Supporting Information

Visible-Light-Promoted Deoxygenation / Isomerization Strategy for Highly *E*-selective Synthesis of α-fluoro-β-arylalkenyl Sulfides

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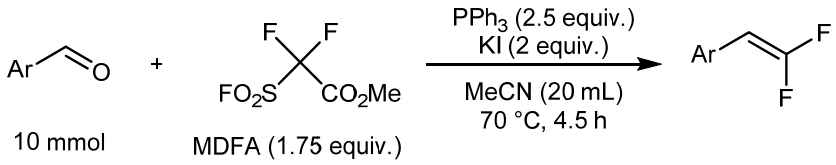
Table of Contents

1. General information

All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere in a sealed tube. Unless otherwise noted, all the solvents and reagents were obtained from commercial suppliers (Strem, Alfa, Aldrich, Adamas-beta®, Innochem, Aladdin, Acros, TCI, bidepharm and so on) and used without further purification. All *gem*-difluoroalkenes[1-3] and sodium sulfinates[4] were prepared following literature procedures. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 °C). Gas chromatographic analyses were performed on Shimadzu GC 2030 gas chromatography instrument with a FID detector and adamantane was added as an internal standard. ^{1}H, ^{13}C and ^{19}F NMR data were recorded with **Bruker AVANCE NEO (600 MHz)** spectrometers and **Agilent DD2 600 (600 MHz)** with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. Singlet (s), doublet (d), doublet of doublet (dd), triplet (t), doublet of triplet (dt), triplet of doublet (td), quartet (q), multiplet (m), doublet of doublet of doublet (ddd) were used to express the signal. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C), respectively. High resolution mass spectra (HRMS) were measured with a Thermo fisher Q-Exactive instrument, accurate masses are reported for the molecular ion ($[M]^+$ or $[M]^-$).

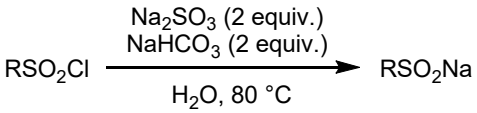
2. General procedure

2.1 Preparation of difluoroalkene substrates[1-3]



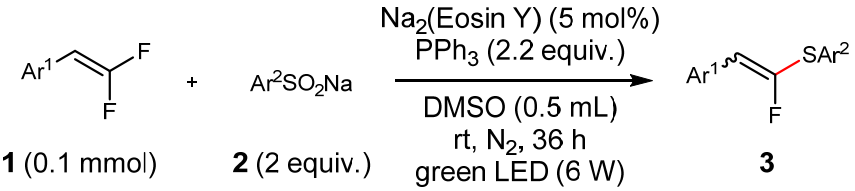
An oven-dried three necked round bottomed flask equipped with a PTFE-coated stir bar was charged with PPh_3 (6.56 g, 25 mmol, 2.5 equiv.), KI (3.32 g, 20 mmol, 2 equiv.) and aldehyde (10 mmol, 1 equiv.). Under the inert, nitrogen atmosphere, acetonitrile (20 mL) was added to the vessel, and the temperature was increased to 70 °C and let stir for 30 min. Then methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA) (3.36 g, 17.5 mmol,1.75 equiv.) was then added slowly over a period 0.5 h. The resulting mixture was stirred for three hours, a nitrogen atmosphere being maintained until the end of the reaction. Then the reaction was quenched with water (50 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by flash column chromatography to afford the difluoroalkenes.

2.2 Preparation of sodium sulfinate substrates[4]



A 25 mL round bottom flask equipped with a PTFE-coated stir bar was charged with Na_2SO_3 (2 equiv), $NaHCO_3$ (2 equiv) and deionized H_2O (10 mL). After stirring for 5 min, the sulfonyl chloride (10 mmol) was added portionwise to the flask. The mixture was heated to 80 °C in an oil bath for 12 h. After this time, the reaction mixture was cooled to rt, and the solvent was removed in vacuo by rotary evaporation, affording the crude sulfinate salt. The impurities were triturated with EtOH and removed by filtration. The solvent was removed from the filtrate in vacuo by rotary evaporation, washing the residue three times by EA to afford the pure sodium sulfinates.

2.3 General procedure for synthesis of α-fluoro-vinyl sulfides



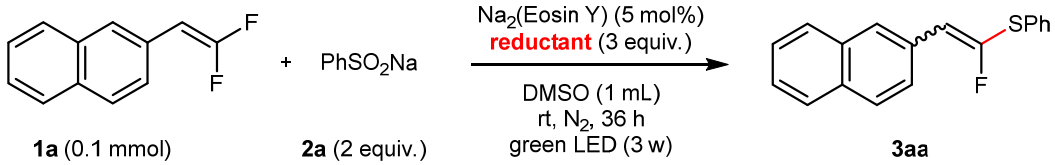
1 (0.1 mmol) **2** (2 equiv.) **3**

A solution of *gem*-difluoroalkene **1** (0.1 mmol), sodium benzenesulfinate **2** (0.2 mmol), PPh_3 (0.22 mmol) and photocatalyst (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether).

3. Optimization of the reaction conditions

3.1 Optimization of the reaction conditions for synthesis of α-fluoro-vinyl sulfides

Table S1: Reductant screening



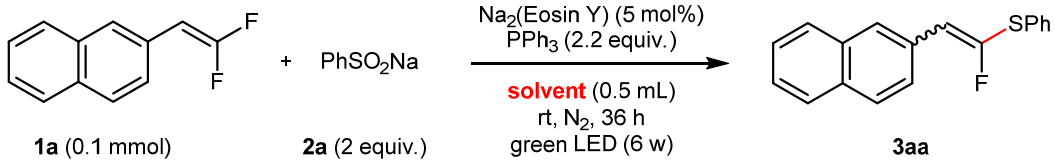
1a (0.1 mmol) **2a** (2 equiv.) **3aa**

Entry	reductant	**3aa** (%)[a, b]
1	Et_3SiH	25 (89:11)
2	$(EtO)_2MeSiH$	trace
3	HE	3 (75:25)
4	TBAI	25 (92:8)
5	$P(4\text{-}OMePh)_3$	88 (92:8)
6	dppp	84 (90:10)
7	$^nBu_3P$	53 (92.5:7.5)
8[c]	PPh_3	88 (92:8)

9[c, d]	PPh_3	93 (92:8)
10[c, d, e]	PPh_3	94 (92.5:7.5)

Reaction conditions: all reactions were performed with **1a** (0.10 mmol), **2a** (2 equiv), Na_2(Eosin Y) (5 mol%), reductant (3 equiv), and DMSO (1.0 mL) by 3 W green LED irradition for 36 h at rt. under N_2 unless otherwise noted. a) GC yield using adamantane as an internal standard. b) The *E:Z* ratio in parenthesis was determined by GC analysis of the crude mixture. c) 6 W green LED. d) 2.2 equiv. PPh_3. e) 0.5 mL DMSO.

Table S2: Solvent screening

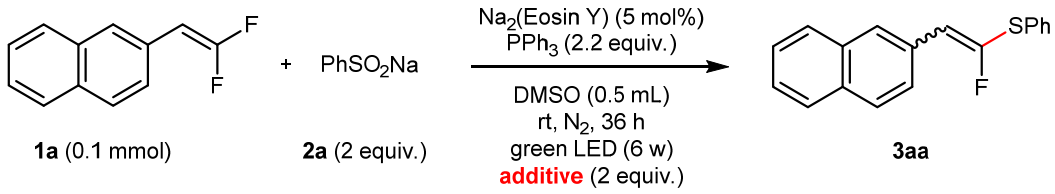


1a (0.1 mmol) **2a** (2 equiv.) **3aa**

Entry	solvent	**3aa** (%)[a, b]
1	DMF	26 (79:21)
2	DMA	20 (79:21)
3	NMP	40 (84:16)
4	DMPU	20 (65:35)
5	MeCN	trace
6	MeOH	trace
7	Acetone	trace
8	THF	N.D.
9	Dioxane	N.D.
10	EA	N.D.
11	DCE	trace
12	toluene	N.D.

Reaction conditions: all reactions were performed with **1a** (0.10 mmol), **2a** (2 equiv), Na_2(Eosin Y) (5 mol%), PPh_3 (2.2 equiv), and DMSO (0.5 mL) by 6 W green LED irradition for 36 h at rt. under N_2 unless otherwise noted. N.D.= not detected a) GC yield using adamantane as an internal standard. b) The *E:Z* ratio in parenthesis was determined by GC analysis of the crude mixture.

Table S3: Additive screening

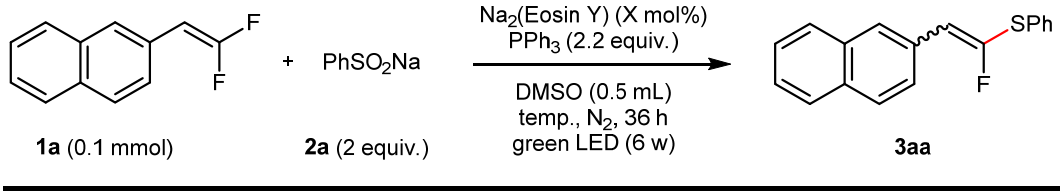


1a (0.1 mmol) **2a** (2 equiv.) **3aa**

Entry	additive	**3aa** (%)[a, b]
1	Li_2CO_3	81 (91:9)
2	Na_2CO_3	47 (89:11)
3	TBAB	30 (86:14)
4	KI	28 (92.5:7.5)
5	$TBAF•3H_2O$	77 (89:11)
6	NaF	85 (92:8)
7	$KF•2H_2O$	83 (91.5:8.5)
8	$MgCl_2$	81 (85:15)
9	$Ca(OH)_2$	82 (90:10)

Reaction conditions: all reactions were performed with **1a** (0.10 mmol), **2a** (2 equiv), Na_2(Eosin Y) (5 mol%), PPh_3 (2.2 equiv), additive (2.0 equiv) and DMSO (0.5 mL) by 6 W green LED irradition for 36 h at rt. under N_2 unless otherwise noted. a) GC yield using adamantane as an internal standard. b) The *E:Z* ratio in parenthesis was determined by GC analysis of the crude mixture.

Table S4: Temperature and amount of PC screening



1a (0.1 mmol) **2a** (2 equiv.) **3aa**

Entry	temp. (°C)	PC (x mol%)	**3aa** (%)[a, b]
1	8	5	78 (92.5:7.5)
2	rt.	5	93 (92.5:7.5)
3	50	5	84 (91.5:8.5)
4	rt.	2	78 (90.5:9.5)
5	rt.	10	80 (92:8)
6	rt.	20	83 (92.7:7.3)

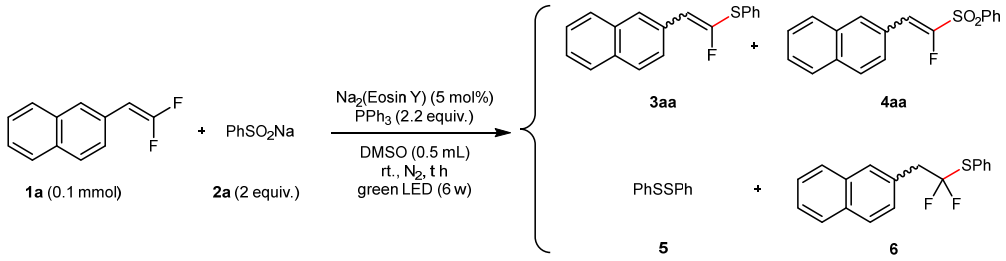
Reaction conditions: all reactions were performed with **1a** (0.10 mmol), **2a** (2 equiv),

Na_2(Eosin Y) (X mol%), PPh_3 (2.2 equiv), and DMSO (0.5 mL) by 6 W green LED irradition for 36 h at temp. under N_2 unless otherwise noted. a) GC yield using adamantane as an internal standard. b) The *E:Z* ratio in parenthesis was determined by GC analysis of the crude mixture.

4. Control experiments

4.1 Table S5: Monitoring the reaction over time.

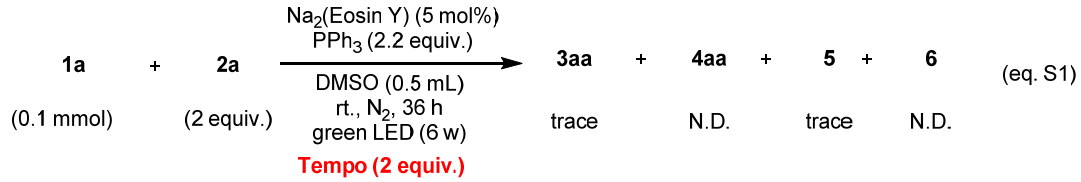
A solution of *gem*-difluoroalkene **1a** (0.1 mmol), sodium benzenesulfinate **2a** (0.2 mmol), PPh_3 (0.22 mmol), Na_2(Eosin Y) (5 mol%) and Ph-Ph (0.1 mmol) as an internal standard in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt.. The reaction was monitoring by GC and the result was listed the following table.



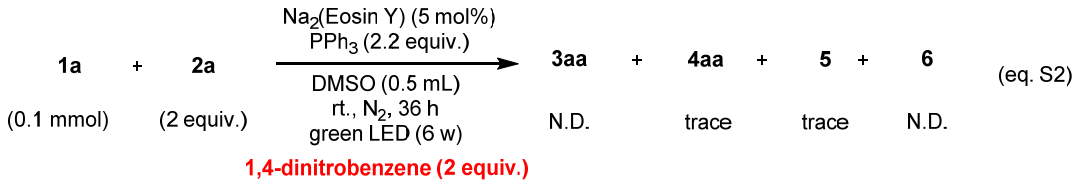
Entry	t (h)	**3aa** (%)	**E/Z (3aa)**	**4aa** (%)	**5** (%)	**6** (%)
1	2	20	66.4:33.6	3	trace	N.D.
2	5	43	75.2:24.8	5	trace	N.D.
3	8	56	83.4:16.6	5	trace	N.D.
4	10	66	86:14	5	trace	N.D.
5	12	84	88:12	3	trace	N.D.
6	16	87	90.1:9.9	1	trace	N.D.
7	21	90	91:9	trace	trace	N.D.
8	24	92	91.3:8.7	0	trace	N.D.
9	30	91	92:8	0	trace	N.D.

10	36	93	92.3:7.7	0	trace	N.D.
11	48	92	92.5:7.5	0	trace	N.D.

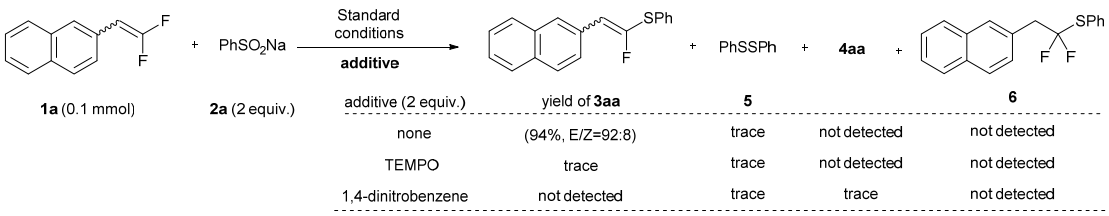
4.2 Radical inhibition experiments



A solution of *gem*-difluoroalkene **1a** (0.1 mmol), sodium benzenesulfinate **2a** (0.2 mmol), PPh_3 (0.22 mmol), Na_2(Eosin Y) (5 mol%) and tempo (0.2 mmol) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then, the resulting mixture was analyzed by GC.



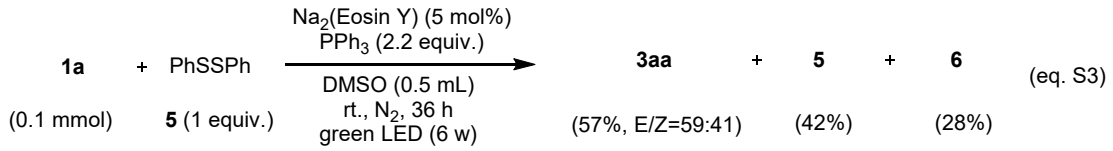
A solution of *gem*-difluoroalkene **1a** (0.1 mmol), sodium benzenesulfinate **2a** (0.2 mmol), PPh_3 (0.22 mmol), Na_2(Eosin Y) (5 mol%) and 1,4-dinitrobenzene (0.2 mmol) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then, the resulting mixture was analyzed by GC.



additive (2 equiv.)	yield of **3aa**	**5**		**6**
none	(94%, E/Z=92:8)	trace	not detected	not detected
TEMPO	trace	trace	not detected	not detected
1,4-dinitrobenzene	not detected	trace	trace	not detected

Conclusion: Those results demonstrate that the transformation may rely on an SET-involved radical process.

4.3 Experimental verification of intermediates



A solution of *gem*-difluoroalkene **1a** (0.1 mmol), 1,2-diphenyldisulfane **5** (0.1 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then, the resulting mixture was analyzed by GC.

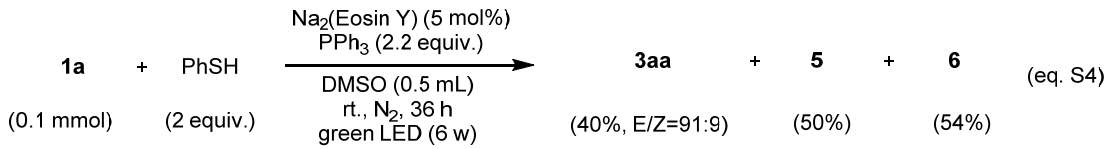
(1,1-difluoro-2-(naphthalen-2-yl)ethyl)(phenyl)sulfane (**6**)**.**

^{1}H NMR (600 MHz, CDCl3) δ 7.83 (t, *J* = 8.8 Hz, 3H), 7.75 (s, 1H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.48 (dt, *J* = 5.4, 3.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 3.59 (t, *J* = 14.7 Hz, 2H).

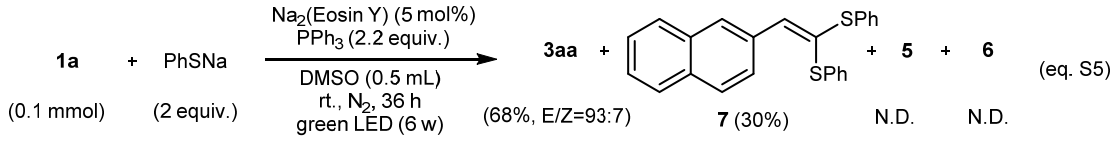
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.19, 133.29, 132.80, 130.71, 129.74, 129.54 (t, *J* = 3.1 Hz), 129.03, 128.85, 128.22, 128.09, 127.84, 127.70, 126.95, 126.22, 126.11, 45.34 (t, *J* = 24.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -71.20.

FTMS: (APCI) calcd for $C_{18}H_{13}F_2S^-$ [M-H^+] 299.07115; found 299.07097.



A solution of *gem*-difluoroalkene **1a** (0.1 mmol), PhSH (0.2 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then, the resulting mixture was analyzed by GC.



A solution of *gem*-difluoroalkene **1a** (0.1 mmol), PhSNa (0.2 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then 2 mL water was

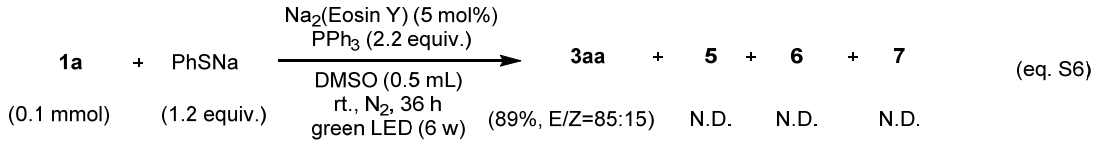
added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel, to obtain **3aa** and **7** in 68% and 30% yields, respectively.

(2-(naphthalen-2-yl)ethene-1,1-diyl)bis(phenylsulfane) (**7**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.84 – 7.74 (m, 4H), 7.47 – 7.42 (m, 2H), 7.37 – 7.27 (m, 8H), 7.26 – 7.25 (m, 1H), 7.24 – 7.21 (m, 2H).

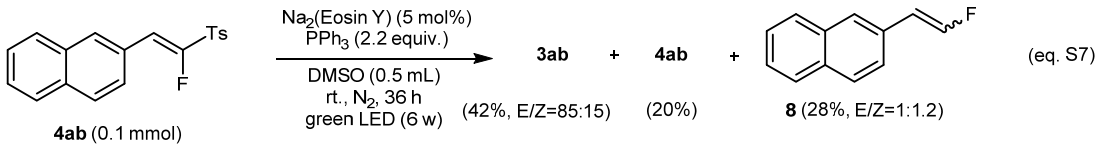
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.47, 133.90, 133.79, 133.42, 133.17, 132.87, 132.28, 131.72, 131.08, 129.03, 129.01, 128.73, 128.33, 127.86, 127.68, 127.58, 127.23, 126.73, 126.41, 126.25.

FTMS: (APCI) calcd for $C_{24}H_{17}S_2^-$ [M-H$^+$] 369.07772; found 369.07709.



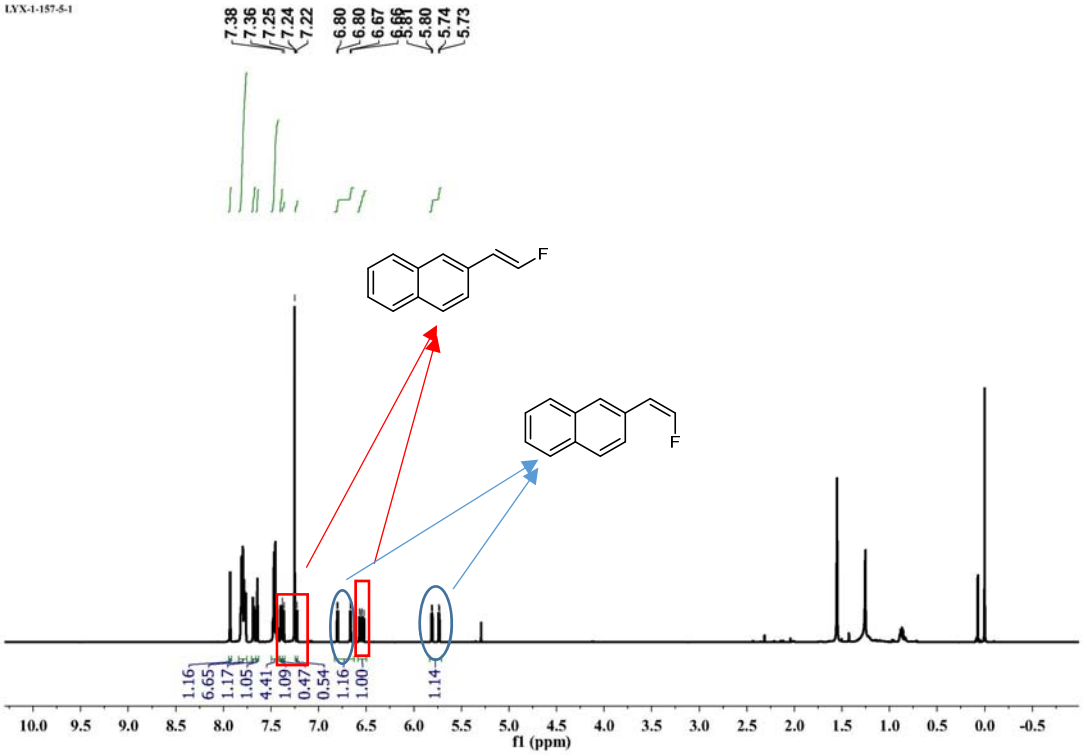
(eq. S6)

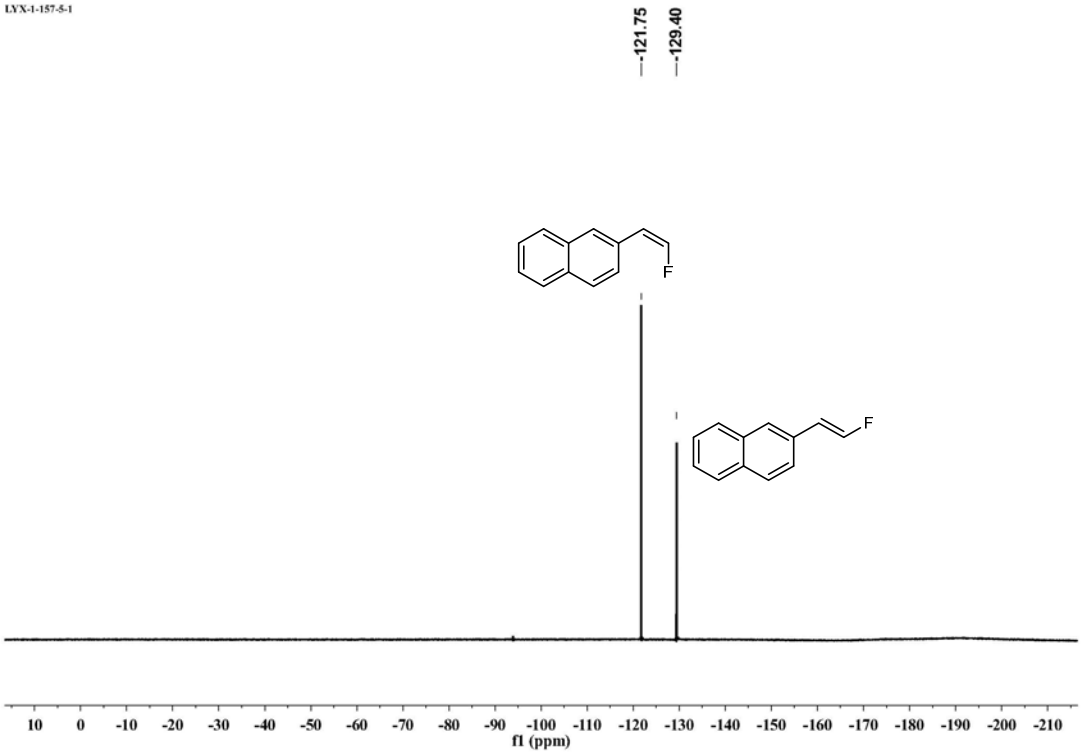
A solution of *gem*-difluoroalkene **1a** (0.1 mmol), PhSNa (0.12 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then, the resulting mixture was analyzed by GC.

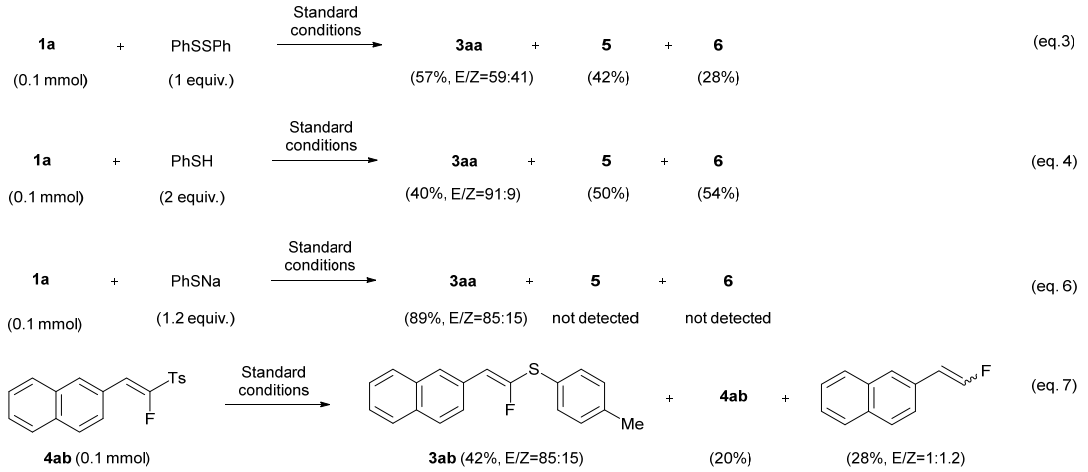


(eq. S7)

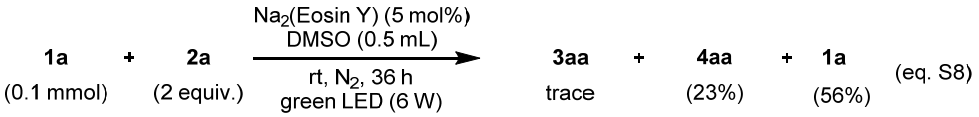
A solution of **4ab** (0.1 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel, to obtain **3ab** and **7**[5] in 42% and 28% yields, respectively. And **4ab** was recovered in 20% yield.


LYX-1-157-5-1
7.38
7.36
7.25
7.24
7.22
6.80
6.80
6.67
6.66
5.81
5.80
5.74
5.73
F
F
1.16
6.65
1.17
1.05
4.41
1.09
0.47
0.54
1.16
1.00
1.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


LYX-1-157-5-1
-121.75
-129.40
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



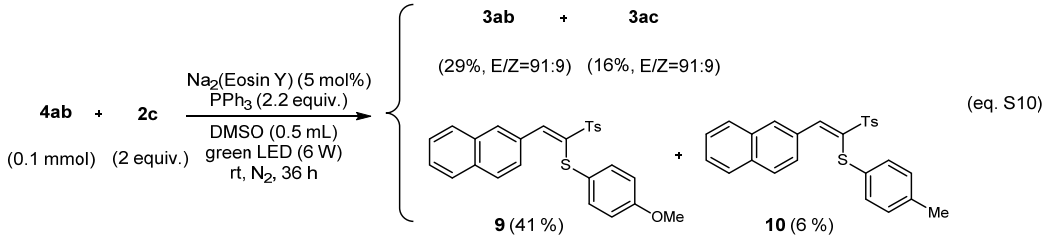
Conclusion: Those results imply that PhSNa and **4ab** may be the intermediate, while 1,2-diphenyldisulfane (PhSSPh) or benzenethiol (PhSH) as the intermediate seems to be ruled out because large amount of byproduct **6** is generated.



A solution of *gem*-difluoroalkene **1a** (0.1 mmol), **2a** (0.2 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then, the resulting mixture was analyzed by GC.

A solution of *gem*-difluoroalkene **1a** (0.1 mmol), **2a** (0.2 mmol), **4ab** (0.1 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 1 h. Then, the resulting mixture was analyzed by GC.

Conclusion: Those results indicate that **3ab** deriving from the reduction of **4ab** is minor.



A solution of **4ab** (0.1 mmol), **2c** (0.2 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel, to obtain **3ab**, **3ac**, **6c** and **9** in 29%, 16%, 6% and 41% yields, respectively.

(*E*)-(4-methoxyphenyl)(2-(naphthalen-2-yl)-1-tosylvinyl)sulfane (**9**)

^{1}H NMR (600 MHz, CDCl3) δ 8.59 (s, 1H), 8.33 (s, 1H), 8.17 (dd, J = 8.7, 1.6 Hz, 1H), 7.83 (d, J = 8.3 Hz, 3H), 7.79 (t, J = 7.7 Hz, 2H), 7.57 – 7.45 (m, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.64 – 6.54 (m, 2H), 3.66 (s, 3H), 2.38 (s, 3H).

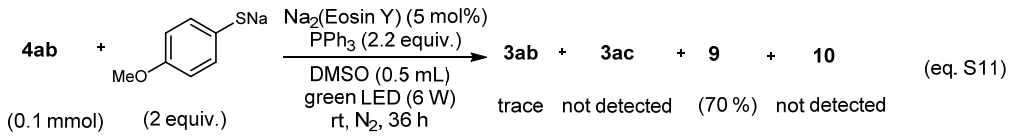
^{13}C NMR (151 MHz, CDCl3) δ 158.94, 146.41, 144.25, 135.79, 135.07, 134.39, 132.99, 132.79, 130.55, 130.00, 129.42, 129.01, 128.93, 128.24, 127.96, 127.61, 126.65, 126.45, 123.98, 114.58, 55.20, 21.55.

(*E*)-(2-(naphthalen-2-yl)-1-tosylvinyl)(p-tolyl)sulfane (**10**)

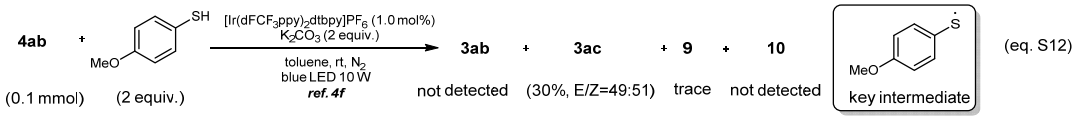
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.33 (s, 1H), 8.15 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.85 – 7.78 (m, 4H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.50 – 7.47 (m, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 2.36 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.21, 144.30, 136.58, 135.62, 134.47, 133.97, 133.16, 132.79, 130.00, 129.95, 129.71, 129.39, 129.08, 128.98, 128.28, 128.00, 127.91, 127.59, 126.64, 126.37, 21.55, 20.87.

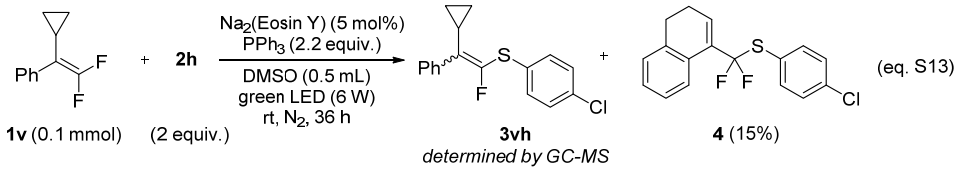
FTMS: (APCI) calcd for $C_{26}H_{21}O_2S_2^-$ [M-H$^+$] 429.09884; found 429.09798.



A solution of **4ab** (0.1 mmol), sodium 4-methoxybenzenethiolate (0.2 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel, to obtain **9** in 70% yield.



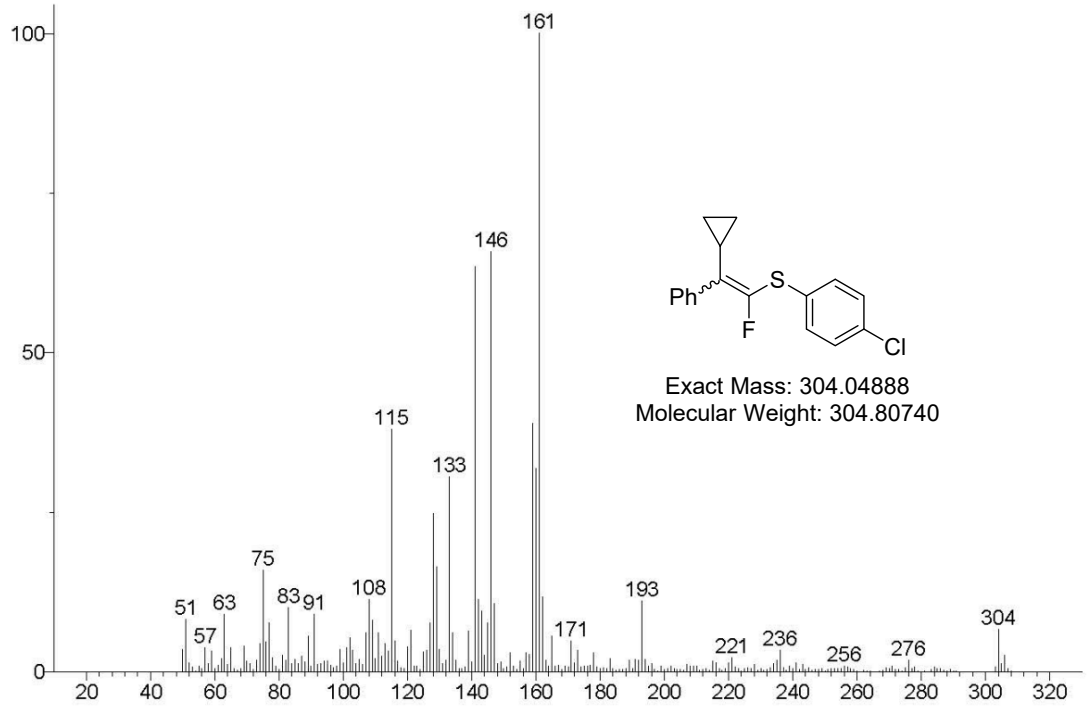
A solution of **4ab** (0.1 mmol), 4-methoxybenzenethiol (0.2 mmol), K_2CO_3 (0.2 mmol) and [Ir(dFCF3ppy)2dtbpy]PF_6 (1 mol%) in degassed toluene (1 mL) were stirred under nitrogen atmosphere and irradiated by 10 W blue LEDs at rt. for 36 h (*Chem. Commun.*, **2019**, 55, 11103. ***ref. 4f***). Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel, to obtain **3ac** in 30% yield.



A solution of *gem*-difluoroalkene **1v** (0.1 mmol), **2h** (0.2 mmol), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography

on silica gel, to obtain **4** in 15% yield.

MS spectra of **3vh**



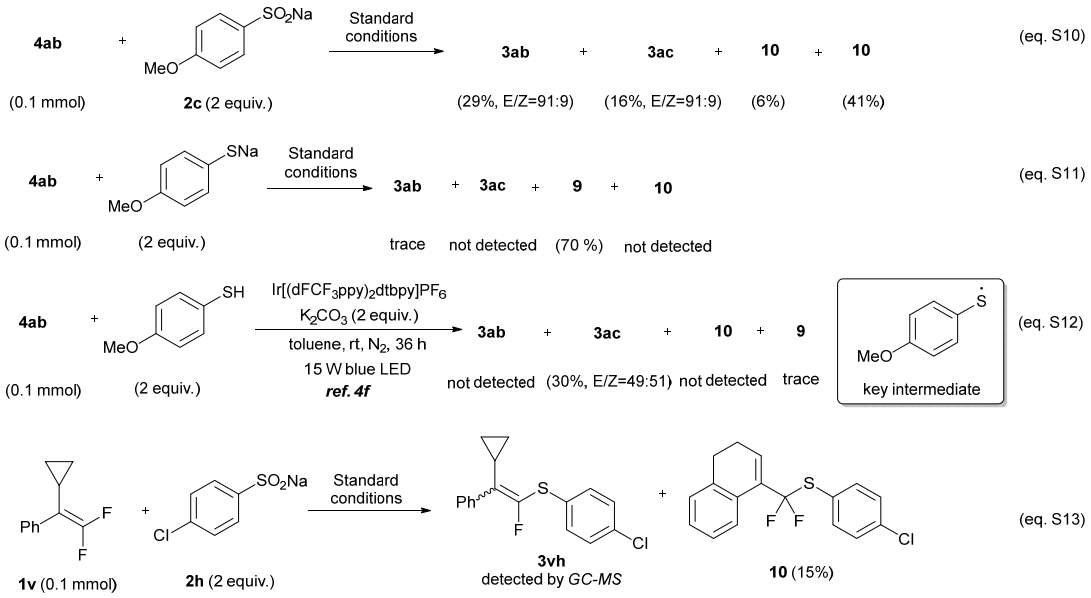
(4-chlorophenyl)((3,4-dihydronaphthalen-1-yl)difluoromethyl)sulfane (**4**)

^{1}H NMR (600 MHz, CDCl3) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 6.42 (t, *J* = 4.7 Hz, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.28 (tdt, *J* = 7.6, 5.0, 2.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.65, 136.42 (d, *J* = 9.9 Hz), 132.40 (t, *J* = 22.2 Hz), 131.76 (t, *J* = 7.9 Hz), 130.13, 129.53, 129.38, 129.15, 127.78, 127.77, 126.42, 126.16, 125.42 (t, *J* = 2.4 Hz), 27.53, 22.69.

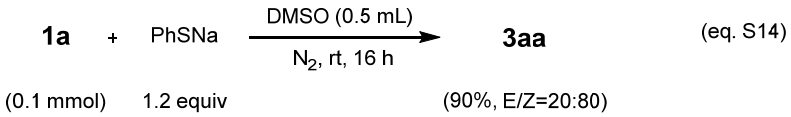
^{19}F NMR (565 MHz, $CDCl_3$) δ -70.94.

FTMS: (APCI) calcd for $C_{17}H_{12}F_2ClS^-$ [M-H$^+$] 321.03218; found 321.03187.

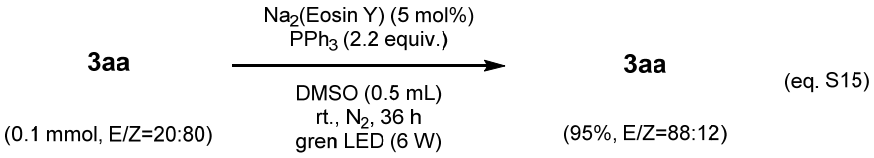


Conclusion: Those results suggest that thiol anion and thiol radical may be initiated from sodium sulfinate under standard conditions in the reaction system.

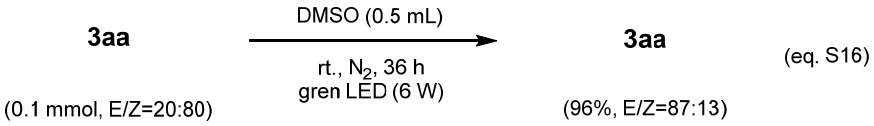
4.4 Visile-light-promoted regioselective *Z*→*E* isomerization



A solution of **1a** (0.1 mmol) and PhSNa (1.2 equiv.) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere at rt. for 16 h. Then 2 mL water was added to the reaction mixture and the aqueous solution was extracted with ethyl acetate (3 × 4 mL). The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel, to obtain **3aa** in 90% yield with 20:80 *E*/*Z* ratio.



A solution of **3aa** (0.1 mmol, E/Z=20:80), PPh_3 (0.22 mmol) and Na_2(Eosin Y) (5 mol%) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. After that time, the mixture was detected by GC. The regioselective *Z*→*E* isomerization of **3aa** occured and the E/Z ratio was 88:12.

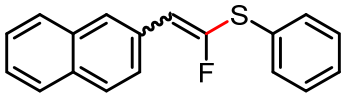


A solution of **3aa** (0.1 mmol, E/Z=20:80) in degassed DMSO (0.5 mL) were stirred under nitrogen atmosphere and irradiated by 6 W green LEDs at rt. for 36 h. After that time, the mixture was detected by GC. The regioselective *Z*→*E* isomerization of **3aa** also occured and the E/Z ratio was 87:13.

Conclusion: Those results intimate that the regioselective *Z*→*E* isomerization of α-fluoro-vinyl sulfides could be promoted by visible light in the absence of photosensitizer Na_2(Eosin Y).

5. Characterization data of products

(1-fluoro-2-(naphthalen-2-yl)vinyl)(phenyl)sulfane (**3aa**)



Chemical Formula: $C_{18}H_{13}FS$
Exact Mass: 280.07220

Isolated yield: 26.5 mg, 94 % yield. The ratio of E/Z is **92.5:7.5** by ^{19}F NMR .

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.82 – 7.78 (m, 3H), 7.68 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.35 (ddd, *J* = 7.0, 6.3, 2.7 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.45 (d, *J* = 32.5 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.60 (d, *J* = 310.2 Hz), 133.36, 132.90, 132.19, 130.50 (d, *J* = 5.4 Hz), 129.98, 129.39, 128.40 (d, *J* = 7.8 Hz), 128.27 (d, *J* = 5.4 Hz), 127.72, 127.63, 126.52, 126.40, 126.36, 126.30, 117.90 (d, *J* = 13.1 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.60 (s, 1F), -85.29 (s, 12.8F).

FTMS: (APCI) calcd for $C_{18}H_{12}FS^-$ [M-H^+] 279.06492; found 279.06415.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(*p*-tolyl)sulfane (**3ab**)

Chemical Formula: $C_{19}H_{15}FS$
Exact Mass: 294.08785

Isolated yield: 23.9 mg, 81 % yield. The ratio of E/Z is **92:8** by ^{19}F NMR .

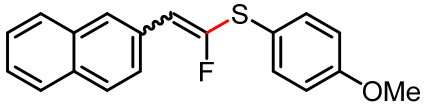
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.81 – 7.76 (m, 3H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 32.7 Hz, 1H), 2.34 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.36 (d, *J* = 310.4 Hz), 138.16, 133.84, 133.71, 133.37, 132.82, 130.82, 130.63 (d, *J* = 5.6 Hz), 130.16, 128.53 (d, *J* = 6.7 Hz), 128.25, 128.20, 127.61, 126.42, 126.36, 126.30, 116.73 (d, *J* = 12.6 Hz), 21.17.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.78 (s, 1F), -85.43 (s, 11F).

FTMS: (APCI) calcd for $C_{19}H_{14}FS^-$ [M-H^+] 293.08057; found 293.08011.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(4-methoxyphenyl)sulfane (**3ac**)



Chemical Formula: $C_{19}H_{15}FOS$
Exact Mass: 310.08276

Isolated yield: 18.0 mg, 58 % yield. The ratio of E/Z is **76:24** by ^{19}F NMR .

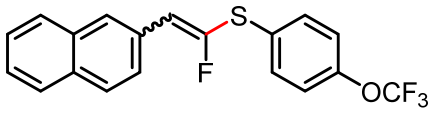
Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 0.33H), 7.91 (s, 1H), 7.82 (dd, *J* = 10.8, 5.4 Hz, 1H), 7.80 – 7.76 (m, 3.2H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.50 (t, *J* = 5.8 Hz, 2H), 7.46 (ddt, *J* = 9.5, 8.6, 5.0 Hz, 3.26H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 0.66H), 6.76 (d, *J* = 16.6 Hz, 0.34H), 6.31 (d, *J* = 33.0 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.11, 154.21 (d, *J* = 309.9 Hz), 133.74, 133.37, 132.73, 130.70 (d, *J* = 5.6 Hz), 128.30 (d, *J* = 4.2 Hz), 128.20, 128.15, 128.07, 127.59, 126.32, 126.27, 121.69, 115.19 (d, *J* = 12.6 Hz), 114.99, 55.42.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.47 (s, 1F), -85.90 (s, 3.2F).

FTMS: (APCI) calcd for $C_{19}H_{14}FOS^-$ [M-H^+] 309.07549; found 309.07483.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(4-(trifluoromethoxy)phenyl)sulfane (**3ad**)



Chemical Formula: $C_{19}H_{12}F_4OS$
Exact Mass: 364.05450

Isolated yield: 23.8 mg, 65 % yield. The ratio of E/Z is **91:9** by ^{19}F NMR .

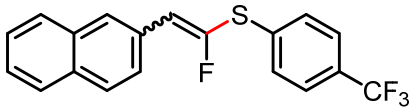
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.83 – 7.78 (m, 3H), 7.67 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.50 – 7.45 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.46 (d, *J* = 32.4 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.79 (d, *J* = 310.6 Hz), 148.80 (d, *J* = 1.7 Hz), 133.30, 132.98 (d, *J* = 1.5 Hz), 131.37, 130.86, 130.84, 130.19 (d, *J* = 6.0 Hz), 128.56 (d, *J* = 7.9 Hz), 128.31, 128.29, 127.63, 126.65, 126.46, 126.23 (d, *J* = 8.3 Hz), 120.41 (q, *J* = 257.6 Hz), 118.51 (d, *J* = 12.4 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -57.91, -80.50 (s, 1F), -85.88 (s, 10.23F).

FTMS: (APCI) calcd for $C_{19}H_{11}F_4OS^-$ [M-H^+] 363.04722; found 363.04648.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(4-(trifluoromethyl)phenyl)sulfane (**3ae**)



Chemical Formula: $C_{19}H_{12}F_4S$
Exact Mass: 348.05958

Isolated yield: 17.5 mg, 50 % yield. The ratio of E/Z is **92:8** by ^{19}F NMR .

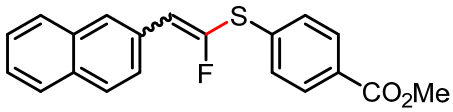
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.83 (dd, *J* = 9.0, 6.7 Hz, 3H), 7.71 – 7.68 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.51 – 7.48 (m, 2H), 6.54 (d, *J* = 32.2 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.55 (d, *J* = 310.4 Hz), 137.85, 133.27, 133.08, 129.99 (d, *J* = 5.7 Hz), 129.34 (q, *J* = 32.9 Hz), 128.81, 128.76, 128.53, 128.39, 128.34, 127.64, 126.79, 126.52, 126.24, 126.17 (q, *J* = 3.3 Hz), 120.16 (d, *J* = 12.1 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.61 (s, 32F), -62.65 (s, 2.92F), -80.48 (s, 1F), -86.08 (s, 11.24F).

FTMS: (APCI) calcd for $C_{19}H_{11}F_4S^-$ [M-H^+] 347.05231; found 347.05154.

methyl 4-((1-fluoro-2-(naphthalen-2-yl)vinyl)thio)benzoate **(3af)**



Chemical Formula: $C_{20}H_{15}FO_2S$
Exact Mass: 338.07768

Isolated yield: 25.6 mg, 76 % yield. The ratio of E/Z is **89:11** by ^{19}F NMR .

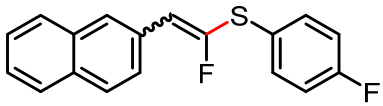
Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (t, *J* = 7.4 Hz, 3H), 7.82 (t, *J* = 8.1 Hz, 3H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.48 (dd, *J* = 8.9, 4.4 Hz, 4H), 6.53 (d, *J* = 32.2 Hz, 1H), 3.90 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.51, 150.58 (d, *J* = 310.4 Hz), 139.27 (d, *J* = 4.2 Hz), 133.29, 133.09, 130.43, 130.08 (d, *J* = 5.7 Hz), 128.81, 128.75 (d, *J* = 1.6 Hz), 128.38, 128.36, 127.78, 127.66, 126.77, 126.52, 126.26 (d, *J* = 8.5 Hz), 20.25 (d, *J* = 12.3 Hz), 52.23.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.14 (s, 1F), -85.91 (s, 8F).

FTMS: (APCI) calcd for $C_{20}H_{14}FO_2S^-$ [M-H^+] 337.07040; found 337.07003.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(4-fluorophenyl)sulfane (**3ag**)



Chemical Formula: $C_{18}H_{12}F_2S$
Exact Mass: 298.06278

Isolated yield: 24.5 mg, 82 % yield. The ratio of E/Z is **93:7** by ^{19}F NMR .

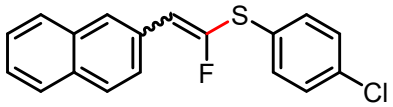
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.80 (dd, *J* = 9.2, 3.5 Hz, 3H), 7.65 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.44 (m, 2H), 7.09 – 7.04 (m, 2H), 6.40 (d, *J* = 32.6 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.76 (d, *J* = 248.4 Hz), 152.83 (d, *J* = 310.8 Hz), 133.33, 132.98, 132.93, 132.88 (d, *J* = 1.6 Hz), 130.38 (d, *J* = 5.7 Hz), 128.36 (d, *J* = 7.9 Hz), 128.26, 127.62, 126.82 (t, *J* = 3.1 Hz), 126.54, 126.42, 126.25 (d, *J* = 8.1 Hz), 117.08 (d, *J* = 12.4 Hz), 116.54 (d, *J* = 22.6 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.56 (s, 1F), -85.89 (s, 13.4F), -113.07 (s, 0.97F), -113.20 (s, 12F).

FTMS: (APCI) calcd for $C_{18}H_{11}F_2S^-$ [M-H$^+$] 297.05550; found 297.05487.

(4-chlorophenyl)(1-fluoro-2-(naphthalen-2-yl)vinyl)sulfane (**3ah**)



Chemical Formula: $C_{18}H_{12}ClFS$
Exact Mass: 314.03323

Isolated yield: 27.5 mg, 87 % yield. The ratio of E/Z is **92:8** by ^{19}F NMR .

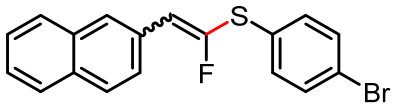
E isomers: ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.81 (t, *J* = 5.7 Hz, 3H), 7.66 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.47 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.29 (m, 2H), 6.44 (d, *J* = 32.4 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.96 (d, *J* = 310.6 Hz), 133.95, 133.31, 132.96, 131.29, 130.64 (d, *J* = 3.3 Hz), 130.26 (d, *J* = 6.0 Hz), 129.54, 128.52 (d, *J* = 8.3 Hz), 128.31, 128.09 (d, *J* = 7.8 Hz), 127.63, 126.63, 126.46, 126.25 (d, *J* = 8.1 Hz), 118.28 (d, *J* = 12.8 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.39 (s, 1F), -85.88 (s, 12F).

FTMS: (APCI) calcd for $C_{18}H_{11}ClFS^-$ [M-H$^+$] 313.02595; found 313.02539.

(4-bromophenyl)(1-fluoro-2-(naphthalen-2-yl)vinyl)sulfane **(3ai)**



Chemical Formula: $C_{18}H_{12}BrFS$
Exact Mass: 357.98271

Isolated yield: 27.3 mg, 76 % yield. The ratio of E/Z is **93:7** by ^{19}F NMR .

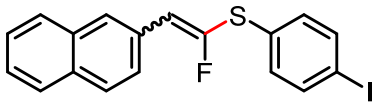
Both isomers: ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.82 – 7.78 (m, 3H), 7.66 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.38 – 7.32 (m, 2H), 6.44 (d, *J* = 32.4 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.71 (d, *J* = 310.4 Hz), 133.26, 132.92 (d, *J* = 1.5 Hz), 132.41, 131.35, 130.18 (d, *J* = 6.2 Hz), 128.50 (d, *J* = 7.8 Hz), 128.27, 128.26, 128.04 (d, *J* = 7.3 Hz), 127.59, 126.59, 126.42, 126.20 (d, *J* = 8.4 Hz), 121.83, 118.43 (d, *J* = 12.2 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.35 (s, 1F), -85.87 (s, 13F).

FTMS: (APCI) calcd for $C_{18}H_{11}FBrS^-$ [M-H$^+$] 356.97544; found 35697532.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(4-iodophenyl)sulfane (**3aj**)



Chemical Formula: $C_{18}H_{12}FIS$
Exact Mass: 405.96884

Isolated yield: 20.3 mg, 50 % yield. The ratio of E/Z is **92.5:7.5** by ^{19}F NMR .

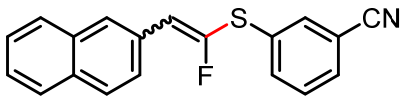
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 3H), 7.69 – 7.64 (m, 3H), 7.51 – 7.45 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 32.4 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.61 (d, *J* = 310.5 Hz), 138.37, 133.30, 132.98 (d, *J* = 1.5 Hz), 132.37 (d, *J* = 3.7 Hz), 131.39, 130.22 (d, *J* = 5.9 Hz), 128.56 (d, *J* = 7.8 Hz), 128.32, 128.31, 127.64, 126.65, 126.47, 126.25 (d, *J* = 8.4 Hz), 118.68 (d, *J* = 12.5 Hz), 93.02.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.30 (s, 1F), -85.85 (s, 12.36F).

FTMS: (APCI) calcd for $C_{18}H_{11}FIS^-$ [M-H$^+$] 404.96157; found 404.96100.

3-((1-fluoro-2-(naphthalen-2-yl)vinyl)thio)benzonitrile (**3ak**)



Chemical Formula: $C_{19}H_{12}FNS$
Exact Mass: 305.06745

Isolated yield: 23.5 mg, 66 % yield. The ratio of E/Z is **84:16** by ^{19}F NMR .

Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.90 (s, 0.2H), 7.86 – 7.79 (m, 3.67H), 7.74 (s, 1H), 7.72 – 7.67 (m, 2.41H), 7.64 (d, *J* = 8.0 Hz, 0.22H), 7.55 (ddd, *J* = 9.2, 5.2, 1.1 Hz, 1.17H), 7.52 – 7.47 (m, 2.44H), 7.47 – 7.41 (m, 1.32H), 7.04 (d, *J* = 16.0 Hz, 0.19H), 6.53 (d, *J* = 32.3 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.20 (d, *J* = 310.6 Hz), 134.89 (d, *J* = 3.6 Hz), 133.21, 133.18, 133.09 (d, *J* = 1.6 Hz), 132.12, 130.82, 129.94, 129.79 (d, *J* = 6.1 Hz), 128.85 (d, *J* = 8.3 Hz), 128.39, 128.32, 127.62, 126.81, 126.51, 126.14 (d, *J* = 8.4

Hz), 120.15 (d, *J* = 12.3 Hz), 117.94, 113.65.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.15 (s, 1F), -86.41 (s, 5.22F).

FTMS: (APCI) calcd for $C_{19}H_{11}FNS^-$ [M-H$^+$] 304.06017; found 304.05945.

(3-bromophenyl)(1-fluoro-2-(naphthalen-2-yl)vinyl)sulfane (**3al**)

Chemical Formula: $C_{18}H_{12}BrFS$
Exact Mass: 357.98271

Isolated yield: 25.5 mg, 71 % yield. The ratio of E/Z is **93:7** by ^{19}F NMR .

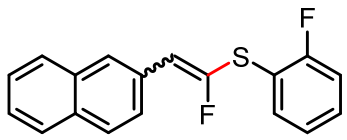
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.84 – 7.78 (m, 3H), 7.68 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.62 (s, 1H), 7.48 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.48 (d, *J* = 32.3 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.37 (d, *J* = 310.6 Hz), 134.61 (d, *J* = 3.4 Hz), 133.30, 133.02, 132.02, 130.68, 130.64, 130.18 (d, *J* = 5.9 Hz), 128.67 (d, *J* = 8.3 Hz), 128.34, 128.11 (d, *J* = 7.7 Hz), 128.03, 127.65, 126.69, 126.48, 126.28 (d, *J* = 8.4 Hz), 123.16, 119.14 (d, *J* = 12.3 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.19 (s, 1F), -85.66 (s, 13.7F).

FTMS: (APCI) calcd for $C_{18}H_{11}FBrS^-$ [M-H$^+$] 356.97544; found 356.97476.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(2-fluorophenyl)sulfane (**3am**)



Chemical Formula: $C_{18}H_{12}F_2S$
Exact Mass: 298.06278

Isolated yield: 23.5 mg, 78 % yield. The ratio of E/Z is **91:9** by ^{19}F NMR .

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.80 (dd, *J* = 8.6, 4.3 Hz, 3H), 7.66 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.34 – 7.26 (m, 1H), 7.18 – 7.09 (m, 2H), 6.47 (d, *J* = 32.5 Hz, 1H).

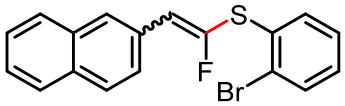
E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.77 (d, *J* = 247.5 Hz), 150.96 (d, *J* = 310.5 Hz), 133.27, 132.89, 132.41, 130.30 (d, *J* = 5.8 Hz), 129.91 (d, *J* = 8.0 Hz),

128.41 (d, J = 8.3 Hz), 128.25, 128.22, 127.58, 126.53, 126.38, 126.22 (d, J = 7.8 Hz), 124.84, 124.81, 118.16 (d, J = 12.0 Hz), 116.13 (d, J = 21.8 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.06 (s, 1F), -85.92 (s, 10.5F), -109.16 (s, 0.92F), -109.73 (s, 9.82F).

FTMS: (APCI) calcd for $C_{18}H_{11}F_2S^-$ [M-H$^+$] 297.05550; found 297.05484.

(2-bromophenyl)(1-fluoro-2-(naphthalen-2-yl)vinyl)sulfane (**3an**)



Chemical Formula: $C_{18}H_{12}BrFS$
Exact Mass: 357.98271

Isolated yield: 22.6 mg, 63 % yield. The ratio of E/Z is **90:10** by ^{19}F NMR .

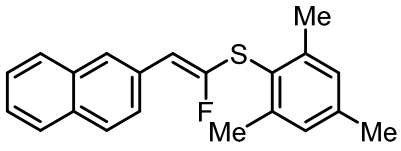
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.82 (t, J = 7.7 Hz, 3H), 7.71 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.49 (dd, J = 12.0, 7.5 Hz, 3H), 7.29 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.56 (d, J = 32.4 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.71 (d, J = 309.9 Hz), 134.66 (d, J = 4.2 Hz), 133.30, 133.09, 130.19 (d, J = 5.9 Hz), 129.23, 128.80, 128.74, 128.37, 128.18, 128.15, 127.66, 126.75, 126.51, 126.33, 126.27, 122.38, 120.67 (d, J = 11.9 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.47 (s, 1F), -86.45 (s, 9F).

FTMS: (APCI) calcd for $C_{18}H_{11}FBrS^-$ [M-H$^+$] 356.97544; found 356.97482.

(*E*)-(1-fluoro-2-(naphthalen-2-yl)vinyl)(mesityl)sulfane (***E*-(3ao)**)



Chemical Formula: $C_{21}H_{19}FS$
Exact Mass: 322.11915

Isolated yield: 15.7 mg, 49 % yield.

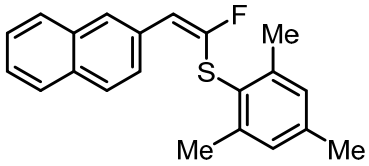
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.78 – 7.71 (m, 3H), 7.56 (dd, J = 8.6, 1.3 Hz, 1H), 7.48 – 7.38 (m, 2H), 6.99 (s, 2H), 5.97 (d, J = 34.8 Hz, 1H), 2.56 (s, 6H), 2.30 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.71 (d, *J* = 306.3 Hz), 143.53, 139.83, 133.39, 132.38, 131.01 (d, *J* = 4.6 Hz), 129.45, 128.00, 127.99, 127.50, 127.22 (d, *J* = 7.8 Hz), 126.18, 126.12, 125.97, 124.36, 110.93 (d, *J* = 10.9 Hz), 21.79, 21.08.

^{19}F NMR (565 MHz, $CDCl_3$) δ -87.87.

FTMS: (APCI) calcd for $C_{21}H_{18}FS^-$ [M-H^+] 321.11187; found 321.11112.

(*Z*)-(1-fluoro-2-(naphthalen-2-yl)vinyl)(mesityl)sulfane (***Z*-(3ao)**)



Chemical Formula: $C_{21}H_{19}FS$
Exact Mass: 322.11915

Isolated yield: 5.6 mg, 17 % yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.88 – 7.81 (m, 3H), 7.73 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 6.94 (s, 2H), 6.65 (d, *J* = 18.2 Hz, 1H), 2.42 (s, 6H), 2.28 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.92 (d, *J* = 296.1 Hz), 143.35, 139.59, 133.31, 132.44, 130.43 (d, *J* = 9.9 Hz), 129.24, 128.02, 127.81, 127.77, 127.61, 126.54 (d, *J* = 2.0 Hz), 126.26, 126.03, 123.65, 112.82 (d, *J* = 30.6 Hz), 21.96, 21.05.

^{19}F NMR (565 MHz, $CDCl_3$) δ -83.75.

FTMS: (APCI) calcd for $C_{21}H_{18}FS^-$ [M-H^+] 321.11187; found 321.11121.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(naphthalen-2-yl)sulfane (**3ap**)

Chemical Formula: $C_{22}H_{15}FS$
Exact Mass: 330.08785

Isolated yield: 28.5 mg, 86 % yield. The ratio of E/Z is **89:11** by ^{19}F NMR .

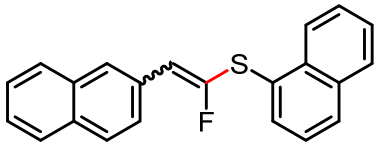
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.82 – 7.79 (m, 5H), 7.79 – 7.77 (m, 1H), 7.69 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.49 – 7.45 (m, 4H), 6.49 (d, *J* = 32.5 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.65 (d, *J* = 310.4 Hz), 133.78, 133.37, 132.92, 132.59, 130.52 (d, *J* = 5.5 Hz), 129.39 (d, *J* = 2.9 Hz), 129.12, 129.09, 128.45 (d, *J* = 7.8 Hz), 128.31, 128.28, 127.84, 127.64, 127.56, 127.21, 126.84, 126.55, 126.53, 126.43, 126.35 (d, *J* = 8.4 Hz), 117.93 (d, *J* = 12.2 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.51 (s, 1F), -85.28 (s, 8.35F).

FTMS: (APCI) calcd for $C_{22}H_{14}FS^-$ [M-H^+] 329.08057; found 329.08044.

(1-fluoro-2-(naphthalen-2-yl)vinyl)(naphthalen-1-yl)sulfane **(3aq)**



Chemical Formula: $C_{22}H_{15}FS$
Exact Mass: 330.08785

Isolated yield: 24.1 mg, 73 % yield. The ratio of E/Z is **76:24** by ^{19}F NMR .

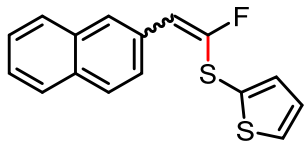
Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1H), 8.26 – 8.19 (m, 0.3H), 7.99 (s, 0.3H), 7.91 (s, 1.12H), 7.88 – 7.73 (m, 8.46H), 7.63 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.60 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.53 (dd, *J* = 9.4, 5.6 Hz, 1.09H), 7.50 – 7.40 (m, 4.61H), 6.88 (d, *J* = 16.6 Hz, 0.31H), 6.43 (d, *J* = 33.0 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.96 (d, *J* = 310.2 Hz), 134.18, 133.29, 133.03, 132.73, 130.88, 130.55 (d, *J* = 6.0 Hz), 129.29, 128.61, 128.40 (d, *J* = 1.8 Hz), 128.31 (d, *J* = 3.6 Hz), 128.18, 128.13, 128.07, 127.54, 126.96, 126.48, 126.35, 126.30, 125.74, 124.89, 116.51 (d, *J* = 12.0 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.60 (s, 1F), -85.64 (s, 3.2F).

FTMS: (APCI) calcd for $C_{22}H_{14}FS^-$ [M-H^+] 329.08057; found 329.08050.

2-((1-fluoro-2-(naphthalen-2-yl)vinyl)thio)thiophene **(3ar)**



Chemical Formula: $C_{16}H_{11}FS_2$
Exact Mass: 286.02862

Isolated yield: 16.6 mg, 58 % yield. The ratio of E/Z is **41:59** by ^{19}F NMR .

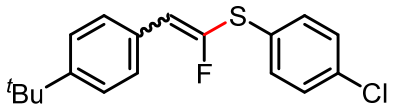
Z isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.84 (dd, *J* = 10.9, 5.8 Hz, 3H), 7.73 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.49 (p, *J* = 6.6 Hz, 2H), 7.45 (d, *J* = 5.3 Hz, 1H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.03 (dd, *J* = 5.3, 3.7 Hz, 1H), 6.70 (d, *J* = 16.2 Hz, 1H).

Z isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.26 (d, *J* = 298.7 Hz), 135.50, 133.23, 132.75, 131.05, 129.80 (d, *J* = 8.7 Hz), 128.44, 128.42, 128.07, 128.00, 127.71, 127.66, 126.67, 126.39, 126.36, 115.49 (d, *J* = 30.5 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -82.10 (s, 1.44F), -86.99 (s, 1F).

FTMS: (APCI) calcd for $C_{16}H_{10}FS_2^-$ [M-H$^+$] 285.02134; found 285.02060.

(2-(4-(tert-butyl)phenyl)-1-fluorovinyl)(4-chlorophenyl)sulfane (**3bh**)



Chemical Formula: $C_{18}H_{18}ClFS$
Exact Mass: 320.08018

Isolated yield: 26.6 mg, 83 % yield. The ratio of E/Z is **93.5:6.5** by ^{19}F NMR .

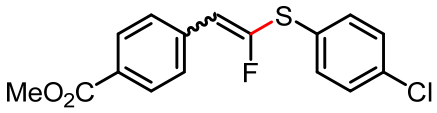
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 4H), 7.31 – 7.28 (m, 2H), 6.29 (d, *J* = 32.6 Hz, 1H), 1.32 (s, 9H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.67 (d, *J* = 2.0 Hz), 150.92 (d, *J* = 309.0 Hz), 133.63, 131.04 (d, *J* = 3.9 Hz), 130.79, 129.91 (d, *J* = 5.6 Hz), 129.42, 128.71 (d, *J* = 7.8 Hz), 125.62, 118.58 (d, *J* = 12.9 Hz), 34.71, 31.19.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.74 (s, 1F), -86.94 (s, 14.54F).

FTMS: (APCI) calcd for $C_{18}H_{17}FClS^-$ [M-H$^+$] 319.07290; found 319.07230.

methyl 4-(2-((4-chlorophenyl)thio)-2-fluorovinyl)benzoate (**3ch**)



Chemical Formula: $C_{16}H_{12}ClFO_2S$
Exact Mass: 322.02306

Isolated yield: 21.9 mg, 68 % yield. The ratio of E/Z is **94:6** by ^{19}F NMR .

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.31 (m, 2H), 6.28 (d, *J* = 32.3 Hz, 1H), 3.91 (s,

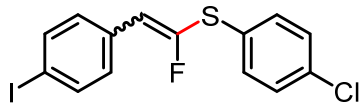
3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.62, 154.03 (d, *J* = 313.1 Hz), 137.08 (d, *J* = 5.6 Hz), 134.47, 132.04, 129.91, 129.62, 129.41 (d, *J* = 2.1 Hz), 128.67, 128.61, 116.08 (d, *J* = 12.0 Hz), 52.19.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -77.69 (s, 1F), -82.90 (s, 16.3F).

FTMS: (APCI) calcd for $C_{16}H_{11}FClO_2S^-$ [M-H$^+$] 321.01578; found 321.01529.

(4-chlorophenyl)(1-fluoro-2-(4-iodophenyl)vinyl)sulfane (**3dh**)



Chemical Formula: $C_{14}H_9ClFIS$
Exact Mass: 389.91422

Isolated yield: 16.8 mg, 43 % yield. The ratio of E/Z is **93:7** by ^{19}F NMR .

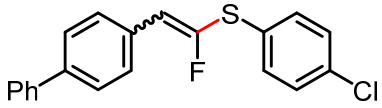
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.19 (d, *J* = 32.1 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.70 (d, *J* = 311.5 Hz), 137.81, 134.18, 132.13 (d, *J* = 5.7 Hz), 131.58, 130.44, 130.39, 129.55, 116.65 (d, *J* = 12.2 Hz), 93.94 (d, *J* = 3.2 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.39 (s, 1F), -84.55 (s, 13.56F).

FTMS: (APCI) calcd for $C_{14}H_8FClIS^-$ [M-H$^+$] 388.90694; found 388.90729.

(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)(4-chlorophenyl)sulfane (**3eh**)



Chemical Formula: $C_{20}H_{14}ClFS$
Exact Mass: 340.04888

Isolated yield: 28.3 mg, 83 % yield. The ratio of E/Z is **92.5:7.5** by ^{19}F NMR .

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (t, *J* = 1.6 Hz, 1H), 7.60 – 7.58 (m, 5H), 7.46 – 7.42 (m, 2H), 7.42 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.33 – 7.30 (m, 2H), 6.33 (d, *J* = 32.5 Hz, 1H).

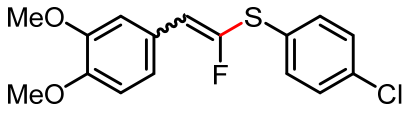
E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.79 (d, *J* = 310.5 Hz), 141.04, 141.03,

140.37, 133.91, 131.74 (d, J = 5.6 Hz), 131.19, 130.69 (d, J = 3.3 Hz), 129.53, 129.36 (d, J = 7.9 Hz), 128.89, 127.63, 127.32, 127.03, 117.93 (d, J = 12.9 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.46 (s, 1F), -85.76 (s, 12.56F).

FTMS: (APCI) calcd for $C_{20}H_{13}FClS^-$ [M-H^+] 339.04160; found 339.04095.

(4-chlorophenyl)(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)sulfane (**3fh**)



Chemical Formula: $C_{16}H_{14}ClFO_2S$
Exact Mass: 324.03871

Isolated yield: 16.8 mg, 50 % yield. The ratio of E/Z is **87.5:12.5** by ^{19}F NMR .

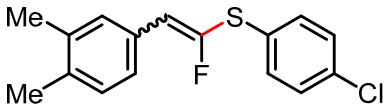
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.15 (d, J = 1.6 Hz, 1H), 7.05 (dd, J = 8.4, 2.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.26 (d, J = 32.4 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.98 (d, J = 307.7 Hz), 149.28 (d, J = 2.4 Hz), 148.84, 133.67, 131.12 (d, J = 4.0 Hz), 130.84, 129.45, 125.71 (d, J = 5.8 Hz), 122.32 (d, J = 7.3 Hz), 118.65 (d, J = 12.8 Hz), 111.61 (d, J = 9.7 Hz), 110.97, 55.89, 55.84.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -82.43 (s, 1F), -88.82 (s, 6F).

FTMS: (APCI) calcd for $C_{16}H_{13}FClS^-$ [M-H^+] 323.03143; found 323.03098.

(4-chlorophenyl)(2-(3,4-dimethylphenyl)-1-fluorovinyl)sulfane (**3gh**)



Chemical Formula: $C_{16}H_{14}ClFS$
Exact Mass: 292.04888

Isolated yield: 14.8 mg, 50 % yield. The ratio of E/Z is **93:7** by ^{19}F NMR .

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, J = 10.8, 3.1 Hz, 2H), 7.32 – 7.29 (m, 3H), 7.27 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 6.26 (d, J = 32.7 Hz, 1H), 2.26 (s, 6H).

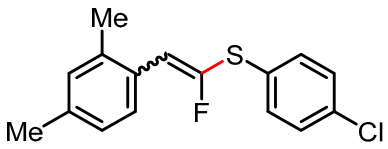
E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.59 (d, J = 308.8 Hz), 137.27, 136.86,

133.61, 131.17 (d, J = 3.7 Hz), 130.78, 130.32 (d, J = 5.6 Hz), 130.11 (d, J = 7.7 Hz), 129.95, 129.43, 126.47 (d, J = 7.9 Hz), 118.87 (d, J = 12.8 Hz), 19.79, 19.68.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -82.31 (s, 1F), -87.15 (s, 13.6F).

FTMS: (APCI) calcd for $C_{16}H_{13}FClS^-$ [M-H^+] 291.04160; found 291.04106.

(4-chlorophenyl)(2-(2,4-dimethylphenyl)-1-fluorovinyl)sulfane (**3hh**)



Chemical Formula: $C_{16}H_{14}ClFS$
Exact Mass: 292.04888

Isolated yield: 19.3 mg, 66 % yield. The ratio of E/Z is **88:12** by ^{19}F NMR .

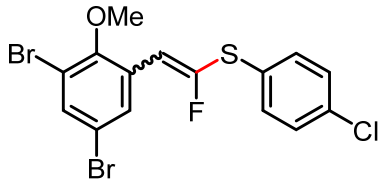
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 8.5 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.32 – 7.29 (m, 2H), 7.01 (d, J = 5.6 Hz, 2H), 6.43 (d, J = 31.8 Hz, 1H), 2.31 (s, 3H), 2.31 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.78 (d, J = 309.3 Hz), 138.28, 135.90, 133.63, 131.07, 130.81, 129.43, 129.15, 129.08, 128.30 (d, J = 5.4 Hz), 126.88, 115.88 (d, J = 13.1 Hz), 21.19, 20.06.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -83.85 (s, 1F), -88.47 (s, 7.35F).

FTMS: (APCI) calcd for $C_{16}H_{13}FClS^-$ [M-H^+] 291.04160; found 291.04102.

(4-chlorophenyl)(2-(3,5-dibromo-2-methoxyphenyl)-1-fluorovinyl)sulfane (**3ih**)



Chemical Formula: $C_{15}H_{10}Br_2ClFOS$
Exact Mass: 449.84917

Isolated yield: 15.3 mg, 34 % yield. The ratio of E/Z is **90:10** by ^{19}F NMR.

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 2.3 Hz, 1H), 7.61 (d, J = 2.3 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.36 – 7.33 (m, 2H), 6.48 (d, J = 32.4 Hz, 1H), 3.80 (s, 3H).

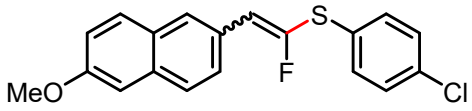
E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.93 (d, J = 313.0 Hz), 153.54, 135.19,

134.73, 132.37, 131.75 (d, J = 15.1 Hz), 129.66, 129.41 (d, J = 5.8 Hz), 129.25 (d, J = 1.9 Hz), 118.23, 117.57, 108.69 (d, J = 10.4 Hz), 61.58.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -77.05 (s, 1F), -82.57 (s, 9.25F).

FTMS: (APCI) calcd for $C_{15}H_{10}FClBr_2S^+$ $[M]^+$ 449.84862; found 84799.

(4-chlorophenyl)(1-fluoro-2-(6-methoxynaphthalen-2-yl)vinyl)sulfane (**3jh**)



Chemical Formula: $C_{19}H_{14}ClFOS$
Exact Mass: 344.04379

Isolated yield: 28.3 mg, 82 % yield. The ratio of E/Z is **92:8** by ^{19}F NMR .

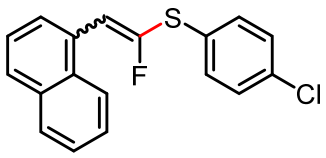
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.70 (d, J = 5.9 Hz, 1H), 7.69 (d, J = 5.5 Hz, 1H), 7.63 (dd, J = 8.6, 1.6 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.33 – 7.28 (m, 2H), 7.14 (dd, J = 9.0, 2.5 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H), 6.42 (d, J = 32.6 Hz, 1H), 3.91 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.37, 151.06 (d, J = 309.5 Hz), 134.28 (d, J = 1.6 Hz), 133.76, 131.00, 129.86, 129.49, 128.74, 128.46, 128.40, 128.11 (d, J = 5.7 Hz), 127.11, 126.85 (d, J = 8.5 Hz), 119.34, 118.80 (d, J = 12.9 Hz), 105.69, 55.36.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.35 (s, 1F), -86.95 (s, 12F).

FTMS: (APCI) calcd for $C_{19}H_{13}ClFOS^-$ $[M\text{-}H^+]$ 343.03651; found 311.03574.

(4-chlorophenyl)(1-fluoro-2-(naphthalen-1-yl)vinyl)sulfane (**3kh**)



Chemical Formula: $C_{18}H_{12}ClFS$
Exact Mass: 314.03323

Isolated yield:27.5 mg, 87 % yield. The ratio of E/Z is **74:26** by ^{19}F NMR .

Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 1.04H), 7.94 (d, J = 7.6 Hz, 0.41H), 7.89 – 7.78 (m, 3.78H), 7.56 – 7.43 (m, 6.54H), 7.35 – 7.29 (m, 2.71H), 7.25 (dt, J = 4.3, 2.4 Hz, 0.93H), 7.22 (s, 0.19H), 6.97 (d, J = 30.4 Hz, 1H).

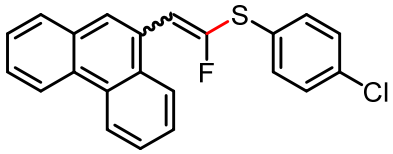
E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.52 (d, J = 309.7 Hz), 133.96, 133.59,

131.81, 131.31, 130.49 (d, J = 3.1 Hz), 129.52, 128.79, 128.75, 128.71, 127.64 (d, J = 10.4 Hz), 126.52, 125.91, 125.44, 123.51, 114.57 (d, J = 13.5 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -82.33 (s, 1F), -87.12 (s, 2.5F).

FTMS: (APCI) calcd for $C_{18}H_{11}ClFS^-$ [M-H^+] 313.02595; found 313.02533.

(4-chlorophenyl)(1-fluoro-2-(phenanthren-9-yl)vinyl)sulfane (**3lh**)



Chemical Formula: $C_{22}H_{14}ClFS$
Exact Mass: 364.04888

Isolated yield: 30.5 mg, 83 % yield. The ratio of E/Z is **69:31** by ^{19}F NMR .

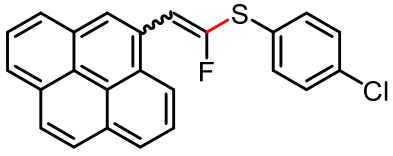
Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 8.3 Hz, 1.52H), 8.64 (dd, J = 11.2, 8.4 Hz, 1.5H), 8.05 (t, J = 3.7 Hz, 2H), 7.99 (d, J = 7.7 Hz, 0.46H), 7.85 (d, J = 7.9 Hz, 1.48H), 7.70 – 7.61 (m, 4.84H), 7.61 – 7.56 (m, 1.46H), 7.51 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 (d, J = 8.6 Hz, 0.85H), 7.25 – 7.23 (m, 0.88H), 7.20 (dd, J = 13.9, 0.9 Hz, 0.45H), 6.94 (d, J = 29.8 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.02 (d, J = 309.4 Hz), 134.13, 132.16, 131.55, 130.50, 130.45 (d, J = 3.1 Hz), 130.26, 130.07, 129.63, 129.42, 129.01, 128.76 (d, J = 2.0 Hz), 127.27, 126.97, 126.92, 126.69, 124.37, 123.24, 122.53, 114.80 (d, J = 13.6 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.35 (s, 1F), -86.95 (s, 12F).

FTMS: (APCI) calcd for $C_{22}H_{13}FClS^-$ [M-H^+] 363.04160; found 363.04083.

(4-chlorophenyl)(1-fluoro-2-(pyren-4-yl)vinyl)sulfane **(3mh)**



Chemical Formula: $C_{24}H_{14}ClFS$
Exact Mass: 388.04888

Isolated yield: 28.7 mg, 74 % yield. The ratio of E/Z is **90:10** by ^{19}F NMR .

Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 9.2

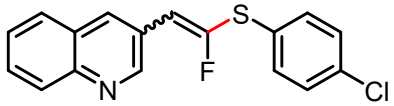
Hz, 1H), 8.20 – 8.16 (m, 2H), 8.12 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 9.2 Hz, 1H), 8.05 (d, J = 8.9 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.53 – 7.47 (m, 2H), 7.37 – 7.33 (m, 2H), 7.26 (s, 0.48H), 7.21 (s, 0.48H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.48 (d, J = 310.8 Hz), 134.02, 131.40, 131.29, 131.20, 130.66, 130.55 (d, J = 3.0 Hz), 129.56, 128.48, 128.14, 127.90, 127.34, 127.13, 127.06, 126.10, 125.67, 125.39, 124.82, 124.77, 124.65, 122.85, 114.89 (d, J = 13.0 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.64 (s, 1F), -87.62 (s, 9F).

FTMS: (APCI) calcd for $C_{24}H_{13}FClS^-$ [M-H$^+$] 387.04160; found 387.04086.

3-(2-((4-chlorophenyl)thio)-2-fluorovinyl)quinoline (**3nh**)



Chemical Formula: $C_{17}H_{11}ClFNS$
Exact Mass: 315.02848

Isolated yield: 26.8 mg, 85 % yield. The ratio of E/Z is **92:8** by ^{19}F NMR .

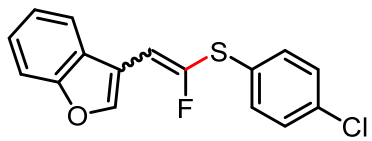
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.35 (d, J = 1.6 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.37 – 7.33 (m, 2H), 6.41 (d, J = 32.5 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.34 (d, J = 312.0 Hz), 150.54 (d, J = 6.2 Hz), 147.23, 135.15 (d, J = 10.7 Hz), 134.55, 132.08, 130.01, 129.66, 129.57 (d, J = 2.6 Hz), 129.21, 128.16, 127.80, 127.19, 126.09 (d, J = 6.0 Hz), 113.85 (d, J = 13.5 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -77.39 (s, 1F), -82.72 (s, 12F).

FTMS: (APCI) calcd for $C_{17}H_{10}FClNS^-$ [M-H$^+$] 314.02120; found 314.02042.

3-(2-((4-chlorophenyl)thio)-2-fluorovinyl)benzofuran (**3oh**)



Chemical Formula: $C_{16}H_{10}ClFOS$
Exact Mass: 304.01249

Isolated yield: 19.1 mg, 51 % yield. The ratio of E/Z is **87.5:12.5** by ^{19}F NMR .

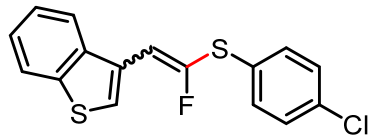
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.42 (m, 3H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.38 (d, *J* = 31.0 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.23, 153.37 (d, *J* = 312.8 Hz), 149.37 (d, *J* = 6.1 Hz), 134.58, 132.10, 129.67, 129.46 (d, *J* = 2.9 Hz), 128.67, 125.08, 123.16, 121.21, 111.15, 107.65 (d, *J* = 11.7 Hz), 107.24 (d, *J* = 15.3 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.56 (s, 7F), -80.95 (s, 1F).

FTMS: (APCI) calcd for $C_{16}H_9FOClS^-$ [M-H^+] 303.00521; found 303.00470.

3-(2-((4-chlorophenyl)thio)-2-fluorovinyl)benzo[b]thiophene (**3ph**)



Chemical Formula: $C_{16}H_{10}ClFS_2$
Exact Mass: 319.98965

Isolated yield: 19.1 mg, 60 % yield. The ratio of E/Z is **92:8** by ^{19}F NMR .

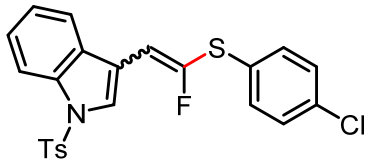
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.41 – 7.37 (m, 1H), 7.35 – 7.30 (m, 2H), 6.67 (d, *J* = 31.7 Hz, 1H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.52 (d, *J* = 309.9 Hz), 139.22, 137.55, 133.98, 131.20, 130.52 (d, *J* = 3.8 Hz), 129.54, 127.34 (d, *J* = 15.2 Hz), 126.99 (d, *J* = 5.3 Hz), 124.74, 124.52, 122.82, 121.11, 109.85 (d, *J* = 15.4 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -82.04 (s, 1F), -83.0 (s, 11.48F).

FTMS: (APCI) calcd for $C_{16}H_9FClS_2^-$ [M-H^+] 318.98237; found 318.98169.

3-(2-((4-chlorophenyl)thio)-2-fluorovinyl)-1-tosyl-1H-indole (**3qh**)



Chemical Formula: $C_{23}H_{17}ClFNO_2S_2$
Exact Mass: 457.03733

Isolated yield: 19.2 mg, 42 % yield. The ratio of E/Z is **94:6** by ^{19}F NMR .

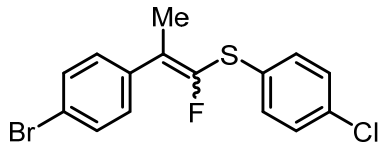
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.95 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.37 – 7.34 (m, 1H), 7.34 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 32.5 Hz, 1H), 2.34 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.03 (d, *J* = 308.6 Hz), 145.23, 135.03, 134.30, 134.07, 131.33, 130.45 (d, *J* = 3.4 Hz), 130.00, 129.54, 128.96, 126.94, 126.42 (d, *J* = 14.8 Hz), 125.17, 123.54, 119.00, 114.14 (d, *J* = 4.8 Hz), 113.65, 108.22 (d, *J* = 18.2 Hz), 21.59.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.58 (s, 16.15F), -81.58 (s, 1F).

FTMS: (APCI) calcd for $C_{23}H_{18}FClNO_2S_2^+[M+H^+]$ 458.04460; found 458.04401.

(2-(4-bromophenyl)-1-fluoroprop-1-en-1-yl)(4-chlorophenyl)sulfane **(3rh)**



Chemical Formula: $C_{15}H_{11}BrClFS$
Exact Mass: 355.94374

Isolated yield: 26.3 mg, 74 % yield. The ratio of E/Z is **51:49** by ^{19}F NMR .

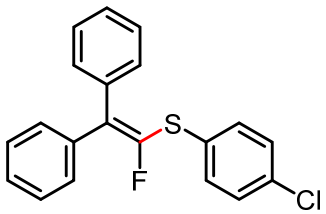
Both isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 4H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 6H), 7.24 – 7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 2.25 (d, *J* = 3.3 Hz, 3H), 2.15 (d, *J* = 4.4 Hz, 3H).

Both isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.11 (d, *J* = 263.6 Hz), 148.11 (d, *J* = 328.1 Hz), 137.90 (d, *J* = 4.4 Hz), 135.76, 133.47, 133.25, 131.37, 130.86 (d, *J* = 3.1 Hz), 130.62, 130.20, 129.83, 129.81, 129.69, 129.66, 129.46, 129.38, 127.69 (d, *J* = 23.3 Hz), 124.68 (d, *J* = 14.9 Hz), 121.82, 19.78, 17.84 (d, *J* = 4.4 Hz).

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -88.78 (s, 1F), -89.39 (s, 0.96F).

FTMS: (APCI) calcd for $C_{15}H_{10}FClBrS^-$ [M-H$^+$] 354.93646; found 354.93598.

(4-chlorophenyl)(1-fluoro-2,2-diphenylvinyl)sulfane (**3sh**)



Chemical Formula: $C_{20}H_{14}ClFS$
Exact Mass: 340.04888

Isolated yield: 25.9 mg, 76 % yield.

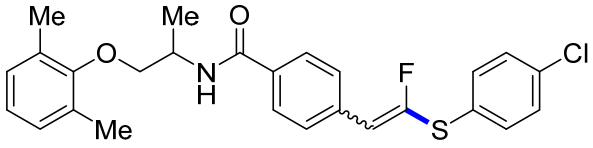
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.31 (dt, *J* = 4.4, 3.4 Hz, 6H), 7.29 – 7.22 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.47 (d, *J* = 304.1 Hz), 138.29 (d, *J* = 4.1 Hz), 136.69 (d, *J* = 2.7 Hz), 133.58, 131.07, 131.02 (d, *J* = 5.7 Hz), 130.96 (d, *J* = 8.8 Hz), 130.18 (d, *J* = 3.1 Hz), 129.72 (d, *J* = 5.4 Hz), 129.45, 128.32, 128.17, 128.09, 128.02.

^{19}F NMR (565 MHz, $CDCl_3$) δ -79.39 (s, 1F), -84.55 (s, 13.56F).

FTMS: (APCI) calcd for $C_{20}H_{13}FClS^-$ [M-H$^+$] 339.04160; found 339.04092.

4-(2-((4-chlorophenyl)thio)-2-fluorovinyl)-N-(1-(2,6-dimethylphenoxy)propan-2-yl)benzamide (**3th**)



Chemical Formula: $C_{26}H_{25}ClFNO_2S$
Exact Mass: 469.12786

Isolated yield: 29.1 mg, 62 % yield. The ratio of E/Z is **94:6** by ^{19}F NMR.

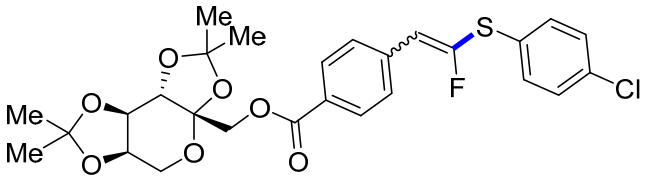
E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.35 – 7.31 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.95 – 6.91 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 6.28 (d, *J* = 32.3 Hz, 1H), 4.59 – 4.51 (m, 1H), 3.92 (dd, *J* = 9.1, 3.8 Hz, 1H), 3.81 (dd, *J* = 9.1, 3.0 Hz, 1H), 2.26 (s, 6H), 1.52 (d, *J* = 6.9 Hz, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.15, 154.82, 153.59 (d, *J* = 312.3 Hz), 135.78 (d, *J* = 5.6 Hz), 134.39, 133.87 (d, *J* = 1.8 Hz), 131.92, 130.74, 129.76 (d, *J* = 2.7 Hz), 129.61, 129.08, 128.94 (d, *J* = 7.9 Hz), 127.26, 124.22, 116.27 (d, *J* = 12.3 Hz), 73.87, 45.96, 17.88, 16.24.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -78.31 (d, *J* = 16.0 Hz, 1F), -83.58 (d, *J* = 32.4 Hz, 15.54F).

FTMS: (APCI) calcd for $C_{26}H_{26}FClNO_2S^-$ [M+H$^+$] 470.13513; found 470.13583.

((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 4-(2-((4-chlorophenyl)thio)-2-fluorovinyl)benzoate (**3uh**)



Chemical Formula: $C_{27}H_{28}ClFO_7S$
Exact Mass: 550.12283

Isolated yield: 27.6 mg, 50 % yield. The ratio of E/Z is **94:6** by ^{19}F NMR.

E isomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.27 (d, *J* = 32.3 Hz, 1H), 4.72 – 4.66 (m, 1H), 4.64 (dd, *J* = 7.8, 2.6 Hz, 1H), 4.46 (d, *J* = 2.6 Hz, 1H), 4.35-4.30 (m, 1H), 4.26 (d, *J* = 7.9 Hz, 1H), 3.96 (dd, *J* = 12.9, 1.5 Hz, 1H), 3.80 (d, *J* = 13.0 Hz, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H).

E isomers: ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.43, 154.19 (d, *J* = 313.7 Hz), 137.24 (d, *J* = 5.7 Hz), 134.50, 132.10, 130.07, 129.60, 129.46 (d, *J* = 2.0 Hz), 128.63, 128.58, 115.86 (d, *J* = 11.8 Hz), 109.17, 108.83, 101.64, 70.78, 70.54, 70.09, 65.33, 61.35, 26.51, 25.88, 25.50, 24.01.

Both isomers: ^{19}F NMR (565 MHz, $CDCl_3$) δ -77.43 (d, *J* = 16.1 Hz, 1F), -82.68 (d, *J* = 32.2 Hz, 15.88F).

FTMS: (APCI) calcd for $C_{27}H_{29}FClO_7S^-$ [M+H$^+$] 551.13011; found 551.13067.

6. Reference

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[2] Krishnamoorthy, S.; Kothandaraman, J.; Saldana, J.; Prakash, G. K. S., Direct Difluoromethylenation of Carbonyl Compounds by Using TMSCF3: The Right Conditions. *Eur. J. Org. Chem.* **2016,** *2016*, 4965-4969.

[3] Thomoson, C. S.; Martinez, H.; Dolbier, W. R., The use of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate as the difluorocarbene source to generate an in situ source of difluoromethylene triphenylphosphonium ylide. *J. Fluorine Chem.* **2013,** *150*, 53-59.

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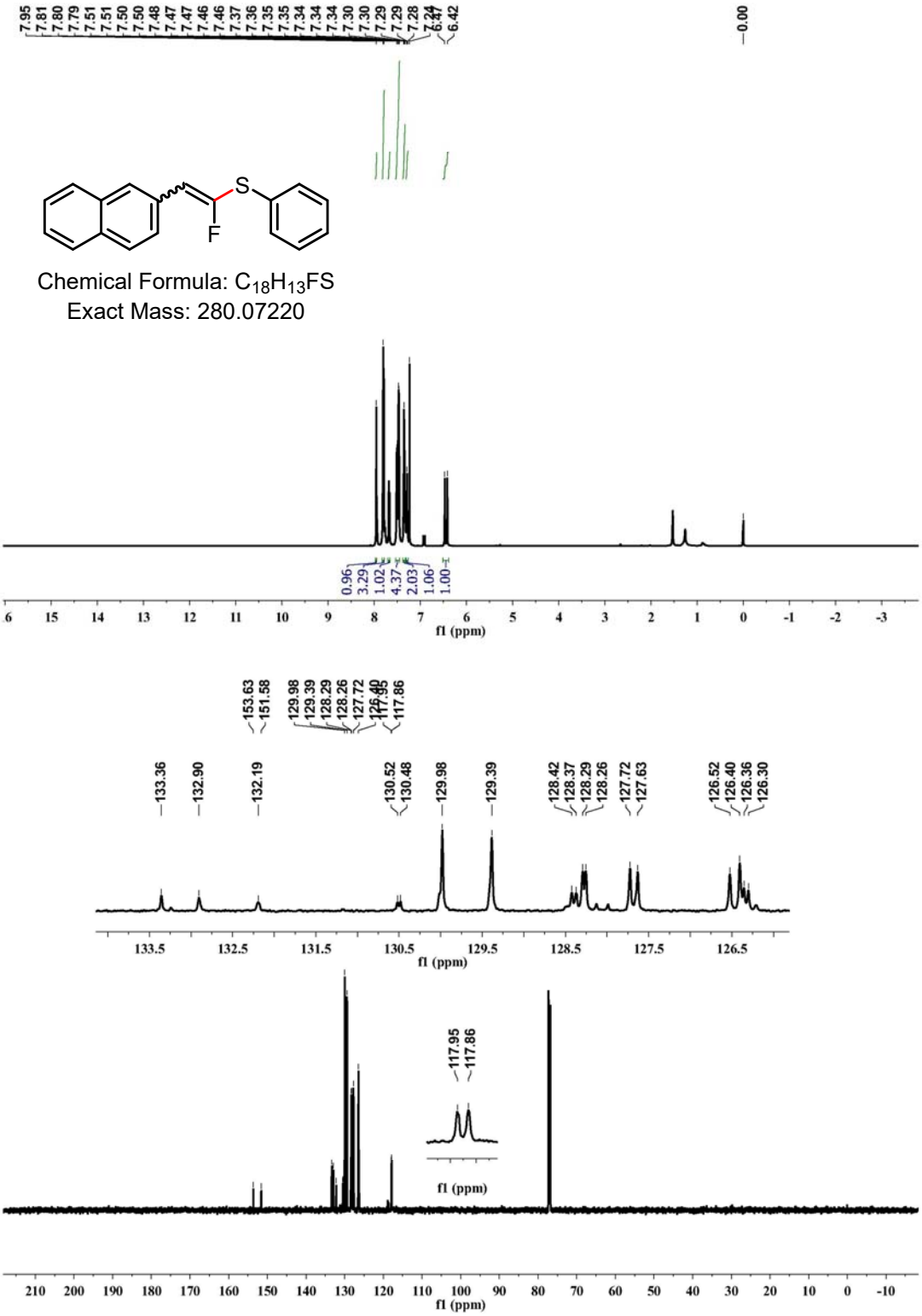
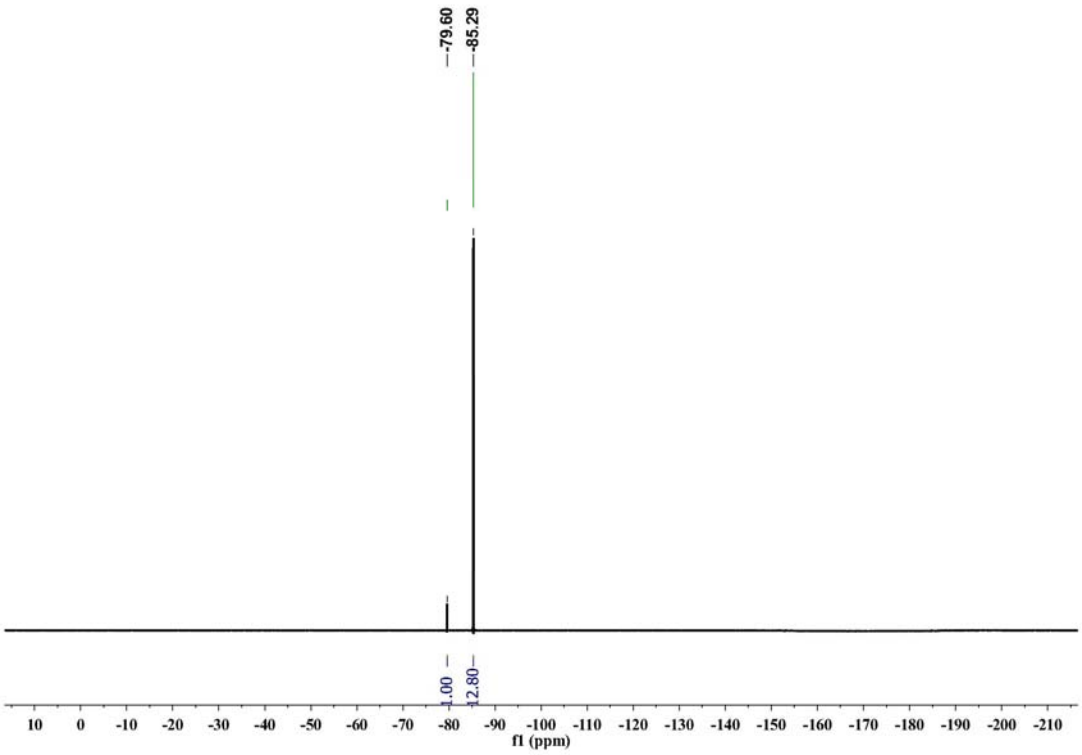
[5] Ma, T.; Chen, Y.; Li, Y.; Ping, Y.; Kong, W., Nickel-Catalyzed Enantioselective Reductive Aryl Fluoroalkenylation of Alkenes. *ACS Catal.* **2019,** *9*, 9127-9133.

7. Copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra

3aa

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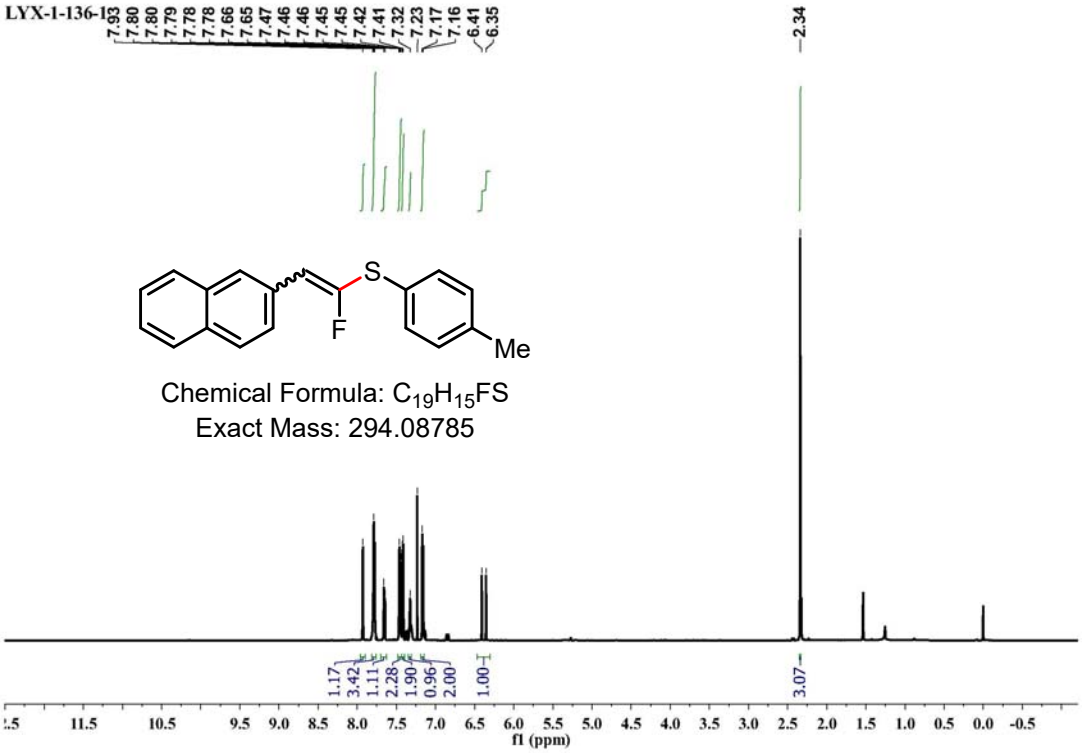
1.00
12.80
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3ab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7.80
7.80
7.79
7.78
7.78
7.66
7.65
7.47
7.46
7.46
7.45
7.45
7.42
7.41
7.32
7.23
7.17
7.16
6.41
6.35
2.34
S
F
Me
Chemical Formula: C19H15FS
Exact Mass: 294.08785
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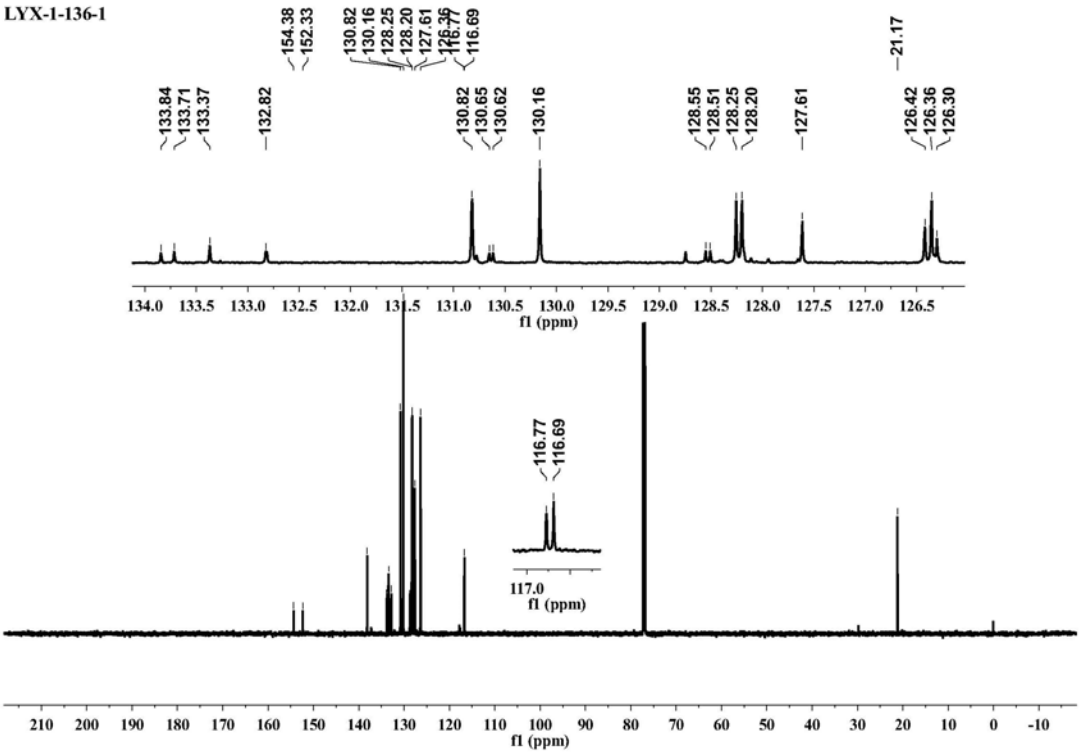
3.42
1.11
2.28
1.90
0.96
2.00
1.00
3.07
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

LYX-1-136-1



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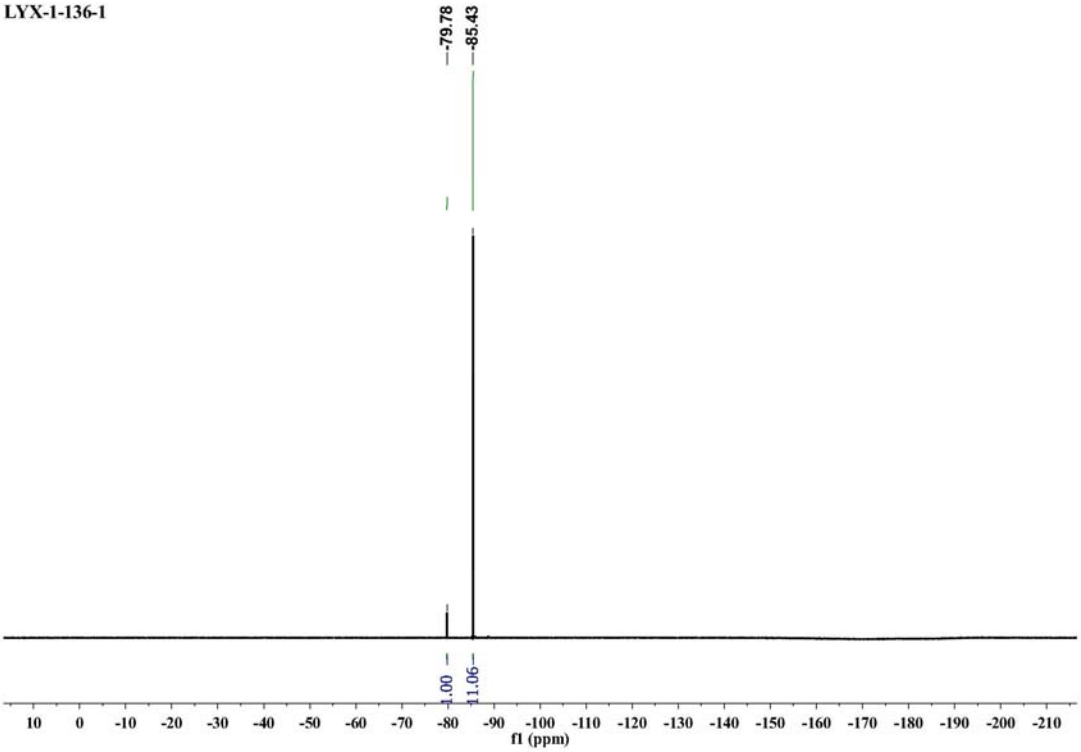

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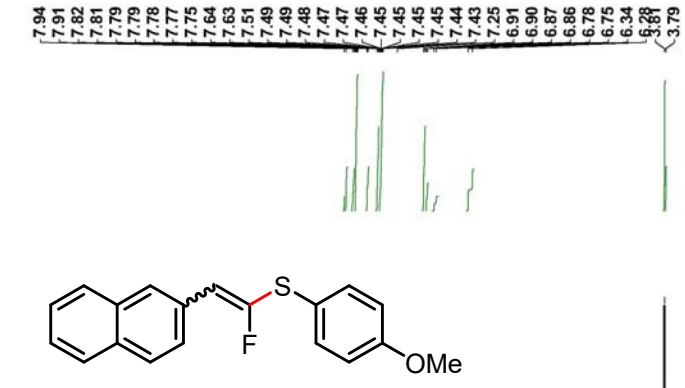
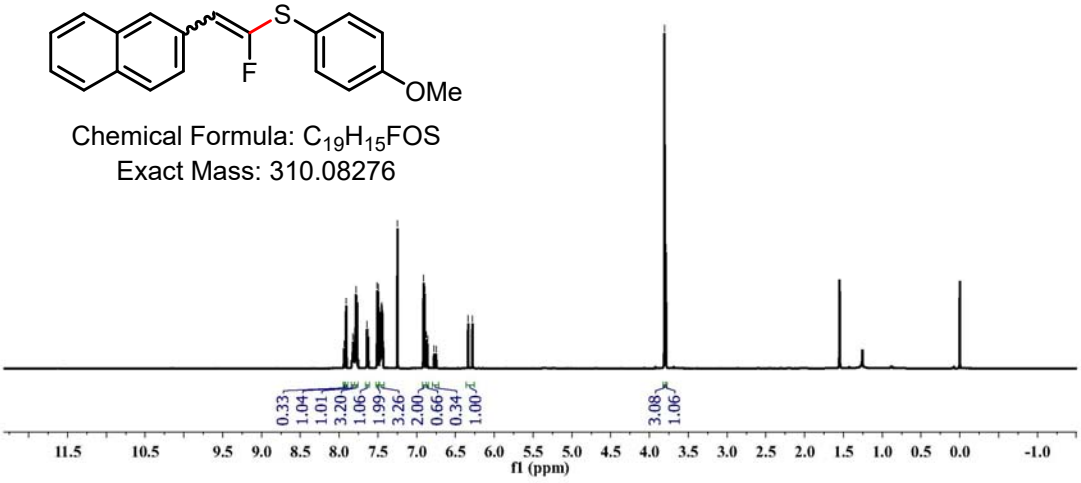


Chemical Formula: $C_{19}H_{15}FOS$
Exact Mass: 310.08276



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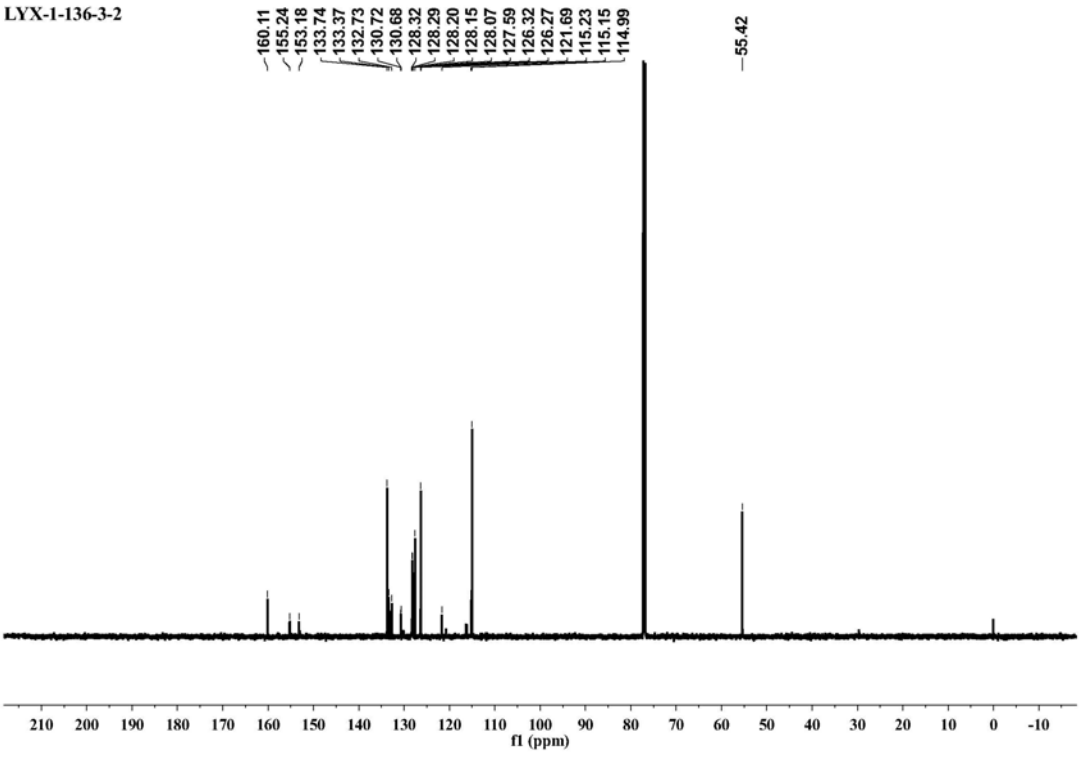
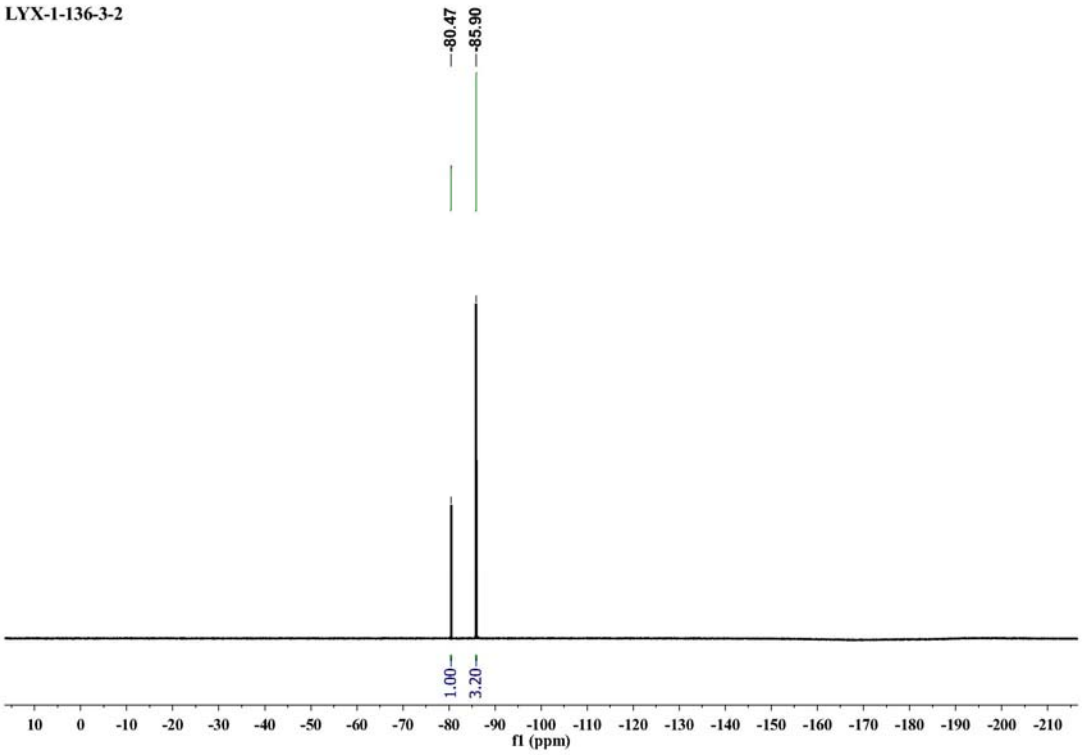
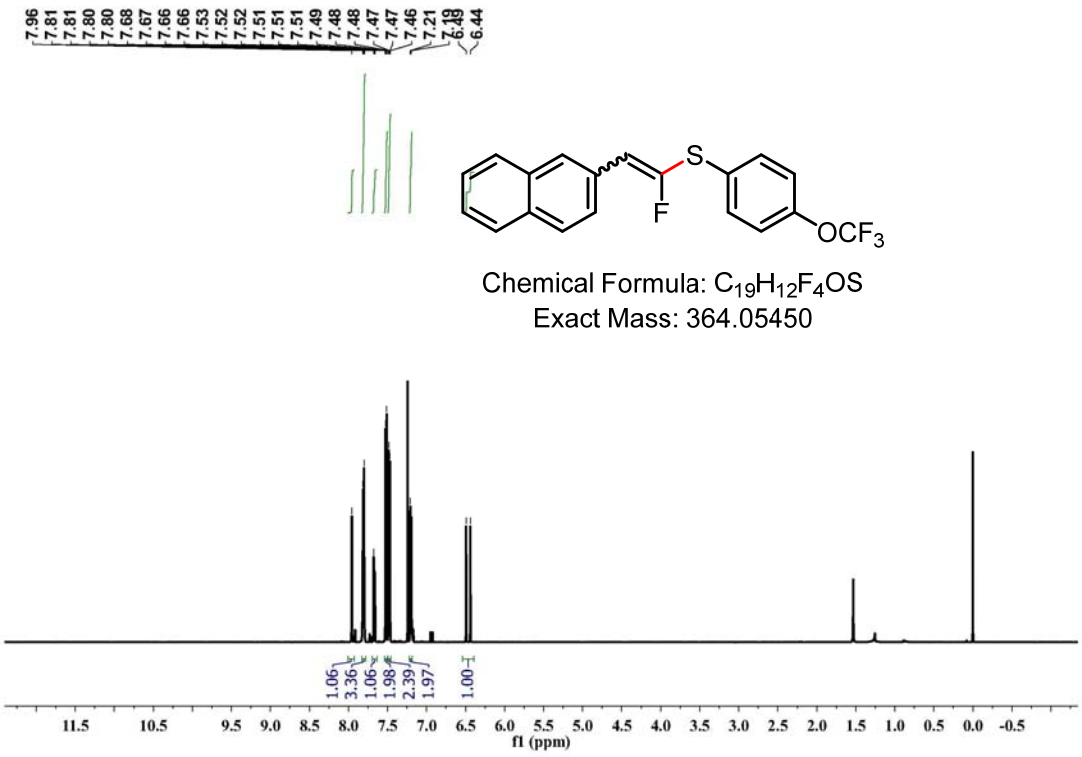
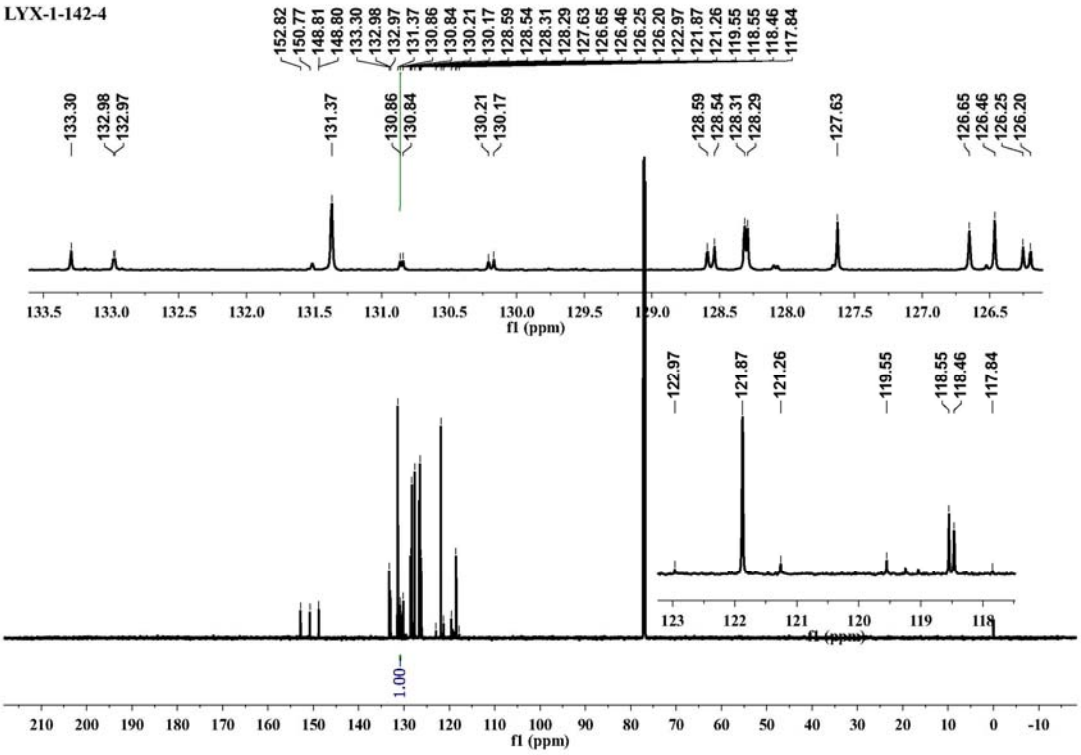




3ad



Chemical Formula: $C_{19}H_{12}F_4OS$
Exact Mass: 364.05450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132.97
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130.86
130.84
130.21
130.17
128.59
128.54
128.31
128.29
127.63
126.65
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126.25
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121.26
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118.46
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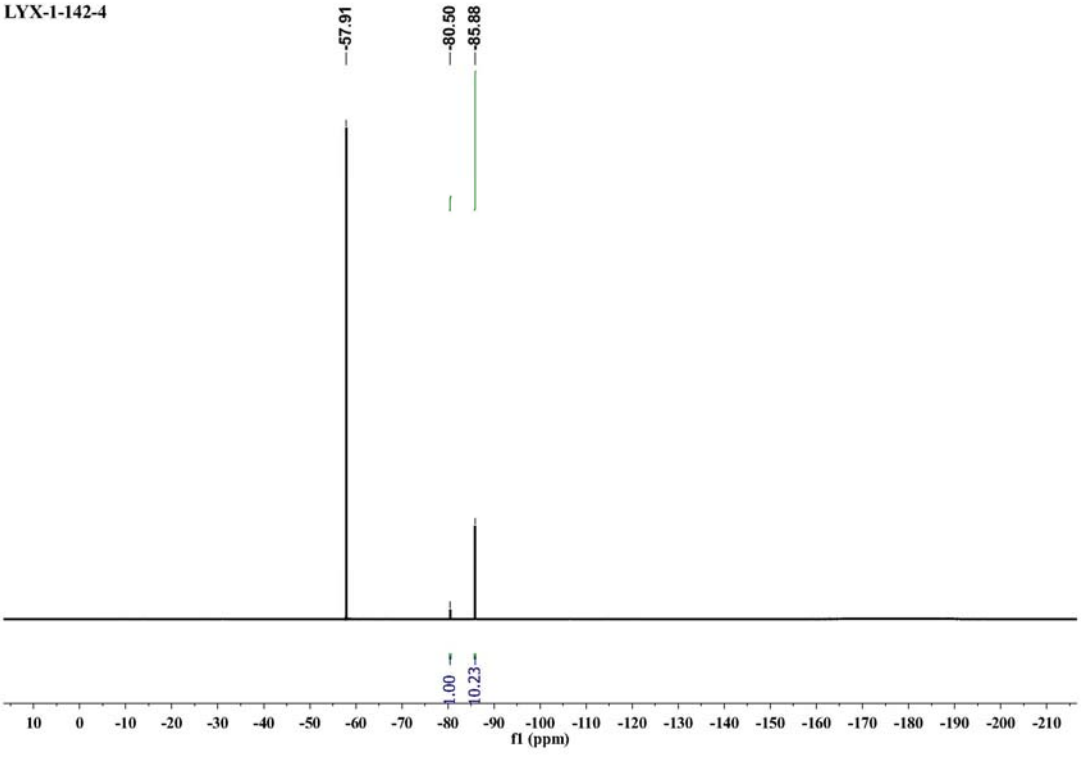
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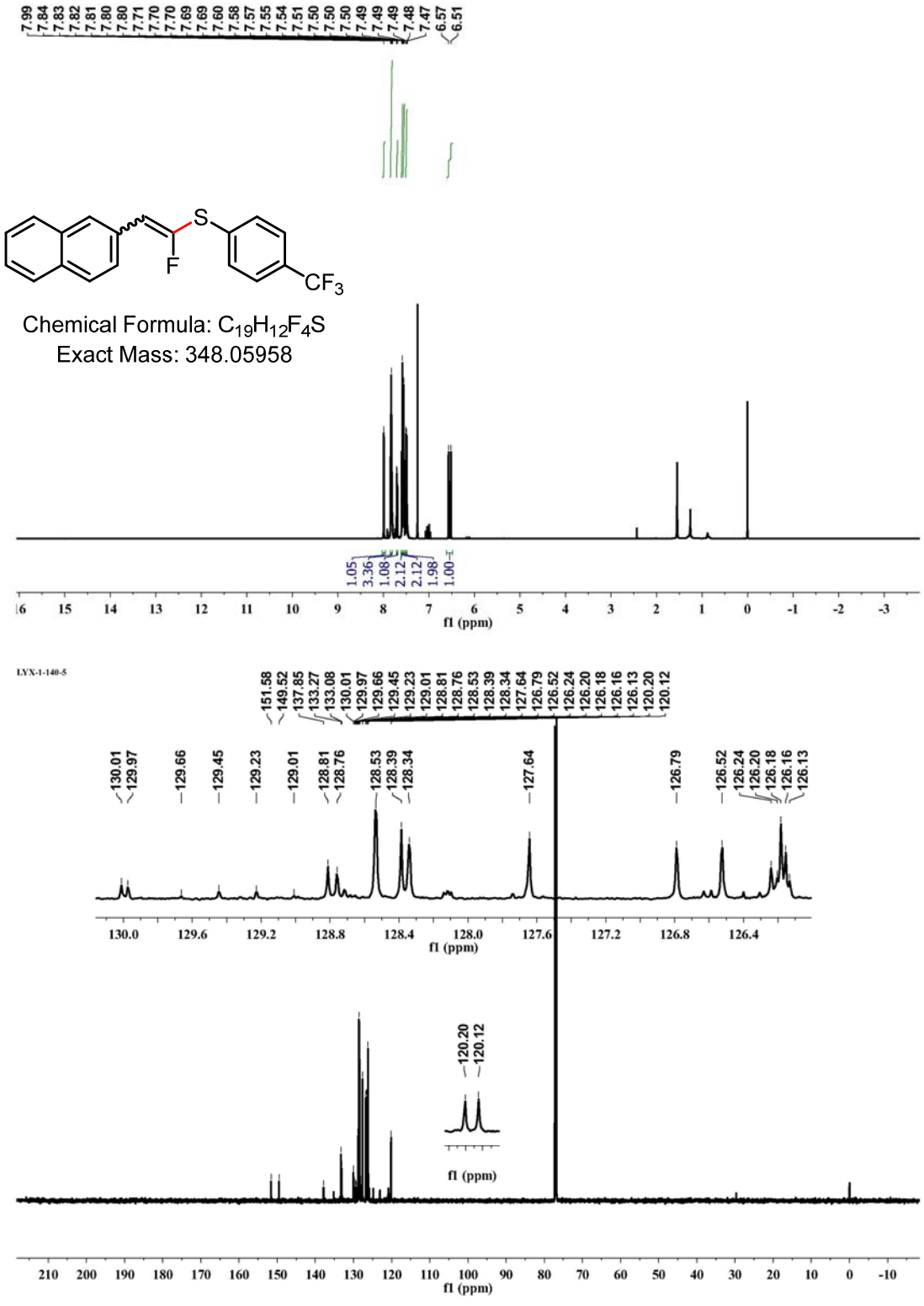
3ae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7.51
7.50
7.50
7.50
7.49
7.49
7.49
7.48
7.47
6.57
6.51
S
F
CF3
Chemical Formula: C19H12F4S
Exact Mass: 348.05958
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2.12
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129.01
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128.34
127.64
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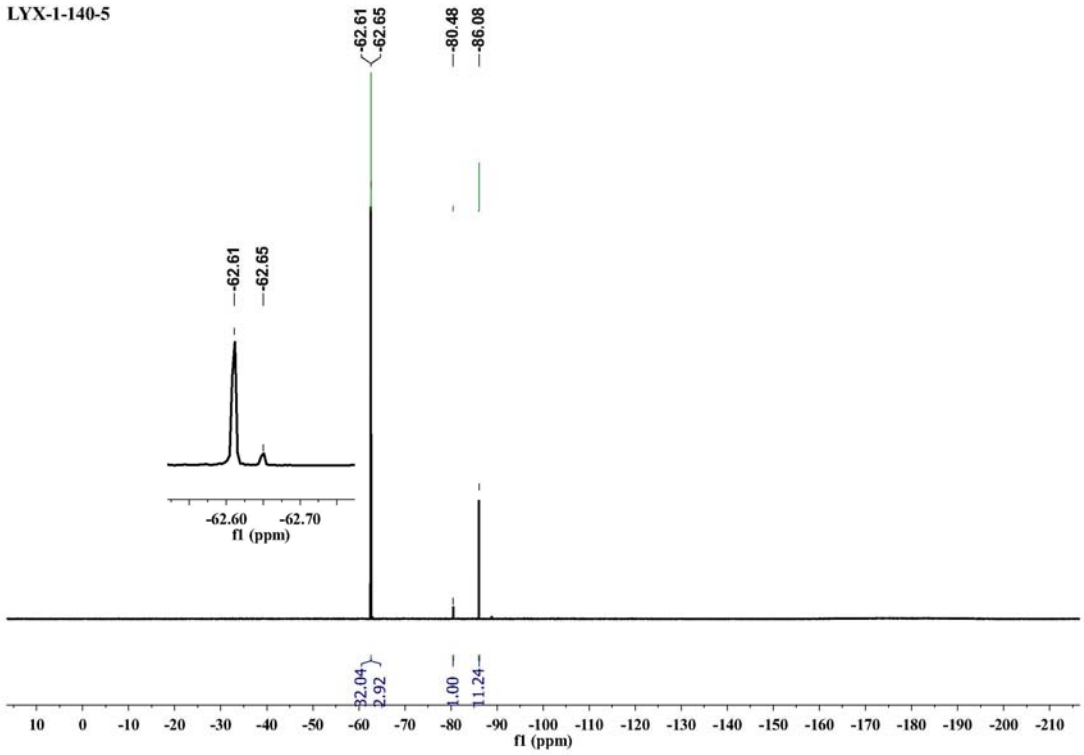
120.20
120.12
f1 (ppm)
f1 (ppm)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f1 (ppm)
32.04
2.92
1.00
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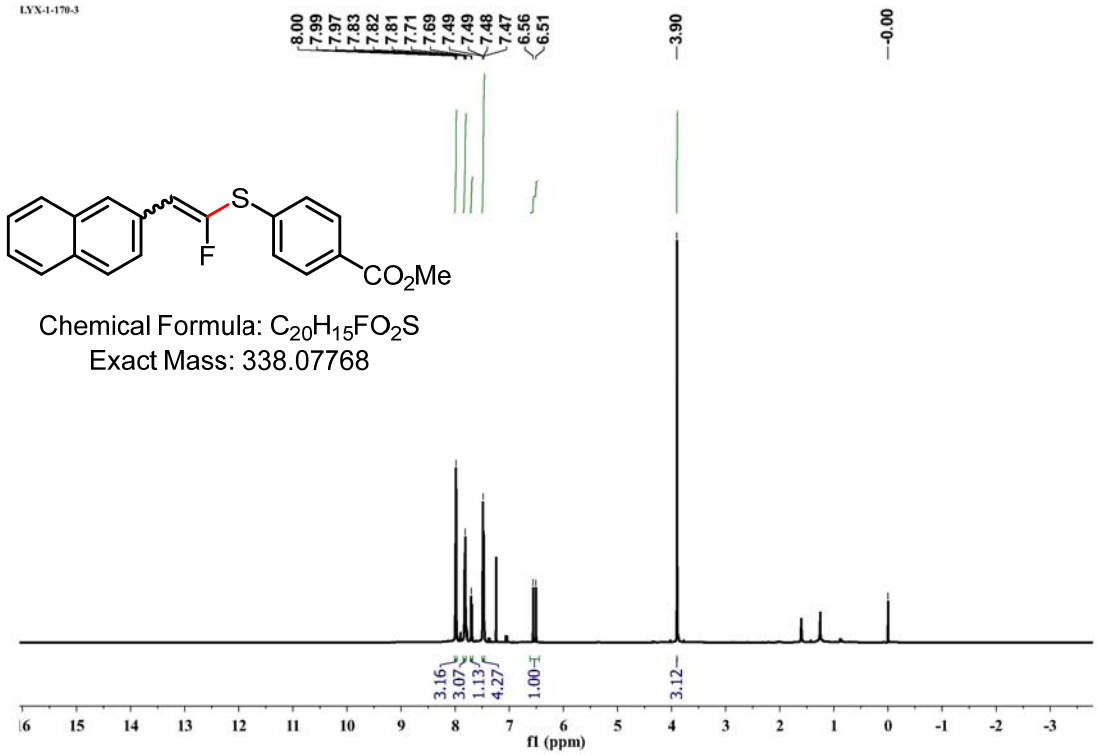
f1 (ppm)

3af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3.90
0.00
S
F
CO2Me
Chemical Formula: C20H15FO2S
Exact Mass: 338.07768
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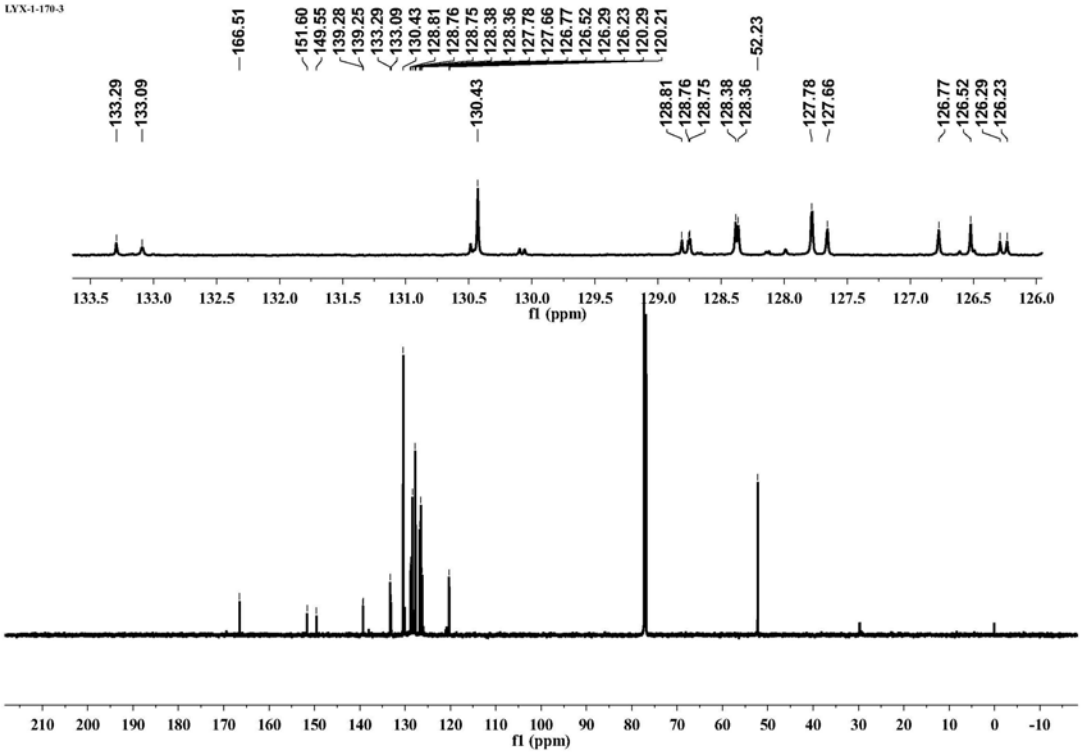
f1 (ppm)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120.29
120.21
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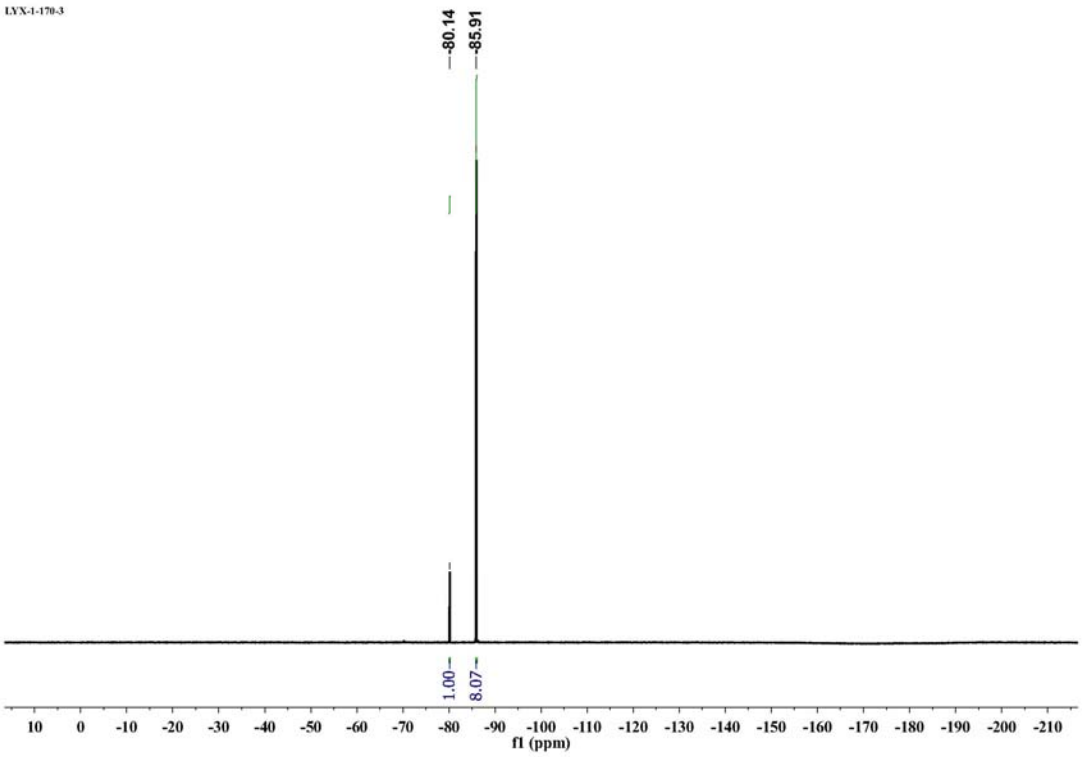
f1 (ppm)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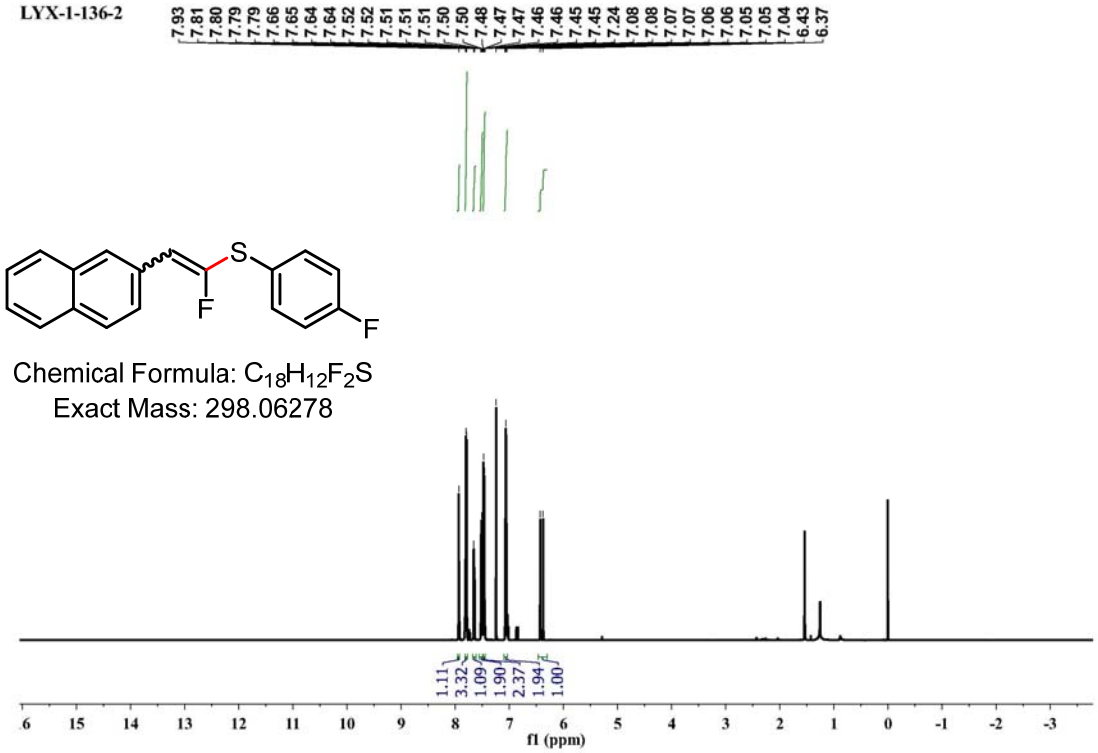
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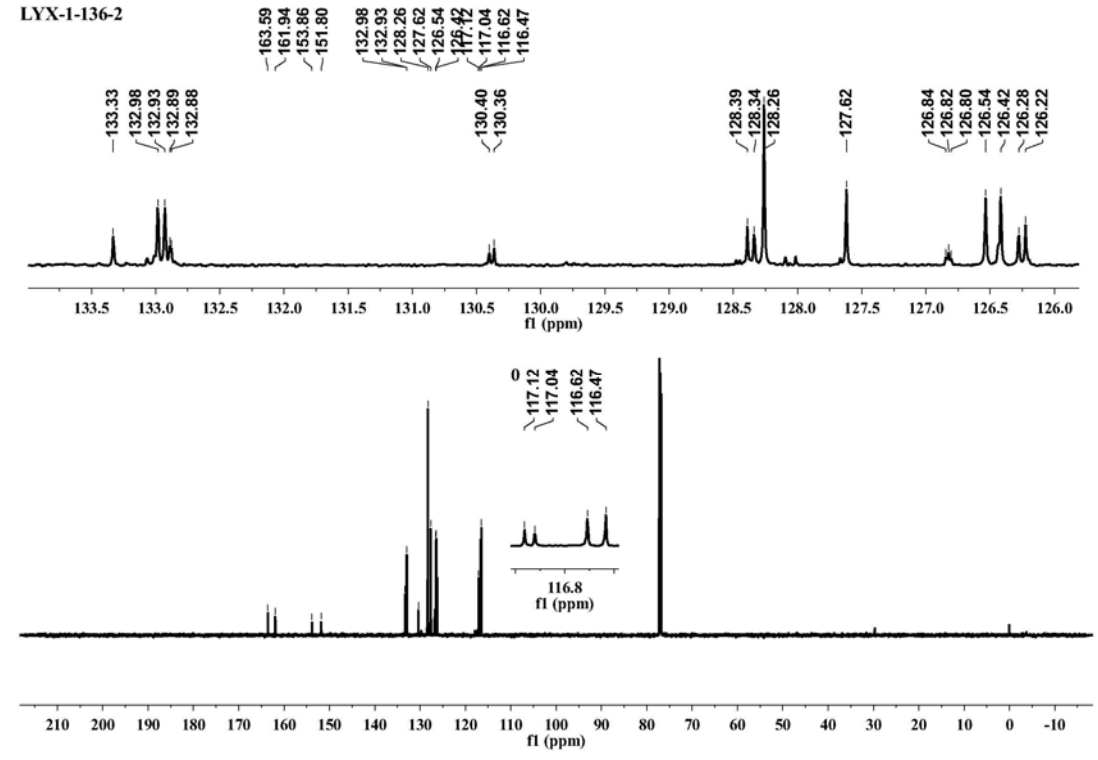
S
F
F
Chemical Formula: C18H12F2S
Exact Mass: 298.06278
1.11 3.32 1.09 1.90 2.37 1.94 1.00
f1 (ppm)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133.33 132.98 132.93 132.89 132.88 130.40 130.36 128.39 128.34 128.26 127.62 126.84 126.82 126.80 126.54 126.42 126.28 126.22
f1 (ppm)
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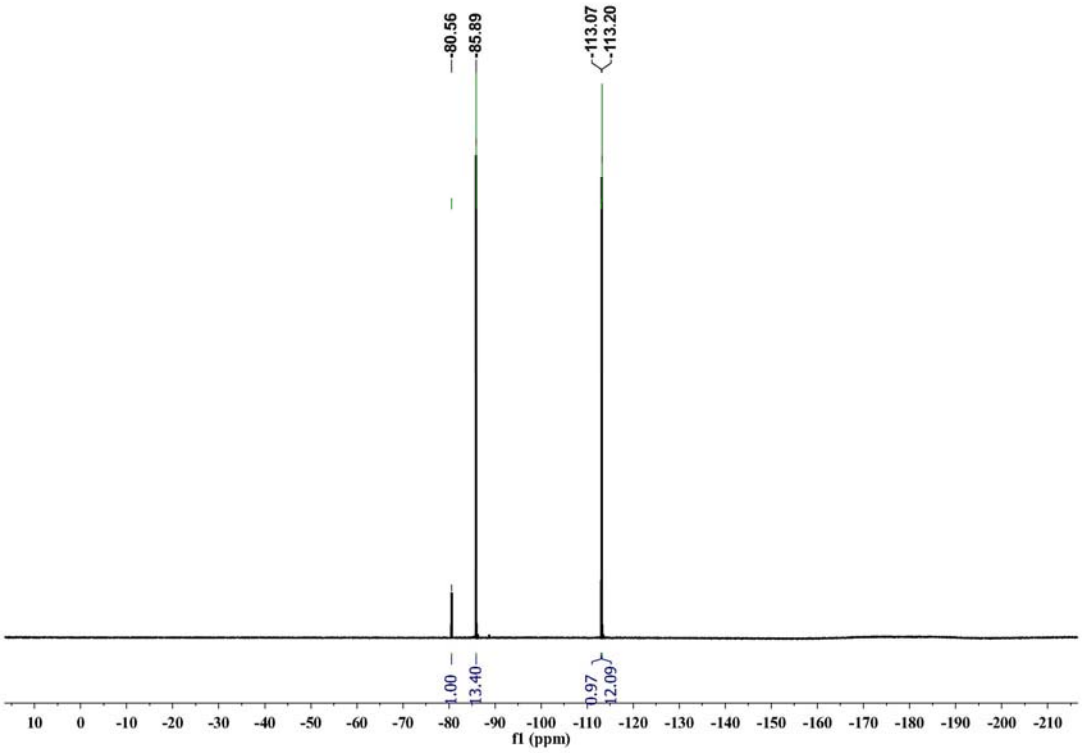
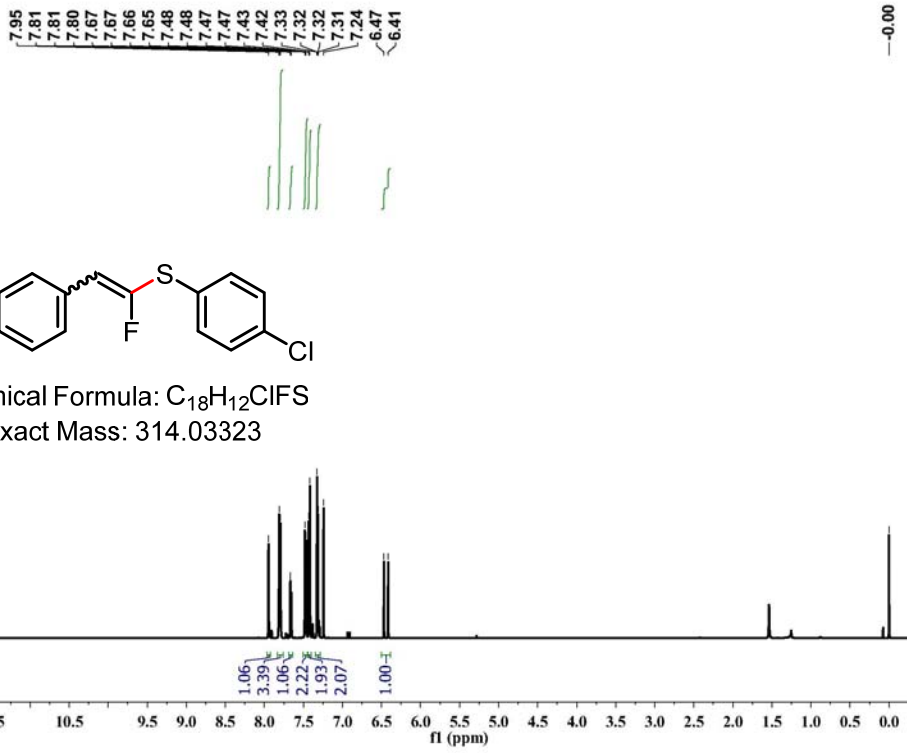
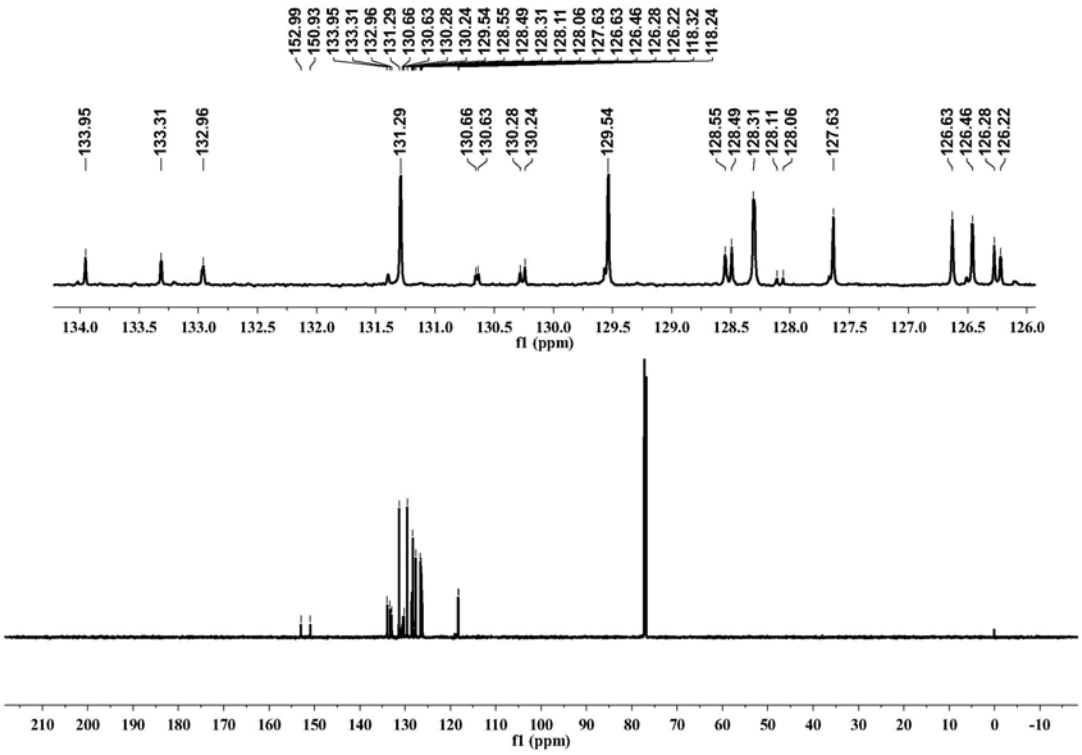
117.12 117.04 116.62 116.47
116.8
f1 (ppm)



3ah



Chemical Formula: $C_{18}H_{12}ClFS$
Exact Mass: 314.03323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130.24
129.54
128.55
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128.31
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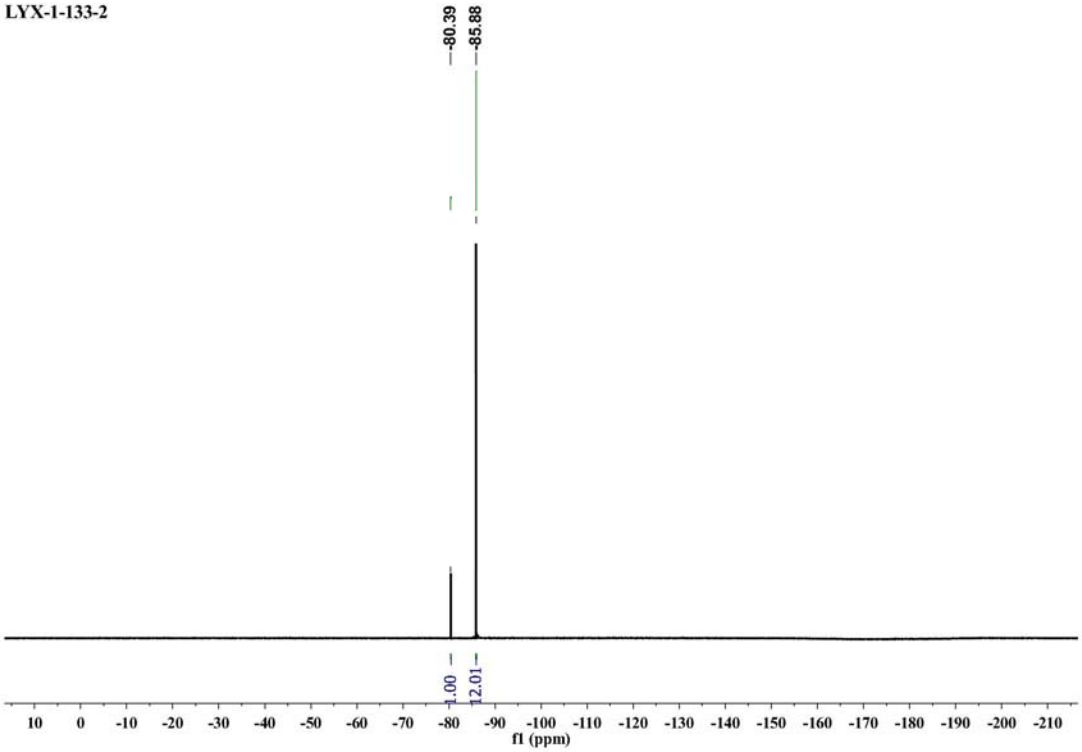
118.32
118.24
f1 (ppm)

LYX-1-133-2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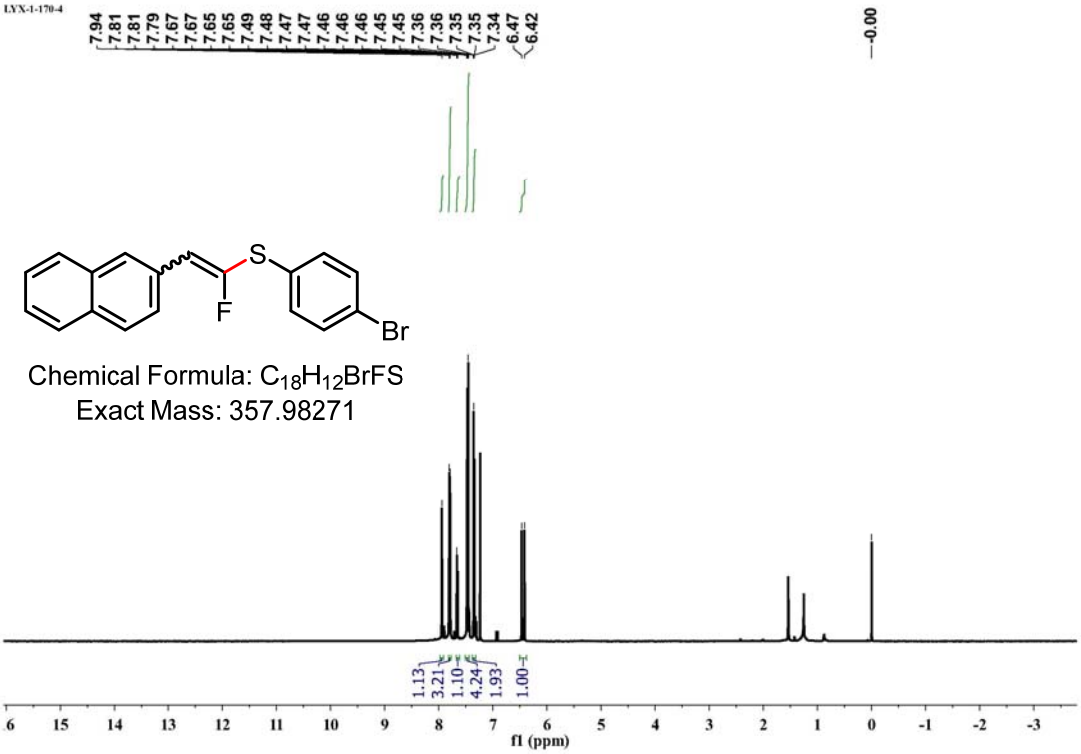
1.00
2.01
f1 (ppm)

3ai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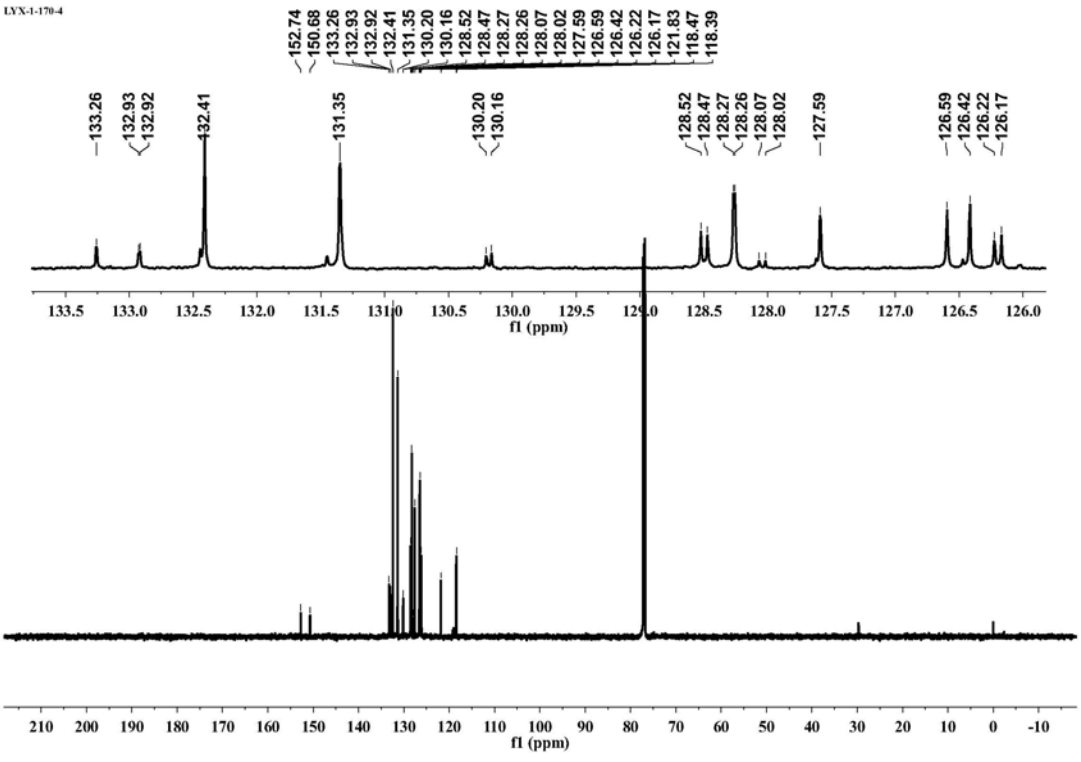
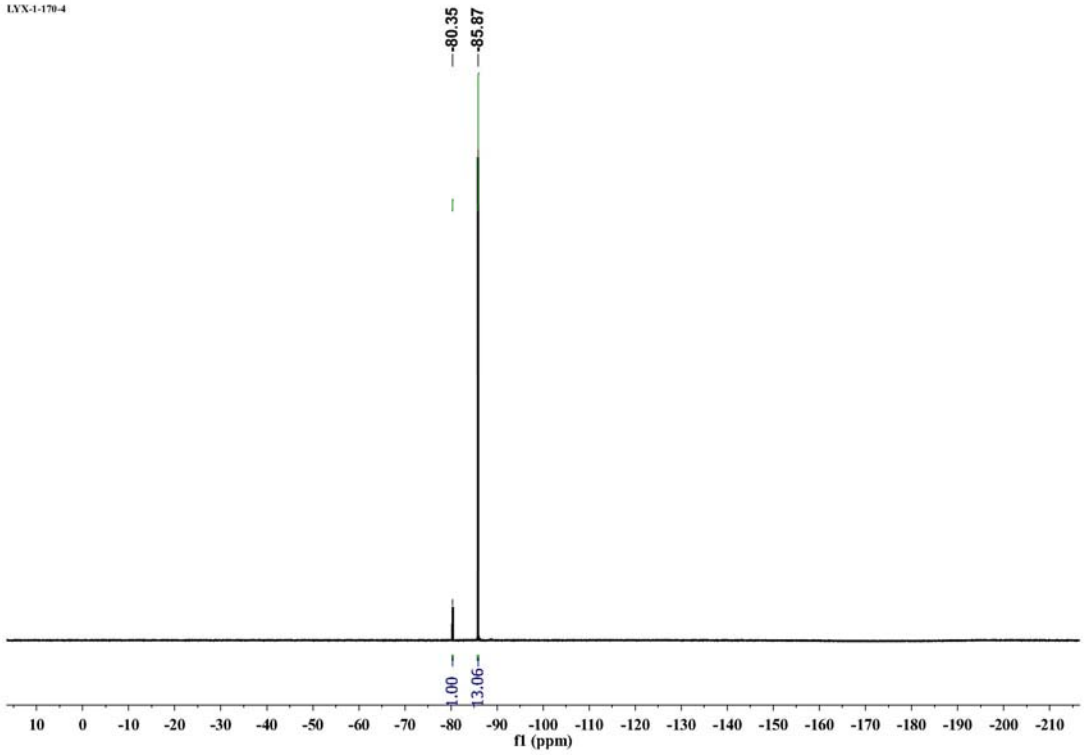
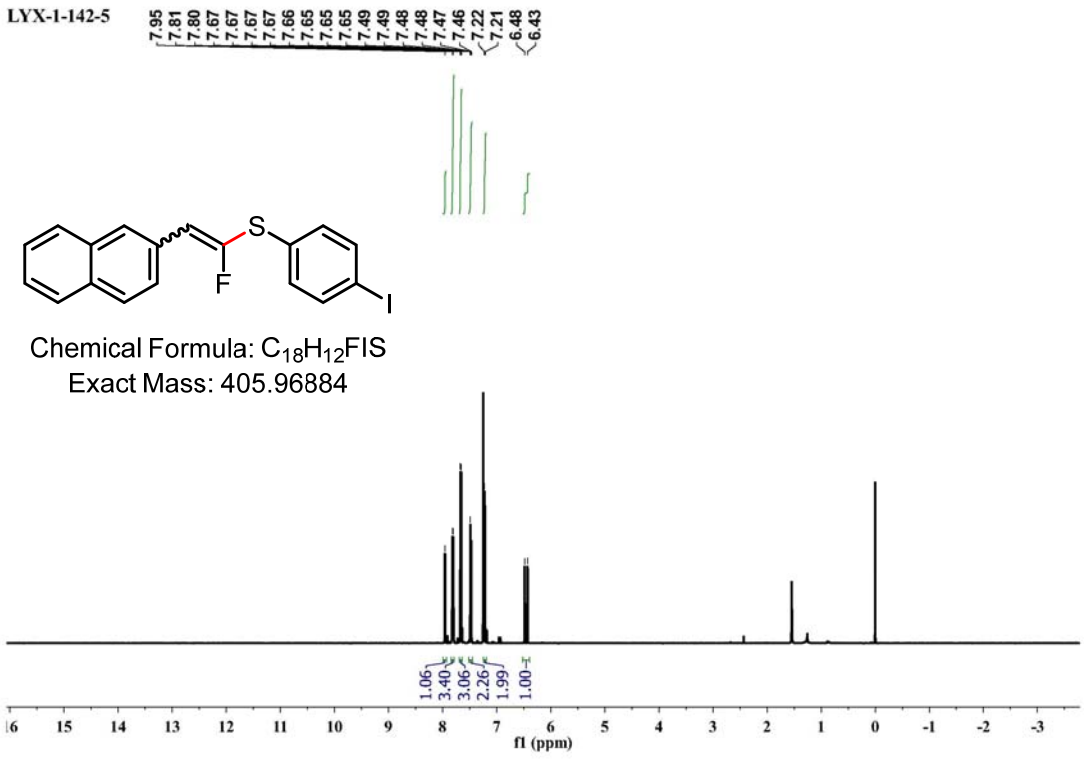
7.47
7.46
7.46
7.46
7.45
7.45
7.36
7.36
7.35
7.35
7.34
6.47
6.42
0.00
S
F
Br
Chemical Formula: C18H12BrFS
Exact Mass: 357.98271
1.13
3.21
1.10
4.24
1.93
1.00
f1 (ppm)


LYX-1-170-4
152.74
150.68
133.26
132.93
132.92
132.41
131.35
130.20
130.16
128.52
128.47
128.27
128.26
128.07
128.02
127.59
126.59
126.42
126.22
126.17
121.83
118.47
118.39
f1 (ppm)

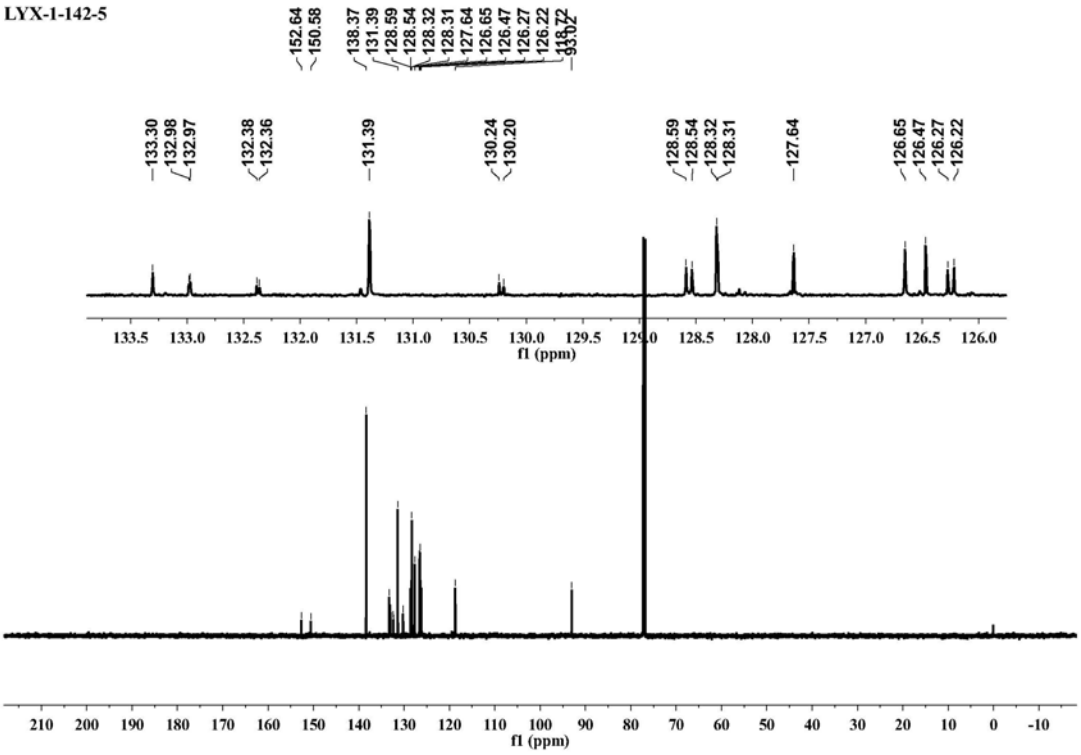


3aj

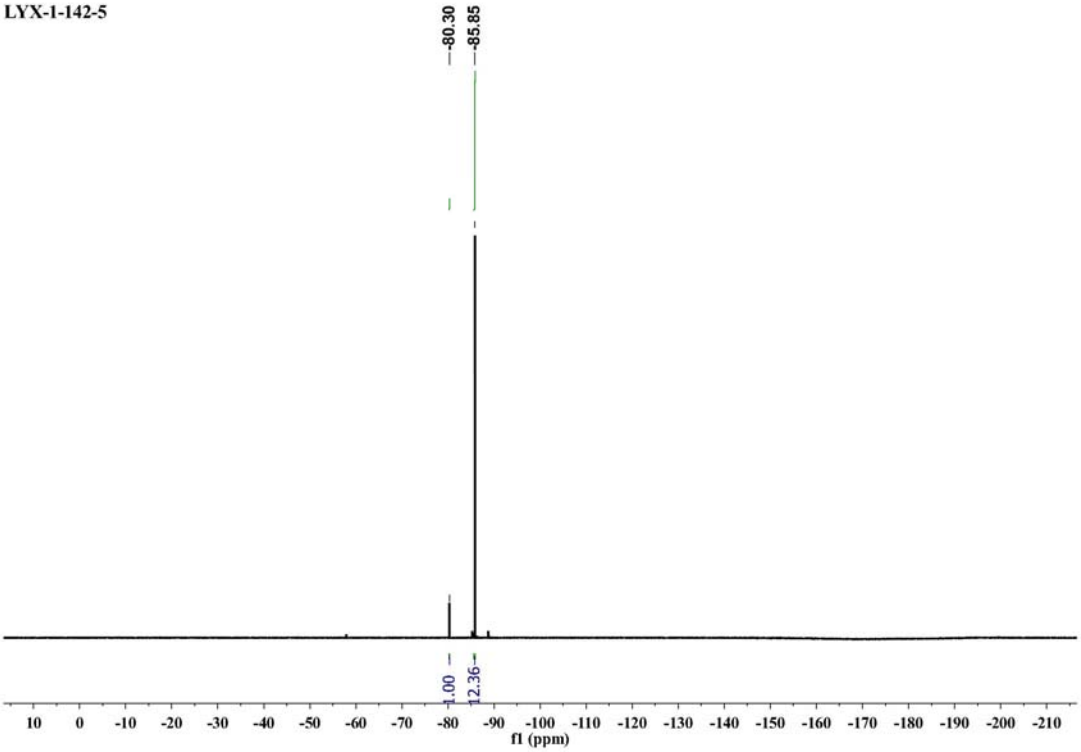


Chemical Formula: $C_{18}H_{12}FIS$
Exact Mass: 405.96884

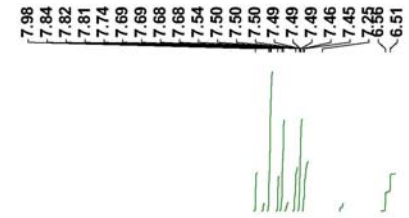
LYX-1-142-5

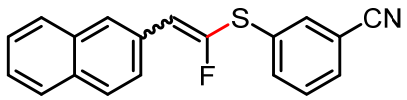


LYX-1-142-5

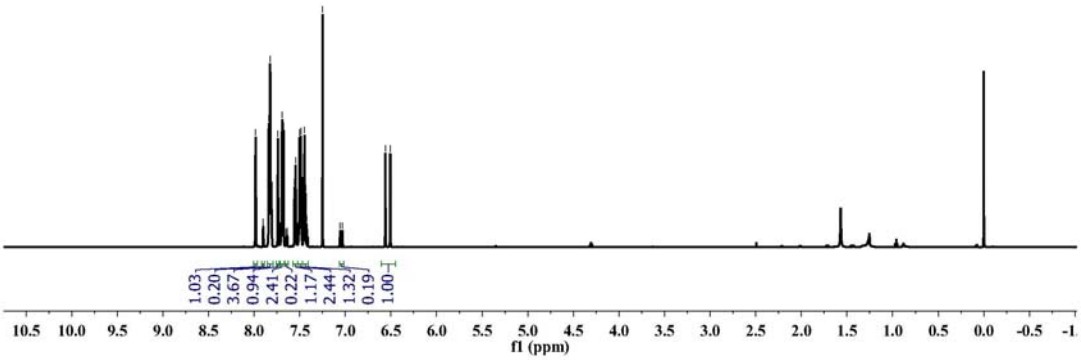


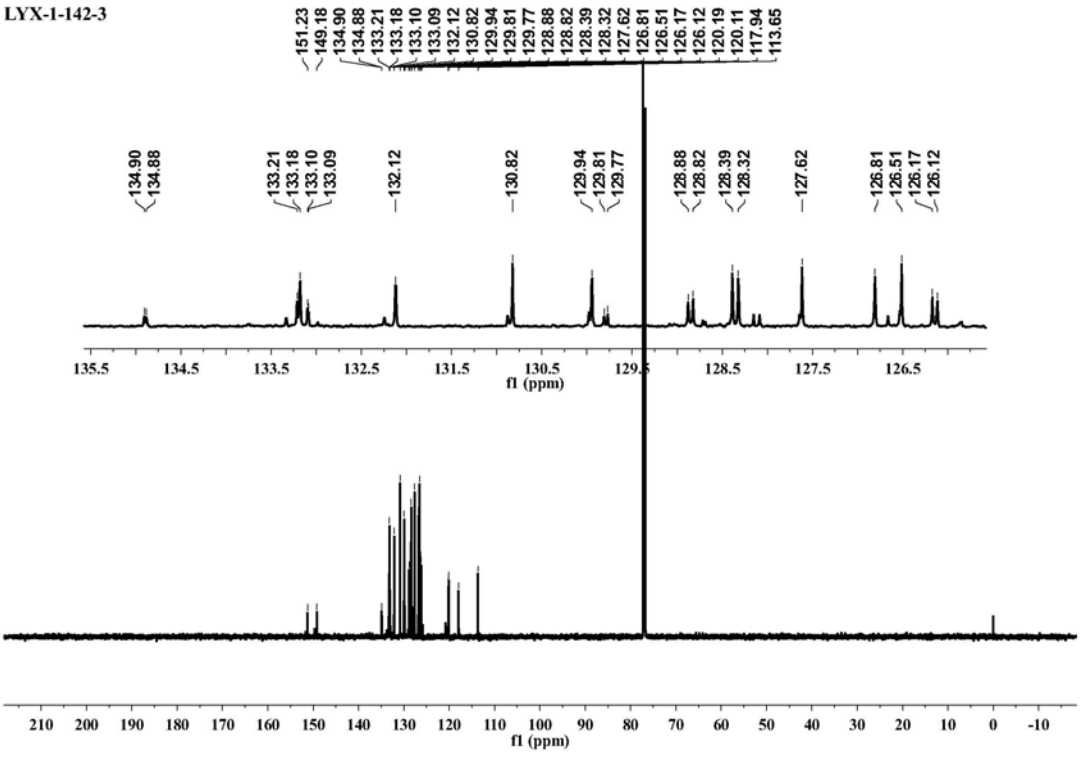
3ak

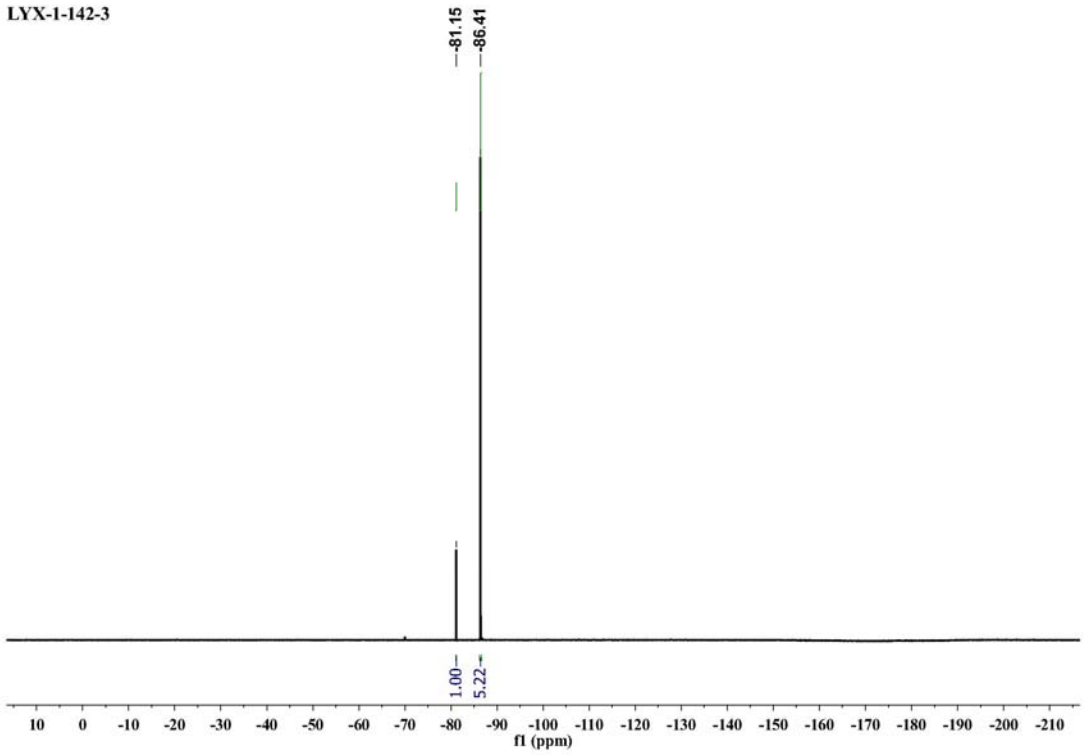




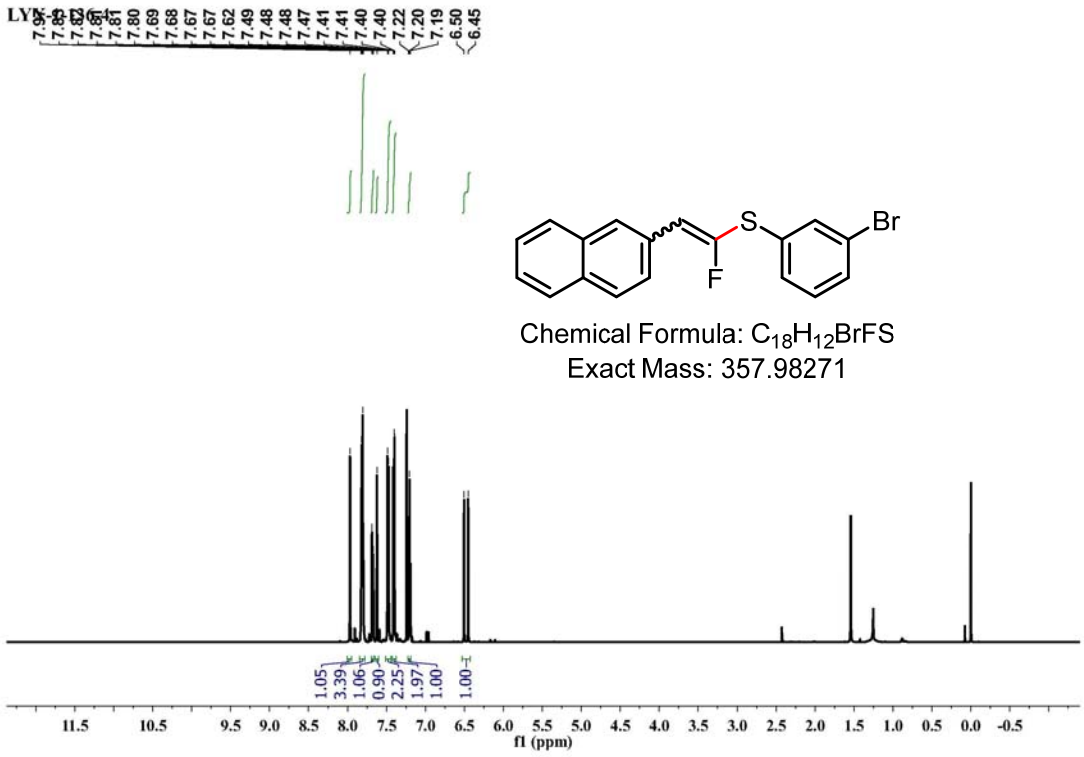
Chemical Formula: $C_{19}H_{12}FNS$
Exact Mass: 305.06745





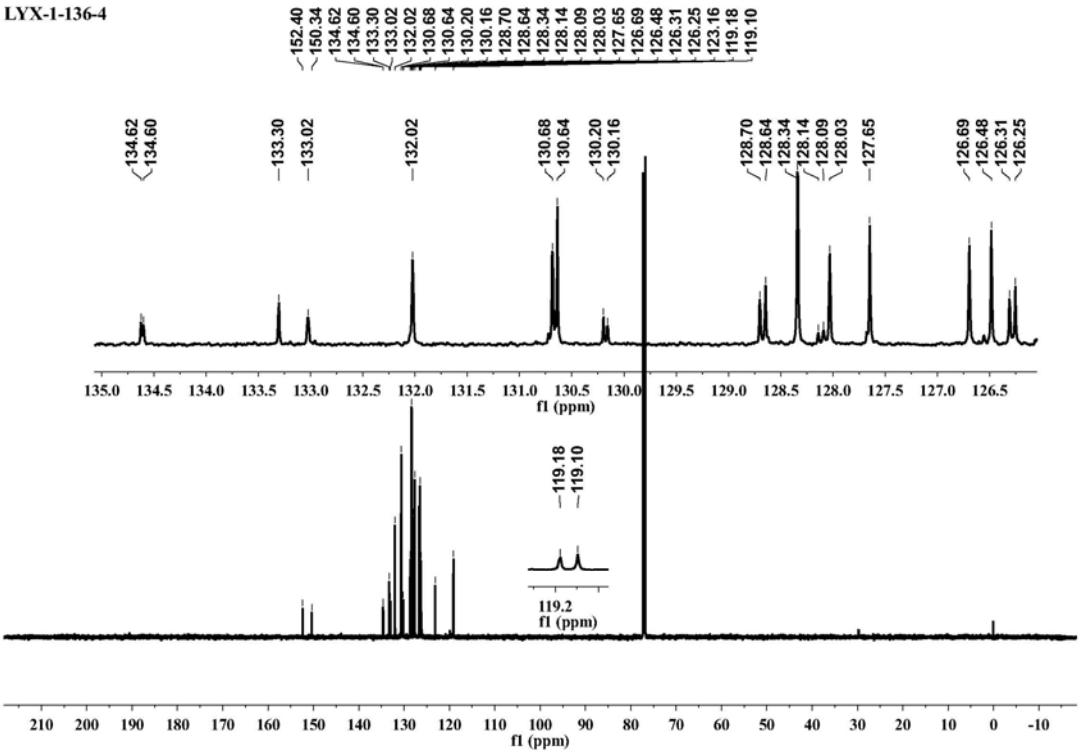


3al

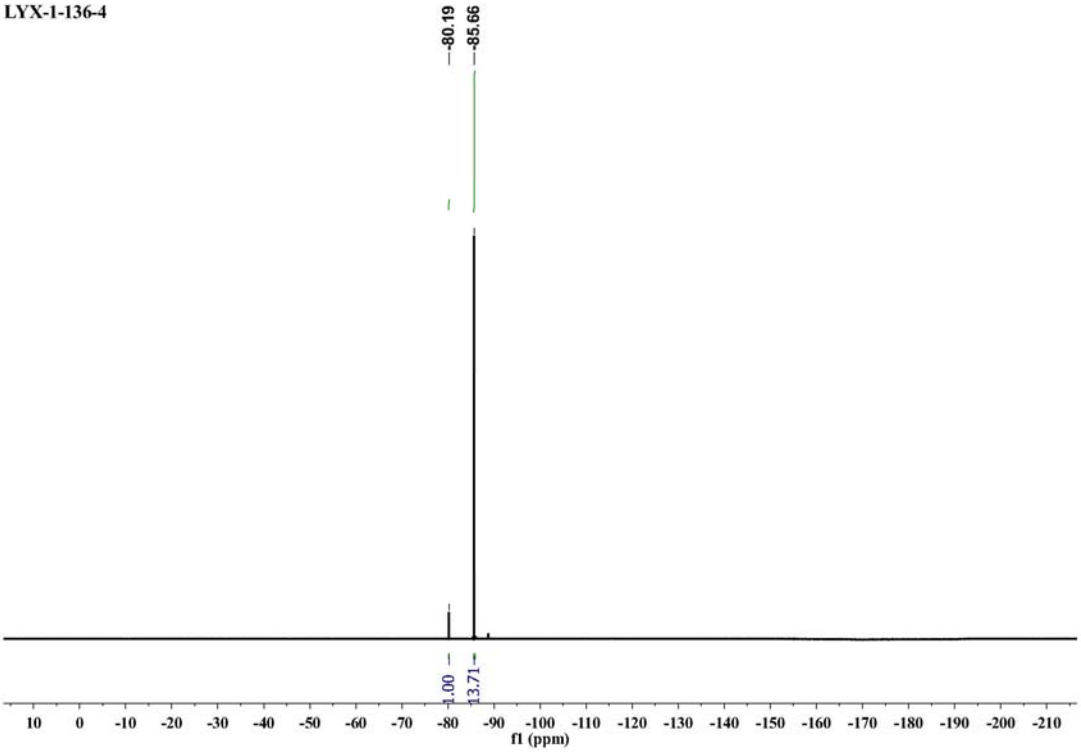


Chemical Formula: $C_{18}H_{12}BrFS$
Exact Mass: 357.98271

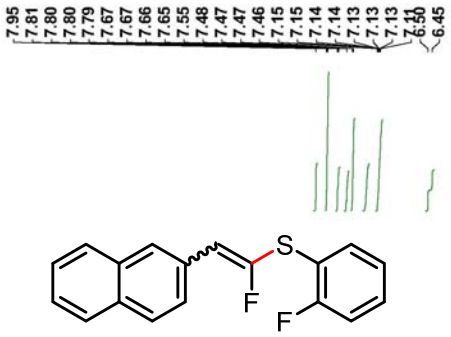
LYX-1-136-4



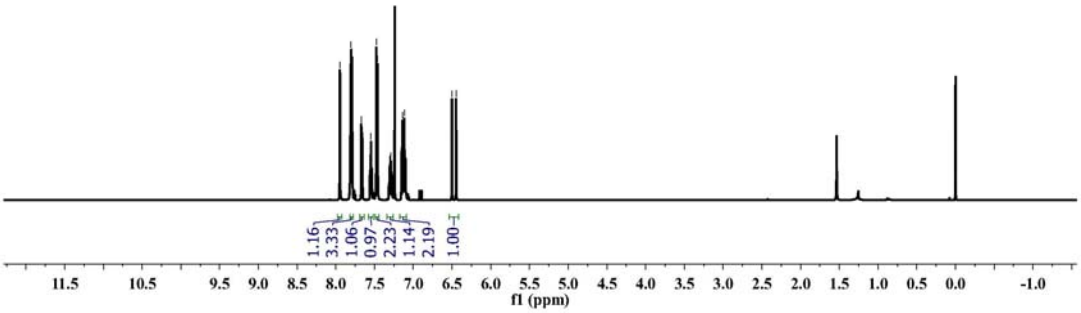
LYX-1-136-4

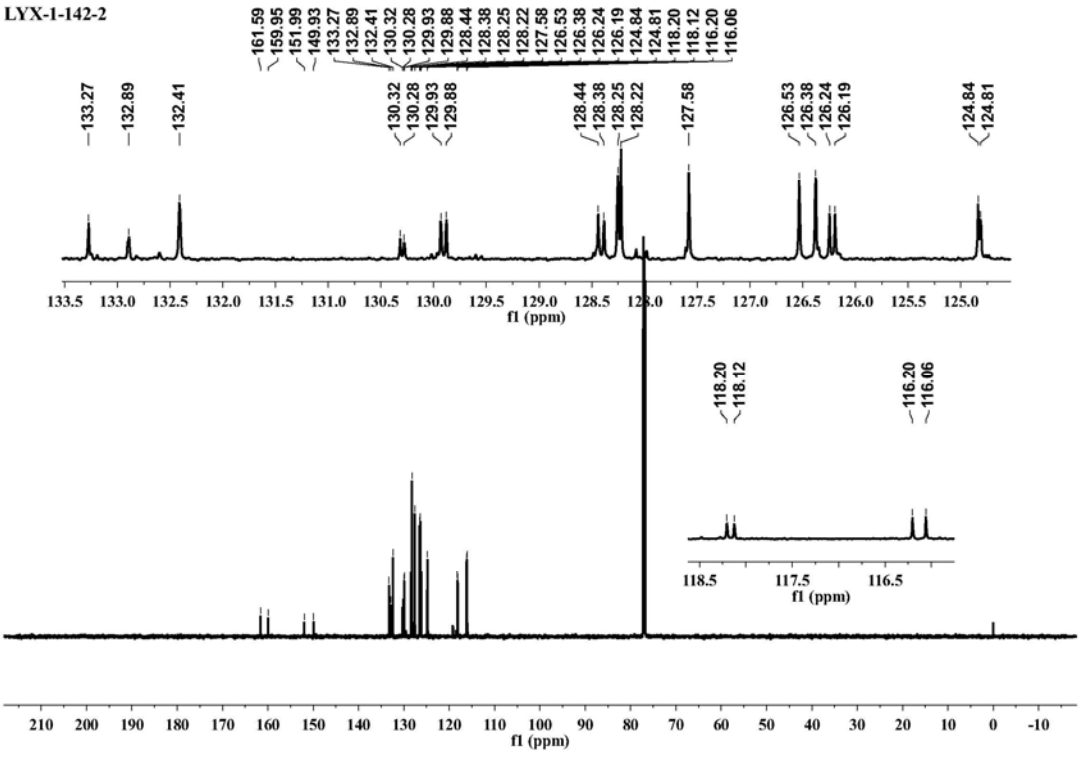


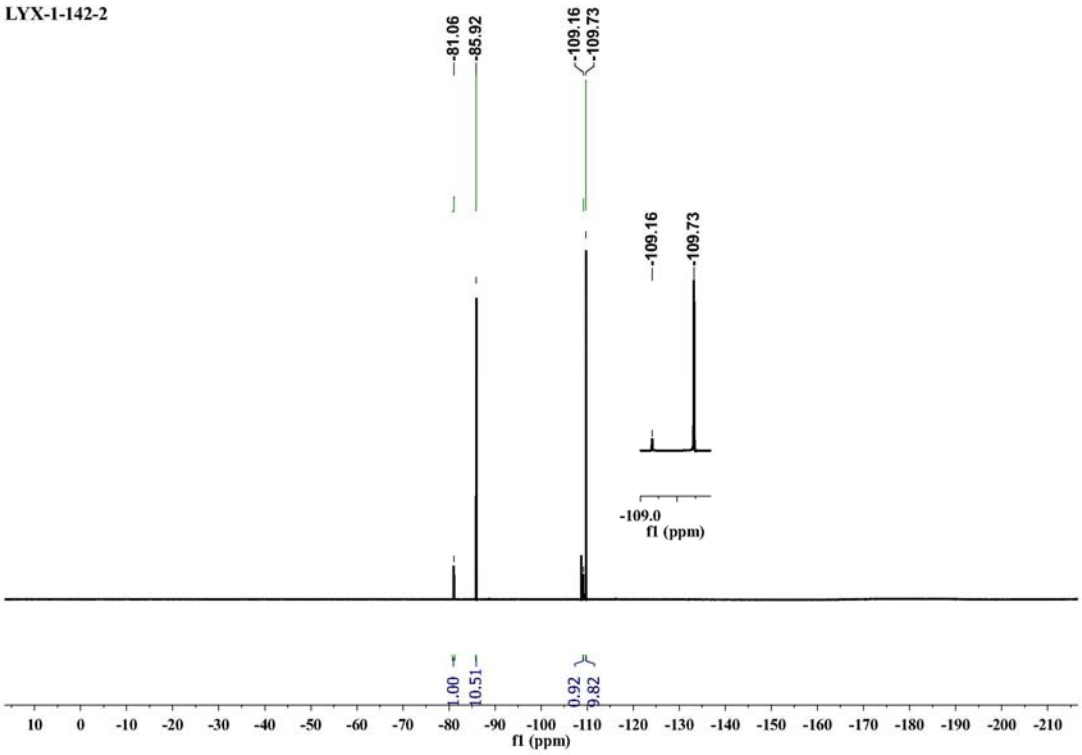
3am



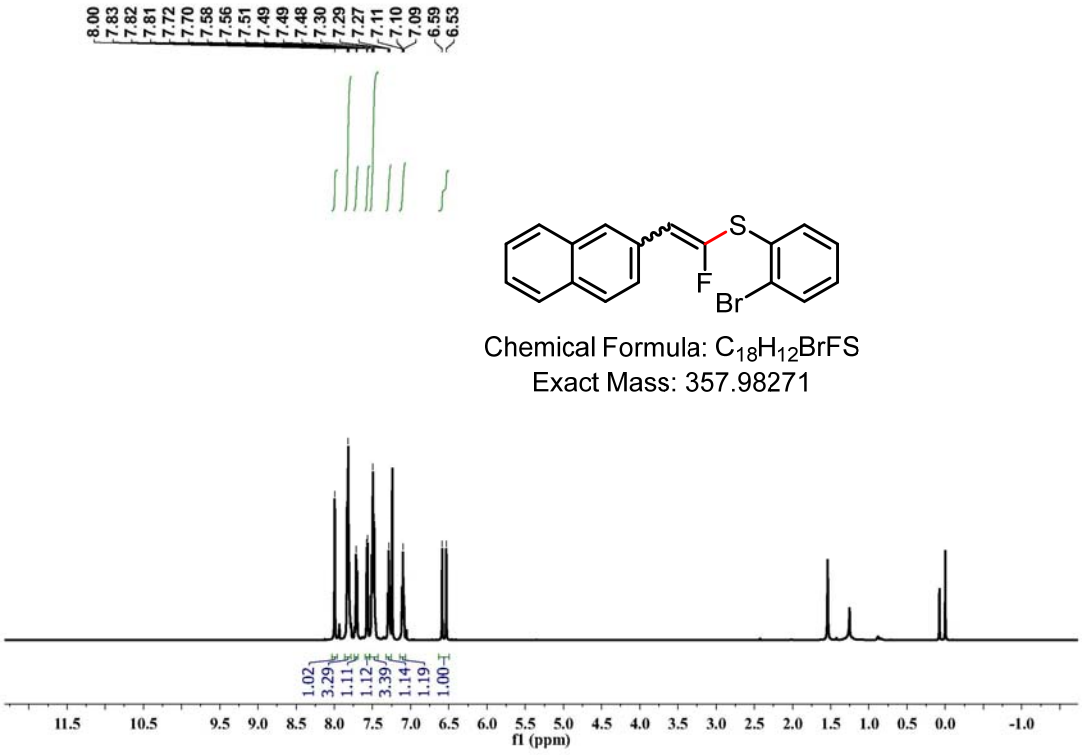
Chemical Formula: $C_{18}H_{12}F_2S$
Exact Mass: 298.06278



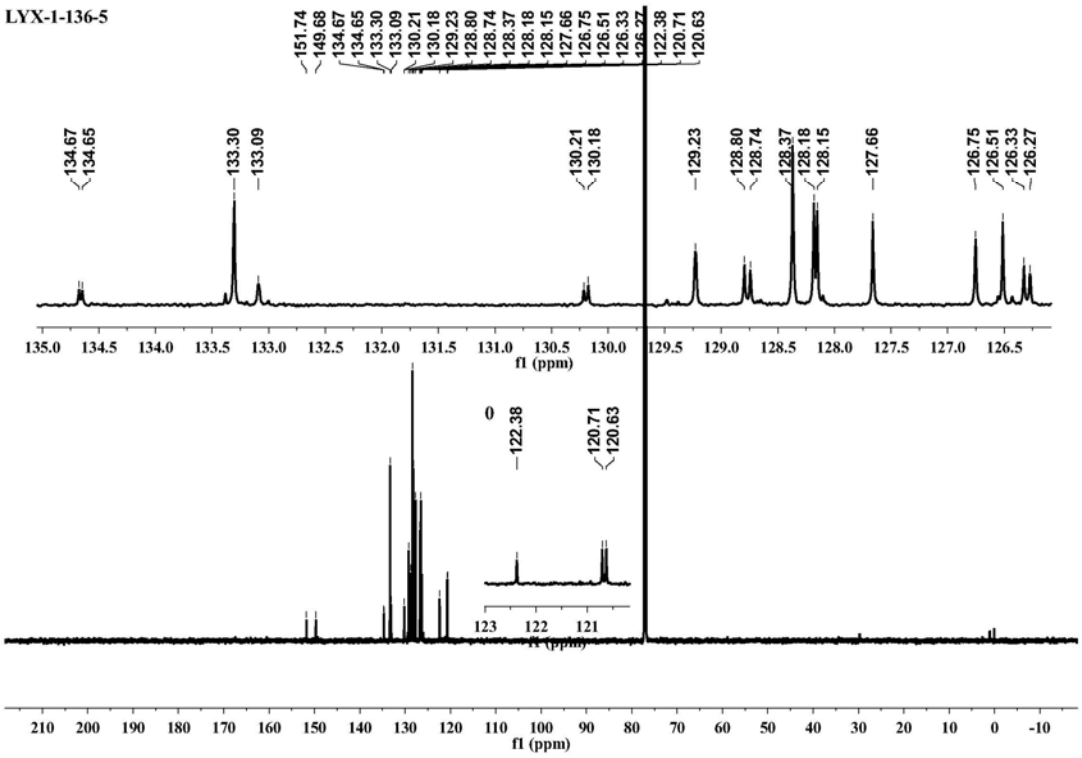


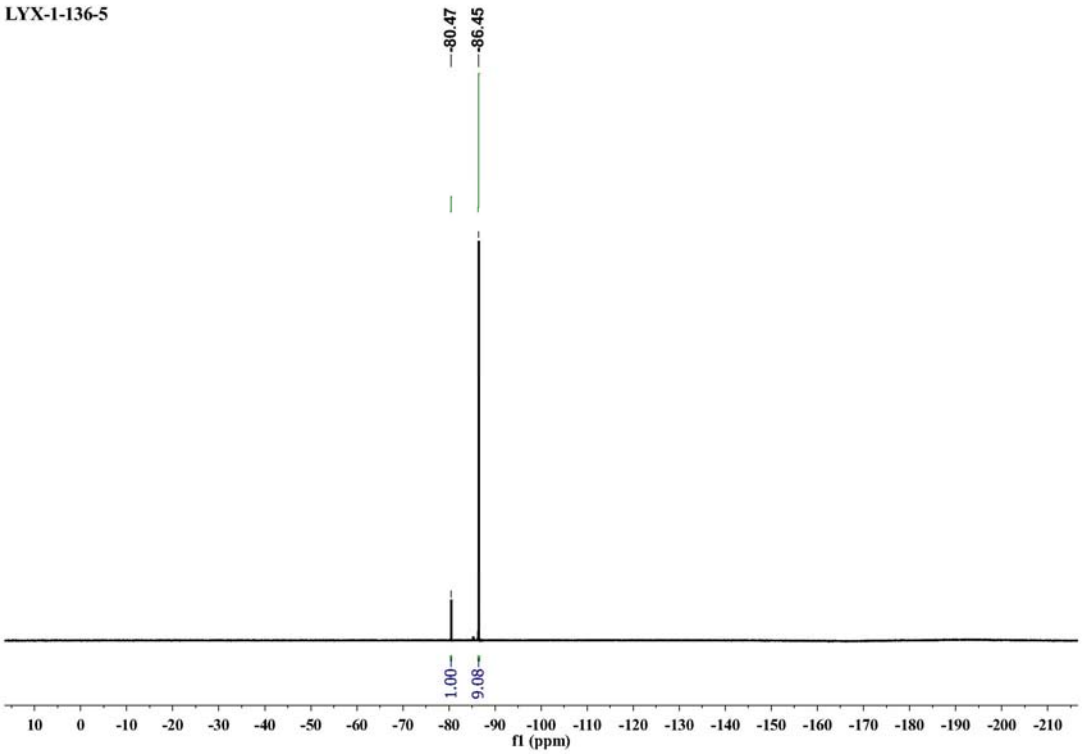


3an

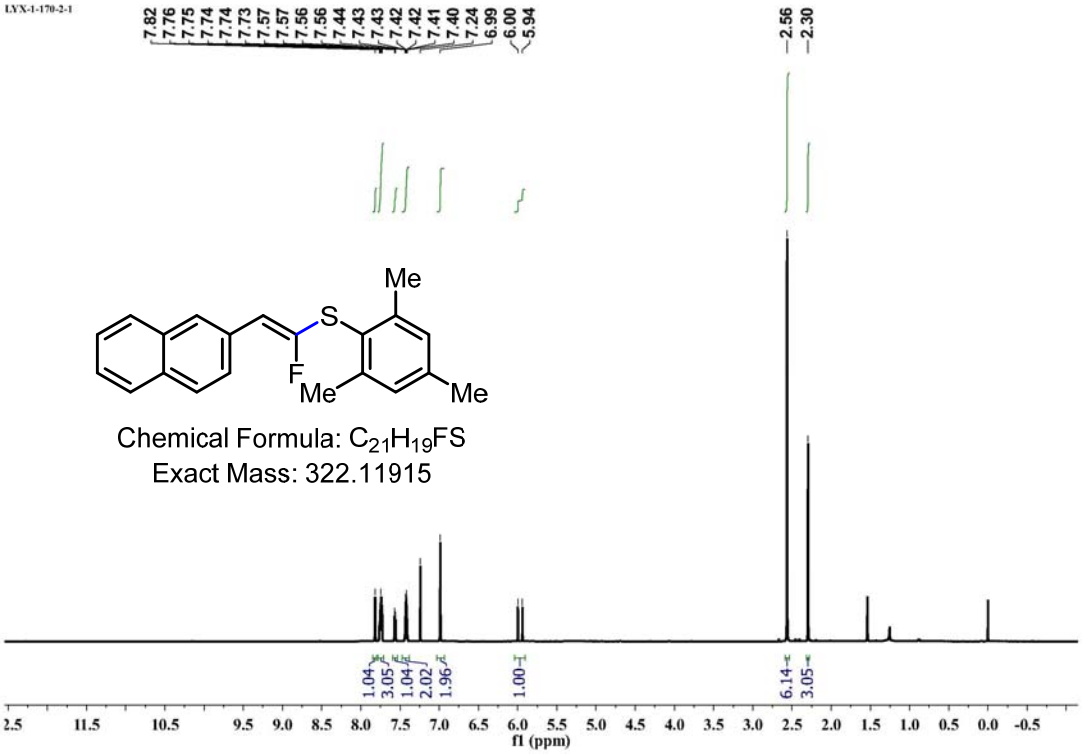


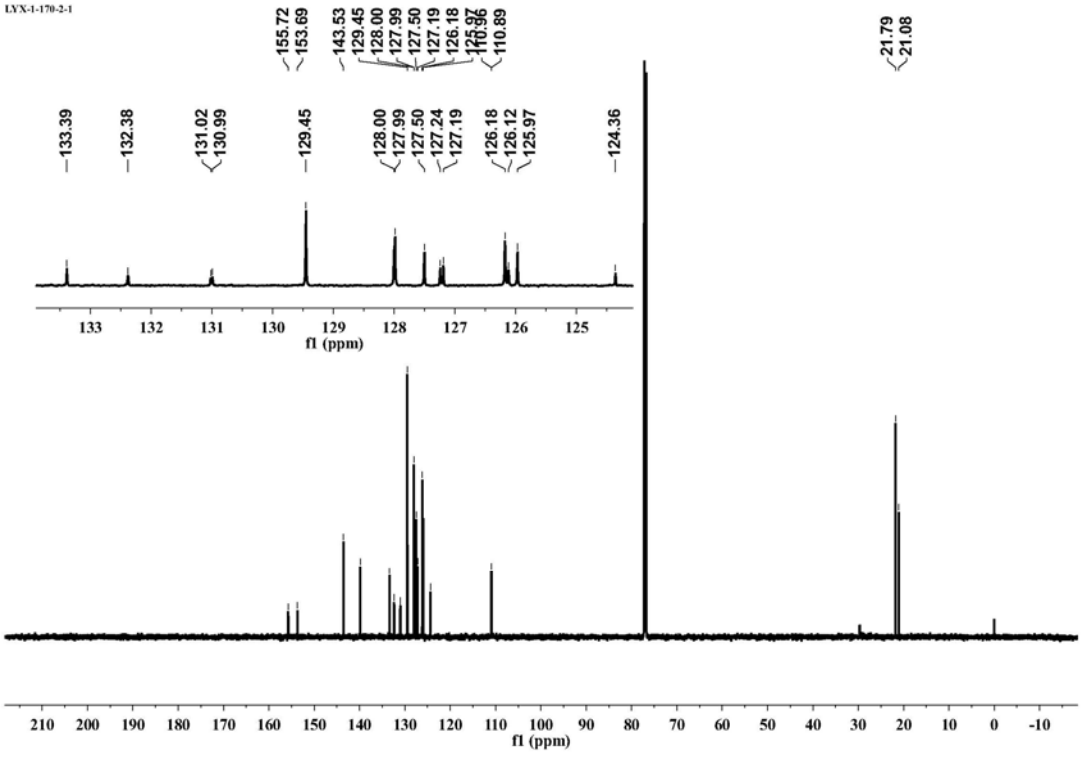
Chemical Formula: $C_{18}H_{12}BrFS$
Exact Mass: 357.98271

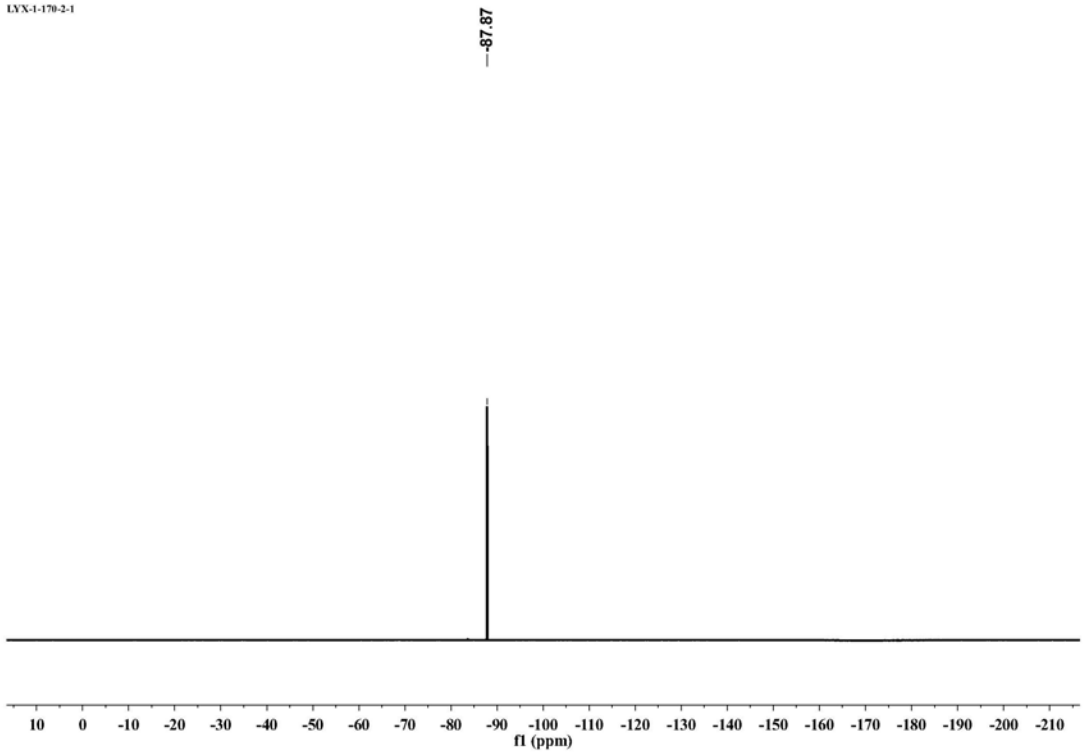

LYX-1-136-5
151.74
149.68
134.67
134.65
133.30
133.09
130.21
130.18
129.23
128.80
128.74
128.37
128.18
128.15
127.66
126.75
126.51
126.33
122.38
120.71
120.63
134.67
134.65
133.30
133.09
130.21
130.18
129.23
128.80
128.74
128.37
128.18
128.15
127.66
126.75
126.51
126.33
126.27
f1 (ppm)
0
122.38
120.71
120.63
123
122
121
f1 (ppm)
f1 (ppm)


LYX-1-136-5
-80.47
-86.45
1.00
9.08
f1 (ppm)

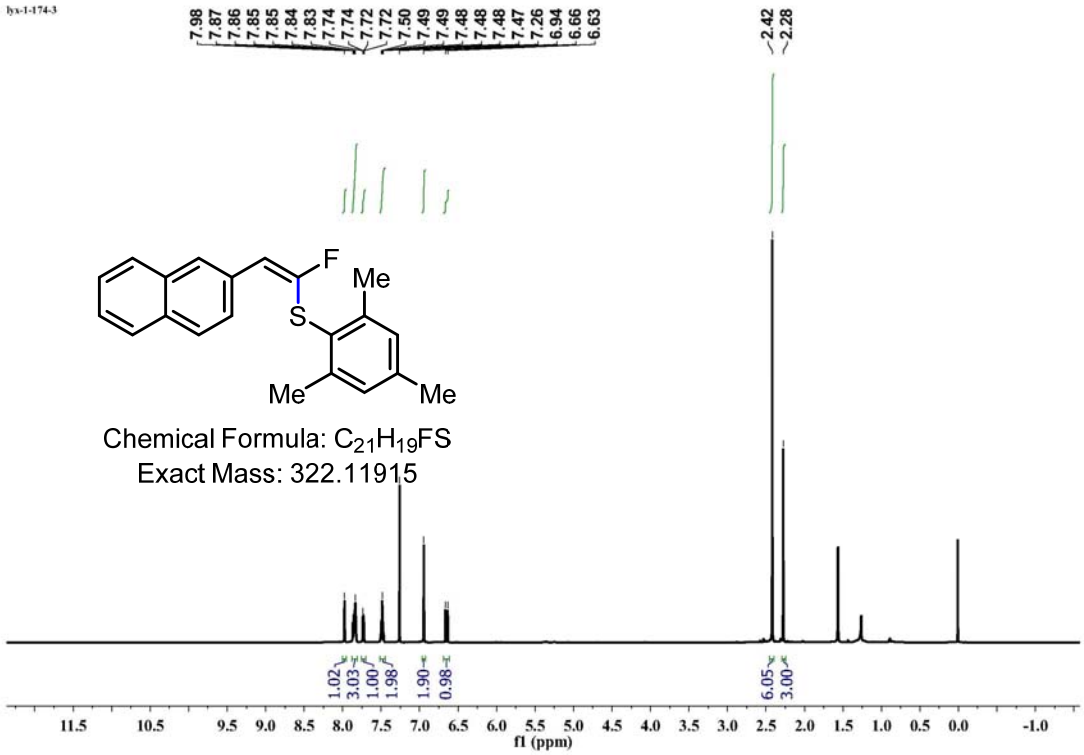
(*E*)-3ao

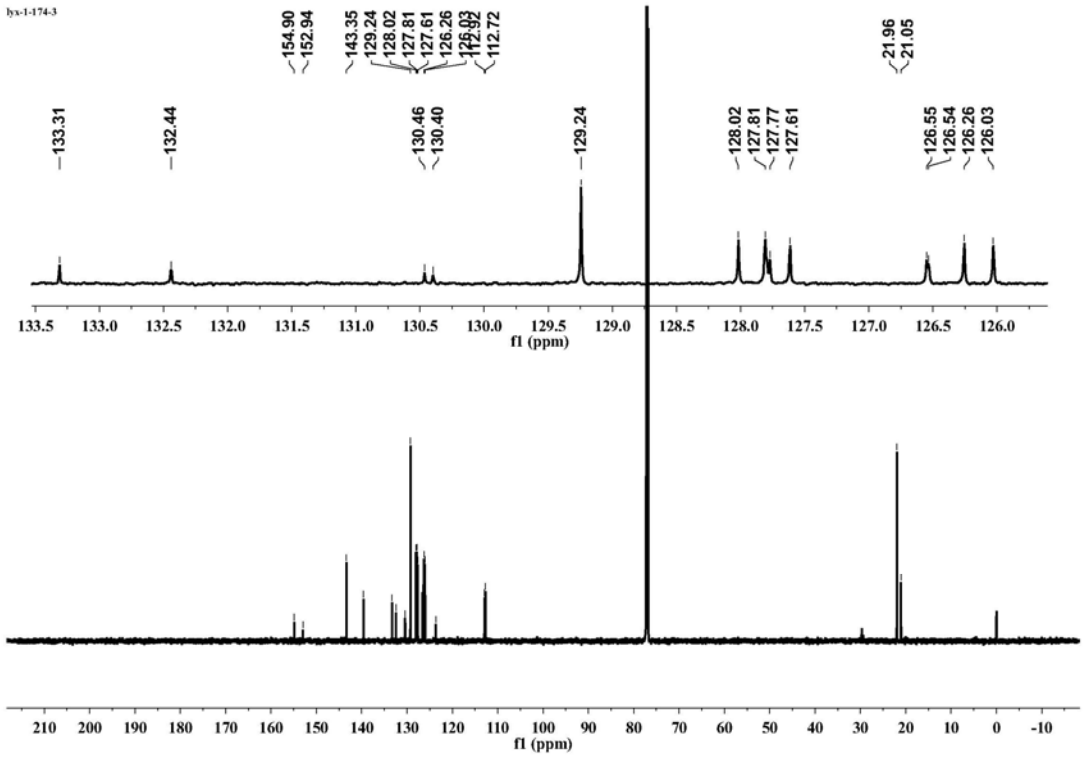

LYX-1-170-2-1
7.82
7.76
7.75
7.74
7.74
7.73
7.57
7.57
7.56
7.56
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.24
6.99
6.00
5.94
2.56
2.30
Me
S
F
Me
Me
Chemical Formula: C21H19FS
Exact Mass: 322.11915
1.04
3.05
1.04
2.02
1.96
1.00
6.14
3.05
f1 (ppm)

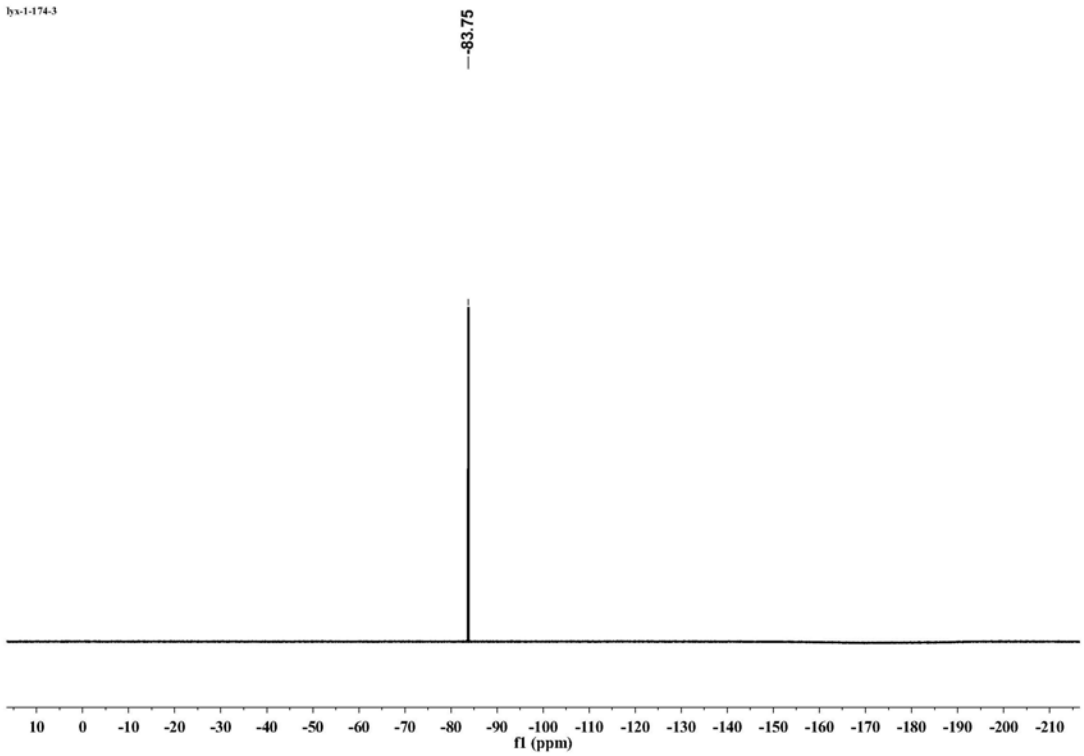

LYX-1-170-2-1
155.72
153.69
143.53
129.45
128.00
127.99
127.50
127.19
126.18
125.97
110.96
110.89
21.79
21.08
133.39
132.38
131.02
130.99
129.45
128.00
127.99
127.50
127.24
127.19
126.18
126.12
125.97
124.36
f1 (ppm)
f1 (ppm)


LYX-1-170-2-1
-87.87
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

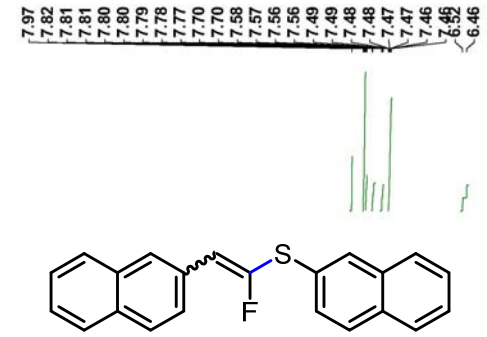
(*E*)-3ao


lyx-1-174-3
7.98 7.87 7.86 7.85 7.85 7.84 7.83 7.74 7.74 7.72 7.72 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.26 6.94 6.66 6.63
2.42 2.28
F
Me
S
Me
Me
Chemical Formula: C21H19FS
Exact Mass: 322.11915
1.02 3.03 1.00 1.98 1.90 0.98 6.05 3.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

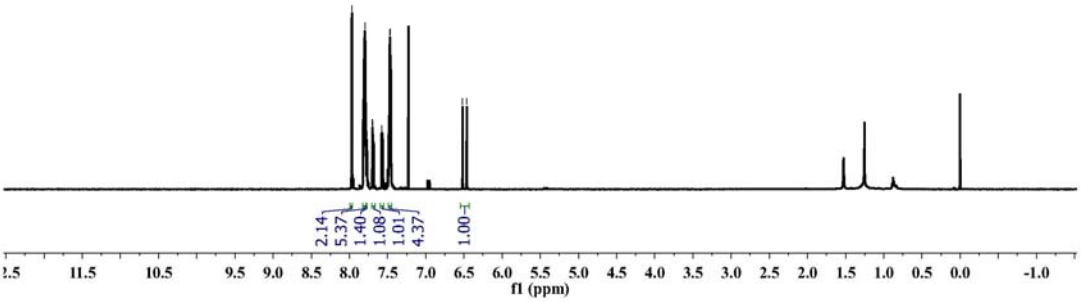

lyx-1-174-3
154.90
152.94
143.35
129.24
128.02
127.81
127.61
126.26
112.72
21.96
21.05
133.31
132.44
130.46
130.40
129.24
128.02
127.81
127.77
127.61
126.55
126.54
126.26
126.03
f1 (ppm)
f1 (ppm)

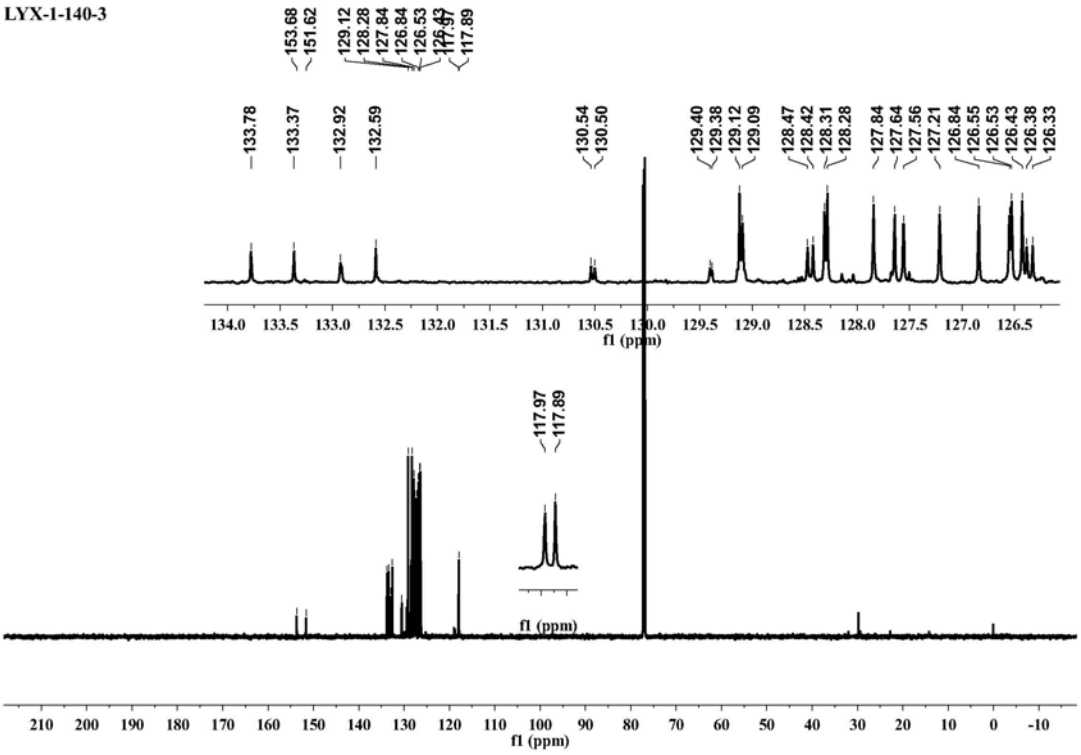

lyx-1-174-3
-83.75
f1 (ppm)

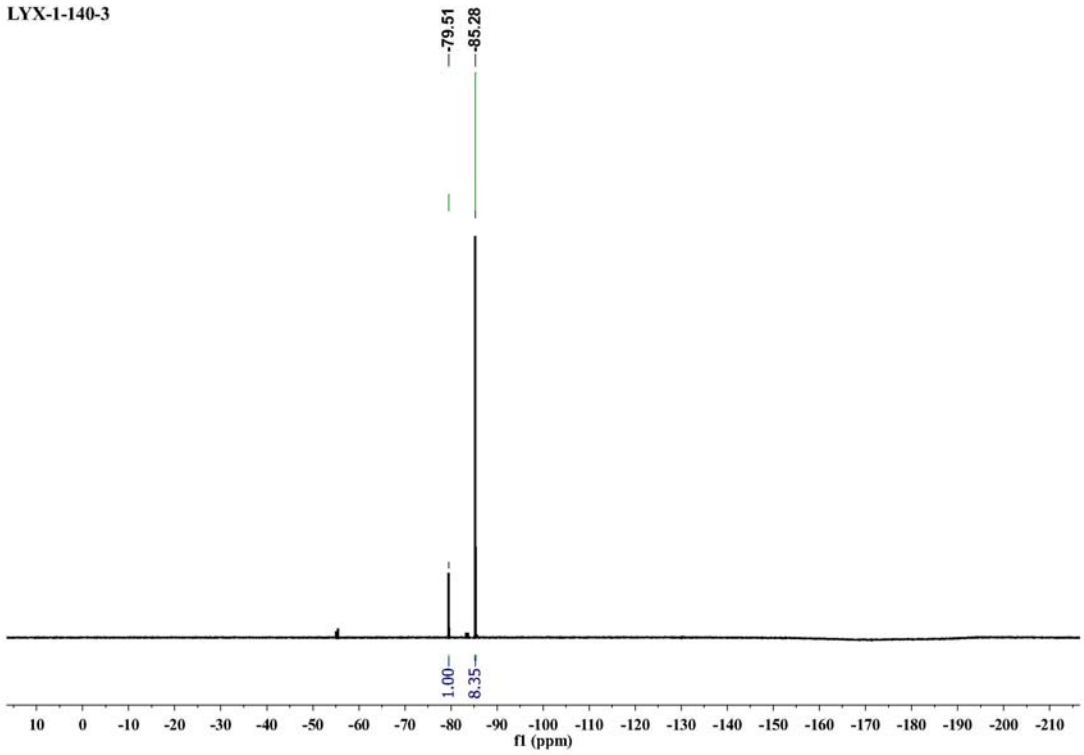
3ap



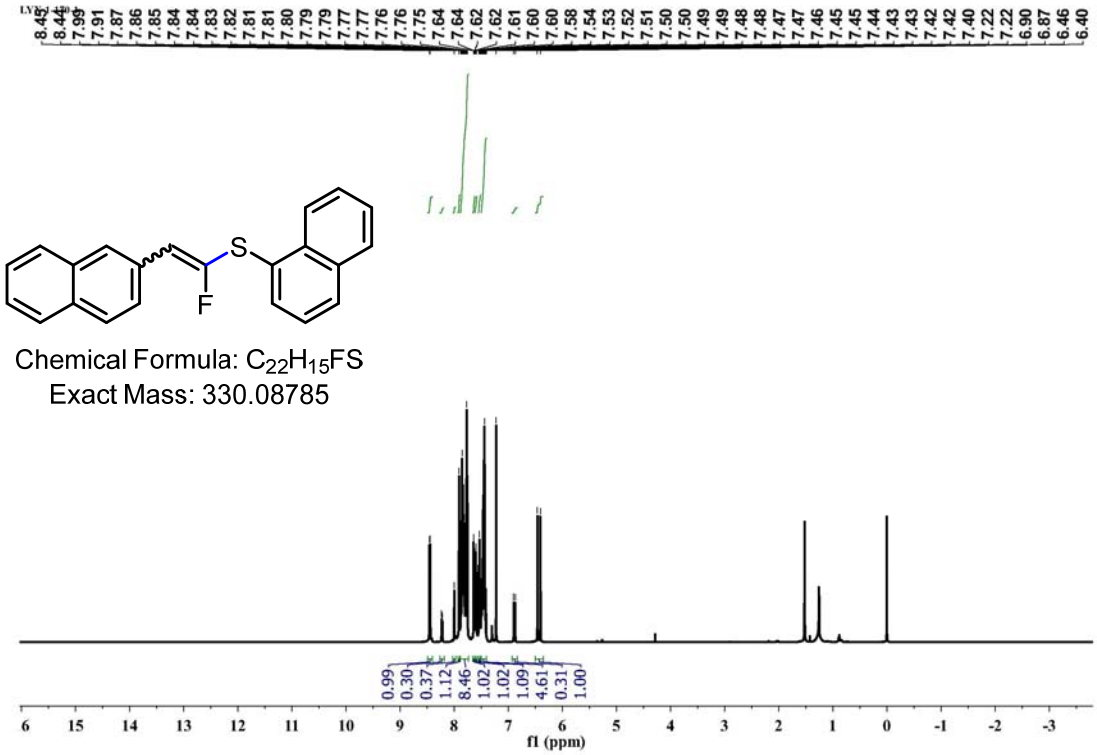
Chemical Formula: $C_{22}H_{15}FS$
Exact Mass: 330.08785



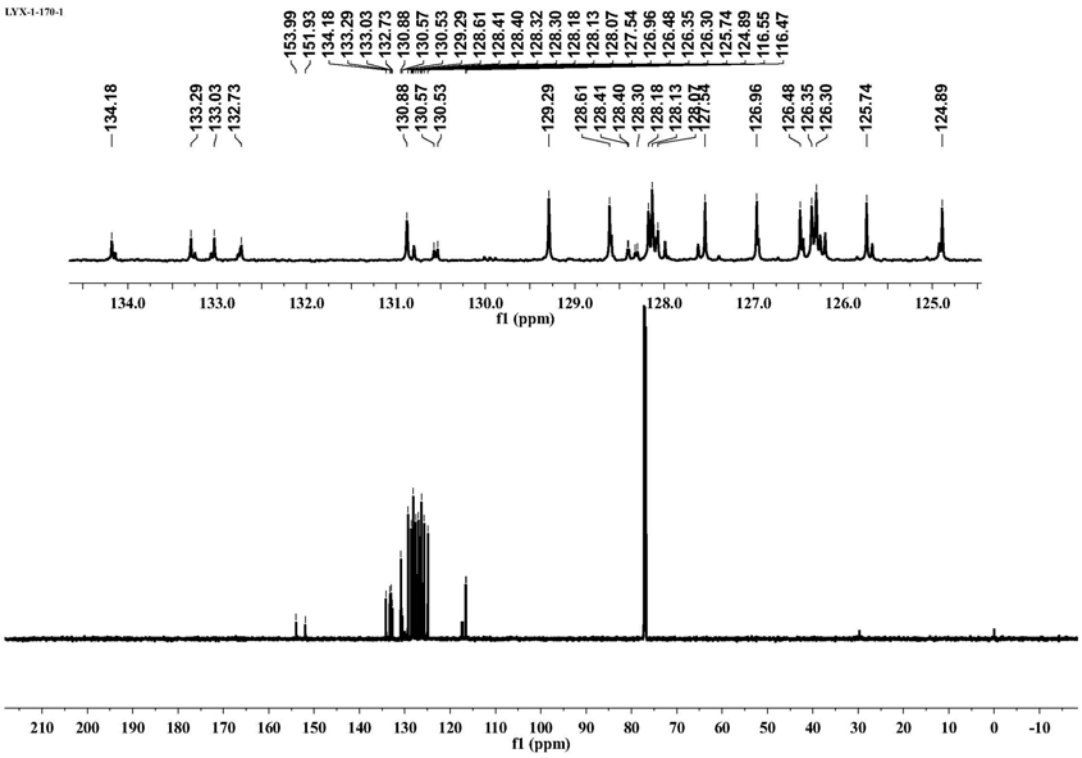


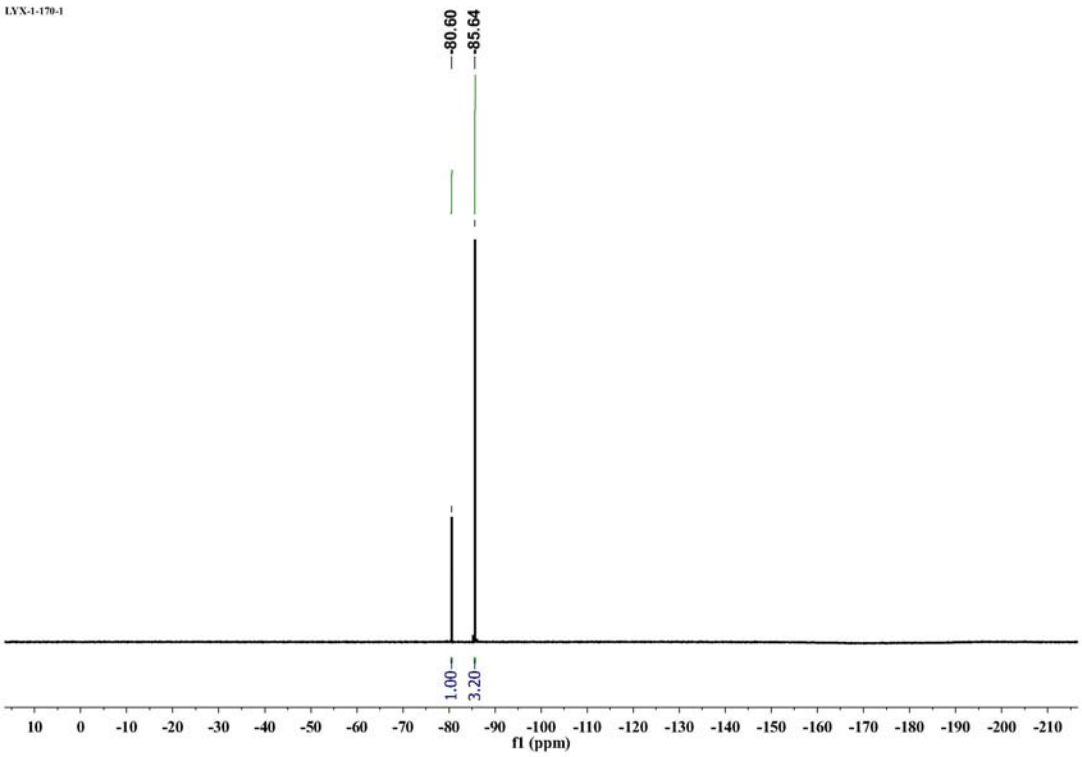


3aq

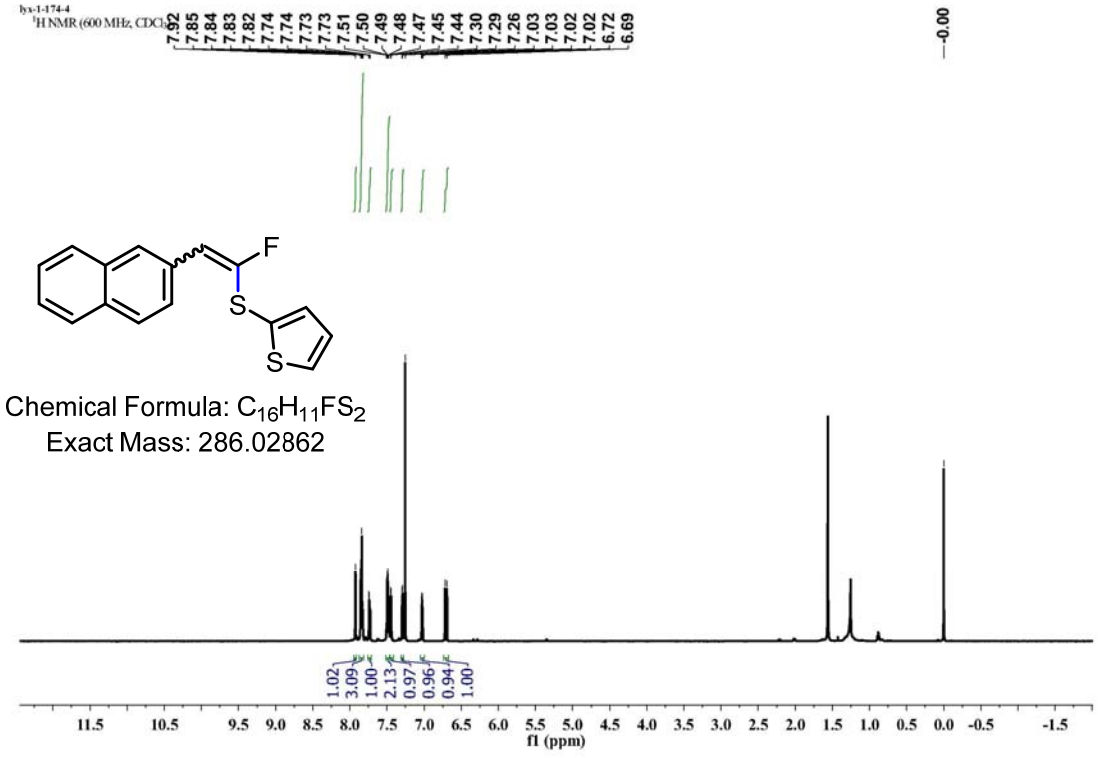


Chemical Formula: $C_{22}H_{15}FS$
Exact Mass: 330.08785

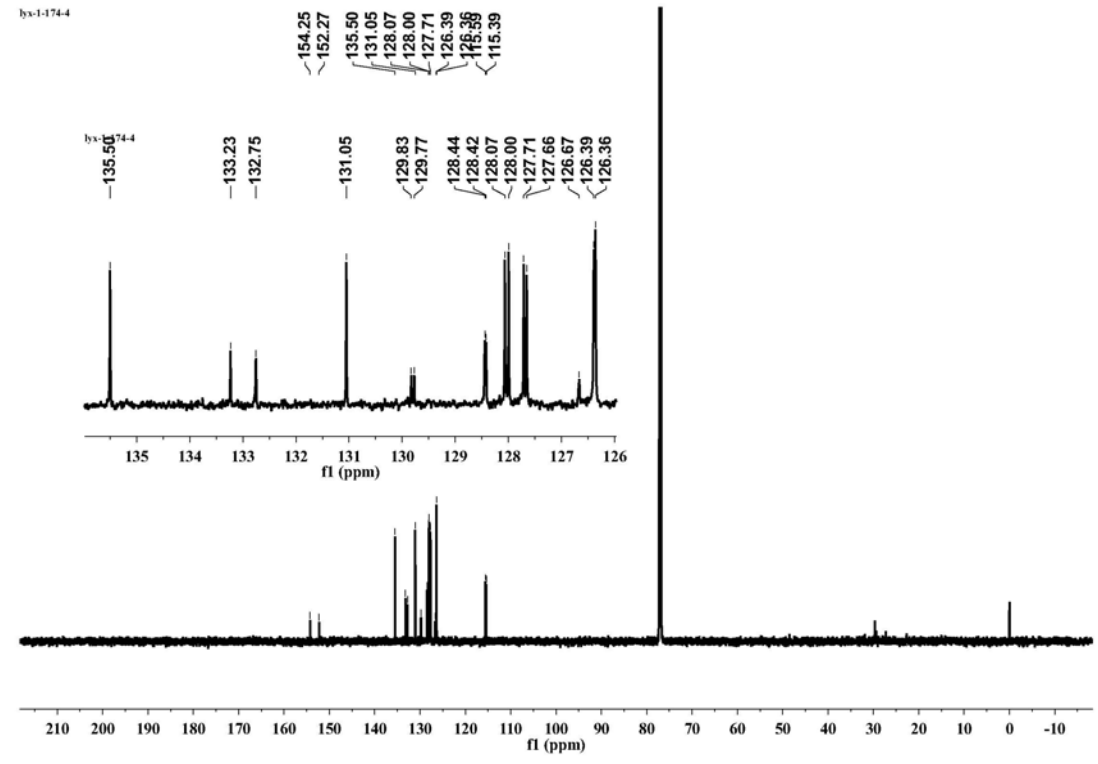

LYX-1-170-1
153.99
151.93
134.18
133.29
133.03
132.73
130.88
130.57
130.53
129.29
128.61
128.41
128.40
128.32
128.30
128.18
128.13
128.07
127.54
126.96
126.48
126.35
126.30
125.74
124.89
116.55
116.47
f1 (ppm)

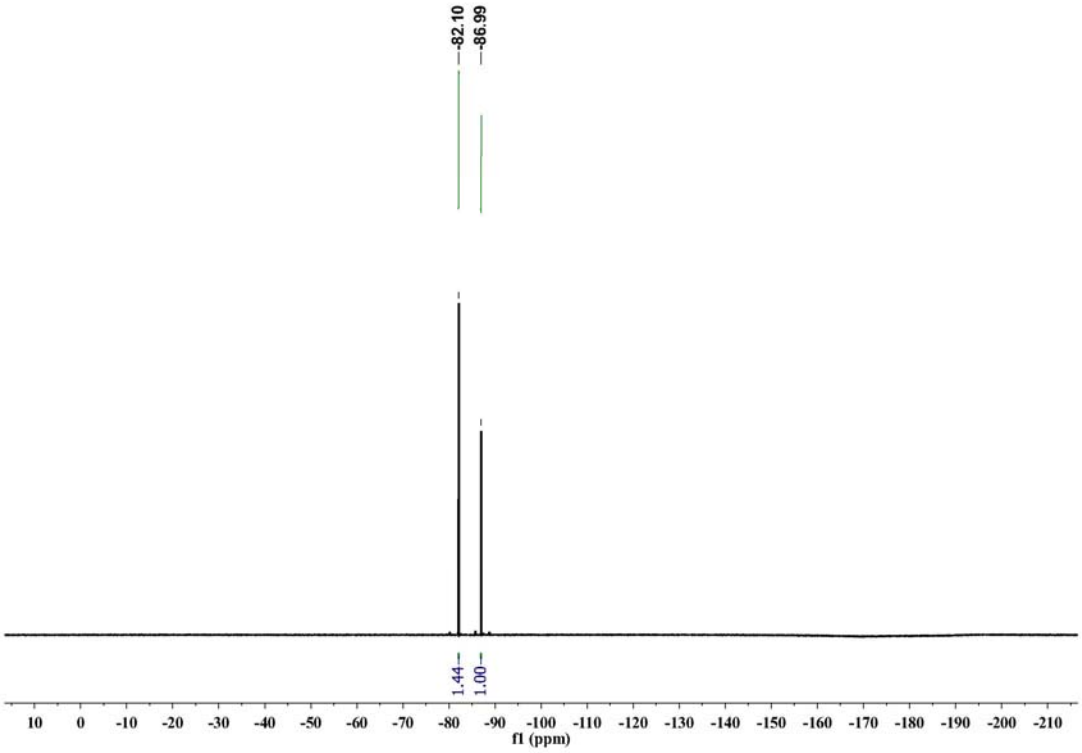

LYX-1-170-1
-80.60
-85.64
1.00
3.20
f1 (ppm)

3ar

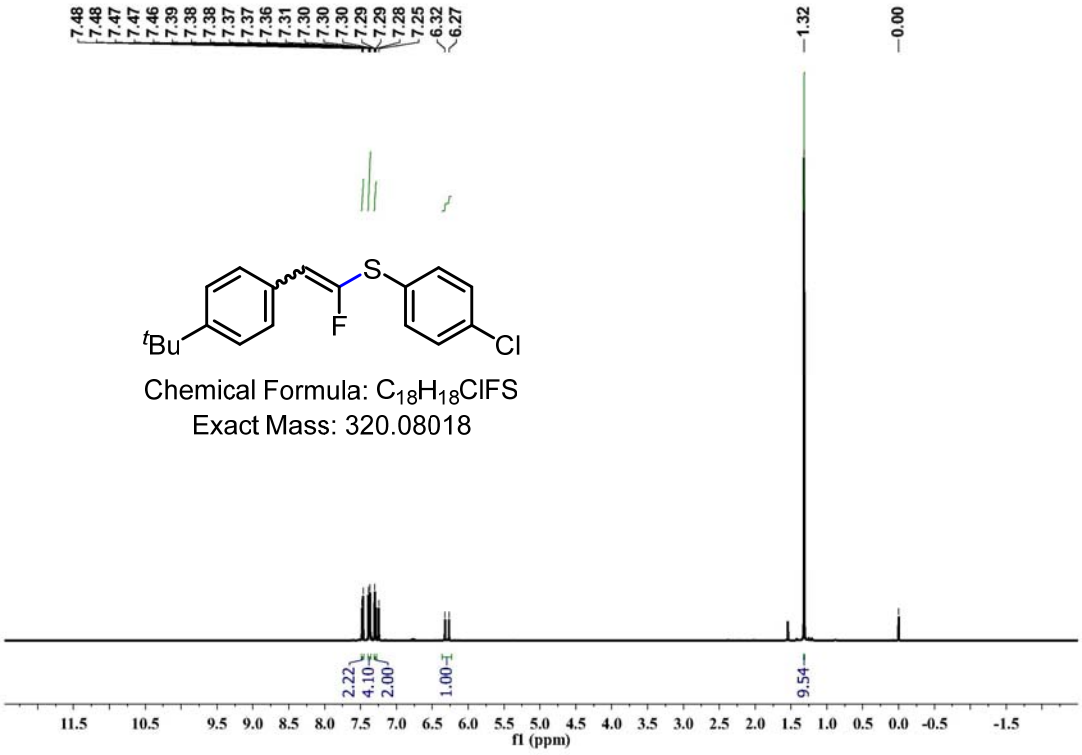


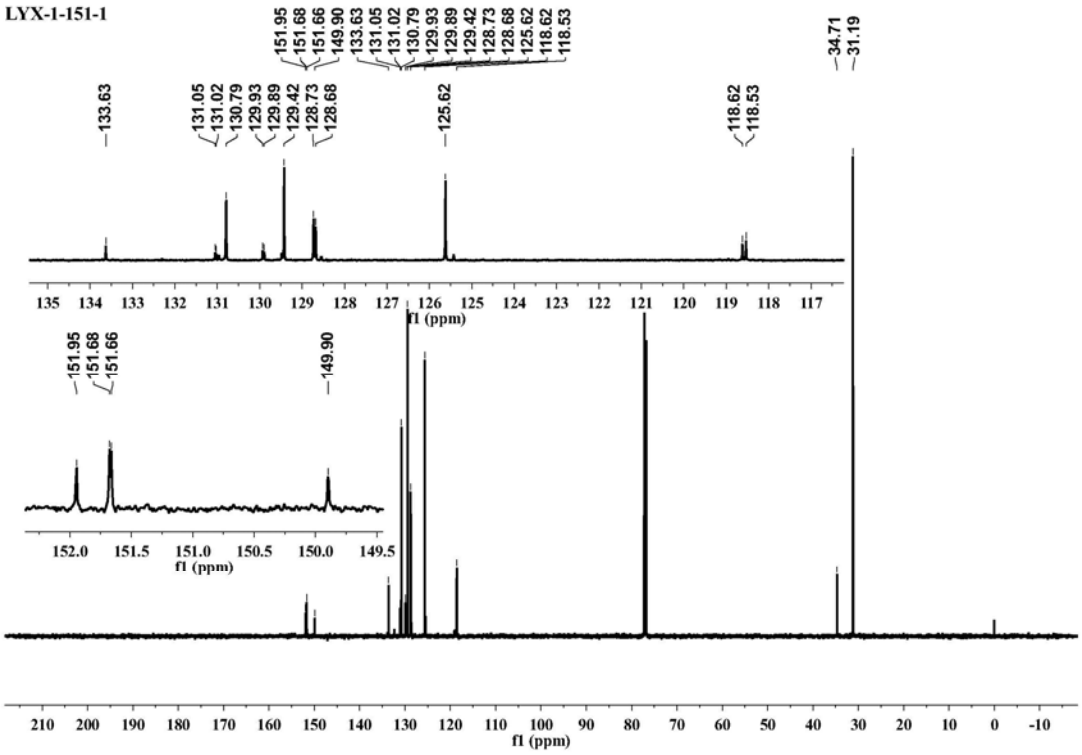
Chemical Formula: $C_{16}H_{11}FS_2$
Exact Mass: 286.02862

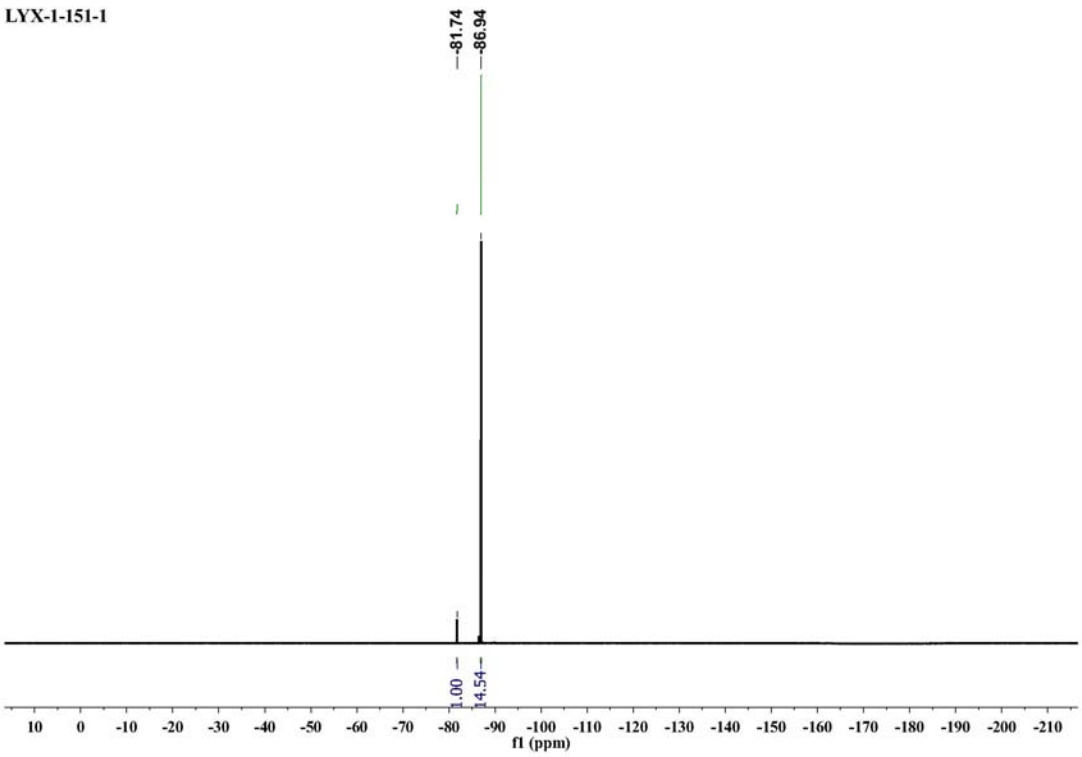



-82.10
-86.99
1.44
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

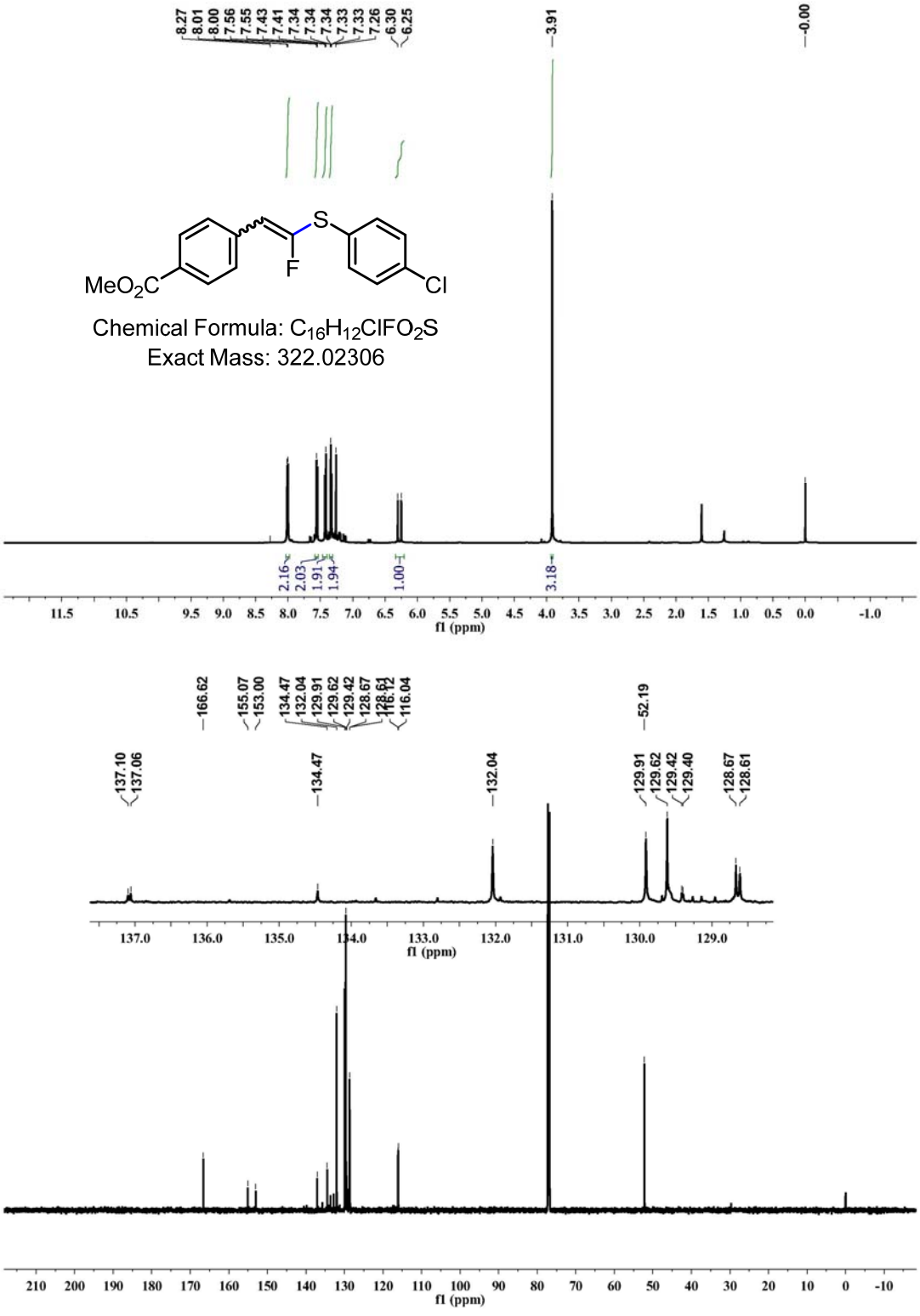
3bh

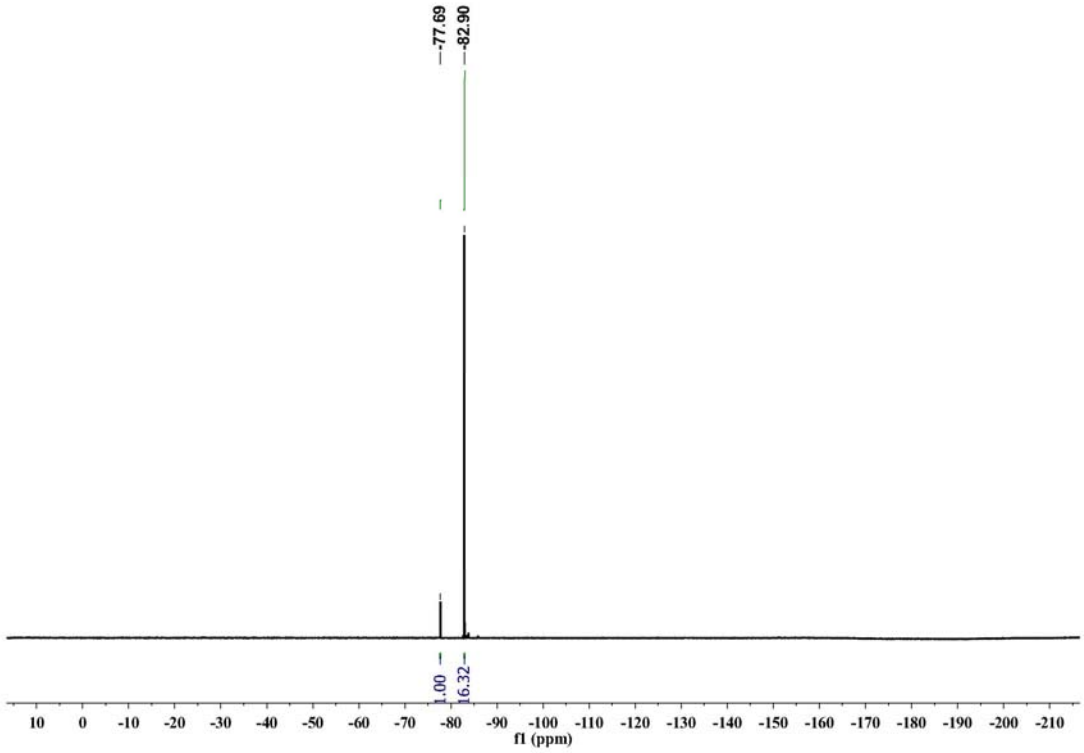

7.48
7.48
7.47
7.47
7.46
7.39
7.38
7.38
7.37
7.37
7.36
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.25
6.32
6.27
1.32
0.00
S
F
tBu
Cl
Chemical Formula: C18H18ClFS
Exact Mass: 320.08018
2.22
4.10
2.00
1.00
9.54
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)


LYX-1-151-1
151.95
151.68
151.66
149.90
133.63
131.05
131.02
130.79
129.93
129.89
129.42
128.73
128.68
125.62
118.62
118.53
34.71
31.19
f1 (ppm)

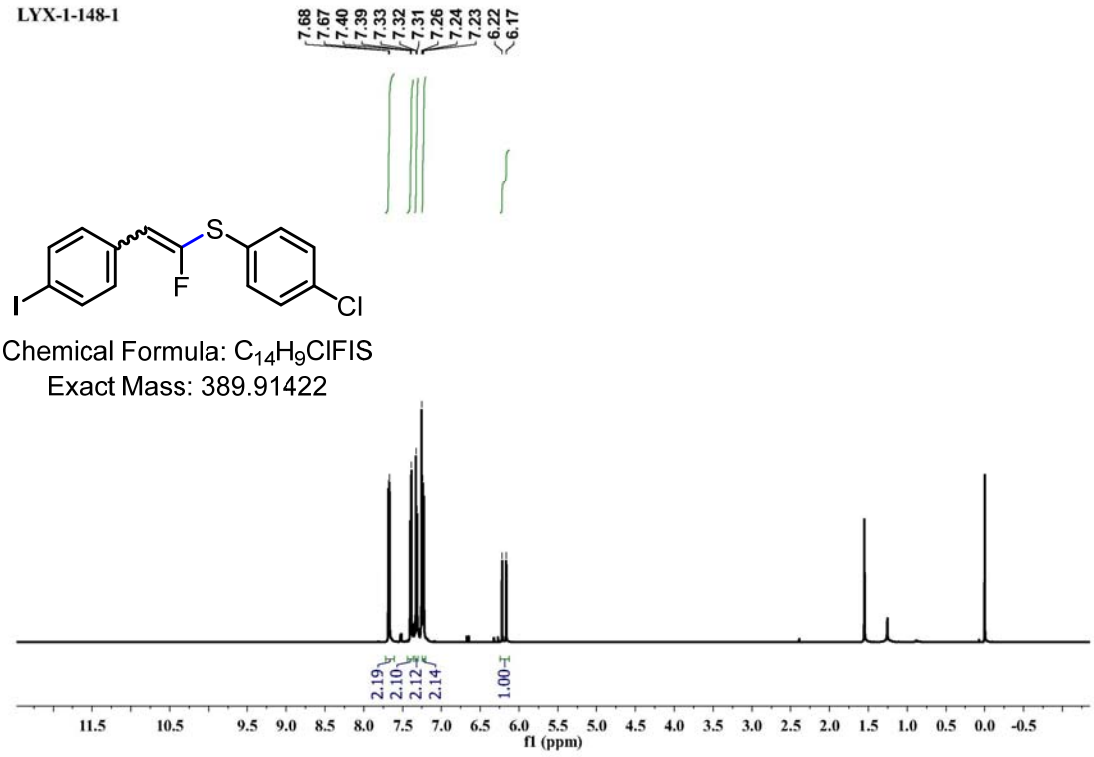

LYX-1-151-1
81.74
86.94
1.00
14.54
f1 (ppm)

3ch

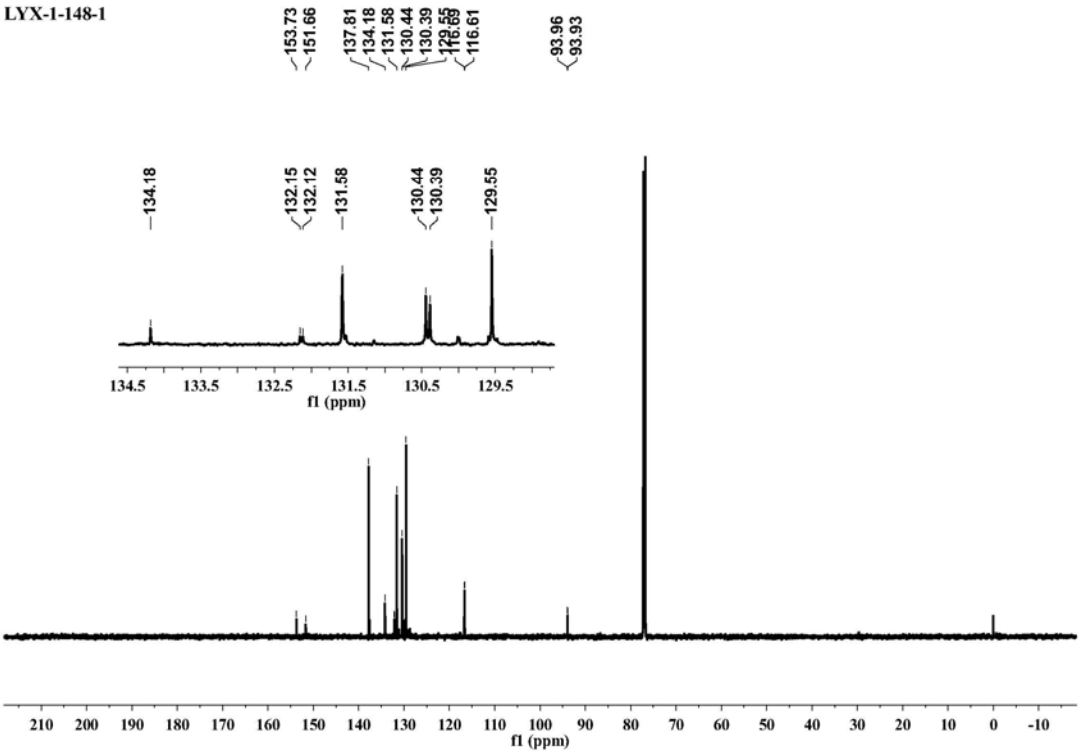

8.27
8.01
8.00
7.56
7.55
7.43
7.41
7.34
7.34
7.34
7.33
7.33
7.26
6.30
6.25
3.91
0.00
S
F
MeO2C
Cl
Chemical Formula: C16H12ClFO2S
Exact Mass: 322.02306
2.16
2.03
1.91
1.94
1.00
3.18
f1 (ppm)
166.62
155.07
153.00
134.47
132.04
129.91
129.62
129.42
128.67
128.61
116.12
116.04
52.19
137.10
137.06
134.47
132.04
129.91
129.62
129.42
129.40
128.67
128.61
f1 (ppm)
f1 (ppm)


-77.69
-82.90
1.00
16.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

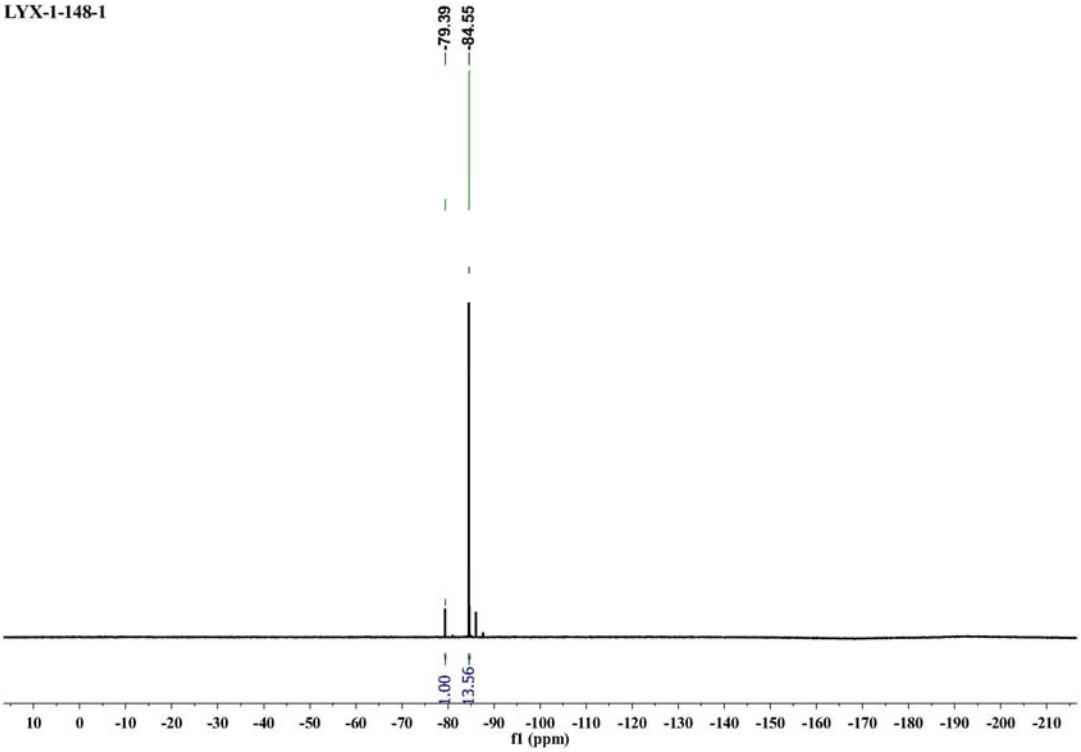
3dh


LYX-1-148-1
7.68
7.67
7.40
7.39
7.33
7.32
7.31
7.26
7.24
7.23
6.22
6.17
S
F
I
Cl
Chemical Formula: C14H9ClFIS
Exact Mass: 389.91422
2.19
2.10
2.12
2.14
1.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

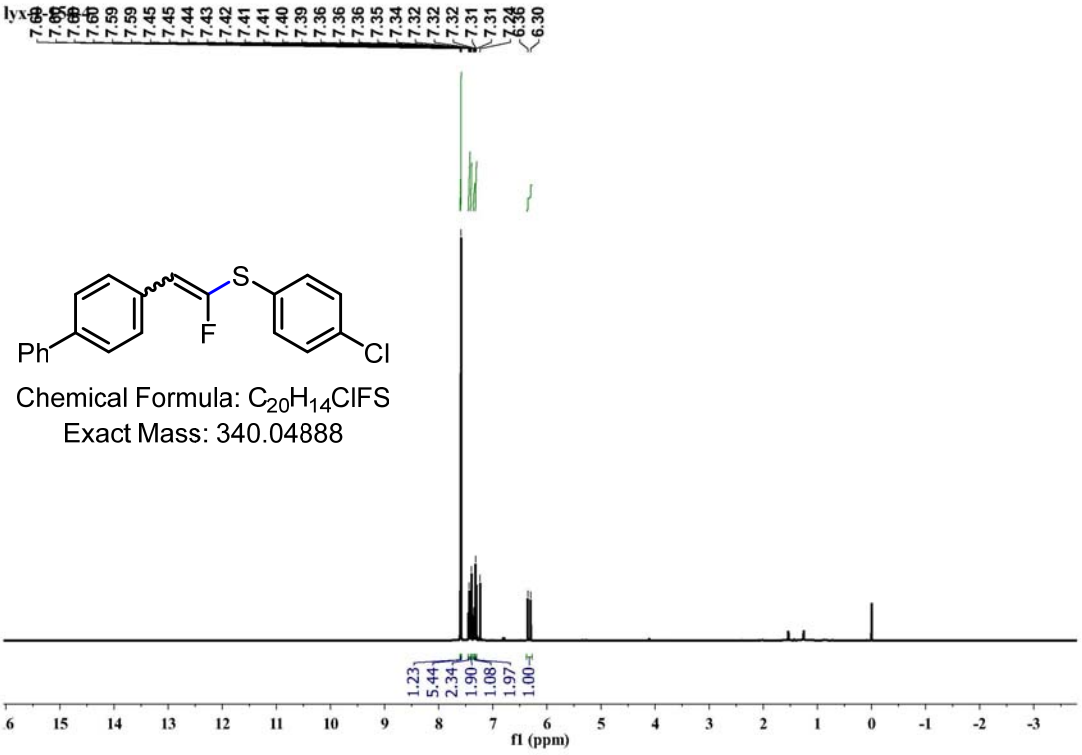
LYX-1-148-1

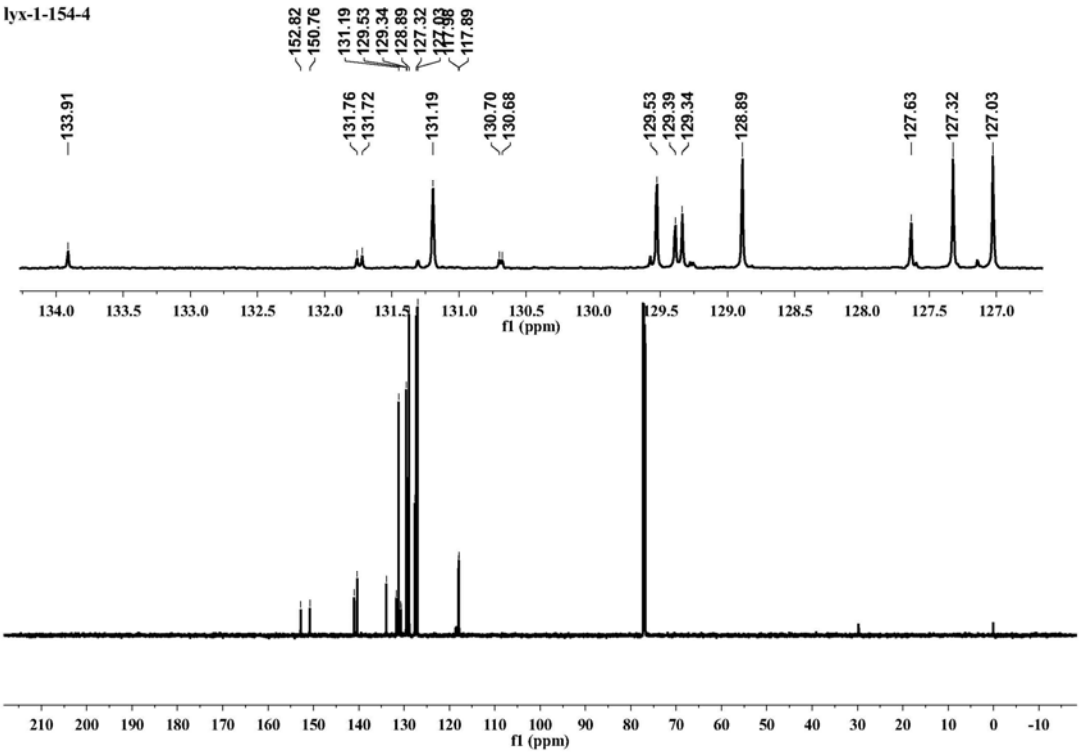


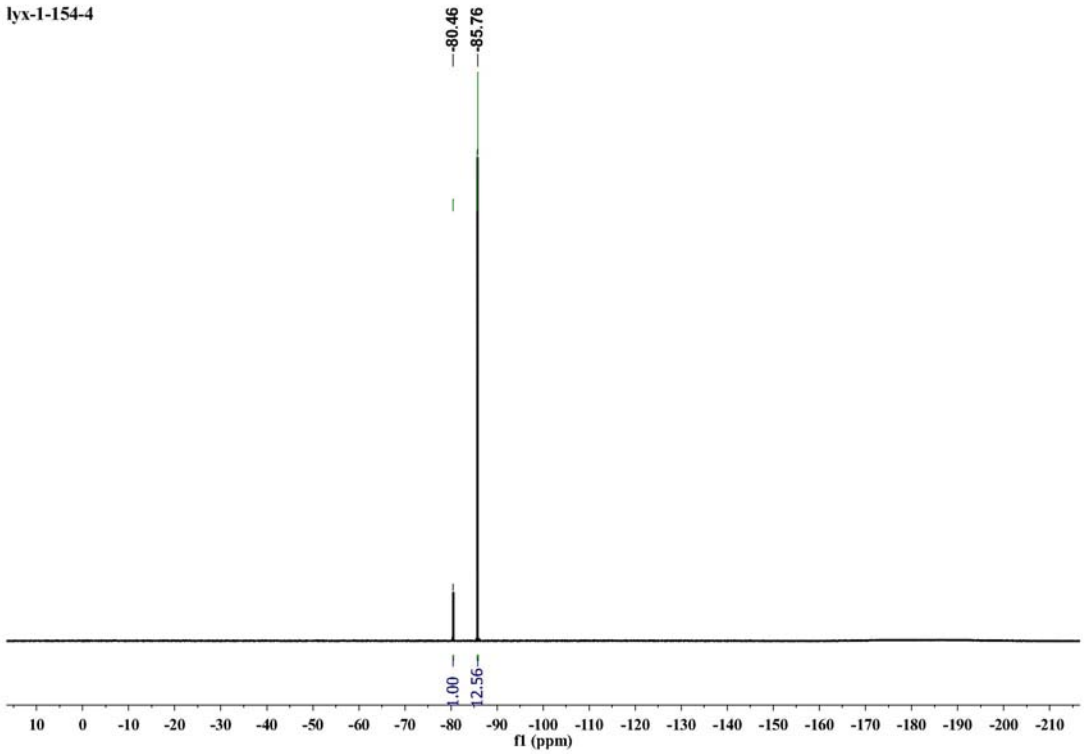
LYX-1-148-1



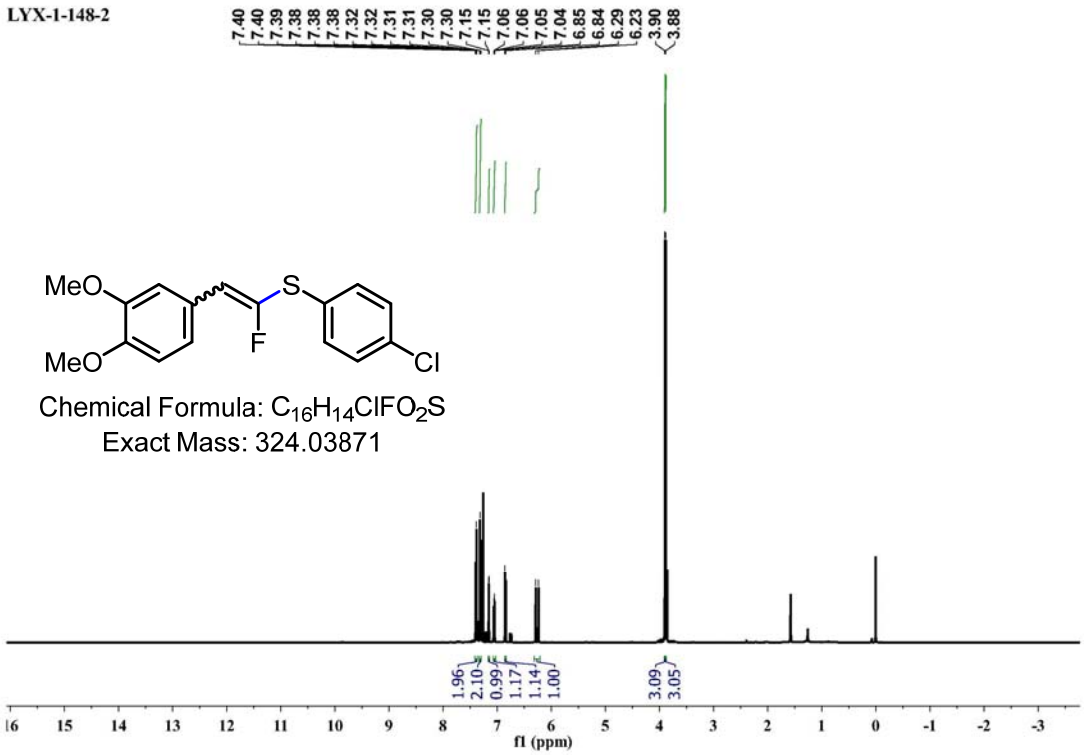
3eh

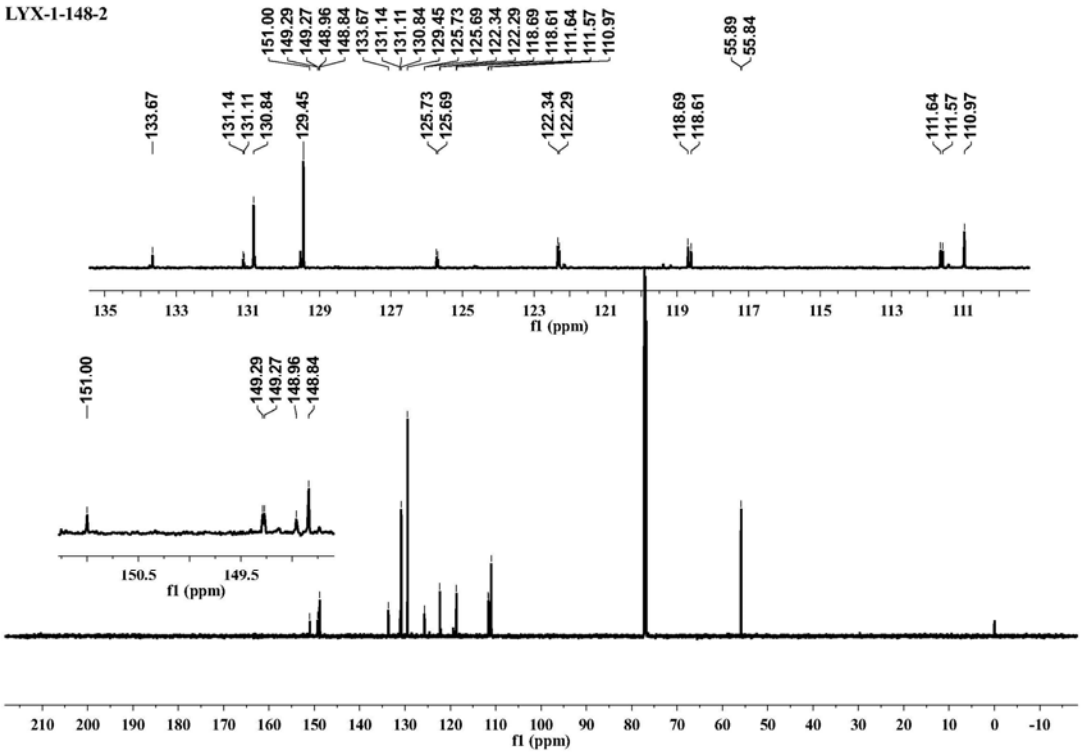

Ph
S
F
Cl
Chemical Formula: C20H14ClFS
Exact Mass: 340.04888
f1 (ppm)

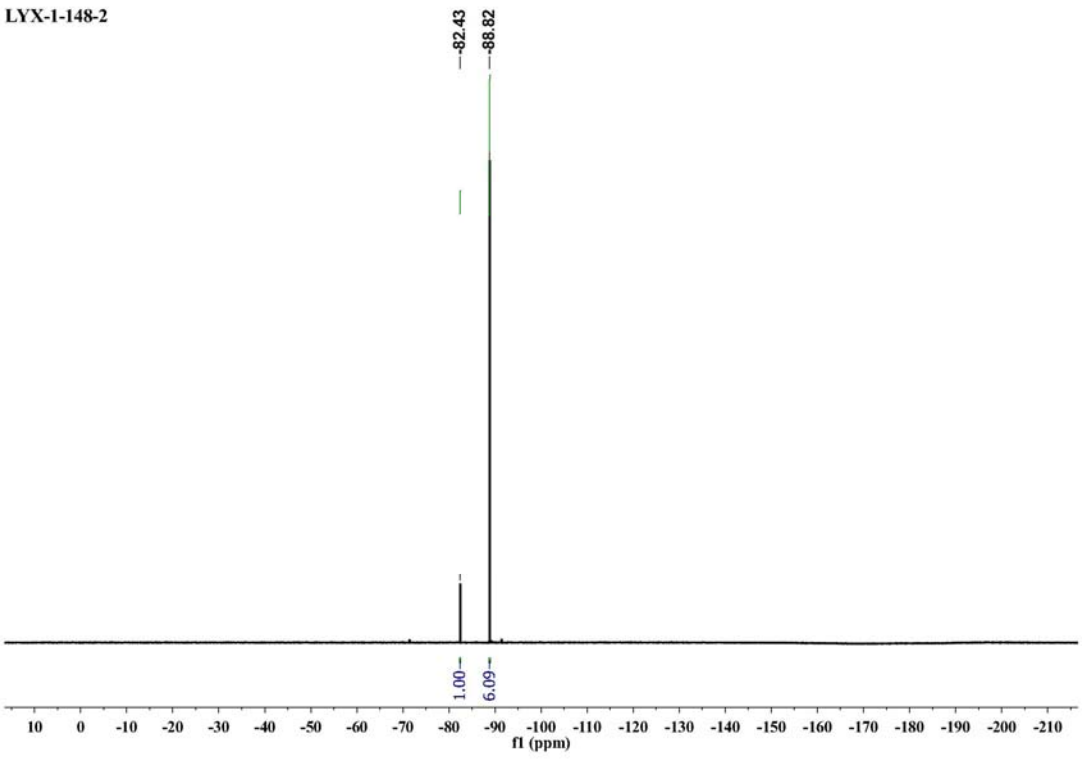

lyx-1-154-4
f1 (ppm)
f1 (ppm)


lyx-1-154-4
-80.46
-85.76
1.00
12.56
f1 (ppm)

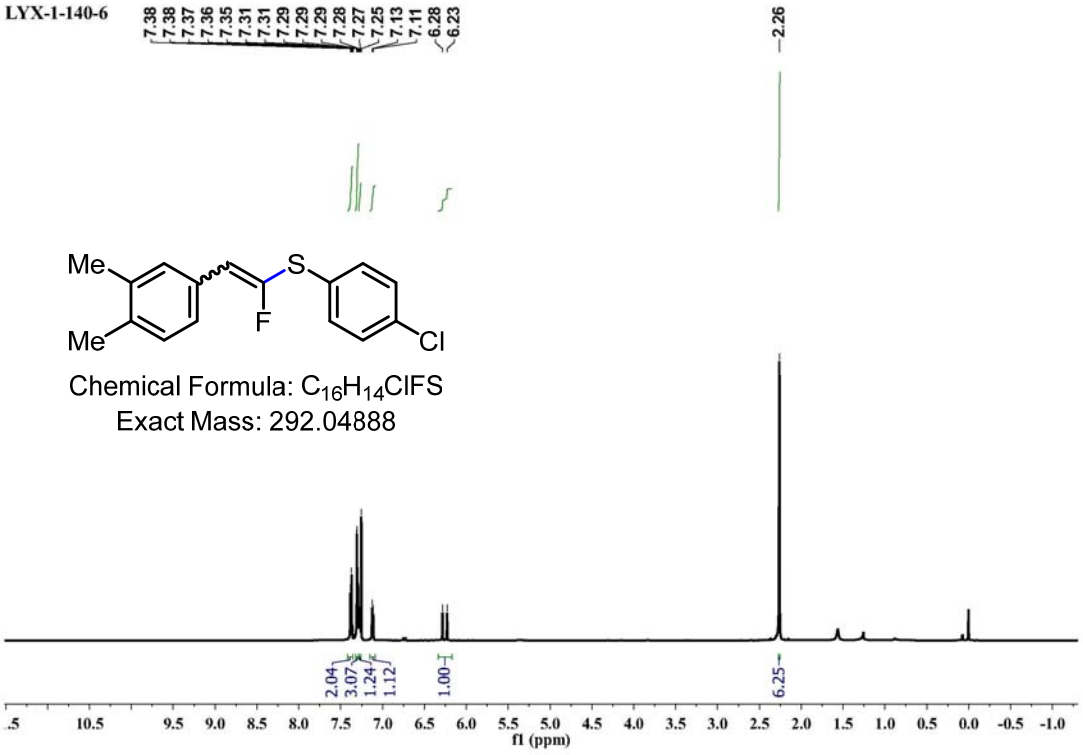
3fh

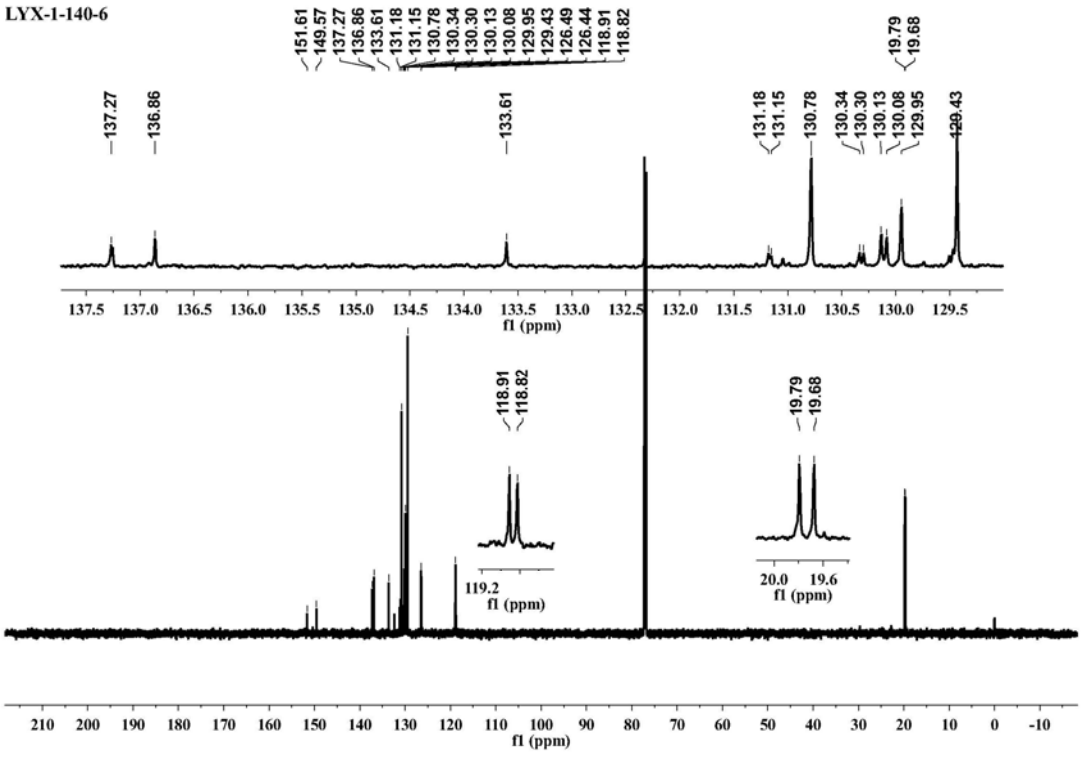

LYX-1-148-2
MeO
MeO
S
F
Cl
Chemical Formula: C16H14ClFO2S
Exact Mass: 324.03871
1.96
2.10
0.99
1.17
1.14
1.00
3.09
3.05
f1 (ppm)

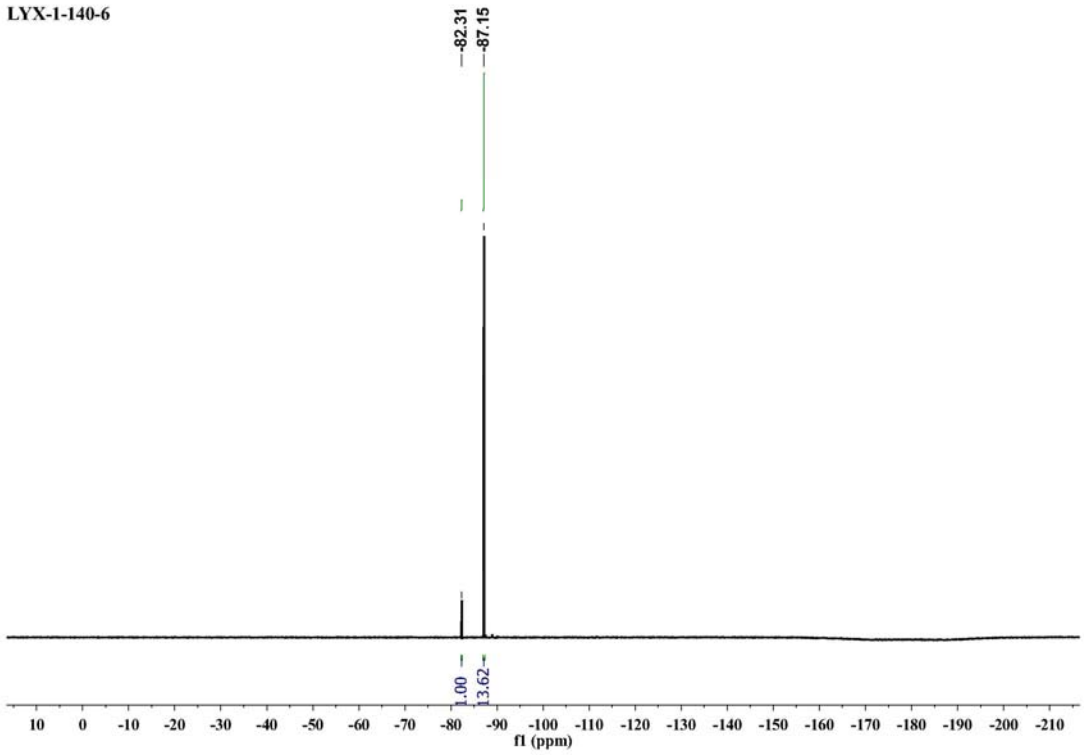

LYX-1-148-2
151.00
149.29
149.27
148.96
148.84
133.67
131.14
131.11
130.84
129.45
125.73
125.69
122.34
122.29
118.69
118.61
111.64
111.57
110.97
55.89
55.84
fl (ppm)


LYX-1-148-2
82.43
88.82
1.00
6.09
fl (ppm)

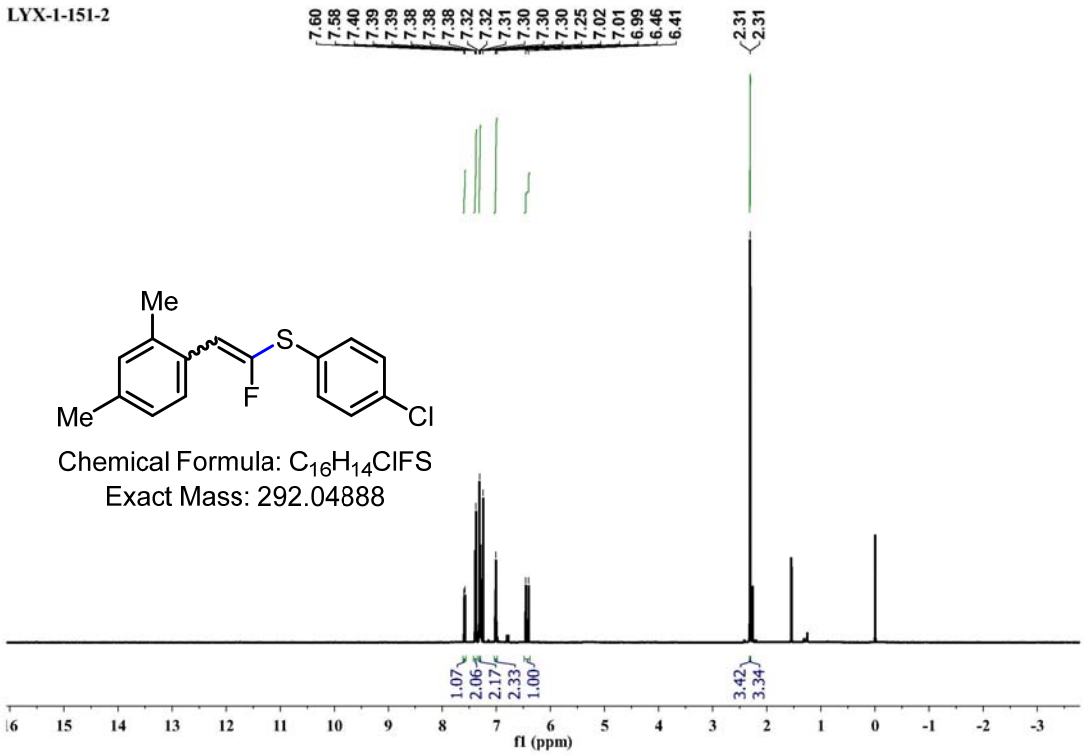
3gh

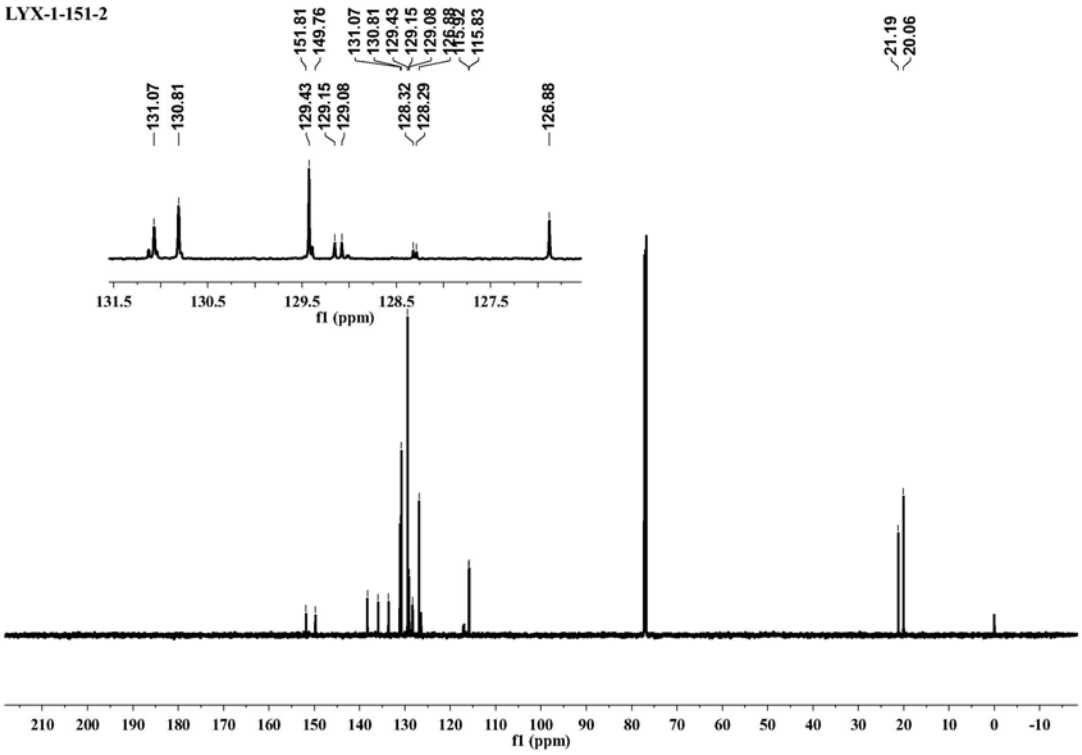

LYX-1-140-6
Me
Me
S
F
Cl
Chemical Formula: C16H14ClFS
Exact Mass: 292.04888
f1 (ppm)

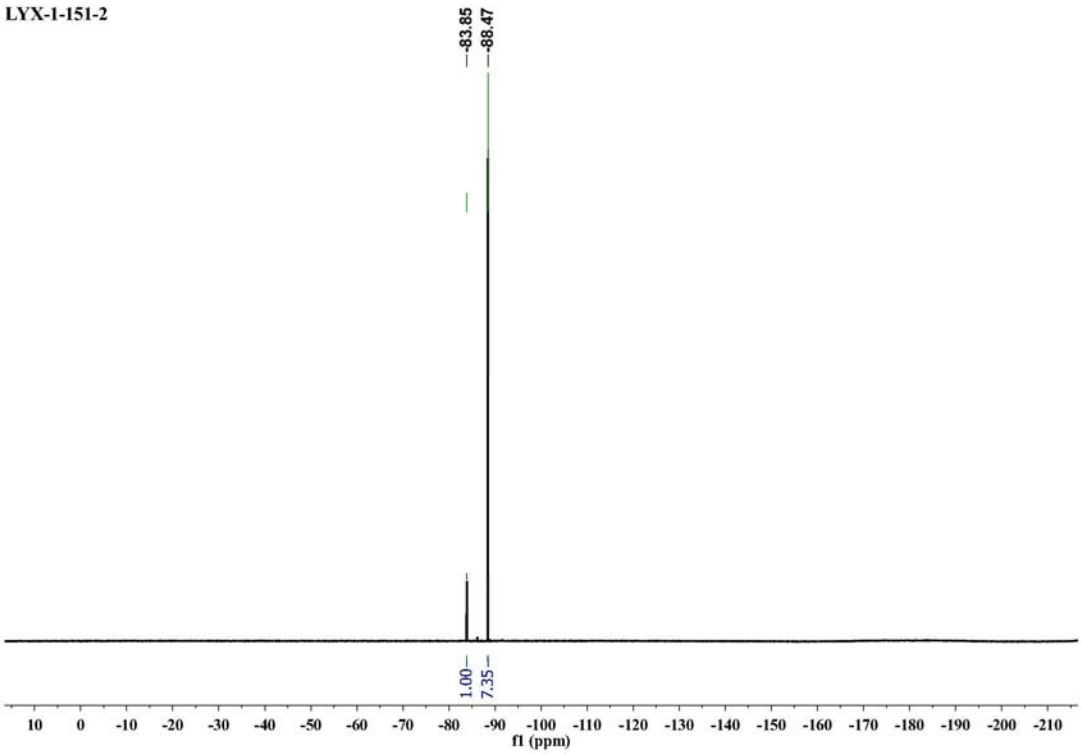

LYX-1-140-6
f1 (ppm)


LYX-1-140-6
-82.31
-87.15
1.00
13.62
f1 (ppm)

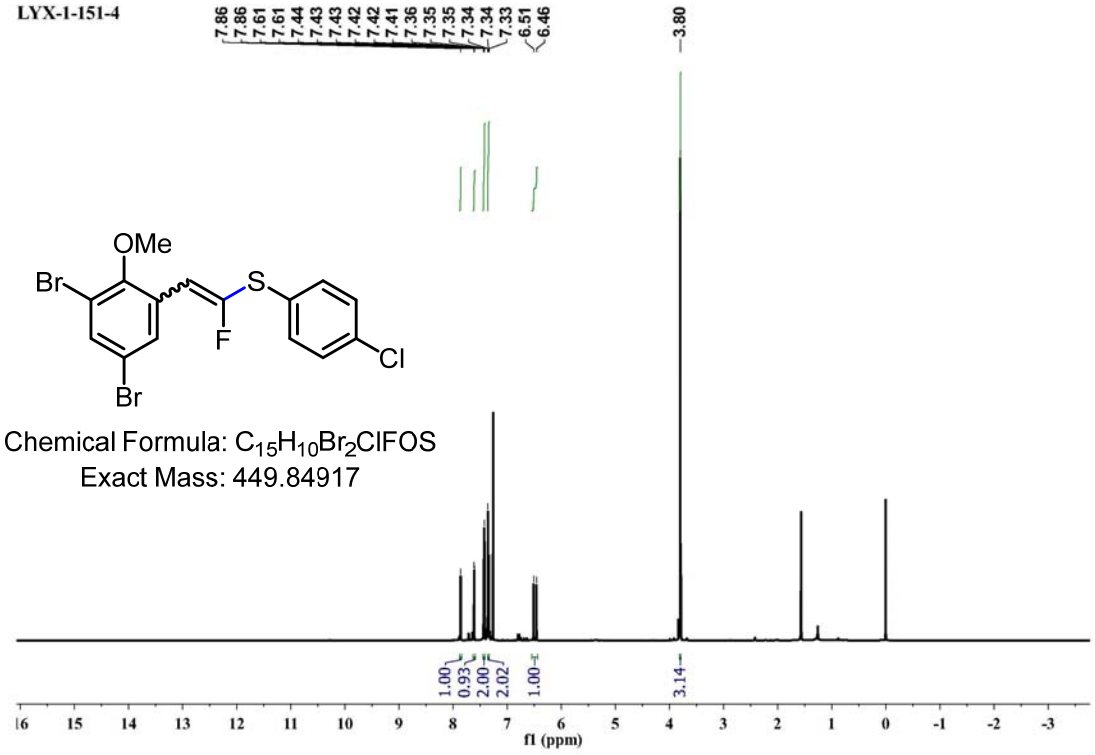
3hh

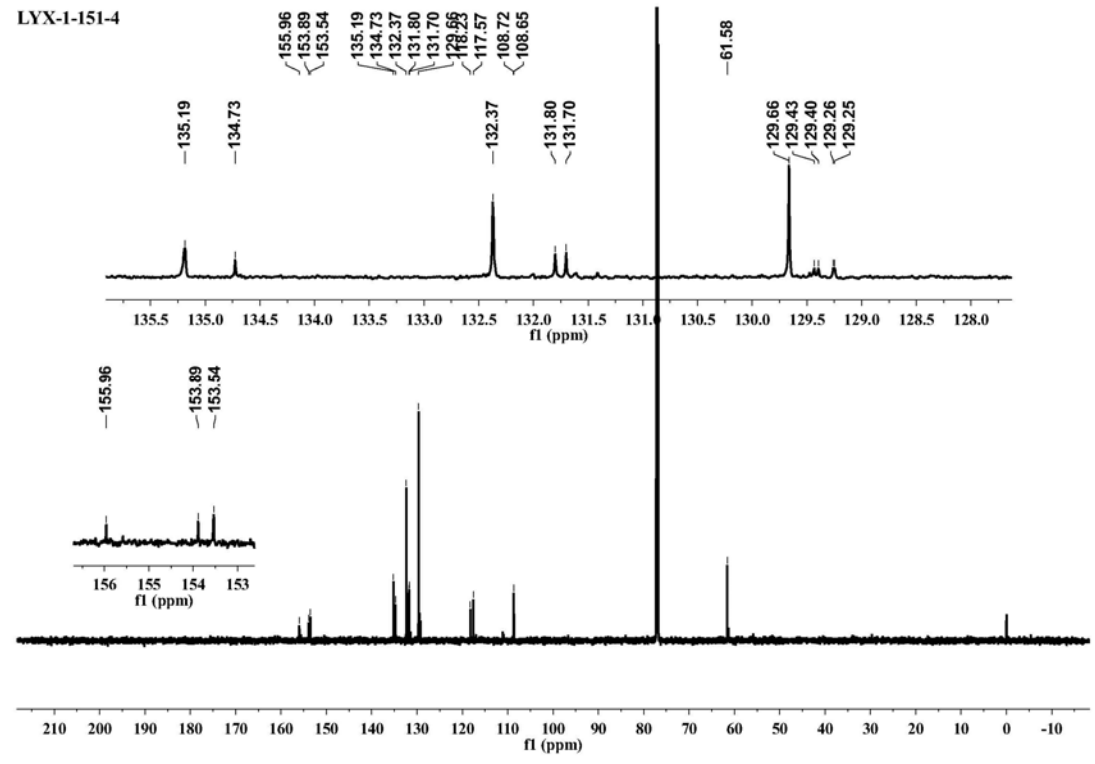

LYX-1-151-2
7.60
7.58
7.40
7.39
7.39
7.38
7.38
7.38
7.32
7.32
7.31
7.30
7.30
7.30
7.25
7.02
7.01
6.99
6.46
6.41
2.31
2.31
Me
S
F
Me
Cl
Chemical Formula: C16H14ClFS
Exact Mass: 292.04888
1.07
2.06
2.17
2.33
1.00
3.42
3.34
f1 (ppm)

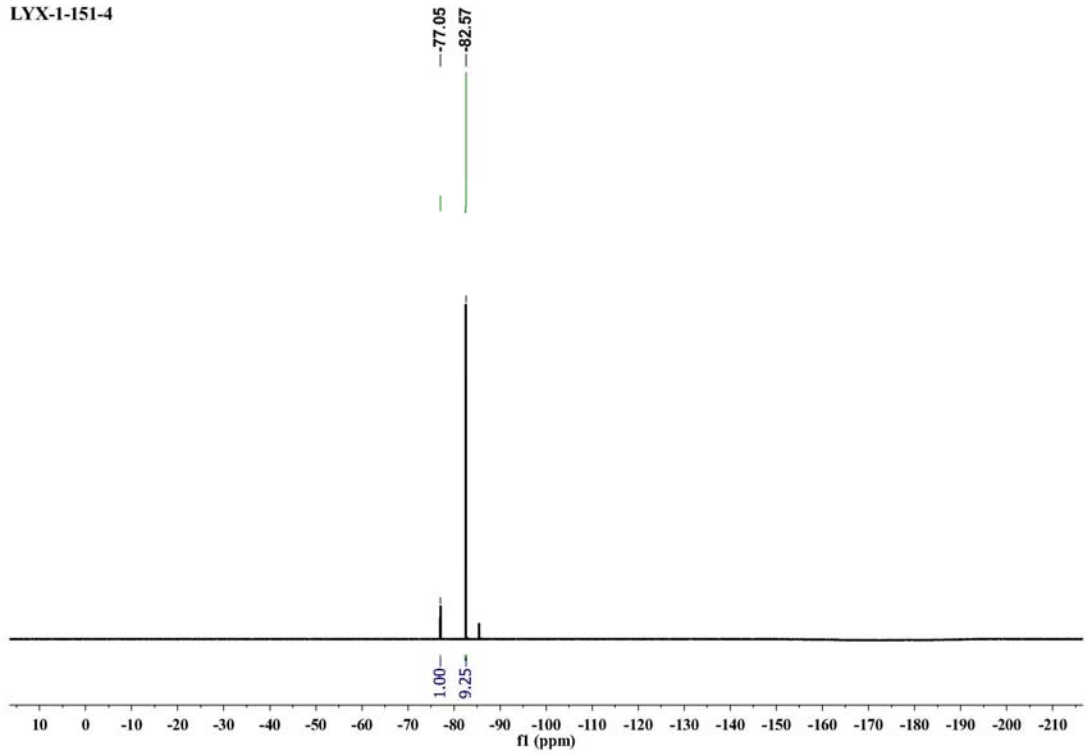

LYX-1-151-2
151.81
149.76
131.07
130.81
129.43
129.15
129.08
128.32
128.29
126.88
115.83
21.19
20.06
131.07
130.81
129.43
129.15
129.08
128.32
128.29
126.88
131.5
130.5
129.5
128.5
127.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LYX-1-151-2
-83.85
-88.47
1.00
7.35
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

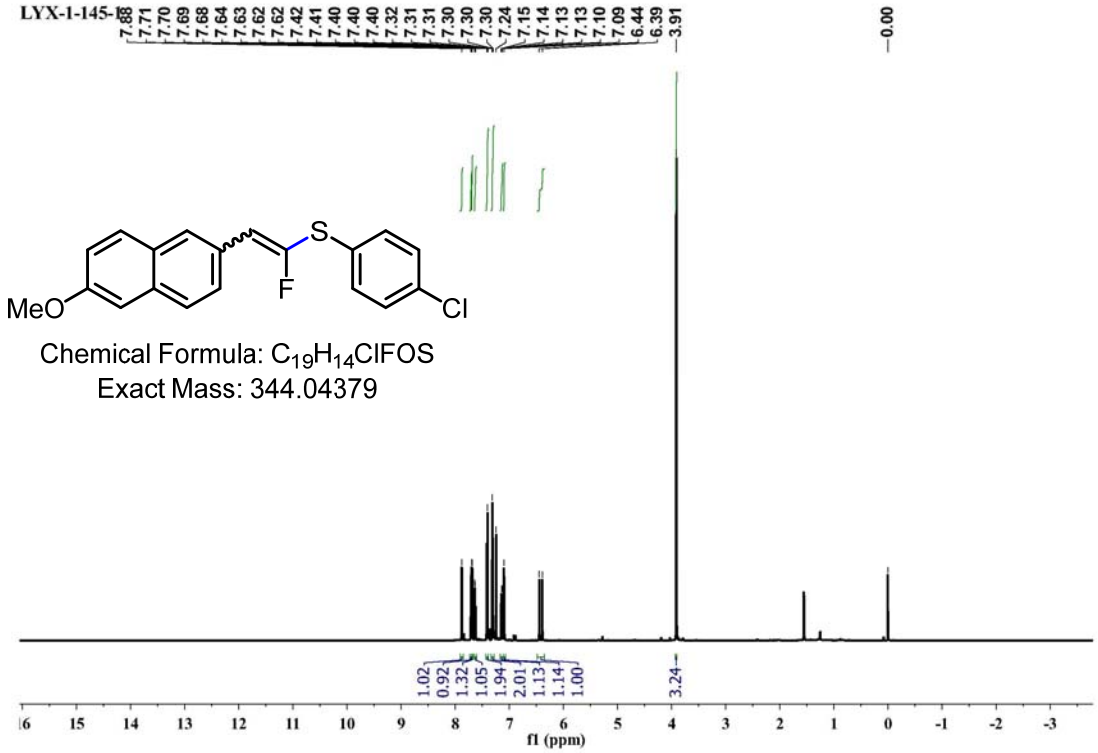
3ih


LYX-1-151-4
7.86
7.86
7.61
7.61
7.44
7.43
7.43
7.42
7.42
7.41
7.36
7.35
7.35
7.34
7.34
7.33
6.51
6.46
3.80
OMe
Br
S
F
Cl
Br
Chemical Formula: C15H10Br2ClFOS
Exact Mass: 449.84917
1.00
0.93
2.00
2.02
1.00
3.14
f1 (ppm)

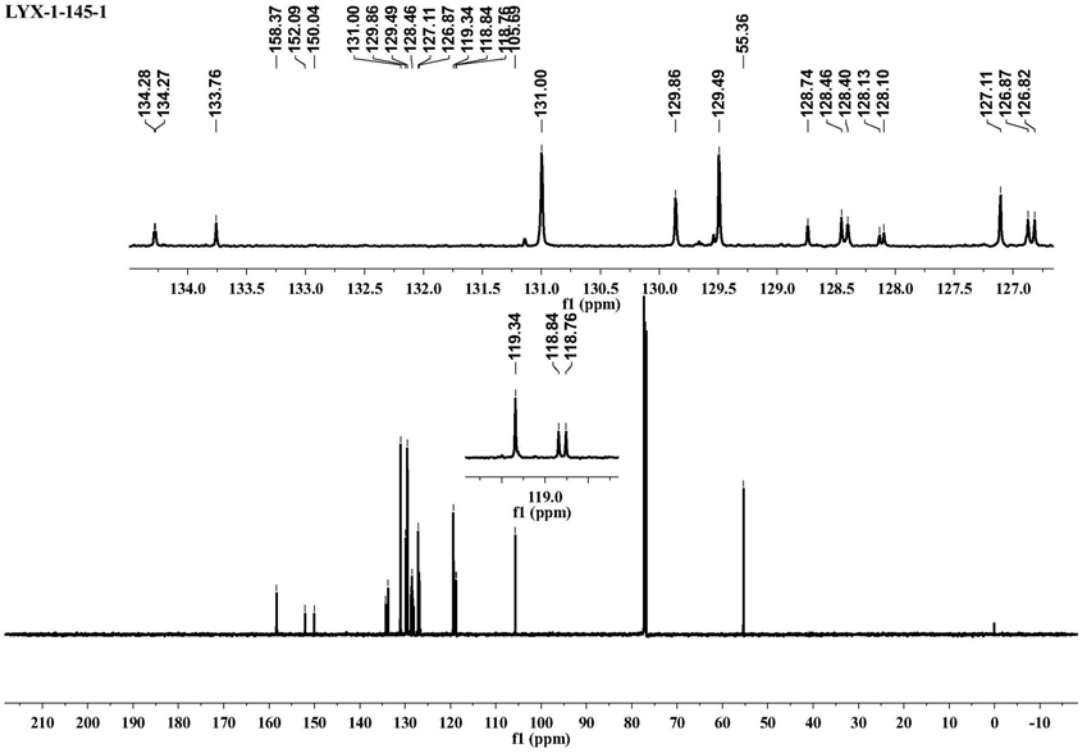

LYX-1-151-4
155.96
153.89
153.54
135.19
134.73
132.37
131.80
131.70
117.57
108.72
108.65
61.58
135.19
134.73
132.37
131.80
131.70
129.66
129.43
129.40
129.26
129.25
f1 (ppm)
155.96
153.89
153.54
f1 (ppm)
f1 (ppm)


LYX-1-151-4
-77.05
-82.57
1.00
9.25
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

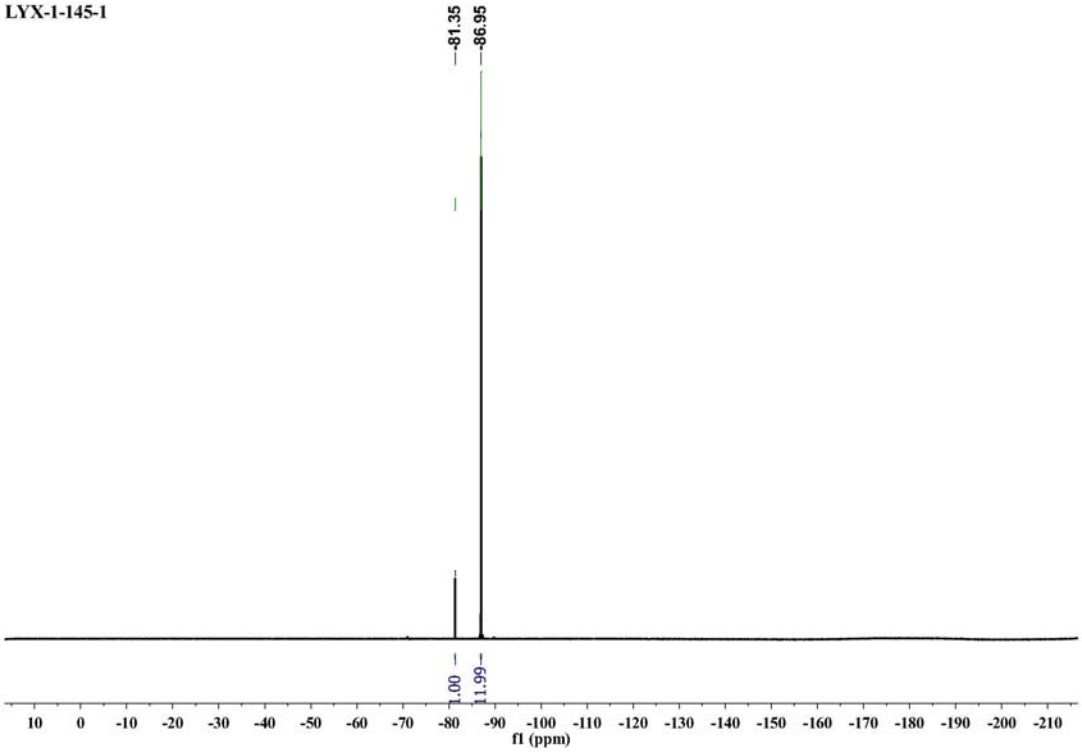
3jh


LYX-1-145-
7.88 7.71 7.70 7.69 7.68 7.64 7.63 7.62 7.62 7.42 7.41 7.40 7.40 7.40 7.32 7.31 7.31 7.30 7.30 7.30 7.24 7.15 7.14 7.13 7.13 7.10 7.09 6.44 6.39 3.91
0.00
S
F
MeO
Cl
Chemical Formula: C19H14ClFOS
Exact Mass: 344.04379
1.02 0.92 1.32 1.05 1.94 2.01 1.13 1.14 1.00
3.24
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

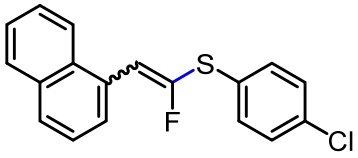
LYX-1-145-1



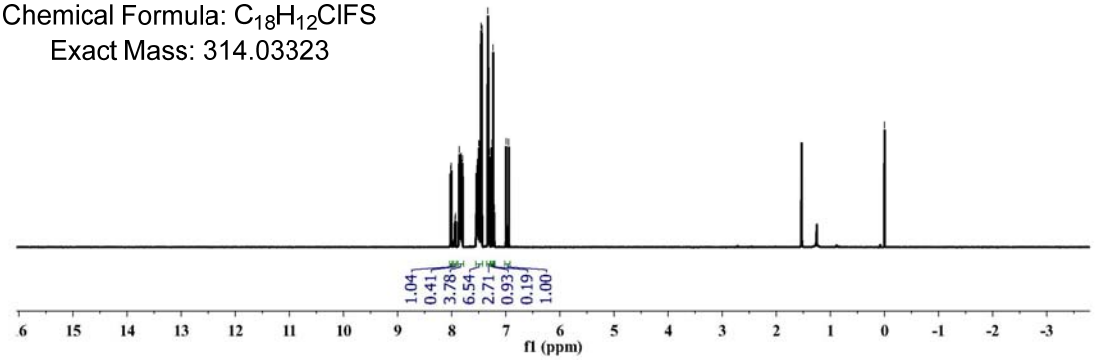
LYX-1-145-1

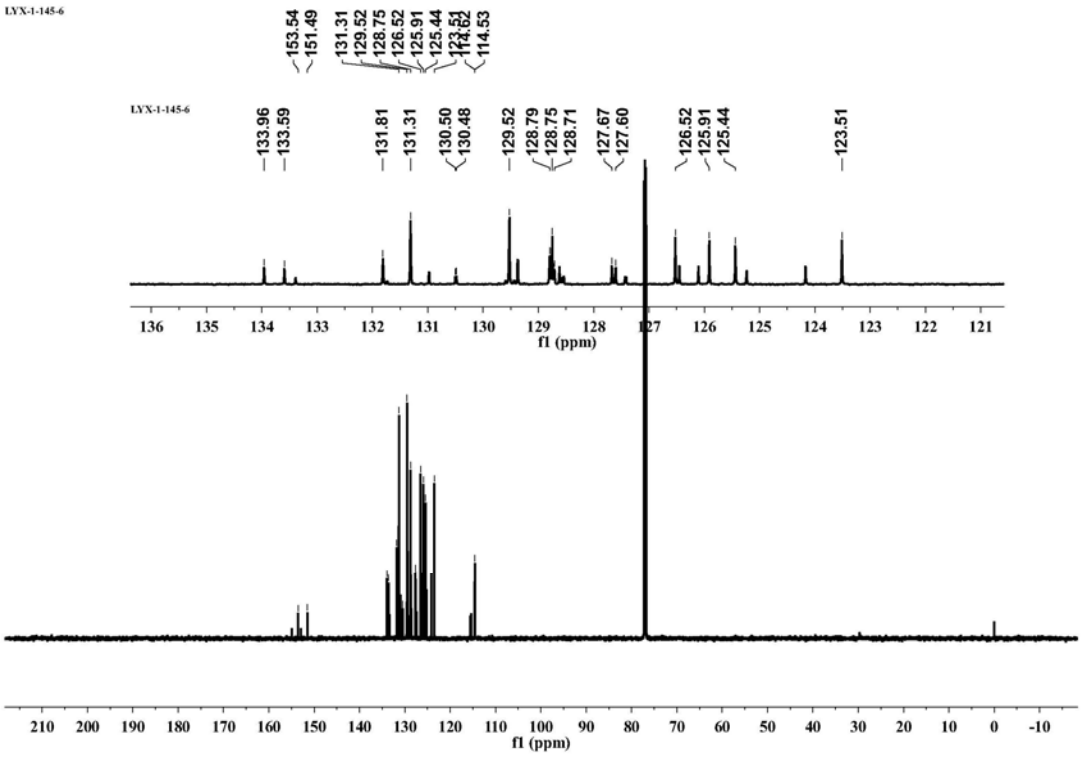


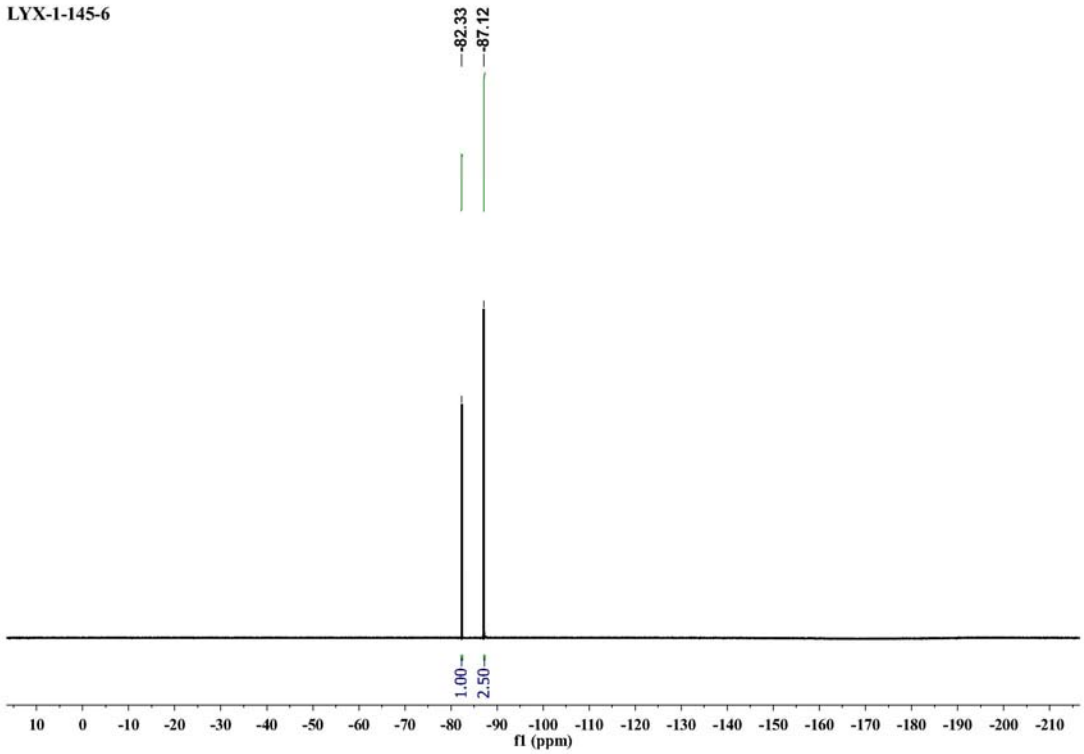
3kh



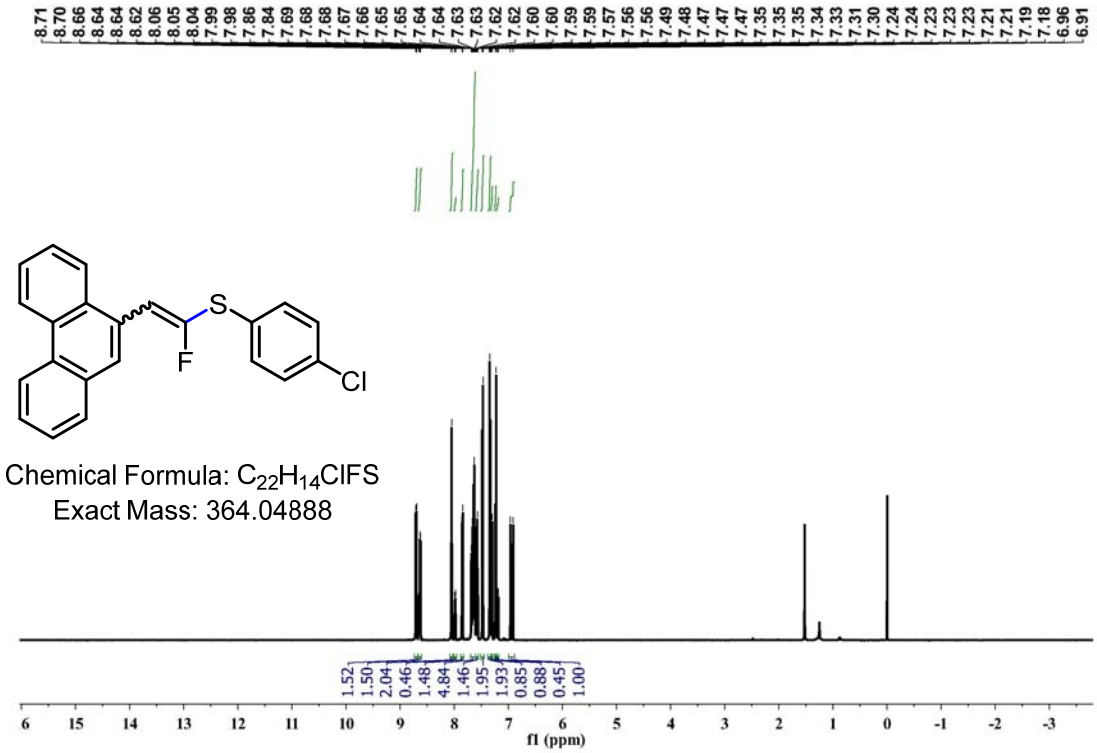
Chemical Formula: $C_{18}H_{12}ClFS$
Exact Mass: 314.03323



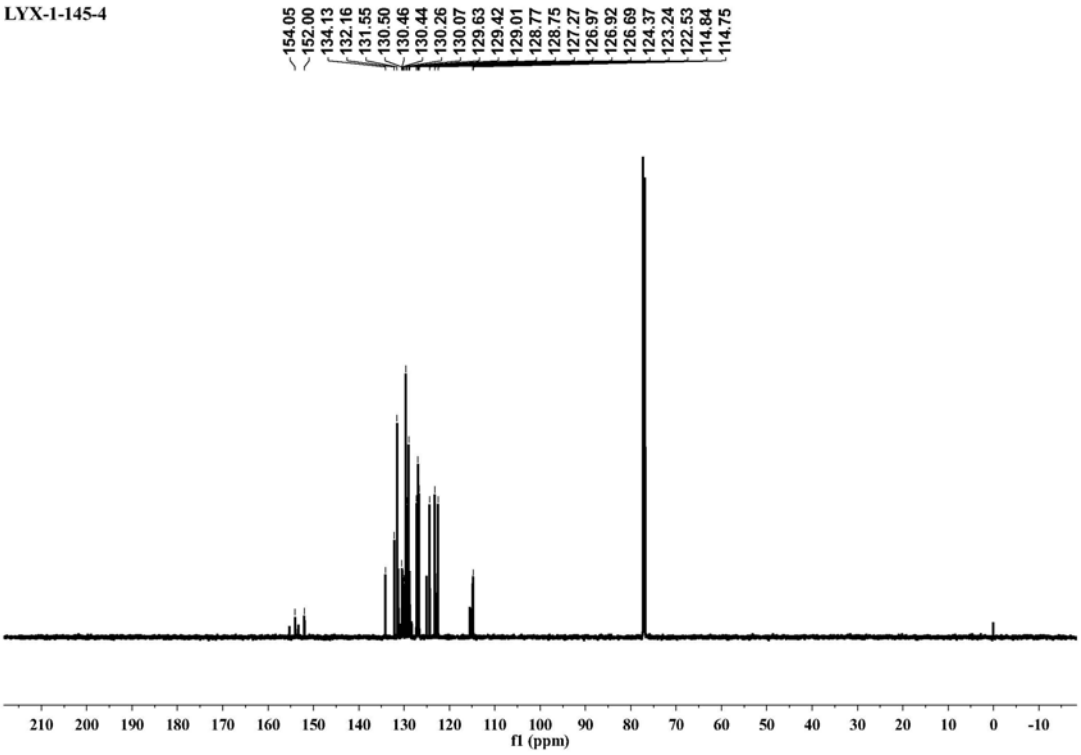



LYX-1-145-6
-82.33
-87.12
1.00
2.50
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

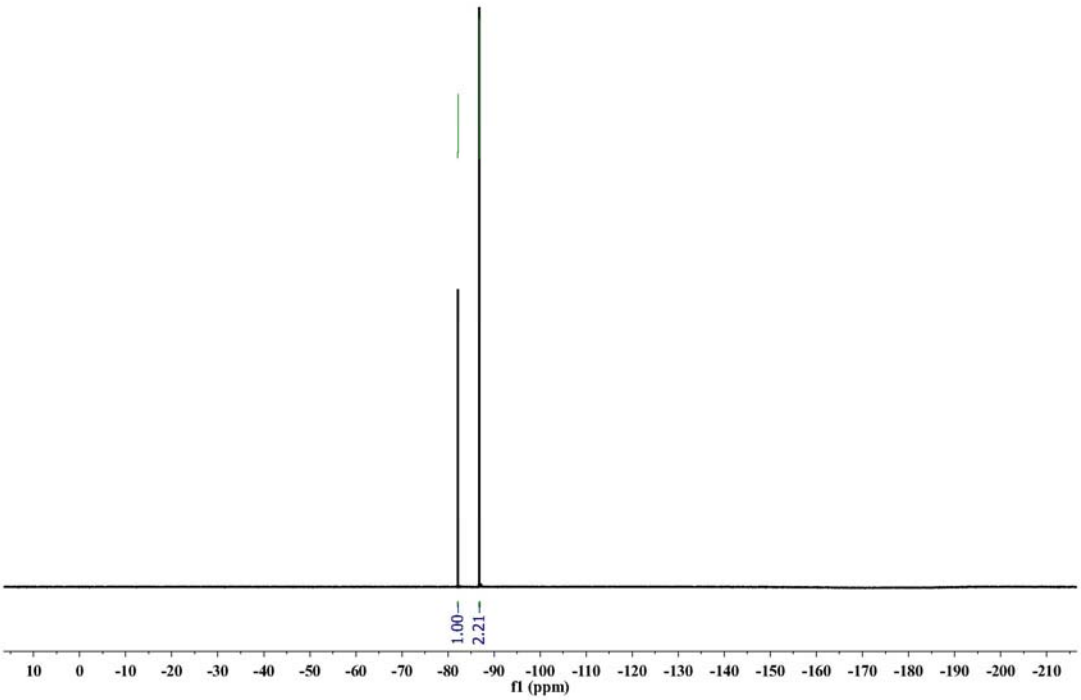
3lh


8.71 8.70 8.66 8.64 8.64 8.62 8.06 8.05 8.04 7.99 7.98 7.86 7.84 7.69 7.68 7.68 7.67 7.66 7.65 7.65 7.64 7.64 7.63 7.63 7.62 7.62 7.60 7.60 7.59 7.59 7.57 7.56 7.56 7.49 7.48 7.47 7.47 7.47 7.35 7.35 7.35 7.34 7.33 7.31 7.30 7.24 7.24 7.23 7.23 7.23 7.21 7.21 7.19 7.18 6.96 6.91
S
F
Cl
Chemical Formula: C22H14ClFS
Exact Mass: 364.04888
1.52 1.50 2.04 0.46 1.48 4.84 1.46 1.95 1.93 0.85 0.88 0.45 1.00
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

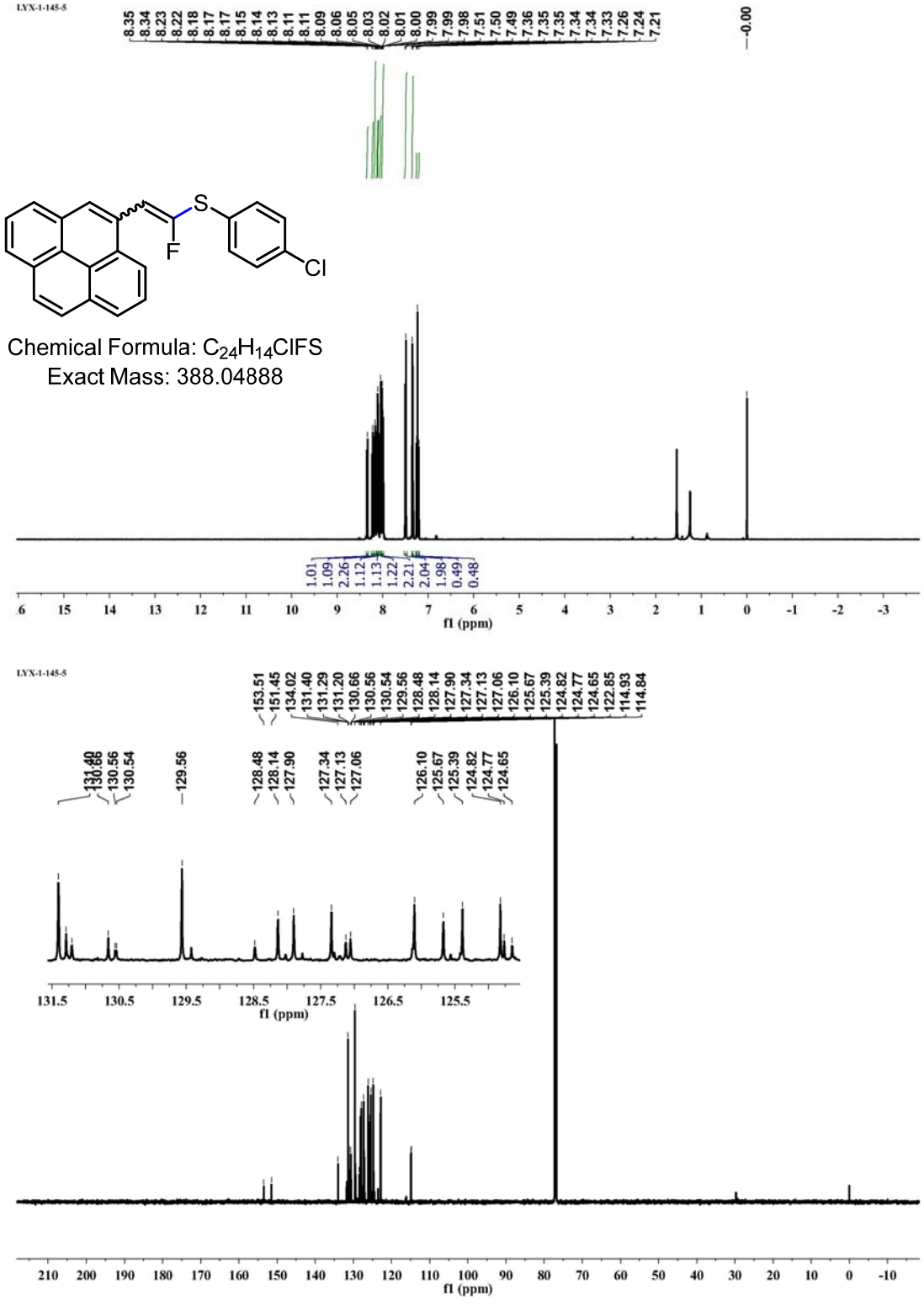
LYX-1-145-4

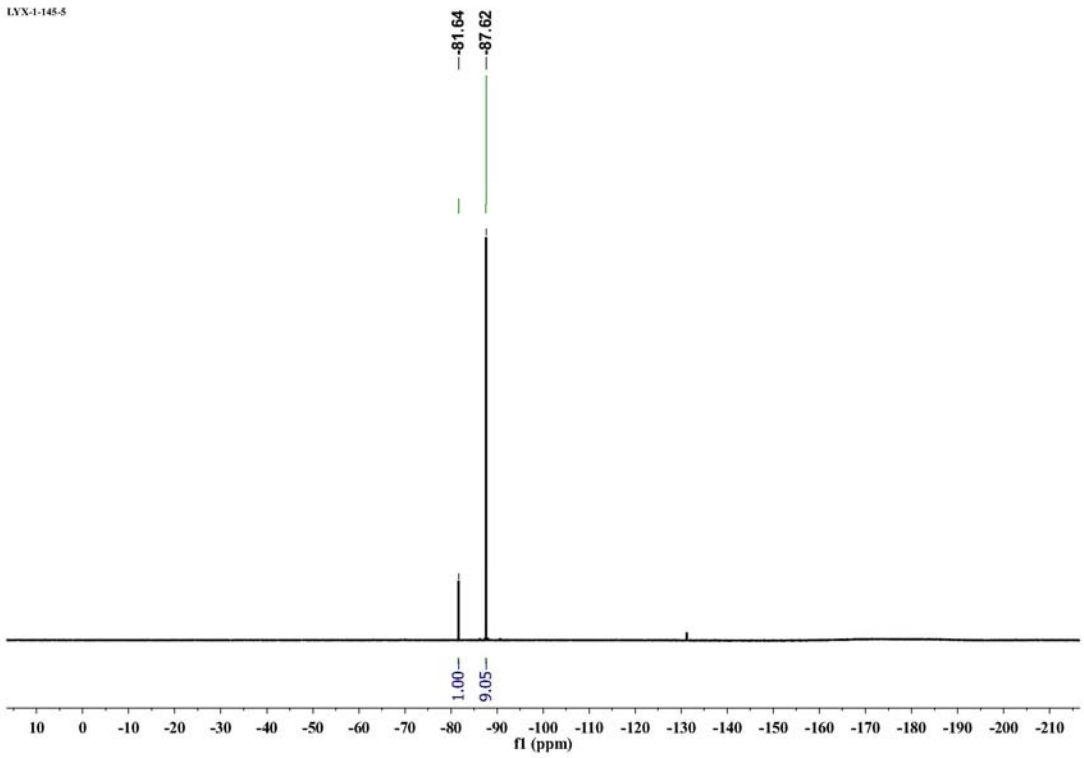


LYX-1-145-4

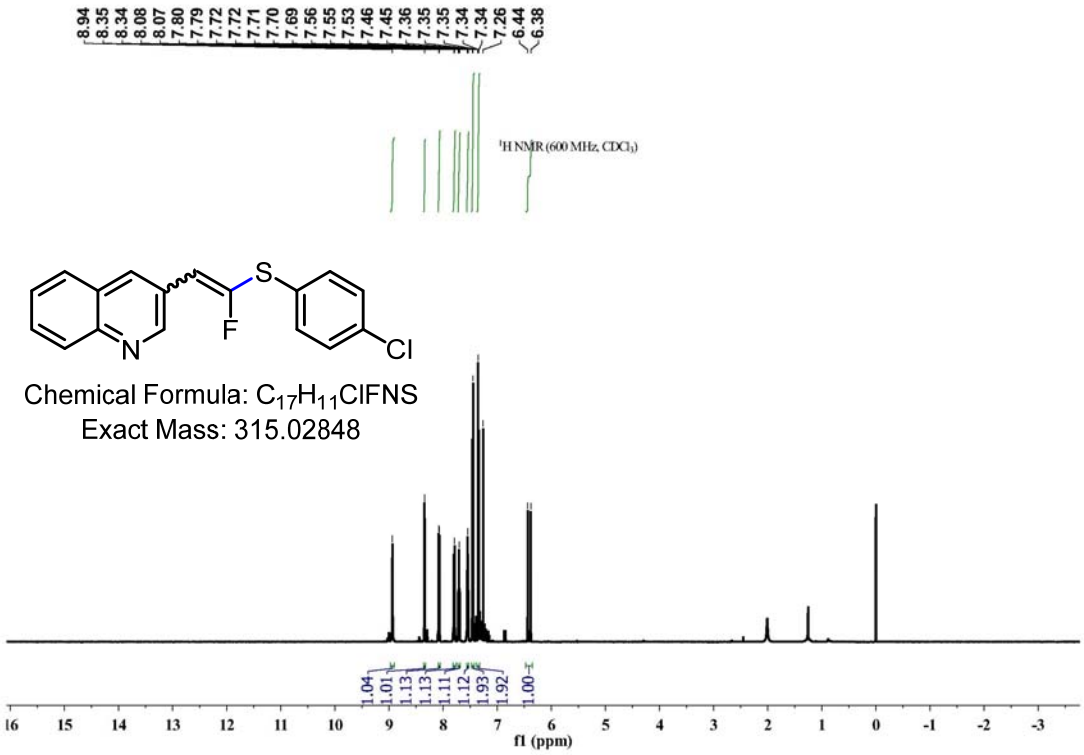


3mh

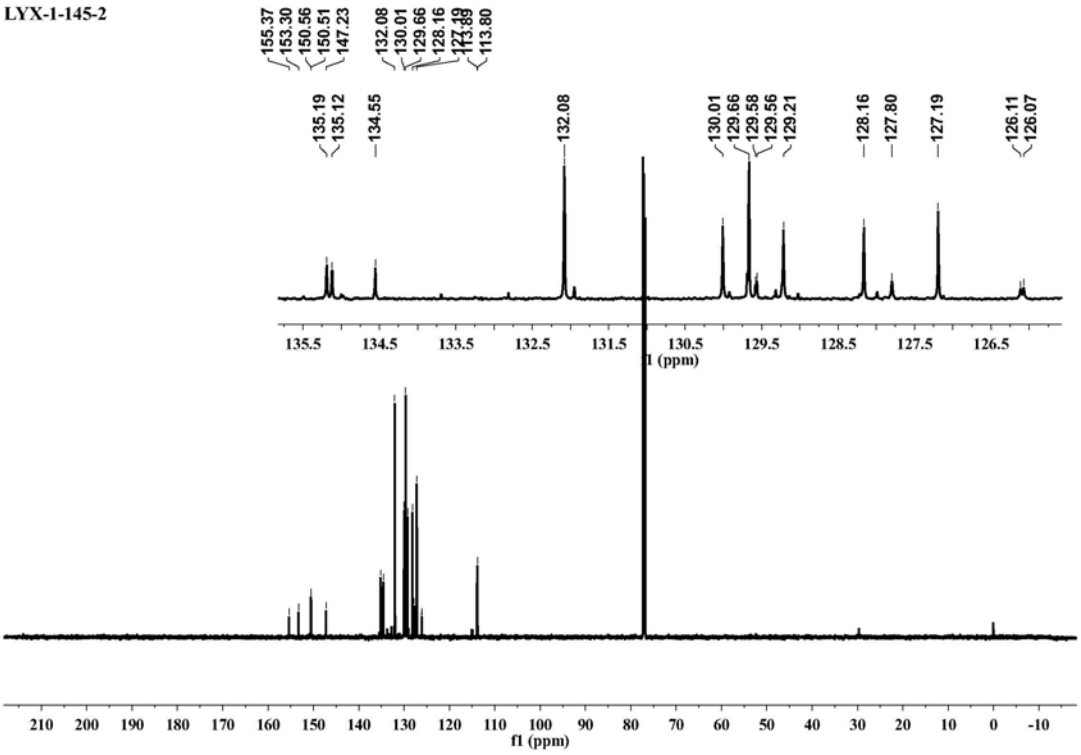

LYX-1-145-5
8.35 8.34 8.23 8.22 8.18 8.17 8.17 8.15 8.14 8.13 8.11 8.11 8.09 8.06 8.05 8.03 8.02 8.01 8.00 7.99 7.99 7.98 7.51 7.50 7.49 7.36 7.35 7.35 7.34 7.34 7.33 7.26 7.24 7.21
0.00
S
F
Cl
Chemical Formula: C24H14ClFS
Exact Mass: 388.04888
1.01 1.09 2.26 1.12 1.13 1.22 2.21 2.04 1.98 0.49 0.48
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
LYX-1-145-5
153.51 151.45 134.02 131.40 131.29 131.20 130.66 130.56 130.54 129.56 128.48 128.14 127.90 127.34 127.13 127.06 126.10 125.67 125.39 124.82 124.77 124.65 122.85 114.93 114.84
131.40 130.66 130.56 130.54 129.56 128.48 128.14 127.90 127.34 127.13 127.06 126.10 125.67 125.39 124.82 124.77 124.65
131.5 130.5 129.5 128.5 127.5 126.5 125.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LYX-1-145-5
-81.64
-87.62
1.00
9.05
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

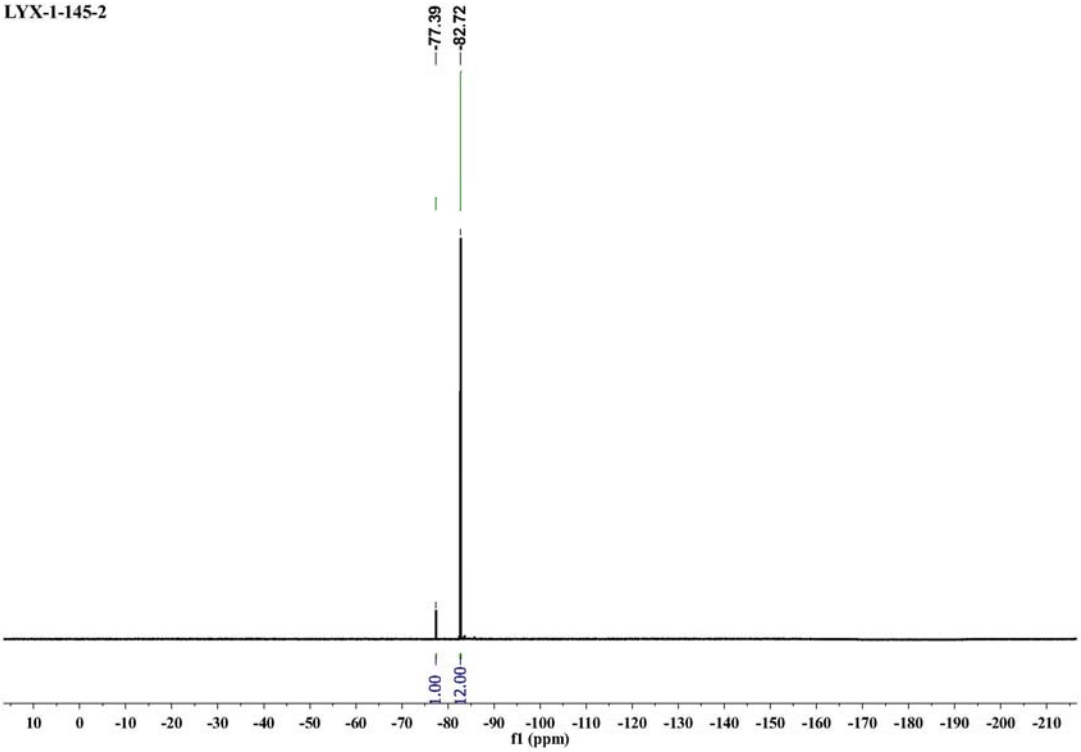
3nh


8.94
8.35
8.34
8.08
8.07
7.80
7.79
7.72
7.72
7.71
7.70
7.69
7.56
7.55
7.53
7.46
7.45
7.36
7.35
7.35
7.34
7.34
7.26
6.44
6.38
¹H NMR (600 MHz, CDCl₃)
S
F
N
Cl
Chemical Formula: C17H11ClFNS
Exact Mass: 315.02848
1.04
1.01
1.13
1.13
1.11
1.12
1.93
1.92
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

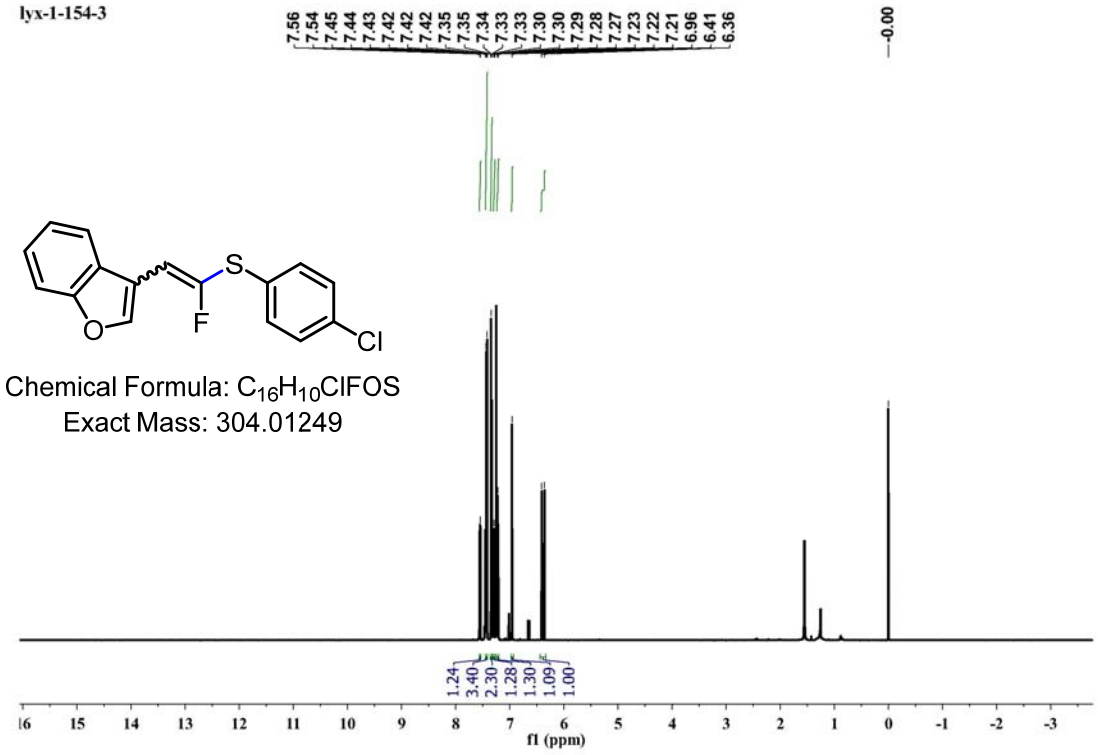
LYX-1-145-2



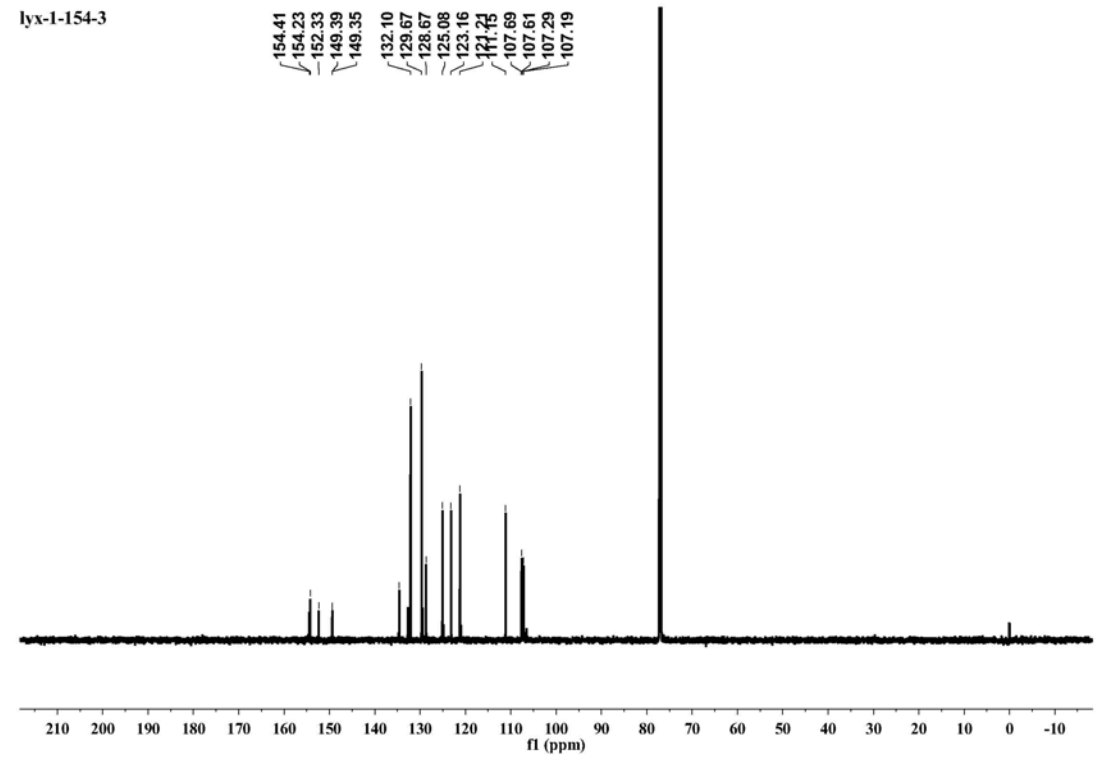
LYX-1-145-2

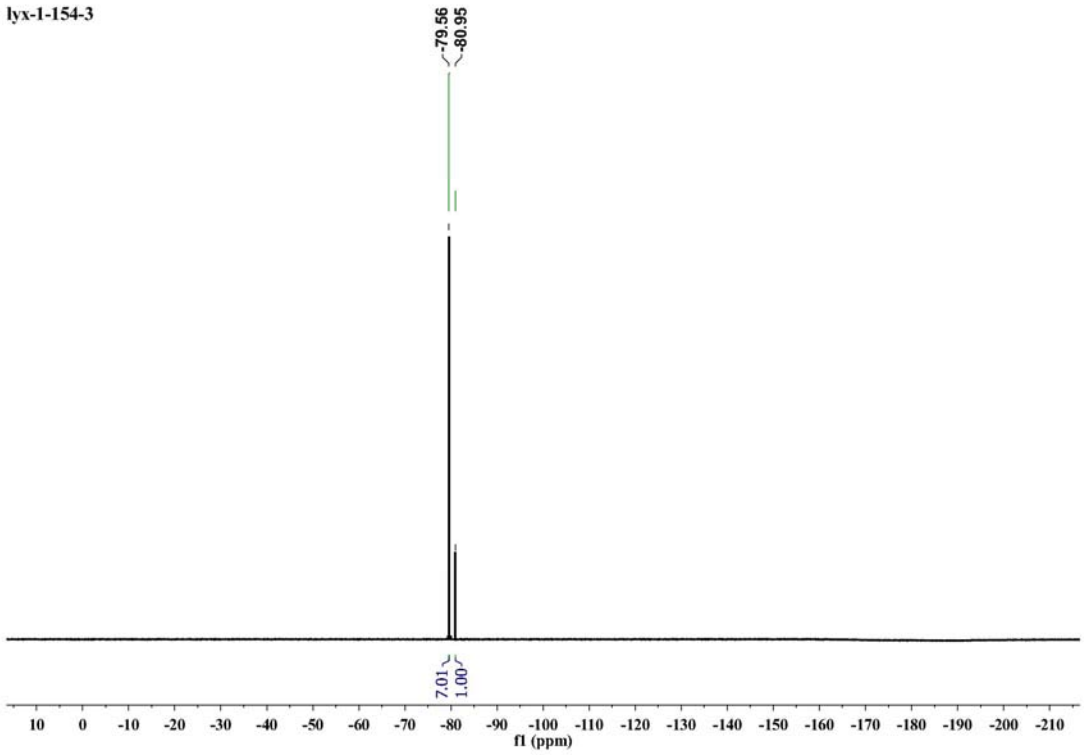


3oh

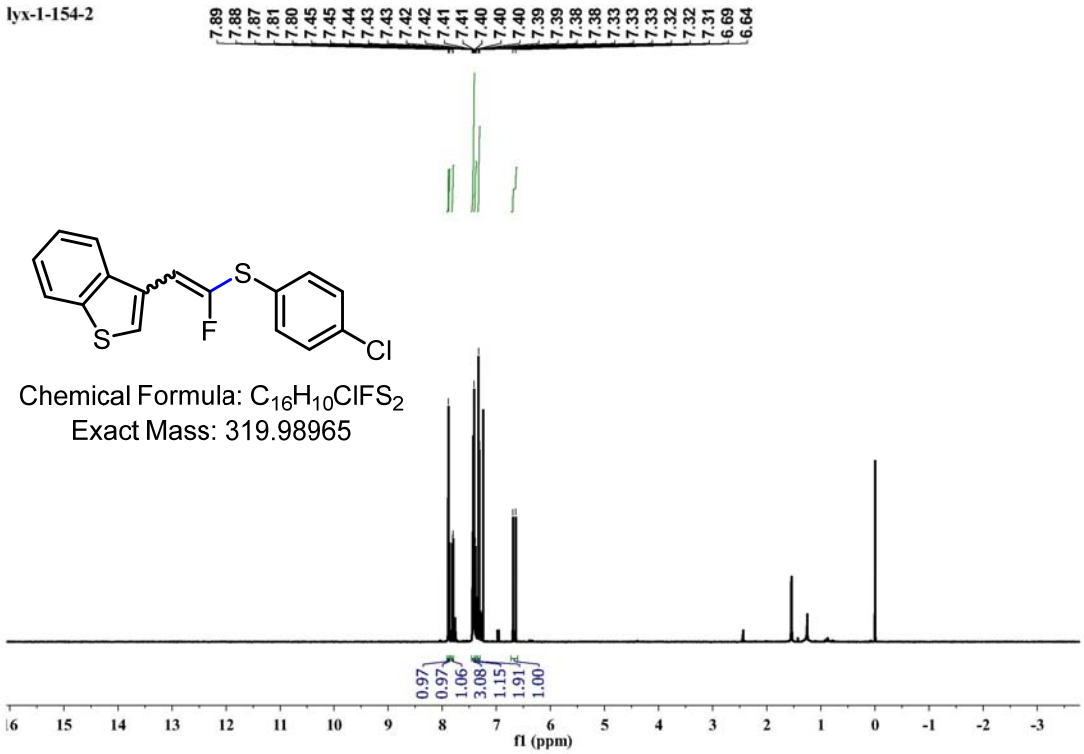


Chemical Formula: $C_{16}H_{10}ClFOS$
Exact Mass: 304.01249

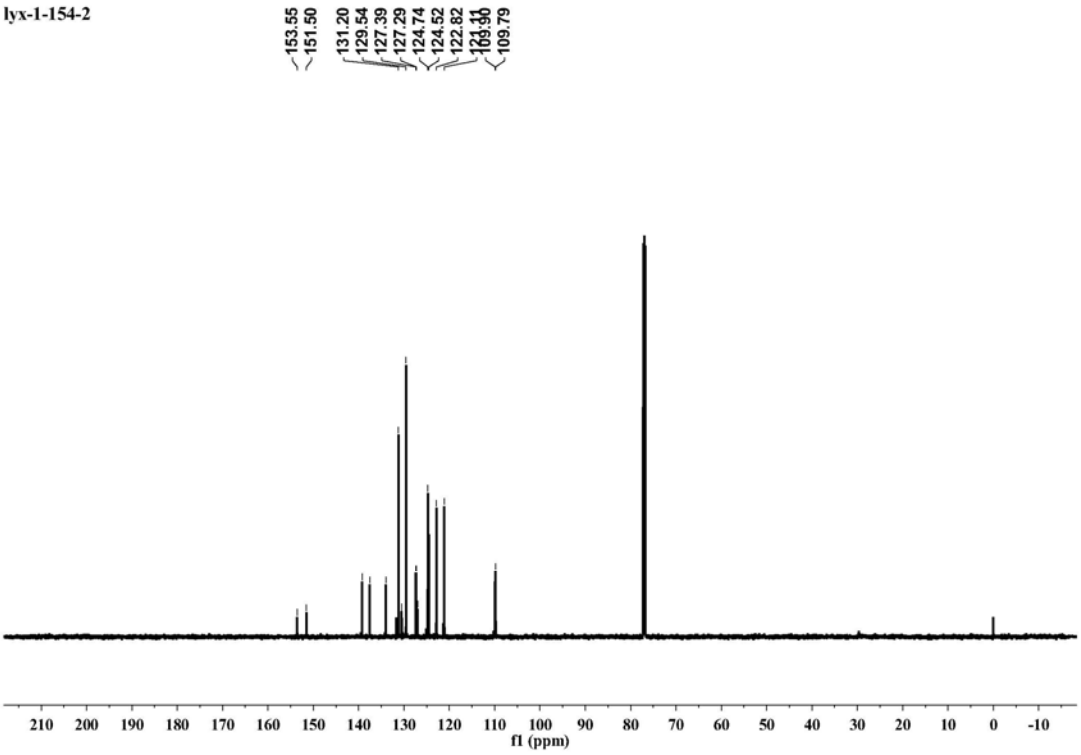



lyx-1-154-3
-79.56
-80.95
7.01
1.00
f1 (ppm)

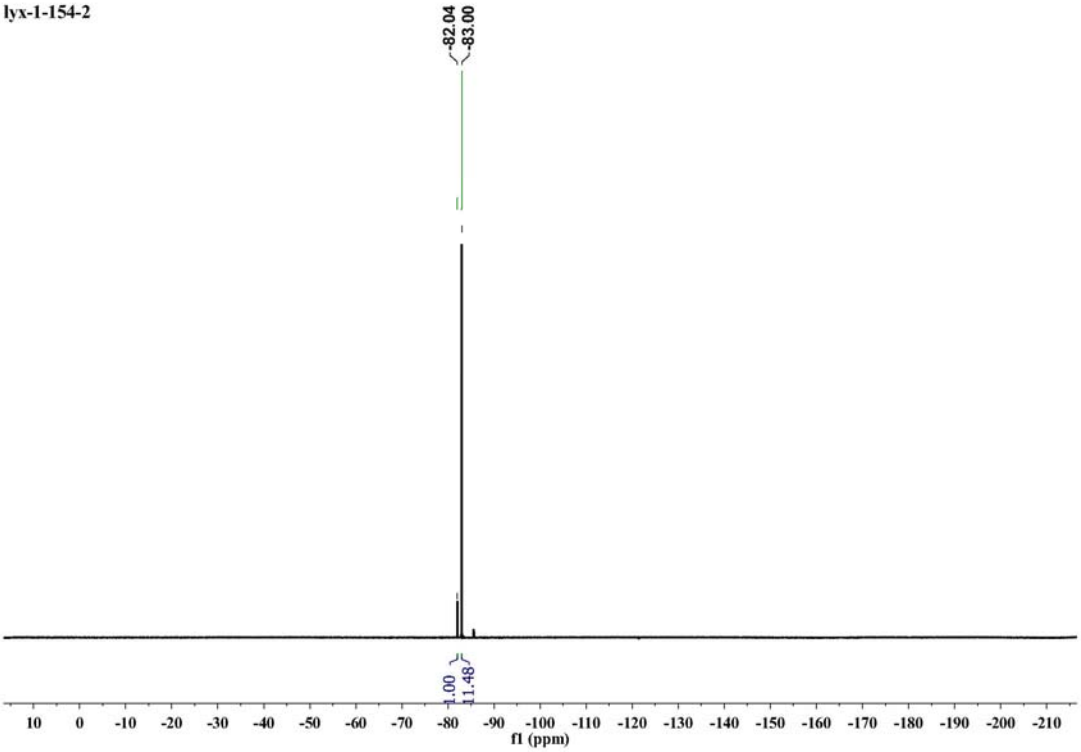
3ph


lyx-1-154-2
7.89
7.88
7.87
7.81
7.80
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.33
7.33
7.32
7.32
7.31
6.69
6.64
S
F
S
Cl
Chemical Formula: C16H10ClFS2
Exact Mass: 319.98965
0.97
0.97
1.06
3.08
1.15
1.91
1.00
f1 (ppm)

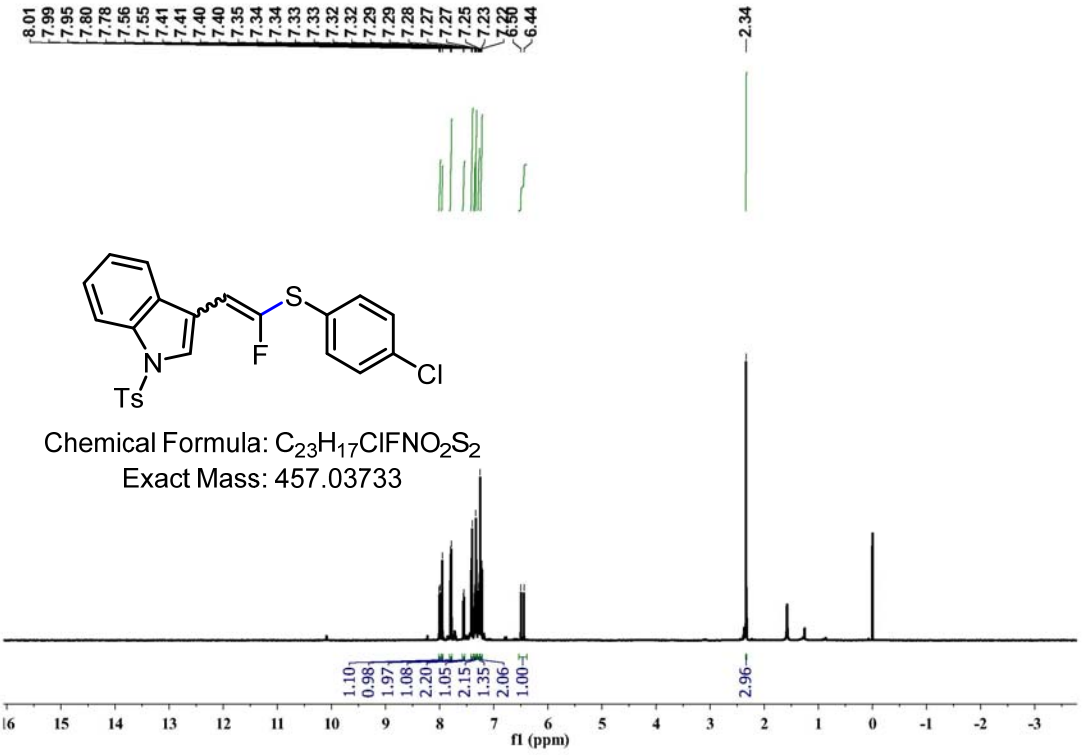
lyx-1-154-2

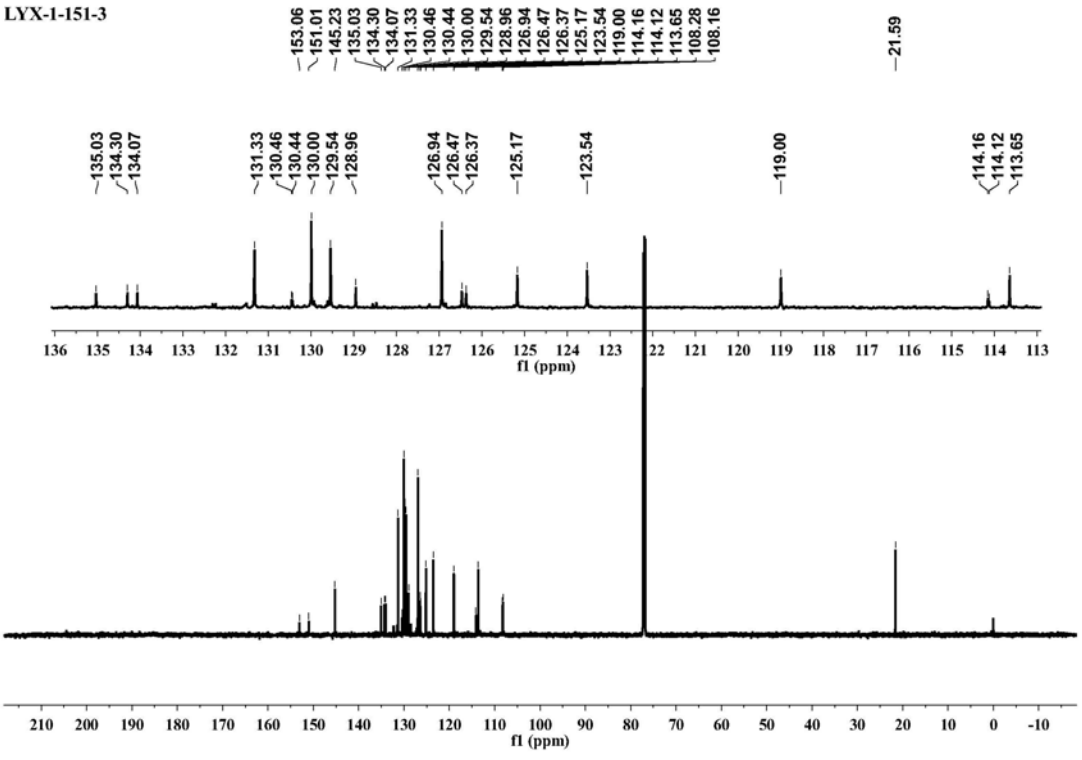


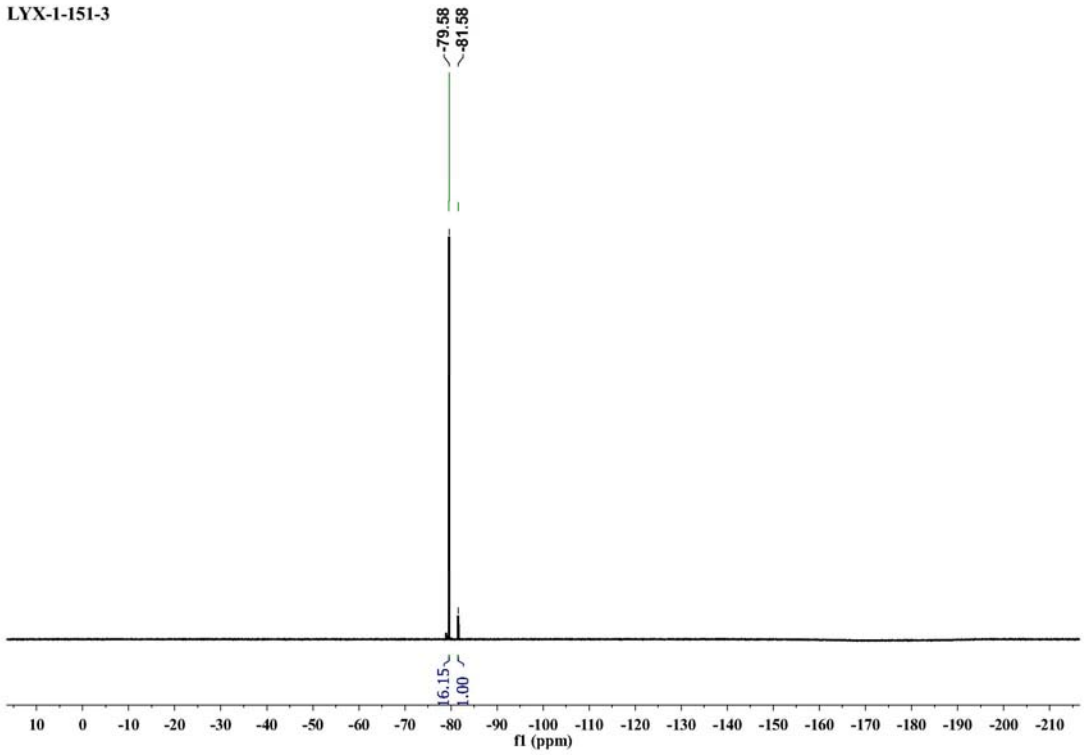
lyx-1-154-2



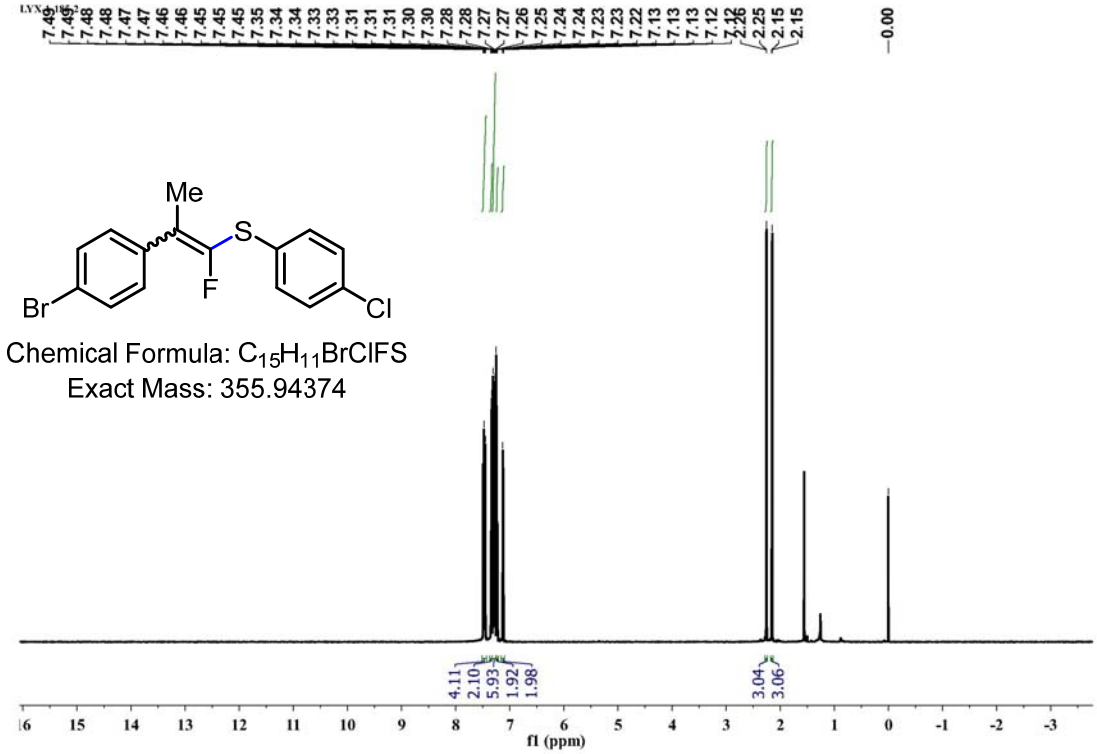
3qh


8.01
7.99
7.95
7.80
7.78
7.56
7.55
7.41
7.41
7.40
7.40
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.29
7.29
7.28
7.27
7.27
7.25
7.23
6.50
6.44
2.34
S
F
N
Ts
Cl
Chemical Formula: C23H17ClFNO2S2
Exact Mass: 457.03733
1.10
0.98
1.97
1.08
2.20
1.05
2.15
1.35
2.06
1.00
2.96
f1 (ppm)

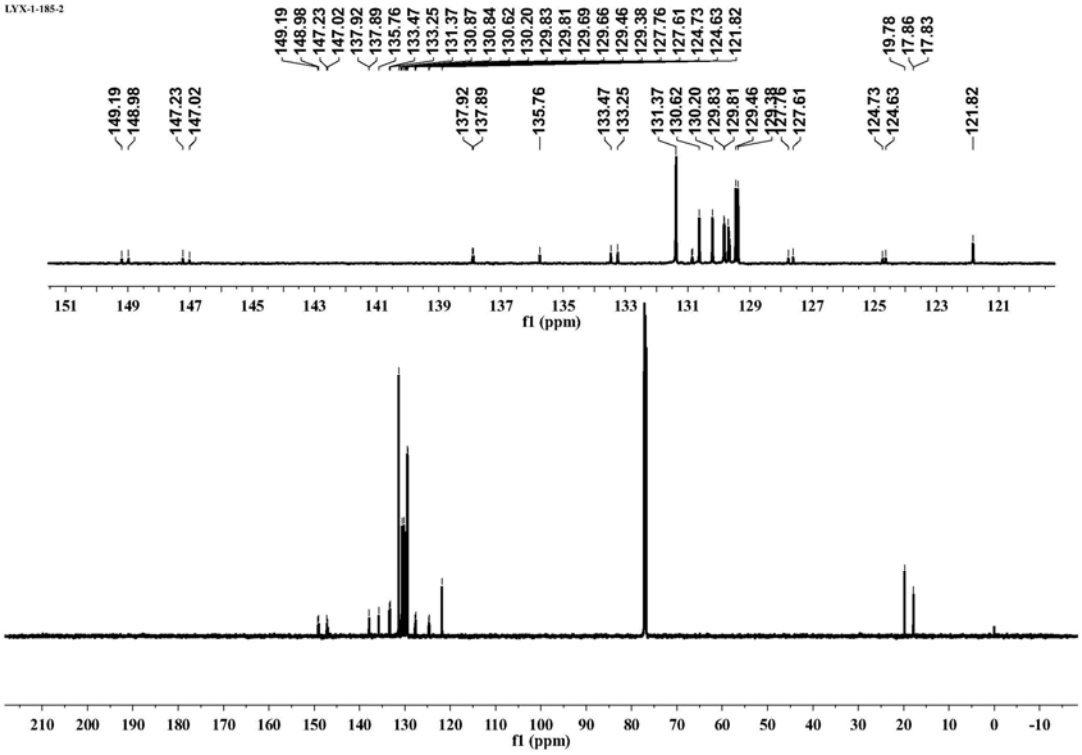

LYX-1-151-3
153.06
151.01
145.23
135.03
134.30
134.07
131.33
130.46
130.44
130.00
129.54
128.96
126.94
126.47
126.37
126.17
125.17
123.54
119.00
114.16
114.12
113.65
108.28
108.16
21.59
f1 (ppm)

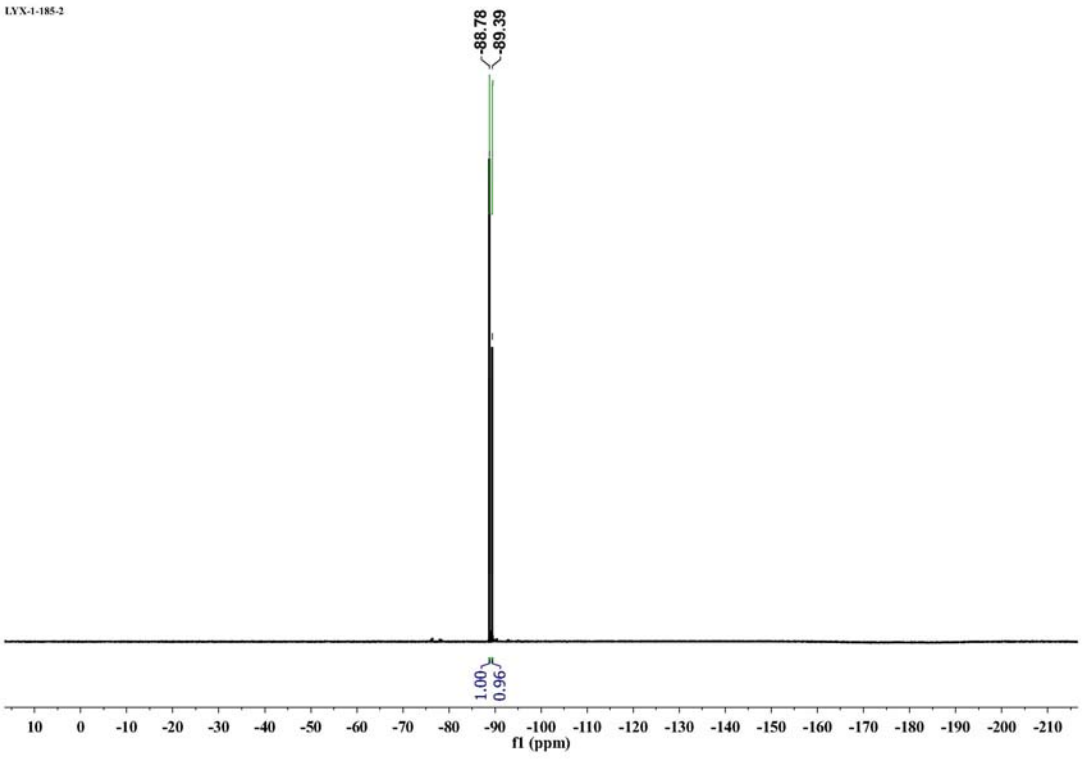


3rh

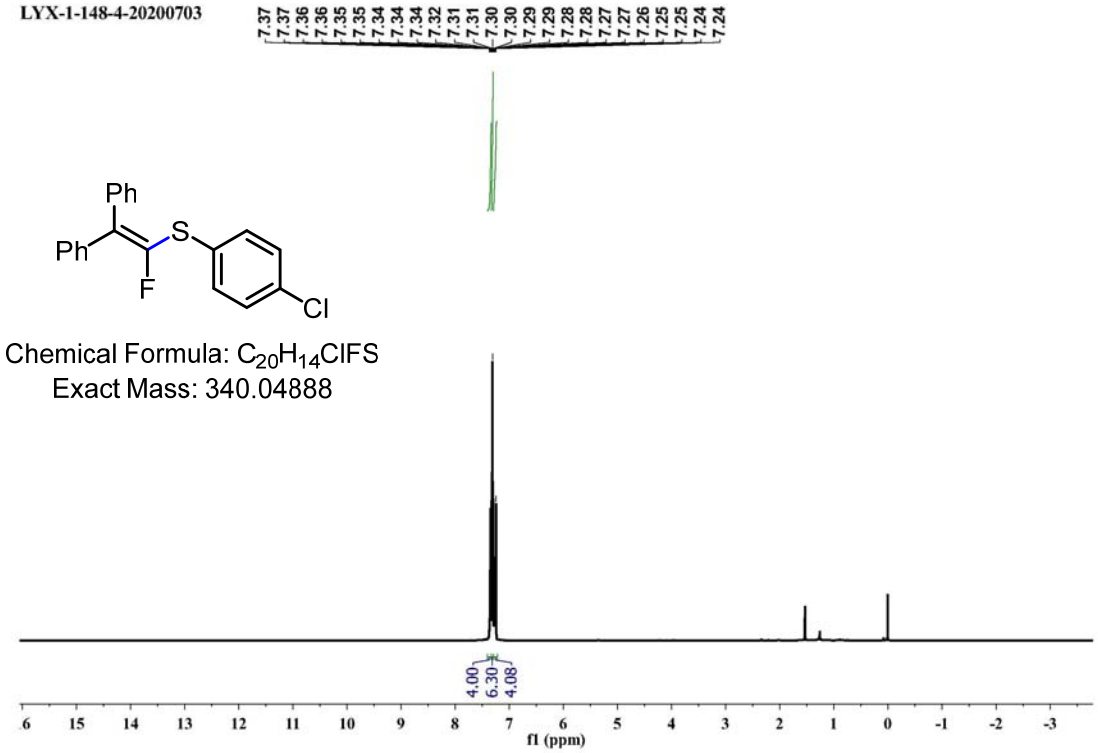


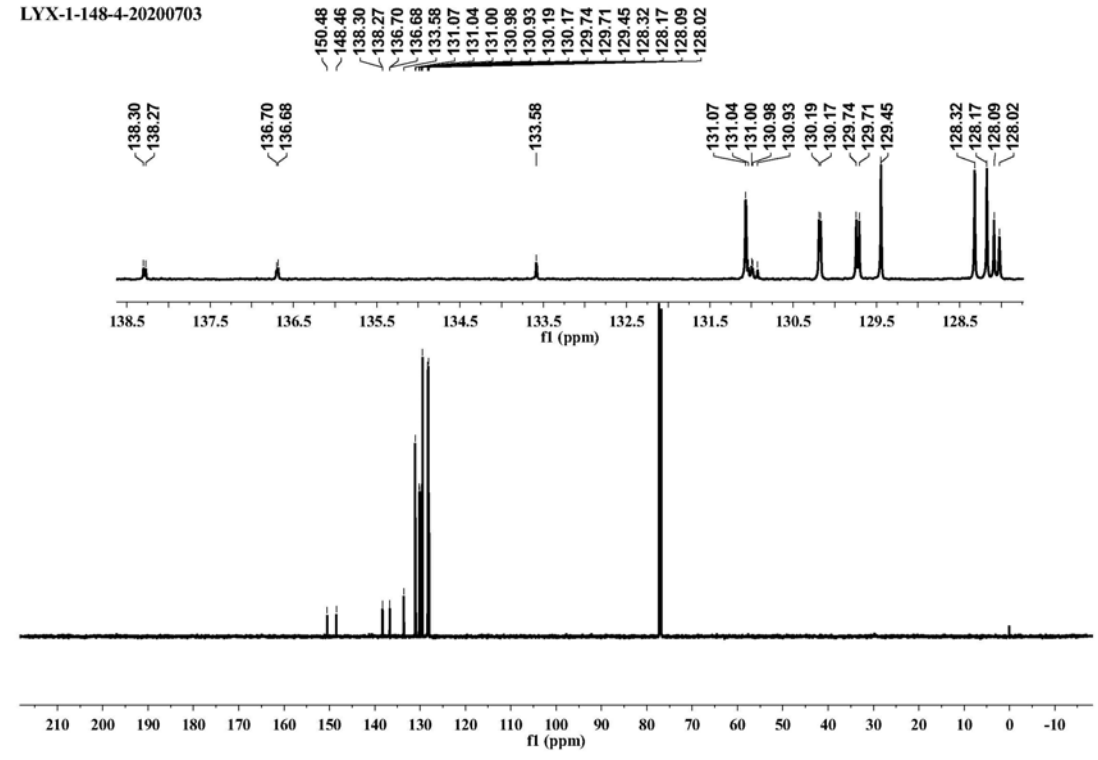
Chemical Formula: $C_{15}H_{11}BrClFS$
Exact Mass: 355.94374

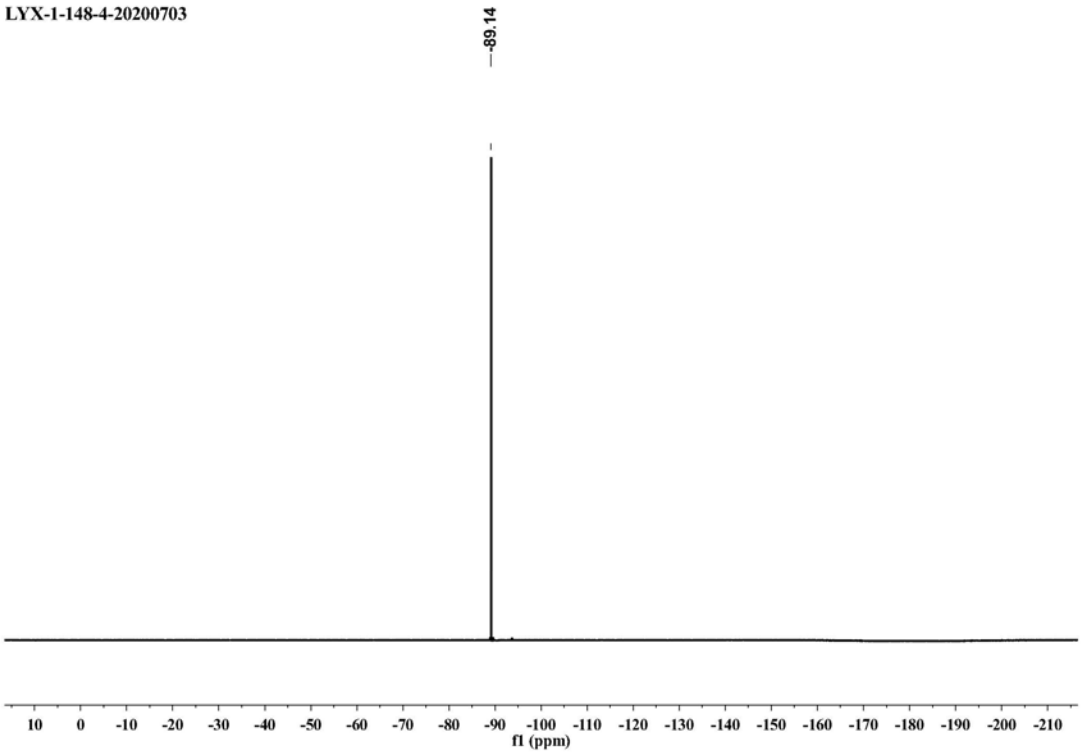

LYX-1-185-2
149.19
148.98
147.23
147.02
137.92
137.89
135.76
133.47
133.25
131.37
130.87
130.84
130.62
130.20
129.83
129.81
129.69
129.66
129.46
129.38
127.76
127.61
124.73
124.63
121.82
19.78
17.86
17.83
f1 (ppm)


LYX-1-185-2
-88.78
-89.39
1.00
0.96
f1 (ppm)

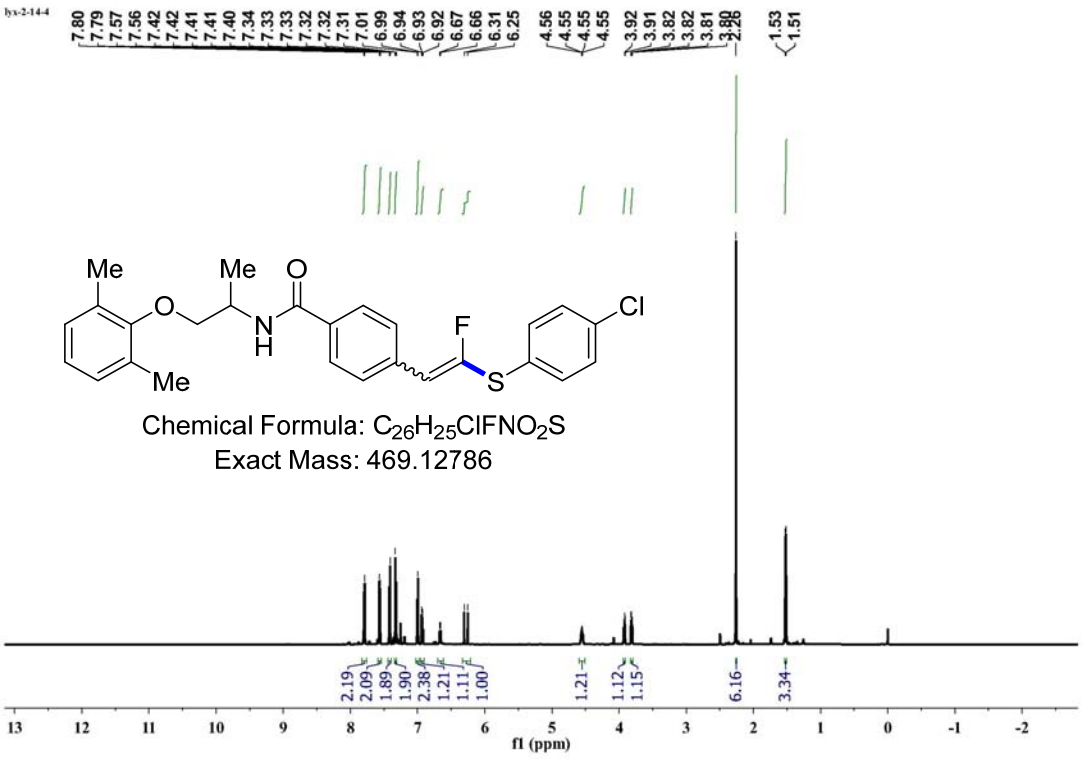
3sh

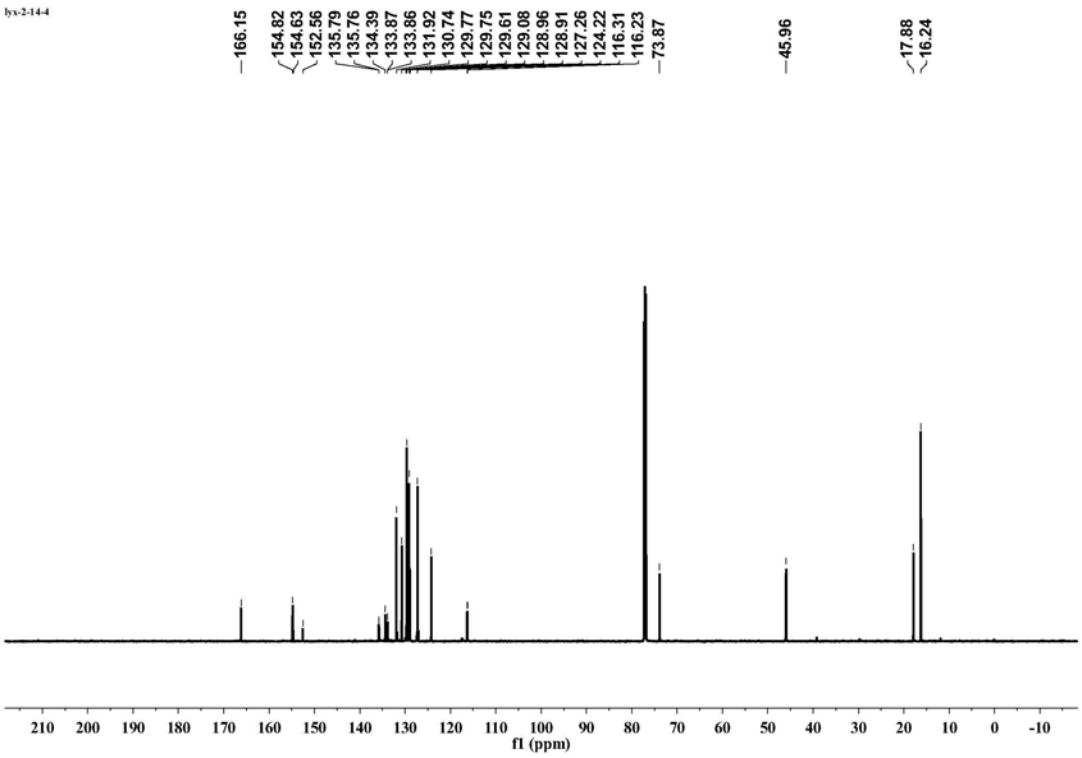

LYX-1-148-4-20200703
Ph
Ph
S
F
Cl
Chemical Formula: C20H14ClFS
Exact Mass: 340.04888
4.00
6.30
4.08
f1 (ppm)

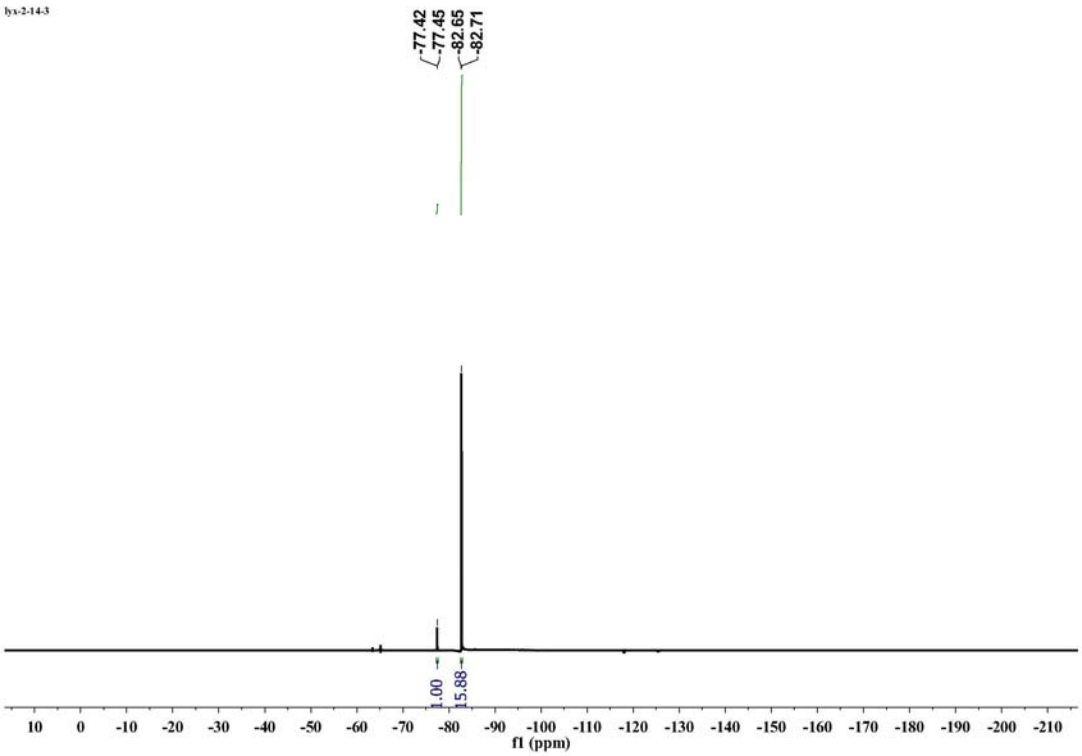

LYX-1-148-4-20200703
f1 (ppm)


LYX-1-148-4-20200703
-89.14
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

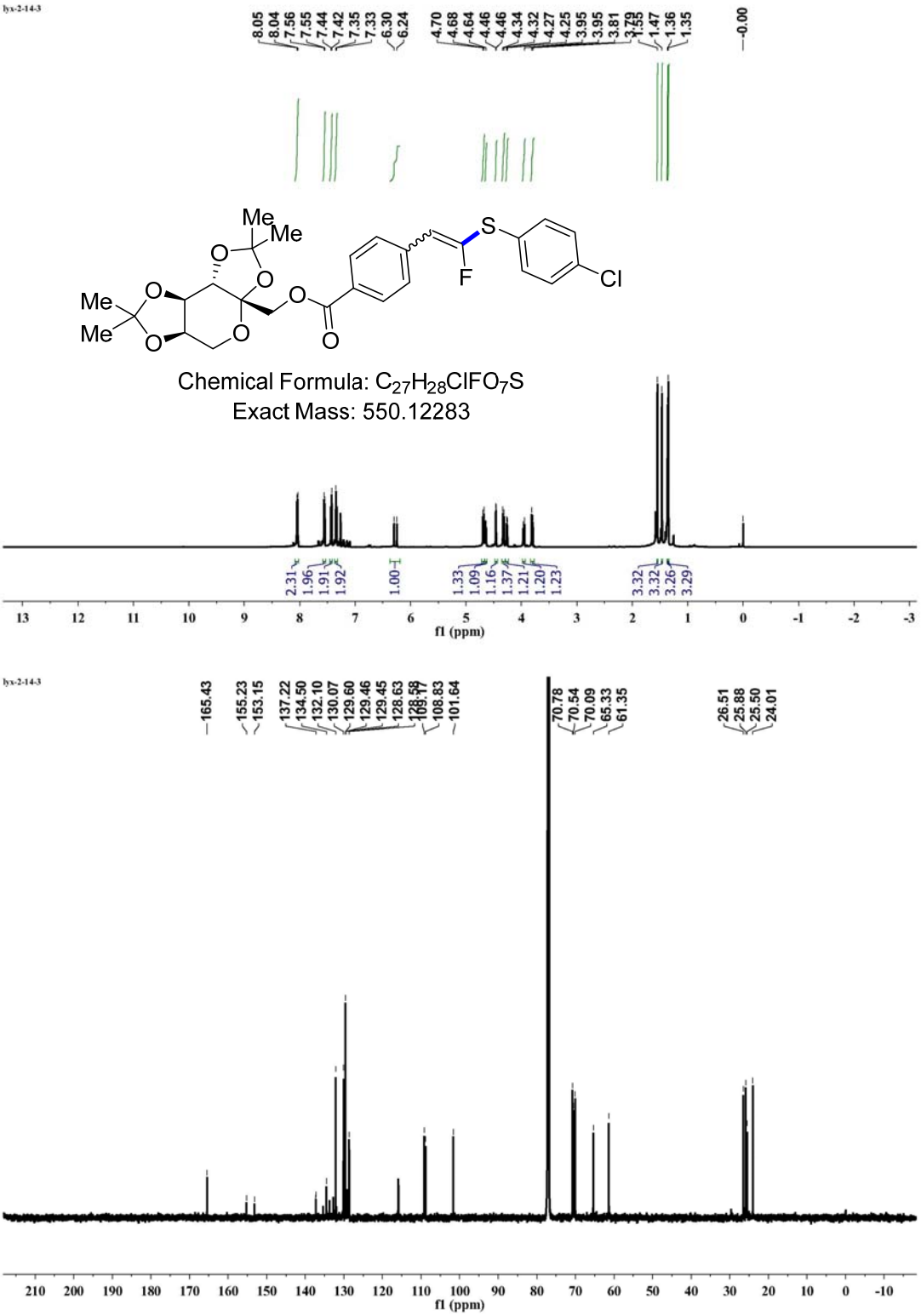
3th

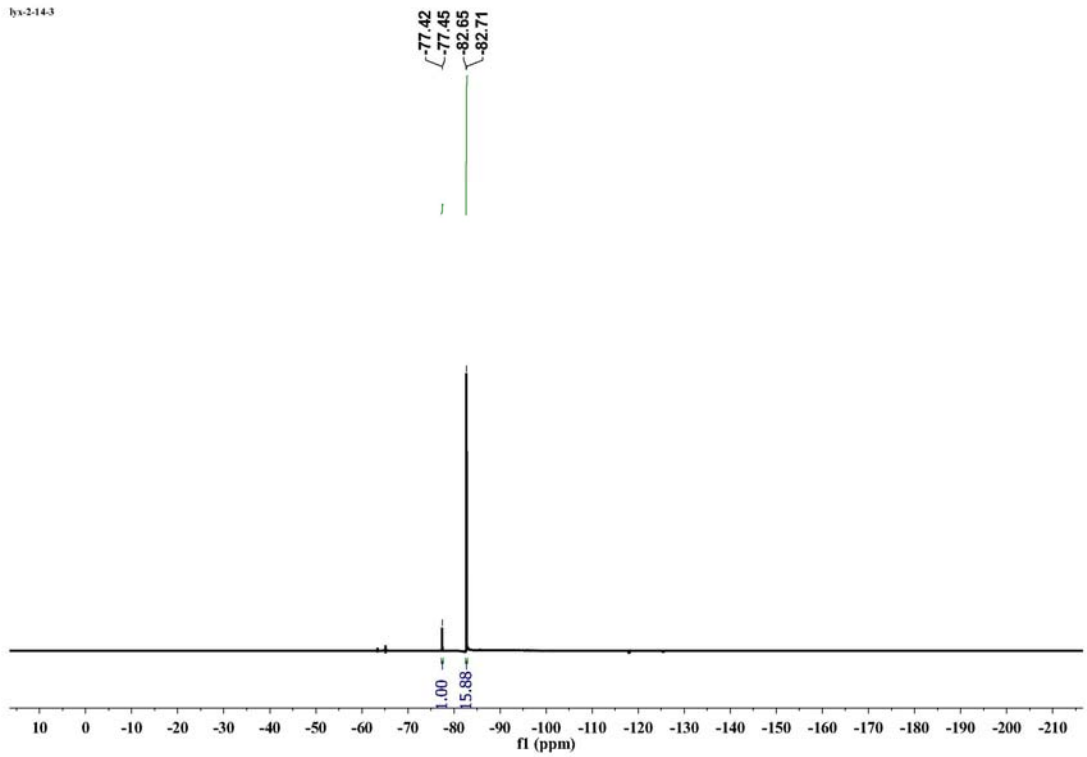

lyx-2-14-4
7.80 7.79 7.57 7.56 7.42 7.42 7.41 7.41 7.40 7.34 7.33 7.33 7.32 7.32 7.31 7.01 6.99 6.94 6.93 6.92 6.67 6.66 6.31 6.25
4.56 4.55 4.55 4.55
3.92 3.91 3.82 3.82 3.81 3.80 2.28
1.53 1.51
Me
Me
O
O
N
H
F
Cl
Me
S
Chemical Formula: C26H25ClFNO2S
Exact Mass: 469.12786
2.19 2.09 1.89 1.90 2.38 1.21 1.11 1.00
1.21 1.12 1.15
6.16
3.34
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


lyx-2-14-4
166.15
154.82
154.63
152.56
135.79
135.76
134.39
133.87
133.86
131.92
130.74
129.77
129.75
129.61
129.08
128.96
128.91
127.26
124.22
116.31
116.23
73.87
45.96
17.88
16.24
f1 (ppm)

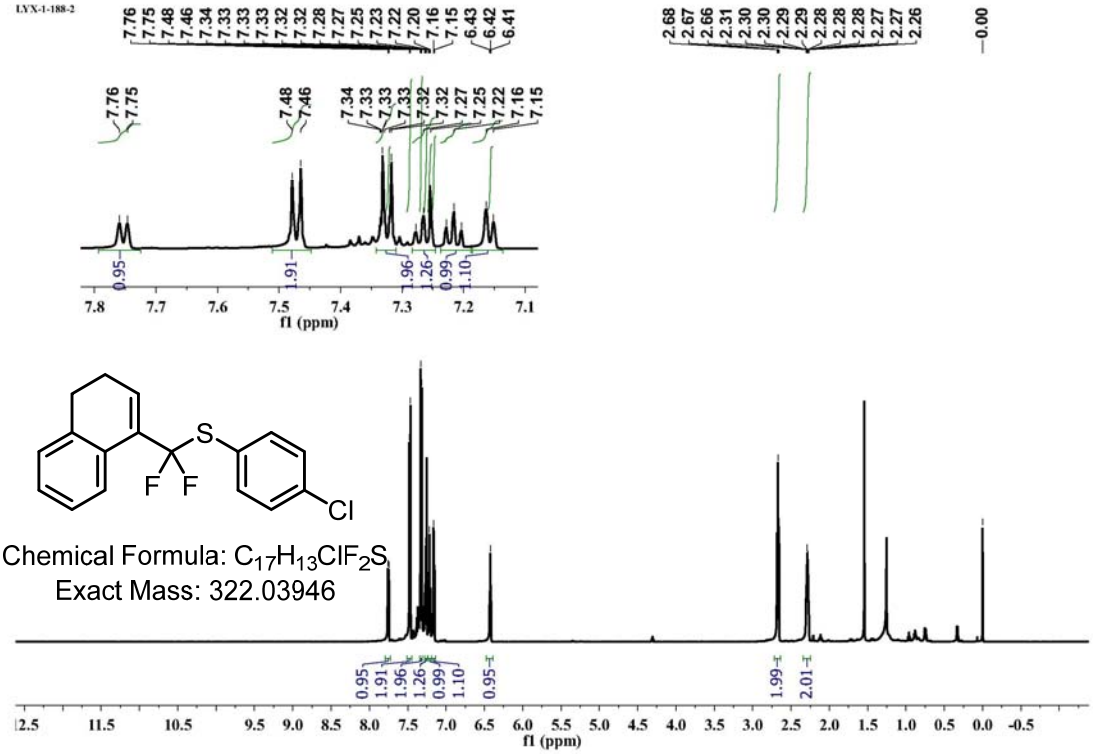

lyx-2-14-3
-77.42
-77.45
-82.65
-82.71
1.00
15.88
f1 (ppm)

3uh

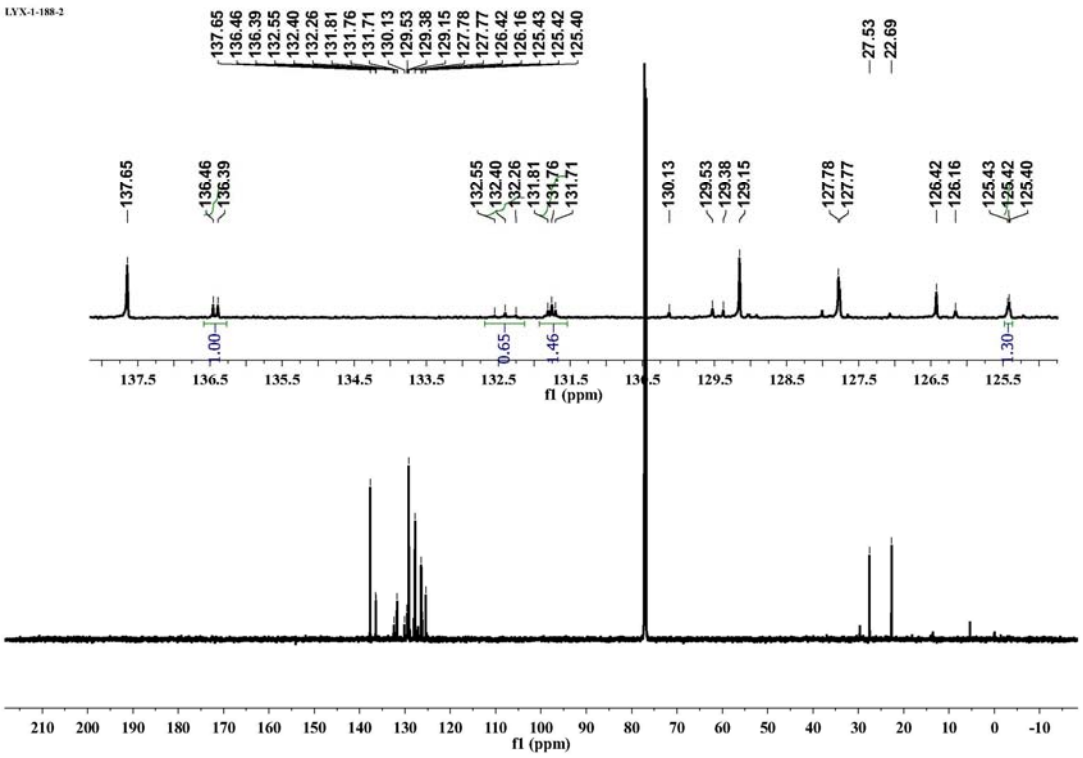

lyx-2-14-3
8.05
8.04
7.56
7.55
7.44
7.42
7.35
7.33
6.30
6.24
4.70
4.68
4.64
4.46
4.46
4.34
4.32
4.27
4.25
3.95
3.81
1.47
1.36
1.35
0.00
Me
Me
O
O
O
Me
Me
O
O
O
O
S
F
Cl
Chemical Formula: C27H28ClFO7S
Exact Mass: 550.12283
2.31
1.96
1.91
1.92
1.00
1.33
1.09
1.16
1.37
1.21
1.20
1.23
3.32
3.32
3.26
3.29
f1 (ppm)
lyx-2-14-3
165.43
155.23
153.15
137.22
134.50
132.10
130.07
129.60
129.46
129.45
128.63
108.83
101.64
70.78
70.54
70.09
65.33
61.35
26.51
25.88
25.50
24.01
f1 (ppm)

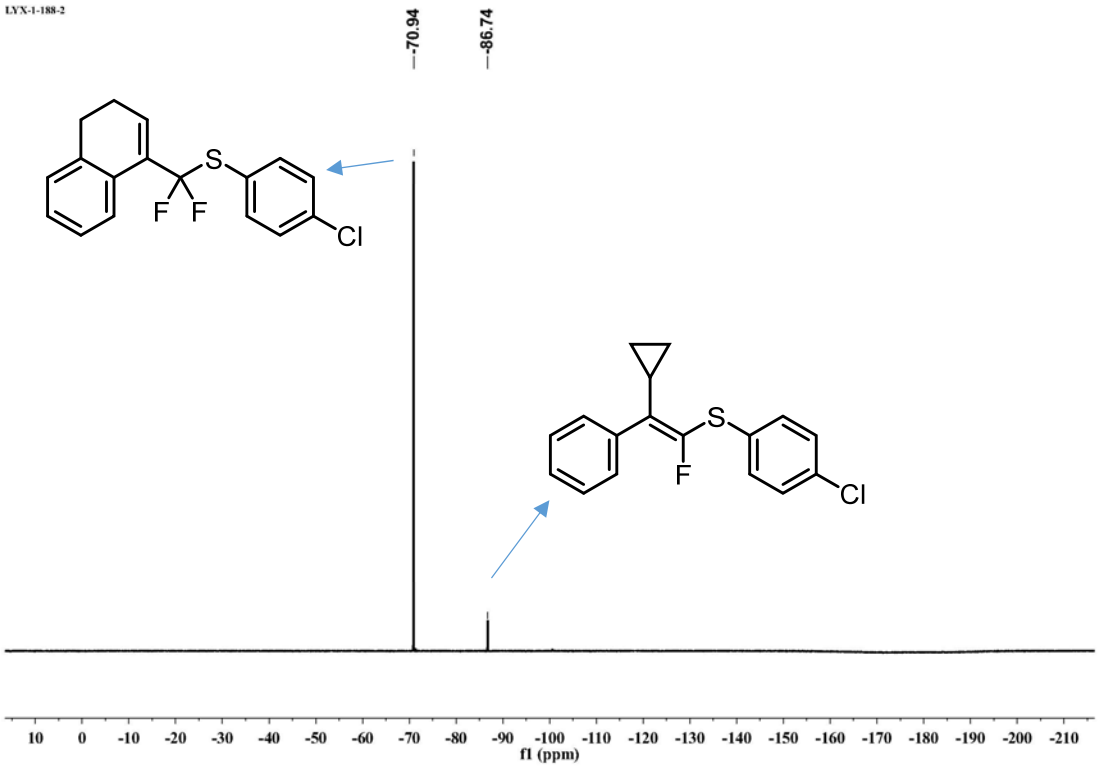


4

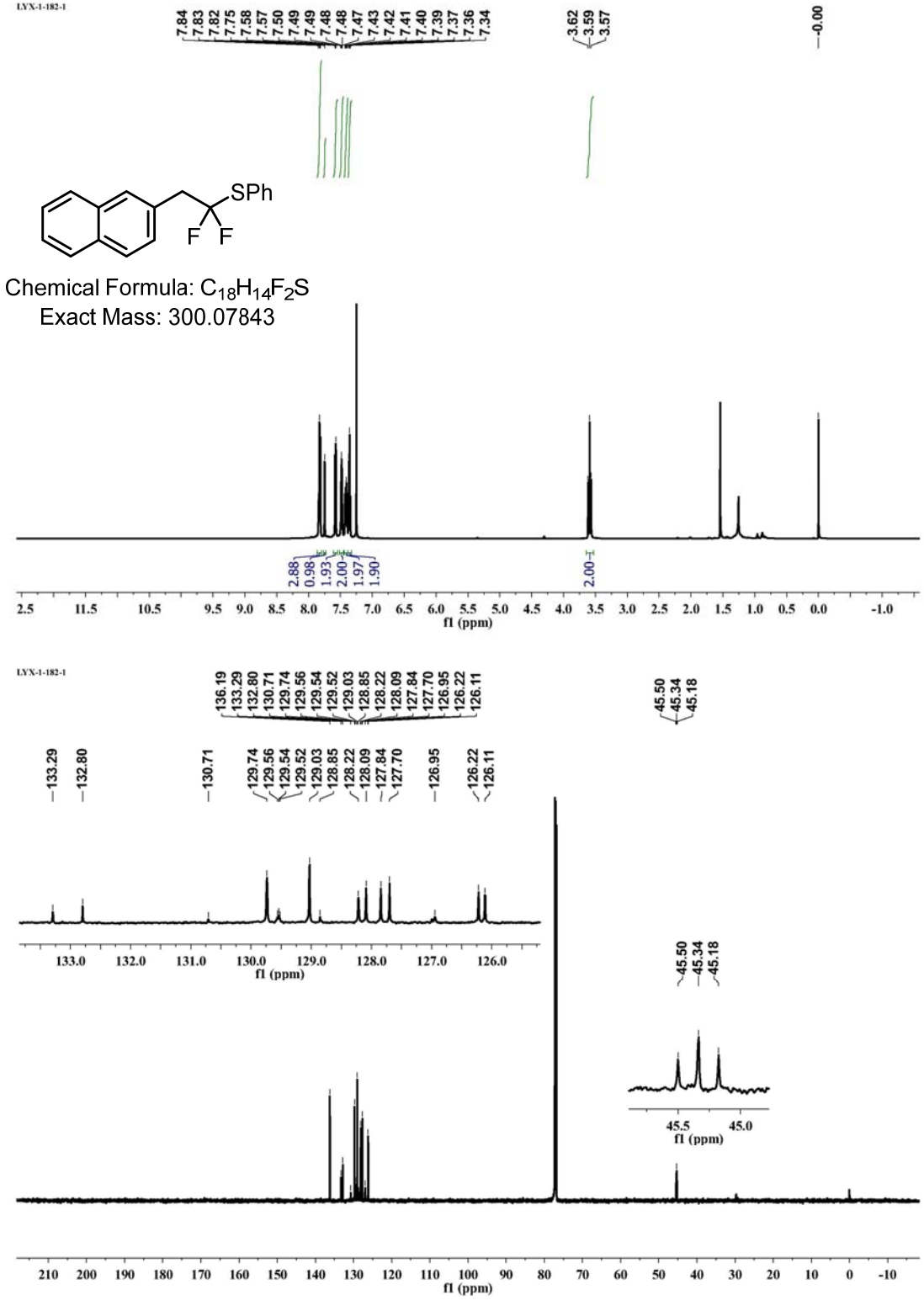


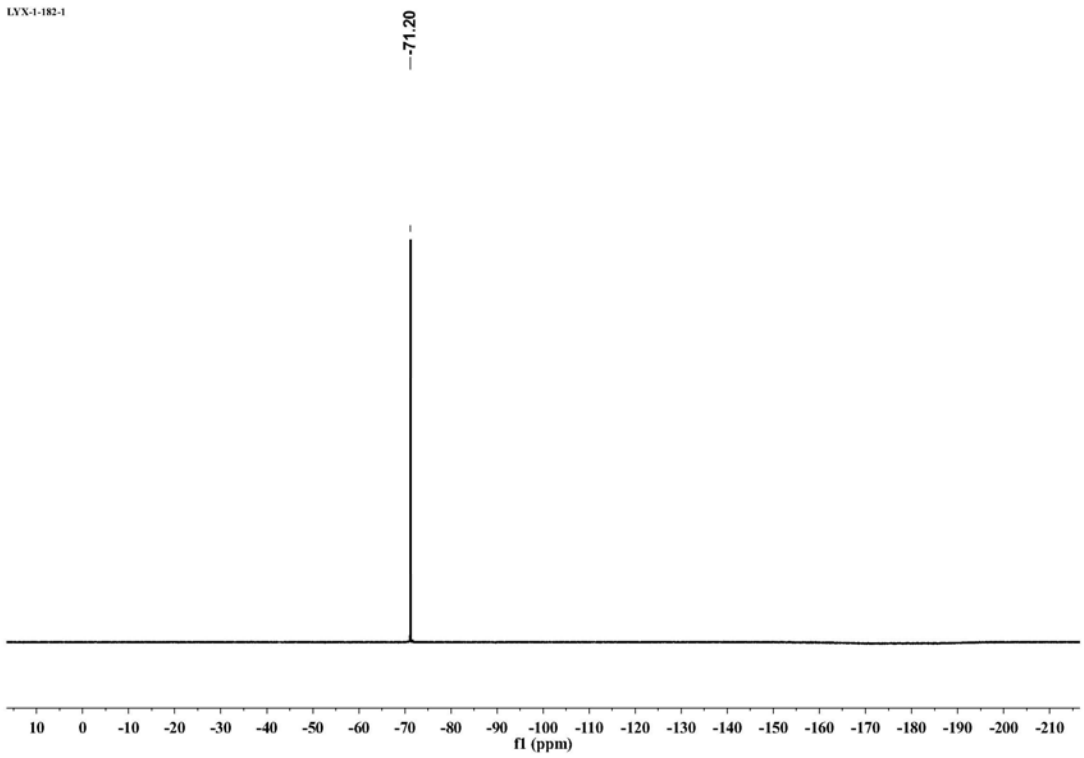
Chemical Formula: $C_{17}H_{13}ClF_2S$
Exact Mass: 322.03946


LYX-1-188-2
137.65
136.46
136.39
132.55
132.40
132.26
131.81
131.76
131.71
130.13
129.53
129.38
129.15
127.78
127.77
126.42
126.16
125.43
125.42
125.40
27.53
22.69
1.00
0.65
1.46
1.30
f1 (ppm)

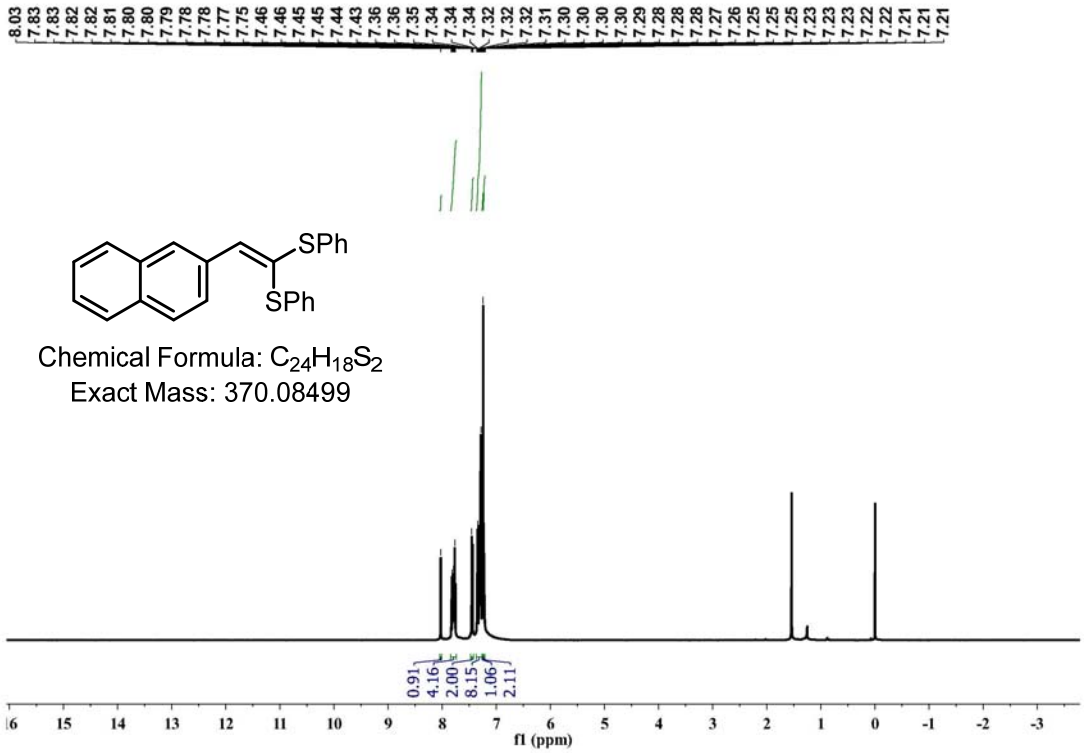

LYX-1-188-2
-70.94
-86.74
S
F
F
Cl
S
F
Cl
f1 (ppm)

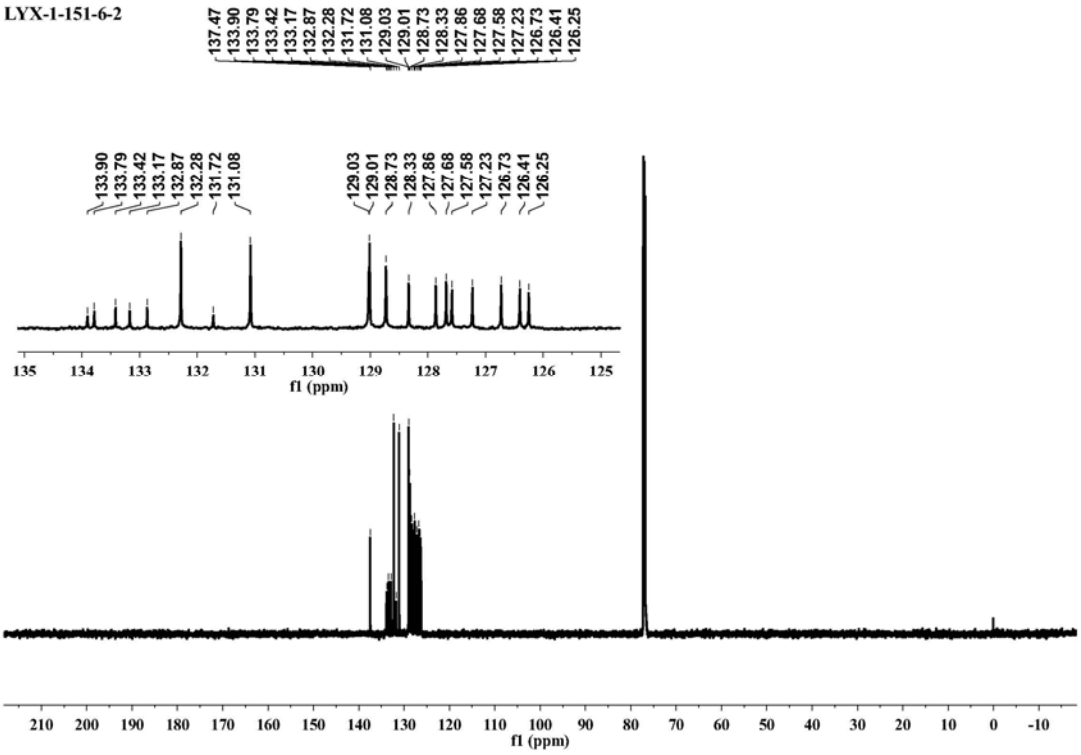
6


LYX-1-182-1
7.84
7.83
7.82
7.75
7.58
7.57
7.50
7.49
7.49
7.48
7.48
7.47
7.43
7.42
7.41
7.40
7.39
7.37
7.36
7.34
3.62
3.59
3.57
0.00
SPh
F F
Chemical Formula: C18H14F2S
Exact Mass: 300.07843
2.88
0.98
1.93
2.00
1.97
1.90
2.00
fl (ppm)
LYX-1-182-1
136.19
133.29
132.80
130.71
129.74
129.56
129.54
129.52
129.03
128.85
128.22
128.09
127.84
127.70
126.95
126.22
126.11
45.50
45.34
45.18
fl (ppm)
fl (ppm)
fl (ppm)

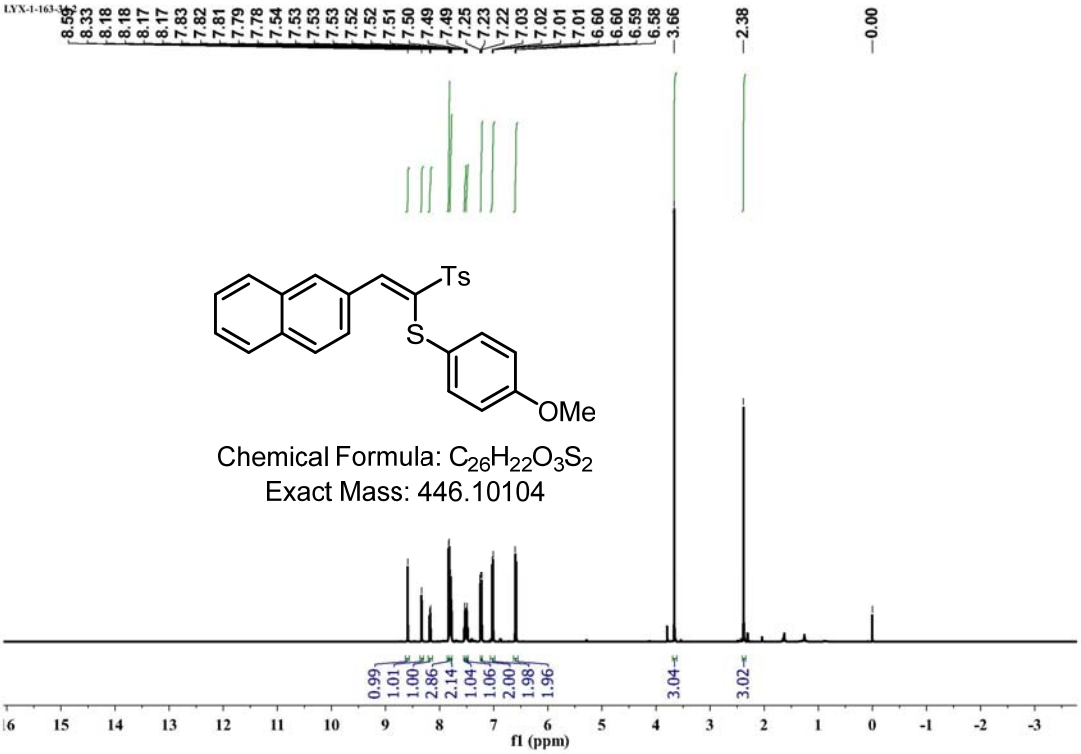

LYX-1-182-1
-71.20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

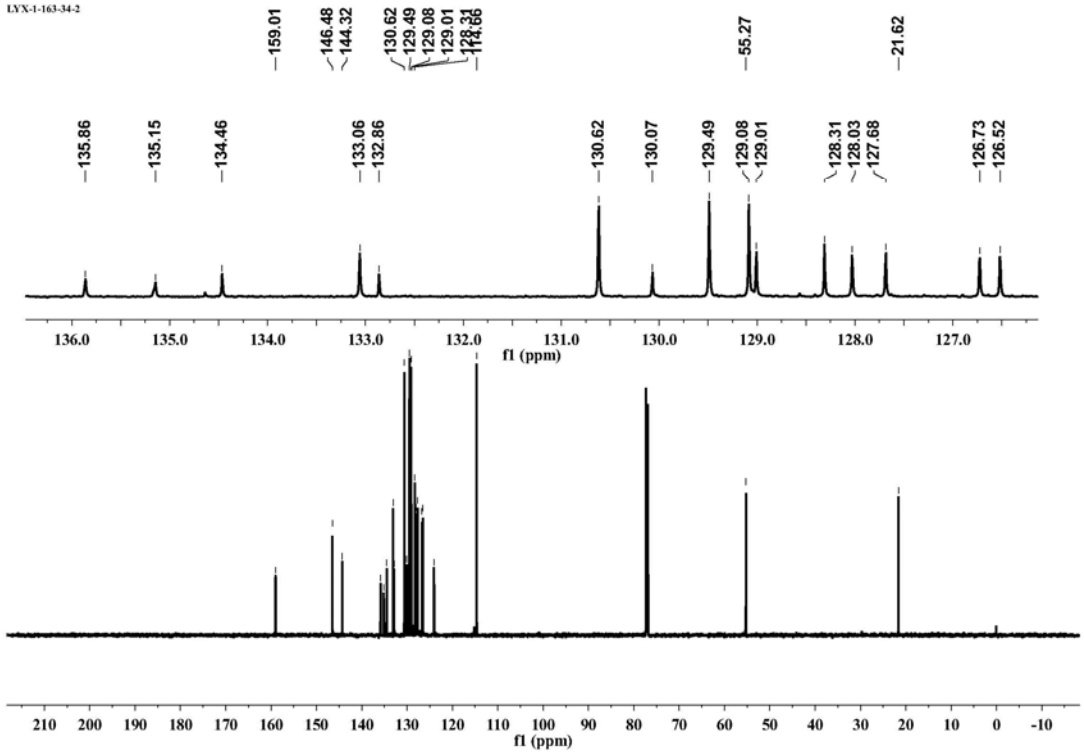
7


SPh
SPh
Chemical Formula: C24H18S2
Exact Mass: 370.08499
0.91
4.16
2.00
8.15
1.06
2.11
f1 (ppm)

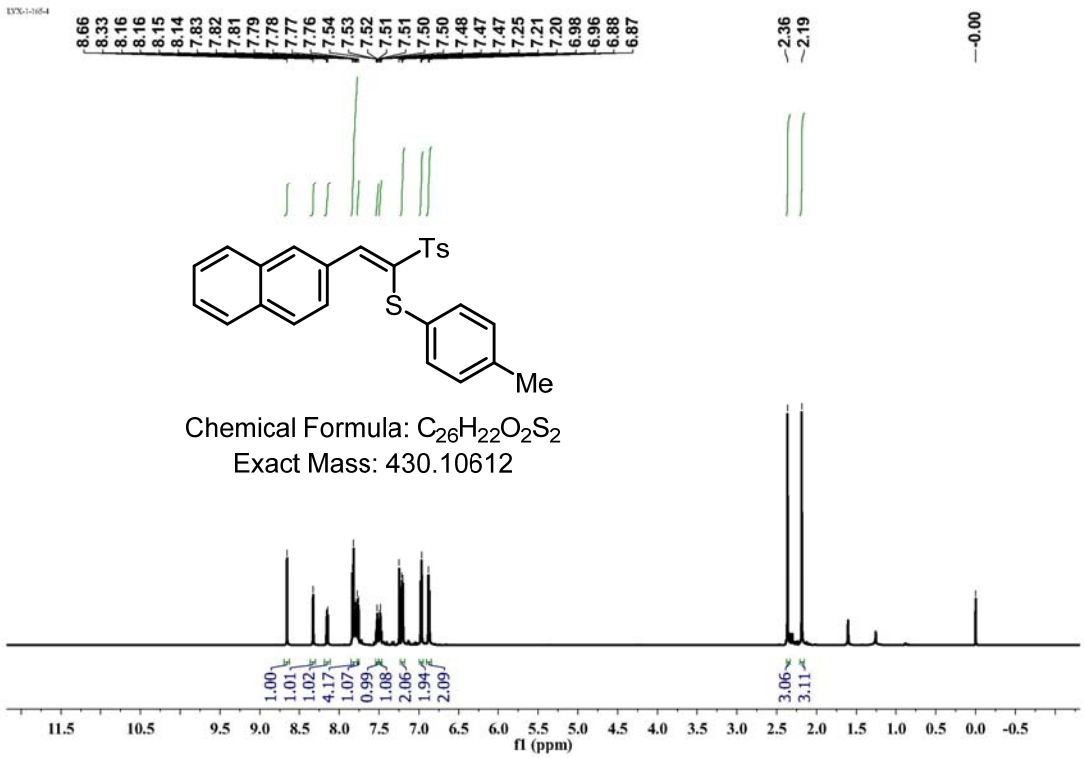

LYX-1-151-6-2
137.47
133.90
133.79
133.42
133.17
132.87
132.28
131.72
131.08
129.03
129.01
128.73
128.33
127.86
127.68
127.58
127.23
126.73
126.41
126.25
f1 (ppm)
f1 (ppm)

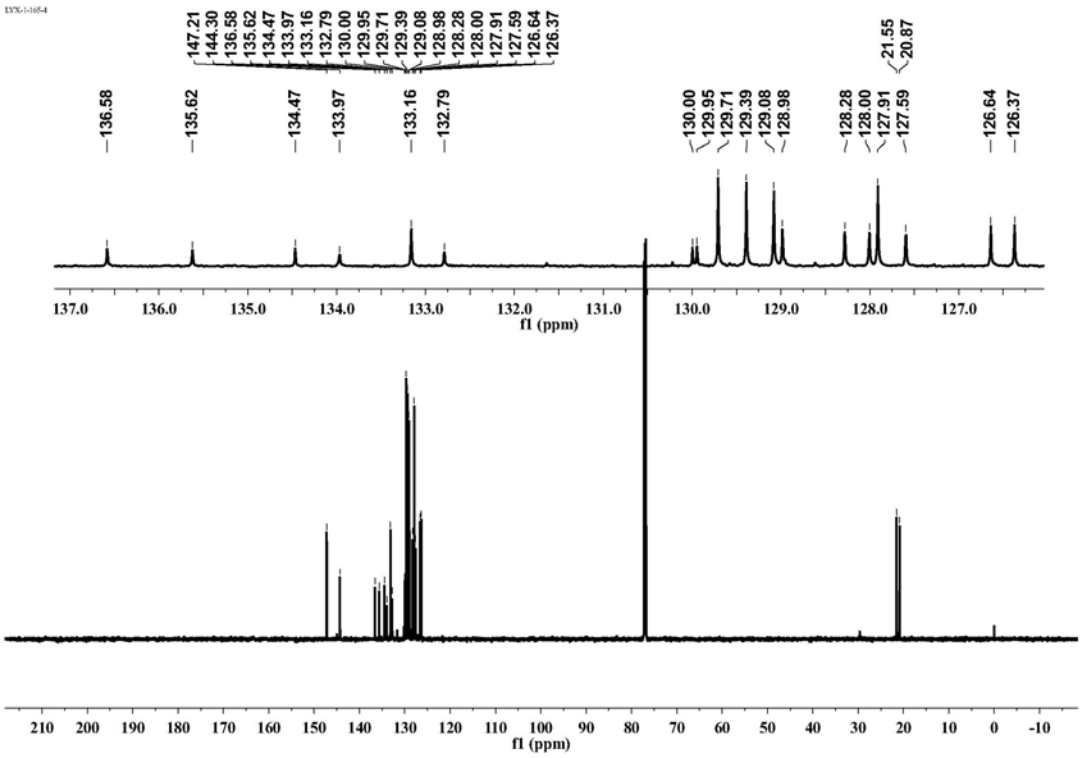
9


8.33
8.18
8.18
8.17
8.17
7.83
7.82
7.81
7.79
7.78
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.25
7.23
7.22
7.03
7.02
7.01
7.01
6.60
6.60
6.59
6.58
3.66
2.38
0.00
Ts
S
OMe
Chemical Formula: C26H22O3S2
Exact Mass: 446.10104
0.99
1.01
1.00
2.86
2.14
1.04
1.06
2.00
1.98
1.96
3.04
3.02
f1 (ppm)


LYX-1-163-34-2
159.01
146.48
144.32
130.62
129.49
129.08
129.01
55.27
21.62
135.86
135.15
134.46
133.06
132.86
130.62
130.07
129.49
129.08
129.01
128.31
128.03
127.68
126.73
126.52
f1 (ppm)

10


8.66
8.33
8.16
8.16
8.15
8.14
7.83
7.82
7.81
7.79
7.78
7.77
7.76
7.54
7.53
7.52
7.51
7.51
7.50
7.50
7.48
7.47
7.47
7.25
7.21
7.20
6.98
6.96
6.88
6.87
2.36
2.19
0.00
Ts
S
Me
Chemical Formula: C26H22O2S2
Exact Mass: 430.10612
1.00
1.01
1.02
4.17
1.07
0.99
1.08
2.06
1.94
2.09
3.06
3.11
f1 (ppm)


147.21
144.30
136.58
135.62
134.47
133.97
133.16
132.79
130.00
129.95
129.71
129.39
129.08
128.98
128.28
128.00
127.91
127.59
126.64
126.37
21.55
20.87
136.58
135.62
134.47
133.97
133.16
132.79
130.00
129.95
129.71
129.39
129.08
128.98
128.28
128.00
127.91
127.59
126.64
126.37
137.0
136.0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
127.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)