Supporting Information

Base-promoted [4+2] cycloaddition of alkynyl 1,3-dithianes and chalcones to access highly substituted pyran derivatives

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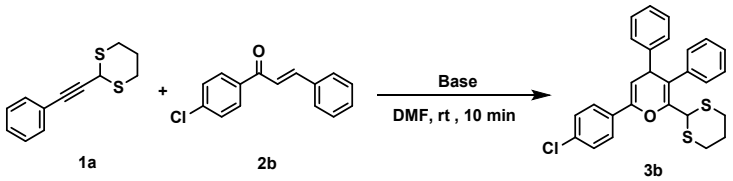
Table of Contents

1. General information

All the commercially available chemicals were purchased from Energy Chemical, Bidepharm, J&K Scientific, Leyan.com, Sigma-Aldrich, Acros Organics and used as received unless otherwise noted. 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). Flash chromatography was performed using XINNUO silica gel (200-300 mesh). Compounds were either visualised under UV-light at 254 nm or dipped the plates either 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.The crystal structure was measured on Rigaku Oxford Diffraction. The melting points were determined on a microscopic apparatus and were uncorrected.

2. The process of optimizing reaction conditions

Table S1. Screening of the Base and Equivalent[a,b]

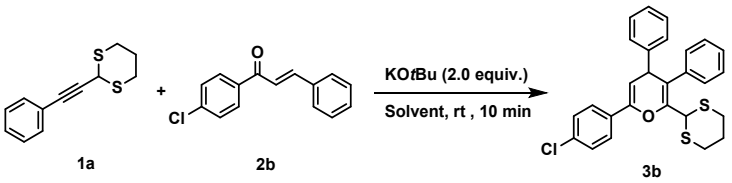


1a 2b 3b

Entry	Base	Equivalent	Yield (%)
1	KO*t*Bu	0.2	10
2	KO*t*Bu	0.5	18
3	KO*t*Bu	1.2	25
4	KO*t*Bu	2.0	39
5	KO*t*Bu	3.0	38
6	NaO*t*Bu	2.0	28
7	LiO*t*Bu	2.0	10
8	$NaOCH_3$	2.0	26
9	NaOEt	2.0	N.R.
10	$KOCH_3$	2.0	21
11	NaOH	2.0	N.D.
12	Et_3N	2.0	N.D.
13	Cs_2CO_3	2.0	21
14	K_2CO_3	2.0	N.D.
14	NaH	2.0	14

[a]Reaction conditions: **1a** (26.4 mg, 0.12 mmol), **2a** (24.3 mg, 0.1 mmol), and Base (x equiv.) dissolved in DMF (3 mL) at 25 °C for 10 min. [b]Isolated yields. N.R. = No Reaction. N.D. = Not detected.

Table S2. Screening of the solvent[a,b]

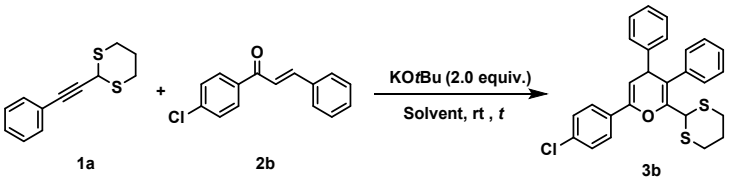


Entry	Solvent	Yield (%)
1	DMF	39
2	DMSO	14
3	THF	30
4	DMAc	21
5	ACN	22
6	Toluene	N.R.
7	HMPA	N.R.
8	NMP	35
9	DMI	24
10	DMF/THF (10:1)	39
11	DMSO/DMF (10:1)	36
12	DMSO/THF (10:1)	32
13	DMSO/DMF (1:1)	8
14	DMSO/THF (1:1)	43
15	DMF/THF (1:1)	27

[a]Reaction conditions: **1a** (26.4 mg, 0.12 mmol), **2a** (24.3 mg, 0.1 mmol), and KO*t*Bu (2.0 equiv.) dissolved in Solvent (3 mL) at 25 °C for 10 min. [b]Isolated yields. N.R. = No Reaction. N.D. = Not detected.

Table S3. Screening of other reaction time[a,b]

Entry	Solvent	t (min)	Yield (%)
1	DMSO/THF (10:1)	0.25	28
2	DMSO/THF (10:1)	0.5	48
3	DMSO/THF (10:1)	1	68
4	DMSO/THF (10:1)	1.5	50
5	DMSO/THF (10:1)	2	40
6	DMSO/THF (10:1)	10	32
7	DMF/DMSO (10:1)	1	48
8	DMF/THF (10:1)	1	45
9	ACN/THF (10:1)	1	N.D.
10	THF/DMSO (10:1)	1	8
11	DMSO/THF (1:1)	1	38
12	DMF	1	48
13	NMP	1	44

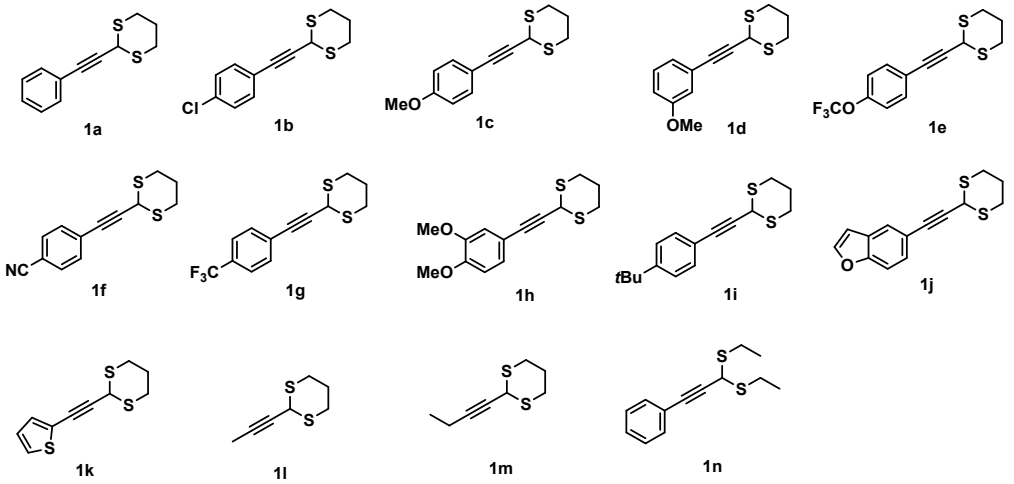


1a 2b 3b

[a]Reaction conditions: **1a** (26.4 mg, 0.12 mmol), **2a** (24.3 mg, 0.1 mmol), and KO*t*Bu (2.0 equiv.) dissolved in Solvent (3 mL) at 25 °C for x min. [b]Isolated yields. N.R. = No Reaction. N.D. = Not detected.

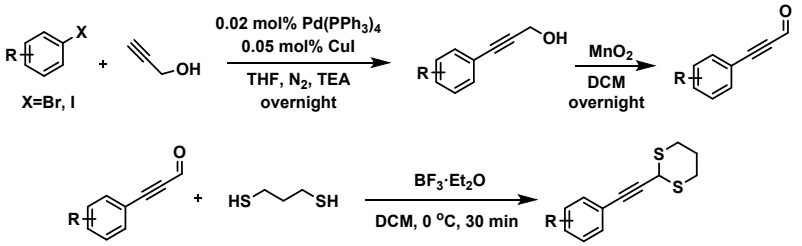
3. Synthesis of substrates

Synthesis of alkynyl 1,3-dithianes



1a-1h, 1l, 1n are known compounds, and all their spectral data have been reported in in our previous publications. [1, 2]

General procedure A for the synthesis of 2-Arylethynyl-1,3-dithiane.[1]



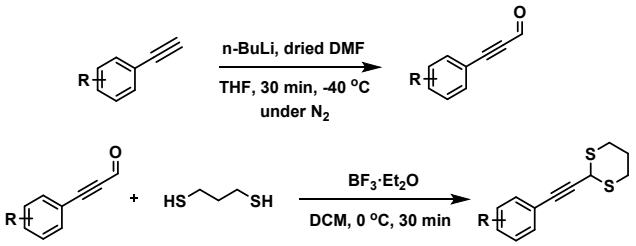
Step 1: A mixture of aryliodobenzene (10.00 mmol, 1.0 equiv.), Pd $(PPh_3)_4$ (0.2 mmol, 0.02 equiv.), CuI (0.5 mmol, 0.05 equiv.) was dissolved in dry THF (20 mL) under N_2 atmosphere. Et_3N (30 mmol) and propargyl alcohol (15.0 mmol, 1.5 equiv.) were sequentially added via syringes, and the resulting mixture was stirred at 75 °C overnight. After completion, the reaction mixture was filtered through a short pad of celite with DCM as eluent. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate (PE/EA = 5:1 to 1:1) affording the corresponding 3-arylprop-2-yn-1-ol.

Step 2: A solution of 3-arylprop-2-yn-1-ol (6.0 mmol, 1.0 equiv.) in dry DCM (20 mL) was added MnO_2 (30.0 mmol, 5.0 equiv.). The mixture was stirred at room temperature overnight. After filtering through a short pad of celite with DCM as eluent and removal

of the solvent under reduced pressure, the crude product was subsequently purified by column chromatography using a gradient of petroleum ether and ethyl acetate (PE/EA = 100:1 to 5:1) affording the corresponding arylpropiolaldehyde as a faint yellow solid.

Step 3: To a solution of arylpropiolaldehyde (6.0 mmol, 1.0 equiv.) and propane-1,3-dithiol (6.0 mmol, 1.0 equiv.) in DCM (20 mL), $BF_3{\cdot}Et_2O$ (0.37 mL, 3 mmol, 0.3 equiv.) was slowly added at 0 °C using an ice-bath. The resulting mixture was allowed to warm up to room temperature and stirred for 30 minutes until the disappearance of arylpropiolaldehyde was confirmed by TLC analysis. After evaporating the solvents under reduced pressure, the residue was purified by flash chromatography on silica gel using a gradient of petroleum ether and ethyl acetate (PE/EA = 200:1 to 5:1) affording the corresponding 2-arylethynyl-1,3-dithiane.

General procedure B for the synthesis of 2-Arylethynyl-1,3-dithiane.[2]



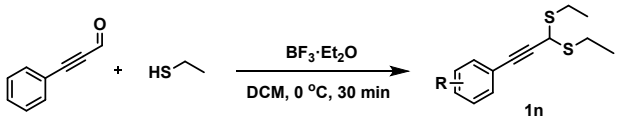
Step 1: *n*-Butyllithium (1.54 M in hexane, 10.0 mmol) was added dropwise to a solution of arylacetylene (10.0 mmol) in dried THF (20 mL) under a nitrogen atmosphere. After 30 min, dry DMF (15.0 mmol) was added and the mixture was stirred at room temperature for 30 minutes. The reaction was quenched by pouring into ice water and slightly acidified with 1.0 M HCl aqueous solution. Neutralization was achieved by adding saturated $NaHCO_3$ aqueous solution until the pH reached 6-7. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried over Na_2SO_4. After filtration and removal of the solvents under reduced pressure, the residue was purified by flash chromatography on silica gel using a gradient of petroleum ether and ethyl acetate (PE/EA = 100:1 to 5:1) affording the corresponding arylpropiolaldehyde.

Step 2: To a solution of arylpropiolaldehyde (6.0 mmol, 1.0 equiv.) and propane-1,3-dithiol (6.0 mmol, 1.0 equiv.) in DCM (20 mL), $BF_3{\cdot}Et_2O$ (0.37 mL, 3 mmol, 0.3 equiv.) was slowly added at 0 °C using an ice-bath. The resulting mixture was allowed

to warm up to room temperature and stirred for 30 minutes until the disappearance of arylpropiolaldehyde was confirmed by TLC analysis. After evaporating the solvents under reduced pressure, the residue was purified by flash chromatography on silica gel using a gradient of petroleum ether and ethyl acetate (PE/EA = 200:1 to 50:1) affording the corresponding 2-arylethynyl-1,3-dithianes.

Synthesis of (3-phenylprop-2-yne-1,1-diyl) bis(ethylsulfane) 1n

General procedure for the synthesis of (3-phenylprop-2-yne-1,1-diyl) bis(ethylsulfane)[2]



To a solution of 3-phenylpropiolaldehyde (6.0 mmol, 1.0 equiv.) and ethanethiol (12.0 mmol, 2.0 equiv.) in DCM (20 mL), $BF_3{\cdot}Et_2O$ (0.22 mL, 1.8 mmol, 0.3 equiv.) was slowly added at 0 °C using an ice-bath. The resulting mixture was allowed to warm up to room temperature and stirred for 30 minutes until the disappearance of 3-phenylpropiolaldehyde was confirmed by TLC analysis. After evaporating the solvents under reduced pressure, the residue was purified by flash chromatography on silica gel using petroleum ether (PE) to give the corresponding (3-phenylprop-2-yne-1,1-diyl) bis (ethylsulfane) **1n**.

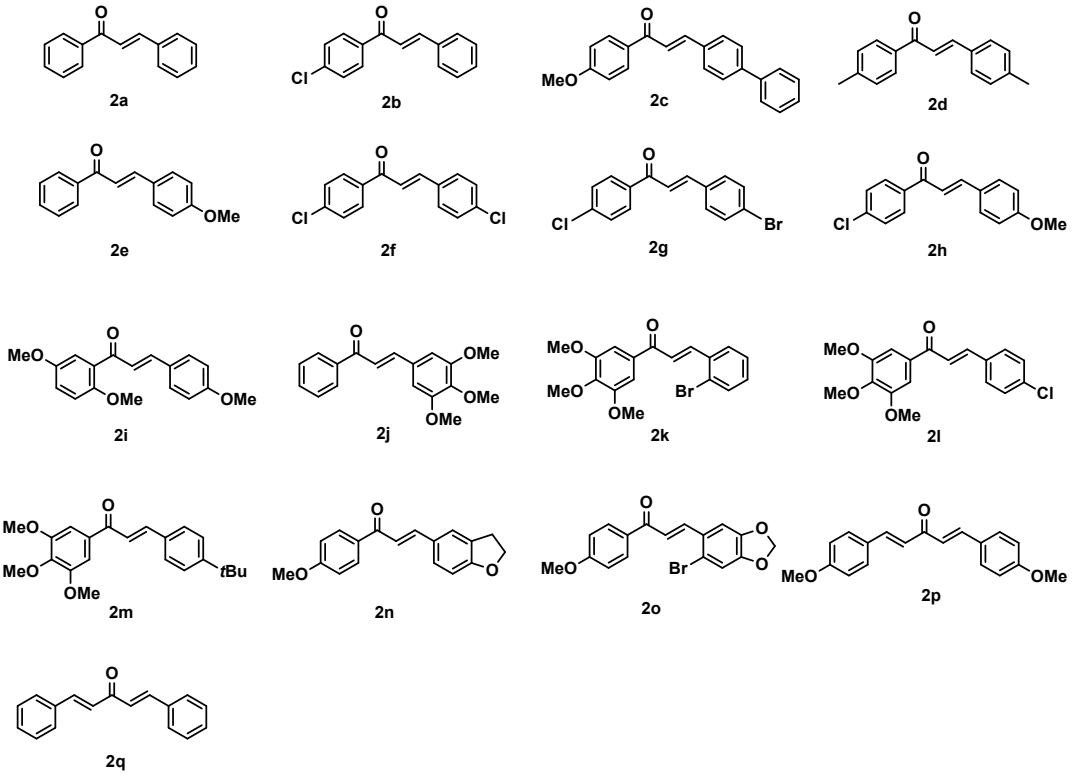
Synthesis of 2-(but-1-yn-1-yl)-1,3-dithiane 1m

General procedure for the synthesis of 2-(but-1-yn-1-yl)-1,3-dithiane[1]

To a solution of pent-2-ynal (340 mg, 5.0 mmol, 1.0 equiv.) and propane-1,3-dithiol (0.5 mL, 5.0 mmol, 1.0 equiv.) in DCM (20 mL) were slowly added $BF_3{\cdot}Et_2O$ (0.19 mL, 1.5 mmol, 0.3 equiv.) at 0 °C (using an ice-bath). The resulting mixture was allowed to warm up to room temperature and continued to stir until the disappearance of methylpropiolic aldehyde as determined by TLC analysis. The reaction was quenched with H_2O (10 mL) and extracted with DCM (3 × 30 mL). 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 with petroleum and ethyl acetate (PE/EA = 200:1 to 50:1) to give the 2-(but-1-yn-1-yl)-1,3-dithiane **1m**.

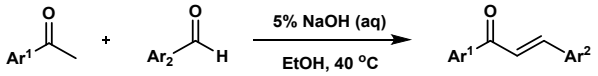
Synthesis of chalcones



Compounds **2a** and **2b** were obtained from commercial suppliers.

2c-**2p** were prepared according to the general procedure A, **2q** and **2r** were prepared according to the general procedure B. All spectral data matched that reported in the literature.

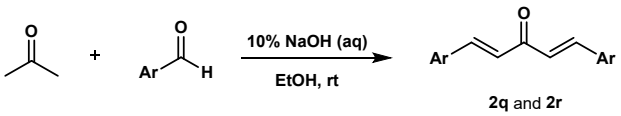
General procedure A for the synthesis of chalcone.[3]



A flamedried 50 mL round bottom flask was charged with aldehyde (10 mmol, 1.0 equiv.), acetone (10 mmol, 1.0 equiv.) and EtOH (20 mL). Then, 5% NaOH (aq) (1 mL) was slowly added and the mixture was heated at 40 °C until the reaction was complete (as determined by TLC analysis), water (20 ml) was added and the mixture was extracted with DCM (3 × 20 mL), the aqueous phase was separated. The combined organic extracts were washed with brine (3 × 20 mL), and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate (PE/EA = 100:1 to 29:1) to yield corresponding *α, β*-unsaturated carbonyl compounds.

Synthesis of 1,4-dien-3-one

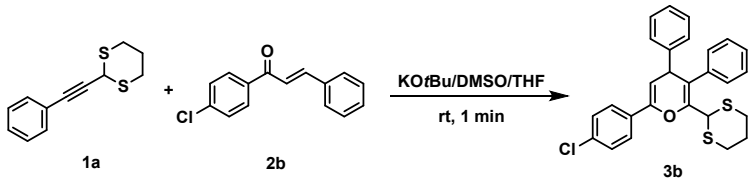
General procedure B for the synthesis of 1,4-dien-3-one.[4]



2q and **2r**

To the solution of acetone (8.0 mmol, 1.0 equiv.) and aldehyde (16.0 mmol, 2.0 equiv.) in ethanol (10 mL), 10% NaOH (aq) (15 mL) was added dropwise and stirred at room temperature to the completion of the reaction (as determined by TLC analysis). The resulted mixture was poured into water (30 mL). The solid was collected by filtration, washed with water (3 × 15 mL), and dried under vacuum to afford the crude product, which was recrystallized with petroleum ether and ethyl acetate (PE/EA = 50:1, v/v) to give corresponding compounds.

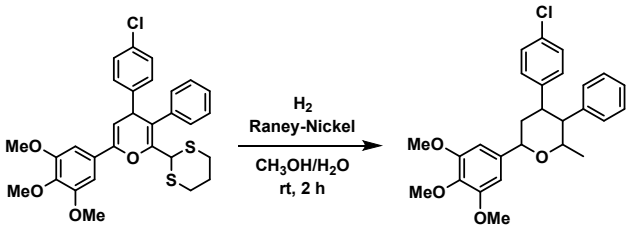
4. General procedure for the synthesis of 4*H*-pyran products



General procedure (illustrated with compound **3b** under standard conditions): To a 25 mL Schlenk flask equipped with a magnetic stir bar was added **1a** (0.12 mmol, 1.2 equiv.), **2b** (0.1 mmol, 1 equiv.), and a mixture of DMSO/THF (10:1, 3 mL). KO*t*Bu (0.2 mmol, 2 equiv.) was then added, and the reaction mixture was stirred at room temperature for 1 minute. The reaction was quenched with H_2O (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a gradient of petroleum ether and ethyl acetate (PE/EA= 50:1 to 10:1), yielding the corresponding 4*H*-pyran product **3b**.

5. Synthetic applications

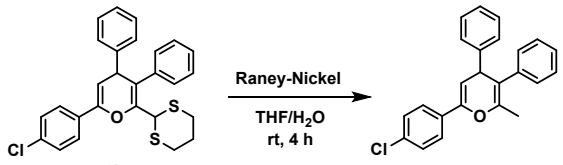
General procedure for the synthesis of 4-(4-chlorophenyl)-2-methyl-3-phenyl-6-(3,4,5-trimethoxyphenyl)tetrahydro-2H-pyran



3l 5a, 90% yield

A solution of compound **3l** (55.3 mg, 0.1 mmol) in methanol (CH_3OH, 10 mL) was treated with Raney Nickel (1 g, Aldrich-2800, 50% aqueous slurry) under a hydrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours, filtered through a Celite pad, and rinsed with dichloromethane (DCM). The resulting organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to yield a crude residue. Purification by flash column chromatography on silica gel eluting with a gradient of petroleum ether and ethyl acetate (PE/EA = 10:1 to 5:1) afforded compound **5a** as a yellow solid (40.4 mg, 90% isolated yield).

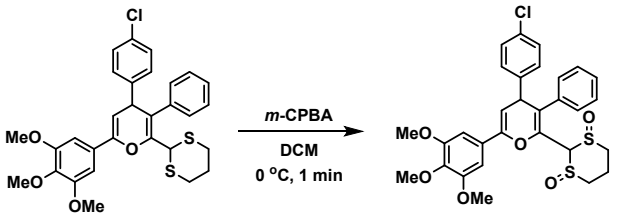
General procedure for the synthesis of 6-(4-chlorophenyl)-2-methyl-3,4-diphenyl-4H-pyran



3b 5b, 85% yield

To a solution of compound **3b** (46.3 mg, 0.1 mmol) in tetrahydrofuran (THF, 10 mL), Raney Nickel (1 g, Aldrich-2800, 50% aqueous slurry) was added. The reaction mixture was stirred at room temperature for 4 hours. After completion, the mixture was filtered through a Celite pad and rinsed with dichloromethane (DCM). The resulting organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to obtain a crude residue. Purification by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (PE/EA = 50:1 to 20:1) afforded compound **5b** as a faint yellow solid (30.5 mg, 85% isolated yield).

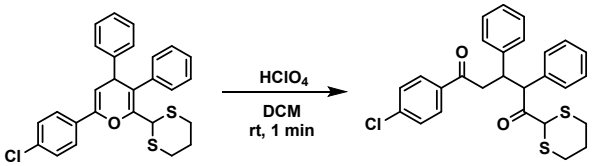
General procedure for the synthesis of 2-(4-(4-chlorophenyl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4H-pyran-2-yl)-1,3-dithiane 1,3-dioxide



3l **5c, 90% yield**

An oven-dried round-bottom flask was charged with dichloromethane (DCM, 2 mL) and compound **3l** (55.3 mg, 0.1 mmol) at 0 °C. The mixture was stirred at 0 °C for 5 minutes, after which m-chloroperbenzoic acid (*m*-CPBA, 17.3 mg, 0.1 mmol) was added under continuous stirring. The reaction mixture was further stirred at 0 °C for 1 minute. After solvent removal under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (PE/EA = 5:1 to 1:1) to yield compound **5c** as a faint yellow solid (52.7 mg, 90% isolated yield).

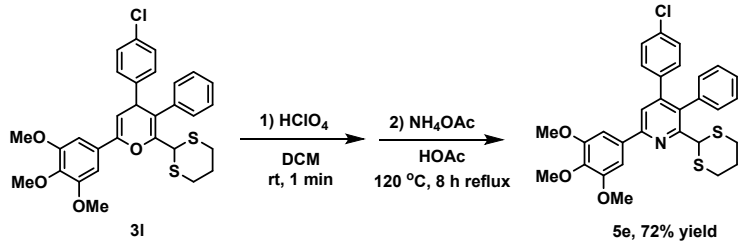
General procedure for the synthesis of 5-(4-chlorophenyl)-1-(1,3-dithian-2-yl)-2,3-diphenylpentane-1,5-dione



3b **5d, 80% yield**

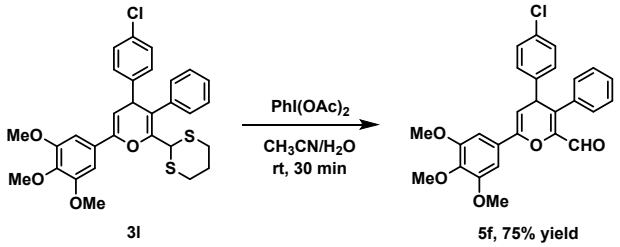
To a solution of compound **3b** (46.3 mg, 0.1 mmol) in dichloromethane (DCM, 10 mL), perchloric acid ($HClO_4$, 0.1 mL, Greagent, 70.0-72.0%) was added. The reaction mixture was stirred at room temperature for 1 minute. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (PE/EA = 30:1 to 10:1) to afford compound **5d** as a yellow solid (38.5 mg, 80% isolated yield).

General procedure for the synthesis of 4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)pyridine



A solution of compound **3l** (46.3 mg, 0.1 mmol) in dichloromethane (DCM, 10 mL) was treated with perchloric acid ($HClO_4$, 0.1 mL, Greagent, 70.0-72.0%) and stirred at room temperature for 1 minute. After solvent removal under reduced pressure, the residue was purified by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (PE/EA = 30:1 to 10:1) to afford a yellow solid. This yellow solid was dissolved in acetic acid (1.5 mL) and treated with ammonium acetate (NH_4OAc, 192.8 mg, 2.5 mmol). The reaction mixture was stirred at 120 °C for 8 hours, cooled to room temperature, quenched with water, and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated. Purification by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1 to 5:1) afforded compound **5e** as a white solid (33.4mg, 72% isolated yield).

General procedure for the synthesis of 4-(4-chlorophenyl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4H-pyran-2-carbaldehyde



Bis(trifluoroacetoxy)iodobenzene (52 mg, 0.16 mmol) was added at 0 °C to a stirred solution of compound **3l** (55.3 mg, 0.1 mmol) in water (1 mL) and acetonitrile (CH_3CN, 9 mL). The reaction mixture was then stirred at room temperature for 30 minutes and subsequently quenched with a saturated solution of sodium bicarbonate ($NaHCO_3$, 10 mL). The volatiles were evaporated under reduced pressure, and the resulting residue was dissolved in ethyl acetate (20 mL). The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4, and

concentrated under reduced pressure to yield a crude product. Purification by column chromatography on silica gel eluting with petroleum ether and ethyl acetate (PE/EA = 10:1 to 5:1) afforded the pure product **5f** (34.7 mg, 75% isolated yield).

6. Crystal data and structure of product 3f

Sample preparation and structure refinement of 3f. The compound **3f** (30 mg) was dissolved in acetonitrile (10 mL) and kept at room temperature for slow evaporation to obtain crystals. Block shaped colorless crystals were formed, which were subjected to X-ray diffraction. A suitable crystal was selected and tested on Rigaku Oxford Diffraction. The crystal was kept at 303.9(3) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

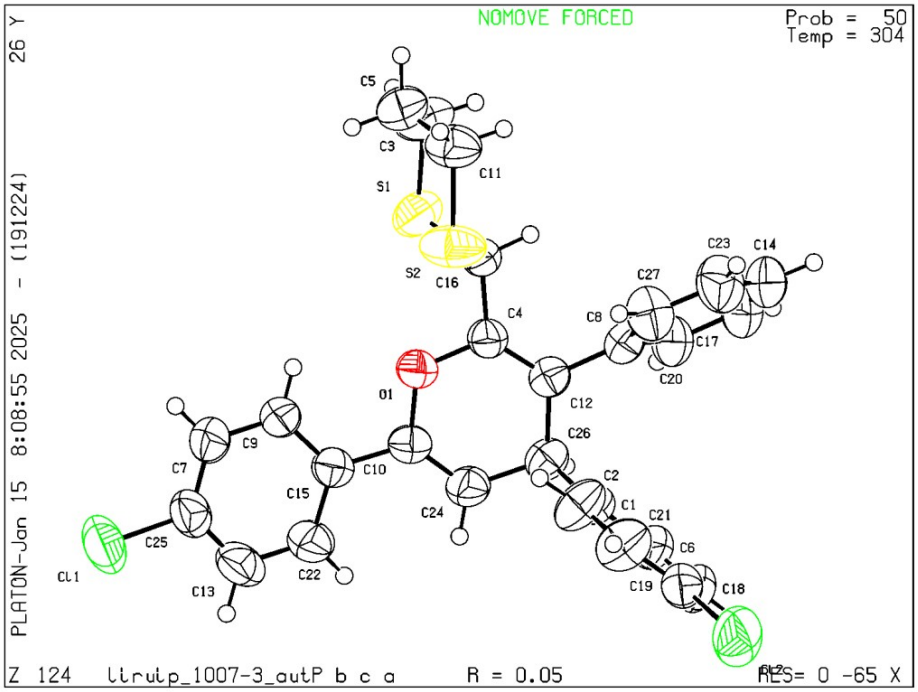


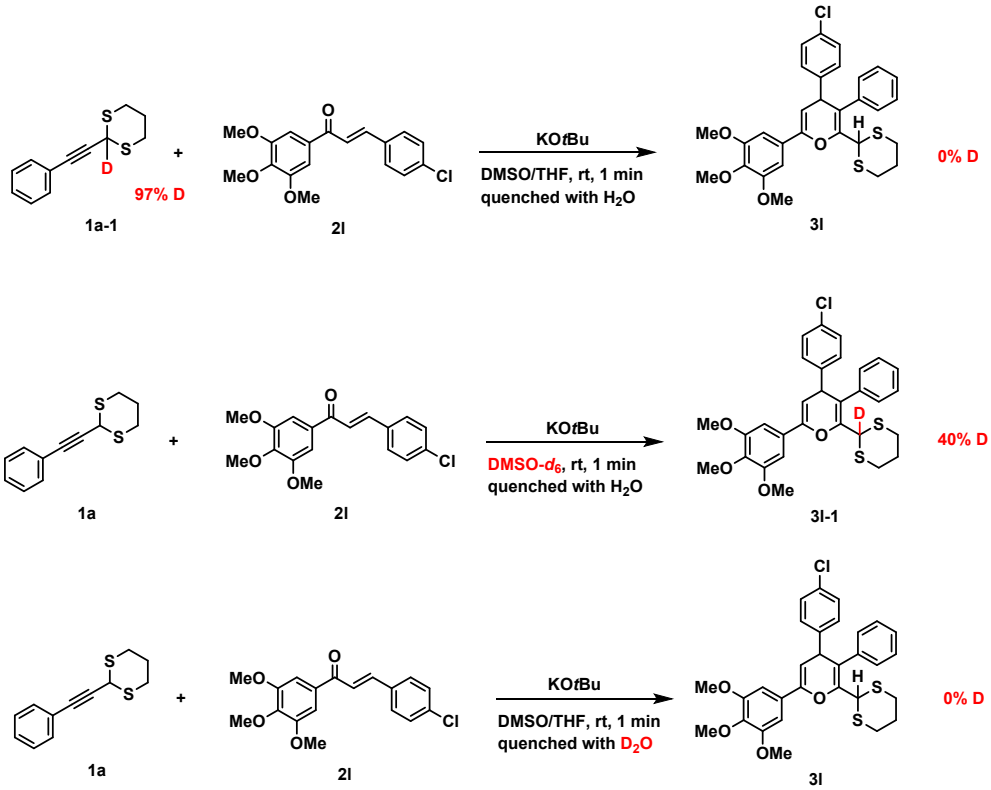
Figure S1 Crystal structure of compound **3f** (CCDC 2417173), thermal ellipsoids are drawn at the 30% probability level.

Table S5. Crystal data and structure refinement for 3f

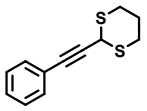
Empirical formula	$C_{27}H_{22}Cl_2OS_2$
Formula weight	497.46
Temperature/K	303.9(3)
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.4331(2)

b/Å	17.0683(3)
c/Å	20.0983(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4951.19(14)
Z	8
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	4.066
F(000)	2064.0
Crystal size/mm^3	0.23 × 0.21 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.8 to 152.064
Index ranges	-17 ≤ h ≤ 6, -20 ≤ k ≤ 21, -25 ≤ l ≤ 25
Reflections collected	18730
Independent reflections	4950 [R_{int} = 0.0347, R_{sigma} = 0.0336]
Data/restraints/parameters	4950/0/289
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1548
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1647
Largest diff. peak/hole / e Å^{-3}	0.49/-0.45

7. Mechanism investigation.



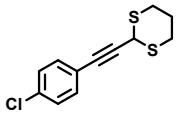
8. Characterization data of products



1a

2-(Phenylethynyl)-1,3-dithiane (1a)[5]

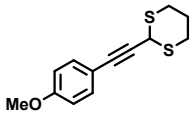
White solid, R_f = 0.6 (PE/EA = 20:1), 793mg, 60%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.42 (m, 2H), 7.34 – 7.26 (m, 3H), 4.80 (s, 1H), 3.35 – 3.15 (m, 2H), 2.87 – 2.70 (m, 2H), 2.13 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.7, 128.5, 128.2, 122.4, 85.8, 85.4, 33.4, 27.9, 25.7.



1b

2-((4-chlorophenyl)ethynyl)-1,3-dithiane (1b)

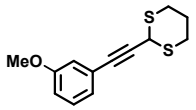
Colorless oil, R_f = 0.4 (PE/EA = 15:1), 887 mg, 58% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 2H), 7.24 – 7.14 (m, 2H), 4.75 (s, 1H), 3.22 – 3.07 (m, 2H), 2.80 – 2.64 (m, 2H), 2.07 – 1.85 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.7, 128.5, 128.2, 122.4, 85.8, 85.4, 33.4, 27.9, 25.7. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{12}H_{11}ClS_2Na^+$ 276.9883, found 276.9880.



1c

2-((4-methoxyphenyl)ethynyl)-1,3-dithiane (1c)

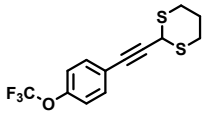
White solid, R_f = 0.4 (PE/EA = 7:1), 691 mg, 46% isolated yield. m.p. 115-117 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.81 (s, 1H), 3.80 (s, 3H), 3.36 – 3.15 (m, 2H), 3.02 – 2.68 (m, 2H), 2.34 – 1.86 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 133.3, 114.5, 113.9, 86.0, 83.9, 55.3, 33.8, 28.2, 25.8. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{13}H_{14}OS_2Na^+$ 273.0378, found.273.0367.



1d

2-((3-Methoxyphenyl)ethynyl)-1,3-dithiane (1d)

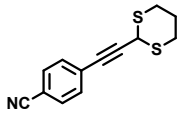
White solid, R_f = 0.6 (PE/EA = 10:1), 600 mg, 40% isolated yield. m.p. 111-113 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 1H), 7.07 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.00 (dd, *J* = 2.6, 1.4 Hz, 29 1H), 6.91 – 6.86 (m, 1H), 4.79 (s, 1H), 3.80 (s, 3H), 3.35 – 3.24 (m, 2H), 2.87 – 2.78 (m, 2H), 2.13 – 2.05 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4, 129.5, 124.5, 123.6, 116.8, 115.3, 86.0, 85.3, 55.4, 33.5, 28.1, 25.9. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{13}H_{14}OS_2Na^+$ 273.0378, found.273.0376.



1e

5-(1,3-dithian-2-yl)-2,3,4-triphenyl-2,3-dihydrooxazole (1e)

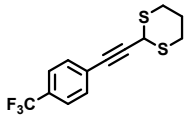
Colorless oil, R_f = 0.5 (PE/EA = 10:1), 1.13 g, 62% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.38 (m, 2H), 7.39 – 6.90 (m, 2H), 4.78 (s, 1H), 3.80 – 3.04 (m, 2H), 3.07 – 2.63 (m, 2H), 2.44 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ149.1, 133.4, 121.3, 120.8, 117.9 (q, *J* = 257.8 Hz), 86.4, 84.3, 33.3, 28.0, 25.7. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{13}H_{11}F_3OS_2Na^+$ 327.0096, found 327.0105.



1f

4-((1,3-dithian-2-yl)ethynyl)benzonitrile (1f)

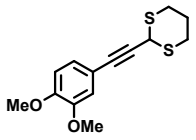
White solid, R_f = 0.4 (PE/EA = 5:1), 1.06 g, 72% isolated yield. m.p. 115-117 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 2H), 7.49 – 7.45 (m, 2H), 4.75 (s, 1H), 3.41 – 3.03 (m, 2H), 2.84 – 2.68 (m, 2H), 2.23 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.2, 131.9, 127.2, 118.2, 111.8, 90.0, 83.8, 32.9, 27.8, 25.5. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{13}H_{11}NS_2Na^+$ 268.0225, found 268.0226.



1g

2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3-dithiane (1g)

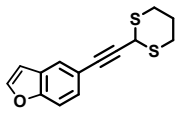
Colorless oil, R_f = 0.4 (PE/EA = 15:1), 986 mg, 57% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 6.83 (m, 4H), 4.78 (s, 1H), 3.34 – 3.08 (m, 2H), 2.89 – 2.69 (m, 2H), 2.19 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.2, 130.4 (q, *J* = 32.8 Hz), 126.4, 125.3 (d, *J* = 5.0 Hz), 121.2 (d, *J* = 272.1 Hz), 88.0, 84.4, 33.2, 28.0, 25.8. ESI-MS (TOF): $[M+Na]^+$calcd. for $C_{13}H_{11}F_3S_2Na^+$ 311.0146, found 311.0145.



1h

2-((3,4-dimethoxyphenyl)ethynyl)-1,3-dithiane (1h)

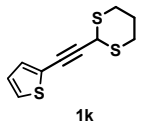
White solid, R_f = 0.3 (PE/EA = 5:1), 892 mg, 53% isolated yield. m.p. 132-133 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.11 – 7.07 (m, 1H), 6.97 (s, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 4.83 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.40 – 3.18 (m, 2H), 2.98 – 2.77 (m, 2H), 2.12 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 148.7, 125.4, 114.7, 114.6, 111.0, 86.1, 83.8, 56.1, 56.0, 33.8, 28.3, 25.9. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{14}H_{16}O_2S_2Na^+$ 303.0484, found 303.0492.



1j

5-((1,3-dithian-2-yl)ethynyl)benzofuran (1j)

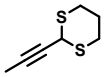
White solid, R_f = 0.4 (PE/EA = 5:1), 969 mg, 62% isolated yield. m.p. 142-143 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.68 (m, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.33 (m, 2H), 6.72 (dt, *J* = 2.0, 1.0 Hz, 1H), 4.82 (s, 1H), 3.43 – 3.18 (m, 2H), 2.88 – 2.74 (m, 2H), 2.12 – 2.00 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 146.0, 128.3, 127.6, 125.1, 117.0, 111.6, 106.5, 86.4, 83.9, 33.7, 28.1, 25.9. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{14}H_{12}OS_2Na^+$ 283.0222, found 283.0218.



1k

2-(thiophen-2-ylethynyl)-1,3-dithiane (1k)

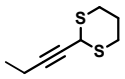
Yellow solid, R_f = 0.6 (PE/EA = 15:1), 747 mg, 55% isolated yield. m.p. 118-119 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 2H), 6.94 – 6.87 (m, 1H), 4.72 (s, 1H), 3.32 – 3.11 (m, 2H), 2.79 – 2.67 (m, 2H), 2.12 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.6, 132.5, 127.6, 127.6, 127.1, 127.1, 122.4, 89.2, 79.2, 33.5, 33.4, 27.9, 25.9. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{10}H_{10}S_3Na^+$ 248.9837, found 248.9847.



1l

2-(prop-1-yn-1-yl)-1,3-dithiane (1l)

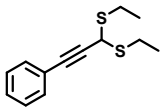
Colorless oil, R_f = 0.5 (PE/EA = 20:1), 541 mg, 57% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.54 (s, 1H), 3.57 – 3.14 (m, 2H), 3.04 – 2.75 (m, 2H), 2.73 (d, *J* = 2.5 Hz, 3H), 2.24 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.3, 75.3, 33.7, 28.5, 25.7, 3.9. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_7H_{10}S_2Na^+$ 181.0116, found 181.0114.



1m

2-(but-1-yn-1-yl)-1,3-dithiane (1m)

Colorless oil, R_f = 0.6 (PE/EA = 25:1), 558 mg, 54% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.63 (s, 1H), 3.22 – 3.09 (m, 2H), 2.85 – 2.75 (m, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.09 – 1.98 (m, 2H), 1.17 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 88.3, 75.5, 33.8, 28.5, 25.8, 13.9, 12.7. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_8H_{13}S_2^+$173.0453, found. 173.0455

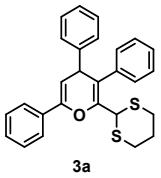


1n

(3-phenylprop-2-yne-1,1-diyl)bis(ethylsulfane) (1n)

Colorless oil, R_f = 0.5 (PE/EA = 30:1), 1.02 g, 72% isolated yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 2H), 7.27 – 7.21 (m, 3H), 4.80 (s, 1H), 2.77 (q, *J* = 7.4 Hz, 4H), 1.27 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 130.7, 127.5,

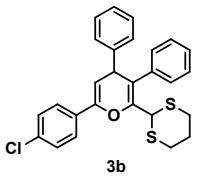
127.2, 121.4, 84.8, 84.3, 37.0, 24.5, 13.3. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{13}H_{16}S_2Na^+$ 259.0586, found 259.0589.



3a

2-(1,3-dithian-2-yl)-3,4,6-triphenyl-4*H*-pyran (3a)

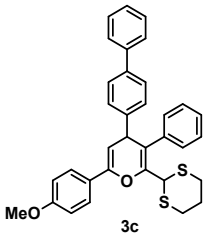
Orange solid, R_f = 0.4 (PE/EA = 10:1), 23.6 mg, 55% isolated yield, m.p. 152-153 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 2H), 7.40 – 7.30 (m, 3H), 7.25 – 7.15 (m, 8H), 7.12 – 7.07 (m, 2H), 5.54 (d, *J* = 4.7 Hz, 1H), 4.81 (s, 1H), 4.29 (d, *J* = 4.7 Hz, 1H), 2.99 – 2.90 (m, 2H), 2.87 – 2.75 (m, 2H), 2.06 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.0, 145.8, 144.8, 138.1, 133.9, 128.9, 128.6, 128.6, 128.5, 128.4, 127.4, 126.9, 124.9, 114.5, 101.1, 46.8, 44.7, 30.9, 30.7, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{27}H_{25}OS_2^+$ 429.1342, found 429.1327.



3b

6-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3,4-diphenyl-4*H*-pyran (3b)

Yellow solid, R_f = 0.4 (PE/EA = 10:1), 31.5 mg, 68% isolated yield, m.p. 108-110 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.62 (m, 2H), 7.36 – 7.32 (m, 2H), 7.27 – 7.14 (m, 8H), 7.11 – 7.06 (m, 2H), 5.52 (d, *J* = 4.7 Hz, 1H), 4.83 (s, 1H), 4.28 (d, *J* = 4.7 Hz, 1H), 3.01 – 2.81 (m, 4H), 2.09 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 145.5, 144.5, 137.9, 134.3, 132.4, 129.1, 128.9, 128.7, 128.5, 128.4, 127.5, 127.0, 126.2, 114.7, 101.6, 47.1, 44.6, 31.0, 30.8, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{27}H_{24}ClOS_2^+$ 463.0952, found 463.0961.

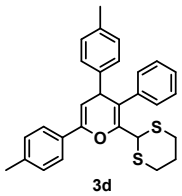


3c

4-([1,1'-biphenyl]-4-yl)-2-(1,3-dithian-2-yl)-6-(4-methoxyphenyl)-3-phenyl-4*H*-

pyran (3c)

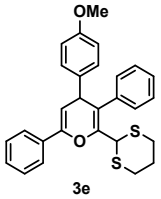
Yellow solid, R_f = 0.3 (PE/EA = 10:1), 28.3 mg, 53% isolated yield, m.p. 128-130 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.61 (m, 2H), 7.59 – 7.50 (m, 2H), 7.52 – 7.43 (m, 2H), 7.45 – 7.35 (m, 2H), 7.35 – 7.26 (m, 2H), 7.29 – 7.19 (m, 5H), 7.16 – 7.11 (m, 2H), 6.94 – 6.89 (m, 2H), 5.45 (d, *J* = 4.8 Hz, 1H), 4.83 (s, 1H), 4.32 (d, *J* = 4.8 Hz, 1H), 3.83 (s, 3H), 2.98 – 2.90 (m, 2H), 2.88 – 2.78 (m, 2H), 2.08 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 148.0, 145.9, 144.1, 141.0, 139.6, 138.2, 129.0, 128.9, 128.8, 128.4, 127.4, 127.3, 127.2, 127.1, 126.7, 126.4, 114.5, 113.9, 99.4, 55.5, 47.0, 44.4, 31.0, 30.7, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{34}H_{31}O_2S_2^+$ 535.1760, found 535.1771.



3d

2-(1,3-dithian-2-yl)-3-phenyl-4,6-di-p-tolyl-4*H*-pyran (3d)

Yellow solid, R_f = 0.5 (PE/EA = 20:1), 20.9 mg, 46% isolated yield, m.p. 178-179 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 2H), 7.26 – 7.16 (m, 6H), 7.11 – 7.02 (m, 6H), 5.47 (d, *J* = 4.7 Hz, 1H), 4.79 (s, 1H), 4.24 (d, *J* = 4.7 Hz, 1H), 3.00 – 2.91 (m, 2H), 2.86 – 2.75 (m, 2H), 2.36 (s, 3H), 2.27 (s, 3H), 2.05 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.0, 145.9, 142.0, 138.3, 136.3, 131.2, 129.3, 129.1, 129.0, 128.4, 128.4, 127.3, 124.9, 114.6, 100.6, 46.7, 44.2, 30.8, 30.6, 25.3, 21.4, 21.2. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{29}H_{29}OS_2^+$ 457.1665, found 457.1645.

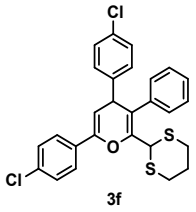


3e

2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-3,6-diphenyl-4*H*-pyran (3e)

Golden yellow solid, R_f = 0.3 (PE/EA = 10:1), 26.6 mg, 58% isolated yield, m.p. 106-108 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.39 – 7.30 (m, 3H), 7.24 – 7.20 (m, 3H), 7.11 – 7.06 (m, 4H), 6.79 – 6.74 (m, 2H), 5.51 (d, *J* = 4.8, 1.6 Hz, 1H), 4.80 (s, 1H), 4.22 (d, *J* = 4.7, 1.6 Hz, 1H), 3.73 (s, 3H), 2.97 – 2.89 (m, 2H), 2.86

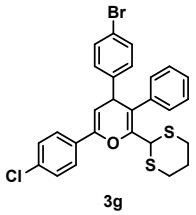
– 2.75 (m, 2H), 2.04 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 147.8, 145.6, 138.2, 137.1, 134.0, 129.5, 129.0, 128.5, 128.4, 127.4, 124.9, 114.8, 114.0, 101.4, 55.3, 46.8, 43.8, 30.9, 30.6, 29.8, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{28}H_{27}O_2S_2^+$ 459.1447, found 459.1432.



3f

4,6-bis(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-phenyl-4*H*-pyran (3f)

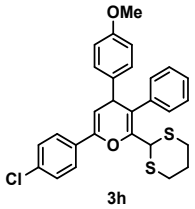
Yellowish black solid, R_f = 0.4 (PE/EA = 10:1), 31.8 mg, 64% isolated yield, m.p. 118-120 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 2H), 7.38 – 7.31 (m, 2H), 7.28 – 7.17 (m, 5H), 7.12 – 7.04 (m, 4H), 5.47 (d, *J* = 4.8 Hz, 1H), 4.81 (s, 1H), 4.28 (d, *J* = 4.8 Hz, 1H), 2.97 – 2.77 (m, 4H), 2.11 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 145.7, 143.0, 137.5, 134.5, 132.7, 132.2, 129.8, 128.8, 128.8, 128.7, 128.5, 127.7, 126.2, 114.3, 101.0, 47.0, 44.0, 31.0, 30.7, 25.2. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{27}H_{23}Cl_2OS_2^+$ 497.0562, found 497.0545.



3g

4-(4-bromophenyl)-6-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-phenyl-4*H*-pyran (3g)

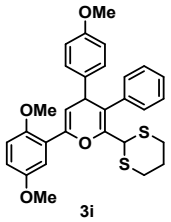
Golden yellow solid, R_f = 0.4 (PE/EA = 10:1), 26.9 mg, 50% isolated yield, m.p. 92-93 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 2H), 7.36 – 7.31 (m, 4H), 7.26 – 7.21 (m, 3H), 7.11 – 7.06 (m, 2H), 7.05 – 7.00 (m, 2H), 5.47 (d, *J* = 4.8 Hz, 1H), 4.81 (s, 1H), 4.27 (d, *J* = 4.7 Hz, 1H), 2.95 – 2.75 (m, 4H), 2.07 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 145.8, 143.6, 137.6, 134.5, 132.2, 131.8, 130.2, 128.8, 128.7, 128.6, 127.7, 126.3, 120.9, 114.3, 100.9, 47.0, 44.1, 31.0, 30.7, 25.2. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{27}H_{22}BrClOS_2Na^+$ 562.9876, found 562.9892.



3h

6-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-3-phenyl-4*H*-pyran (3h)

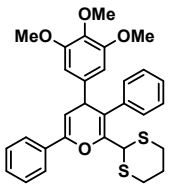
Orange solid, R_f = 0.3 (PE/EA = 10:1), 25.1 mg, 51% isolated yield, m.p. 88-90 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 2H), 7.34 – 7.31 (m, 2H), 7.23 – 7.20 (m, 3H), 7.10 – 7.04 (m, 4H), 6.79 – 6.74 (m, 2H), 5.49 (d, *J* = 4.9 Hz, 1H), 4.80 (s, 1H), 4.21 (d, *J* = 4.9 Hz, 1H), 3.74 (s, 3H), 2.94 – 2.77 (m, 4H), 2.05 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 146.9, 145.3, 138.0, 136.8, 134.3, 132.5, 129.5, 128.9, 128.7, 128.4, 127.5, 126.2, 115.0, 114.0, 101.8, 55.3, 47.1, 43.7, 31.0, 30.8, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{28}H_{26}ClO_2S_2^+$ 493.1057, found 493.1038.



3i

6-(2,5-dimethoxyphenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-3-phenyl-4*H*-pyran (3i)

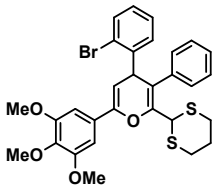
Faint yellow solid, R_f = 0.5 (PE/EA = 3:1), 27.5 mg, 53% isolated yield, m.p. 166-168 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 1H), 7.26 – 7.19 (m, 4H), 7.13 – 7.06 (m, 4H), 6.86 – 6.80 (m, 2H), 6.80 – 6.74 (m, 2H), 5.87 (d, *J* = 8.2 Hz, 1H), 4.75 (s, 1H), 4.24 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.03 – 2.72 (m, 4H), 2.04 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.4, 153.6, 151.4, 146.1, 144.6, 138.4, 137.4, 129.5, 129.1, 128.3, 127.2, 123.9, 114.6, 114.3, 113.9, 113.9, 112.9, 106.5, 56.4, 55.9, 55.3, 46.1, 44.0, 30.5, 30.3, 25.4. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{31}O_4S_2^+$ 519.1659, found 519.1653.



3j

2-(1,3-dithian-2-yl)-3,6-diphenyl-4-(3,4,5-trimethoxyphenyl)-4*H*-pyran (3j)

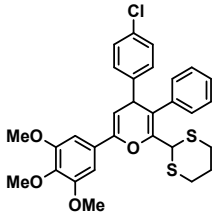
Orange solid, R_f = 0.5 (PE/EA = 3:1), 31.6 mg, 61% isolated yield, m.p. 83-84.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 2H), 7.39 – 7.30 (m, 3H), 7.26 – 7.22 (m, 3H), 7.15 – 7.11 (m, 2H), 6.41 (s, 2H), 5.56 (d, *J* = 5.1 Hz, 1H), 4.88 (s, 1H), 4.17 (d, *J* = 5.0 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 6H), 2.94 – 2.78 (m, 4H), 2.05 – 1.92 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 148.2, 146.0, 140.6, 138.1, 136.8, 133.9, 128.9, 128.6, 128.5, 128.4, 127.5, 124.9, 114.5, 105.2, 101.1, 60.9, 56.2, 47.1, 44.7, 31.0, 30.6, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{31}O_4S_2^+$ 519.1659, found 519.1652.



3k

4-(2-bromophenyl)-2-(1,3-dithian-2-yl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (3k)

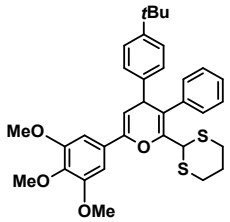
Faint yellow solid, R_f = 0.5 (PE/EA = 3:1), 29.8 mg, 50% isolated yield, m.p. 168-169.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.59 (m, 1H), 7.56 – 7.52 (m, 1H), 7.36 – 7.31 (m, 1H), 7.27 – 7.20 (m, 4H), 7.11 – 7.08 (m, 2H), 6.48 (s, 2H), 5.26 (d, *J* = 4.6 Hz, 1H), 4.70 (s, 1H), 4.17 (d, *J* = 4.6 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 6H), 3.03 – 2.96 (m, 1H), 2.94 – 2.87 (m, 1H), 2.78 – 2.67 (m, 2H), 1.98 – 1.88 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 148.4, 146.8, 140.3, 138.1, 136.7, 136.2, 133.3, 131.1, 130.3, 129.1, 128.4, 127.5, 122.9, 113.7, 105.8, 105.5, 61.0, 56.2, 45.0, 44.7, 30.3, 30.1, 25.1. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{30}BrO_4S_2^+$ 597.0764, found 597.0747.



3l

4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (3l)

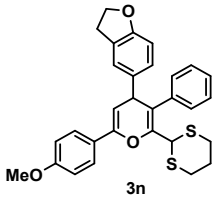
Faint yellow solid, R_f = 0.5 (PE/EA = 3:1), 32.6 mg, 59% isolated yield, m.p. 160-161 ^{o}C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 5H), 7.13 – 7.08 (m, 4H), 6.97 (s, 2H), 5.42 (d, *J* = 4.8 Hz, 1H), 4.81 (s, 1H), 4.28 (d, *J* = 4.8 Hz, 1H), 3.90 (s, 6H), 3.86 (s, 3H), 2.99 – 2.92 (m, 2H), 2.86 – 2.78 (m, 2H), 2.07 – 2.02 (m, 1H), 1.96 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 148.1, 146.0, 143.3, 138.6, 137.6, 132.6, 129.8, 129.7, 129.4, 128.8, 128.7, 128.5, 127.6, 114.2, 102.3, 100.3, 61.0, 56.2, 46.3, 44.1, 30.6, 30.4, 25.4. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{30}ClO_4S_2^+$ 553.1269, found 553.1258.



3m

4-(4-(tert-butyl)phenyl)-2-(1,3-dithian-2-yl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (3m)

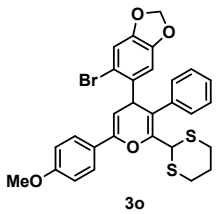
Faint yellow solid, R_f = 0.2 (PE/EA = 4:1), 27.4 mg, 53% isolated yield, m.p. 170-171.5 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 5H), 7.14 – 7.07 (m, 4H), 6.98 (s, 2H), 5.49 (d, *J* = 5.0 Hz, 1H), 4.82 (s, 1H), 4.22 (d, *J* = 5.0 Hz, 1H), 3.90 (s, 6H), 3.86 (s, 3H), 3.00 – 2.92 (m, 2H), 2.87 – 2.76 (m, 2H), 2.08 – 2.01 (m, 1H), 1.98 – 1.88 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 149.8, 147.9, 145.9, 141.8, 138.5, 138.1, 129.8, 129.0, 128.4, 128.1, 127.4, 125.6, 114.9, 102.5, 101.2, 61.0, 56.3, 46.6, 44.2, 34.6, 31.5, 30.7, 30.5, 25.6. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{30}O_4S_2^+$ 518.1580, found 518.1582.



3n

5-(2-(1,3-dithian-2-yl)-6-(4-methoxyphenyl)-3-phenyl-4*H*-pyran-4-yl)-2,3-dihydrobenzofuran (3n)

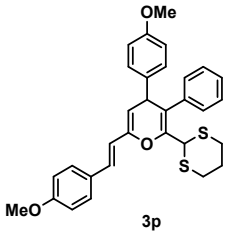
Orange solid, R_f = 0.2 (PE/EA = 10:1), 25.5 mg, 51% isolated yield, m.p. 78-80 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 2H), 7.23 (d, *J* = 6.7 Hz, 3H), 7.12 – 7.08 (m, 2H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.84 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 5.40 (d, *J* = 4.7 Hz, 1H), 4.80 (s, 1H), 4.51 (t, *J* = 8.7 Hz, 2H), 4.18 (d, *J* = 4.7 Hz, 1H), 3.82 (s, 3H), 3.13 (td, *J* = 8.6, 3.8 Hz, 2H), 2.97 – 2.89 (m, 2H), 2.86 – 2.77 (m, 2H), 2.06 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 160.3, 151.0, 137.7, 130.3, 130.1, 128.9, 128.6, 128.5, 127.5, 127.2, 127.0, 127.0, 125.3, 123.6, 113.6, 109.2, 98.1, 79.7, 71.5, 55.4, 48.5, 31.2, 31.0, 29.7, 25.0. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{30}H_{28}O_3S_2Na^+$ 523.1372, found 523.1372.



3o

5-(2-(1,3-dithian-2-yl)-6-(4-methoxyphenyl)-3-phenyl-4*H*-pyran-4-yl)-6-bromobenzo[*d*][1,3]dioxole (3o)

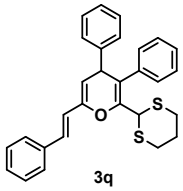
Faint yellow solid, R_f = 0.4 (PE/EA = 3:1), 30.2 mg, 52% isolated yield, m.p. 107-108 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.29 – 7.22 (m, 5H), 7.01 (s, 1H), 6.93 – 6.89 (m, 2H), 6.83 (s, 1H), 5.94 – 5.88 (m, 2H), 5.39 (d, *J* = 4.7 Hz, 1H), 4.92 (s, 1H), 4.88 (d, *J* = 4.8 Hz, 1H), 3.82 (s, 3H), 3.01 – 2.82 (m, 4H), 2.07 – 1.97 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 148.2, 148.2, 147.2, 147.1, 137.6, 137.1, 128.8, 128.5, 127.6, 126.5, 126.3, 113.9, 113.4, 113.1, 112.2, 110.4, 101.8, 98.2, 55.5, 46.8, 42.8, 31.0, 30.7, 25.3. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{29}H_{25}BrO_4S_2Na^+$ 603.0270, found 603.0274.



3p

(*E*)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-6-(4-methoxystyryl)-3-phenyl-*4H*-pyran (3p)

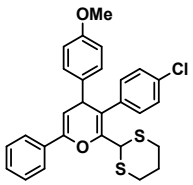
Dark yellow solid, R_f = 0.4 (PE/EA = 5:1), 24.7 mg, 48% isolated yield, m.p. 93-94 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.39 (m, 2H), 7.23 – 7.19 (m, 3H), 7.07 – 7.03 (m, 5H), 6.88 – 6.85 (m, 2H), 6.78 – 6.75 (m, 2H), 6.39 – 6.35 (m, 1H), 5.08 (d, *J* = 4.7 Hz, 1H), 4.71 (s, 1H), 4.16 (d, *J* = 4.6 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.09 – 3.01 (m, 2H), 2.84 – 2.76 (m, 2H), 2.06 – 2.02 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 158.5, 147.4, 146.2, 138.3, 137.1, 129.8, 129.5, 129.0, 128.6, 128.4, 128.1, 127.3, 120.0, 114.2, 114.1, 113.9, 105.8, 55.4, 55.3, 45.7, 43.9, 30.5, 30.2, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{31}H_{31}O_3S_2^+$ 515.1709, found 515.1701.



3q

(*E*)-2-(1,3-dithian-2-yl)-3,4-diphenyl-6-styryl-4*H*-pyran (3q)

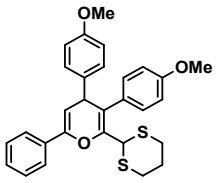
Brown yellow solid, R_f = 0.4 (PE/EA = 10:1), 19.9 mg, 44% isolated yield, m.p. 208-210 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.45 (m, 2H), 7.35 – 7.32 (m, 2H), 7.26 – 7.19 (m, 6H), 7.17 – 7.14 (m, 3H), 7.12 – 7.09 (m, 1H), 7.07 – 7.04 (m, 2H), 6.52 – 6.48 (m, 1H), 5.15 (d, *J* = 4.7 Hz, 1H), 4.73 (s, 1H), 4.23 (d, *J* = 4.7 Hz, 1H), 3.10 – 3.02 (m, 2H), 2.85 – 2.77 (m, 2H), 2.06 – 2.02 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.4, 146.4, 144.6, 138.1, 136.9, 129.3, 129.0, 128.7, 128.6, 128.6, 128.4, 128.0, 127.9, 127.4, 126.9, 126.9, 121.9, 113.8, 106.6, 45.6, 44.8, 30.5, 30.2, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{29}H_{27}OS_2^+$ 455.1498, found 455.1484.



4a

3-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-6-phenyl-4*H*-pyran (4a)

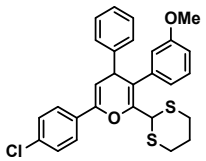
Golden yellow solid, R_f = 0.3 (PE/EA = 10:1), 28.5 mg, 58% isolated yield, m.p. 74-76 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.66 (m, 2H), 7.39 – 7.30 (m, 3H), 7.21 – 7.17 (m, 2H), 7.08 – 6.99 (m, 4H), 6.80 – 6.75 (m, 2H), 5.50 (d, *J* = 4.7 Hz, 1H), 4.72 (s, 1H), 4.18 (d, *J* = 4.6 Hz, 1H), 3.75 (s, 3H), 2.96 – 2.89 (m, 2H), 2.86 – 2.76 (m, 2H), 2.07 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 147.8, 145.7, 136.8, 136.6, 133.8, 133.3, 130.4, 129.5, 128.6, 128.6, 128.5, 124.9, 114.1, 113.7, 101.2, 55.3, 47.0, 43.7, 31.0, 30.7, 25.2. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{28}H_{26}ClO_2S_2^+$ 493.1057, found 493.1035.



4b

2-(1,3-dithian-2-yl)-3,4-bis(4-methoxyphenyl)-6-phenyl-4*H*-pyran (4b)

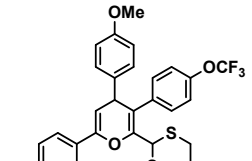
Golden yellow solid, R_f = 0.4 (PE/EA = 5:1), 29.8 mg, 61% isolated yield, m.p. 82-83 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 7.12 – 7.07 (m, 2H), 7.04 – 6.99 (m, 2H), 6.80 – 6.74 (m, 4H), 5.51 (d, *J* = 4.7 Hz, 1H), 4.82 (s, 1H), 4.19 (d, *J* = 4.7 Hz, 1H), 3.77 (d, 6H), 2.98 – 2.92 (m, 2H), 2.87 – 2.80 (m, 2H), 2.05 – 1.97 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.8, 158.5, 147.8, 145.5, 137.3, 134.1, 130.5, 130.1, 129.6, 128.5, 124.9, 114.4, 114.0, 113.7, 101.3, 55.3, 55.3, 47.0, 43.9, 31.0, 30.7, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{29}H_{29}O_3S_2^+$ 489.1553, found 489.1564.



4c

6-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-(3-methoxyphenyl)-4-phenyl-4*H*-pyran (4c)

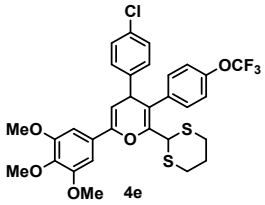
Faint yellow solid, R_f = 0.3 (PE/EA = 10:1), 31.0 mg, 63% isolated yield, m.p. 83-85 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 7.21 – 7.11 (m, 4H), 6.78 – 6.74 (m, 1H), 6.72 – 6.68 (m, 1H), 6.62 (s, 1H), 5.52 (d, *J* = 4.7 Hz, 1H), 4.88 (s, 1H), 4.27 (d, *J* = 4.8 Hz, 1H), 3.65 (s, 3H), 2.94 – 2.82 (m, 4H), 2.06 – 1.95 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3, 147.0, 145.5, 144.6, 139.2, 134.3, 132.4, 129.4, 128.7, 128.7, 128.5, 127.0, 126.2, 121.2, 114.5, 113.9, 113.7, 101.6, 55.2, 47.1, 44.5, 31.0, 30.7, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{28}H_{26}ClO_2S_2^+$ 493.1058, found 493.1035.



4d

6-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)-4*H*-pyran (4d)

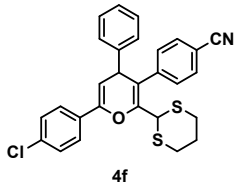
Golden yellow solid, R_f = 0.4 (PE/EA = 5:1), 24.8 mg, 43% isolated yield, m.p. 75-77 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.36 – 7.32 (m, 2H), 7.13 – 7.05 (m, 6H), 6.82 – 6.76 (m, 2H), 5.50 (d, *J* = 4.7 Hz, 1H), 4.74 (s, 1H), 4.17 (d, *J* = 4.7 Hz, 1H), 3.76 (s, 3H), 2.97 – 2.79 (m, 4H), 2.10 – 1.92 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.7, 148.6, 146.9, 145.7, 136.6, 136.5, 134.4, 132.3, 130.4, 129.5, 128.7, 126.2, 120.7, 120.5 (d, *J* = 257.3 Hz) ,114.2, 113.7, 101.6, 55.3, 47.1, 43.7, 31.0, 30.8, 25.2. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{29}H_{25}ClF_3O_3S_2^+$ 577.0880, found 577.0891.



4e

4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-(4-(trifluoromethoxy)phenyl)-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (4e)

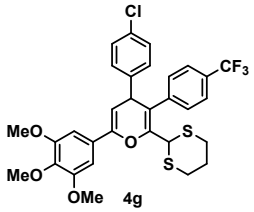
Golden yellow solid, R_f = 0.4 (PE/EA = 3:1), 38.7 mg, 61% isolated yield, m.p. 170-171 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 2H), 7.14 – 7.09 (m, 6H), 6.96 (s, 2H), 5.43 (d, *J* = 4.8 Hz, 1H), 4.75 (s, 1H), 4.24 (d, *J* = 4.8 Hz, 1H), 3.90 (s, 6H), 3.87 (s, 3H), 3.00 – 2.93 (m, 2H), 2.90 – 2.80 (m, 2H), 2.11 – 2.04 (m, 1H), 1.99 – 1.89 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 148.6, 148.6 (q, *J* = 1.9 Hz), 148.1, 146.4, 142.9, 138.6, 136.2, 132.8, 130.4, 129.7, 129.2, 128.9, 120.8, 120.5 (q, *J* = 257.5 Hz), 112.9, 102.3, 100.2, 61.0, 56.2, 46.3, 44.1, 30.7, 30.4, 25.3. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{31}H_{28}ClF_3O_5S_2Na^+$ 659.0911, found 659.0904.



4f

4-(6-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-4-phenyl-4*H*-pyran-3-yl)benzonitrile (4f)

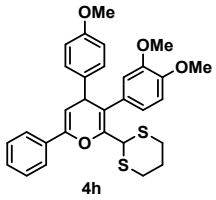
Faint yellow solid, R_f = 0.4 (PE/EA = 10:1), 29.2 mg, 60% isolated yield, m.p. 136-138 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 2H), 7.55 – 7.50 (m, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.17 (m, 5H), 7.16 – 7.11 (m, 2H), 5.53 (d, *J* = 4.7 Hz, 1H), 4.68 (s, 1H), 4.27 (d, *J* = 4.7 Hz, 1H), 2.96 – 2.78 (m, 4H), 2.10 – 1.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 146.2, 143.8, 142.9, 134.6, 132.3, 132.0, 129.8, 128.9, 128.8, 128.4, 127.4, 126.2, 118.8, 113.3, 111.5, 101.3, 47.1, 44.3, 31.1, 30.8, 25.1. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{28}H_{22}ClNOS_2Na^+$ 510.0723, found 510.0724.



4g

4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-(4-(trifluoromethyl)phenyl)-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (4g)

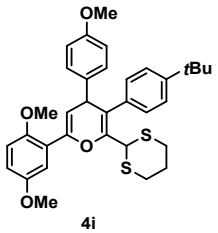
Orange solid, R_f = 0.5 (PE/EA = 4:1), 40.4 mg, 65% isolated yield, m.p. 174-175 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 – 7.50 (m, 2H), 7.25 – 7.21 (m, 4H), 7.13 – 7.10 (m, 2H), 6.97 (s, 2H), 5.45 (d, *J* = 4.8 Hz, 1H), 4.72 (s, 1H), 4.28 (d, *J* = 4.8 Hz, 1H), 3.91 (s, 6H), 3.87 (s, 3H), 2.98 – 2.80 (m, 4H), 2.10 – 2.03 (m, 1H), 1.98 – 1.89 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.2, 148.1, 146.5, 142.7, 141.4, 141.4, 138.6, 132.9, 129.7, 129.6 (q, *J* = 32.4 Hz), 129.2, 129.1, 128.9, 125.49 (q, *J* = 3.9 Hz), 124.1(q, *J* = 272.1 Hz), 113.0, 102.3, 100.1, 61.0, 56.2, 46.4, 44.0, 30.6, 30.4, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{31}H_{29}ClF_3O_4S_2^+$ 621.1143, found 621.1131.



4h

3-(3,4-dimethoxyphenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-6-phenyl-4*H*-pyran (4h)

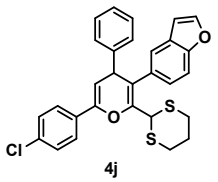
Dark yellow solid, R_f = 0.5 (PE/EA = 3:1), 26.4 mg, 51% isolated yield, m.p. 85-87 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.26 (s, 1H), 7.14 – 7.09 (m, 2H), 6.82 – 6.78 (m, 2H), 6.75 – 6.72 (m, 1H), 6.68 – 6.64 (m, 1H), 6.61 – 6.57 (m, 1H), 5.52 (d, *J* = 4.7 Hz, 1H), 4.86 (s, 1H), 4.19 (d, *J* = 4.7 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 2.99 – 2.91 (m, 2H), 2.89 – 2.80 (m, 2H), 2.09 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 148.3, 148.1, 147.7, 145.5, 137.4, 134.0, 130.7, 129.6, 128.5, 124.9, 121.1, 114.5, 114.0, 112.3, 110.8, 101.3, 55.8, 55.4, 47.1, 43.8, 31.0, 30.7, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{31}O_4S_2^+$ 519.1659, found 519.1641.



4i

3-(4-(tert-butyl)phenyl)-6-(2,5-dimethoxyphenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-4*H*-pyran (4i)

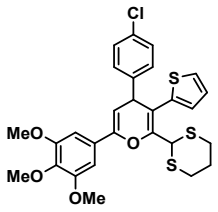
Brown yellow solid, R_f = 0.2 (PE/EA = 4:1), 28.7 mg, 50% isolated yield, m.p. 194-196 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.45 (m, 1H), 7.24 – 7.21 (m, 2H), 7.16 – 7.12 (m, 2H), 7.05 – 7.01 (m, 2H), 6.83 – 6.77 (m, 4H), 5.87 (d, *J* = 5.0 Hz, 1H), 4.84 (s, 1H), 4.20 (d, *J* = 5.1 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 6H), 3.03 – 2.95 (m, 2H), 2.86 – 2.76 (m, 2H), 2.05 – 1.93 (m, 2H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.3, 153.6, 151.4, 150.0, 146.5, 144.5, 137.7, 135.3, 129.5, 128.5, 125.2, 123.9, 114.6, 114.0, 113.9, 113.9, 112.8, 106.8, 56.3, 55.9, 55.3, 45.8, 43.8, 34.6, 31.5, 31.4, 31.3, 30.4, 30.1, 25.5. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{34}H_{39}O_4S_2^+$ 575.2285, found 575.2274.



4j

5-(4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran-3-yl)benzofuran (4j)

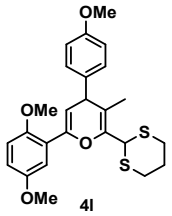
Orange solid, R_f = 0.2 (PE/EA = 10:1), 33.2 mg, 56% isolated yield, m.p. 103-105 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.60 – 7.57 (m, 1H), 7.37 – 7.33 (m, 3H), 7.31 – 7.29 (m, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.15 (m, 3H), 7.03 – 6.99 (m, 1H), 6.68 (s, 1H), 5.54 (d, *J* = 4.7 Hz, 1H), 4.82 (s, 1H), 4.30 (d, *J* = 4.7 Hz, 1H), 2.94 – 2.76 (m, 4H), 2.04 – 1.93 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) 159.9, 159.0, 147.5, 145.4, 138.3, 137.4, 129.0, 128.3, 128.1, 127.4, 127.3, 126.8, 126.3, 125.1, 115.1, 113.8, 108.9, 100.0, 71.4, 55.5, 47.1, 44.0, 31.0, 30.7, 29.9, 25.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{32}H_{30}ClO_5S_2^+$ 593.1218, found 593.1208.



4k

4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-(thiophen-2-yl)-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (4k)

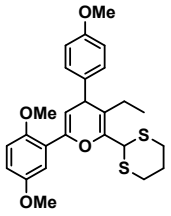
Faint yellow solid, R_f = 0.4 (PE/EA = 3:1), 27.4 mg, 49% isolated yield, m.p. 215-216 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 5H), 6.93 – 6.87 (m, 4H), 5.40 (d, *J* = 4.9 Hz, 1H), 5.18 (s, 1H), 4.27 (d, *J* = 4.9 Hz, 1H), 3.88 (s, 6H), 3.84 (s, 3H), 3.05 – 2.85 (m, 4H), 2.13 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 147.9, 147.6, 143.3, 139.1, 138.7, 132.9, 129.8, 129.1, 128.9, 127.2, 126.9, 125.7, 107.4, 102.4, 100.5, 61.0, 56.2, 46.3, 44.5, 30.6, 30.4, 25.4. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{28}H_{28}ClO_4S_3^+$ 559.0833, found 559.0822.



4l

6-(2,5-dimethoxyphenyl)-2-(1,3-dithian-2-yl)-4-(4-methoxyphenyl)-3-methyl-4*H*-pyran (4l)

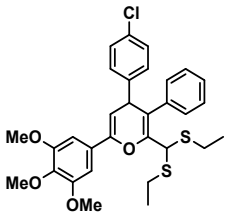
Brown red solid, R_f = 0.4 (PE/EA = 4:1), 21.9 mg, 48% isolated yield, m.p. 131-132 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 1H), 7.23 – 7.19 (m, 2H), 6.87 – 6.83 (m, 2H), 6.82 – 6.76 (m, 2H), 5.71 (d, *J* = 4.5 Hz, 1H), 5.12 (s, 1H), 3.92 (d, *J* = 4.6 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.03 – 2.92 (m, 4H), 2.15 – 2.07 (m, 1H), 2.00 – 1.90 (m, 1H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 153.5, 151.3, 144.1, 143.0, 137.6, 129.4, 123.9, 114.3, 113.9, 113.8, 112.8, 108.5, 105.6, 56.3, 55.9, 55.4, 46.9, 43.8, 31.4, 31.3, 25.6, 15.9. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{25}H_{29}O_4S_2^+$ 457.1502, found 457.1496.



4m

6-(2,5-dimethoxyphenyl)-2-(1,3-dithian-2-yl)-3-ethyl-4-(4-methoxyphenyl)-4*H*-pyran (4m)

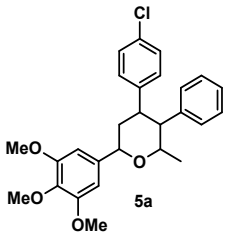
Brown red solid, R_f = 0.5 (PE/EA = 4:1), 21.6 mg, 46% isolated yield, m.p. 74-75 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 2.7, 0.8 Hz, 1H), 7.24 – 7.20 (m, 2H), 6.87 – 6.83 (m, 2H), 6.82 – 6.76 (m, 2H), 5.75 (d, *J* = 4.7 Hz, 1H), 5.14 (s, 1H), 4.08 (d, *J* = 4.6 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.04 – 2.93 (m, 4H), 2.21 – 2.08 (m, 2H), 1.98 – 1.81 (m, 2H), 1.57 (s, 1H), 1.26 (s, 1H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 153.6, 151.4, 144.1, 142.8, 138.0, 129.5, 124.0, 114.4, 114.2, 114.0, 113.8, 112.9, 106.0, 56.4, 55.9, 55.4, 46.6, 40.8, 31.4, 31.3, 25.7, 22.7, 12.8. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{26}H_{30}O_4S_2Na^+$ 493.1478, found 493.1479.



4n

2-(bis(ethylthio)methyl)-4-(4-chlorophenyl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran (4n)

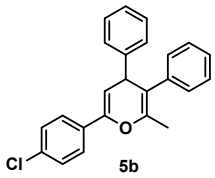
Brown solid, R_f = 0.5 (PE/EA = 3:1), 21.6 mg, 38% isolated yield, m.p. 66-68 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 5H), 7.15 – 7.12 (m, 2H), 7.04 – 7.01 (m, 2H), 6.98 (s, 2H), 5.48 (d, *J* = 4.7 Hz, 1H), 4.58 (s, 1H), 4.28 (d, *J* = 4.9 Hz, 1H), 3.89 (s, 6H), 3.87 (s, 3H), 2.74 – 2.65 (m, 2H), 2.59 – 2.53 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.3, 148.3, 145.9, 143.4, 138.7, 137.7, 132.7, 129.8, 129.4, 129.3, 128.8, 128.6, 127.6, 113.9, 102.2, 100.1, 61.1, 56.3, 47.8, 44.4, 26.3, 26.0, 14.7. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{31}H_{33}ClO_4S_2Na^+$ 591.1401, found 591.1395.



5a

4-(4-chlorophenyl)-2-methyl-3-phenyl-6-(3,4,5-trimethoxyphenyl)tetrahydro-2*H*-pyran (5a)

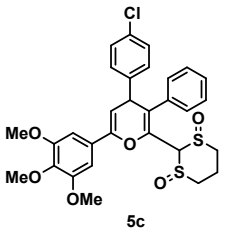
Faint yellow solid, R_f = 0.4 (PE/EA = 5:1), 40.7 mg, 90% isolated yield, m.p. 170-171 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.06 (m, 7H), 6.80 – 6.72 (m, 4H), 4.71 – 4.65 (m, 1H), 4.31 – 4.25 (m, 1H), 3.93 (s, 6H), 3.86 (s, 3H), 3.51 – 3.44 (m, 1H), 2.95 – 2.89 (m, 1H), 2.34 – 2.24 (m, 1H), 1.87 – 1.81 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 142.9, 138.8, 137.8, 137.5, 131.4, 127.9, 127.9, 127.4, 126.3, 126.2, 103.2, 80.7, 77.9, 61.0, 56.3, 51.9, 47.7, 33.2, 20.2. ESI-MS (TOF): $[M+Na]^+$ calcd. for $C_{27}H_{29}ClO_4Na^+$ 475.1646, found 475.1631.



5b

6-(4-chlorophenyl)-2-methyl-3,4-diphenyl-4*H*-pyran (5b)

Dark yellow solid, R_f = 0.4 (PE/EA = 10:1), 30.4 mg, 85% isolated yield, m.p. 62-63.5 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.14 (m, 8H), 6.97 – 6.93 (m, 2H), 5.54 (d, *J* = 4.6 Hz, 1H), 4.29 (d, *J* = 4.7 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.8, 145.5, 144.8, 139.6, 134.2, 132.9, 129.5, 128.6, 128.6, 128.5, 128.4, 128.2, 126.7, 126.0, 113.0, 101.9, 44.5, 17.3. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{24}H_{20}ClO^+$ 359.1197, found 359.1194.

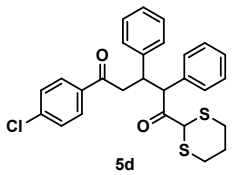


5c

2-(4-(4-chlorophenyl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran-2-yl)-1,3-dithiane 1,3-dioxide (5c)

Faint yellow solid, 52.6 mg, 90% total isolated yield, dr=1:1. isomer 1 ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.20 (m, 9H), 6.86 (s, 2H), 5.45 (d, *J* = 4.7 Hz, 1H), 4.48 (s, 1H), 4.38 (d, *J* = 4.7 Hz, 1H), 3.88 (s, 6H), 3.86 (s, 3H), 3.53 – 3.46 (m, 1H), 2.61 – 2.52 (m, 3H), 2.46 – 2.39 (m, 1H), 2.36 – 2.25 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.3, 147.2, 142.5, 139.8, 138.9, 136.8, 132.8, 130.0, 129.9, 129.0, 128.9, 128.6, 127.8, 120.6, 102.3, 100.6, 66.3, 61.1, 56.3, 54.9, 44.8, 30.6, 30.0.

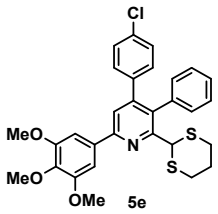
isomer 2 ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 5H), 7.15 – 7.09 (m, 4H), 6.88 (s, 2H), 5.45 (d, *J* = 4.7 Hz, 1H), 4.42 (s, 1H), 4.36 (d, *J* = 4.8 Hz, 1H), 3.89 (s, 6H), 3.86 (s, 3H), 3.49 – 3.42 (m, 1H), 2.64 – 2.57 (m, 2H), 2.55 – 2.47 (m, 1H), 2.44 – 2.37 (m, 1H), 2.34 – 2.24 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.3, 147.8, 143.0, 140.0, 138.9, 136.7, 132.8, 130.0, 129.6, 129.1, 128.9, 128.6, 127.9, 120.8, 102.4, 100.5, 66.4, 61.1, 56.3, 54.5, 44.5, 30.8, 29.9. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{29}ClO_6S_2Na^+$ 607.0986, found 607.0962.



5d

5-(4-chlorophenyl)-1-(1,3-dithian-2-yl)-2,3-diphenylpentane-1,5-dione (5d)

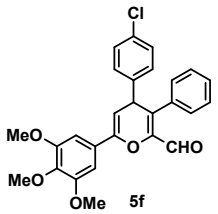
Yellow solid, R_f = 0.4 (PE/EA = 5:1), 38.4 mg, 80% isolated yield, m.p. 85-87 ˚C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 2H), 7.42 – 7.38 (m, 2H), 7.26 (s, 1H), 7.13 – 7.10 (m, 2H), 7.06 – 6.94 (m, 7H), 4.42 (d, *J* = 10.4 Hz, 1H), 4.14 (s, 1H), 4.10 – 4.03 (m, 1H), 3.56 – 3.42 (m, 3H), 3.00 – 2.93 (m, 1H), 2.67 – 2.61 (m, 1H), 2.52 – 2.46 (m, 1H), 2.14 – 2.09 (m, 1H), 2.05 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.8, 197.3, 140.6, 139.4, 135.7, 129.8, 129.2, 129.0, 128.9, 128.4, 128.2, 127.8, 126.7, 61.8, 46.0, 44.9, 43.3, 26.2, 26.1, 25.1. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{27}H_{25}ClO_2S_2Na^+$ 503.0876, found 503.0890.



5e

4-(4-chlorophenyl)-2-(1,3-dithian-2-yl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)pyridine (5e)

Orange solid, R_f = 0.5 (PE/EA = 3:1), 37.3 mg, 68% isolated yield, m.p. 176-178 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.37 (s, 2H), 7.31 – 7.28 (m, 3H), 7.23 – 7.16 (m, 4H), 7.04 – 7.00 (m, 2H), 4.99 (s, 1H), 3.97 (s, 6H), 3.92 (s, 3H), 3.32 – 3.25 (m, 2H), 2.80 – 2.73 (m, 2H), 2.12 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.8, 155.9, 153.6, 149.6, 139.4, 138.0, 136.4, 134.6, 133.9, 131.8, 130.7, 130.5, 128.4, 128.4, 127.8, 120.1, 104.6, 61.1, 56.4, 30.0, 25.7. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{30}H_{28}ClNO_3S_2Na^+$ 572.1091, found 572.1101.



5f

4-(4-chlorophenyl)-3-phenyl-6-(3,4,5-trimethoxyphenyl)-4*H*-pyran-2-carbaldehyde (5f)

Faint yellow solid, R_f = 0.4 (PE/EA = 2:1), 34.7 mg, 75% isolated yield, m.p. 146-147 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 7.34 – 7.22 (m, 6H), 7.13 – 7.10 (m, 2H), 7.07 – 7.03 (m, 2H), 6.97 (s, 2H), 5.50 (d, *J* = 4.5 Hz, 1H), 4.46 (d, *J* = 4.5 Hz, 1H), 3.91 (s, 6H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.9, 153.4, 148.1, 144.6, 141.9, 139.2, 134.6, 134.2, 133.5, 130.1, 129.7, 129.1, 129.0, 128.7, 128.6, 102.4, 99.1, 61.1, 56.4, 45.1. ESI-MS (TOF): $[M+H]^+$ calcd. for $C_{27}H_{23}ClO_5Na^+$ 485.1126, found 485.1138.

9. Reference

[1] R.-P. Li, X. Xu, Z. Zhang, X. Gong and S. Tang, *Org. Lett.,* 2024, **26**, 7601–7606.

[2] X. Xu, R.-P. Li, Z. Zhang, X. Gong, Y. Zheng and S. Tang, *Org. Lett.,* 2024, **26**, 6825–6829.

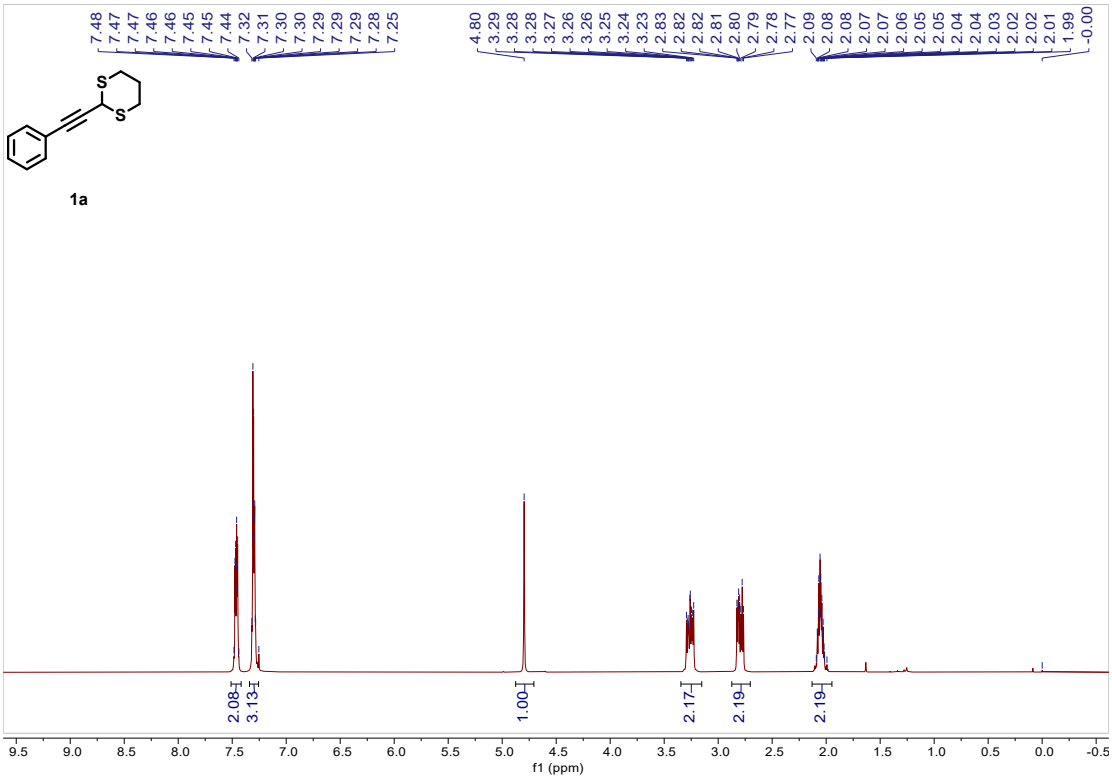
[3] Y. Liang, J. Lai, T. Liu and S. Tang, *Org. Lett.,* 2016, **18**, 5086–5089

[4] X. Liu, X. Xu, L. Pan, Q. Zhang and Q. Liu, *Org. Biomol. Chem.,* 2013, **11**, 6703-6706.

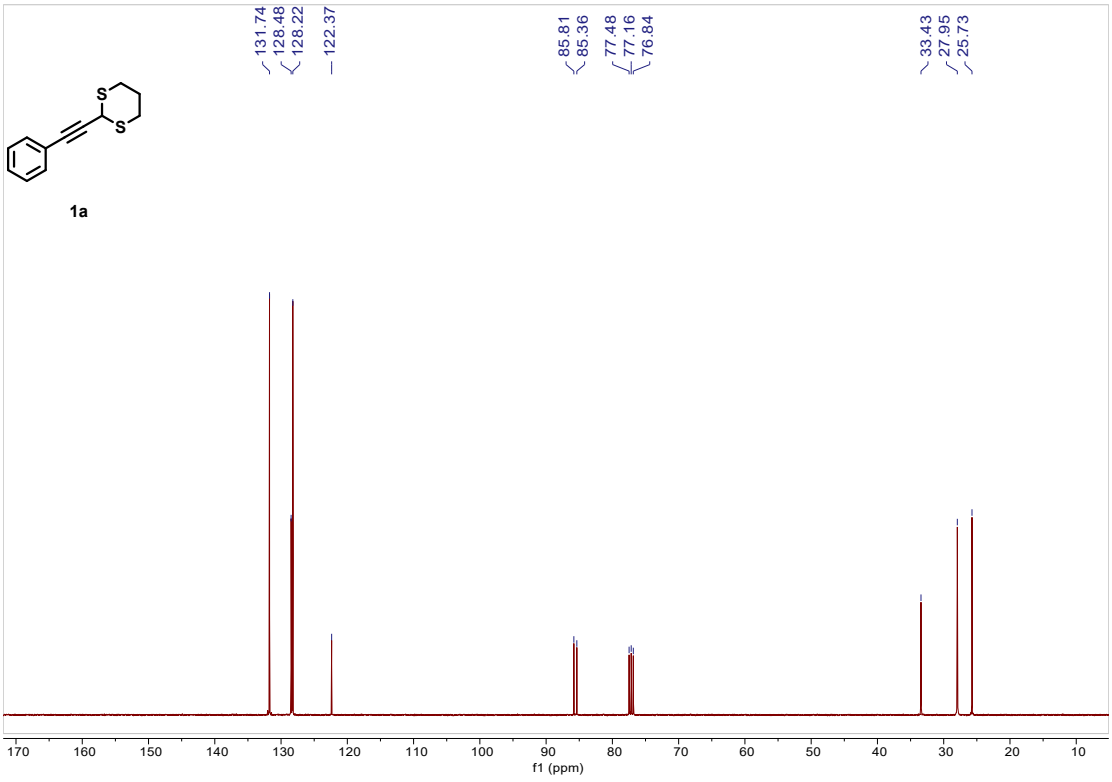
[5] X. Zhao, Z. Zhong, L. Peng, W. Zhang and J. Wang, *Chem. Commun.,* 2009, 2535-2537.

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

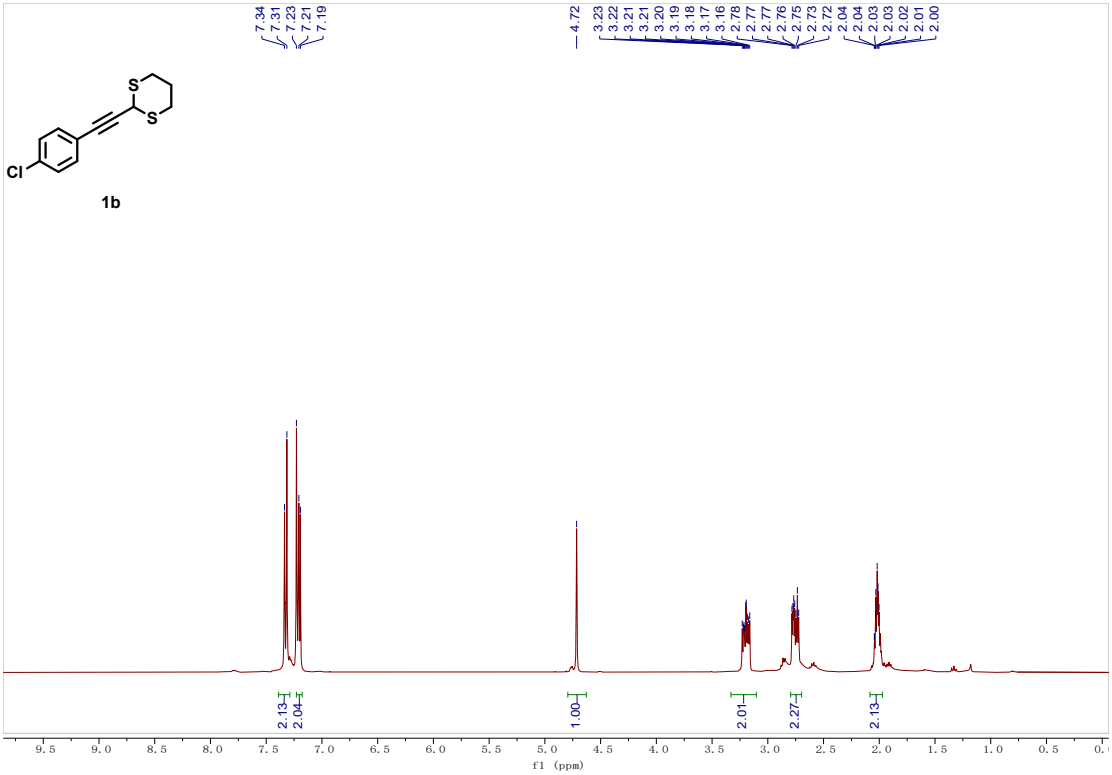
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 1a



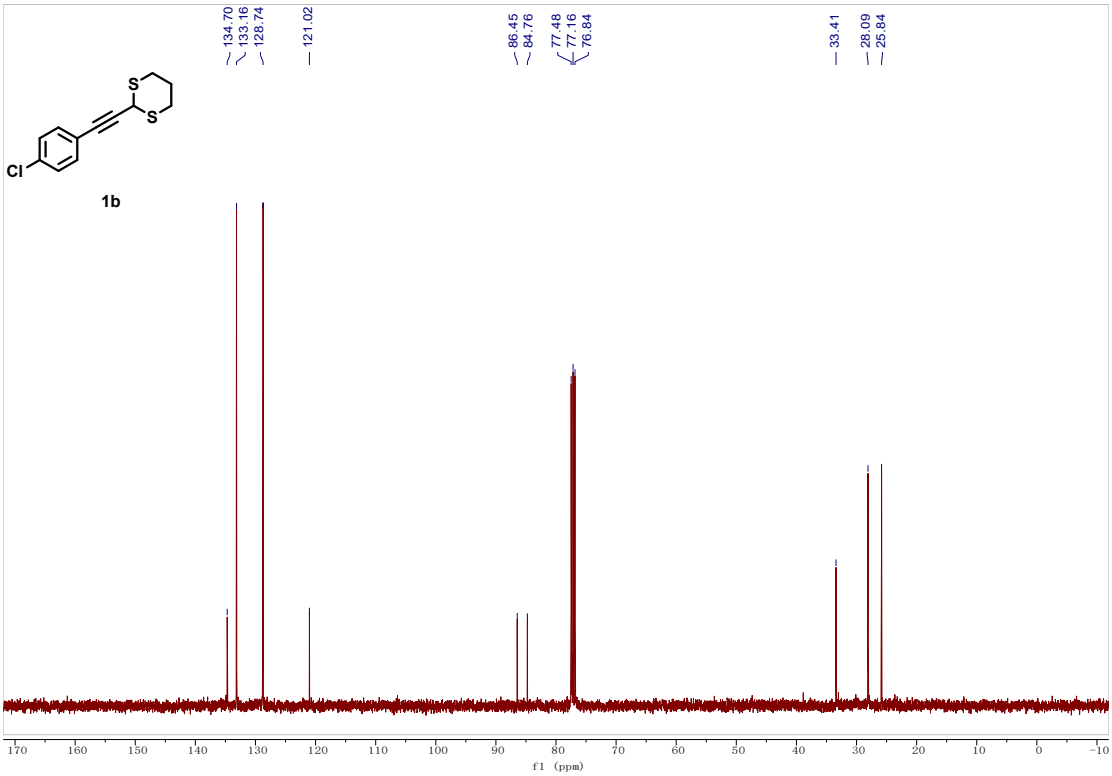
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 1a



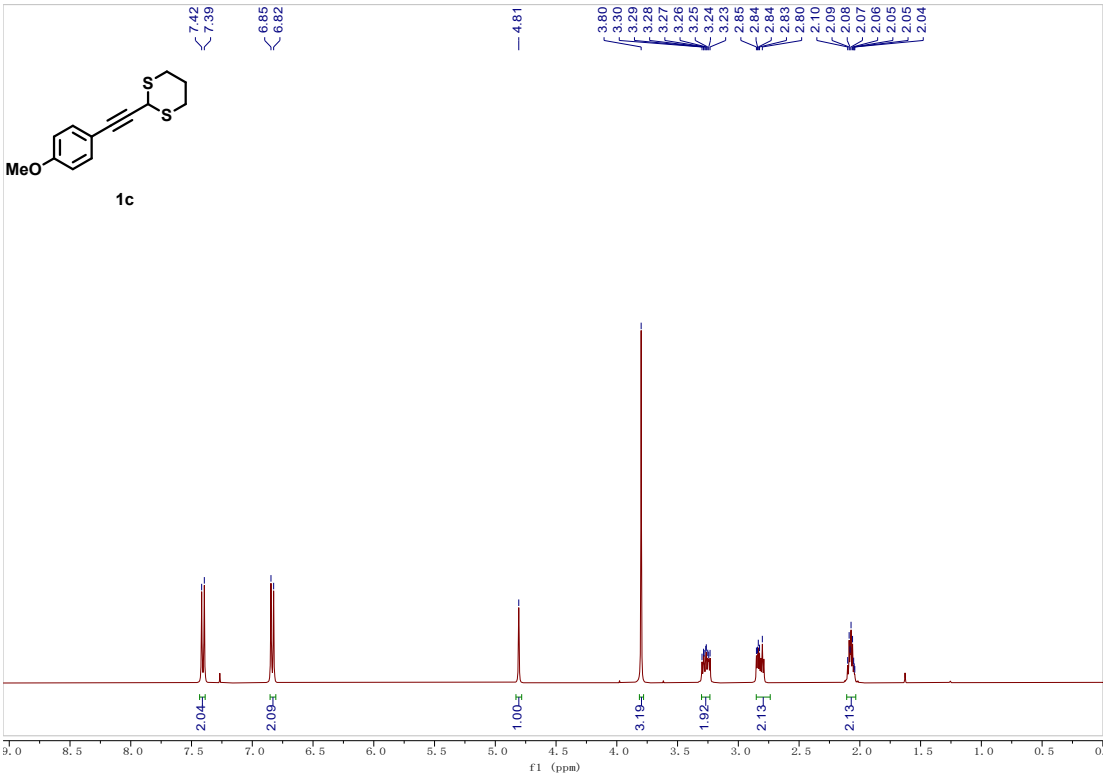
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 1b



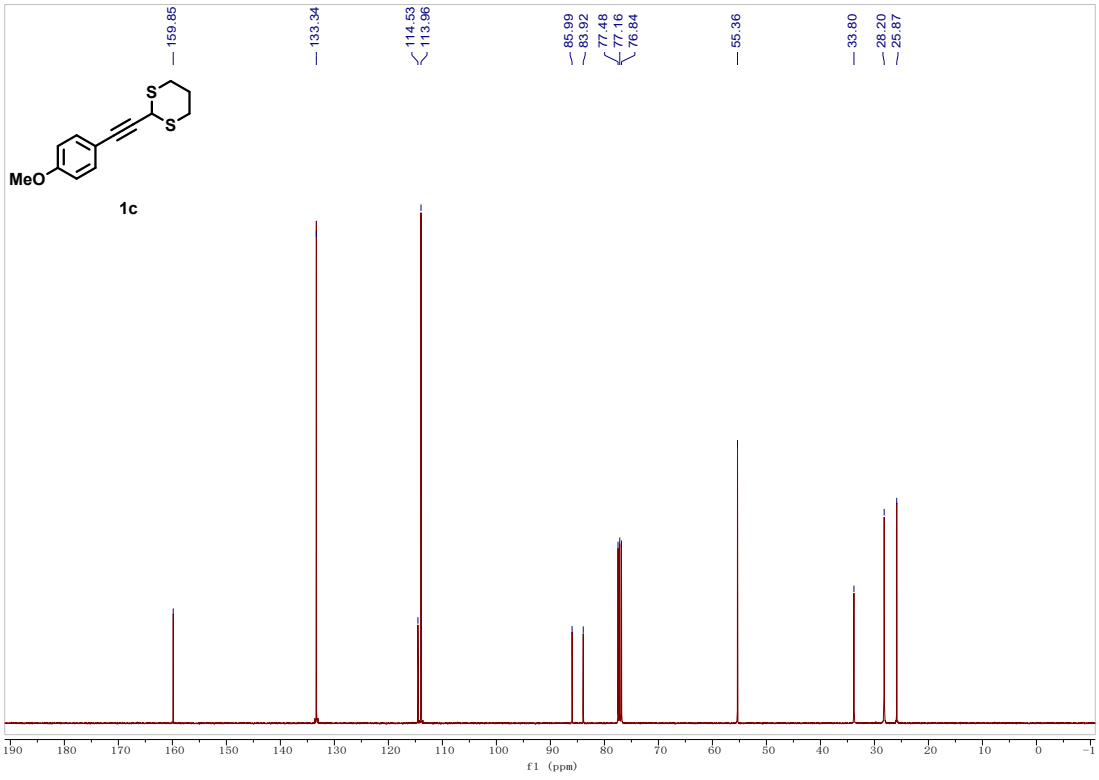
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 1b



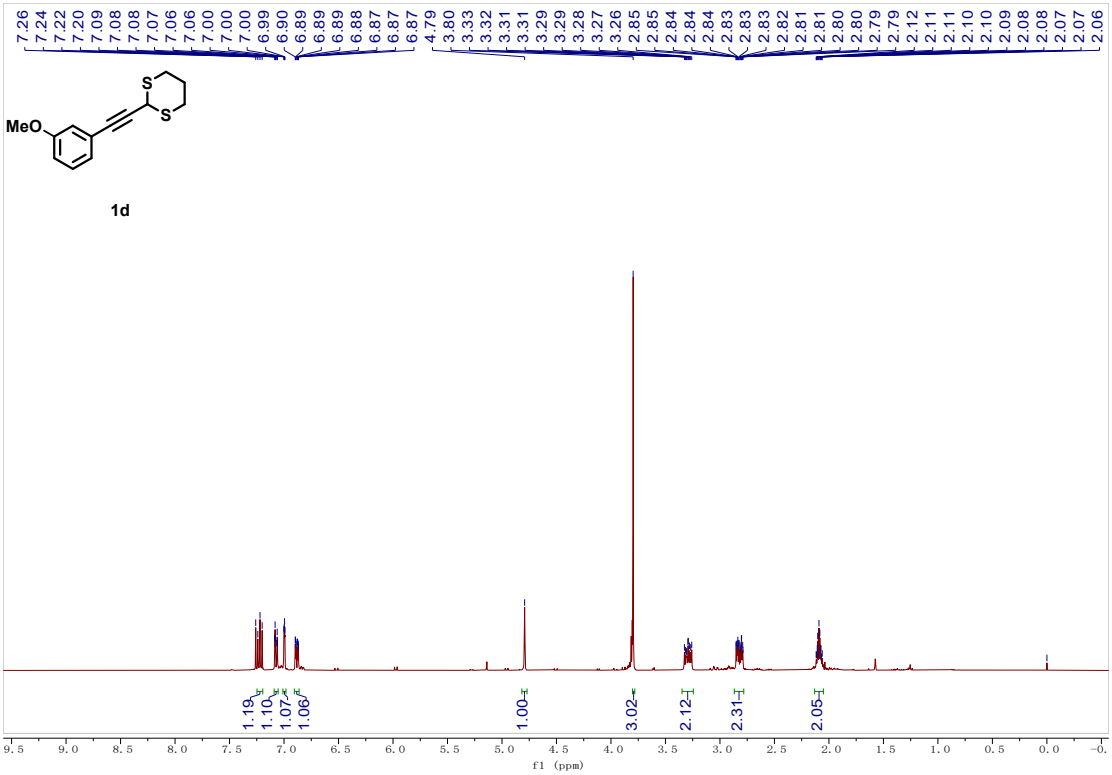
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 1c



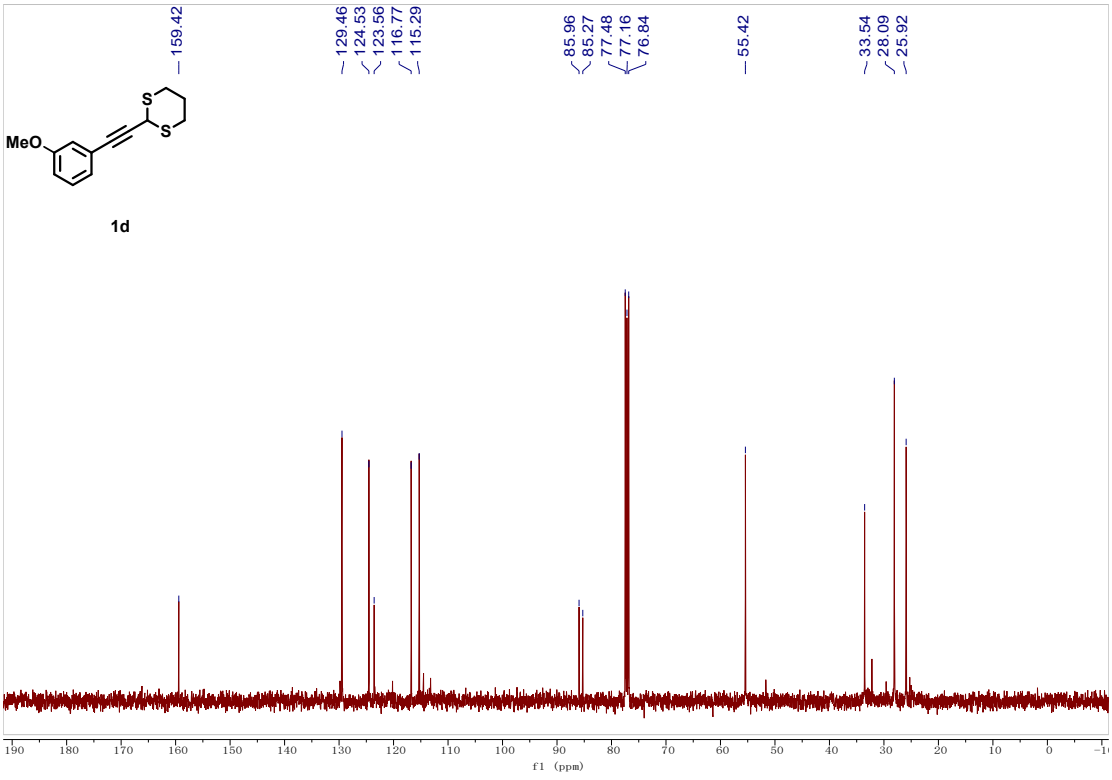
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 1c



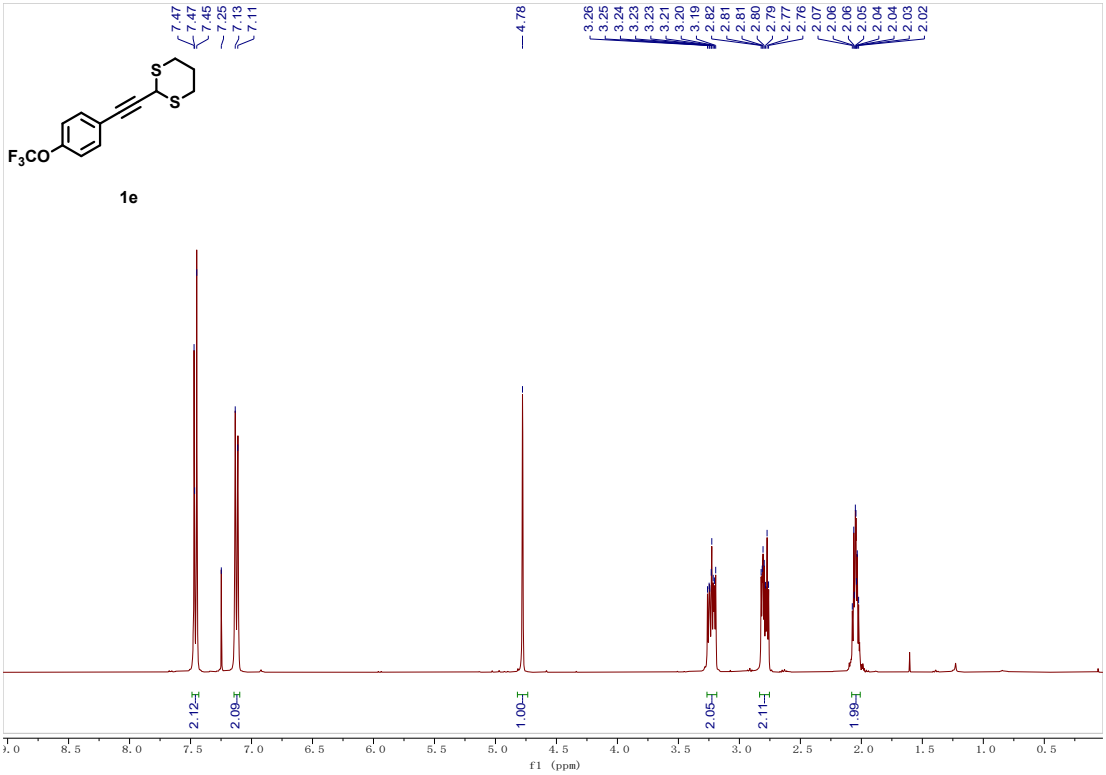
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 1d



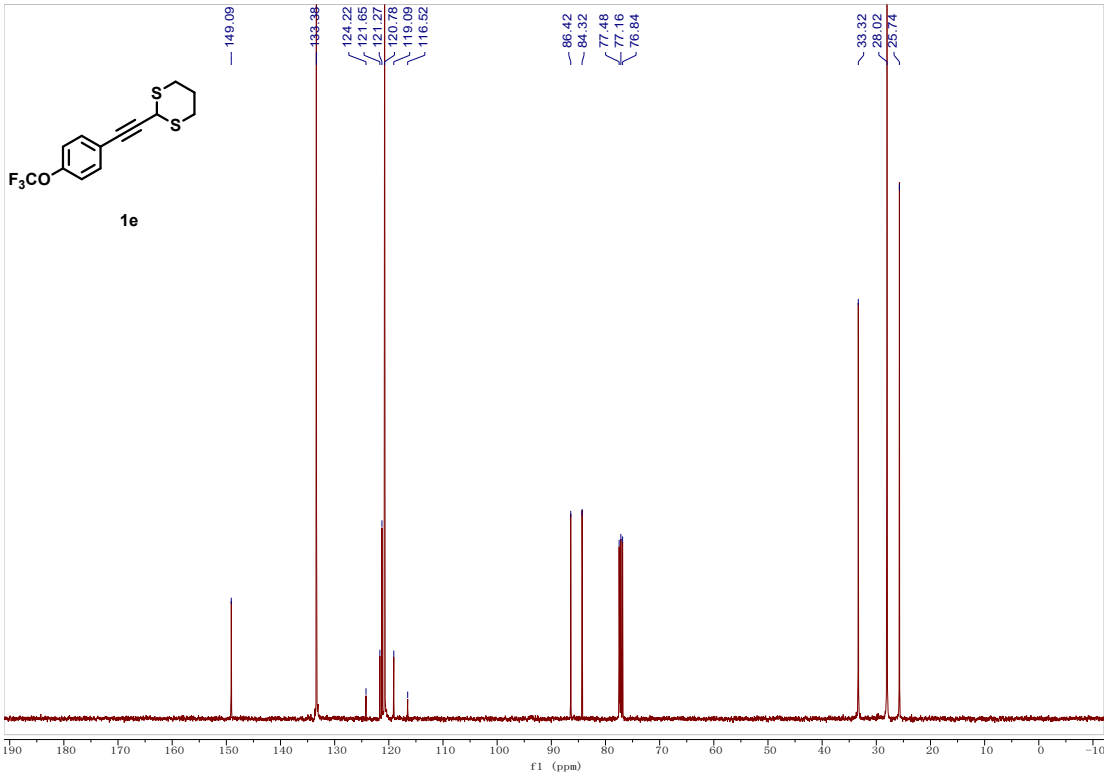
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 1d



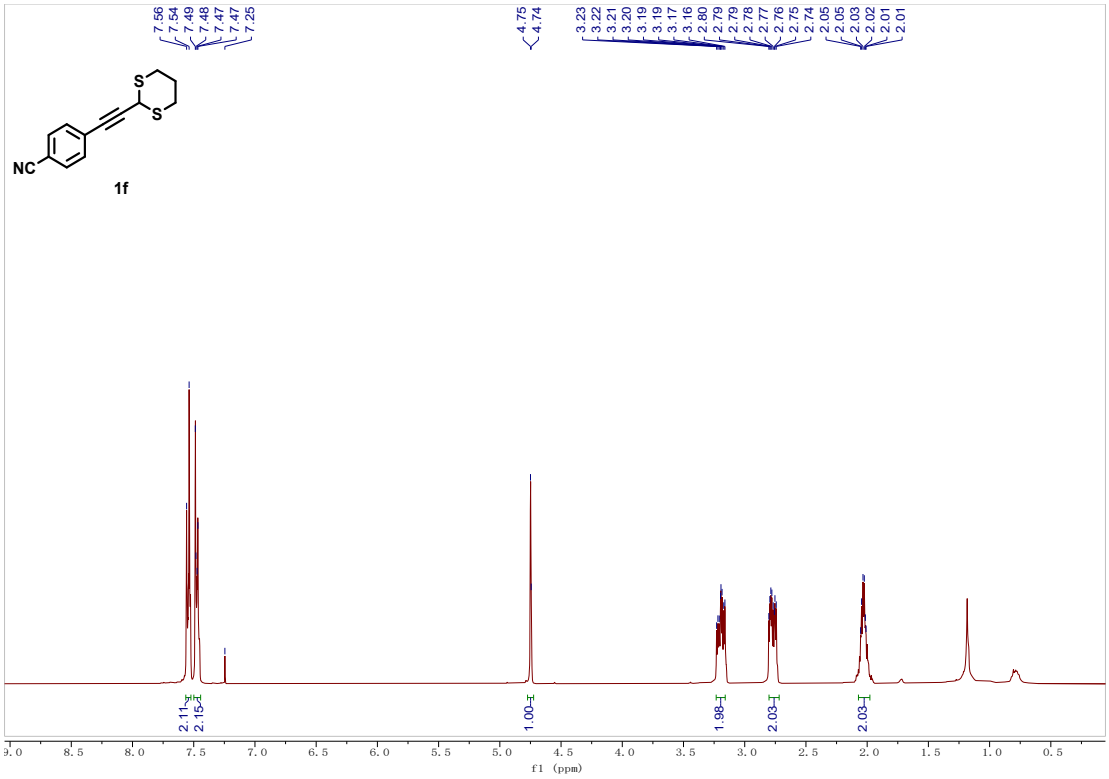
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 1e



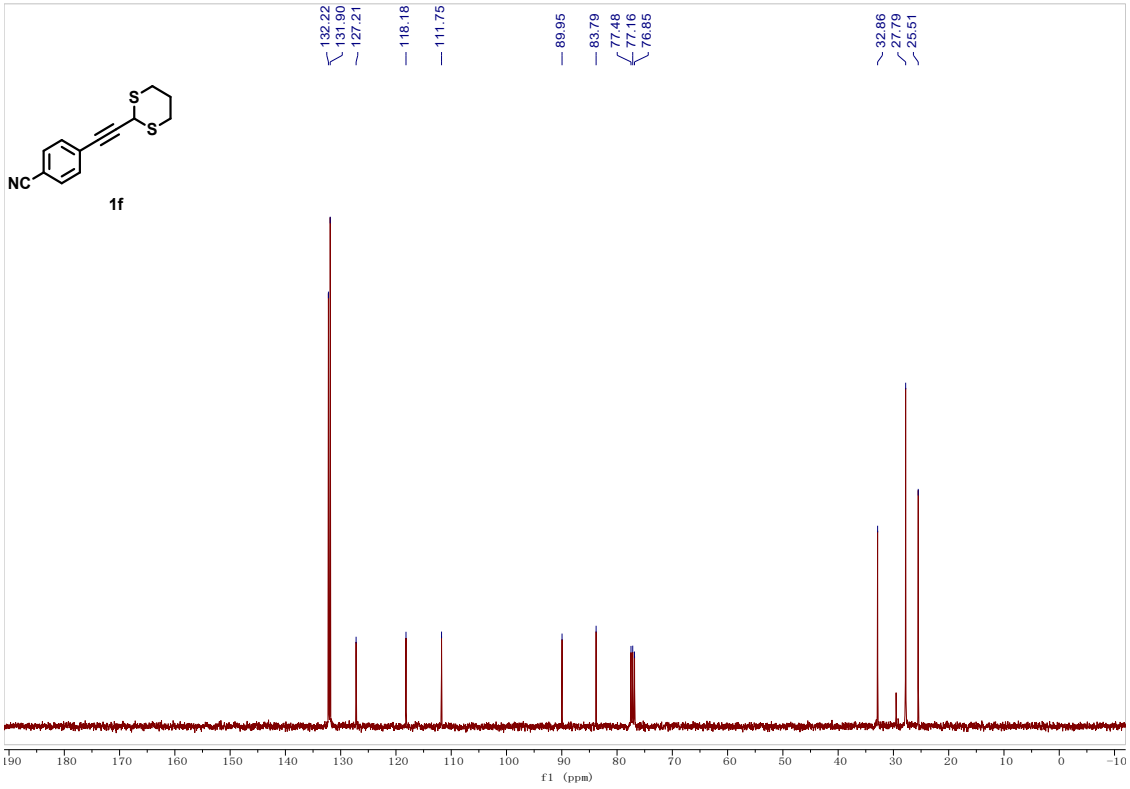
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 1e



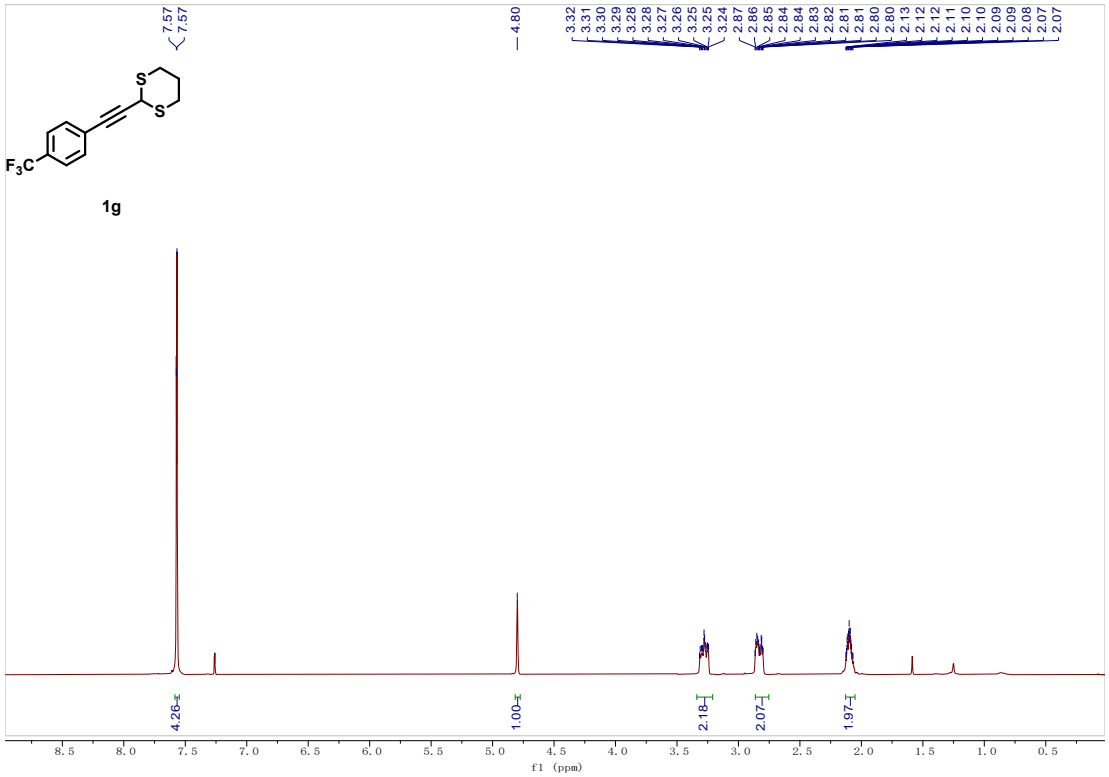
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1f



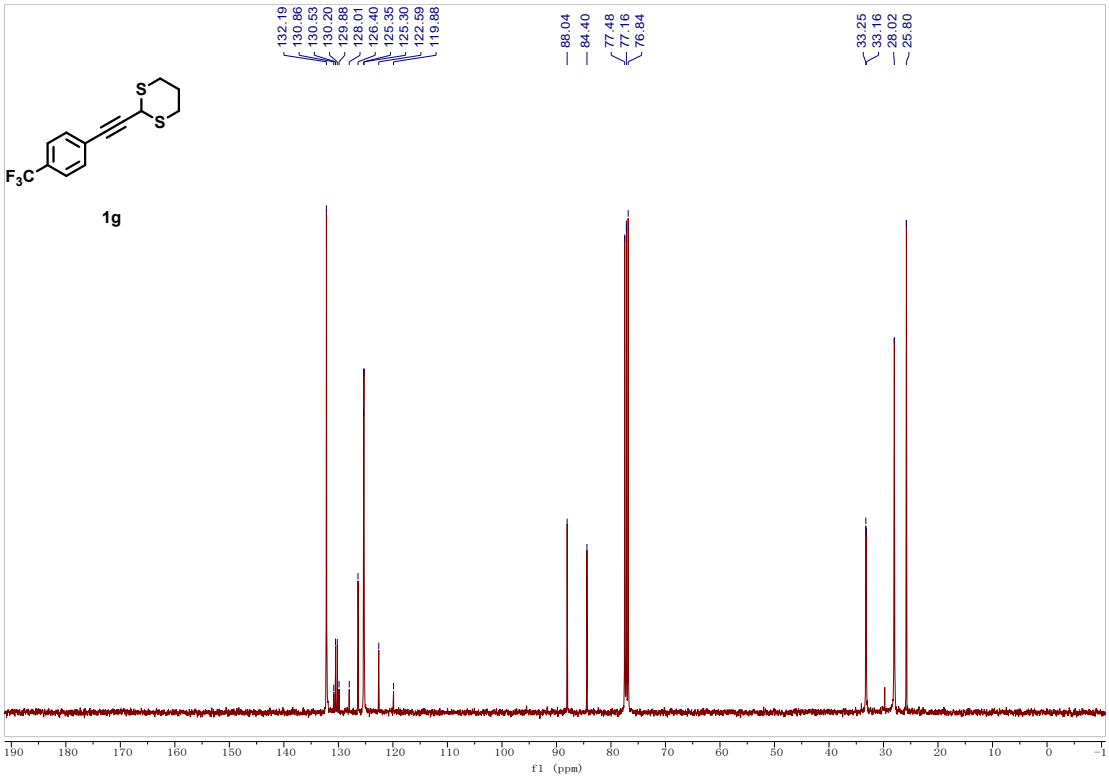
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 1f



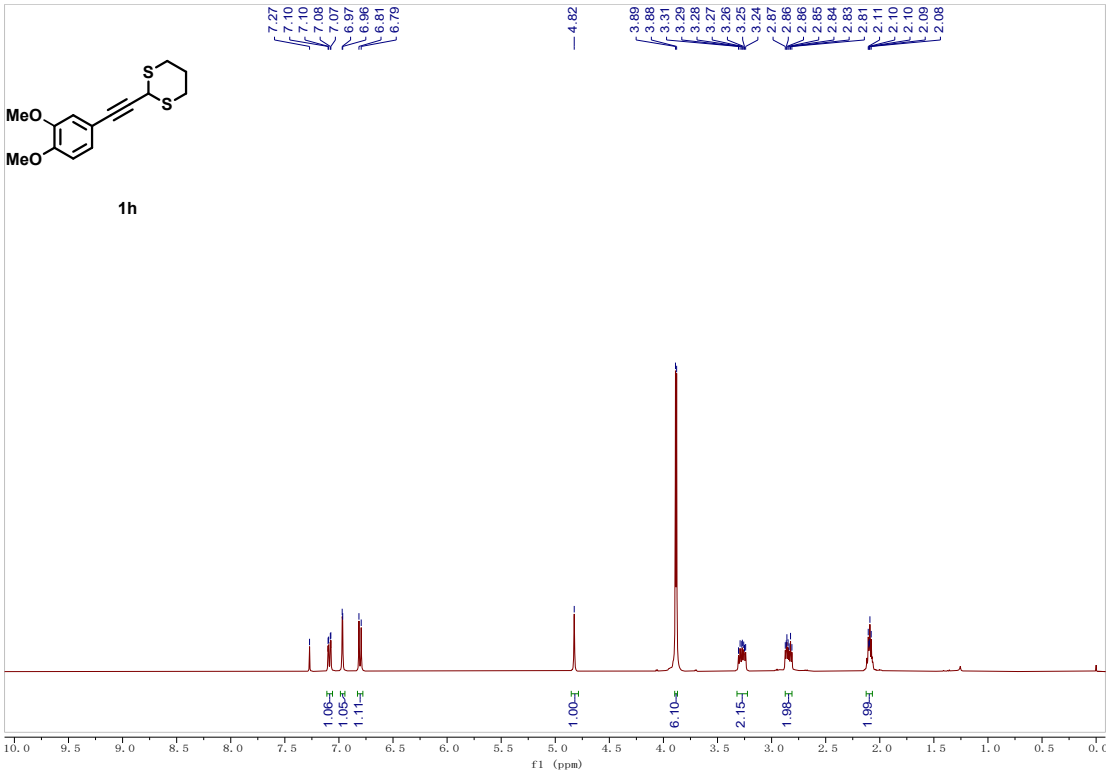
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1g



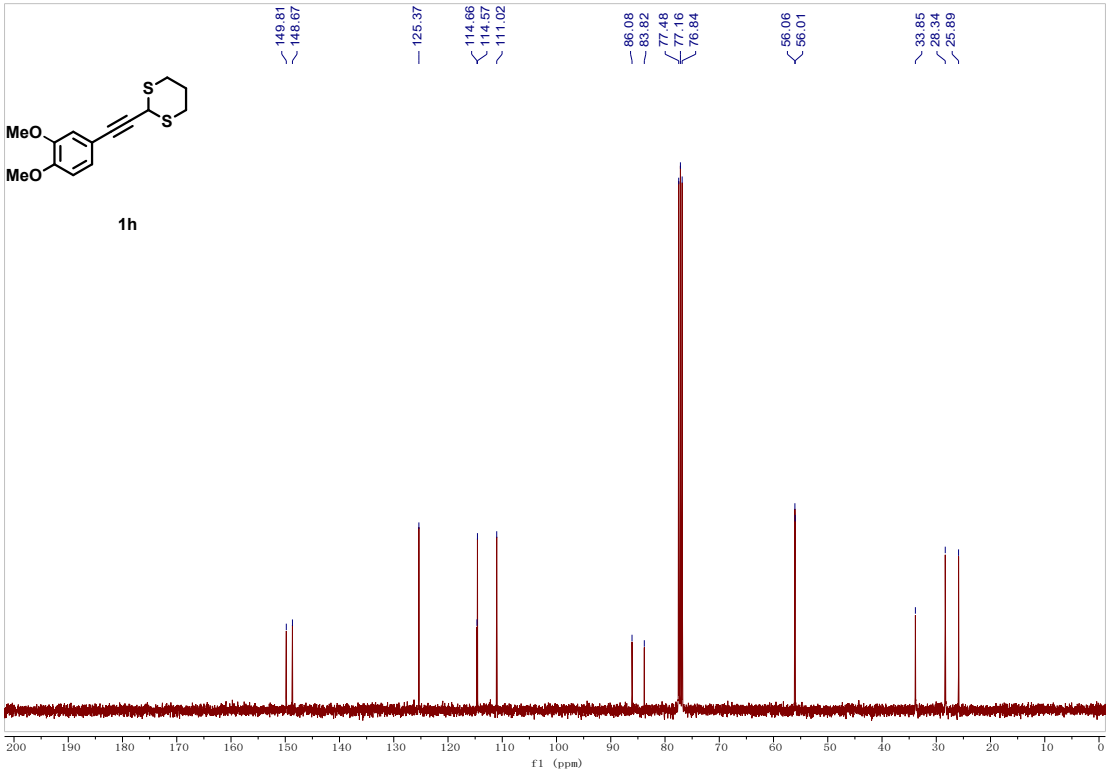
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 1g



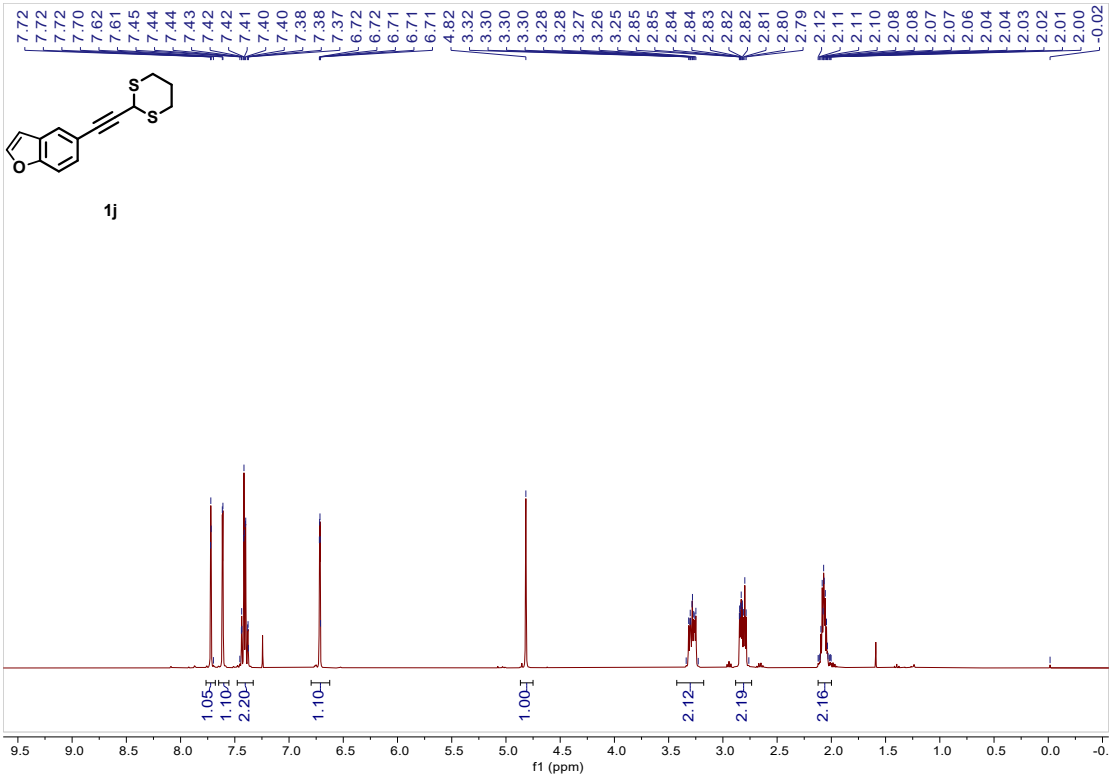
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1h



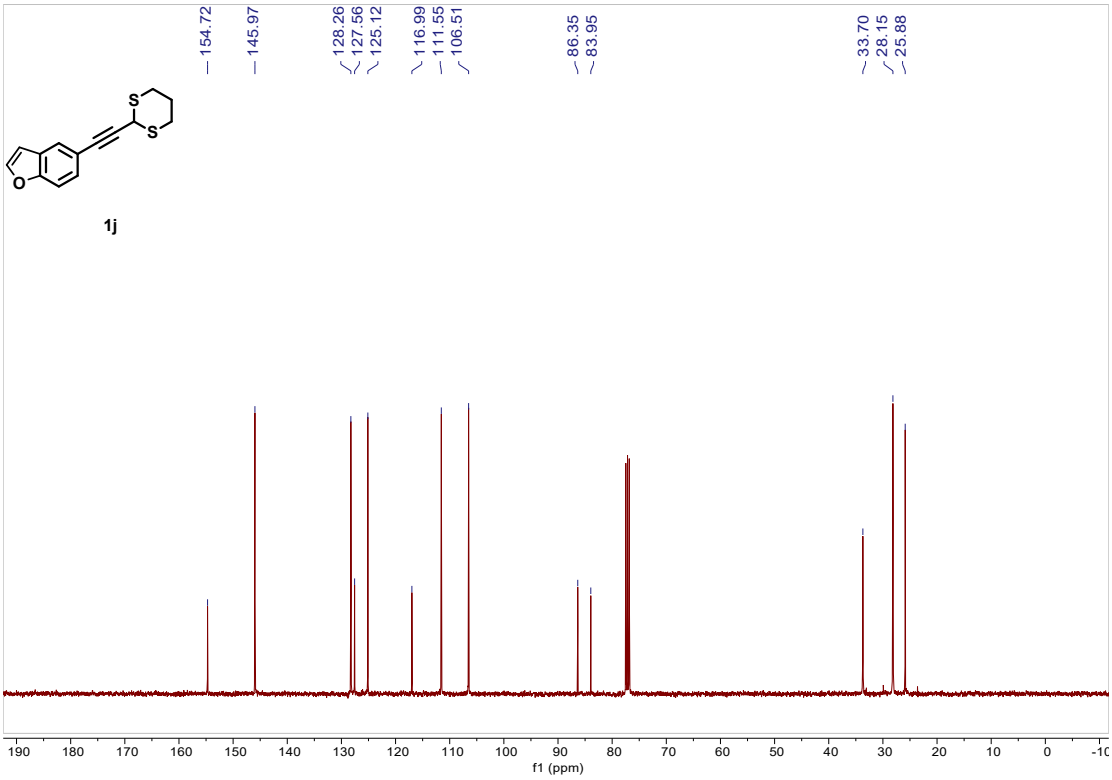
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 1h



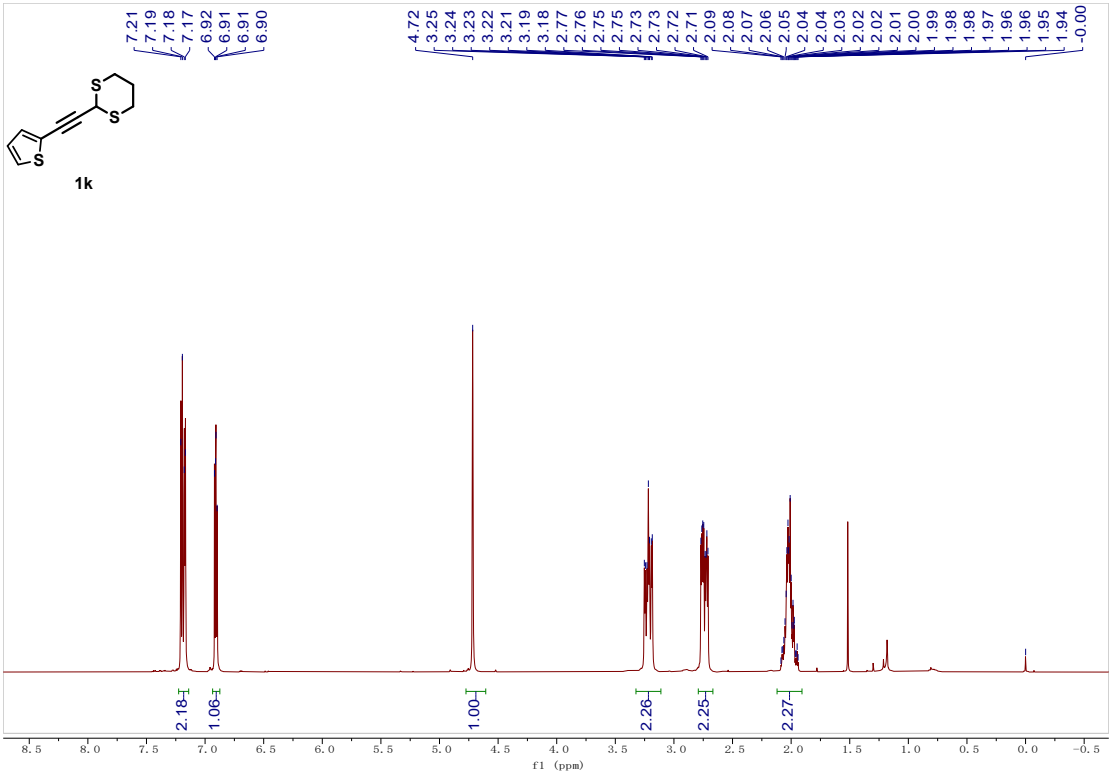
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1j



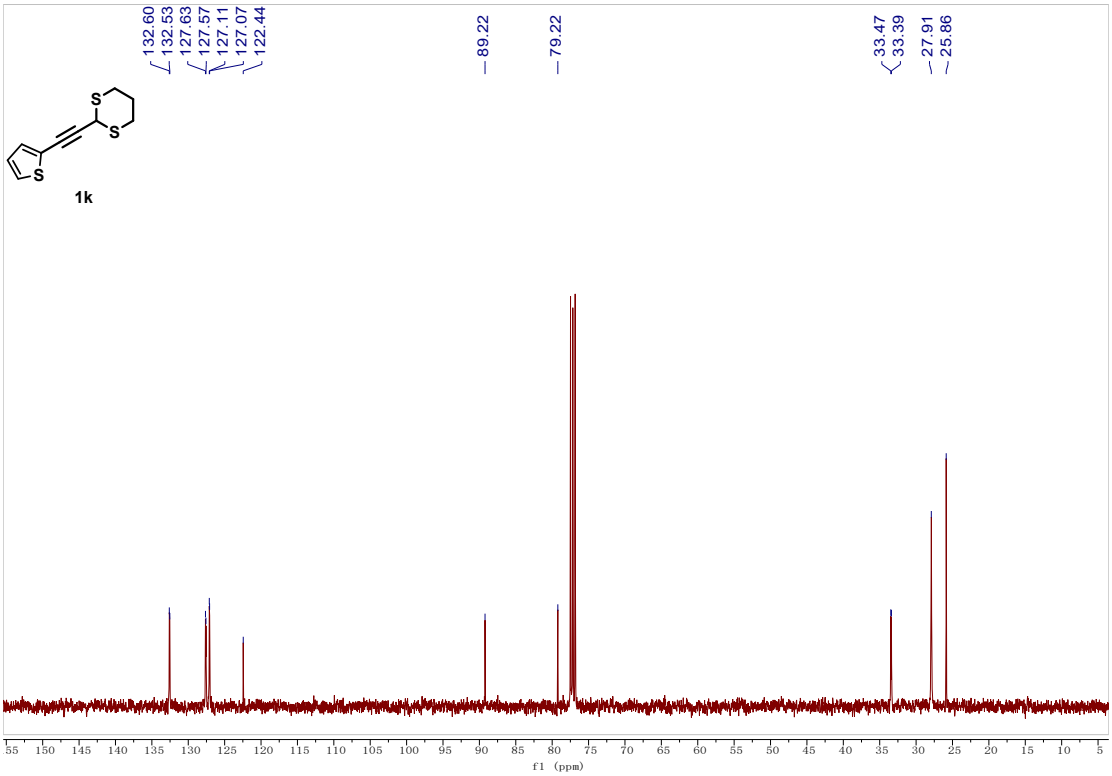
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1j



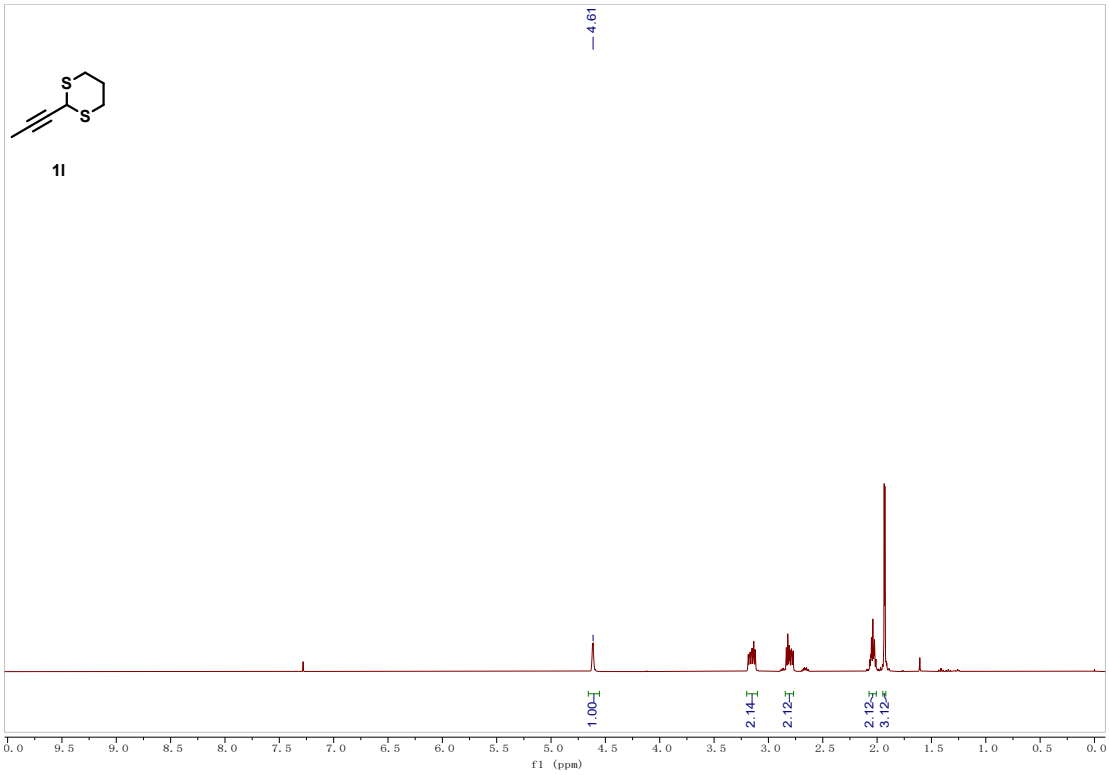
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1k



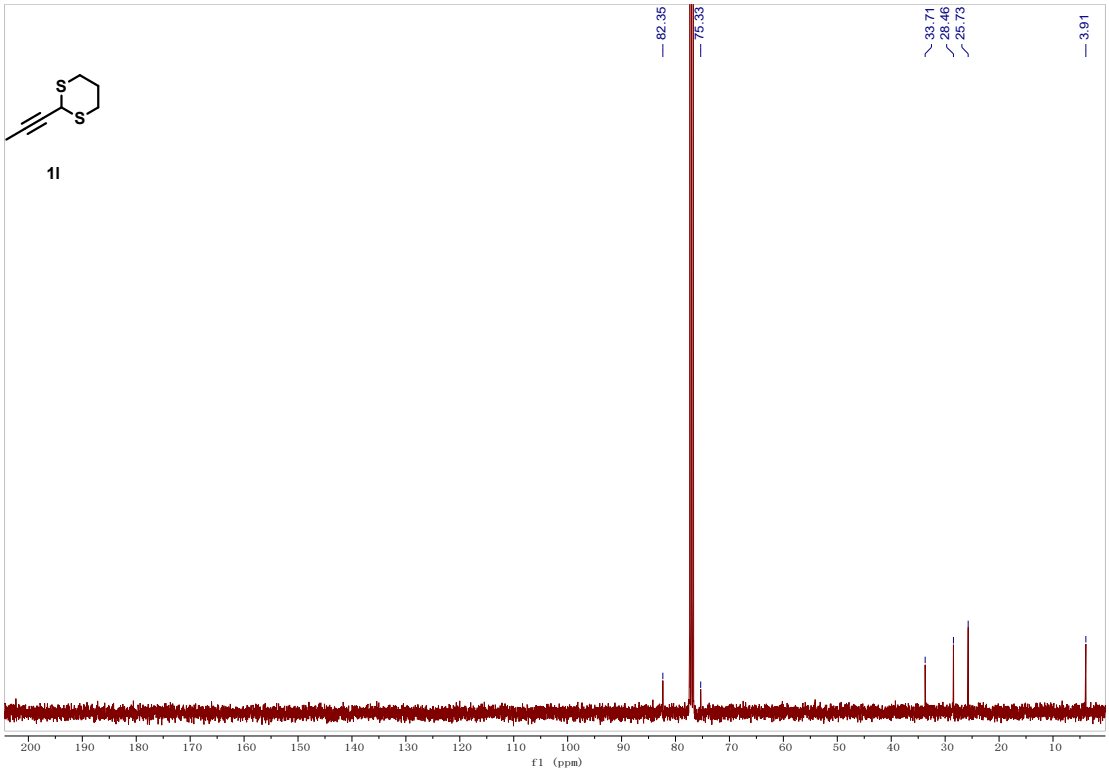
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1k



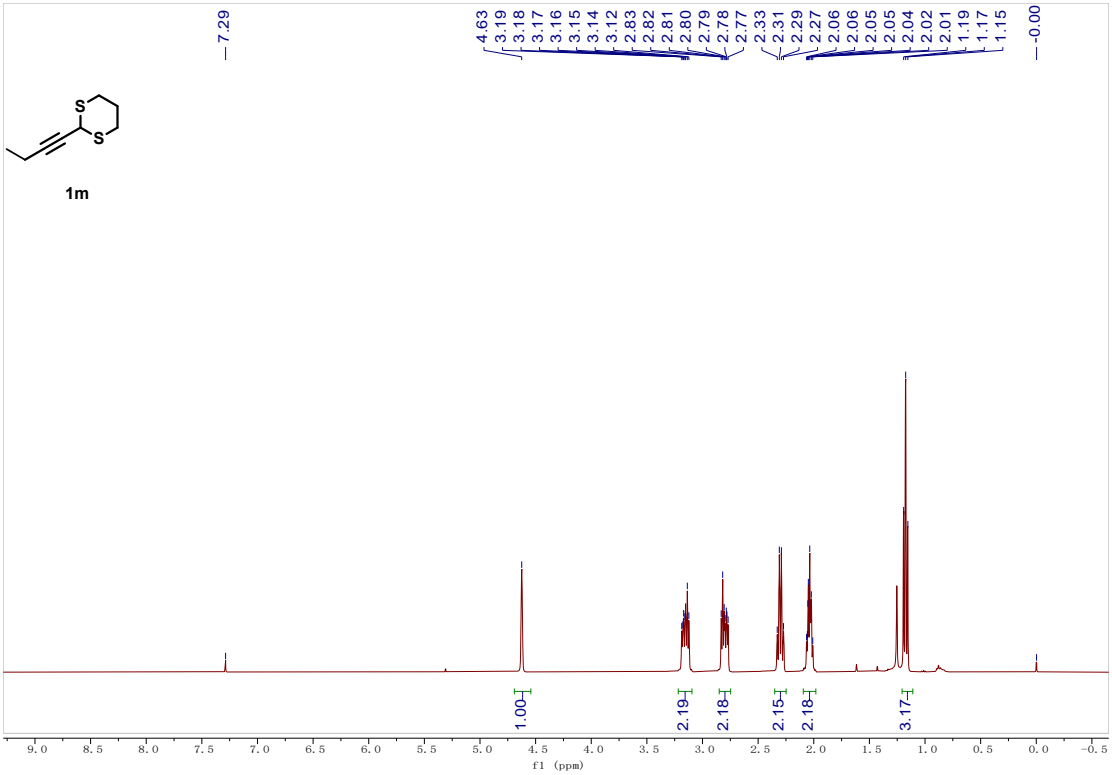
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1l



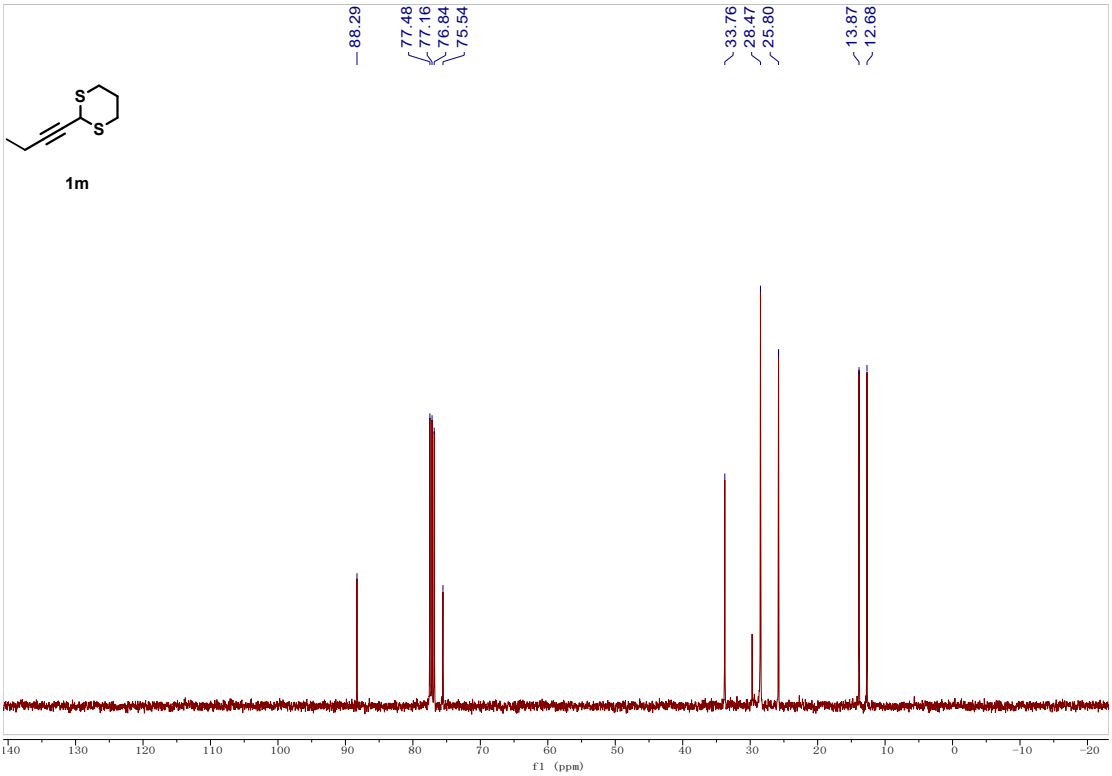
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 1l



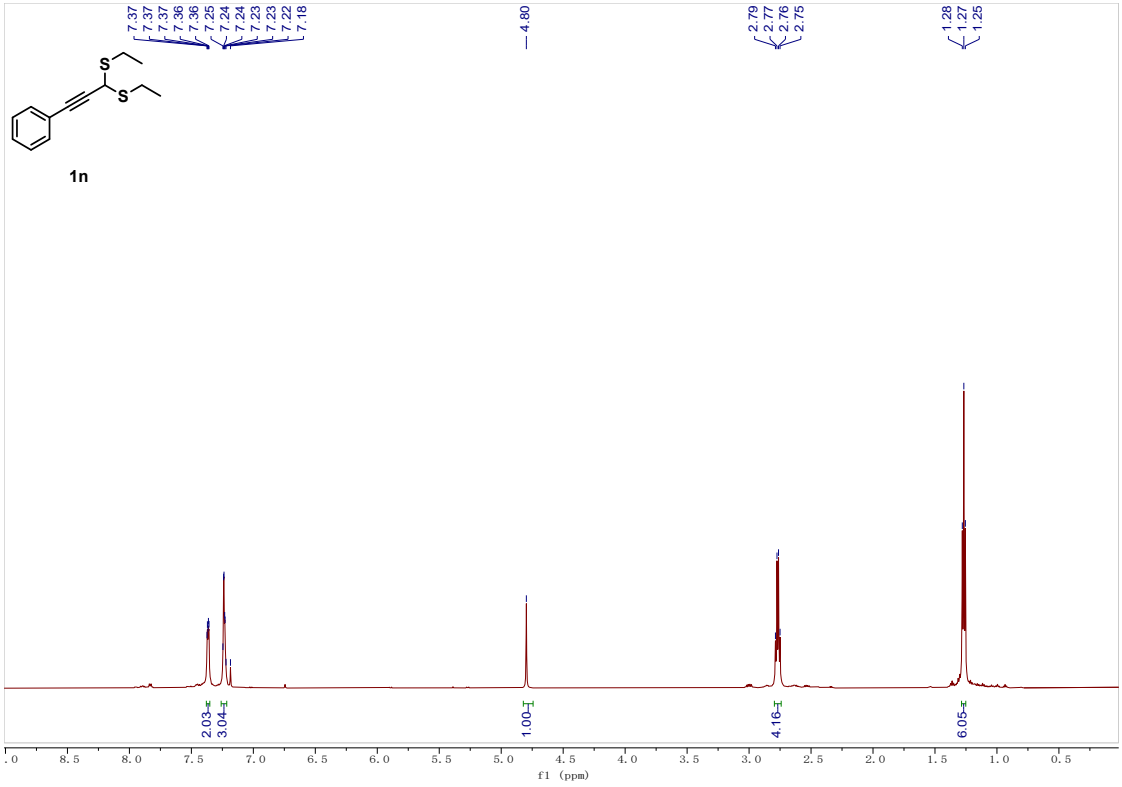
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1m



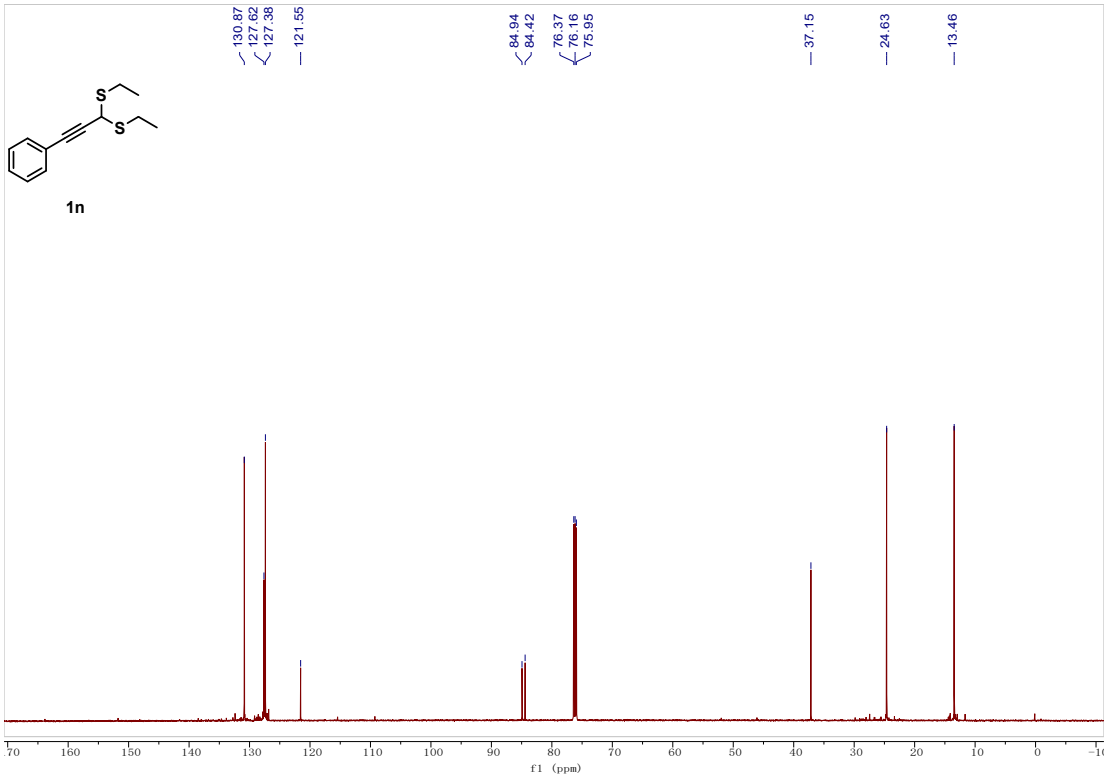
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 1m



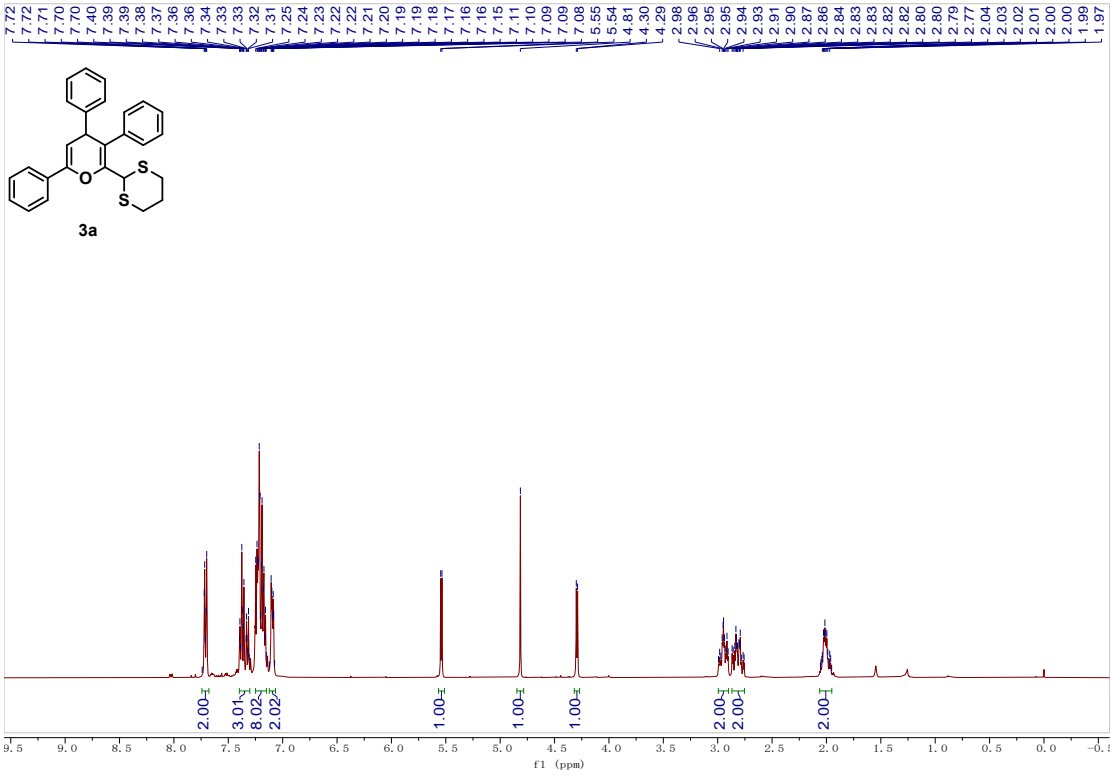
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 1n



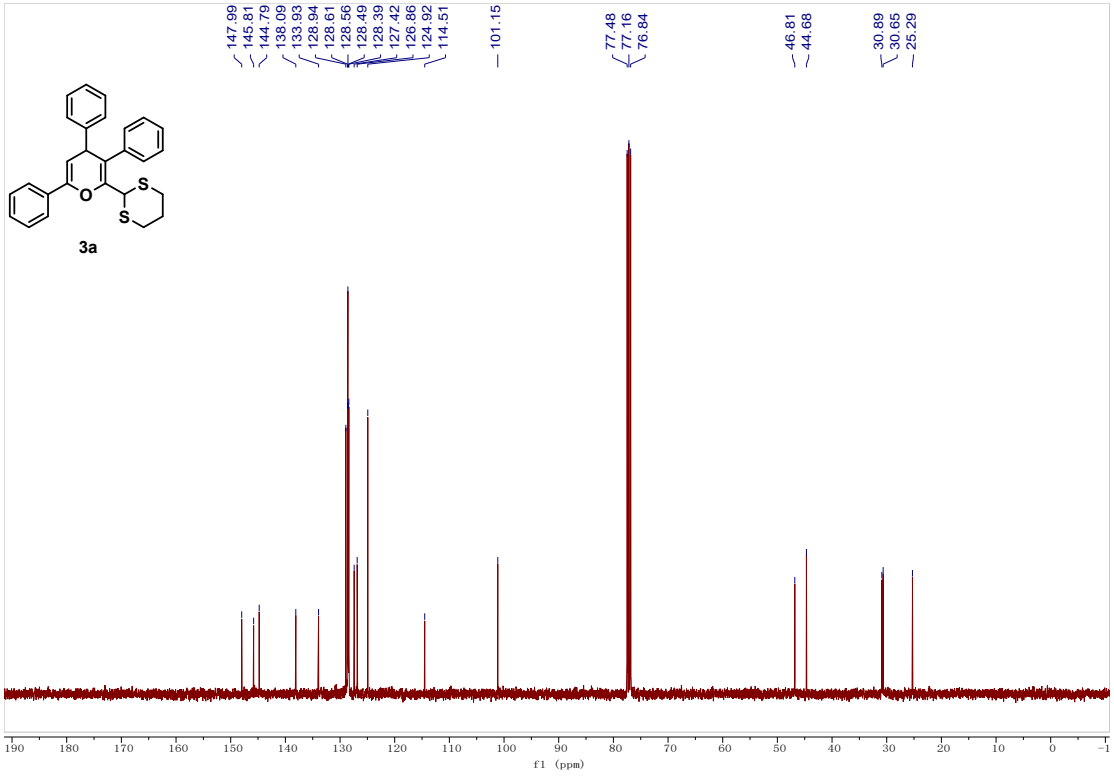
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 1n



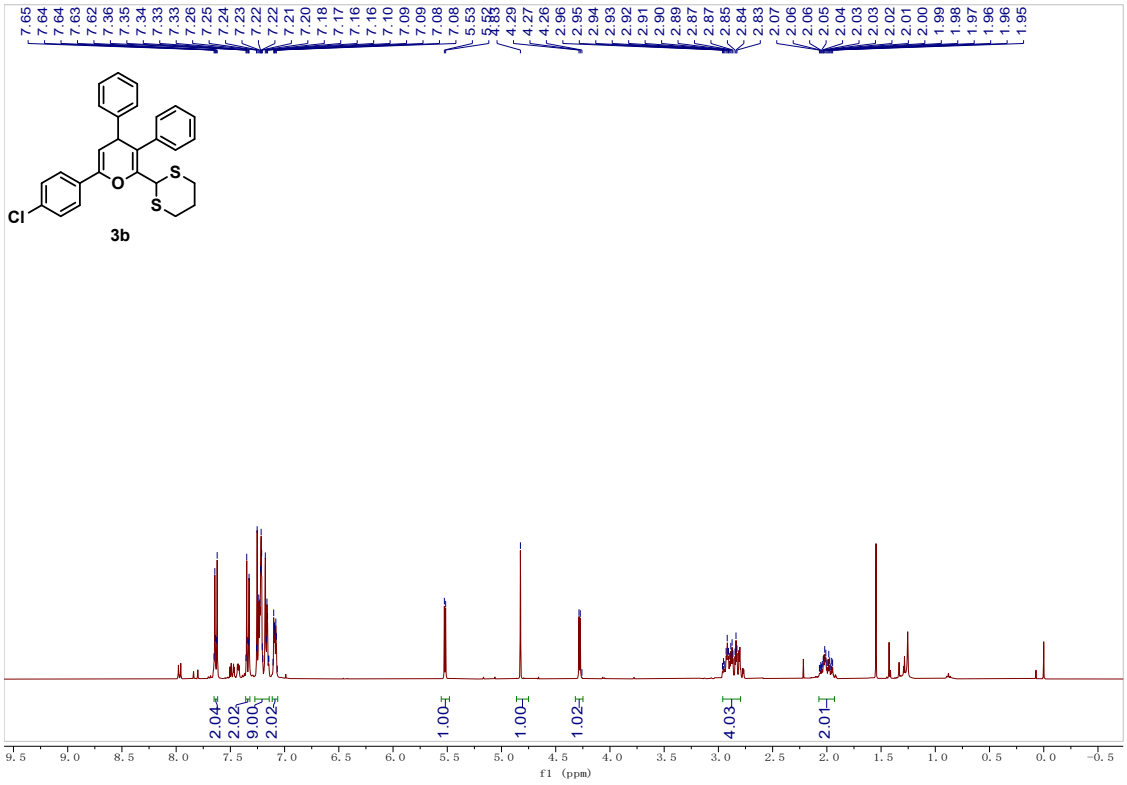
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3a



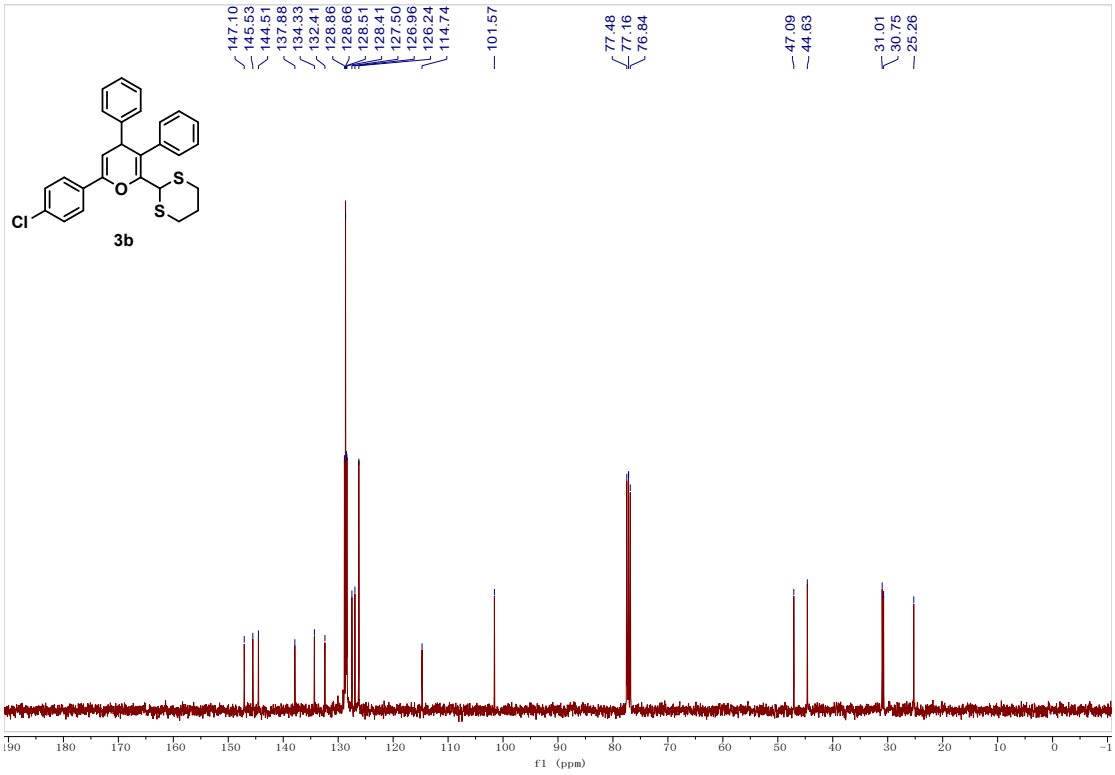
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3a



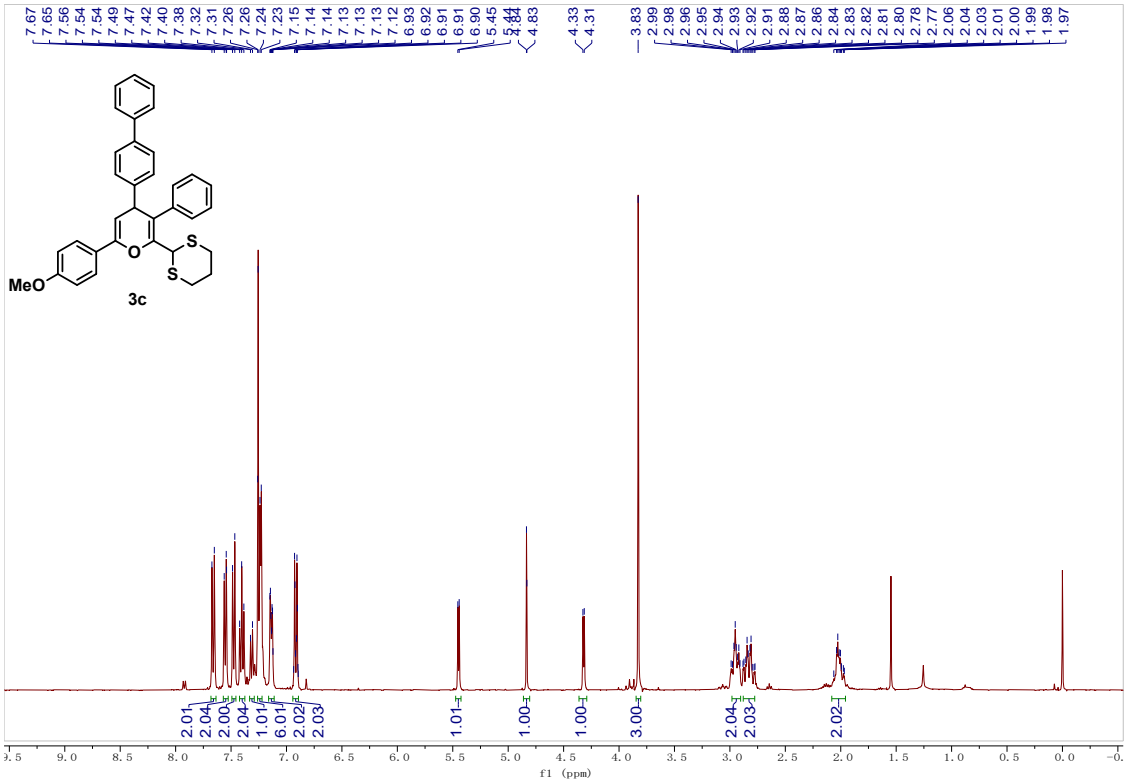
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3b



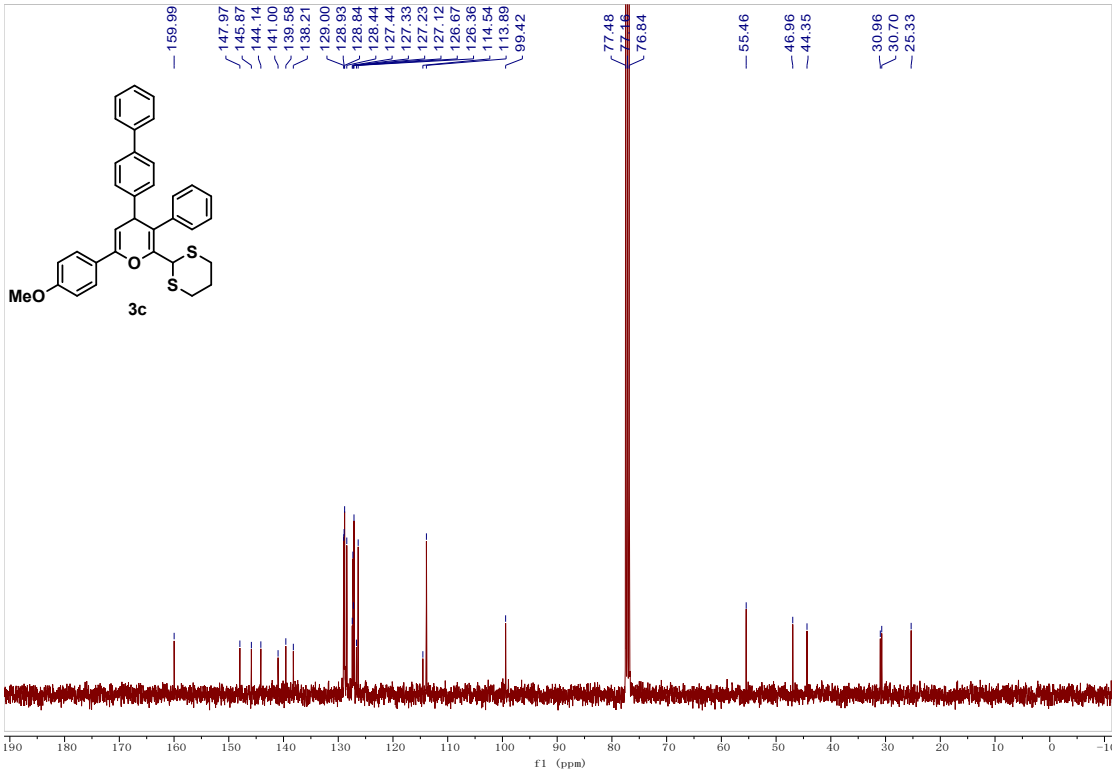
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3b



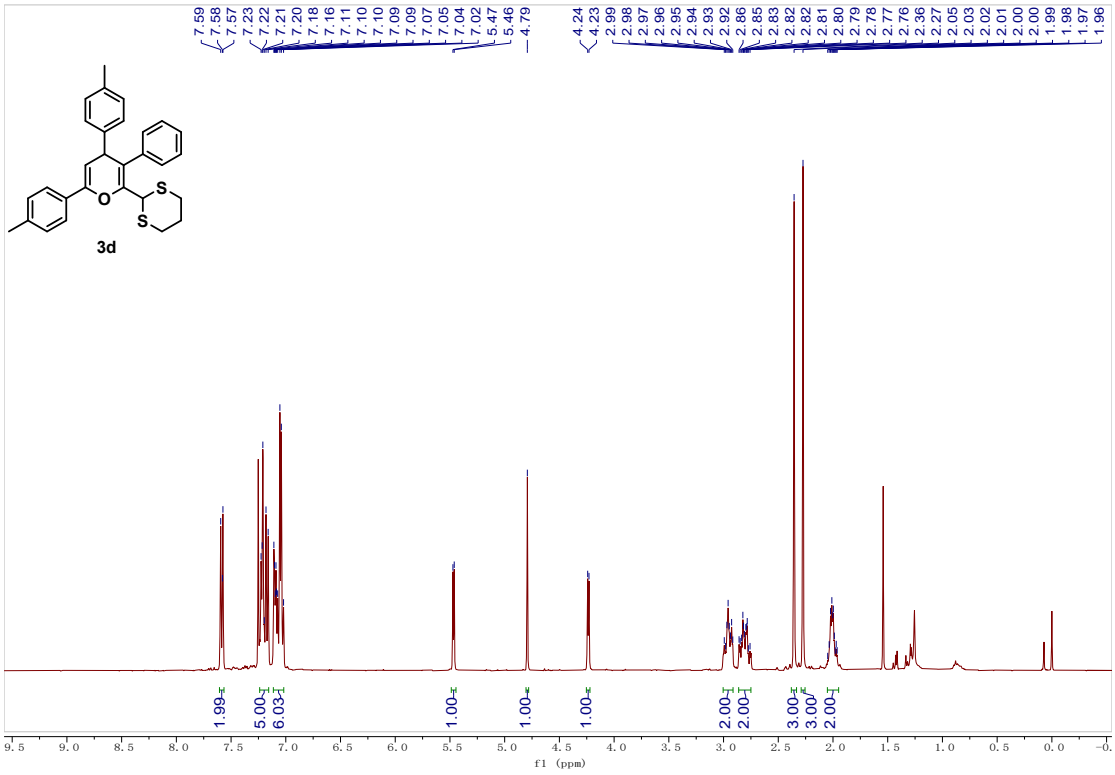
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3c



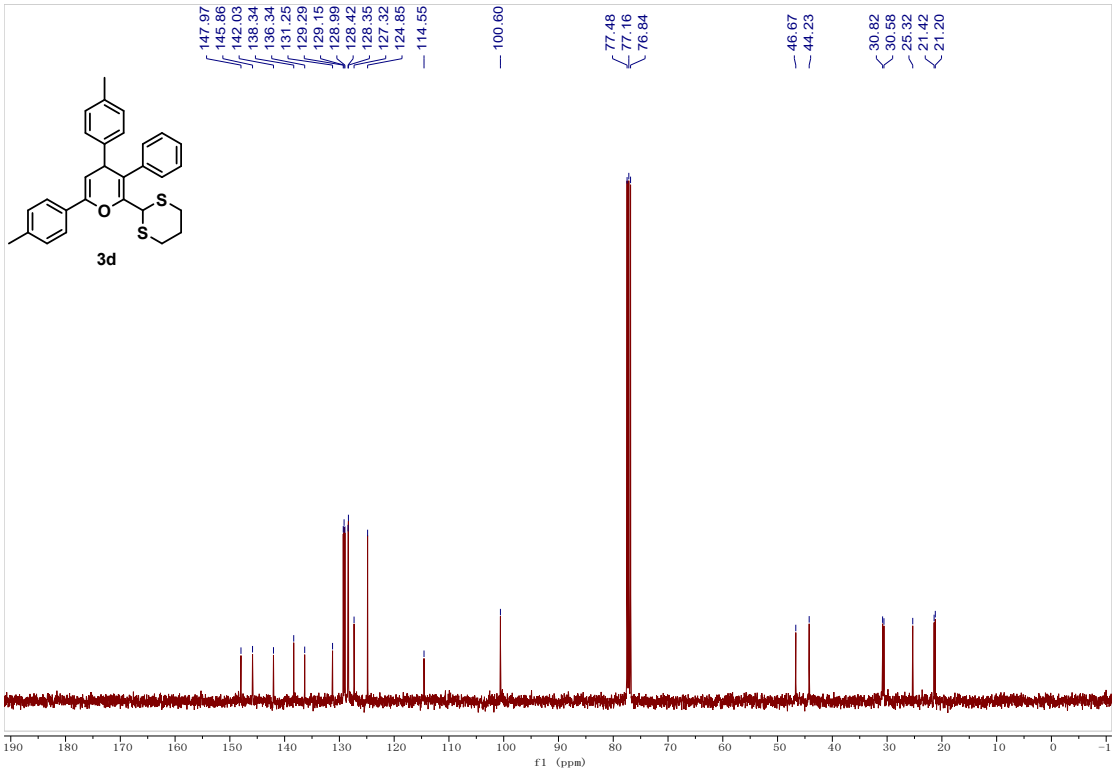
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3c



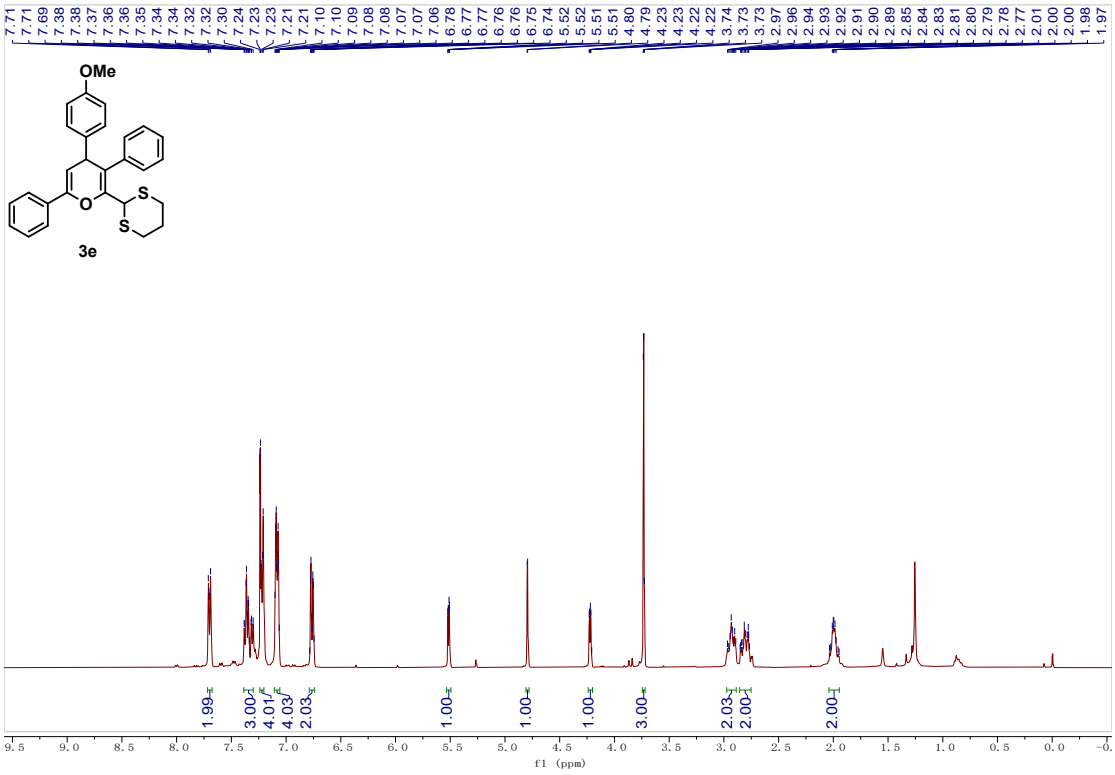
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3d



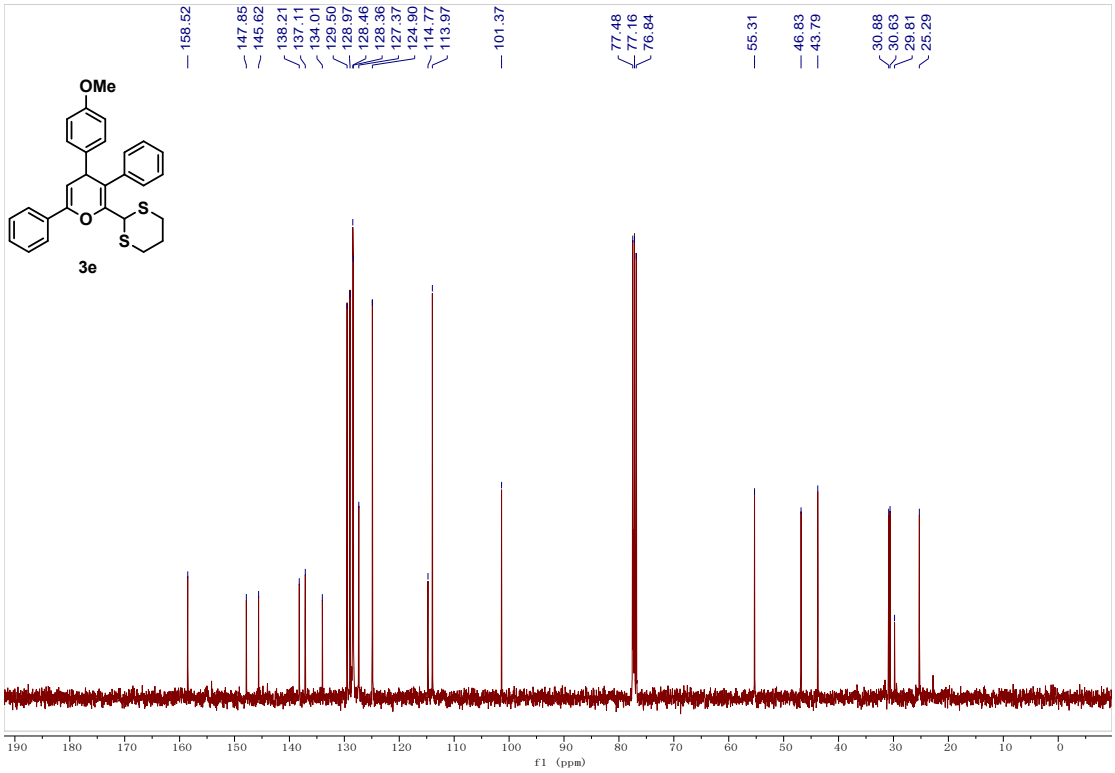
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3d



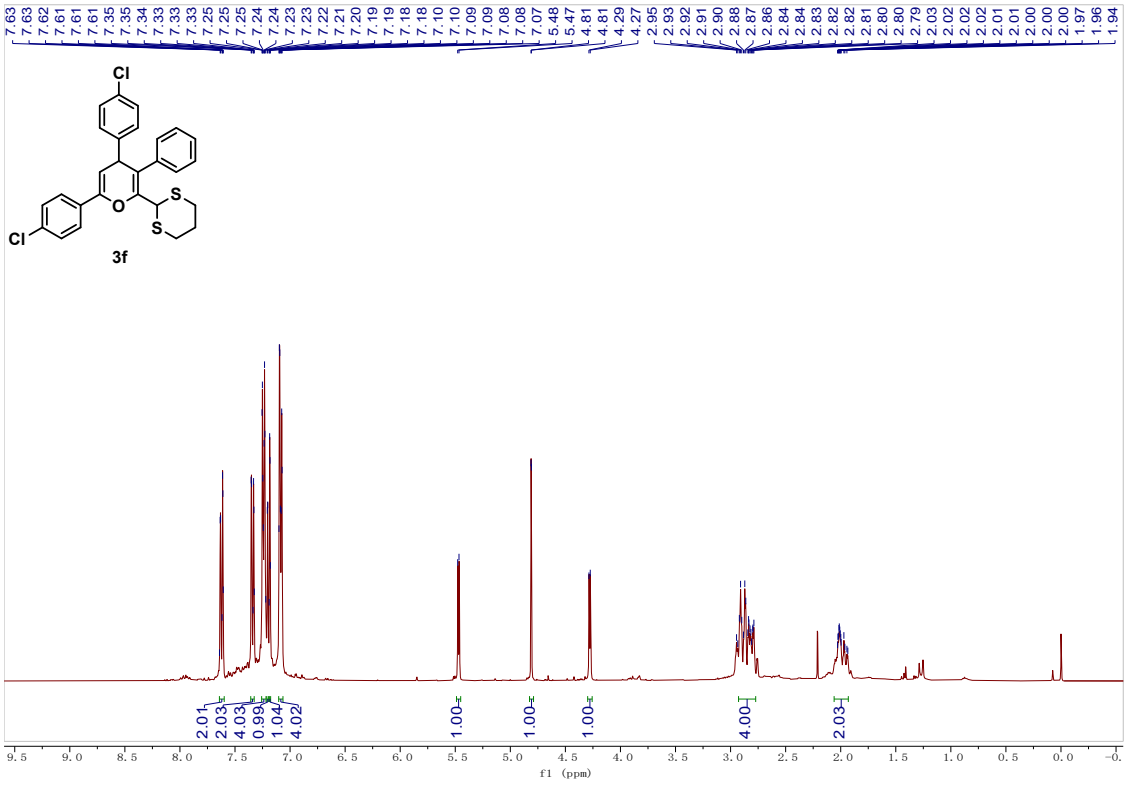
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3e



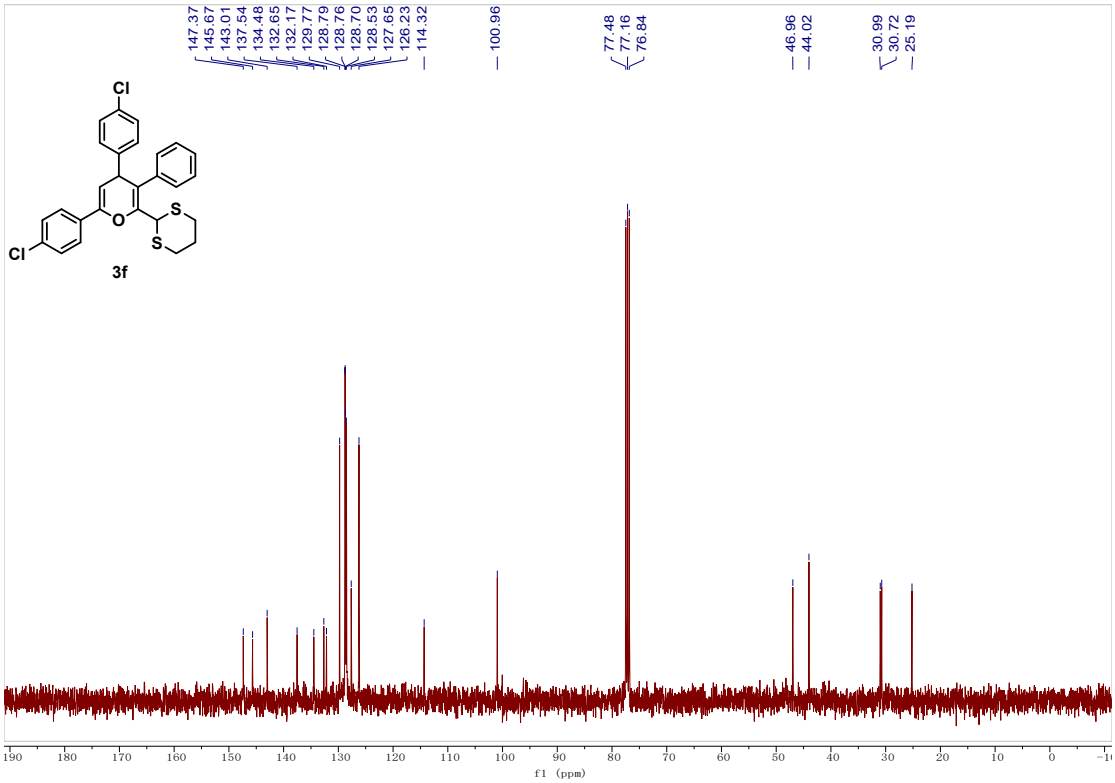
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3e



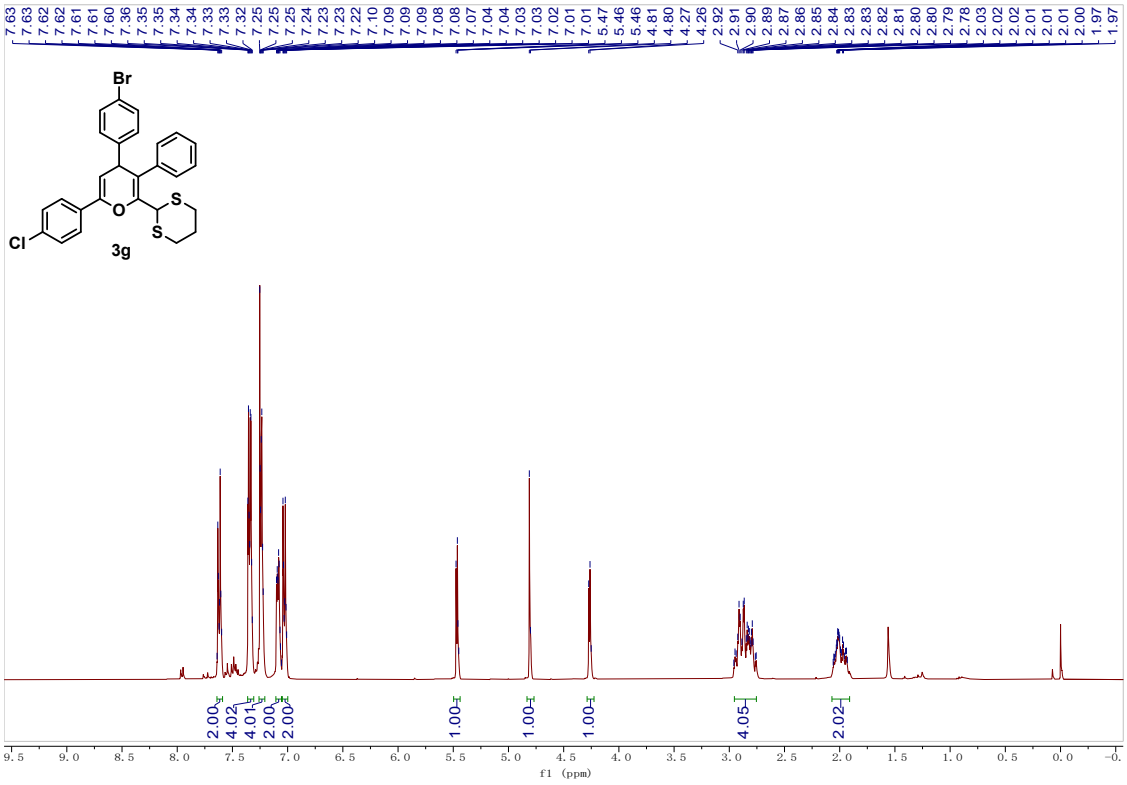
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3f



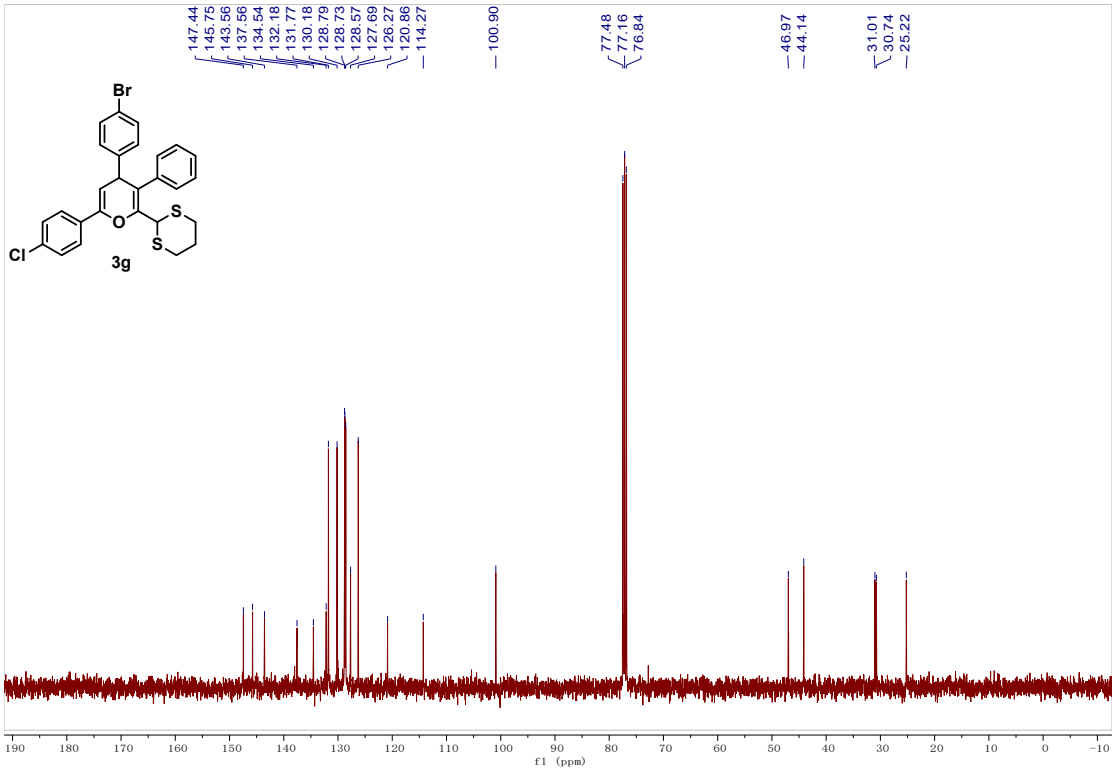
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3f



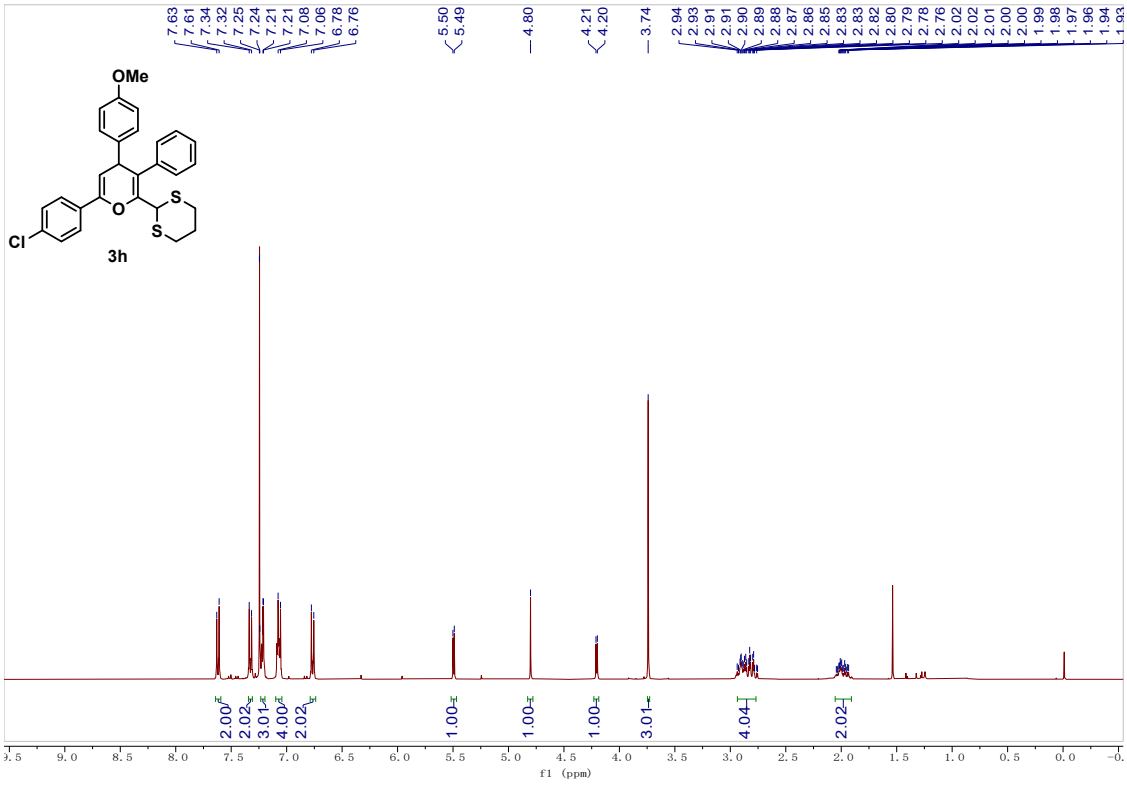
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3g



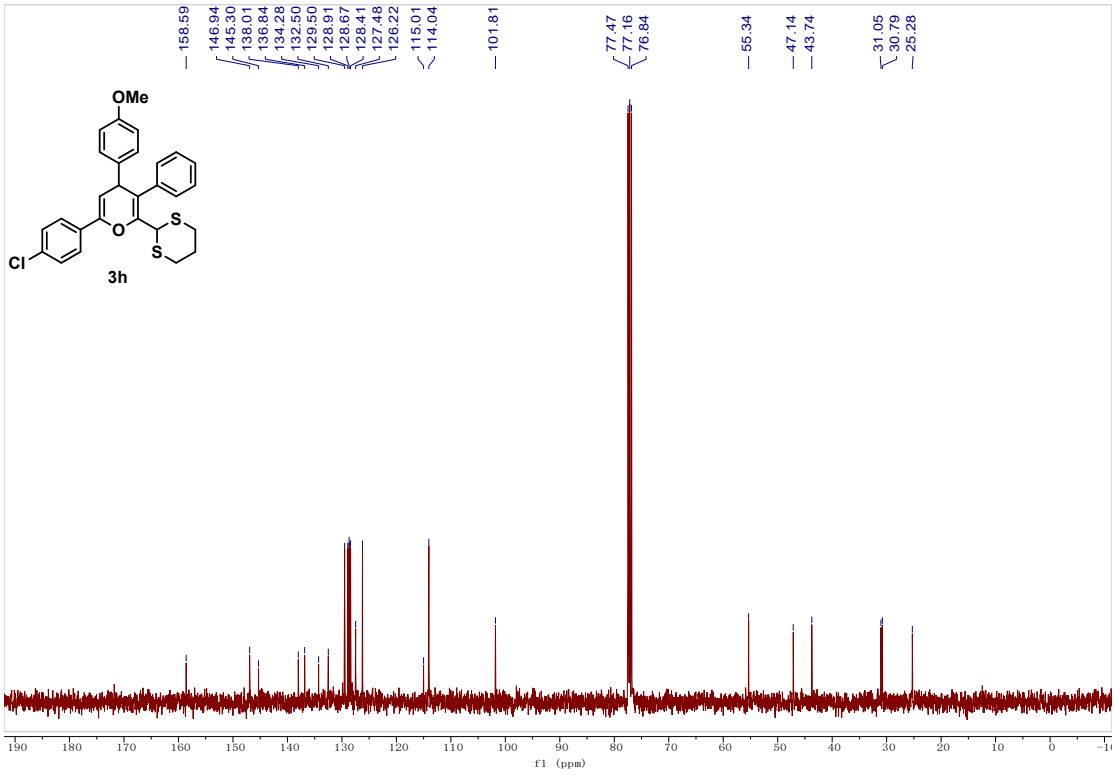
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3g



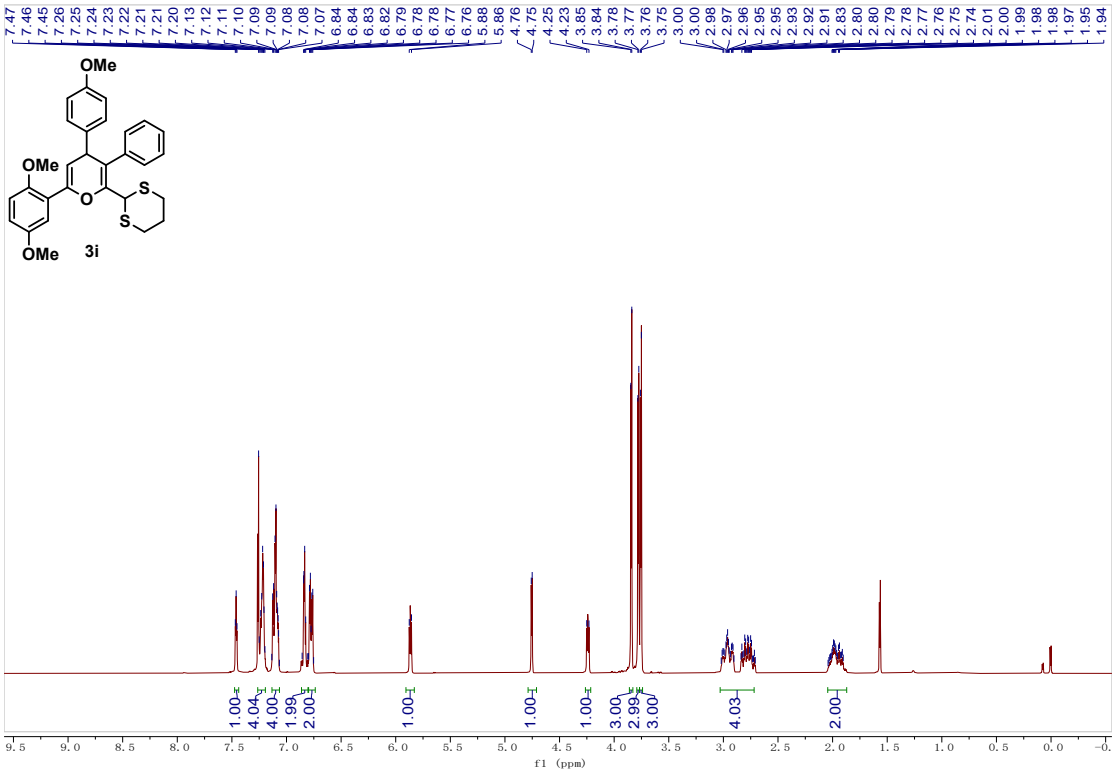
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3h



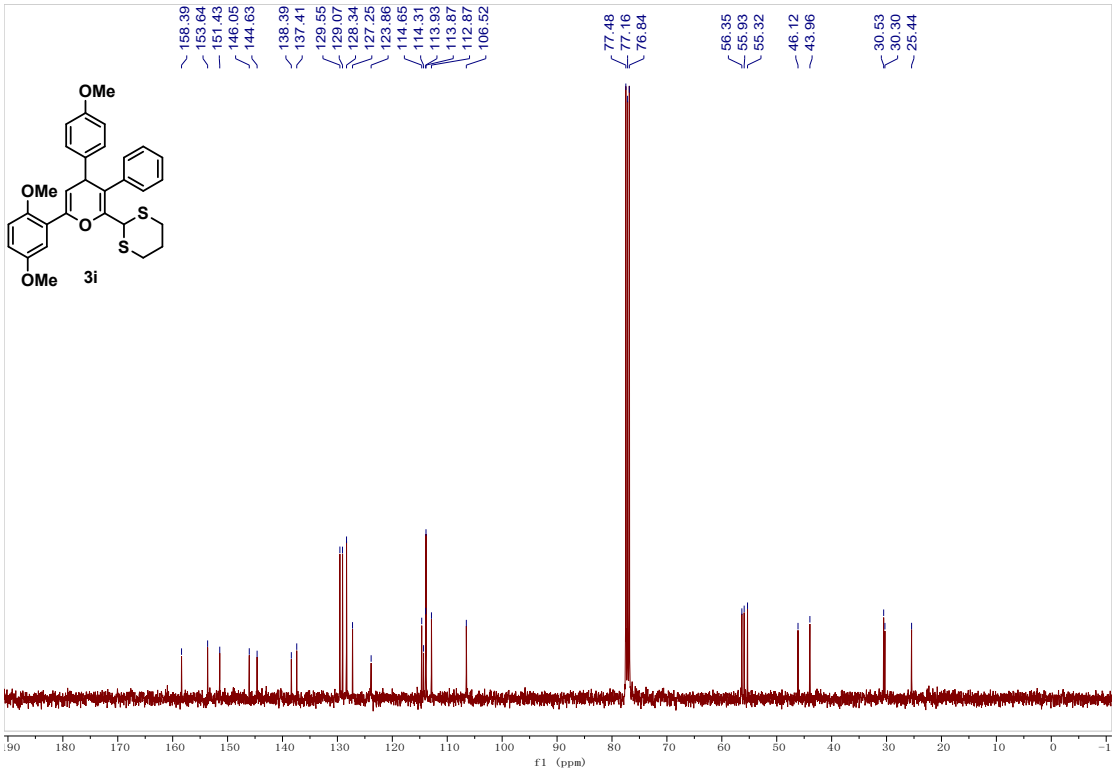
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3h



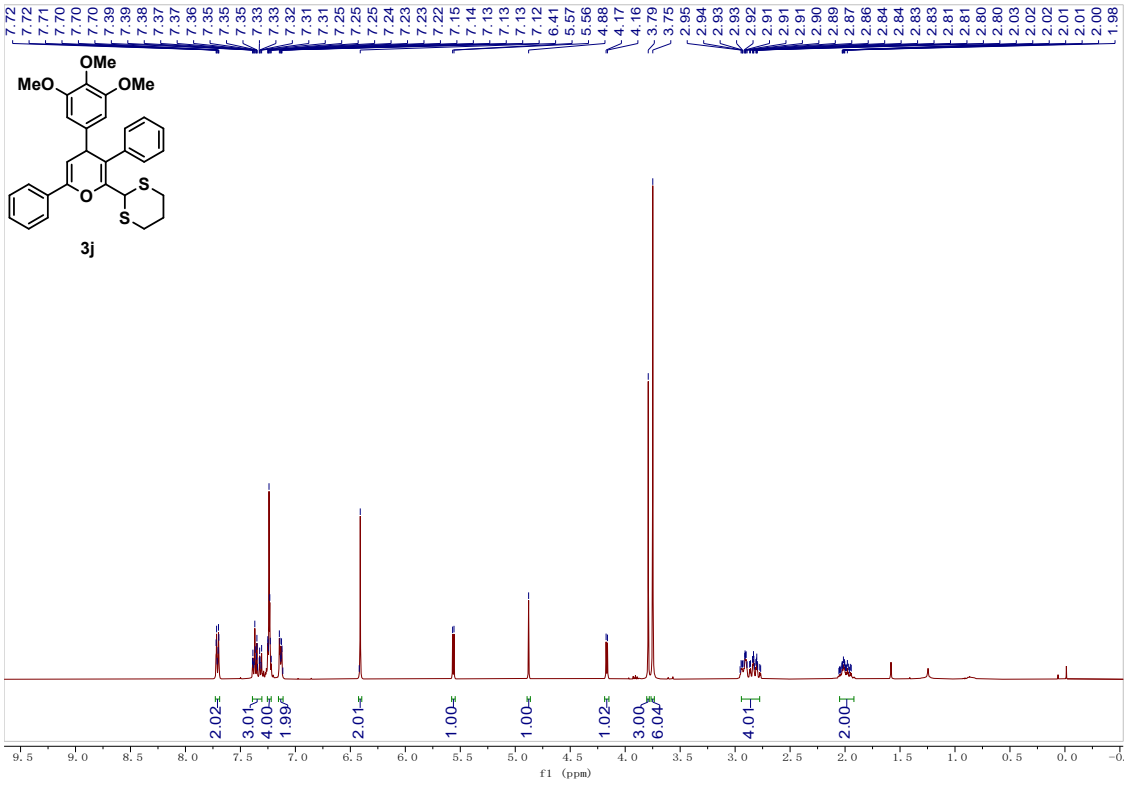
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3i



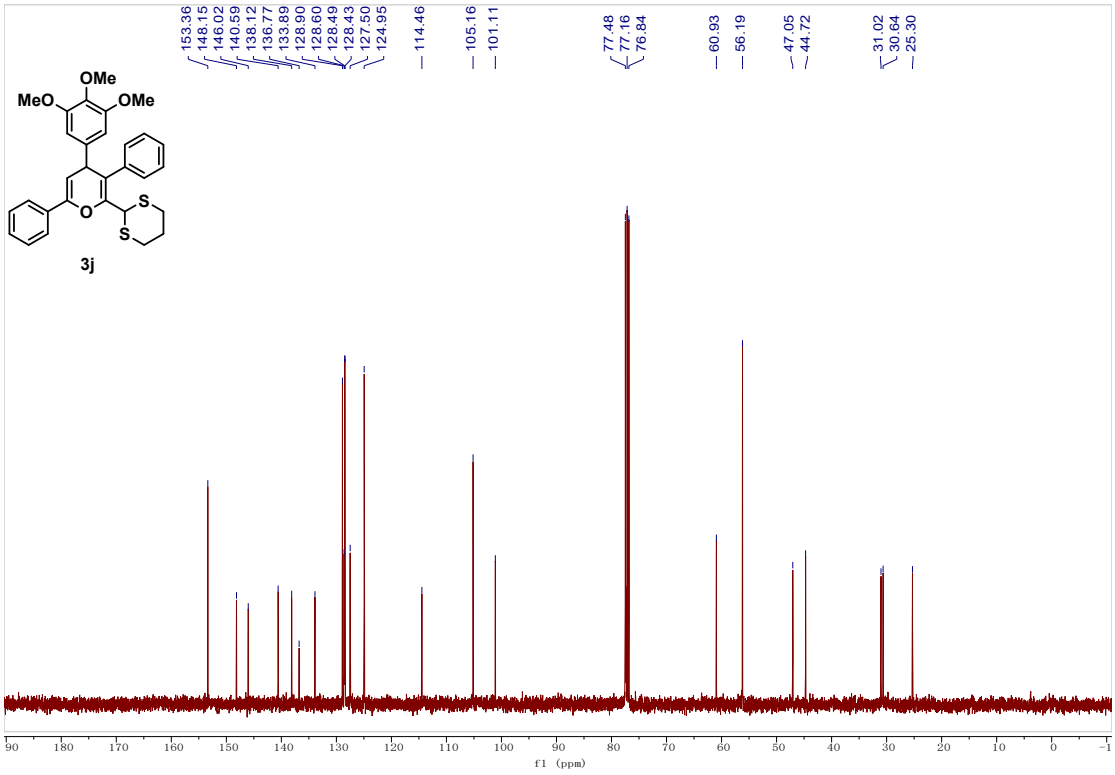
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3i



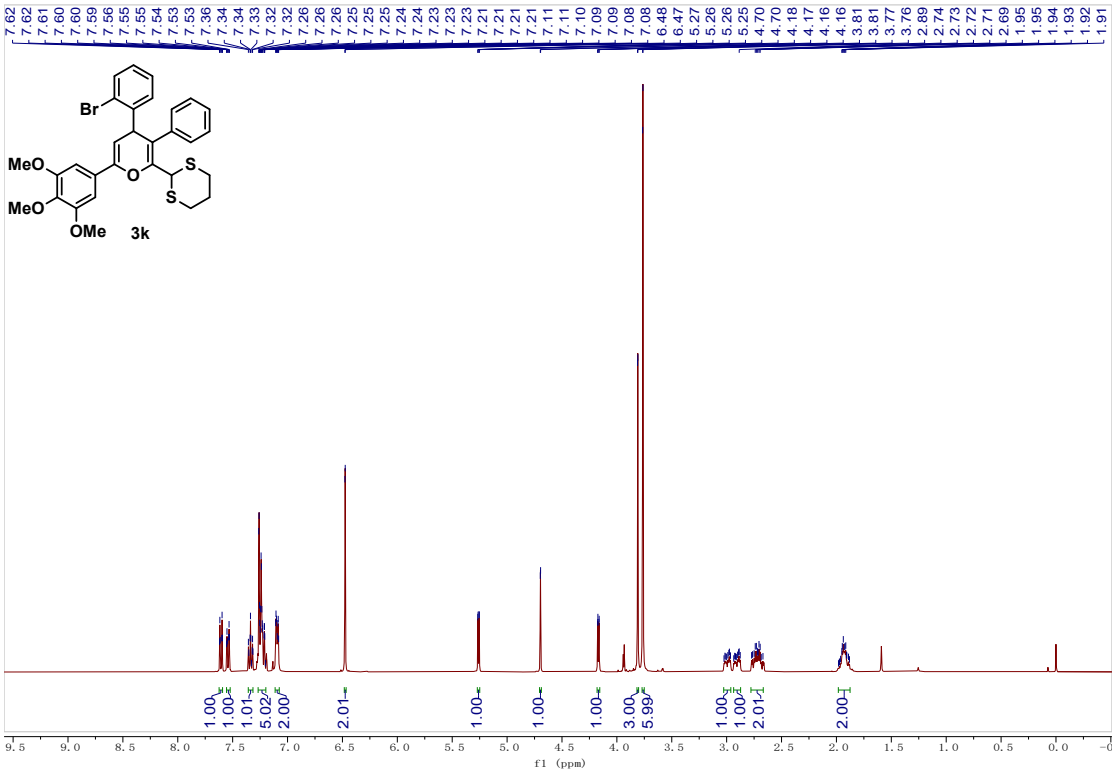
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3J



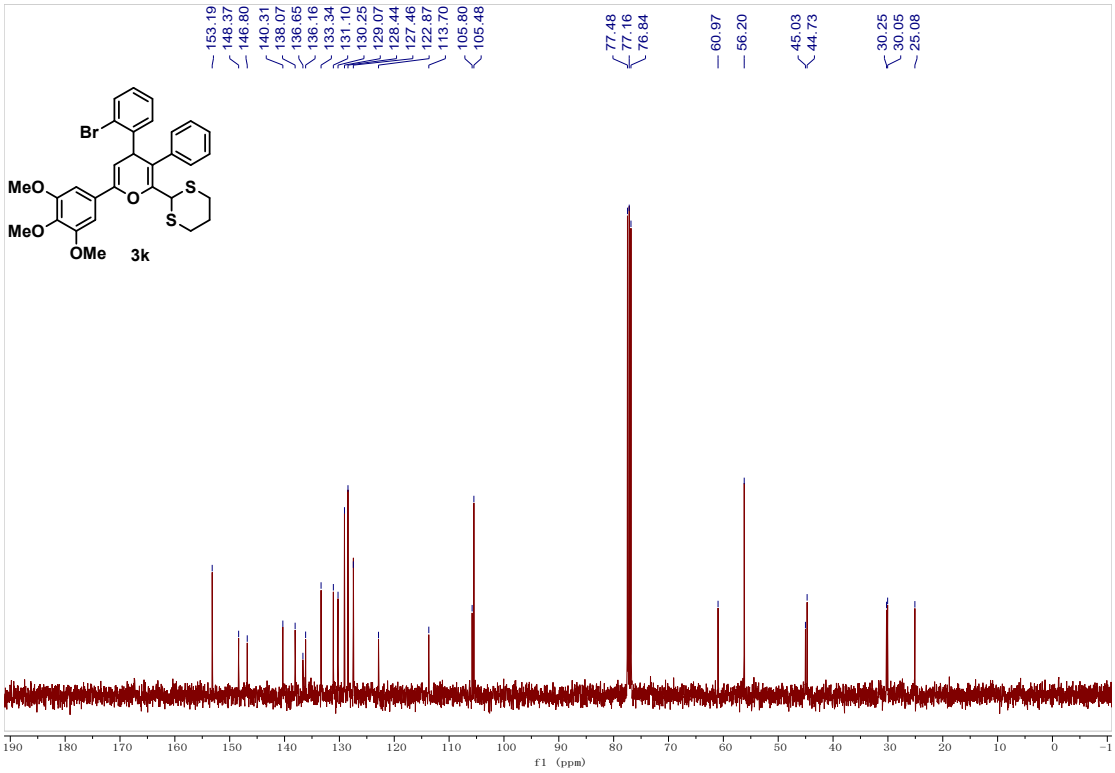
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3J



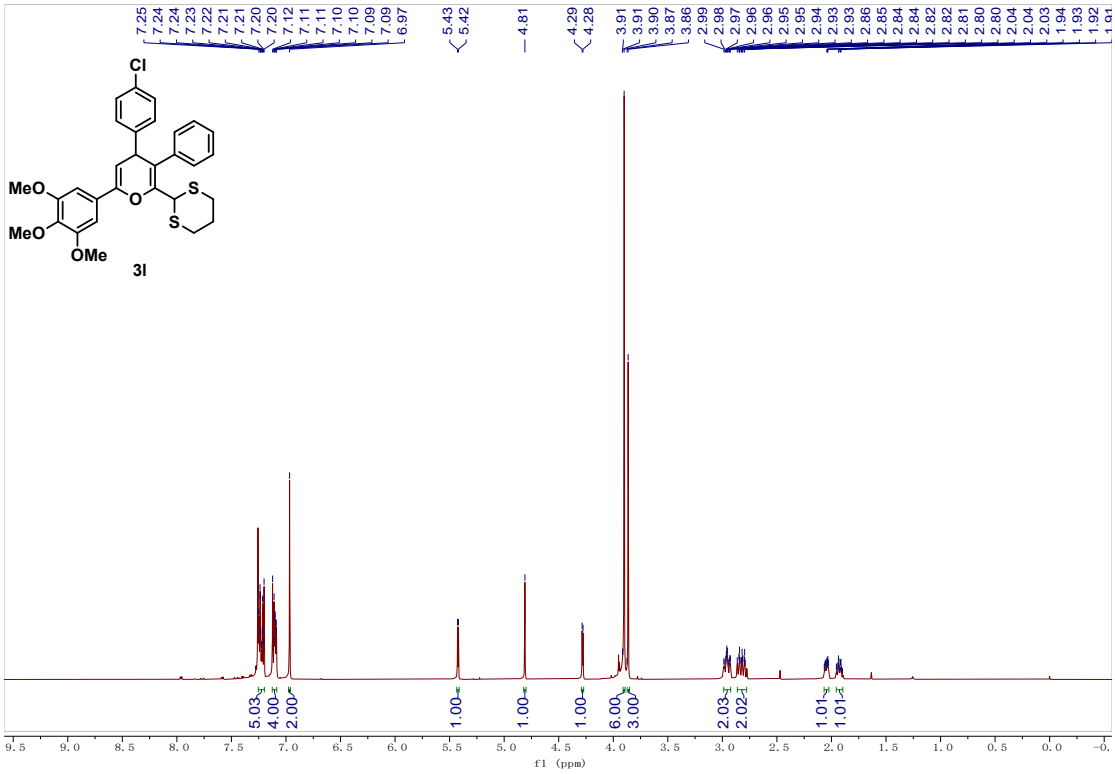
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3k



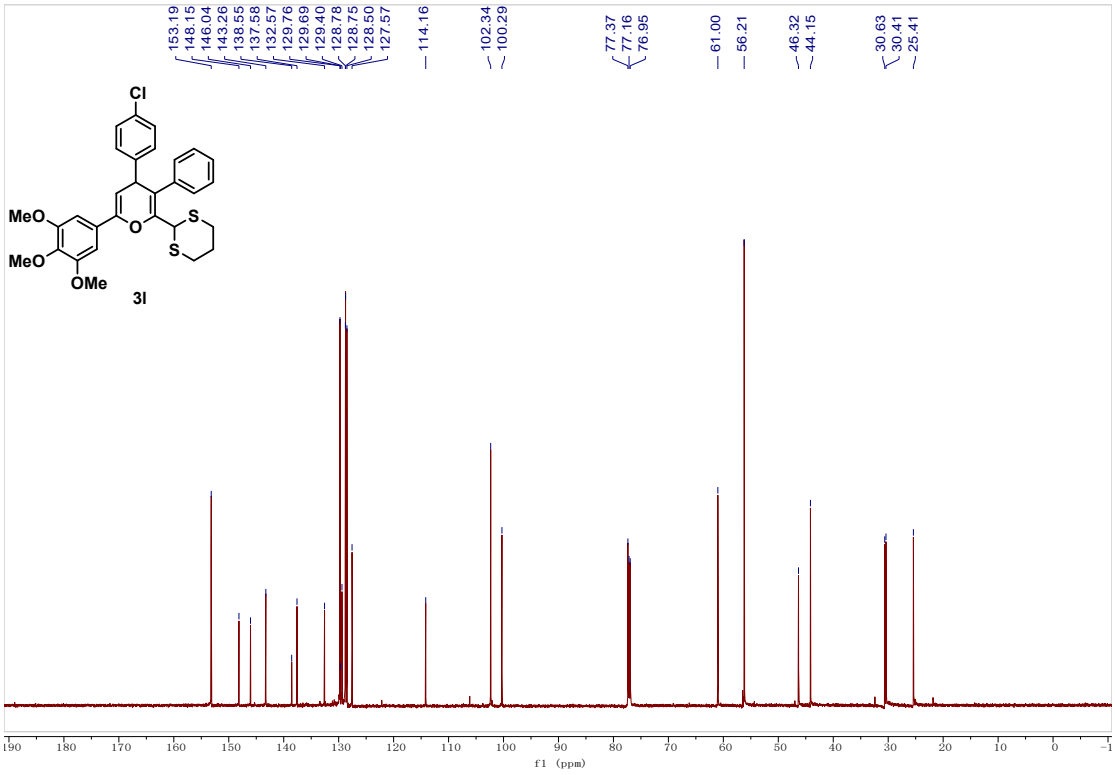
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3k



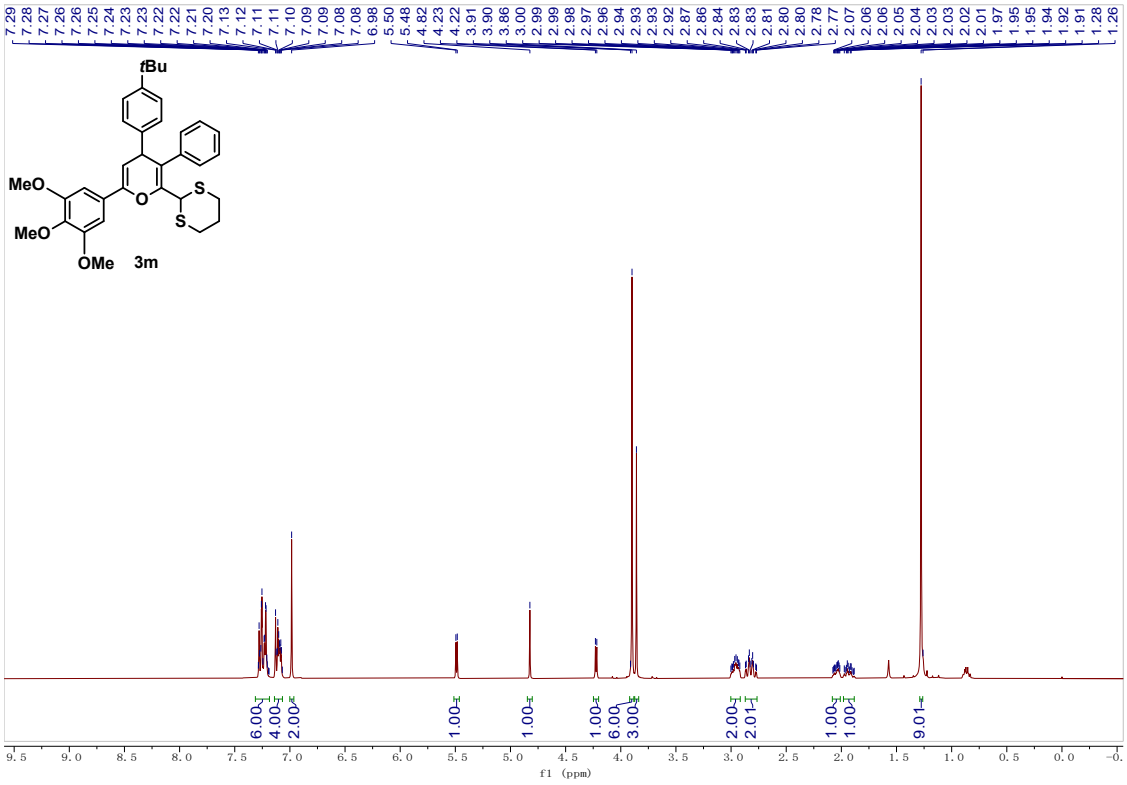
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3l



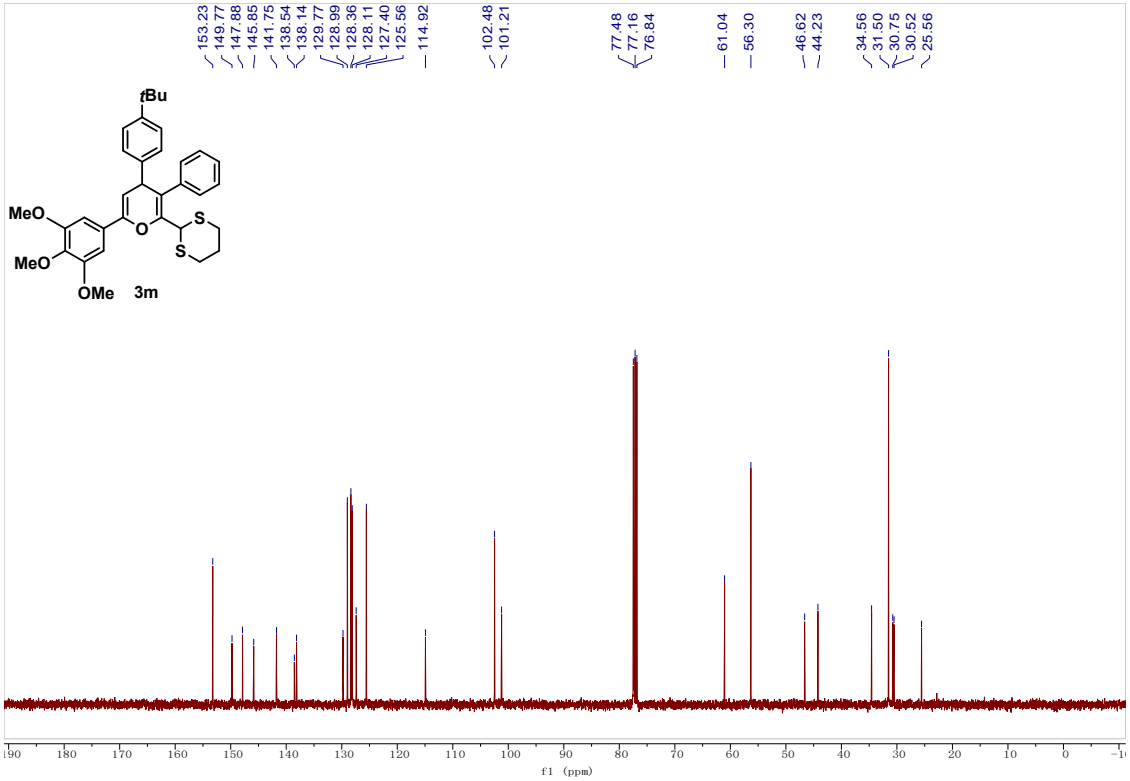
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3l



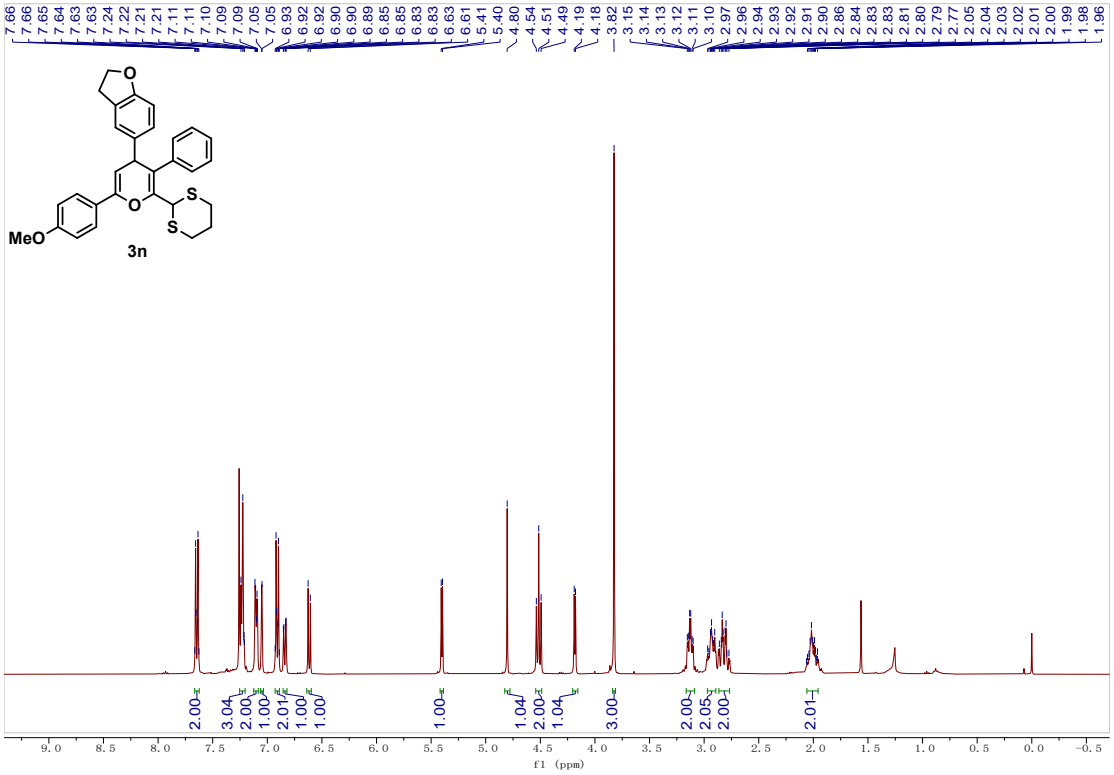
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3m



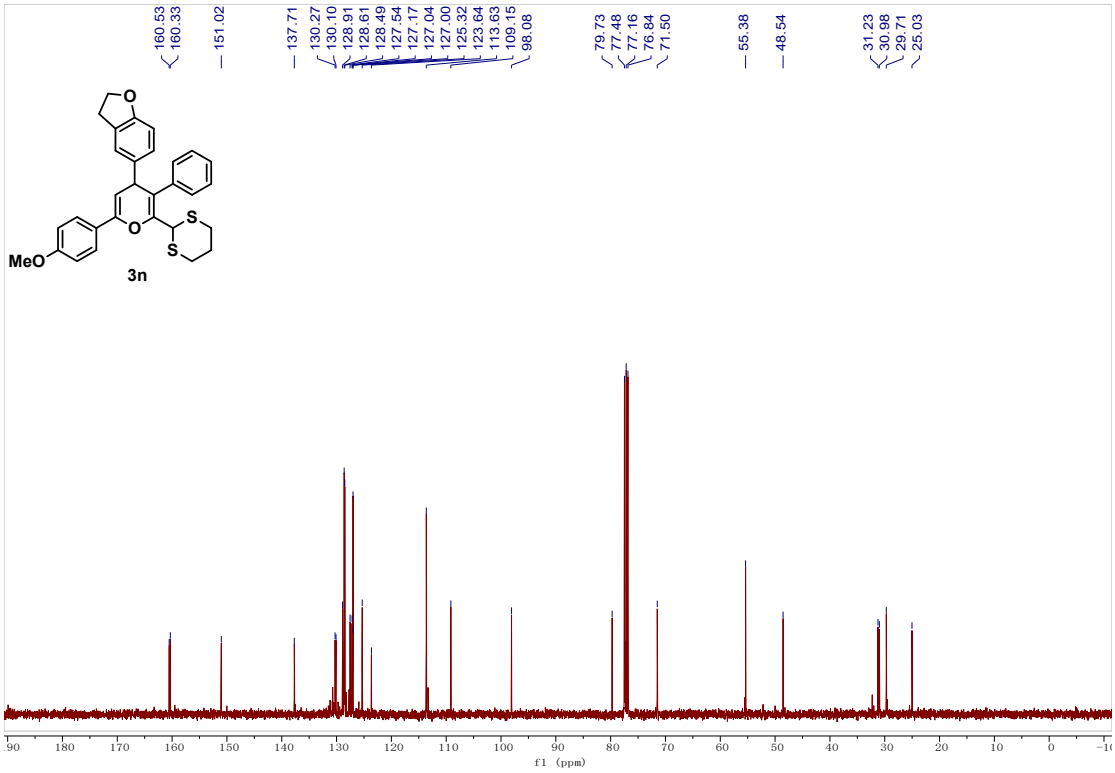
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3m



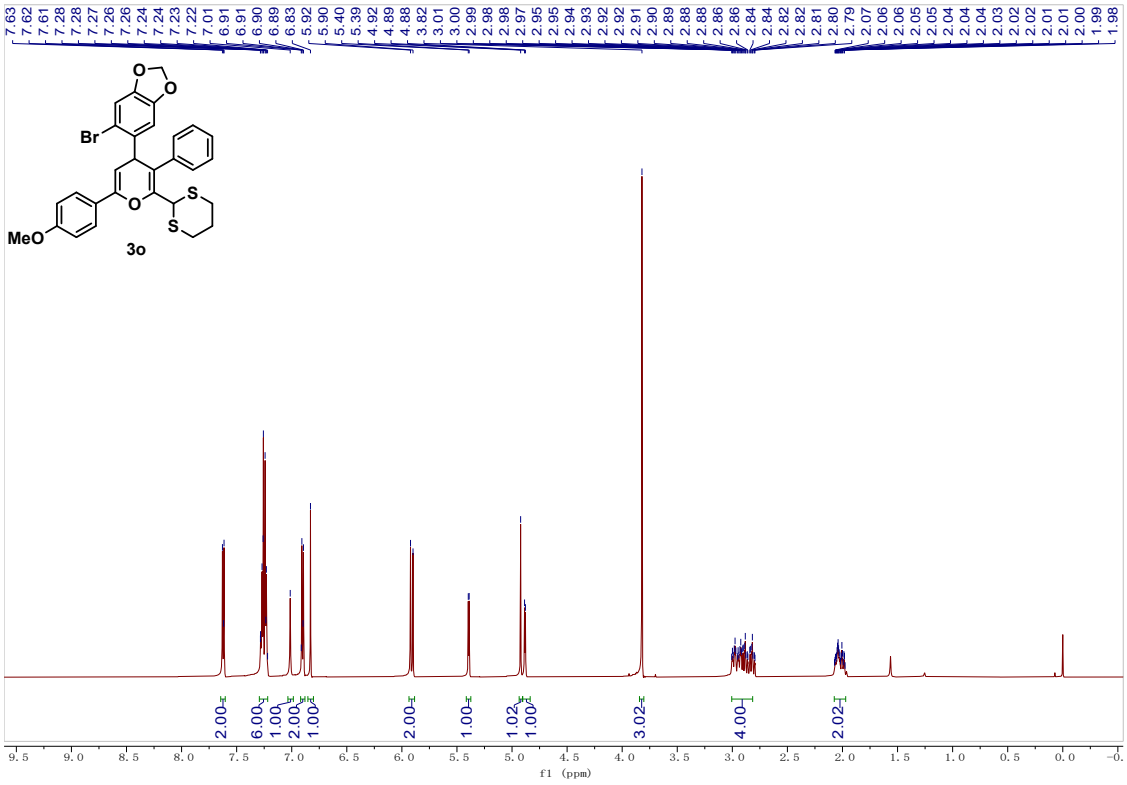
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3n



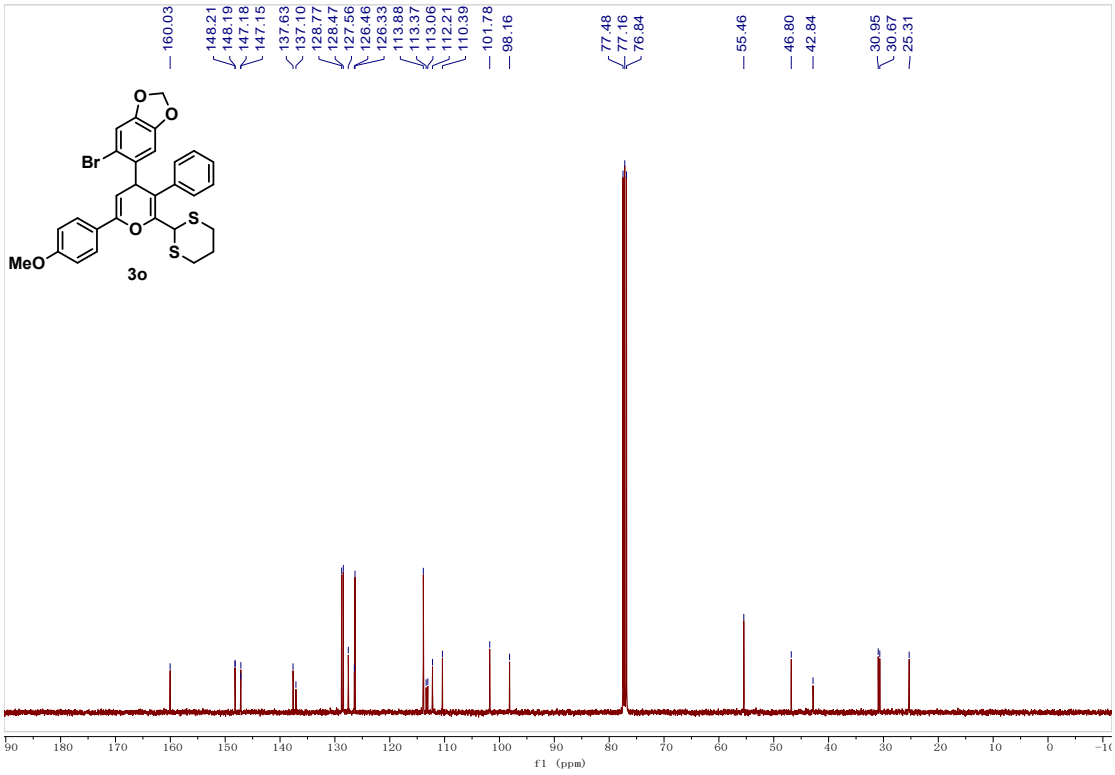
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3n



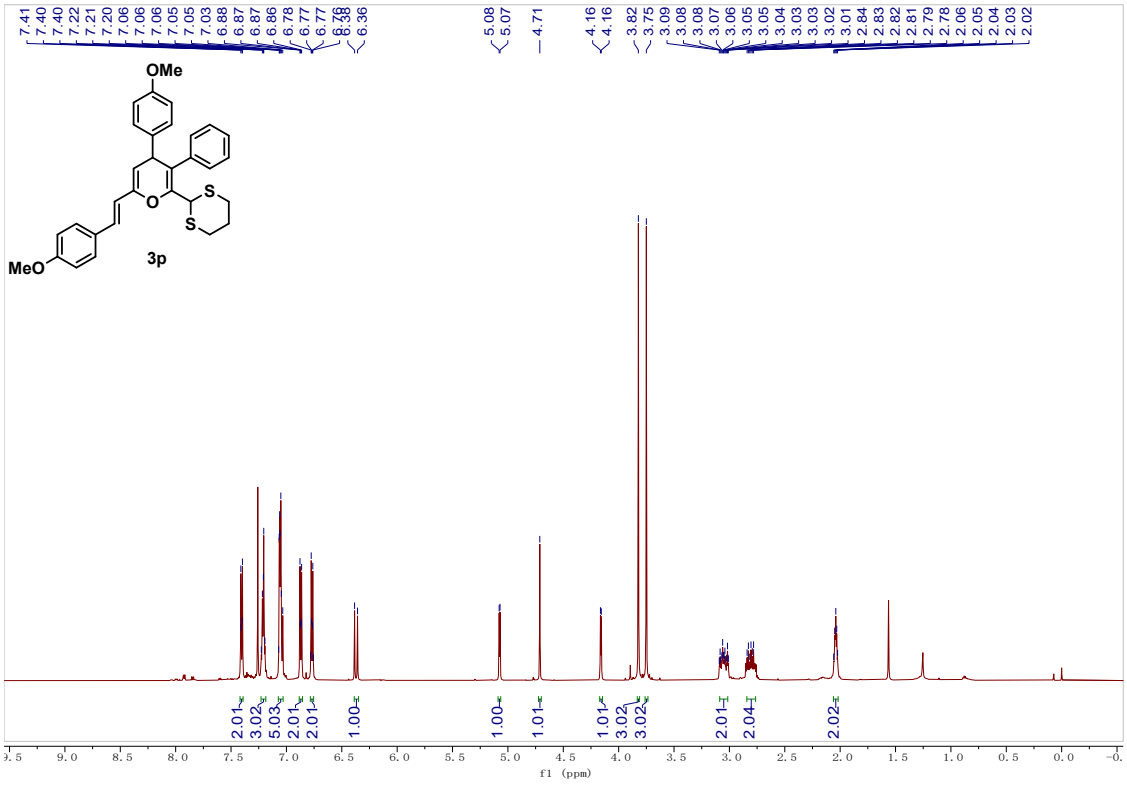
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3o



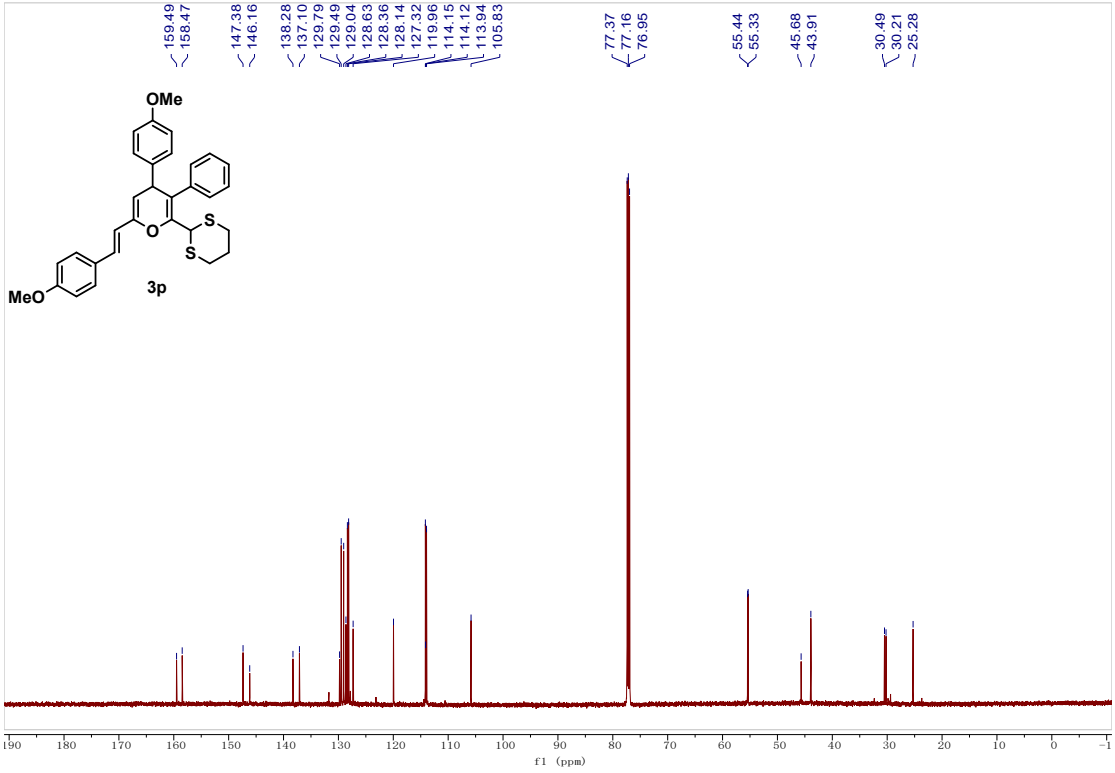
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3o



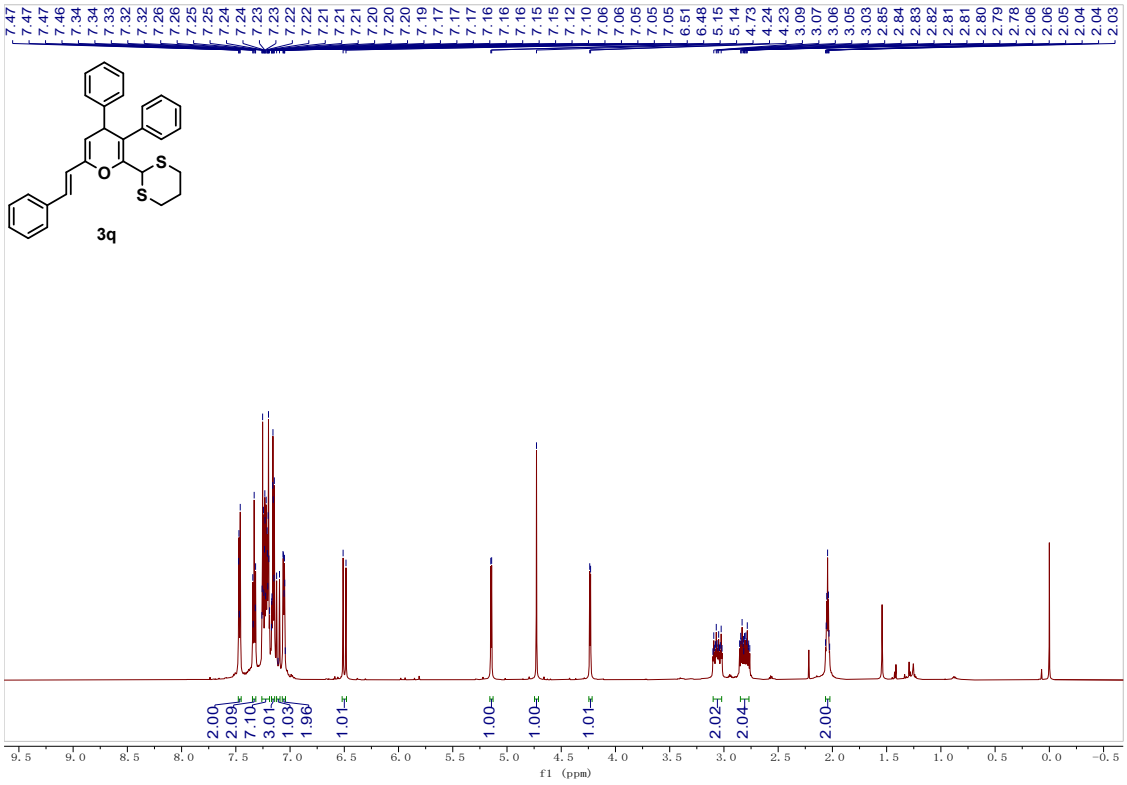
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3p



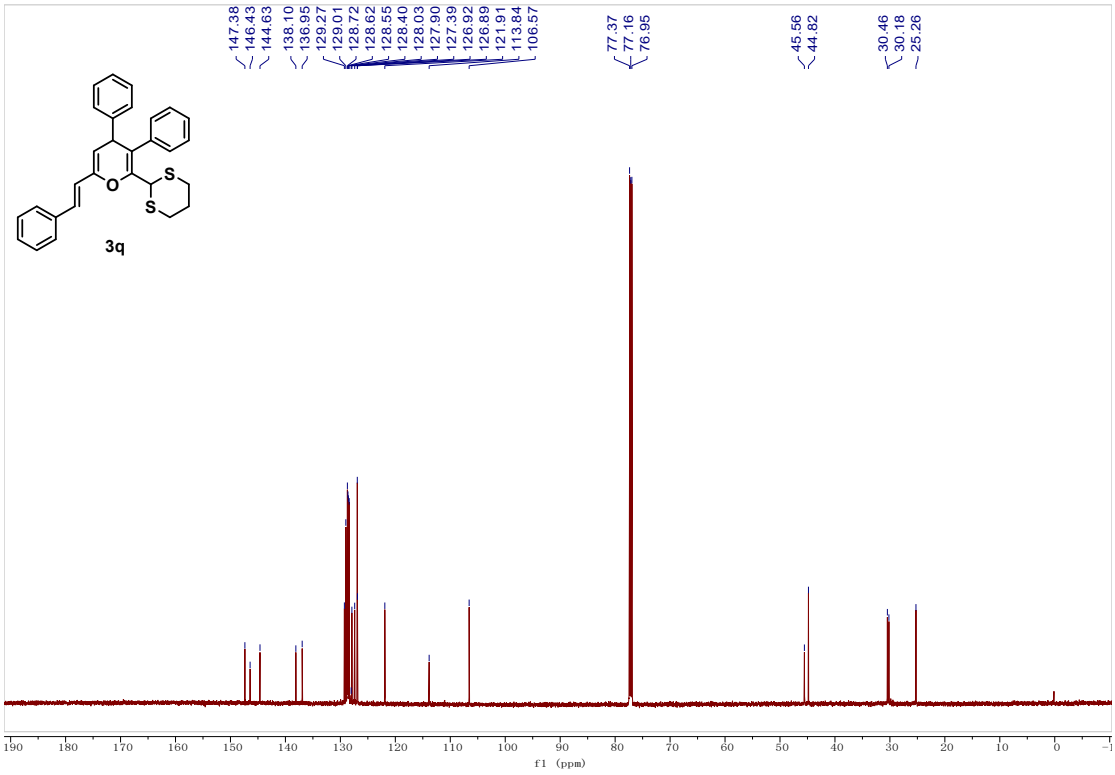
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3p



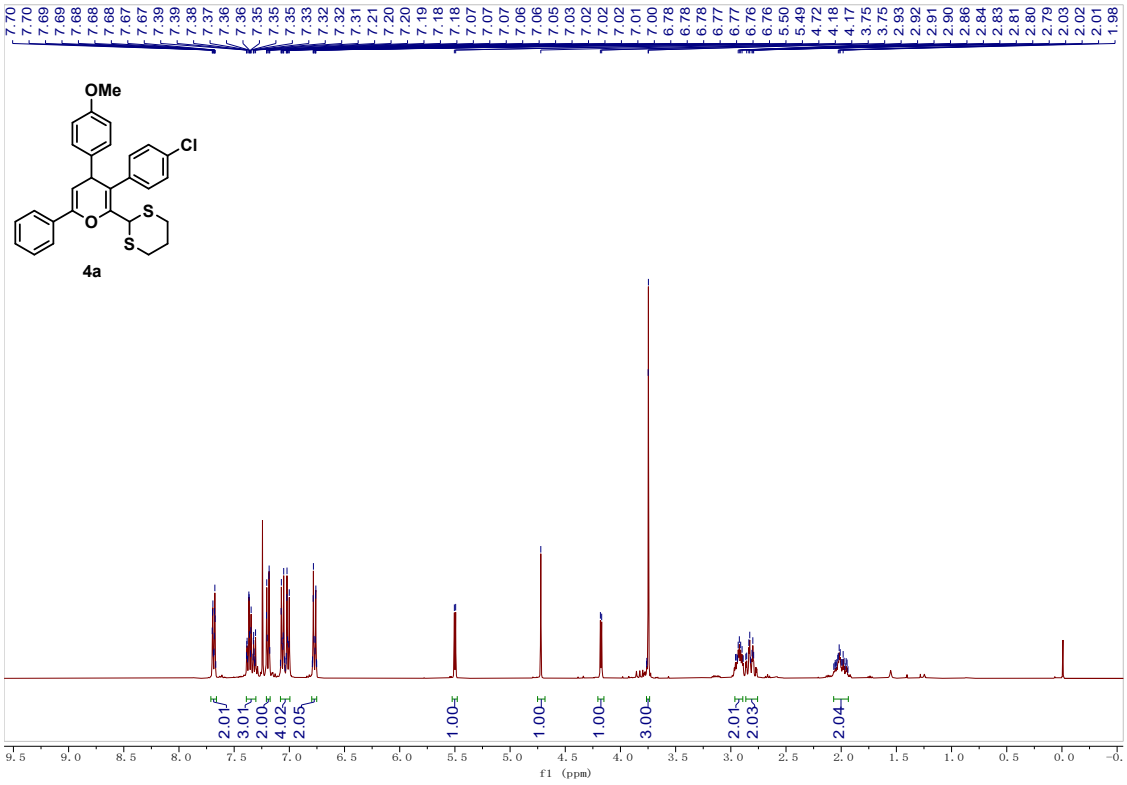
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3q



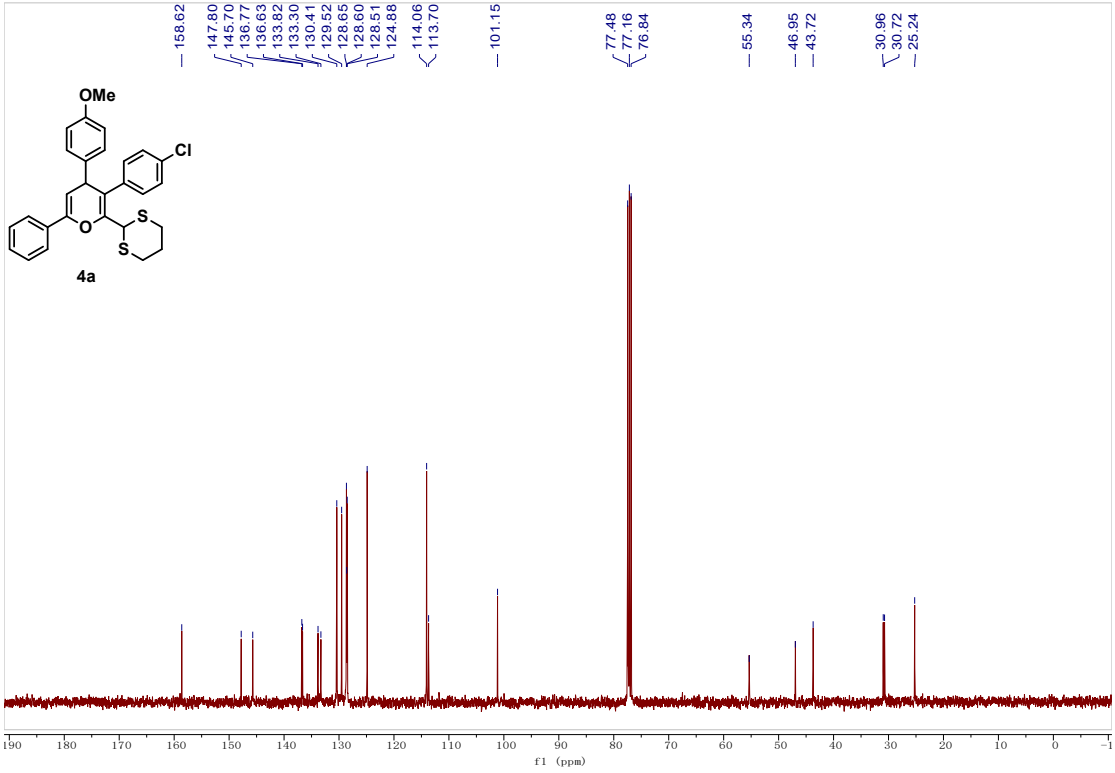
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3q



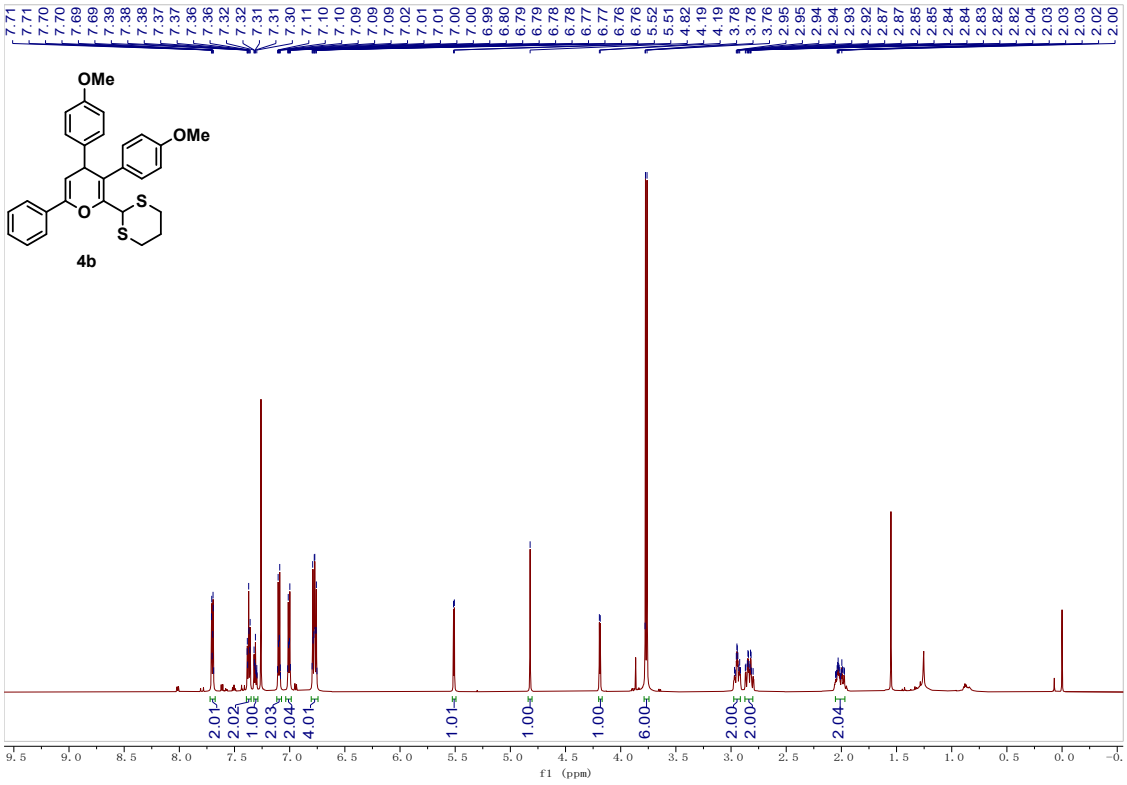
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4a



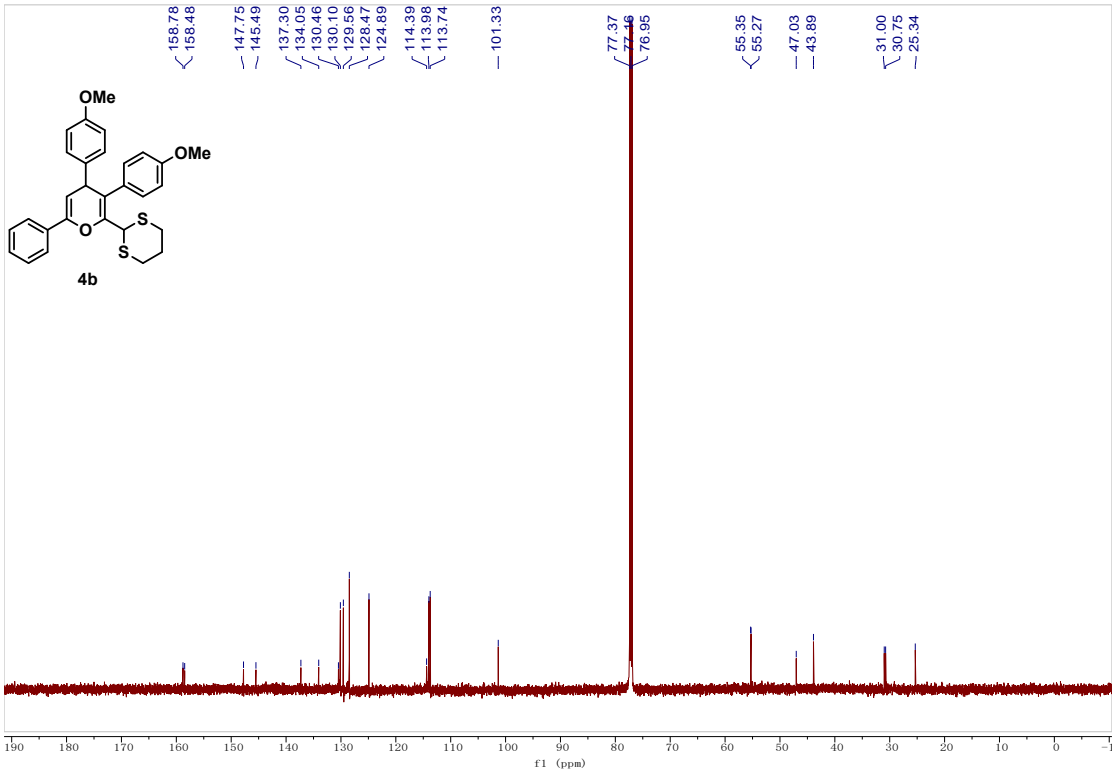
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4a



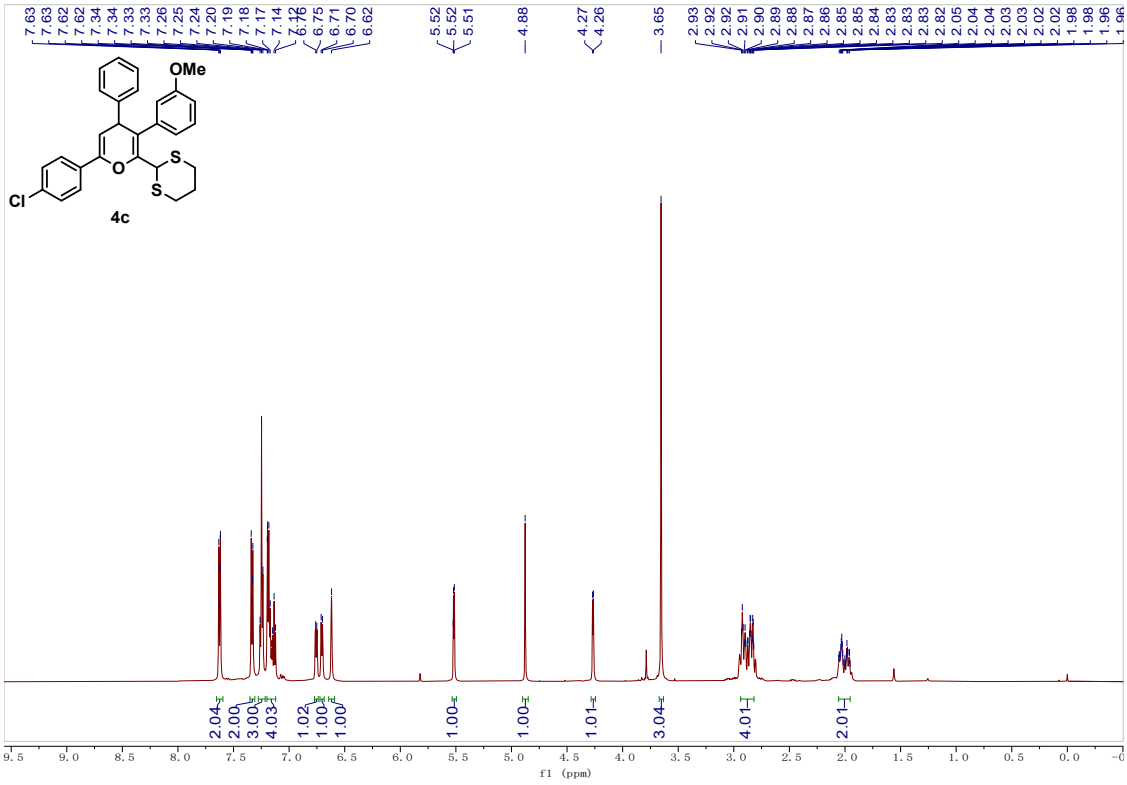
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4b



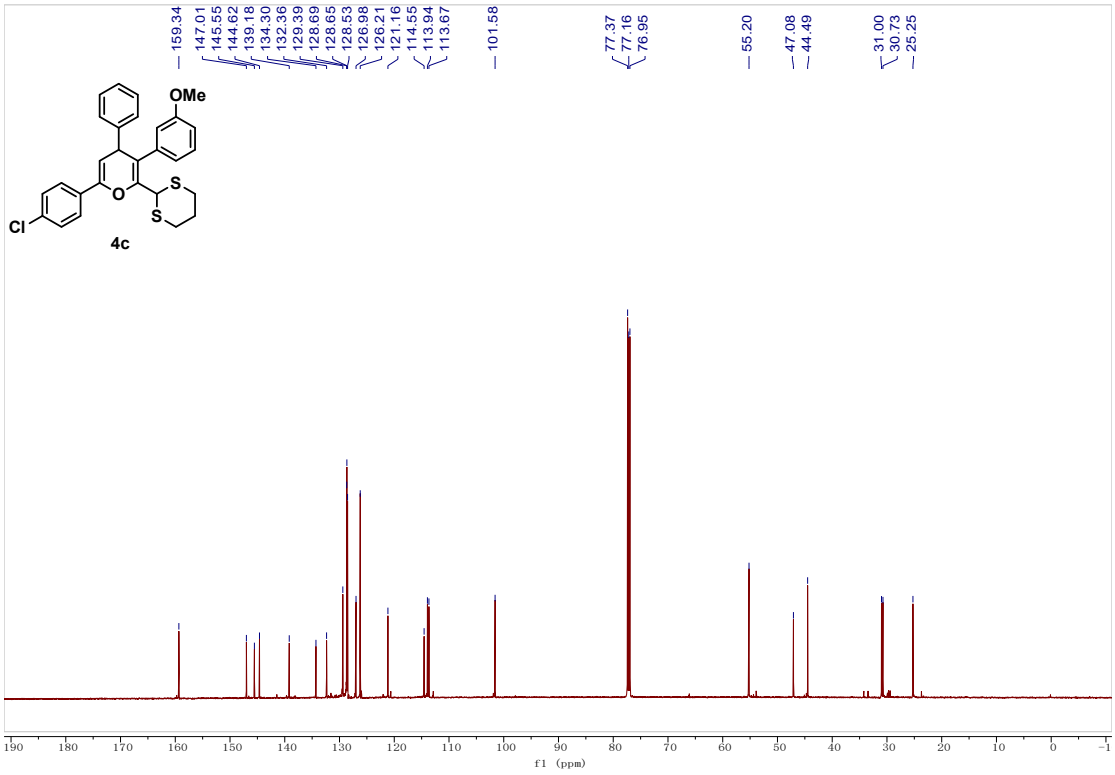
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4b



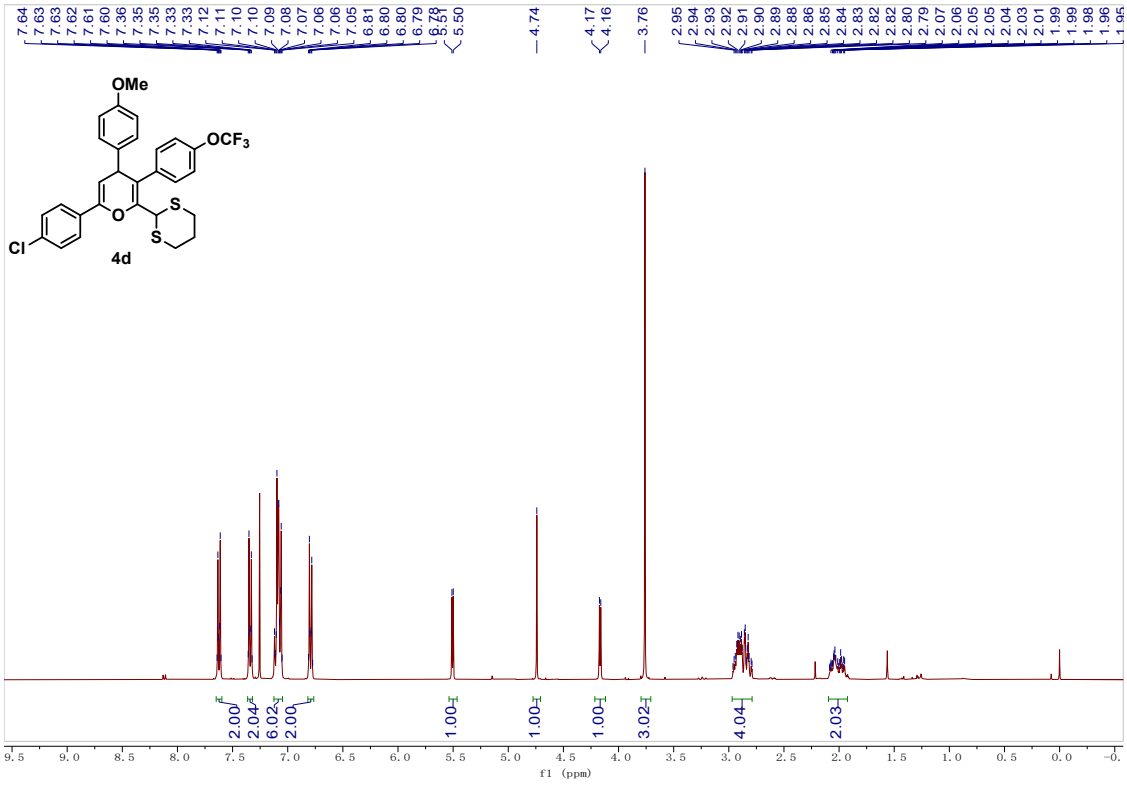
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4c



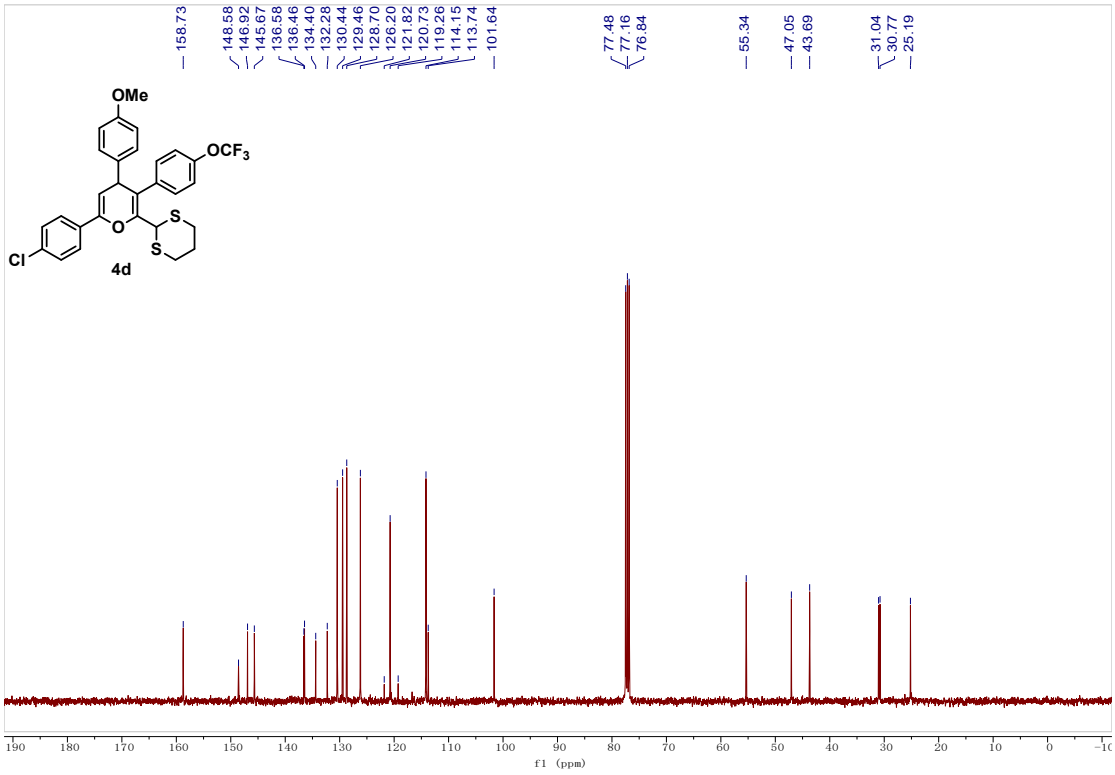
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4c



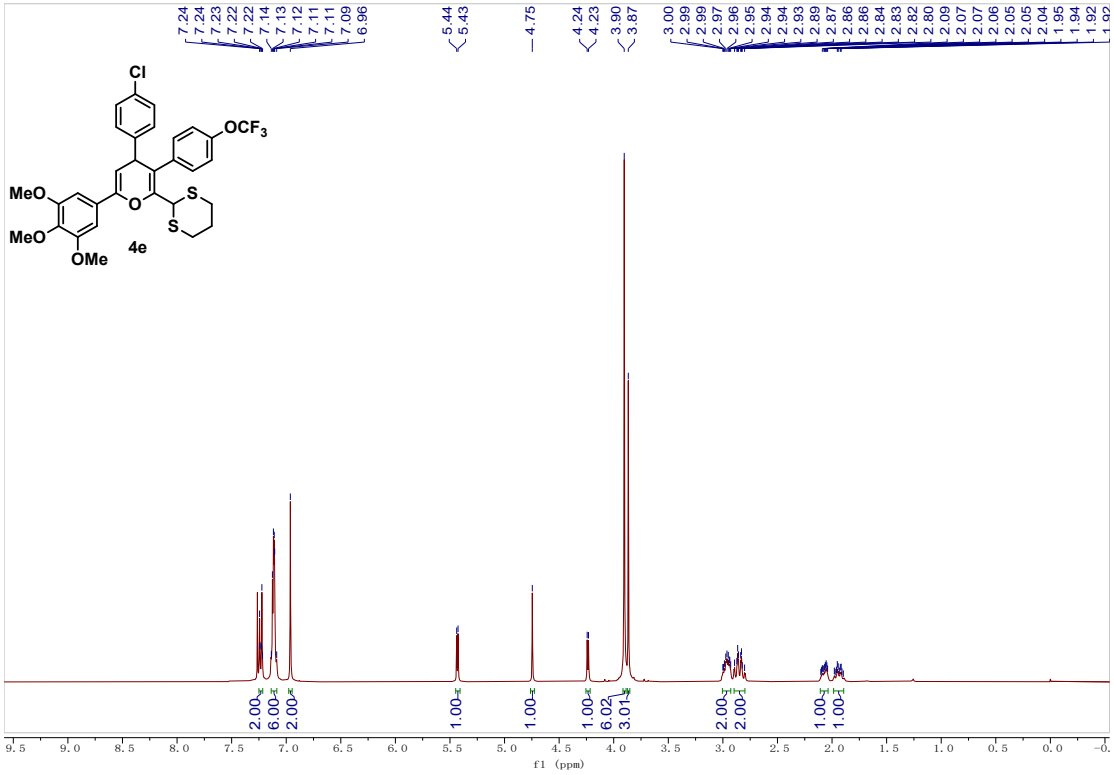
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4d



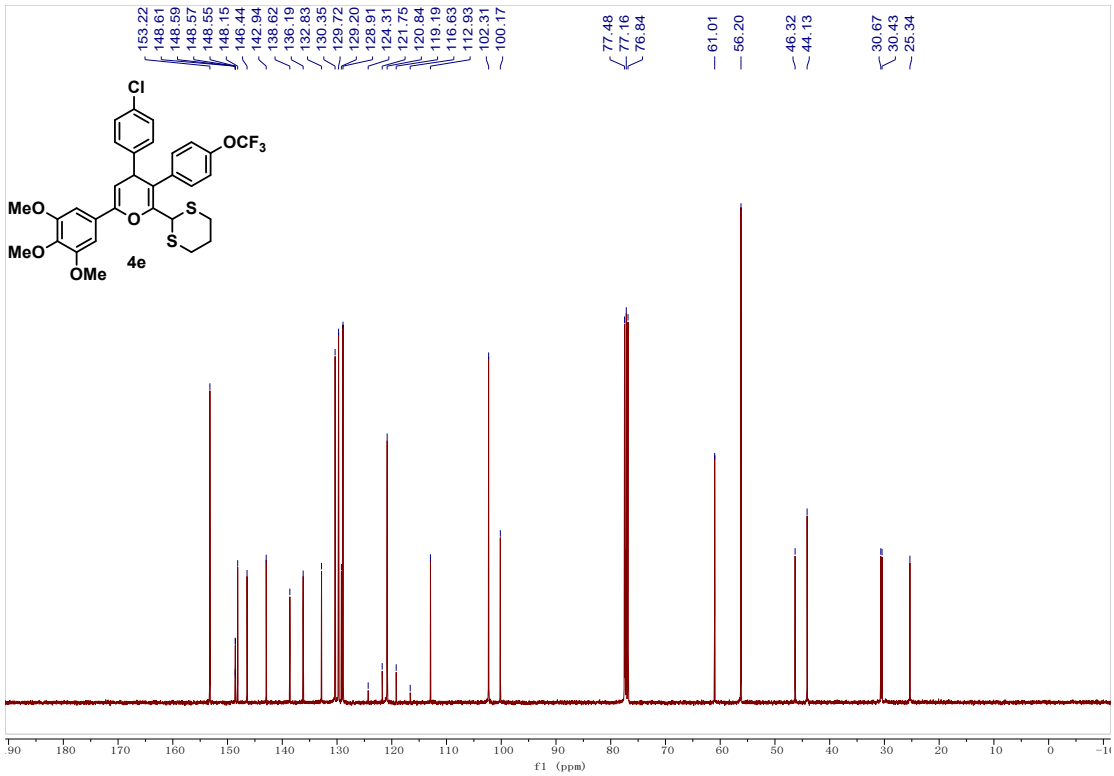
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4d



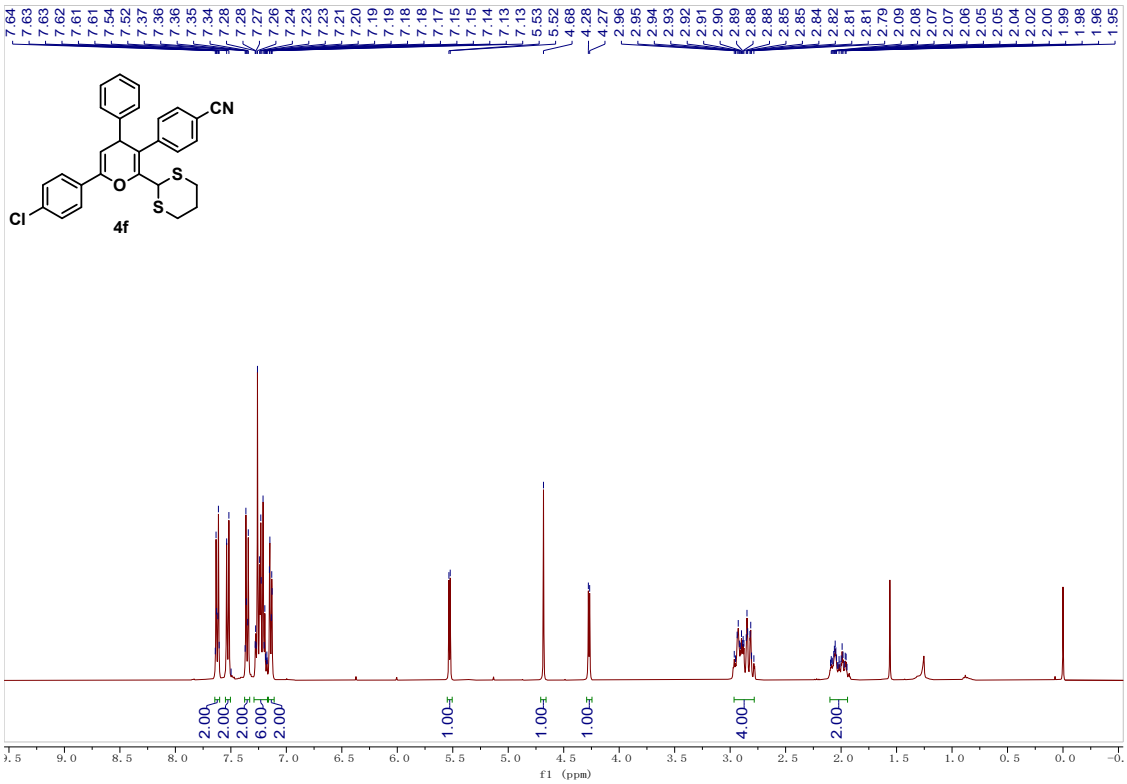
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4e



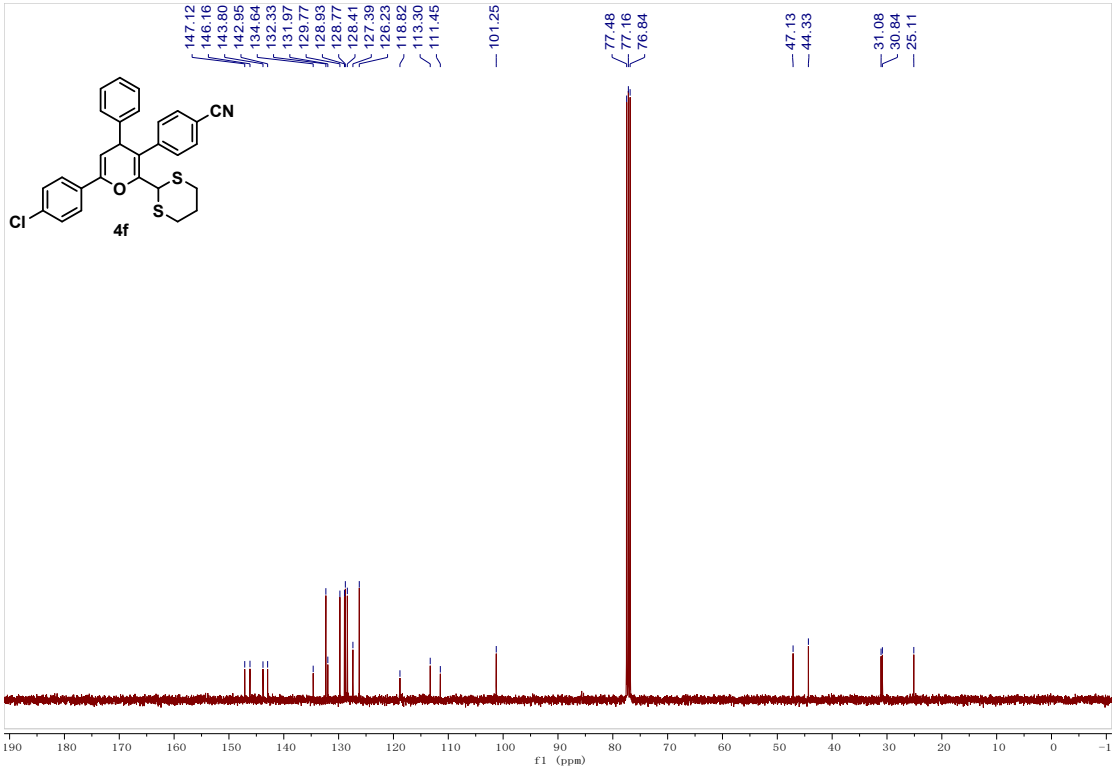
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4e



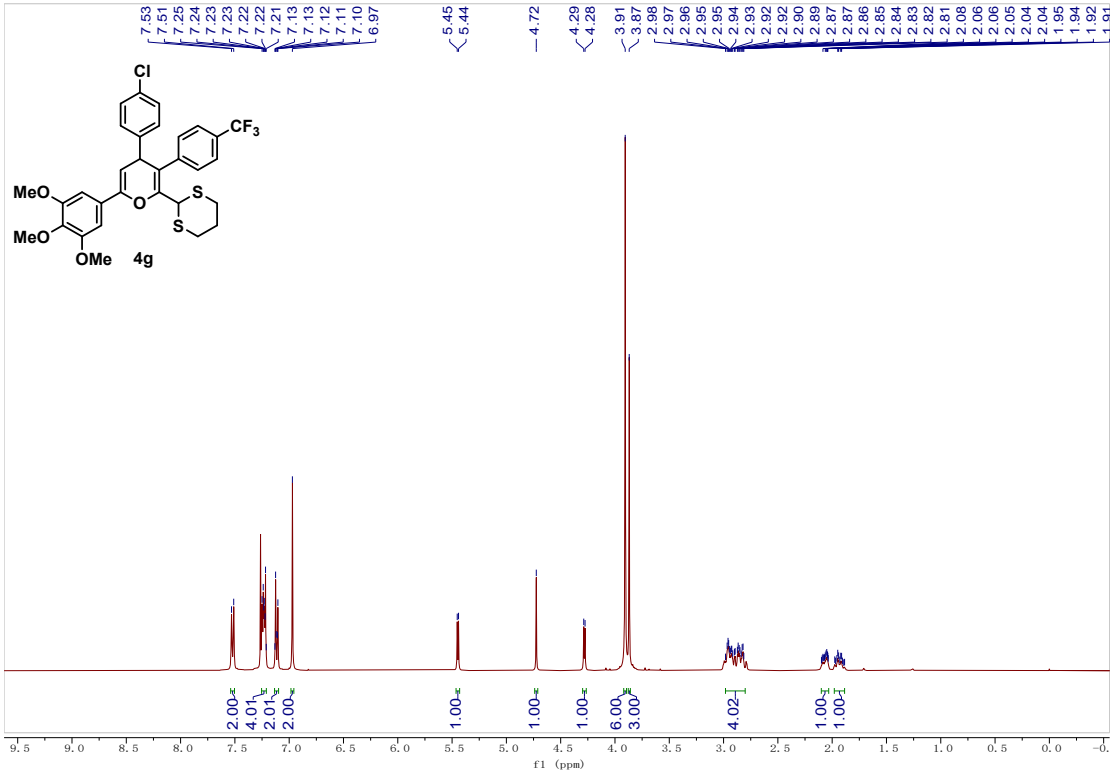
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4f



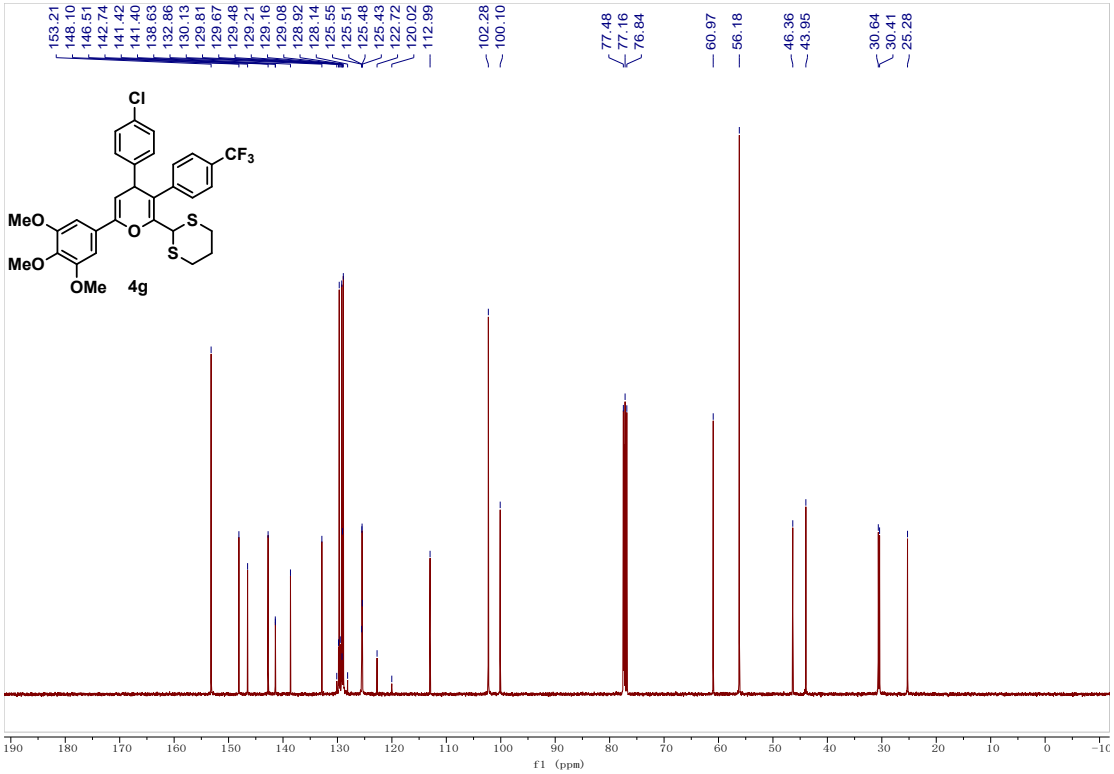
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4f



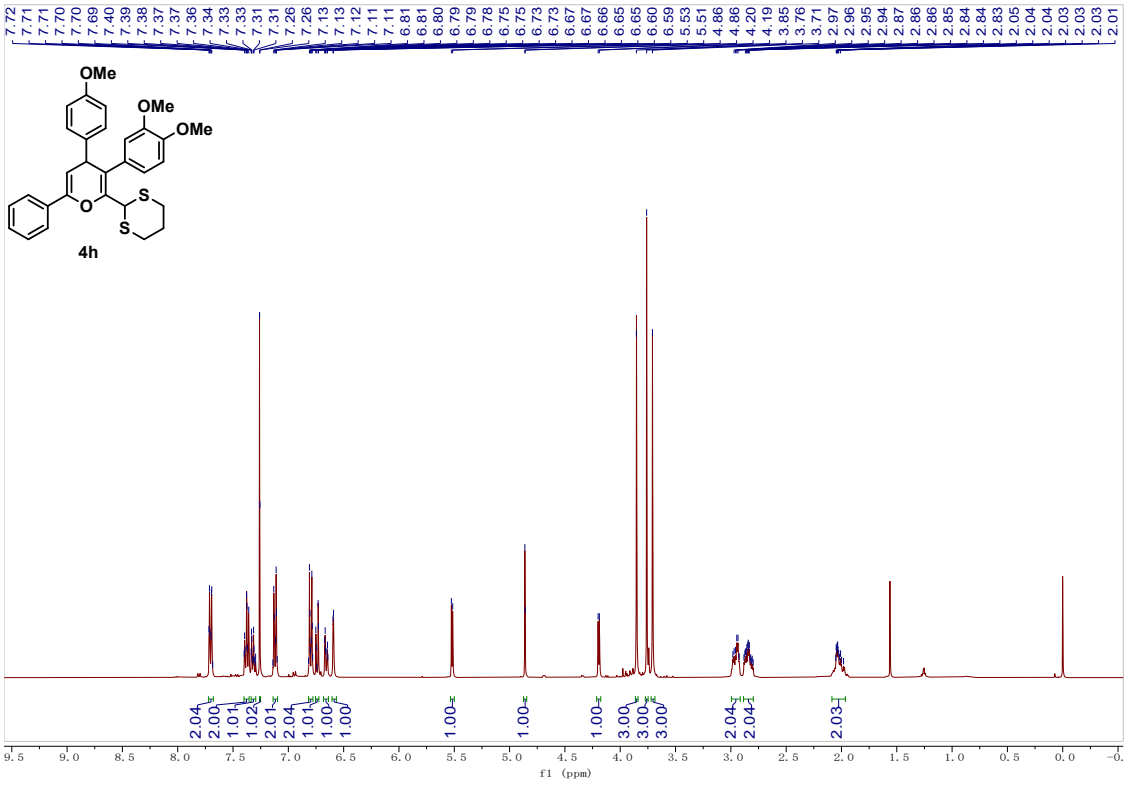
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4g



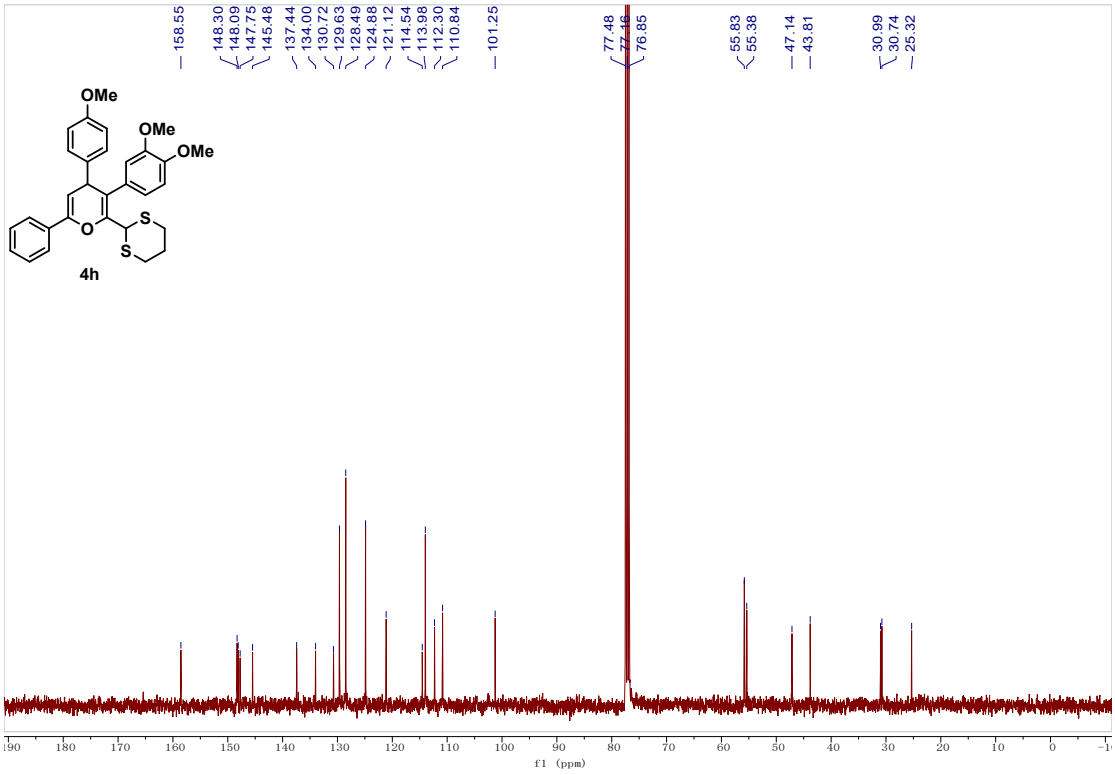
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4g



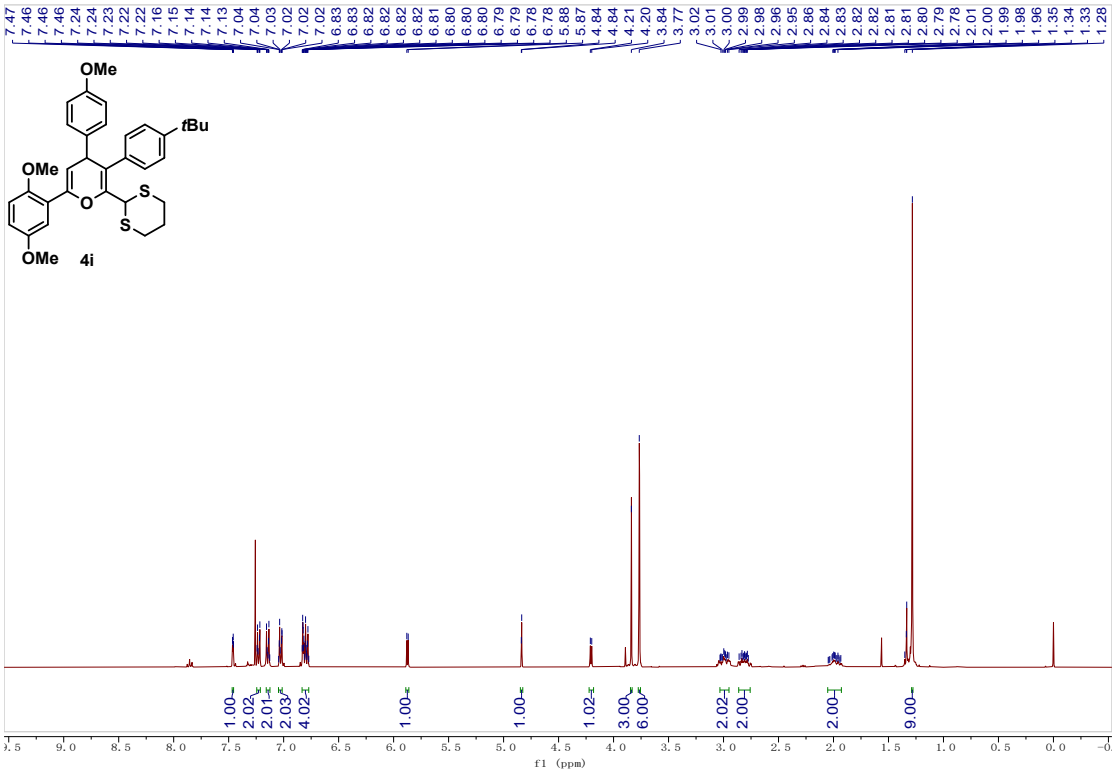
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4h



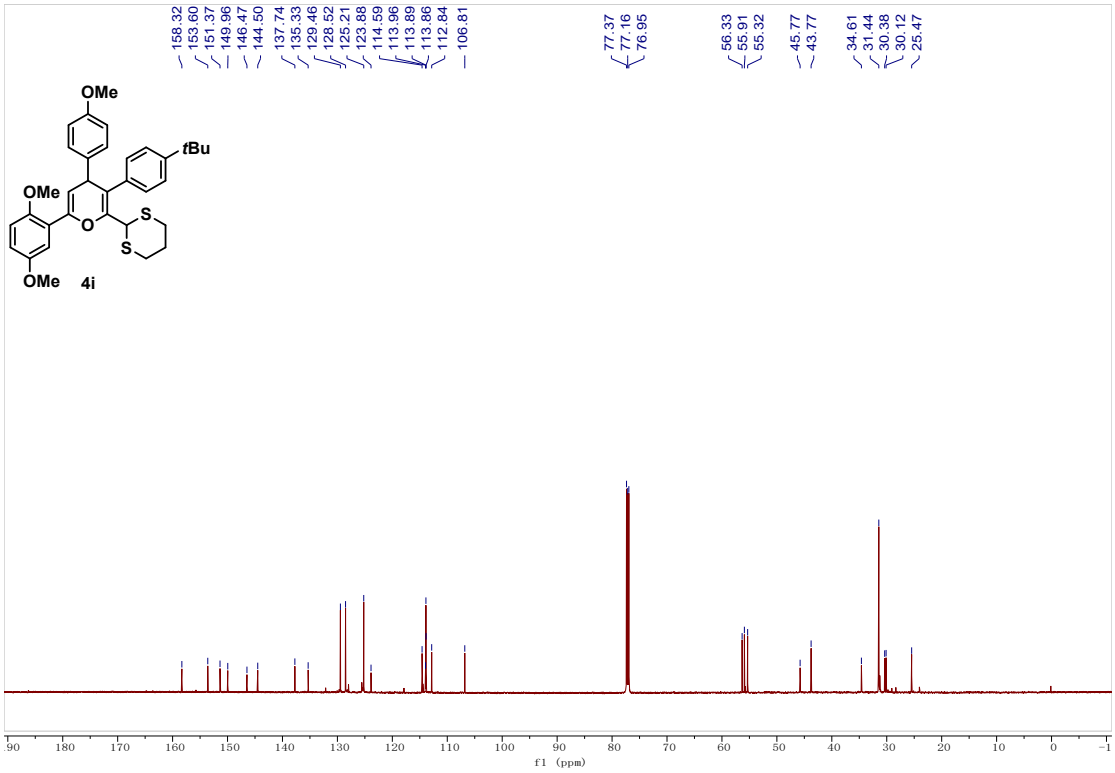
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4h



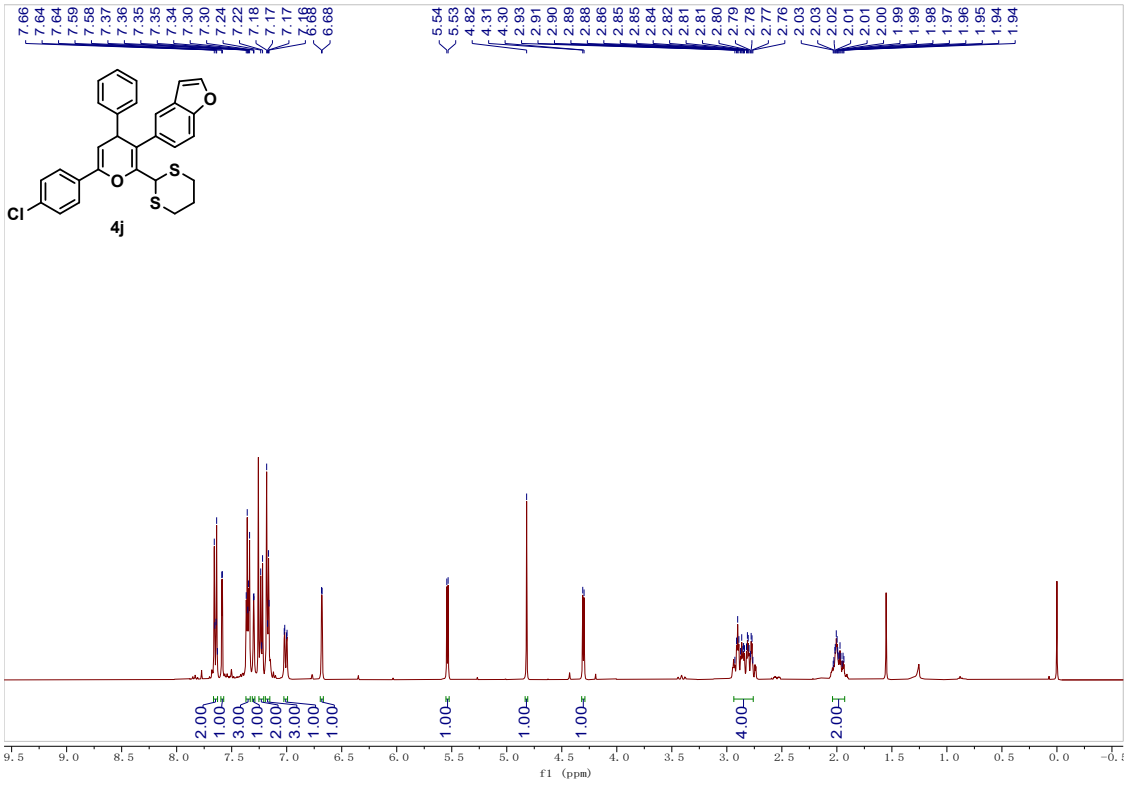
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4i



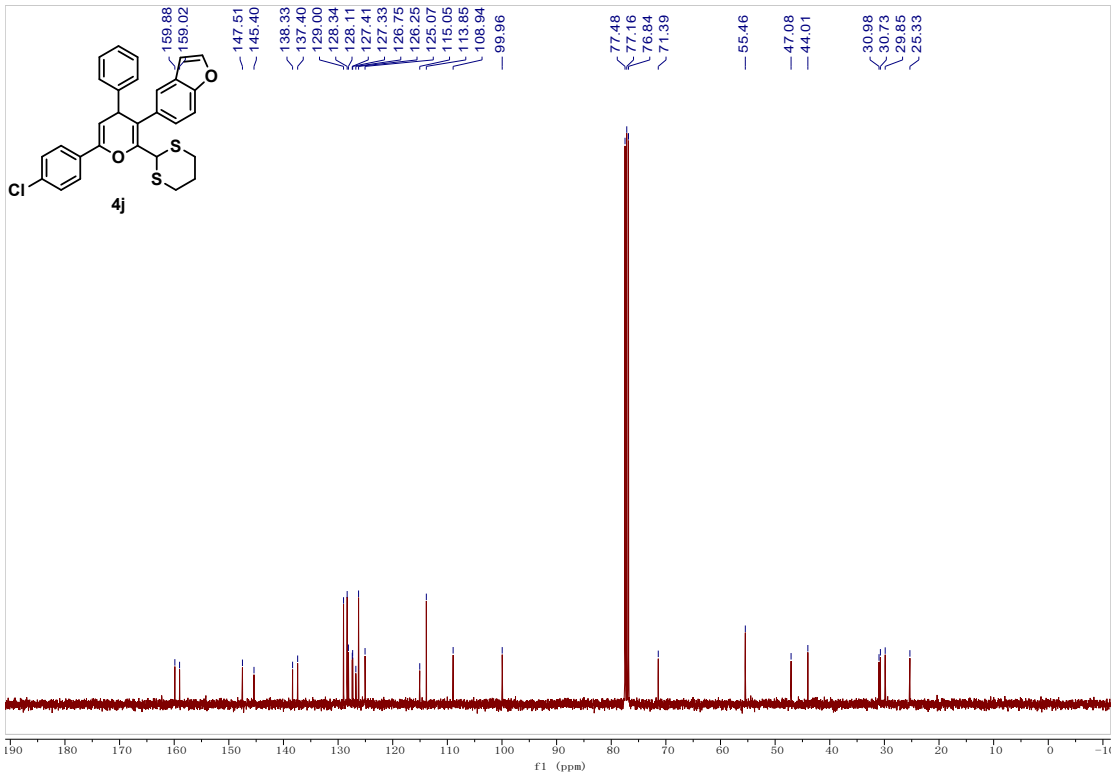
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4i



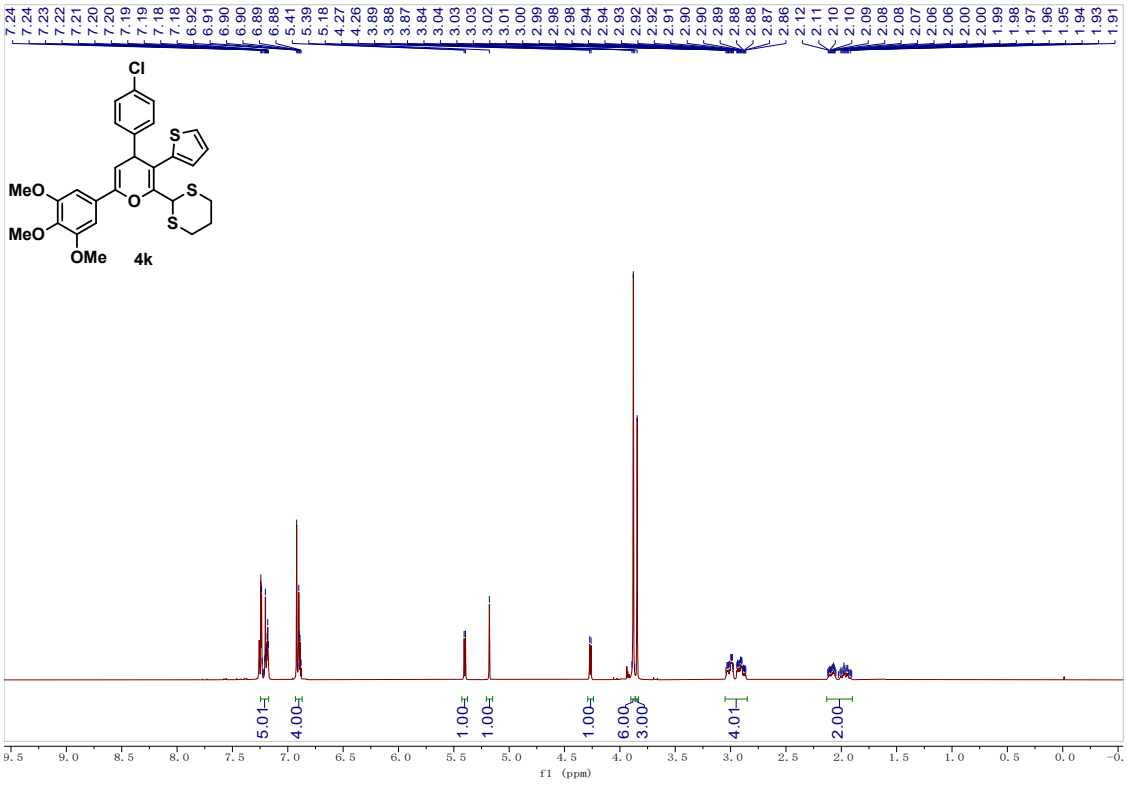
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4J



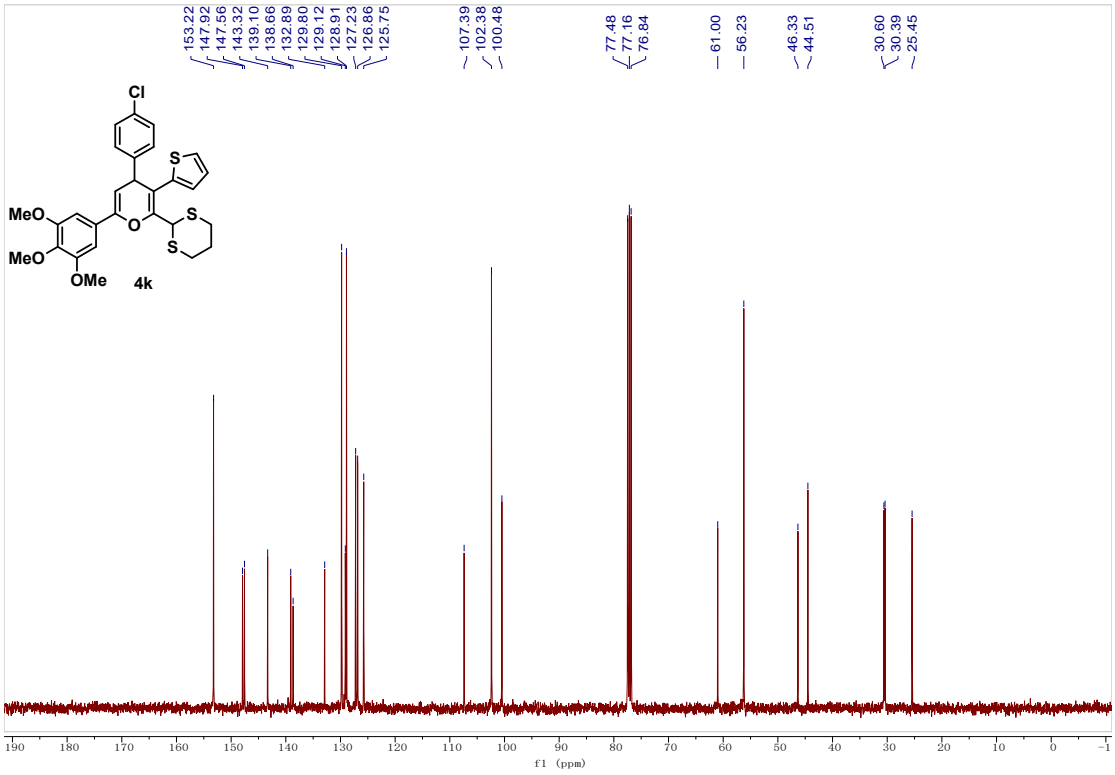
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4J



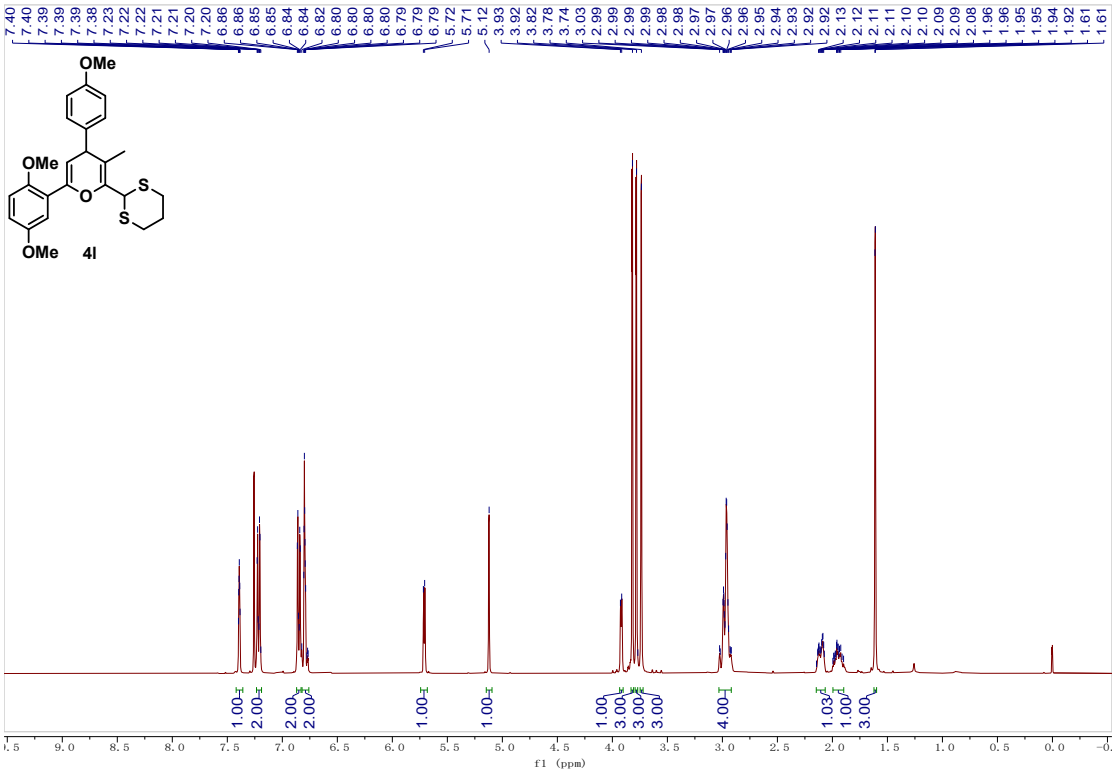
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4k



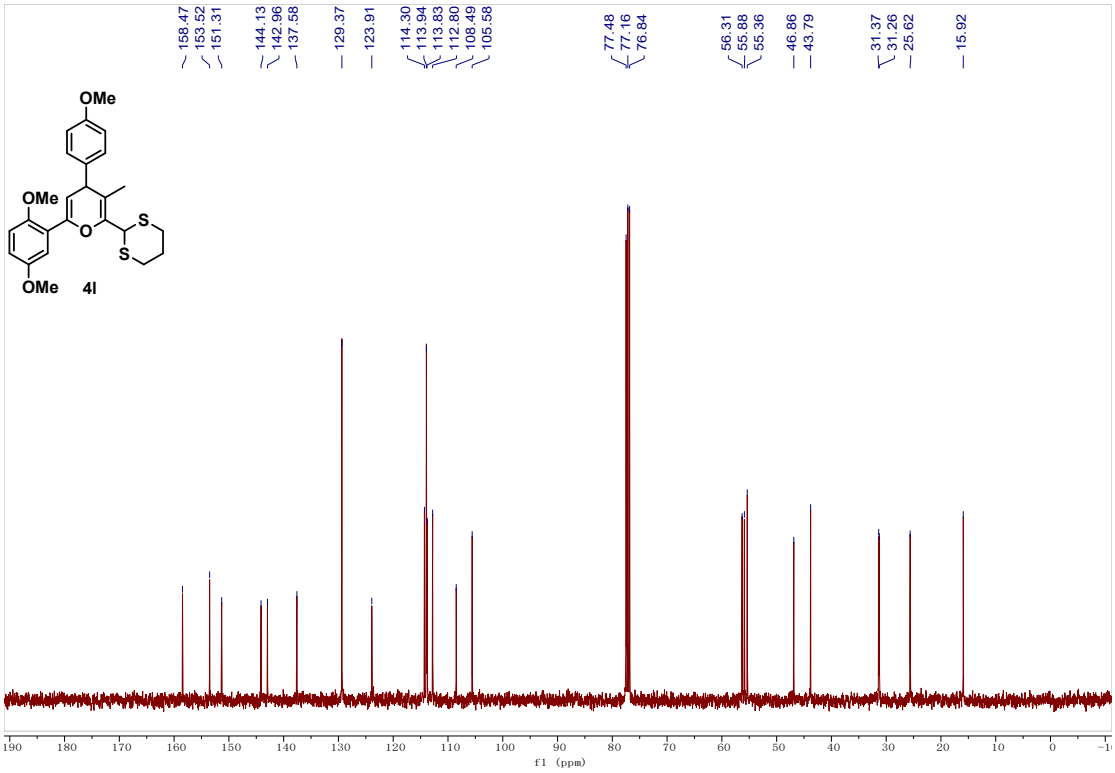
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4k



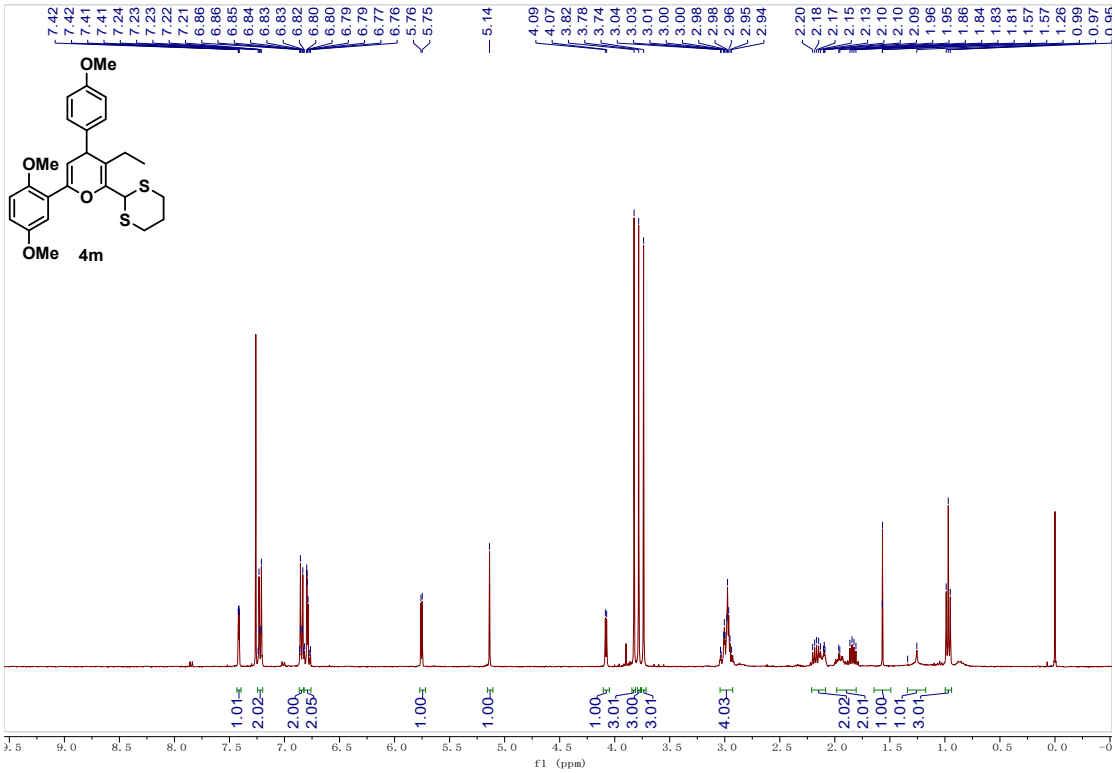
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4l



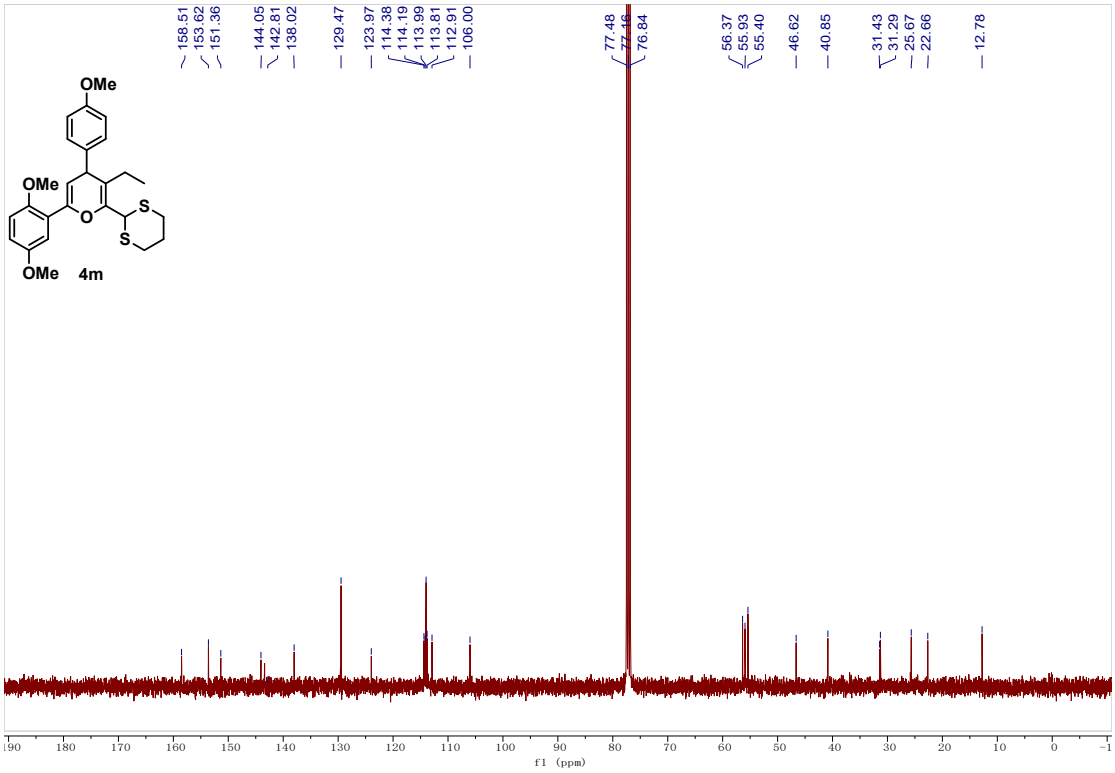
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4l



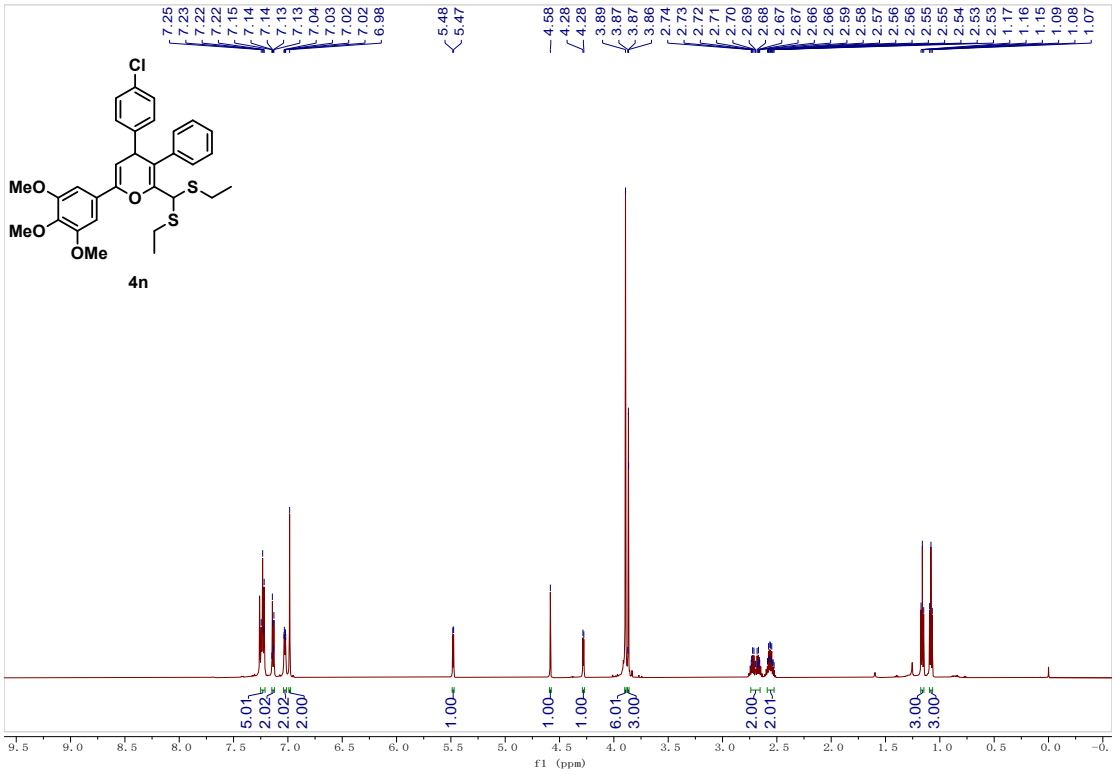
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4m



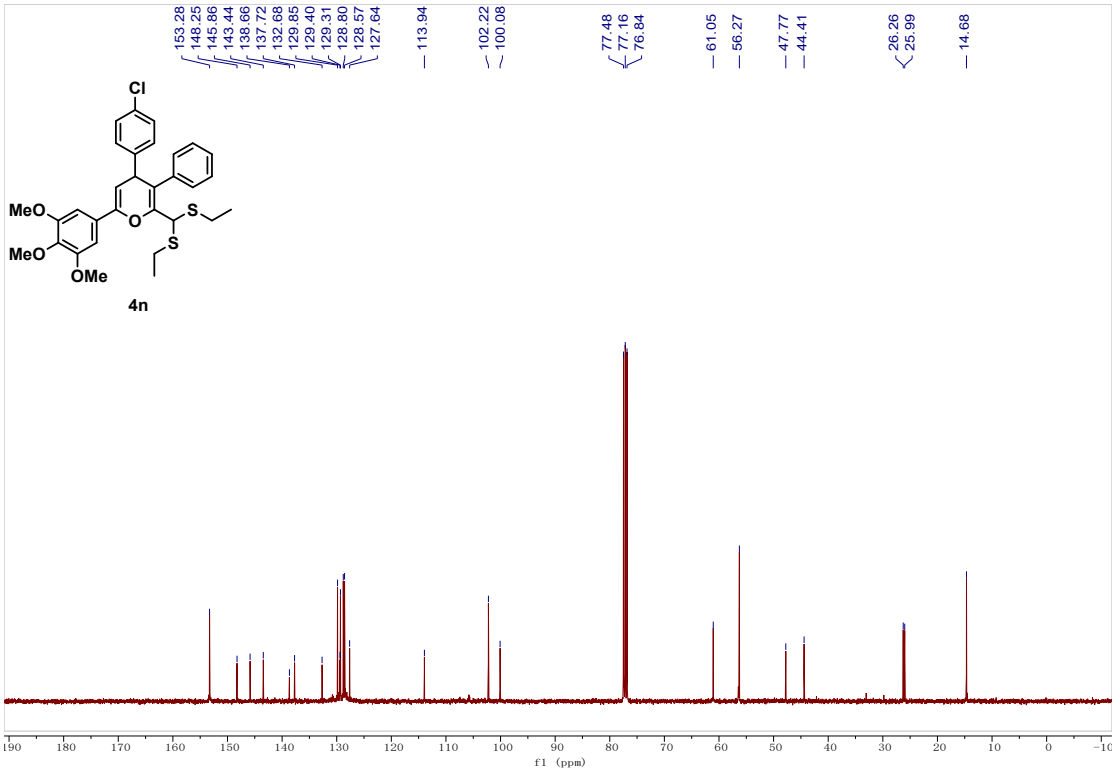
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4m



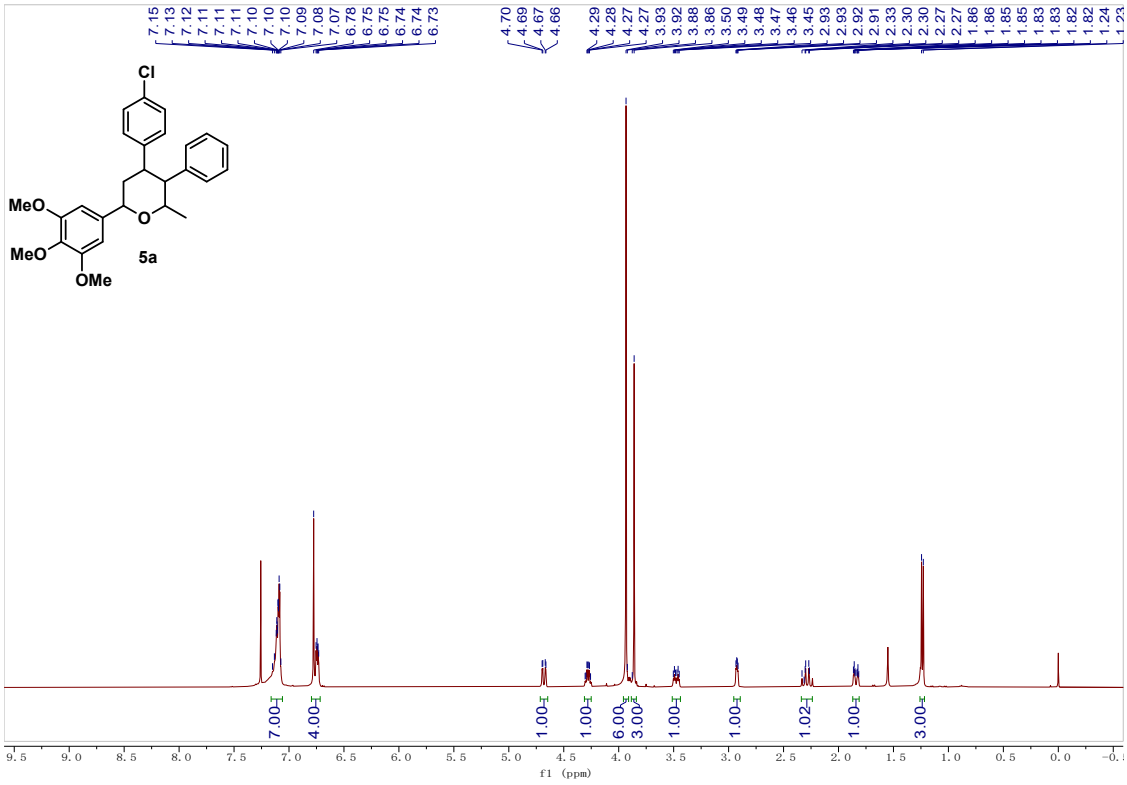
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4n



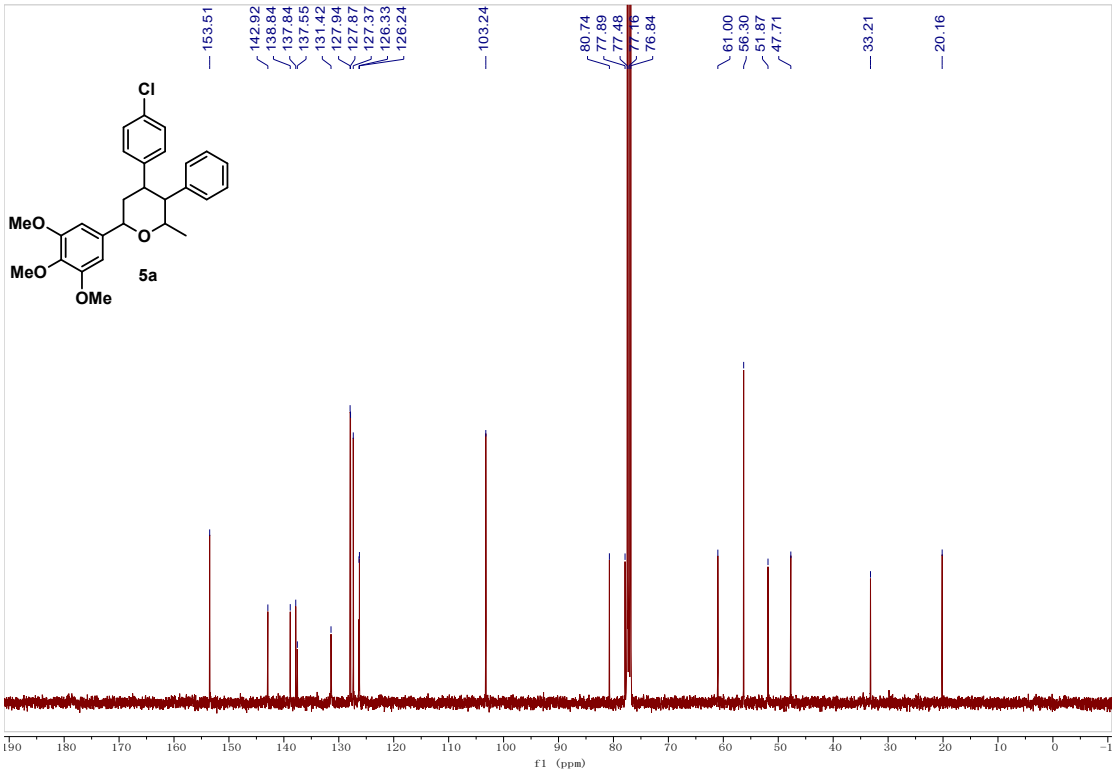
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 4n



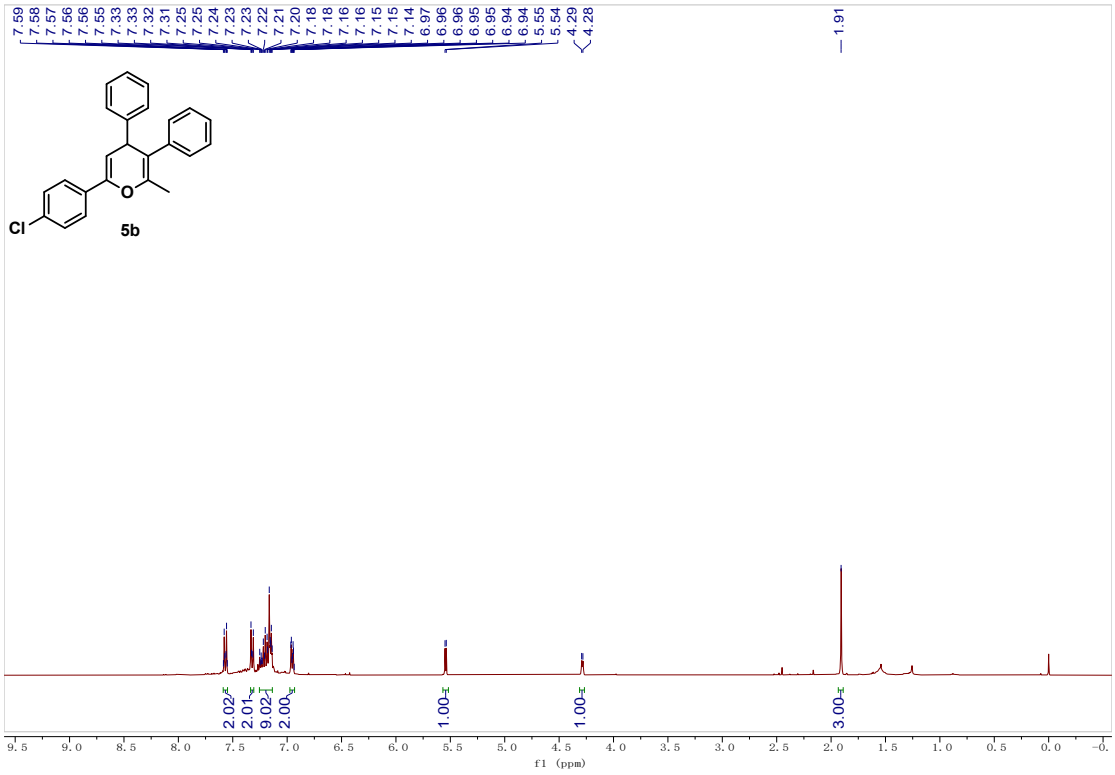
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5a



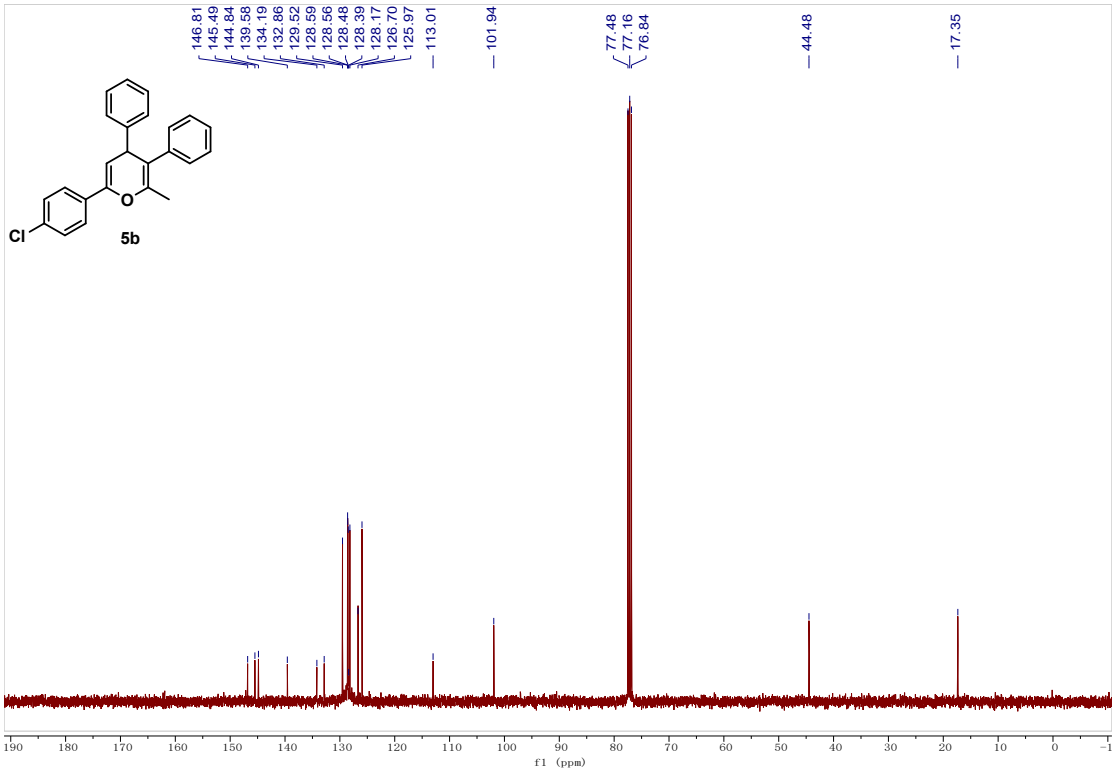
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5a



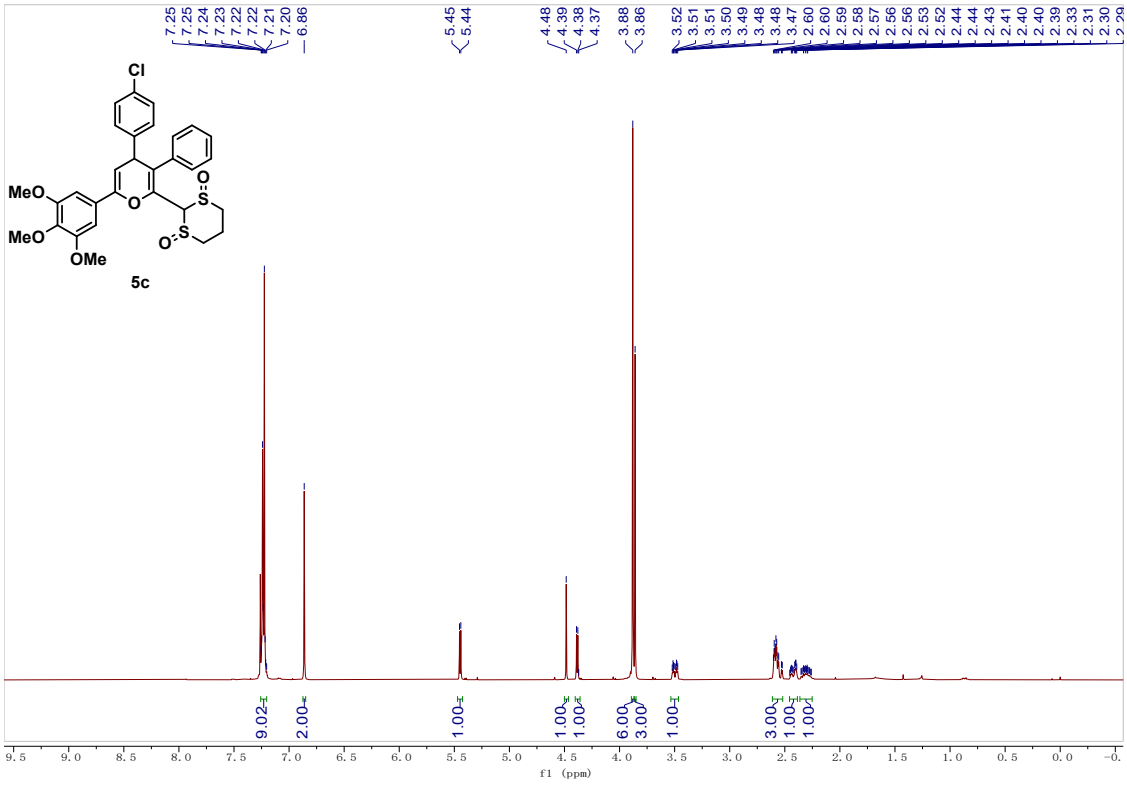
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5b



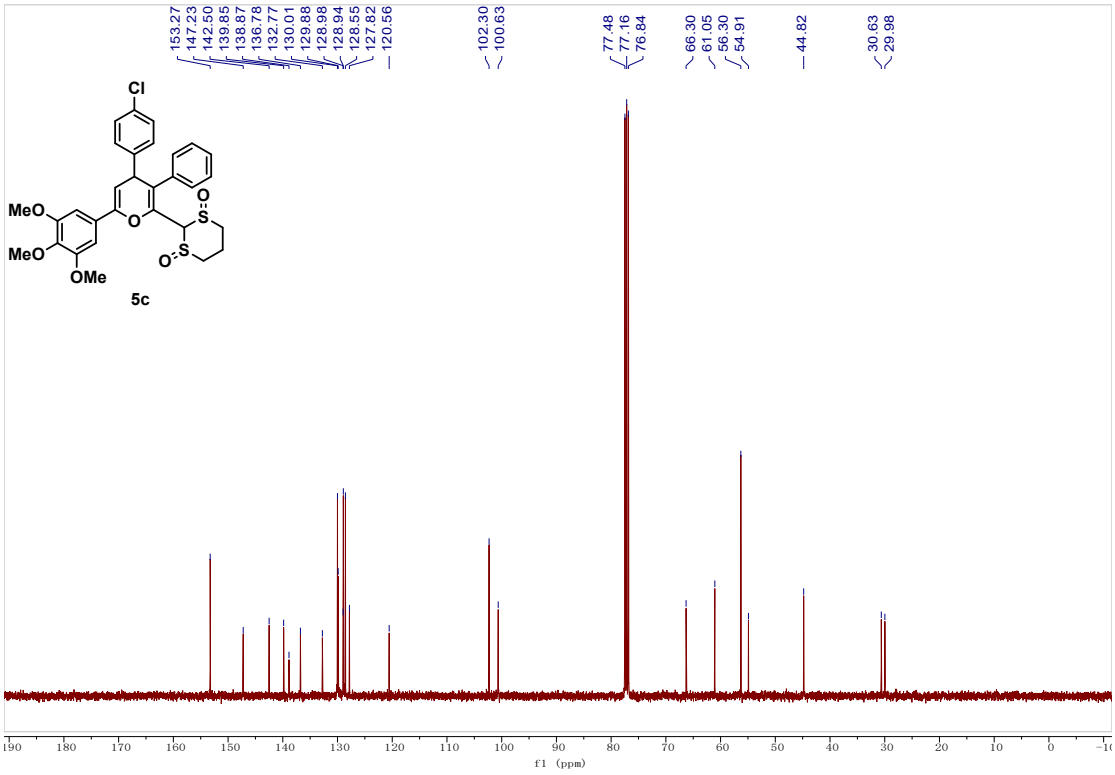
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5b



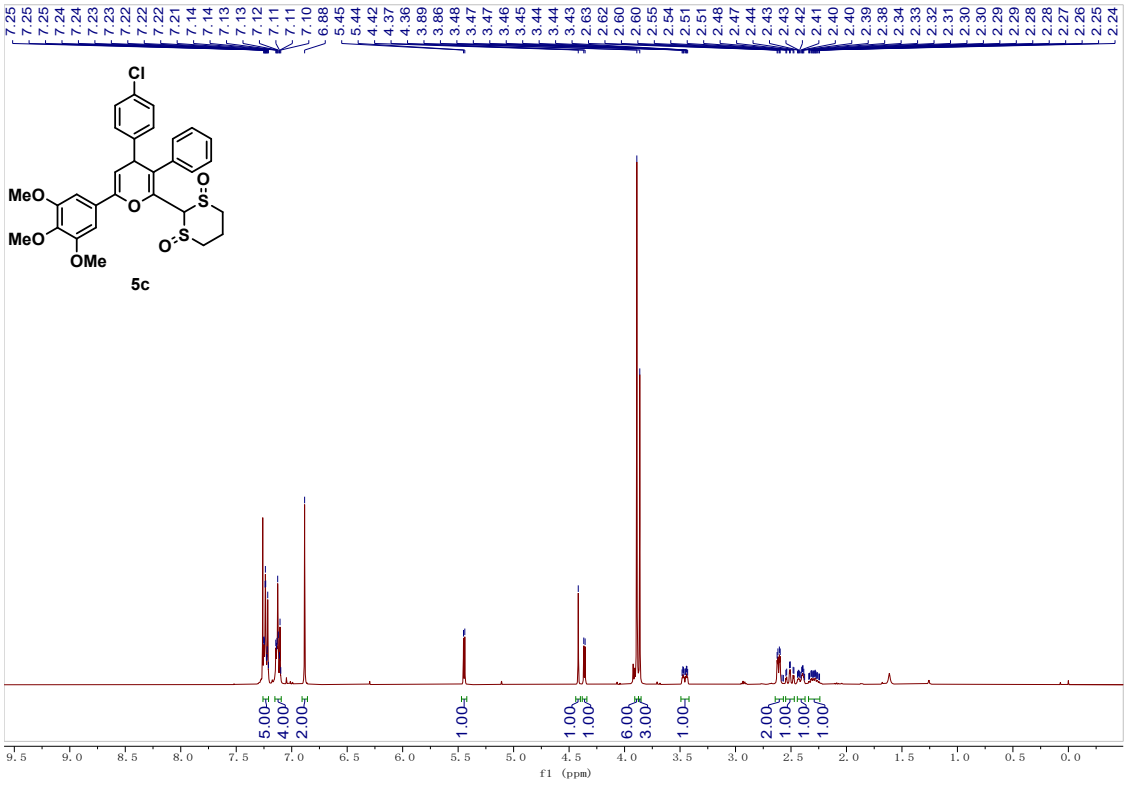
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5c (isomer 1)



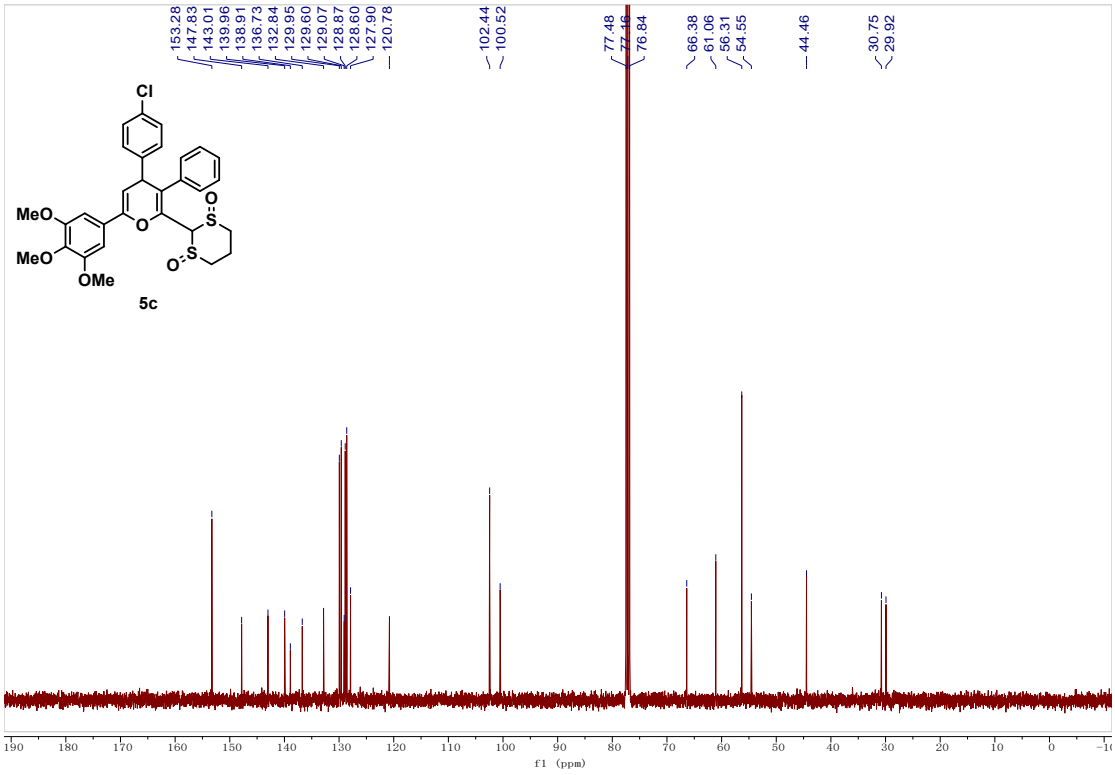
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5c (isomer 1)



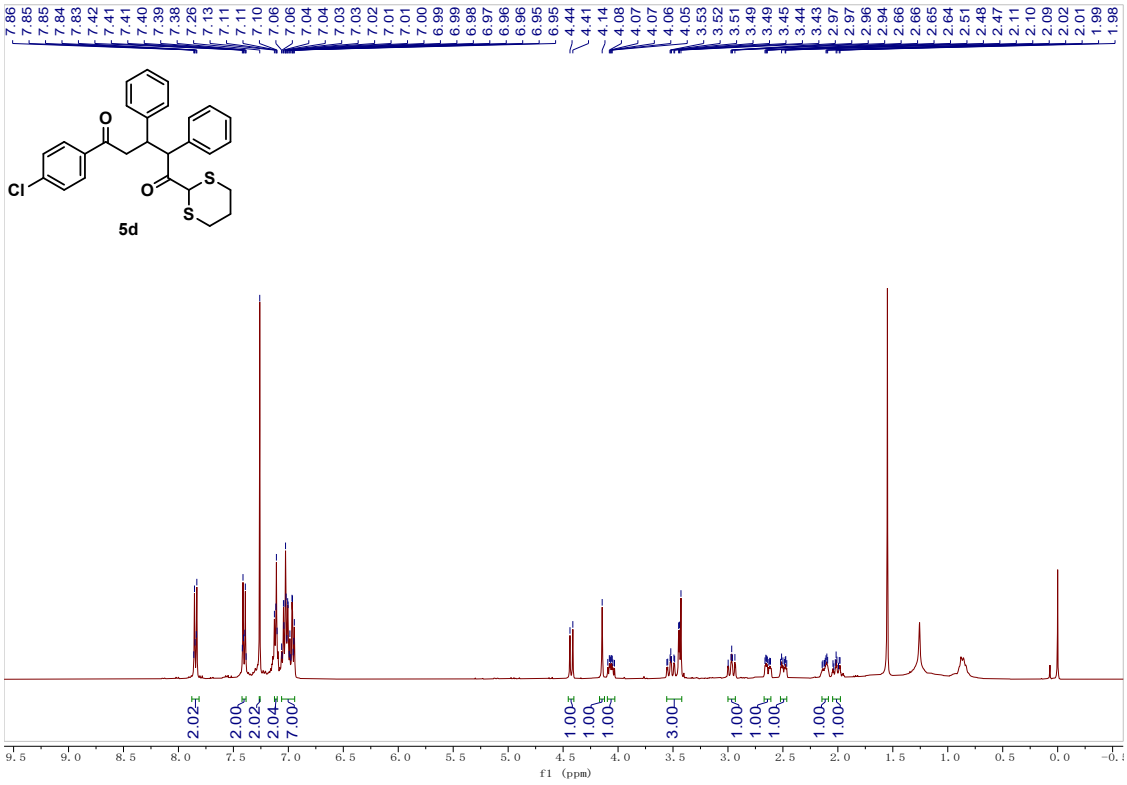
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5c (isomer 2)



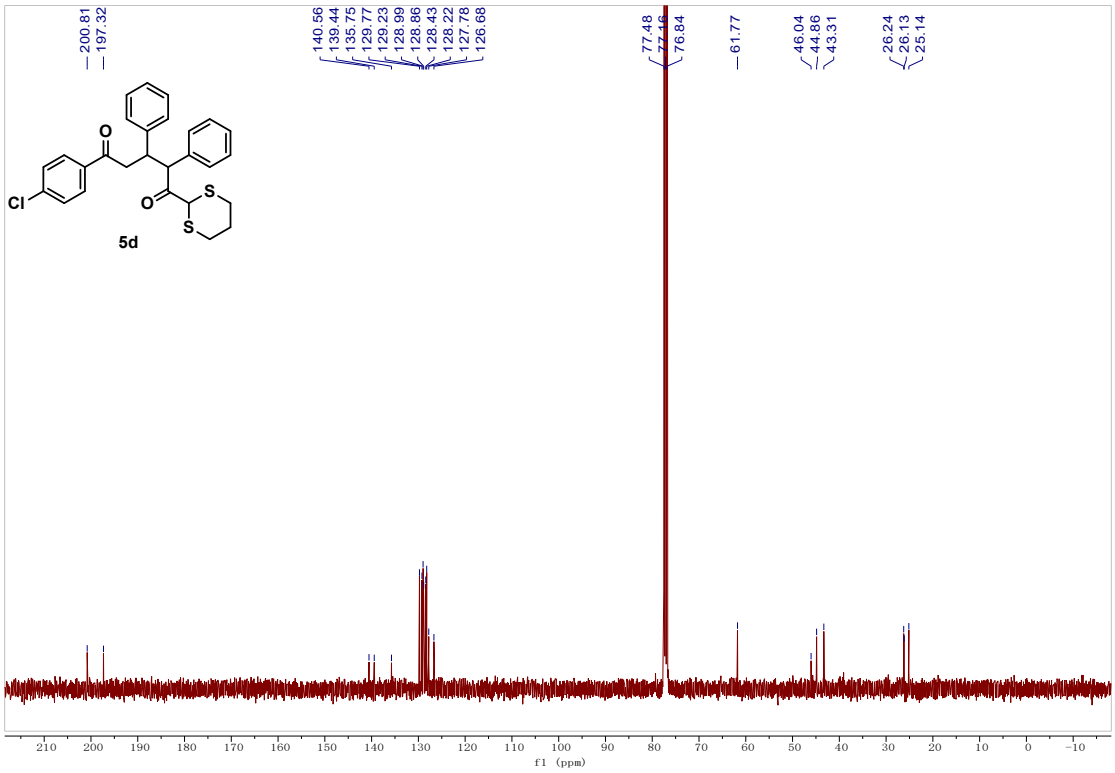
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5c (isomer 2)



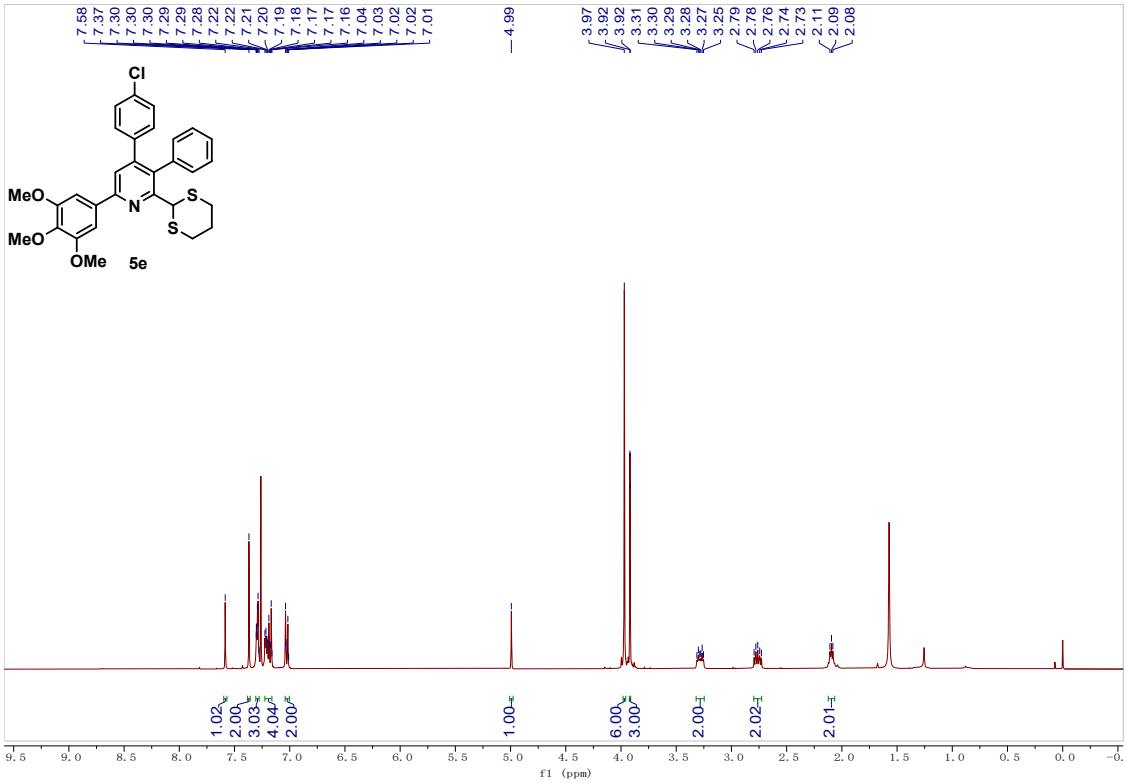
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5d



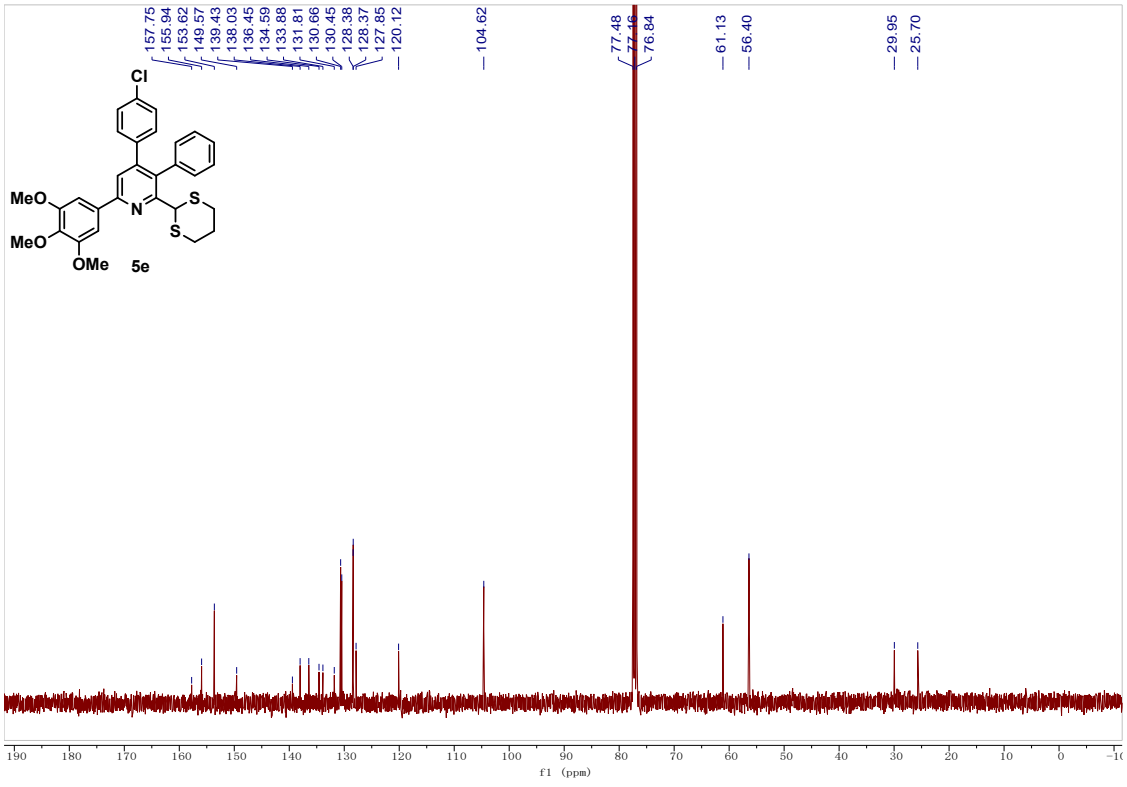
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5d



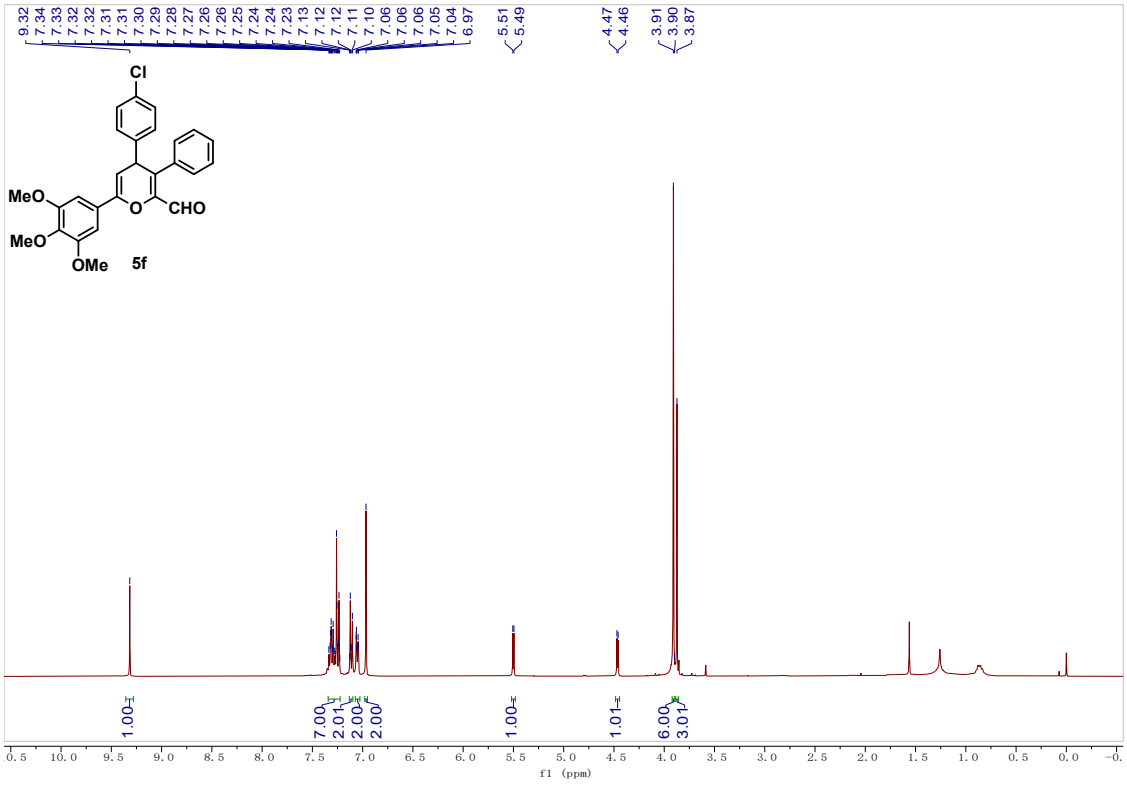
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5e



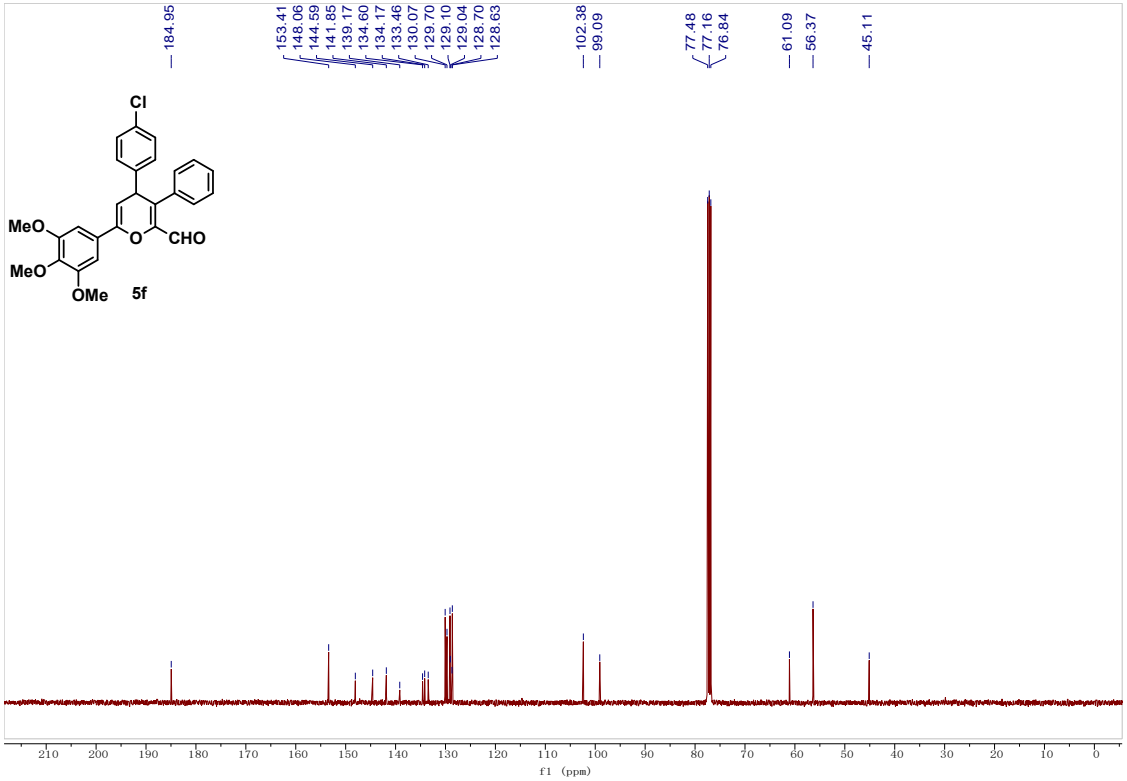
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5e



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 5f



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 5f



^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3l-1