Visible-Light Induced Radical Perfluoroalkylation/Cyclization Strategy to Access 2-Perfluoroalkylbenzothiazoles/benzoselenazoles by EDA Complex

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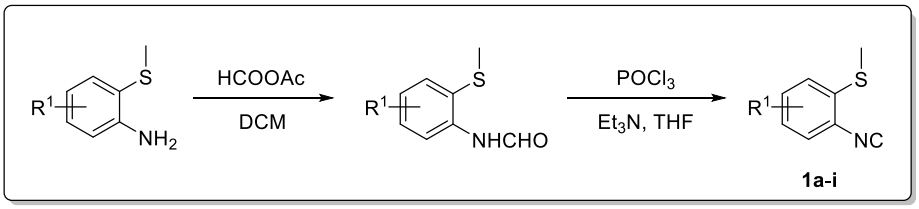
1. General Methods

All reagents were used without further purification. TLC was performed on silica gel plates (F254, 200-300 mesh) using UV light (254/366 nm) for detection and column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Proton chemical shifts δ were given in ppm using tetramethylsilane as internal standard. All NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 3 °C). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet. ^{1}H and ^{13}C chemical shifts are quoted in parts per million downfield from TMS. High resolution mass spectra (HRMS) were taken with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system using the ESI technique. X-ray single-crystal diffraction data were collected on a Bruker SMART1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at variable temperatures. EPR spectrum was recorded by Bruker EMX-10/12 EPR spectrometer. UV−Vis spectra were measured on an Agilent 8453 and fluorescence spectra were obtained with Hitachi F-4600 spectrophotometer, respectively.

2. Experimental Procedures

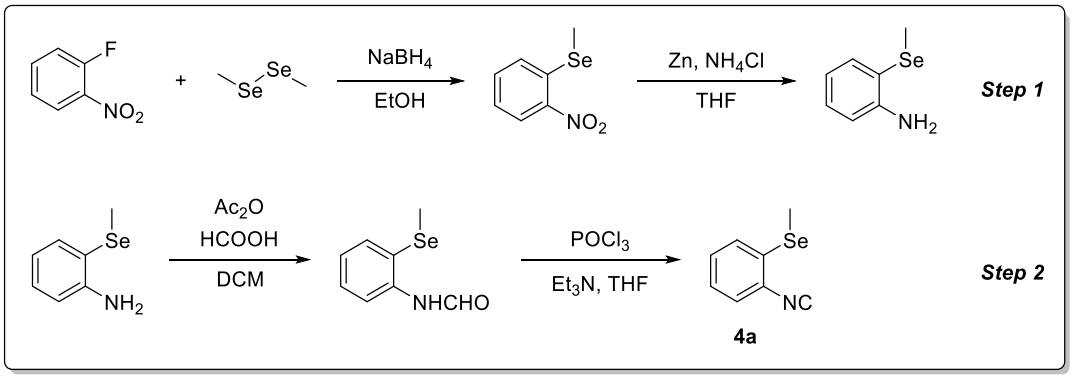
2.1 Preparation of Starting Materials

2.1.1 General Procedures for the Synthesis of (2-isocyanophenyl)(methyl)sulfanes (1a-j)[1]



Acetic formic anhydride (11.3 mmol, 0.89 mL) was added dropwise to a stirring solution of anilines (4.3 mmol) at 0 °C in DCM (8 mL). The mixture was stirred for 2 h at room temperature. Then, the mixture was quenched with saturated Na_2CO_3 solution and extracted with DCM for three times. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the formamides. The crude products were used for subsequent dehydration without further purification. The formamides obtained above and NEt_3 (4.3 mL) were dissolved in THF (8 mL) under nitrogen atmosphere. $POCl_3$ (7.5 mmol, 0.7 mL) in THF (2 mL) was added slowly to the solution *via* syringe for a period of 1 h at 0 °C. The reaction mixture was then stirred for another 2 h at 0 °C. After that, the reaction mixture was diluted with 15 mL ethyl acetate at 0 °C and slowly quenched with saturated Na_2CO_3 solution with continuous stirring for another 30 min. The crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give (2-isocyanophenyl)(methyl)sulfanes (**1a**-**j**).

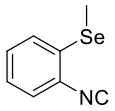
2.1.2 General Procedures for the Synthesis of (2-isocyanophenyl)(methyl)selane (4a)



Step 1[2]: To a solution of dimethyl diselenide (5 mmol, 0.47 mL) in 25 mL of ethanol was added $NaBH_4$ (10.9 mmol, 0.41 g). The solution was stirred until the color disappeared, and then 0.97 mL (9.2 mmol) of 2-fluoronitrobenzene was added. The solution was stirred for 12 h at room temperature. After that, the solvent was removed, water (20 mL) was added, and the mixture was extracted with DCM. The organic layers were combined, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give crude product for next step without further purification. A suspension of methylseleno-2-nitrobenzene (8 mmol, 1.5g), zinc powder (75 mmol, 4.9 g), and ammonium chloride (48 mmol, 2.6 g) in THF (70 mL) was reflux for 20 hunder N_2 atmosphere. The resulting suspension was filtered and the solid was washed with dichloromethane. The organic layer was then dried over $MgSO_4$, concentrated under reduced

pressure to give crude product. The crude product was purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give pure 2-methylselenoaniline.

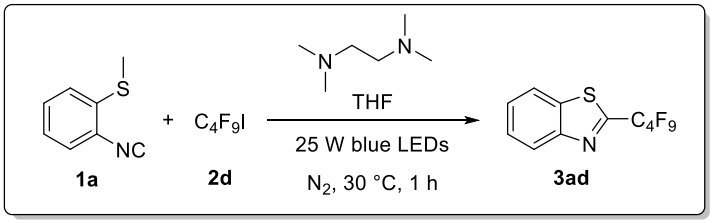
Step 2: Acetic formic anhydride (11.3 mmol, 0.89 mL) was added dropwise to a stirring solution of 2-methylselenoaniline (4.30 mmol) at 0 °C in DCM (8 mL). The mixture was stirred for 2 h at room temperature. Then, the mixture was quenched with saturated aqueous solution of Na_2CO_3 and extracted with DCM for three times. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give *N*-(2-(methylselanyl)phenyl)formamide. The crude product was used for the subsequent dehydration without further purification. THF (8 mL) and NEt_3 (4.3 mL) were added to a flask containing the formamide obtained above under nitrogen atmosphere. $POCl_3$ (7.5 mmol, 0.7 mL) in 2 mL of THF was added slowly *via* syringe for a period of 1 h at 0 °C, and the mixture was stirred for another 2 h at 0 °C. After then, the reaction mixture was diluted with 15 mL ethyl acetate at 0 °C and slowly quenched with saturated aqueous solution of Na_2CO_3 with stirring for 30 min. The crude compound was purified by column chromatography using petroleum ether/ethyl acetate as eluent to give (2-isocyanophenyl)(methyl)selane (**4a**).



4a

(2-isocyanophenyl)(methyl)selane (4a): yellow oil (491.3 mg, 58% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 3H), 7.24 – 7.15 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.56, 130.70, 129.80, 129.19, 127.07, 126.36, 6.62. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for C_8H_8NSe 197.9816, found 197.9831.

2.2 General procedure for the synthesis of 2-Fluoroalkylated Benzothiazoles and Benzoselenazoles

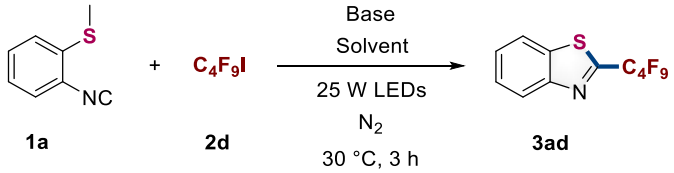


In a 25 mL flask, (2-isocyanophenyl)(methyl)sulfane **1a** (1.0 equiv, 0.2 mmol) was dissolved in THF (2 mL, 0.1 M), then perfluoro-4-iodobutane **2d** (2.0 equiv,0.4 mmol) and TMEDA (2.0 equiv, 1.0 mmol) were added. The mixture was allowed to stir at 30 ºC with irradiation of 25 W LEDs under N_2 atmosphere at 30 °C for 1 h. The reactionwas monitored by TLC. After substrate **1a** was completely consumed, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **3ad**.

2.3 Optimization of Reaction Conditions

We initiated our study by establishing optimal experimental conditions using the model reaction of (2-isocyanophenyl)(methyl)sulfane (**1a**) with nonafluoroalkyl iodide (**2d**) in the presence of various bases under irradiation of 25 W LEDs with N_2 protection at 30 °C for 3 h, as summarized in Table 1. All yields of desired product **3ad** (2-(perfluorobutyl)benzothiazole) were determined by ^{19}F NMR. Initially, a group of bases, including Cs_2CO_3, 1,4-diazabicyclo[2.2.2]octane (DABCO), 8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,1,3,3-tetramethylguanidine (TMG), (*N*,*N*,*N*',*N*'-tetramethylethane-1,2-diamine) TMEDA, *N*,*N*,*N*',*N*'-tetraethylethane-1,2-diamine (TEEDA), *N*,*N*-diisopropyl-ethylanmin (DIPEA), dibenzyl amine and 2,6-lutidine, were examined in CH_3CN under irradiation of white light (entries 1-10), respectively. As it can be seen, DBU, TBD, TMEDA, TEEDA and DIPEA resulted in positive results, delivering **3ad** in 10-44% yields, and among them, TMEDA rendered the highest yield (44%) (entry 6). In contrast, Cs_2CO_3, DABCO, TMG, dibenzyl amine and 2,6-lutidine gave no or trace amount of product **3ad** (entries 1-2, 5, 9-10). Then the effects of solvents on the model reaction were investigated (entries 6, 11-17). It was interesting to observe that the yields of **3ad** were obviously improved when the reaction being carried out in some other solvents tested, including DCE, toluene, DMF, DMSO, THF, 1,4-dioxane and DME (yields: from 62 up to 97%). Among all the solvents tested, THF resulted in a remarkably high yield (97%) (entry 15). Subsequently, effects of different light sources on the model reaction were investigated (entries 15, 18-22). As can be seen, red，yellow or green light gave no or trace amount of product **3ad**, and the reaction did not occur in the dark (for more evidence see supporting information Figure S2). Surprisingly, up to 97% yield of **3ad** could be obtained under irradiation of blue light for only 1 h (entry 20), sharply compared with the 3 h required by using white light as light source (entry 15). Afterward, the amount of TMEDA on the model reaction was examined (entries 20, 23-24). The results showed that 0.2 mmol of TMEDA was still the best choice (entry 20). Following this investigation, we doubled the reaction scale (entry 25), and in this case, we still obtained product **3ad** in 97% yield. Thus, the optimized reaction conditions were established as follows: **1a** (0.2 mmol), **2d** (2.0 equiv) and TMEDA (2.0 equiv) were mixed in THF (2 mL) under irradiation of 25 W blue LEDs with N_2 protection at 30 °C for 1 h.

Table S1. Optimization of Reaction Conditions[a]



1a 2d 3ad

Entry	Base	Solvent	LEDs	Yield (%)[b]
1	Cs_2CO_3	MeCN	White light	0
2	DABCO	MeCN	White light	Trace
3	DBU	MeCN	White light	38
4	TBD	MeCN	White light	10
5	TMG	MeCN	White light	Trace
6	TMEDA	MeCN	White light	44
7	TEEDA	MeCN	White light	19
8	DIPEA	MeCN	White light	16
9	dibenzyl amine	MeCN	White light	Trace
10	2,6-lutidine	MeCN	White light	0
11	TMEDA	DCE	White light	79
12	TMEDA	toluene	White light	67
13	TMEDA	DMF	White light	81
14	TMEDA	DMSO	White light	80
15	TMEDA	THF	White light	97
16	TMEDA	1,4-dioxane	White light	62
17	TMEDA	DME	White light	77
18	TMEDA	THF	Red light	0
19	TMEDA	THF	Yellow light	Trace
20[c]	TMEDA	THF	Blue light	97
21	TMEDA	THF	Green light	6
22	TMEDA	THF	In the dark	0
23[c, d]	TMEDA	THF	Blue light	20
24[c, e]	TMEDA	THF	Blue light	46
25[c, f]	TMEDA	THF	Blue light	97

[a] Reaction conditions: **1a** (0.1 mmol), **2d** (0.2 mmol) and base (0.2 mmol) in solvent (1 mL) under irradiation of 25 W LEDs with N_2 protection at 30 °C for 3 h unless noted otherwise. [b] The yields of **3ad** were determined by ^{19}F NMR [c] Reaction time was 1 h. [d] TMEDA (0.05 mmol) was used. [e] TMEDA (0.1 mmol) was used. [f] Double-sale: **1a** (0.2 mmol), **2d** (0.4 mmol) and TMEDA (0.4 mmol) in THF (2 mL).

*2.4 Specially designed reactor for the gram-scale synthesis of **3ad***

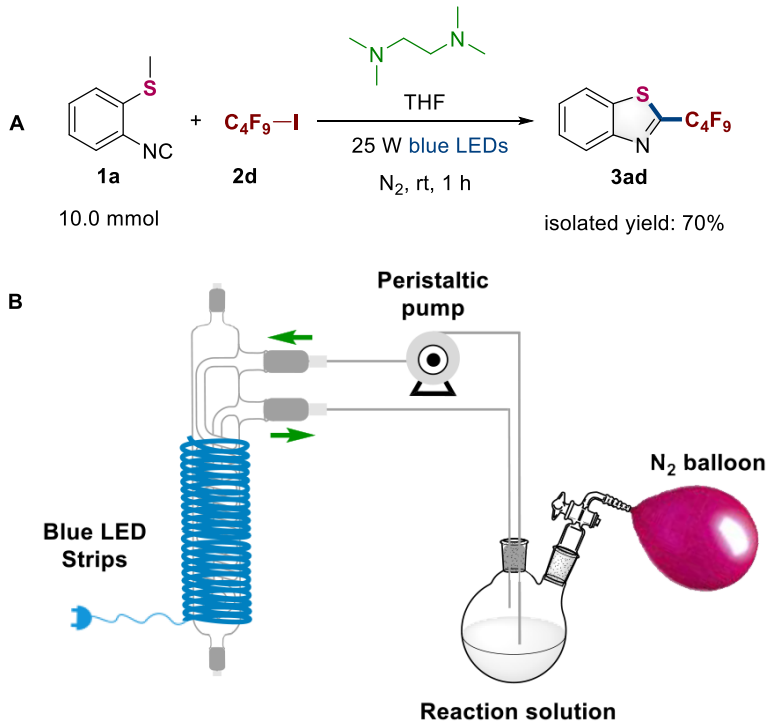


Figure S1. Specially designed reactor for the gram-scale synthesis. **A:** Gram-scale synthesis of **3ad** with blue LEDs light irradiation: **1a** (10.0 mmol, 1.49 g), **2a** (20.0 mmol, 3.45 g), TMEDA (20.0 mmol, 1.16 g) in 100 mL THF with N_2 protection at rt for 1 h with the assistance of specially designed reactor. Isolated yield of **3ad** was given; **B:** A specially designed apparatus for gram-scale synthesis of **3ad**.

2.5 *"On/off" LED irradiation experiment*

"On/off" LED irradiation experiment was used to explore the essential role of visible light in this transformation, as descripted in Figure S2. The model reaction of **1a** and **2d** was designed to be irradiated under successive on/off LED irradiation conditions at every 20 min interval for a total of 100 min. The yield of **3ad** was determined by ^{19}F NMR every 20 min. As can be seen, obvious increases in yield were observed once the reaction was irradiated with blue light. In contrast, almost no increase in yield was observed when the reaction was conducted in dark, demonstrating an essential role of the visible-light irradiation in this transformation.

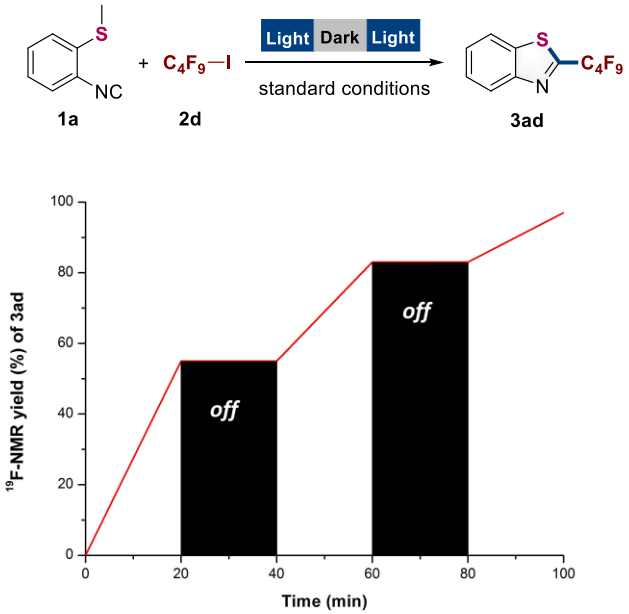


Figure S2. "On/off" LED irradiation experiment for the synthesis of **3ad**.

2.6 Titration experiments of C_4F_9I with TMEDA

^{19}F NMR spectra of mixtures of C_4F_9I and TMEDA in $CDCl_3$ were recorded at 298 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of C_4F_9I (0.03 mmol) was kept constant at 0.5 M, and that of TMEDA was varied from 0 to 2.0 M. The molar ratios of C_4F_9I: TMEDA were 1:0, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:10, 1:20, 1:30, 1:40. Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.0660) was used as an internal standard. The ^{19}F NMR signal of $-CF_2I$ group in C_4F_9I shifted upfield along with increasing the amount of TMEDA, indicating the formation of EDA complex of C_4F_9I with TMEDA (Figure S2).

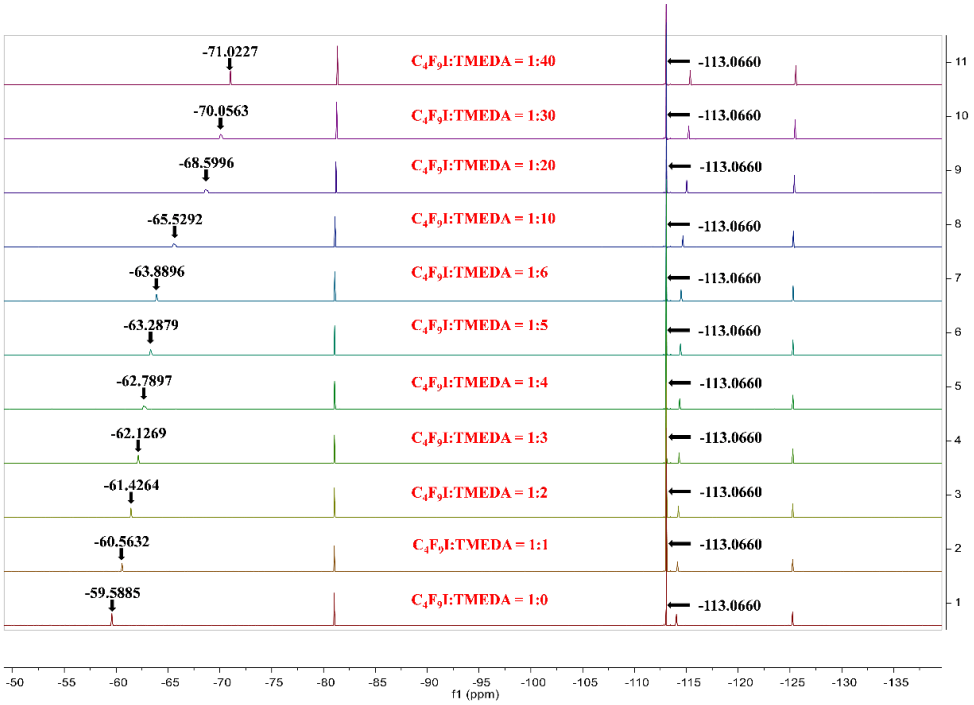


Figure S3. ^{19}F NMR shift of C_4F_9I with TMEDA.

2.7 Determination of the association constant (K_{TMEDA})

^{19}F NMR spectra of mixtures of C_4F_9I and TMEDA in $CDCl_3$ were recorded at 298 K. In an NMR tube, the total volume of mixture was 0.6 mL, the concentration of C_4F_9I (0.03 mmol) was kept constant at 0.5 M, while that of TMEDA was varied from 0 to 2.0 M. The molar ratios of C_4F_9I: TMEDA were 1:0, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:10, 1:20, 1:30, 1:40. Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.0660) was used as an internal standard. ^{19}F NMR for each sample was recorded and the changes of chemical shift ($\Delta\delta$) for -CF_2I group in C_4F_9I were used to draw the plot. The association constant of C_4F_9I with TMEDA (K_{TMEDA}) was calculated: $K_{TMEDA} = c/a = 0.0695/0.0478 = 1.45\ M^{-1}$

Enty	[C_4F_9I] (M)	1/[TMEDA] (M)	δ (ppm)	Δδ (ppm)	1/Δδ (ppm)
1	0	0.5	-71.0227	11.4372	0.0874
2	0.05	0.67	-70.0563	10.4708	0.0955
3	0.05	1	-68.5966	9.0111	0.1110
4	0.05	2	-65.5292	5.9437	0.1682
5	0.05	3.33	-63.8896	4.3041	0.2323
6	0.05	4	-63.2879	3.7024	0.2701
7	0.05	5	-62.7897	3.2042	0.3121
8	0.05	6.67	-62.1269	2.5414	0.3935
9	0.05	10	-61.4264	1.8409	0.5432
10	0.05	20	-60.5632	0.9777	1.0228
11	0.05	--	-59.5855	--	--

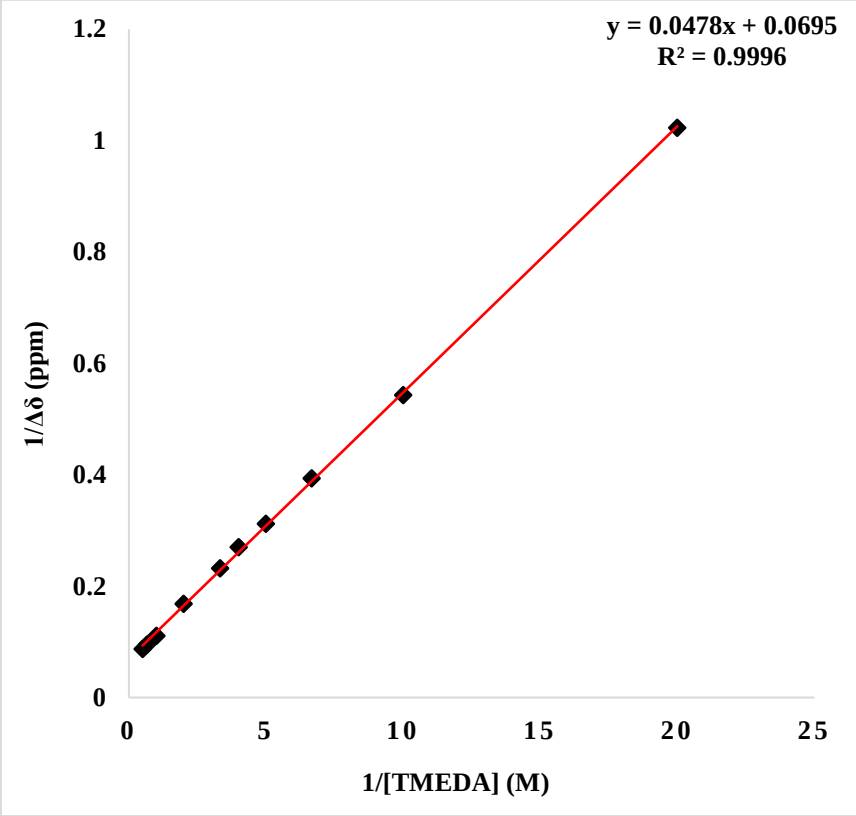


Figure S4. Plot for determination of the association constant (K_{TMEDA}).

2.8 Determination of binding stoichiometry of EDA complex

The binding stoichiometry between C_4F_9I and TMEDA was evaluated using Job's plot analysis: ^{19}F NMR spectra mixtures of C_4F_9I and TMEDA in $CDCl_3$ were recorded at 298 K. Fluorobenzene ($\delta_{F\text{-}Ph}$ = -113.066) was used as an internal standard. The total volume of the mixture was 0.5 mL, and the total amount of C_4F_9I and TMEDA was kept constant at 0.25 mmol (0.5 M), while the amount of C_4F_9I was varied from 0 to 0.25 mmol (0-0.5 M). The molar ratios of $[C_4F_9I]/[C_4F_9I + TMEDA]$ were 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. ^{19}F NMR for each sample was recorded and the changes of chemical shift ($\Delta\delta$) for $-CF_2I$ group in C_4F_9I were used to draw the plot. The stoichiometry was determined by plotting ratios of $[C_4F_9I]\times\Delta\delta$ against ratios of $[C_4F_9I]/[C_4F_9I + TMEDA]$ to afford a maximum value. $X_{max} = b/(-2a) = 6.3701/-2\times-6.2269 = 0.51$. These data indicate that the formation of EDA complex of C_4F_9I with TMEDA in a binding stoichiometry of 1:1.

Enty	$[C_4F_9I]$ (M)	$\Delta\delta$ (ppm)	$[C_4F_9I]/[C_4F_9I + TMEDA]$	$[C_4F_9I]\times\Delta\delta$ (M.ppm)
1	0	0	0	0
2	0.05	5.7487	0.1	0.57487
3	0.10	5.0797	0.2	1.01594
4	0.15	4.6486	0.3	1.39458
5	0.20	3.7404	0.4	1.49616
6	0.25	2.7246	0.5	1.3623
7	0.30	2.7059	0.6	1.62354
8	0.35	2.1659	0.7	1.51613
9	0.40	1.4824	0.8	1.18592
10	0.45	0.8315	0.9	0.74835
11	0.50	0	1.0	0

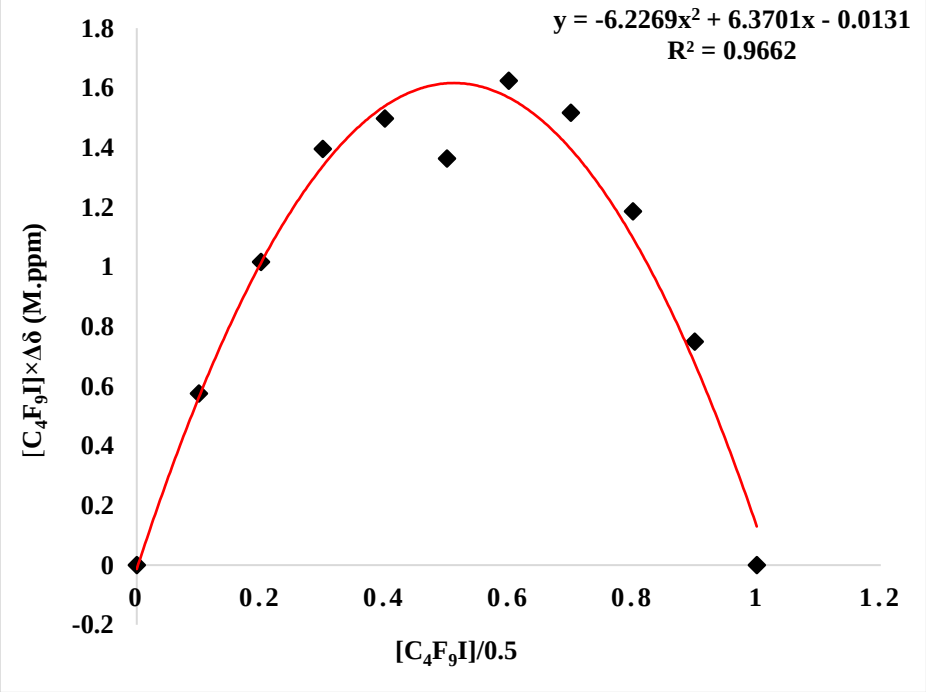


Figure S5. Job's plot.

2.9 UV-vis absorbance experiment

A UV-vis absorbance experiment has been carried out for confirming the formation of EDA complex as illustrated below in Figure S6. In Figure S6, the red UV absorbance line came from C_4F_9I solution, black one came from TMEDA solution, and blue one came from the mixed solution of C_4F_9I and TMEDA. UV-vis spectra revealed that upon mixing C_4F_9I with TMEDA, an obvious bathochromic shift of the UV-vis absorbance was observed, strongly suggesting that C_4F_9I-TMEDA EDA complex might indeed be formed in the mixed solution.

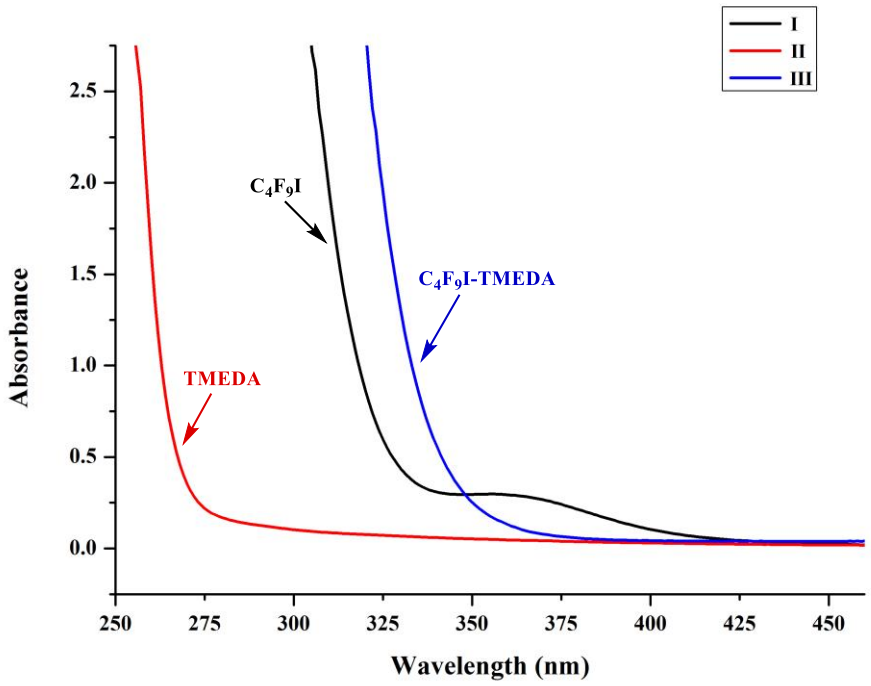
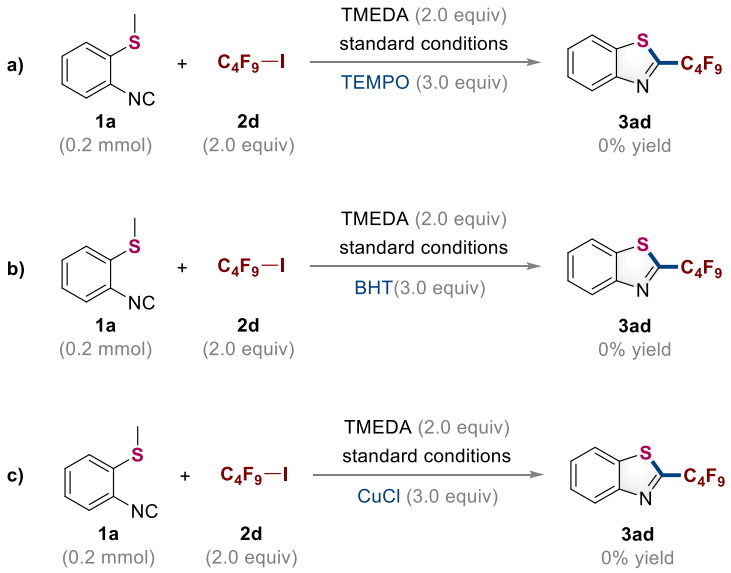


Figure S6. UV-vis absorption spectra. Line I: C_4F_9I (**2d)** (0.2 mmol) in 2 mL MeCN; Line II: TMEDA (0.2 mmol) in 2 mL MeCN; Line III: **2d** (0.2 mmol) and TMEDA (0.2 mmol) in 2 mL MeCN. All the UV-vis absorption spectra were recorded in 1 cm path quartz cuvettes using Agilent 8543 UV/Vis spectrophotometer.

2.10 Control Experiments

We carried out three control experiments using TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)-oxidanyl), BHT (2,6-di-*tert*-butyl-4-methylphenol), and CuCl as radical scavengers, respectively, as illustrated in Scheme S1. As it can be seen, the three reactions were totally suppressed, and no desired product **3ad** was obtained in each case. The results strongly remind of a radical-involved process.

Scheme S1. **Control Experiments**[a]



[a] Reaction conditions: **1a** (0.1 mmol), **2d** (2.0 equiv), TMEDA (2.0 equiv), and quenchers (3.0 equiv) in 2 mL THF under irradiation of 25 W blue LEDs with N_2 protection at 30 °C for 1 h. The yields of **3ad** were determined by ^{19}F NMR.

2.11 Measurement of quantum yield

A measurement on quantum yield of the photoreaction was conducted following the methods published[3] The result of the quantum yield measurement indicated that 0.2 equivalent of product was formed for every photon absorbed, ruling out the possibility of chain propagation process, which is basically consistent with our proposed mechanism shown in Scheme 5 of our manuscript. The measurement on the quantum yield of the photoreaction is described in details as follows:

- **Determination of the light intensity at 468 nm**

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 468 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 468 nm. A non-irradiated sample was also prepared and the absorbance at 468 nm measured. Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = \frac{V*\Delta A}{L*\mathcal{E}} \qquad (1)$$

where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 468 nm between the irradiated and non-irradiated solutions, L is the path length (1.000 cm), and ε is the molar absorptivity (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi*t*f} \qquad (2)$$

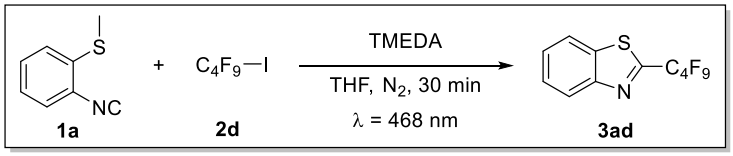
Where Φ is the quantum yield for the ferrioxalate actinometer (0.93 for 0.15 M solution at λ = 468 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 468 nm (0.906, *vide infra*). The photon flux was calculated to be 3.94×10^{-9} einstein s^{-1}.

Sample calculation:

$$\text{mol } Fe^{2+} = \frac{0.00235 \text{ L}*1.4123}{1.0000 \text{ cm}*11100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 2.99 * 10^{-7} \text{ mol}$$

$$\text{photon flux} = \frac{2.99\times10^{-7} \text{ mol}}{0.93*90 \ s*0.906} = 3.94 * 10^{-9} \text{ einstein } s^{-1}$$

- **Determination of quantum yield:**



A cuvette was pumped into the glovebox. A mixture of **1a** (0.2 mmol), **4d** (0.4 mmol), and TMEDA (0.4 mmol) were dissolved in THF (2 mL) under N_2 atmosphere. The cuvette sealed with a cap and septa. The

sample was stirred and irradiated (λ = 468 nm) at room temperature for 30 min. After irradiation, the yield of product formed was determined by ^{19}F NMR. The quantum yield was determined using eq 3.

$$\Phi = \frac{\text{mol product}}{\text{flux}*t*f} \quad (3)$$

$$f = 1 - 10^{-A} \quad (4)$$

- **Absorbance of EDA complex:**

The absorbance of EDA complex was measured at the reaction concentration. The absorbance at 468 nm is 0.1. The fraction of light absorbed (*f*) by this solution was calculated using eq 4.

$$f = 1 - 10^{-0.1} = 0.2$$

- **Sample quantum yield calculation:**

$$\Phi = \frac{3*10^{-7}\ \text{mol}}{3.94*10^{-9}\ \text{einstein}\ \text{s}^{-1}*1800\ \text{s}*0.2} = 0.2$$

2.12 HRMS analysis of model reaction solution

In order to have a deeper insight of reaction mechanism, we employed high resolution mass spectrometry (HRMS) to analyze the reaction solution of the model reaction as illustrated below in Figure7. As it can be seen, three high peaks appearing at *m/z* 115.1230, 117.1386, and 131.1538, corresponding to ions $[C_6H_{15}N_2]^+$, $[C_6H_{17}N_2]^+$, and $[C_7H_{19}N_2]^+$ respectively, were observed. The peak of $[C_6H_{17}N_2]^+$ appearing at *m/z* 117.1386 obviously corresponds to the molecular ion [TMEDA + H]$^+$. Reasonably, the peak of $[C6H15N_2]^+$ appearing at *m/z* 115.1230 should correspond to the iminium ion **8**, and the peak of $[C7H19N_2]^+$ appearing at *m/z* 131.1538 to quaternary ammonium **9**.

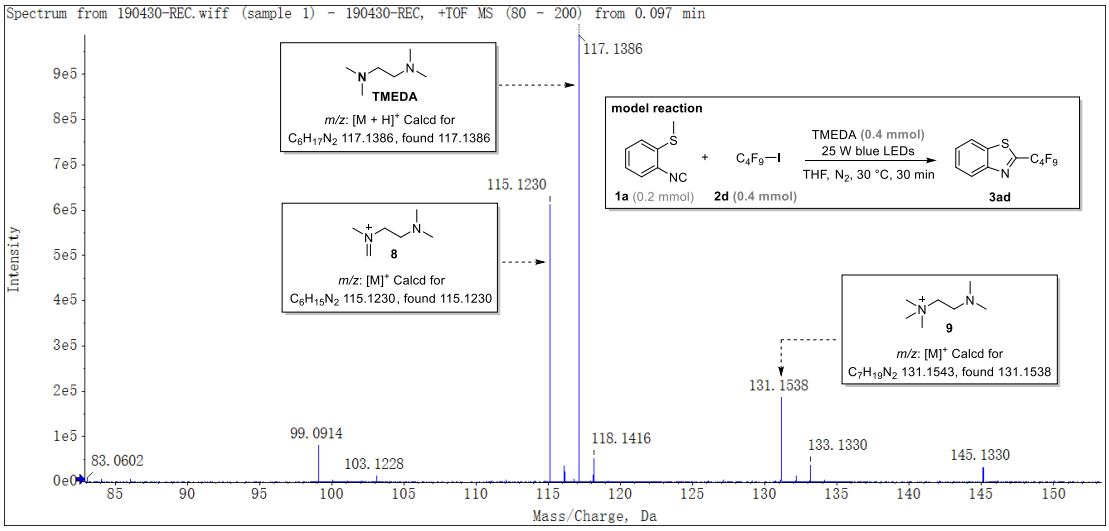


Figure S7. HRMS analysis of model reaction solution (*m/z* from 80 to 150).

Reference

(1) (a) Yang, W. C.; Wei, K.; Sun, X.; Zhu, J.; Wu, L. *Org. Lett.* **2018**, *20*, 3144. (b) Yuan, Y.; Dong, W.; Gao, X.; Xie, X.; Zhang, Z. *Org. Lett.* **2019**, *21*, 469.

(2) (a) Zang, H.; Sun, J.-G.; Dong, X.; Li, P.; Zhang, B. *Adv. Synth. Catal.* **2016**, *358*, 1746. (b) Bubrin, M.; Schweinfurth, D.; Ehret, F.; Záliš, S.; Kvapilová, H.; Fiedler, J.; Zeng, Q.; Hartl, F.; Kaim, W. *Organometallics* **2014**, *33*, 4973.

(3) (a) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426. (b) Kandukuri, S. R.; Bahamonde, A.; Chatterjee, I.; Jurberg, I. D.; Escudero-Adan, E. C.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2015**, *54*, 1485.

3. Crystal data and structure refinement for 3ae and 5ad

Identification code	CCDC 1905456
Empirical formula	CHNOFS
Formula weight	94.09
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.849(3)
b/Å	5.3065(4)
c/Å	11.1102(8)
α/°	90
β/°	94.384(10)
γ/°	90
Volume/Å^3	1401.9(2)
Z	16
ρ_{calc}g/cm^3	1.783
μ/mm^{-1}	6.888
F(000)	752.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/	7.436 to 147.126
Index ranges	-29 ≤ h ≤ 28, -5 ≤ k ≤ 6, -13 ≤ l ≤ 12
Reflections collected	8524
Independent reflections	2730 [R_{int} = 0.0387, R_{sigma} = 0.0334]
Data/restraints/parameters	2730/0/226
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0947, wR_2 = 0.2723
Final R indexes [all data]	R_1 = 0.1008, wR_2 = 0.2783
Largest diff. peak/hole / e Å^{-3}	1.14/-0.65

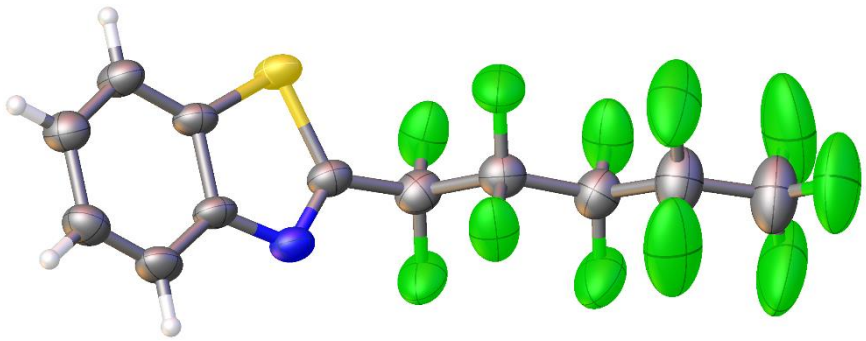


Figure S8. ORTEP view (30% ellipsoid contour probability) of X-crystal structure of **3ae.**

Identification code	CCDC 1905455
Empirical formula	$C_{11}H_4F_9NSe$
Formula weight	400.11
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.6570(9)
b/Å	5.3921(2)
c/Å	11.3053(4)
α/°	90
β/°	99.237(4)
γ/°	90
Volume/Å^3	1303.08(9)
Z	4
ρ_{calc}g/cm^3	2.039
μ/mm^{-1}	4.956
F(000)	768.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.134 to 146.412
Index ranges	$-25 \leq h \leq 26$, $-6 \leq k \leq 6$, $-13 \leq l \leq 13$
Reflections collected	5575
Independent reflections	2512 [R_{int} = 0.0386, R_{sigma} = 0.0496]
Data/restraints/parameters	2512/36/199
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0744, wR_2 = 0.2133
Final R indexes [all data]	R_1 = 0.0783, wR_2 = 0.2172
Largest diff. peak/hole / e Å^{-3}	1.61/-0.98

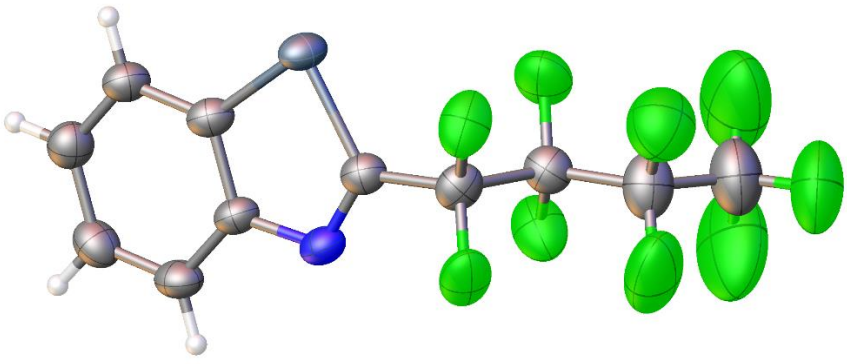
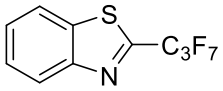


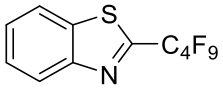
Figure S9. ORTEP view (30% ellipsoid contour probability) of X-crystal structure of **5ad**.

4. Characterization data



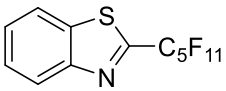
3ac

2-(perfluoropropyl)benzo[d]thiazole (3ac): colorless oil (54.5 mg, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.55 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.64 (t, *J* = 30.0 Hz), 152.67, 135.32, 127.45, 127.30, 125.08, 121.87, 119.50 – 107.94 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.18 (t, *J* = 9.3 Hz, 3F), -107.01 – -107.14 (m, 2F), -125.81 – -125.87 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{10}H_5F_7NS$ 304.0025, found 304.0040.



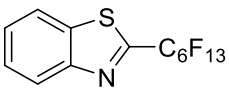
3ad

2-(perfluorobutyl)benzo[d]thiazole (3ad): colorless oil (64.9 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.51 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.79 (t, *J* = 29.8 Hz), 152.66, 135.34, 127.49, 127.35, 125.12, 121.91, 119.11 – 108.31 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.29 – -81.36 (m, 3F), -106.37 – -106.45 (m, 2F), -122.27 – -122.37 (m, 2F), -125.72 – -125.85 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{11}H_5F_9NS$ 353.9994, found 354.0013.



3ae

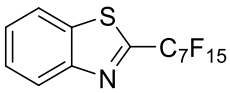
2-(perfluoropentyl)benzo[d]thiazole (3ae): white solid (73.3 mg, 91% yield), mp 47.6 – 48.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.55 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.86 (t, *J* = 29.9 Hz), 152.68, 135.35, 127.45, 127.30, 125.10, 121.86, 119.01 – 108.26 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.91 – -80.98 (m, 3F), -106.14 – -106.23 (m, 2F), -121.46 – -121.56 (m, 2F), -122.18 – -122.35 (m, 2F), -126.23 – -126.35 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{12}H_5F_{11}NS$ 403.9962, found 403.9988.



3af

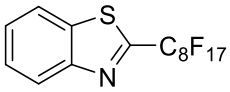
2-(perfluorohexyl)benzo[d]thiazole (3af): white solid (75.2 mg, 83% yield), mp 69.8 – 71.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.55 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.88 (t, *J* = 29.9 Hz), 152.66, 135.35, 127.50, 127.36, 125.14, 121.93, 118.92 – 108.36 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.75 – -80.81 (m, 3F), -106.05 – -

106.15 (m, 2F), -121.19 – -121.42 (m, 4F), -122.68 – -122.84 (m, 2F), -126.09 – -126.18 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_5F_{13}NS$ 453.9930, found 453.9940.



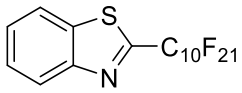
3ag

2-(perfluoroheptyl)benzo[d]thiazole (3ag): white solid (89.5 mg, 89% yield), mp 74.2 – 75.6 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.89 (t, *J* = 30.0 Hz), 152.67, 135.34, 127.37, 127.22, 125.05, 121.79, 118.87 – 107.11 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.22 (t, *J* = 9.8 Hz, 3F), -106.23 – -106.31 (m, 2F), -121.32 – -121.49 (m, 4F), -122.12 – -122.24 (m, 2F), -122.90 – -123.03(m, 2F), -126.42 – -126.51(m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_5F_{15}NS$ 503.9898, found 503.9886.



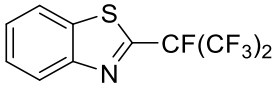
3ah

2-(perfluorooctyl)benzo[d]thiazole (3ah): white solid (89.6 mg, 81% yield), mp 76.6 – 77.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.90 (t, *J* = 29.7 Hz), 152.67, 135.35, 127.48, 127.34, 125.14, 121.90, 118.87 – 107.34 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.76 – -80.87 (m, 3F), -106.03 – -106.12 (m, 2F), -121.13 – -121.23 (m, 4F), -121.76 – -121.94 (m, 4F), -122.70 – -122.78 (m, 2F), -126.09 – -126.23 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_5F_{17}NS$ 553.9866, found 553.9846.



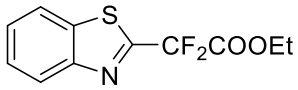
3aj

2-(perfluorodecyl)benzo[d]thiazole (3aj): white solid (121.5 mg, 93% yield), mp 102.5 – 104.6 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.55 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.91 (t, *J* = 29.8 Hz), 152.67, 135.36, 127.50, 127.35, 125.15, 121.93, 118.85 – 107.01 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.81 (t, *J* = 10.0 Hz, 3F), -106.10 (t, *J* = 13.3 Hz, 2F), -121.19 (s, 4F), -121.75 (s, 6F), -121.95 (s, 2F), -122.76 (s, 2F), -126.13 – -126.22 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_5F_{21}NS$ 653.9802, found 653.9828.



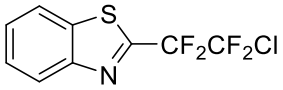
3ak

2-(perfluoropropan-2-yl)benzo[d]thiazole (3ak): colorless oil (43.0 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.48 (d, *J* = 29.5 Hz), 152.98, 134.79 (d, *J* = 2.1 Hz), 127.13, 127.05, 124.78, 121.67, 119.57 (dd, *J* = 288.0, 26.7 Hz), 92.55 – 89.20 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.04 – -75.10 (m, 6F), -174.42 – -174.52 (m, 1F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{10}H_5F_7NS$ 304.0025, found 304.0038.



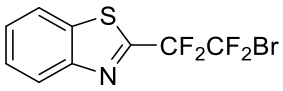
3al

Ethyl 2-(benzo[d]thiazol-2-yl)-2,2-difluoroacetate (3al): yellow oil (45.2 mg, 88% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.48 (m, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.68 (t, *J* = 32.2 Hz), 160.22 (t, *J* = 32.6 Hz), 152.39, 135.04, 127.04, 127.00, 124.64, 122.01, 110.31 (t, *J* = 252.5 Hz), 64.00, 13.85. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -98.28 (s, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{11}H_{10}F_2NO_2S$ 258.0395, found 258.0384.



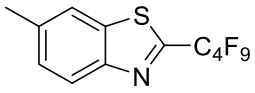
3am

2-(2-chloro-1,1,2,2-tetrafluoroethyl)benzo[d]thiazole (3am): colorless oil (40.9 mg, 76% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.50 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.99 (t, *J* = 30.5 Hz), 152.59, 135.35, 127.34, 127.20, 124.93, 121.78, 122.55 (tt, *J* = 300.7, 38.3 Hz), 111.78 (tt, *J* = 257.6, 34.5 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -69.51 – -69.54 (m, 2F), -105.16 (t, *J* = 4.9 Hz, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_9H_5ClF_4NS$ 269.9762, found 269.9744.



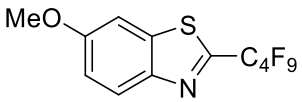
3an

2-(2-bromo-1,1,2,2-tetrafluoroethyl)benzo[d]thiazole (3an): colorless oil (41.9 mg, 67% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.77 (t, *J* = 30.8 Hz), 152.60, 135.39, 127.37, 127.24, 124.96, 121.82, 115.92 (tt, *J* = 313.6, 40.6 Hz), 111.78 (tt, *J* = 257.1, 32.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.39 (t, *J* = 6.1 Hz, 2F), -102.99 (t, *J* = 6.1 Hz, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_9H_5BrF_4NS$ 313.9257, found 313.9273.



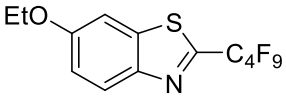
3bd

6-methyl-2-(perfluorobutyl)benzo[d]thiazole (3bd): colorless oil (63.9 mg, 87% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.38 (dd, *J* = 8.5, 1.6 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.47 (t, *J* = 29.9 Hz), 150.87, 138.06, 135.57, 128.92, 124.38, 121.17, 21.22. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.37 – -81.44 (m, 3F), -106.32 – -106.41 (m, 2F), -122.31 – -122.44 (m, 2F), -125.78 – -125.90 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{12}H_7F_9NS$ 368.0150, found 368.0158.



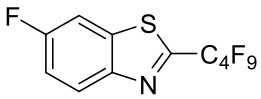
3cd

6-methoxy-2-(perfluorobutyl)benzo[d]thiazole (3cd): colorless oil (71.2 mg, 93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 9.1 Hz, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.16 (dd, *J* = 9.1, 2.6 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.39, 152.50 (t, *J* = 29.9 Hz), 147.20, 137.12, 125.44, 117.47, 103.08, 55.46. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.40 (t, *J* = 9.7 Hz, 3F), -106.26 – -106.34 (m, 2F), -122.41 – -122.48 (m, 2F), -125.83 – -125.95 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{12}H_7F_9NOS$ 384.0099, found 384.0116.



3dd

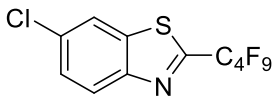
6-ethoxy-2-(perfluorobutyl)benzo[d]thiazole (3dd): white solid (69.8 mg, 88% yield), mp 58.5 – 60.6 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 9.1 Hz, 1H), 7.36 (d, *J* = 2.5 Hz, 1H), 7.20 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.76, 152.42 (t, *J* = 30.0 Hz), 147.12, 137.13, 125.53, 117.87, 103.83, 64.18, 14.49. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.13 – -81.19 (m, 3F), -106.14 – -106.23 (m, 2F), -122.25 – -122.38 (m, 2F), -125.66 – -125.78 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{13}H_9F_9NOS$ 398.0256, found 398.0241.



3ed

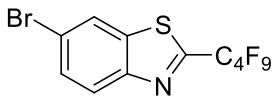
6-fluoro-2-(perfluorobutyl)benzo[d]thiazole (3ed): white solid (31.9 mg, 43% yield), mp 67.1 – 69.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 9.1, 4.7 Hz, 1H), 7.66 (dd, *J* = 7.8, 2.6 Hz, 1H), 7.36 (td, *J* = 8.9, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.68 (d, *J* = 250.3 Hz), 155.45 (t, *J* =

30.2 Hz), 149.33 (d, *J* = 1.7 Hz), 136.51 (d, *J* = 11.6 Hz), 126.34 (d, *J* = 9.8 Hz), 116.50 (d, *J* = 25.2 Hz), 107.84 (d, *J* = 27.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.00 – -81.12 (m, 3F), -106.31 – -106.41 (m, 2F), -111.46 – -111.51 (m, 1F), -122.20 – -122.31 (m, 2F), -125.58 – -122.72 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_4F_{10}NS$ 371.9899, found 371.9920.



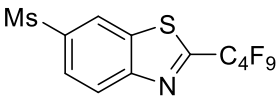
3fd

6-chloro-2-(perfluorobutyl)benzo[d]thiazole (3fd): white solid (37.1 mg, 48% yield), mp 79.8 – 81.6 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.60 (dd, *J* = 8.8, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.23 (t, *J* = 30.0 Hz), 151.16, 136.46, 133.90, 128.43, 125.87, 121.47. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.07 – -81.14 (m, 3F), -106.39 – -106.48 (m, 2F), -122.18 – -122.31 (m, 2F), -125.51 – -125.73 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_4ClF_9NS$ 387.9604, found 387.9627.



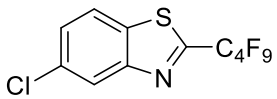
3gd

6-bromo-2-(perfluorobutyl)benzo[d]thiazole (3gd): white solid (46.5 mg, 54% yield), mp 92.2 – 94.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 1.9 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 8.8, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.25 (t, *J* = 30.2 Hz), 151.47, 136.86, 131.11, 126.15, 124.46, 121.64. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.15 (t, *J* = 9.7 Hz, 3F), -106.43 – -106.51 (m, 2F), -122.20 – -122.33 (m, 2F), -125.64 – -125.77 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_4BrF_9NS$ 431.9099, found 431.9106.



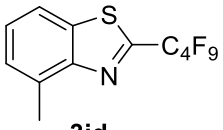
3hd

6-(methylsulfonyl)-2-(perfluorobutyl)benzo[d]thiazole (3hd): white solid (70.8 mg, 82% yield), mp 116.8 – 118.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.52 (t, *J* = 30.3 Hz), 155.32, 139.62, 135.81, 126.25, 125.90, 122.87, 44.71. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.98 (t, *J* = 9.3 Hz, 3F), -106.53 (t, *J* = 11.6 Hz, 2F), -122.09 – -122.18 (m, 2F), -125.53 – -125.61 (m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_7F_9NO_2S_2$ 431.9769, found 431.9755.



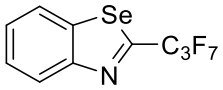
3id

5-chloro-2-(perfluorobutyl)benzo[d]thiazole (3id): white solid (42.6 mg, 55% yield), mp 96.6 – 98.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.57 (dd, *J* = 8.7, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.64 (t, *J* = 30.2 Hz), 153.40, 133.67, 133.54, 128.22, 124.83, 122.65. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.99 – -81.05 (m, 3F), -106.43 – -106.52 (m, 2F), -122.15 – -122.28 (m, 2F), -125.55 – -125.67 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{11}H_4ClF_9NS$ 387.9604, found 387.9599.



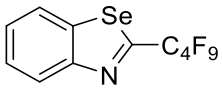
3jd

4-methyl-2-(perfluorobutyl)benzo[d]thiazole (3jd): colorless oil (65.4 mg, 89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.41 (m, 2H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.29 (t, *J* = 30.1 Hz), 152.34, 135.52, 135.32, 127.57, 127.42, 119.16, 116.30 – 105.56 (m), 18.14. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.97 (t, *J* = 9.7 Hz, 2F), -105.79 – -106.05 (m, 2F), -121.81 – -122.28 (m, 2F), -125.31 – -125.55 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{12}H_7F_9NS$ 368.0150, found 368.0156.



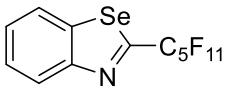
5ac

2-(perfluoropropyl)benzo[d][1,3]selenazole (5ac): colorless oil (38.6 mg, 55% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.82 (t, *J* = 31.8 Hz), 154.15, 139.37, 127.35, 127.24, 126.87, 124.92, 119.20 – 104.92 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.98 – -80.04 (m, 3F), -104.97 – -105.06 (m, 2F), -125.52 (s, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{10}H_5F_7NSe$ 351.9470, found 351.9460.



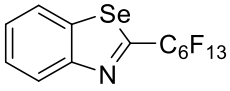
5ad

2-(perfluorobutyl)benzo[d][1,3]selenazole (5ad): white solid (44.9 mg, 56% yield), mp 57.1 – 58.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.07 (t, *J* = 31.8 Hz), 154.15, 139.37, 127.31, 127.19, 126.87, 124.88. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.23 (t, *J* = 9.8 Hz, 3F), -104.29 – -104.36 (m, 2F), -121.96 – - 122.04 (m, 2F), -125.54 – -125.67 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{11}H_5F_9NSe$ 401.9438, found 401.9452.



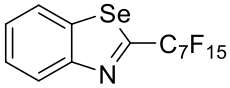
5ae

2-(perfluoropentyl)benzo[d][1,3]selenazole (5ae): white solid (44.2 mg, 49% yield), mp 73.9 – 75.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.57 (dt, *J* = 46.8, 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.03 (t, *J* = 31.7 Hz), 154.15, 139.38, 127.34, 127.22, 126.88, 124.90. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.79 – -80.86 (m, 3F), -104.11 – -104.20 (m, 2F), -121.16 – -121.26 (m, 2F), -122.02 – -122.18 (m, 2F), -126.17 – -126.27 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{12}H_5F_{11}NSe$ 451.9406, found 451.9399.



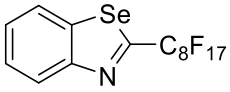
5af

2-(perfluorohexyl)benzo[d][1,3]selenazole (5af): white solid (41.1 mg, 41% yield), mp 82.5 – 84.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.58 (dt, *J* = 47.2, 8.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.06 (t, *J* = 31.3 Hz), 154.14, 139.38, 127.35, 127.24, 126.89, 124.92. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.24 – -81.36 (m, 3F), -104.55 – -104.65 (m, 2F), -121.43 – -121.55 (m, 2F), -121.67 – -121.83 (m, 2F), -123.25 – -123.30 (m, 2F), -126.57 – -126.70 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{13}H_5F_{13}NSe$ 501.9374, found 501.9390.



5ag

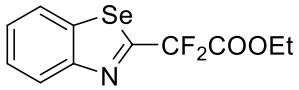
2-(perfluoroheptyl)benzo[d][1,3]selenazole (5ag): white solid (48.5 mg, 44% yield), mp 94.9 – 96.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.58 (dt, *J* = 46.6, 7.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.07 (t, *J* = 31.4 Hz), 154.15, 139.38, 127.34, 127.22, 126.89, 124.90. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.64 – -80.69 (m, 3F), -103.92 – -103.99 (m, 2F), -120.78 – -121.00 (m, 4F), -121.80 – -121.83 (m, 2F), -122.55 – -123.57 (m, 2F), -125.97 – -126.06 (m, 2F). HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{14}H_5F_{15}NSe$ 551.9342, found 551.9364.



5ah

2-(perfluorooctyl)benzo[d][1,3]selenazole (5ah): white solid (74.5 mg, 62% yield), mp 103.5 – 105.0 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.07 (t, *J* = 31.8 Hz), 154.15, 139.37, 127.31, 127.19, 126.87, 124.88. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.92 (t, *J* = 9.9 Hz, 3F), -104.13 (t, *J* = 13.9 Hz, 2F), -120.94 – -121.10 (m, 4F), -121.85 – -121.97 (m, 4F), -122.73 – -122.89 (m, 2F), -126.19 – -126.29

(m, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_5F_{17}NSe$ 601.9310, found 601.9322.

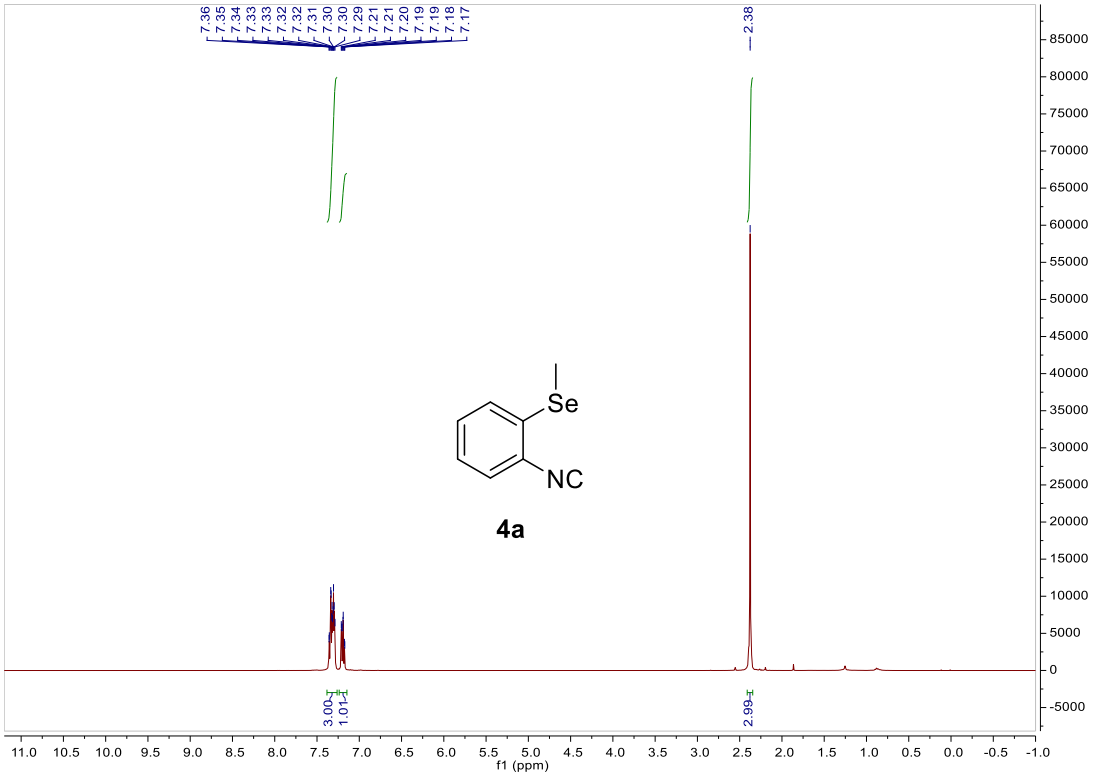


5al

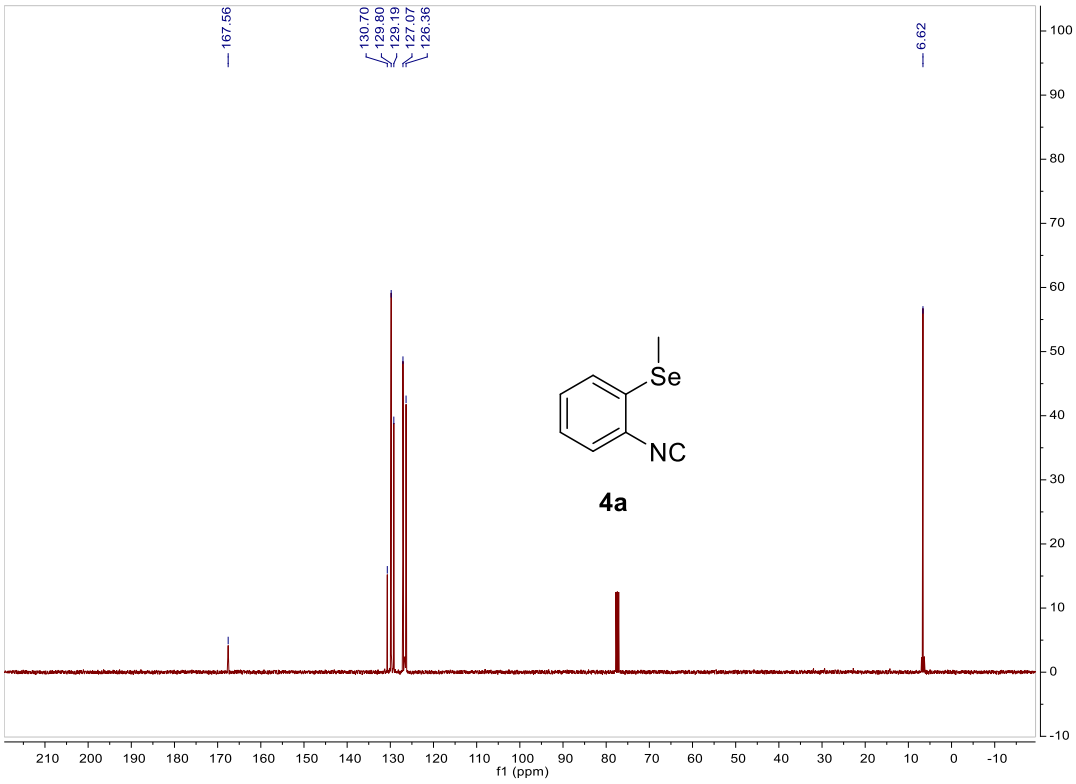
Ethyl 2-(benzo[d][1,3]selenazol-2-yl)-2,2-difluoroacetate (5al): yellow oil (47.6 mg, 78% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.48 – 7.41 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.68 (t, *J* = 34.8 Hz), 161.69 (t, *J* = 32.4 Hz), 153.88, 138.95, 126.90, 126.43, 125.02, 111.35 (t, *J* = 251.9 Hz), 63.93, 13.90. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.35 (s, 2F). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{10}F_2NO_2Se$ 305.9839, found 305.9851.

5. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

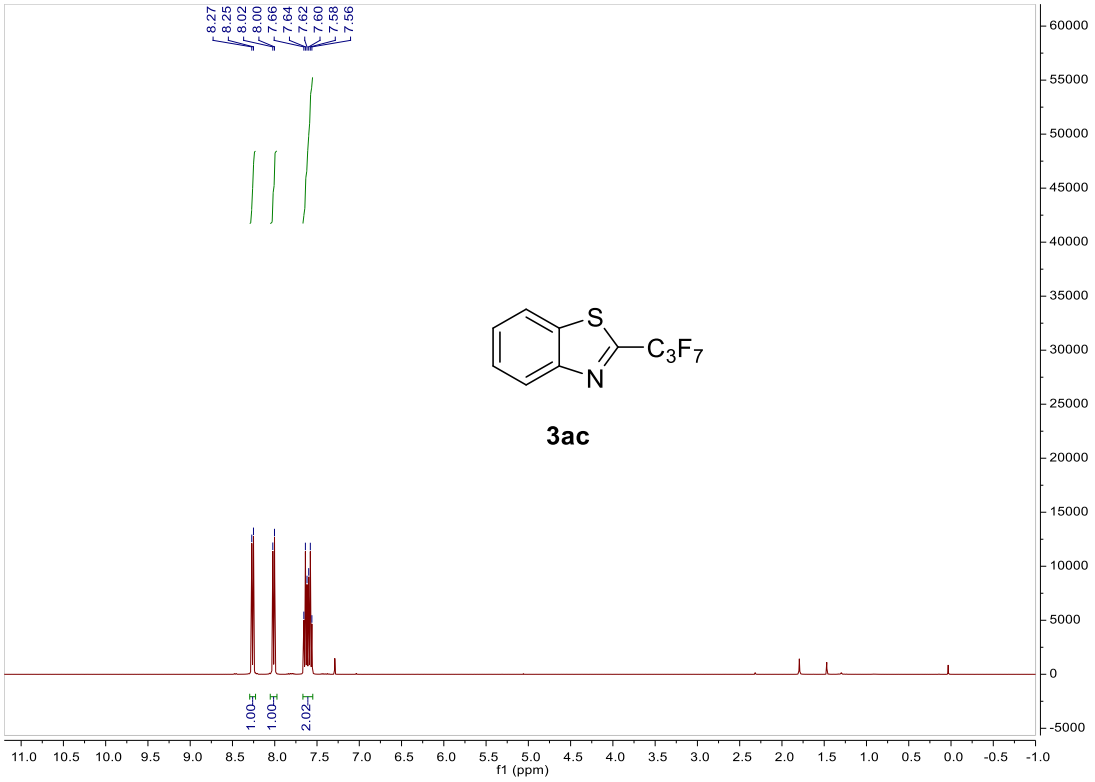
^{1}H NMR spectrum of 4a



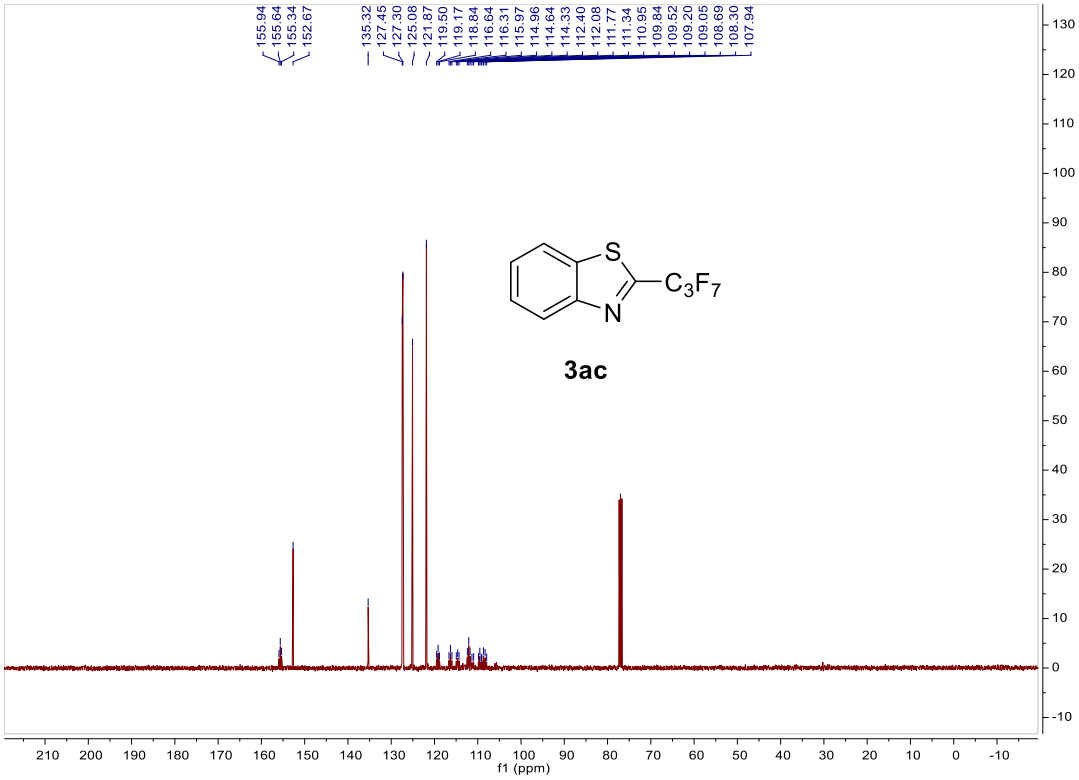
^{13}C NMR spectrum of 4a



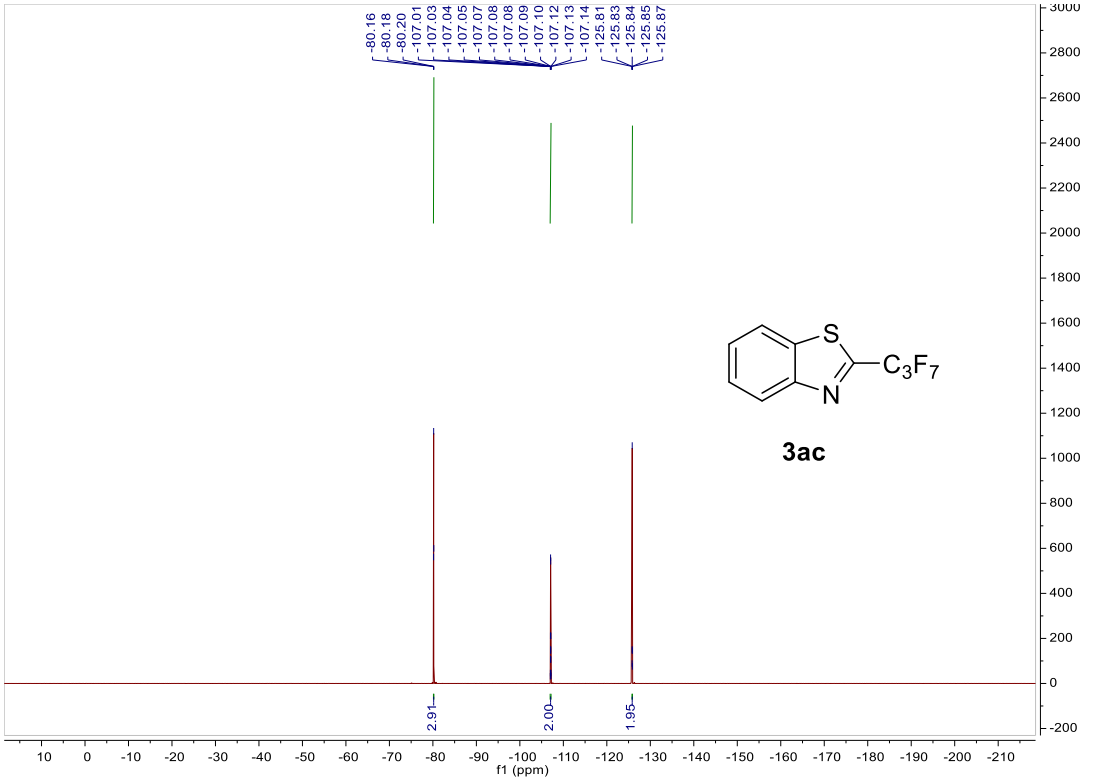
^{1}H NMR spectrum of 3ac



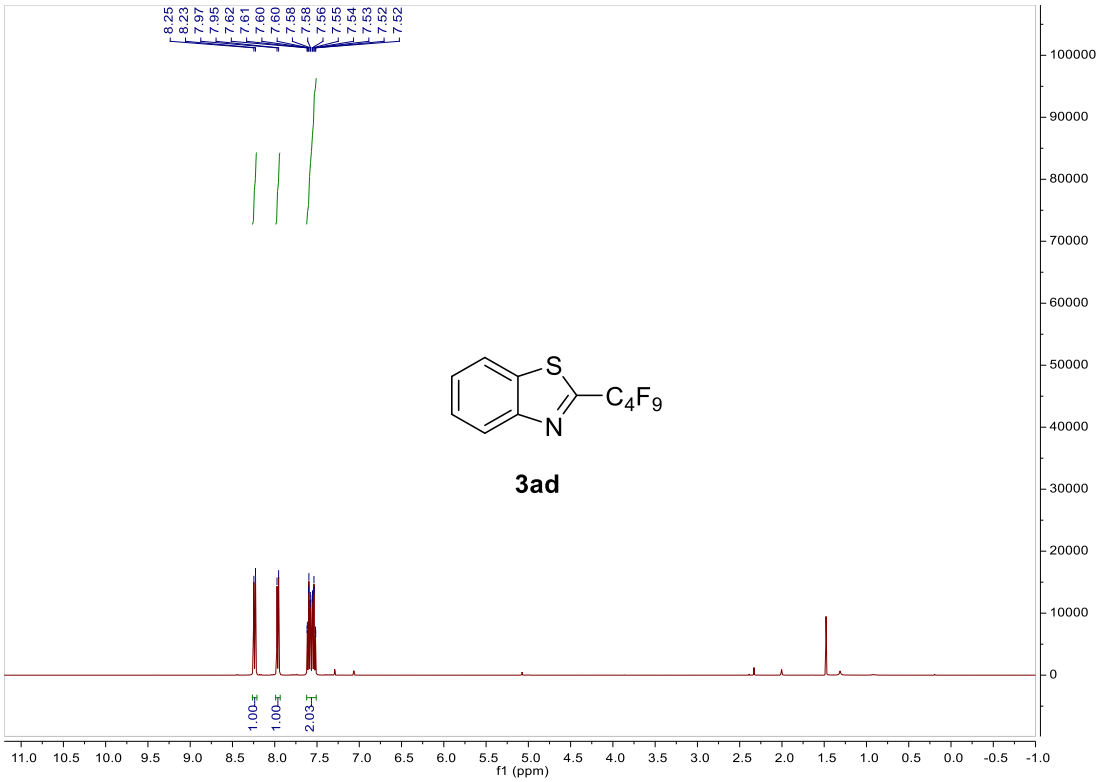
^{13}C NMR spectrum of 3ac



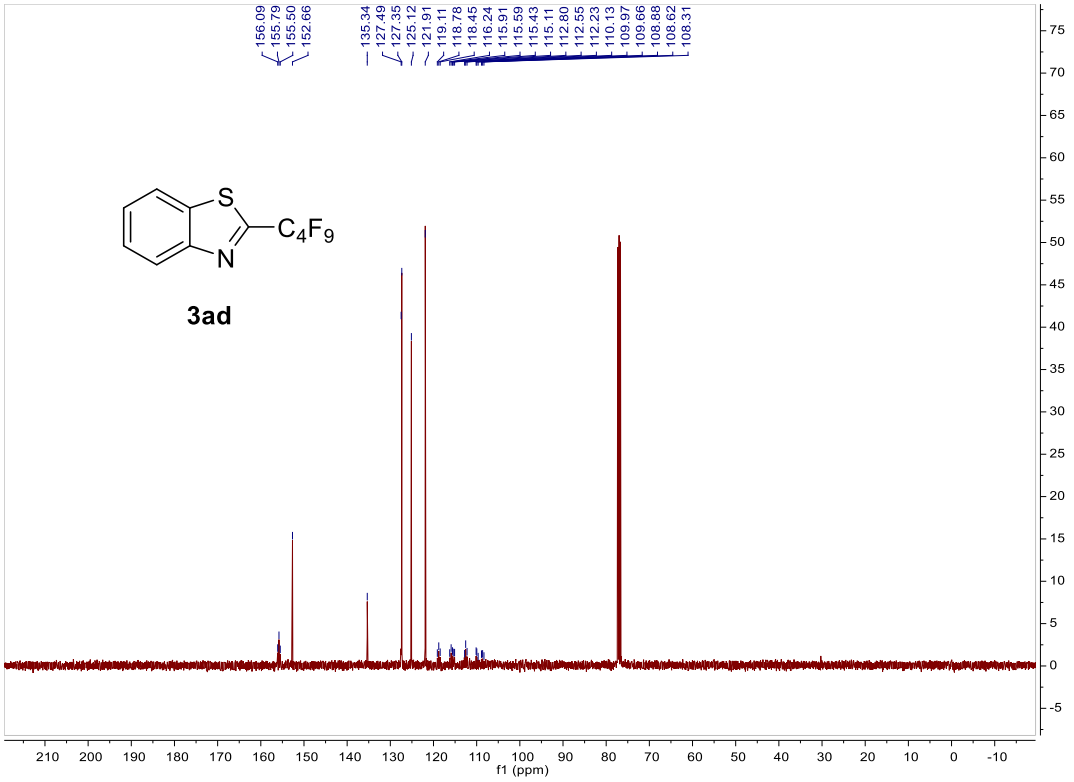
^{19}F NMR spectrum of 3ac



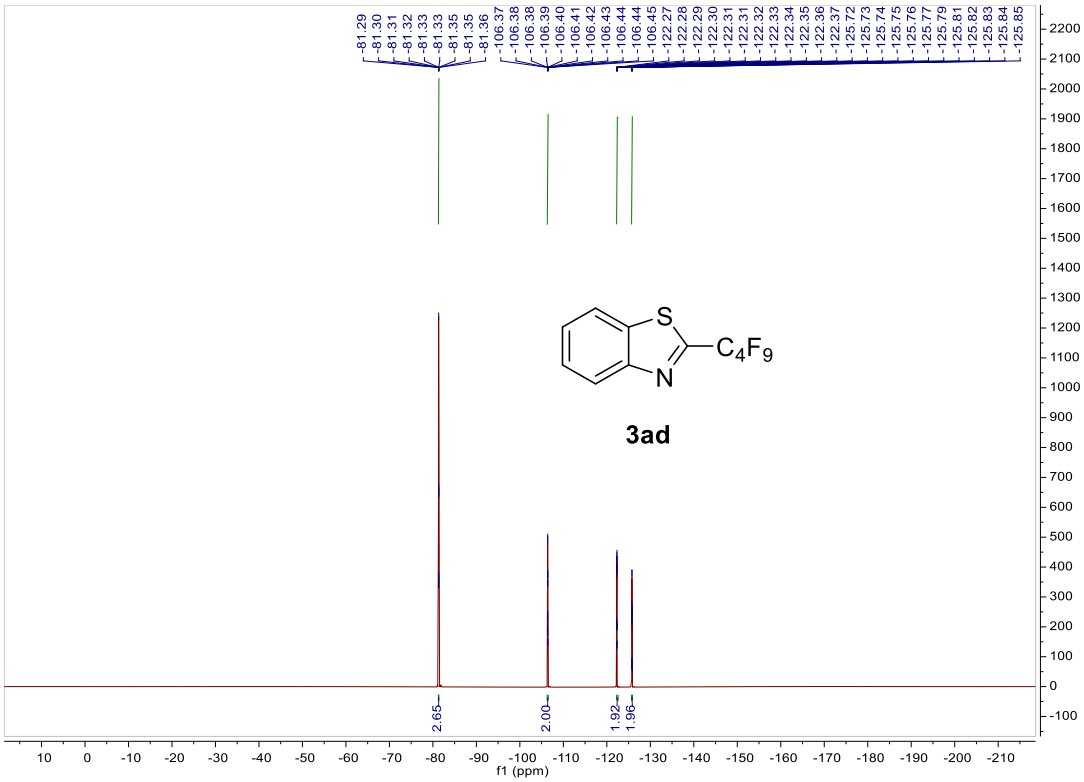
^{1}H NMR spectrum of 3ad



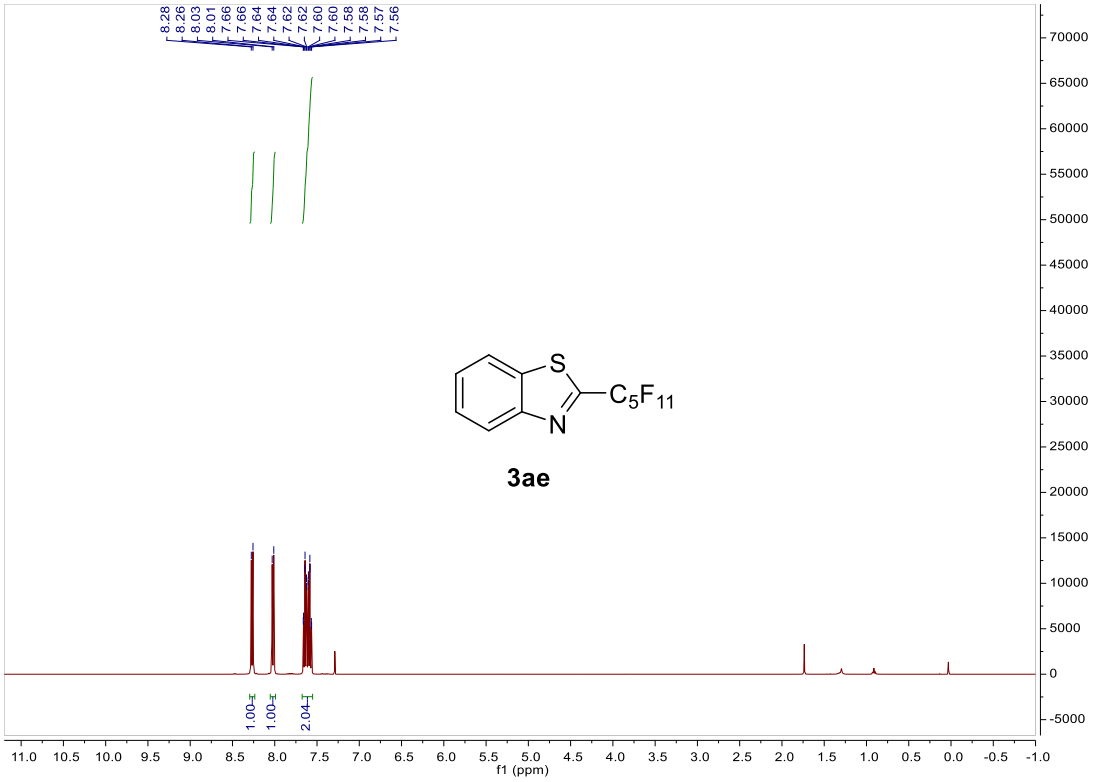
^{13}C NMR spectrum of 3ad



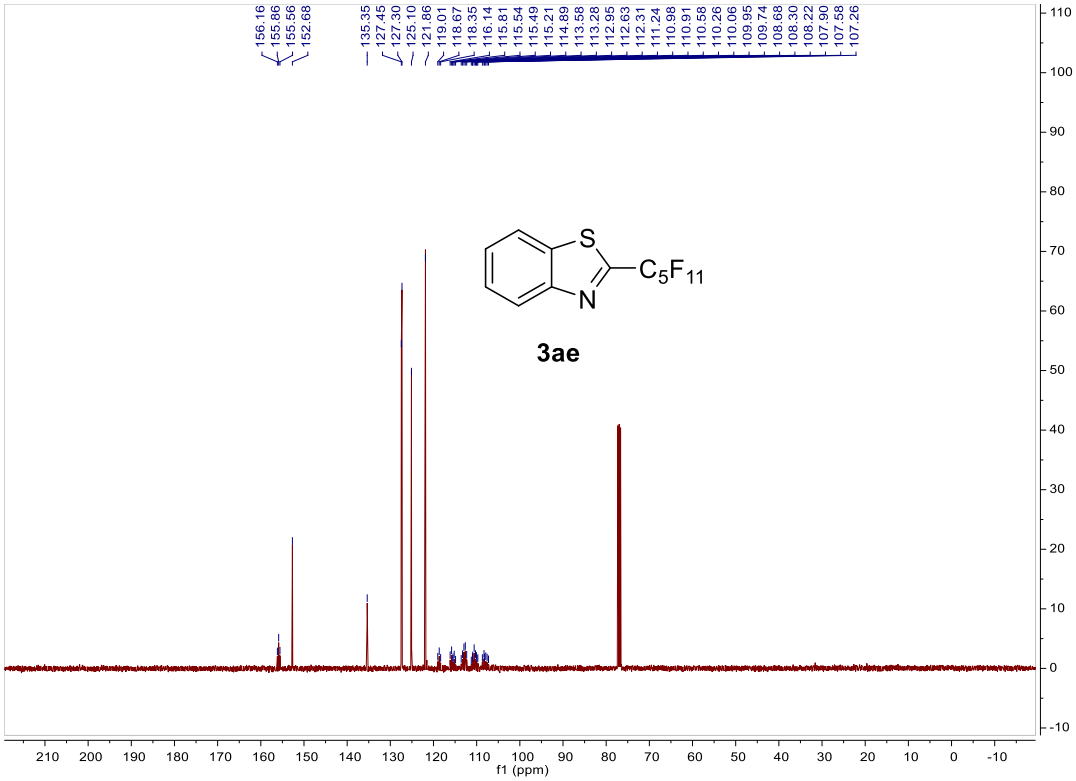
^{19}F NMR spectrum of 3ad



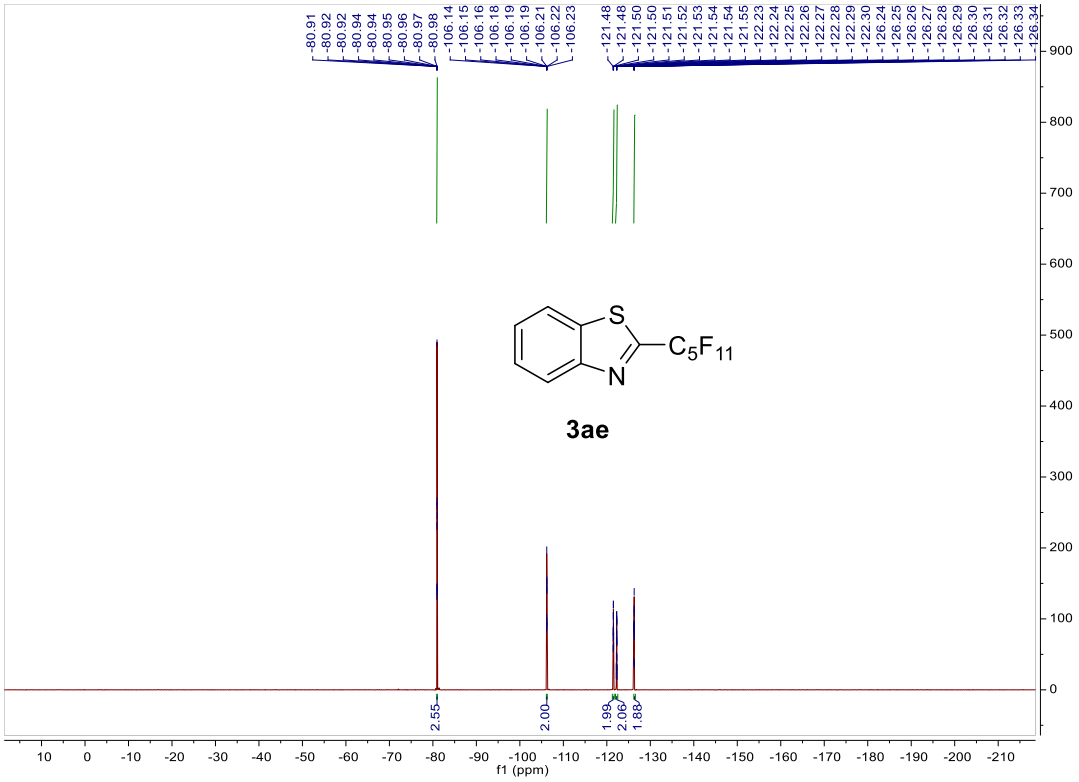
^{1}H NMR spectrum of 3ae



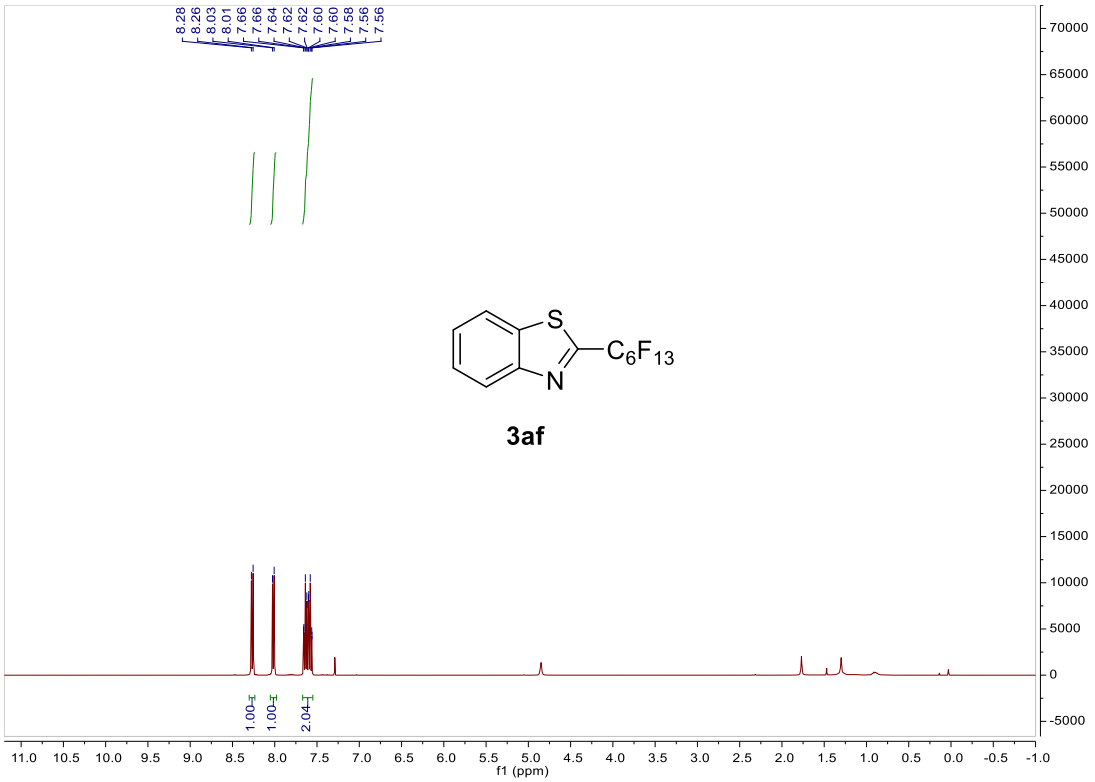
^{13}C NMR spectrum of 3ae



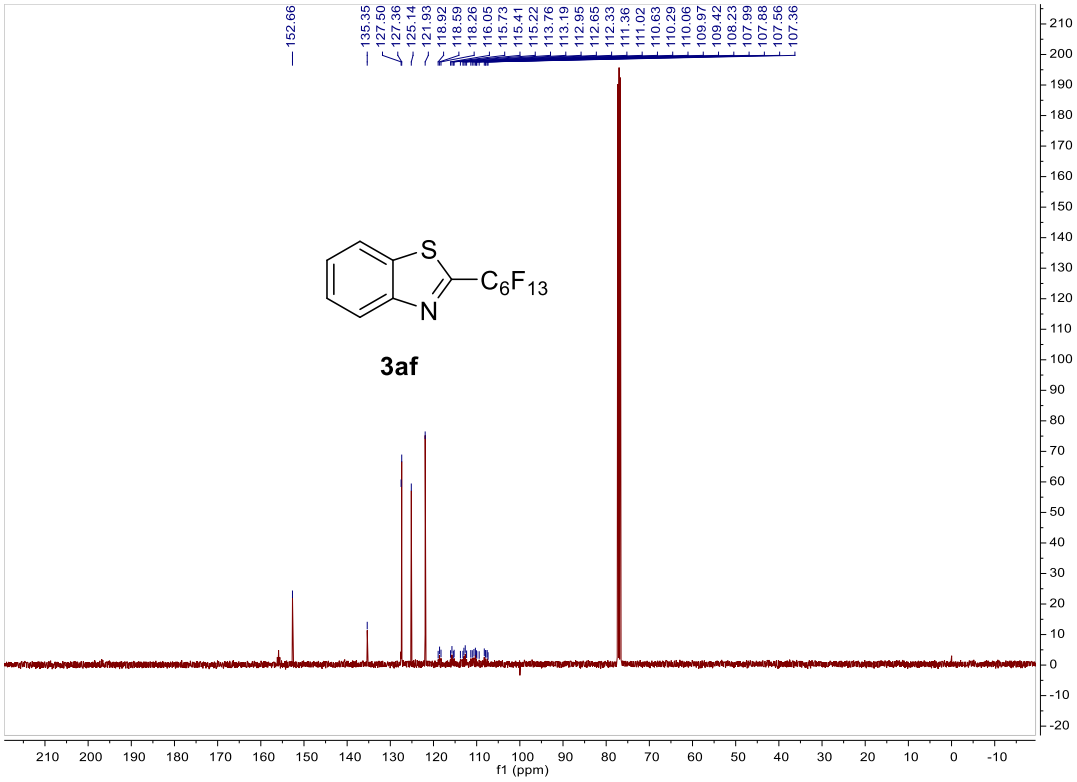
^{19}F NMR spectrum of 3ae



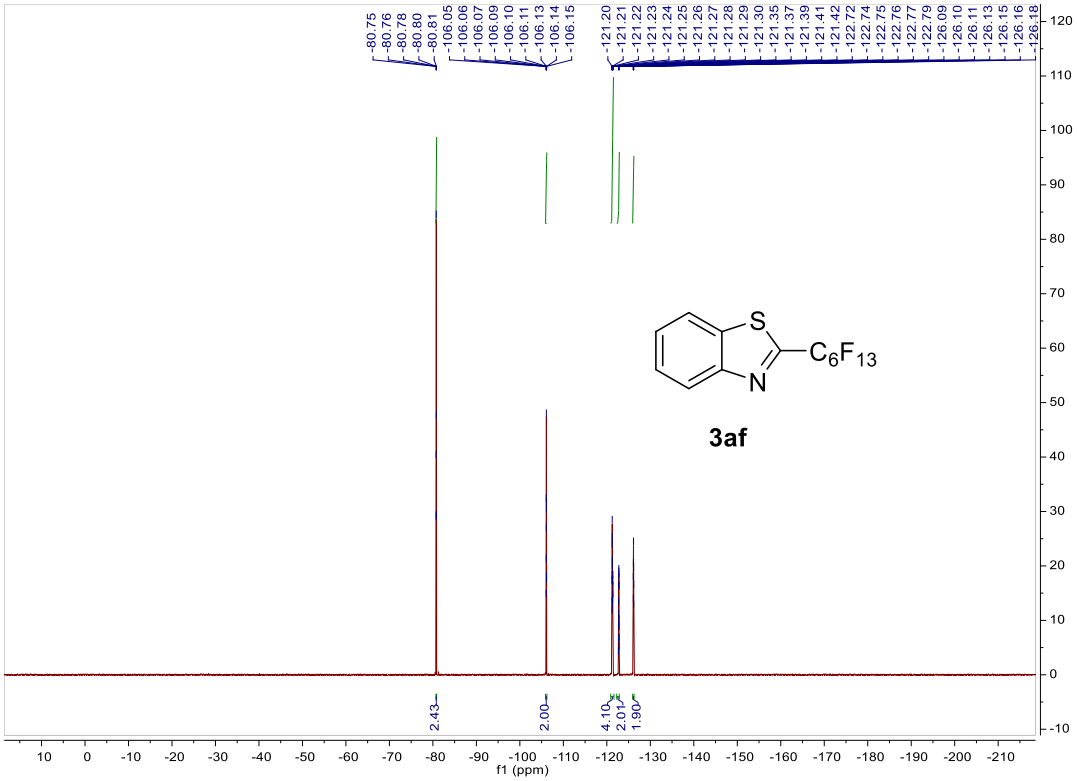
^{1}H NMR spectrum of 3af



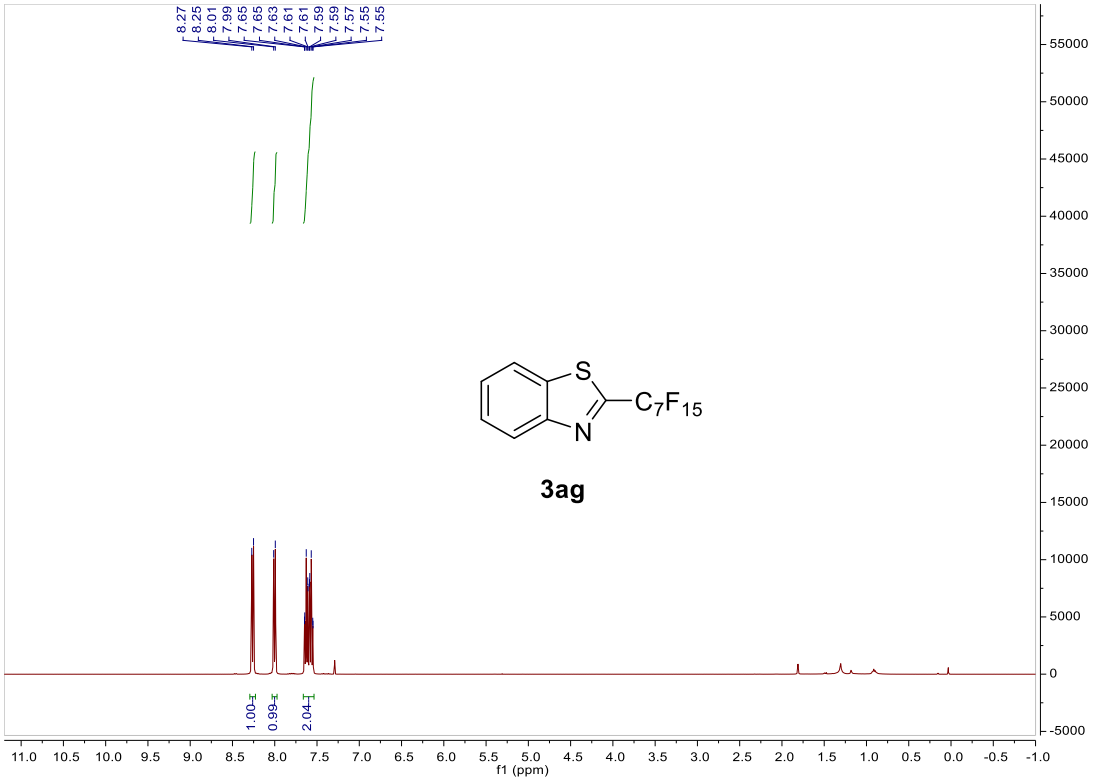
^{13}C NMR spectrum of 3af



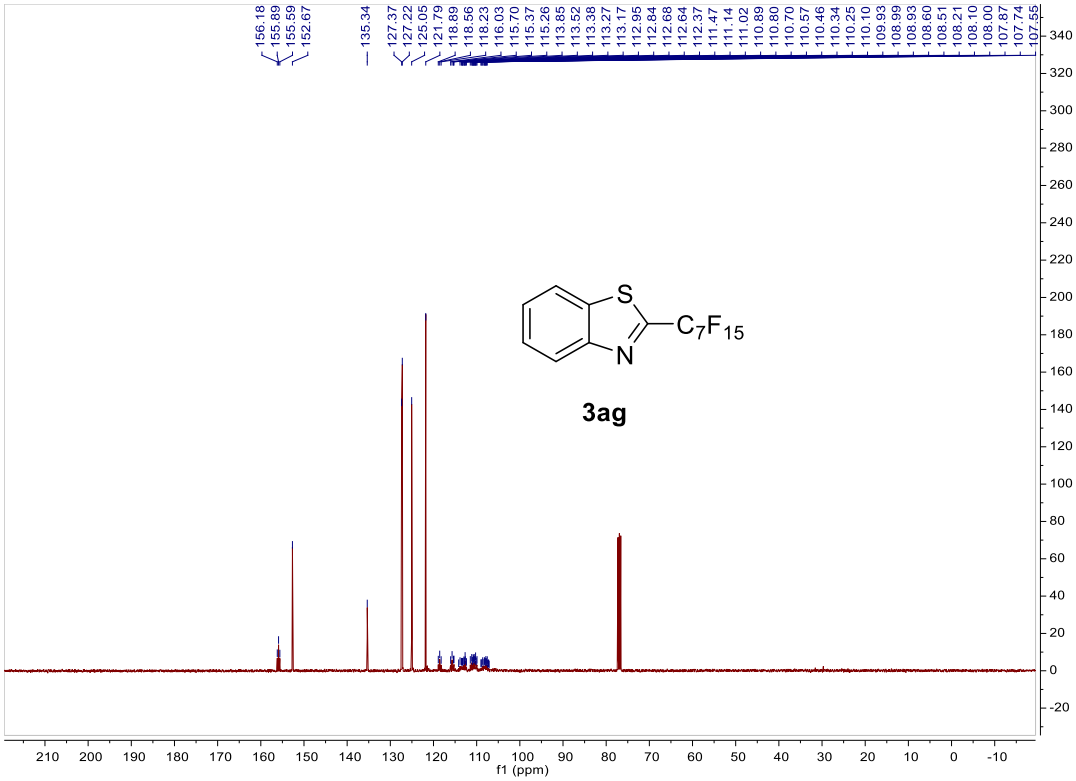
^{19}F NMR spectrum of 3af



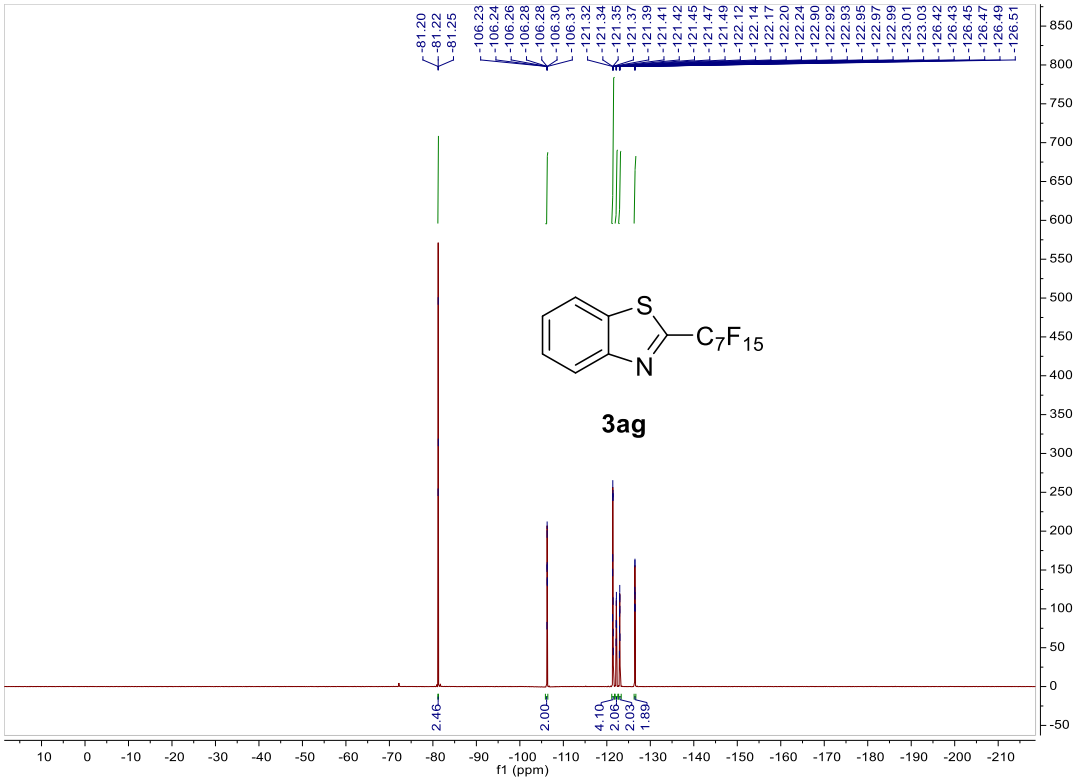
^{1}H NMR spectrum of 3ag



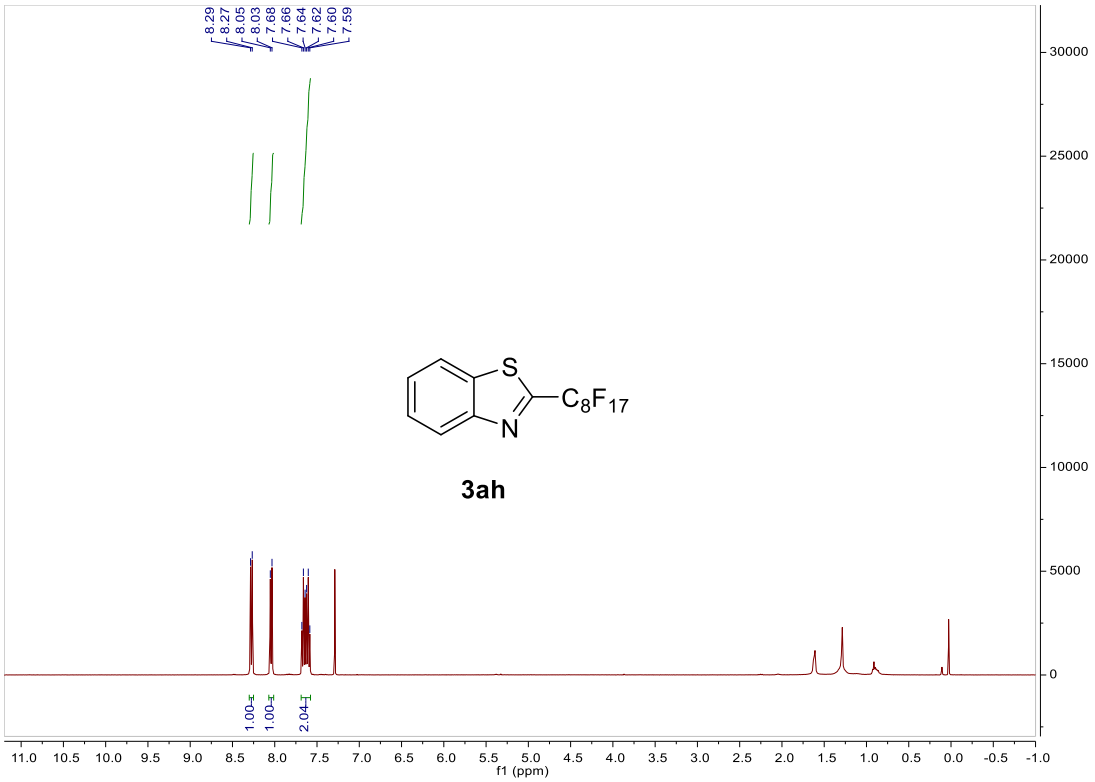
^{13}C NMR spectrum of 3ag



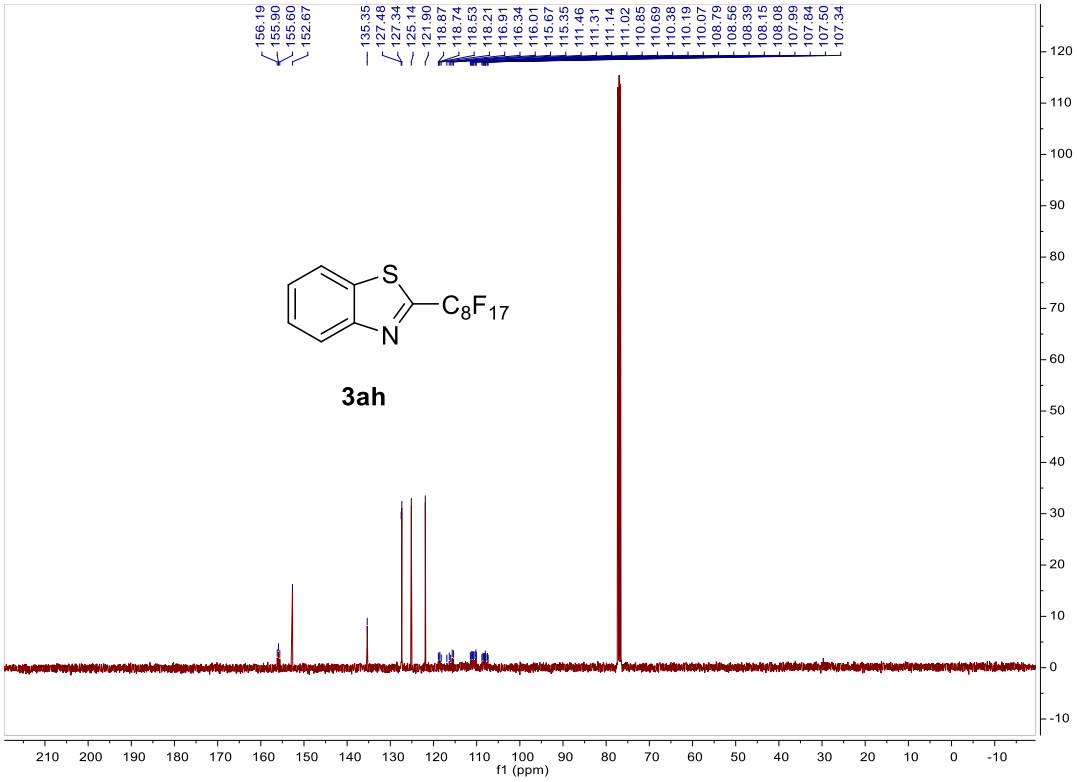
^{19}F NMR spectrum of 3ag



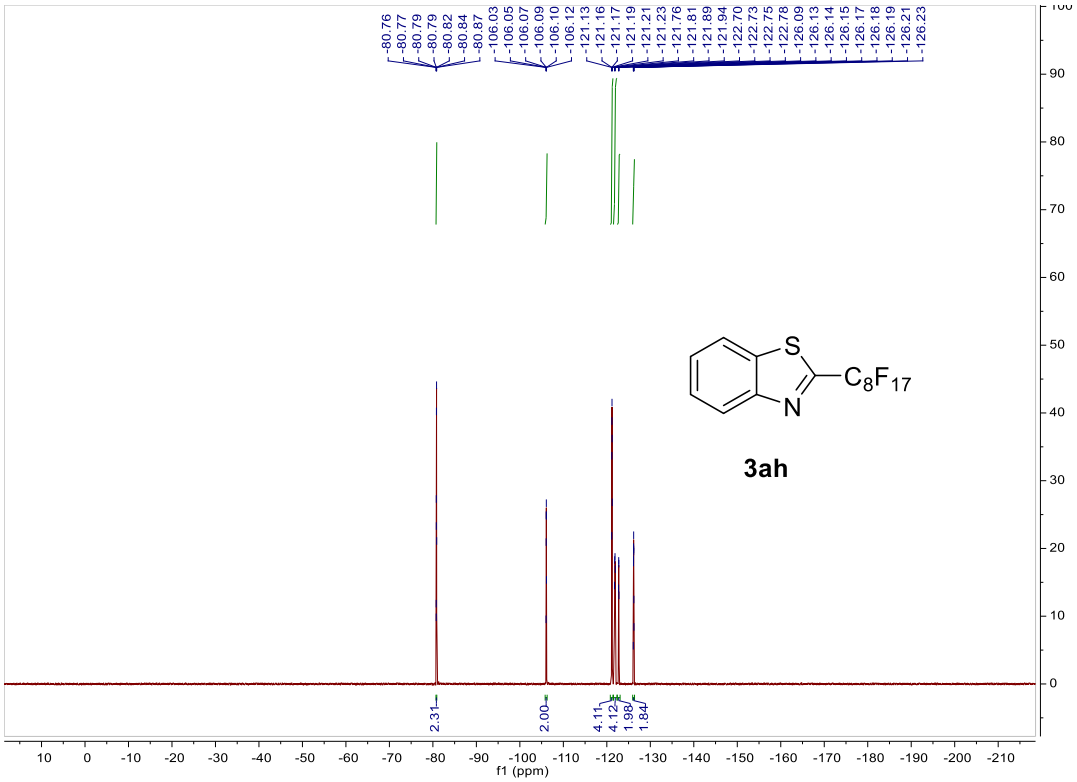
^{1}H NMR spectrum of 3ah



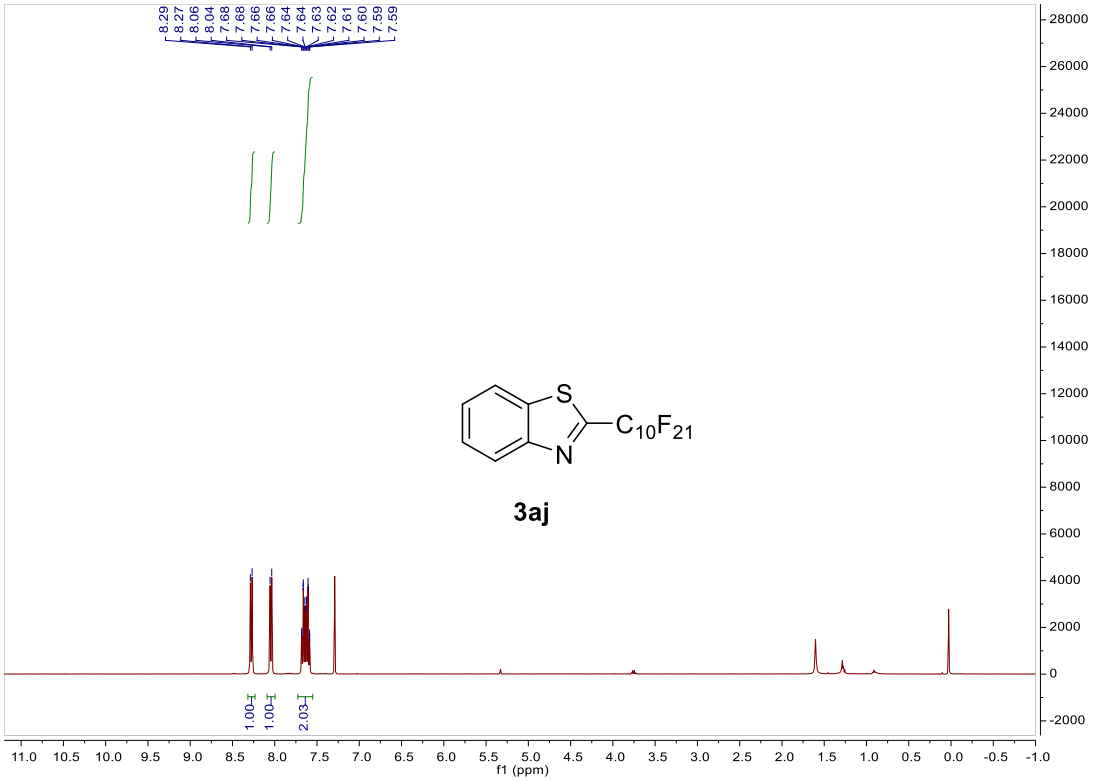
^{13}C NMR spectrum of 3ah



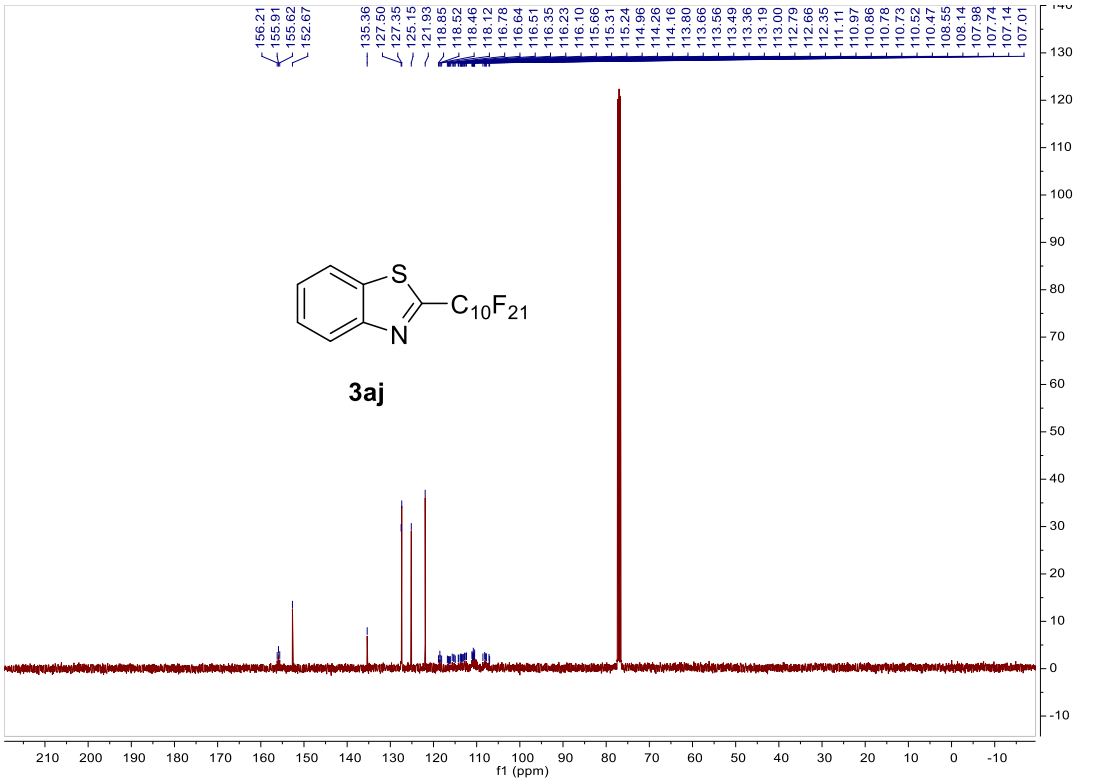
^{19}F NMR spectrum of 3ah



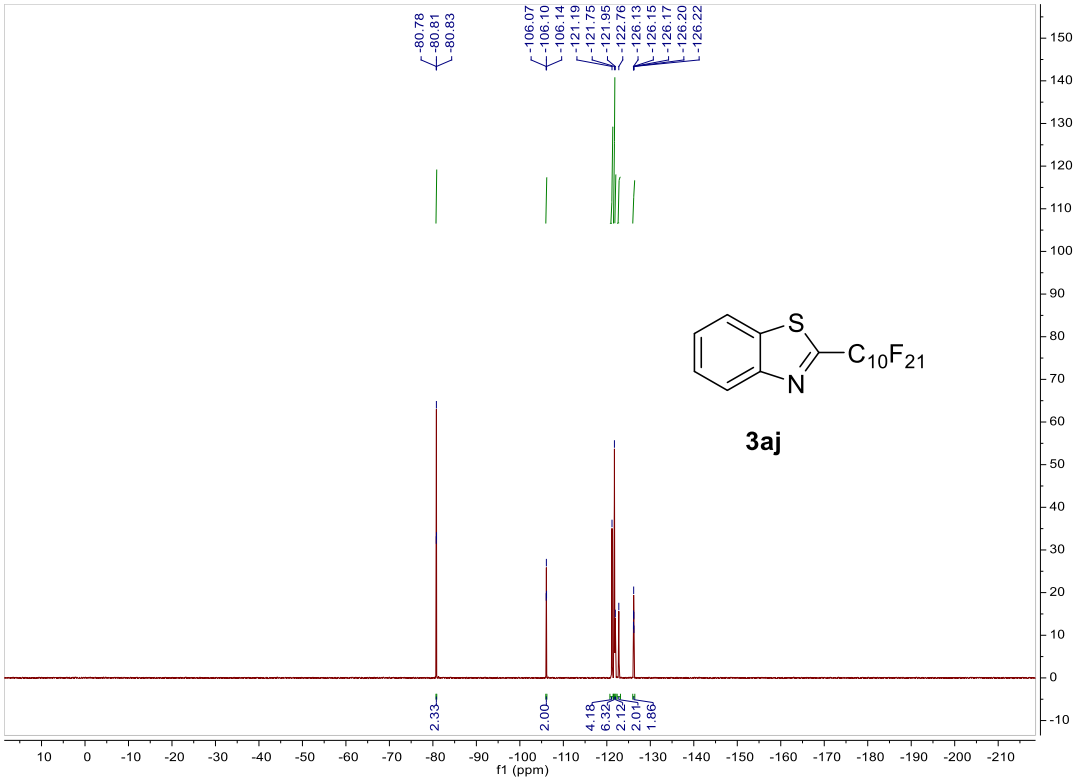
^{1}H NMR spectrum of 3aj



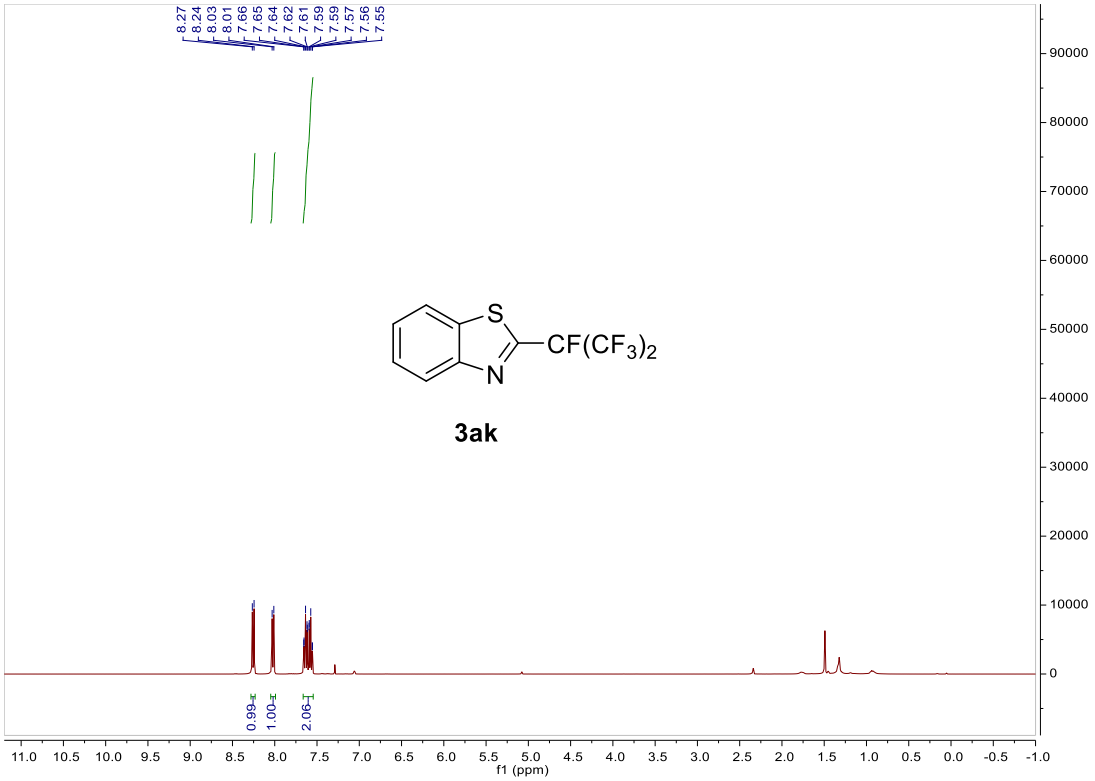
^{13}C NMR spectrum of 3aj



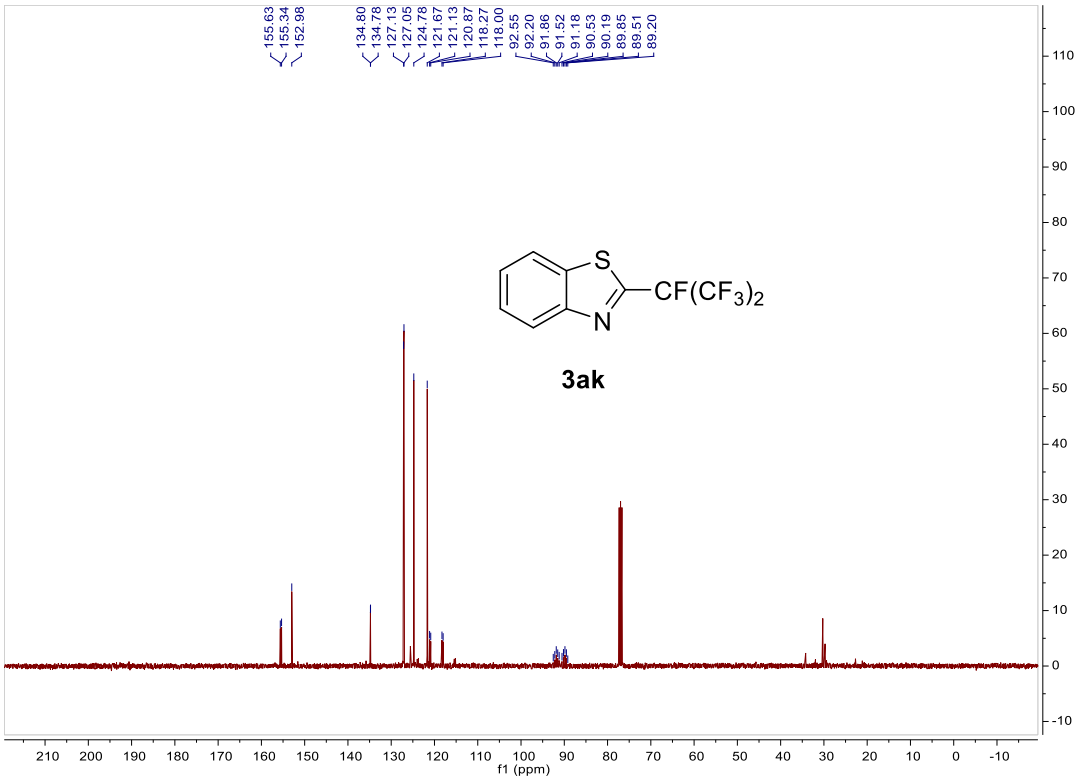
^{19}F NMR spectrum of 3aj



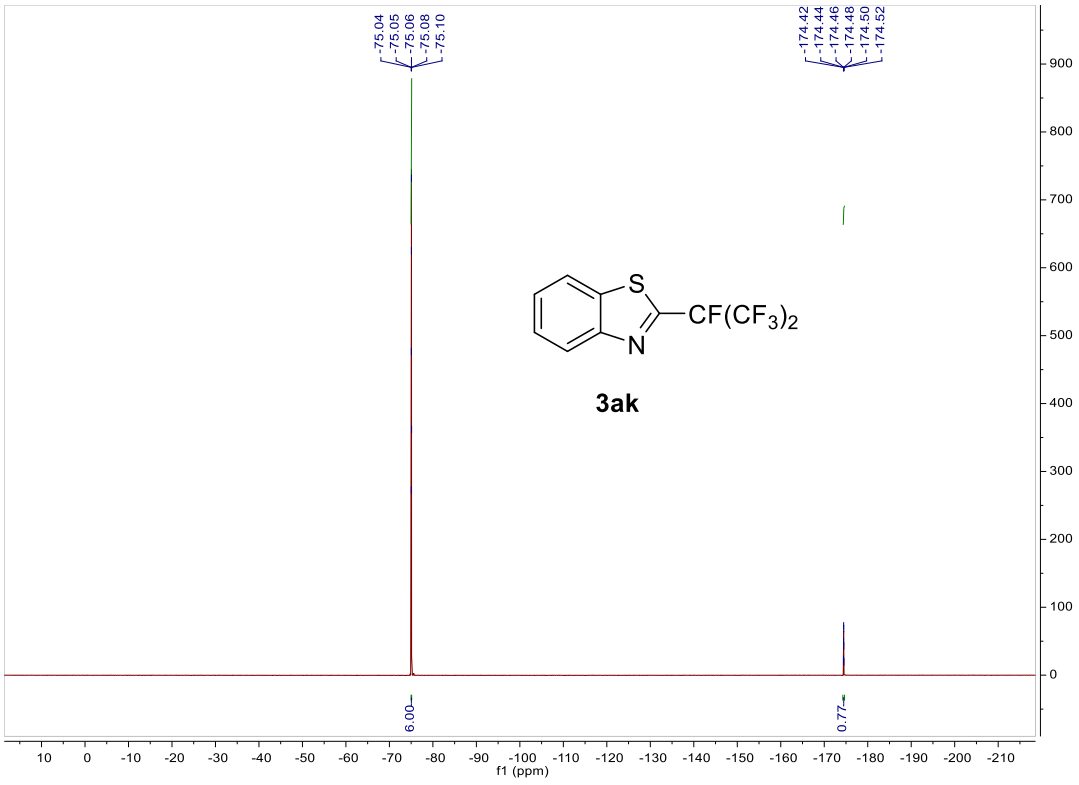
^{1}H NMR spectrum of 3ak



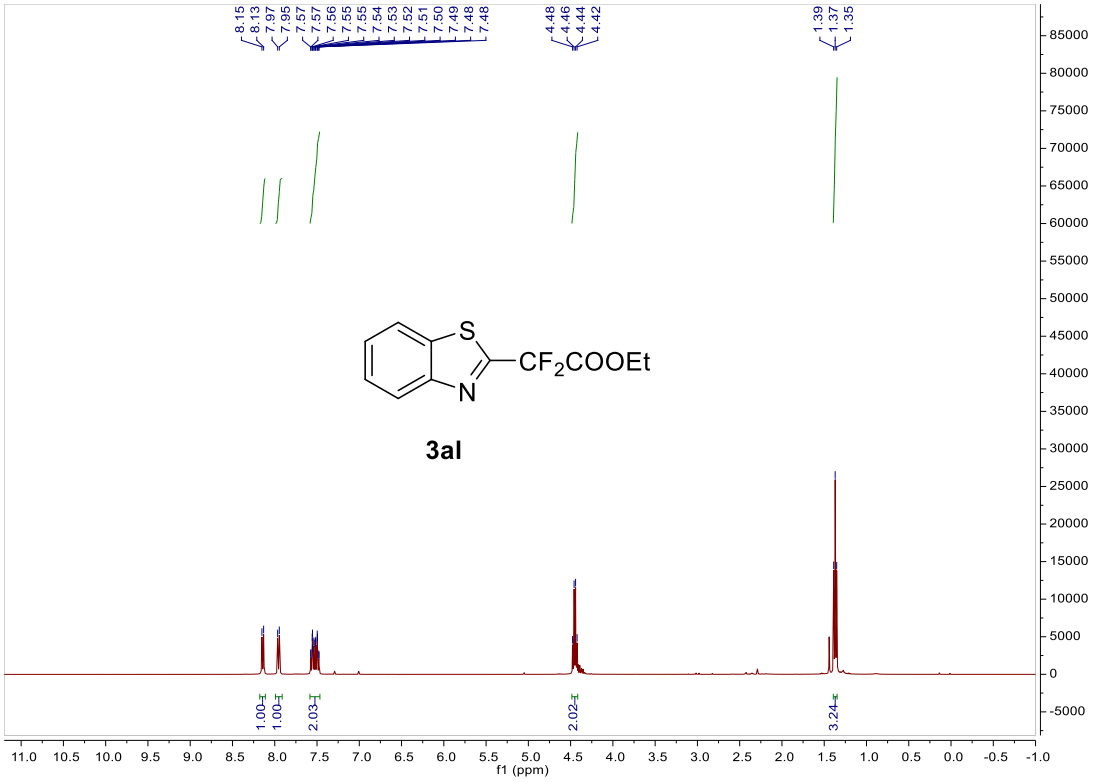
^{13}C NMR spectrum of 3ak



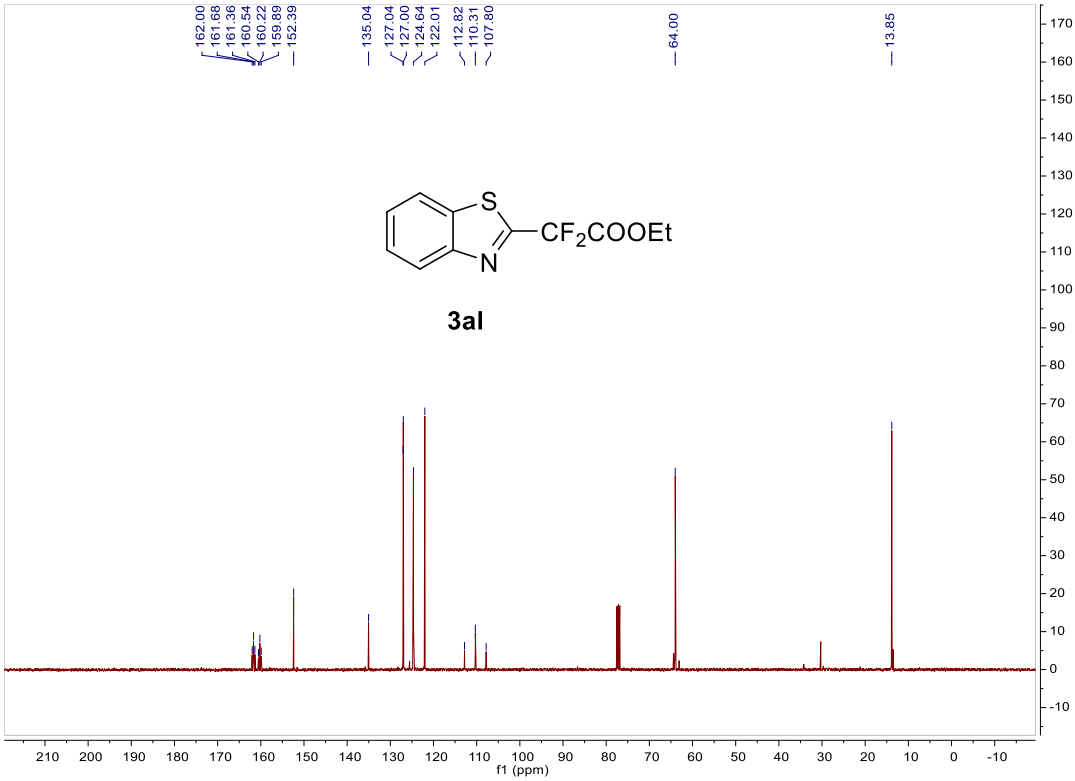
^{19}F NMR spectrum of 3ak



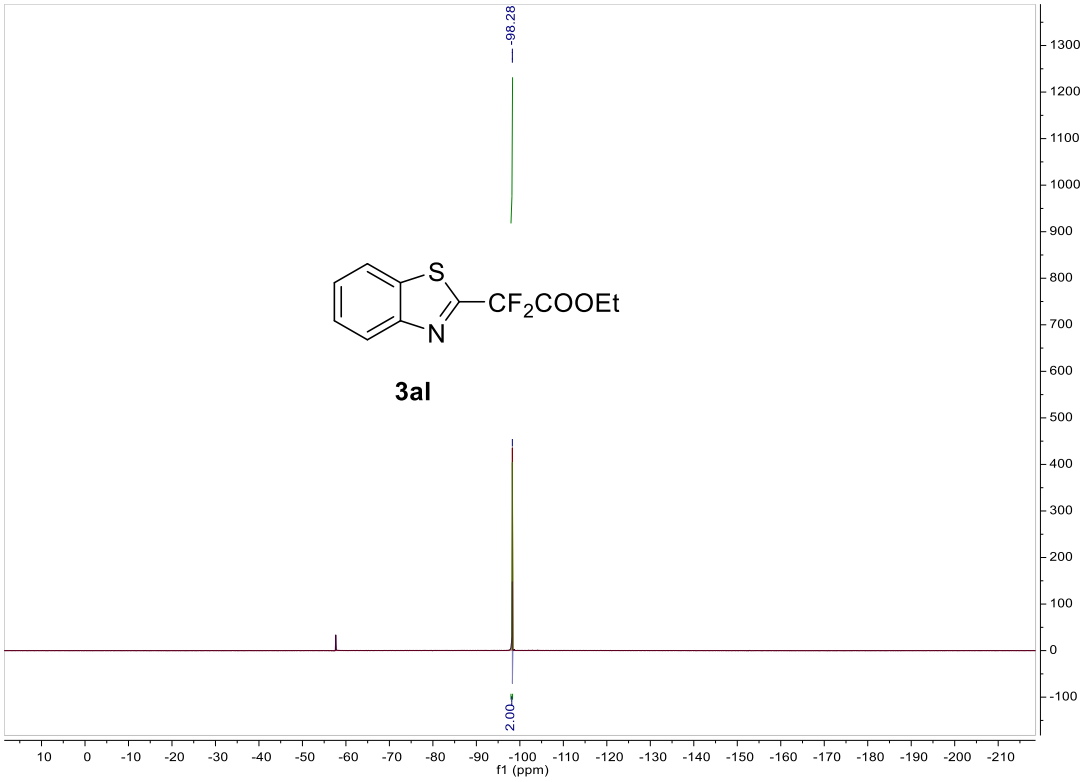
^{1}H NMR spectrum of 3al



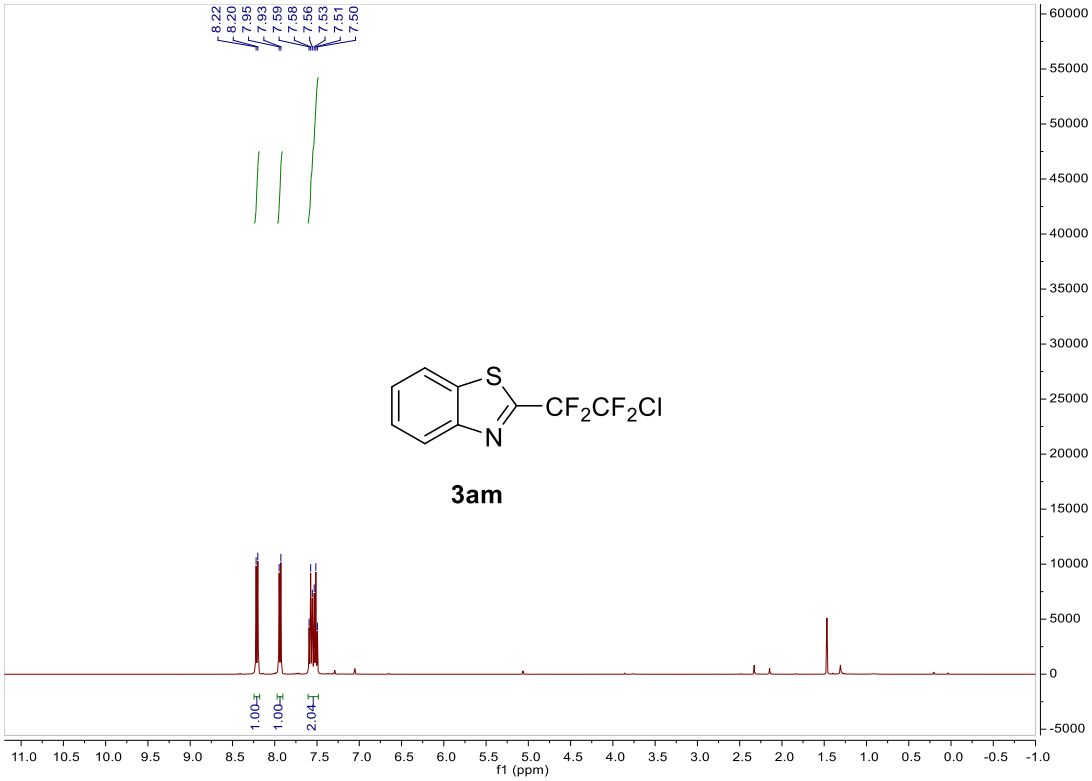
^{13}C NMR spectrum of 3al



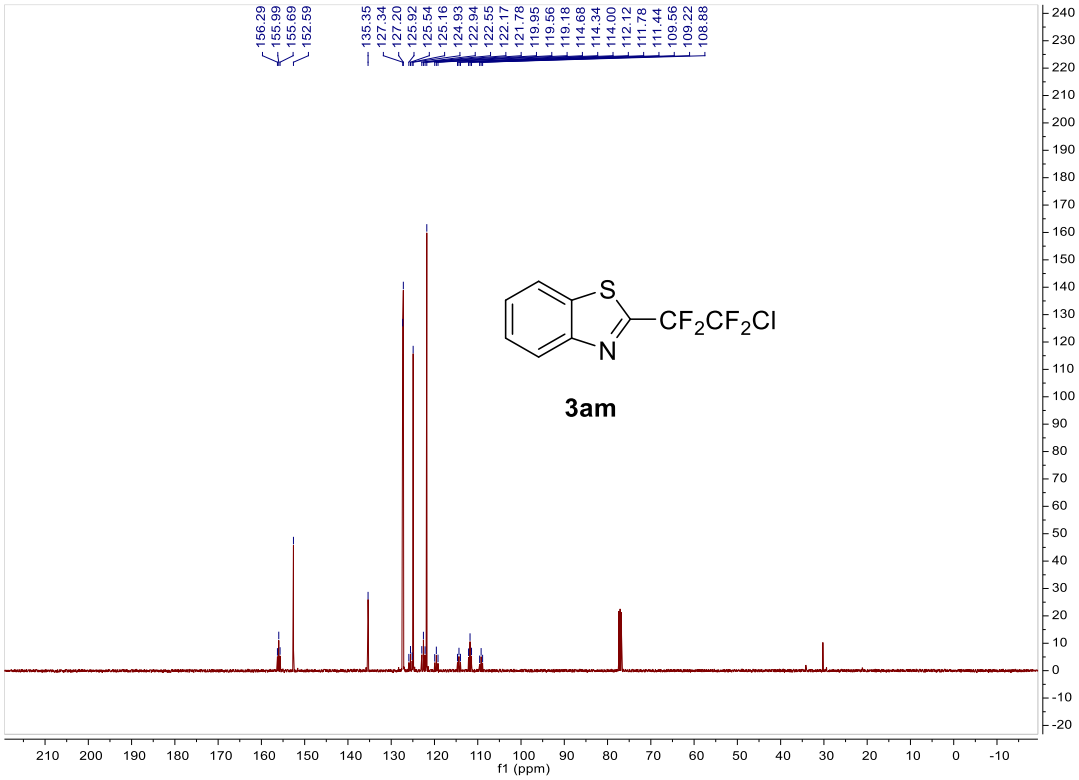
^{19}F NMR spectrum of 3al



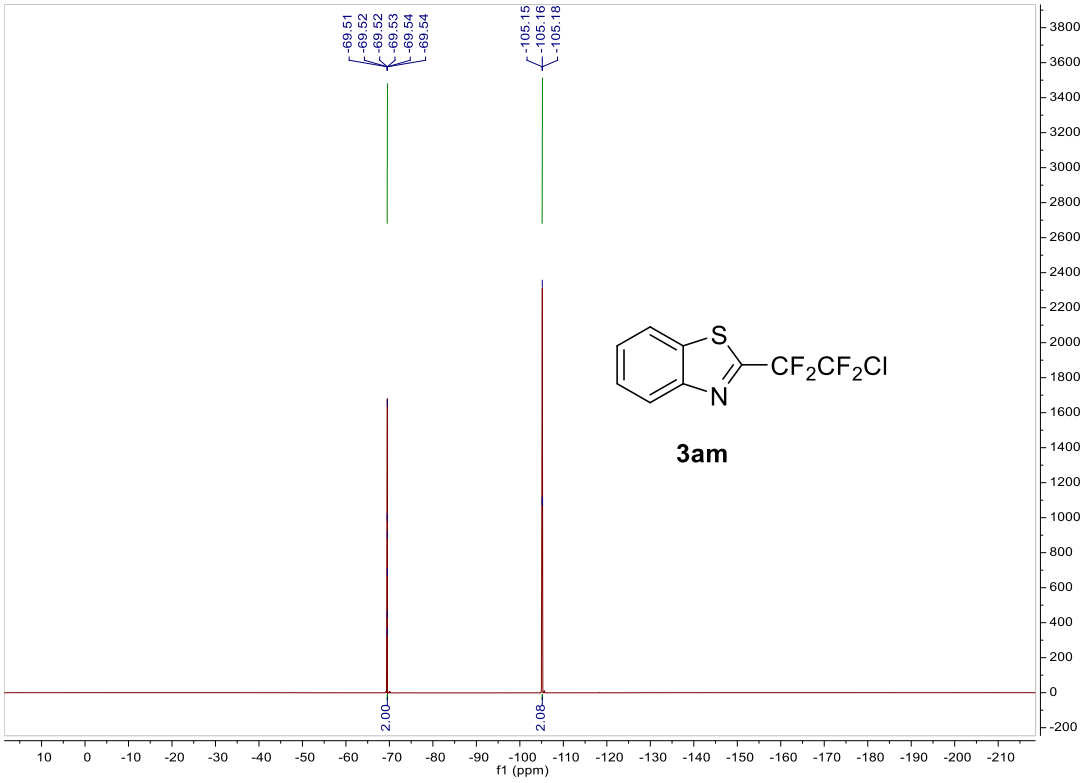
^{1}H NMR spectrum of 3am



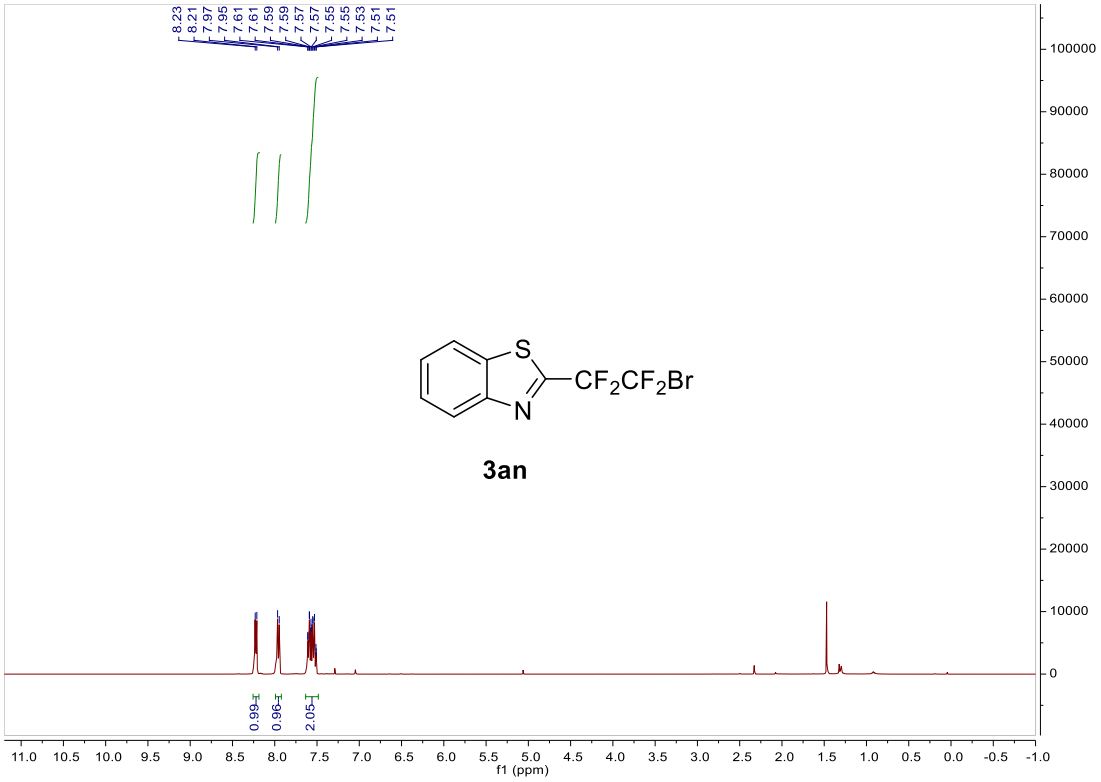
^{13}C NMR spectrum of 3am



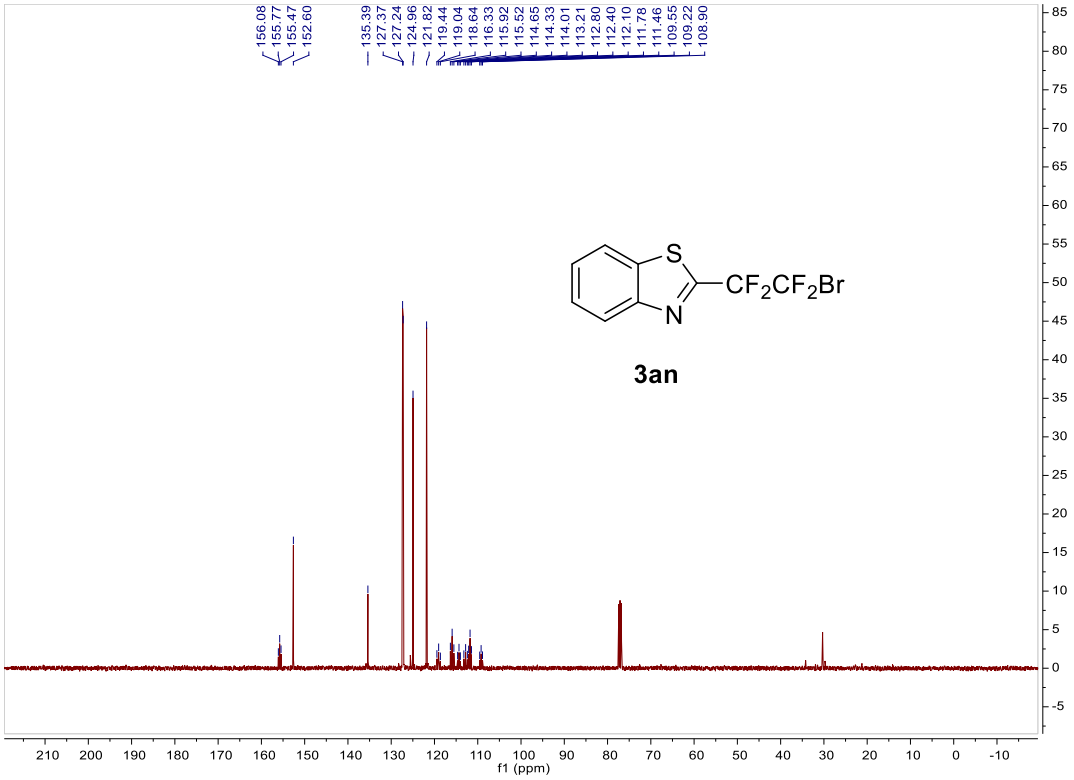
^{19}F NMR spectrum of 3am



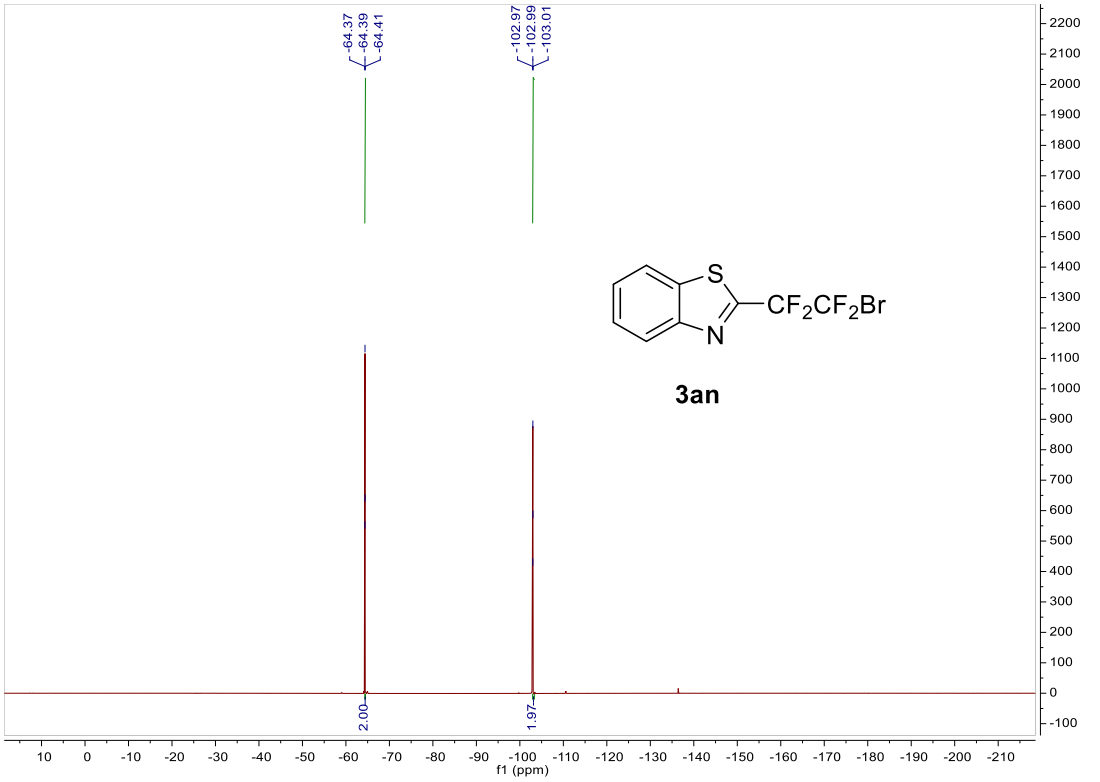
^{1}H NMR spectrum of 3an



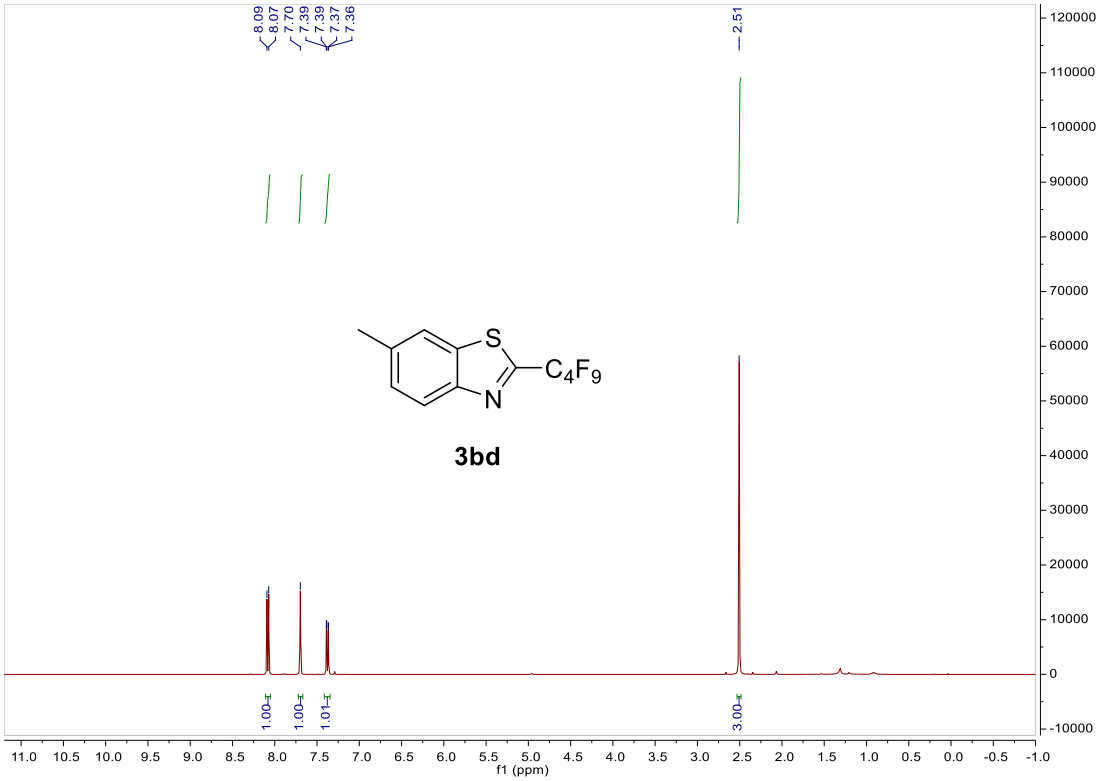
^{13}C NMR spectrum of 3an



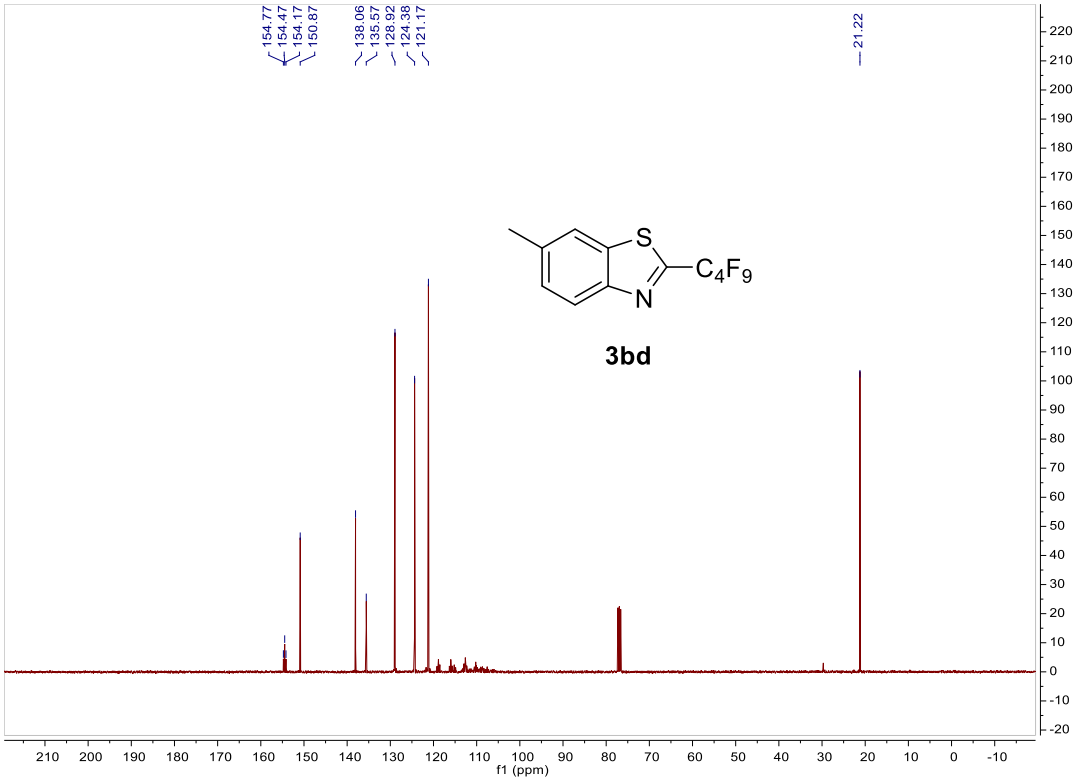
^{19}F NMR spectrum of 3an



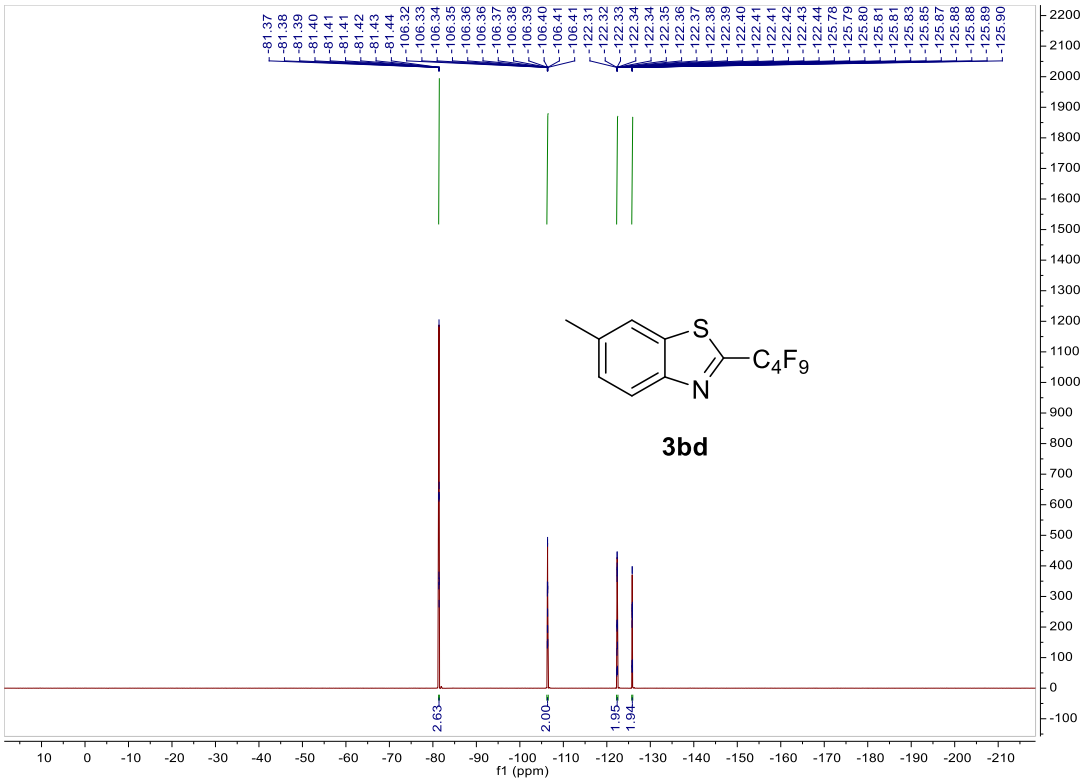
^{1}H NMR spectrum of 3bd



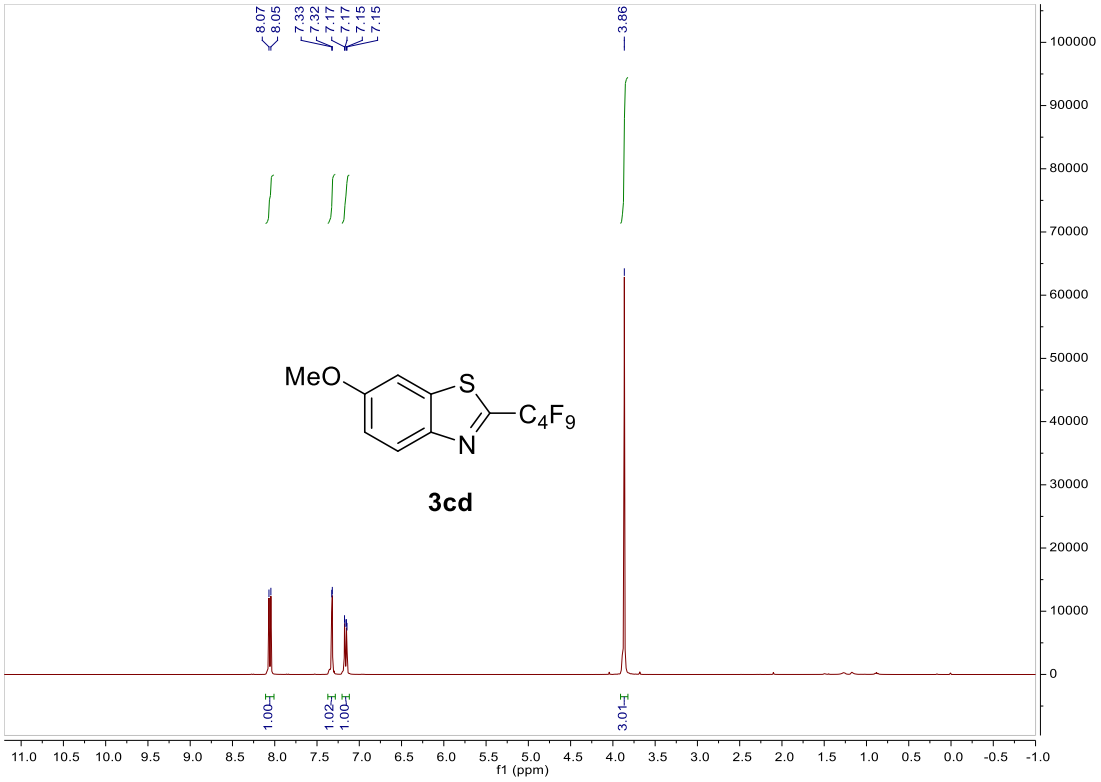
^{13}C NMR spectrum of 3bd



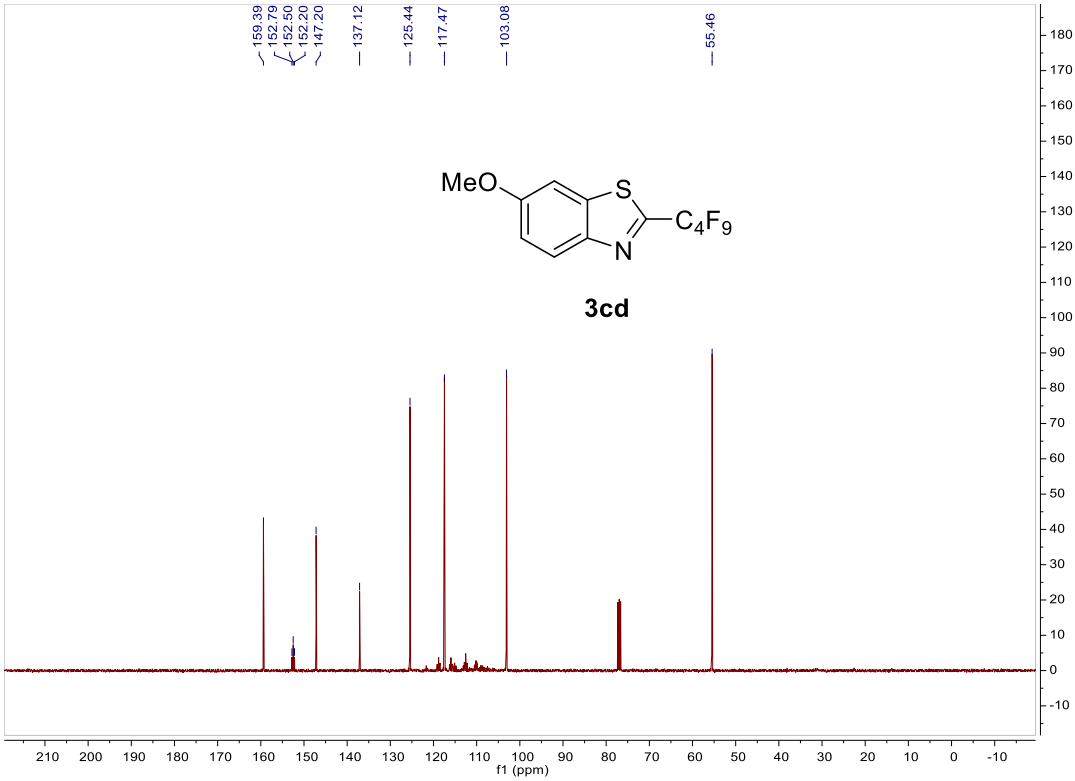
^{19}F NMR spectrum of 3bd



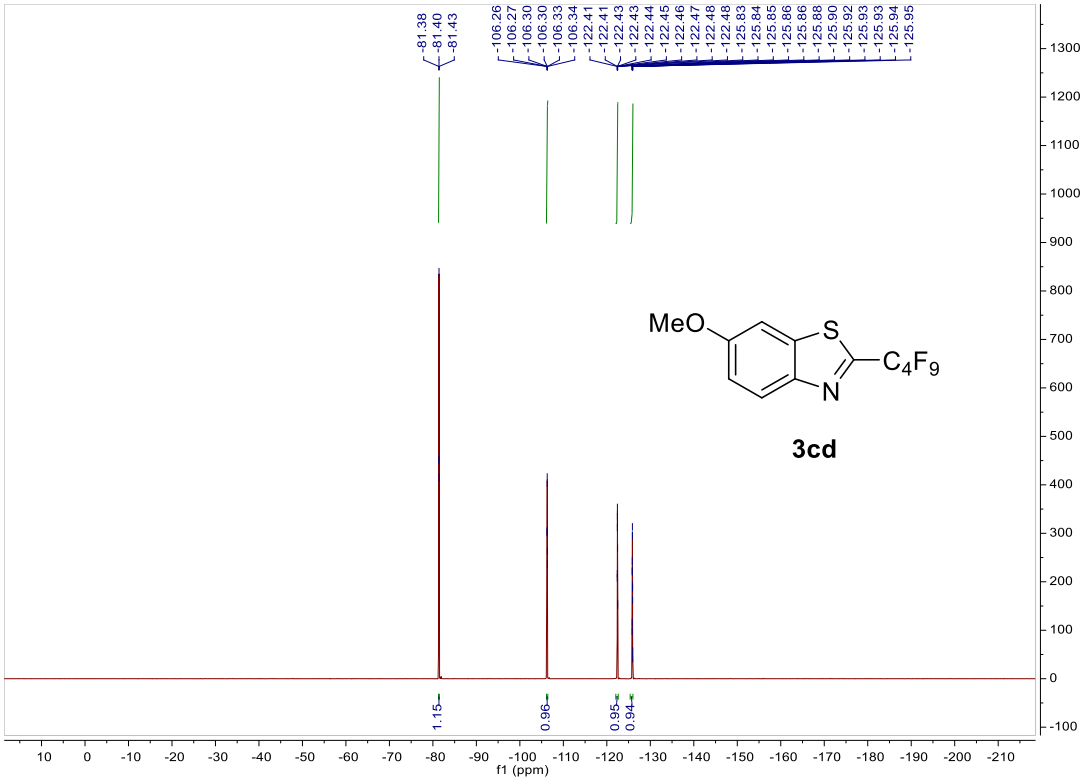
^{1}H NMR spectrum of 3cd



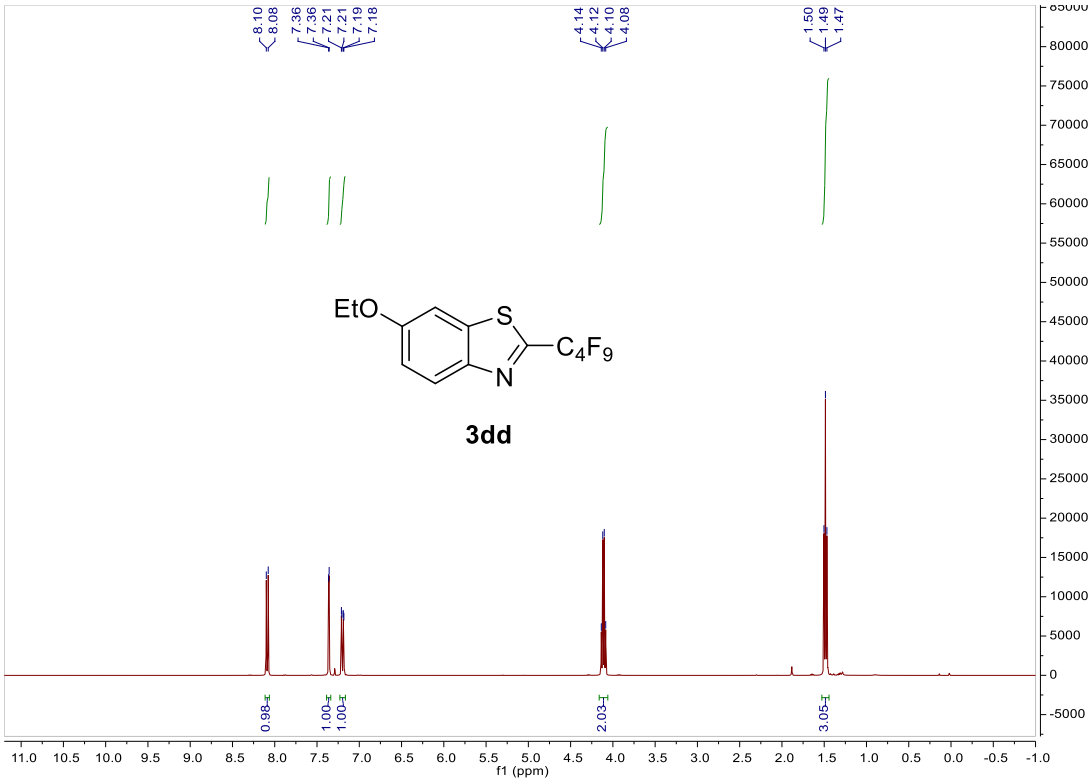
^{13}C NMR spectrum of 3cd



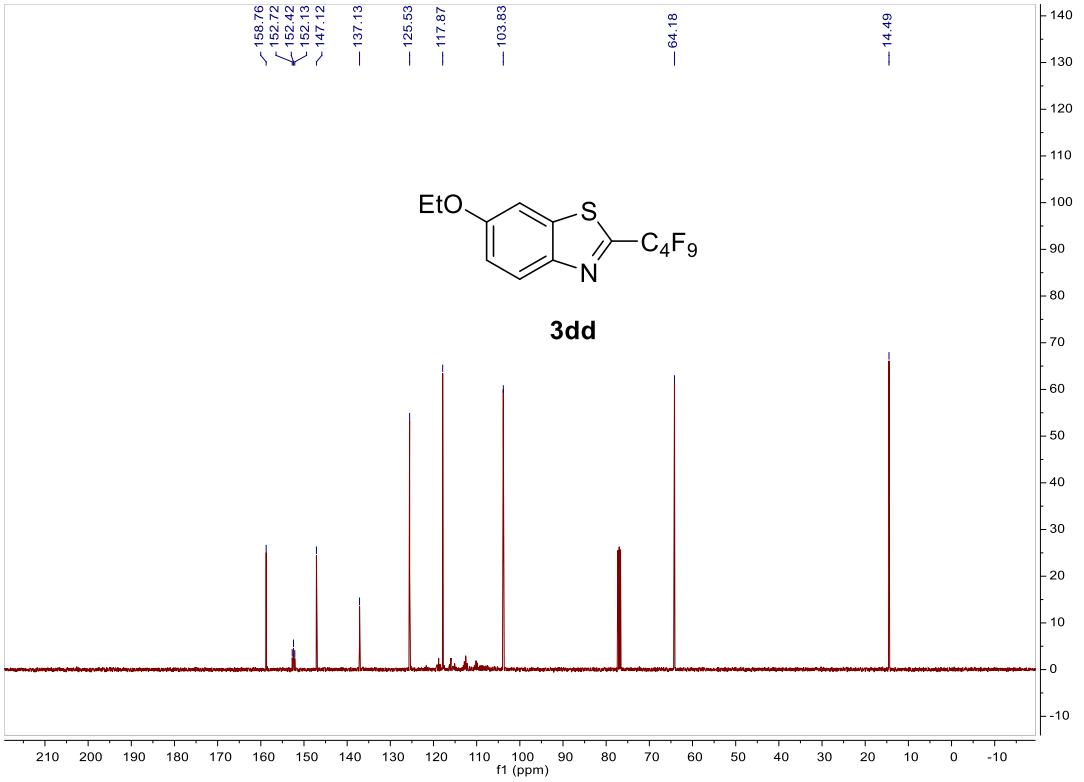
^{19}F NMR spectrum of 3cd



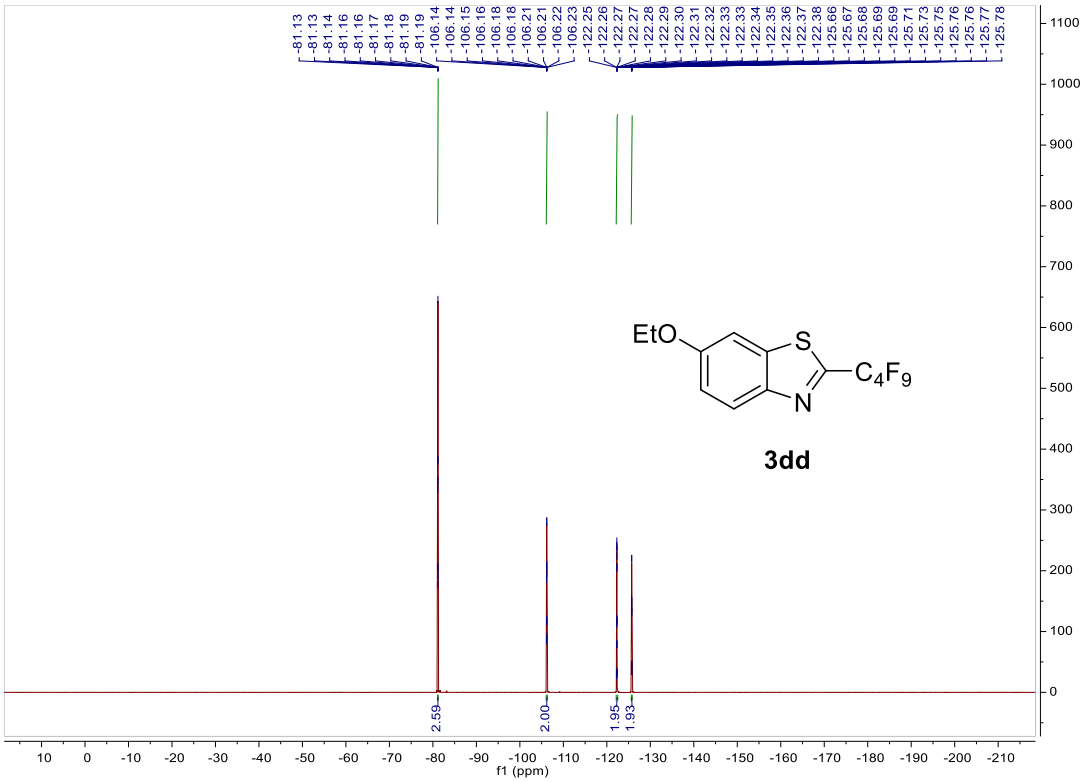
^{1}H NMR spectrum of 3dd



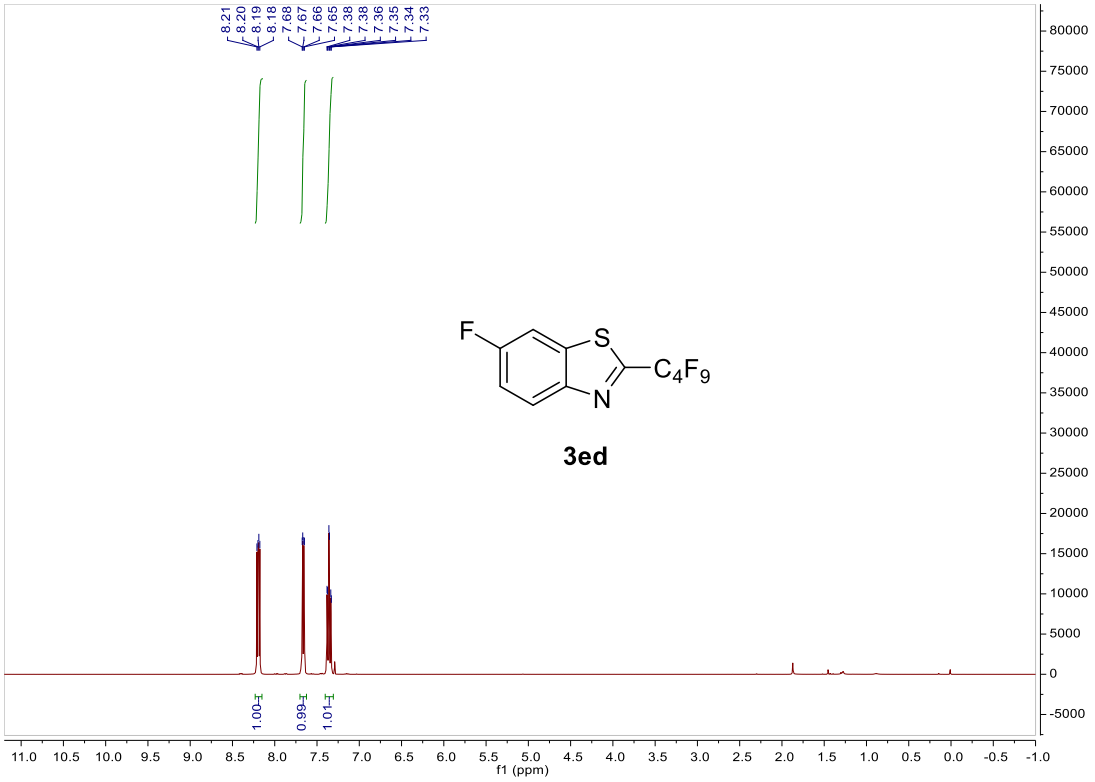
^{13}C NMR spectrum of 3dd



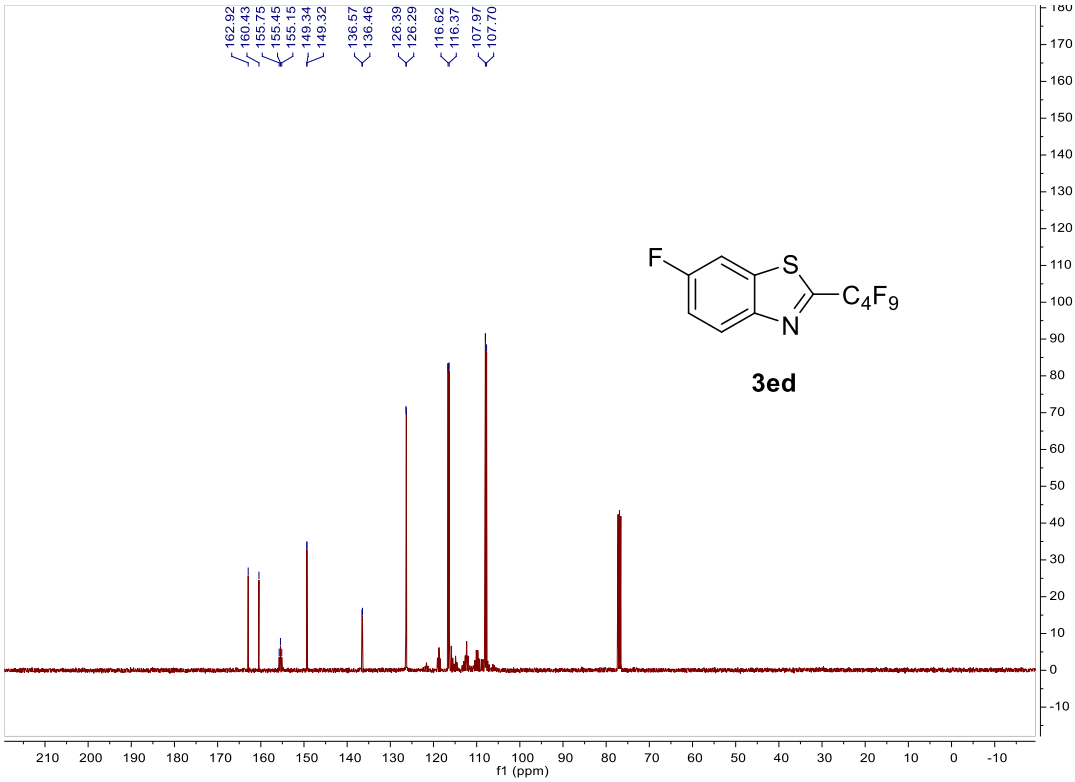
^{19}F NMR spectrum of 3dd



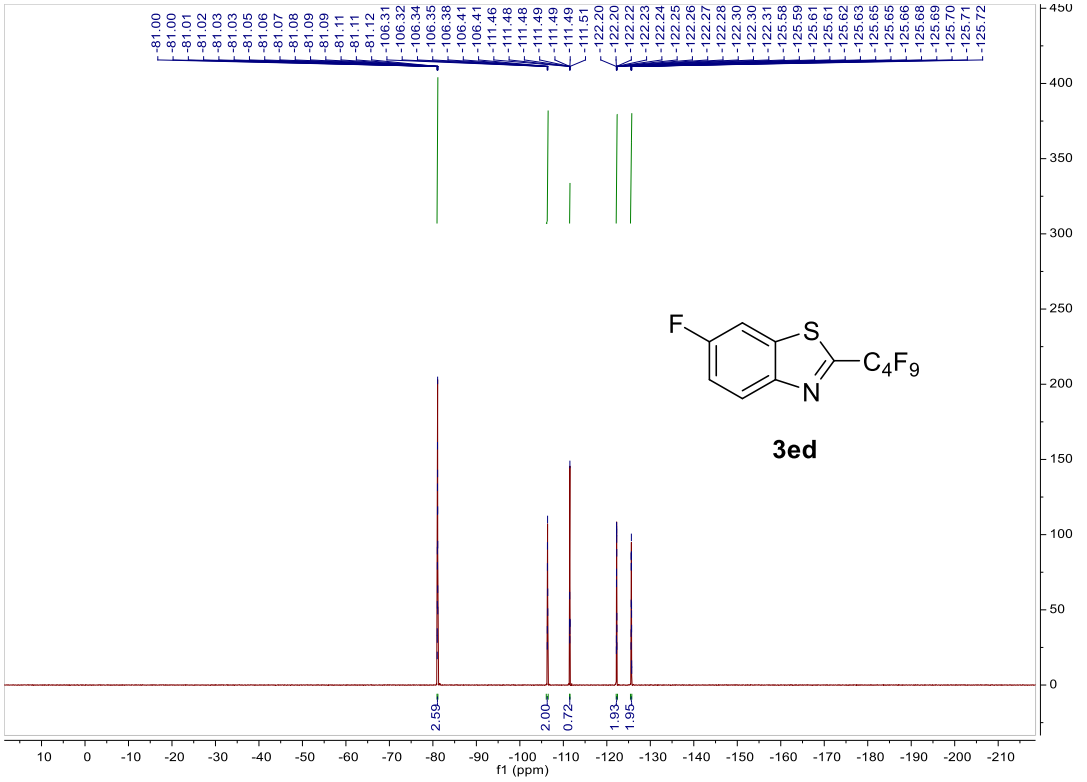
^{1}H NMR spectrum of 3ed



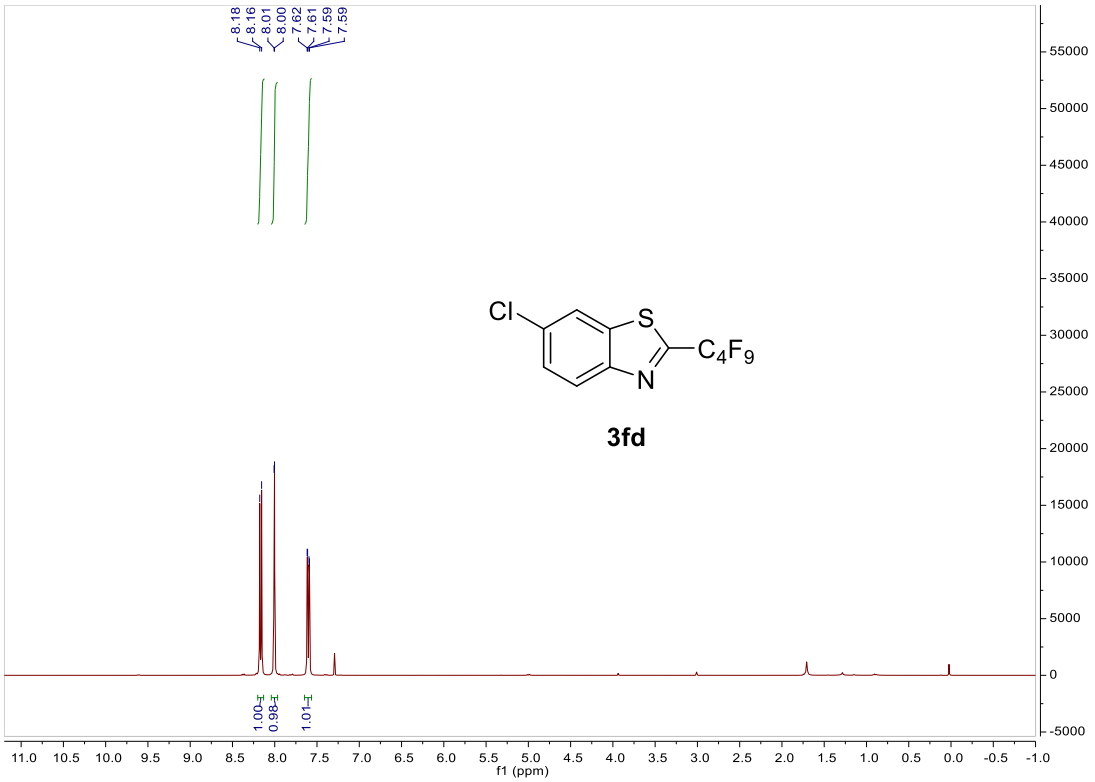
^{13}C NMR spectrum of 3ed



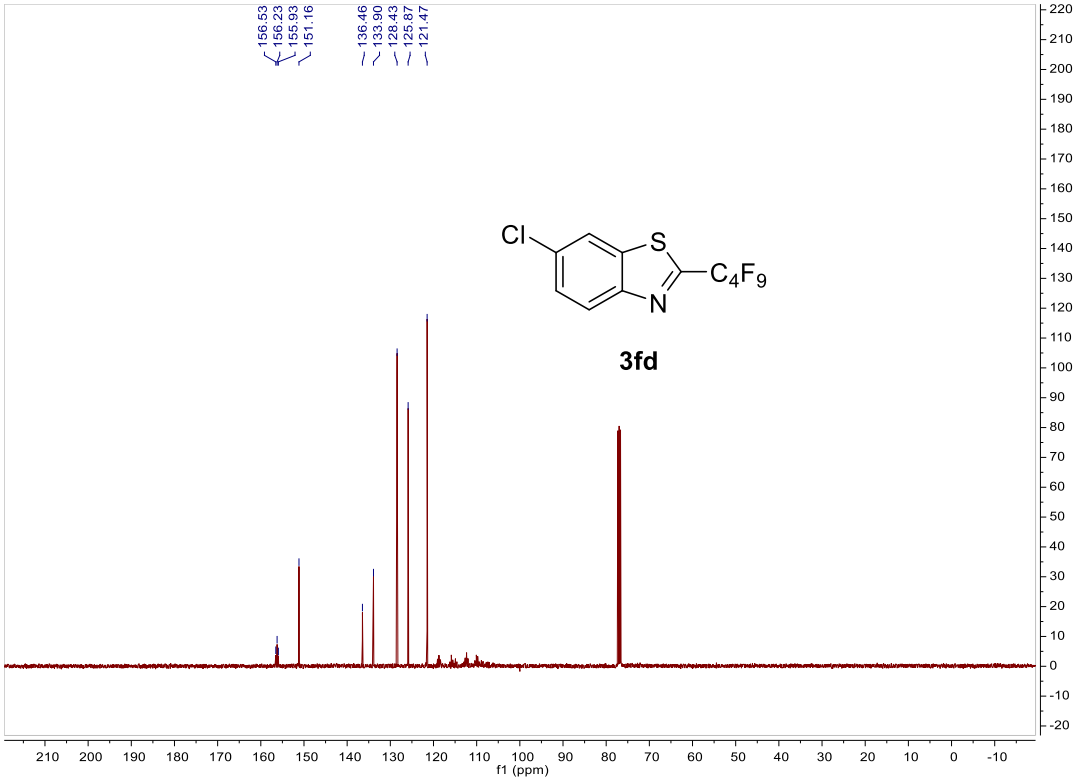
^{19}F NMR spectrum of 3ed



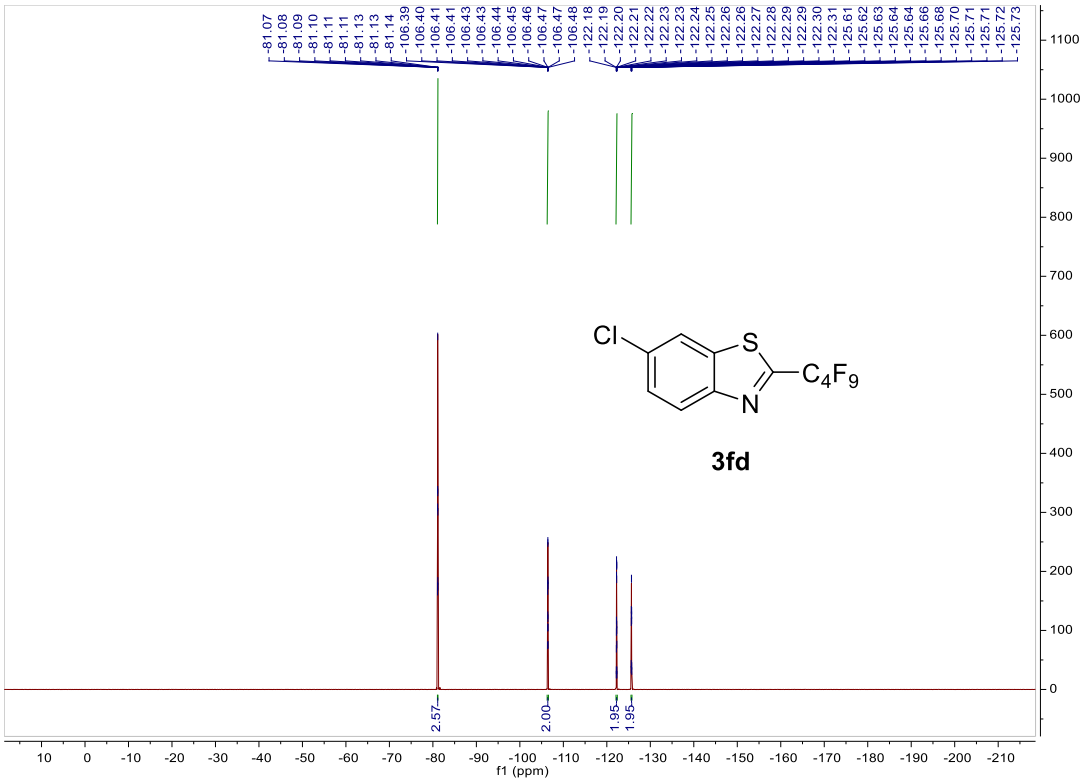
^{1}H NMR spectrum of 3fd



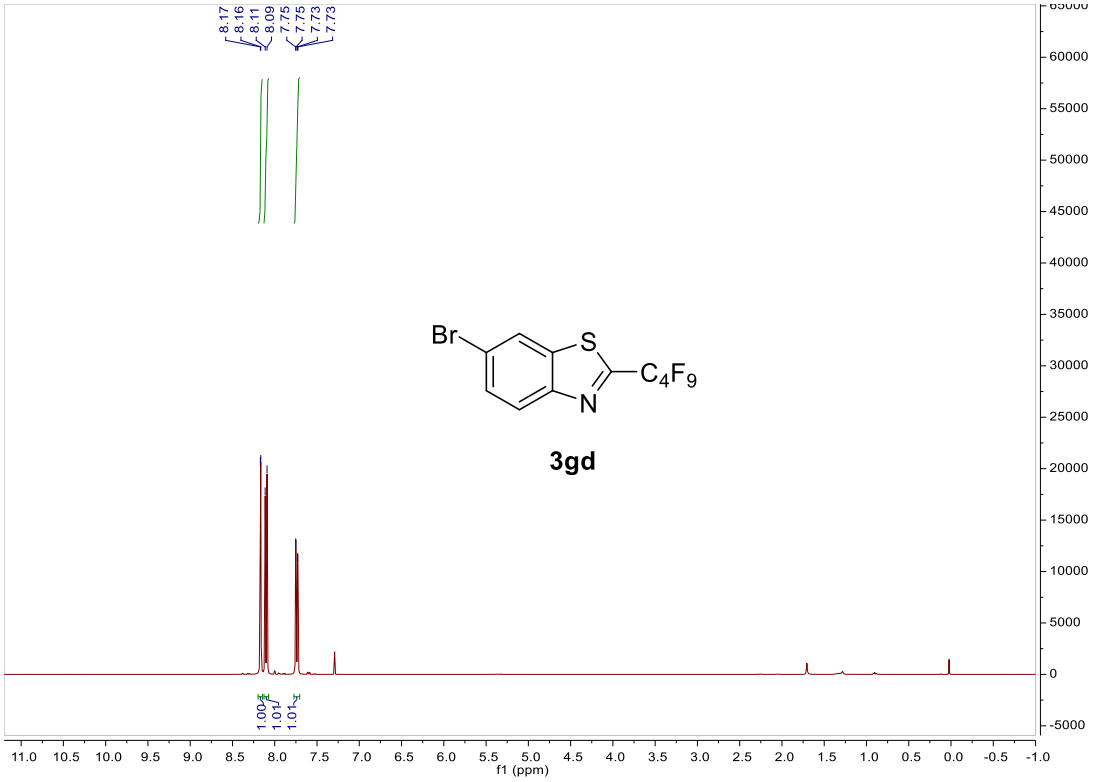
^{13}C NMR spectrum of 3fd



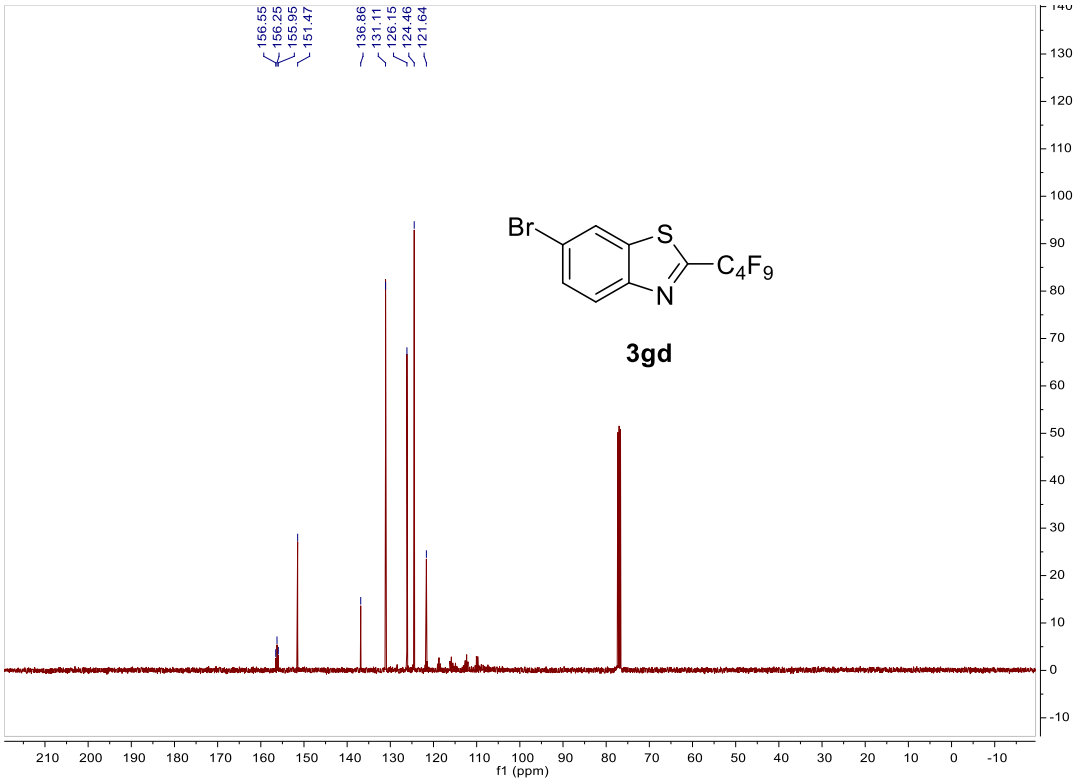
^{19}F NMR spectrum of 3fd



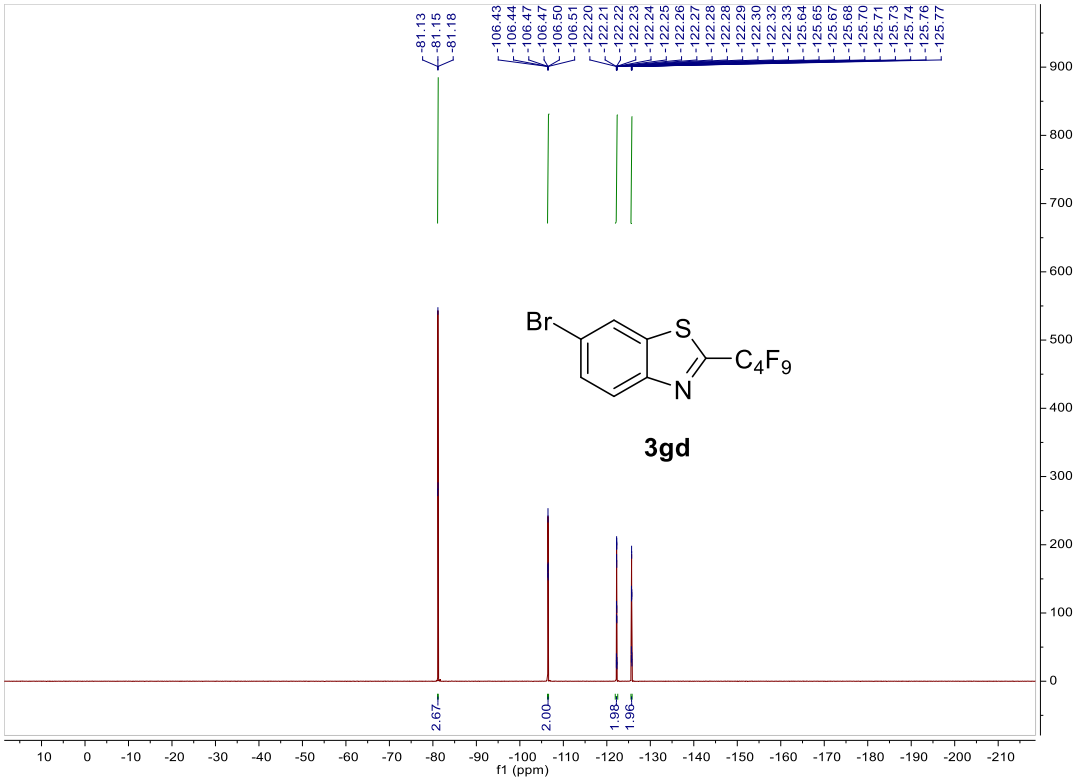
^{1}H NMR spectrum of 3gd



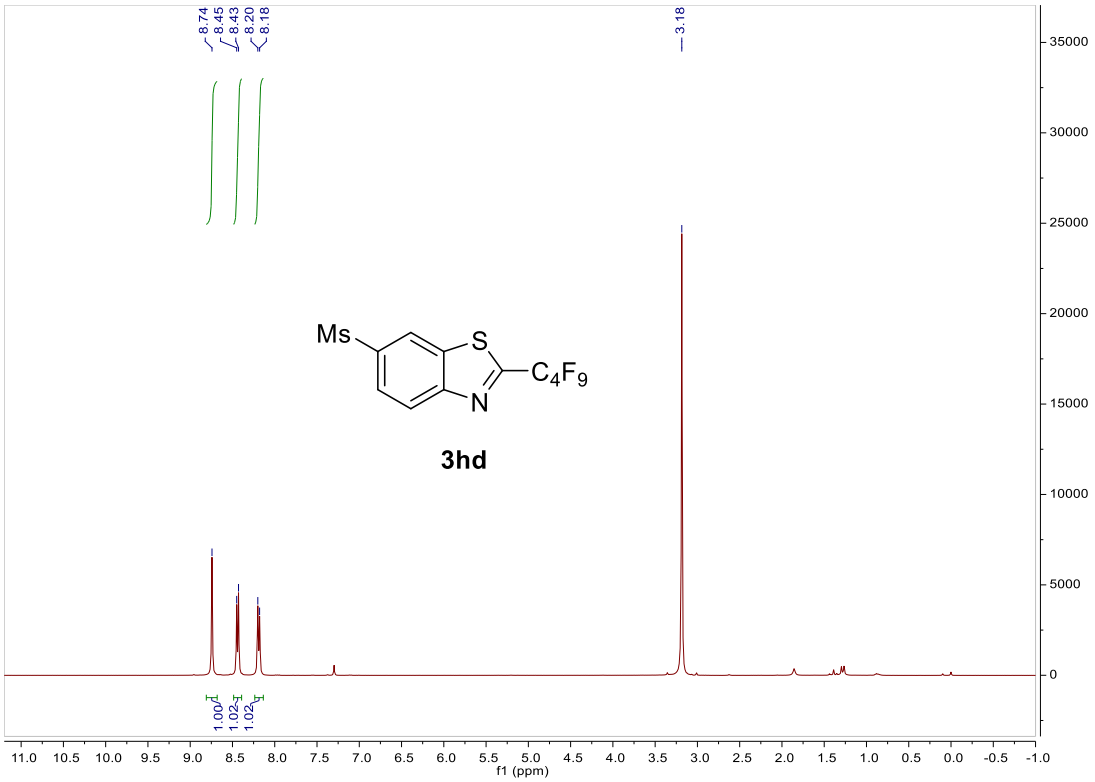
^{13}C NMR spectrum of 3gd



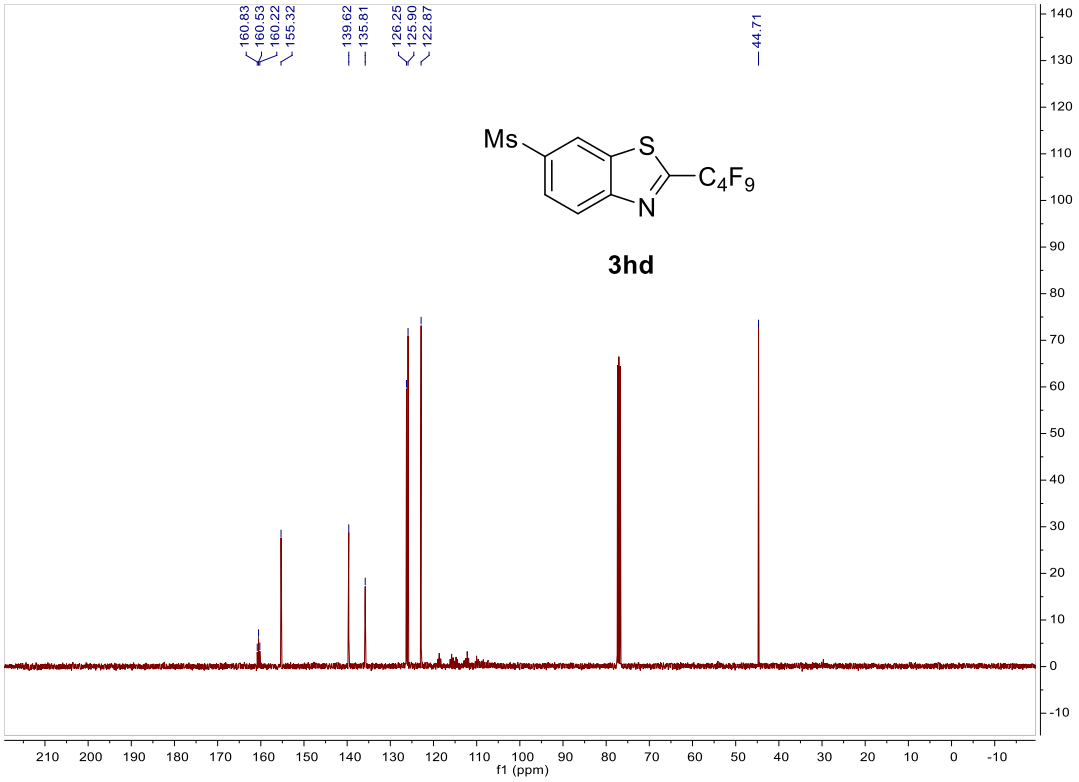
^{19}F NMR spectrum of 3gd



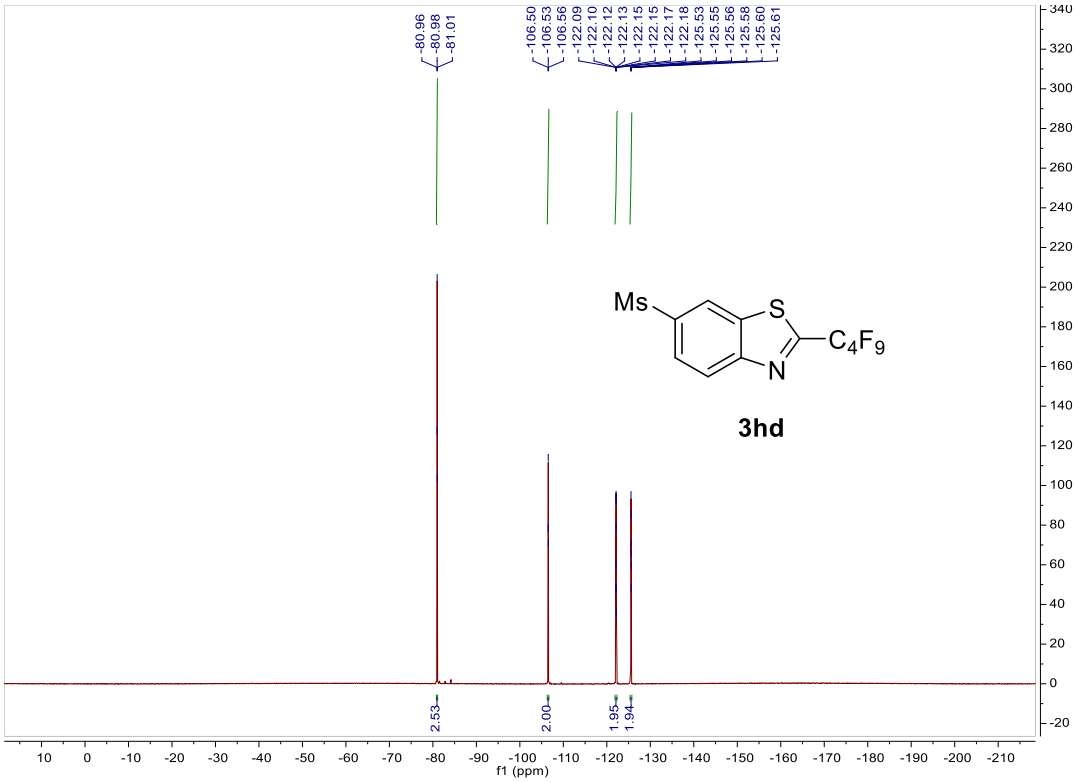
^{1}H NMR spectrum of 3hd



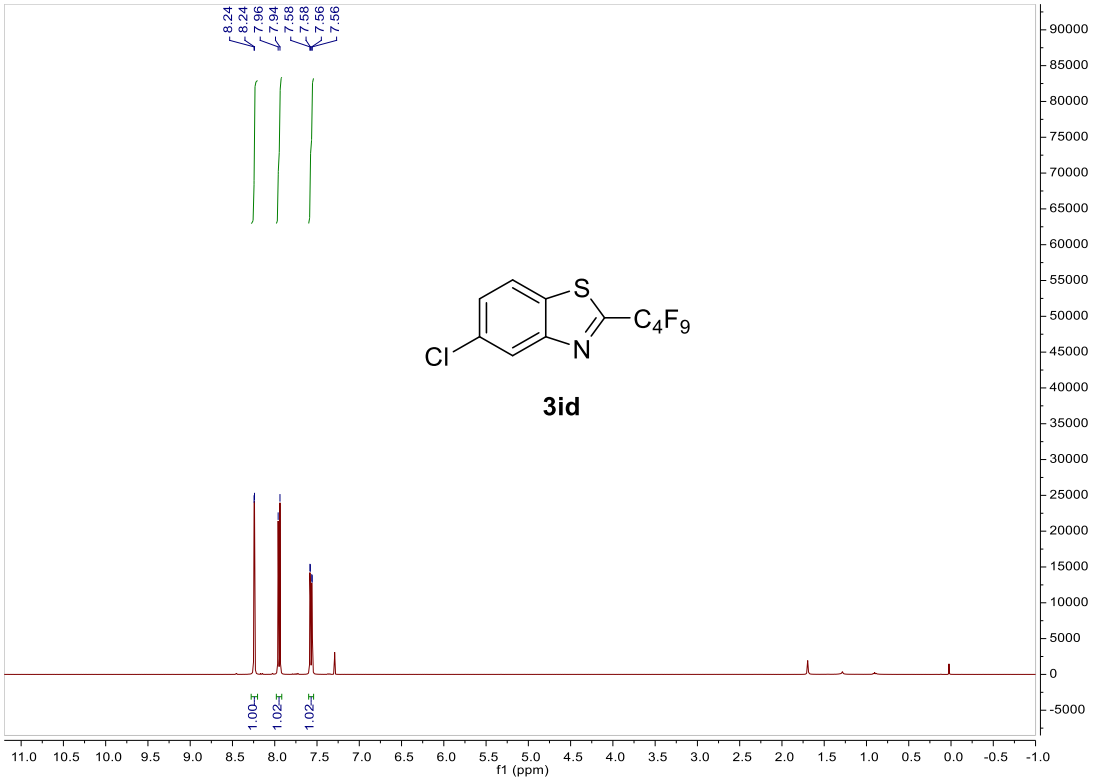
^{13}C NMR spectrum of 3hd



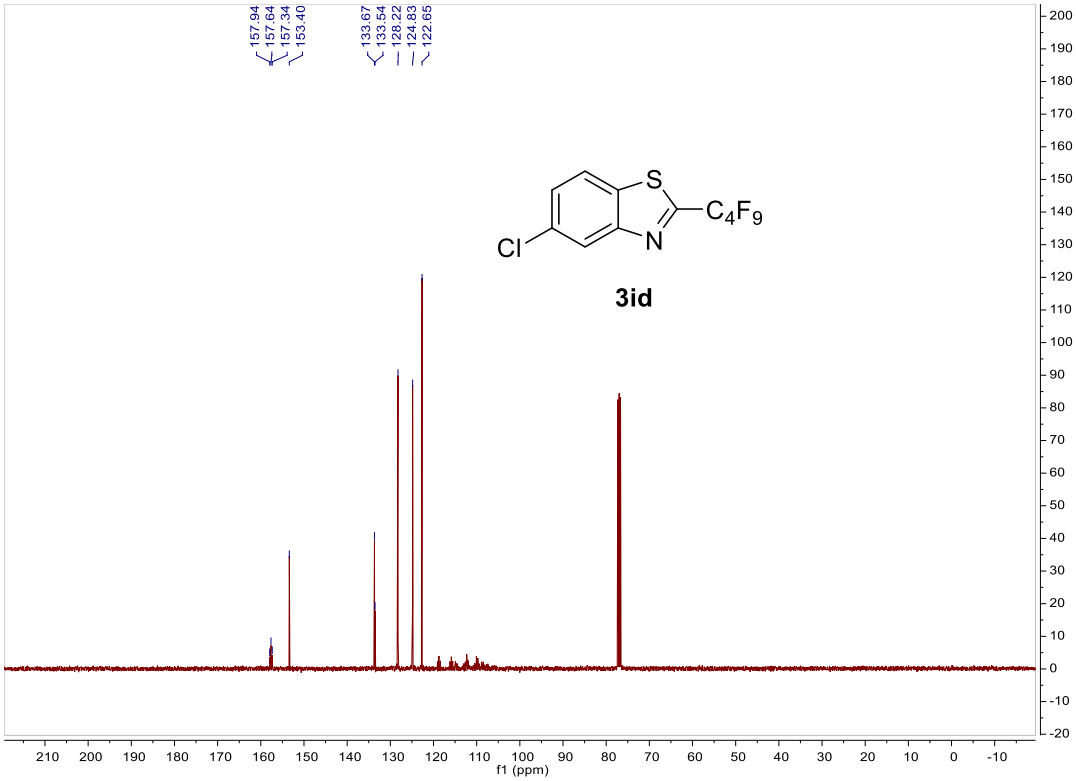
^{19}F NMR spectrum of 3hd



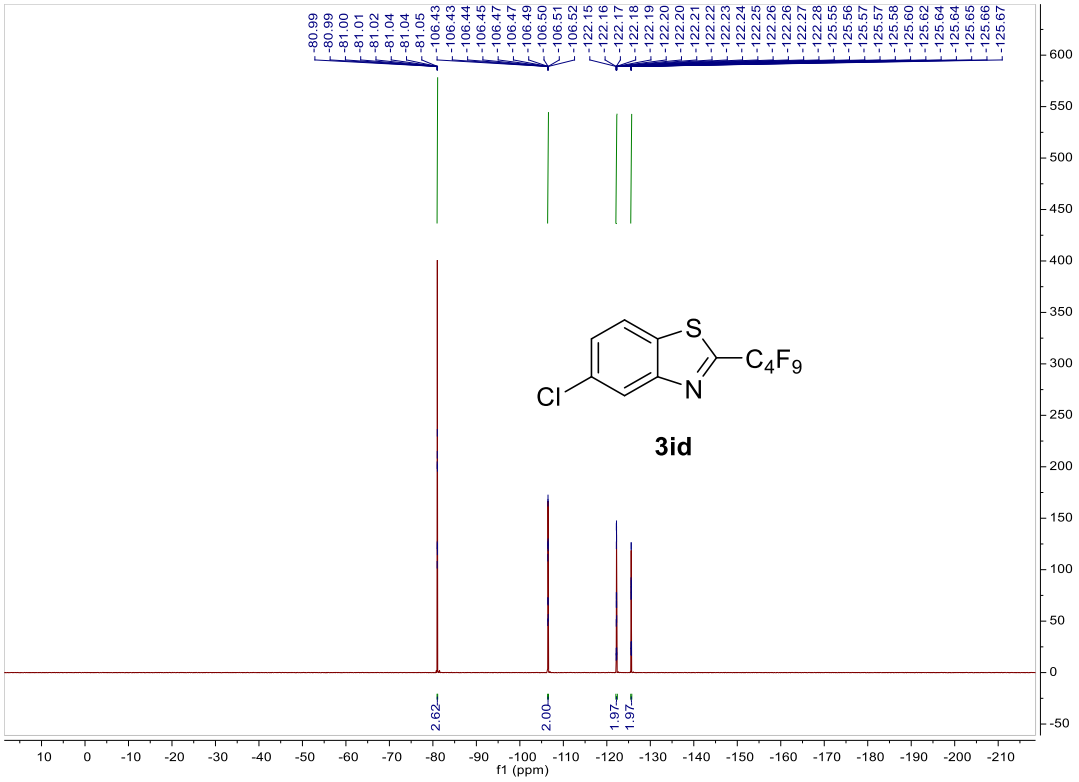
^{1}H NMR spectrum of 3id



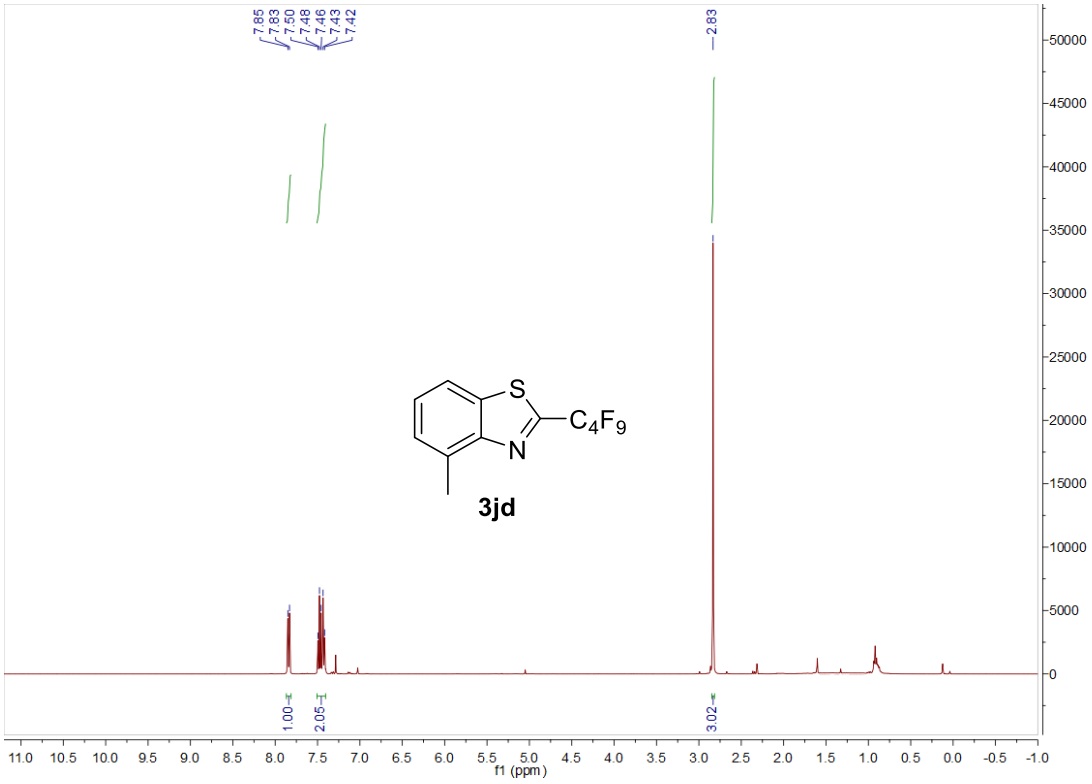
^{13}C NMR spectrum of 3id



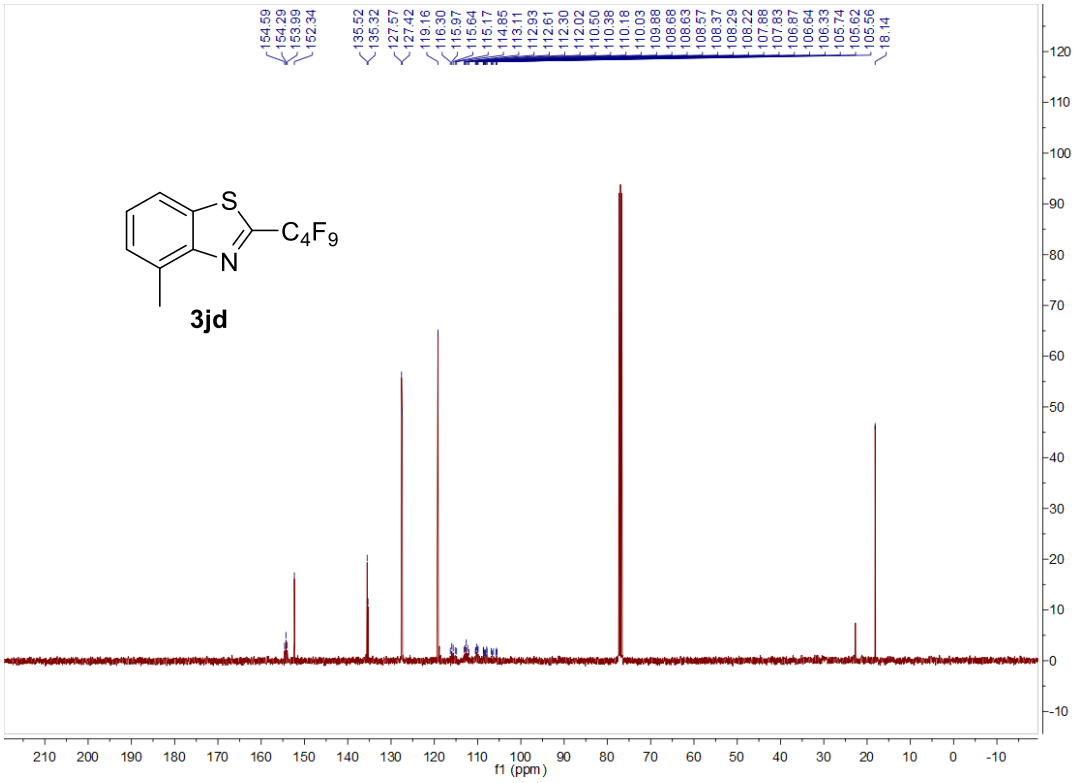
^{19}F NMR spectrum of 3id



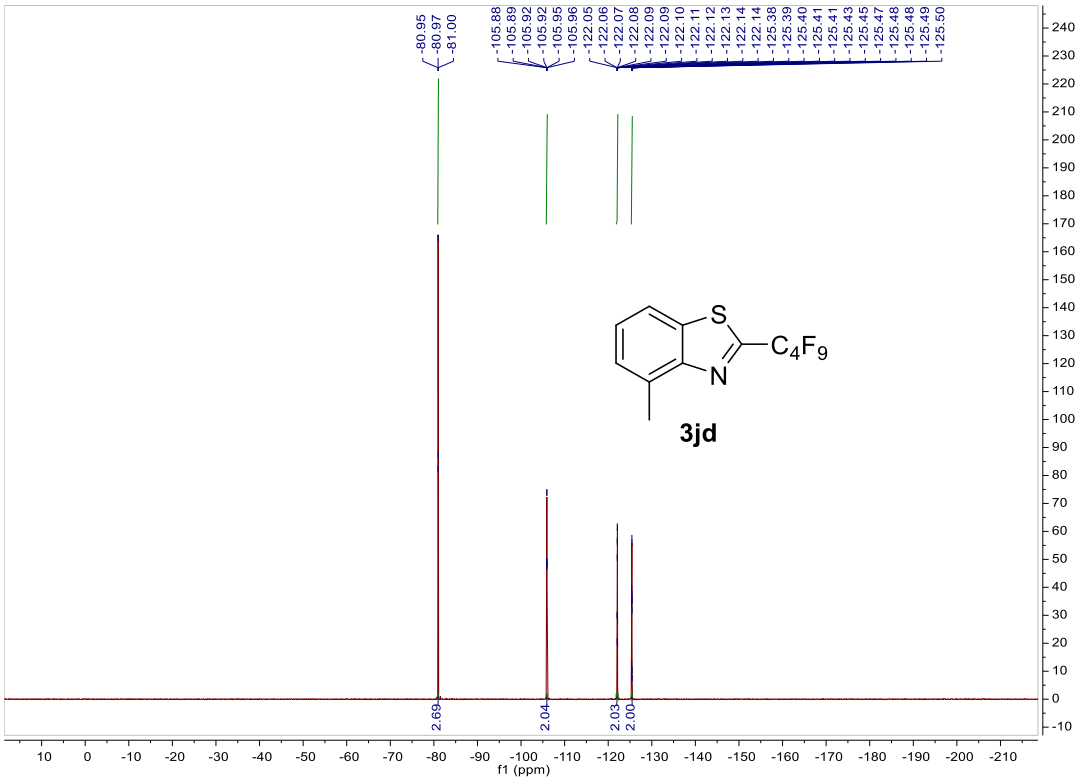
^{1}H NMR spectrum of 3jd



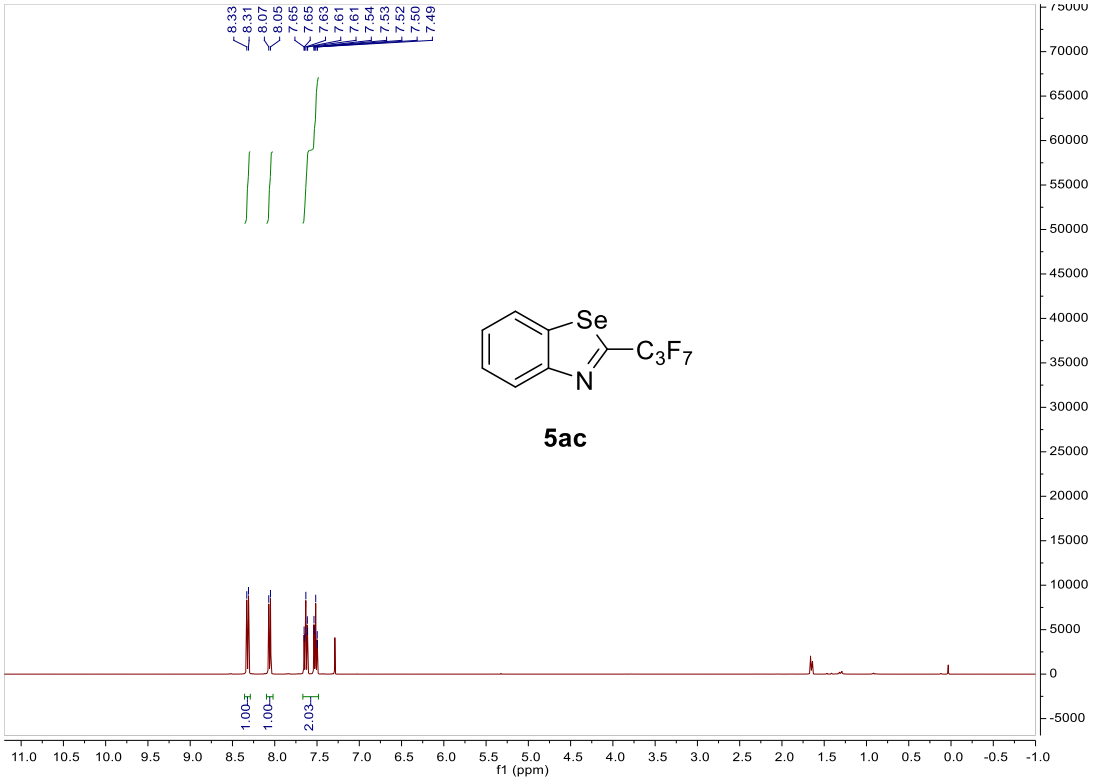
^{13}C NMR spectrum of 3jd



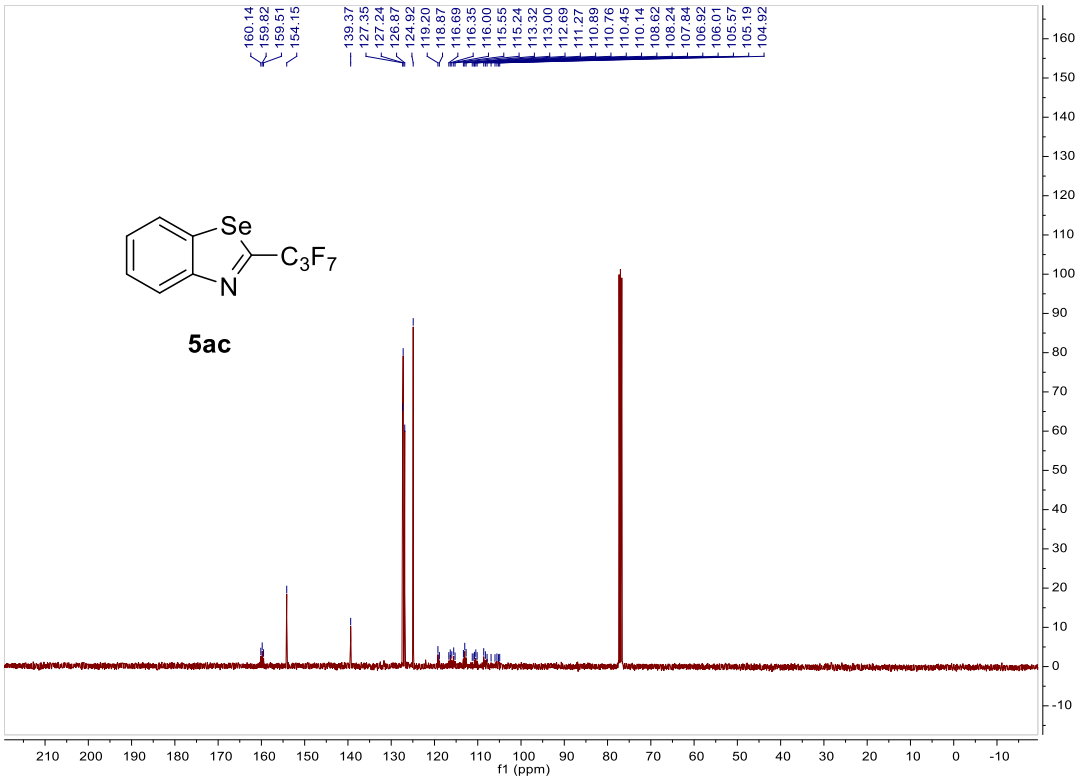
^{19}F NMR spectrum of 3jd



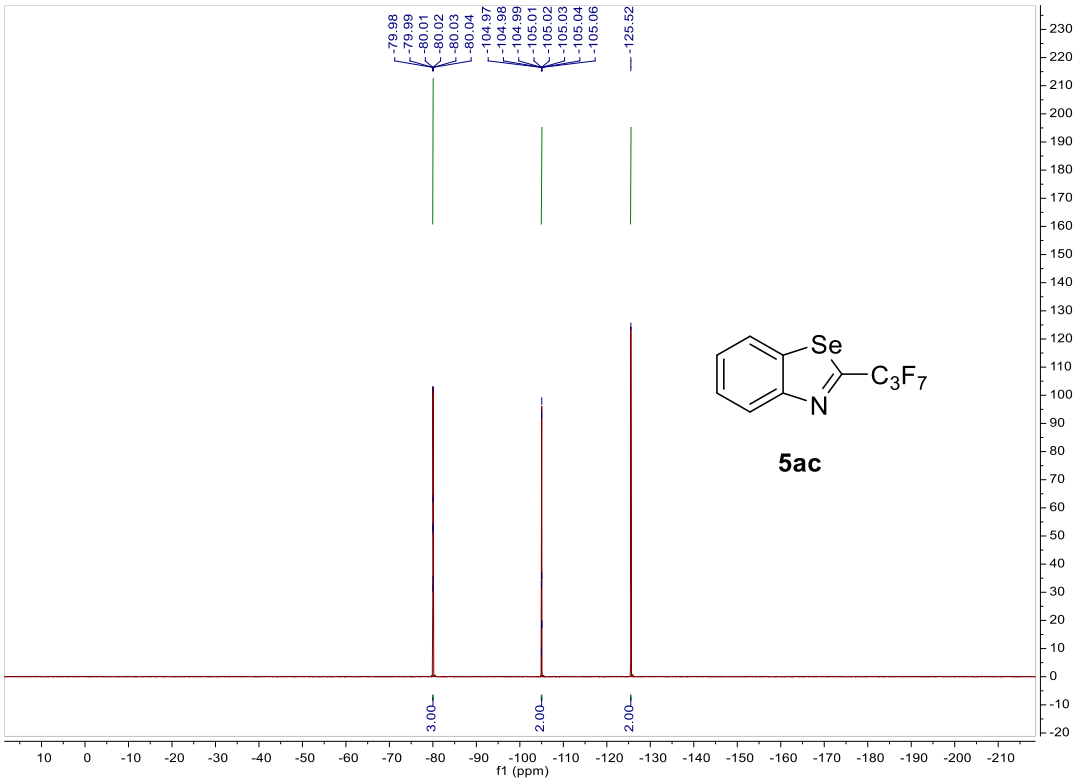
^{1}H NMR spectrum of 5ac



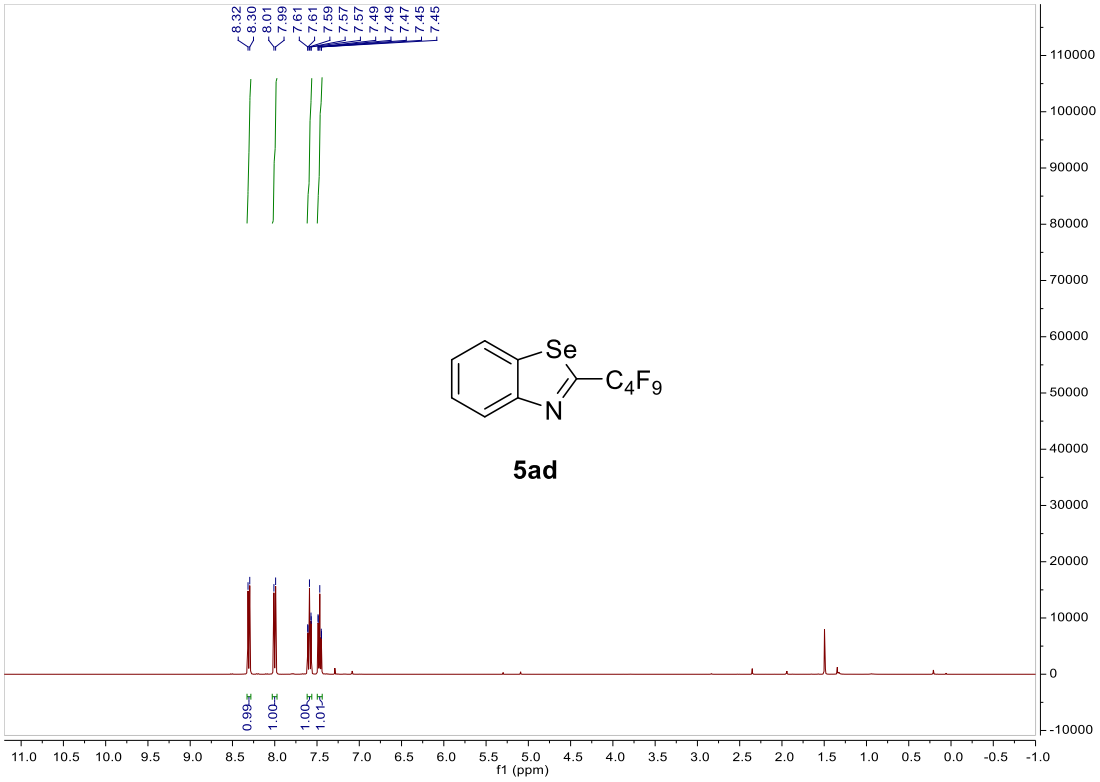
^{13}C NMR spectrum of 5ac



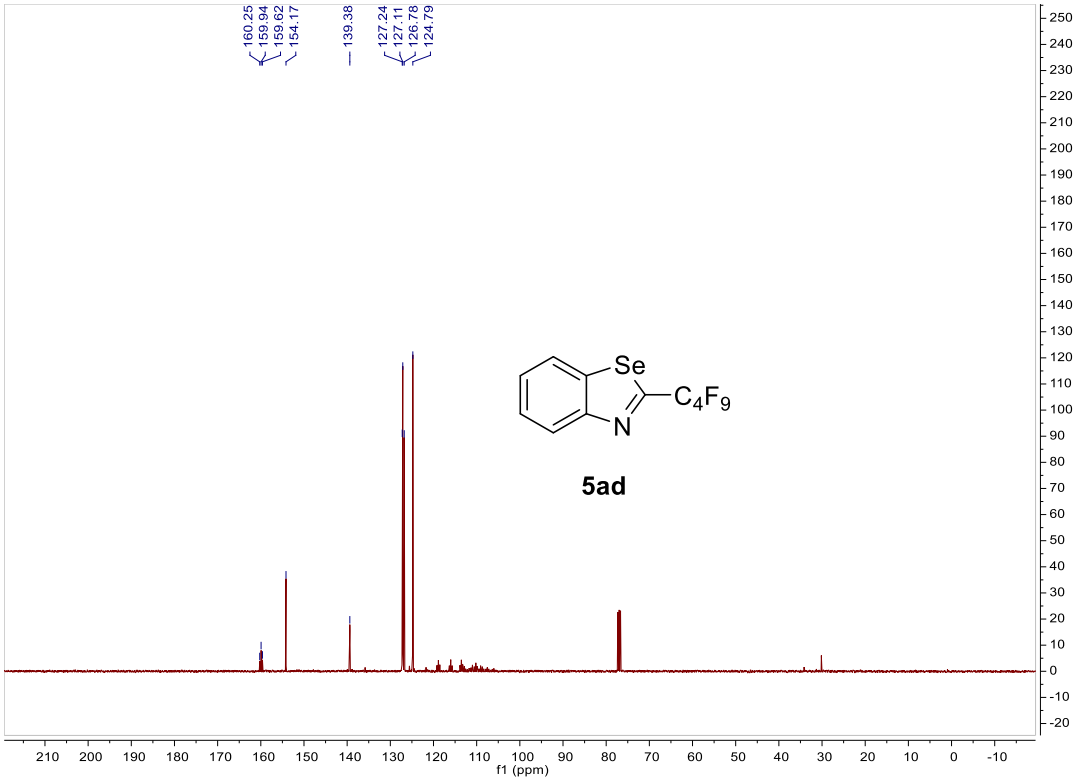
^{19}F NMR spectrum of 5ac



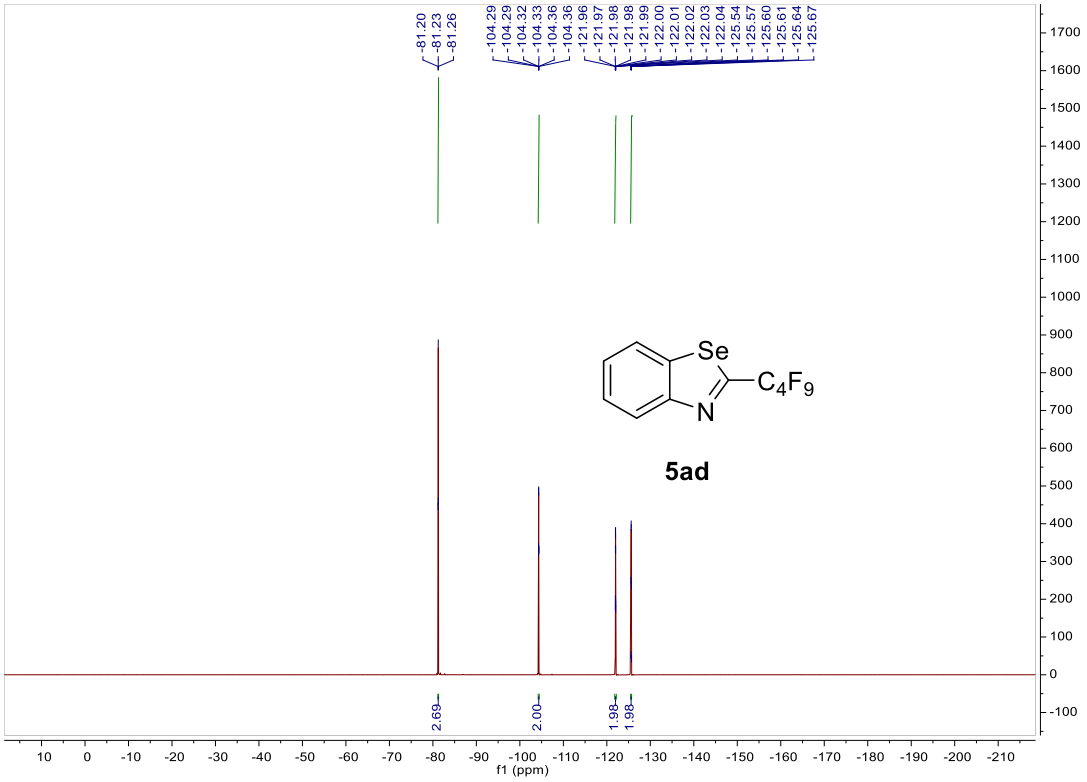
^{1}H NMR spectrum of 5ad



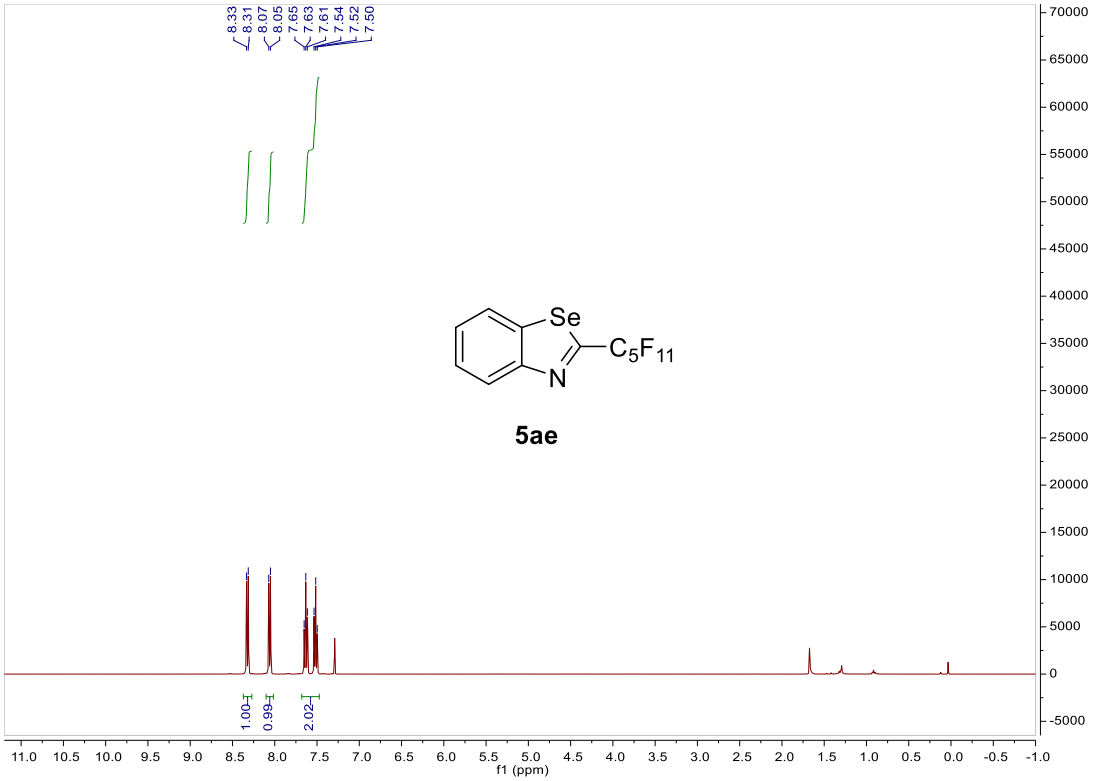
^{13}C NMR spectrum of 5ad



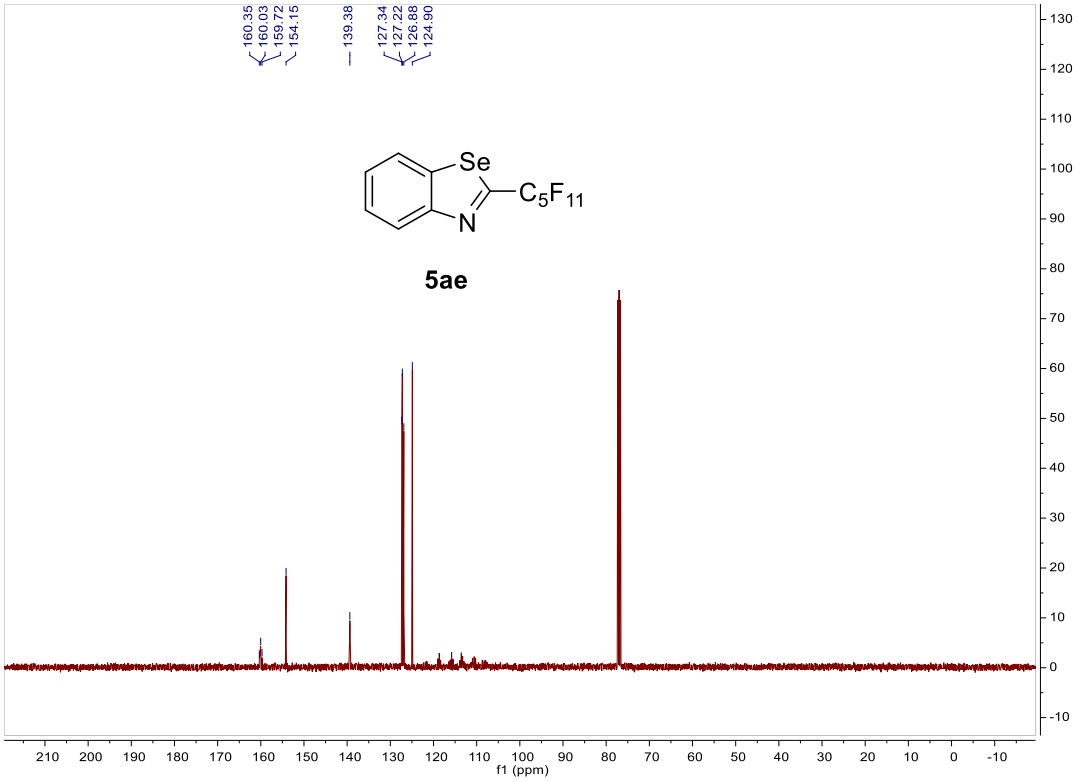
^{19}F NMR spectrum of 5ad



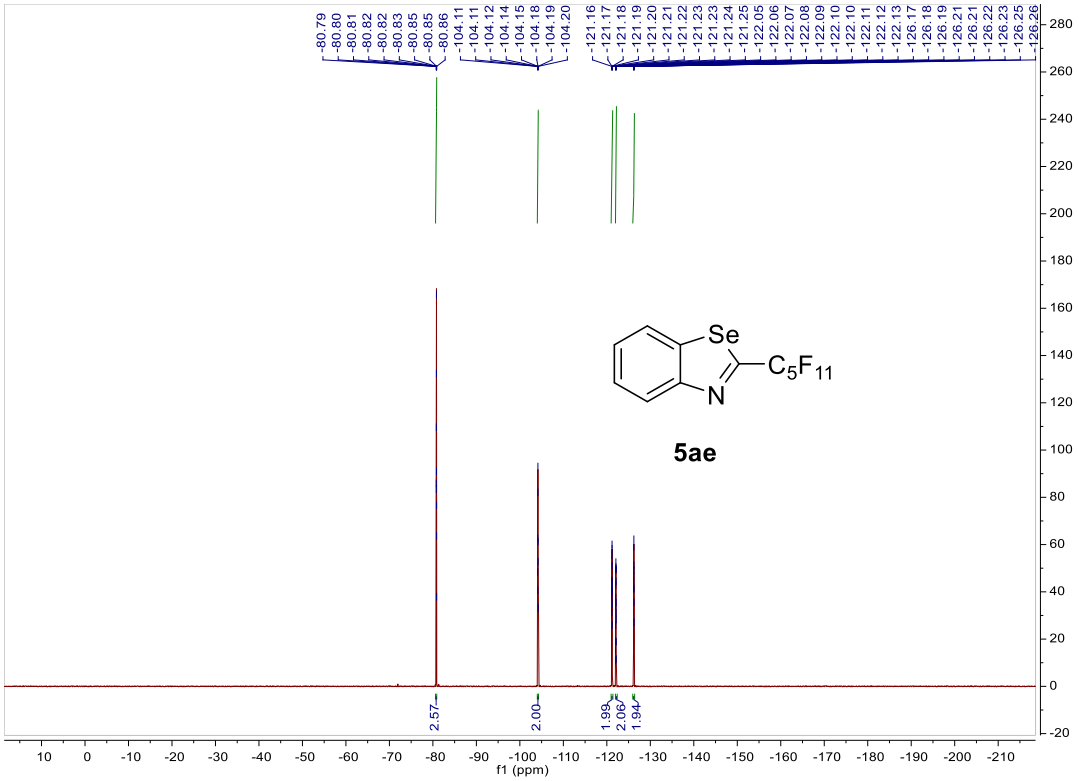
^{1}H NMR spectrum of 5ae



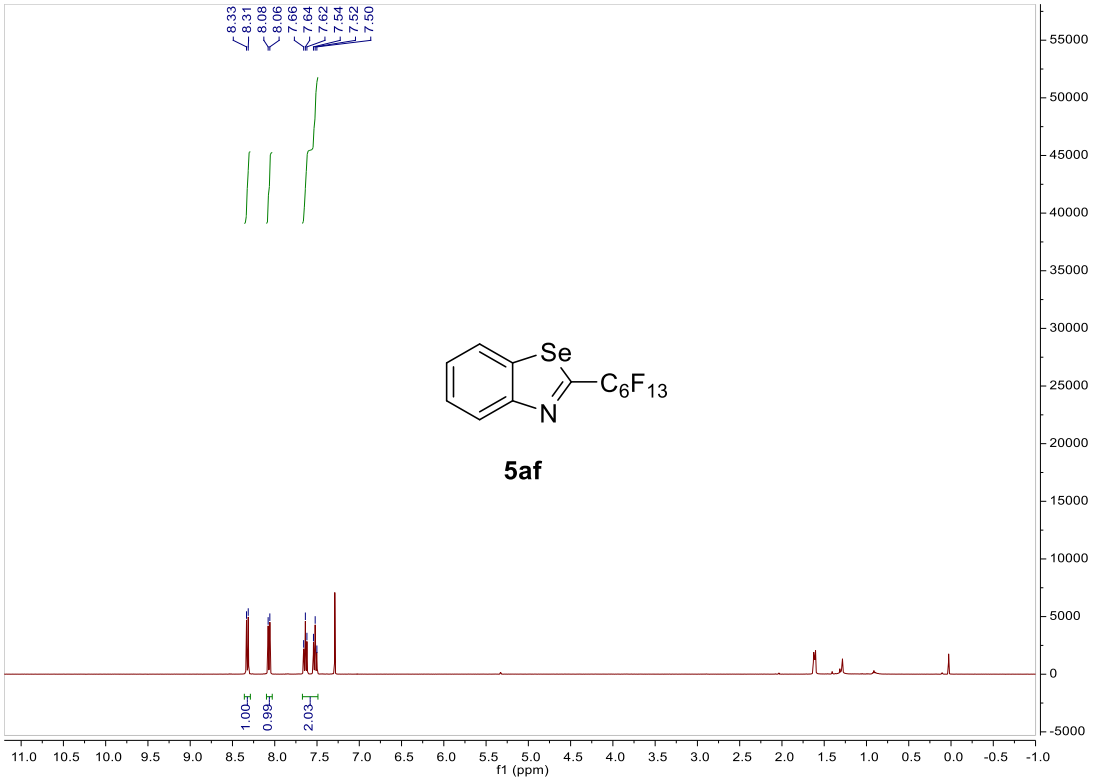
^{13}C NMR spectrum of 5ae



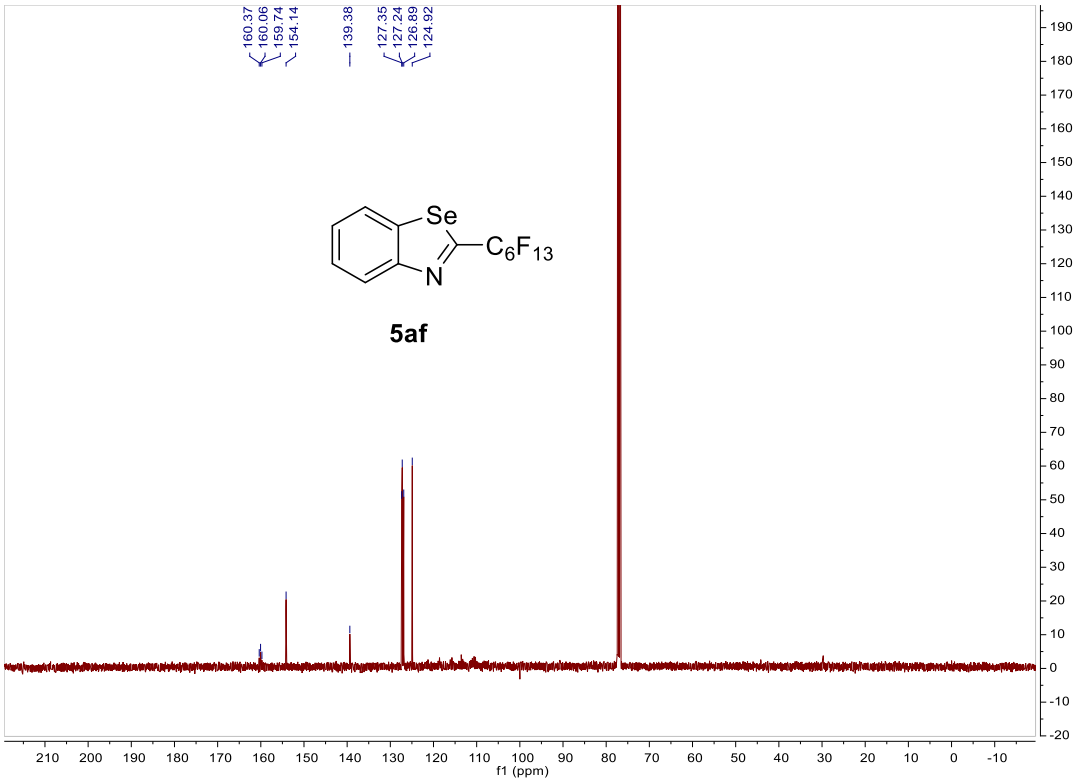
^{19}F NMR spectrum of 5ae



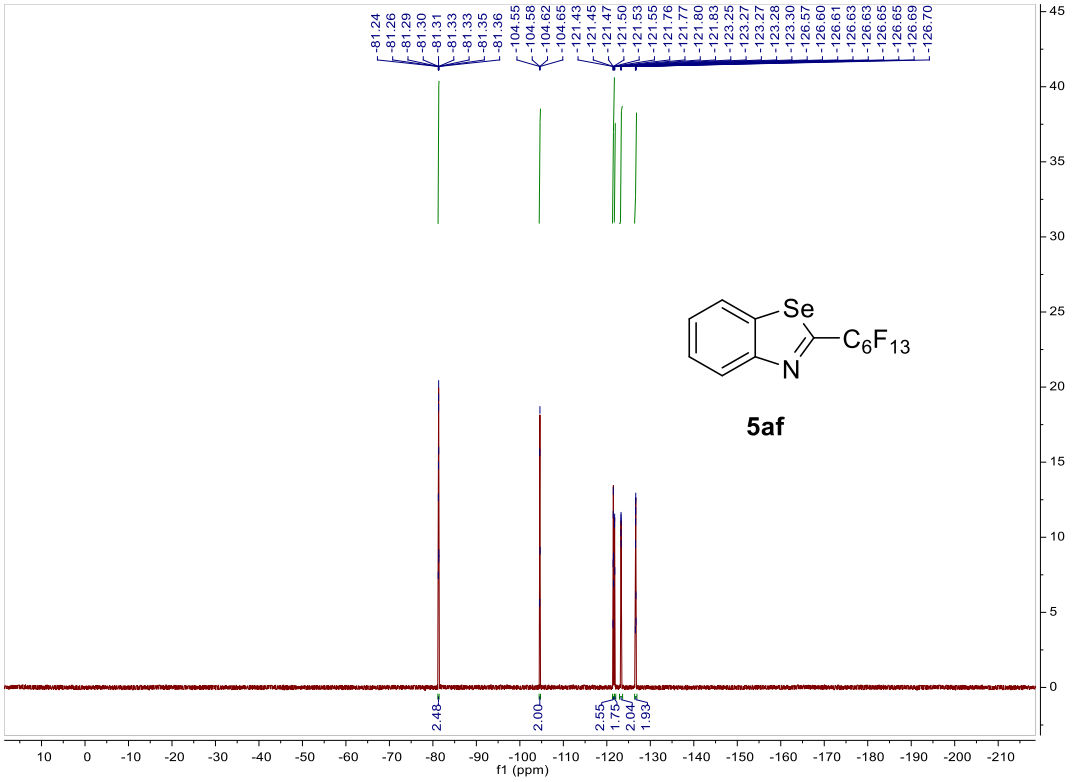
^{1}H NMR spectrum of 5af



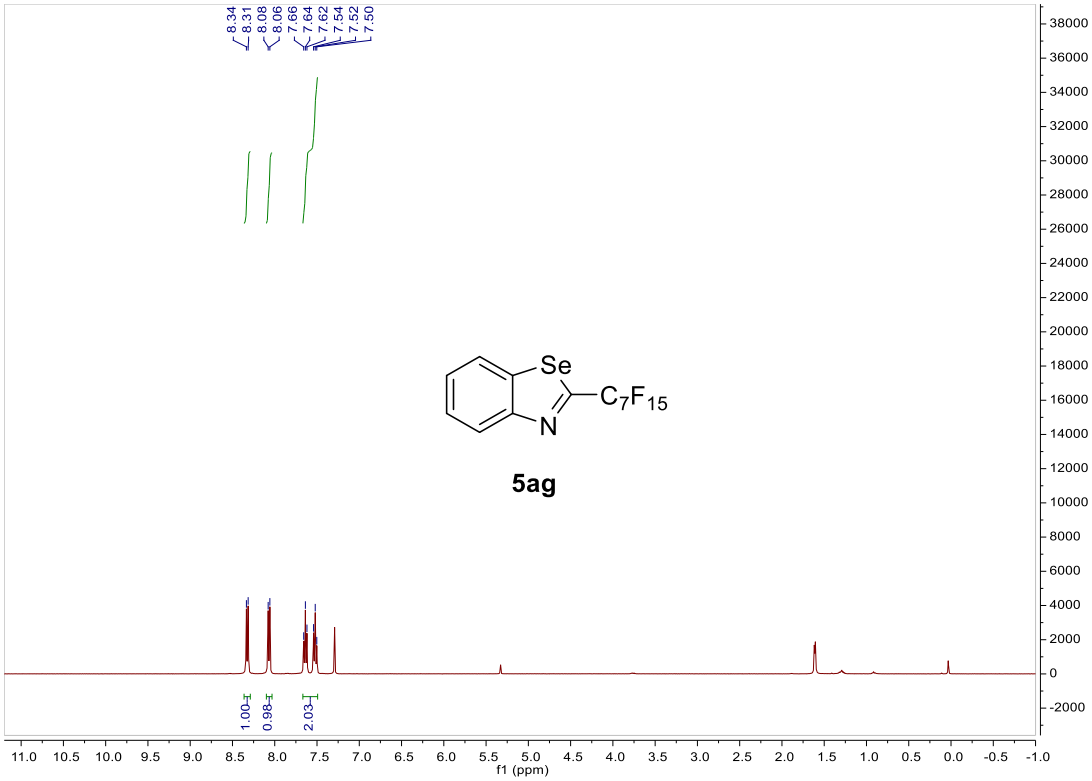
^{13}C NMR spectrum of 5af



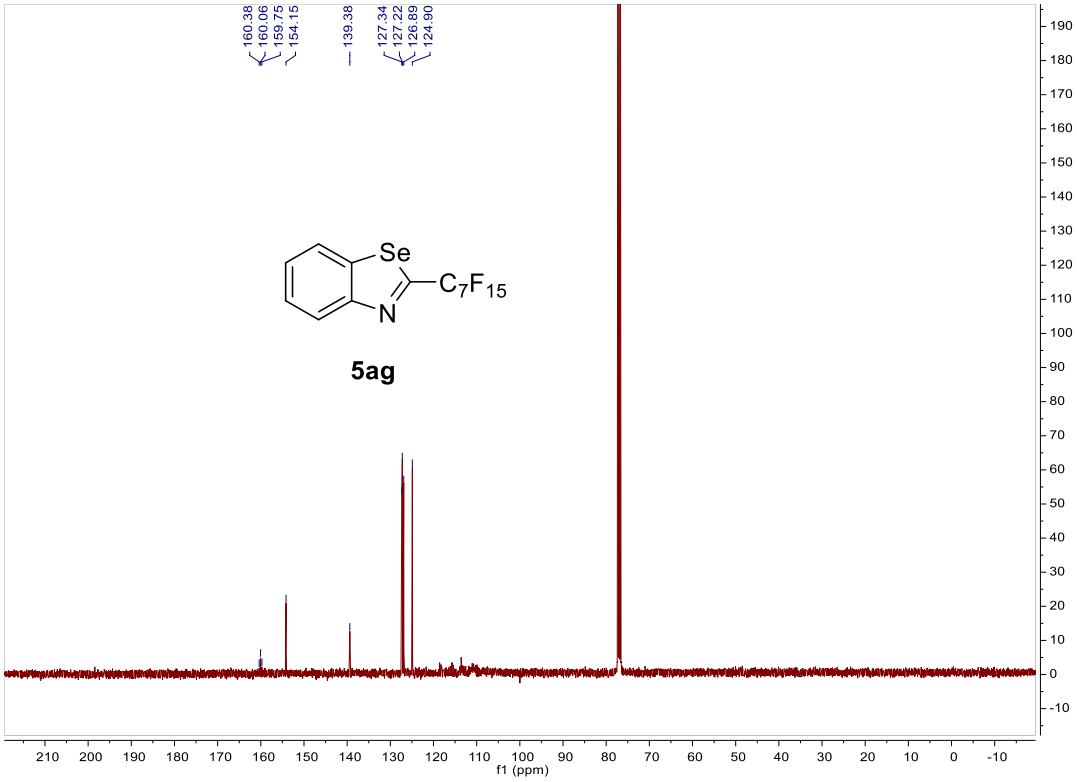
^{19}F NMR spectrum of 5af



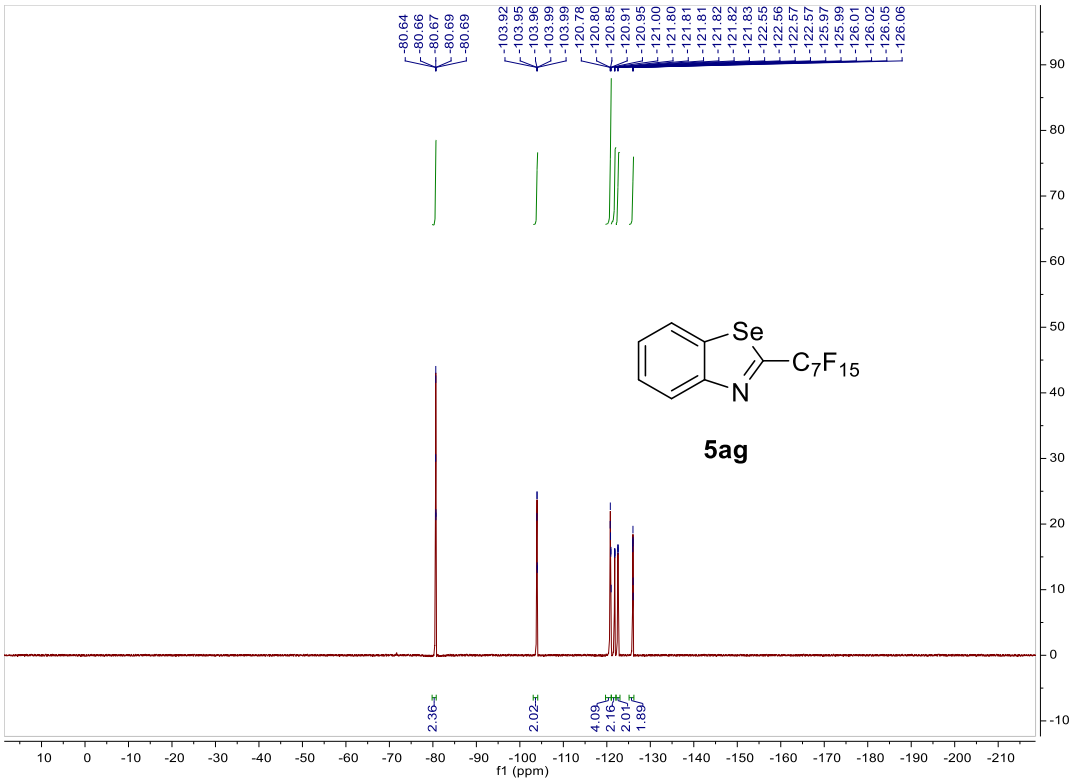
^{1}H NMR spectrum of 5ag



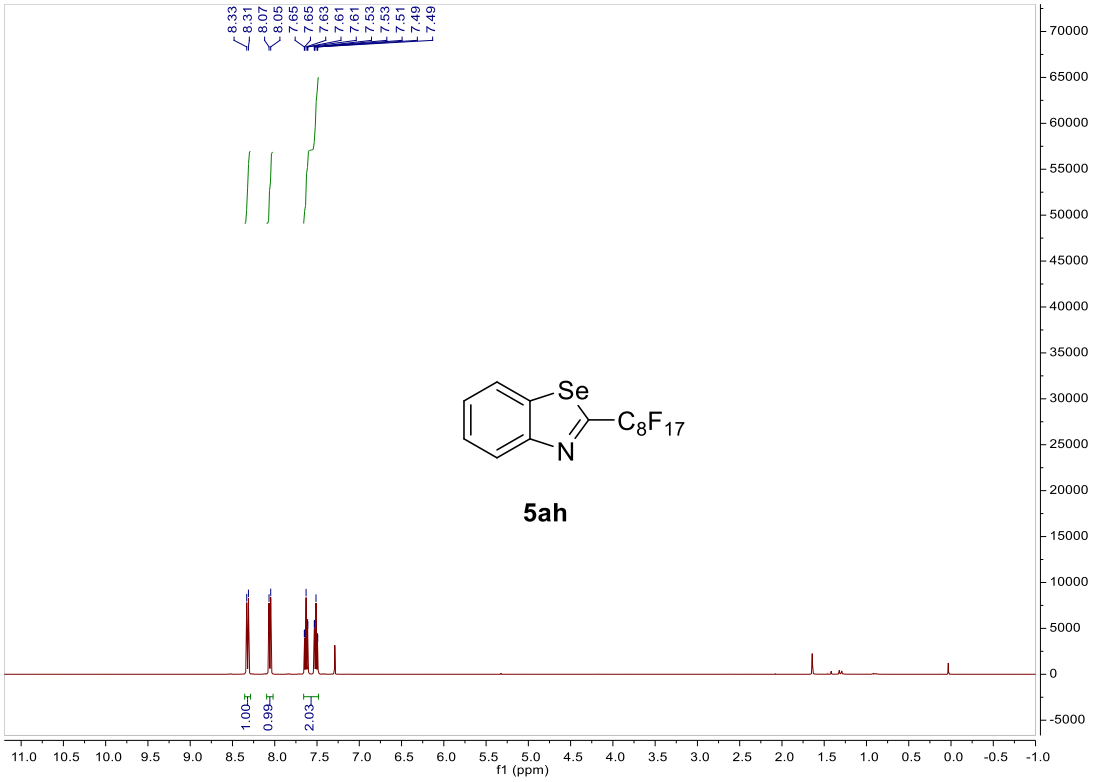
^{13}C NMR spectrum of 5ag



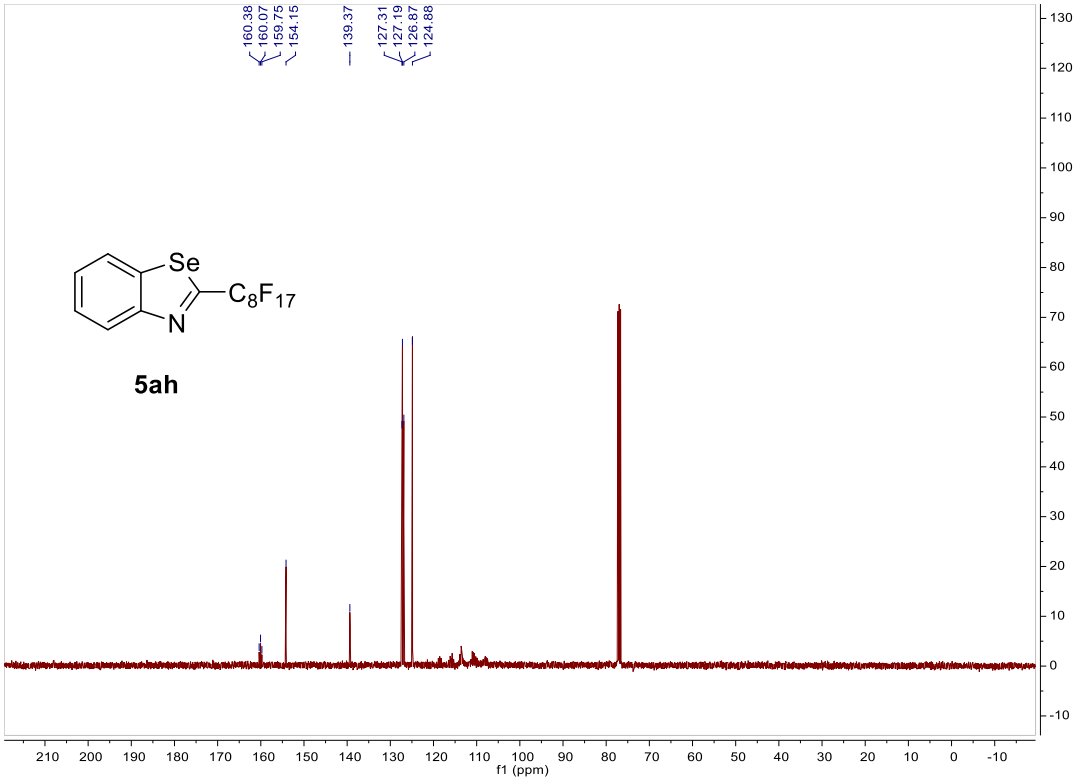
^{19}F NMR spectrum of 5ag



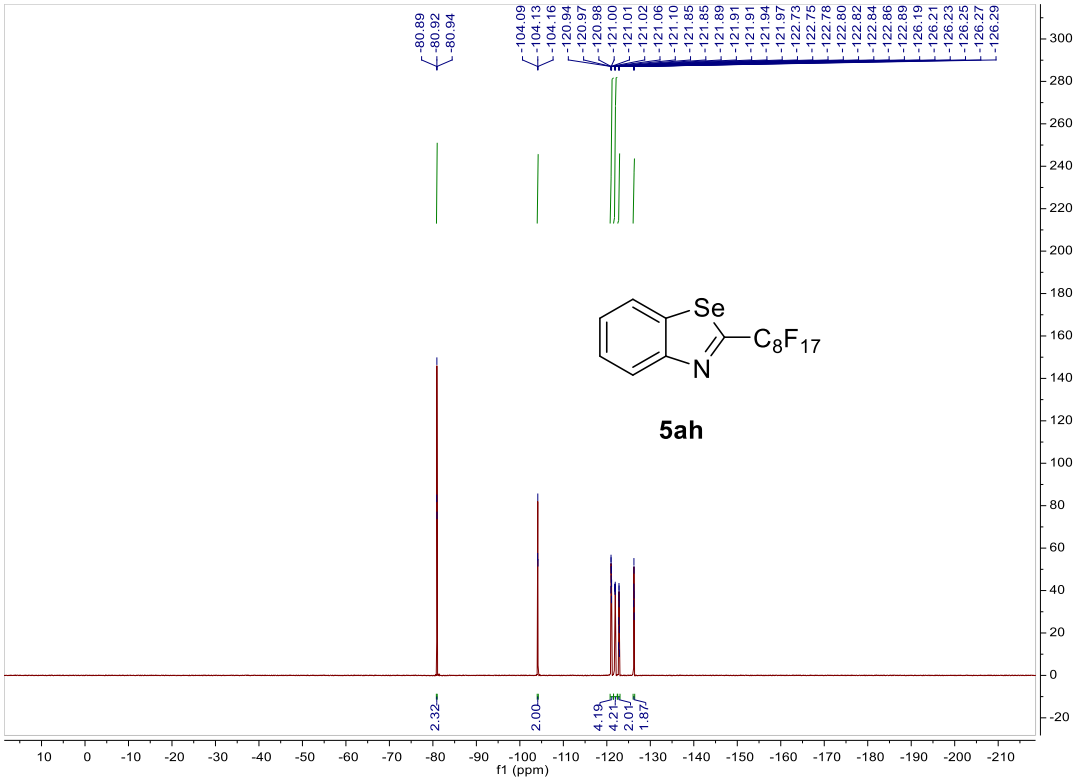
^{1}H NMR spectrum of 5ah



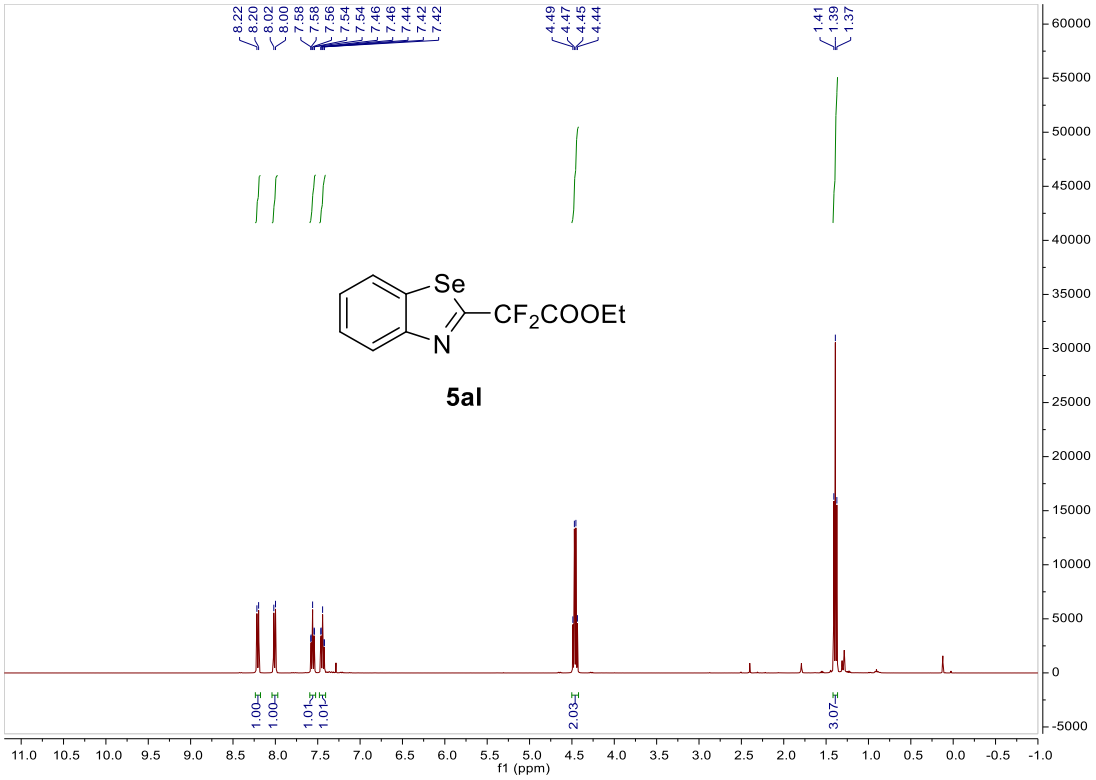
^{13}C NMR spectrum of 5ah



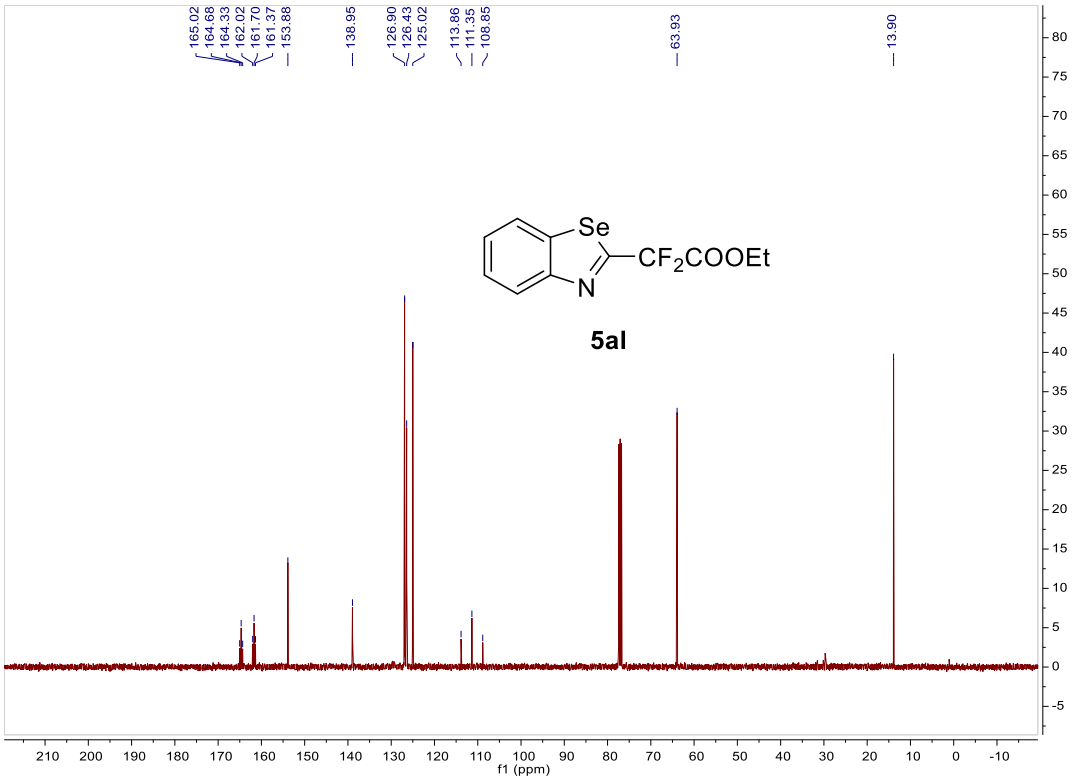
^{19}F NMR spectrum of 5ah



^{1}H NMR spectrum of 5ai



^{13}C NMR spectrum of 5ai



^{19}F NMR spectrum of 5ai