Supporting Information

Indium-Catalyzed Inter- and Intramolecular Dithianyl-Alkyne Metathesis Reaction

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1. General information

All the commercially available chemicals and solvents were purchased from Energy Chemical, Bidepharm, J&K Scientific, Leyan.com, Sigma-Aldrich, Acros Organics and used as received. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Reactions requiring heating were carried out using an oil bath. Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (GF254).

The products were purified by Flash chromatography using petroleum/ethyl acetate as eluents. Compounds were either visualized under UV-light at 254 nm or dipped the plates in an aqueous phosphomolybdic solution followed by heating.

^{1}H and ^{13}C NMR spectra were collected on a Bruker AVANCE III 400 MHz, JEOL JNM-ECS 400 MHz, and Agilent-NMR-Inova 600 MHz spectrometer at room temperature. ^{1}H NMR spectra were reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were referenced to the signal of TMS (0 ppm). ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

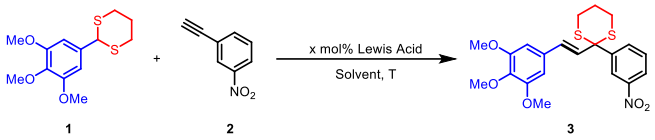
High resolution mass (HRMS) data were obtained using an Agilent UPLC-IM- QTOF instrument with ESI source. Optical rotations were measured on an AUTOPOL IV Automatic polarimeter (Rudolph Research Analytical).

The X-RAY was measured on Rigaku Oxford Diffraction.

The melting points were determined on a microscopic apparatus and were uncorrected.

2. The process of optimizing of reaction conditions

Table S1. Screening of the Lewis acid

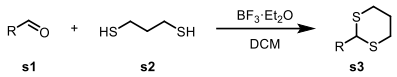


Entry	Lewis acid	Solvent	Temperature (°C)	mol %	Yield (%)
1	None	DCE	r.t.	0	N.R.
2	$BF_3{\cdot}Et_2O$	DCE	r.t.	10	17
3	BCl_3	DCE	r.t.	10	< 5
4	$B(C_6F_5)_3$	DCE	r.t.	10	N.R.
5	$AlCl_3$	DCE	r.t.	10	14
6	$InCl_3$	DCE	r.t.	10	54
7	$InBr_3$	DCE	r.t.	10	57
8	InI_3	DCE	r.t.	10	20
9	$FeCl_3$	DCE	r.t.	10	8
10	$InBr_3$	DCM	r.t.	10	36
11	$InBr_3$	TCM	r.t.	10	33
12	$InBr_3$	PhCl	r.t.	10	11
13	$InBr_3$	Toluene	r.t.	10	15
14	$InBr_3$	MeCN	r.t.	10	< 5
15	$InBr_3$	EtOH	r.t.	10	N.R.
16	$InBr_3$	EA	r.t.	10	N.R.
17	$InBr_3$	THF	r.t.	10	N.R.
18	$InBr_3$	Ethyl ether	r.t.	10	N.R.
19	$InBr_3$	Anisole	r.t.	10	< 5
20	$InBr_3$	Anisole	30	10	22
21	$InBr_3$	Anisole	50	10	73
22	$InBr_3$	Anisole	80	10	72
23	$InBr_3$	Anisole	50	5	34
24	$InBr_3$	Anisole	50	30	69
25	$InBr_3$	Anisole	50	50	48

Reaction conditions: **1** (28 mg, 0.1 mmol, 1.0 equiv.), **2** (18 mg, 0.12 mmol, 1.2 equiv.), and Lewis acid dissolved in solvent (1.0 mL), Isolated yields. N.R. = No reaction.

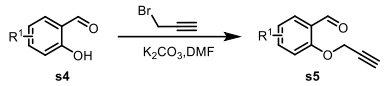
3. Synthesis of substrates

General procedure 1: Synthesis of Dithianes



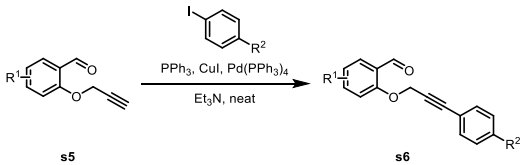
To a solution of aryl aldehyde **s1** (10 mmol, 1.0 equiv.) and propane-1,3-dithiol **s2** (1.1 mL, 11 mmol, 1.1 equiv.) in DCM (10 mL) were slowly added $BF_3{\cdot}Et_2O$ (0.37 mL, 3 mmol, 30 mol%) at 0 °C. The resulting mixture was allowed to warm up to room temperature and continued to stir for 1–3 hours until the disappearance of aldehyde as determined by TLC analysis. The reaction was quenched with H_2O and extracted with EA. The combined organic layers were washed with brine and dried with Na_2SO_4. After filtration and removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give the corresponding dithiane **s3**.

General procedure 2: Synthesis of O-Propargylated 2-hydroxyarylaldehydes[1]



To a solution of salicylaldehyde derivative **s4** (2.0 mmol, 1.0 equiv.) and K_2CO_3 (1.38 g, 10 mmol, 5.0 equiv.) in DMF (10 mL), propargylic bromide (2.4 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature until the disappearance of salicylaldehyde derivative as determined by TLC analysis. The reaction mixture was poured into water and filtered to obtain almost all product **s5** without further purification.

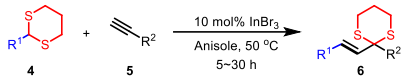
General procedure 3: O-propargylated 2-hydroxyarylaldehydes via Sonogashira coupling[2]



To a two-neck round bottom flask equipped with a stirrer bar was added 2-(prop-2-yn-1-yloxy)benzaldehyde **s5** (0.32 g, 2.0 mmol,), aryl iodide (2.2 mmol, 1.1 equiv.), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 5 mol%), PPh_3(13 mg, 0.10 mmol, 5 mol%) and CuI (19 mg, 0.10 mmol, 5 mol%) under argon. After 15 minutes, triethylamine (5 mL) was added to the reaction. The resulting mixture was stirred at room temperature for 18 hours. After the reaction was complete, the volatiles were removed by reduced pressure and extracted with DCM. The combined organic layer was washed with saturated NH_4Cl and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the O-propargylated 2-hydroxyarylaldehydes **s6** as off-white solids or yellow oil.

4. General procedure for the synthesis of 2-vinyl-dithiane and dithianyl-2*H*-chromene

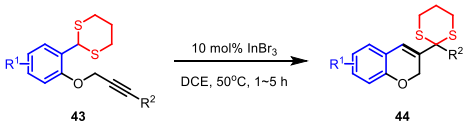
Intermolecular DAM reaction



4 5 6

To a magnetically stirred solution of dithiane **4** (0.10 mmol, 1 equiv.) and alkyne **5** (0.12 mmol, 1.2 equiv.) in anisole (1 mL) were added $InBr_3$ (3 mg, 10 mol%). The resulting mixture was stirred at 50 °C for 5-30 h until the disappearance of dithiane determined by TLC analysis. The mixture was quenched with 1N $NaHCO_3$ (10 mL) and extracted with EA. The organic layer was separated, and the aqueous phase was re-extracted with EA. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel to give the desired product **6**.

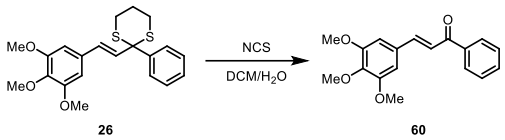
Intramolecular DAM reaction



43 44

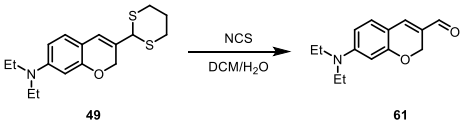
To a magnetically stirred solution of dithiane **43** (0.1 mmol) in DCE (10 mL) were added $InBr_3$ (3 mg, 10 mol%). The resulting mixture was stirred at 50 °C for 1-5 h until the disappearance of dithiane determined by TLC analysis. The mixture was quenched with 1N $NaHCO_3$ (10 mL) and extracted with EA. The organic layer was separated, and the aqueous phase was re-extracted with EA. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel to give the desired product **44**.

5. Representative synthetic applications



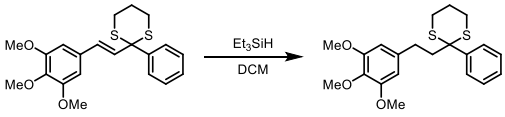
26 60

To a stirred solution of **26** (39 mg, 0.1 mmol, 1.0 equiv.) in DCM/H_2O = 5:1 (3 mL) was added NCS (13 mg, 0.1 mmol, 1.0 equiv.). The resulting mixture was stirred at room temperature until the disappearance of **26** as determined by TLC analysis. The mixture was diluted with DCM, washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography (PE/EA = 50:1 ~ 20:1) on silica gel to give the **60** (25 mg, isolated yield 83%) as a yellow oil.



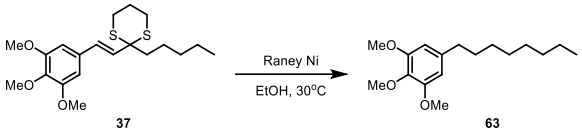
49 61

To a stirred solution of **49** (32 mg, 0.1 mmol, 1.0 equiv.) in DCM/H_2O = 5:1 (3 mL) was added NCS (13 mg, 0.1 mmol, 1.0 equiv.). The resulting mixture was stirred at room temperature until the disappearance of **49** as determined by TLC analysis. The mixture was diluted with DCM, washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography (PE/EA = 100:1 ~ 50:1) on silica gel to give the **61** (17 mg, isolated yield 71%) as a yellow oil.



26 62

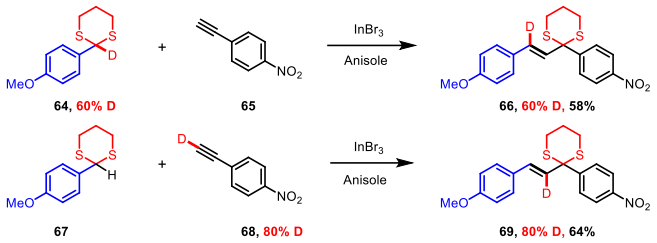
To a stirred solution of **26** (39 mg, 0.1 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (10 mg, 0.02 mmol, 0.02 equiv.) in DCM (3 mL), Et_3SiH (35 mg, 0.3 mmol, 3.0 equiv.) was added, and the resulting mixture was stirred at room temperature until the disappearance of **26** as determined by TLC analysis. 10% NaOH aq. was added, and the mixture was extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography (PE/EA = 50:1 ~ 20:1) on silica gel to give the **62** (27 mg, isolated yield 70%) as a colorless oil



37 63

To a solution of **37** (38 mg, 0.1 mmol) in EtOH (5 mL), Raney-nickel (1 g, Aldrich-2800 50% slurry in water) was added and stirred at 30 ºC for 36 h. Then was filtered through a Celite pad and washed with DCM. The ethanol was removed in vacuo and the mixture was subsequently dissolved in DCM and the water was removed by liquid separation and further dried over anhydrous Na_2SO_4 and purified by flash column chromatography (PE/EA = 30:1) to obtain the desired product **63** (20 mg, isolated yield 70%).

6. Deuterium experiment

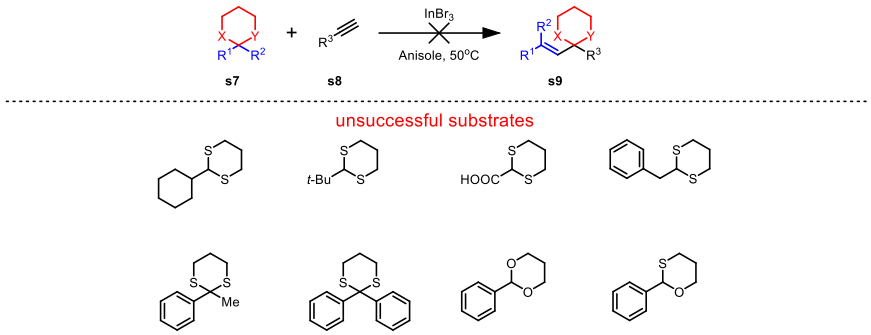


To a magnetically stirred solution of deuterated dithiane **64** (12 mg, 0.05 mmol, 1 equiv.) and alkyne **65** (9 mg, 0.6 mmol, 1.2 equiv.) in anisole (1 mL) were added $InBr_3$ (2 mg, 10 mol%). The resulting mixture was stirred at 50 °C for 5 h until the disappearance of dithiane determined by TLC analysis. The mixture was quenched with 1N $NaHCO_3$ (10 mL) and extracted with EA. The organic layer was separated, and the aqueous phase was re-extracted with EA. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo. The mixture was purified by flash column chromatography on silica gel to give desired deuterated product **66** (11 mg, 58% isolated yield).

The similar reaction of dithiane **67** with deuterated alkyne **68** catalyzed by $InBr_3$ was stopped after 5 hours, affording the 80% deuterated product **69** (12 mg, 64% isolated yield). These results indicate that deuterium of the dithianes and alkynes were not shift during the DAM reaction.

Scheme S1. Control Experiment

7. Unsuccessful substrates



In the interest of expanding the reaction scope, we focused on the aliphatic dithiane. Under optimized reaction conditions, we did not obtain desired products. We believed that these aliphatic dithianes were not tolerated under our reaction conditions. On the other hand, dithiane analogues and H-substituted dithiane also did not provide corresponding products under the current conditions.

8. Gram-scale reaction

To a stirred solution of dithiane **1** (0.572 g, 2 mmol, 1 equiv.) and hept-1-yne **s10** (0.389 g, 3.6 mmol, 1.2 equiv.) in anisole (10 mL) were added $InBr_3$ (0.07 g, 0.2 mmol, 10 mol%). The resulting mixture was stirred at 50 °C for 5 h. The mixture was quenched with 1M $NaHCO_3$ (100 mL) and extracted with EA. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography (PE/EA = 100:1 ~ 20:1) to give the pure desired product **37** (0.610 g, 1.59 mmol, 79%) as colorless oil.

9. Crystal data and structure of 16

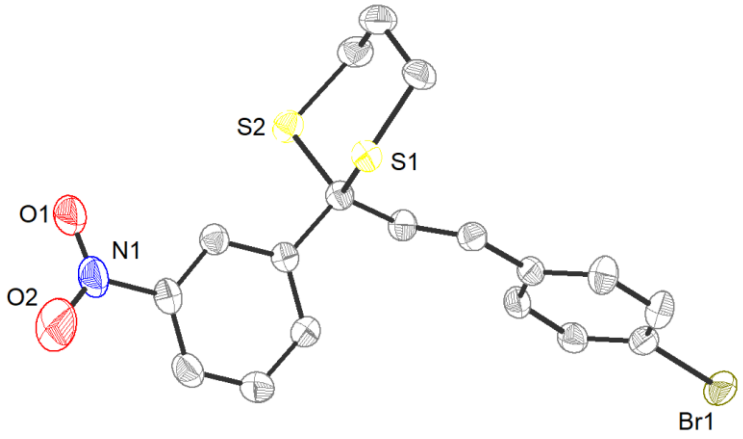


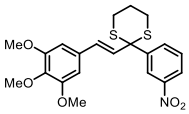
Figure S1 Crystal structure of compound **16** (CCDC 2308103), thermal ellipsoids are drawn at the 30% probability level. H-atoms omitted for clarity.

Table S2 Crystal data and structure refinement for chenxi_tshch_0313_auto

Identification code	chenxi_tshch_0313_auto
Empirical formula	$C_{18}H_{16}BrNO_2S_2$
Formula weight	422.35
Temperature/K	300.49(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	18.3295(3)
b/Å	10.5061(2)
c/Å	18.8191(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3624.02(11)
Z	8
ρcalcg/cm^3	1.548
μ/mm-1	5.331
F(000)	1712.0
Crystal size/mm^3	0.15 × 0.12 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.398 to 153.042
Index ranges	-22 ≤ h ≤ 22, -11 ≤ k ≤ 12, -23 ≤ l ≤ 18
Reflections collected	12880
Independent reflections	3578 [R_{int} = 0.0344, R_{sigma} = 0.0274]
Data/restraints/parameters	3578/0/217
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.1201
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.1231
Largest diff. peak/hole / e Å^{-3}	0.78/-0.56

10.Characterization data of products

(*E*)-2-(3-nitrophenyl)-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (3)



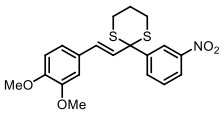
Yellow oil, 32 mg, R_f= 0.07 (PE/EA = 10:1), 73% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.65 (s, 2H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 3.89 (s, 6H), 3.86 (d, *J* = 0.9 Hz, 3H), 3.00 – 2.91 (m, 2H), 2.80 – 2.71 (m, 2H), 2.09 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 148.7, 144.2, 138.7, 135.2, 135.0, 131.4, 130.7, 129.7, 124.3, 123.2, 104.1, 61.1, 58.4, 56.3, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{24}NO_5S_2^+$ 434.1090, found 434.1091.

(*E*)-2-(3,4-dimethoxystyryl)-2-(3-nitrophenyl)-1,3-dithiane (7)



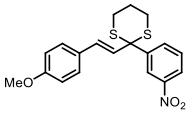
White solid, 25 mg, R_f= 0.11 (PE/EA = 10:1), 62% isolated yield, m.p: 116-118 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 6.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 11.4 Hz, 6H), 3.00 – 2.88 (m, 2H), 2.79 – 2.71 (m, 2H), 2.08 – 1.96 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.6, 149.2, 148.6, 144.3, 135.2, 134.7, 129.5, 129.3, 128.7, 124.2, 123.0, 120.3, 111.2, 109.1, 58.4, 56.0, 56.0, 28.6, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{22}NO_4S_2^+$ 404.0985, found 404.0982.

(*E*)-2-(4-methoxystyryl)-2-(3-nitrophenyl)-1,3-dithiane (8)



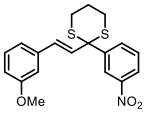
Colorless oil, 20 mg, R_f= 0.25 (PE/EA = 30:1), 54% isolated yield

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 2.99 – 2.91 (m, 2H), 2.78 – 2.71 (m, 2H), 2.09 – 1.96 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.0, 148.7, 144.5, 135.2, 134.5, 129.6, 129.2, 128.6, 128.2, 124.2, 123.0, 114.3, 58.5, 55.5, 28.7, 24.3.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_3S_2^+$ 374.0879, found 374.0871.

(*E*)-2-(3-methoxystyryl)-2-(3-nitrophenyl)-1,3-dithiane (9)



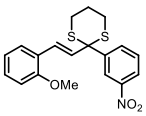
Colorless oil, 21 mg, R_f= 0.25 (PE/EA = 30:1), 56% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.18 (t, *J* = 9.2 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.26 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 6.85 (d, *J* = 8.3, 2.6 Hz, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 3.00 – 2.93 (m, 2H), 2.80 – 2.71 (m, 2H), 2.09 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.1, 148.7, 144.2, 137.2, 135.1, 135.0, 131.6, 129.9, 129.6, 124.2, 123.2, 119.6, 114.4, 112.1, 58.3, 55.4, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_3S_2^+$ 374.0879, found 374.0874.

(*E*)-2-(2-methoxystyryl)-2-(3-nitrophenyl)-1,3-dithiane (10)



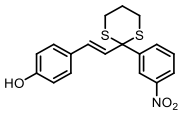
Colorless oil, 19 mg, R_f= 0.33 (PE/EA = 30:1), 51% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.75 (t, *J* = 2.1 Hz, 1H), 8.22 – 8.19 (m, 1H), 8.18 – 8.14 (m, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 3.05 – 2.99 (m, 2H), 2.78 – 2.73 (m, 2H), 2.10 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.2, 148.6, 144.6, 135.1, 131.6, 130.4, 129.6, 129.5, 127.5, 124.9, 124.1, 123.1, 120.8, 111.1, 58.7, 55.6, 28.7, 24.3.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_3S_2^+$ 374.0879, found 374.0877.

(*E*)-4-(2-(2-(3-nitrophenyl)-1,3-dithian-2-yl)vinyl)phenol (11)



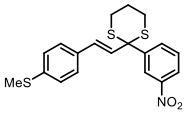
White solid, 18 mg, R_f= 0.03 (PE/EA = 10:1), 50% isolated yield, m.p: 117-119 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 2.98 – 2.90 (m, 2H), 2.77 – 2.71 (m, 2H), 2.08 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 148.7, 144.5, 135.2, 134.5, 129.6, 129.3, 128.8, 128.5, 124.2, 123.1, 115.8, 58.5, 28.7, 24.3.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{18}H_{18}NO_3S_2^+$ 360.0723, found 360.0714.

(*E*)-2-(4-(methylthio)styryl)-2-(3-nitrophenyl)-1,3-dithiane (12)



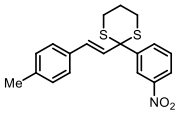
Yellow oil, 26 mg, R_f= 0.33 (PE/EA = 30:1), 66% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 8.17 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 3.00 – 2.91 (m, 2H), 2.78 – 2.71 (m, 2H), 2.48 (s, 3H), 2.11 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 144.2, 139.2, 135.1, 134.3, 132.6, 130.7, 129.6, 127.3, 126.6, 124.1, 123.1, 58.3, 28.7, 24.2, 15.8.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_2S_3^+$ 390.0651, found 390.0642.

(*E*)-2-(4-methylstyryl)-2-(3-nitrophenyl)-1,3-dithiane (13)



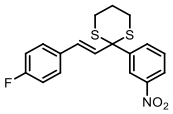
Yellow oil, 18 mg, R_f= 0.48 (PE/EA = 50:1), 50% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 3.04 – 2.89 (m, 2H), 2.83 – 2.70 (m, 2H), 2.35 (s, 3H), 2.10 – 1.93 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.6, 144.4, 138.6, 135.2, 135.0, 133.0, 130.3, 129.5, 126.9, 124.2, 123.1, 58.4, 28.7, 24.2, 21.4.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_2S_2^+$ 358.0930, found 358.0925.

(*E*)-2-(4-fluorostyryl)-2-(3-nitrophenyl)-1,3-dithiane (14)



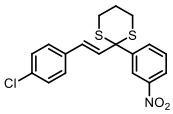
White solid, 24 mg, R_f= 0.37 (PE/EA = 50:1), 66% isolated yield, m.p: 119-121 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.23 – 8.14 (m, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 2.98 – 2.91 (m, 2H), 2.78 – 2.72 (m, 2H), 2.10 – 1.96 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.9 (d, *J* = 248.2 Hz), 148.6, 144.2, 135.1, 133.7, 132.0, 131.2, 129.6, 128.6 (d, *J* = 8.1 Hz), 124.1, 123.1, 115.79 (d, *J* = 21.8 Hz), 58.2, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{18}H_{17}FNO_2S_2^+$ 362.0679, found 362.0673.

(*E*)-2-(4-chlorostyryl)-2-(3-nitrophenyl)-1,3-dithiane (15)



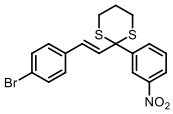
White solid, 24 mg, R_f= 0.38 (PE/EA = 50:1), 63% isolated yield, m.p: 123-124 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.19 (t, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 2.98 – 2.89 (m, 2H), 2.80 – 2.72 (m, 2H), 2.12 – 1.96 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 144.1, 135.1, 134.3, 133.7, 132.1, 129.7, 129.1, 128.2, 124.2, 123.2, 100.0, 58.2, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{18}H_{17}ClNO_2S_2^+$ 378.0384 found 378.0370.

(*E*)-2-(4-bromostyryl)-2-(3-nitrophenyl)-1,3-dithiane (16)



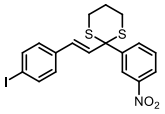
White solid, 28 mg, R_f= 0.37 (PE/EA = 50:1), 67% isolated yield, m.p: 128-131 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.19 (t, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 2.99 – 2.86 (m, 2H), 2.81 – 2.70 (m, 2H), 2.11 – 1.96 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 148.7, 144.2, 138.7, 135.2, 135.0, 131.4, 130.7, 129.7, 124.3, 123.2, 104.1, 61.1, 58.4, 56.3, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{18}H_{17}BrNO_2S_2^+$ 421.9879, found 421.9877.

(*E*)-2-(4-iodostyryl)-2-(3-nitrophenyl)-1,3-dithiane (17)



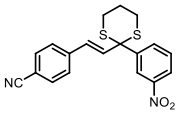
White solid, 31 mg, R_f= 0.36 (PE/EA = 50:1), 66% isolated yield, m.p: 145-146 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.17 (dd, *J* = 15.2, 8.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 2.97 – 2.90 (m, 2H), 2.78 – 2.71 (m, 2H), 2.09 – 1.96 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.6, 143.9, 137.8, 135.3, 135.0, 133.8, 132.2, 129.6, 128.6, 124.0, 123.1, 94.0, 58.1, 28.6, 24.1.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{18}H_{17}INO_2S_2^+$ 469.9740 found 469.9745 .

(*E*)-4-(2-(2-(3-nitrophenyl)-1,3-dithian-2-yl)vinyl)benzonitrile (18)



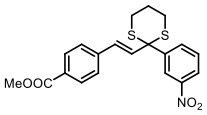
Colorless oil, 31 mg, R_f= 0.13 (PE/EA = 10:1), 84% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.20 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 2.97 – 2.91 (m, 2H), 2.80 – 2.75 (m, 2H), 2.12 – 1.99 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 143.6, 140.3, 135.3, 135.0, 133.0, 132.7, 129.8, 127.5, 124.1, 123.4, 118.8, 111.8, 58.0, 28.6, 24.0.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{17}N_2O_2S_2^+$ 369.0726, found 369.0731.

methyl (*E*)-4-(2-(2-(3-nitrophenyl)-1,3-dithian-2-yl)vinyl)benzoate (19)



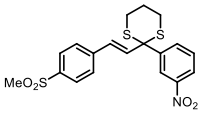
White solid, 35 mg, R_f= 0.17 (PE/EA = 10:1), 87% isolated yield, m.p: 142-144 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.19 (t, *J* = 8.1 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 3.92 (s, 3H), 3.03 – 2.89 (m, 2H), 2.86 – 2.70 (m, 2H), 2.18 – 1.92 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 148.7, 143.9, 140.2, 135.0, 134.0, 133.9, 130.1, 129.9, 129.7, 126.8, 124.1, 123.2, 58.2, 52.3, 28.6, 24.1.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{20}NO_4S_2^+$ 402.0828, found 402.0826.

(*E*)-2-(4-(methylsulfonyl)styryl)-2-(3-nitrophenyl)-1,3-dithiane (20)



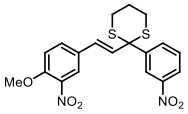
White solid, 38 mg, R_f= 0.01 (PE/EA = 5:1), 90% isolated yield, m.p: 157-159 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.24 – 8.18 (m, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.60 (dd, *J* = 17.3, 8.3 Hz, 3H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 3.06 (s, 3H), 3.00 – 2.90 (m, 2H), 2.82 – 2.74 (m, 2H), 2.14 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 143.6, 141.2, 140.0, 135.5, 135.0, 132.9, 129.8, 128.0, 127.7, 124.0, 123.4, 58.0, 44.7, 28.6, 24.0.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_4S_3^+$ 422.0549, found 422.0544.

(*E*)-2-(4-methoxy-3-nitrostyryl)-2-(3-nitrophenyl)-1,3-dithiane (21)



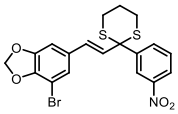
Yellow oil, 15 mg, R_f= 0.06 (PE/EA = 5:1), 36% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (t, *J* = 2.1 Hz, 1H), 8.23 – 8.16 (m, 2H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 3.98 (s, 3H), 2.98 – 2.88 (m, 2H), 2.81 – 2.71 (m, 2H), 2.12 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.9, 148.7, 143.9, 139.9, 135.1, 132.4, 132.3, 132.1, 129.8, 128.7, 124.2, 123.9, 123.2, 113.9, 58.1, 56.8, 28.7, 24.1.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{19}N_2O_5S_2^+$ 419.0730, found 419.0727.

(*E*)-4-bromo-6-(2-(2-(3-nitrophenyl)-1,3-dithian-2-yl)vinyl)benzo[*d*][1,3]dioxole (22)



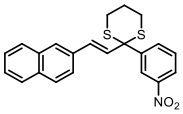
Yellow oil, 20 mg, R_f= 0.33 (PE/EA = 50:1), 43% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.08 – 6.97 (m, 3H), 6.22 (d, *J* = 15.7 Hz, 1H), 5.99 (s, 2H), 3.10 – 2.98 (m, 2H), 2.81 – 2.72 (m, 2H), 2.16 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 148.6, 147.9, 144.1, 135.0, 134.2, 132.3, 129.6, 129.2, 124.0, 123.2, 115.6, 112.9, 106.5, 102.1, 58.2, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{17}BrNO_4S_2^+$ 465.9777, found 465.9779.

(*E*)-2-(2-(naphthalen-2-yl)vinyl)-2-(3-nitrophenyl)-1,3-dithiane (23)



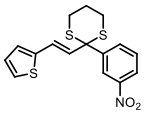
Colorless oil, 31 mg, R_f= 0.36 (PE/EA = 50:1), 79% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.19 – 8.16 (m, 1H), 7.79 (dd, *J* = 14.4, 7.4 Hz, 4H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.49 – 7.43 (m, 2H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.59 (d, *J* = 15.8 Hz, 1H), 3.04 – 2.93 (m, 2H), 2.80 – 2.72 (m, 2H), 2.11 – 1.96 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.7, 144.3, 135.2, 135.1, 133.6, 133.4, 133.2, 131.7, 129.6, 128.5, 128.2, 127.8, 127.4, 126.6, 126.4, 124.2, 123.6, 123.1, 58.4, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{22}H_{20}NO_2S_2^+$ 394.0930, found 394.0925.

(*E*)-2-(3-nitrophenyl)-2-(2-(thiophen-2-yl)vinyl)-1,3-dithiane (24)



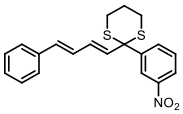
Yellow oil, 16 mg, R_f= 0.44 (PE/EA = 100:1), 46% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.18 (dd, *J* = 8.1, 2.1 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 5.1 Hz, 1H), 7.03 (d, *J* = 3.5 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 3.02 – 2.92 (m, 2H), 2.80 – 2.71 (m, 2H), 2.11 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 144.2, 140.7, 135.1, 130.7, 129.7, 128.4, 127.8, 127.3, 125.6, 124.2, 123.2, 58.2, 28.8, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{16}H_{16}NO_2S_2^+$ 350.0338, found 350.0332.

2-(3-nitrophenyl)-2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)-1,3-dithiane (25)



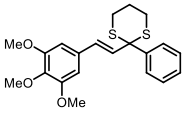
Yellow oil, 12mg, R_f= 0.40 (PE/EA = 100:1), 32% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (t, *J* = 2.1 Hz, 1H), 8.23 – 8.12 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.88 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.42 (dd, *J* = 15.1, 10.5 Hz, 1H), 6.06 (d, *J* = 15.3 Hz, 1H), 3.00 – 2.85 (m, 2H), 2.80 – 2.68 (m, 2H), 2.12 – 1.91 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 144.3, 136.8, 135.4, 135.1, 134.8, 129.6, 128.8, 128.1, 127.3, 126.7, 124.1, 124.1, 123.1, 58.3, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{20}NO_2S_2^+$ 370.0930, found 370.0928.

(*E*)-2-phenyl-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (26)



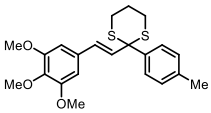
White solid, 22 mg, R_f = 0.19 (PE/EA = 20:1), 57% isolated yield, m.p: 114-116 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 8.3, 3.0 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 6.66 (s, 2H), 6.58 (d, *J* = 12.3 Hz, 1H), 6.40 (d, *J* = 15.5 Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.04 – 2.91 (m, 2H), 2.85 – 2.71 (m, 2H), 2.12 – 1.92 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 141.5, 138.3, 134.1, 132.0, 131.9, 128.8, 128.7, 128.1, 103.9, 61.1, 59.1, 56.3, 28.8, 24.6.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{25}O_3S_2^+$ 389.1240, found 389.1240.

(*E*)-2-(p-tolyl)-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (27)



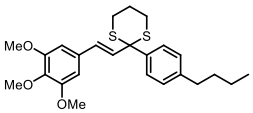
Colorless oil, 26 mg, R_f = 0.19 (PE/EA = 20:1), 64% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 2H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.03 – 2.90 (m, 2H), 2.83 – 2.69 (m, 2H), 2.36 (s, 3H), 2.08 – 1.89 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 138.4, 138.2, 138.0, 134.0, 132.0, 129.6, 129.4, 128.6, 103.9, 61.1, 58.9, 56.3, 28.9, 24.7, 21.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{22}H_{27}O_3S_2^+$ 403.1396, found 403.1378.

(*E*)-2-(4-butylphenyl)-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (28)



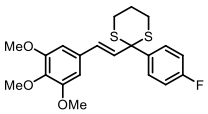
Colorless oil, 29 mg, R_f = 0.20 (PE/EA = 20:1), 65% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.68 (s, 2H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 3.88 (s, 6H), 3.86 (s, 3H), 3.03 – 2.95 (m, 2H), 2.81 – 2.73 (m, 2H), 2.61 (t, 2H), 2.10 – 1.92 (m, 2H), 1.63 – 1.57 (m, 2H), 1.40 – 1.31 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.5, 143.0, 138.6, 138.1, 133.9, 132.0, 132.0, 128.7, 128.4, 103.8, 61.1, 58.8, 56.2, 35.3, 33.6, 28.9, 24.7, 22.5, 14.1.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{25}H_{33}O_3S_2^+$ 445.1866 found 445.1868.

(*E*)-2-(4-fluorophenyl)-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (29)



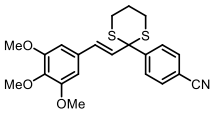
Yellow oil, 28 mg, R_f = 0.14 (PE/EA = 20:1), 69% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 9.0, 5.3 Hz, 2H), 7.06 (t, 2H), 6.66 (s, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 2.99 – 2.92 (m, 2H), 2.80 – 2.71 (m, 2H), 2.09 – 1.92 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.42 (d, *J* = 247.9 Hz), 153.5, 138.4, 137.2, 134.4, 131.8, 131.7, 130.76 (d, *J* = 8.1 Hz), 115.47 (d, *J* = 21.6 Hz), 103.9, 61.1, 58.5, 56.3, 28.9, 24.5.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{24}FO_3S_2^+$ 407.1145, found 407.1144.

(*E*)-4-(2-(3,4,5-trimethoxystyryl)-1,3-dithian-2-yl)benzonitrile (30)



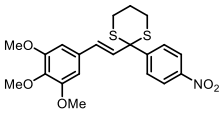
Yellow oil, 30mg, R_f = 0.26 (PE/EA = 10:1), 72% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 6.63 (s, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.02 – 2.87 (m, 2H), 2.87 – 2.68 (m, 2H), 2.12 – 1.92 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 153.5, 146.5, 138.5, 134.5, 131.7, 131.3, 130.0, 129.8, 129.1, 103.9, 61.0, 59.0, 56.3, 52.3, 28.7, 24.4.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{22}H_{24}NO_3S_2^+$ 414.1192, found 414.1193.

(*E*)-2-(4-nitrophenyl)-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (31)



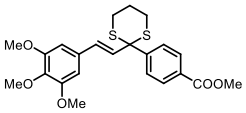
Yellow oil, 30 mg, R_f = 0.07 (PE/EA = 10:1), 69% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H), 6.63 (s, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.00 – 2.90 (m, 2H), 2.81 – 2.71 (m, 2H), 2.10 – 1.98 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.5, 148.9, 147.5, 138.7, 135.0, 131.3, 130.7, 130.2, 123.8, 104.0, 61.1, 58.6, 56.3, 28.7, 24.2.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{24}NO_5S_2^+$ 434.1090, found 434.1096

methyl (*E*)-4-(2-(3,4,5-trimethoxystyryl)-1,3-dithian-2-yl)benzoate (32)



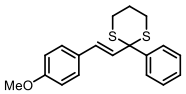
Colorless oil, 32 mg, R_f = 0.07 (PE/EA = 10:1), 72% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 6.63 (s, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 6H), 3.85 (s, 3H), 3.02 – 2.85 (m, 2H), 2.81 – 2.69 (m, 2H), 2.11 – 1.92 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 153.5, 146.5, 138.5, 134.5, 131.7, 131.3, 130.0, 129.8, 129.2, 103.9, 61.0, 59.0, 56.3, 52.3, 28.7, 24.4.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{23}H_{27}O_5S_2^+$ 447.1294, found 447.1294.

(*E*)-2-(4-methoxystyryl)-2-phenyl-1,3-dithiane (33)



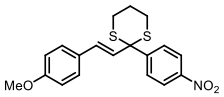
Yellow oil, 18 mg, R_f = 0.50 (PE/EA = 100:1), 55% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 3.02 – 2.91 (m, 2H), 2.81 – 2.68 (m, 2H), 2.11 – 1.90 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 141.8, 133.6, 130.4, 129.2, 128.8, 128.6, 128.1, 128.0, 114.2, 59.2, 55.5, 28.8, 24.7.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{21}OS_2^+$ 329.1028, found 329.1025.

(*E*)-2-(4-methoxystyryl)-2-(4-nitrophenyl)-1,3-dithiane (34)



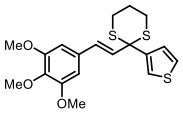
Yellow oil, 23 mg, R_f = 0.30 (PE/EA = 20:1), 61% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 9.0 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 2.98 – 2.92 (m, 2H), 2.77 – 2.72 (m, 2H), 2.09 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 149.3, 147.4, 134.5, 130.2, 129.1, 128.5, 128.2, 123.7, 114.3, 58.7, 55.5, 55.4, 32.3, 28.7, 24.3.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{20}NO_3S_2^+$ 374.0881, found 374.0871.

(*E*)-2-(thiophen-3-yl)-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (35)



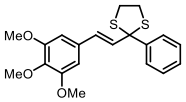
Colorless oil, 15 mg, R_f = 0.17 (PE/EA = 20:1), 38% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 (s, 1H), 7.35 (d, *J* = 2.3 Hz, 2H), 6.63 (s, 2H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.40 (d, *J* = 15.5 Hz, 1H), 3.87 (s, 6H), 3.84 (s, 3H), 2.97 – 2.87 (m, 2H), 2.87 – 2.77 (m, 2H), 2.05 – 1.95 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.4, 143.1, 138.3, 133.5, 131.8, 131.7, 128.4, 126.2, 124.9, 103.9, 61.0, 56.3, 55.4, 28.6, 24.6.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{19}H_{23}O_3S_3^+$ 395.0804, found 395.0805.

(*E*)-2-phenyl-2-(3,4,5-trimethoxystyryl)-1,3-dithiolane (36)



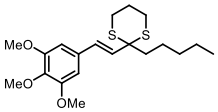
Yellow oil, 21 mg, R_f = 0.14 (PE/EA = 20:1), 56% isolated yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.62 (s, 2H), 6.56 (d, *J* = 15.2 Hz, 1H), 6.49 (d, *J* = 15.3 Hz, 1H), 3.86 (s, 6H), 3.84 (s, 3H), 3.41 (dd, *J* = 6.6, 1.8 Hz, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 141.7, 138.0, 133.1, 132.1, 130.1, 128.3, 128.2, 127.9, 103.9, 74.1, 61.0, 56.2, 39.9.

ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{23}O_3S_2^+$ 375.1083, found 375.1071.

(*E*)-2-pentyl-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (37)



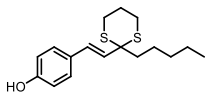
Colorless oil, 33mg, R_f = 0.14 (PE/EA = 20:1), 86% isolated yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 15.7 Hz, 1H), 6.68 (s, 2H), 6.12 (d, *J* = 15.7 Hz, 1H), 3.91 (s, 6H), 3.86 (s, 3H), 2.99 – 2.92 (m, 2H), 2.72 – 2.66 (m, 2H), 2.09 – 2.01 (m, 1H), 1.93 – 1.85 (m, 3H), 1.52 – 1.45 (m, 2H), 1.33 – 1.24 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 138.1, 133.2, 132.4, 132.2, 103.7, 61.0, 56.2, 55.4, 42.6, 32.0, 27.4, 25.6, 23.5, 22.5, 14.1.

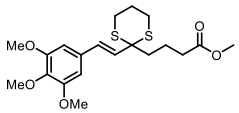
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{31}O_3S_2^+$ 383.1709, found 383.1696.

(*E*)-4-(2-(2-pentyl-1,3-dithian-2-yl)vinyl)phenol (38)



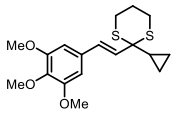
Colorless oil, 22mg, R_f = 0.15 (PE/EA = 20:1), 71% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.06 (d, *J* = 15.8 Hz, 1H), 5.13 (br, 1H), 3.00 – 2.89 (m, 2H), 2.72 – 2.63 (m, 2H), 2.09 – 1.98 (m, 1H), 1.92 – 1.85 (m, 3H), 1.53 – 1.42 (m, 2H), 1.34 – 1.21 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.4, 132.6, 130.9, 129.7, 128.1, 115.7, 55.5, 42.7, 32.0, 27.4, 25.7, 23.6, 22.5, 14.1.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{17}H_{25}OS_2^+$ 309.1341, found 309.1332.

methyl (*E*)-4-(2-(3,4,5-trimethoxystyryl)-1,3-dithian-2-yl)butanoate (39)



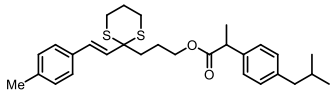
White solid, 29 mg, R_f = 0.07 (PE/EA = 10:1), 70% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.74 (d, *J* = 15.8 Hz, 1H), 6.68 (s, 2H), 6.11 (d, *J* = 15.7 Hz, 1H), 3.91 (s, 6H), 3.85 (s, 3H), 3.66 (s, 3H), 2.99 – 2.89 (m, 2H), 2.77 – 2.69 (m, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.08 – 1.77 (m, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 153.3, 138.0, 133.4, 131.9, 131.6, 103.7, 60.8, 56.1, 54.7, 51.5, 41.4, 33.8, 27.2, 25.3, 19.5.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{29}O_5S_2^+$ 413.1451, found 413.1440.

(*E*)-2-cyclopropyl-2-(3,4,5-trimethoxystyryl)-1,3-dithiane (40)



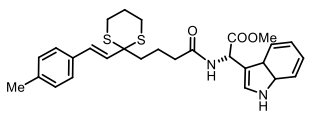
Yellow oil, 25mg, R_f = 0.26 (PE/EA = 30:1), 71% isolated yield.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.71 (d, *J* = 15.7 Hz, 1H), 6.65 (s, 2H), 5.91 (d, *J* = 15.7 Hz, 1H), 3.90 (s, 6H), 3.85 (s, 3H), 3.01 – 2.89 (m, 2H), 2.73 – 2.58 (m, 2H), 2.11 – 1.99 (m, 1H), 1.97 – 1.84 (m, 1H), 1.38 – 1.32 (m, 1H), 0.56 – 0.49 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 138.3, 135.4, 132.0, 128.5, 103.8, 61.0, 56.2, 55.9, 27.8, 25.4, 21.7, 1.5.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{18}H_{25}O_3S_2^+$ 353.1240, found 353.1232.

(*E*)-3-(2-(4-methylstyryl)-1,3-dithian-2-yl)propyl 2-(4-isobutylphenyl)propanoate (41)



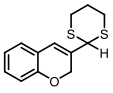
Colorless oil, 32mg, R_f = 0.50 (PE/EA = 100:1), 66% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 6.2 Hz, 2H), 7.20 – 7.12 (m, 4H), 7.06 (d, *J* = 6.1 Hz, 2H), 6.75 (d, *J* = 15.8 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 4.09 – 3.98 (m, 2H), 3.66 (q, *J* = 7.3, 6.2 Hz, 1H), 2.95 – 2.84 (m, 2H), 2.66 (d, *J* = 16.1 Hz, 2H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 2.05 – 1.95 (m, 1H), 1.93 – 1.73 (m, 6H), 1.47 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 140.6, 137.9, 133.7, 133.4, 131.5, 129.4, 129.4, 127.3, 126.6, 64.5, 54.8, 45.2, 45.2, 38.6, 30.2, 27.3, 25.5, 23.6, 22.5, 21.3, 18.6.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{29}H_{39}O_2S_2^+$ 483.2386, found 483.2382.

methyl (2*S*)-2-(3a,7a-dihydro-1*H*-indol-3-yl)-2-(4-(2-((*E*)-4-methylstyryl)-1,3-dithian-2-yl)butanamido)acetate (42)



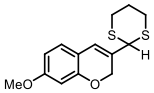
Yellow oil, 27 mg, R_f= 0.01 (PE/EA = 5:1), 53% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.28 (s, 1H), 7.17 – 7.12 (m, 3H), 7.10 – 7.06 (m, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.13 (d, *J* = 15.8 Hz, 1H), 5.95 (d, *J* = 7.8 Hz, 1H), 4.94 – 4.88 (m, 1H), 3.66 (s, 3H), 3.34 – 3.24 (m, 2H), 2.97 – 2.85 (m, 2H), 2.68 (d, *J* = 15.7 Hz, 2H), 2.36 (s, 3H), 2.12 (t, *J* = 6.8 Hz, 2H), 2.05 – 1.97 (m, 1H), 1.94 – 1.75 (m, 5H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 172.0, 137.9, 136.2, 133.7, 133.3, 131.5, 129.5, 127.7, 126.7, 123.0, 122.3, 119.8, 118.6, 111.4, 110.0, 55.0, 52.8, 52.4, 41.6, 36.4, 27.7, 27.3, 25.5, 21.3, 20.4.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{28}H_{35}N_2O_3S_2^+$ 511.2084, found 511.2088.

3-(1,3-dithian-2-yl)-2*H*-chromene (45)



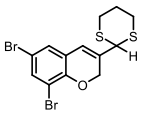
Colorless oil, 17 mg, R_f= 0.40 (PE/EA = 100:1), 68% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.08 (m, 1H), 7.05 – 6.99 (m, 1H), 6.91 – 6.84 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 4.84 (s, 2H), 4.64 (s, 1H), 2.96 – 2.87 (m, 4H), 2.17 – 2.08 (m, 1H), 1.98 – 1.85 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 131.0, 129.6, 127.2, 123.2, 122.3, 121.7, 115.7, 67.0, 48.4, 30.5, 25.4.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{13}H_{15}OS_2^+$ 251.0559, found 251.0556.

3-(1,3-dithian-2-yl)-7-methoxy-2*H*-chromene (46)



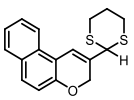
White solid, 17 mg, R_f= 0.28 (PE/EA = 50:1), 60% isolated yield, m.p: 99-101 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.92 (d, *J* = 8.3 Hz, 1H), 6.57 (s, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 6.39 (s, 1H), 4.81 (s, 2H), 4.64 (s, 1H), 3.76 (s, 3H), 2.95 – 2.84 (m, 4H), 2.17 – 2.06 (m, 1H), 1.97 – 1.83 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 154.9, 127.8, 127.7, 122.9, 115.5, 107.4, 101.6, 67.0, 55.5, 48.5, 30.6, 25.4.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{14}H_{17}O_2S_2^+$ 281.0664, found 281.0668.

6,8-dibromo-3-(1,3-dithian-2-yl)-2*H*-chromene (47)



White solid, 30 mg, R_f= 0.36 (PE/EA = 50:1), 74% isolated yield, m.p: 132-134 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.07 (s, 1H), 6.52 (s, 1H), 4.95 (s, 2H), 4.61 (s, 1H), 2.93 – 2.85 (m, 4H), 2.17 – 2.07 (m, 1H), 1.97 – 1.85 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 134.6, 133.2, 128.7, 124.8, 121.6, 113.5, 110.4, 67.7, 47.5, 30.3, 25.2.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{13}H_{13}Br_2OS_2^+$ 406.8769, found 406.8760.

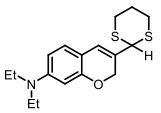
2-(1,3-dithian-2-yl)-3*H*-benzo[f]chromene (48)



Colorless oil, 20 mg, R_f= 0.36 (PE/EA = 50:1), 66% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.07 (d, *J* = 8.8 Hz, 1H), 4.89 (s, 2H), 4.78 (s, 1H), 3.02 – 2.82 (m, 4H), 2.17 – 2.05 (m, 1H), 1.99 – 1.84 (m, 1H).

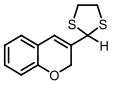
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 130.1, 129.9, 129.5, 129.2, 128.6, 126.9, 123.9, 121.6, 119.5, 117.4, 115.3, 66.9, 48.9, 30.4, 25.3.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{17}H_{17}OS_2^+$ 301.0715, found 301.0704.

3-(1,3-dithian-2-yl)-N,N-diethyl-2*H*-chromen-7-amine (49)



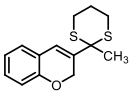
Yellow oil, 27 mg, R_f= 0.36 (PE/EA = 50:1), 83% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (d, *J* = 8.5 Hz, 1H), 6.54 (s, 1H), 6.20 (d, *J* = 8.5 Hz, 1H), 6.15 (s, 1H), 4.78 (s, 2H), 4.66 (s, 1H), 3.36 – 3.26 (m, 4H), 2.96 – 2.84 (m, 4H), 2.15 – 2.05 (m, 1H), 1.95 – 1.82 (m, 1H), 1.18 – 1.09 (m, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1, 149.3, 128.0, 124.6, 123.4, 110.6, 105.0, 98.6, 67.0, 48.9, 44.6, 30.7, 25.4, 12.8.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{17}H_{24}NO_2S_2^+$ 322.1294, found 322.1285.

3-(1,3-dithiolan-2-yl)-2*H*-chromene (50)



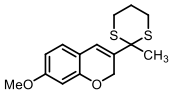
Yellow oil, 11 mg, R_f= 0.45 (PE/EA = 100:1), 46% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 5.32 (s, 1H), 4.90 (s, 2H), 3.40 – 3.23 (m, 4H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.7, 131.9, 129.5, 127.0, 122.4, 121.8, 121.6, 115.7, 65.8, 55.0, 39.9.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{12}H_{13}OS_2^+$ 237.0402, found 237.0413.

3-(2-methyl-1,3-dithian-2-yl)-2*H*-chromene (51)



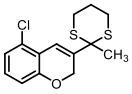
Colorless oil, 12 mg, R_f= 0.55 (PE/EA = 100:1), 45% isolated yield, m.p: 99-101 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.08 (m, 2H), 6.96 – 6.83 (m, 3H), 4.78 (s, 2H), 2.89 – 2.79 (m, 2H), 2.68 (d, *J* = 14.9 Hz, 2H), 2.06 – 1.97 (m, 1H), 1.92 – 1.79 (m, 1H), 1.66 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 134.5, 129.4, 127.3, 123.8, 123.1, 121.7, 115.6, 66.0, 52.0, 28.7, 28.1, 24.5.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{14}H_{17}OS_2^+$ 265.0715, found 265.0704.

7-methoxy-3-(2-methyl-1,3-dithian-2-yl)-2*H*-chromene (52)



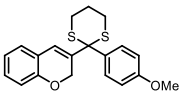
Colorless oil, 10 mg, R_f= 0.41 (PE/EA = 50:1), 34% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.51 – 6.47 (m, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 4.76 (s, 2H), 3.79 (s, 3H), 2.88 – 2.79 (m, 2H), 2.71 – 2.63 (m, 2H), 2.06 – 1.97 (m, 1H), 1.91 – 1.82 (m, 1H), 1.65 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.9, 154.7, 131.2, 127.9, 123.5, 116.3, 107.6, 101.5, 66.1, 55.6, 52.1, 28.8, 28.1, 24.6.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{15}H_{19}O_2S_2^+$ 295.0821, found 295.0827.

5-chloro-3-(2-methyl-1,3-dithian-2-yl)-2*H*-chromene (53)



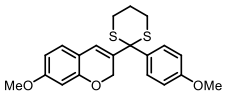
Colorless oil, 16 mg, R_f = 0.75 (PE/EA = 100:1), 54% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (s, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.72 (d, *J* = 1.1 Hz, 2H), 2.90 – 2.80 (m, 2H), 2.73 – 2.63 (m, 2H), 2.07 – 1.98 (m, 1H), 1.91 – 1.77 (m, 1H), 1.66 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 135.9, 131.9, 129.2, 122.4, 121.5, 120.3, 114.3, 65.6, 51.9, 28.5, 28.0, 24.4.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{14}H_{16}ClOS_2^+$ 299.0326, found 299.0330.

3-(2-(4-methoxyphenyl)-1,3-dithian-2-yl)-2*H*-chromene (54)



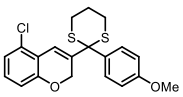
Colorless oil, 21 mg, R_f = 0.41 (PE/EA = 100:1), 59% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.00 (s, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.90 – 6.84 (m, 3H), 4.64 (s, 2H), 3.79 (s, 3H), 3.01 – 2.90 (m, 2H), 2.76 – 2.67 (m, 2H), 2.11 – 1.87 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 153.7, 132.6, 132.3, 129.5, 127.4, 126.3, 123.2, 121.7, 115.8, 114.1, 66.9, 59.9, 55.4, 29.3, 24.4.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{21}O_2S_2^+$ 357.0977, found 357.0989.

7-methoxy-3-(2-(4-methoxyphenyl)-1,3-dithian-2-yl)-2*H*-chromene (55)



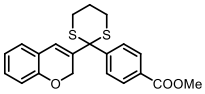
Colorless oil, 19 mg, R_f = 0.33 (PE/EA = 50:1), 49% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.93 (s, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.47 (s, 1H), 4.62 (s, 2H), 3.78 (s, 6H), 2.94 (t, *J* = 12.7 Hz, 2H), 2.70 (d, *J* = 14.1 Hz, 2H), 2.09 – 1.85 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 159.6, 154.9, 132.5, 129.5, 129.2, 128.1, 126.0, 116.2, 114.0, 107.7, 101.5, 67.0, 60.0, 55.5, 55.3, 29.3, 24.3.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{23}O_3S_2^+$ 387.1083, found 387.1072.

5-chloro-3-(2-(4-methoxyphenyl)-1,3-dithian-2-yl)-2*H*-chromene (56)



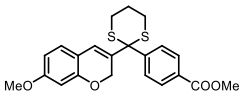
Colorless oil, 30 mg, R_f = 0.61 (PE/EA = 100:1), 77% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.39 (s, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.56 (s, 2H), 3.79 (s, 3H), 3.00 (t, *J* = 12.0 Hz, 2H), 2.78 – 2.70 (m, 2H), 2.08 – 1.87 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 154.9, 133.9, 132.1, 132.1, 129.3, 122.9, 122.4, 121.7, 114.5, 114.1, 66.6, 59.8, 55.4, 29.3, 24.3.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{20}H_{20}ClO_2S_2^+$ 391.0588, found 391.0588.

methyl 4-(2-(2*H*-chromen-3-yl)-1,3-dithian-2-yl)benzoate (57)



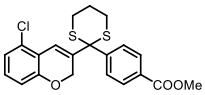
White solid, 28 mg, R_f = 0.27 (PE/EA = 50:1), 73% isolated yield, m.p: 130-133 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.15 (m, 2H), 6.99 – 6.93 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.64 (s, 2H), 3.91 (s, 3H), 2.97 (t, *J* = 11.3 Hz, 2H), 2.80 – 2.71 (m, 2H), 2.13 – 1.91 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 153.7, 145.4, 131.9, 130.3, 130.1, 129.8, 128.5, 127.6, 126.8, 122.9, 121.9, 115.8, 66.8, 60.3, 52.4, 29.0, 24.2.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{21}O_3S_2^+$ 385.0927, found 385.0939.

methyl 4-(2-(7-methoxy-2*H*-chromen-3-yl)-1,3-dithian-2-yl)benzoate (58)



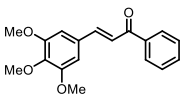
Colorless oil, 21 mg, R_f = 0.18 (PE/EA = 30:1), 51% isolated yield, m.p: 136-138 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 1H), 5.89 (t, *J* = 4.6 Hz, 1H), 5.63 (s, 1H), 4.69 (d, *J* = 4.6 Hz, 2H), 3.92 (s, 3H), 3.38 (s, 3H), 3.12 (t, *J* = 12.5 Hz, 2H), 2.90 (d, *J* = 14.5 Hz, 2H), 2.22 – 2.12 (m, 1H), 1.99 – 1.85 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 156.1, 153.0, 145.7, 136.0, 129.7, 128.9, 128.4, 126.9, 121.9, 119.8, 112.8, 105.5, 77.5, 77.4, 77.2, 76.8, 65.0, 55.2, 52.1, 43.6, 32.4, 25.3.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{22}H_{23}O_4S_2^+$ 415.1032, found 415.1015.

methyl 4-(2-(5-chloro-2*H*-chromen-3-yl)-1,3-dithian-2-yl)benzoate (59)



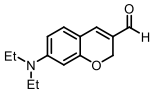
Colorless oil, 34 mg, R_f = 0.33 (PE/EA = 50:1), 81% isolated yield, m.p: 125-127 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 5.2 Hz, 2H), 7.85 (d, *J* = 5.1 Hz, 2H), 7.38 (s, 1H), 7.11 (t, *J* = 6.5 Hz, 1H), 7.02 (d, *J* = 4.9 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.56 (s, 2H), 3.91 (s, 3H), 3.08 – 2.93 (m, 2H), 2.77 (d, *J* = 11.2 Hz, 2H), 2.18 – 1.89 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 154.9, 145.2, 133.1, 132.1, 130.4, 130.1, 129.6, 128.3, 123.4, 122.5, 121.4, 114.6, 66.5, 60.1, 52.3, 29.0, 24.1.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{20}ClO_3S_2^+$ 419.0537, found 419.0532.

(*E*)-1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (60)[3]



Yellow oil, 25 mg, R_f = 0.15 (PE/EA = 20:1), 83% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 6.9 Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 15.7 Hz, 1H), 6.87 (s, 2H), 3.91 (d, *J* = 7.4 Hz, 9H).

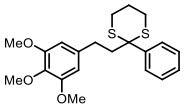
7-(diethylamino)-2*H*-chromene-3-carbaldehyde (61)



Yellow oil, 17 mg, R_f = 0.30 (PE/EA = 50:1), 71% isolated yield.

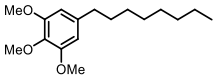
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.18 (s, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.27 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.13 (d, *J* = 2.5 Hz, 1H), 5.00 (s, 2H), 3.38 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.0, 158.4, 152.3, 142.8, 131.2, 126.0, 109.4, 105.8, 98.0, 63.8, 44.8, 12.8.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{14}H_{18}NO_2^+$ 232.1332, found 232.1344.

2-phenyl-2-(3,4,5-trimethoxyphenethyl)-1,3-dithiane (62)



Colorless oil, 27 mg, R_f= 0.20 (PE/EA = 20:1), 60% isolated yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.42 (t, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.25 (s, 2H), 3.79 (d, *J* = 4.7 Hz, 9H), 2.77 – 2.67 (m, 4H), 2.55 – 2.48 (m, 2H), 2.33 – 2.26 (m, 2H), 2.02 – 1.92 (m, 2H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.2, 141.7, 137.3, 136.2, 129.0, 128.7, 127.2, 105.3, 60.9, 58.9, 56.2, 47.1, 30.9, 27.8, 25.4.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{21}H_{27}O_3S_2^+$ 391.1396, found 391.1399.

1,2,3-trimethoxy-5-octylbenzene (63)



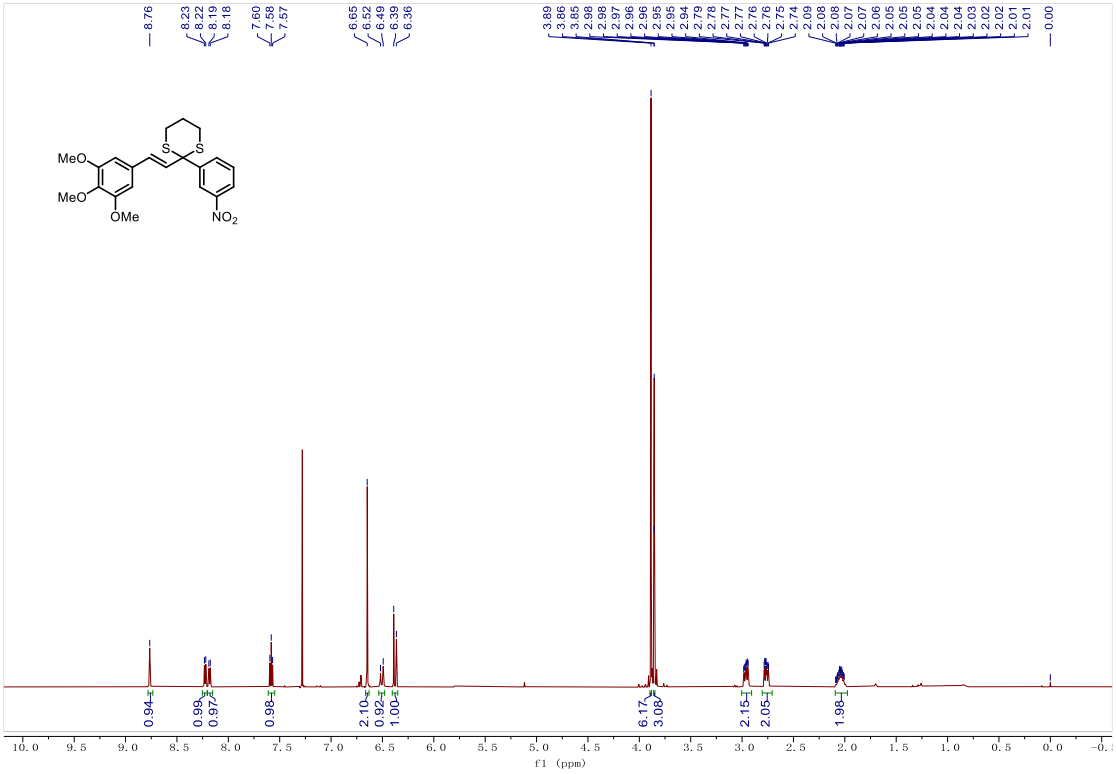
Colorless oil, 20 mg, R_f= 0.20 (PE/EA = 30:1), 75% isolated yield.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.40 (s, 2H), 3.84 (d, *J* = 14.9 Hz, 9H), 2.57 – 2.51 (m, 2H), 1.64 – 1.57 (m, 2H), 1.38 – 1.23 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.1, 138.9, 136.0, 105.3, 60.9, 56.1, 36.5, 32.0, 31.7, 29.6, 29.5, 29.4, 22.8, 14.2.
ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{17}H_{29}O_3^+$ 281.2111, found 281.4167.

11. Reference

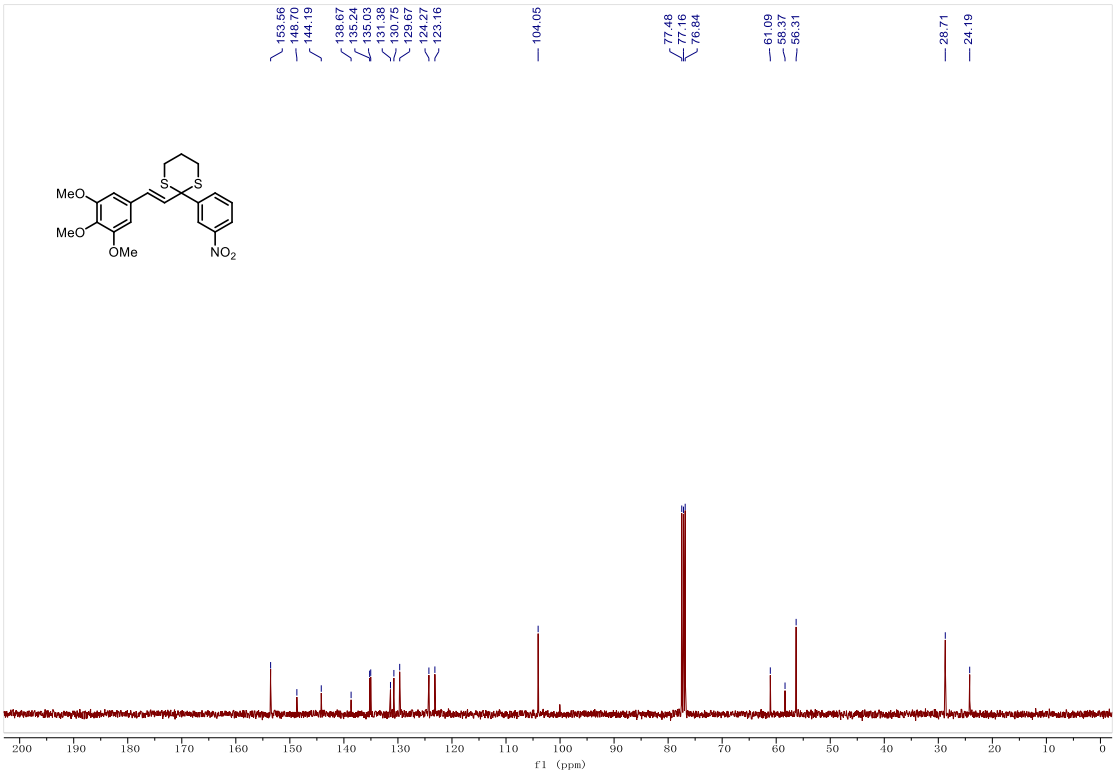
1. M. Zheng, C. Huang, J.-Z. Yan, S.-L. Xie, S.-J. Ke, H.-D. Xia and Y.-N. Duan, The J. Org. Chem., 2023, 88, 1504-1514.
2. C. H. Guo, D. Q. Chen, S. Chen and X. Y. Liu, *Adv. Synth. Catal.*, 2017, 359, 2901-2906.
3. S. Vedachalam, Q. L. Wong, B. Maji, J. Zeng, J. Ma and X. W. Liu, *Adv. Synth. Catal.*, 2011, 353, 219-225.

12. Copies of ^{1}H NMR and ^{13}C NMR spectra

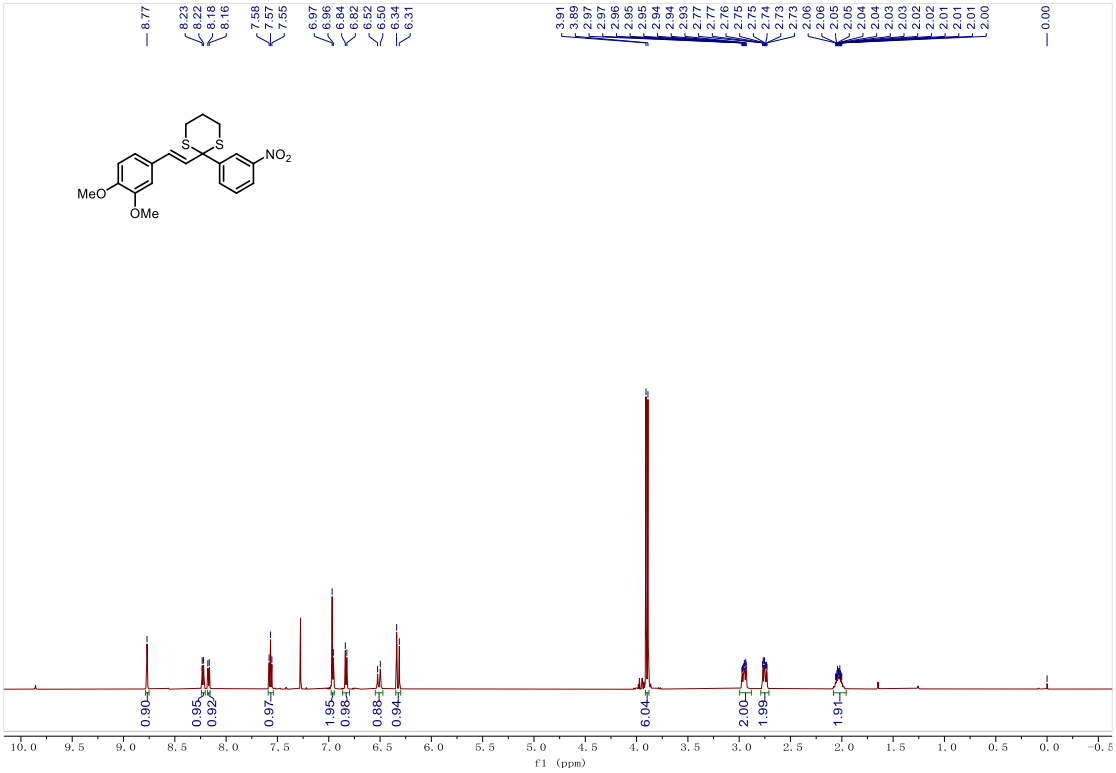
^{1}H NMR (600 MHz, Chloroform-*d*) of 3



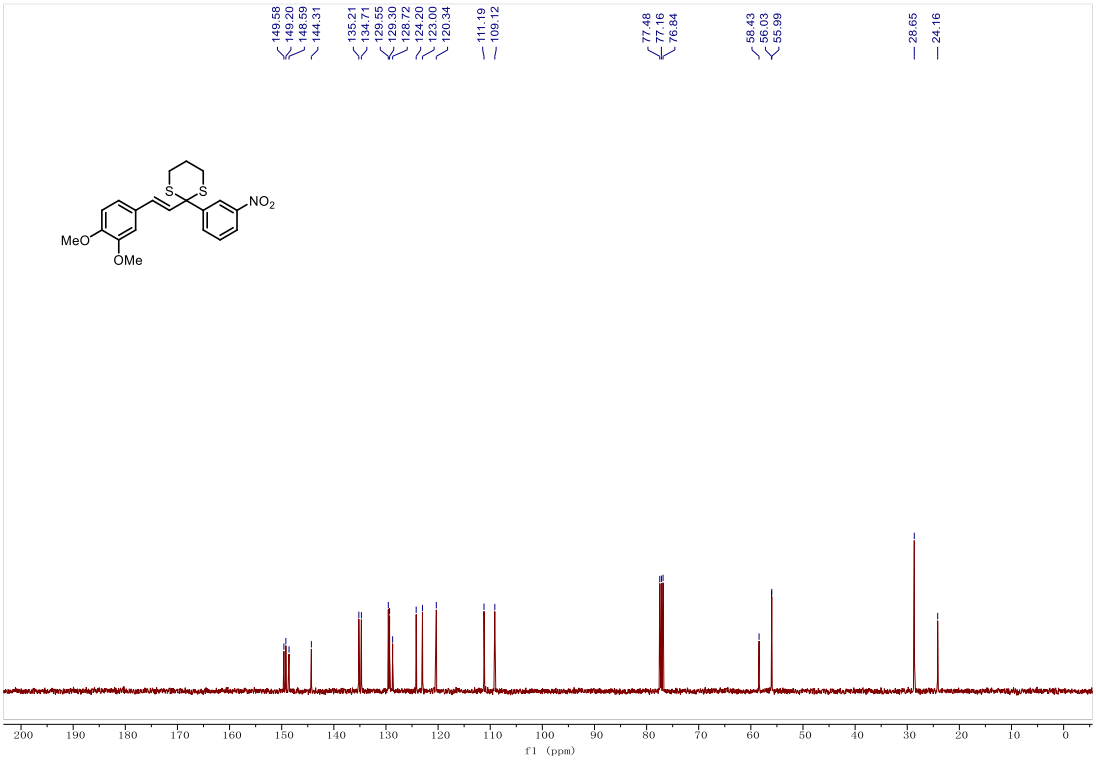
^{13}C NMR (101 MHz, Chloroform-*d*) of 3



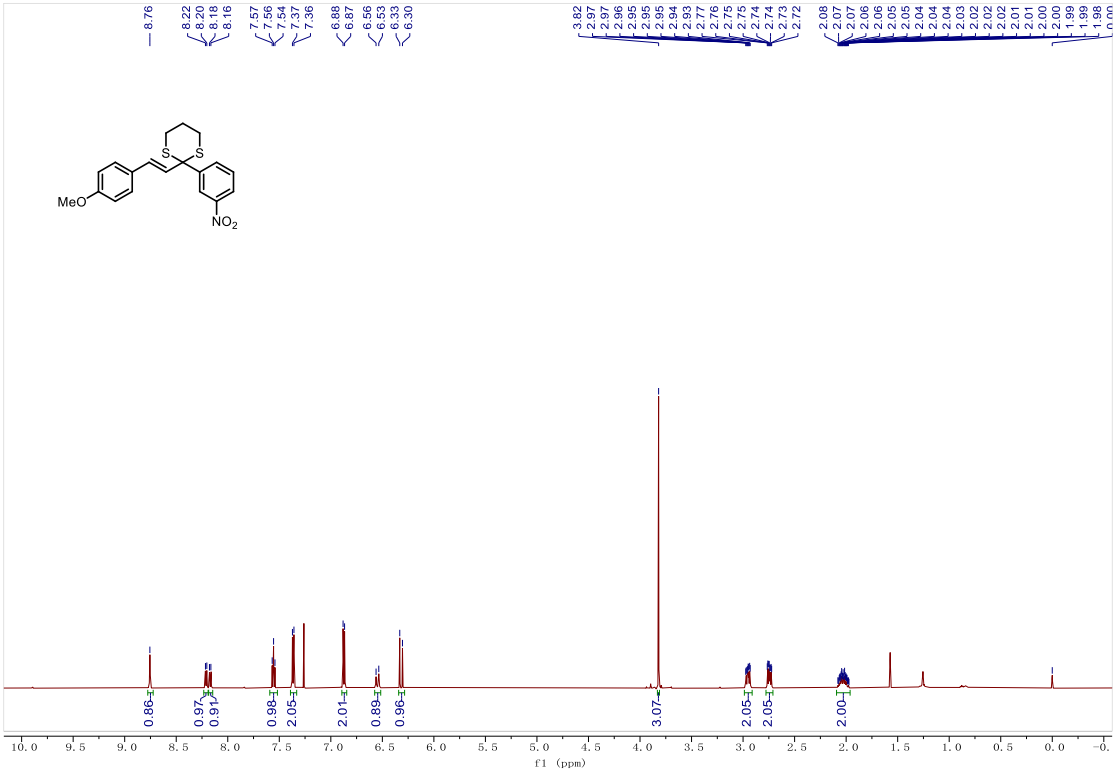
^{1}H NMR (600 MHz, Chloroform-*d*) of 7



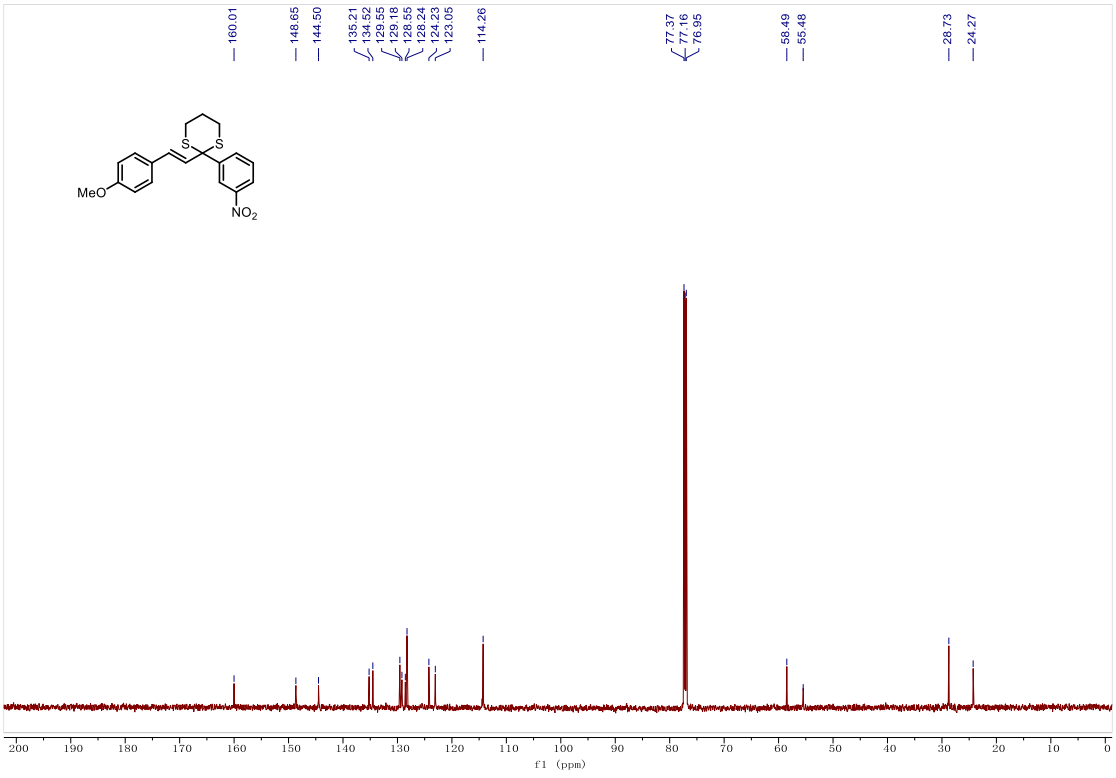
^{13}C NMR (101 MHz, Chloroform-*d*) of 7



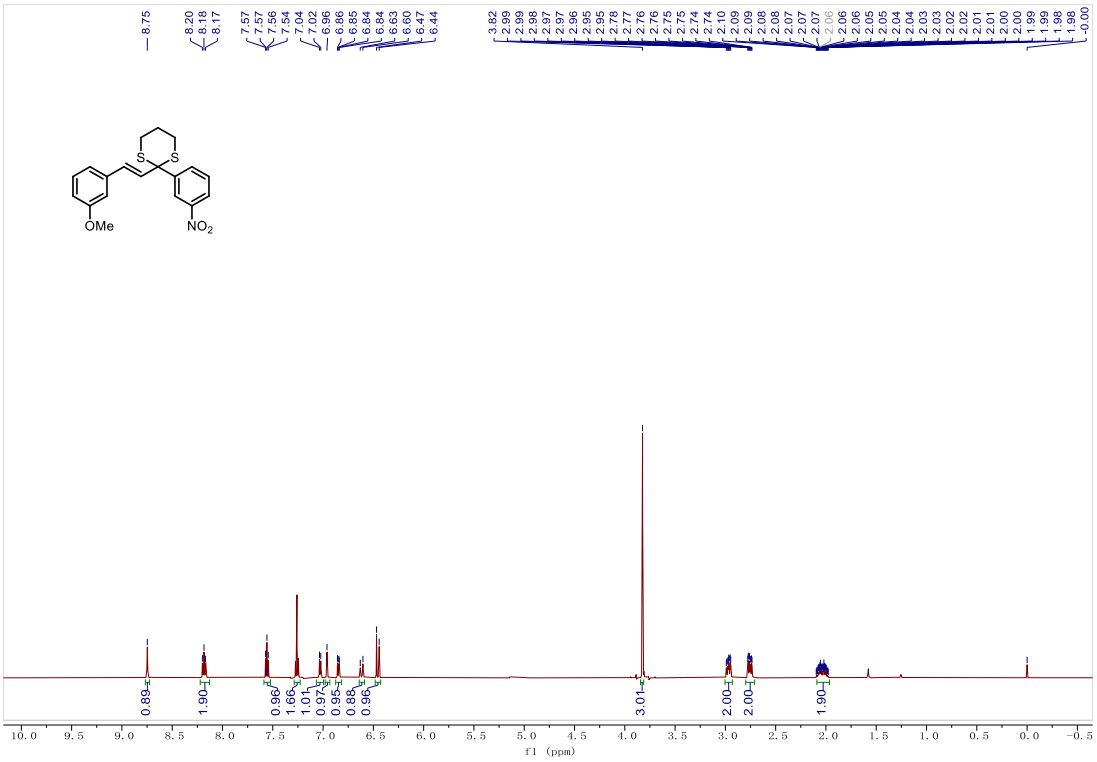
^{1}H NMR (600 MHz, Chloroform-*d*) of 8



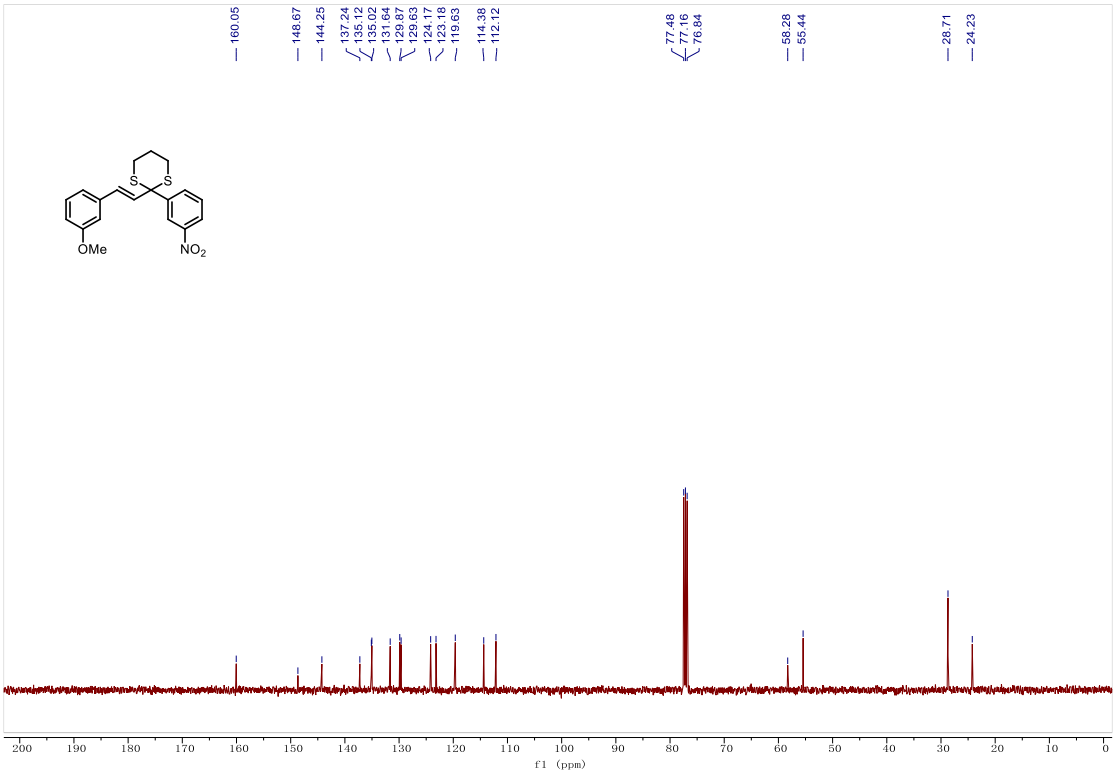
^{13}C NMR (151 MHz, Chloroform-*d*) of 8



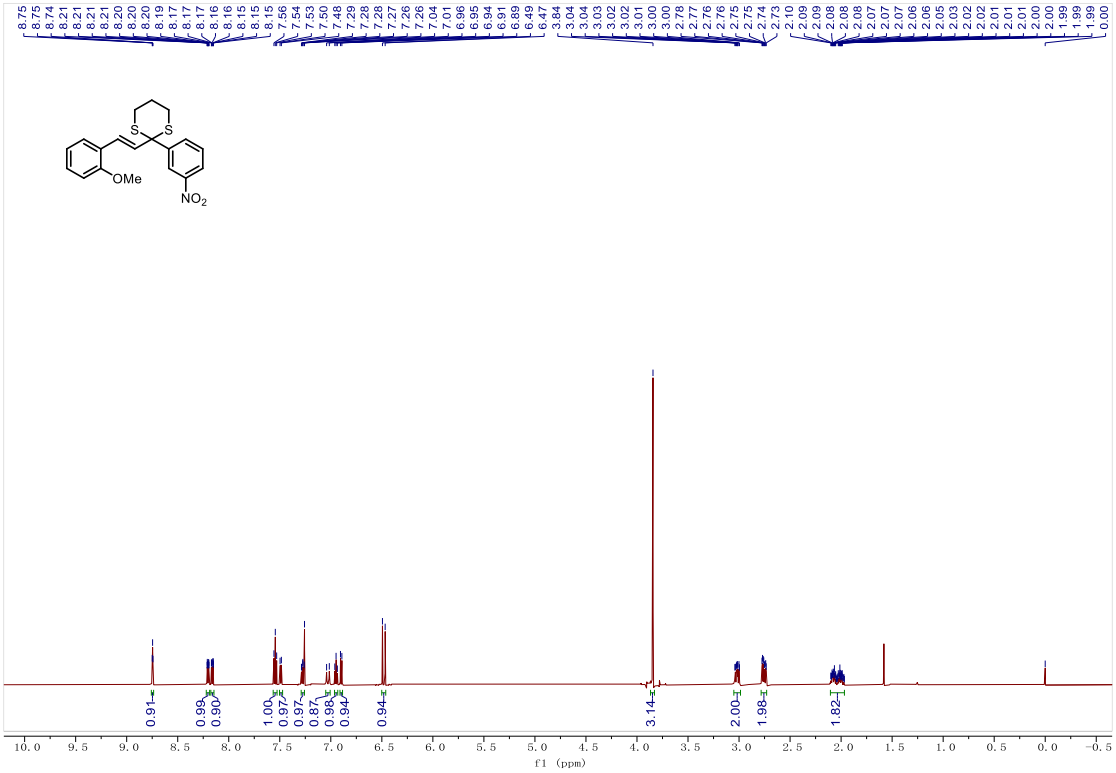
^{1}H NMR (600 MHz, Chloroform-*d*) of 9



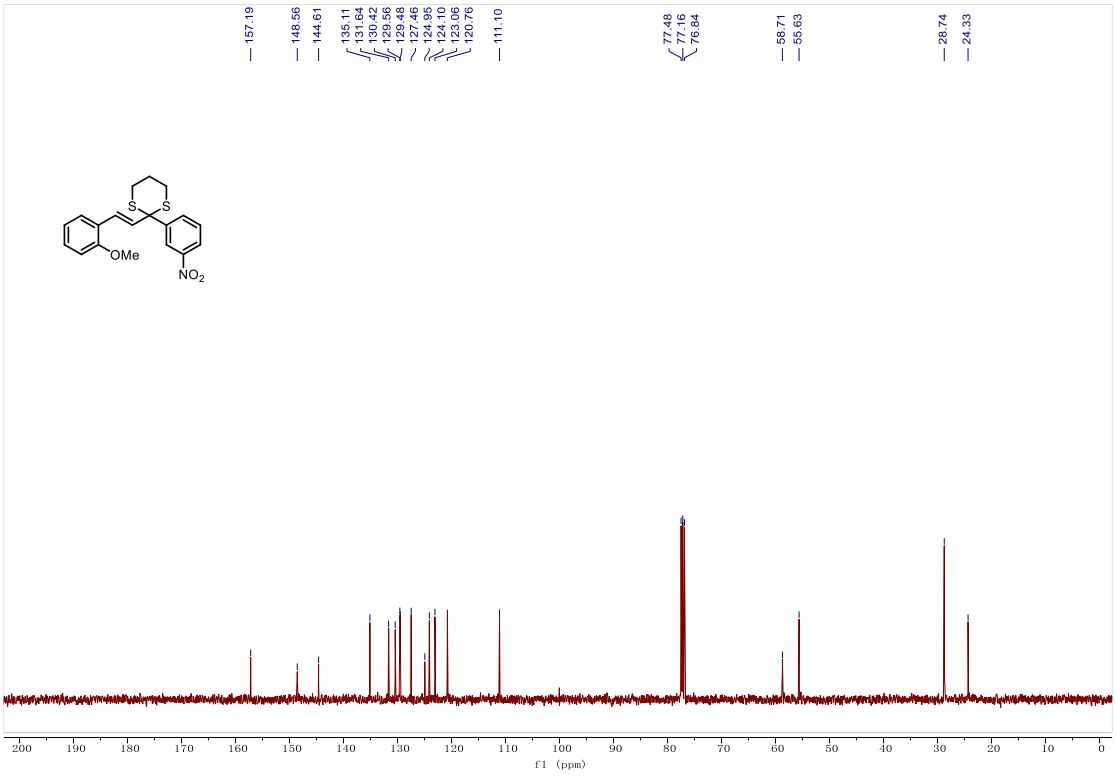
^{13}C NMR (101 MHz, Chloroform-*d*) of 9



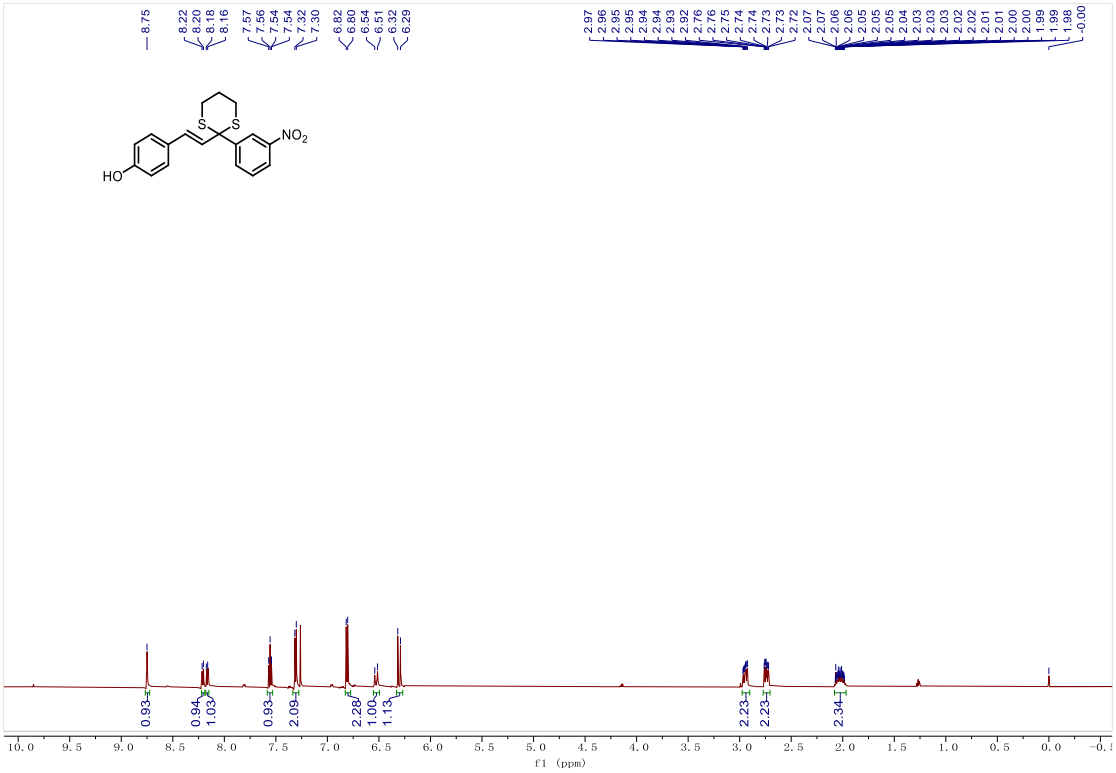
^{1}H NMR (600 MHz, Chloroform-*d*) of 10



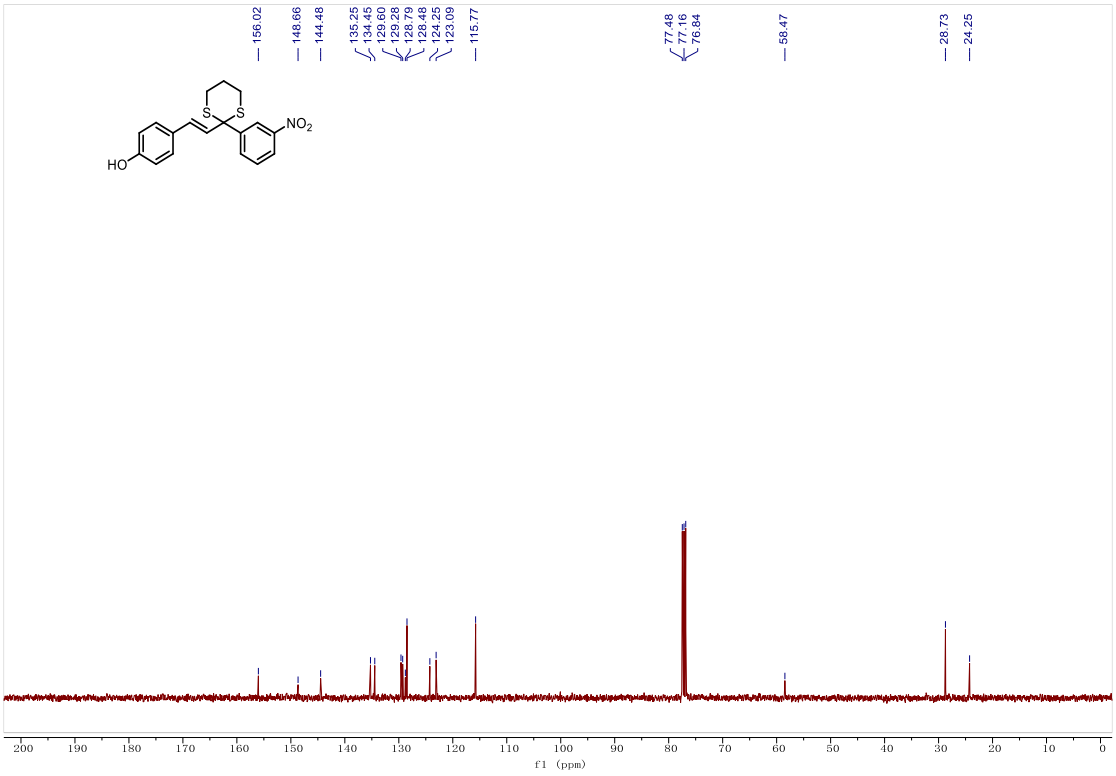
^{13}C NMR (101 MHz, Chloroform-*d*) of 10



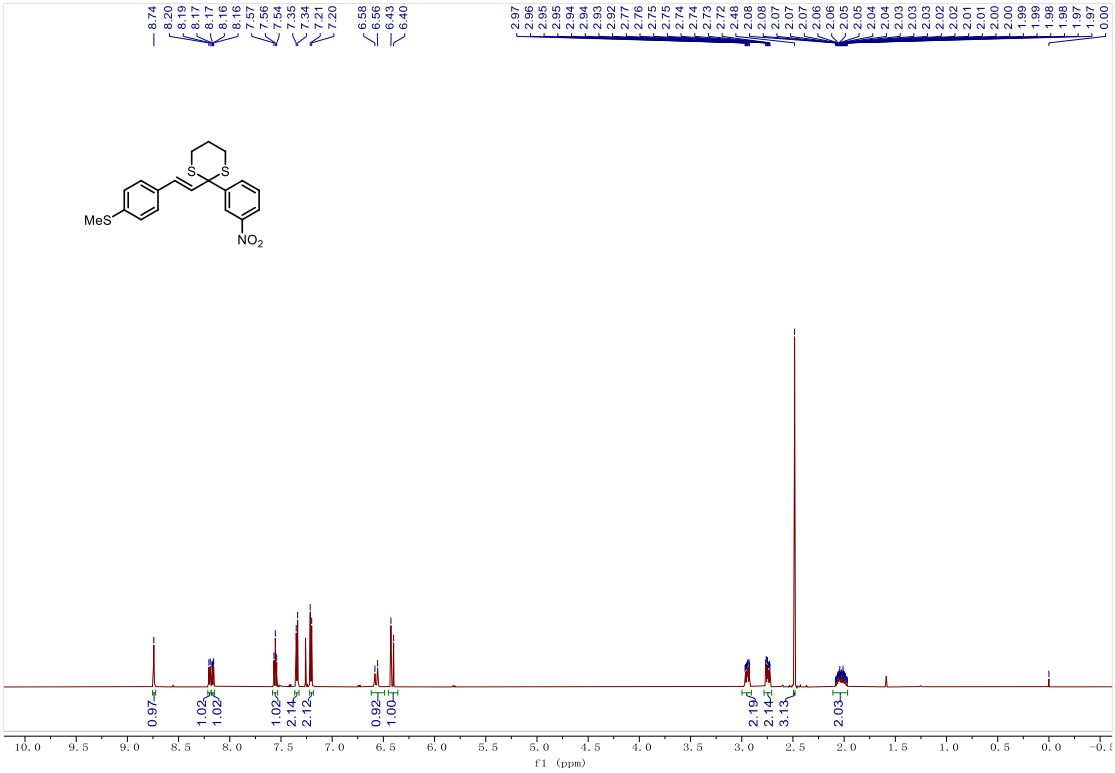
^{1}H NMR (600 MHz, Chloroform-*d*) of 11



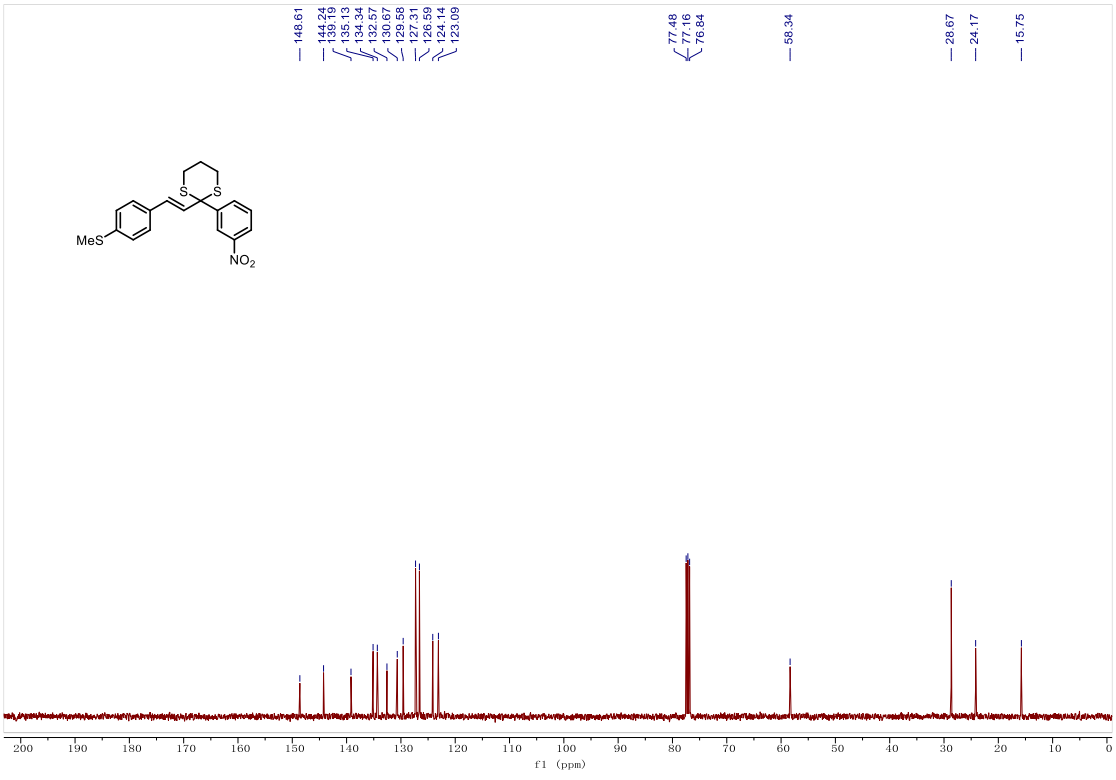
^{13}C NMR (101 MHz, Chloroform-*d*) of 11



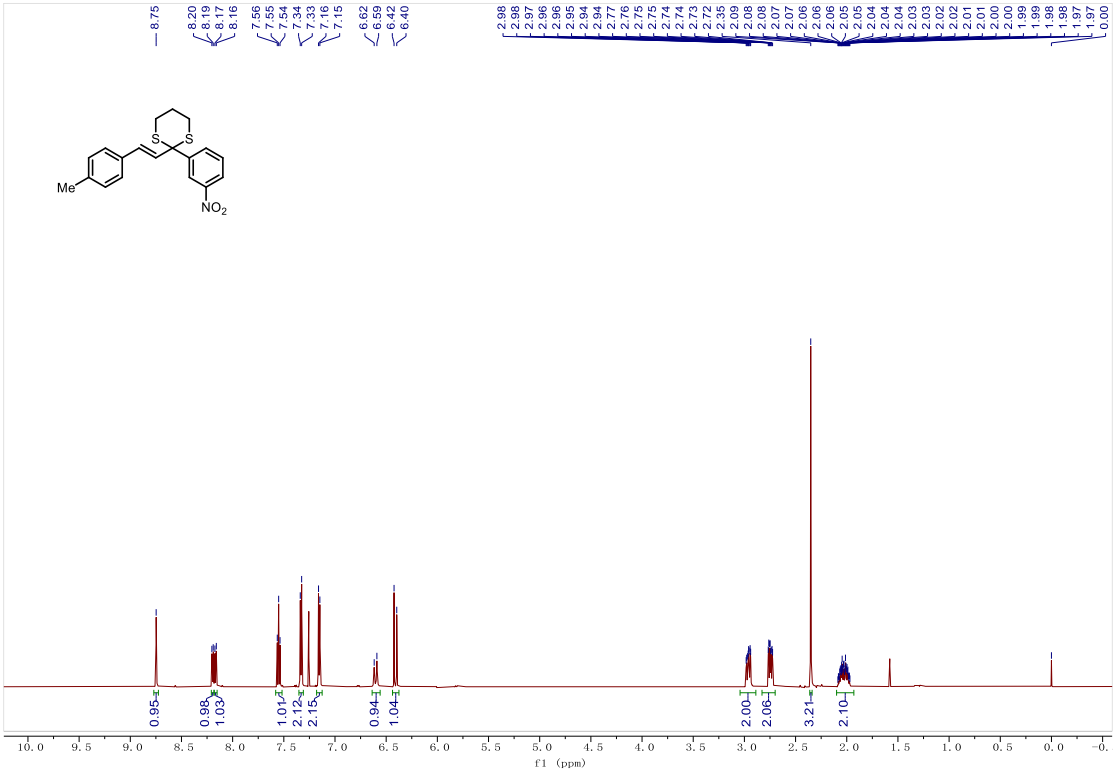
^{1}H NMR (600 MHz, Chloroform-*d*) of 12



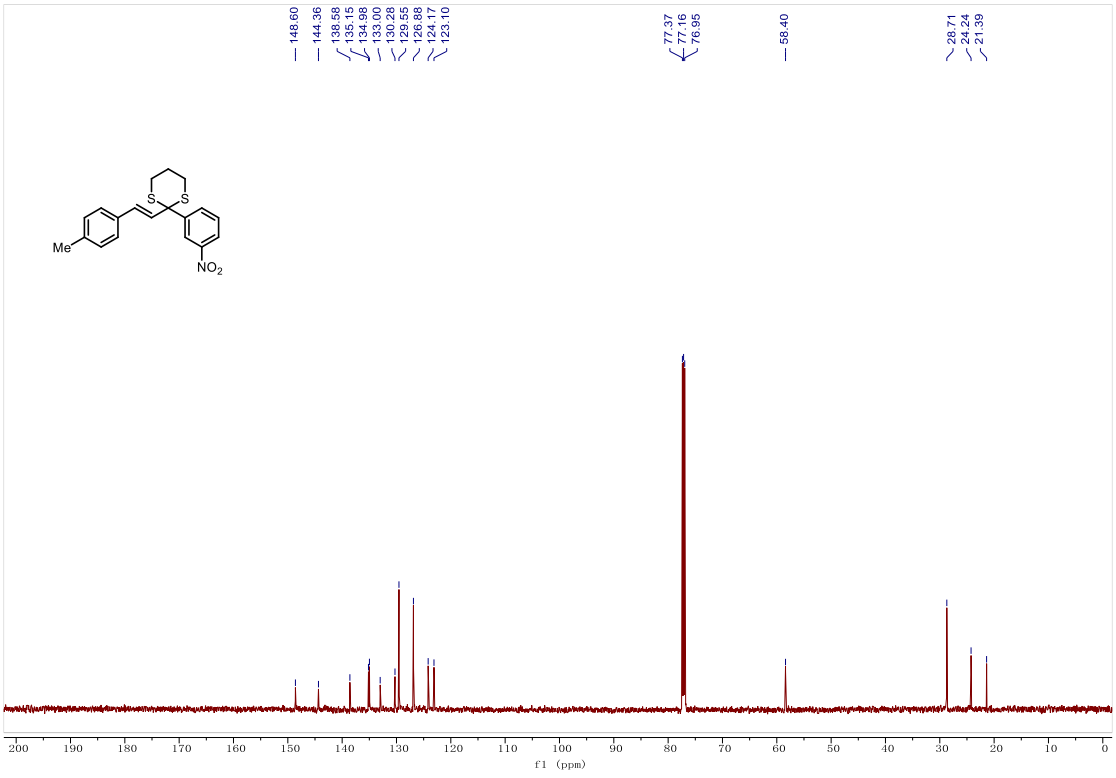
^{13}C NMR (101 MHz, Chloroform-*d*) of 12



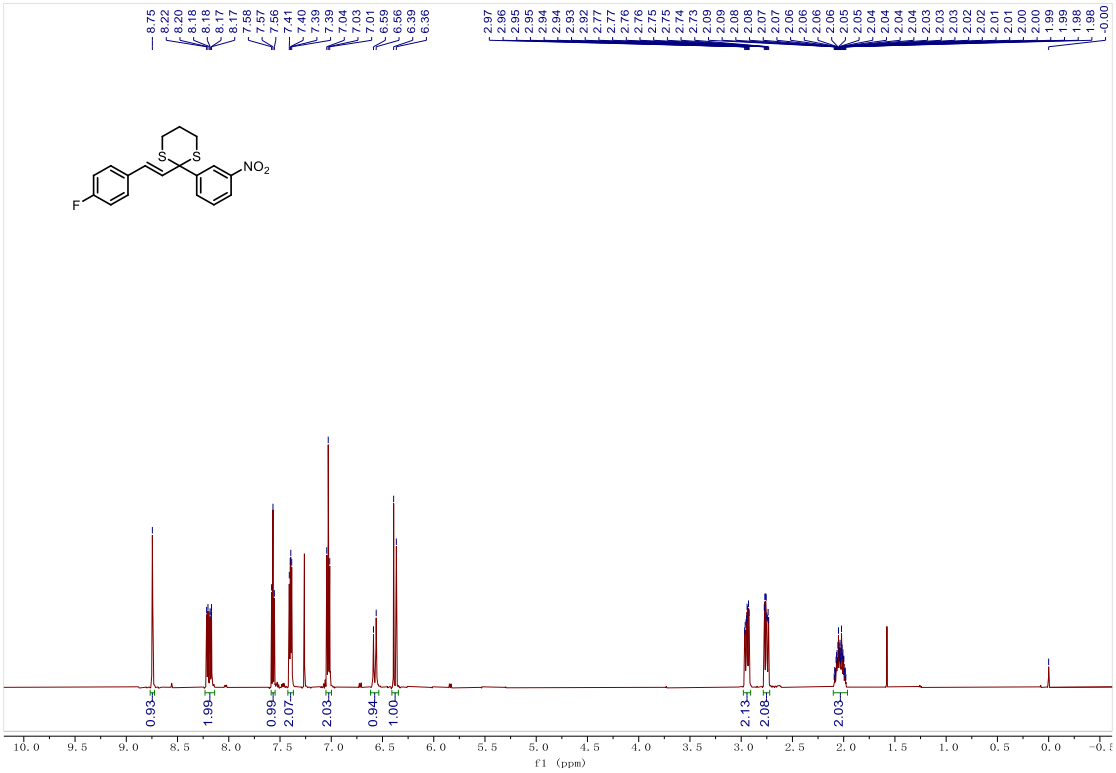
^{1}H NMR (600 MHz, Chloroform-*d*) of 13



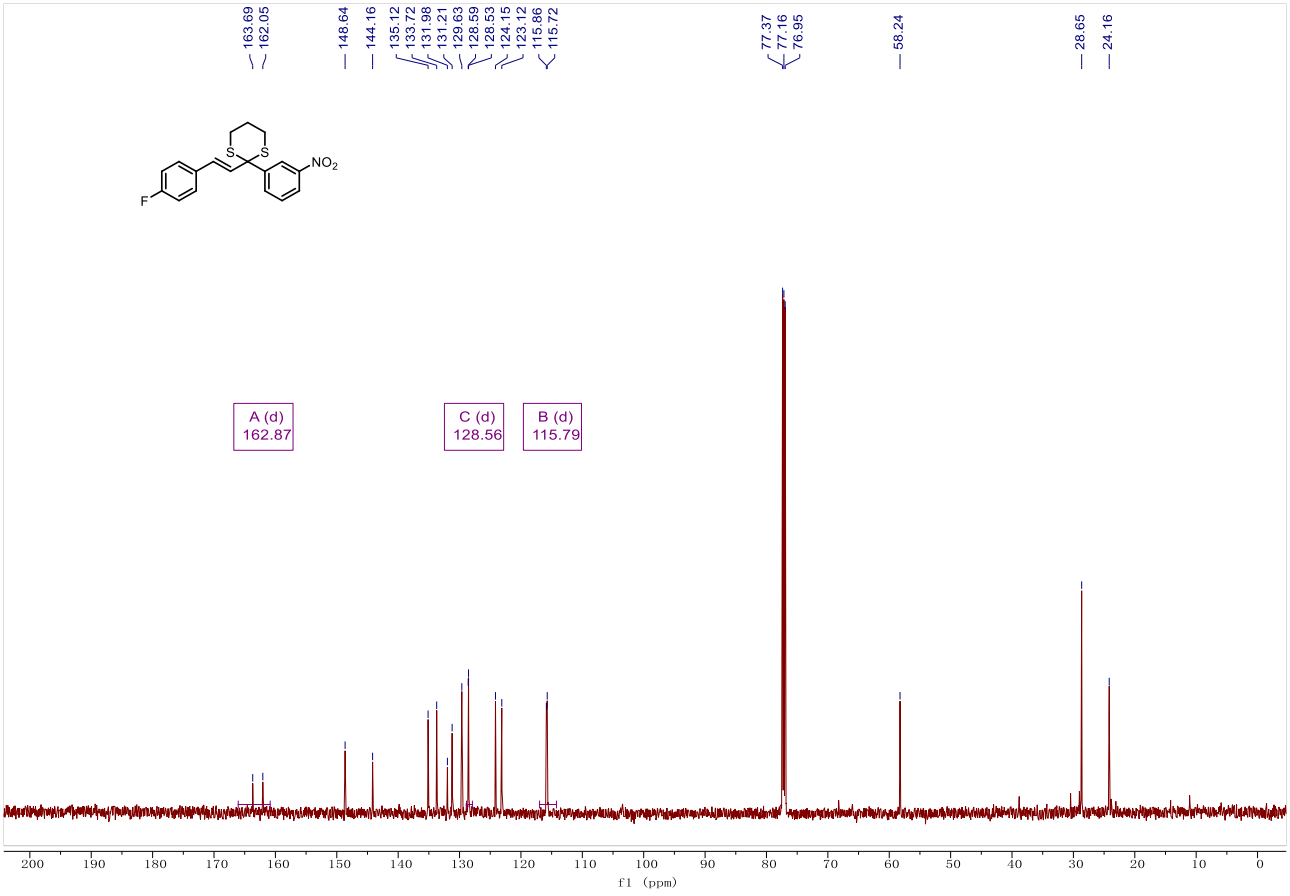
^{13}C NMR (151 MHz, Chloroform-*d*) of 13



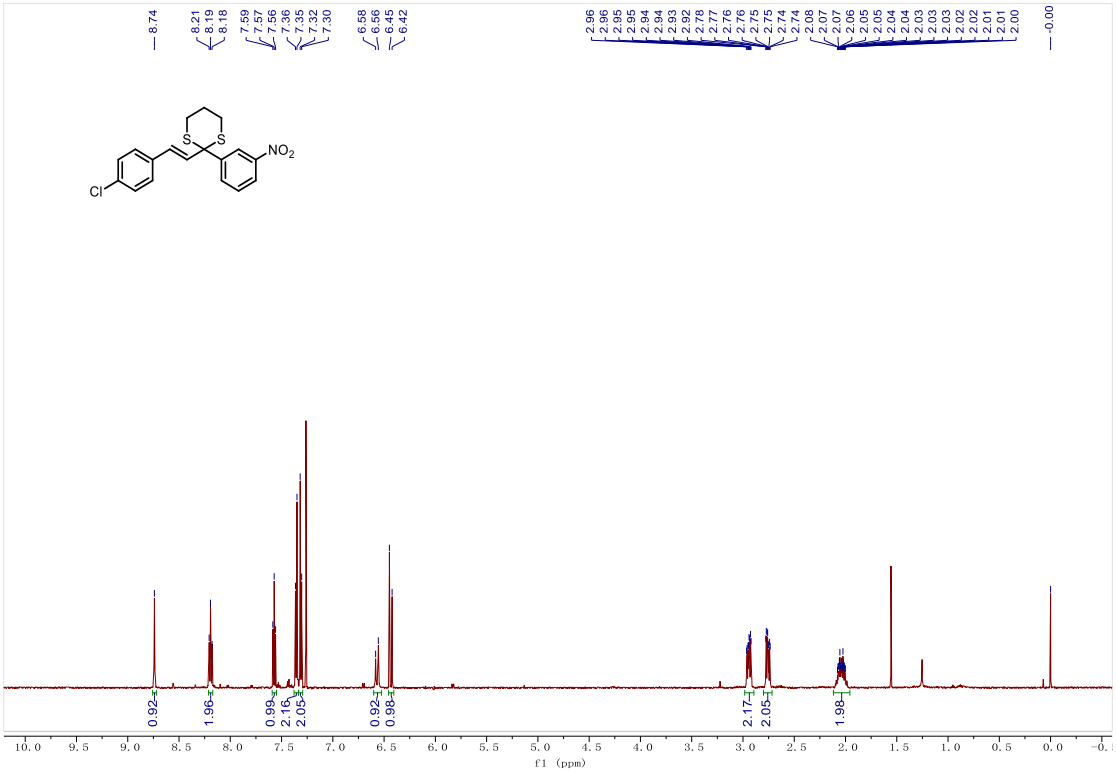
^{1}H NMR (600 MHz, Chloroform-*d*) of 14



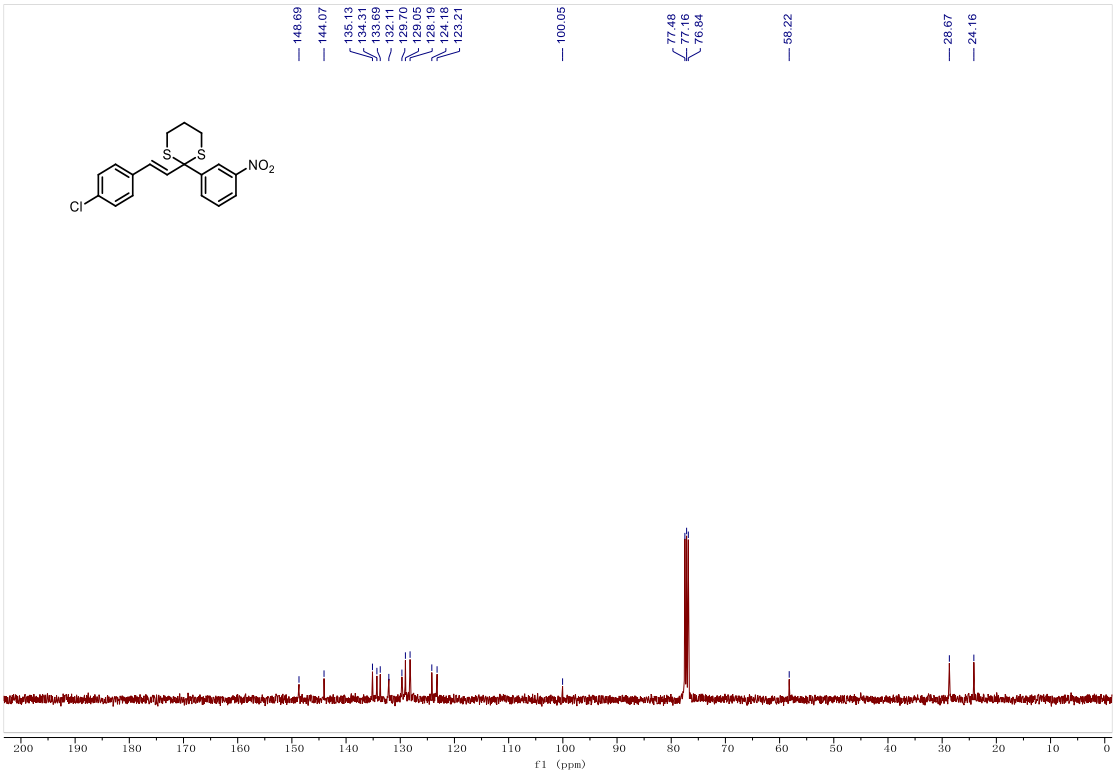
^{13}C NMR (151 MHz, Chloroform-*d*) of 14



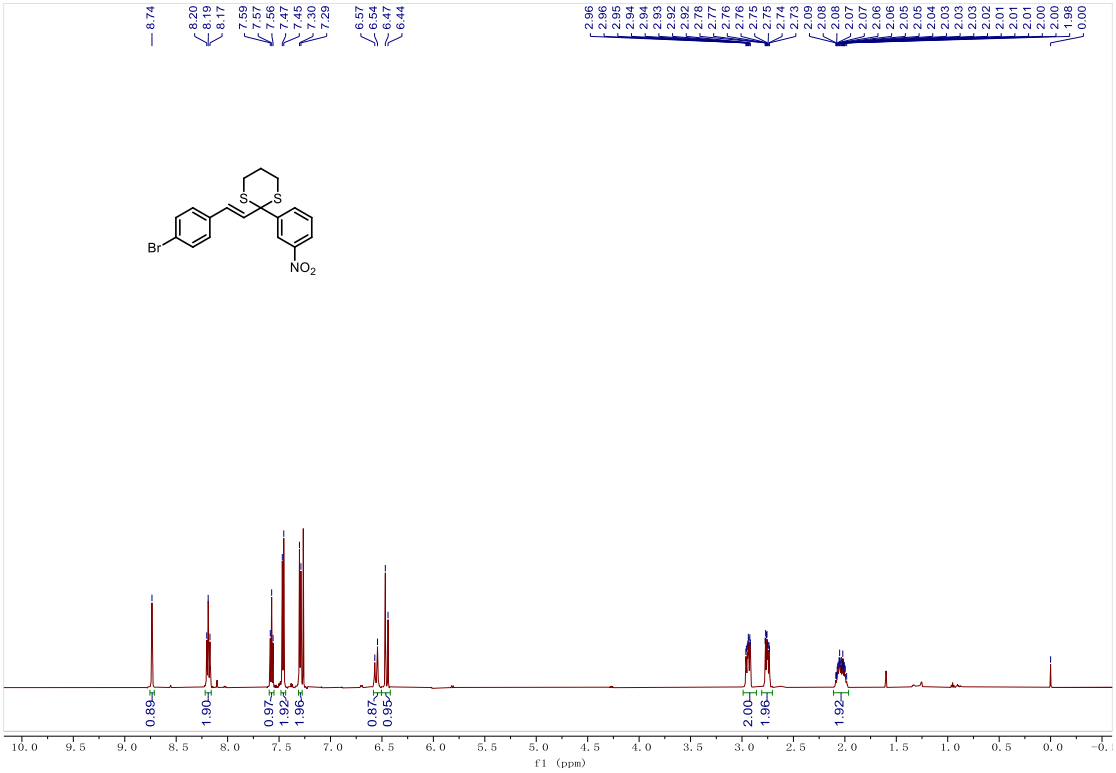
^{1}H NMR (600 MHz, Chloroform-*d*) of 15



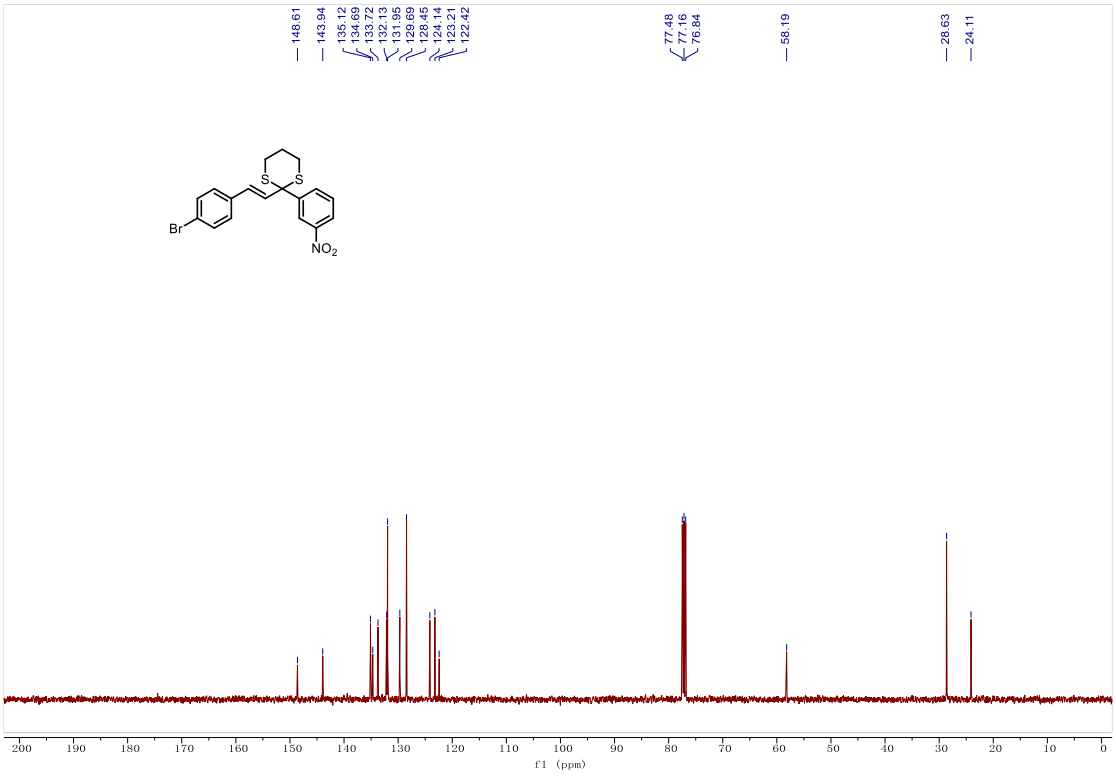
^{13}C NMR (101 MHz, Chloroform-*d*) of 15



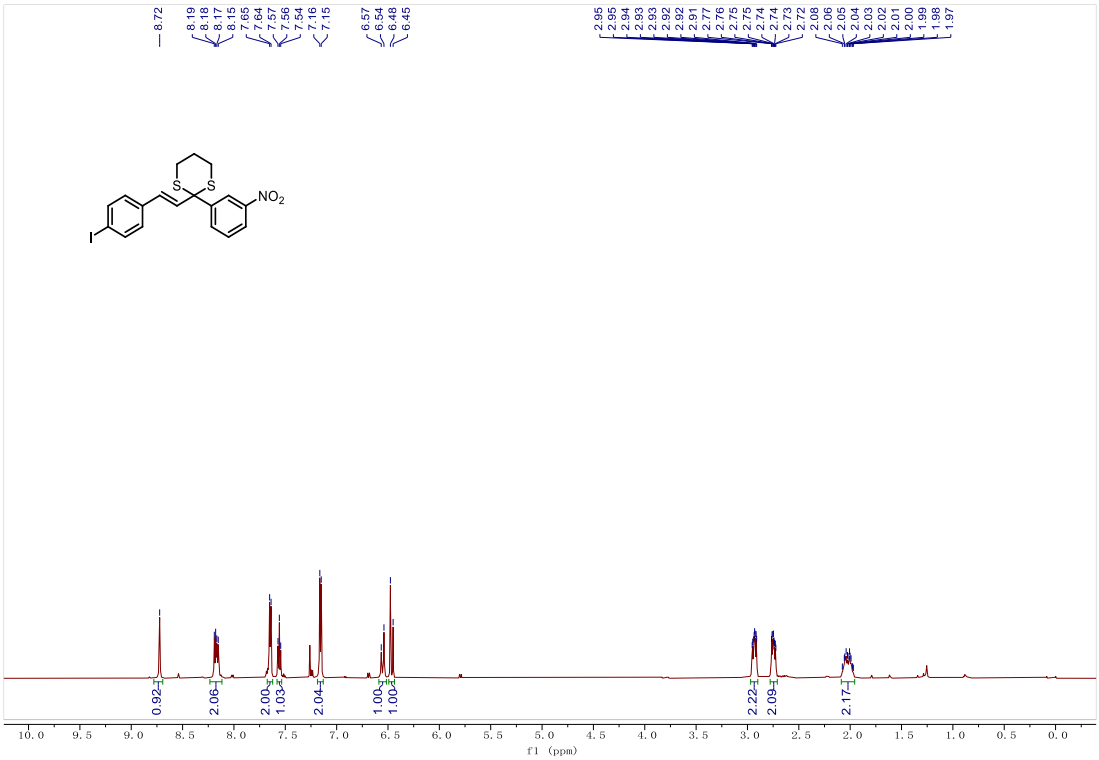
^{1}H NMR (600 MHz, Chloroform-*d*) of 16



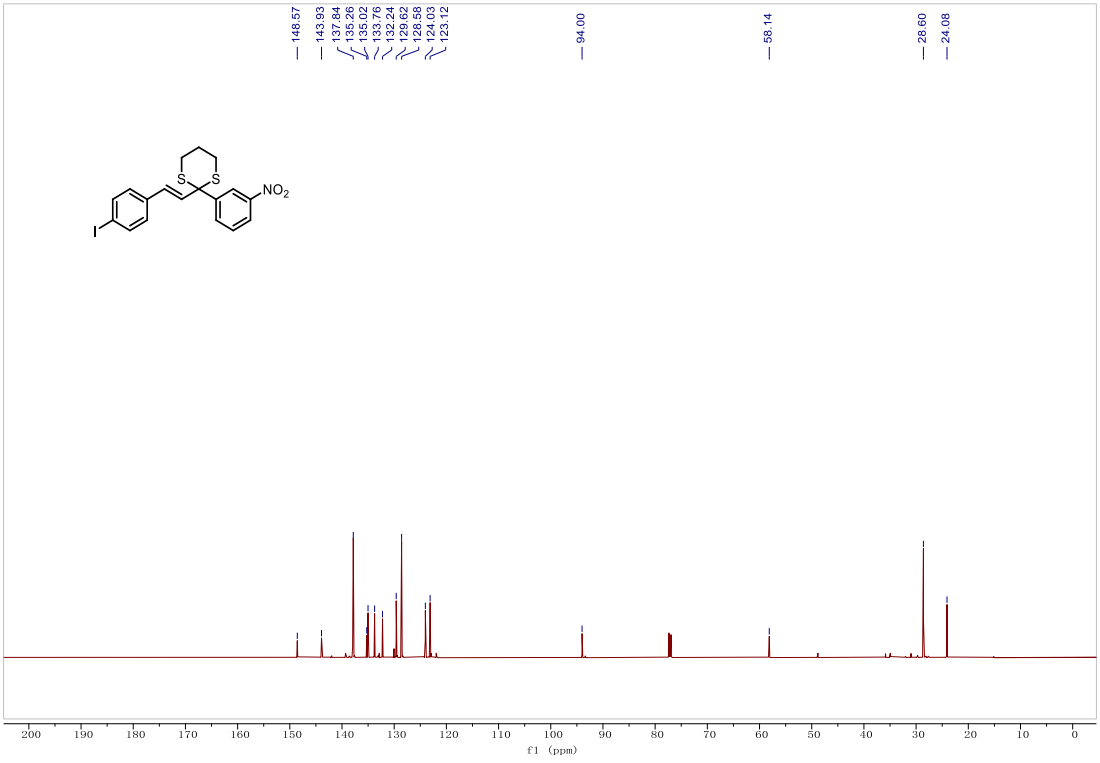
^{13}C NMR (101 MHz, Chloroform-*d*) of 16



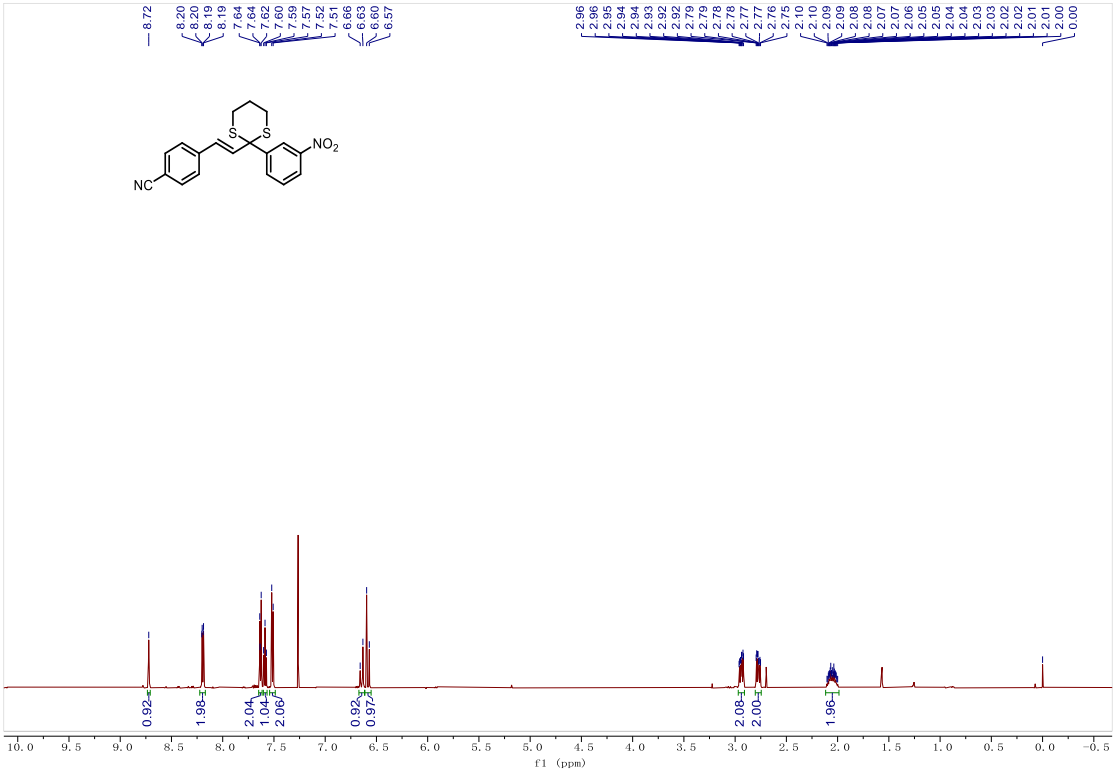
^{1}H NMR (600 MHz, Chloroform-*d*) of 17



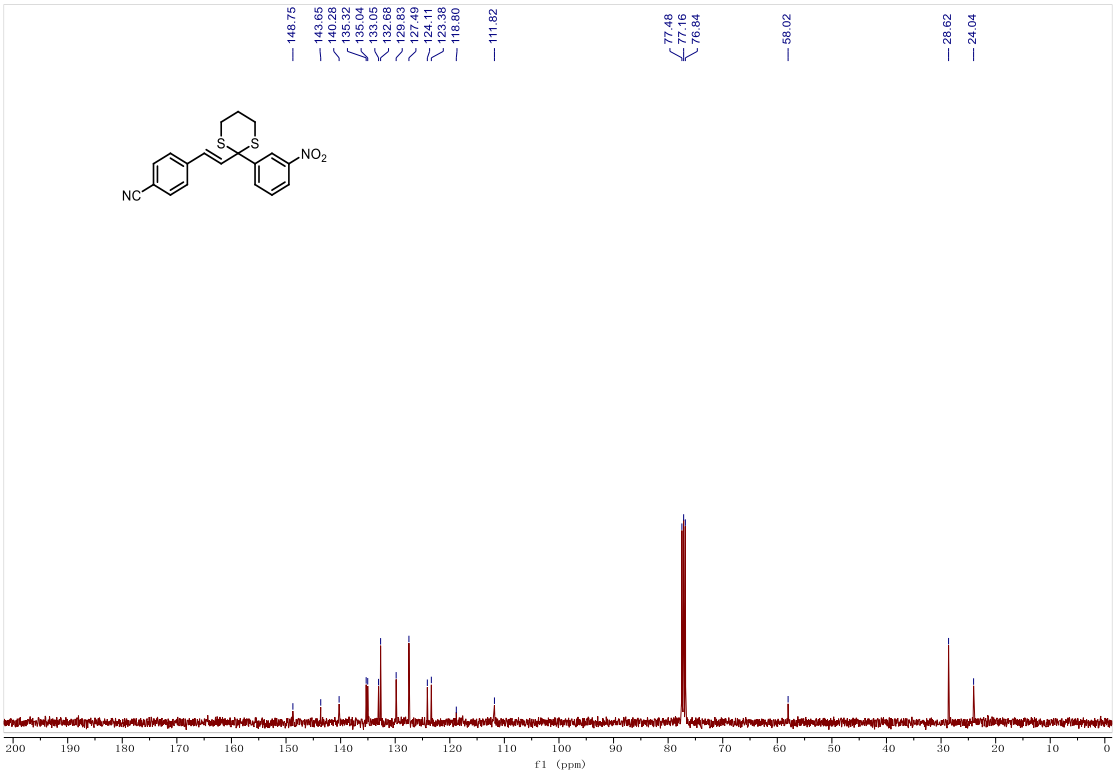
^{13}C NMR (101 MHz, Chloroform-*d*) of 17



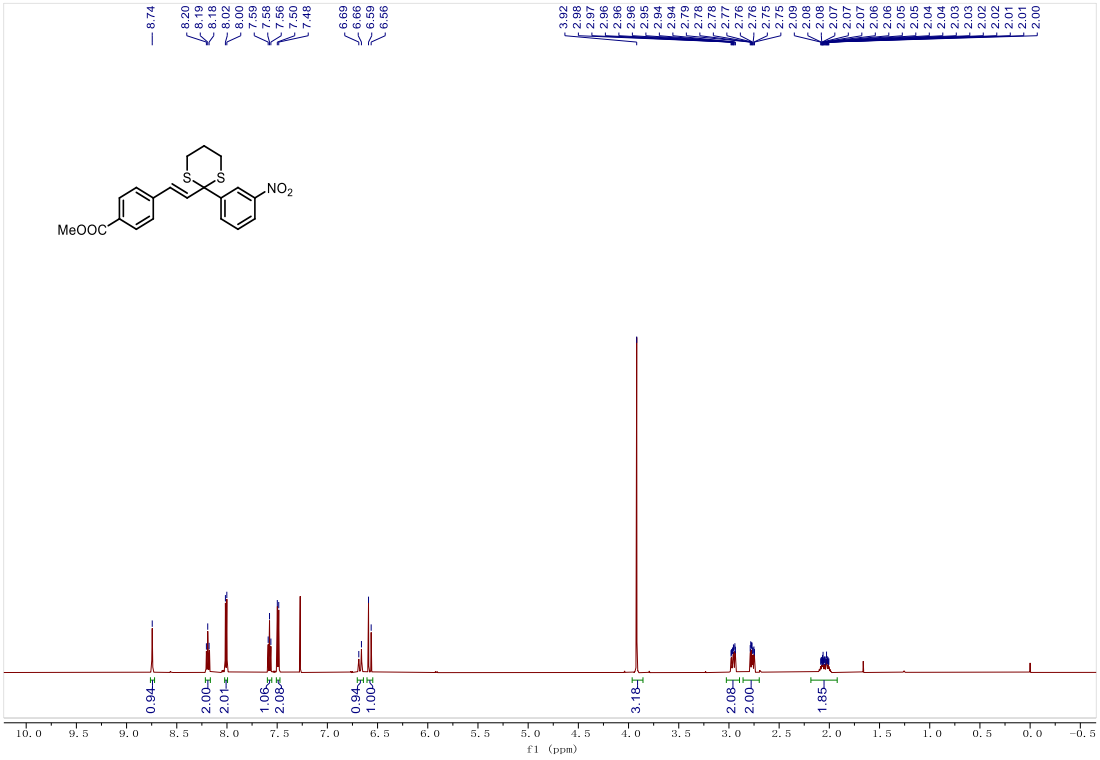
^{1}H NMR (600 MHz, Chloroform-*d*) of 18



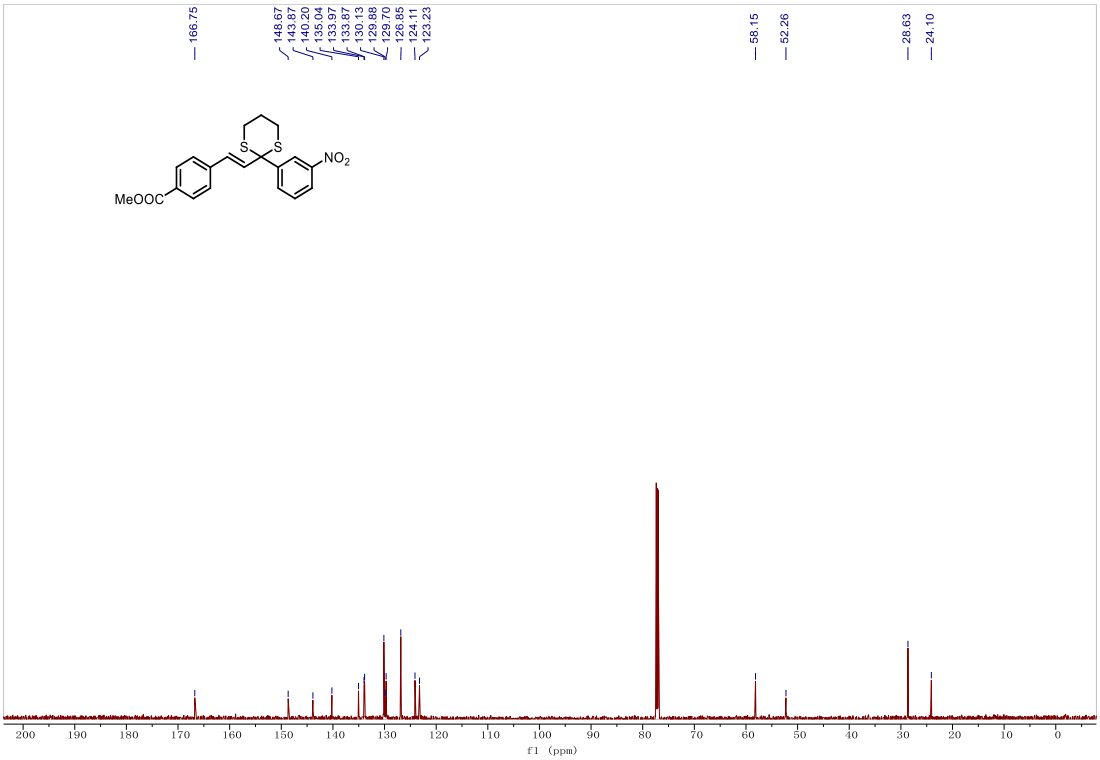
^{13}C NMR (101 MHz, Chloroform-*d*) of 18



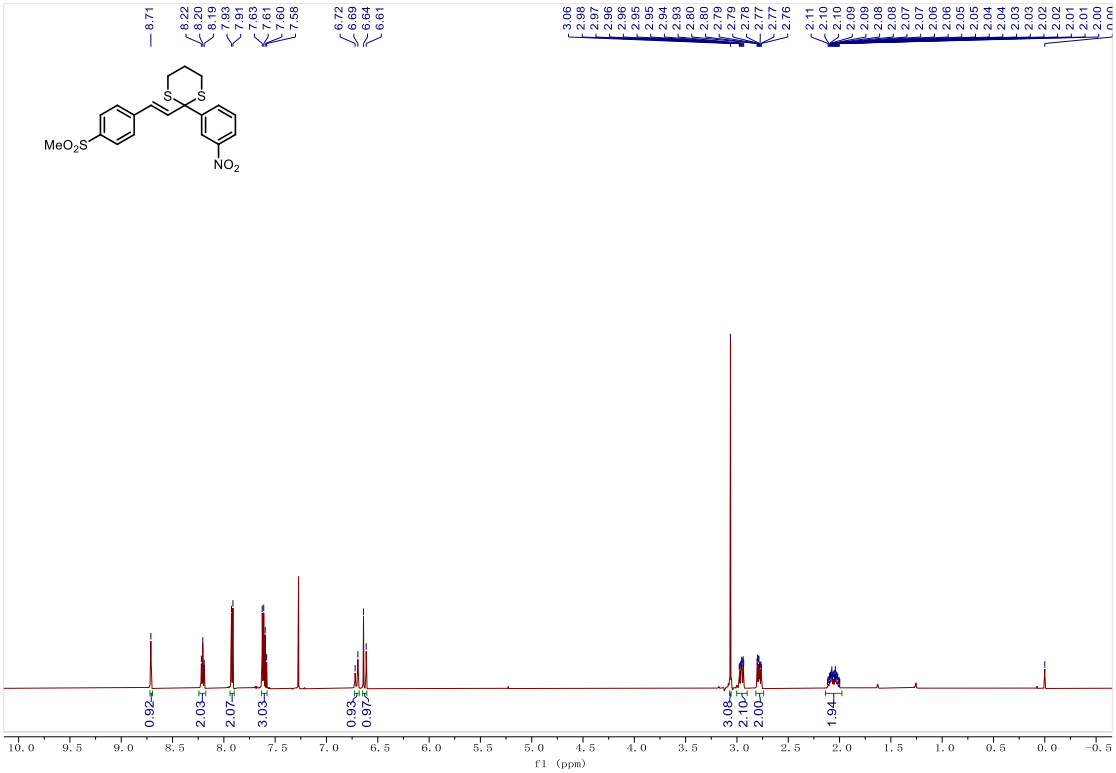
^{1}H NMR (600 MHz, Chloroform-*d*) of 19



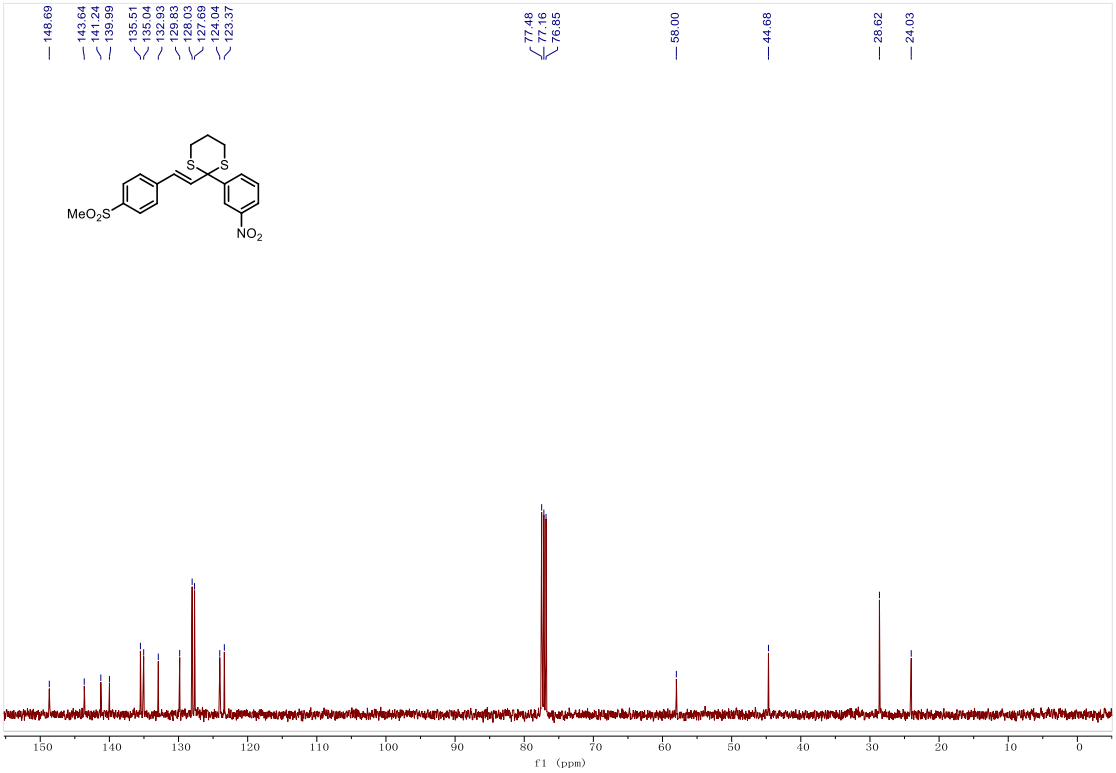
^{13}C NMR (101 MHz, Chloroform-*d*) of 19



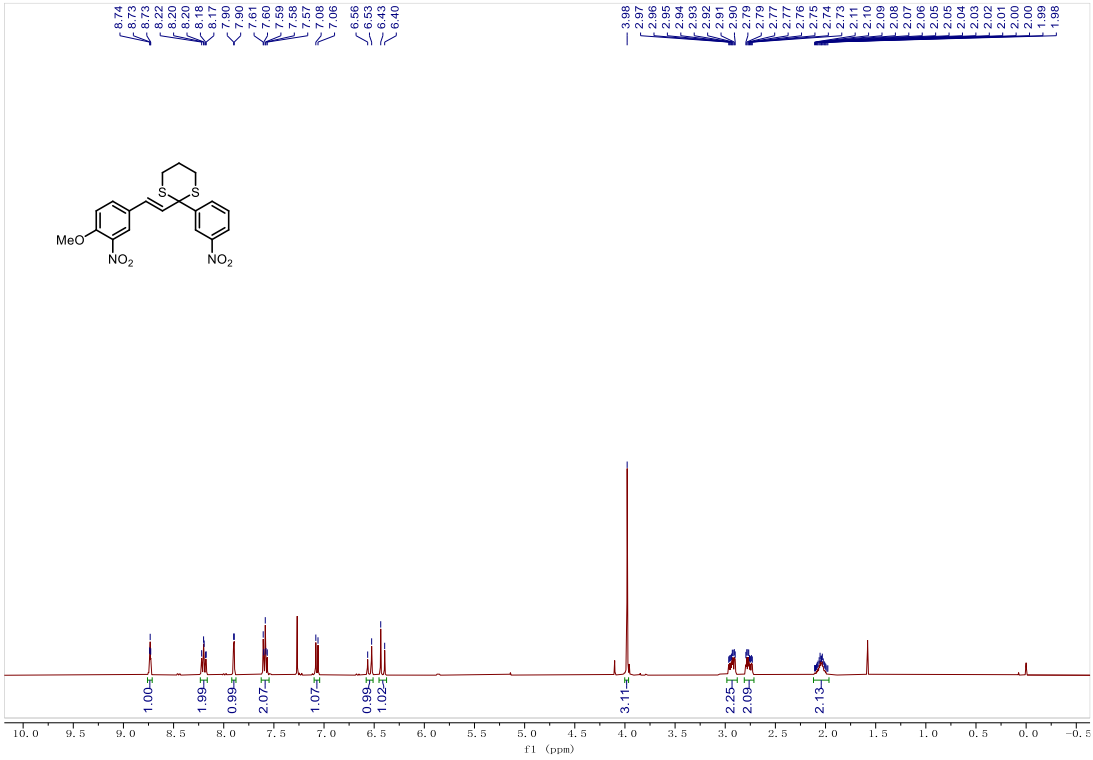
^{1}H NMR (600 MHz, Chloroform-*d*) of 20



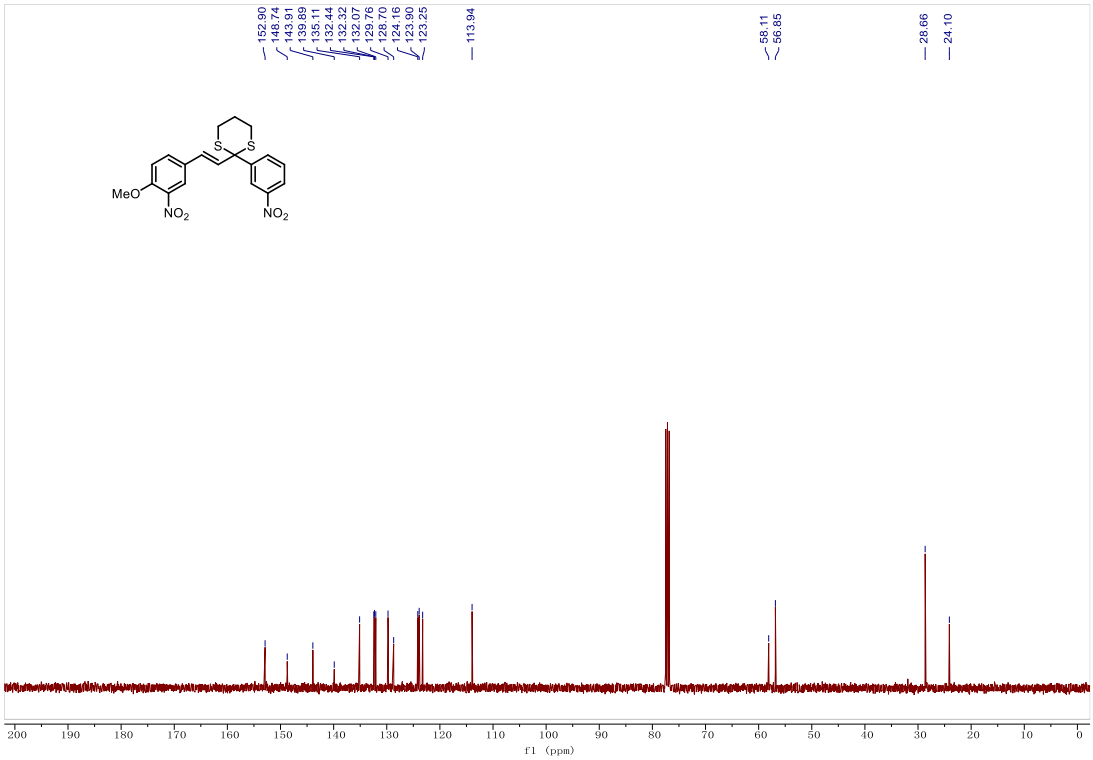
^{13}C NMR (101 MHz, Chloroform-*d*) of 20



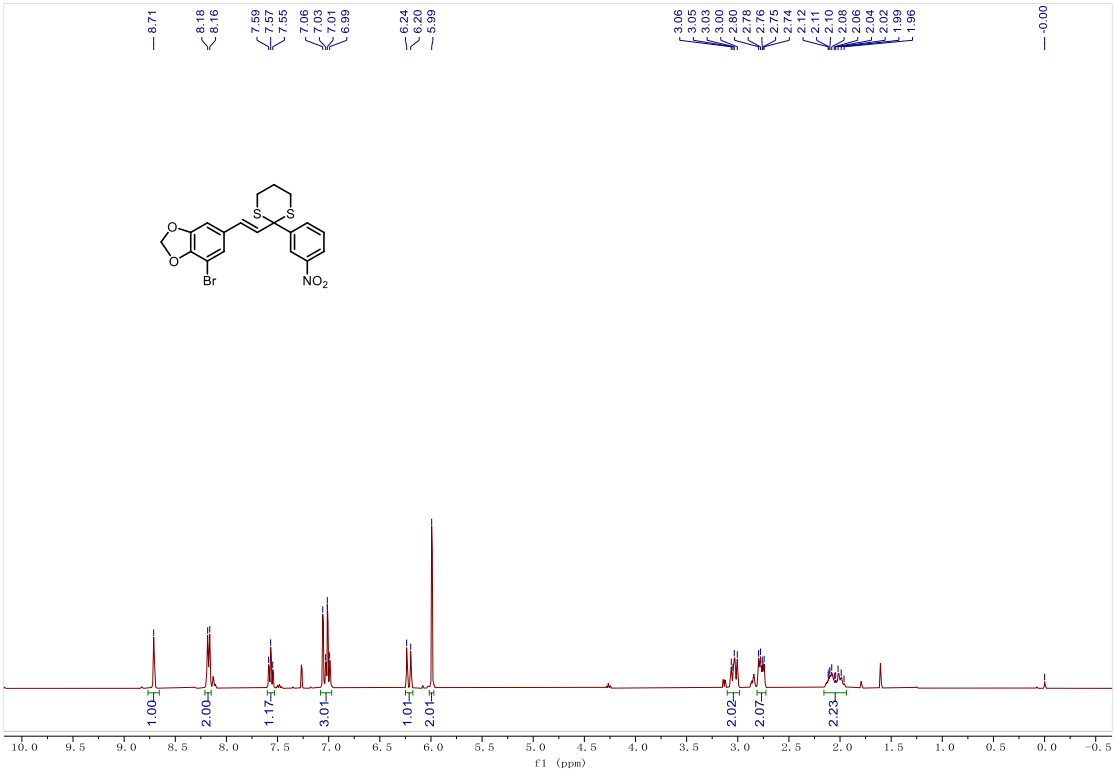
^{1}H NMR (400 MHz, Chloroform-*d*) of 21



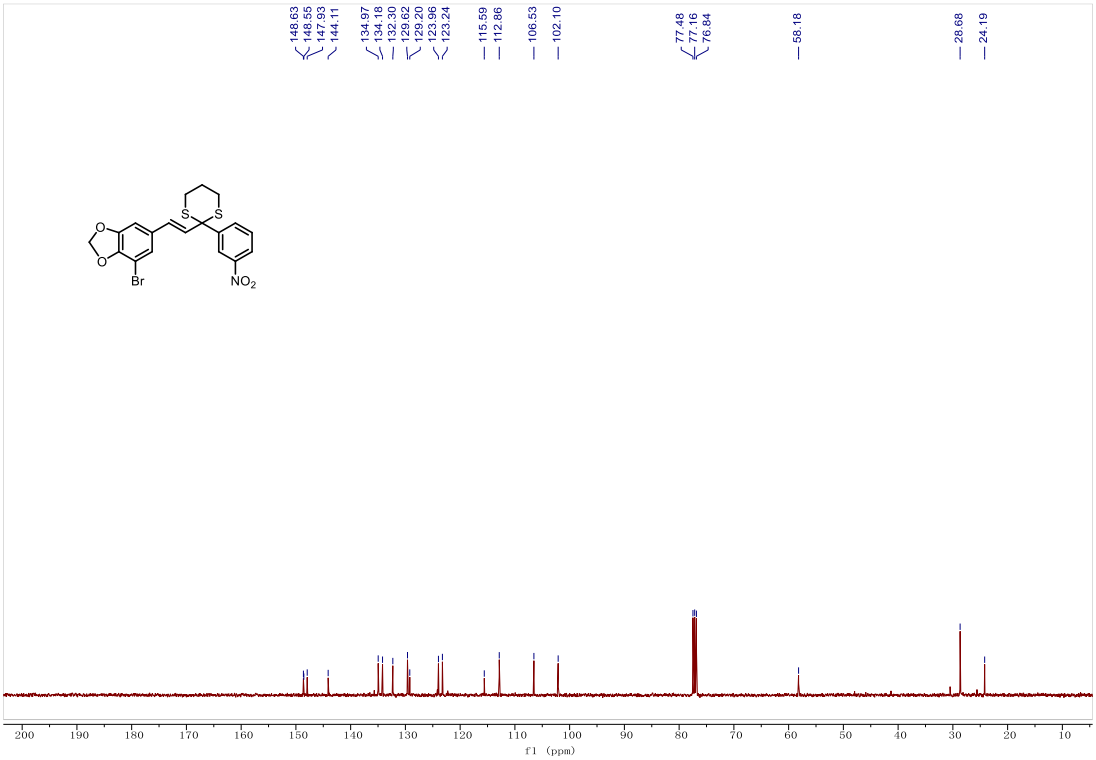
^{13}C NMR (101 MHz, Chloroform-*d*) of 21



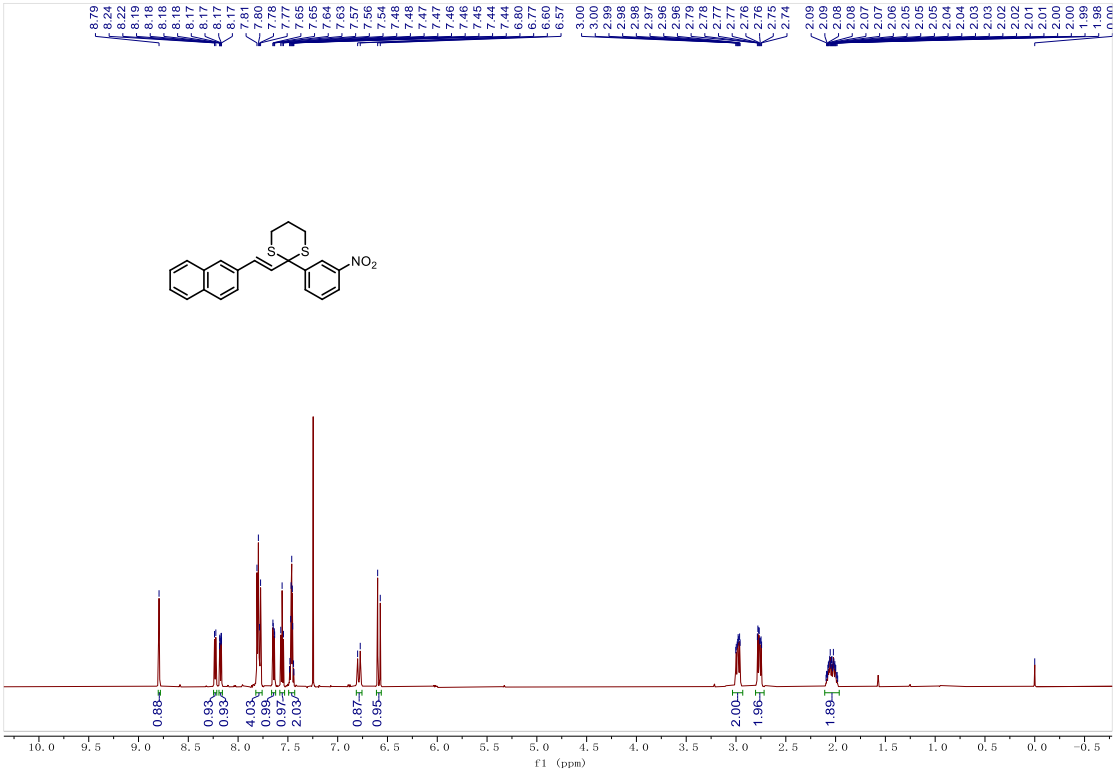
^{1}H NMR (400 MHz, Chloroform-*d*) of 22



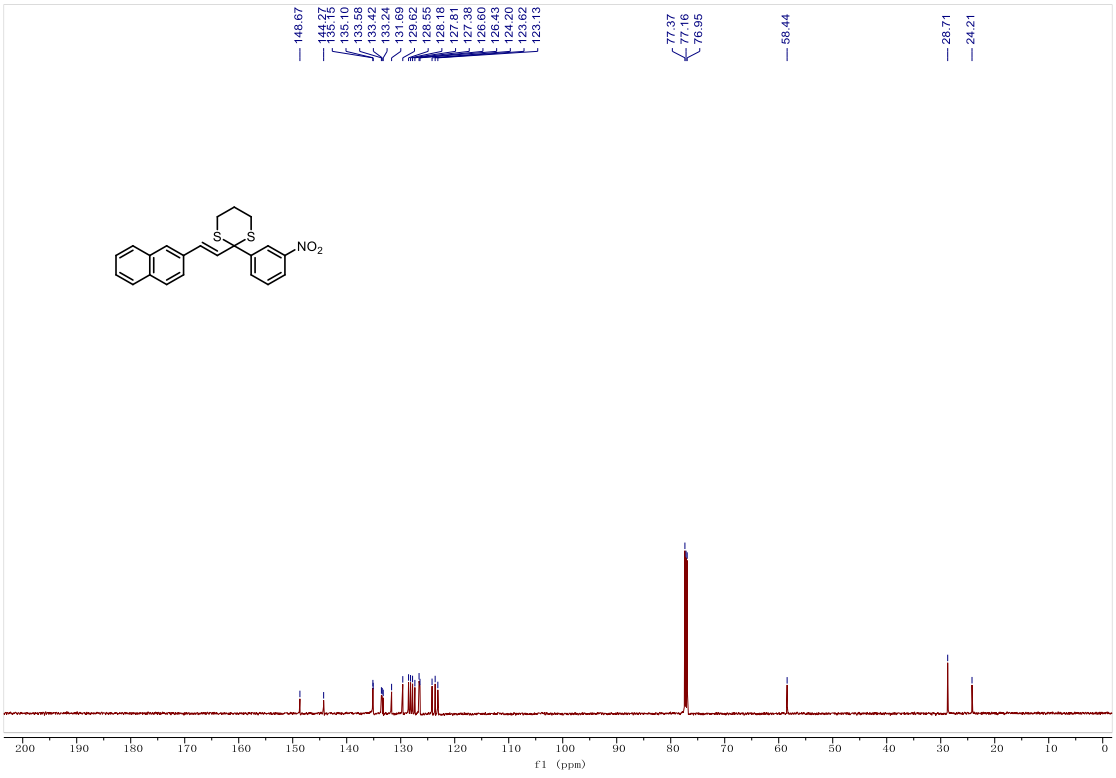
^{13}C NMR (101 MHz, Chloroform-*d*) of 22



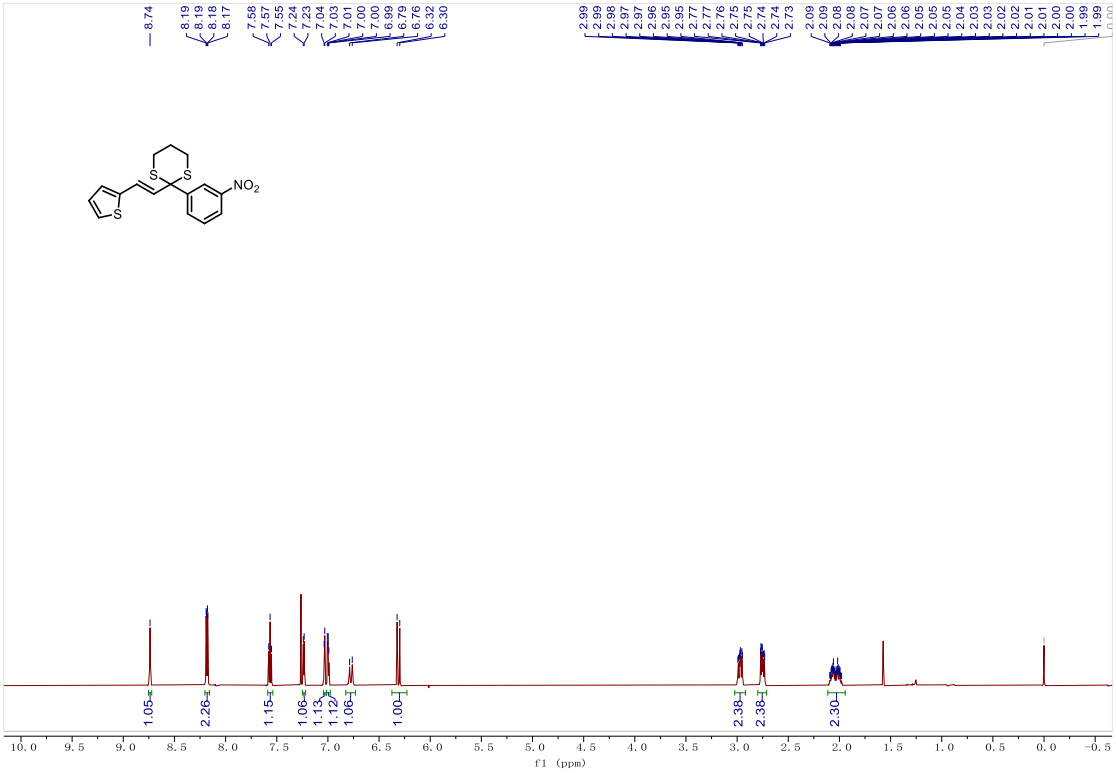
^{1}H NMR (600 MHz, Chloroform-*d*) of 23



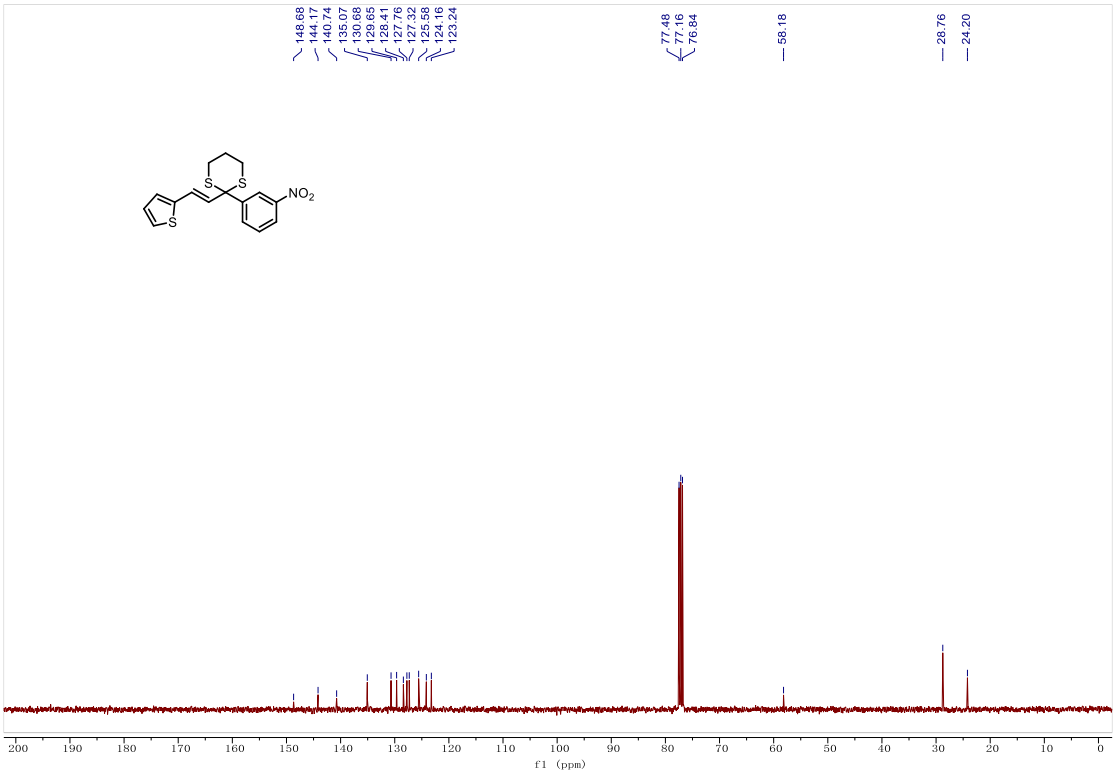
^{13}C NMR (151 MHz, Chloroform-*d*) of 23



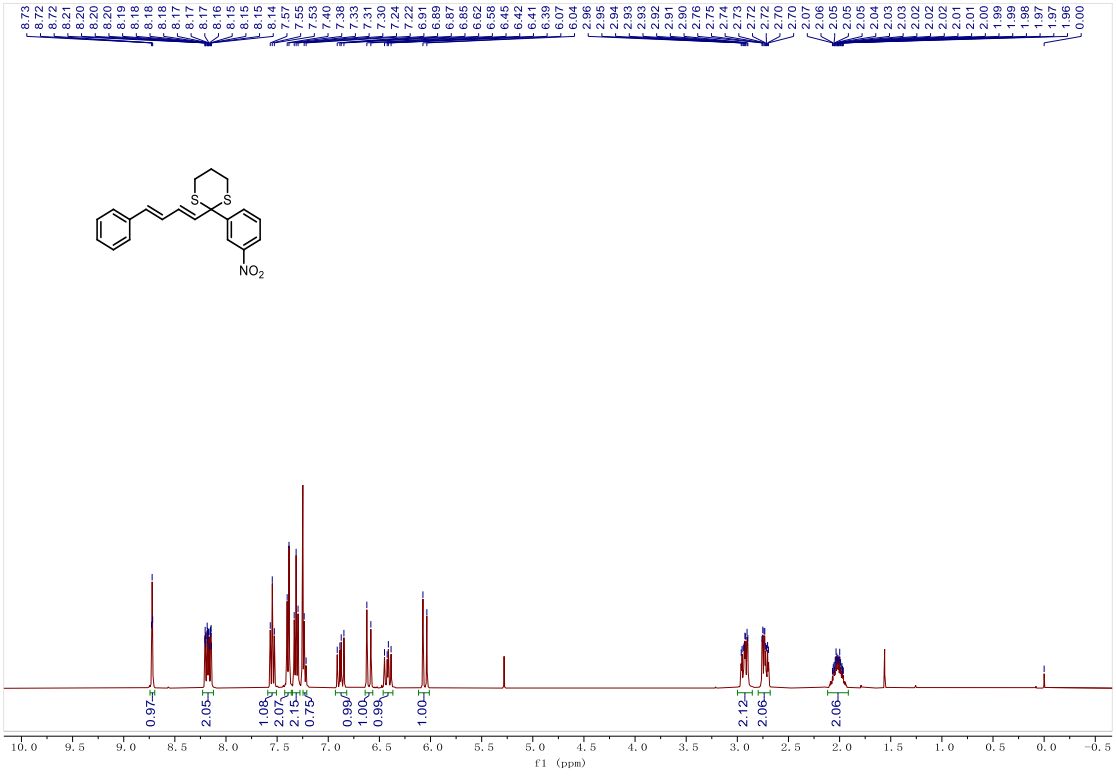
^{1}H NMR (600 MHz, Chloroform-*d*) of 24



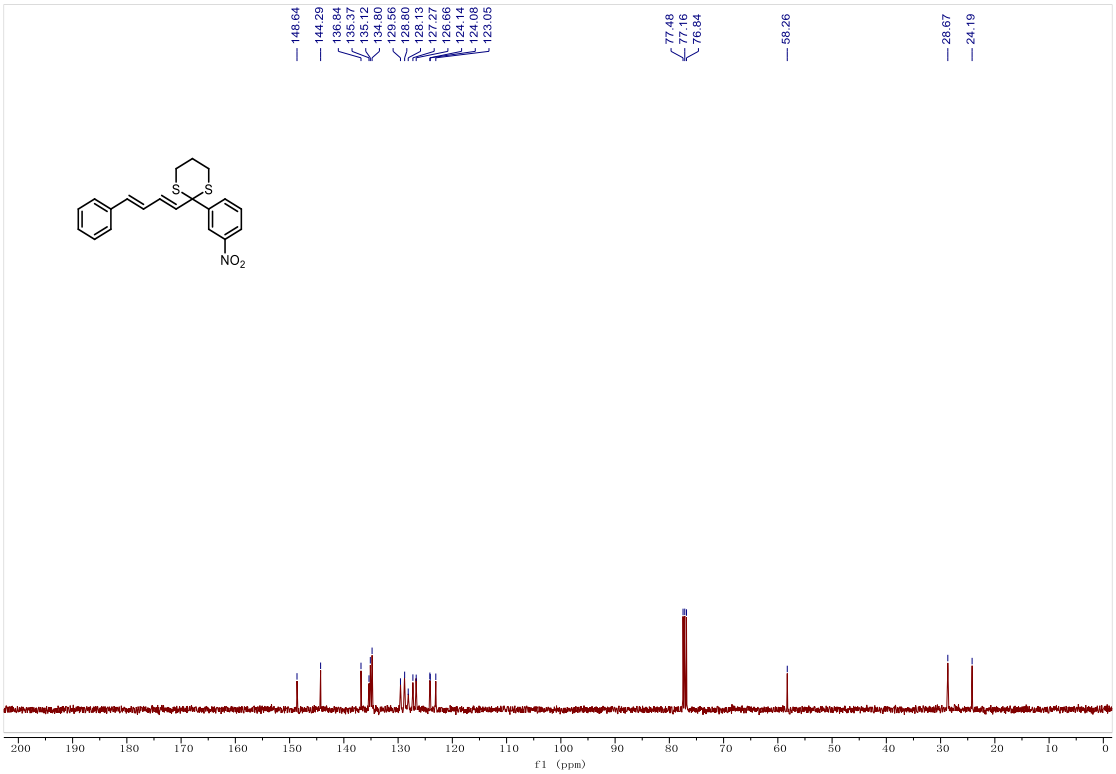
^{13}C NMR (101 MHz, Chloroform-*d*) of 24



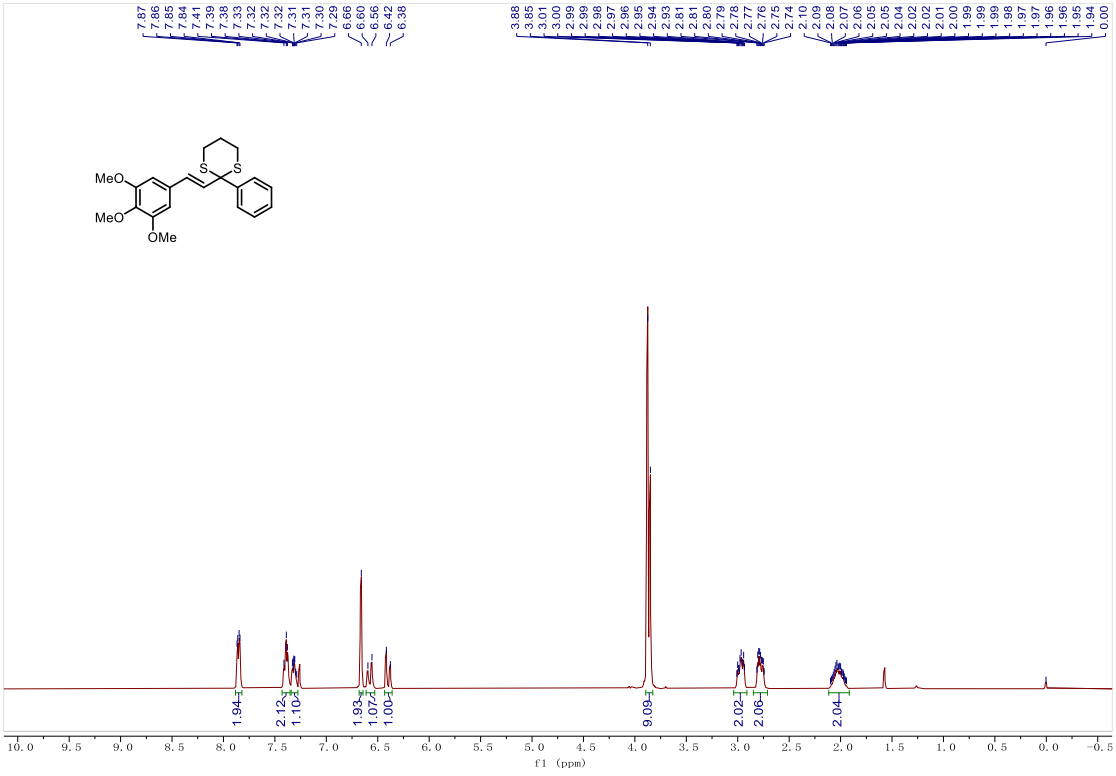
^{1}H NMR (400 MHz, Chloroform-*d*) of 25



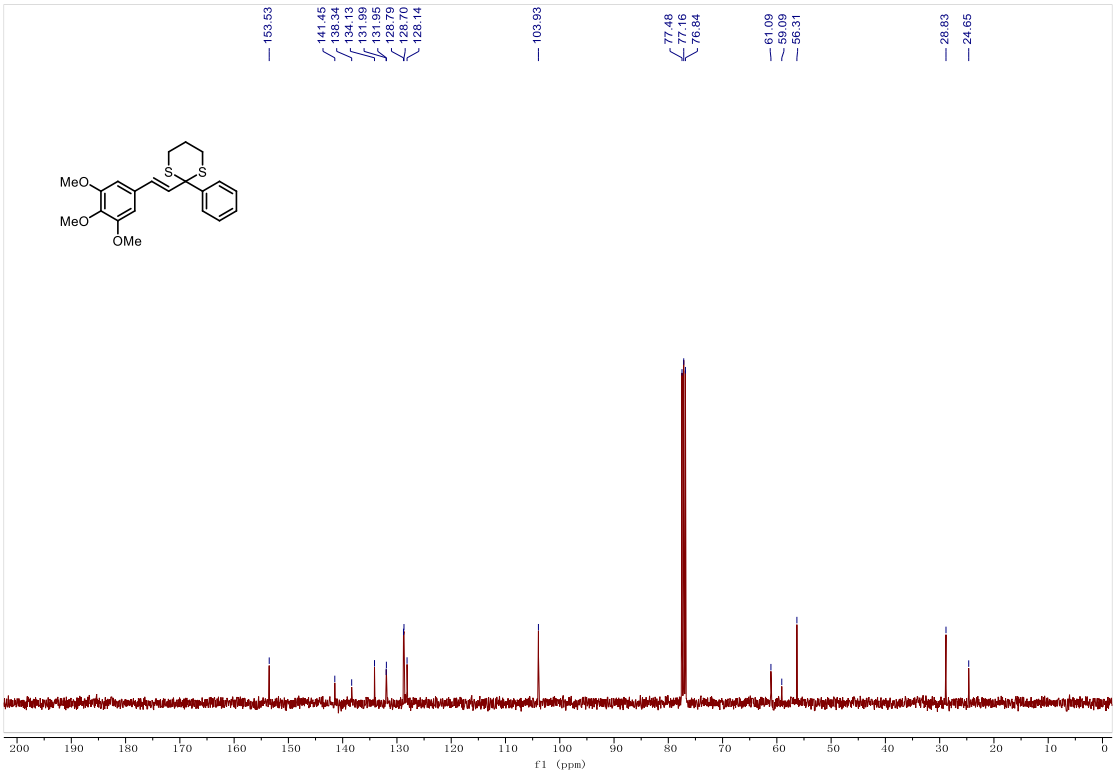
^{13}C NMR (101 MHz, Chloroform-*d*) of 25



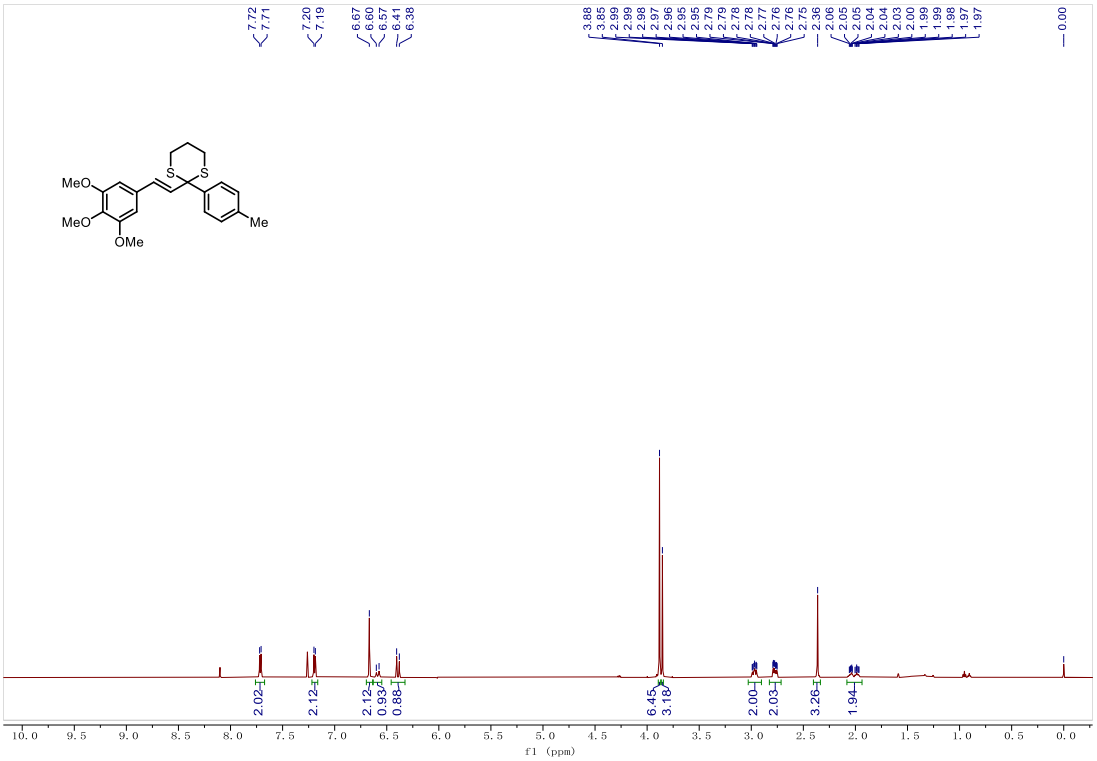
^{1}H NMR (400 MHz, Chloroform-*d*) of 26



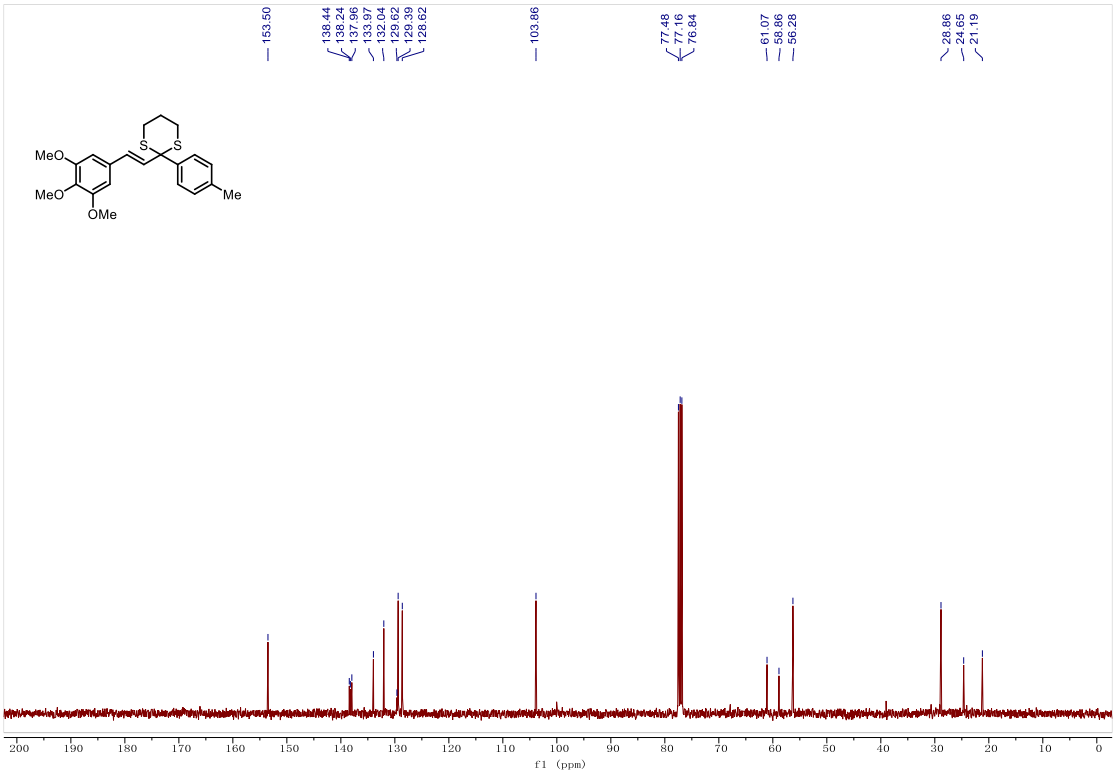
^{13}C NMR (101 MHz, Chloroform-*d*) of 26



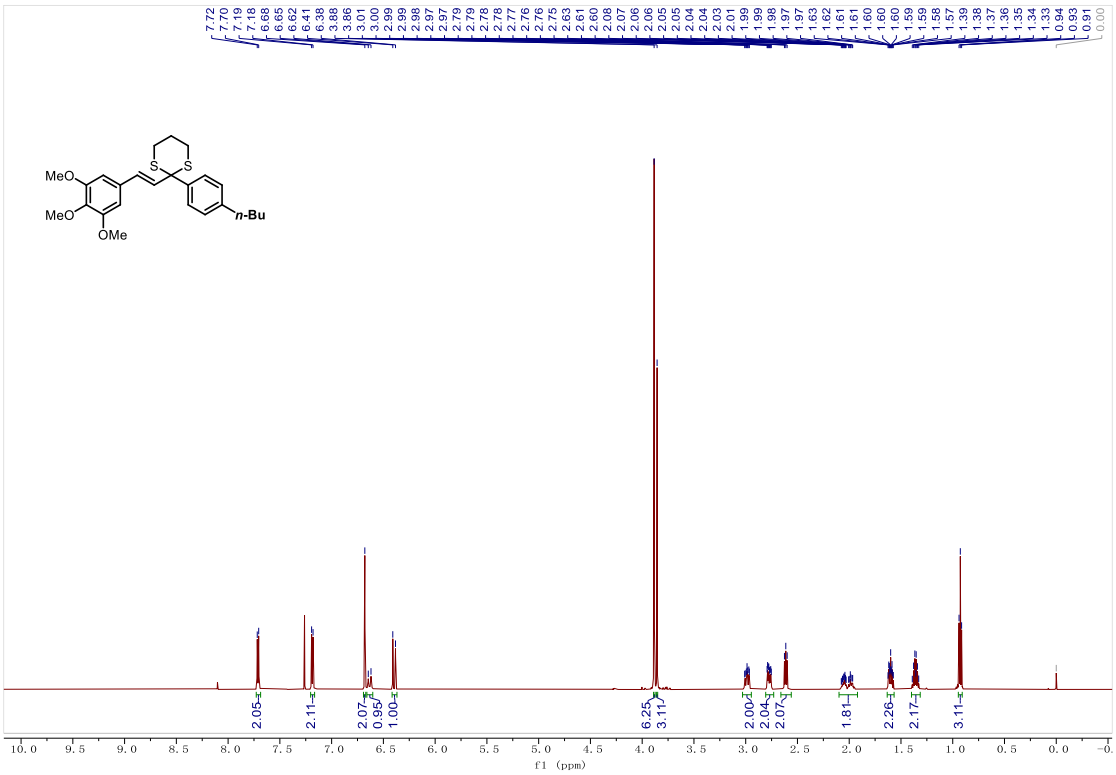
^{1}H NMR (600 MHz, Chloroform-*d*) of 27



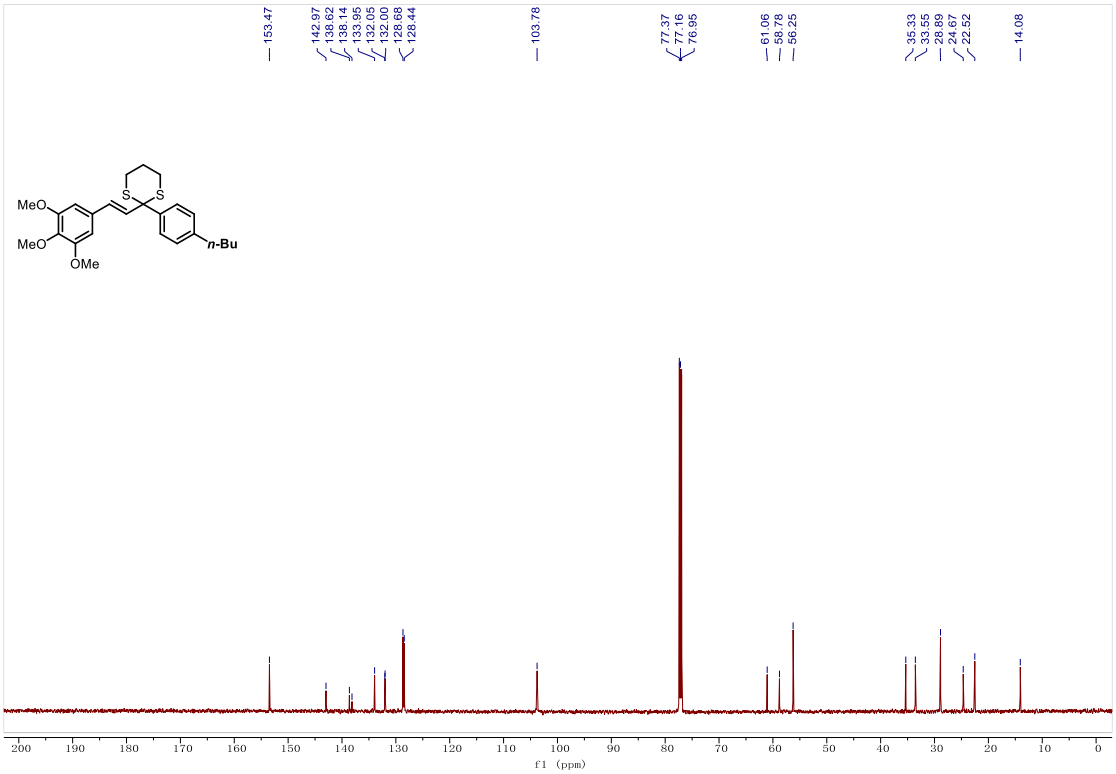
^{13}C NMR (101 MHz, Chloroform-*d*) of 27



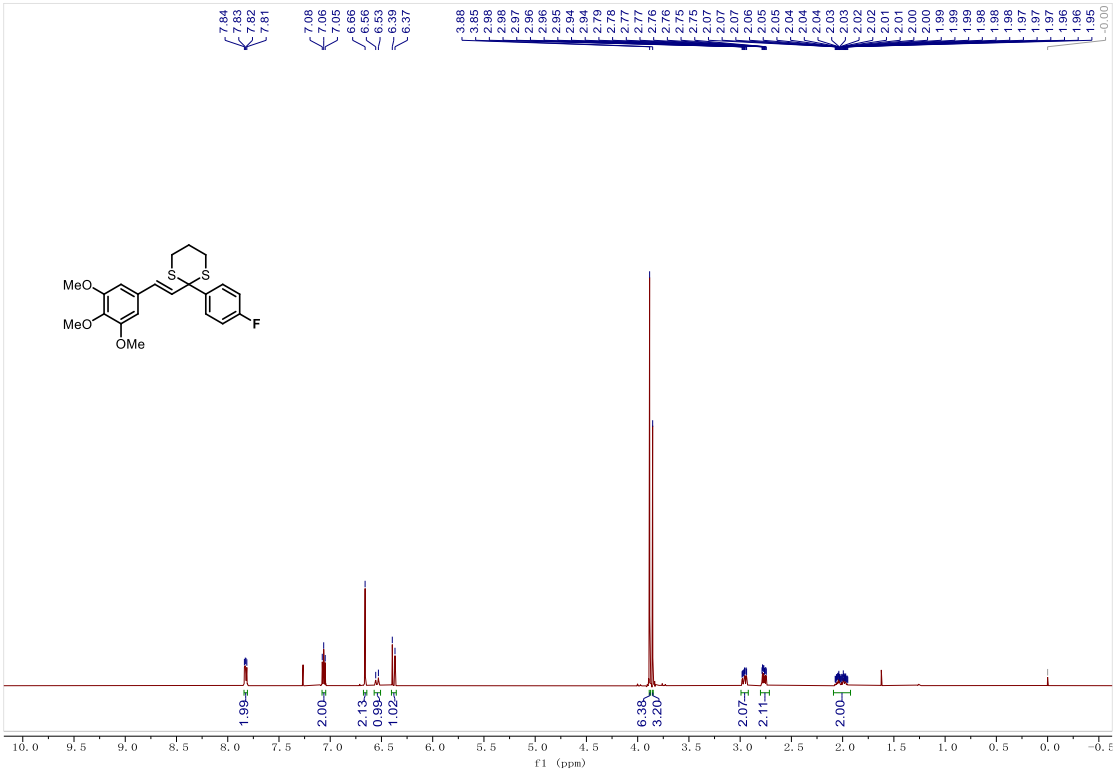
^{1}H NMR (600 MHz, Chloroform-*d*) of 28



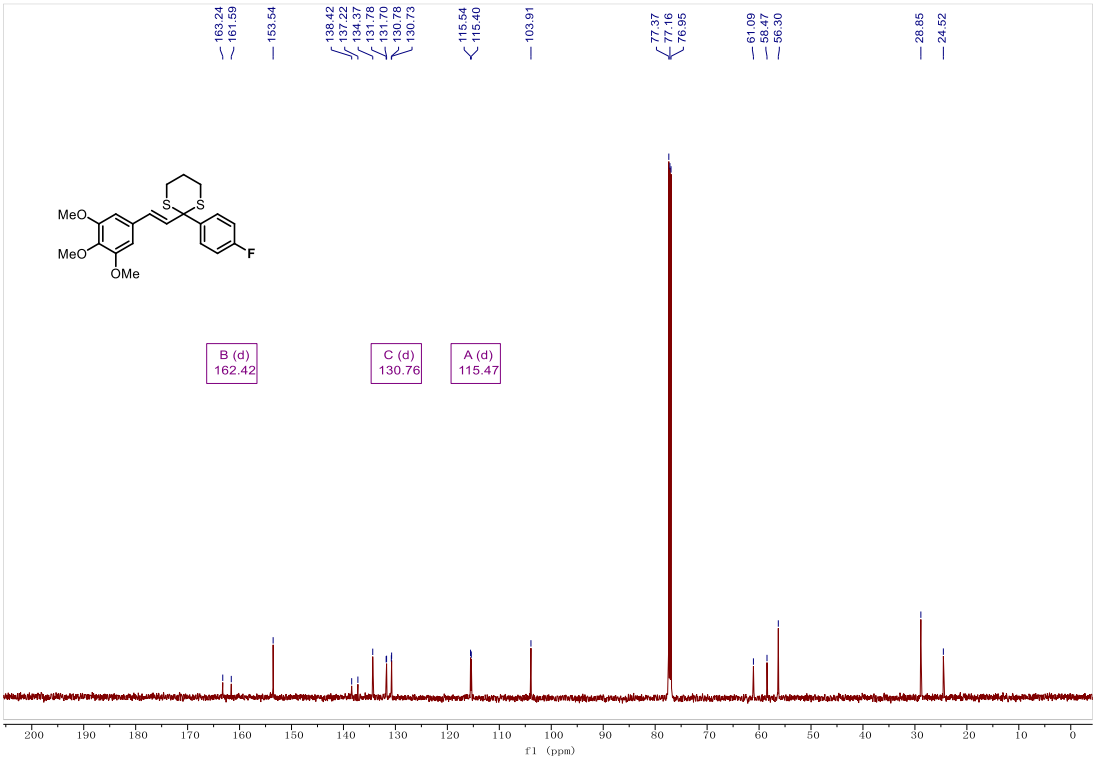
^{13}C NMR (151 MHz, Chloroform-*d*) of 28



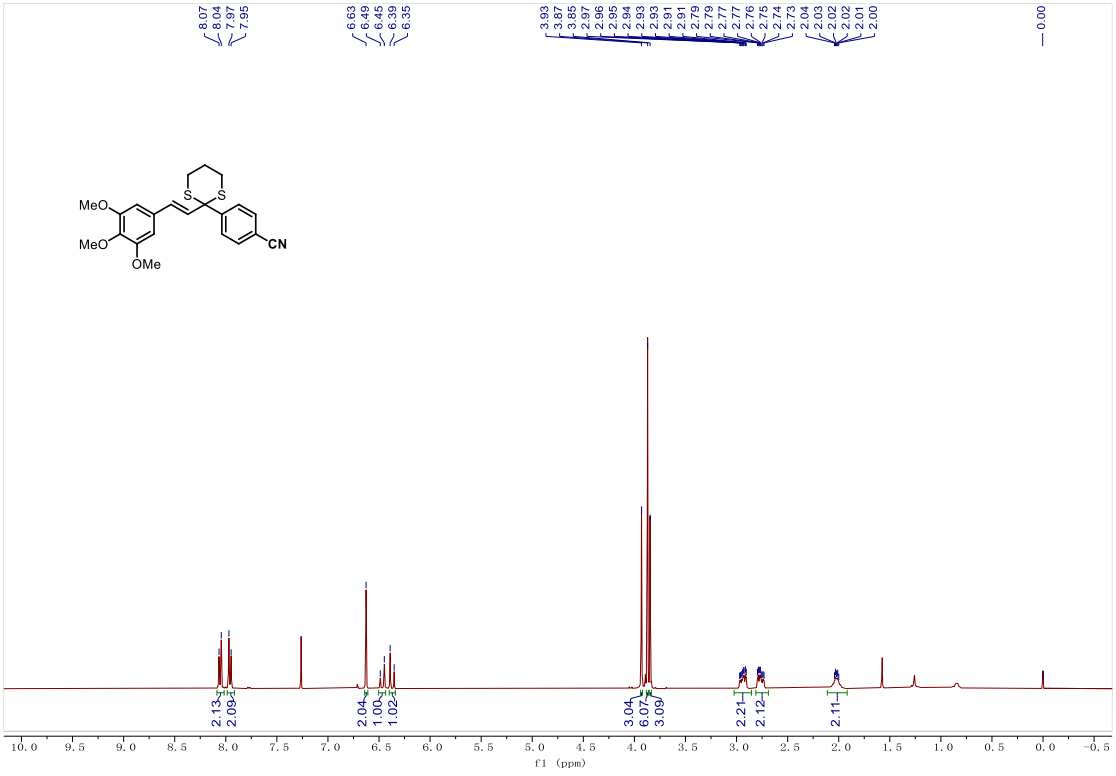
^{1}H NMR (600 MHz, Chloroform-*d*) of 29



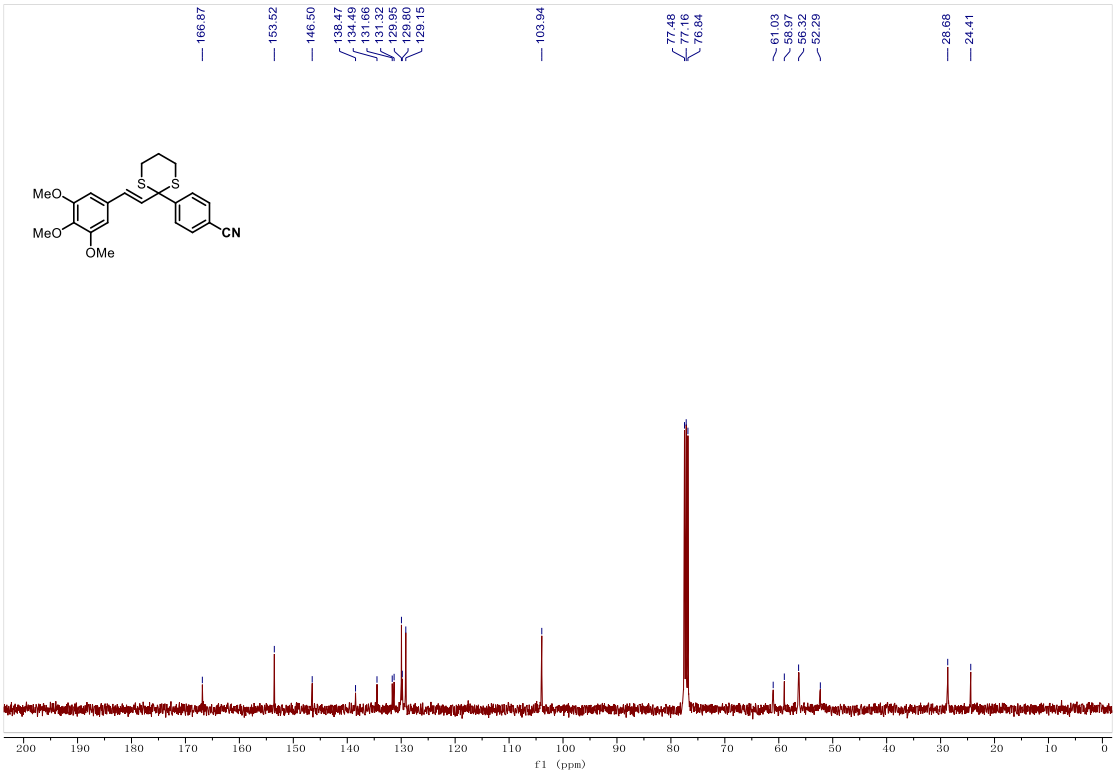
^{13}C NMR (151 MHz, Chloroform-*d*) of 29



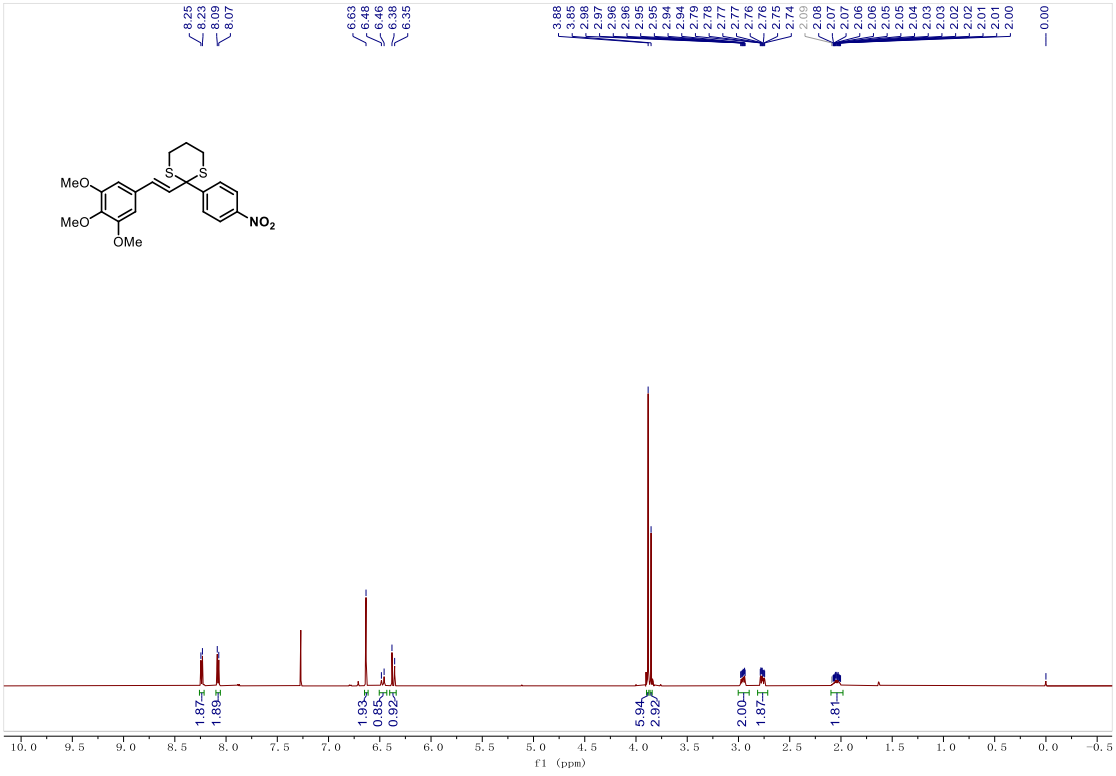
^{1}H NMR (400 MHz, Chloroform-*d*) of 30



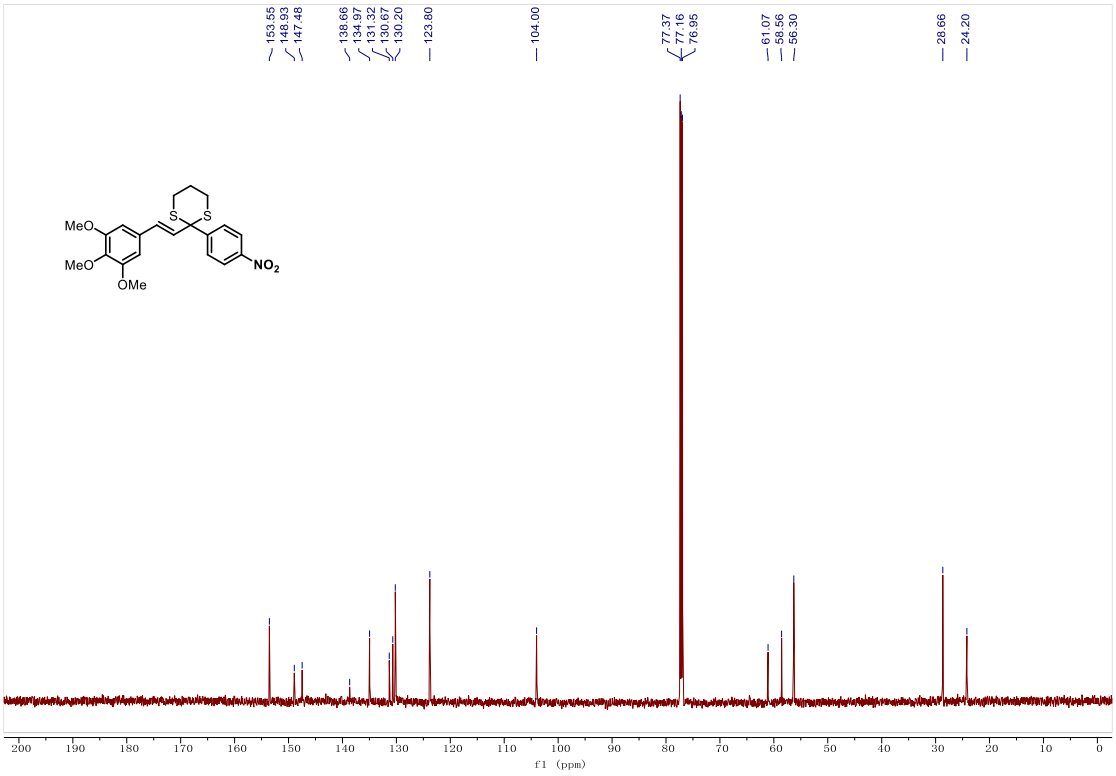
^{13}C NMR (101 MHz, Chloroform-*d*) of 30



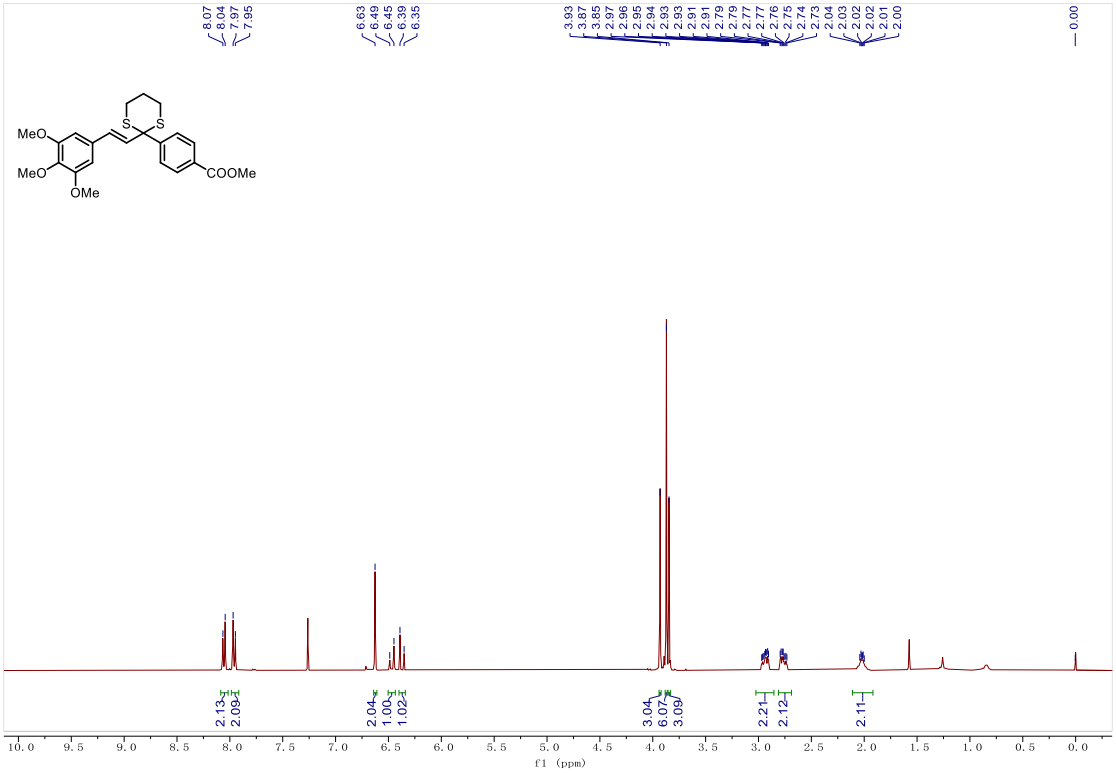
^{1}H NMR (600 MHz, Chloroform-*d*) of 31



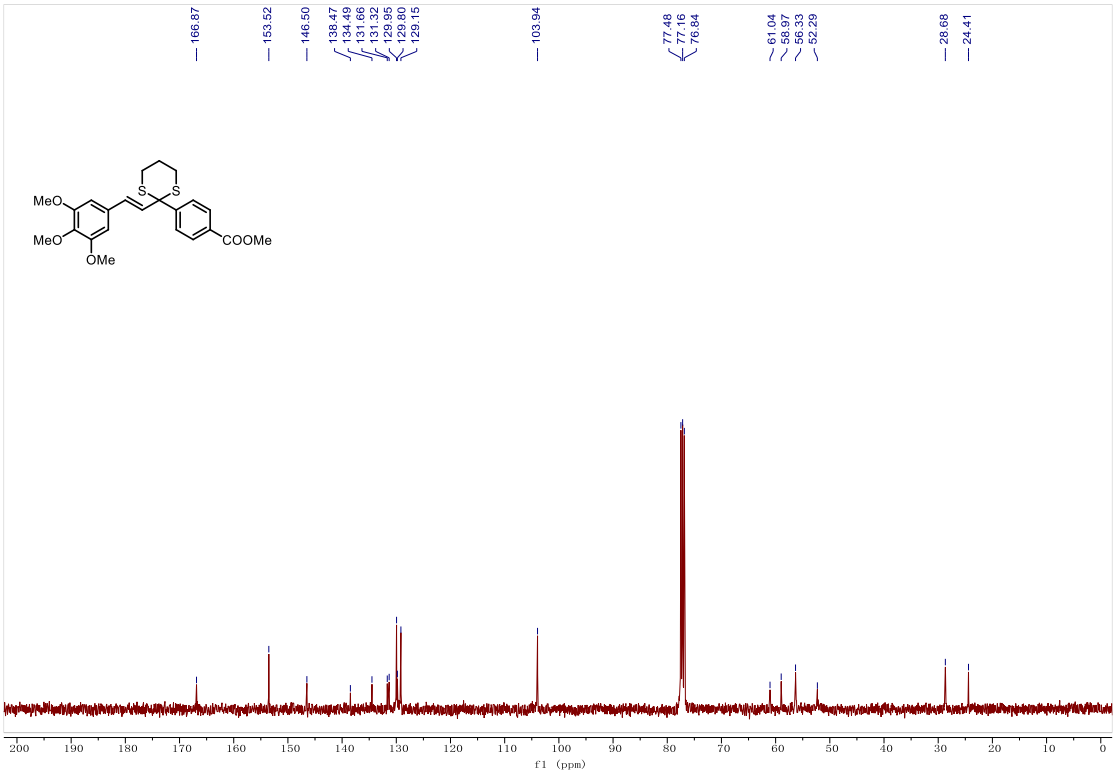
^{13}C NMR (151 MHz, Chloroform-*d*) of 31



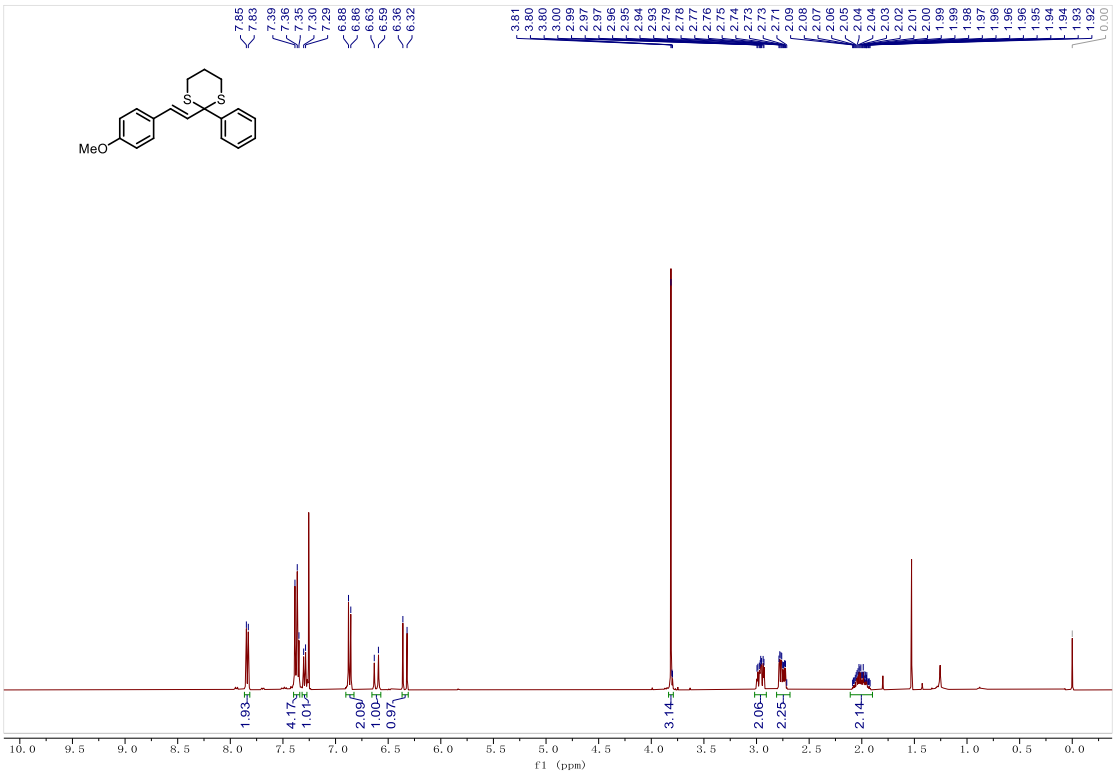
^{1}H NMR (400 MHz, Chloroform-*d*) of 32



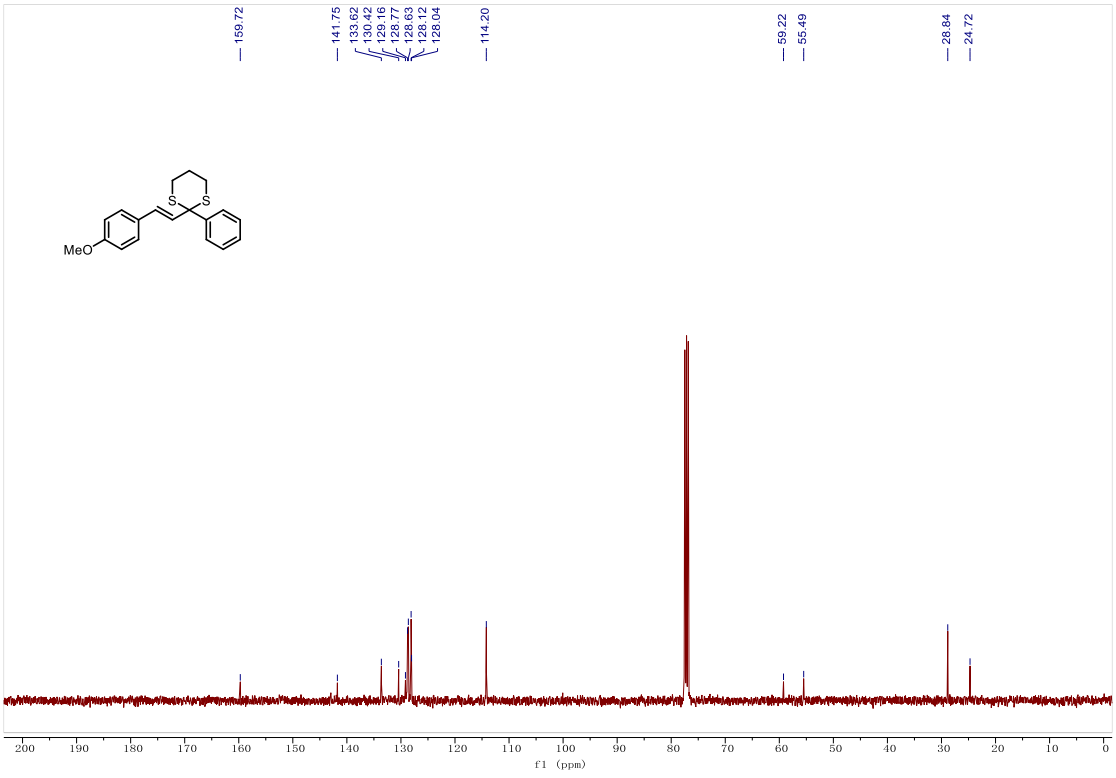
^{13}C NMR (101 MHz, Chloroform-*d*) of 32



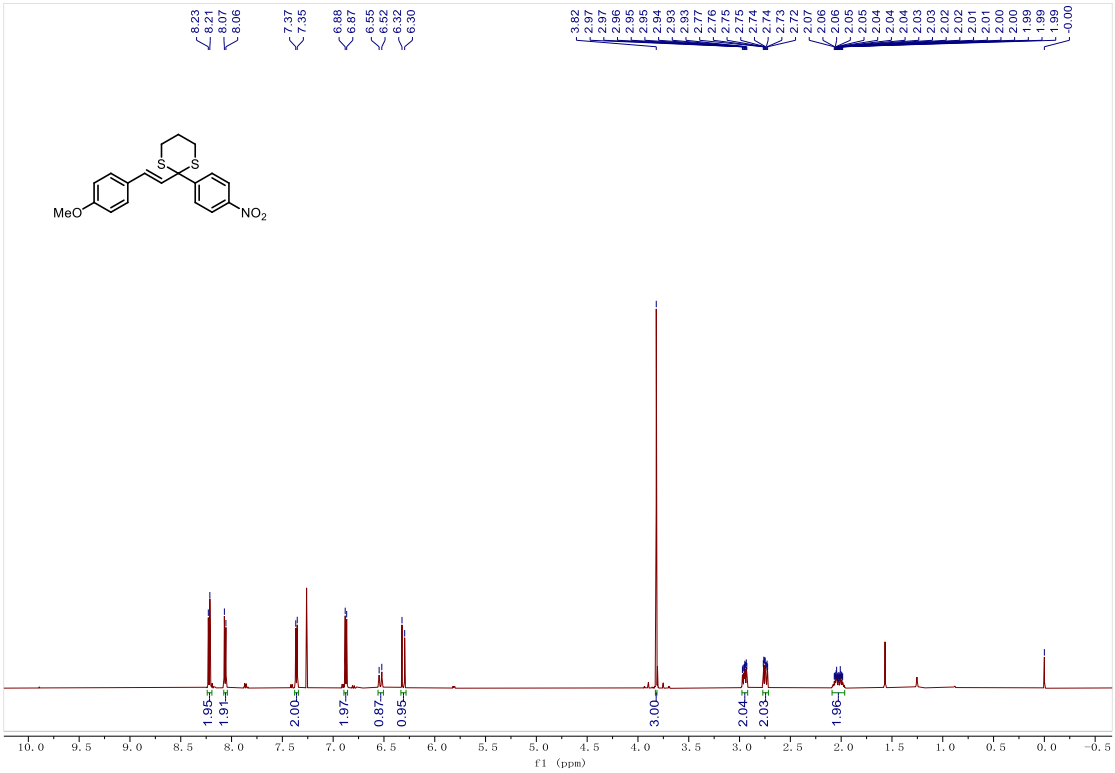
^{1}H NMR (400 MHz, Chloroform-*d*) of 33



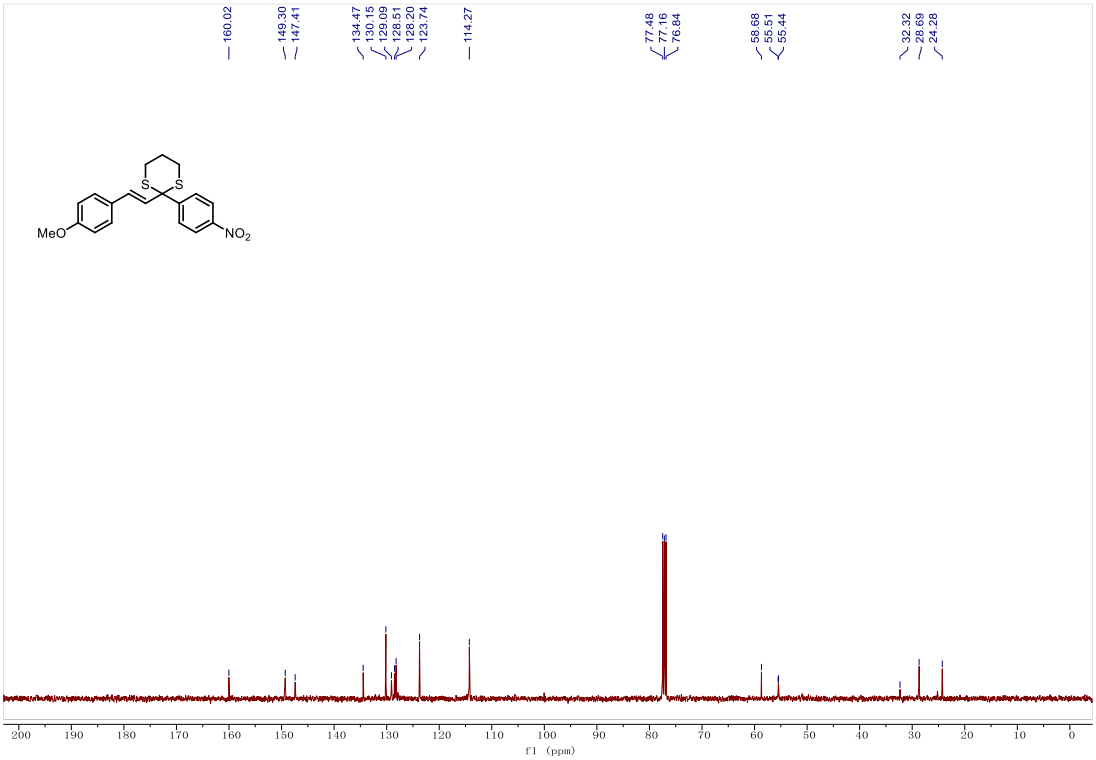
^{13}C NMR (101 MHz, Chloroform-*d*) of 33



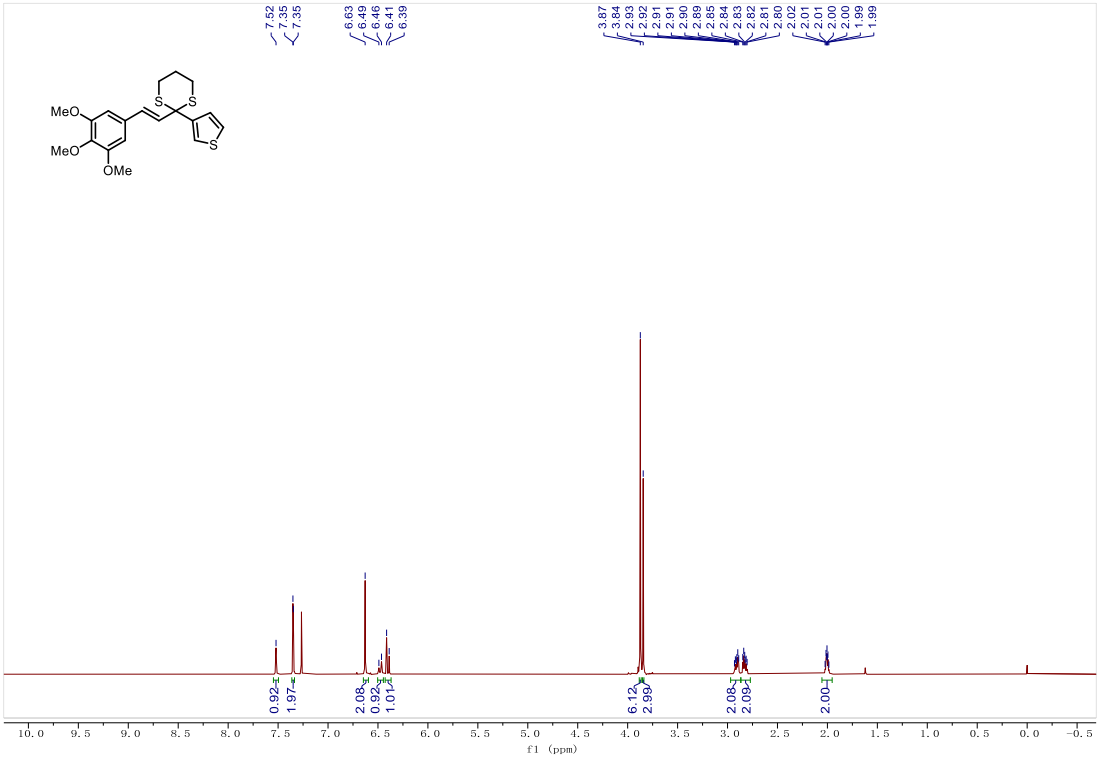
^{1}H NMR (600 MHz, Chloroform-*d*) of 34



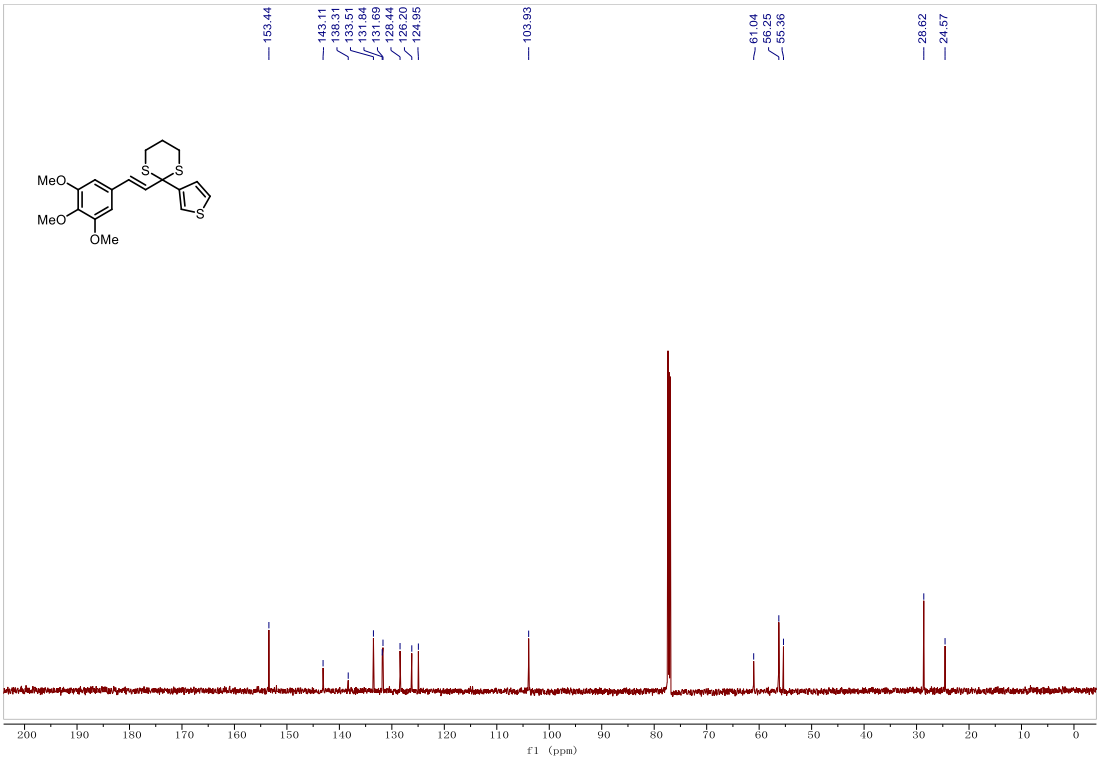
^{13}C NMR (101 MHz, Chloroform-*d*) of 34



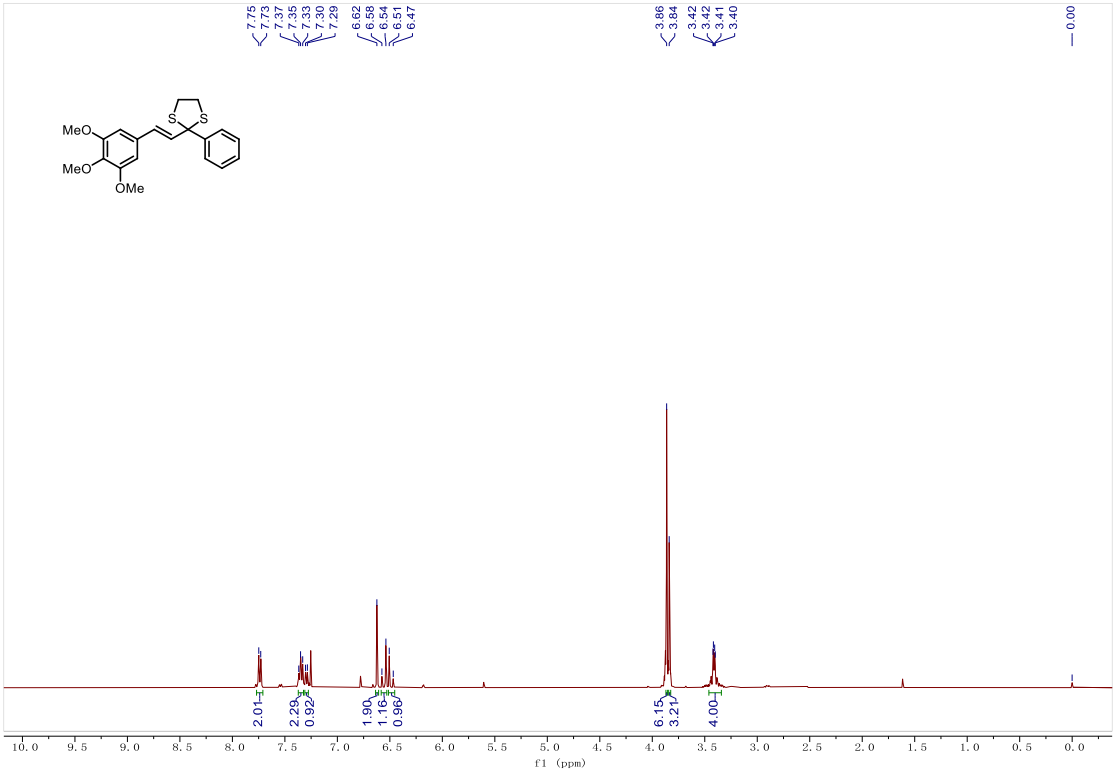
^{1}H NMR (600 MHz, Chloroform-*d*) of 35



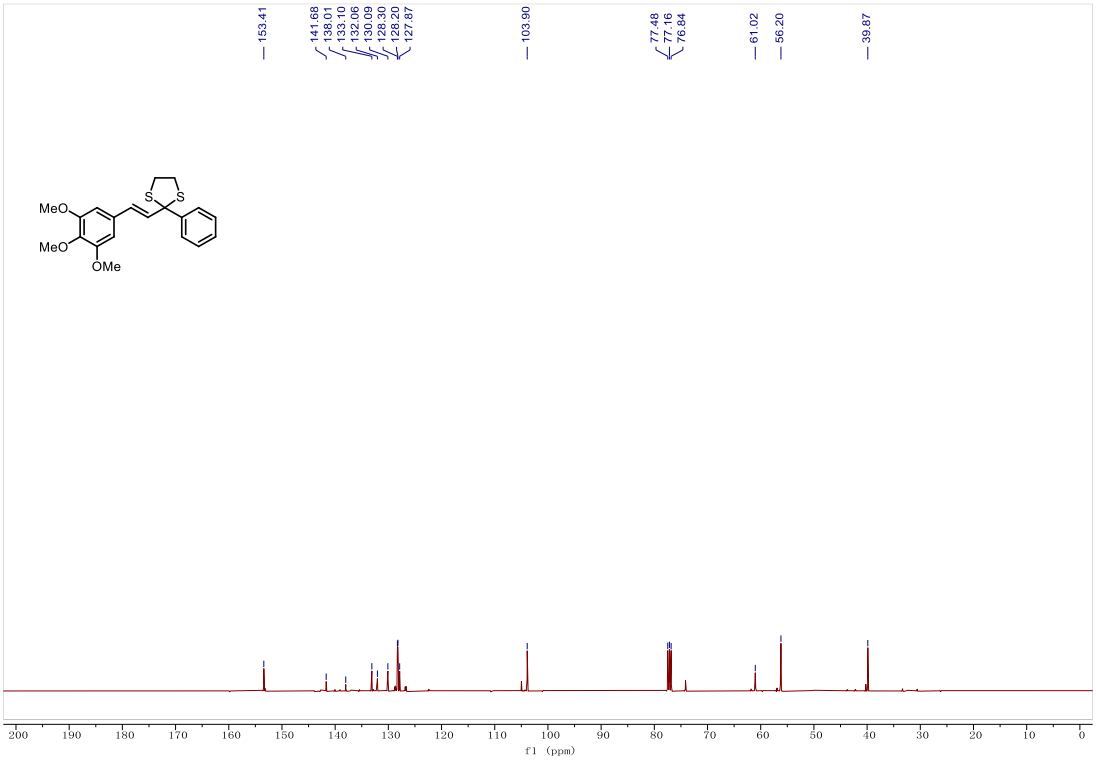
^{13}C NMR (101 MHz, Chloroform-*d*) of 35



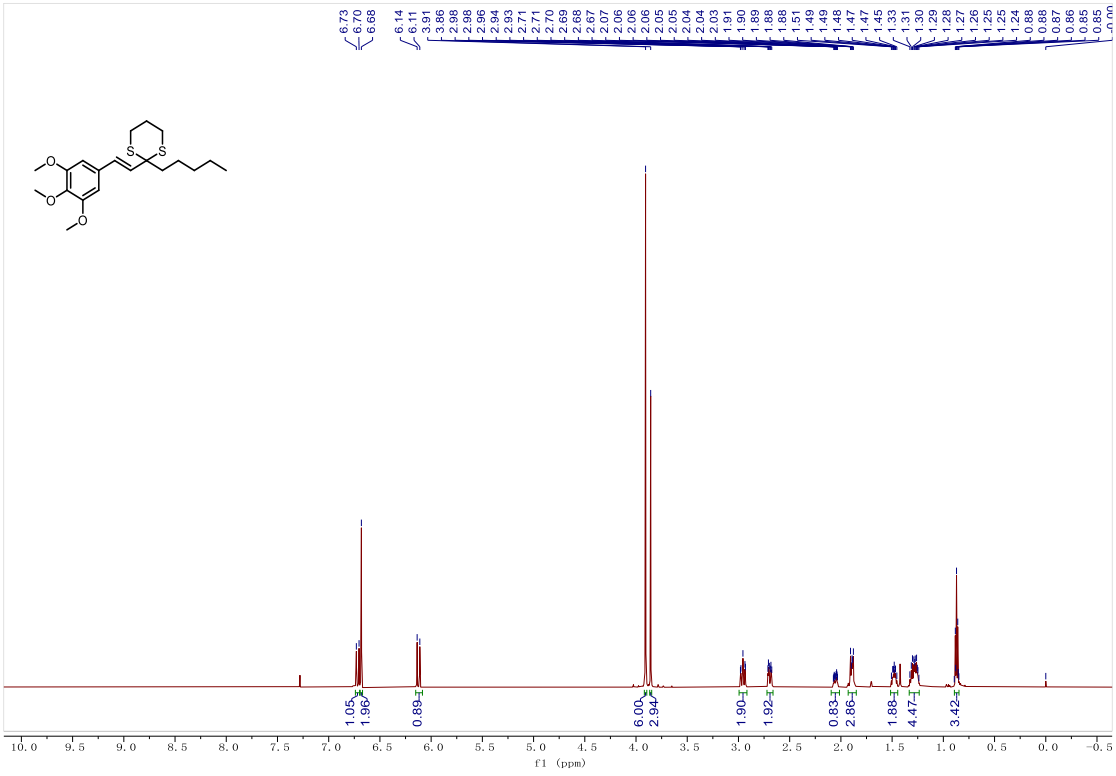
^{1}H NMR (400 MHz, Chloroform-*d*) of 36



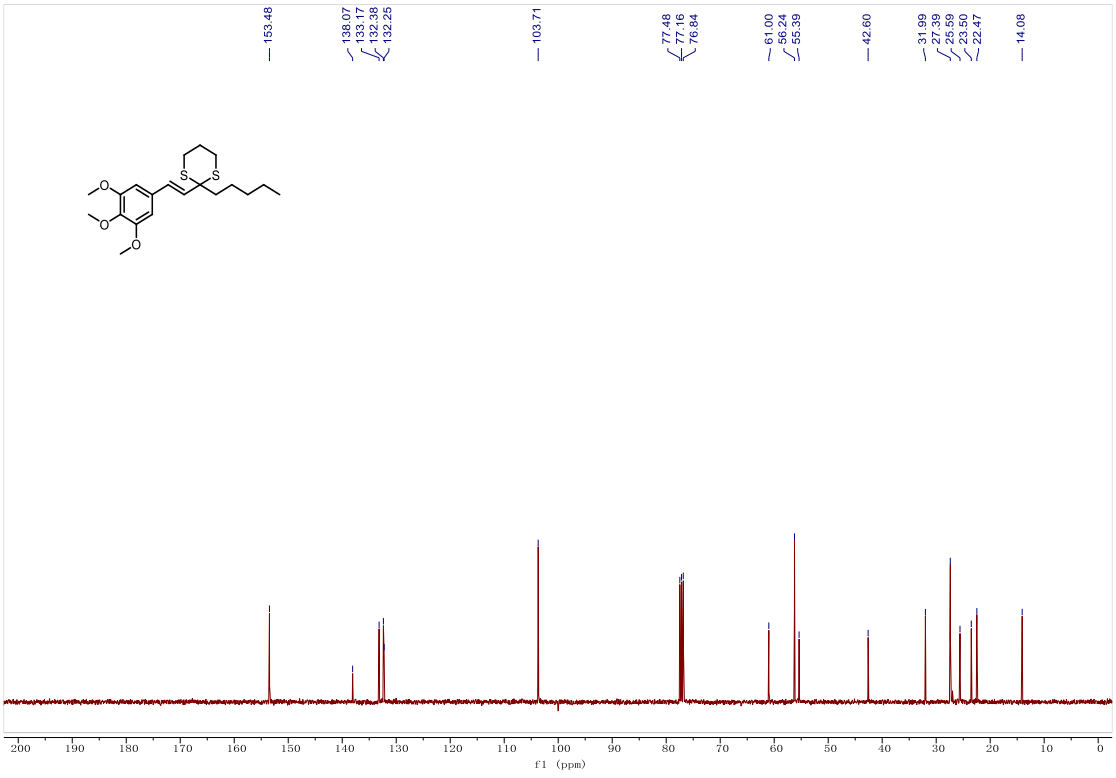
^{13}C NMR (101 MHz, Chloroform-*d*) of 36



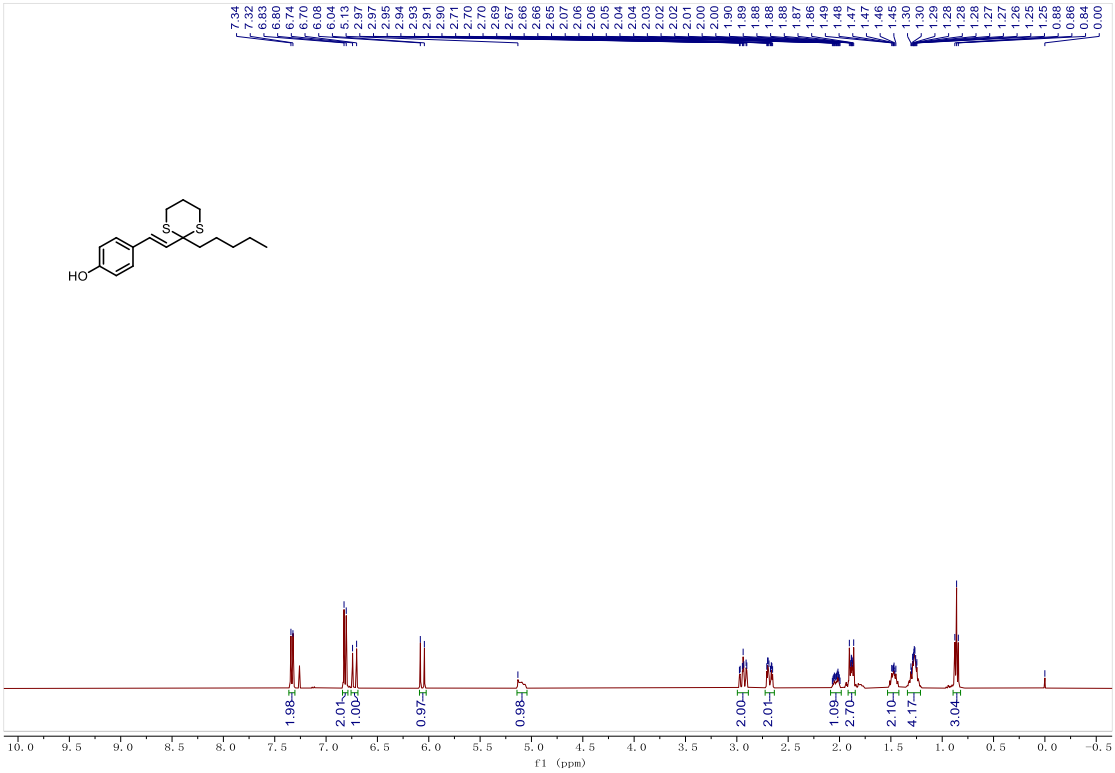
^{1}H NMR (600 MHz, Chloroform-*d*) of 37



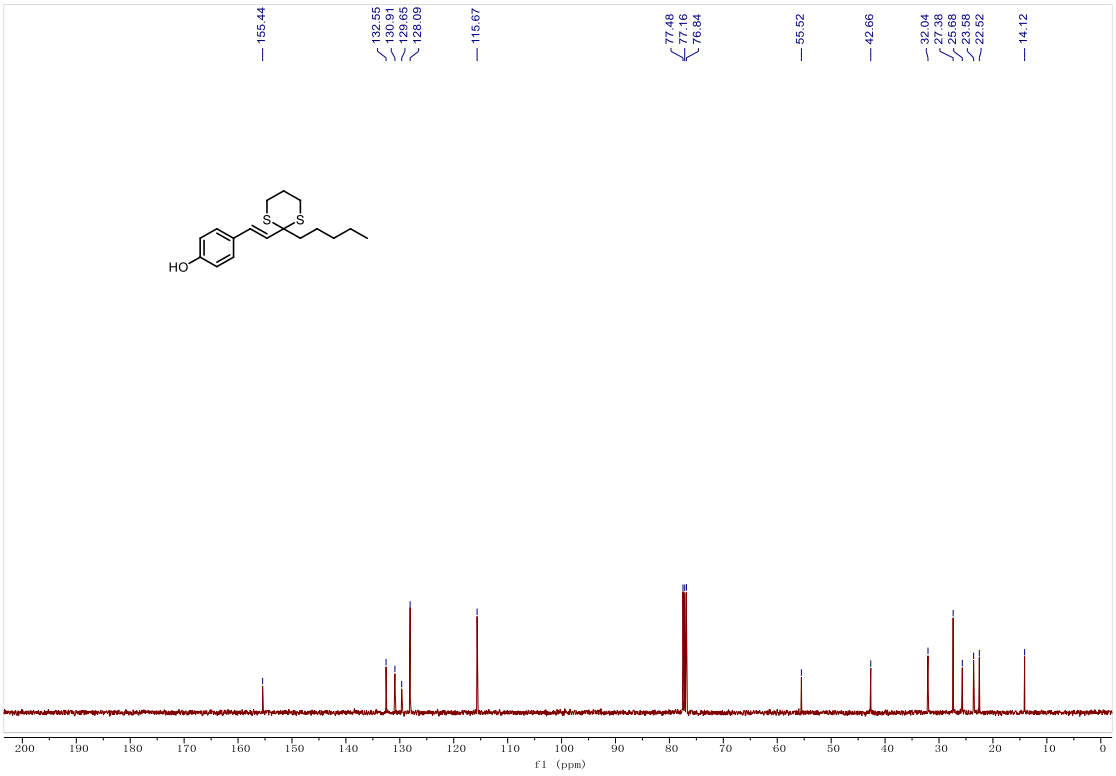
^{13}C NMR (101 MHz, Chloroform-*d*) of 37



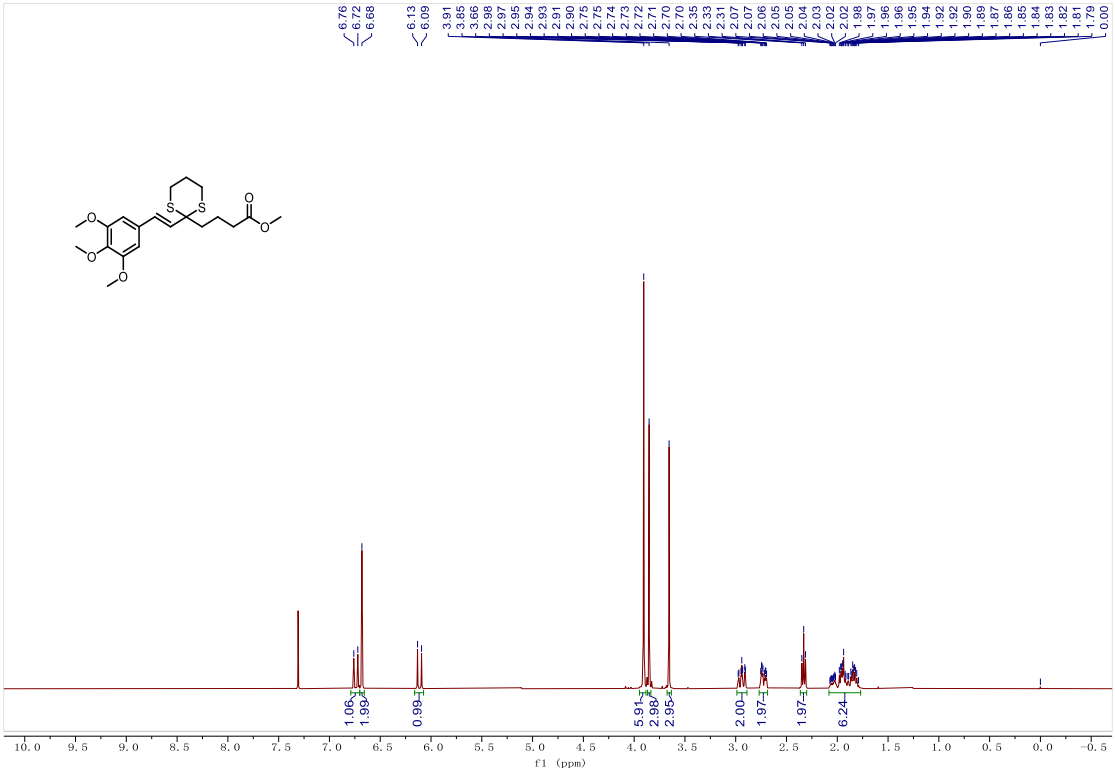
^{1}H NMR (400 MHz, Chloroform-*d*) of 38



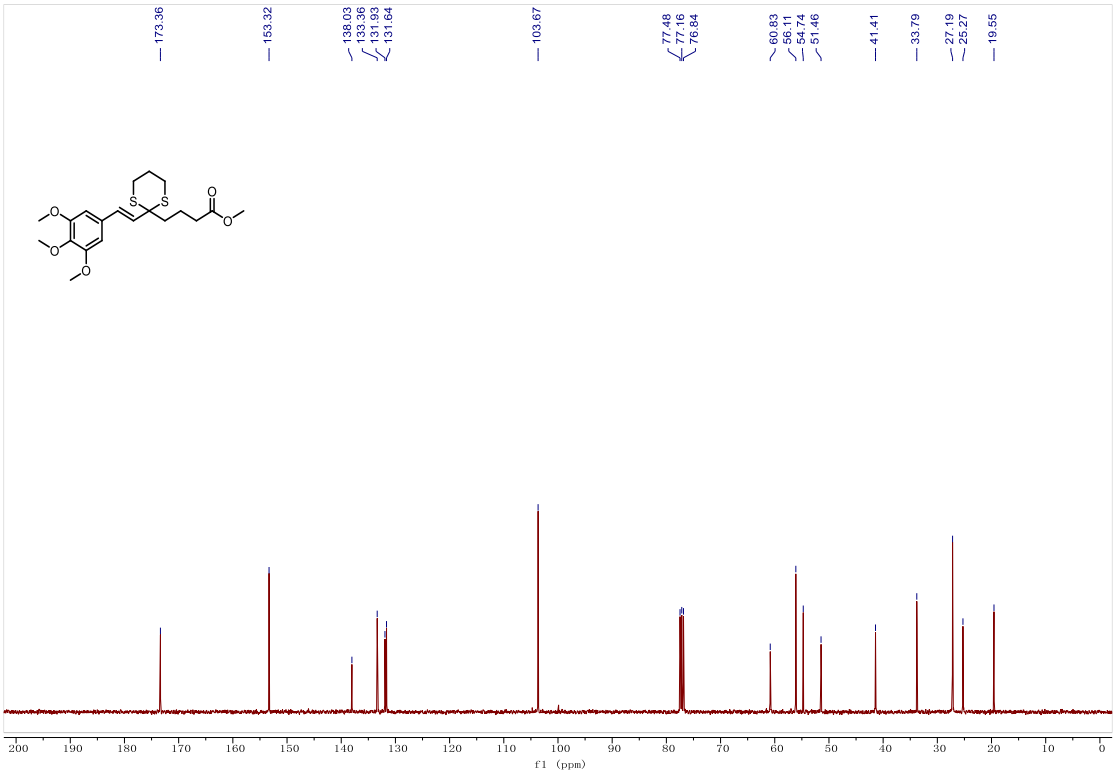
^{13}C NMR (101 MHz, Chloroform-*d*) of 38



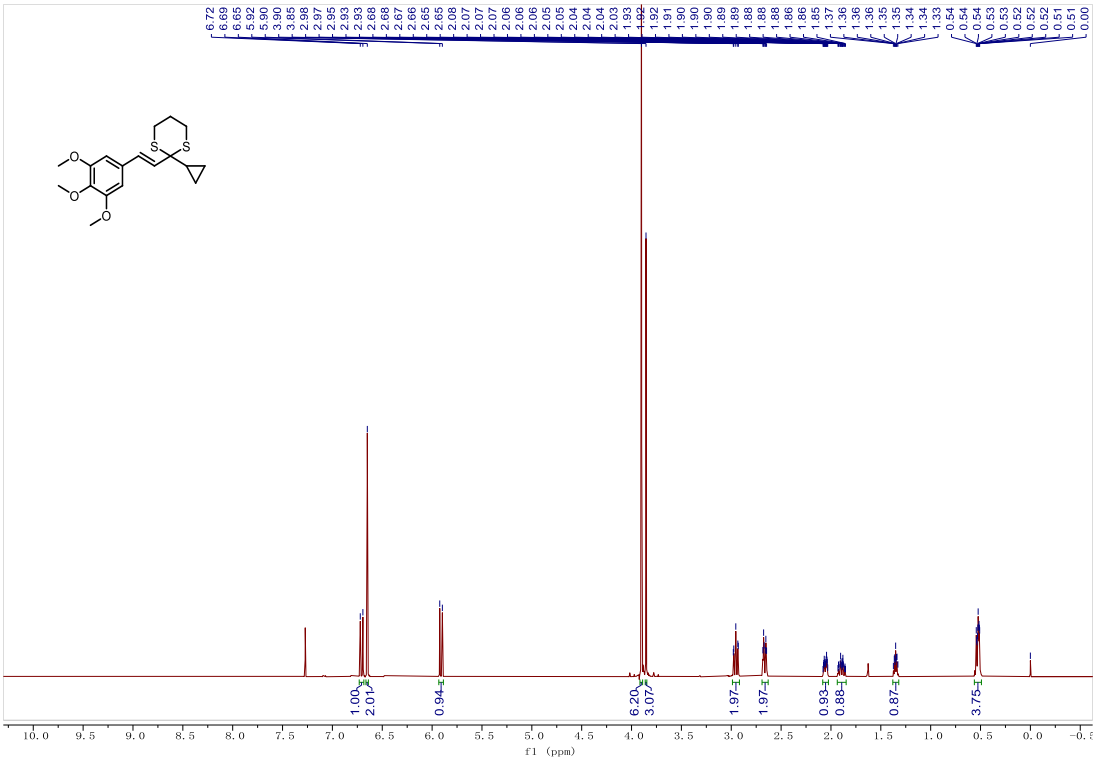
^{1}H NMR (400 MHz, Chloroform-*d*) of 39



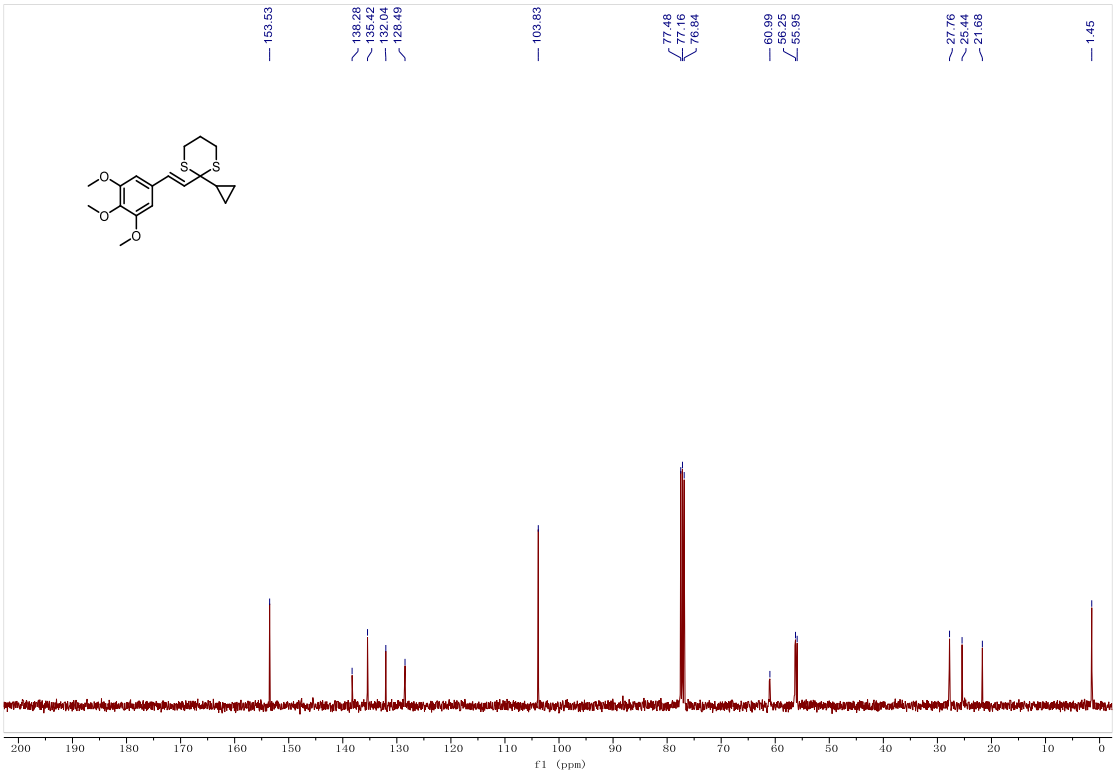
^{13}C NMR (101 MHz, Chloroform-*d*) of 39



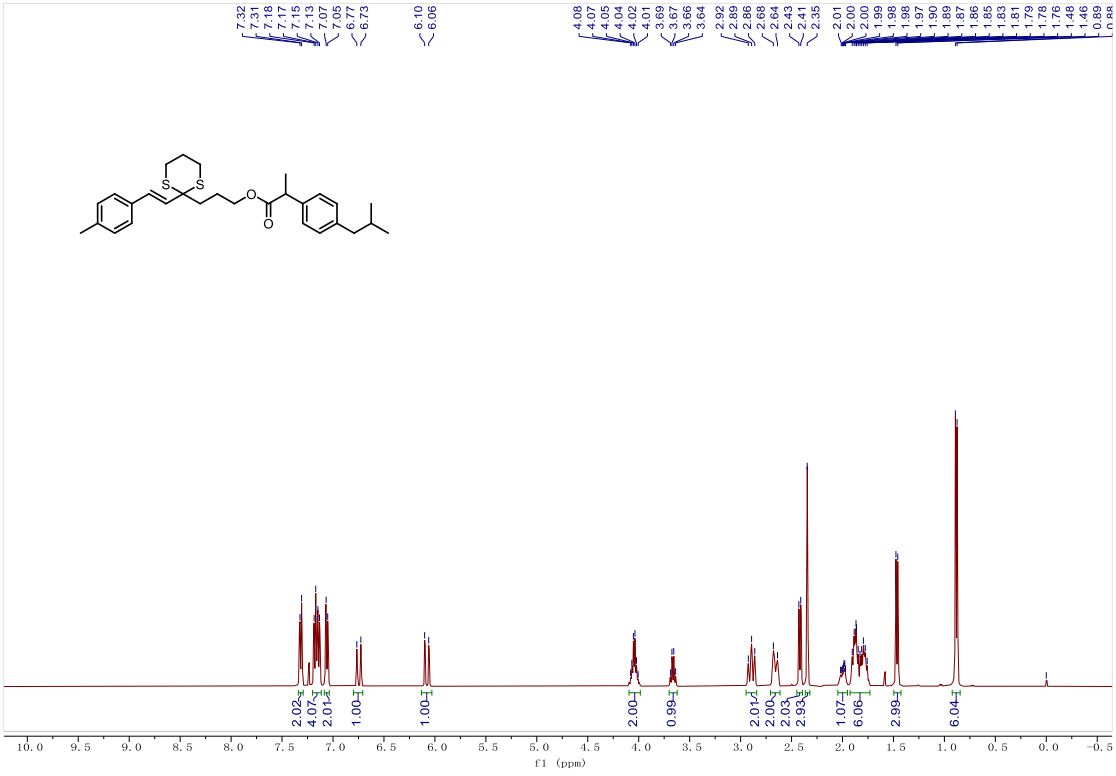
^{1}H NMR (600 MHz, Chloroform-*d*) of 40



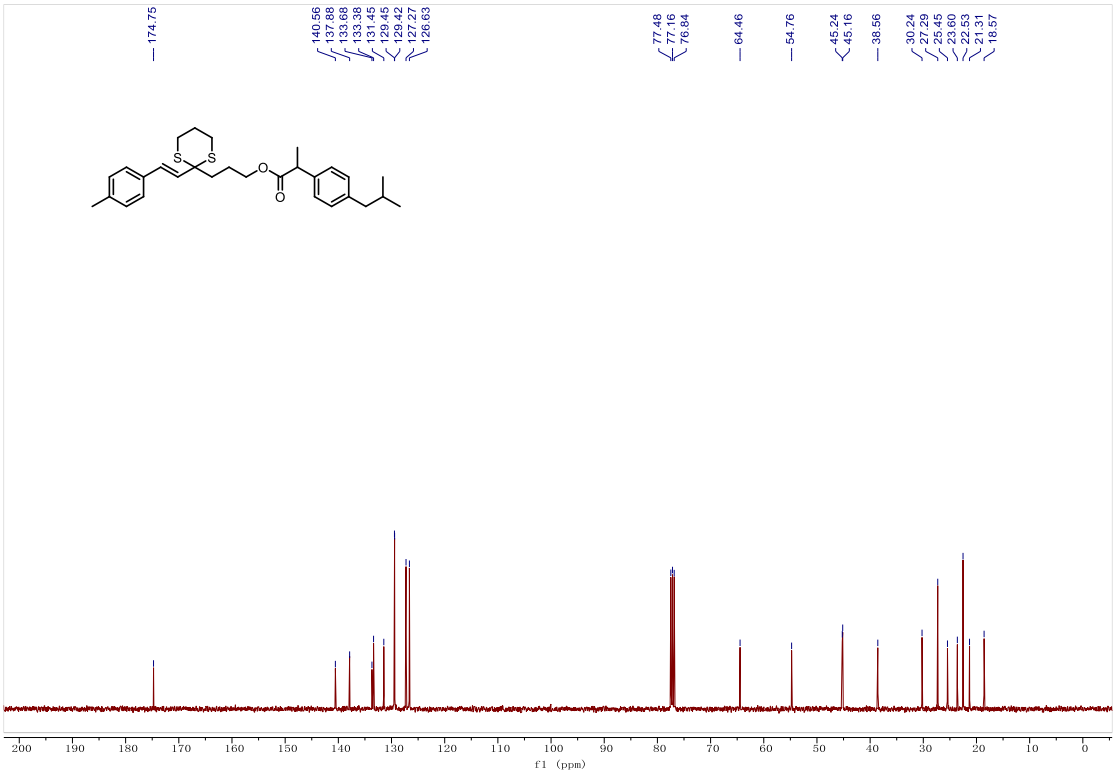
^{13}C NMR (101 MHz, Chloroform-*d*) of 40



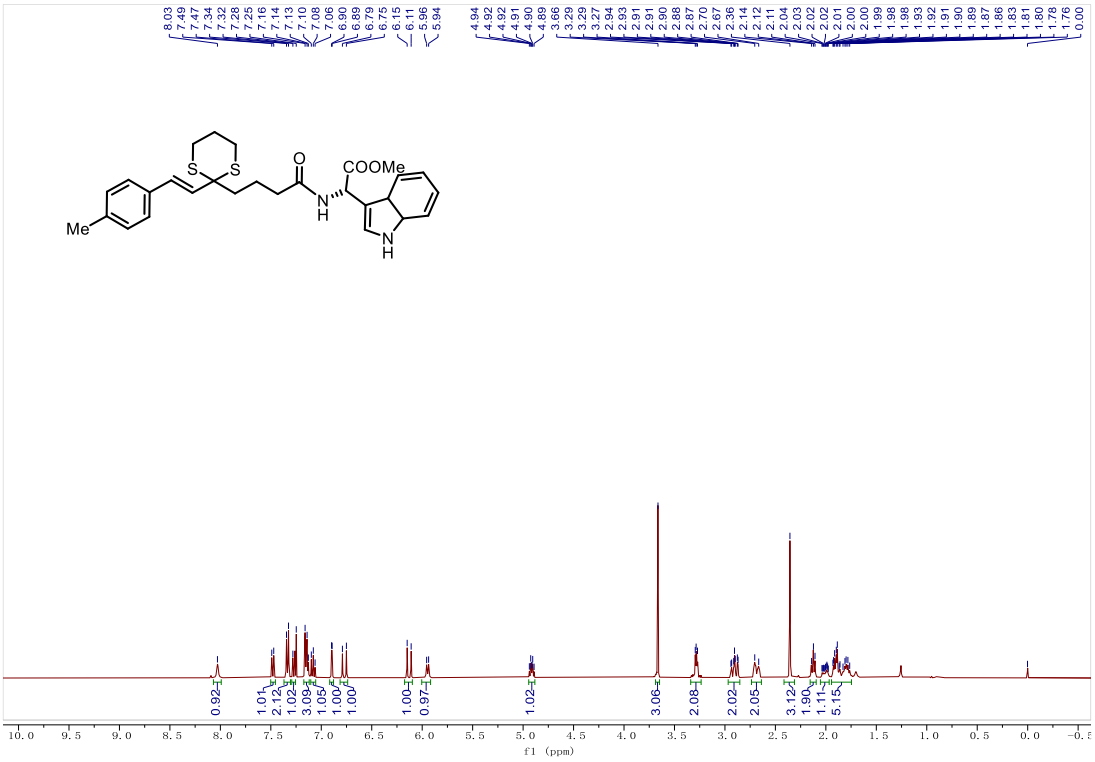
^{1}H NMR (400 MHz, Chloroform-*d*) of 41



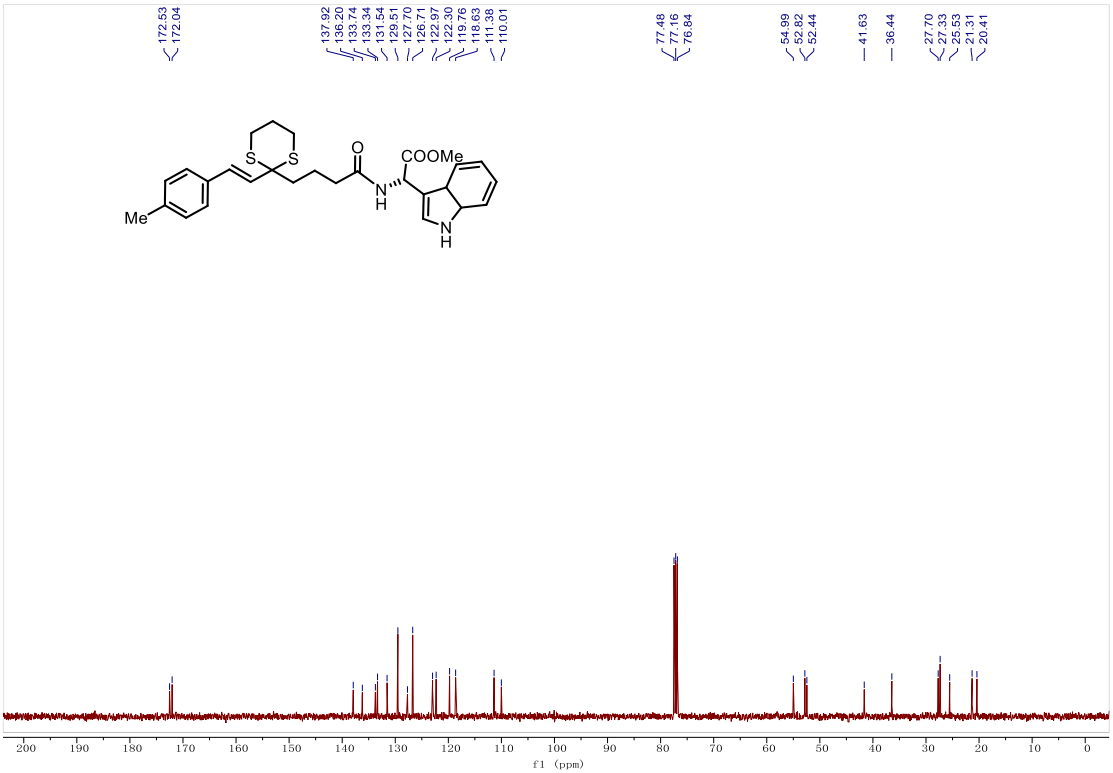
^{13}C NMR (101 MHz, Chloroform-*d*) of 41



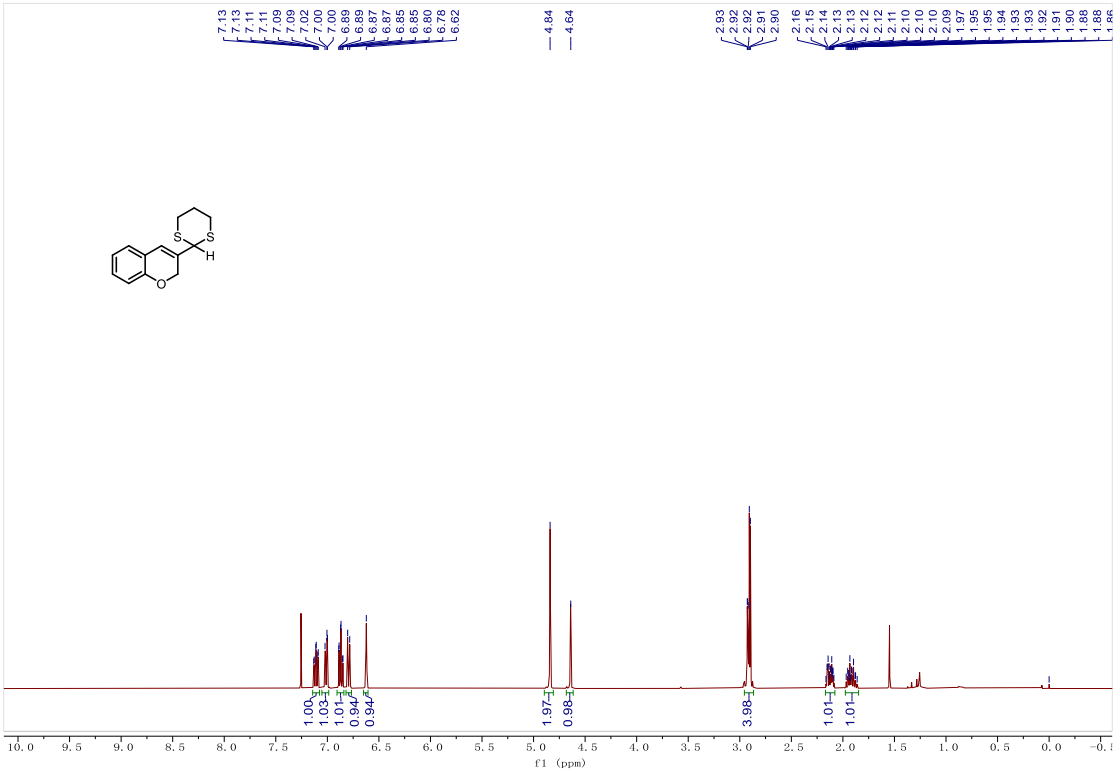
^{1}H NMR (400 MHz, Chloroform-*d*) of 42



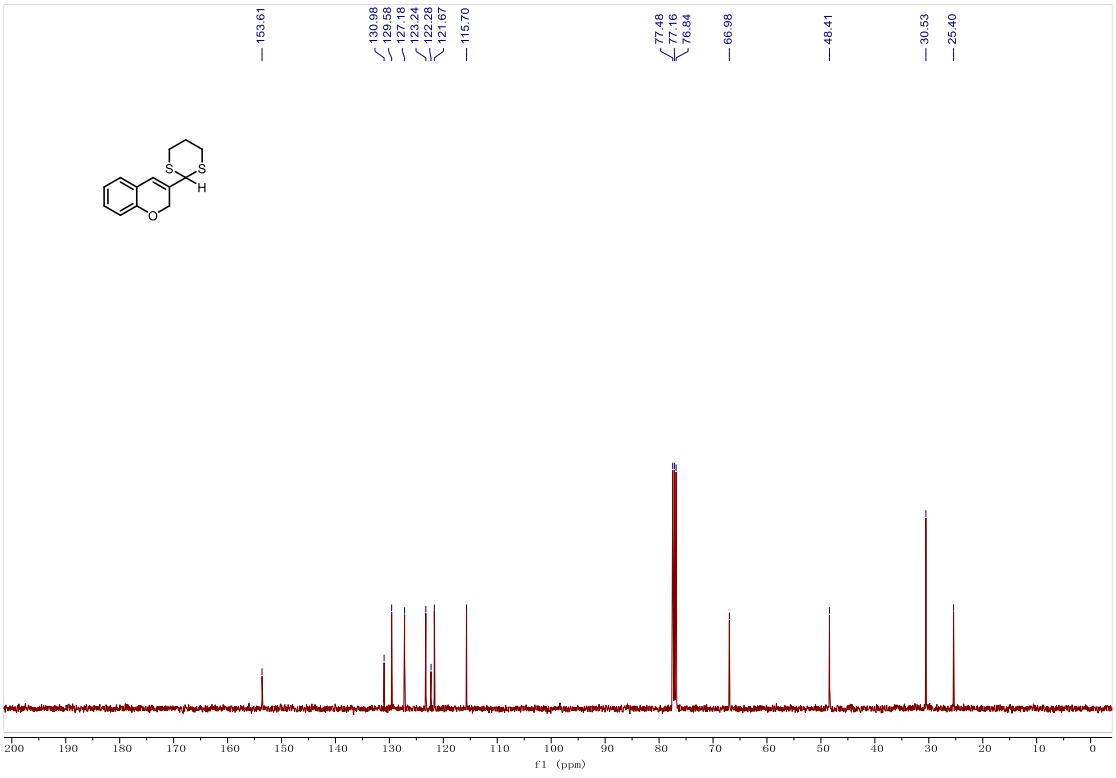
^{13}C NMR (101 MHz, Chloroform-*d*) of 42



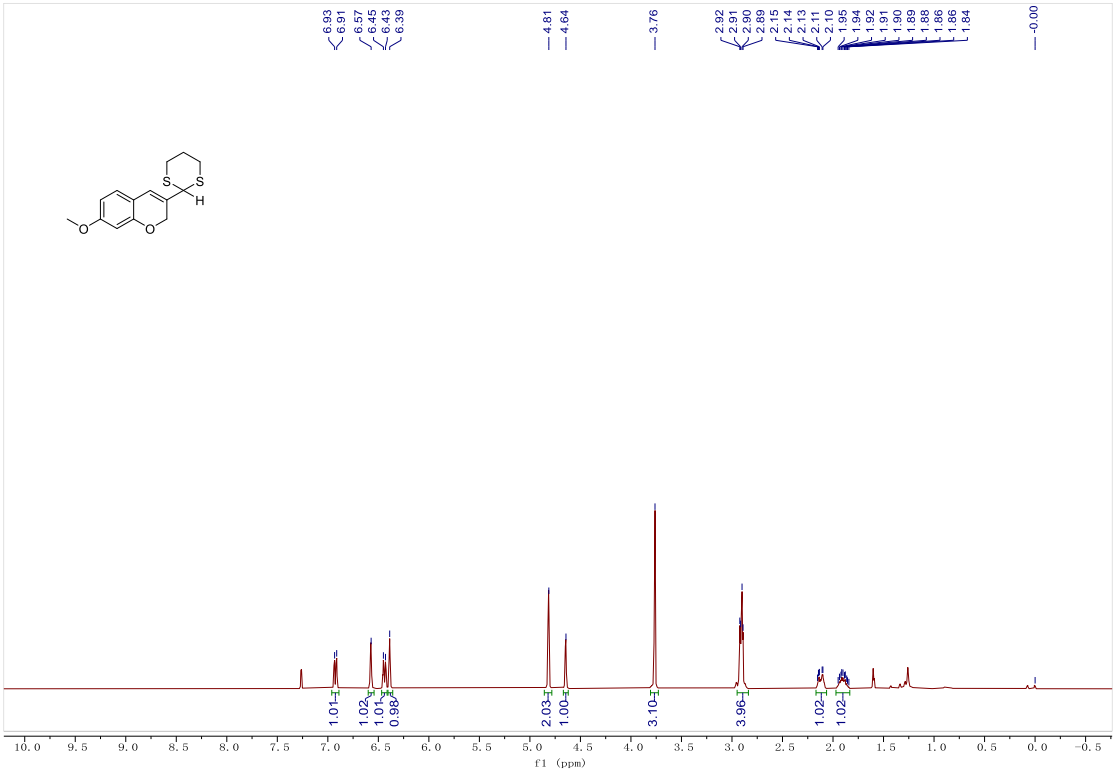
^{1}H NMR (400 MHz, Chloroform-*d*) of 45



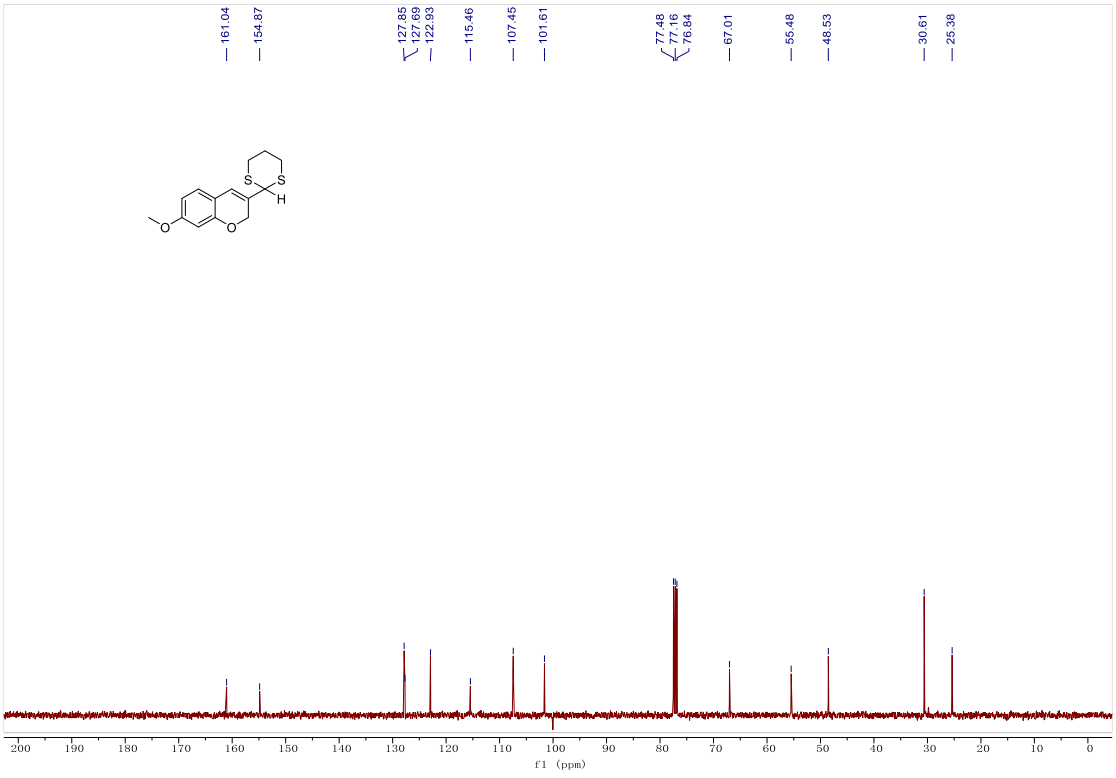
^{13}C NMR (101 MHz, Chloroform-*d*) of 45



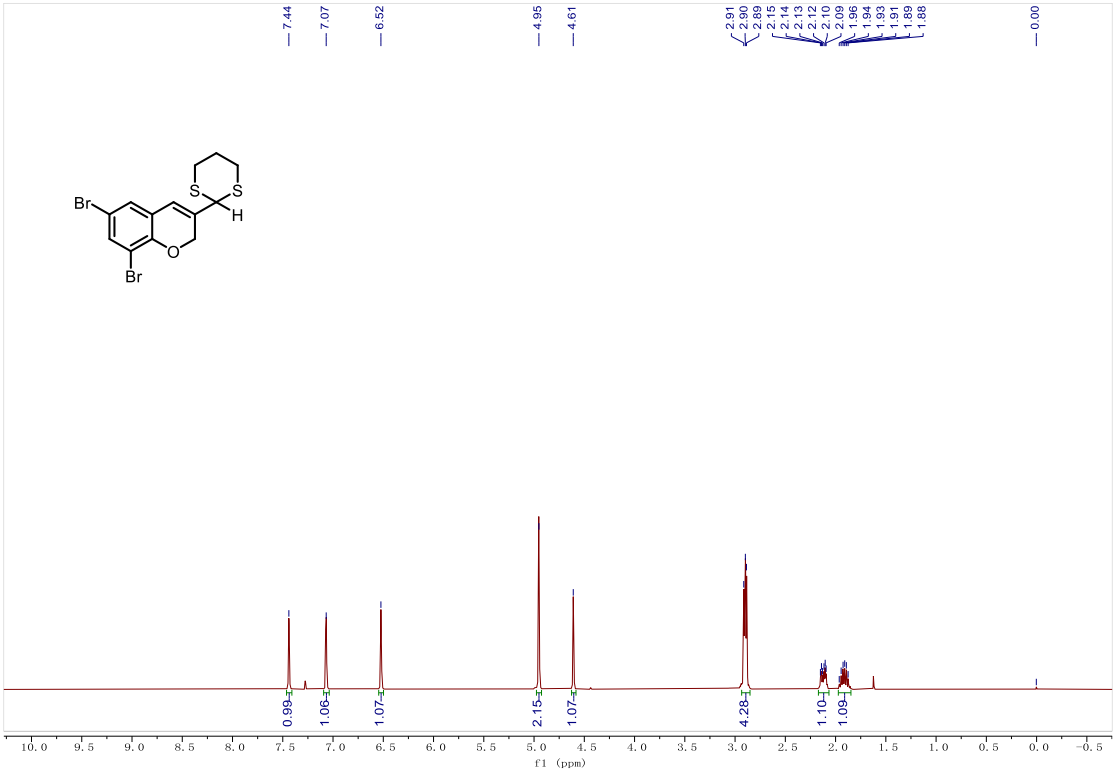
^{1}H NMR (400 MHz, Chloroform-*d*) of 46



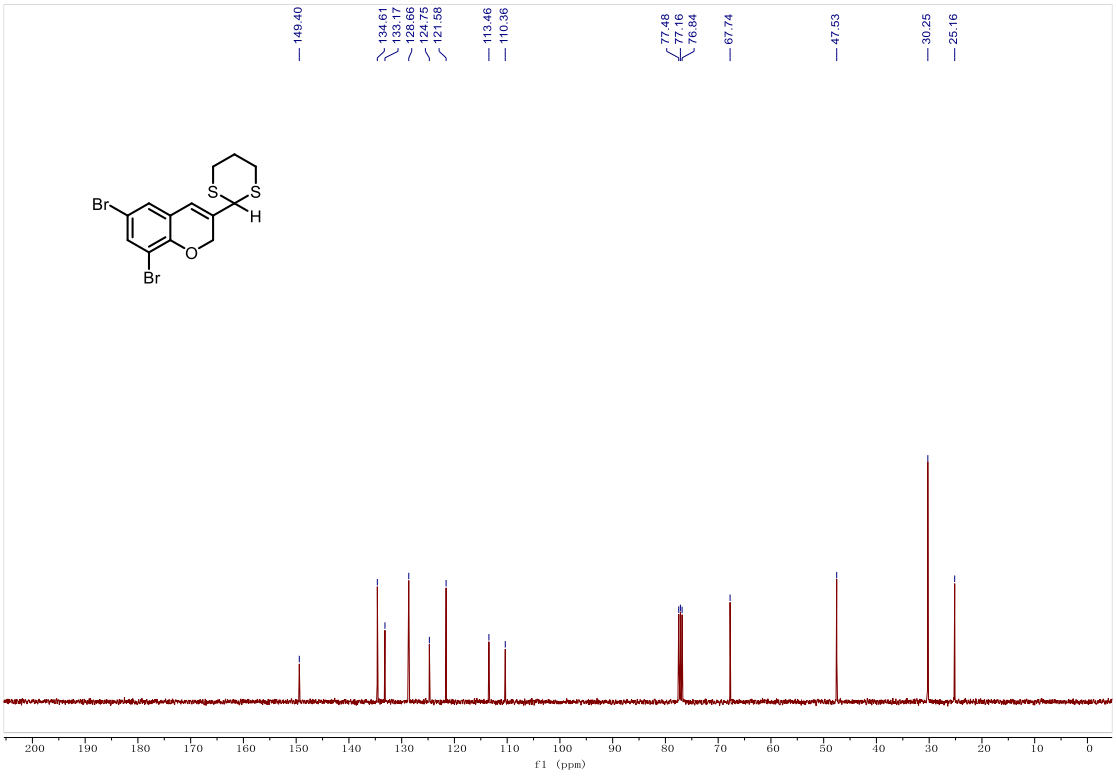
^{13}C NMR (101 MHz, Chloroform-*d*) of 46



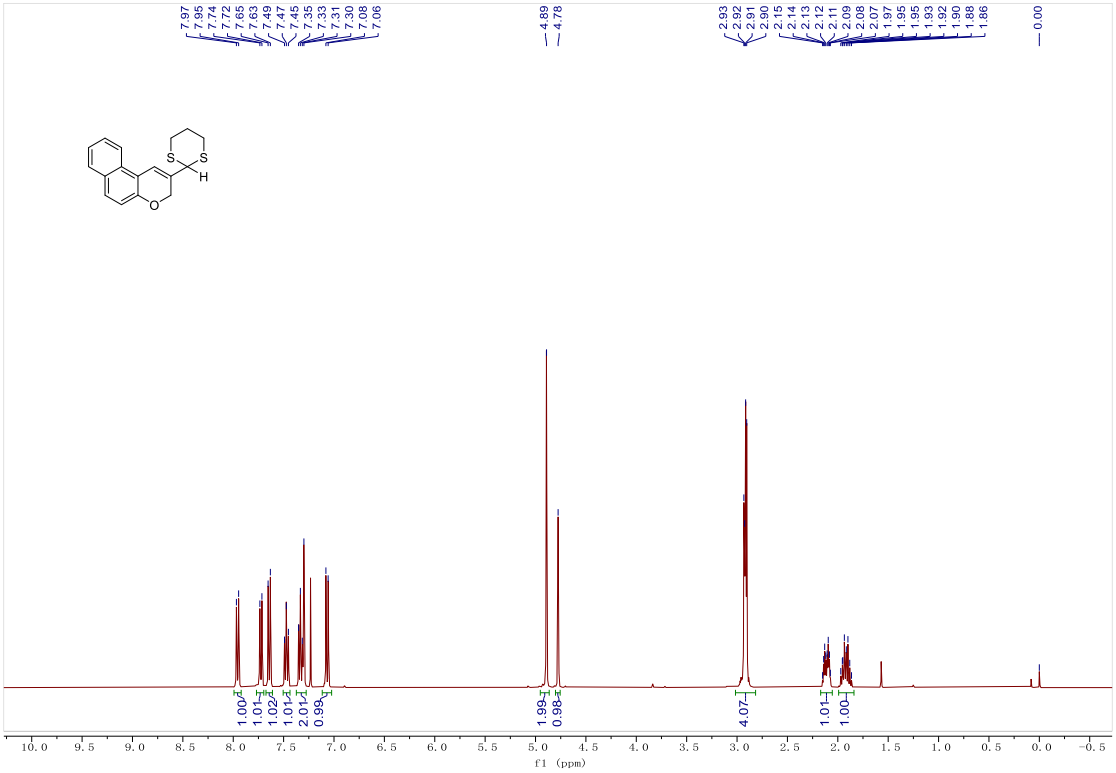
^{1}H NMR (400 MHz, Chloroform-*d*) of 47



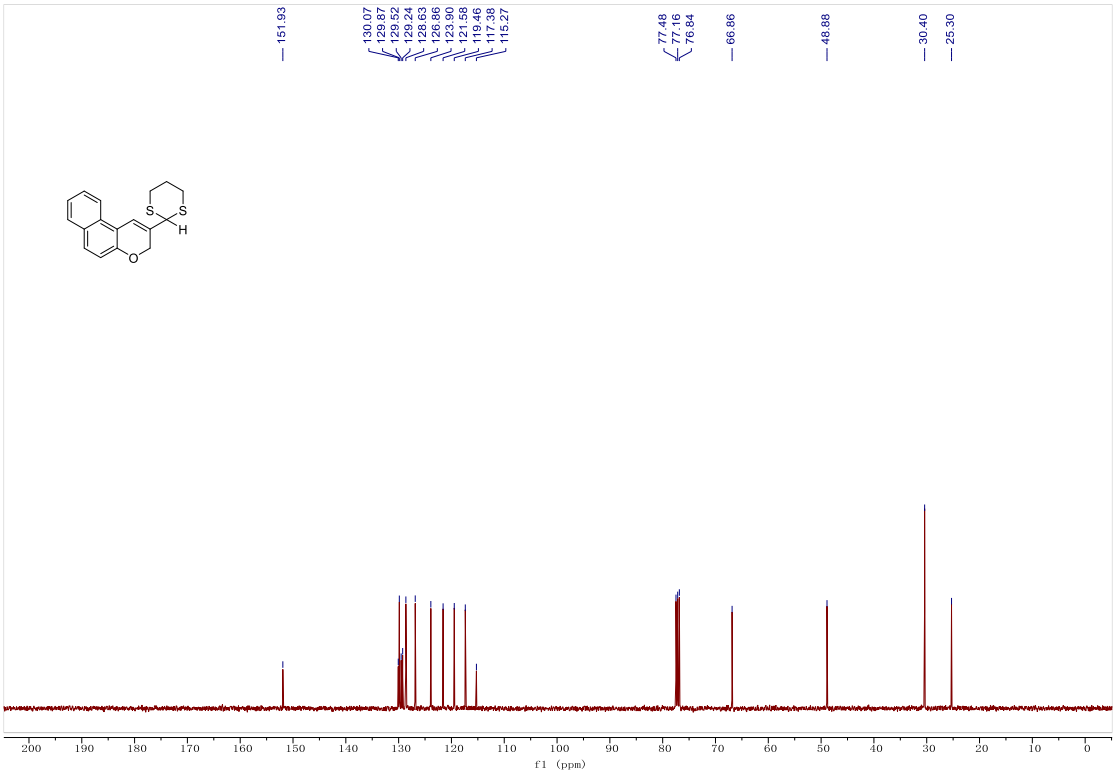
^{13}C NMR (101 MHz, Chloroform-*d*) of 47



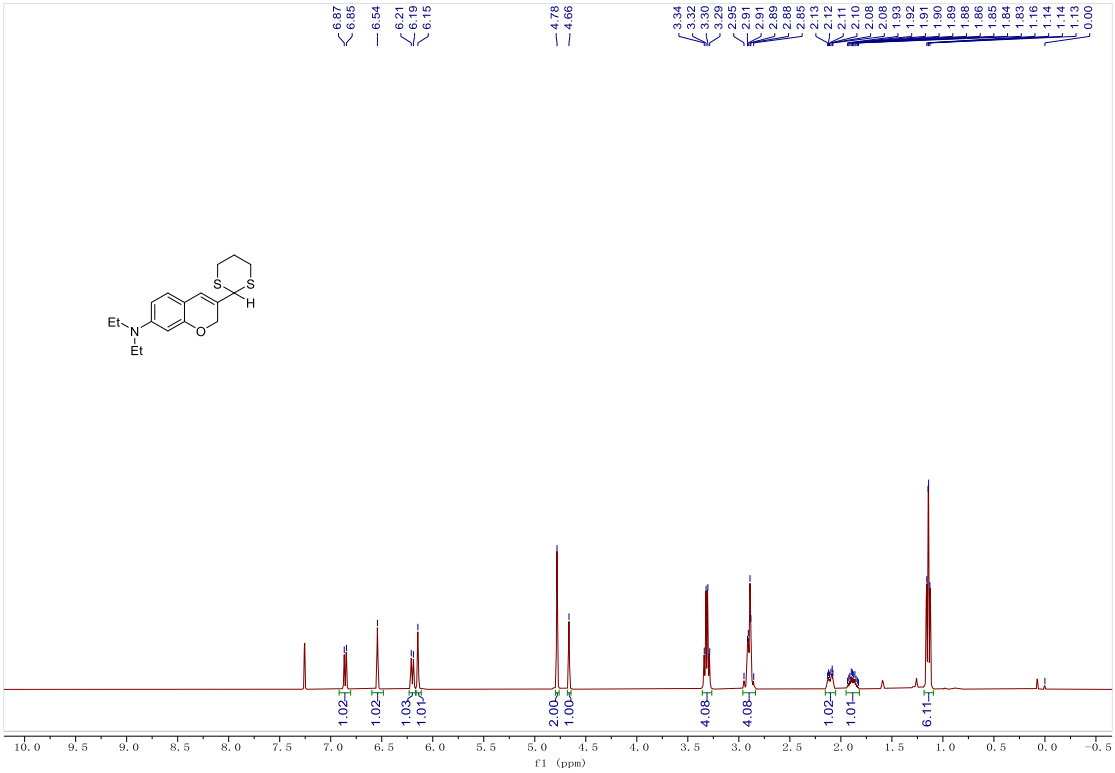
^{1}H NMR (400 MHz, Chloroform-*d*) of 48



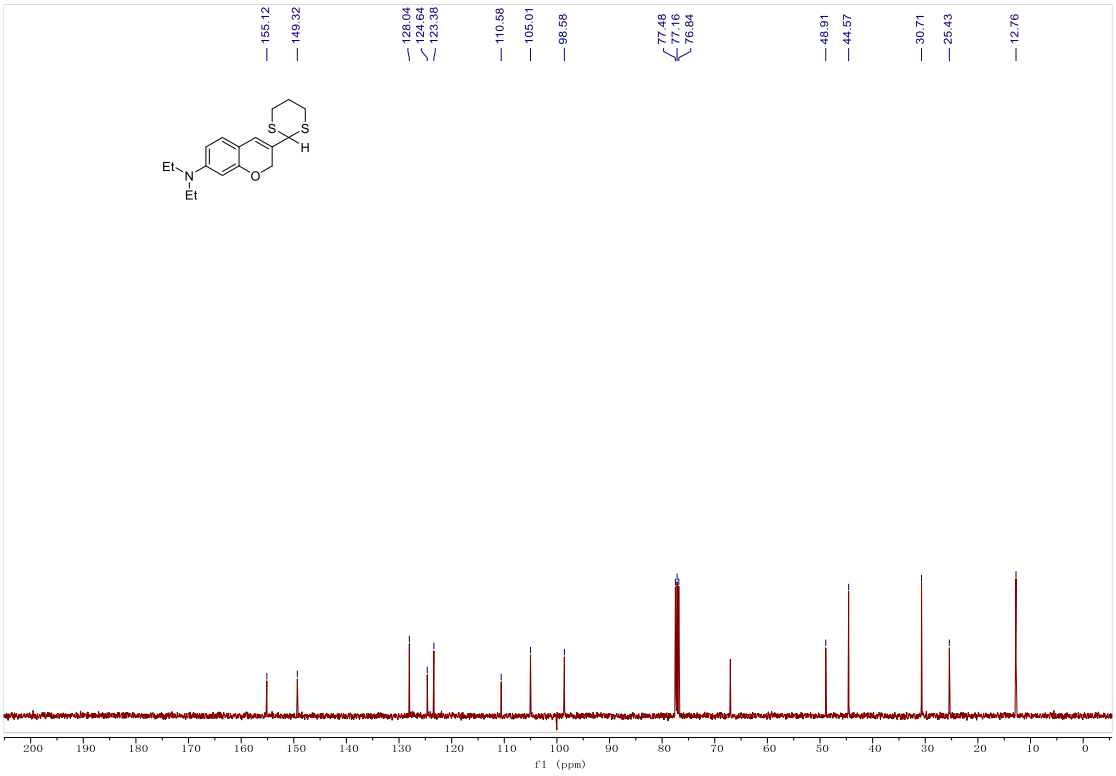
^{13}C NMR (101 MHz, Chloroform-*d*) of 48



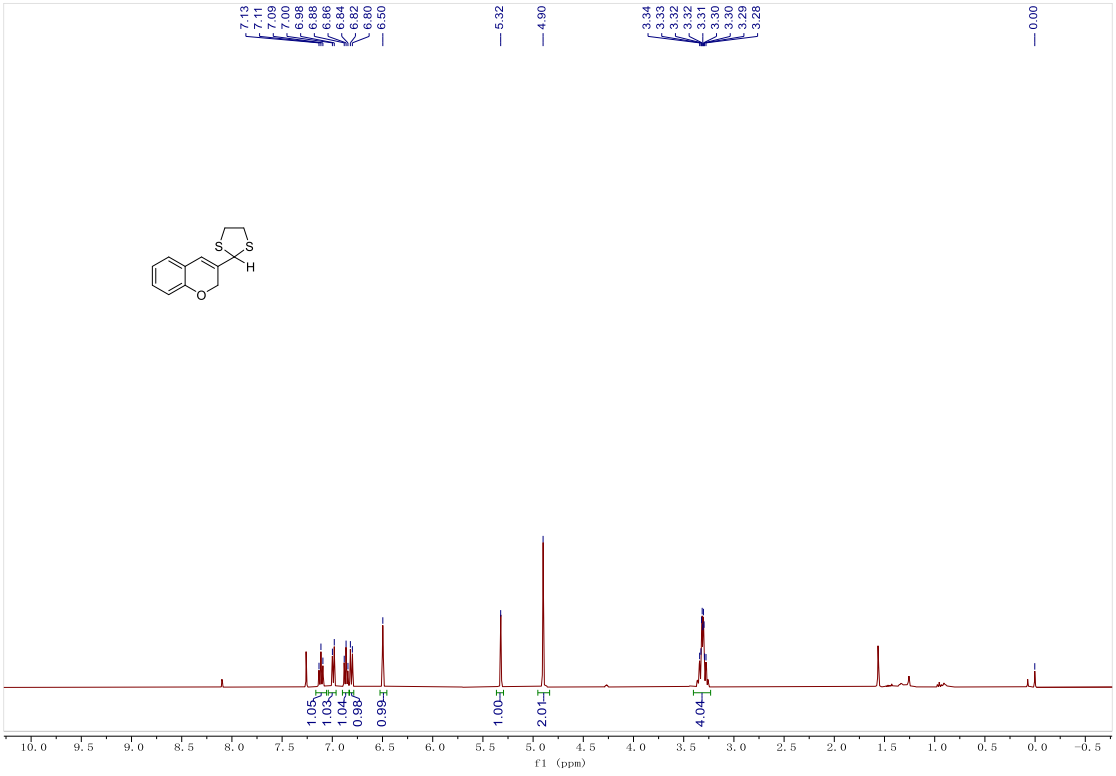
^{1}H NMR (400 MHz, Chloroform-*d*) of 49



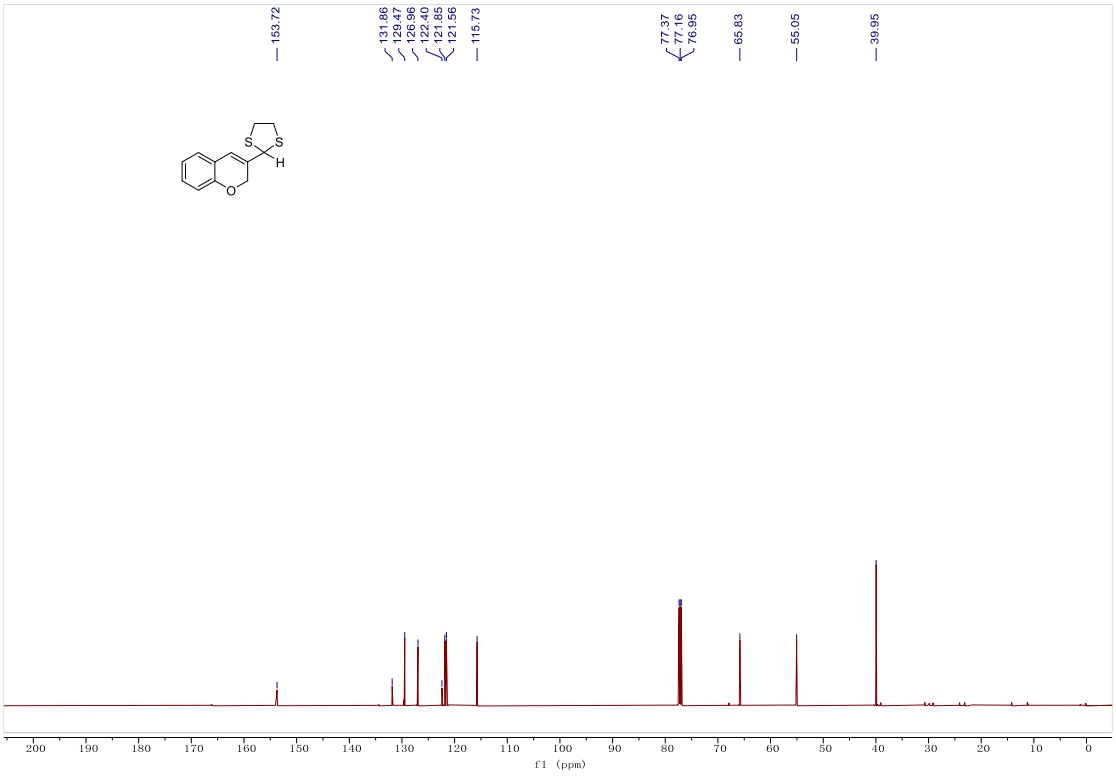
^{13}C NMR (101 MHz, Chloroform-*d*) of 49



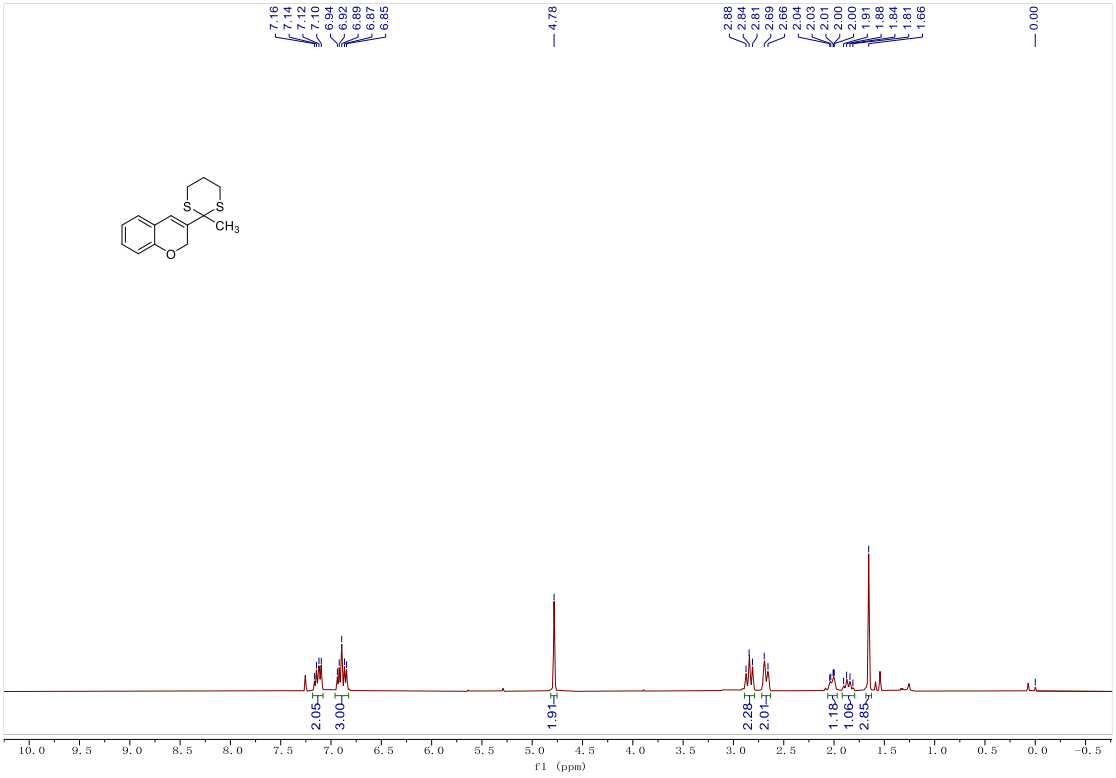
^{1}H NMR (400 MHz, Chloroform-*d*) of 50



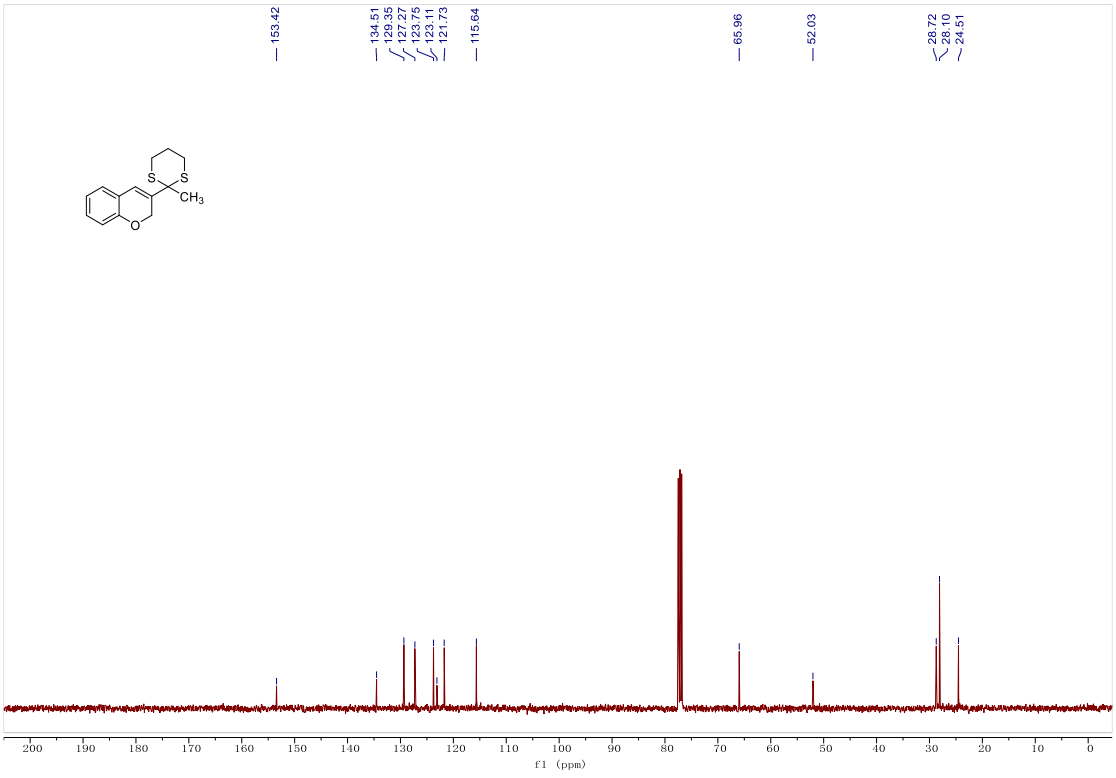
^{13}C NMR (151 MHz, Chloroform-*d*) of 50



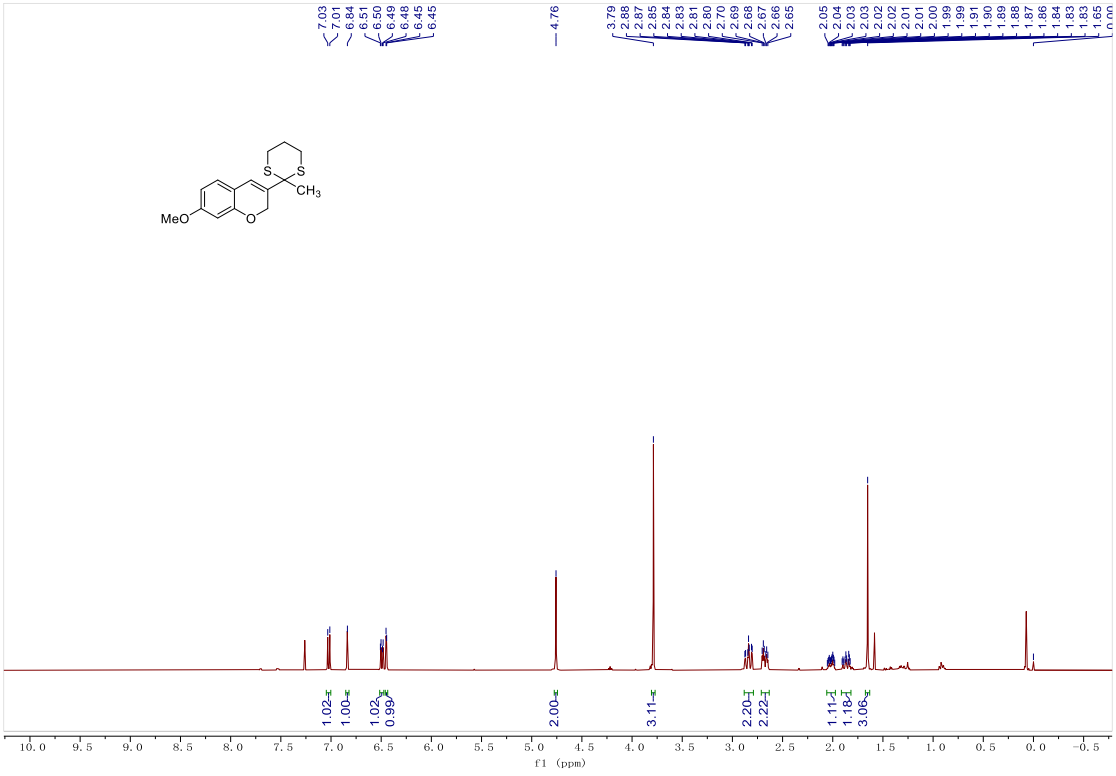
^{1}H NMR (400 MHz, Chloroform-*d*) of 51



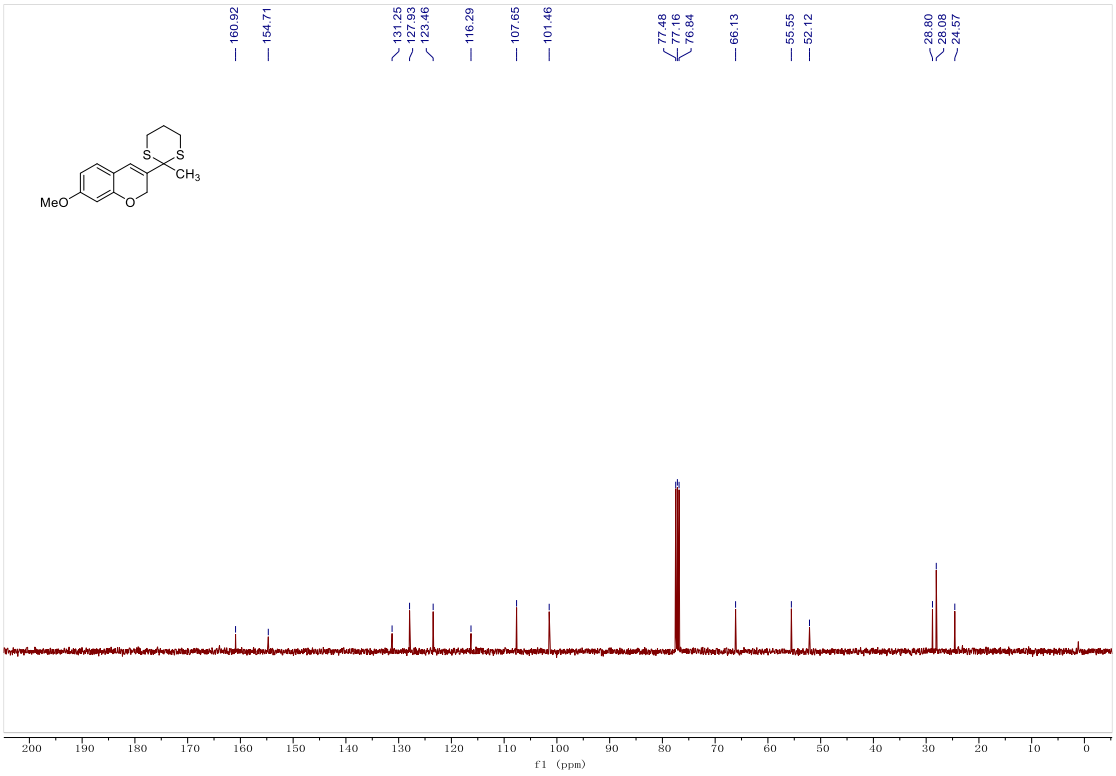
^{13}C NMR (101 MHz, Chloroform-*d*) of 51



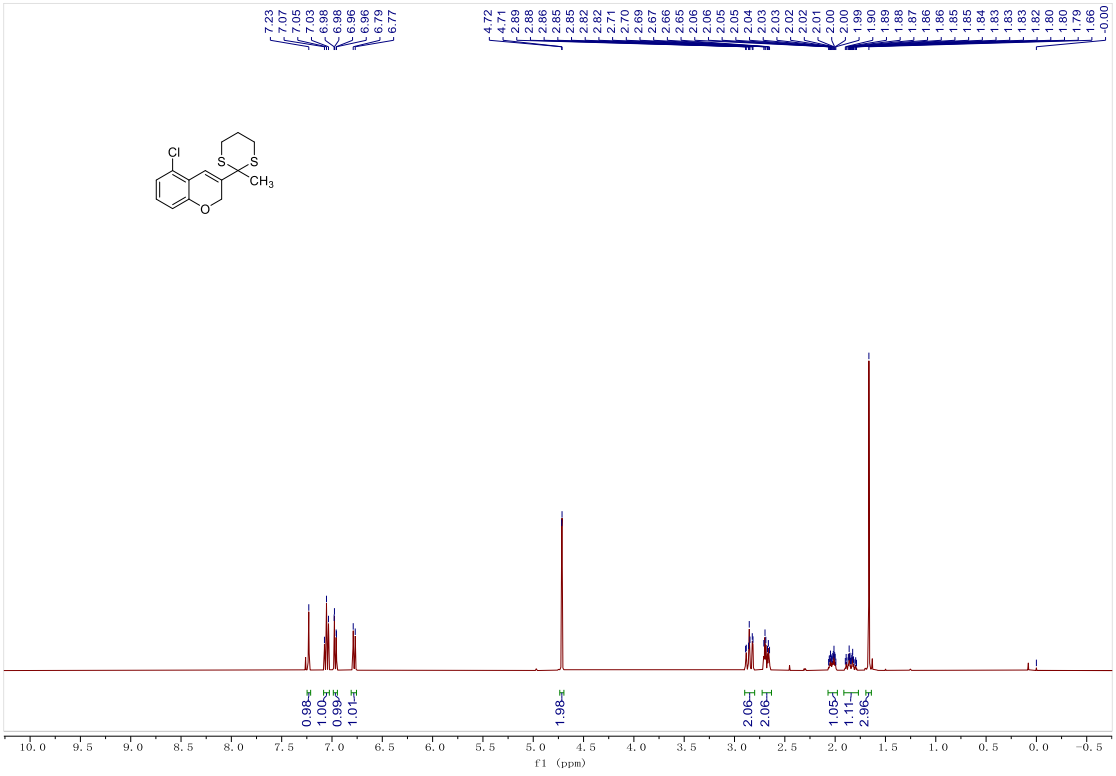
^{1}H NMR (400 MHz, Chloroform-*d*) of 52



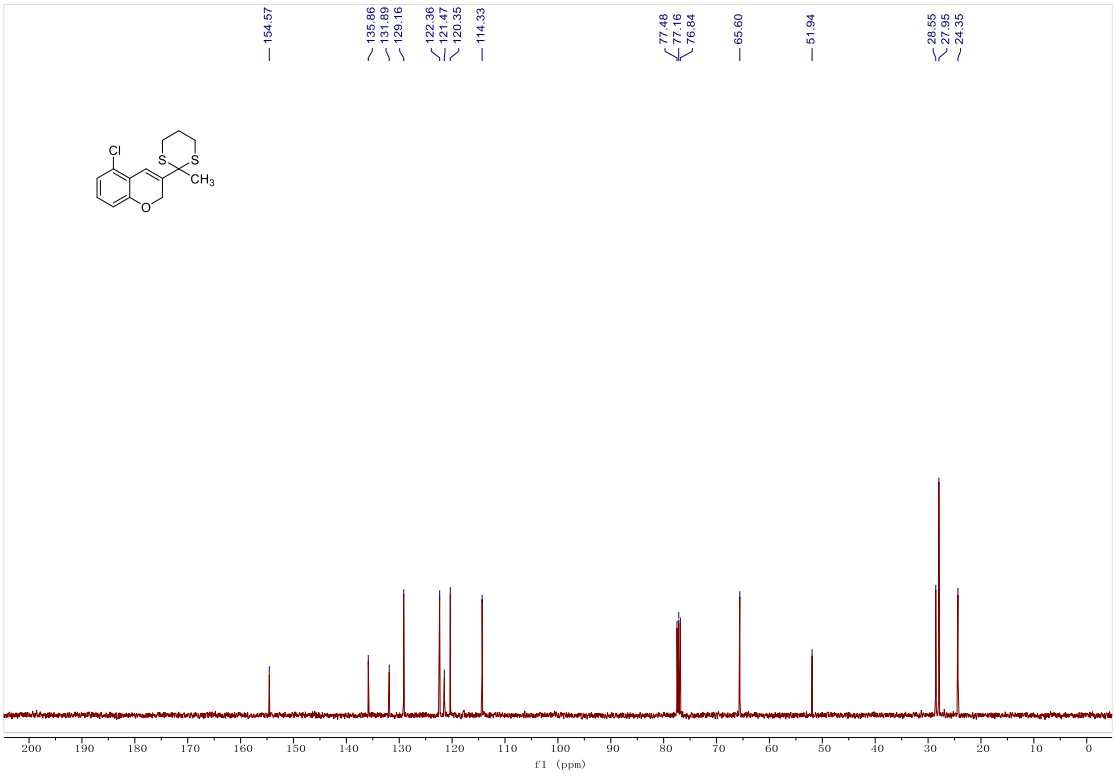
^{13}C NMR (101 MHz, Chloroform-*d*) of 52



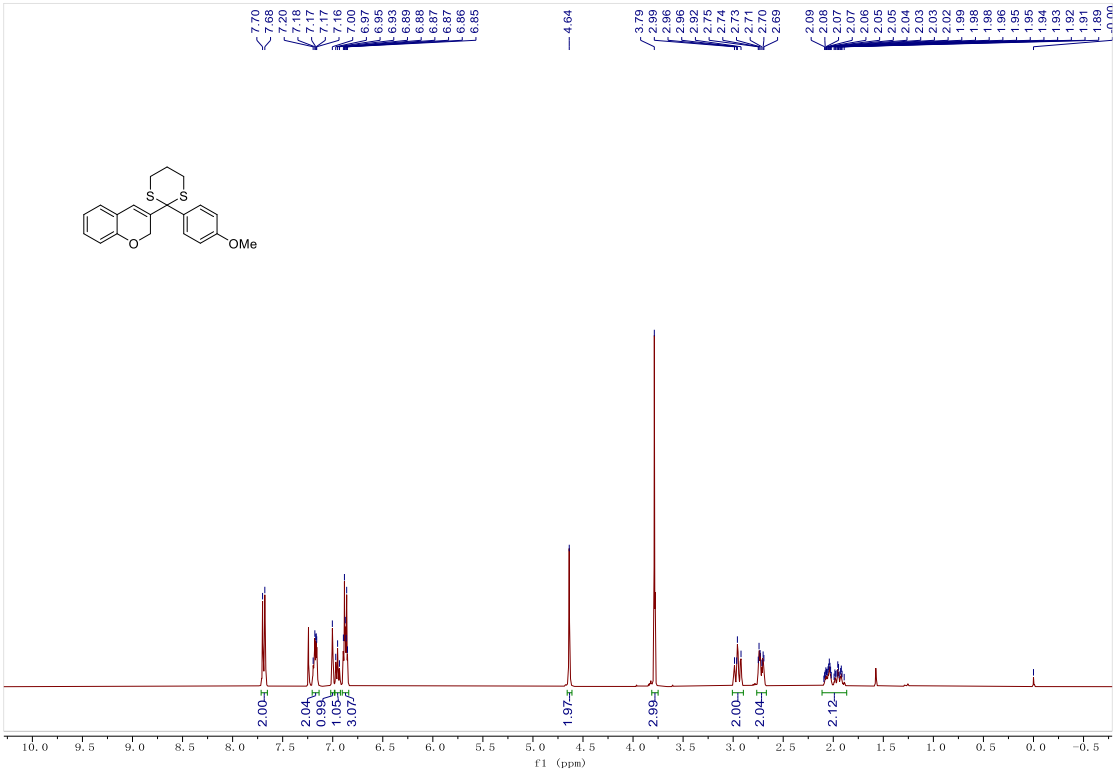
^{1}H NMR (400 MHz, Chloroform-*d*) of 53



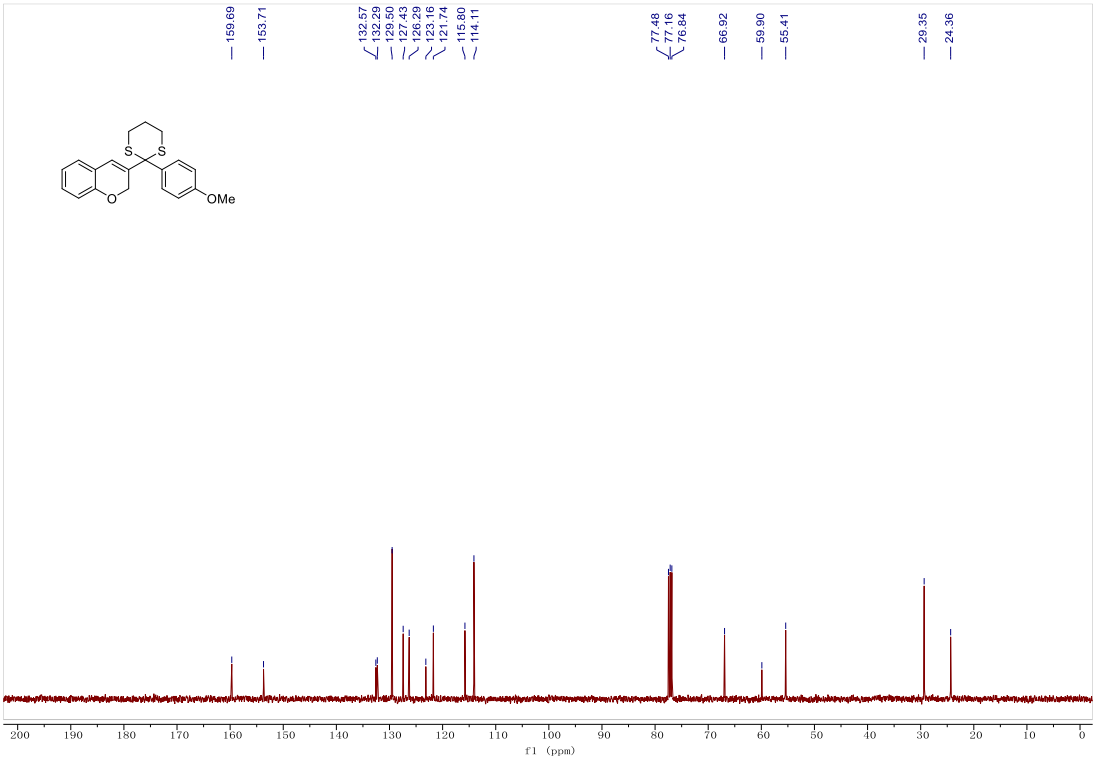
^{13}C NMR (101 MHz, Chloroform-*d*) of 53



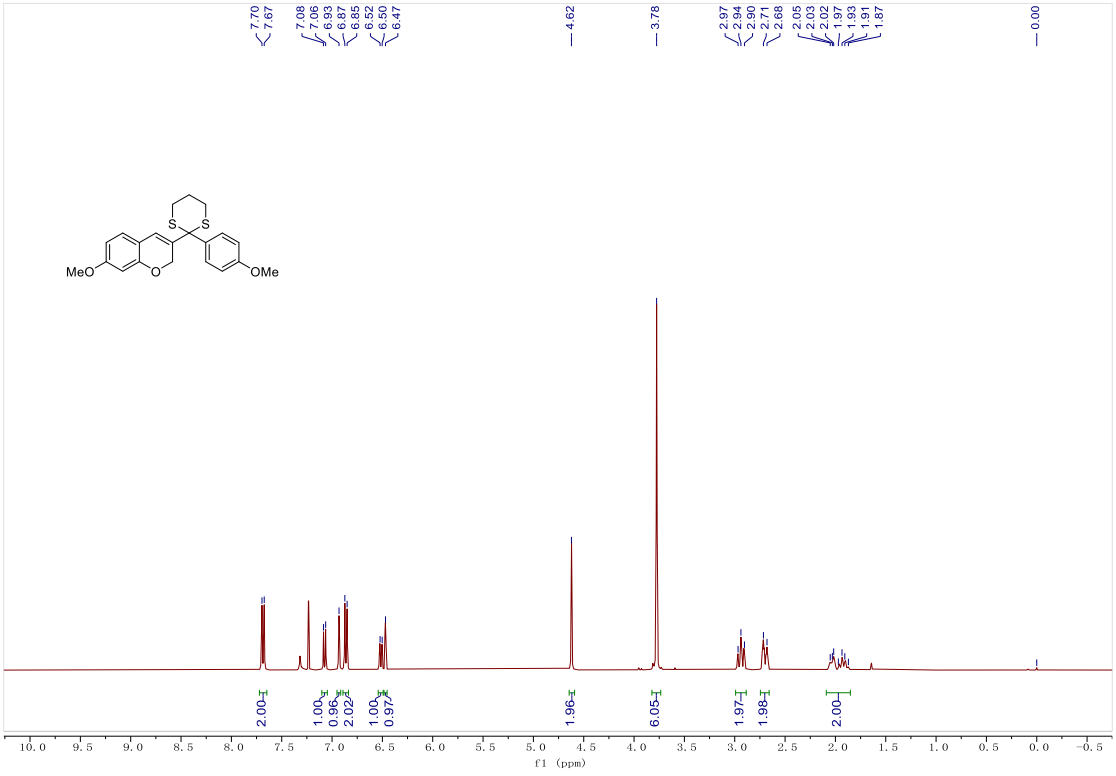
^{1}H NMR (400 MHz, Chloroform-*d*) of 54



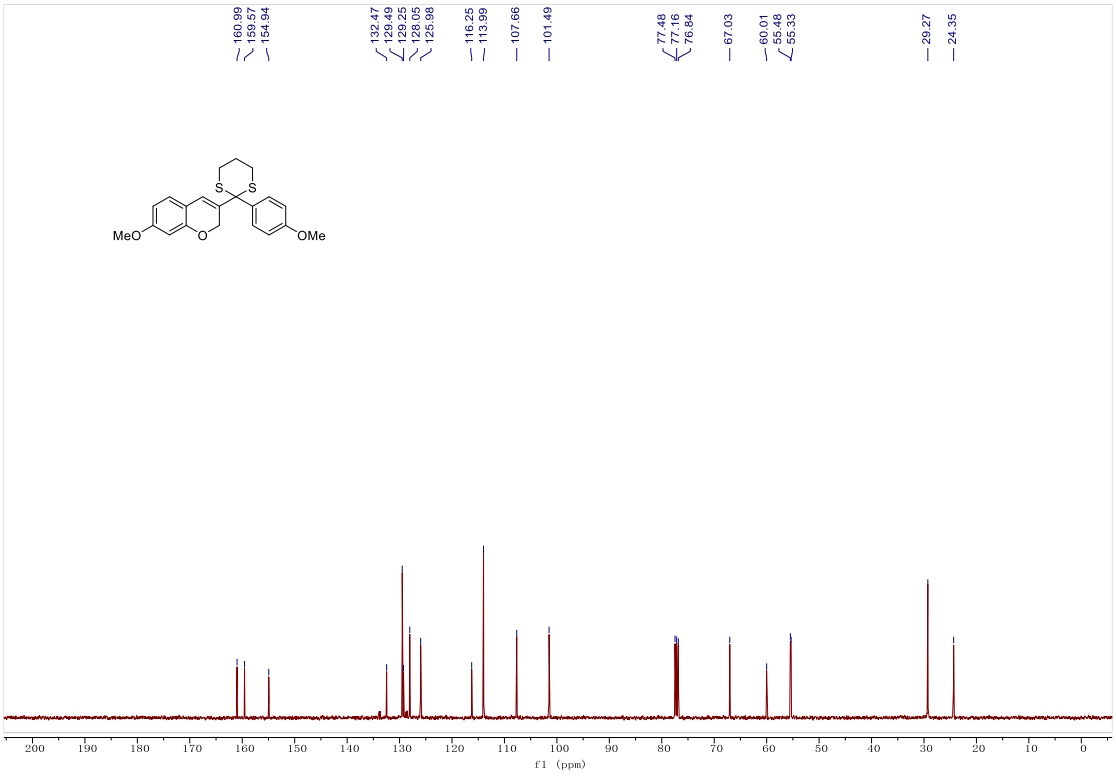
^{13}C NMR (101 MHz, Chloroform-*d*) of 54



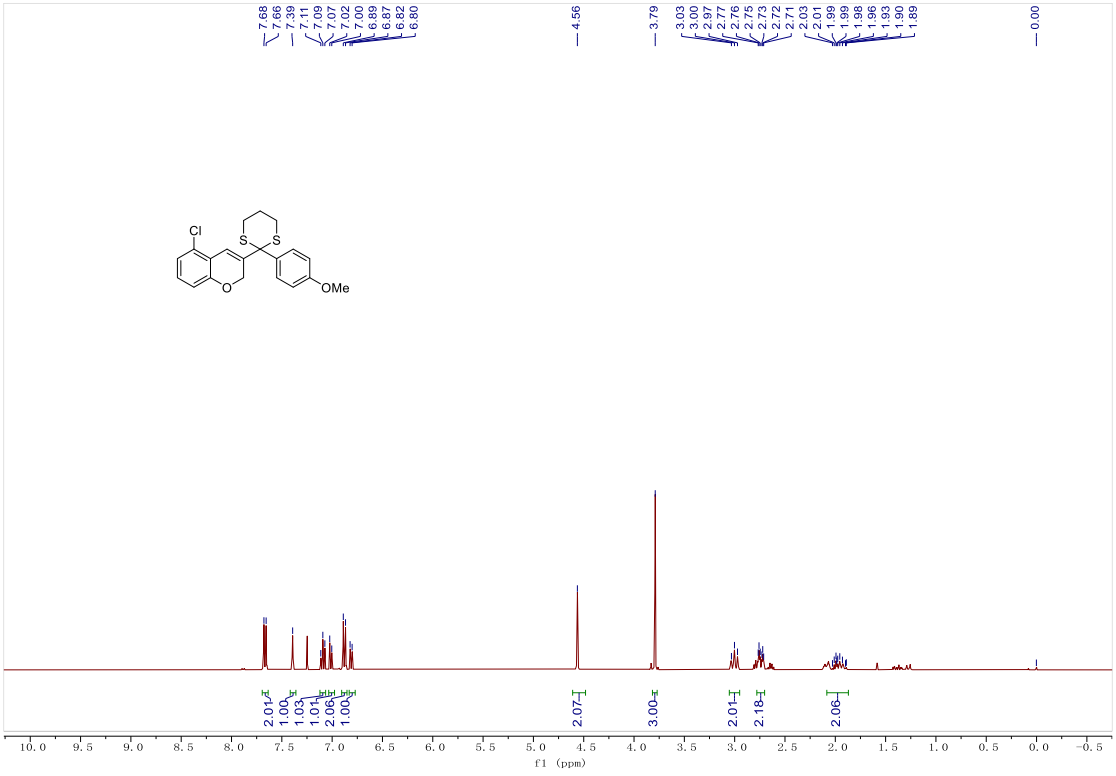
^{1}H NMR (400 MHz, Chloroform-*d*) of 55



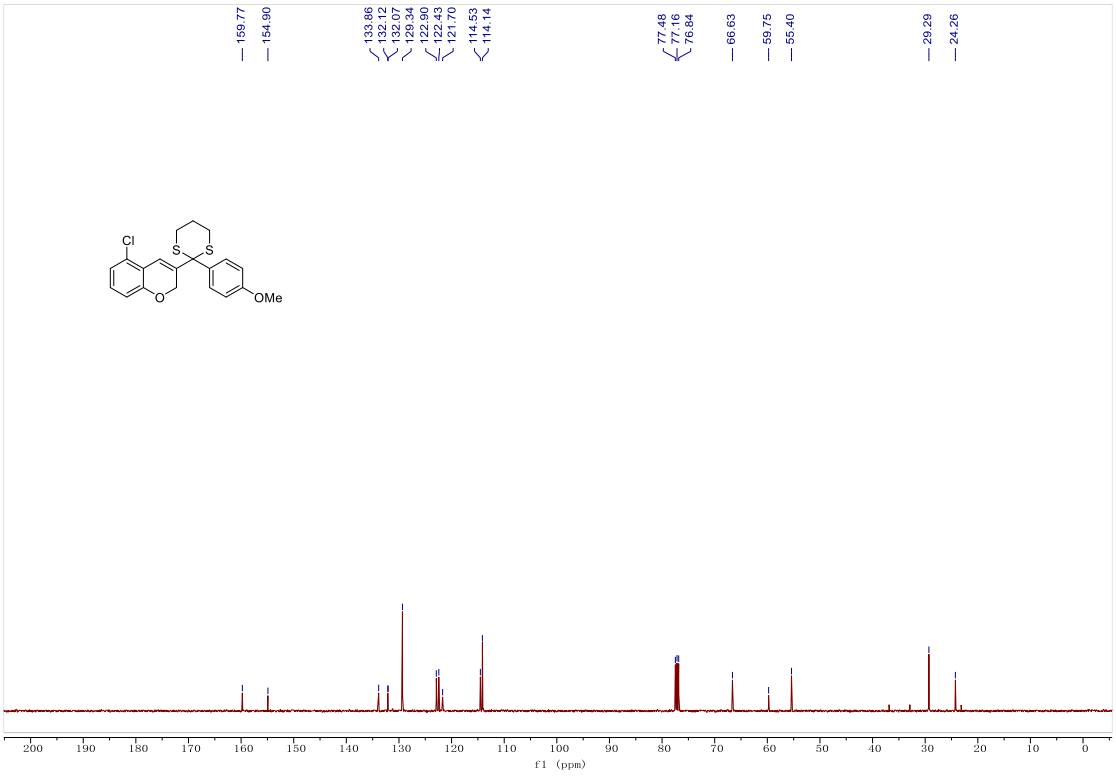
^{13}C NMR (101 MHz, Chloroform-*d*) of 55



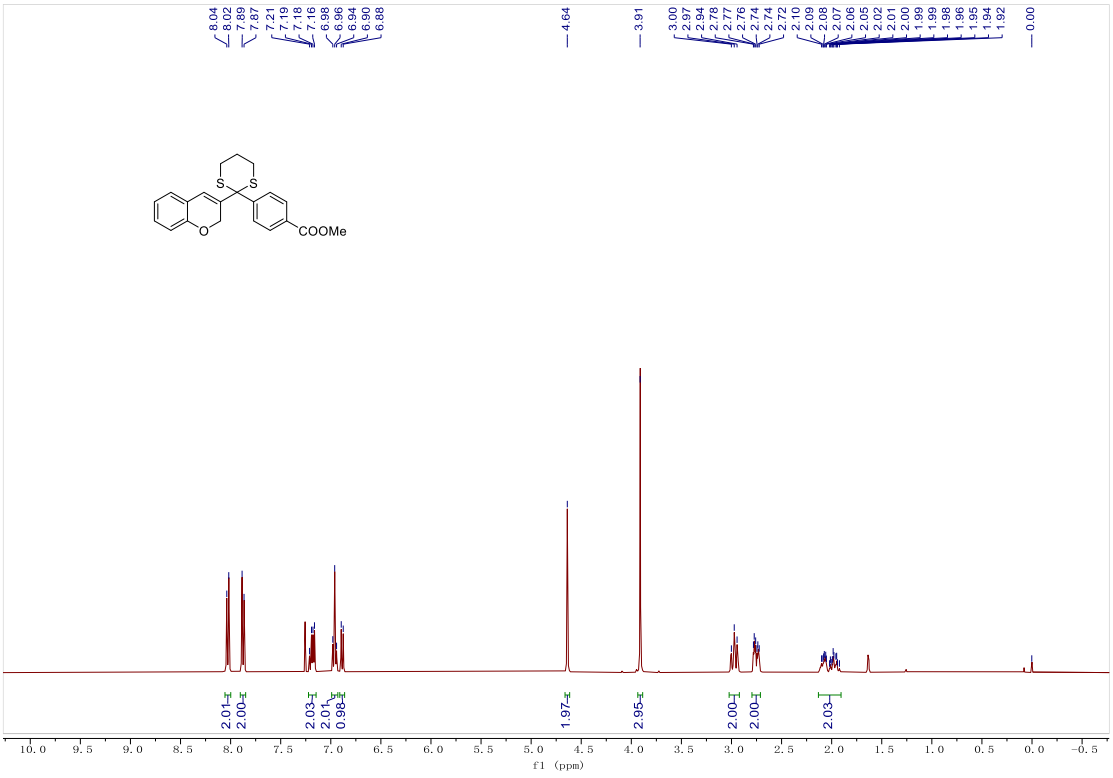
^{1}H NMR (400 MHz, Chloroform-*d*) of 56



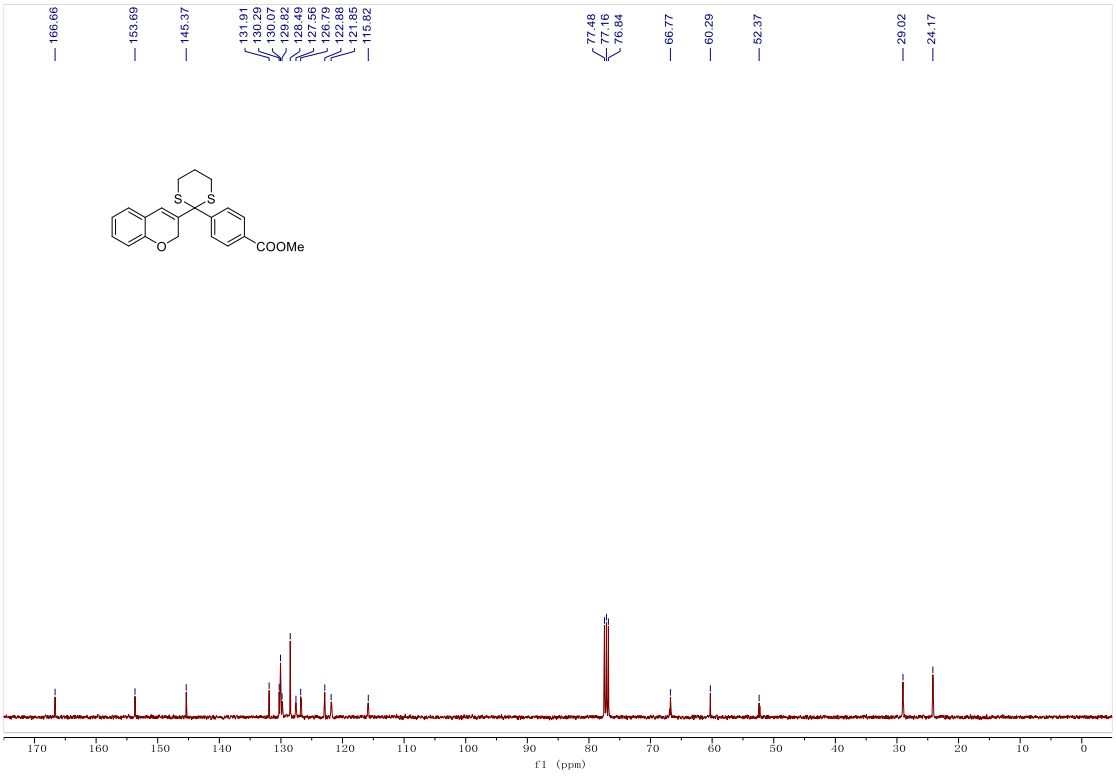
^{13}C NMR (101 MHz, Chloroform-*d*) of 56



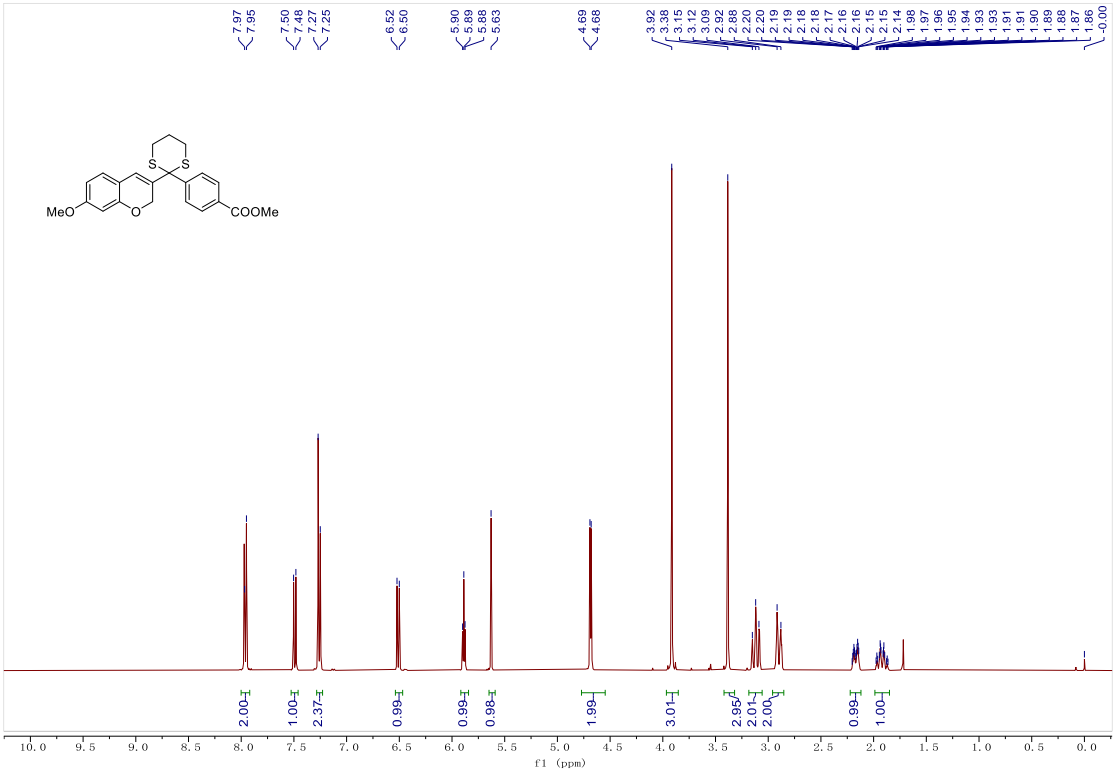
^{1}H NMR (400 MHz, Chloroform-*d*) of 57



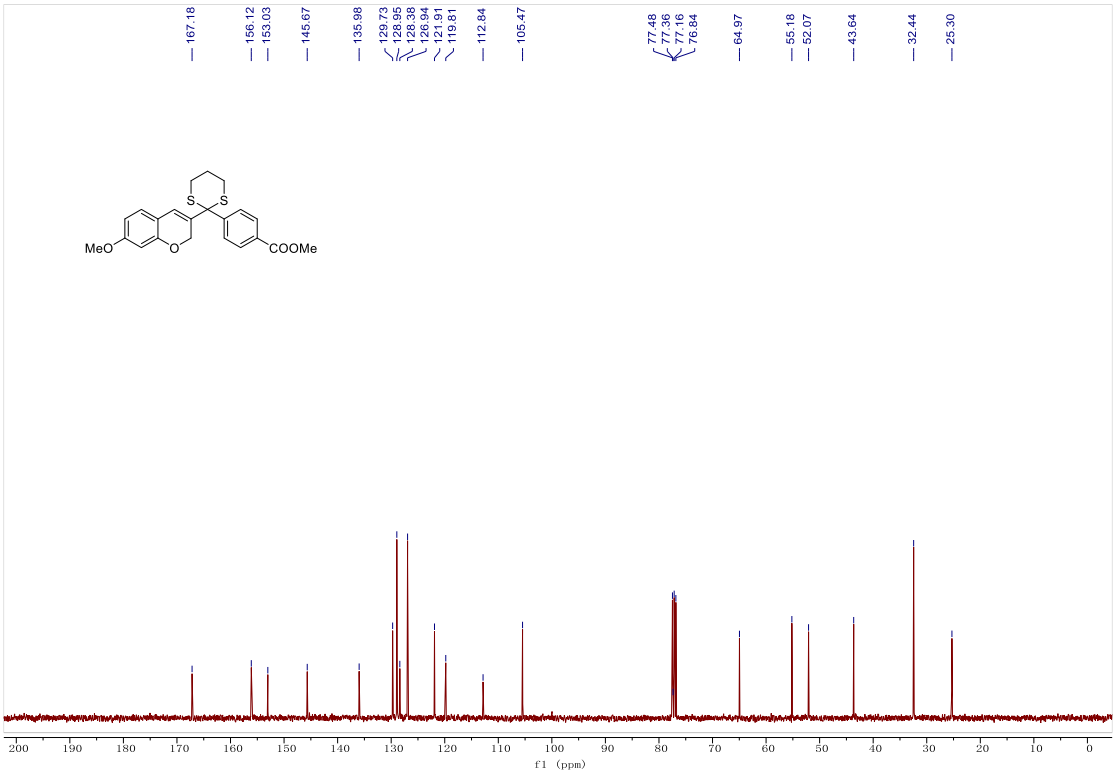
^{13}C NMR (101 MHz, Chloroform-*d*) of 57



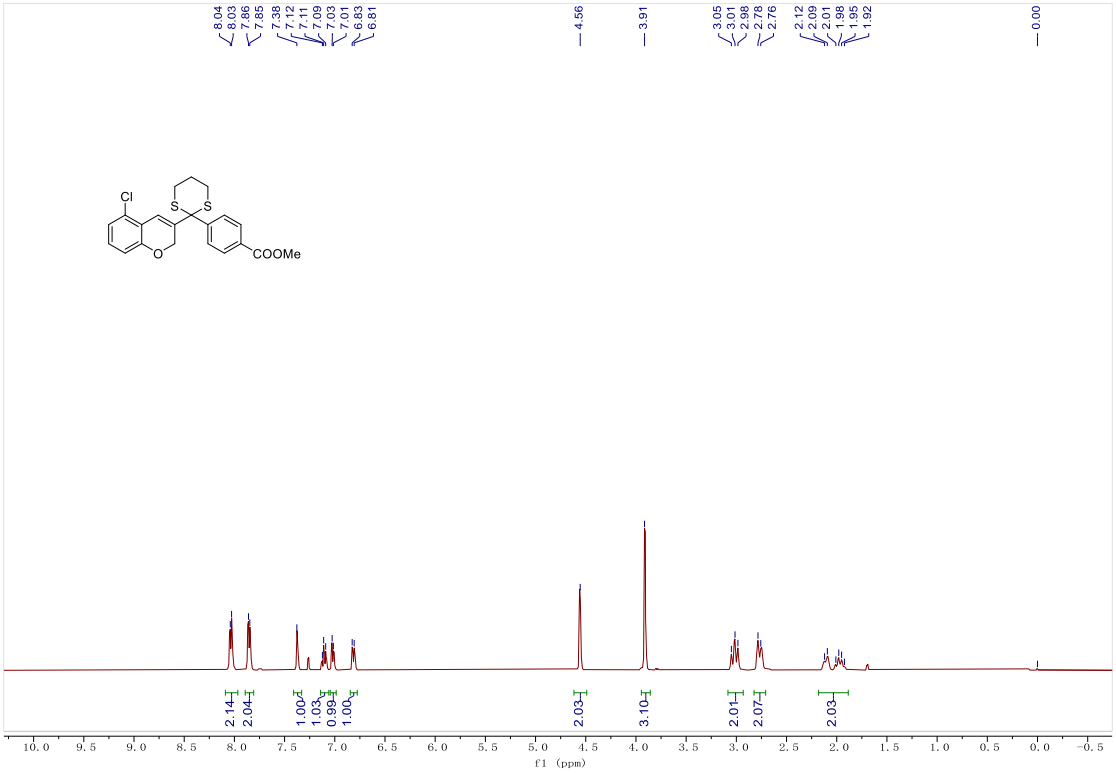
^{1}H NMR (400 MHz, Chloroform-*d*) of 58



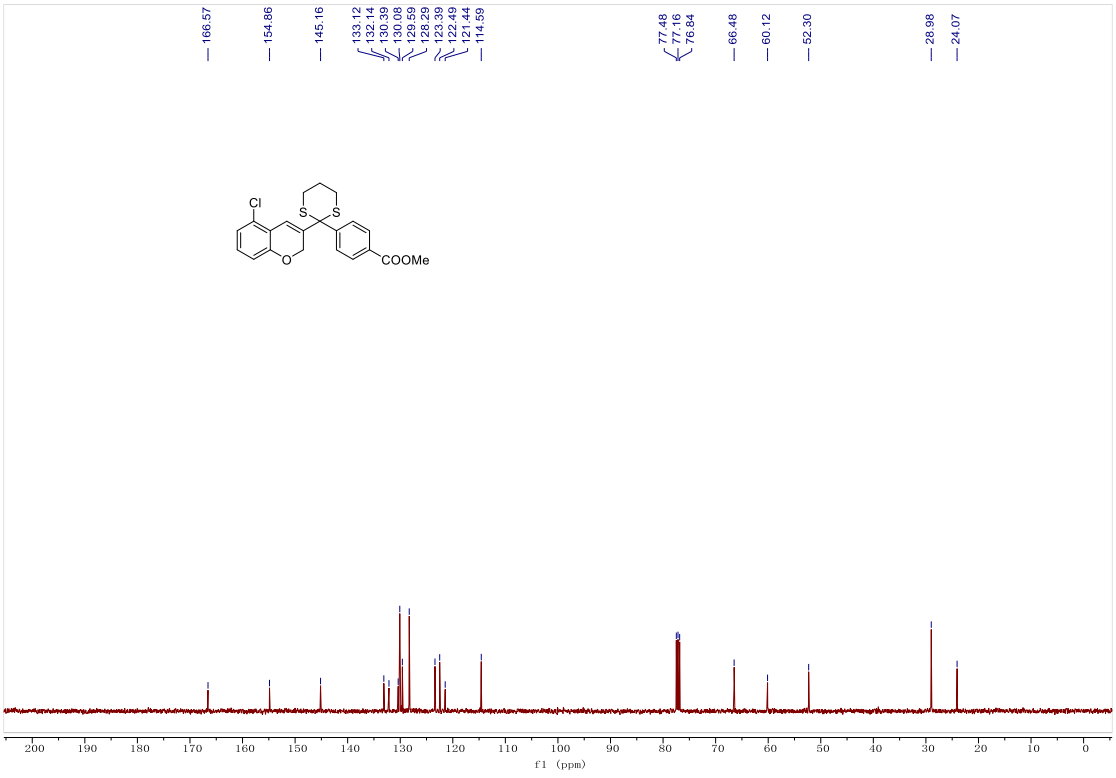
^{13}C NMR (101 MHz, Chloroform-*d*) of 58



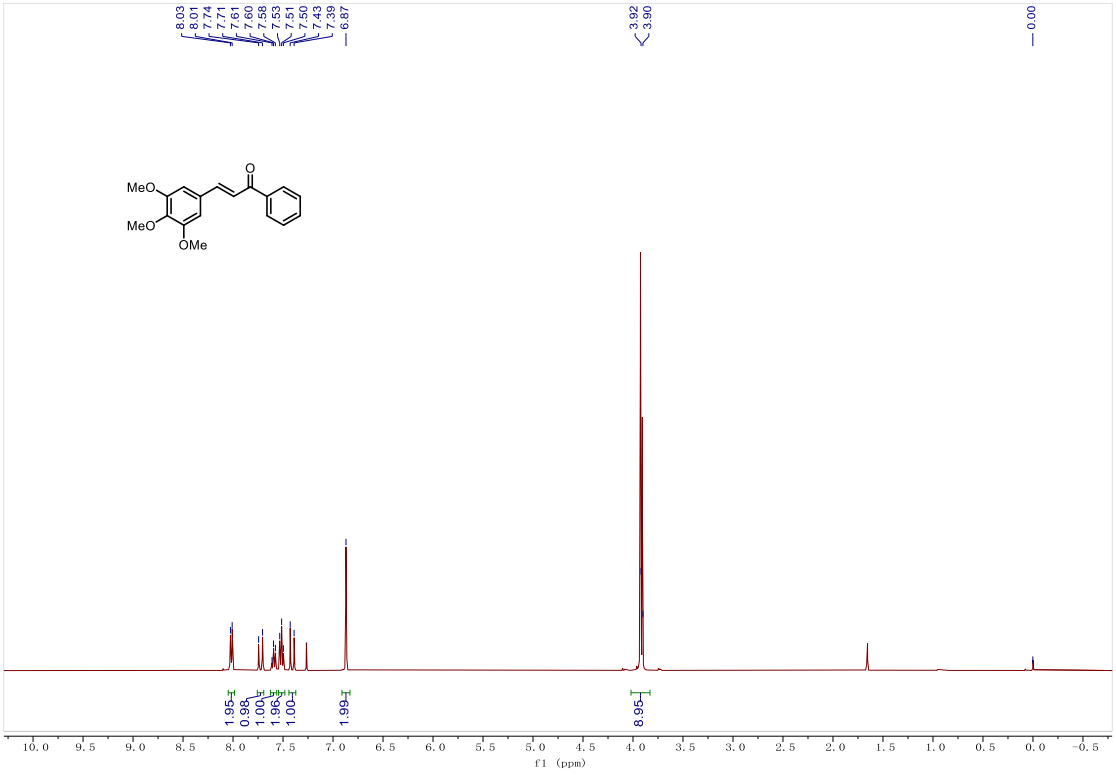
^{1}H NMR (400 MHz, Chloroform-*d*) of 59



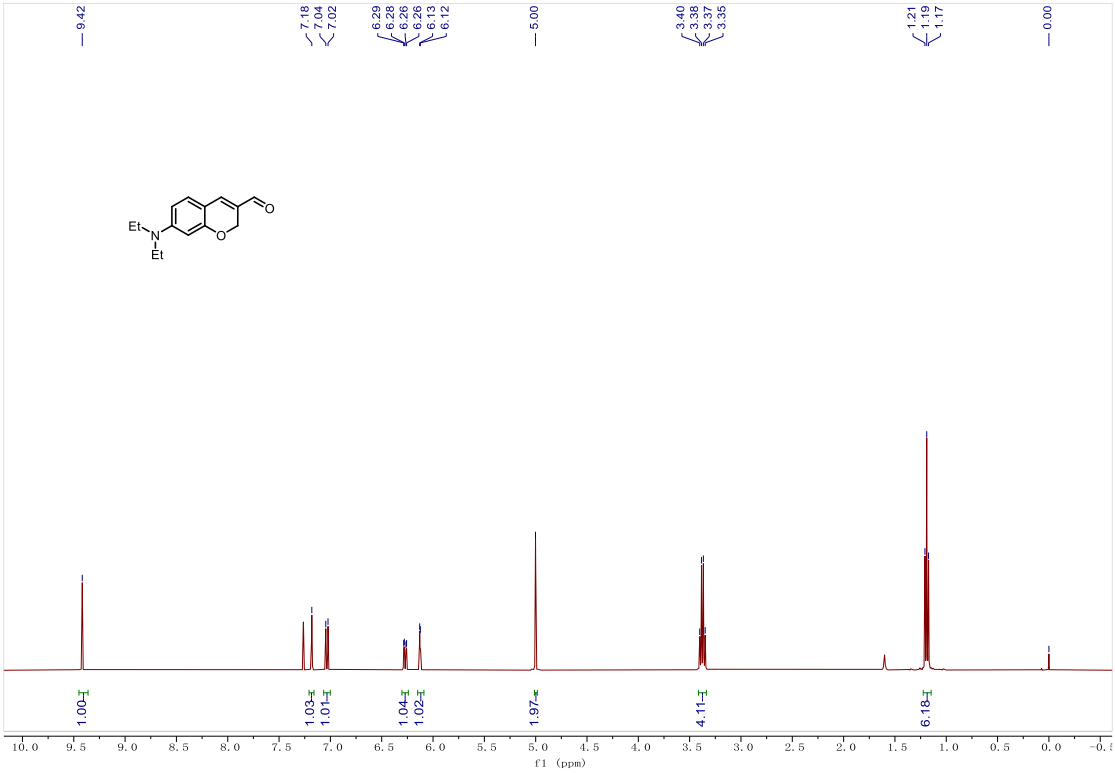
^{13}C NMR (101 MHz, Chloroform-*d*) of 59



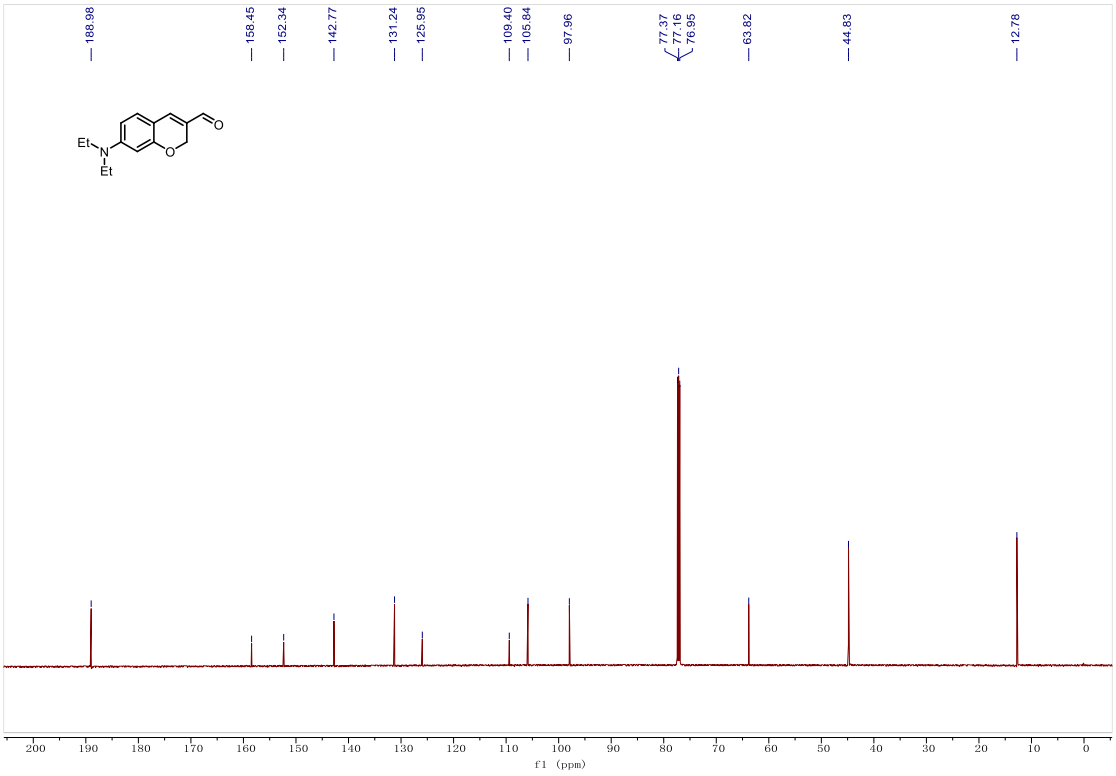
^{1}H NMR (400 MHz, Chloroform-*d*) of 60



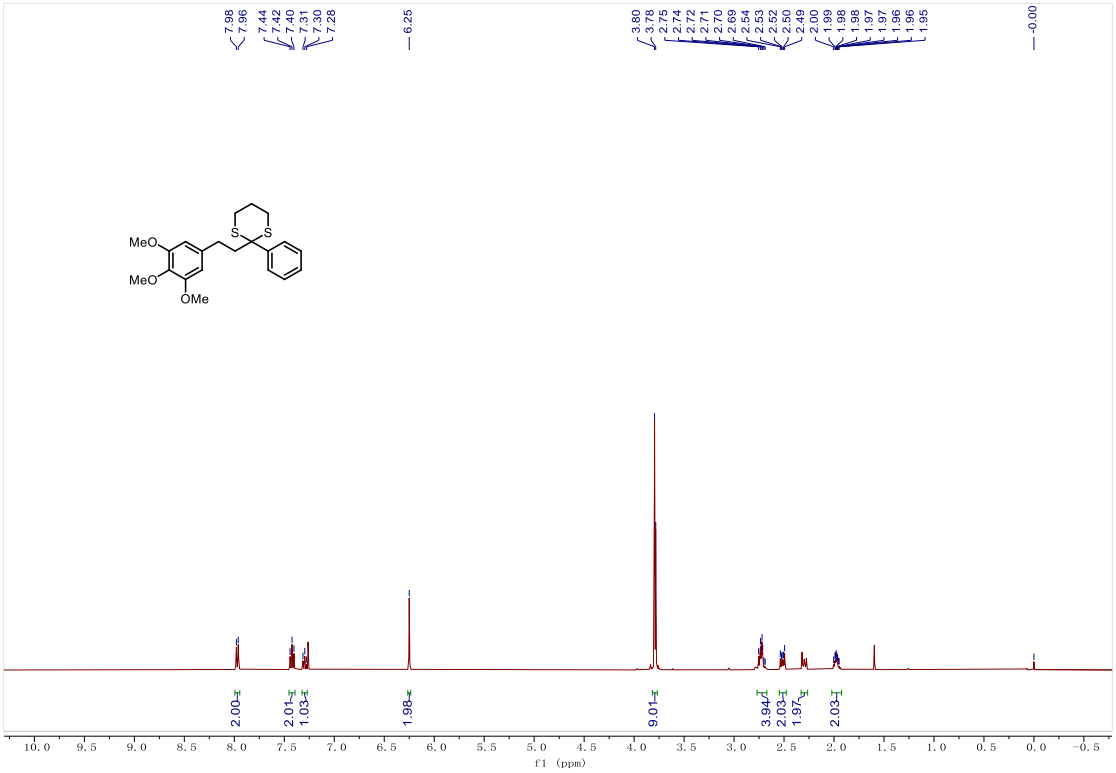
^{1}H NMR (400 MHz, Chloroform-*d*) of 61



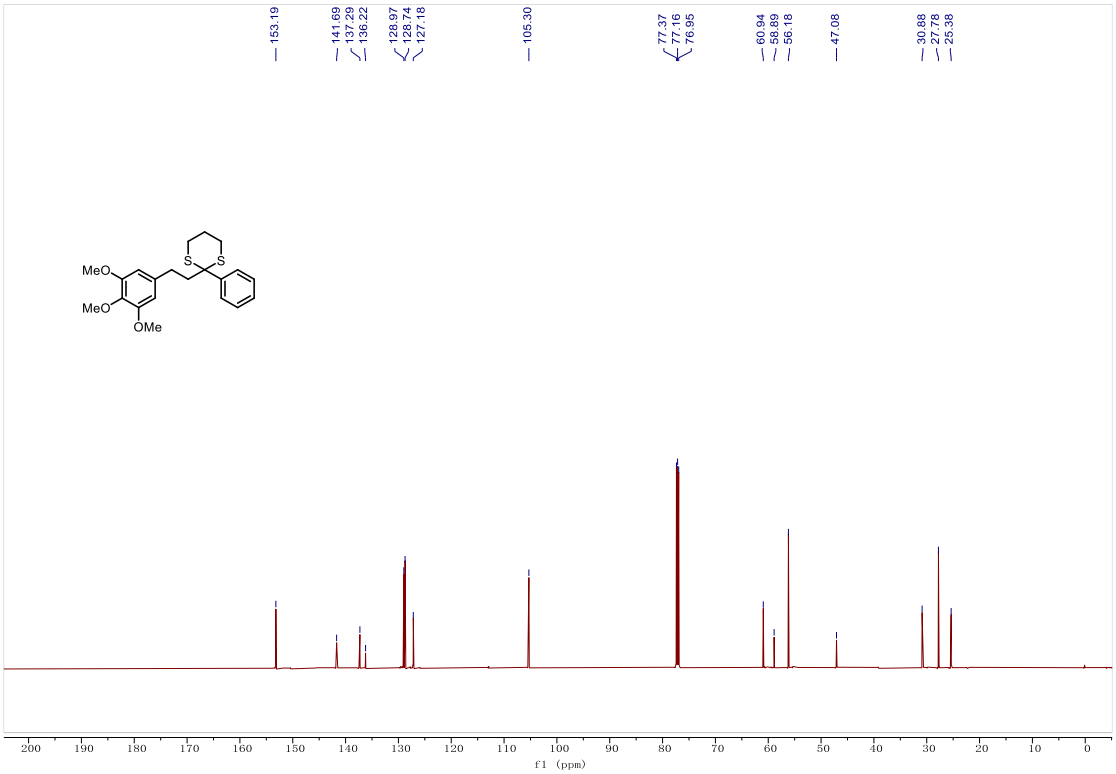
^{13}C NMR (151 MHz, Chloroform-*d*) of 61



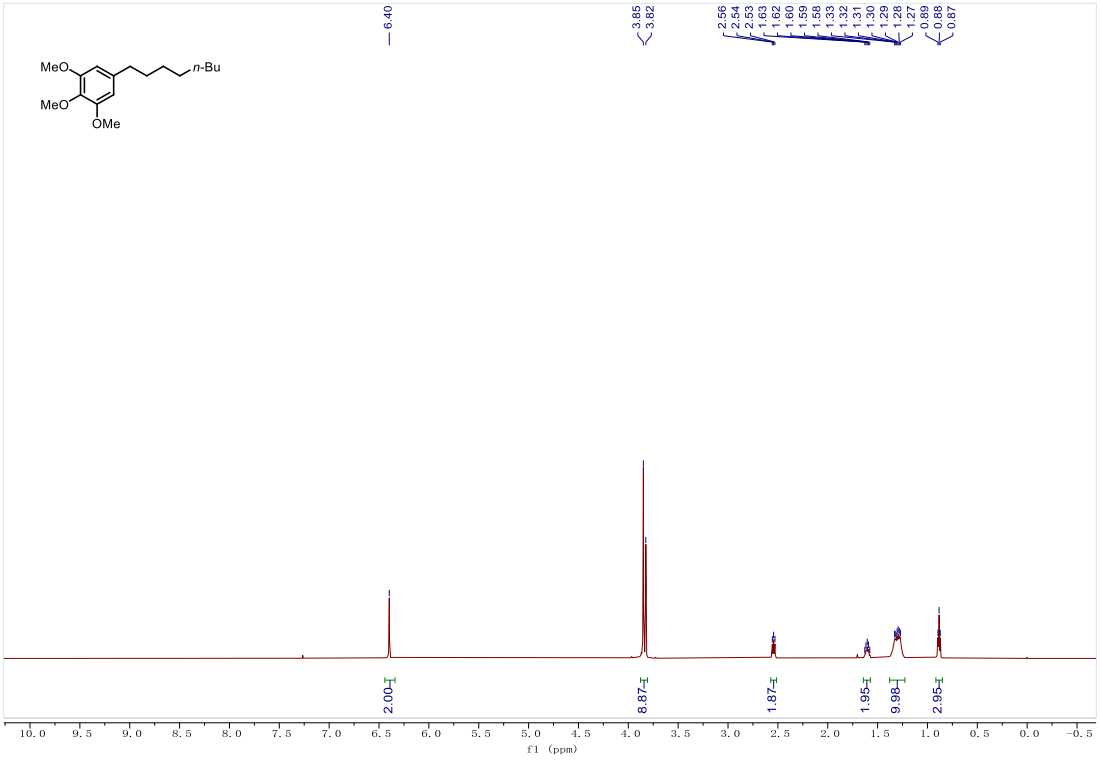
^{1}H NMR (400 MHz, Chloroform-*d*) of 62



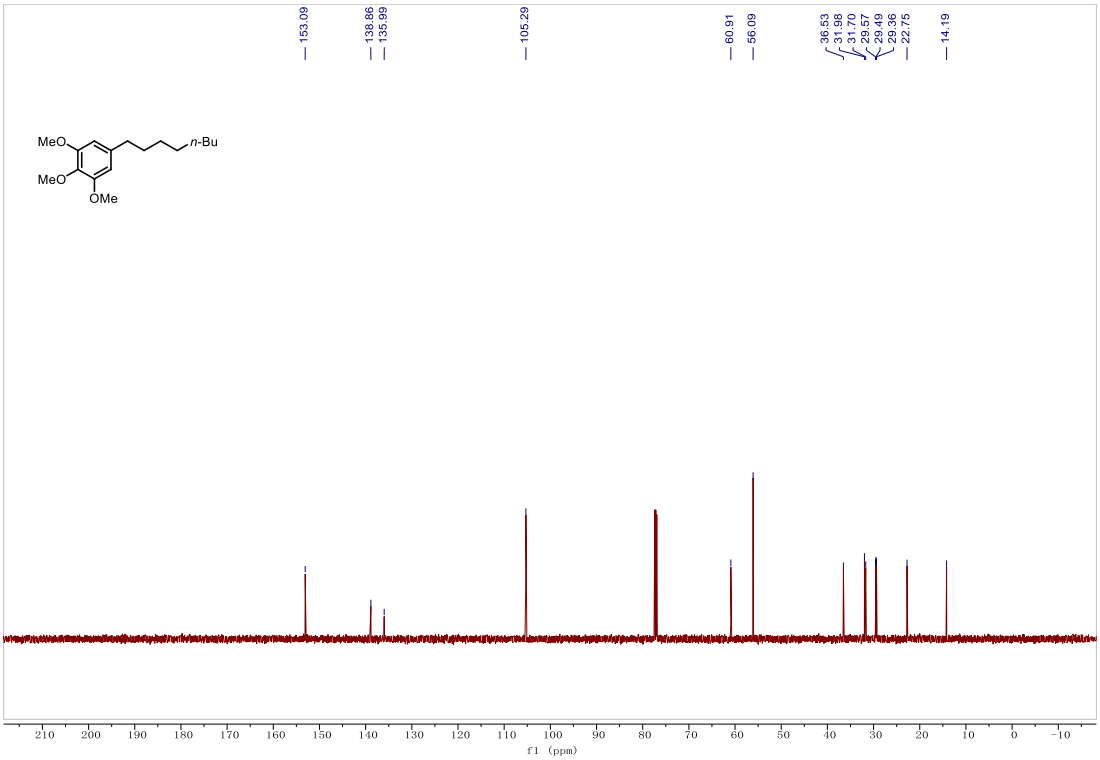
^{13}C NMR (151 MHz, Chloroform-*d*) of 62



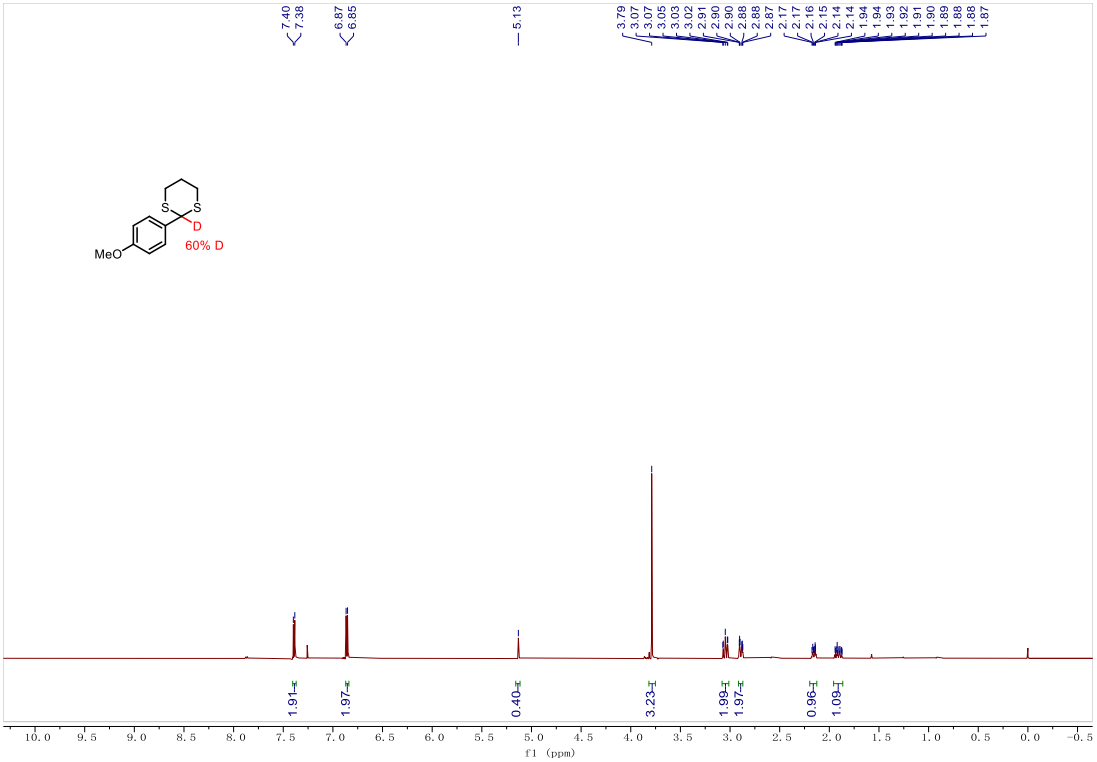
^{1}H NMR (600 MHz, Chloroform-*d*) of 63



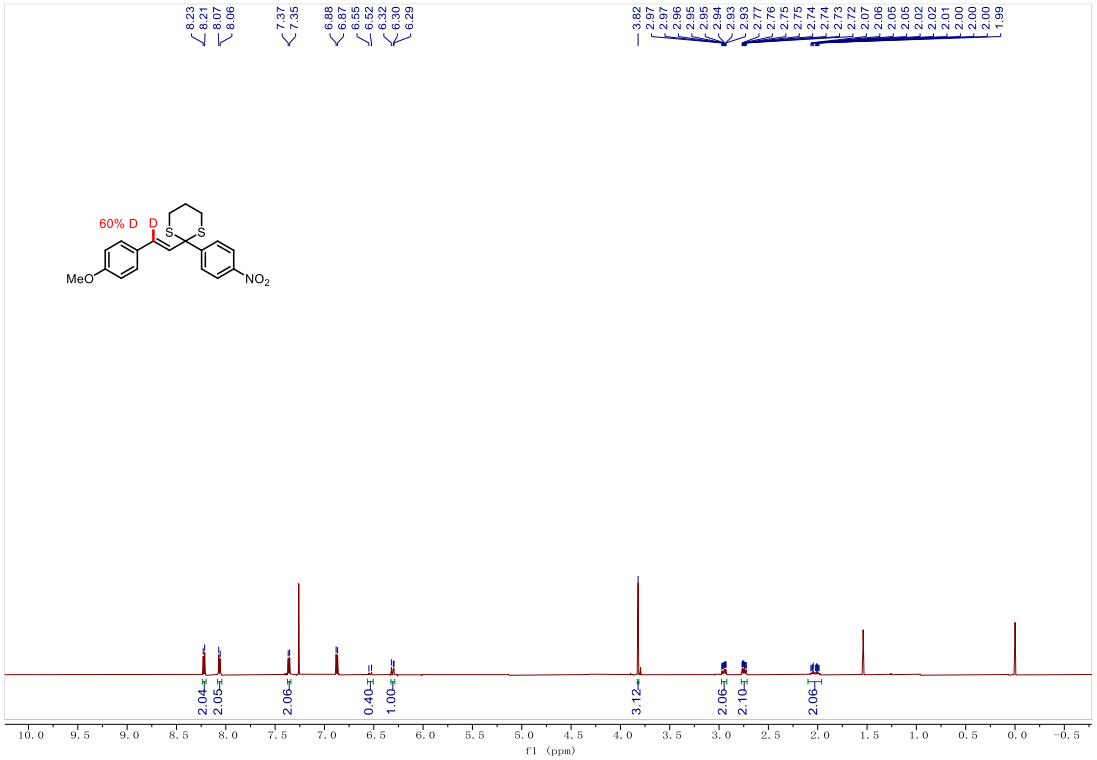
^{13}C NMR (151 MHz, Chloroform-*d*) of 63



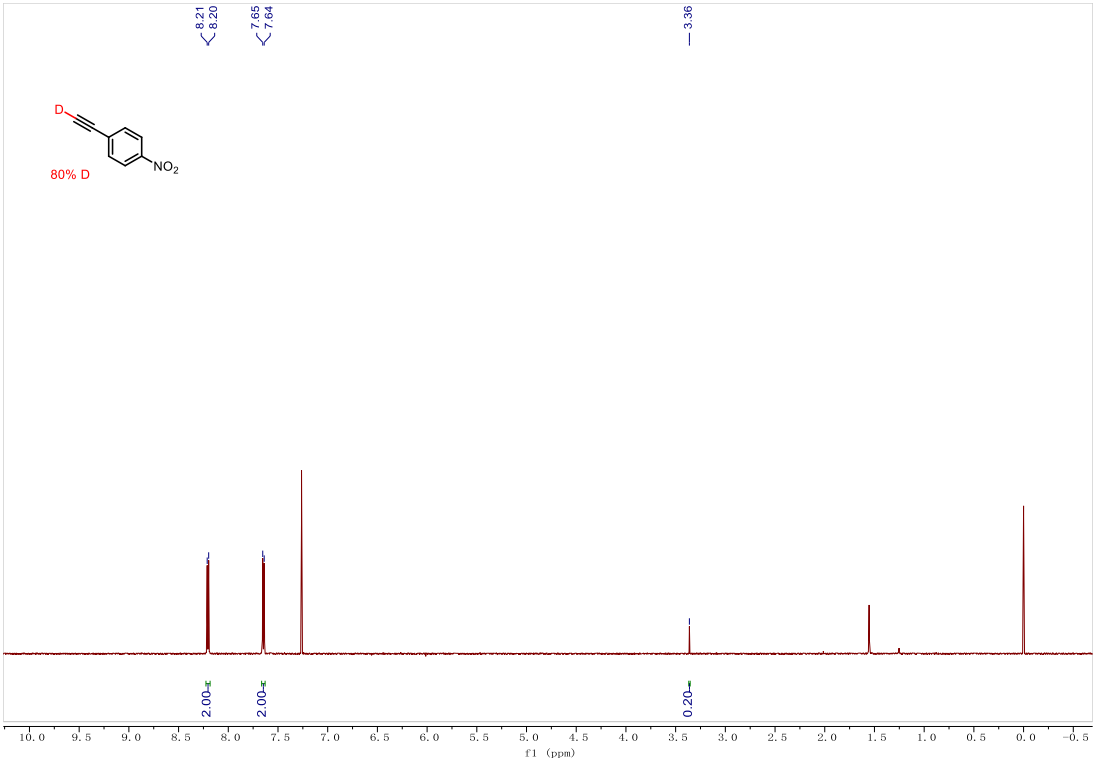
^{1}H NMR (600 MHz, Chloroform-*d*) of 64



^{1}H NMR (600 MHz, Chloroform-*d*) of 66



^{1}H NMR (600 MHz, Chloroform-*d*) of 68



^{1}H NMR (600 MHz, Chloroform-*d*) of 69