Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoinduced Regioselective Trifluoroalkylation of Ketene Dithioacetals with CF_3SO_2Na

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1. General Information

1.1. Solvents, Reagents and Starting Materials

All reagents were used as received unless otherwise stated from Sigma-Aldrich, Energy Chemical, Adamas-beta®, and Bidepharm. Water is de-ionised and brine refers to a saturated aqueous solution of NaCl. MeCN was anhydrous, purchased from Energy Chemical and Adamas-beta® and used as received. Dichloromethane (CH_2Cl_2) was anhydrous (purification using a column composed of activated alumina). 4CzIPN and R_f SO_2Na was prepared following the method of papers.[1]

1.2. Chromatography and Instrumentation

Flash column chromatography was carried out using silica gel (Aldrich, silica gel 60, 40-63 μm). Analytical thin-layer chromatography (TLC) was performed using aluminium-backed silica plates (0.25 mm, Merck, silica gel 60 F254). Compounds were visualised under UV light or by staining with aqueous basic potassium permanganate, an ethanolic solution of phosphomolybdic acid (PMA), or an ethanolic solution of ninhydrin.

^1H, ^{13}C and ^{11}B NMR spectra were acquired at various field strengths, as indicated, using Bruker 400 MHz, Varian VNMR 400 MHz, Varian VNMR 500 MHz, and Bruker Cryo 500 MHz spectrometers. All NMR spectra were recorder at 25 ℃ unless otherwise stated. Chemical shifts (δ) are given in parts per million (ppm) and referenced to $CDCl_3$ (^1H: 7.26 ppm) or DMSO-d_6 (^1H: 2.50 ppm). Coupling constants (*J*) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, h = heptet, m = multiplet, dd = doublet of doublets, etc.). The ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons).

Gas chromatography (GC) was performed on an Agilent Technologies 6890N Network GC System using an Agilent HP-5 column (15 m × 0.25 mm × 0.25 μm).

High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF instrument using electrospray ionisation (ESI). Low-resolution mass spectra (LRMS) were recorded on an Agilent 7820A GC-MS equipped with a HP-5MS UI column (30 m x 0.25 mm x 0.25 μm) using electron ionisation (EI).

Infra-red (IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer as a thin film. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}).

Melting points were recorded in degrees Celsius (℃), using a Kofler hot-stage microscope apparatus and are reported uncorrected.

Optical rotation ($[\alpha]_D^T$) was measured on a Bellingham and Stanley Ltd. ADP220 polarimeter and is quoted in (°mL) $(g\ dm)^{-1}$.

For quantum yield experiments, commercially available potassium ferrioxalate trihydrate (Alfa Aesar) was used for actinometry, and all the absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis Spectrophotometer.

1.3. Photochemical Equipment and Setup

The blue LED lamps were either 30 W 420nm blue LED with a fan or 40 W Kessil PR160-427 nm LED Photoredox Lights were used with the intensity dial set to 100.

During the course of the photoredox reactions, heat generated from the LED lamps resulted in warming of the reaction mixtures to approximately 40 ℃. For reactions performed in MeCN, fan cooling was used to maintain a temperature of 25–30 ℃.

2. Optimization studies

Table 1. Optimization studies[a]

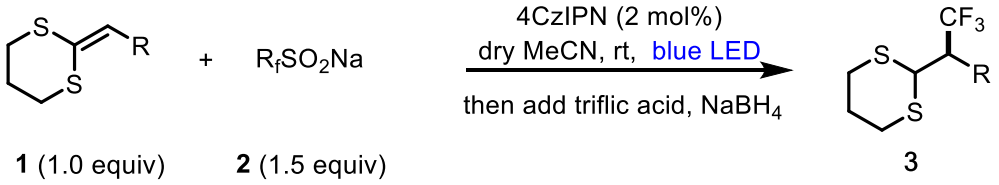
1a (1.0 equiv) **2a** (1.5 equiv) **3a** **4CzIPN**

Entry	Variation from standard conditions	3a%
1	none	93
2	**2a** (1.2 equiv)	89
3	MeOH instead of MeCN	trace
4	DMF instead of MeCN	57
5	DCM instead of MeCN	40
6	THF instead of MeCN	trace
7	DCE instead of MeCN	33
8	1 mol% 4CzIPN	85
9	0.1 mol% 4CzIPN	83
10[b]	1 mol% *fac*-Ir(ppy)$_3$	2
11[c]	1 mol% [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$)	80
12	1 mol% Eosin Y	42
13[d]	1 mol% Ru(phen)$_3$(PF$_6$)$_2$	trace
14[c]	1 mol% Ru(bpy)$_3$Cl$_2$	trace
15	2 mol% DPAIPN	81
16	No 4CzIPN	23

17	Under air	70
18[e]	No light	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), photocatalyst (2 mol%), solvent (2.0 mL), 25 ℃, 20 h, 420 nm blue LED, N_2. Then add triflic acid (0.6 mmol) and NaBH4 (0.5 mmol) to the system. Yields were determined after aqueous workup by ^{1}H NMR or ^{19}F analysis using crude mixture, 1,3,5-trimethoxybenzene as internal standard. [b] ppy = 2-phenylpyridine. [c] dF(CF_3)ppy = 5-trifluoromethyl-2-pyridyl-2,4-difluorophenyl; bpy = 2,2-bipyridine; dtbbpy = 4,4′-di-*tert*-butyl-2,2'-bipyridine. [d] phen = 1,10-phenanthroline. [e] Reaction performed in the dark.

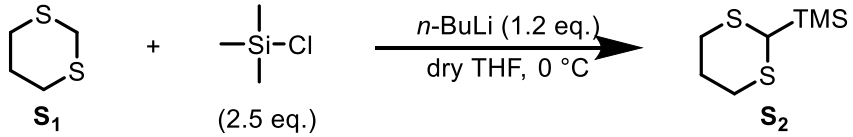
3. General Procedures for Photo Reaction



To a 7 mL vial equipped with a magnetic stir bar was added the **1** (1.00 equiv), 4CzIPN (2.0 mol%) and R_fSO_2Na (1.50 equiv). Then anhydrous MeCN (0.05 M) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for typical 24-48 h with TLC monitoring. After the reaction complete, triflic acid (8.00 equiv) and $NaBH_4$ (6.00 equiv) were added to the mixture and stirred until the TLC detection reaction is complete. Then, DCM and water was added and the phases were separated. The aqueous phase was extracted into DCM (3 × 15 mL) and the combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was then purified by flash column chromatography gave the corresponding product **3**.

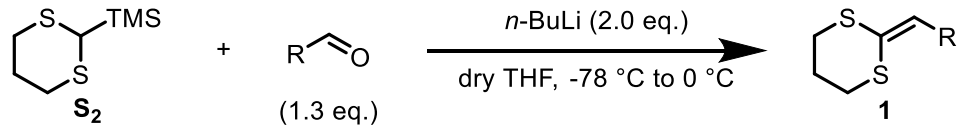
4. Synthesis of Starting Materials

General Procedure A:



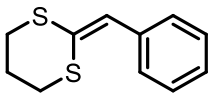
S₂ was prepared following a modified literature procedure:[2] A solution of 1,3-dithiane **S₁** (1.0 equiv) in anhydrous THF was treated with *n*-BuLi (1.6 M in hexanes, 1.2 equiv) at 0 ℃ under N_2. The resulting solution was stirred for 15 min, chlorotrimethylsilane (2.5 equiv) was added and the reaction allowed warm to rt. 2 M HCl (15 mL) was added, the residue extracted with diethyl ether (3 × 15 mL), organic layers were combined, washed with brine, dried over $MgSO_4$ and concentrated to dryness. The residue was purified by flash column chromatography gave 2-trimethylsilyl-1,3-dithiane **S₂**.

General Procedure B:



2-Trimethylsilyl-1,3-dithiane **S₂** (1.0 equiv) was dissolved in anhydrous THF under nitrogen with stirring. The solution was cooled to -78 ℃ and *n*-BuLi (1.6 M solution in hexanes: 2.0 equiv) was added. The solution was allowed to warm to 0 ℃ over 5 hours. The solution was re-cooled to -78 ℃ and aldehydes (1.3 equiv) was added. The solution was allowed to warm to room temperature until the TLC detection reaction is complete. The reaction solution was poured onto H_2O (20 mL) and extracted with EA (3 × 20 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by flash column chromatography gave the substrate **1**.

2-benzylidene-1,3-dithiane (1a)



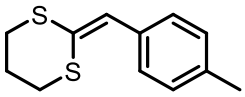
Prepared following General Procedure B using benzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1a** (708 mg, 3.4 mmol, 85%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 3.05 – 2.92 (m, 4H), 2.26 – 2.15 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.1, 130.6, 128.9, 128.1, 126.8, 29.8, 29.2, 24.3 ppm.

HRMS (ESI^+): calcd. for $C_{11}H_{12}S_2$ $[M+H]^+$ 209.0459, found 209.0460.

2-(4-methylbenzylidene)-1,3-dithiane (1b)



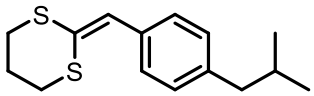
Prepared following General Procedure B using 4-methylbenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1b** (889 mg, 4.0 mmol, 55%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.85 (s, 1H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.2 Hz, 2H), 2.33 (s, 3H), 2.23 – 2.17 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.6, 133.2, 129.3, 129.0, 128.7 (d, *J* = 10.7 Hz), 29.8, 29.1, 24.3, 21.2 ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{14}S_2$ $[M+H]^+$ 223.0615, found 223.0616.

2-(4-isobutylbenzylidene)-1,3-dithiane (1c)



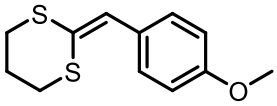
Prepared following General Procedure B using 4-isobutylbenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1c** (555 mg, 2.1 mmol, 52%) as a colourless oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.88 (s, 1H), 3.03 – 2.93 (m, 4H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.24 – 2.15 (m, 2H), 1.94 – 1.83 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 140.4, 133.4, 129.2, 129.0, 128.7 (d, *J* = 9.4 Hz), 45.1, 30.1, 29.8, 29.2, 24.3, 22.3 ppm.

HRMS (ESI^+): calcd. for $C_{15}H_{20}S_2$ $[M+H]^+$ 265.1085, found 265.1086.

2-(4-methoxybenzylidene)-1,3-dithiane (1d)



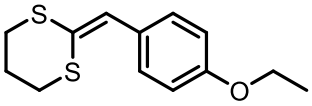
Prepared following General Procedure B using 4-methoxybenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1d** (1.19 g, 5.0 mmol, 62%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.84 (s, 1H), 3.81 (s, 3H), 3.02 – 2.90 (m, 4H), 2.25 – 2.15 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 158.4, 130.4, 129.6, 128.8, 127.1, 113.5, 55.2, 30.1, 29.4, 24.5 ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{14}OS_2$ $[M+H]^+$ 239.0564, found 239.0565.

2-(4-ethoxybenzylidene)-1,3-dithiane (1e)



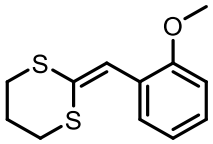
Prepared following General Procedure B using 4-ethoxybenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1e** (681 mg, 2.7 mmol, 52%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.00 – 2.89 (m, 4H), 2.22 – 2.13 (m, 2H), 1.41 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 157.7, 130.3, 129.4, 128.6, 126.9, 113.9, 63.2, 29.9, 29.2, 24.4, 14.7 ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{16}OS_2$ $[M+H]^+$ 253.0721, found 253.0722.

2-(2-methoxybenzylidene)-1,3-dithiane (1f)



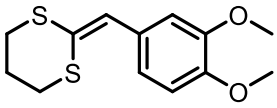
Prepared following General Procedure B using 2-methoxybenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1f** (596 mg, 2.5 mmol, 63%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.14 (m, 1H), 7.07 (s, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H), 2.94 (t, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 6.1 Hz, 2H), 2.18 – 2.08 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 156.2, 129.8, 129.6, 128.3, 124.5, 119.6, 110.0, 55.2, 29.7, 29.1, 24.3 ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{14}OS_2$ $[M+H]^+$ 239.0564, found 239.0565.

2-(3,4-dimethoxybenzylidene)-1,3-dithiane (1g)



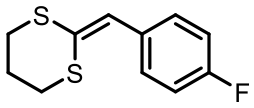
Prepared following General Procedure B using 3,4-dimethoxybenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1g** (778 mg, 2.9 mmol, 35%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.11 (d, *J* = 2.1 Hz, 1H), 7.00 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.83 (d, *J* = 9.4 Hz, 2H), 3.88 (d, *J* = 2.6 Hz, 6H), 3.02 – 2.92 (m, 4H), 2.24 – 2.17 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.3, 147.9, 129.4, 129.1, 127.7, 122.1, 111.9, 110.6, 55.8 (d, *J* = 4.1 Hz), 30.0, 29.3, 24.5 ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{16}O_2S_2$ $[M+H]^+$ 269.0670, found 269.0671.

2-(4-fluorobenzylidene)-1,3-dithiane (1h)



Prepared following General Procedure B using 4-fluorobenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1h** (1.04 g, 4.6 mmol, 61%) as a yellow oil liquid.

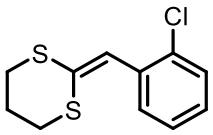
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.81 (s, 1H), 3.01 – 2.92 (m, 4H), 2.22 – 2.14 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.4, 160.0, 132.1 (d, *J* = 3.4 Hz), 130.5 (d, *J* = 7.9 Hz), 130.2 (d, *J* = 2.2 Hz), 127.6, 115.0, 114.8, 29.6, 29.0, 24.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -114.2 – -114.3 (m) ppm.

HRMS (ESI^+): calcd. for $C_{11}H_{11}FS_2$ $[M+H]^+$ 227.0364, found 227.0365.

2-(2-chlorobenzylidene)-1,3-dithiane (1i)



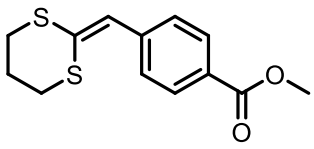
Prepared following General Procedure B using 2-chlorobenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1i** (689 mg, 2.8 mmol, 57%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.56 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (td, *J* = 7.6, 1.7 Hz, 1H), 6.95 (s, 1H), 2.99 – 2.93 (m, 2H), 2.90 – 2.85 (m, 2H), 2.17 – 2.10 (m, 2H) ppm.

^{13}C NMR (101 MHZ, $CDCl_3$): δ_C 133.8, 133.7, 132.9, 130.4, 129.3, 128.0, 126.0, 124.9, 29.5, 28.9, 24.1 ppm.

HRMS (ESI$^+$): calcd. for $C_{11}H_{11}ClS_2$ $[M+H]^+$ 243.0069, found 243.0070.

methyl 4-((1,3-dithian-2-ylidene)methyl)benzoate (1j)



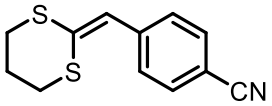
Prepared following General Procedure B using methyl 4-formylbenzoate. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **1j** (266 mg, 1.0 mmol, 23%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 6.79 (s, 1H), 3.88 (s, 3H), 3.03 – 2.94 (m, 4H), 2.22 – 2.13 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.7, 140.5, 135.6, 129.3, 128.4, 127.4, 126.2, 51.9, 29.3, 28.8, 23.8 ppm.

HRMS (ESI$^+$): calcd. for $C_{13}H_{14}O_2S_2$ $[M+H]^+$ 267.0513, found 267.0514.

4-((1,3-dithian-2-ylidene)methyl)benzonitrile (1k)



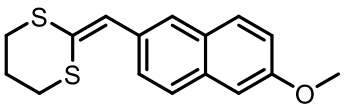
Prepared following General Procedure B using 4-formylbenzonitrile. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **1k** (443 mg, 1.9 mmol, 25%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53 (q, *J* = 8.5 Hz, 4H), 6.71 (s, 1H), 3.03 – 2.97 (m, 4H), 2.22 – 2.15 (m, 2H) ppm.

^{13}C NMR (101 MHZ, $CDCl_3$): δ_C 140.4, 138.1, 131.7, 128.8, 124.7, 119.0, 108.9, 29.1, 28.7, 23.6 ppm.

HRMS (ESI$^+$): calcd. for $C_{12}H_{11}NS_2$ $[M+H]^+$ 234.0406, found 234.0403.

2-((6-methoxynaphthalen-2-yl)methylene)-1,3-dithiane (1l)



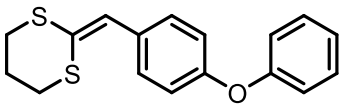
Prepared following General Procedure B using 6-methoxy-2-naphthaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1l** (750 mg, 2.6 mmol, 34%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.87 (s, 1H), 7.70 (dd, *J* = 16.6, 8.7 Hz, 2H), 7.57 (dt, *J* = 8.6, 1.6 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.99 (s, 1H), 3.92 (s, 3H), 3.05 – 2.96 (m, 4H), 2.27 – 2.19 (m, 2H) ppm.

^{13}C NMR (101 MHZ, $CDCl_3$): δ_C 157.8, 133.4, 131.5, 129.6, 129.4, 128.6, 127.9, 127.7, 126.4, 118.9, 105.6, 55.3, 29.9, 29.3, 24.4 ppm.

HRMS (ESI^+): calcd. for $C_{16}H_{16}OS_2$ $[M+H]^+$ 289.0721, found 289.0722.

2-(4-phenoxybenzylidene)-1,3-dithiane (1m)



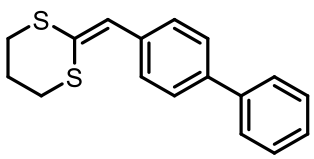
Prepared following General Procedure B using 4-phenoxybenzaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1m** (721 mg, 2.4 mmol, 59%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 – 7.27 (m, 3H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.16 (s, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.87 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.79 (s, 1H), 3.03 – 2.93 (m, 4H), 2.23 – 2.15 (m, 2H) ppm.

^{13}C NMR (101 MHZ, $CDCl_3$): δ_C 157.1, 156.9, 137.7, 132.2, 129.7, 129.3, 127.7, 123.9, 123.1, 119.1, 118.9, 117.2, 29.6, 29.0, 24.1 ppm.

HRMS (ESI^+): calcd. for $C_{17}H_{16}OS_2$ $[M+H]^+$ 301.0715, found 301.0716.

2-([1,1'-biphenyl]-4-ylmethylene)-1,3-dithiane (1n)



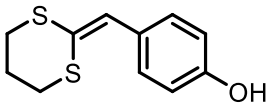
Prepared following General Procedure B using [1,1'-biphenyl]-4-carbaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1n** (569 mg, 2.0 mmol, 55%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64 – 7.54 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 3.06 – 2.96 (m, 4H), 2.26 – 2.19 (m, 2H) ppm.

^{13}C NMR (101 MHZ, $CDCl_3$): δ_C 140.6, 139.3, 135.1, 130.9, 129.3, 128.7, 128.4, 127.2, 126.9, 126.7, 29.8, 29.2, 24.3 ppm.

HRMS (ESI^+): calcd. for $C_{17}H_{16}S_2$ $[M+H]^+$ 285.0772, found 285.0773.

4-((1,3-dithian-2-ylidene)methyl)phenol (1o)



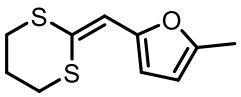
Prepared following General Procedure B using 4-formylphenyl acetate. Purification by flash column chromatography (20% EtOAc/hexane) gave the title compound **1o** (516 mg, 2.3 mmol, 23%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 6.5 Hz, 2H), 6.79 (s, 1H), 5.20 (s, 1H), 2.98 (t, *J* = 6.3 Hz, 2H), 2.93 (t, 2H), 2.23 – 2.16 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 154.4, 130.6, 129.5, 129.0, 127.2, 115.0, 30.0, 29.3, 24.4 ppm.

HRMS (ESI^+): calcd. for $C_{11}H_{12}OS_2$ $[M+H]^+$ 225.0408, found 225.0409.

2-((1,3-dithian-2-ylidene)methyl)-5-methylfuran (1p)



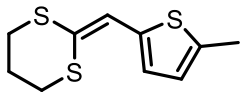
Prepared following General Procedure B using 5-methylfuran-2-carbaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1p** (637 mg, 3.0 mmol, 68%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.64 (s, 1H), 6.47 (s, 1H), 6.02 (s, 1H), 3.01 – 2.94 (m, 4H), 2.29 (s, 3H), 2.22 – 2.14 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 150.9, 149.8, 126.7, 117.2, 111.1, 107.8, 29.7, 28.8, 24.1, 13.6 ppm.

HRMS (ESI^+): calcd. for $C_{10}H_{12}OS_2$ $[M+H]^+$ 213.0408, found 213.0409.

2-((5-methylthiophen-2-yl)methylene)-1,3-dithiane (1q)



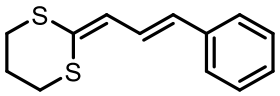
Prepared following General Procedure B using 5-methylthiophene-2-carbaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1q** (228 mg, 1.0 mmol, 25%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.96 (s, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H), 3.05 – 2.91 (m, 4H), 2.47 (s, 3H), 2.27 – 2.15 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 140.8, 137.3, 128.3, 124.9, 124.6, 124.3, 30.3, 29.8, 24.4, 15.3 ppm.

HRMS (ESI^+): calcd. for $C_{10}H_{12}S_3$ $[M+H]^+$ 229.0179, found 229.0180.

(E)-2-(3-phenylallylidene)-1,3-dithiane (1r)



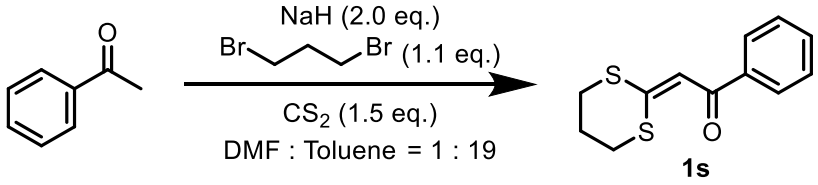
Prepared following General Procedure B using cinnamaldehyde. Purification by flash column chromatography (hexane) gave the title compound **1r** (890 mg, 3.8 mmol, 77%) as a yellow oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.14 (m, 2H), 6.59 (d, *J* = 10.9 Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 1H), 2.98 – 2.92 (m, 4H), 2.25 – 2.17 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 137.4, 131.8, 130.7, 128.6, 127.5, 126.4, 123.9, 29.9, 29.3, 24.7 ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{14}S_2$ $[M+H]^+$ 235.0615, found 235.0616.

2-(1,3-dithian-2-ylidene)-1-phenylethan-1-one (1s)



1s was prepared following a modified literature procedure:[3] 1,3-Dibromopropane (1.1 equiv) was added dropwise to a stirred mixture of acetophenone (1.0 equiv), NaH (60% in oil, 2.0

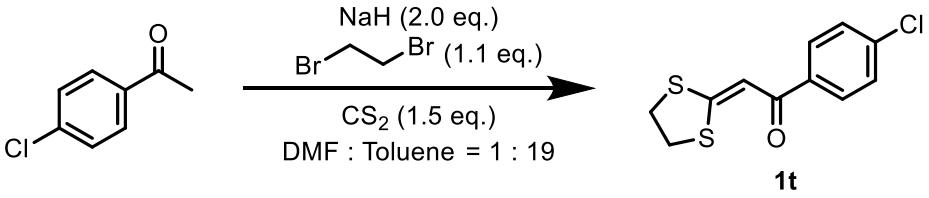
equiv), CS_2 (1.5 equiv), and 1.0 mL DMF in 19.0 mL toluene at 0 ℃. The reaction was complete within 24 h by TLC monitoring. The resulting mixture was poured into 20 g of ice water, extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$, and filtered. All the volatiles were removed under reduced pressure and the resultant residue was purified by silica gel column chromatography (20% EtOAc/hexane), affording **1s** (476 mg, 2.0 mmol, 40%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 (d, *J* = 7.1 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.29 (s, 1H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.93 (t, *J* = 6.5 Hz, 2H), 2.26 – 2.17 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 186.0, 164.2, 138.2, 131.8, 128.3, 127.6, 117.2, 28.7, 28.0, 23.6 ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{12}OS_2$ $[M+H]^+$ 237.0408, found 237.0409.

1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)ethan-1-one (1t)



1t

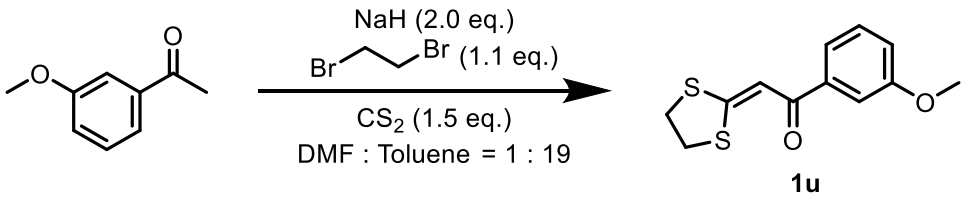
1t was prepared following a modified literature procedure:[3] 1,2-Dibromoethane (1.1 equiv) was added dropwise to a stirred mixture of 1-(4-chlorophenyl)ethan-1-one (1.0 equiv), NaH (60% in oil, 2.0 equiv), CS_2 (1.5 equiv), and 1.0 mL DMF in 19.0 mL toluene at 0 ℃. The reaction was complete within 24 h by TLC monitoring. The resulting mixture was poured into 20 g of ice water, extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$, and filtered. All the volatiles were removed under reduced pressure and the resultant residue was purified by silica gel column chromatography (5% EtOAc/hexane), affording **1t** (673 mg, 2.6 mmol, 52%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 – 7.84 (m, 2H), 7.42 – 7.36 (m, 2H), 7.27 (s, 1H), 3.50 – 3.43 (m, 2H), 3.41 – 3.34 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 184.5, 169.1, 138.2, 136.5, 129.1, 128.7, 107.7, 38.9, 35.4 ppm.

HRMS (ESI^+): calcd. for $C_{11}H_9ClOS_2$ $[M+H]^+$ 256.9856, found 256.9856.

2-(1,3-dithiolan-2-ylidene)-1-(3-methoxyphenyl)ethan-1-one (1u)



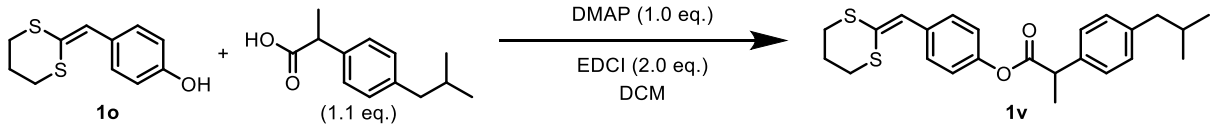
1u was prepared following a modified literature procedure:[3] 1,2-Dibromoethane (1.1 equiv) was added dropwise to a stirred mixture of 1-(3-methoxyphenyl)ethan-1-one (1.0 equiv), NaH (60% in oil, 2.0 equiv), CS_2 (1.5 equiv), and 1.0 mL DMF in 19.0 mL toluene at 0 ℃. The reaction was complete within 24 h by TLC monitoring. The resulting mixture was poured into 20 g of ice water, extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$, and filtered. All the volatiles were removed under reduced pressure and the resultant residue was purified by silica gel column chromatography (20% EtOAc/hexane), affording **1u** (312 mg, 1.2 mmol, 25%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.51 – 7.45 (m, 2H), 7.34 – 7.28 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.82 (d, *J* = 1.6 Hz, 3H), 3.44 (t, *J* = 6.0 Hz, 2H), 3.34 (t, *J* = 5.9 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 185.5, 168.3, 159.6, 139.4, 129.3, 120.0, 118.5, 112.0, 108.1, 55.2, 38.8, 35.3 ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{12}O_2S_2$ $[M+H]^+$ 253.0357, found 253.0358.

4-((1,3-dithian-2-ylidene)methyl)phenyl 2-(4-isobutylphenyl)propanoate (1v)



1v was prepared following a modified literature procedure:[4] **1o** (1.0 equiv), 2-(4-isobutylphenyl)propanoic acid (1.1 equiv), and 4-dimethylaminopyridine (DMAP) (1.0 equiv) were dissolved in dichloromethane (30 mL) at 0 ℃. To this solution, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (2.0 equiv) in dichloromethane (10 mL) was added dropwise. The mixture was then stirred at room temperature for 12 h, detected by TLC. Upon completion of the reaction, the dichloromethane was removed by rotary evaporation. The crude product was dissolved with ethyl acetate, washed with saturated aqueous $NaHCO_3$ and H_2O, dried over $MgSO_4$, filtered, and then concentrated. The residue was purified by silica gel column chromatography (5% EtOAc/hexane) to obtain **1v** as a colourless oil liquid.

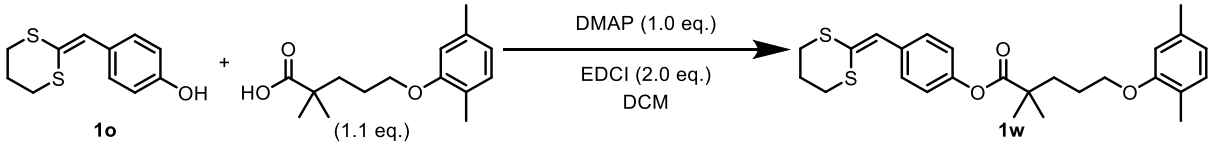
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.51 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.86 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 1H), 3.01 – 2.91 (m, 4H), 2.54 (d, *J* =

7.2 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.99 – 1.88 (m, 1H), 1.66 (d, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.7, 149.0, 140.4, 137.0, 133.5, 130.9, 129.6, 129.2, 127.3, 127.0, 120.8, 45.0, 44.8, 29.9, 29.4, 28.8, 23.9, 22.2, 18.3 ppm.

HRMS (ESI^+): calcd. for $C_{24}H_{28}O_2S_2$ $[M+H]^+$ 419.1609, found 419.1610.

4-((1,3-dithian-2-ylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (1w)



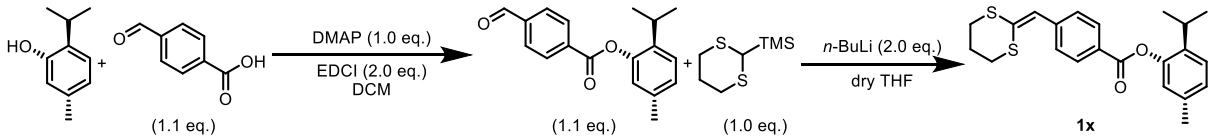
1w was prepared following a modified literature procedure:[5] **1o** (1.0 equiv), 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (1.1 equiv), and 4-dimethylaminopyridine (DMAP) (1.0 equiv) were dissolved in dichloromethane (30 mL) at 0 ℃. To this solution, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (2.0 equiv) in dichloromethane (10 mL) was added dropwise. The mixture was then stirred at room temperature for 12 h, detected by TLC. Upon completion of the reaction, the dichloromethane was removed by rotary evaporation. The crude product was dissolved with ethyl acetate, washed with saturated aqueous $NaHCO_3$ and H_2O, dried over $MgSO_4$, filtered, and then concentrated. The residue was purified by silica gel column chromatography (5% EtOAc/hexane) to obtain **1w** as a colourless oil liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 3H), 6.91 (s, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 4.06 (t, *J* = 5.2 Hz, 2H), 3.06 – 2.97 (m, 4H), 2.41 (s, 3H), 2.30 (s, 3H), 2.25 – 2.17 (m, 2H), 1.97 (s, 4H), 1.47 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.8, 156.6, 149.2, 136.1, 133.5, 130.8, 130.1, 129.6, 127.4, 123.2, 120.9, 120.5, 111.6, 67.4, 42.1, 36.9, 29.4, 28.8, 24.9 (d, *J* = 10.7 Hz), 24.0, 21.2, 15.6 ppm.

HRMS (ESI^+): calcd. for $C_{27}H_{34}O_3S_2$ $[M+H]^+$ 471.2028, found 471.2029.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-((1,3-dithian-2-ylidene)methyl)benzoate (1x)



2-isopropyl-5-methylphenol (1.0 equiv), 4-formylbenzoic acid (1.1 equiv), and 4-dimethylaminopyridine (DMAP) (1.0 equiv) were dissolved in dichloromethane (30 mL) at 0 ℃. To this solution, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (2.0 equiv) in dichloromethane (10 mL) was added dropwise. The mixture was then stirred at room temperature for 12 h, detected by TLC. Upon completion of the reaction, the dichloromethane was removed by rotary evaporation. The crude product was dissolved with ethyl acetate, washed with saturated aqueous $NaHCO_3$ and H_2O, dried over $MgSO_4$, filtered, and then concentrated. The residue was purified by silica gel column chromatography (5% EtOAc/hexane) to obtain 2-isopropyl-5-methylphenyl 4-formylbenzoate as a colourless oil liquid. Then **1x** was prepared following General Procedure B using 2-isopropyl-5-methylphenyl 4-formylbenzoate and $\mathbf{S_1}$. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **1x** (234 mg, 0.6 mmol, 25%) as a colourless oil liquid.

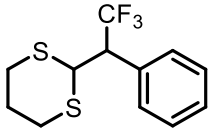
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 6.79 (s, 1H), 4.95 – 4.86 (m, 1H), 3.01 – 2.91 (m, 4H), 2.19 – 2.06 (m, 3H), 2.00 – 1.90 (m, 1H), 1.69 (d, *J* = 11.6 Hz, 2H), 1.52 (t, *J* = 11.7 Hz, 2H), 1.17 – 1.02 (m, 2H), 0.90 (dd, *J* = 6.9, 3.9 Hz, 8H), 0.77 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.5, 140.2, 135.3, 129.2, 128.3, 128.1, 126.2, 74.4, 47.0, 40.8, 34.1, 31.2, 29.2, 28.7, 26.3, 23.8, 23.4, 21.9, 20.6, 16.3 ppm.

HRMS (ESI^+): calcd. for $C_{22}H_{30}O_2S_2$ $[M+H]^+$ 391.1765, found 391.1766.

5. Product Characterisation

2-(2,2,2-trifluoro-1-phenylethyl)-1,3-dithiane (3a)



Prepared following the General Procedure using **1a** (625 mg, 3.0 mmol, 1.00 equiv), 4CzIPN (47 mg, 0.06 mmol, 2.0 mol%), CF_3SO_2Na (702 mg, 4.5 mmol, 1.50 equiv) and MeCN (30.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (1% EtOAc/hexane) gave the title compound **3a** (718 mg, 2.6 mmol, 86%), as a yellow oil.

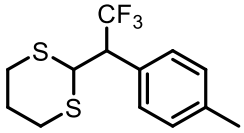
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 – 7.34 (m, 5H), 4.64 (dd, *J* = 7.0, 2.4 Hz, 1H), 3.73 – 3.62 (m, 1H), 3.05 – 2.76 (m, 4H), 2.11 – 2.01 (m, 1H), 1.88 – 1.75 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 131.9, 129.6, 128.9, 128.5, 125.6 (q, *J* = 281.7 Hz), 55.0 (q, *J* = 27.0 Hz), 47.1, 30.9 (d, *J* = 7.1 Hz), 25.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.8 – -63.9 (m) ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{13}F_3S_2$ $[M+Na]^+$ 301.0308, found 301.0314.

2-(2,2,2-trifluoro-1-(p-tolyl)ethyl)-1,3-dithiane (3b)



Prepared following the General Procedure using **1b** (173 mg, 0.78 mmol, 1.00 equiv), 4CzIPN (12 mg, 0.016 mmol, 2.0 mol%), CF_3SO_2Na (146 mg, 0.94 mmol, 1.50 equiv) and MeCN (15.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3b** (157 mg, 0.54 mmol, 69%), as a yellow oil.

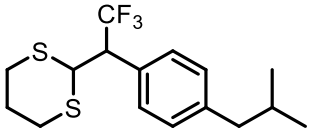
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.64 (d, *J* = 7.0 Hz, 1H), 3.70 – 3.60 (m, 1H), 3.04 – 2.77 (m, 4H), 2.37 (s, 3H), 2.10 – 2.01 (m, 1H), 1.87 – 1.75 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 138.8, 129.3 (d, *J* = 14.2 Hz), 128.7, 125.6 (q, *J* = 282.0 Hz), 54.5 (q, *J* = 27.1 Hz), 47.2, 30.9 (d, *J* = 8.0 Hz), 25.0, 21.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.9 – -64.1 (m) ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{15}F_3S_2$ $[M+H]^+$ 293.0646, found 293.0647.

2-(2,2,2-trifluoro-1-(4-isobutylphenyl)ethyl)-1,3-dithiane (3c)



Prepared following the General Procedure using **1c** (277 mg, 1.05 mmol, 1.00 equiv), 4CzIPN (17 mg, 0.021 mmol, 2.0 mol%), CF_3SO_2Na (246 mg, 1.6 mmol, 1.50 equiv) and MeCN (15.0 mL), which was

irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3c** (261 mg, 0.78 mmol, 74%), as a colourless oil.

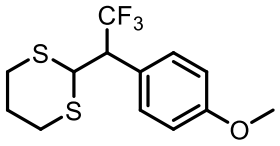
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.32 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.65 (d, *J* = 6.9 Hz, 1H), 3.73 – 3.61 (m, 1H), 3.04 – 2.76 (m, 4H), 2.50 (d, *J* = 7.2 Hz, 2H), 2.10 – 1.99 (m, 1H), 1.96 – 1.75 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 142.4, 129.1 (d, *J* = 9.5 Hz), 128.9, 125.6 (q, *J* = 281.8 Hz), 54.5 (q, *J* = 27.0 Hz), 47.1, 45.0, 30.8 (d, *J* = 8.5 Hz), 29.9, 24.9, 22.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.9 (d, *J* = 9.2 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{16}H_{21}F_3S_2$ $[M+H]^+$ 335.1115, found 335.111.

2-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)-1,3-dithiane (3d)



Prepared following the General Procedure using **1d** (221 mg, 0.92 mmol, 1.00 equiv), 4CzIPN (14 mg, 0.018 mmol, 2.0 mol%), CF_3SO_2Na (172 mg, 1.10 mmol, 1.50 equiv) and MeCN (15.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3d** (139 mg, 0.45 mmol, 49%), as a yellow oil.

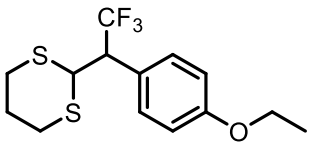
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.33 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.64 (d, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 3.70 – 3.59 (m, 1H), 3.03 – 2.77 (m, 4H), 2.09 – 2.00 (m, 1H), 1.86 – 1.74 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.8, 130.7, 125.6 (q, *J* = 281.7 Hz), 123.5, 113.7, 55.0, 54.0 (q, *J* = 27.0 Hz), 47.3, 30.8 (d, *J* = 6.4 Hz), 24.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.3 (d, *J* = 7.7 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{15}F_3OS_2$ $[M+Na]^+$ 331.0414, found 331.0414.

2-(1-(4-ethoxyphenyl)-2,2,2-trifluoroethyl)-1,3-dithiane (3e)



Prepared following the General Procedure using **1e** (76 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (5 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3e** (56 mg, 0.17 mmol, 56%), as a yellow oil.

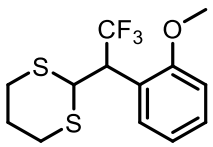
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.31 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.67 – 3.56 (m, 1H), 3.02 – 2.76 (m, 4H), 2.09 – 2.00 (m, 1H), 1.86 – 1.73 (m, 1H), 1.41 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.3, 130.7, 125.6 (q, *J* = 281.9 Hz), 123.4, 114.2, 63.3, 54.1 (q, *J* = 27.2 Hz), 47.4, 30.9 (d, *J* = 6.7 Hz), 25.0, 14.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.3 (d, *J* = 9.4 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{14}H_{17}F_3OS_2$ $[M+H]^+$ 323.0751, found 323.0752.

2-(2,2,2-trifluoro-1-(2-methoxyphenyl)ethyl)-1,3-dithiane (3f)



Prepared following the General Procedure using **1f** (119 mg, 0.50 mmol, 1.00 equiv), 4CzIPN (8 mg, 0.01 mmol, 2.0 mol%), CF_3SO_2Na (117 mg, 0.75 mmol, 1.50 equiv) and MeCN (10.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3f** (109 mg, 0.35 mmol, 71%), as a yellow oil.

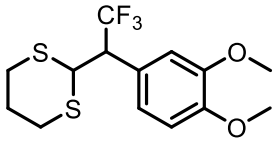
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.66 – 4.53 (m, 2H), 3.86 (s, 3H), 2.99 – 2.79 (m, 4H), 2.09 – 1.98 (m, 1H), 1.95 – 1.81 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 157.6, 129.8, 128.8, 125.8 (q, *J* = 281.8 Hz), 121.0, 120.4, 110.8, 55.7, 46.8, 30.2 (d, *J* = 30.7 Hz), 25.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.2 ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{15}F_3OS_2$ $[M+H]^+$ 305.0595, found 305.0597.

2-(1-(3,4-dimethoxyphenyl)-2,2,2-trifluoroethyl)-1,3-dithiane (3g)



Prepared following the General Procedure using **1g** (161 mg, 0.60 mmol, 1.00 equiv), 4CzIPN (9 mg, 0.012 mmol, 2.0 mol%), CF_3SO_2Na (140 mg, 0.90 mmol, 1.50 equiv) and MeCN (12.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3g** (135 mg, 0.4 mmol, 66%), as a yellow oil.

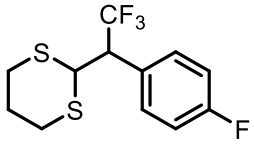
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.97 – 6.90 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 4.63 (d, *J* = 6.5 Hz, 1H), 3.89 (d, *J* = 6.6 Hz, 6H), 3.67 – 3.56 (m, 1H), 3.04 – 2.79 (m, 4H), 2.11 – 2.01 (m, 1H), 1.87 – 1.74 (m, 1H) ppm.

^{13}C NMR (400 MHz, $CDCl_3$): δ_C 149.4, 148.6, 125.6 (q, *J* = 281.6, 281.1 Hz), 123.8, 122.3, 112.4, 110.6, 55.9, 55.7, 54.5 (q, *J* = 27.0 Hz), 47.5, 31.0 (d, *J* = 4.5 Hz), 25.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.33 (d, *J* = 9.4 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{14}H_{17}F_3O_2S_2$ $[M+H]^+$ 339.0700, found 339.0701.

2-(2,2,2-trifluoro-1-(4-fluorophenyl)ethyl)-1,3-dithiane (3h)



Prepared following the General Procedure using **1h** (131 mg, 0.58 mmol, 1.00 equiv), 4CzIPN (9 mg, 0.012 mmol, 2.0 mol%), CF_3SO_2Na (135 mg, 0.87 mmol, 1.50 equiv) and MeCN (11.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3h** (130 mg, 0.44 mmol, 76%), as a yellow oil.

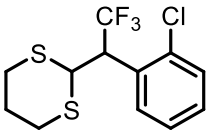
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.07 (t, *J* = 8.1 Hz, 2H), 4.62 (d, *J* = 6.6 Hz, 1H), 3.73 – 3.62 (m, 1H), 3.04 – 2.78 (m, 4H), 2.11 – 2.02 (m, 1H), 1.87 – 1.73 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.2, 161.7, 131.4 (d, *J* = 8.3 Hz), 127.5, 125.4 (q, *J* = 281.8 Hz), 115.6, 115.4, 54.2 (q, *J* = 27.4 Hz), 47.0, 30.9, 24.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.3 (d, *J* = 9.2 Hz), -112.4 – -112.5 (m) ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{12}F_4S_2$ $[M+H]^+$ 297.0389, found 297.0382.

2-(1-(2-chlorophenyl)-2,2,2-trifluoroethyl)-1,3-dithiane (3i)



Prepared following the General Procedure using **1i** (235 mg, 0.97 mmol, 1.00 equiv), 4CzIPN (15 mg, 0.019 mmol, 2.0 mol%), CF_3SO_2Na (227 mg, 1.5 mmol, 1.50 equiv) and MeCN (12.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3i** (199 mg, 0.64 mmol, 66%), as a yellow oil.

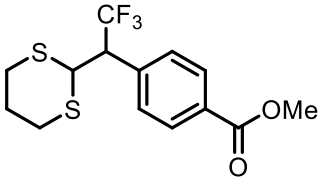
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 – 7.55 (m, 1H), 7.47 – 7.43 (m, 1H), 7.34 – 7.29 (m, 2H), 4.72 – 4.60 (m, 1H), 4.55 (d, *J* = 8.6 Hz, 1H), 2.94 – 2.89 (m, 2H), 2.88 – 2.81 (m, 2H), 2.09 – 2.01 (m, 1H), 1.95 – 1.83 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 135.6, 130.7, 129.8 (d, *J* = 14.2 Hz), 129.2, 127.0, 125.3 (q, *J* = 282.3 Hz), 48.9 (q, *J* = 27.2 Hz), 46.4, 30.2, 29.7, 24.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.3 (d, *J* = 9.2 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{12}ClF_3S_2$ $[M+H]^+$ 313.0099, found 313.0100.

methyl 4-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)benzoate (3j)



Prepared following the General Procedure using **3j** (91 mg, 0.34 mmol, 1.00 equiv), 4CzIPN (5 mg, 0.007 mmol, 2.0 mol%), CF_3SO_2Na (80 mg, 0.51 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3j** (61 mg, 0.18 mmol, 53%), as a yellow solid.

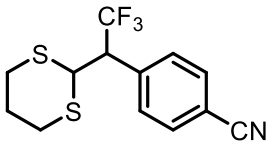
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.05 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 4.63 (d, *J* = 7.0 Hz, 1H), 3.91 (s, 3H), 3.80 – 3.69 (m, 1H), 3.03 – 2.75 (m, 4H), 2.10 – 1.99 (m, 1H), 1.86 – 1.72 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.4, 136.7, 130.6, 129.6, 125.2 (q, *J* = 282.0 Hz), 54.8 (q, *J* = 27.4 Hz), 52.1, 46.5, 30.7, 24.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.6 (d, *J* = 9.1 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{14}H_{15}F_3O_2S_2$ $[M+H]^+$ 337.0544, found 337.0545.

4-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)benzonitrile (3k)



Prepared following the General Procedure using **1k** (117 mg, 0.50 mmol, 1.00 equiv), 4CzIPN (8 mg, 0.01 mmol, 2.0 mol%), CF_3SO_2Na (117 mg, 0.75 mmol, 1.50 equiv) and MeCN (10.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **3k** (94 mg, 0.31 mmol, 62%), as a yellow solid.

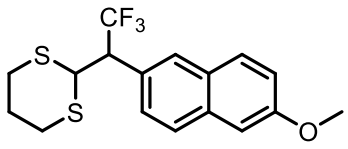
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68 (d, *J* = 6.7 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 4.64 (d, *J* = 6.7 Hz, 1H), 3.80 – 3.69 (m, 1H), 3.04 – 2.78 (m, 4H), 2.12 – 2.02 (m, 1H), 1.86 – 1.72 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.8, 132.2, 130.5, 125.0 (q, *J* = 282.1 Hz), 118.2, 113.1, 54.8 (q, *J* = 27.4 Hz), 46.3, 30.8 (d, *J* = 6.8 Hz), 24.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.8 (d, *J* = 9.0 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{12}F_3NS_2$ $[M+H]^+$ 304.0442, found 304.0443.

2-(2,2,2-trifluoro-1-(6-methoxynaphthalen-2-yl)ethyl)-1,3-dithiane (3l)



Prepared following the General Procedure using **1l** (182 mg, 0.63 mmol, 1.00 equiv), 4CzIPN (10 mg, 0.013 mmol, 2.0 mol%), CF_3SO_2Na (147 mg, 0.94 mmol, 1.50 equiv) and MeCN (12.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **3l** (122 mg, 0.34 mmol, 54%), as a white solid.

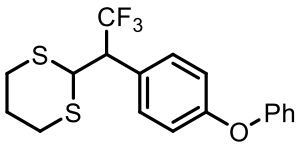
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.77 (d, *J* = 10.4 Hz, 3H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.22 – 7.10 (m, 2H), 4.73 (d, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 3.86 – 3.77 (m, 1H), 3.05 – 2.73 (m, 4H), 2.10 – 1.97 (m, 1H), 1.86 – 1.71 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 158.2, 134.5, 129.6, 129.2, 128.3, 127.0, 126.9, 125.7 (q, *J* = 281.9 Hz), 119.3, 105.5, 55.3, 54.9 (q, *J* = 27.0 Hz), 47.1, 30.8 (d, *J* = 10.6 Hz), 25.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.8 (d, *J* = 9.8 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{17}H_{17}F_3OS_2$ $[M+H]^+$ 359.0751, found 359.0752.

2-(2,2,2-trifluoro-1-(4-phenoxyphenyl)ethyl)-1,3-dithiane (3m)



Prepared following the General Procedure using **1m** (180 mg, 0.60 mmol, 1.00 equiv), 4CzIPN (9 mg, 0.012 mmol, 2.0 mol%), CF_3SO_2Na (140 mg, 0.90 mmol, 1.50 equiv) and MeCN (12.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3m** (179 mg, 0.48 mmol, 81%), as a colourless oil.

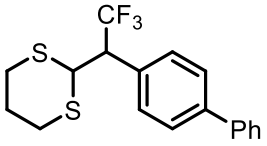
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 – 7.31 (m, 3H), 7.19 – 7.09 (m, 3H), 7.09 – 6.99 (m, 3H), 4.62 (d, *J* = 7.2 Hz, 1H), 3.73 – 3.60 (m, 1H), 3.04 – 2.78 (m, 4H), 2.13 – 2.00 (m, 1H), 1.91 – 1.75 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 157.0, 156.7, 133.6, 129.7 (d, *J* = 3.6 Hz), 125.4 (q, *J* = 281.9 Hz), 124.2, 123.4, 120.1, 119.0, 118.9, 54.6 (q, *J* = 27.2 Hz), 46.8, 30.7 (d, *J* = 7.4 Hz), 24.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.8 (d, *J* = 9.1 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{18}H_{17}F_3OS_2$ $[M+H]^+$ 371.0751, found 371.0752.

2-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)-1,3-dithiane (3n)



Prepared following the General Procedure using **1n** (85.3 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (4.7 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70.2 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3n** (70.1 mg, 0.20 mmol, 66%), as a white solid.

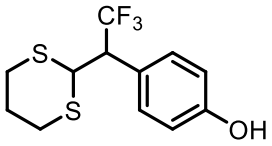
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 (d, *J* = 5.9 Hz, 4H), 7.52 – 7.40 (m, 4H), 7.40 – 7.32 (m, 1H), 4.69 (d, *J* = 6.7 Hz, 1H), 3.81 – 3.69 (m, 1H), 3.08 – 2.80 (m, 4H), 2.13 – 2.02 (m, 1H), 1.92 – 1.76 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 141.7, 140.2, 130.6, 130.0, 128.7, 127.5, 127.1 (q, *J* = 4.3 Hz), 125.6 (d, *J* = 281.8 Hz), 54.6 (q, *J* = 27.2 Hz), 47.1, 30.9 (d, *J* = 3.0 Hz), 25.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.7 (d, *J* = 6.7 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{18}H_{17}F_3S_2$ $[M+H]^+$ 355.0797, found 355.0799.

4-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)phenol (3o)



Prepared following the General Procedure using **1o** (67 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (5 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (20% EtOAc/hexane) gave the title compound **3o** (62 mg, 0.21 mmol, 71%), as a white solid.

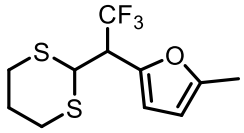
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.17 (s, 1H), 4.62 (d, *J* = 6.6 Hz, 1H), 3.68 – 3.56 (m, 1H), 3.04 – 2.77 (m, 4H), 2.11 – 2.01 (m, 1H), 1.86 – 1.74 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 156.0, 131.0, 125.6 (q, *J* = 281.7 Hz), 123.7, 115.4, 54.1 (q, *J* = 27.2 Hz), 47.4, 30.9 (d, *J* = 2.2 Hz), 25.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.4 (d, *J* = 9.4 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{13}F_3OS_2$ $[M+H]^+$ 295.0438, found 295.0439.

2-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)-5-methylfuran (3p)



Prepared following the General Procedure using **1p** (64 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (5 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 96 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3p** (43 mg, 0.15 mmol, 51%), as a yellow oil.

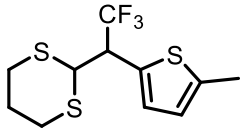
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.36 (d, *J* = 3.1 Hz, 1H), 5.99 (d, *J* = 1.9 Hz, 1H), 4.58 (d, *J* = 6.4 Hz, 1H), 3.88 – 3.77 (m, 1H), 3.02 – 2.80 (m, 4H), 2.30 (s, 3H), 2.11 – 2.03 (m, 1H), 1.91 – 1.79 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 152.8, 143.0, 124.5 (q, *J* = 282.0 Hz), 111.9, 106.7, 49.0 (q, *J* = 28.6 Hz), 45.8, 30.7, 30.5, 25.0, 13.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -65.2 (d, *J* = 8.8 Hz) ppm

HRMS (ESI^+): calcd. for $C_{11}H_{13}F_3OS_2$ $[M+H]^+$ 283.0438, found 283.0439.

2-(2,2,2-trifluoro-1-(5-methylthiophen-2-yl)ethyl)-1,3-dithiane (3q)



Prepared following the General Procedure using **1q** (114 mg, 0.50 mmol, 1.00 equiv), 4CzIPN (8 mg, 0.01 mmol, 2.0 mol%), CF_3SO_2Na (117 mg, 0.75 mmol, 1.50 equiv) and MeCN (10.0 mL), which was irradiated with 30 W blue LED for 96 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3q** (111 mg, 0.37 mmol, 75%), as a yellow solid.

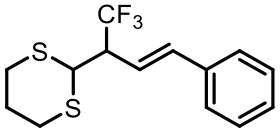
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.94 (d, *J* = 3.5 Hz, 1H), 6.68 (d, *J* = 2.3 Hz, 1H), 4.60 (d, *J* = 5.5 Hz, 1H), 4.00 – 3.89 (m, 1H), 3.07 – 2.80 (m, 4H), 2.48 (s, 3H), 2.13 – 2.01 (m, 1H), 1.90 – 1.75 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 141.4, 129.6, 129.3, 124.8, 124.8 (q, *J* = 281.8 Hz), 50.6 (q, *J* = 28.6 Hz), 47.7, 31.1, 30.9, 25.0, 15.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -65.8 (d, *J* = 9.1 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{11}H_{13}F_3S_3$ $[M+H]^+$ 299.0210, found 299.0211.

(E)-2-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)-1,3-dithiane (3r)



Prepared following the General Procedure using **1r** (199 mg, 0.85 mmol, 1.00 equiv), 4CzIPN (13 mg, 0.017 mmol, 2.0 mol%), CF_3SO_2Na (199 mg, 1.27 mmol, 1.50 equiv) and MeCN (15.0 mL), which was irradiated with 30 W blue LED for 72 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **3r** (46 mg, 0.15 mmol, 18%), as a yellow oil.

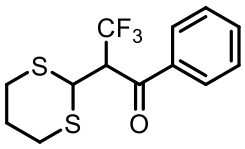
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 – 7.22 (m, 5H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.25 – 6.13 (m, 1H), 4.55 (d, *J* = 4.2 Hz, 1H), 3.34 – 3.14 (m, 1H), 3.08 – 2.67 (m, 4H), 2.16 – 2.03 (m, 1H), 1.94 – 1.77 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 138.0, 135.7, 128.6, 128.4, 126.8, 125.4 (q, *J* = 281.8 Hz), 118.4, 53.0 (q, *J* = 27.5 Hz), 46.9, 31.1, 30.7, 25.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -66.6 (d, *J* = 8.8 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{14}H_{15}F_3S_2$ $[M+H]^+$ 305.0646, found 305.0647.

2-(1,3-dithian-2-yl)-3,3,3-trifluoro-1-phenylpropan-1-one (3s)



Prepared following the General Procedure using **1s** (70.9 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (4.7 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70.2 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was

irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (20% EtOAc/hexane) gave the title compound **3s** (59 mg, 0.19 mmol, 64%), as a yellow solid.

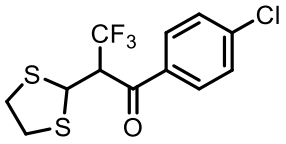
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 4.76 – 4.62 (m, 2H), 2.97 – 2.89 (m, 2H), 2.84 – 2.78 (m, 2H), 2.12 – 2.02 (m, 1H), 2.01 – 1.89 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 192.0, 137.0, 134.2, 129.0, 128.6, 123.5 (q, *J* = 282.8 Hz), 52.0 (q, *J* = 25.5 Hz), 42.9, 29.2, 28.7, 24.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -61.8 (d, *J* = 7.3 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{13}F_3OS_2$ $[M+H]^+$ 307.0438, found 307.0439.

1-(4-chlorophenyl)-2-(1,3-dithiolan-2-yl)-3,3,3-trifluoropropan-1-one (3t)



Prepared following the General Procedure using **1t** (77 mg, 0.30 mmol, 1.00 equiv.), 4CzIPN (4.7 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70.2 mg, 0.45 mmol, 1.50 equiv.) and MeCN (6.0 mL), which was irradiated with 30 W blue LED for 72 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (20% EtOAc/hexane) gave the title compound **3t** (43 mg, 0.13 mmol, 44%), as a yellow solid.

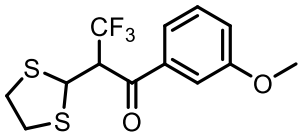
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.90 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 5.16 (d, *J* = 10.2 Hz, 1H), 4.48 – 4.38 (m, 1H), 3.32 – 3.28 (m, 2H), 3.20 – 3.12 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 191.7, 140.9, 135.0, 130.2, 129.3, 123.2 (q, *J* = 283.7 Hz), 57.2 (q, *J* = 23.9 Hz), 49.4, 39.4, 38.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.2 (d, *J* = 7.6 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{12}H_{10}ClF_3OS_2$ $[M+H]^+$ 326.9892, found 326.9893.

2-(1,3-dithiolan-2-yl)-3,3,3-trifluoro-1-(3-methoxyphenyl)propan-1-one (3u)



Prepared following the General Procedure using **1u** (126 mg, 0.50 mmol, 1.00 equiv), 4CzIPN (8 mg, 0.01 mmol, 2.0 mol%), CF_3SO_2Na (117 mg, 0.75 mmol, 1.50 equiv) and MeCN (10.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (20% EtOAc/hexane) gave the title compound **3u** (45 mg, 0.14 mmol, 28%), as a yellow solid.

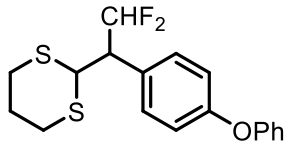
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 – 7.48 (m, 2H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 4.54 – 4.41 (m, 1H), 3.87 (s, 3H), 3.34 – 3.27 (m, 2H), 3.20 – 3.12 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 192.7, 160.0, 138.0, 129.8, 123.3 (q, *J* = 283.4 Hz), 121.6, 120.8, 112.9, 57.2 (q, *J* = 23.8 Hz), 55.5, 49.5, 39.3, 38.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.2 (d, *J* = 7.5 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{13}F_3O_2S_2$ $[M+H]^+$ 323.0387, found 323.0388.

2-(2,2-difluoro-1-(4-phenoxyphenyl)ethyl)-1,3-dithiane (4a)



Prepared following the General Procedure using **1m** (153 mg, 0.51 mmol, 1.00 equiv), 4CzIPN (8 mg, 0.010 mmol, 2.0 mol%), HCF_2SO_2Na (106 mg, 0.76 mmol, 1.50 equiv) and MeCN (10.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **4a** (49 mg, 0.14 mmol, 27%), as a yellow oil.

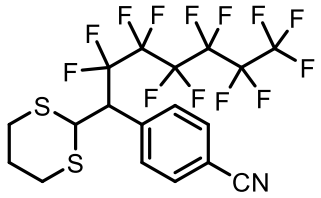
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34 (q, *J* = 7.6 Hz, 3H), 7.14 – 7.05 (m, 3H), 7.05 – 7.01 (m, 2H), 7.01 – 6.97 (m, 1H), 6.37 (td, *J* = 55.9, 3.9 Hz, 1H), 4.47 (d, 1H), 3.47 – 3.33 (m, 1H), 2.98 – 2.79 (m, 4H), 2.13 – 2.05 (m, 1H), 1.94 – 1.83 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 156.9 (d, *J* = 3.4 Hz), 134.8 (d, *J* = 4.1 Hz), 129.7, 129.5, 124.5, 123.3, 120.3, 118.8, 118.6, 114.9 (t, *J* =245.4 Hz), 53.5 (t, *J* = 21.3 Hz), 47.1 (t, *J* = 4.4 Hz), 30.1 (d, *J* = 15.0 Hz), 25.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -119.8 (dd, *J* = 55.7, 7.7 Hz), -120.6 (dd, *J* = 55.8, 7.8 Hz), -123.8 (dd, *J* = 56.1, 21.7 Hz), -124.6 (dd, *J* = 56.0, 21.7 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{18}H_{18}F_2OS_2$ $[M+H]^+$ 353.0845, found 353.0846.

4-(1-(1,3-dithian-2-yl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)benzonitrile (4b)



Prepared following the General Procedure using **1k** (70 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (4.7 mg, 0.006 mmol, 2.0 mol%), $C_6F_{13}SO_2Na$ (183 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 9 d. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **4b** (92 mg, 0.17 mmol, 55%), as a yellow solid.

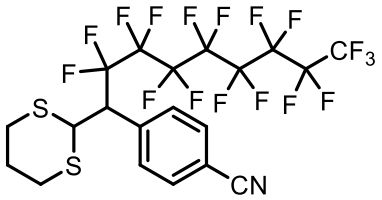
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 4.80 (d, *J* = 4.2 Hz, 1H), 3.93 – 3.82 (m, 1H), 3.09 – 2.91 (m, 2H), 2.87 – 2.78 (m, 2H), 2.08 – 2.00 (m, 1H), 1.80 – 1.65 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 135.6 (d, *J* = 5.8 Hz), 131.9, 131.3, 118.2, 113.3, 52.3 (t, *J* = 20.7 Hz), 46.9 (d, *J* = 3.8 Hz), 31.5, 31.0, 24.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -80.8 (t, *J* = 10.0 Hz), -108.0 – -112.6 (m), -117.6 – -120.4 (m), -120.5 – -124.1 (m), -124.9 – -127.5 (m) ppm.

HRMS (ESI^+): calcd. for $C_{18}H_{12}F_{13}NS_2$ $[M+H]^+$ 554.0282, found 554.0283.

4-(1-(1,3-dithian-2-yl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)benzonitrile (4c)



Prepared following the General Procedure using **1k** (70 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (5 mg, 0.006 mmol, 2.0 mol%), $C_8F_{17}SO_2Na$ (228 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 10 d. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (2% EtOAc/hexane) gave the title compound **4c** (157 mg, 0.24 mmol, 80%), as a yellow solid.

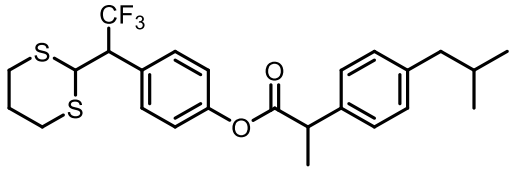
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 4.2 Hz, 1H), 3.99 – 3.78 (m, 1H), 3.09 – 2.91 (m, 2H), 2.87 – 2.75 (m, 2H), 2.08 – 1.98 (m, 1H), 1.81 – 1.65 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 135.6 (d, J = 6.1 Hz), 131.8, 131.3, 118.2, 113.2, 52.2 (t, J = 20.5 Hz), 46.9 (d, J = 3.7 Hz), 31.5, 31.0, 24.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -81.0 (t, *J* = 9.7 Hz), -108.1 – -112.5 (m), -117.8 – -120.4 (m), -120.5 – -123.9 (m), -125.4 – -127.4 (m) ppm.

HRMS (ESI^+): calcd. for $C_{20}H_{12}F_{17}NS_2$ $[M+H]^+$ 654.0218, found 654.0219.

4-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)phenyl 2-(4-isobutylphenyl)propanoate (5a)



Prepared following the General Procedure using **1v** (123 mg, 0.30 mmol, 1.00 equiv), 4CzIPN (5 mg, 0.006 mmol, 2.0 mol%), CF_3SO_2Na (70 mg, 0.45 mmol, 1.50 equiv) and MeCN (6.00 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **5a** (51 mg, 0.1 mmol, 35%), as a colourless oil.

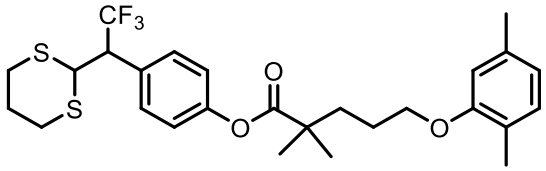
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 4.60 (d, *J* = 6.7 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 1H), 3.75 – 3.60 (m, 1H), 3.03 – 2.75 (m, 4H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.10 – 1.98 (m, 1H), 1.95 – 1.72 (m, 2H), 1.61 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.7, 151.2, 140.8, 137.0, 130.6, 129.5, 129.0, 127.1, 125.4 (q, *J* = 281.5 Hz), 121.3, 54.3 (q, *J* = 27.4 Hz), 47.0, 45.2, 45.0, 30.8 (d, *J* = 2.8 Hz), 30.1, 24.9, 22.3, 18.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.0 (d, *J* = 9.3 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{25}H_{29}F_3O_2S_2$ $[M+H]^+$ 483.1639, found 483.1640.

4-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (5b)



Prepared following the General Procedure using **1w** (288 mg, 0.63 mmol, 1.00 equiv), 4CzIPN (10 mg, 0.013 mmol, 2.0 mol%), CF_3SO_2Na (147 mg, 0.94 mmol, 1.50 equiv) and MeCN (12.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **5b** (190 mg, 0.36 mmol, 57%), as a colourless oil.

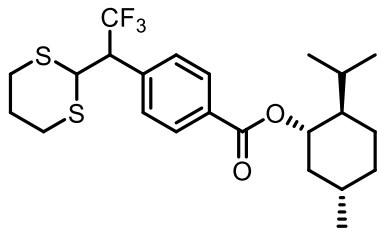
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.01 – 3.96 (m, 2H), 3.73 – 3.64 (m, 1H), 3.03 – 2.77 (m, 4H), 2.32 (s, 3H), 2.19 (s, 3H), 2.10 – 2.01 (m, 1H), 1.88 (s, 4H), 1.85 – 1.78 (m, 1H), 1.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.9, 156.8, 151.4, 136.5, 130.7, 130.3, 129.0, 125.4 (q, *J* = 281.6 Hz), 123.6, 121.5, 120.7, 111.9, 67.7, 54.4 (q, *J* = 27.3 Hz), 47.0, 42.4, 37.1, 30.8 (d, *J* = 3.3 Hz), 29.7, 25.1 (t, *J* = 12.8 Hz), 21.4, 15.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -64.1 (d, *J* = 9.2 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{27}H_{33}F_3O_3S_2$ $[M+H]^+$ 527.1901, found 527.1902.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(1-(1,3-dithian-2-yl)-2,2,2-trifluoroethyl)benzoate (5c)



Prepared following the General Procedure using **1x** (218 mg, 0.56 mmol, 1.00 equiv), 4CzIPN (9 mg, 0.011 mmol, 2.0 mol%), CF_3SO_2Na (131 mg, 0.84 mmol, 1.50 equiv) and MeCN (11.0 mL), which was irradiated with 30 W blue LED for 48 h. Then triflic acid and $NaBH_4$ were added to the mixture and stirred until the TLC detection reaction is complete. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **5c** (150 mg, 0.33 mmol, 58%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.06 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 4.93 (td, *J* = 10.9, 4.4 Hz, 1H), 4.65 (d, *J* = 6.9 Hz, 1H), 3.82 – 3.68 (m, 1H), 3.03 – 2.77 (m, 4H), 2.13 – 2.01 (m, 2H), 2.01 – 1.92 (m, 1H), 1.86 – 1.77 (m, 1H), 1.77 – 1.67 (m, 2H), 1.62 – 1.48 (m, 2H), 1.19 – 1.02 (m, 2H), 0.92 (dd, *J* = 6.8, 2.7 Hz, 7H), 0.78 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.4, 136.4, 131.4, 129.6 (d, *J* = 7.9 Hz), 125.2 (q, *J* = 282.1 Hz), 74.9, 54.7 (q, *J* = 27.3 Hz), 47.1, 46.6, 40.8, 34.2, 31.4, 30.7, 26.3, 24.8, 23.4, 22.0, 20.8, 16.3 ppm.

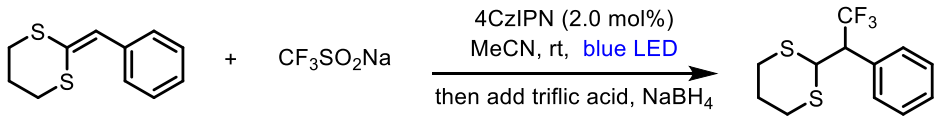
^{19}F NMR (376 MHz, $CDCl_3$): δ_F -63.7 (d, *J* = 9.0 Hz) ppm.

HRMS (ESI^+): calcd. for $C_{23}H_{31}F_3O_2S_2$ $[M+H]^+$ 461.1796, found 461.1797.

6. Follow-up chemistry

(a) Gram-scale synthesis

a) Gram-scale synthesis of **3a**:



1a
625 mg, 3.0 mmol

2a
(1.5 equiv)

3a
86% yield
718 mg, 2.58 mmol

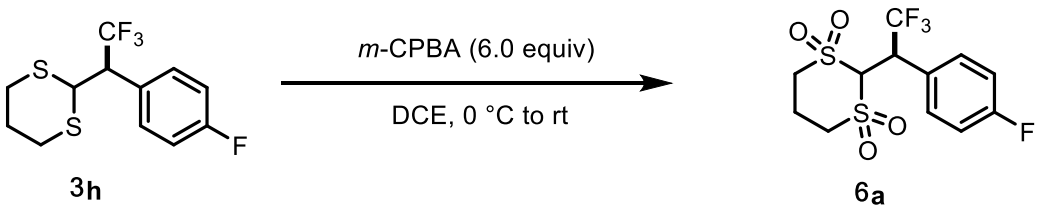
Prepared following the modified General Procedure. 4CzIPN (47 mg, 0.06 mmol, 2.0 mol%) was added to a solution of **1a** (625 mg, 3.00 mmol, 1.00 equiv), CF_3SO_2Na (702 mg, 4.50 mmol, 1.50 equiv) and dry MeCN (30.0 mL) under N_2 at room temperature. The mixture was irradiated with 2 × 30 W blue LED for 72 h. Then triflic acid (2.1 mL, 24.0 mmol, 8.00 equiv) and $NaBH_4$ (681 mg, 18.0 mmol, 6.00 equiv) were added to the mixture and stirred until the TLC detection reaction is complete. Water (20 mL) was added to the reaction mixture. The phases were separated and the aqueous phase was extracted into DCM (2 ×30 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (2% EtOAc/hexane) gave the title compound **3a** (718 mg, 2.58 mmol, 86%), as a yellow oil.

b) Reaction set-up:

Figure S1. Photoredox reaction setup for scale up.

(b) Reprehensive product transformations

a) Oxidation of **3h**:



3h

6a

Dissolve **3h** (113 mg, 0.38 mmol, 1.00 equiv) in DCM (4.00 mL) and *m*-CPBA (394 mg, 2.28 mmol, 6.00 equiv) in DCM (2.00 mL), then add the solution of *m*-CPBA to **3h** in an ice bath and stir at room temperature for 48 h. Water (15 mL) was added to the reaction mixture. The phases were separated and the aqueous phase was extracted into DCM (3 × 15 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by recrystallization (EtOAc/hexane) gave the corresponding compound **6a** (130 mg, 0.36 mmol, 95%) as white solid.

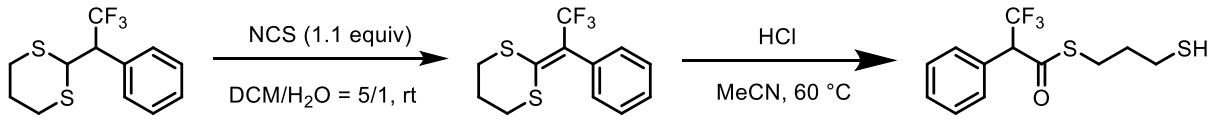
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ_H 7.59 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.21 (t, *J* = 8.9 Hz, 2H), 5.93 (d, *J* = 2.4 Hz, 1H), 4.86 – 4.76 (m, 1H), 3.72 – 3.63 (m, 1H), 3.63 – 3.51 (m, 2H), 3.48 – 3.41 (m, 1H), 2.45 – 2.35 (m, 1H), 2.15 – 2.00 (m, 1H) ppm.

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ_C 164.0, 161.6, 133.8 (d, *J* = 8.6 Hz), 126.0, 125.6 (d, J = 281.5 Hz), 115.5, 115.3, 76.9, 52.7, 51.6, 42.4 (q, *J* = 30.1 Hz), 17.4 ppm.

^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ_F -64.1 (d, *J* = 10.6 Hz), -113.1 – -113.2 (m) ppm.

HRMS (ESI$^+$): calcd. for $C_{12}H_{12}F_4O_4S_2$ $[M+H]^+$ 361.0191, found 361.0192.

b) Reduction of **3a**:



3a **6b** **6c**

NCS (29.4 mg, 0.22 mmol, 1.10 equiv) was added to a solution of **3a** (55.7 mg, 0.20 mmol, 1.00 equiv) in DCM/H_2O = 5/1 (3.00 mL). The mixture was stirred at rt for 48 h. Then partitioned between DCM (15 mL) and H_2O (15 mL). The phases were separated and the aqueous phase was extracted into DCM (2 × 15 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (1% EtOAc/hexane) gave the corresponding compound **6b** (23.2 mg, 0.08 mmol, 42%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 – 7.31 (m, 3H), 7.26 – 7.16 (m, 2H), 3.01 (t, *J* = 7.0 Hz, 2H), 2.87 (t, *J* = 6.8 Hz, 2H), 2.12 – 2.03 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 147.8, 134.7, 130.1, 128.5, 124.3, 122.8 (q, *J* = 241.7 Hz), 28.4 (d, *J* = 5.1 Hz), 22.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -56.1 ppm.

HRMS (ESI$^+$): calcd. for $C_{12}H_{11}F_3S_2$ $[M+H]^+$ 277.0333, found 277.0334.

HCl (1.5 mL) was added to a solution of **6a** (239 mg, 0.86 mmol, 1.00 equiv) in MeCN (10.0 mL). The mixture was stirred at 60 ℃ for 48 h. Then partitioned between DCM (15 mL) and H_2O (15 mL). The phases were separated and the aqueous phase was extracted into DCM (2 × 15 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (2% EtOAc/hexane) gave the corresponding compound **6c** (180 mg, 0.61 mmol, 71%) as colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46 – 7.38 (m, 5H), 4.46 (q, *J* = 8.5 Hz, 1H), 3.04 (t, *J* = 6.6 Hz, 2H), 2.53 (q, *J* = 7.3 Hz, 2H), 1.87 (p, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 8.1 Hz, 1H) ppm.

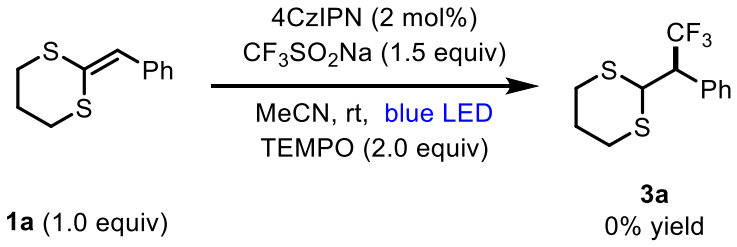
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 191.4, 129.5, 129.4, 129.0, 123.3 (q, *J* = 281.6 Hz), 62.2 (q, *J* = 27.7 Hz), 33.0, 28.0, 23.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -66.4 (d, *J* = 8.5 Hz) ppm.

HRMS (ESI$^+$): calcd. for $C_{12}H_{13}F_3OS_2$ $[M+H]^+$ 295.0438, found 295.0439.

7. Mechanistic Studies

(a) Radical inhibition experiments:

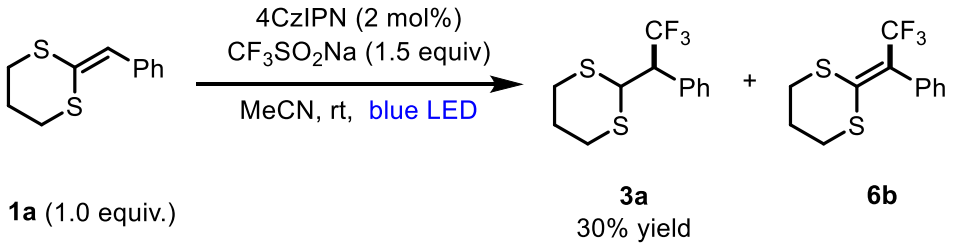


1a (1.0 equiv)

3a
0% yield

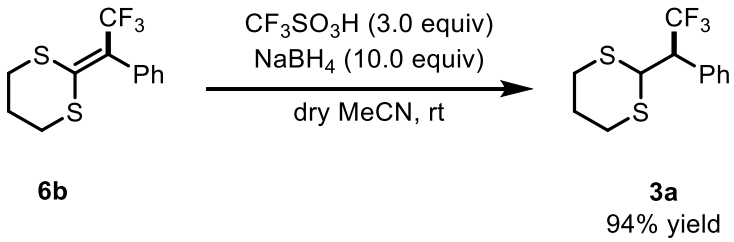
To a 5 mL vial equipped with a magnetic stir bar was added the olefin **1a** (20.8 mg, 0.10 mmol, 1.00 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 2.0 mol%) and CF_3SO_2Na (23.4 mg, 0.15 mmol, 1.50 equiv). Then anhydrous MeCN (2.00 mL) and TEMPO (31.2 mg, 0.20 mmol, 2.00 equiv) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for 24 h. ^{1}HNMR analysis of this reaction crude mixture showed that no product **3a** or **3a'** was observed, the reaction was completely inhibited.

(b) Selective experiments:



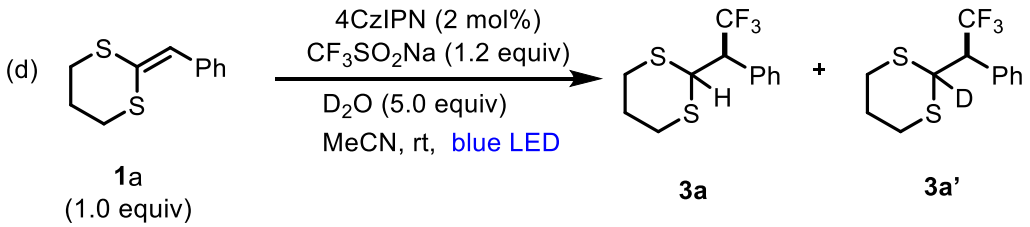
To a 5 mL vial equipped with a magnetic stir bar was added the olefin **1a** (20.8 mg, 0.10 mmol, 1.00 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 2.0 mol%) and CF_3SO_2Na (23.4 mg, 0.15 mmol, 1.50 equiv). Then anhydrous MeCN (2.00 mL) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for 24 h. ^{1}HNMR analysis of this reaction crude mixture showed that product **3a** or **6b** was observed. The separation yield of **3a** and **6b** is 30% and 20%, respectively.

(c) Reduction reaction



CF_3SO_3H (0.021 mL, 0.24 mmol, 3.00 equiv) was added to a solution of **6b** (22.1 mg, 0.08 mmol, 1.00 equiv) in MeCN (2.00 mL). The mixture was stirred at room temperature for 15 min. Then $NaBH_4$ (30.0 mg, 0.8 mmol, 10.0 equiv) were added to the mixture at 0 ℃ and stirred until the TLC detection reaction is complete. Water (15 mL) was added to the reaction mixture. The phases were separated and the aqueous phase was extracted into DCM (2 × 10 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (2% EtOAc/hexane) gave the title compound **3a** (20.8 mg, 0.075 mmol, 94%), as a yellow oil.

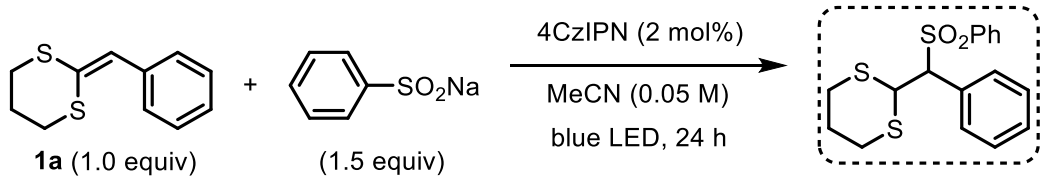
(d) Deuterium experiment



To a 15 mL vial equipped with a magnetic stir bar was added the **1a** (1.00 equiv), 4CzIPN (2.0 mol%), CF_3SO_2Na (1.50 equiv) and D_2O (5.00 equiv). Then anhydrous MeCN (0.05 M) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 400 rpm and irradiated with a 30 W blue LED lamp with fan cooling for typical 36 h with TLC monitoring. Then, purification by flash column chromatography (1% EtOAc/hexane) gave the compound **3a**, along with the deuterated product **3a′** determined by nuclear magnetic resonance hydrogen spectroscopy.

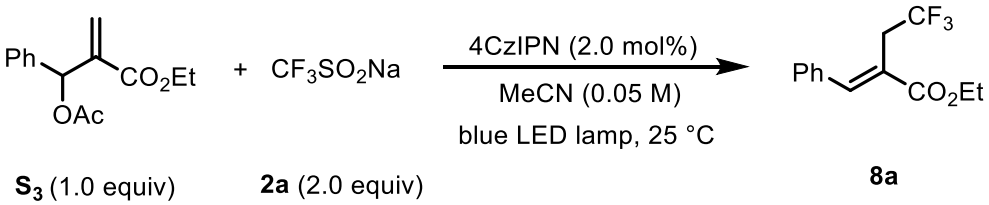
(e) Other radical source experiments

Phenyl sulfinate was tried in this reaction, and failed to give desired product.



Prepared following the General Procedure using **1a** (27.8 mg, 0.10 mmol, 1.00 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 2.0 mol%), $PhSO_2Na$ (0.15 mmol, 1.50 equiv) and MeCN (2.00 mL), which was irradiated with 30 W blue LED for 24 h. No obvious changes were observed by TLC determination. 95% **1a** was recovered after purification by flash column chromatography.

(f) anion trapping experiments:



To a 7 mL vial equipped with a magnetic stir bar was added the $\mathbf{S_3}$ (23.4 mg, 0.10 mmol, 1.00 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 2.0 mol%), CF_3SO_2Na (31.2 mg, 0.20 mmol, 2.00 equiv.) and MeCN (2.00 mL). The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for 38 h. Then partitioned between DCM (15 mL) and water (20 mL). The phases were separated and the aqueous phase was extracted into DCM (2 × 15 mL). The combined organic phases dried ($MgSO_4$),

filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (5% EtOAc/hexane) gave the title compound **8a** (17.4 mg, 0.067 mmol, 67%, E/Z = 95/5) as a yellow oil. All recorded spectroscopic data matched those previously reported in our previous work[5].

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (s, 1H), 7.50 – 7.35 (m, 5H), 4.36 (q, *J* = 7.0 Hz, 2H), 3.47 (q, *J* = 10.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 167.0, 145.0, 134.3, 129.2, 128.9, 128.8, 125.7 (q, *J* = 279.3 Hz), 122.8, 61.5, 32.1 (q, *J* = 30.6 Hz), 14.2 ppm.

8. References

[1] a) Luo, J.; Zhang, J. *ACS Catal.* **2016**, *6*, 873; b) Zheng, Z.; van der Werf, A.; Deliaval, M.; Selander, N. *Org. Lett.* **2020**, *22*, 2791.

[2] Manvar, A.; O'Shea, D. F. *Eur. J. Org. Chem.* **2015**, *33*, 1099.

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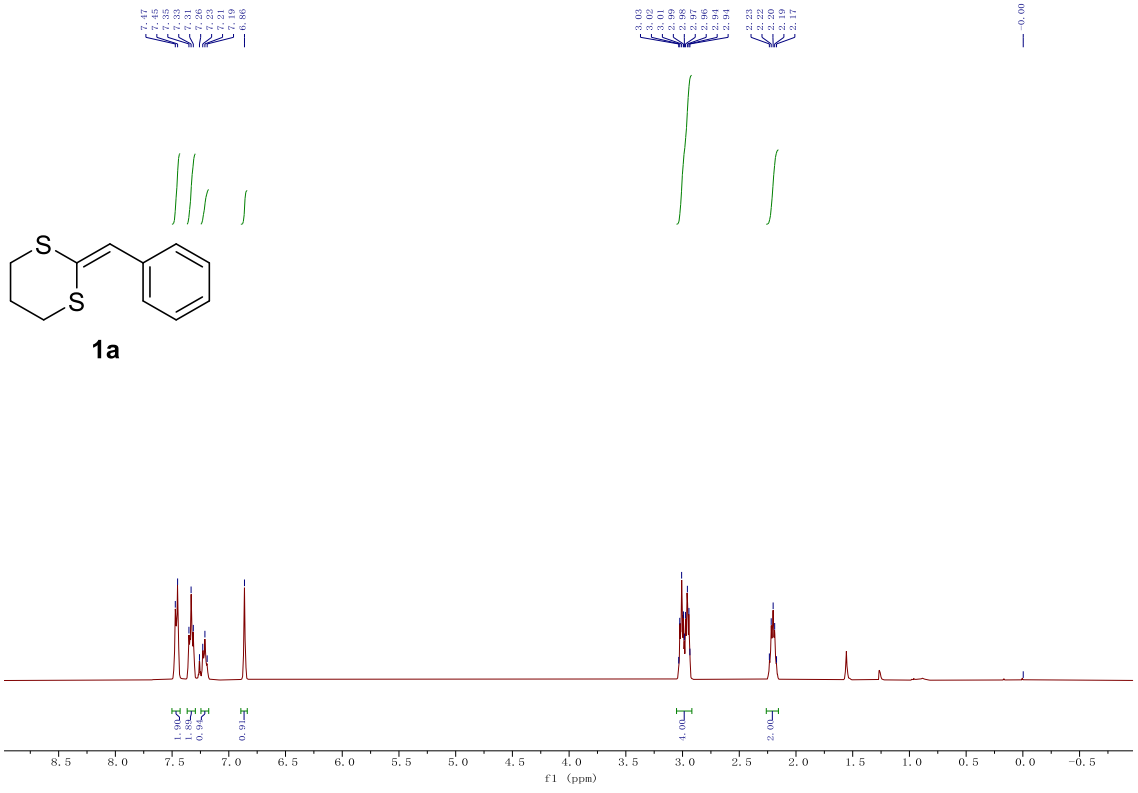
[4] Lv, P.; Chen, Y.; Wang, D.; Wu, X.; Li, Q.; Hua, R. *Engineering.* **2020**, *6*, 560.

[5] Li, H.; Zhang, Y.; Yang, X.; Deng, Z.; Zhu, Z.; Zhou, P.; Ouyang, X.; Yuan, Y.; Chen, X.; Yang, L.; Liu, M.; Shu, C. *Angew. Chem. Int. Ed.* **2023**, *62*, e202300159.

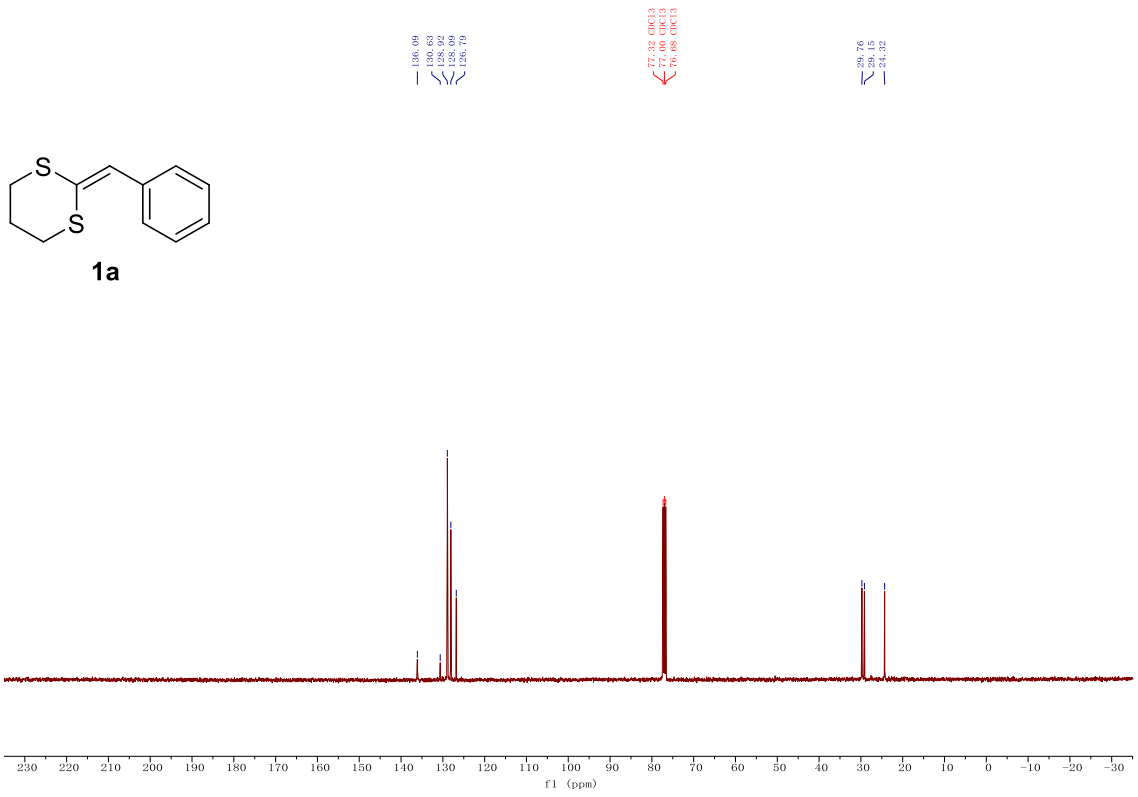
9. NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$)



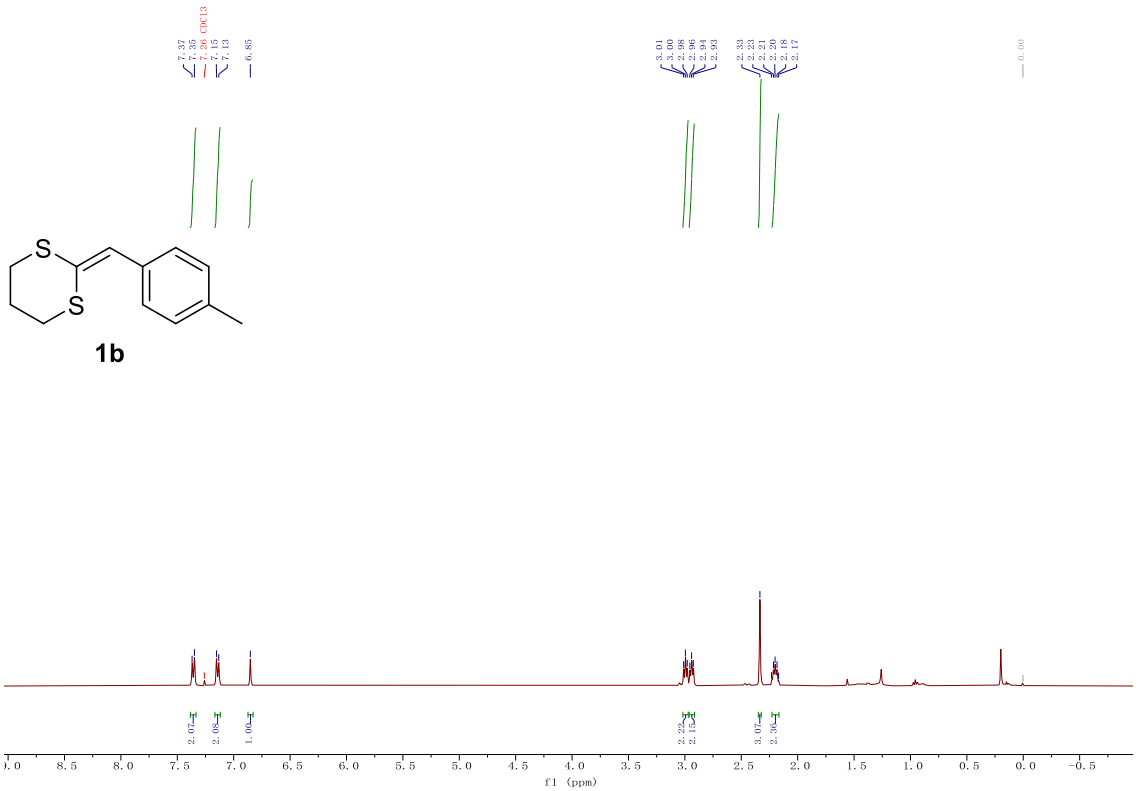
1a

^{13}C NMR (101 MHz, $CDCl_3$)

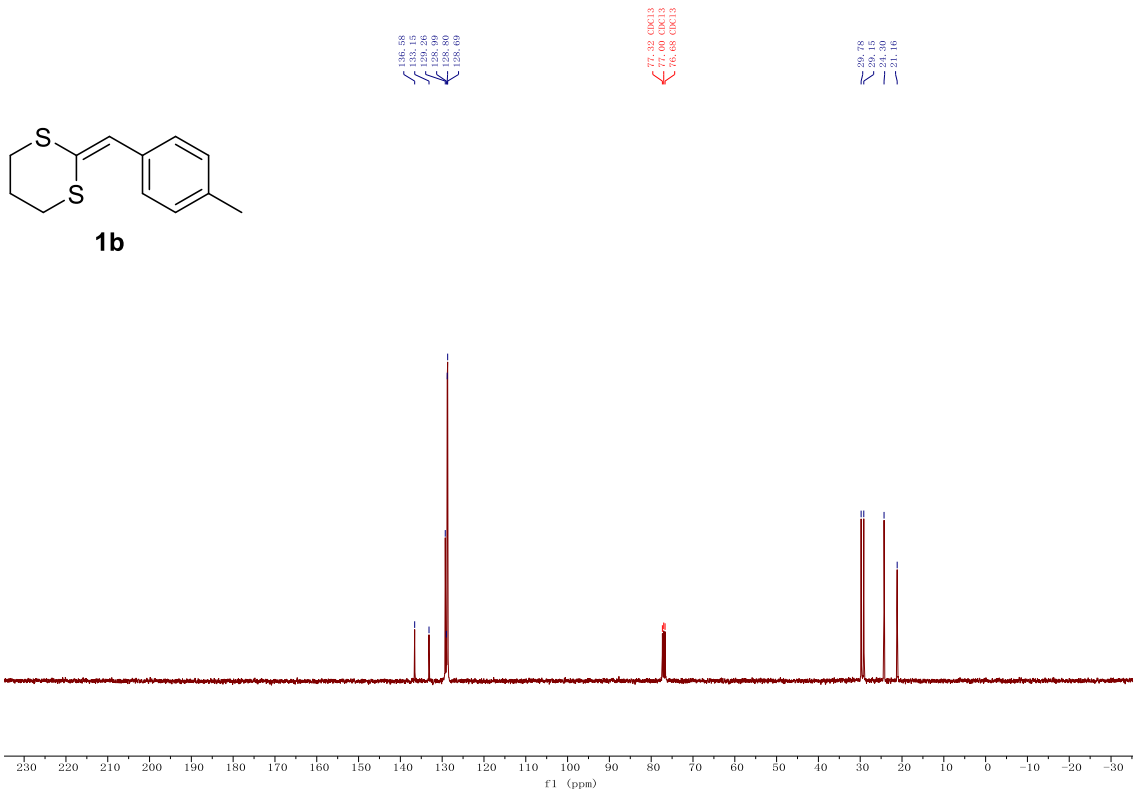


1a

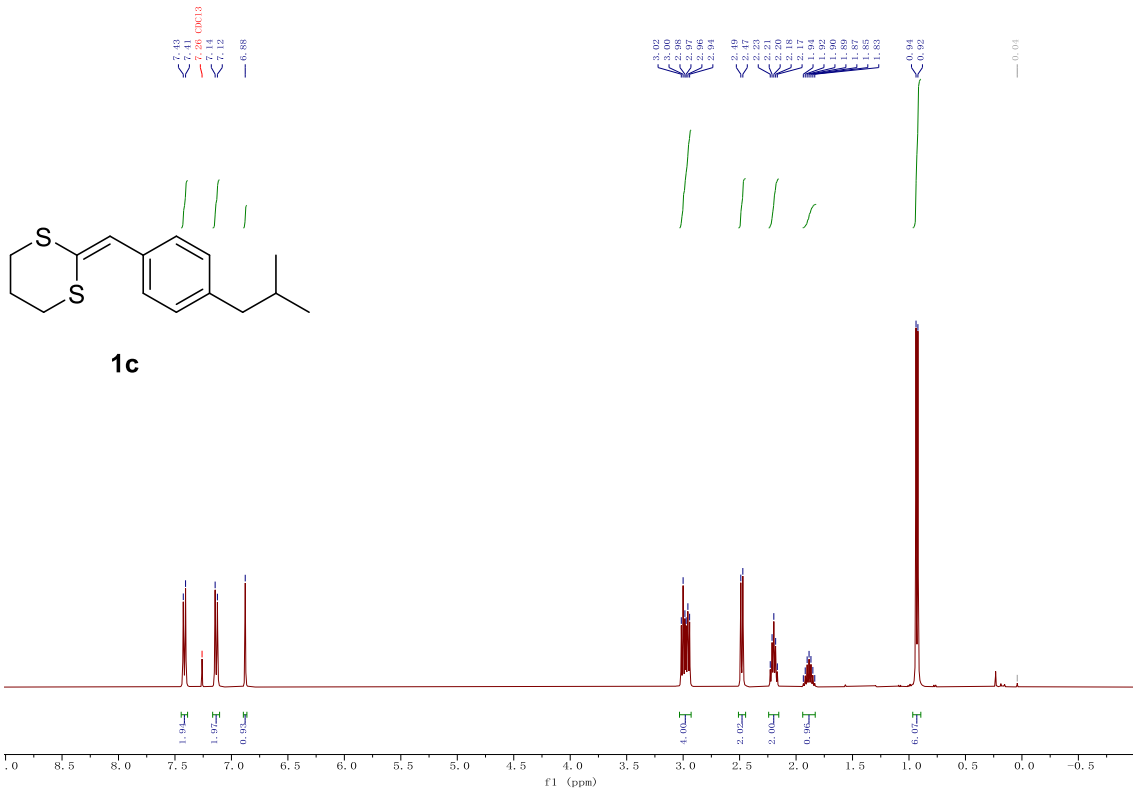
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

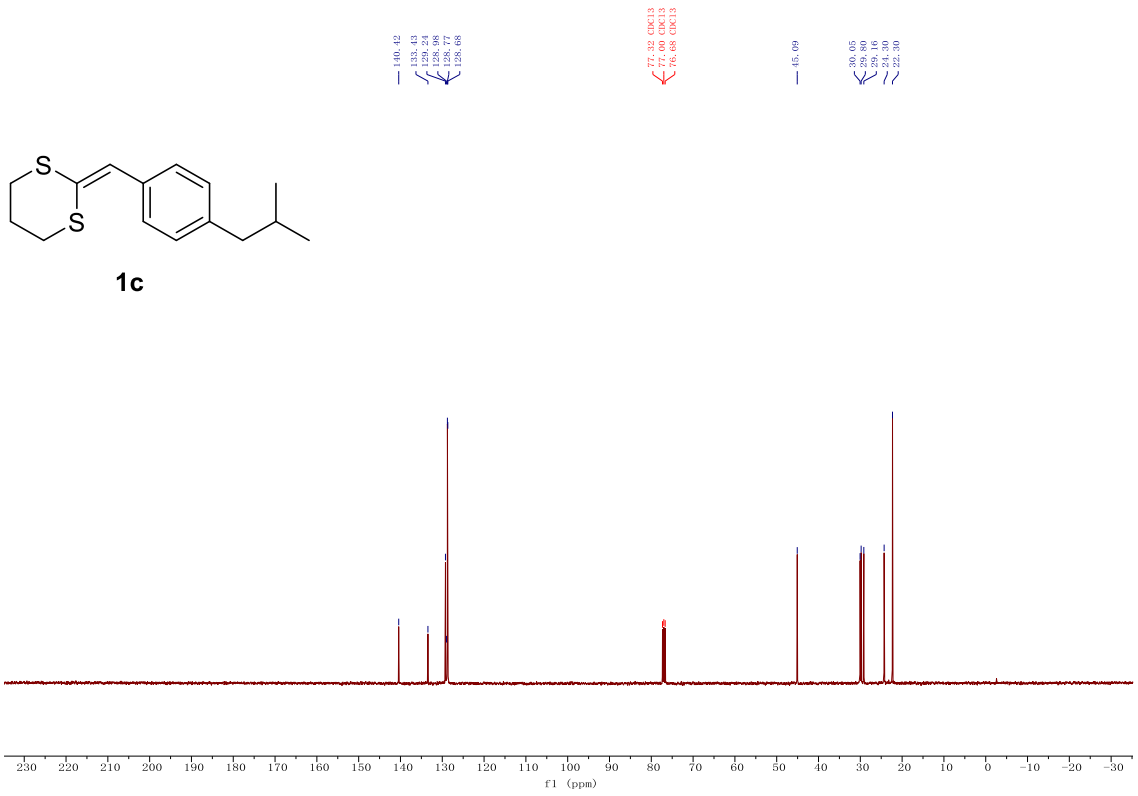


^{1}H NMR (400 MHz, $CDCl_3$)



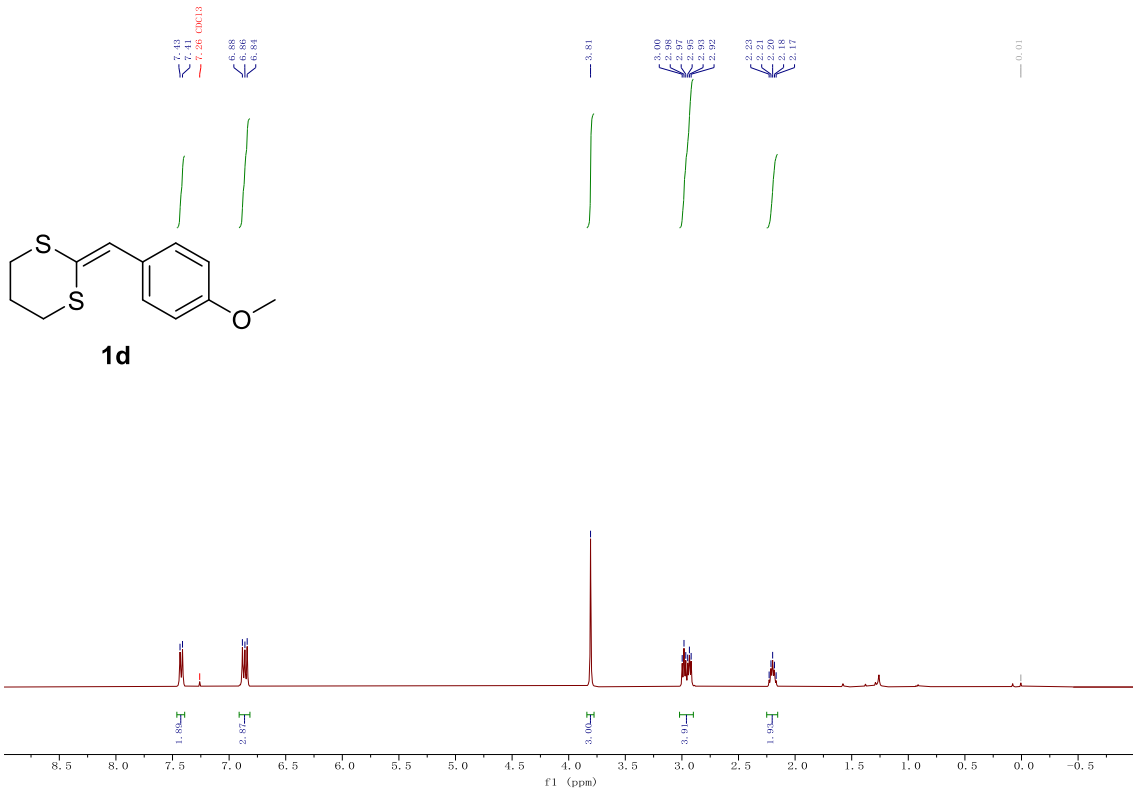
1c

^{13}C NMR (101 MHz, $CDCl_3$)

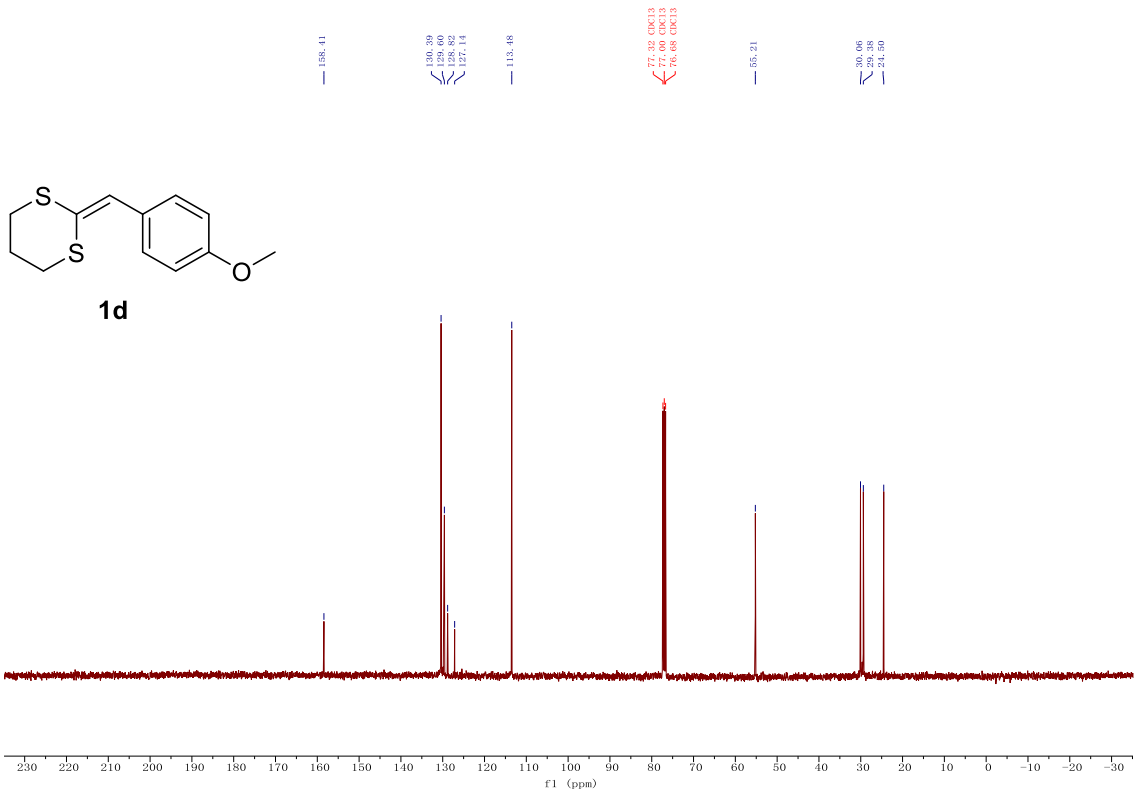


1c

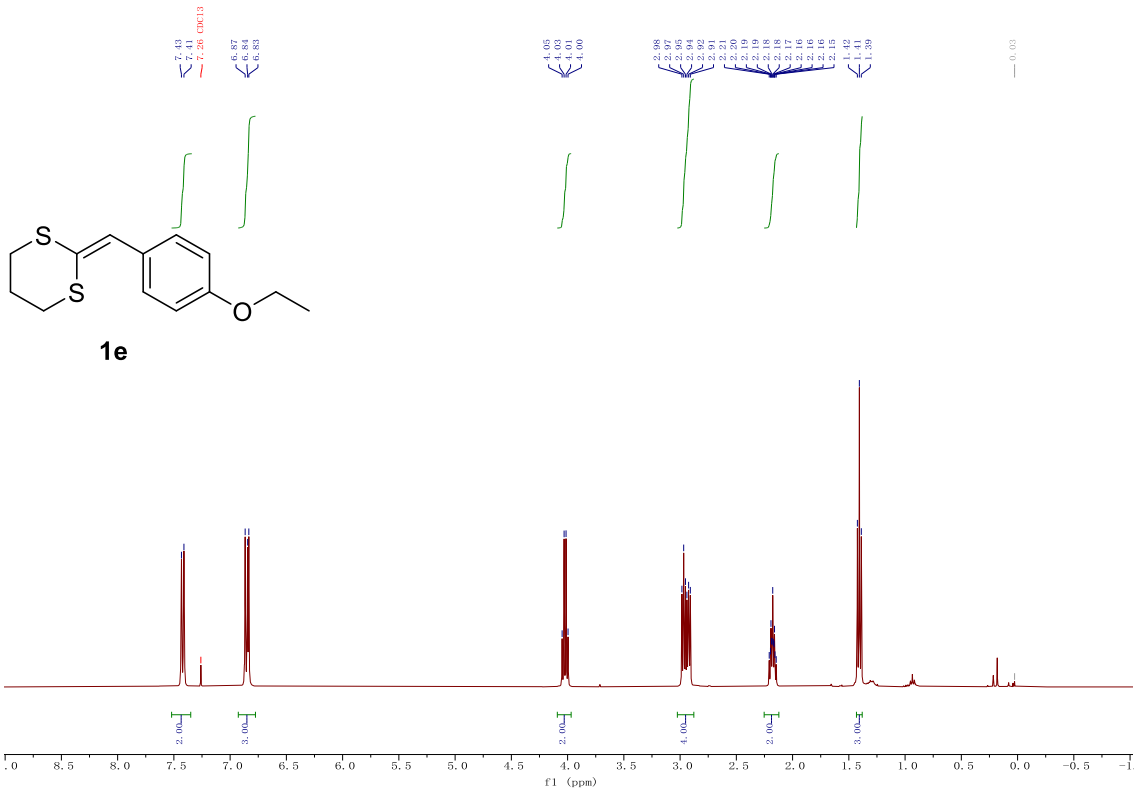
^{1}H NMR (400 MHz, $CDCl_3$)



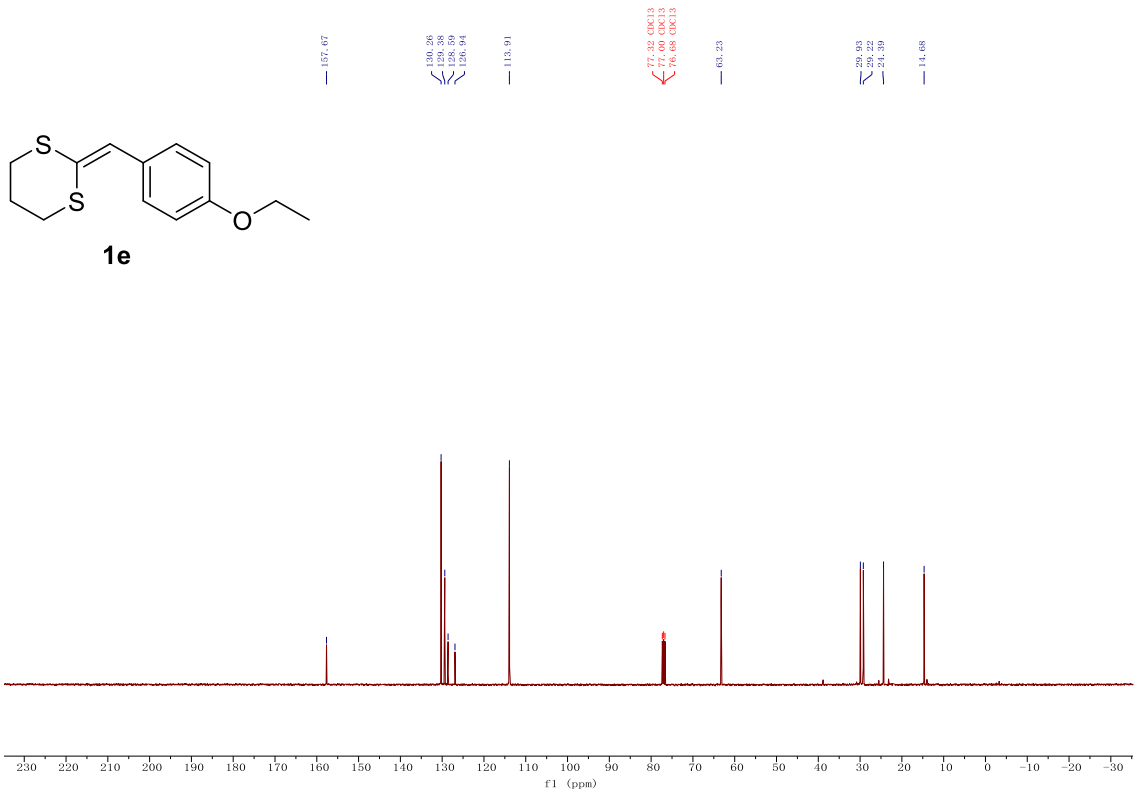
^{13}C NMR (101 MHz, $CDCl_3$)



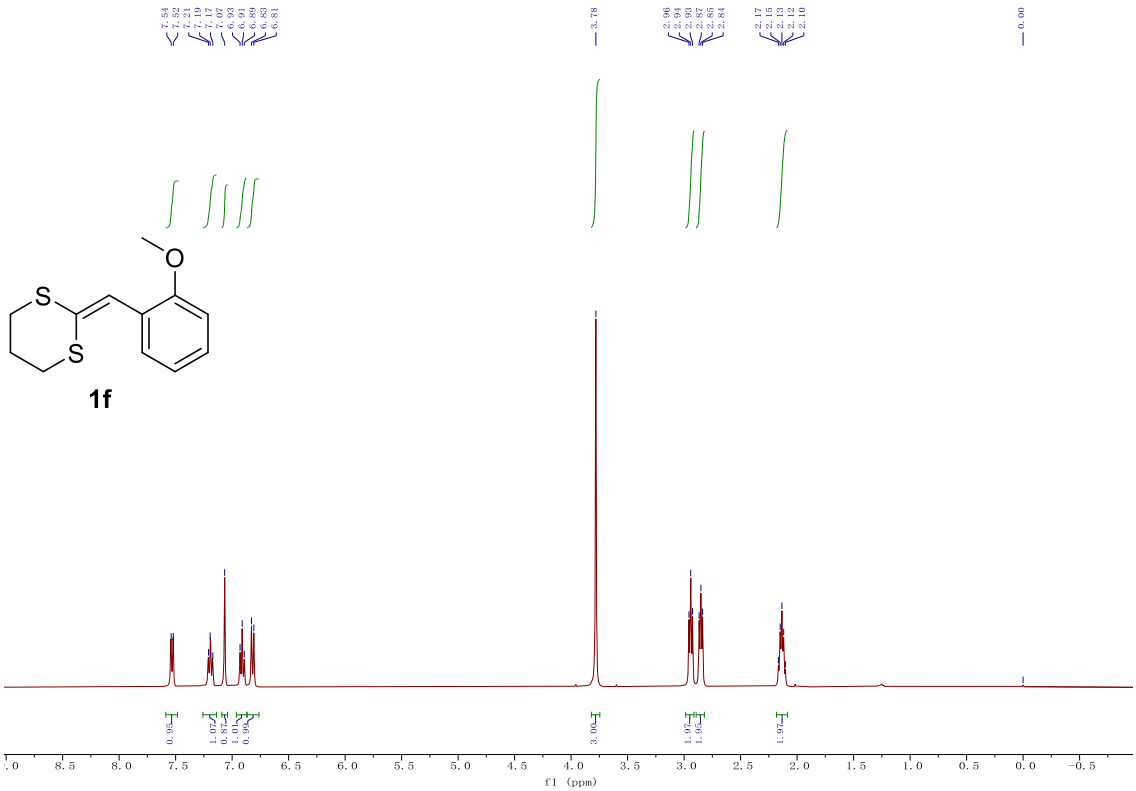
^{1}H NMR (400 MHz, $CDCl_3$)



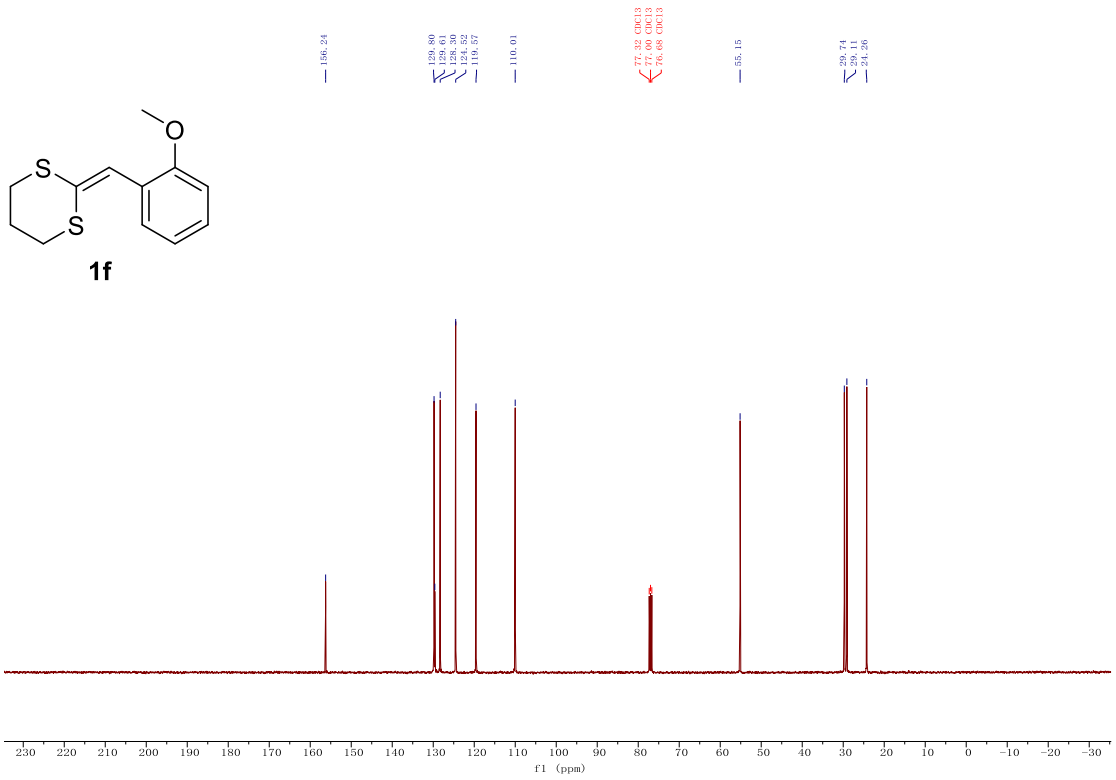
^{13}C NMR (101 MHz, $CDCl_3$)



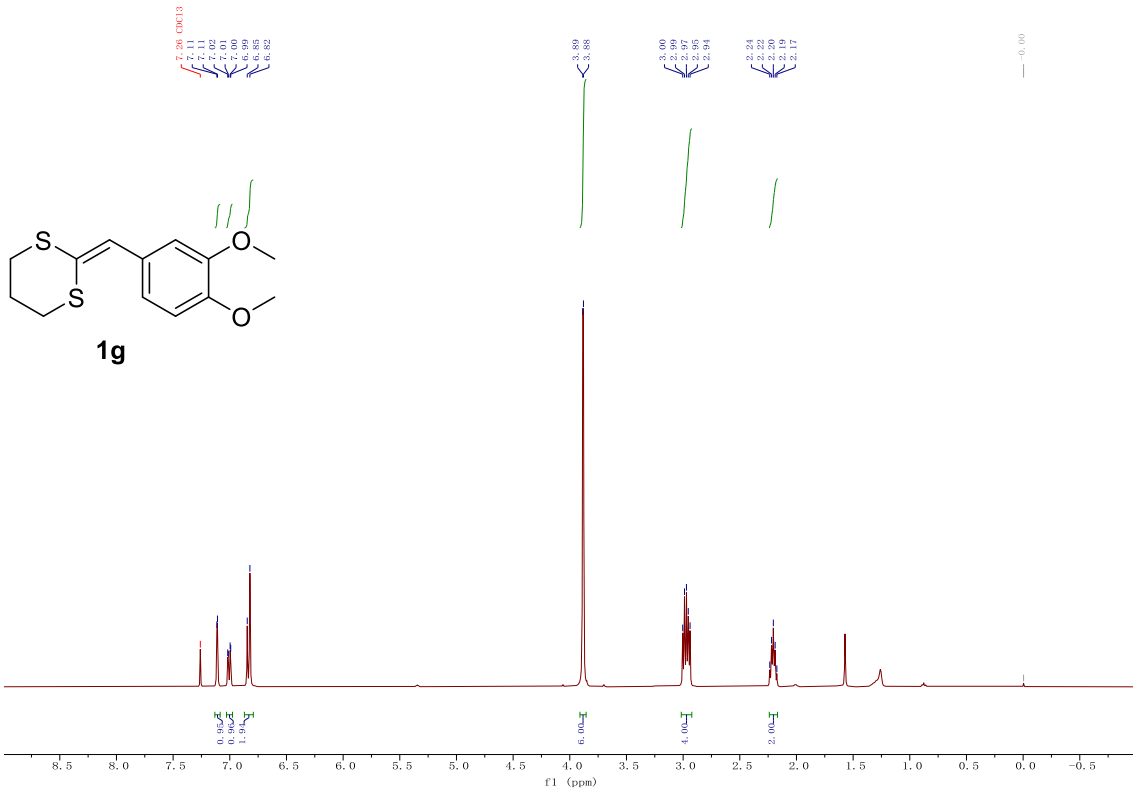
^{1}H NMR (400 MHz, $CDCl_3$)



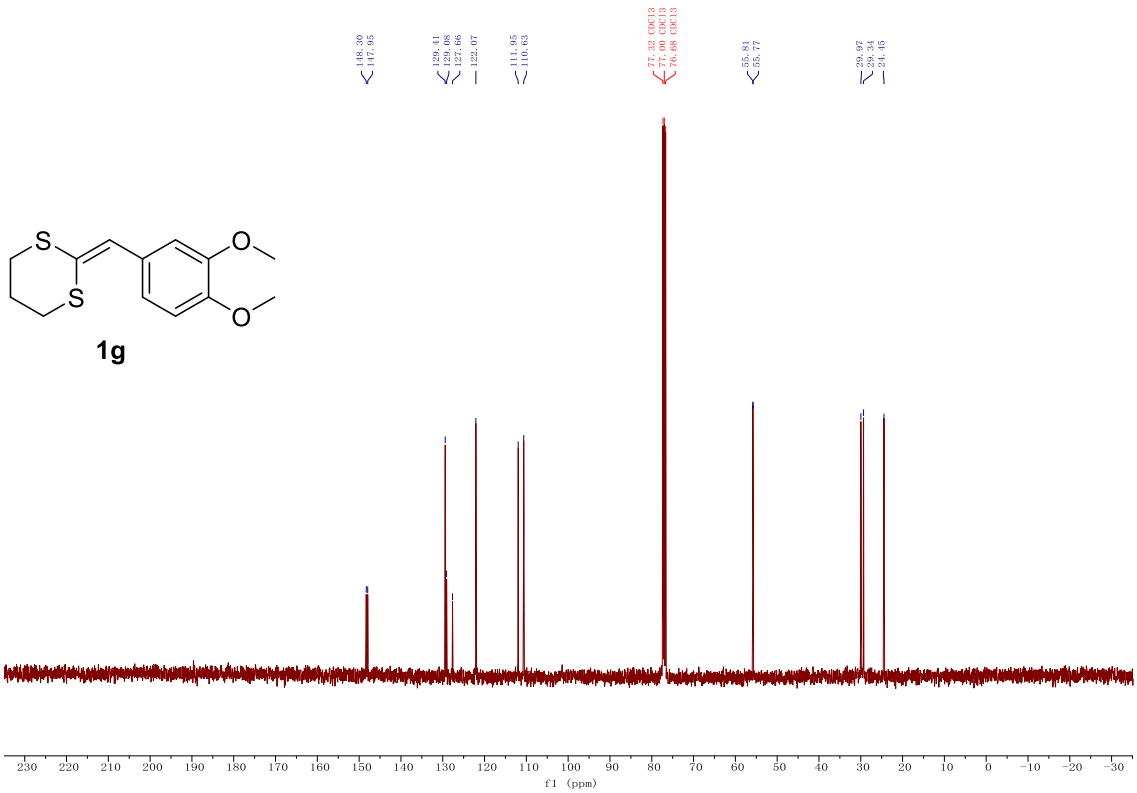
^{13}C NMR (101 MHz, $CDCl_3$)



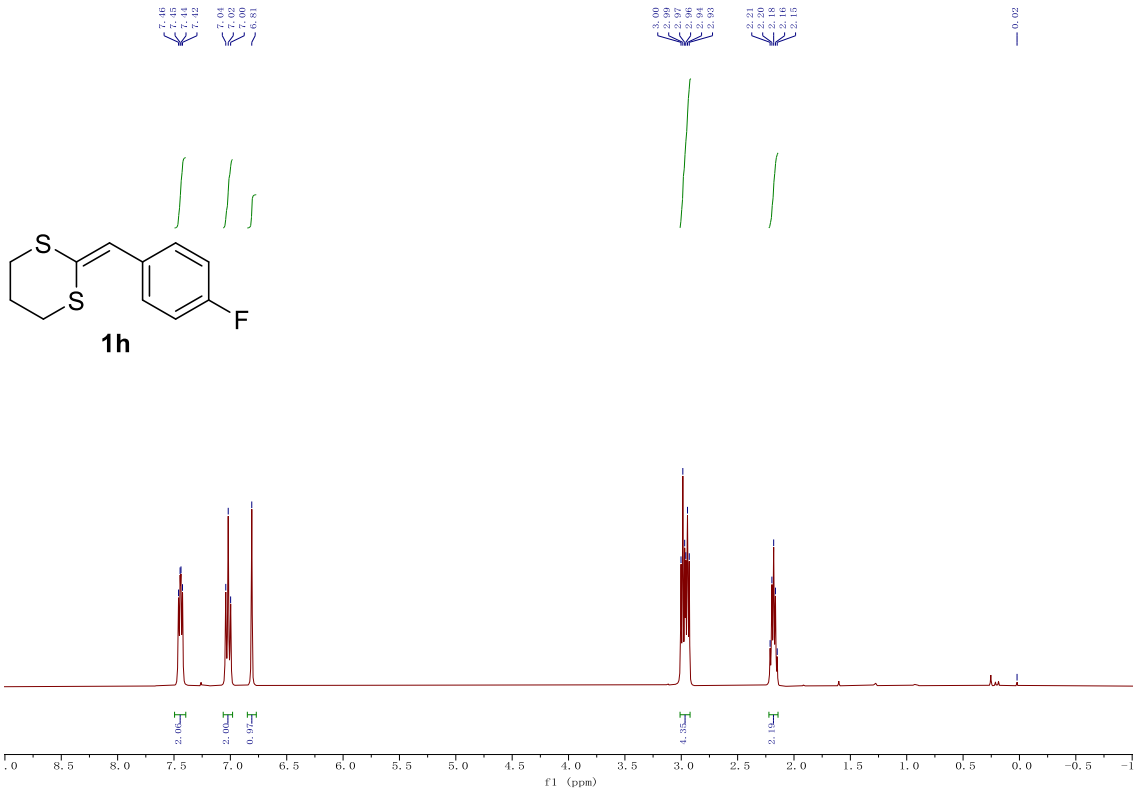
^{1}H NMR (400 MHz, $CDCl_3$)



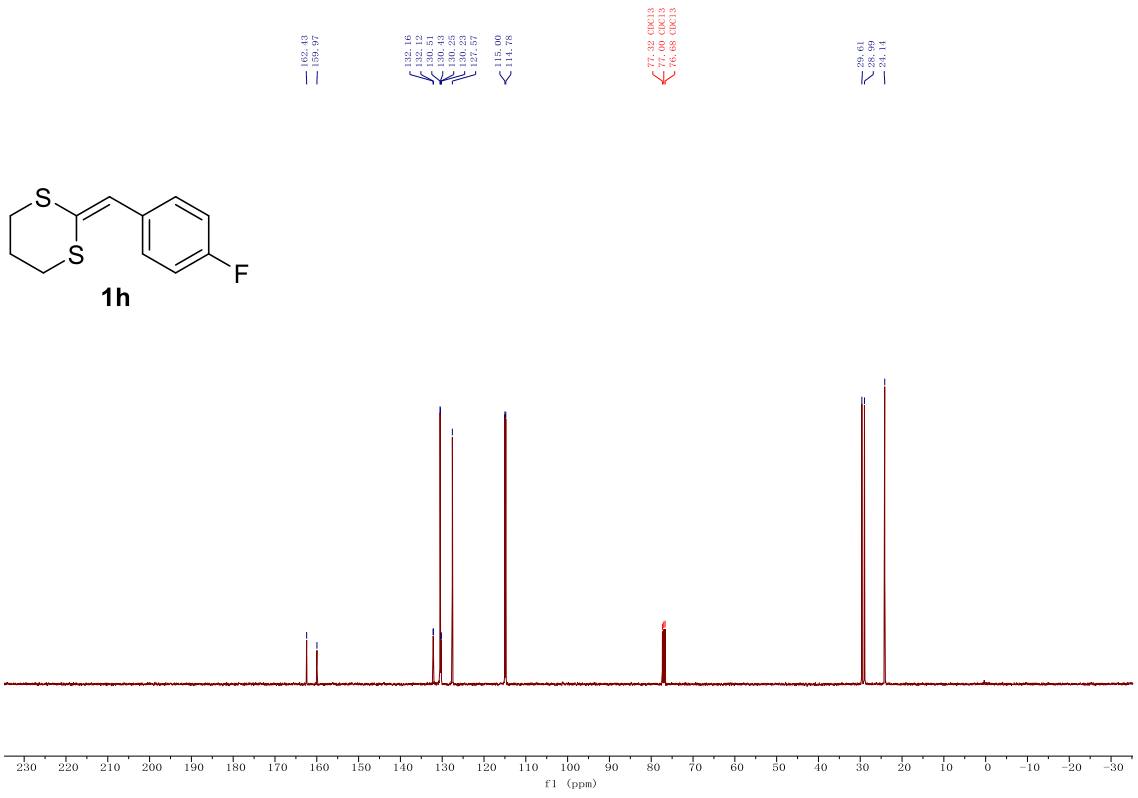
^{13}C NMR (101 MHz, $CDCl_3$)



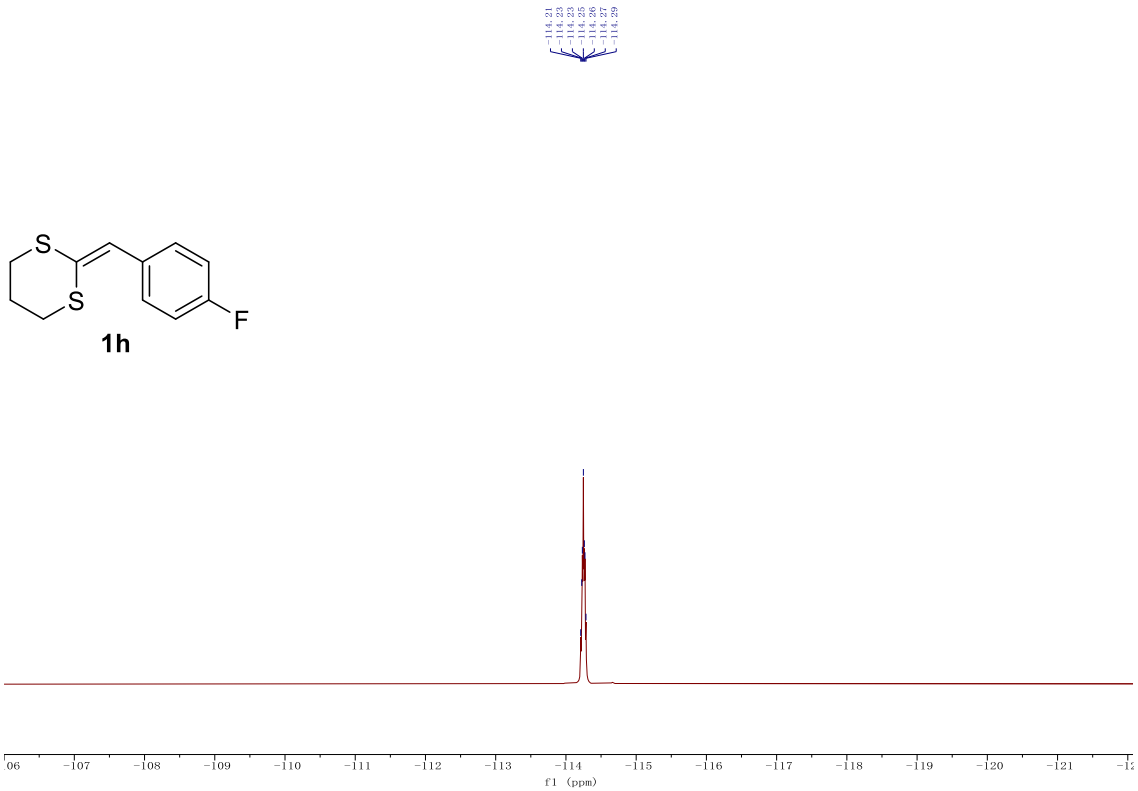
^{1}H NMR (400 MHz, $CDCl_3$)



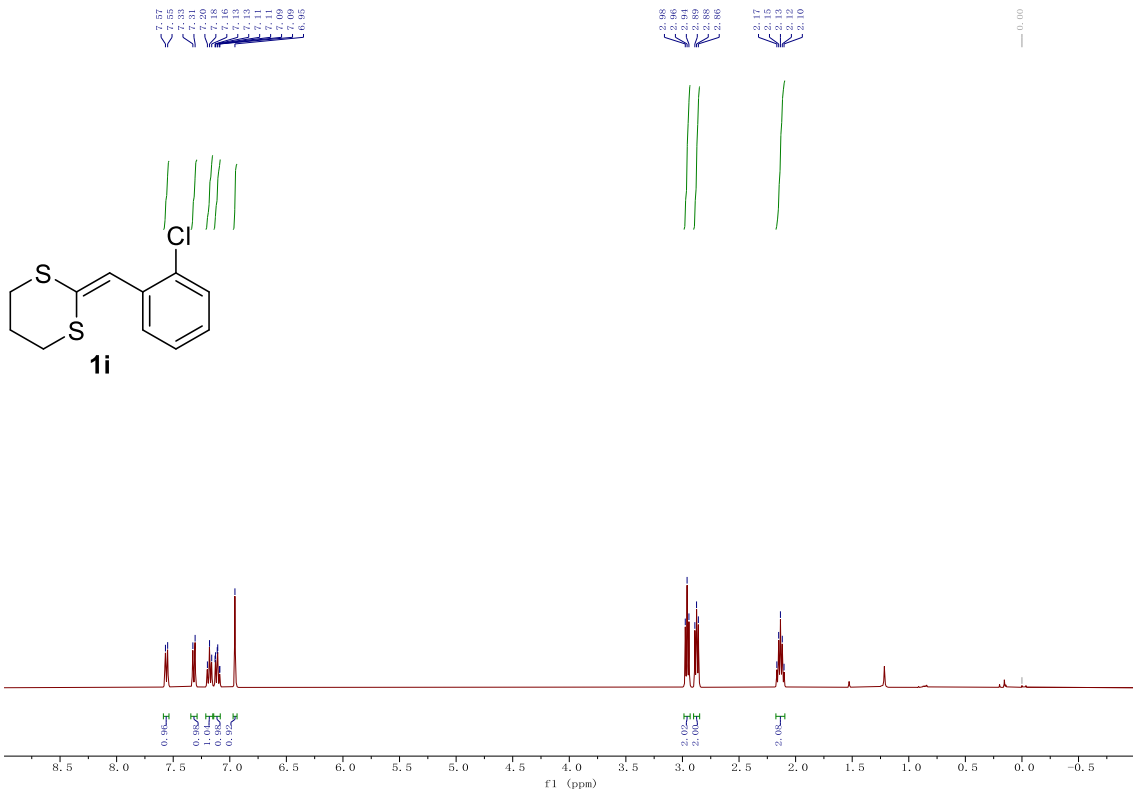
^{13}C NMR (101 MHz, $CDCl_3$)



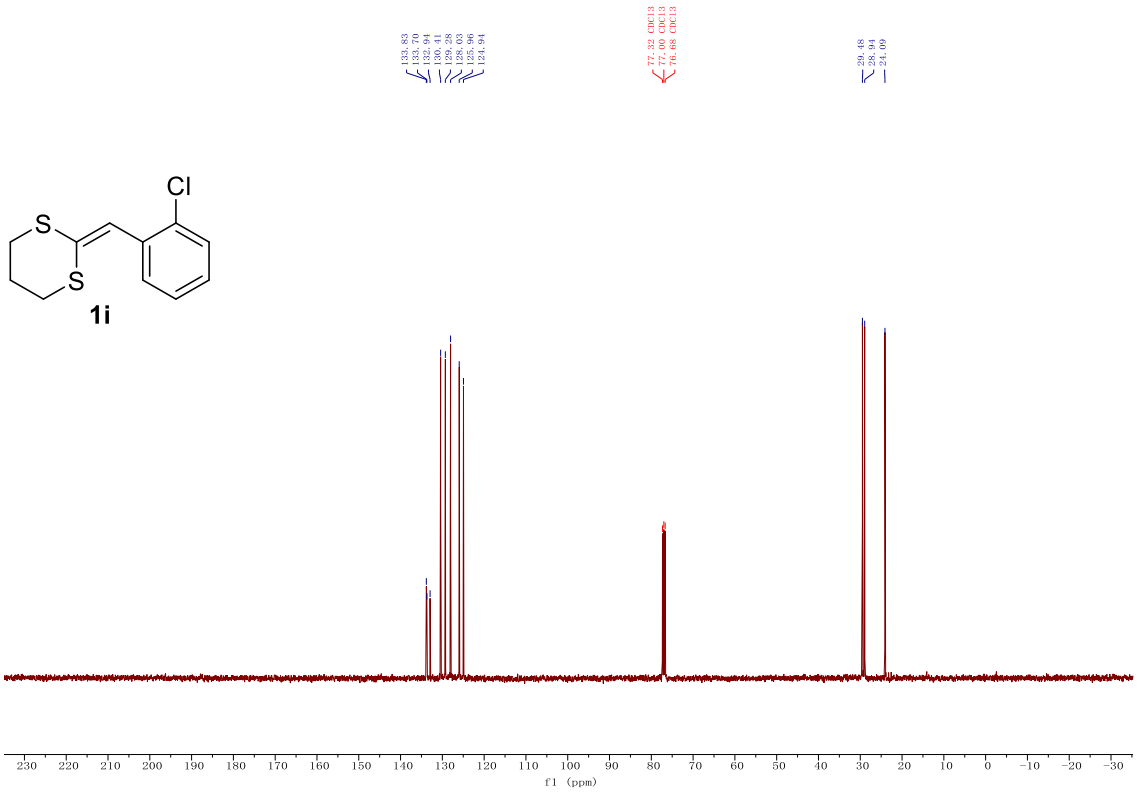
^{19}F NMR (376 MHz, $CDCl_3$)



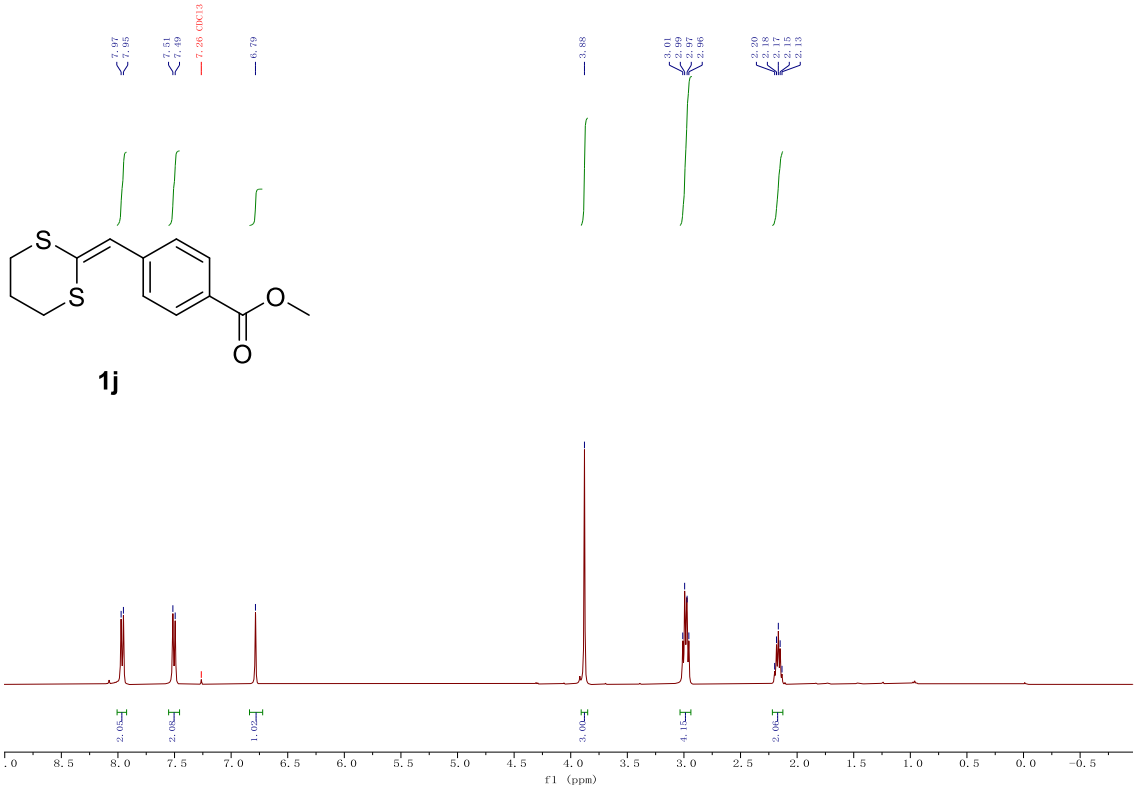
^{1}H NMR (400 MHz, $CDCl_3$)



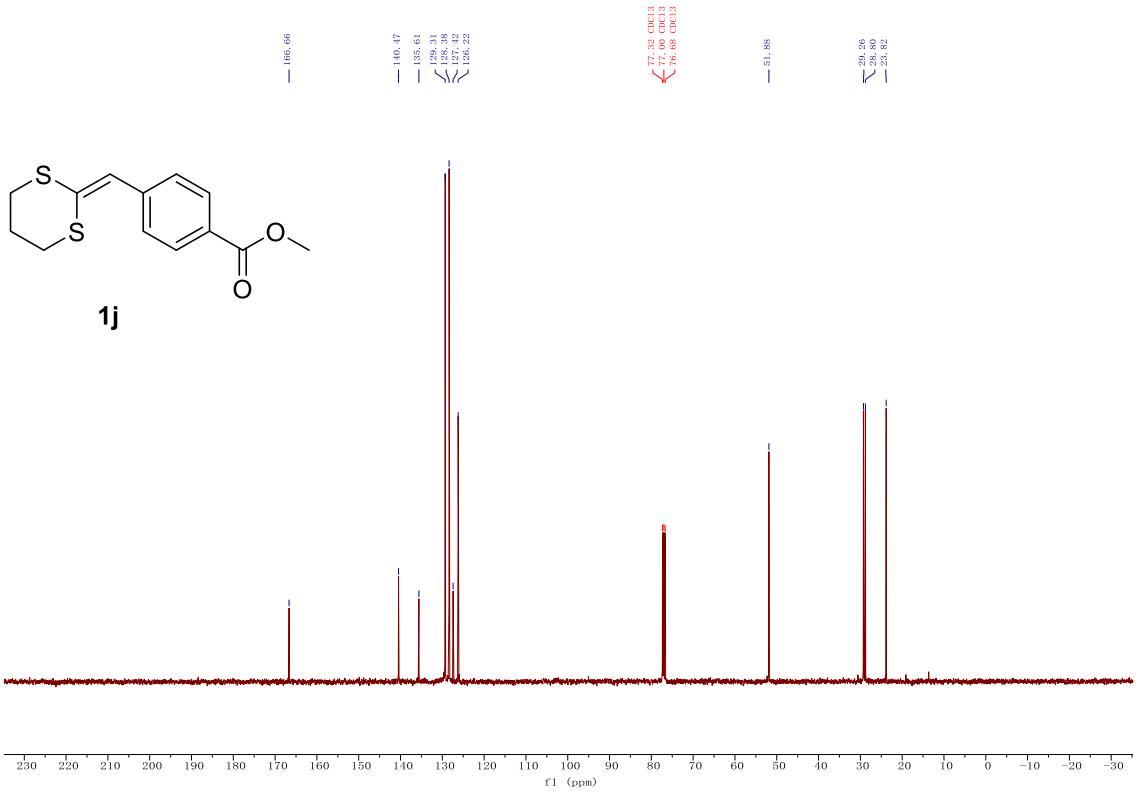
^{13}C NMR (101 MHz, $CDCl_3$)



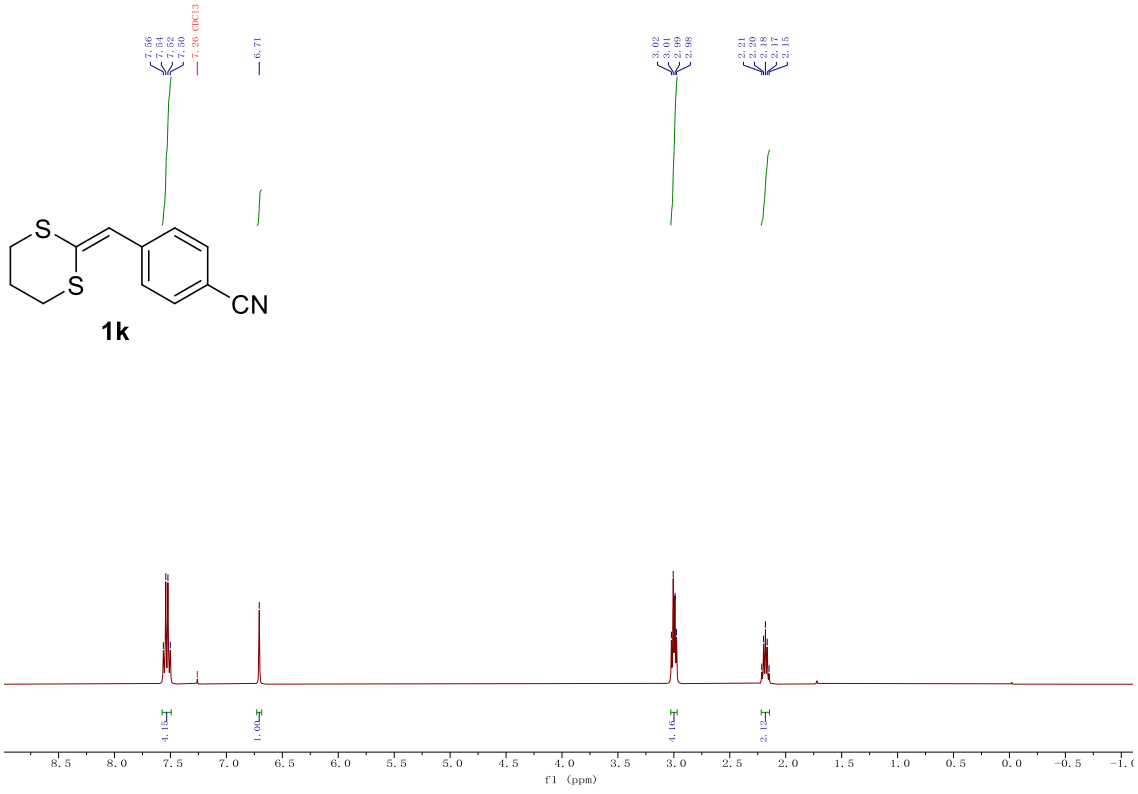
^{1}H NMR (400 MHz, $CDCl_3$)



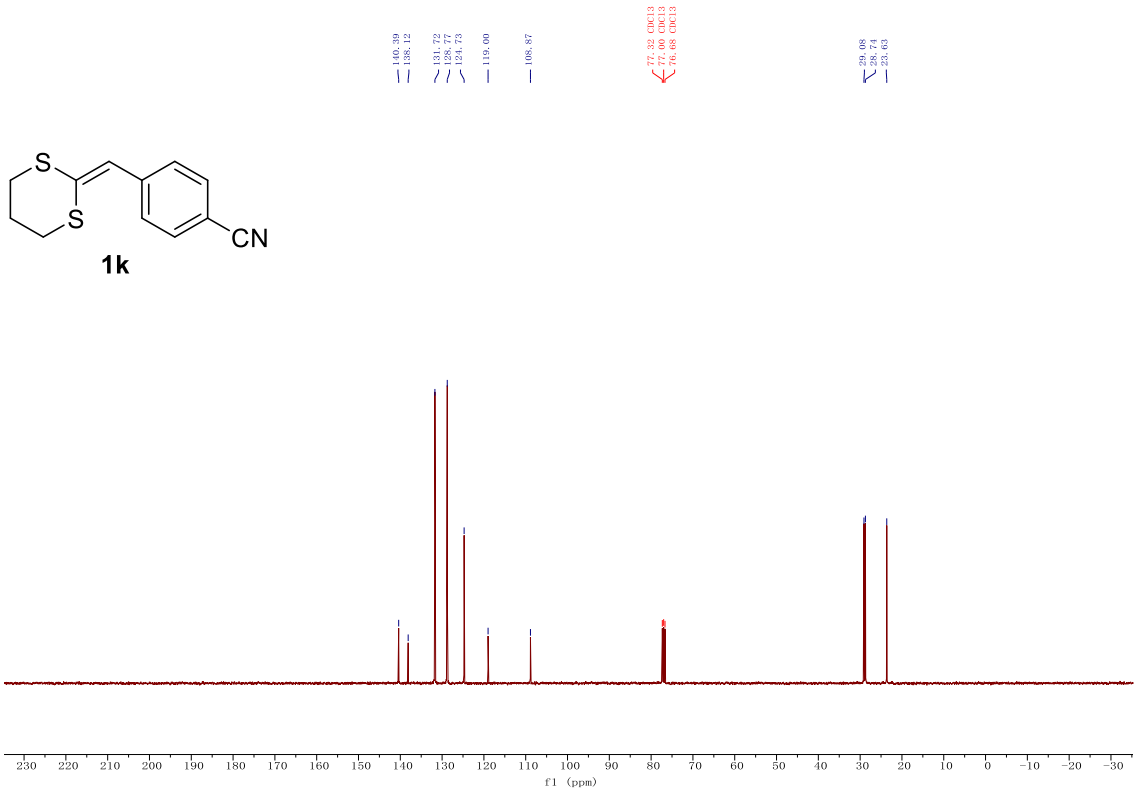
^{13}C NMR (101 MHz, $CDCl_3$)



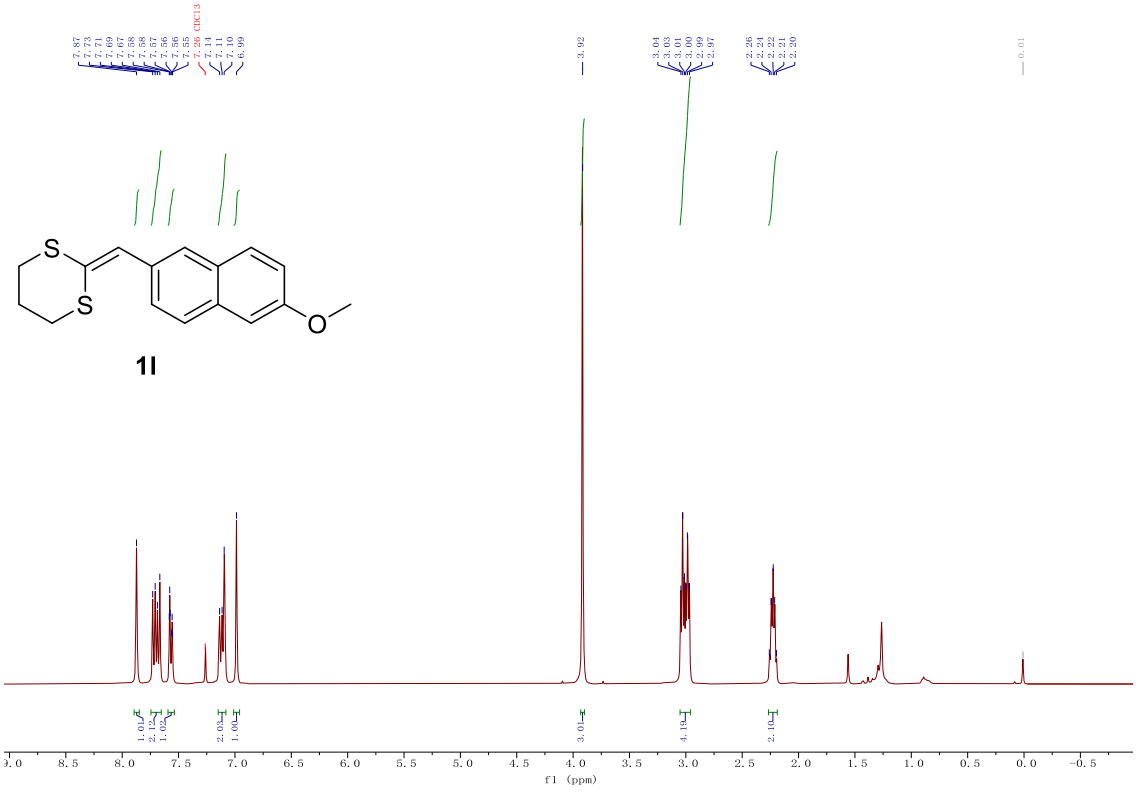
^{1}H NMR (400 MHz, $CDCl_3$)



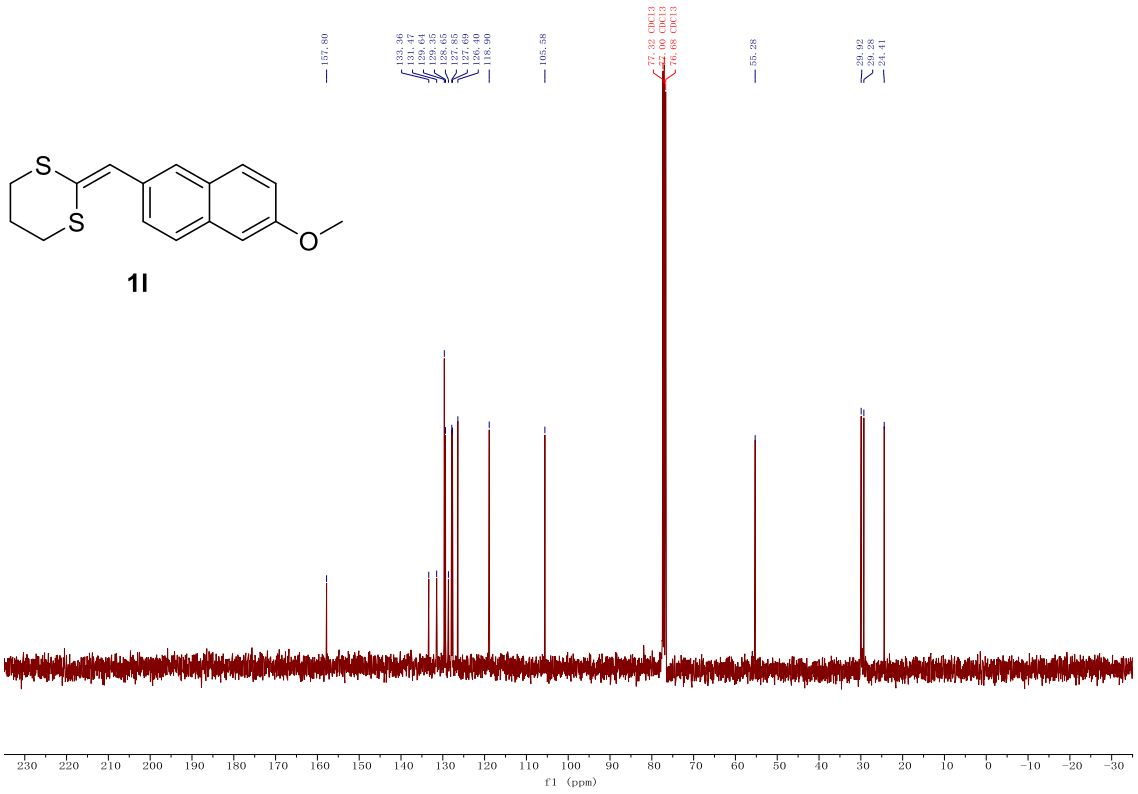
^{13}C NMR (101 MHz, $CDCl_3$)



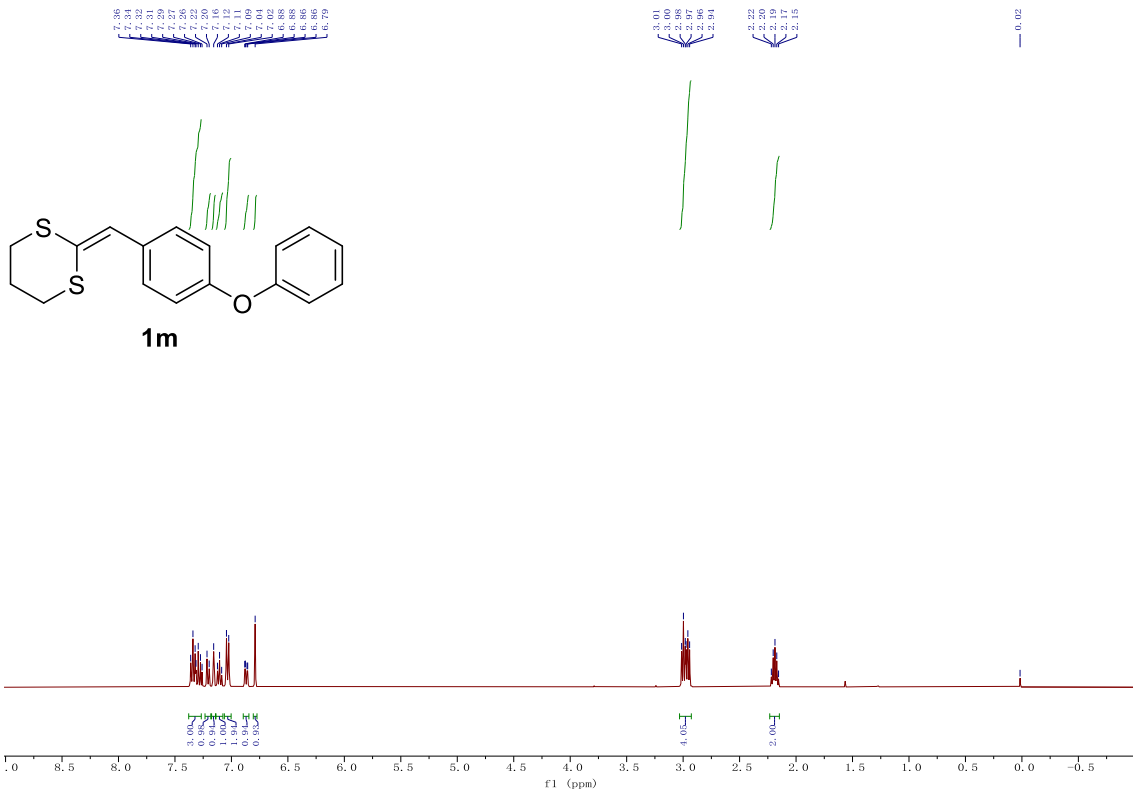
^{1}H NMR (400 MHz, $CDCl_3$)



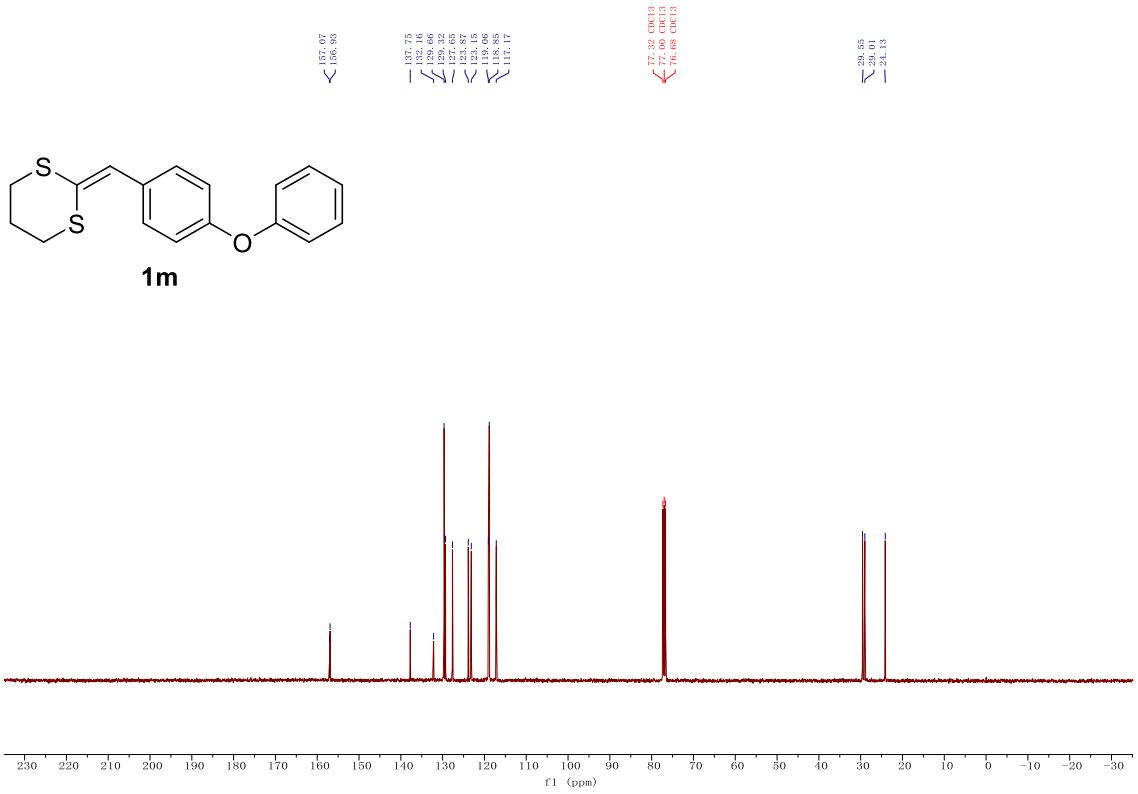
^{13}C NMR (101 MHz, $CDCl_3$)



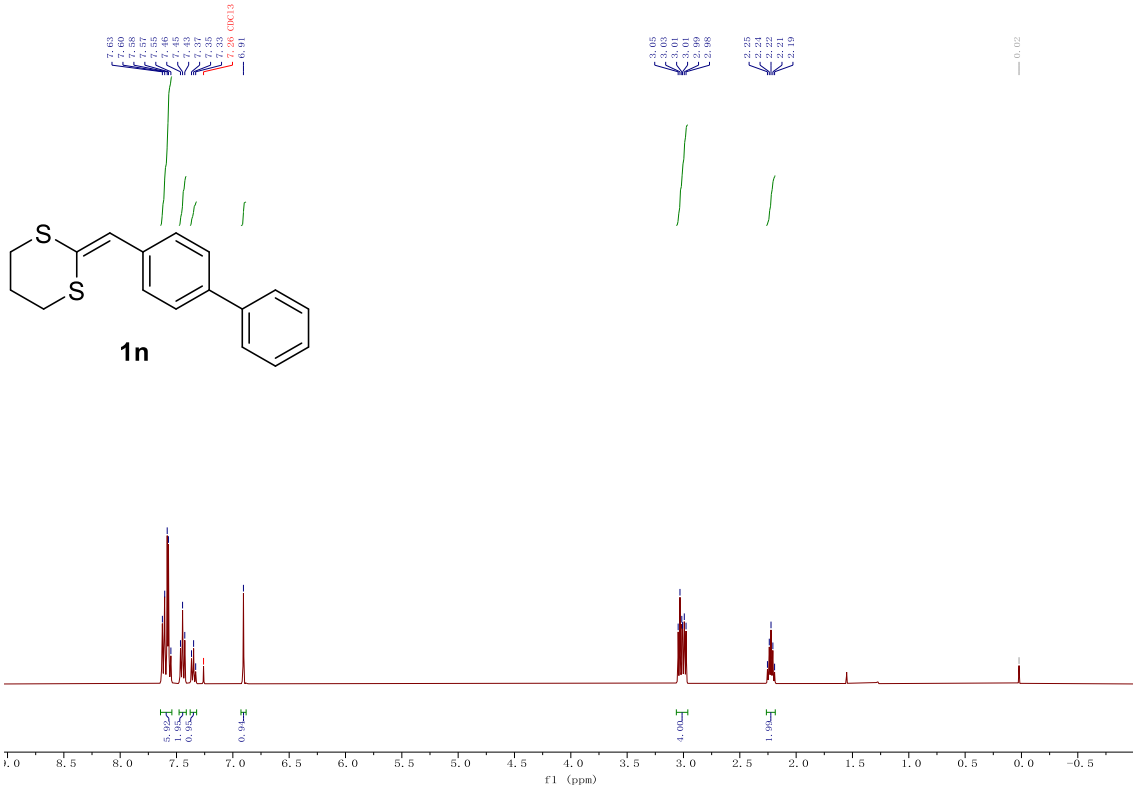
^{1}H NMR (400 MHz, $CDCl_3$)



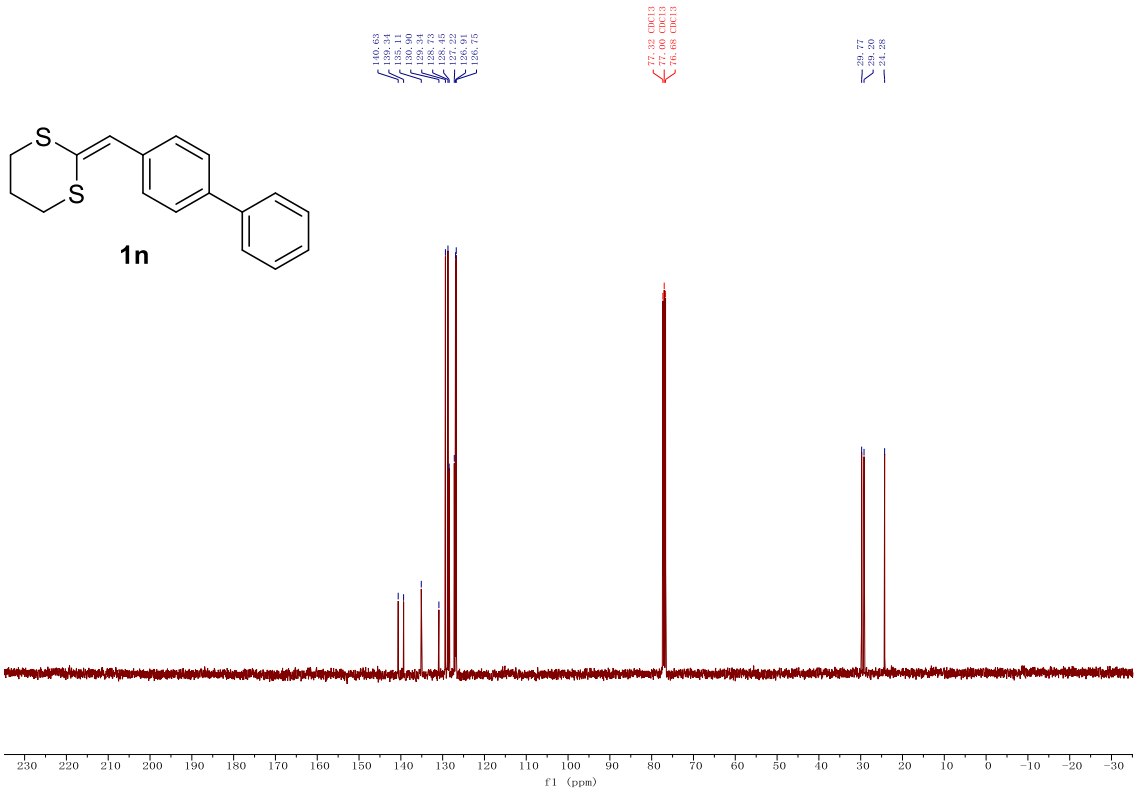
^{13}C NMR (101 MHz, $CDCl_3$)



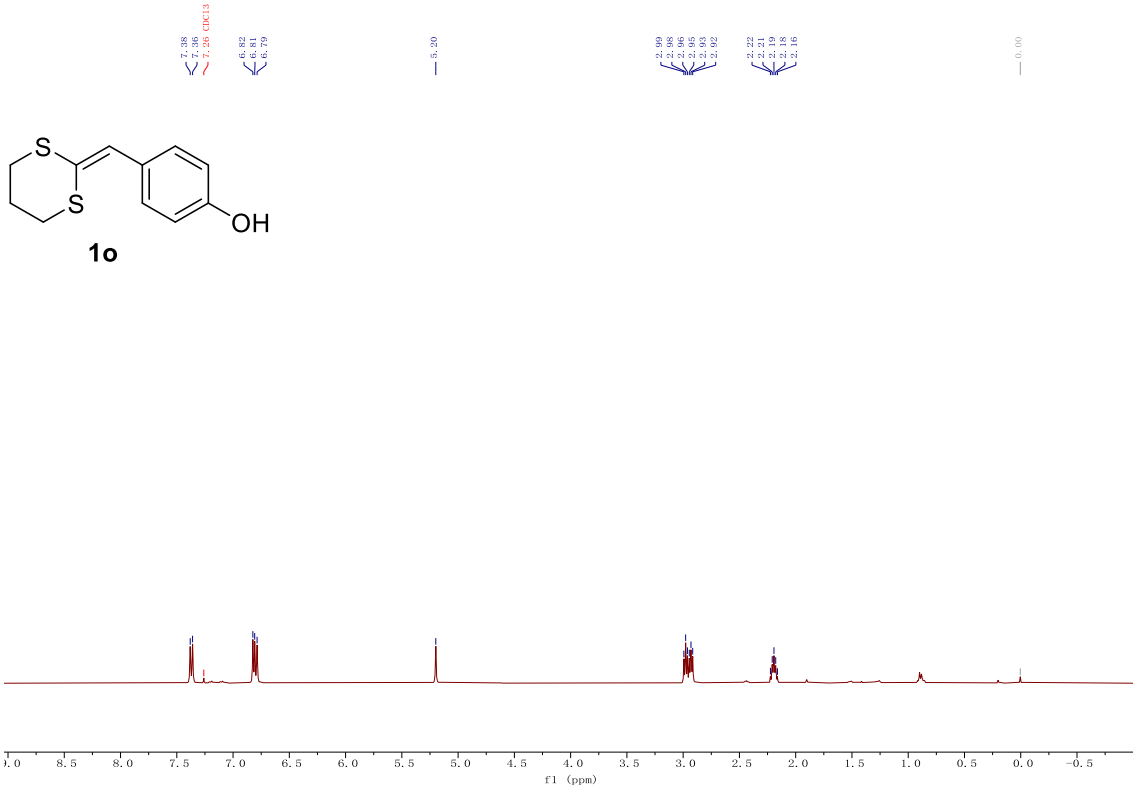
^{1}H NMR (400 MHz, $CDCl_3$)



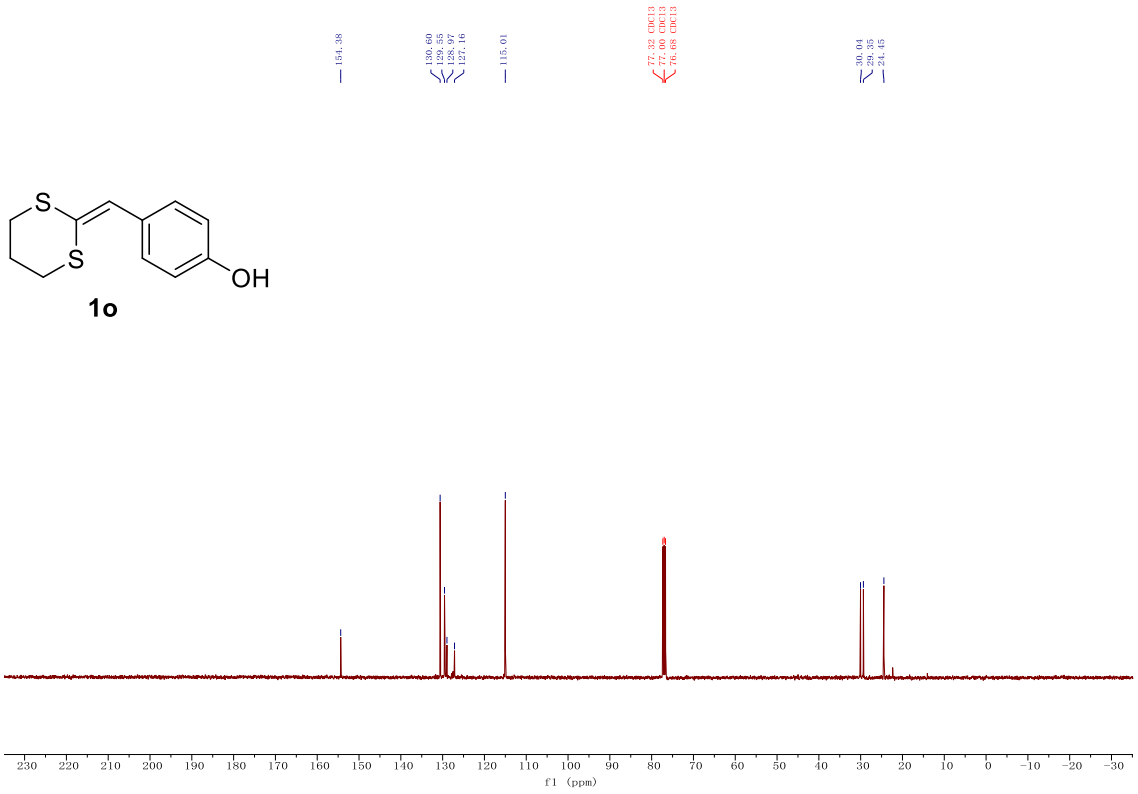
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

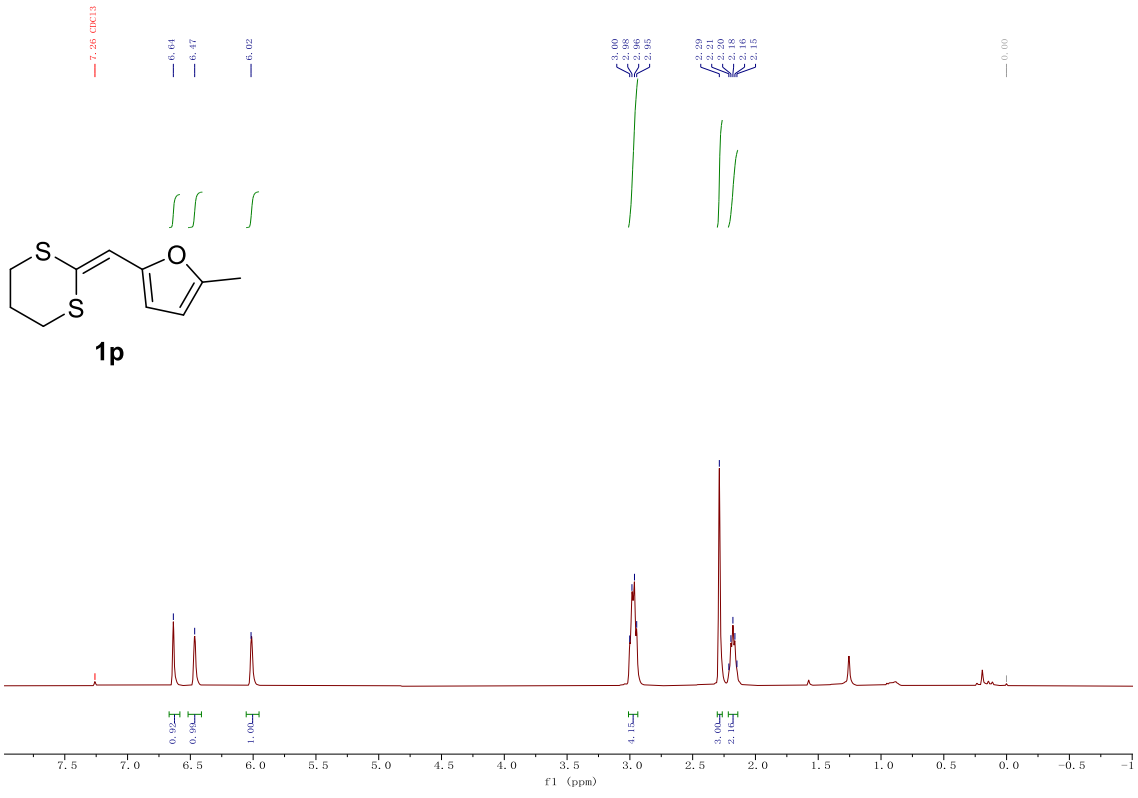


^{13}C NMR (101 MHz, $CDCl_3$)



1o

^{1}H NMR (400 MHz, $CDCl_3$)



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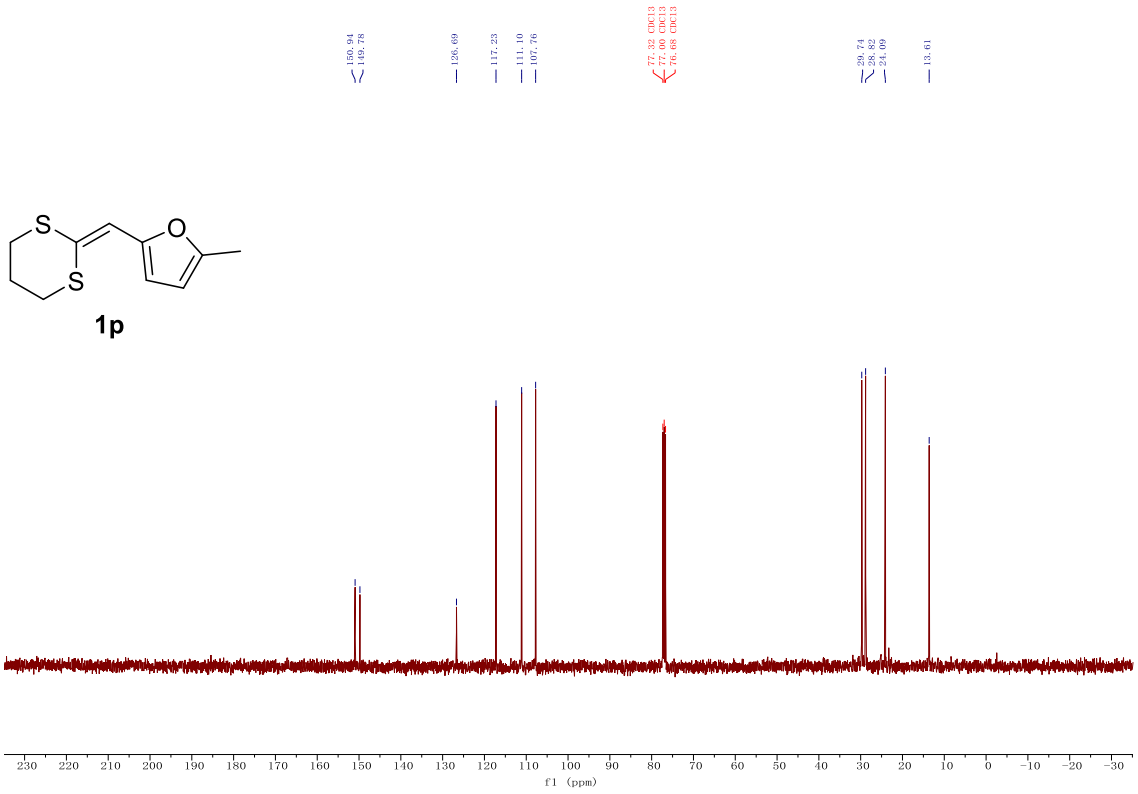
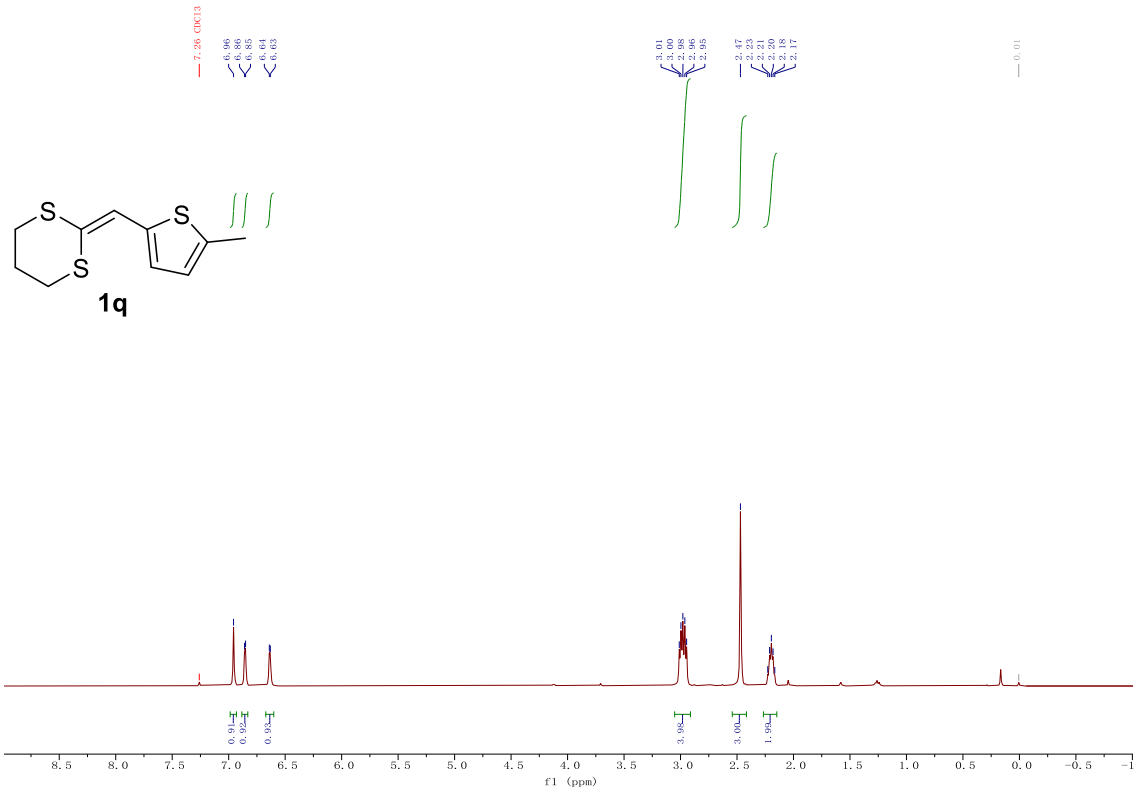
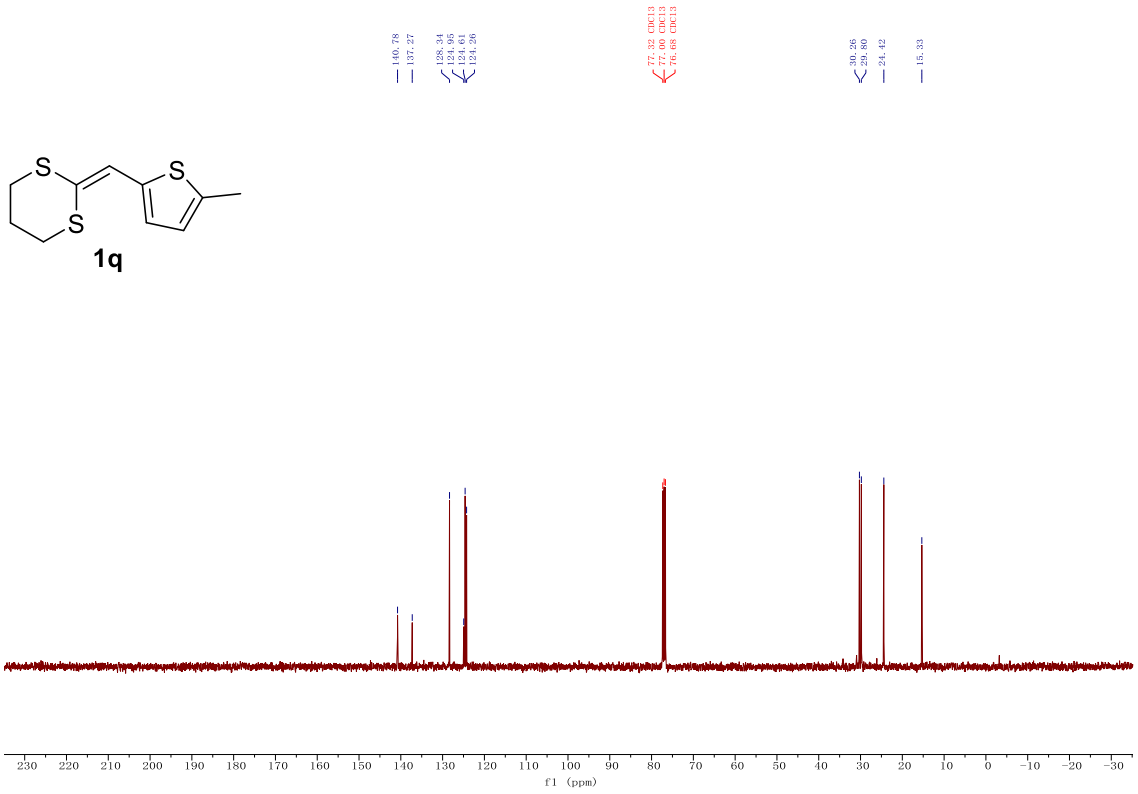
^{13}C NMR (101 MHz, $CDCl_3$)



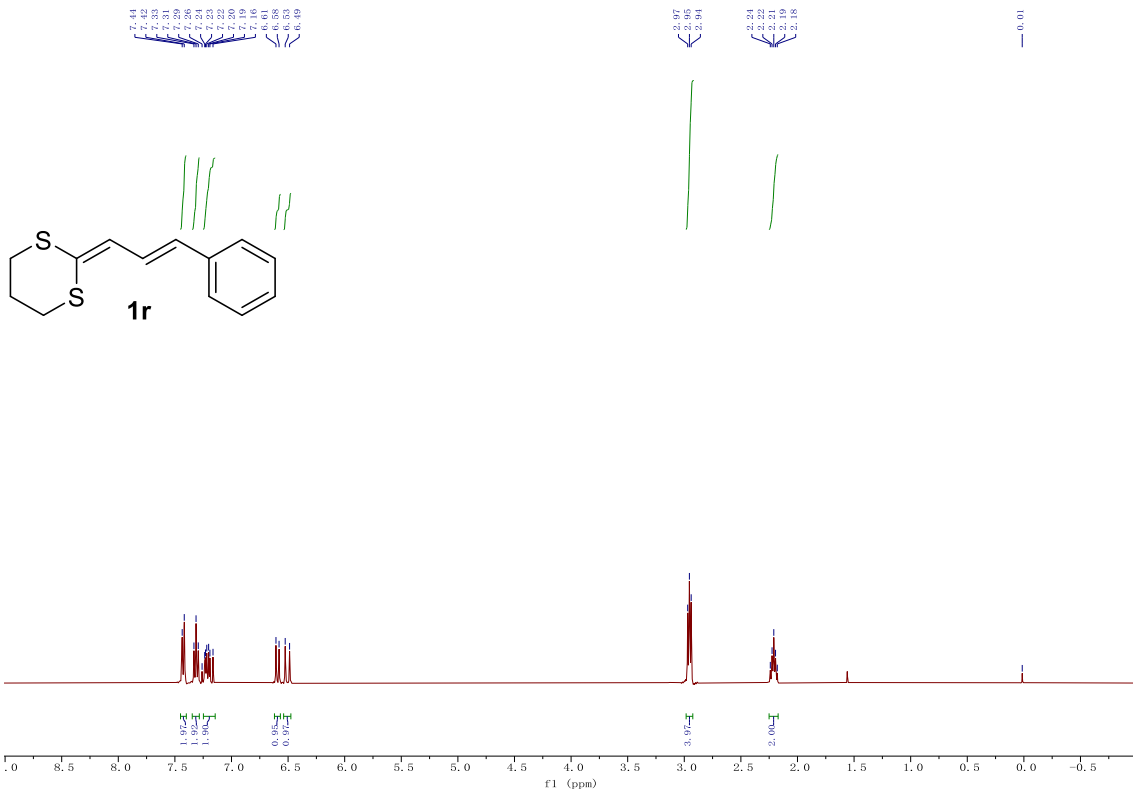
^{1}H NMR (400 MHz, $CDCl_3$)



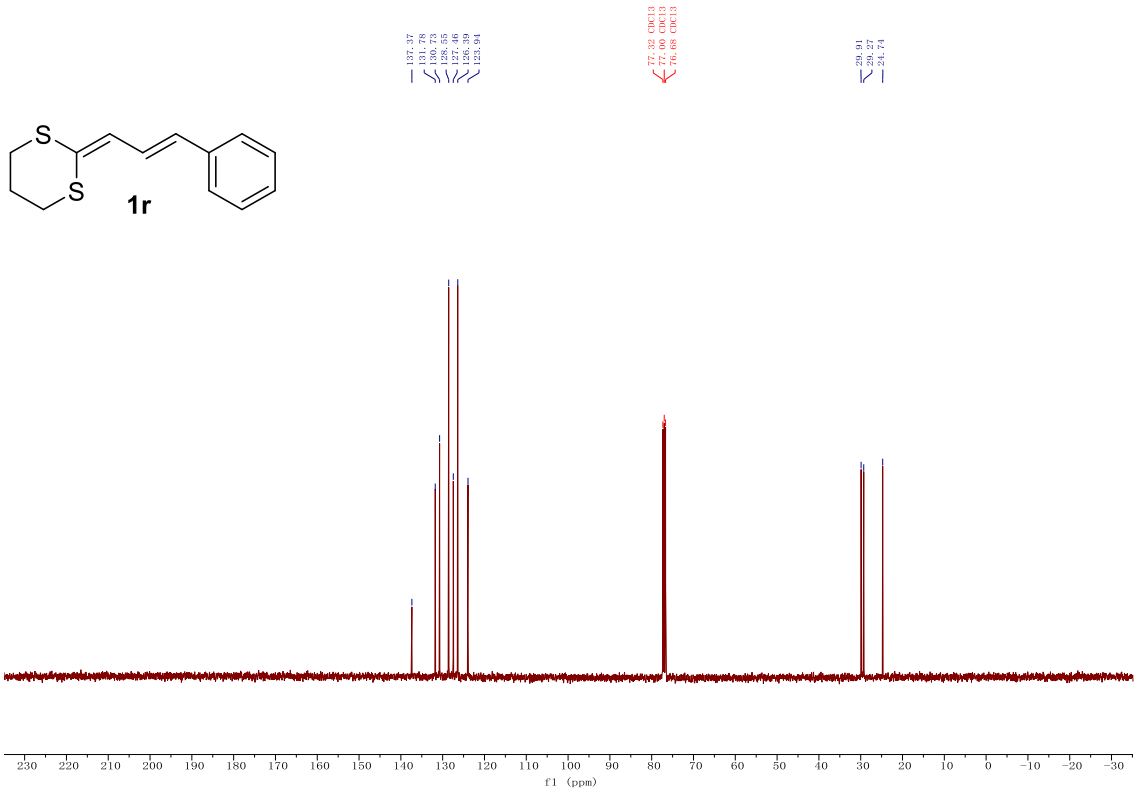
^{13}C NMR (101 MHz, $CDCl_3$)



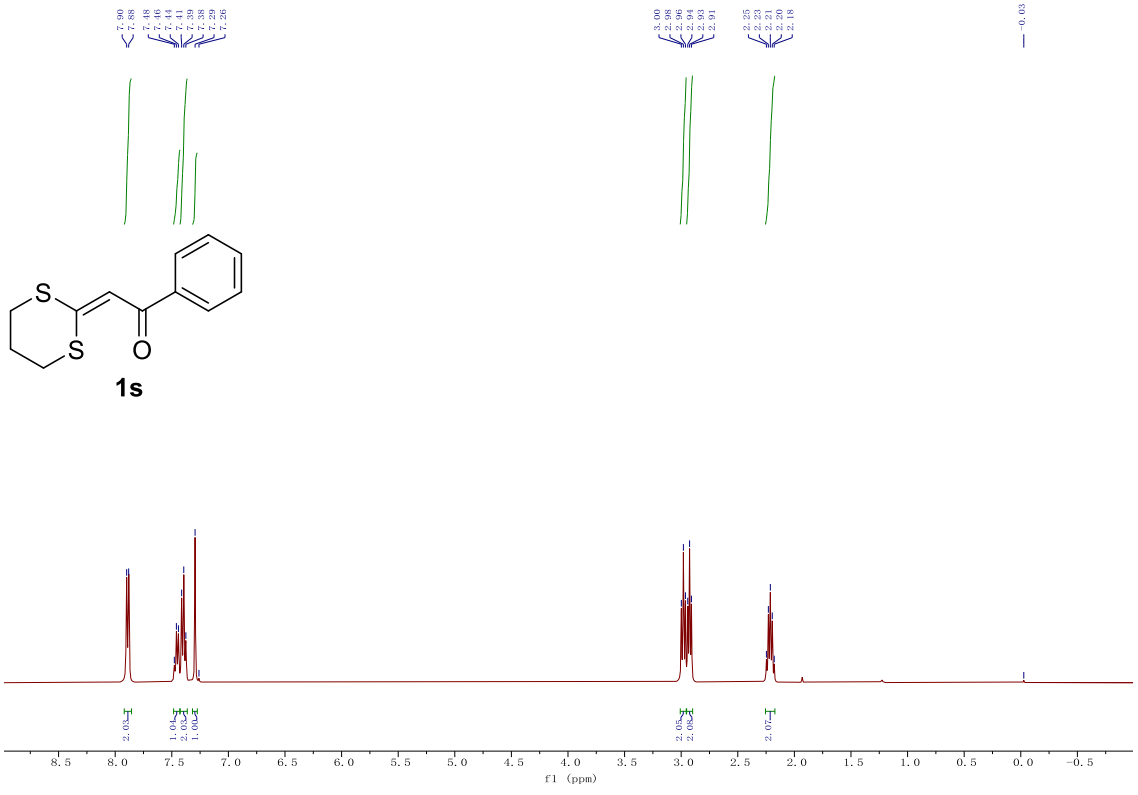
^{1}H NMR (400 MHz, $CDCl_3$)



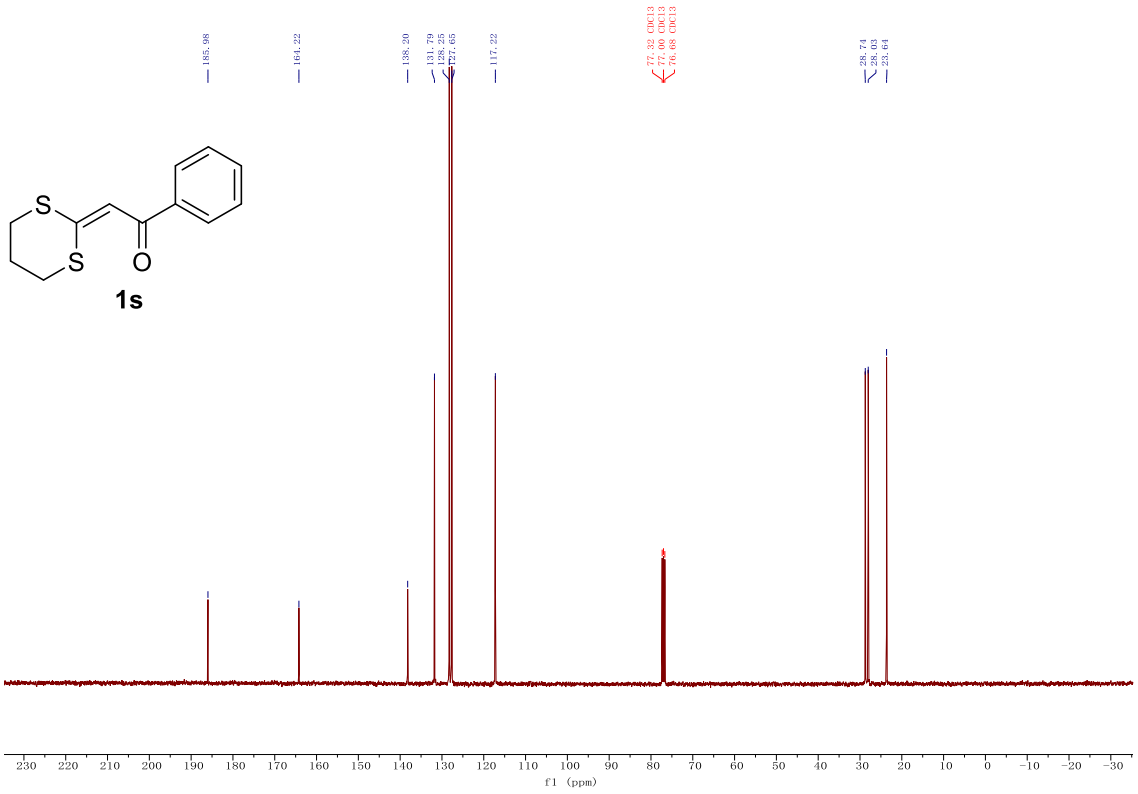
^{13}C NMR (101 MHz, $CDCl_3$)



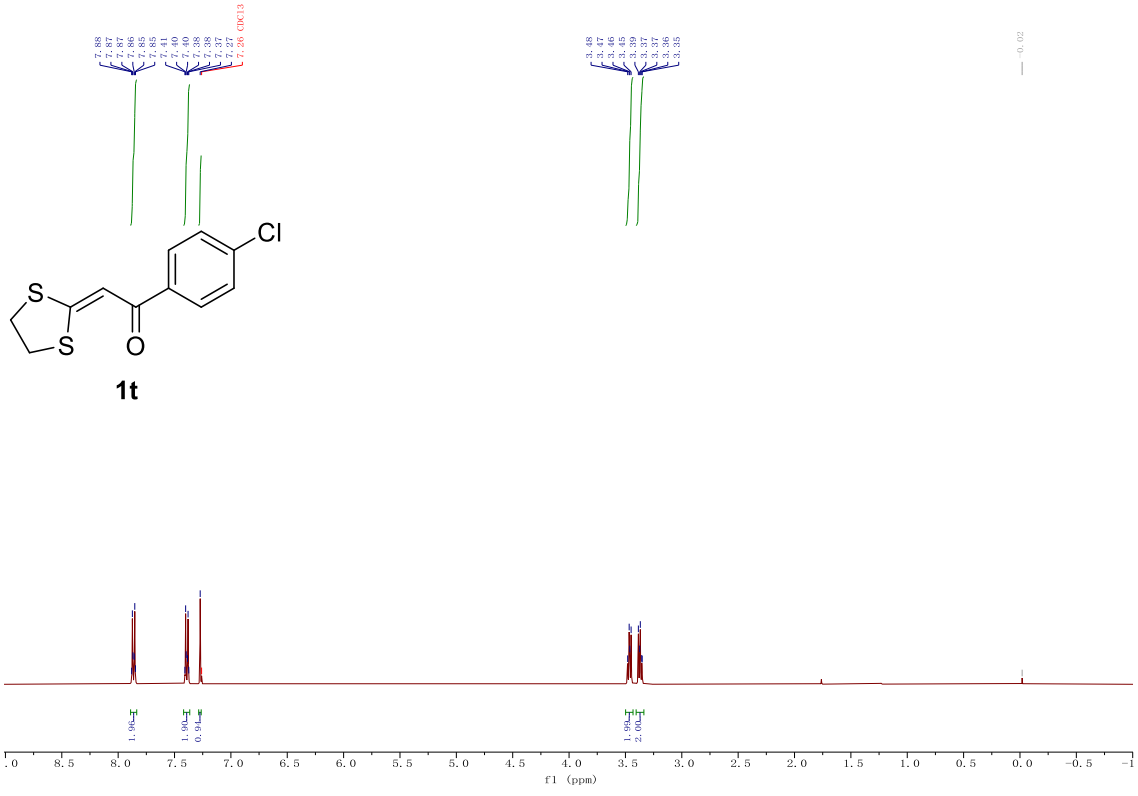
^{1}H NMR (400 MHz, $CDCl_3$)



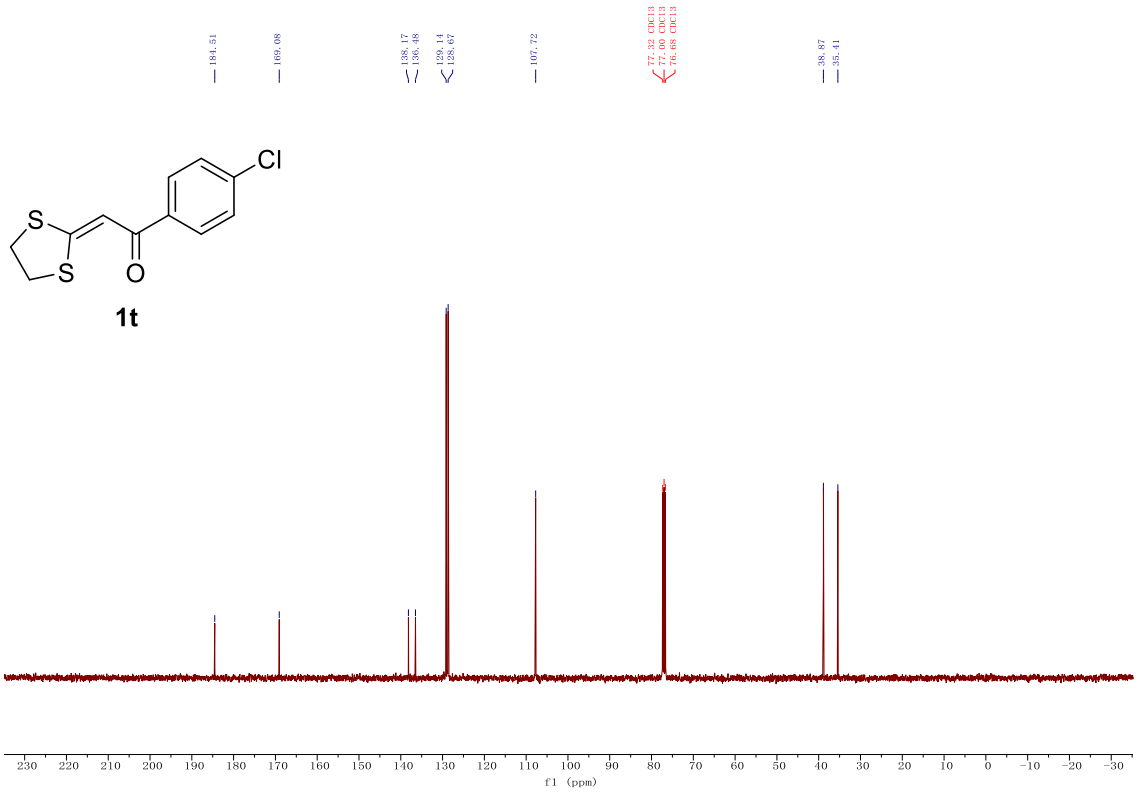
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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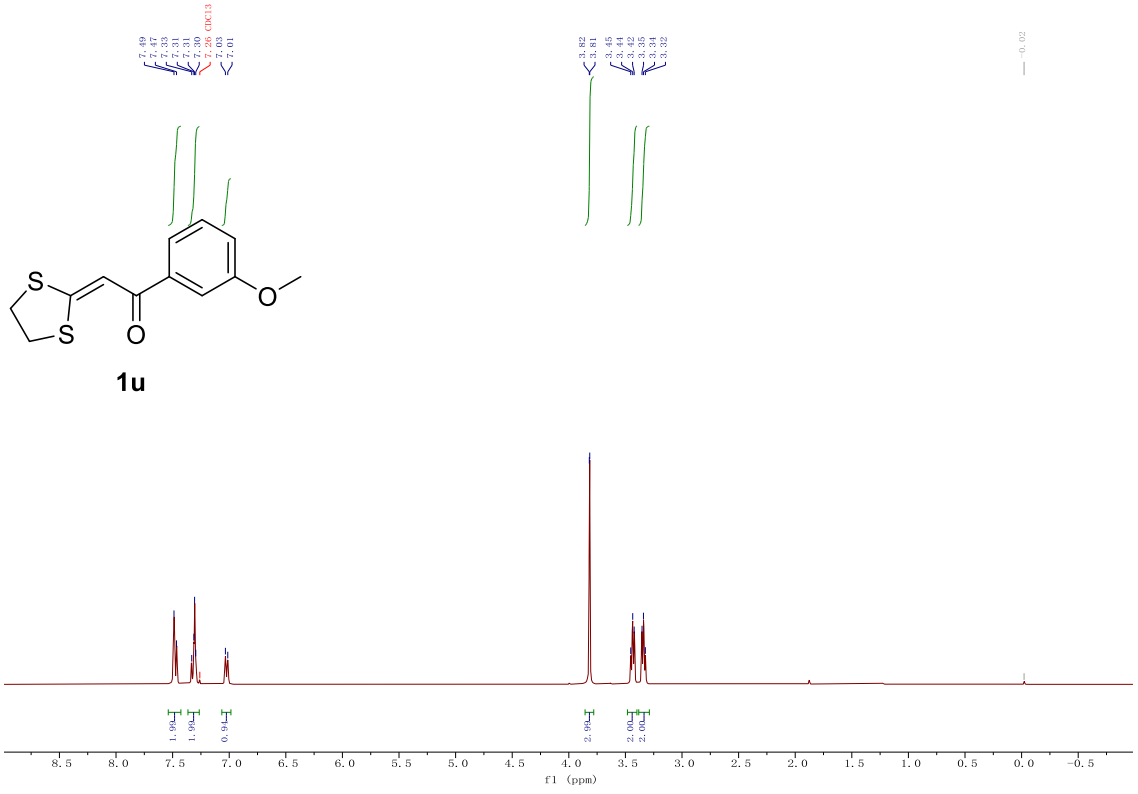
^{1}H NMR (400 MHz, $CDCl_3$)



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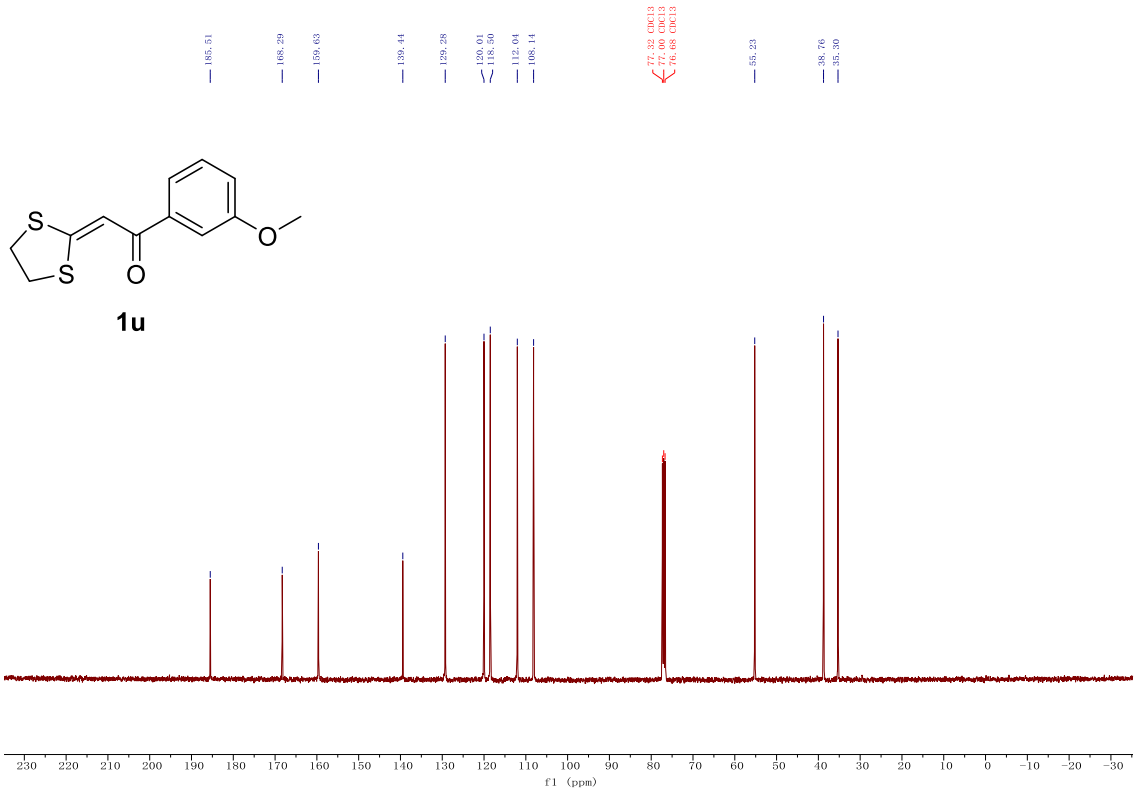
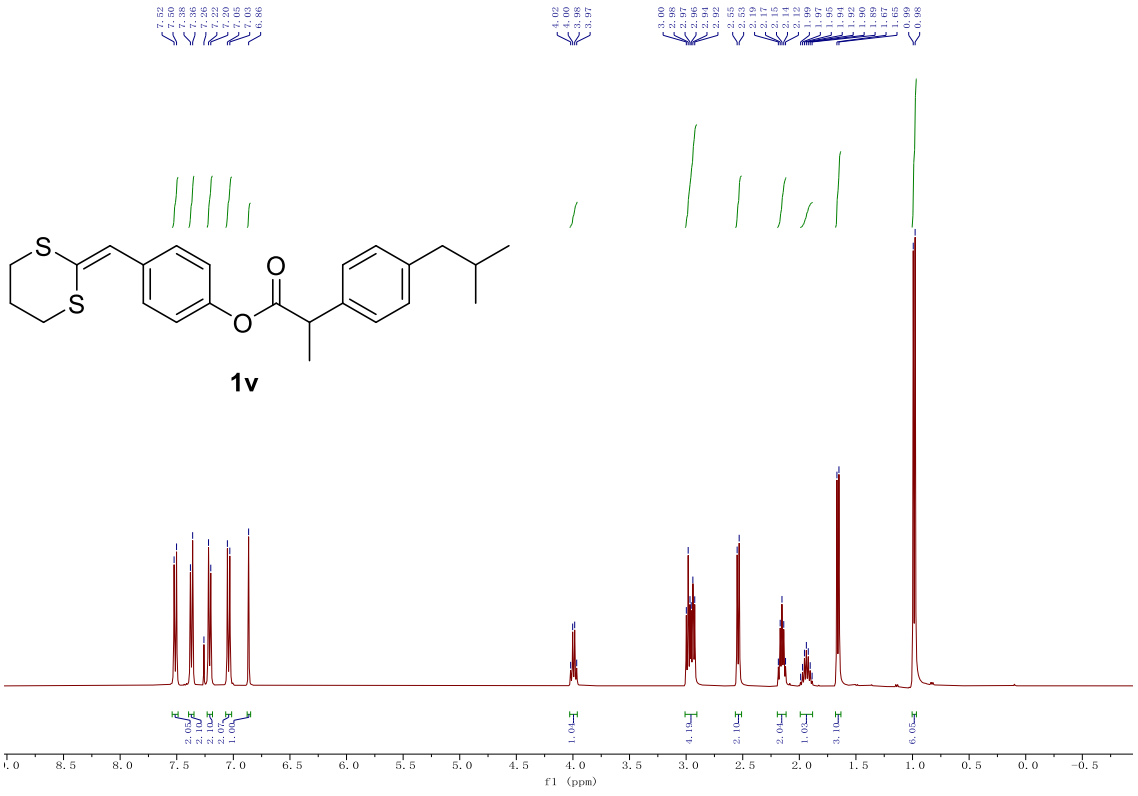
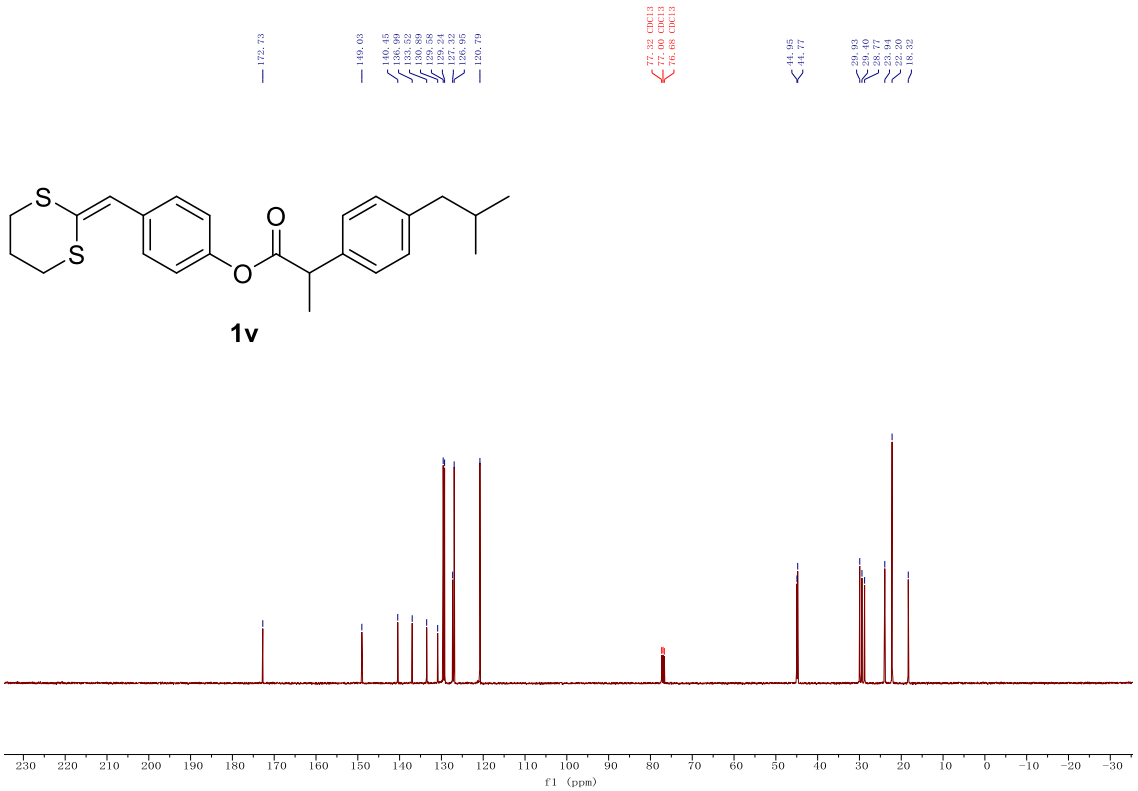
^{13}C NMR (101 MHz, $CDCl_3$)



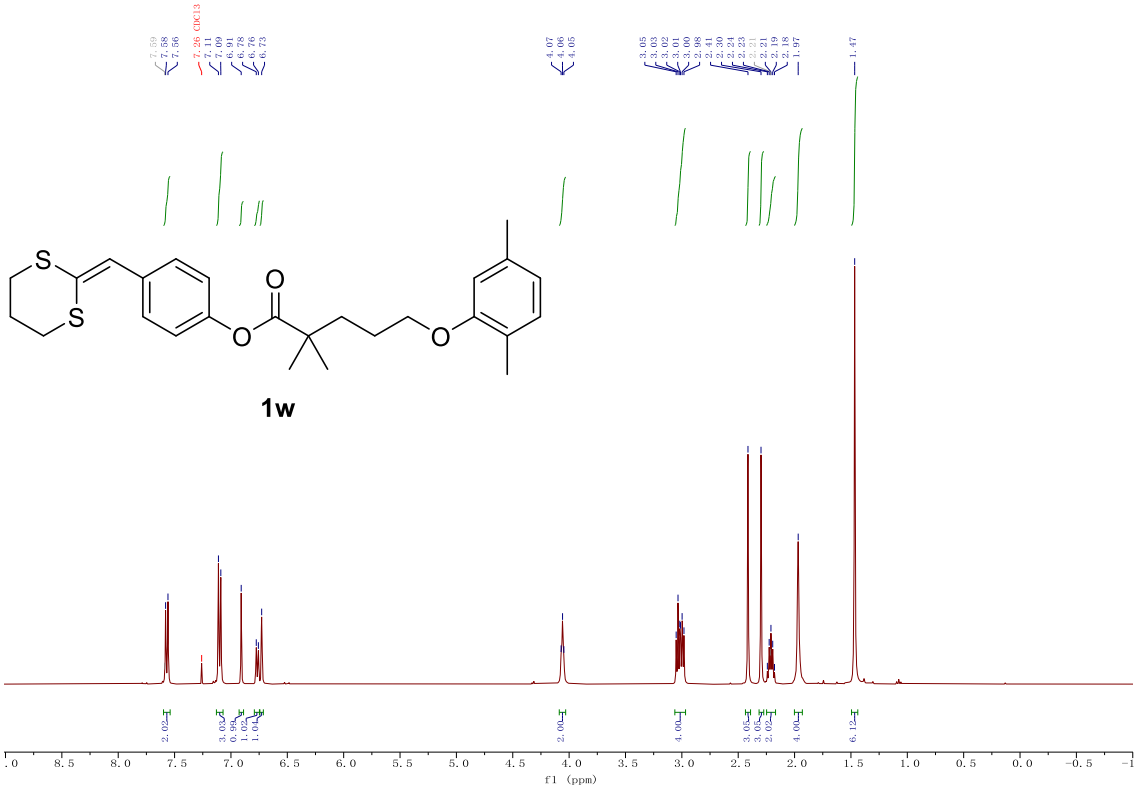
^{1}H NMR (400 MHz, $CDCl_3$)



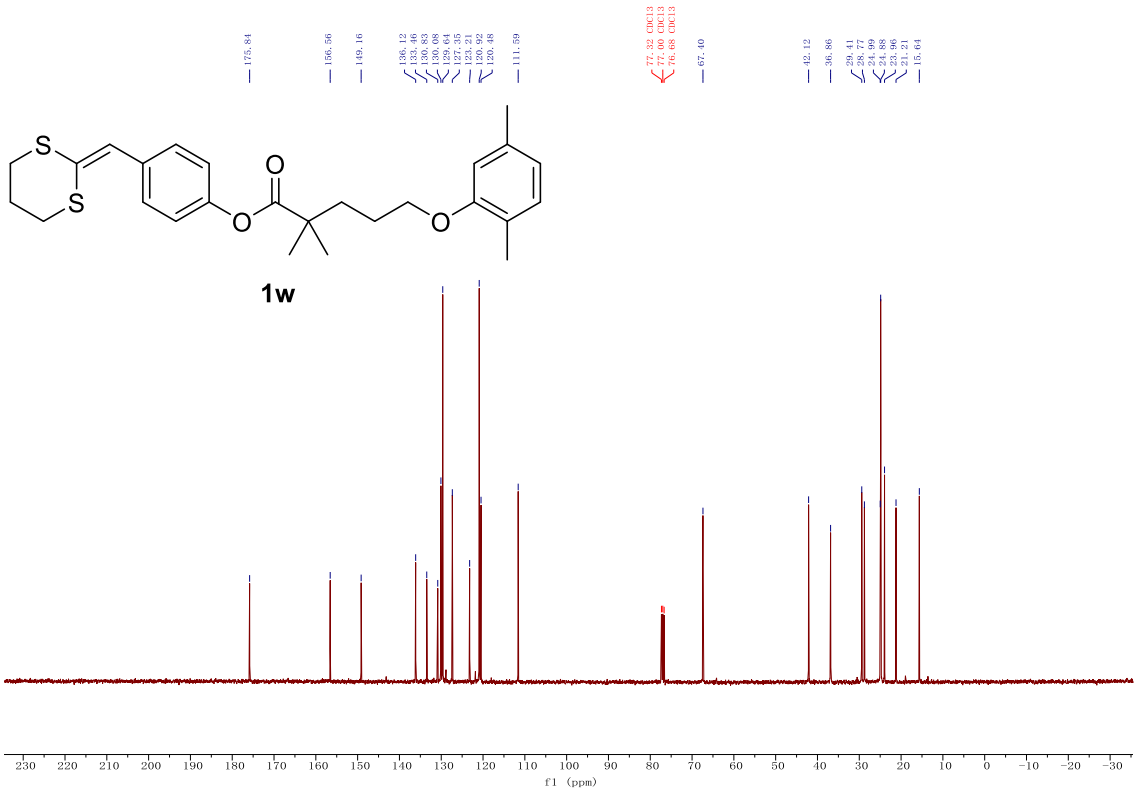
^{13}C NMR (101 MHz, $CDCl_3$)



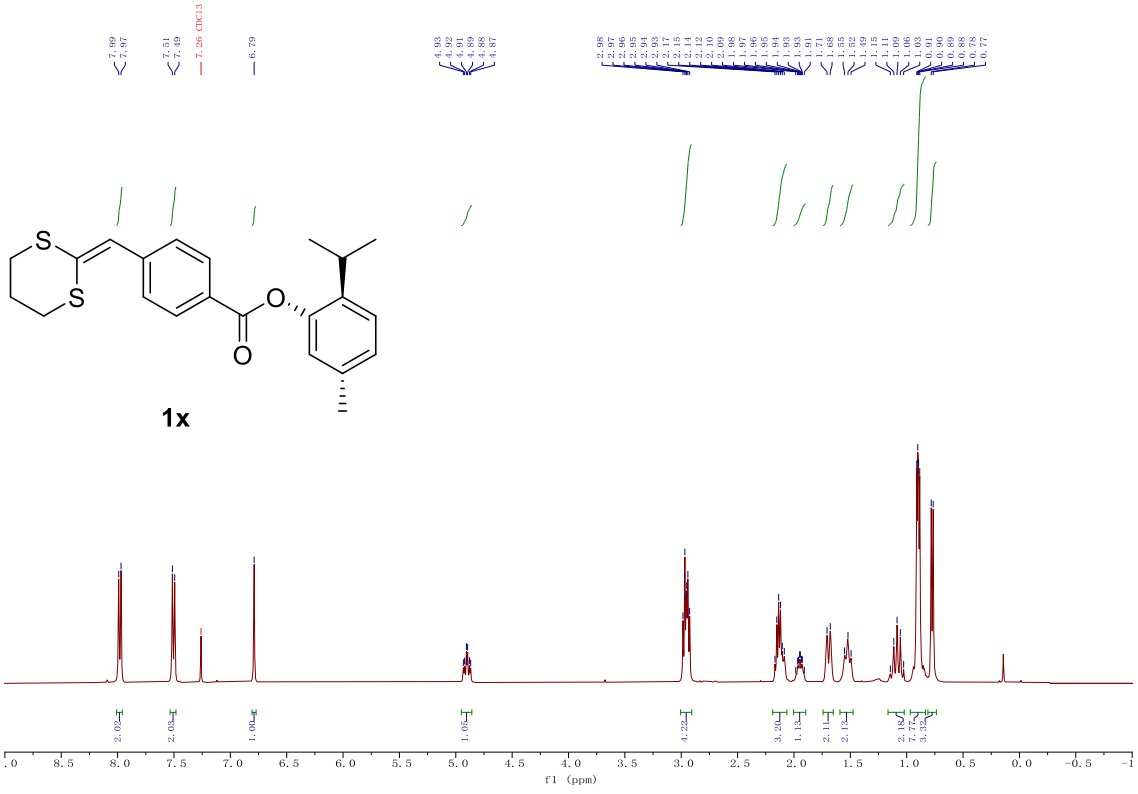
^{1}H NMR (400 MHz, $CDCl_3$)



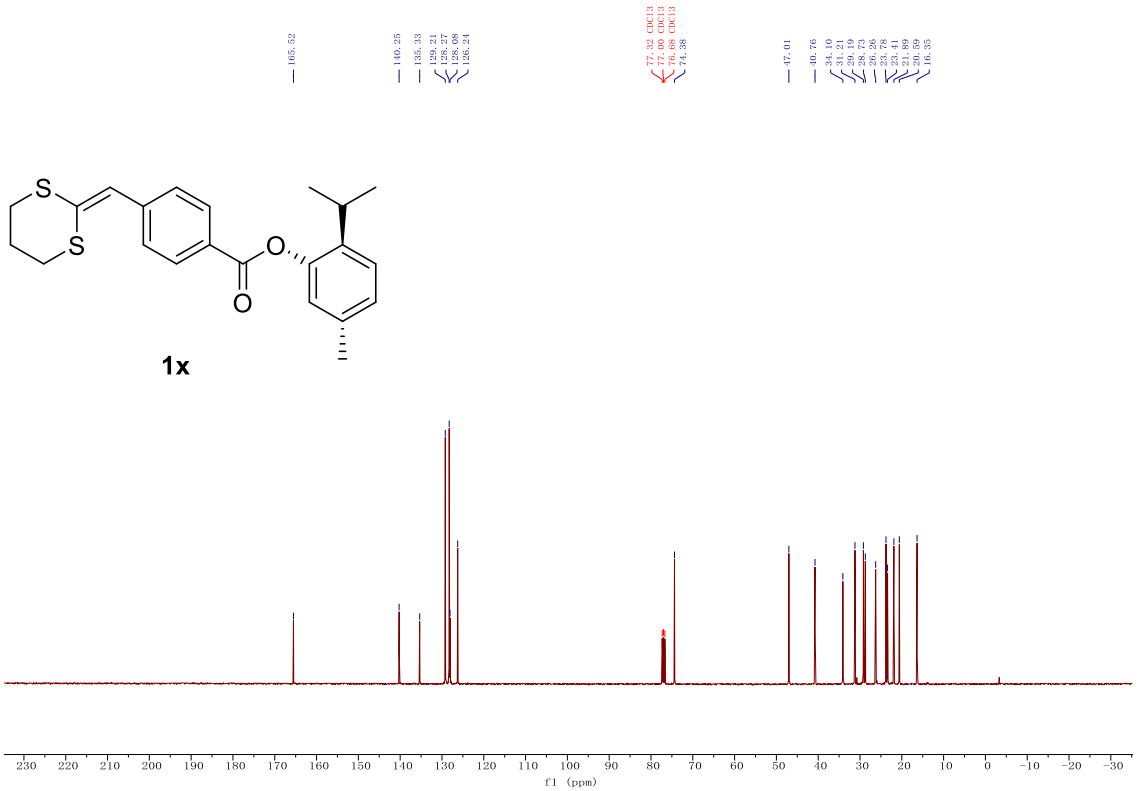
^{13}C NMR (101 MHz, $CDCl_3$)



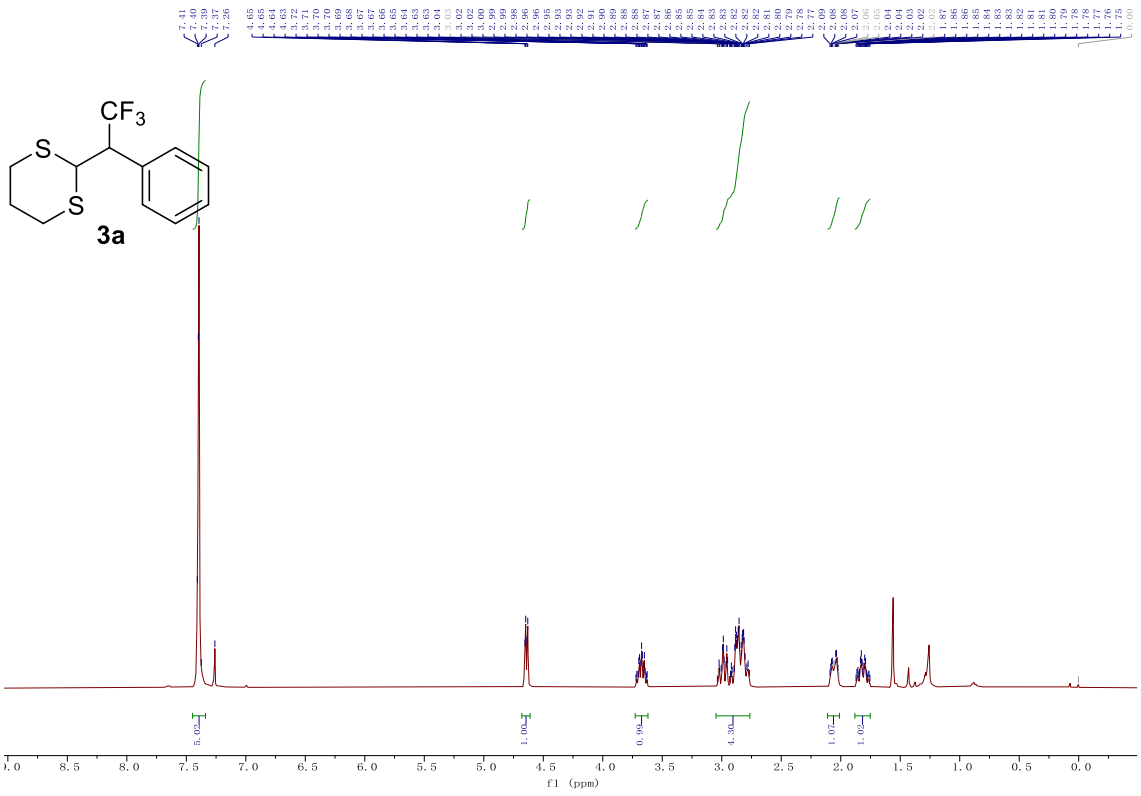
^{1}H NMR (400 MHz, $CDCl_3$)



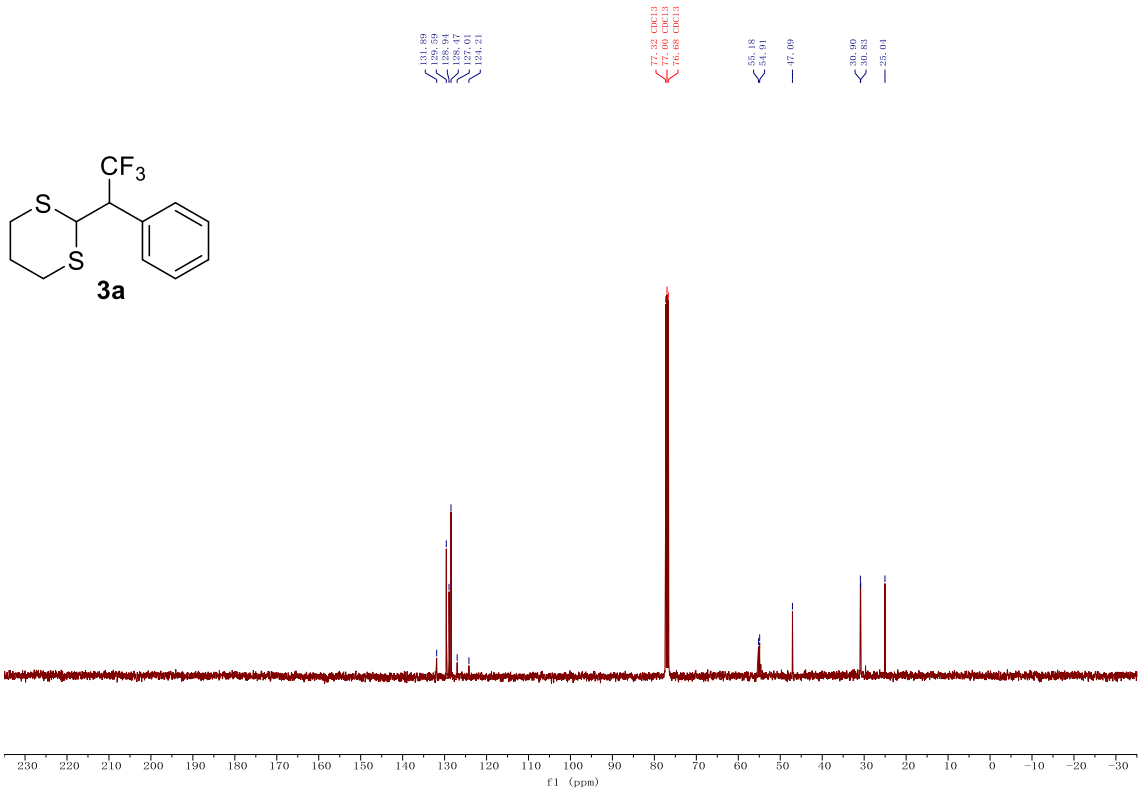
^{13}C NMR (101 MHz, $CDCl_3$)



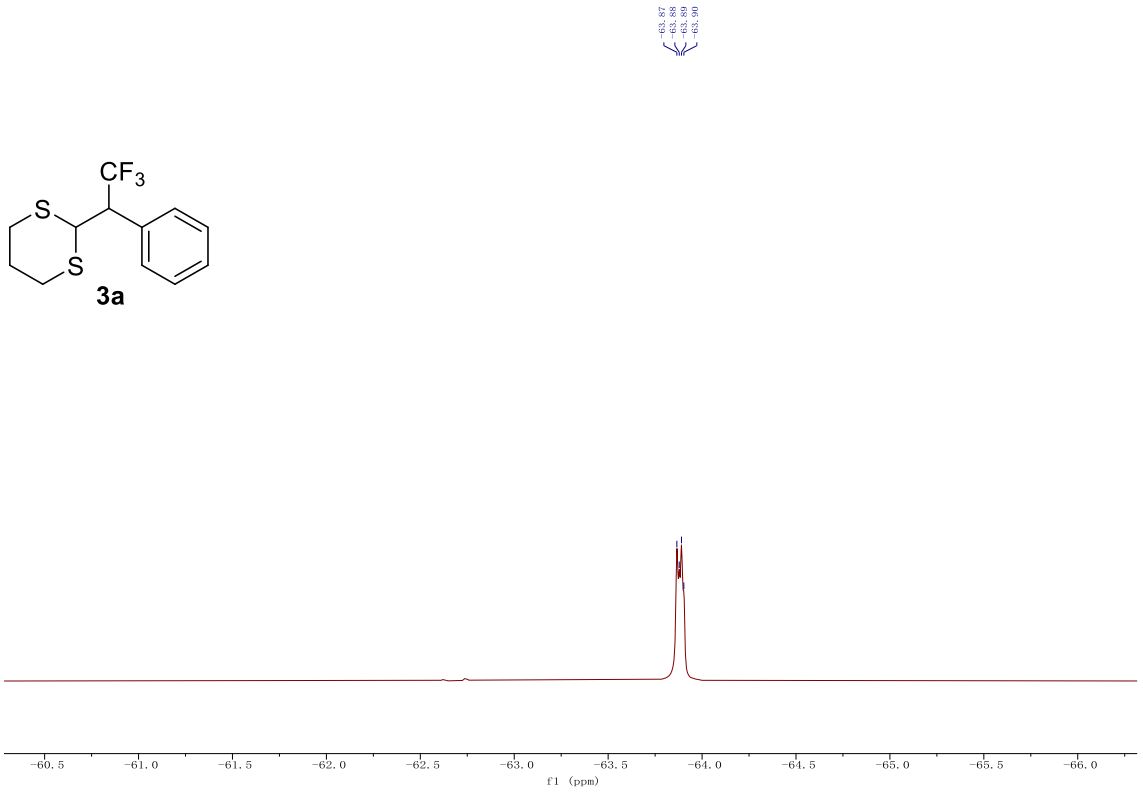
^{1}H NMR (400 MHz, $CDCl_3$)



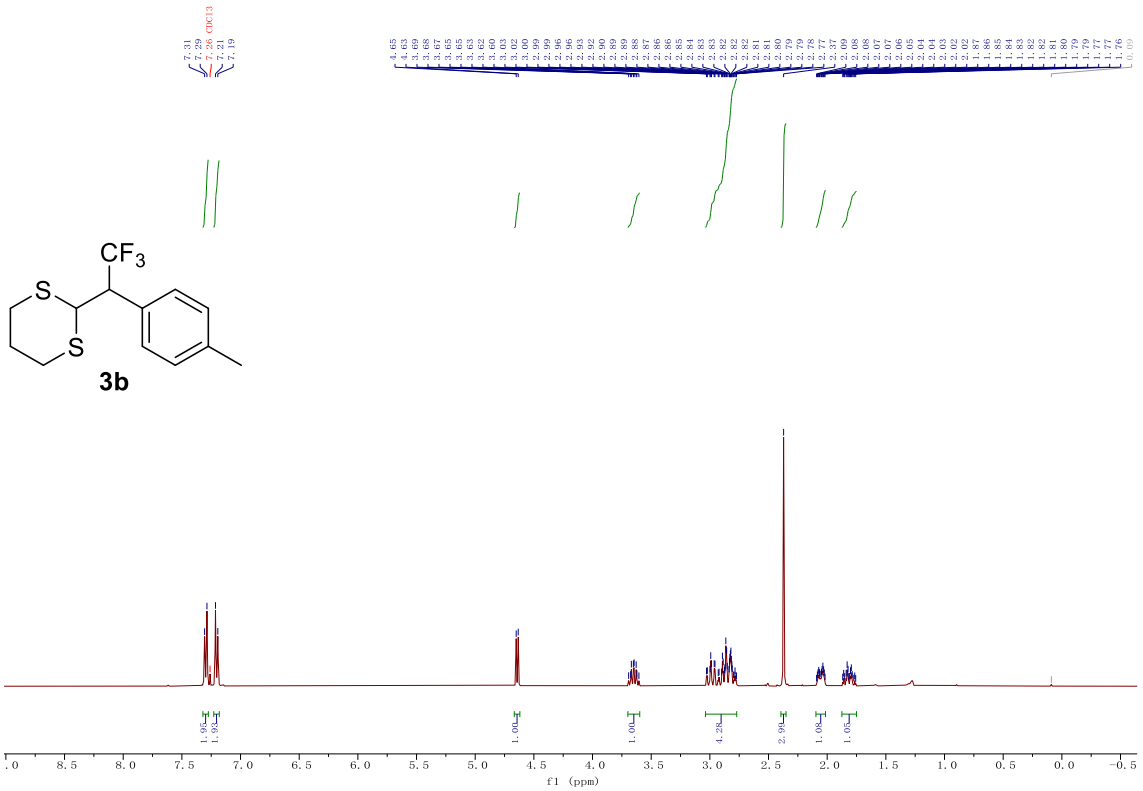
^{13}C NMR (101 MHz, $CDCl_3$)



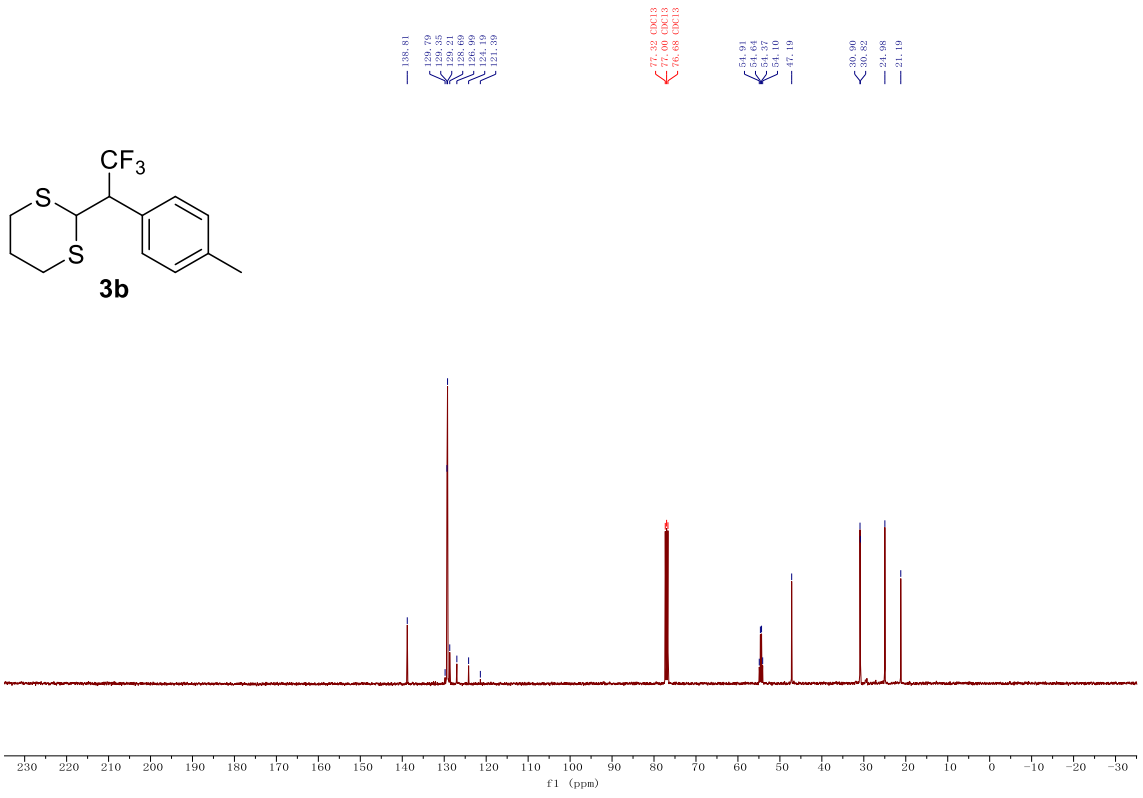
^{19}F NMR (376 MHz, $CDCl_3$)



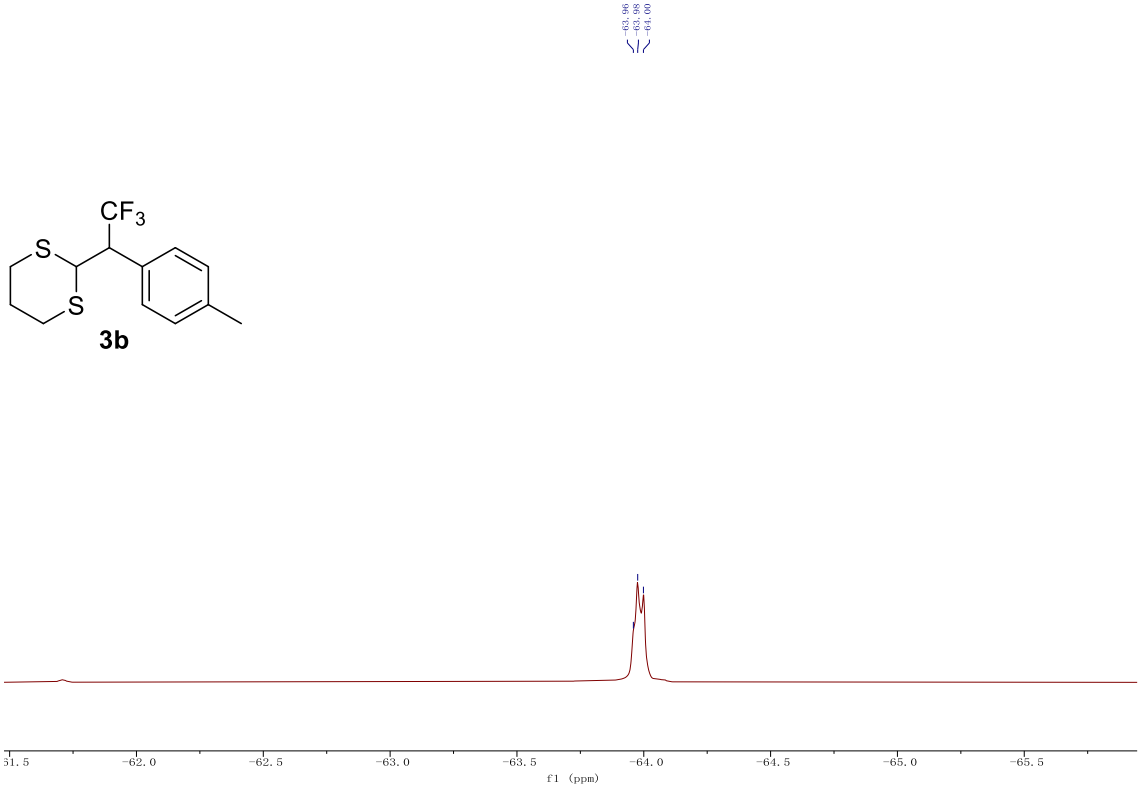
^{1}H NMR (400 MHz, $CDCl_3$)



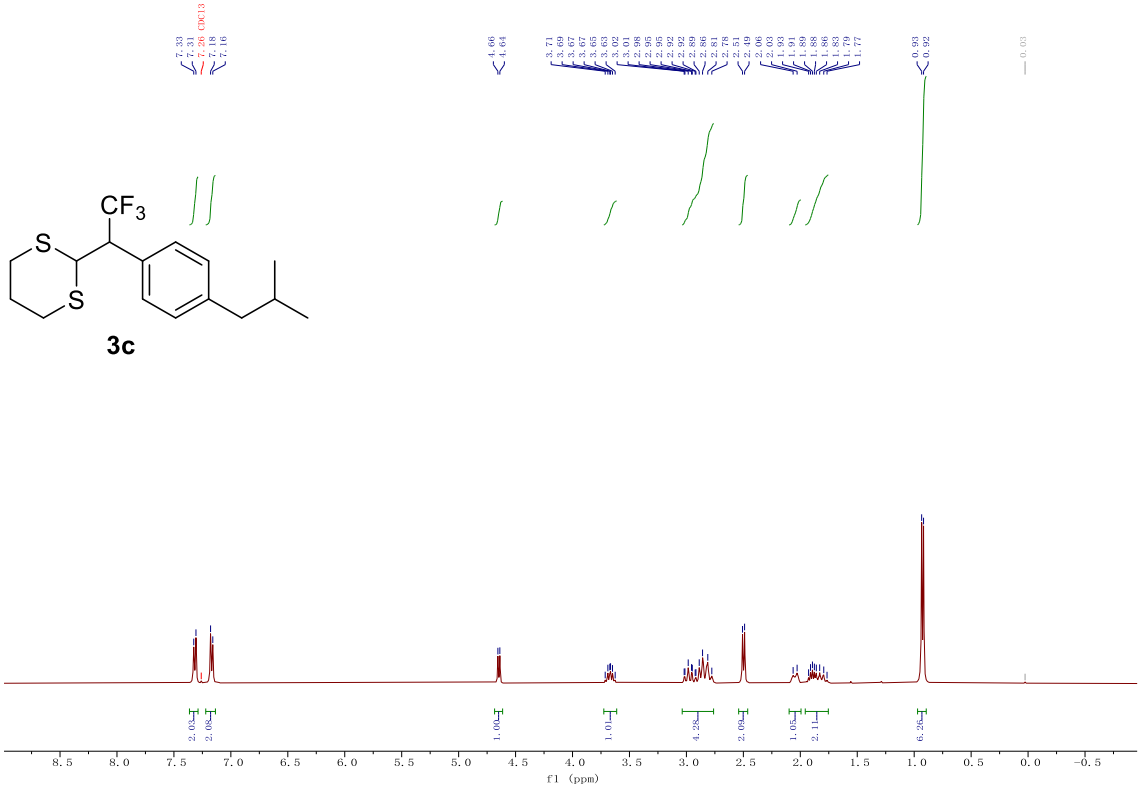
^{13}C NMR (101 MHz, $CDCl_3$)



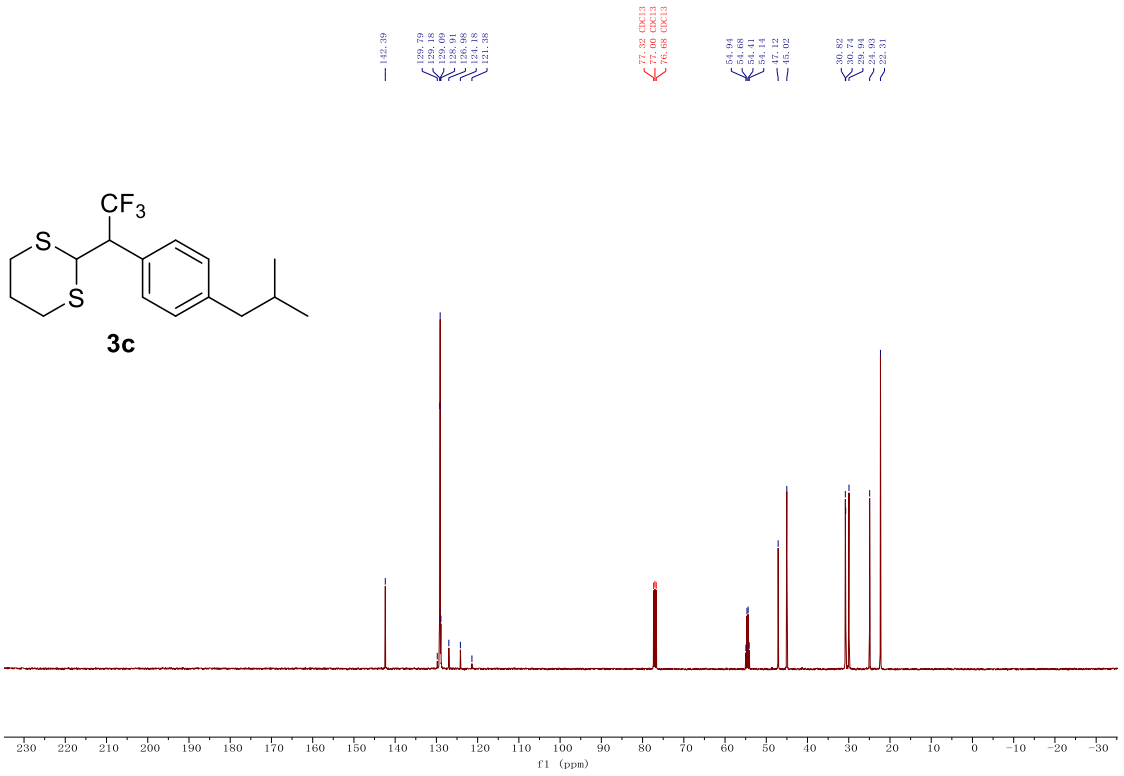
^{19}F NMR (376 MHz, $CDCl_3$)



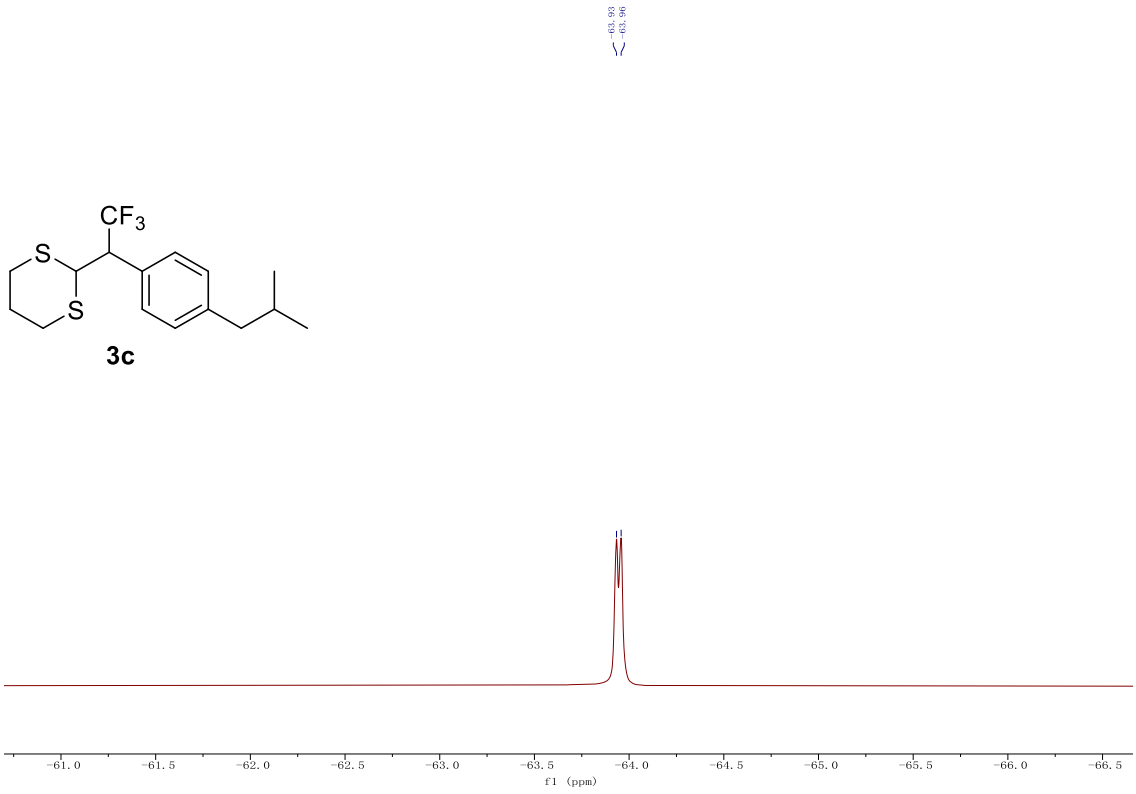
^{1}H NMR (400 MHz, $CDCl_3$)



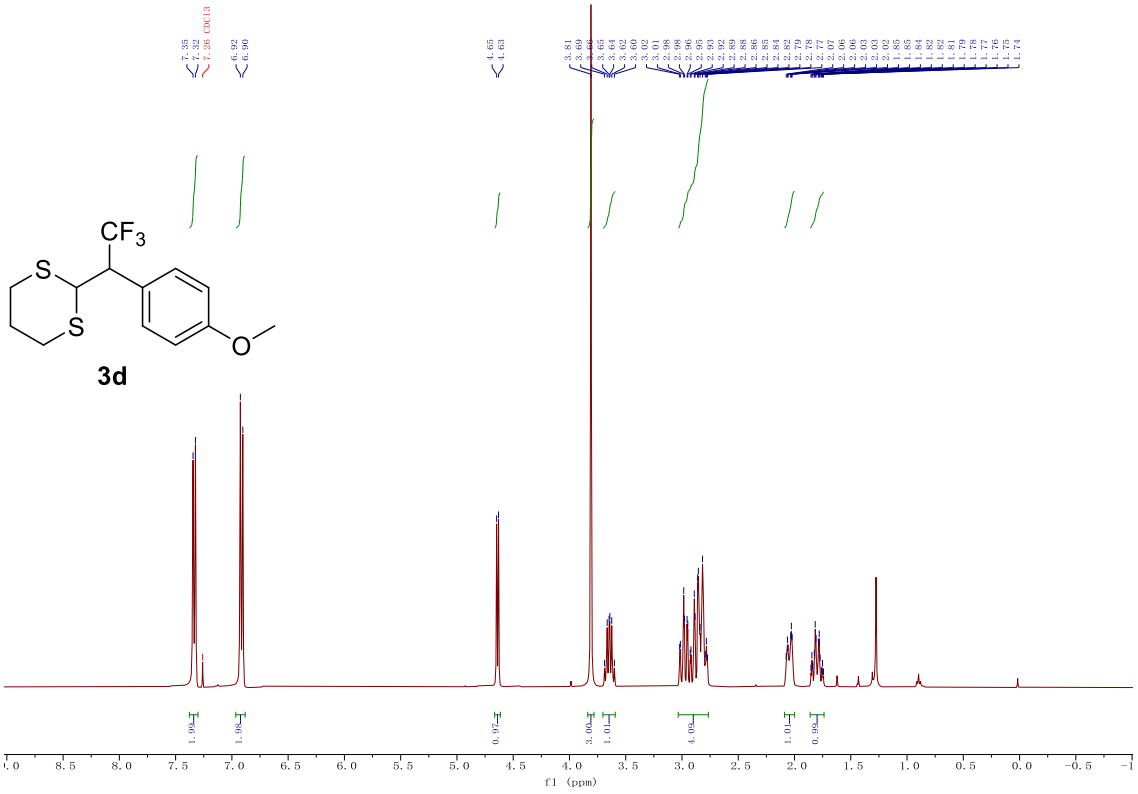
^{13}C NMR (101 MHz, $CDCl_3$)



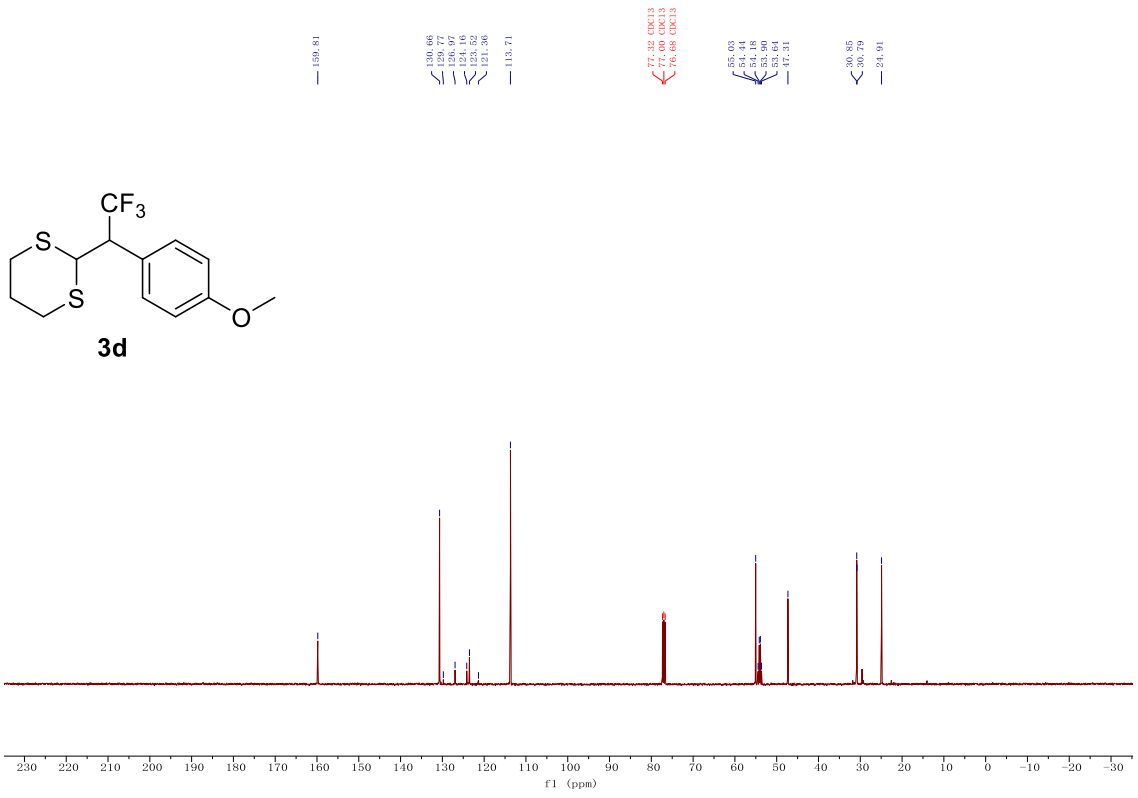
^{19}F NMR (376 MHz, $CDCl_3$)



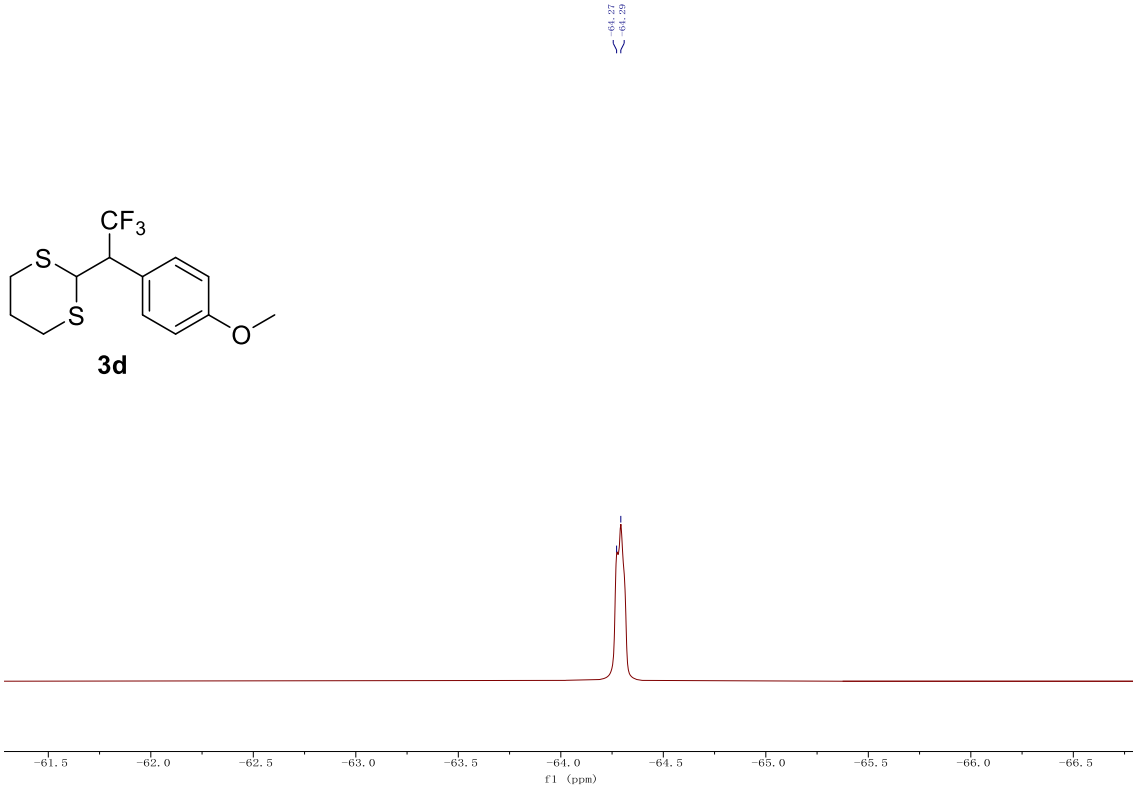
^{1}H NMR (400 MHz, $CDCl_3$)



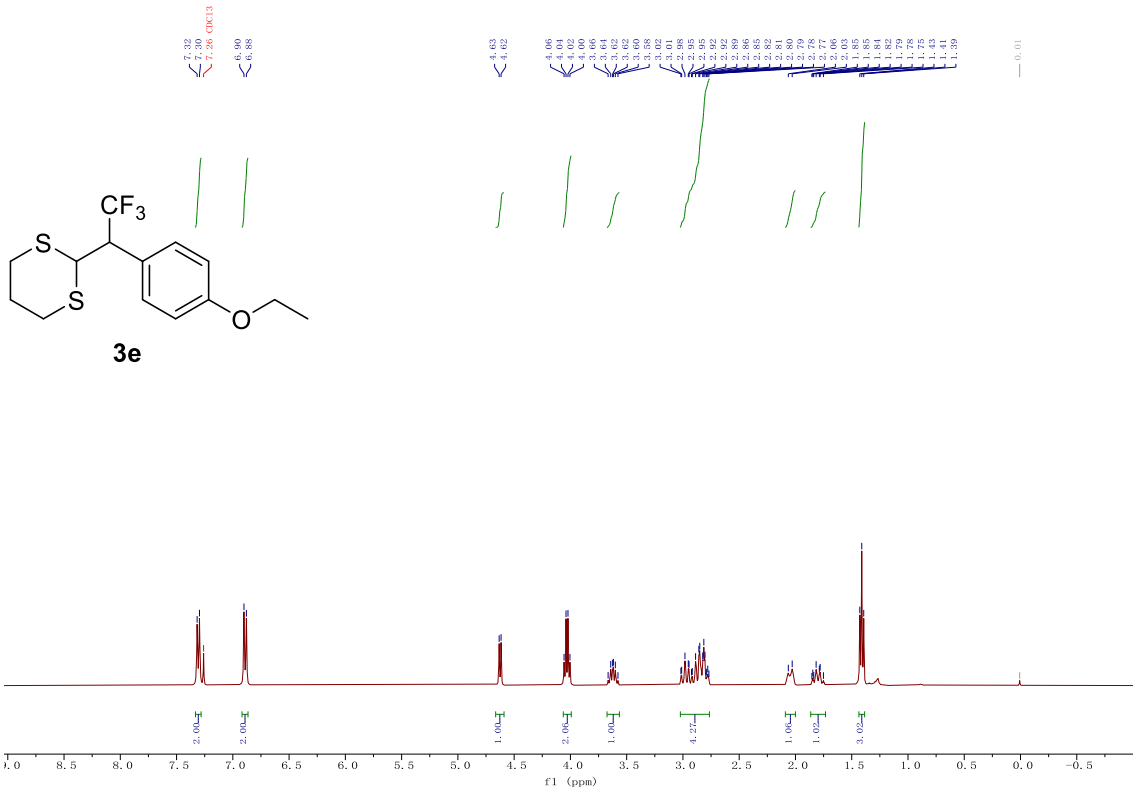
^{13}C NMR (101 MHz, $CDCl_3$)



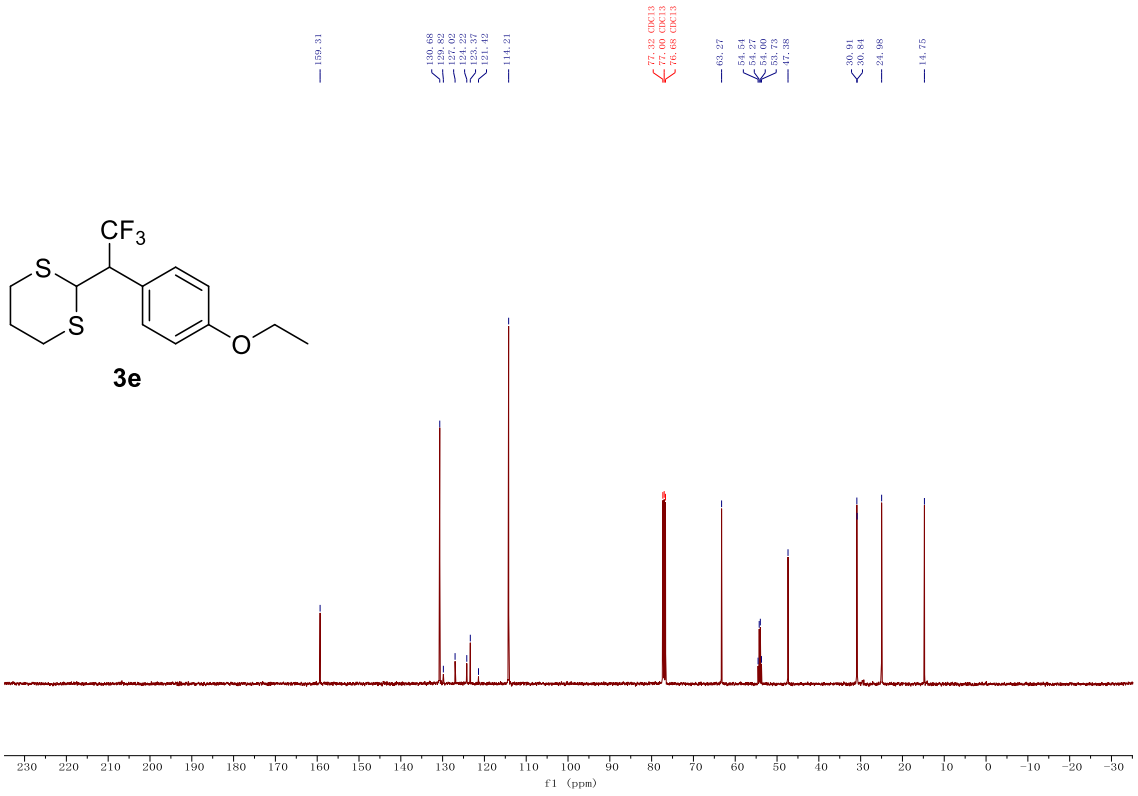
^{19}F NMR (376 MHz, $CDCl_3$)



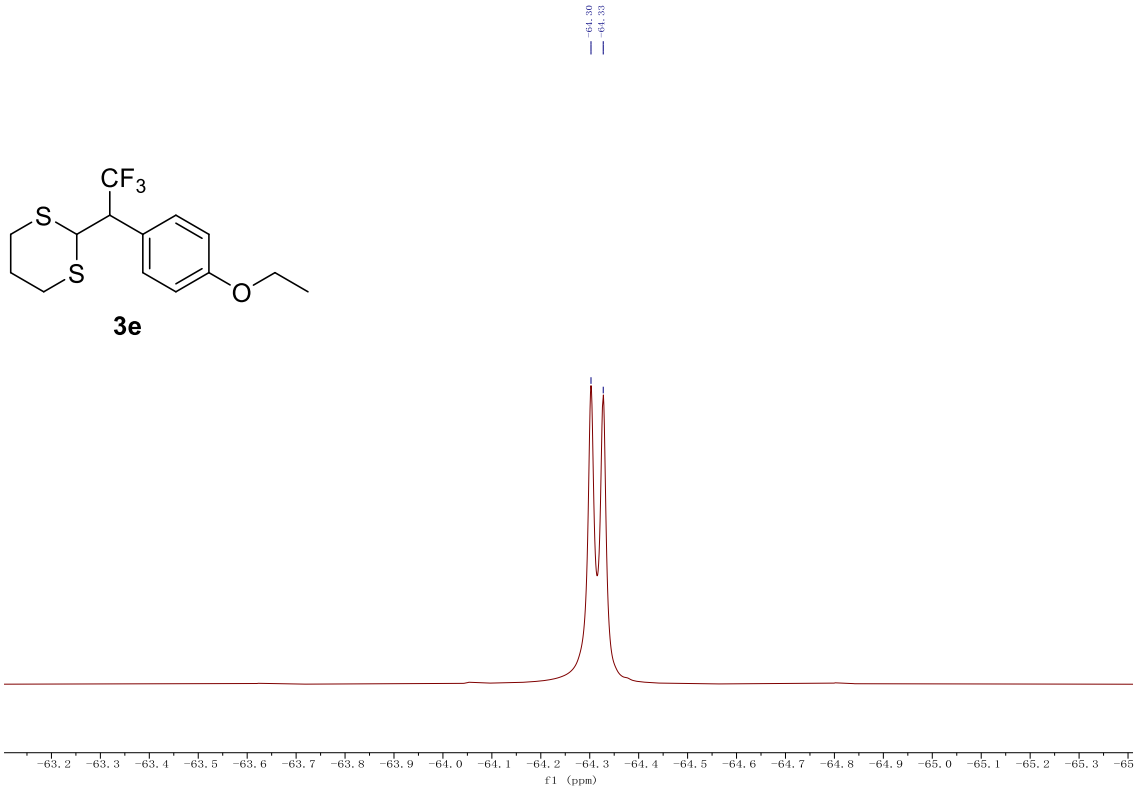
^{1}H NMR (400 MHz, $CDCl_3$)



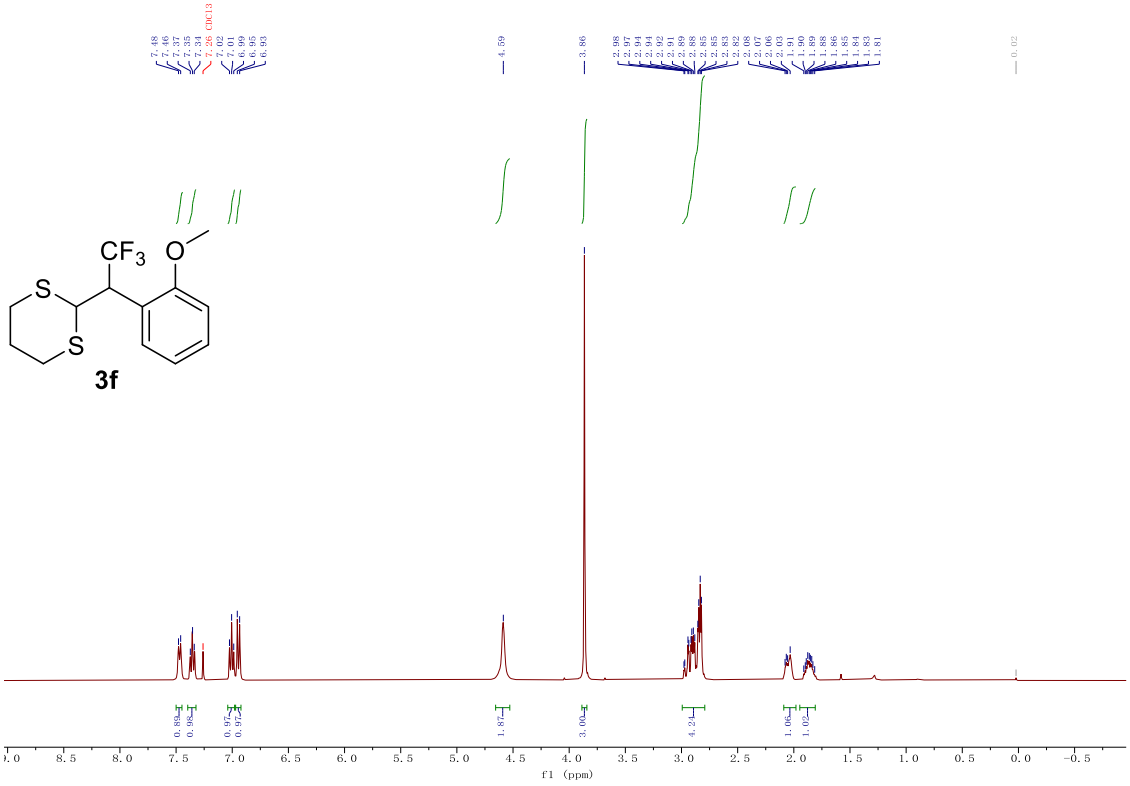
^{13}C NMR (101 MHz, $CDCl_3$)



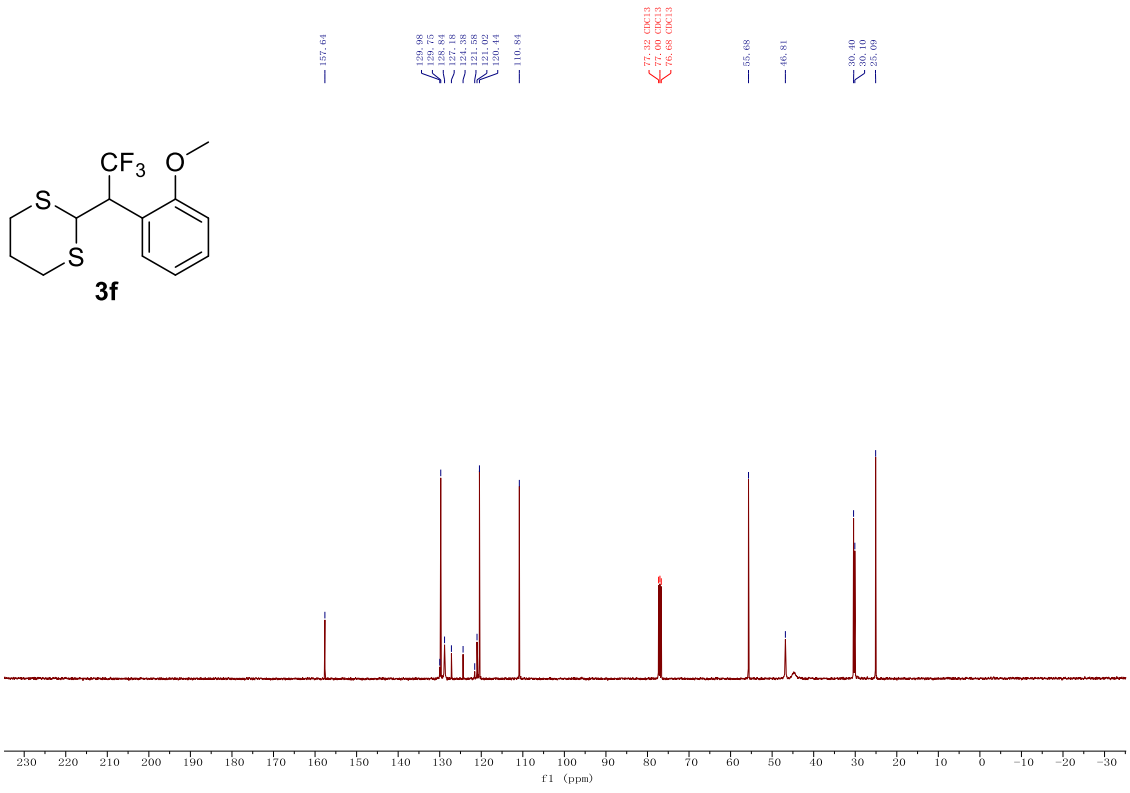
^{19}F NMR (376 MHz, $CDCl_3$)



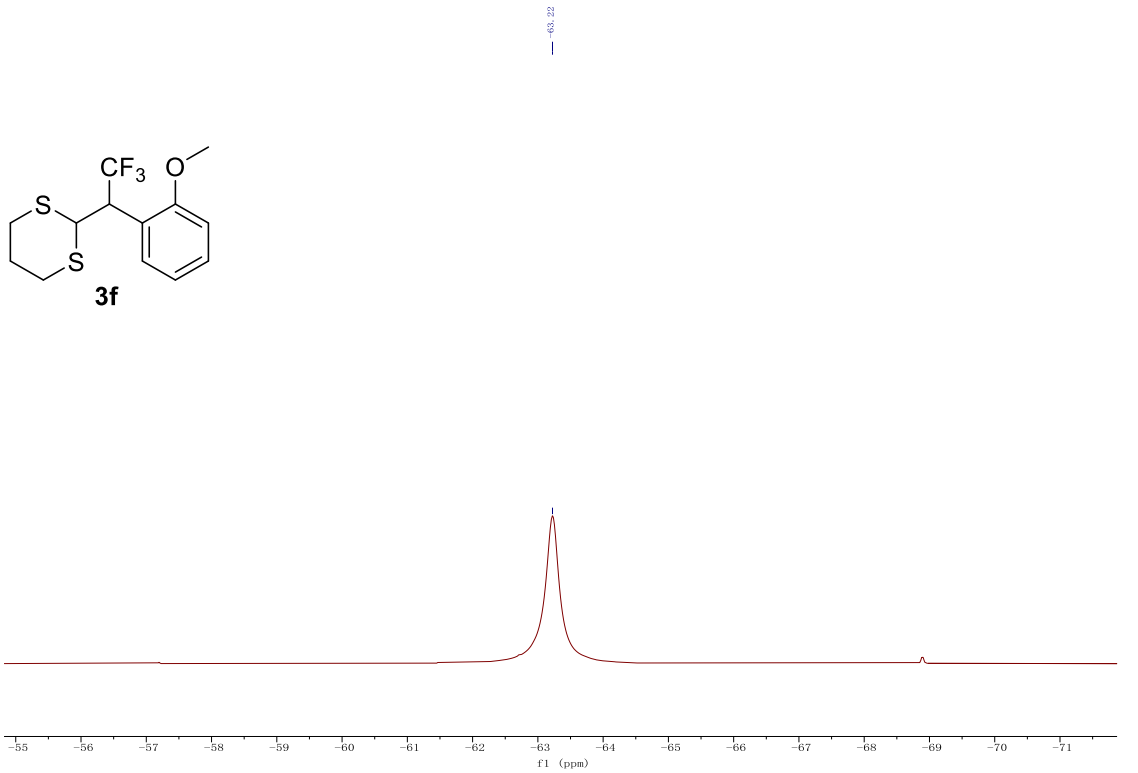
^{1}H NMR (400 MHz, $CDCl_3$)



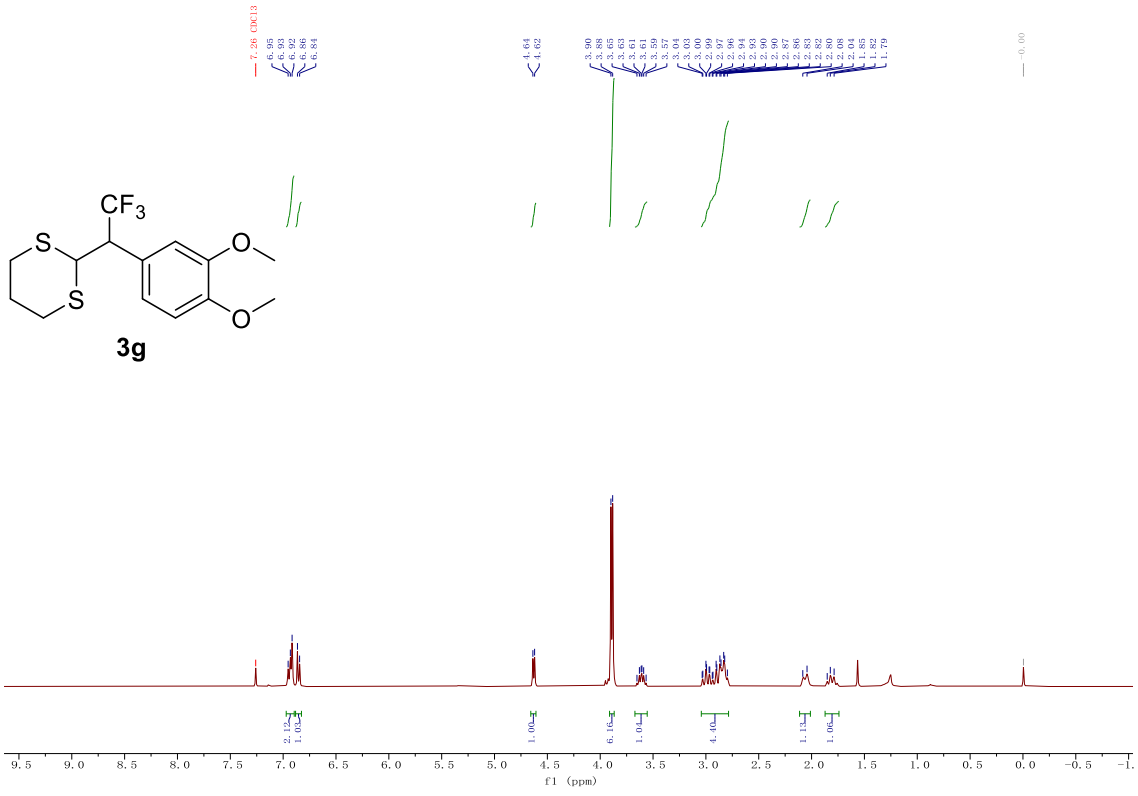
^{13}C NMR (101 MHz, $CDCl_3$)



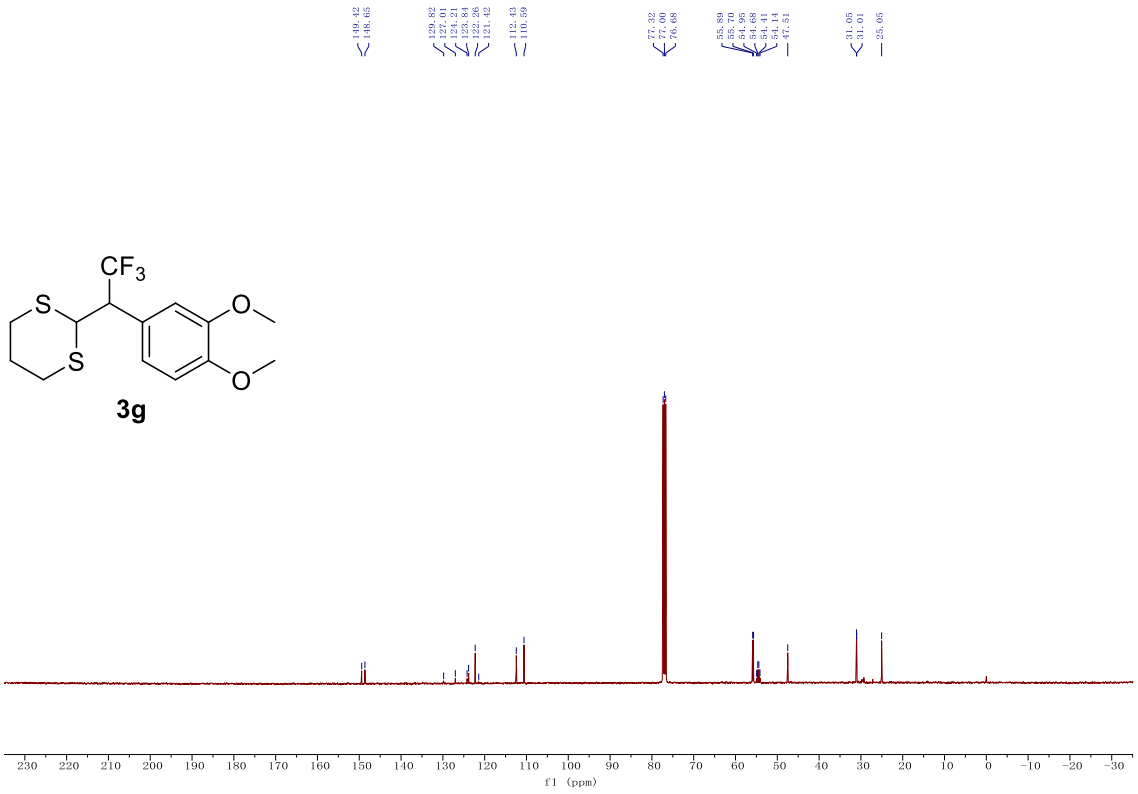
^{19}F NMR (376 MHz, $CDCl_3$)



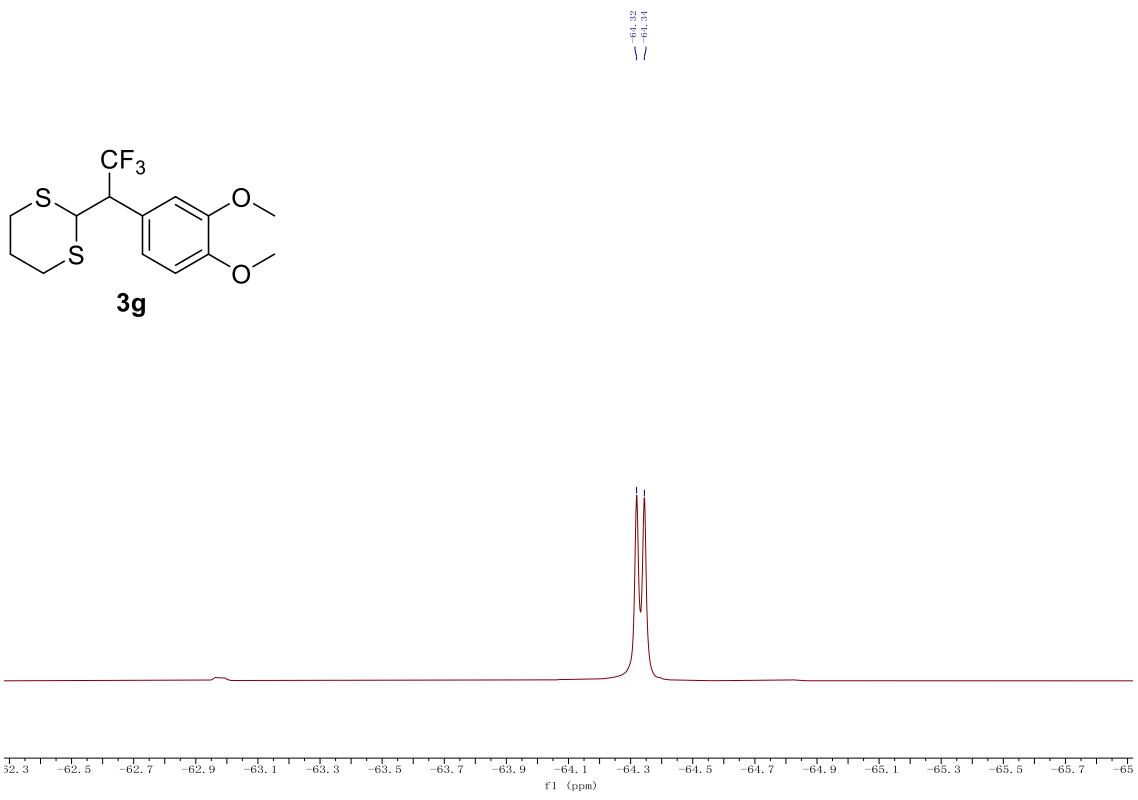
^{1}H NMR (400 MHz, $CDCl_3$)



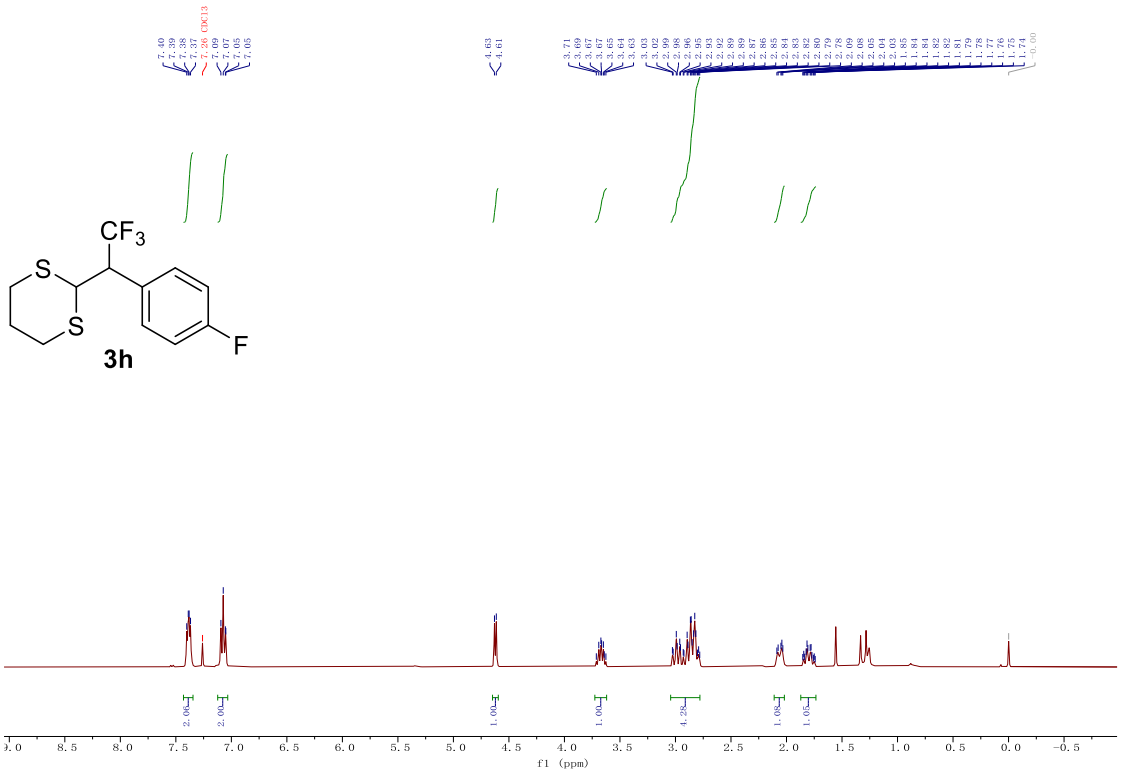
^{13}C NMR (101 MHz, $CDCl_3$)



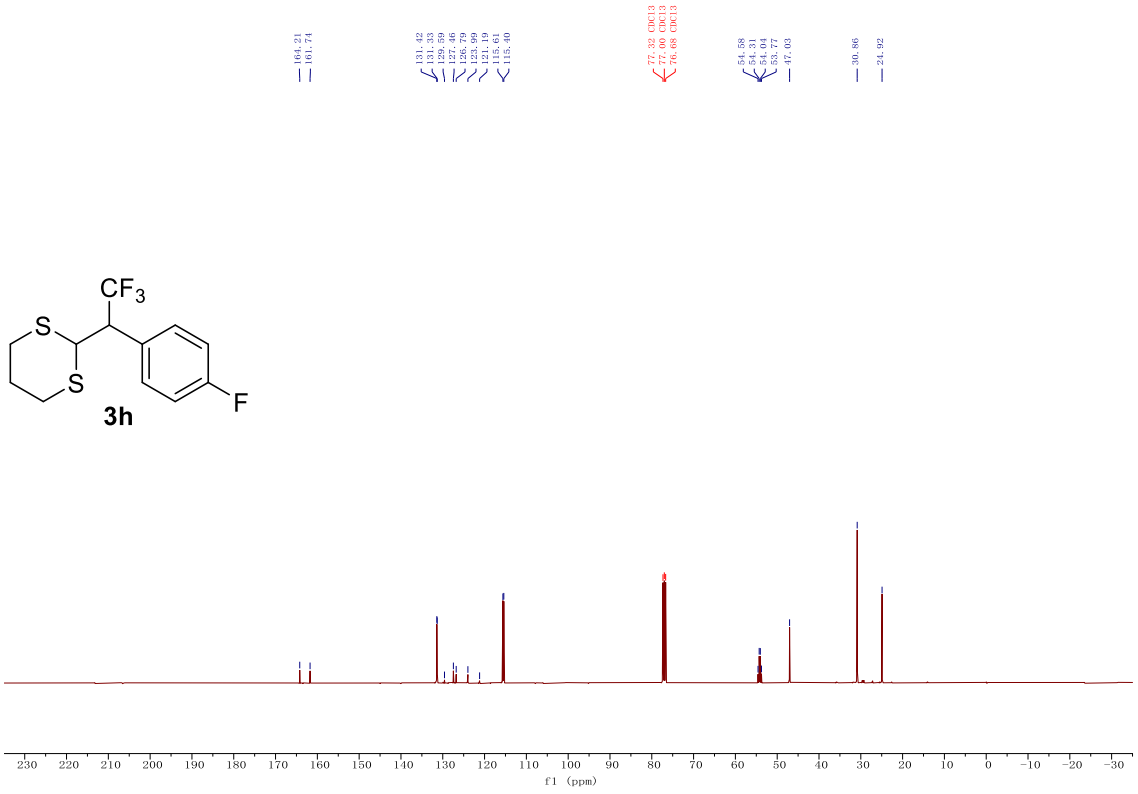
^{19}F NMR (376 MHz, $CDCl_3$)



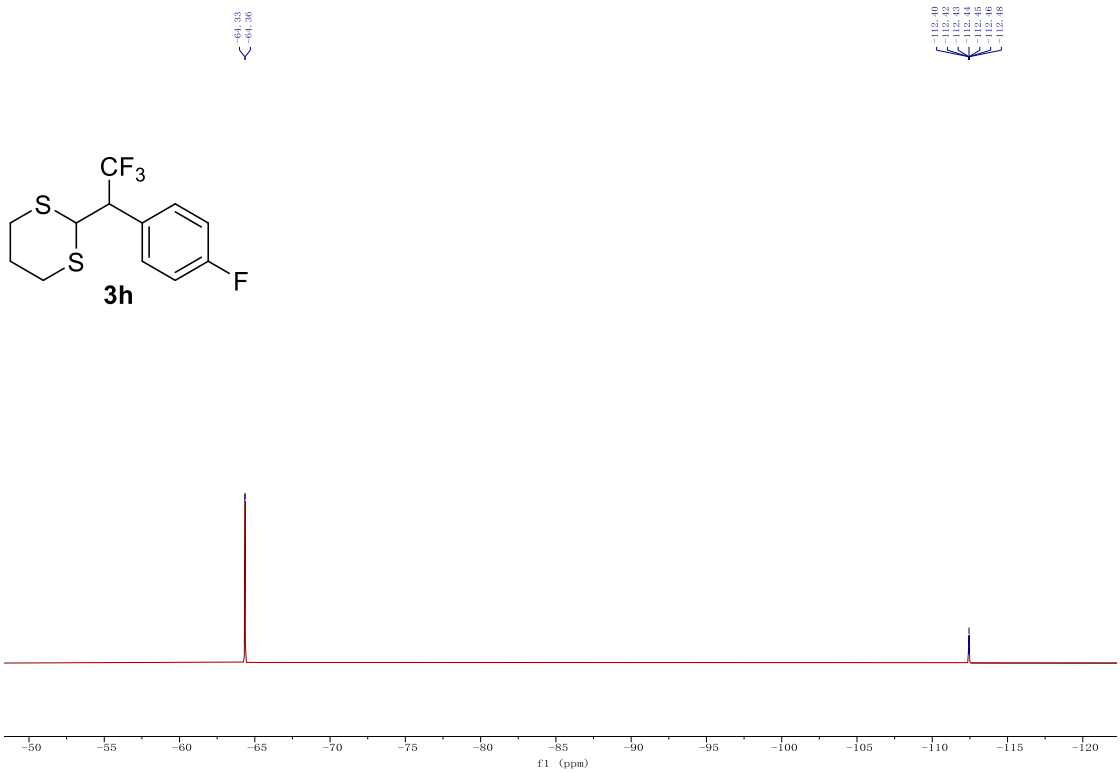
^{1}H NMR (400 MHz, $CDCl_3$)



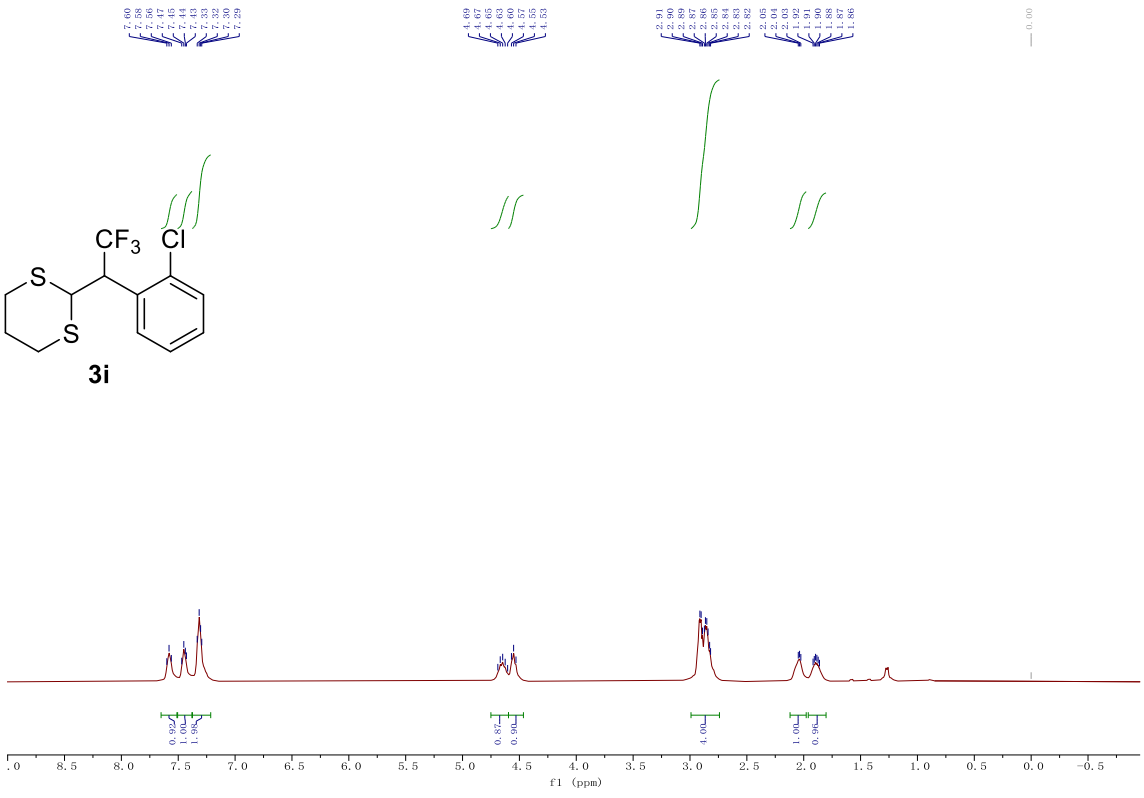
^{13}C NMR (101 MHz, $CDCl_3$)



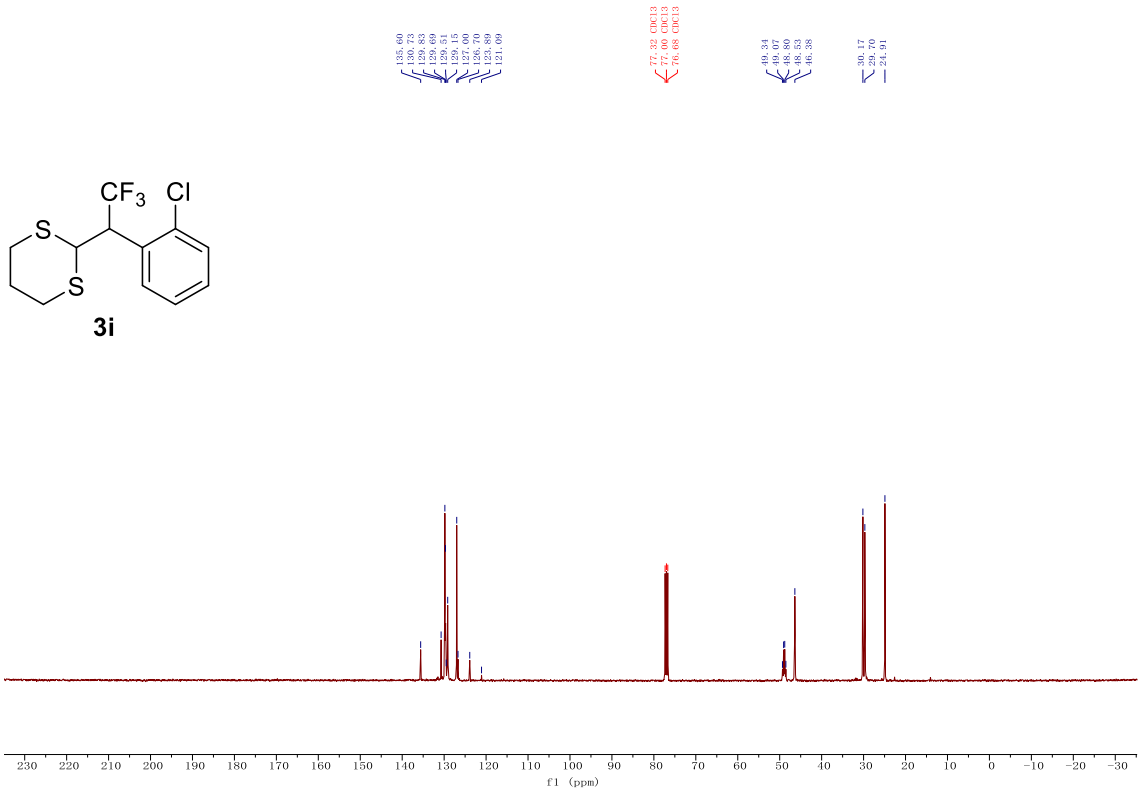
^{19}F NMR (376 MHz, $CDCl_3$)



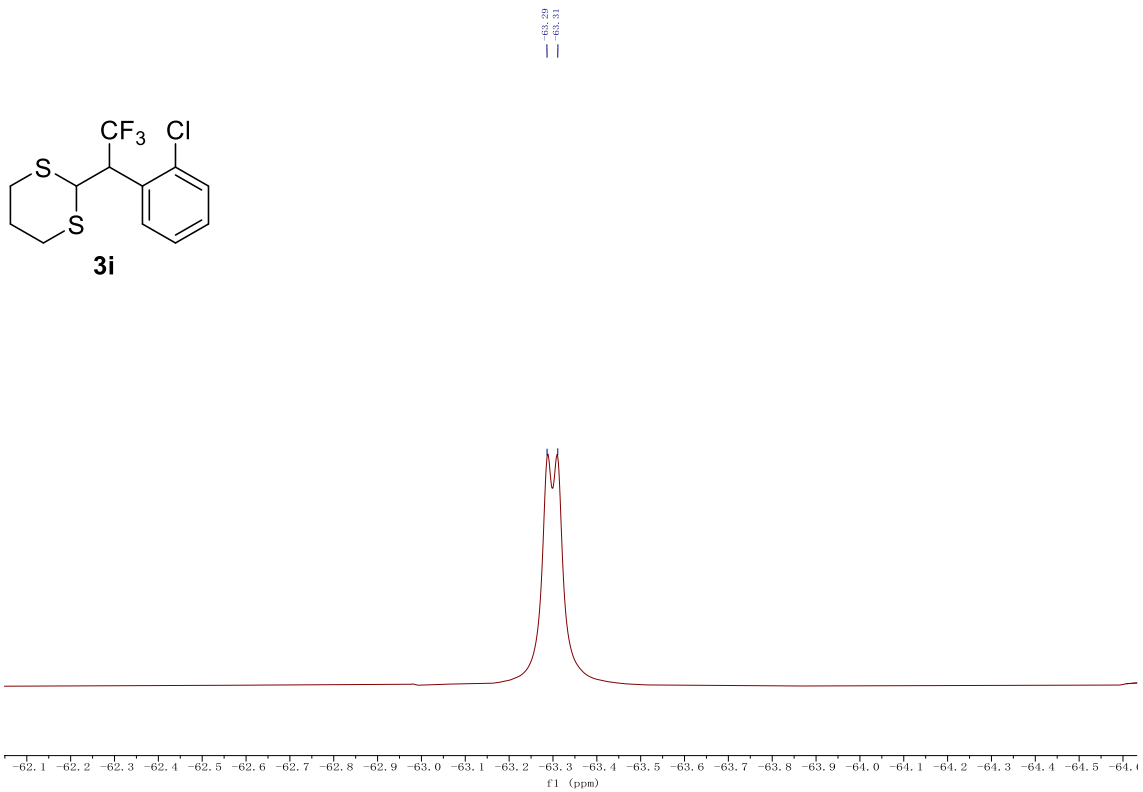
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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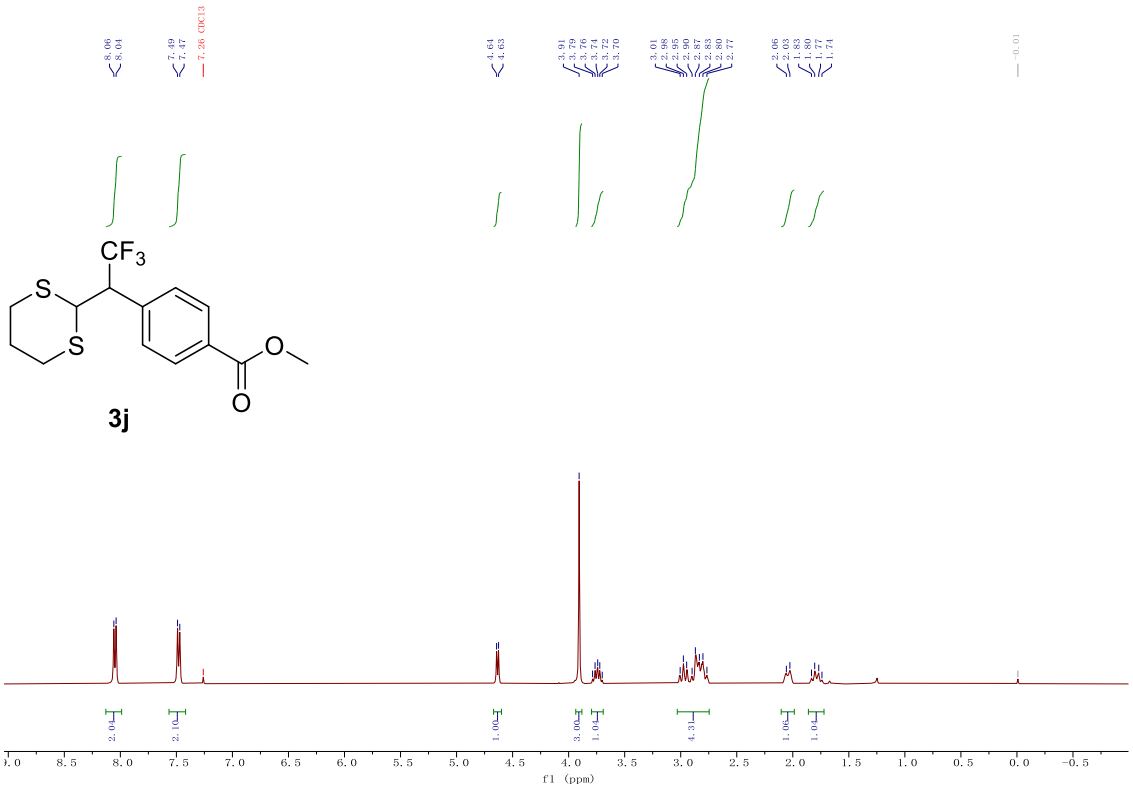
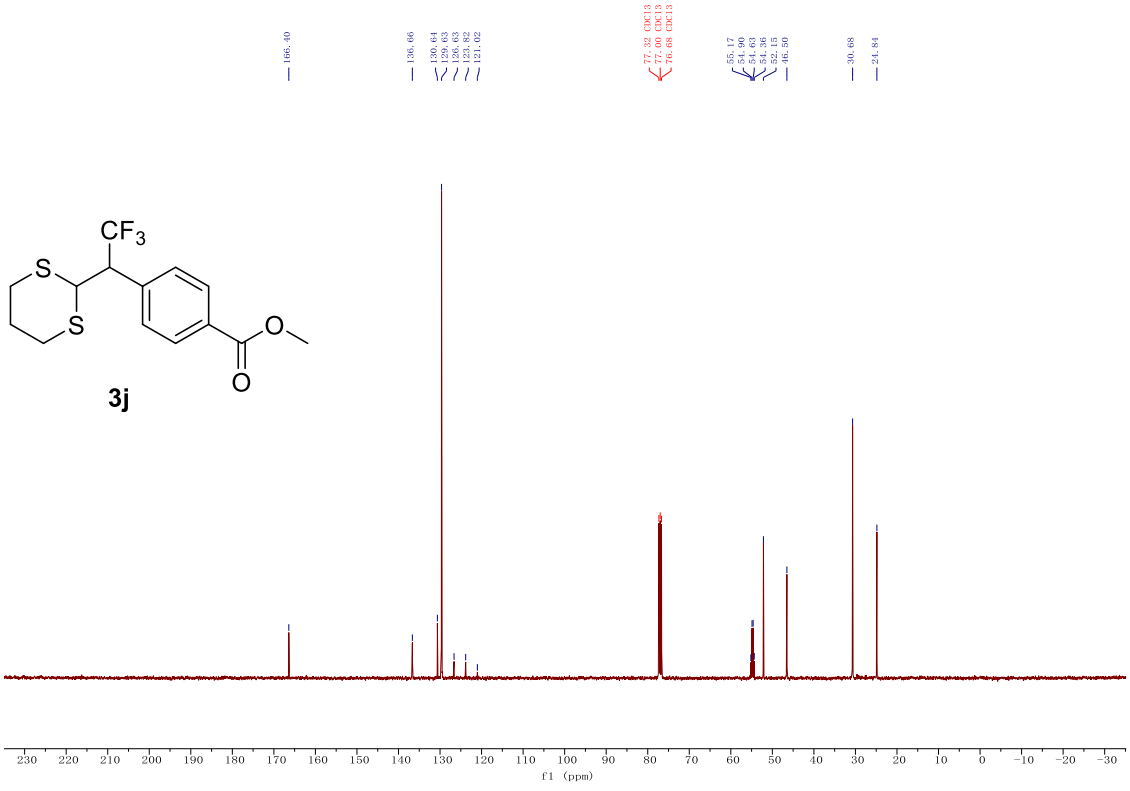
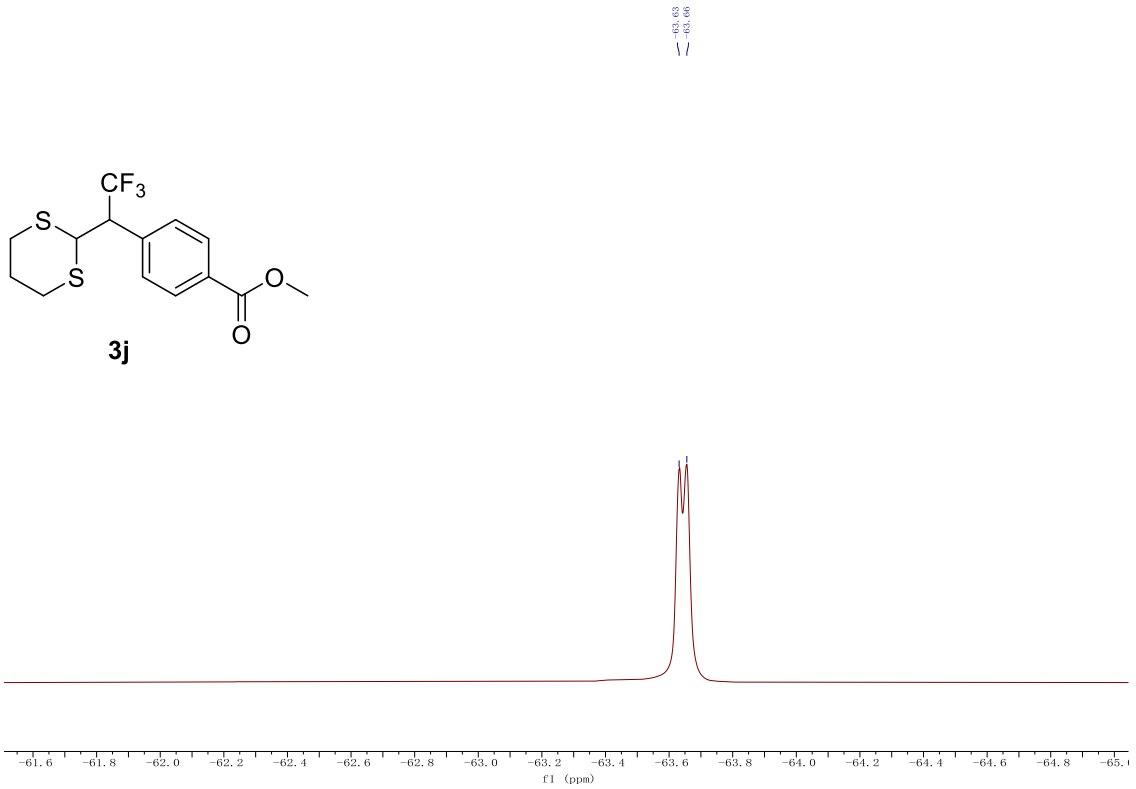


^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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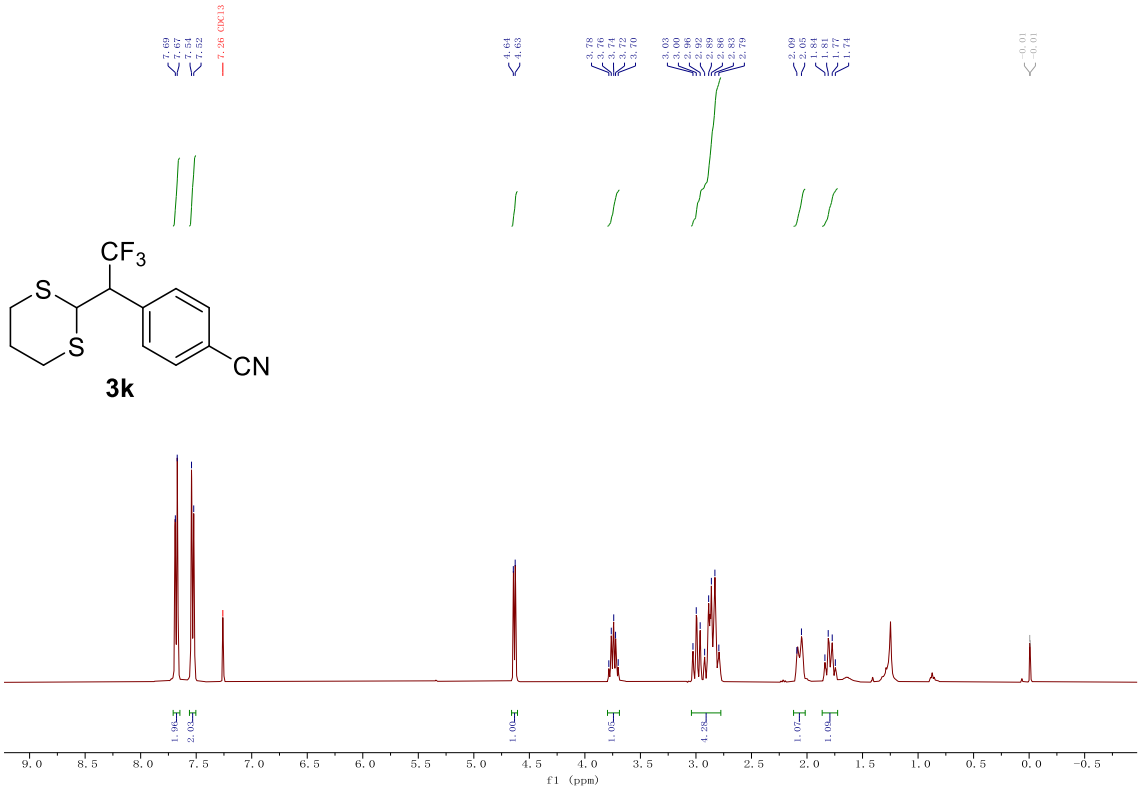
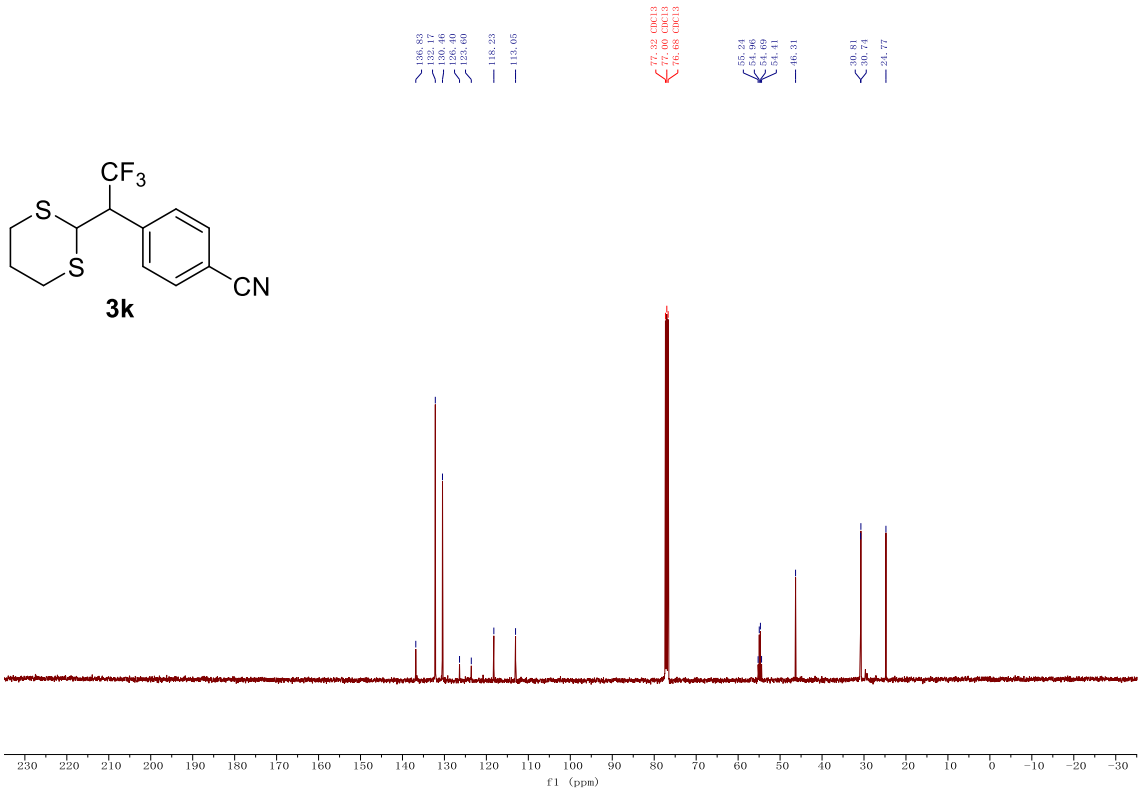
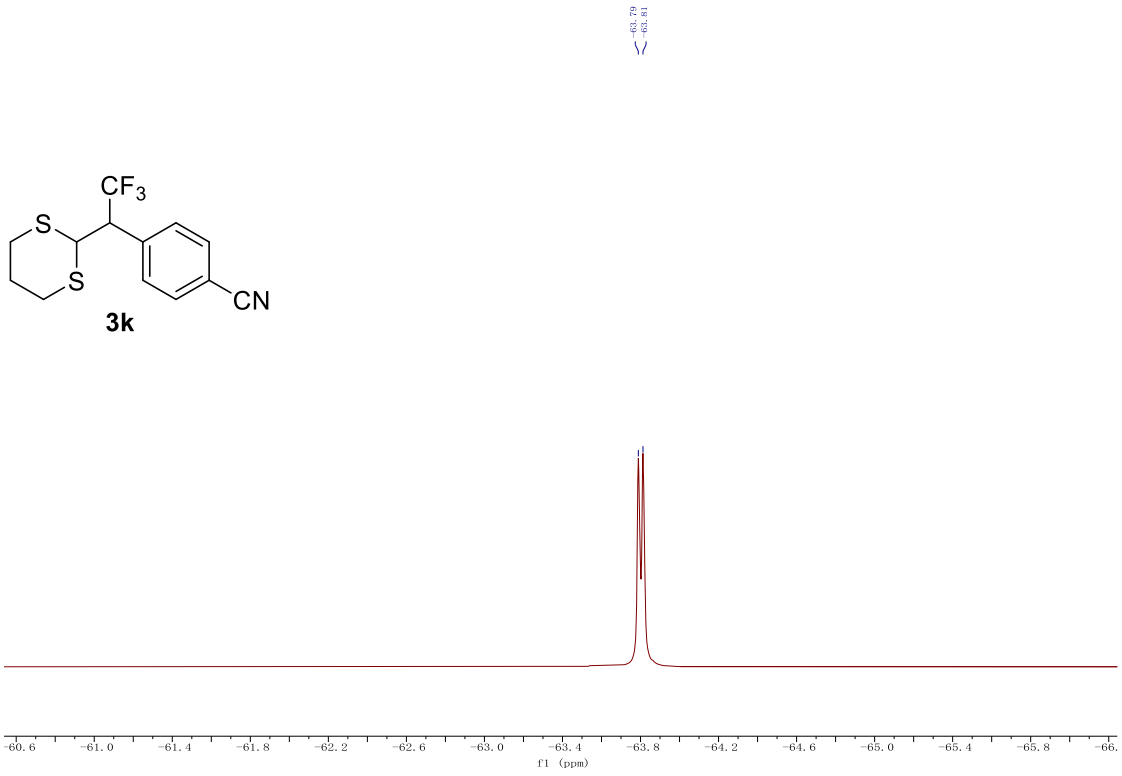


^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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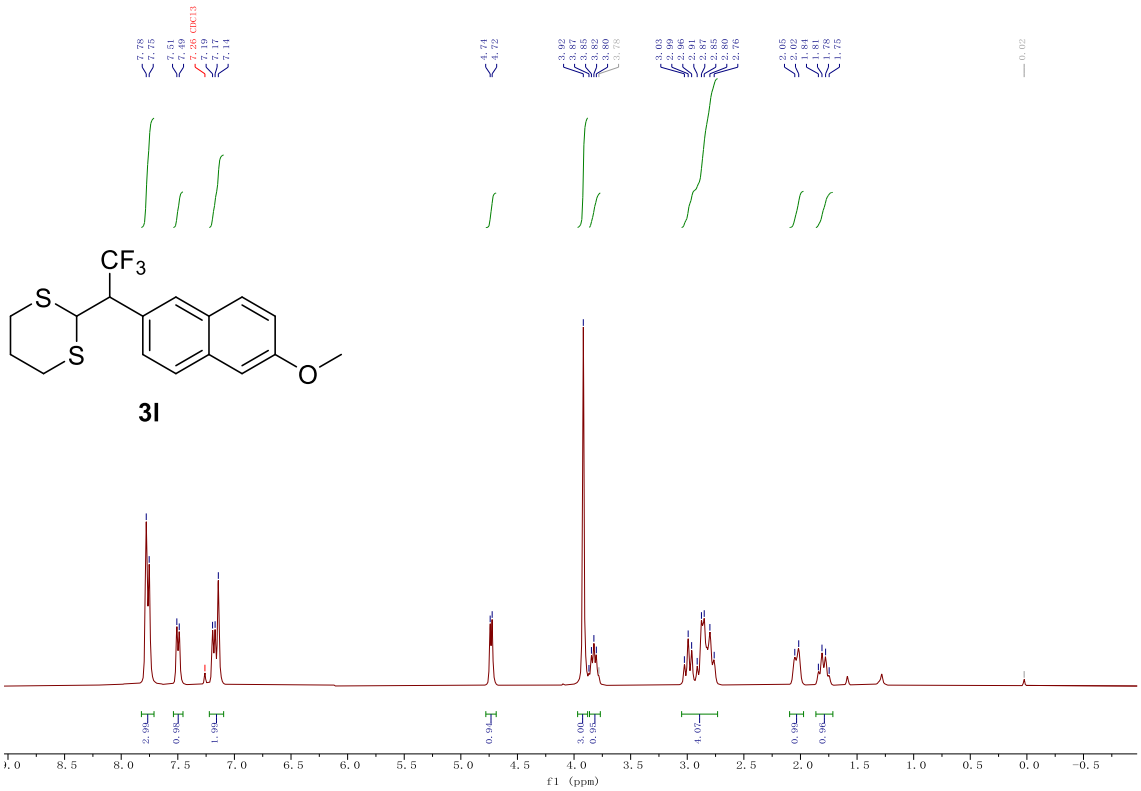
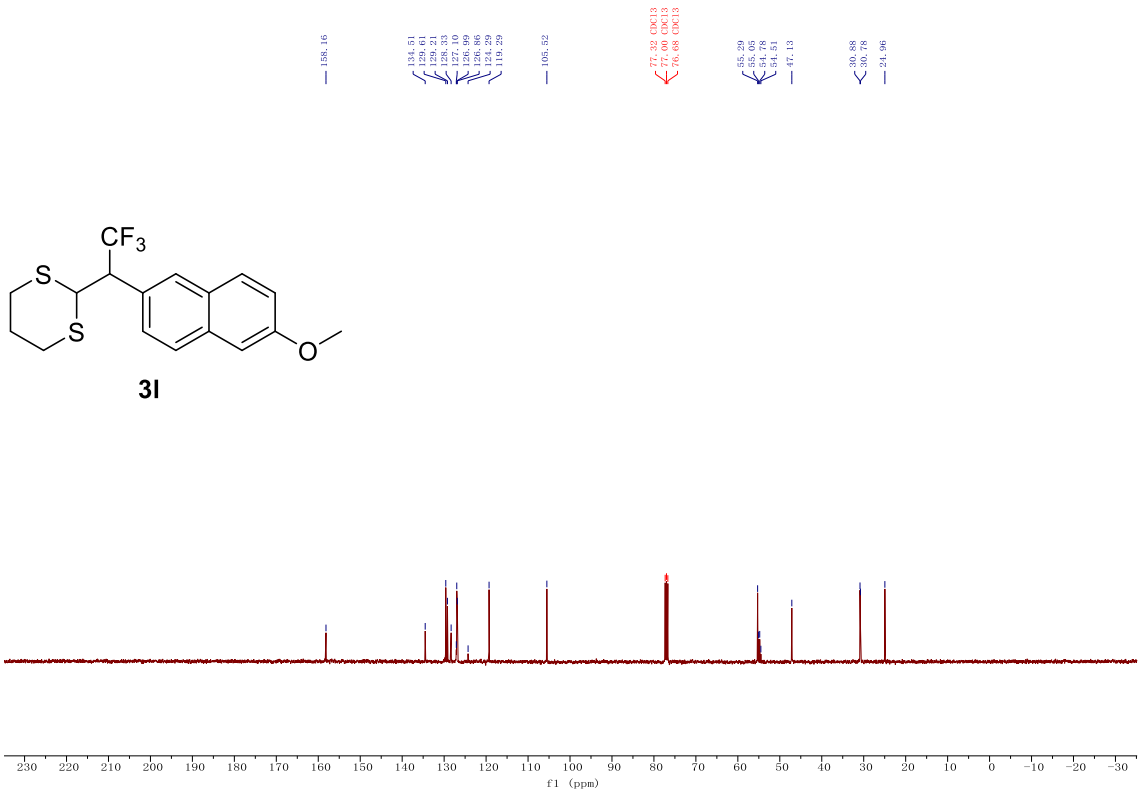
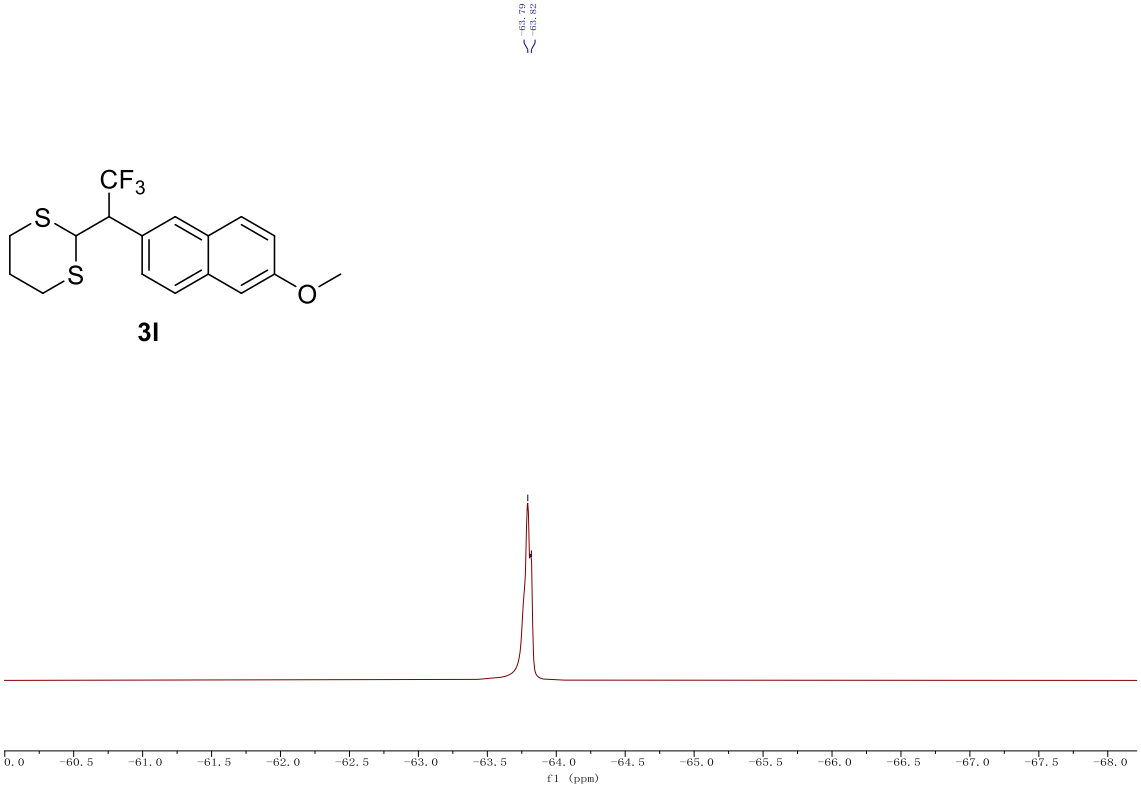


^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



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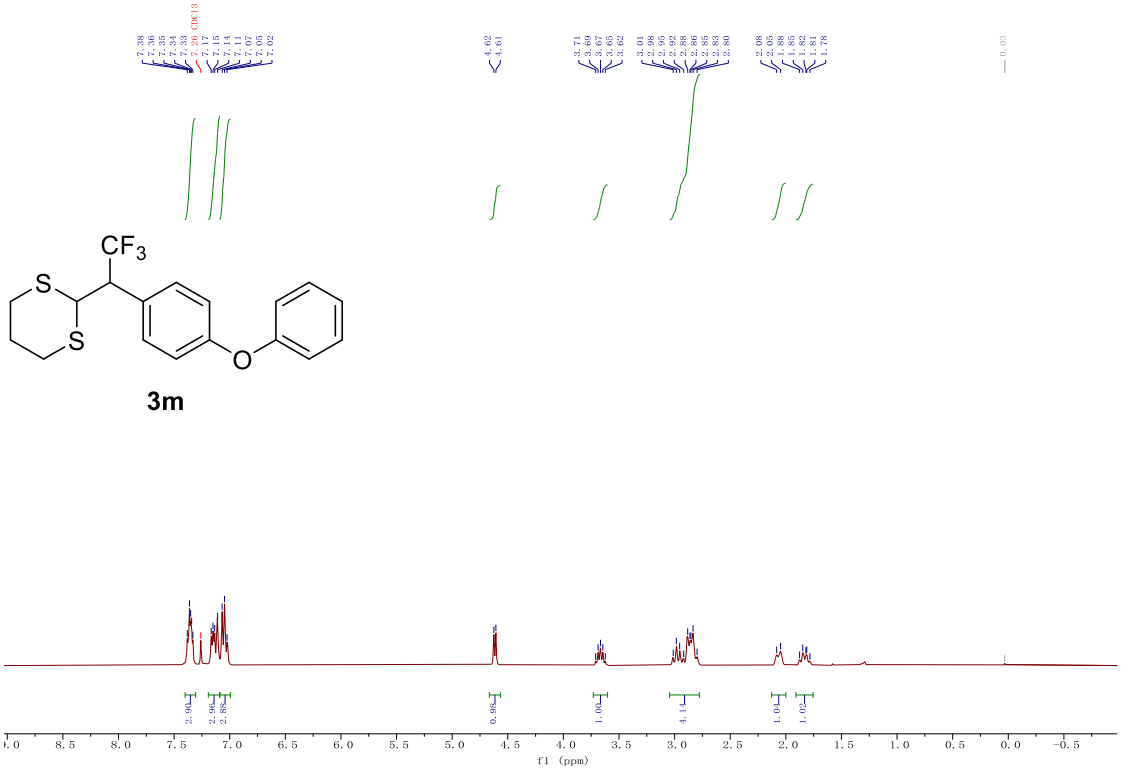

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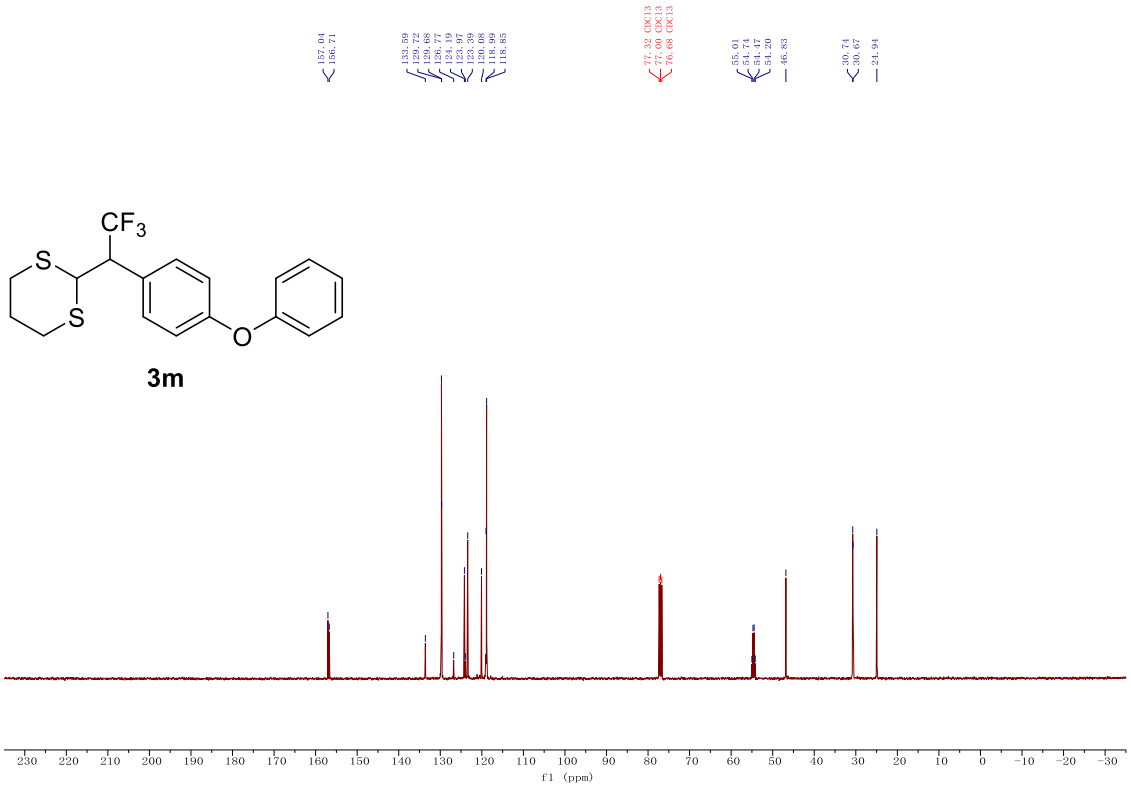

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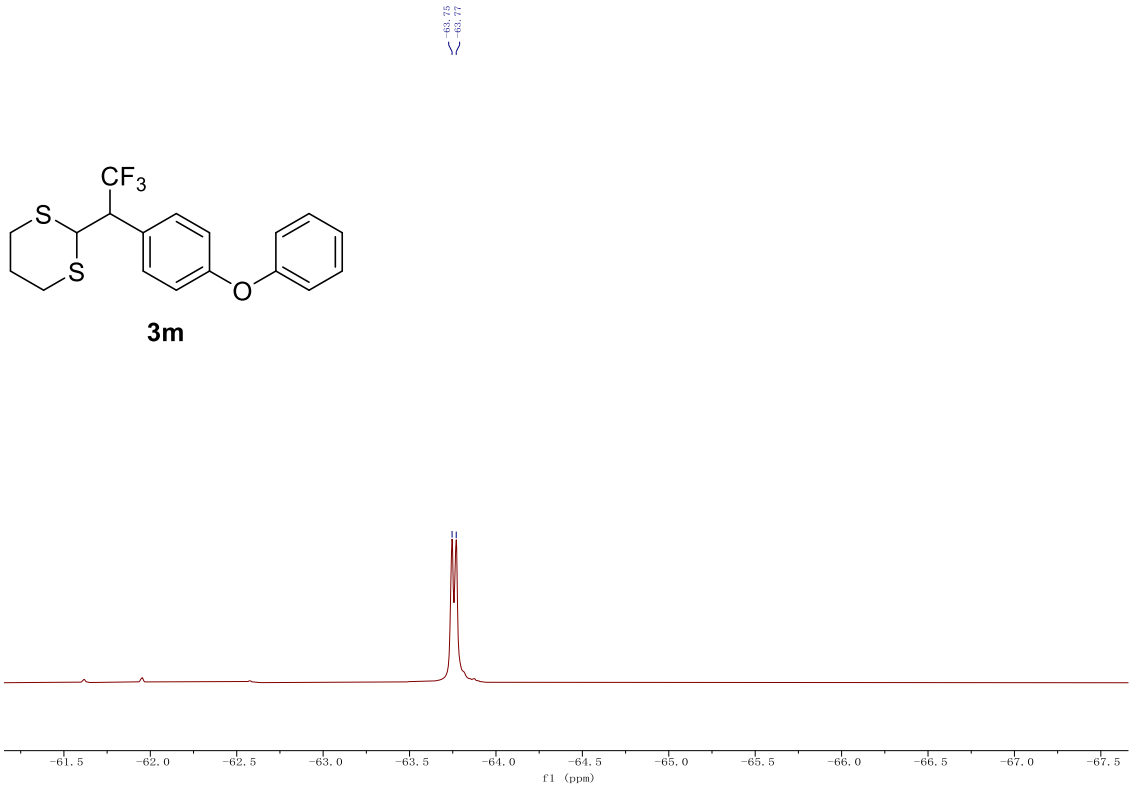
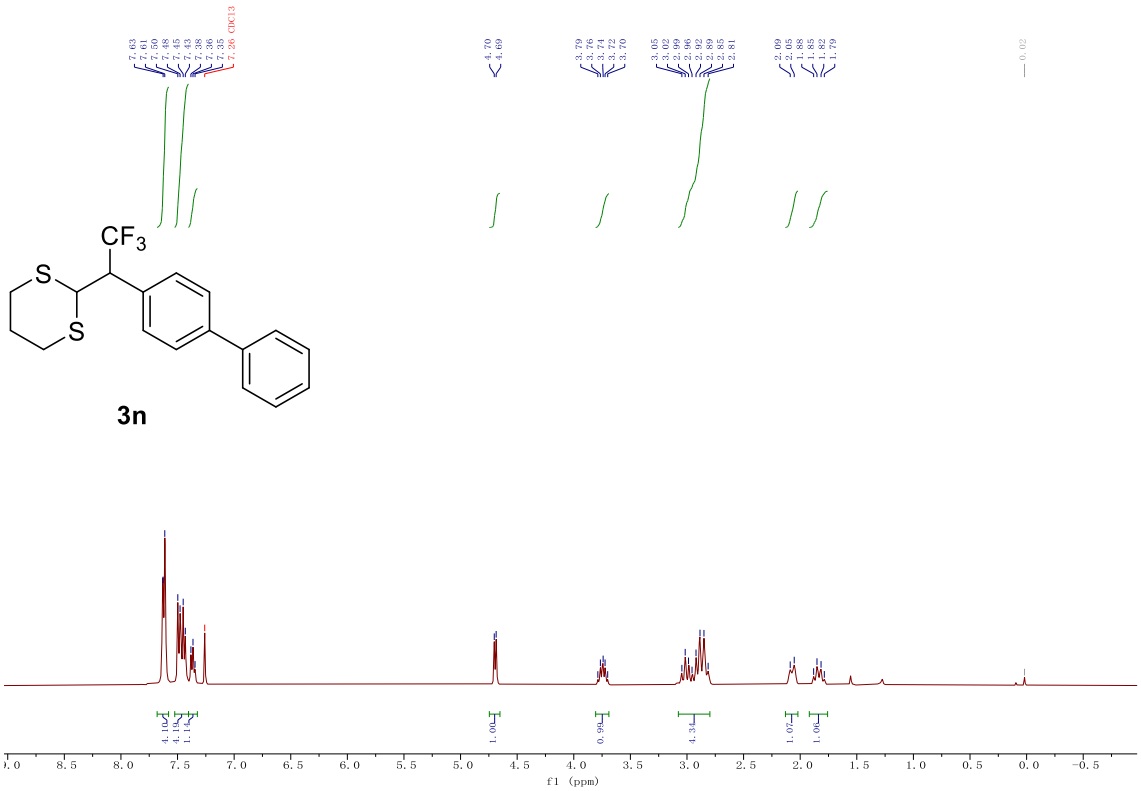
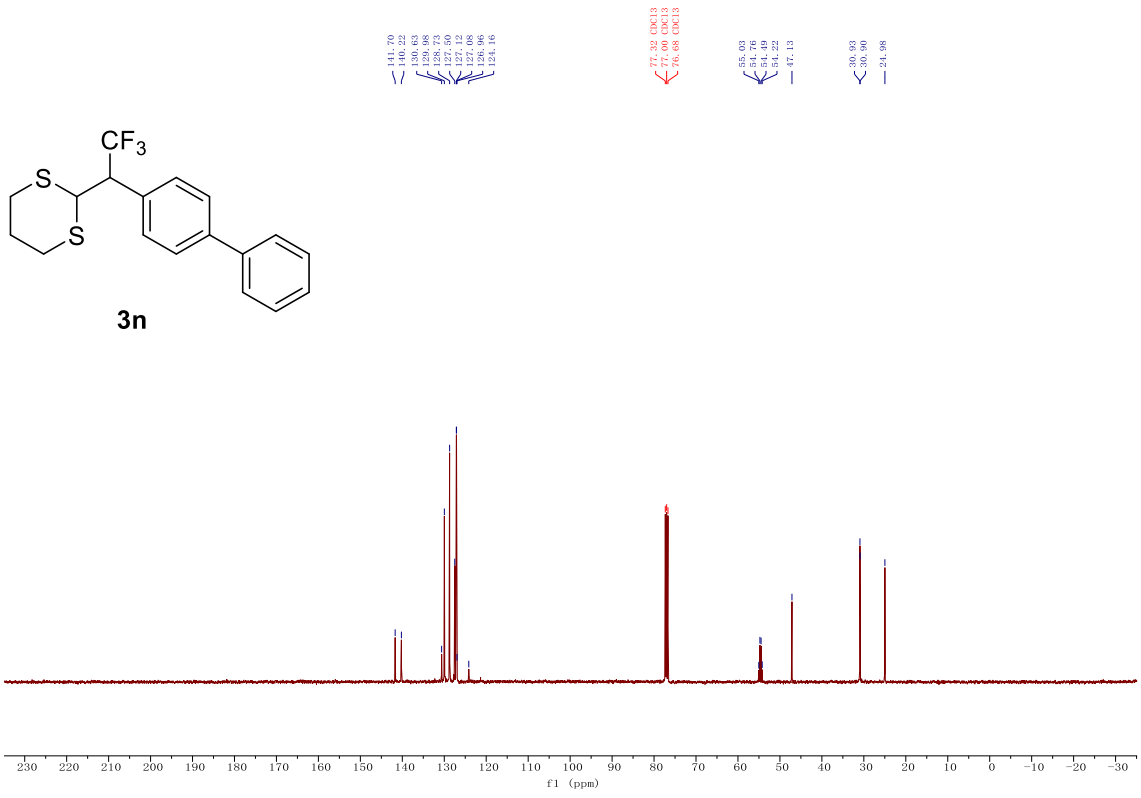


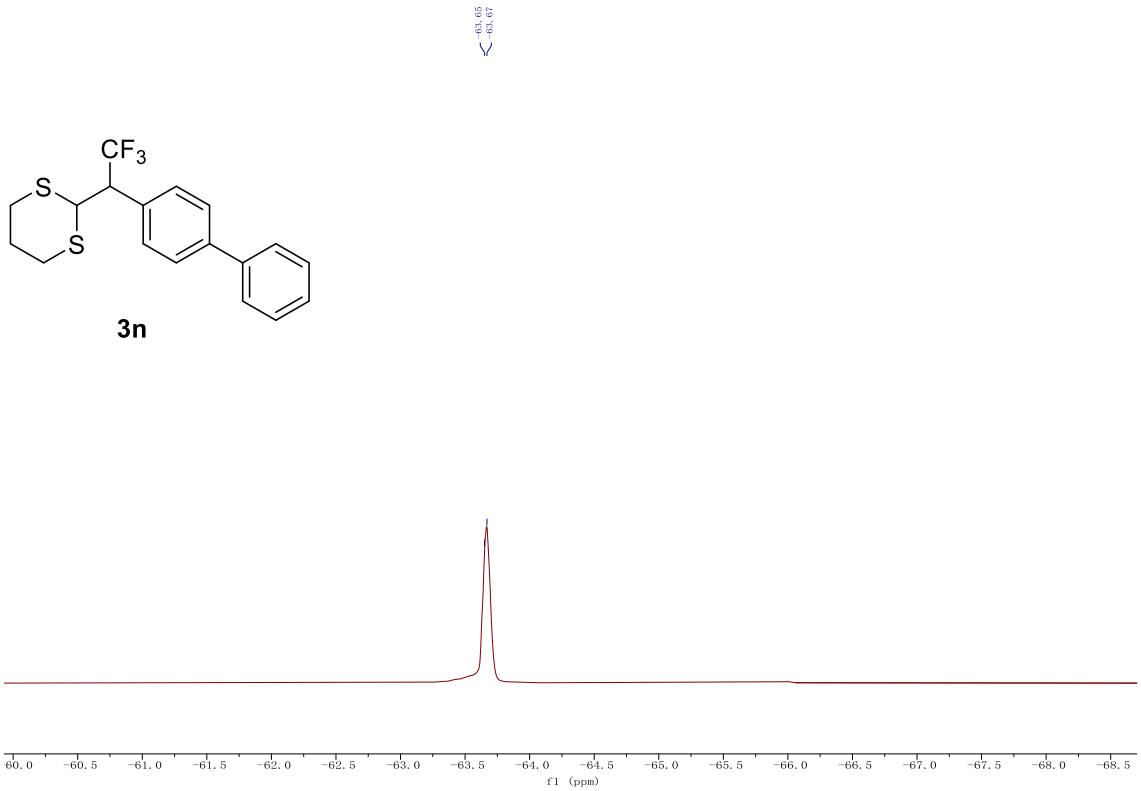
^{1}H NMR (400 MHz, $CDCl_3$)



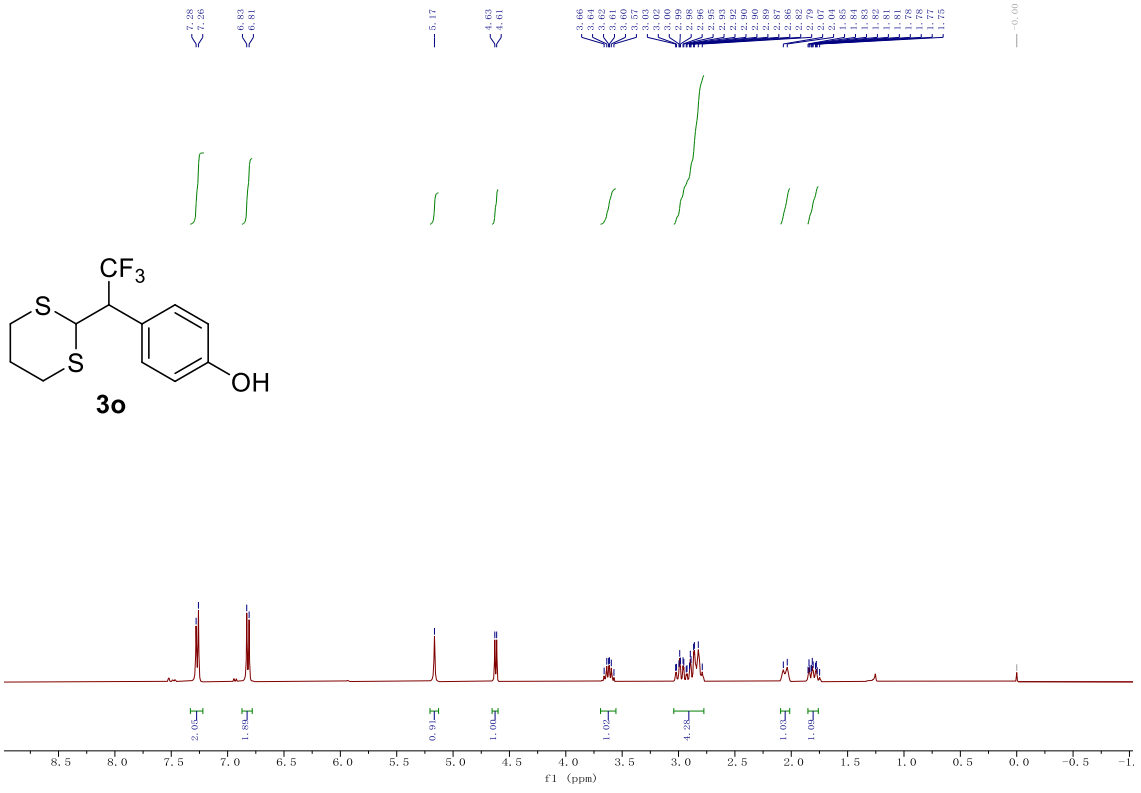
^{13}C NMR (101 MHz, $CDCl_3$)



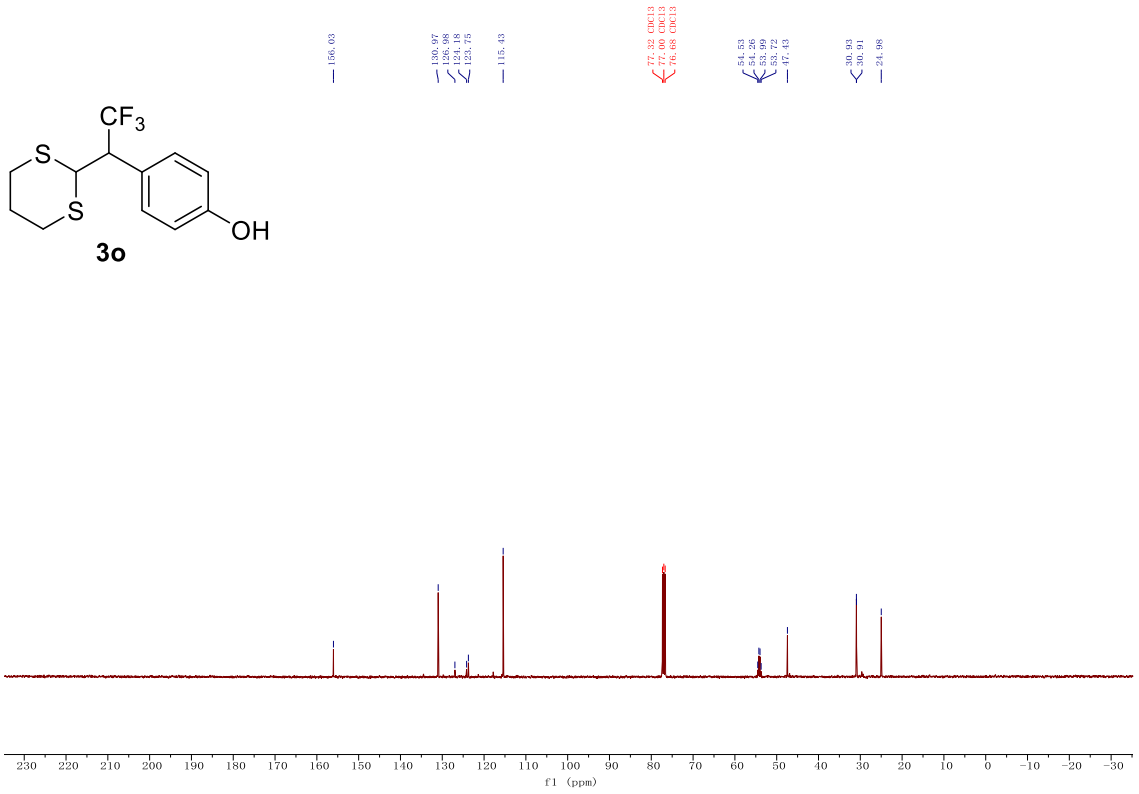
^{19}F NMR (376 MHz, $CDCl_3$)



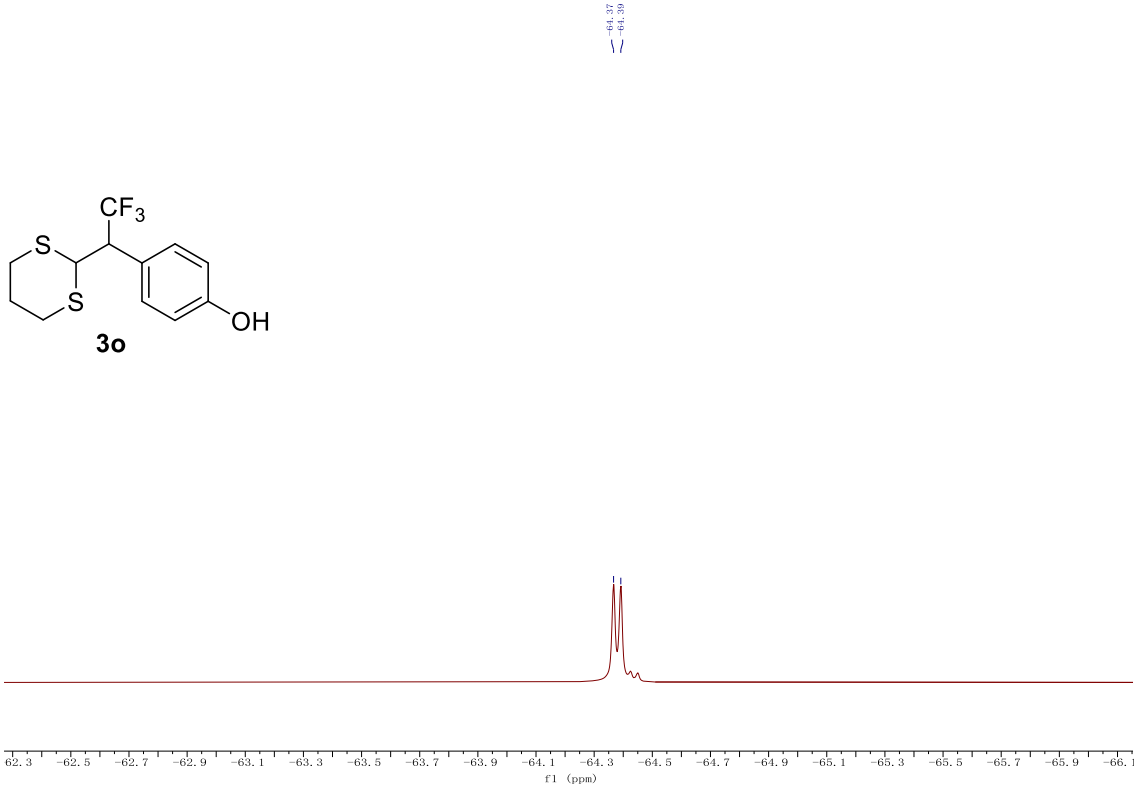
^{1}H NMR (400 MHz, $CDCl_3$)



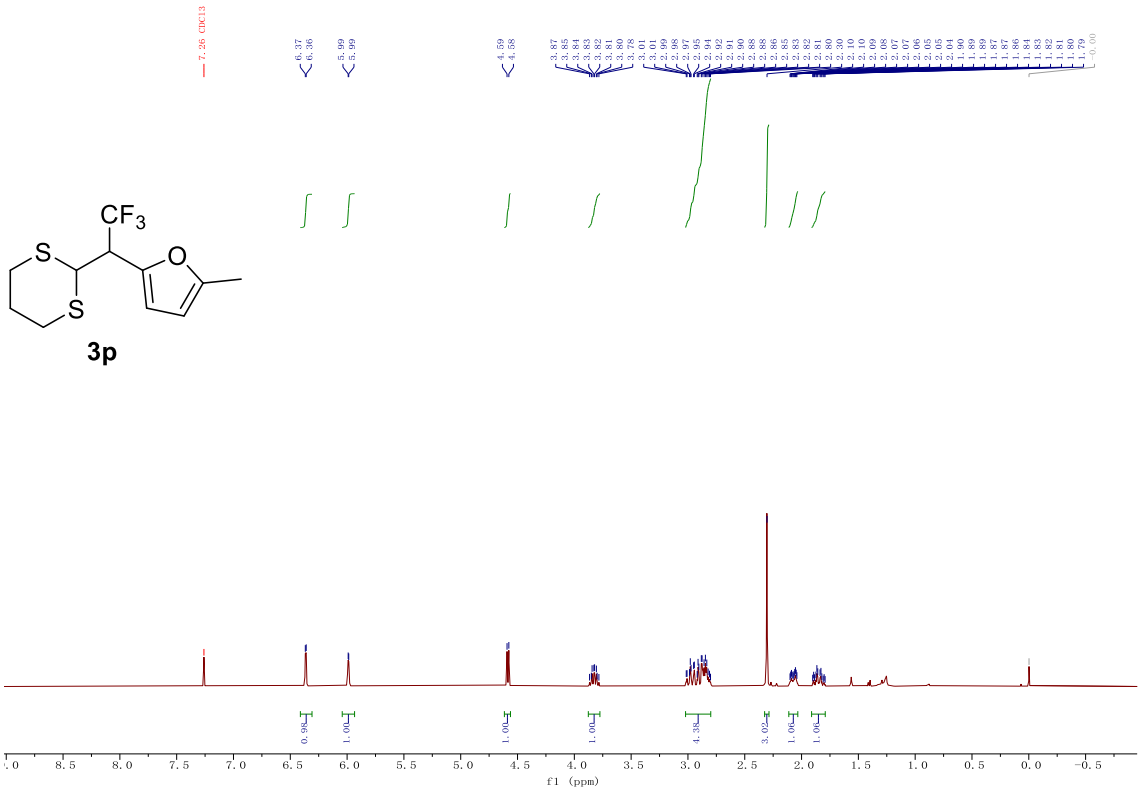
^{13}C NMR (101 MHz, $CDCl_3$)



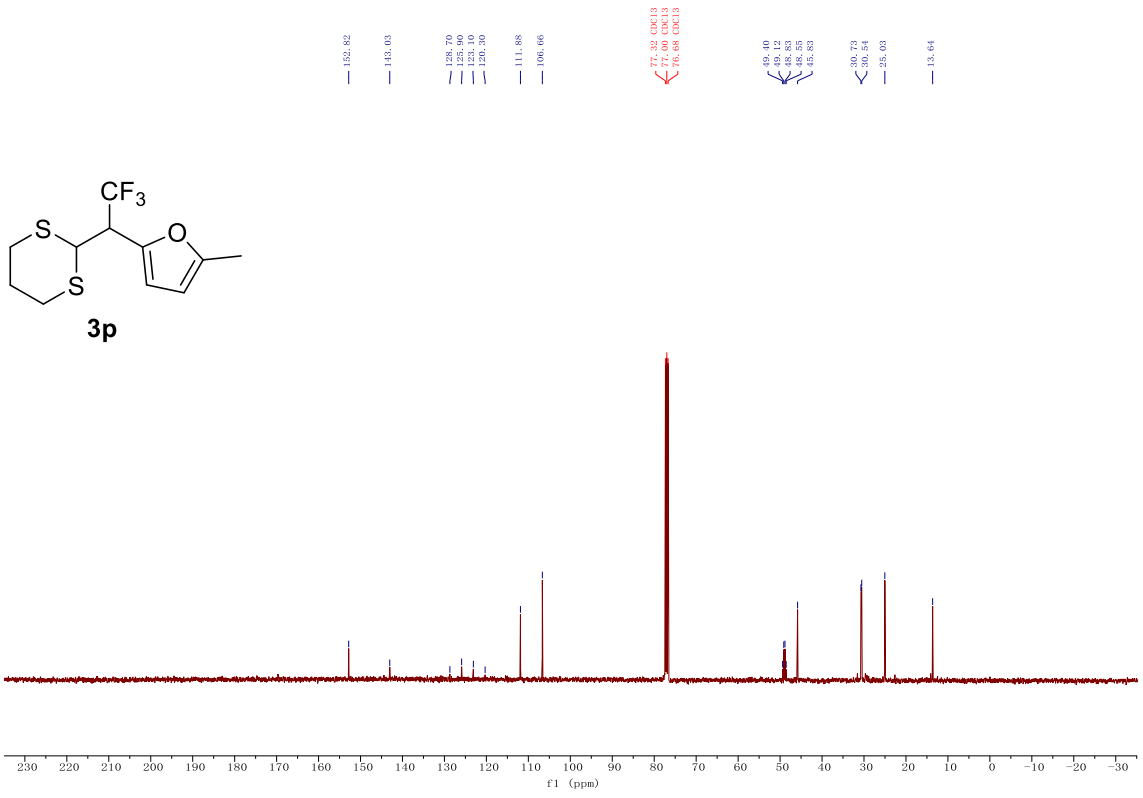
^{19}F NMR (376 MHz, $CDCl_3$)



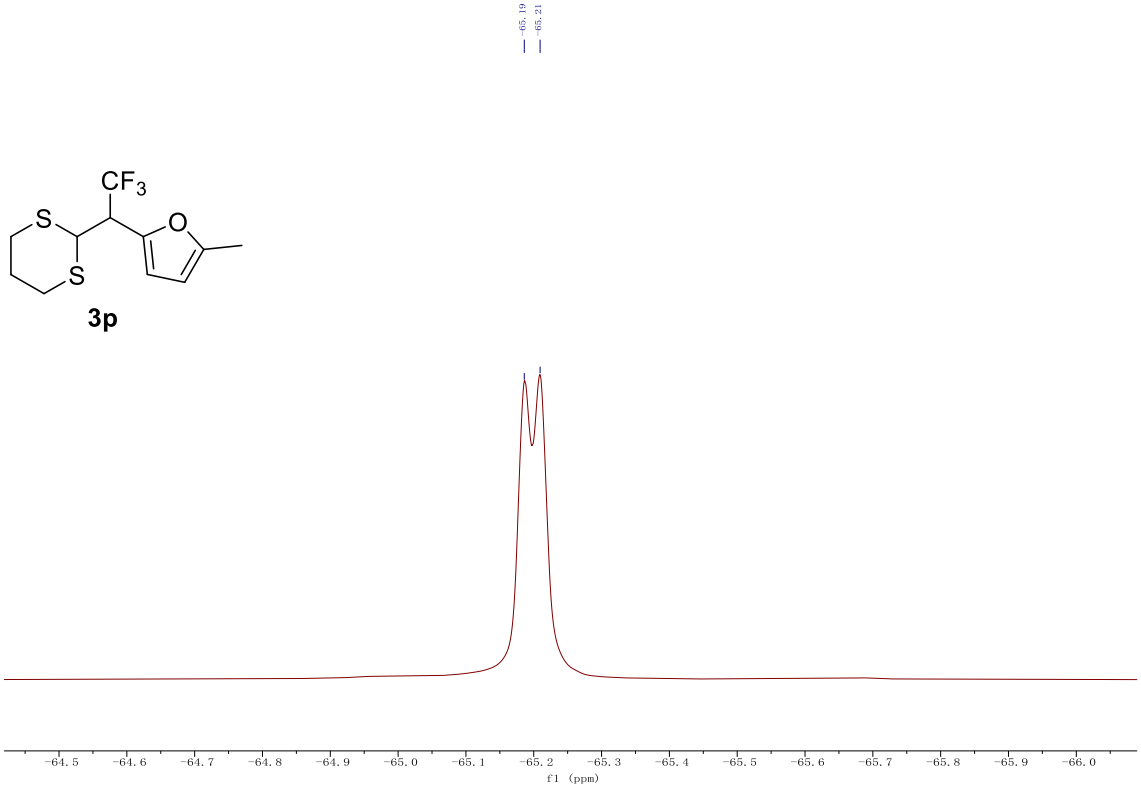
^{1}H NMR (400 MHz, $CDCl_3$)



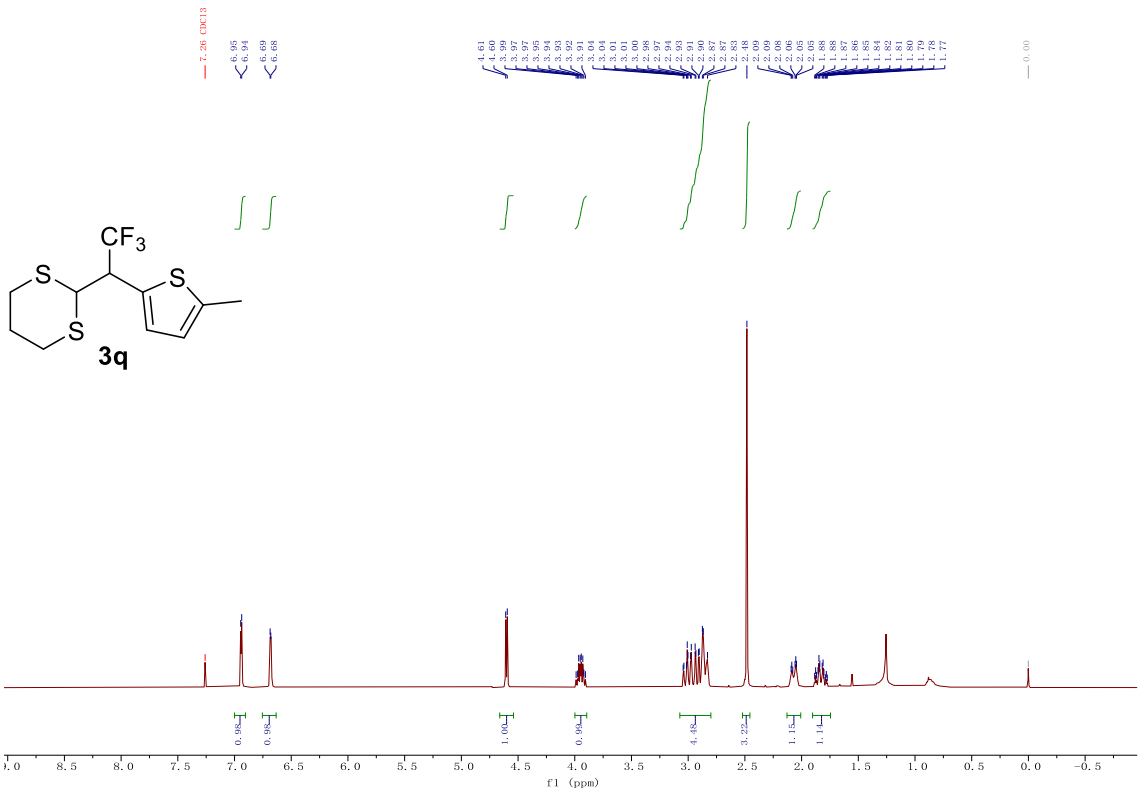
^{13}C NMR (101 MHz, $CDCl_3$)



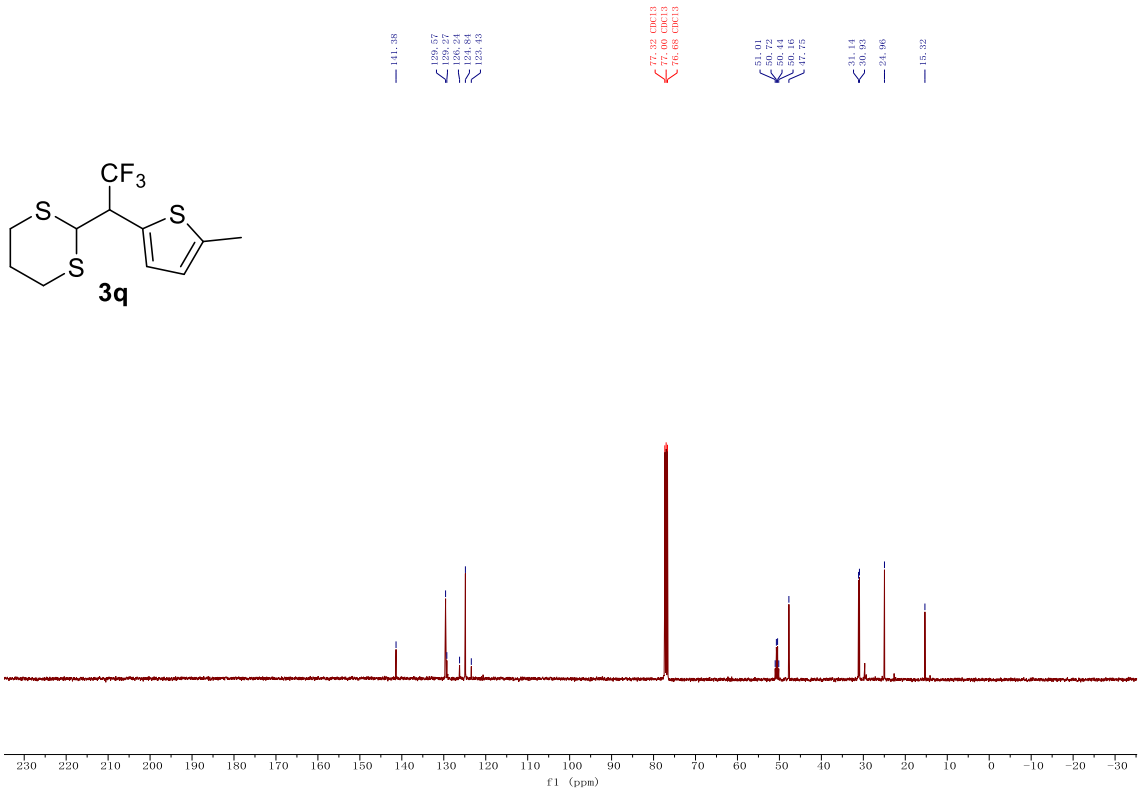
^{19}F NMR (376 MHz, $CDCl_3$)



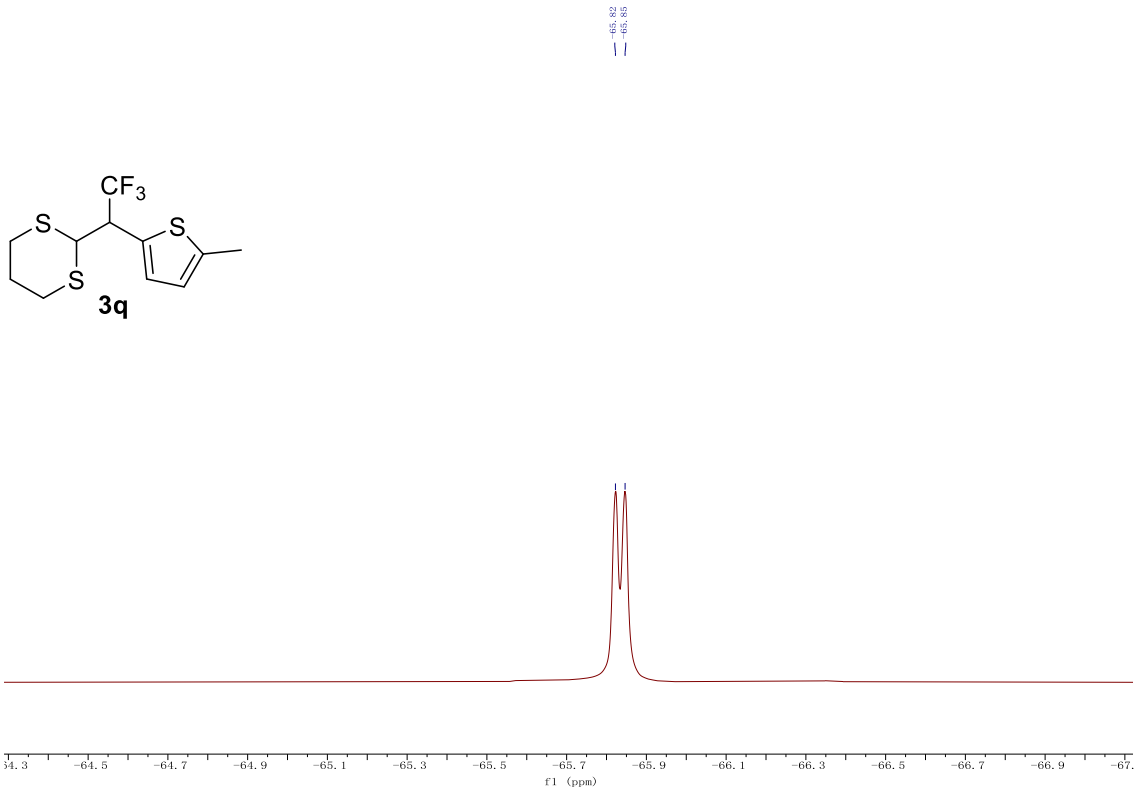
^{1}H NMR (400 MHz, $CDCl_3$)



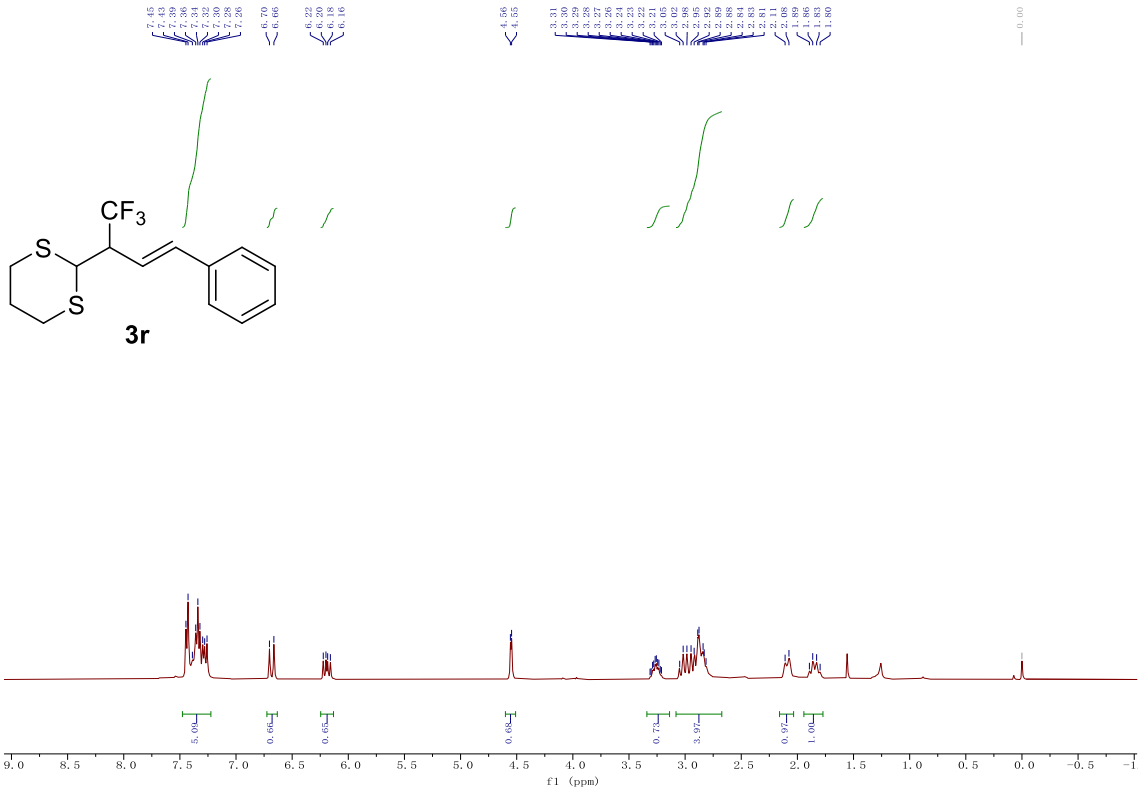
^{13}C NMR (101 MHz, $CDCl_3$)



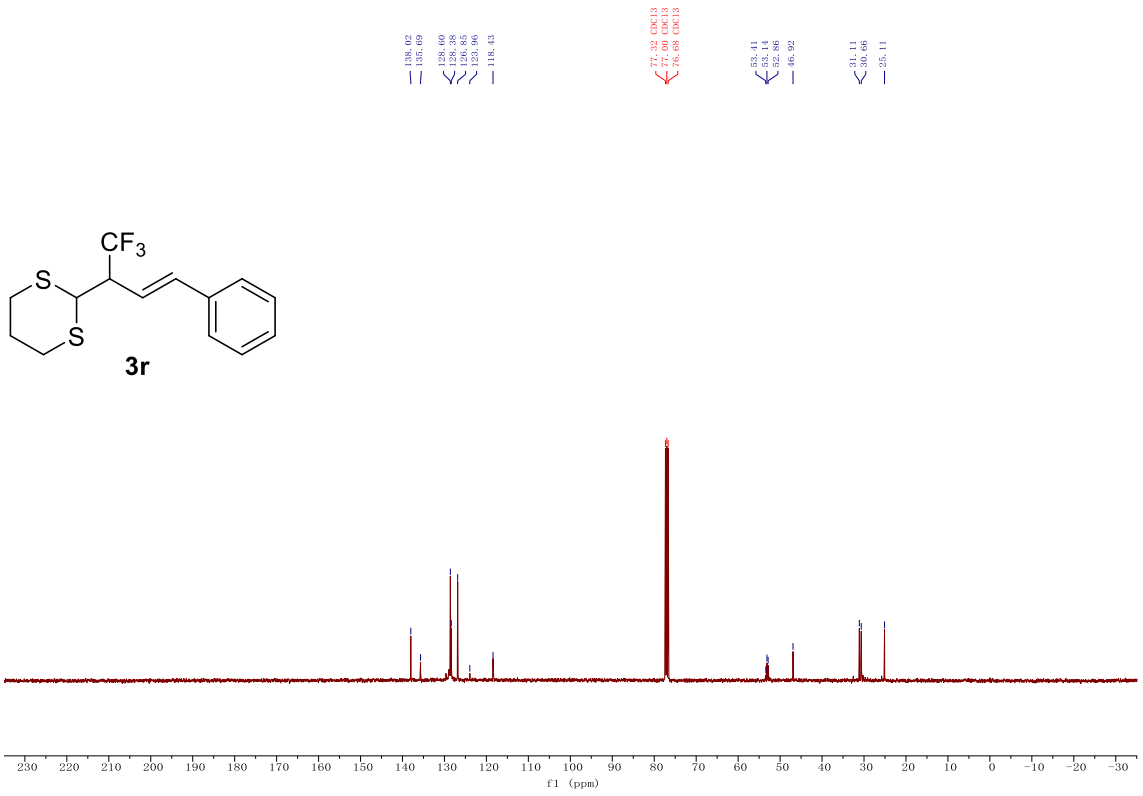
^{19}F NMR (376 MHz, $CDCl_3$)



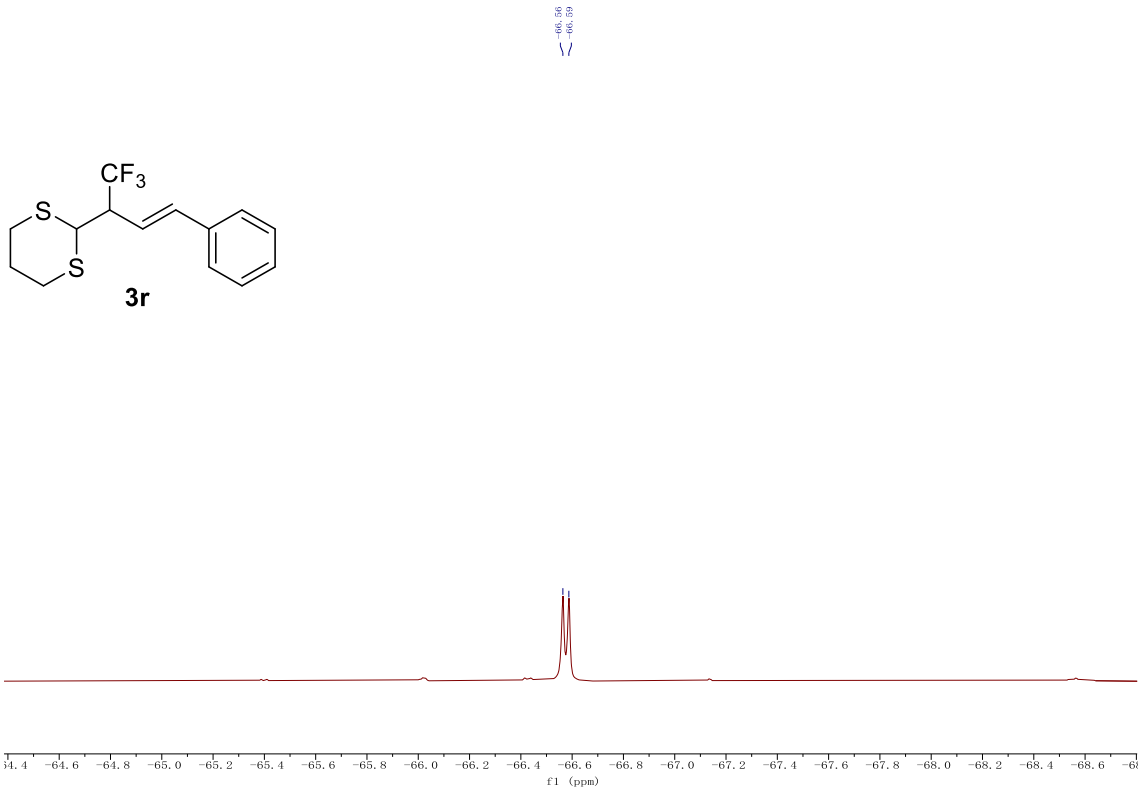
^{1}H NMR (400 MHz, $CDCl_3$)



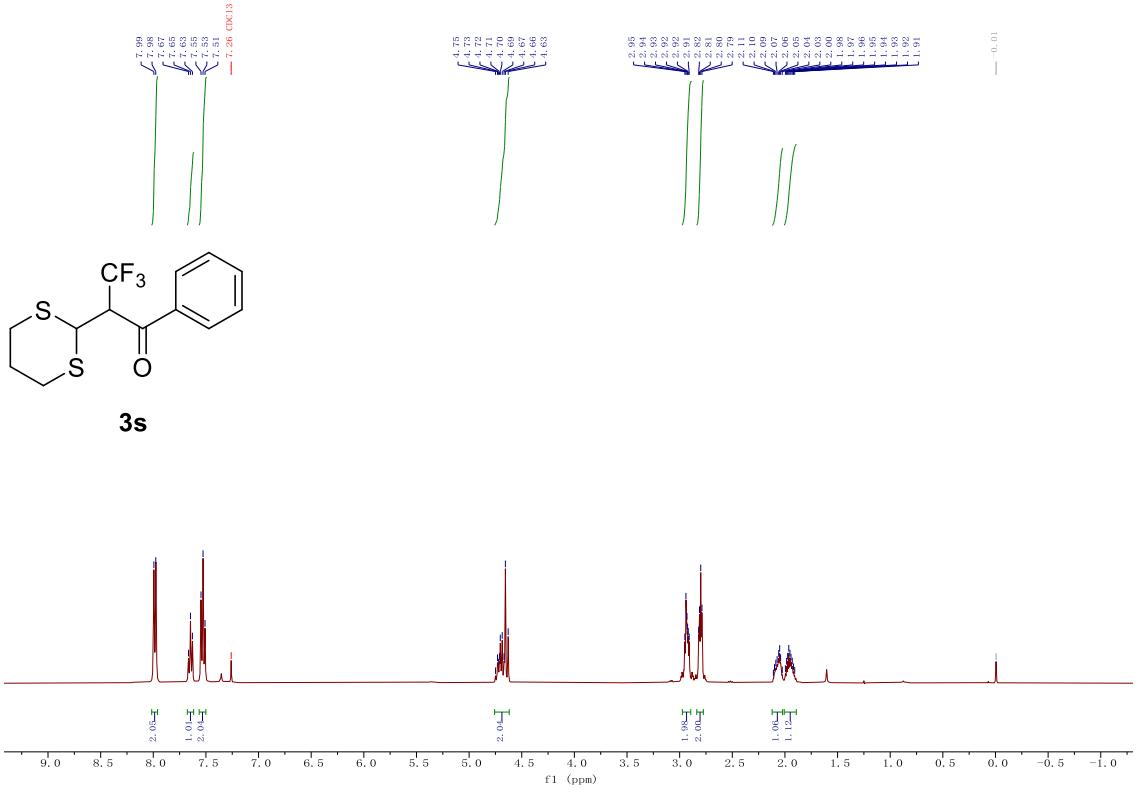
^{13}C NMR (101 MHz, $CDCl_3$)



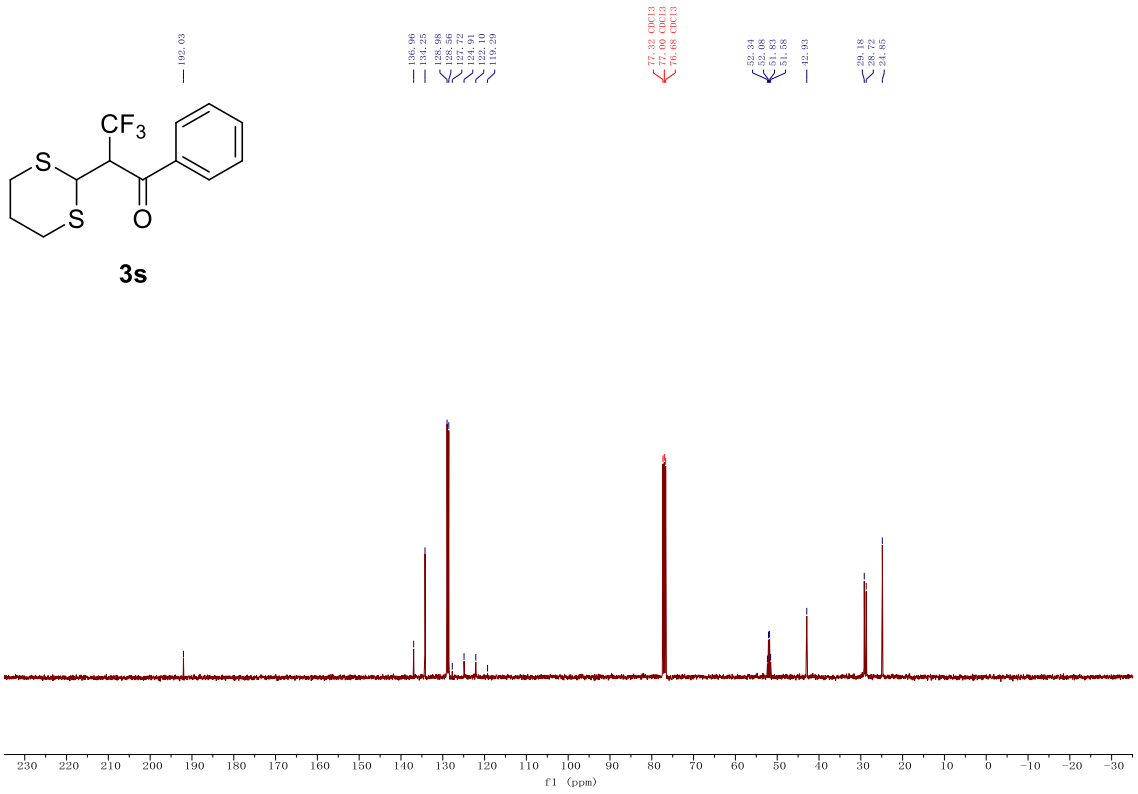
^{19}F NMR (376 MHz, $CDCl_3$)



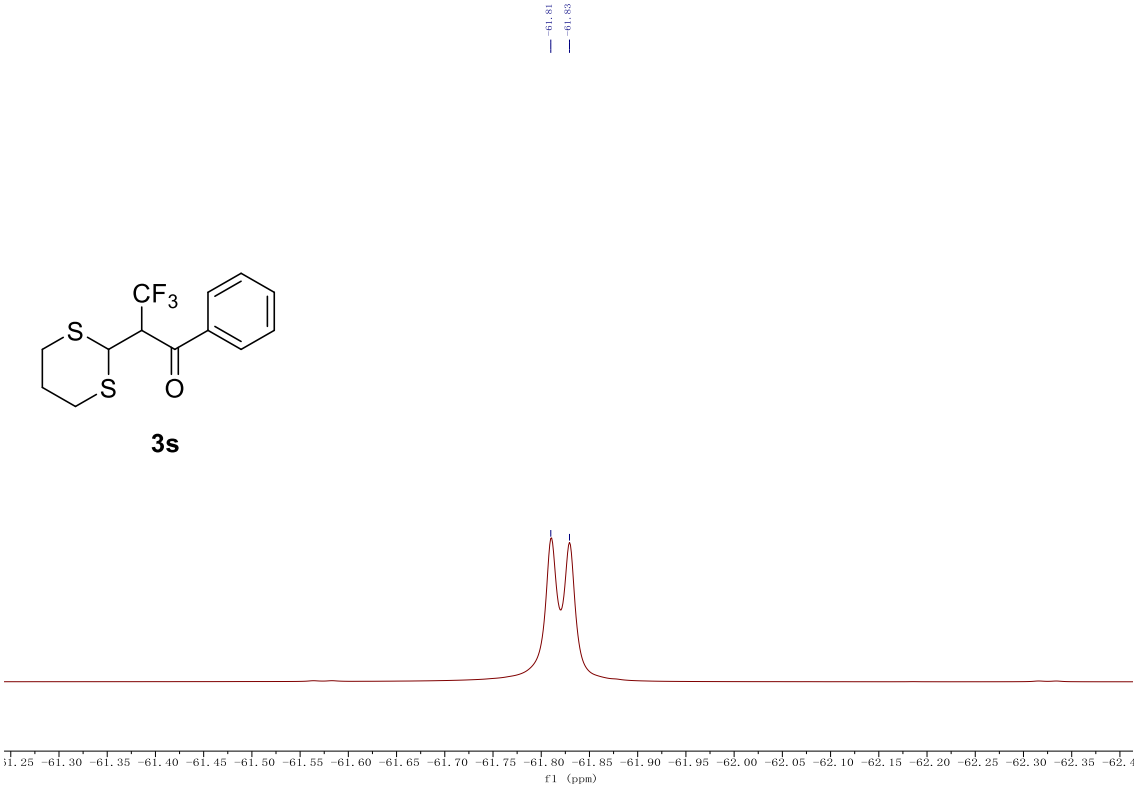
^{1}H NMR (400 MHz, $CDCl_3$)



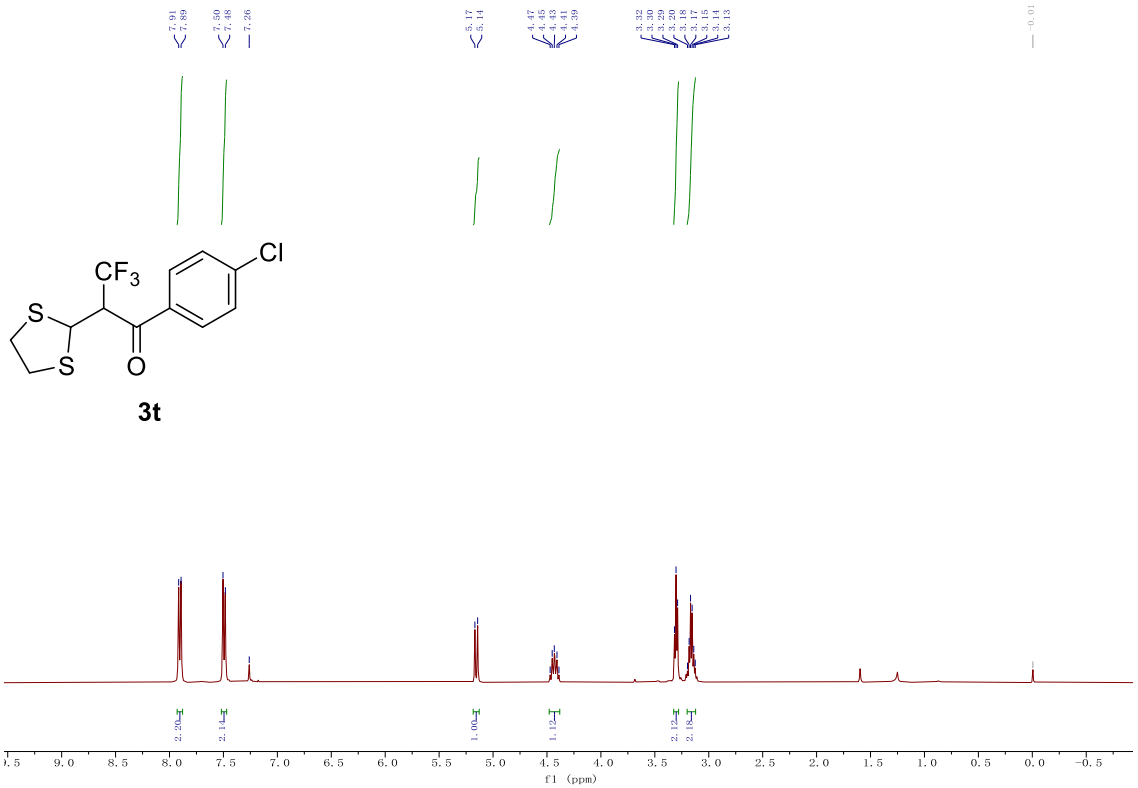
^{13}C NMR (101 MHz, $CDCl_3$)



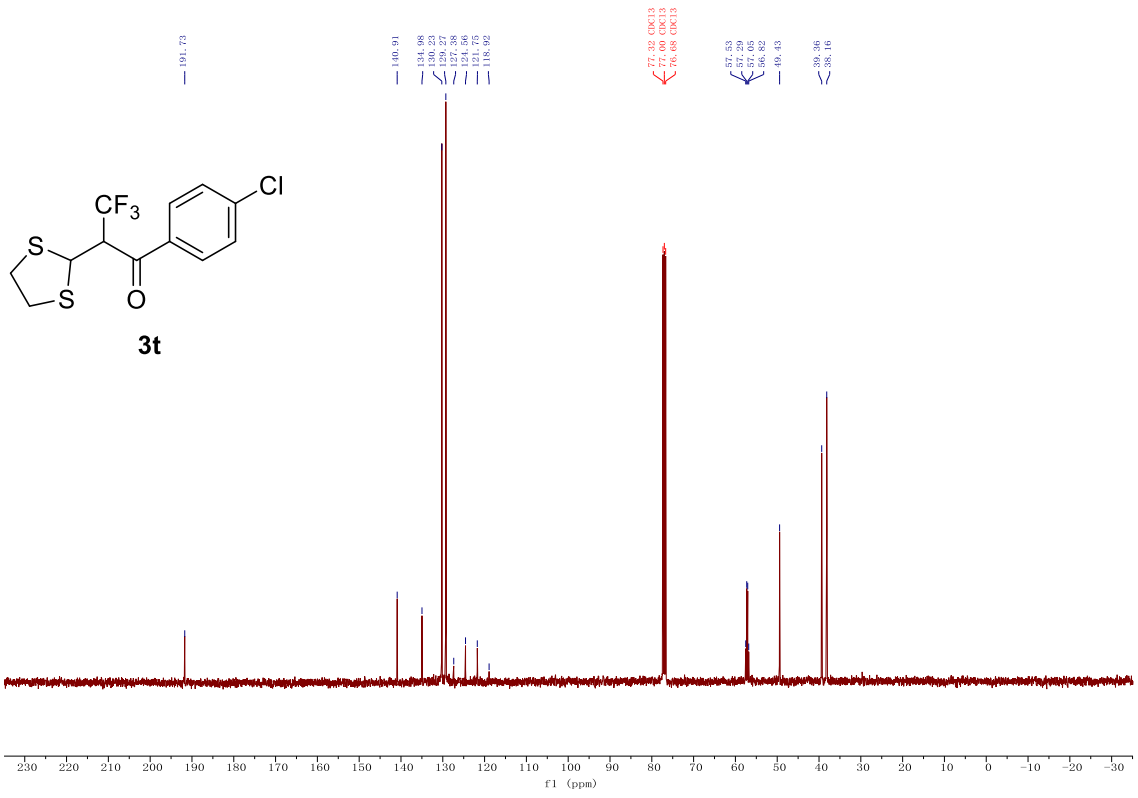
^{19}F NMR (376 MHz, $CDCl_3$)



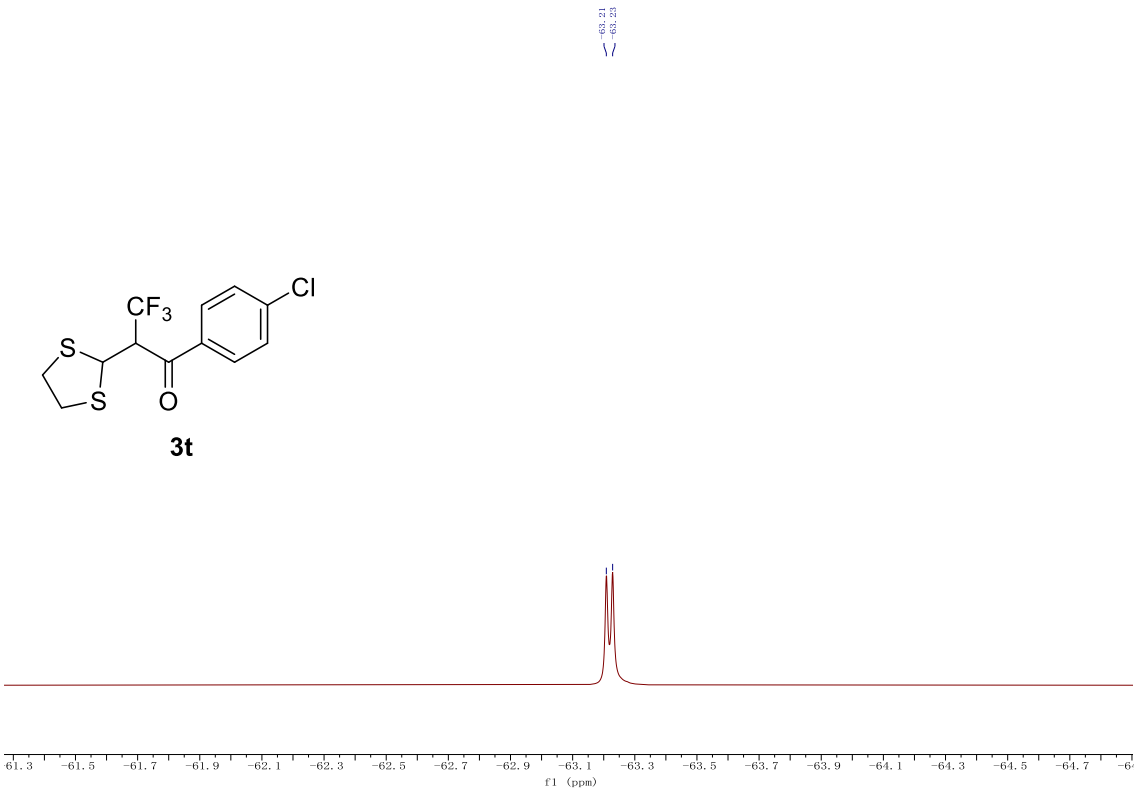
^{1}H NMR (400 MHz, $CDCl_3$)



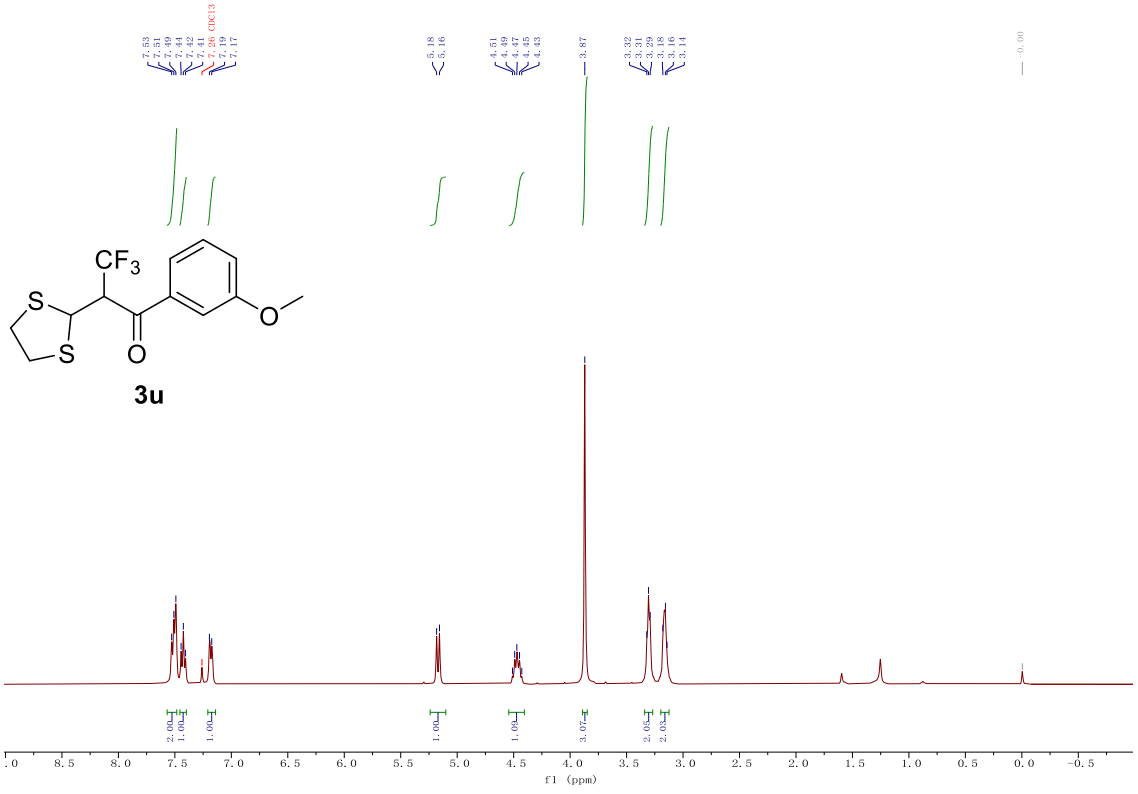
^{13}C NMR (101 MHz, $CDCl_3$)



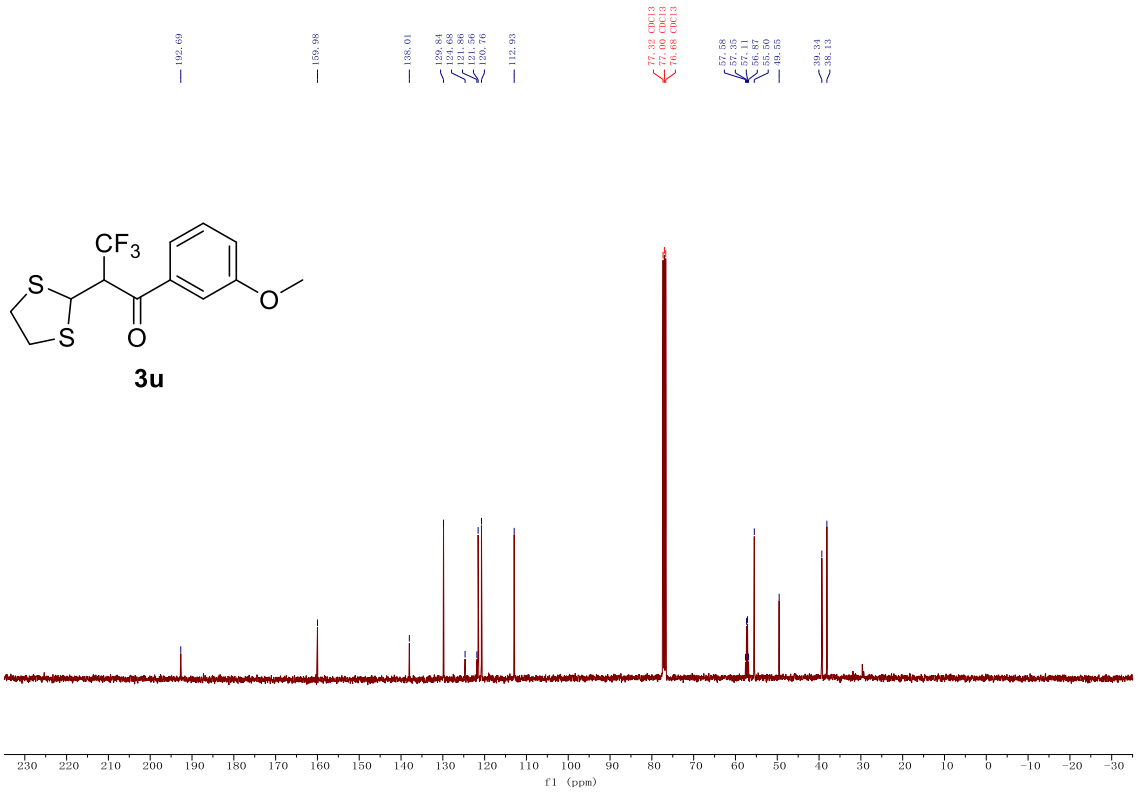
^{19}F NMR (376 MHz, $CDCl_3$)



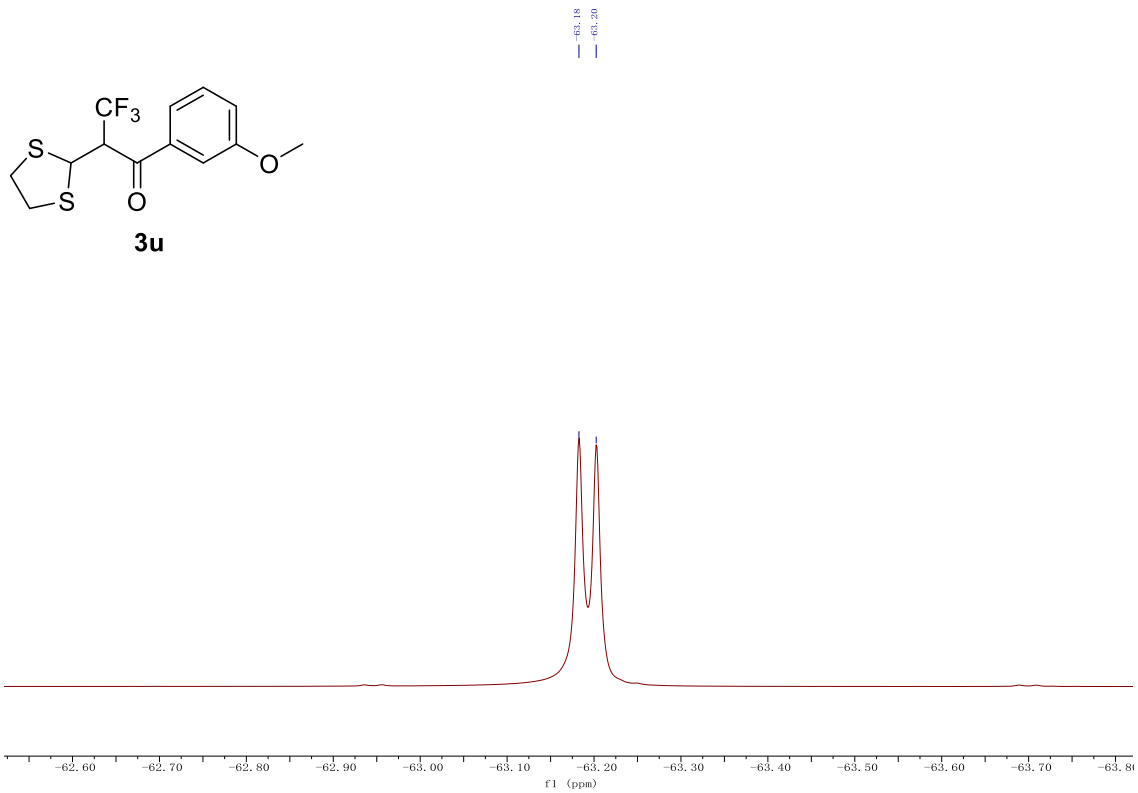
^{1}H NMR (400 MHz, $CDCl_3$)



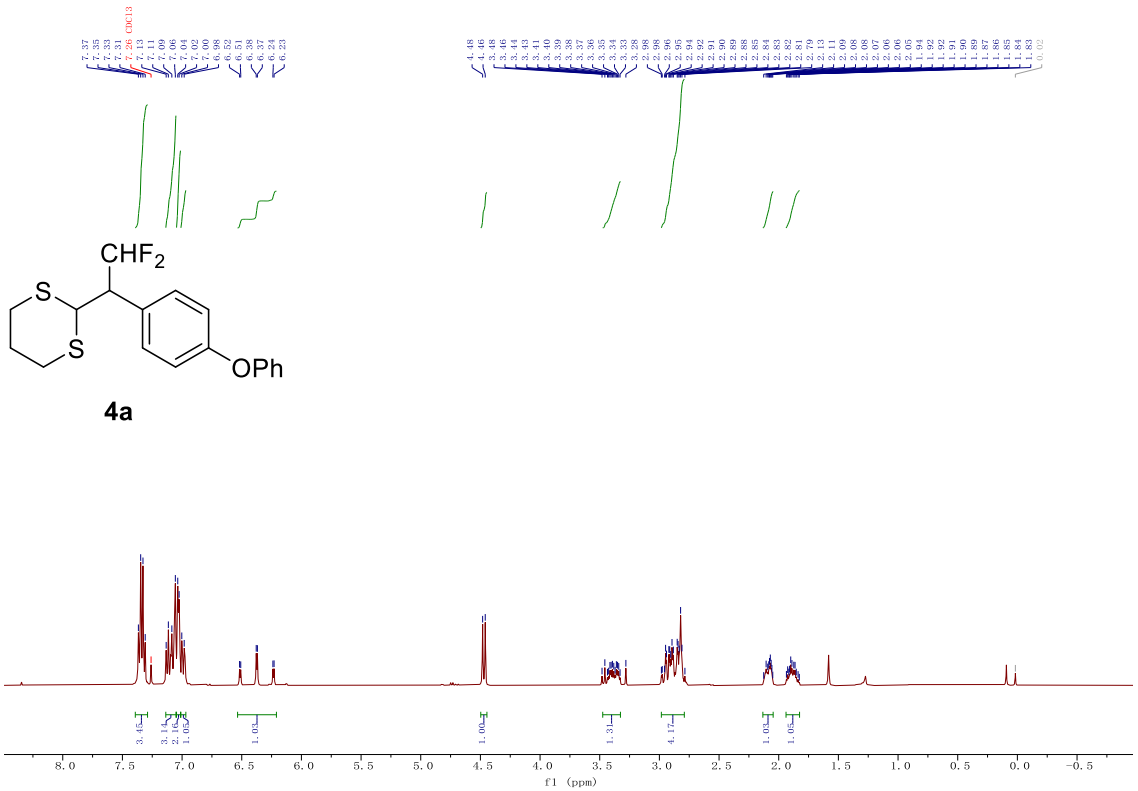
^{13}C NMR (101 MHz, $CDCl_3$)



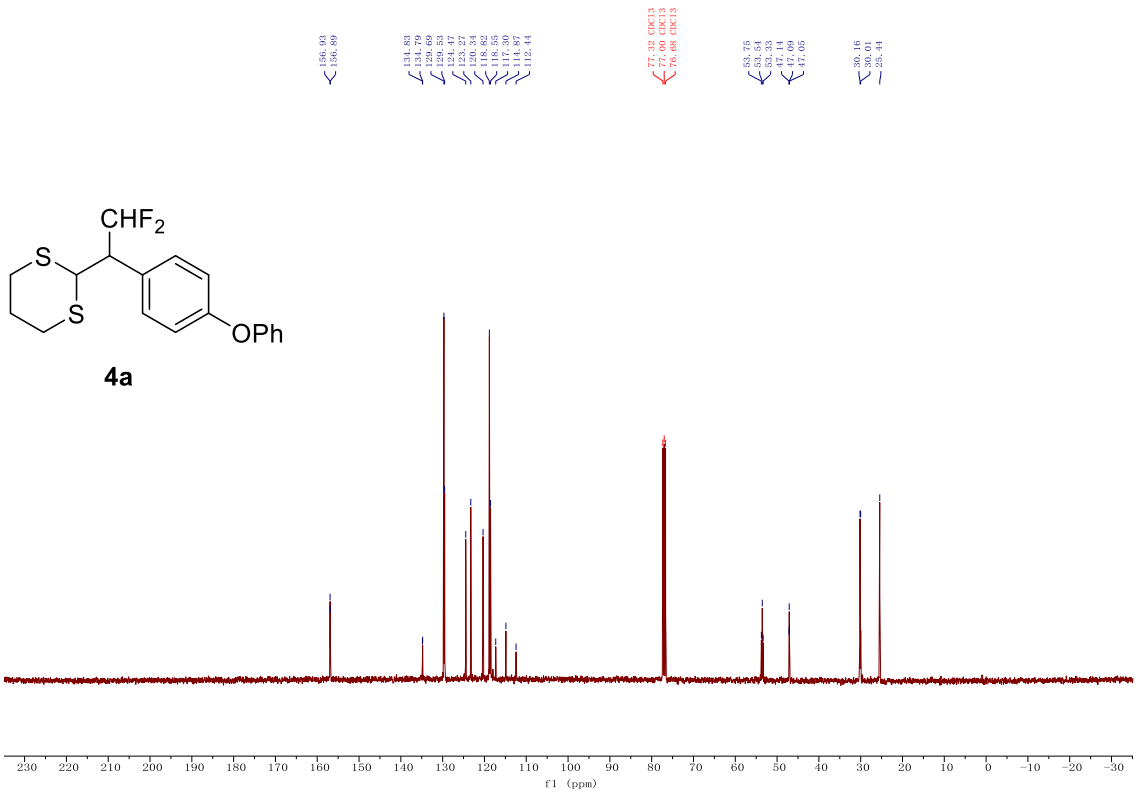
^{19}F NMR (376 MHz, $CDCl_3$)



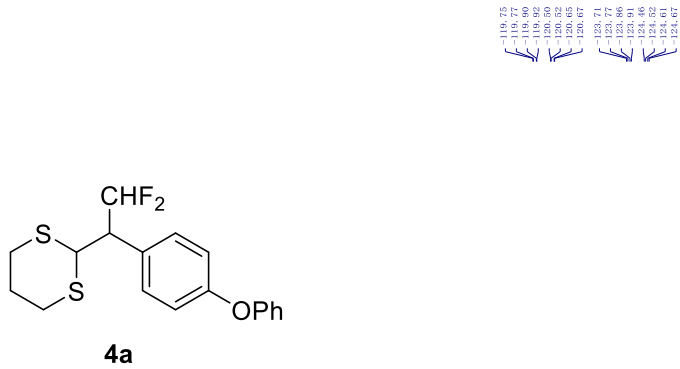
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

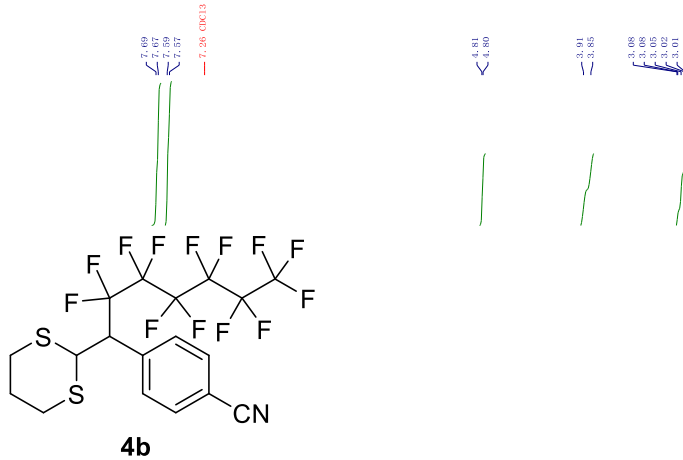


^{19}F NMR (376 MHz, $CDCl_3$)



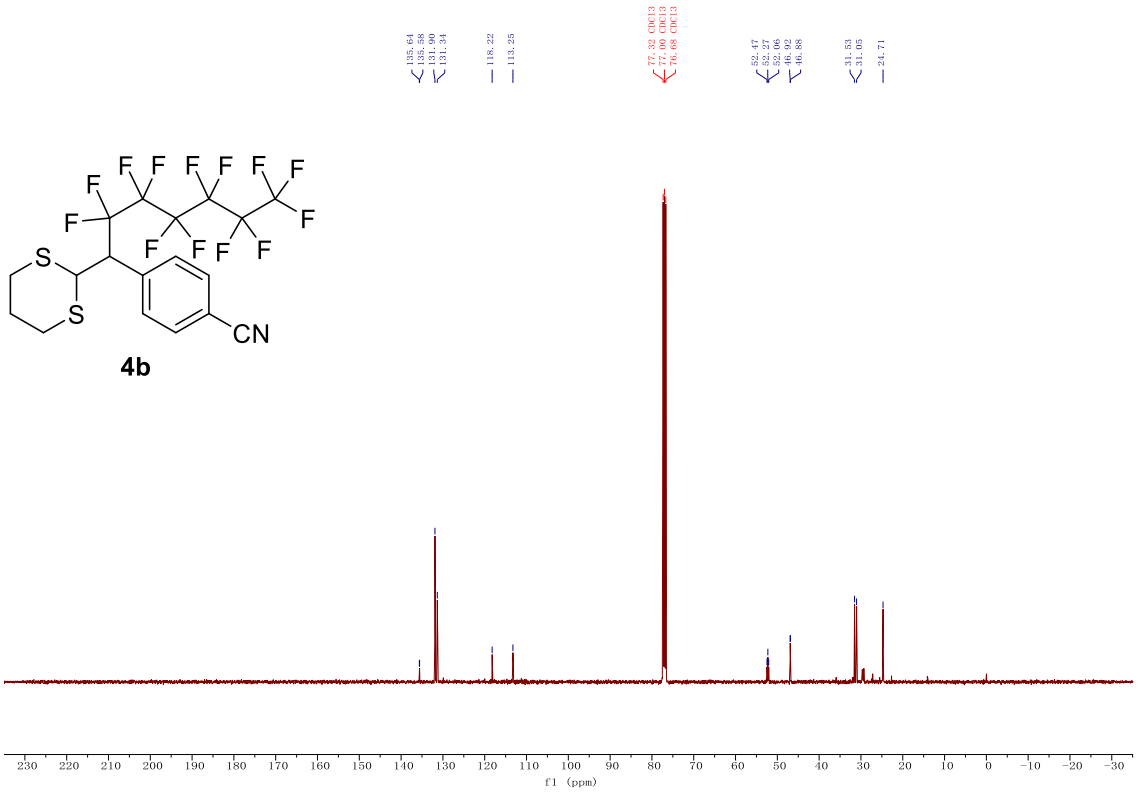
4a

^{1}H NMR (400 MHz, $CDCl_3$)

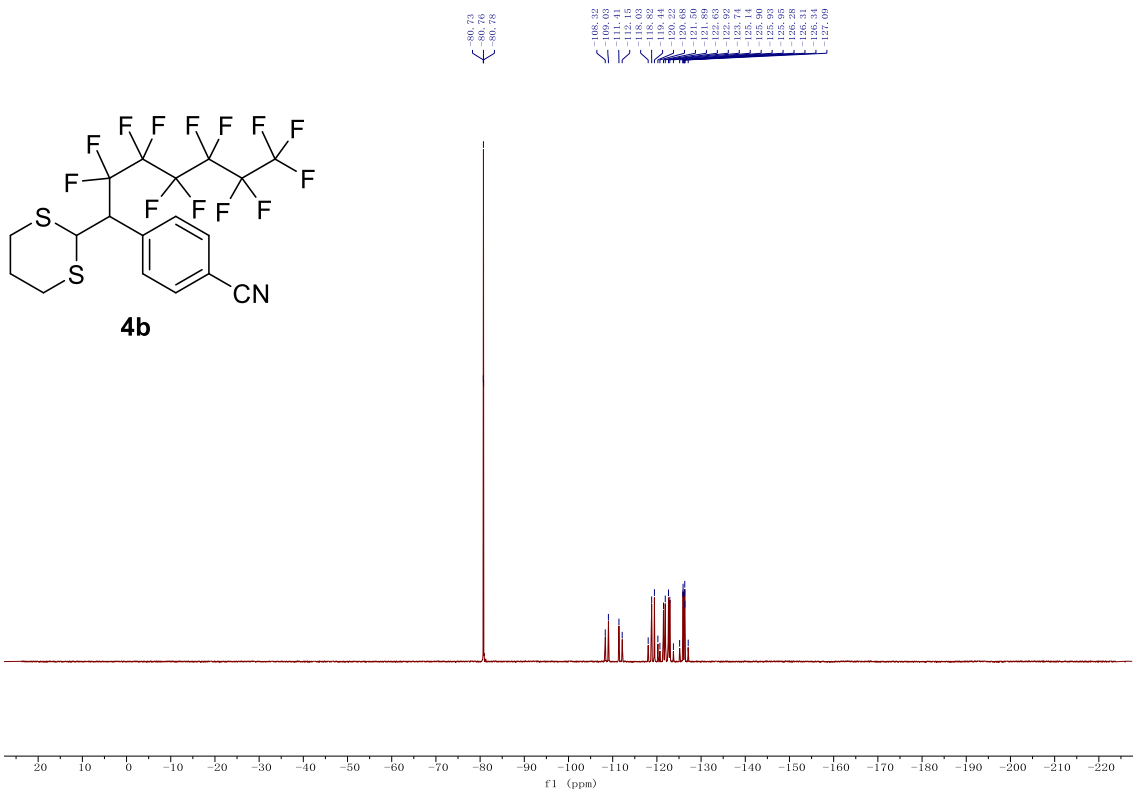


4b

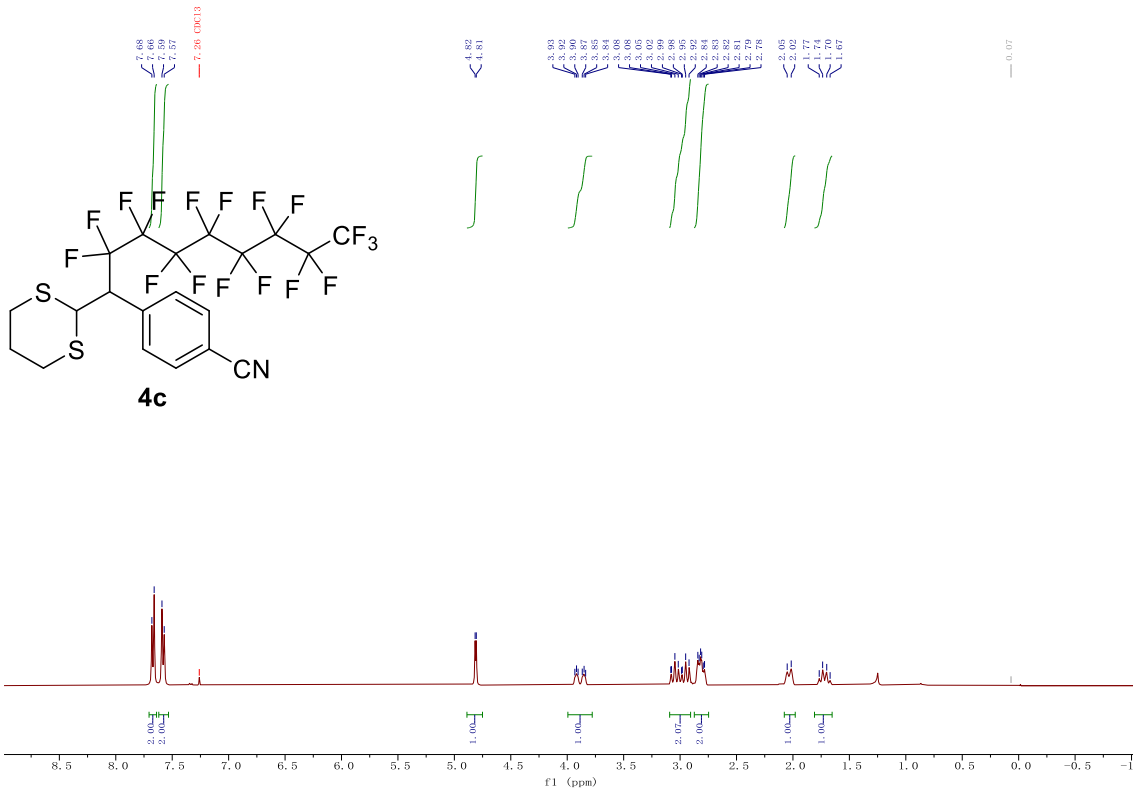
^{13}C NMR (101 MHz, $CDCl_3$)



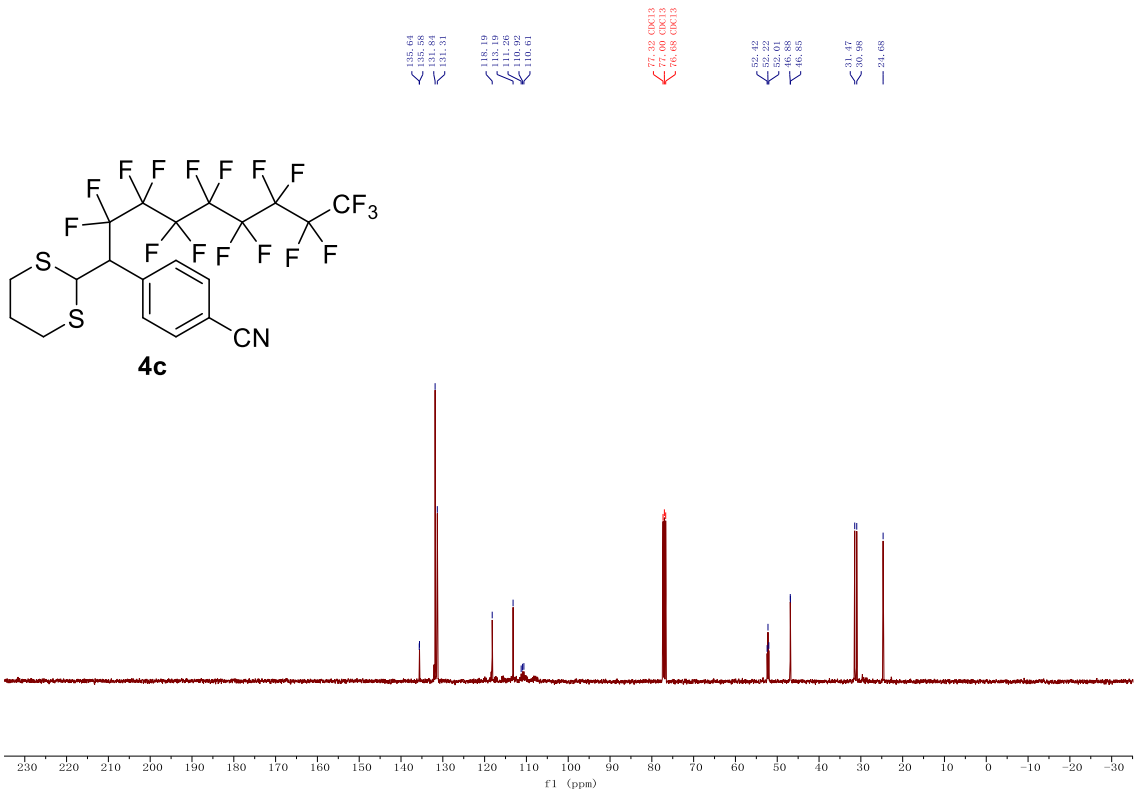
^{19}F NMR (376 MHz, $CDCl_3$)



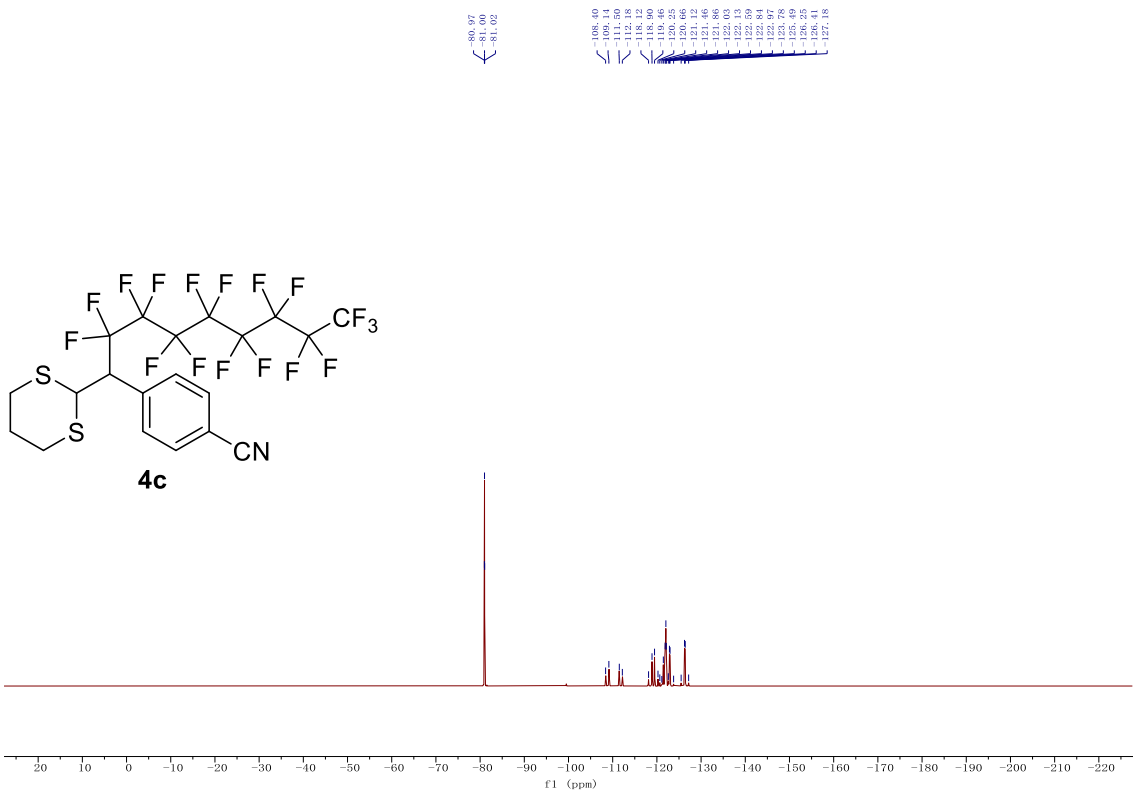
^{1}H NMR (400 MHz, $CDCl_3$)



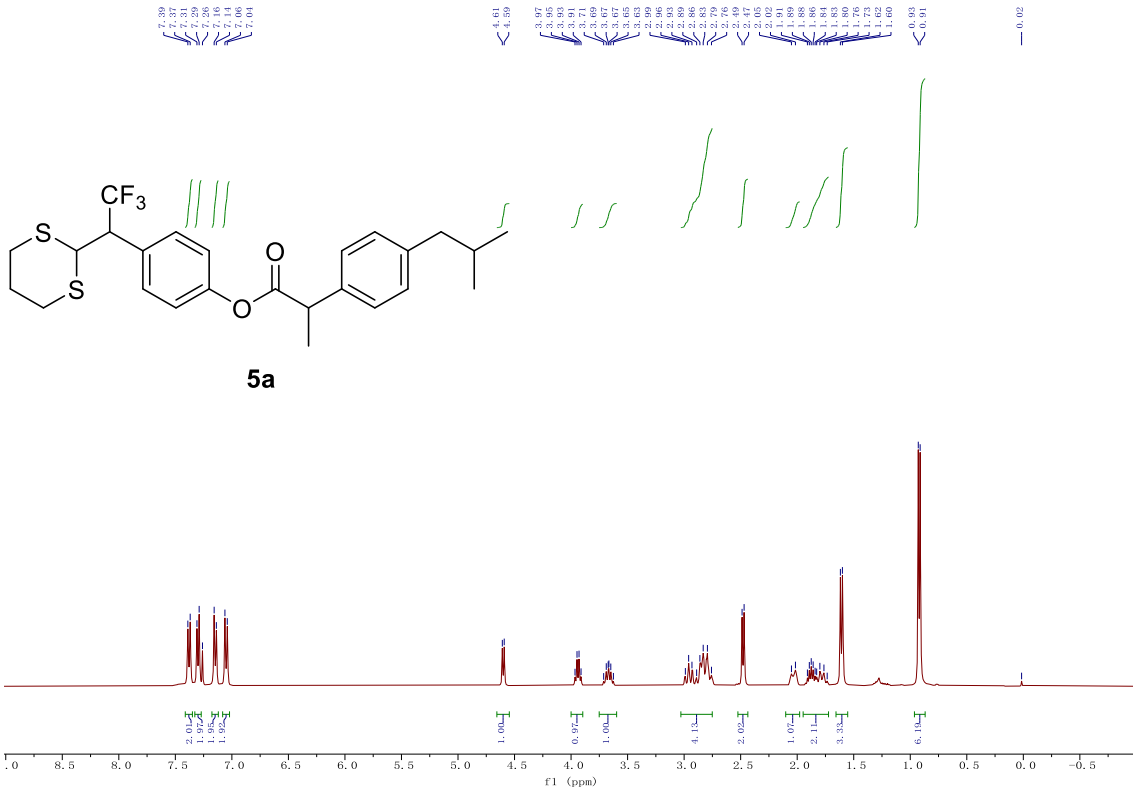
^{13}C NMR (101 MHz, $CDCl_3$)



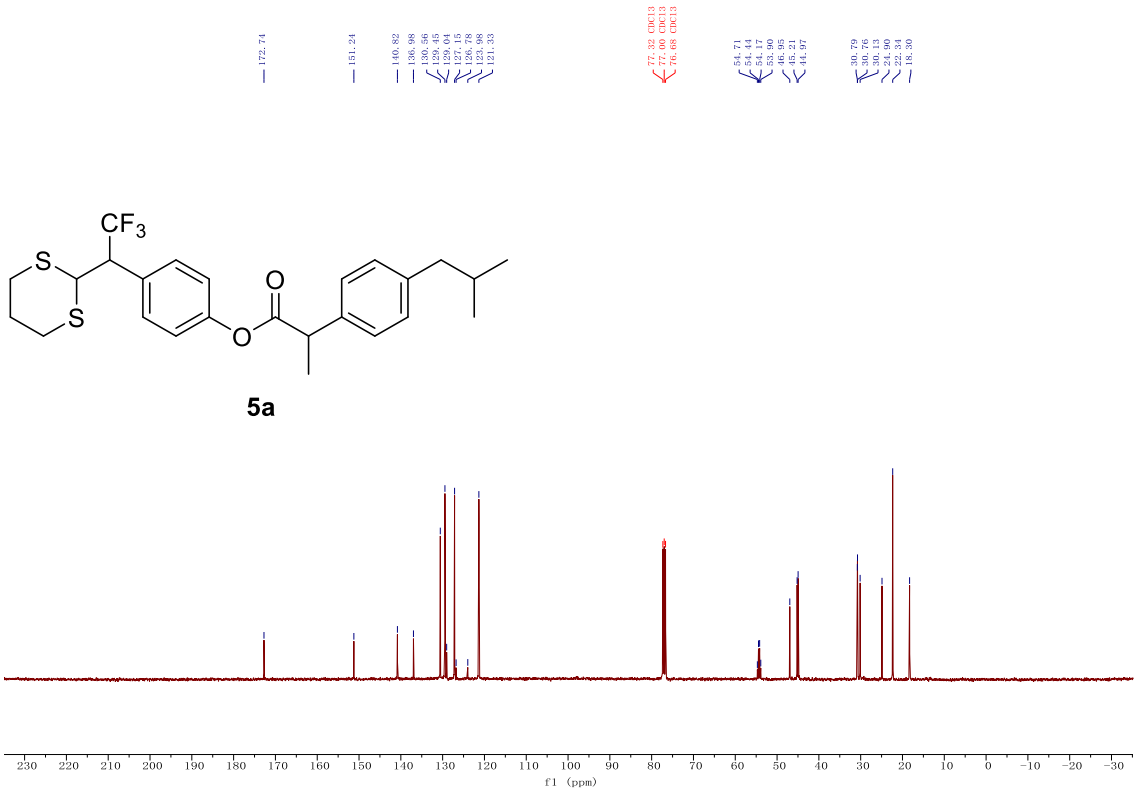
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

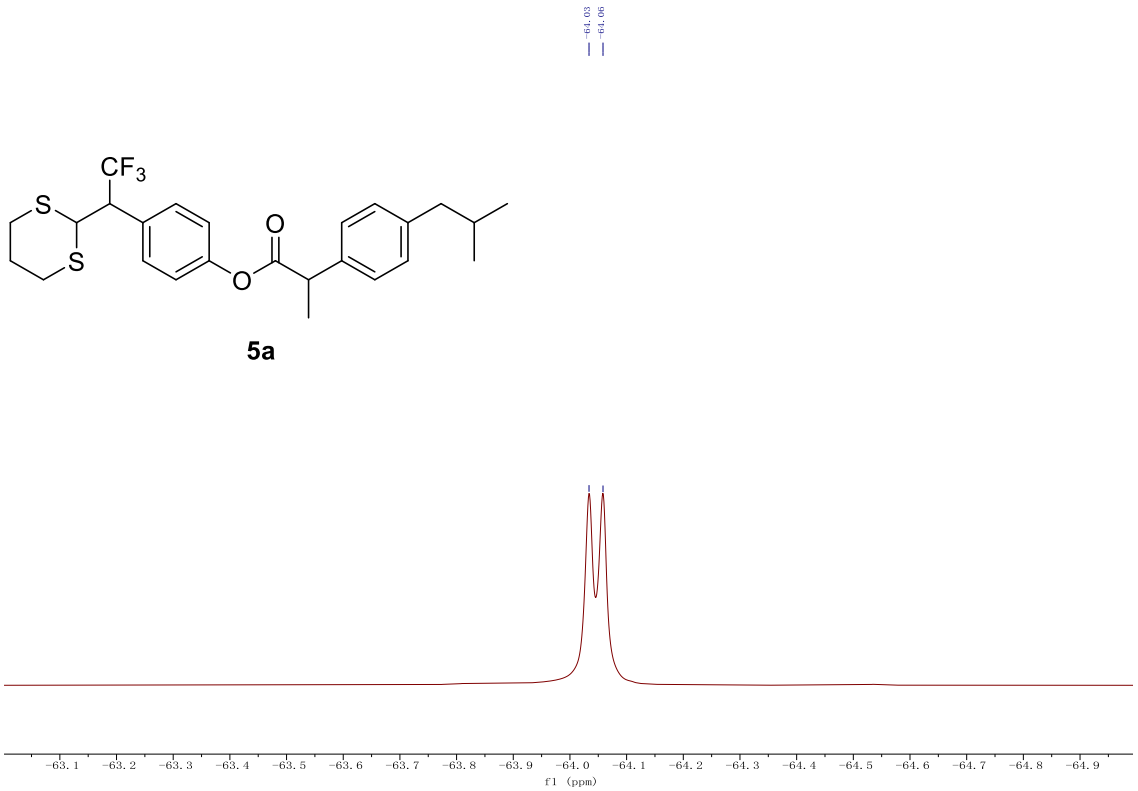


^{13}C NMR (101 MHz, $CDCl_3$)



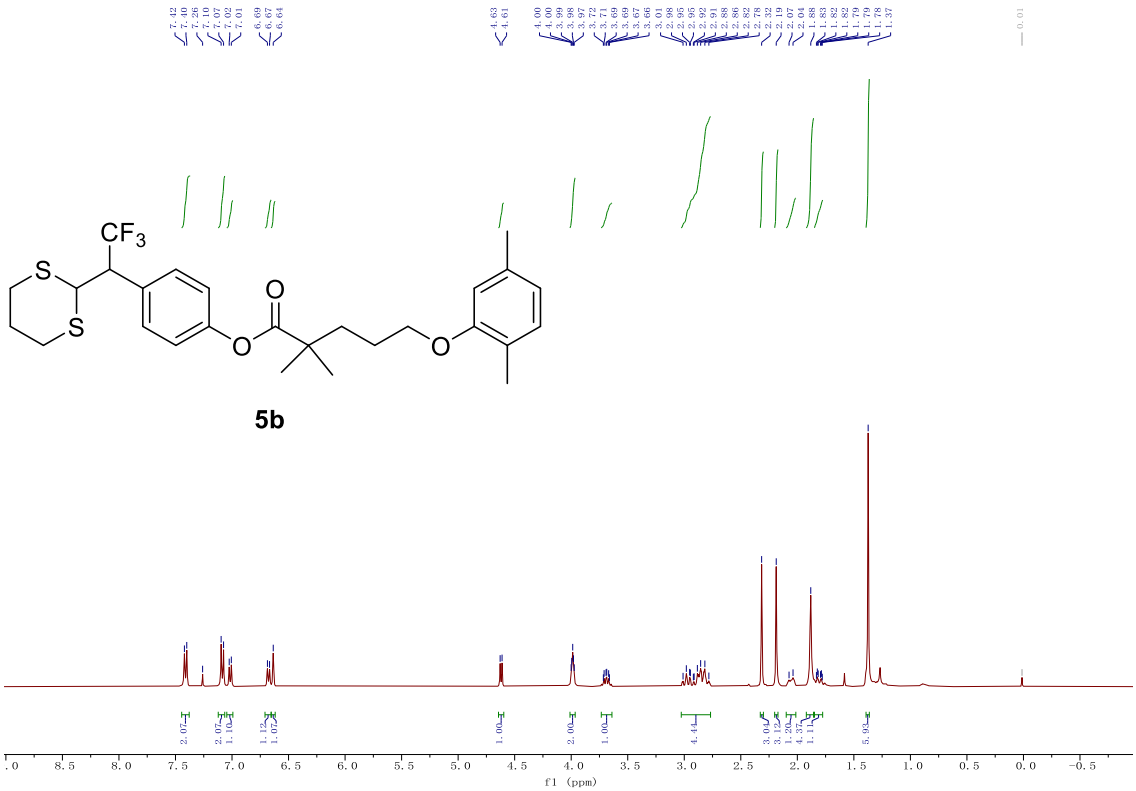
5a

^{19}F NMR (376 MHz, $CDCl_3$)

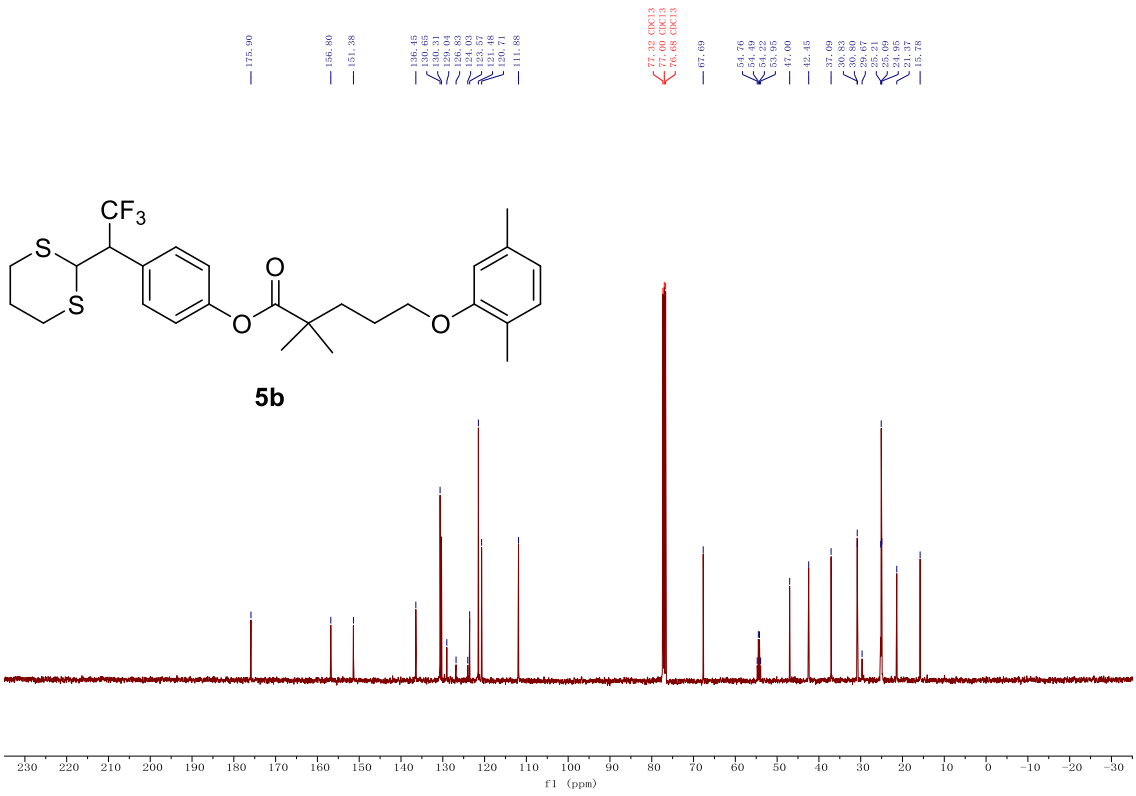


5a

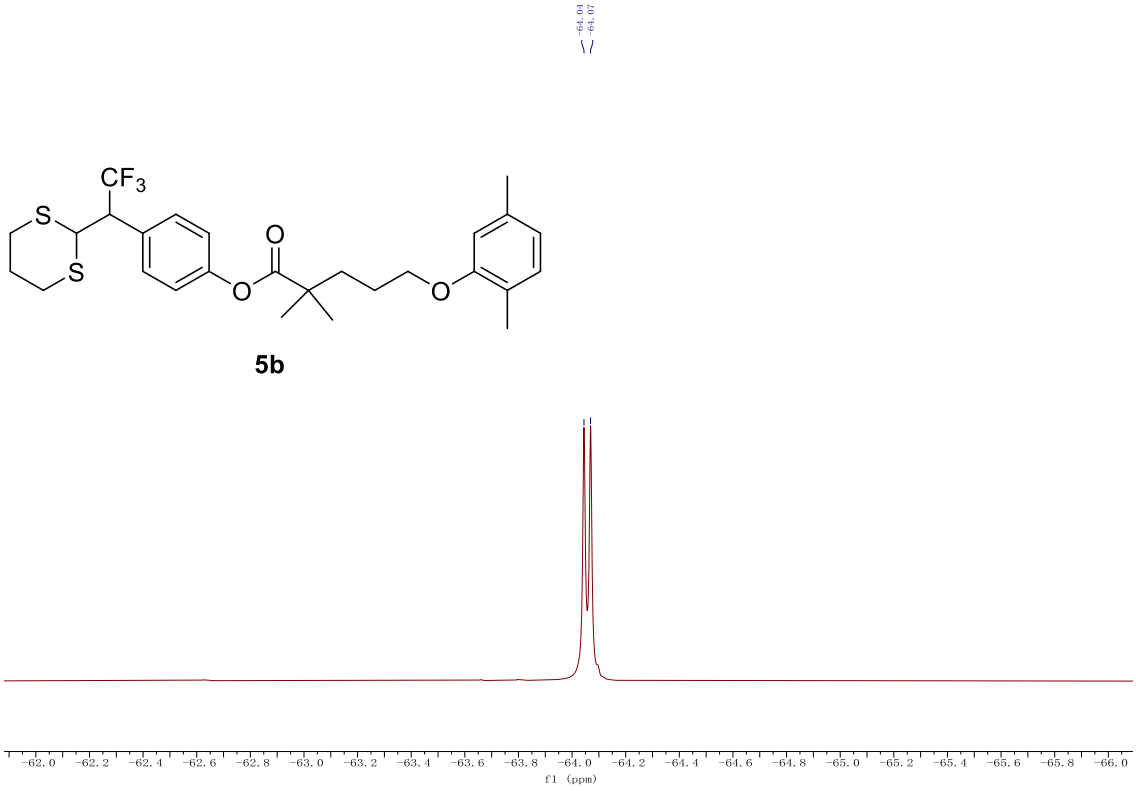
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

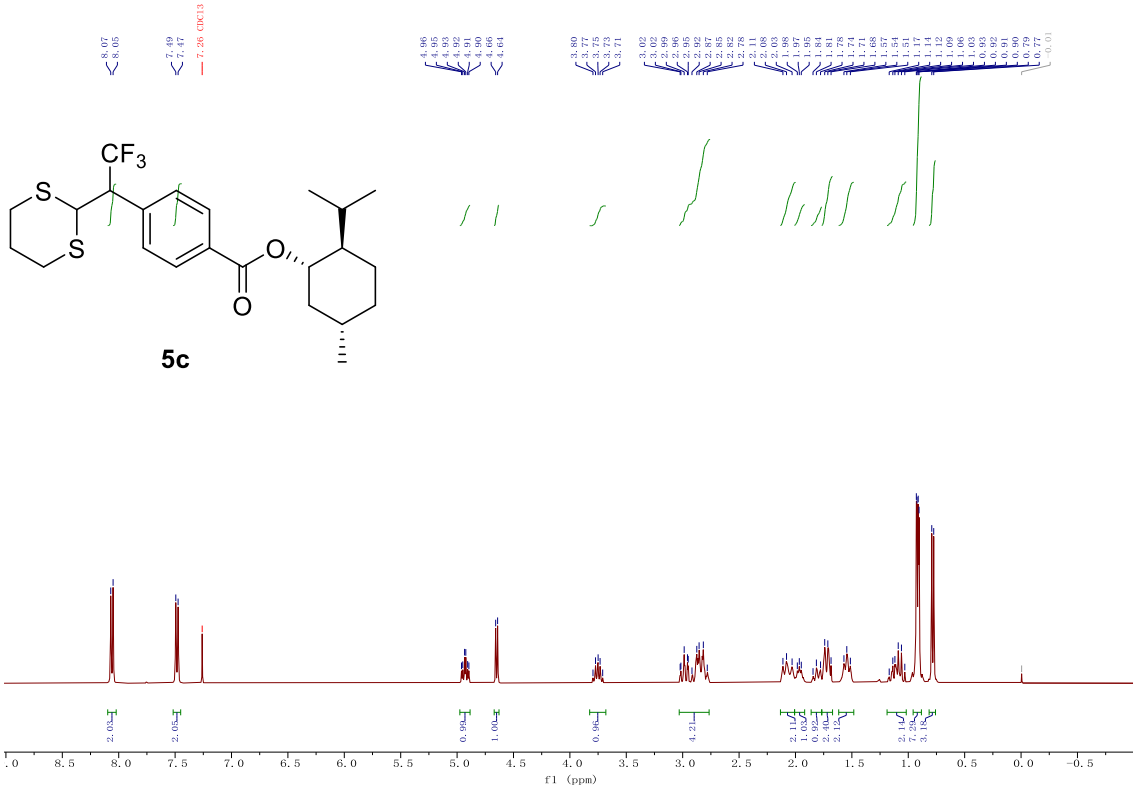


^{19}F NMR (376 MHz, $CDCl_3$)



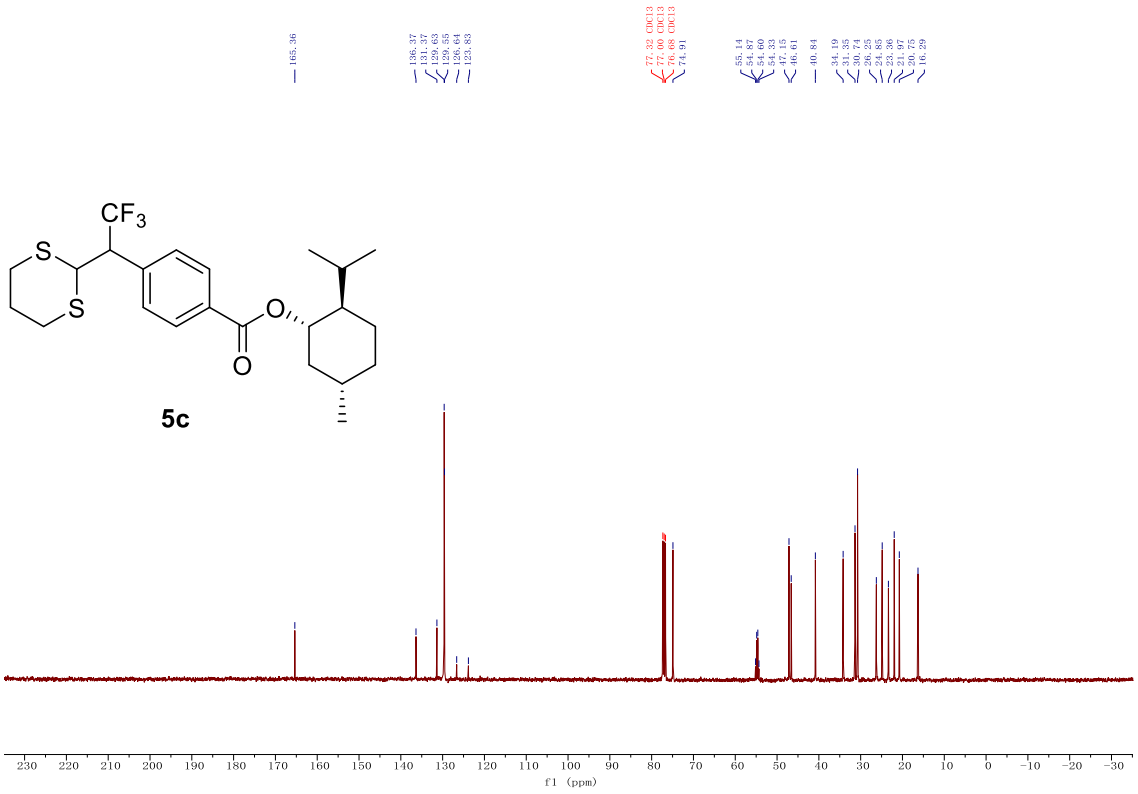
5b

^{1}H NMR (400 MHz, $CDCl_3$)

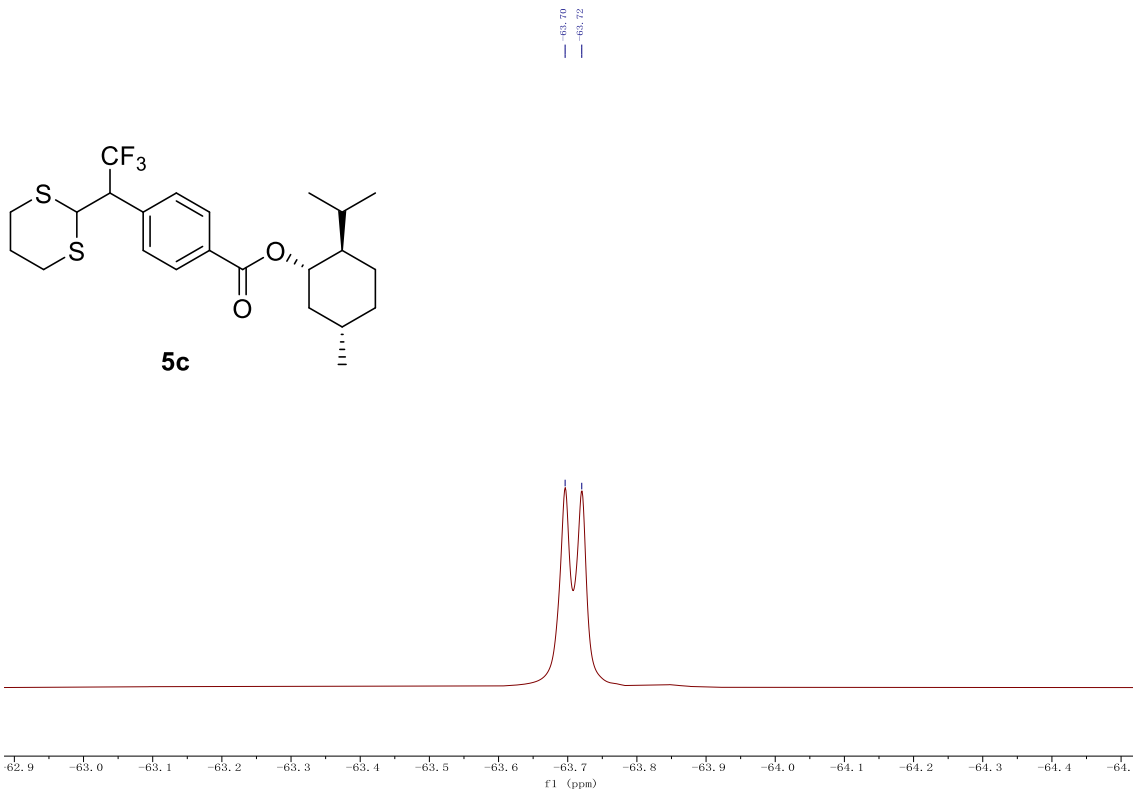


5c

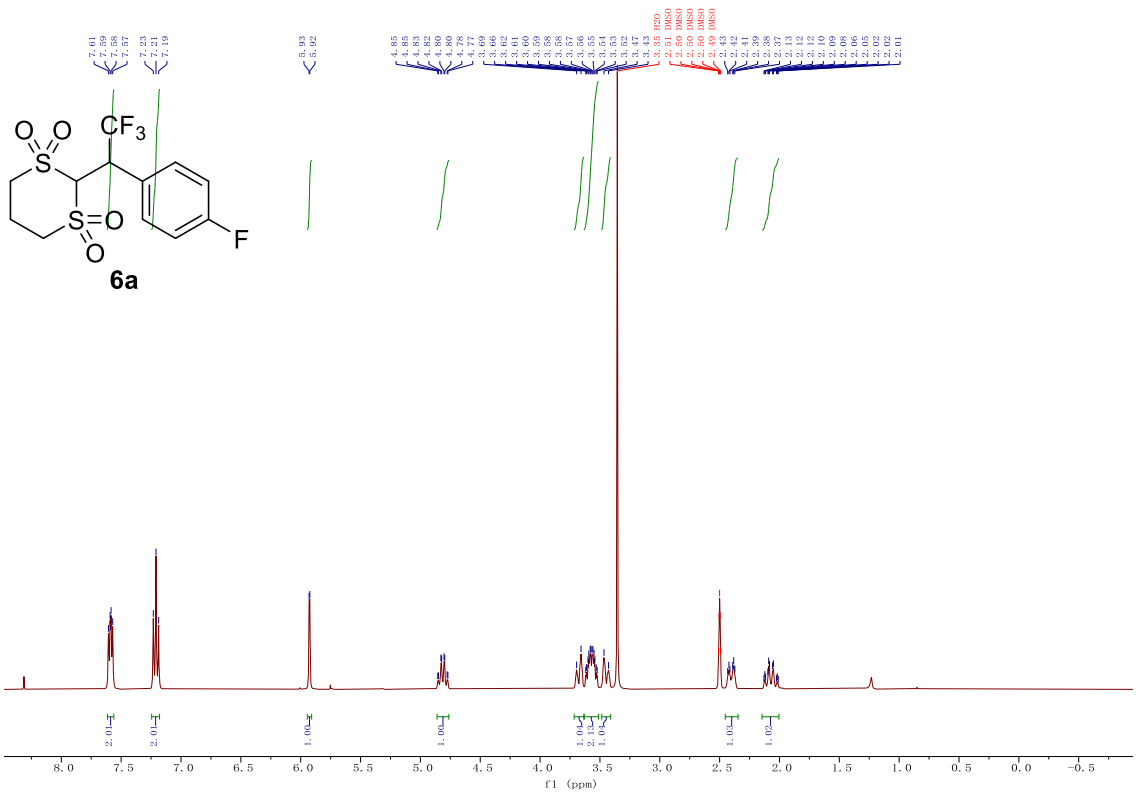
^{13}C NMR (101 MHz, $CDCl_3$)



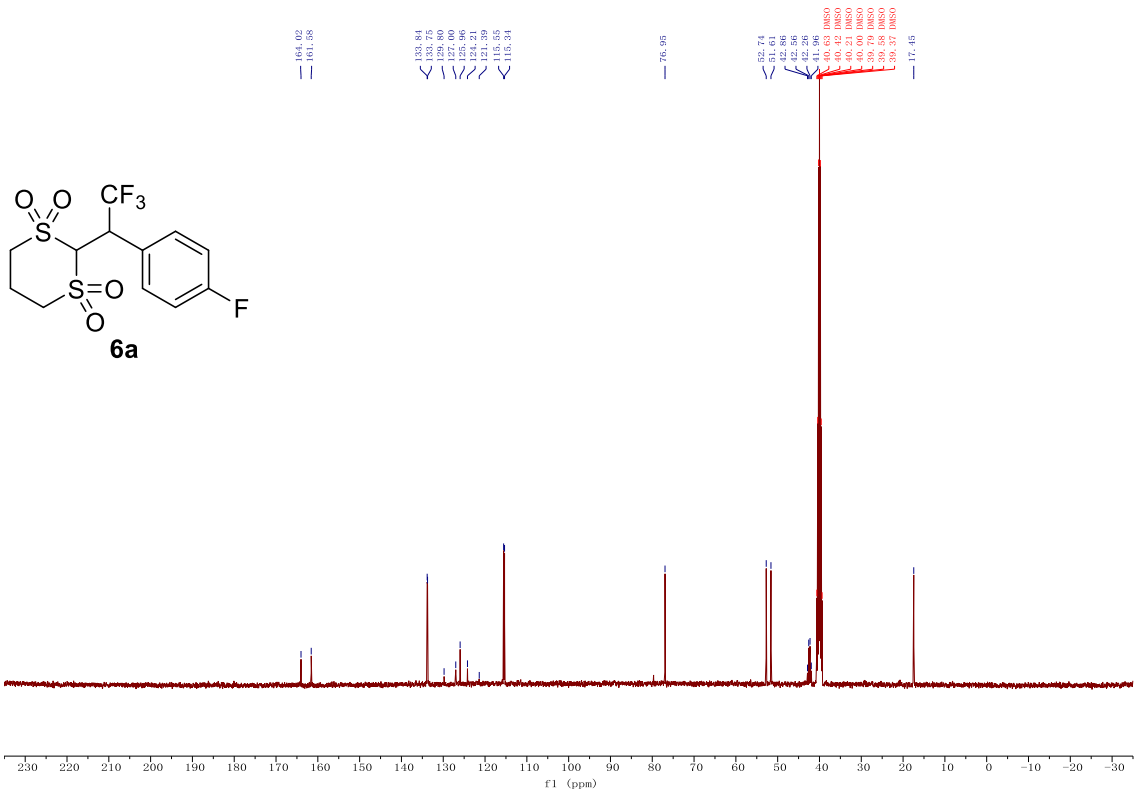
^{19}F NMR (376 MHz, $CDCl_3$)



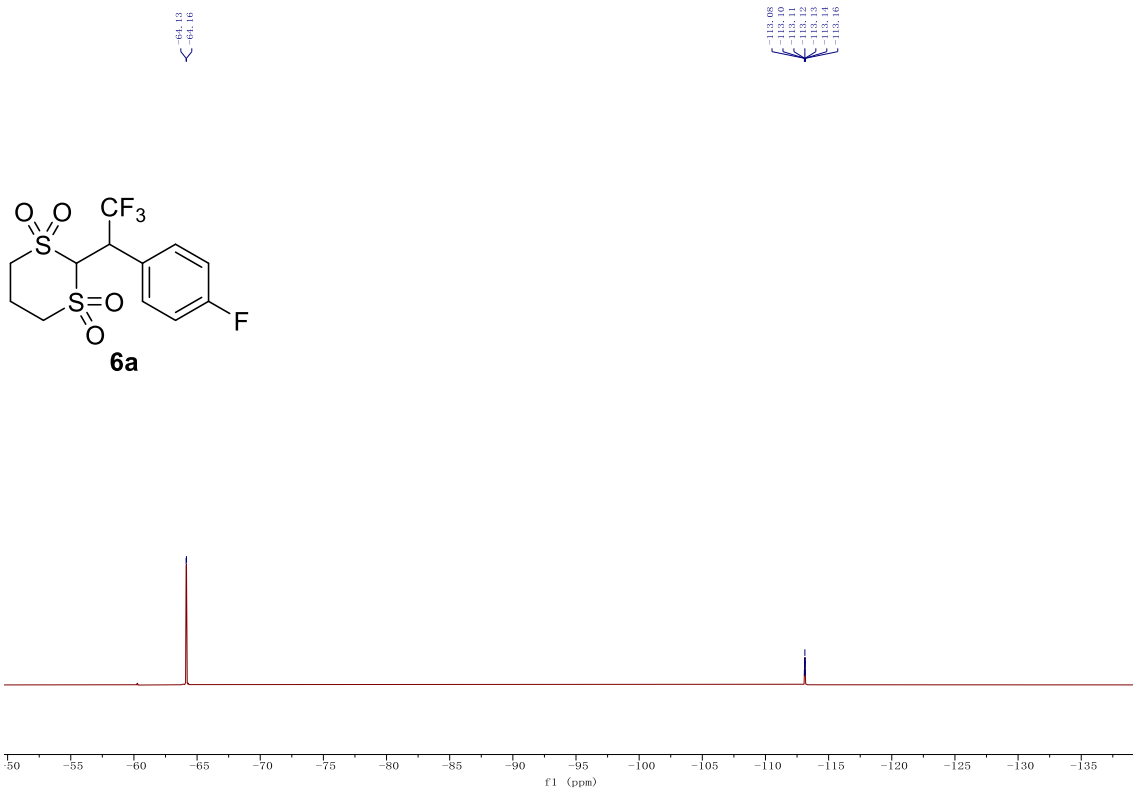
^{1}H NMR (400 MHz, DMSO-d_6)



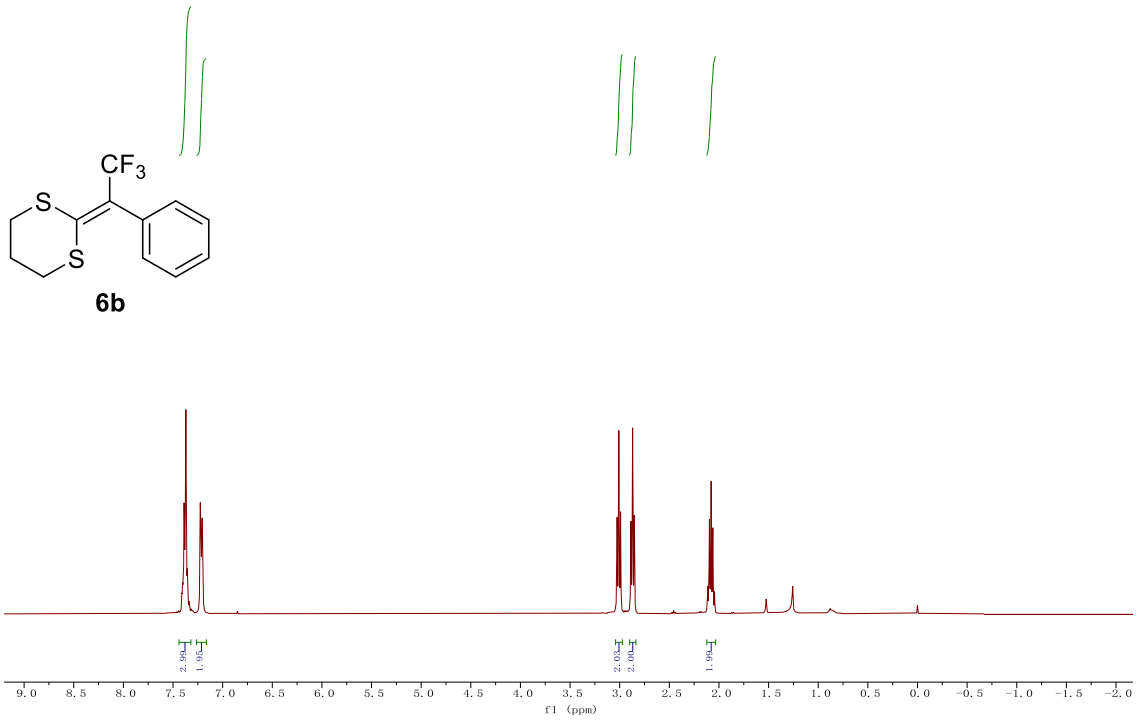
^{13}C NMR (101 MHz, DMSO-d_6)



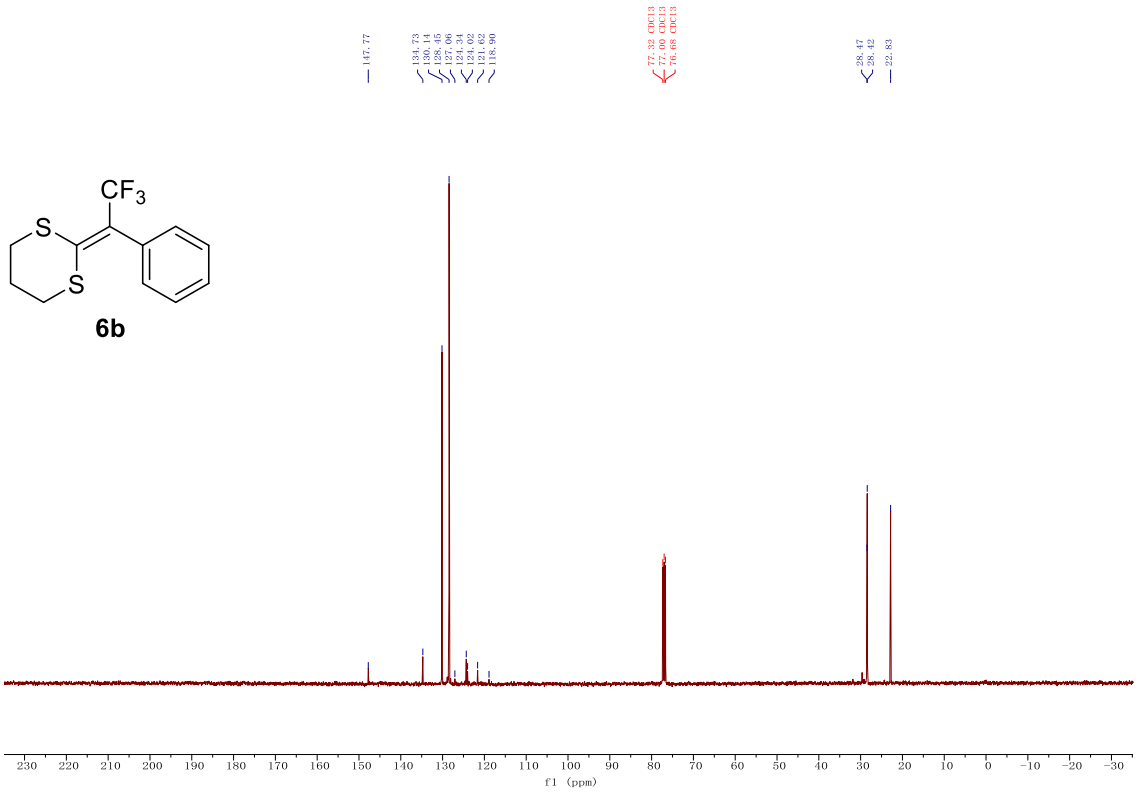
^{19}F NMR (376 MHz, DMSO-d_6)



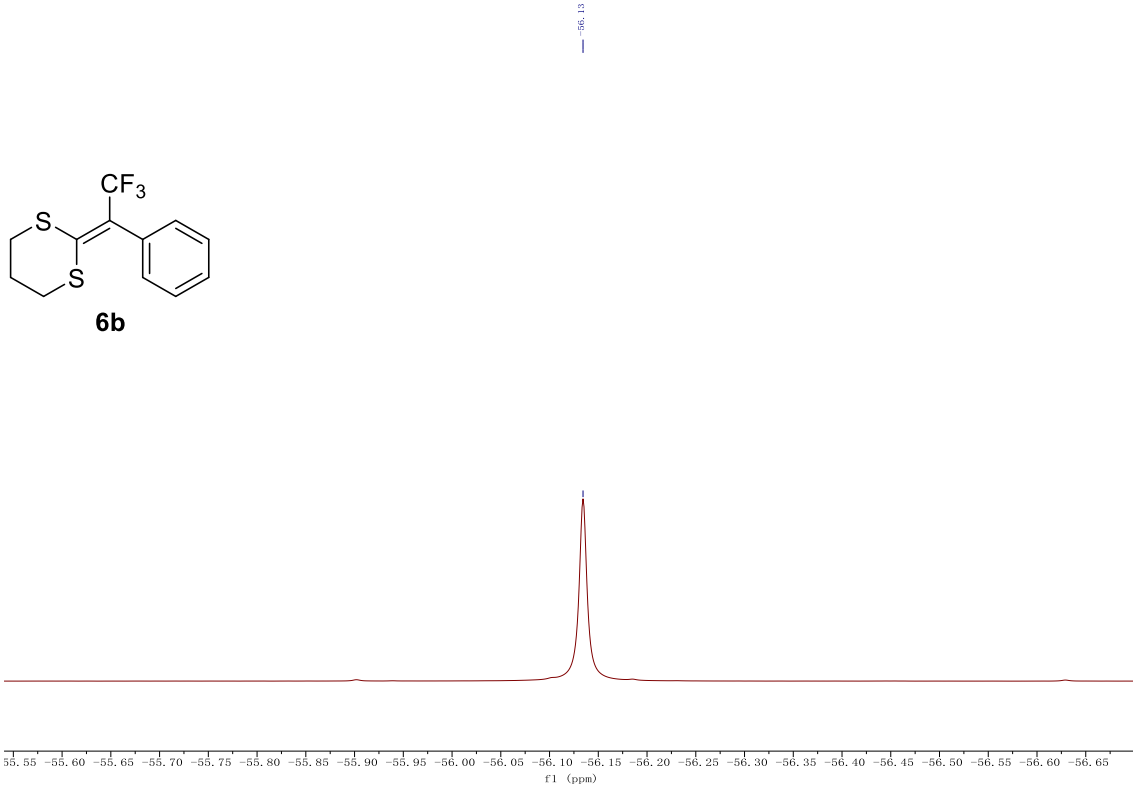
^{1}H NMR (400 MHz, $CDCl_3$)



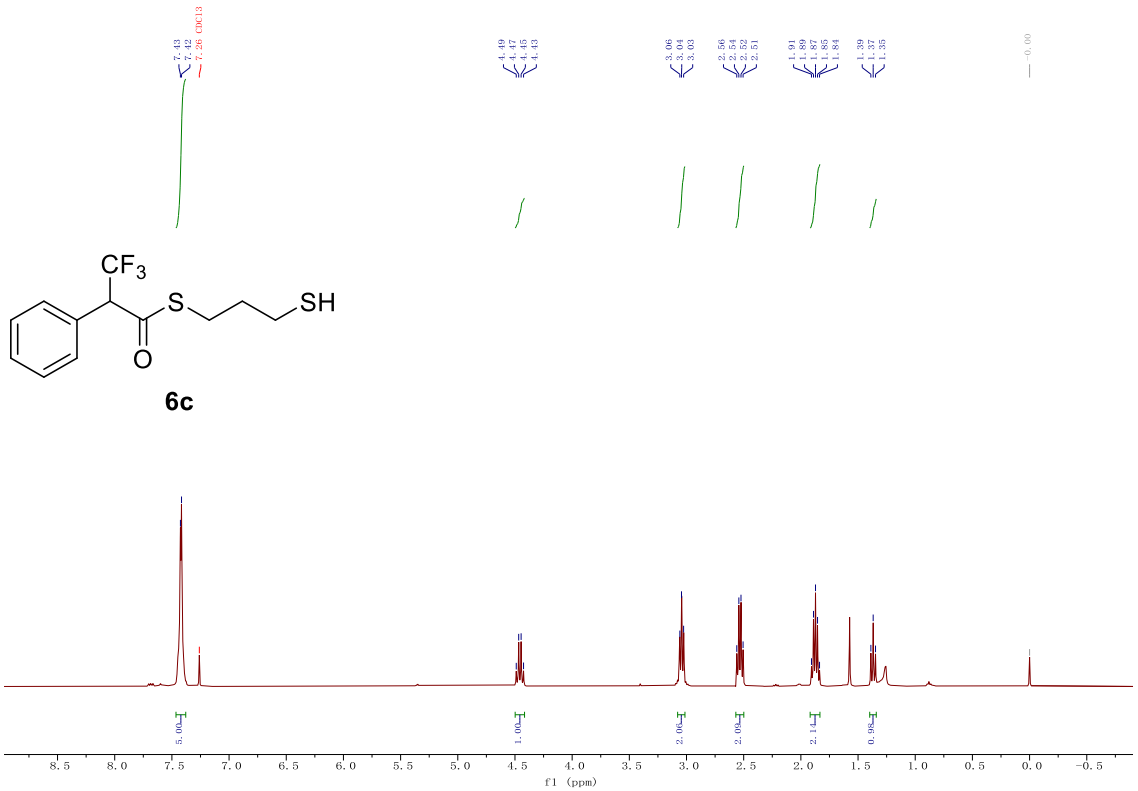
^{13}C NMR (101 MHz, $CDCl_3$)



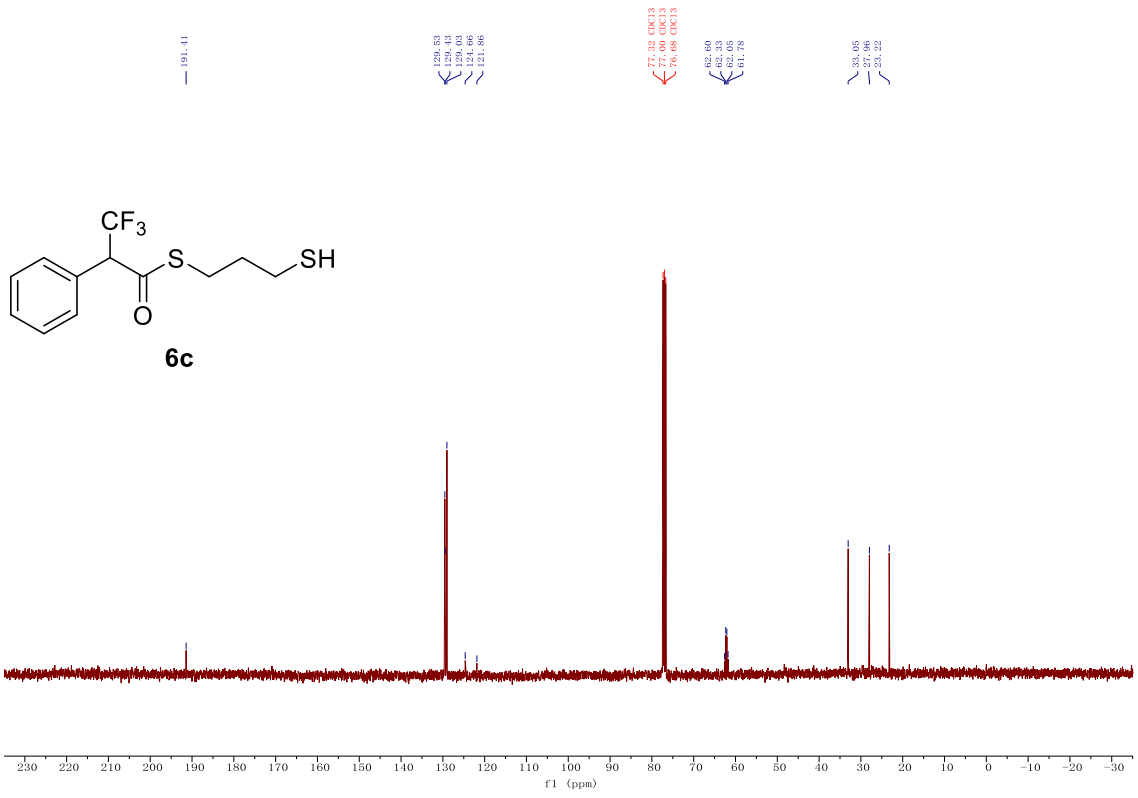
^{19}F NMR (376 MHz, $CDCl_3$)



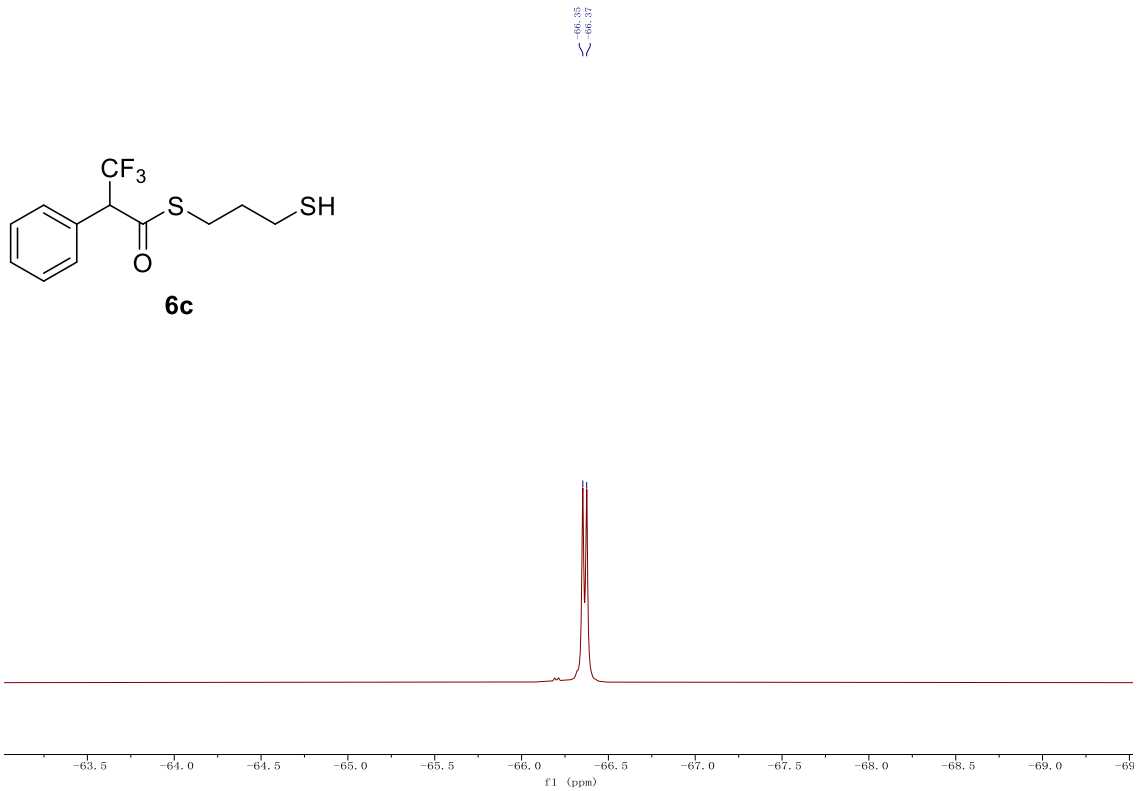
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)