Supporting Information

Harnessing Visible Light for Metal-Free Trifluoromethylation/Cyclization of Unactivated Alkenes

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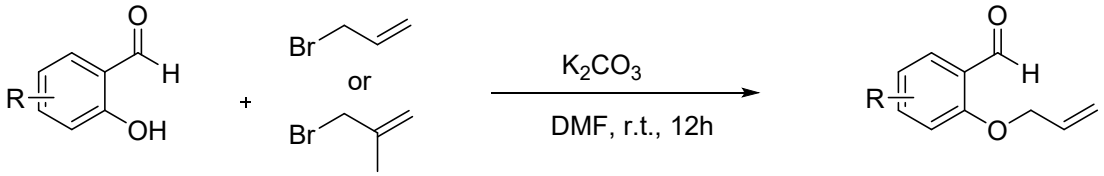
Contents

1. General comments

Chemicals were purchased from Adamas, Bidepharm., TCI, Aladdin and used as such unless stated otherwise. All solvents like acetonitrile, tetrahydrofuran, *N*, *N*-dimethylmethanamide, 1,4-dioxane were purchased from Adamas (Water ≤ 30 ppm (by K.F.), 99.9%, SafeDry, with molecular sieves, Safeseal). NMR spectra were recorded on Bruker AV 400 or Bruker Fourier 300 spectrometer. Chemical shifts (ppm) are given relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C solvent. Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), m (multiplet) and br.s (broad singlet). High-resolution mass spectra HRMS spectra were recorded on a Thermo Scientific Exactive Orbitrap Mass Spectrometer under Electron Spray Ionization conditions preparing sample solution in methanol. The data are given as mass units per charge (m/z). GC yields were calculated using dodecane as an internal standard. Gas chromatography analysis was performed on an Agilent 6820 instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using nitrogen as carrier gas. The light sources used in the reaction include a 40 W Kessil Blue LEDs with a wavelength of 456 nm, an AC 220 V blue l LEDs (450-460 nm) from Xuzhou Aijia Electronics Technology, an AC 220 V purple LEDs (380-390 nm) from Xuzhou Aijia Electronics Technology, and an AC 220 V green LEDs (530-540 nm) from Xuzhou Aijia Electronics Technology. The products were isolated from the reaction mixture by column chromatography on silica gel., 54-74 μm, 200-300 mesh (Yucheng Chemical CO., LTD, Shanghai). LED lamps were purchased from the Chinese Taobao branded as "JiaDeng". (https://item.taobao.com/item.htm?spm=a1z09.2.0.0.2ad62e8dHqtY75&id=613485925423&_u=s23 m2hbk30f5). Unless otherwise noted, the wavelength of the LEDs used under standard conditions is 530-540 nm. The light intensity on the 4 mL reaction vials is 39 mW/cm^2. Substrates **1b-1s** were prepared according to previous reports[1 2 3 4].

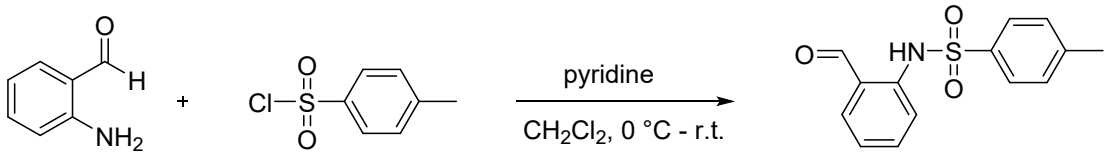
2. General Procedures

2.1 General Procedures for the synthesis of substrate 1b-1n, 1p-1q,1s[1]:

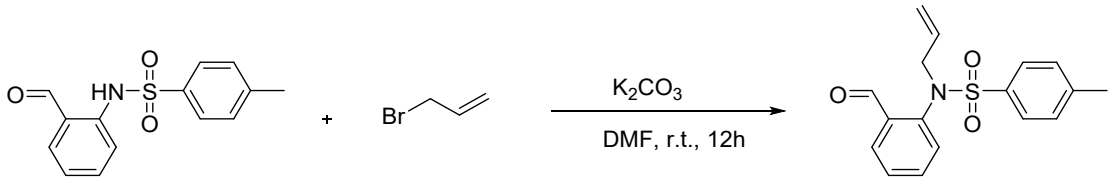


To a 50 mL round-bottomed flask with a stir bar was added 2-hydroxyarylaldehyde (5 mmol), DMF (15 mL), then was added potassium carbonate (5.5 mmol), followed by the dropwise addition of allyl bromide (5.5 mmol). The reaction mixture was then stirred for 12 h at room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over Na_2SO4, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired 2-(allyloxy)arylaldehydes.

2.2 General Procedures for the synthesis of substrate 1o[2 3]:



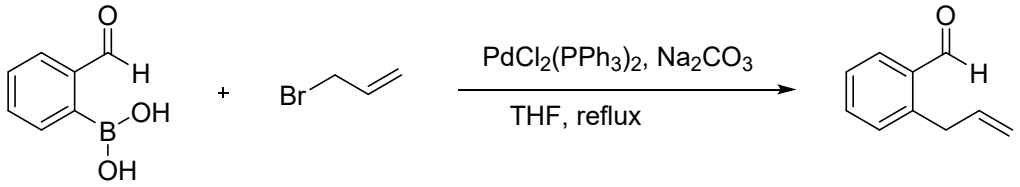
A 50 mL round-bottomed flask with a stir bar was added 2-aminobenzaldehyde (8 mmol), CH_2Cl_2 (20 mL). Then reaction is cooled to 0 °C, and was added pyridine (17.6 mmol), followed by the addition of tosyl chloride (8.8 mmol). The reaction mixture was then stirred for 16 h, poured into brine and extracted with EtOAc. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the N-(2-formylphenyl)-4-methylbenzenesulfonamide.



To an ordinary vial with a stir bar was added salicylaldehyde (5 mmol), DMF (15 mL), then was added potassium carbonate (5.5 mmol), followed by the dropwise addition of allyl bromide (5.5 mmol). The reaction mixture was then stirred for 12 h at room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over Na_2SO_4, filtered, and evaporated. The residue was

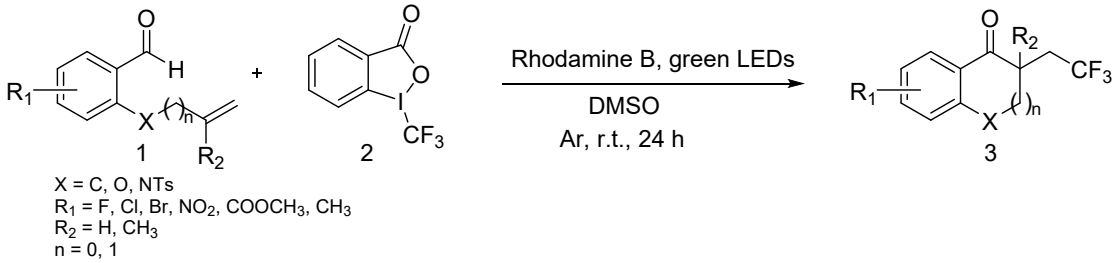
purified by column chromatography (petroleum ether /EtOAc) to afford the desired N-allyl-N-(2-formylphenyl)-4-methylbenzenesulfonamide.

2.3 General Procedures for the synthesis of substrate 1r[4]:



To a solution of the 2-formylphenylboronic acid and corresponding allyl halide (1.5 equiv) in THF (0.2 M) in a round-bottom flask were added $PdCl_2(PPh_3)_2$ (2.5 mol %). The reaction mixture was heated to 50 °C, then aq Na_2CO_3 (1 M, 2 equiv) solution was added dropwise over a period of 1 h and the heating continued in reflux for 3-4 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc) to afford the desired yellow product.

2.4 General Procedures for the synthesis of 3

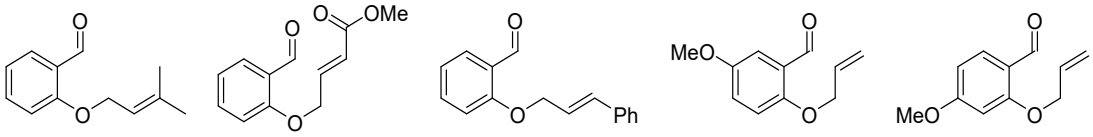


X = C, O, NTs
R_1 = F, Cl, Br, NO_2, $COOCH_3$, CH_3
R_2 = H, CH_3
n = 0, 1

An oven-dried ordinary vial (5 mL) was equipped with a magnetic stir bar, Substrate 1 (0.05 mmol), Togni's Reagent II 2 (2 equiv, 0.1 mmol), Rhodamine B (10 mol%). 2mL DMSO was added with syringe under Ar. Then the vial was evacuated and backfilled with Ar for 3 times. The vial was placed

exposed to green light bulb (530-540 nm) at room temperature. Meanwhile, a fan was placed next to the reaction apparatus to help dissipate heat from the light bulb. After the reaction was finished, DMSO was washed by using 10 volumes of brine and the organic product was extracted with EtOAc. The organic layers were combined together and the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether / EtOAc) on silica gel to obtain the desired product 3.

2.5 Unsuccessful examples



3t low yield, part of **1t** remain

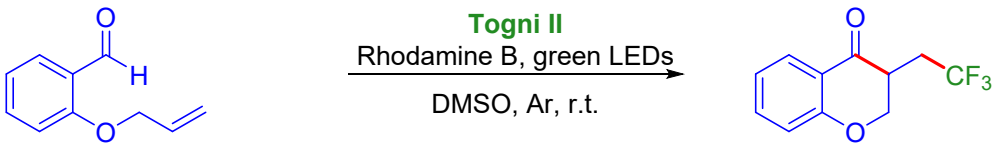
3u low yield, part of **1u** remain

3v, 0% **1v** remain

1w, trace

1x, trace

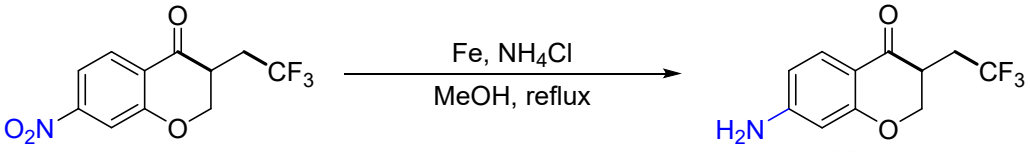
2.6 Large-scale synthesis and further functional groups transformations



1a, 1 mmol

3a, 62%, 0.143 g

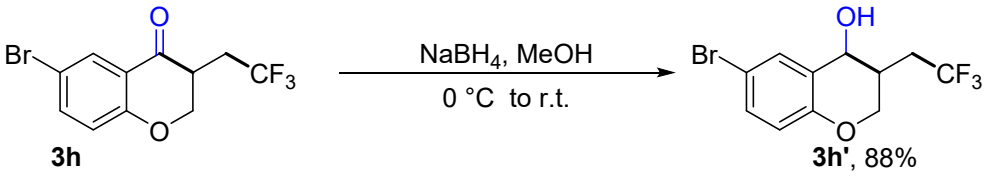
An oven-dried flask (100 mL) was equipped with a magnetic stir bar, Substrate 1a (1 mmol), Togni's Reagent II 2 (1.5 equiv, 2 mmol), Rhodamine B (10 mol%). 50 mL DMSO was added with syringe under Ar. Then the vial was evacuated and backfilled with Ar for 3 times. The vial was placed exposed to green light bulb (530-540 nm) at room temperature. Meanwhile, a fan was placed next to the reaction apparatus to help dissipate heat from the light bulb. After 24 hours, another 0.5 equivalent of Togni's Reagent II was added to the reaction mixture to achieve full conversion of substrate **1a**. When the reaction was finished, DMSO was washed by using 10 volumes of brine and the organic product was extracted with EtOAc. The organic layers were combined together and the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether / EtOAc) on silica gel to obtain the desired product **3a** (0.143 g, 62%).



3k

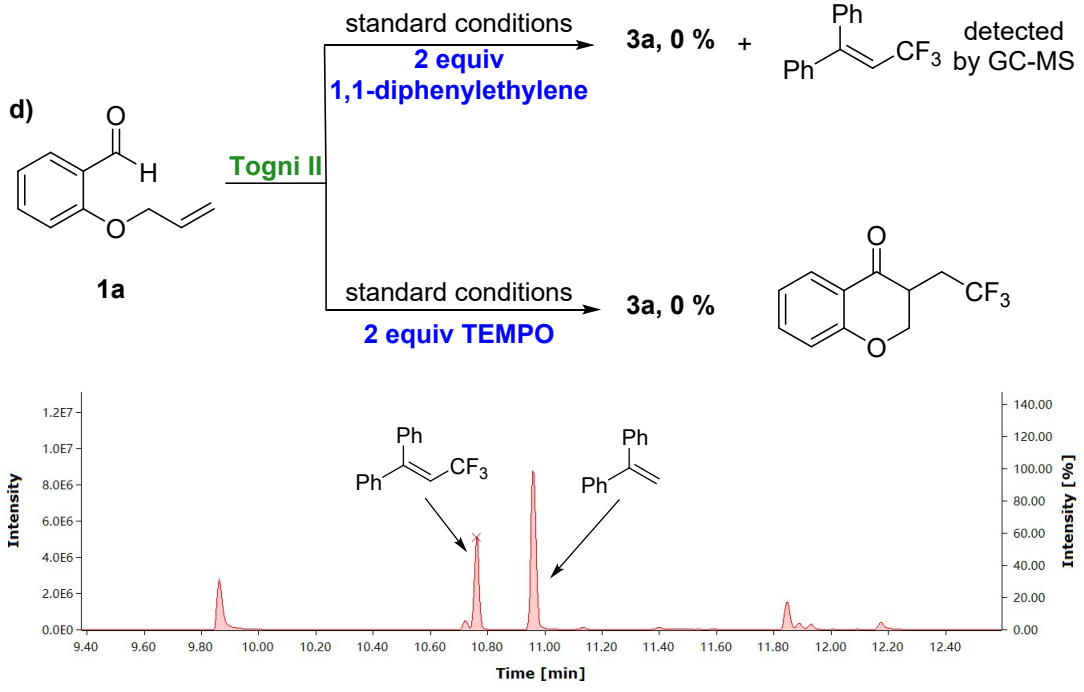
3k', 72%

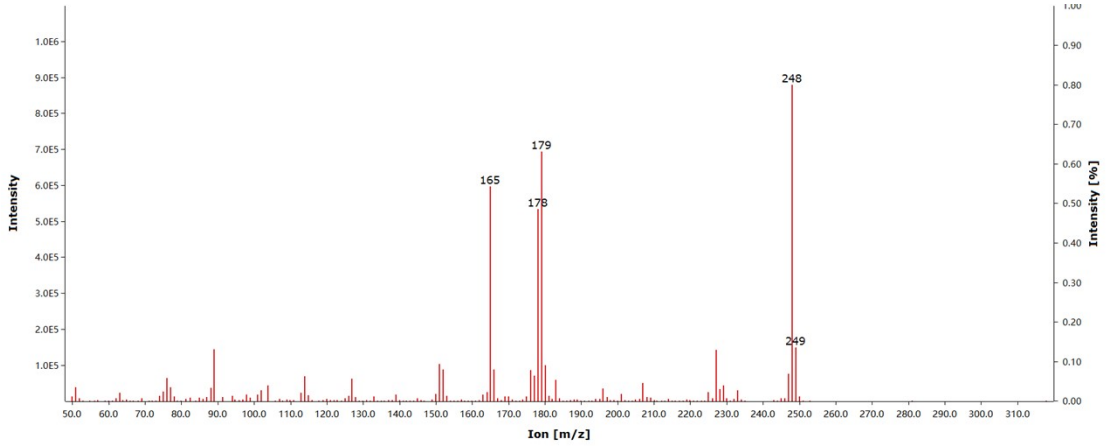
To a suspension of compound **3k** (0.2 mmol, 1.0 eq) in MeOH (2.0 mL) and water (0.5 ml) was added $NHCl_4$ (2.0 mmol, 10 eq) and iron powder (2 mmol, 10 eq). The reaction was stirred at reflux for 2 hours. After completion of the reaction, the mixture was partitioned between water and EtOAC, and filtered through celite. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to obtain the crude product. The crude product was purified by column chromatography to provide **3k'** in 72% yield.



Add $NaBH_4$ (0.3 mmol) to a cooled methanolic solution of **3h** (0.2 mmol) at 0°C. Stir the mixture for an hour until the disappearance of the starting material is monitored by the TLC. Later, add 3 drops of concentrated AcOH to quench the reaction mixture. Evaporate the methanol under vacuum. Extract the reaction mass in EtOAc (10 mL x 3). Dry the combined organic layers over Na_2SO_4 and concentrate the combined organic layers under a vacuum. The crude product was purified by column chromatography to provide **3h'** in 88% yield.

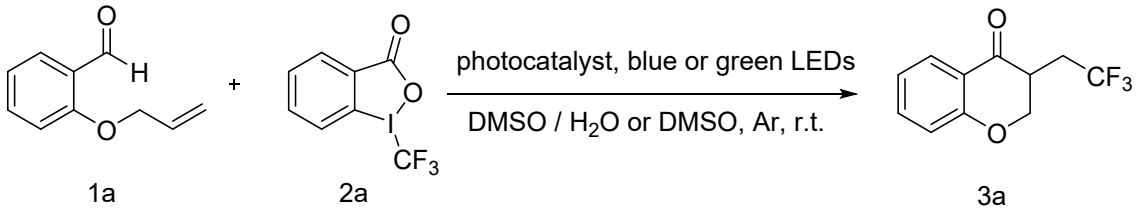
2.7 Radical trapping experiment




Intensity
Intensity [%]
Ion [m/z]
248
179
165
178
249

3. Optimization of reaction conditions

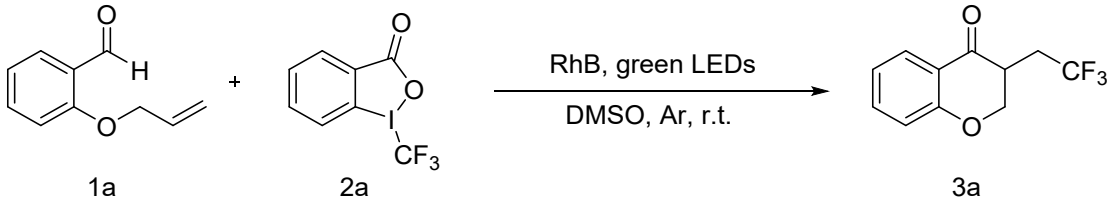
3.1 Optimization of the concentration of substrate 1a and photocatalysts



Entry	1a	Photocatalyst	Solvents	Yield (%)
1[a]	0.1 M	Eosin Y	DMSO / H_2O = 1/1 (mL)	10.2
2[a]	0.1 M	4CZIPN	DMSO / H_2O = 1/1 (mL)	0
3[a]	0.1 M	3CzClIPN	DMSO / H_2O = 1/1 (mL)	3.9
4[a]	0.1 M	g-C_3N_4	DMSO / H_2O = 1/1 (mL)	6.3
5[a]	0.1 M	TPPTFB	DMSO / H_2O = 1/1 (mL)	22.7
6[b]	0.1 M	TPPTFB	DMSO = 2 mL	32.8
7[b]	0.05 M	TPPTFB	DMSO = 2 mL	34.2
8[b]	0.025 M	TPPTFB	DMSO = 2 mL	37.2
9[c]	0.025 M	Eosin B	DMSO = 2 mL	23.8
10[c]	0.025 M	AQ	DMSO = 2 mL	33.2
11[c]	0.025 M	FL	DMSO = 2 mL	33.4
12[d]	0.025 M	Rh 6G	DMSO = 2 mL	18.6
13[d]	**0.025 M**	**RhB**	**DMSO = 2 mL**	**48.2**

(Reaction conditions a: **1a** (32 μL, 0.2 mmol, 1.0 equivalent), **2a** (126.5 mg, 0.4 mmol, 2.0 equivalent), photocatalyst (3 mol%), blue LEDs (450-460 nm) and DMSO / H_2O = 1/1 (2 mL), r.t., under Ar, 16 h, GC yields.
Reaction conditions b: **1a** (1.0 equivalent), **2a** (2.0 equivalent), TPPTFB (3 mol%), blue LEDs (450-460 nm) and DMSO = 2 mL, r.t., under Ar, 16 h, GC yields.
Reaction conditions c: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), photocatalyst (3 mol%), blue LEDs (450-460 nm) and DMSO = 2 mL, r.t., under Ar, 16 h, GC yields.
Reaction conditions d: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), photocatalyst (3 mol%), green LEDs (530-540 nm) and DMSO = 2 mL, r.t., under Ar, 16 h, GC yields.
TPPTFB: 2,4,6-triphenylpyrylium tetrafluoroborate, AQ: Anthraquinone, FL: Fluorescein, Rh 6G: Rhodamine 6G, RhB: Rhodamine B.)

3.2 Optimization of the equivalents of substrate 2a and light source



Entry	Togni II（eq）	Yield (%)
1[a]	1	Trace
2[a]	1.5	Trace
3[a]	**2**	**59.7**
4[a]	2.5	58.5
5[a]	3	51.2
6[b]	2	47.2
7[c]	2	Trace

(Reaction conditions a: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (Togni's Reagent II), RhB (5 mol%), green LEDs (530-540 nm) and DMSO (2 mL), r.t., under Ar, 18 h, GC yields; RhB: Rhodamine B.
Reaction conditions b: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (Togni's Reagent II), RhB (5 mol%), blue LEDs (450-460 nm) and DMSO (2 mL), r.t., under Ar, 18 h, GC yields; RhB: Rhodamine B.
Reaction conditions c: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (Togni's Reagent II), RhB (5 mol%), purple LEDs (380-390 nm) and DMSO (2 mL), r.t., under Ar, 18 h, GC yields; RhB: Rhodamine B.)

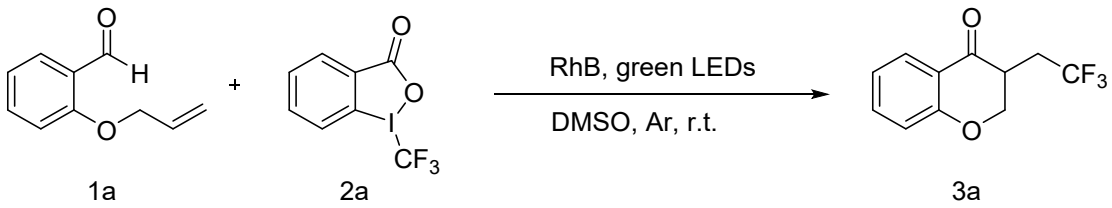
3.3 Optimization of the amount of photocatalyst and the influence of air

Entry	RhB（mol %）	Yield (%)
1[a]	1	Trace
2[a]	4	52.9
3[a]	5	58.3
4[a]	6	62.2

5[a]	8	63.5
6[a]	**10**	**67.9**
7[a]	12	60.5
8[b]	10	51.7

(Reaction conditions a: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), RhB (Rhodamine B), green LEDs (530-540 nm) and DMSO (2 mL), r.t., under Ar, 24 h, GC yields.
Reaction conditions b: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), RhB (Rhodamine B), green LEDs (530-540 nm) and DMSO (2 mL), r.t., under air, 24 h, GC yields.)

3.4 Control Experiment

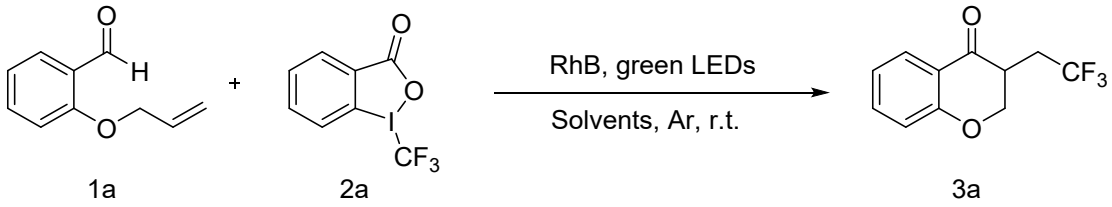


1a 2a 3a

Entry	RhB	Light source	Yield (%)
1	-	green LEDs	n.r.
2	10 mol%	dark	n.r.

(Reaction conditions: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), RhB (10 mol%), green LEDs (530-540 nm) and DMSO (2 mL), r.t., under Ar, 24 h, GC yields; RhB: Rhodamine B, n.r.: no reaction.)

3.5 Optimization of the reaction solvents



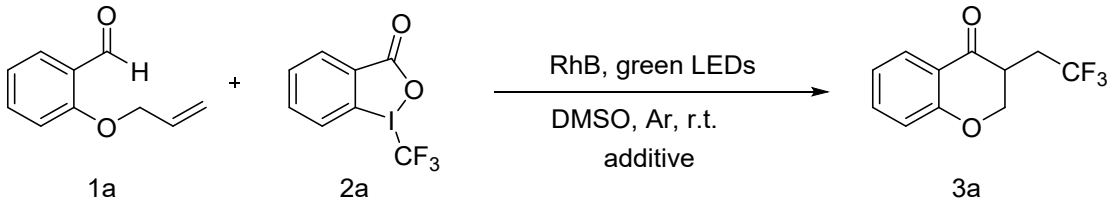
1a 2a 3a

Entry	Solvents	Yield (%)
1	DCM	22.7
2	Toluene	n.r.
3	EA	29.0
4	NMP	15.1

5	DMAC	32.6
6	**DMSO**	**68.2**
7	DMSO / DMF = 4/1	trace
8	DMSO / DMAC = 4/1	47.8
9	DMSO / THF =4 /1	trace
10	DMSO / dixoane = 4/1	55.6
11	DMSO / dixoane = 5/1	58.4
12	DMSO / dixoane = 9/1	60.3
13	DMSO / CH_3CN = 4/1	56.7
14	DMSO / Kpi buffer = 1.9/0.1	34.9
15	DMSO / Kpi buffer = 1.8/0.2	49.1
16	DMSO / Kpi buffer = 1.7/0.3	57.0
17	DMSO / Kpi buffer = 1.5/0.5	37.4
18	DMSO / H_2O = 1.9/0.1	24.3
19	DMSO / H_2O= 1.8/0.2	60.3
20	DMSO / H_2O= 1.7/0.3	46.5
21	DMSO / H_2O= 1.6/0.4	37.6

(Reaction conditions: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), RhB (10 mol%), green LEDs (530-540 nm) and solvents (2 mL), r.t., under Ar, 24 h, GC yields; RhB: Rhodamine B, Kpi buffer: K_2HPO_4, KH_2PO_4 and d H_2O (0.1 M, pH = 7.5), n.r.: no reaction)

3.6 Optimization of the additives



Entry	Additives	Yield (%)
1	H_2O 10 eq	51.5
2	H_2O 20 eq	60.9
3	H_2O 30 eq	65.6

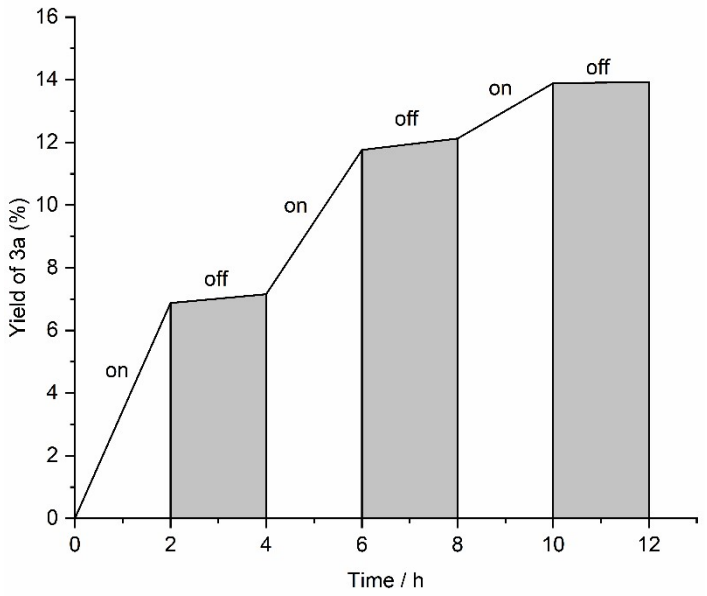
4	$^{n}Bu_4NNO_3$ 2.0 eq	51.6
5	$^{n}Bu_4OAc$ 2.0 eq	39.8
6	Et_4NCl 2.0 eq	53.3
7	Et_4NBr 2.0 eq	59.7
8	Me_4NCl 2.0 eq	43.7
9	$ZnBr_2$ 3.0 eq	52.9
10	$ZnBr_2$ 2.0 eq	60.4
11	$ZnBr_2$ 1.0 eq	55.8
12	$AgBF_4$ 2.0 eq	54.5
13	$LiBF_4$ 3.0 eq	66.0
14	$LiBF_4$ 2.0 eq	60.8
15	TFA 2.0 eq	58.8
16	PTSA 2.0 eq	46.6
17	HOAc 1.0 eq	60.4
18	Salicylic acid 2.0 eq	61.6
19	KH_2PO_4 1.0 eq	53.9
20	K_2CO_3 1.0 eq	44.7
21	Cs_2CO_3 2.0 eq	19.7
22	tBuOK 2.0 eq	25.8
23	NaF 2.0 eq	53.8
24	DBU 2.0 eq	40.3
25	Et_3N 2.0 eq	41.7
26	Et_3N 1.0 eq	58.0
27	DIPEA 1.0 eq	51.0
28	Pyridine 2.0 eq	43.1
29	Pyridine 1.0 eq	54.9
30	$PhI(OA)_2$ 2.0 eq	48.0
31	tBuOOH 2.0 eq	28.3
32	$K_2S_2O_8$ 2.0 eq	50.9

33	BQ 1.0 eq	n.r.

(Reaction conditions: **1a** (8 μL, 0.05 mmol, 1.0 equivalent), **2a** (31.6 mg, 0.1 mmol, 2.0 equivalent), RhB (10 mol%), green LEDs (530-540 nm) and DMSO (2 mL), additive, r.t., under Ar, 24 h, GC yields; RhB: Rhodamine B, n.r.: no reaction)

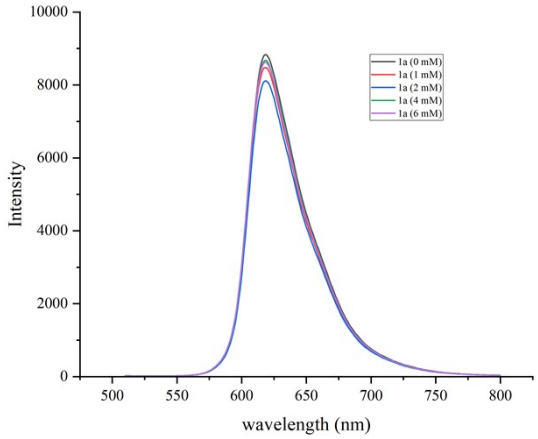
4. "On/off" irradiation experiments for the reaction

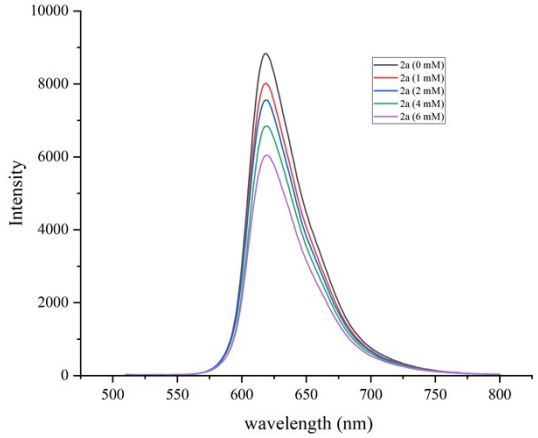
1a (0.2 mmol), 2a (0.4 mmol), Rhodamine B (10 mol%, 0.02 mmol) and DMSO (8 mL) were placed in a glass tube. The tube was evacuated and back-filled with argon. The reaction mixture was then stirred at room temperature under green LEDs irradiation. Once the mixture was stirred for 2 hours, 20 μL of the reaction mixture was taken out via syring. The mixture was monitored by GC yields using dodecane as an internal standard. The resulting mixture in the tube continued to react at dark for 2h, and 20 μL of the reaction mixture was taken out via syring. The mixture was monitored by GC yields using dodecane as an internal standard. The above process was repeated for several times. The results showed that the yield of 3a was obviously increased upon irradiating the reaction with green LEDs. In contrast, the increase of the yield of 3a was not observed upon performing the reaction in the dark. These results indicated the necessity of continuous visible light irradiation for photoredox-catalyzed.

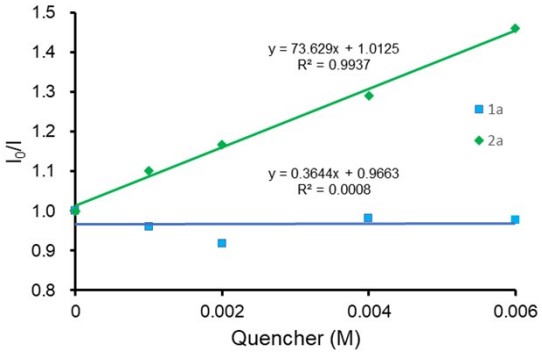


5. Stern-Volmer fluorescence quenching experiment

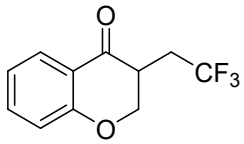
In the Stern-Volmer fluorescence quenching experiments, the DMSO was degassed by argon for 30 minutes， which was used to prepare the Rhodamine B solution (1 mM) and quenchers 2-(allyloxy) arylaldehydes (1a) and Togni's Reagent II (2a) with the concentrations of 1 mM, 2 mM, 4 mM, and 6 mM. All solutions were excited at 500 nm and the emission intensity was collected at 510-800 nm. The solution of samples was stirred for 3-5 minutes before testing, and the corresponding emission spectra of the samples were collected. The results showed that 2a efficiently quenches photoexcited Rhodamine B, while 1a has no quenching effect.






y = 73.629x + 1.0125
R² = 0.9937
y = 0.3644x + 0.9663
R² = 0.0008
1a
2a
I0/I
Quencher (M)
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0
0.002
0.004
0.006

6. Characterization data of products



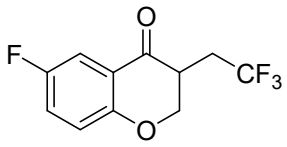
3-(2,2,2-trifluoroethyl)chroman-4-one(3a): (30.6 mg, coloress oil, yield: 67 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.07 – 7.02 (m, 1H), 6.98 (dd, 1H), 4.71 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.22 (t, *J* = 11.8 Hz, 1H), 3.17 – 3.03 (m, 2H), 2.13 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 161.5, 136.4, 127.6, 126.6 (q, J_{CF} = 276.3 Hz), 121.8, 120.0, 117.9, 69.7(q, J_{CF} = 1.5 Hz), 40.5 (q, J_{CF} = 2.2 Hz), 29.6 (q, J_{CF} = 30.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



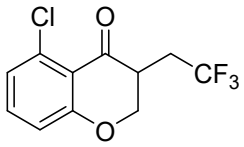
6-fluoro-3-(2,2,2-trifluoroethyl)chroman-4-one(3b): (22.8 mg, white solid, m.p. = 65-67 ℃, yield: 46 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.2, 3.2 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.98 (dd, *J* = 9.1, 4.2 Hz, 1H), 4.70 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.22 (t, *J* = 11.8 Hz, 1H), 3.18 – 3.01 (m, 2H), 2.14 – 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0 (d, J_{CF} = 2.0 Hz), 157.8 (d, J_{CF} = 1.7 Hz), 157.3 (d, J_{CF} = 242.5 Hz), 126.5 (q, J_{CF} = 277.8 Hz), 124.0 (d, J_{CF} = 24.6 Hz), 120.4 (d, J_{CF} = 6.6 Hz), 119.6 (d, J_{CF} = 7.4 Hz), 112.4 (d, J_{CF} = 23.5 Hz), 69.9 (q, J_{CF} = 1.9 Hz), 40.4 (q, J_{CF} = 2.0 Hz), 29.5 (q, J_{CF} = 30.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1, -120.8.

The analytical data are consistent with those reported in the literature[5].



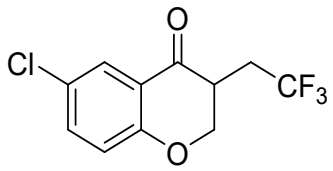
5-chloro-3-(2,2,2-trifluoroethyl)chroman-4-one(3c): (31.5 mg, coloress oil, yield: 60 %**)**

H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.4, 1.1 Hz, 1H), 4.70 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.23 (t, *J* = 11.8 Hz, 1H), 3.22 – 3.01 (m, 2H), 2.16 – 2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 162.8, 135.1, 134.6, 127.0 (q, J_{CF} = 277.9 Hz), 124.9, 117.3, 116.9, 69.2 (q, J_{CF} = 1.9 Hz), 41.0 (q, J_{CF} = 2.2 Hz), 29.5 (q, J_{CF} = 30.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



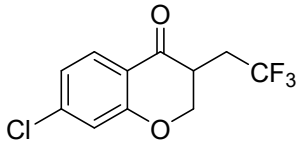
6-chloro-3-(2,2,2-trifluoroethyl)chroman-4-one(3d): (25.3 mg, white solid, m.p. = 60-62 ℃, yield: 48 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.7 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 4.72 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.23 (t, *J* = 11.8 Hz, 1H), 3.18 – 3.02 (m, 2H), 2.13 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 160.0, 136.2, 127.4, 126.8, 126.5(q, J_{CF} = 277.8 Hz), 120.8, 119.6, 69.8 (q, J_{CF} = 2.0 Hz), 40.3 (q, J_{CF} = 2.0 Hz), 29.5 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



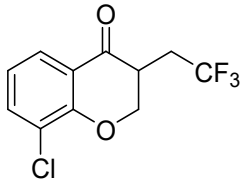
7-chloro-3-(2,2,2-trifluoroethyl)chroman-4-one(3e): (26.5 mg, white solid, m.p. = 55-57 ℃, yield: 50 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, 1H), 7.05 – 6.98 (m, 2H), 4.73 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.24 (t, *J* = 11.8 Hz, 1H), 3.19 – 3.03 (m, 2H), 2.12 – 2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 161.8, 142.3, 128.8, 126.5 (q, J_{CF} = 277.8 Hz), 122.6, 118.6, 118.0, 70.0 (q, J_{CF} = 2.0 Hz), 40.3 (q, J_{CF} = 2.0 Hz), 29.4 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



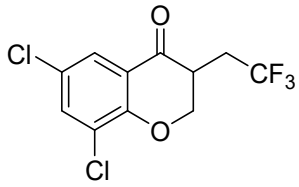
8-chloro-3-(2,2,2-trifluoroethyl)chroman-4-one(3f): (26.2 mg, white solid, m.p. = 77-79 ℃ yield: 50 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 4.88 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.31 (t, *J* = 12.0 Hz, 1H), 3.25 – 3.04 (m, 2H), 2.16 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 157.0, 136.4, 126.5 (q, J_{CF} = 276.7 Hz), 126.1, 122.7, 121.9, 121.3, 70.2 (q, J_{CF} = 2.0 Hz), 40.2 (q, J_{CF} = 2.0 Hz), 29.5 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[6].



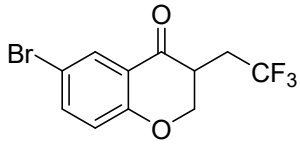
6,8-dichloro-3-(2,2,2-trifluoroethyl)chroman-4-one(3g): (33.1 mg, white solid, m.p. = 81-83 ℃, yield: 55 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.6 Hz, 1H), 7.57 (d, *J* = 2.6 Hz, 1H), 4.88 (dd, *J* = 11.6, 5.3 Hz, 1H), 4.30 (t, *J* = 12.0 Hz, 1H), 3.24 – 3.01 (m, 2H), 2.18 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 155.7, 135.9, 127.1, 126.1 (q, J_{CF} = 277.8 Hz), 125.6, 123.9, 121.5, 70.3 (q, J_{CF} = 2.0 Hz), 40.1 (q, J_{CF} = 2.0 Hz), 29.4 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

HRMS (ESI-TOF) Calc. for $C_{11}H_8O_2Cl_2F_3$ [M+H]+: 298.9853; found: 298.9847.



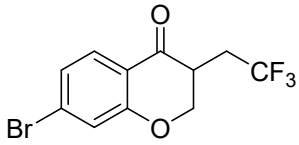
6-bromo-3-(2,2,2-trifluoroethyl)chroman-4-one(3h): (33.8 mg, white solid, m.p. = 56-58 ℃ yield: 55 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.5 Hz, 1H), 7.58 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 4.73 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.23 (t, *J* = 11.9 Hz, 1H), 3.18 – 3.02 (m, 2H), 2.13 – 2.02 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 160.4, 139.0, 130.0, 126.5(q, J_{CF} = 276.7 Hz), 121.3, 120.0, 114.5, 69.8 (q, J_{CF} = 2.0 Hz), 40.3 (q, J_{CF} = 2.0 Hz), 29.5 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



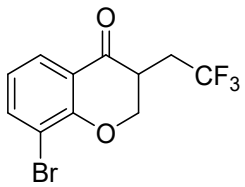
7-bromo-3-(2,2,2-trifluoroethyl)chroman-4-one(3i): (34.3 mg, white solid, m.p. = 68-70 ℃, yield: 55 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.13 (m, 2H), 4.73 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.23 (t, *J* = 11.8 Hz, 1H), 3.19 – 2.99 (m, 2H), 2.12 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 161.7, 130.9, 128.7, 126.5 (q, J_{CF} = 276.7 Hz), 125.5, 121.1, 118.9, 70.0 (q, J_{CF} = 2.0 Hz), 40.3 (q, J_{CF} = 2.0 Hz), 29.5 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



8-bromo-3-(2,2,2-trifluoroethyl)chroman-4-one(3j): (35.7 mg, white solid, m.p. = 91-93 ℃, yield:

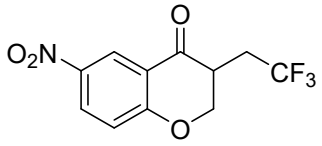
58%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 4.87 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.31 (t, *J* = 12.0 Hz, 1H), 3.23 – 3.02 (m, 2H), 2.09 (dt, *J* = 15.6, 10.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 157.9, 139.6, 126.9, 126.4 (q, J_{CF} = 277.8 Hz), 122.5, 121.3, 111.5, 70.3 (q, J_{CF} = 2.0 Hz), 40.1 (q, J_{CF} = 2.0 Hz), 29.5 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[6].

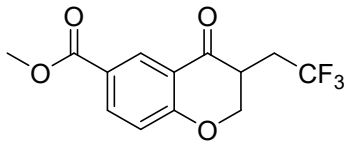


6-nitro-3-(2,2,2-trifluoroethyl)chroman-4-one(3k): (37.8 mg, white solid, m.p. = 105-107 ℃, yield: 69 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.8 Hz, 1H), 8.34 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.14 (d, *J* = 9.1 Hz, 1H), 4.87 (dd, *J* = 11.7, 5.4 Hz, 1H), 4.35 (t, *J* = 12.1 Hz, 1H), 3.28 – 3.06 (m, 2H), 2.20 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 165.3, 142.3, 130.6, 126.3 (q, J_{CF} = 277.8 Hz), 124.0, 119.6, 119.3, 70.1 (q, J_{CF} = 2.0 Hz), 40.2 (q, J_{CF} = 2.0 Hz), 29.3 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.



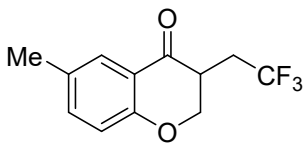
methyl 4-oxo-3-(2,2,2-trifluoroethyl)chromane-6-carboxylate(3l): (24 mg, white solid, m.p. = 124-126 ℃, yield: 42 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.2 Hz, 1H), 8.17 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 4.80 (dd, *J* = 11.6, 5.3 Hz, 1H), 4.29 (t, *J* = 11.9 Hz, 1H), 3.92 (s, 3H), 3.24 – 3.03 (m, 2H), 2.15 – 2.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 165.7, 164.4, 136.9, 129.9, 126.4 (q, J_{CF} = 276.7 Hz), 124.0, 119.5, 118.2, 69.8 (q, J_{CF} = 2.0 Hz), 52.2, 40.2 (q, J_{CF} = 2.0 Hz), 29.4 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[6].



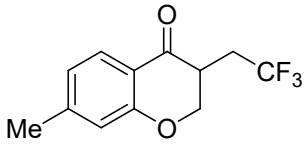
6-methyl-3-(2,2,2-trifluoroethyl)chroman-4-one(3m): (16.4 mg, coloress oil, yield: 34 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 4.67 (dd, *J* = 11.3, 5.1 Hz, 1H), 4.20 (t, *J* = 11.7 Hz, 1H), 3.16 – 3.01 (m, 2H), 2.31 (s, 3H), 2.15 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 159.6, 137.4, 131.3, 127.0, 126.6 (q, J_{CF} = 277.8 Hz), 119.6, 117.6, 69.7 (q, J_{CF} = 1.9 Hz), 40.5 (q, J_{CF} = 2.1 Hz), 29.6 (q, J_{CF} = 30.1 Hz), 20.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



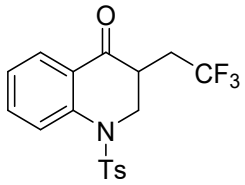
7-methyl-3-(2,2,2-trifluoroethyl)chroman-4-one(3n): (11.8 mg, white solid, m.p. = 64-66 ℃, yield: 24 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 4.69 (dd, *J* = 11.6, 5.0 Hz, 1H), 4.20 (t, *J* = 11.6 Hz, 1H), 3.14 – 3.03 (m, 2H), 2.36 (s, 3H), 2.11 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 161.6, 148.0, 128.0, 127.4, 125.3, 123.2, 117.8, 69.8 (q, J_{CF} = 2.0 Hz), 40.4 (q, J_{CF} = 2.0 Hz), 29.4 (q, J_{CF} = 30.3 Hz), 21.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

The analytical data are consistent with those reported in the literature[5].



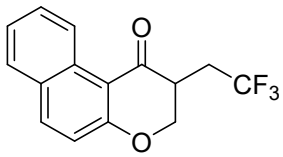
1-tosyl-3-(2,2,2-trifluoroethyl)-2,3-dihydroquinolin-4(1H)-one（3o）: (25.7 mg, white solid, m.p. = 120-122 ℃, yield: 34 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.83 (m, 2H), 7.63 – 7.52 (m, 3H), 7.29 – 7.21 (m, 3H), 4.74 (dd, *J* = 14.4, 5.0 Hz, 1H), 3.67 (t, *J* = 13.9 Hz, 1H), 3.05 – 2.89 (m, 1H), 2.52 – 2.42 (m, 1H), 2.38 (s, 3H), 1.94 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 144.9, 142.1, 136.5, 135.1, 130.2, 128.2, 126.8, 126.5 (q, J_{CF} = 276.7 Hz), 125.6, 124.3, 124.0, 50.0 (q, J_{CF} = 2.0 Hz), 39.5 (q, J_{CF} = 2.0 Hz), 30.7 (q, J_{CF} = 30.3 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8.

The analytical data are consistent with those reported in the literature[5].



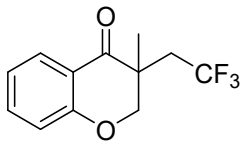
1-tosyl-3-(2,2,2-trifluoroethyl)-2,3-dihydroquinolin-4(1H)-one(3p): (18.1 mg, white solid, m.p. = 93-95 ℃, yield: 32 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.68 – 7.61 (m, 1H), 7.48 – 7.41 (m, 1H), 7.10 (d, *J* = 9.0 Hz, 1H), 4.79 (dd, *J* = 11.3, 5.2 Hz, 1H), 4.36 (t, *J* = 11.5 Hz, 1H), 3.25 – 3.09 (m, 2H), 2.21 – 2.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 163.5, 137.9, 131.5, 129.9, 129.2, 128.5, 126.8 (q, J_{CF} = 277.8 Hz), 125.6, 125.1, 118.4, 111.7, 69.6 (q, J_{CF} = 2.0 Hz), 40.9 (q, J_{CF} = 2.0 Hz), 29.9 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.9.

The analytical data are consistent with those reported in the literature[5].



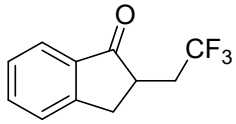
1-methyl-3-(2,2,2-trifluoroethyl)chroman-4-one(3q): (29.0 mg, coloress oil, yield: 59 %**)**

H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.09 – 7.03 (m, 1H), 6.99 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.38 (d, *J* = 11.8 Hz, 1H), 4.32 (d, *J* = 11.8 Hz, 1H), 2.62 – 2.52 (m, 2H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 160.8, 136.2, 128.1, 126.8 (q, J_{CF} = 278.8 Hz), 122.0, 118.8, 117.7, 73.9 (q, J_{CF} = 2.0 Hz), 42.6 (q, J_{CF} = 2.0 Hz), 36.2 (q, J_{CF} = 30.3 Hz), 18.5 (q, J_{CF} = 2.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.5.

The analytical data are consistent with those reported in the literature[5].



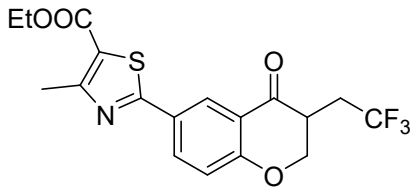
2-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-inden-1-one(3r): (18.1 mg, coloress oil, yield: 42 %**)**

H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.52 – 7.47 (m, 1H), 7.43 – 7.37 (m, 1H), 3.51 (dd, *J* = 17.2, 7.9 Hz, 1H), 3.03 – 2.89 (m, 3H), 2.16 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 153.0, 135.5, 135.3, 127.8, 127.0 (q, J_{CF} = 277.8 Hz), 126.5, 124.2, 41.8 (q, J_{CF} = 2.0 Hz), 34.9 (q, J_{CF} = 30.3 Hz), 33.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8.

The analytical data are consistent with those reported in the literature[5].



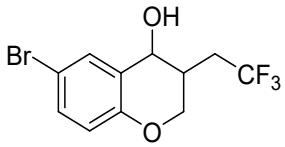
ethyl 4-methyl-2-(4-oxo-3-(2,2,2-trifluoroethyl)chroman-6-yl)thiazole-5-carboxylate(3s): (25.2 mg, white solid, m.p. = 116-118 ℃, yield: 33 %**)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.4 Hz, 1H), 8.09 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 4.76 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.35 – 4.29 (m, 2H), 4.26 (t, 1H), 3.22 – 3.04 (m, 2H), 2.70 (s, 3H), 2.14 – 2.03 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 167.8, 163.0, 162.0, 160.9, 134.0, 127.0, 126.5 (q, J_{CF} = 277.8 Hz), 126.0, 121.7, 119.9, 118.7, 69.8 (q, J_{CF} = 2.0 Hz), 61.2, 40.3 (q, J_{CF} = 2.0 Hz), 29.4 (q, J_{CF} = 30.3 Hz), 17.3, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0.

HRMS (ESI-TOF) Calc. for $C_{18}H_{17}N_4F_3S$ $[M+H]^+$: 400.0830; found: 400.0834



6-Bromo-3-(2,2,2-trifluoroethyl)chroman-4-ol (3h'): (54.6 mg, colorless liquid, yield: 88 %**)**

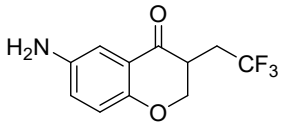
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.12 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 1H), 4.72 – 4.23 (m,

2H), 4.16 – 3.99 (m, 1H), 2.31 – 2.24 (m, 1H), 2.21 – 2.01 (m, 2H).

^{13}C NMR (101 MHz, cdcl$_3$) δ 153.1, 133.01, 132.5, 126.6 (q, J_{CF} = 277.8 Hz), 124.2, 119.0, 113.1, 67.1, 64.9, 34.1, 32.3 (q, J_{CF} = 30.3 Hz).

^{19}F NMR (376 MHz, CDCl$_3$) δ -64.0.

GC-MS: 312 (68), 310 (67), 202 (87), 201 (60), 200 (100), 200 (59).



6-Amino-3-(2,2,2-trifluoroethyl)chroman-4-one (3k'): (35.3 mg, yellow solid, yield: 72 %**)**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13 (d, *J* = 2.9 Hz, 1H), 6.93 – 6.70 (m, 2H), 4.61 (dd, *J* = 11.3, 5.1 Hz, 1H), 4.15 (t, *J* = 11.6 Hz, 1H), 3.59 (s, 2H), 3.17 – 2.87 (m, 2H), 2.22 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, cdcl$_3$) δ 191.1, 154.9, 140.9, 126.7 (q, J_{CF} = 277.8 Hz), 124.8, 120.2, 118.6, 111.1, 69.8, 40.7, 29.7 (q, J_{CF} = 30.3 Hz)..

^{19}F NMR (376 MHz, CDCl$_3$) δ -64.00, -64.03, -64.06.

GC-MS:246 (20), 245 (100), 135 (68), 107 (25), 79 (40).

7. References

1. H. Hu, X. Chen, K. Sun, J. Wang, Y. Liu, H. Liu, L. Fan, B. Yu, Y. Sun, L. Qu, Y. Zhao, *Org. Lett.* **2018**, *20* (19), 6157–6160.
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6. Y. Lv, H. Luo, X. Z. Jiang, Y. Yu, C. Ding, Y. Xie Zhang, *Eur. J. Org.* **2025**, *28*, e202401013.

8. Copies of NMR Spectra of products

Figure S1 ^{1}H NMR spectrum for compound 3a

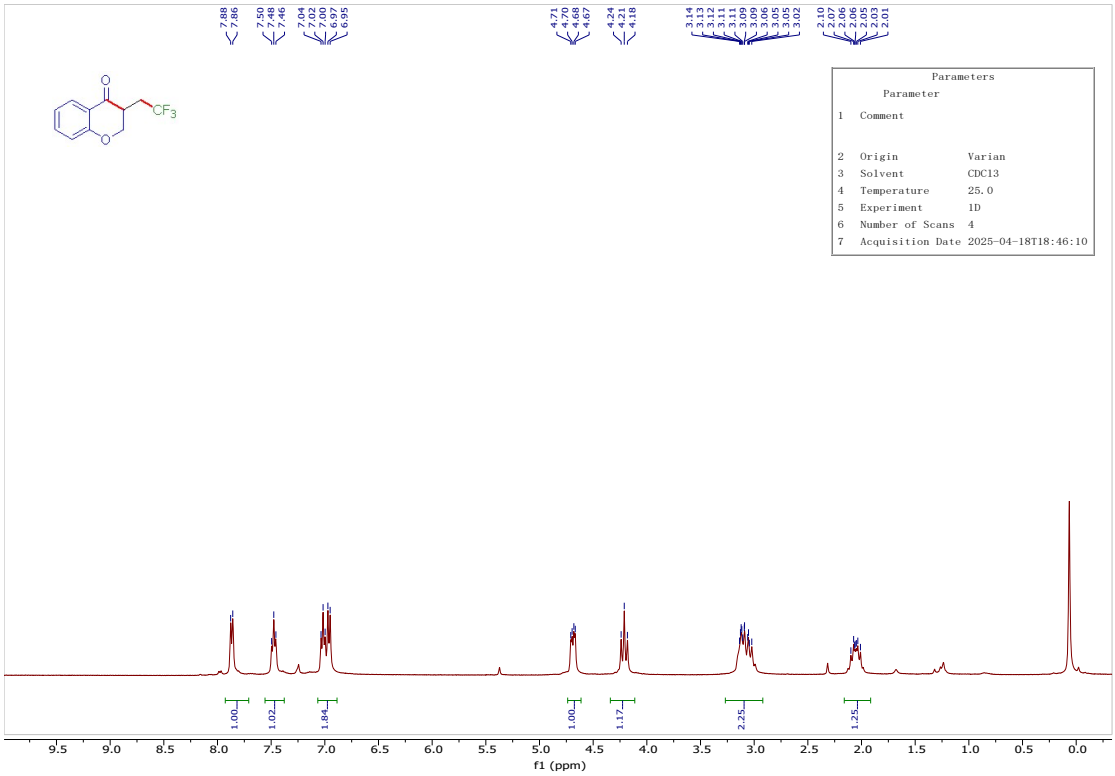


Figure S2 ^{13}C NMR spectrum for compound 3a

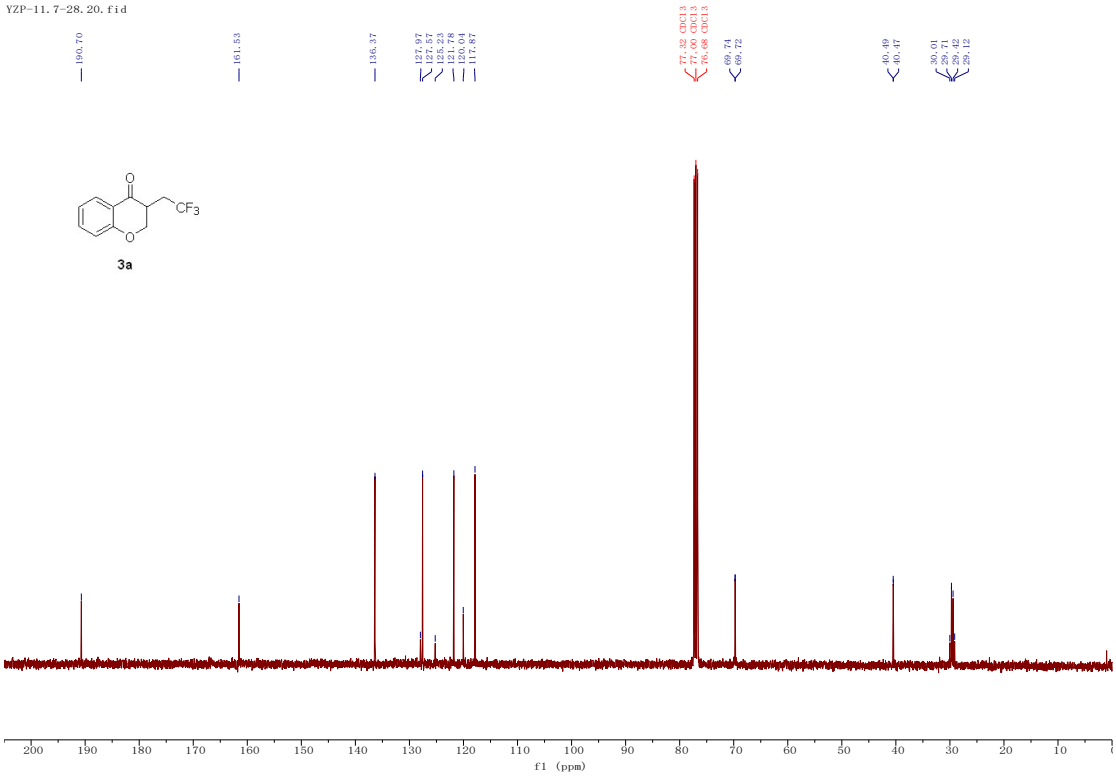


Figure S3 ^{19}F NMR spectrum for compound 3a

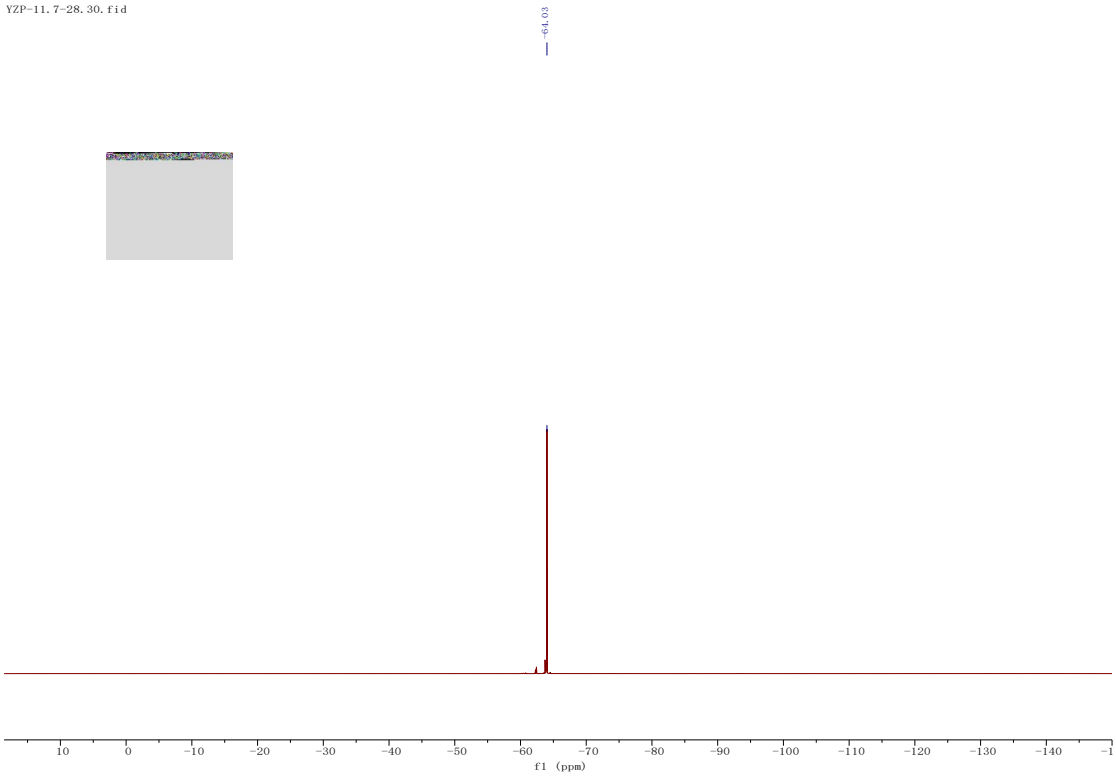


Figure S4 ^{1}H NMR spectrum for compound 3b

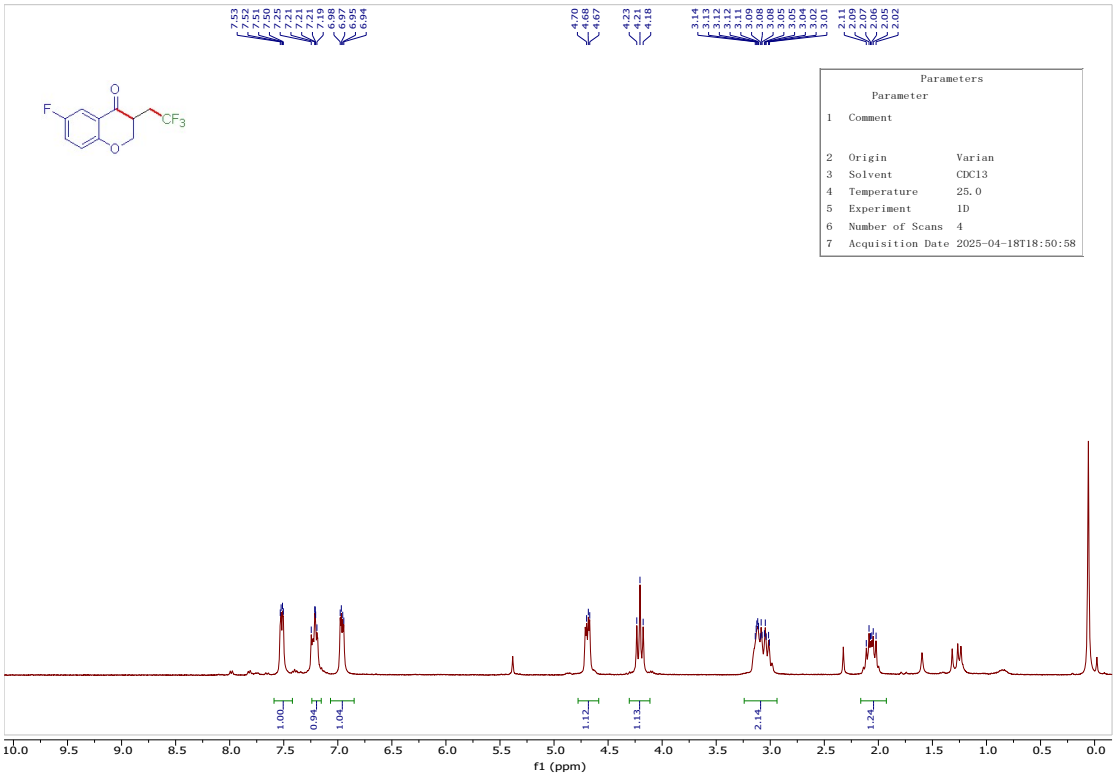


Figure S5 ^{13}C NMR spectrum for compound 3b

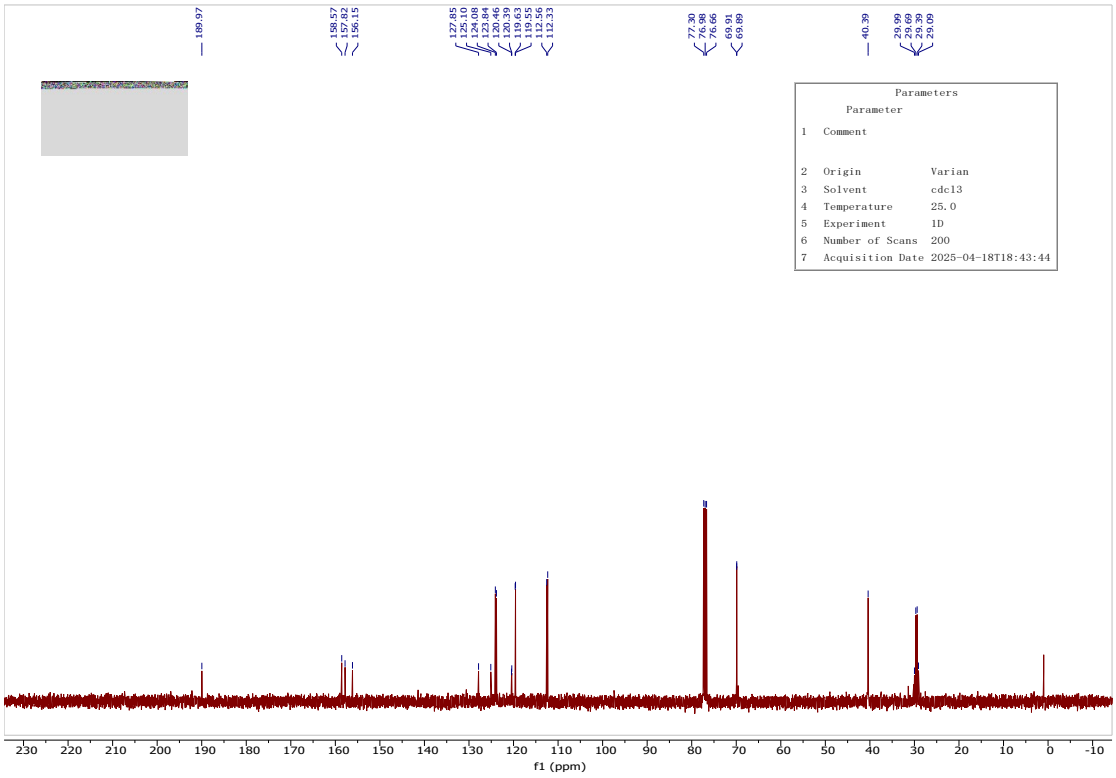


Figure S6 ^{19}F NMR spectrum for compound 3b

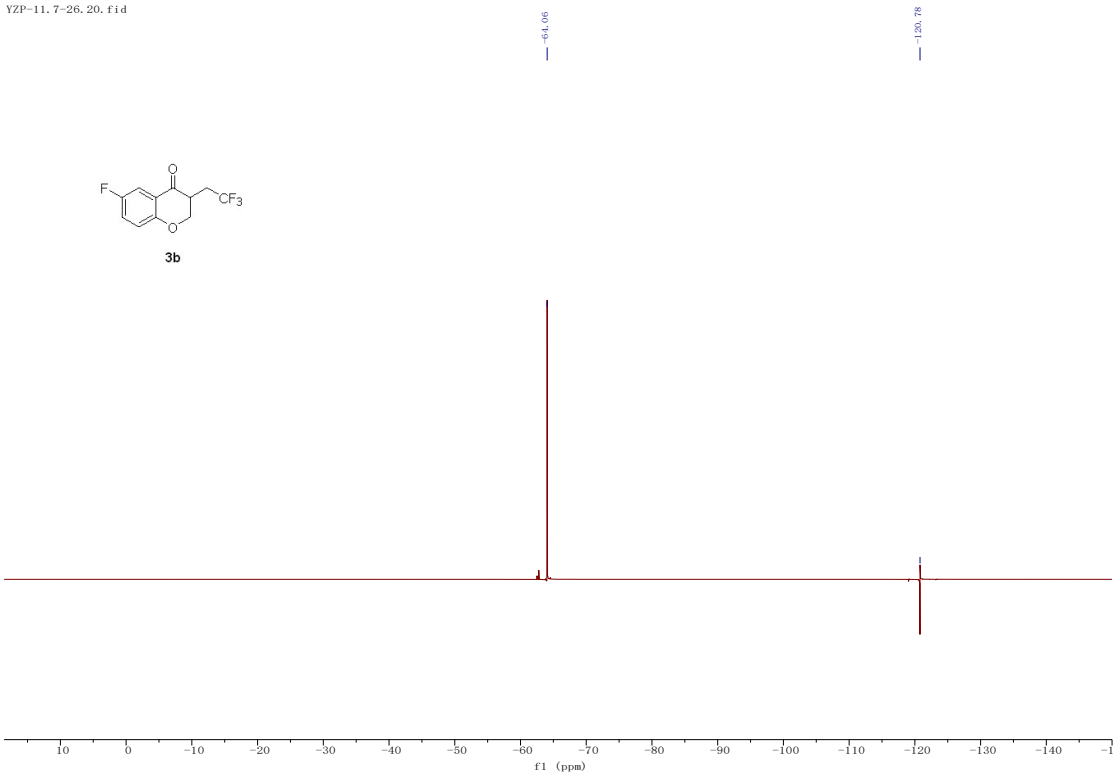


Figure S7 ^{1}H NMR spectrum for compound 3c

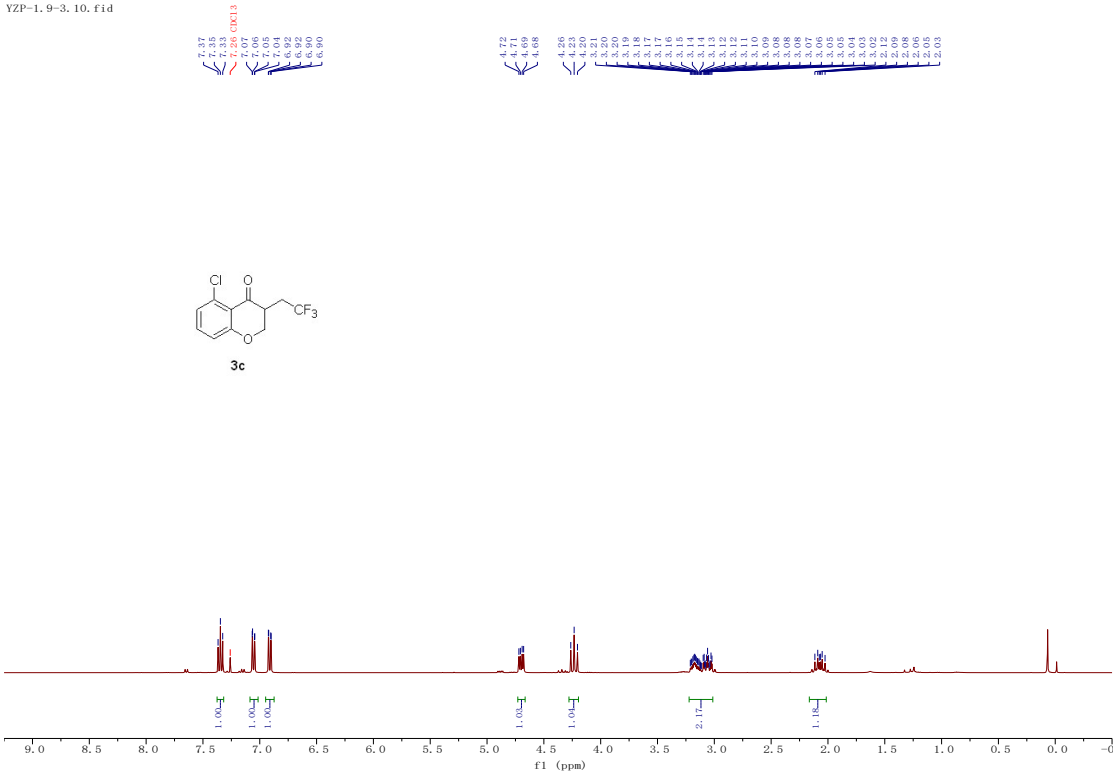


Figure S8 ^{13}C NMR spectrum for compound 3c

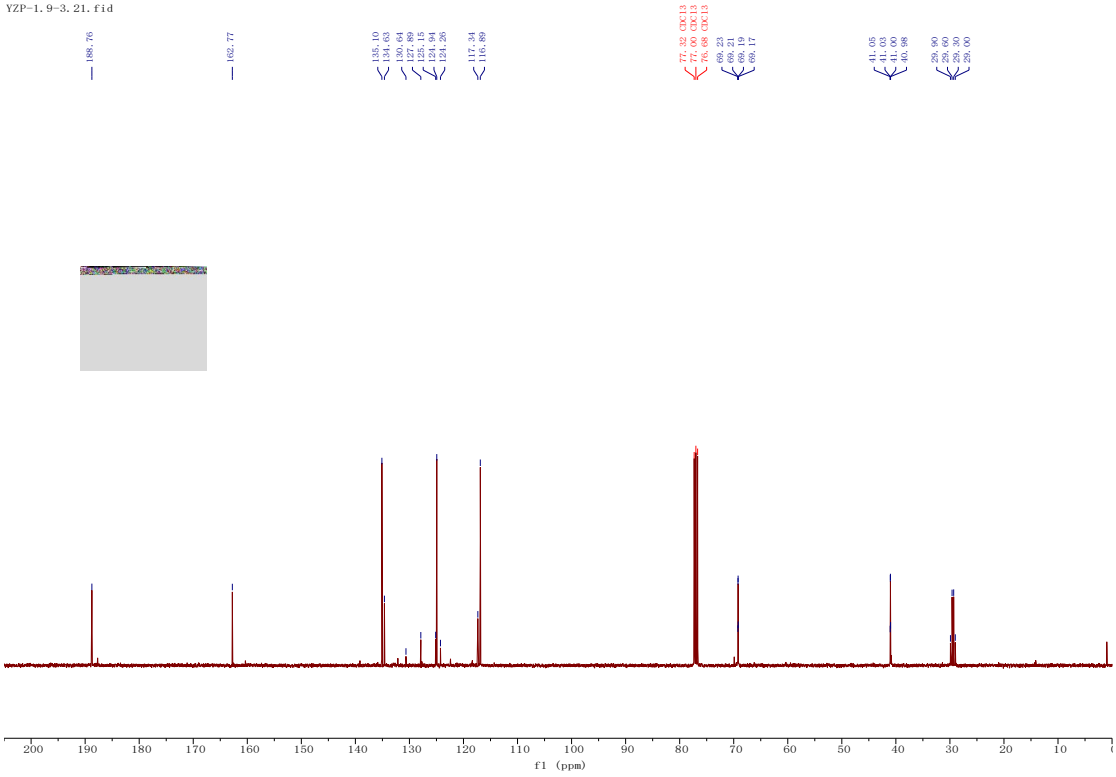


Figure S9 ^{19}F NMR spectrum for compound 3c

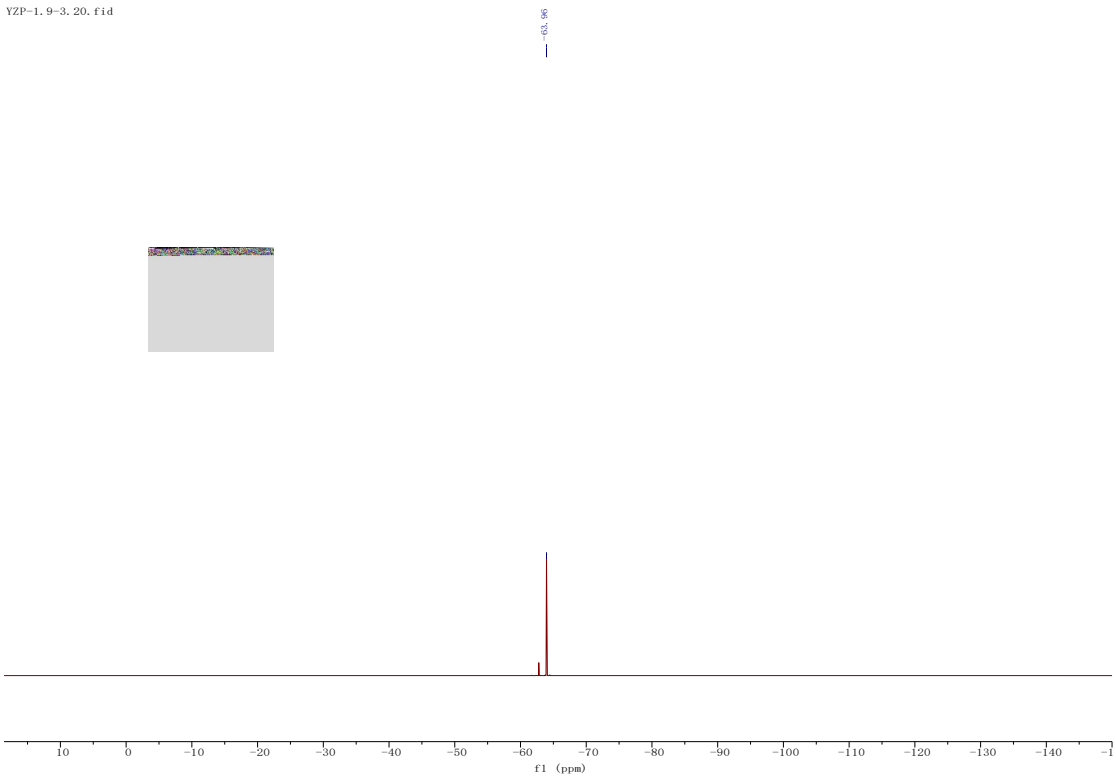


Figure S10 ^{1}H NMR spectrum for compound 3d

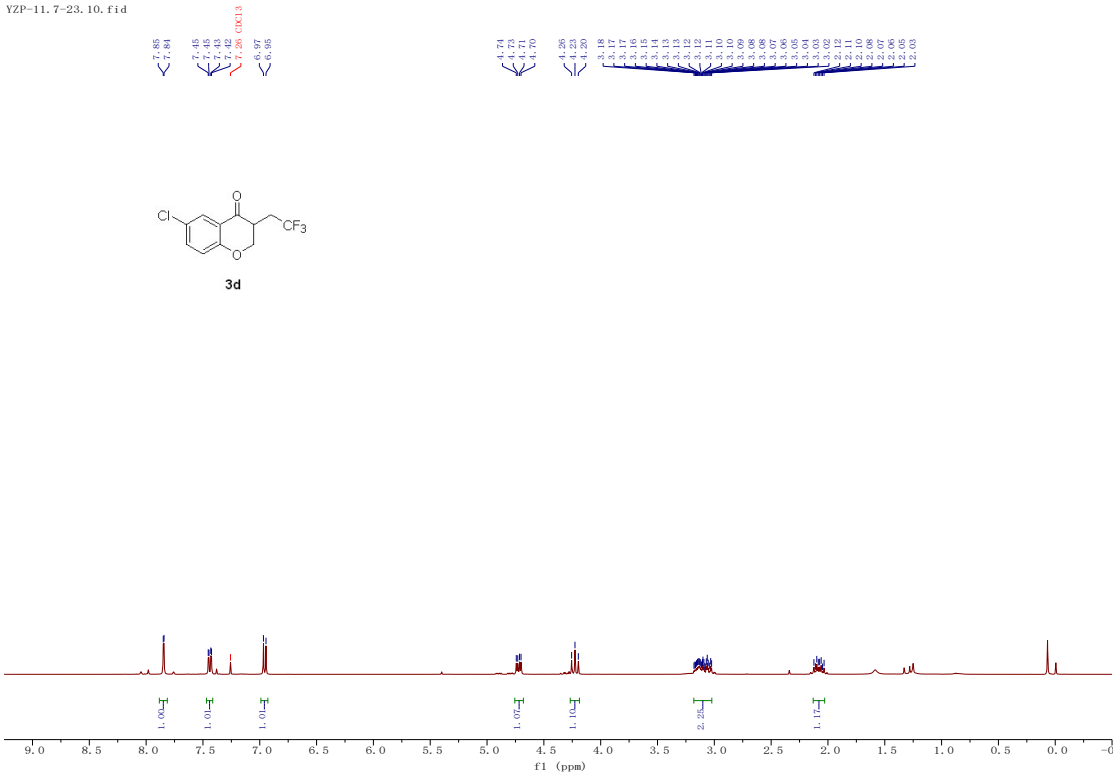


Figure S11 ^{13}C NMR spectrum for compound 3d

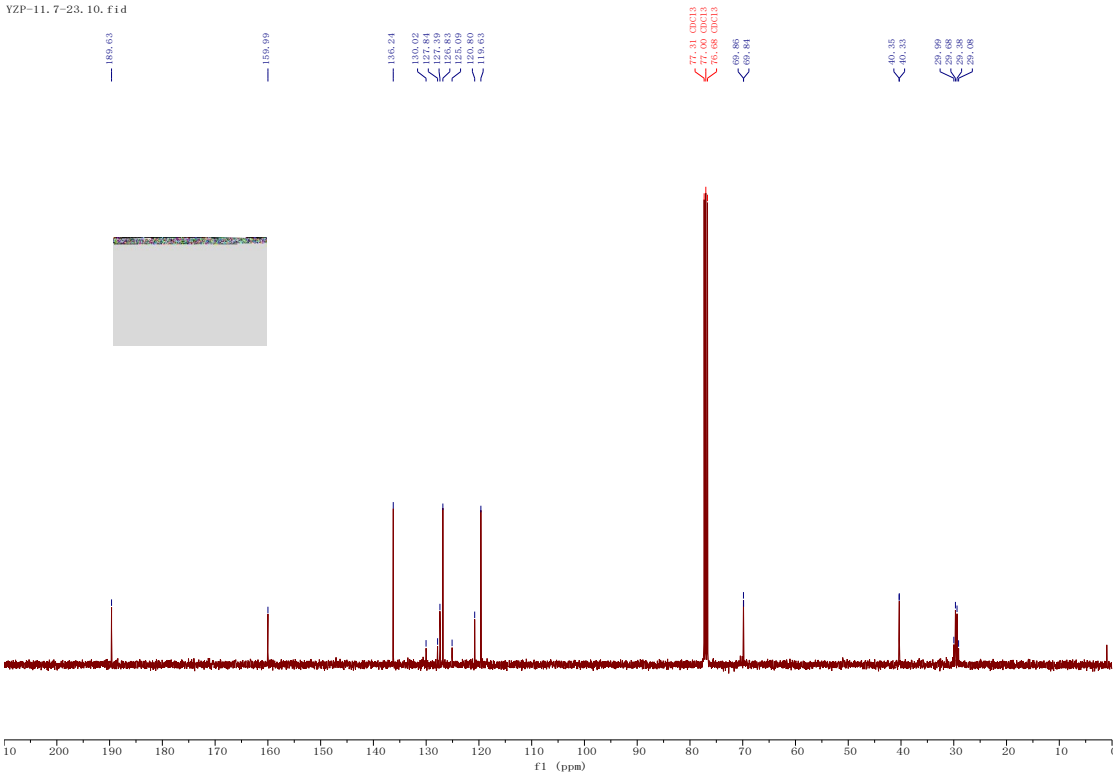


Figure S12 ^{19}F NMR spectrum for compound 3d

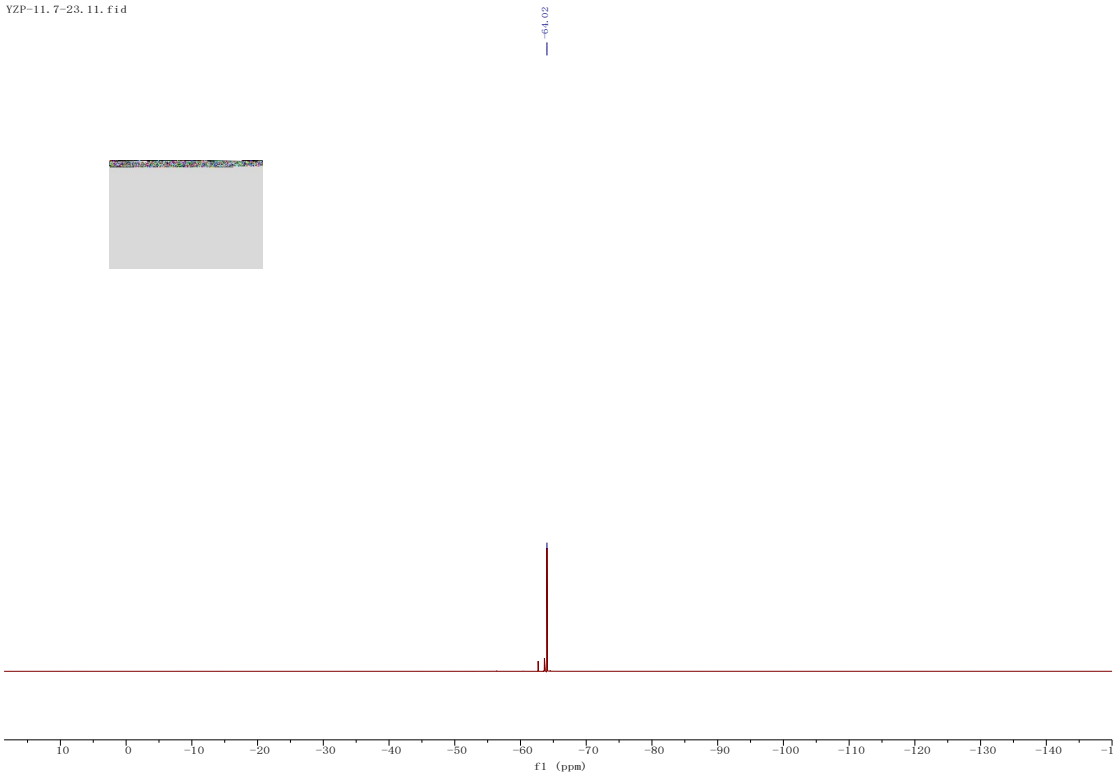


Figure S13 ^{1}H NMR spectrum for compound 3e

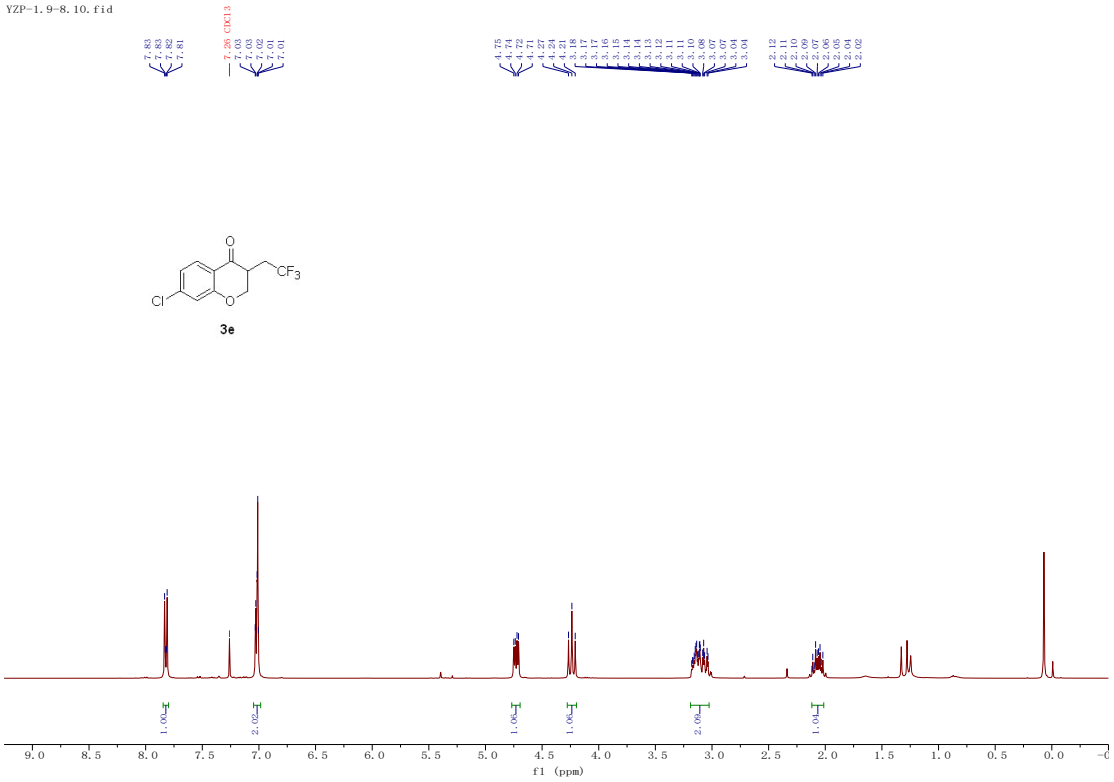


Figure S14 ^{13}C NMR spectrum for compound 3e

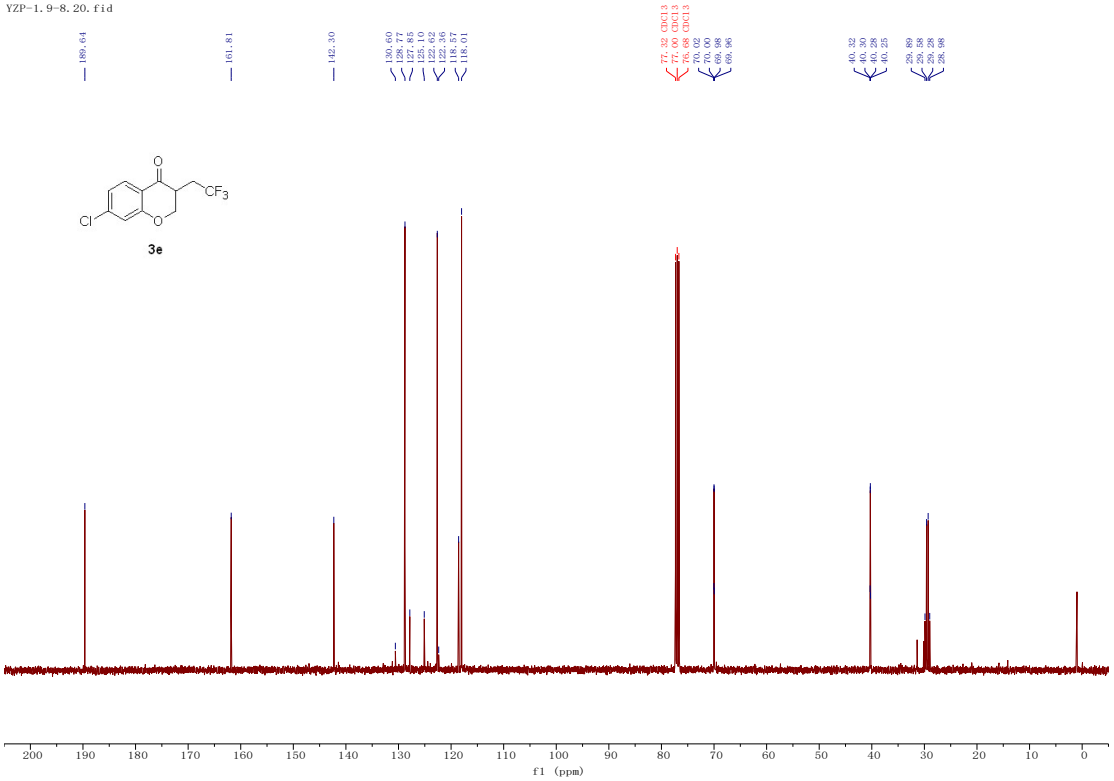


Figure S15 ^{19}F NMR spectrum for compound 3e

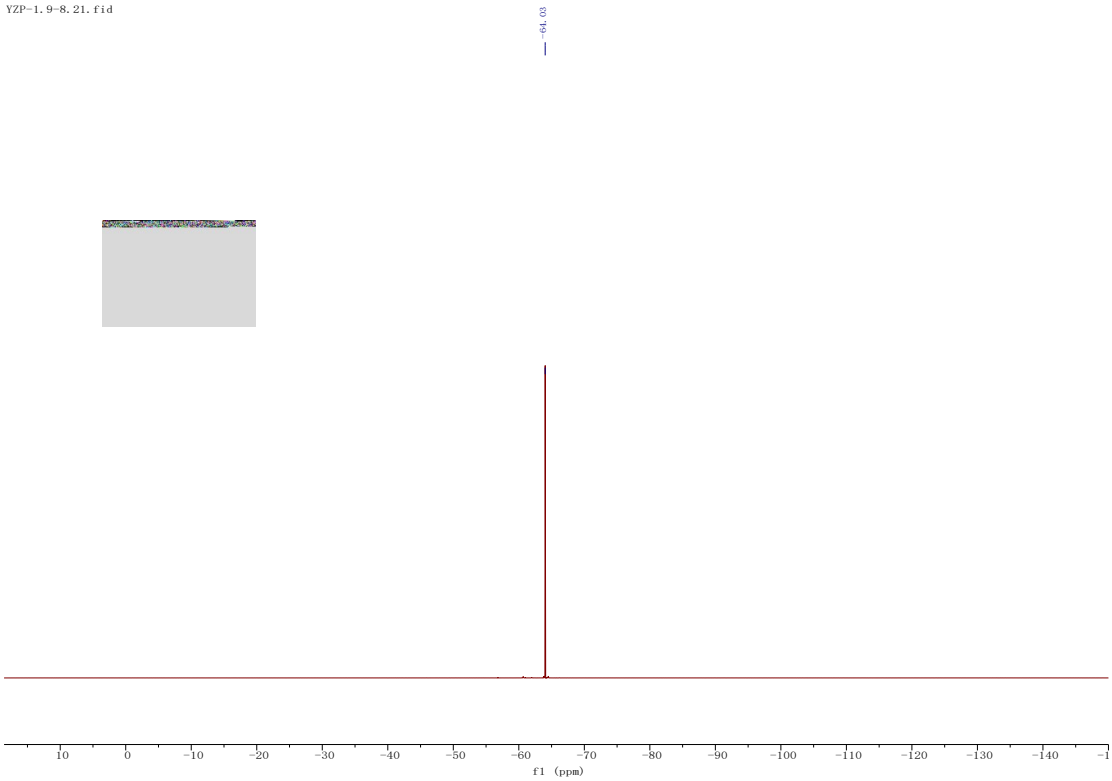


Figure S16 ^{1}H NMR spectrum for compound 3f

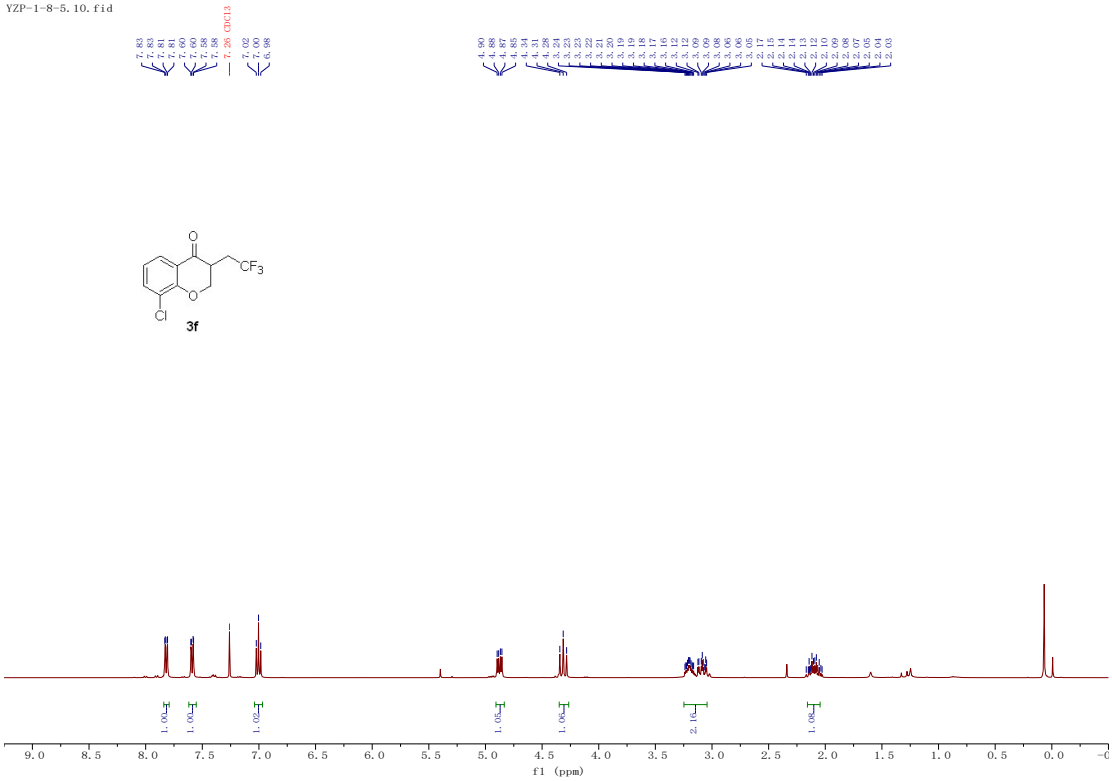


Figure S17 ^{13}C NMR spectrum for compound 3f

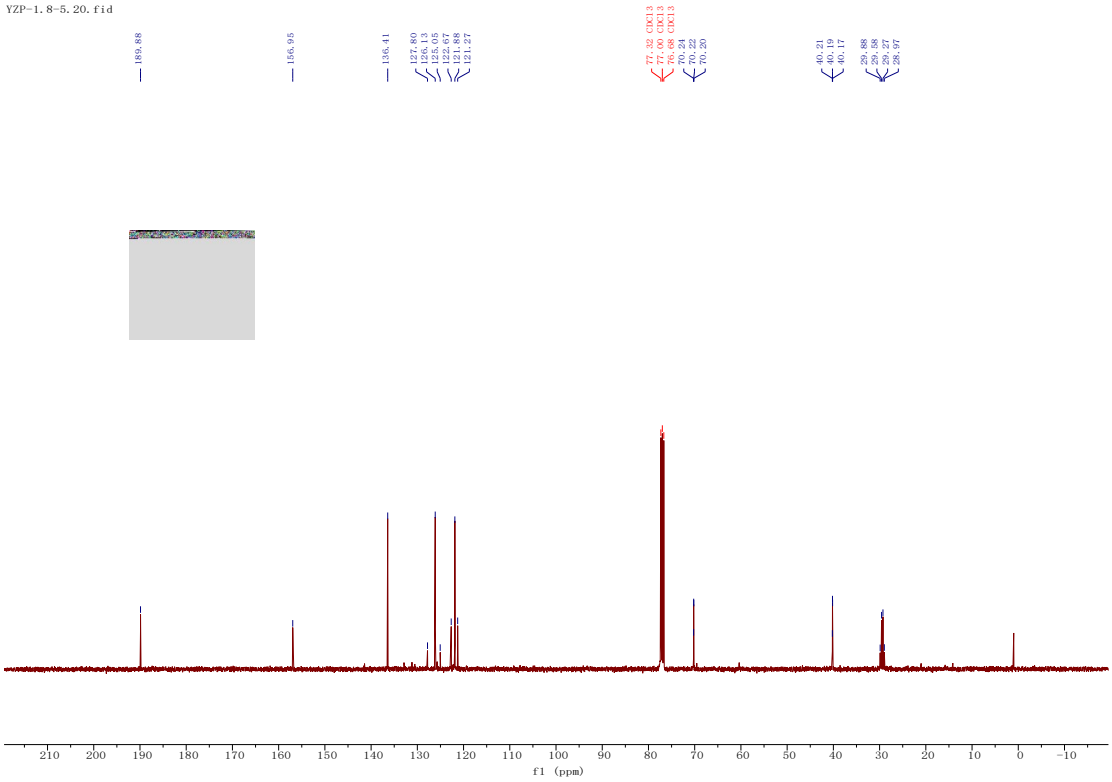


Figure S18 ^{19}F NMR spectrum for compound 3f

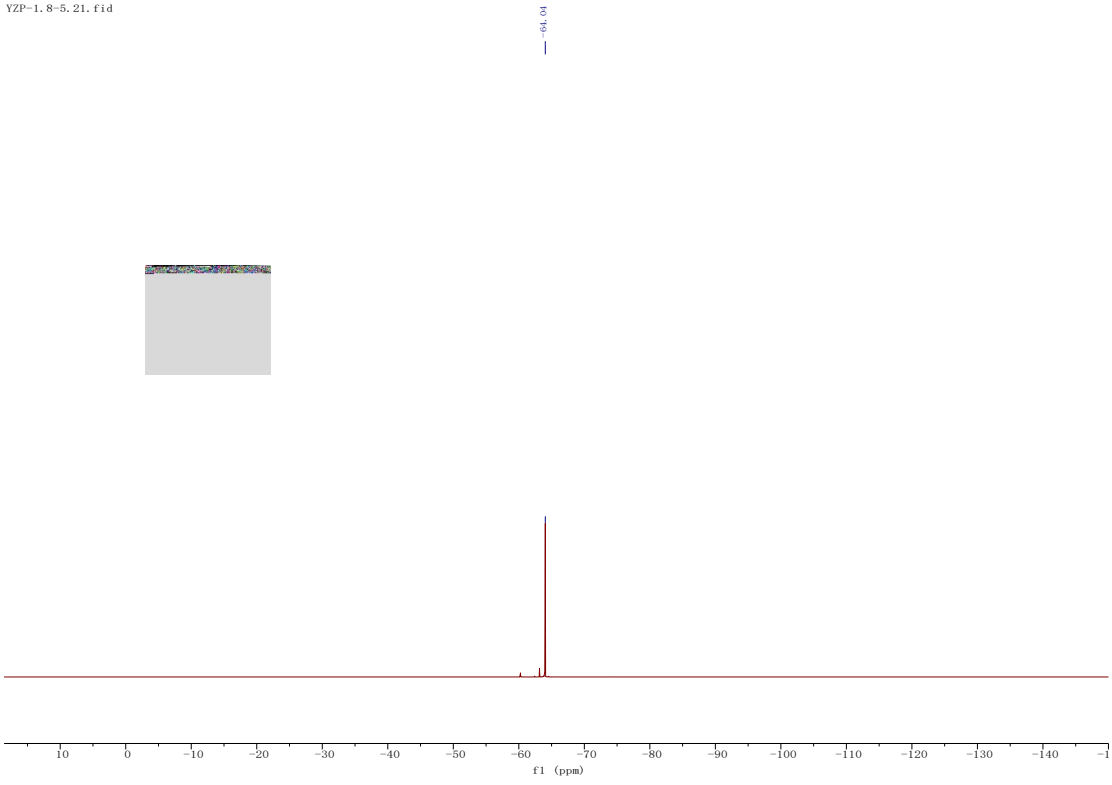


Figure S19 ^{1}H NMR spectrum for compound 3g

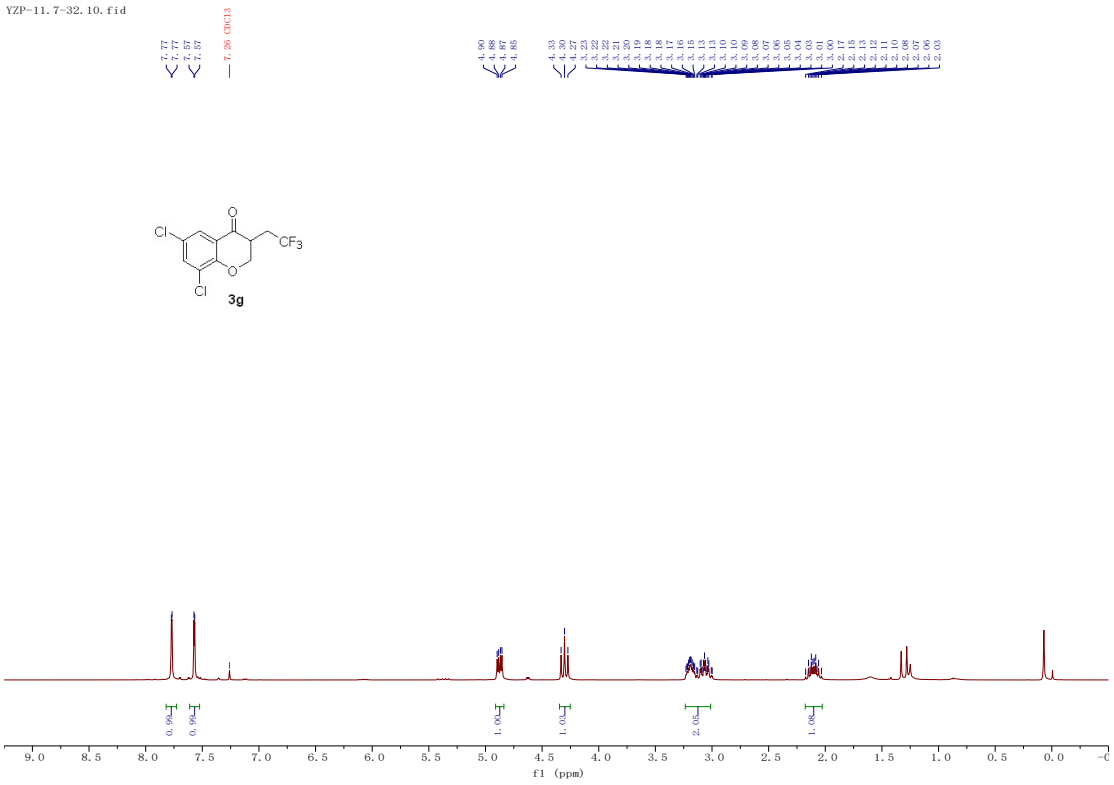


Figure S20 ^{13}C NMR spectrum for compound 3g

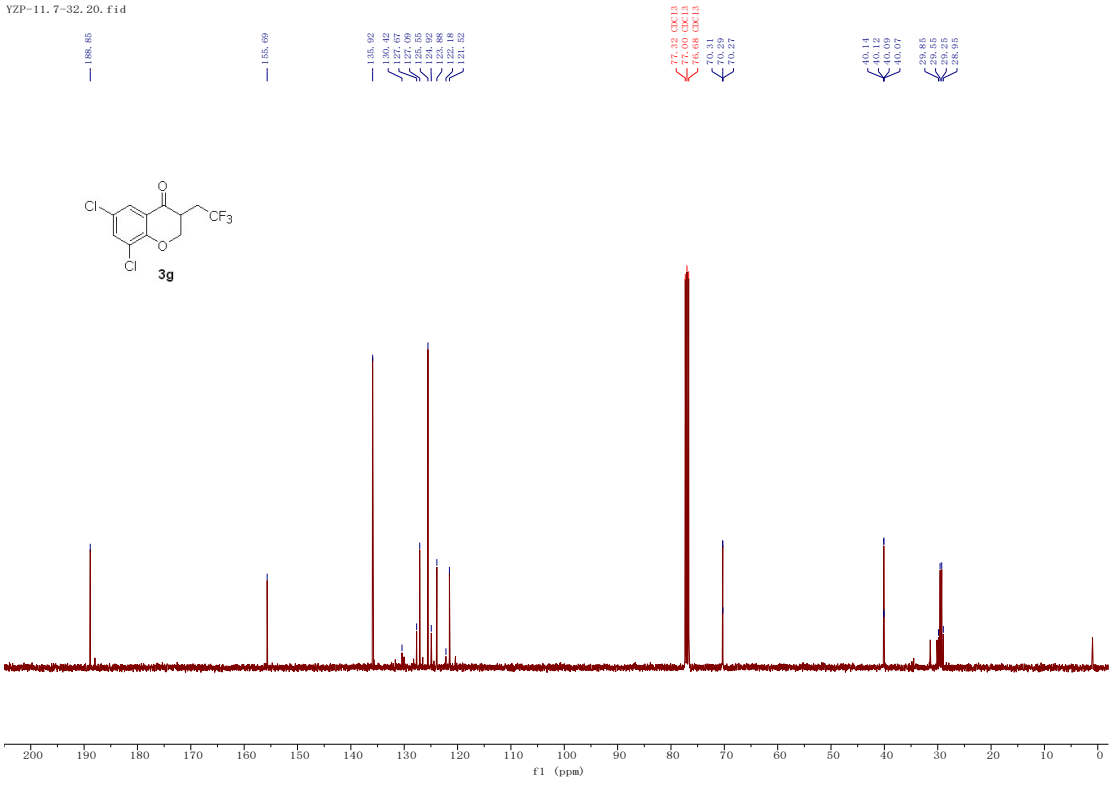
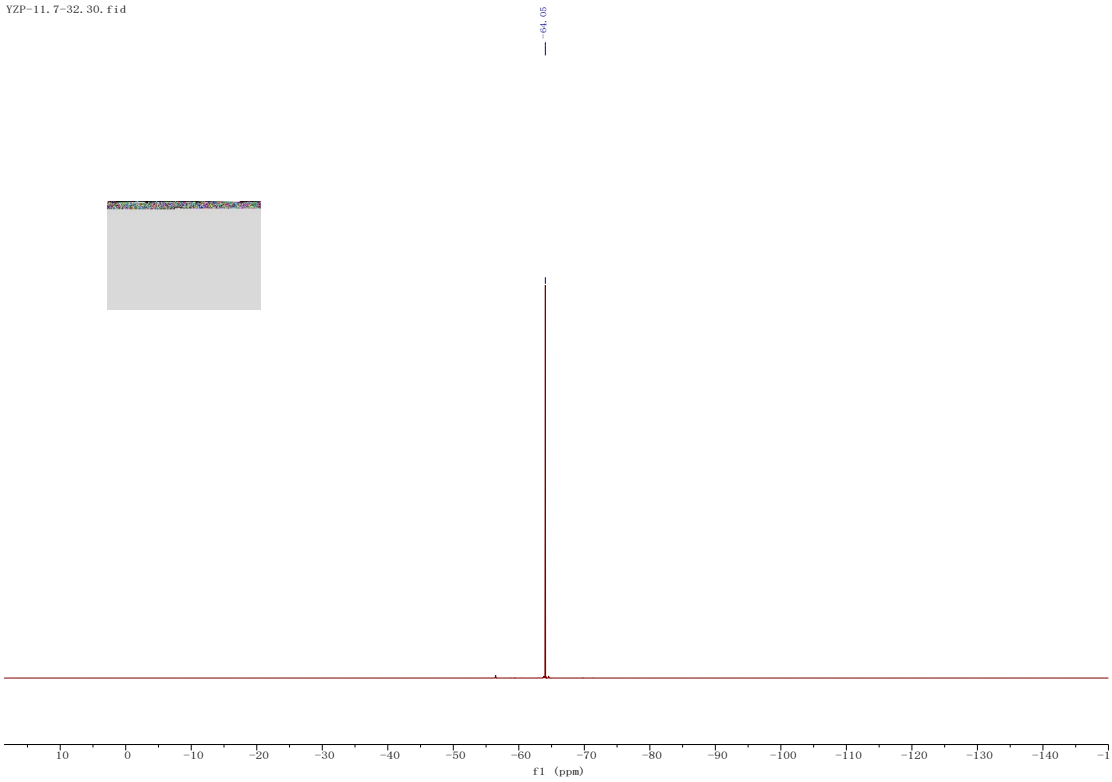


Figure S21 ^{19}F NMR spectrum for compound 3g



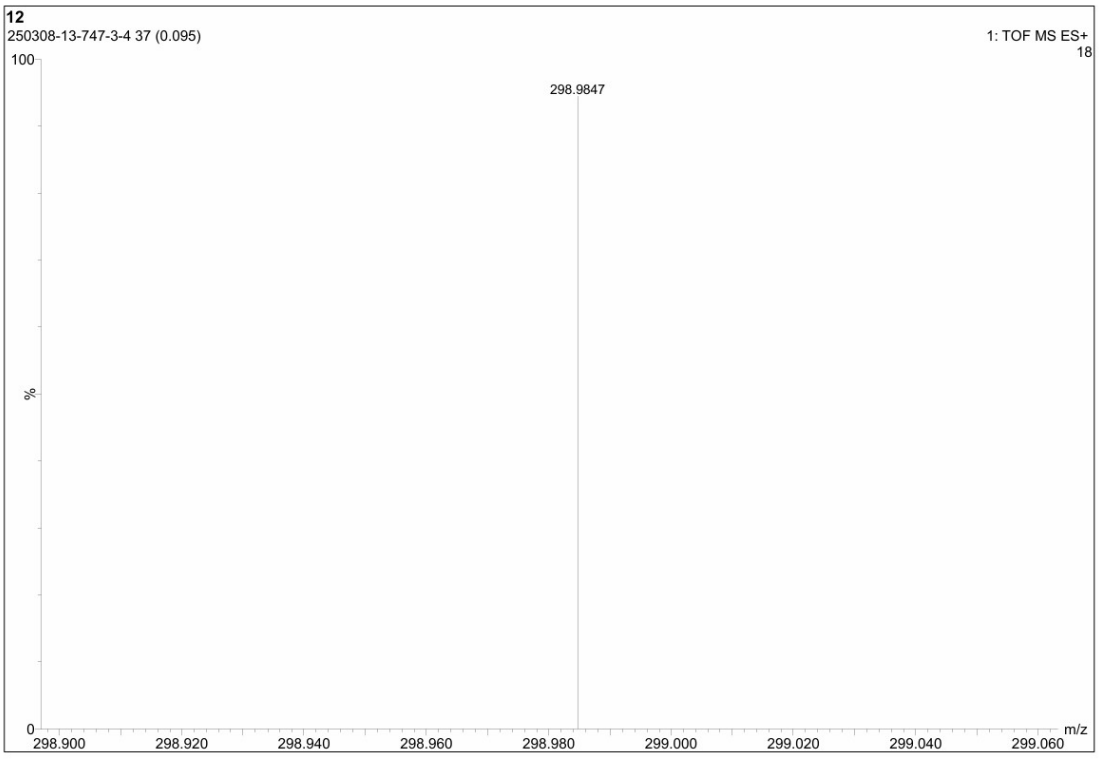


Figure S22 ^{1}H NMR spectrum for compound 3h

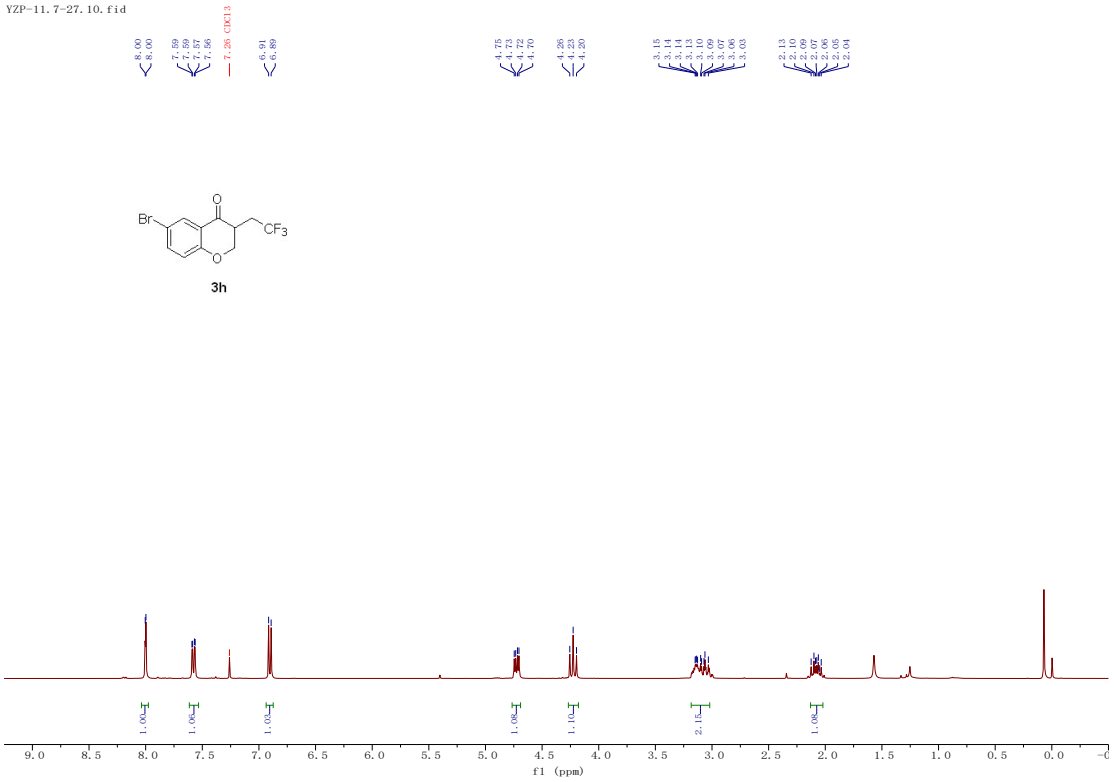


Figure S23 ^{13}C NMR spectrum for compound 3h

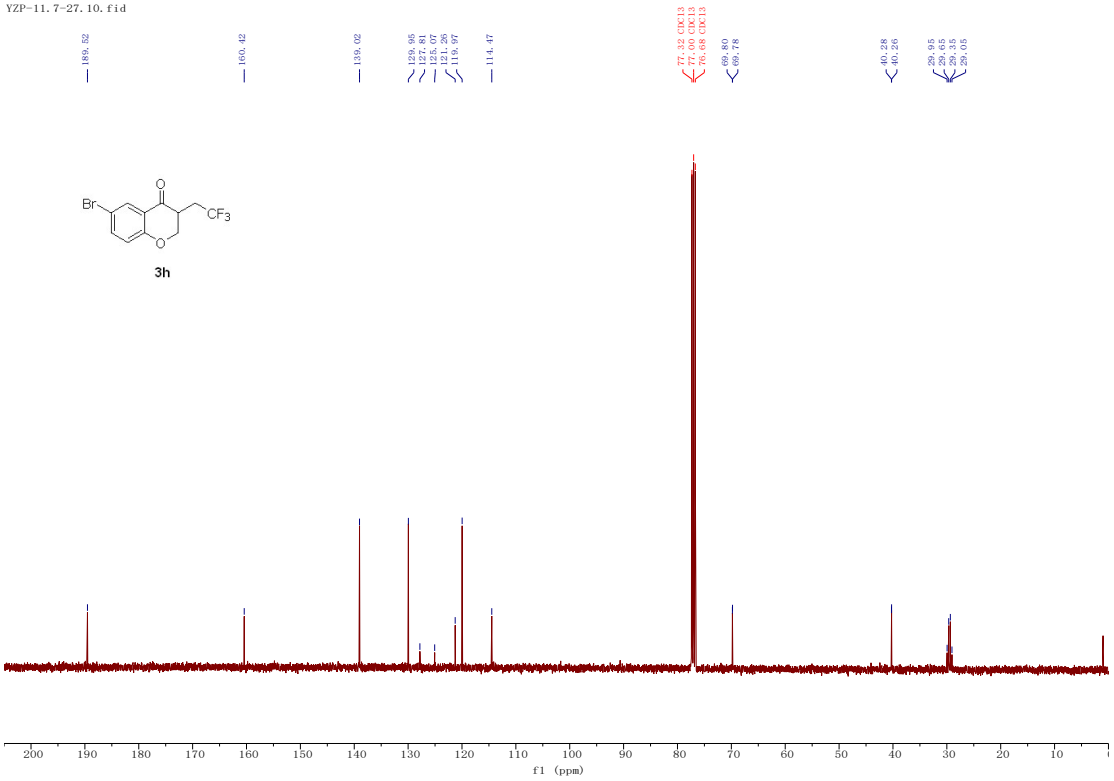


Figure S24 ^{19}F NMR spectrum for compound 3h

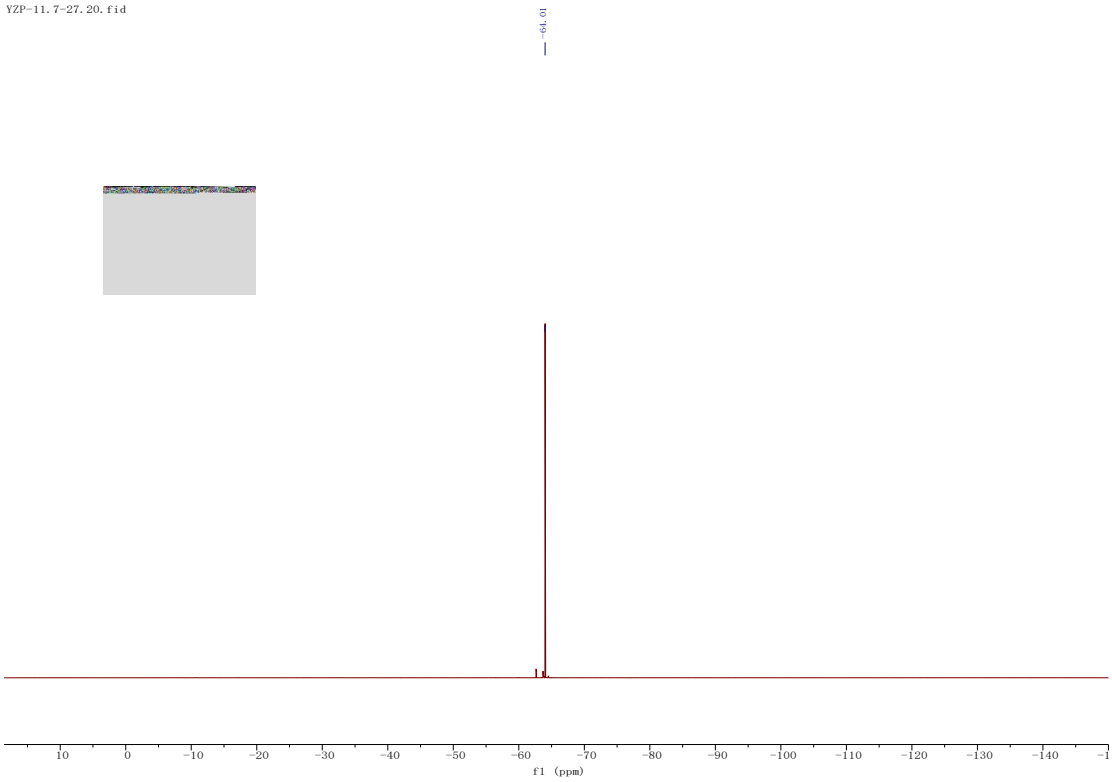


Figure S25 ^{1}H NMR spectrum for compound 3i

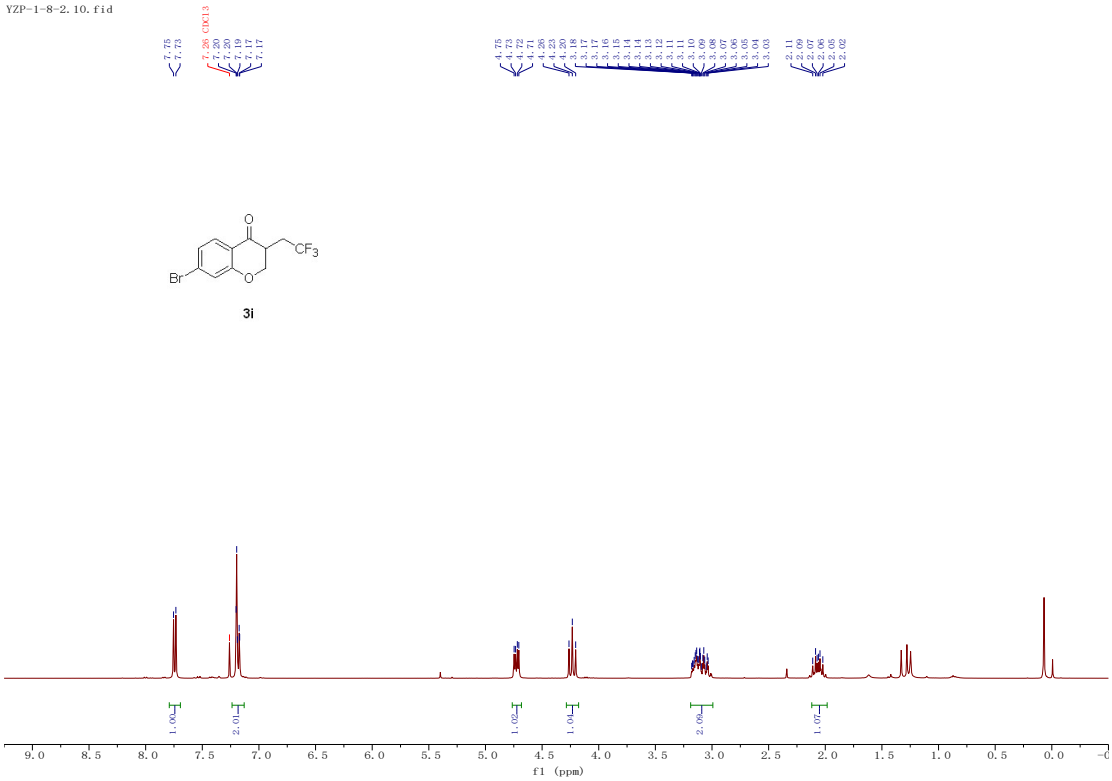


Figure S26 ^{13}C NMR spectrum for compound 3i

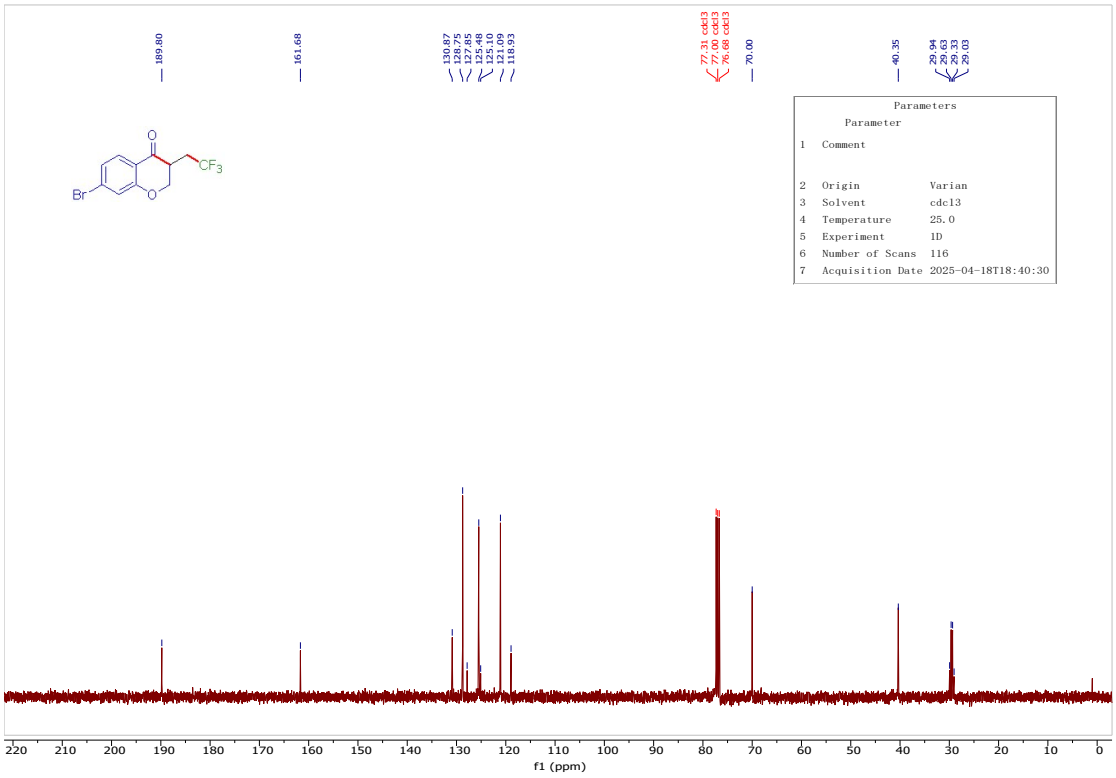


Figure S27 ^{19}F NMR spectrum for compound 3i

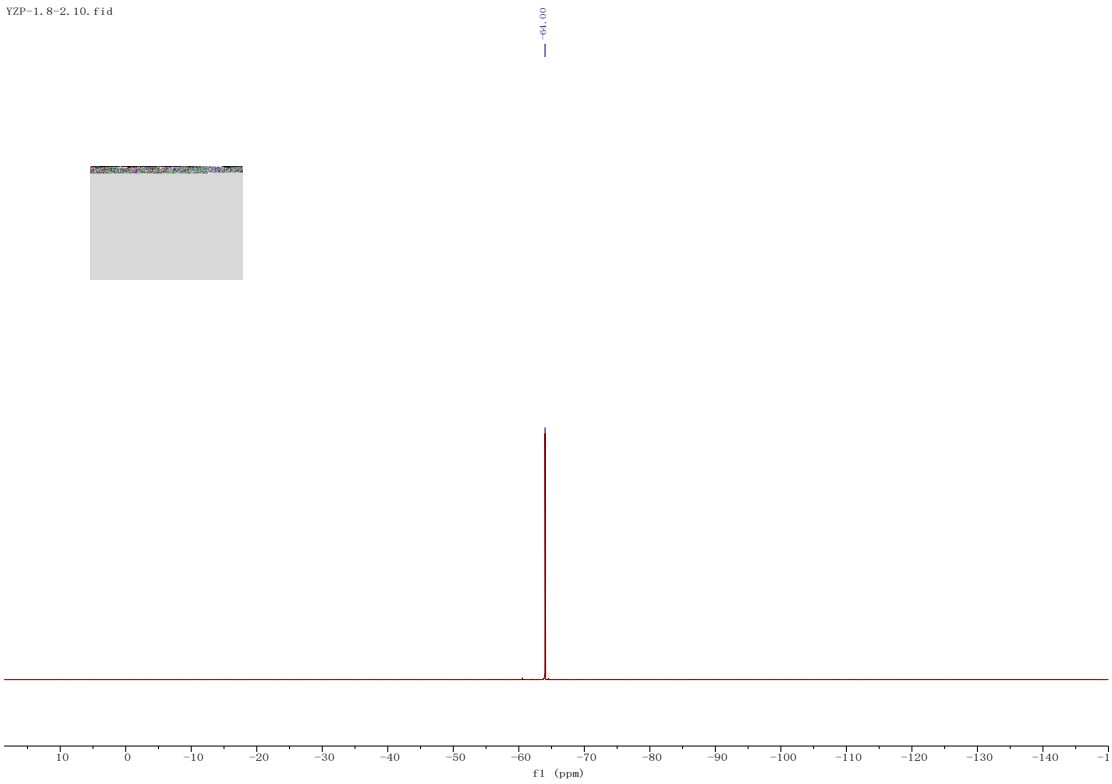


Figure S28 ^{1}H NMR spectrum for compound 3j

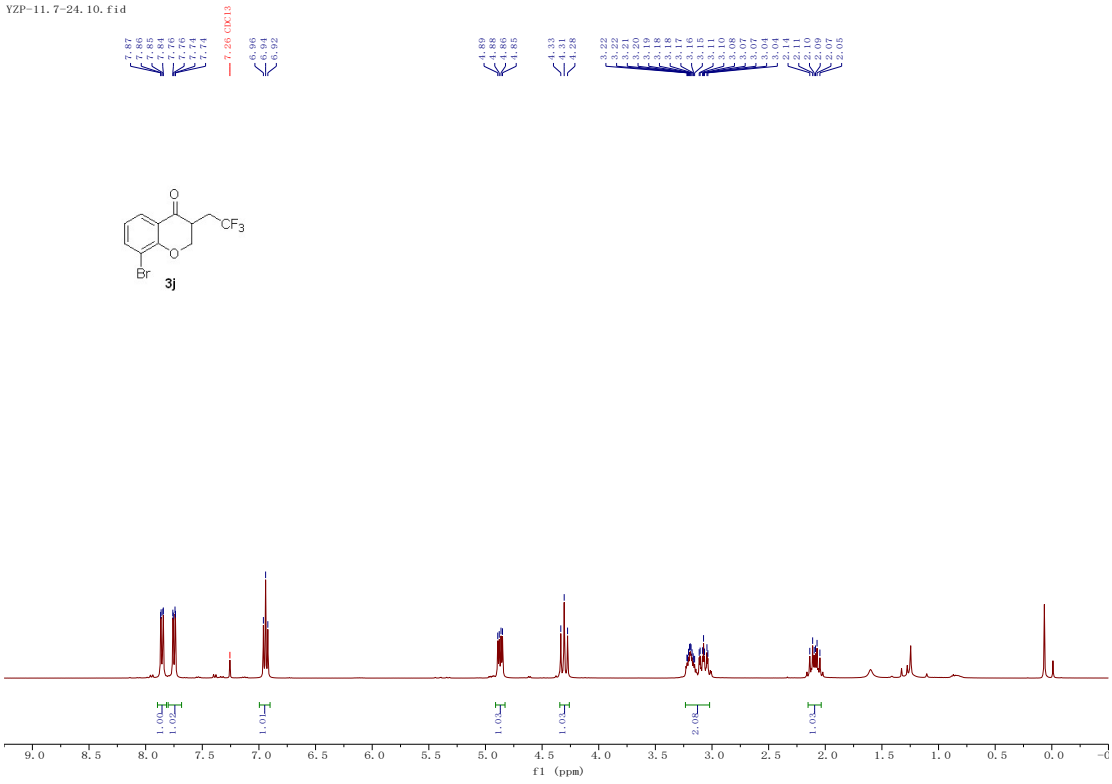


Figure S29 ^{13}C NMR spectrum for compound 3j

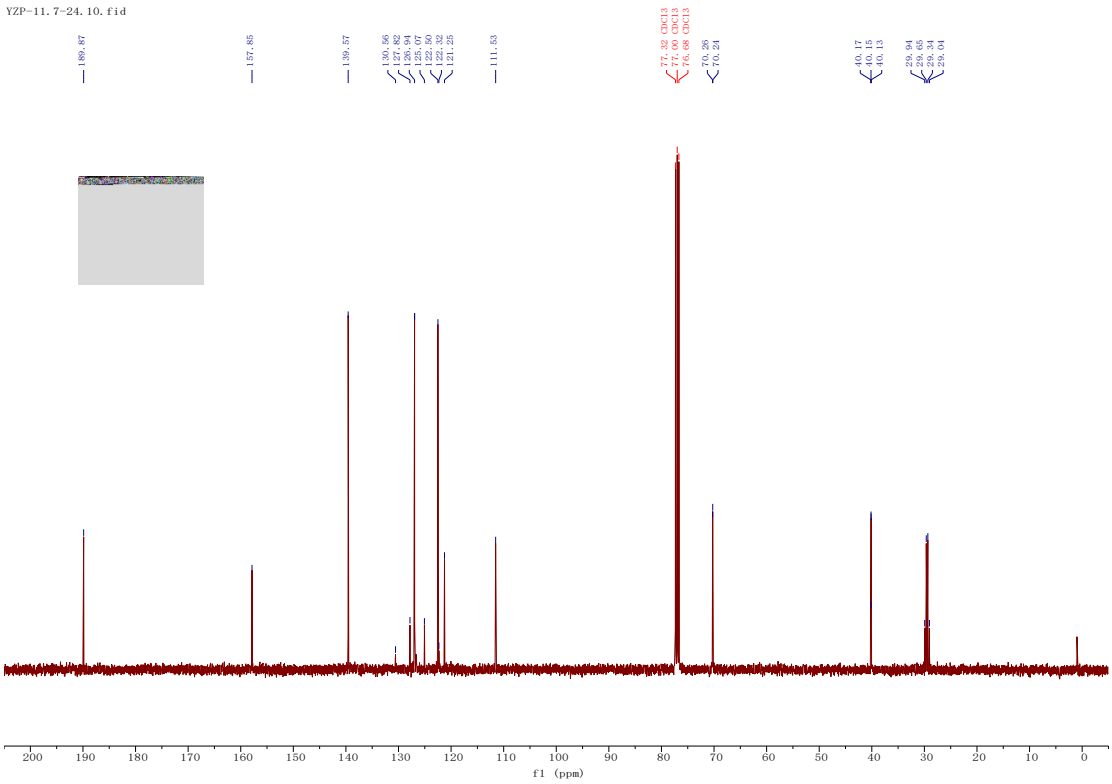


Figure S30 ^{19}F NMR spectrum for compound 3j

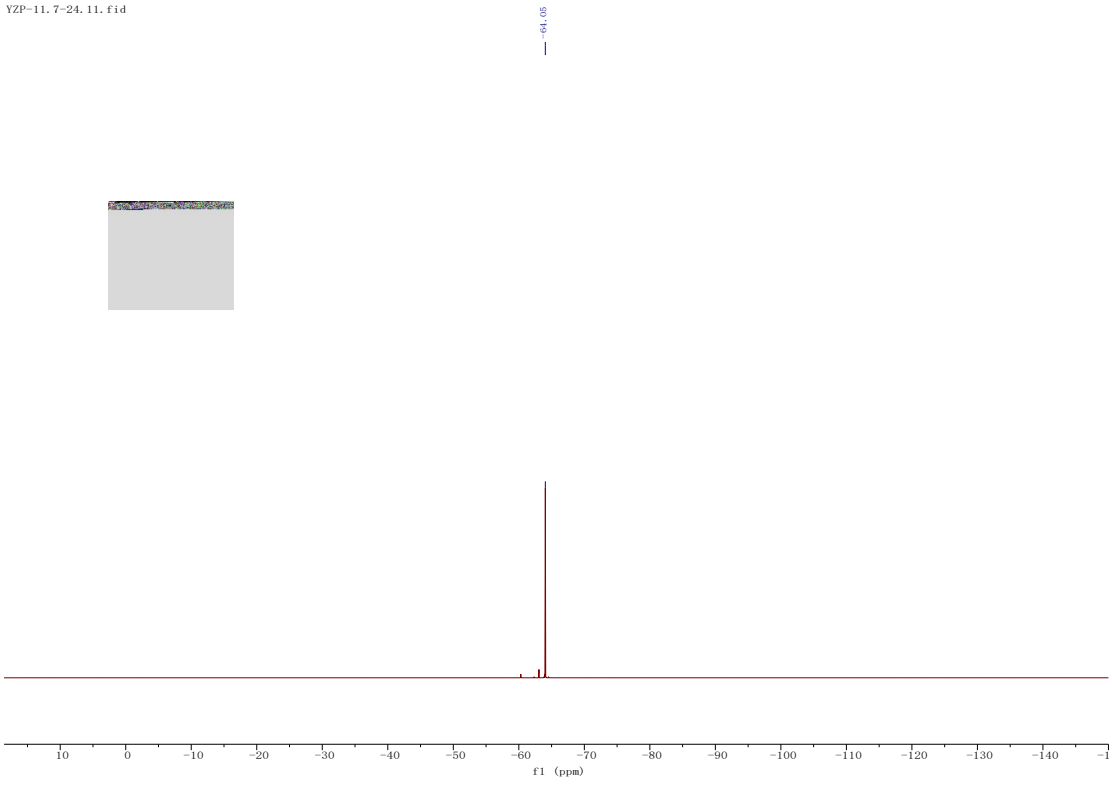


Figure S31 ^{1}H NMR spectrum for compound 3k

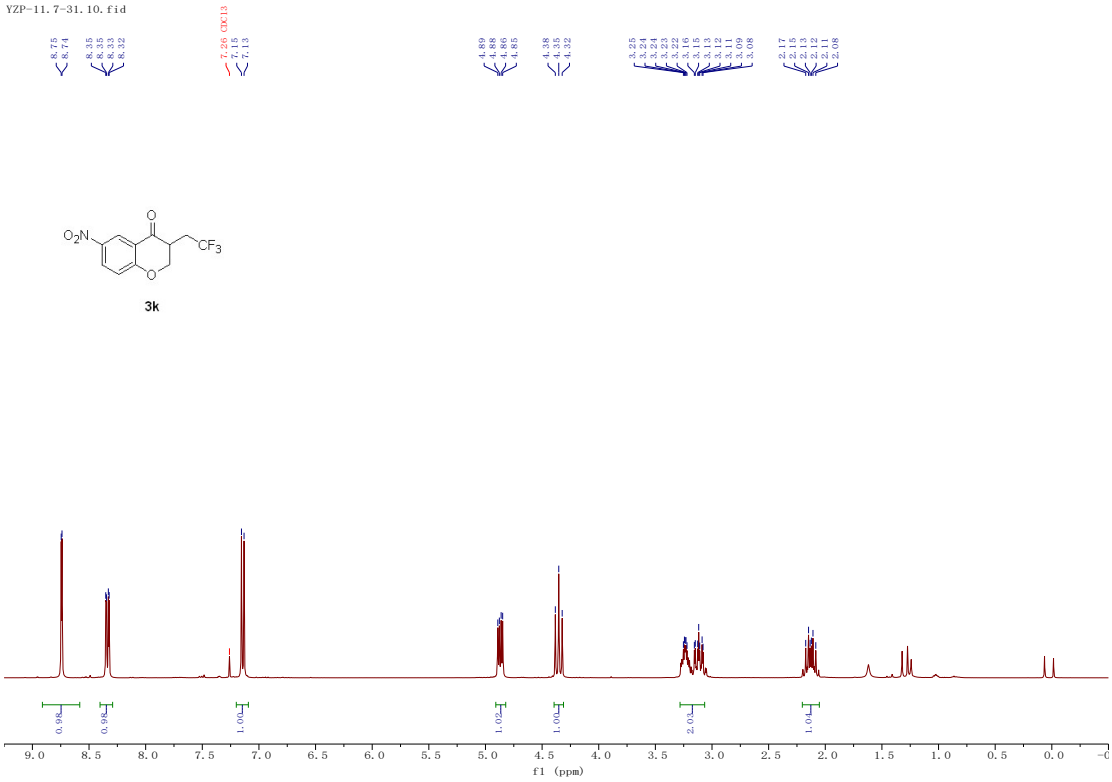


Figure S32 ^{13}C NMR spectrum for compound 3k

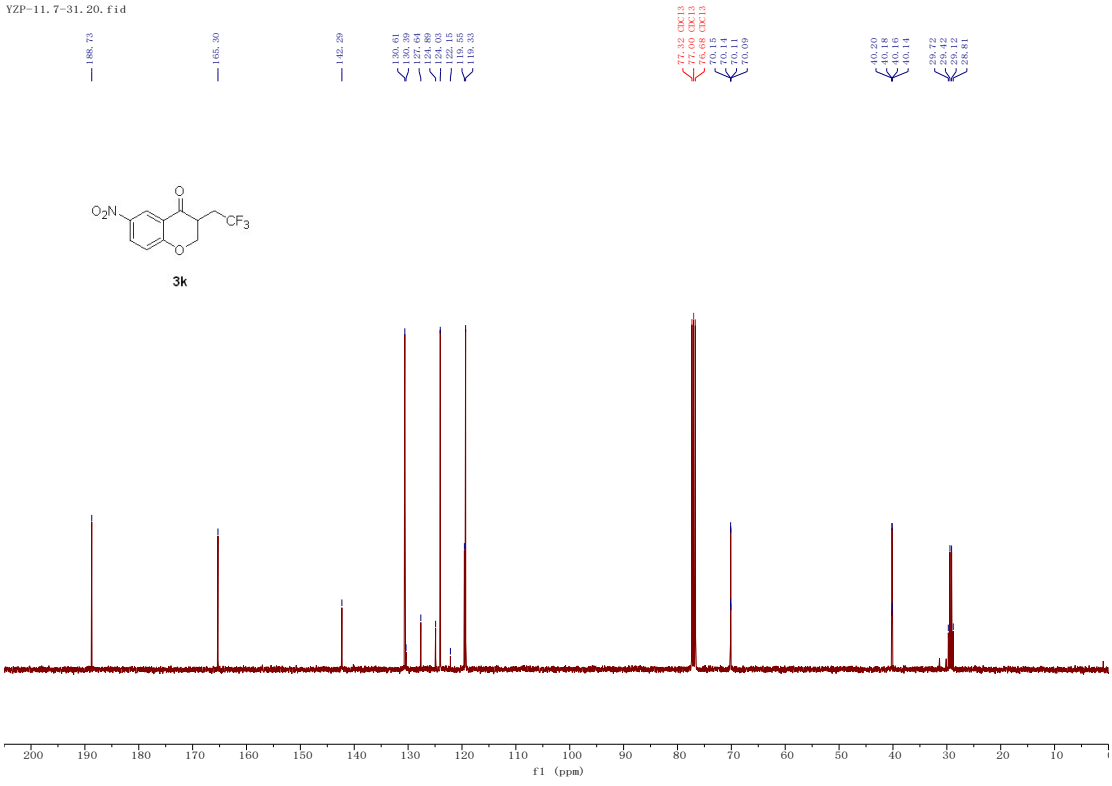


Figure S33 ^{19}F NMR spectrum for compound 3k

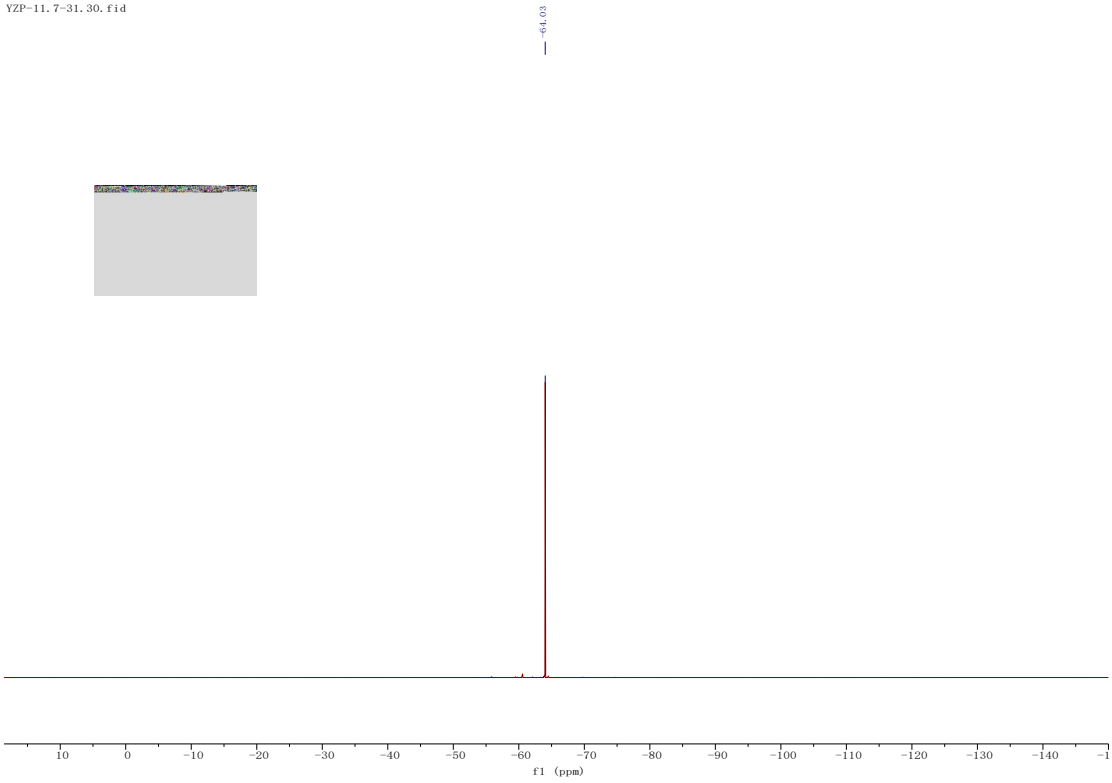


Figure S34 ^{1}H NMR spectrum for compound 3l

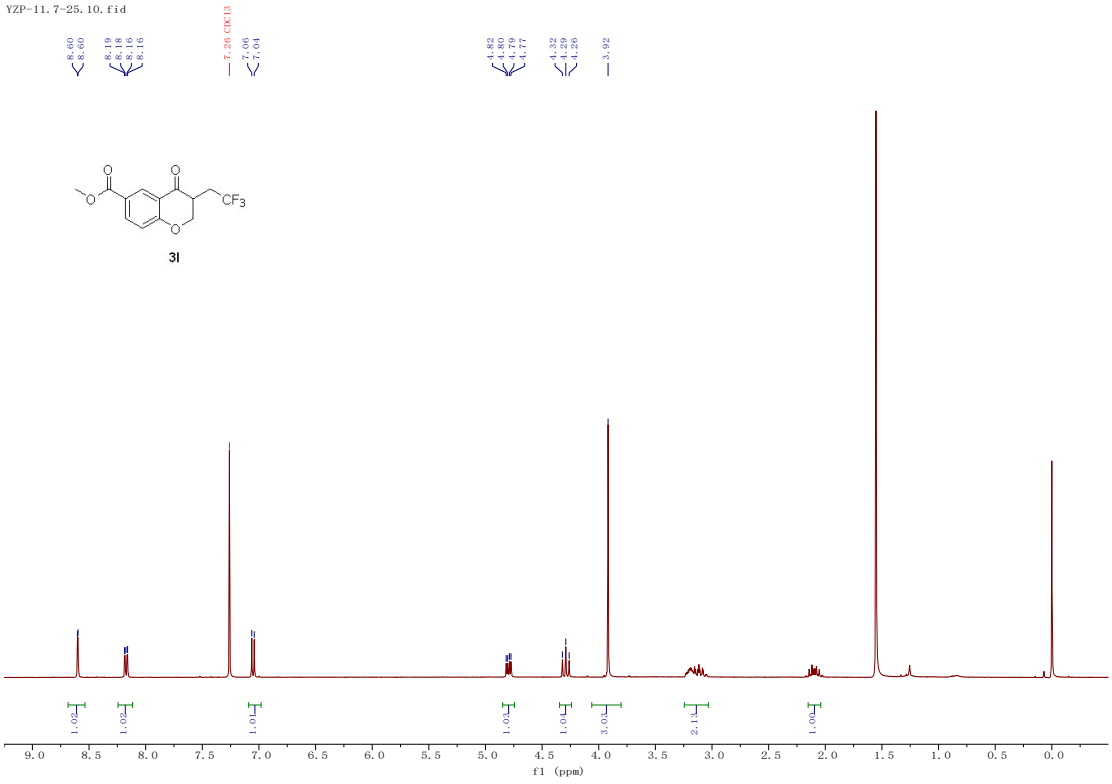


Figure S35 ^{13}C NMR spectrum for compound 3l

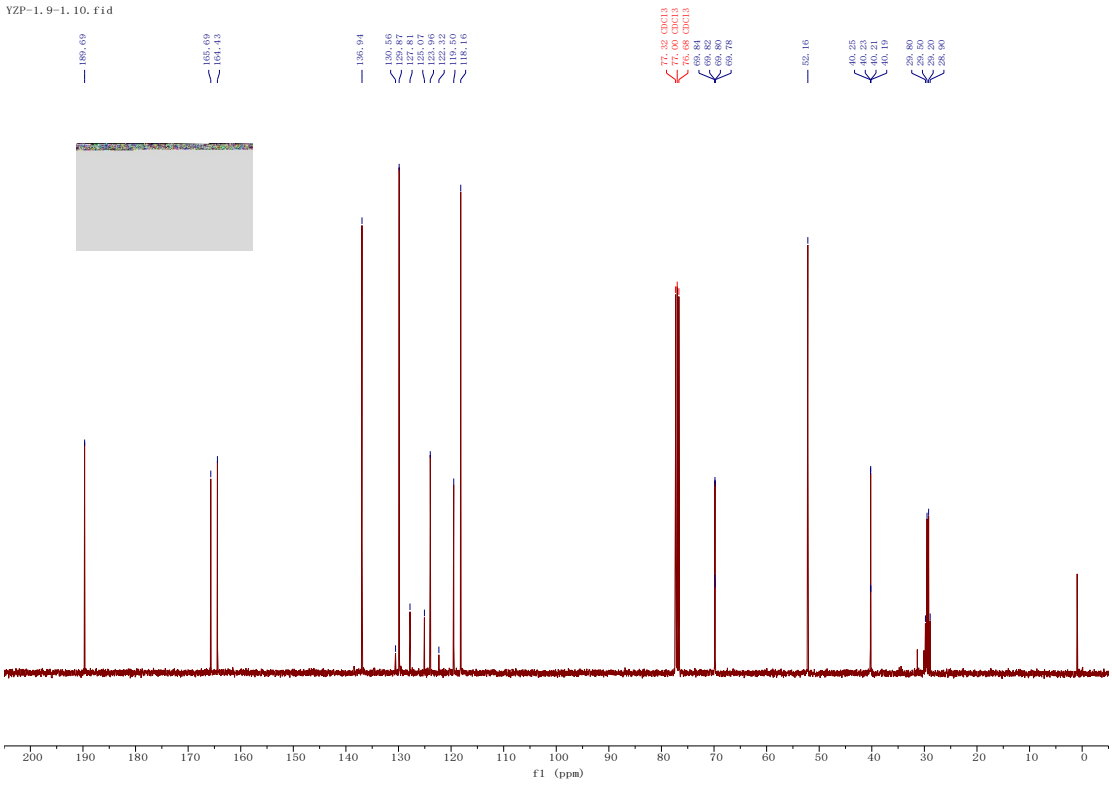


Figure S36 ^{19}F NMR spectrum for compound 3l

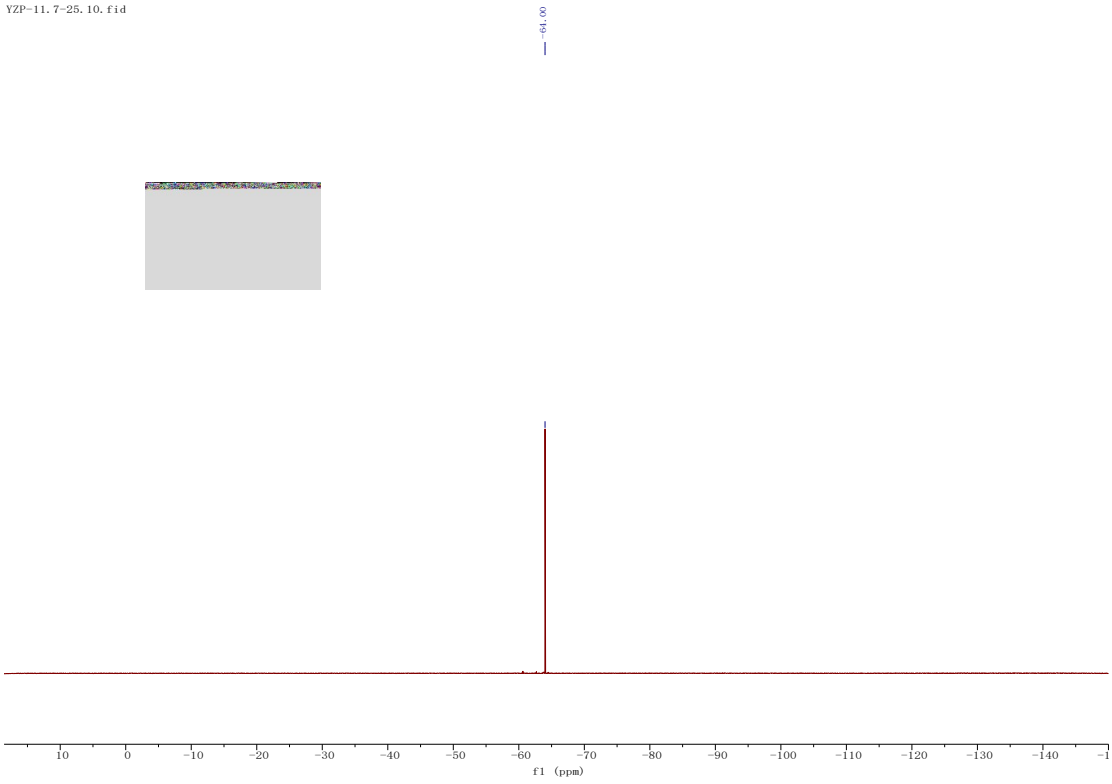


Figure S37 ^{1}H NMR spectrum for compound 3m

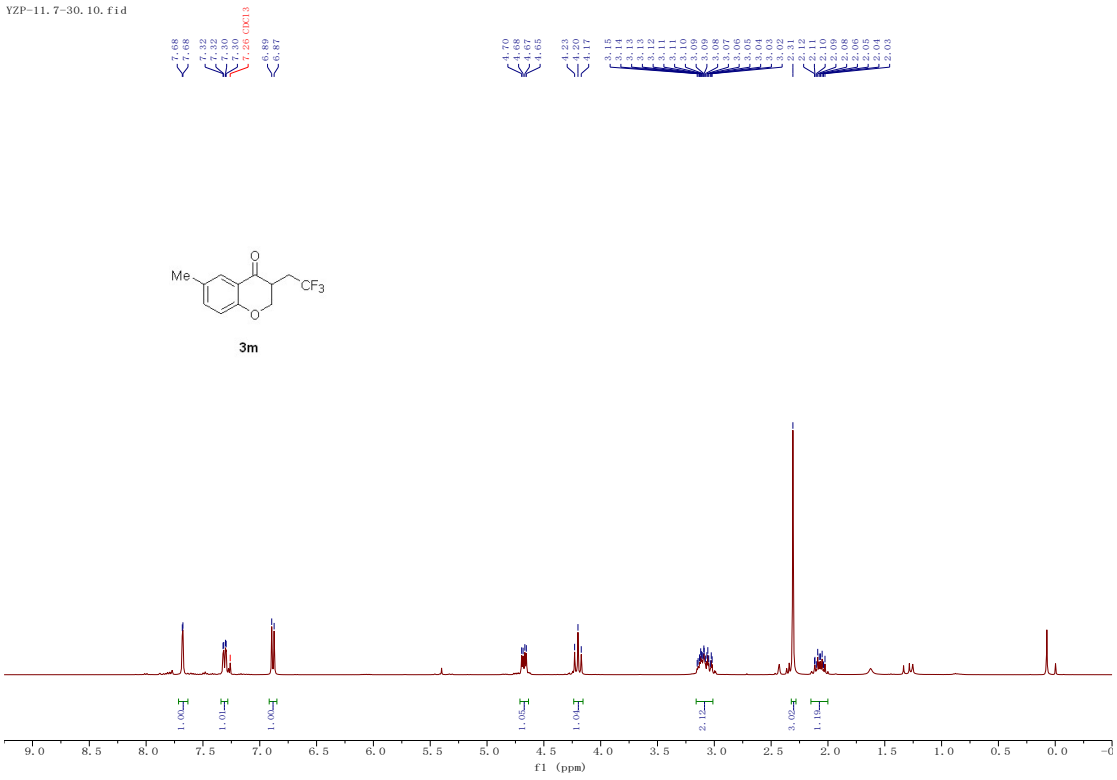


Figure S38 ^{13}C NMR spectrum for compound 3m

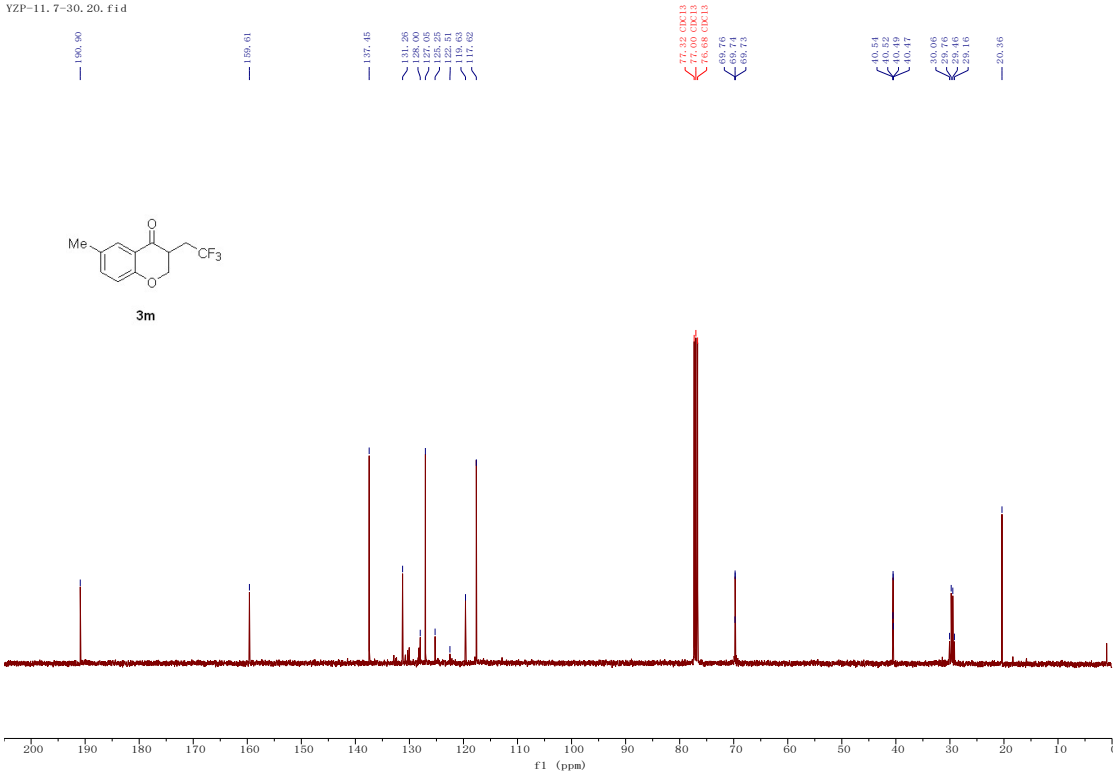


Figure S39 ^{19}F NMR spectrum for compound 3m

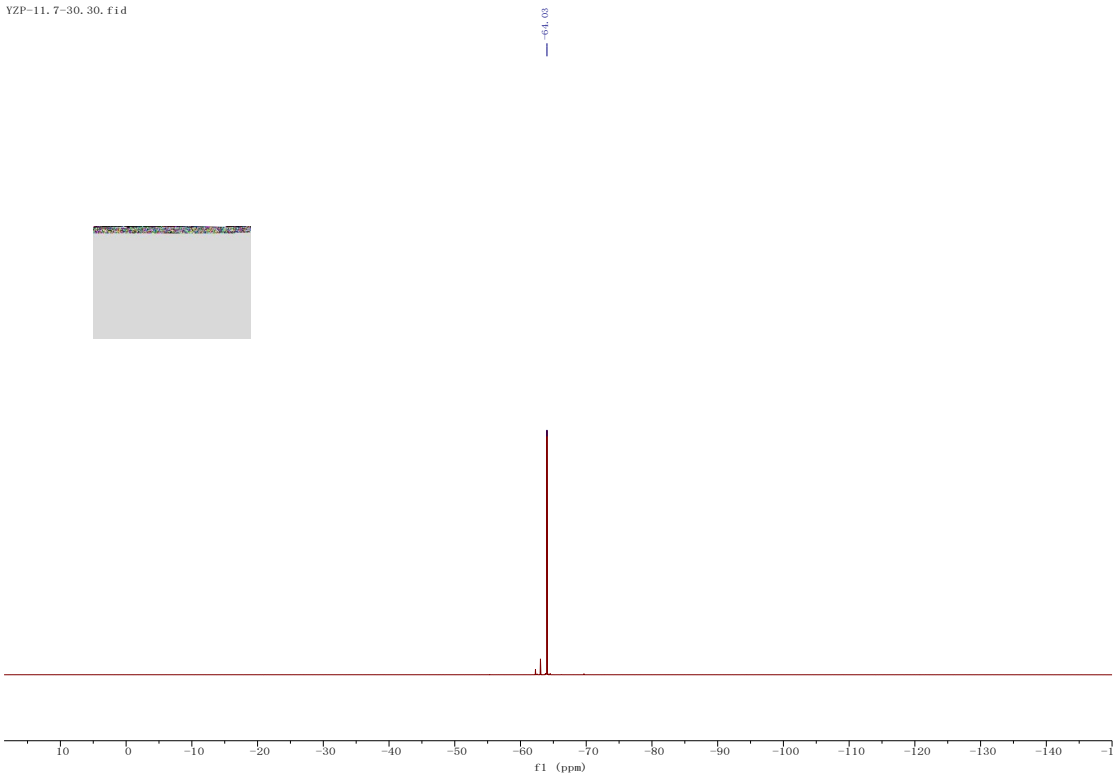


Figure S40 ^{1}H NMR spectrum for compound 3n

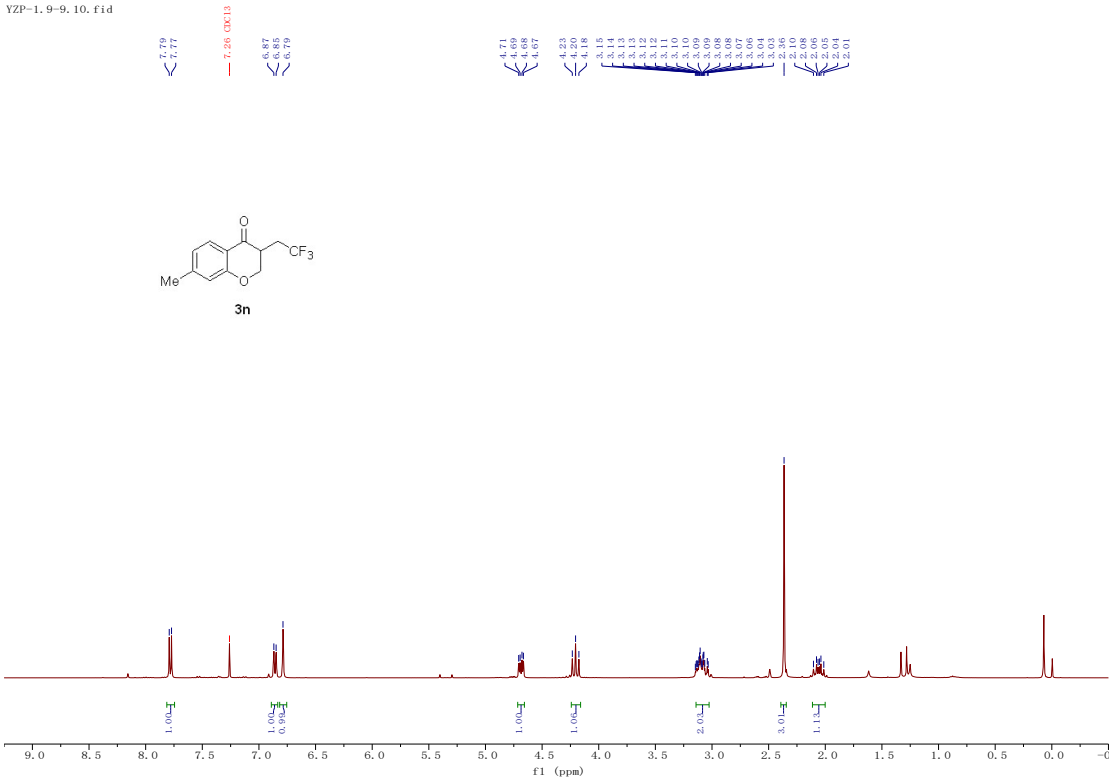


Figure S41 ^{13}C NMR spectrum for compound 3n

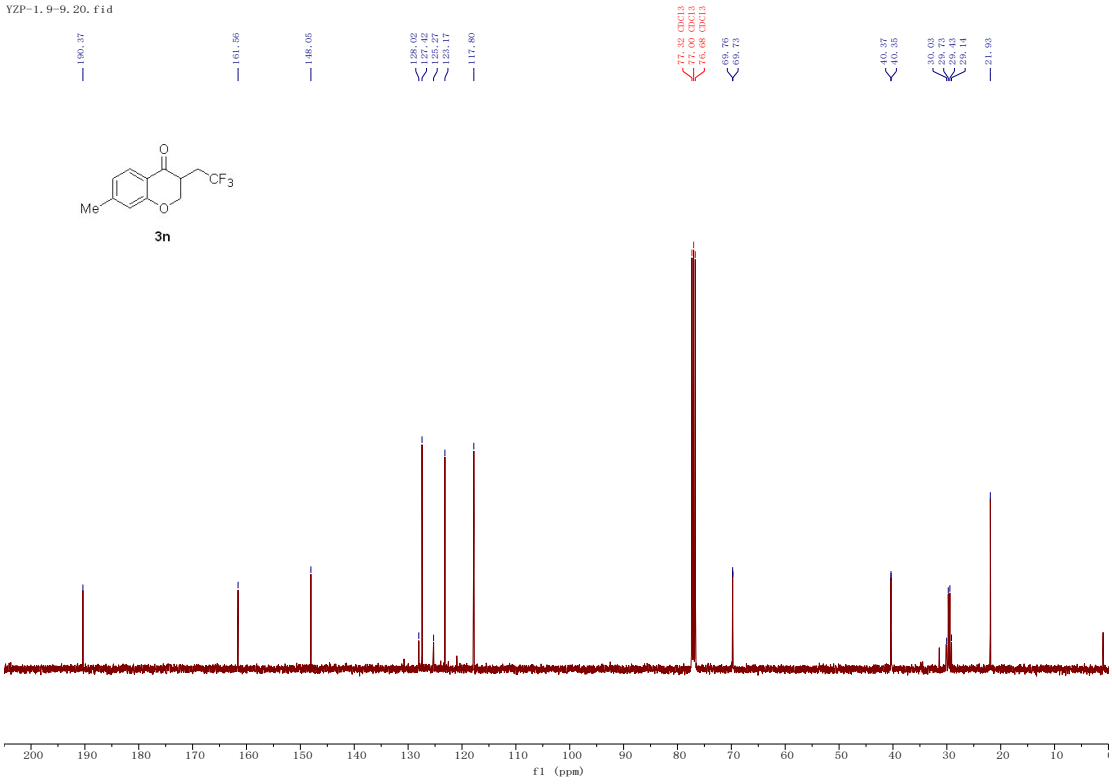


Figure S42 ^{19}F NMR spectrum for compound 3n

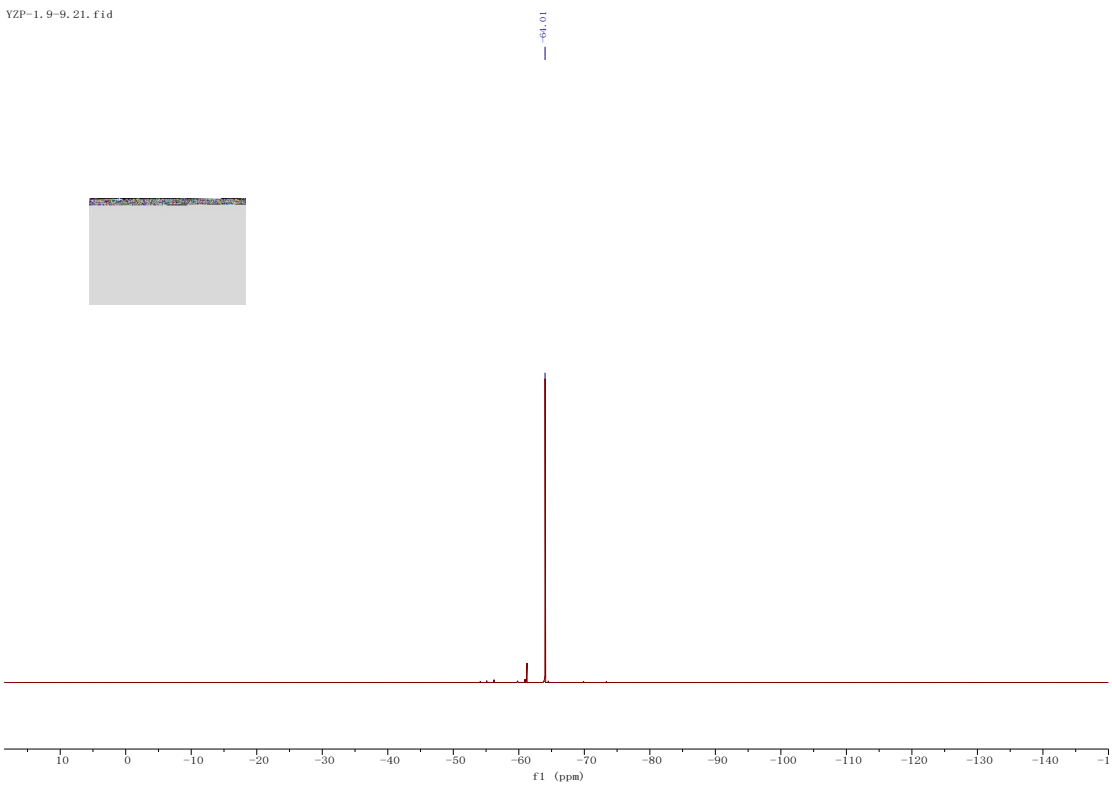


Figure S43 ^{1}H NMR spectrum for compound 3o

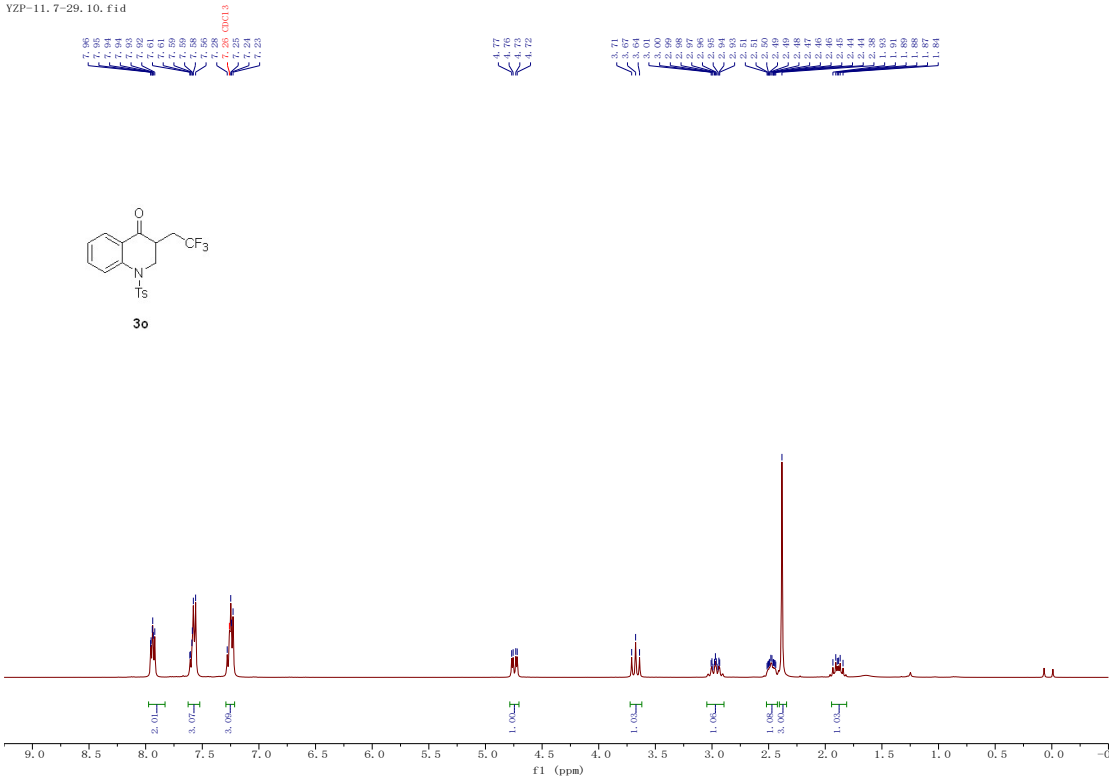


Figure S44 ^{13}C NMR spectrum for compound 3o

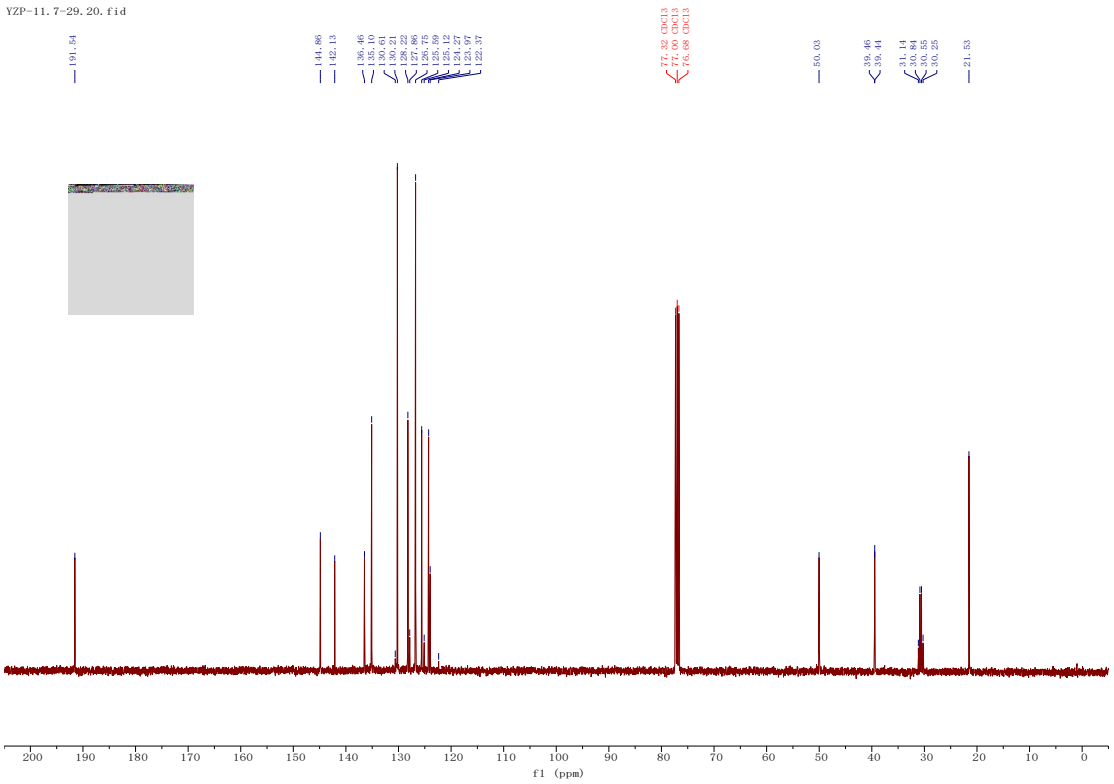


Figure S45 ^{19}F NMR spectrum for compound 3o

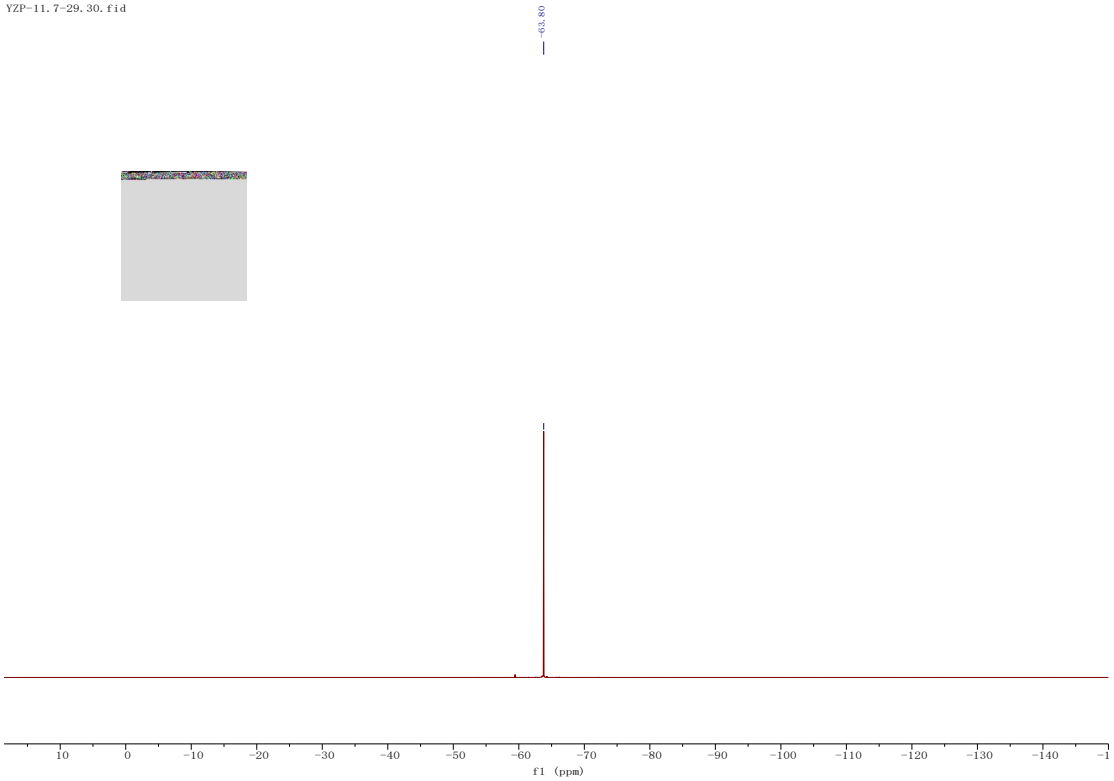


Figure S46 ^{1}H NMR spectrum for compound 3p

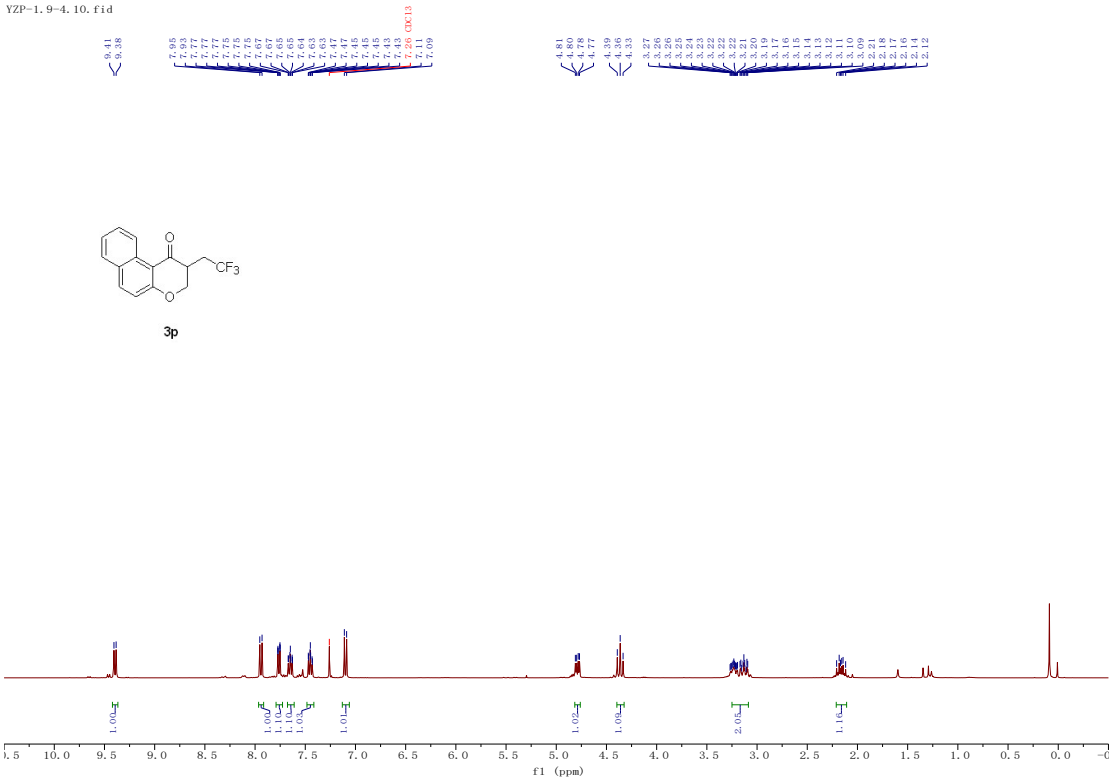


Figure S47 ^{13}C NMR spectrum for compound 3p

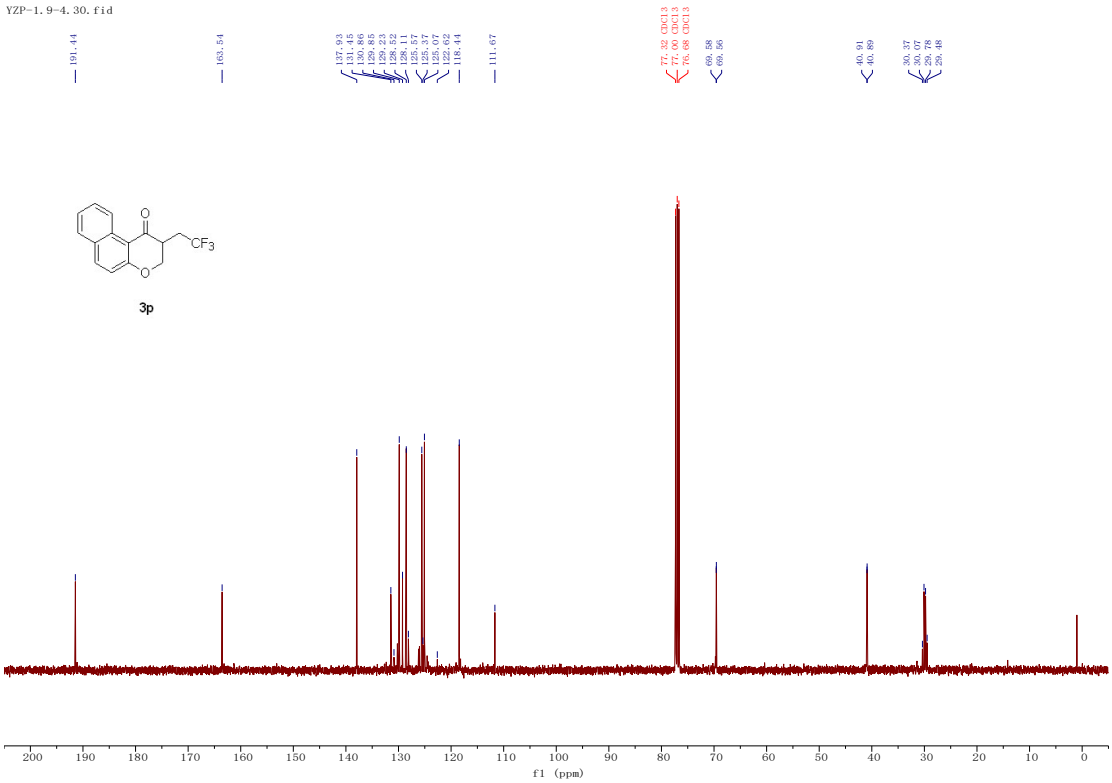


Figure S48 ^{19}F NMR spectrum for compound 3p

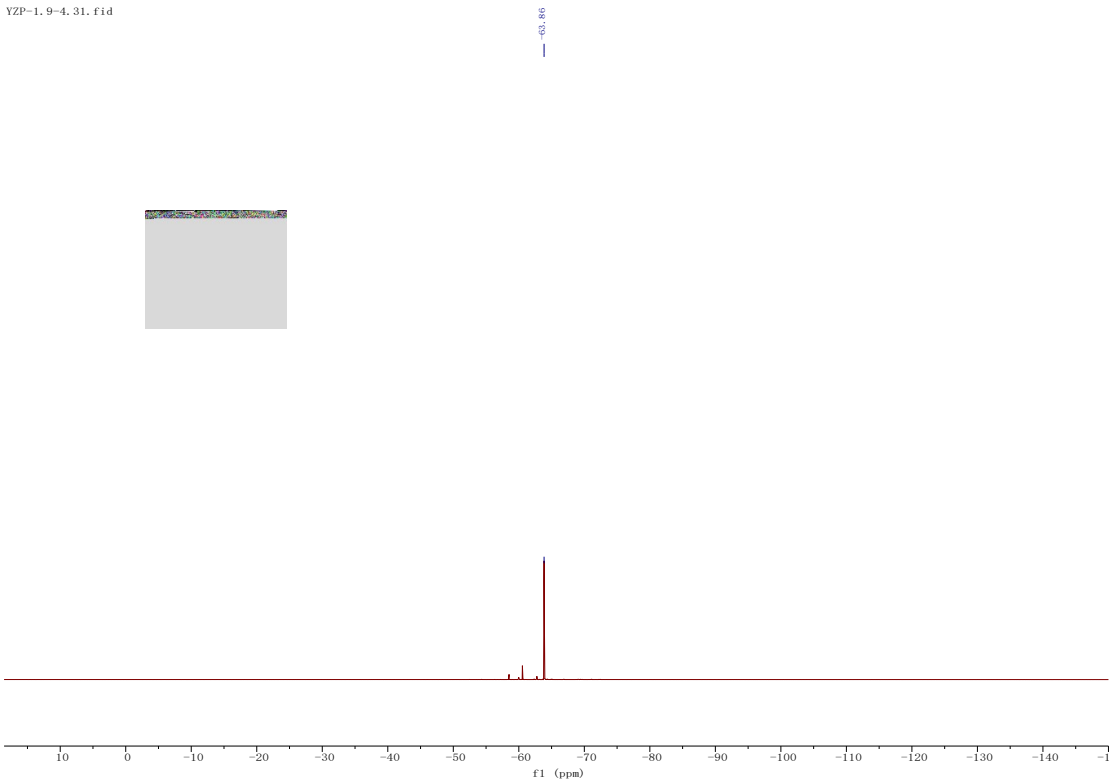


Figure S49 ^{1}H NMR spectrum for compound 3q

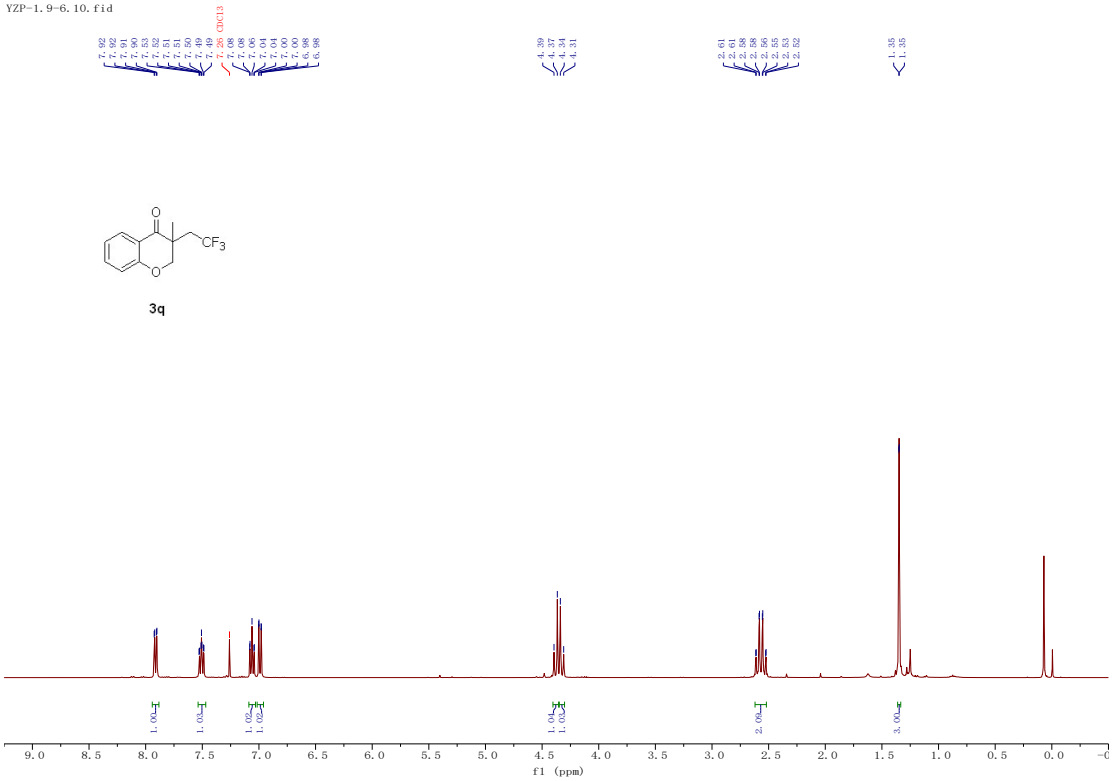


Figure S50 ^{13}C NMR spectrum for compound 3q

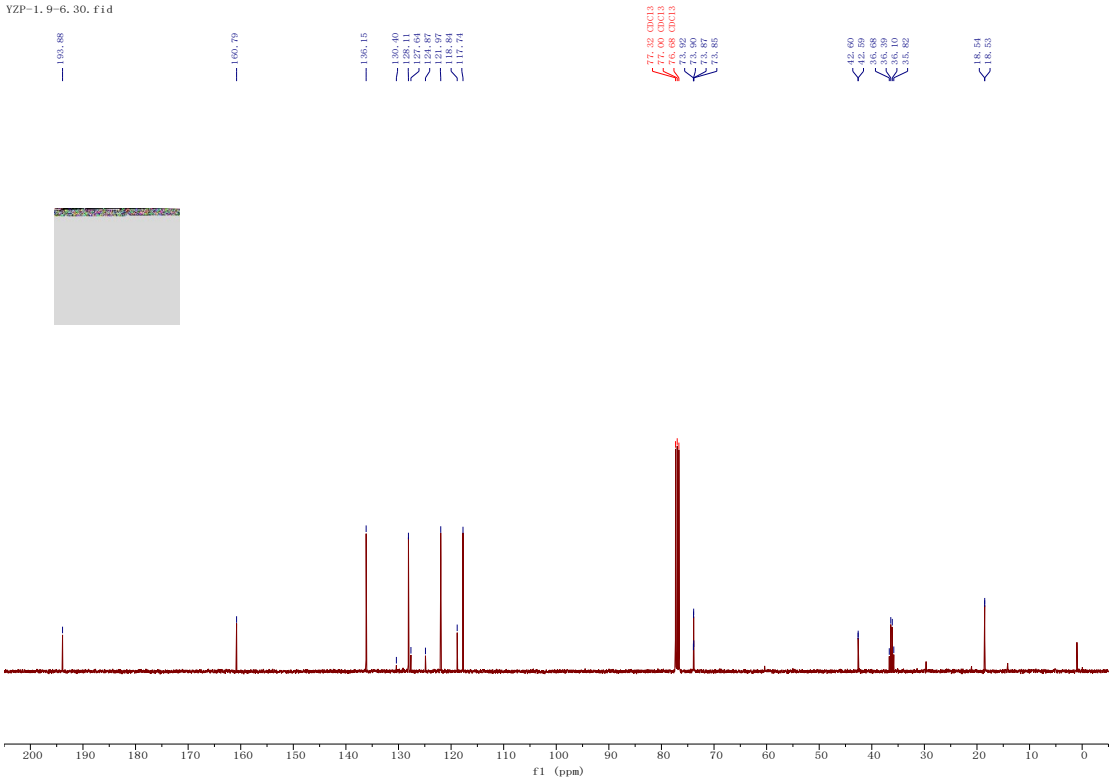


Figure S51 ^{19}F NMR spectrum for compound 3q

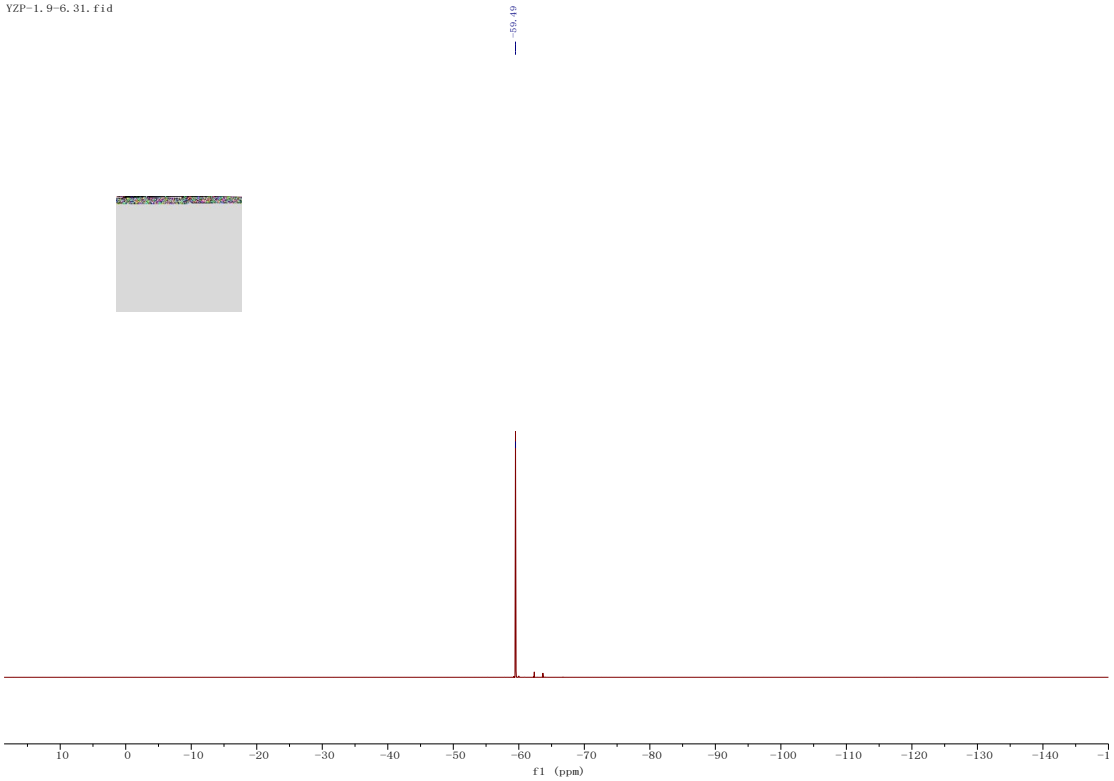


Figure S52 ^{1}H NMR spectrum for compound 3r

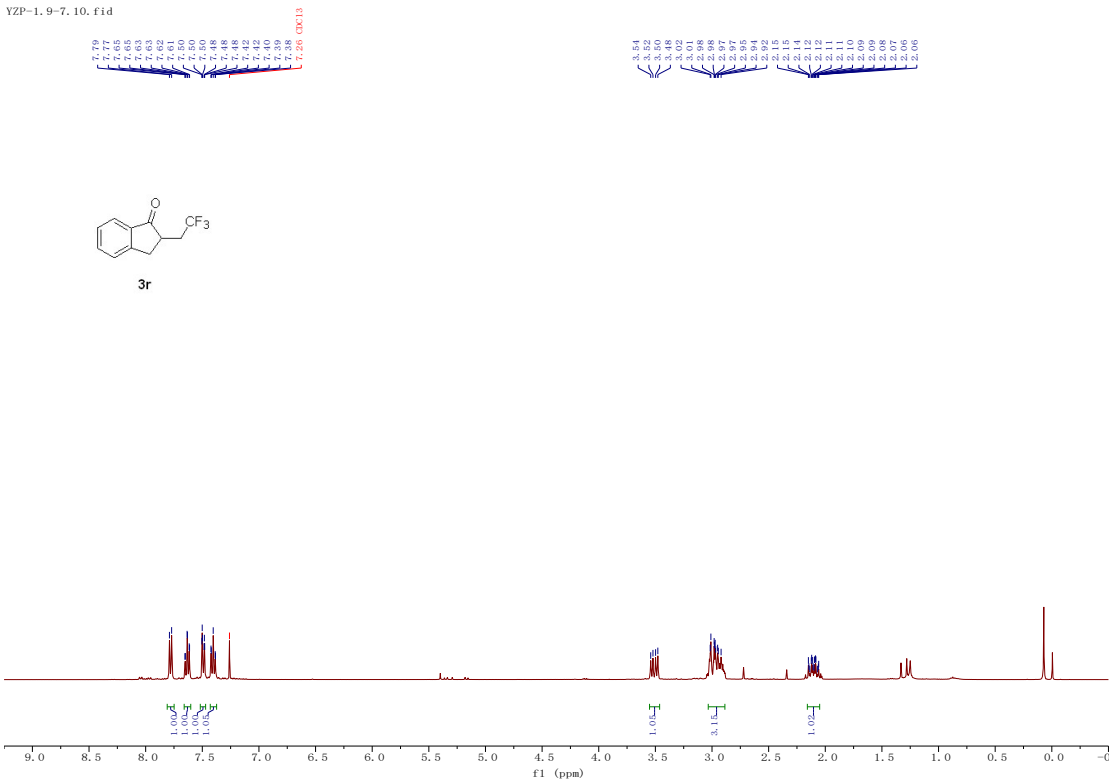


Figure S53 ^{13}C NMR spectrum for compound 3r

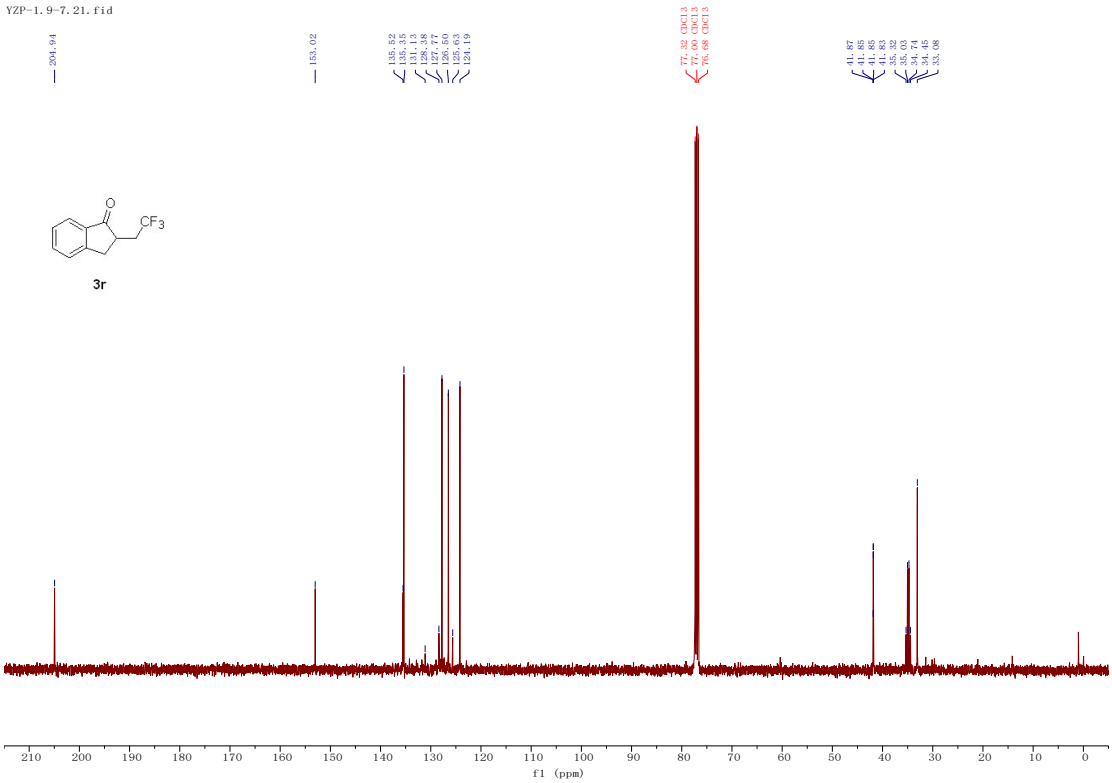


Figure S54 ^{19}F NMR spectrum for compound 3r

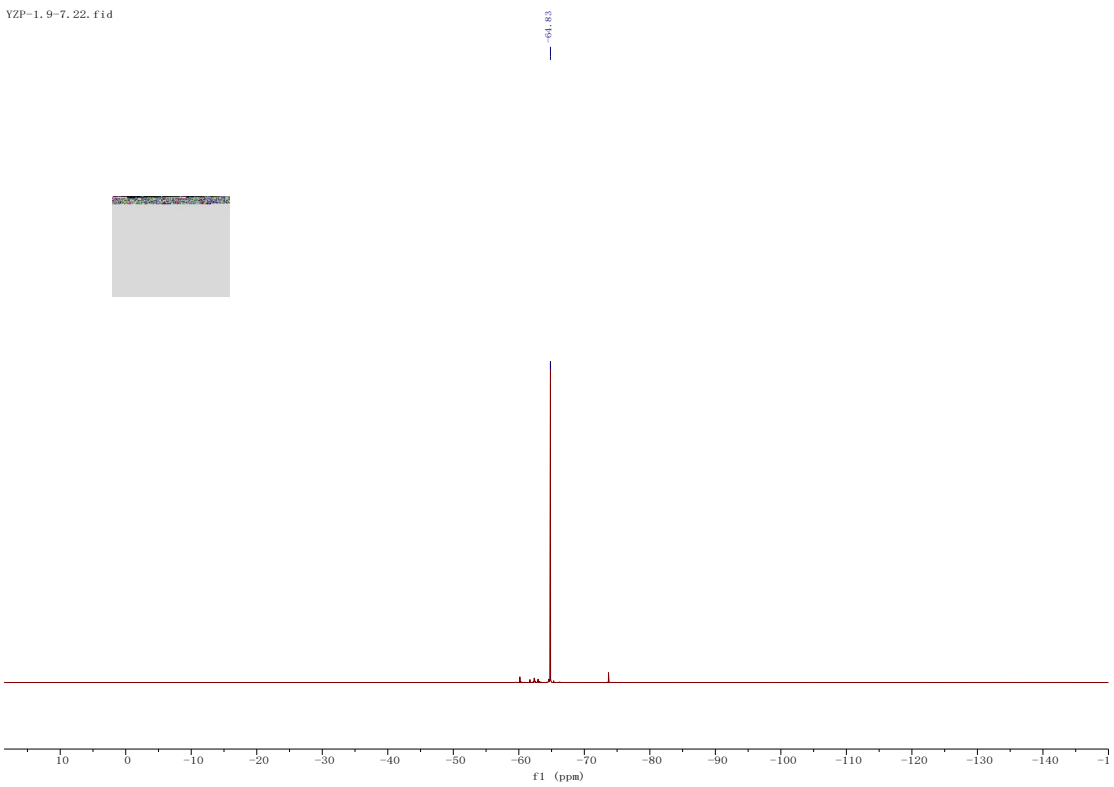


Figure S55 ^{1}H NMR spectrum for compound 3s

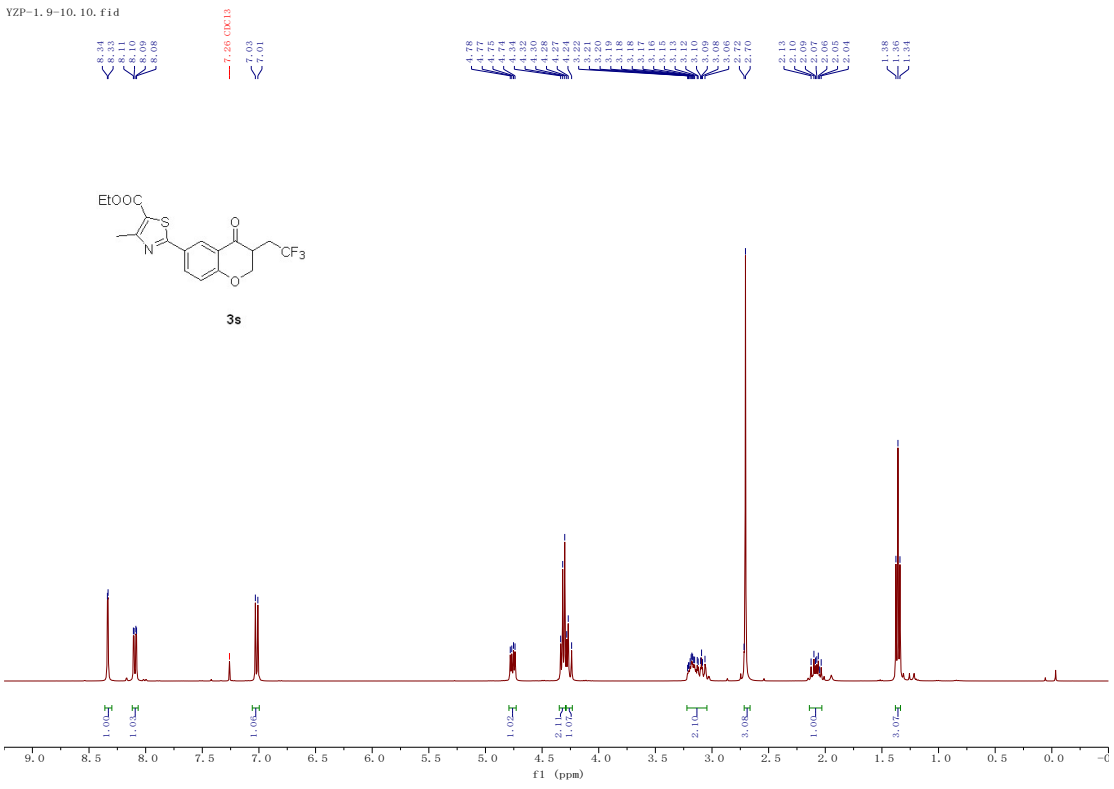


Figure S56 ^{13}C NMR spectrum for compound 3s

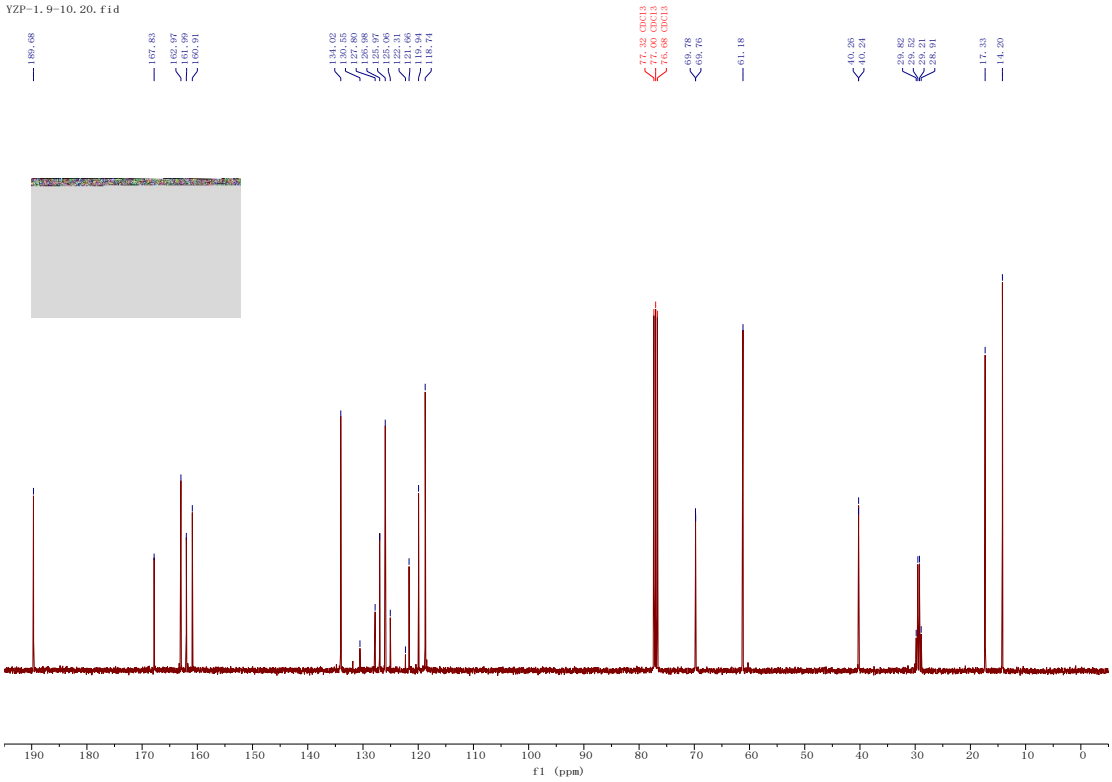
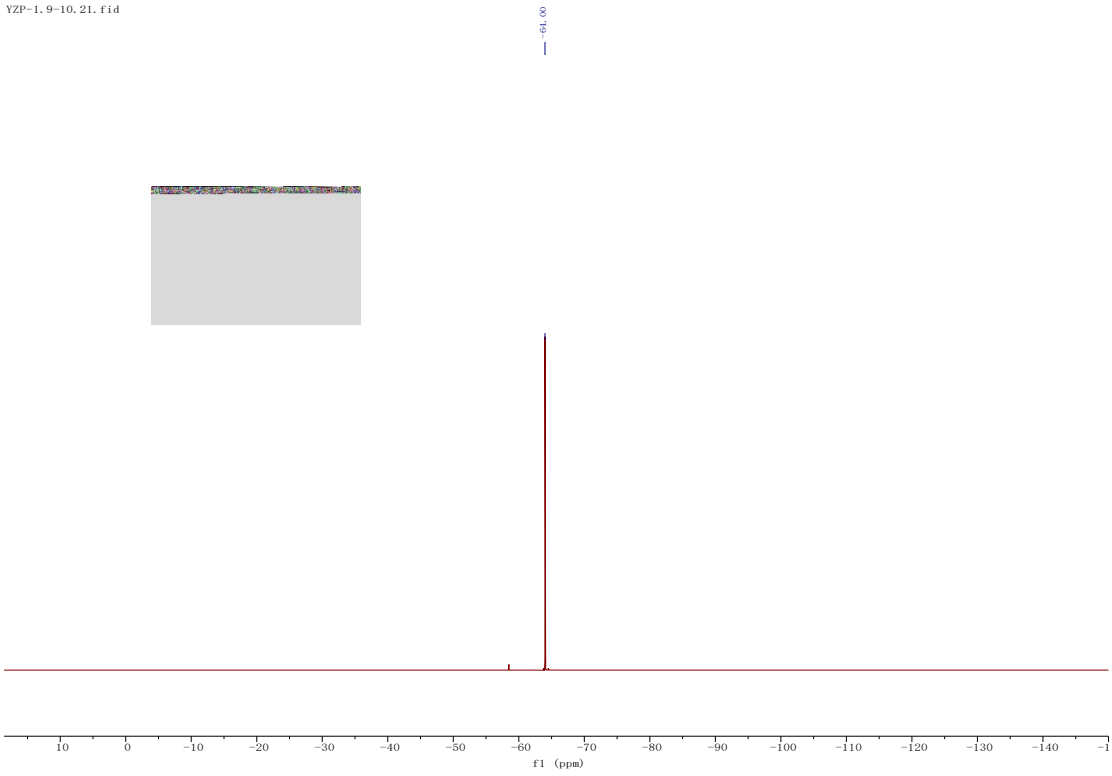


Figure S57 ^{19}F NMR spectrum for compound 3s



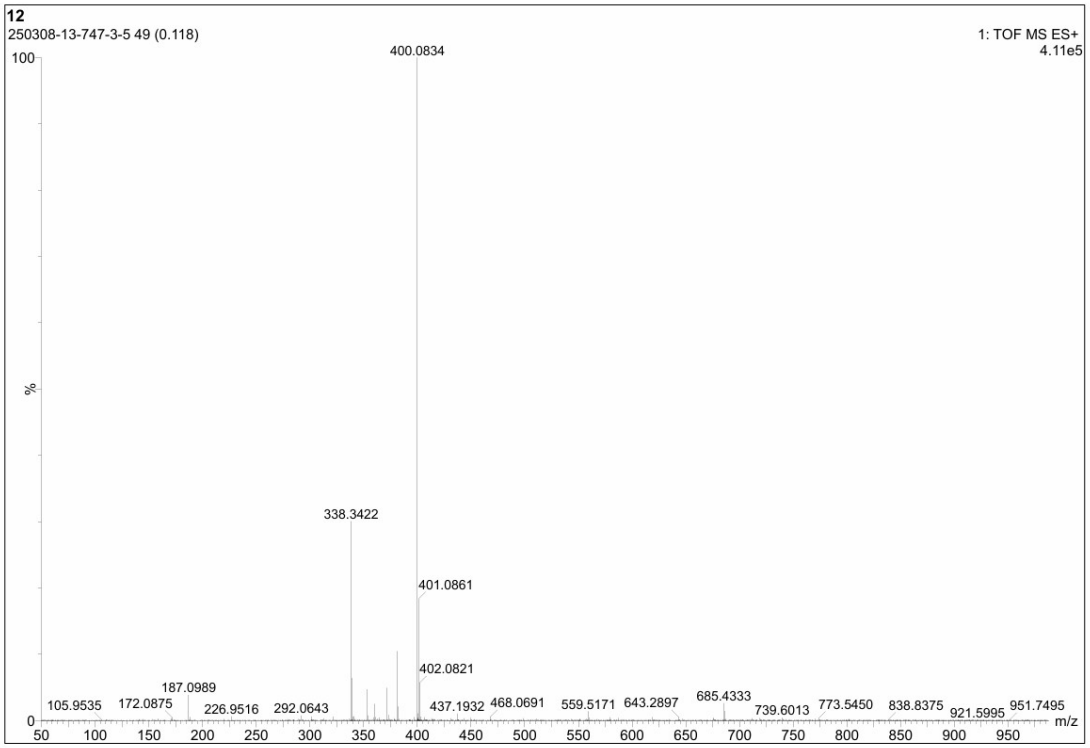


Figure S58 ^{1}H NMR spectrum for compound 3h'

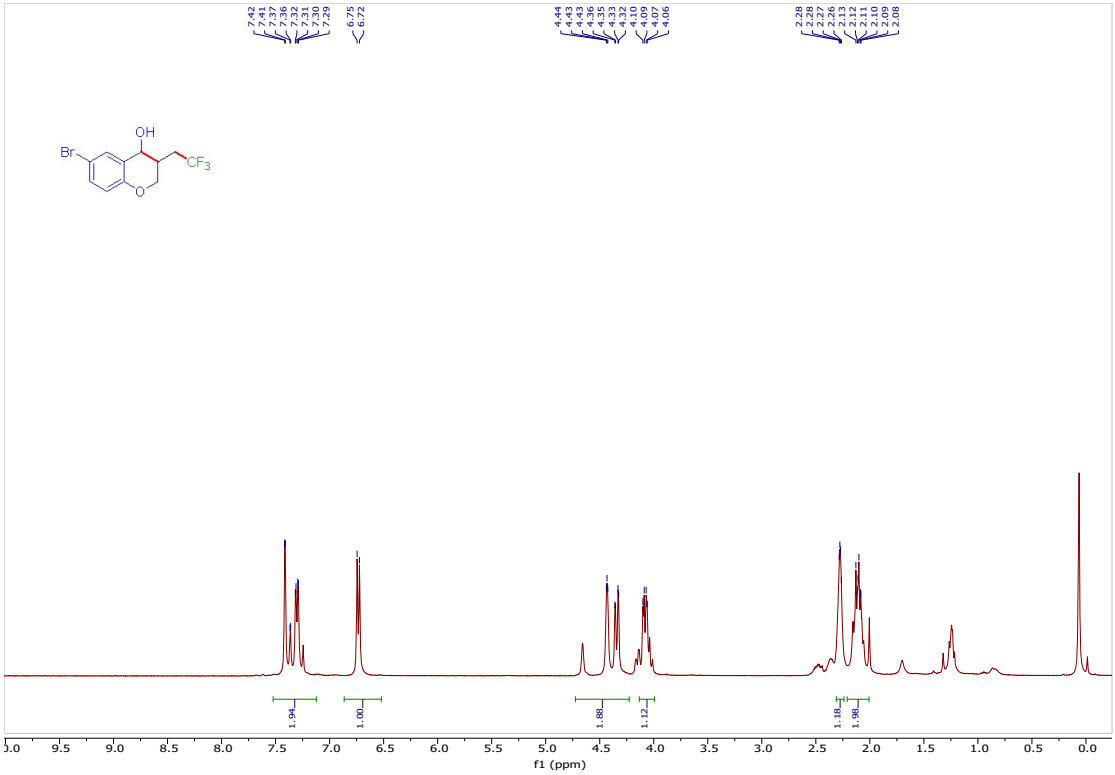


Figure S59 ^{13}C NMR spectrum for compound 3h'

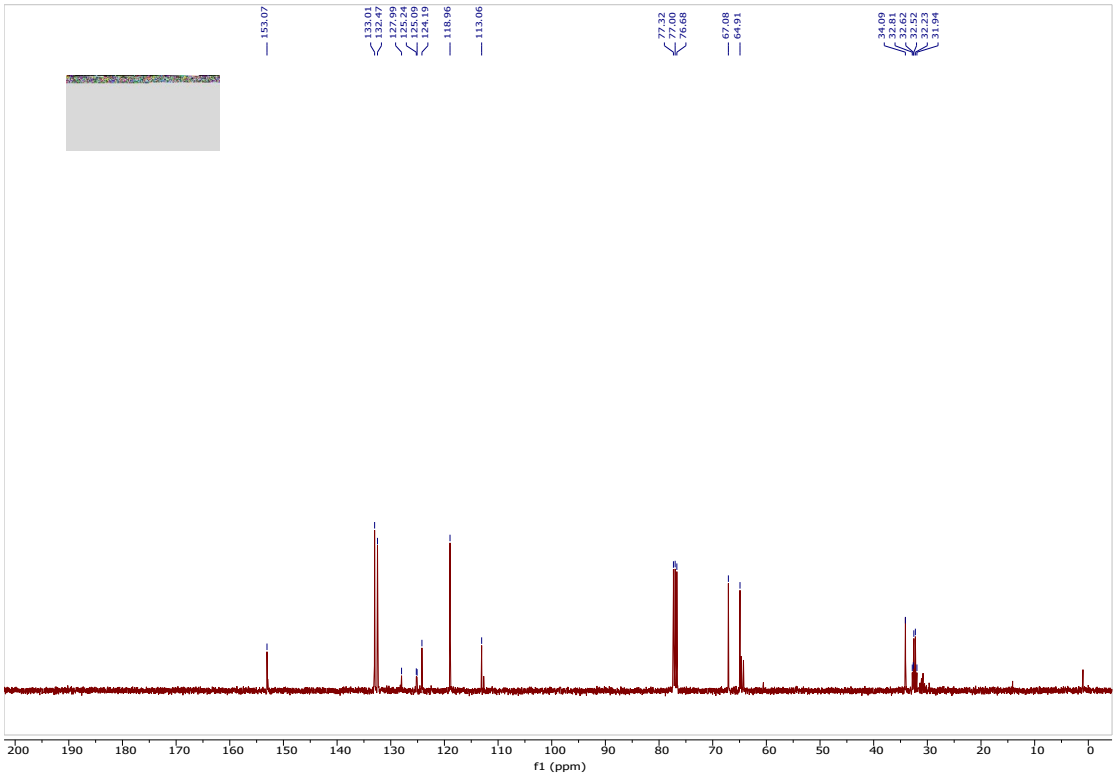


Figure S60 ^{19}F NMR spectrum for compound 3h'

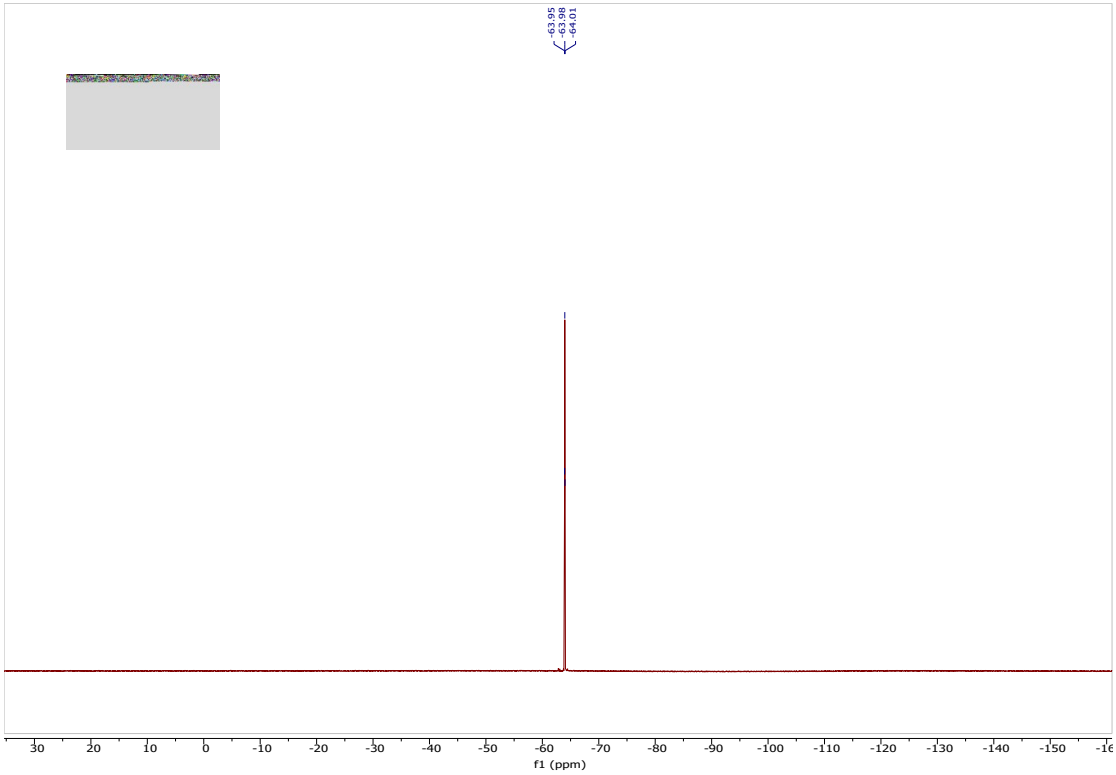


Figure S61 ^{1}H NMR spectrum for compound 3k'

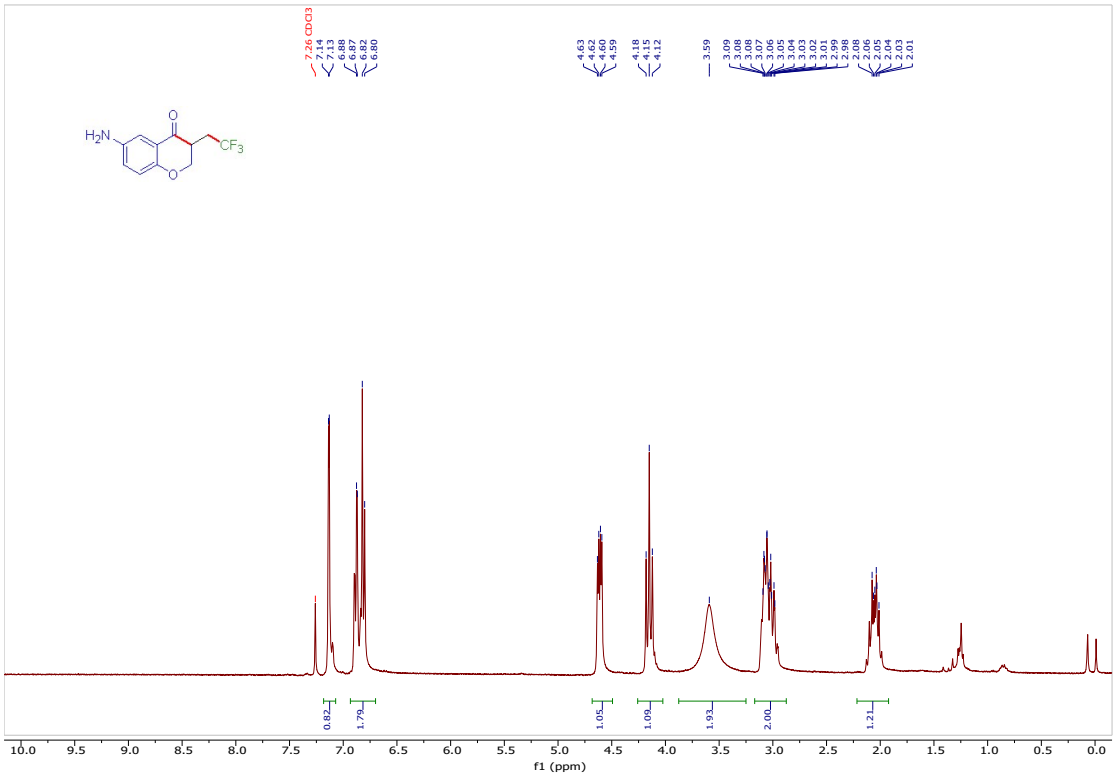


Figure S62 ^{13}C NMR spectrum for compound 3k'

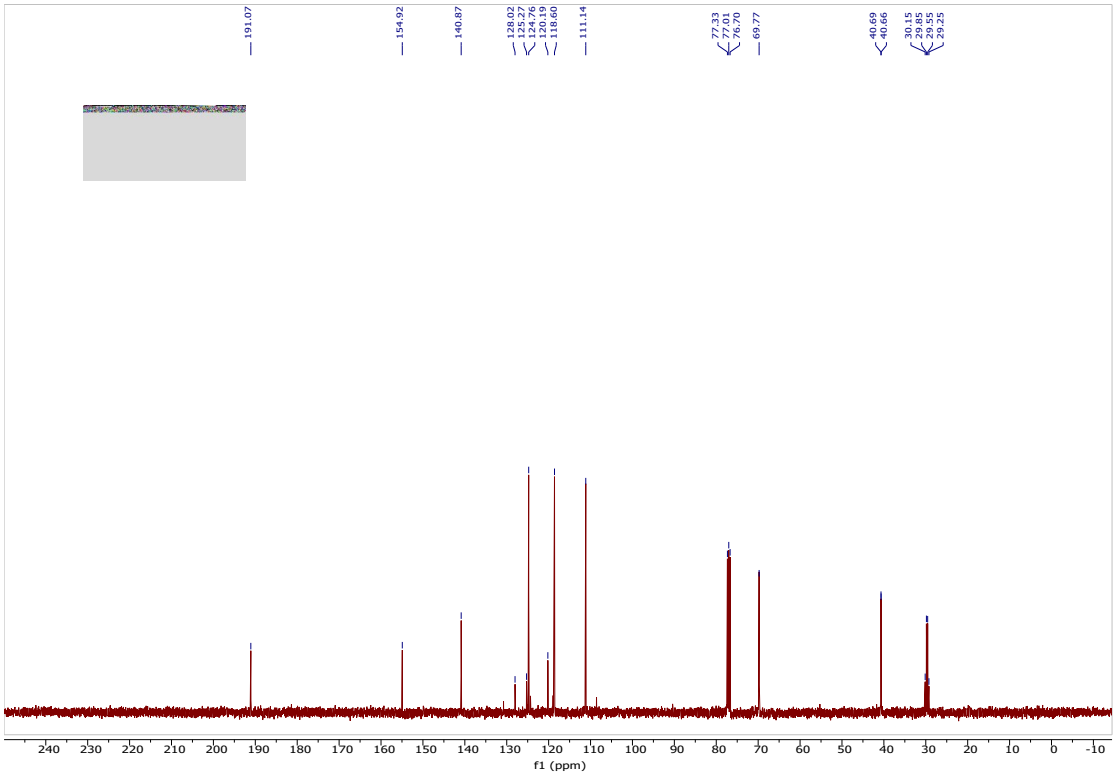


Figure S63 ^{19}F NMR spectrum for compound 3k'