Supporting Information

Iridium-Cobaloxime mediated Alkene C(sp^2)−CF_2H Cross-coupling: Difluoromethylation of Ketene dithioacetal

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I. General Information

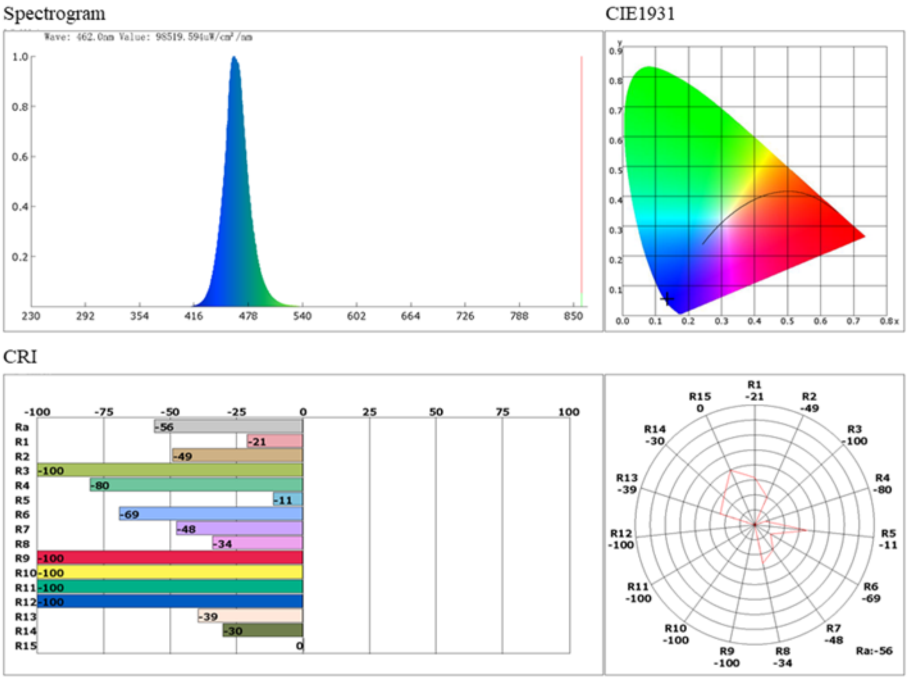
All reagents and catalysts, with the exception of several cobaloximes, were purchased from commercial sources and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254) using UV light as visualizing agent. Tsingdao silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 565 MHz) and Varian 500 (^{1}H: 500 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to $CDCl_3$ (7.26 ppm) for ^{1}H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR, (trifluoromethyl)benzene (δ -62.9 ppm) as the internal standard for ^{19}F NMR. Coupling constants are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focusspectrometer (ESI).

UV-vis absorption analysis was performed on Varian cary 50. Stern-Volmer fluorescence quenching experiments was performed on Full-featured fluorescence spectroscopy system (Edinburgh FLS920P010404) and Cyclic Voltammetry experiments was performed on CH Instruments (CHI 660E).

Photoreactor: The source of the 7 W blue LED using Wattecs Parallel Light Reactor (blue LED Light source, every tube hole groove, 7 W 465 nm).

Emission Spectrum

Spectrogram of blue light (7 W)



II. Additional Optimizations[a]

Photosensitizer screening

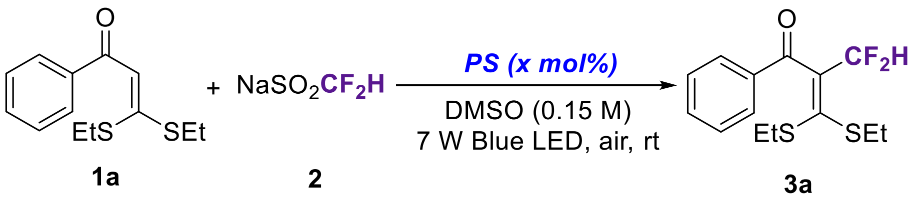


Table S1. Photosensitizer screening[b]

Entry	Photosensitizer (mol%)	Yield[b] (%)
1	$Ru(bpy)_3(PF_6)_2$ (5.0)	15
2	$[Ir(ppy)_2(dtbbpy)][PF_6]$ (5.0)	29
3	EosinY(5.0)	33
4	*p*-$MeOC_6H_4SH$ (5.0)	8
5	Mes-Acr$^+$-Me BF_4^- (5.0)	17
6	Thioxanthone (5.0)	*N.O.*
7	$[Ir[dFCF_3ppy]_2(bpy)][PF_6]$ (5.0)	31
8	*fac*-$Ir(ppy)_3$ (5.0)	37
9	*fac*-$Ir(ppy)_3$ (1.0)	26
10	*fac*-$Ir(ppy)_3$ (3.0)	37

[a]Yields were determined by ^{19}F NMR analysis using $PhCF_3$ as the internal standard; [b]**1a** (0.3 mmol), **2** (5.0 equiv.), photosensitizer (x mol%), DMSO (0.15 M), 7 W Blue LED, air, rt.

Solvent screening

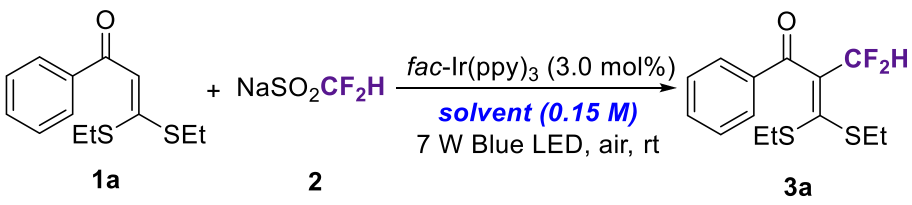


Table S2. Solvent screening[c]

Entry	Solvent (mL)	Time (h)	Yield[b] (%)
10	DMF (2)	24	13
11	DCE (2)	24	24
12	DMAc (2)	24	26
13	THF (2)	24	18
14	MeCN (2)	24	37
15	EtOAc (2)	24	18
16	1,4-dioxane (2)	24	19
17	NMP (2)	24	trace
18	Acetone (2)	24	39
19	MeCN (2)	48	45
20	MeCN (2)	72	37
21	DMSO-MeCN (2, v/v = 7/1)	24	45

[c]**1a** (0.3 mmol), **2** (5.0 equiv.), *fac*-Ir(ppy)$_3$ (3.0 mol%), solvent (0.15 M), 7 W Blue LED, air, rt.

Base screening

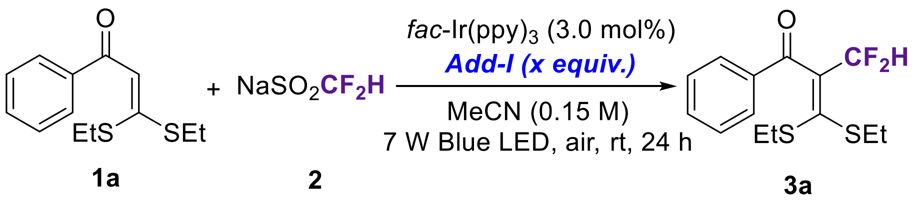
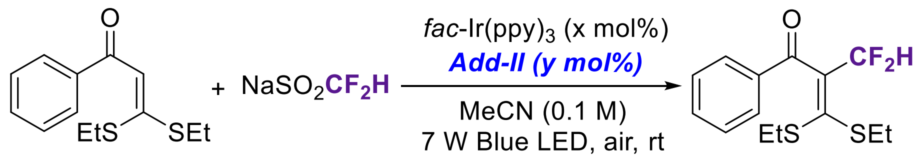


Table S3. Base screening[d]

Entry	Additive-I (equiv.)	Yield[b] (%)
22	quinone (1.0)	10
23	DBU (1.0)	0
24	$NaHCO_3$ (1.2)	42
25	K_2HPO_4 (1.2)	43
26	$NaHSO_4$ (1.2)	45
27	2,6-dimethylpyridine (1.2)	40
28	TBAI (1.2)	0

[d]**1a** (0.3 mmol), **2** (5.0 equiv.), *fac*-Ir(ppy)$_3$ (3.0 mol%), Additive-I (*x* equiv.), MeCN (0.15 M), 7 W Blue LED, air, rt, 24 h.

Cobalt catalysts screening



1a 2 3a

Table S4. Cobalt catalysts screening[e]

Entry	[Co] (mol %)	Time (h)	Yield[b] (%)
29	[Co-1] (10.0)	24	38
30	[Co-2] (10.0)	24	42
31	[Co-3] (10.0)	24	22
32	[Co-4] (10.0)	24	45
33	[Co-5] (10.0)	24	57
34	[Co-6] (10.0)	24	42
35	[Co-7] (10.0)	24	32
36	[Co-8] (10.0)	24	46
37	[Co-9] (10.0)	24	75
38[f]	[Co-5] (7.0)	24	51
39	[Co-5] (7.0), $K_2S_2O_8$ (1.0 equiv.)	24	66
40	[Co-5] (7.0), DIPEA (1.0 equiv.)	24	0
41	[Co-9] (7.0)	72	64
42[g]	*[Co-9](7.5)*	*72*	*76*

[e]**1a** (0.3 mmol), **2** (5.0 equiv.), *fac*-Ir(ppy)3 (3.0 mol%), Additive-II (*y* mol% or equiv.), MeCN (0.1 M), 7 W Blue LED, air, rt; [f]MeCN-H_2O (3 mL, v:v = 24:1); [g]*fac*-Ir(ppy)3 (5 mol%).

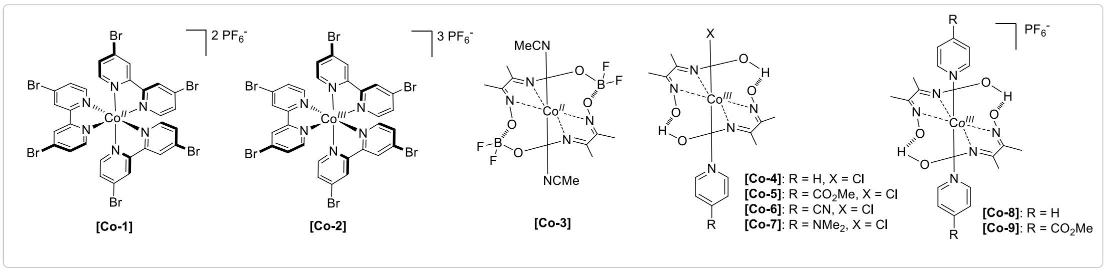
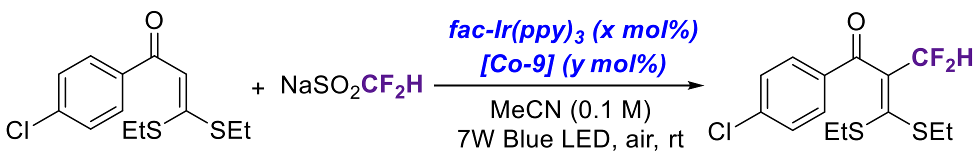


Figure S1. Structures of the cobaloximes used.

Fine-tuning (take 1h as example)



1h 2 3h

Table S5. Fine-tuning (take 1h as example)[h]

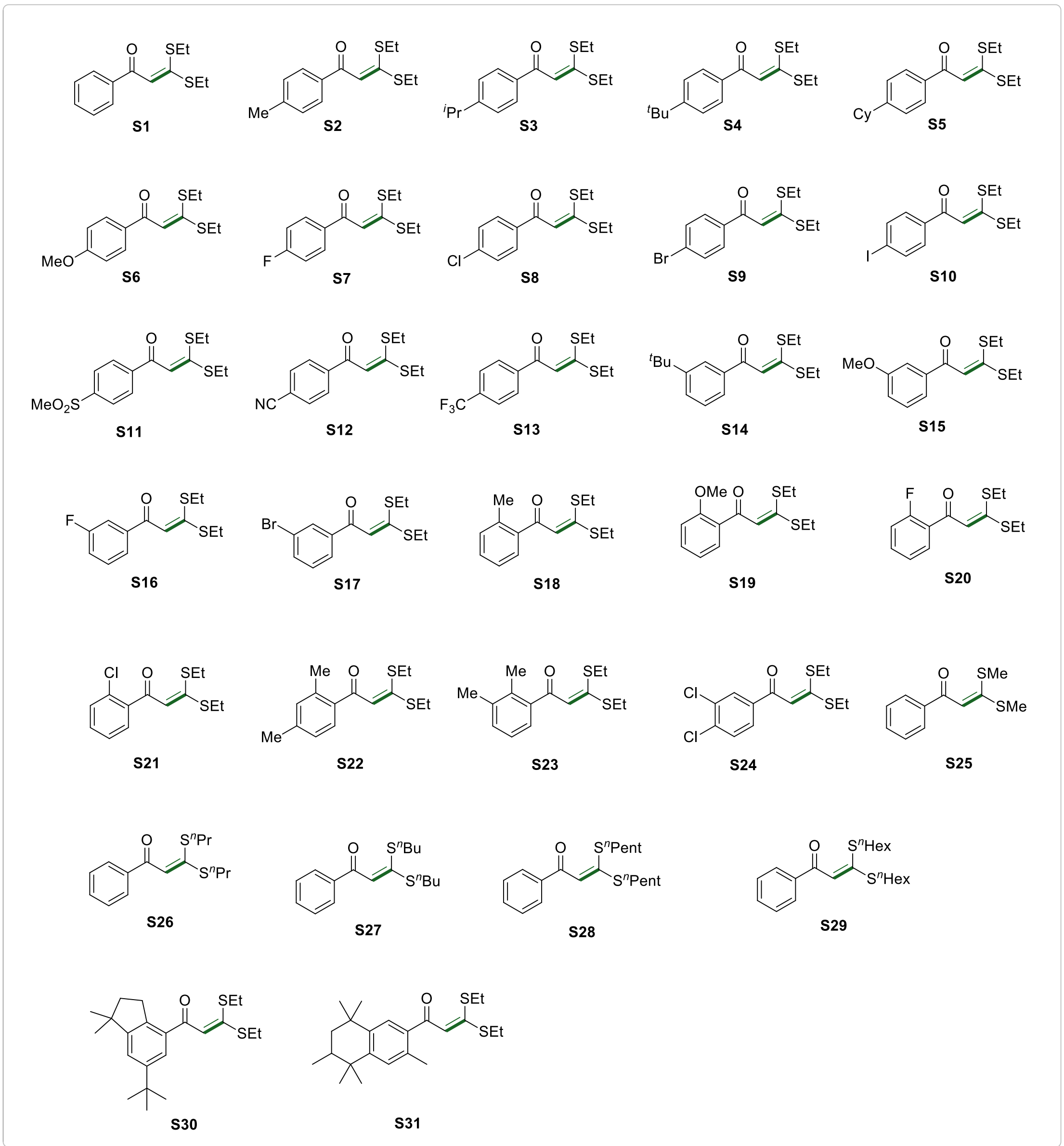
Entry	Photosensitizer (mol %)	[Co] (mol %)	Yield[b] (%)
43	*fac*-Ir(ppy)3 (5.0)	[Co-9] (7.0)	66

44	*fac*-Ir(ppy)3 (5.0)	[Co-9] (15.0)	56
45	*fac*-Ir(ppy)3 (7.0)	[Co-9] (7.0)	10
46	*fac*-Ir(ppy)3 (5.0)	[Co-9] (8.0)	60
47	*fac*-Ir(ppy)3 (5.0)	[Co-9] (6.0)	56
48	***fac-Ir(ppy)3 (5.0)***	***[Co-9] (7.5)***	***70***
49	*fac*-Ir(ppy)3 (4.0)	[Co-9] (7.0)	4
50[i]	*fac*-Ir(ppy)3 (5.0)	[Co-9] (7.5)	63

[h] **1a** (0.3 mmol), **2** (5 eq), *fac*-Ir(ppy)3 (*x* mol%), [Co-9] (*y* mol%), MeCN (0.1 M), 7 W Blue LED, air, rt; [i] **2** (5.5 equiv.)

III. Experimental Sections

1. Synthesis and characterization of substrates



S1~S31 were synthesized following the reported literature.

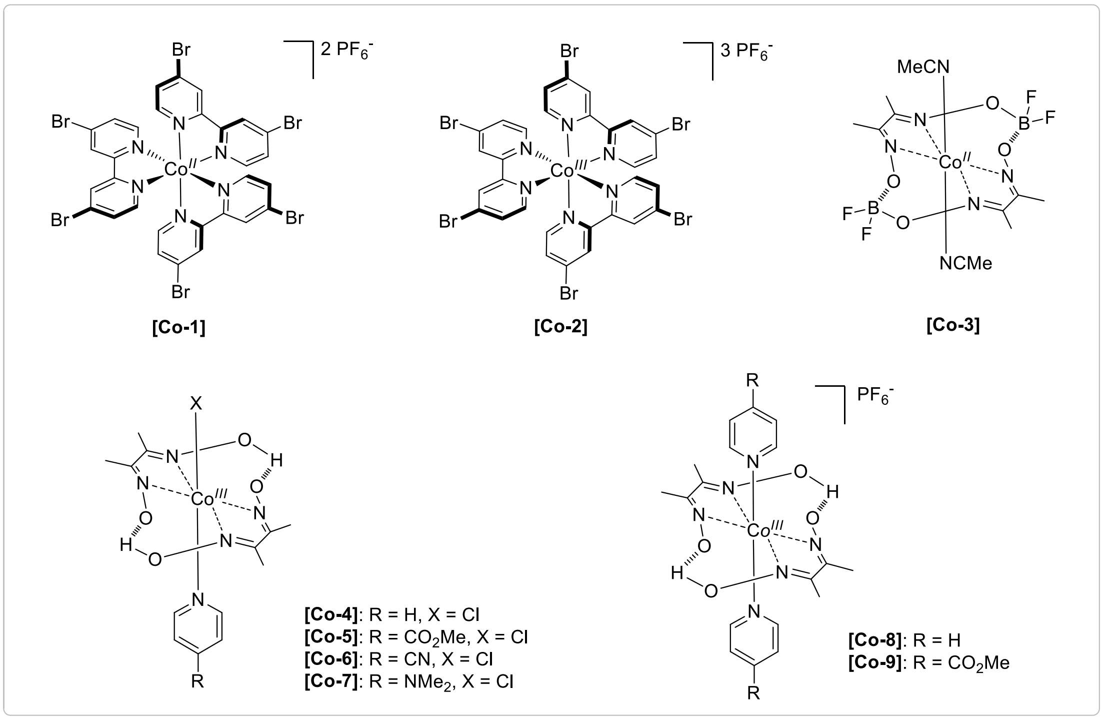
General Procedure:[1-5]

To a 100 mL round bottom flask, DMF (20 mL), sodium hydride (2.0 equiv.) and acetophenone (5.0 mmol) were added sequentially, and after stirring for 30 min at room temperature, the solution was transferred to 0 °C and carbon disulfide (1.2 equiv.) was added dropwise. After stirring for 1 h, bromoethane (2.2 equiv.) was added dropwise to the mixture, and the reaction was warmed to room temperature. When completed, 20 mL of distilled water was added into the system to quench the reaction; extracted with ethyl acetate (20 mL×3) and then reverse extracted with distilled water (20 mL×3). The whole organic layer was concentrated by evaporation and The residue was separated and purified via column chromatography (petroleum ether/ethyl acetate) to obtain product.

S1-S3, **S6~S13**, **S16~S18**, **S21**, **S22**, **S25** were known compounds as reported.

S4, **S5**, **S14**, **S15**, **S19**, **S20**, **S23**, **S24**, **S26-S31** were new compounds prepared following the procedure above.

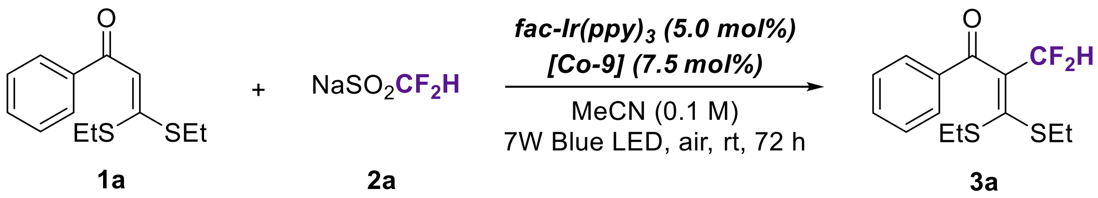
2. Synthesis of the cobaloximes



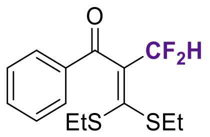
[Co-1], **[Co-2]**;[6] **[Co-3]**;[7] **[Co-5]**, **[Co-6]**, **[Co-7]**[8-9] and **[Co-9]**[10-11] were synthesized according to previous reported methods. Others were purchased from commercial sources.

[Co-9]: $Co(NO_3)_2{\cdot}6H_2O$ (1.4552 g, 5.0 mmol) was dissolved in 50 mL of methanol, then treated with methyl iso-nicotinate (5.32 mL, 9.0 mol), dimethylglyoxime ($dmgH_2$) (1.1612 g, 10.0 mmol). The solution was stirred with air passed through for 3.5 h. Afterwards, it became cloudy and was filtered to remove a fraction of brown material, which was discarded. The filtrate was treated with ammonium hexafluorophosphate (0.8150 g, 5.0 mol), and the product precipitated as a light gold powder, which was collected and washed with water (5 mL×1), methanol (5 mL×2), and diethyl ether (5 mLc×3). Then the product should be dried under vacuum to give usable **[Co-9]** (2.8964 g, 82%). The product could be recrystallized further from acetone to give purer [Co-9]. **^{1}H NMR** (600 MHz, DMSO-d_6) δ (ppm) 8.77 (dd, J = 4.2 Hz, 1H), 8.34 (dd, J = 5.4 Hz, 4H), 7.95 (d, J = 5.4 Hz, 4H), 7.80 (d, J = 4.2 Hz, 1H), 3.87 (s, 1H), 3.84 (s, 6H), 2.24 (s, 12H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ (ppm) 165.3, 163.7, 156.9, 152.2, 150.9, 140.2, 136.9, 125.7, 122.6, 53.5, 52.9, 40.0, 39.9, 39.7, 39.6, 39.5, 39.3, 39.2, 13.5. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{28}CoN_6O_8$ ($[M-(PF_6)]^{3+}$) 563.1295. Found 563.1289.

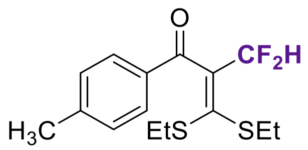
3. Synthesis of difluoromethylated α- phenacyl ketene dithioacetals



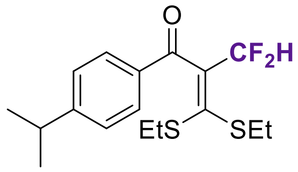
General synthesis procedure (with **3a** as an example): To a 15 ml flask equipped with a stir-bar was add α-phenacyl ketene dithioacetals **1a** (76 mg, 0.3 mmol), sodium difluoromethyl sulfinate **2** (207 mg, 5.0 equiv.), *fac*-Ir(ppy)$_3$ (9.8 mg, 5.0 mol%), [Co-9] (15.9 mg, 7.5 mol%) and dry MeCN (3 mL, 0.1 M versus **1**) was added into a 15 mL glass tube containing a stir bar. The whole apparatus was then assembled and stirred (800 rpm) under the irradiation of 7 W Blue LED at room temperature (ca. 25 ℃) for 72 h. When finished, the crude mixture was poured into 10 mL saturated $NaHCO_3$ aqueous and immediately separated the water phase. The latter was extracted with EtOAc (5 mL×2) and combined with the previous organic phase. The whole organic phase was washed with 5 mL saturated NaCl aqueous, discarding the water phase. Concentrating to remove the violated components and purified via flash column chromatography (PE/EA = 120/1 to 100/1, v/v) to get the target molecule **3** (yellow oil, 68.8 mg, 76%).



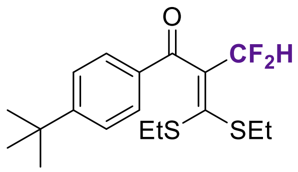
3a: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-phenylprop-2-en-1-on: yellow oil (68.8 mg, 76%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 55.2 Hz, 1H), 2.89 (q, *J* = 7.2 Hz, 2H), 2.72 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) = 191.7, 144.3 (t, *J* = 10.1 Hz), 140.1 (t, *J* = 24.8 Hz), 136.7, 133.7, 129.5, 128.6, 111.9 (t, *J* = 238.4 Hz), 28.2, 28.0, 15.1, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) = -110.47 (d, *J* = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{16}F_2NaOS_2$ $(M+Na)^+$ 325.0503. Found 325.0500. Characterization data were consistent with literature values.[12]



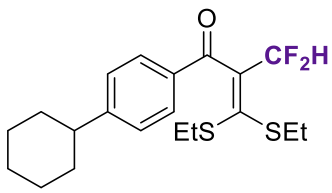
3b: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(*p*-tolyl)prop-2-en-1-one: light yellow oil (71.2 mg, 75%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.83 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 55.2 Hz, 1H), 2.88 (q, *J* = 7.2 Hz, 2H), 2.72 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.3, 144.8, 143.7 (t, *J* = 10.1 Hz), 140.2 (t, *J* = 24.8 Hz), 134.1, 129.7, 129.3, 111.9 (t, *J* = 238.3 Hz), 28.1, 27.9, 21.7, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.49 (d, *J* = 55.3 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{18}F_2NaOS_2$ $(M+Na)^+$ 339.0659. Found 339.0648.



3c: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(4-isopropylphenyl)prop-2-en-1-one: light yellow oil (65.0 mg, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.86 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 6.95 (t, J = 55.2 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.07 (t, J = 7.2 Hz, 3H). **^{13}C NMR** δ (ppm) 191.4, 155.4, 143.7 (t, J = 10.2 Hz), 140.4 (t, J = 24.9 Hz), 134.5, 129.8, 126.7, 112.0 (t, J = 238.4 Hz), 34.3, 28.1, 27.9, 23.6, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.49 (d, J = 55.2 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{17}H_{22}F_2NaOS_2$ $(M+Na)^+$ 367.0972. Found 367.0963.

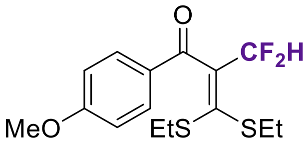


3d: 1-(4-(*tert*-butyl)phenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (79.5 mg, 74%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.86 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 6.95 (t, J = 55.2 Hz, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.34 (s, 9H), 1.33 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.3, 157.6, 143.8 (t, J = 10.1 Hz), 140.4 (t, J = 24.7 Hz), 134.1, 129.5, 125.6, 112.0 (t, J = 238.3 Hz), 35.2, 31.0, 28.1, 27.9, 15.1, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.47 (d, J = 55.3 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{18}H_{24}F_2NaOS_2$ $(M+Na)^+$ 381.1129. Found 381.1126.

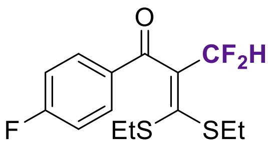


3e: 1-(4-cyclohexylphenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: yellow oil (80.7 mg, 70%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.85 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 6.94 (t, J = 55.2 Hz, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.72

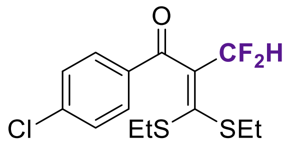
(q, J = 7.2 Hz, 2H), 2.57 (m, 1H), 1.91 – 1.82 (m, 4H), 1.79 – 1.72 (m, 1H), 1.47 – 1.36 (m, 4H), 1.33 (t, J = 7.2 Hz, 3H), 1.30 – 1.21 (m, 1H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.3, 154.5, 143.7 (t, J = 10.2 Hz), 140.4 (t, J = 24.7 Hz), 134.5, 129.7, 127.1, 112.0 (t, J = 238.3 Hz), 44.7, 34.0, 28.1, 27.9, 26.7, 26.0, 15.1, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.48 (d, J = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{20}H_{26}F_2NaOS_2$ $(M+Na)^+$ 407.1285. Found 407.1295.



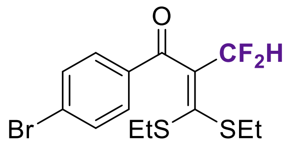
3f: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(4-methoxyphenyl)prop-2-en-1-one: yellow oil (69.7 mg, 70%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.91 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 2H), 6.94 (t, J = 55.8 Hz, 1H), 3.87 (s, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.3, 164.2, 143.4 (t, J = 10.1 Hz), 140.4 (t, J = 24.8 Hz), 132.0, 129.7, 113.9, 112.0 (t, J = 238.2 Hz), 55.5, 28.1, 27.9, 15.1, 14.8. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.50 (d, J = 55.2 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{18}F_2NaO_2S_2$ $(M+Na)^+$ 335.0608. Found 335.0601.



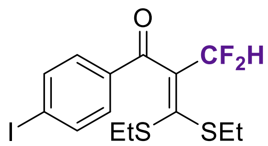
3g: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(4-fluorophenyl)prop-2-en-1-one: light yellow oil (74.9 mg, 78%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 9.0, 5.4 Hz, 2H), 7.14 (t, J = 9.0 Hz, 2H), 6.94 (t, J = 55.2 Hz, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.1, 166.14 (d, J = 256.1 Hz), 144.6 (t, J = 10.1 Hz), 139.6 (t, J = 24.8 Hz), 133.1 (d, J = 2.8 Hz), 132.2 (d, J = 9.4 Hz), 115.8 (d, J = 22.0 Hz), 111.9 (t, J = 238.3 Hz), 28.1, 28.0, 15.0, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -103.84 (tt, J = 8.5, 5.5 Hz, 1F), -110.38 (d, J = 55.0 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}F_3NaOS_2$ $(M+Na)^+$ 343.0409. Found 343.0406.



3h: 1-(4-chlorophenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (76.6 mg, 76%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 6.84 (t, J = 55.2 Hz, 1H), 2.78 (q, J = 7.2 Hz, 2H), 2.63 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.5, 144.9 (t, J = 10.0 Hz), 140.2, 139.3 (t, J = 24.8 Hz), 135.0, 130.8, 128.9, 111.8 (t, J = 238.4 Hz), 28.1, 28.0, 15.0, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.33 (d, J = 55.2 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}ClF_2NaOS_2$ $(M+Na)^+$ 359.0113. Found 359.0108.

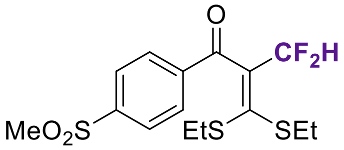


3i: 1-(4-bromophenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (85.5 mg, 75%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.79 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 6.94 (t, J = 55.2 Hz, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.7, 145.0 (t, J = 10.1 Hz), 139.3 (t, J = 24.7 Hz), 135.5, 131.9, 130.9, 129.0, 111.9 (t, J = 238.4 Hz), 28.2, 28.1, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.35 (d, J = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}BrF_2NaOS_2$ $(M+Na)^+$ 402.9608. Found 402.9612.

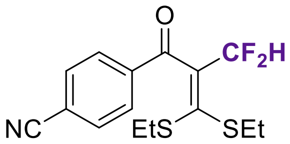


3j: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(4-iodophenyl)prop-2-en-1-one: yellow oil (66.7 mg, 52%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.84 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 6.93 (t, J = 55.2 Hz, 1H), 2.88 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.0, 145.0 (t, J = 10.0 Hz), 139.4 (t, J = 24.8 Hz), 137.9, 136.0, 130.7, 111.8

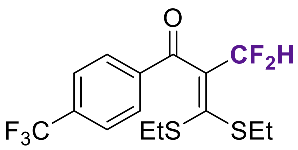
(t, J = 238.4 Hz), 102.0, 28.2, 28.1, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.36 (d, J = 55.2 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}IF_2NaOS_2$ $(M+Na)^+$ 428.9650. Found 428.9640.



3k: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(4-(methylsulfonyl)phenyl)prop-2-en-1-one: dark brown oil (74.2 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.10 – 8.02 (m, 4H), 6.95 (t, J = 55.2 Hz, 1H), 3.08 (s, 3H), 2.89 (q, J = 7.2 Hz, 2H), 2.72 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.3, 146.7 (t, J = 9.8 Hz), 144.4, 140.9, 138.5 (t, J = 24.9 Hz), 130.0, 127.7, 111.8 (t, J = 238.6 Hz), 44.3, 28.3, 28.2, 15.0, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.17 (d, J = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{19}F_2O_3S_3$ $(M+Na)^+$ 381.0459. Found 381.0453.

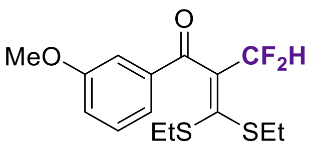


3l: 4-(2-(difluoromethyl)-3,3-bis(ethylthio)acryloyl)benzonitrile: light yellow oil (37.1 mg, 38%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.00 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 6.95 (t, J = 55.2 Hz, 1H), 2.89 (q, J = 7.2 Hz, 2H), 2.72 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.02 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.3, 146.6 (t, J = 9.8 Hz), 140.0, 138.5 (t, J = 24.9 Hz), 132.42, 129.60, 117.9, 116.6, 111.8 (t, J = 238.6 Hz), 28.3, 28.2, 15.0, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.18 (d, J = 55.0 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{15}F_2NNaOS_2$ $(M+Na)^+$ 350.0455. Found 350.0449.

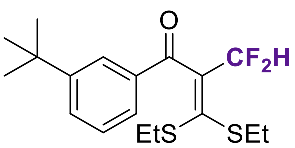


3m: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one: light yellow oil (48.3 mg, 44%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.03

(d, J = 7.8 Hz, 2H), 7.74 (m, 2H), 6.96 (t, J = 55.2 Hz, 1H), 2.90 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.7, 145.9 (t, J = 9.9 Hz), 139.5, 139.1 (t, J = 24.8 Hz), 134.8 (q, J = 32.5 Hz), 129.7, 125.6 (q, J = 3.9 Hz), 123.6 (q, J = 272.7 Hz), 111.9 (t, J = 238.5 Hz), 28.3, 28.2, 15.1, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -63.14(s, 3F), -110.30 (d, J = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{15}F_5NaOS_2$ $(M+Na)^+$ 393.0377. Found 393.0381.

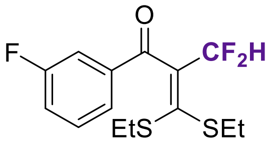


3n: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(3-methoxyphenyl)prop-2-en-1-one: light yellow oil (54.6 mg, 55%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.50 (t, J = 1.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H)., 7.37 (t, J = 7.8 Hz, 1H), 7.14 (dd, J = 8.4, 2.4 Hz, 1H), 6.94 (t, J = 55.2 Hz, 1H), 3.86 (s, 3H), 2.89 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.5, 159.8, 144.3 (t, J = 10.1 Hz), 140.1 (t, J = 24.6 Hz), 138.0, 129.5, 122.7, 120.7, 112.9, 111.9 (t, J = 238.8 Hz), 55.4, 28.2, 28.0, 15.1, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.45 (d, J = 55.2 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{18}F_2NaO_2S_2$ $(M+Na)^+$ 355.0608. Found 355.0598.

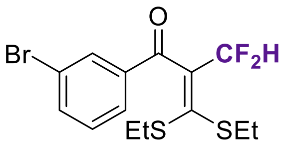


3o: 1-(3-(*tert*-butyl)phenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (67.6 mg, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.99 (s, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.63 (m, 1H), 7.40 (t, J = 7.8 Hz, 1H), 6.95 (t, J = 55.2 Hz, 1H), 2.89 (q, J = 7.2 Hz, 2H), 2.72 (q, J = 7.2 Hz, 2H), 1.34 (s, 9H), 1.33 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 192.1, 151.6, 143.8 (t, J = 10.2 Hz), 140.6 (t, J = 24.8 Hz), 136.5, 131.0, 128.3, 127.0, 126.4, 111.9 (t, J = 238.4 Hz), 34.8, 31.2, 28.1, 27.9, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.44 (d, J = 55.0 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{18}H_{24}F_2NaOS_2$ $(M+Na)^+$

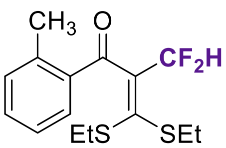
381.1129. Found 381.1120.



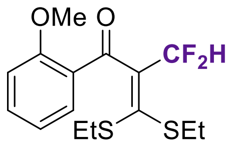
3p: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(3-fluorophenyl)prop-2-en-1-one: light brown oil (62.4 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.70 (d, J = 7.8 Hz, 1H), 7.62 (dt, J = 9.0, 2.4 Hz, 1H), 7.45 (td, J = 7.8, 5.4 Hz, 1H), 7.29 (td, J = 8.4, 2.4 Hz, 1H), 6.94 (t, J = 55.2 Hz, 1H), 2.89 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.5 (d, J = 2.2 Hz), 162.8 (d, J = 241.6 Hz), 145.3 (t, J = 10.0 Hz), 139.3 (t, J = 24.9 Hz), 138.9 (d, J = 6.4 Hz), 130.2 (d, J = 7.8 Hz), 125.3 (d, J = 2.9 Hz), 120.7 (d, J = 21.6 Hz), 115.9 (d, J = 22.6 Hz), 111.9 (t, J = 238.6 Hz), 28.24, 28.09, 15.07, 14.62. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.39 (d, J = 55.1 Hz, 2F), -111.88 (td, J = 8.7, 5.4 Hz,1F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}F_3NaOS_2$ $(M+Na)^+$ 343.0409. Found 343.0396.



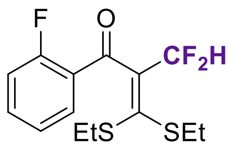
3q: 1-(3-bromophenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (52.4 mg, 46%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.06 (t, J = 1.8 Hz, 1H), 7.83 (dt, J = 7.8, 1.2 Hz, 1H), 7.70 (m, 1H), 7.35 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 55.2 Hz, 1H), 2.89 (q, J = 7.2 Hz, 2H), 2.73 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.3, 145.5 (t, J = 10.0 Hz), 139.1 (t, J = 24.7 Hz), 138.5, 136.4, 132.2, 130.1, 128.0, 122.9, 111.8 (t, J = 238.5 Hz), 28.2, 28.1, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.39 (d, J = 55.0 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}BrF_2NaOS_2$ $(M+Na)^+$ 402.9608. Found 402.9609.



3r: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(o-tolyl)prop-2-en-1-one: light brown oil (68.3 mg, 72%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.62 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 5.4 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 55.2 Hz, 1H), 2.87 (q, *J* = 7.2 Hz, 2H), 2.66 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ (ppm) 193.5, 145.5 (t, *J* = 9.7 Hz), 141.6 (t, *J* = 24.3 Hz), 140.3, 136.9, 132.1, 131.8, 130.9, 125.4, 112.1 (t, *J* = 238.7 Hz), 28.2, 28.0, 21.4, 15.0, 14.6. ^{19}**F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.47 (d, *J* = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{18}F_2NaOS_2$ $(M+Na)^+$ 339.0659. Found 339.0647.

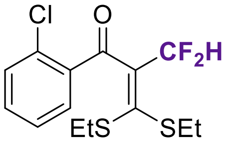


3s: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(2-methoxyphenyl)prop-2-en-1-one: light brown oil (61.6 mg, 62%). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.49 (td, *J* = 7.8, 7.2, 1.8 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.85 (t, *J* = 55.2 Hz, 1H), 3.84 (s, 3H), 2.85 (q, *J* = 7.2 Hz, 2H), 2.68 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.5, 159.4, 143.3 (t, *J* = 23.5 Hz), 141.5 (t, *J* = 9.5 Hz), 134.5, 131.6, 127.3, 120.5, 112.2 (t, *J* = 241.6 Hz), 111.8, 55.7, 27.9, 27.8, 15.1, 14.5. ^{19}**F NMR** (565 MHz, $CDCl_3$) δ (ppm) -111.24 (d, *J* = 55.3 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{15}H_{19}F_2O_2S_2$ $(M+H)^+$ 333.0789. Found 333.0792.

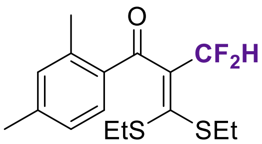


3t: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(2-fluorophenyl)prop-2-en-1-one: light brown oil (40.4 mg, 42%). ^{19}**F yield**: 60%. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.90 (td, *J* = 7.8, 1.8 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.27 (q, *J* = 7.8 Hz, 1H), 7.12 (m, 1H), 6.96 (t, *J* = 54.6 Hz, 1H), 2.89 (q, *J* = 7.2 Hz, 2H), 2.75 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ (ppm) 188.1, 161.8 (d, *J* = 258.1 Hz), 144.6 (td, *J* = 10.5, 3.4 Hz), 141.6 (t, *J* = 24.2 Hz), 135.0 (d, *J*

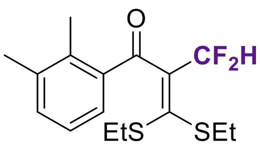
= 9.1 Hz), 131.2, 126.2 (d, J = 9.3 Hz), 124.2 (d, J = 3.8 Hz), 116.6 (d, J = 22.1 Hz), 112.1 (t, J = 239.0 Hz), 28.1 (d, J = 5.1 Hz), 15.0, 14.4. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.85 (ddq, J = 11.7, 8.1, 4.0 Hz, 1F), -111.09 (dd, J = 54.9, 3.7 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{16}F_3OS_2$ $(M+H)^+$ 321.0589. Found 321.0585.



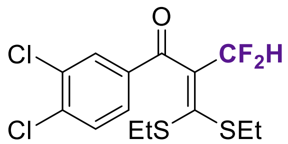
3u: 1-(2-chlorophenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: yellow oil (22.2 mg, 2%). **^{19}F yield**: 63%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.64 (d, J = 7.2 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.31 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 54.6 Hz, 1H), 2.89 (q, J = 7.2 Hz, 2H), 2.70 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 190.2, 149.6 (t, J = 8.7 Hz), 139.6 (t, J = 23.4 Hz), 137.6, 133.4, 132.4, 130.1, 130.9, 126.4, 112.3 (t, J = 239.6 Hz), 28.8, 28.4, 15.1, 14.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.29 (d, J = 54.8 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{16}ClF_2OS_2$ $(M+H)^+$ 337.0294. Found 337.0284.



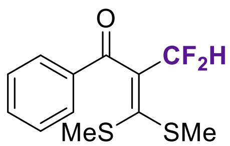
3v: 2-(difluoromethyl)-1-(2,4-dimethylphenyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (64.3 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.40 (d, J = 7.8 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.93 (t, J = 55.2 Hz, 1H), 2.87 (q, J = 7.2 Hz, 2H), 2.67 (q, J = 7.2 Hz, 2H), 2.48 (s, 3H), 2.34 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 194.0, 146.4 (t, J = 9.6 Hz), 141.7 (t, J = 24.5 Hz), 138.1 (d, J = 4.1 Hz), 133.5, 128.0, 124.6, 112.2 (t, J = 238.8 Hz), 28.3, 28.1, 20.4, 16.4, 15.0, 14.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.34 (d, J = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{16}H_{21}F_2OS_2$ $(M+H)^+$ 331.0996. Found 331.0989.



3w: 2-(difluoromethyl)-1-(2,3-dimethylphenyl)-3,3-bis(ethylthio)prop-2-en-1-one: light yellow oil (69.4 mg, 70%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.53 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.93 (t, J = 55.2 Hz, 1H), 2.86 (q, J = 7.2 Hz, 2H), 2.68 (q, J = 7.2 Hz, 2H), 2.60 (s, 3H), 2.36 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 193.0, 144.3 (t, J = 9.8 Hz), 143.0, 141.8 (t, J = 24.4 Hz), 140.6, 133.9, 132.8, 131.7, 126.0, 112.1 (t, J = 238.5 Hz), 28.0 (d, J = 4.4 Hz), 21.6, 21.5, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.48 (d, J = 55.2 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{16}H_{20}F_2NaOS_2$ $(M+Na)^+$ 353.0816. Found 353.0815.

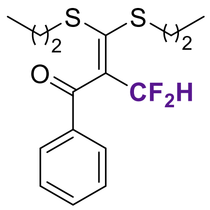


3x: 1-(3,4-dichlorophenyl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: yellow oil (32.2 mg, 29%). **^{19}F yield**: 63%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.00 (d, J = 1.8 Hz, 1H), 7.74 (dd, J = 8.4, 1.8 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 6.94 (t, J = 55.2 Hz, 1H), 2.89 (q, J = 7.2 Hz, 2H), 2.75 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 189.5, 145.9 (t, J = 10.0 Hz), 138.7 (t, J = 24.9 Hz), 138.3, 136.4, 133.4, 131.2, 130.8, 128.4, 111.82 (t, J = 238.5 Hz), 28.3, 28.2, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.33 (d, J = 55.0 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}Cl_2F_2OS_2$ $(M+H)^+$ 370.9904. Found 370.9908.

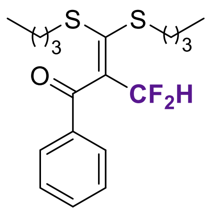


3y: 2-(difluoromethyl)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one: light brown oil (44.4 mg, 54%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.93 (d, J = 7.8 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 6.90 (t, J = 55.2 Hz, 1H), 2.42 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.4, 147.2 (t, J = 10.0 Hz), 137.4 (t, J = 24.6 Hz), 136.7, 133.7, 129.4, 128.7, 111.8 (t, J = 238.5 Hz), 16.9, 16.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.42 (d, J = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for

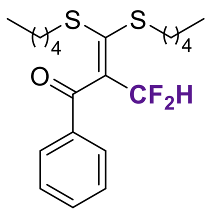
$C_{12}H_{13}F_2OS_2$ $(M+H)^+$ 275.0370. Found 275.0367. Characterization data were consistent with literature values[12].



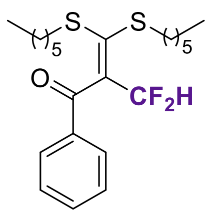
3z: 2-(difluoromethyl)-1-phenyl-3,3-bis(propylthio)prop-2-en-1-one： light yellow oil (48.3 mg, 49%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 6.95 (t, *J* = 55.2 Hz, 1H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.67 (m, 2H), 1.38 (m, 2H), 1.03 (t, *J* = 7.8 Hz, 3H), 0.73 (t, *J* = 7.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.7, 145.1 (t, *J* = 10.2 Hz), 139.5 (t, *J* = 24.7 Hz), 136.8, 133.6, 129.4, 128.5, 112.0 (t, *J* = 238.4 Hz), 35.9, 35.6, 23.2, 22.8, 13.2, 12.9. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.32 (d, *J* = 55.3 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{16}H_{20}F_2NaOS_2$ $(M+Na)^+$ 353.0816. Found 353.0813.



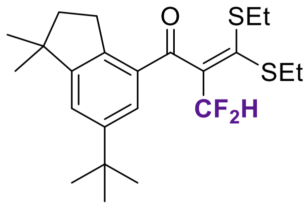
3aa: 3,3-bis(butylthio)-2-(difluoromethyl)-1-phenylprop-2-en-1-one: light yellow oil (44.0 mg, 41%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 55.2 Hz, 1H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 1.63 (m, 2H), 1.44 (m, 2H), 1.32 (m, 2H), 1.14 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.7, 145.2 (t, *J* = 10.1 Hz), 139.4 (t, *J* = 24.6 Hz), 136.8, 133.6, 129.5, 128.5, 112.0 (t, *J* = 238.4 Hz), 33.6, 33.4, 31.9, 31.4, 21.8, 21.5, 13.5, 13.4. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.30 (d, *J* = 55.3 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{18}H_{24}F_2NaOS_2$ $(M+Na)^+$ 381.1129. Found 381.1121.



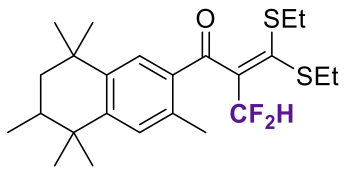
3ab: 2-(difluoromethyl)-3,3-bis(pentylthio)-1-phenylprop-2-en-1-one: light brown oil (34.6 mg, 30%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 55.2 Hz, 1H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 1.64 (m, 2H), 1.36 (m, 6H), 1.12 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.7, 145.3 (t, *J* = 10.1 Hz), 139.3 (t, *J* = 24.7 Hz), 136.8, 133.6, 129.5, 128.5, 112.0 (t, *J* = 238.3 Hz), 33.9, 33.7, 30.8, 30.6, 29.5, 29.1, 22.1, 22.0, 13.9, 13.8. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.30 (d, *J* = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{20}H_{28}F_2NaOS_2$ $(M+Na)^+$ 409.1442. Found 409.1438.



3ac: 2-(difluoromethyl)-3,3-bis(hexylthio)-1-phenylprop-2-en-1-one: light brown oil (55.9 mg, 45%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 55.2 Hz, 1H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 1.64 (m, 2H), 1.42 (m, 2H), 1.37 – 1.27 (m, 6H), 1.18 (m, 2H), 1.14 – 1.08 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 191.7, 145.3 (t, *J* = 10.0 Hz), 139.3 (t, *J* = 24.7 Hz), 136.8, 133.6, 129.4, 128.5, 112.0 (t, *J* = 238.4 Hz), 34.0, 33.7, 31.2, 31.1, 29.8, 29.4, 28.3, 28.1, 22.4, 22.3, 13.9, 13.8. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.28 (d, *J* = 55.1 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{22}H_{32}F_2NaOS_2$ $(M+Na)^+$ 437.1755. Found 437.1758.

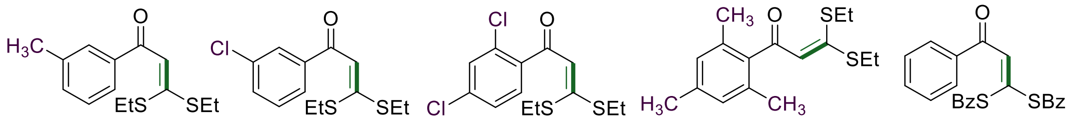


3ad: 1-(6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)-2-(difluoromethyl)-3,3-bis(ethylthio)prop-2-en-1-one: light brown oil (83.2 mg, 65%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.58 (d, J = 1.8 Hz, 1H), 7.34 (d, J = 1.8 Hz, 1H), 6.94 (t, J = 55.2 Hz, 1H), 3.24 (t, J = 7.2 Hz, 2H), 2.88 (q, J = 7.2 Hz, 2H), 2.69 (q, J = 7.2 Hz, 2H), 1.96 (t, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.31 (s, 6H), 1.27 (s, 6H), 1.01 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 193.1, 154.1, 149.5, 143.4 (t, J = 10.2 Hz), 142.3, 141.9 (t, J = 24.5 Hz), 132.7, 126.8, 123.8, 112.0 (t, J = 238.4 Hz), 43.4, 41.4, 34.6, 31.4, 30.3, 28.8, 28.0, 27.8, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.39 (d, J = 55.3 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{23}H_{32}F_2NaOS_2$ $(M+Na)^+$ 449.1755. Found 449.1758.

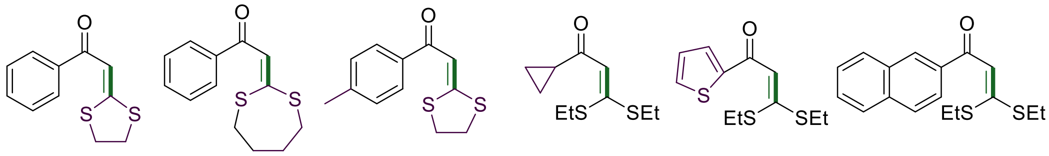


3ae: 2-(difluoromethyl)-3,3-bis(ethylthio)-1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)prop-2-en-1-one: light yellow solid (85.8 g, 65%). mp: 94-95 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.60 (s, 1H), 7.21 (s, 1H), 6.94 (t, J = 55.2 Hz, 1H), 2.87 (q, J = 7.2 Hz, 2H), 2.66 (q, J = 7.2 Hz, 2H), 2.59 (s, 3H), 1.91 – 1.80 (m, 1H), 1.61 (t, J = 13.2 Hz, 1H), 1.38 (dd, J = 13.8, 2.4 Hz, 1H), 1.35 – 1.30 (m, 6H), 1.24 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 0.99 (d, J = 6.6 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 193.1, 150.9, 143.9 (t, J = 9.9 Hz), 142.4 (t, J = 24.5 Hz), 141.8, 136.9, 133.8, 130.7, 130.3, 112.1 (t, J = 238.5 Hz), 43.3, 37.9, 34.4, 33.9, 32.2, 31.8, 28.2, 28.0, 27.9, 24.6, 21.3, 16.7, 15.1, 14.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.34 (dd, J = 55.4, 4.8 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{24}H_{34}F_2NaOS_2$ $(M+Na)^+$ 463.1911. Found 463.1915.

4. Unsuccessful Examples



1o 1r 1z 1ab 1ah



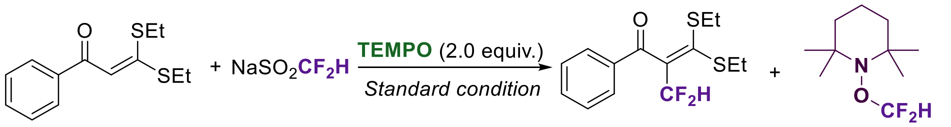
1ai 1aj 1ak 1al 1am 1ao

Figure S2. Unsuccessful Examples.

IV. Mechanism Investigations

A. Radical capture experiments

a. TEMPO



1a 2 **3a**, 7% (^{19}F NMR yield) **7**, 23% (^{19}F NMR yield)

In a 15 mL glass tube added **1a** (76 mg, 0.3 mmol), **2** (207 mg, 5.0 equiv.), *fac*-$Ir(ppy)_3$ (9.8 mg, 5.0 mol%), [Co-9] (15.9 mg, 7.5 mol%), and TEMPO (93.8 mg, 2.0 equiv.). Then the dry MeCN (0.1 M) was added into the tube. The whole apparatus was assembled and irradiated by Blue LEDs (7 W) under room temperature. When finished, $PhCF_3$ (0.0812 mmol, 10 μL) was added for indicating the crude mixture from **^{19}F NMR** analysis. From the **^{19}F NMR** spectrum we found that the yield of **3a** was 7% (sharply decreased) and the yield of **7** was 23%.[13-14] This suggested that the generation of difluoromethylation radical in the reaction.

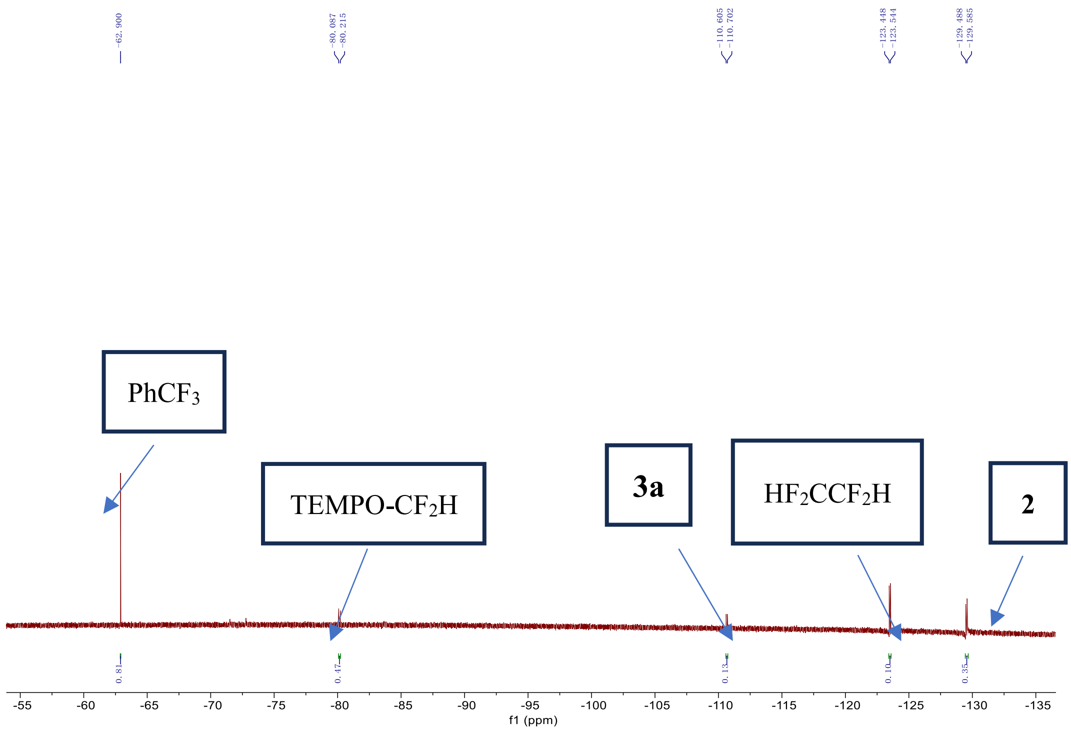


Figure S3. **^{19}F NMR** analysis of the crude mixture (TEMPO as the radical scavenger).

Characterization data of **7**: ^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm) -80.15 (d, J = 72.8 Hz, 2F). **HRMS**(ESI-TOF) Calcd for $C_{10}H_{20}F_2NONa$ $(M+2H)^+$ 209.2. Found 209.2.

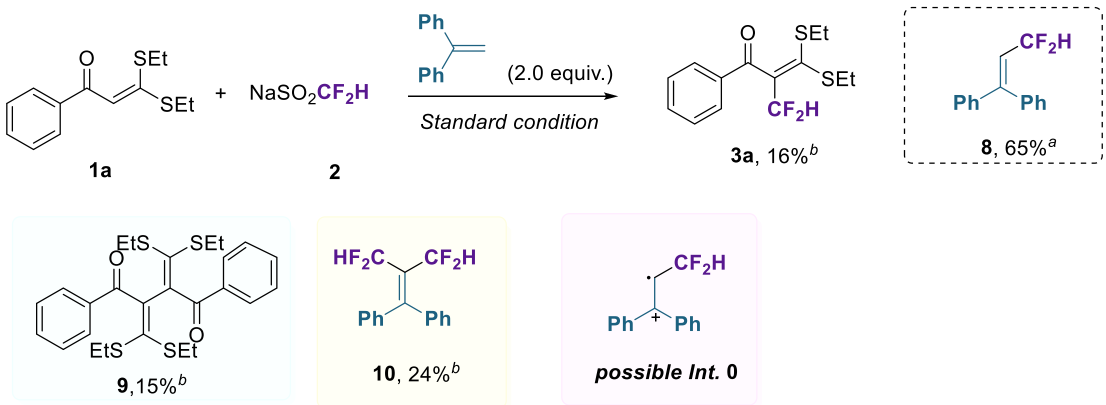
Note: Owing to the TEMPO containing tertiary amine sub-structure, the nitrogen atom could abstract a proton from [Co^{III}-H] species, viz. be pronated.[15]

b. 1, 1-diphenylethene

In a 15 mL glass tube added **1a** (76 mg, 0.3 mmol), **2** (207 mg, 5.0 equiv.), *fac*-Ir(ppy)$_3$ (9.8 mg, 5.0 mol%), [Co-9] (15.9 mg, 7.5 mol%). Then the dry MeCN (0.1 M) and 1,1-diphenylethene (35.3 μL, 2.0 equiv.) was added into the tube. The whole apparatus was assembled and irradiated by Blue LEDs (7 W) under room temperature. When finished, $PhCF_3$ (0.0812 mmol, 10 μL) was added for analysis. From the corresponding **^{19}F NMR**, we could note the generation of **8**[13] (**^{19}F yield**: 65%). However, we could not distinguish some peaks because they were not clearly apart from each other. Then we try to isolate them. Afterwards, we obtained the product **3a** (14.7 mg, 16%) and **10** (19.9 mg, 24%), and two **1a** molecules directly coupling product **9** (22.7 mg, 15%) (68% **1a** remained intact).

This might due to **1a** could be a stability factor for preventing the **Int-0** to back electron transfer (BET),[16] which could be of value to the radical controllable fluorine chain propagation (CFCE).[14]

However, when we attempted to use the **1ai** for stabling the distonic radical cation[16] (**Int-0**), which could be beneficial for the generation of **10**, we eventually failed. Therefore, the use of catalytic amount cobaloxime to replace the stoichiometric base commonly used to realize milder radical CFCE is of elegant future.



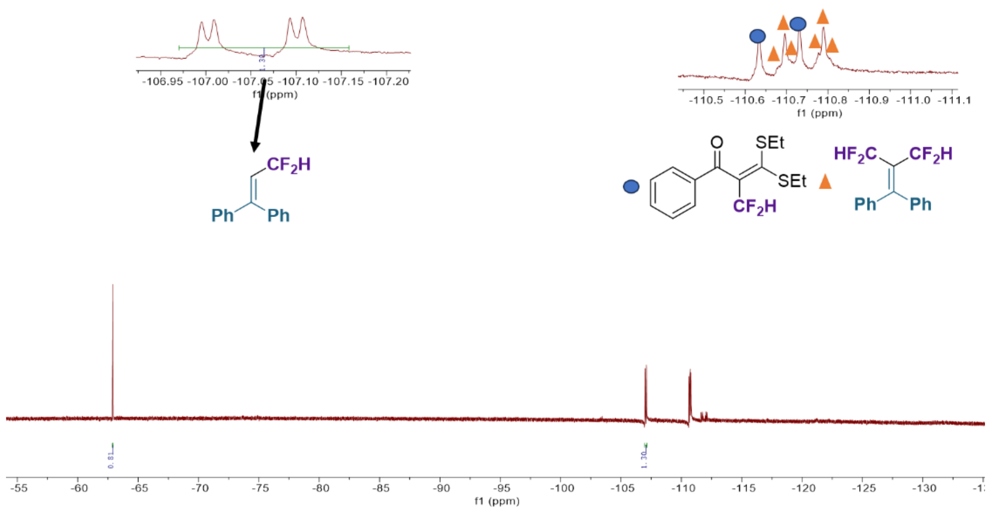


Figure S4. [19]F NMR analysis of the crude mixture (1,1-diphenylethene as the radical scavenger).

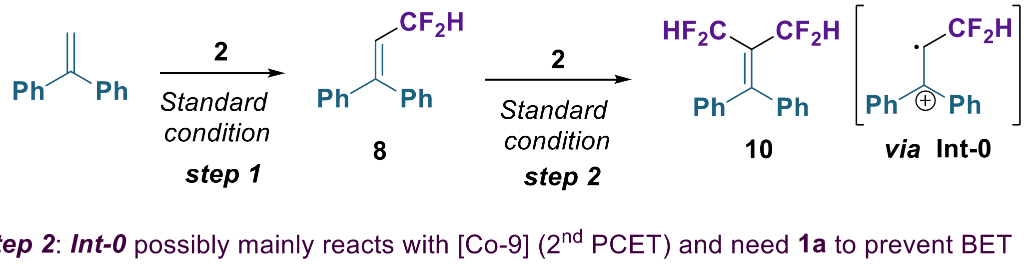


Figure S5 Possible pathway for the generation of **10**.

Characterization data of **8**: **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -107.05 (dd, J = 55.5, 7.9 Hz), **^{19}F yield**:65%. Characterization data were consistent with literature values.[13]

Characterization data of **10**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.44 – 7.37 (m, 6H), 7.21 (d, J = 7.2 Hz, 4H), 6.39 – 6.05 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 155.89 (t, J = 8.4 Hz), 137.61, 129.59, 128.48, 124.24 (t, J = 22.3 Hz), 113.46 (td, J = 238.7, 1.8 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -110.50 (dt, J = 52.9, 8.9 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{16}H_{12}F_4Na$ $(M+Na)^+$ 281.0875. Found 281.0940.

Characterization data of **9**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.91 (dd, J = 7.8, 1.2 Hz, 4H), 7.63 – 7.56 (m, 2H), 7.48 (t, J = 7.8 Hz, 4H), 2.97 (q, J = 7.2 Hz, 4H), 2.68 (q, J = 7.2 Hz, 4H), 1.35 (t, J = 7.2 Hz, 6H), 1.09 (t, J = 7.2 Hz, 6H). Characterization data were consistent with literature values.[17]

B. UV-vis spectra analysis

Amounts and concentrations of the components:

Components	1a	2	*fac*-Ir(ppy)$_3$	[Co-5]	[Co-9]
Amount(mol)	1.5×10^{-2}	2.0×10^{-4}	5.0×10^{-3}	1.0×10^{-5}	1.0×10^{-5}
Concentration(M)	1.5×10^{-4}	2.0×10^{-2}	5.0×10^{-5}	1.0×10^{-3}	1.0×10^{-3}

a. No Blue LEDs irradiation

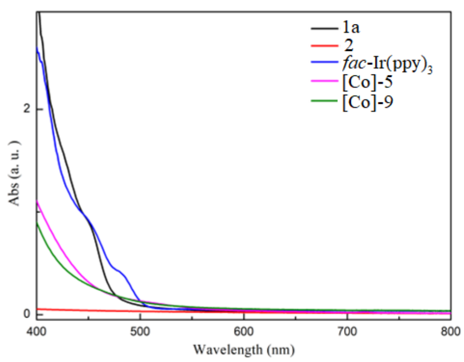


Figure S5. UV-Vis spectrum of each component (No Blue LED irradiation).

We could find that the *fac*-Ir(ppy)$_3$ was the best photosensitizer of the reaction.

b. With Blue LED irradiation

To demonstrate the cobaloxime could oxidize *fac*-Ir(ppy)$_3$, we executed the following measurement: mixing *fac*-Ir(ppy)$_3$ and **[Co-5]**(or **[Co-9]**) under air atmosphere, and the mixture was irradiated with Blue LEDs (15 W), stirring for several minutes. The aim was to monitor whether the [Co^I] could be generated (ca. 550 nm exists its absorption peak)[18]. Unfortunately, we failed to monitor **[Co-9]** being reduced to the corresponding [Co^I]. We could only see weak absorption peak in ca. 580 nm when using **[Co-5]**. Thus, we suggest that excited *fac*-Ir(ppy)$_3$ could be oxidized by **[Co-5]**(or **[Co-9]**). The weak new absorption peak might owe to the short irradiation time,

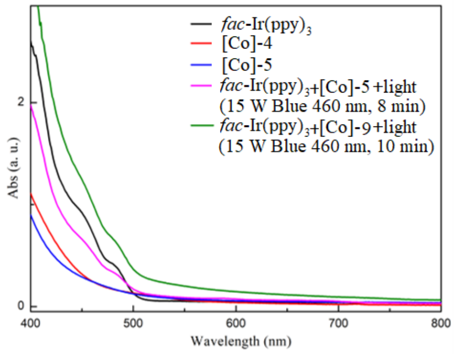


Figure S6. UV-Vis spectrum: *fac*-Ir(ppy)$_3$, [Co], and mixture (With Blue LED irradiation).

C. Emission quenching experiments

Emission intensities were recorded using Full-featured fluorescence spectroscopy system (Edinburgh FLS920P010404) at ambient temperature. All solutions of *fac*-Ir(ppy)$_3$ were excited at 365 nm and the emission intensity at 514 nm was observed. Firstly, the emission spectrum of a 5×10^{-5} M solution of *fac*-Ir(ppy)$_3$ in MeCN was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum was collected. The Stern-Volmer emission quenching studies telled us that the **[Co-9]** are easier than **[Co-5]** to quench the excited photosensitizer ([Ir^{IV}]), which both easier than **1a**.

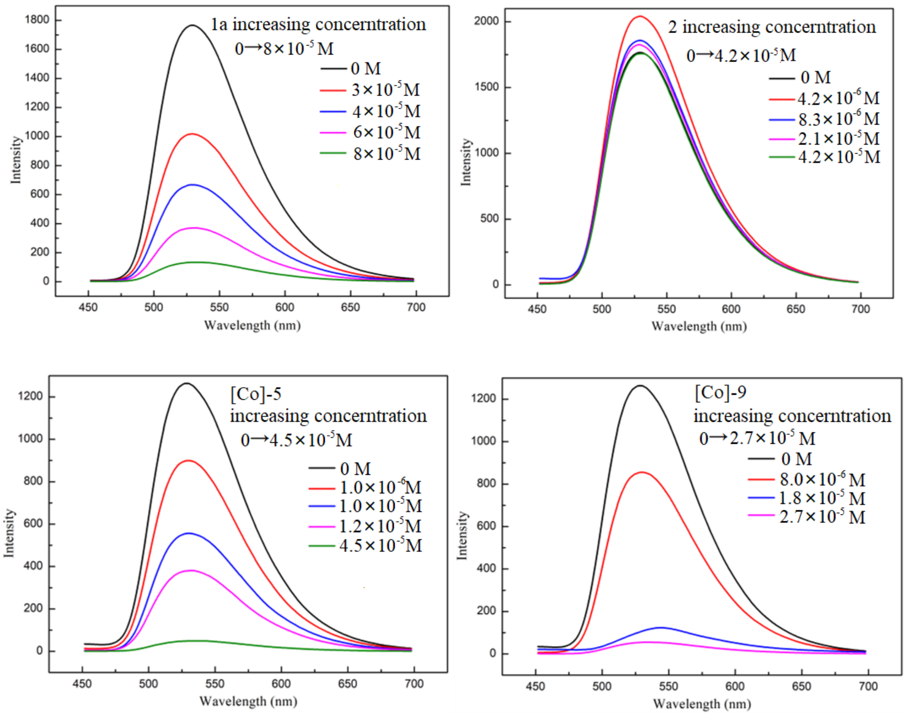


Figure S7. Emission quenching of *fac*-Ir(ppy)$_3$ with **1a**, **2**, [Co-5], [Co-9] in MeCN.

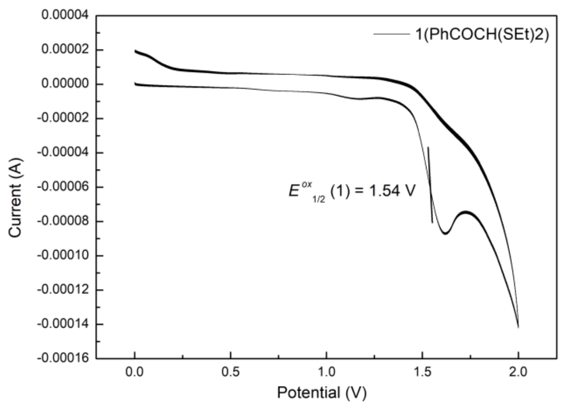
Table S7. Comparison: slope of the Stern-Volmer plots

Quencher	1a	2a	[Co-5]	[Co-9]
k_{sv} (1/nm)	2.05×10^5	2.94×10^3	6.04×10^5	1.14×10^6

D. Cyclic voltammetry (CV) experiments

A three-electrode system connected to an electrochemical station was used: (1) the reference electrode (Ag/AgCl in 0.1 M KCl); (2) a glassy carbon electrode as working electrode; (3) a Pt wire as counter electrode. All electrochemical measurements were performed in degassed dry MeCN under N_2 atmosphere.

The *fac*-Ir(ppy)$_3$ was in 5×10^{-2} M solution; others were in 3×10^{-2} M solution.



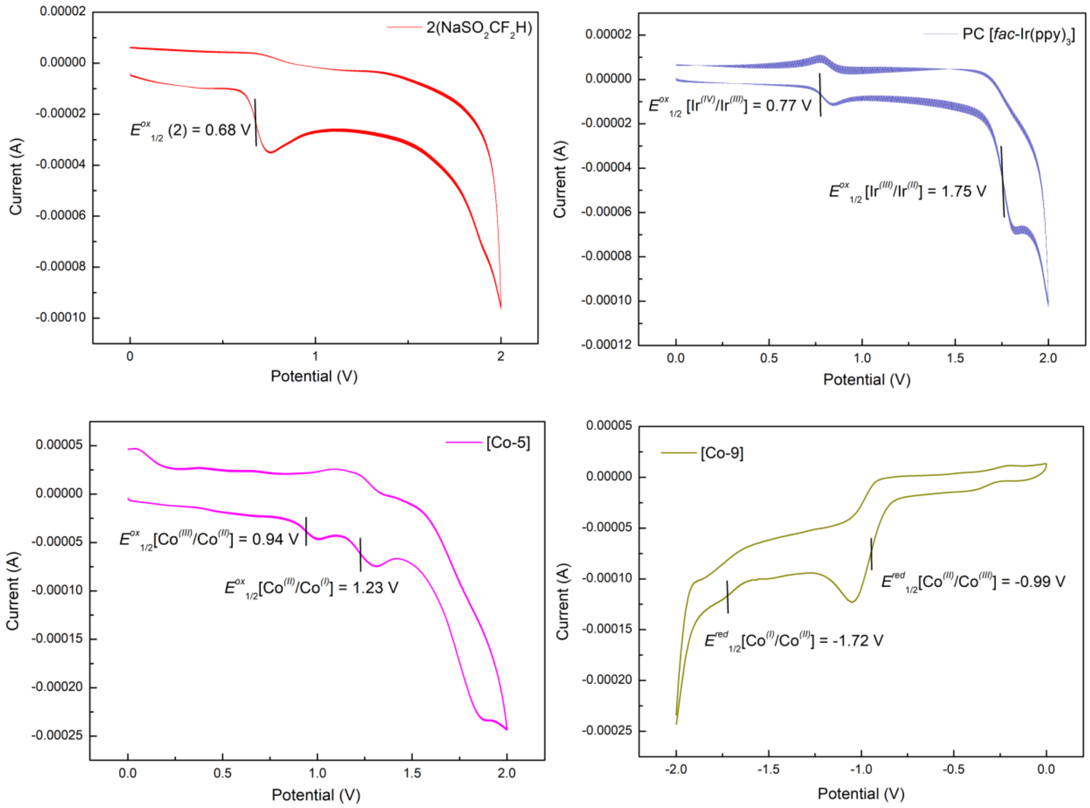


Figure S8. CV spectra in TBAPF$_6$ (0.1 M) in degassed MeCN with scan rate 100 mV/s.

Analysis:

a. $E^{ox}_{1/2}(2^-/2^\cdot)$ = 0.64 V vs SCE < $E^{ox}_{1/2}[\mathrm{Ir}^{(IV)}/\mathrm{Ir}^{(III)}]$ = 0.73 V vs SCE. Hence **2** could be oxidized by *fac*-Ir(ppy)$_3$.

b. $E^{ox}_{1/2}(O_2/O_2^{\cdot-})$ = 0.87 V, -0.87 V < -0.90 V (-0.94 V). Hence O_2 might help **[Co-5]** or **[Co-9]** turnover.[19]

c. According to literature reports:[20]

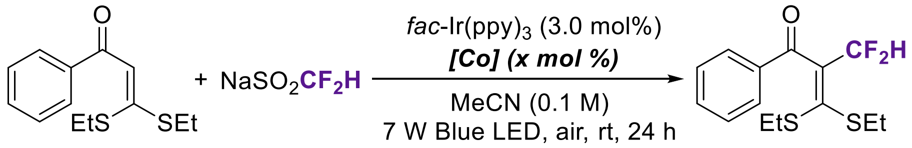
$$E_{0\text{-}0} = h\frac{c}{\lambda_{is}} = \frac{6.626 * 10^{-34}\ \mathrm{J{\cdot}s} * 2.998 * 10^{8}\ \mathrm{m{\cdot}s^{-1}}}{485 * 10^{-9}\ \mathrm{m} * 1.602 * 10^{-19}\ \mathrm{J{\cdot}eV^{-1}}} = 2.56\ \mathrm{eV}$$

$$E^{ox}_{1/2}[\mathrm{Ir}^{IV}/\,^{*}\mathrm{Ir}^{III}] = E^{ox}_{1/2}[\mathrm{Ir}^{IV}/\mathrm{Ir}^{III}] - E_{0\text{-}0} = -1.79\ \mathrm{V\ vs\ Ag/AgCl}$$

$$E^{ox}_{1/2}[\mathrm{Ir}^{IV}/\,^{*}\mathrm{Ir}^{III}] = -1.79\ \mathrm{V} - 0.039\ \mathrm{V} = -1.83\ \mathrm{V\ vs\ SCE}$$

Comparing relevant redox potentials, we suggest that the iridium photosensitizer could easily reduce [Co^{III}] to [Co^{II}], itself being oxidized to [Ir^{IV}].

E. Further reaction parameter analysis (necessity consideration)



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

Table S8. Further parameter considerations[j]

Entry	[Co] (mol %)	Atmo	Yield[b] (%)
60	[Co-3] (10.0)	Air	22
61	[Co-3] (10.0)	N_2	0
62	[Co-4] (10.0)	Air	56
63	[Co-4] (10.0)	N_2	21
64	[Co-5] (7.0)	Air	57
65	[Co-5] (7.0)	N_2	23
66[k]	[Co-5] (7.0)	N_2	40
67[l]	——	O_2	0
68	——	O_2	46

[j]Reaction conditions： **1a** (0.3 mmol), **2** (5.0 equiv.), *fac*-Ir(ppy)$_3$ (3.0 mol%), [Co] (*x* mol%), MeCN (0.1 M), 7 W Blue LED, air, rt, 24 h; [b]Yields were determined by ^{19}F NMR analysis using PhCF$_3$ as the internal standard; [k]Add PhNO$_2$ (1.0 equiv.); [l]**2** (2.5 equiv.)。

a. For the comparison of [Co^{II}] & [Co^{III}]: The latter might be more efficient, possibly owing to their photo-stabilities, quenching efficiencies and redox potentionals.[7-9, 18]

b. For the comparison of reaction atmosphere, we could conclude that:

i) Air was superior to O_2, and O_2 was superior to N_2.

ii) Air was superior to add another oxidant under N_2 atmosphere.

These phenomena might due to the product **3a** was tend to hydrolyse,[21-22] where O_2 terminally turned into H_2O[13]. Meantime, H_2O could also ruin **2** for effectively generating sufficient ·CF_2H[23].

F. Possible side reactions (Take 1m as example)

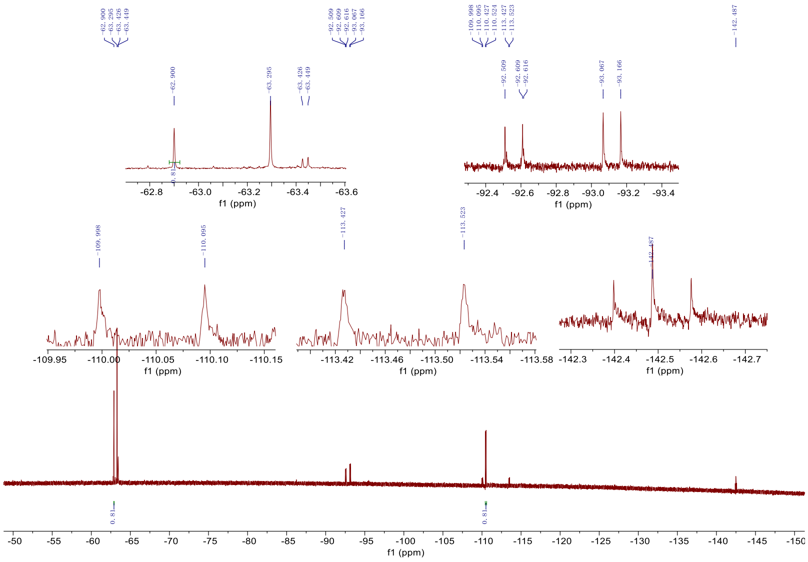
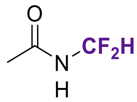
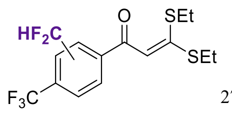
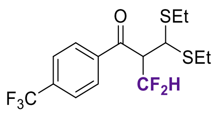


Figure S9. Crude **^{19}F NMR** peak identification (take **1m** as example).

According to reported literature, we defer the peaks to the corresponding side reactions (see below).

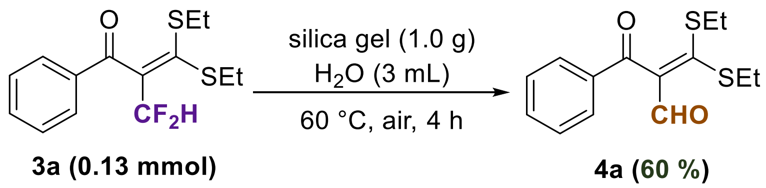
Table S9. Peak identifications

δ (ppm)	Identifications
-62.90 (s)	$PhCF_3$
-63.30 (s)	CF_3 in **3m**
-63.44 (d, *J* = 12.7 Hz, 1F), -93.12 (d, J = 56.4 Hz, 1F)	2F of [Co]-CF_2H[24] (ligand exchange)[25]
-92.58 (dt, *J* = 56.6, 5.6 Hz, 2F)	 26
-110.05 (d, *J* = 55.2, 2F)	 27
-110.48 (d, *J* = 55.0 Hz, 2F)	CF_2H in **3m**
-113.48 (dd, *J* = 54.3, 1.3 Hz, 2F)	 28
-142.49 (t, *J* = 50.5 Hz, 2F)	CF_2H_2[29]

We noticed the generation of CF_2H_2 during the reaction[29]. Thus, we conclude that ·CF_2H might be a short-living radical (non-persistent radical)[30-31].

V. Downstream Applications

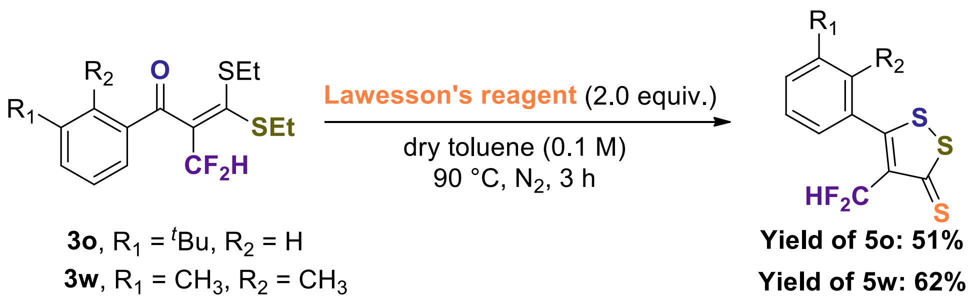
A. converted to aldehyde (hydrolysis)



In a 25 mL round bottom flask, fresh **3a** was added, followed by silica gel (1.0 g), which was rinsed with 3 mL water. Afterwards, it was heated under 60 ℃ oil bath for 4 h. When finished, the crude mixture was poured into saturated $NaHCO_3$ aqueous (10 mL), and quickly distracted by DCM (5 mL×3). Then the solvent was evaporated and the residue was purified via flash column chromatography (PE/EA = 30/1 to 4/1) to obtain target aldehyde **4a** (21.7 mg, 60%).

4a: 2-benzoyl-3,3-bis(ethylthio)acrylaldehyde: light yellow oil (21.7 mg, 60%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 10.24 (s, 1H), 7.83 (dd, J = 7.8, 1.2 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H), 3.05 – 2.82 (m, 4H), 1.39 – 1.14 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 194.0, 186.9, 161.6, 144.3, 136.2, 133.7, 129.2, 128.6, 29.5, 14.8. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{16}NaO_2S_2$ $(M+Na)^+$ 303.0484. Found 303.0477.

B. cyclization to 3*H*-1,2-dithio-2-thione(s)



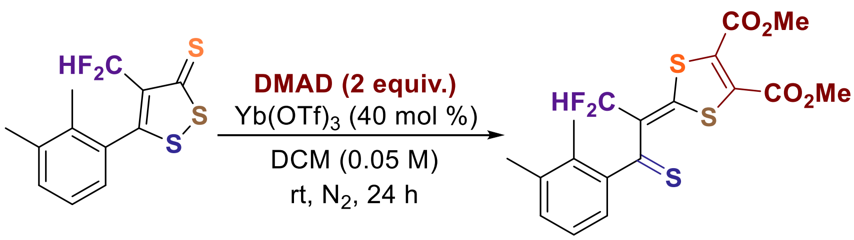
In a glove box (N_2) to a 15 mL pressure tube, fresh **3** (75.9 mg, 0.23 mmol), Lawesson's reagent (94.0 mg, 2.0 equiv) and dry toluene (3 mL, ca. 0.1 M versus **3**) was added. Then the whole system was transferred to an 90 ℃ oil bath, refluxing for 3 h. After the reaction completed, the toluene was evaporated and the residue was purified by column chromatography (PE/EA = 130/1 to 125/1) to get **5w** (41.1 mg, 62%).[32-36]

5w: 4-(difluoromethyl)-5-(2,3-dimethylphenyl)-3*H*-1,2-dithiole-3-thione: bright orange solid (41.1 mg, 62%). mp: 113-114 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.30 (dd, J = 7.2, 1.8 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.72 (t, J = 53.4 Hz, 1H), 2.34 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 213.4 (t, J = 5.0 Hz), 177.8, 137.9, 137.3 (t, J = 22.8 Hz), 135.0, 132.4, 129.2, 126.9, 125.5, 112.2 (t, J = 241.5 Hz), 20.2, 17.0 (d, J = 2.1 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -116.37 (dd, J = 309.3, 53.4 Hz, 1F), -119.25 (dd, J = 309.4, 53.4 Hz, 1F). **HRMS** (ESI-TOF) Calcd for $C_{12}H_{11}F_2S_3$ $(M+H)^+$ 288.9985. Found 288.9985.

Procedures to obtain **5o** is similar to that of **5w**: Using **3o** (60.9 mg, 0.17 mmol), and get **5o** (27.3 mg, 51%).

5o: 5-(3-(*tert*-butyl)phenyl)-4-(difluoromethyl)-3*H*-1,2-dithiole-3-thione: bright orange solid (27.3 mg, 51%). mp: 108-109 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.65 (d, J = 1.8 Hz, 1H), 7.61 (ddd, J = 5.4, 3.6, 1.8 Hz, 1H), 7.46 – 7.42 (m, 2H), 6.85 (t, J = 53.4 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 213.7 (t, J = 5.3 Hz), 178.2, 152.2, 135.7 (t, J = 23.2 Hz), 130.4, 128.9, 128.6, 125.9 (t, J = 2.3 Hz), 125.6 (t, J = 1.7 Hz), 112.6 (t, J = 241.7 Hz), 34.9, 31.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -114.52 (d, J = 53.5 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}F_2S_3$ $(M+H)^+$ 317.0298. Found 317.0294.

C. further transformation



5w (0.15 mmol) **6w** (44%)

In a glove box (N_2) to a 25 mL round bottom flask, fresh 5**w** (43.2 mg, 0.15 mmol), DMAD (37.0 μL, 2.0 equiv.), anhydrous Yb(OTf)$_3$ (37.2 mg, 40 mol%) were added sequentially. Then dry DCM (4 mL) was added, and the flask was tightly sealed. Removing the flask out of the glove box and stirring overnight. After 24 h, the DCM was evaporated. The residue was purified by column chromatography (PE/EA = 20/1 to 4/1). Evenetually, we obtained **6w** (28.5 mg, 44%)[37].

6w: dimethyl 2-(1-(2,3-dimethylphenyl)-3,3-difluoro-1-thioxopropan-2-ylidene)-1,3-dithiole-4,5-dicarboxylate: dark green solid (28.5 mg, 44%). mp: 121-122 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 7.18 – 7.08 (m, 2H), 6.90 (d, J = 7.2 Hz, 1H), 6.53 (t, J = 53.4 Hz, 1H), 3.99 (m, 6H), 2.29 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) 213.3 (t, J = 4.7 Hz), 166.7, 160.2, 159.1, 146.1, 137.73, 133.5 (t, J = 3.6 Hz), 131.3, 130.8, 129.9, 126.4 (t, J = 21.4 Hz), 125.8, 123.8, 114.7 (t, J = 240.8 Hz), 54.0, 53.9, 20.3, 16.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (ppm) -115.07 (dd, J = 103.0, 53.7 Hz, 2F). **HRMS** (ESI-TOF) Calcd for $C_{18}H_{17}F_2O_4S_3$ $(M+H)^+$ 431.0252. Found 431.0247.

VI. Crystal Datas of Compound 5w

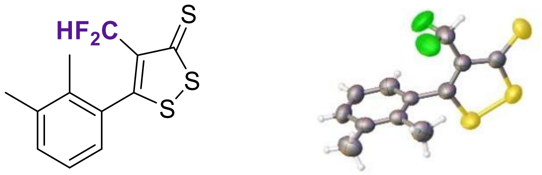


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Table S10. Crystallographic data and structural refinement for **5w**

Empirical formula	$C_{14}H_{16}F_2S_3$
Formula weight	288.38
Crystal system	monoclinic
Space group	P-1
a (Å)	11.9779 (9)
b (Å)	8.2686 (6)
c (Å)	13.1934 (10)
α (deg)	90
β (deg)	98.869(5)
γ (deg)	90
Volume (Å^3)	1291.06

Z	4
Calculated density (mg/m^3)	1.484
Absorption coefficient (mm^{-1})	5.264
F(000)	592.0
Theta range for data collection (deg)	3.735 to 64.091
Reflections collected/unique	10789/2112
Goodness-of-fit on F^2	1.089
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0543, WR2 = 0.1998
R indices (all data)	R1 = 0.0693, WR2 = 0.2179

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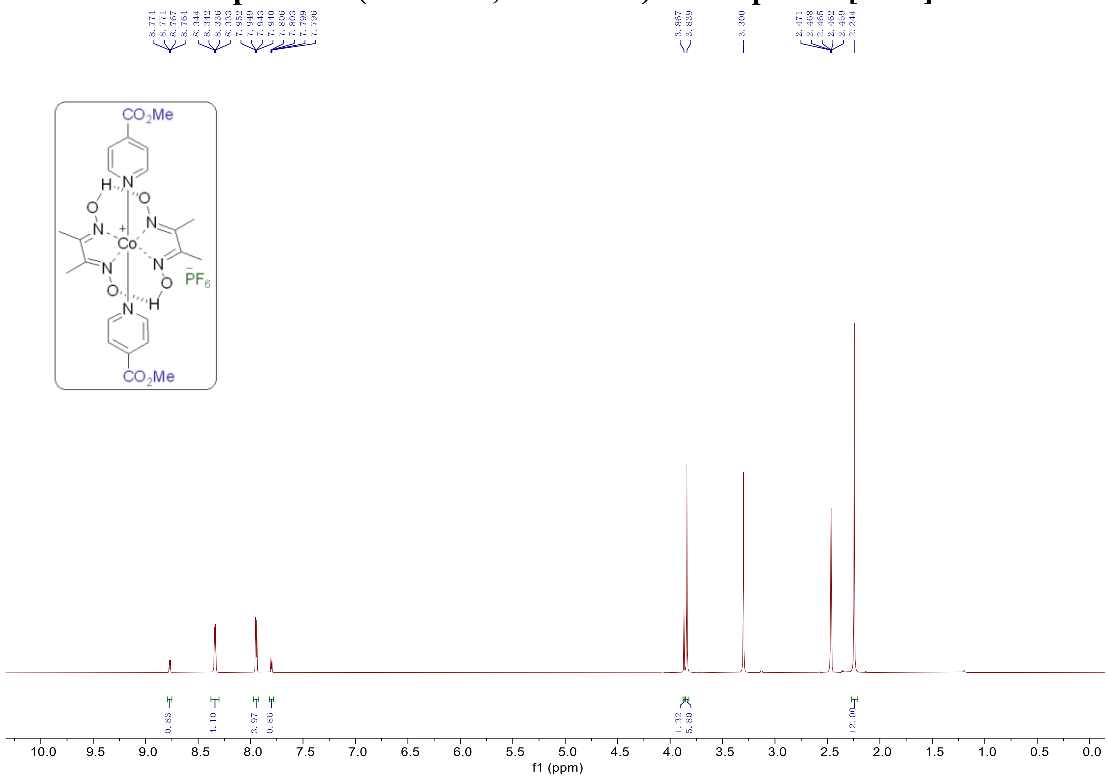
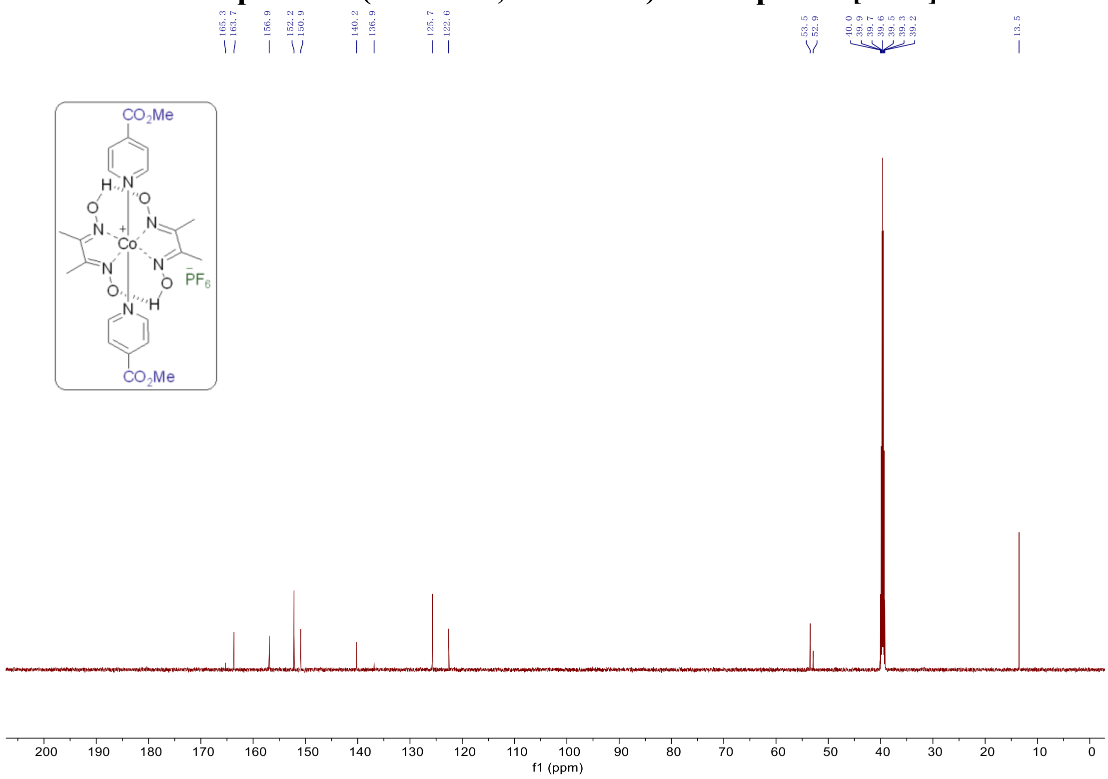
VIII. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

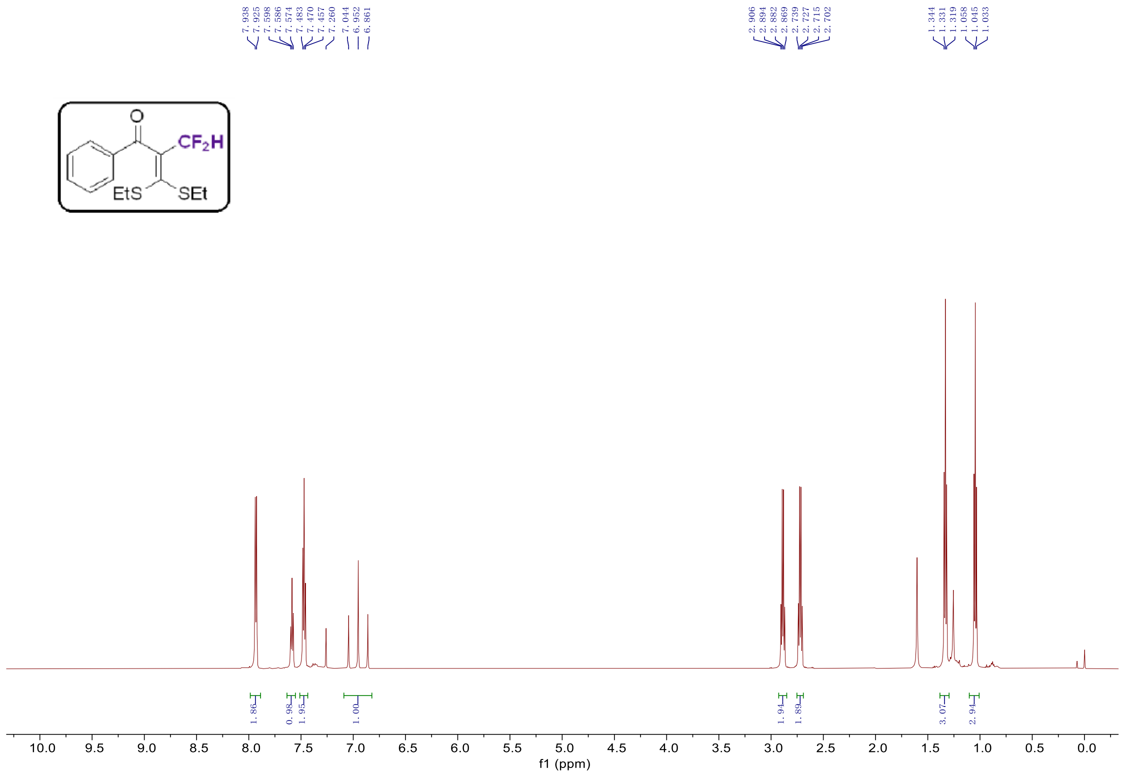
^{1}H spectrum (600 MHz, DMSO-d_6) of compound [Co-9]



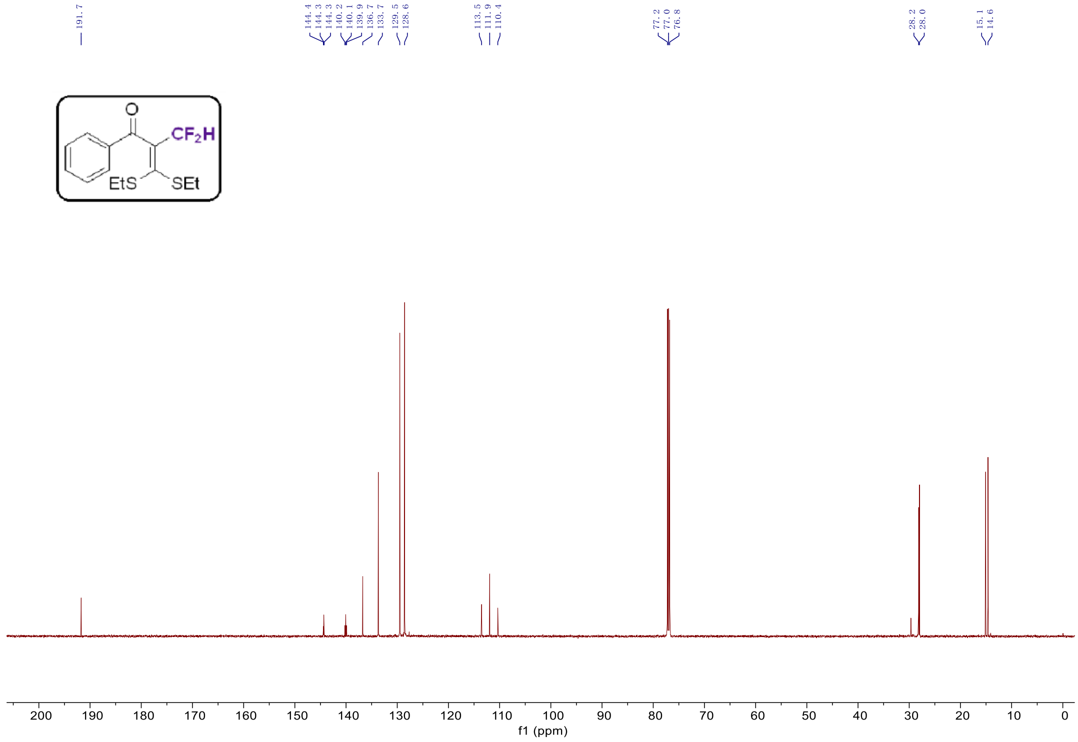
^{13}C spectrum (151 MHz, DMSO-d_6) of compound [Co-9]



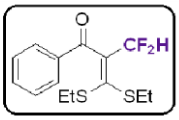
[1]H spectrum (600 MHz, CDCl3) of compound 3a

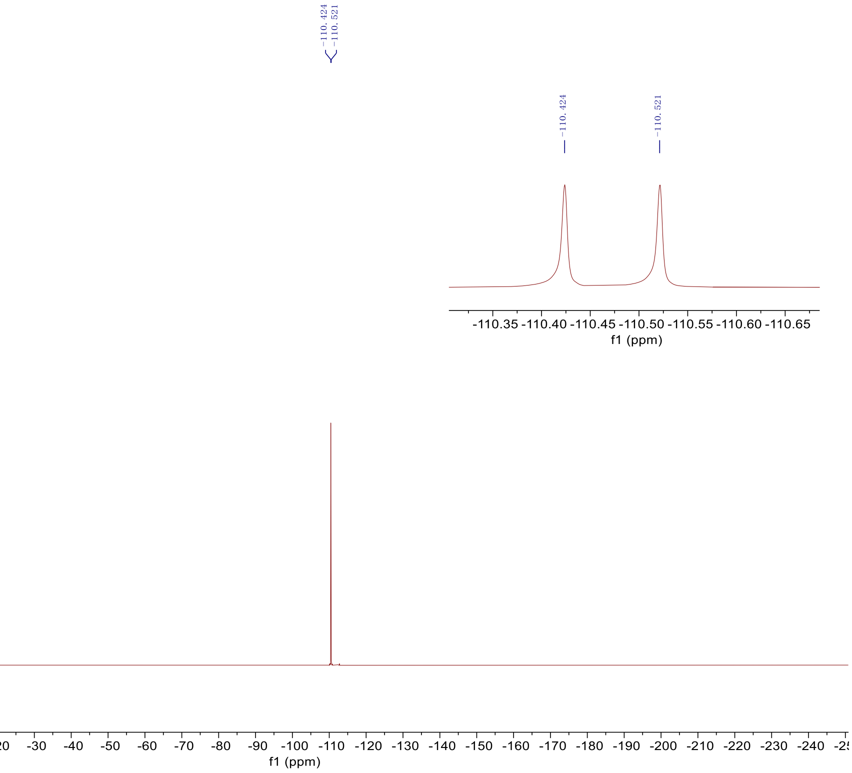


[13]C spectrum (151 MHz, CDCl3) of compound 3a

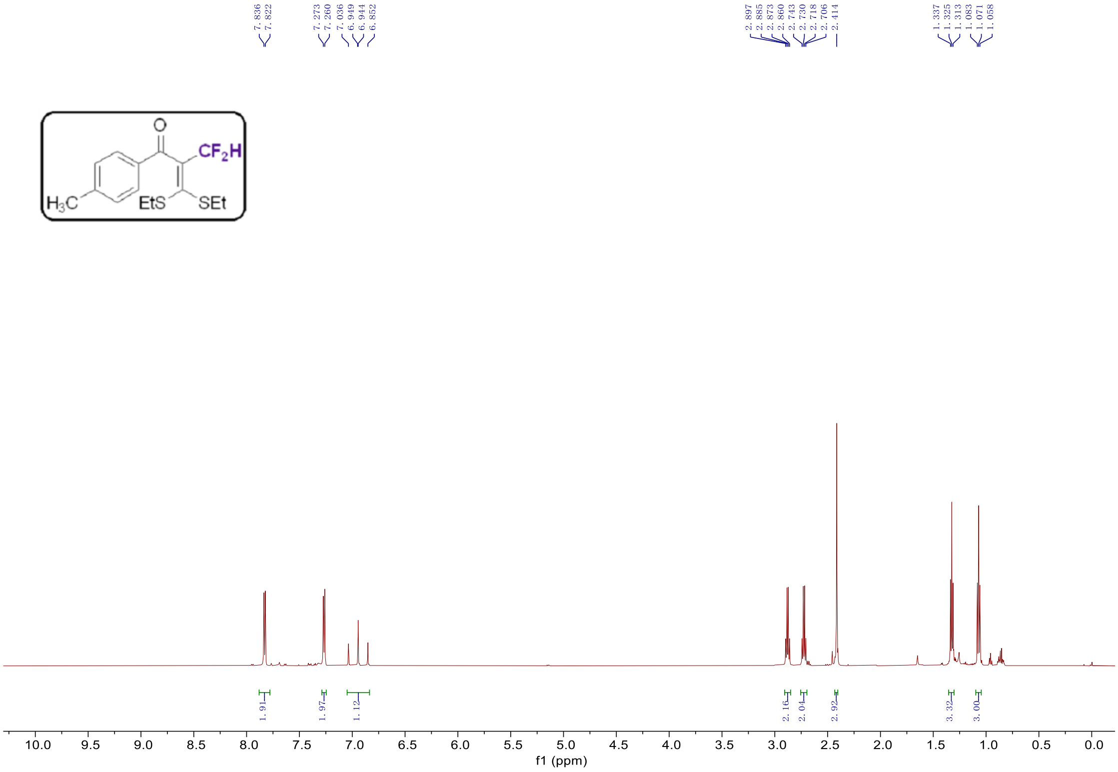


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3a

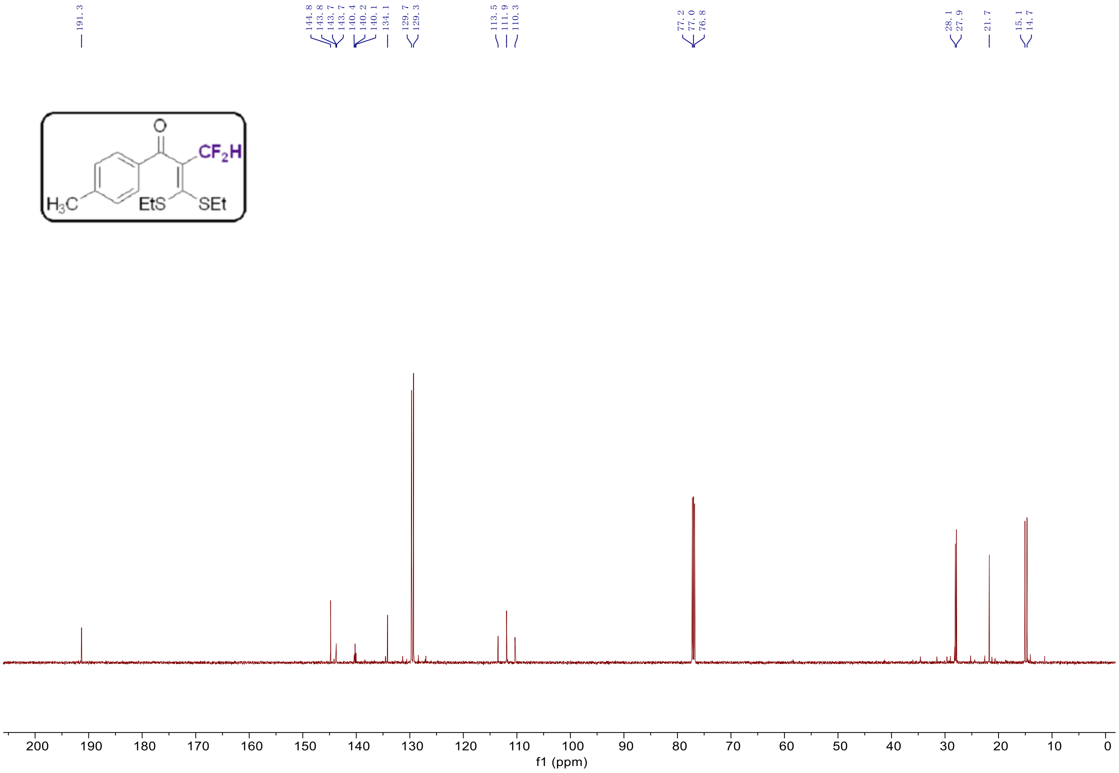




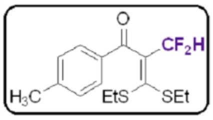
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3b

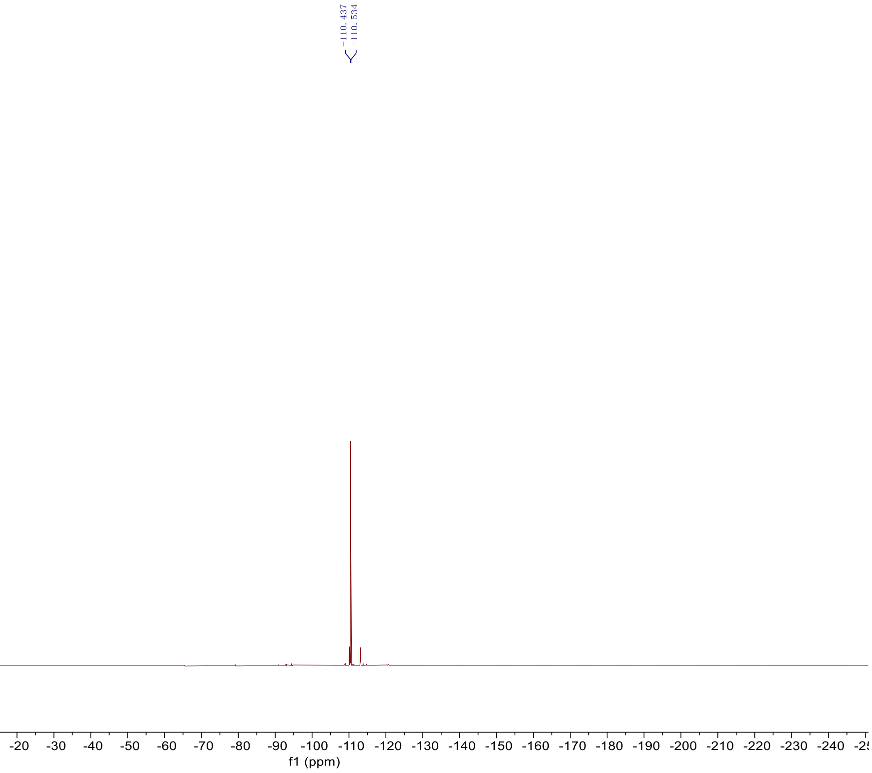


^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3b

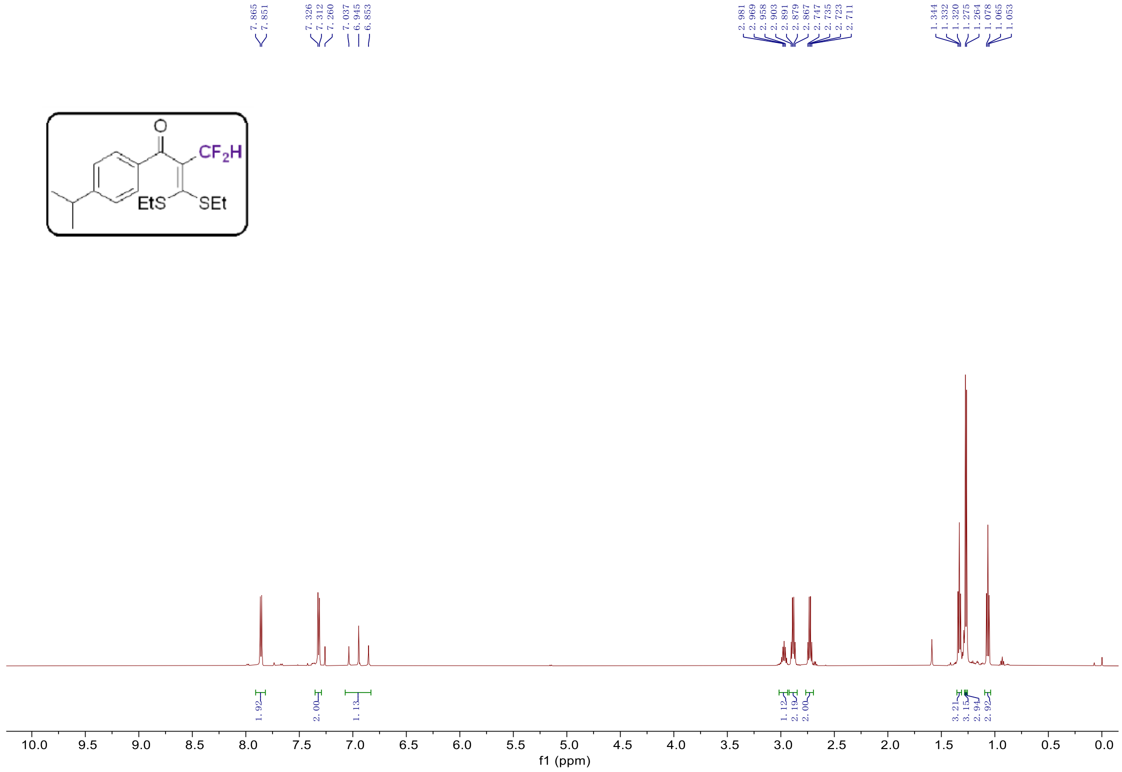


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3b

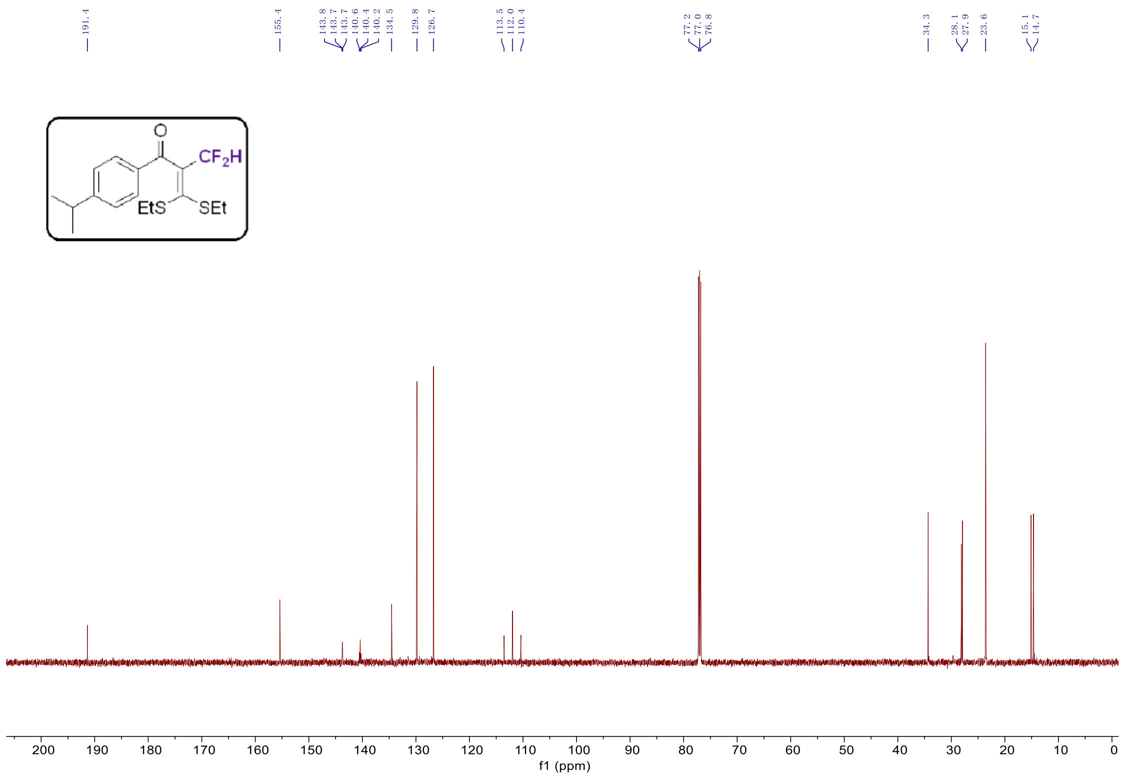




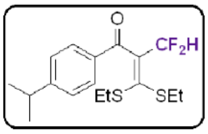
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3c

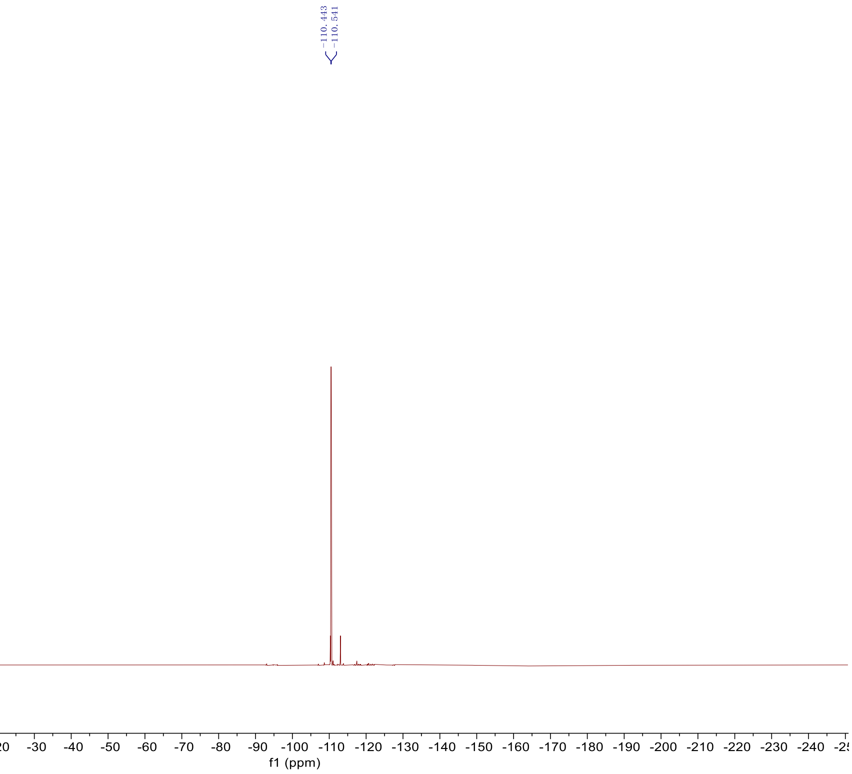


^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3c

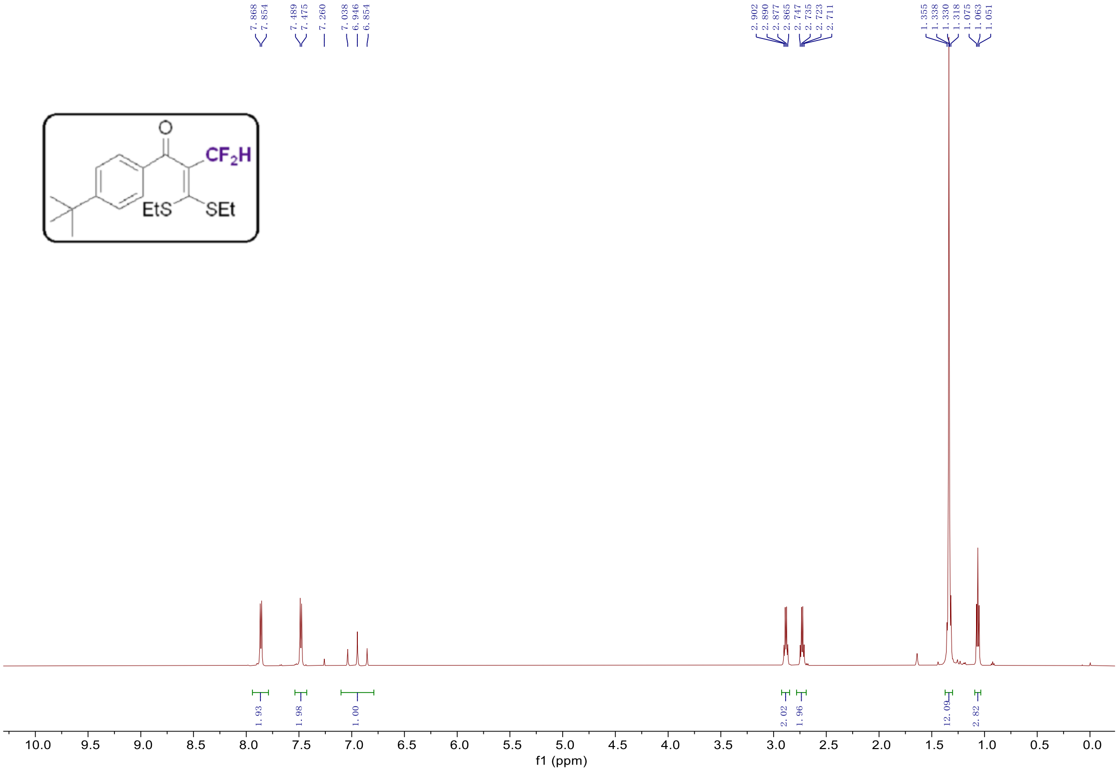


[19]F spectrum (565 MHz, $CDCl_3$) of compound 3c

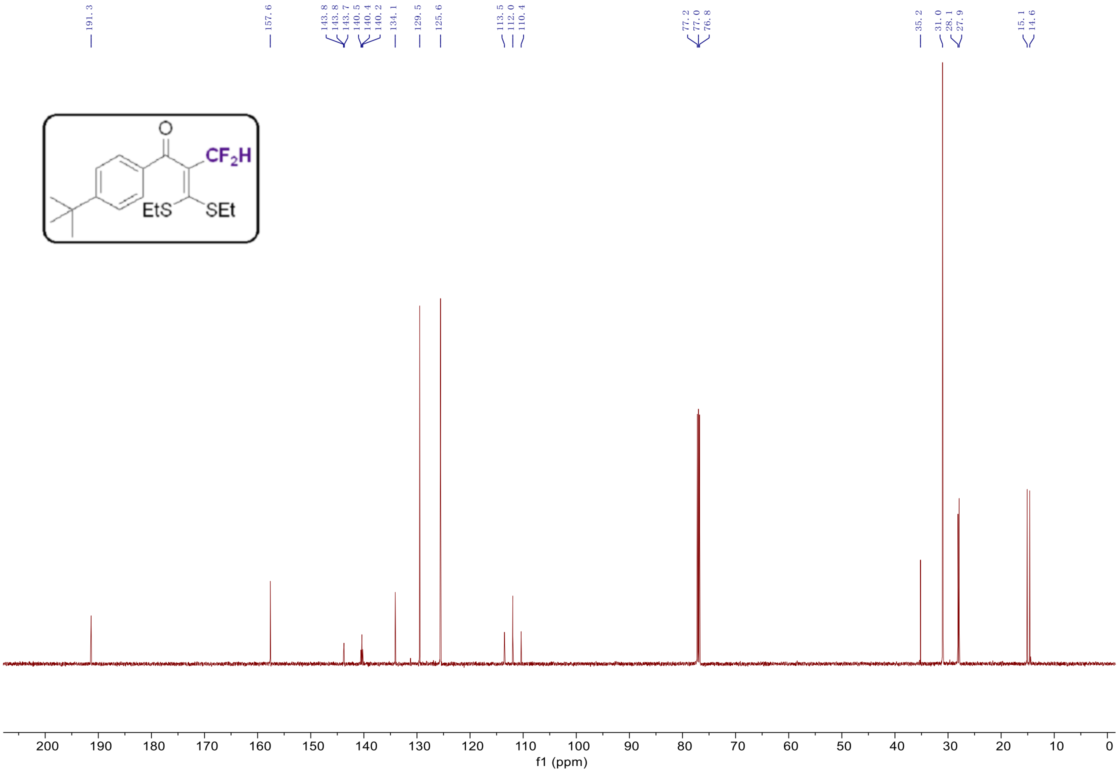




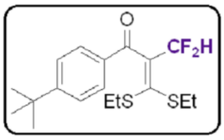
^{1}H spectrum (600 MHz, CDCl₃) of compound 3d

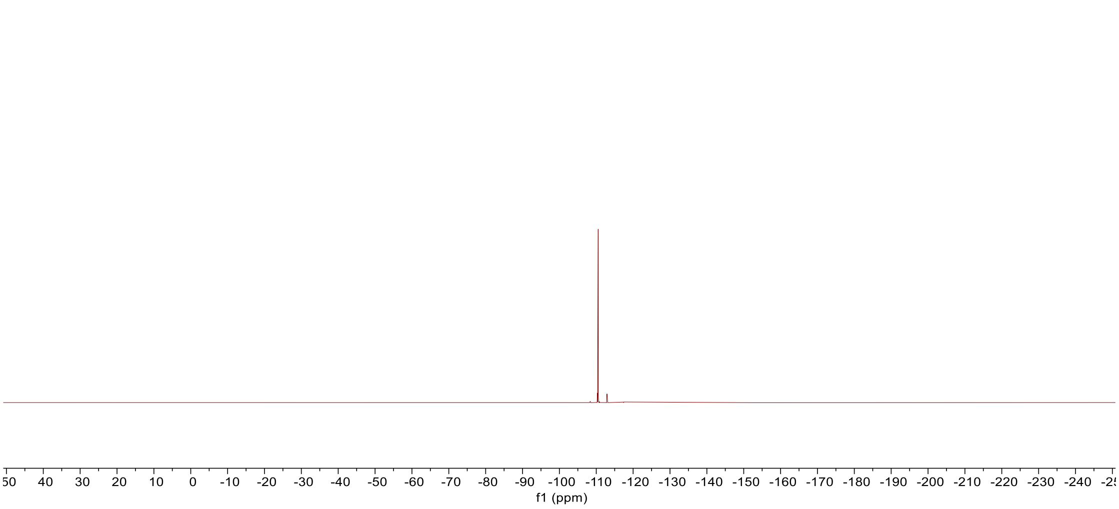


^{13}C spectrum (151 MHz, CDCl₃) of compound 3d

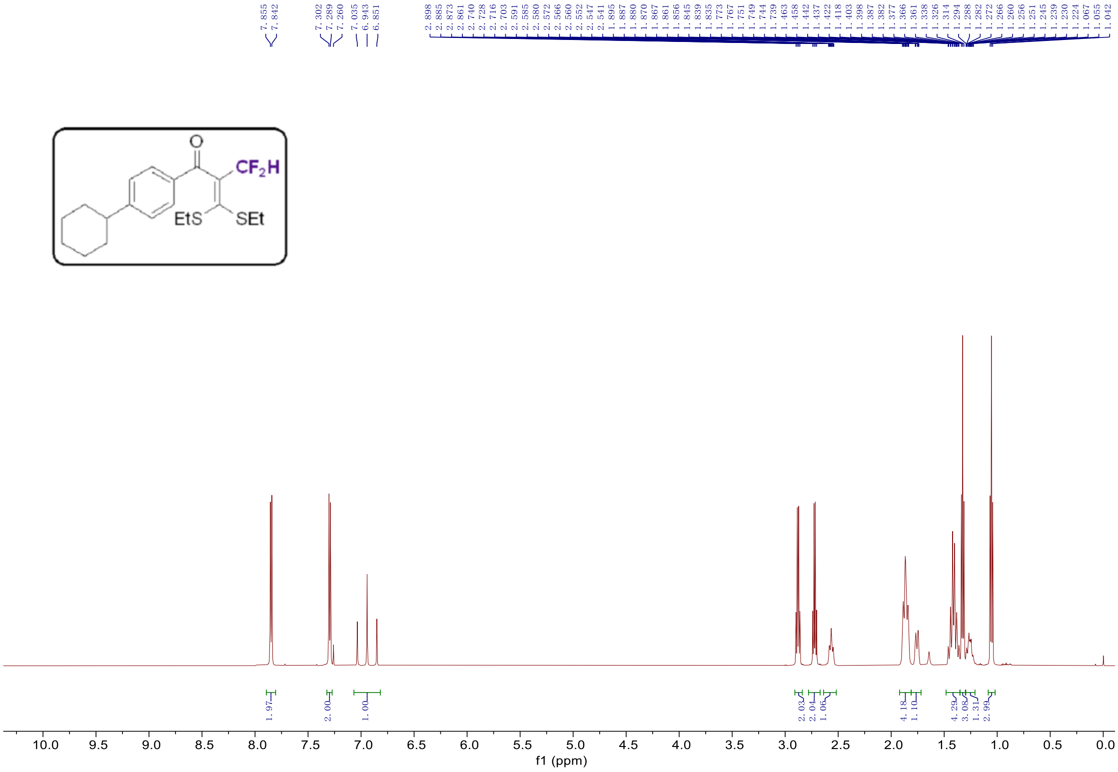


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3d

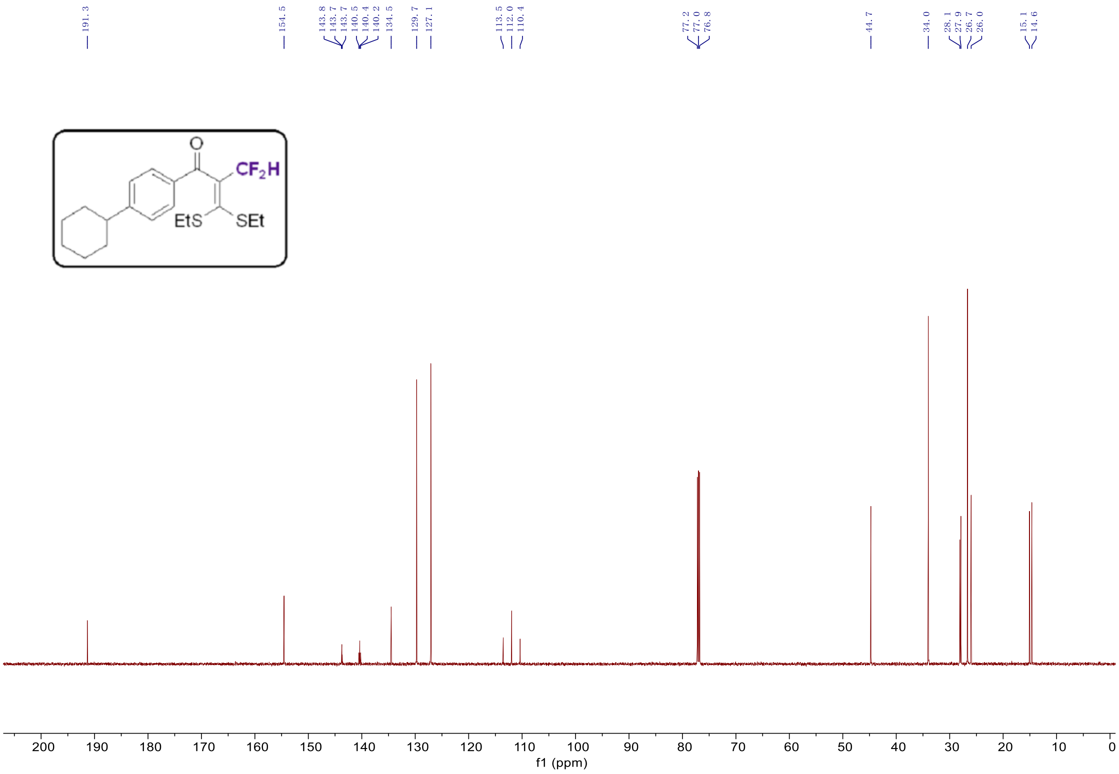




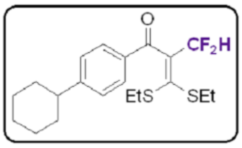
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3e

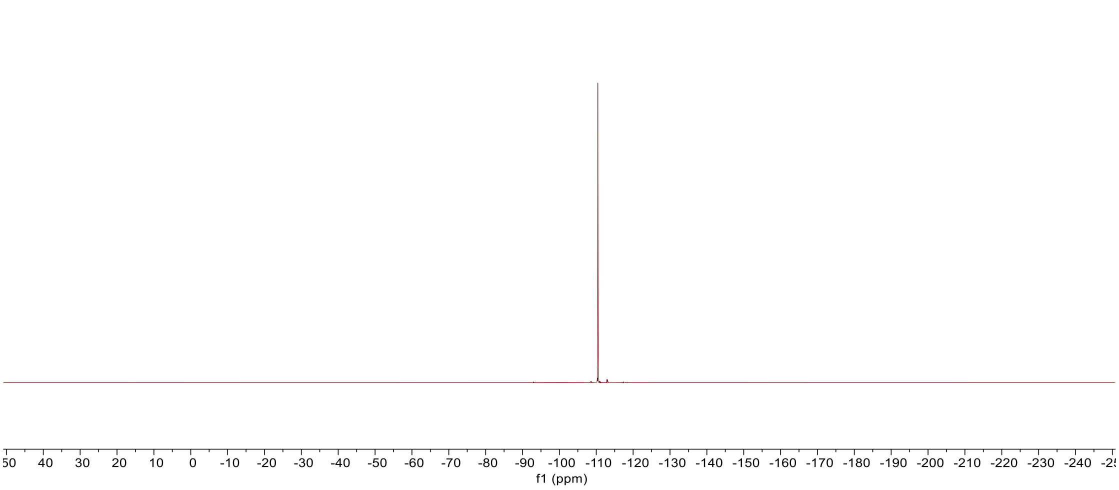


^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3e



[19]F spectrum (565 MHz, $CDCl_3$) of compound 3e





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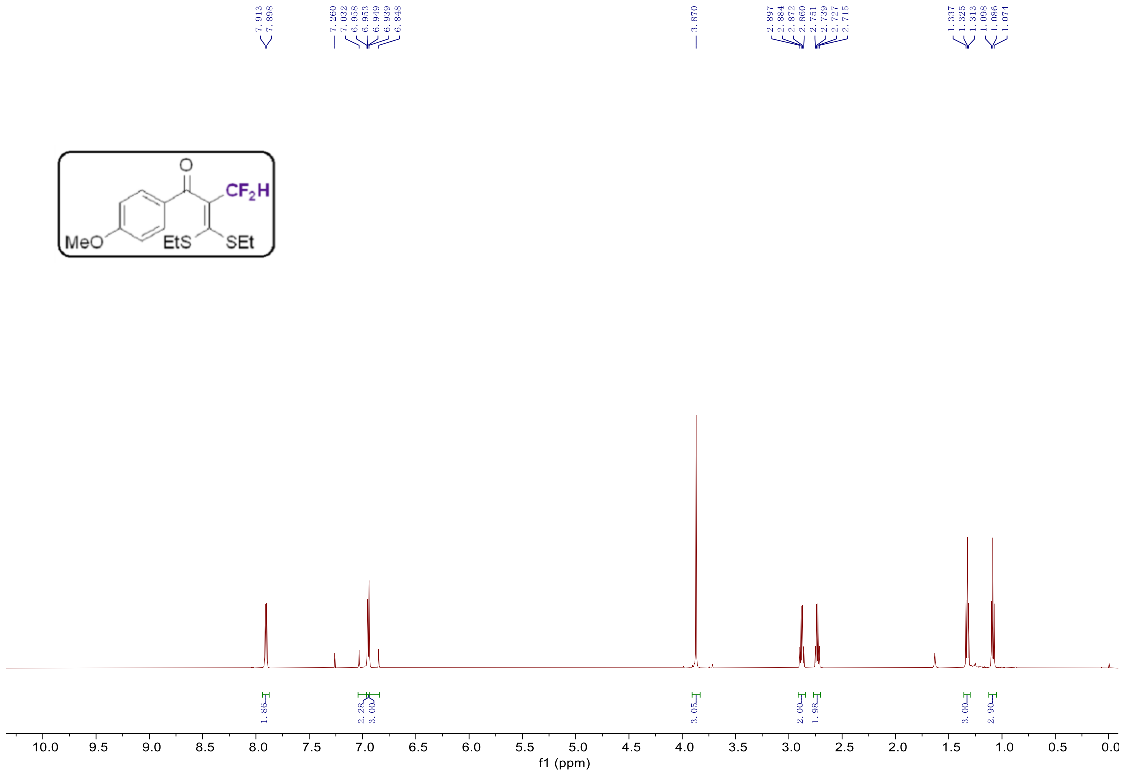
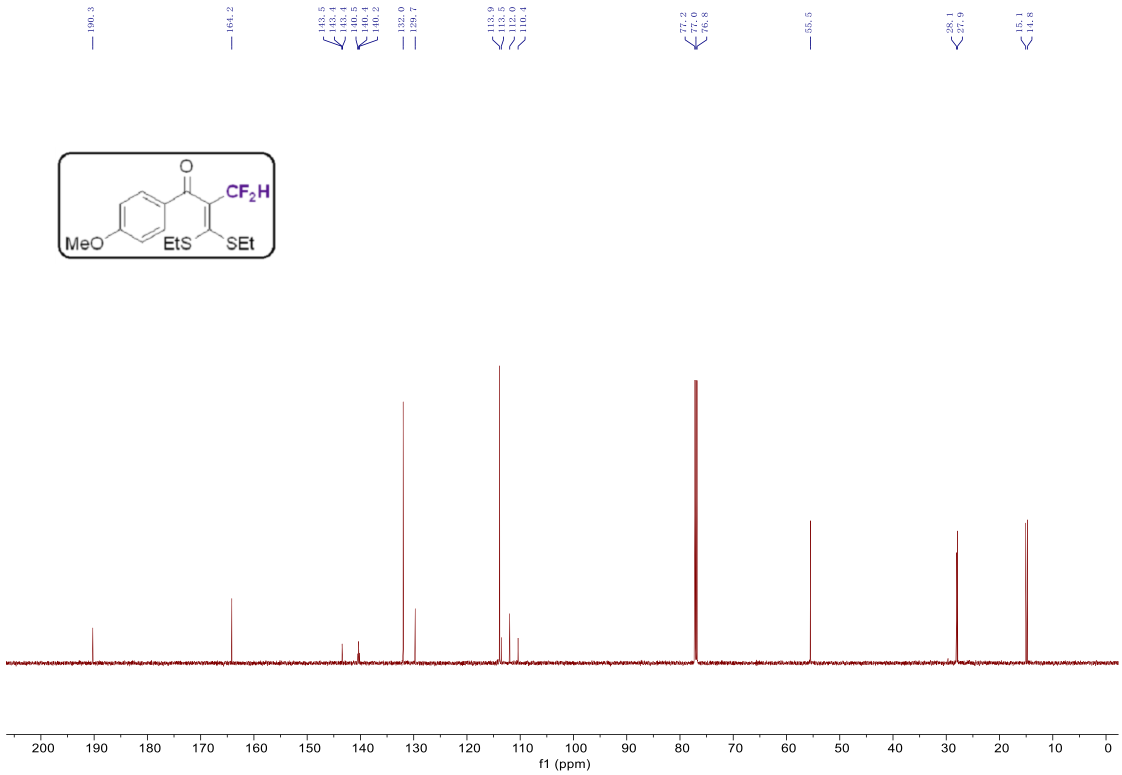
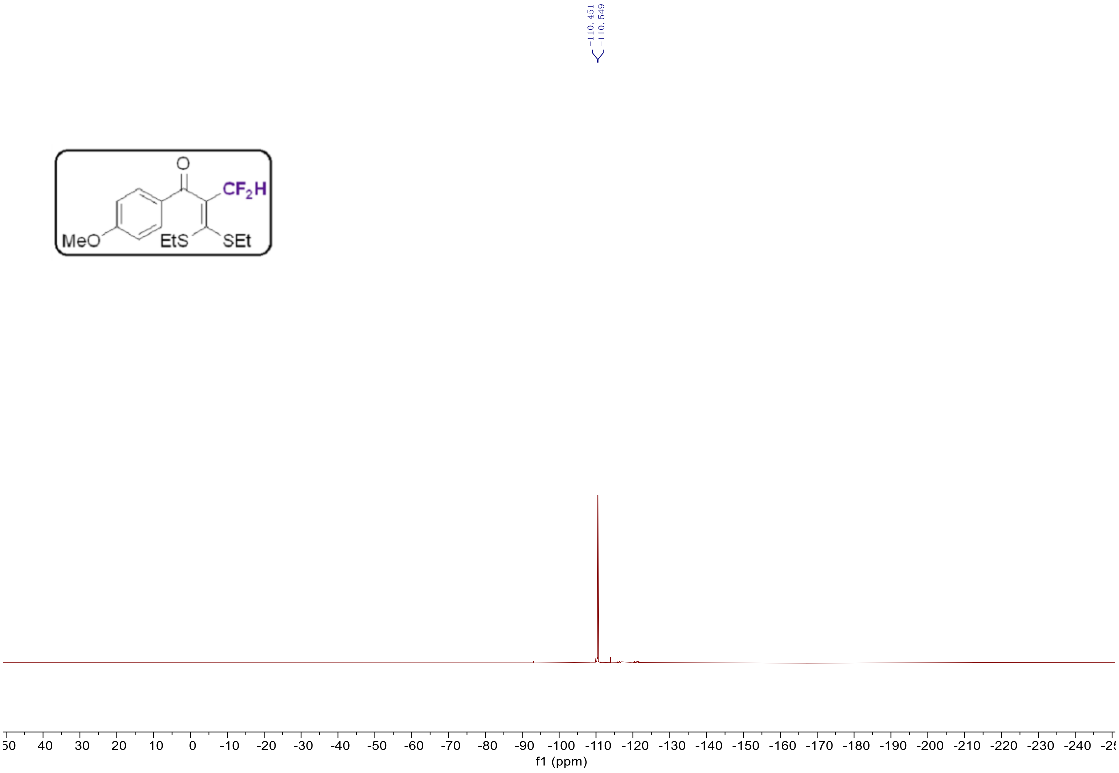


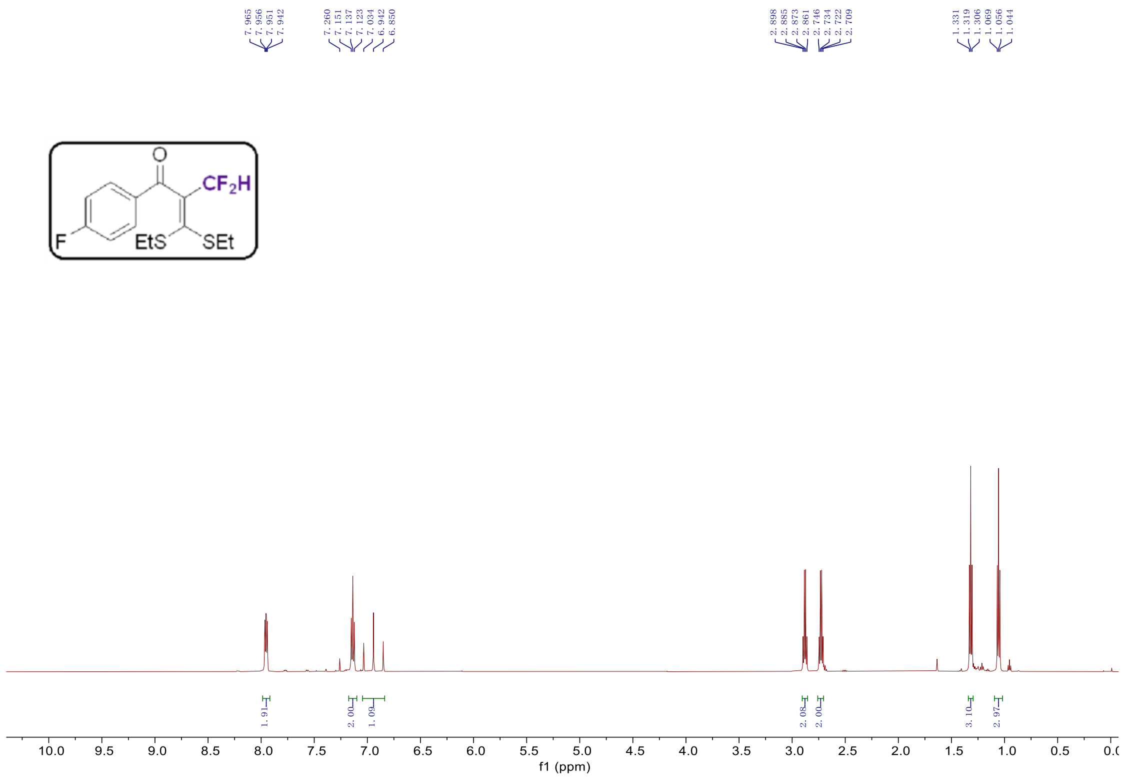
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3f



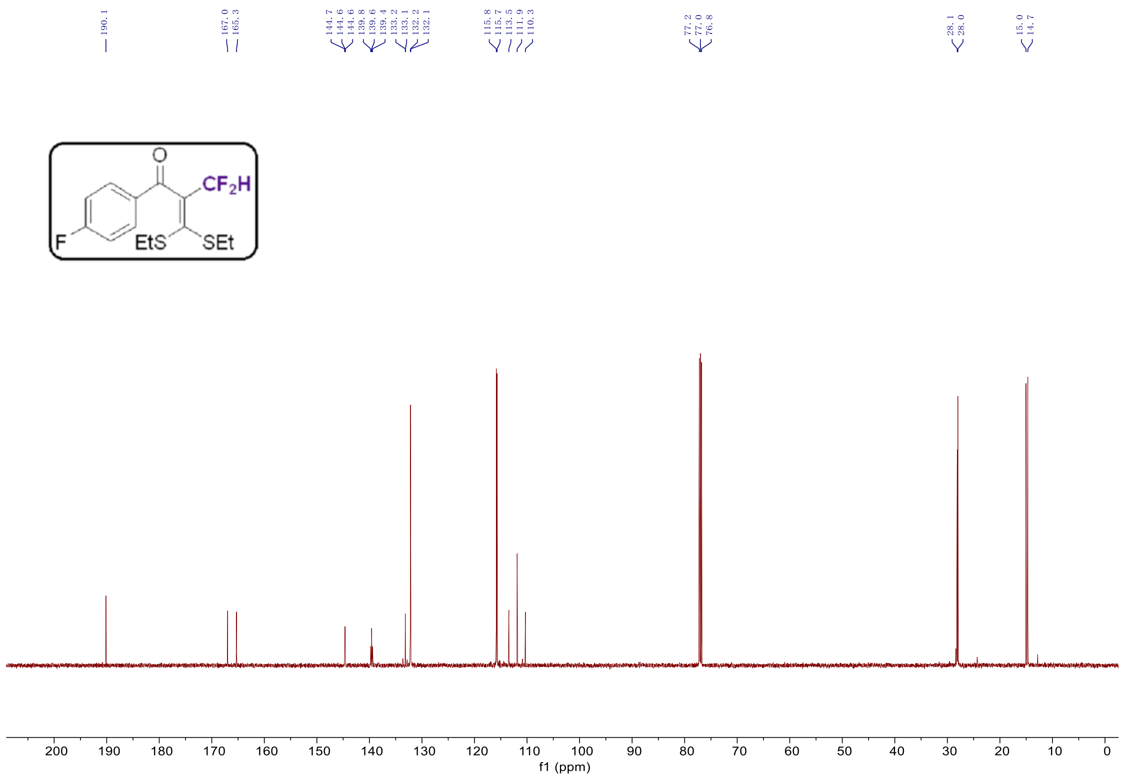
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3f



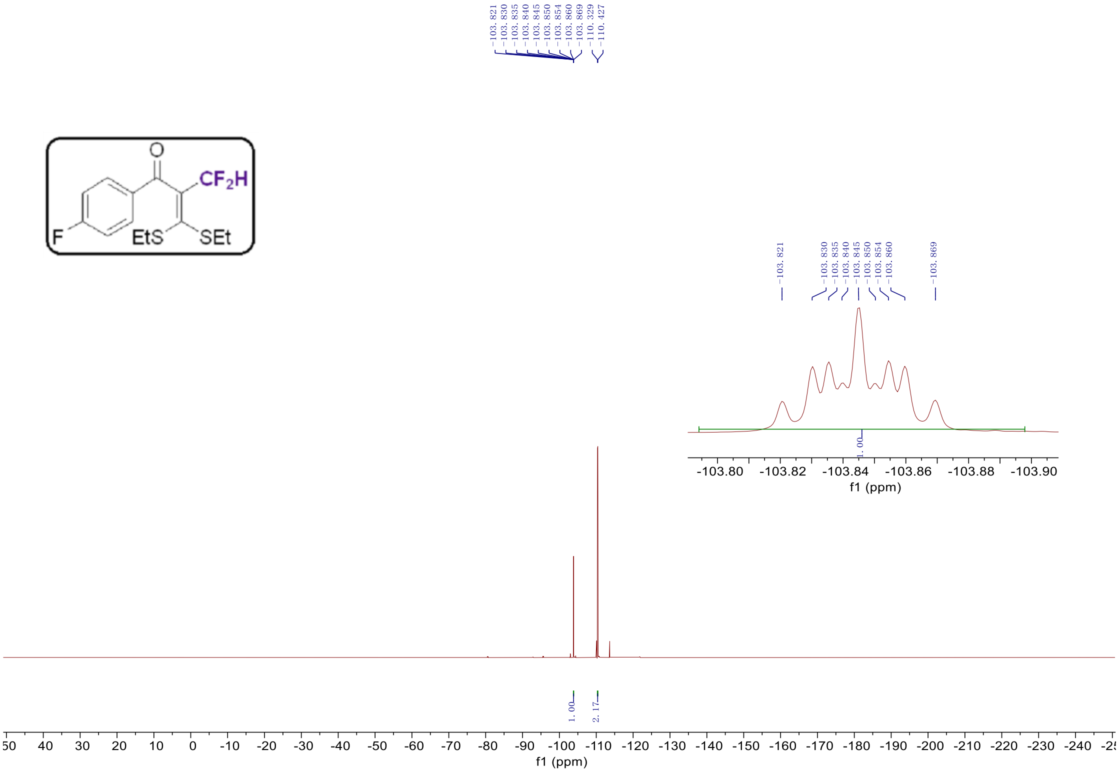
[1]H spectrum (600 MHz, $CDCl_3$) of compound 3g



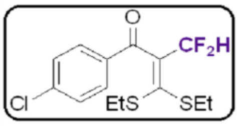
[13]C spectrum (151 MHz, $CDCl_3$) of compound 3g

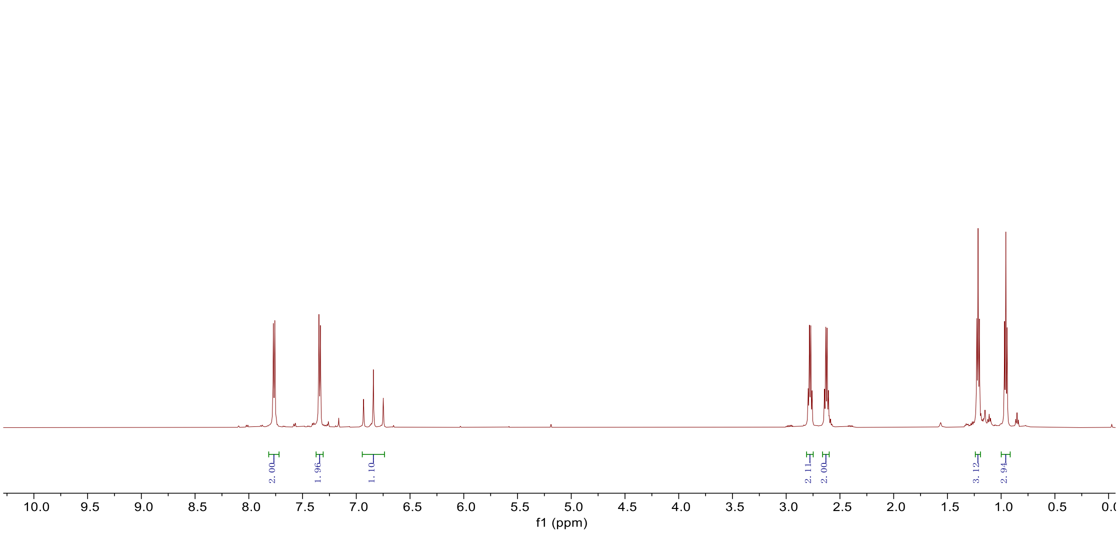


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3g

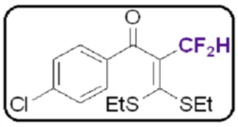


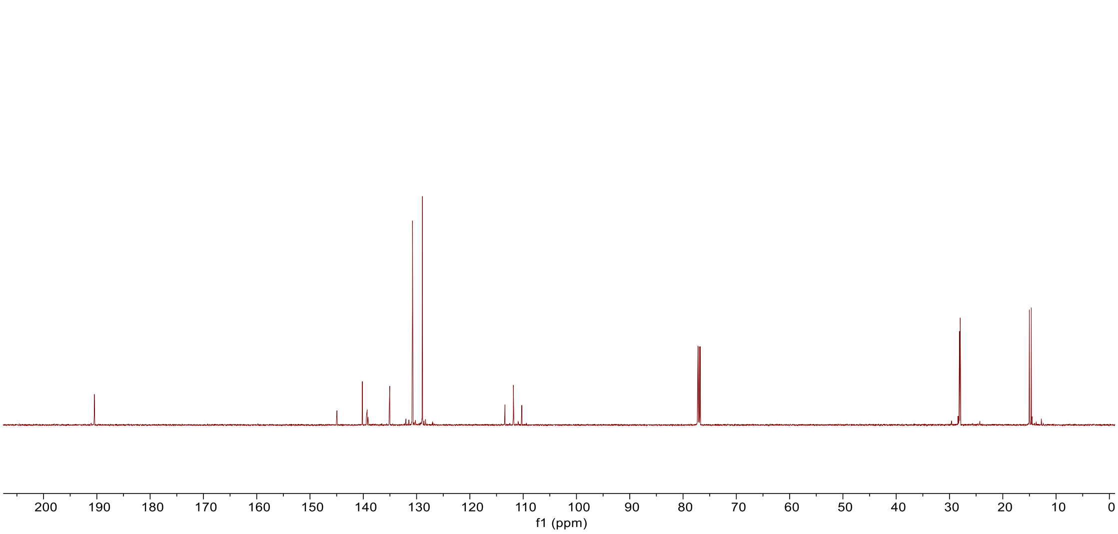
[1]H spectrum (600 MHz, CDCl3) of compound 3h



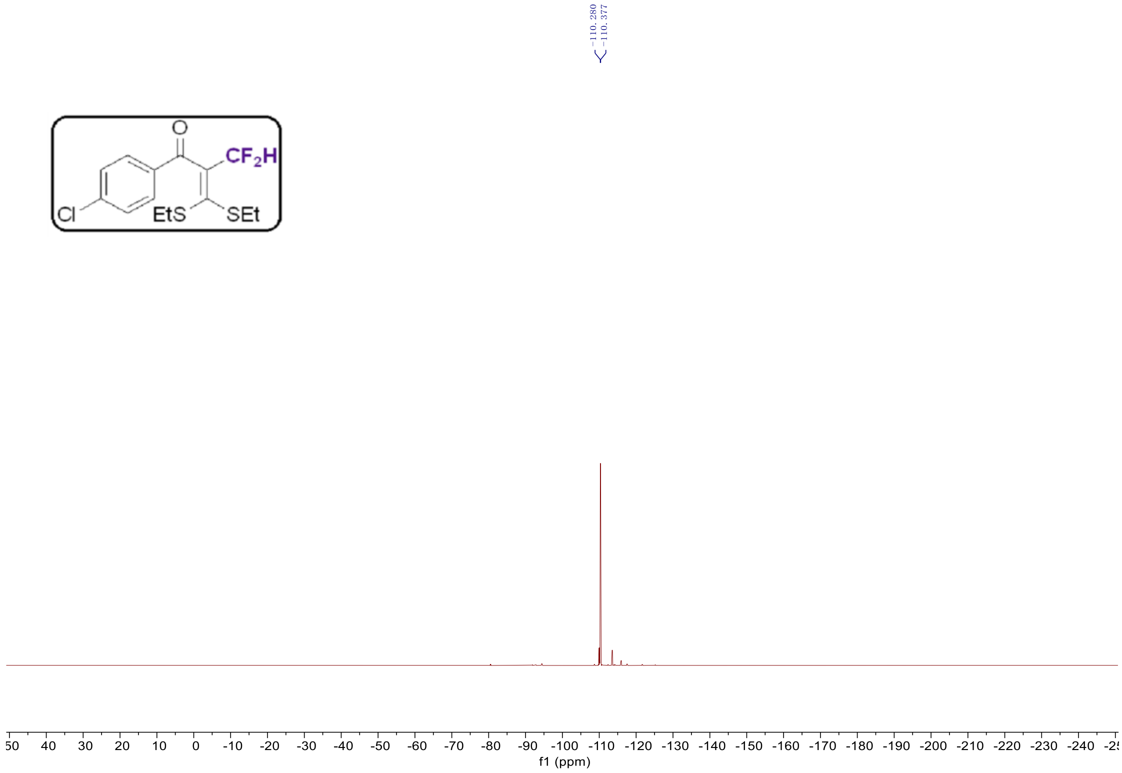


[13]C spectrum (151 MHz, CDCl3) of compound 3h

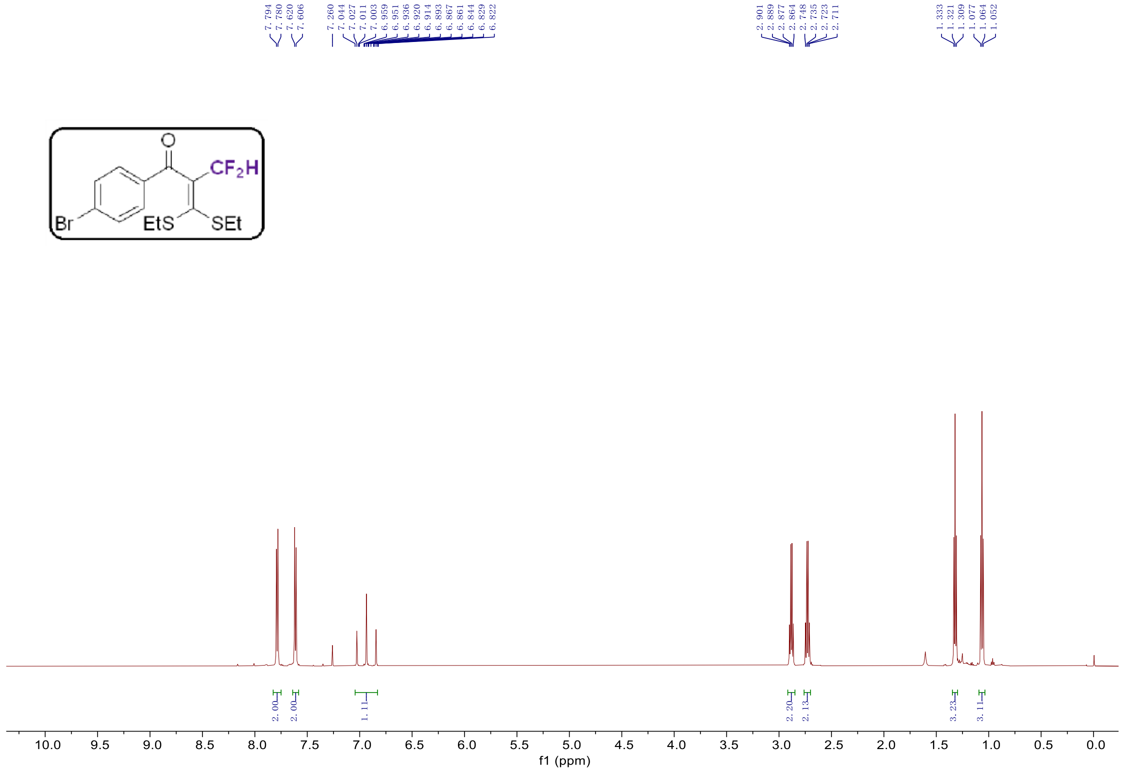




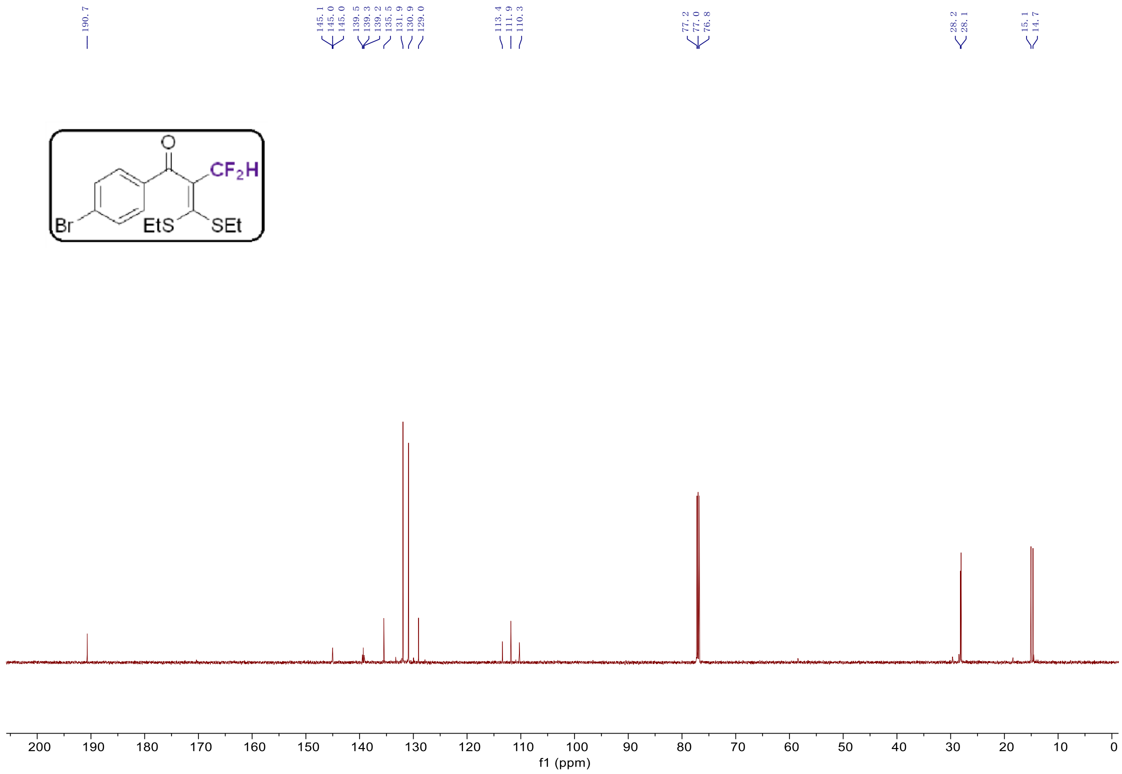
[19]F spectrum (565 MHz, $CDCl_3$) of compound 3h



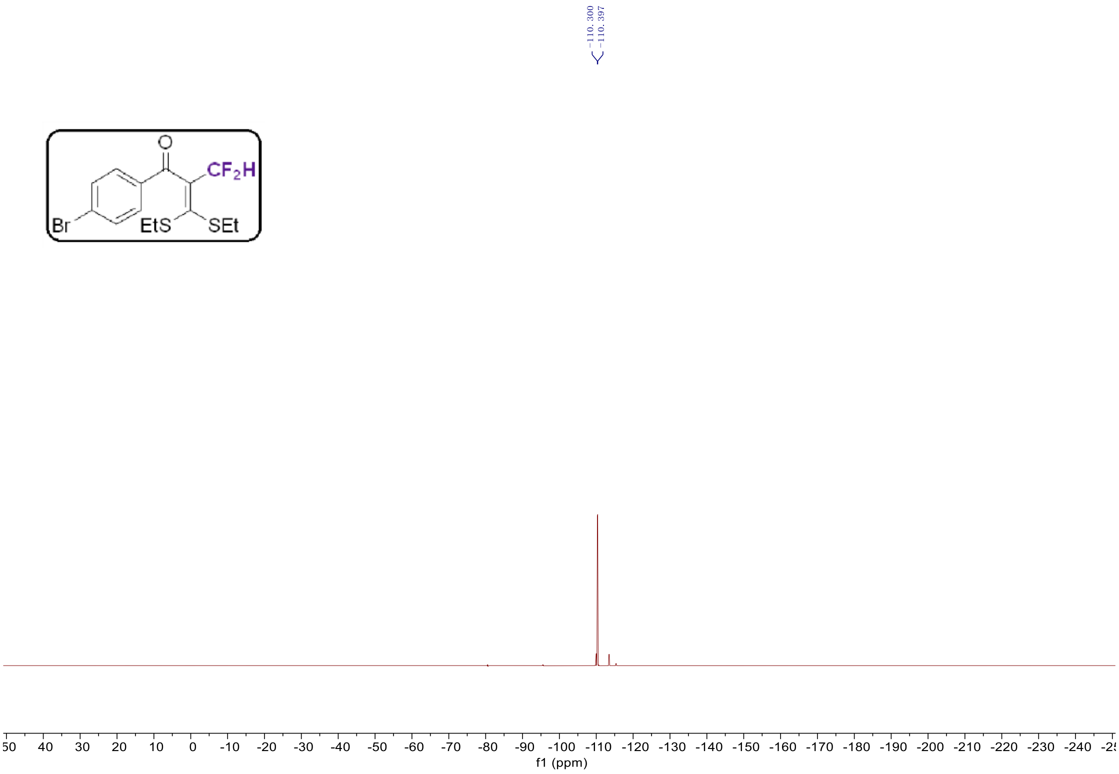
[1]H spectrum (600 MHz, $CDCl_3$) of compound 3i



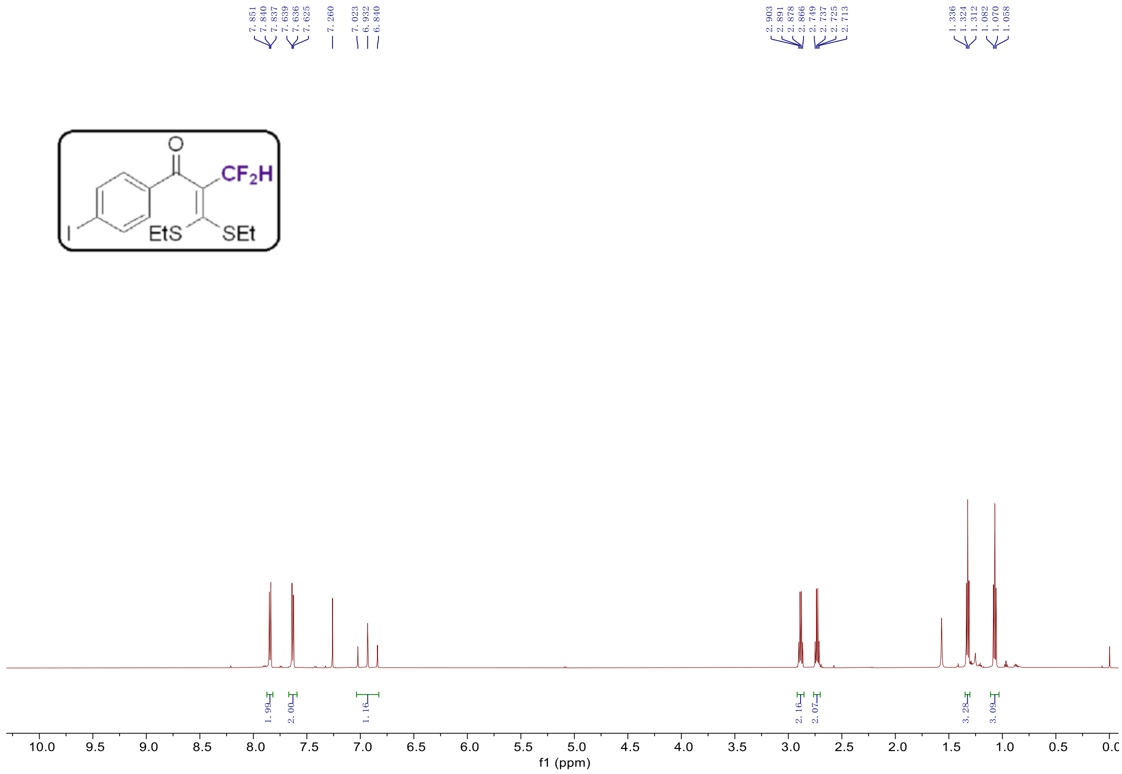
[13]C spectrum (151 MHz, $CDCl_3$) of compound 3i



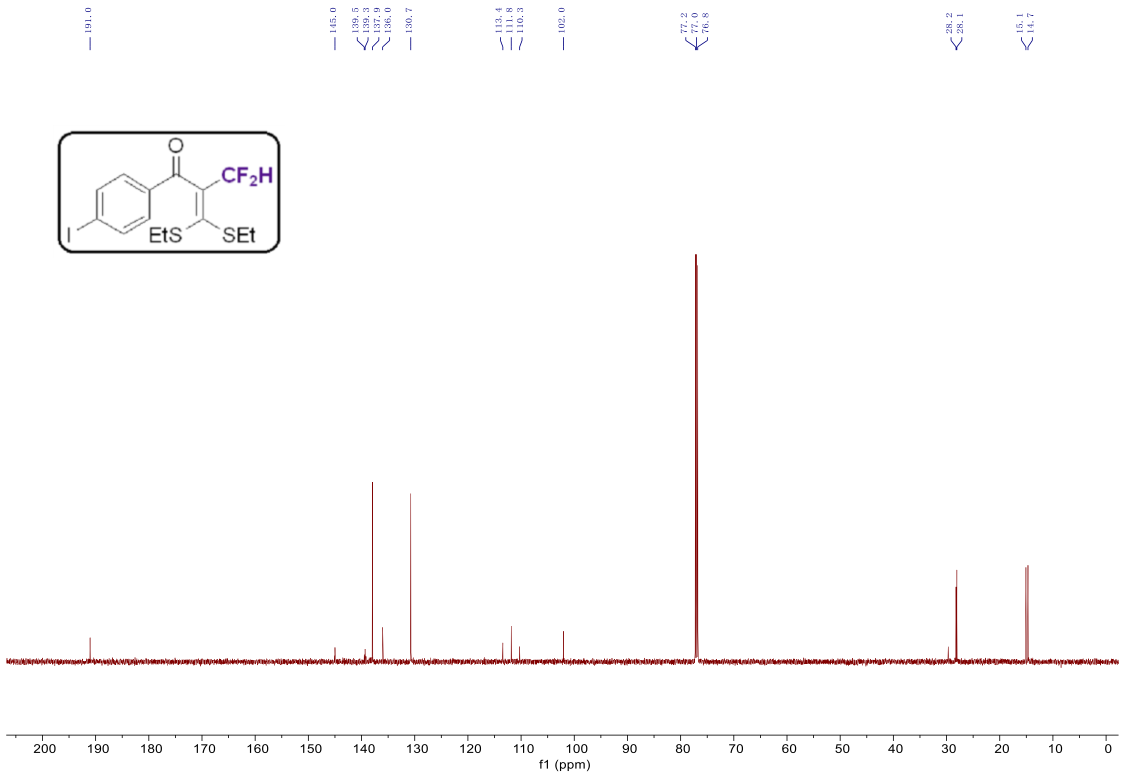
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3i



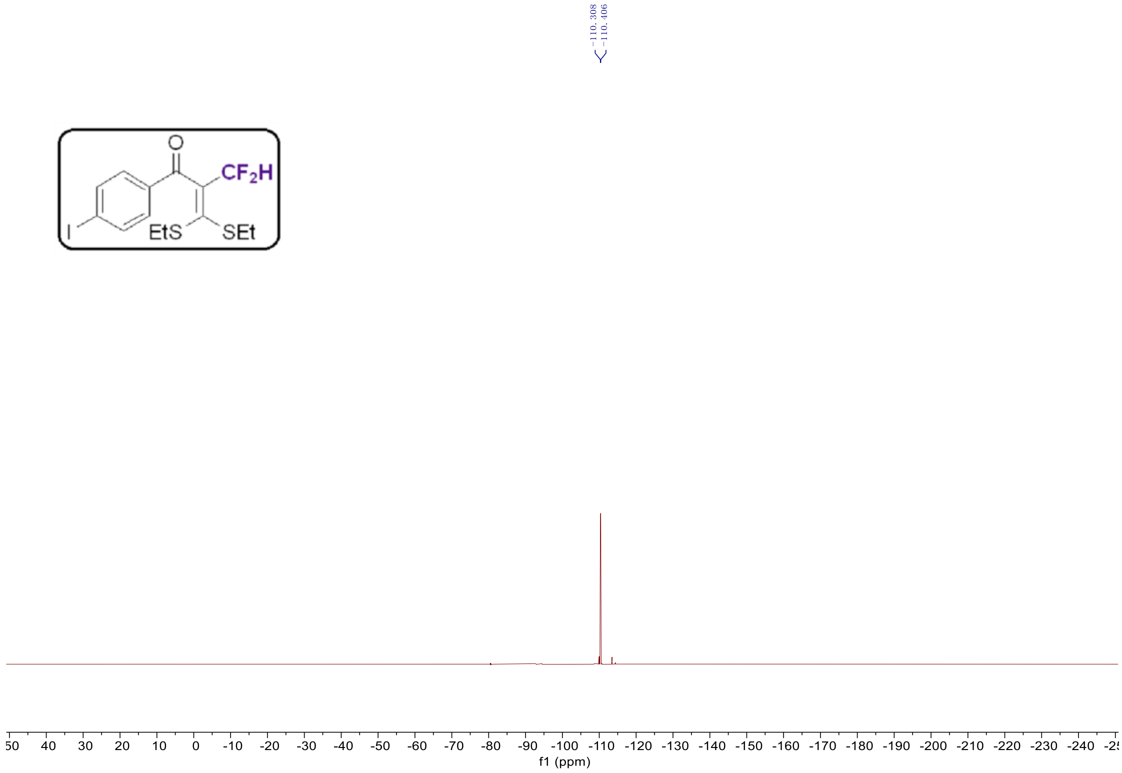
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3j



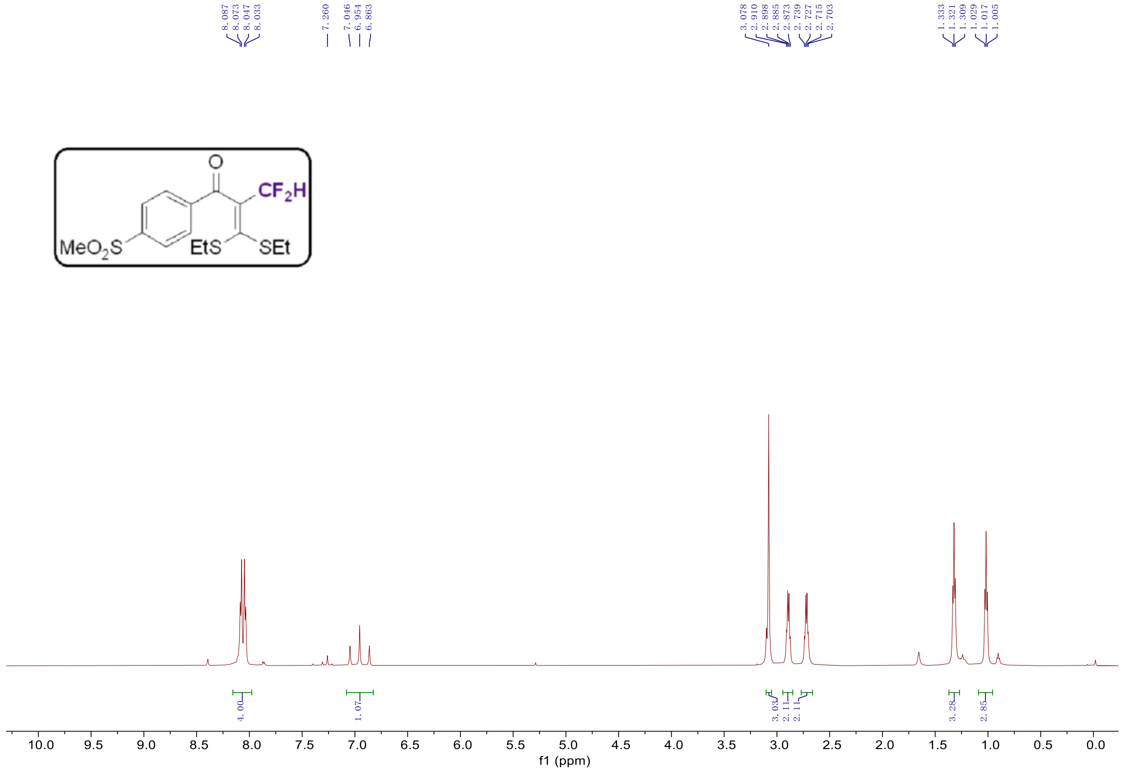
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3j



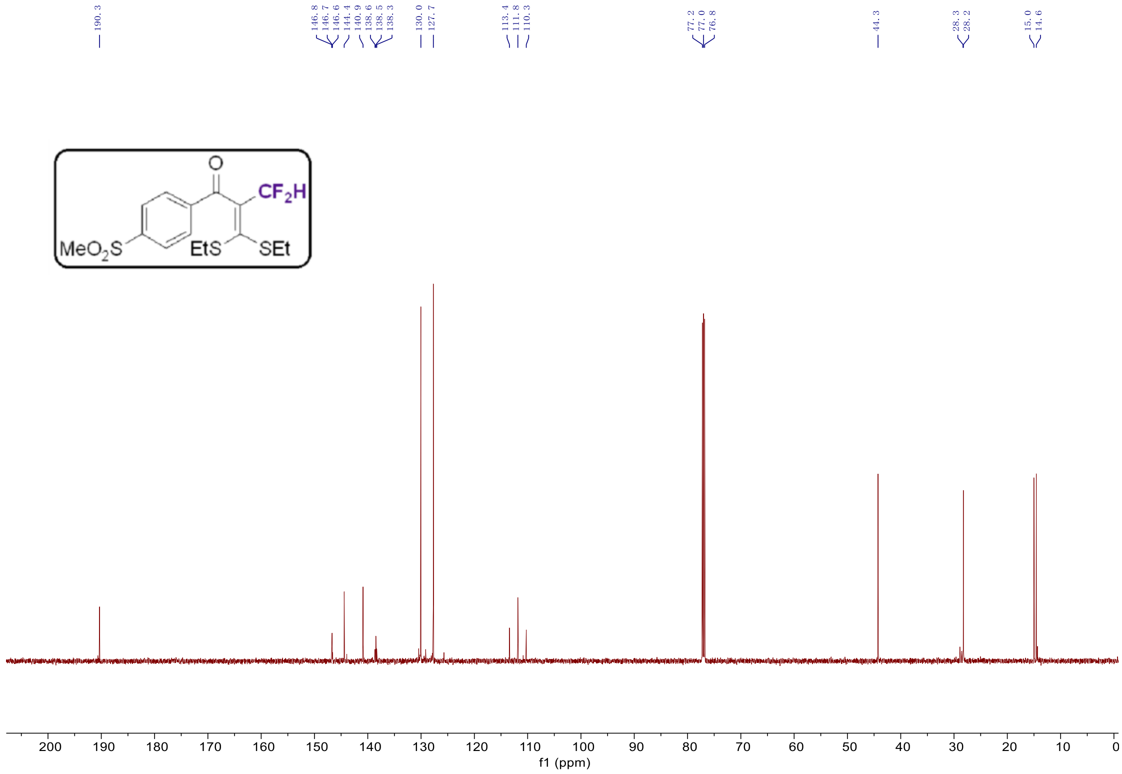
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3j



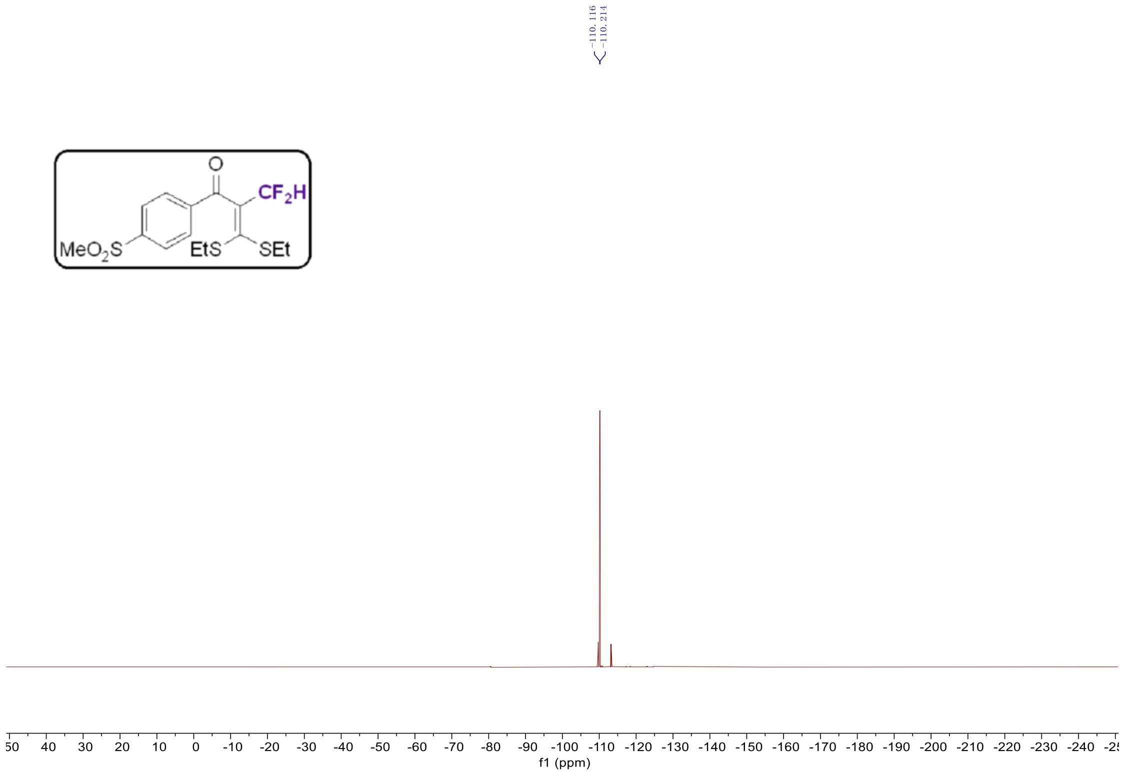
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3k



^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3k



[19]F spectrum (565 MHz, CDCl₃) of compound 3k



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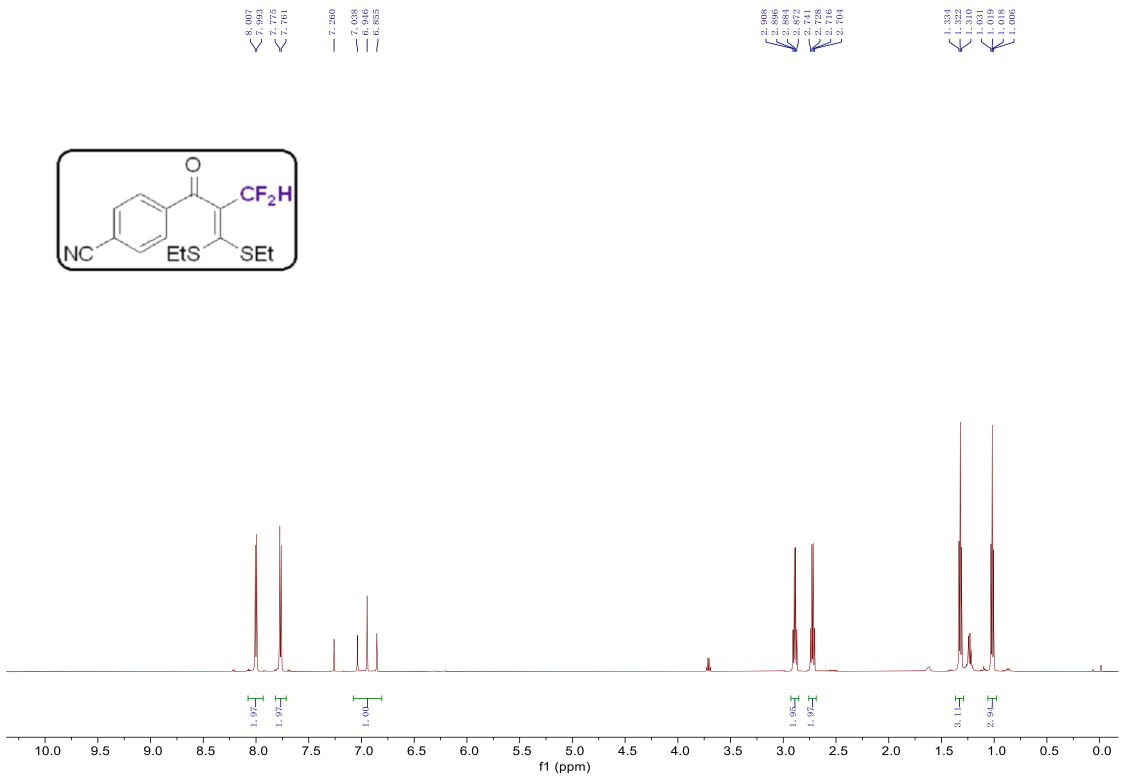
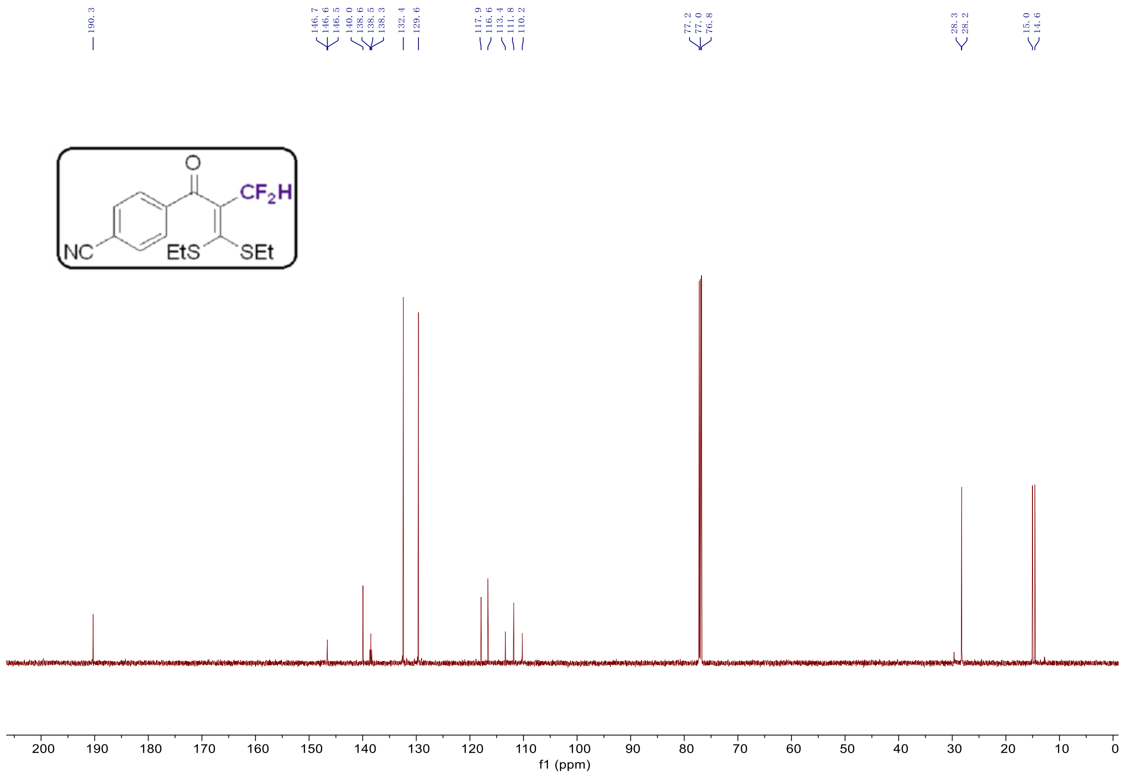


^{13}C spectrum (151 MHz, CDCl$_3$) of compound 3l



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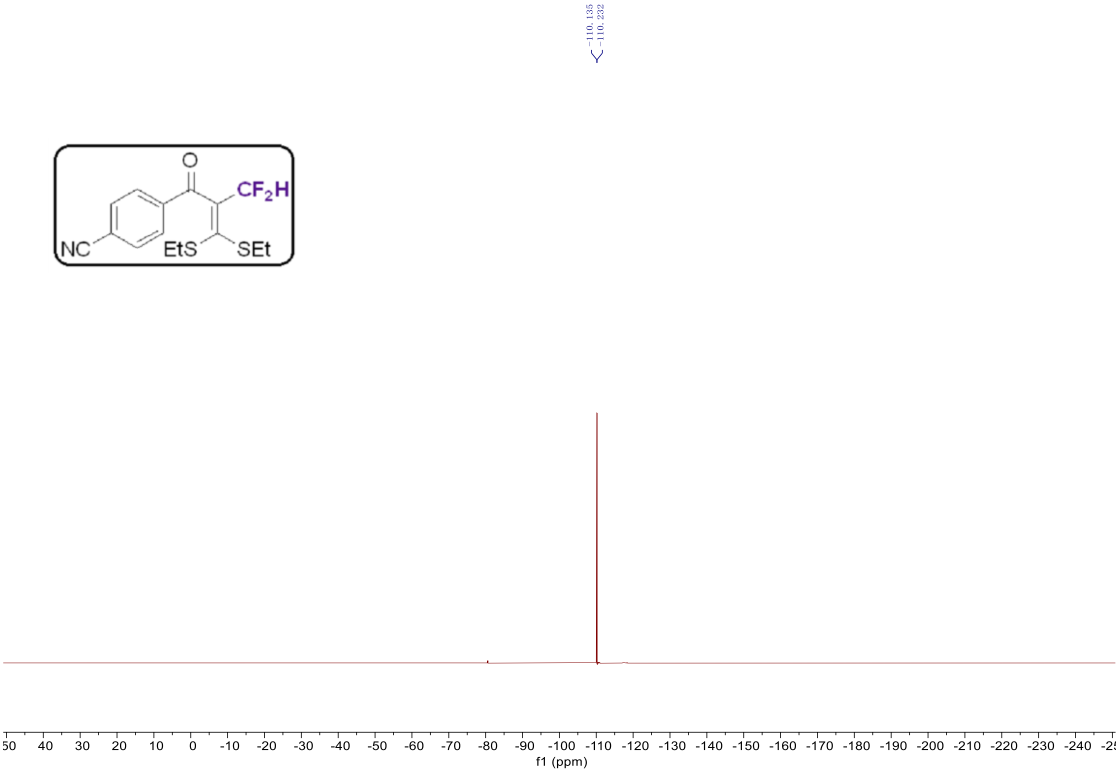

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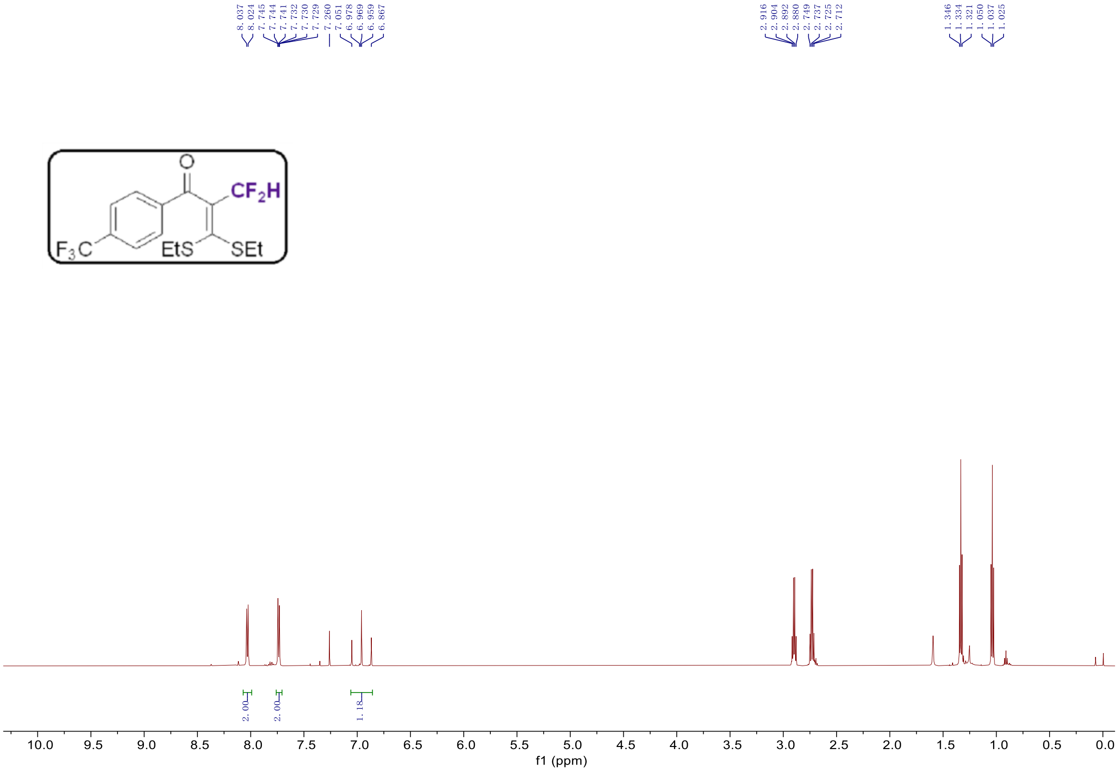
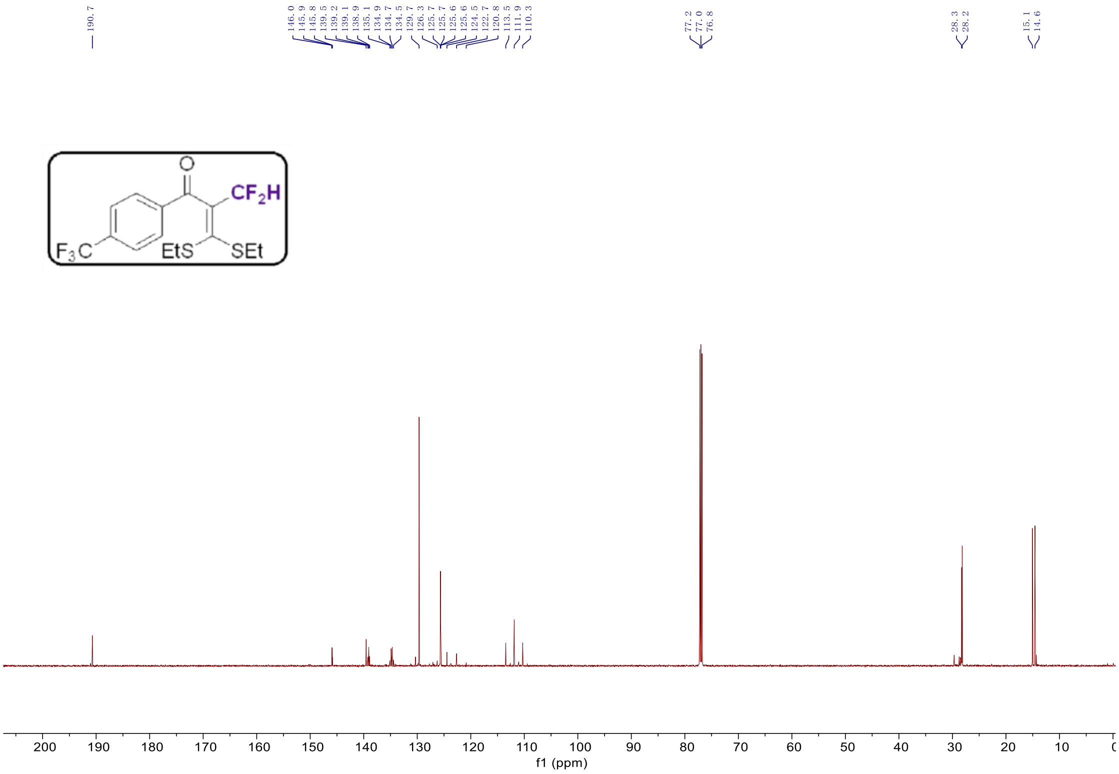


^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3m



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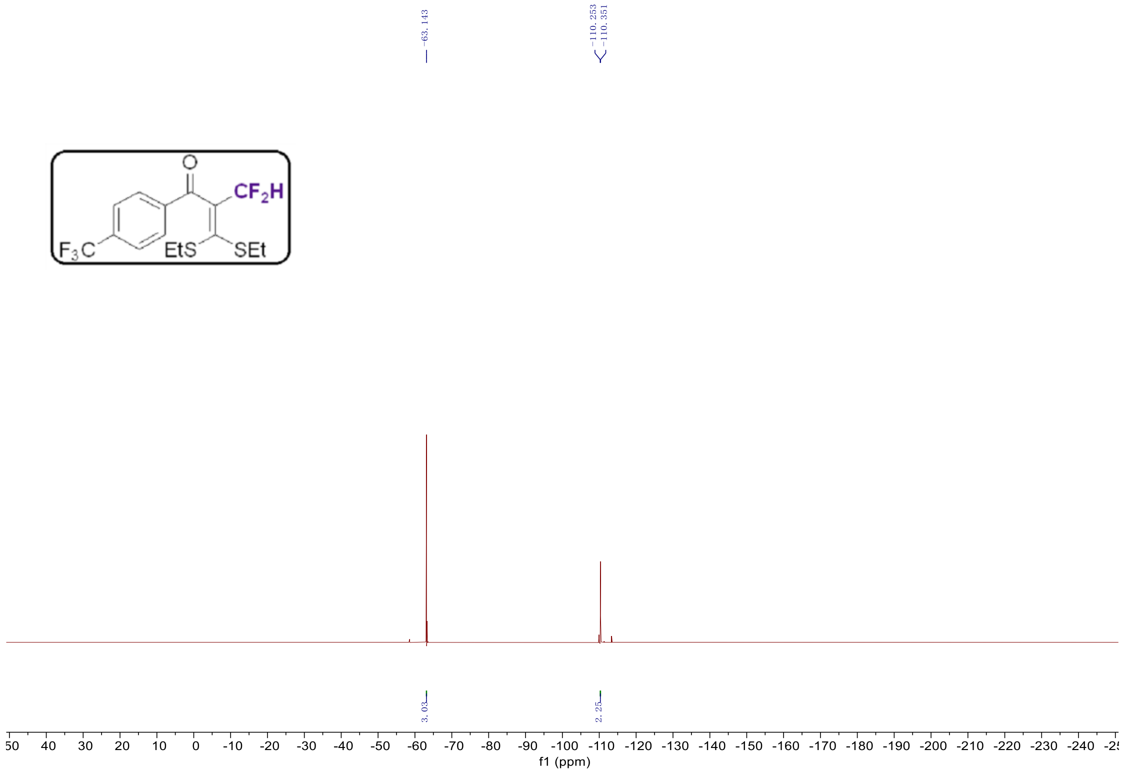

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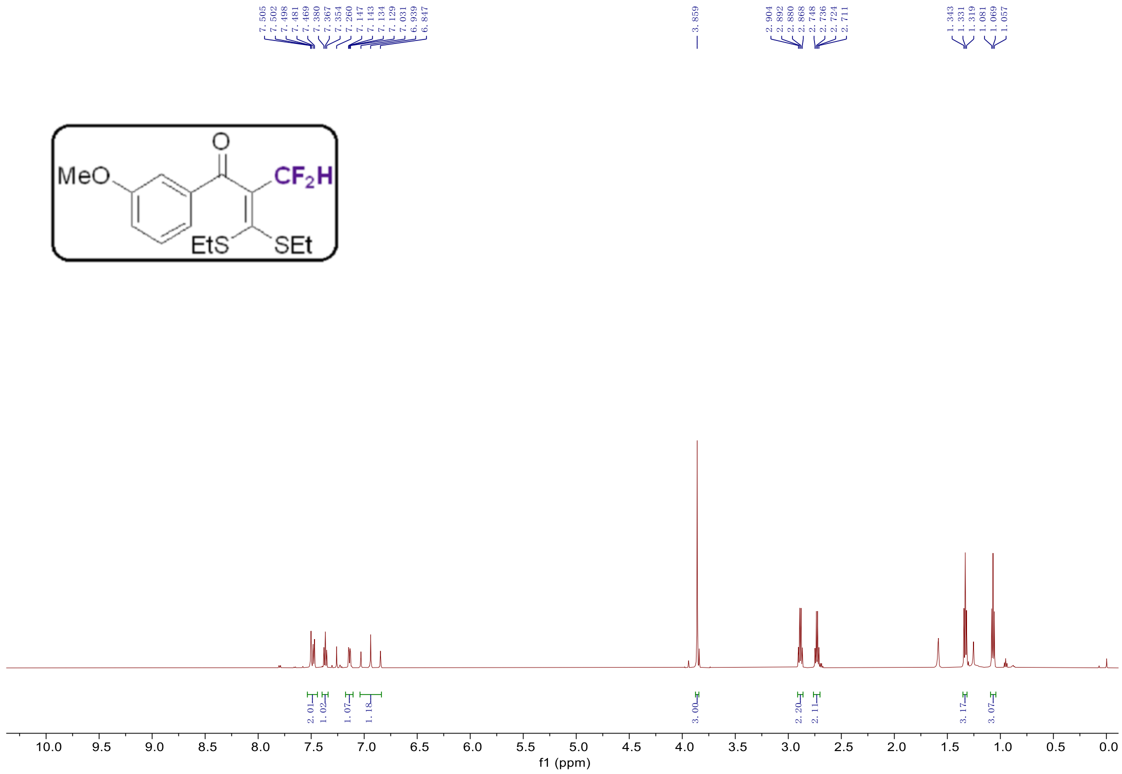
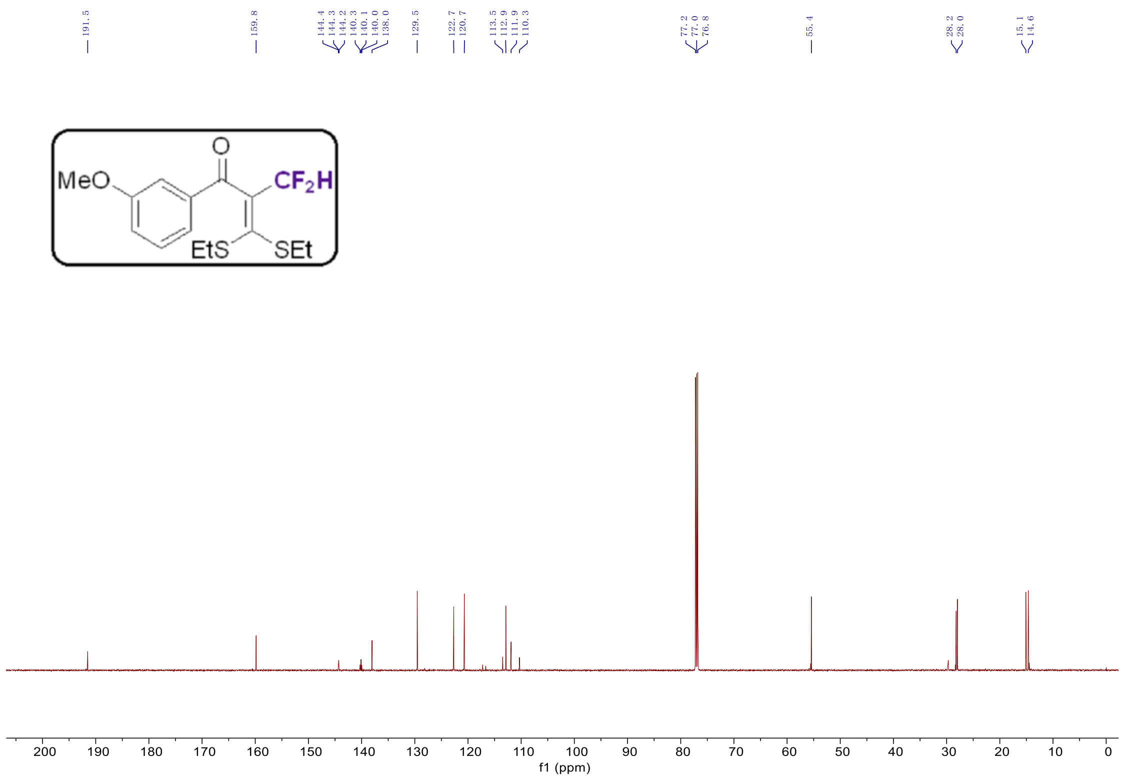


^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3n



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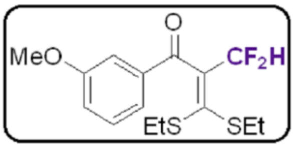

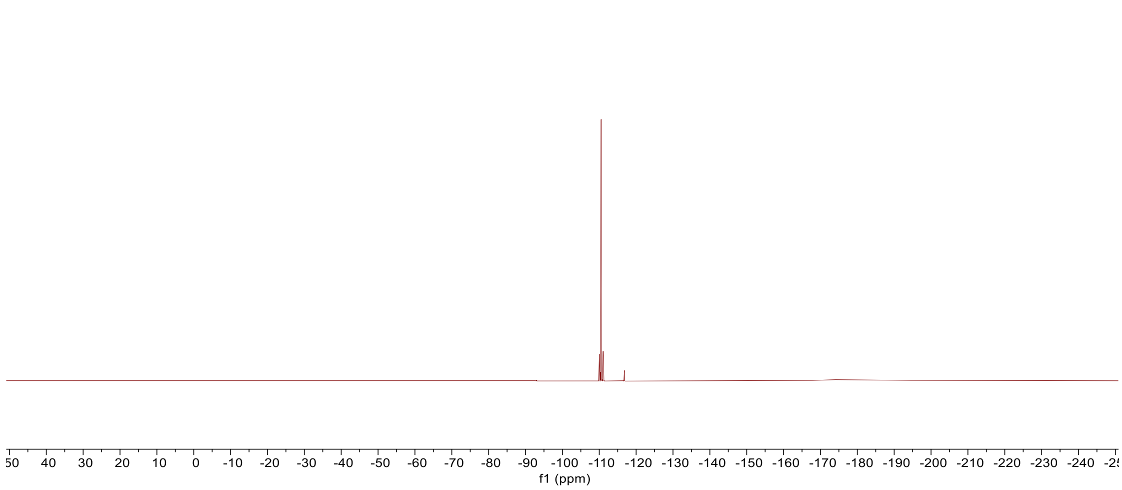

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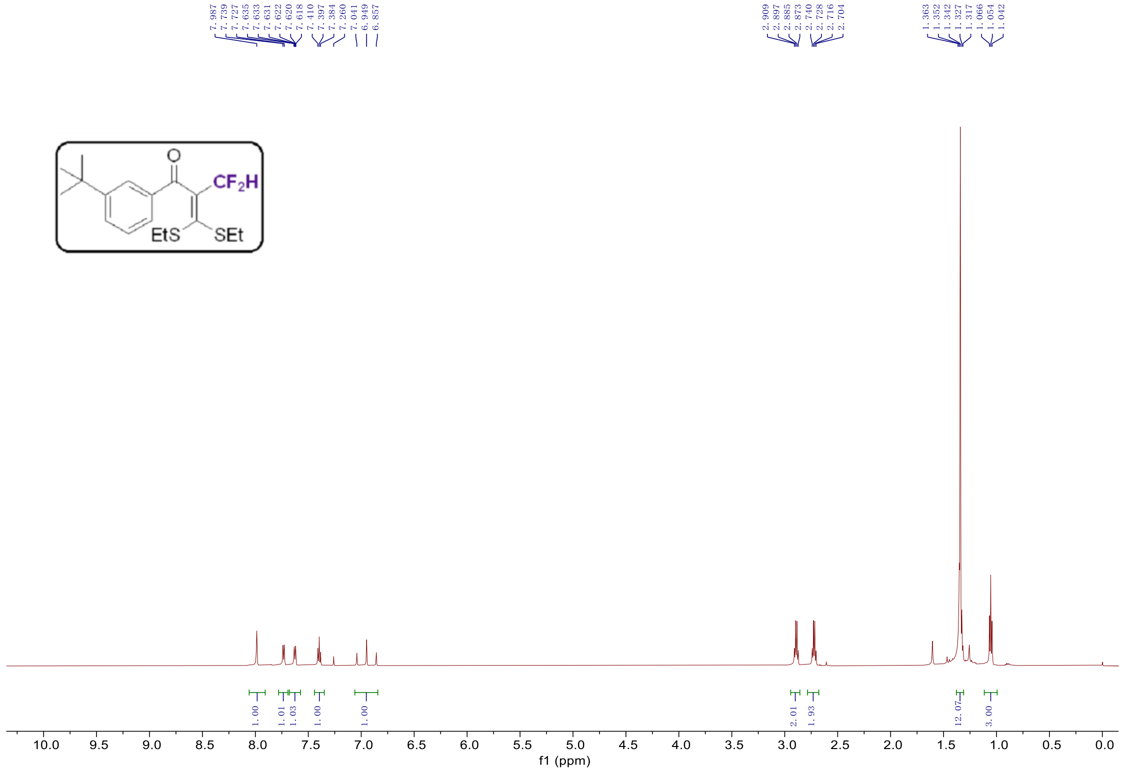
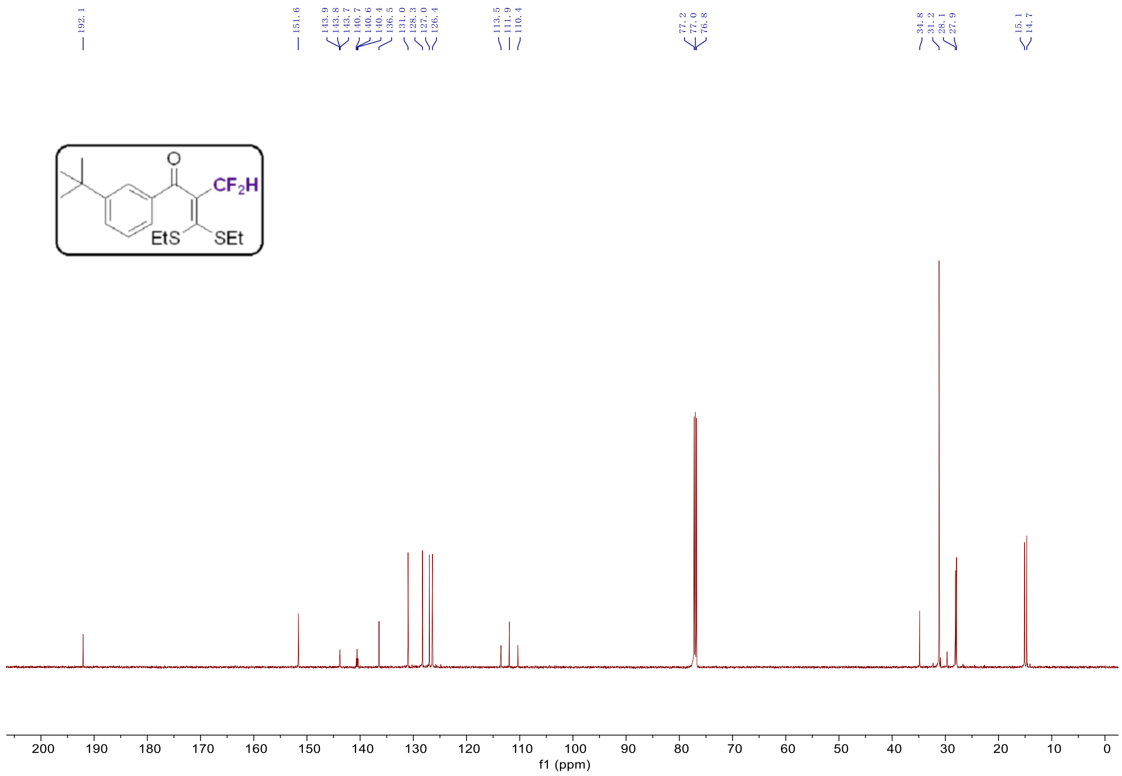
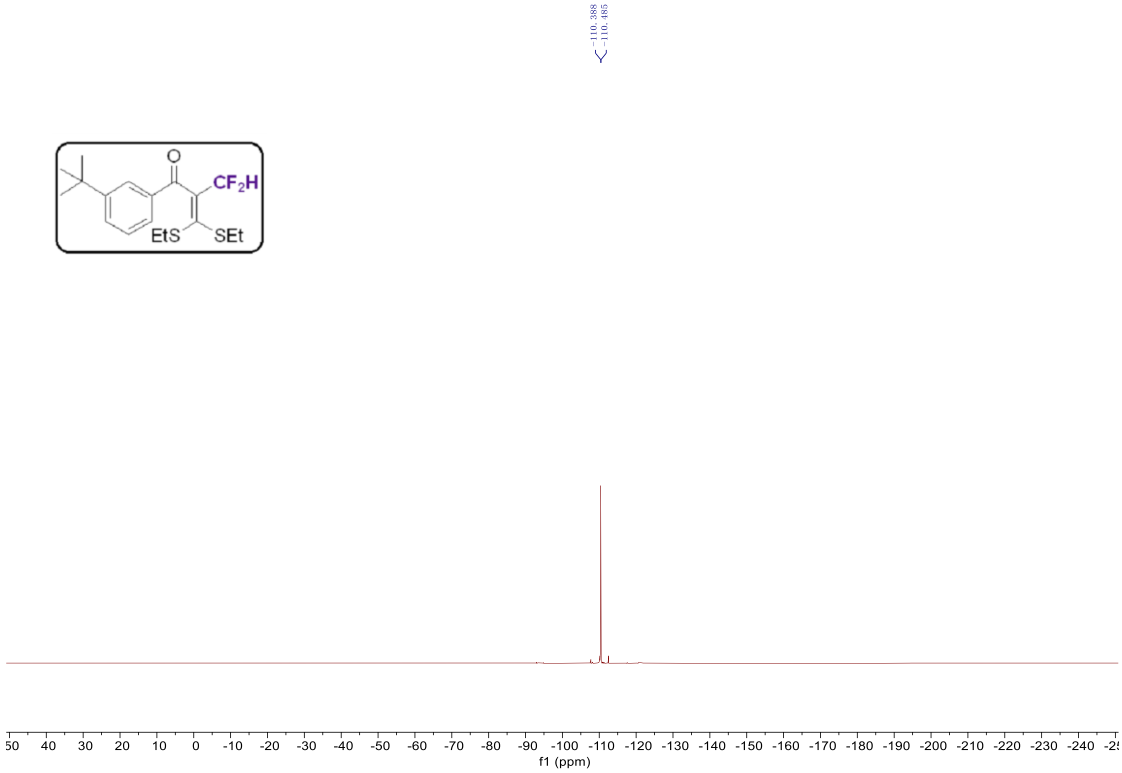


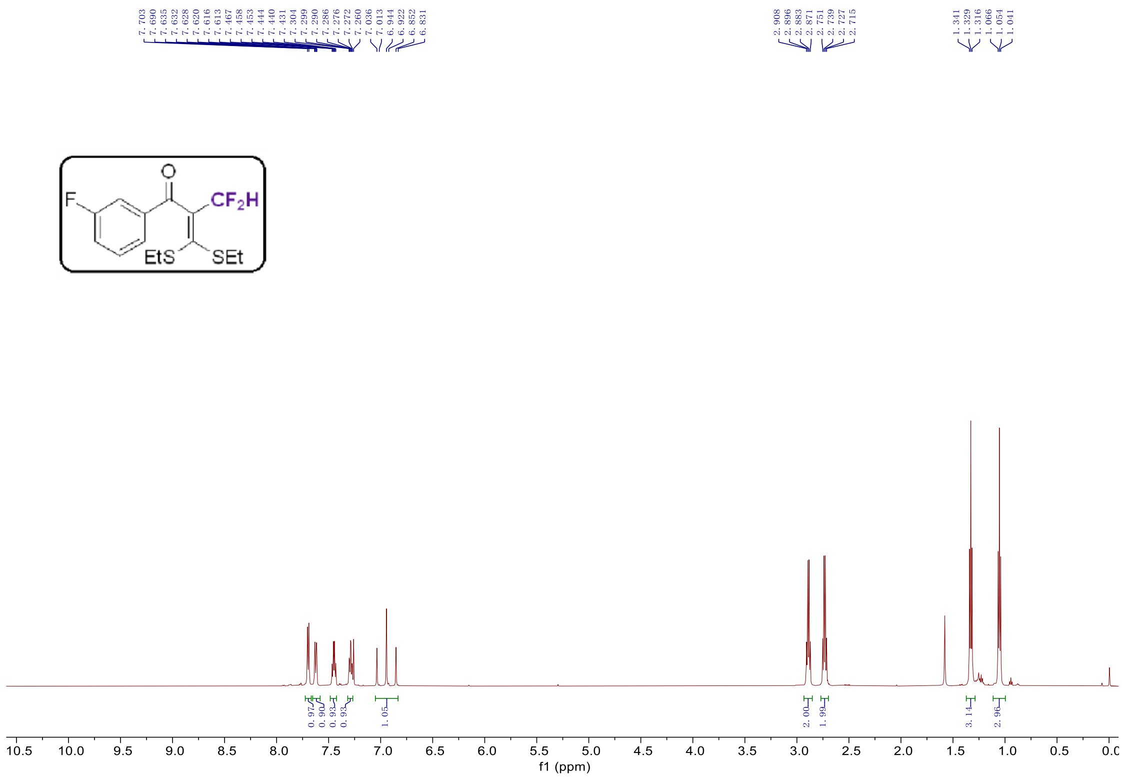
[13]C spectrum (151 MHz, CDCl3) of compound 3p



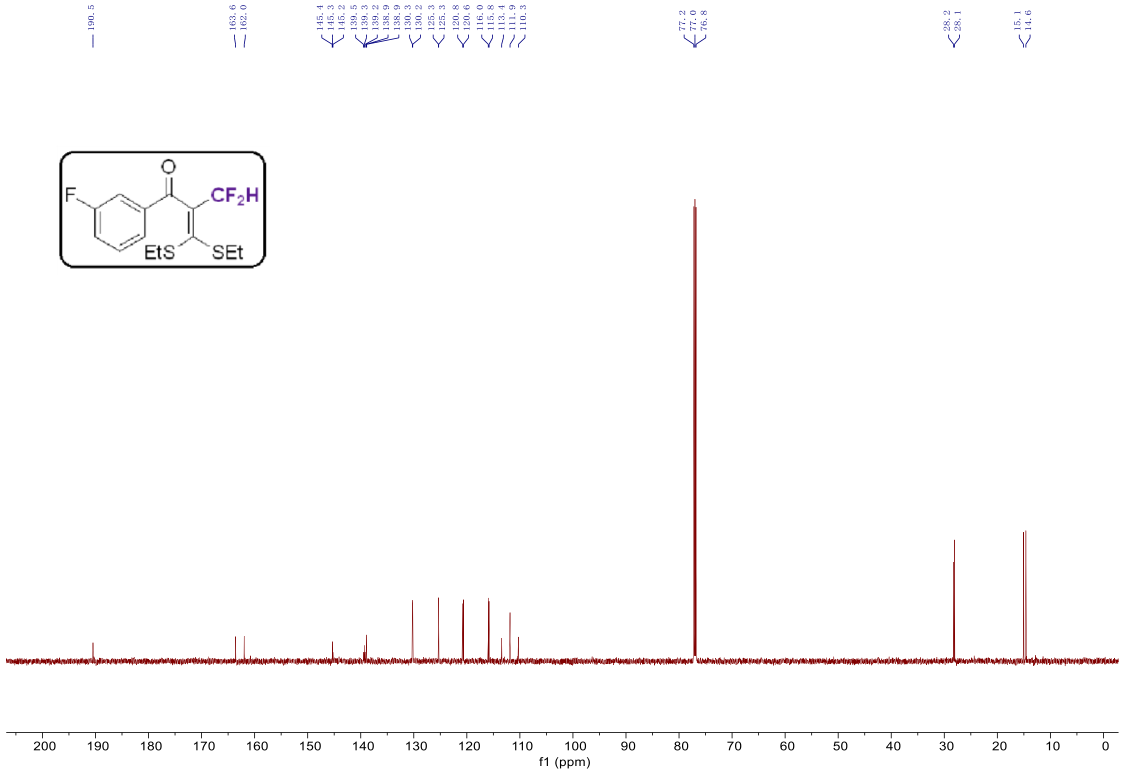
[19]F spectrum (565 MHz, $CDCl_3$) of compound 3p



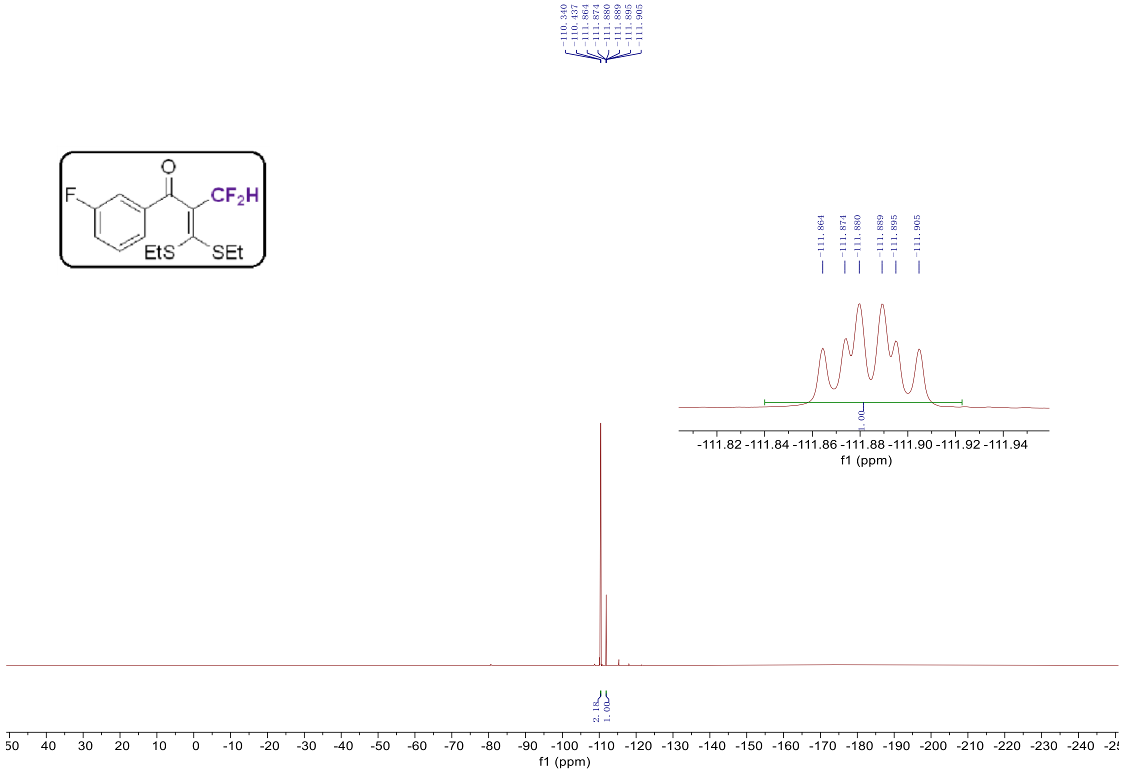
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3p



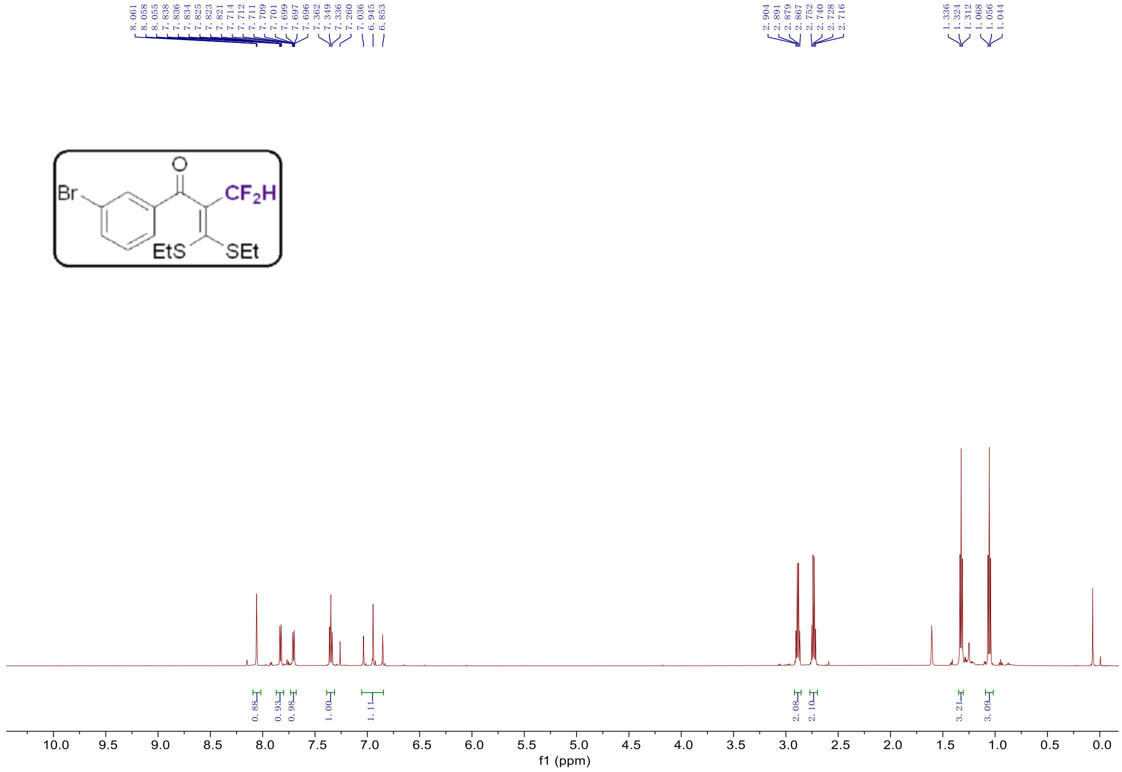
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3p



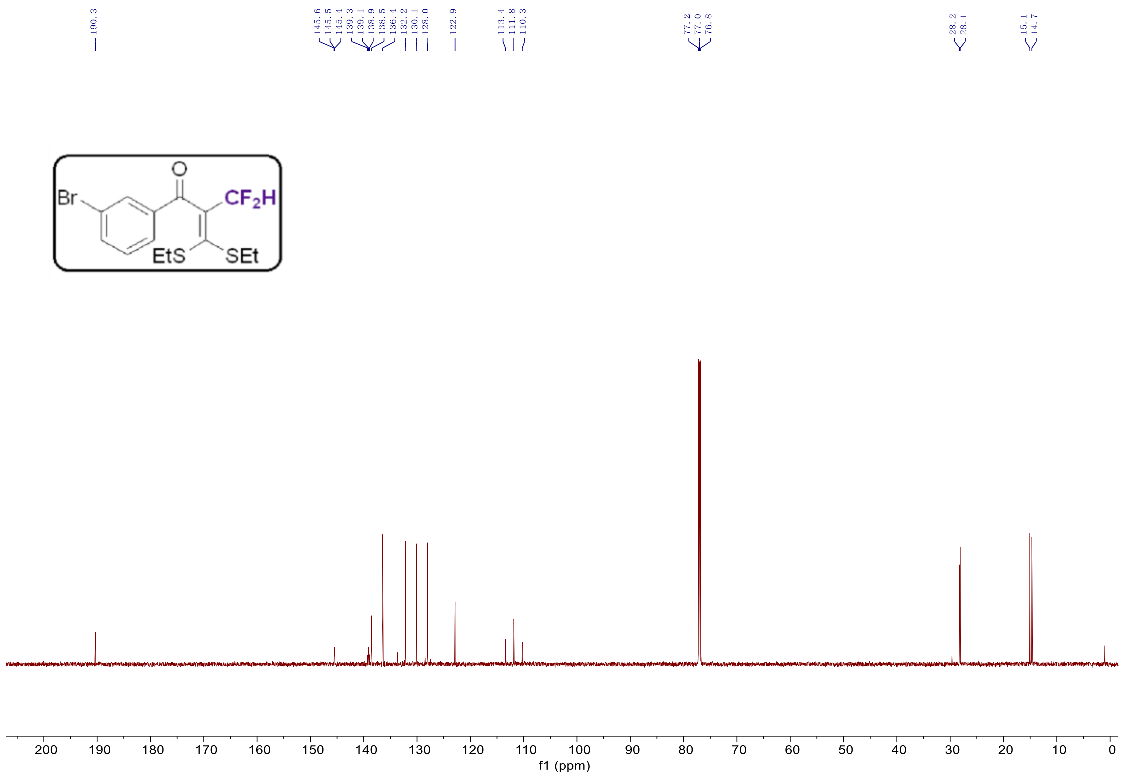
^{19}F spectrum (565 MHz, CDCl$_3$) of compound 3p



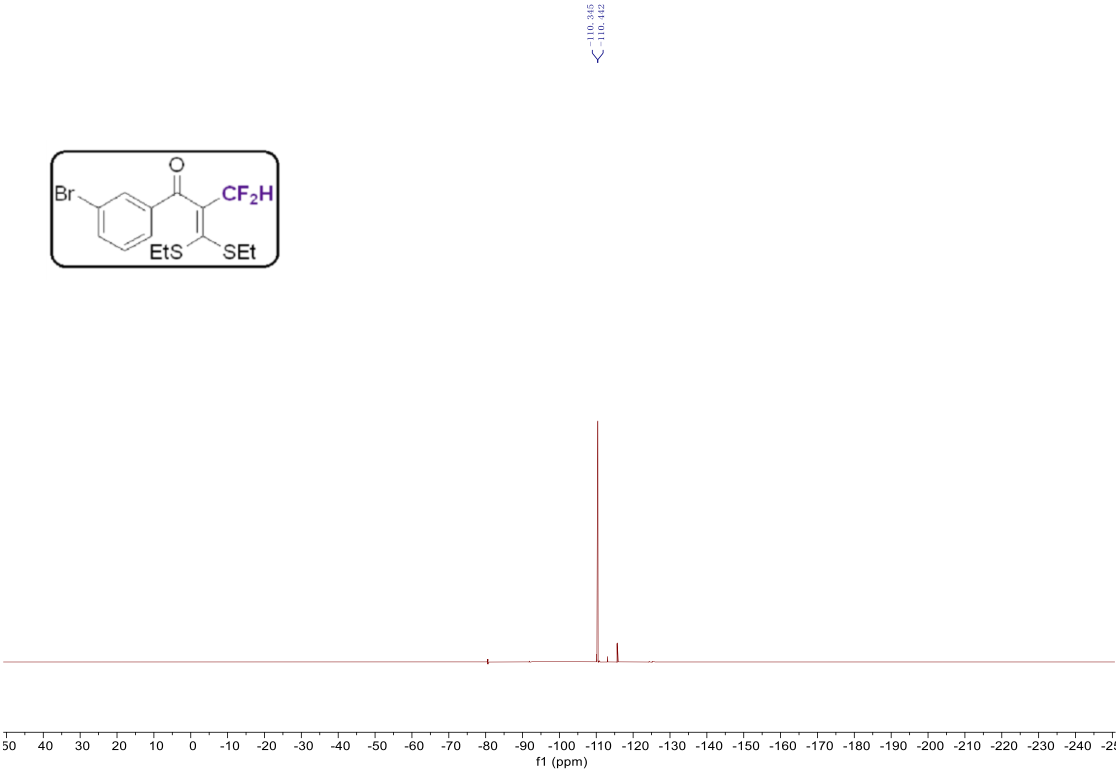
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3q



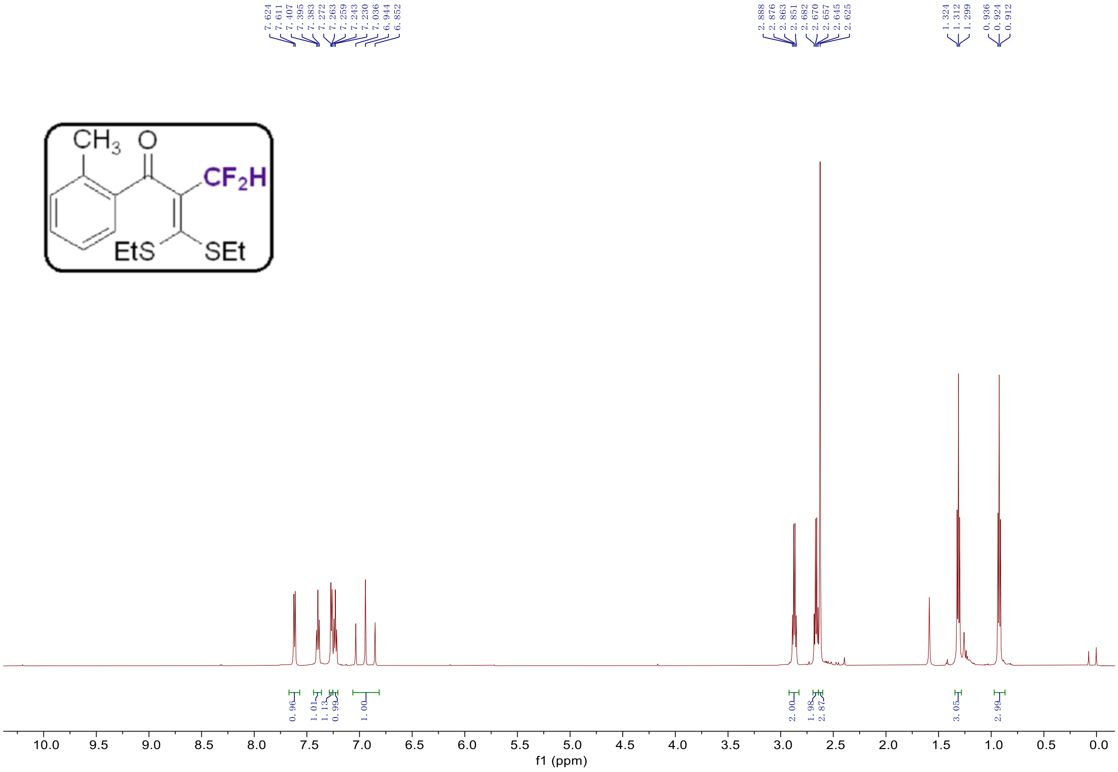
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3q



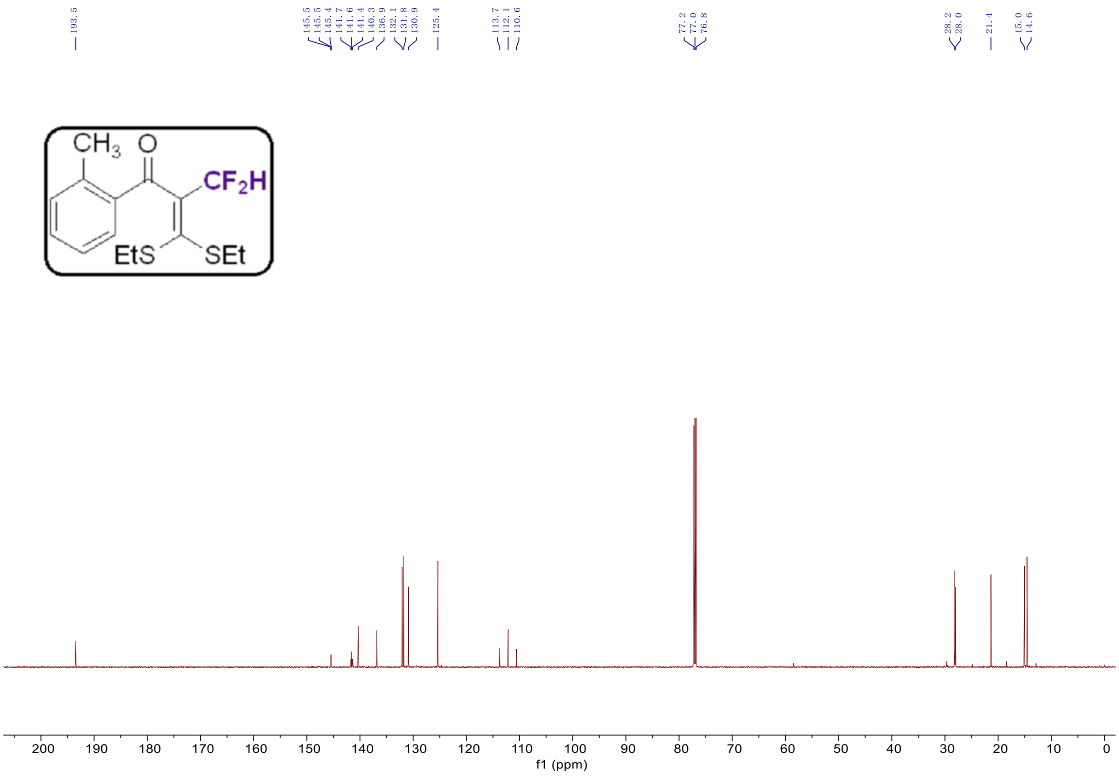
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3q



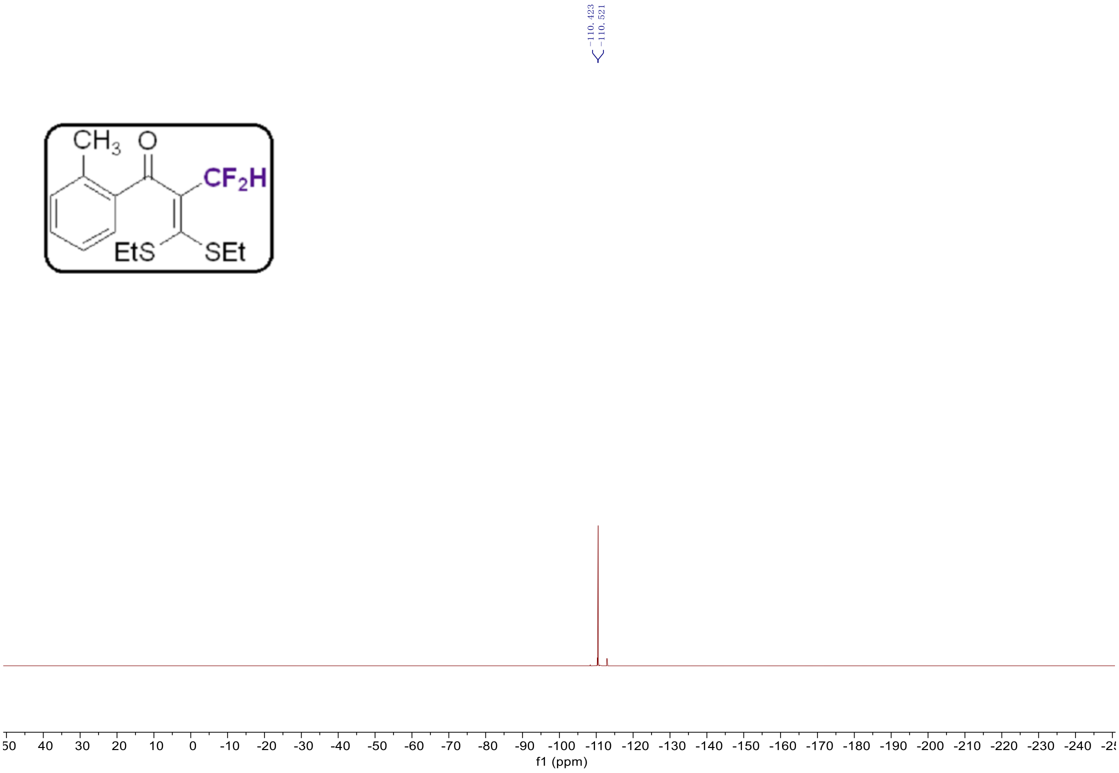
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3r



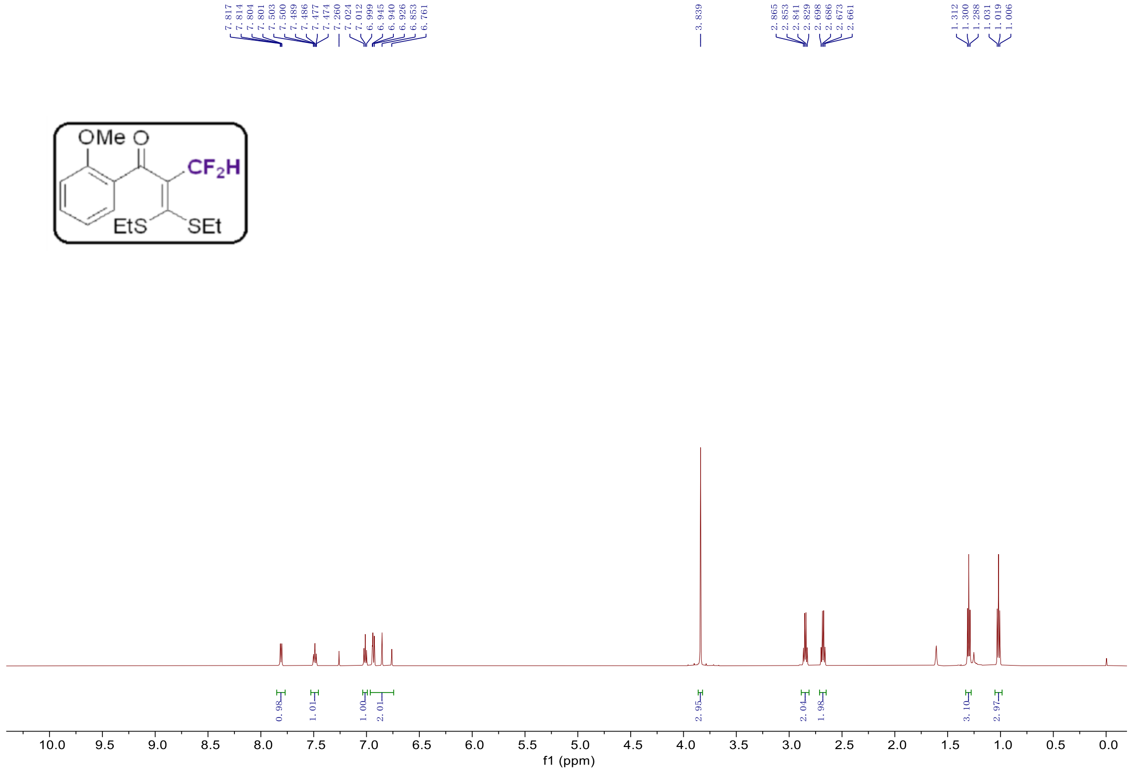
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3r



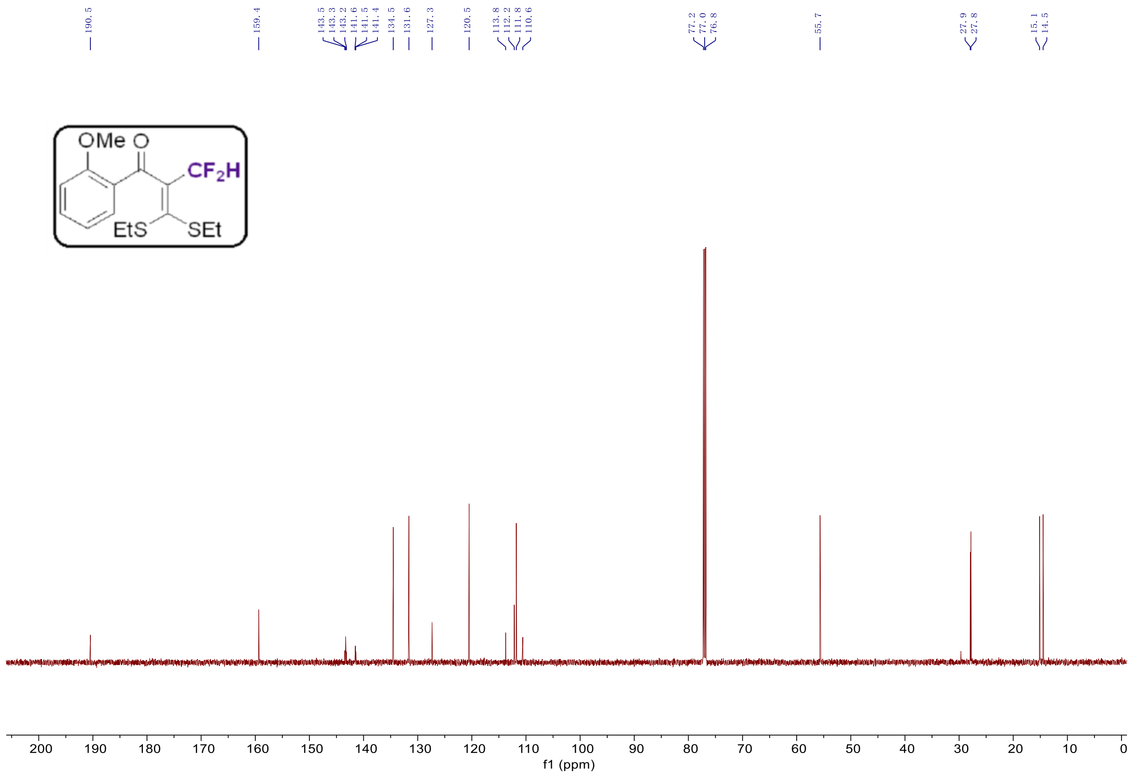
[19]F spectrum (565 MHz, $CDCl_3$) of compound 3r



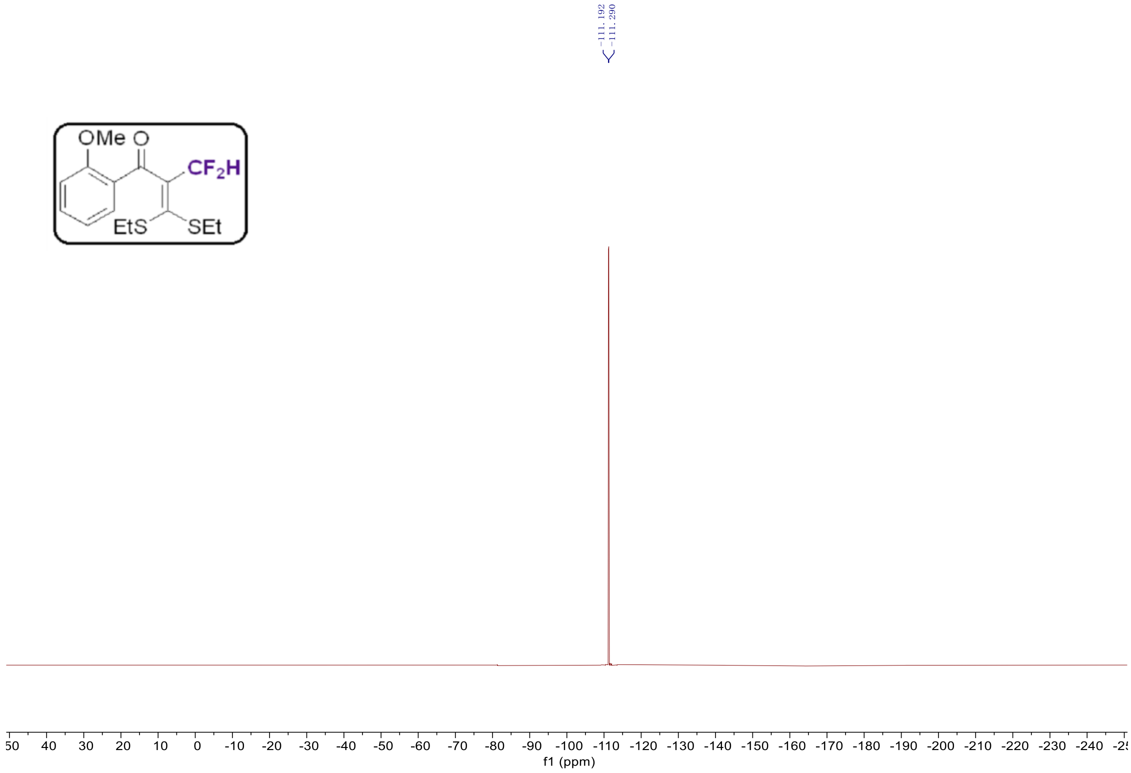
^{1}H spectrum (600 MHz, CDCl3) of compound 3s



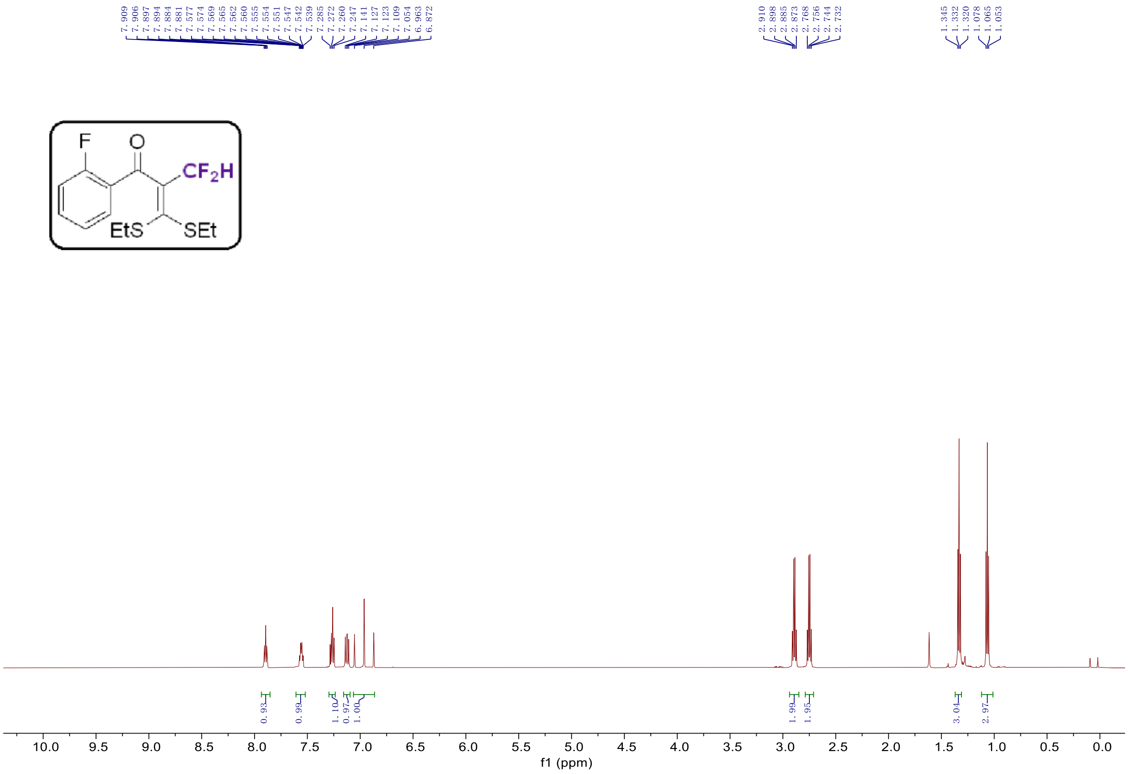
^{13}C spectrum (151 MHz, CDCl3) of compound 3s



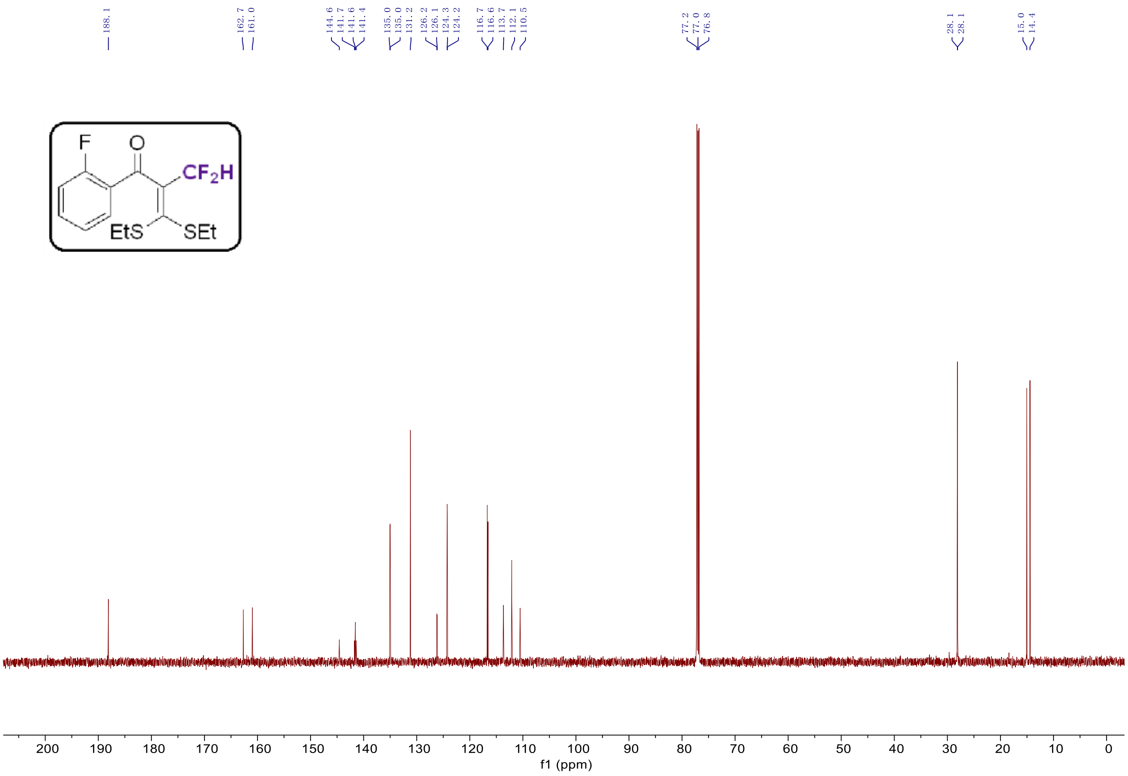
^{19}F spectrum (565 MHz, CDCl$_3$) of compound 3s



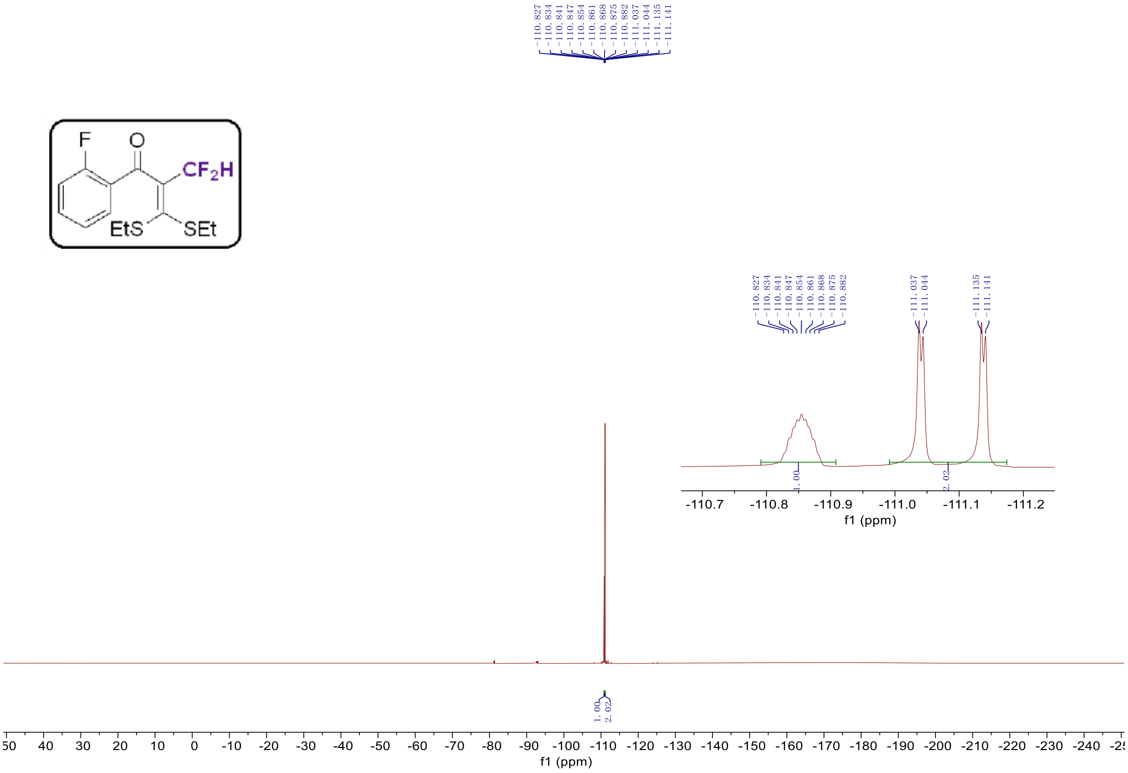
[1]H spectrum (600 MHz, CDCl3) of compound 3t



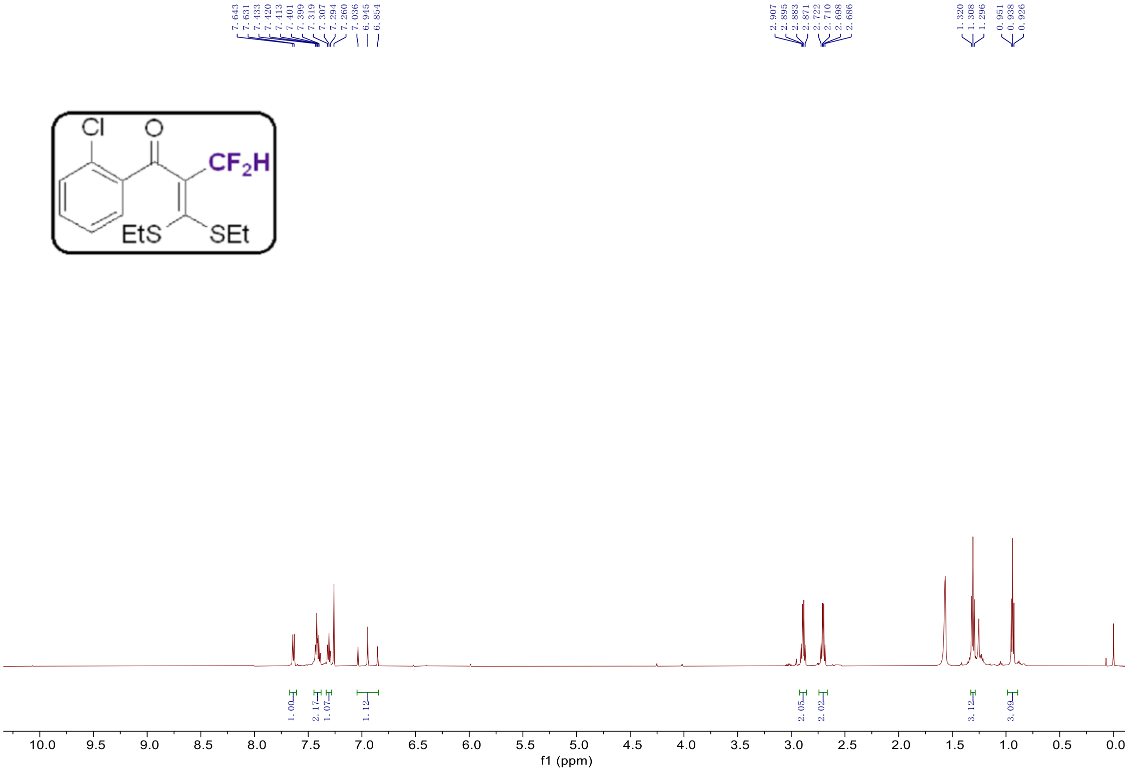
[13]C spectrum (151 MHz, CDCl3) of compound 3t



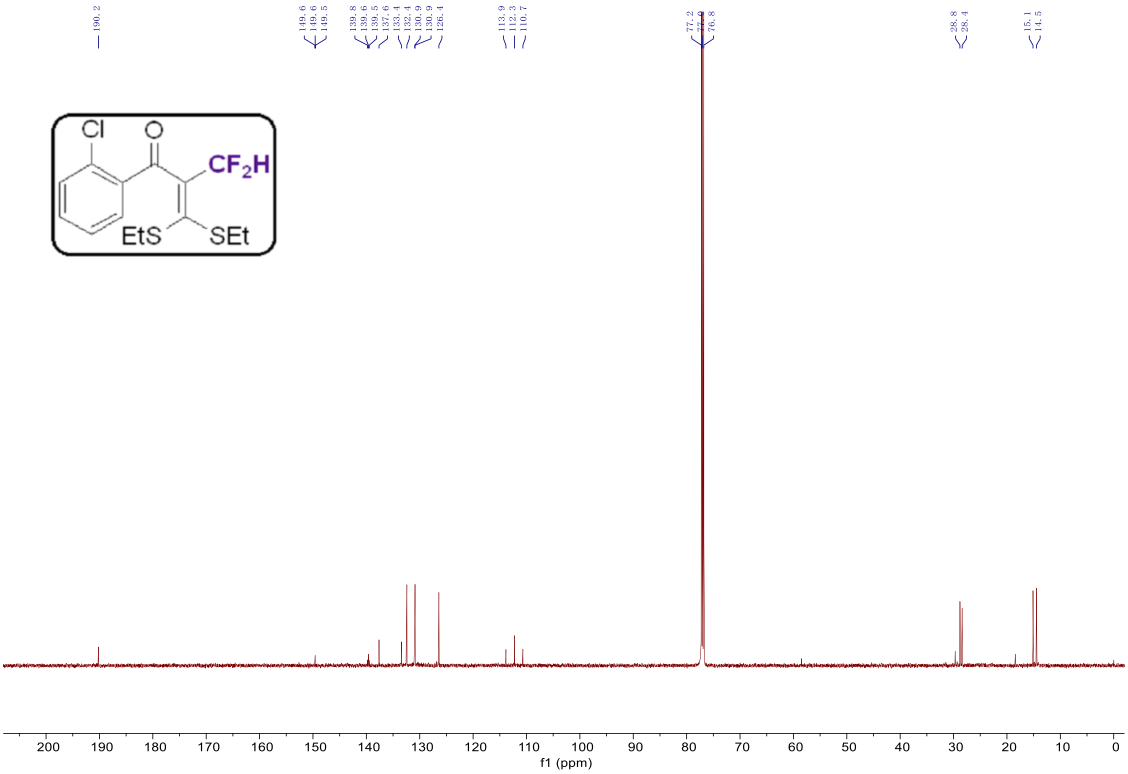
^{19}F spectrum (565 MHz, CDCl$_3$) of compound 3t



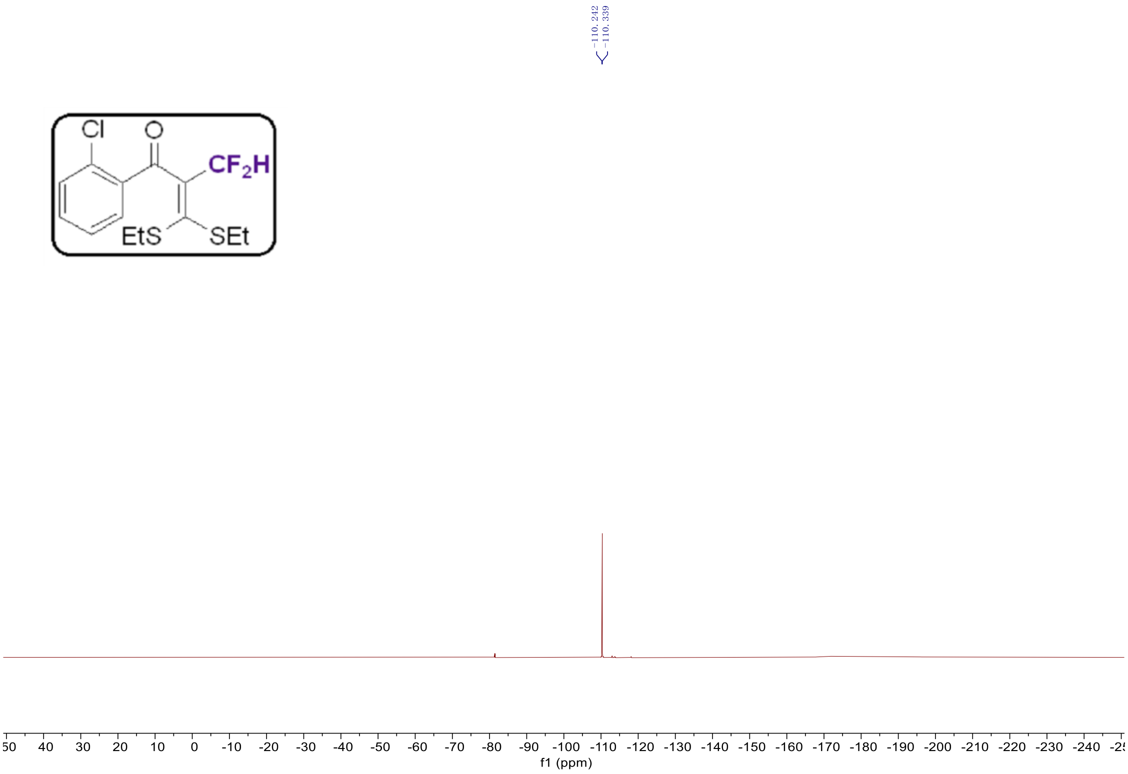
[1]H spectrum (600 MHz, CDCl3) of compound 3u



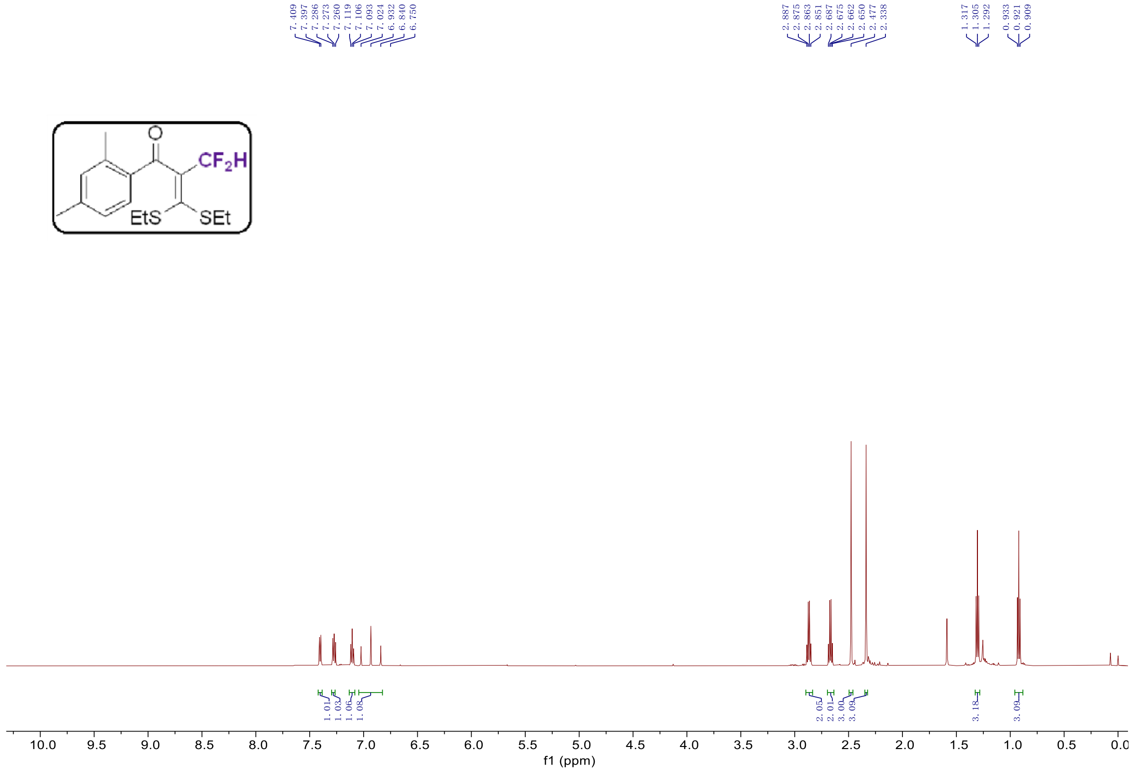
[13]C spectrum (151 MHz, CDCl3) of compound 3u



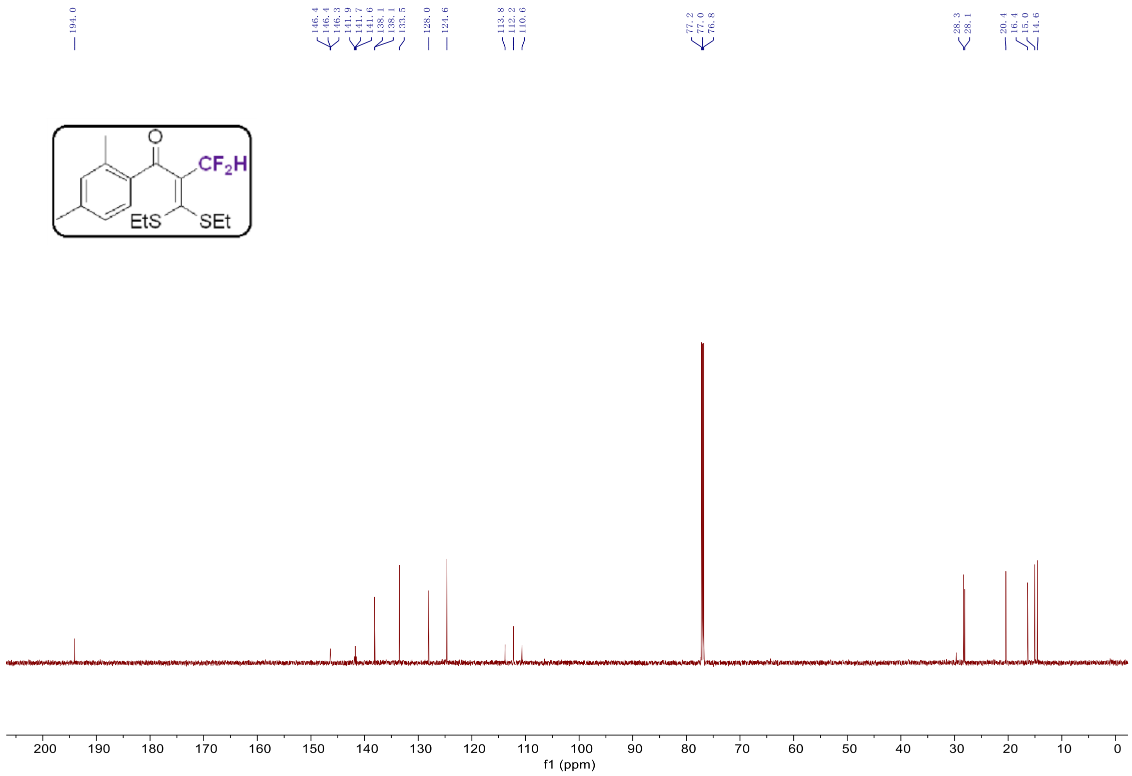
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3u



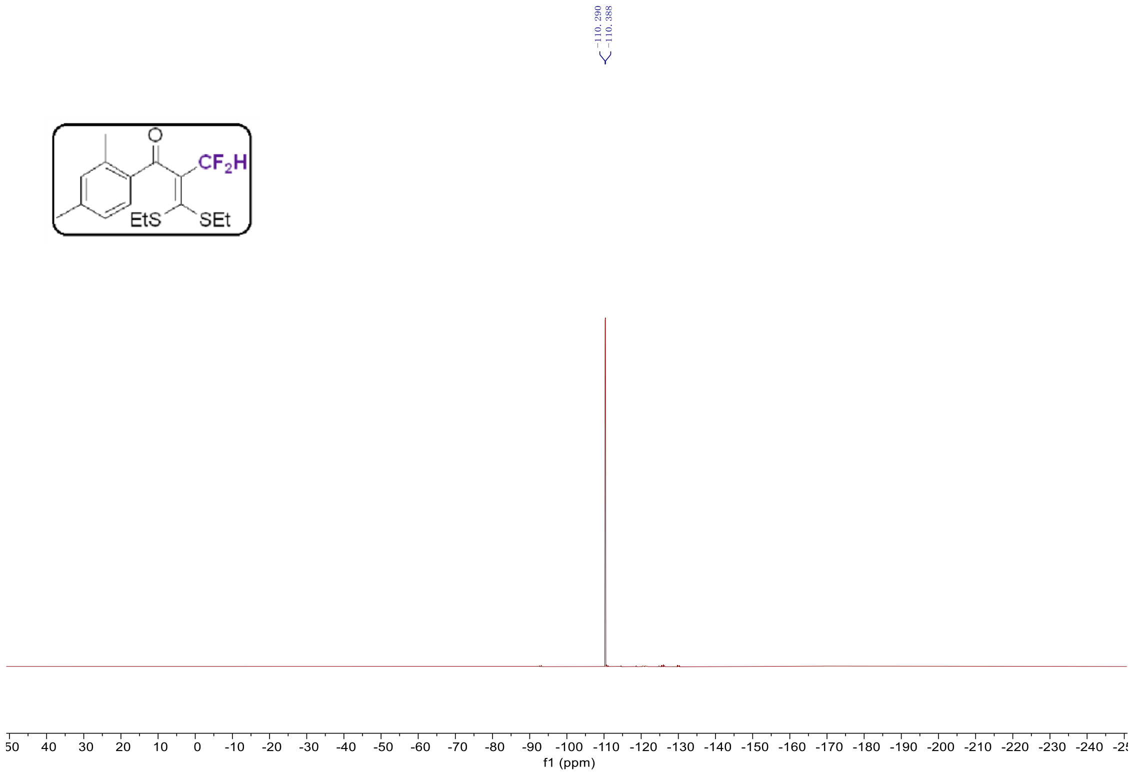
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3v



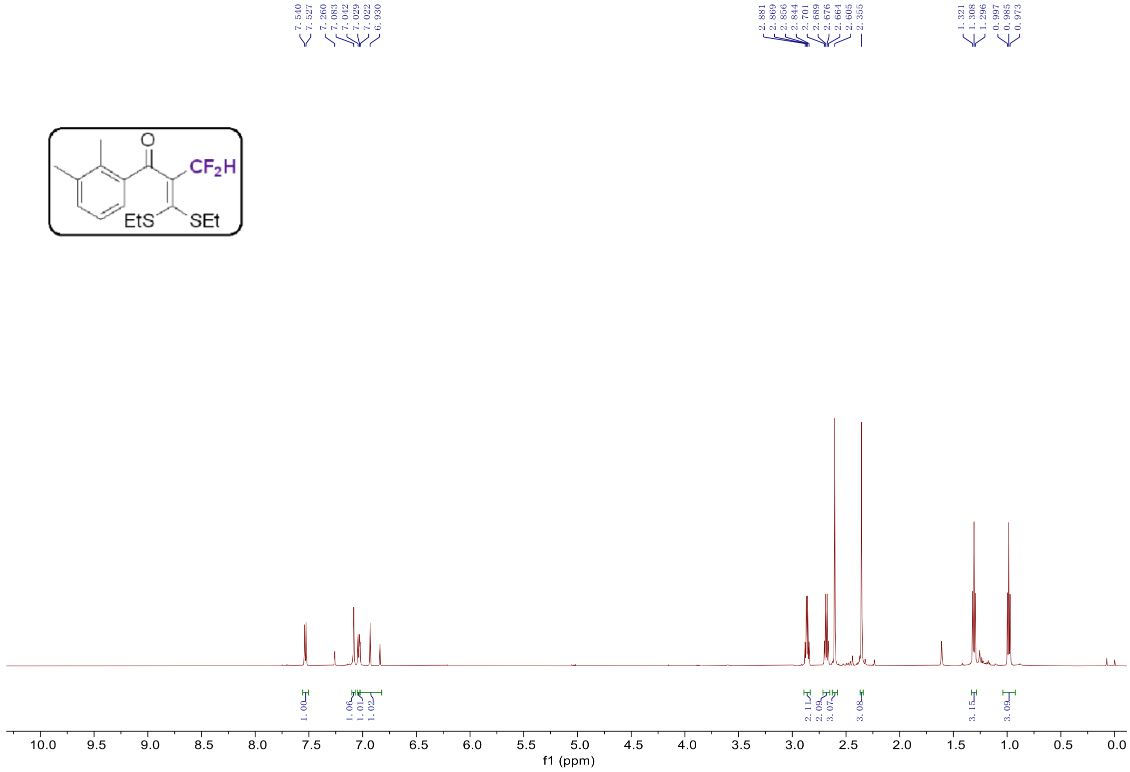
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3v



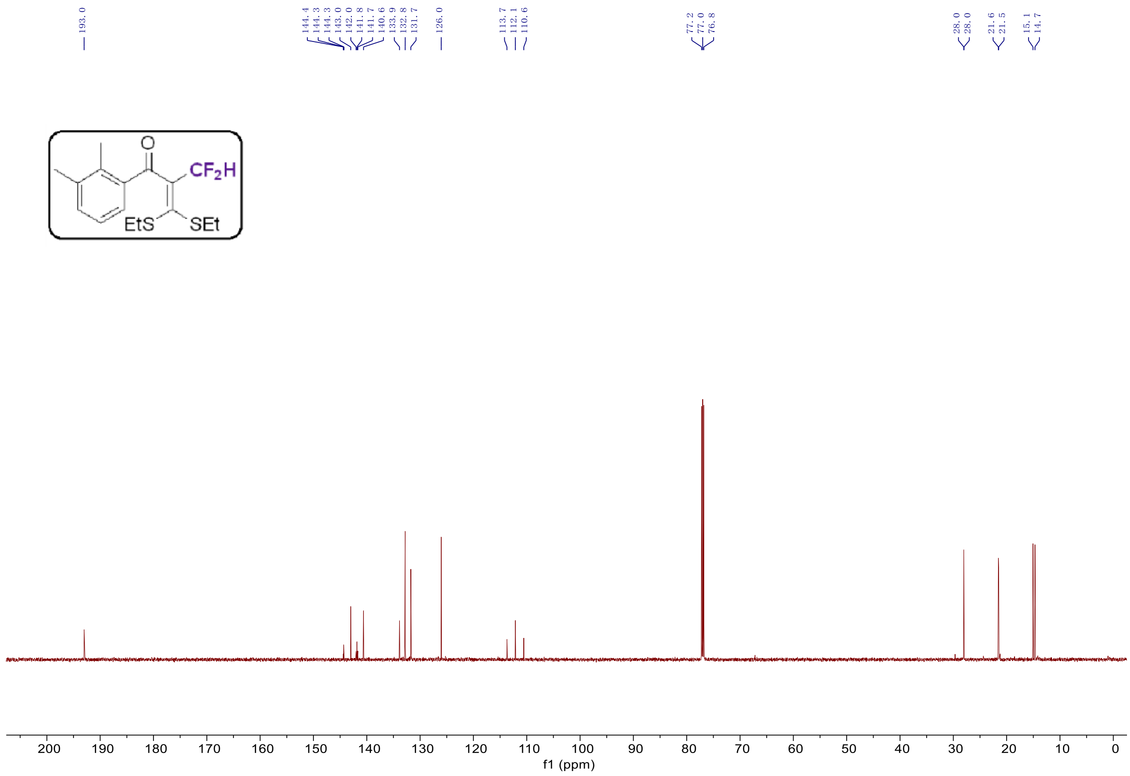
[19]F spectrum (565 MHz, CDCl3) of compound 3v



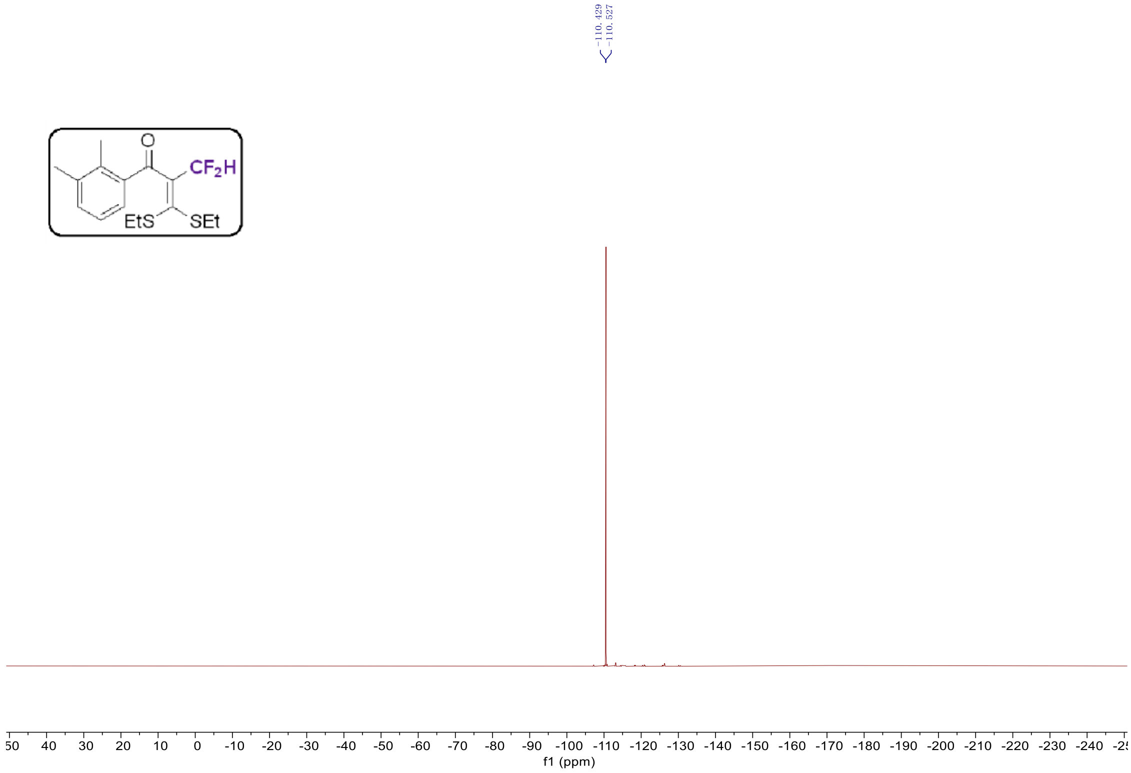
[1]H spectrum (600 MHz, $CDCl_3$) of compound 3w



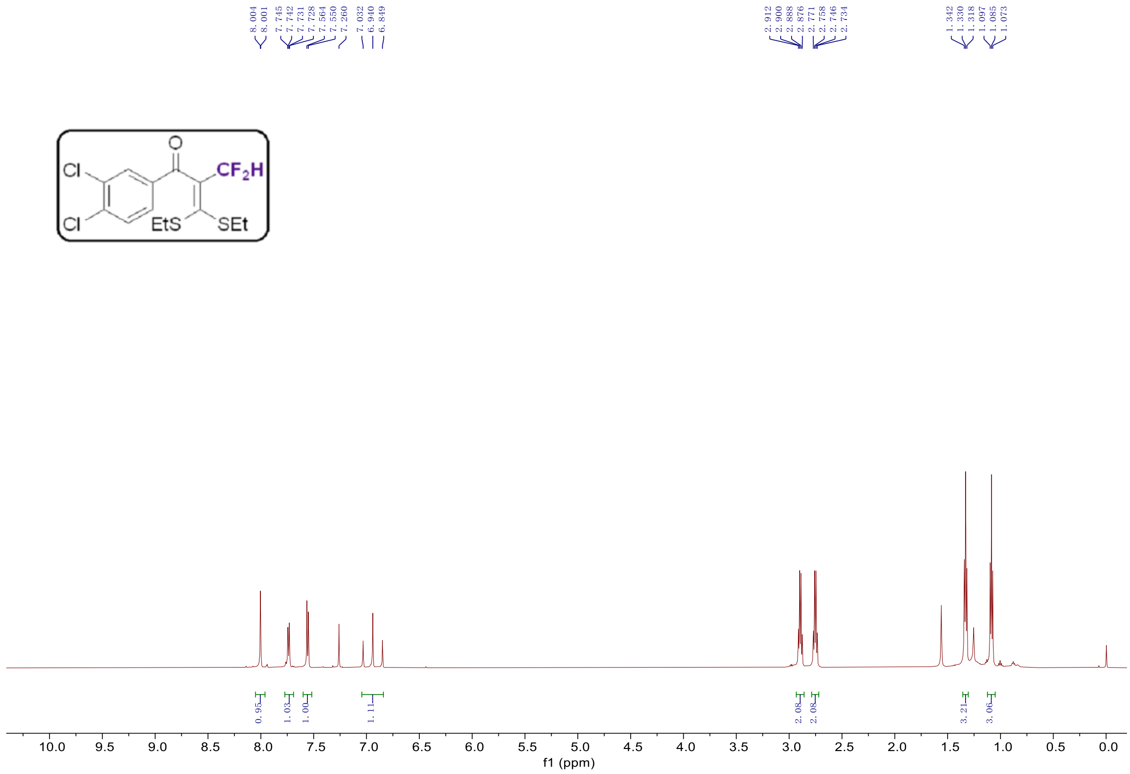
[13]C spectrum (151 MHz, $CDCl_3$) of compound 3w



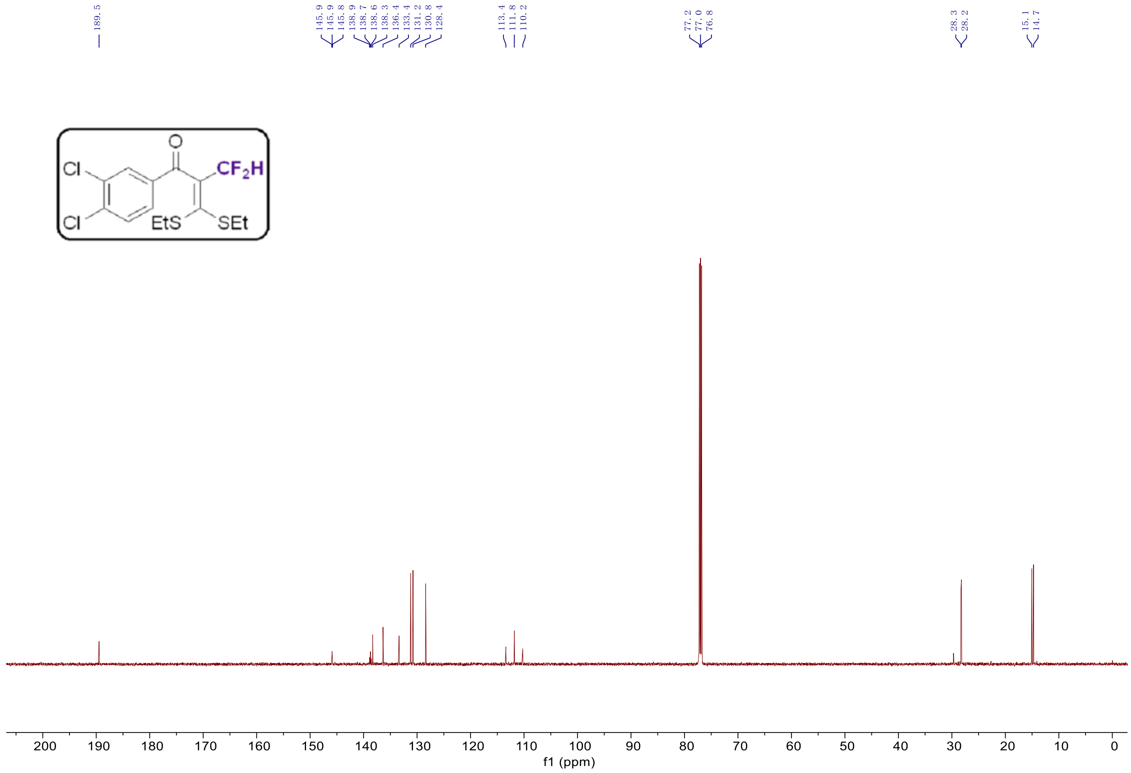
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3w



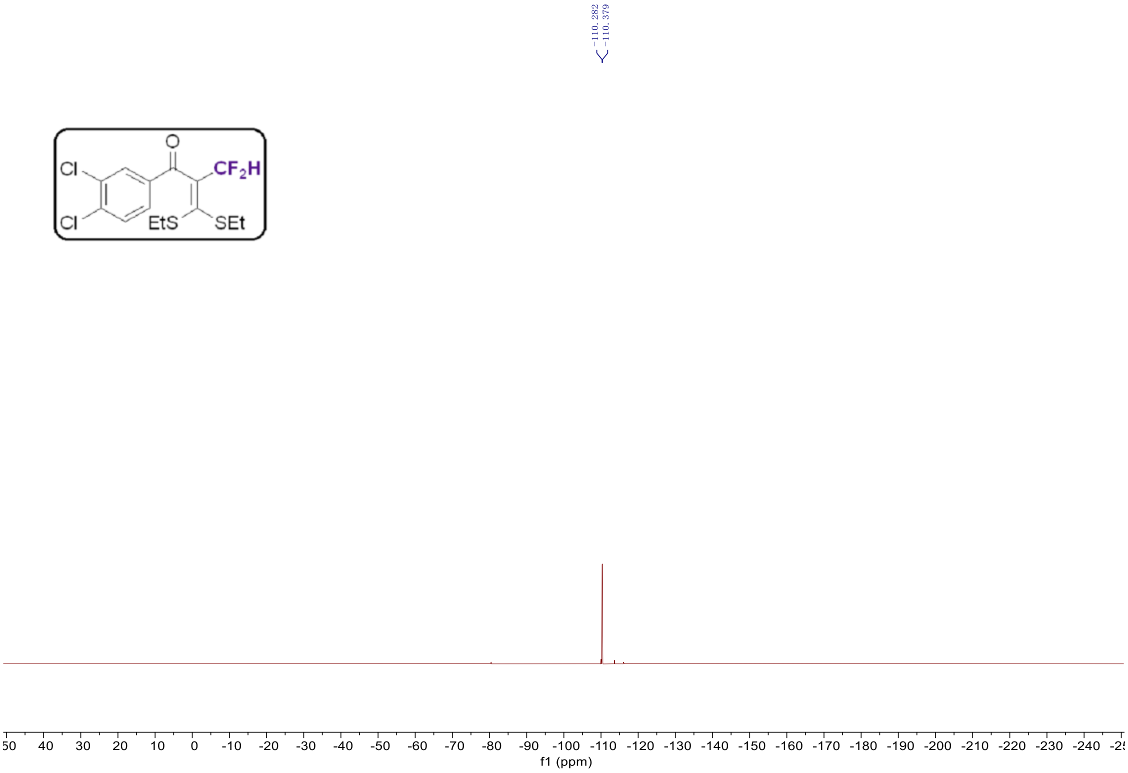
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3x



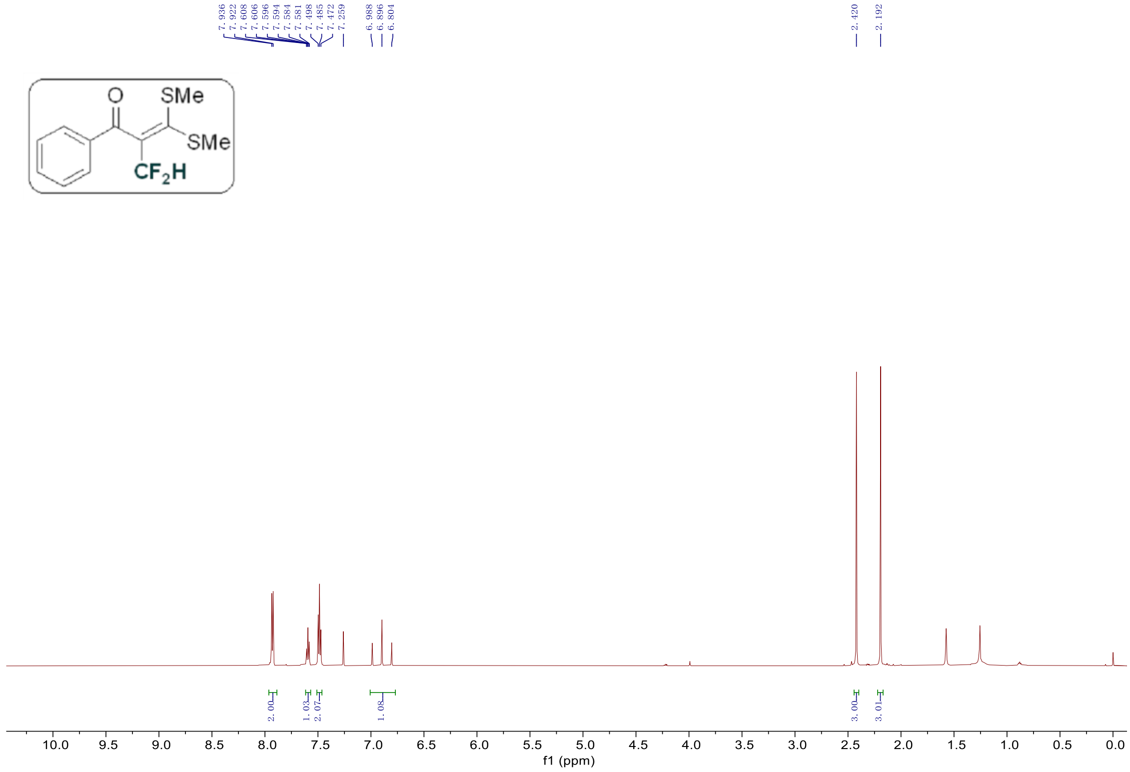
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3x



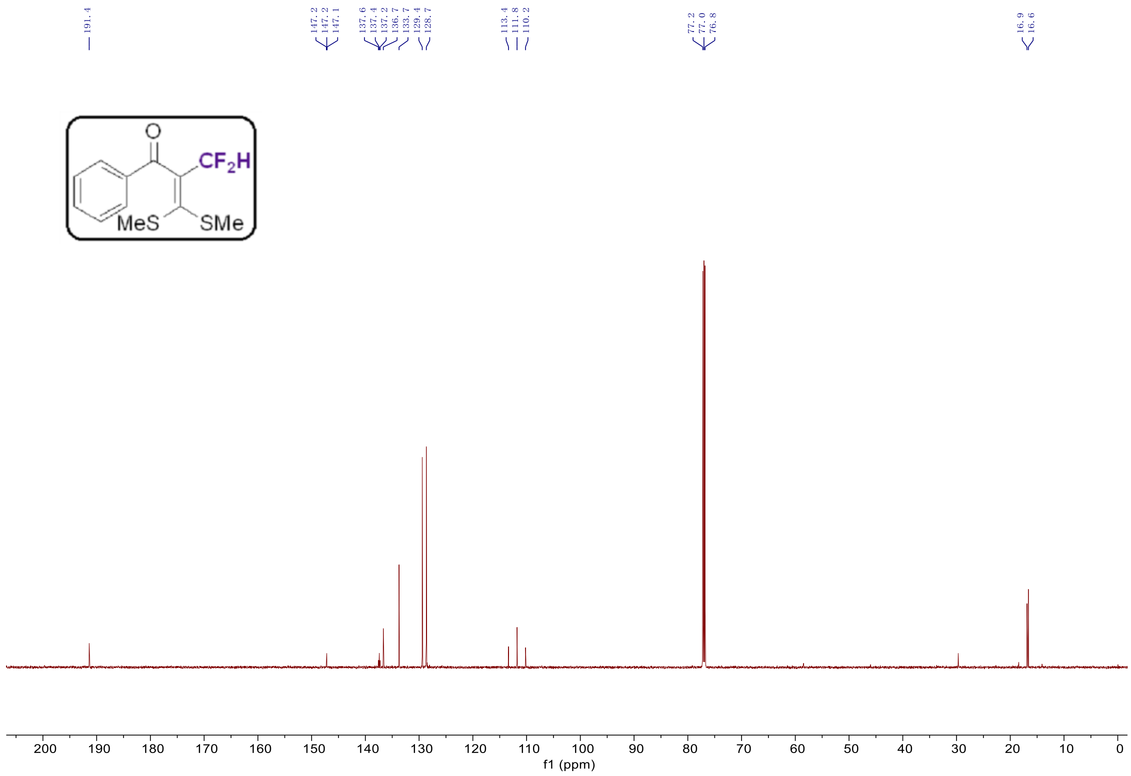
[19]F spectrum (565 MHz, $CDCl_3$) of compound 3x



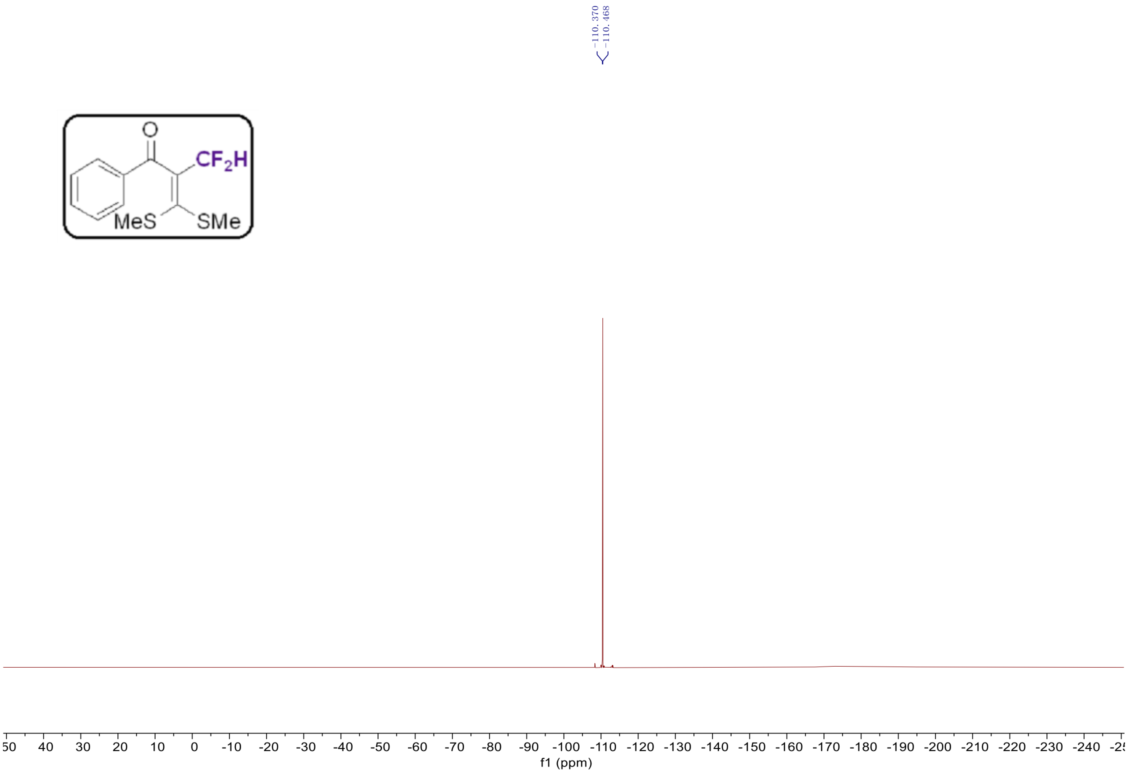
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3y



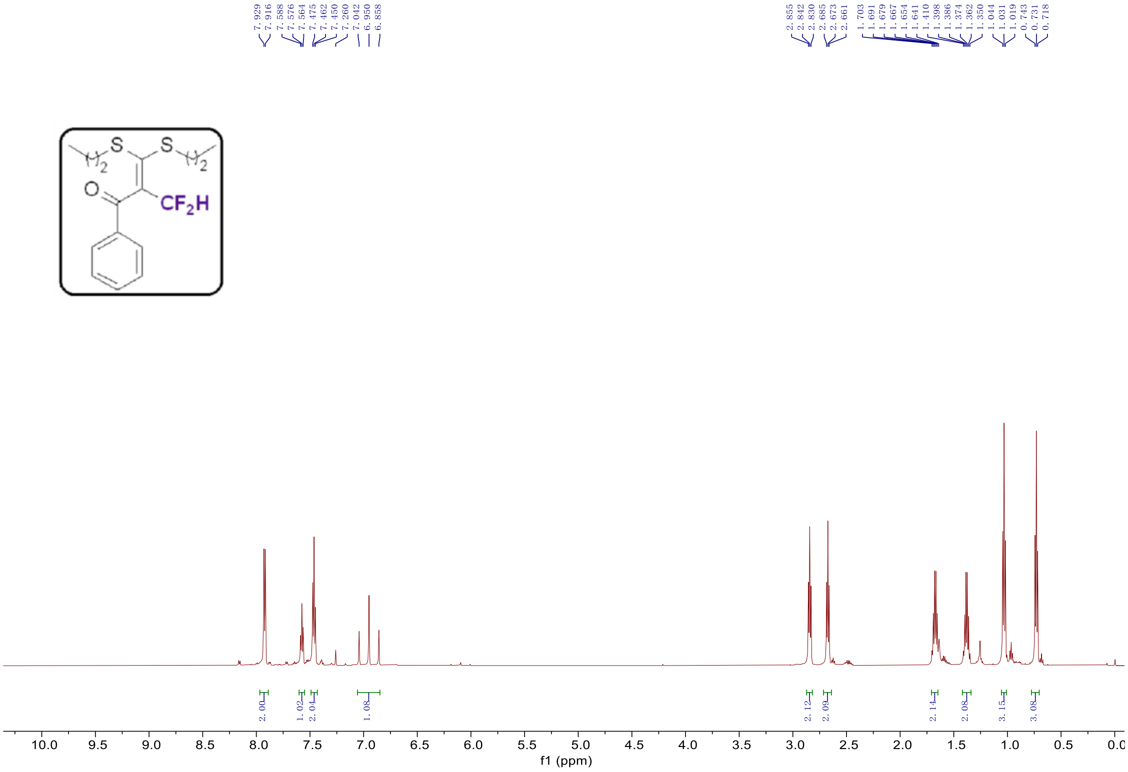
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3y



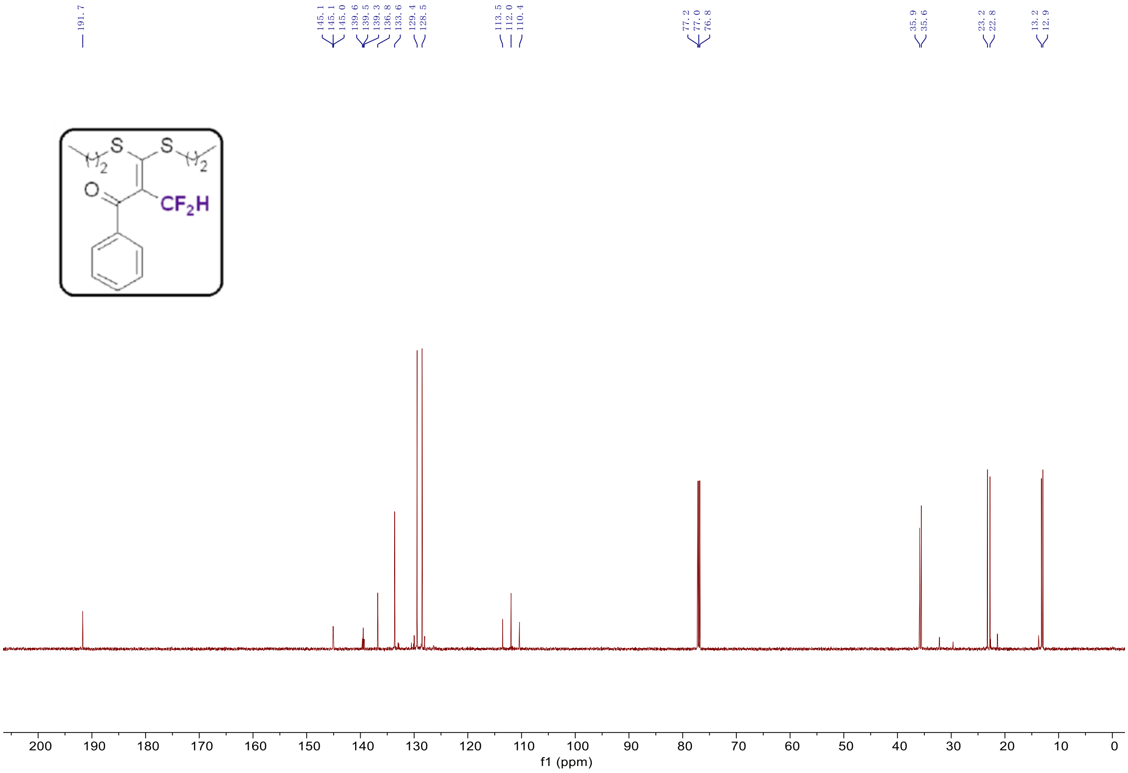
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3y



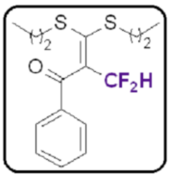
¹H spectrum (600 MHz, CDCl₃) of compound 3z

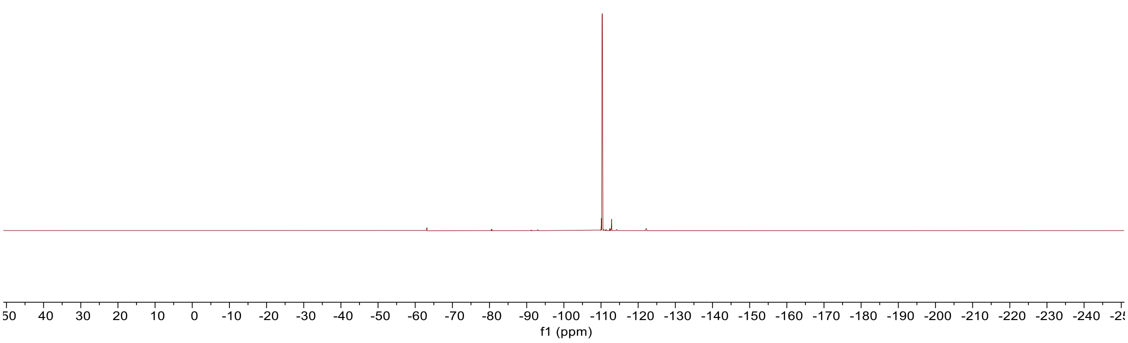


¹³C spectrum (151 MHz, CDCl₃) of compound 3z

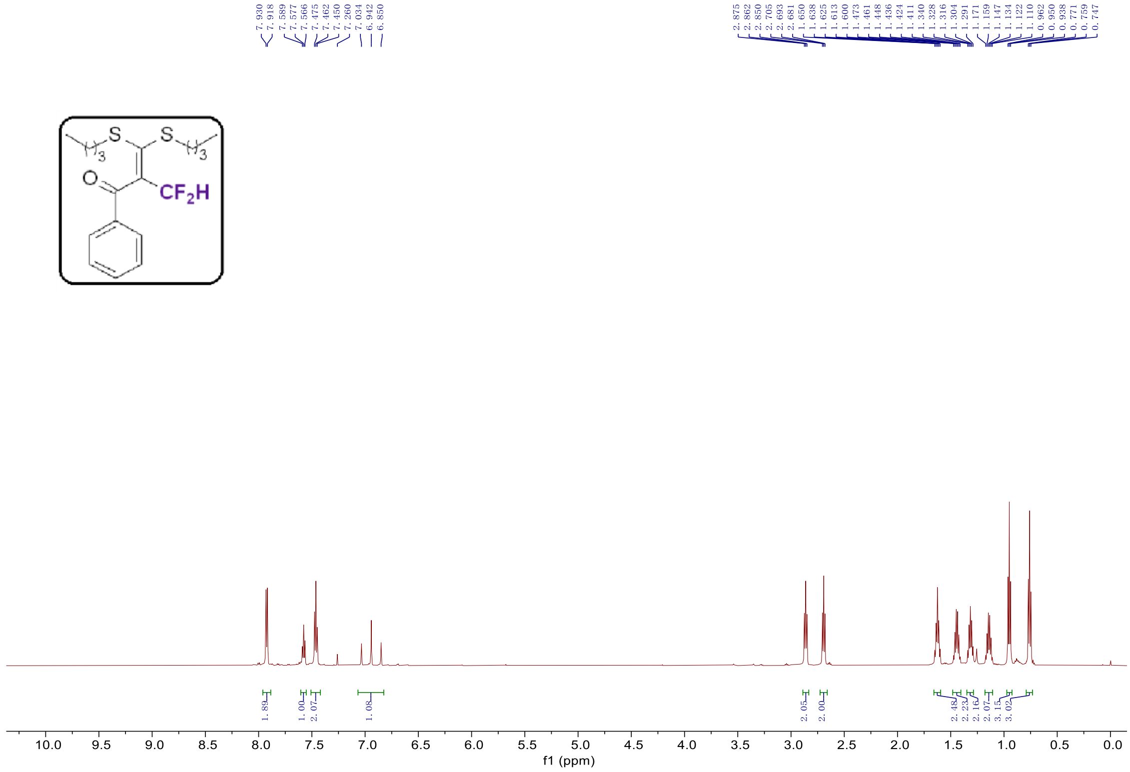


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3z

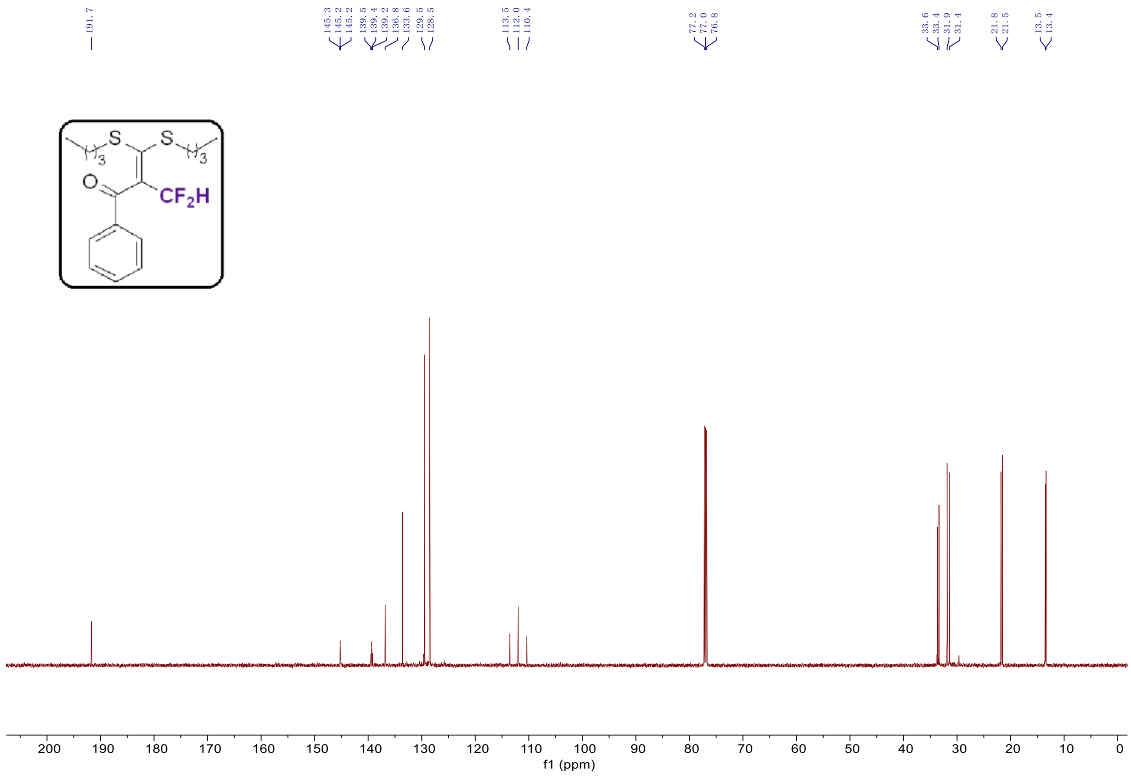




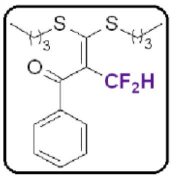
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 3aa

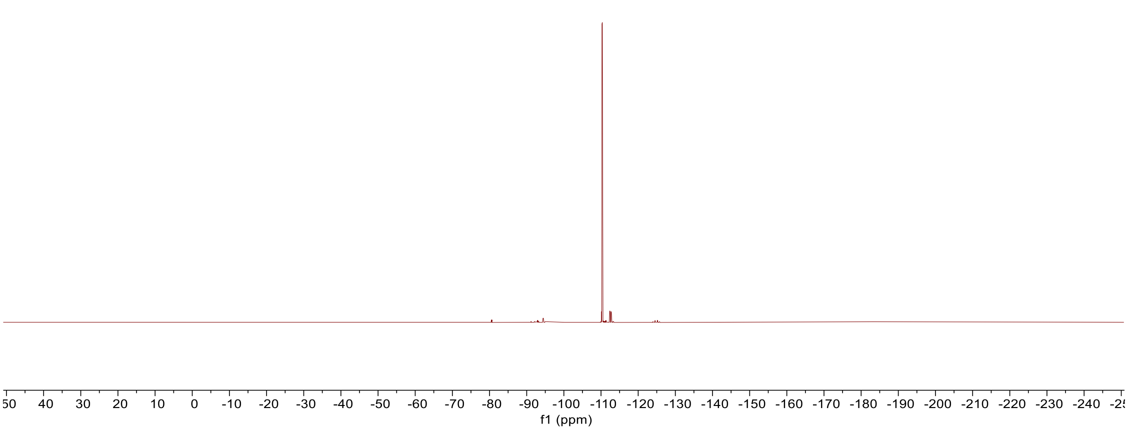


^{13}C spectrum (151 MHz, $CDCl_3$) of compound 3aa

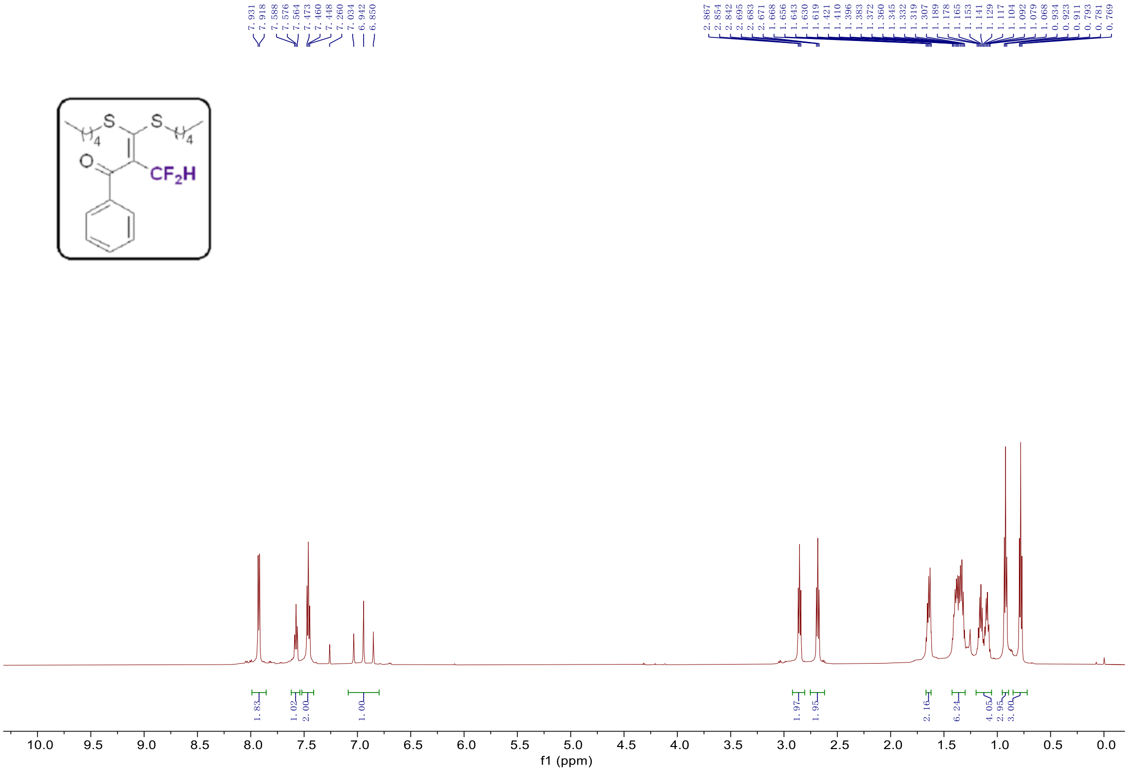


^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3aa

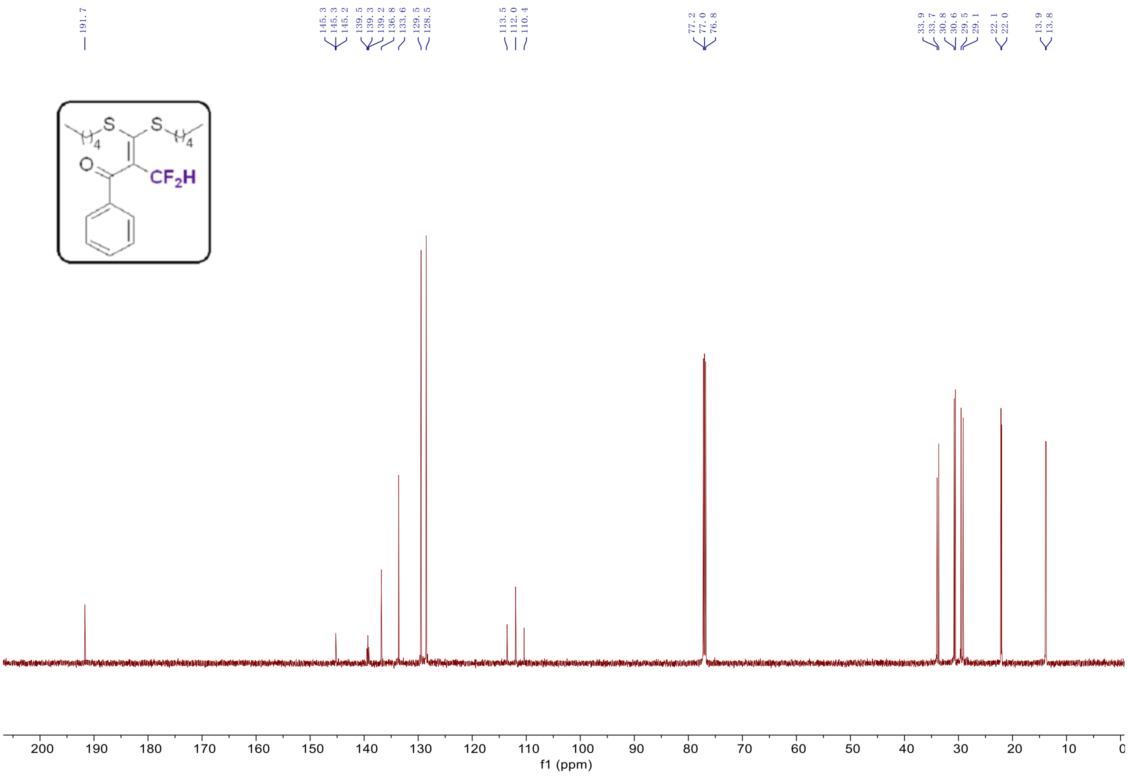




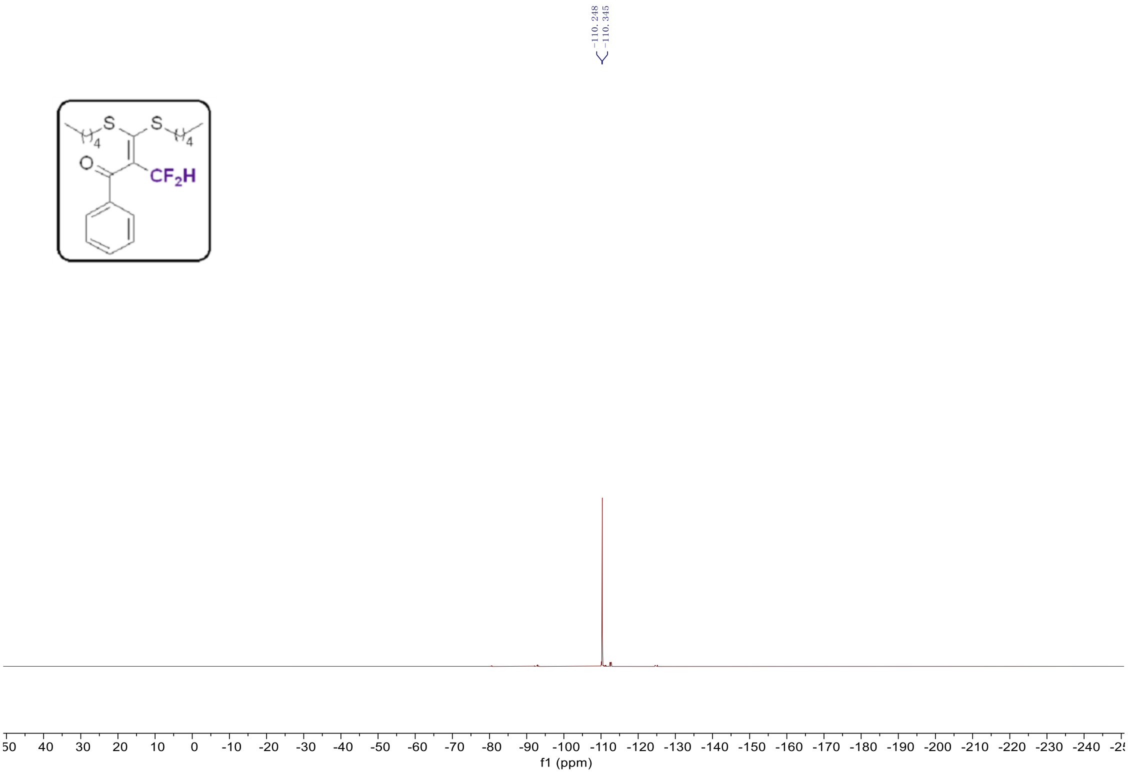
[1]H spectrum (600 MHz, CDCl3) of compound 3ab



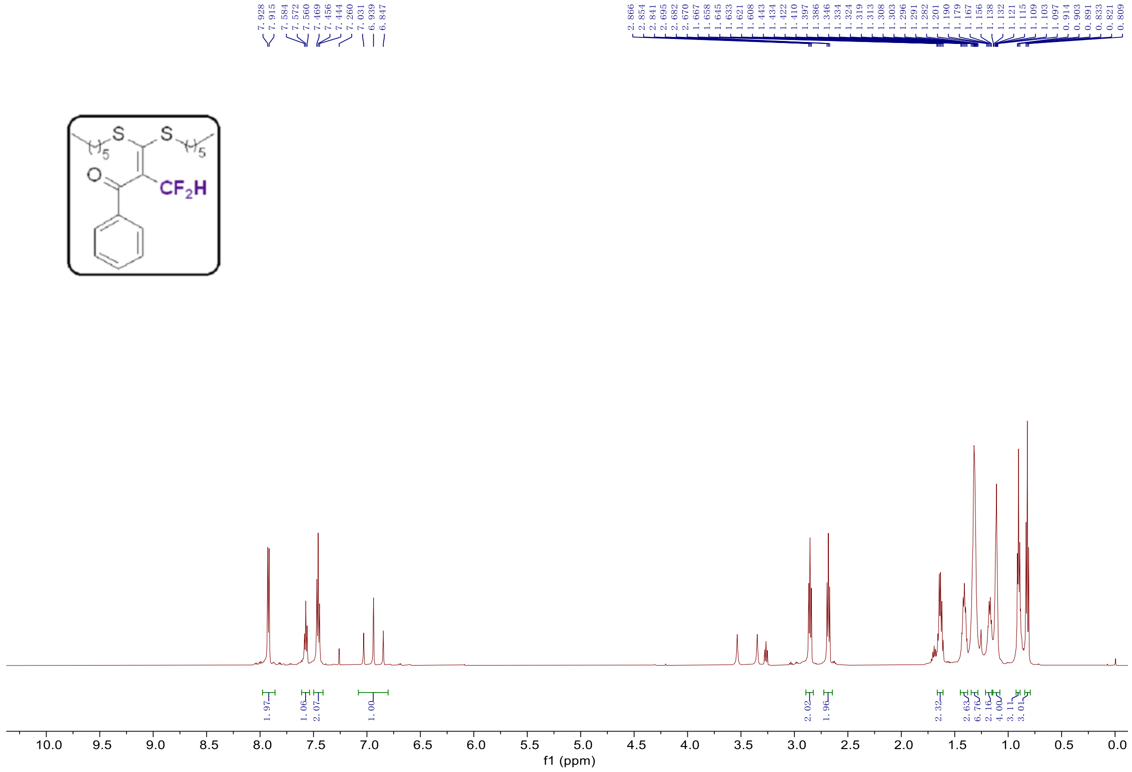
[13]C spectrum (151 MHz, CDCl3) of compound 3ab



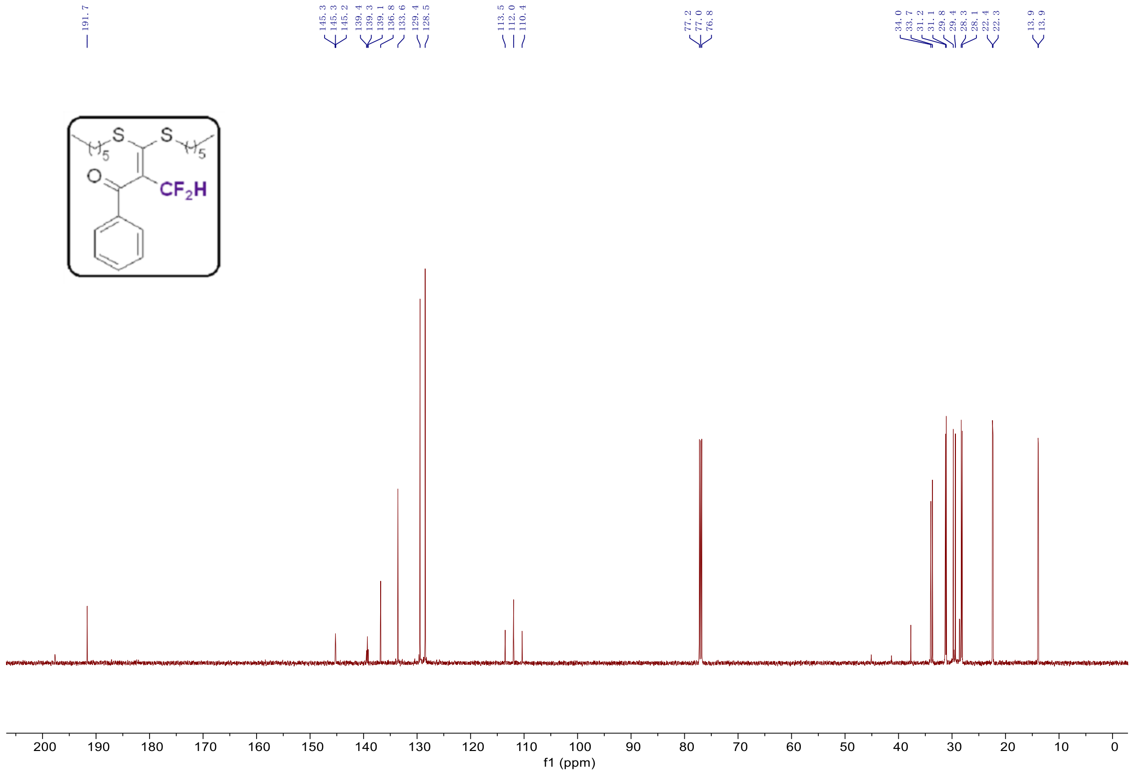
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3ab



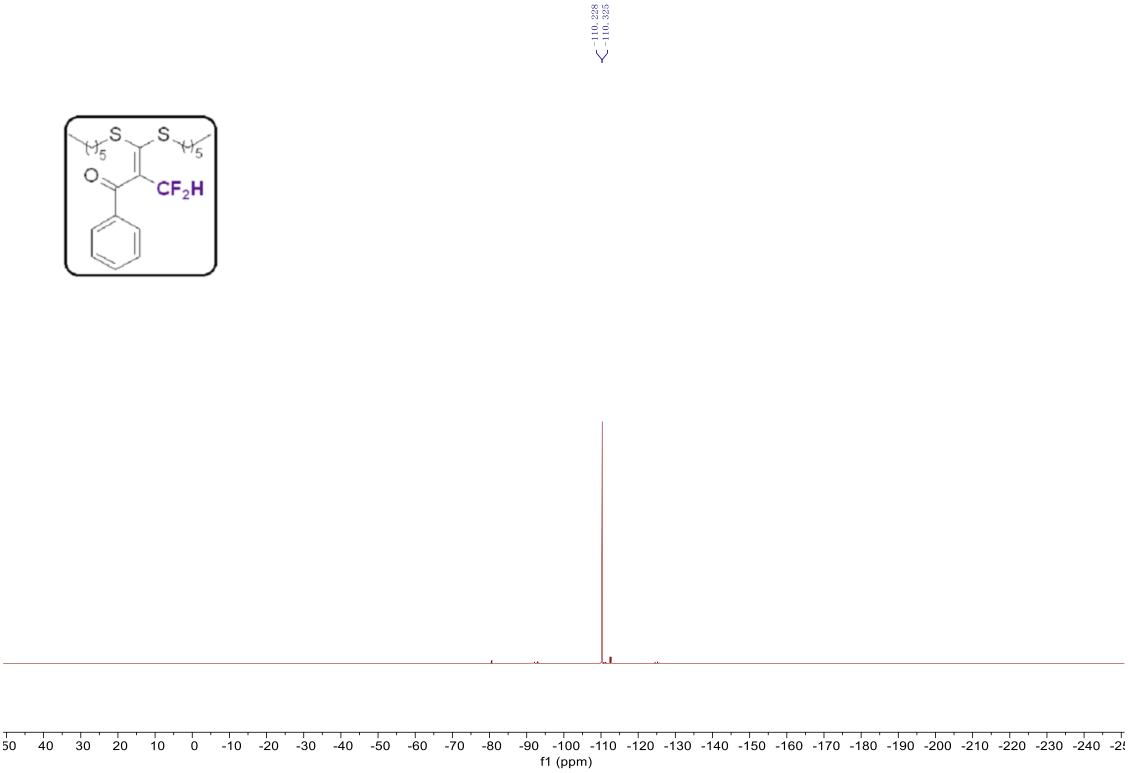
^{1}H spectrum (600 MHz, CDCl$_3$) of compound 3ac



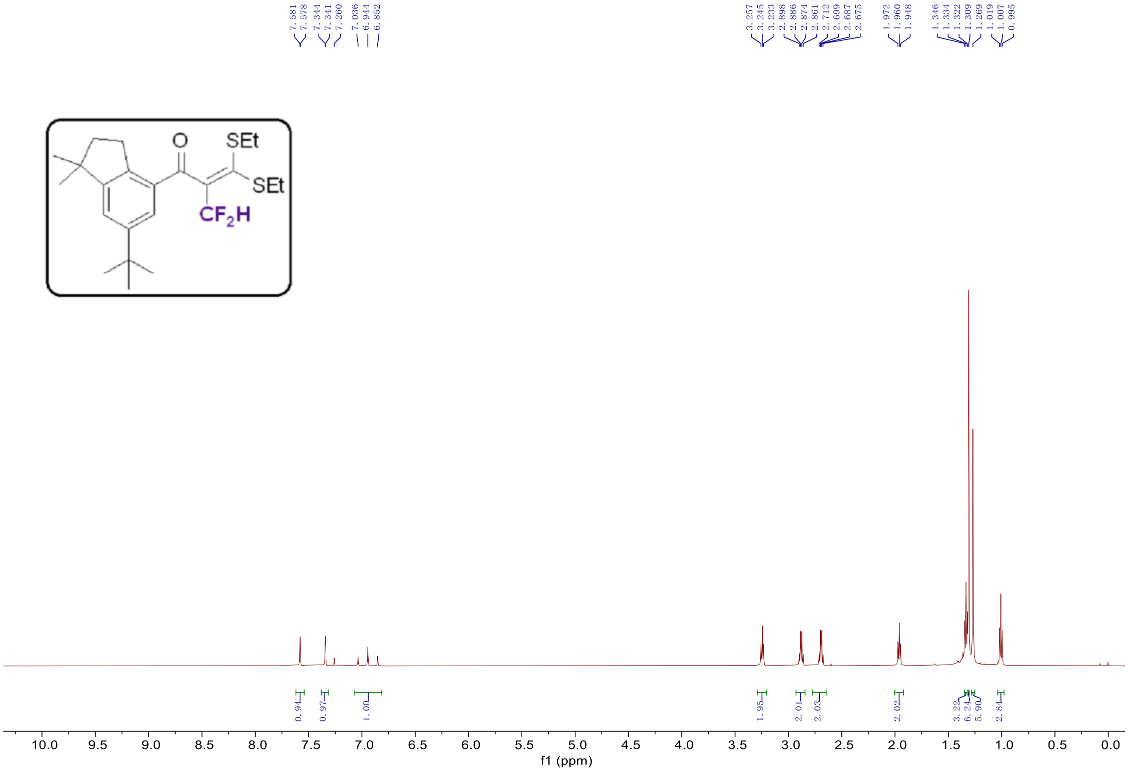
^{13}C spectrum (151 MHz, CDCl$_3$) of compound 3ac



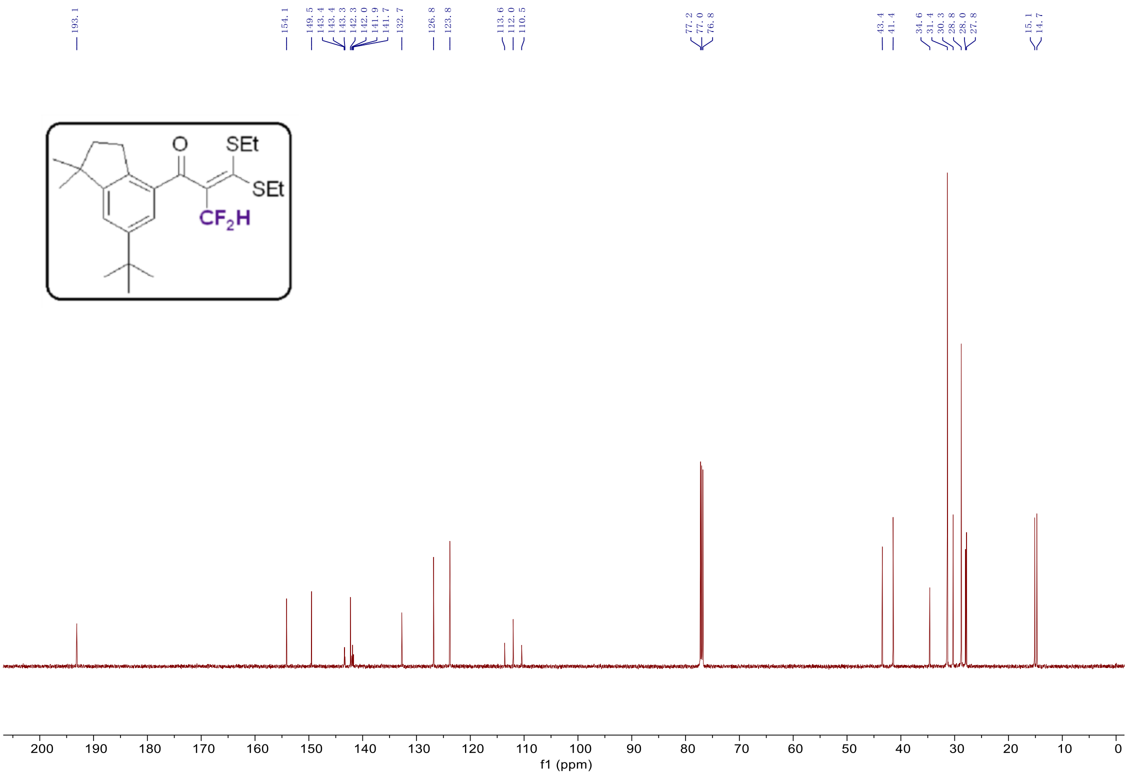
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 3ac



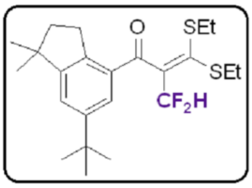
[1]H spectrum (600 MHz, CDCl3) of compound 3ad

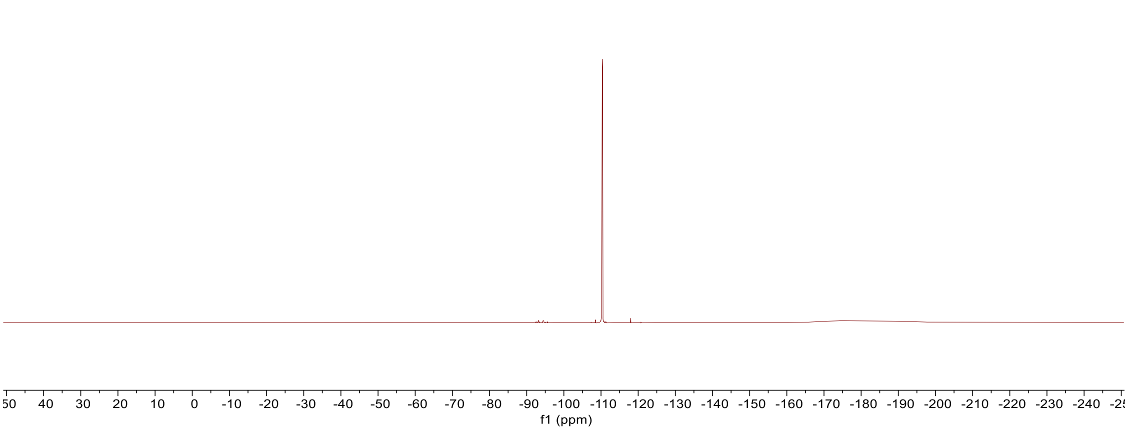


[13]C spectrum (151 MHz, CDCl3) of compound 3ad

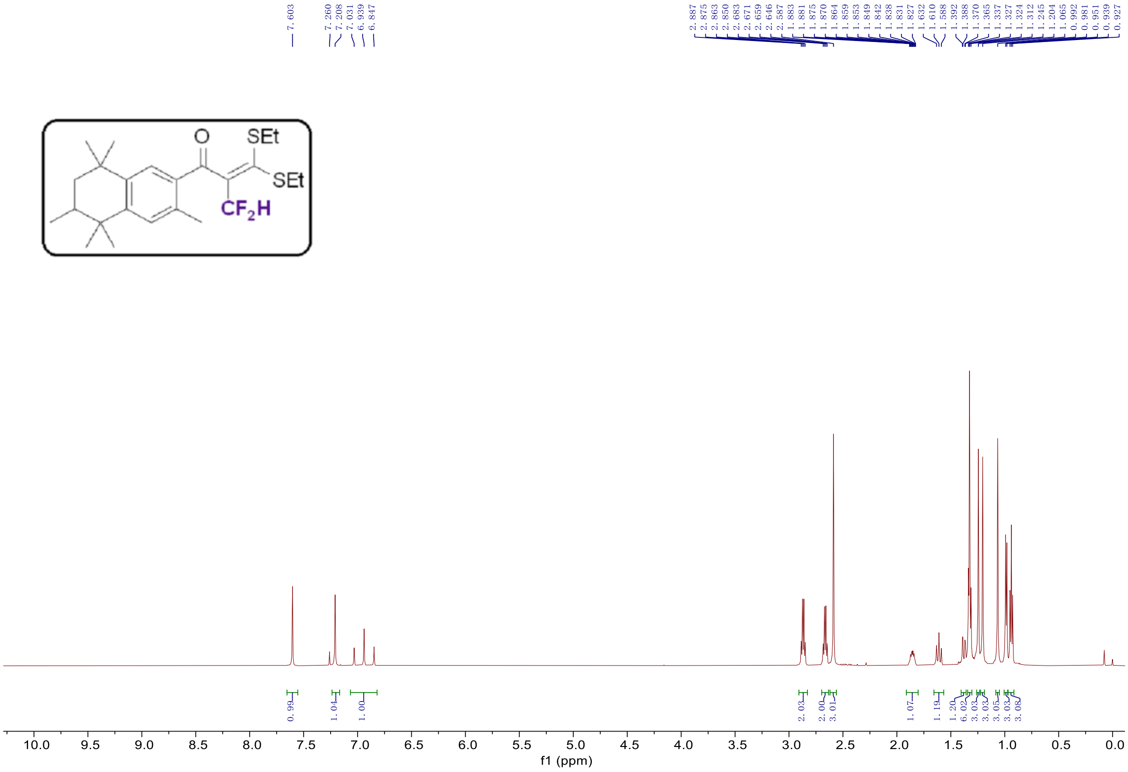


^{19}F spectrum (565 MHz, CDCl$_3$) of compound 3ad

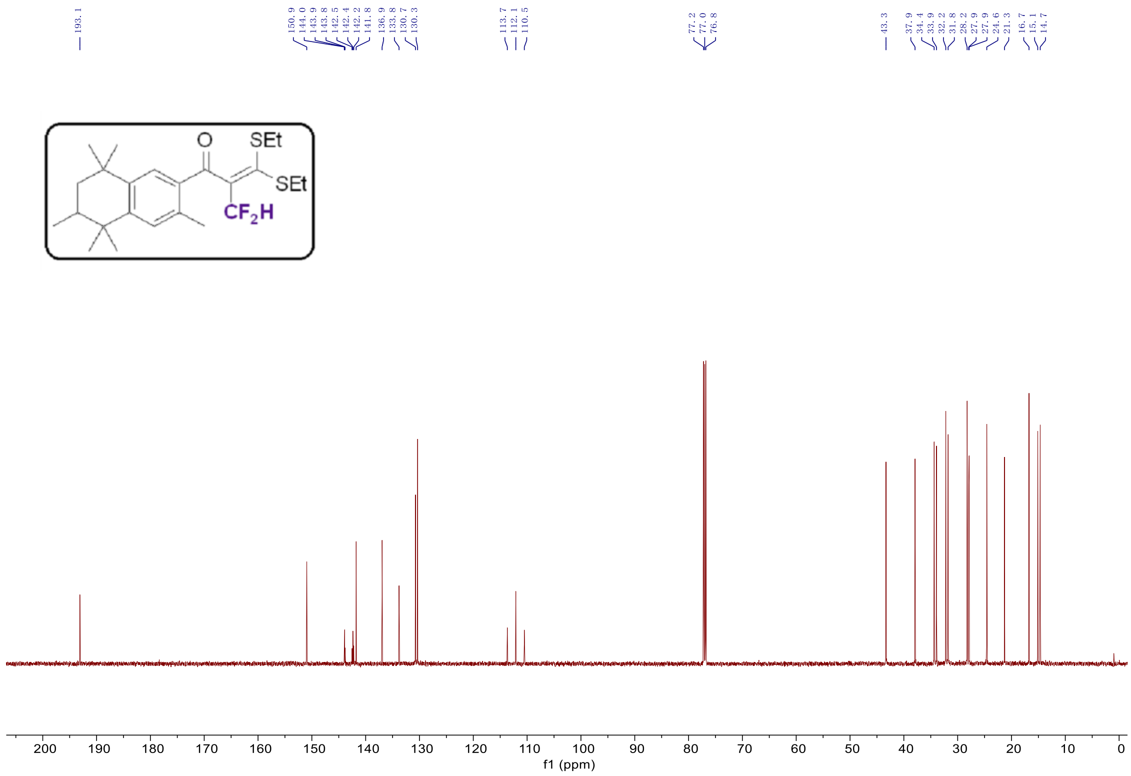




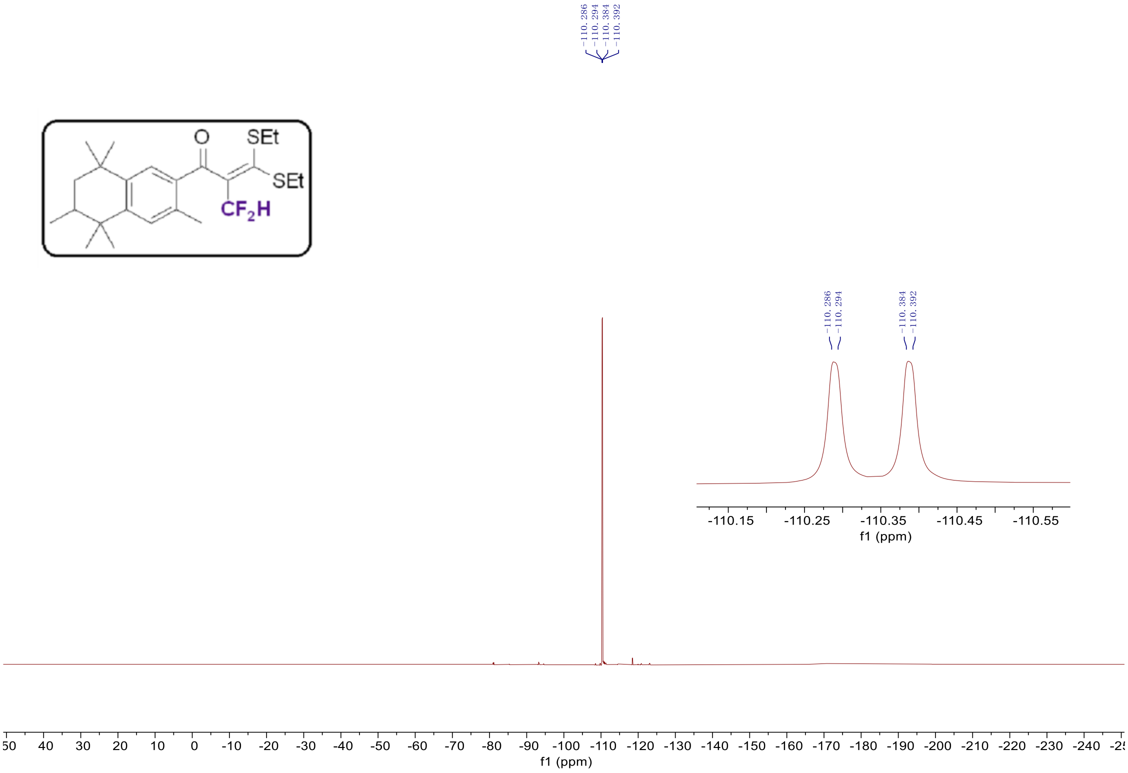
[1]H spectrum (600 MHz, $CDCl_3$) of compound 3ae



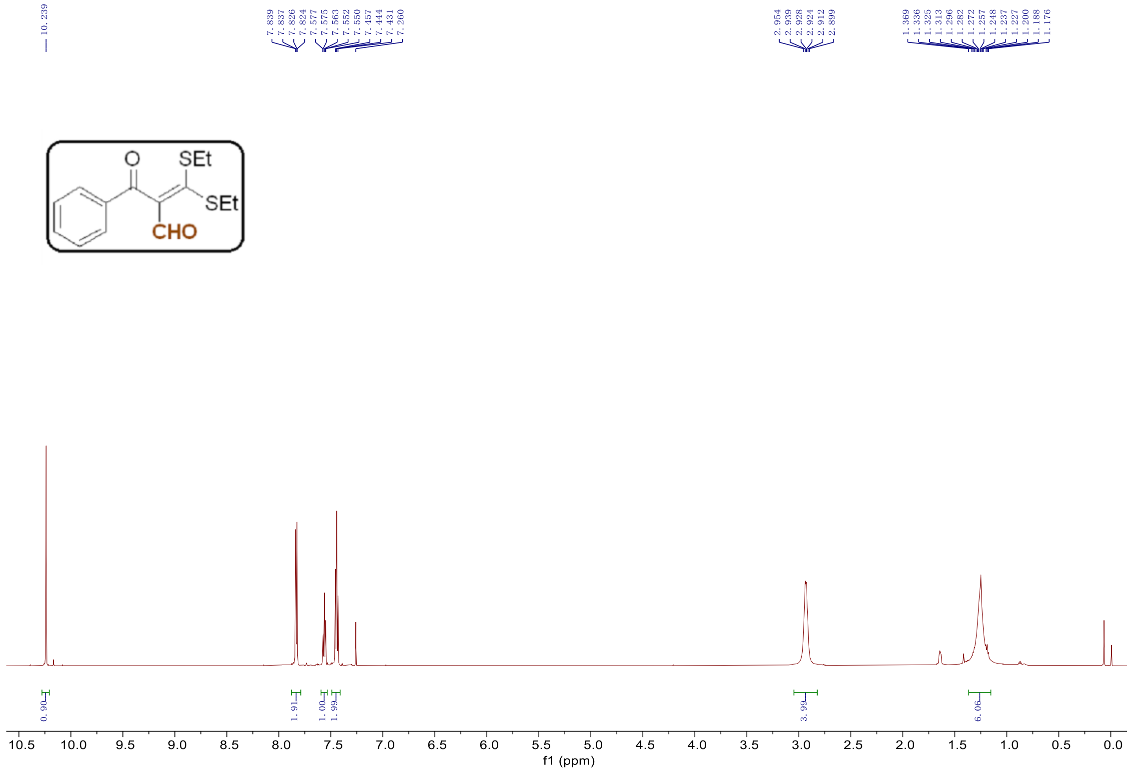
[13]C spectrum (151 MHz, $CDCl_3$) of compound 3ae



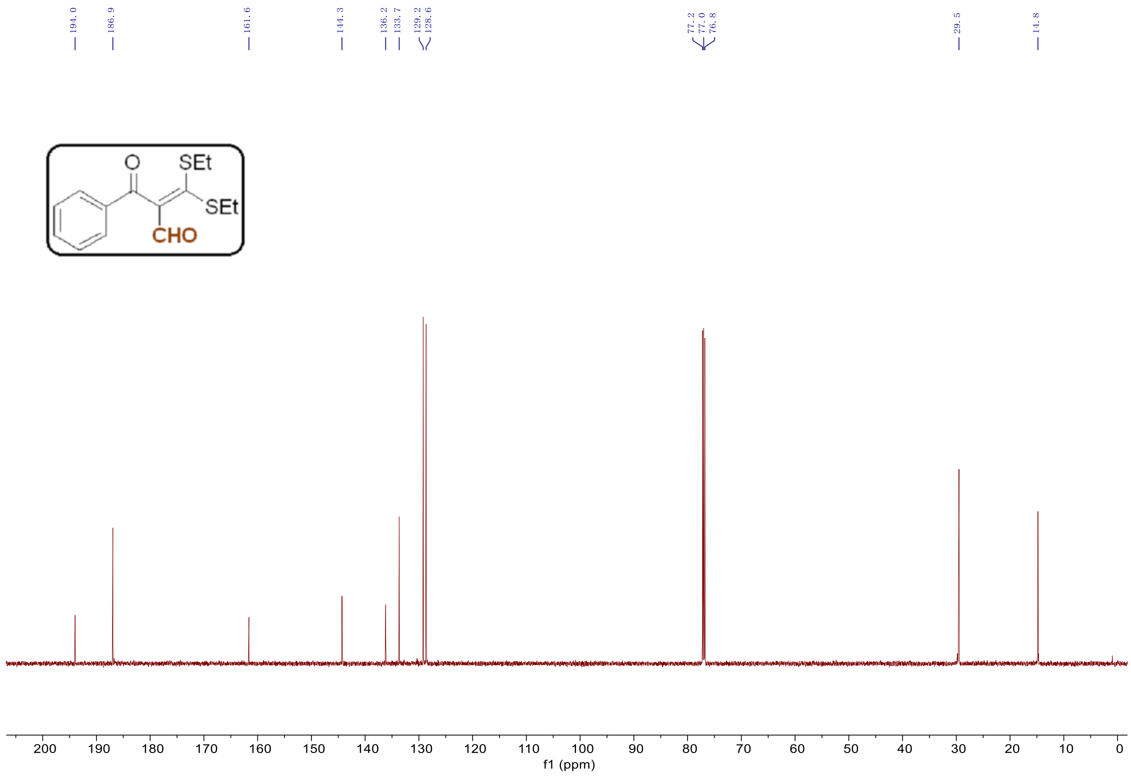
[19]F spectrum (565 MHz, $CDCl_3$) of compound 3ae



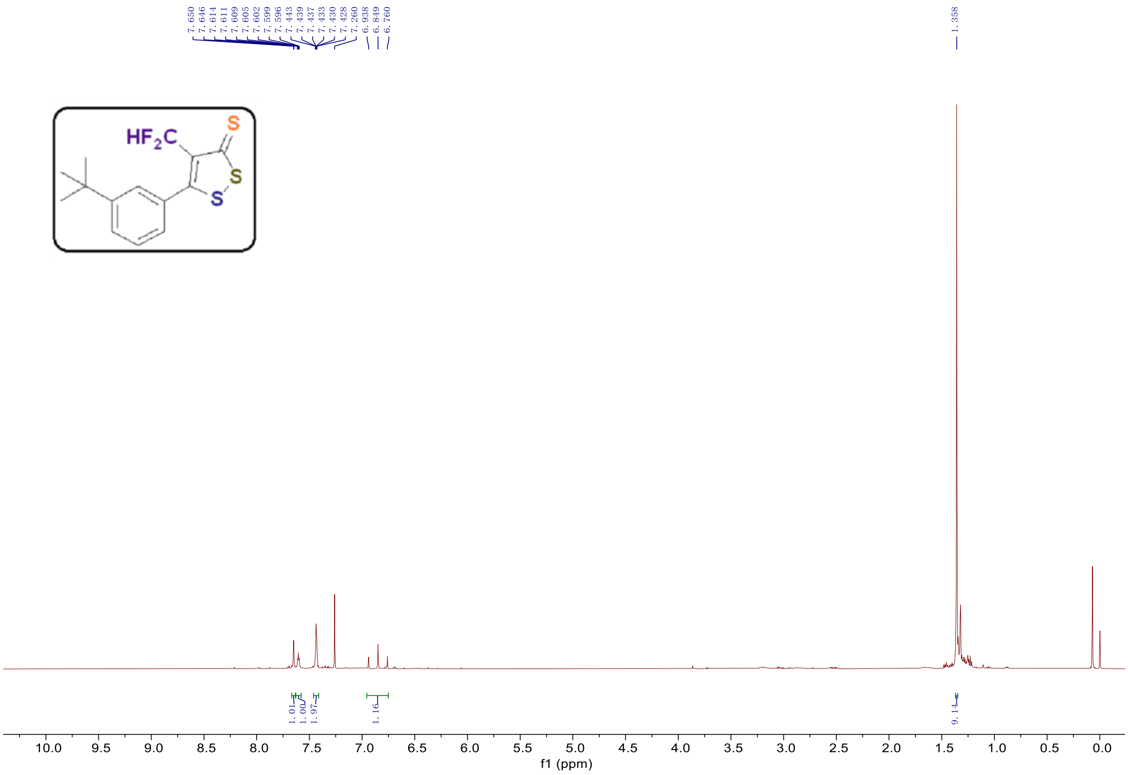
^{1}H spectrum (600 MHz, $CDCl_3$) of compound 4a



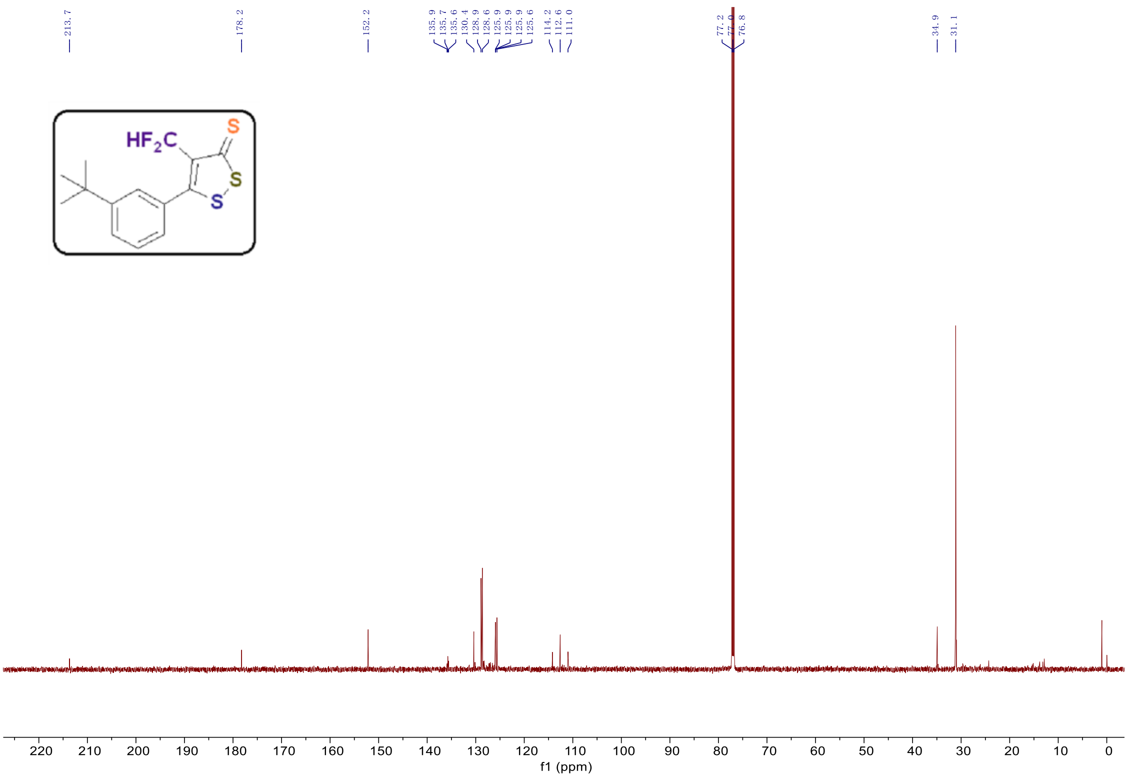
^{13}C spectrum (151 MHz, $CDCl_3$) of compound 4a



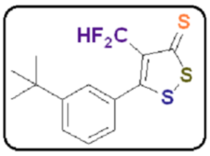
[1]H spectrum (600 MHz, CDCl3) of compound 5o

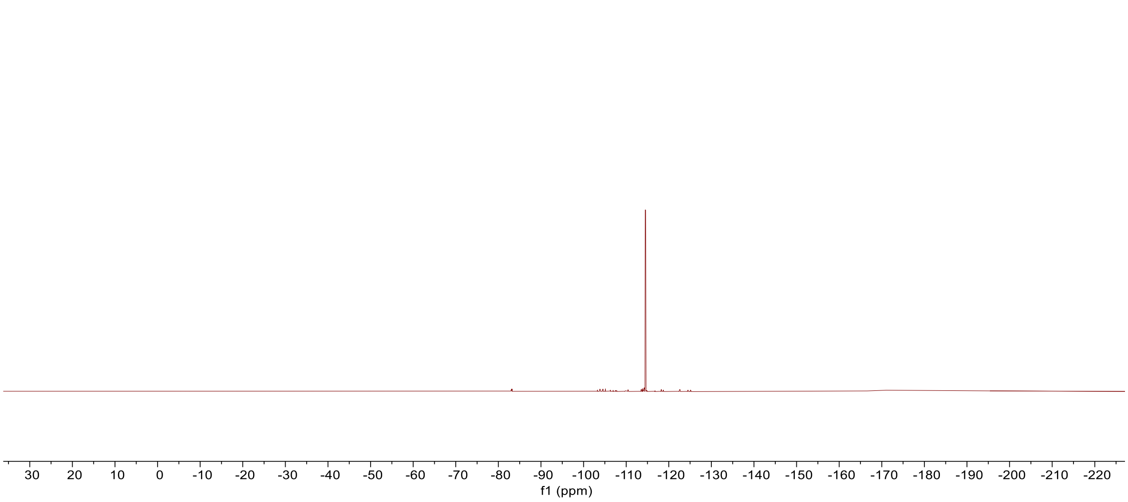


[13]C spectrum (151 MHz, CDCl3) of compound 5o

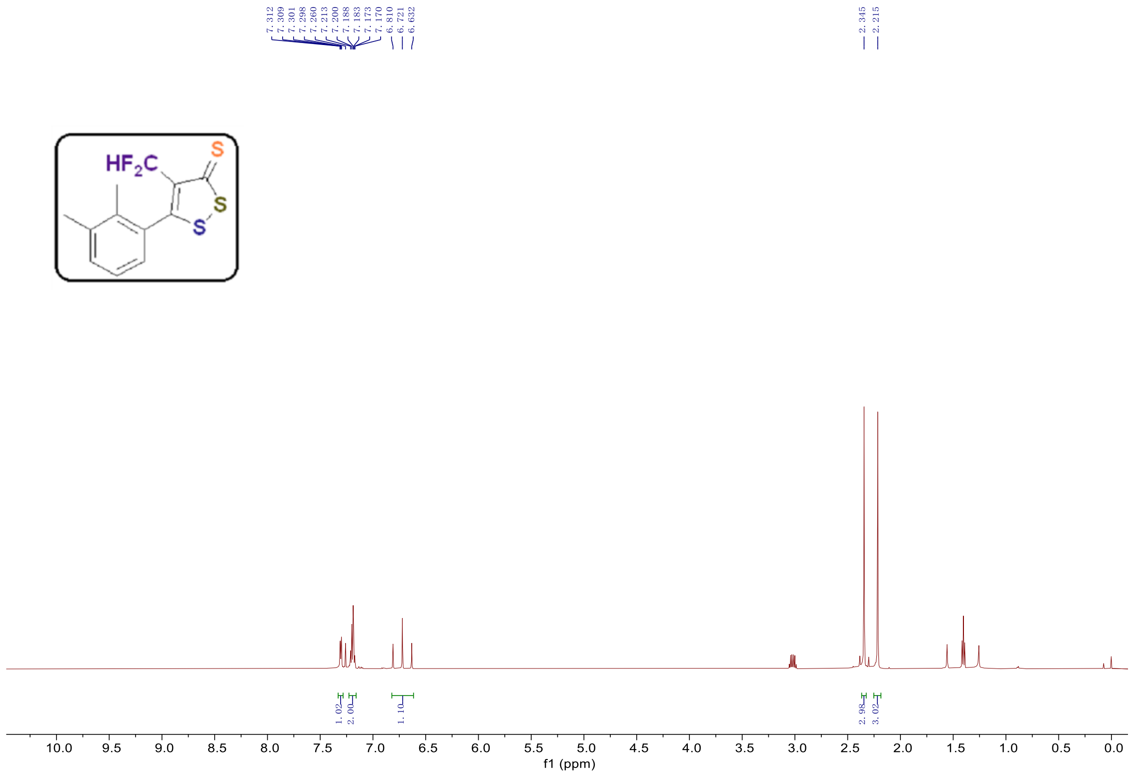


^{19}F spectrum (565 MHz, CDCl$_3$) of compound 5o

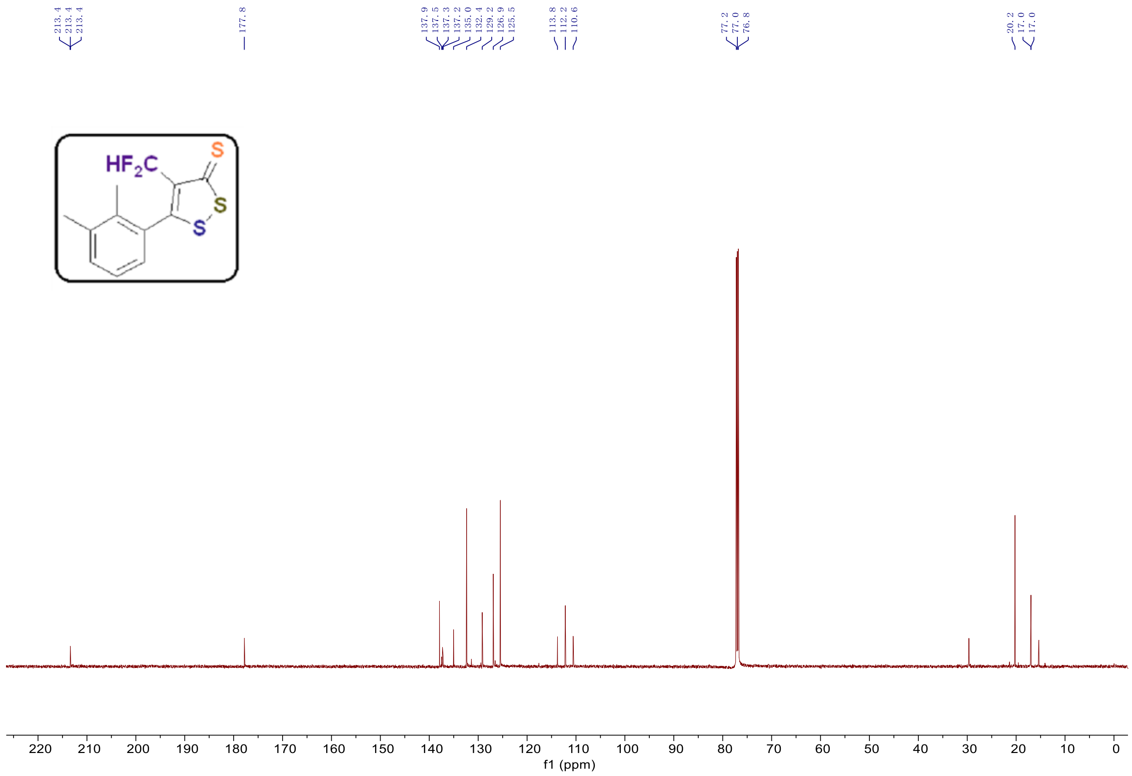




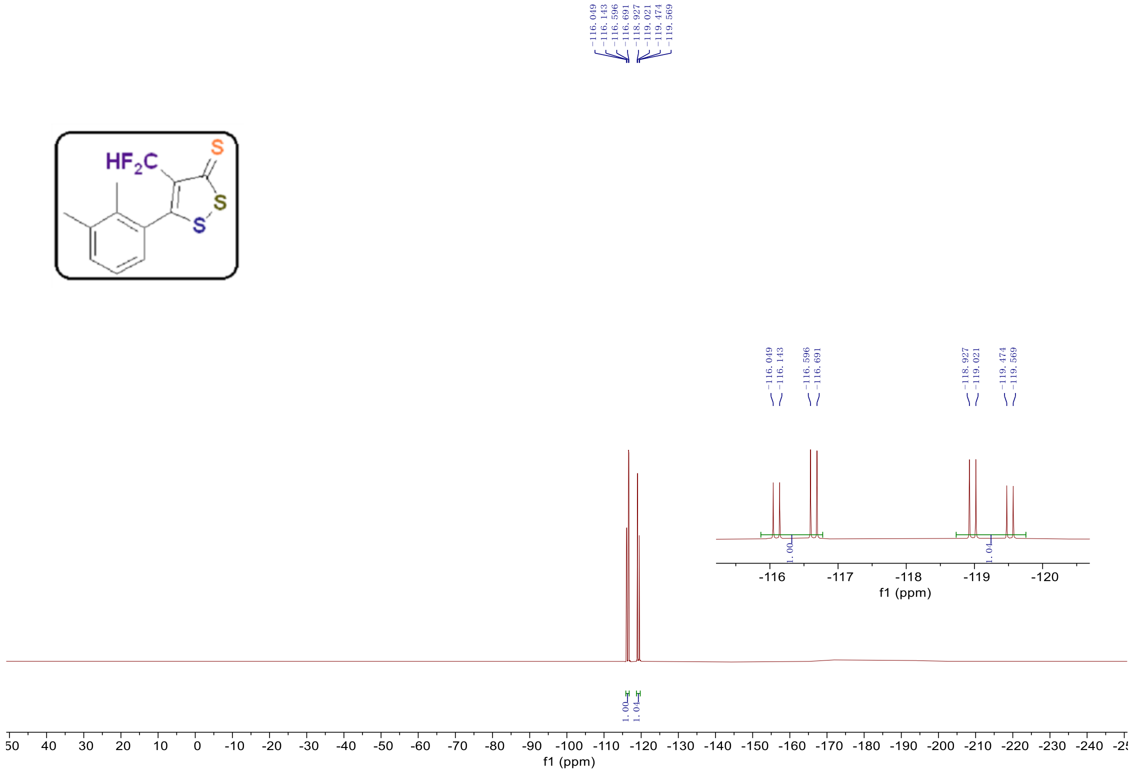
[1]H spectrum (600 MHz, $CDCl_3$) of compound 5w



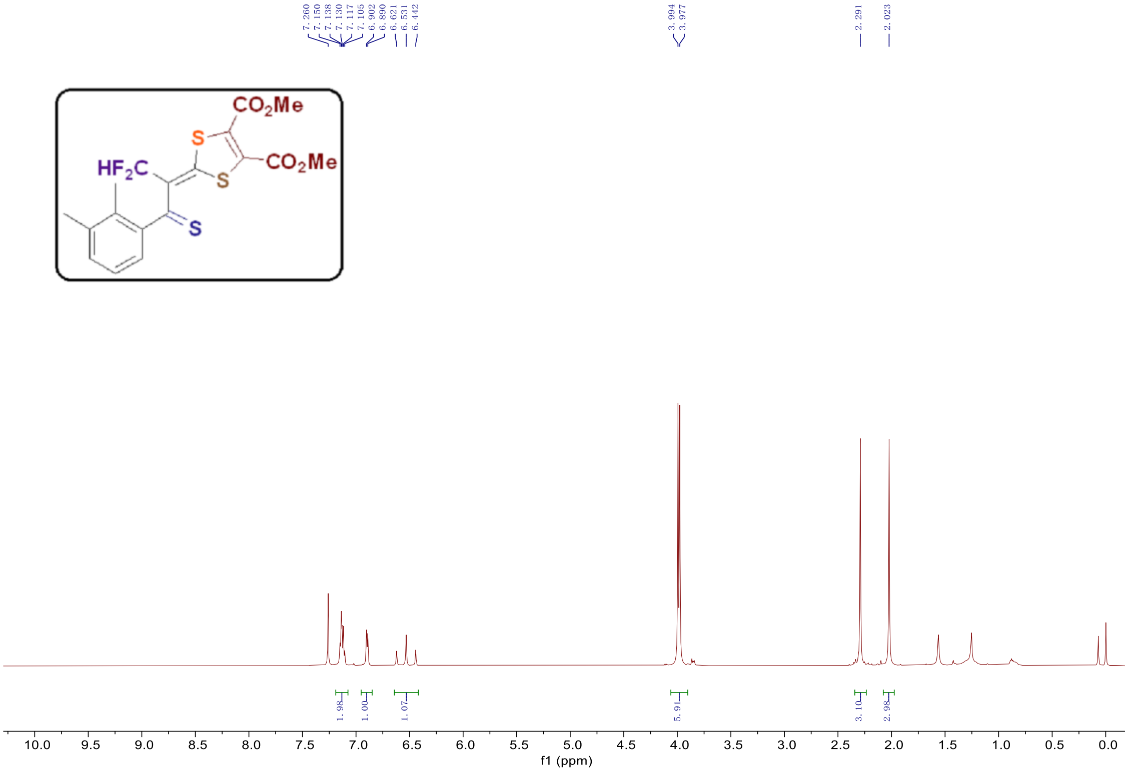
[13]C spectrum (151 MHz, $CDCl_3$) of compound 5w



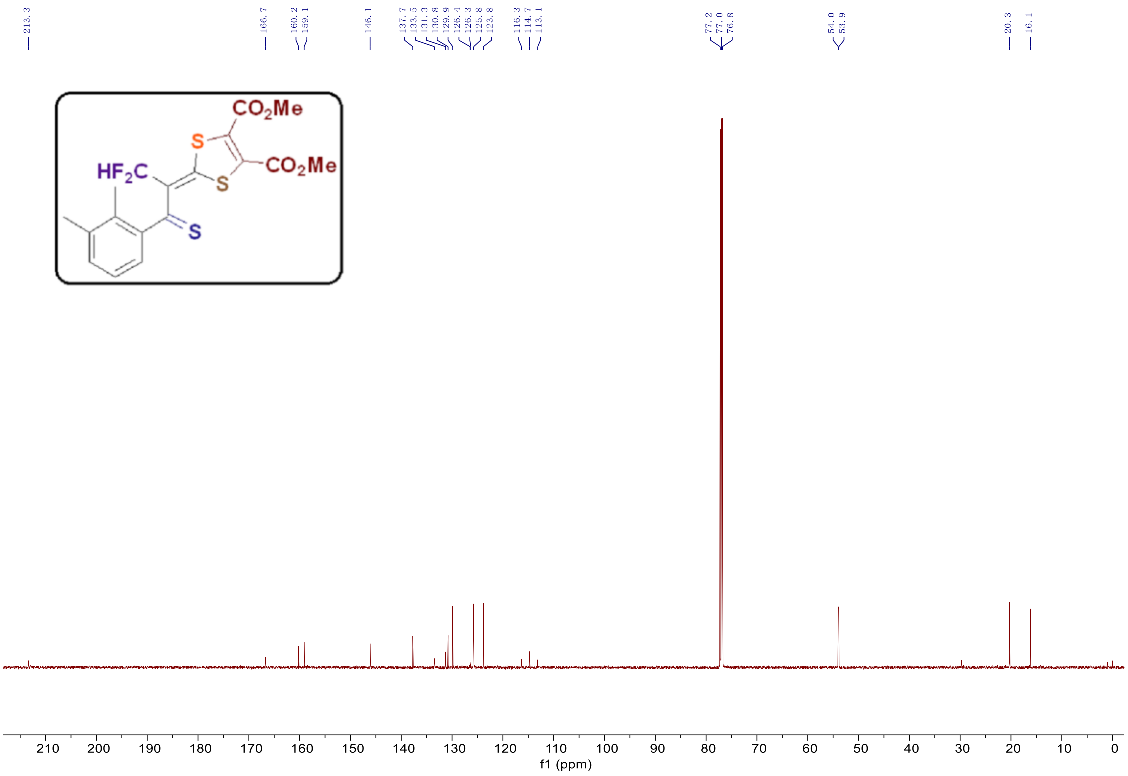
^{19}F spectrum (565 MHz, $CDCl_3$) of compound 5w



^1H spectrum (600 MHz, $CDCl_3$) of compound 6w



^{13}C spectrum (151 MHz, $CDCl_3$) of compound 6w



^{19}F spectrum (565 MHz, $CDCl_3$) of compound 6w