Supplementary Information

For

Visible-Light-Mediated Defluorinative Cross-Coupling of *gem*-Difluoroalkenes with Thiols

Junlei Wang, Binbin Huang, Chao Yang* and Wujiong Xia*

State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology (Shenzhen), Shenzhen, China 518055.

E-mail: xyyang@hit.edu.cn ;

xiawj@hit.edu.cn (W. X.)

Contents

1. General Information

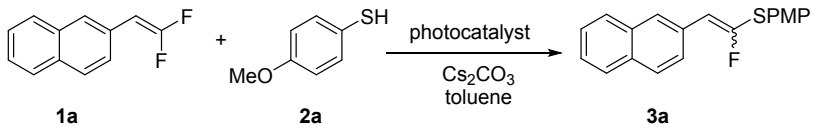
All of the reagents were purchased from Energy-Chemical and Sigma-Aldrich without further purification. Uncommercial available multifluoroarenes were obtained according to literature. Solvents were purified according to the method of Grubbs.[1] ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AV-400 or 600 (^{1}H NMR at 400 MHz or 600 M, ^{13}C NMR at 100 MHz or 151 M, ^{19}F NMR at 376 MHz) spectrometers using tetramethylsilane (TMS) as internal standard. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). High resolution massspectra (HRMS) were collected on Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was conducted on a 7890A-5975C/Agilent.

2. General Procedure for the Preparation of Starting Materials

All of the gem-difluoroalkenes (**1a - 1s**) were prepared according to the previous literatures.[2-3]

3. Optimization Studies

Table S1. Screening of photocatalyst.[a]

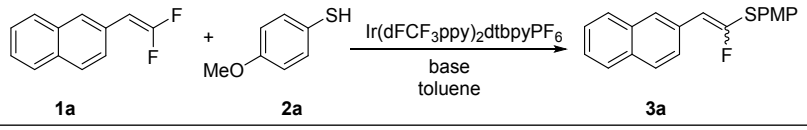


1a **2a** **3a**

Entry	Photocatalyst	Base	Solvent	Y(%)[b]
1	$Ru(bpy)_3Cl_2$	Cs_2CO_3	toluene	3
2	$Ru(bpy)_3PF_6$	Cs_2CO_3	toluene	0
3	Eosin Y	Cs_2CO_3	toluene	0
4	fac-$Ir(ppy)_3$	Cs_2CO_3	toluene	5
5	fac-$Ir(dFppy)_3$	Cs_2CO_3	toluene	0
6	$Ir(dFppy)_2bpyPF_6$	Cs_2CO_3	toluene	57
7	$Ir(dFCF_3ppy)_2dtbpyPF_6$	Cs_2CO_3	toluene	85
8	$Ir(ppy)_2dtbpyPF_6$	Cs_2CO_3	toluene	47

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv), Cs_2CO_3 (2 equiv), toluene (1 mL), room temperature, N_2 atmosphere, 15 W blue leds. [b] The isolated yields are shown. [c] with the conversion of 80%.

Table S2. Screening of base.[a]

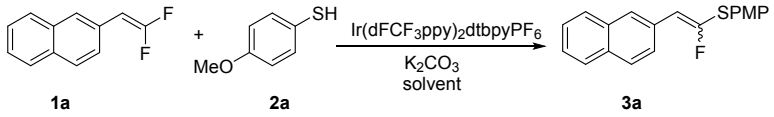


1a **2a** **3a**

Entry	Photocatalyst	Base	Solvent	Y(%)[b]
1	$Ir(dFCF_3ppy)_2dtbpyPF_6$	NaOAc	toluene	0
2	$Ir(dFCF_3ppy)_2dtbpyPF_6$	K_2HPO_4	toluene	0
3	$Ir(dFCF_3ppy)_2dtbpyPF_6$	K_2CO_3	toluene	90

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv), base (2 equiv), toluene (1 mL), room temperature, N_2 atmosphere, 15 W blue leds. [b] The isolated yields are shown.

Table S3. Screening of solvents.[a]

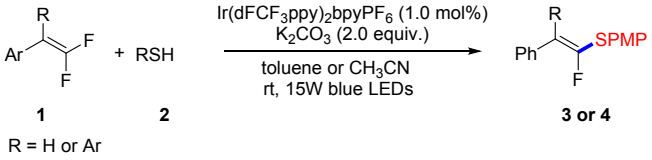


1a **2a** **3a**

Entry	Photocatalyst	Base	Solvent	Y(%)[b]
1	$Ir(dFCF_3ppy)_2dtbpyPF_6$	DCE	toluene	3
2	$Ir(dFCF_3ppy)_2dtbpyPF_6$	CH_3CN	toluene	83
3	$Ir(dFCF_3ppy)_2dtbpyPF_6$	CF_3CH_2OH	toluene	0
4	$Ir(dFCF_3ppy)_2dtbpyPF_6$	DMSO	toluene	78
5	$Ir(dFCF_3ppy)_2dtbpyPF_6$	K_2CO_3	toluene	0
6	--	K_2CO_3	toluene	0
7	$Ir(dFCF_3ppy)_2dtbpyPF_6$	--	toluene	0

[a] Reaction conditions: photocatalyst (1 mol%), **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2 equiv), base (2 equiv), toluene (1 mL), room temperature, N_2 atmosphere, 15 W blue leds. [b] The isolated yields are shown. [c] the reaction was conducted in dark.

4. Typical Procedure for Cross-coupling Reactions

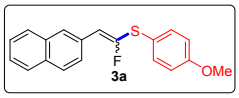


1 **2** **3 or 4**

R = H or Ar

General procedure: 1 (0.1 mmol), **2** (0.15 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1 mL solvent (CH_3CN or toluene) was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. The filtrate was concentrated and purification by chromatography on silica gel to afford the desired product.

5. Product Characterization



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

The reaction was performed according to the general procedure using 2-(2,2-difluorovinyl)naphthalene with toluene as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3a** (27.9 mg, 90% yield) as a yellow solid. Yellow solid, mp. 59-61 °C, 90% isolated yield.

Both isomers:[1]H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (d, J = 10.9 Hz, 1H), 7.86 - 7.74 (m, 3.55H), 7.64 (dd, J = 8.6, 1.5 Hz, 0.45H), 7.55 - 7.42 (m, 4H), 6.94 - 6.85 (m, 2H), 6.78 (d, J = 16.6 Hz, 0.51H), 6.32 (d, J = 33.0 Hz, 0.38H), 3.82 (s, 1.34H), 3.80 (s, 1.66H).

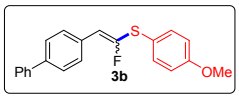
E isomer: [13]C NMR (101 MHz, $CDCl_3$): δ_C 160.1, 154.2 (d, J = 309.9 Hz), 133.3, 132.7, 128.2, 128.1, 127.9, 127.6 (d, J = 5.6 Hz), 126.3, 121.7, 117.2, 116.8 (d, J = 88.6 Hz), 116.3, 115.2, 115.0, 55.4.

Z isomer: [13]C NMR (101 MHz, $CDCl_3$): δ_C 160.07, 154.00 (d, J = 296.8 Hz), 133.4, 132.7, 130.7 (d, J = 5.5 Hz), 130.1 (d, J = 9.0 Hz), 128.3, 128.2, 128.0, 127.6 (d, J = 5.6 Hz), 126.2, 120.7, 116.0, 115.6 (d, J = 82.6 Hz), 115.1, 115.0, 55.4

[19]F NMR (376 MHz, $CDCl_3$): δ_F -80.39 (d, J = 16.6 Hz, 0.55F), -85.85 (d, J = 33.0 Hz, 0.45F).

GC-MS (EI, QMS, m/z): 139.0, 202.1, 247.1, 277.1, 290.1, 310.1.

HRMS (ESI): calcd for $C19H16FOS^+$, $(M+H)^+$, 311.0900, found, 311.0909.



(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)(4-methoxyphenyl)sulfane (3b)

The reaction was performed according to the general procedure using 4-(2,2-difluorovinyl)-1,1'-biphenyl with toluene as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3b** (27.9 mg, 83% yield) as a yellow solid. Yellow solid, mp. 68-71 °C, 83% isolated yield.

Both isomers:[1]H NMR (400 MHz, $CDCl_3$): δ_H 7.73 - 7.59 (m, 6H), 7.57 - 7.46 (m, 4H), 7.44 - 7.37 (m, 1H), 6.99 - 6.91 (m, 2H), 6.71 (d, J = 16.7 Hz, 0.36H), 6.26 (d, J = 33.0 Hz, 0.53H), 3.87 (s, 1.79H), 3.85 (s, 1.21H).

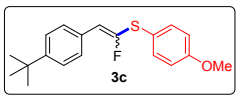
E isomer: [13]C NMR (101 MHz, $CDCl_3$): δ_C 160.4, 154.4 (d, J = 309.9 Hz), 140.8 (d, J = 4.5 Hz), 133.8, 132.4 (d, J = 5.3 Hz), 129.4 (d, J = 12.3 Hz), 129.0, 127.6, 127.4, 127.1, 122.1, 115.2, 115.1 (d, J = 2.4 Hz), 114.9 (d, J = 2.0 Hz), 55.6.

Z isomer: [13]C NMR (101 MHz, $CDCl_3$): δ_C 160.36, 154.2 (d, J = 268.9 Hz), 140.7 (d, J = 6.4 Hz), 133.8, 131.9 (d, J = 9.4 Hz), 129.4 (d, J = 12.3 Hz), 128.97, 127.6, 127.4, 127.1, 121.1, 116.1 (d, J = 2.5 Hz), 115.8 (d, J = 2.7 Hz), 115.2, 55.6.

[19]F NMR (376 MHz, $CDCl_3$): δ_F -80.56 (d, J = 16.7 Hz, 0.40F), -85.73 (d, J = 33.0 Hz, 0.60F).

GC-MS (EI, QMS, m/z): 197.1, 273.1, 291.1, 316.1, 336.2.

HRMS (ESI): calcd for $C_{21}H_{18}FOS^+$, $(M+H)^+$, 337.1057, found, 337.1056.



(2-(4-(tert-butyl)phenyl)-1-fluorovinyl)(4-methoxyphenyl)sulfane (3c)

The reaction was performed according to the general procedure using 1-(tert-butyl)-4-(2,2-difluorovinyl)benzene with toluene as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3c** (23.7 mg, 75% yield) as a colorless oil. Colorless oil, 75% isolated yield.

Both isomers: [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.54 (dd, J = 24.4, 7.3 Hz, 2H), 7.49 - 7.44 (m, 2H), 7.39 (dd, J = 27.9, 19.5 Hz, 2H), 6.66 (d, J = 16.8 Hz, 0.29H), 6.23 (d, J = 33.0 Hz, 0.58H), 3.86 (s, 1.8H), 3.85 (s, 1.2H), 1.38 (s, 3.0H), 1.36 (s, 6H).

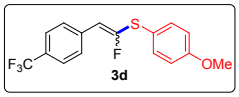
E isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.9, 153.1 (d, J = 309.0 Hz), 133.2 (s), 130.3 (d, J = 5.2 Hz), 128.4, 125.5, 122.16 (d, J = 1.9 Hz), 121.05, 116.4, 115.6 (d, J = 13.1 Hz), 114.9, 55.4, 31.2.

Z isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 152.94 (d, J = 295.8 Hz), 150.8, 133.3, 130.2, 128.4, 125.3, 121.1, 116.2 (d, J = 31.5 Hz), 55.4, 34.6, 31.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -81.85 (d, J = 16.8 Hz, 0.31F), -86.79 (d, J = 33.0 Hz, 0.69F).

GC-MS (EI, QMS, m/z): 207.1, 259.1, 281.1, 301.1, 316.2.

HRMS (ESI): calcd for $C_{19}H_{22}FOS^+$, $(M+H)^+$, 317.1370, found, 317.1368.



3d

(1-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)(4-methoxyphenyl)sulfane (3d)

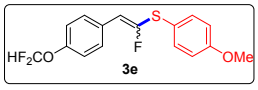
The reaction was performed according to the general procedure using 1-(2,2-difluorovinyl)-4-(trifluoromethyl)benzene with toluene as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3d** (18.0 mg, 55% yield) as a colorless oil. Colorless oil, 55% isolated yield.

Both isomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.73 - 7.57 (m, 4H), 7.56 - 7.44 (m, 2H), 6.99 - 6.90 (m, 2H), 6.63 (d, J = 16.3 Hz, 0.31H), 6.15 (d, J = 32.7 Hz, 0.6H), 3.87 (s, 2H), 3.86 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.8, 160.7, 134.6, 134.3, 129.2 (d, J = 1.3 Hz), 128.9, 128.8, 125.6, 125.5, 122.9 (d, J = 4.1 Hz), 121.0, 120.0, 115.3, 114.2 (d, J = 33.8 Hz), 112.6 (d, J = 3.9 Hz), 112.5 (d, J = 2.8 Hz), 55.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -62.56 (s, 1F), -62.62 (s, 2F), -78.04 (d, J = 16.3 Hz, 0.33F), -83.62 (d, J = 32.7 Hz, 0.67F).

HRMS (ESI): calcd for $C_{16}H_{13}F_4OS^+$, $(M+H)^+$, 329.0618, found, 329.0612.



3e

(2-(4-(difluoromethyl)phenyl)-1-fluorovinyl)(4-methoxyphenyl)sulfane (3e)

The reaction was performed according to the general procedure using 1-(difluoromethyl)-4-(2,2-difluorovinyl)benzene with toluene as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3e** (28.8 mg, 93% yield) as a colorless oil. Colorless oil, 93% isolated yield.

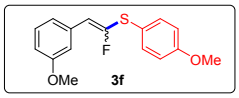
Both isomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64 - 7.38 (m, 4H), 7.14 (dd, J = 16.6, 8.7 Hz, 2H), 6.98 - 6.90 (m, 2H), 6.74 (d, J = 9.0 Hz, 0.23H), 6.62 (d, J = 16.3 Hz, 0.23H), 6.56 (d, J = 9.0 Hz, 0.46H), 6.38 (d, J = 9.0 Hz, 0.22H), 6.17 (d, J = 32.6 Hz, 0.67H), 3.86 (s, 2.13H), 3.85 (s, 0.87H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.3, 133.9, 133.8, 130.6 (d, J = 5.4 Hz), 130.4 (d, J = 2.8 Hz), 130.3 (d, J = 8.1 Hz), 121.6, 120.5, 119.6, 119.5, 118.5, 116.0, 115.9, 115.1, 114.9, 114.8, 113.9 (d, J = 12.8 Hz), 113.3, 55.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -80.61 (d, J = 16.3 Hz, 0.26F), -80.70 (d, J = 23.5 Hz, 1F), -80.90 (d, J = 23.5 Hz, 1F), -86.46 (d, J = 32.6 Hz, 0.74F).

GC-MS (EI, QMS, m/z): 139.1, 263.1, 281.1, 306.1, 326.1.

HRMS (ESI): calcd for $C_{16}H_{14}F_3O_2S^+$, $(M+H)^+$, 327.0661, found, 327.0667.



(1-fluoro-2-(3-methoxyphenyl)vinyl)(4-methoxyphenyl)sulfanemethyl (3f)

The reaction was performed according to the general procedure using 1-(2,2-difluorovinyl)-3-methoxybenzene with toluene as the solvent. The reaction was run for 72 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3f** (20.3 mg, 70% yield) as a colorless oil. Colorless oil, 70% isolated yield.

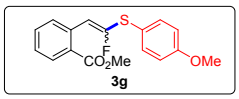
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 11.4 Hz, 1H), 7.07 - 7.03 (m, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 6.63 - 6.53 (d, 0.12H), 6.13 (d, J = 32.8 Hz, 0.63H), 3.80 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ_C, 160.0, 159.7, 154.18 (d, J = 310.3 Hz), 134.5 (d, J = 5.5 Hz), 133.8, 132.8, 129.6, 128.6, 121.7, 121.5 (d, J = 7.3 Hz), 115.1 (d, J = 12.2 Hz), 115.1, 114.7, 114.0 (d, J = 2.1 Hz), 113.8 (d, J = 8.8 Hz), 55.5, 55.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -80.84 (d, J = 16.9 Hz, 0.08F), -85.47 (d, J = 32.8 Hz, 0.92F).

GC-MS (EI, QMS, m/z): 139.1, 242.1, 257.1, 278.1, 290.1.

HRMS (ESI): calcd for $C_{16}H_{15}FNaO_2S^+$, $(M+Na)^+$, 313.0669, found, 313.0666.



methyl 2-(2-fluoro-2-((4-methoxyphenyl)thio)vinyl)benzoate (3g)

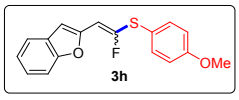
The reaction was performed according to the general procedure using methyl 2-(2,2-difluorovinyl)benzoate with toluene as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3g** (25.7 mg, 81% yield) as a colorless oil. Colorless oil, 81% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 (dd, J = 28.1, 7.9 Hz, 1H), 7.77 (d, J = 7.9 Hz, 0.29H), 7.61 - 7.49 (m, 2.44H), 7.45 - 7.38 (m, 2H), 7.37 - 7.20 (m, 1H), 6.99 - 6.86 (m, 2H), 3.96 - 3.90 (m, 3H), 3.85 (d, J = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ_C, 167.7, 167.3, 160.2, 159.9, 154.8 (d, J = 309.7 Hz), 154.2 (d, J = 296.6 Hz), 138.3, 134.6 (d, J = 9.8 Hz), 133.6 (d, J = 4.2 Hz), 134.1, 133.4, 133.2, 132.1, 132.0, 131.8, 131.3 (d, J = 2.0 Hz), 130.8, 130.7, 130.6, 129.3 (d, J = 3.2 Hz), 128.7, 127.9, 127.8, 127.5, 121.5, 121.1, 116.4, 116.1, 115.0, 115.0, 114.6, 112.5 (d, J = 10.5 Hz), 55.5, 55.47, 52.3, 52.27.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -83.02 (d, J = 15.2 Hz, 0.62 F), -88.46 (d, J = 32.4 Hz, 0.38 F).

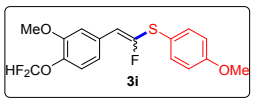
HRMS (ESI): calcd for $C_{17}H_{15}FNaO_3S^+$, $(M+Na)^+$, 341.0618, found, 341.0610.



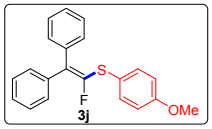
2-(2-fluoro-2-((4-methoxyphenyl)thio)vinyl)benzofuran (3h)

The reaction was performed according to the general procedure using 2-(2,2-difluorovinyl)benzofuran with toluene as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3h** (21.6 mg, 72% yield) as a colorless oil. Colorless oil, 72% isolated yield.

Both isomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 - 7.45 (m, 4H), 7.36 - 7.22 (m, 2H), 7.08 - 6.91 (m, 3H), 6.56 (d, J = 14.3 Hz, 0.2H), 6.24 (d, J = 31.8 Hz, 0.67H), 3.87 (s, 2.22H), 3.86 (s, 0.71H).
E isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.7, 156.3 (d, J = 310.5 Hz), 154.2, 150.1 (d, J = 5.8 Hz), 134.7, 129.0, 124.8, 123.1, 121.1, 120.5, 115.3, 111.1, 106.7 (d, J = 11.4 Hz), 104.1 (d, J = 14.9 Hz), 55.6.
Z isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.65, 156.3 (d, J = 304.0 Hz), 154.2 (s), 150.1 (d, J = 5.8 Hz), 135.0, 128.9, 124.6, 123.1, 121.0, 120.5, 115.1, 111.1, 106.0 (d, J = 6.6 Hz), 104.7 (d, J = 37.0 Hz), 55.57.
^{19}F NMR (376 MHz, $CDCl_3$): δ_F -79.83 (d, J = 31.8 Hz, 0.78F), -81.17 (d, J = 14.3 Hz, 0.22F).
GC-MS (EI, QMS, m/z): 165.1, 237.1, 267.1, 285.1, 300.1.
HRMS (ESI): calcd for $C_{17}H_{14}FO_2S^+$, $(M+H)^+$, 301.0693, found, 301.0691.



(2-(4-(difluoromethyl)-3-methoxyphenyl)-1-fluorovinyl)(4-methoxyphenyl)sulfane (3i)
The reaction was performed according to the general procedure using 1-(difluoromethyl)-4-(2,2-difluorovinyl)-2-methoxybenzene with toluene as the solvent. The reaction was run for 42 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3i** (28.9.0 mg, 85% yield) as a colorless oil. Colorless oil, 85% isolated yield.
Both isomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (dd, J = 24.8, 8.8 Hz, 2H), 7.33 (dd, J = 9.7, 7.7 Hz, 1H), 7.16 (dd, J = 15.2, 8.3 Hz, 1H), 7.07 (ddd, J = 32.9, 8.3, 1.8 Hz, 1H), 6.94 (dd, J = 10.5, 8.9 Hz, 2H), 6.87 (d, J = 8.7 Hz, 0.3H), 6.79 (d, J = 9.3 Hz, 0.2H), 6.60 (dd, J = 12.9, 3.5 Hz, 0.73H), 6.41 (d, J = 9.3 Hz, 0.21H), 6.15 (d, J = 32.5 Hz, 0.65H), 3.92 (d, J = 13.9 Hz, 3H), 3.86 (d, J = 4.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.38, 160.34, 154.6 (d, J = 309.6 Hz), 154.20 (d, J = 297.4 Hz), 151.1, 150.9, 139.6, 134.1, 133.8, 131.9 (d, J = 5.3 Hz), 131.4 (d, J = 8.8 Hz), 122.2, 122.2, 122.0 (d, J = 2.8 Hz), 121.8 (d, J = 6.9 Hz), 121.4, 120.4, 118.8, 116.2 (d, J = 3.6 Hz), 115.4, 115.2, 115.1, 114.8, 114.0 (d, J = 12.4 Hz), 113.7 (d, J = 3.7 Hz), 113.0 (d, J = 1.8 Hz), 112.8 (d, J = 9.8 Hz), 56.2, 56.1, 55.6.
^{19}F NMR (376 MHz, $CDCl_3$): δ_F -80.18 (d, J = 16.6 Hz, 0.27F), -81.32 (d, J = 21.3 Hz, 1F), -81.52 (d, J = 21.3 Hz, 1F), -86.14 (d, J = 32.5 Hz, 0.73F).
GC-MS (EI, QMS, m/z): 139.1, 256.1, 293.1, 323.2, 356.2.
HRMS (ESI): calcd for $C_{17}H_{16}F_3O_3S^+$, $(M+H)^+$, 357.0767, found, 357.0775.



(1-fluoro-2,2-diphenylvinyl)(4-methoxyphenyl)sulfane (3j)
The reaction was performed according to the general procedure using (2,2-difluoroethene-1,1-diyl)dibenzene with CH_3CN as the solvent. The reaction was run for 40 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3j** (30.6 mg, 91% yield) as a yellow solid. Yellow solid, mp. 81-84 ^{o}C, 91% isolated yield.

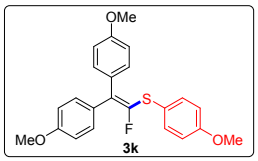
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 - 7.39 (m, 5H), 7.37 - 7.26 (m, 7H), 6.97 - 6.88 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.0, 151.4 (d, J = 304.7 Hz), 137.9 (dd, J = 149.4, 3.0 Hz), 133.6, 130.6 (d, J = 2.7 Hz), 129.8 (d, J = 5.3 Hz), 128.4, 128.2 (s), 128.0, 127.9, 127.7, 122.1, 115.0, 55.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.74 (s, 1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 215.1, 228.1, 316.2, 336.2.

HRMS (ESI): calcd for $C_{21}H_{18}FO_3S^+$, $(M+H)^+$, 337.1057, found, 337.1055.



(1-fluoro-2,2-bis(4-methoxyphenyl)vinyl)(4-methoxyphenyl)sulfane (3k)

The reaction was performed according to the general procedure using 4,4'-(2,2-difluoroethene-1,1-diyl)bis(methoxybenzene) with CH_3CN as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (20:1) to afford **3k** (22.2 mg, 56% yield) as a white solid. White solid, mp. 82-85 °C, 56% isolated yield.

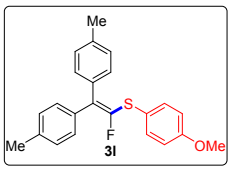
^{1}H NMR (400 MHz, $CDCl_3$): δ_H δ 7.46 - 7.39 (m, 2H), 7.32 - 7.21 (m, 4H), 6.98 - 6.84 (m, 6H), 3.89 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.8, 159.3, 159.1, 149.9 (d, J = 302.4 Hz), 133.1, 131.8 (d, J = 2.5 Hz), 131.2 (d, J = 5.3 Hz), 129.9 (d, J = 2.6 Hz), 128.1, 128.0, 122.9, 115.0, 113.7, 113.5, 55.5, 55.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -90.50 (s, 1F).

GC-MS (EI, QMS, m/z): 211.2, 226.2, 245.1, 365.2, 396.3.

HRMS (ESI): calcd for $C_{23}H_{22}FO_3S^+$, $(M+H)^+$, 397.1268, found, 397.1264.



(1-fluoro-2,2-di-p-tolylvinyl)(4-methoxyphenyl)sulfane (3l)

The reaction was performed according to the general procedure using 4,4'-(2,2-difluoroethene-1,1-diyl)bis(methylbenzene) with CH_3CN as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (50:1) to afford **3l** (31.3 mg, 86% yield) as a colorless oil. Colorless oil, 86% isolated yield.

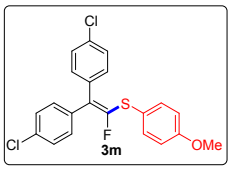
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 (d, J = 8.8 Hz, 2H), 7.25 (m, J = 7.3 Hz, 6H), 7.16 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.7, 150.3 (d, J = 303.5 Hz), 137.5 (d, J = 12.8 Hz), 135.8 (d, J = 4.0 Hz), 134.3 (d, J = 2.9 Hz), 133.2, 130.3 (d, J = 3.0 Hz), 129.6 (d, J = 5.4 Hz), 129.5, 129.2, 128.9, 128.7, 122.3, 114.8, 55.4, 21.4, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -89.76 (s, 1F).

GC-MS (EI, QMS, m/z): 129.2, 194.2, 229.2, 349.2, 364.2.

HRMS (ESI): calcd for $C_{23}H_{22}FOS^+$, $(M+H)^+$, 365.1370, found, 365.1371.



(2,2-bis(4-chlorophenyl)-1-fluorovinyl)(4-methoxyphenyl)sulfane (3m)

The reaction was performed according to the general procedure using 4,4'-(2,2-difluoroethene-1,1-diyl)bis(chlorobenzene) with CH_3CN as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3m** (27.5 mg, 68% yield) as a colorless oil. Colorless oil, 68% isolated yield.

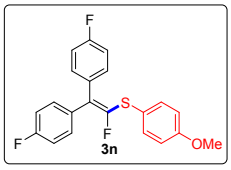
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 - 7.38 (m, 4H), 7.30 (dt, J = 6.8, 2.2 Hz, 2H), 7.24 (dd, J = 10.8, 4.7 Hz, 4H), 6.96 - 6.89 (m, 2H), 3.85 (d, J = 3.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.3, 152.3(d, J = 306.3 Hz), 136.6 (d, J = 4.1 Hz), 135.2 (d, J = 2.3 Hz), 134.2, 134.1, 133.7, 132.0 (d, J = 2.6 Hz), 131.0 (d, J = 5.6 Hz), 128.8, 128.5, 125.4 (d, J = 17.5 Hz), 121.2 (s), 115.1 (s), 55.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -86.84 (s, 1F).

GC-MS (EI, QMS, m/z): 199.1, 234.1, 262.1, 336.2, 369.2, 406.2.

HRMS (ESI): calcd for $C_{21}H_{16}Cl_2FOS^+$, $(M+H)^+$, 405.0277, found, 405.0270.



(1-fluoro-2,2-bis(4-fluorophenyl)vinyl)(4-methoxyphenyl)sulfane (3n)

The reaction was performed according to the general procedure using 4,4'-(2,2-difluoroethene-1,1-diyl)bis(fluorobenzene) with CH_3CN as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3n** (29.1 mg, 78% yield) as a white solid. white solid, mp. 64-67 °C, 78% isolated yield.

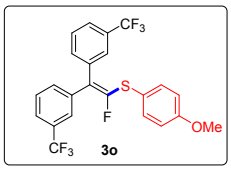
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 - 7.38 (m, 4H), 7.30 (dt, J = 6.8, 2.2 Hz, 2H), 7.24 (dd, J = 10.8, 4.7 Hz, 4H), 6.96 - 6.89 (m, 2H), 3.85 (d, J = 3.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.6 (d, J = 42.0 Hz), 161.1 (d, J = 42.7 Hz), 160.2, 151.7 (d, J = 304.6 Hz), 134.4 (t, J = 3.4 Hz), 133.8, 133.0, 132.3 (dd, J = 7.9, 2.7 Hz), 131.5 (dd, J = 7.4, 6.2 Hz), 126.0 (d, J = 17.8 Hz), 121.7 (s), 115.6, 115.4, 115.33, 115.1, 115.1, 55.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -88.25 (s,1F), -113.03 - -114.19 (m, 2F).

GC-MS (EI, QMS, m/z): 201.1, 264.1, 339.2, 252.2, 372.3.

HRMS (ESI): calcd for $C_{21}H_{16}F_3OS^+$, $(M+H)^+$, 373.0868, found, 373.0869.



(1-fluoro-2,2-bis(3-(trifluoromethyl)phenyl)vinyl)(4-methoxyphenyl)sulfane (3o)

The reaction was performed according to the general procedure using 3,3'-(2,2-difluoroethene-1,1-diyl)bis((trifluoromethyl)benzene) with toluene as the solvent. The reaction was run for 36 h, and the

desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3o** (31.1 mg, 66% yield) as a colorless oil. Colorless oil, 66% isolated yield.

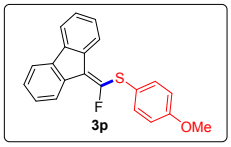
^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.64 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 3.6 Hz, 2H), 7.52 (dd, J = 13.1, 7.1 Hz, 2H), 7.46 (d, J = 7.7 Hz, 1H), 7.40 (dd, J = 13.5, 7.6 Hz, 3H), 7.35 (d, J = 7.9 Hz, 1H), 6.88 (d, J = 7.4 Hz, 2H), 3.81 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ_C 160.4 (s), 155.0, 152.9, 138.5 (d, J = 4.4 Hz), 137.1 (d, J = 2.6 Hz), 134.6, 133.9 (d, J = 1.3 Hz), 132.8 (d, J = 4.3 Hz), 130.9 (dq, J = 35.6, 32.4 Hz), 129.1, 128.8, 127.5 - 127.3 (m), 126.6, 126.2 (dq, J = 7.5, 3.8 Hz), 125.0 (q, J = 3.6 Hz), 124.8, 124.6 (dd, J = 7.0, 3.4 Hz), 124.3, 124.2, 123.0, 55.40.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -62.52 (s, 3F), -62.62 (s, 3F), -85.15 (s, 1F).

GC-MS (EI, QMS, m/z): 233.1, 257.1, 271.1, 319.1, 334.2.

HRMS (ESI): calcd for $C_{23}H_{16}F_7OS^+$, $(M+H)^+$, 473.0805, found, 473.0800.



((9H-fluoren-9-ylidene)fluoromethyl)(4-methoxyphenyl)sulfane (3p)

The reaction was performed according to the general procedure using 9-(difluoromethylene)-9H-fluorene with CH_3CN as the solvent. The reaction was run for 18 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3p** (27.0 mg, 81% yield) as a colorless oil. Colorless oil, 81% isolated yield.

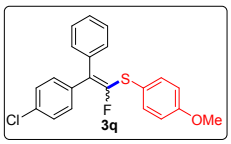
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.57 - 8.45 (m, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.85 - 7.73 (m, 2H), 7.63 - 7.58 (m, 2H), 7.42 (tt, J = 8.2, 3.6 Hz, 3H), 7.34 (td, J = 7.5, 1.0 Hz, 1H), 7.00- 6.93 (m, 2H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.7, 154.5 (d, J = 315.1 Hz), 140.4 (d, J = 4.3 Hz), 138.8, 136.3 (d, J = 4.2 Hz), 135.5 (d, J = 7.6 Hz), 134.87, 128.3 (d, J = 2.0 Hz), 128.1 (d, J = 1.8 Hz), 127.7, 127.2, 126.1 (d, J = 15.9 Hz), 124.5 (d, J = 2.3 Hz), 120.00, 119.6, 119.6, 115.2, 55.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -72.18 (s, 1F).

GC-MS (EI, QMS, m/z): 183.1,257.1, 271.1, 319.1, 334.2.

HRMS (ESI): calcd for $C_{21}H_{16}FOS^+$, $(M+H)^+$, 335.0900, found, 335.0897.



(2-(4-chlorophenyl)-1-fluoro-2-phenylvinyl)(4-methoxyphenyl)sulfane (3q)

The reaction was performed according to the general procedure using 1-chloro-4-(2,2-difluoro-1-phenylvinyl)benzene with CH_3CN as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (100:1) to afford **3q** (31.5 mg, 85% yield) as a colorless oil. Colorless oil, 85% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46 - 7.39 (m, 4H), 7.38 - 7.24 (m, 7H), 6.93 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).

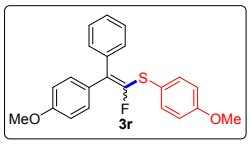
Major isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.0, 151.6 (d, J = 305.2 Hz), 137.0 (d, J = 4.3 Hz), 136.7 (d, J = 1.6 Hz), 133.6, 132.7, 131.8 (d, J = 2.5 Hz), 129.6 (d, J = 5.3 Hz), 128.5, 128.1, 127.8, 126.9 (d, J = 17.8 Hz), 121.6, 114.9, 55.4.

Minor isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.1, 151.96 (d, J = 305.8 Hz), 138.2 (d, J = 3.7 Hz), 135.6, 133.97, 133.4, 131.1 (d, J = 5.7 Hz), 130.6 (d, J = 2.6 Hz), 128.5, 128.4, 128.2, 126.5 (d, J = 16.9 Hz), 121.60, 115.0, 55.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -87.47 (s, 0.64F), -88.07 (s, 0.36F).

GC-MS (EI, QMS, m/z): 165.1, 200.1, 228.1, 302.1, 335.2, 370.2.

HRMS (ESI): calcd for $C_{21}H_{17}ClFOS^+$, $(M+H)^+$, 371.0667, found, 371.0667.



(1-fluoro-2-(4-methoxyphenyl)-2-phenylvinyl)(4-methoxyphenyl)sulfane (3r)

The reaction was performed according to the general procedure using 1-(2,2-difluoro-1-phenylvinyl)-4-methoxybenzene with CH_3CN as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (30:1) to afford **3r** (30.0 mg, 82% yield) as a colorless oil. Colorless oil, 82% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 - 7.38 (m, 4H), 7.34 (d, J = 4.4 Hz, 2H), 7.33 - 7.25 (m, 3H), 6.98 - 6.85 (m, 4H), 3.89 (s, 1H), 3.85 (s, 1H), 3.85 (s, 2H), 3.84 (s, 2H).

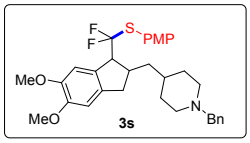
Major isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.7, 158.9, 150.4 (d, J = 303.1 Hz), 139.0 (d, J = 4.0 Hz), 133.2, 131.0 (d, J = 5.9 Hz), 130.44, 129.53, 129.52 (d, J = 2.7 Hz), 128.3, 127.9, 122.7, 115.0, 113.6, 55.5, 55.4.

Minor isomer: ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.8, 159.2, 150.7 (d, J = 303.9 Hz), 137.3 (d, J = 1.3 Hz), 133.3, 131.7 (d, J = 2.6 Hz), 130.8 (d, J = 3.6 Hz), 129.7 (d, J = 5.3 Hz), 128.0, 127.5, 122.2, 114.8, 113.6, 55.4, 55.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -89.23 (s, 0.33F), -90.07 (s, 0.67F).

GC-MS (EI, QMS, m/z): 183.1, 196.1, 258.1, 346.2, 366.2.

HRMS (ESI): calcd for $C_{22}H_{20}FO_2S^+$, (M+H)+, 367.1163, found, 367.1165.



1-benzyl-4-((1-(difluoro((4-methoxyphenyl)thio)methyl)-5,6-dimethoxy-2,3-dihydro-1H-inden-2-yl)methyl)piperidine (3s)

The reaction was performed according to the general procedure using 1-benzyl-4-((1-(difluoromethylene)-5,6-dimethoxy-2,3-dihydro-1H-inden-2-yl)methyl)piperidine with CH_3CN as the solvent. The reaction was run for 72 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (10:1) to afford **3s** (41.3 mg, 79% yield) as a colorless oil. Red oil, 79% isolated yield.

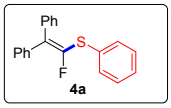
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 (dd, J = 13.0, 8.8 Hz, 2H), 7.31 (dd, J = 7.5, 5.5 Hz, 4H), 7.28 - 7.22 (m, 1H), 6.95 - 6.82 (m, 3H), 6.74 (d, J = 16.9 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.52

(s, 2H), 3.50 - 3.42 (m, 1H), 3.30 (dd, J = 15.9, 8.3 Hz, 1H), 2.95 - 2.79 (m, 3H), 2.51 (dd, J = 15.9, 3.0 Hz, 1H), 1.98 (t, J = 11.2 Hz, 2H), 1.74 (t, J = 12.3 Hz, 2H), 1.48 (dd, J = 12.3, 6.5 Hz, 1H), 1.43 - 1.25 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.0, 149.6, 148.1, 138.2, 136.2, 129.3, 128.1, 126.9, 117.0, 114.46, 109.5, 107.4, 63.5, 59.72 (t, J = 21.8 Hz), 56.0, 55.8, 55.3, 53.8, 43.6, 38.5, 38.1, 33.5, 32.6, 32.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -74.16 (dd, J = 33.2, 12.3 Hz, 2F).

HRMS (ESI): calcd for $C_{32}H_{37}F_2NNaO_3S^+$, $(M+Na)^+$, 576.2354, found, 576.2363.



4a

(1-fluoro-2,2-diphenylvinyl)(phenyl)sulfane (4a)

The reaction was performed according to the general procedure using benzenethiol with CH_3CN as the solvent. The reaction was run for 24 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4a** (23.0 mg, 75% yield) as a colorless oil. Colorless oil, 75% isolated yield.

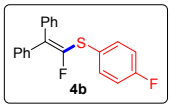
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.50 - 7.45 (m, 2H), 7.42 - 7.38 (m, 7H), 7.37 - 7.29 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 149.4 (d, J = 304.0 Hz), 137.7 (d, J = 3.6 Hz), 136.2 (d, J = 2.4 Hz), 131.8 (d, J = 1.8 Hz), 129.7 (d, J = 17.4 Hz), 129.4 (d, J = 2.1 Hz), 129.2, 128.9 (d, J = 5.2 Hz), 128.4, 127.4, 127.3, 127.0, 127.0, 126.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.49(s, 1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 228.1, 386.1, 306.1.

HRMS (ESI): calcd for $C_{20}H_{16}FS^+$, $(M+H)^+$, 307.0951, found, 307.0958.



4b

(1-fluoro-2,2-diphenylvinyl)(4-fluorophenyl)sulfane (4b)

The reaction was performed according to the general procedure using 4-fluorobenzenethiol with CH_3CN as the solvent. The reaction was run for 72 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4b** (17.2 mg, 53% yield) as a colorless oil. White solid, mp. 70-72 ^{o}C, 53% isolated yield.

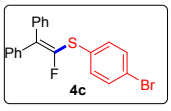
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 - 7.43 (m, 2H), 7.43 - 7.38 (m, 3H), 7.37 - 7.34 (m, 4H), 7.33 - 7.30 (m, 3H), 7.11 - 7.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.7 (d, J = 248.0 Hz), 150.4 (d, J = 304.3 Hz), 138.5 (d, J = 3.5 Hz), 136.9, 132.9 (d, J = 8.2 Hz), 130.4 (d, J = 2.3 Hz), 129.80 (d, J = 5.2 Hz), 128.7, 128.4, 128.25 (s), 128.1, 128.0, 127.2, 116.54 (d, J = 22.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -89.00 (s, 1F), -113.40 - -113.81 (m, 1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 228.1, 286.1, 306.1, 324.1.

HRMS (ESI): calcd for $C_{20}H_{15}F_2S^+$, $(M+H)^+$, 325.0857, found, 325.0860.



4c

(4-bromophenyl)(1-fluoro-2,2-diphenylvinyl)sulfane (4c)

The reaction was performed according to the general procedure using 4-bromobenzenethiol with CH_3CN as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (100:1) to afford **4c** (35.0 mg, 91% yield) as a colorless oil. White solid, mp. 74-77 °C, 91% isolated yield.

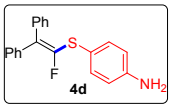
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 - 7.47 (m, 2H), 7.42 - 7.38 (m, 3H), 7.36 (t, J = 4.8 Hz, 4H), 7.34 - 7.28 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 149.5 (d, J = 303.9 Hz), 138.3 (d, J = 3.4 Hz), 136.7 (d, J = 2.3 Hz), 132.3, 131.8 (d, J = 1.7 Hz), 131.3, 130.1, 129.7, 129.6, 128.2, 128.1, 128.0, 127.9, 121.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.98 (s, 1F).

GC-MS (EI, QMS, m/z): 196.1, 228.1, 272.1, 366.1, 384.1.

HRMS (ESI): calcd for $C_{20}H_{15}BrFS^+$, $(M+H)^+$, 385.0056, found, 385.0048.



4-((1-fluoro-2,2-diphenylvinyl)thio)aniline (4d)

The reaction was performed according to the general procedure using 4-aminobenzenethiol with CH_3CN as the solvent. The reaction was run for 24 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4e** (29.5 mg, 92% yield) as a colorless oil. Yellow solid, mp. 89-91 °C, 92% isolated yield.

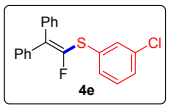
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (t, J = 7.9 Hz, 3H), 7.41 - 7.27 (m, 9H), 6.70 (d, J = 8.3 Hz, 2H), 3.83 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 151.9 (d, J = 304.7 Hz), 147.0, 138.7 (d, J = 4.0 Hz), 137.2, 134.2 , 130.6 (d, J = 2.5 Hz), 129.7 (d, J = 5.3 Hz), 128.2, 128.0, 127.7, 127.5, 126.9 (d, J = 17.1 Hz), 118.5, 115.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.76 (s, 1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 228.1, 288.1, 321.1.

HRMS (ESI): calcd for $C_{20}H_{17}FNS^+$, (M+H)+, 322.1060, found, 322.1055.



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

The reaction was performed according to the general procedure using 3-chlorobenzenethiol with CH_3CN as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4e** (17.0 mg, 50% yield) as a colorless oil. Colorless oil, 50% isolated yield.

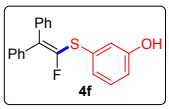
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (s, 1H), 7.39 - 7.34 (m, 7H), 7.31 - 7.25 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.2 (d, J = 304.1 Hz), 137.4 (d, J = 3.4 Hz), 135.8 (d, J = 2.3 Hz), 134.2, 133.8 (d, J = 2.2 Hz), 131.0, 130.8, 129.4, 129.3 (d, J = 2.7 Hz), 128.9 (d, J = 5.3 Hz), 128.1, 127.4, 127.3, 127.2, 126.6, 126.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -89.01 (s, 1F).

GC-MS (EI, QMS, m/z): 168.1, 196.1, 228.1, 272.1, 320.1, 340.2.

HRMS (ESI): calcd for $C_{20}H_{15}ClFS^+$, $(M+H)^+$, 341.0562, found, 341.0568.



3-((1-fluoro-2,2-diphenylvinyl)thio)phenol (4f)

The reaction was performed according to the general procedure using 3-hydroxythiophenol with CH_3CN as the solvent. The reaction was run for 72 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4f** (24.2 mg, 75% yield) as a colorless oil. Colorless oil, 75% isolated yield.

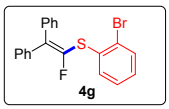
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41 - 7.36 (m, 7H), 7.34 - 7.30 (m, 3H), 7.24 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.95 (t, J = 2.0 Hz, 1H), 6.77 (ddd, J = 8.1, 2.4, 0.7 Hz, 1H), 5.14 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 155.3, 149.0 (d, J = 303.9 Hz), 137.7 (d, J = 3.4 Hz), 136.1 (d, J = 2.4 Hz), 133.3 (d, J = 1.8 Hz), 130.3 (d, J = 17.1 Hz), 129.4, 128.9, 128.9, 127.4, 127.3, 127.1, 127.1, 121.1, 115.5, 113.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.33 (s, 1F).

GC-MS (EI, QMS, m/z): 165.2, 195.9, 208.2, 268.6, 322.2.

HRMS (ESI): calcd for $C_{20}H_{16}FOS^+$, $(M+H)^+$, 323.0900, found,323.0901.



(2-bromophenyl)(1-fluoro-2,2-diphenylvinyl)sulfane (4g)

The reaction was performed according to the general procedure using 2-bromobenzenethiol with CH_3CN as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4g** (24.2 mg, 63% yield) as a colorless oil. Colorless oil, 63% isolated yield.

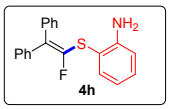
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.58 (t, J = 6.9 Hz, 2H), 7.44 - 7.35 (m, 8H), 7.35 - 7.28 (m, 3H), 7.19-7.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.6 (d, J = 303.0 Hz), 138.3 (d, J = 3.4 Hz), 136.9 (d, J = 1.4 Hz), 134.7 (d, J = 2.0 Hz), 133.4, 133.0, 132.8, 130.1 (d, J = 2.4 Hz), 129.9 (d, J = 5.1 Hz), 129.5, 128.4, 128.3, 128.2, 122.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -89.99 (s, 1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 272.1, 285.1, 384.2.

HRMS (ESI): calcd for $C_{20}H_{15}BrFS^+$, $(M+H)^+$, 385.0056, found, 385.0057.



2-((1-fluoro-2,2-diphenylvinyl)thio)aniline (4h)

The reaction was performed according to the general procedure using 2-aminobenzenethiol with CH_3CN as the solvent. The reaction was run for 48 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4h** (24.0 mg, 75% yield) as a colorless oil. Colorless oil, 75% isolated yield.

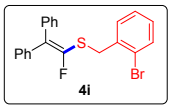
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 - 7.40 (m, 4H), 7.39 - 7.34 (m, 2H), 7.34 - 7.27 (m, 5H), 7.22 (td, J = 7.9, 1.5 Hz, 1H), 6.81- 6.70 (m, 2H), 4.15 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 150.6 (d, J = 305.7 Hz), 148.6, 138.5 (d, J = 4.1 Hz), 137.0, 136.5, 131.1, 130.6 (d, J = 2.6 Hz), 129.7 (d, J = 5.4 Hz), 128.48, 128.1, 127.7, 127.6, 127.4, 118.7, 115.5, 112.94.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.73 (s, 1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 267.1, 301.1, 321.1.

HRMS (ESI): calcd for $C_{20}H_{17}FNS^+$, (M+H)+, 322.1060, found, 322.1069.



4i

(2-bromobenzyl)(1-fluoro-2,2-diphenylvinyl)sulfanemethyl (4i)

The reaction was performed according to the general procedure using 2-bromobenzylthiol with CH_3CN as the solvent. The reaction was run for 24 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate (100:1) to afford **4i** (31.8 mg, 80% yield) as a colorless oil. Colorless oil, 80% isolated yield.

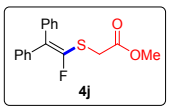
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 (dd, J = 7.9, 0.9 Hz, 1H), 7.37 - 7.29 (m, 5H), 7.28 - 7.23 (m, 5H), 7.19 (td, J = 7.7, 1.8 Hz, 1H), 6.87 (dd, J = 7.7, 1.4 Hz, 2H), 4.16 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 150.3 (d, J = 302.6 Hz), 137.5 (d, J = 4.3 Hz), 136.4 (d, J = 1.7 Hz), 135.8, 132.3, 130.2, 129.3, 128.8, 128.7, 128.6, 128.2, 127.2, 127.2, 126.6, 126.6, 123.8, 36.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -89.40 (s,1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 229.2, 398.1, 400.1.

HRMS (ESI): calcd for $C_{21}H_{17}BrFS^+$, $(M+H)^+$, 399.0213, found, 399.0211.



4j

methyl 2-((1-fluoro-2,2-diphenylvinyl)thio)acetate (4j)

The reaction was performed according to the general procedure using methyl thioglycolate with CH_3CN as the solvent. The reaction was run for 24 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4j** (30.0 mg, 86% yield) as a colorless oil. Colorless oil, 86% isolated yield.

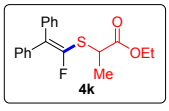
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 - 7.37 (m, 3H), 7.37 - 7.27 (m, 7H), 3.78 (s, 3H), 3.58 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 169.5, 150.0 (d, J = 303.3 Hz), 138.1 (d, J = 4.4 Hz), 137.0, 130.5 (d, J = 2.5 Hz), 129.7 (d, J = 5.1 Hz), 128.40 128.21 128.1, 127.9, 127.8, 52.8, 33.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -93.31 (s,1F).

GC-MS (EI, QMS, m/z): 165.1, 196.1, 208.1, 229.1, 302.1.

HRMS (ESI): calcd for $C_{17}H_{16}FO_2S^+$, $(M+H)^+$, 303.0850, found, 303.0841.



4k

ethyl 2-((1-fluoro-2,2-diphenylvinyl)thio)propanoate (4k)

The reaction was performed according to the general procedure using ethyl 2-mercaptopropionate with CH_3CN as the solvent. The reaction was run for 18 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4k** (31.5 mg, 95% yield) as a colorless oil. Colorless oil, 95% isolated yield.

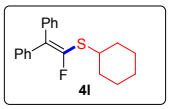
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 - 7.35 (m, 4H), 7.35 - 7.30 (m, 4H), 7.27 - 7.23 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.92 (q, J = 7.2 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 171.8, 150.4 (d, J = 302.3 Hz), 138.3 (d, J = 4.0 Hz), 137.1, 130.5 (d, J = 2.4 Hz), 129.8 (d, J = 5.0 Hz), 129.7, 128.3, 128.2, 128.0, 127.8, 61.62 42.62 17.1, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.08 (s,1F).

GC-MS (EI, QMS, m/z):165.1, 196.1, 209.1, 228.6, 257.1, 330.1;

HRMS (ESI): calcd for $C_{18}H_{18}FO_2S^+$, $(M+H)^+$, 317.1006, found, 317.1004.



cyclohexyl(1-fluoro-2,2-diphenylvinyl)sulfaneethyl (4l)

The reaction was performed according to the general procedure using cyclohexanethiol with CH_3CN as the solvent. The reaction was run for 36 h, and the desired product was purified by flash column chromatography with Petroleum ether/Ethyl acetate to afford **4l** (26.5 mg, 85% yield) as a colorless oil. White solid, mp. 59-61 °C, 85% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 - 7.29 (m, 7H), 7.26 (ddd, J = 7.3, 3.0, 1.6 Hz, 3H), 3.28 - 3.18 (m, 1H), 2.03 (dd, J = 9.3, 4.1 Hz, 2H), 1.76 (dd, J = 9.0, 3.8 Hz, 2H), 1.62 (dd, J = 13.3, 5.2 Hz, 1H), 1.48 - 1.32 (m, 4H), 1.31 - 1.22 (m, 1H).

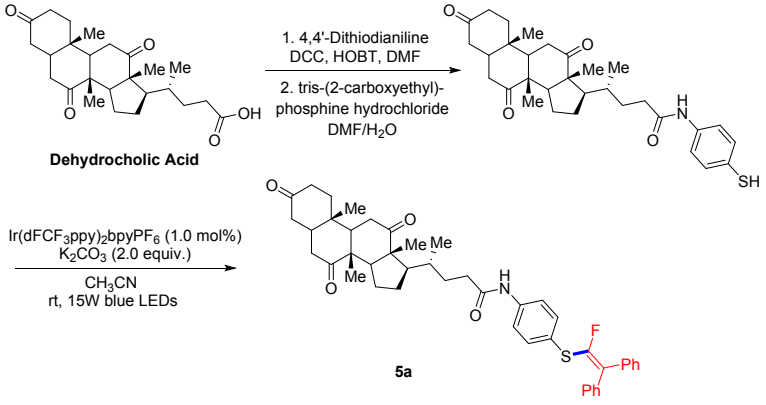
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 152.2 (d, J = 301.7 Hz), 138.9 (d, J = 4.6 Hz), 137.6 (s), 130.7 (d, J = 3.2 Hz), 129.7 (d, J = 5.3 Hz), 128.2, 128.1, 127.6, 127.4, 45.2, 33.4, 26.1, 25.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -87.21 (s, 1F).

GC-MS (EI, QMS, m/z): 55.1, 165.1, 196.1, 210.1, 231.1, 312.3.

HRMS (ESI): calcd for $C_{20}H_{22}FS^+$, $(M+H)^+$, 313.1421, found, 313.1416.

6. Late-stage Monofluoroalkenylation of complex molecules



Dehydrocholic Acid (416 mg, 1.0 mmol), 1-hydroxybenzotriazole hydrate (HOBT) (135 mg, 1mmol) and 1,3-dicyclohexylcarbodiimide (DCC) (206 mg, 1.0 mmol) were added in DMF (10 mL) at 0-5 °C. After 1 h of stirring at the same temperature, 4,4'-Dithiodianilineaniline (124 mg, 0.5 mmol) was added,

and the resulting mixture was left stirring overnight at room temperature. DMF was distilled off, the crude was diluted with EA (20 mL), washed with 1 N HCl (2 × 10mL), with a saturated solution of $NaHCO_3$ (2 × 10 mL), and with brine, dried over Na_2SO_4, and evaporated to give a crude product.

The residues without further purification and dissolved in 20 mL DMF/H2O (V/V = 1:1), and the resulting mixture was stirred for 12 hours at room temperature. DMF was removed and then extracted with EA (15 mL for three times). The solvent was concentrated and purification by chromatography on silica gel to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 3.46 (s, 1H), 3.03 - 2.84 (m, 4H), 2.54 - 2.24 (m, 9H), 2.23 - 2.13 (m, 2 H), 2.12 – 2.05 (m, 3H), 2.04 - 1.96 (m, 2H), 1.89 (td, J = 11.4, 7.1 Hz, 1H), 1.73 - 1.62 (m, 3H), 1.45 (s, 4H), 1.41 (s, 1H), 1.30 (s, 1H), 1.12 (s, 3H), 0.92 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 212.1, 209.1, 208.8, 171.5, 136.2, 130.7, 125.0, 120.5, 56.9, 51.8, 49.0, 46.8, 45.5, 45.0, 42.8, 38.7, 36.5, 36.0, 35.4, 35.3, 34.4, 30.8, 28.1, 27.6, 25.1, 21.9, 18.8, 11.9.

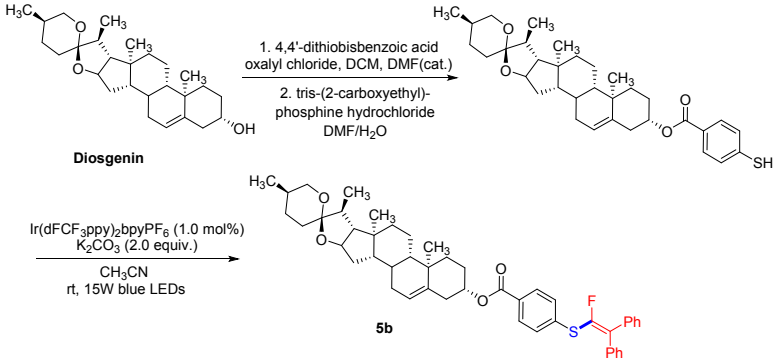
Synthesis of **5a**: **1b** (0.2 mmol), Dehydrocholic Acid derivative (0.1 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (2.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. The filtrate was concentrated and purification by chromatography on silica gel to afford the desired product **5a**.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 - 7.52 (m, 3H), 7.44 - 7.37 (m, 5H), 7.31 (d, J = 6.0 Hz, 6H), 3.01 - 2.83 (m, 3H), 2.48 (ddd, J = 16.0, 11.1, 5.0 Hz, 2H), 2.42 - 2.31 (m, 4H), 2.30 - 2.13 (m, 4H), 2.13 - 1.95 (m, 6H), 1.88 (dd, J = 18.4, 11.2 Hz, 1H), 1.74 (s, 1H), 1.65 (td, J = 14.4, 3.8 Hz, 1H), 1.55 (dd, J = 8.8, 4.8 Hz, 1H), 1.42 (d, J = 10.6 Hz, 5H), 1.36 - 1.27 (m, 2H), 1.10 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ_C 212.2, 209.2, 209.0, 171.7, 150.3 (d, J = 304.7 Hz), 138.4 (d, J = 3.8 Hz), 137.9, 136.9 (d, J = 2.7 Hz), 131.5, 130.3 (d, J = 2.9 Hz), 129.7 (d, J = 5.3 Hz), 128.3, 128.1, 127.9 (s), 127.9, 120.4, 60.4, 56.9), 51.8, 49.0, 46.85, 45.5, 45.0, 42.8, 38.7, 36.5, 36.0, 35.3, 35.3, 34.4, 30.8, 27.7, 25.2, 21.9, 18.8, 14.2, 11.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -88.79 (s, 1F).

HRMS (ESI): calcd for $C_{45}H_{51}FNO_4S^+$, $(M+H)^+$, 720.3517, found, 720.3519.



In a 25 mL dried Schelenk flask, 4,4'-dithiobisbenzoic acid (306 mg, 1.0 mmol) was dissolved in 5 mL dry DCM, oxalyl chloride (280 mg, 2.2 equiv) slowly (one drop of DMF was added) was added in the reaction system. The reaction system was stirred at rt for 4 hours. The solvent was removed in vacuo to afford chloride. Then, Diosgenin (828 mg, 2.0 mmol), Et_3N (222 mg, 2.2 mmol) and DMAP (5 mol%)

was dissolved in 20 mL dry DCM, the chloride was added to the reaction system at room temperature. The resulting mixture was refluxed under N_2 for 12 hours. 10 mL water was added and extracted with DCM (10 mL* 3). The combined DCM phases were dried over $MgSO_4$ and the solvent was removed in vacuo.

The residues without further purification and dissolved in 20 mL DMF/H_2O (V/V = 1:1), and the resulting mixture was stirred for 12 hours at room temperature. DMF was removed and then extracted with EA for three times. The solvent was concentrated and purification by chromatography on silica gel to afford the desired product.

^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.77 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 11.2 Hz, 2H), 5.19 (d, J = 51.4 Hz, 2H), 4.35 (dd, J = 14.3, 7.0 Hz, 1H), 3.52 (s, 1H), 3.41 (d, J = 9.7 Hz, 1H), 3.31 (t, J = 10.8 Hz, 1H), 2.51 (d, J = 14.9 Hz, 1H), 2.27 (d, J = 15.1 Hz, 1H), 1.96 - 1.89 (m, 2H), 1.82 (dt, J = 23.8, 15.9 Hz, 3H), 1.71 (dd, J = 20.7, 12.3 Hz, 2H), 1.66 - 1.47 (m, 9H), 1.45 - 1.35 (m, 3H), 1.22 (dt, J = 13.0, 9.8 Hz, 1H), 1.12 (dd, J = 28.1, 12.9 Hz, 2H), 1.00 (s, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.73 (d, J = 9.8 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$): δ_C 164.6, 137.6, 137.1, 129.3, 127.2, 121.2, 108.5, 80.0, 70.3, 66.0, 61.2, 55.6, 49.4, 40.8, 39.4, 38.9, 36.4, 35.7, 33.1, 31.2, 31.0, 30.5, 29.4, 27.9, 25.5, 19.7, 18.1, 16.3, 15.5, 13.7.

Synthesis of **5b**: **1b** (0.2 mmol), diosgenin derivative (0.1 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (2.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. The filtrate was concentrated and purification by chromatography on silica gel to afford the desired product **5b**.

^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.94 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 7.7 Hz, 2H), 7.37 - 7.30 (m, 8H), 7.25 (s, 2H), 5.28 (d, J = 45.4 Hz, 2H), 4.41 (d, J = 6.9 Hz, 1H), 3.47 (s, 1H), 3.38 (t, J = 10.7 Hz, 1H), 2.58 (d, J = 14.7 Hz, 1H), 2.34 (d, J = 15.1 Hz, 1H), 1.99 (d, J = 11.0 Hz, 2H), 1.95 - 1.82 (m, 3H), 1.77 (dd, J = 19.8, 10.8 Hz, 2H), 1.73 - 1.67 (m, 2H), 1.66 - 1.54 (m, 6H), 1.48 (dd, J = 27.4, 13.4 Hz, 3H), 1.28 (dd, J = 19.1, 7.0 Hz, 2H), 1.20 (dd, J = 25.3, 11.1 Hz, 2H), 1.13 (d, J = 14.2 Hz, 1H), 1.07 (s, 3H), 0.98 (d, J = 5.6 Hz, 3H), 0.79 (d, J = 10.1 Hz, 6H).

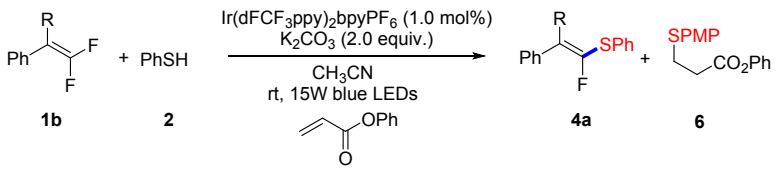
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.5, 148.5 (d, J = 303.5 Hz), 139.4 (d, J = 3.2 Hz), 138.6, 136.7 (d, J = 2.5 Hz), 130.4, 130.1 (d, J = 2.8 Hz), 129.9 (d, J = 5.3 Hz), 128.4, 128.4 (d, J = 4.1 Hz), 128.3 (d, J = 4.3 Hz), 127.6, 122.3, 109.4, 80.8, 71.2, 66.9, 62.1, 56.5, 50.2, 41.6, 40.3, 39.8, 37.3, 36.6, 33.9, 32.1, 31.8, 31.4, 30.3, 28.8, 26.3, 20.6, 19.0, 17.2, 16.3, 14.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -89.35 (s, 1F).

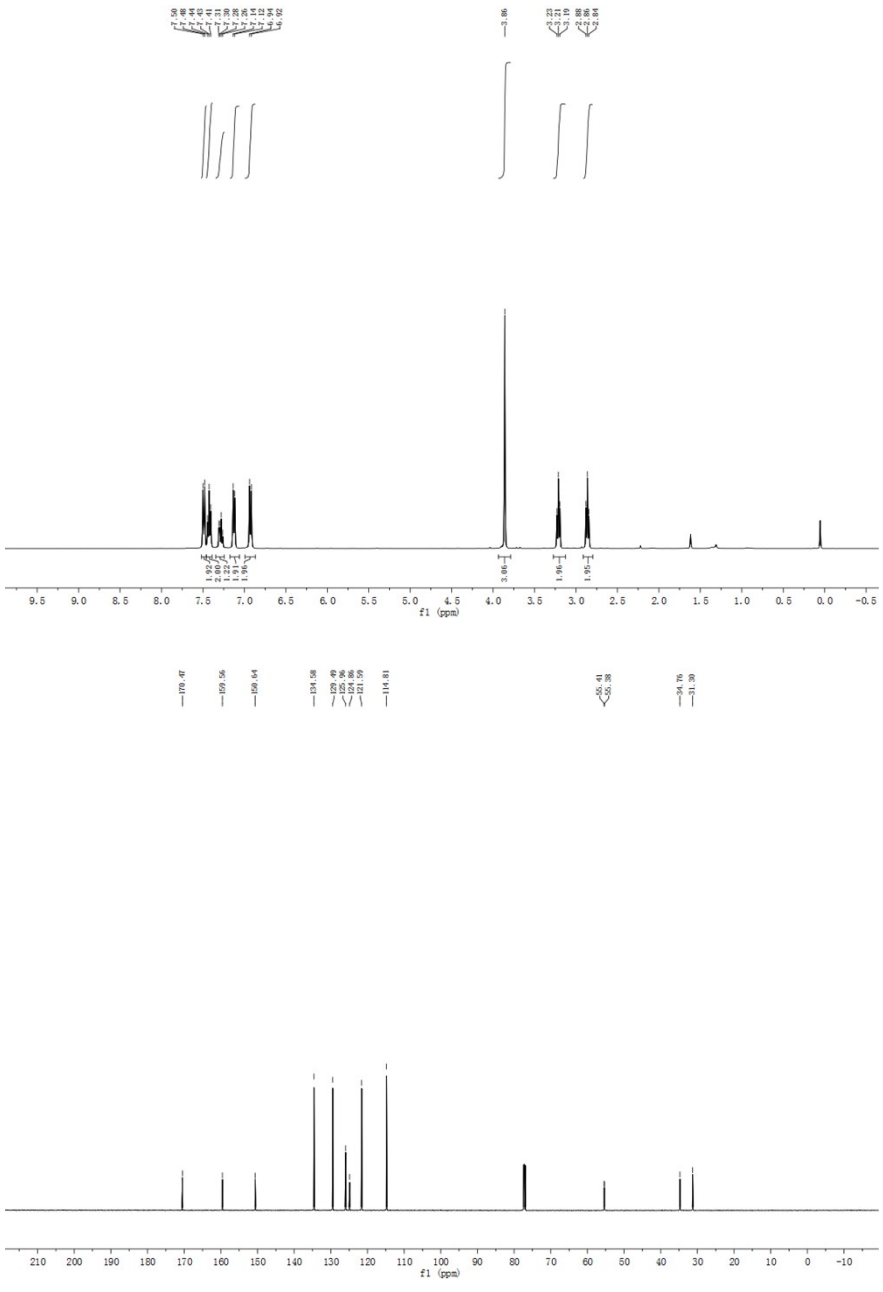
HRMS (ESI): calcd for $C_{48}H_{56}FO_4S^+$, $(M+H)^+$, 747.3878, found, 747.3883.

7. Mechanistic studies

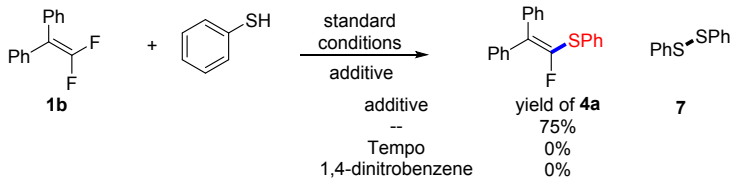
a) Radical intermediate trapping experiment



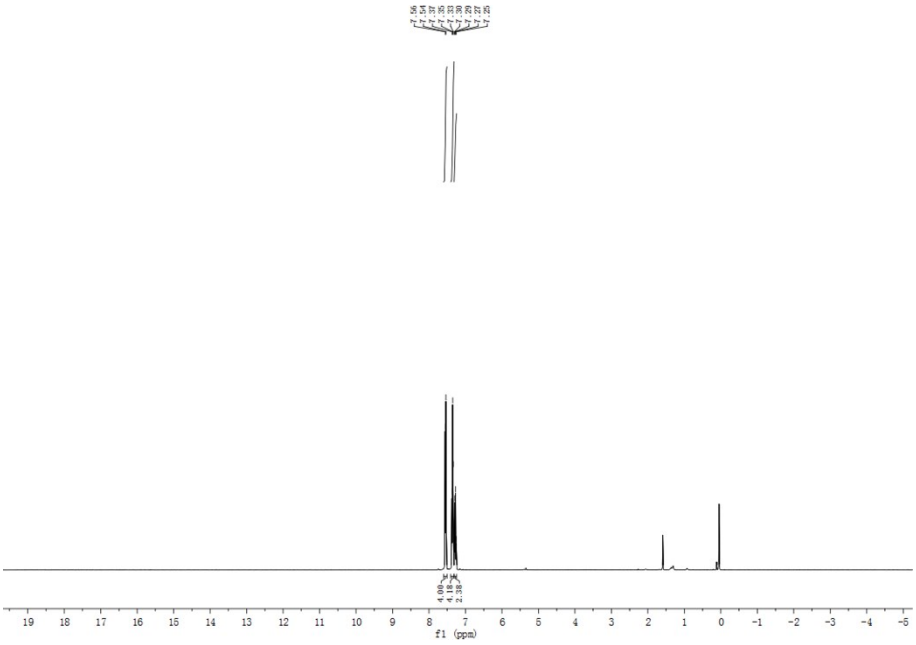
1b (0.1 mmol), **2** (0.15 mmol), phenylacrylate (0.2 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1 mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. The filtrate was concentrated and purification by chromatography on silica gel to afford the desired product **4a** and **6**. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 8.6 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.29 (dd, J = 13.0, 5.5 Hz, 1H), 7.13 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 3.21 (t, J = 7.3 Hz, 2H), 2.86 (t, J = 7.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 170.5, 159.6, 150.6, 134.6, 129.5, 126.0, 124.9, 121.6, 114.8, 55.4, 55.4, 34.8, 31.3.

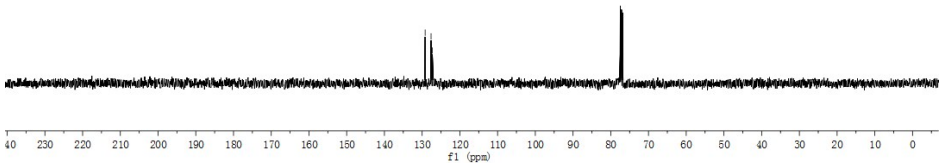


b) Radical inhibition experiments

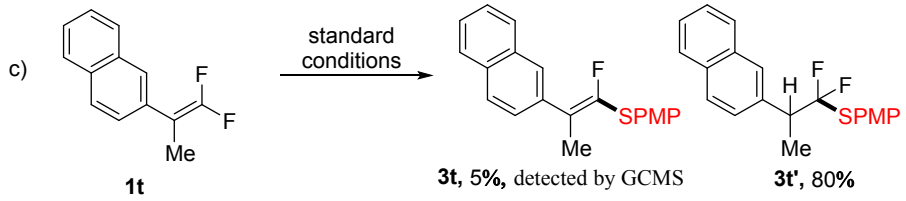


1b (0.1 mmol), thiophenol **2** (0.15 mmol), radical inhibitor (0.2 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1 mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. Subsequently, the reaction mixture was detected on GC-MS. The addition of radical inhibitor directly inhibited this transformation, which indicate the radical involved in the transformation through a single-electron transfer. The ^1H NMR (400 MHz, $CDCl_3$)：δ_H 7.55 (d, J = 7.5 Hz, 4H), 7.35 (t, J = 7.5 Hz, 4H), 7.28 (dd, J = 13.3, 6.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ_H 129.2, 127.6, 127.3.



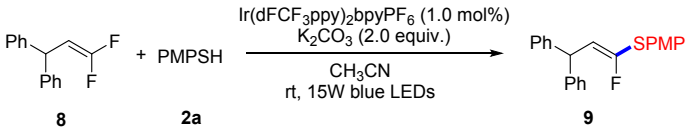


c) Control experiment to rule out the radical addition/elimination pathway



1t (0.1 mmol), thiophenol **2** (0.15 mmol), (0.2 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1 mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. Subsequently, the reaction mixture was detected on GC-MS, which 3t' was the main product indicate the radical addition/elimination process.

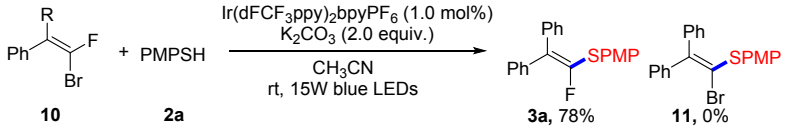
d) Radical intermediate trapping experiment



8 (0.1 mmol), **2a** (0.15 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1 mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 °C. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was

removed with evaporator and then filtered through an inch of silica gel. Subsequently, the reaction mixture was detected on GC-MS and there was no desired detected.

e) Radical intermediate trapping experiment



10 (0.1 mmol), **2a** (0.15 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mol %), K_2CO_3 (0.2 mmol), was combined in a 10 mL flask. 1 mL solvent CH_3CN was added. The flask was caped and degassed oxygen with N_2 for three times at -78 ^oC. Then, the reaction flask was exposed to 15 W blue leds until full completely consumed of *gem*-difluoroalkenes (monitored by TLC). After the reaction finished, the solvent was removed with evaporator and then filtered through an inch of silica gel. The filtrate was concentrated and purification by chromatography on silica gel to afford the desired product **3a** rather than the defluorination product **11** . ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.48 - 7.39 (m, 5H), 7.37 - 7.26 (m, 7H), 6.97 - 6.88 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.0, 151.4 (d, J = 304.7 Hz), 137.9 (dd, J = 149.4, 3.0 Hz), 133.6, 130.6 (d, J = 2.7 Hz), 129.8 (d, J = 5.3 Hz), 128.4, 128.2 (s), 128.0, 127.9, 127.7, 122.1, 115.0, 55.5.

8. Reference

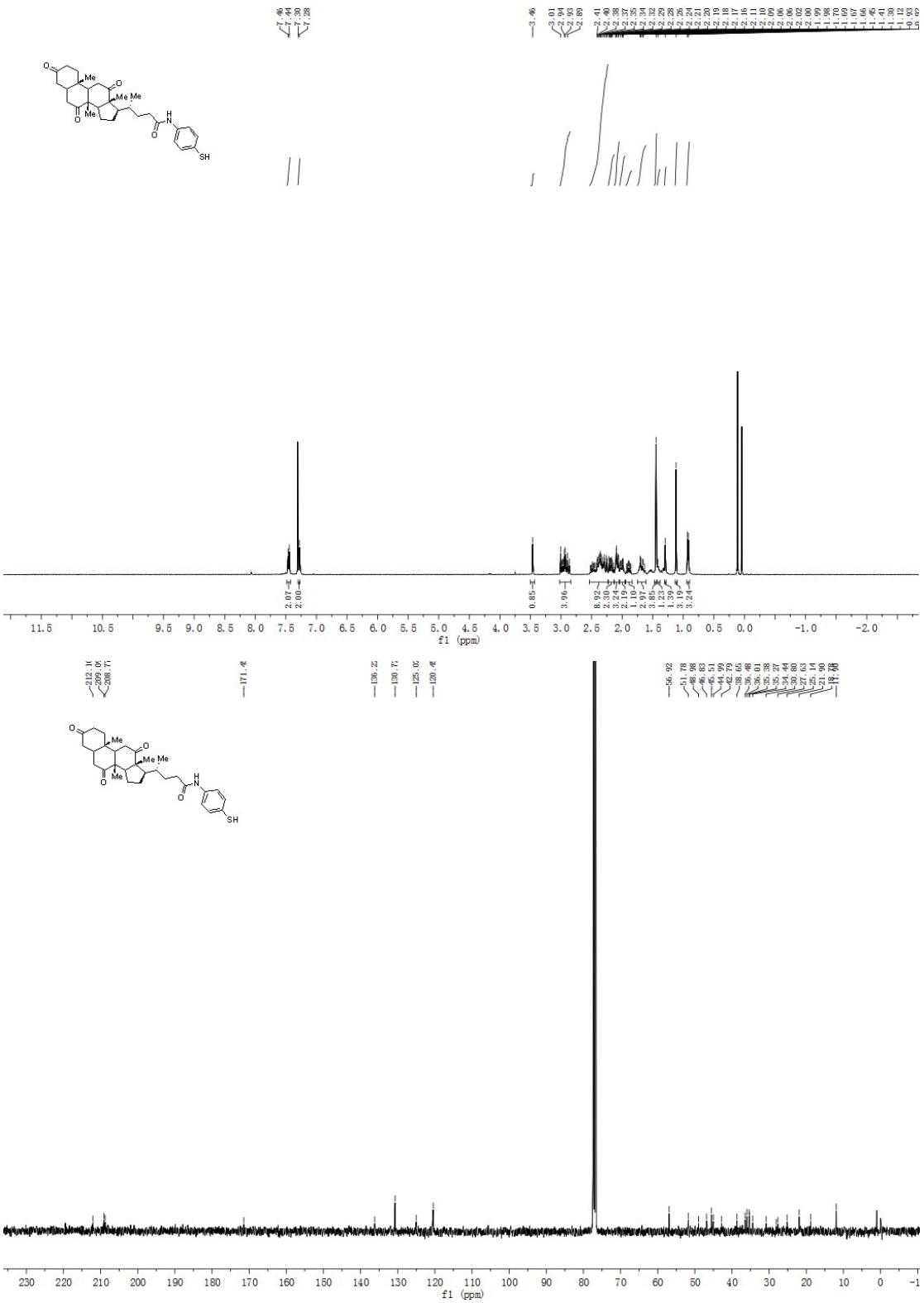
1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15* , 1518.

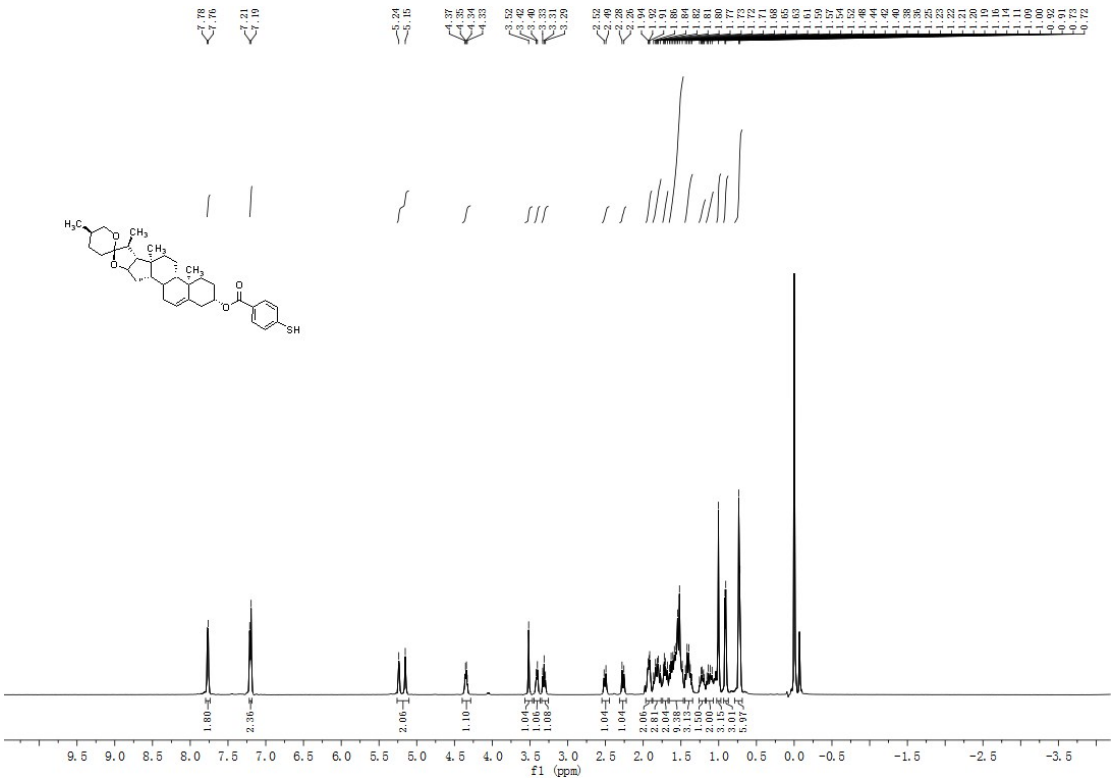
2. Zheng, J.; Cai, J.; Lin, J.-H.; Guo, Y.; Xiao, J.-C. *Chem. Commun.* **2013**, *49*, 7513.

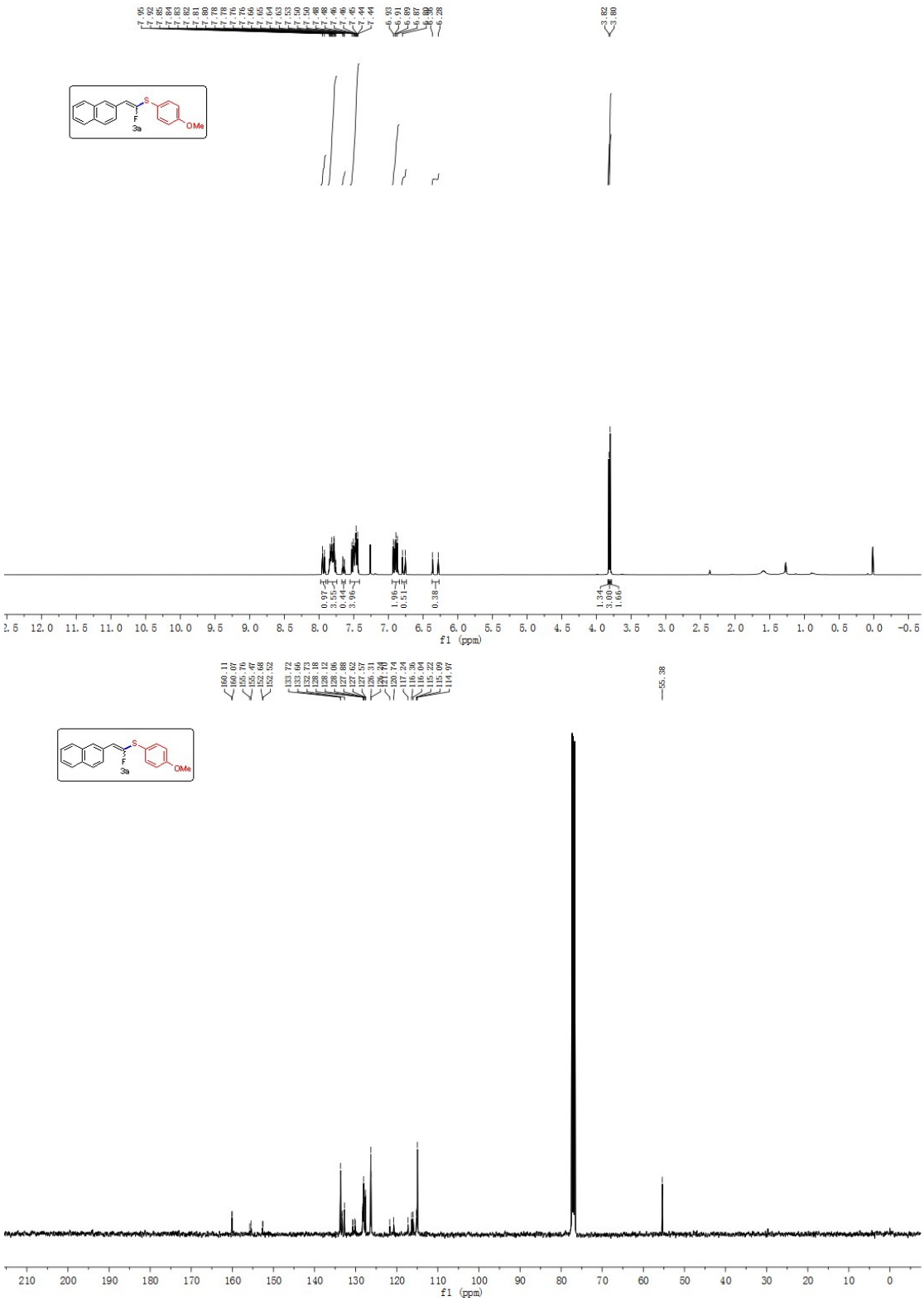
3. Hu, M.; He, Z.; Gao, B.; Li, L.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2013**, *135*, 17302.

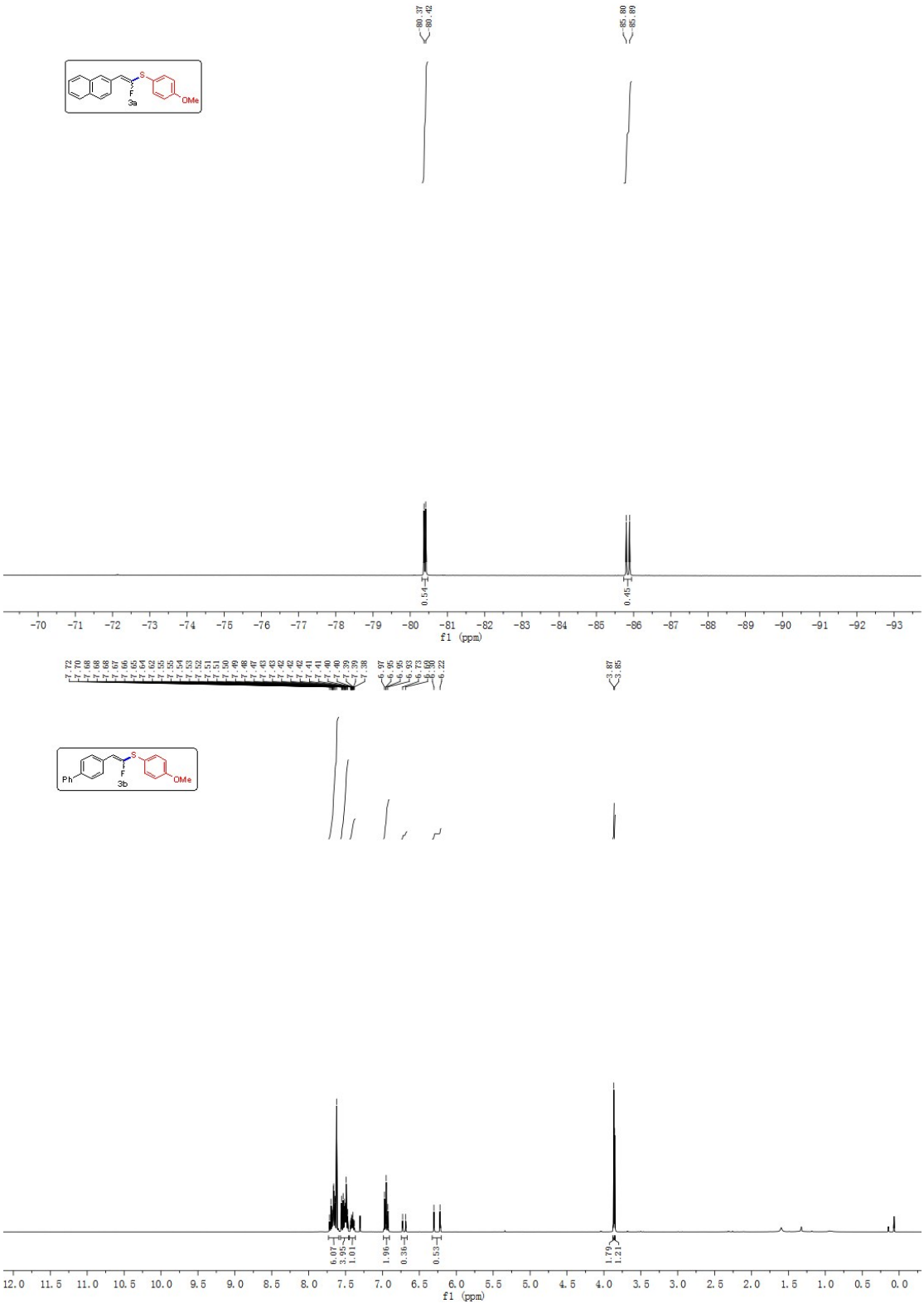
4. Li, Y.; Hu, J. *J. Fluo. Chem*. **2008**, *129*, 382.

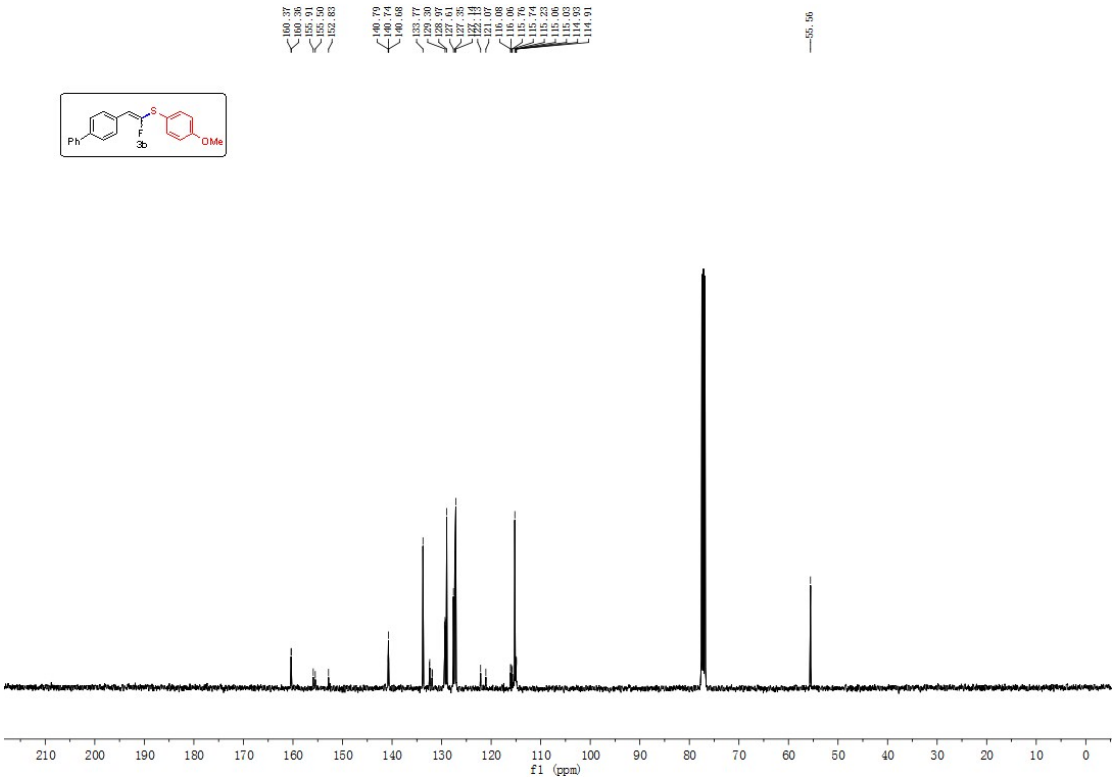
9. Spectra for Substrates and Products Product Characterization

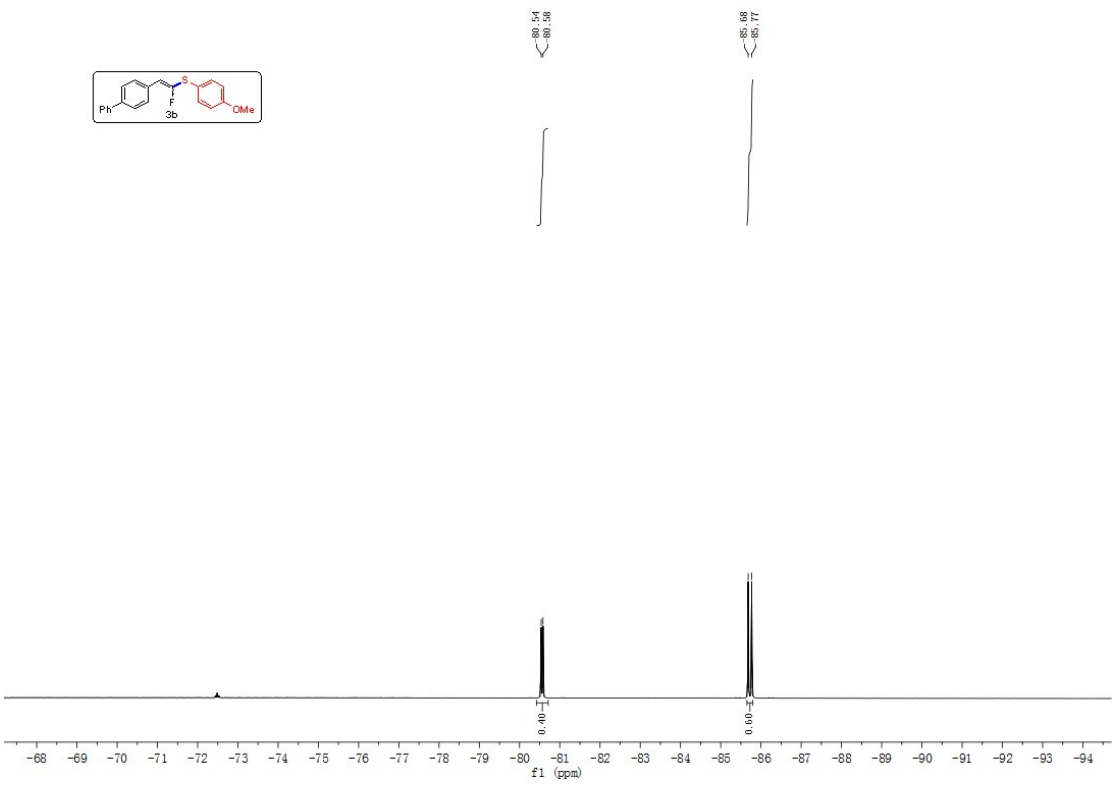


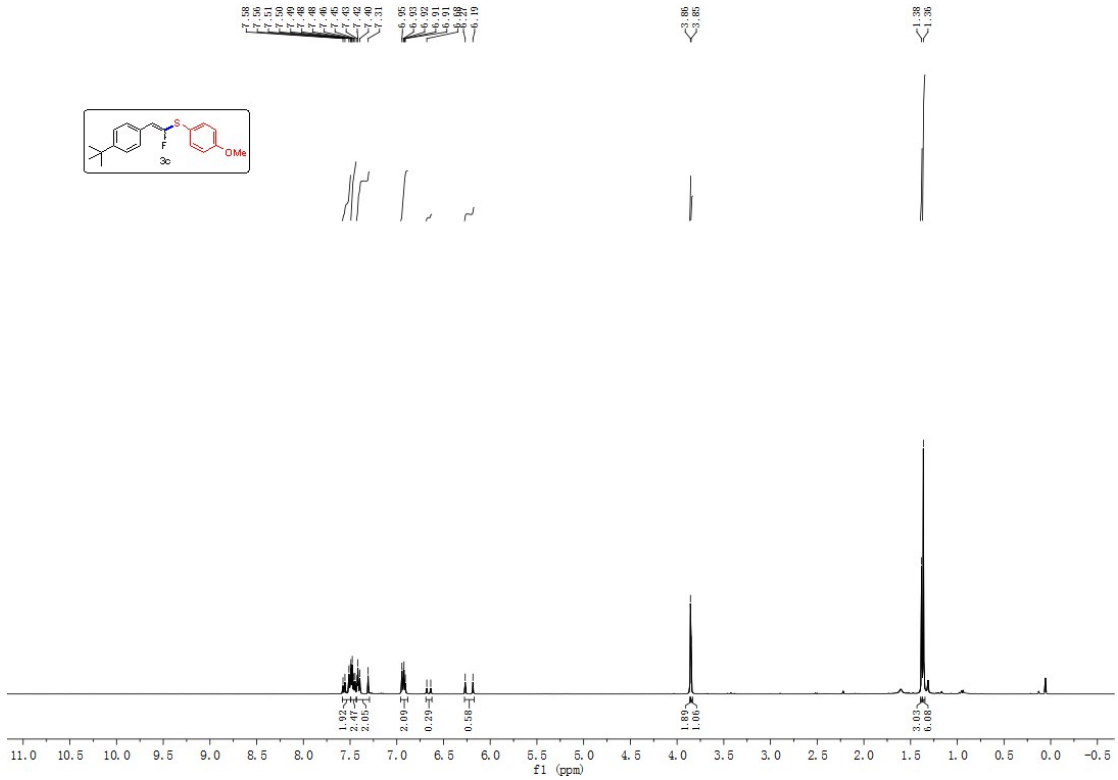

7.78
7.76
7.21
7.19
5.24
5.15
4.37
4.35
4.34
4.33
3.52
3.48
3.46
3.33
3.31
3.29
2.52
2.49
2.28
2.26
1.94
1.92
1.91
1.88
1.86
1.84
1.82
1.81
1.80
1.77
1.73
1.72
1.71
1.68
1.65
1.63
1.61
1.59
1.57
1.54
1.52
1.48
1.44
1.42
1.40
1.38
1.36
1.25
1.23
1.22
1.21
1.20
1.19
1.15
1.14
1.11
1.09
1.00
0.92
0.91
0.73
0.72
1.80
2.36
2.06
1.10
1.04
1.06
1.08
1.04
1.04
2.06
2.81
2.04
9.38
1.15
1.50
2.09
3.15
3.01
5.97
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 -2.5 -3.5
f1 (ppm)
165.64
138.62
138.08
130.32
128.23
122.20
109.46
80.98
71.26
67.00
62.23
56.62
50.37
41.75
40.40
37.39
36.09
34.10
31.97
31.52
30.44
28.93
28.43
19.11
17.29
16.46
14.69
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)

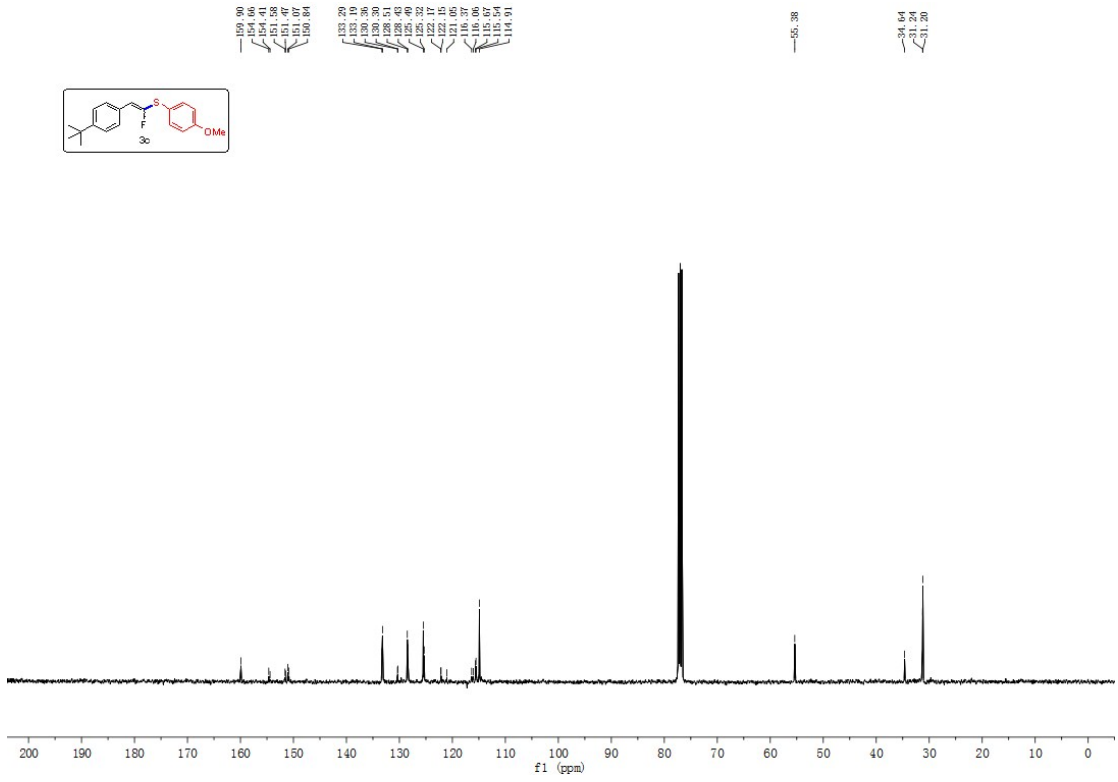

3a
OMe
f1 (ppm)
3a
OMe
f1 (ppm)

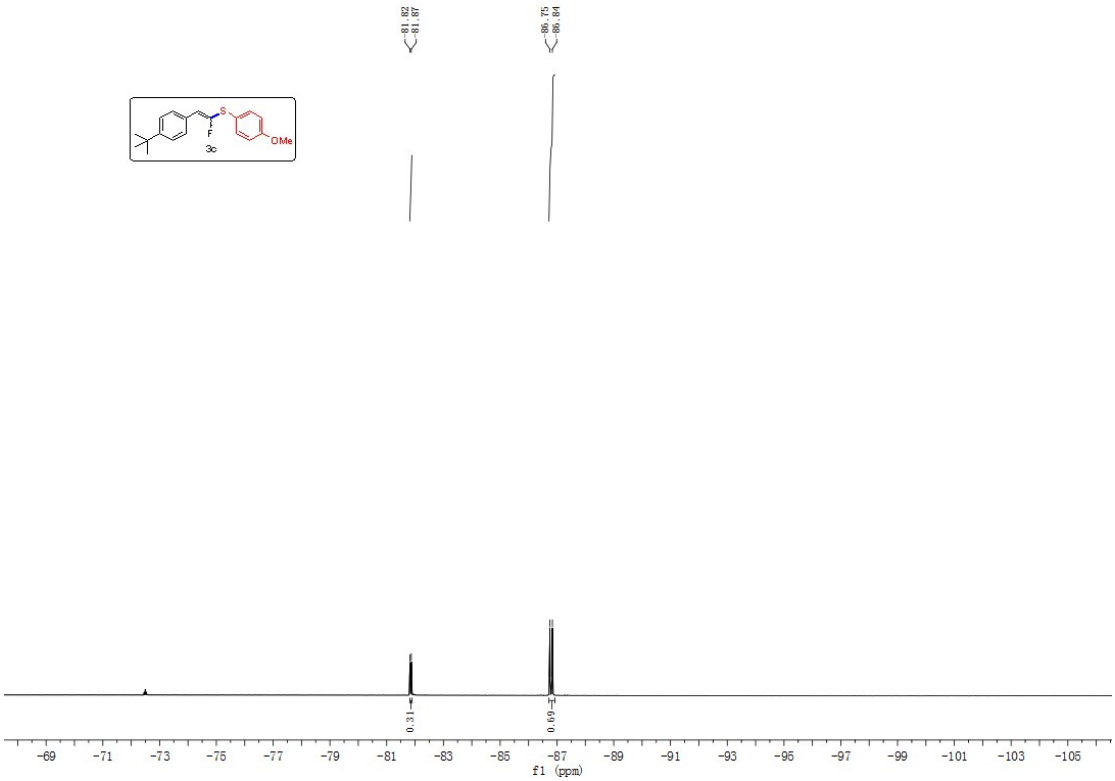

3a
OMe
-80.37
-80.42
-85.80
-85.89
0.54
0.46
f1 (ppm)
3b
Ph
OMe
3.87
3.85
6.07
3.95
1.01
1.96
0.36
0.53
1.79
1.21
f1 (ppm)

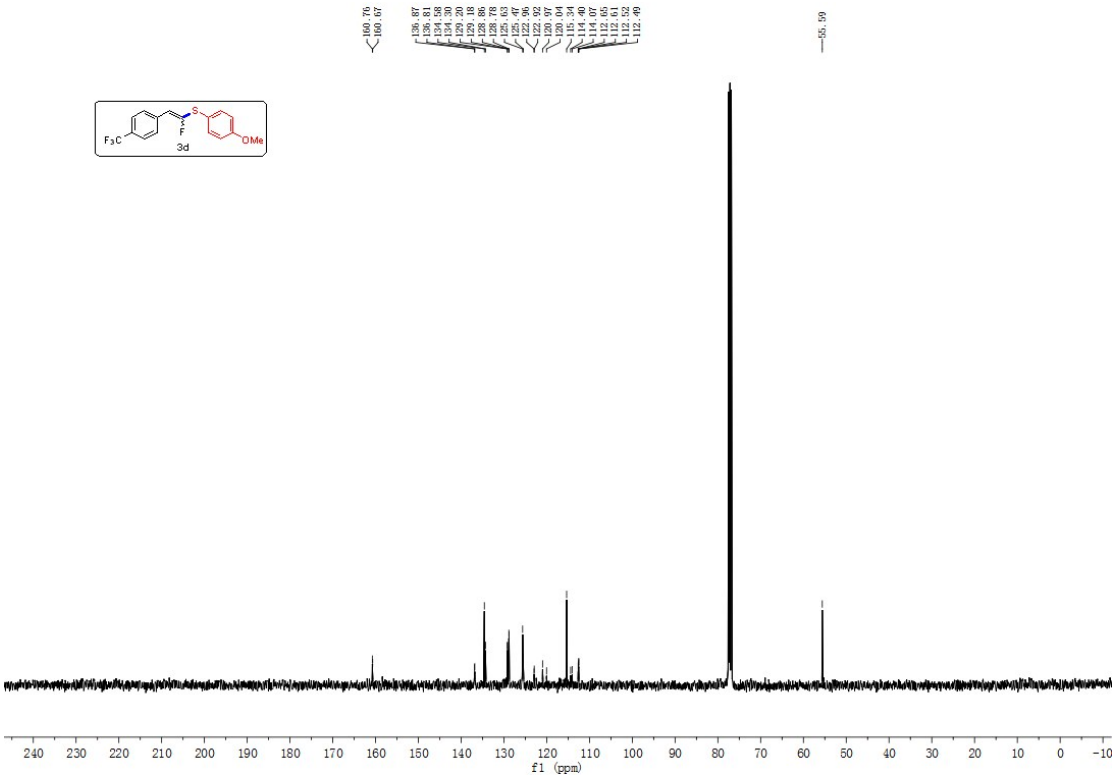

160.37
160.36
155.91
155.50
152.83
140.79
140.74
140.68
133.77
129.30
128.97
127.61
127.35
122.14
121.97
121.07
116.08
116.06
115.76
115.74
115.23
115.06
115.03
114.93
114.91
55.56
Ph
F
S
OMe
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

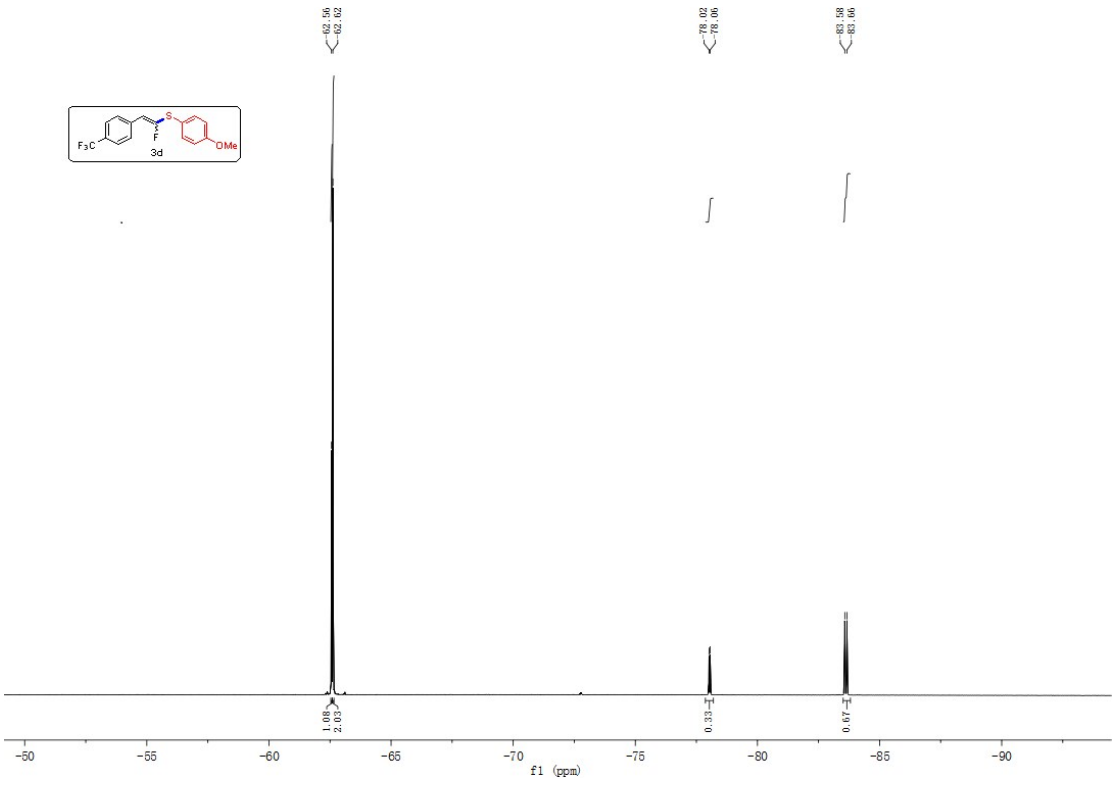

80.54
80.50
85.68
85.77
Ph
F
S
OMe
3b
0.40
0.60
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
-80
-81
-82
-83
-84
-85
-86
-87
-88
-89
-90
-91
-92
-93
-94
f1 (ppm)

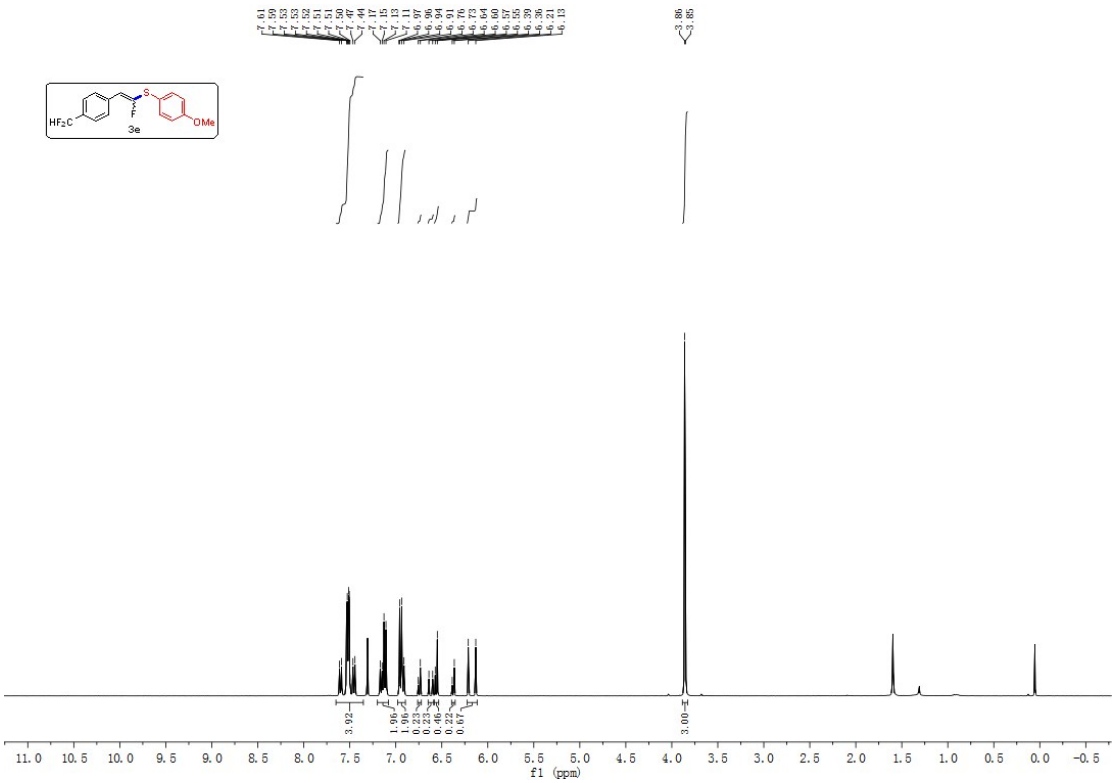

3c
OMe
f1 (ppm)

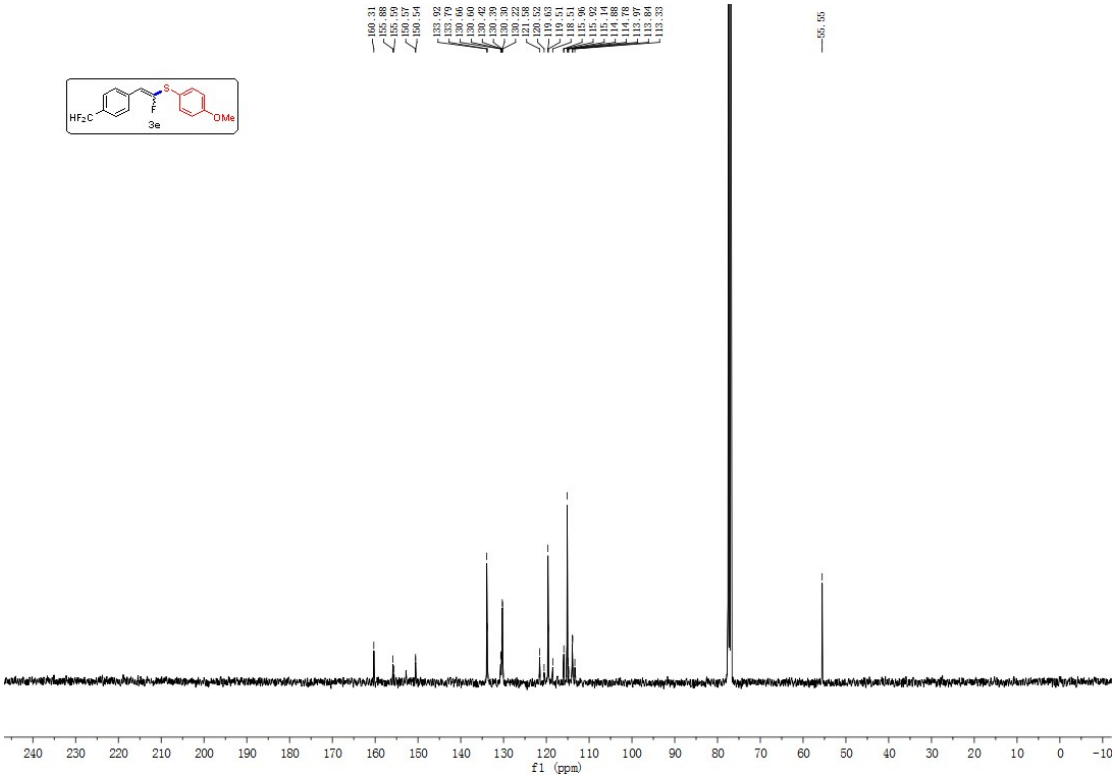

3c
OMe
f1 (ppm)

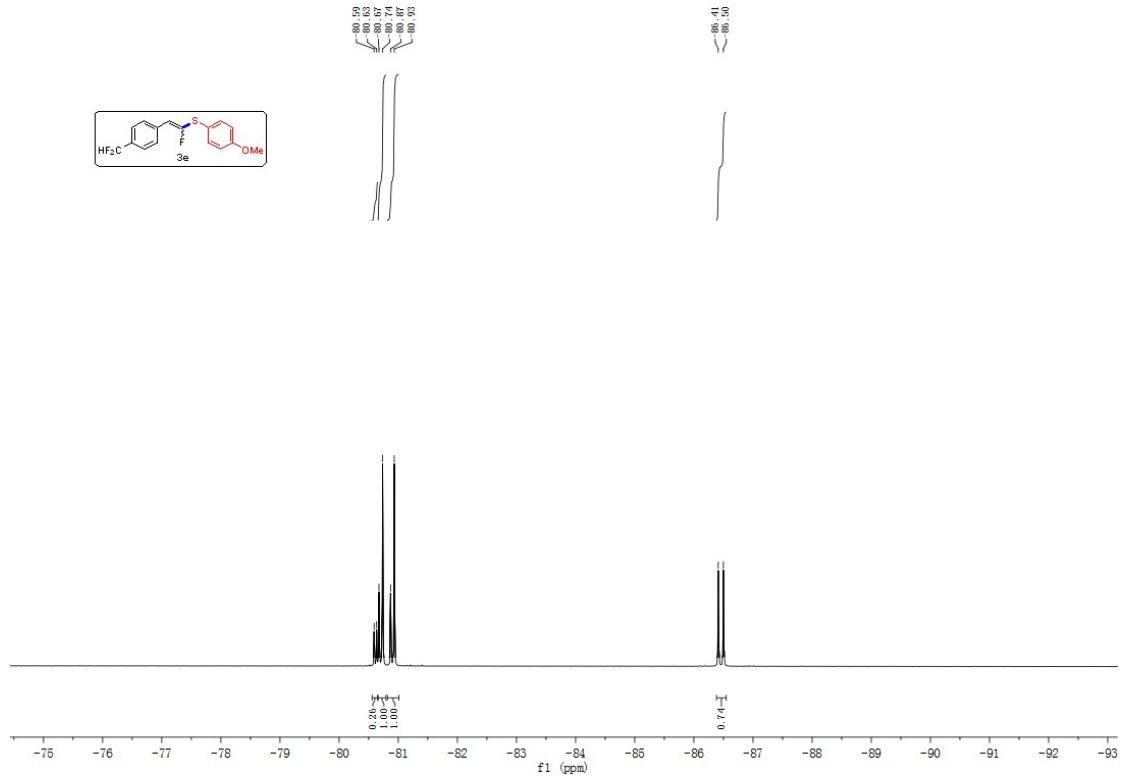

-81.82
-81.87
-86.75
-86.84
3c
OMe
0.31
0.69
f1 (ppm)
7.71
7.69
7.67
7.64
7.61
7.55
7.54
7.53
7.53
7.48
7.47
7.46
7.46
7.31
6.97
6.95
6.84
6.83
6.61
6.19
6.11
3.87
3.86
3d
F3C
OMe
3.97
1.98
1.97
0.31
0.60
1.99
1.05
f1 (ppm)

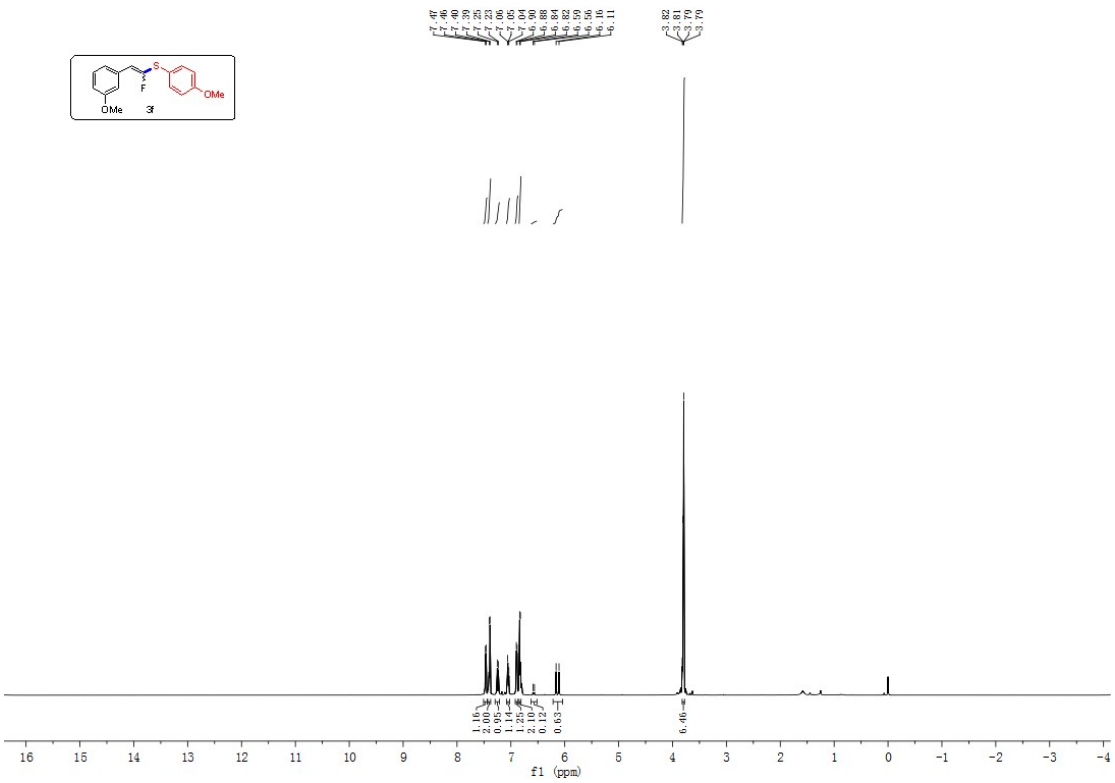

160.76
160.67
136.87
136.81
134.58
134.30
129.20
129.18
128.86
128.78
125.53
125.47
122.96
122.92
120.97
120.04
115.34
114.40
114.07
113.65
112.61
112.52
112.49
55.59
F3C
F
S
OMe
3d
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

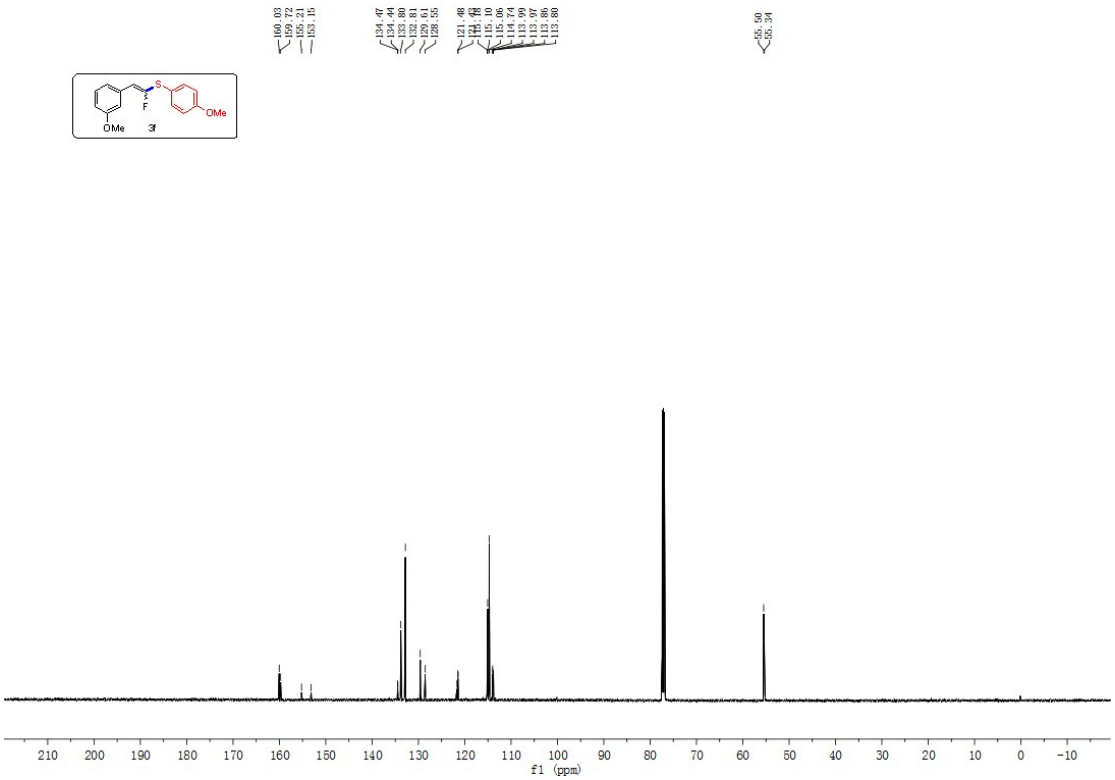

62.56
62.52
78.02
78.00
83.58
83.66
F3C
F
S
OMe
3d
1.08
2.03
0.33
0.67
-50 -55 -60 -65 -70 -75 -80 -85 -90
f1 (ppm)

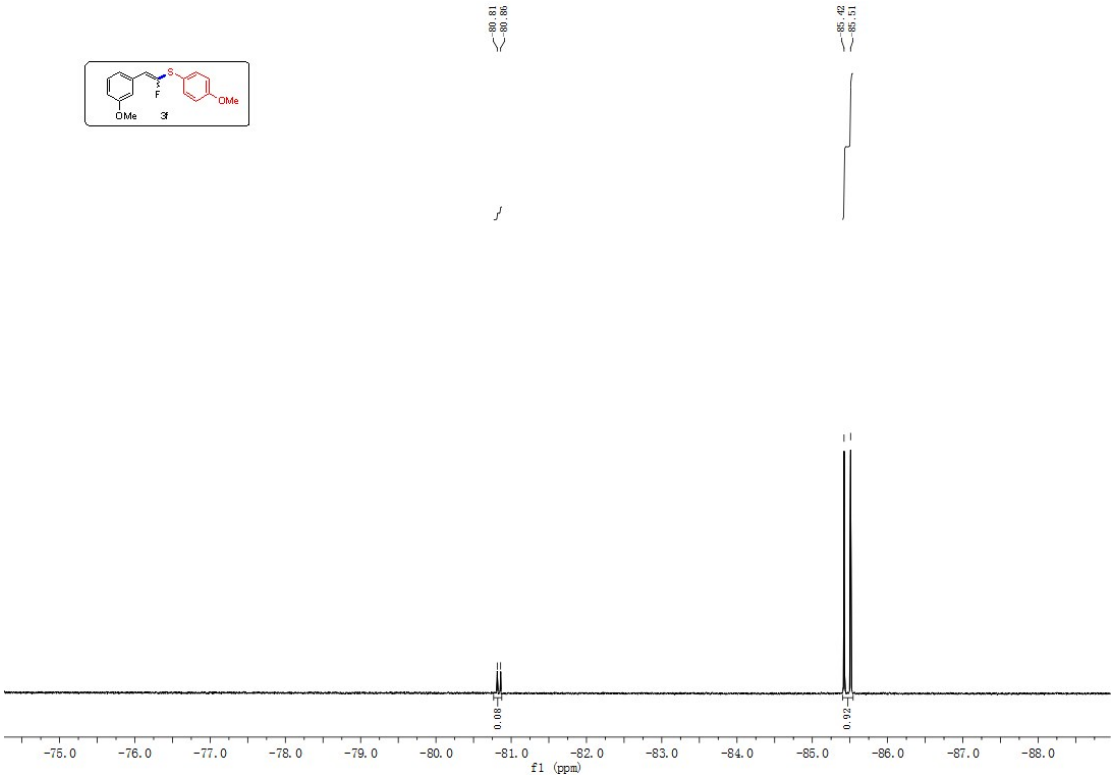

HF2C
3e
OMe
f1 (ppm)

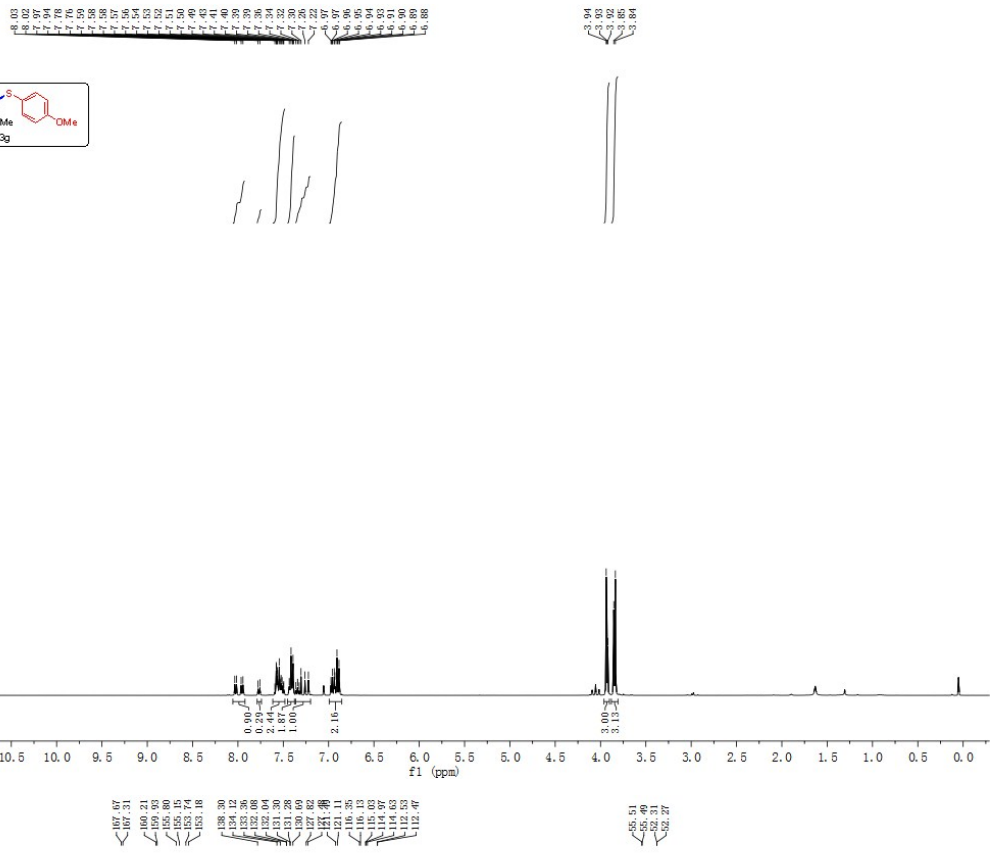

HF2C
3e
OMe
f1 (ppm)

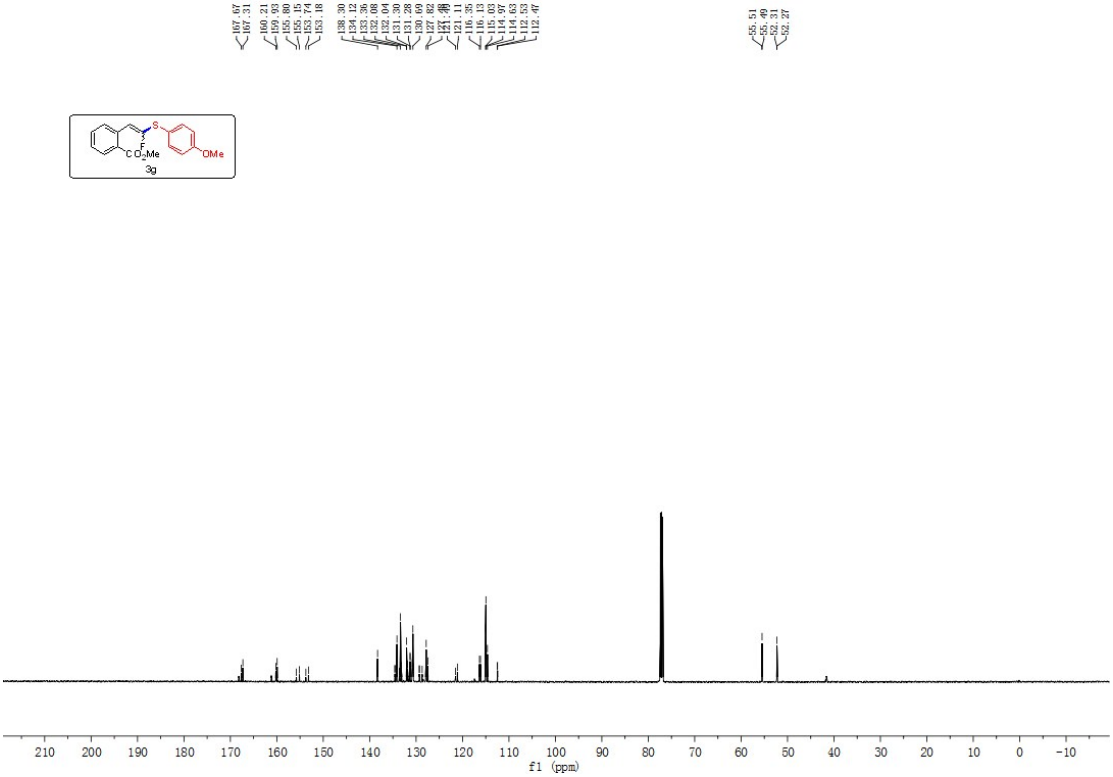

-80.59
-80.63
-80.67
-80.74
-80.87
-80.93
-86.41
-86.50
HF2C
S
F
OMe
3e
0.26
1.00
1.00
0.74
-75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87 -88 -89 -90 -91 -92 -93
f1 (ppm)

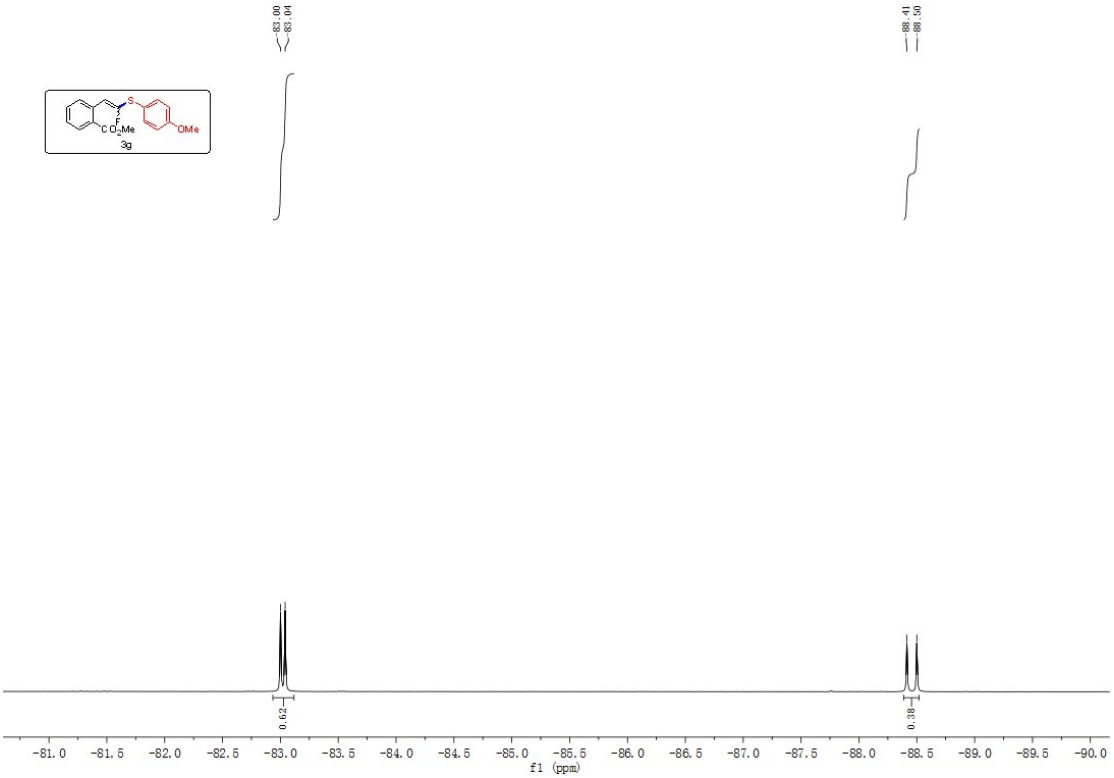

7.47
7.46
7.40
7.39
7.25
7.23
7.06
7.05
7.04
6.90
6.88
6.84
6.82
6.59
6.56
6.16
6.11
3.82
3.81
3.79
3.79
S
F
OMe
OMe
3f
1.16
2.00
0.95
1.14
1.15
2.10
0.12
0.63
6.46
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

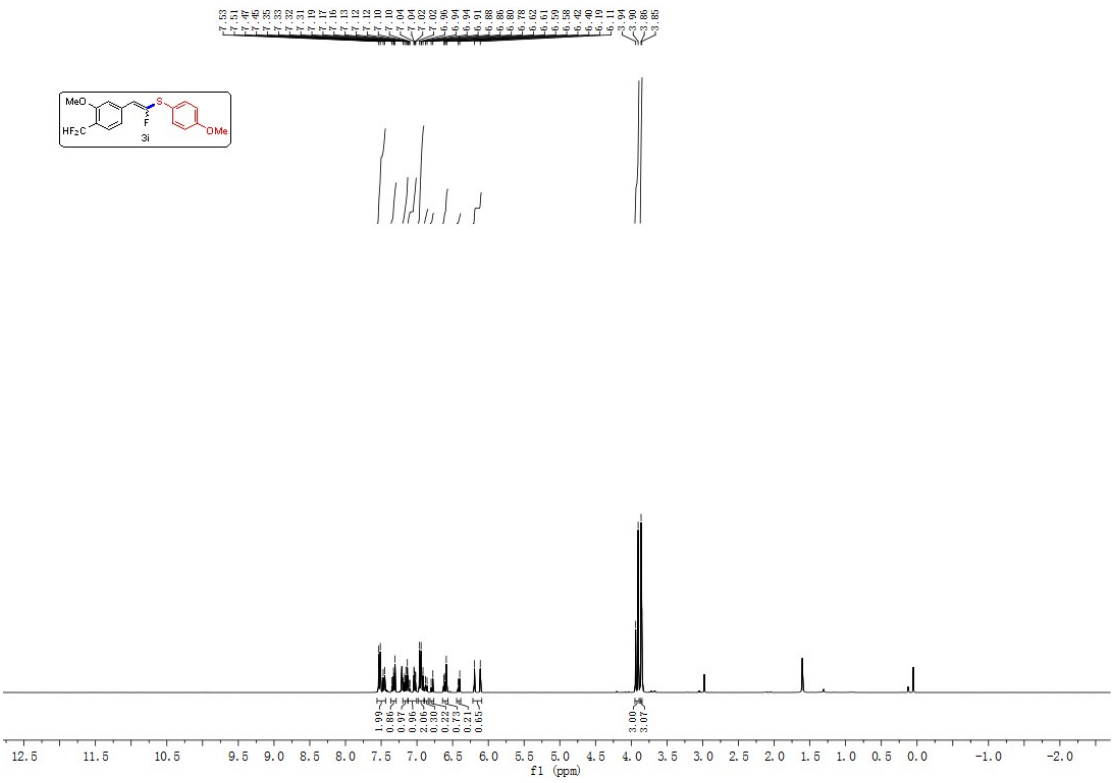

160.03
159.72
155.21
153.15
134.47
134.44
133.80
132.81
129.61
129.55
121.48
121.46
115.10
115.06
114.74
113.99
113.97
113.86
113.80
55.50
55.34
OMe
F
S
OMe
3f
f1 (ppm)

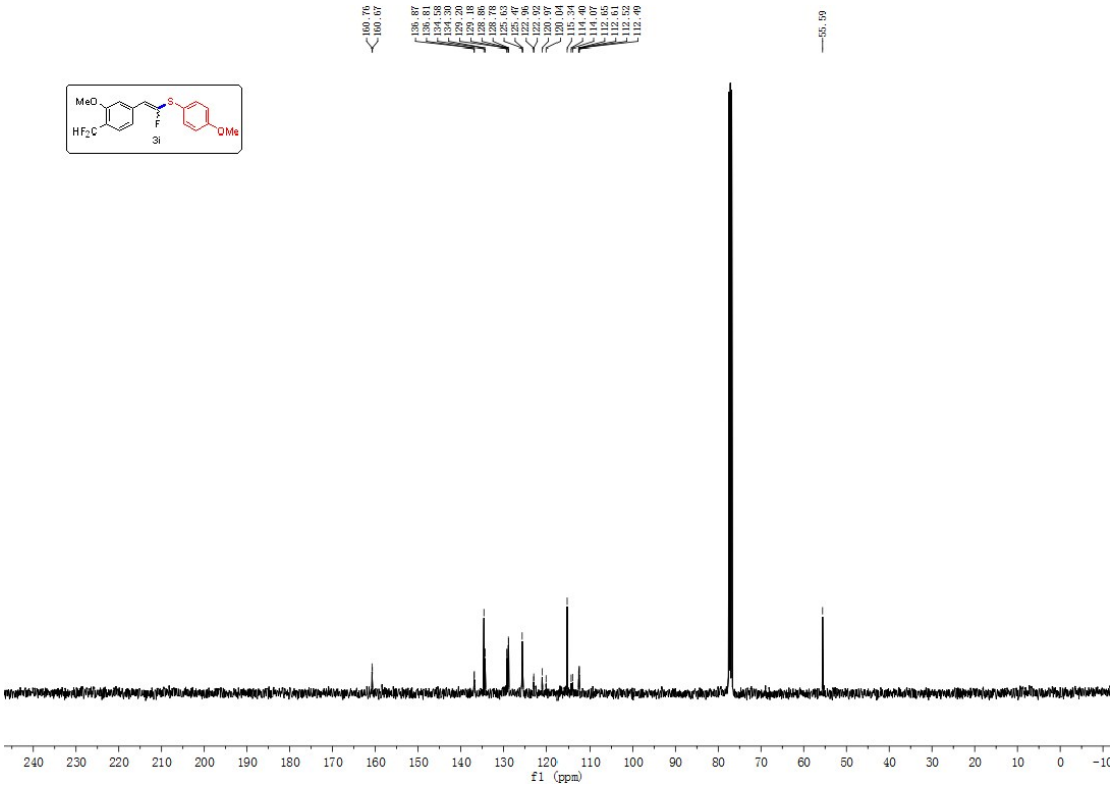

80.81
80.86
85.42
85.51
OMe
F
S
OMe
3f
0.08
0.92
f1 (ppm)

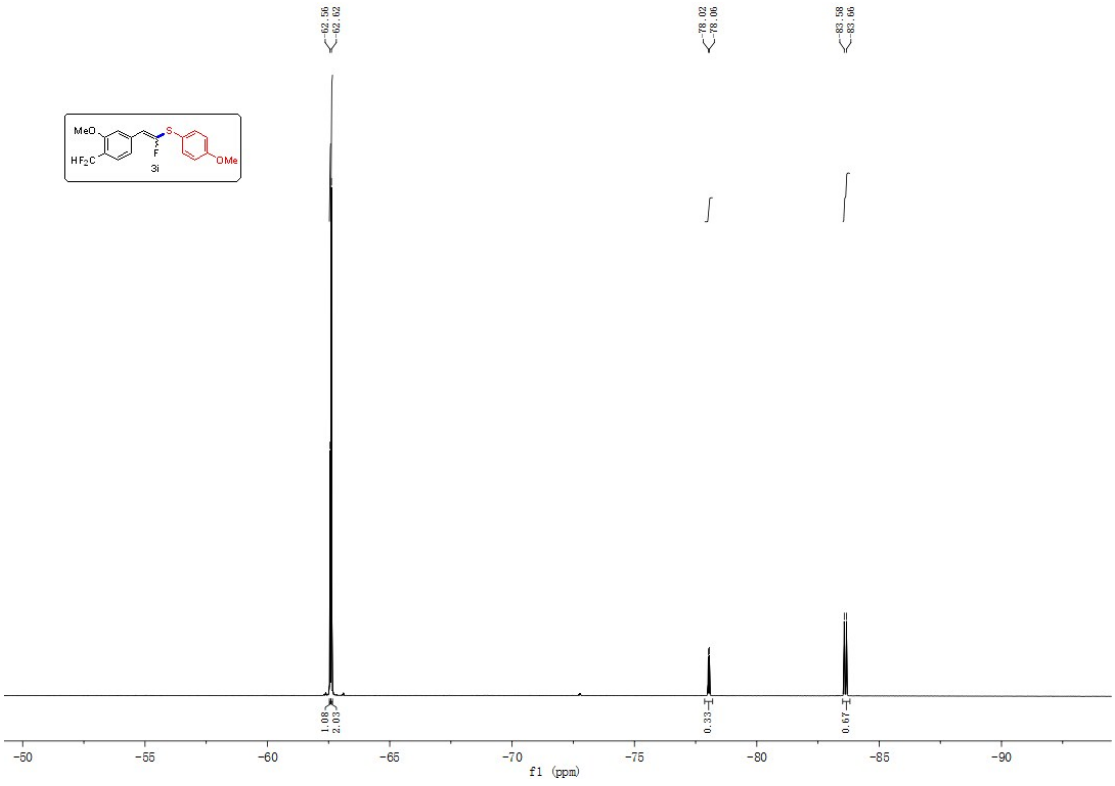

3g
f1 (ppm)

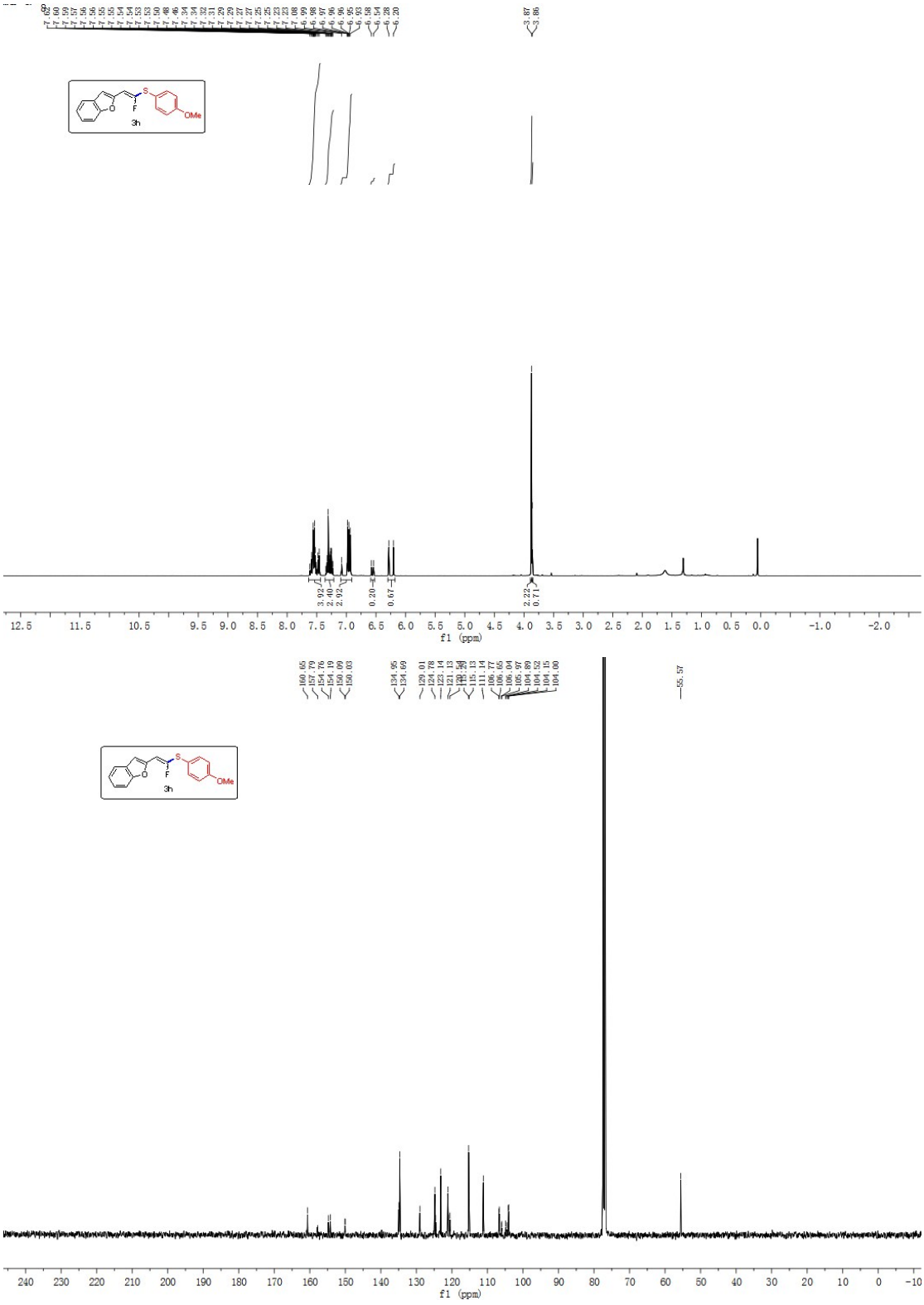

3g
f1 (ppm)

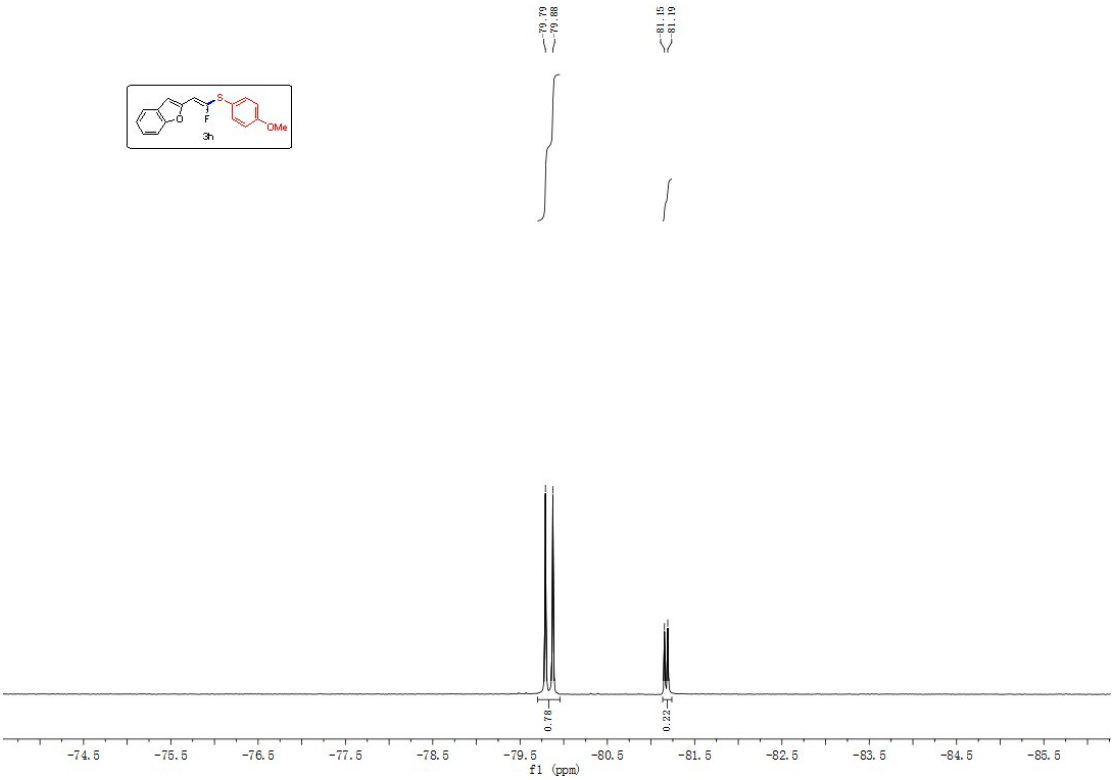

-83.00
-83.04
-88.41
-88.50
3g
0.62
0.38
-81.0 -81.5 -82.0 -82.5 -83.0 -83.5 -84.0 -84.5 -85.0 -85.5 -86.0 -86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0
f1 (ppm)

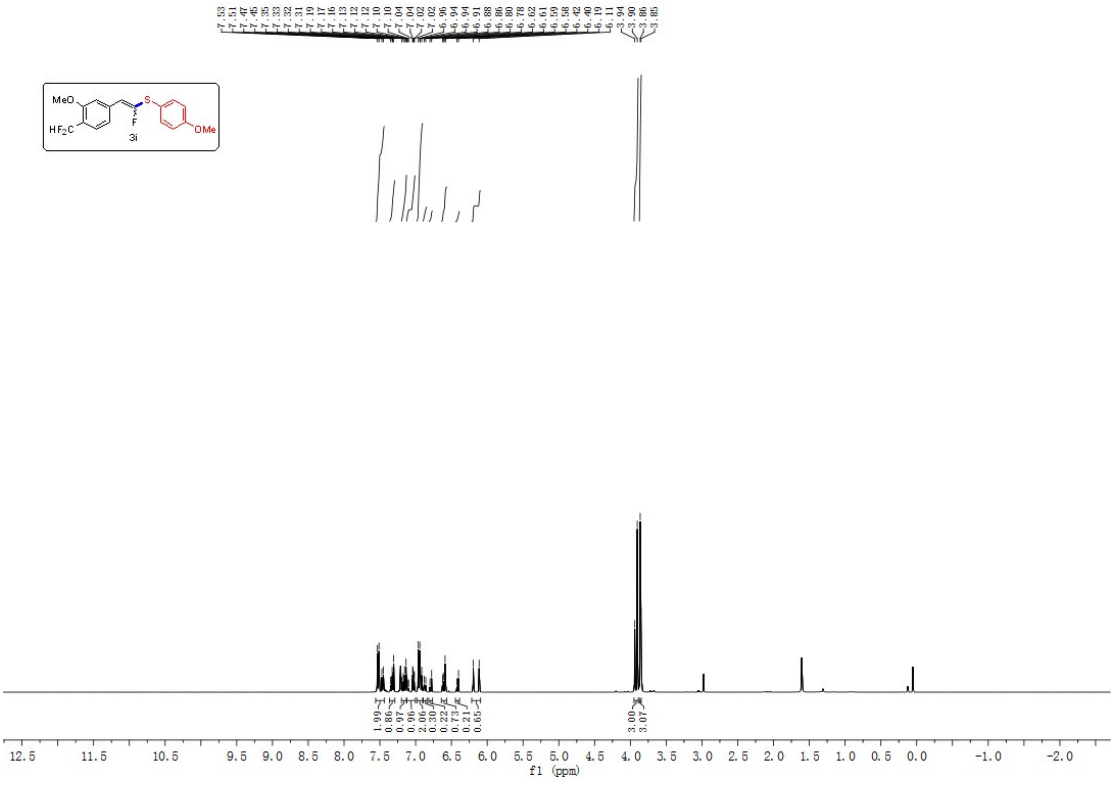

3i
1.99
0.86
0.97
0.96
2.06
1.00
0.22
0.73
0.21
0.65
3.00
3.07
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0
f1 (ppm)

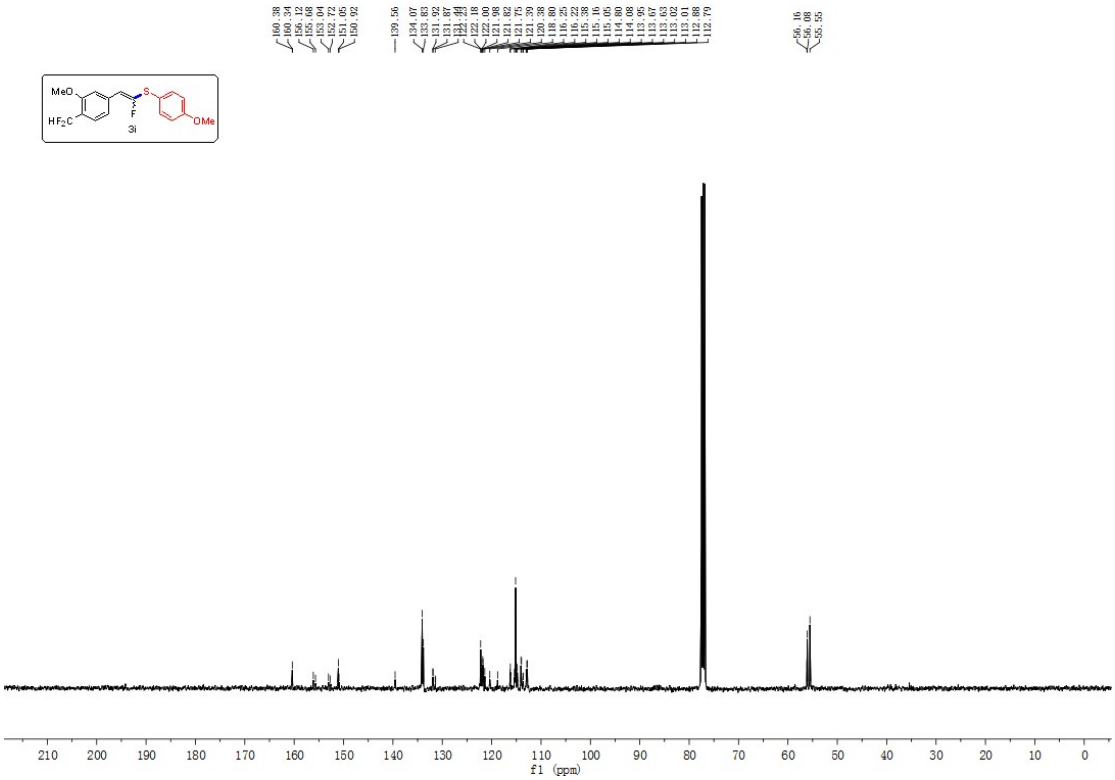

160.76
160.67
136.87
136.81
134.38
134.30
129.20
129.18
128.86
128.78
125.15
125.07
122.96
122.92
120.97
120.04
115.34
114.40
114.07
112.65
112.61
112.52
112.49
55.59
MeO
HF2C
S
F
OMe
3i
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

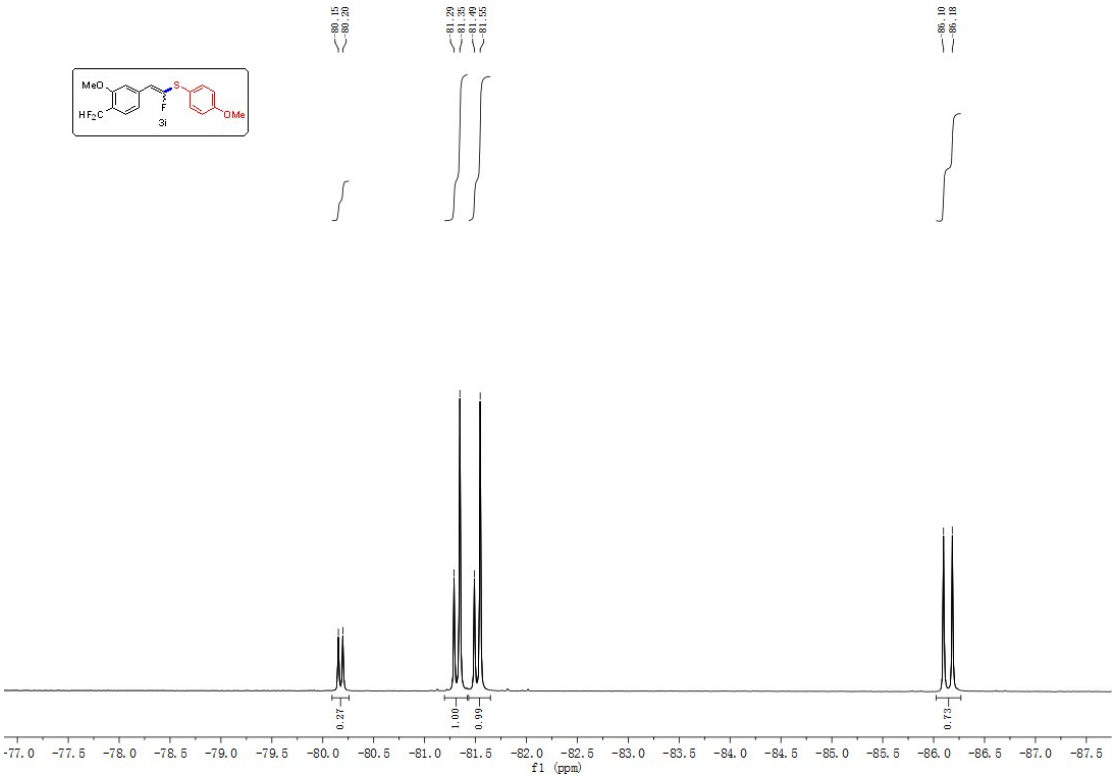

62.56
62.62
78.02
78.06
83.58
83.66
MeO
HF2C
S
F
OMe
3i
1.08
2.03
0.33
0.67
-50 -55 -60 -65 -70 -75 -80 -85 -90
f1 (ppm)

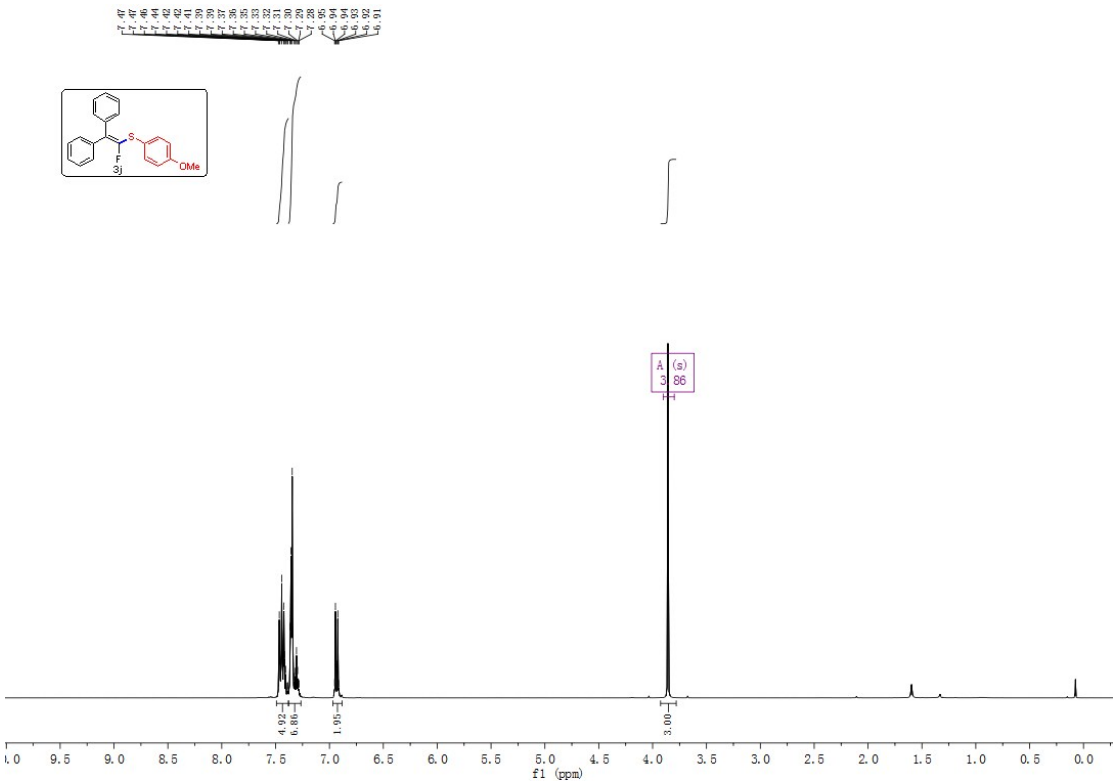

3h
OMe
f1 (ppm)
f1 (ppm)

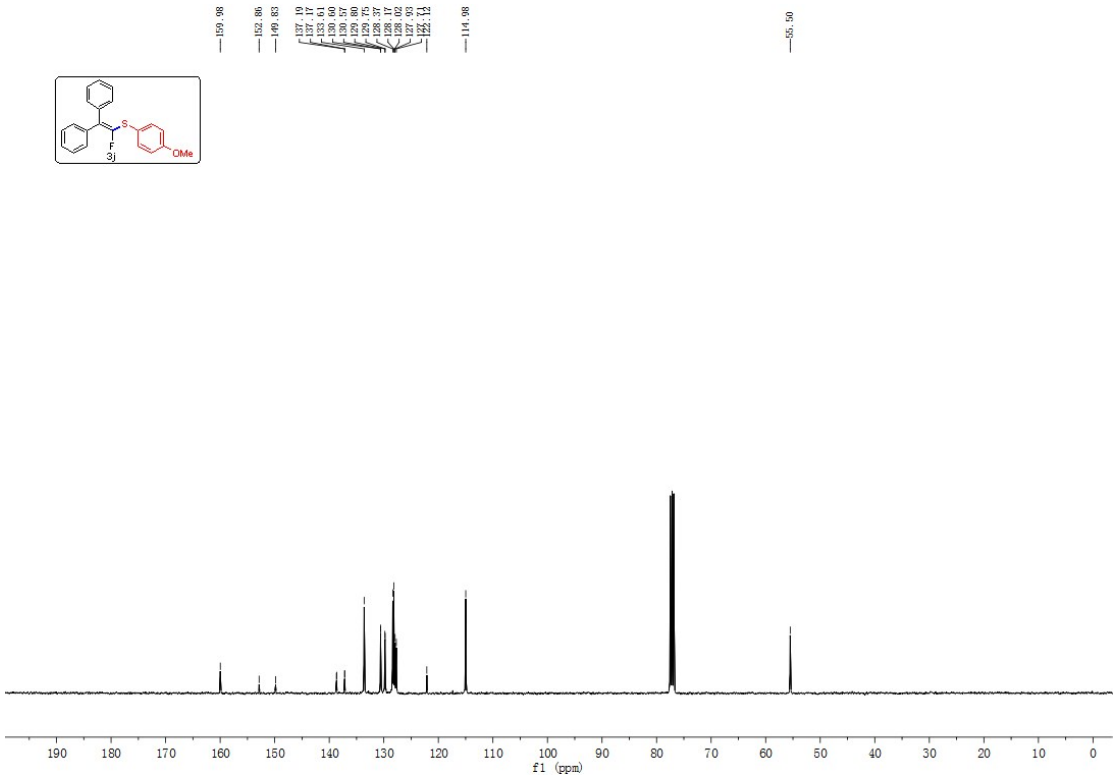

3h
-79.79
-79.88
-81.15
-81.19
0.78
0.22
f1 (ppm)

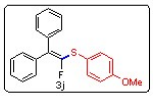

3i
MeO
HF2C
OMe
1.99
0.86
0.97
0.96
2.00
0.22
0.73
0.21
0.65
3.00
3.07
f1 (ppm)


MeO
HF2C
F
S
OMe
3i
f1 (ppm)

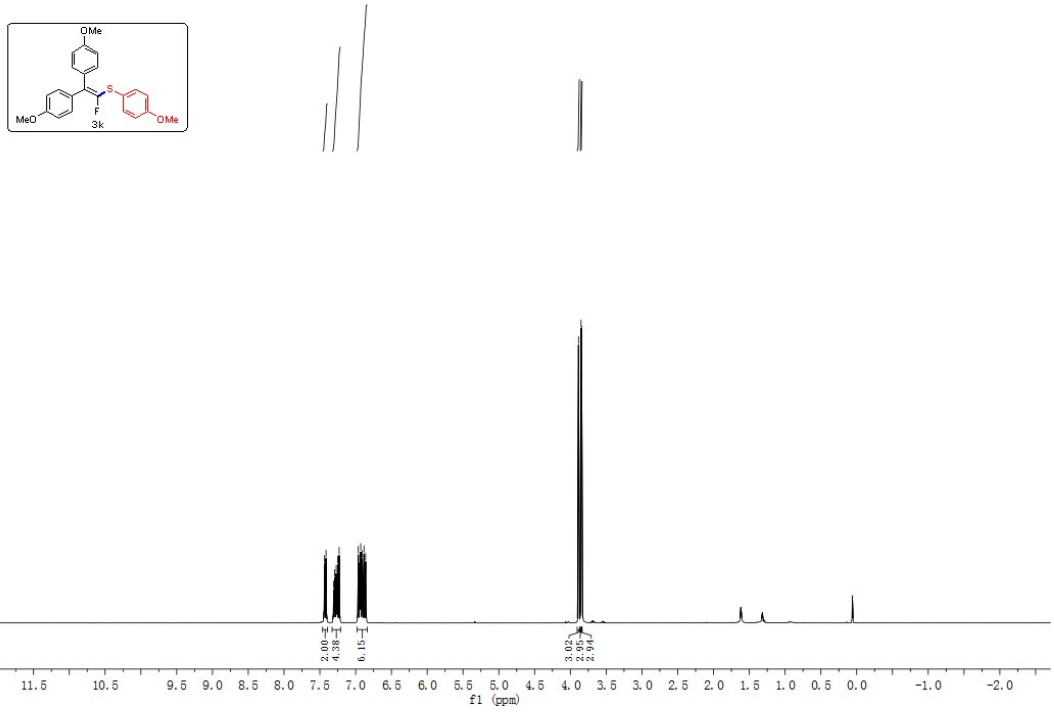

MeO
HF2C
F
S
OMe
3i
0.27
1.00
0.99
0.73
f1 (ppm)


7.47 7.46 7.44 7.42 7.41 7.39 7.38 7.37 7.36 7.35 7.33 7.32 7.31 7.30 7.29 7.28 6.95 6.94 6.94 6.93 6.92 6.91
S
F
3j
OMe
A (s) 3.86
4.92
6.86
1.95
3.00
f1 (ppm)

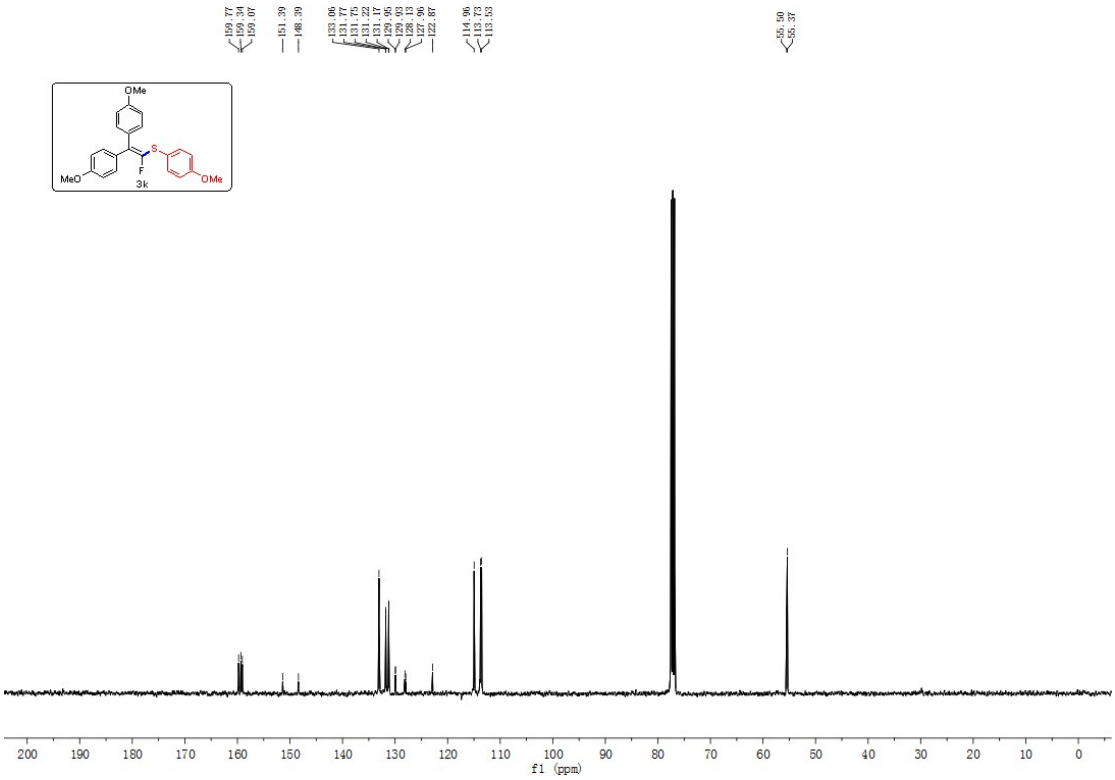

159.98
152.86
149.83
137.19
137.17
133.61
130.57
130.00
129.75
128.37
128.17
128.02
127.93
127.71
122.12
114.98
55.50
S
F
3j
OMe
f1 (ppm)

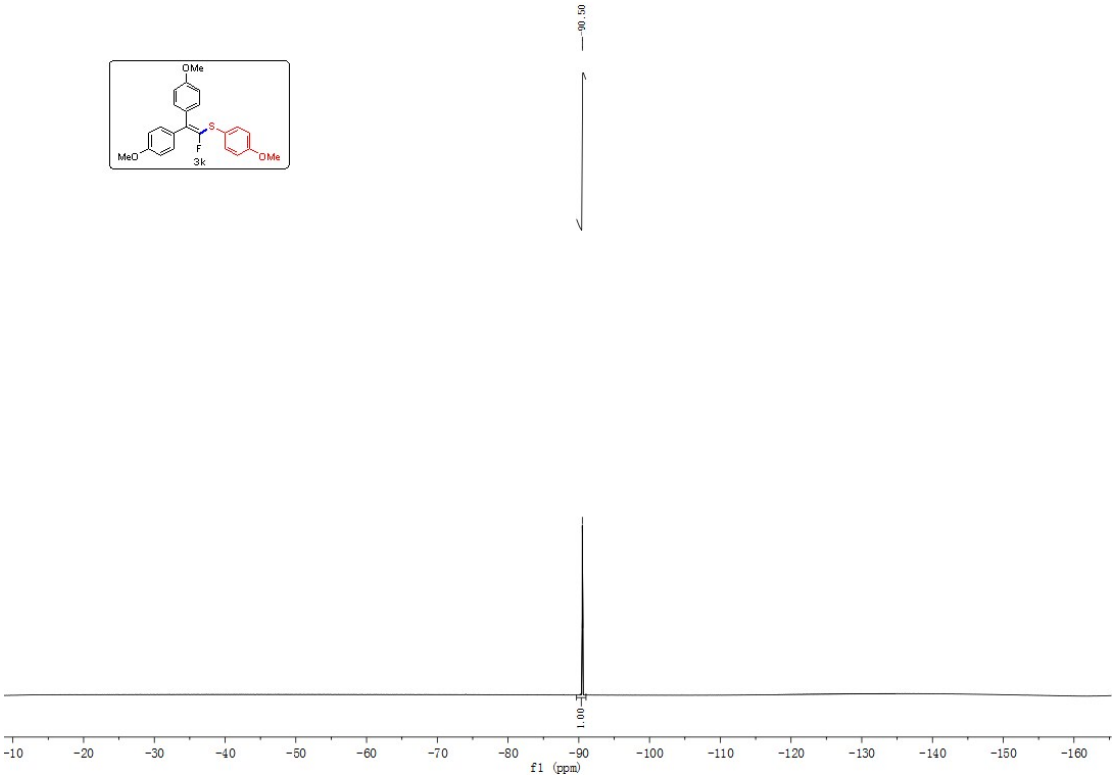

S
F
OMe
3j

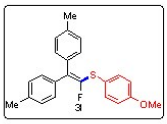
-88.74
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


7.44 7.43 7.42 7.41 7.31 7.29 7.27 7.25 7.24 7.23 6.96 6.95 6.94 6.93 6.92 6.91 6.88 6.88 6.87 6.86
3.89 3.85 3.84
2.00 4.38 6.15 3.02 2.95 2.94
12.5 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 -2.0
f1 (ppm)

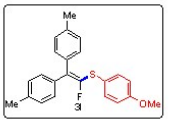
OMe
S
F
MeO
OMe
3k


159.77
159.34
159.07
151.39
146.39
133.06
131.77
131.75
131.23
131.17
129.95
129.93
128.13
127.96
122.87
114.96
113.73
113.53
55.50
55.37
OMe
MeO
F
S
OMe
3k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

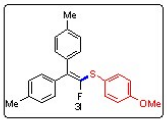

-90.50
OMe
MeO
F
S
OMe
3k
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


Me
Me
S
F
Cl
OMe

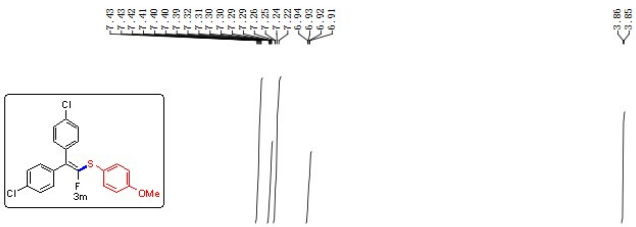
7.46
7.44
7.26
7.24
7.17
7.15
6.94
6.92
3.86
2.45
2.39
1.83
5.76
1.82
2.05
3.13
2.81
3.31
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
f1 (ppm)


Me
Me
S
F
Cl
OMe

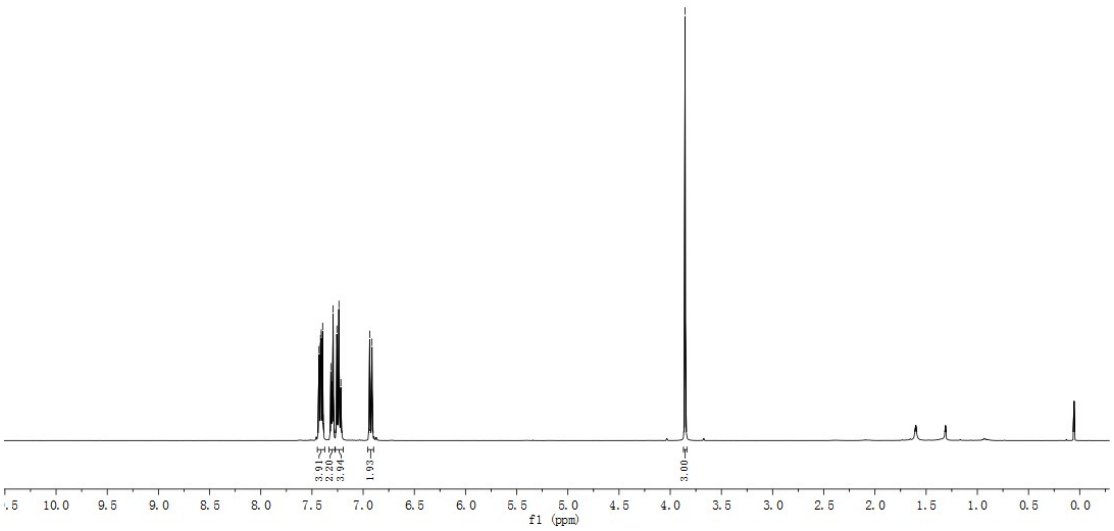
159.68
151.84
148.82
137.58
137.46
133.15
130.32
130.29
129.63
129.57
128.94
122.39
114.81
55.37
21.35
21.23
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

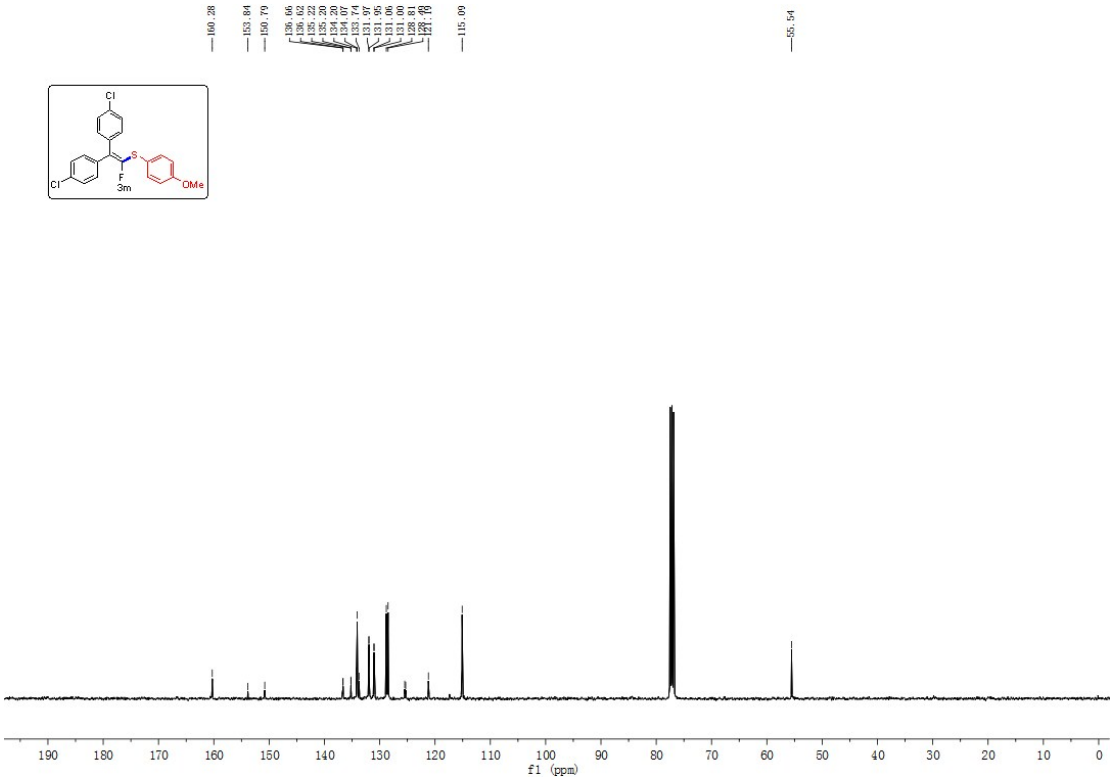

Me
S
F
3l
Me
OMe

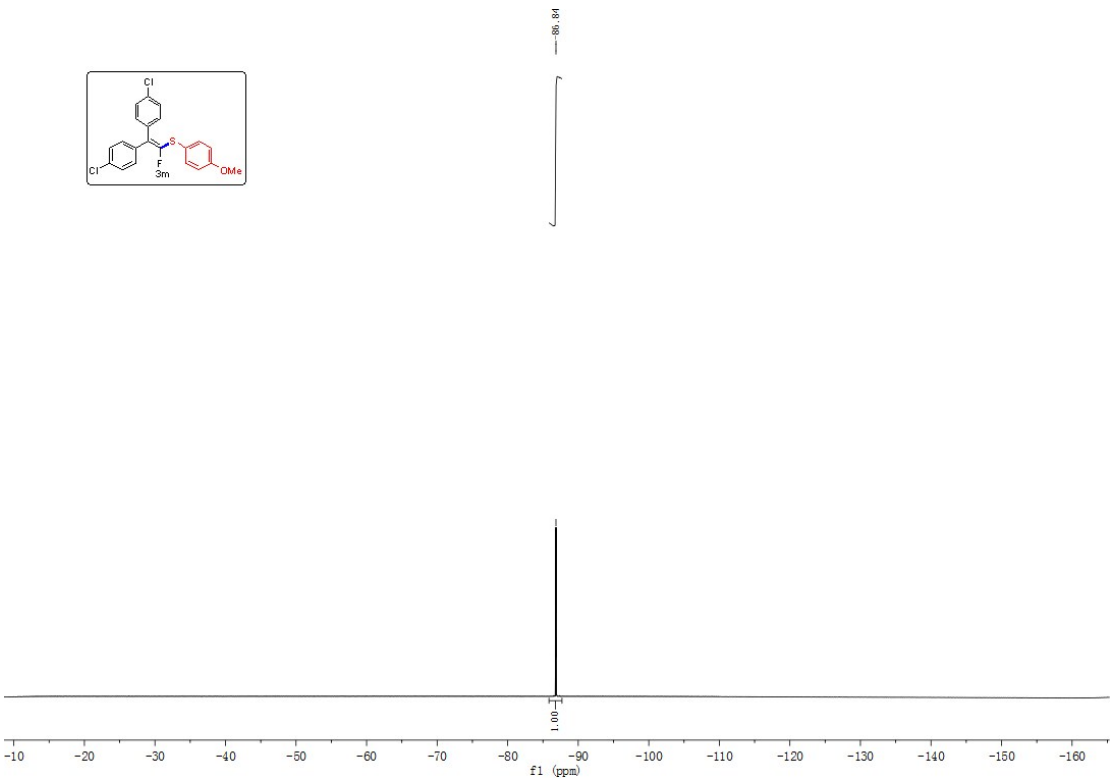
-89.76
1.00
-84.5 -85.0 -85.5 -86.0 -86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0 -93.5 -94.0 -94.5 -95.0 -95.5
f1 (ppm)

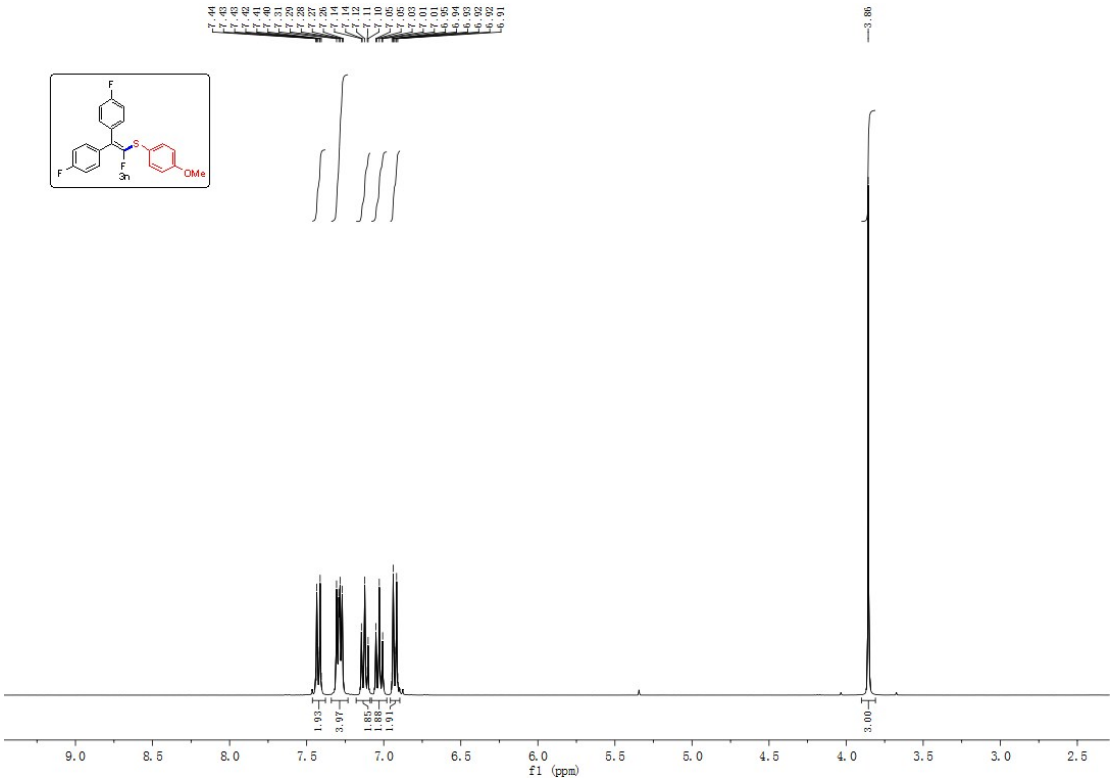

7.43
7.42
7.41
7.40
7.39
7.32
7.31
7.30
7.30
7.29
7.26
7.25
7.24
7.24
6.94
6.93
6.92
6.91
3.86
3.85

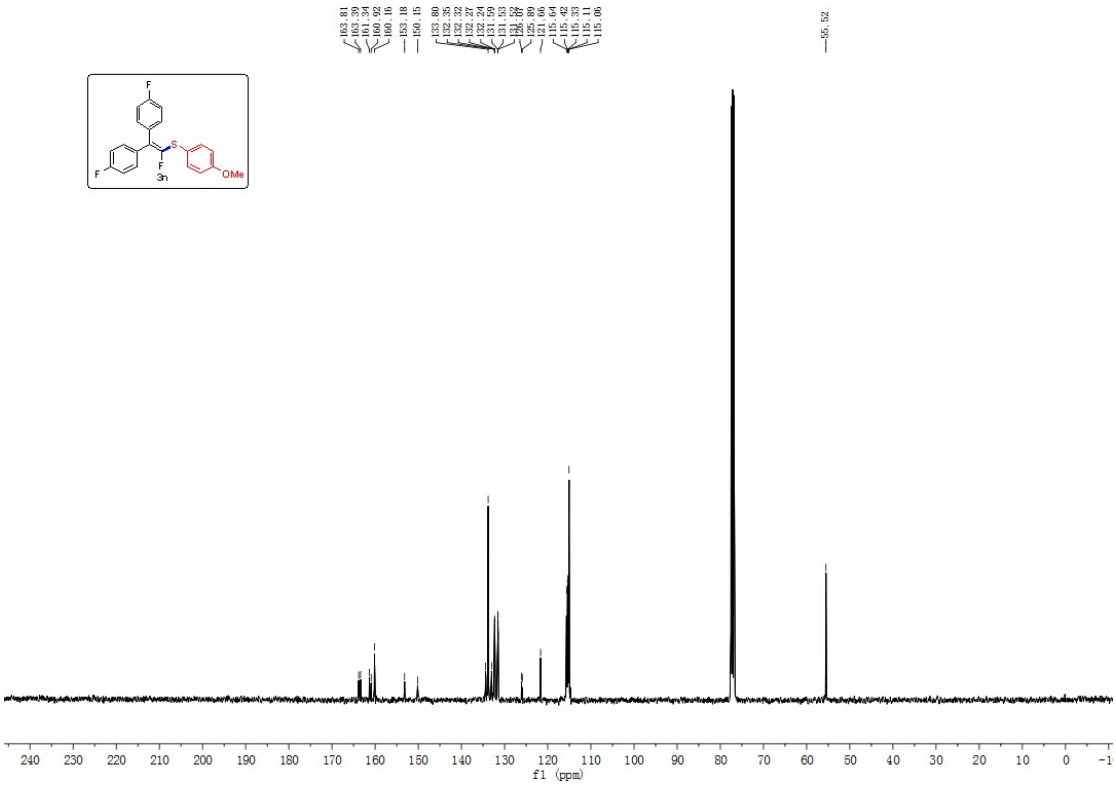
Cl
S
F
3m
Cl
OMe

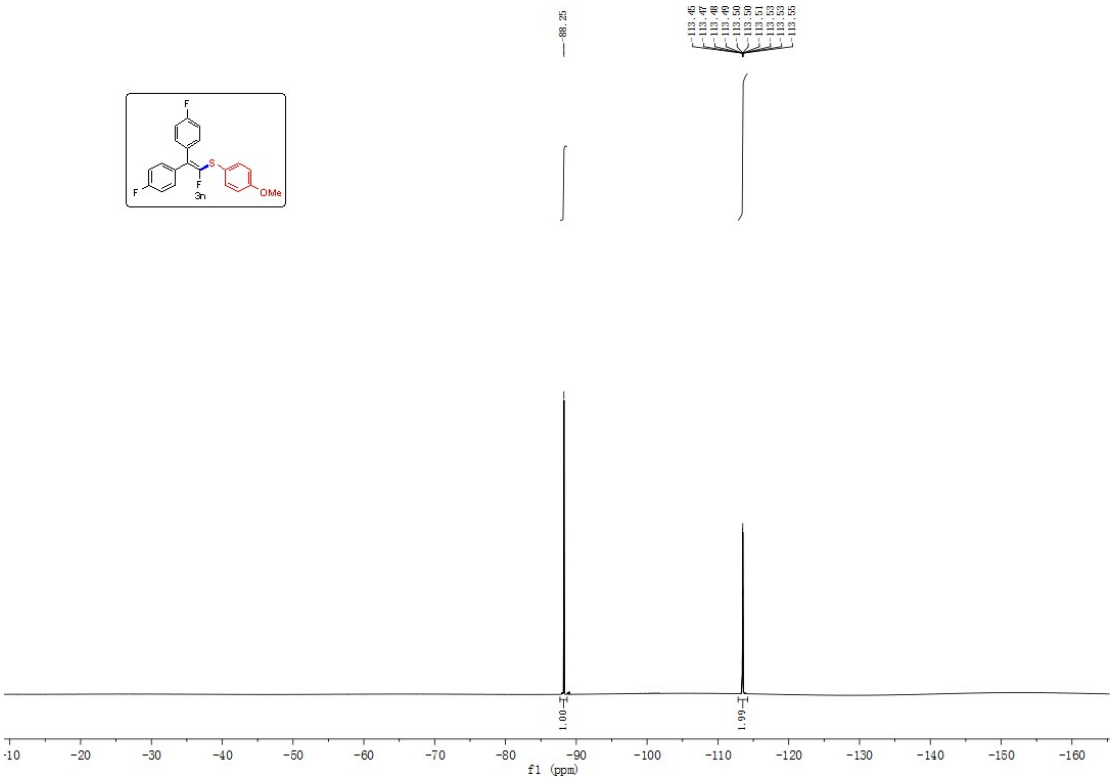

3.91
2.20
3.94
1.93
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

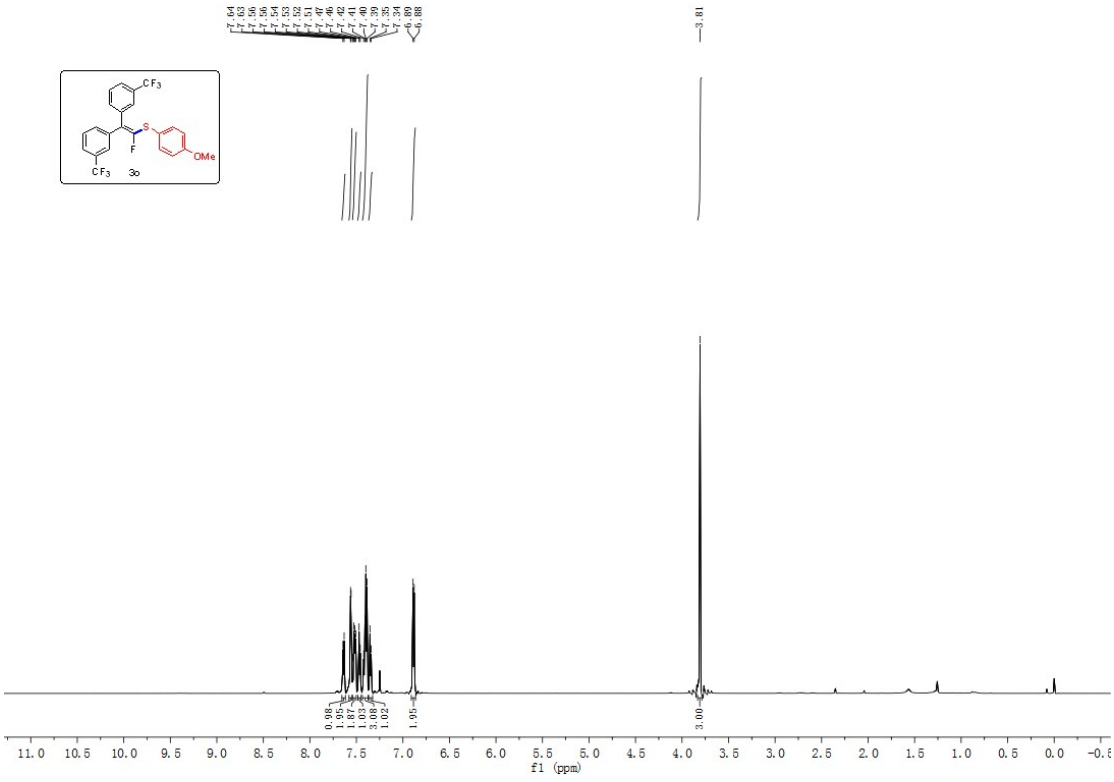

160.28
153.84
150.79
136.66
136.62
135.22
135.20
134.20
134.07
133.74
131.97
131.95
131.06
131.00
128.81
127.79
115.09
55.54
Cl
S
F
3m
Cl
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

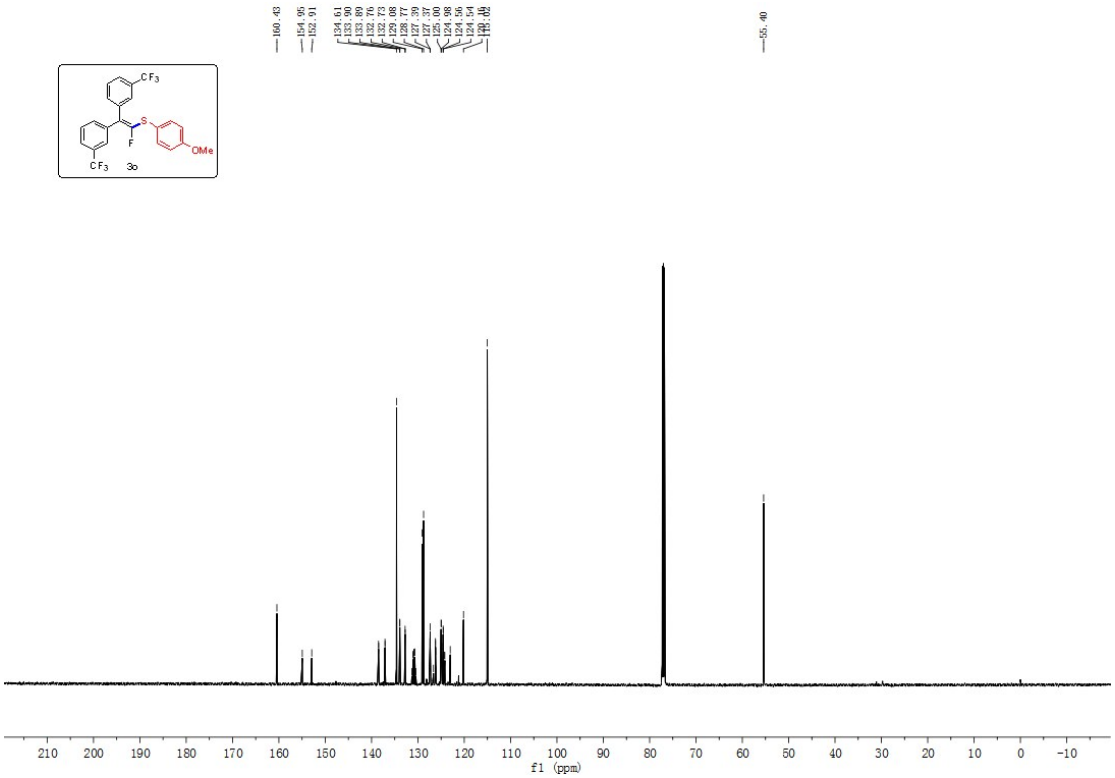

-86.84
Cl
S
F
3m
Cl
OMe
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

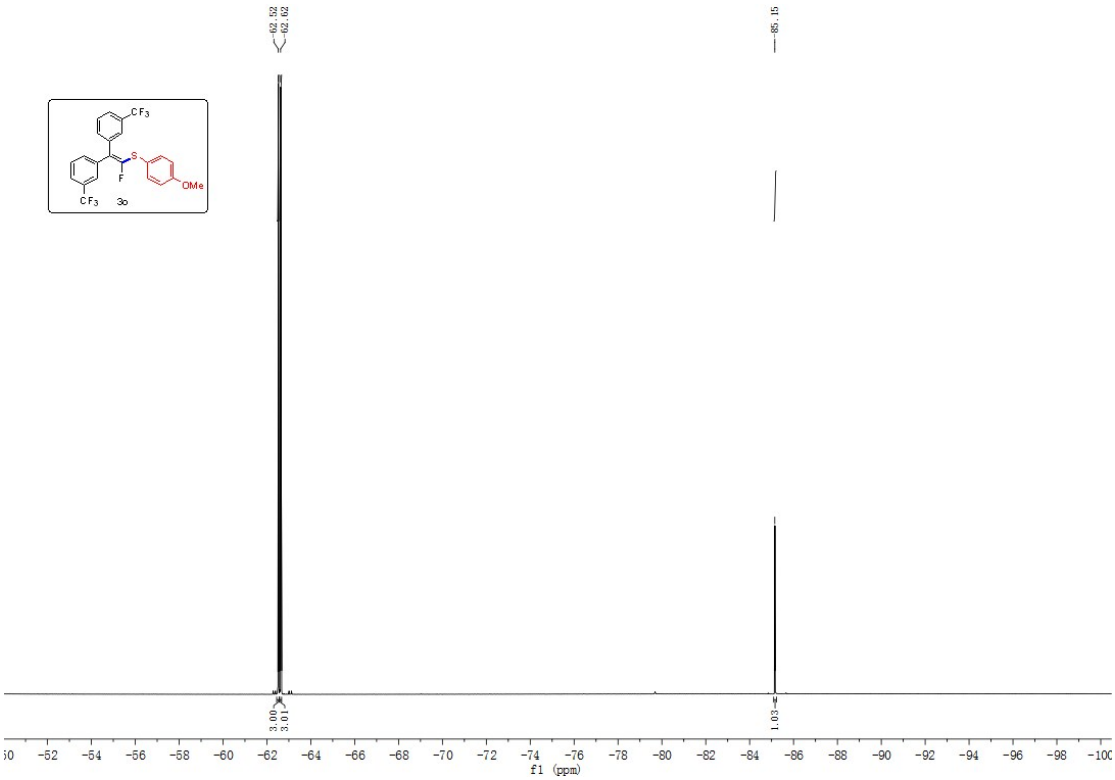

F
F
S
F
3n
OMe
7.44
7.43
7.43
7.42
7.41
7.40
7.31
7.29
7.28
7.27
7.26
7.19
7.14
7.12
7.11
7.10
7.05
7.05
7.03
7.01
7.01
6.95
6.94
6.93
6.92
6.92
6.91
3.86
1.93
3.97
1.85
1.88
1.91
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

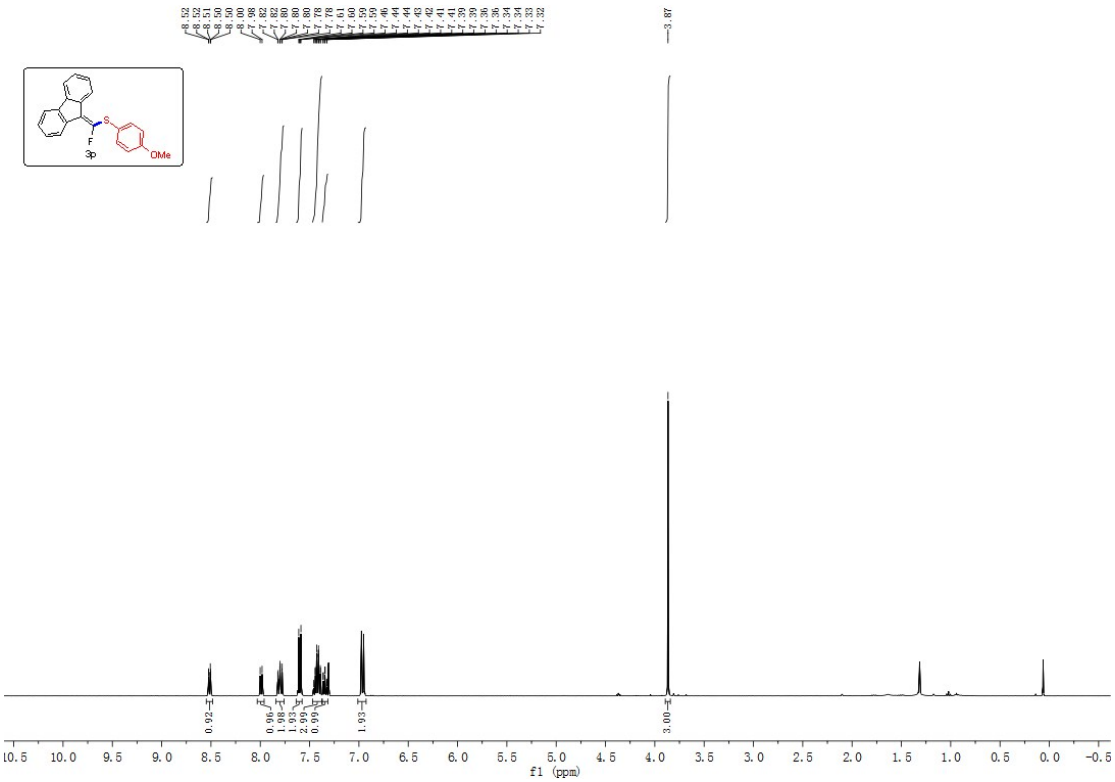

F
F
S
F
3n
OMe
163.81
163.39
161.92
160.92
160.16
153.18
150.15
133.80
132.35
132.32
132.27
132.24
131.59
131.53
125.89
121.66
115.64
115.42
115.33
115.11
115.06
55.52
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

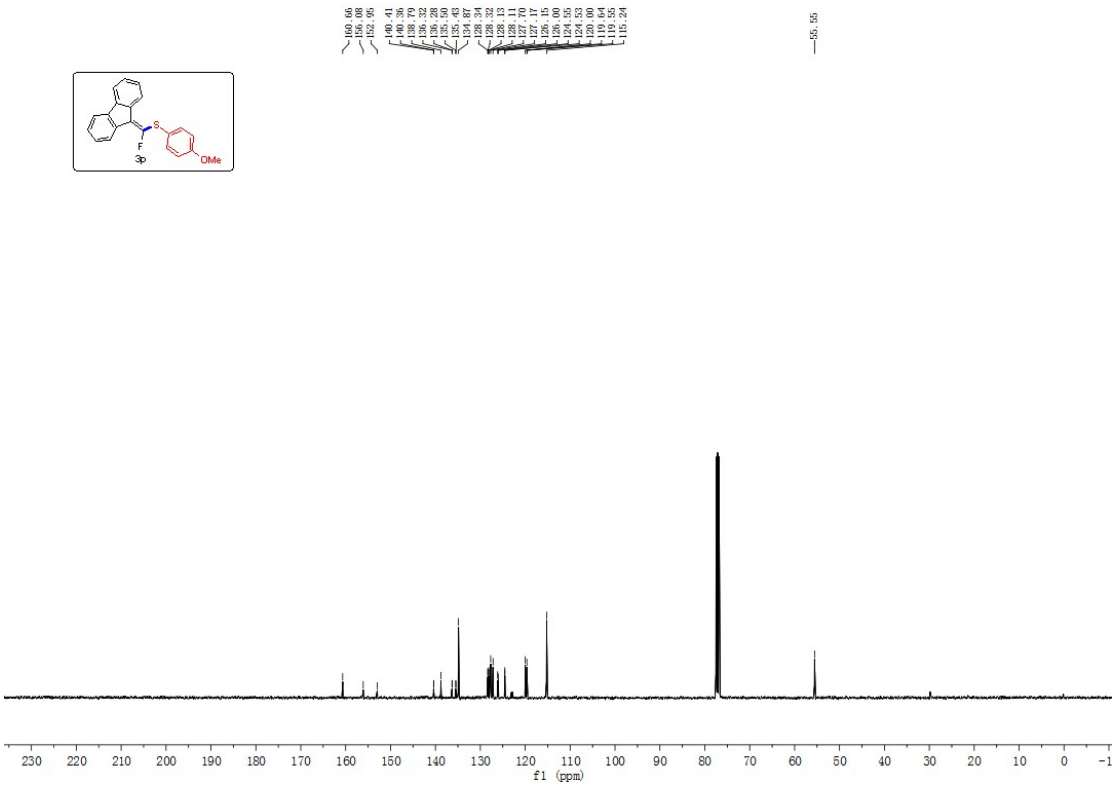

F
S
F
F
OMe
3n
-88.25
113.45
113.47
113.48
113.49
113.50
113.50
113.51
113.52
113.53
113.55
1.00
1.99
f1 (ppm)

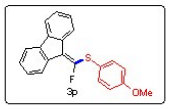

CF3
S
F
OMe
CF3
3o
7.64
7.63
7.56
7.56
7.54
7.53
7.52
7.51
7.47
7.46
7.42
7.41
7.40
7.39
7.35
7.34
7.09
6.88
3.81
0.98
1.95
1.97
1.03
3.08
1.02
1.95
3.00
f1 (ppm)


160.43
154.95
152.91
134.61
133.90
133.89
132.76
132.73
129.06
128.77
127.39
127.37
125.00
124.98
124.56
124.54
55.40
CF3
S
F
OMe
CF3
3o
f1 (ppm)

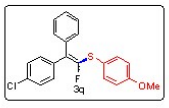

62.52
62.62
-85.15
CF3
S
F
OMe
CF3
3o
3.00
3.01
1.03
f1 (ppm)


8.52
8.52
8.51
8.50
8.50
8.08
8.08
7.82
7.80
7.80
7.80
7.78
7.78
7.61
7.60
7.59
7.59
7.46
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.39
7.36
7.34
7.34
7.33
7.32
3.87
0.92
0.96
1.00
1.93
2.99
0.99
1.93
3.00
10.5 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)

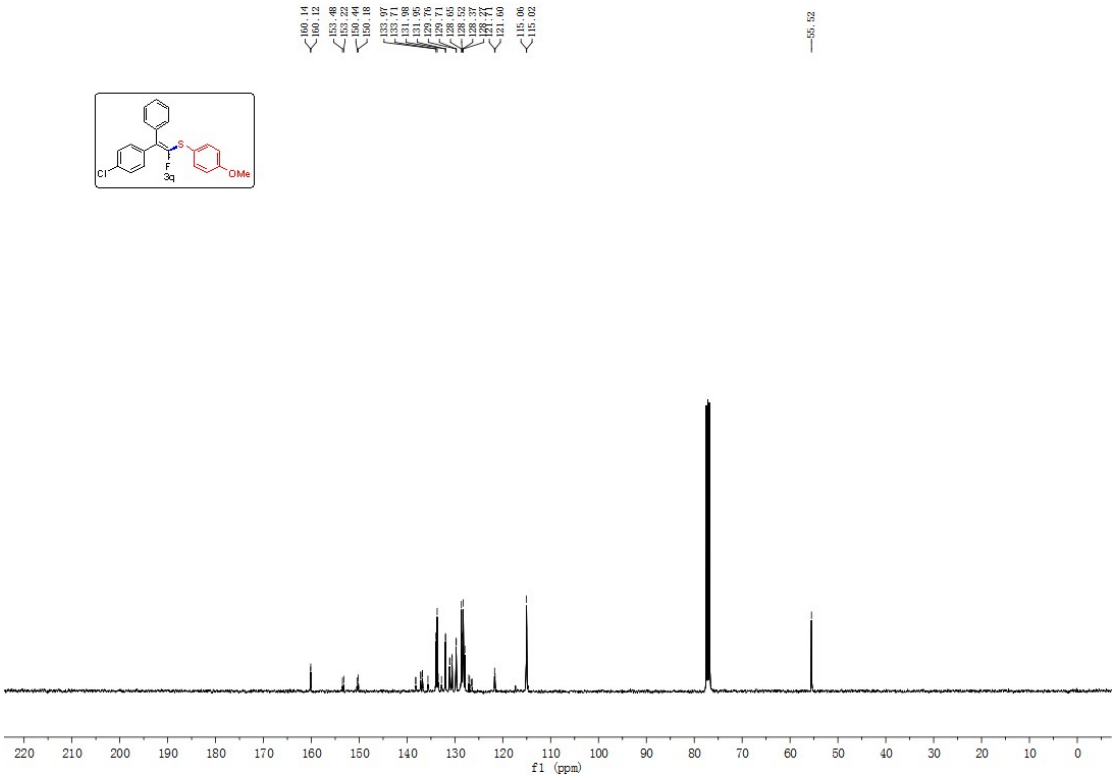

160.66
156.08
152.96
140.41
140.36
138.79
136.32
136.28
135.43
135.50
134.87
128.94
128.32
128.13
128.11
127.70
127.17
126.15
126.00
124.55
124.53
120.00
119.64
119.55
115.24
55.55
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

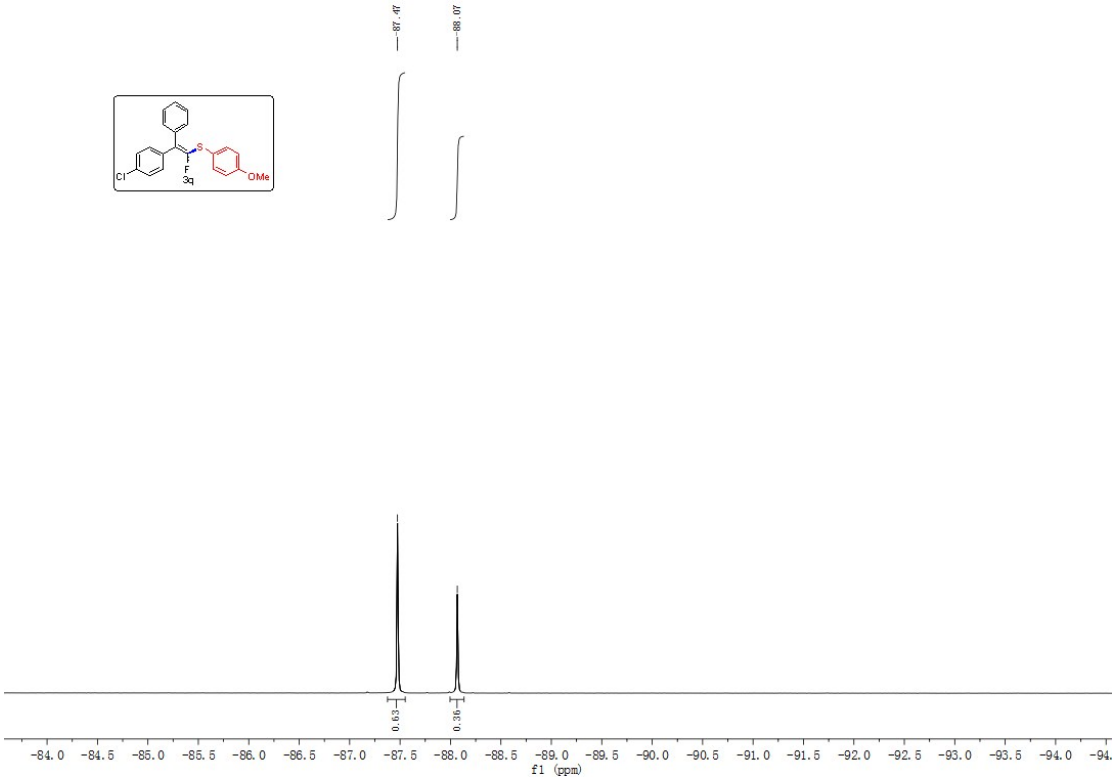

F
3p
OMe

-72.18
1.00
f1 (ppm)

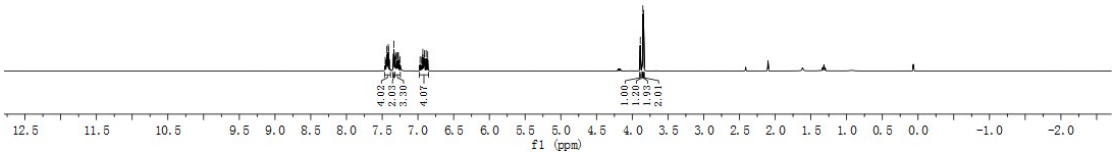

Cl
F
3q
OMe

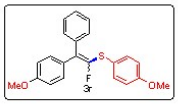
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.40
7.35
7.34
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
6.95
6.92
3.86
4.26
7.01
2.00
3.16
f1 (ppm)

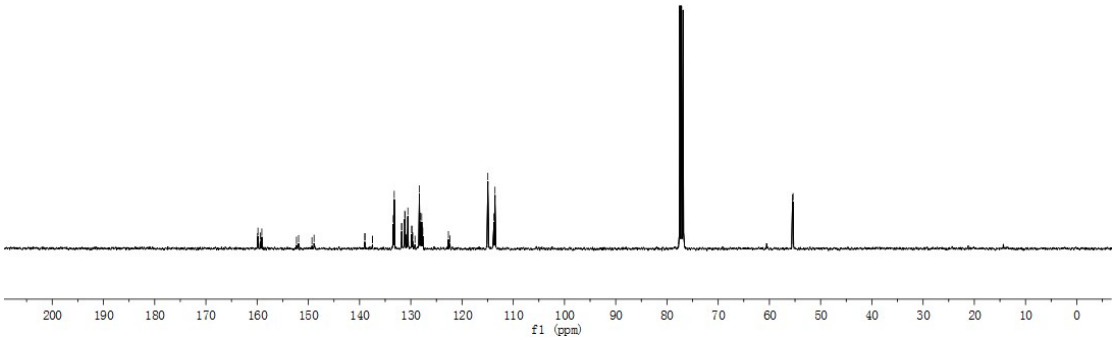

160.14
160.12
153.48
153.22
150.44
150.18
133.97
131.71
131.98
131.95
129.76
129.71
128.65
128.52
128.37
121.77
121.60
115.06
115.02
55.52
Cl
S
F
OMe
3q
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

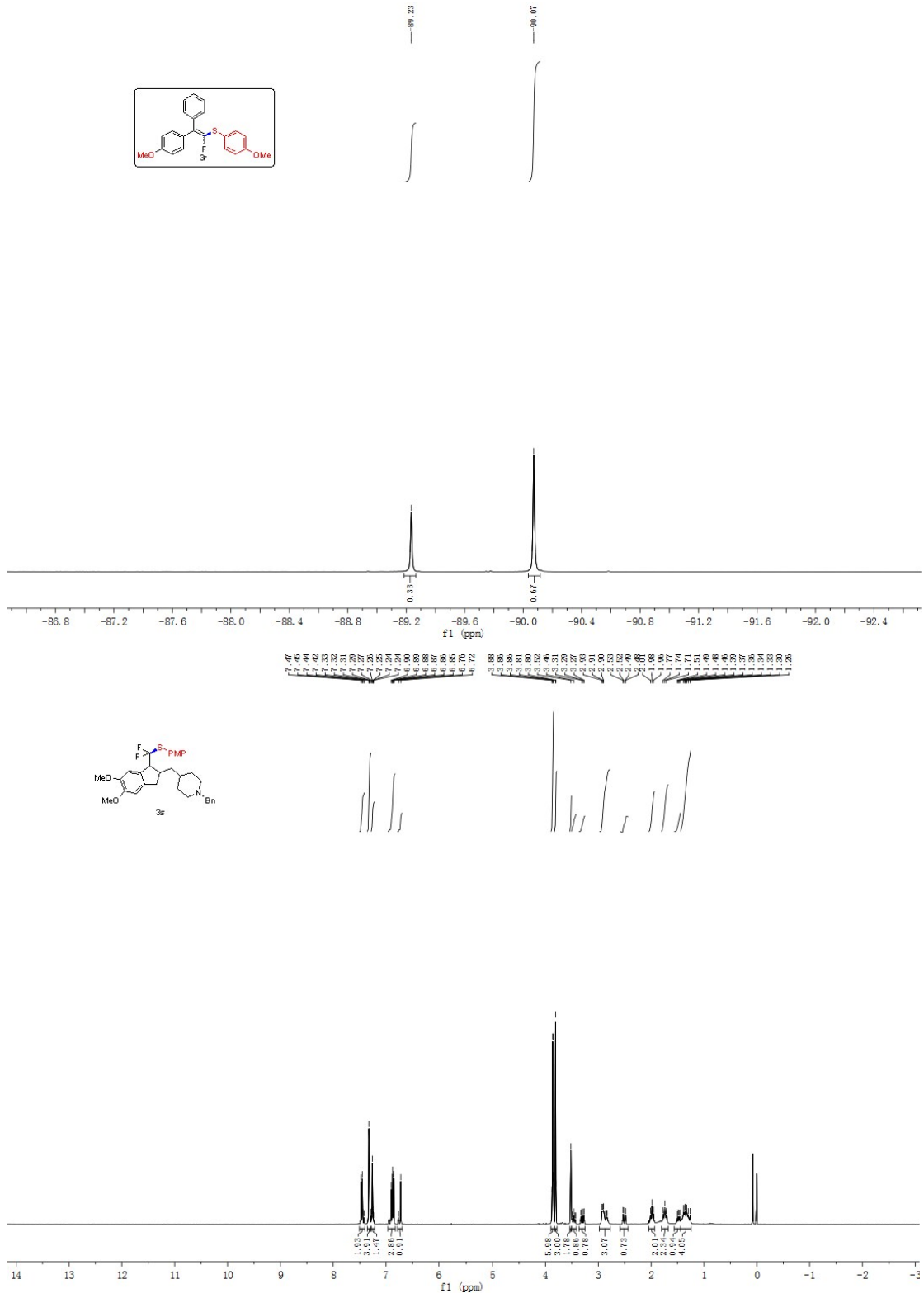

-87.47
-88.07
Cl
S
F
OMe
3q
0.63
0.36
-84.0 -84.5 -85.0 -85.5 -86.0 -86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0 -93.5 -94.0 -94.
f1 (ppm)

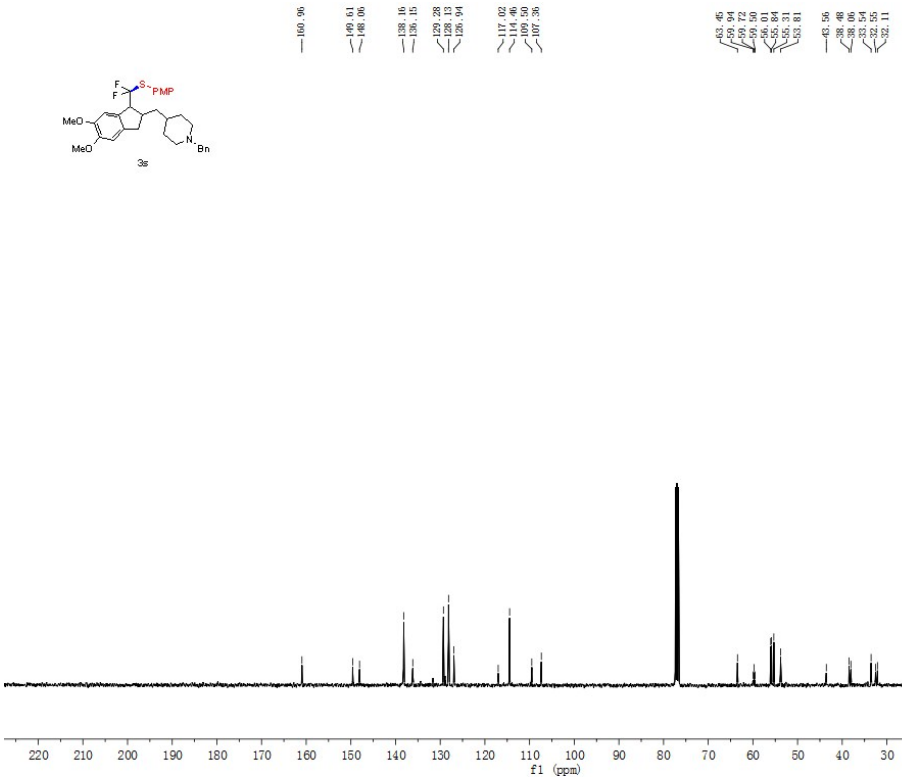

MeO
OMe

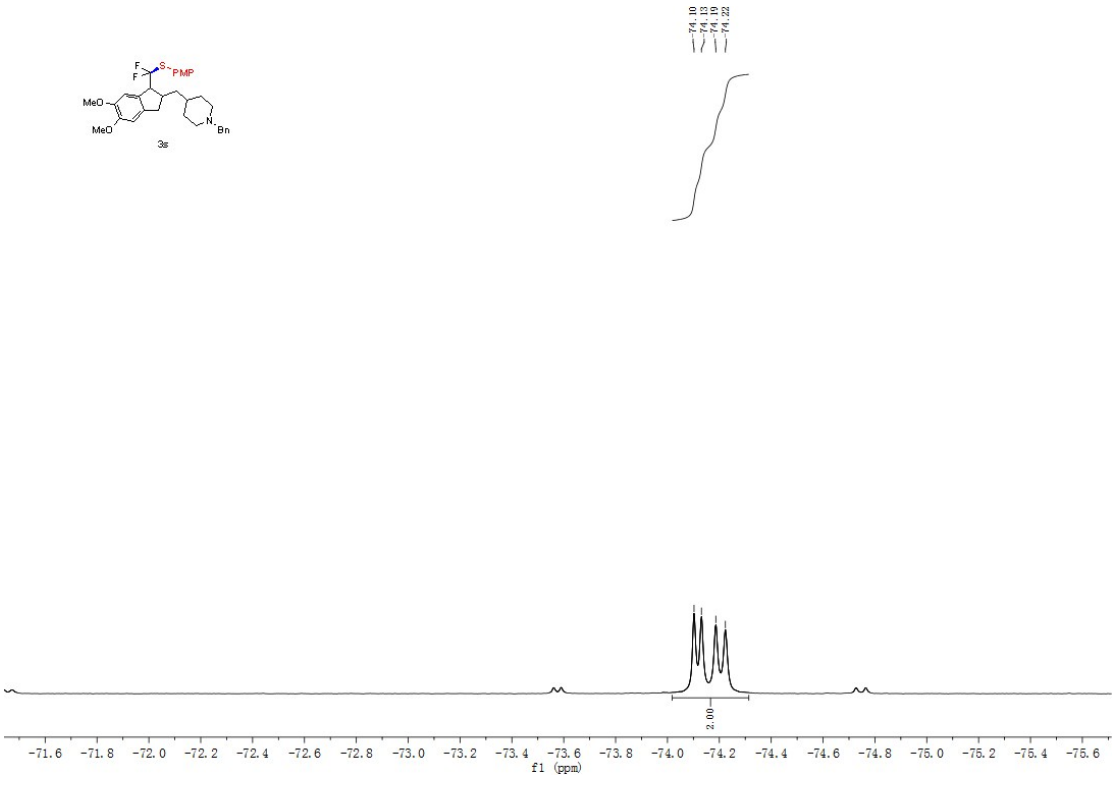

f1 (ppm)


MeO
OMe

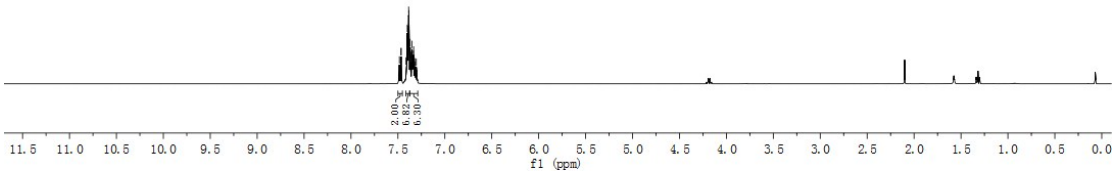

f1 (ppm)


-89.23
-90.07
MeO
OMe
3r
0.33
0.67
f1 (ppm)
PMP
MeO
MeO
N
Bn
3s
1.93
3.91
1.47
2.86
0.91
5.08
3.00
1.78
0.86
0.78
3.07
0.73
2.01
2.04
0.94
4.05
f1 (ppm)

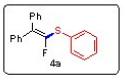

160.96
149.61
148.06
138.16
136.15
129.28
128.15
126.94
117.02
114.46
109.50
107.36
63.45
59.94
59.72
59.50
56.01
55.84
55.31
53.81
43.56
38.48
38.06
33.54
32.55
32.11
PMP
MeO
MeO
N
Bn
3s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

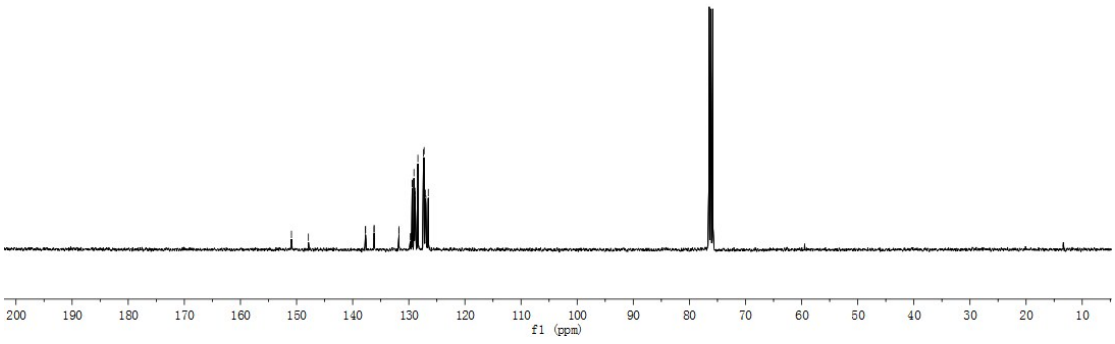

74.10
74.13
74.19
74.22
PMP
MeO
MeO
N
Bn
3s
2.00
-71.6 -71.8 -72.0 -72.2 -72.4 -72.6 -72.8 -73.0 -73.2 -73.4 -73.6 -73.8 -74.0 -74.2 -74.4 -74.6 -74.8 -75.0 -75.2 -75.4 -75.6
f1 (ppm)

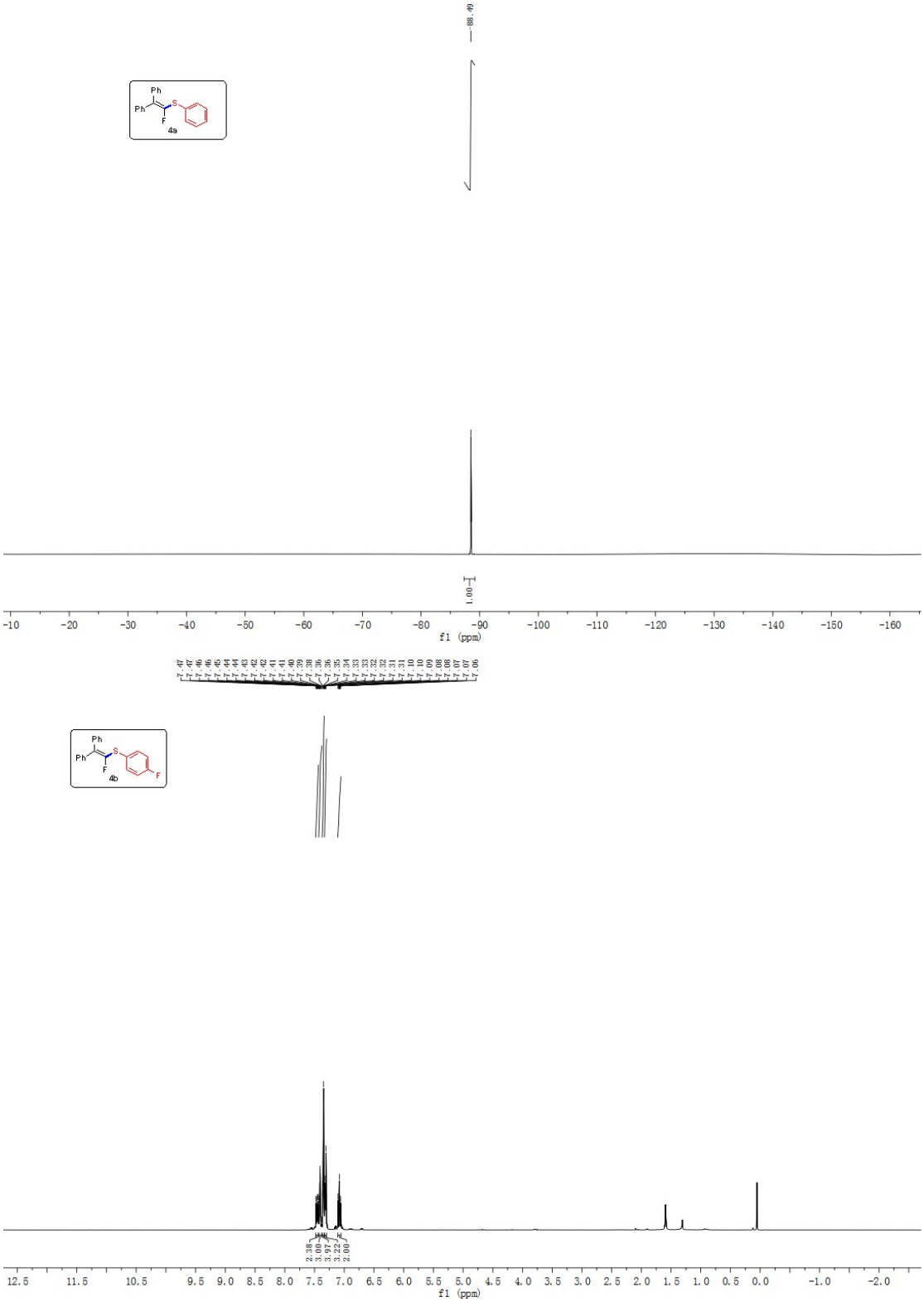

7.48
7.47
7.47
7.47
7.41
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
Ph
Ph
S
F
4a

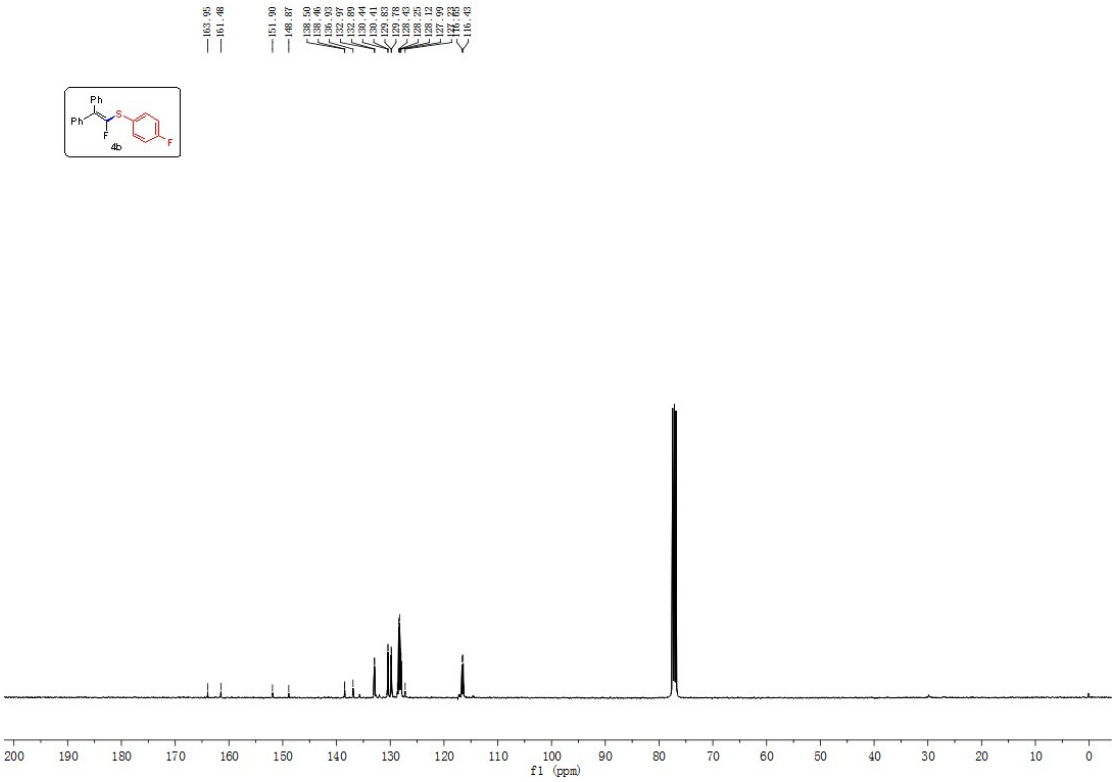

2.00
3.82
6.30
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

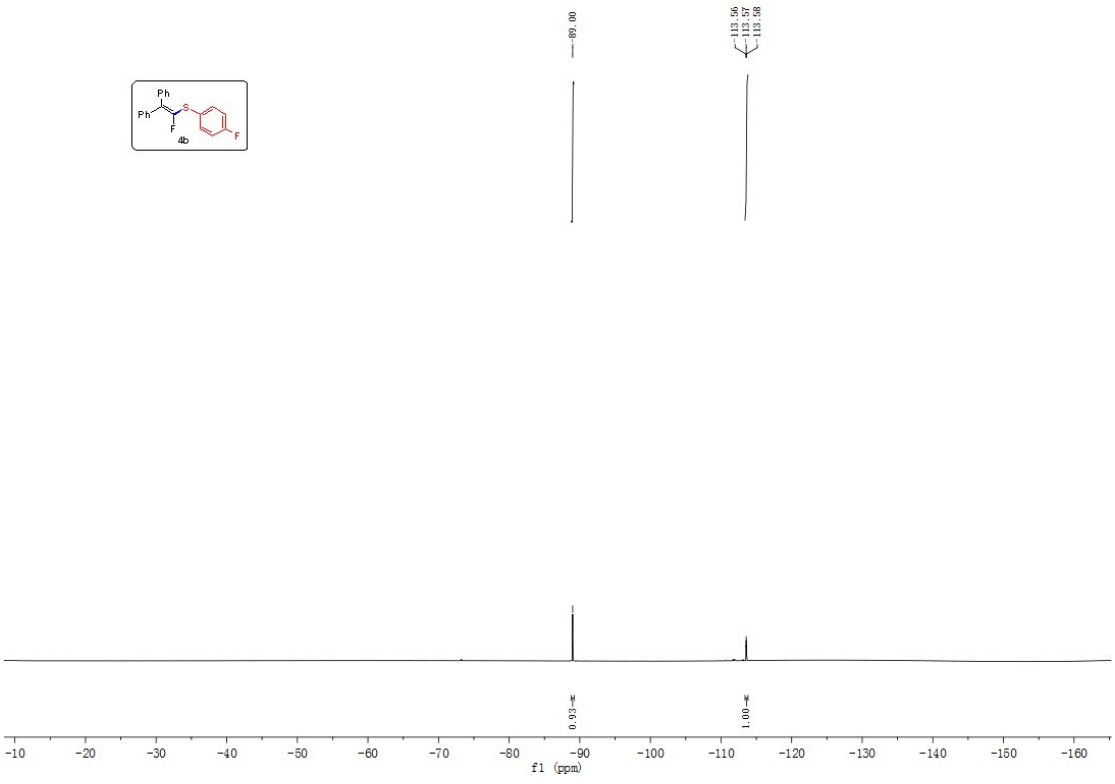

150.91
147.89
137.74
137.70
136.20
135.18
131.78
131.76
129.76
129.58
129.45
129.40
129.08
128.89
128.84
128.38
127.39
127.26
127.04
126.96
126.53

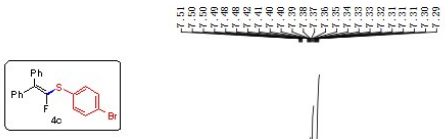

Ph
Ph
S
F
4a

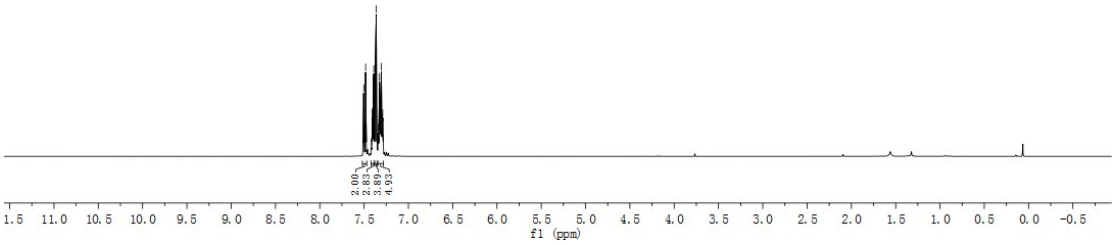

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

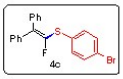

Ph
Ph
S
F
4a
-88.40
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)
7.47 7.47 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.40 7.39 7.38 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.10 7.10 7.09 7.08 7.08 7.07 7.07 7.06
Ph
Ph
S
F
F
4b
2.38
3.00
3.17
3.23
2.00
12.5 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 -2.0
f1 (ppm)

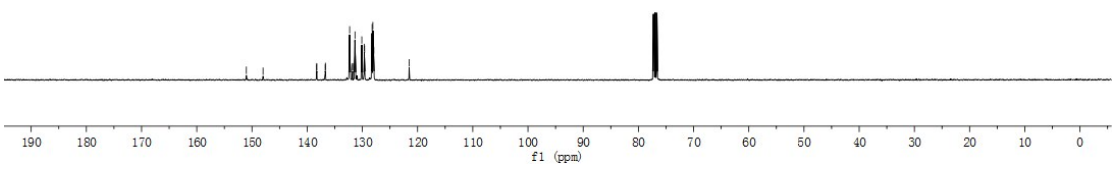

163.95
161.48
151.90
148.87
138.50
138.46
136.53
132.97
132.89
130.44
130.41
129.83
129.78
129.45
128.25
128.12
127.99
117.33
116.43
Ph
Ph
S
F
F
4b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

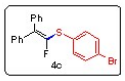

89.00
113.56
113.57
113.58
Ph
Ph
S
F
F
4b
0.93
1.00
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


Ph
Ph
S
F
Br
4c


2.00
3.83
3.89
4.93
f1 (ppm)


Ph
Ph
S
F
Br
4c

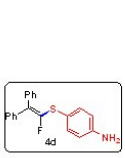

f1 (ppm)

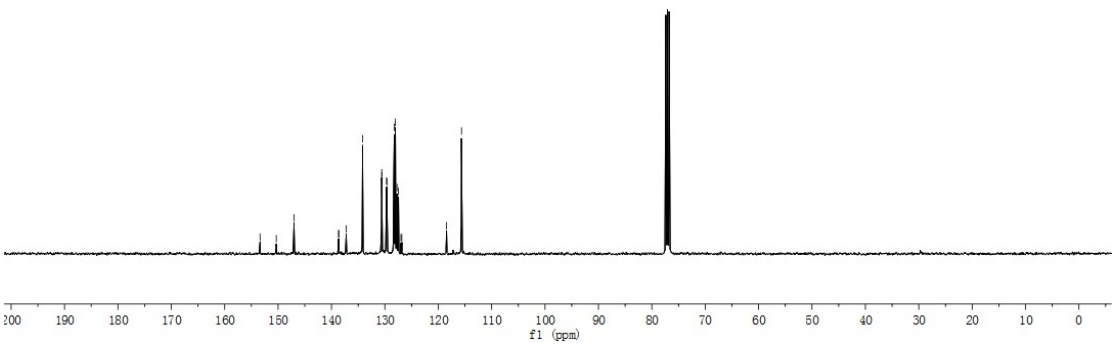

Ph
Ph
S
F
Br
4c

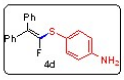
-88.98
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

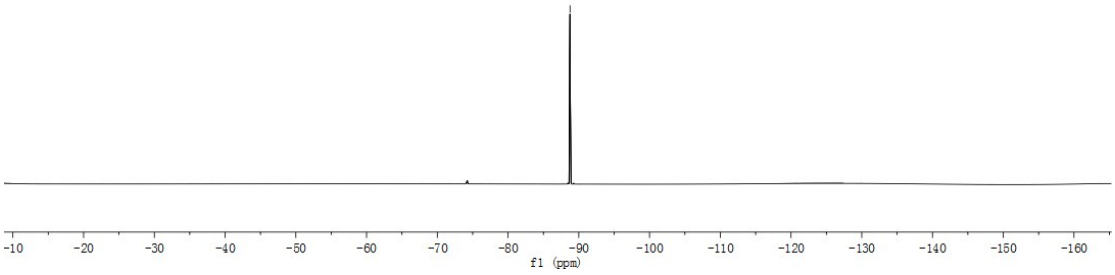

Ph
Ph
S
F
NH2
4d

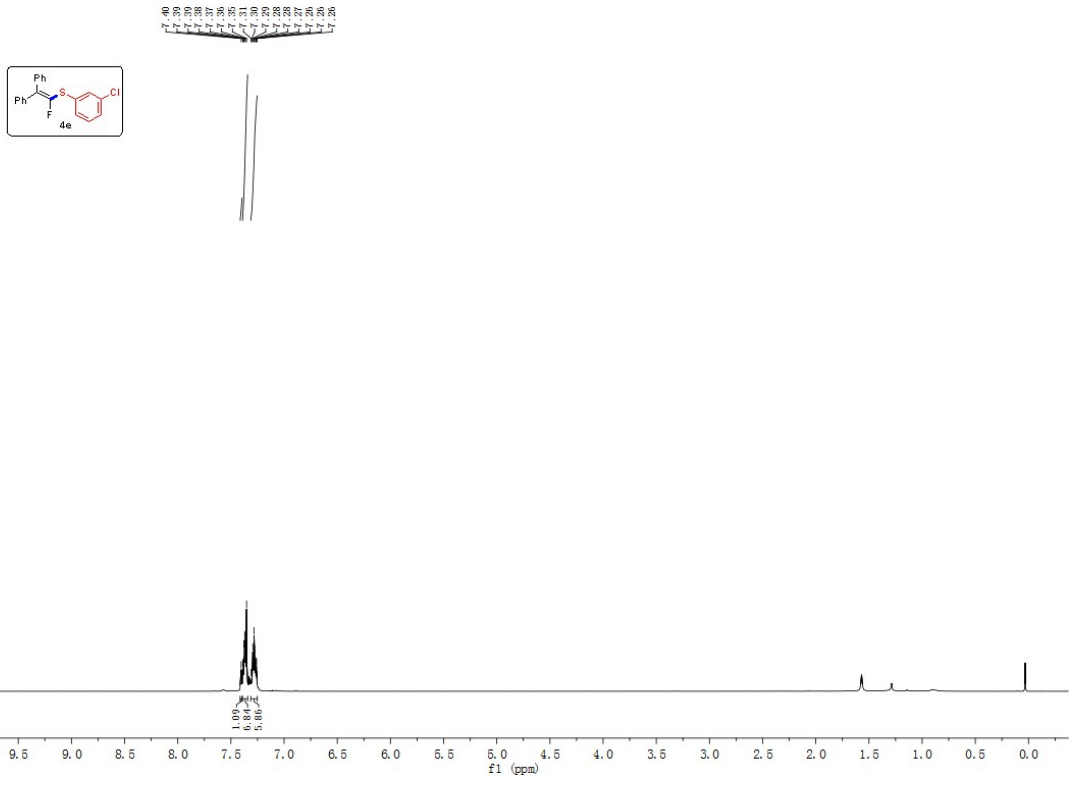
7.46
7.44
7.42
7.39
7.36
7.36
7.34
7.32
7.31
7.30
7.29
7.27
6.71
6.69
3.83
2.99
9.28
2.00
1.73
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

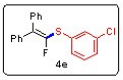

Ph
Ph
S
F
NH2
4d


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


Ph
Ph
S
F
NH2
4d


-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

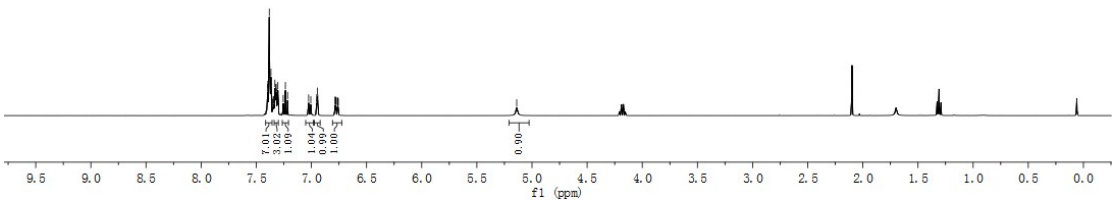

Ph
Ph
S
Cl
F
4e
f1 (ppm)
Ph
Ph
S
Cl
F
4e
f1 (ppm)

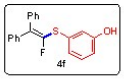

Ph
Ph
S
F
Cl
4e

-89.01
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

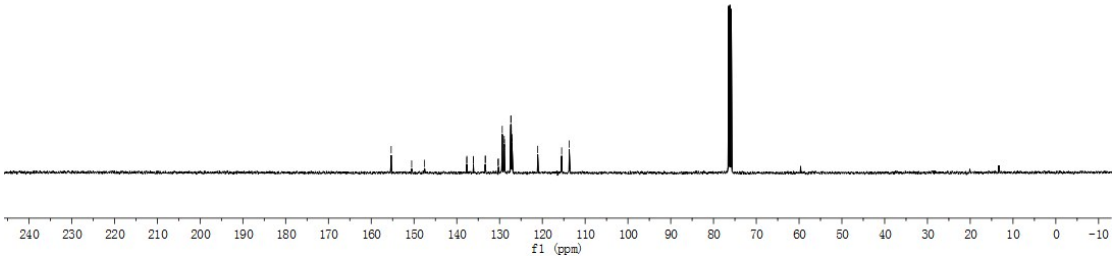

7.40
7.40
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.26
7.24
7.22
7.03
7.01
6.95
6.94
6.79
6.78
6.78
6.76
6.76
6.76
6.76
5.14

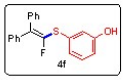
Ph
Ph
S
F
OH
4f


7.01
3.02
1.09
1.04
0.99
1.00
0.90
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
f1 (ppm)

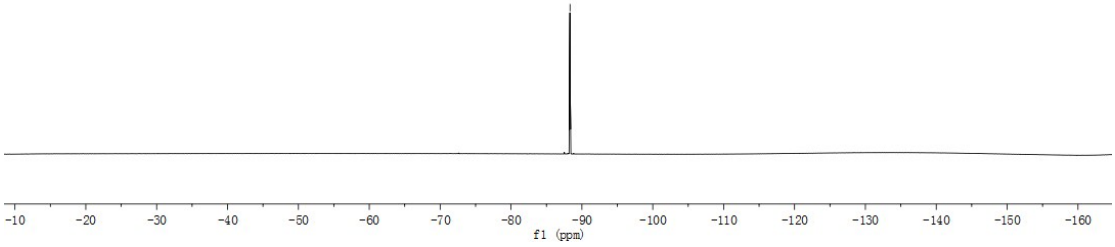

Ph
Ph
S
F
OH
4f

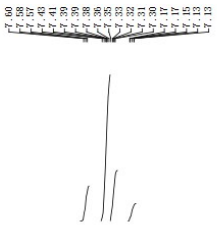

155.24
149.55
147.53
133.35
133.33
129.38
128.91
128.86
127.39
127.28
127.09
121.68
121.68
115.49
113.72

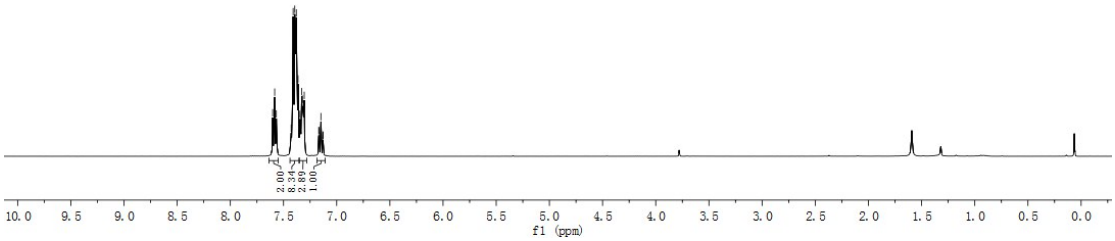

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Ph
S
F
OH
4f

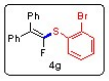
-88.33


-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

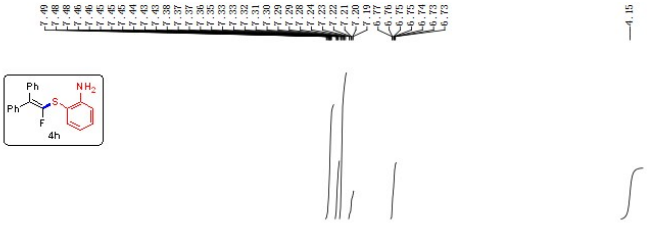

7.60
7.58
7.57
7.43
7.41
7.39
7.38
7.36
7.35
7.33
7.32
7.31
7.30
7.17
7.15
7.13
7.13
Ph
Ph
S
F
Br
4g


2.00
8.34
2.89
1.00
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
f1 (ppm)

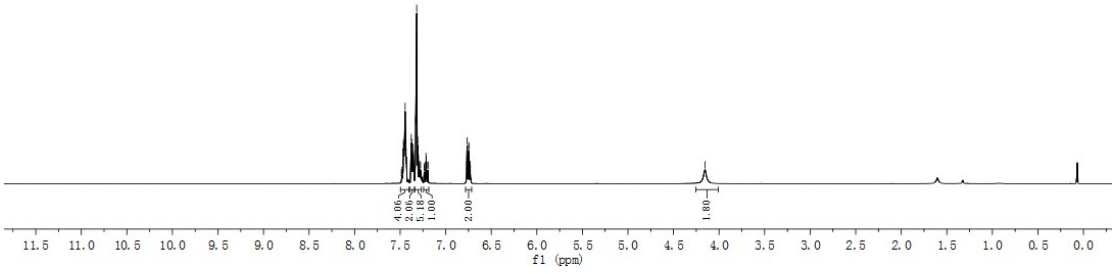

150.12
147.11
136.91
133.42
130.09
130.06
129.91
129.86
129.50
128.43
128.31
Ph
Ph
S
F
Br
4g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

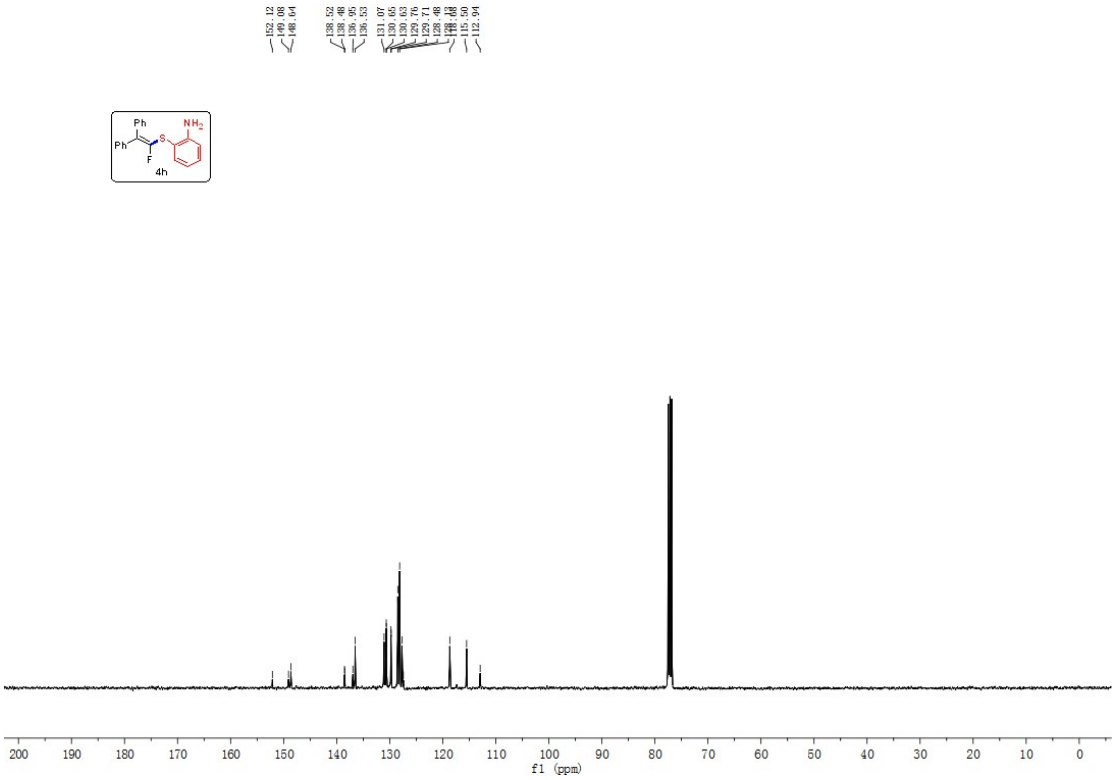

Ph
Br
Ph
S
F
4g

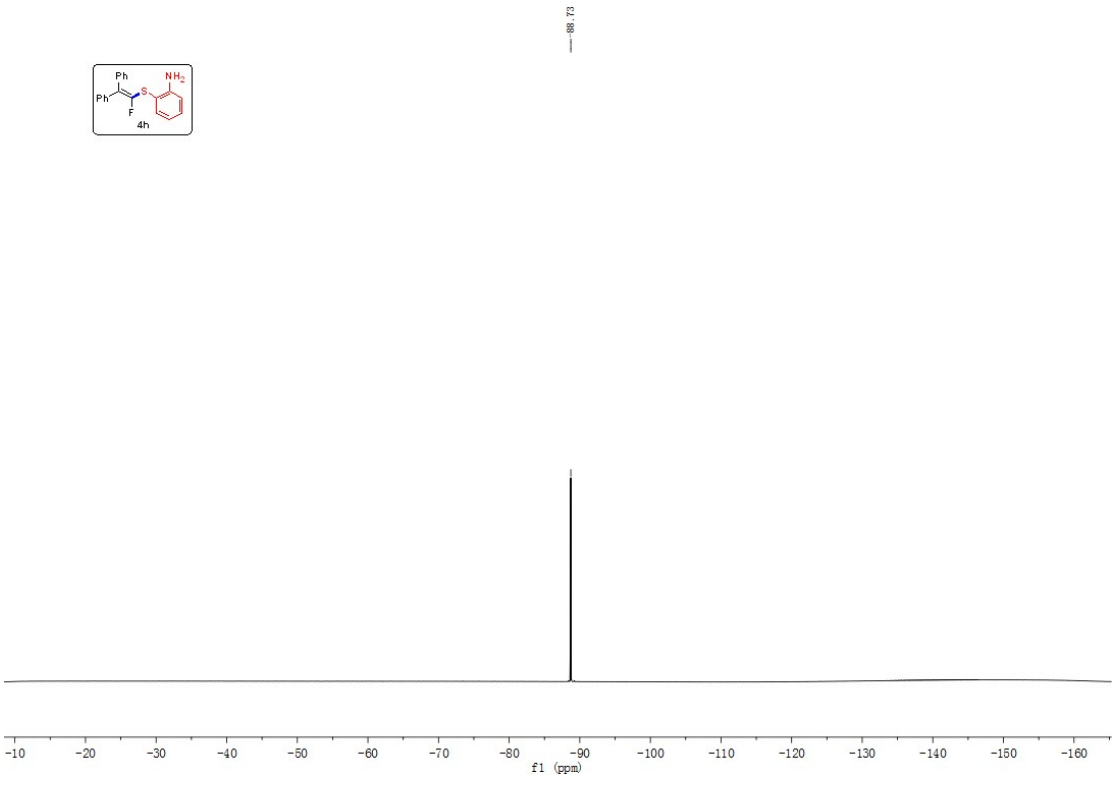
-89.99
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

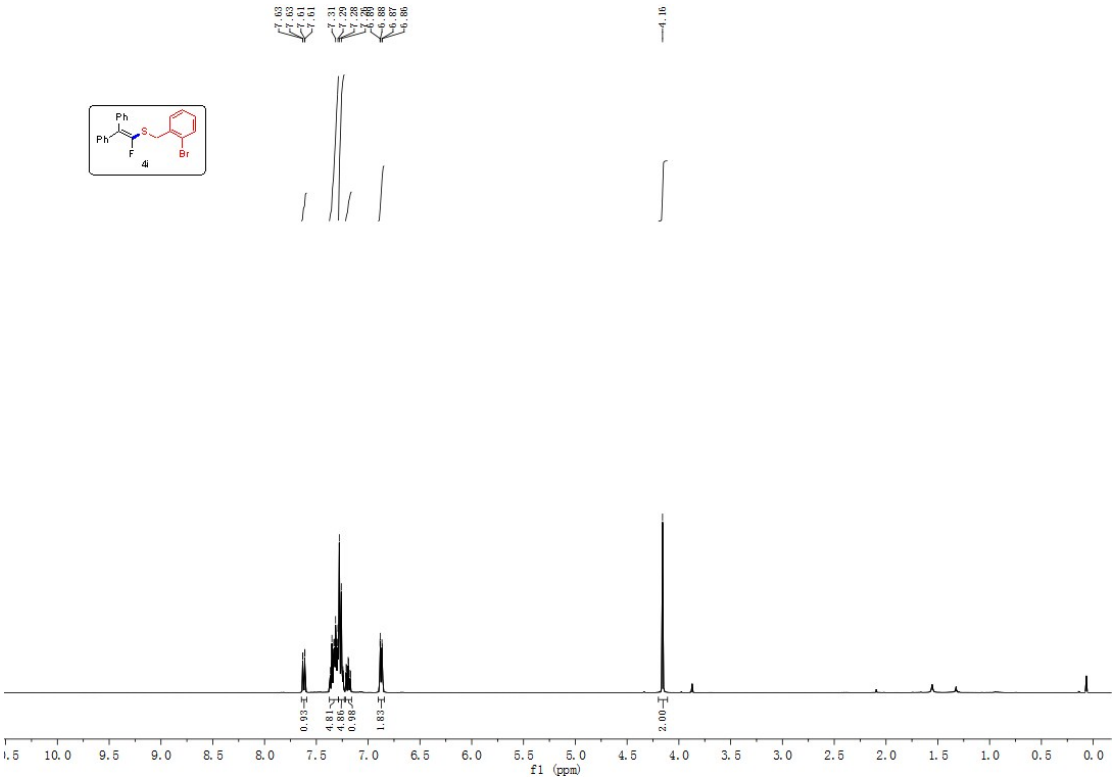

4.15

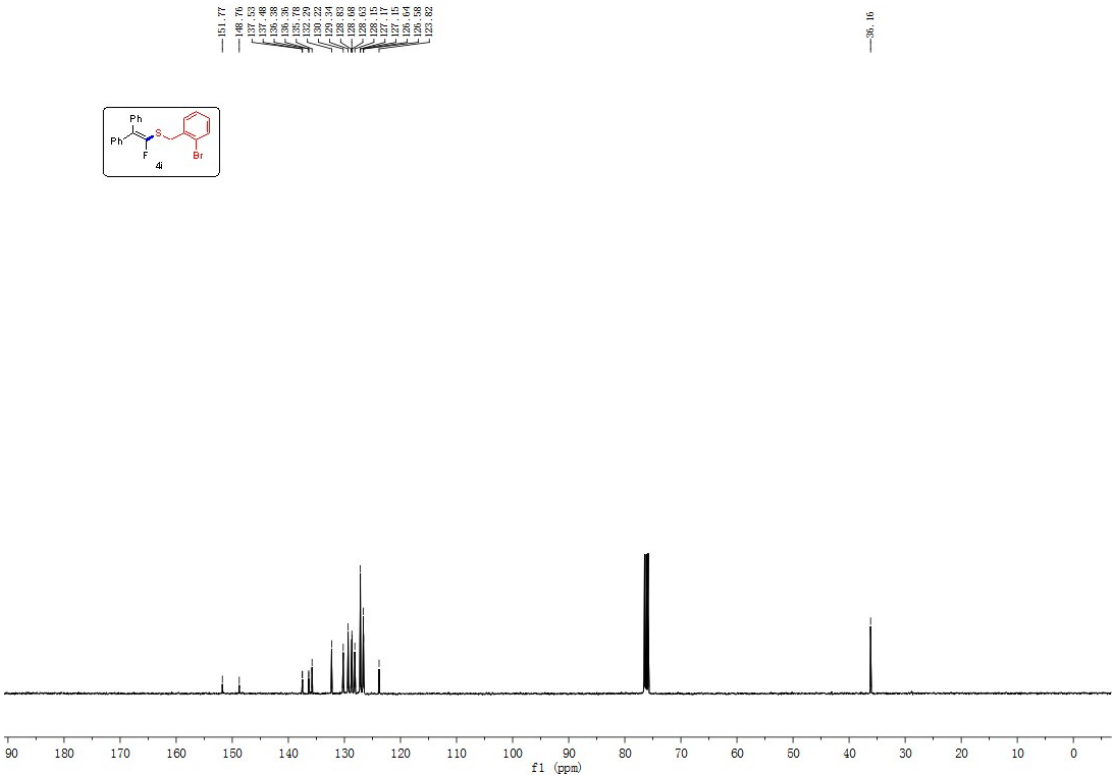
Ph
NH2
Ph
S
F
4h

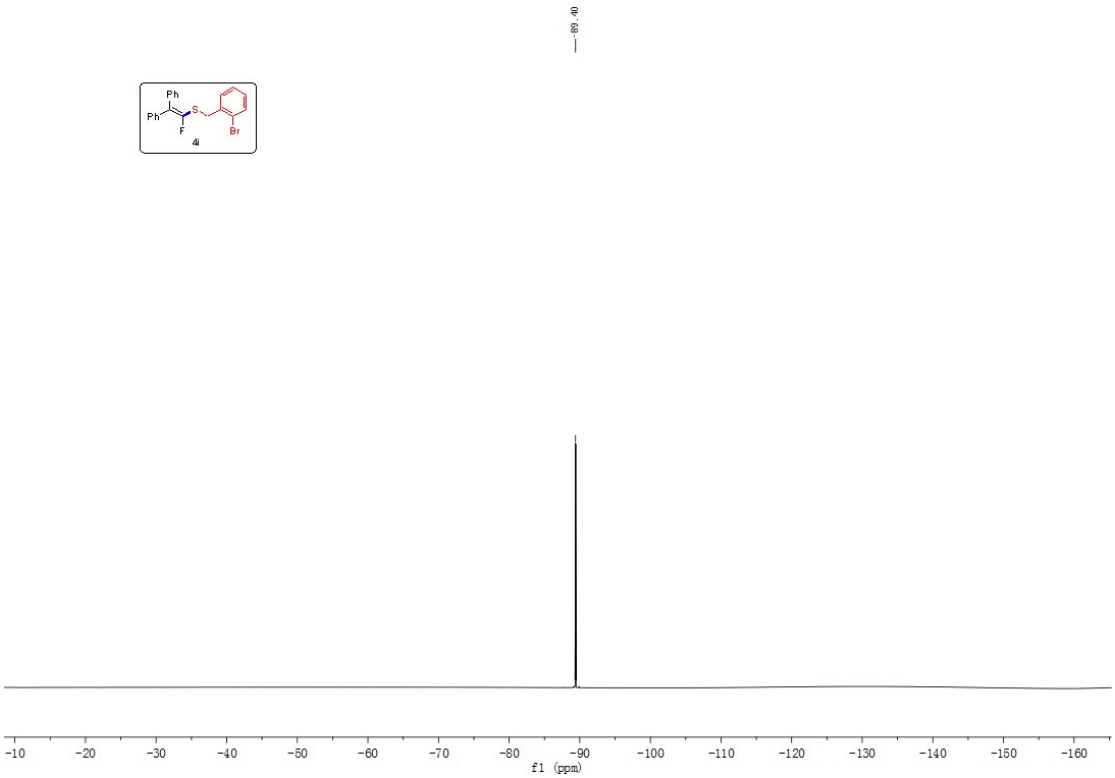

4.05
2.10
1.15
1.00
2.00
1.80
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

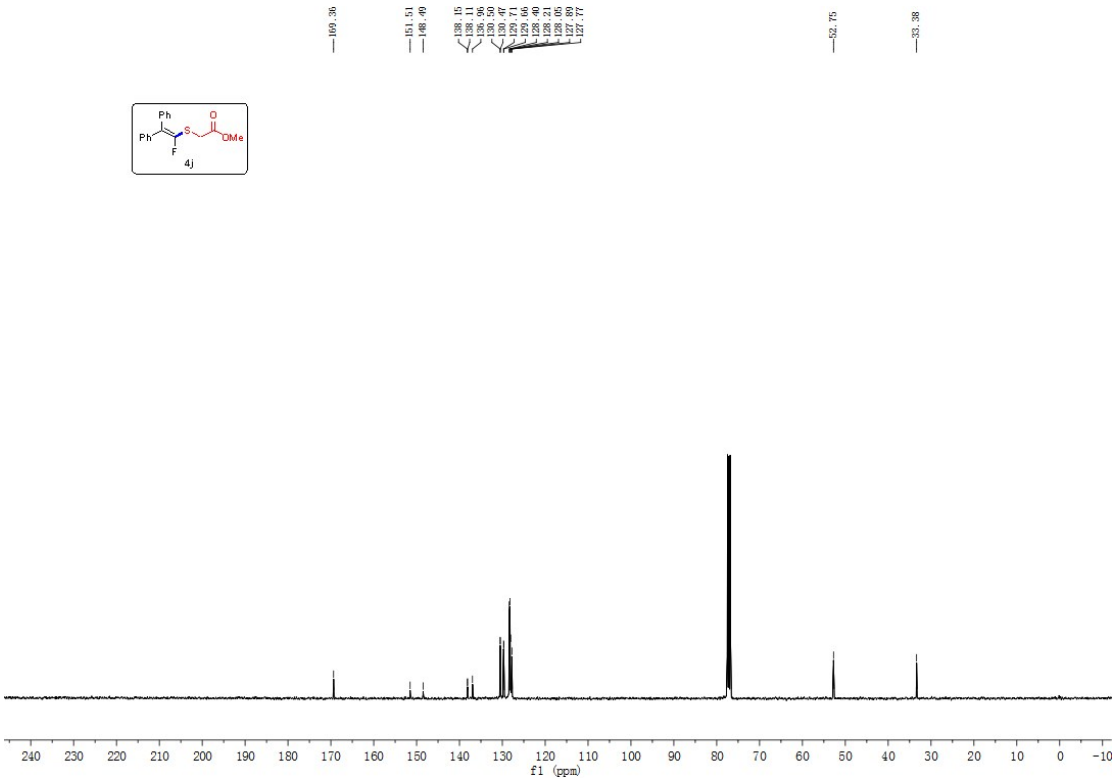

152.12
149.08
148.64
138.52
138.48
136.65
136.53
131.07
130.65
130.03
129.76
129.71
128.48
115.59
112.94
Ph
Ph
S
F
NH2
4h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

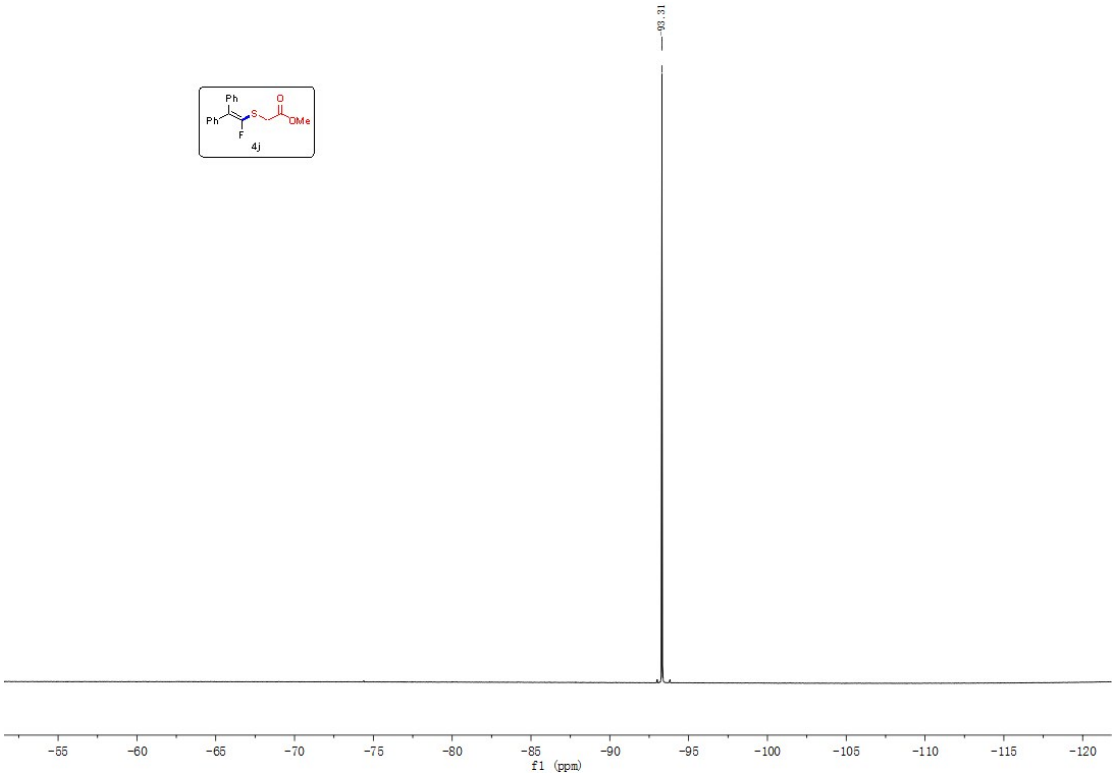

-88.73
Ph
Ph
S
F
NH2
4h
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

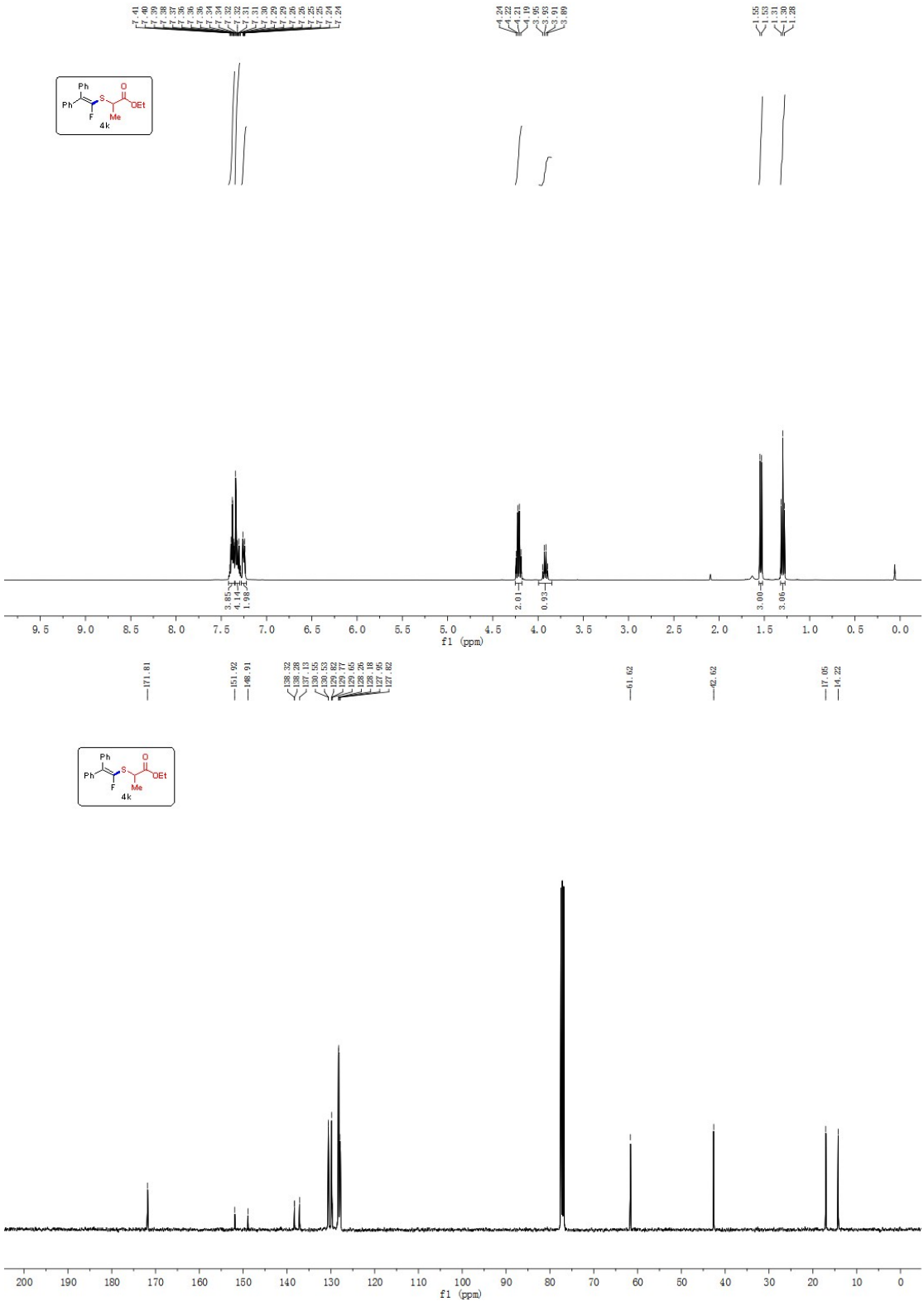

7.63
7.63
7.61
7.61
7.31
7.29
7.28
7.28
6.88
6.87
6.86
4.16
Ph
Ph
S
F
Br
4i
0.93
4.81
4.86
0.98
1.83
2.00
f1 (ppm)

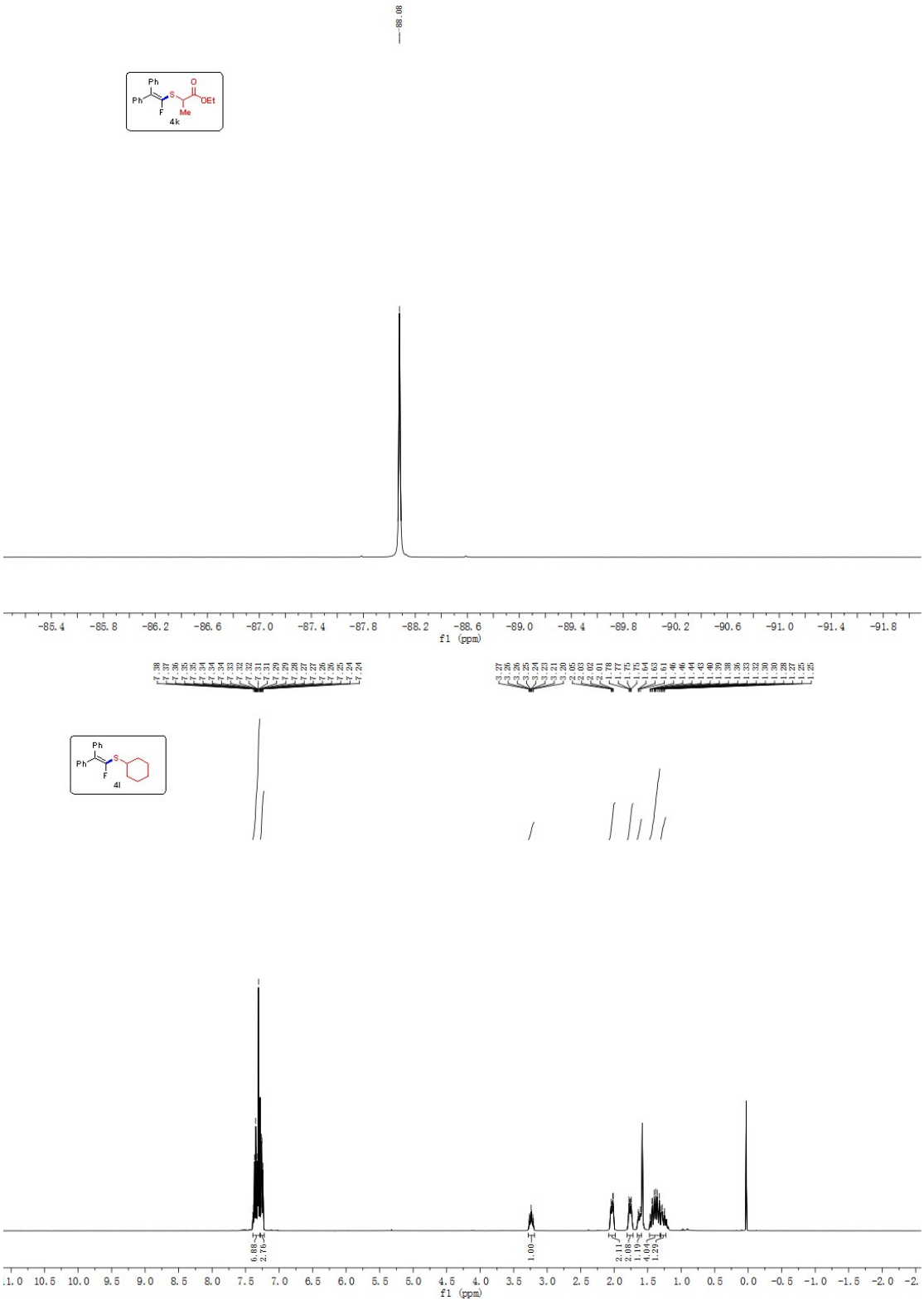

151.77
148.76
137.53
137.48
136.38
136.36
135.78
132.29
130.22
129.34
128.83
128.66
128.63
128.15
127.17
127.15
126.64
126.58
123.82
36.16
Ph
Ph
S
F
Br
4i
f1 (ppm)

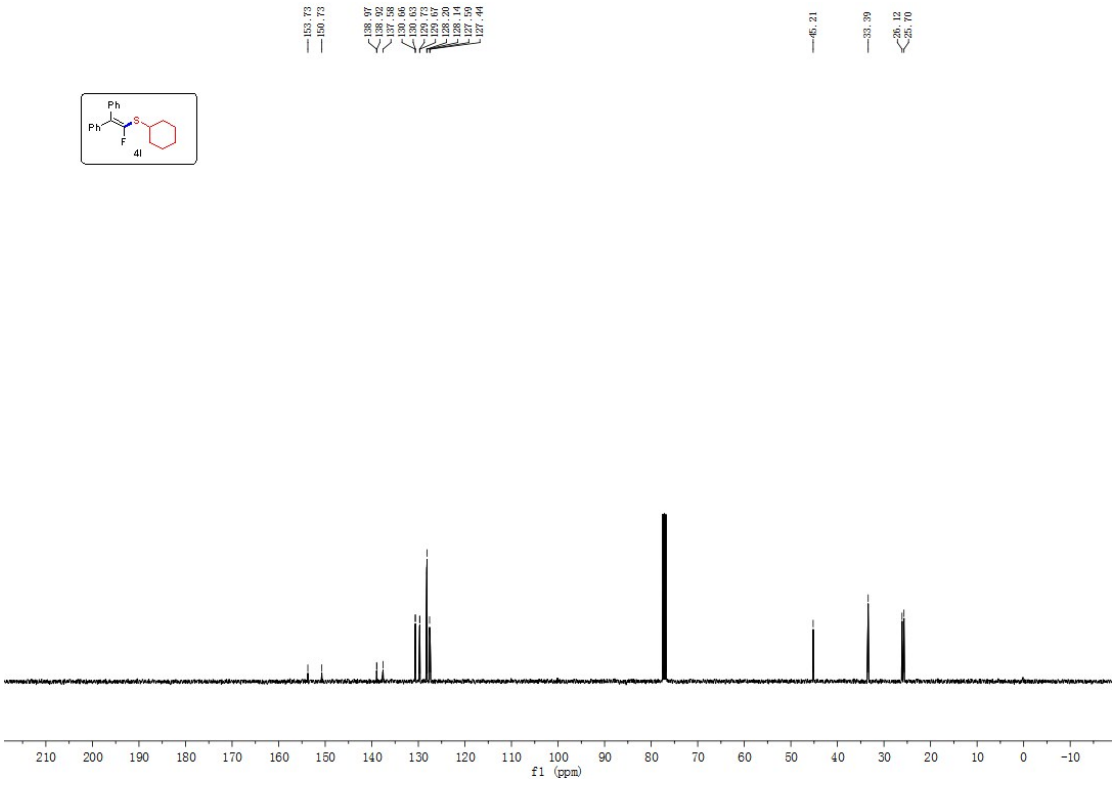

-89.40
4i
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)
3.78
3.58
4j
3.04
7.04
3.01
2.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0
f1 (ppm)

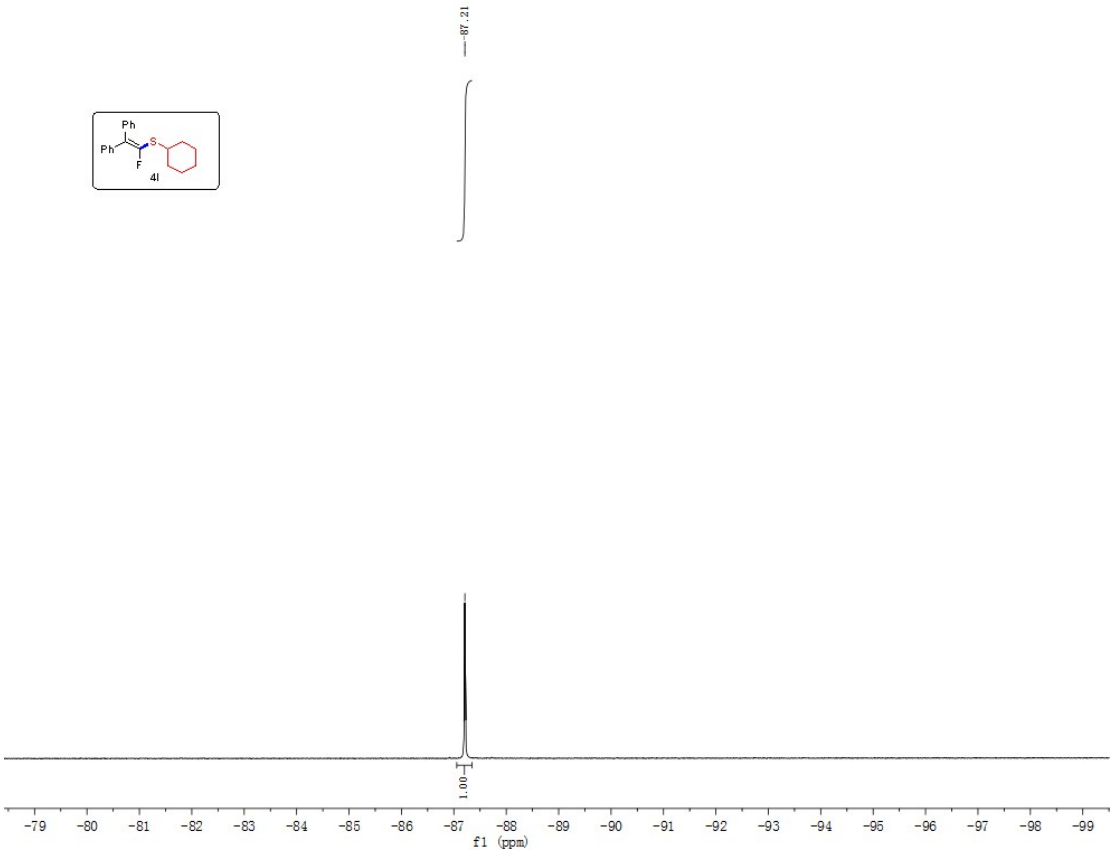

169.36
151.51
148.49
138.15
138.11
135.96
135.59
130.47
129.71
129.66
128.40
128.21
128.05
127.89
127.77
52.75
33.38
Ph
Ph
S
F
O
OMe
4j
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

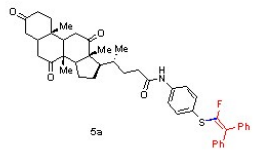

-93.31
Ph
Ph
S
F
O
OMe
4j
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)


7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.26 7.25 7.24 7.24
4.24 4.22 4.21 4.19 3.95 3.93 3.91 3.89
1.55 1.53 1.31 1.30 1.28
Ph
Ph
S
O
OEt
F
Me
4k
3.85
4.14
1.98
2.01
0.93
3.00
3.06
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
f1 (ppm)
171.81
151.92
148.91
138.32
138.28
137.13
130.55
130.53
129.82
129.77
129.65
128.26
128.18
127.95
127.82
61.62
42.62
17.05
14.22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

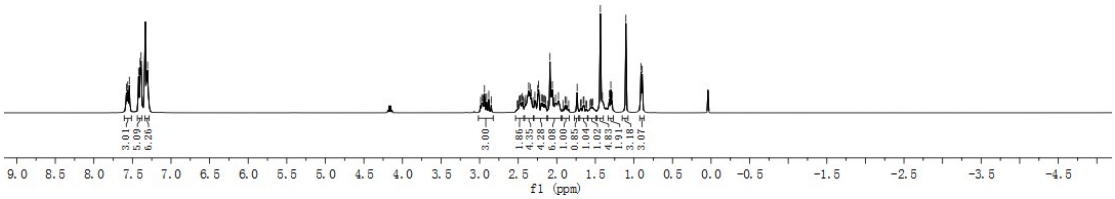

-88.08
Ph
Ph
S
F
O
OEt
Me
4k
-85.4 -85.8 -86.2 -86.6 -87.0 -87.4 -87.8 -88.2 -88.6 -89.0 -89.4 -89.8 -90.2 -90.6 -91.0 -91.4 -91.8
f1 (ppm)
Ph
Ph
S
F
4l
6.88
2.76
1.00
2.11
2.08
2.19
4.04
1.29
f1 (ppm)

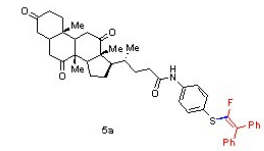

153.73
150.73
138.97
138.92
137.58
130.66
130.63
129.73
129.07
128.20
128.14
127.59
127.44
45.21
33.39
26.12
25.70
Ph
Ph
S
F
4l
f1 (ppm)


87.21
Ph
Ph
S
F
4l
1.00
f1 (ppm)

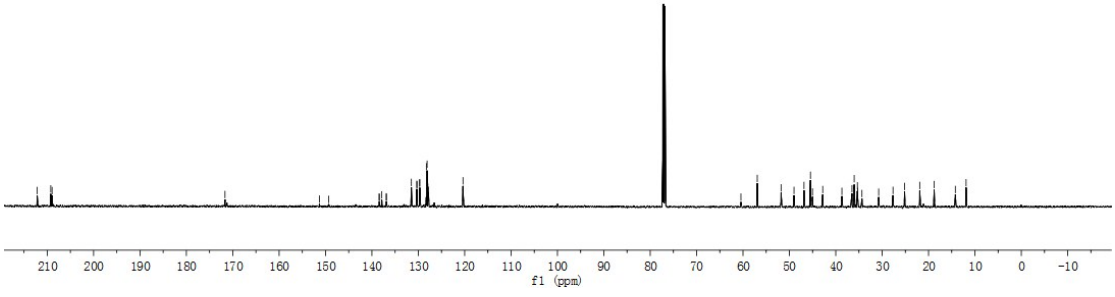


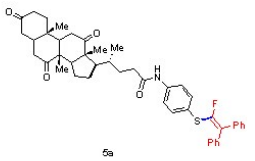
5a





5a

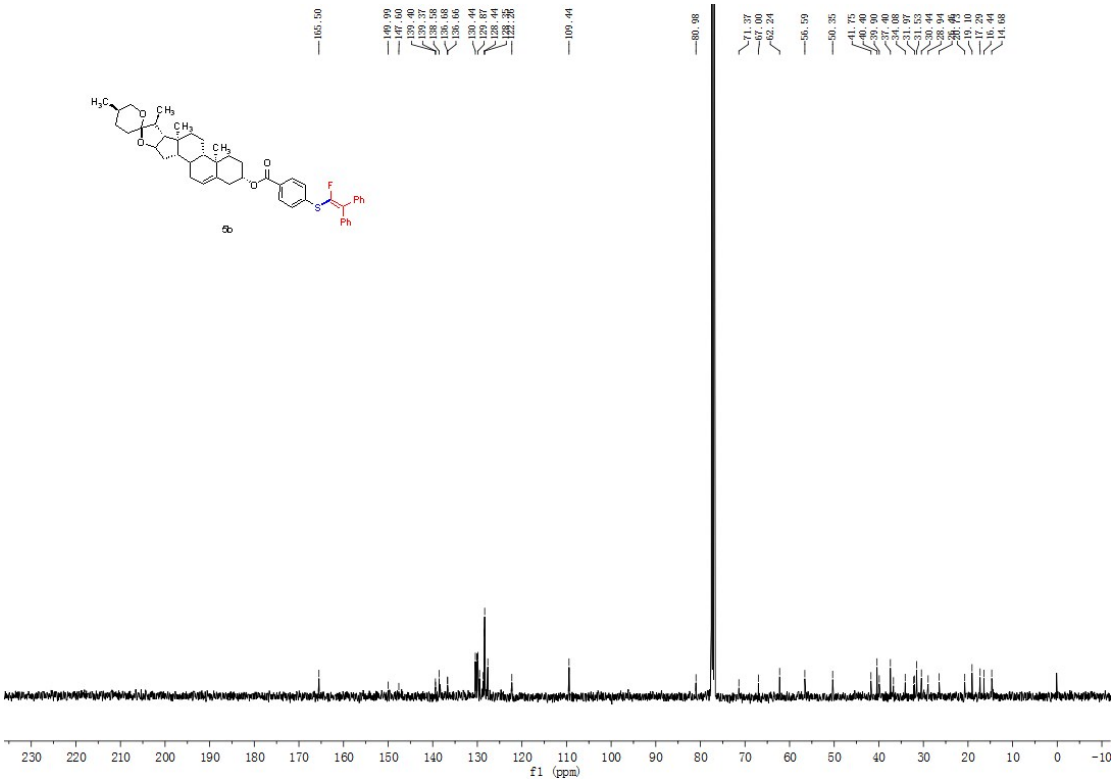


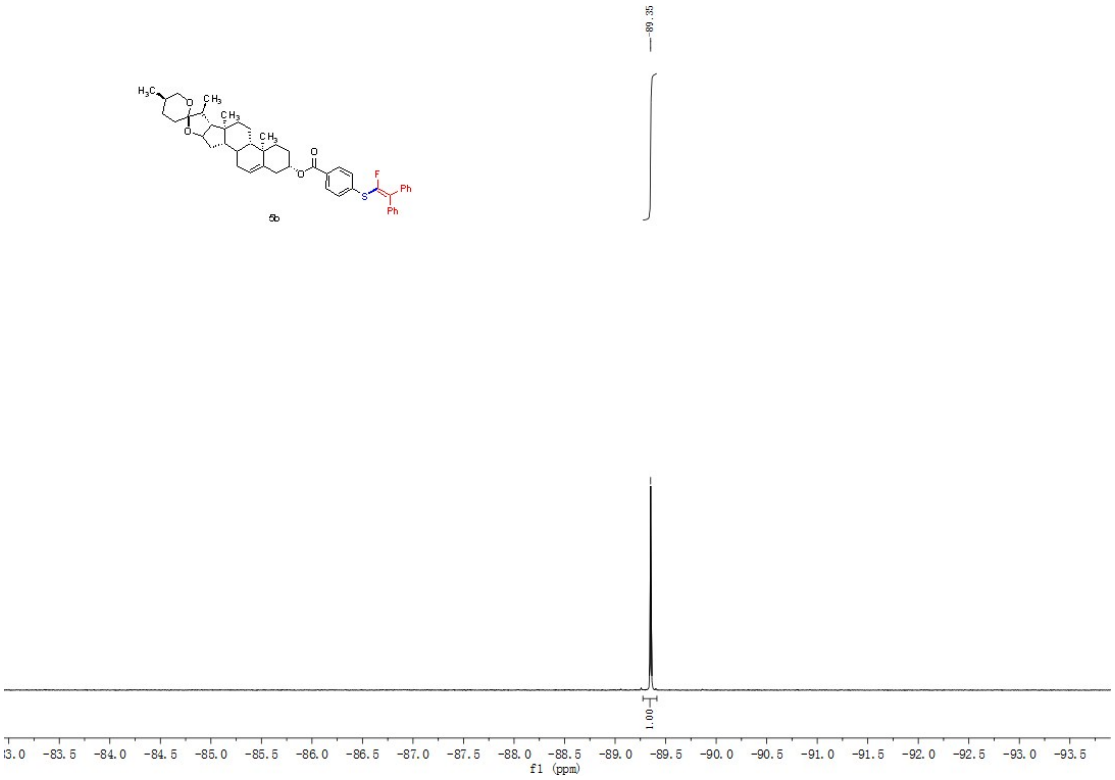

Me
Me
Me
Me
O
O
O
H
N
F
S
Ph
Ph

5a

88.79
1.00
f1 (ppm)
7.94
7.93
7.41
7.40
7.35
7.34
7.34
7.25
5.32
5.24
4.42
4.40
3.47
3.40
3.38
3.36
2.60
2.57
2.35
2.33
2.00
1.99
1.93
1.91
1.88
1.87
1.85
1.82
1.80
1.79
1.77
1.75
1.72
1.70
1.68
1.65
1.64
1.61
1.51
1.49
1.47
1.44
1.39
1.29
1.27
1.26
1.23
1.21
1.19
1.17
1.14
1.12
1.07
1.07
0.98
0.97
0.80
0.79
2.00
1.94
7.85
2.12
2.00
1.04
1.03
1.01
0.99
1.00
3.04
2.12
2.15
6.23
1.82
1.94
1.17
1.85
2.99
6.07
f1 (ppm)

6b


165.50
149.99
147.60
139.40
138.37
138.18
136.68
136.66
130.44
129.87
128.44
122.35
109.44
89.98
71.37
67.00
62.24
56.59
50.35
41.75
40.40
39.90
37.40
34.98
31.97
31.53
30.44
28.94
28.13
20.10
17.29
16.44
14.68
5b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


89.35
5b
1.00
-83.0 -83.5 -84.0 -84.5 -85.0 -85.5 -86.0 -86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0 -93.5
f1 (ppm)