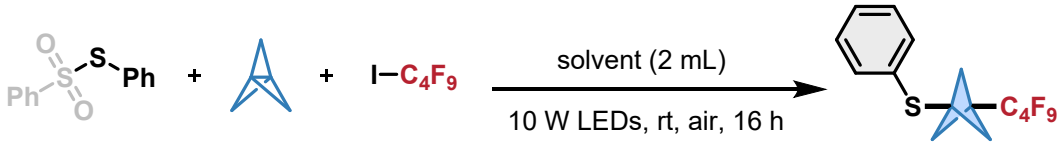
Entry	Wavelength	Solvent	Additive	Yield (%)[b]
1	365 nm	NMP	-	65
2	395 nm	NMP	-	53
3	420 nm	NMP	-	71
4	455 nm	NMP	-	59
5	420 nm	Acetone	-	55
6	420 nm	DMC	-	46
7	420 nm	H_2O	-	23
8	420 nm	NMP:H_2O 1:1	-	23
9	420 nm	EA	-	60
10	420 nm	NMP	K_2CO_3	46
11	420 nm	NMP	DBU	57
12	420 nm	NMP	DIPEA	65
13[c]	420 nm	NMP	-	67
14[d]	420 nm	NMP	-	56
15[e]	420 nm	NMP	-	69
16	In dark	NMP	-	0
17[f]	420 nm	NMP	-	51
18[g]	420 nm	NMP	-	70

[a]Reaction conditions: **1a** (0.20 mmol), **2** (0.40 mmol), **3a** (0.30 mmol), additive (1.0 equiv), solvent (2.0 mL), 10 W LEDs, air, rt, 8 h. [b]Isolated yields. [c]in N_2 atmosphere. [d]4 h. [e]16 h. [f]**3a** (0.20 mmol). [g]**3a** (0.40 mmol).

The optimal conditions for the multi-component reaction were systematically evaluated by examining various factors, including additives, light sources, solvents, and reaction atmospheres. As illustrated in Table 1, a reaction involving *S*-phenyl benzenethiosulfonate (**1a**), [1.1.1]propellane (**2**), and perfluorobutyl iodide (**3a**) in NMP as the solvent, conducted for 8 h, achieved a yield of 71% for the desired product. In an effort to develop a more environmentally benign synthetic approach, we explored the use of green solvents such as acetone and water as alternatives to NMP. Unfortunately, these substitutions did not yield better results (Table S1, entries 5-9). Additionally,

the introduction of various additives, including K_2CO_3, DBU, and DIPEA, into the reaction system did not significantly enhance the reaction yield (Table S1, Entries 10-12). Conducting the reaction under a N_2 atmosphere also failed to inprove the outcome (Table S1, entry 13). Furthermore, varying the reaction time by shortening or extending it beyond the optimal 8-hour duration did not result in a higher yield, suggesting that the reaction kinetics had reached a saturation point (Table S1, entries 14-15). Notably, in the absence of light, the reaction did not proceed, and no product was formed (Table S1, entry 16). Moreover, we have noticed that the excessive use of per- and polyfluoroalkyl substances could pose health and environmental concerns. In order to reduce environmental pollution, we screened the amount of per- and polyfluoroalkyl substances and found that the reaction proceeded best when 1.5 equivalents were used (Table S1, entries 17-18).

Table S2. Screening for green solvents.

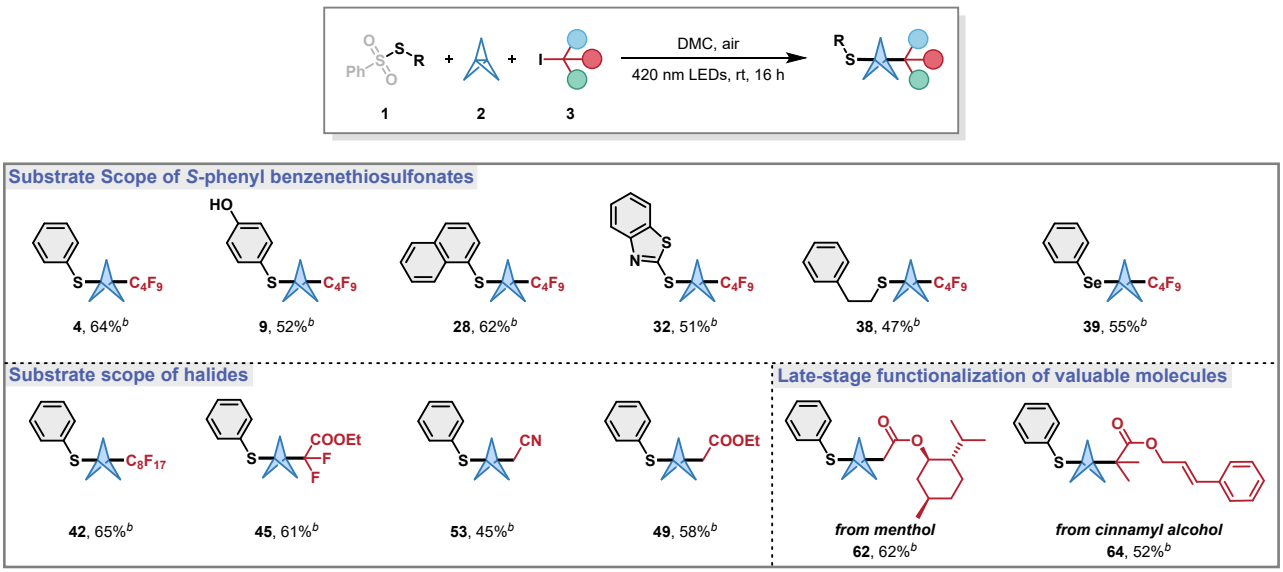


1a **2** **3a** **4**

Entry	Wavelength	Solvent	Yield (%)[b]
1	420 nm	NMP	70
2	420 nm	H_2O	25
3	420 nm	Acetone	61
4	420 nm	EtOH	18
5	420 nm	DMC	64
6	420 nm	DHLG (Dihydrolevoglucosenone)	41

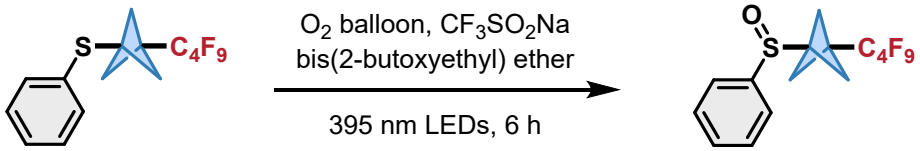
[a]Reaction conditions: **1a** (0.20 mmol), **2** (0.40 mmol), **3a** (0.30 mmol), solvent (2.0 mL), 10 W LEDs, air, rt, 16 h. [b]Isolated yields.

In order to make the reaction greener, based on the optimization of reaction conditions, we further screened green solvents (i.e., solvents recommended by the Sanofi and GSK green solvent guidelines) (Table S2). When the reaction time was extended to 16 hours, we found that the green solvent DMC also achieved a good yield. Therefore, we further explored whether other substrates could react in DMC. We attempted to synthesize some representative substrates and found that they could be obtained in moderate to good yields as shown in the figure below, which confirmed that the reaction could proceed in green solvents.



[b] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), **3** (0.3 mmol), DMC (2.0 mL), 420 nm LEDs, air, rt, 16 h, isolated yields.

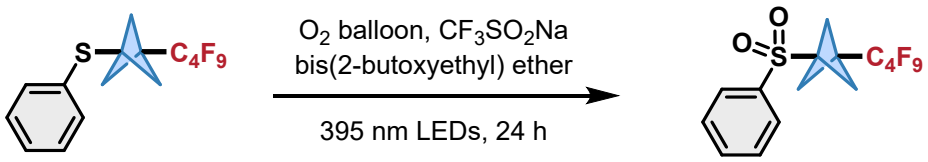
2.7 General procedure for the synthesis of compound 66



4 **66**, 78%

To a 10 mL quartz tube equipped with an O_2 balloon, a mixture of (3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (**4**, 1.0 mmol), trifluoromethanesulfonate sodium (CF_3SO_2Na, 0.25 mmol) and bis(2-butoxyethyl)ether (1.0 mL) was introduced. The reaction was carried out at room temperature under irradiation from 395 nm LEDs (10 W) for 6 h. The progress of the reaction was monitored using TLC or GC-MS. Upon completion of the reaction, water (20 mL) was added to the reaction mixture. The mixture was then extracted with CH_2Cl_2 (5 mL×3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subsequently purified by column chromatography on silica gel to afford the desired compound, (*S*)-1-(perfluorobutyl)-3-(phenylsulfinyl)bicyclo[1.1.1]pentane (**66**).

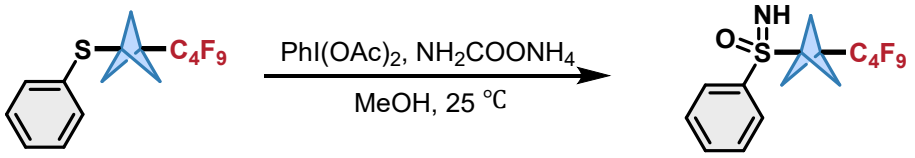
2.8 General procedure for the synthesis of compound 67



4 **67**, 67%

In a 10 mL quartz tube equipped with an O_2 balloon, a reaction mixture of (3-perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (**4**, 1.0 mmol), CF_3SO_2Na (0.25 mmol) and bis(2-butoxyethyl)ether (1.0 mL) was introduced. The reaction was carried out at room temperature under irradiation from 395 nm LEDs (10 W) for 24 h. The progress of the reaction was monitored using TLC or GC-MS. Upon completion of the reaction, water (20 mL) was added to the reaction mixture. The mixture was then extracted with CH_2Cl_2 (5 mL×3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subsequently purified by column chromatography on silica gel to afford the desired compound, 1-(perfluorobutyl)-3-(phenylsulfonyl)bicyclo[1.1.1]pentane (**67**).

2.9 General procedure for the synthesis of compound 68



4 **68**, 67%

To a 25-mL Schlenk tube, a reaction mixture of (3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (**4**, 1.0 mmol), diphenyl iodonium acetate ($PhI(OAc)_2$, 2.5 mmol), ammonium carbamate (NH_2COONH_4, 2.5 mmol) and MeOH (3.0 mL) was introduced. The reaction was carried out at room temperature for 12 h. The progress of the reaction was monitored by TLC or GC-MS. After the reaction was complete, the solvent was carefully removed under reduced pressure. The resulting residue was further purified by silica gel column chromatography using 200-300 mesh silica gel. The purification process afforded the desired product,, imino(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)-λ^6-sulfanone (**68**).

2.10 Continuous-flow reactions

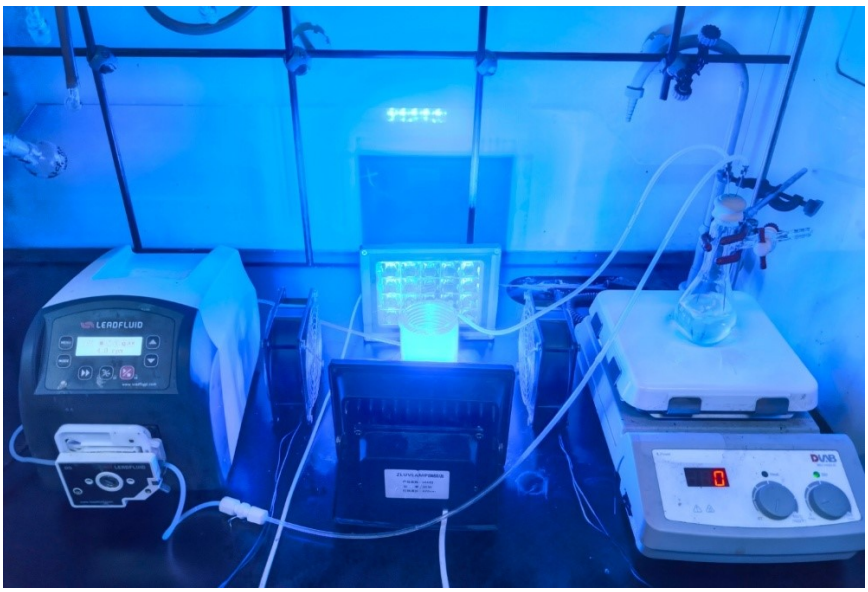
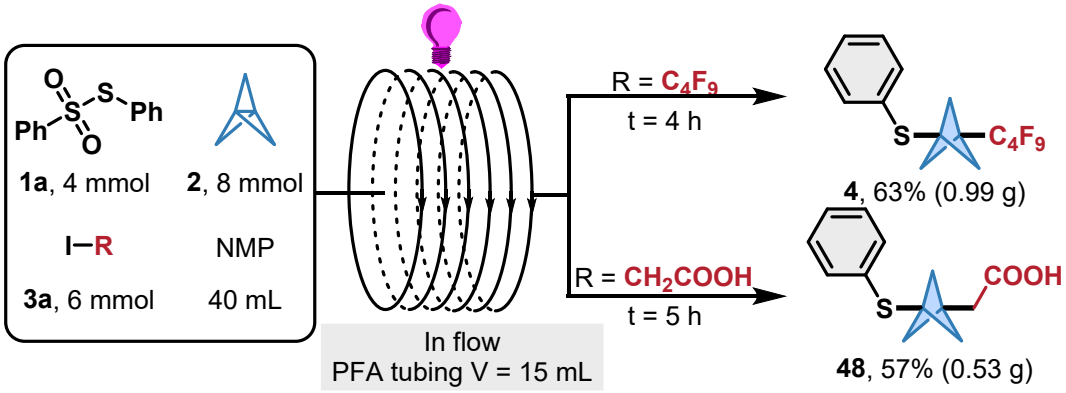


Figure S2. Schematic diagram of flow settings for continuous-flow photochemical reactions.



we prepared a reaction mixture in a 100 mL Schlenk tube containing *S*-phenyl benzenethiosulfonate (**1a**, 4.0 mmol), [1.1.1]propellane (**2**, 8.0 mmol), and iodohydrocarbon (**3**, 6.0 mmol) dissovled to NMP (40 mL). This mixture was stirred thoroughly before being transferred to a flow reactor via a PFA (perfluoroalkoxy) tubing with a volume of 15 mL. The PFA tubing was irradiated with 420 nm light-emitting diodes (LEDs, 10 W) at room temperature. The progress of the reaction was monitored in real time using liquid-phase analysis techniques. Our findings revealed that the flow reactor system significantly shortened the reaction time compared to the batch process while simultaneously increasing the overall reaction efficiency. This approach thus offers a promising strategy for scaling up the reaction while maintaining high productivity and operational simplicity.

3. Mechanistic Studies

3.1 Visible light irradiation on/off experiments

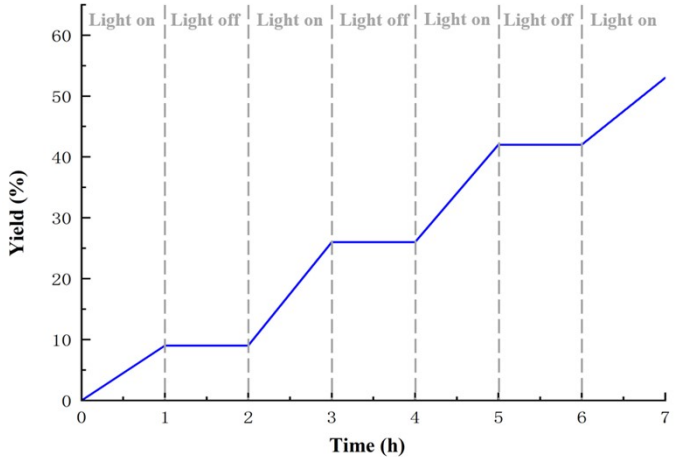
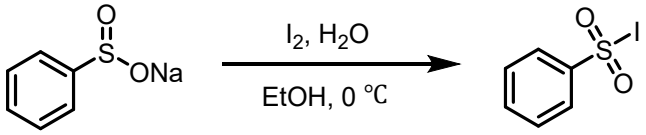


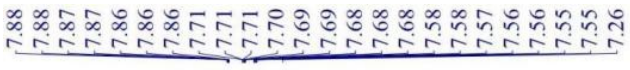
Figure S3 Visible light irradiation on/off experiments.

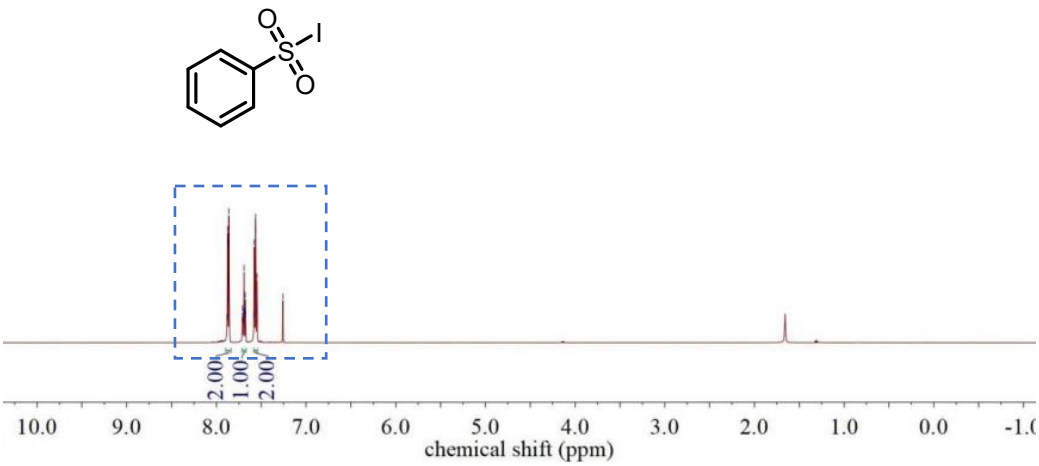
3.2 Determine the formation of iodosulfonic acid in the reaction solution.

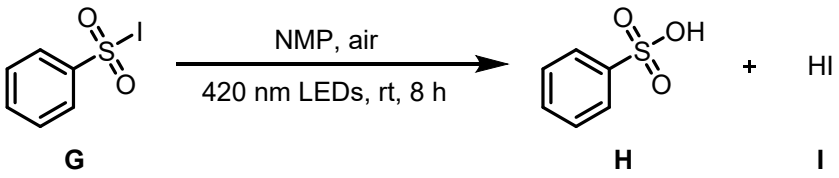


G

In a 10 mL round-bottom flask, sodium sulfinate (2.0 mmol, 1.0 equiv) was dissolved in 5.0 mL of distilled water while maintaining the solution at 0 °C. A saturated solution of iodine (1.0 mmol, 1.0 equiv, 0.254 g) in ethanol (0.6 mL) was prepared separately. This iodine solution was then added dropwise to the sodium sulfinate solution, ensuring that a slight excess of iodine was ultimately present. Throughout the addition, a yellow precipitate gradually formed. Once the addition was complete, the precipitate was collected by filtration, washed thoroughly with cold water, and then carefully dried at room temperature. This procedure yielded the desired sulfonyl iodide (**G**).







G **H** **I**

To investigate the inherent instability of sulfonyl iodide (**G**), we designed and conducted the following experiment: A mixture of **G** (0.5 mmol) and NMP (2.0 mL) was prepared in a 25 mL Schlenk tube. The mixture was stirred under the irradiation of 420 nm LEDs (10 W) at room temperature in an air atmosphere for 8 h. Upon completion of the reaction, we employed TLC to analyze the reaction mixture and observed that **G** had almost completely reacted. High-resolution mass spectrometry (HRMS) was subsequently used to identify the products formed during the decomposition of **G**. The presence of sulfonic acid (**H**) and HI (**I**) was confirmed through the detection of their respective ions. The HRMS data were as follows: for **H**, $[M-H]^-$ calculated 156.9965, found 156.9972; for **I**, $[M-H]^-$ calculated 126.9050, found 126.9053. These results indicate that **G** formed in our reaction system is inherently unstable and readily undergoes decomposition under the given conditions. During the extraction process, both **H** and **I** preferentially partitioned into the aqueous phase. This preferential extraction behavior explains the absence of **H** or **I** in the isolated products.

3.3 Job's plot experiments.

The stoichiometry of the EDA complex *S*-phenyl benzenethiosulfonate (**1a**) and perfluorobutyl iodide (**3a**) was calculated using the Job's plot method. The Job's plot of the EDA complex between **1a** and **3a** was calculated by measuring the absorption of NMP solutions at 420 nm with different donor/acceptor ratios and constant concentration (0.02 M) of the two components. The absorbance values were plotted against the molar fraction of **3a**. The Job's plot analysis of the EDA complex between **1a** and **3a** showed a maximal absorbance at a molar fraction of 0.5 for **1a**, indicating the 1:1 stoichiometry of the EDA complex in solution.

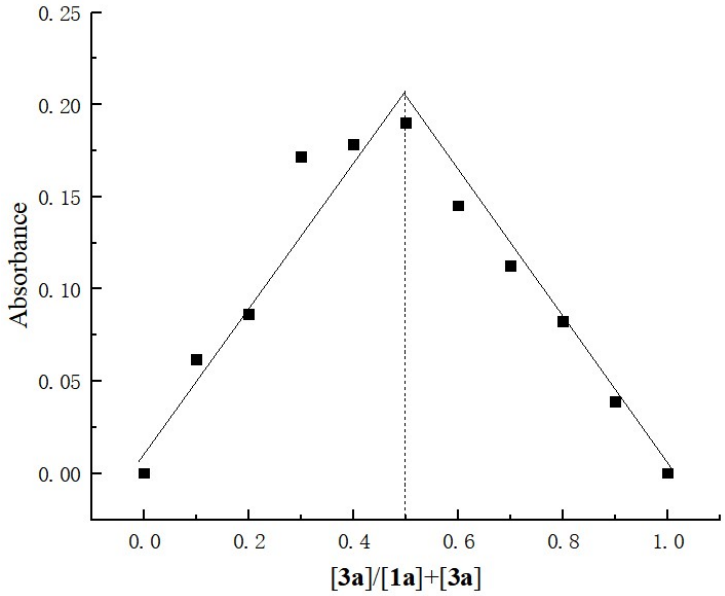


Figure S4. Job's plot between $PhSO_2Ph$ (**1a**) and C_4F_9I (**3a**).

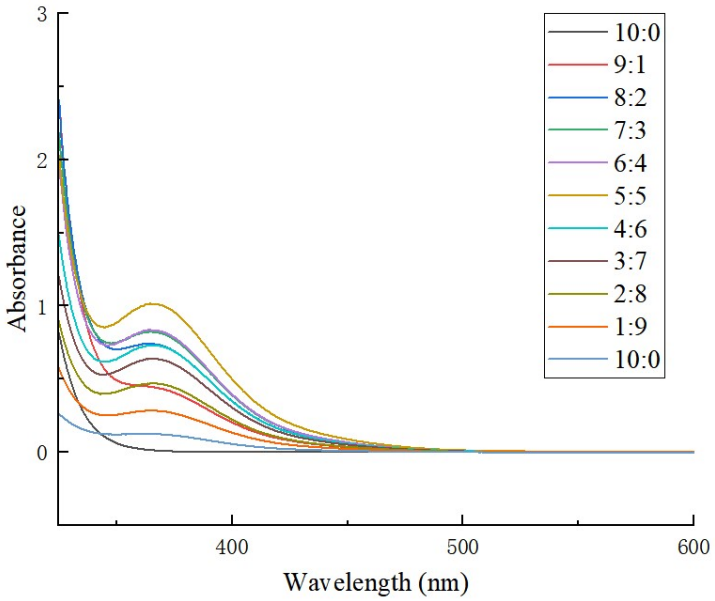


Figure S5. Job's curve UV/vis absorption spectra of different $PhSO_2SPh/C_4F_9I$ ratios.

3.4 Quantum yield measurement

To determine the photon flux of the LED (λ_{max} = 420 nm) according to the procedure of Yoon,[4] we employed standard ferrioxalate actinometry. First, a 0.15 M ferrioxalate solution was prepared by dissolving potassium ferrioxalate hydrate (1.474 g) in 20 mL of a 0.05 M H_2SO_4 solution. Additionally, a buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (5.0 mg) and sodium acetate (1.13 g) in 5.0 mL of a 0.5 M H_2SO_4 solution. Both solutions were stored in the dark to prevent premature photolysis. To measure the photon flux, 3.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90 seconds at λ_{max} = 420 nm. Following irradiation, 0.525 mL of the 1,10-phenanthroline solution was added to the cuvette. The mixture was then stirred in the dark for 1 h to allow the ferrous ions to fully coordinate with the phenanthroline. The absorbance of the resulting solution was measured at 510 nm. For comparison, a nonirradiated sample was also prepared, and its absorbance at 510 nm was measured. The photon flux was calculated using Equation (1), based on the difference in absorbance between the irradiated and nonirradiated samples.

	Non-irrad	Irrad 1	Irrad 2	Irrad 3
A_{510nm}	0.526	3.647	3.712	3.674
Average $A_{510\ nm}$ of irradiated samples		3.678		

$$mol\ Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} \quad (1)$$

$$mol\ Fe^{2+} = \frac{(3.525 \times 10^{-3} L) \times (3.678 - 0.526)}{(1.00\ cm) \times \left(11{,}110 \frac{L}{mol} \times cm^{-1}\right)} = 9.9965 \times 10^{-7} mol$$

Where V represents the total volume of the solution after addition of 1,10-phenanthroline (0.003525 L), ΔA denotes the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, 1 is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L • $mol^{-1}cm^{-1}$)[5]. The photon flux can be calculated using Equation (2).

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \times t \times f} \quad (2)$$

$$photon\ flux = \frac{9.9965 \times 10^{-7}}{(0.96) \times (90s) \times (0.99986)} = 1.157 \times 10^{-8} einstein\ s^{-1}$$

Where Φ represents the quantum yield of the ferrioxalate actinometer, which is 0.96 at a wavelength of 420 nm,[6] The irradiation time, t, is 90 s. The fraction of light absorbed at 420 nm by the ferrioxalate actinometer, denoted as f, is determined using Equation (3). This fraction is calculated based on the absorbance of the ferrioxalate solution at 420 nm, $A_{420\ nm}$. The measured absorbance of the ferrioxalate solution at 420 nm was found to be 3.528, which corresponds to an absorbed light fraction (f) of 0.99970.

$$f = 1 - 10^{-A_{420\,nm}} \quad (3)$$

The photon flux was thus calculated to be 1.157×10^{-8} $einstein\ s^{-1}$.

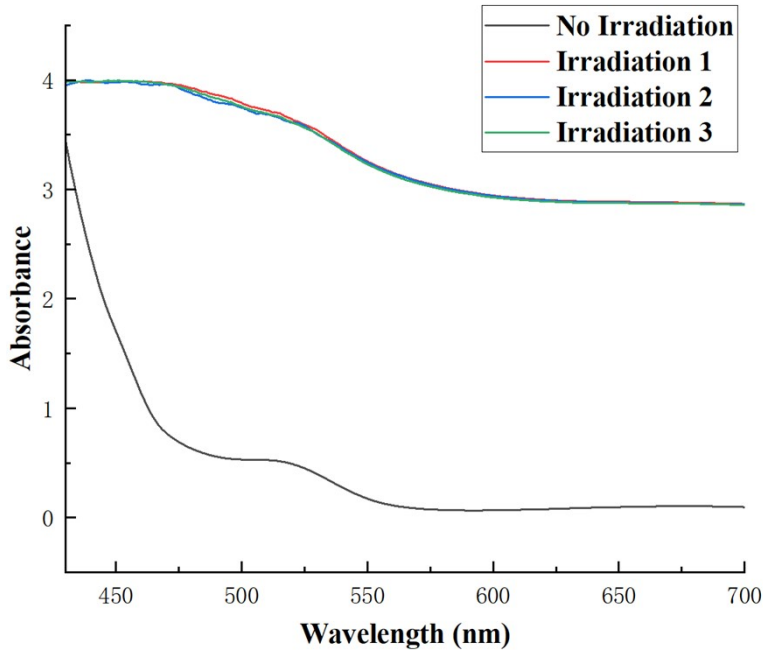
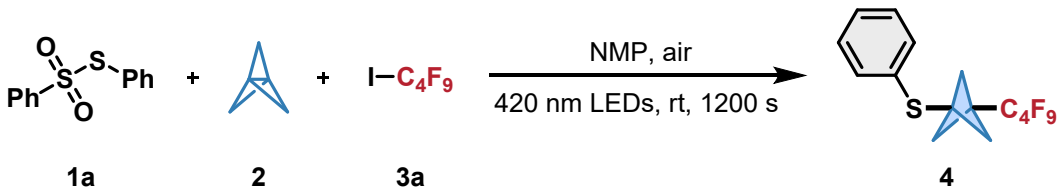


Figure S6. Absorption spectra of three irradiation experiments and one non-irradiation experiment.



The reaction mixture was stirred and exposed to irradiation from a 420 nm LED for 1200 s. The yield of the product was quantified through ^{1}H NMR analysis, employing 1,3,5-trimethoxybenzene

as an internal standard. The yield of product **4** was found to be 3.5%, corresponding to 7.00×10^{-6} mol of **4**. The reaction quantum yield, Φ, was calculated using Equation 4, where the photon flux is 8.816×10^{-9} $einstein\ s^{-1}$(as determined by actinometry as described above), t is the reaction time (1200 s), and f is the fraction of incident light absorbed by the catalyst, determined using Equation 3. The absorbance of the reaction liquid at 420 nm was measured to be 3.7148. indicating that the fraction of absorbed light, f, is 0.99981.

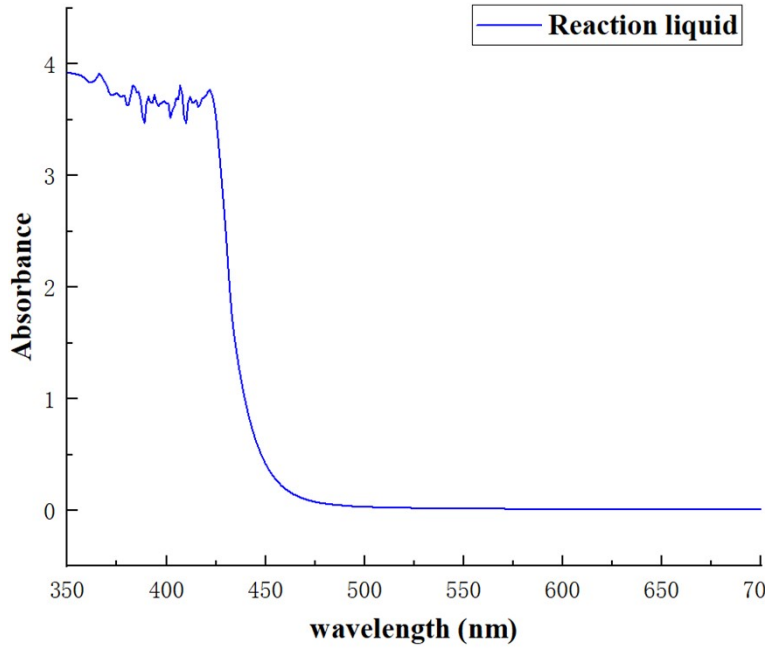


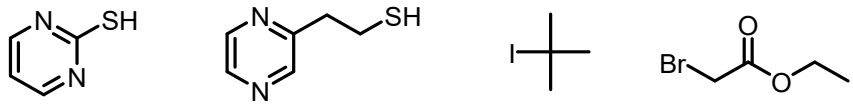
Figure S7. Absorption spectra of reaction liquid

$$\Phi = \frac{mol\ of\ product}{flux \times t \times f}$$

$$\Phi = \frac{7.00\ \times\ 10^{-6}\ mol}{1.157 \times 10^{-8} einstein\ s^{-1} \times 1200\ s \times\ 0.99981} = 0.504$$

3.5 Ineffective substrates for the multicomponent reaction

In an effort to broaden the substrate scope of our method, we explored a range of additional *S*-aryl/alkyl benzenesulfonothioates and halogenated hydrocarbons. Specifically, we tested substrates such as pyrimidine, pyrazinyl ethanethiol, tert-butyl iodide, and ethyl bromoacetate. However, these substrates were found to be incompatible with the current method.



Scheme S1. Ineffective substrates for the multi-component reaction

4. References

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2. Y. Li, J. Xu, Y. Wang, R. Xu, Y. Zhao and W. Li, *J. Org. Chem.*, 2025, **90**, 1683-1696.
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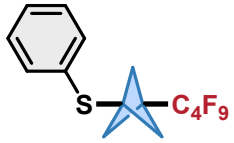
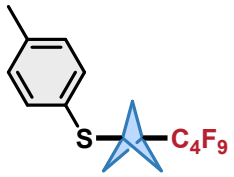
5. Characterization of Products

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (4)



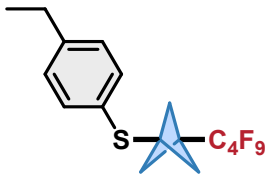
Obtained as a light yellow liquid (56 mg, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.41 (m, 2H), 7.34 (q, J = 3.1, 2.6 Hz, 3H), 2.13 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 132.0, 129.1, 128.4, 52.8, 42.5, 38.1 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.80–-81.86 (m), -115.69–-115.83 (m), -122.22–-122.33 (m), -126.06–-126.18 (m); HRMS (ESI+): Calculated for $C_{15}H_{11}F_9SONa$: $[M+Na+O]^+$ 433.0279, Found 433.0272.

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(p-tolyl)sulfane (5)



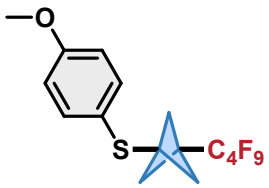
Obtained as a yellow liquid (60 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.32 (m, 2H), 7.14 (d, J = 7.8 Hz, 2H), 2.35 (s, 3H), 2.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 134.6, 129.9, 128.4, 52.7, 42.6, 37.9 (t, J = 30.7 Hz), 21.16, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.03–-81.21 (m), -115.74–-115.85 (m), -122.20–-122.37 (m), -126.05–-126.19 (m); HRMS (ESI+): Calculated for $C_{16}H_{13}F_9SONa$: $[M+Na+O]^+$ 447.0436, Found 447.0454.

(4-Ethylphenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (6)



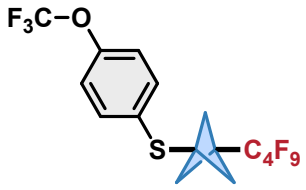
Obtained as a light yellow liquid (61 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.19–7.14 (m, 2H), 2.65 (q, J = 7.6 Hz, 2H), 2.11 (s, 6H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 134.6, 128.7, 128.6, 52.8, 42.6, 38.0 (t, J = 30.8 Hz), 28.5, 15.3, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.07–-81.16 (m), -115.76–-115.84 (m), -122.27–-122.34 (m), -126.12–-126.19 (m); HRMS (ESI+): Calculated for $C_{17}H_{15}F_9SONa$: $[M+Na+O]^+$ 434.0357, Found 434.0289.

(4-Methoxyphenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (7)



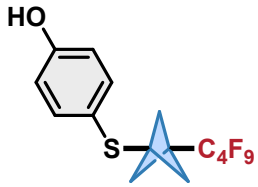
Obtained as a yellow liquid (64 mg, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 6.89–6.84 (m, 2H), 3.82 (s, 3H), 2.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 135.4, 121.5, 113.6, 54.3, 51.5, 41.8, 36.8 (t, J = 30.6 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.07–-81.16 (m), -115.75–-81.83 (m), -122.29–-122.34 (m), -126.05–-126.19 (m); HRMS (ESI+): Calculated for $C_{16}H_{13}F_9O_2SNa$: $[M+Na+O]^+$ 463.0385, Found 463.0375.

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)sulfane (8)



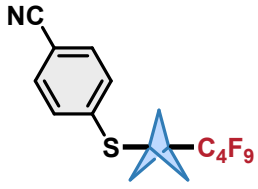
Obtained as a light yellow liquid (64 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.21–7.17 (m, 2H), 2.15 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 135.7, 130.7, 121.4, 52.8, 42.4, 38.1 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.94, -81.13–-81.21 (m), -115.74–-115.89 (m), -122.21–-122.37 (m), -126.09–-126.23 (m); HRMS (ESI+): Calculated for $C_{16}H_{10}F_{12}O_2SNa$: $[M+Na+O]^+$ 517.0102, Found 517.0120.

4-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)phenol (9)



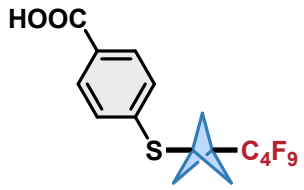
Obtained as a light yellow liquid (56 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 5.17 (s, 1H), 2.08 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 136.7, 122.7, 116.2, 52.5, 42.8, 37.9 (t, J = 30.7 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.99–-81.29 (m), -115.43–-116.12 (m), -121.90–-122.12 (m), -125.81–-125.92 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}F_9OS$: $[M-H]^+$ 409.0314, Found 409.0341.

4-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)benzonitrile (10)



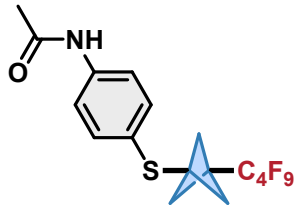
Obtained as a light yellow solid (53 mg, 63% yield); M. P. = 66–67 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 2.25 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 132.8, 132.5 118.3, 111.4, 53.3, 41.7, 38.7 (t, J = 31.0 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.10–-81.15 (m), -115.71–-115.87 (m), -122.22–-122.32 (m), -126.05–-126.17 (m); HRMS (ESI+): Calculated for $C_{16}H_{10}F_9NSONa$: $[M+Na+O]^+$ 442.0282, Found 442.0300.

4-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)benzoic acid (11)



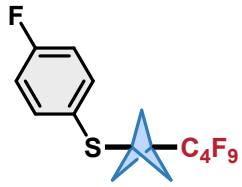
Obtained as a white solid (53 mg, 61% yield); M. P. = 86–87 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.04 (s, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.3, 139.1, 131.6, 130.5, 130.1, 53.2, 41.5, 38.3 (t, J = 30.4 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, DMSO-d_6) δ -80.46–-89.65 (m), -114.41–-114.57 (m), -121.79–-121.92 (m), -125.55–-125.67 (m); HRMS (ESI+): Calculated for $C_{16}H_{10}F_9O_2S$: $[M-H]^+$ 437.0263, Found 437.0282.

***N*-(4-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)phenyl)acetamide (12)**



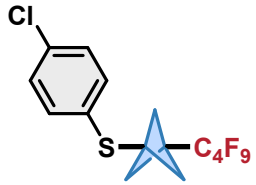
Obtained as a light yellow solid (51 mg, 56% yield); M. P. = 92–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 2.18 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 138.5, 135.4, 126.8, 120.2, 52.7, 42.6, 38.0 (t, J = 30.7 Hz), 24.6, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.98–-81.32 (m), -115.61–-115.89 (m), -122.08–-122.46 (m), -125.89–-126.01 (m); HRMS (ESI+): Calculated for $C_{17}H_{14}F_9NOSNa$: $[M+Na]^+$ 474.0545, Found 474.0541.

(4-Fluorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (13)



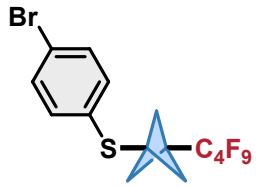
Obtained as a light yellow liquid (58 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.40 (m, 2H), 7.10–7.00 (m, 2H), 2.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, J = 248.8 Hz), 136.6 (d, J = 8.2 Hz), 127.1 (d, J = 3.3 Hz), 116.3 (d, J = 21.8 Hz), 52.7, 42.6, 38.1 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.11–-81.17 (m), -112.53, -115.79–-115.92 (m), -122.28–-122.37 (m), -126.13–-126.23 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}F_{10}SONa$: $[M+Na+O]^+$ 451.0185, Found 451.0185.

(4-Chlorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (14)



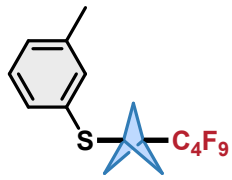
Obtained as a light yellow liquid (58 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.43 (m, 2H), 7.29 (d, J = 8.4 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 134.9, 130.5, 129.3, 52.8, 42.4, 38.1 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.12–-81.17 (m), -115.71–-115.84 (m), -122.21–-122.33 (m), -126.07–-126.17 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}ClF_9SONa$: $[M+Na+O]^+$ 466.9889, Found 466.9890.

(4-Bromophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (15)



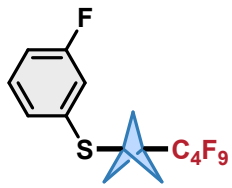
Obtained as a purple solid (57 mg, 60% yield); M. P. = 90–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 2.13 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 132.3, 132.2, 123.0, 52.8, 42.3, 38.1 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.10–-81.22 (m), -115.66–-115.92 (m), -122.19–-122.37 (m), -126.04–-126.27 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}BrF_9SONa$: $[M+Na+O]^+$ 510.9384, Found 510.9438.

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(m-tolyl)sulfane (16)



Obtained as a light yellow liquid (56 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 3H), 7.23–7.17 (m, 1H), 2.40 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 134.9, 131.7, 131.3, 129.2, 128.9, 52.8, 42.4, 38.0 (t, J = 30.7 Hz), 21.3, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.07–-81.18 (m), -115.75–-115.84 (m), -122.16–-122.38 (m), -126.06–-126.21 (m); HRMS (ESI+): Calculated for $C_{16}H_{13}F_9SONa$: $[M+Na+O]^+$ 447.0436, Found 447.0418.

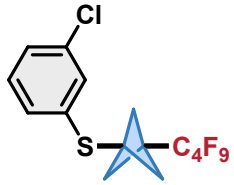
(3-Fluorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (17)



Obtained as a light yellow liquid (52 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m,

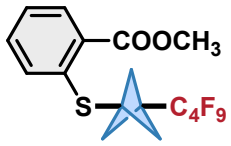
1H), 7.25–7.19 (m, 1H), 7.19–7.13 (m, 1H), 7.08–7.00 (m, 1H), 2.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (d, J = 249.4 Hz), 134.3 (d, J = 7.9 Hz), 130.3 (d, J = 8.2 Hz), 129.6 (d, J = 3.1 Hz), 120.7 (d, J = 21.7 Hz), 115.5 (d, J = 21.0 Hz), 53.0, 42.3, 38.2 (t, J = 30.7 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.06–-81.15 (m), -111.69, -115.76–-115.85 (m), -122.18–-122.35 (m), -126.01–-126.23 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}F_{10}SONa$: $[M+Na+O]^+$ 451.0185, Found 451.0204.

(3-Chlorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (18)



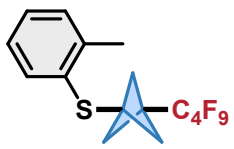
Obtained as a yellow liquid (52 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, J = 1.9 Hz, 1H), 7.29–7.22 (m, 2H), 7.22–7.18 (m, 1H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 134.1, 133.8, 132.2, 130.1, 128.6, 52.9, 42.3, 38.2 (t, J = 30.9 Hz); ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.05–-81.20 (m), -115.66–-115.86 (m), -122.14–-122.36 (m), -126.03–-126.22 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}ClF_9SONa$: $[M+Na+O]^+$ 466.9889, Found 466.9881.

Methyl 2-((3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)benzoate (19)



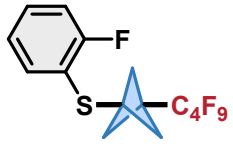
Obtained as a light yellow liquid (61 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.8, 1.6 Hz, 1H), 7.54 (dd, J = 8.0, 1.3 Hz, 1H), 7.46 (td, J = 7.6, 1.5 Hz, 1H), 7.31 (td, J = 7.5, 1.2 Hz, 1H), 3.91 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 135.5 132.8, 132.3, 131.6, 130.4, 126.8, 53.2, 52.3, 42.0, 38.9 (t, J = 30.8 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.01–-81.17 (m), -115.77–-115.89 (m), , -122.10–-122.30 (m), -125.96–-126.20 (m); HRMS (ESI+): Calculated for $C_{17}H_{13}F_9O_2SNa$: $[M+Na]^+$ 475.0385, Found 475.0383.

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(o-tolyl)sulfane (20)



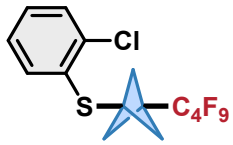
Obtained as a light yellow liquid (59 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 7.0 Hz, 2H), 7.22–7.13 (m, 1H), 2.46 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 136.0, 131.4, 130.6, 128.8, 126.5, 52.8, 42.6, 38.1 (t, J = 30.7 Hz), 21.1, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.11–-81.30 (m), -115.41–-116.16 (m), -121.95–-122.66 (m), -125.91–-126.52 (m); HRMS (ESI+): Calculated for $C_{16}H_{13}F_9SONa$: $[M+Na+O]^+$ 447.0436, Found 447.0449.

(2-Fluorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (21)



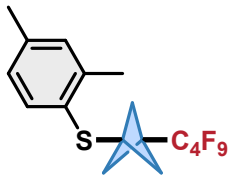
Obtained as a light yellow liquid (54 mg, 66% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.44 (m, 1H), 7.39–7.33 (m, 1H), 7.18–7.08 (m, 2H), 2.14 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 137.1, 131.1, 131.1, 124.6, 116.2, 116.0, 53.1, 42.2, 37.7 (t, J = 30.5 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.12–-81.23 (m), -106.95, -115.67–-115.84 (m), -122.24–-122.40 (m), -126.10–-126.24 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}F_{10}SONa$: $[M+Na+O]^+$ 451.0185, Found 451.0199.

(2-Chlorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (22)



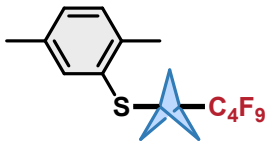
Obtained as a light yellow liquid (68 mg, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.5, 1.9 Hz, 1H), 7.47 (dd, J = 7.8, 1.6 Hz, 1H), 7.30–7.23 (m, 2H), 2.19 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 136.5, 131.4, 130.2, 129.9, 127.3, 53.1, 53.1, 53.1, 42.3, 38.2 (t, J = 30.7 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.08–-81.19 (m), -115.65–-115.80 (m), -122.18–-122.34 (m), -126.05–-126.23 (m); HRMS (ESI+): Calculated for $C_{15}H_{10}ClF_9SONa$: $[M+Na+O]^+$ 466.9889, Found 466.9877.

(2,4-Dimethylphenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (23)



Obtained as a light yellow liquid (62 mg, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 7.8 Hz, 1H), 7.11–7.06 (m, 1H), 6.97 (dd, J = 7.8, 1.9 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 2.08 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 141.0, 138.3, 133.4, 129.7, 129.3, 54.7, 44.7, 40.0 (t, J = 30.7 Hz), 31.7, 23.1, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.08–-81.17 (m), -115.75–-115.82 (m), -122.28–-122.33 (m), -126.05–-126.22 (m); HRMS (ESI+): Calculated for $C_{17}H_{15}F_9SONa$: $[M+Na+O]^+$ 461.0592, Found 461.0600.

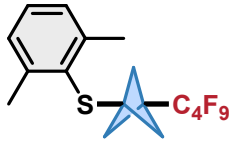
(2,5-Dimethylphenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (24)



Obtained as a light yellow liquid (56 mg, 66% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.25 (m, 1H), 7.14 (d, J = 7.7 Hz, 1H), 7.05 (dd, J = 7.7, 1.9 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 2.10 (s, 6H);

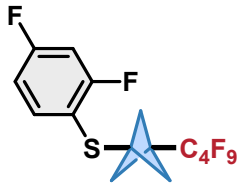
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 136.6, 136.1, 130.8, 130.4, 129.7, 52.8, 42.6, 38.0 (t, J = 30.6 Hz), 20.8, 20.6, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.09–-81.20 (m), -115.63–-115.83 (m), -122.14–-122.39 (m), -126.03–-126.25 (m); HRMS (ESI+): Calculated for $C_{17}H_{15}F_9SONa$: $[M+Na+O]^+$ 461.0592, Found 461.0599.

(2,6-Dimethylphenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (25)



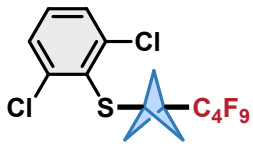
Obtained as a light yellow liquid (51 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.08 (m, 3H), 2.51 (s, 6H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 130.3, 128.9, 128.2, 53.0, 42.8, 37.7 (t, J = 30.5 Hz), 22.2, 21.4, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.07–-81.20 (m), -115.63–-115.80 (m), -122.20–-122.33 (m), -126.07–-126.22 (m); HRMS (ESI+): Calculated for $C_{17}H_{15}F_9SONa$: $[M+Na+O]^+$ 461.0592, Found 461.0591.

(2,4-Difluorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (26)



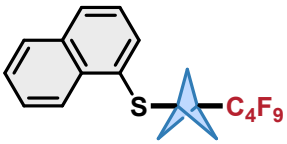
Obtained as a light yellow liquid (59 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.42 (m, 1H), 6.97–6.83 (m, 2H), 2.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.49 (dd, J = 59.6, 11.7 Hz), 162.50 (dd, J = 56.8, 11.9 Hz), 138.30 (d, J = 9.4 Hz), 112.07 (dd, J = 21.4, 4.0 Hz), 104.9 (d, J = 25.6 Hz), 104.7 (d, J = 25.8 Hz), 53.0, 42.2, 37.8 (d, J = 30.6 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.07–-81.19 (m), -101.72 (d, J = 10.2 Hz), -106.98 (d, J = 9.7 Hz), -115.68–-115.82 (m), -122.22–-122.39 (m), -126.06–-126.23 (m); HRMS (ESI+): Calculated for $C_{15}H_9F_{11}SONa$: $[M+Na+O]^+$ 469.0091, Found 469.0115.

(2,6-Dichlorophenyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (27)



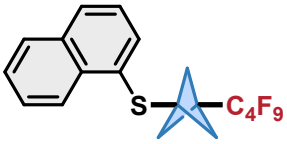
Obtained as a light yellow liquid (53 mg, 57% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 2H), 7.24 (t, J = 8.0 Hz, 1H), 2.19 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 130.8, 130.2, 128.7, 53.4, 42.6, 37.9 (t, J = 30.7 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.06–-81.19 (m), -115.51–-115.67 (m), -122.18–-122.32 (m), -126.14–-126.20 (m); HRMS (ESI+): Calculated for $C_{15}H_9Cl_2F_9SONa$: $[M+Na+O]^+$ 500.9500, Found 500.9528.

Naphthalen-1-yl(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (28)



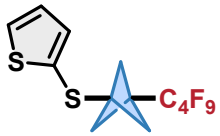
Obtained as a light yellow liquid (67 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57–8.49 (m, 1H), 7.91–7.85 (m, 2H), 7.76 (dd, J = 7.0, 1.2 Hz, 1H), 7.59 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.54 (ddd, J = 8.0, 6.8, 1.3 Hz, 1H), 7.45 (dd, J = 8.2, 7.1 Hz, 1H), 2.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 134.9, 134.2, 129.9, 129.4, 128.5, 126.9, 126.4, 126.1, 125.6, 53.0, 43.0, 37.5 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.09–-81.19 (m), -115.71–-115.80 (m), -122.29–-122.36 (m), -126.16–-126.27 (m); HRMS (ESI+): Calculated for $C_{19}H_{13}F_9SONa$: $[M+Na+O]^+$ 483.0436, Found 483.0455.

Naphthalen-2-yl(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (29)



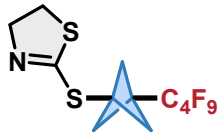
Obtained as a light yellow liquid (57 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 1.7 Hz, 1H), 7.86–7.80 (m, 3H), 7.55–7.48 (m, 3H), 2.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 133.6, 132.9, 131.3, 129.4, 128.7, 127.7, 127.7, 126.8, 126.6, 53.0, 42.6, 38.1 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.06–-81.15 (m), -115.74–-115.81 (m), -122.26–-122.32 (m), -126.05–-126.18 (m); HRMS (ESI+): Calculated for $C_{19}H_{13}F_9SONa$: $[M+Na+O]^+$ 483.0436, Found 483.0432.

2-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)thiophene (30)



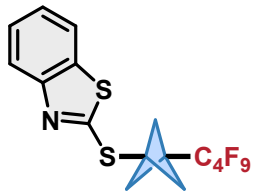
Obtained as a brown liquid (50 mg, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 5.3, 1.3 Hz, 1H), 7.13 (dd, J = 3.6, 1.3 Hz, 1H), 7.03 (dd, J = 5.4, 3.5 Hz, 1H), 2.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.3, 130.7, 130.0, 127.8, 52.5, 43.6, 37.4 (t, J = 30.9 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.06–-81.16 (m), -115.71–-115.85 (m), -122.16–-122.37 (m), -126.12–-126.20 (m); HRMS (ESI+): Calculated for $C_{13}H_9F_9S_2ONa$: $[M+Na+O]^+$ 438.9843, Found 438.9857.

2-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)-4,5-dihydrothiazole (31)



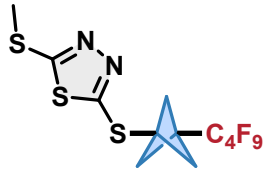
Obtained as a yellow solid (51 mg, 63% yield); M. P. = 37–38 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (t, J = 7.0 Hz, 2H), 2.77 (t, J = 7.0 Hz, 2H), 2.16 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.9, 45.4, 40.8, 38.1 (t, J = 30.8 Hz), 31.1, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02–-81.15 (m), -115.88–-115.96 (m), -122.21–-122.30 (m), -125.98–-126.17 (m); HRMS (ESI+): Calculated for $C_{12}H_{10}F_9NS_2ONa$: $[M+Na+O]^+$ 441.9952, Found 441.9910.

2-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)benzo[d]thiazole (32)



Obtained as a light yellow liquid (59 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 1H), 7.87–7.74 (m, 1H), 7.50–7.42 (m, 1H), 7.41–7.30 (m, 1H), 2.53 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 153.2, 135.7, 126.3, 124.9, 122.4, 121.0, 53.9, 41.0, 39.4 (t, J = 30.9 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02–-81.16 (m), -115.53–-115.69 (m), -122.11–-122.26 (m), -125.99–-126.16 (m); HRMS (ESI+): Calculated for $C_{16}H_{11}F_9NS_2$: $[M+H]^+$ 452.0184, Found 452.0184.

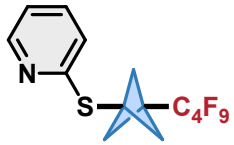
2-(Methylthio)-5-((3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)-1,3,4-thiadiazole (33)



Obtained as a yellow liquid (51 mg, 57% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.79 (s, 3H), 2.45 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 160.6, 53.8, 41.2, 39.2 (t, J = 30.8 Hz), 16.2, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02–-81.12 (m), -115.55–-115.72

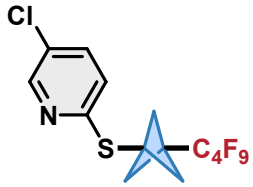
(m), -122.20–-122.28 (m), -126.01–-126.15 (m); HRMS (ESI+): Calculated for $C_{12}H_9F_9N_2S_3ONa$: $[M+Na+O]^+$ 486.9695, Found 486.9787.

2-((3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)pyridine (34)



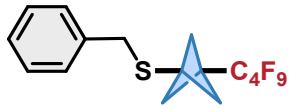
Obtained as a yellow liquid (47 mg, 60% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52–8.42 (m, 1H), 7.53 (td, J = 7.7, 1.7 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 7.07 (dd, J = 7.4, 4.7 Hz, 1H), 2.44 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 148.8, 135.2, 123.2, 119.6, 52.5, 38.8 (t, J = 30.7 Hz), 28.7, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.03–-81.12 (m), -115.65–-115.73 (m), -122.22–-122.29 (m), -126.08–-126.16 (m); HRMS (ESI+): Calculated for $C_{14}H_{10}F_9NSONa$: $[M+Na+O]^+$ 434.0232, Found 434.0232.

5-Chloro-2-((3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)thio)pyridine (35)



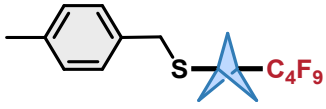
Obtained as a light yellow liquid (52 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, J = 2.5 Hz, 1H), 7.49 (dd, J = 8.5, 2.6 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 2.44 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 148.5, 136.0, 129.1, 124.5, 53.5, 40.2, 40.0 (t, J = 30.7 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.97–-81.21 (m), -115.65–-115.79 (m), -122.22–-122.35 (m), -125.99–-126.17 (m); HRMS (ESI+): Calculated for $C_{14}H_{10}ClF_9NS$: $[M+H]^+$ 430.0073, Found 430.0073.

Benzyl(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (36)



Obtained as a light yellow liquid (55 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.30 (m, 4H), 7.26 (d, J = 4.1 Hz, 1H), 3.79 (s, 2H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 136.8, 131.3, 130.5, 54.7, 43.1, 40.4 (t, J = 30.5 Hz), 37.3, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.01–-81.18 (m), -115.90–-116.02 (m), -122.27–-122.40 (m), -126.00–-126.25 (m); HRMS (ESI+): Calculated for $C_{16}H_{13}F_9SONa$: $[M+Na+O]^+$ 447.0436, Found 447.0389.

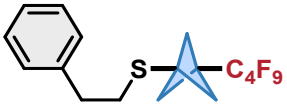
(4-Methylbenzyl)(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)sulfane (37)



Obtained as a light yellow solid (59 mg, 70% yield); M. P. = 57–58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 3.76 (s, 2H), 2.34 (s, 3H), 2.09 (s, 6H); ^{13}C

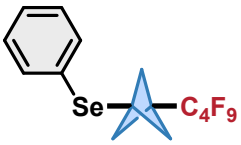
NMR (126 MHz, $CDCl_3$) δ 136.9, 134.8, 129.3, 128.5, 52.7, 41.1, 38.4 (t, J = 30.5 Hz), 35.3, 21.1, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.96–-81.23 (m), -115.83–-116.00 (m), -122.13–-122.38 (m), -126.01–-126.19 (m); HRMS (ESI+): Calculated for $C_{17}H_{15}F_9SONa$: $[M+Na+O]^+$ 461.0592, Found 461.0623.

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenethyl)sulfane (38)



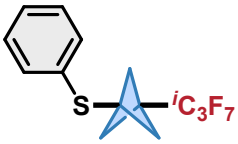
Obtained as a light yellow liquid (50 mg, 59% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.2, 6.9 Hz, 2H), 7.25–7.18 (m, 3H), 2.89 (dd, J = 8.7, 5.8 Hz, 2H), 2.81 (ddd, J = 8.4, 6.6, 1.3 Hz, 2H), 2.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 128.6, 128.5, 126.6, 52.7, 41.1, 38.1 (t, J = 30.6 Hz), 36.8, 32.6, ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02–-81.15 (m), -115.71–-115.97 (m), -122.23–-122.35 (m),, -125.90–-126.27 (m); HRMS (ESI+): Calculated for $C_{17}H_{15}F_9SONa$: $[M+Na+O]^+$ 461.0592, Found 461.0599.

(3-(Perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)selane (39)



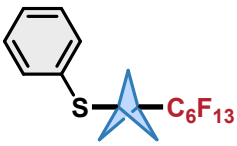
Obtained as a light yellow liquid (49 mg, 58% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.59–7.55 (m, 2H), 7.37–7.29 (m, 3H), 2.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 129.1, 128.4, 127.4, 53.7, 34.4 (t, J = 30.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.07–-81.25 (m), -115.67–-115.89 (m), -122.25–-122.43 (m), -126.05–-126.27 (m); HRMS (ESI+): Calculated for $C_{15}H_{11}F_9SeNa$: $[M+Na]^+$ 458.9834, Found 458.9838.

(3-(Perfluoropropan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (40)



Obtained as a light yellow liquid (48 mg, 70% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.41 (m, 2H), 7.37–7.31 (m, 3H), 2.14 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 132.0, 129.1, 128.4, 53.9, 53.8, 42.1, 36.6 (d, J = 25.9 Hz), ^{13}C NMR for $^iC_3F_7$ could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.80 (d, J = 8.8 Hz), -182.11–-182.16 (m); HRMS (ESI+): Calculated for $C_{14}H_{11}F_7SONa$: $[M+Na+O]^+$ 383.0311, Found 383.0303.

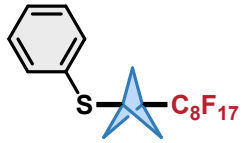
(3-(Perfluorohexyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (41)



Obtained as a light yellow solid (73 mg, 74% yield); M. P. = 46–47 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49–7.42 (m, 2H), 7.38–7.30 (m, 3H), 2.13 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 132.1,

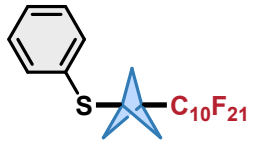
129.1, 128.4, 52.8, 42.5, 38.2 (t, J = 30.7 Hz), ^{13}C NMR for C_6F_{13} could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.82–-80.95 (m), -115.34–-115.82 (m), -121.31–-121.44 (m), -122.02–-122.16 (m), -123.01–-123.17 (m), -126.00–-126.47 (m); HRMS (ESI+): Calculated for $C_{17}H_{11}F_{13}SONa$: $[M+Na+O]^+$ 533.0215, Found 533.0618.

(3-(Perfluorooctyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (42)



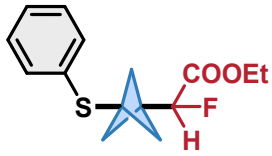
Obtained as a white solid (87 mg, 73% yield); M. P. = 62–63 °C; H NMR (500 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.38–7.31 (m, 3H), 2.13 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 132.1, 129.1, 128.4, 52.8, 42.5, 38.2 (t, J = 30.7 Hz), ^{13}C NMR for C_8F_{17} could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.76–-80.98 (m), -115.39–-115.79 (m), -121.26–-121.41 (m), -121.55–-121.90 (m), -122.04–-121.22 (m), -122.81–-122.97 (m), -126.22–-126.31 (m); HRMS (ESI+): Calculated for $C_{19}H_{11}F_{17}SONa$: $[M+Na+O]^+$ 633.0151, Found 633.0126.

(3-(Perfluorodecyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)sulfane (43)



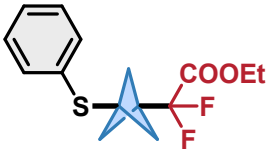
Obtained as a white solid (105 mg, 76% yield); M. P. = 86–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.43 (m, 2H), 7.42–7.28 (m, 3H), 2.14 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 132.1, 129.1, 128.4, 52.8, 42.4, 38.2 (t, J = 30.9 Hz), ^{13}C NMR for $C_{10}F_{21}$ could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.08–-81.20 (m), -115.75–-115.84 (m), -121.34–-121.48 (m), -121.92–-122.08 (m), -122.13–-122.28 (m), -122.93–-122.39 (m), -126.36–-126.44 (m); HRMS (ESI+): Calculated for $C_{21}H_{11}F_{21}SONa$: $[M+Na+O]^+$ 733.0087, Found 733.0061.

Ethyl (*S*)-2-fluoro-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (44)



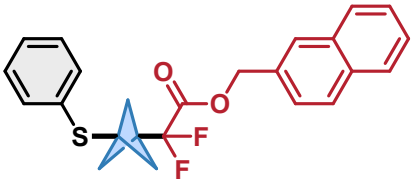
Obtained as a light yellow liquid (35 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.35–7.28 (m, 3H), 4.82 (d, J = 49.3 Hz, 1H), 4.24 (dd, J = 8.6, 7.1 Hz, 2H), 1.96 (s, 6H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5 (d, J = 24.5 Hz), 134.0, 133.0, 128.9, 128.0, 86.8 (d, J = 185.7 Hz), 61.5, 53.0, 42.3, 39.2 (d, J = 26.3 Hz), 14.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -192.73 (s); HRMS (ESI+): Calculated for $C_{15}H_{17}FO_3SNa$: $[M+Na+O]^+$ 319.0775, Found 319.0752.

Ethyl 2,2-difluoro-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (45)



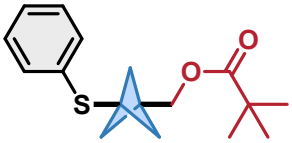
Obtained as a yellow liquid (41 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.37–7.29 (m, 3H), 4.30 (q, J = 7.1 Hz, 2H), 2.03 (s, 6H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (t, J = 33.1 Hz), 134.2, 132.4, 129.0, 128.2, 111.5 (t, J = 30.8 Hz), 62.8, 52.2, 42.1, 39.5 (t, J = 32.0 Hz), 14.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.48 (s); HRMS (ESI+): Calculated for $C_{15}H_{16}F_2O_3SNa$: $[M+Na+O]^+$ 337.0680, Found 337.0661.

Naphthalen-2-ylmethyl 2,2-difluoro-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (46)



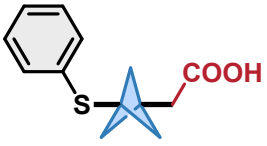
Obtained as a brown liquid (49 mg, 60% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86–7.80 (m, 4H), 7.55–7.49 (m, 2H), 7.42 (d, J = 1.8 Hz, 1H), 7.39–7.33 (m, 2H), 7.30–7.24 (m, 3H), 5.40 (s, 2H), 1.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9 (t, J = 33.4 Hz), 134.1, 133.4, 133.1, 132.4, 131.6, 129.0, 128.7, 128.2, 128.2, 128.1, 127.8, 126.7, 126.6, 125.8, 111.6 (t, J = 250.8 Hz), 68.5, 52.2, 52.2, 52.2, 42.1, 39.6 (t, J = 31.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.17 (s); HRMS (ESI+): Calculated for $C_{24}H_{20}F_2O_3SNa$: $[M+Na+O]^+$ 449.0993, Found 449.0963.

(3-(Phenylthio)bicyclo[1.1.1]pentan-1-yl)methyl pivalate (47)



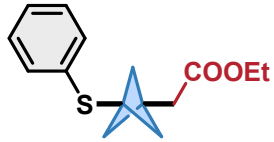
Obtained as a yellow liquid (30 mg, 51% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.33–7.28 (m, 3H), 4.07 (s, 2H), 1.87 (s, 6H), 1.18 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 133.6, 128.8, 127.7, 63.1, 53.4, 42.5, 38.9, 38.9, 27.2; HRMS (ESI+): Calculated for $C_{17}H_{23}O_2S$: $[M+H]^+$ 291.1413, Found 291.1412.

2-(3-(Phenylthio)bicyclo[1.1.1]pentan-1-yl)acetic acid (48)



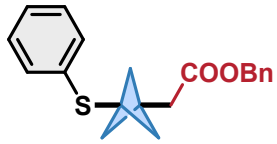
Obtained as a light yellow solid (30 mg, 64% yield); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.04 (s, 1H), 7.38–7.35 (m, 2H), 7.35–7.31 (m, 2H), 7.28 (d, J = 7.0 Hz, 1H), 2.42 (s, 2H), 1.84 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.4, 134.2, 132.8, 129.5, 127.9, 54.9, 41.7, 37.7, 36.8; HRMS (ESI+): Calculated for $C_{13}H_{13}O_2S$: $[M-H]^+$ 233.0642, Found 233.0645.

Ethyl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (49)



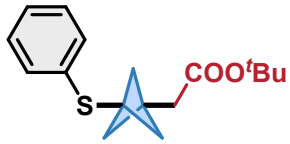
Obtained as a orange liquid (35 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.32–7.27 (m, 3H), 4.10 (q, J = 7.1 Hz, 2H), 2.51 (s, 2H), 1.92 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 137.2, 137.0, 132.2, 131.0, 63.8, 58.3, 45.3, 40.5, 33.1, 17.7; HRMS (ESI+): Calculated for $C_{15}H_{18}O_3SNa$: $[M+Na+O]^+$ 301.0869, Found 301.0882.

Benzyl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (50)



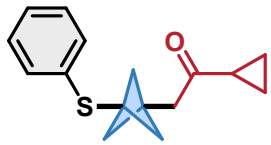
Obtained as a brown liquid (40 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.37–7.33 (m, 3H), 7.33–7.27 (m, 5H), 5.09 (s, 2H), 2.57 (s, 2H), 1.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 134.7, 134.4, 129.7, 129.5, 129.3, 129.2, 128.4, 67.2, 55.8, 42.8, 37.9; HRMS (ESI+): Calculated for $C_{20}H_{20}O_3SNa$: $[M+Na+O]^+$ 363.1025, Found 363.1005.

Tert-butyl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (51)



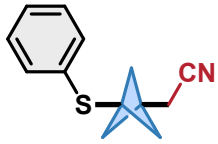
Obtained as a yellow liquid (37 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.33–7.24 (m, 3H), 2.41 (s, 2H), 1.91 (s, 6H), 1.42 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 133.9, 133.5, 128.8, 127.5, 54.9, 41.9, 38.4, 37.3, 28.2; HRMS (ESI+): Calculated for $C_{17}H_{22}O_3SNa$: $[M+Na+O]^+$ 329.1182, Found 329.1164.

1-Cyclopropyl-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)ethan-1-one (52)



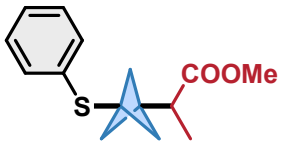
Obtained as a brown liquid (30 mg, 59% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.32–7.26 (m, 3H), 2.73 (s, 2H), 1.93 (s, 6H), 1.85–1.80 (m, 1H), 0.99 (dd, J = 4.5, 3.3 Hz, 2H), 0.86 (d, J = 7.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.5, 133.8, 133.6, 128.8, 127.6, 55.1, 45.7, 42.3, 37.1, 20.9, 11.0; HRMS (ESI+): Calculated for $C_{16}H_{18}O_2SNa$: $[M+Na+O]^+$ 297.0920, Found 297.0906.

2-(3-(Phenylthio)bicyclo[1.1.1]pentan-1-yl)acetonitrile (53)



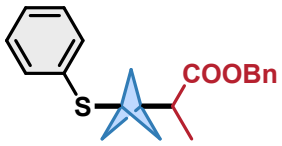
Obtained as a yellow liquid (23.0 mg, 54% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.36–7.28 (m, 3H), 2.58 (s, 2H), 1.95 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 133.0, 129.0, 128.0, 116.9, 54.3, 41.9, 35.7, 20.9; HRMS (ESI+): Calculated for $C_{13}H_{13}NSONa$: $[M+Na+O]^+$ 254.0610, Found 254.0619.

Methyl (S)-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (54)



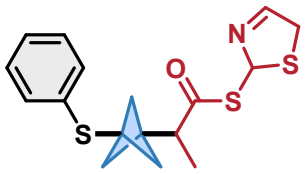
Obtained as a yellow liquid (34 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.32–7.27 (m, 3H), 3.64 (s, 3H), 2.61 (q, J = 7.0 Hz, 1H), 1.82 (s, 6H), 1.07 (d, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 133.7, 133.7, 128.8, 127.6, 53.0, 51.5, 41.8, 41.2, 40.6, 13.6; HRMS (ESI+): Calculated for $C_{15}H_{18}O_3SNa$: $[M+Na+O]^+$ 301.0869, Found 301.0858.

Benzyl (S)-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (55)



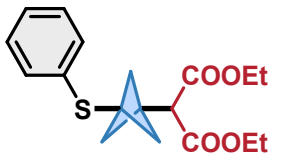
Obtained as a yellow liquid (44 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.35 (d, J = 5.1 Hz, 3H), 7.33–7.27 (m, 5H), 5.13–5.06 (m, 2H), 2.66 (q, J = 7.0 Hz, 1H), 1.80 (s, 6H), 1.09 (d, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 136.0, 133.6, 128.8, 128.6, 128.4, 128.3, 127.6, 66.2, 53.0, 41.8, 41.3, 40.7, 13.6; HRMS (ESI+): Calculated for $C_{21}H_{22}O_3SNa$: $[M+Na+O]^+$ 377.1182, Found 377.1155.

***S*-(2,5-Dihydrothiazol-2-yl) (2S)-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanethioate (56)**



Obtained as a yellow liquid (36 mg, 51% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.35–7.28 (m, 3H), 4.20 (q, J = 7.2 Hz, 1H), 3.74 (td, J = 7.2, 2.7 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.10 (s, 6H), 1.69 (d, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 170.8, 133.9, 133.1, 128.9, 128.0, 57.3, 43.8, 42.2, 41.5, 40.8, 28.5, 19.0; HRMS (ESI+): Calculated for $C_{17}H_{19}NO_2S_3Na$: $[M+Na+O]^+$ 388.0470, Found 388.0446.

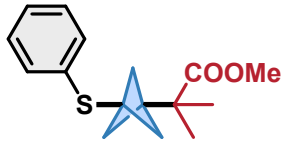
Diethyl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)malonate (57)



Obtained as a yellow liquid (45 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.32–7.26 (m, 3H), 4.16 (q, J = 7.2 Hz, 4H), 3.52 (s, 1H), 2.00 (s, 6H), 1.24 (t, J = 7.1 Hz, 6H); ^{13}C

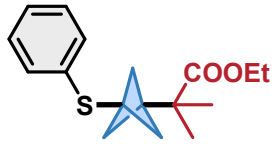
NMR (126 MHz, $CDCl_3$) δ 167.2, 133.7, 133.5, 128.8, 127.7, 61.3, 54.3, 53.0, 42.1, 37.9, 14.1; HRMS (ESI+): Calculated for $C_{18}H_{22}O_5SNa$: $[M+Na+O]^+$ 373.1080, Found 373.1061.

Methyl 2-methyl-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (58)



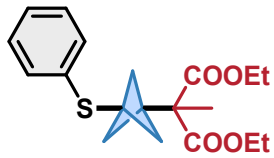
Obtained as a yellow liquid (35 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.33–7.27 (m, 3H), 3.63 (s, 3H), 1.79 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 133.8, 133.8, 128.8, 127.6, 51.7, 51.6, 46.0, 42.4, 40.4, 21.9; HRMS (ESI+): Calculated for $C_{16}H_{20}O_3SNa$: $[M+Na+O]^+$ 315.1025, Found 315.1018.

Ethyl 2-methyl-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (59)



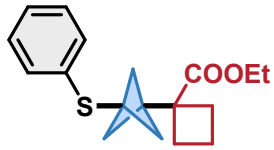
Obtained as a yellow liquid (41 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.32–7.27 (m, 3H), 4.09 (q, J = 7.1 Hz, 2H), 1.80 (s, 6H), 1.22 (t, J = 7.1 Hz, 3H), 1.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 133.8, 133.7, 128.8, 127.6, 60.4, 51.8, 46.0, 42.2, 40.5, 21.9, 14.4; HRMS (ESI+): Calculated for $C_{17}H_{22}O_3SNa$: $[M+Na+O]^+$ 329.1182, Found 329.1172.

Diethyl 2-methyl-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)malonate (60)



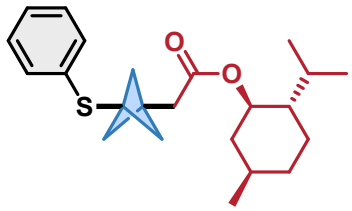
Obtained as a yellow liquid (48 mg, 69% yield);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.39 (m, 2H), 7.32–7.23 (m, 3H), 4.18–4.09 (m, 4H), 1.94 (s, 6H), 1.33 (s, 3H), 1.21 (t, J = 7.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 133.7, 133.6, 128.8, 127.7, 61.2, 53.9, 52.9, 42.6, 41.3, 18.4, 14.1; HRMS (ESI+): Calculated for $C_{19}H_{24}O_5SNa$: $[M+Na+O]^+$ 387.1237, Found 387.1217.

Ethyl 1-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)cyclobutane-1-carboxylate (61)



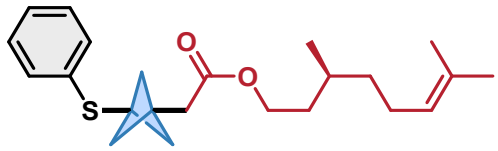
Obtained as a yellow liquid (36 mg, 59% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.35 (m, 2H), 7.26–7.19 (m, 3H), 4.05 (q, J = 7.1 Hz, 2H), 2.30–2.22 (m, 2H), 1.92–1.85 (m, 2H), 1.81 (s, 6H), 1.72–1.64 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 133.8, 133.7, 128.8, 127.6, 60.4, 51.8, 47.3, 43.7, 41.1, 27.3, 15.3, 14.4; HRMS (ESI+): Calculated for $C_{18}H_{22}O_3SNa$: $[M+Na+O]^+$ 341.1182, Found 341.1165.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (62)



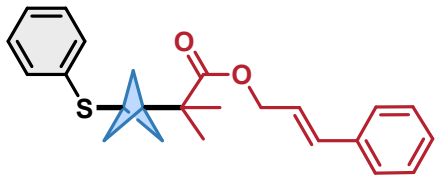
Obtained as a light yellow solid (51 mg, 69% yield); M. P. = 95–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.33–7.26 (m, 3H), 4.65 (td, J = 10.9, 4.4 Hz, 1H), 2.49 (d, J = 3.1 Hz, 2H), 1.92 (s, 6H), 1.82 (ddd, J = 9.8, 7.1, 3.6 Hz, 1H), 1.70–1.60 (m, 4H), 1.51–1.43 (m, 1H), 1.33 (s, 1H), 1.28 (s, 1H), 1.07–1.00 (m, 1H), 0.89 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H), 0.72 (d, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 133.8, 133.5, 128.8, 127.5, 74.4, 54.9, 46.9, 41.9, 41.0, 37.5, 37.2, 34.2, 31.4, 26.2, 23.3, 22.0, 20.8, 16.2; HRMS (ESI+): Calculated for $C_{23}H_{32}O_3SNa$: $[M+Na+O]^+$411.1964, Found 411.1960.

(*S*)-3,7-Dimethyloct-6-en-1-yl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (63)



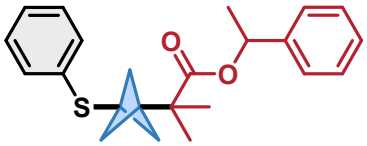
Obtained as a light yellow solid (48 mg, 65% yield); M. P. = 109–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.40 (m, 2H), 7.32–7.26 (m, 2H), 5.11–5.04 (m, 1H), 4.12–4.03 (m, 2H), 2.51 (s, 2H), 1.92 (s, 6H), 1.68 (q, J = 1.4 Hz, 3H), 1.69–1.59 (m, 1H), 1.60 (d, J = 1.3 Hz, 5H), 1.56–1.48 (m, 1H), 1.45–1.36 (m, 1H), 1.36–1.30 (m, 1H), 1.33– 1.26 (m, 1H), 1.21–1.13 (m, 1H), 0.89 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 133.8, 133.6, 131.4, 128.8, 127.6, 124.5, 63.0, 54.9 41.9, 37.1, 37.1, 37.0, 35.5, 29.4, 25.7, 25.4, 19.3, 17.7; HRMS (ESI+): Calculated for $C_{23}H_{32}O_3SNa$: $[M+Na+O]^+$411.1964, Found 411.1966.

Cinnamyl 2-methyl-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (64)



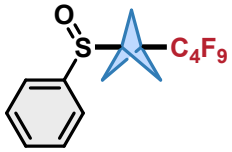
Obtained as a yellow solid (46 mg, 61% yield); M. P. = 123–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.38 (m, 2H), 7.40–7.32 (m, 3H), 7.32 (d, J = 7.7 Hz, 1H), 7.30–7.23 (m, 4H), 6.66–6.58 (m, 1H), 6.27–6.19 (m, 1H), 4.69 (dd, J = 6.5, 1.4 Hz, 2H), 1.81 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 136.2, 134.1, 133.8, 133.7, 128.8, 128.7, 128.1, 127.6, 126.6, 123.3, 65.1, 51.8, 46.0, 42.5, 40.5, 22.0; HRMS (ESI+): Calculated for $C_{24}H_{26}O_3SNa$: $[M+Na+O]^+$ 417.1495, Found 417.1485.

1-Phenylethyl 2-methyl-2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (65)



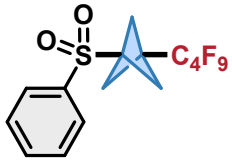
Obtained as a yellow solid (47 mg, 64% yield); M. P. = 95–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.39 (m, 2H), 7.38–7.29 (m, 5H), 7.33–7.27 (m, 3H), 5.85 (q, J = 6.6 Hz, 1H), 1.79 (s, 6H), 1.51 (d, J = 6.6 Hz, 3H), 1.11 (d, J = 1.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 141.7, 133.6, 128.8, 128.5, 127.9, 127.6, 126.1, 126.1, 72.4, 51.8, 46.0, 42.3, 40.5, 22.4, 21.9; HRMS (ESI+): Calculated for $C_{23}H_{26}O_3SNa$: $[M+Na+O]^+$ 405.1495, found 405.1480.

(*S*)-1-(Perfluorobutyl)-3-(phenylsulfinyl)bicyclo[1.1.1]pentane (66)



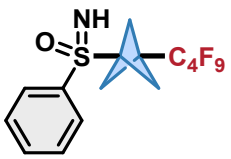
Obtained as a yellow solid (64 mg, 78% yield); M. P. = 62–63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 5H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 131.5, 129.3, 124.0, 51.8, 48.3, 37.7 (t, J = 31.5 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.11–-81.30 (m), -116.25–-116.62 (m), -122.13–-122.60 (m), -125.97–-126.48 (m) ; HRMS (ESI+): Calculated for $C_{15}H_{11}F_9OSNa$: $[M+Na]^+$ 433.0279, Found 433.0287.

1-(Perfluorobutyl)-3-(phenylsulfonyl)bicyclo[1.1.1]pentane (67)



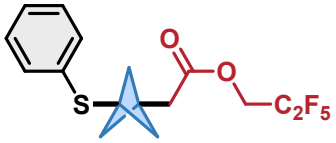
Obtained as a white solid (57 mg, 67% yield); M. P. = 113–114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H), 7.73–7.66 (m, 1H), 7.64–7.56 (m, 2H), 2.30 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 134.3, 129.5, 128.6, 51.3, 50.0, 36.7 (t, J = 31.8 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.04–-81.24 (m), -116.52–-116.79 (m), -122.24–-122.48 (m), -126.01–-126.32 (m); HRMS (ESI+): Calculated for $C_{15}H_{11}F_9O_2SNa$: $[M+Na]^+$ 449.0228, Found 449.0237.

Imino(3-(perfluorobutyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)-λ^6-sulfanone (68)



Obtained as a yellow solid (54 mg, 64% yield); M. P. = 98–99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95–7.87 (m, 2H), 7.65–7.60 (m, 1H), 7.54 (dd, J = 8.4, 7.0 Hz, 2H), 2.83 (s, 1H), 2.23 (t, J = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 133.5, 129.3, 128.9, 52.6, 49.8, 35.8 (t, J = 31.6 Hz), ^{13}C NMR for C_4F_9 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.08–-81.37 (m), -116.25–-116.78 (m), -122.09–-122.67 (m), -125.97–-126.50 (m); HRMS (ESI+): Calculated for $C_{15}H_{12}F_9NOSNa$: $[M+Na]^+$ 448.0388, Found 448.0373.

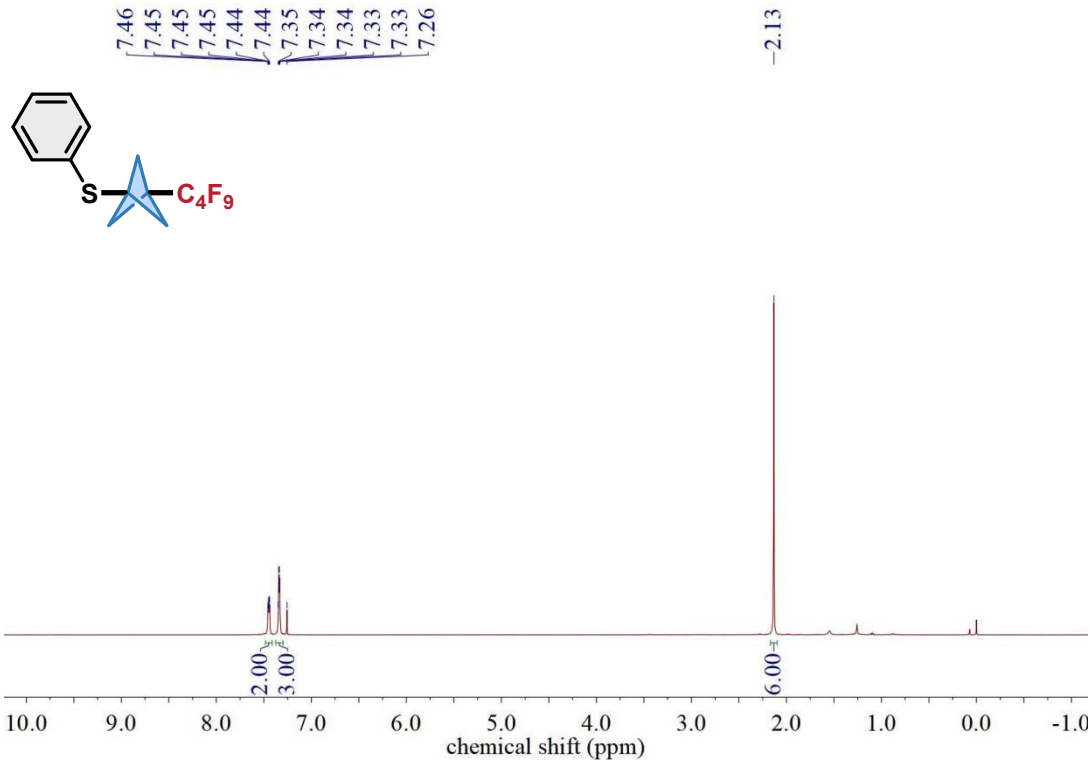
2,2,3,3,3-Pentafluoropropyl 2-(3-(phenylthio)bicyclo[1.1.1]pentan-1-yl)acetate (71)



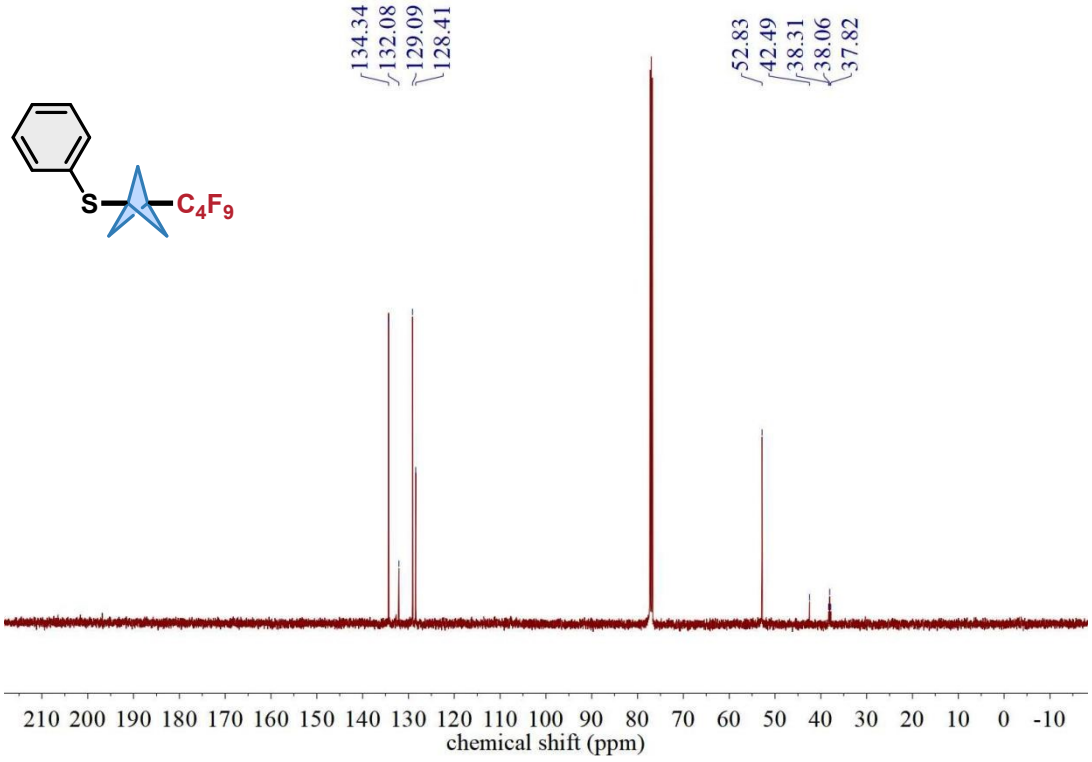
Obtained as a light yellow solid (62 mg, 85% yield); M. P. = 105–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.40 (m, 2H), 7.30 (dd, J = 10.4, 5.3 Hz, 3H), 4.51 (t, J = 13.0 Hz, 2H), 2.64 (s, 2H), 1.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 133.7, 133.6, 128.8, 127.7, 59.0 (t, J = 27.3 Hz), 54.8, 42.0, 36.5, 36.4, ^{13}C NMR for C_2F_5 could not be assigned; ^{19}F NMR (471 MHz, $CDCl_3$) δ -83.84, -123.46; HRMS (ESI+): Calculated for $C_{16}H_{15}F_5O_3SNa$: $[M+Na+O]^+$ 405.0554, Found 405.0541.

6. Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra

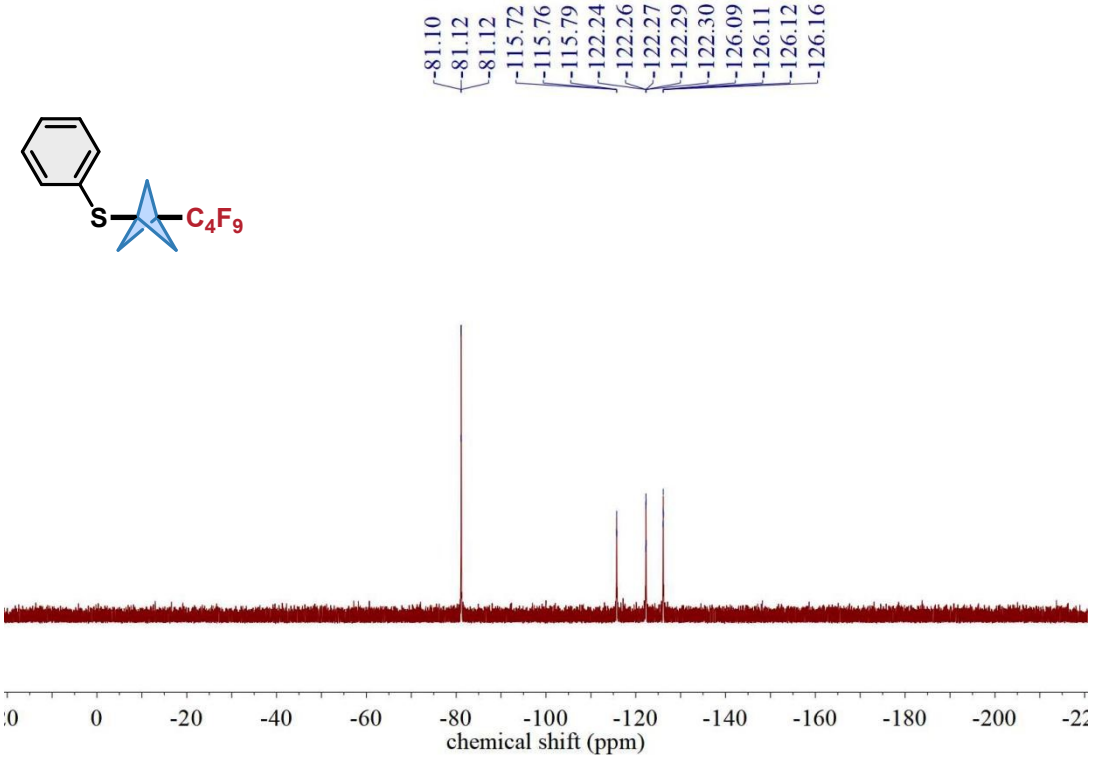
4 ^{1}H NMR (500 MHz, $CDCl_3$)



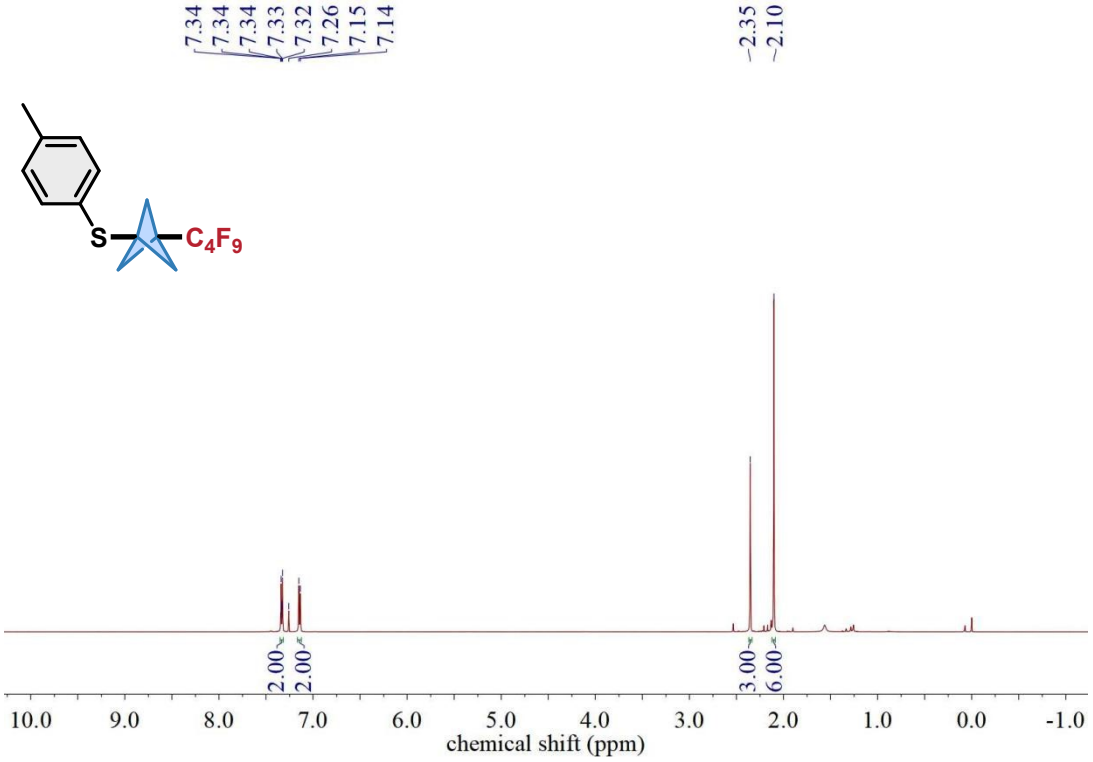
4 ^{13}C NMR (126 MHz, $CDCl_3$)



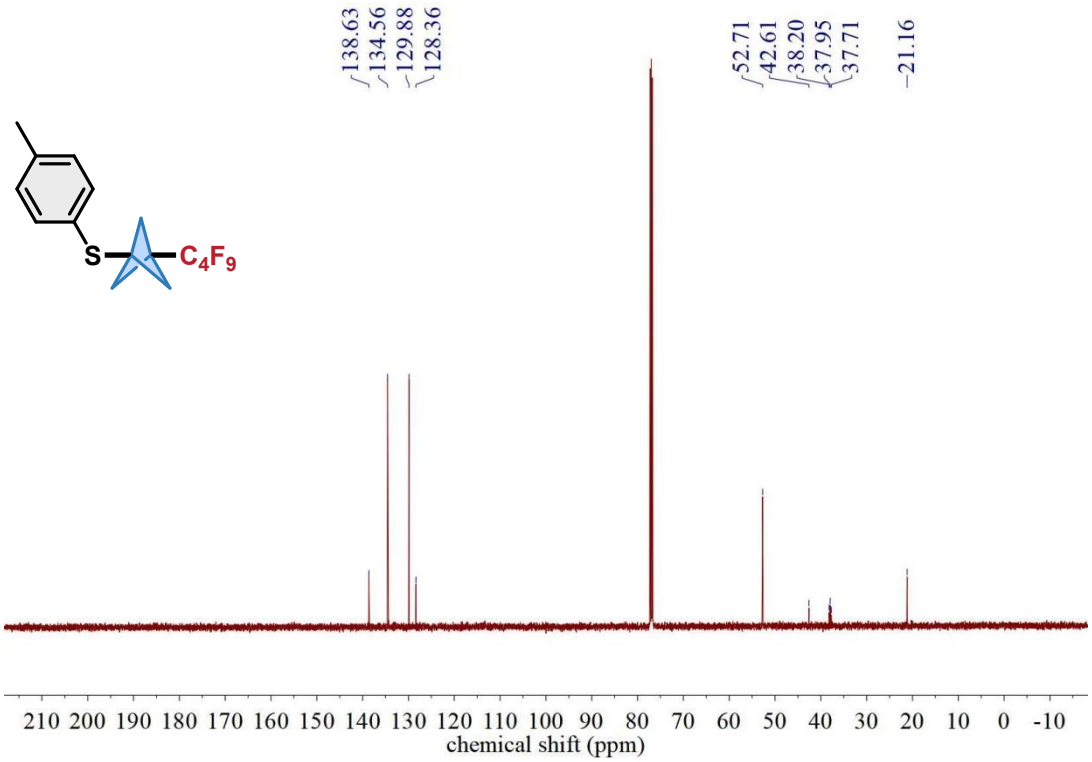
4 ^{19}F NMR (471 MHz, $CDCl_3$)



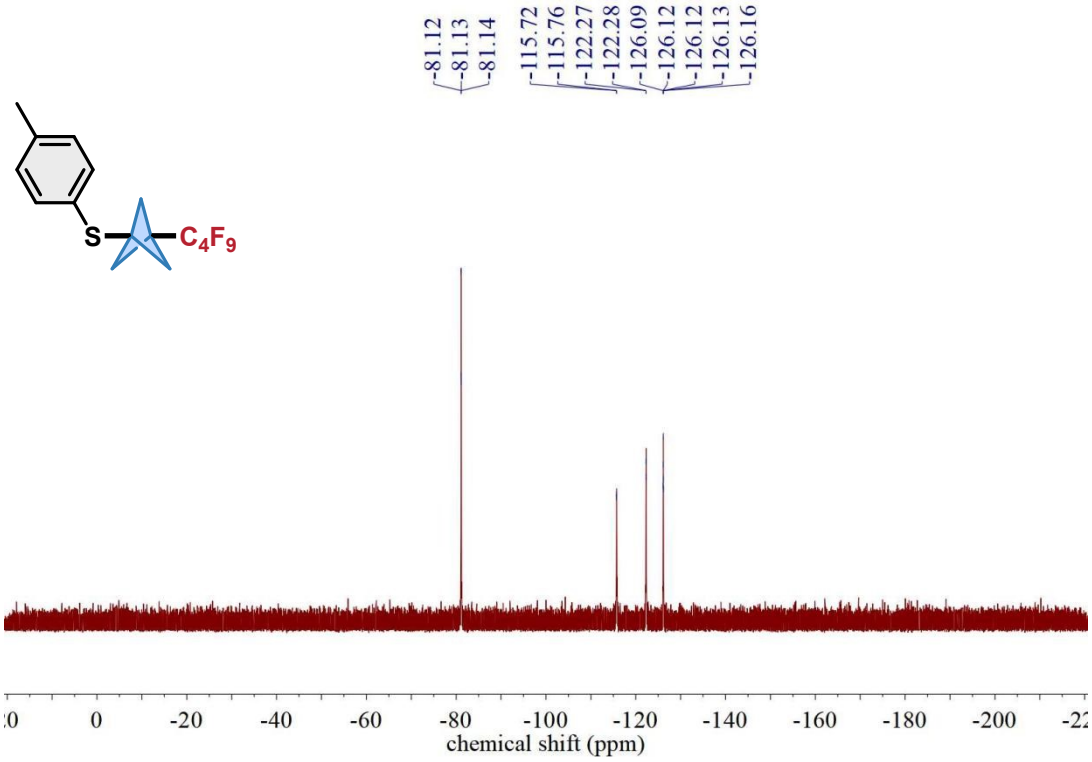
5 ^{1}H NMR (500 MHz, $CDCl_3$)



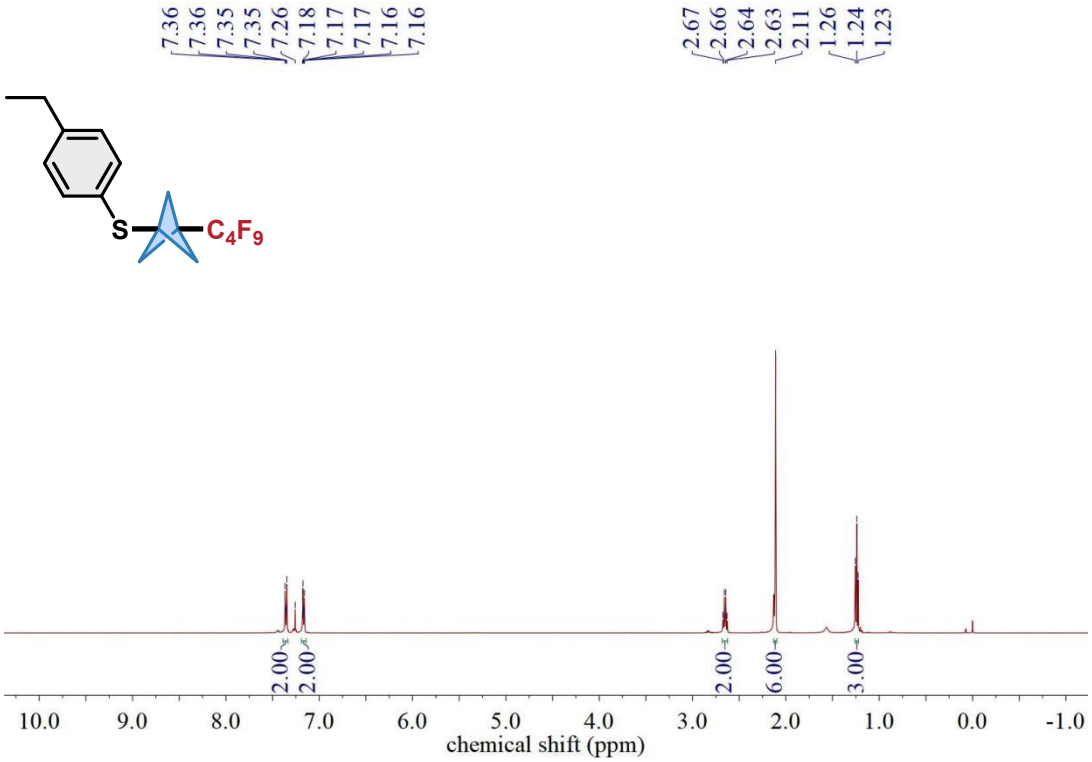
5 ^{13}C NMR (126 MHz, $CDCl_3$)



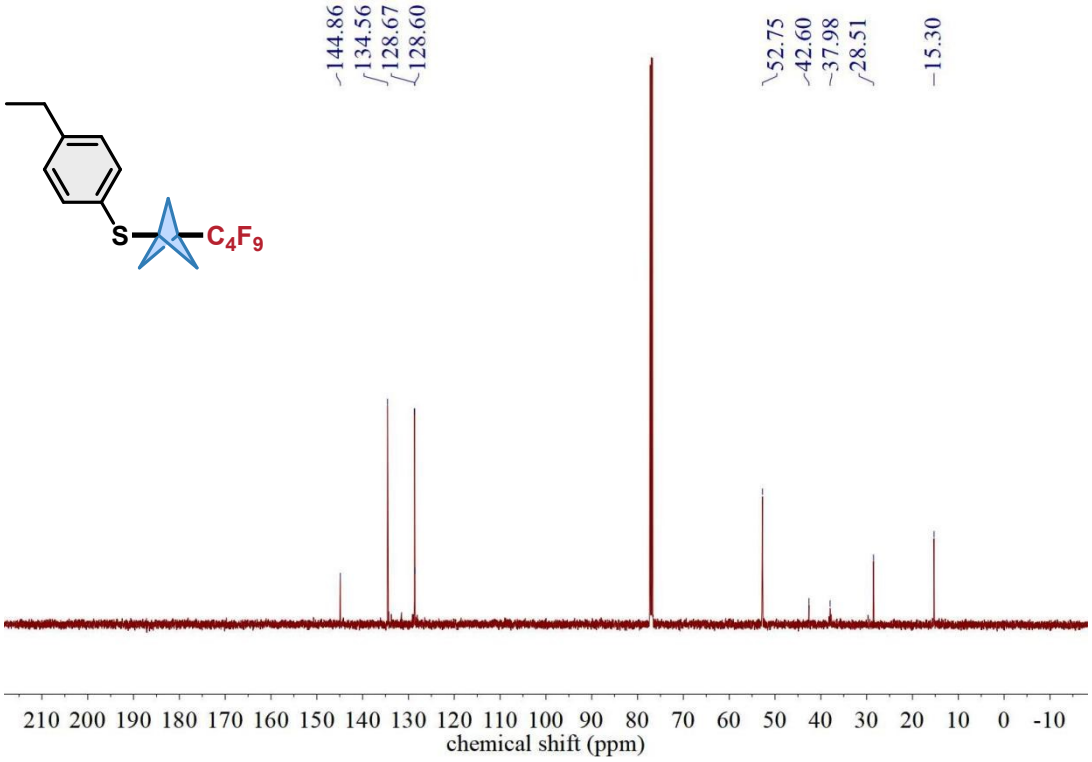
5 ^{19}F NMR (471 MHz, $CDCl_3$)



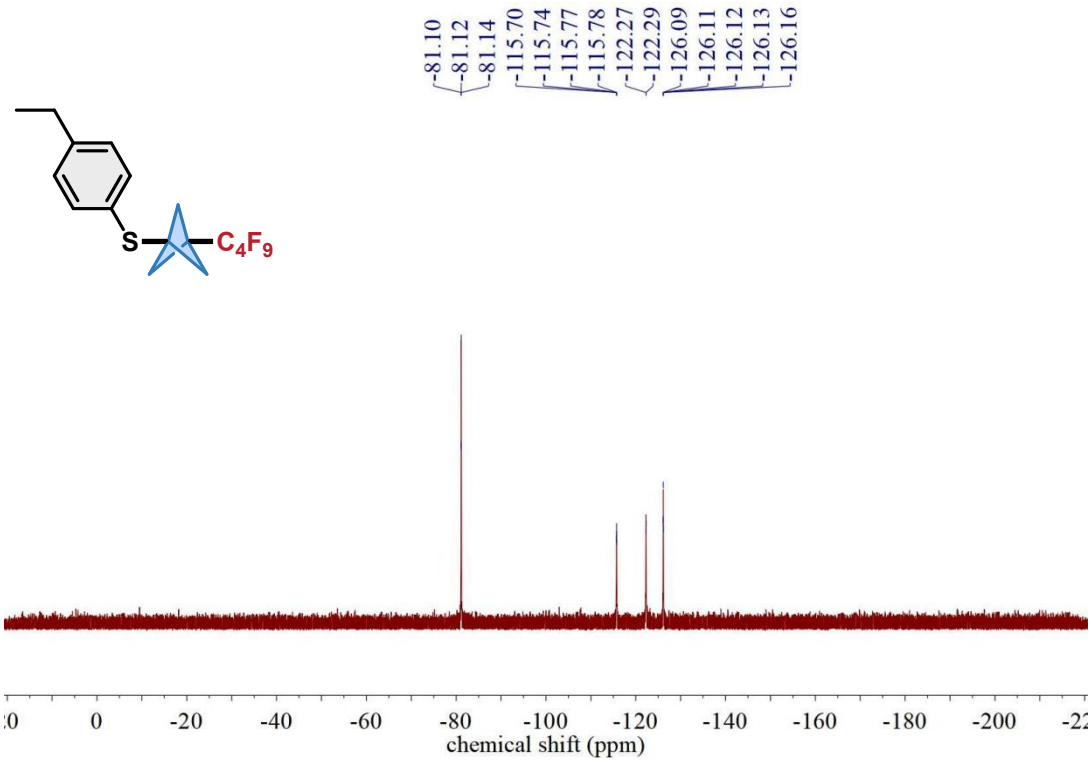
6 ^{1}H NMR (500 MHz, $CDCl_3$)



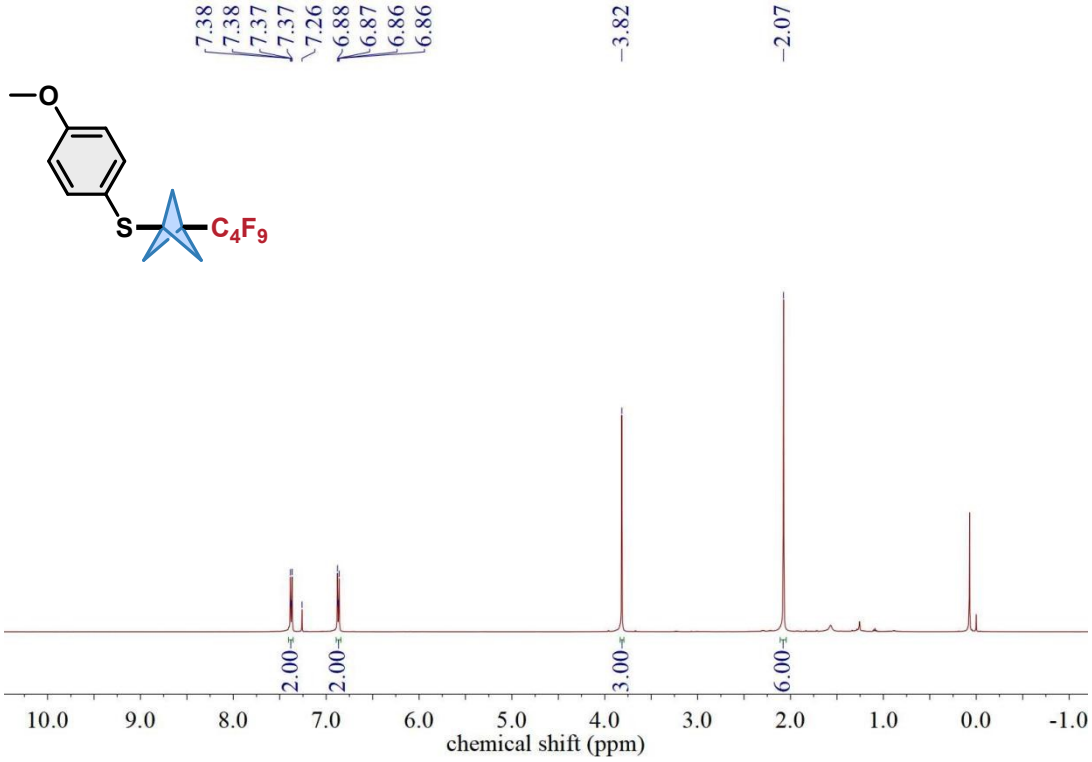
6 ^{13}C NMR (126 MHz, $CDCl_3$)



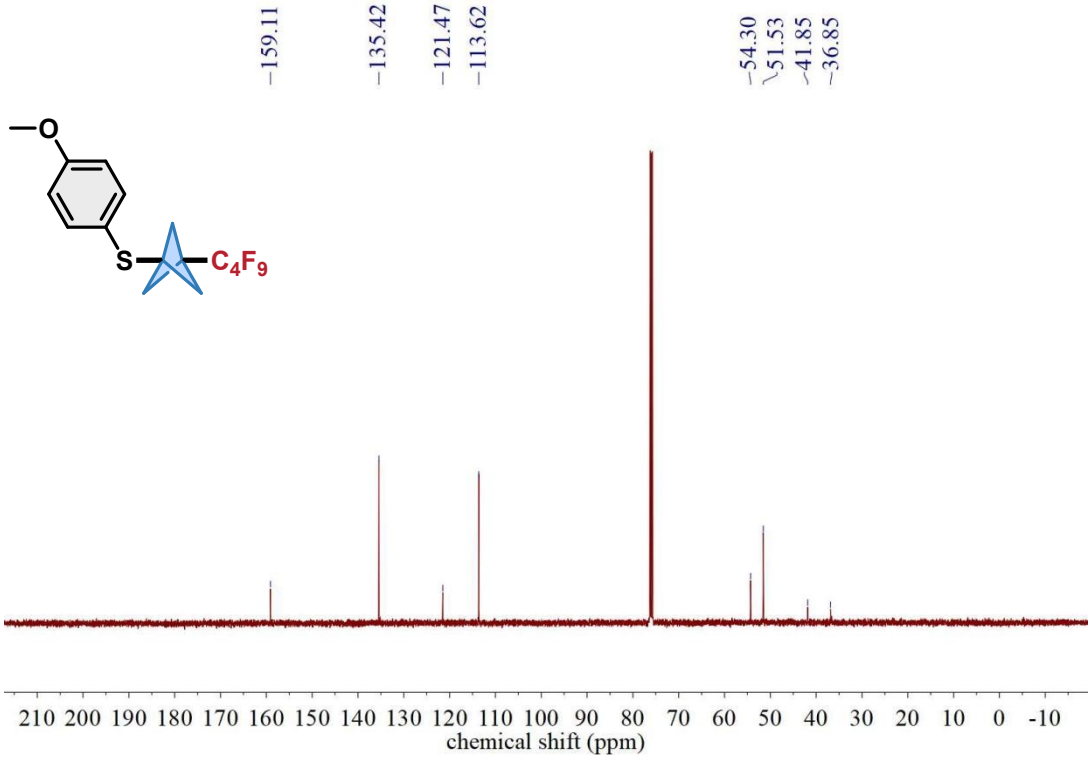
6 ^{19}F NMR (471 MHz, $CDCl_3$)



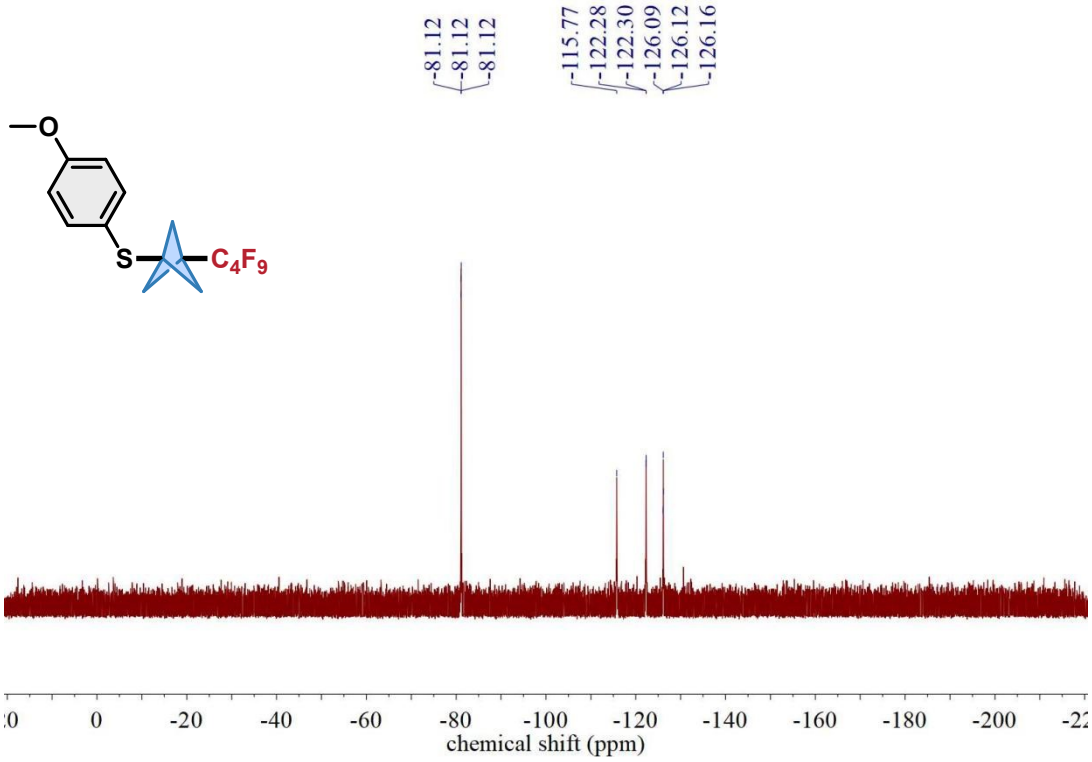
7 ^{1}H NMR (500 MHz, $CDCl_3$)



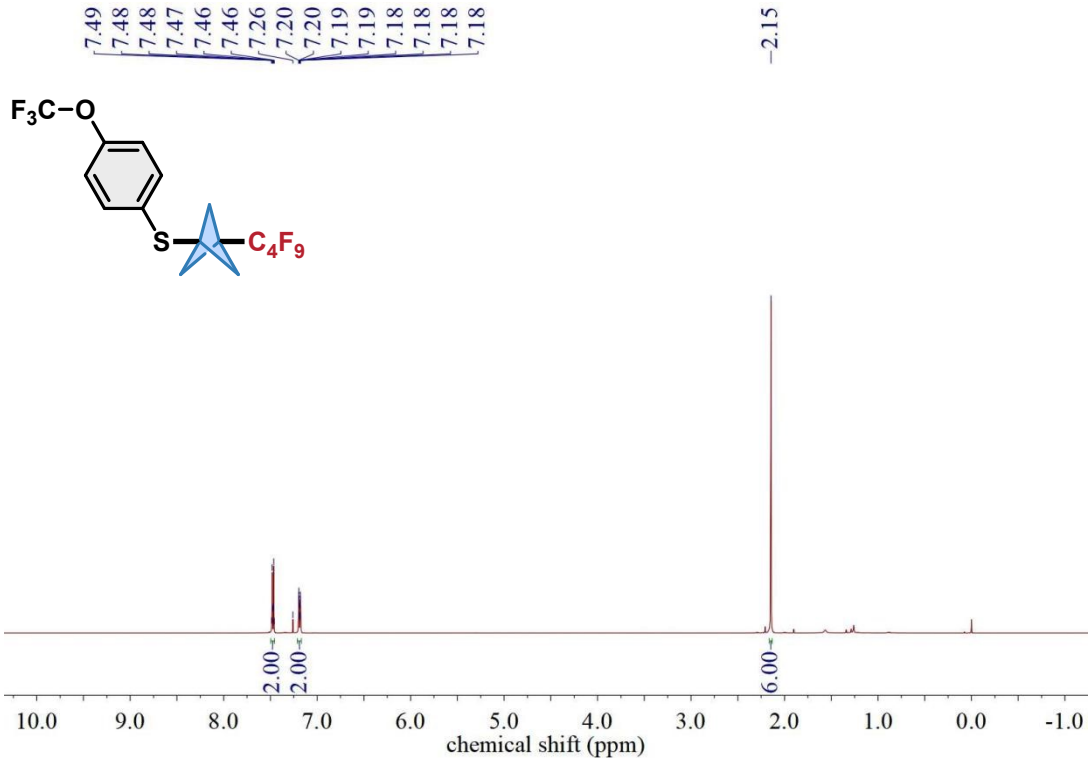
7 ^{13}C NMR (126 MHz, $CDCl_3$)



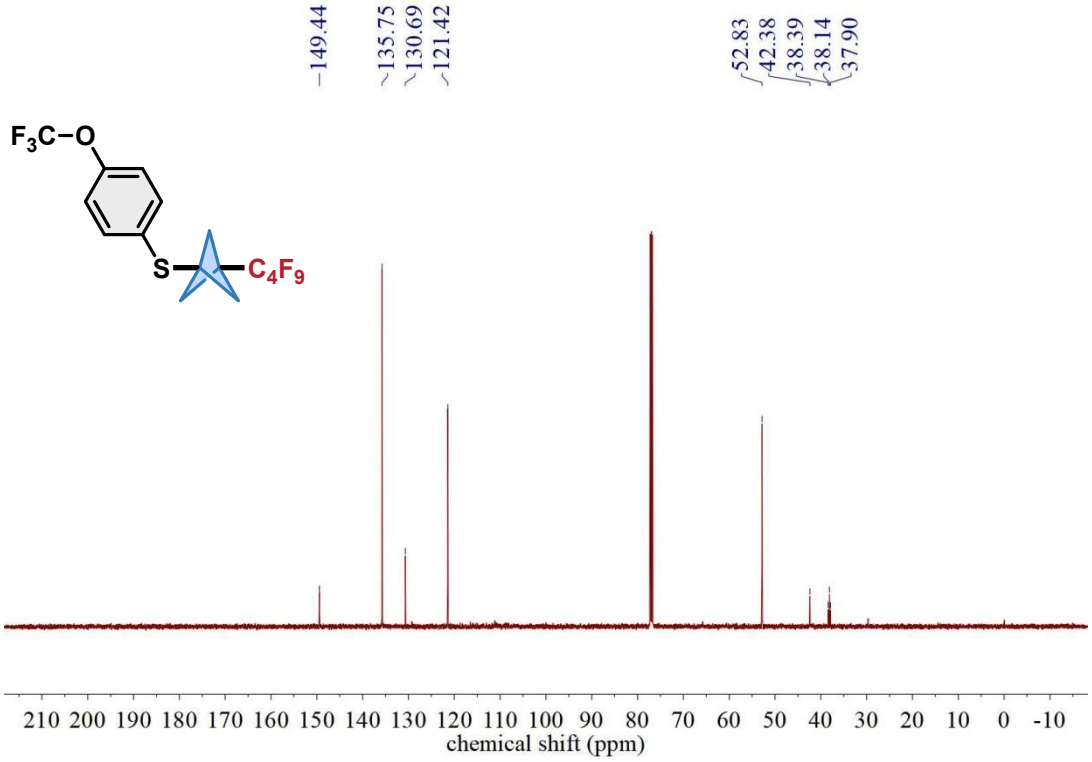
7 ^{19}F NMR (471 MHz, $CDCl_3$)



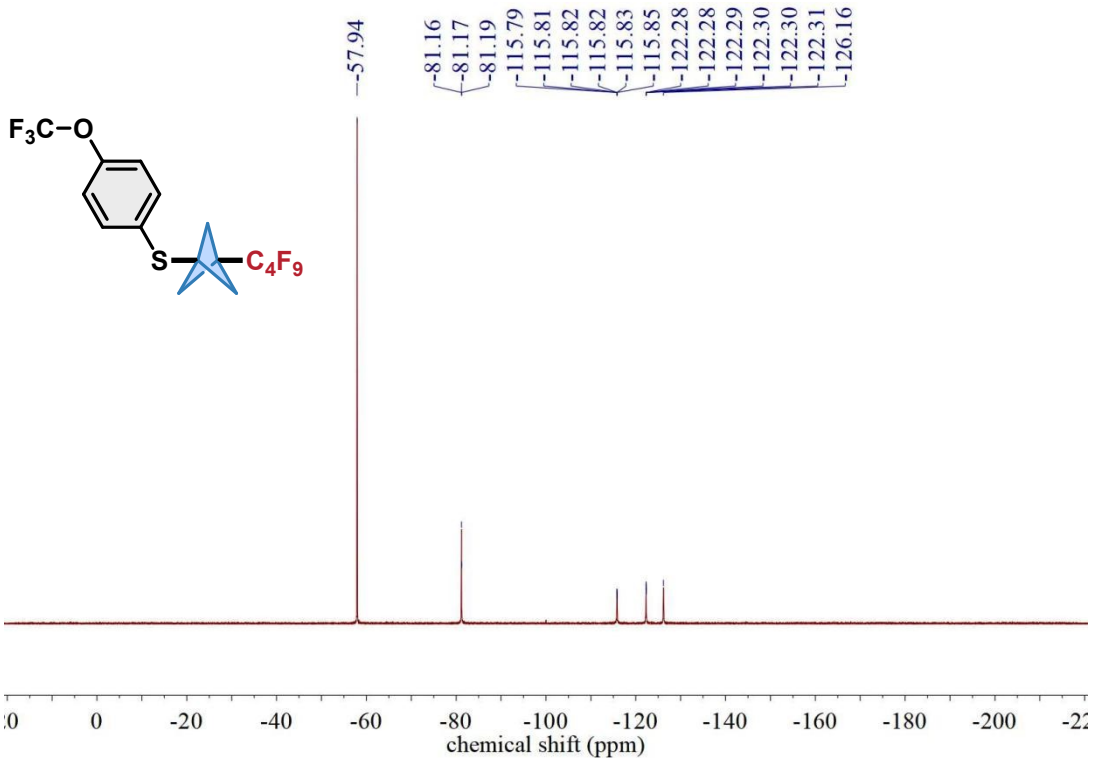
8 ^{1}H NMR (500 MHz, $CDCl_3$)



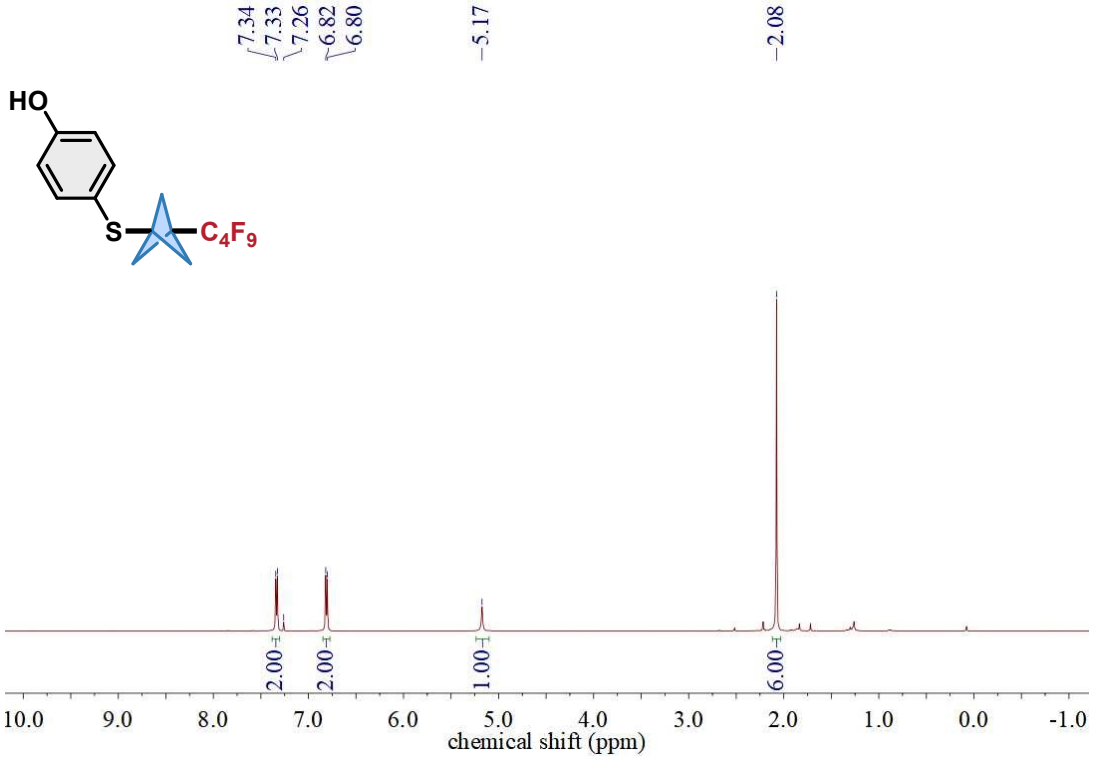
8 ^{13}C NMR (126 MHz, $CDCl_3$)



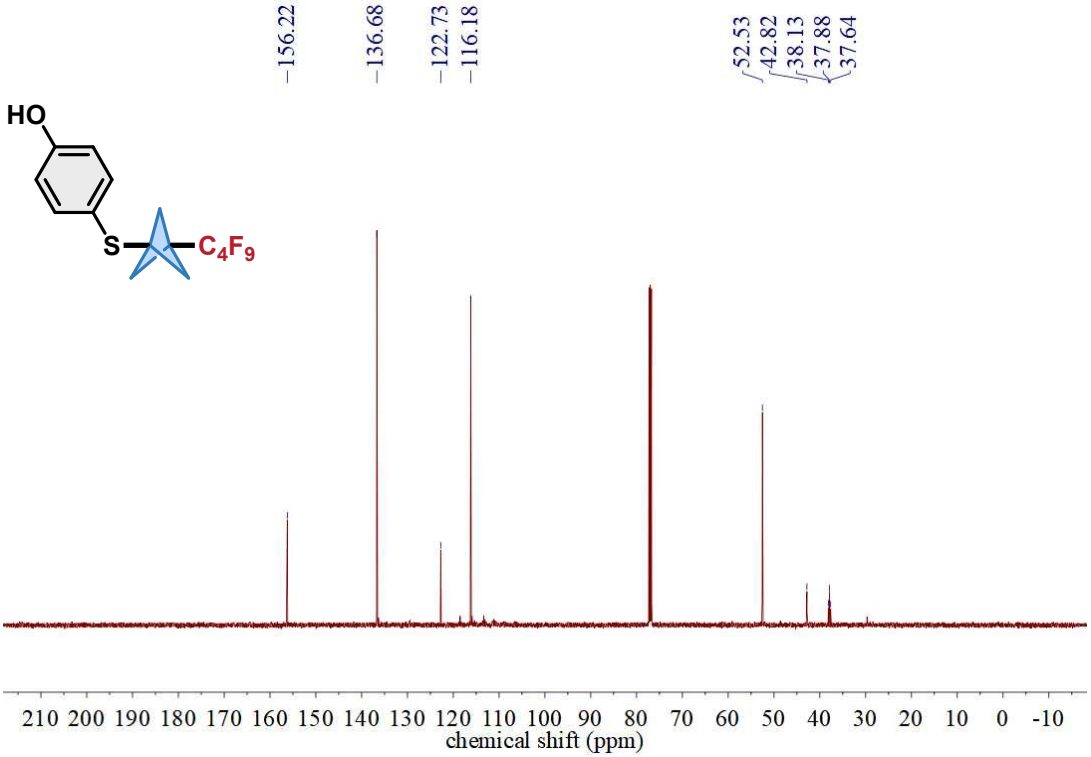
8 ^{19}F NMR (471 MHz, $CDCl_3$)



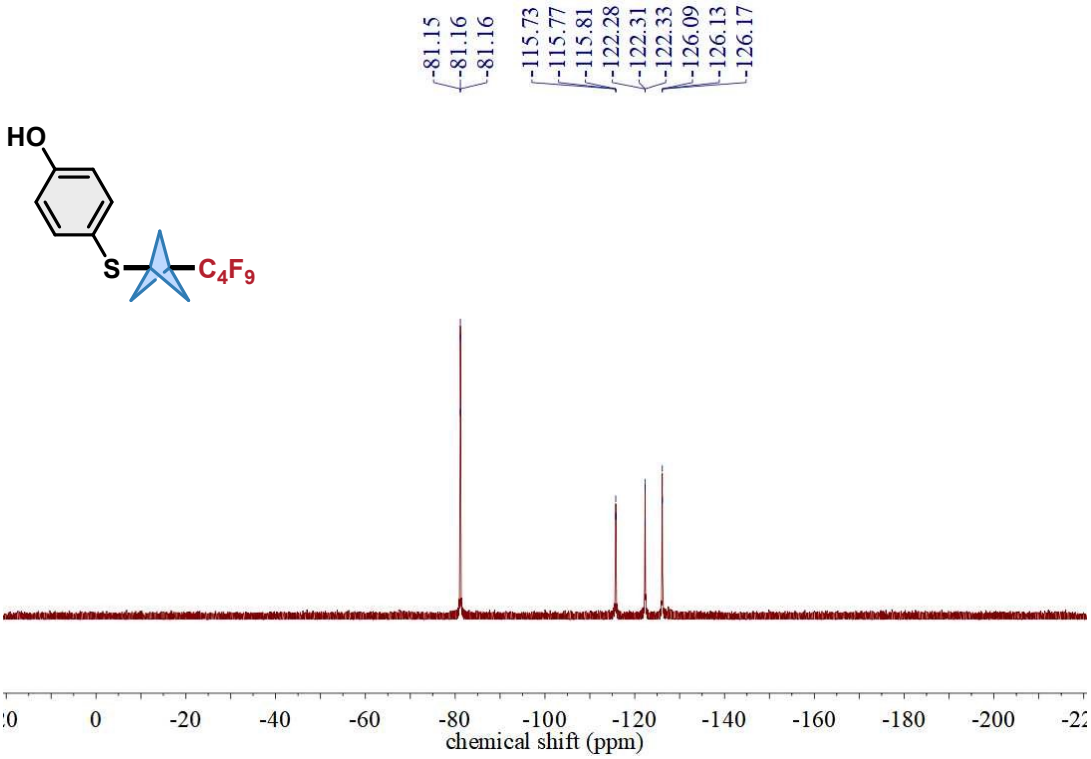
9 ^{1}H NMR (500 MHz, $CDCl_3$)



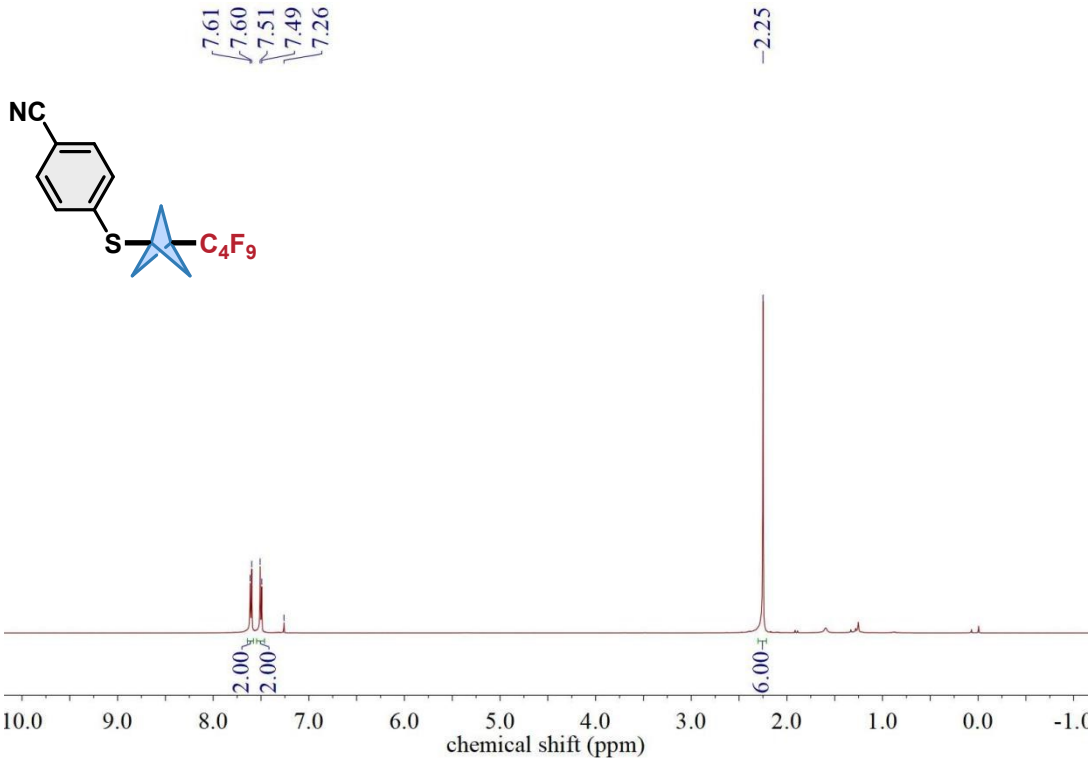
9 ^{13}C NMR (126 MHz, $CDCl_3$)



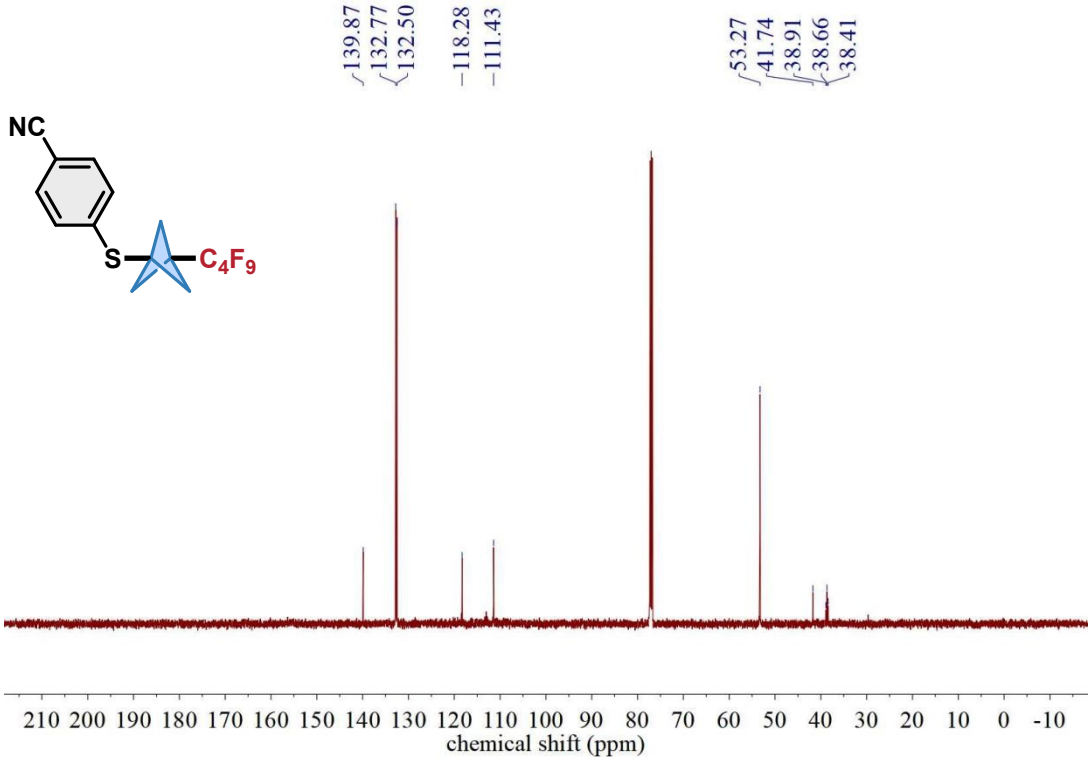
9 ^{19}F NMR (471 MHz, $CDCl_3$)



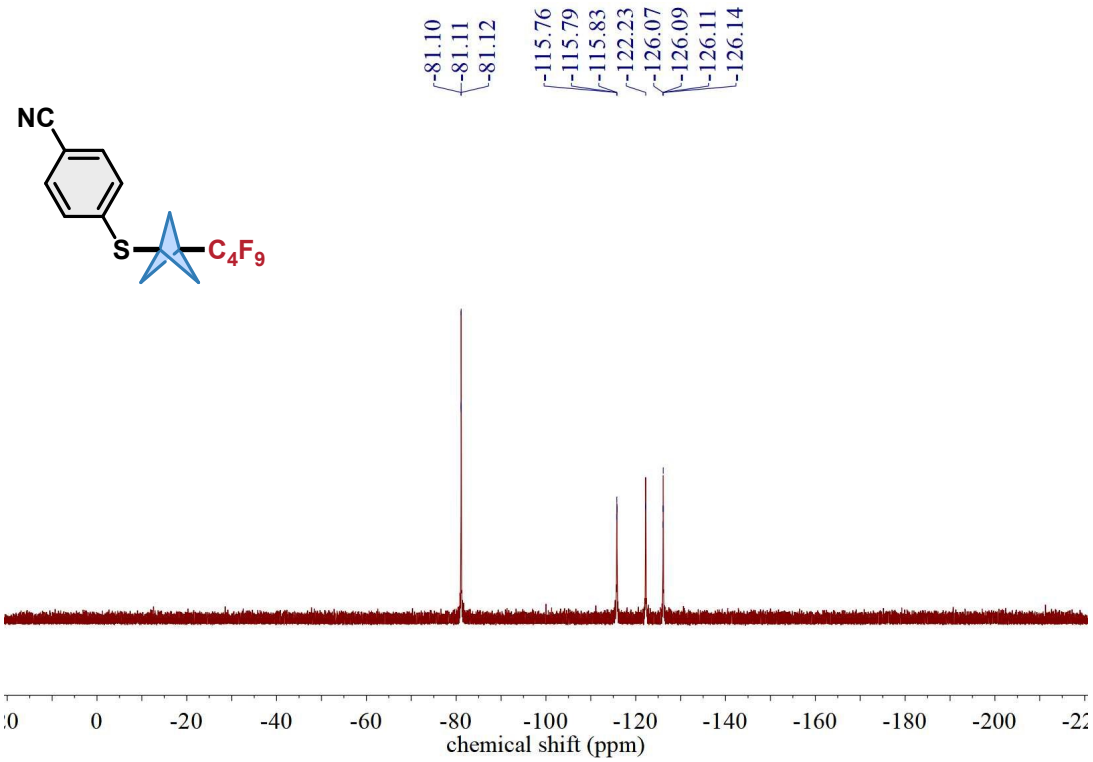
10 ^{1}H NMR (500 MHz, $CDCl_3$)



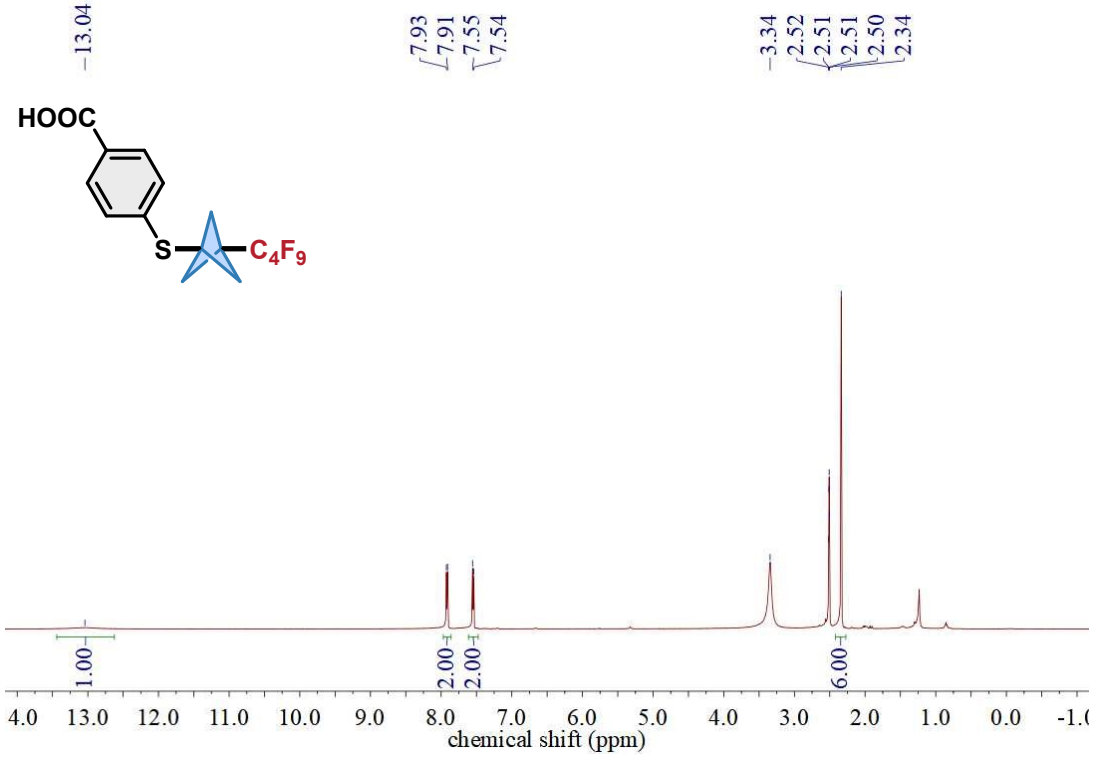
10 ^{13}C NMR (126 MHz, $CDCl_3$)



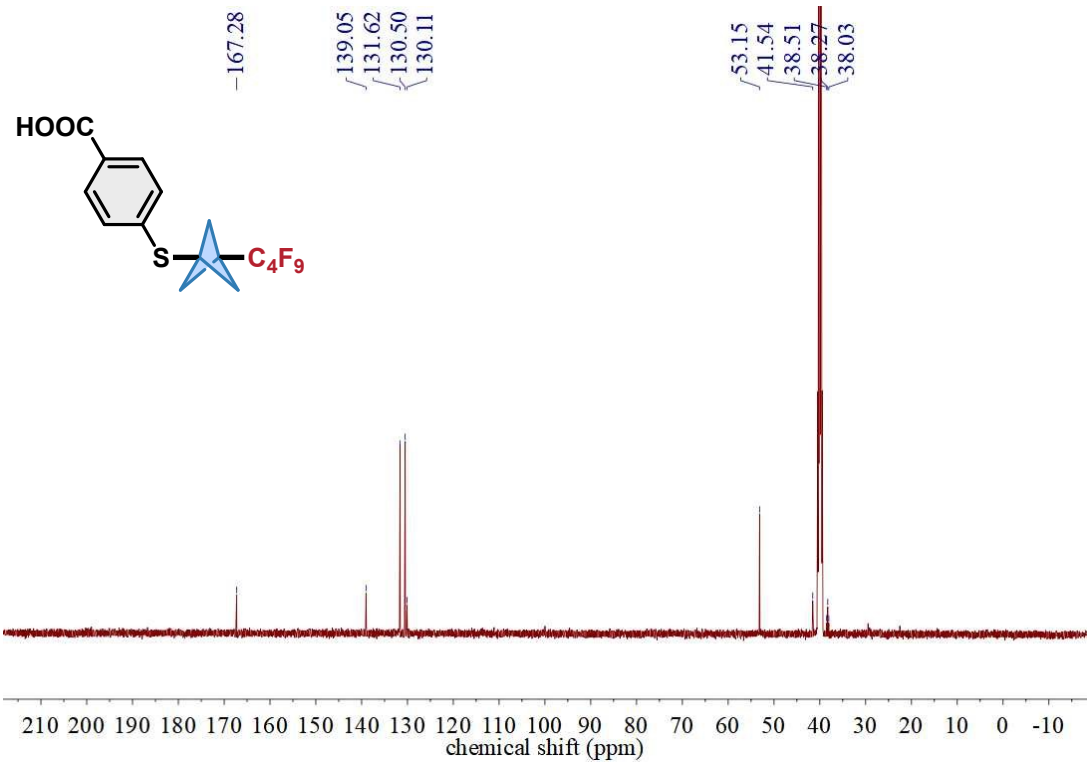
10 ^{19}F NMR (471 MHz, $CDCl_3$)



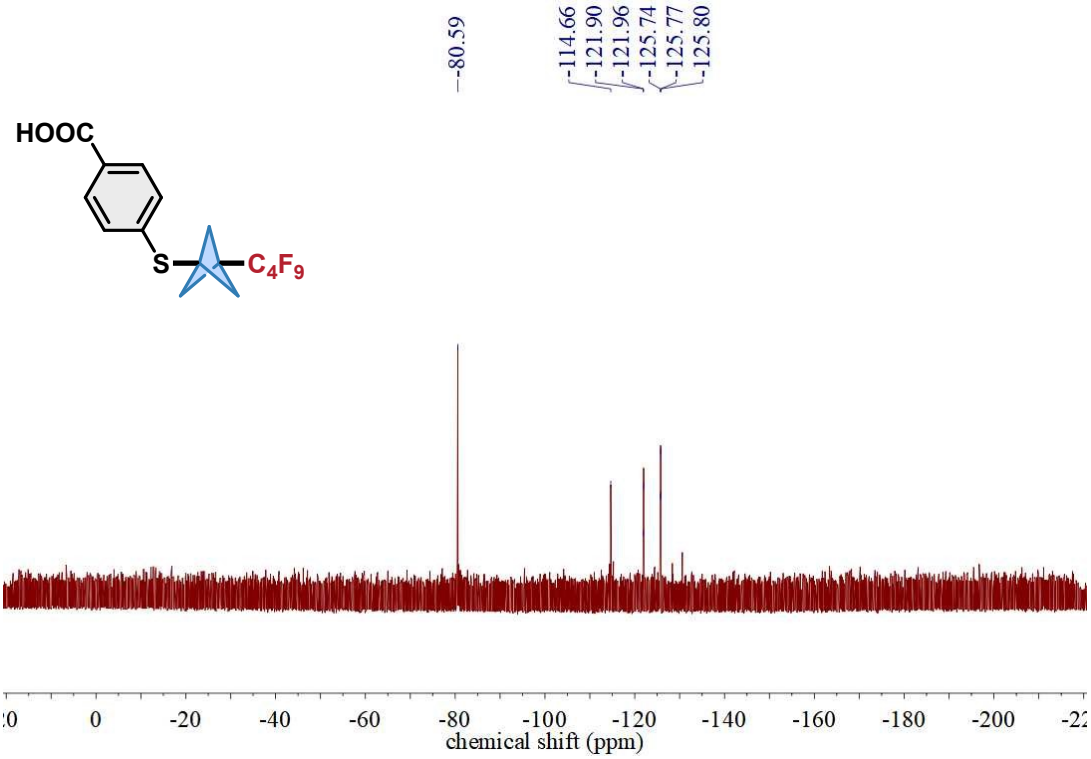
11 ^{1}H NMR (500 MHz, DMSO-d_6)



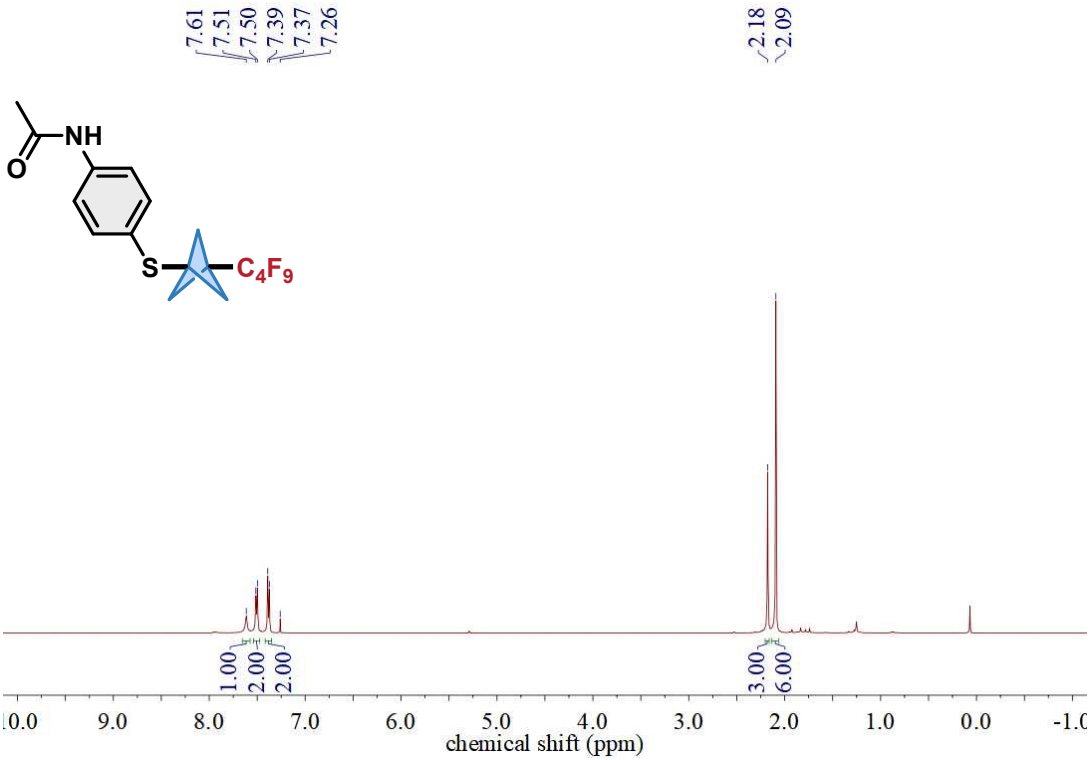
11 ^{13}C NMR (126 MHz, DMSO-d_6)



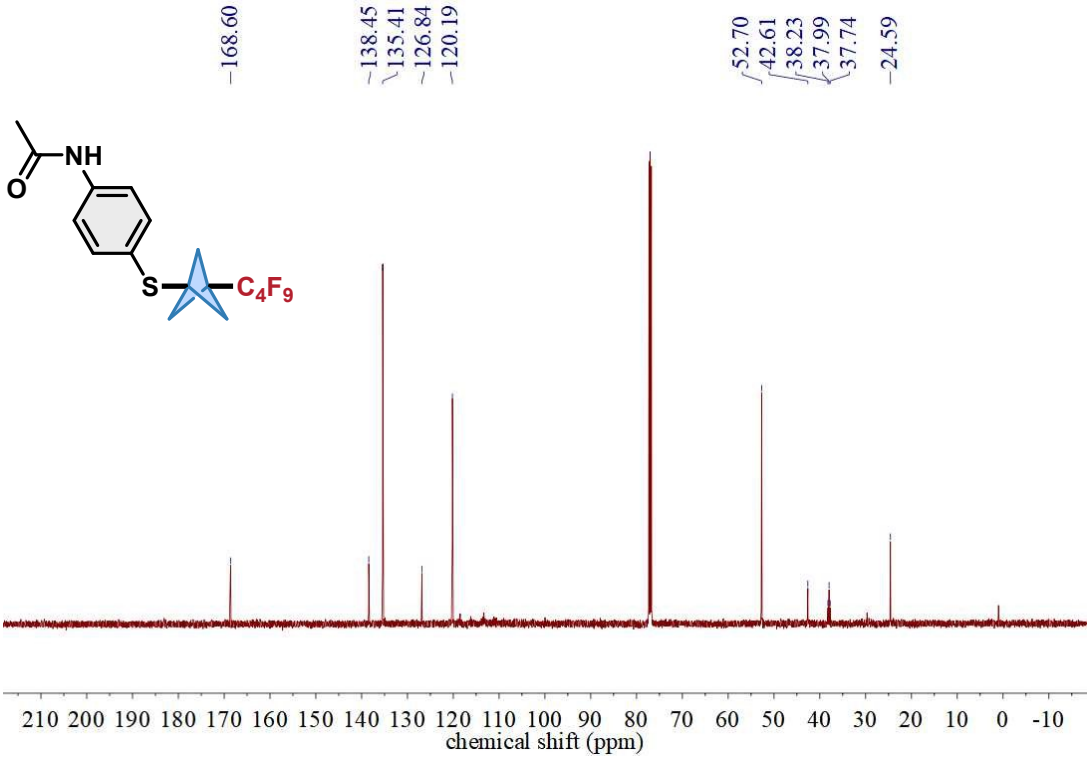
11 ^{19}F NMR (471 MHz, DMSO-d_6)



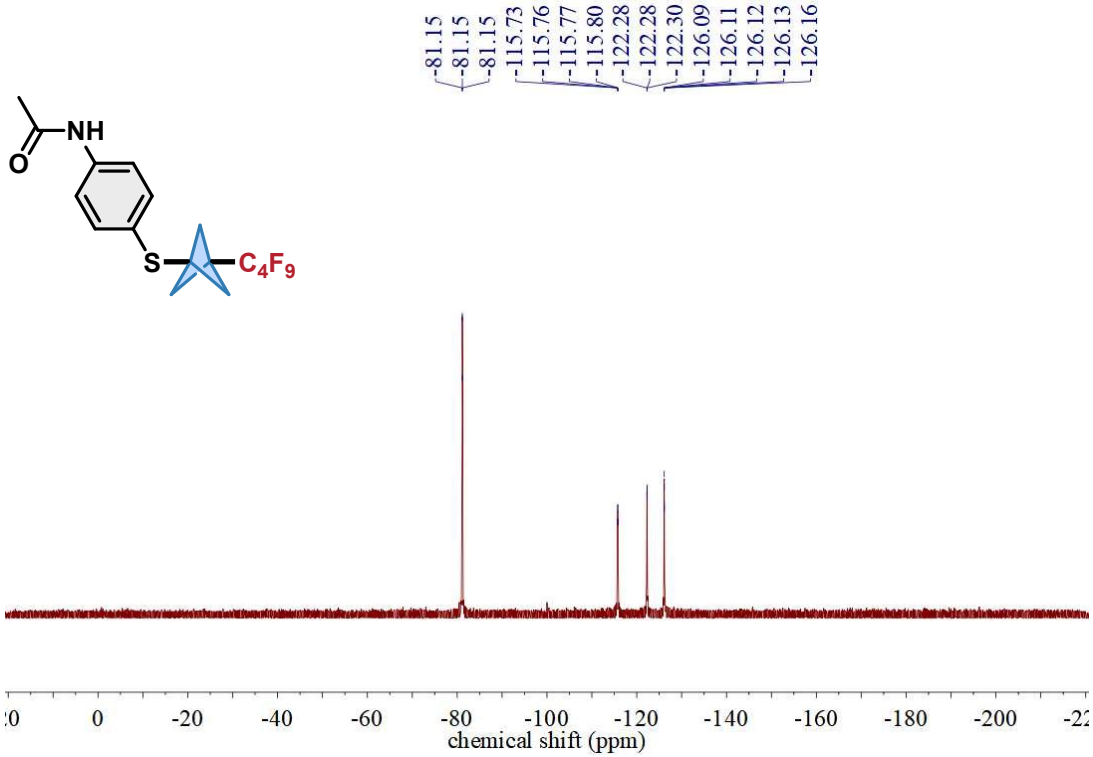
12 ^{1}H NMR (500 MHz, $CDCl_3$)



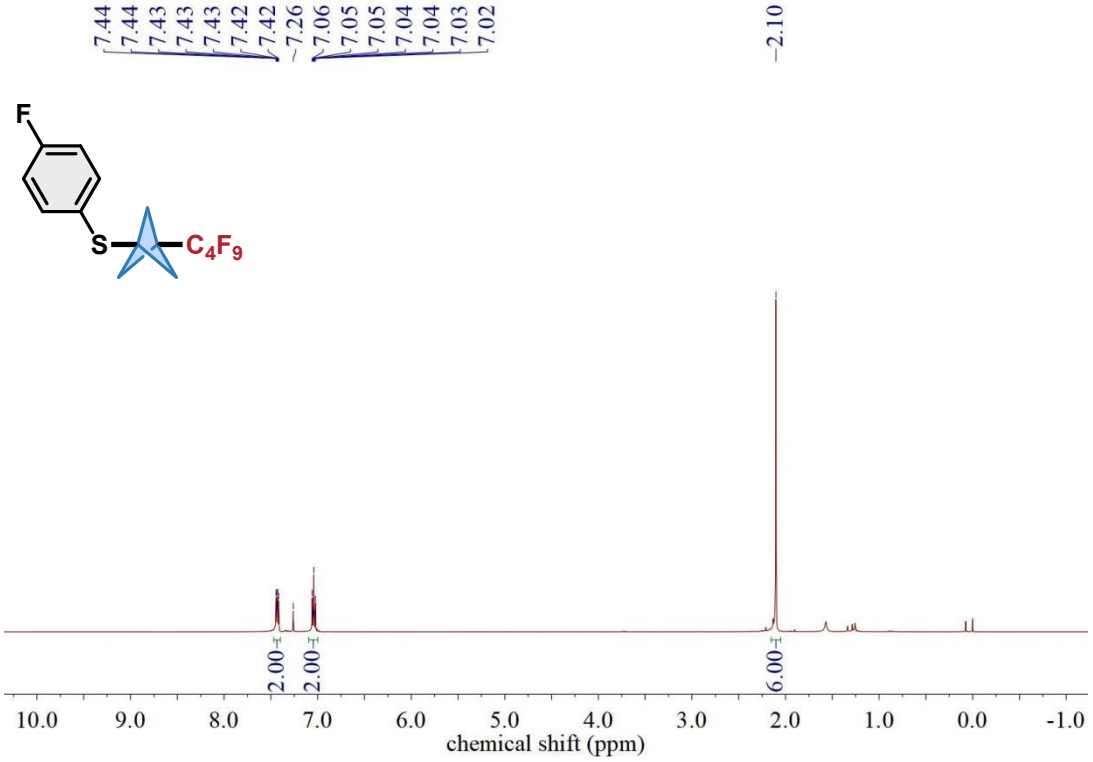
12 ^{13}C NMR (126 MHz, $CDCl_3$)



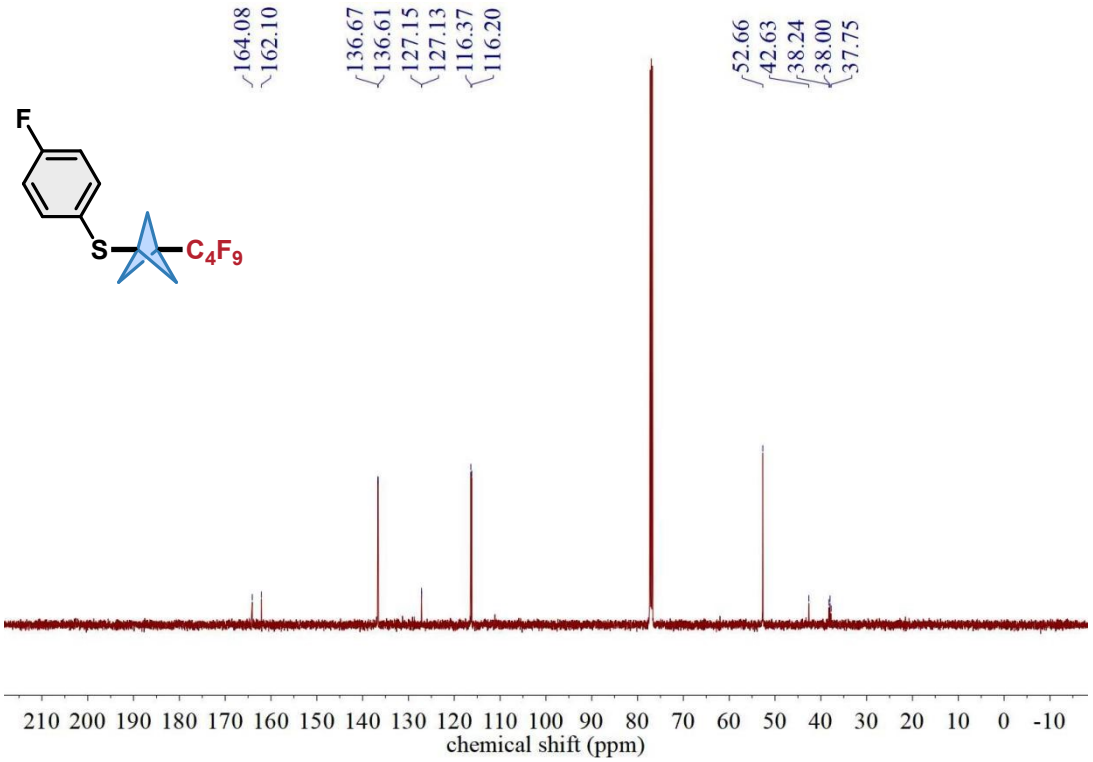
12 ^{19}F NMR (471 MHz, $CDCl_3$)



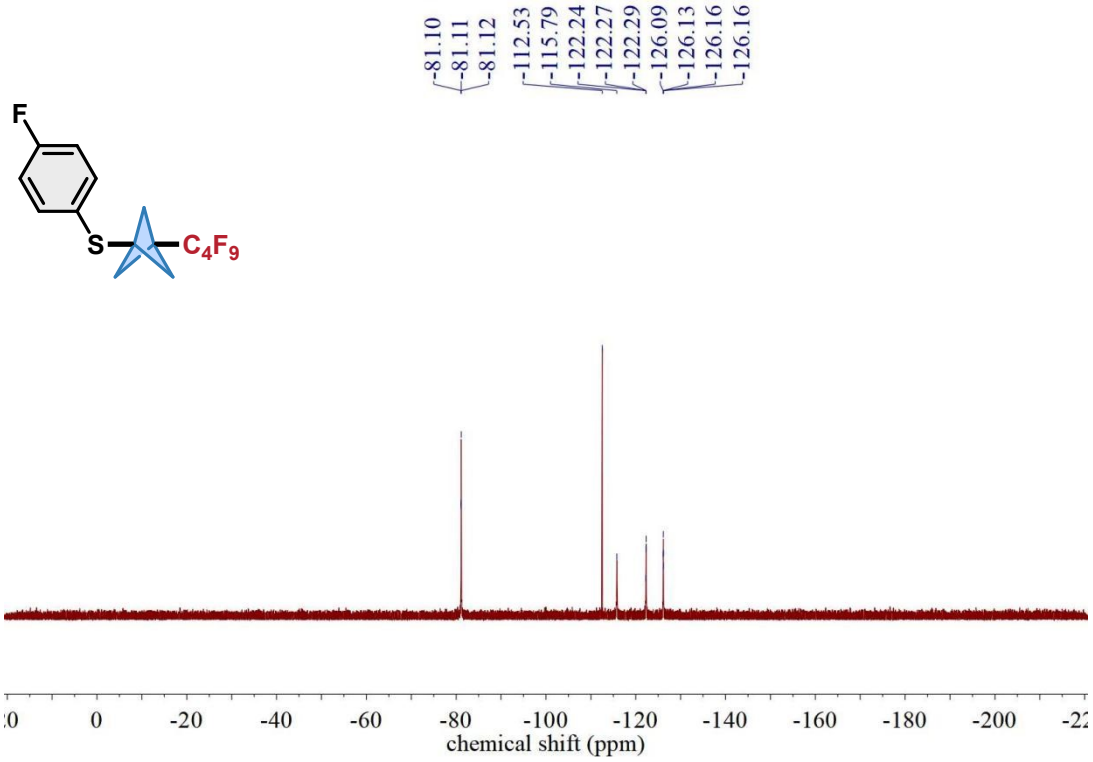
13 ^{1}H NMR (500 MHz, $CDCl_3$)



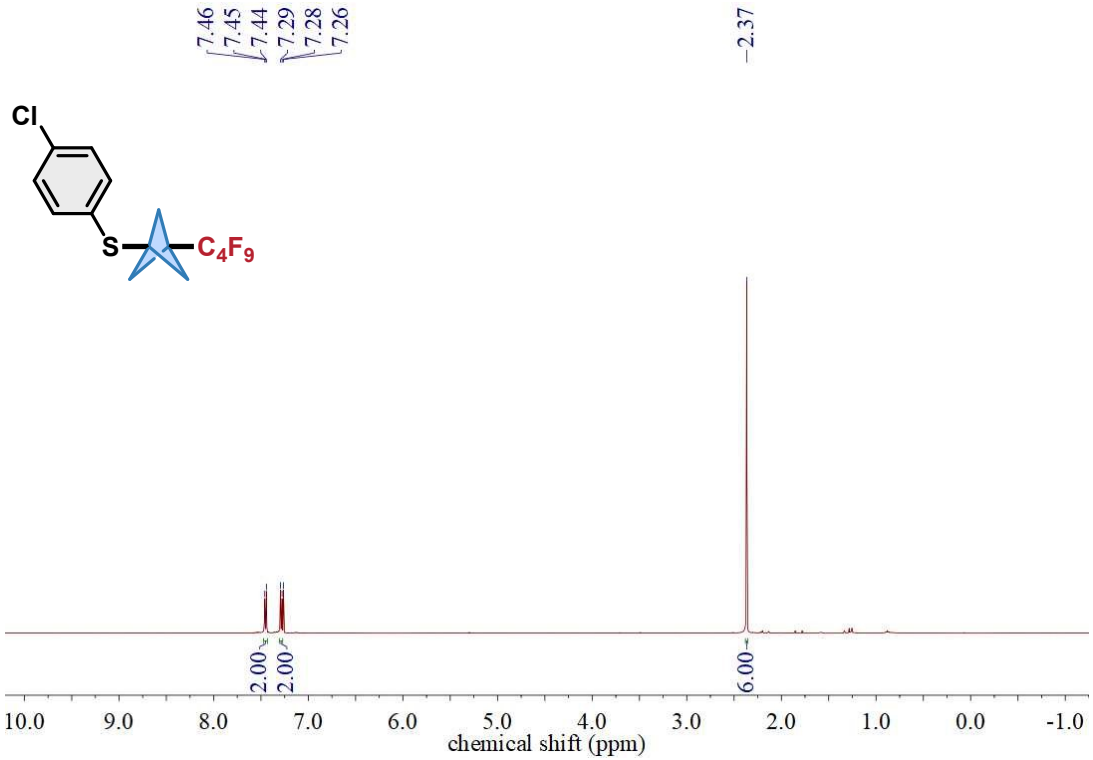
13 ^{13}C NMR (126 MHz, $CDCl_3$)



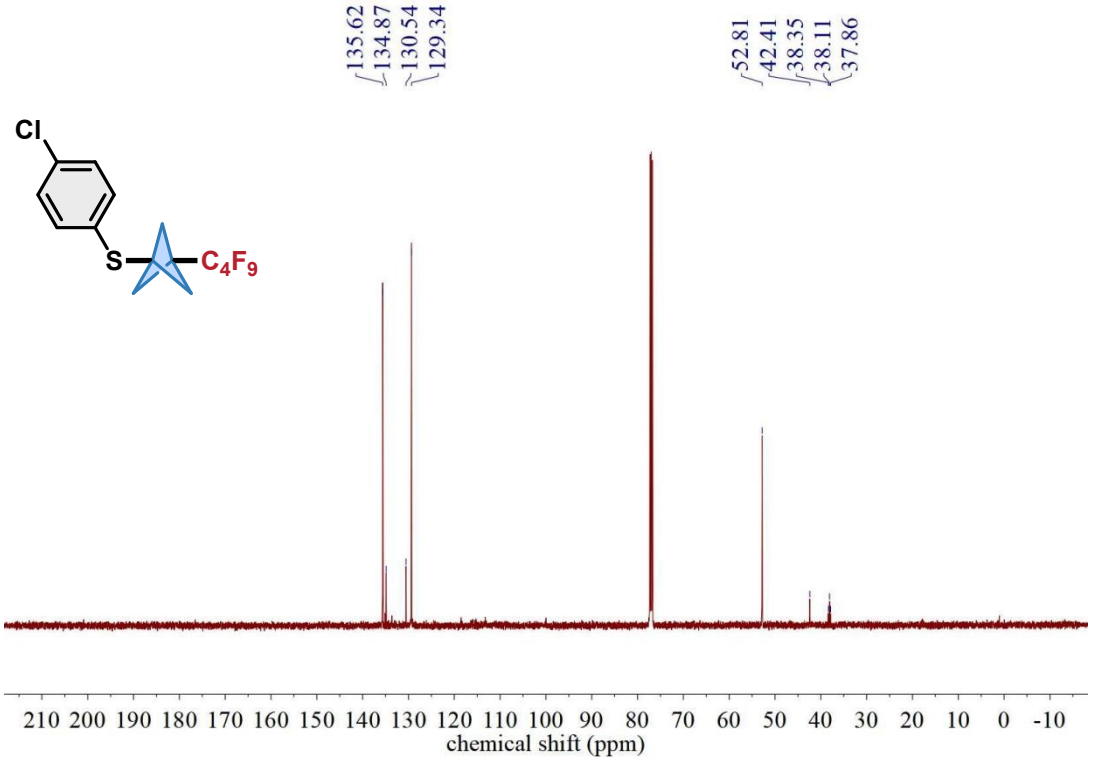
13 ^{19}F NMR (471 MHz, $CDCl_3$)



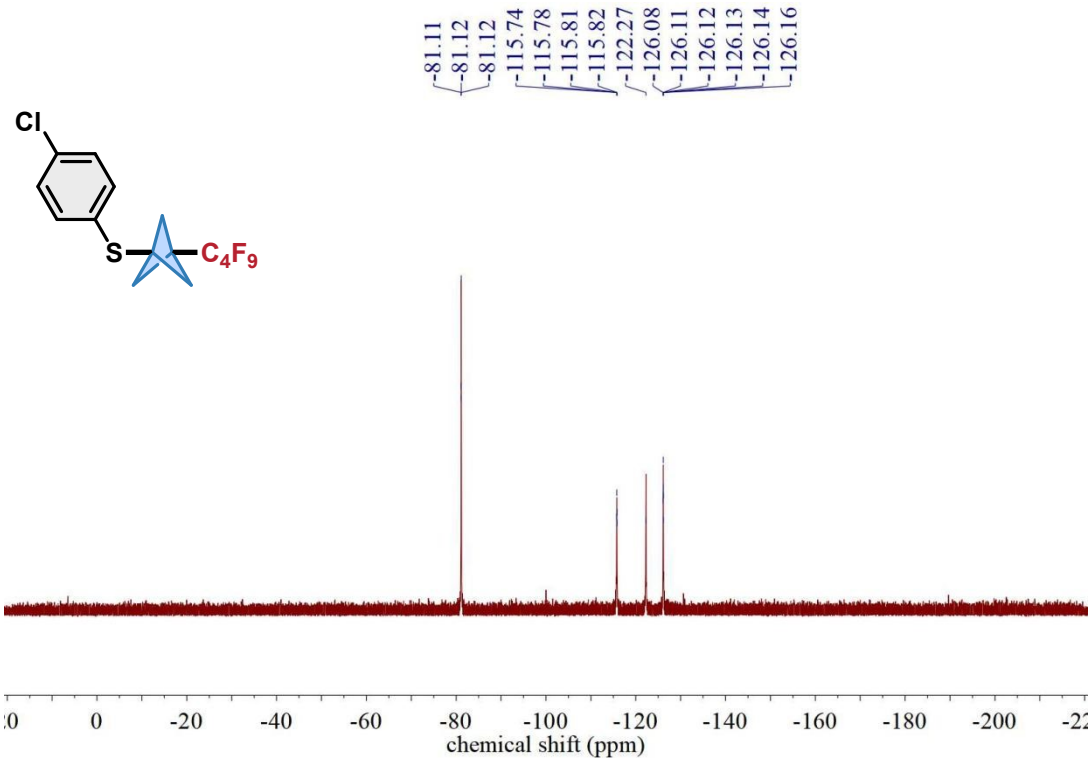
14 ^{1}H NMR (500 MHz, $CDCl_3$)



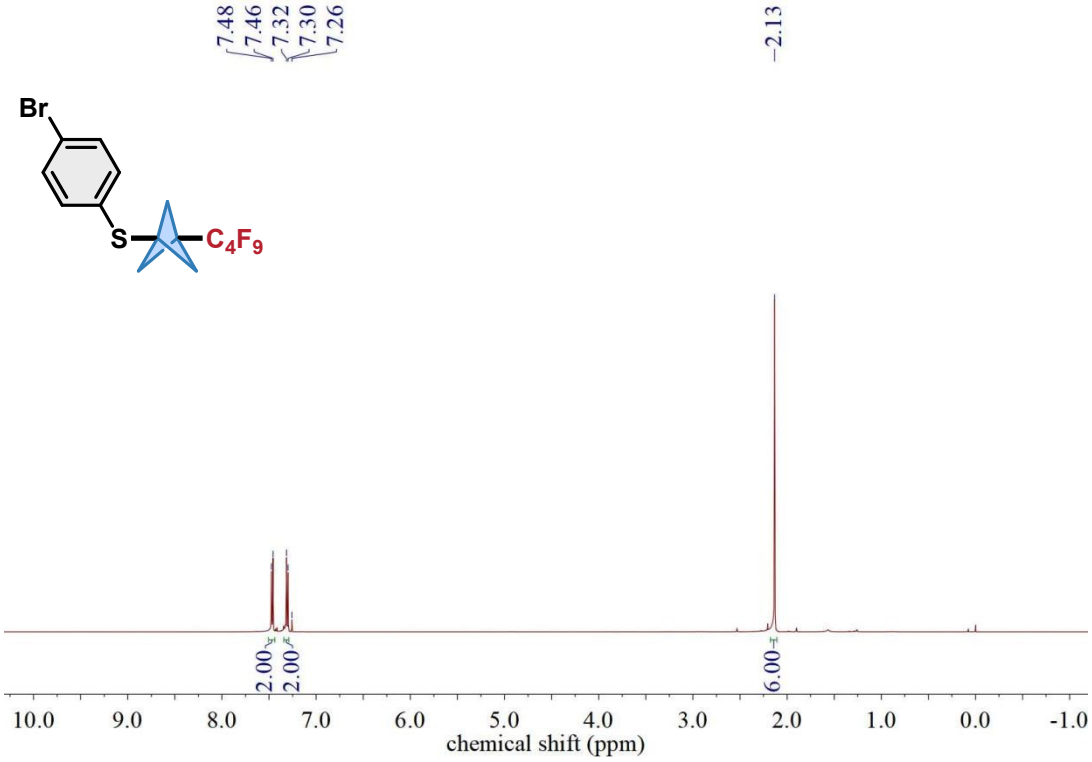
14 ^{13}C NMR (126 MHz, $CDCl_3$)



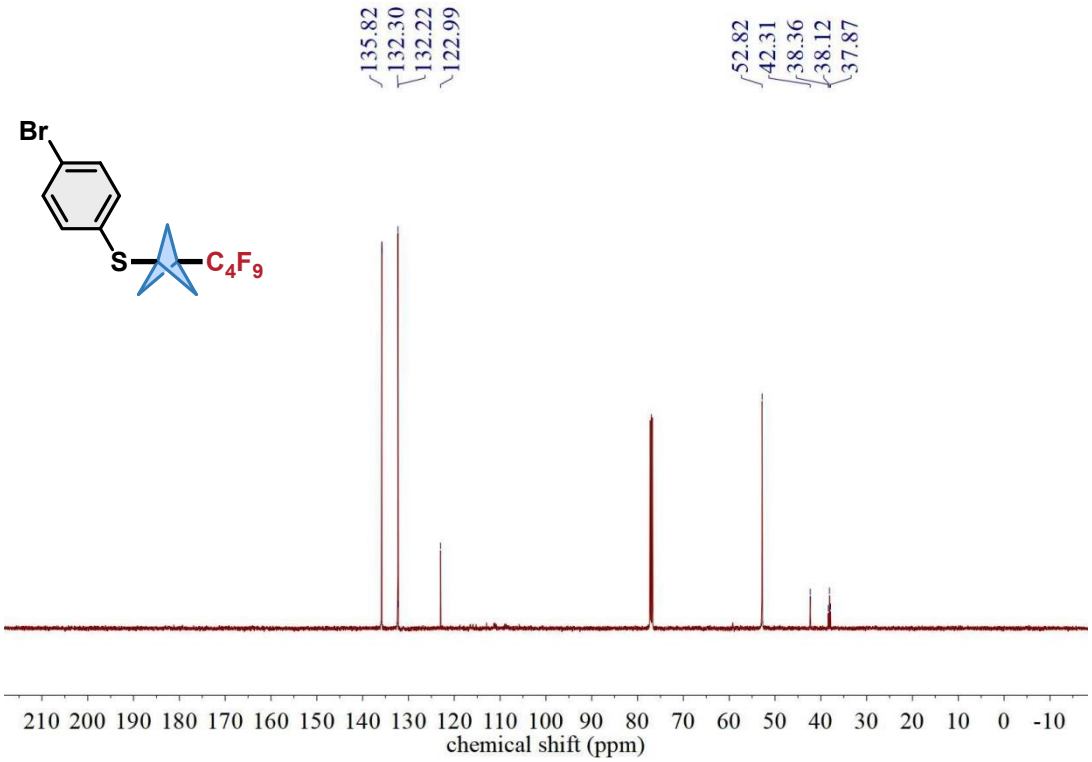
14 ^{19}F NMR (471 MHz, $CDCl_3$)



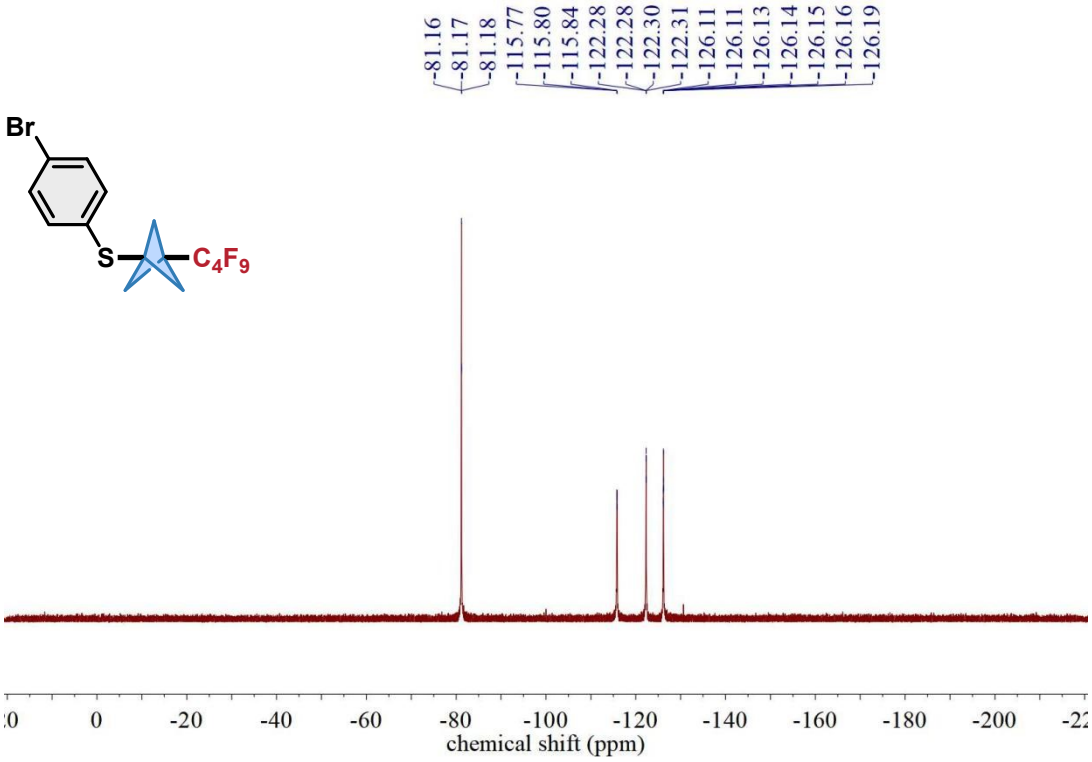
15 ^{1}H NMR (500 MHz, $CDCl_3$)



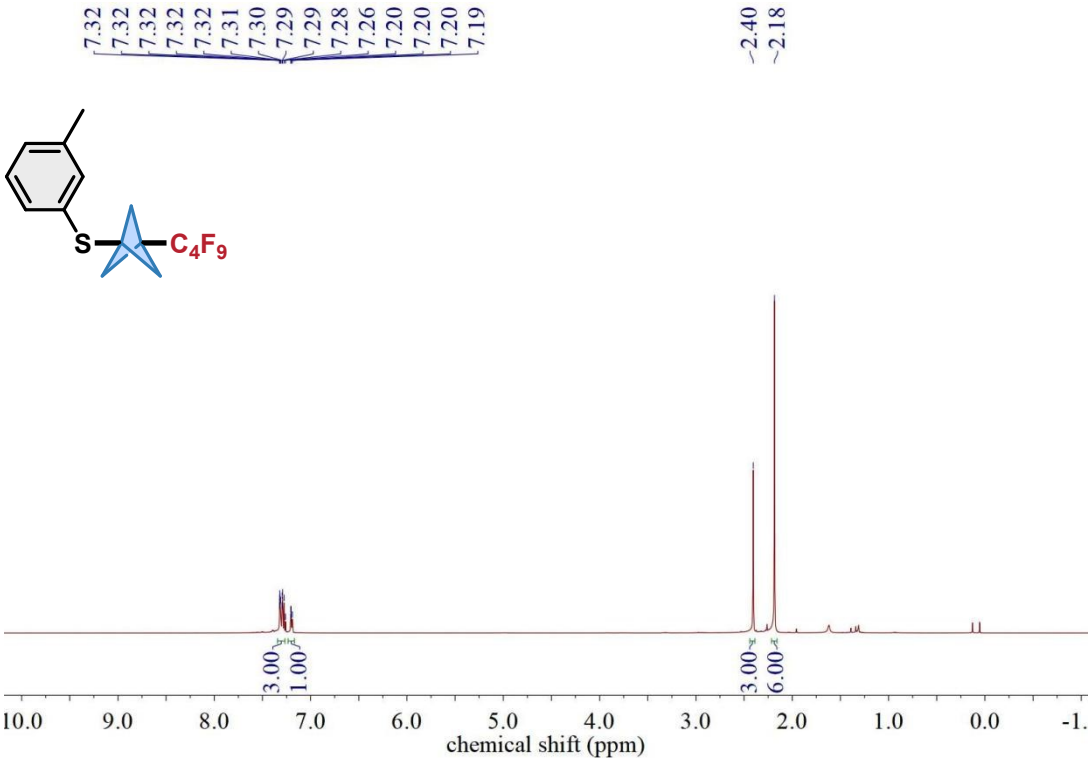
15 ^{13}C NMR (126 MHz, $CDCl_3$)



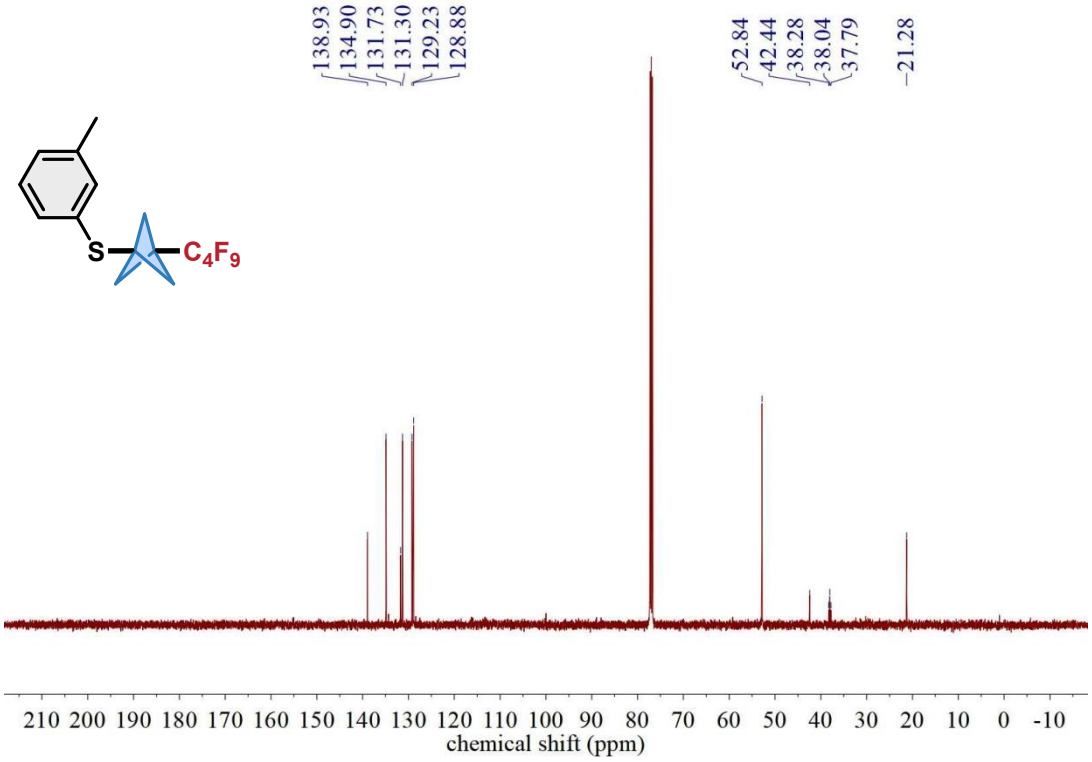
15 ^{19}F NMR (471 MHz, $CDCl_3$)



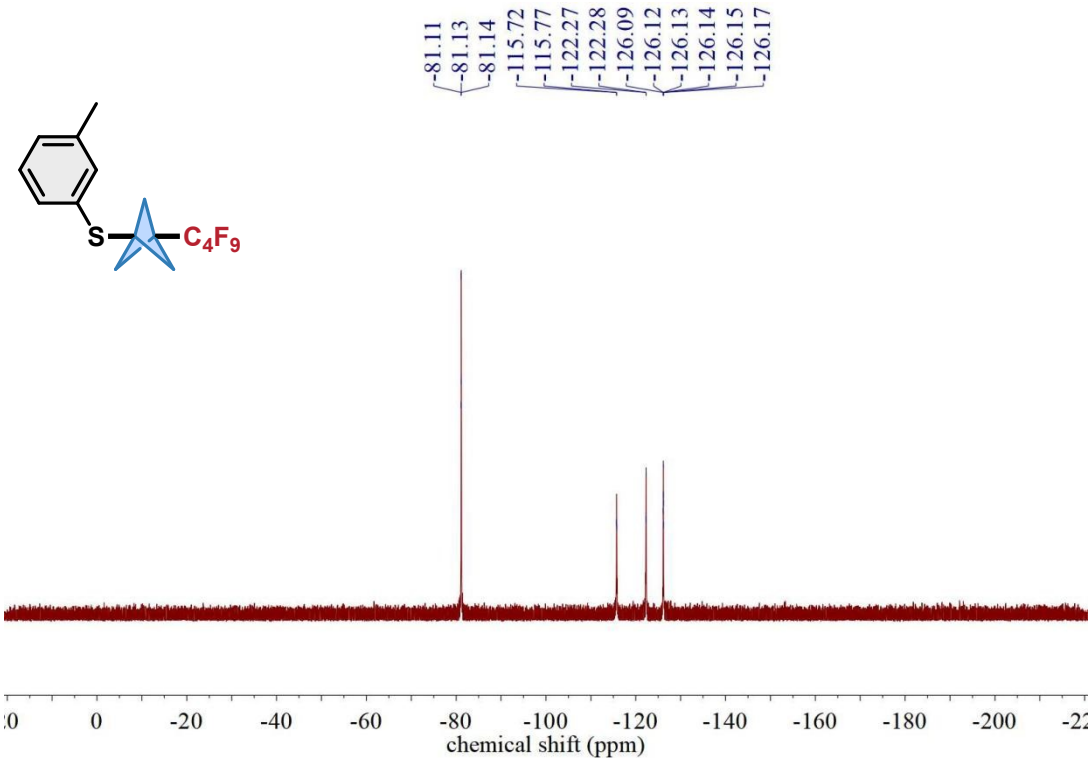
16 ^{1}H NMR (500 MHz, $CDCl_3$)



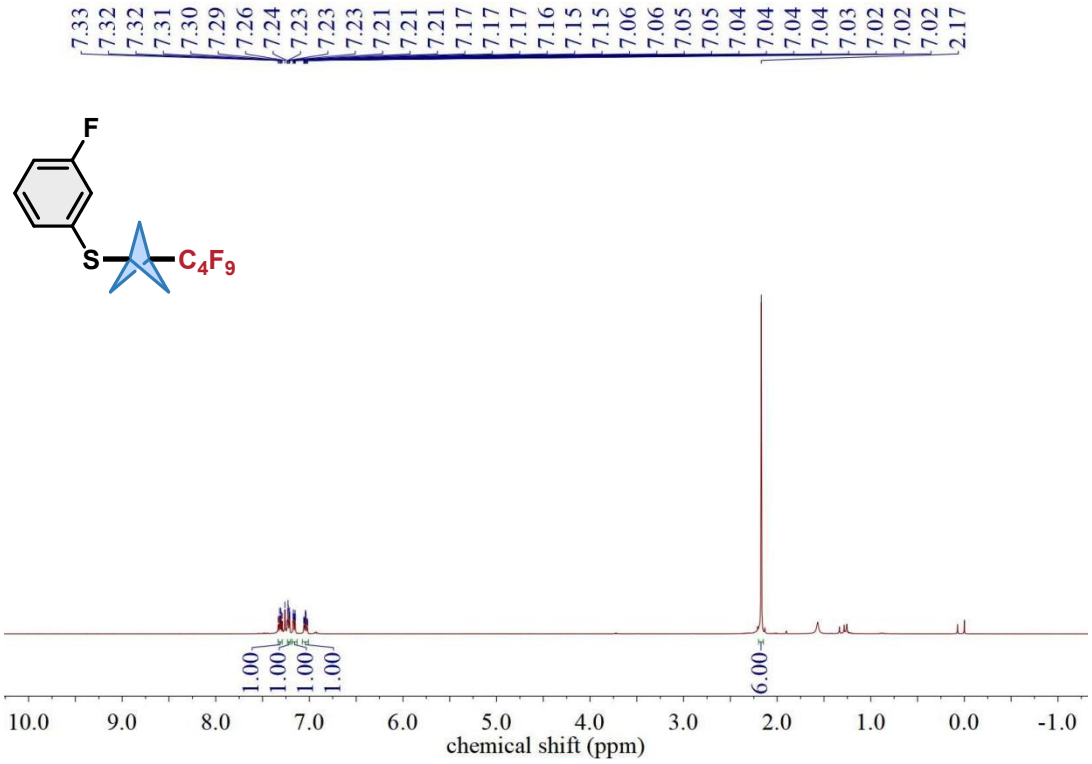
16 ^{13}C NMR (126 MHz, $CDCl_3$)



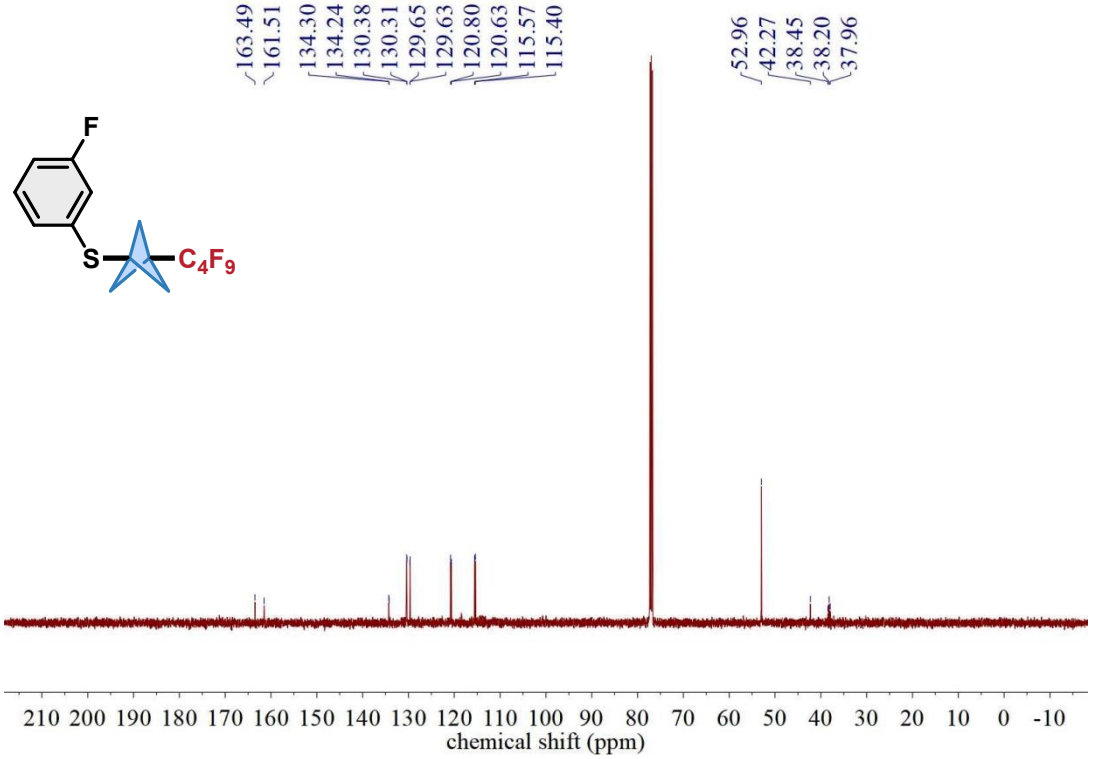
16 ^{19}F NMR (471 MHz, $CDCl_3$)



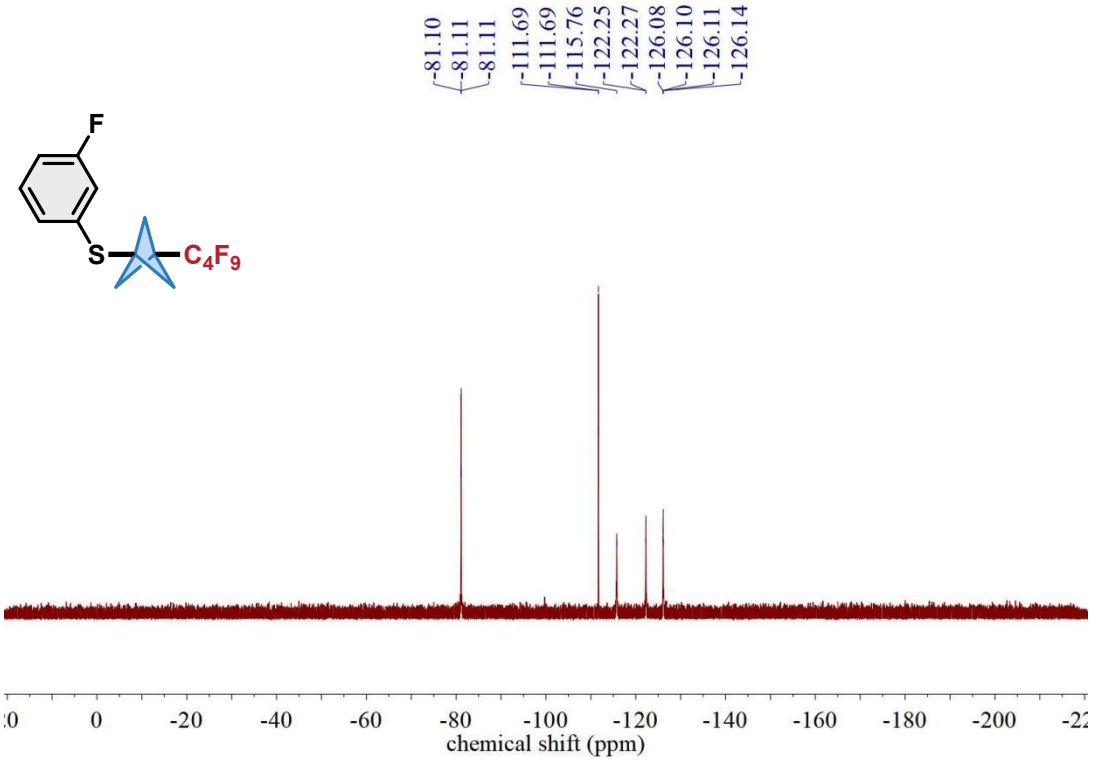
17 ^{1}H NMR (500 MHz, $CDCl_3$)



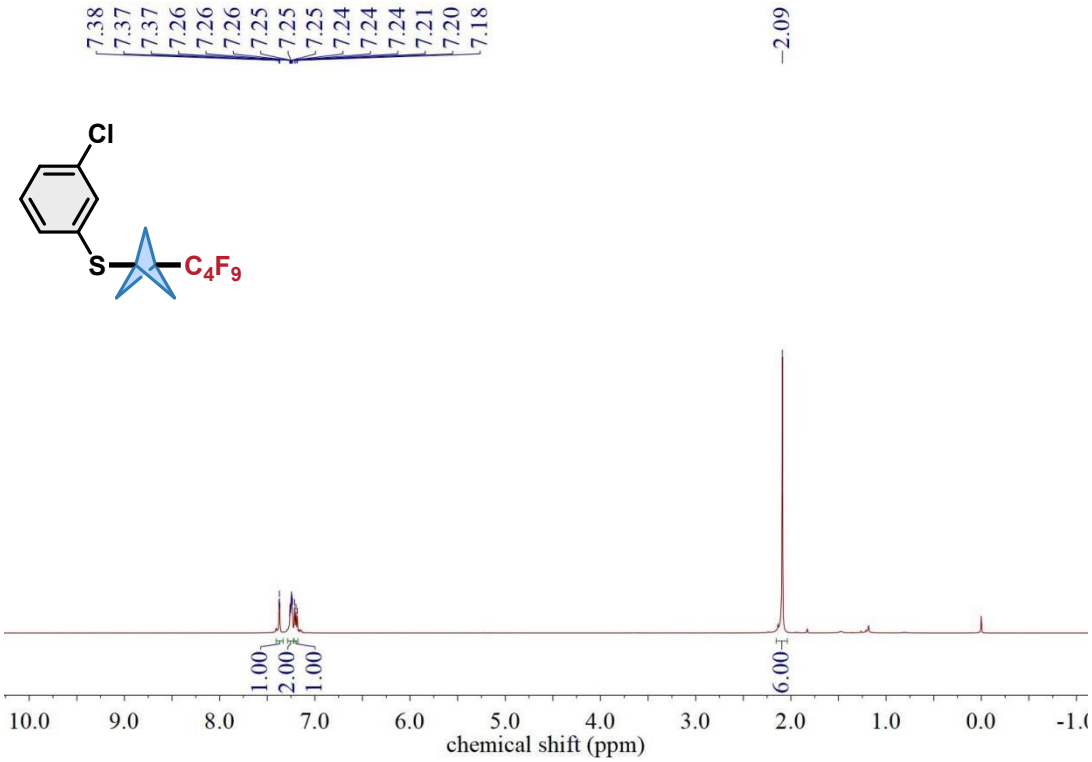
17 ^{13}C NMR (126 MHz, $CDCl_3$)



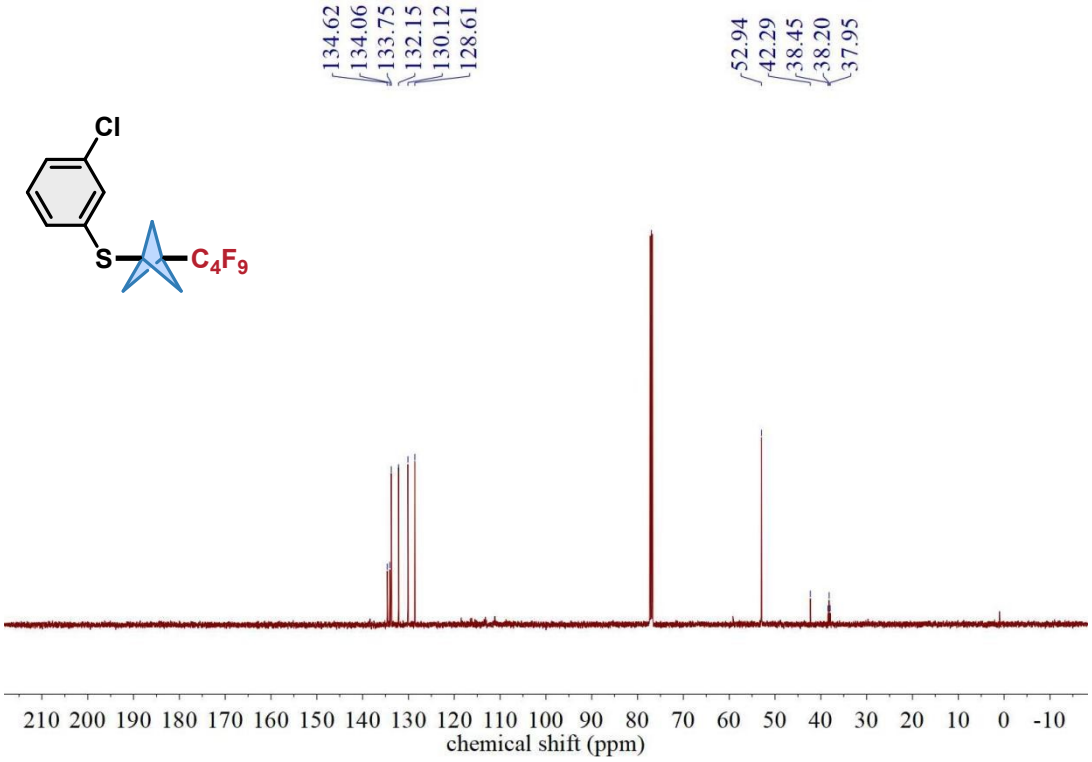
17 ^{19}F NMR (471 MHz, $CDCl_3$)



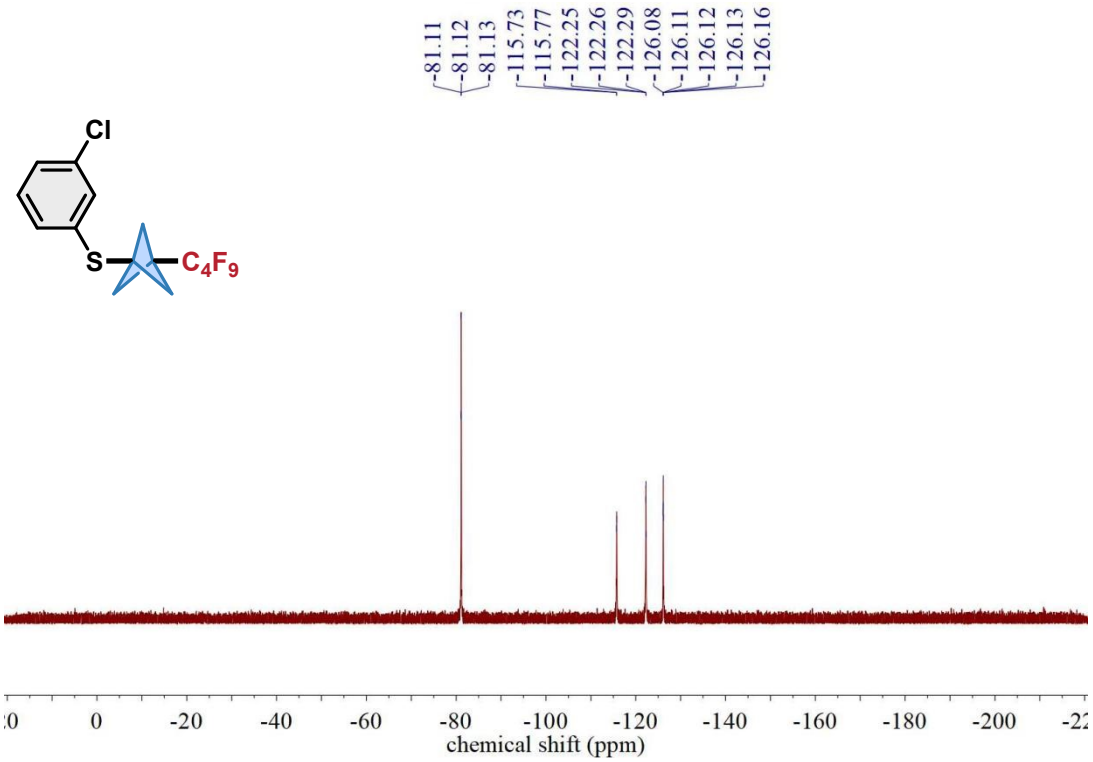
18 ^{1}H NMR (500 MHz, $CDCl_3$)



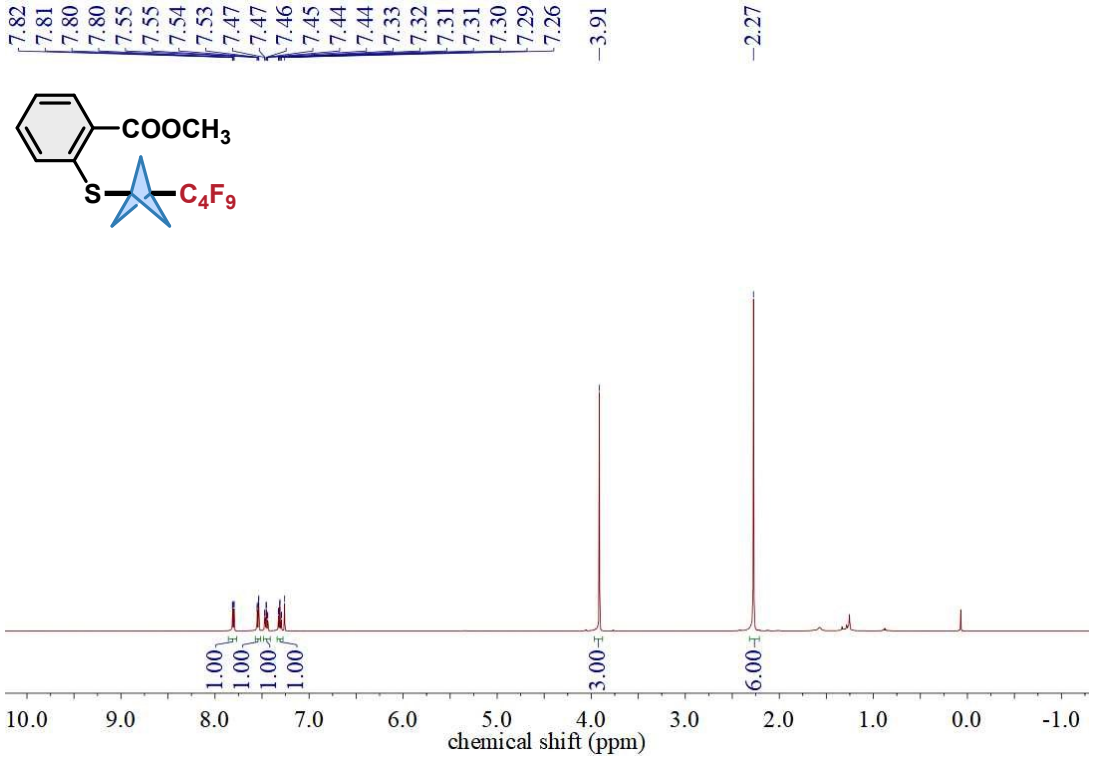
18 ^{13}C NMR (126 MHz, $CDCl_3$)



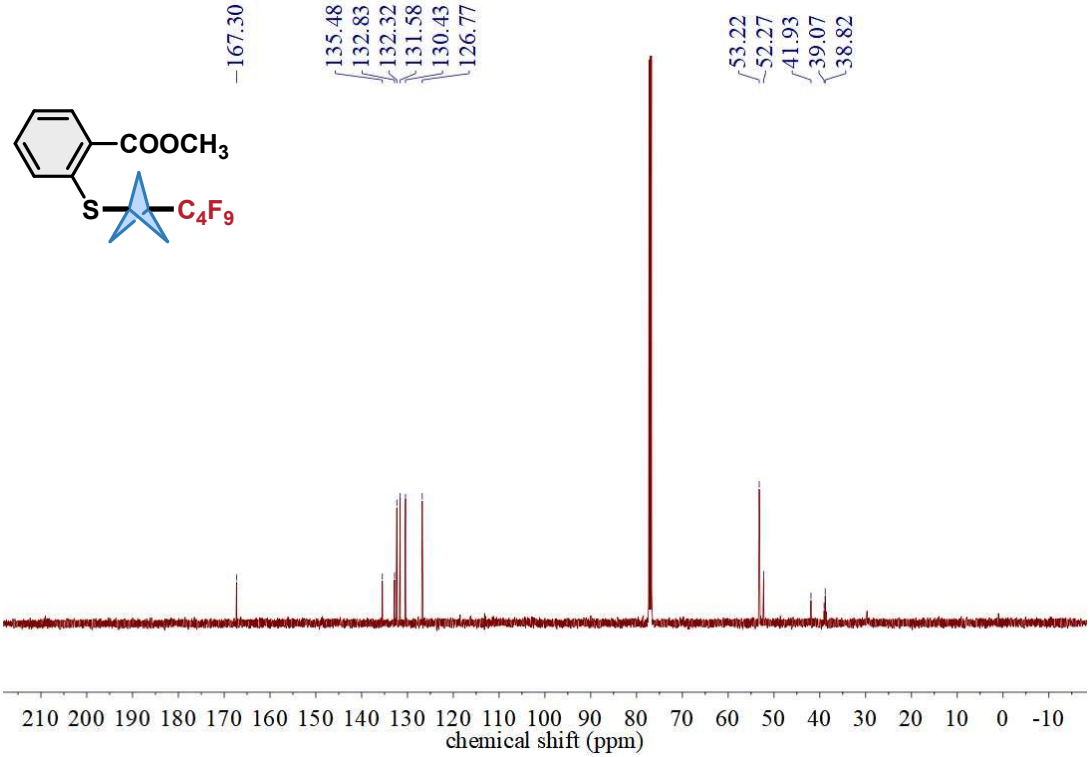
18 ^{19}F NMR (471 MHz, $CDCl_3$)



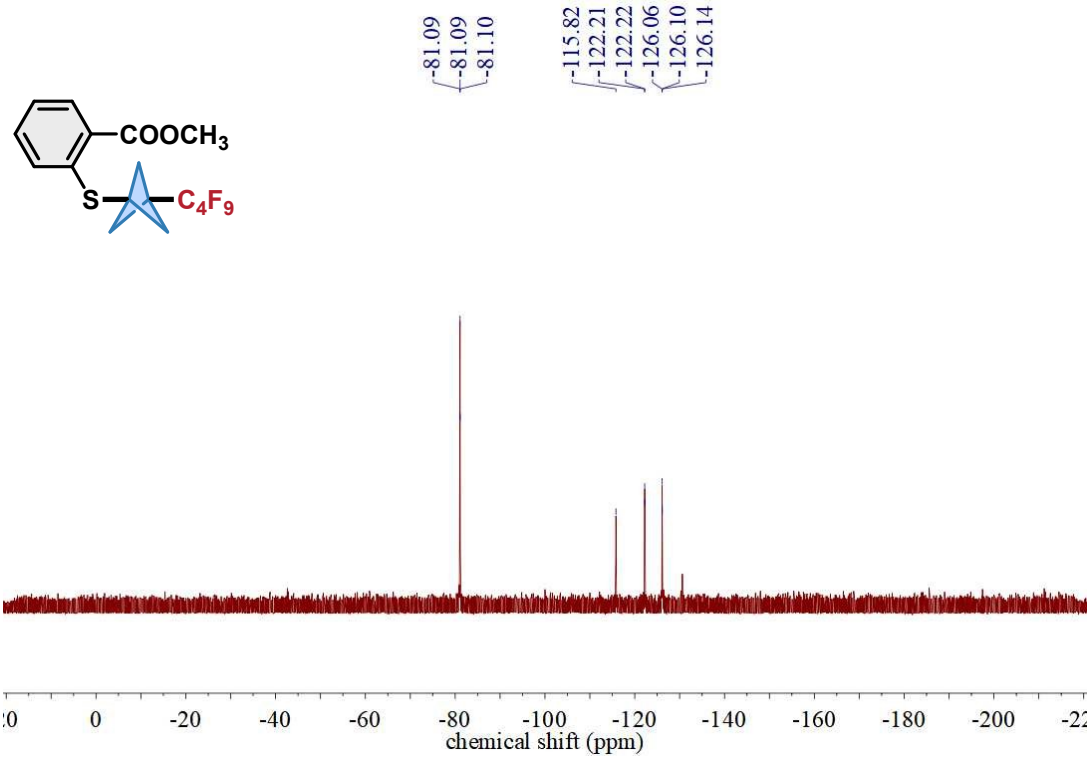
19 ^{1}H NMR (500 MHz, $CDCl_3$)



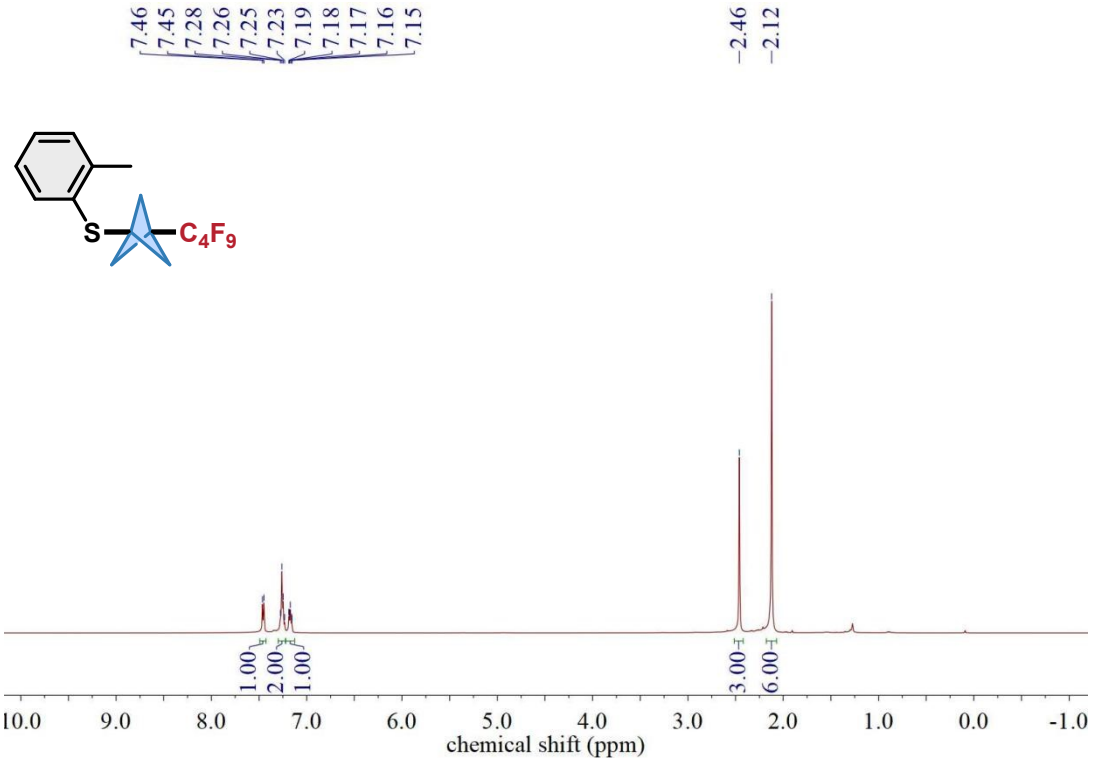
19 ^{13}C NMR (126 MHz, $CDCl_3$)



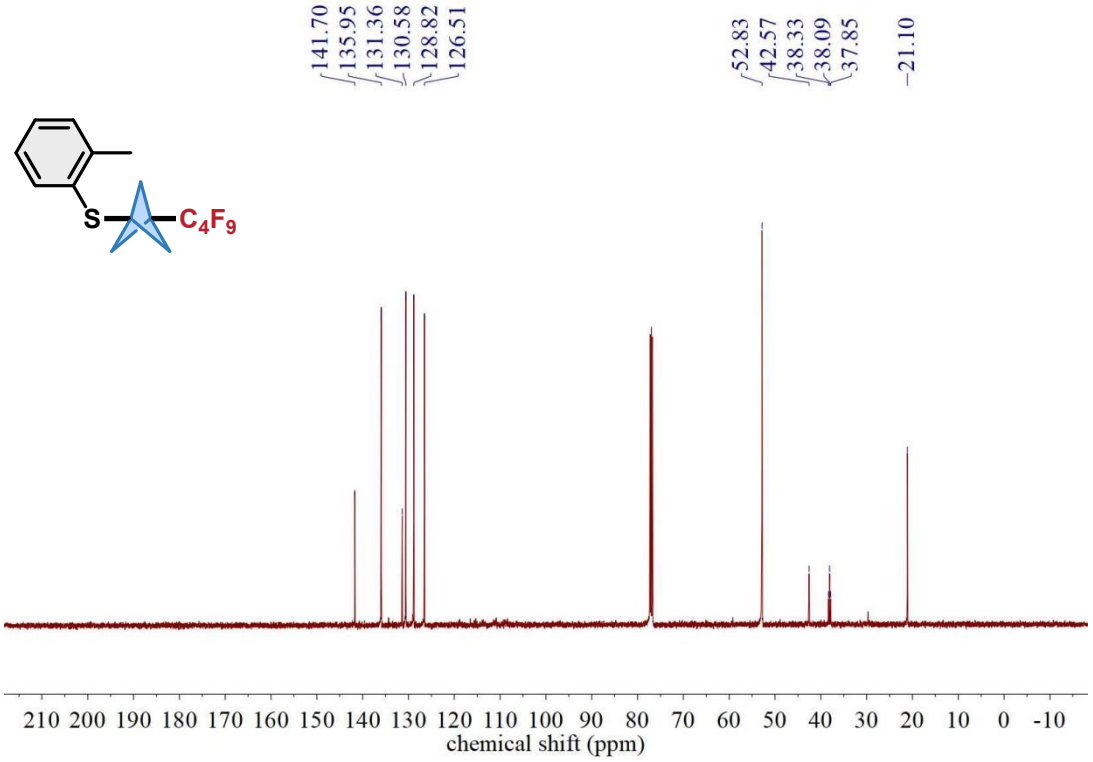
19 ^{19}F NMR (471 MHz, $CDCl_3$)



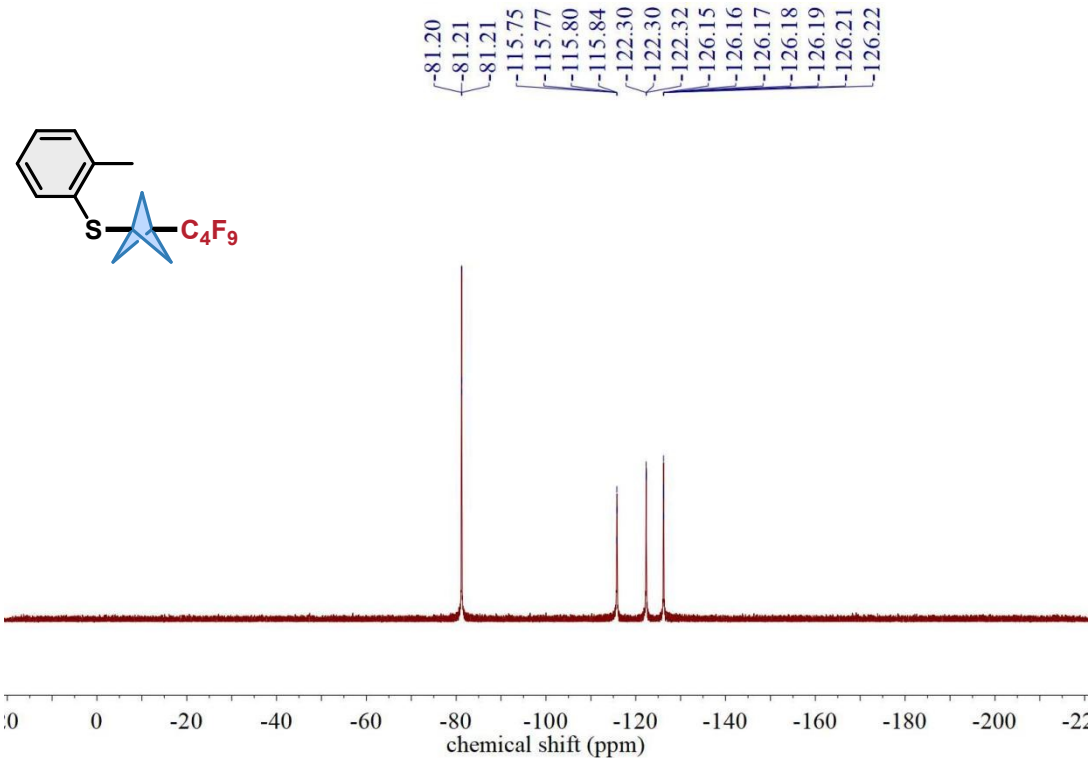
20 ^{1}H NMR (500 MHz, $CDCl_3$)



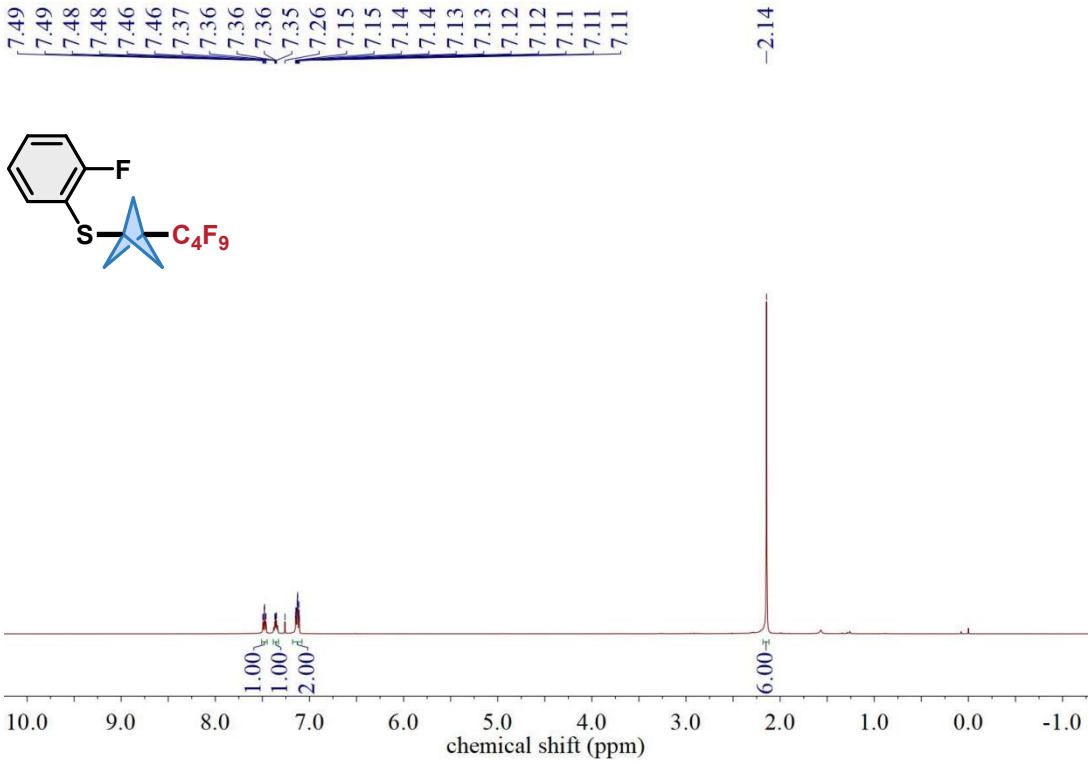
20 ^{13}C NMR (126 MHz, $CDCl_3$)



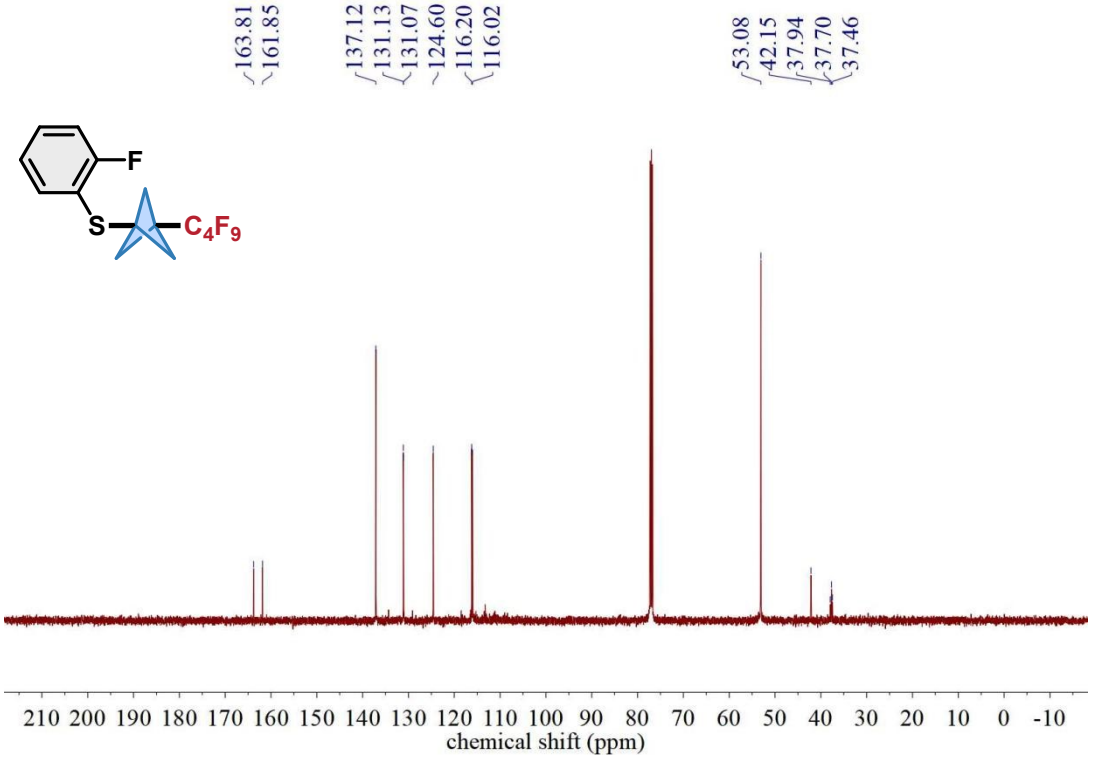
20 ^{19}F NMR (471 MHz, $CDCl_3$)



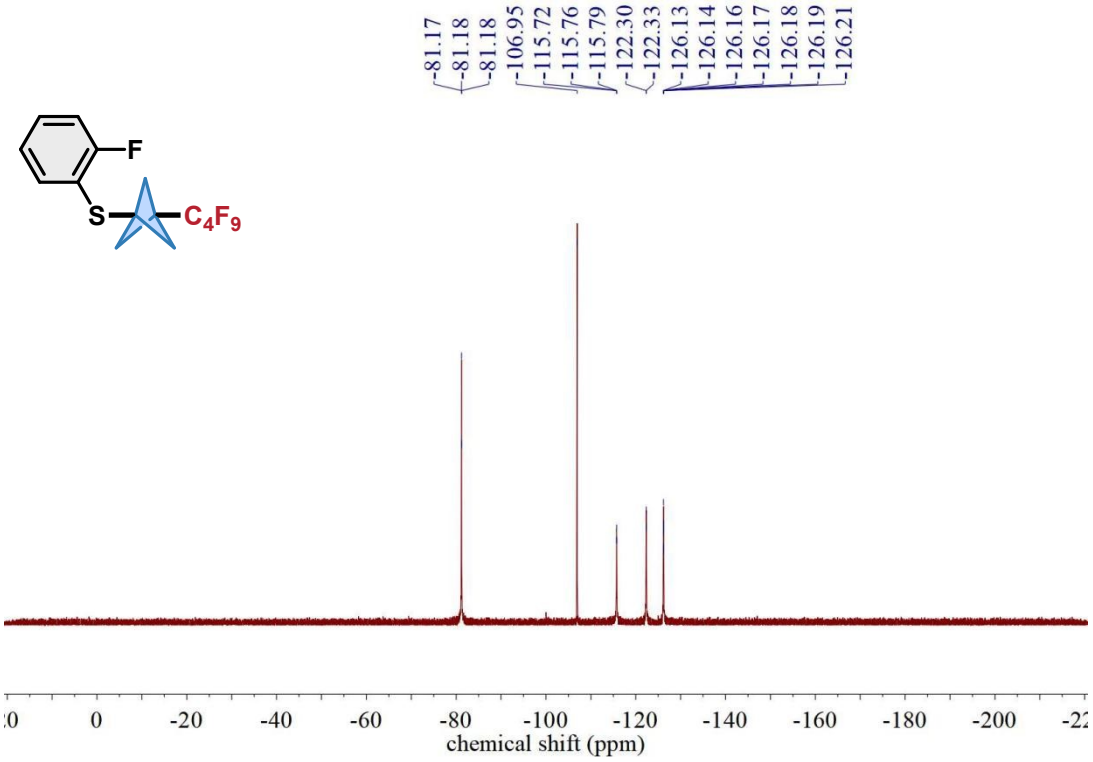
21 ^{1}H NMR (500 MHz, $CDCl_3$)



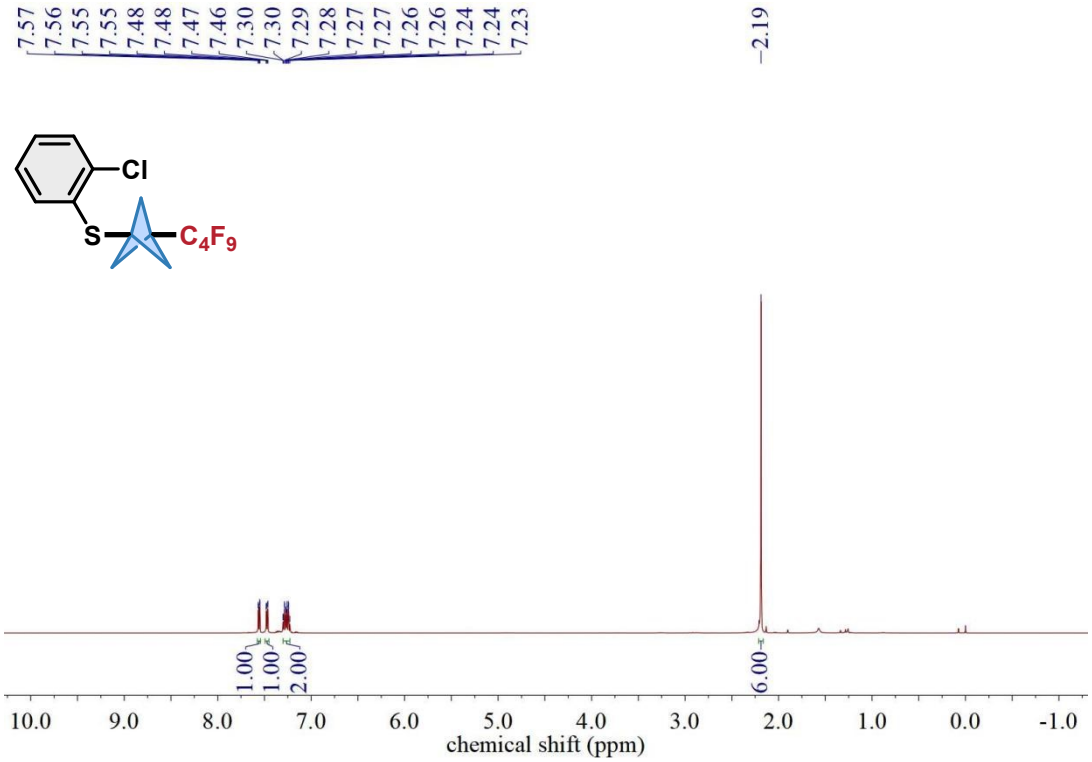
21 ^{13}C NMR (126 MHz, $CDCl_3$)



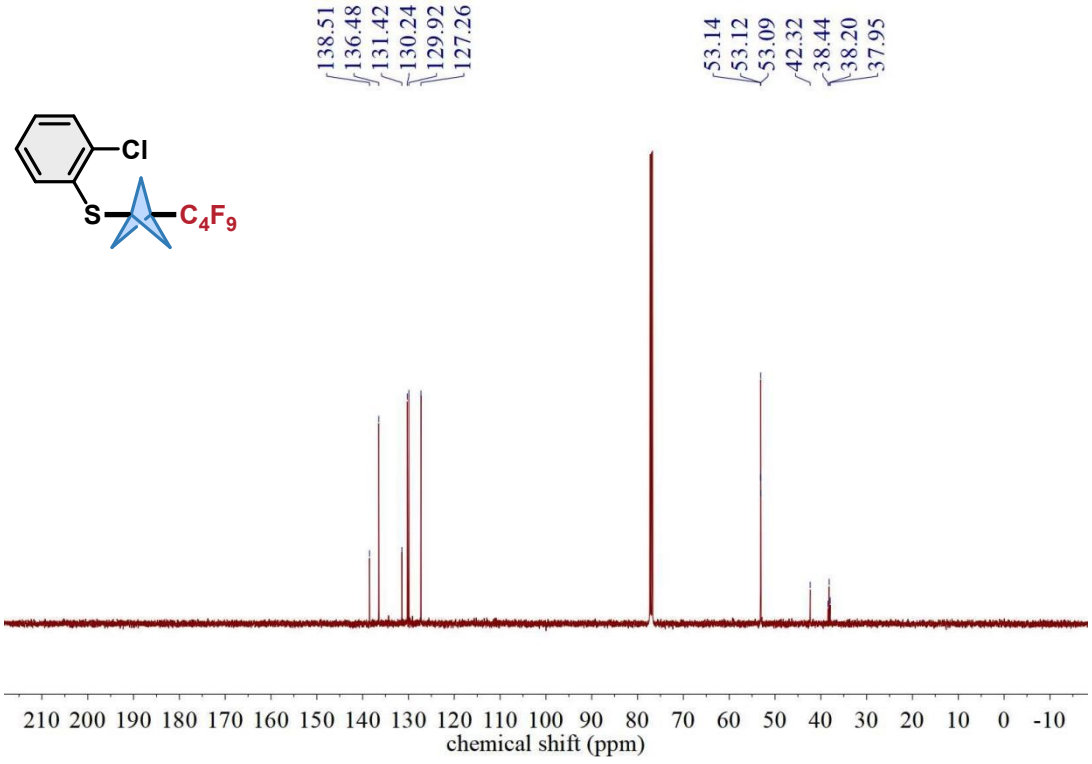
21 ^{19}F NMR (471 MHz, $CDCl_3$)



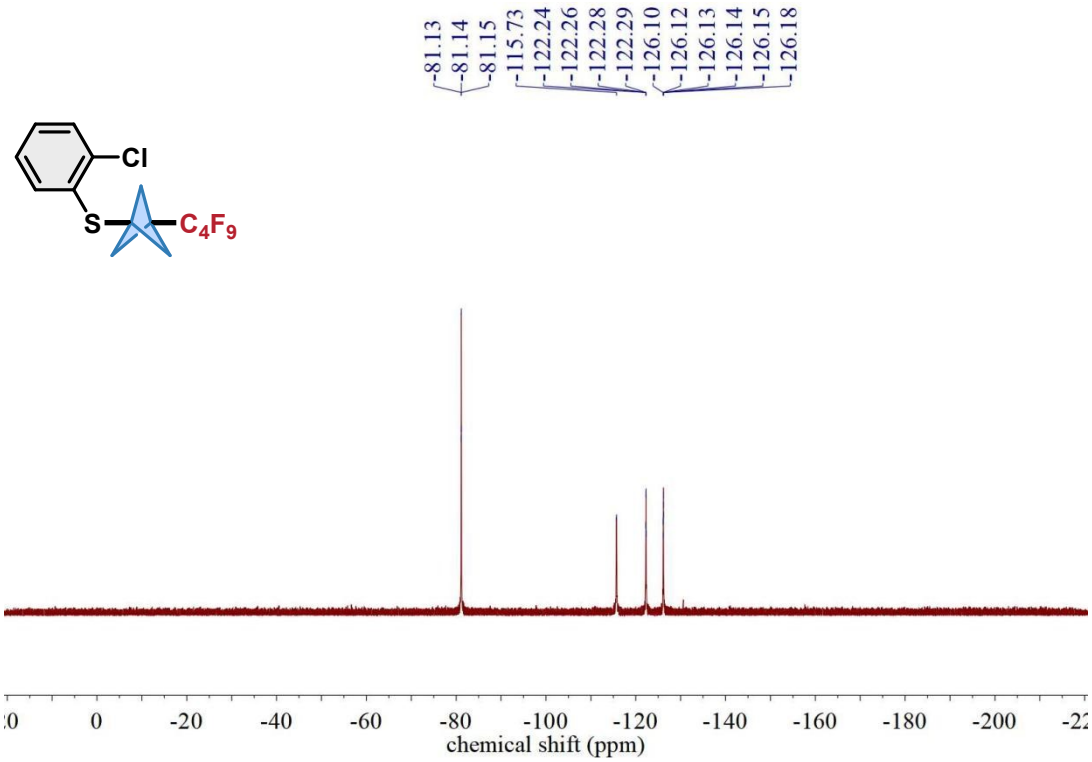
22 ^{1}H NMR (500 MHz, $CDCl_3$)



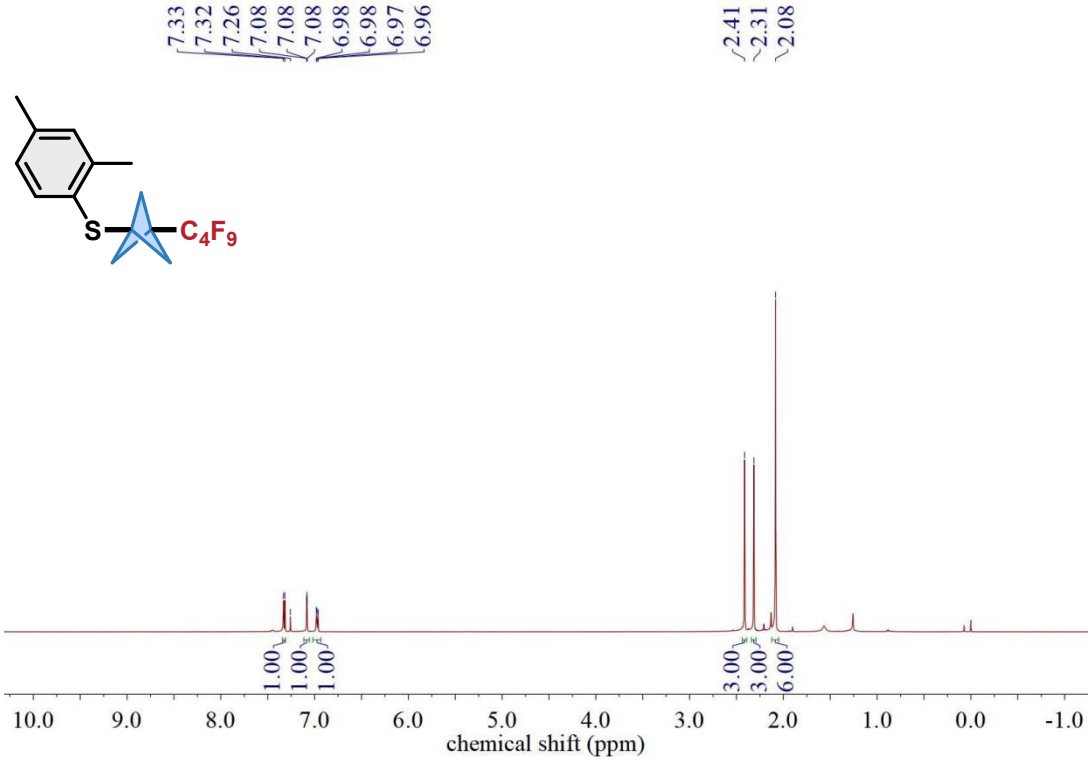
22 ^{13}C NMR (126 MHz, $CDCl_3$)



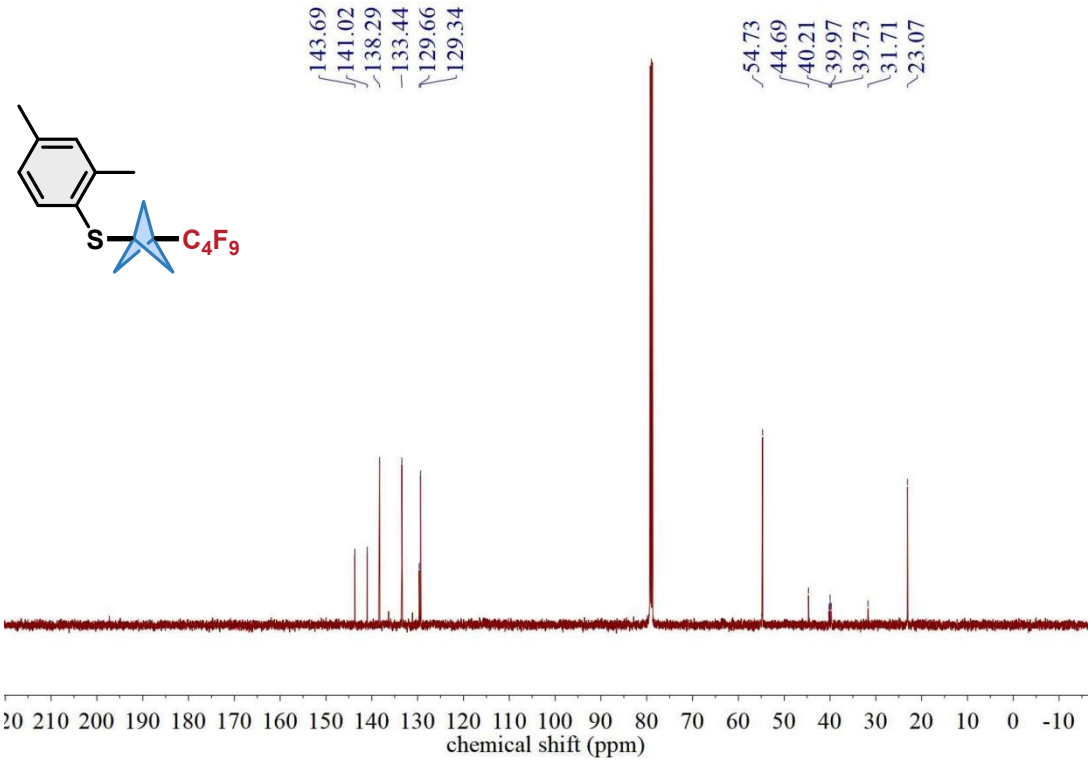
22 ^{19}F NMR (471 MHz, $CDCl_3$)



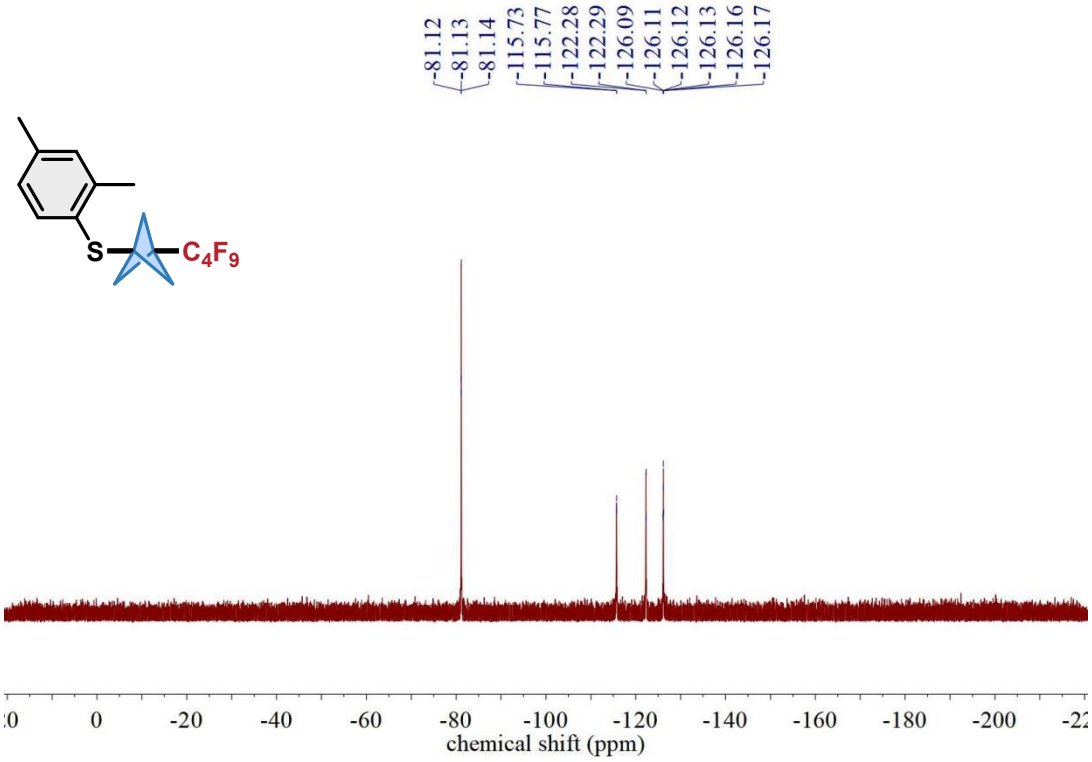
23 ^{1}H NMR (500 MHz, $CDCl_3$)



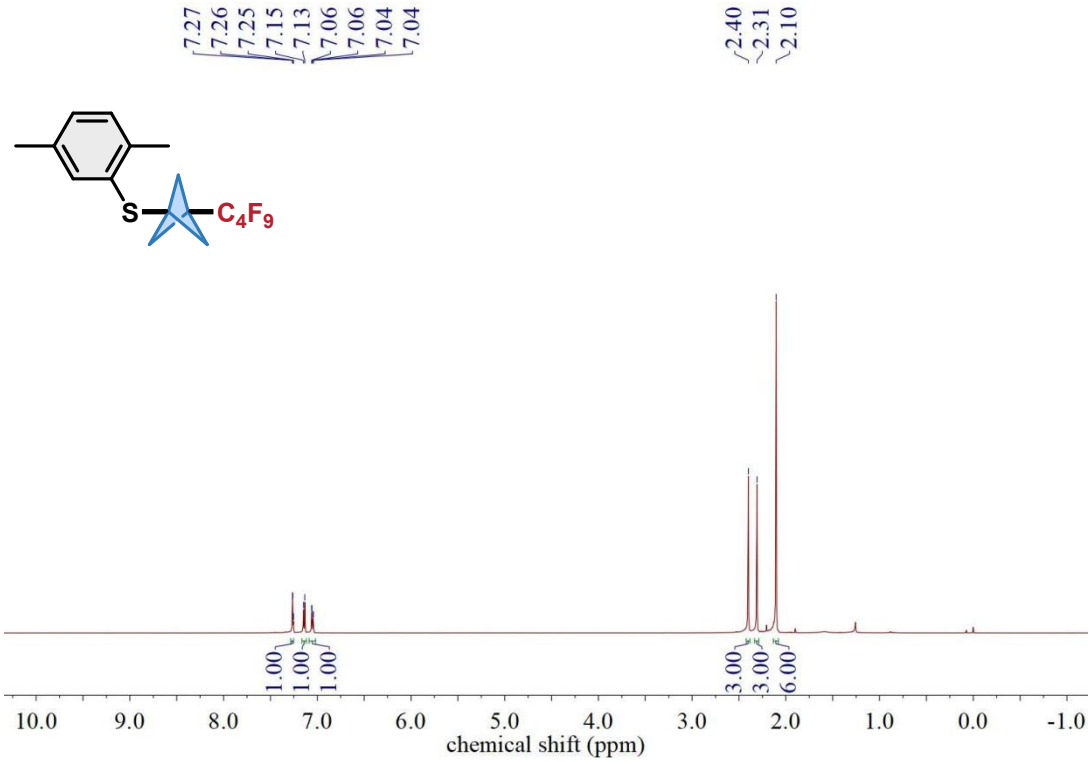
23 ^{13}C NMR (126 MHz, $CDCl_3$)



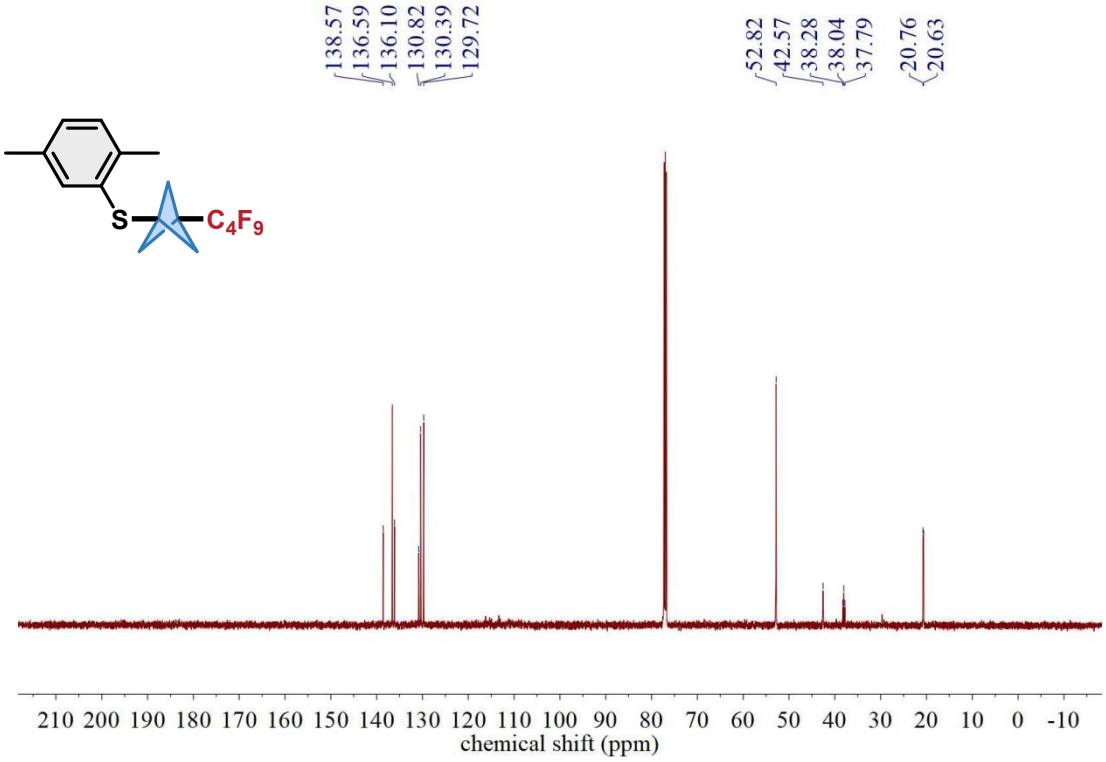
23 ^{19}F NMR (471 MHz, $CDCl_3$)



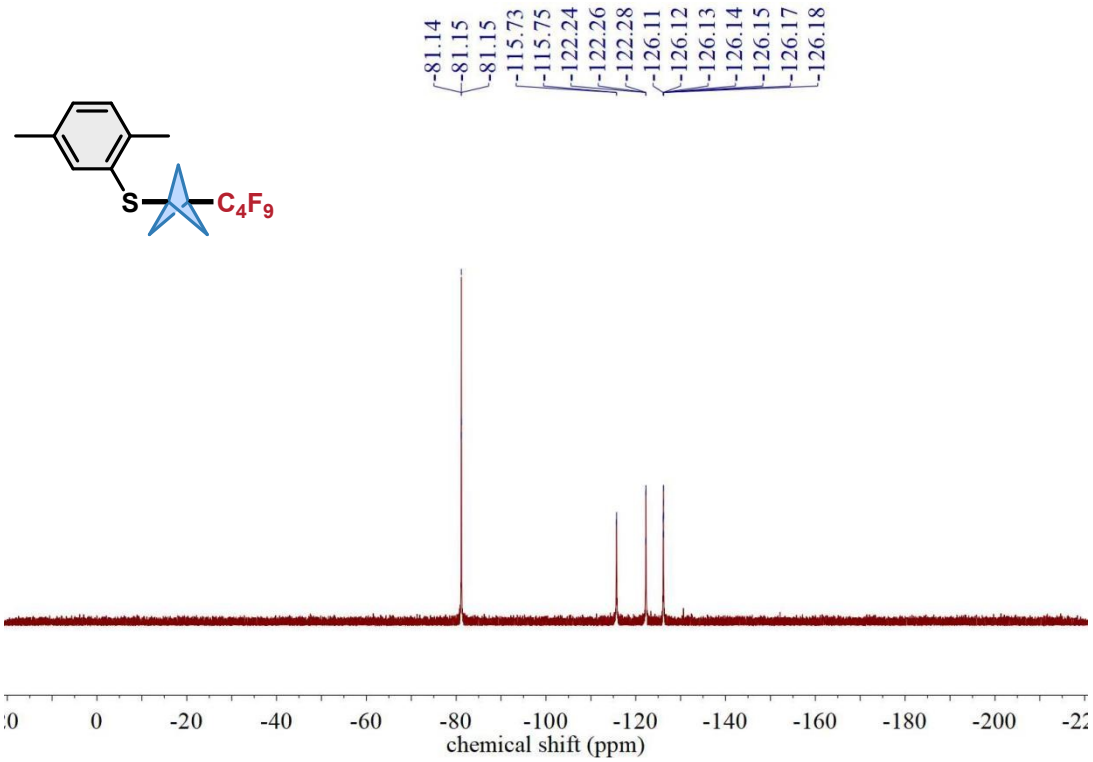
24 ^{1}H NMR (500 MHz, $CDCl_3$)



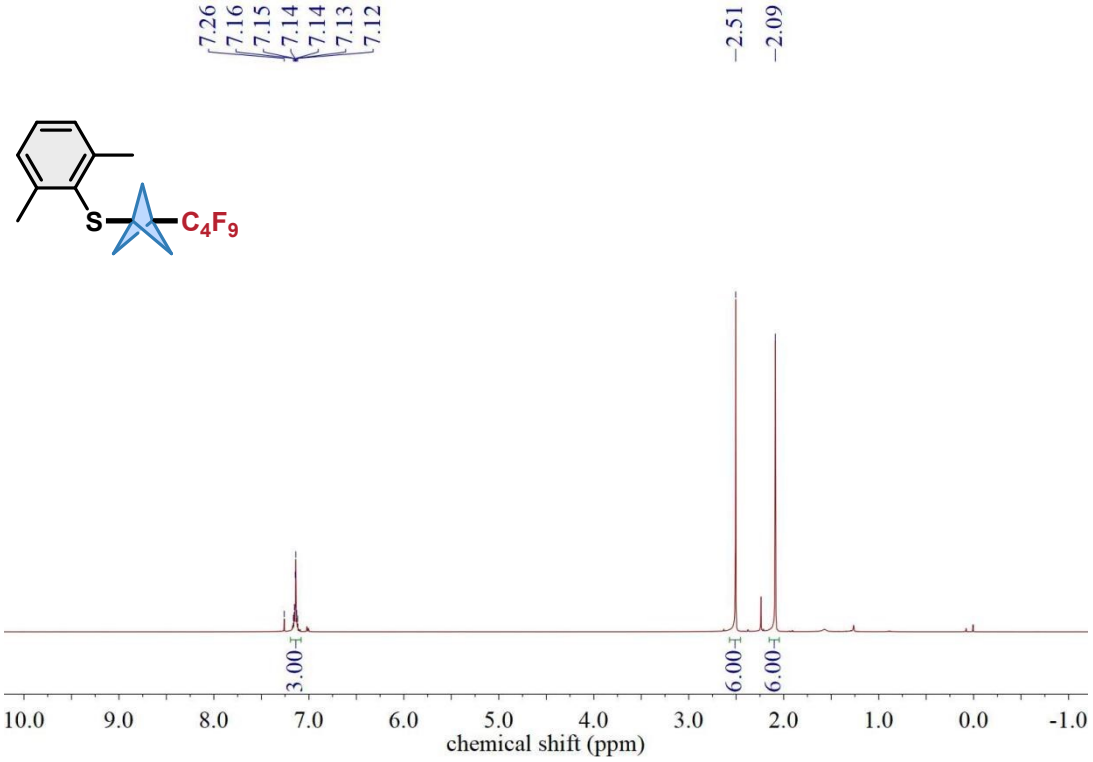
24 ^{13}C NMR (126 MHz, $CDCl_3$)



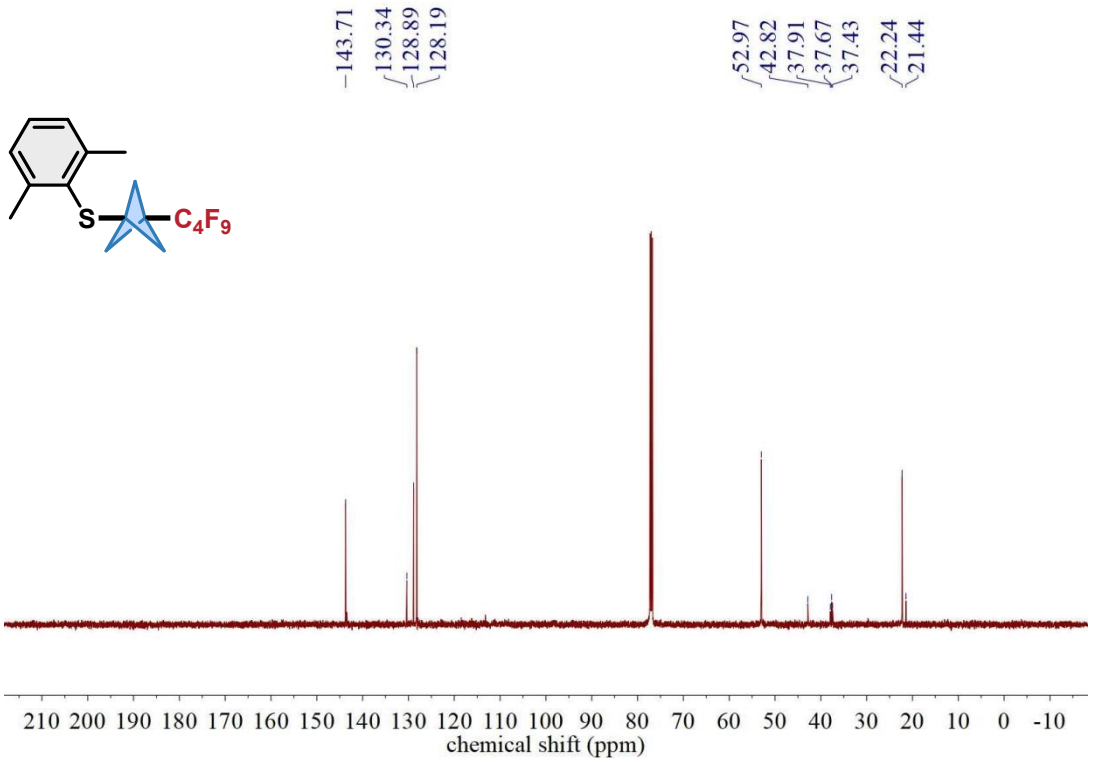
24 ^{19}F NMR (471 MHz, $CDCl_3$)



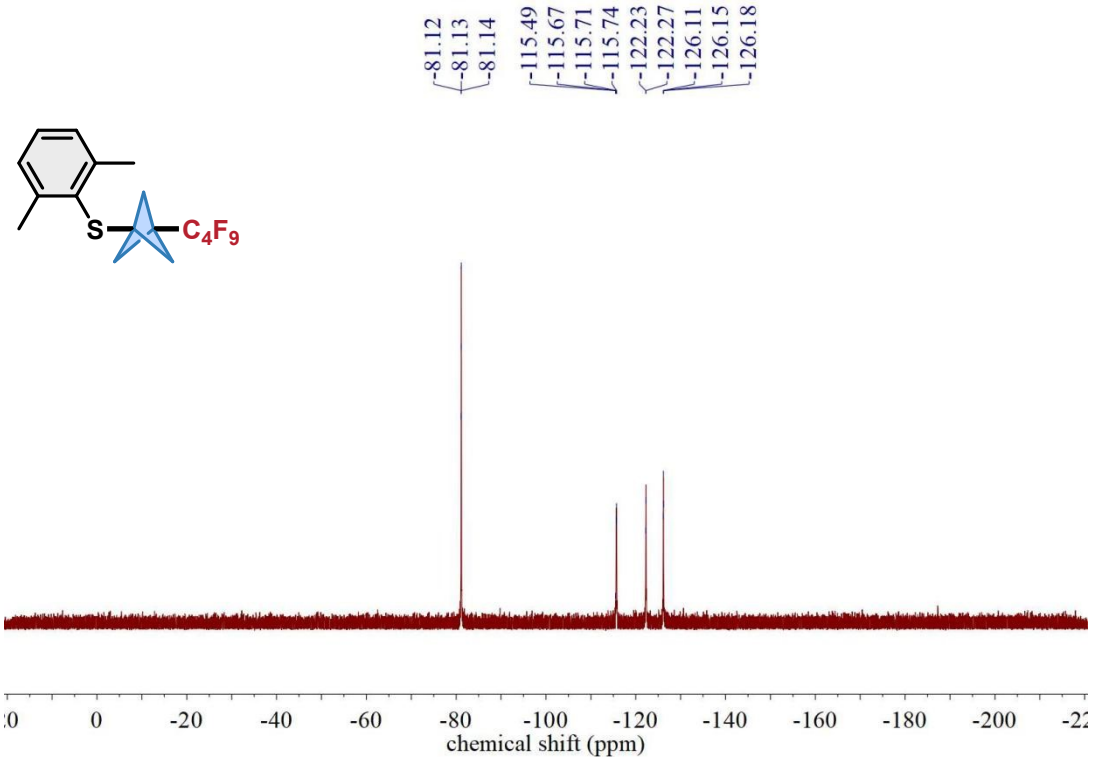
25 ^{1}H NMR (500 MHz, $CDCl_3$)



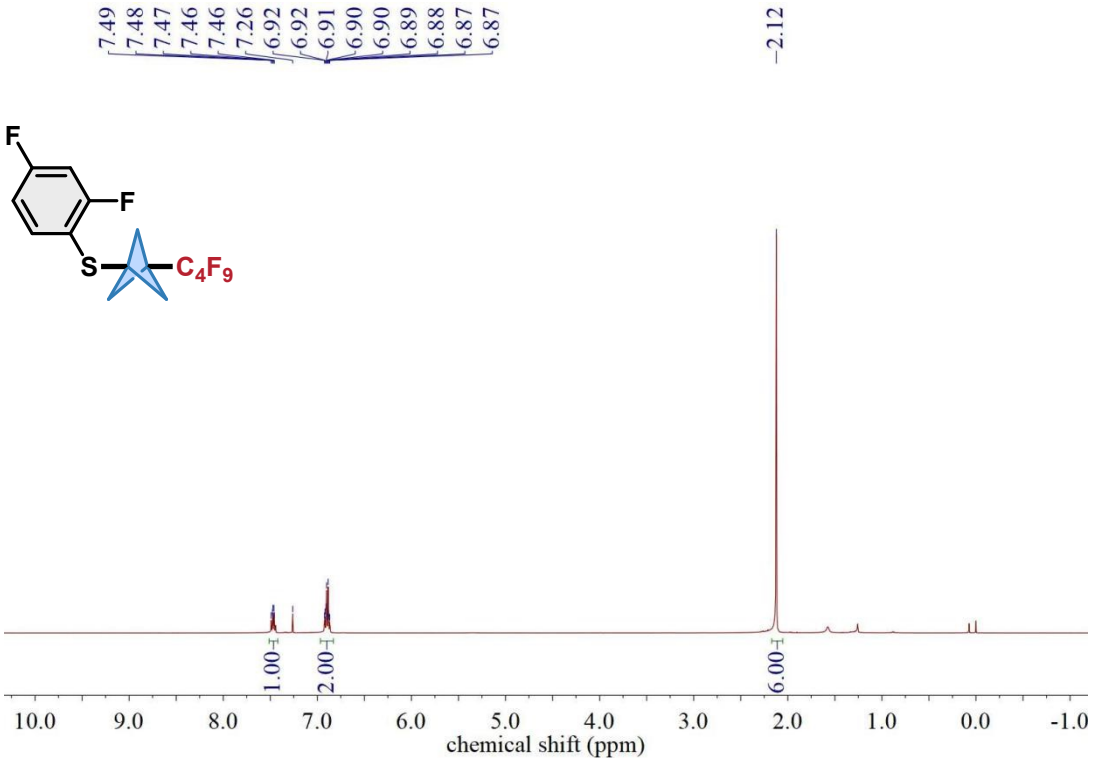
25 ^{13}C NMR (126 MHz, $CDCl_3$)



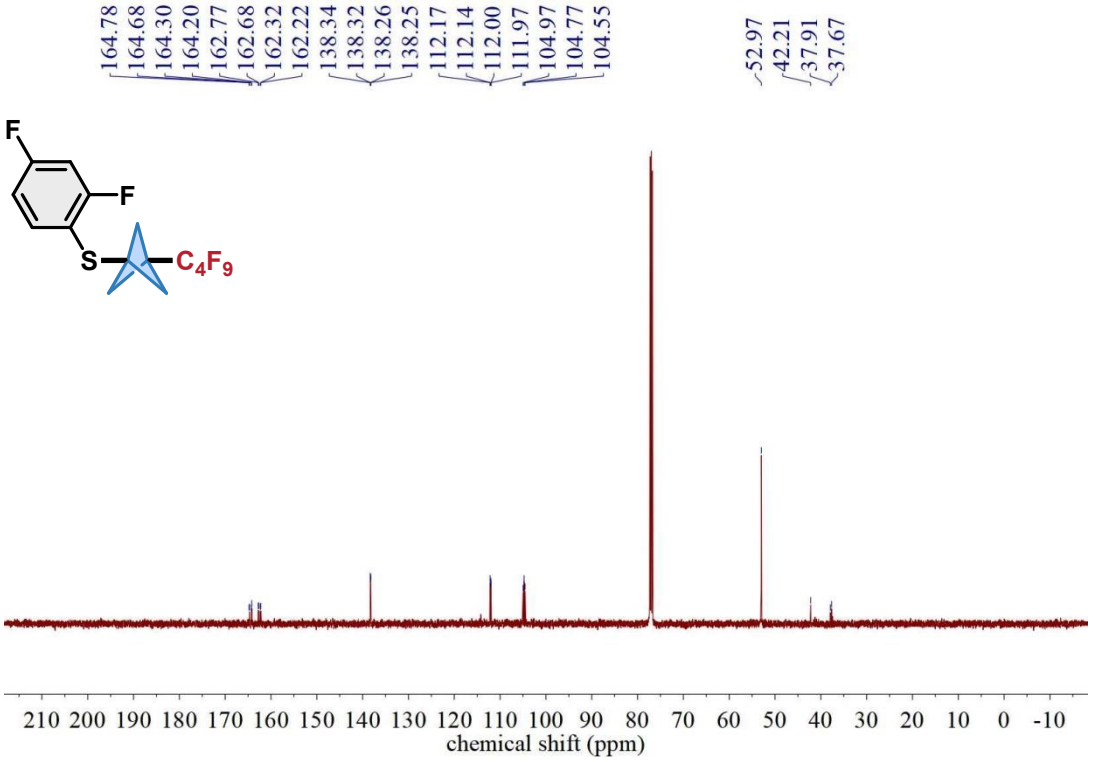
25 ^{19}F NMR (471 MHz, $CDCl_3$)



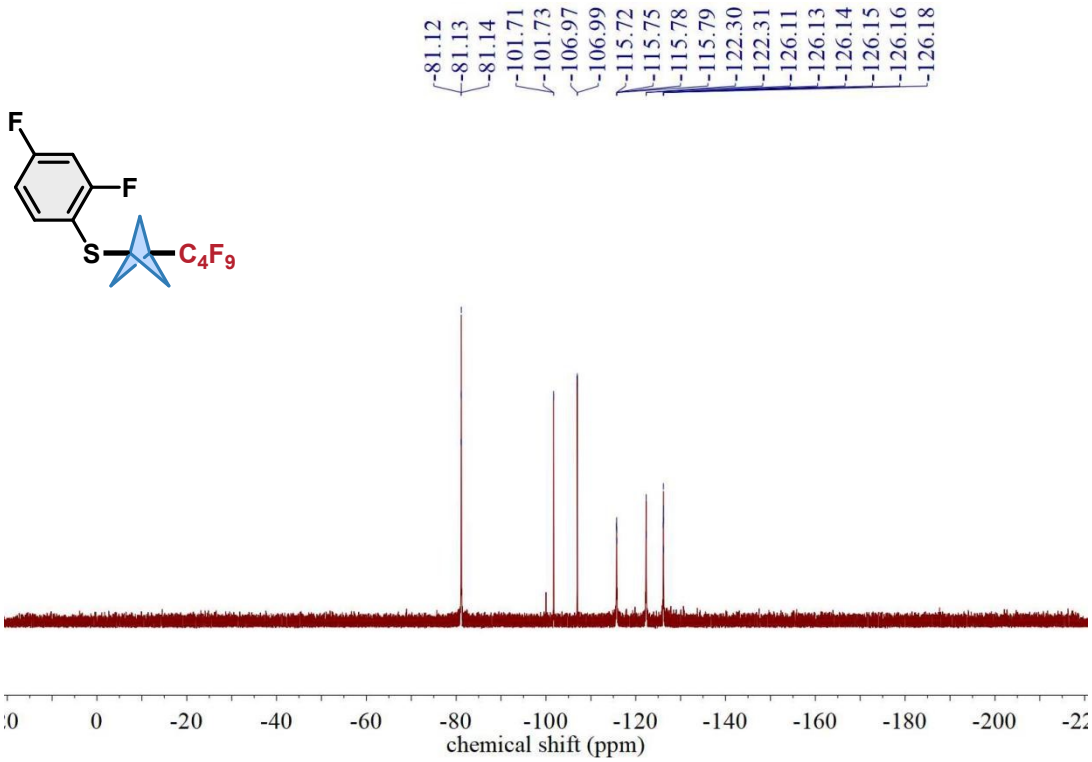
26 ^{1}H NMR (500 MHz, $CDCl_3$)



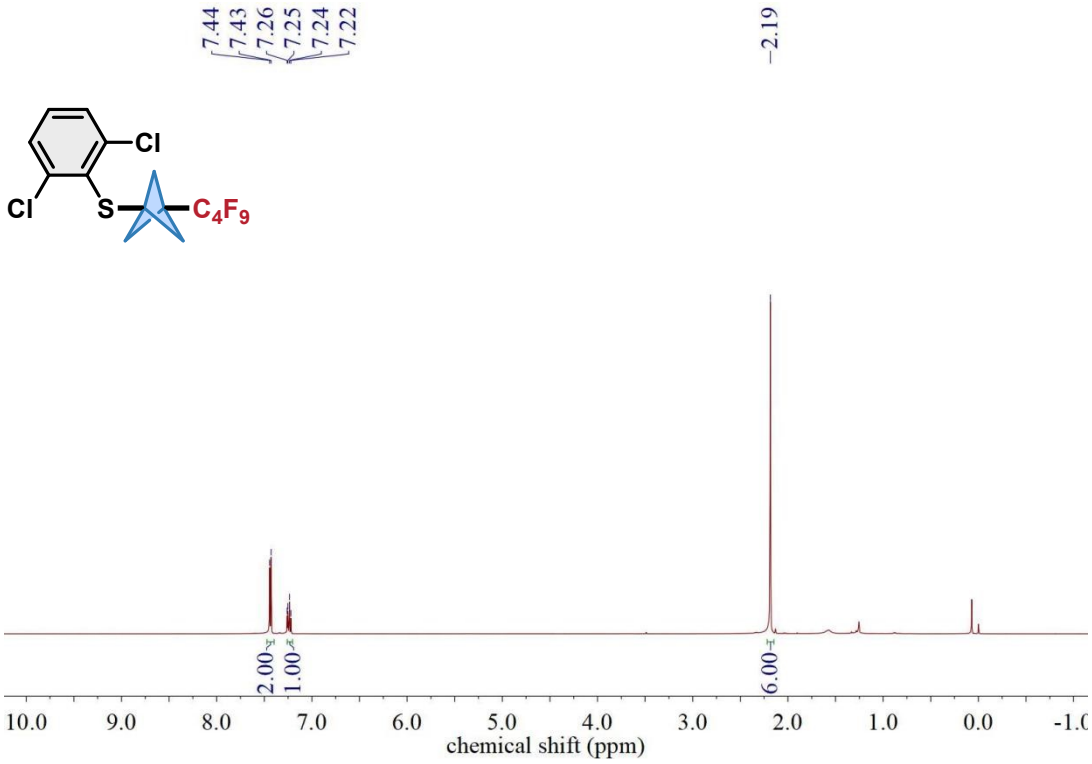
26 ^{13}C NMR (126 MHz, $CDCl_3$)



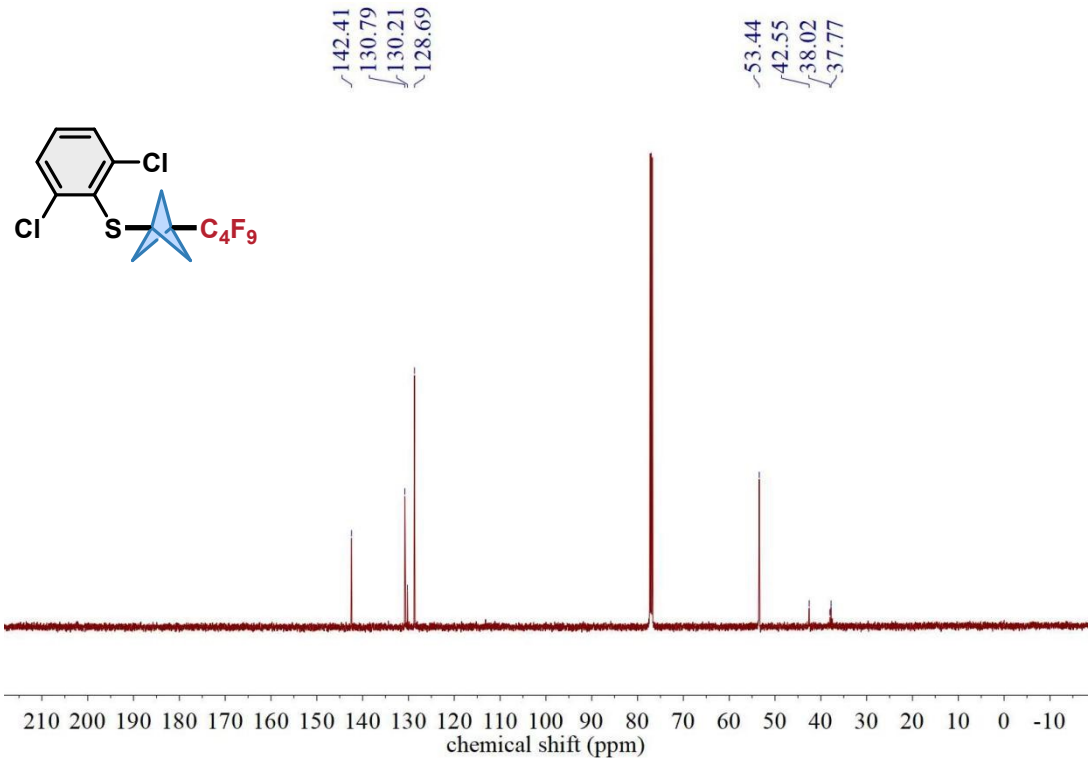
26 ^{19}F NMR (471 MHz, $CDCl_3$)



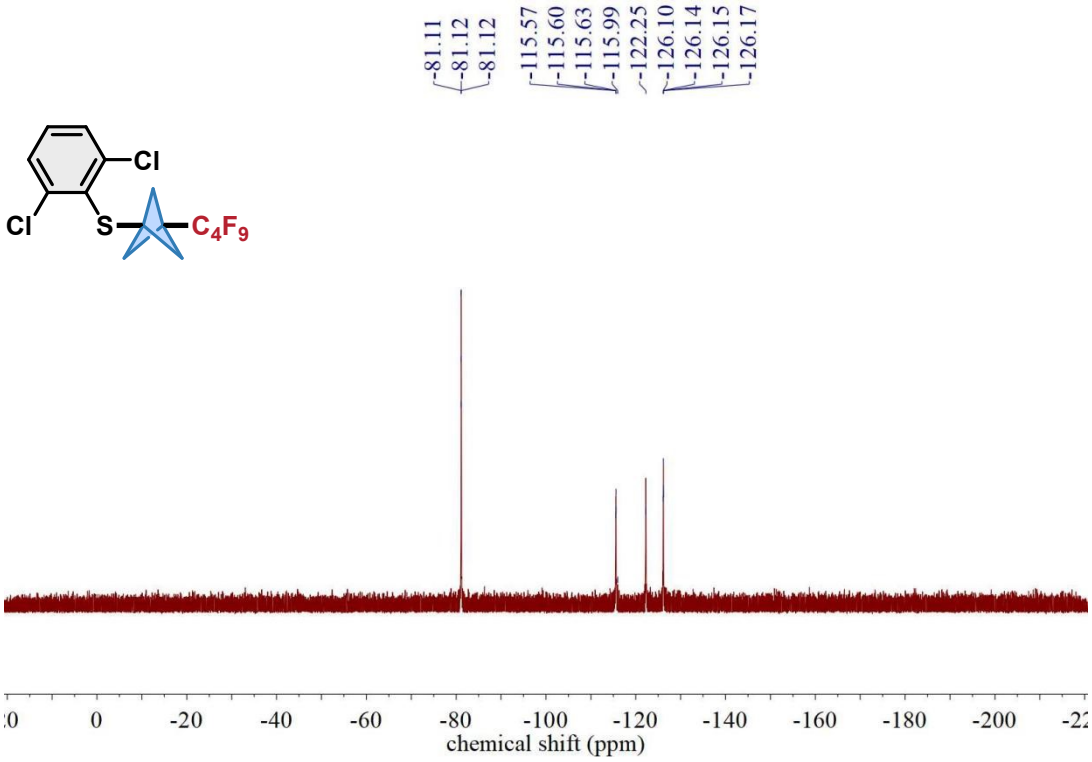
27 ^{1}H NMR (500 MHz, $CDCl_3$)



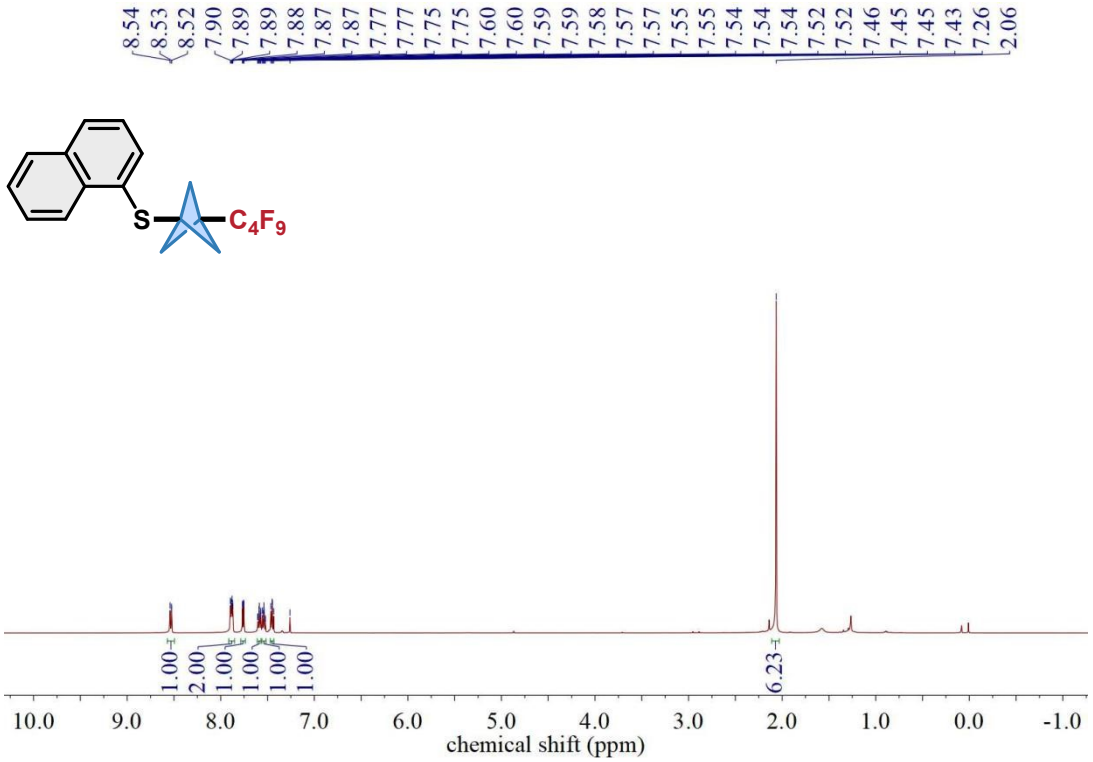
27 ^{13}C NMR (126 MHz, $CDCl_3$)



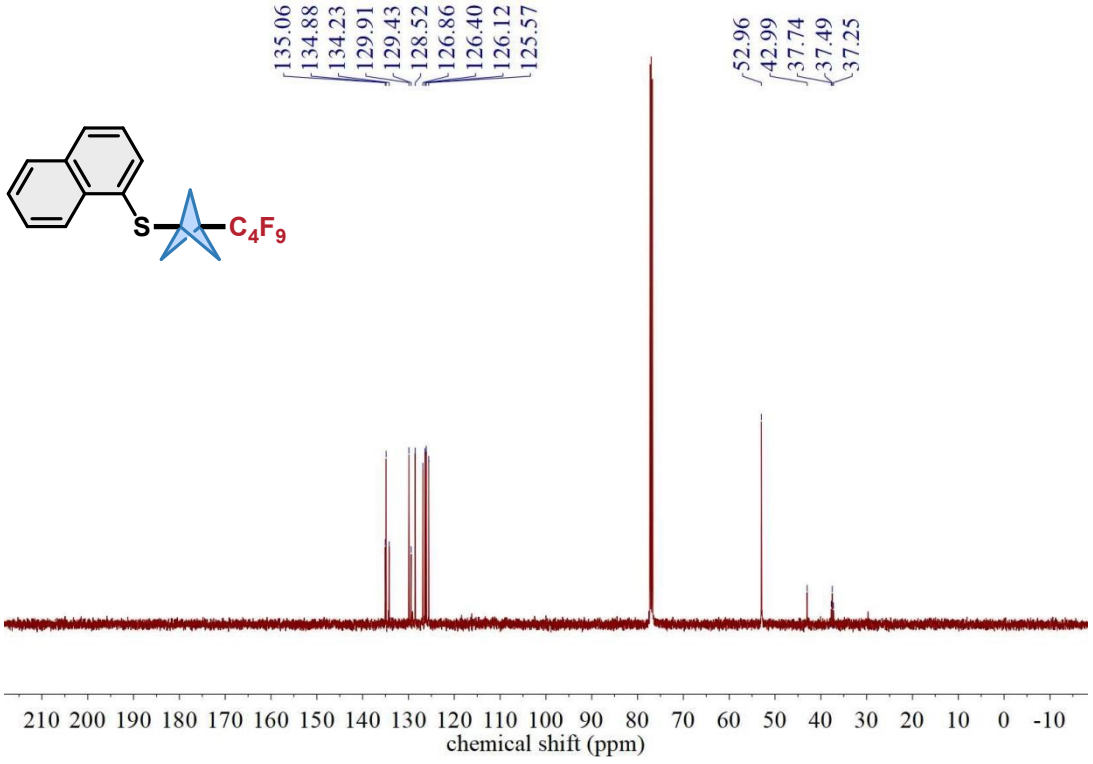
27 ^{19}F NMR (471 MHz, $CDCl_3$)



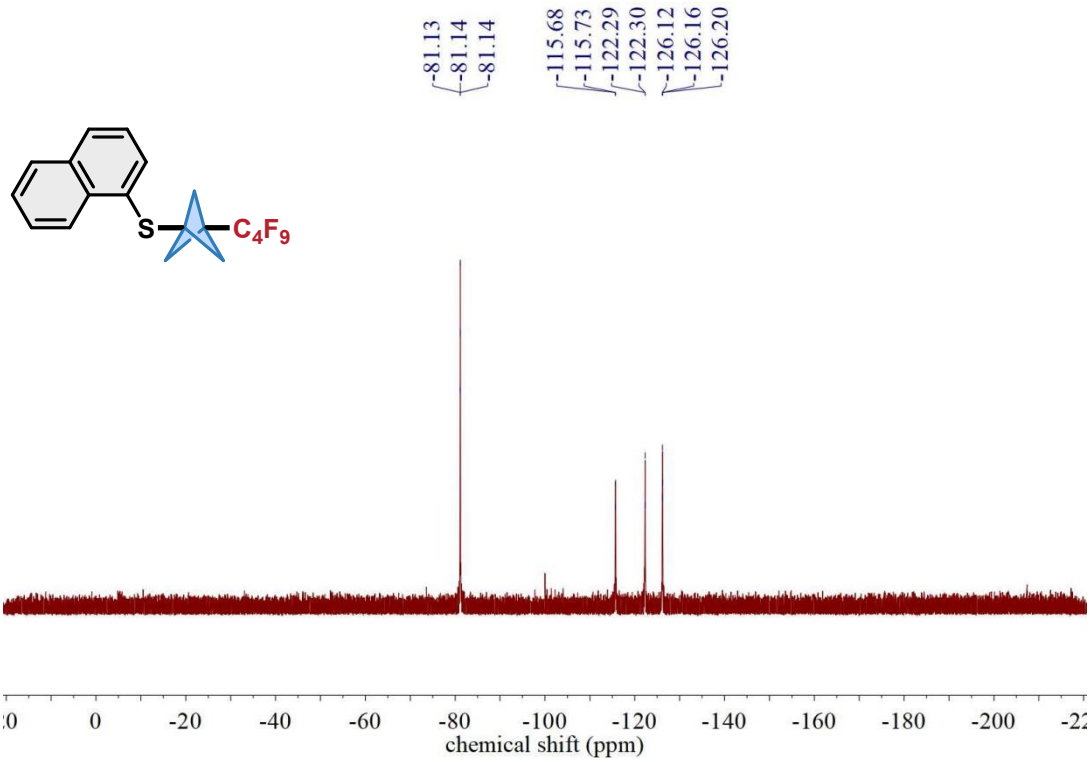
28 ^{1}H NMR (500 MHz, $CDCl_3$)



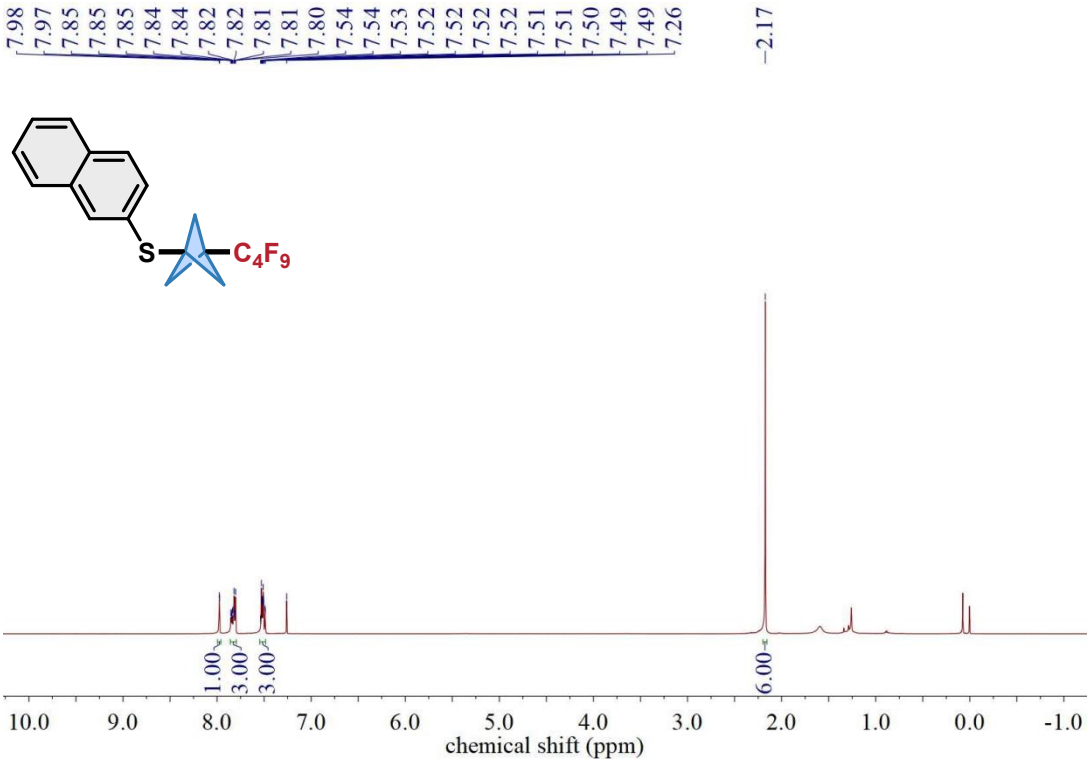
28 ^{13}C NMR (126 MHz, $CDCl_3$)



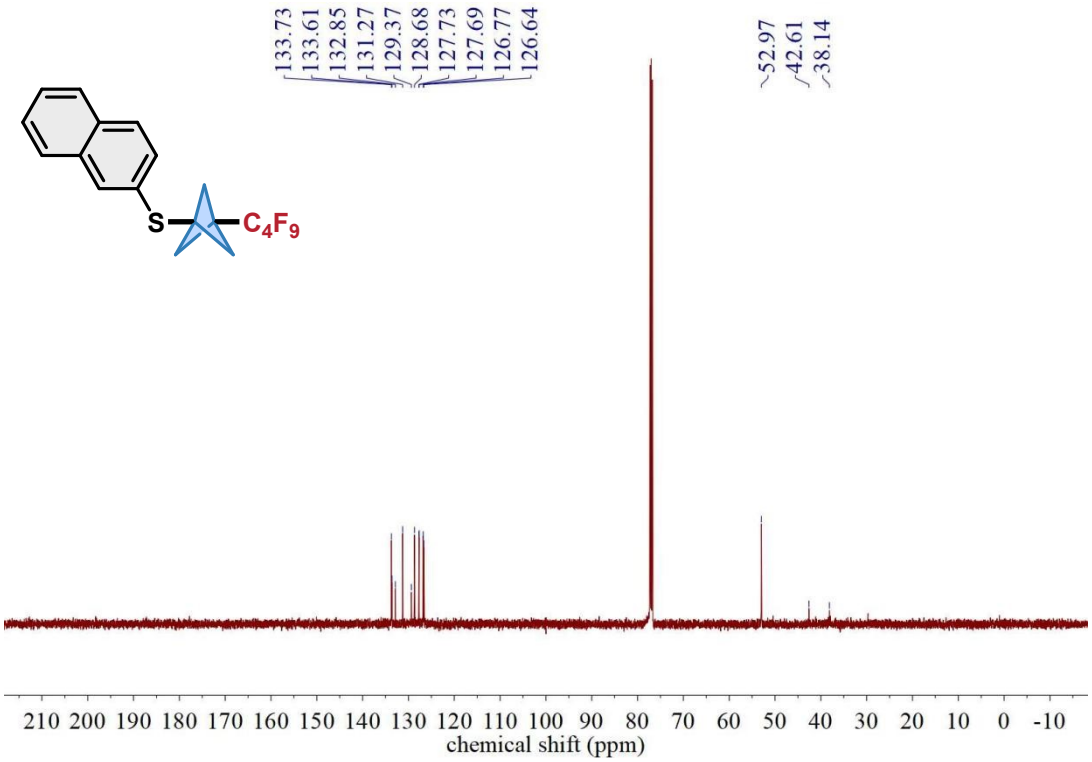
28 ^{19}F NMR (471 MHz, $CDCl_3$)



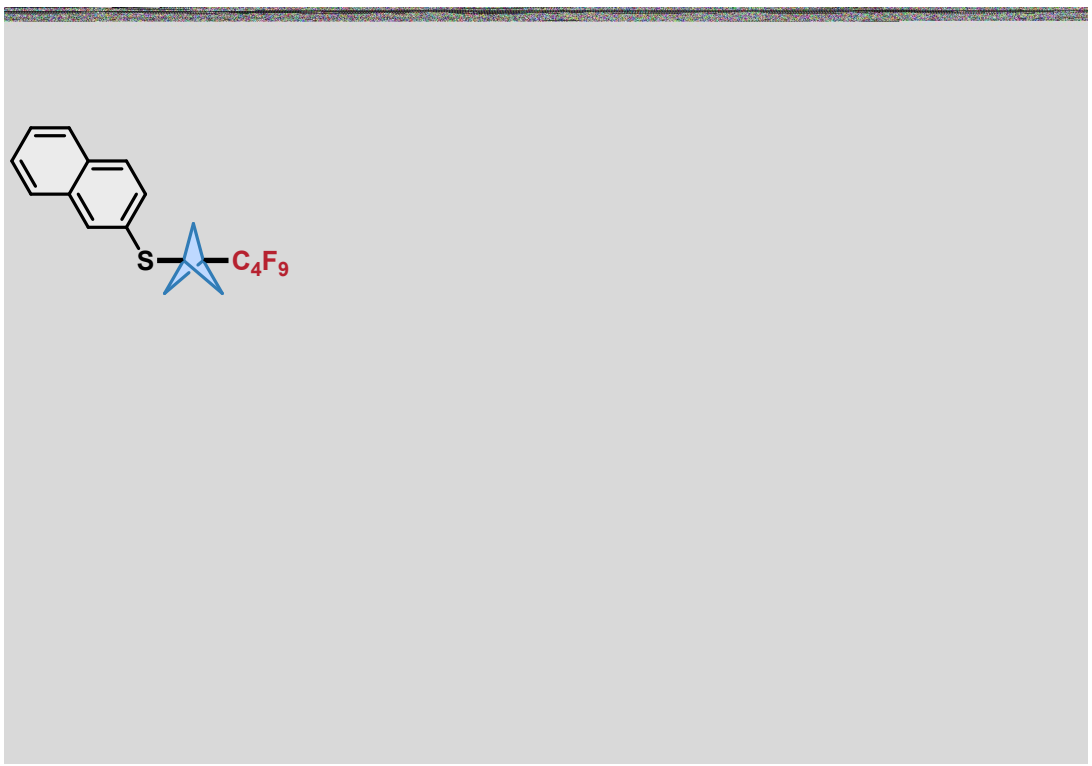
29 ^{1}H NMR (500 MHz, $CDCl_3$)



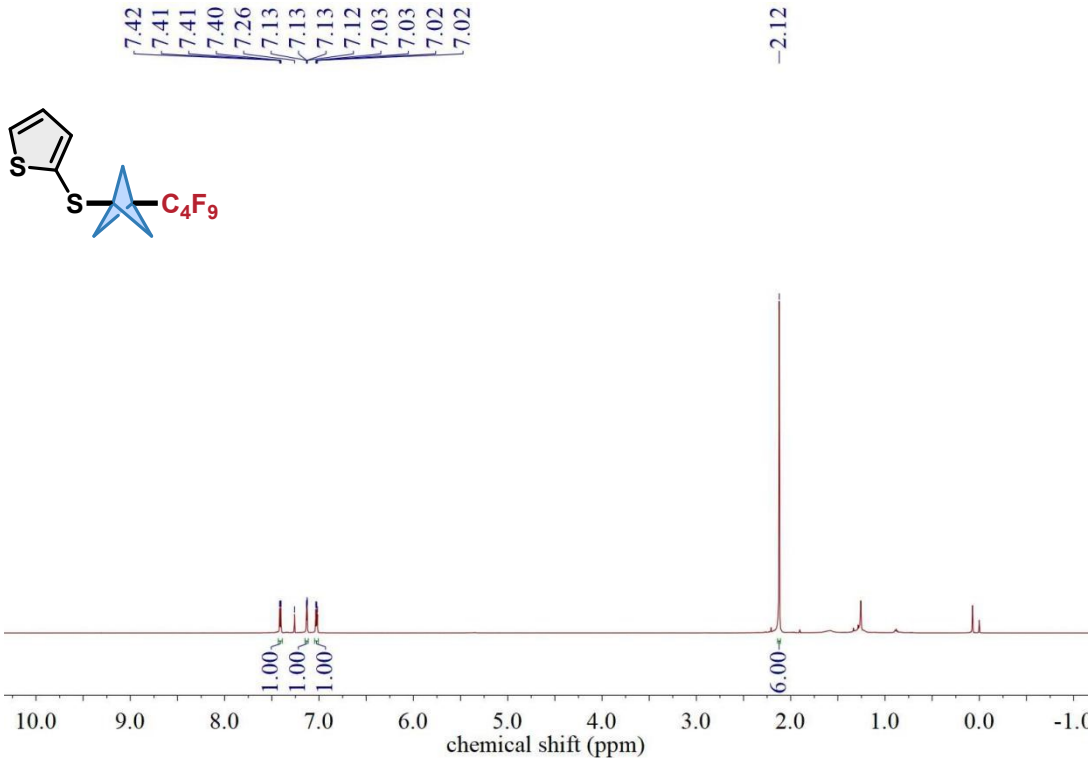
29 ^{13}C NMR (126 MHz, $CDCl_3$)



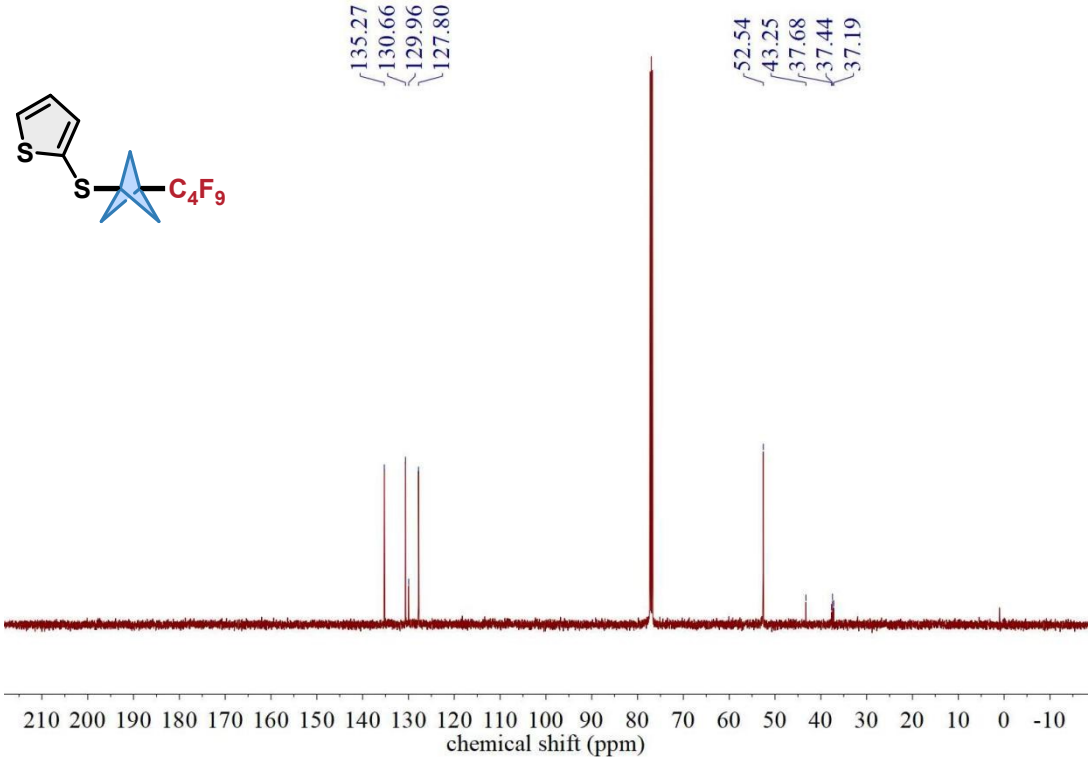
29 ^{19}F NMR (471 MHz, $CDCl_3$)



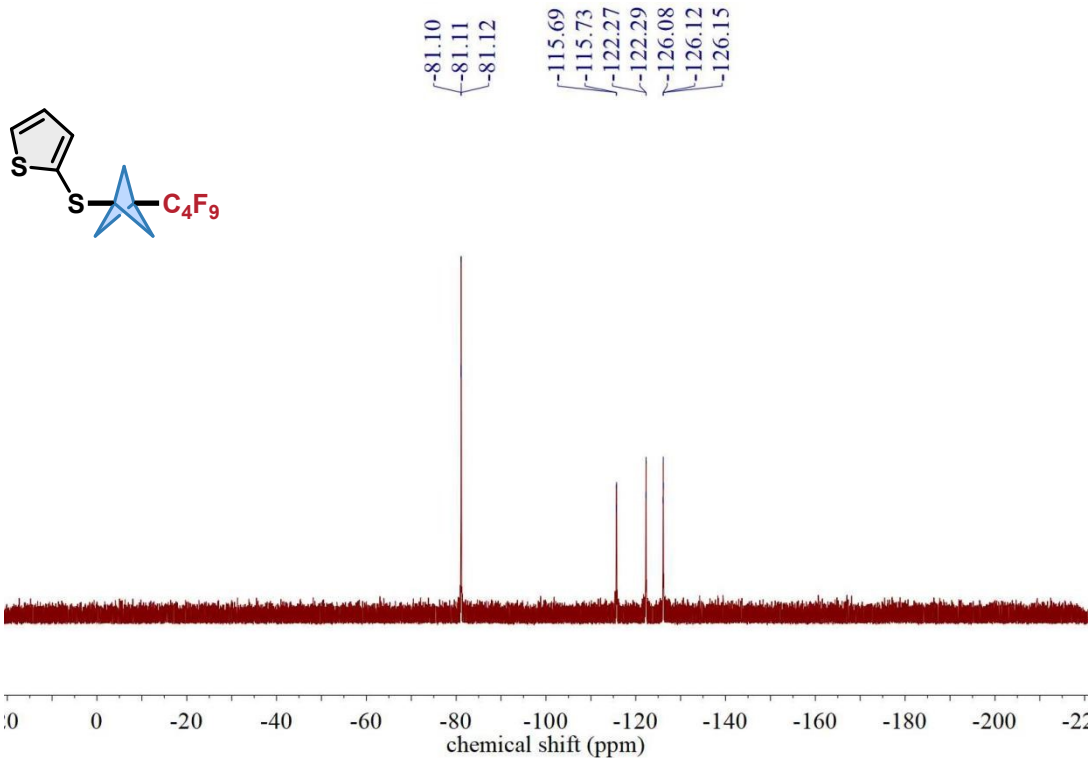
30 ^{1}H NMR (500 MHz, $CDCl_3$)



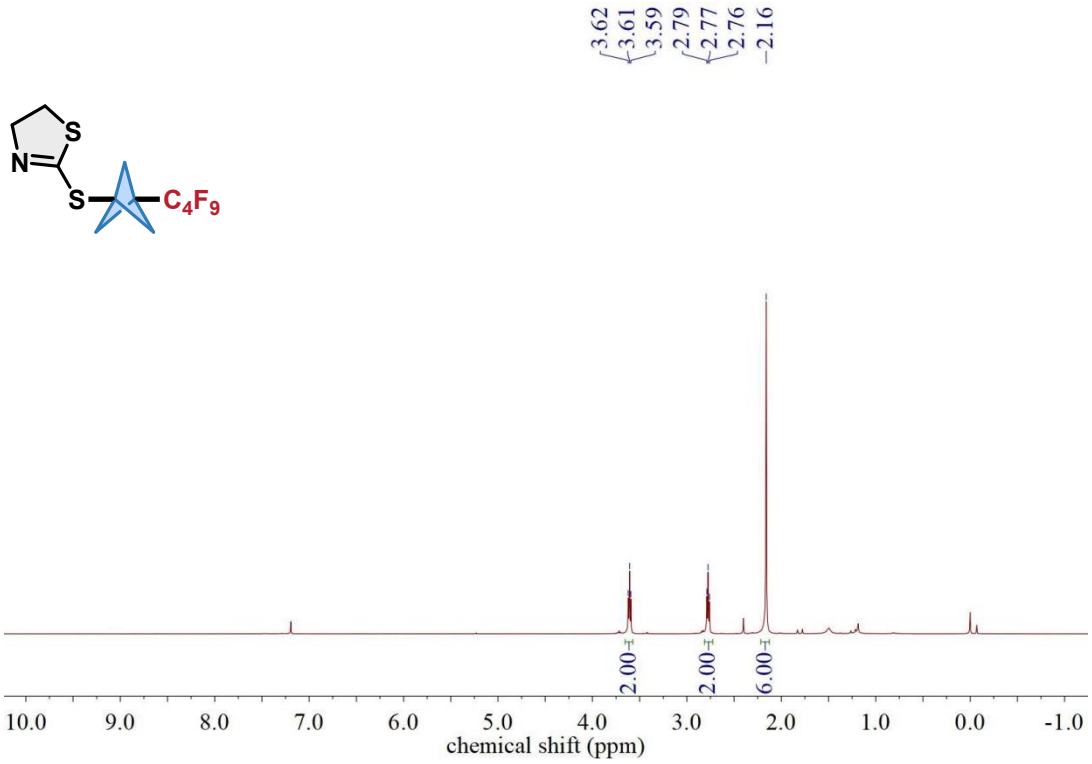
30 ^{13}C NMR (126 MHz, $CDCl_3$)



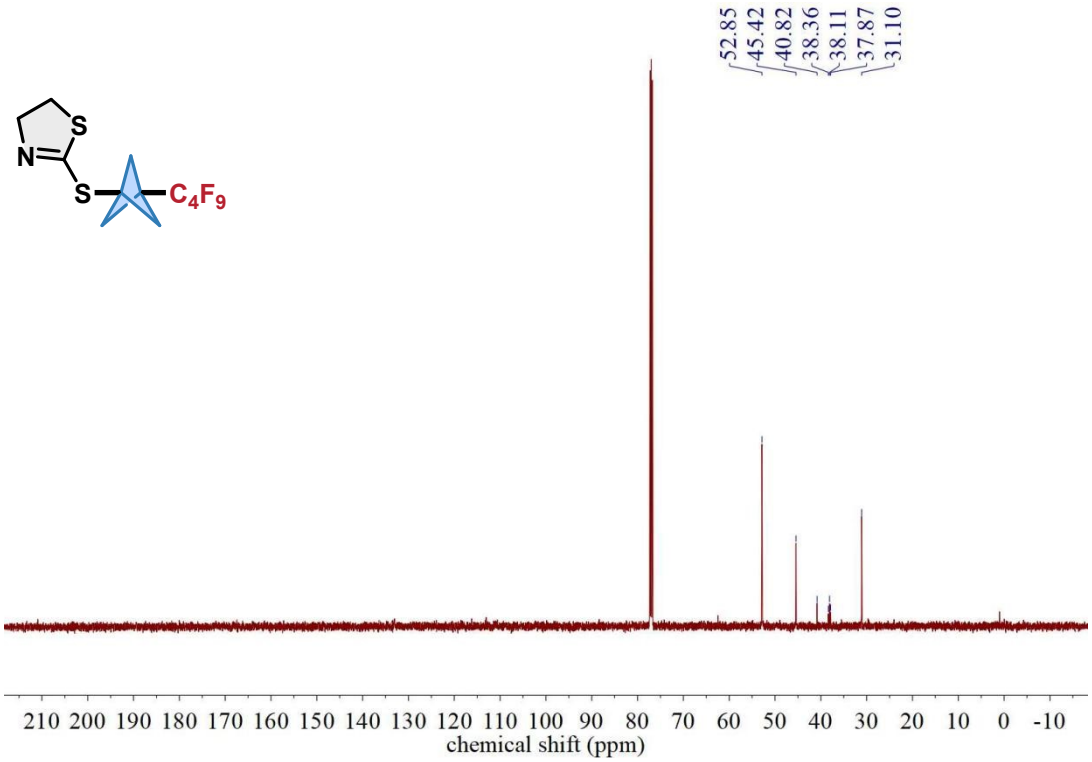
30 ^{19}F NMR (471 MHz, $CDCl_3$)



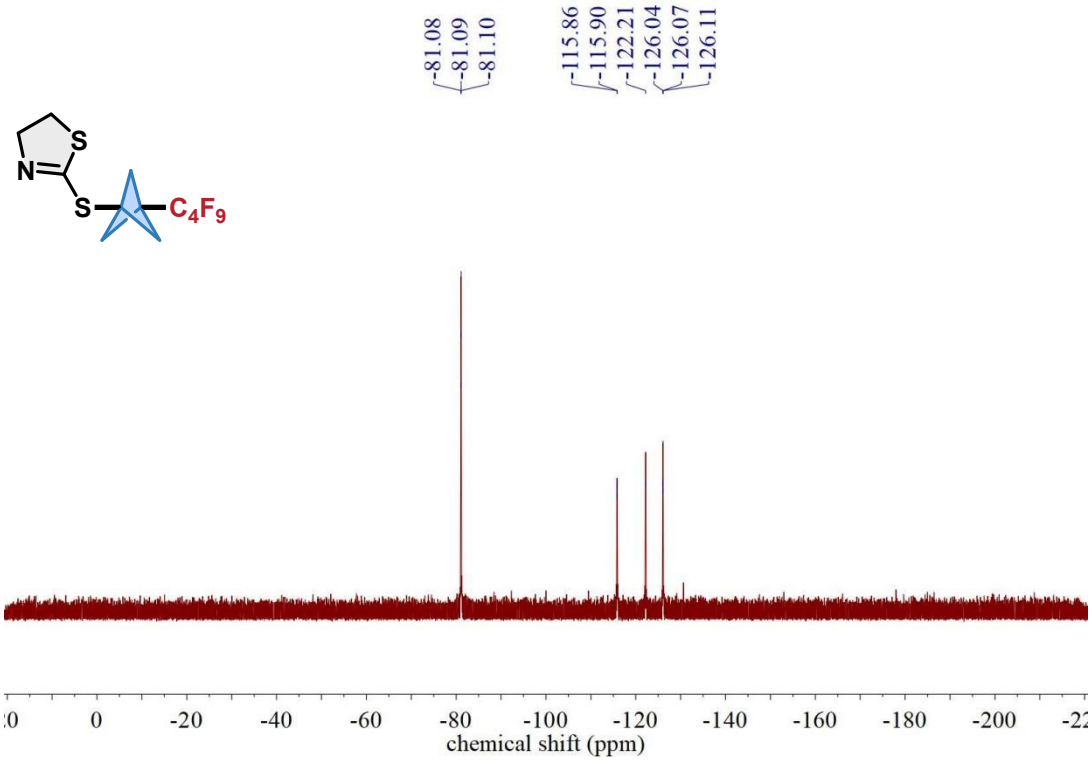
31 ^{1}H NMR (500 MHz, $CDCl_3$)



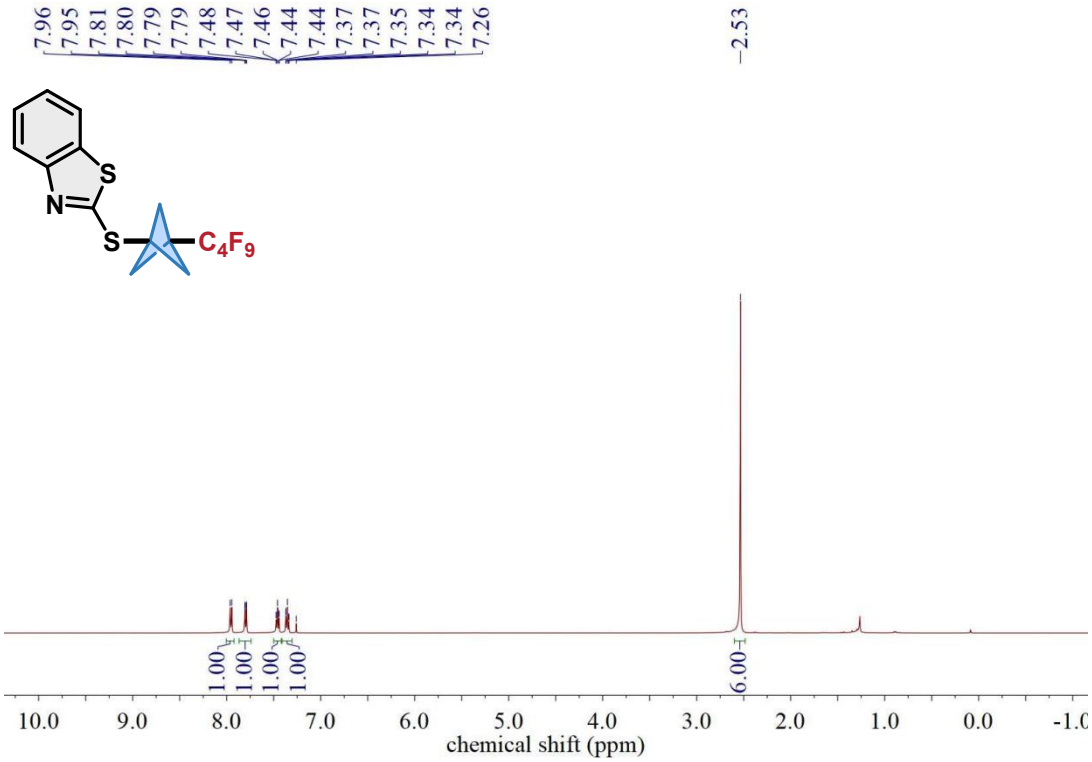
31 ^{13}C NMR (126 MHz, $CDCl_3$)



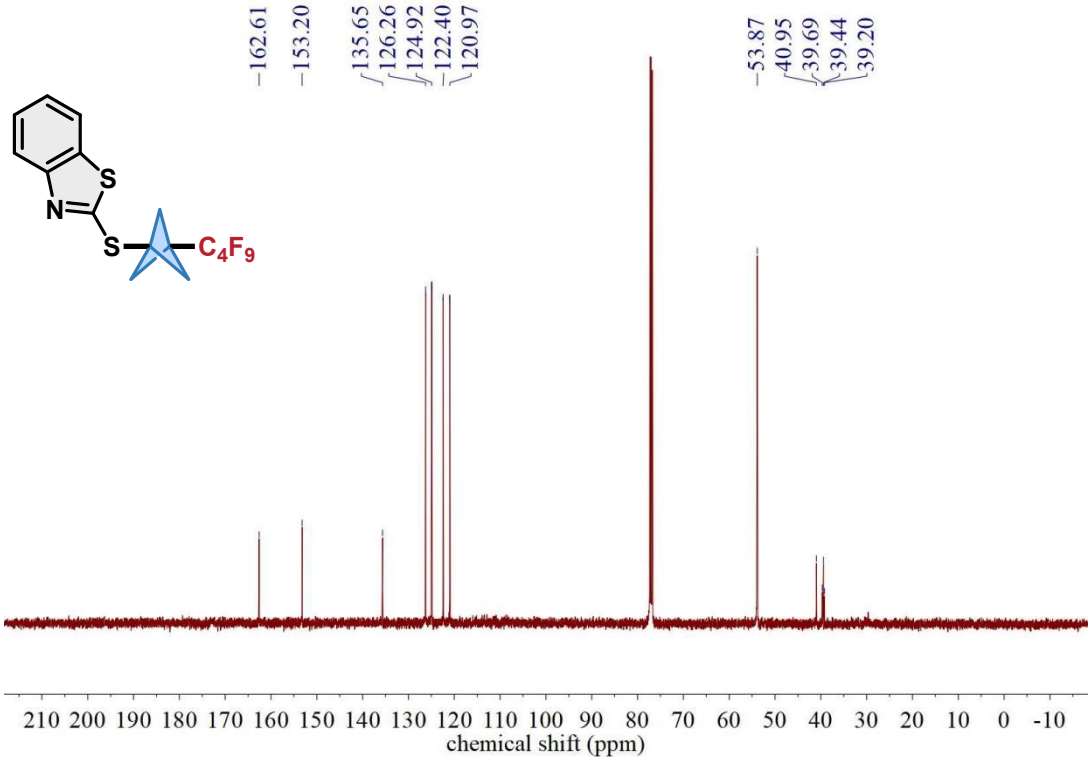
31 ^{19}F NMR (471 MHz, $CDCl_3$)



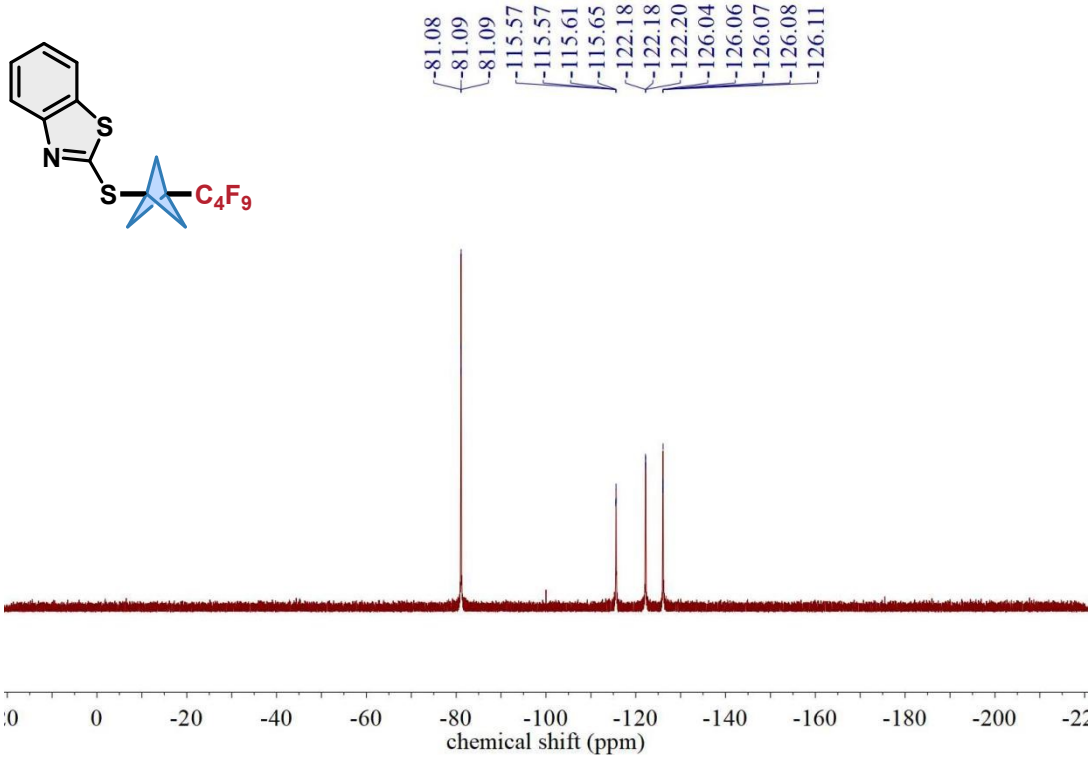
32 ^{1}H NMR (500 MHz, $CDCl_3$)



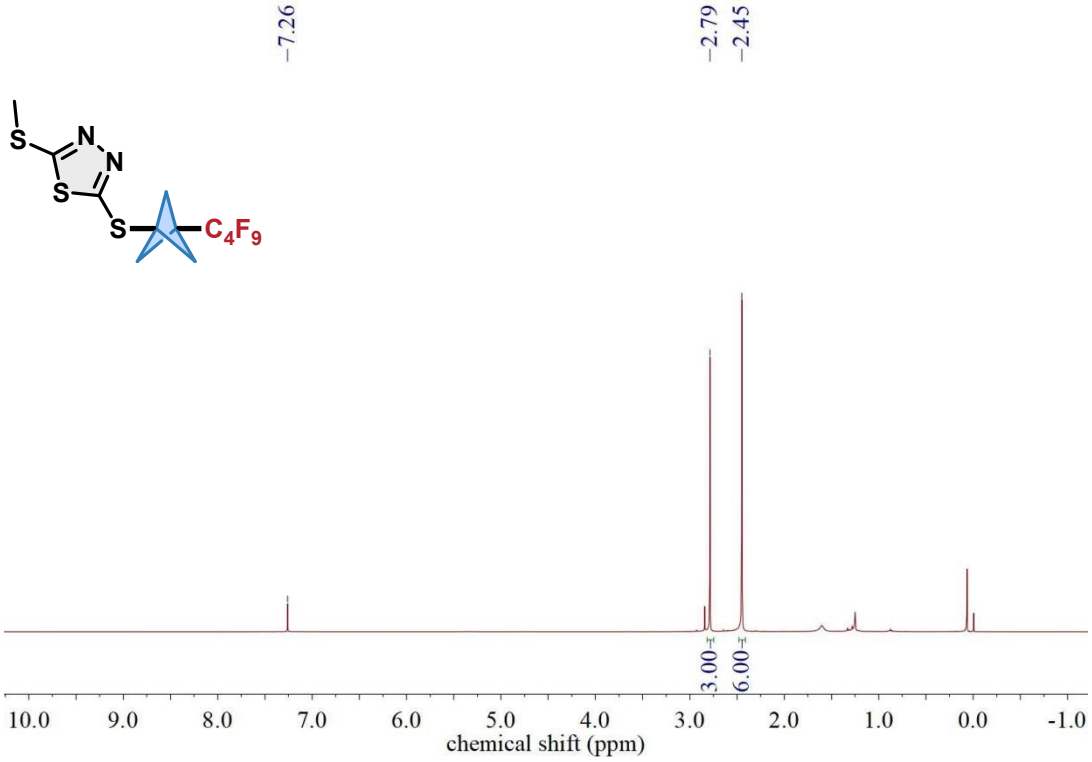
32 ^{13}C NMR (126 MHz, $CDCl_3$)



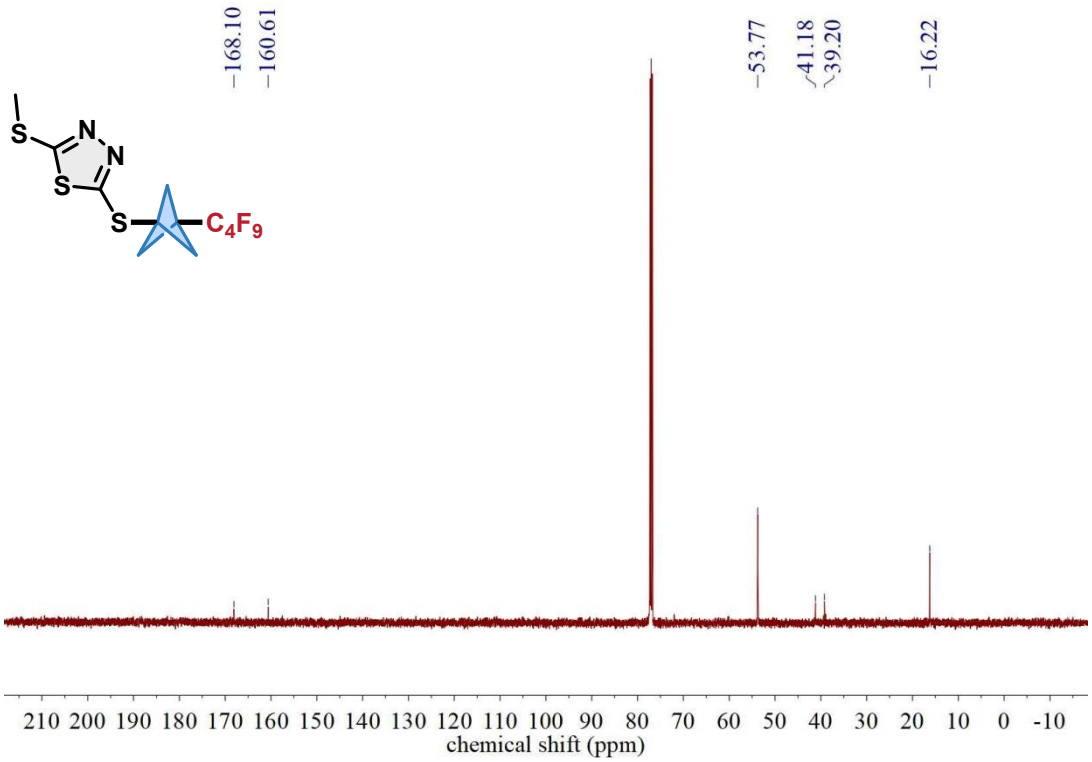
32 ^{19}F NMR (471 MHz, $CDCl_3$)



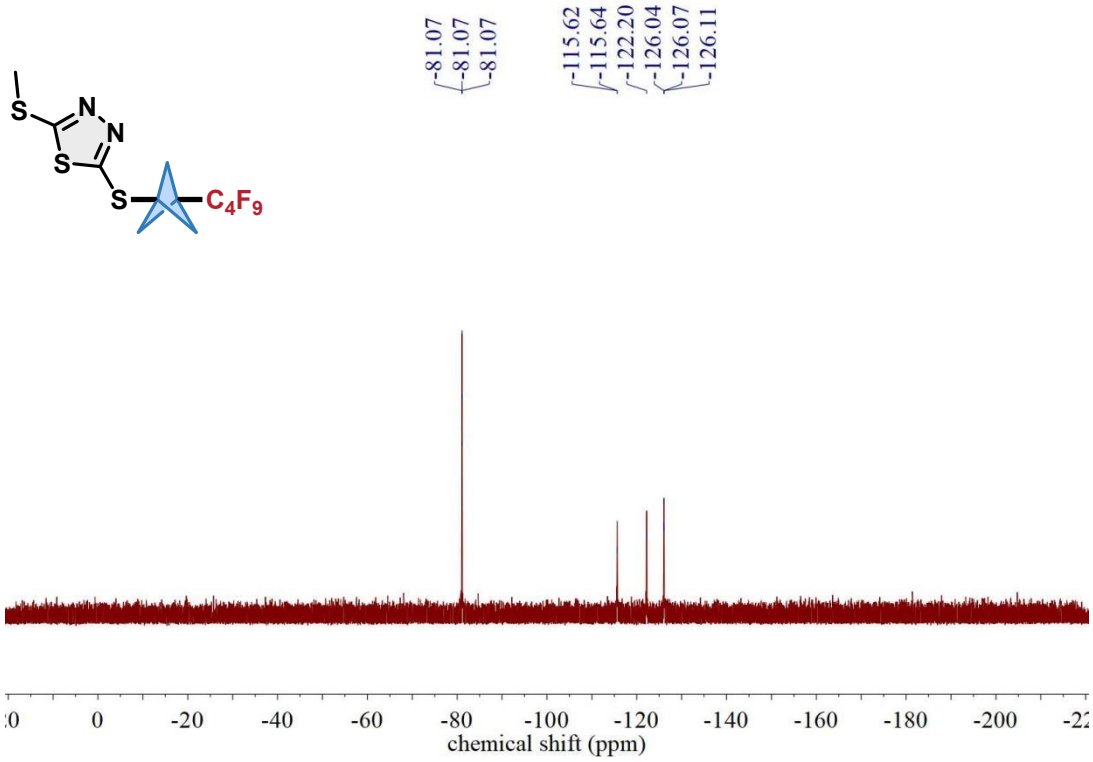
33 ^{1}H NMR (500 MHz, $CDCl_3$)



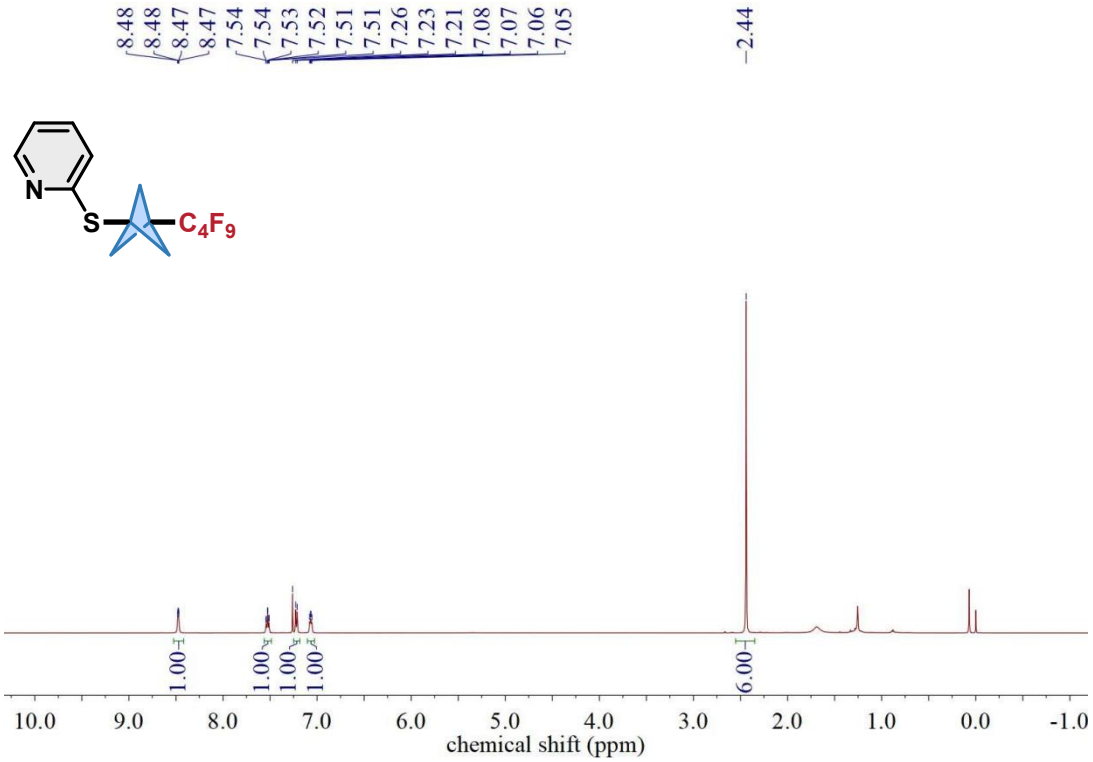
33 ^{13}C NMR (126 MHz, $CDCl_3$)



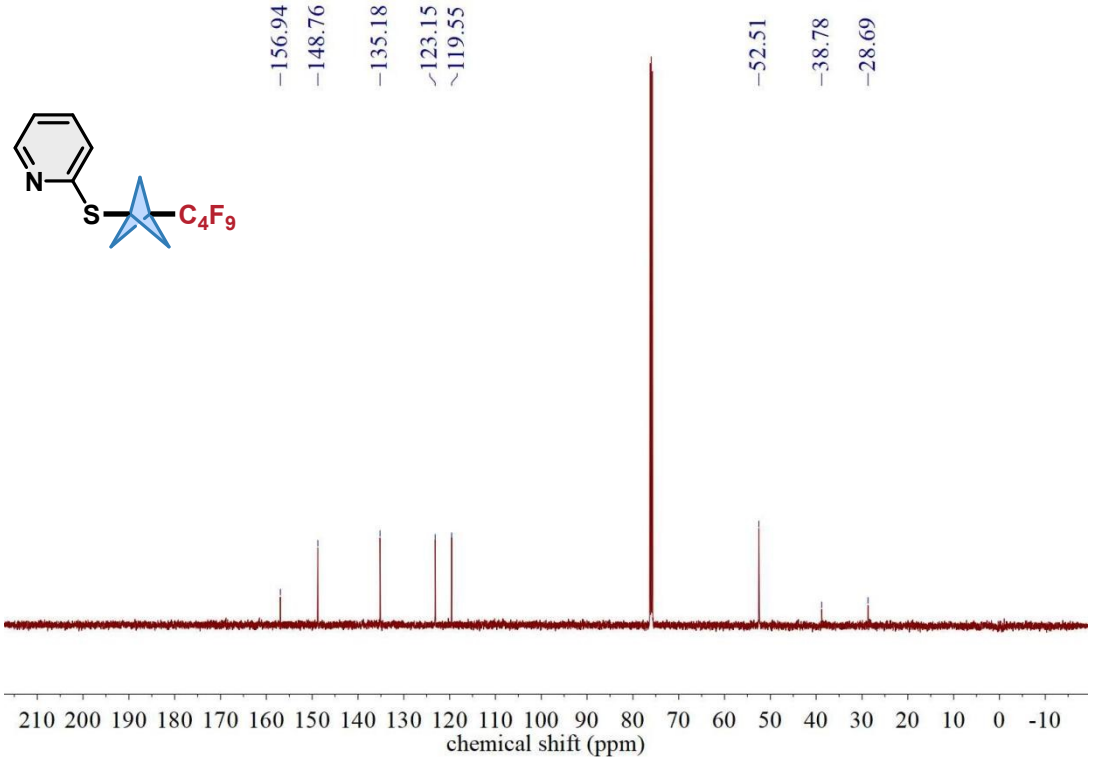
33 ^{19}F NMR (471 MHz, $CDCl_3$)



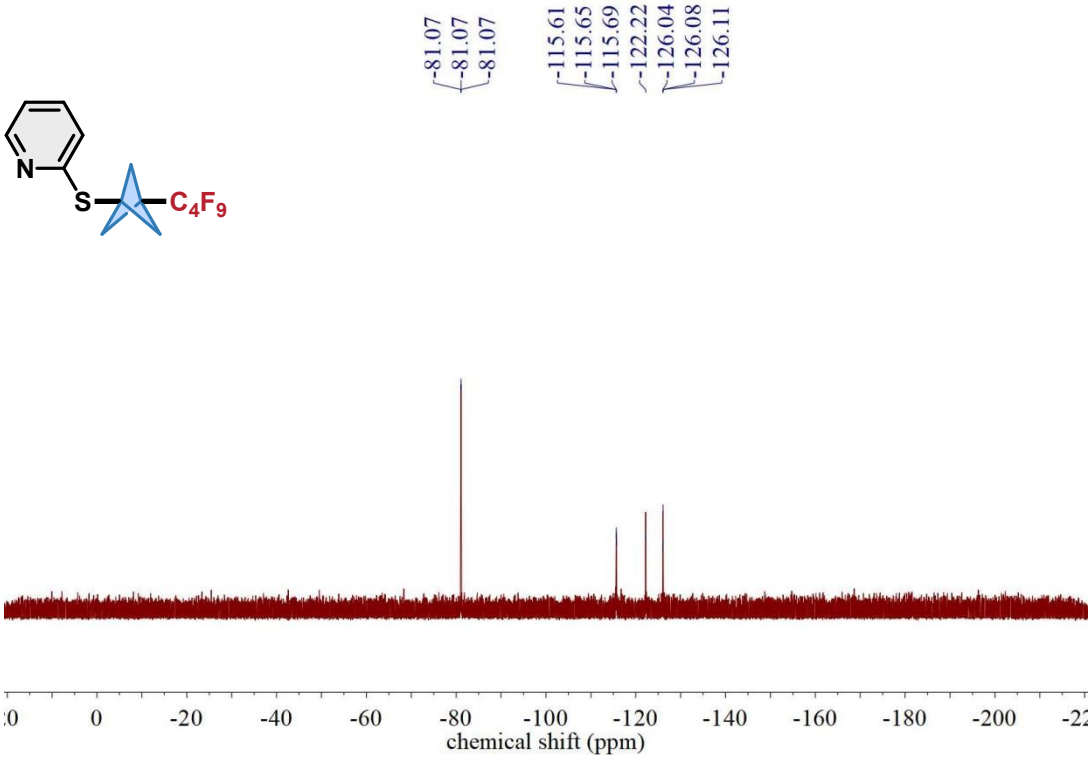
34 ^{1}H NMR (500 MHz, $CDCl_3$)



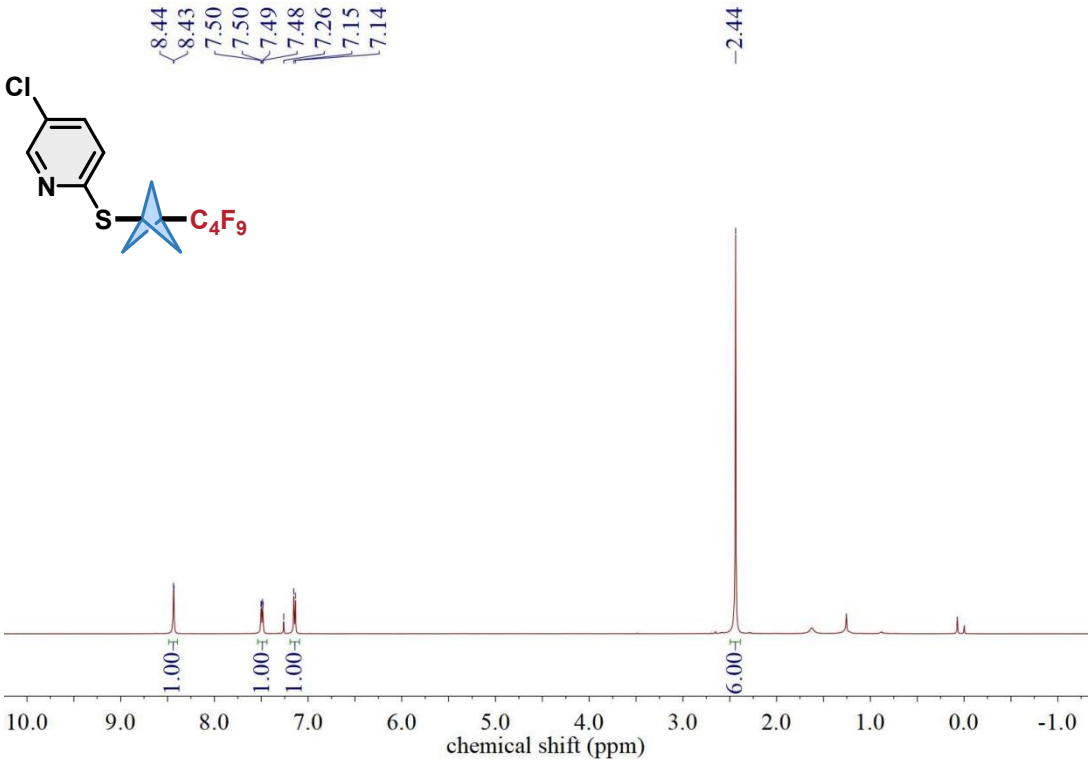
34 ^{13}C NMR (126 MHz, $CDCl_3$)



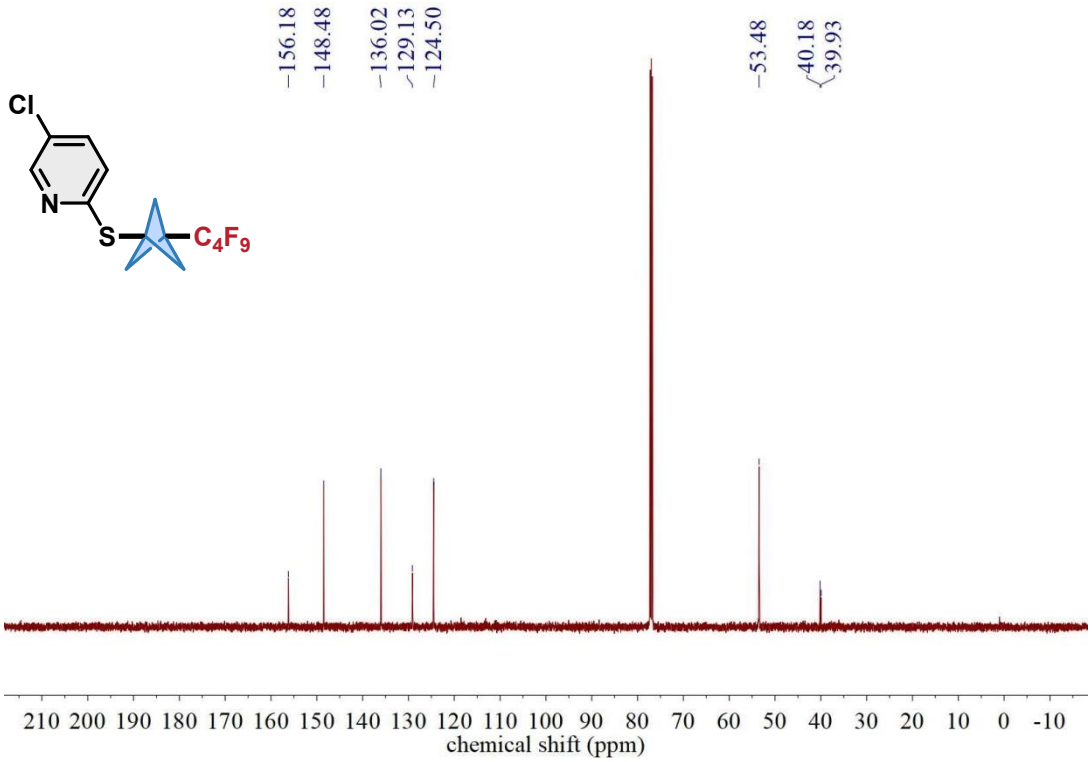
34 ^{19}F NMR (471 MHz, $CDCl_3$)



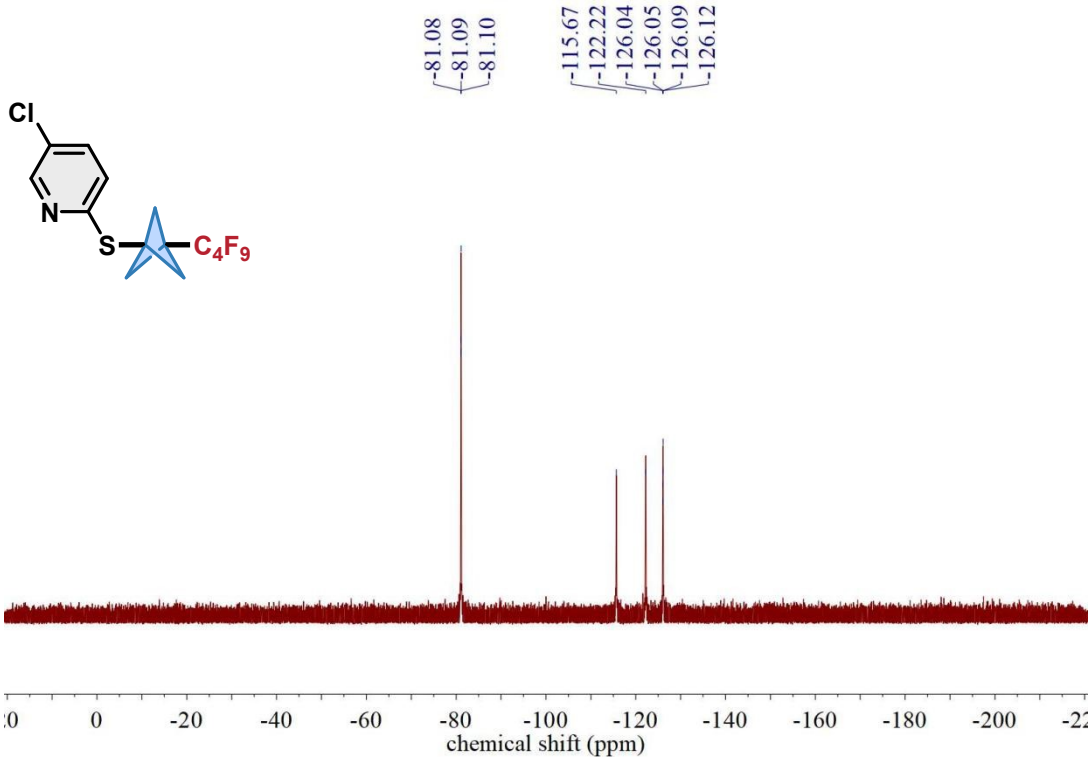
35 ^{1}H NMR (500 MHz, $CDCl_3$)



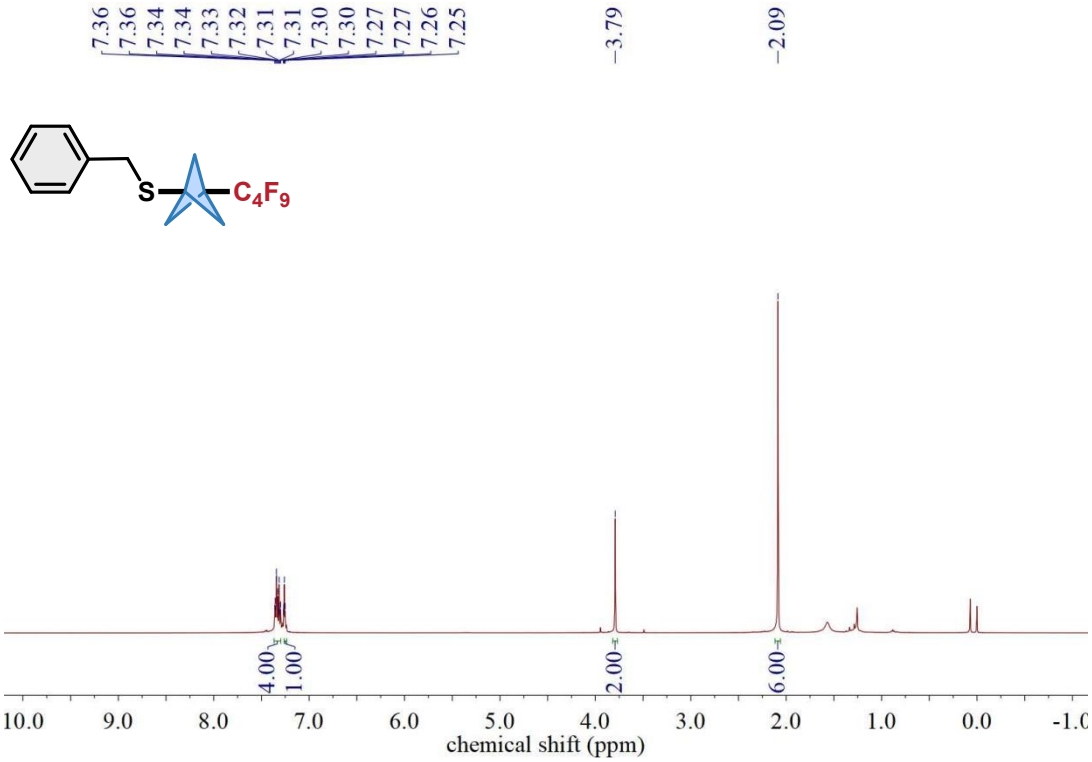
35 ^{13}C NMR (126 MHz, $CDCl_3$)



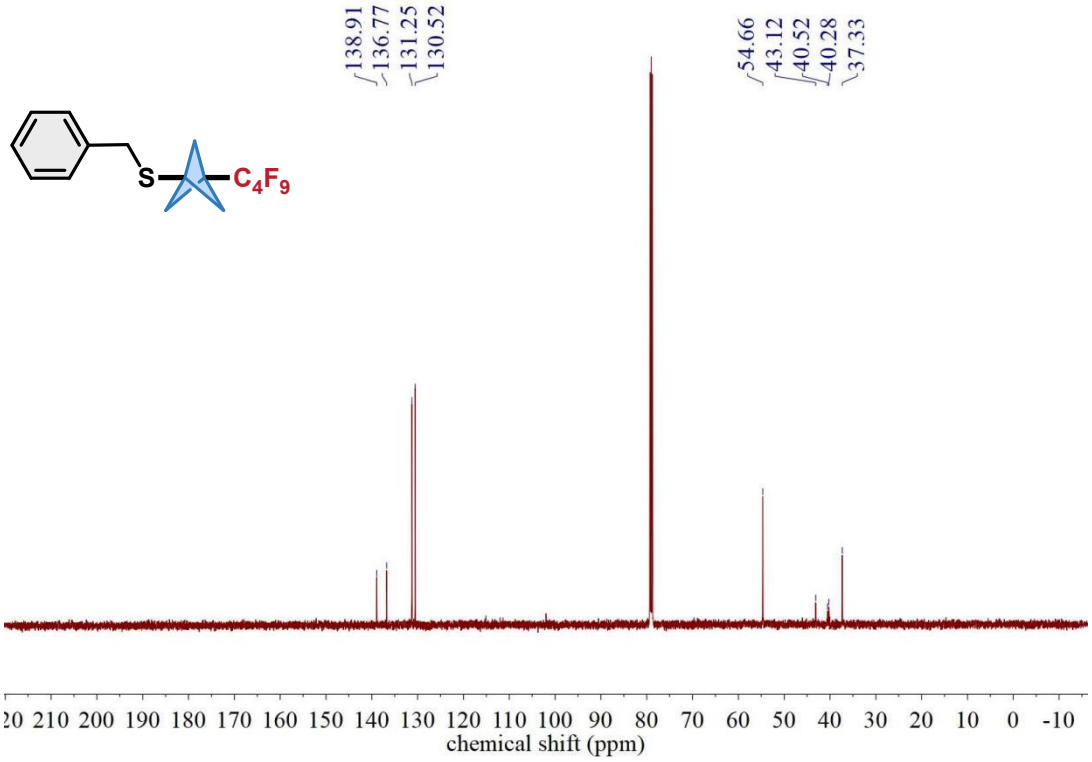
35 ^{19}F NMR (471 MHz, $CDCl_3$)



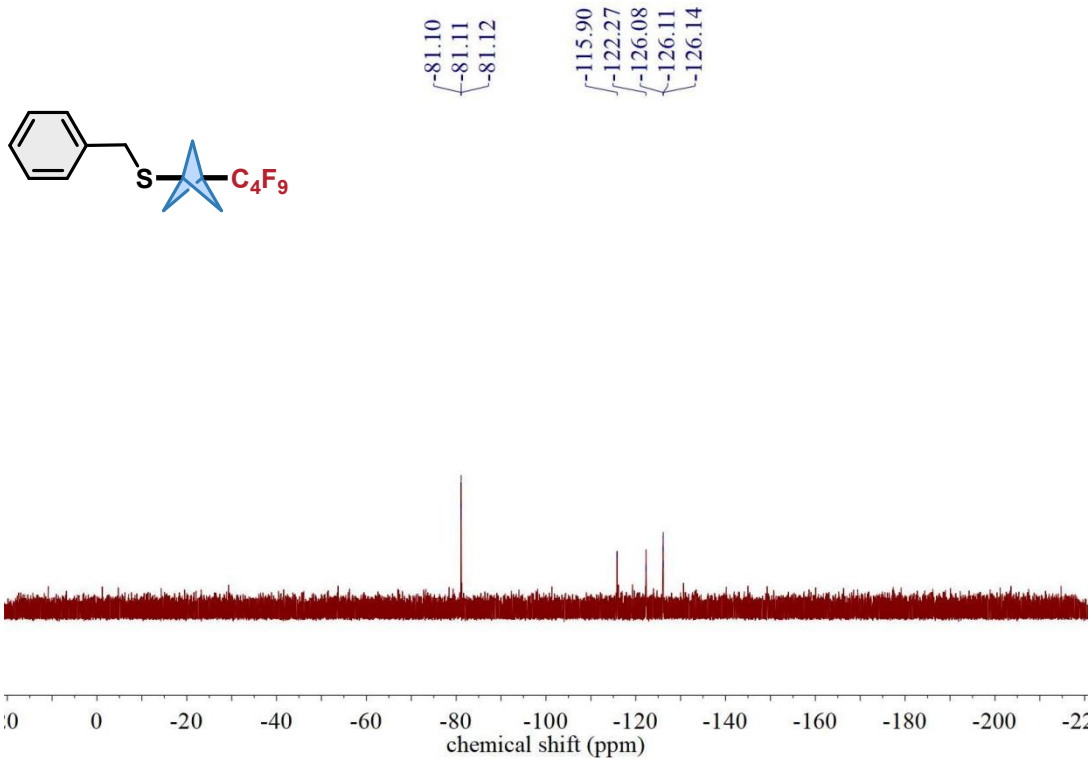
36 ^{1}H NMR (500 MHz, $CDCl_3$)



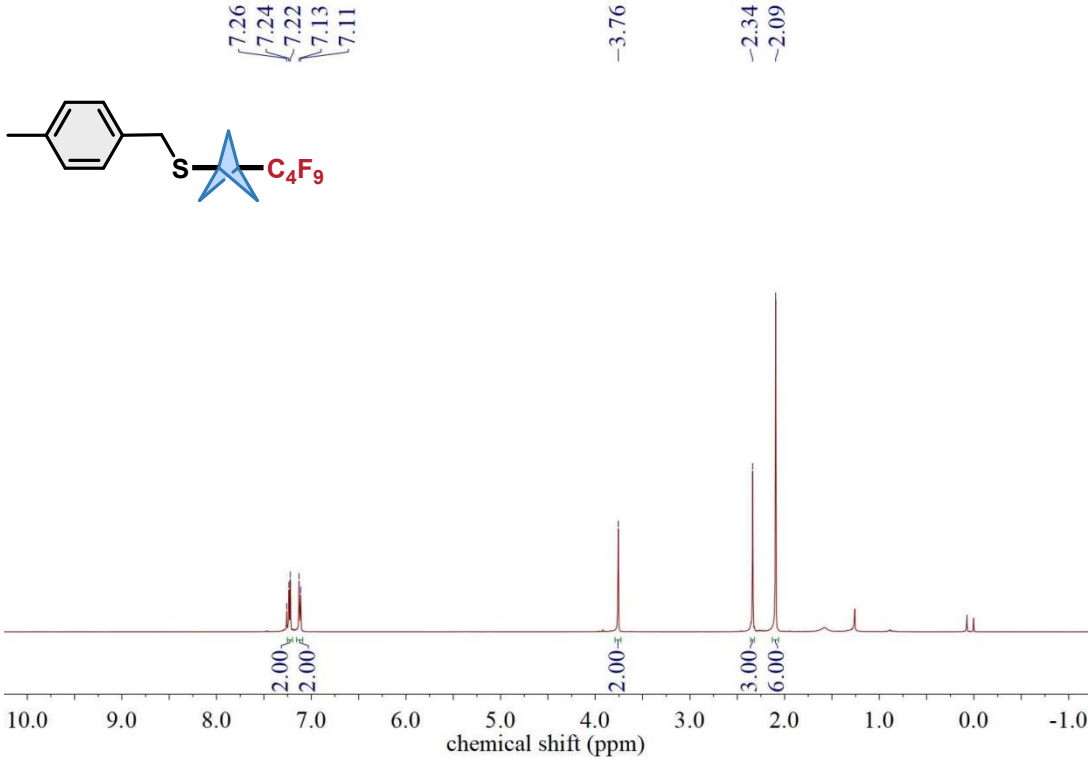
36 ^{13}C NMR (126 MHz, $CDCl_3$)



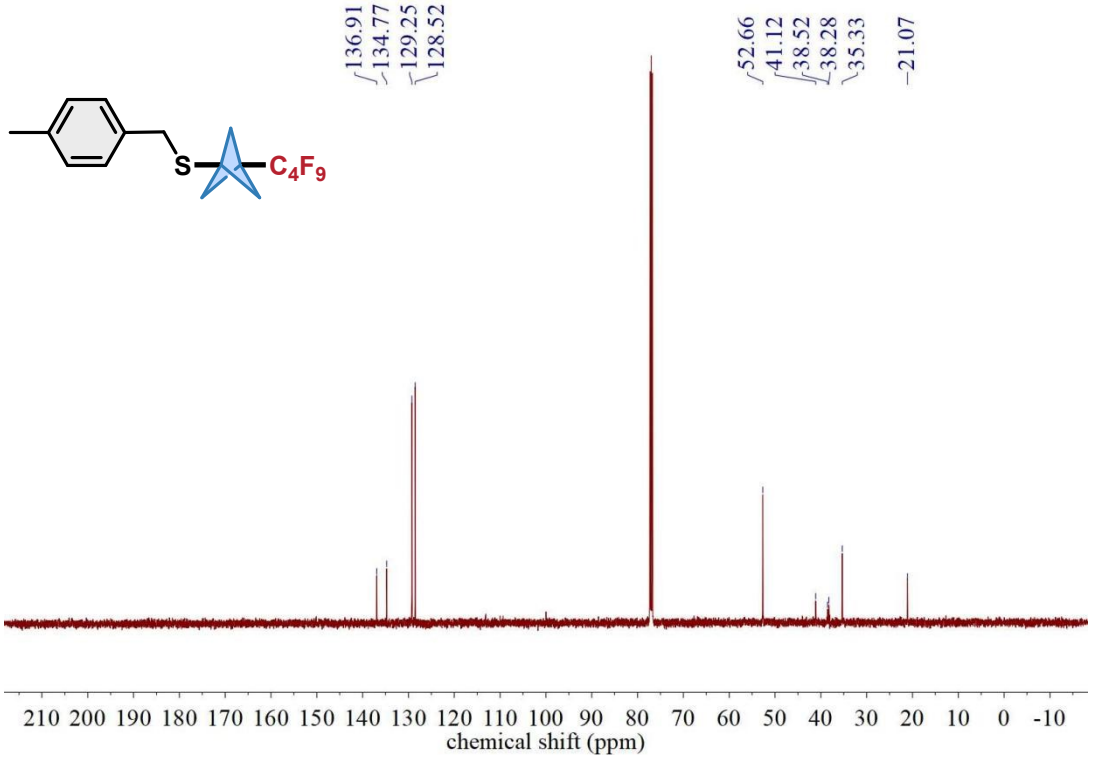
36 ^{19}F NMR (471 MHz, $CDCl_3$)



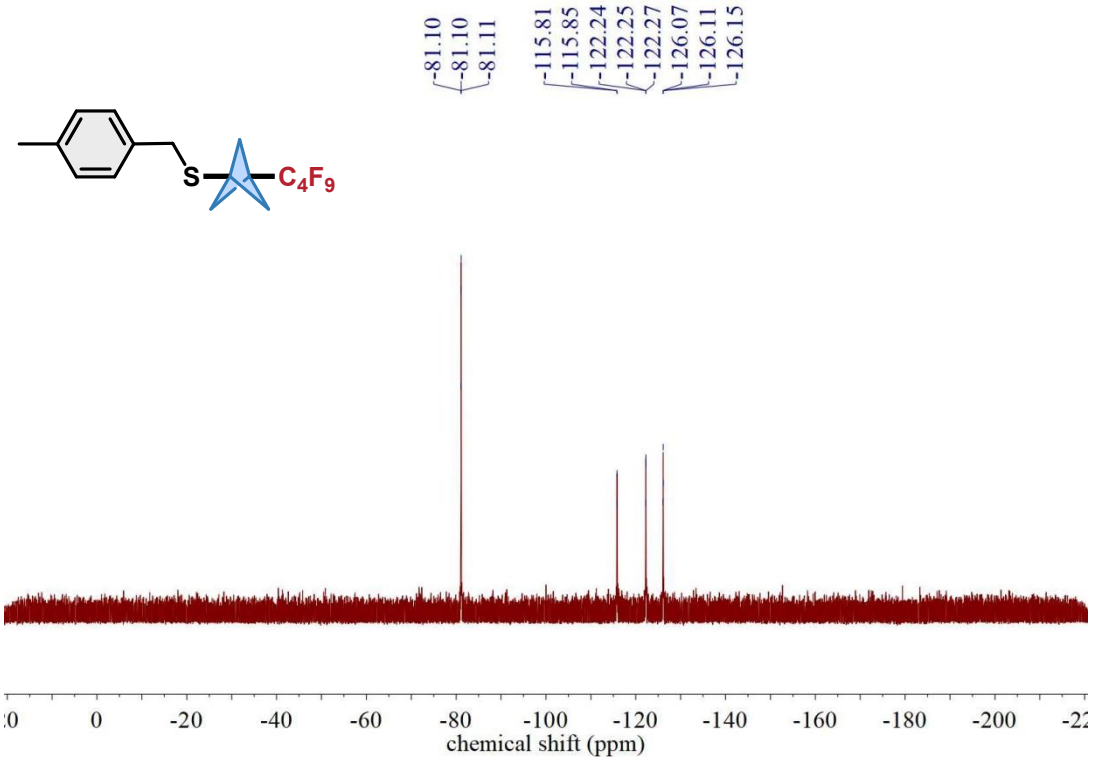
37 ^{1}H NMR (500 MHz, $CDCl_3$)



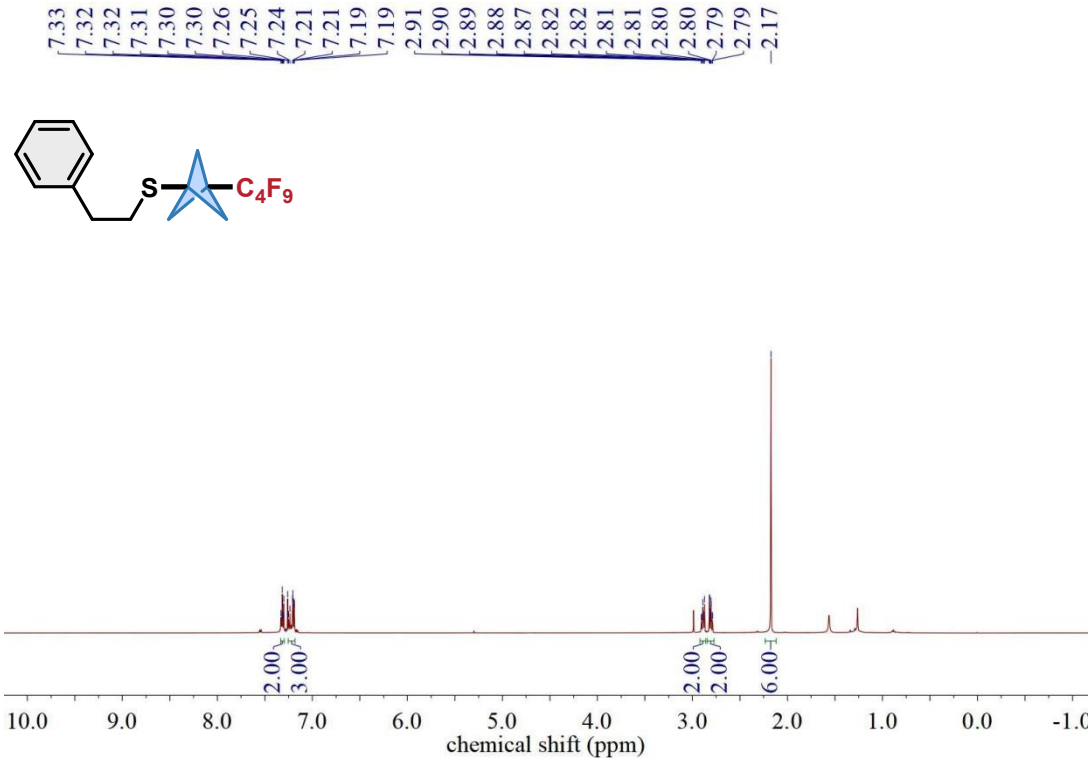
37 ^{13}C NMR (126 MHz, $CDCl_3$)



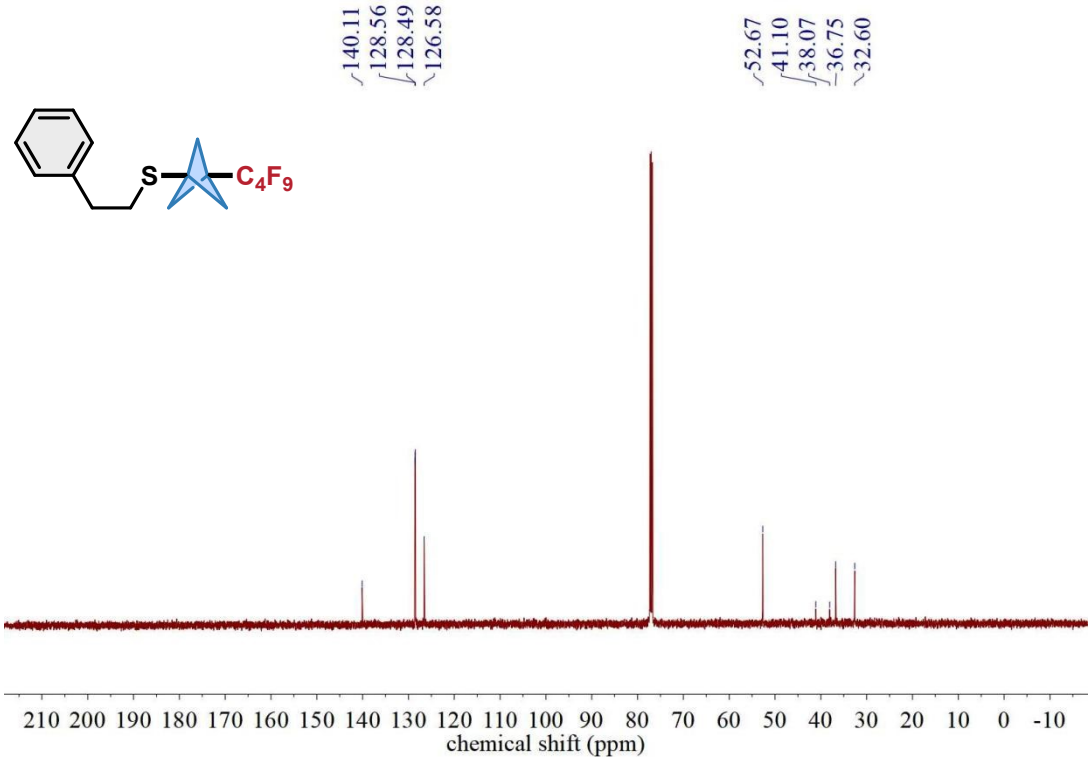
37 ^{19}F NMR (471 MHz, $CDCl_3$)



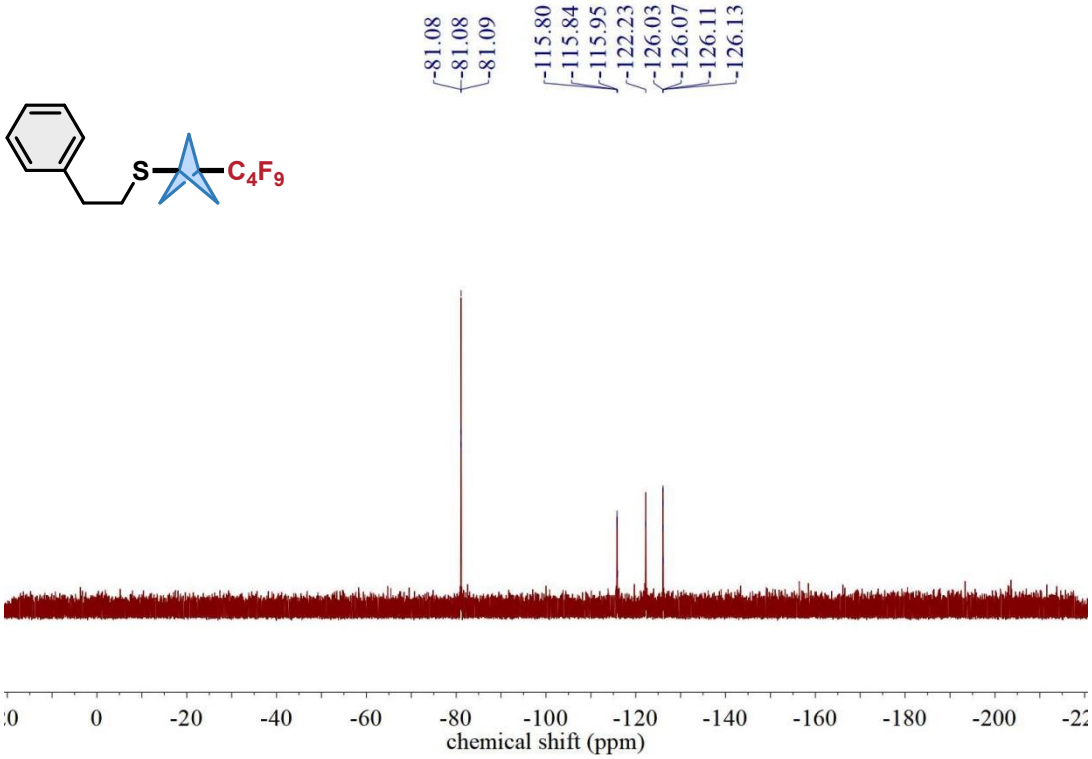
38 ^{1}H NMR (500 MHz, $CDCl_3$)



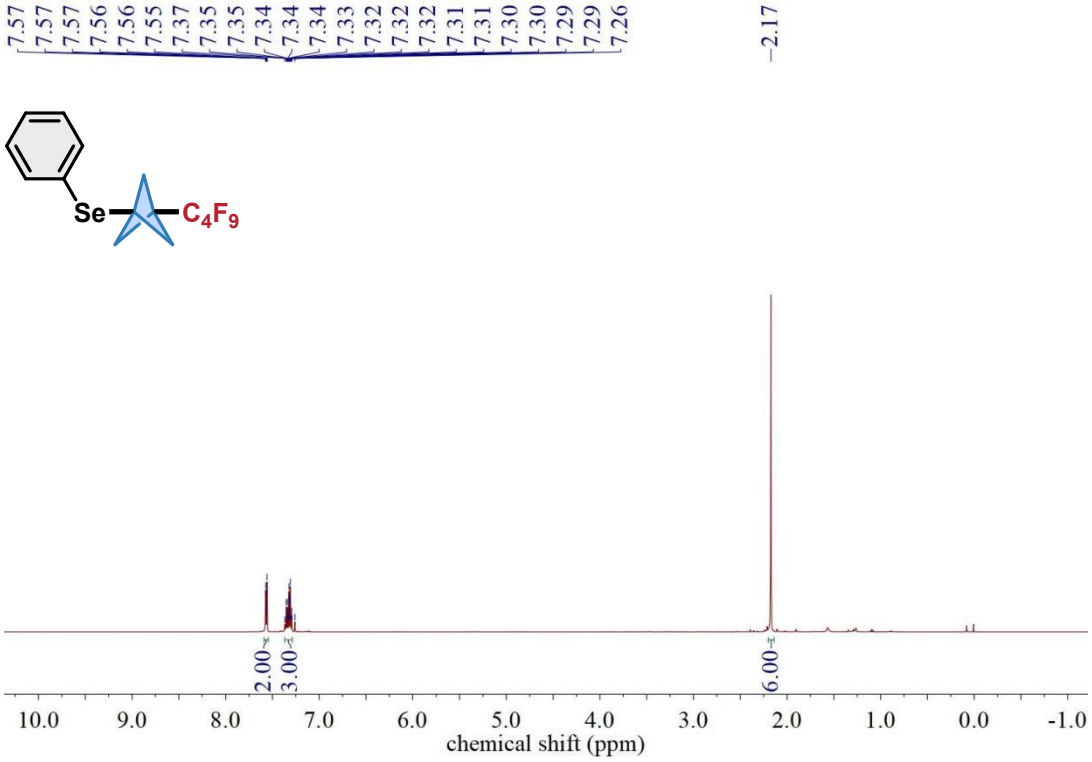
38 ^{13}C NMR (126 MHz, $CDCl_3$)



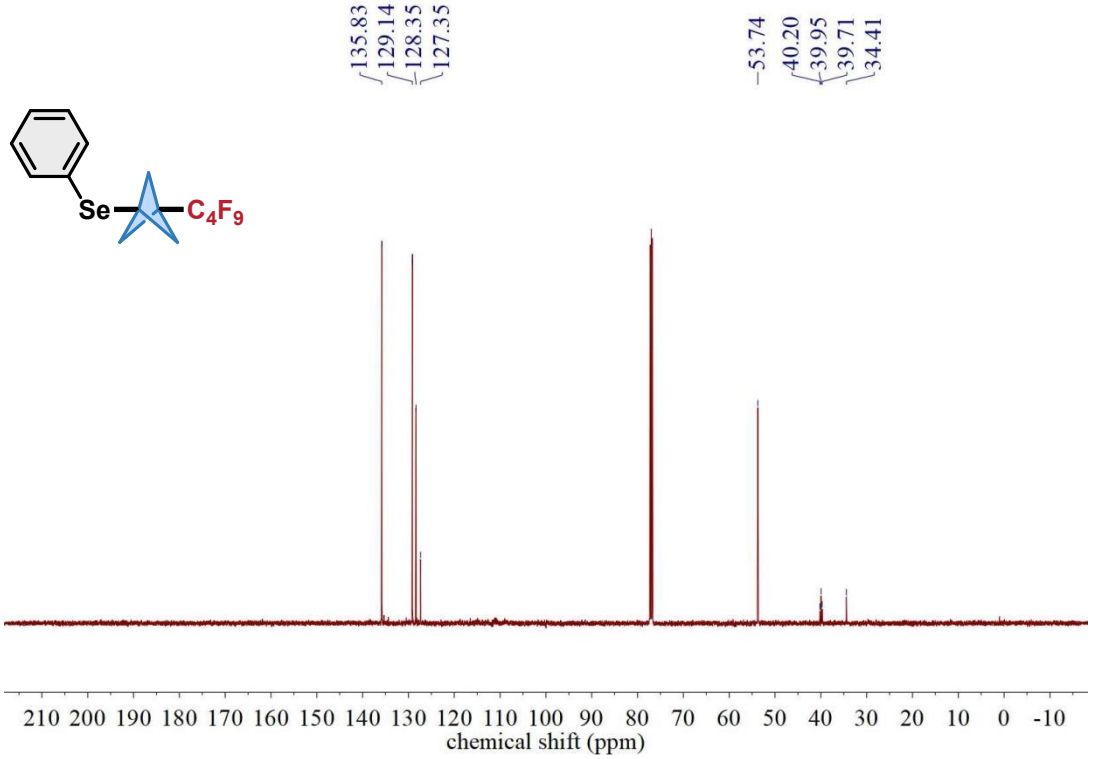
38 ^{19}F NMR (471 MHz, $CDCl_3$)



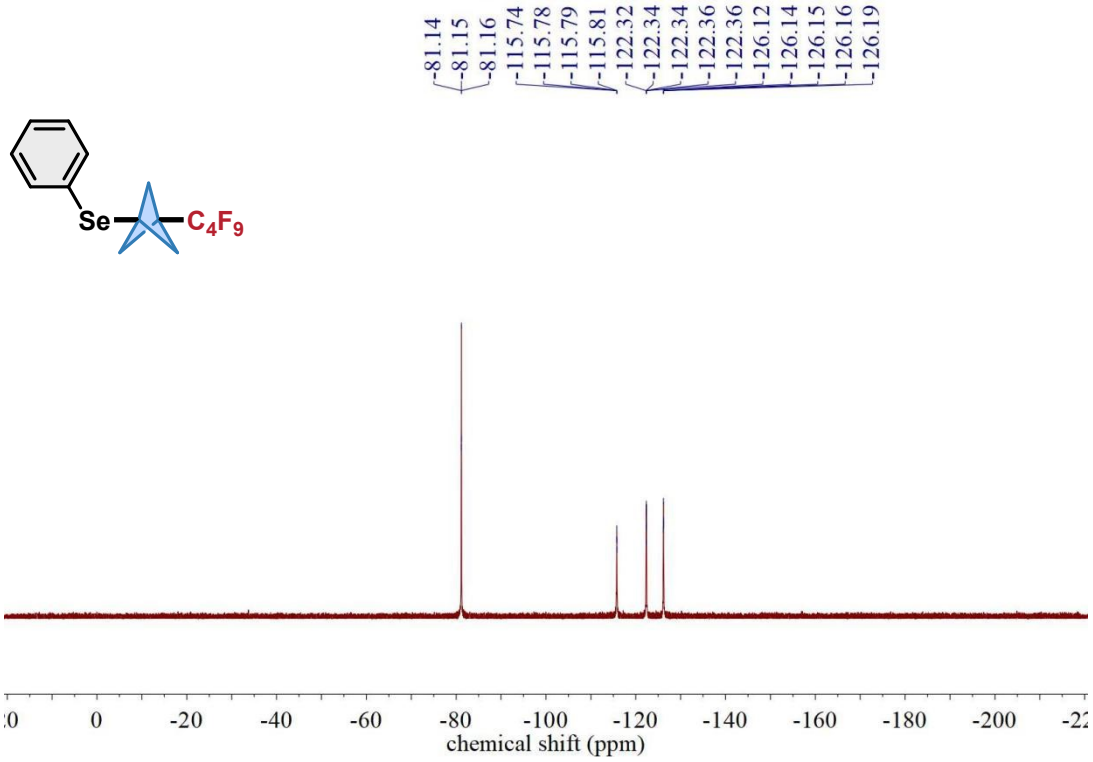
39 ^{1}H NMR (500 MHz, $CDCl_3$)



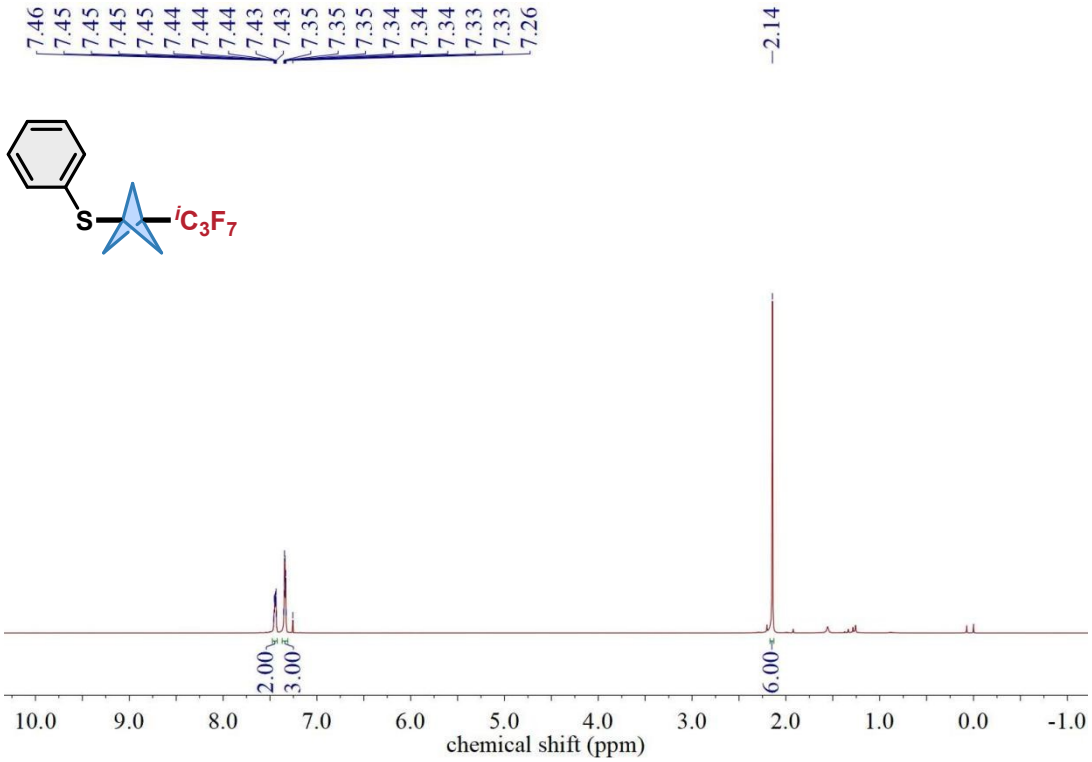
39 ^{13}C NMR (126 MHz, $CDCl_3$)



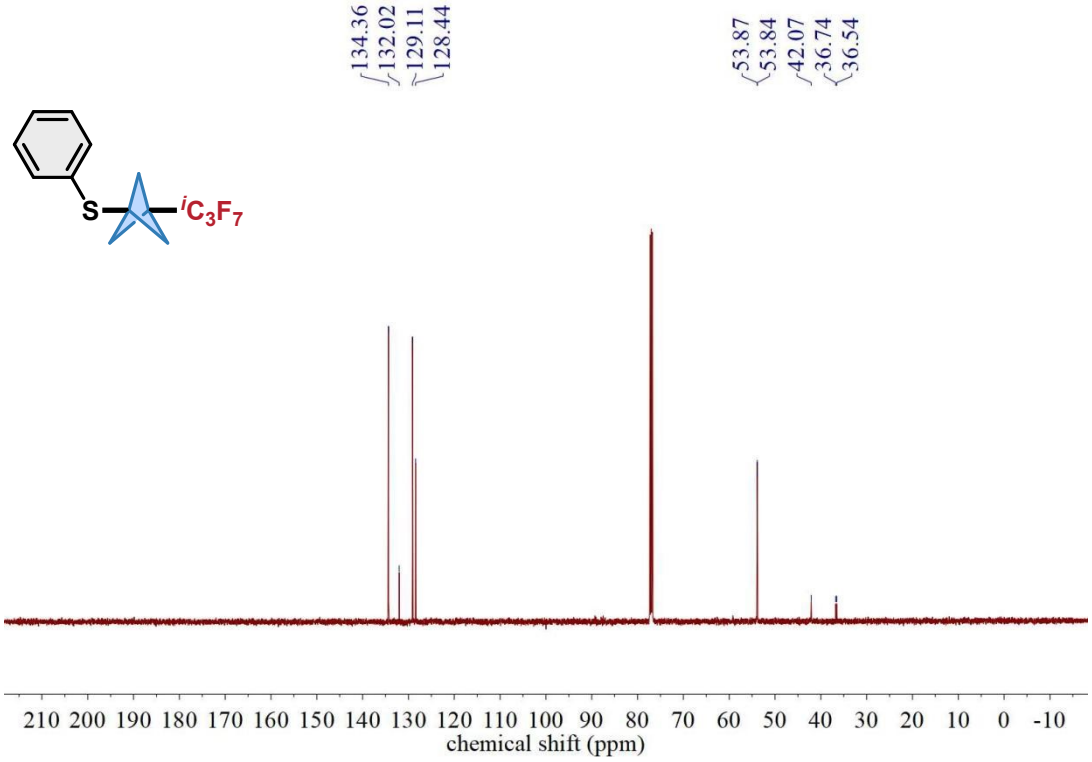
39 ^{19}F NMR (471 MHz, $CDCl_3$)



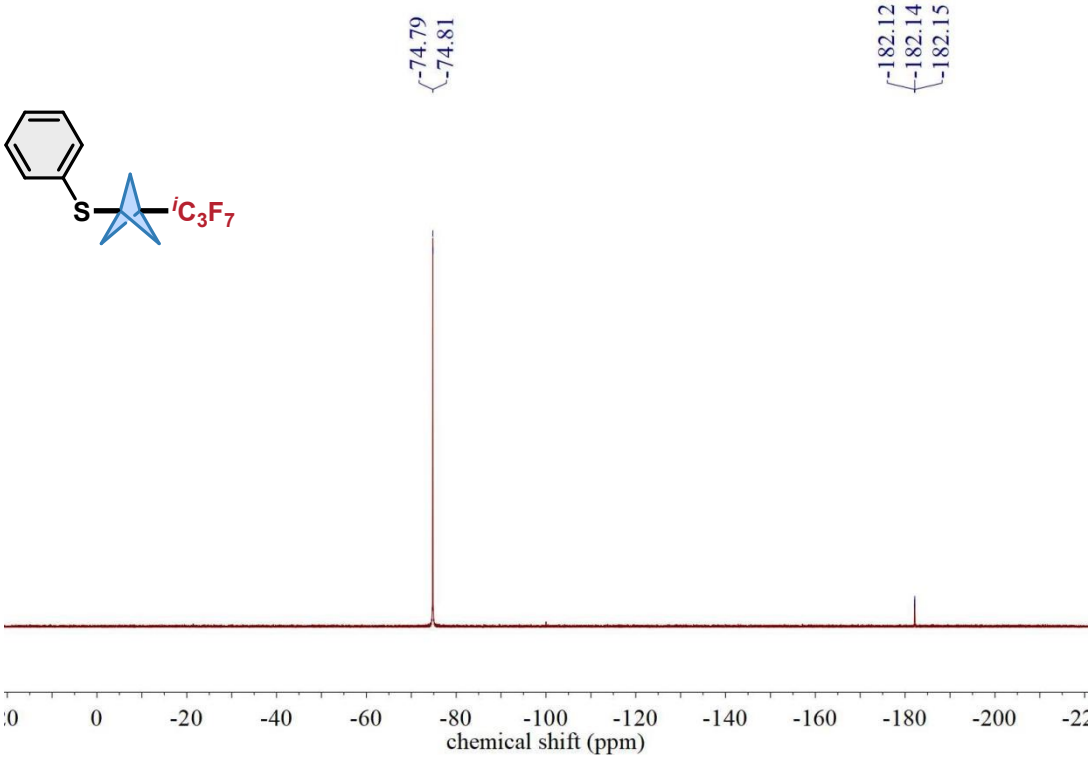
40 ^{1}H NMR (500 MHz, $CDCl_3$)



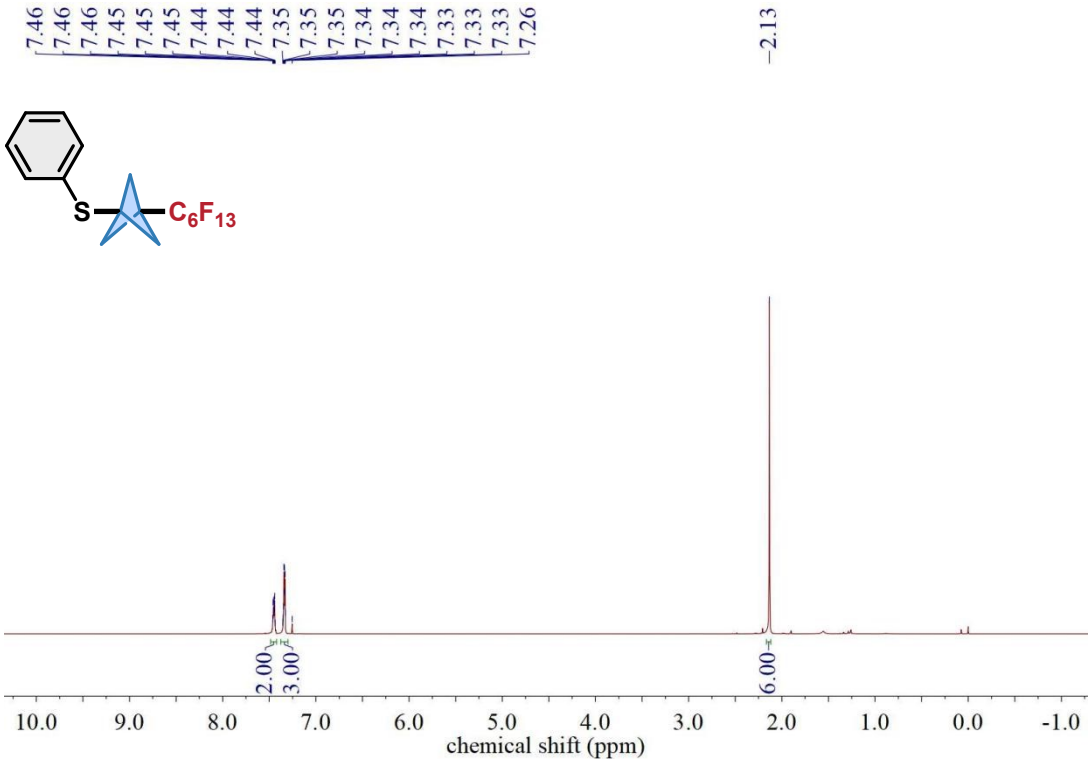
40 ^{13}C NMR (126 MHz, $CDCl_3$)



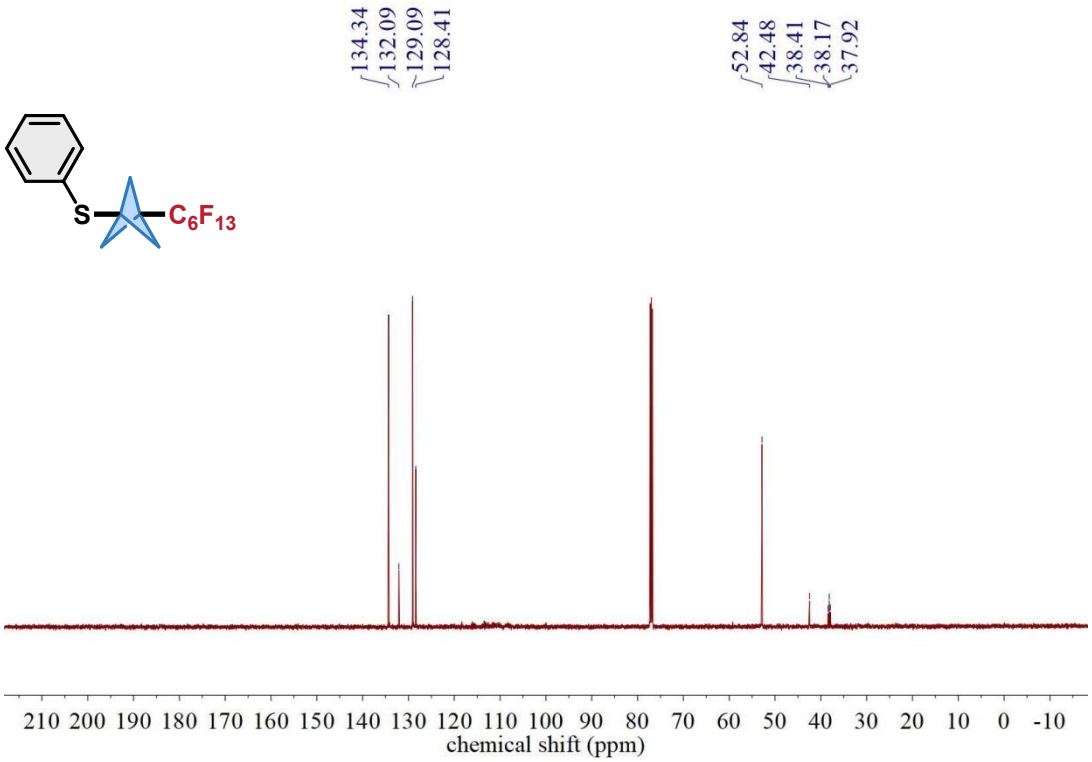
40 ^{19}F NMR (471 MHz, $CDCl_3$)



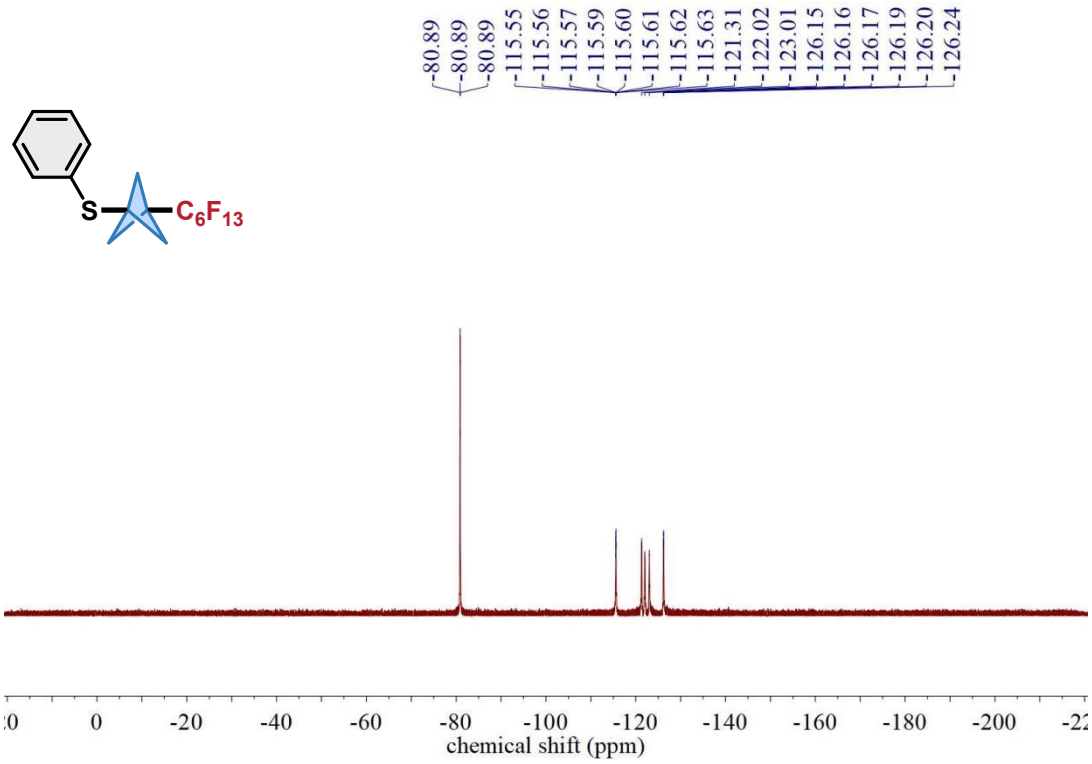
41 ^{1}H NMR (500 MHz, $CDCl_3$)



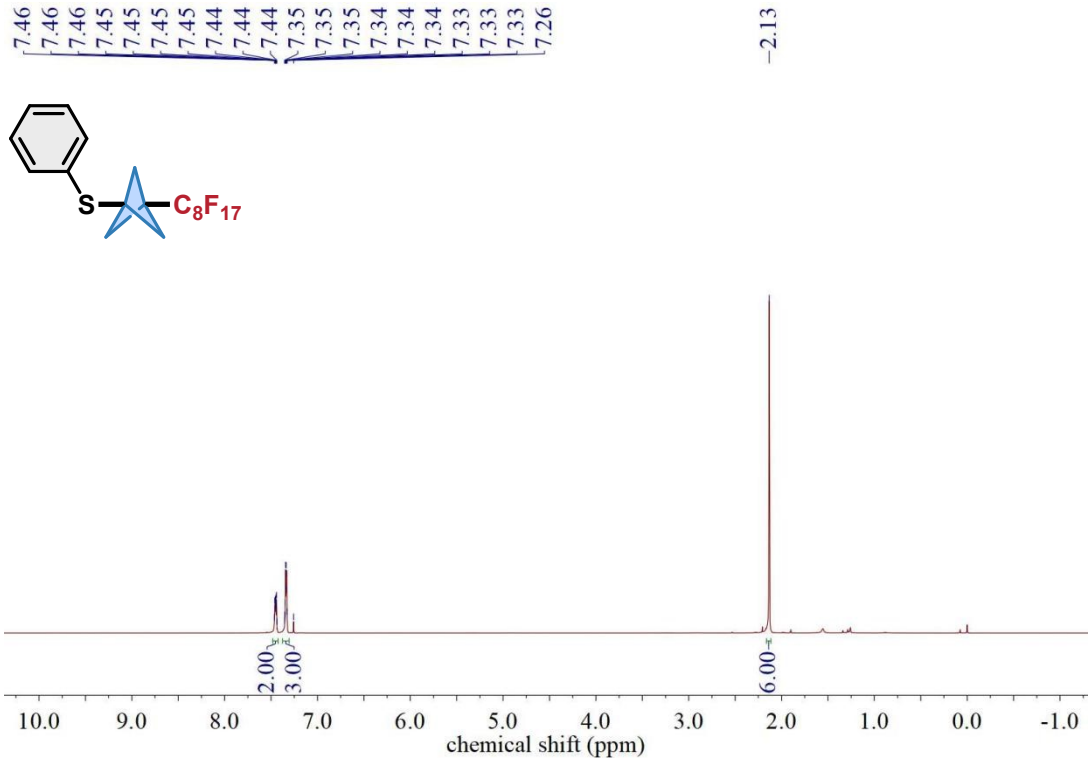
41 ^{13}C NMR (126 MHz, $CDCl_3$)



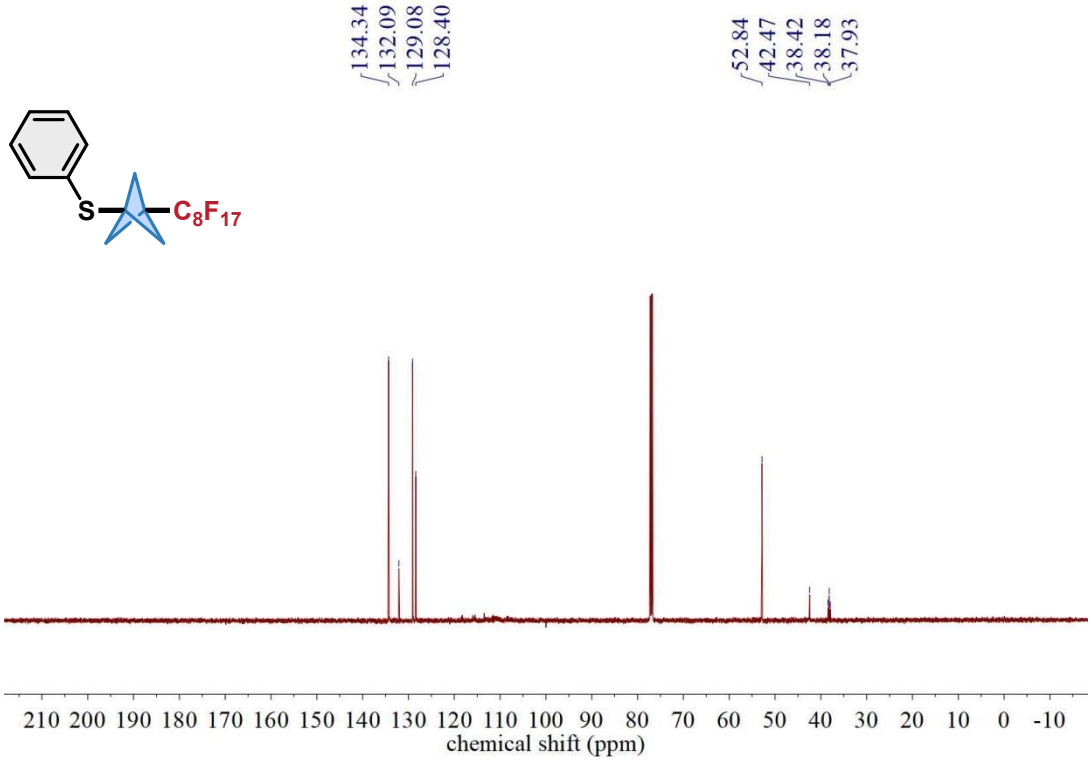
41 ^{19}F NMR (471 MHz, $CDCl_3$)



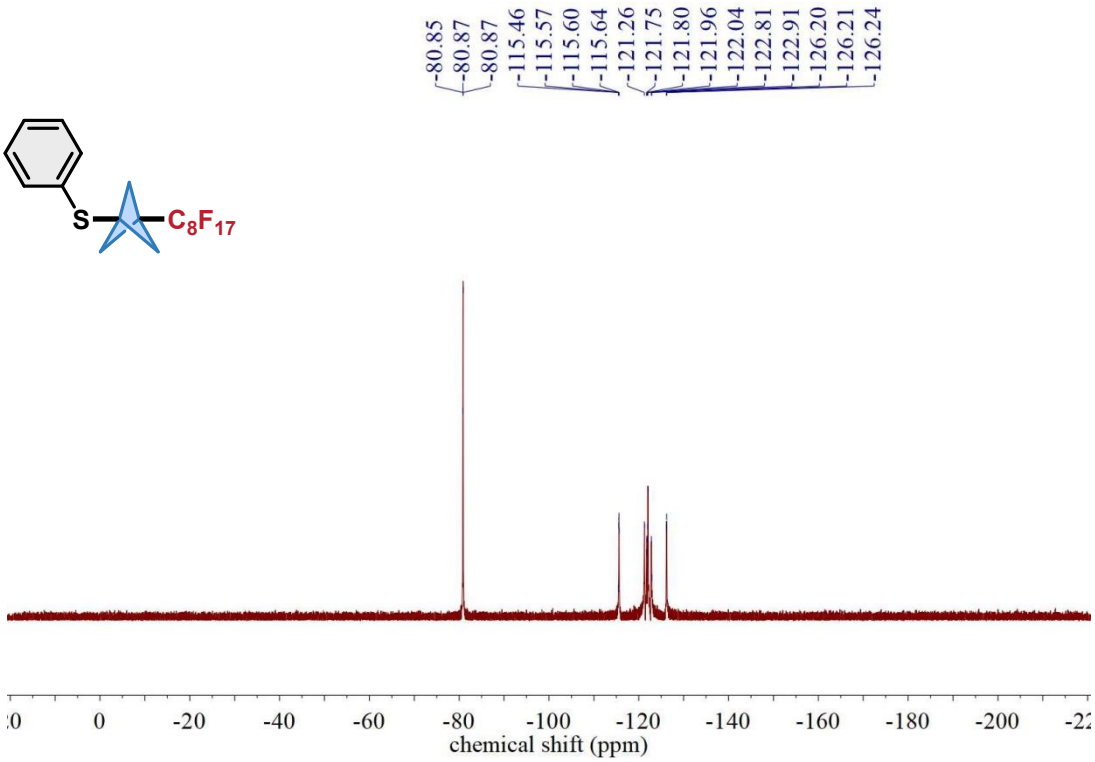
42 ^{1}H NMR (500 MHz, $CDCl_3$)



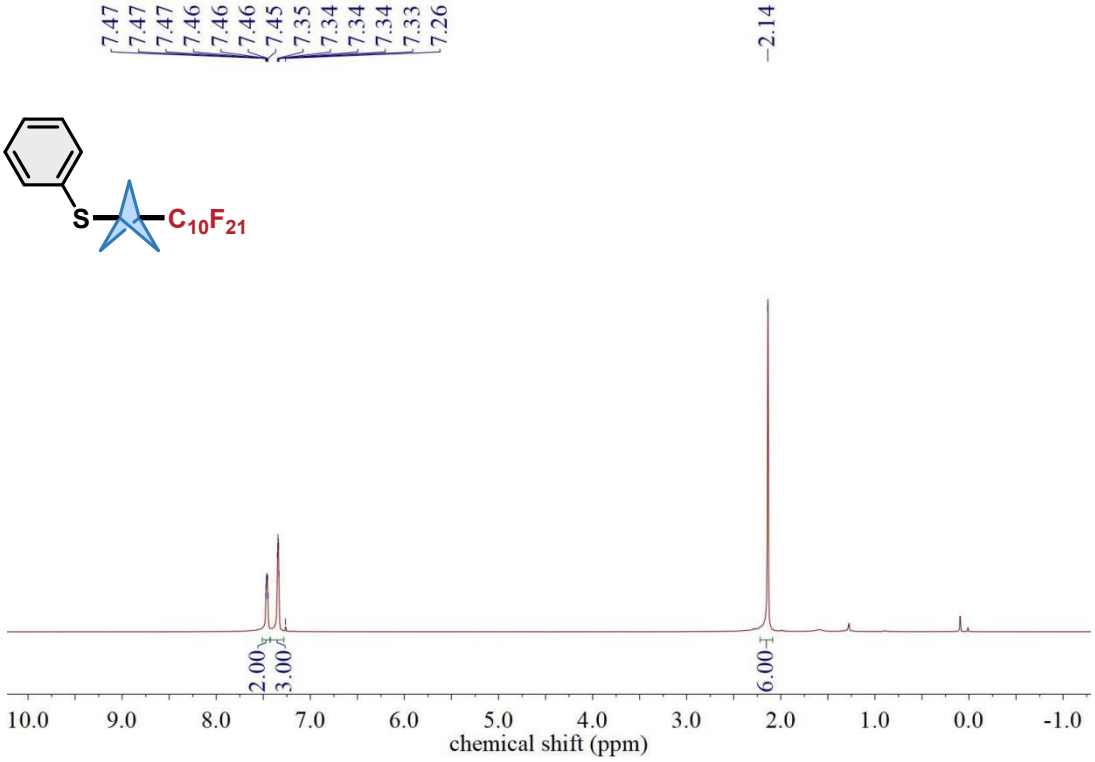
42 ^{13}C NMR (126 MHz, $CDCl_3$)



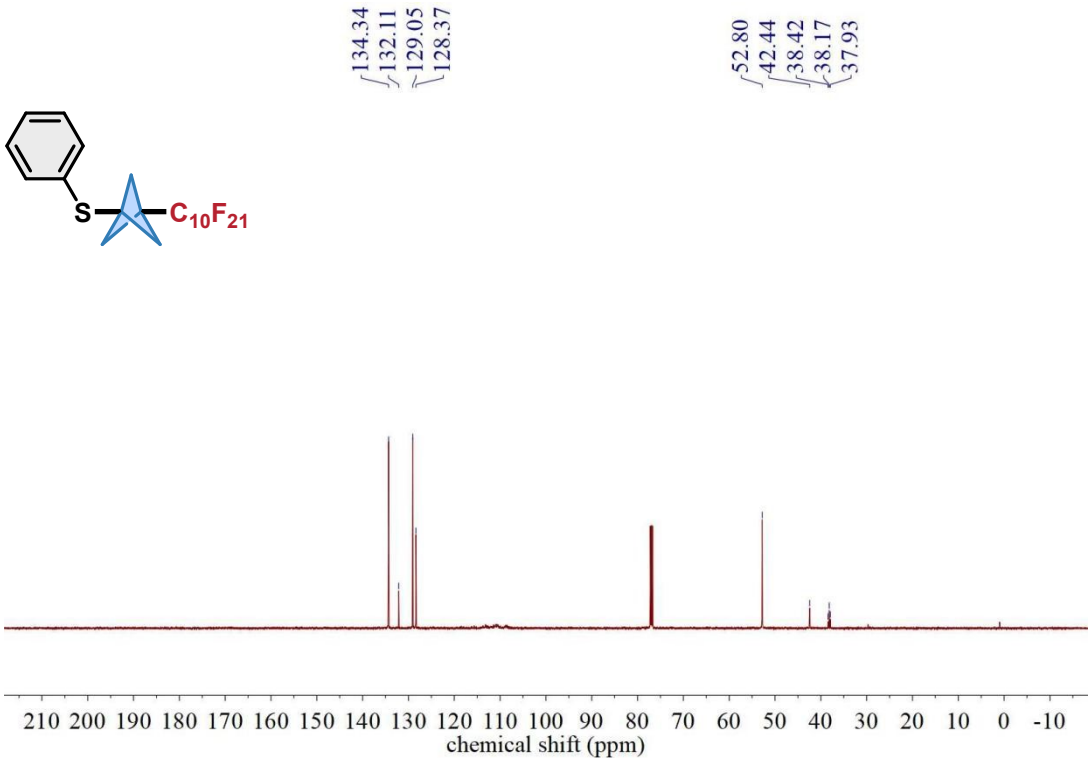
42 ^{19}F NMR (471 MHz, $CDCl_3$)



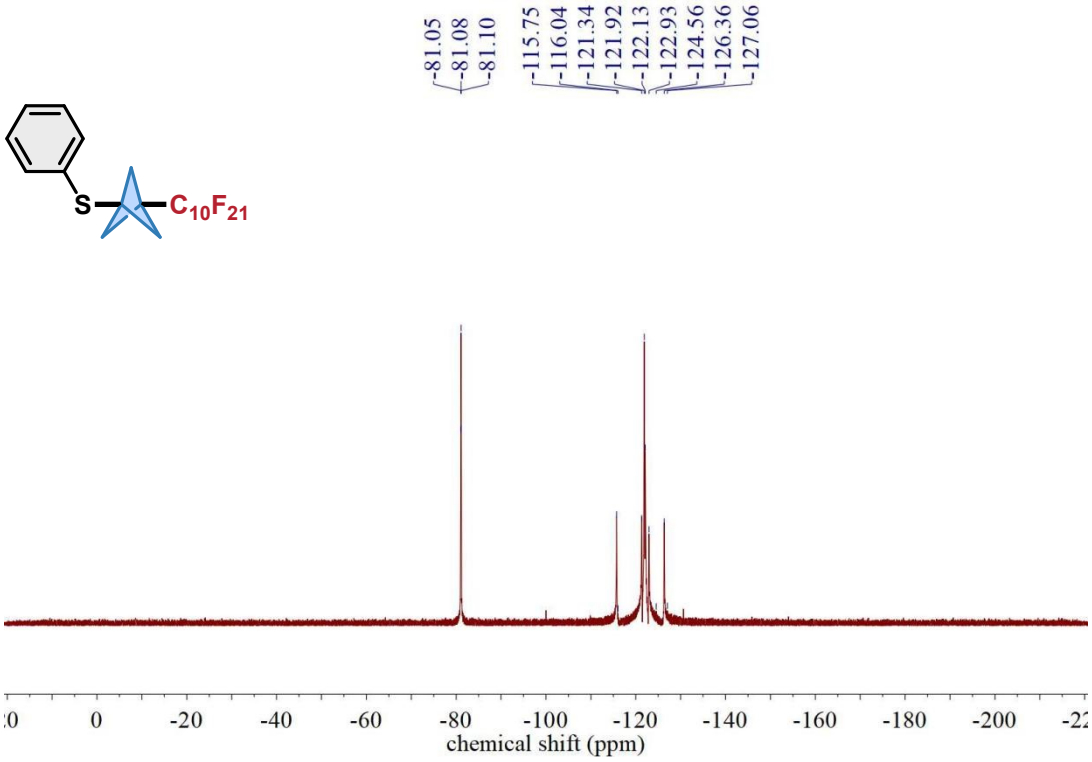
43 ^{1}H NMR (500 MHz, $CDCl_3$)



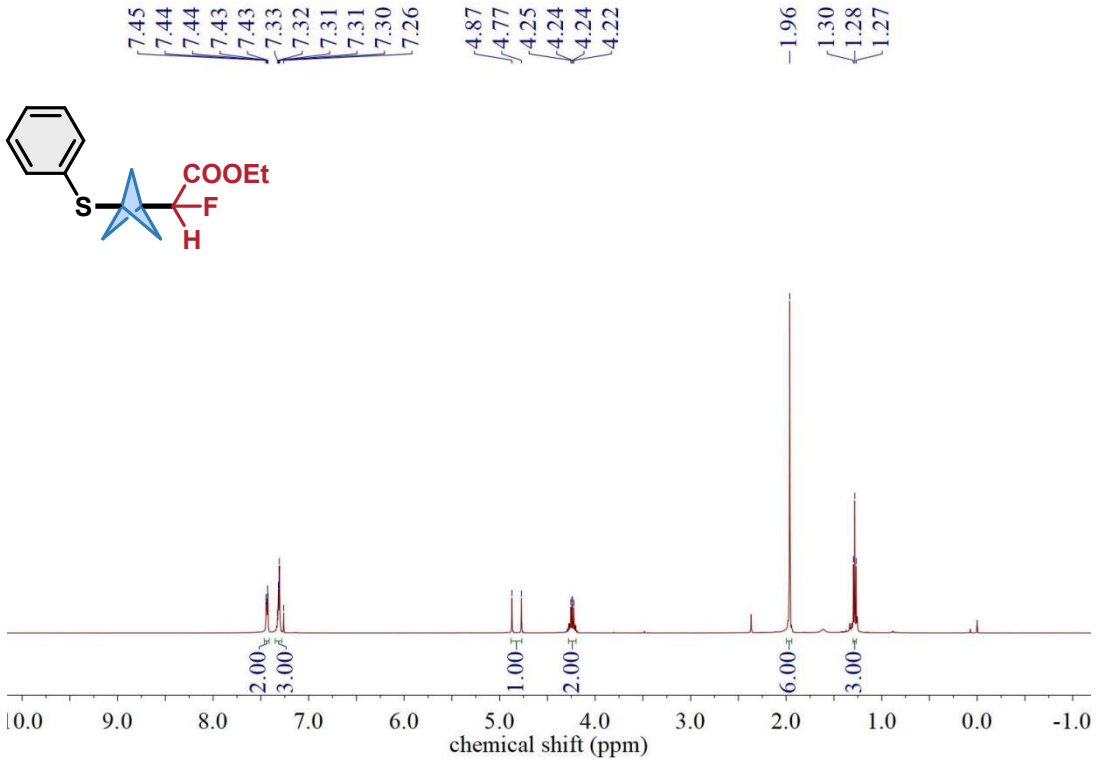
43 ^{13}C NMR (126 MHz, $CDCl_3$)



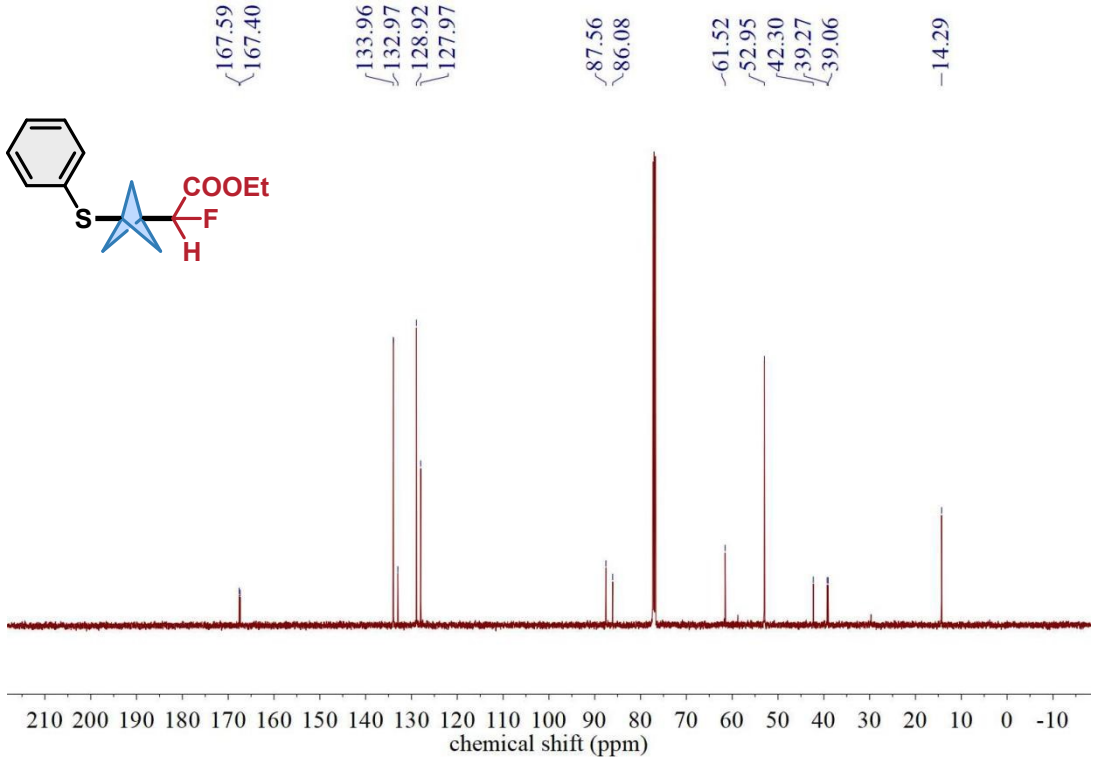
43 ^{19}F NMR (471 MHz, $CDCl_3$)



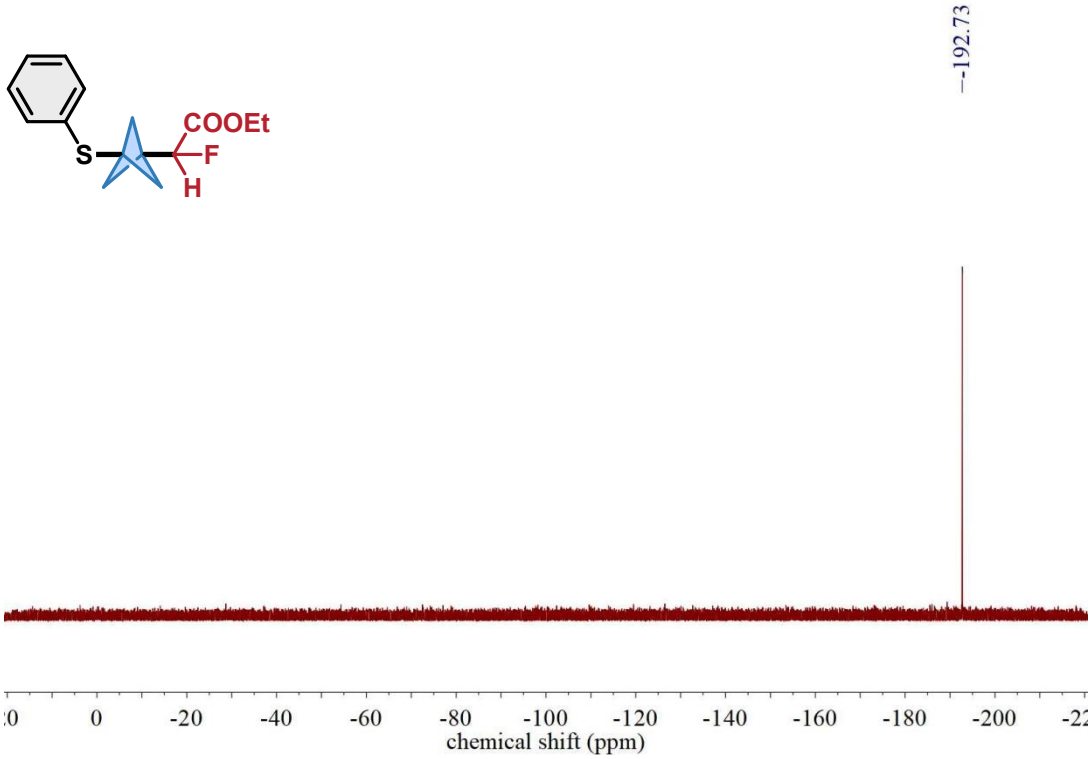
44 ^{1}H NMR (500 MHz, $CDCl_3$)



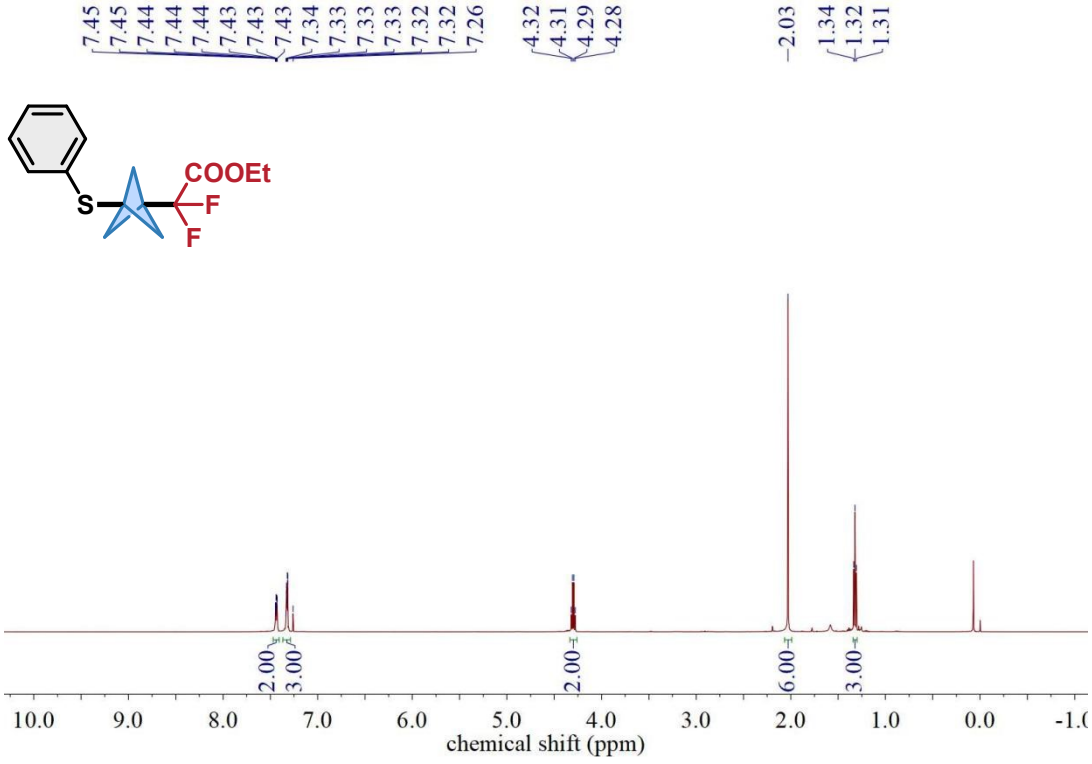
44 ^{13}C NMR (126 MHz, $CDCl_3$)



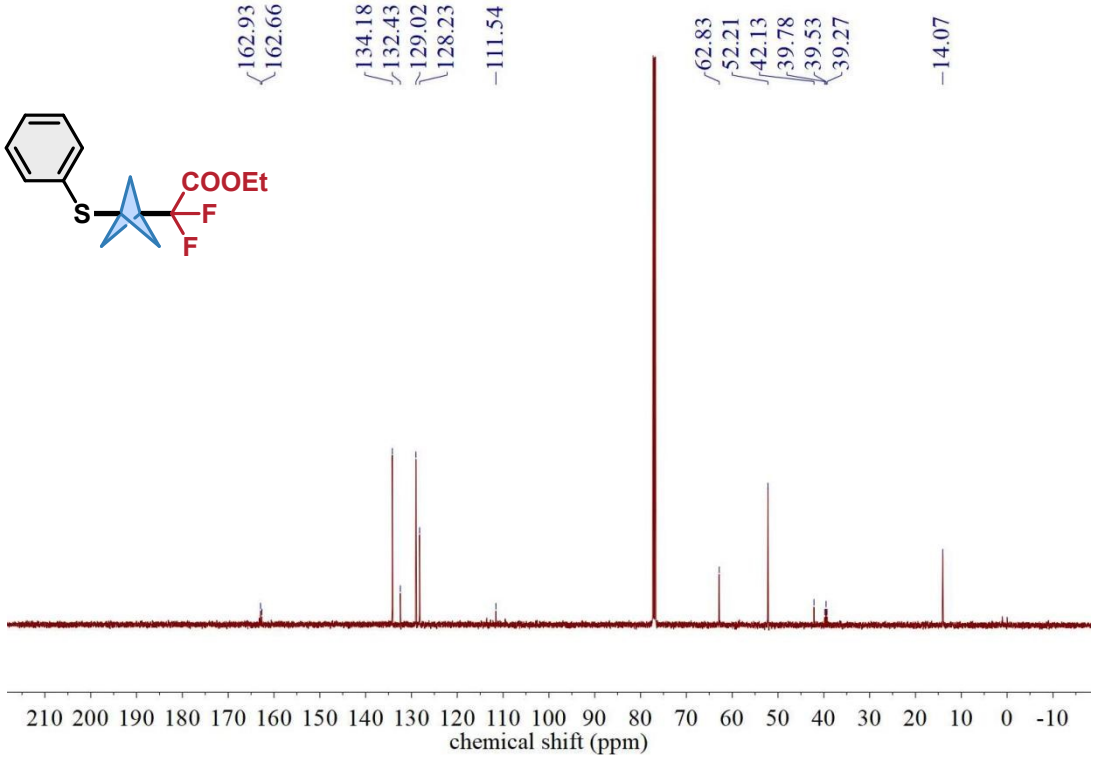
44 ^{19}F NMR (471 MHz, $CDCl_3$)



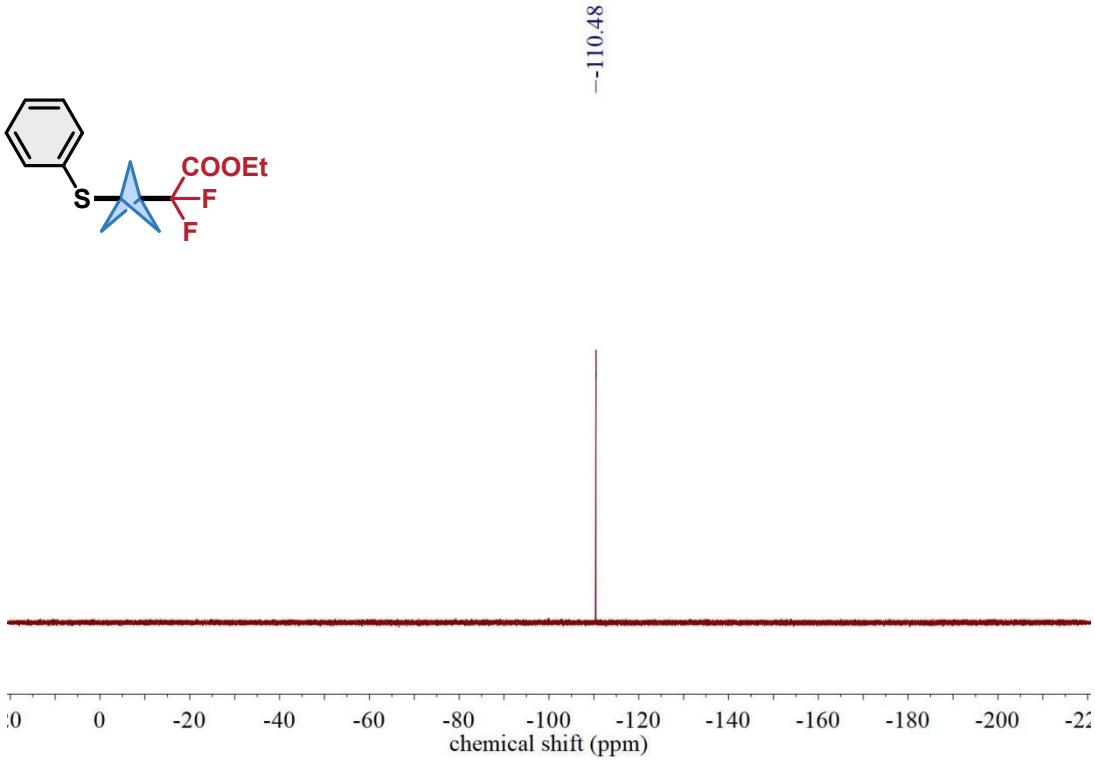
45 ^{1}H NMR (500 MHz, $CDCl_3$)



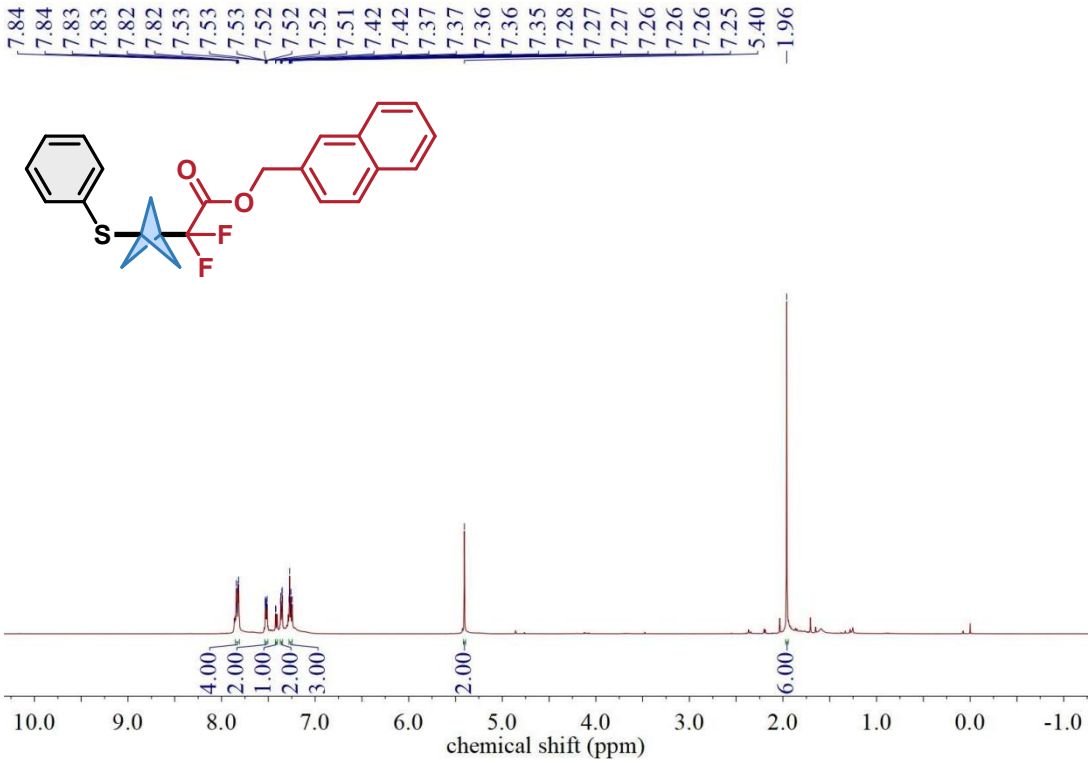
45 ^{13}C NMR (126 MHz, $CDCl_3$)



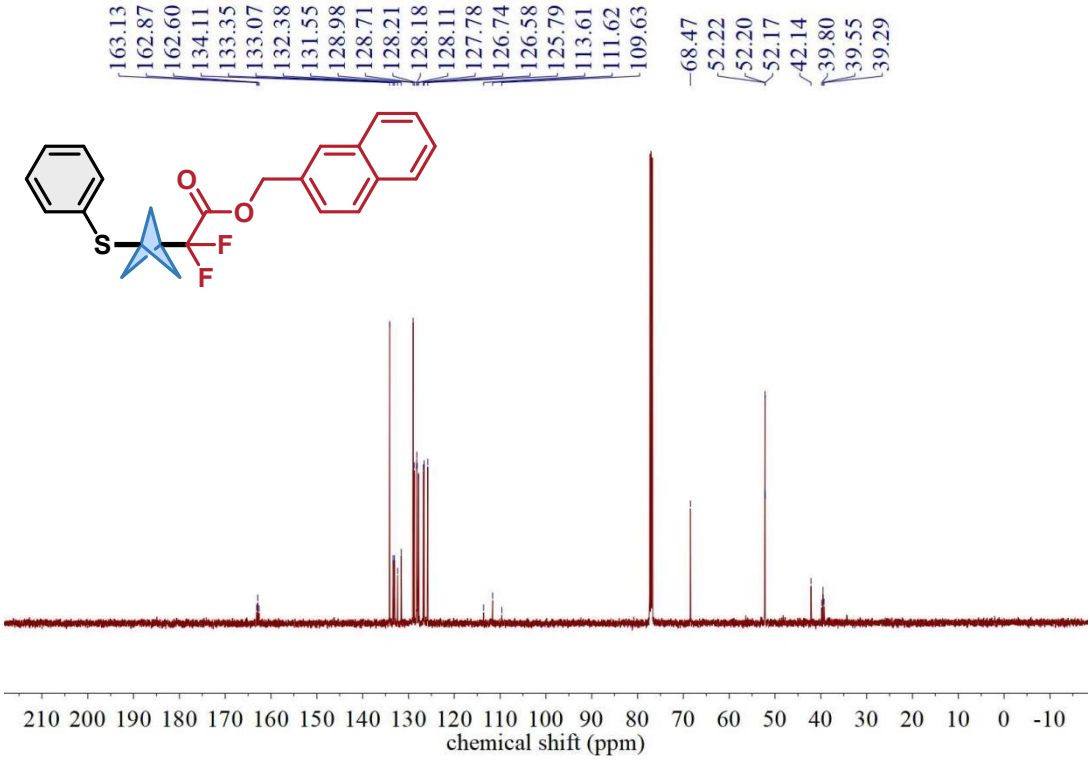
45 ^{19}F NMR (471 MHz, $CDCl_3$)



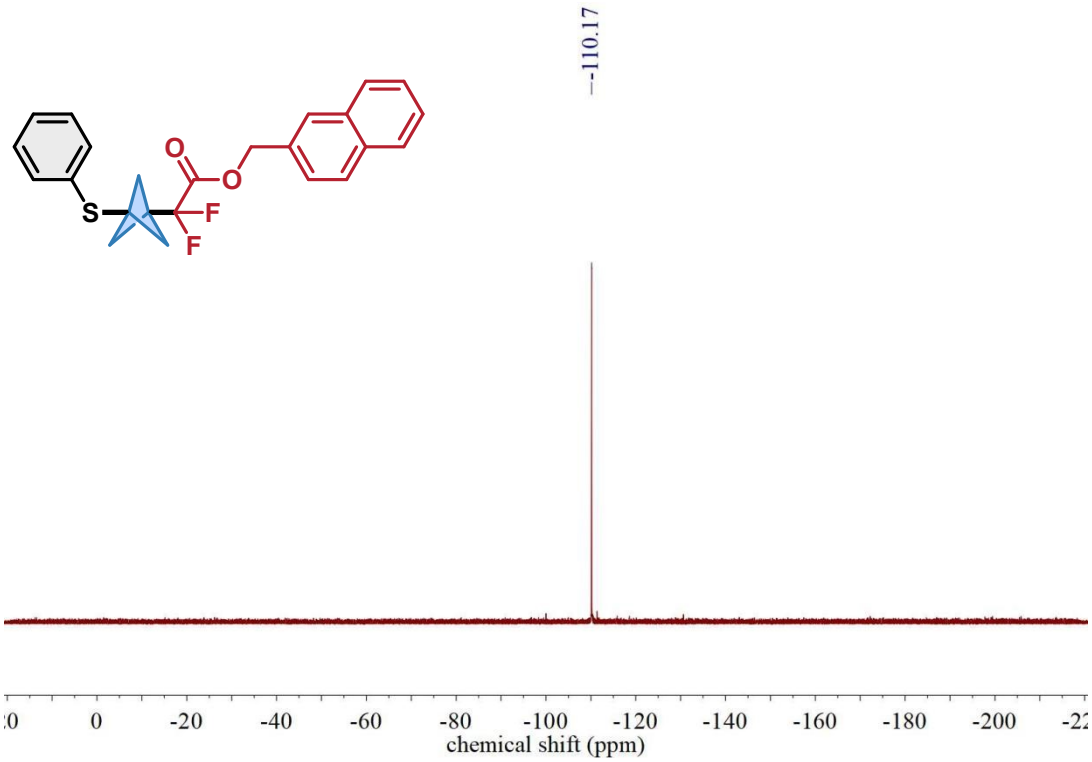
46 ^{1}H NMR (500 MHz, $CDCl_3$)



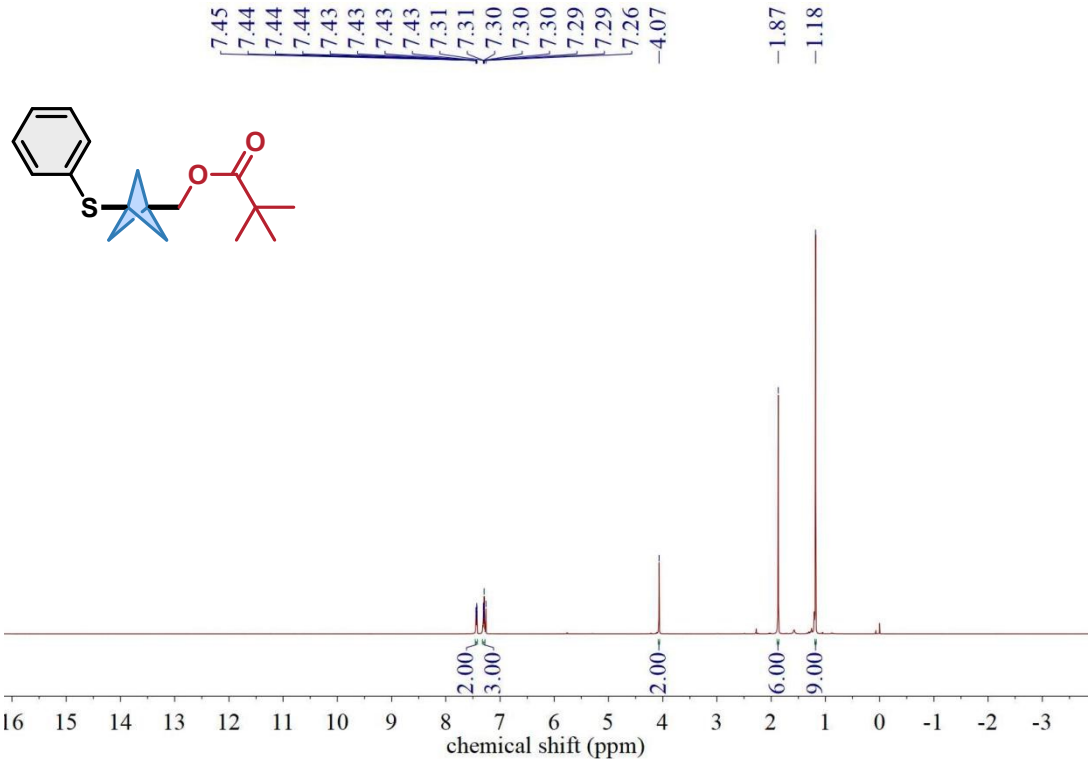
46 ^{13}C NMR (126 MHz, $CDCl_3$)



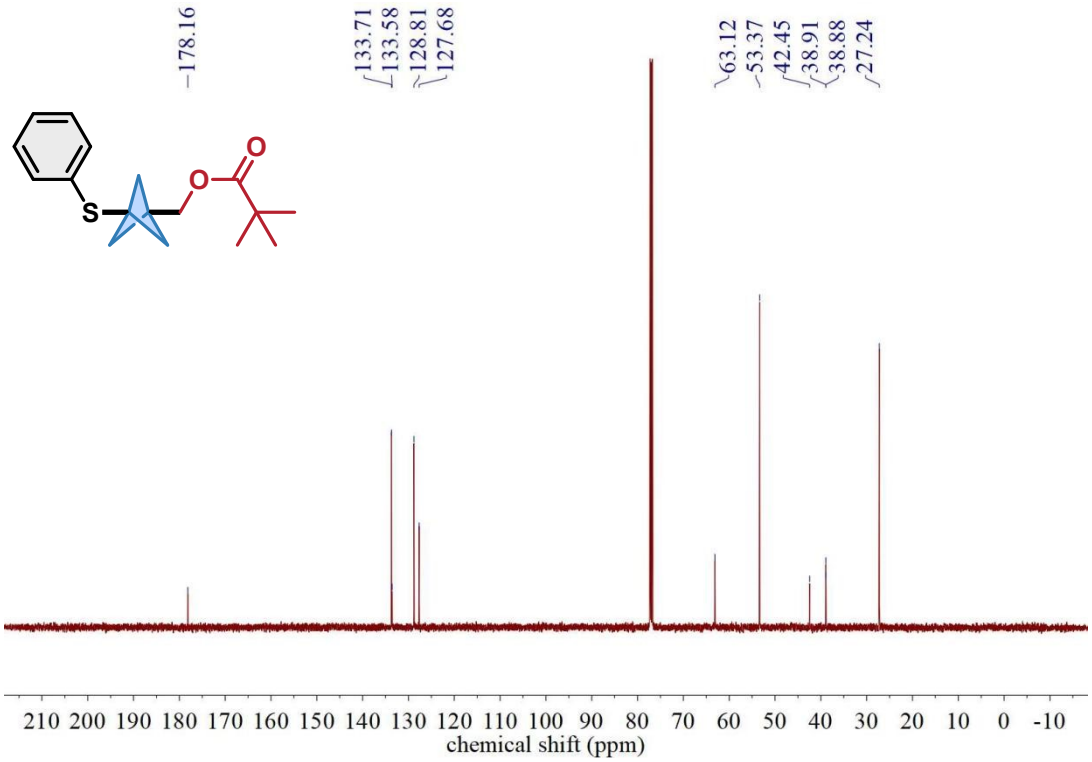
46 ^{19}F NMR (471 MHz, $CDCl_3$)



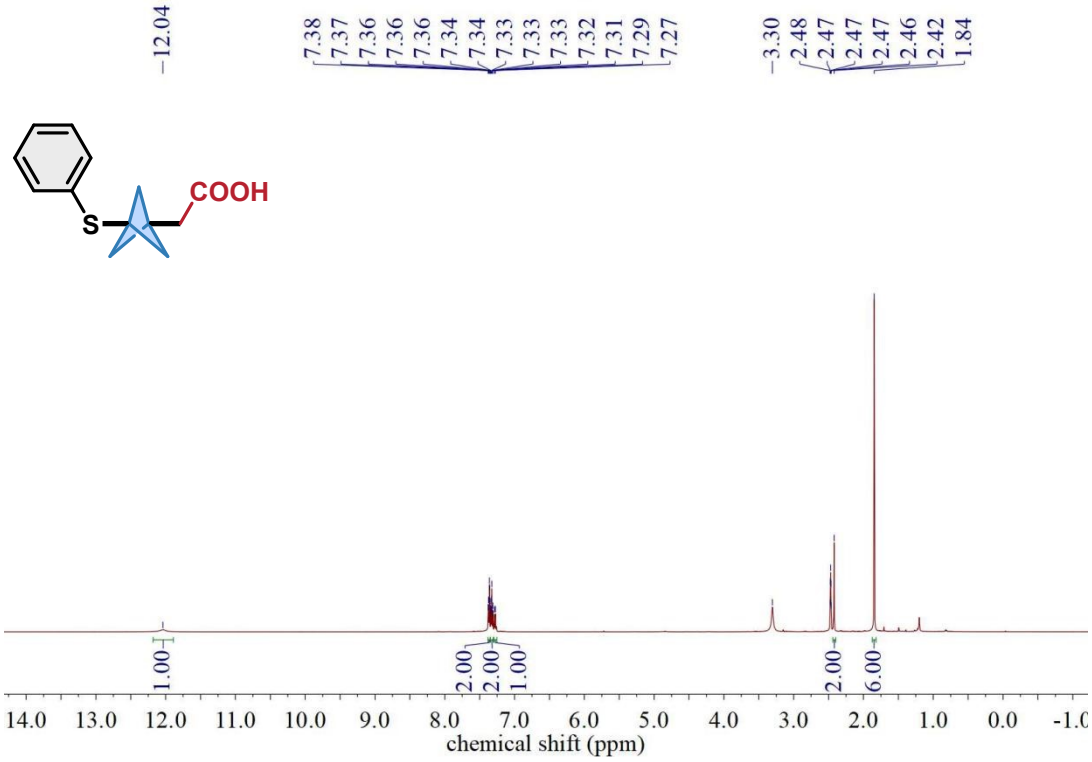
47 ^{1}H NMR (500 MHz, $CDCl_3$)



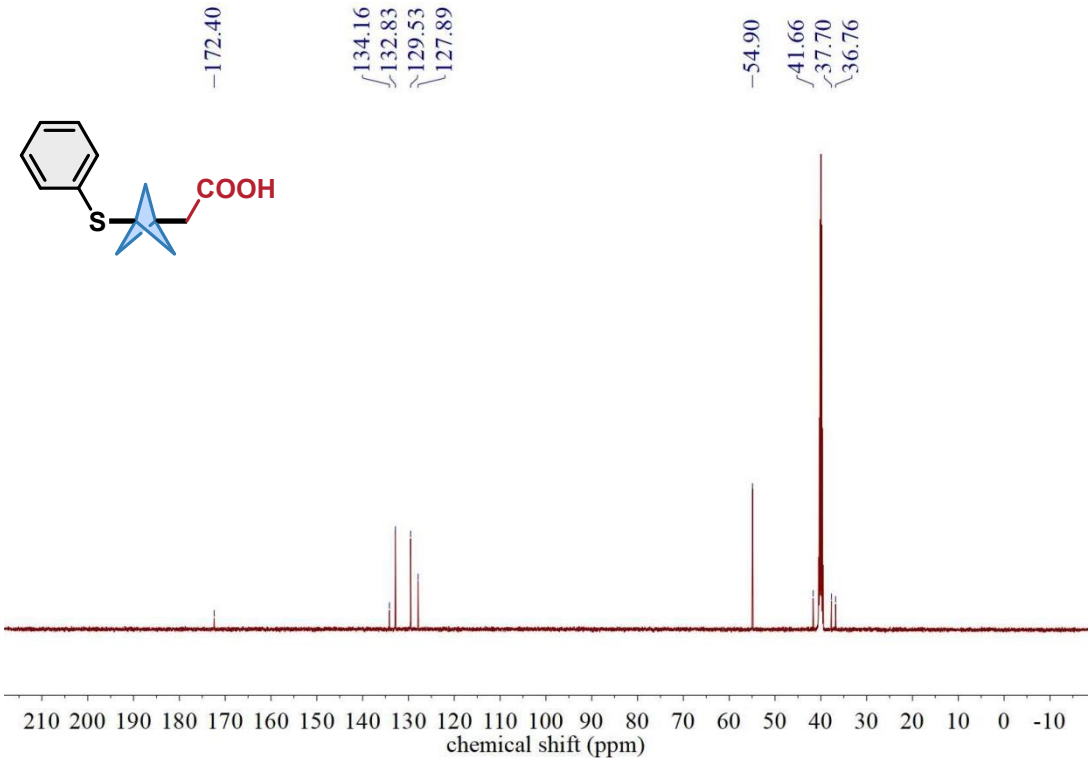
47 ^{13}C NMR (126 MHz, $CDCl_3$)



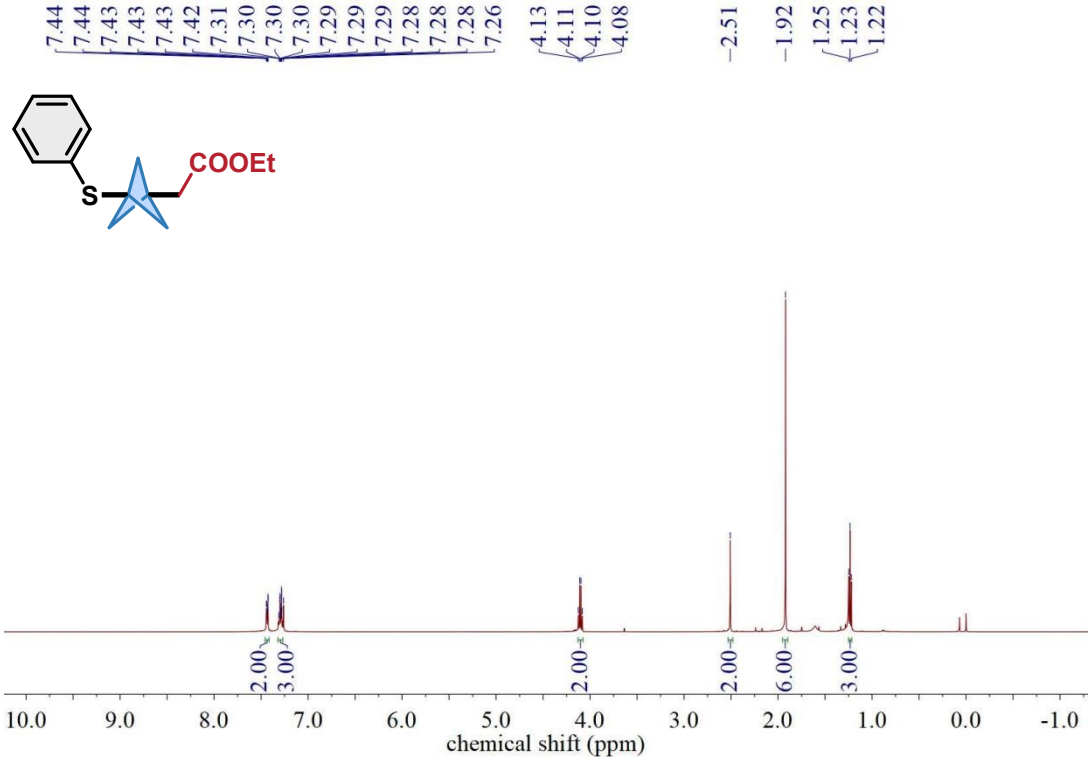
48 ^{1}H NMR (500 MHz, DMSO-d_6)



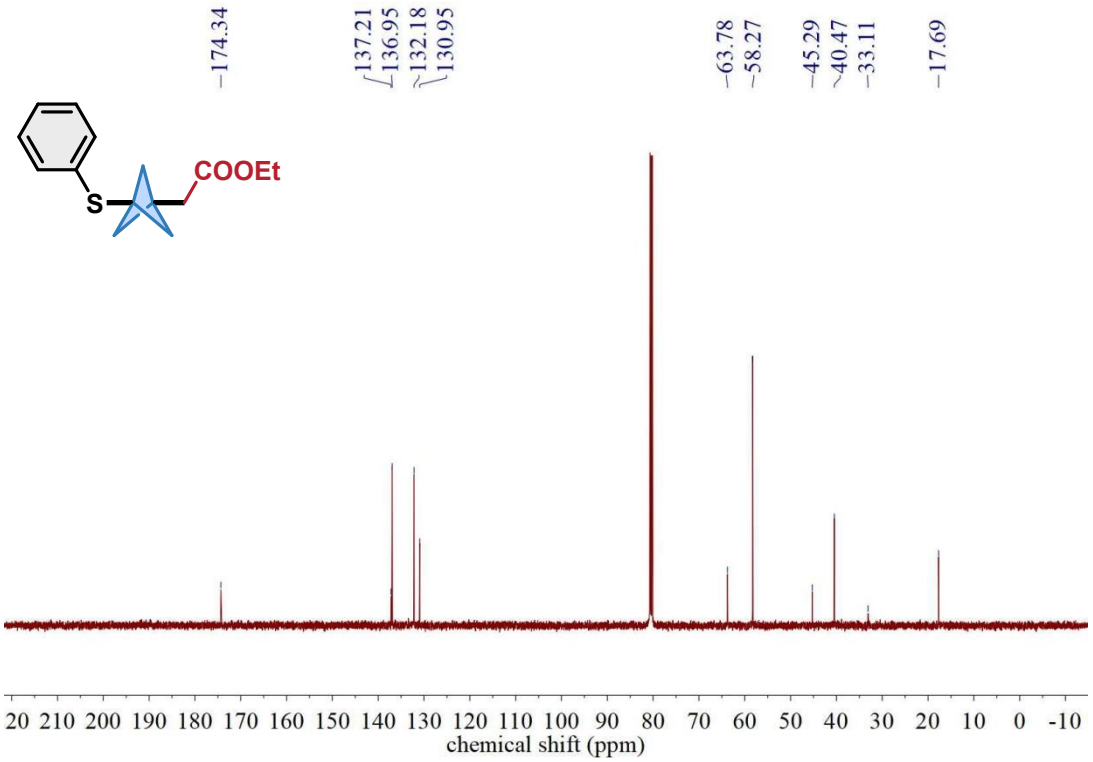
48 ^{13}C NMR (126 MHz, DMSO-d_6)



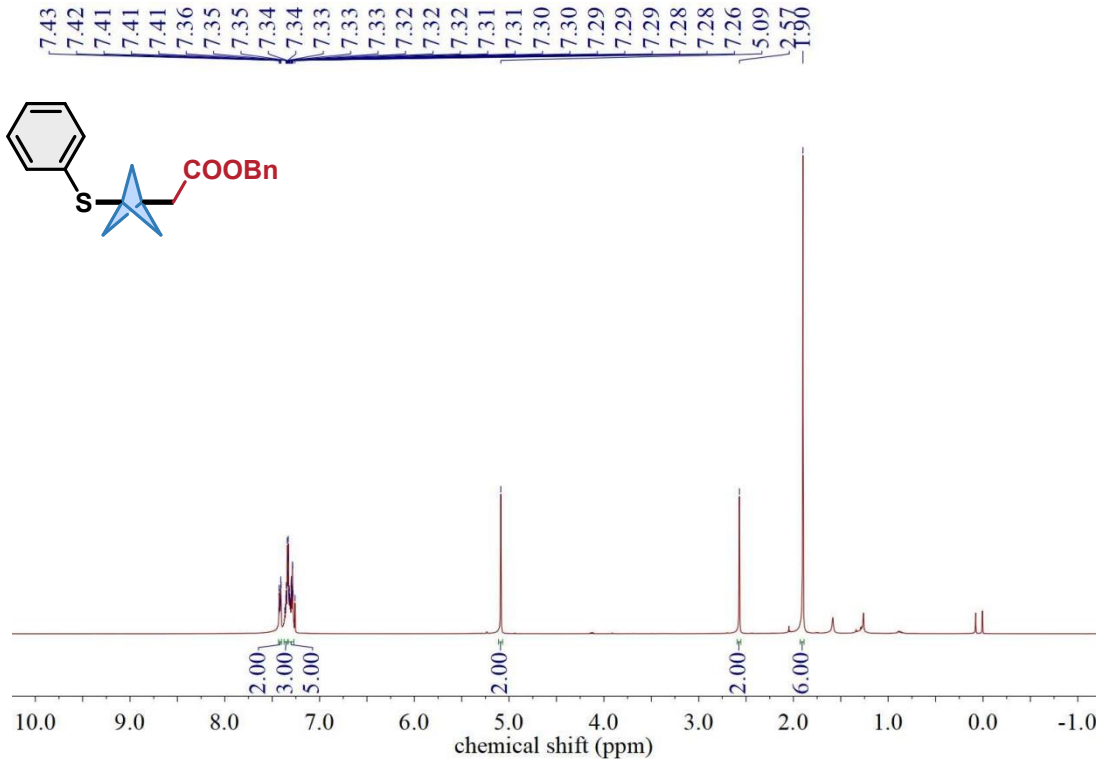
49 ^{1}H NMR (500 MHz, $CDCl_3$)



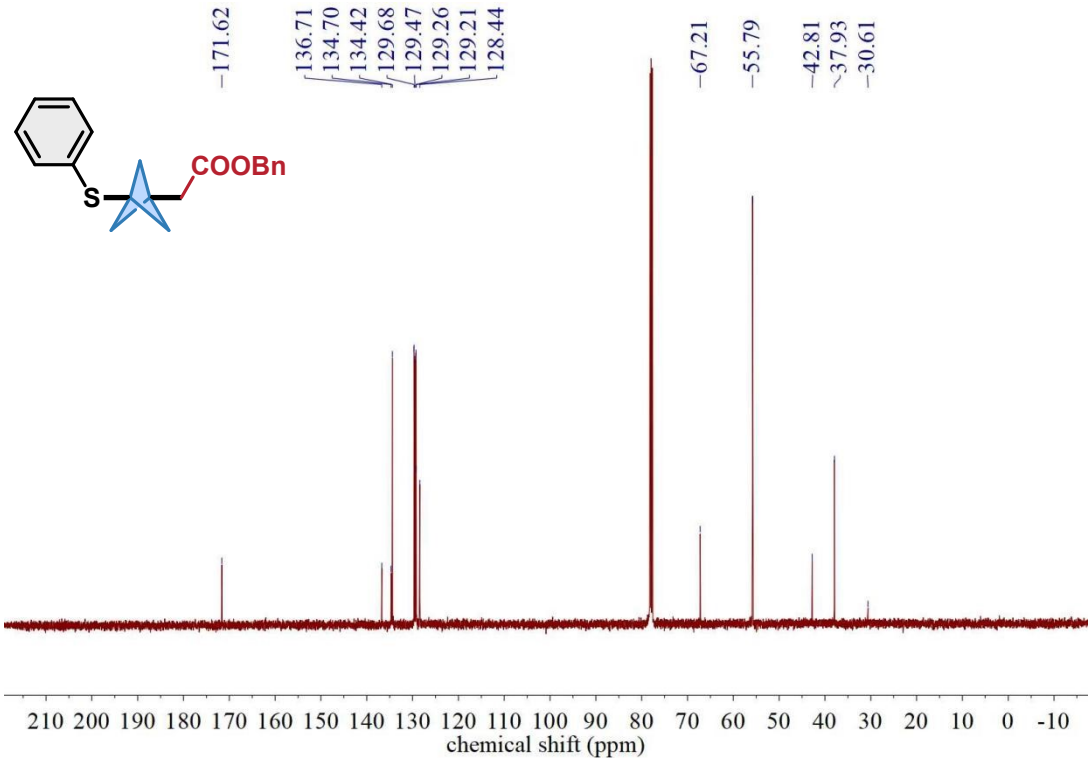
49 ^{13}C NMR (126 MHz, $CDCl_3$)



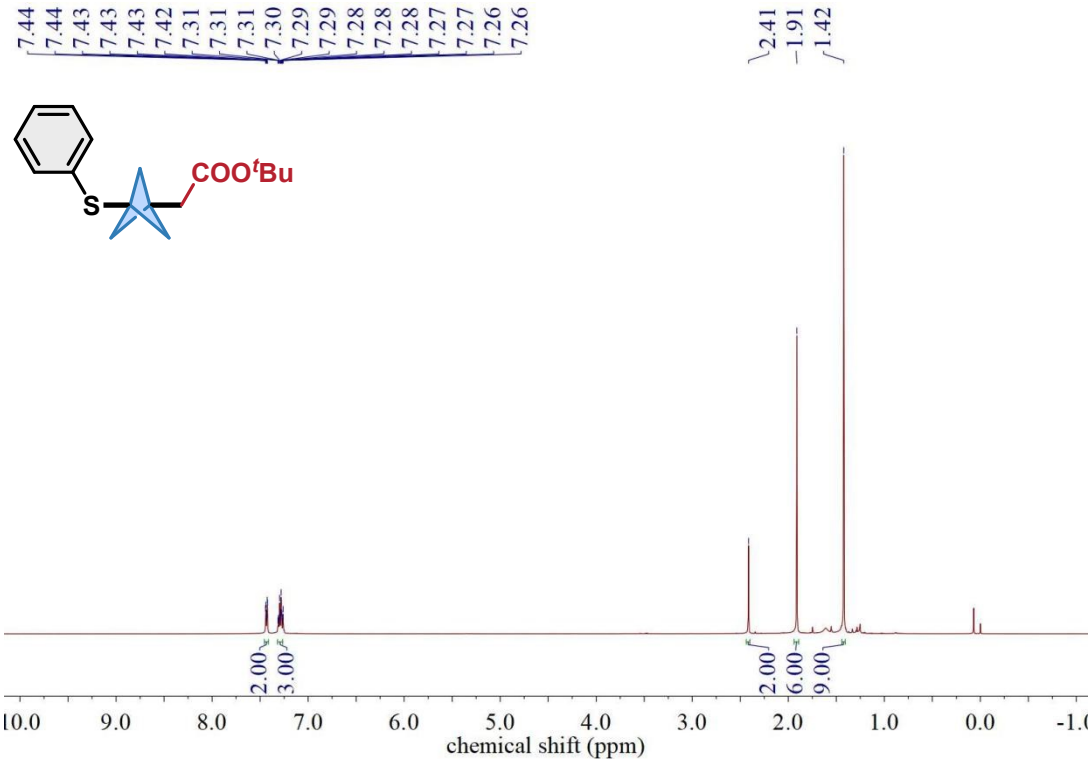
50 ^{1}H NMR (500 MHz, $CDCl_3$)



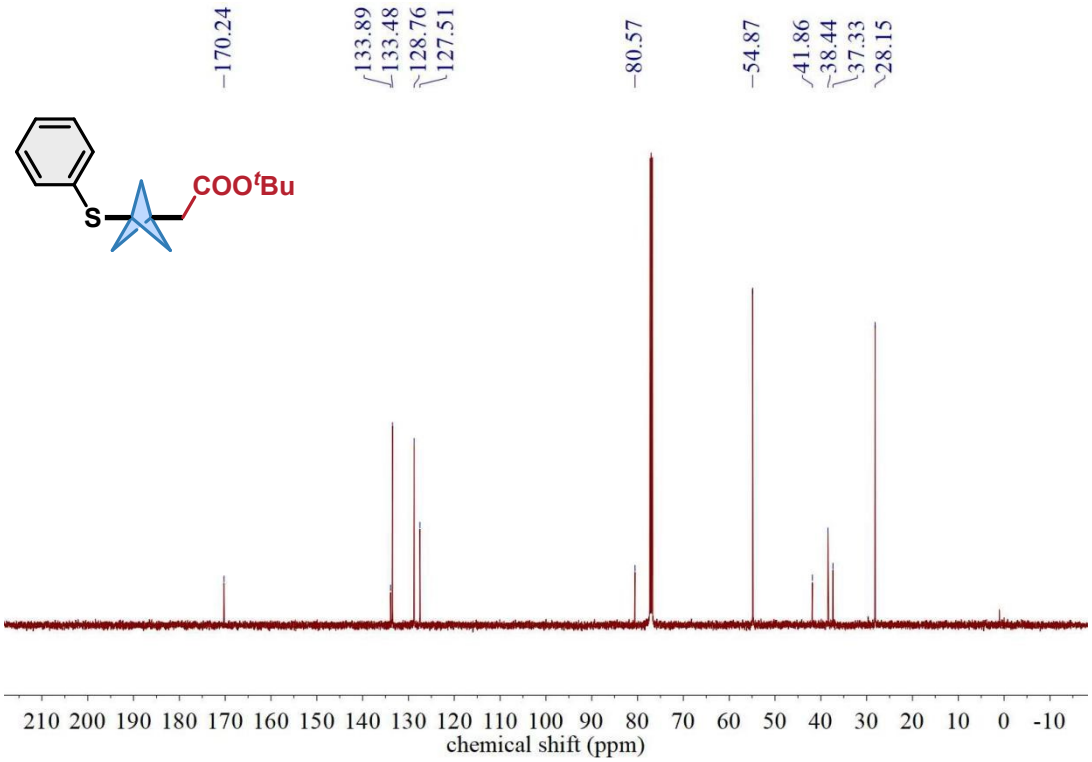
50 ^{13}C NMR (126 MHz, $CDCl_3$)



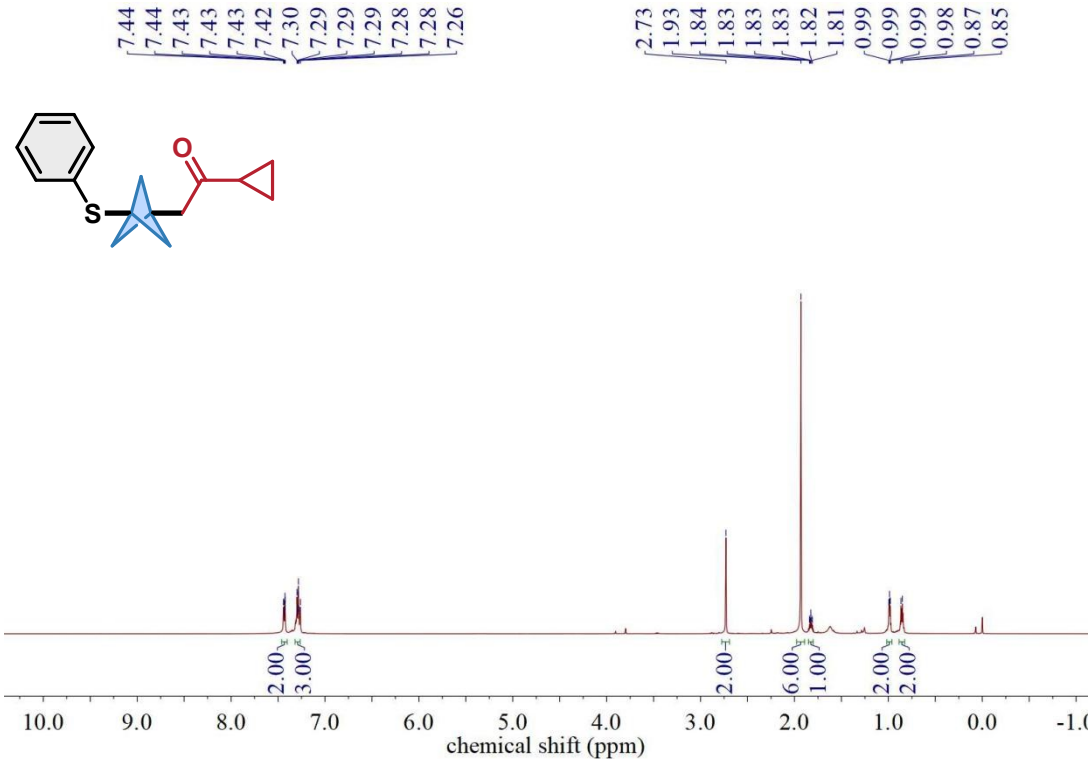
51 ^{1}H NMR (500 MHz, $CDCl_3$)



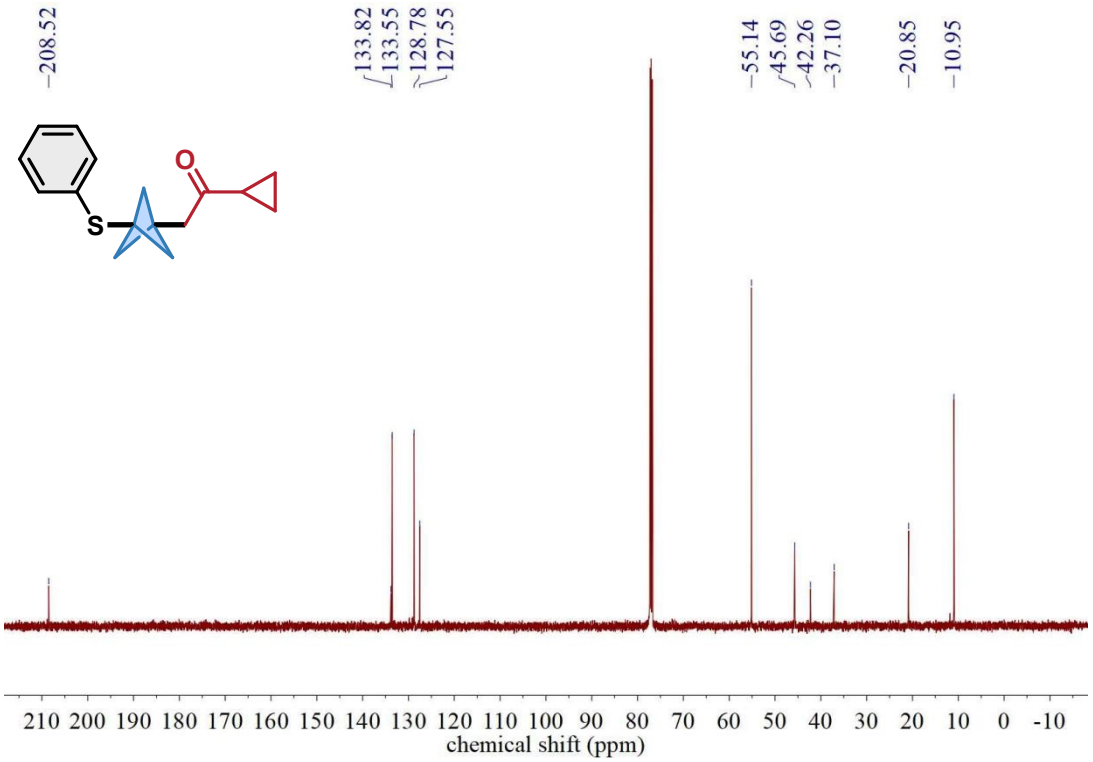
51 ^{13}C NMR (126 MHz, $CDCl_3$)



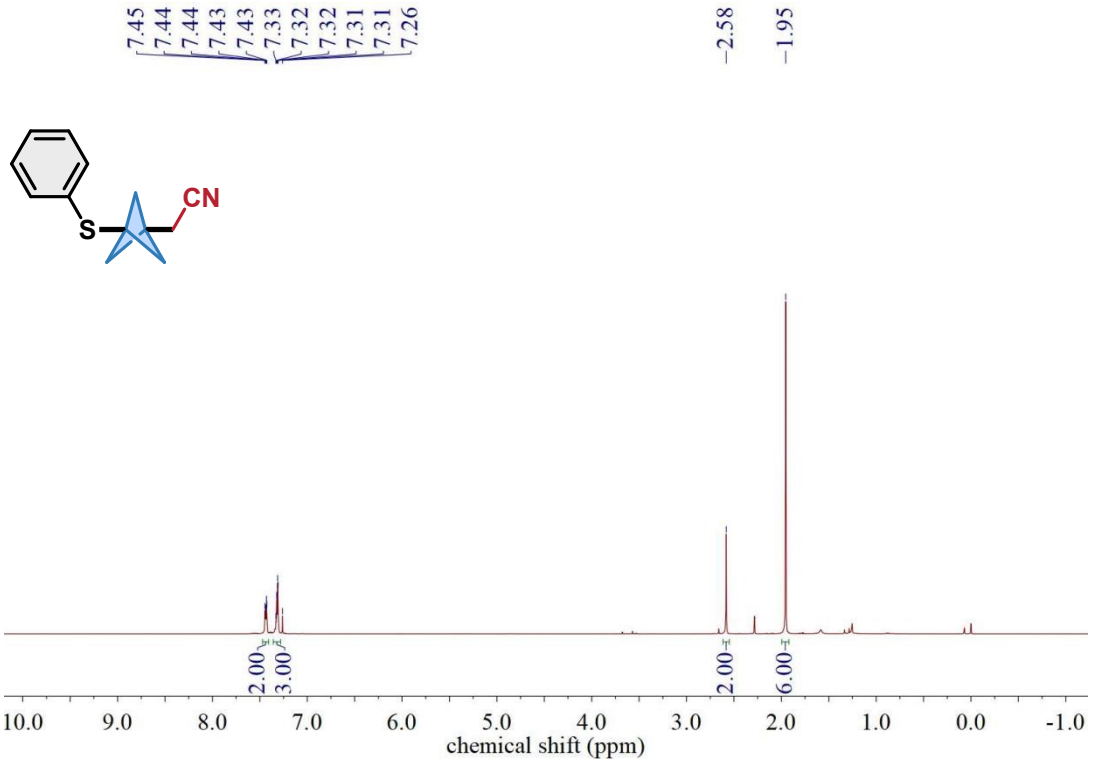
52 ^{1}H NMR (500 MHz, $CDCl_3$)



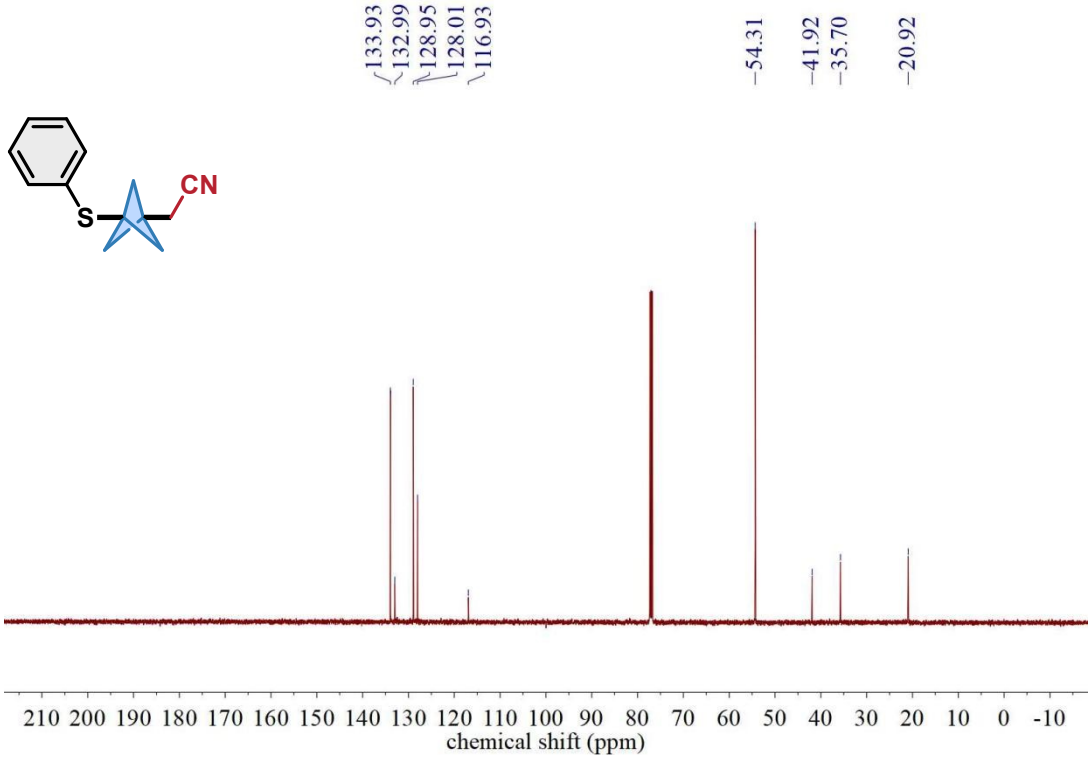
52 ^{13}C NMR (126 MHz, $CDCl_3$)



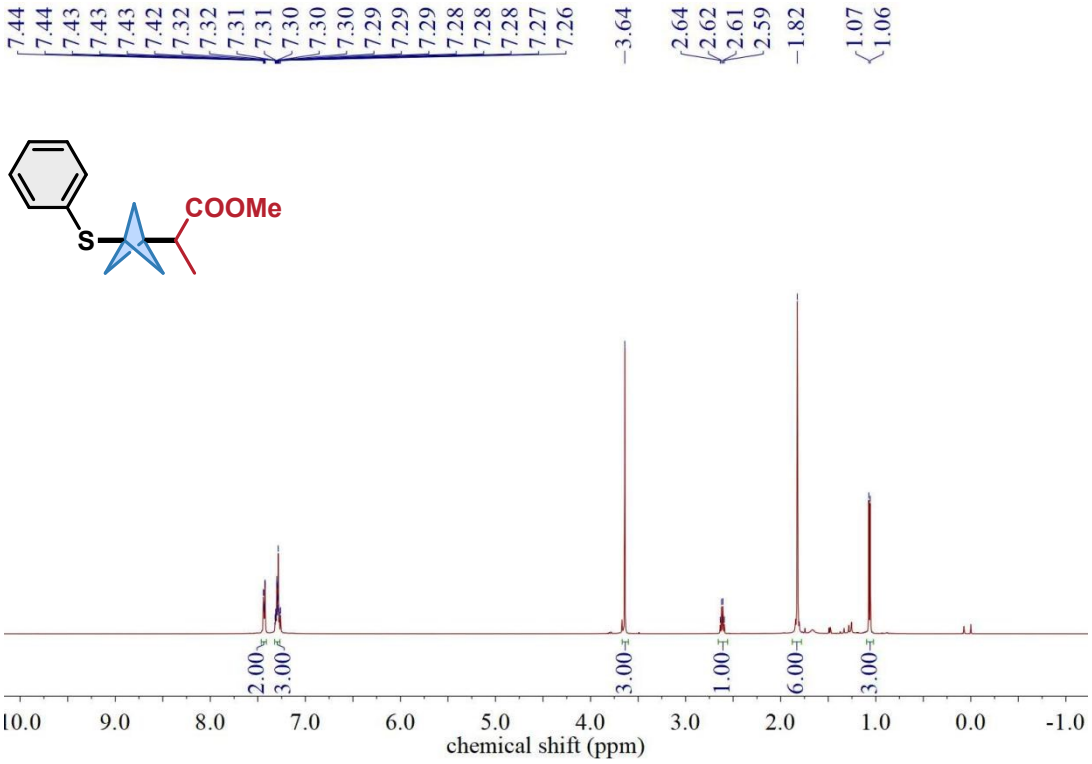
53 ^{1}H NMR (500 MHz, $CDCl_3$)



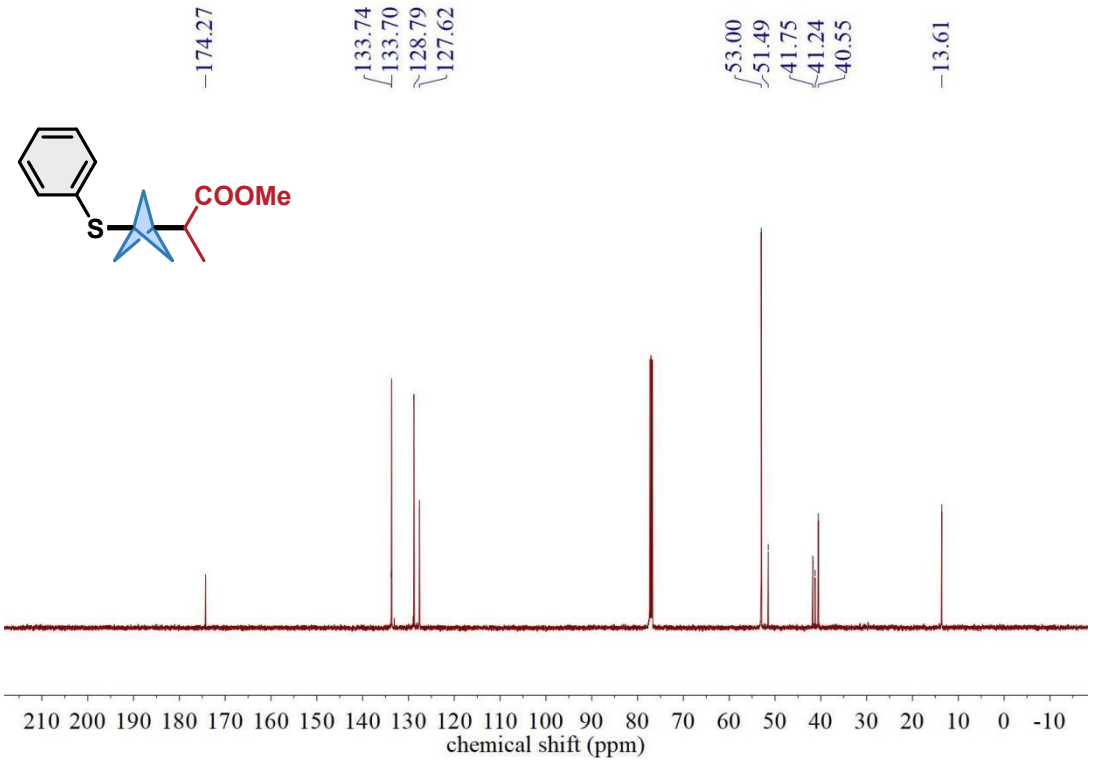
53 ^{13}C NMR (126 MHz, $CDCl_3$)



54 ^{1}H NMR (500 MHz, $CDCl_3$)



54 ^{13}C NMR (126 MHz, $CDCl_3$)



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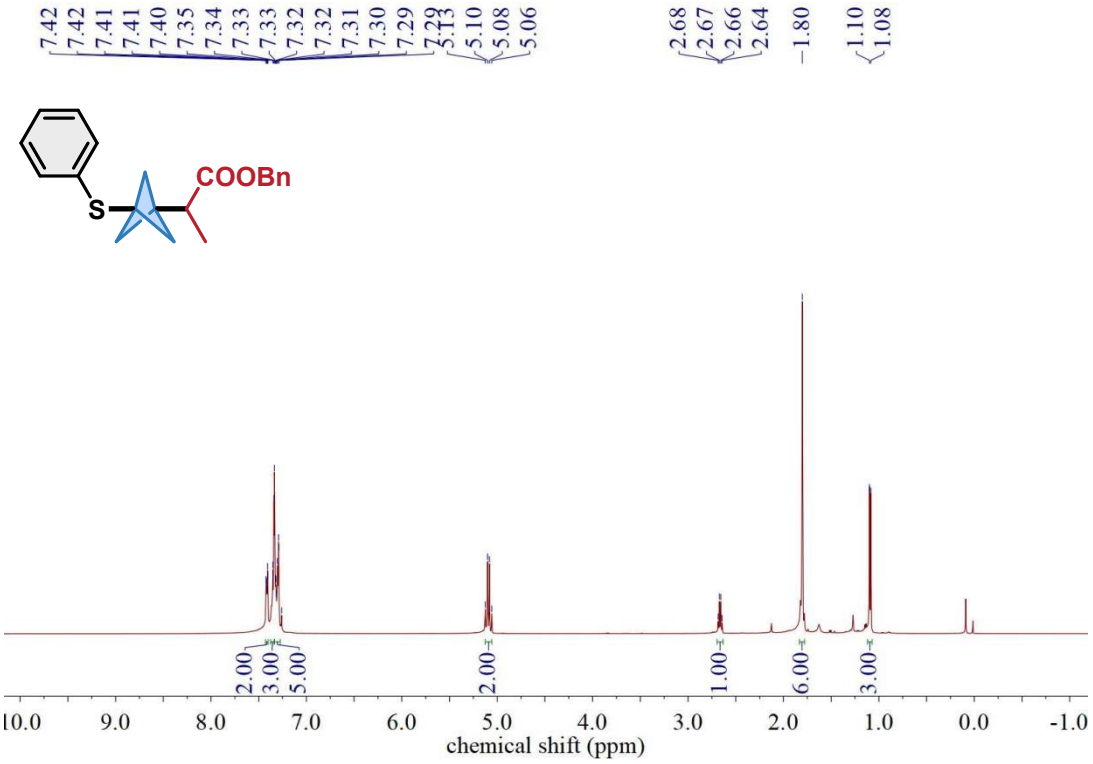
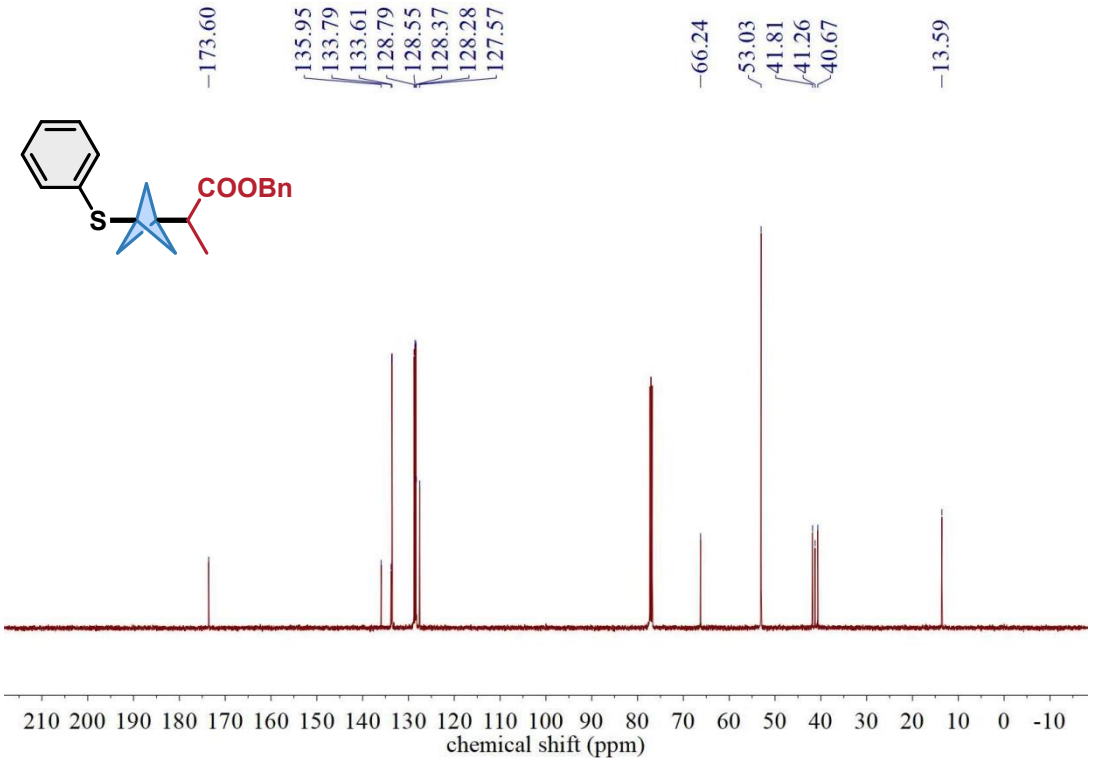
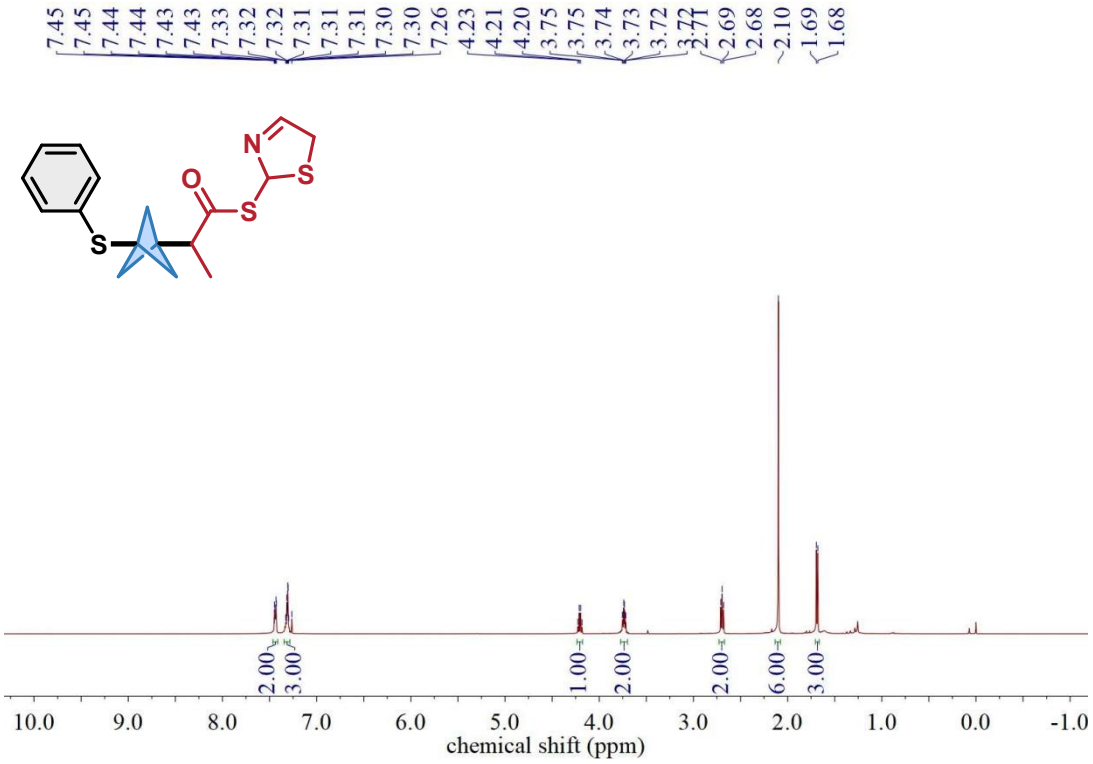


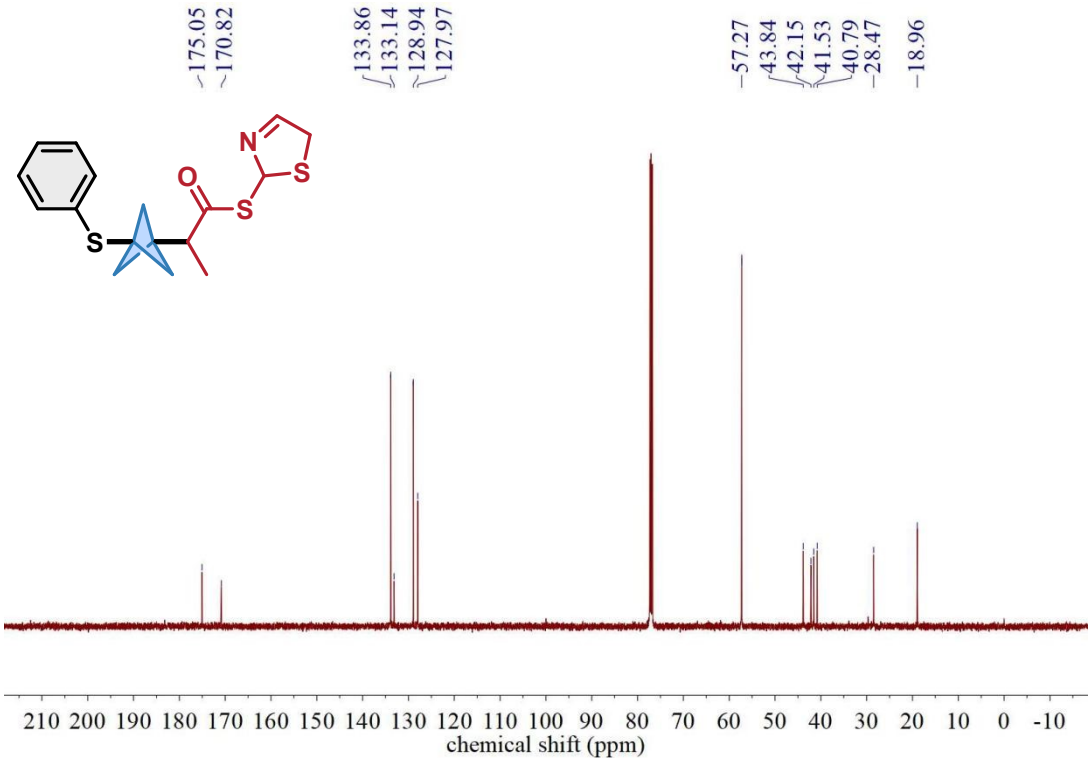
55 ^{13}C NMR (126 MHz, $CDCl_3$)



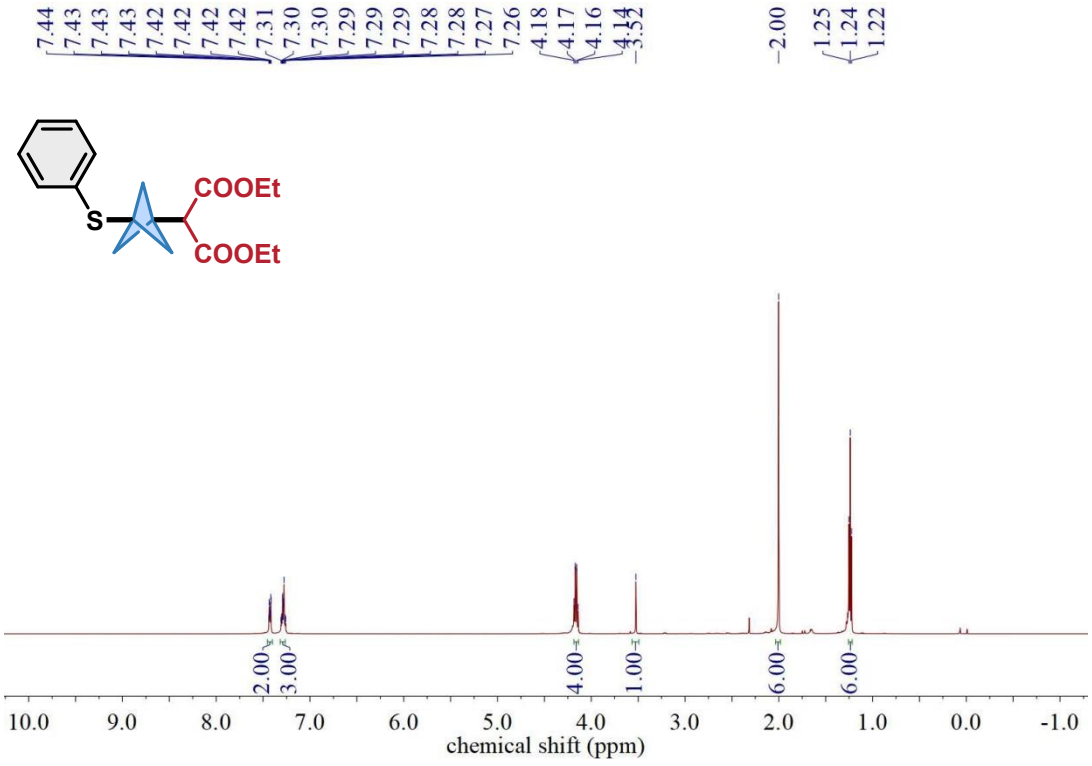
56 ^{1}H NMR (500 MHz, $CDCl_3$)



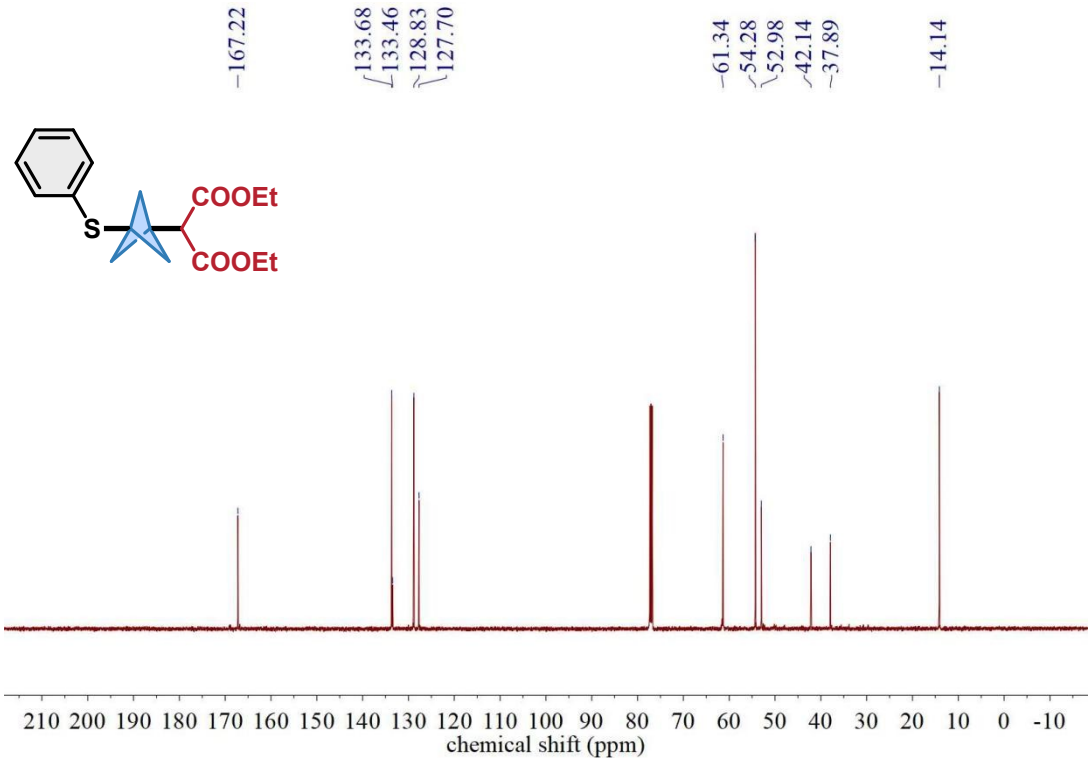
56 ^{13}C NMR (126 MHz, $CDCl_3$)



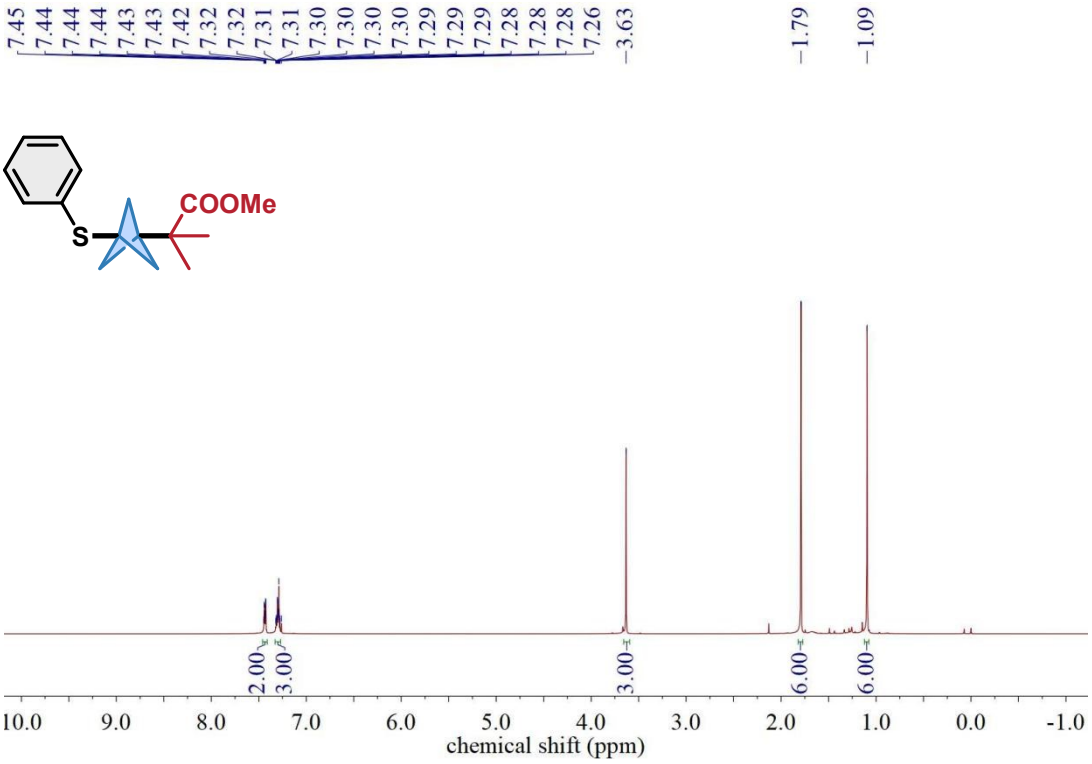
57 ^{1}H NMR (500 MHz, $CDCl_3$)



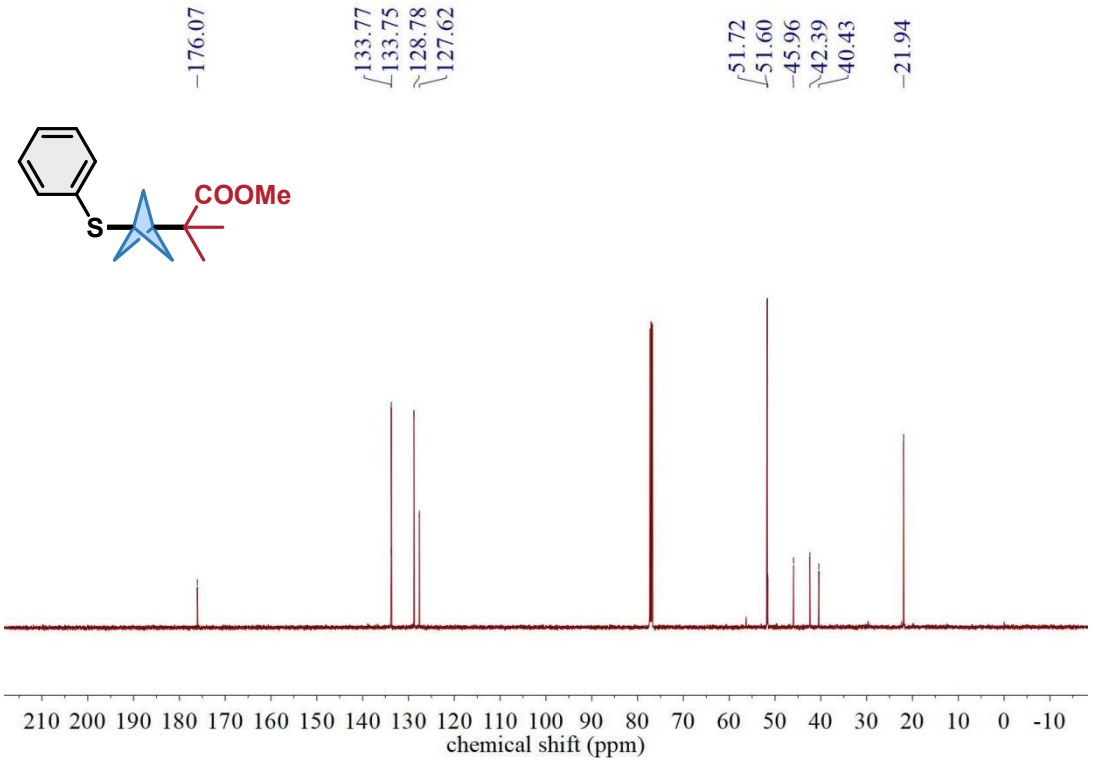
57 ^{13}C NMR (126 MHz, $CDCl_3$)



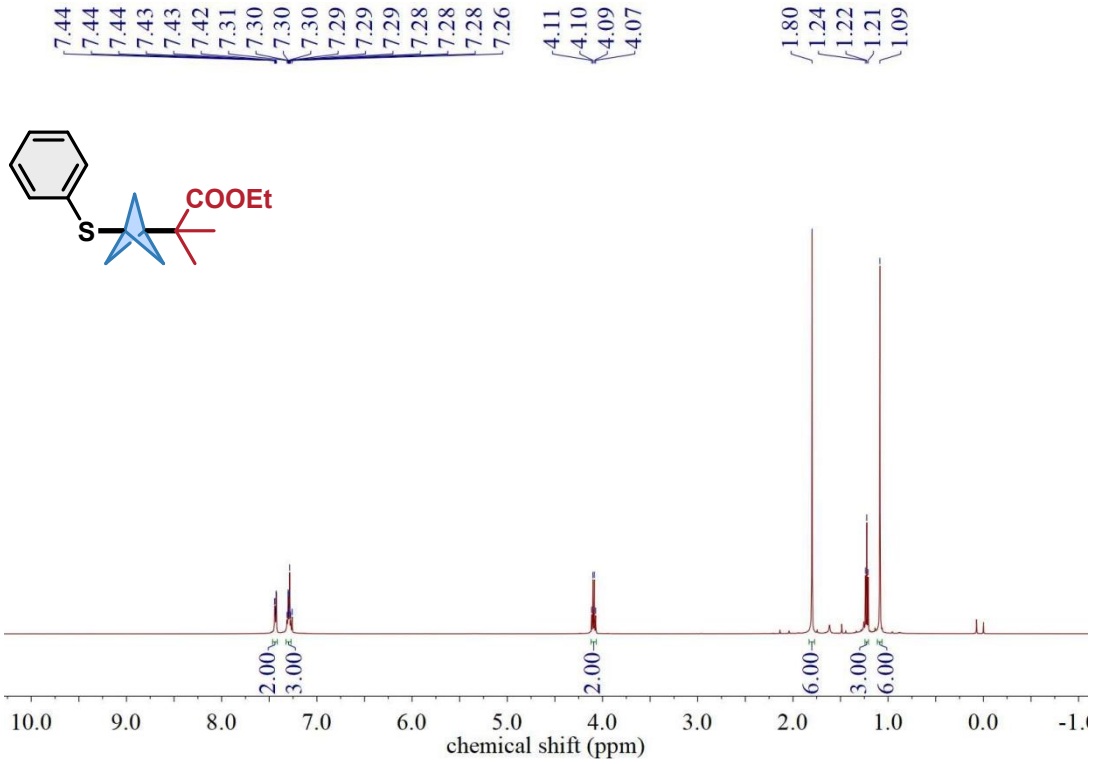
58 ^{1}H NMR (500 MHz, $CDCl_3$)



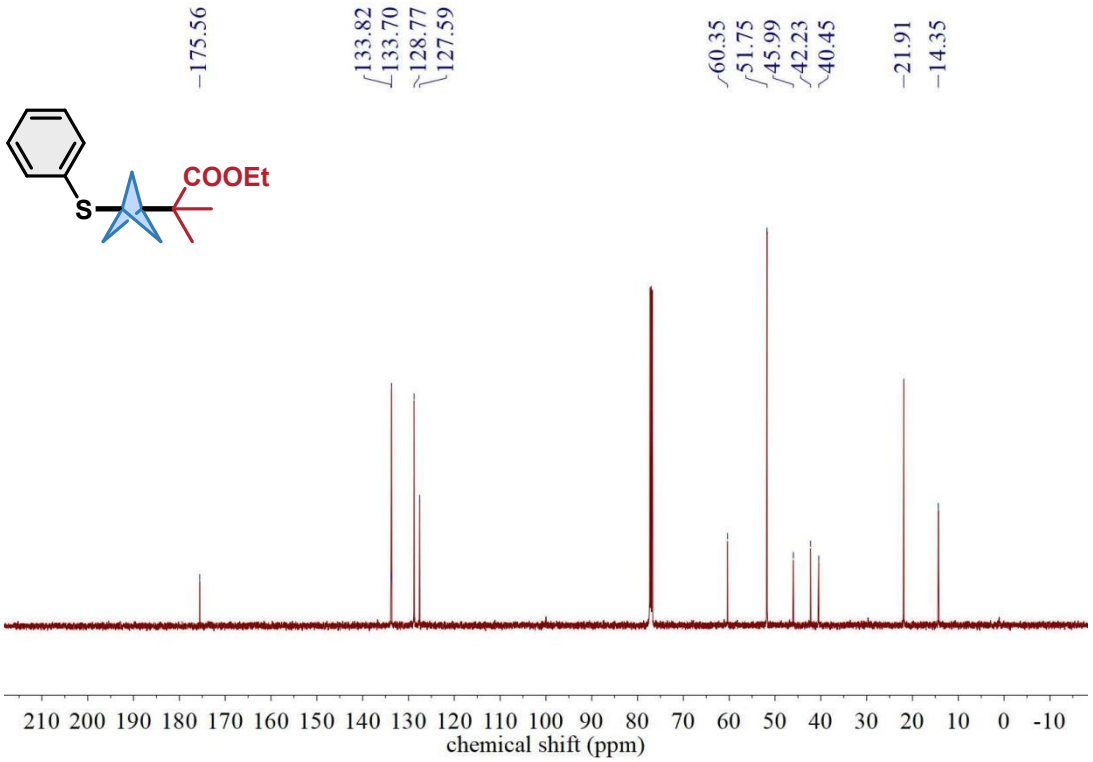
58 ^{13}C NMR (126 MHz, $CDCl_3$)



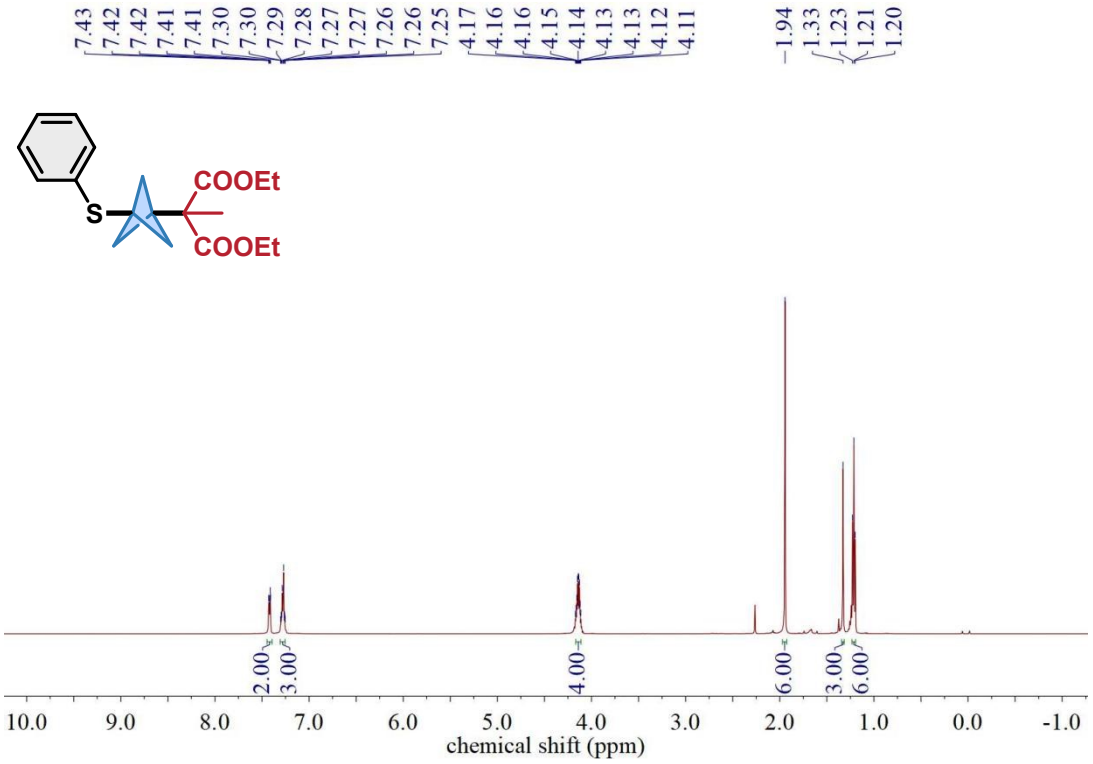
59 ^{1}H NMR (500 MHz, $CDCl_3$)



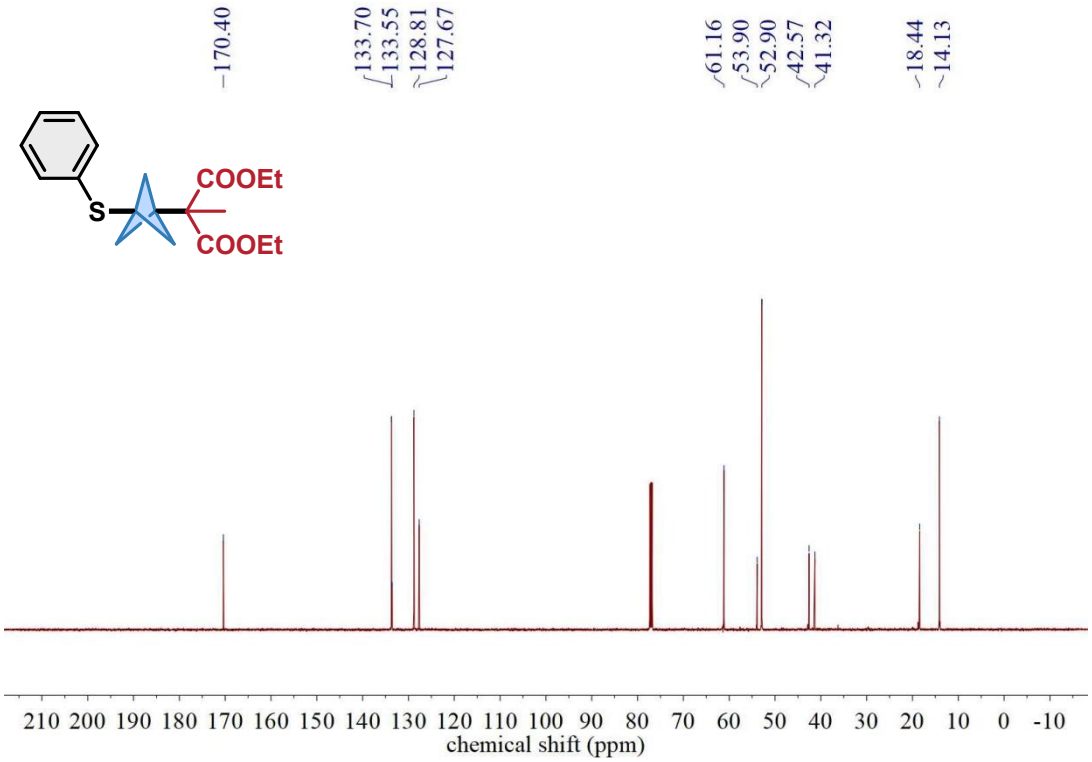
59 ^{13}C NMR (126 MHz, $CDCl_3$)



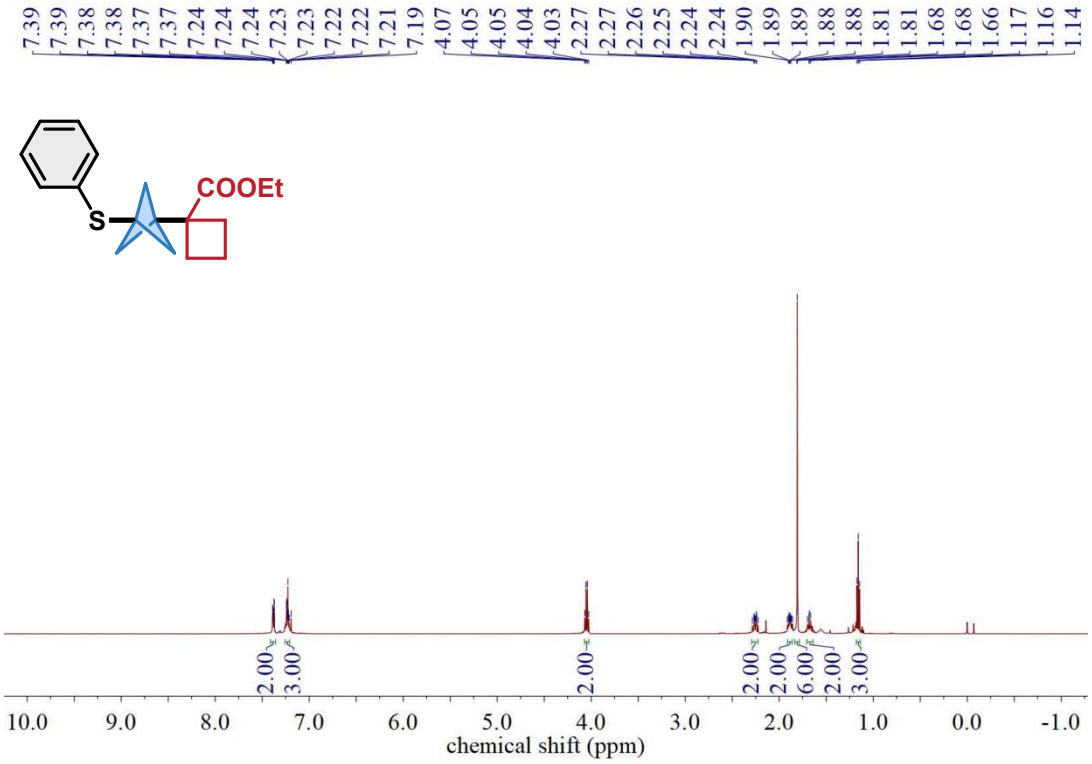
60 ^{1}H NMR (500 MHz, $CDCl_3$)



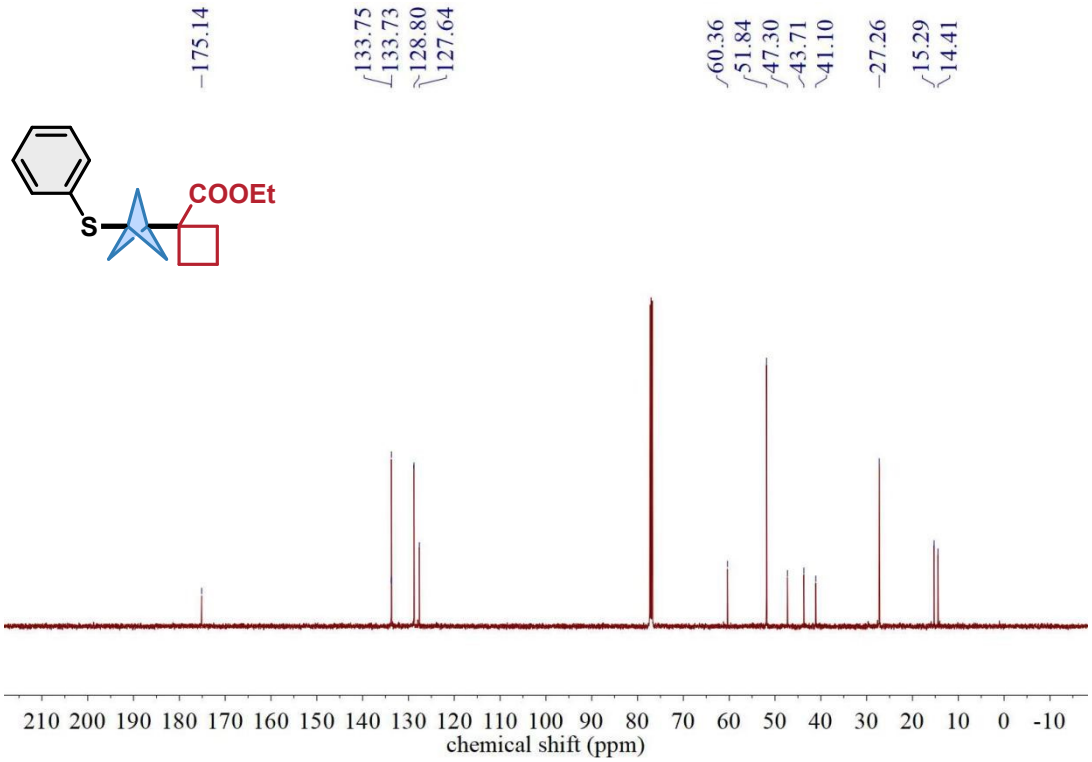
60 ^{13}C NMR (126 MHz, $CDCl_3$)



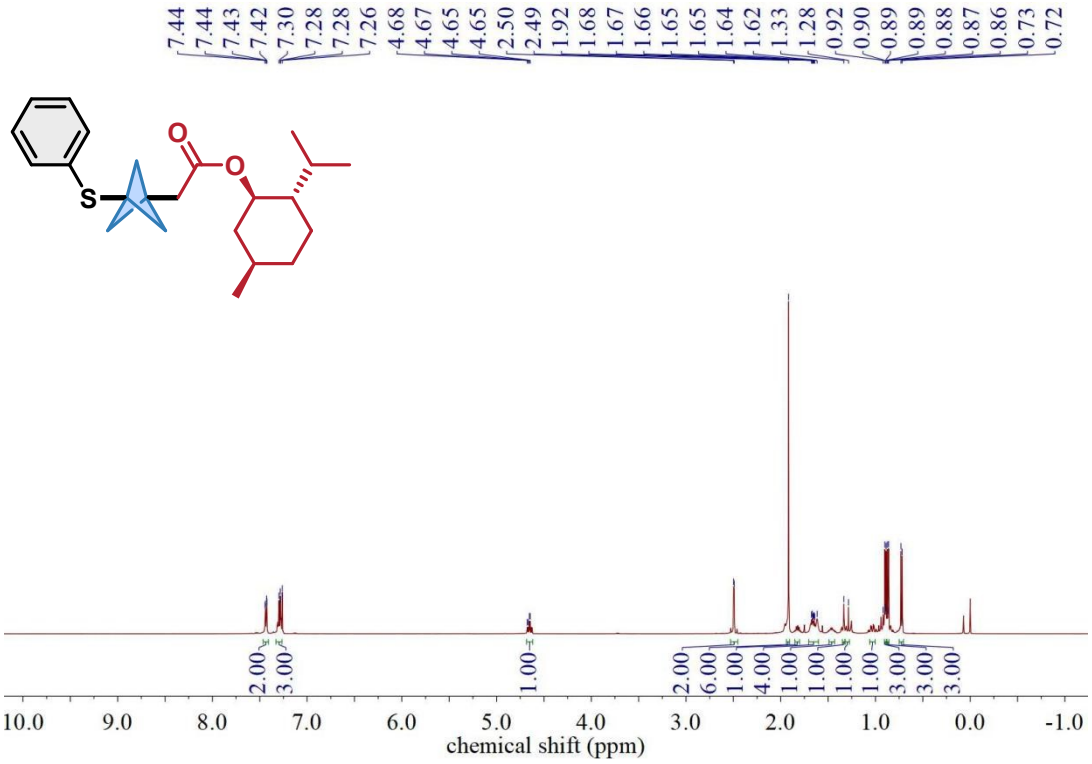
61 ^{1}H NMR (500 MHz, $CDCl_3$)



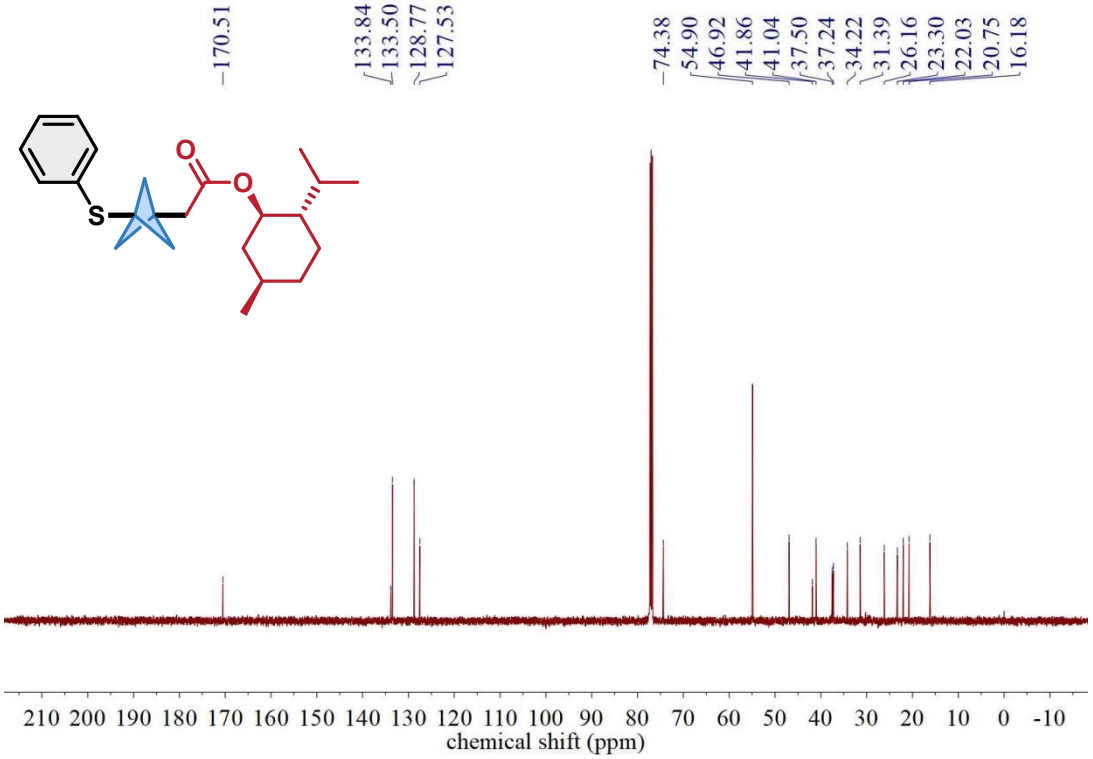
61 ^{13}C NMR (126 MHz, $CDCl_3$)



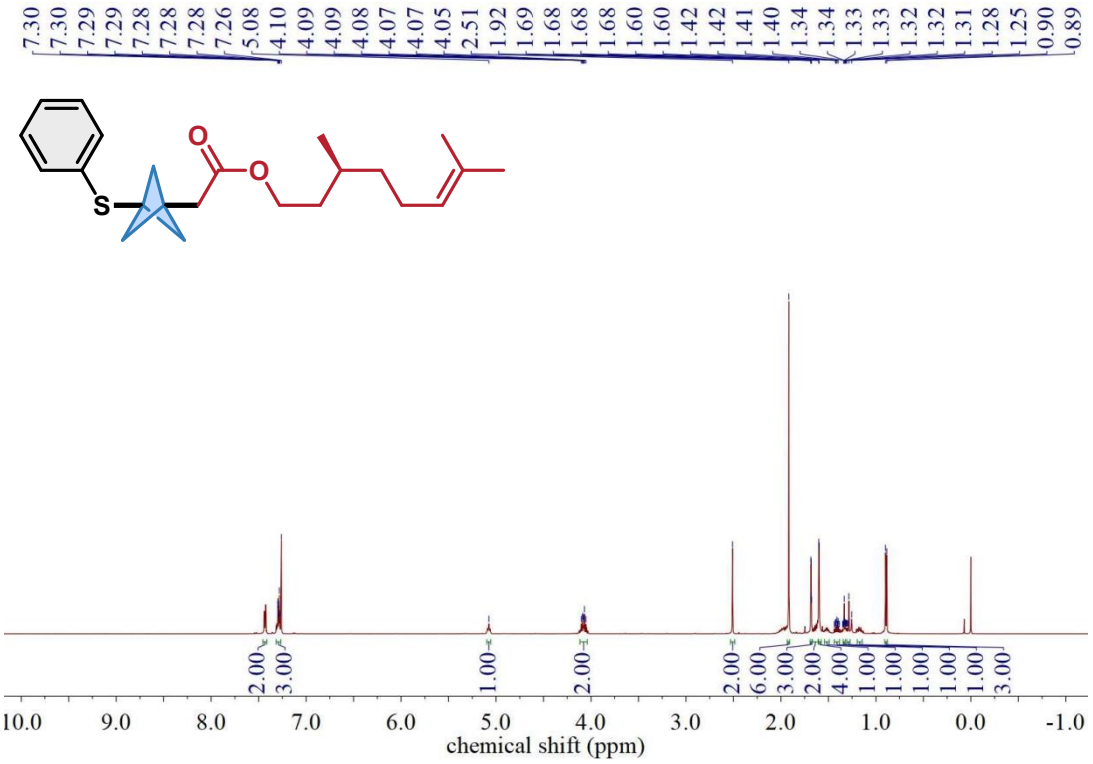
62 ^{1}H NMR (500 MHz, $CDCl_3$)



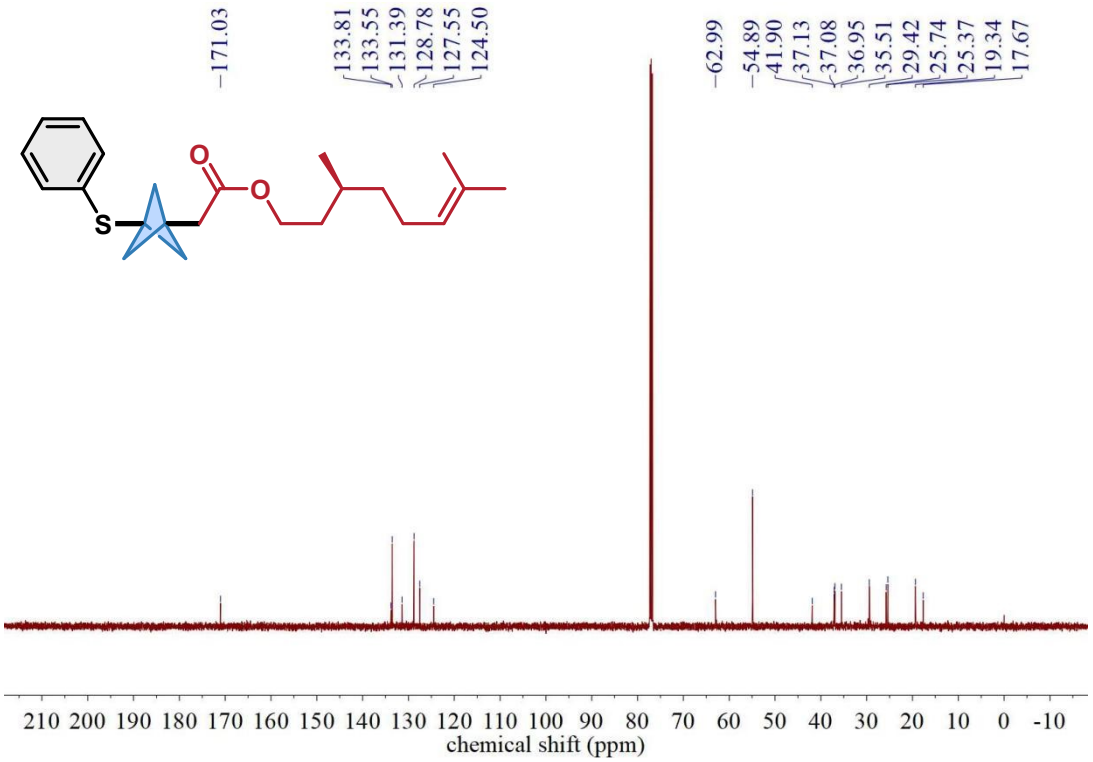
62 ^{13}C NMR (126 MHz, $CDCl_3$)



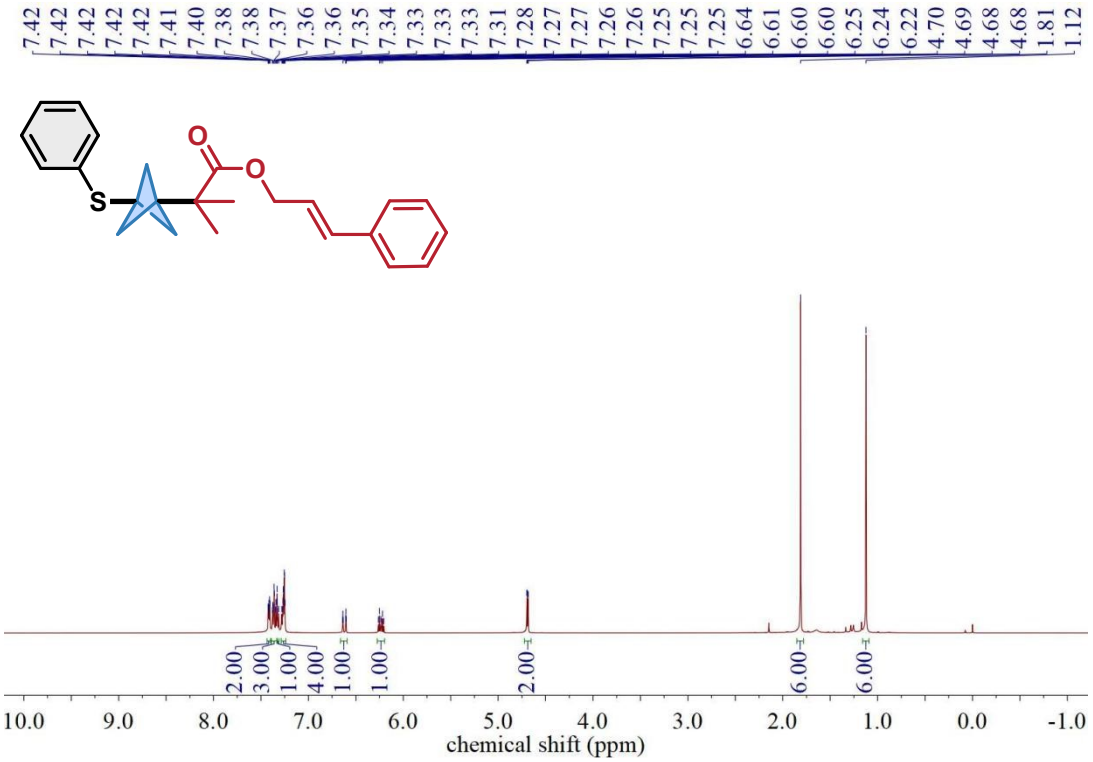
63 ^{1}H NMR (500 MHz, $CDCl_3$)



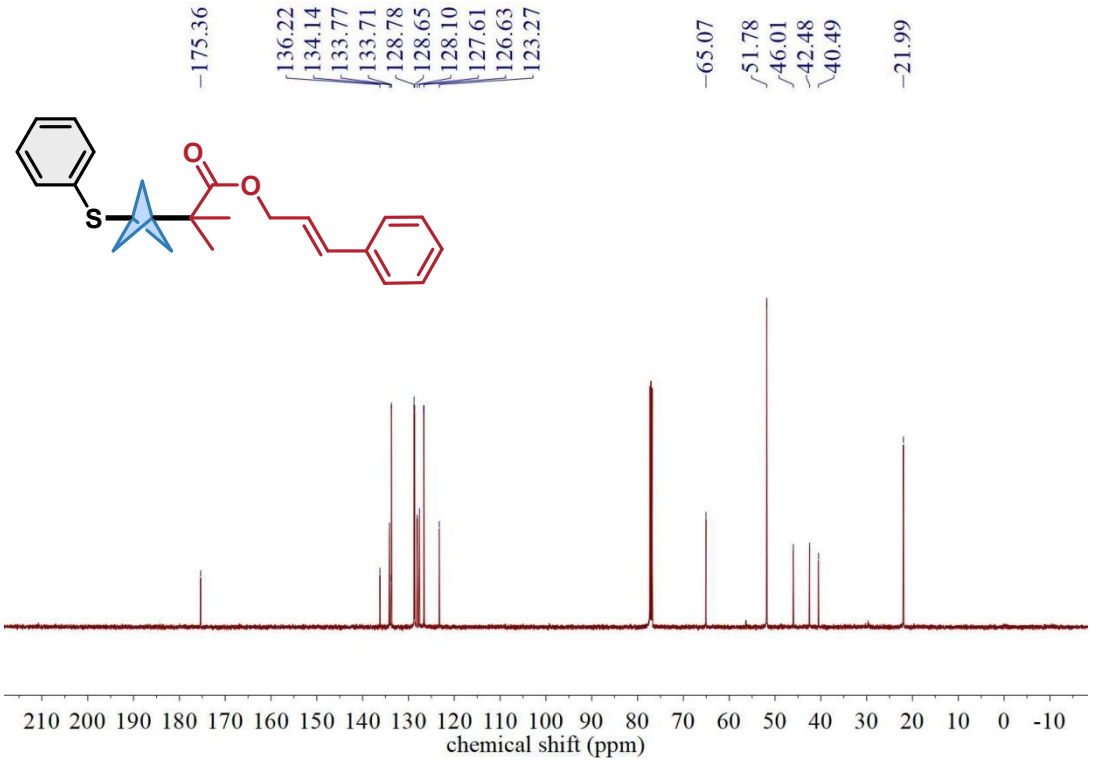
63 ^{13}C NMR (126 MHz, $CDCl_3$)



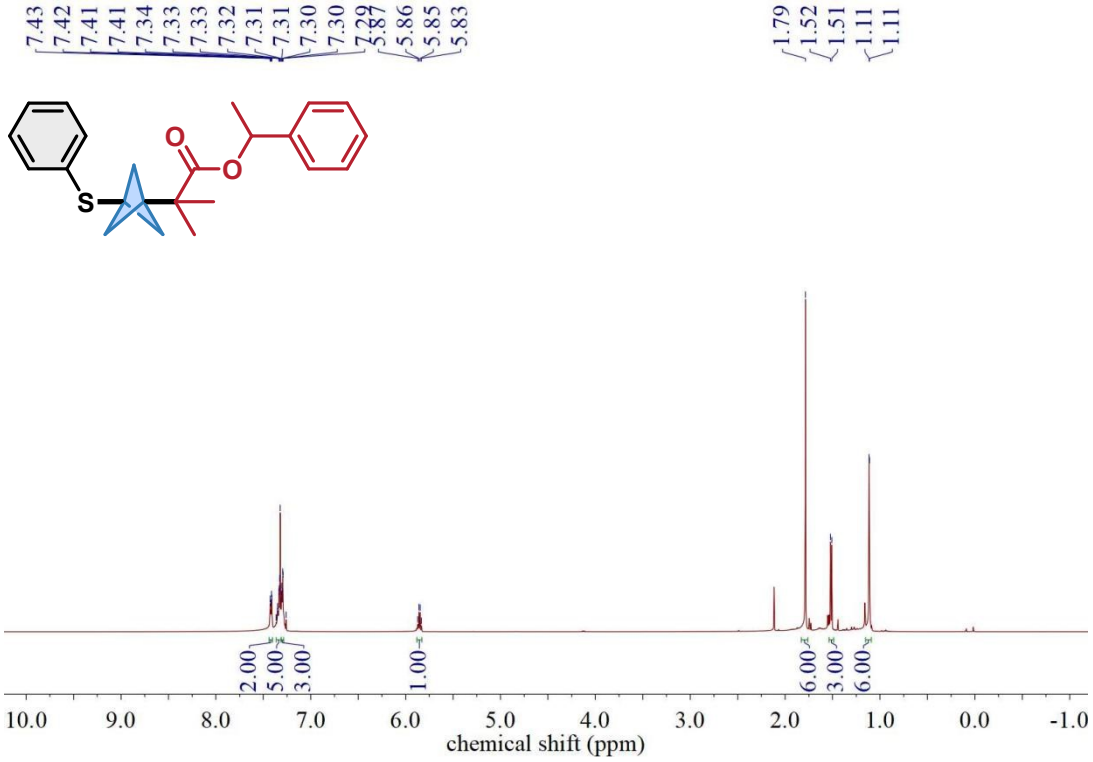
64 ^{1}H NMR (500 MHz, $CDCl_3$)



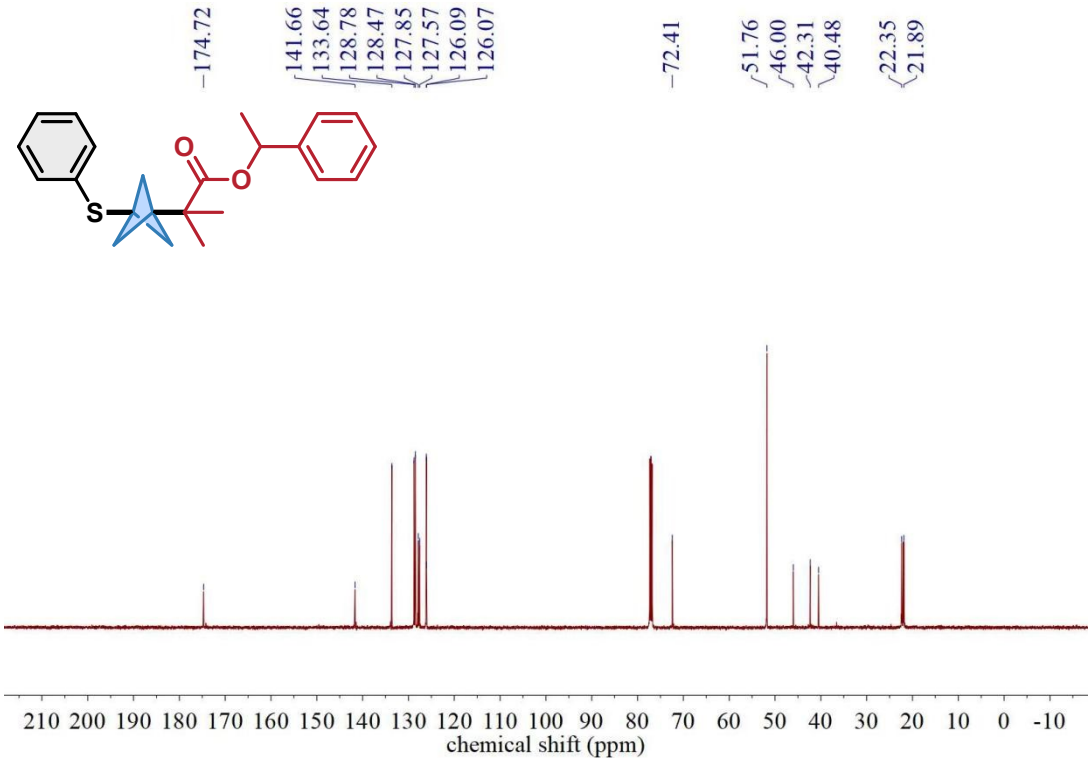
64 ^{13}C NMR (126 MHz, $CDCl_3$)



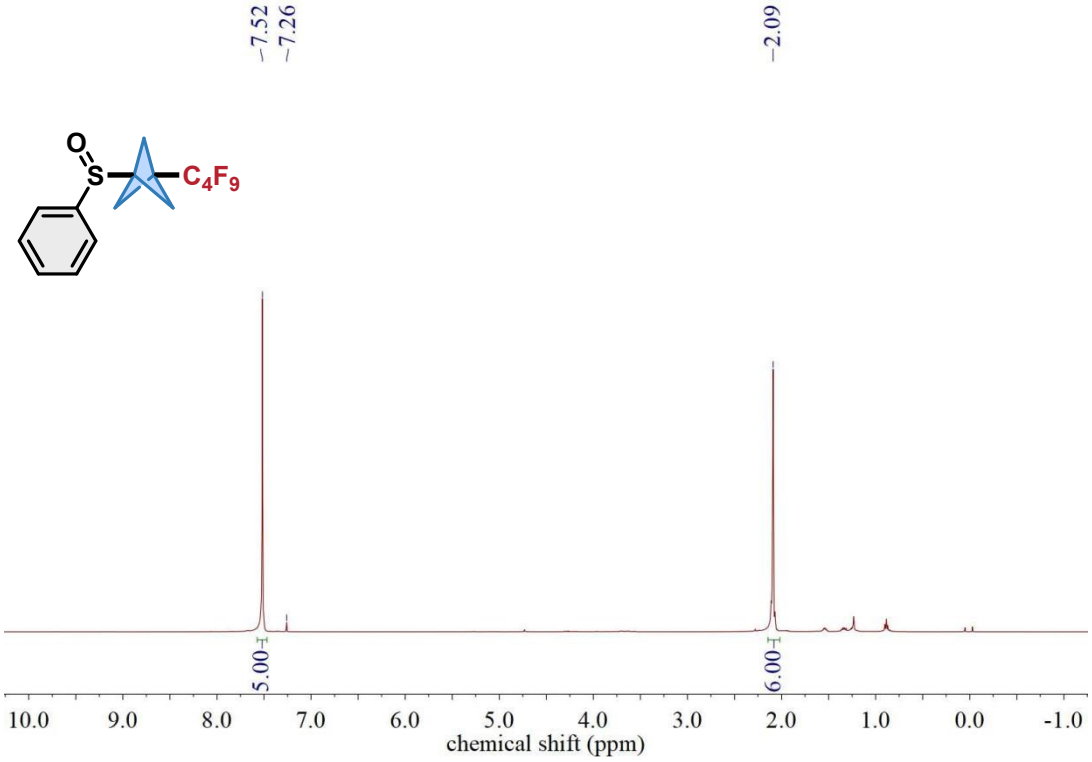
65 ^{1}H NMR (500 MHz, $CDCl_3$)



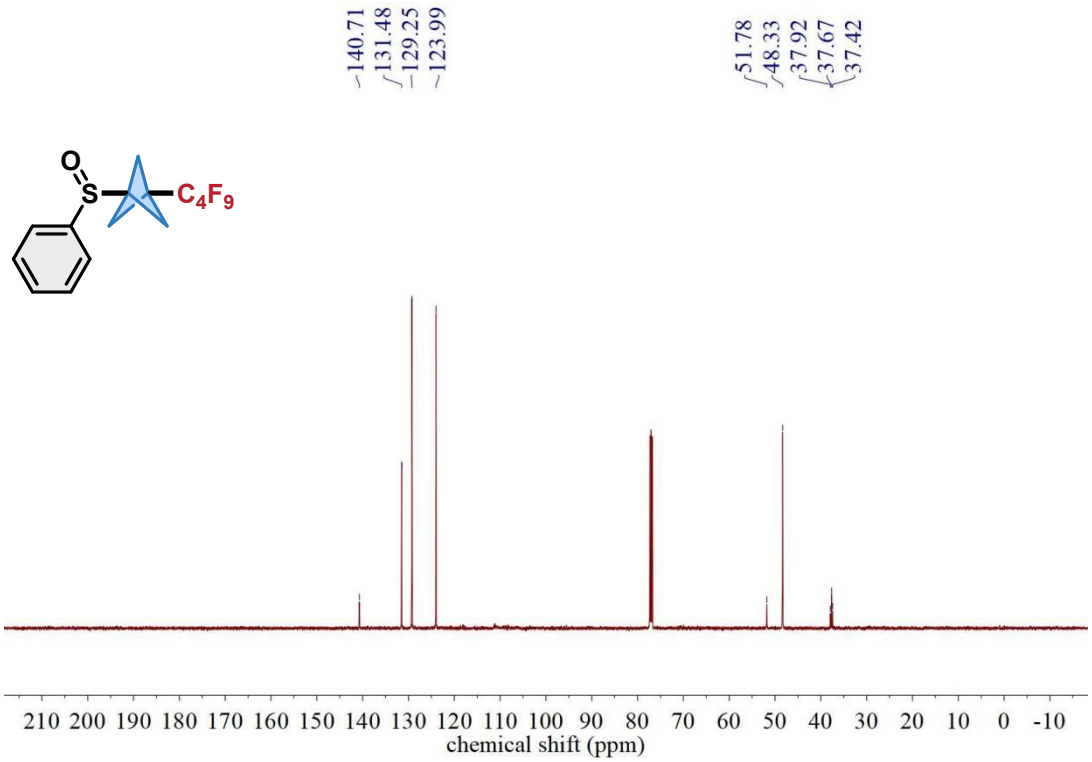
65 ^{13}C NMR (126 MHz, $CDCl_3$)



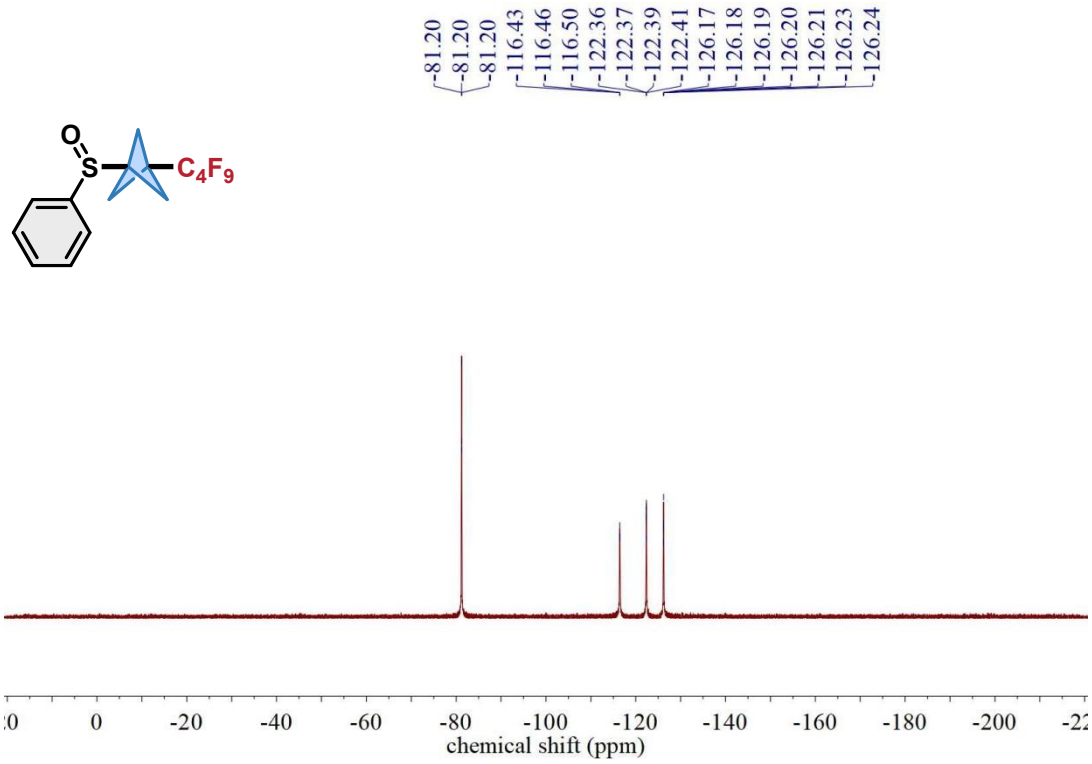
66 ^{1}H NMR (500 MHz, $CDCl_3$)



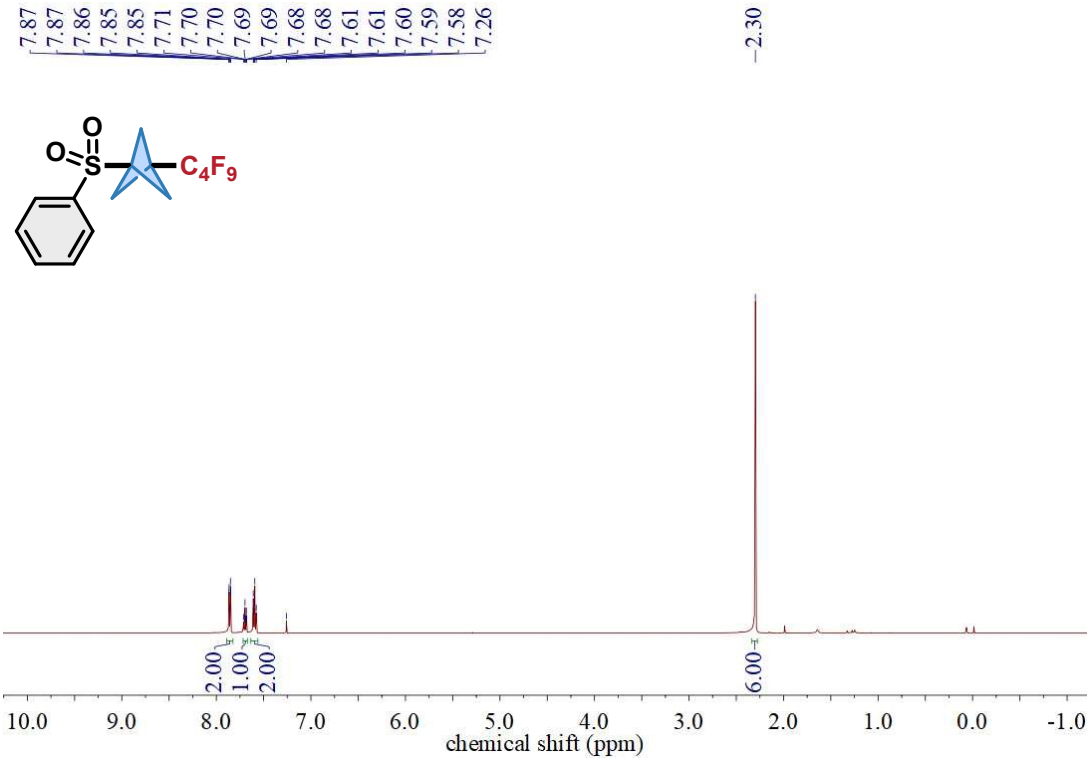
66 ^{13}C NMR (126 MHz, $CDCl_3$)



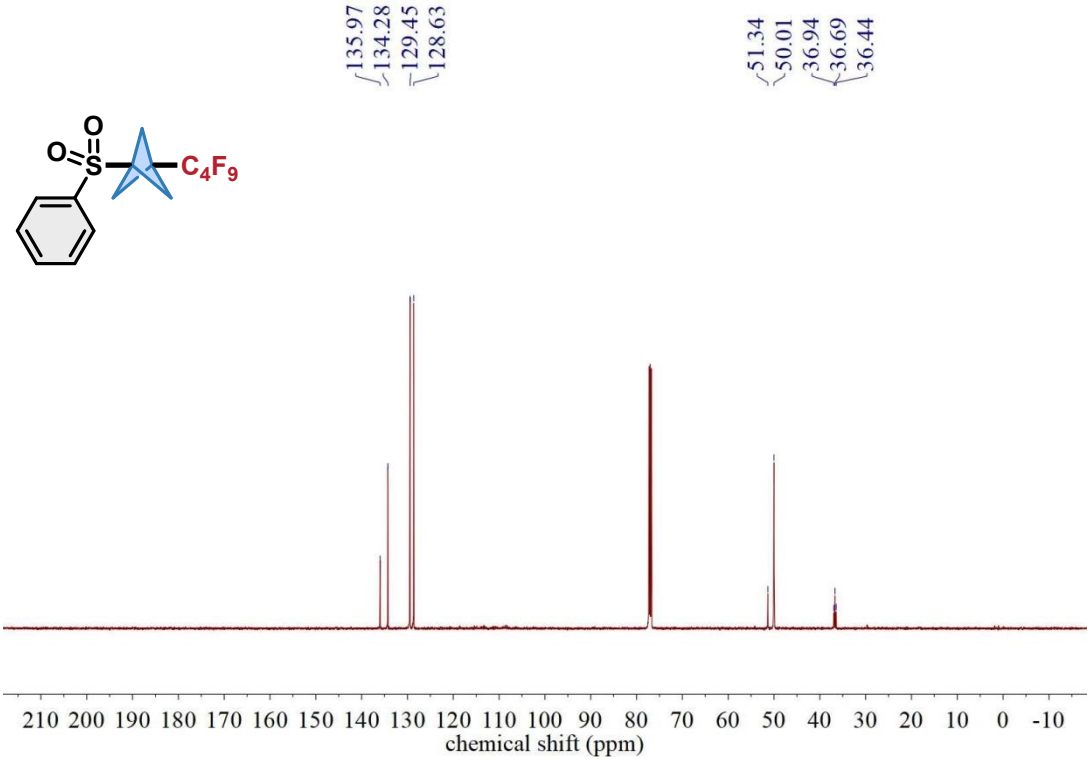
66 ^{19}F NMR (471 MHz, $CDCl_3$)



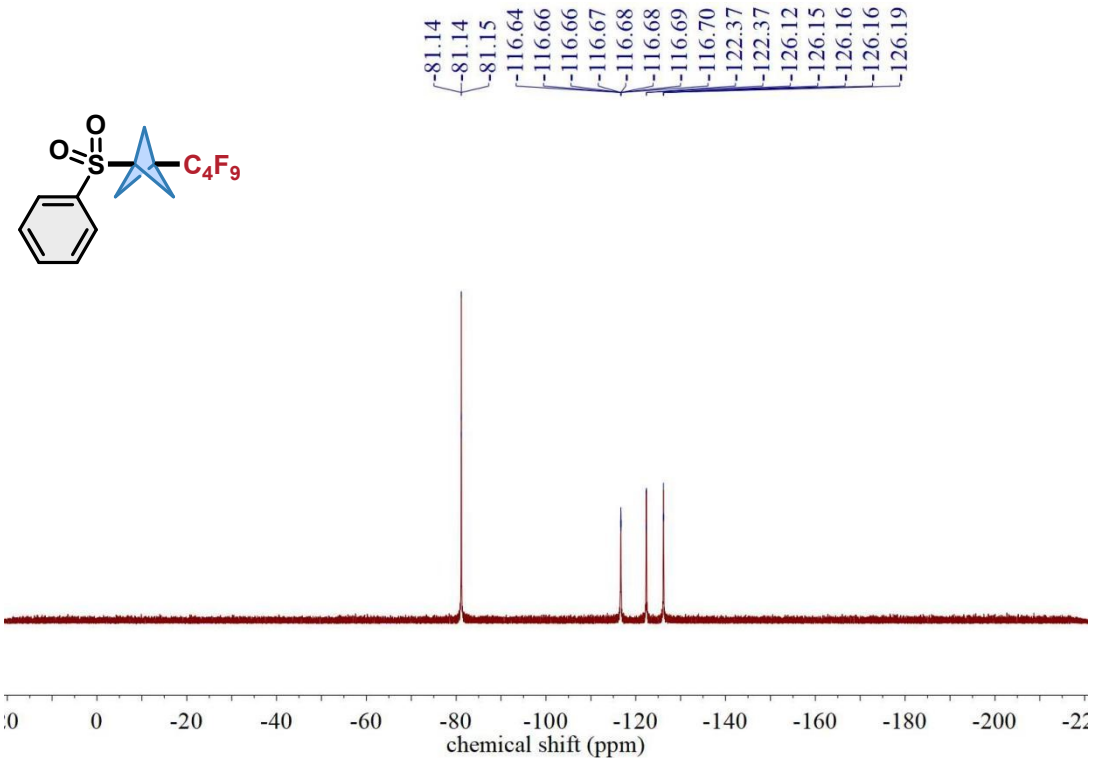
67 ^{1}H NMR (500 MHz, $CDCl_3$)



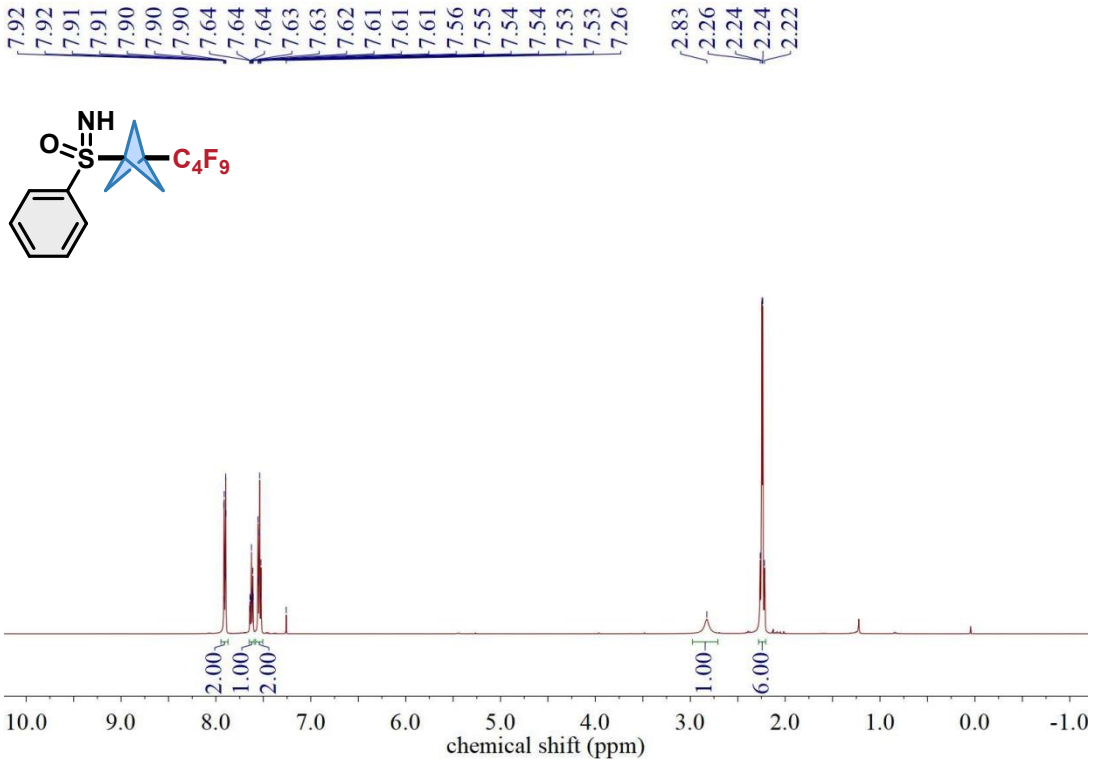
67 ^{13}C NMR (126 MHz, $CDCl_3$)



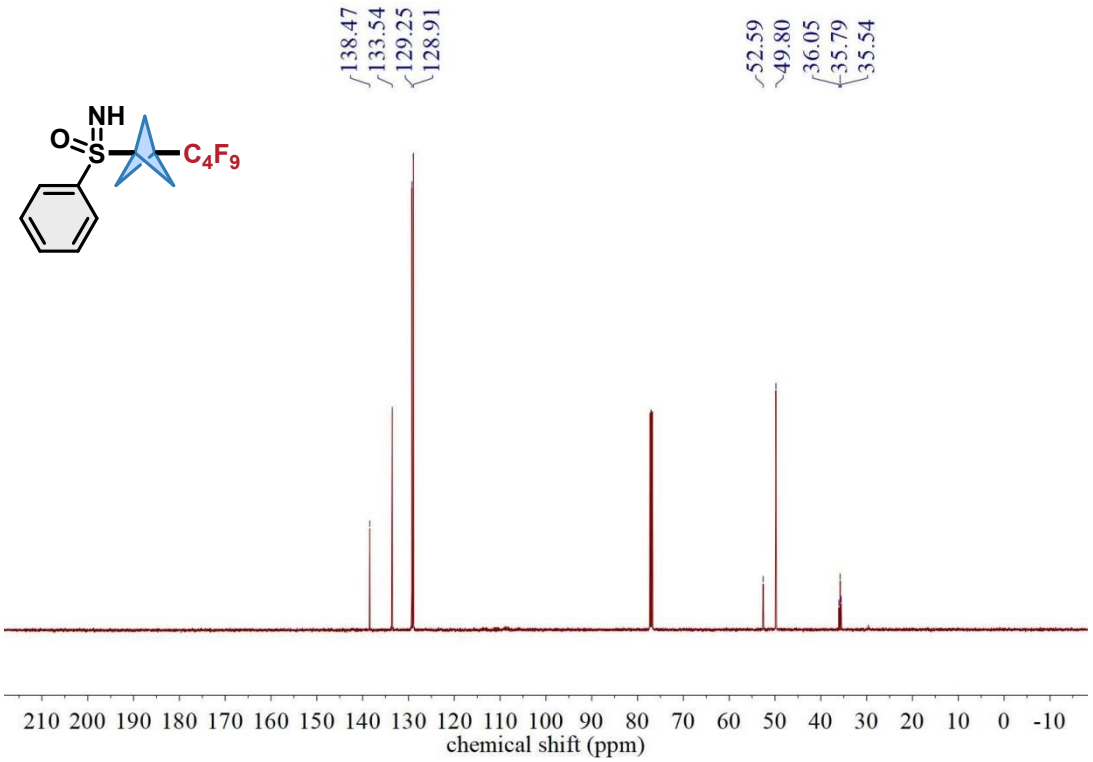
67 ^{19}F NMR (471 MHz, $CDCl_3$)



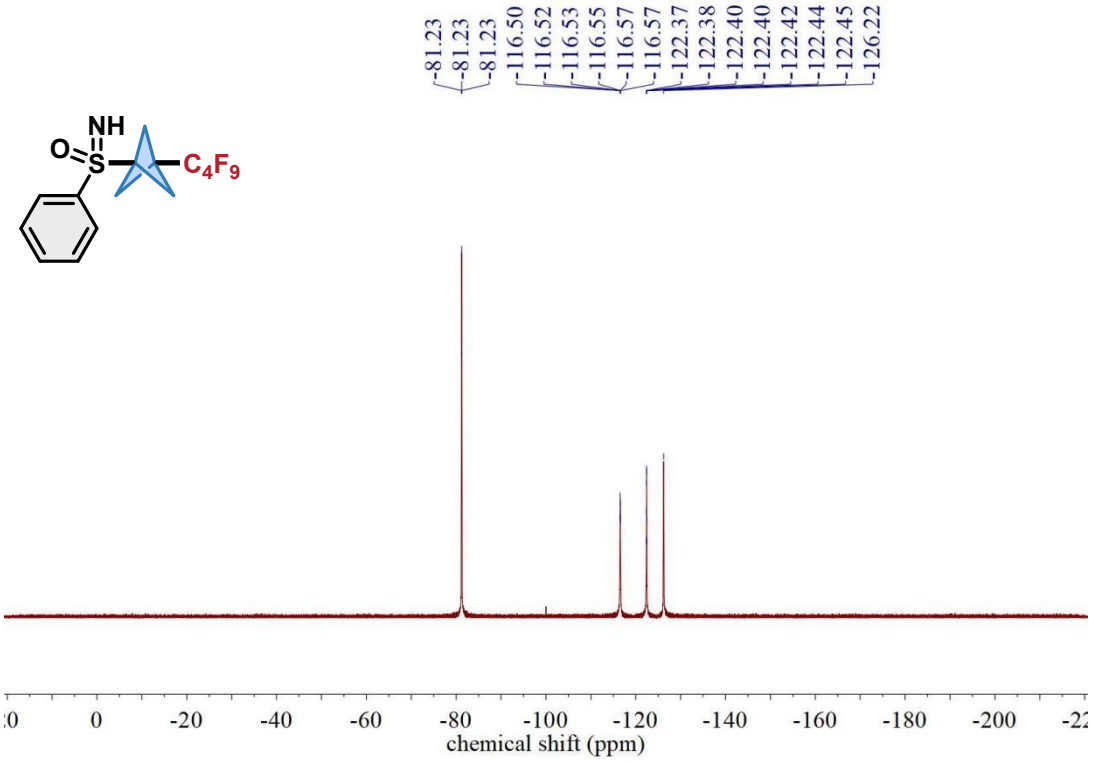
68 ^{1}H NMR (500 MHz, $CDCl_3$)



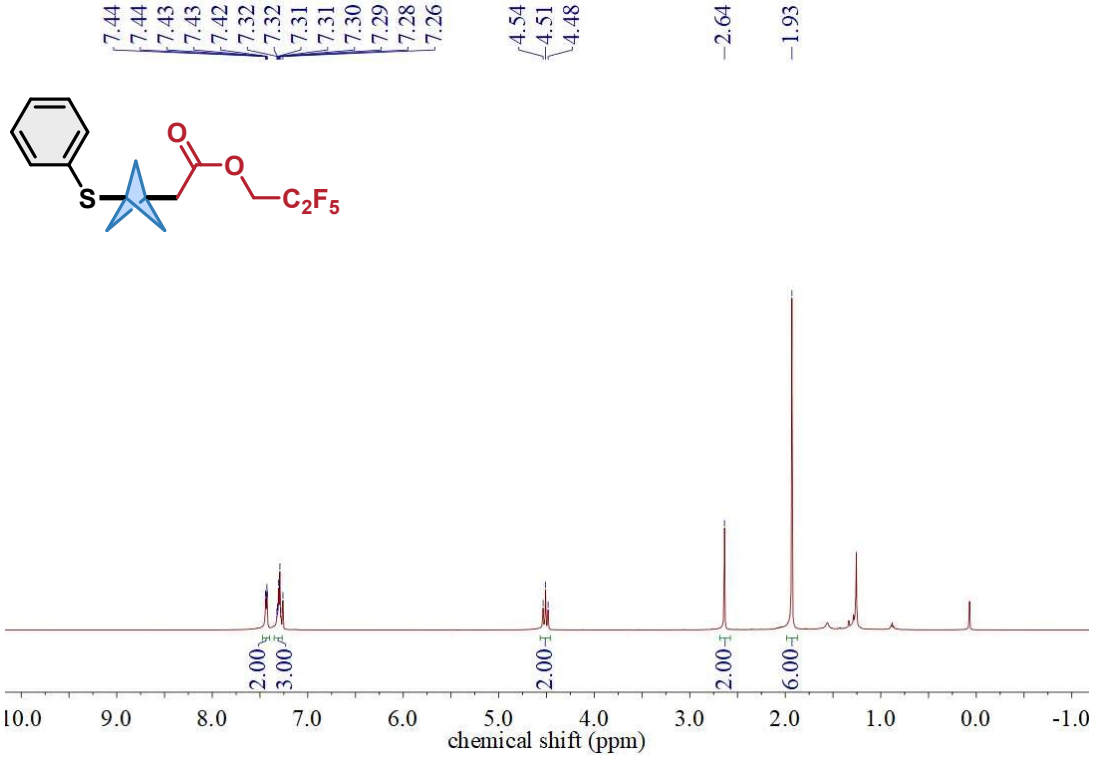
68 ^{13}C NMR (126 MHz, $CDCl_3$)



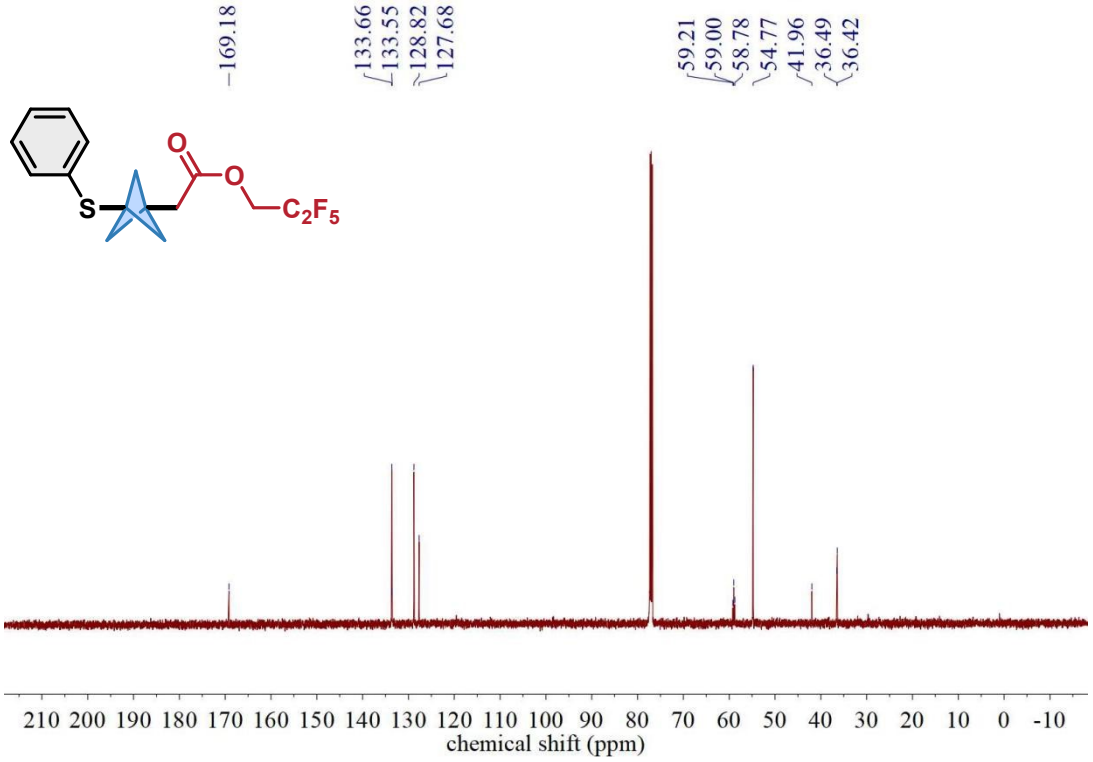
68 ^{19}F NMR (471 MHz, $CDCl_3$)



71 ^{1}H NMR (500 MHz, $CDCl_3$)



71 ^{13}C NMR (126 MHz, $CDCl_3$)



71 ^{19}F NMR (471 MHz, $CDCl_3$)