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Supporting Information

Lewis Acid Catalyzed Cyclization of Pyridinium 1,4-Zwitterionic Thiolates with Propargyl Alcohols and Fluorescence Applications

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General remarks

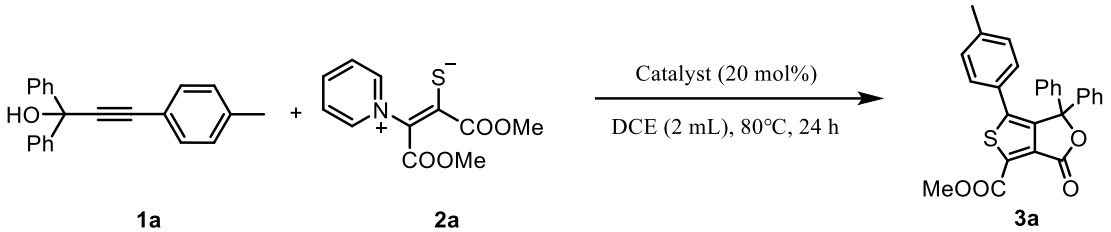
Unless otherwise noted, all of these reactions were carried out under an air atmosphere. For column chromatography, silica gel (200-300 mesh) was employed. Solvent was freshly distilled prior to use unless otherwise noted.

Instrumentation

Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H NMR spectra were recorded on Bruker AANCE III 400, 600 with a 400 MHz and 600 MHz frequencies, and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 and 600 with 100 MHz and 150 MHz frequencies. ^{19}F NMR spectra were recorded on a Bruker AVANCE III 600 spectrometer with a ^{19}F operating frequency of 565 MHz. Chemical shifts (ppm) were recorded with TMS (tetramethylsilane) as the internal reference standard. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal (TMS $\delta = 0$ for ^{1}H NMR and $CDCl_3$ $\delta = 77.0$ for ^{13}C NMR). Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). Data collection for crystal structure was performed using Mo Kα radiation on a Bruker APEXII diffractometer. HRMS obtained using a Q-TOF instrument equipped with an ESI source. UV-vis spectra (200–800 nm, for liquid samples) were recorded with a Yoke T2618S Ultraviolet-visible Spectrophotometer (Yoke, Shanghai, China). Fluorescence spectral data was obtained by a fluorescence spectrometer (FLS1000, Edinburgh Instrument) with a 450 W xenon lamp source. HORIBA FluoroLog-3 spectrofluorometer (HORIBA Scientific, Piscataway, USA) equipped with Spectra LED Pulsed LED sources.

Parameter optimization.

Table S1. Screening of catalysts[a]

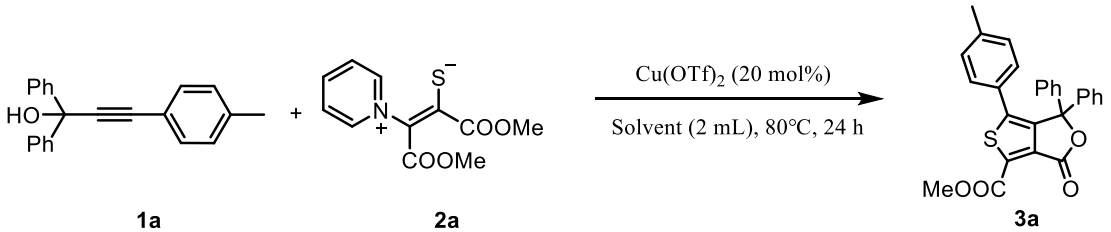


1a **2a** **3a**

Entry	Catalyst	Yield(%)
1	$Yb(OTf)_3$	15
2	$Sc(OTf)_3$	18
3	$Zn(OTf)_2$	12
4	AgOTf	21
5	$Cu(OTf)_2$	24
6	$FeCl_3$	15
7	$CuCl_2$	17
8	$ZnCl_2$	14
9	$BF_3 \cdot Et_2O$	15
10	TfOH	7
11	CF_3COOH	10

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2a** (0.1 mmol, 1.0 equiv.), catalyst (0.2 equiv.) in DCE (0.05 M) at 80°C for 24 h under air atmosphere, isolated yields.

Table S2. Screening of solvent[a]

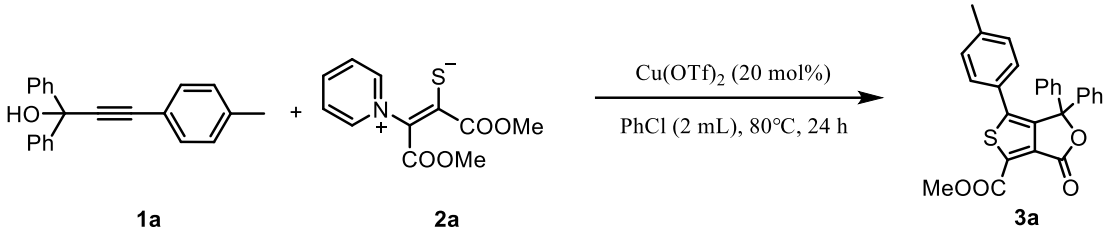


1a **2a** **3a**

Entry	solvent	Yield(%)
1	DCE	24
2	$PhCH_3$	28
3	CH_3CN	27
4	1,4-dioxane	23
5	PhCl	30

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (0.2 equiv.) in a solvent (0.05 M) at 80°C for 24 h under air atmosphere, isolated yields.

Table S3. Screening of temperature[a]

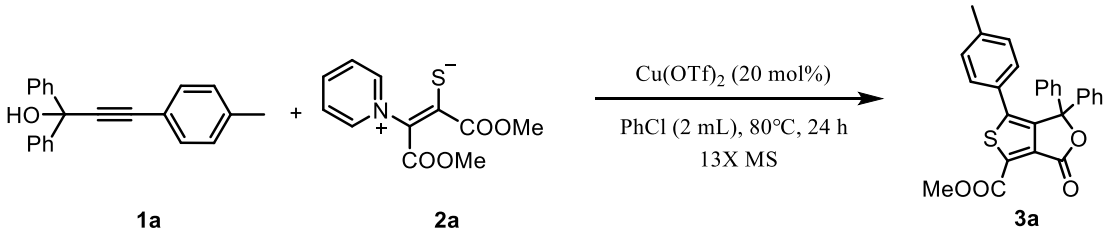


1a **2a** **3a**

Entry	Temperature(℃)	Yield(%)
1	60	23
2	80	30
3	100	31
4	110	45
5	120	58
6	125	72
7	130	64

[a]Reaction conditions: **1a** (0.2mmol, 2.0 equiv.), **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (0.2 equiv.) in PhCl (0.05 M) for 24 h under air atmosphere, isolated yields.

Table S4. Screening of molecular sieves[a]

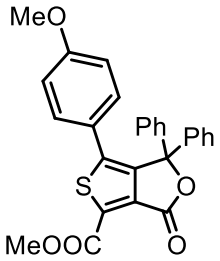


1a **2a** **3a**

Entry	molecular sieve(mg)	Yield(%)
1	10	57
2	20	72
3	30	52
4	---	64

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (0.2 equiv.) and molecular sieves in PhCl (0.05 M) at 125℃ for 24 h under air atmosphere, MS= molecular sieves, isolated yields.

X-ray single crystal diffraction data of 3f



Sample preparation: A solution of compound **3f** (40 mg) in ethyl acetate (0.5 mL) was placed in a vial (5 mL). Petroleum ether was added to the vial with a dropper. The single crystal **3f** was obtained by slowly evaporating mixed solvent at room temperature under the ambient conditions.

Crystal measurement: X-ray crystal structures were determined at 303 K. Thermal ellipsoids are drawn at 50% probability level (CCDC Number: 2448585).

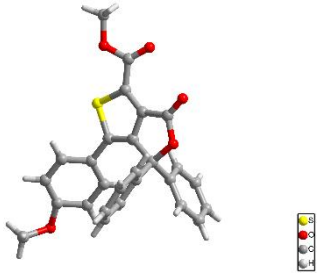


Table S5 Crystal data of compound **3f**

Bond precision:	C-C = 0.0058 A		Wavelength=0.71073
Cell:	a=14.2771(4)	b=37.754(1)	c=17.4551(5)
	alpha=90	beta=107.017(3)	gamma=90
Temperature:	303 K		

	Calculated	Reported
Volume	8996.7(5)	8996.7(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C27 H20 O4 S	C27 H20 O4 S
Sum formula	C27 H20 O4 S	C27 H20 O4 S
Mr	456.49	456.49
Dx,g cm-3	1.348	1.348
Z	16	16
Mu (mm-1)	0.181	0.181
F000	3808.0	3808.0
F000'	3811.86	
h,k,l_{max}	20,54,25	19,53,23
Nref	28085	22645
Tmin,T_{max}	0.971,0.979	0.641,1.000
Tmin'	0.971	

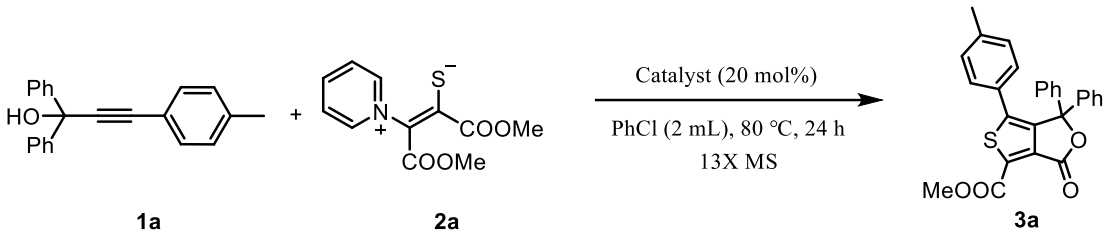
Correction method= # Reported T Limits: T_{min}=0.641 T_{max}=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.806 Theta(max)= 30.758

R(reflections)= 0.1055(14135) wR2(reflections)= 0.3114(22645)

S = 1.039 Npar= 1260

General procedure for the synthesis of 3a

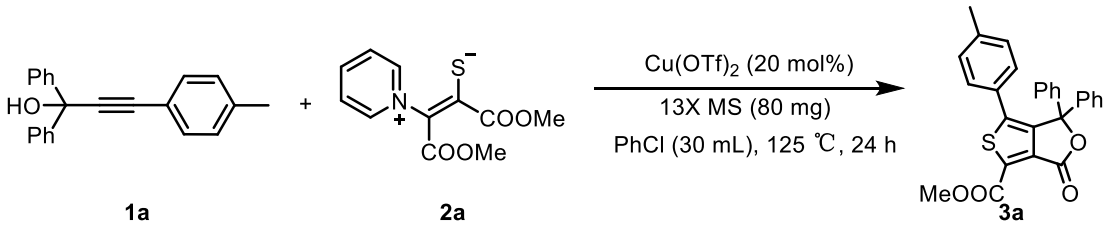


1a **2a** **3a**

The reaction of propargylic alcohol **1a** (0.2 mmol, 2.0 equiv.), pyridinium 1,4-Zwitterionic thiolates **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (20 mol %), 13X MS (20 mg) in PhCl (2.0 mL) was performed at 125 °C under an air atmosphere. The reaction was completed within 24 h by TLC monitoring. The resulting mixture was cooled down to room temperature. The mixture was evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford **3a**.

Compounds **1** and **2** are known compounds synthesized based on the literature[1, 2].

Gram-scale reaction of 3a



1a 8 mmol, 2.38 g **2a** 4 mmol, 1.01 g **3a** 1.39 g, 79 %

Propargyl alcohol **1a** (2.38 g, 2.0 equiv.), pyridinium 1,4-Zwitterionic thiolates **2a** (4 mmol, 1.0 equiv.), $Cu(OTf)_2$ (20 mol%), 13X MS (80 mg), PhCl (30 mL), 125°C, air atmosphere. By TLC monitoring, the reaction was completed within 24 h. The resulting mixture is cooled to room temperature. The mixture evaporates under reduced pressure.

The residue was further purified by silica gel (petroleum ether/ethyl acetate = 10:1) column chromatography to obtain compound **3a (**1.39 g).

UV absorption spectra of 3a in different solvents

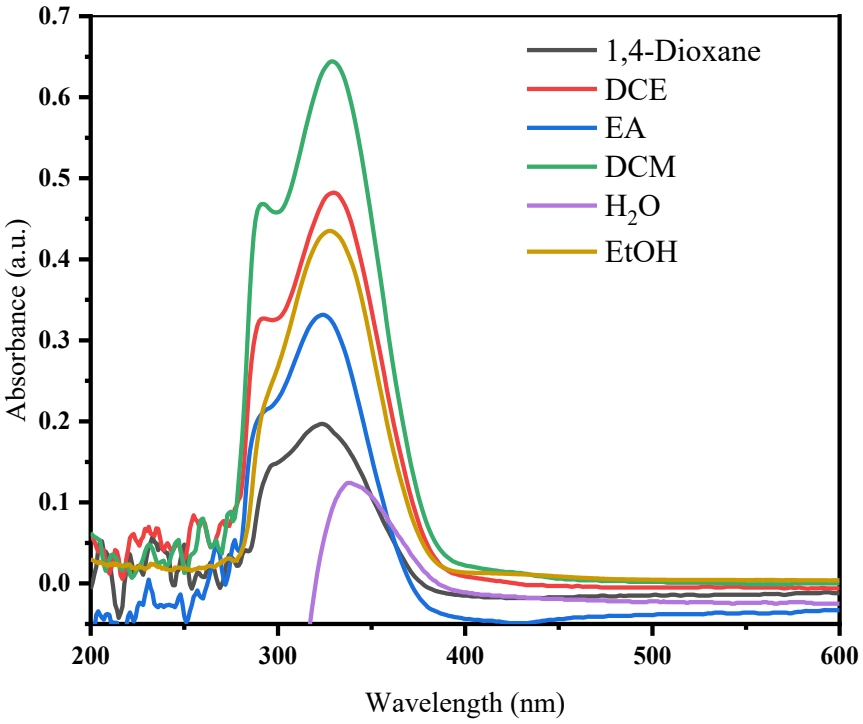


Fig. S1 UV absorption spectra of **3a** in different solvents

Test conditions: Compound **3a** was dissolved in six different solvents (1,4-dioxane, 1,2-dichloroethane, ethyl acetate, dichloromethane, H_2O, EtOH) to prepare a solution with a concentration of 5×10^{-5} mol/L, and then its UV-visible absorption spectra in different solvents were tested.

Fluorescence spectrum

Test conditions: Compounds **3a**, **3f**, **3j**, **3q**, **3m**, **and 3n** were dissolved in dichloromethane to prepare a solution with a concentration of 5×10^{-5} mol/L, scanning range is 300-700 nm.

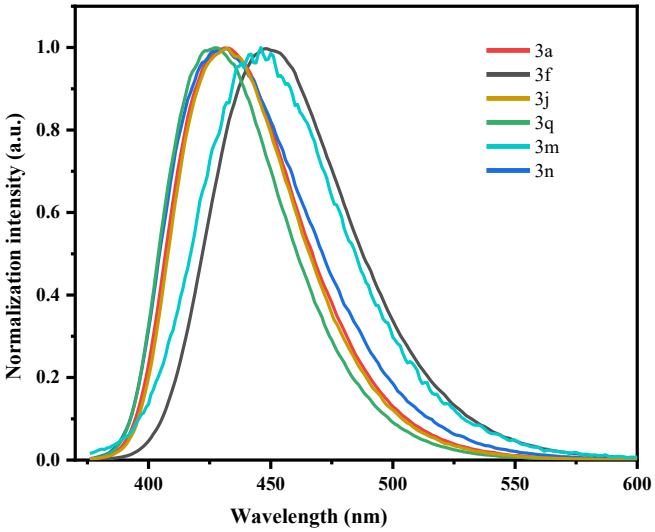


Fig. S2 Fluorescence spectra of different compounds

Table S6 Fluorescence spectral data of compounds

Compounds	λ_{ex}(nm)	λ_{em}(nm)	Stokes shift	Φ_F(%)
3a	340	417	77	74.61
3f	356	450	94	30.19
3j	334	405	71	23.35
3m	350	440	90	5.44
3n	334	420	86	30.40
3q	336	400	64	30.07

Fluorescence quenching experiments

A total of five metal ions were detected, including: Na^+, Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, 0.1mol/L aqueous solution. In addition, 20 mg of compound **3a** was dissolved in 20 mL of water and sonicated for 15 min to prepare a suspension of 1 g/L. A total of 200 μL of the above analyte solutions were added dropwise to 3 mL of suspension containing **3a**, and the corresponding fluorescence spectra were recorded in Fig. S3 (scanning range: 350-600 nm).

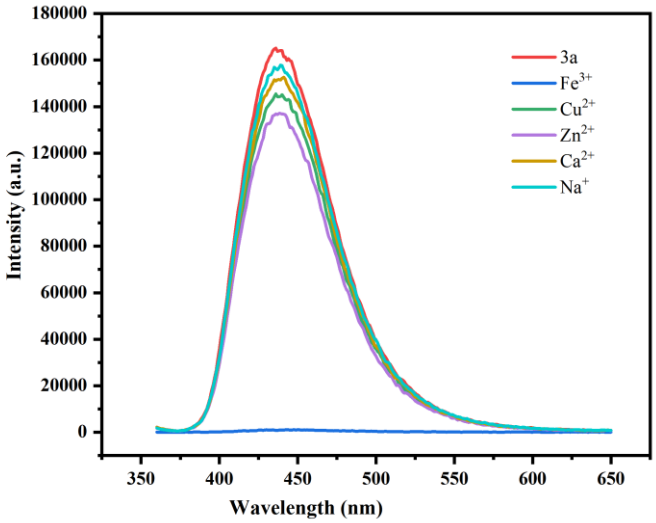


Fig. S3 The fluorescence quenching intensity of **3a** by different analytes

Fluorescence titration experiment

Compound **3a** (20 mg) was dissolved in 20 mL of ethanol and sonicated for 15 minutes to prepare the 1 mg/mL suspension. Separately, 1 mmol/L $FeCl_3$ chloride ethanol solution was prepared. A total of 1000 μL of the ferric chloride solution was added in portions to 3 mL of the suspension containing **3a**, and the corresponding fluorescence spectra were recorded in Fig. S4 (scanning range: 350-600 nm).

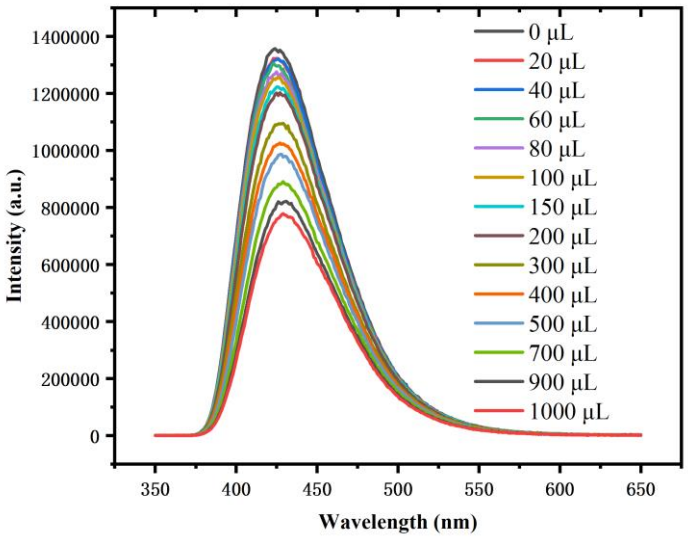


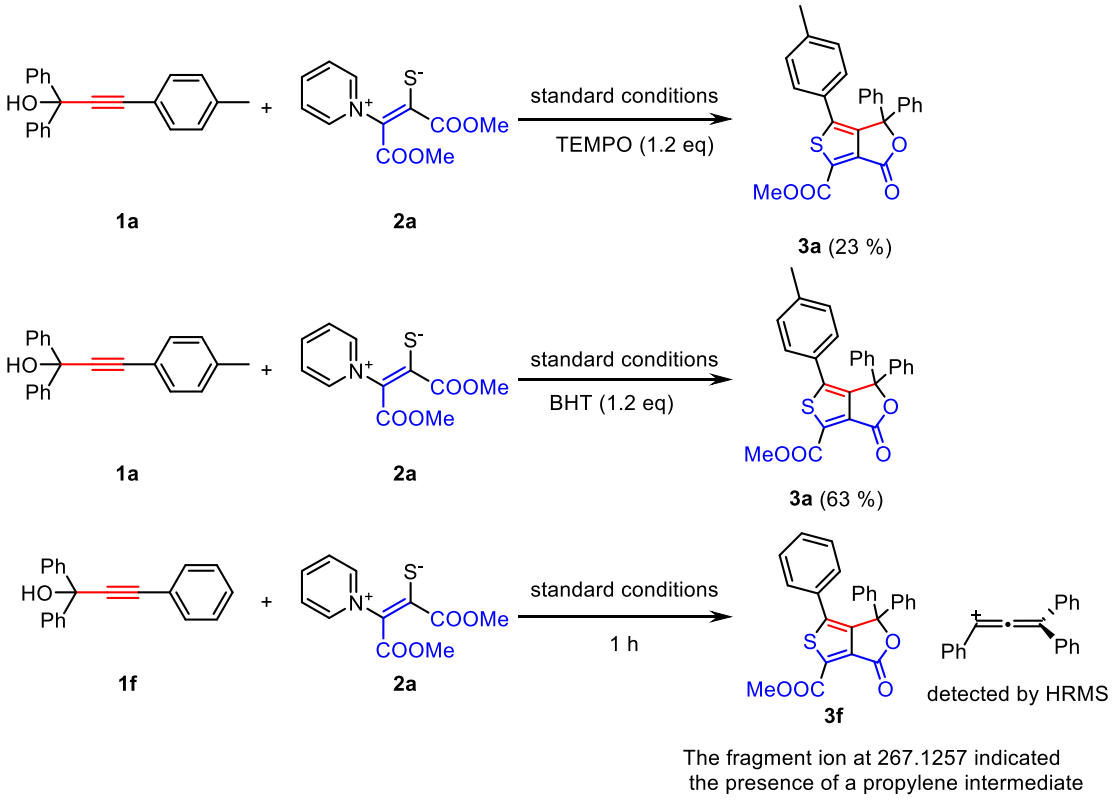
Fig. S4 Fluorescence spectra of **3a** in EtOH with various concentrations (lex = 365 nm)

Anti-counterfeiting Experiments

Experiments of Dynamic Anti-Counterfeiting and Encryption: First, a mixture of **3a (**0.2 g), Polydimethylsiloxane (1.0 g, PDMS, Sylgard 184, Dow Corning) base resin, and 0.1 g curing agent were added into a ceramic dish, which was then mechanically stirred for 5 min and printed on a filter paper by screen printing method. After curing at 60 ℃ for 2 h, the PL images based on PDMS were obtained for anti-counterfeiting labels experiments.

The screen-printed patterns were initially photographed under a 365 nm ultraviolet lamp using a mobile phone. Subsequently, a 1 M $FeCl_3$ solution was uniformly applied to the patterns, which were then re-imaged under identical ultraviolet illumination conditions. Finally, the patterns were gently rinsed with water, dried, and photographed once more under a 365 nm ultraviolet lamp to document the photoluminescent changes.

Mechanistic Investigation



The reaction of propargylic alcohol **1a** (0.2 mmol, 2.0 equiv.), pyridinium 1,4-Zwitterionic thiolates **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (20 mol %), 13X MS (20 mg) and TEMPO (0.12 mmol, 1.2 equiv.) in PhCl (2.0 mL) was performed at 125 °C

under an air atmosphere. The reaction was completed within 24 h by TLC monitoring. The resulting mixture was cooled down to room temperature. The mixture was evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford **3a** in 23% yield.

The reaction of propargylic alcohol **1a** (0.2 mmol, 2.0 equiv.), pyridinium 1,4-Zwitterionic thiolates **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (20 mol %), 13X MS (20 mg) and BHT (0.12 mmol, 1.2 equiv.) in PhCl (2.0 mL) was performed at 125 °C under an air atmosphere. The reaction was completed within 24 h by TLC monitoring. The resulting mixture was cooled down to room temperature. The mixture was evaporated under reduced pressure. The residue was further purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to afford **3a** in 63% yield.

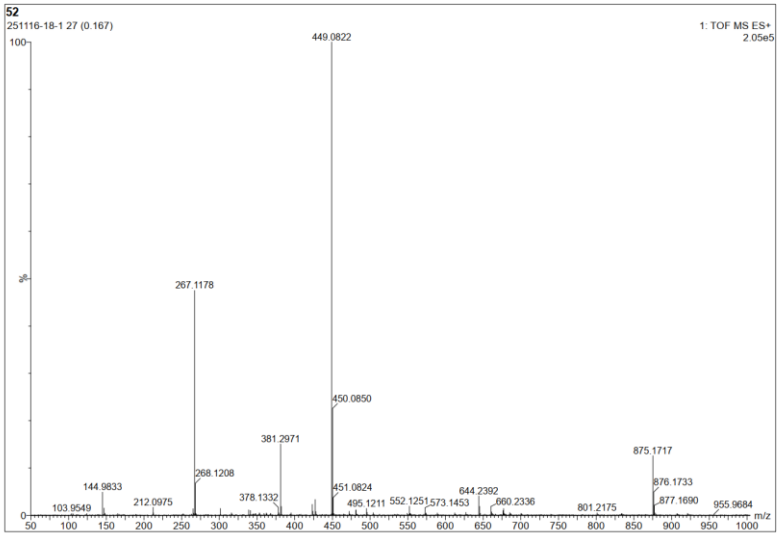


Fig. S5 High-Resolution Mass Spectrometry (HRMS)

The reaction of propargylic alcohol **1a** (0.2 mmol, 2.0 equiv.), pyridinium 1,4-Zwitterionic thiolates **2a** (0.1 mmol, 1.0 equiv.), $Cu(OTf)_2$ (20 mol %), 13X MS (20 mg) in PhCl (2.0 mL) was performed at 125 °C under an air atmosphere, after one hour and analyzed the crude mixture by high-resolution mass spectrometry (HRMS).

Fluorescence Lifetime Measurements

Fluorescence lifetime measurements were performed using the time-correlated single-photon counting (TCSPC) technique. A solution of compound **3a** in ethanol at a

concentration of 1 mg/mL was prepared. The measurements were conducted using a spectrophotometer equipped with a picosecond pulsed diode laser as the excitation source. The excitation wavelength was set to 373.5 nm, and the emission was monitored at 450 nm using a PMT detector. The instrument response function (IRF) was recorded using Ludox scatterers. The temperature was maintained at 25 °C during measurements.

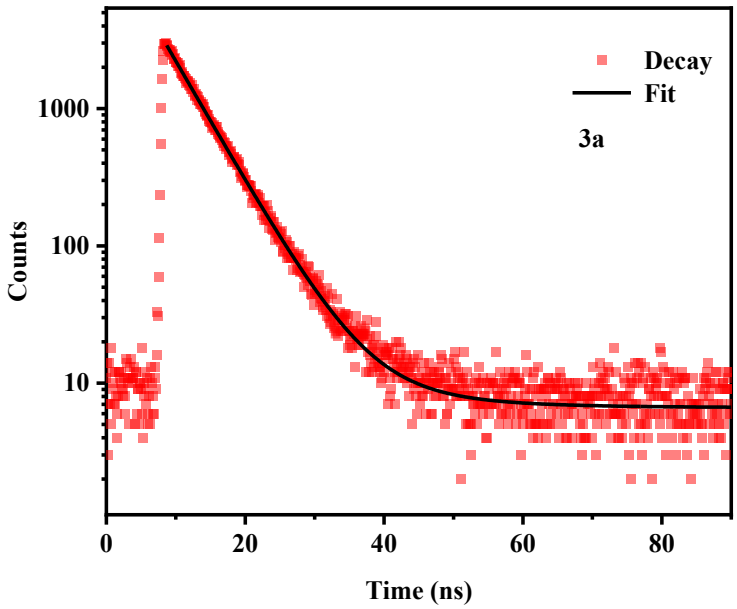


Fig. S6 The lifetime decays and fitting curves of **3a**

Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy

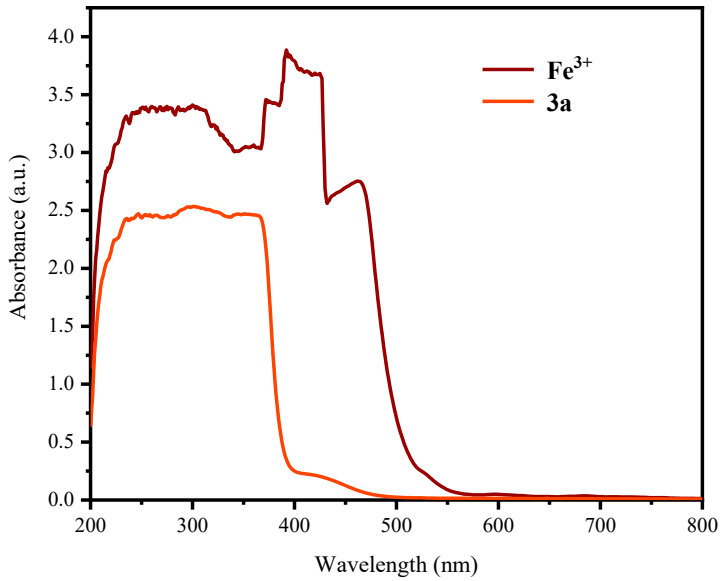


Fig. S7 Absorption spectra of **3a** and Fe^{3+}.

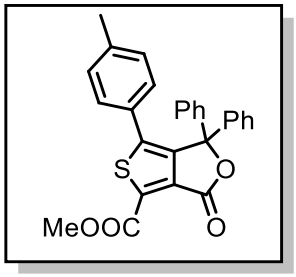
Compound **3a** was dissolved in ethanol and sonicated for 15 min to prepare a 1 mg/mL solution. A 0.1 mol/L $FeCl_3$ ethanol solution was prepared separately. The absorption spectra of ethanol were measured over the wavelength range of 200–800 nm, with baseline correction using pure ethanol as the reference. The corresponding absorption spectra are shown in Fig. S7.

References

[1] X.-R. Song, B. Song, Y.-F. Qiu, Y.-P. Han, Z.-H. Qiu, X.-H. Hao, X.-Y. Liu and Y.-M. Liang, J. Org. Chem. 2014, 79, 7616-7625.

[2] (a) Moafi, L.; Ahadi, S.; Khavasi, H. R.; Bazgir, A. Synthesis., 2011(09): 1399-1402. (a) Cheng, B.; Bao, B.; Xu, W.; Li, Y.; Li, H.; Zhang, X.; Li, Y.; Wang, T.; Zhai, H., *Org. Biomol. Chem.* **2020**, *18*(15): 2949-2955.

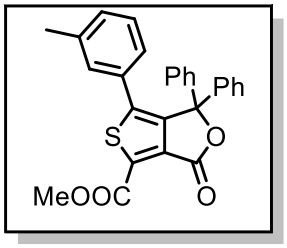
Characterization data



methyl 3-oxo-1,1-diphenyl-6-(p-tolyl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3a)**

Yield: 31.8 mg, 72%; yellow solid; mp:145-147°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.22 (m, 2H), 7.22–7.18 (m, 4H), 7.16–7.13 (m, 4H), 6.94–6.92 (m, 2H), 6.77–6.75 (m, 2H), 3.92 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.1, 149.8, 142.0, 139.8, 139.6, 134.6, 130.8, 129.5, 128.9, 128.8, 128.3, 128.1, 127.9, 89.7, 52.9, 21.2.

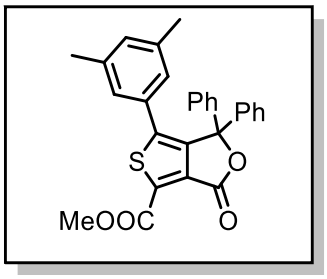
HRMS (ESI-TOF) m/z: $[M+H]^+$, Calcd for $C_{27}H_{21}O_4S$ 441.1155; found 441.1145.



methyl 3-oxo-1,1-diphenyl-6-(m-tolyl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3b)**

Yield: 20.6 mg, 47%; yellow solid; mp:100-102°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35–7.32 (m, 2H), 7.30–7.27 (m, 4H), 7.22–7.20 (m, 4H), 7.14–7.12 (m, 2H), 6.90–6.89 (m, 1H), 6.51 (s, 1H), 3.99 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.3, 160.1, 150.1, 141.9, 139.7, 138.5, 134.6, 131.1, 130.6, 130.3, 129.8, 128.8, 128.7, 128.3, 128.1, 126.1, 89.7, 52.9, 21.2.

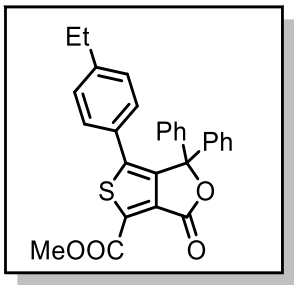
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}O_4S$ 441.1155; found 441.1143.



***methyl 6-(3,5-dimethylphenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate* (3c)**

Yield: 21.3 mg, 47%; yellow solid; mp:159-161°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.34 (m, 1H), 7.33–7.32 (m, 1H), 7.31–7.28 (m, 3H), 7.28–7.27 (m, 1H), 7.22– 7.20 (m, 4H), 6.93 (s, 1H), 6.48 (s, 2H), 3.99 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.2, 150.0, 142.3, 139.8, 138.4, 134.6, 131.2, 130.9, 130.6, 128.7, 128.3, 128.1, 126.8, 89.7, 52.9, 21.1.

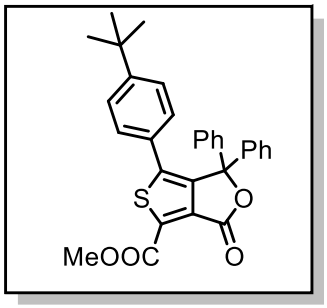
HRMS (ESI-TOF) m/z: $[M+H]^+$, Calcd for $C_{28}H_{23}O_4S$ 455.1312; found 455.1301.



***Methyl 6-(4-ethylphenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate* (3d)**

Yield: 25.1 mg, 55%; yellow solid; mp:160-162°C; column chromatography (eluent: PE: EA = 10:1, v/v).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.29–7.25 (m, 4H), 7.24–7.21 (m, 4H), 7.03–7.01 (m, 2H), 6.89–6.86 (m, 2H), 3.99 (s, 3H), 2.60 (q, J=7.6 Hz， 2H), 1.19 (t, J=7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.1, 149.8, 146.1, 142.0, 139.5, 134.6, 130.8, 129.0, 128.8, 128.3, 128.3, 128.1, 128.0, 89.7, 52.9, 28.5, 15.1.

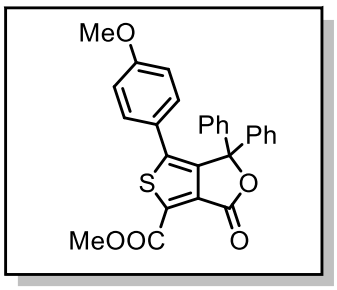
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{23}O_4S$ 455.1312; found 455.1301.



methyl 6-(4-(tert-butyl)phenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3e)**

Yield: 36.8 mg, 76%; yellow solid; mp:155-157°C; column chromatography (eluent: PE:EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.31 (m, 2H), 7.30–7.27 (m, 3H), 7.26–7.23 (m, 4H), 7.23–7.18 (m, 3H), 6.92–6.90 (m, 2H), 3.99 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.1, 153.0, 149.7, 142.0, 139.5, 134.7, 130.8, 128.8, 128.7, 128.3, 128.1, 127.8, 125.7, 89.8, 52.9, 34.7, 31.1.

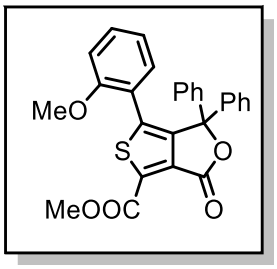
HRMS (ESI-TOF) m/z: $[M+H]^+$, Calcd for $C_{30}H_{27}O_4S$ 483.1625; found: 483.1614.



methyl 6-(4-methoxyphenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3f)**

Yield: 25.7 mg, 56%; yellow solid; mp:111-113°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.30 (m, 3H), 7.30–7.28 (m, 3H), 7.24-7.21 (m, 4H), 6.90–6.86 (m, 2H), 6.72–6.68 (m, 2H), 3.98 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 160.3, 160.1, 149.5, 141.9, 139.5, 134.6, 130.5, 128.8, 128.3, 128.1, 123.0, 114.2, 89.6, 55.3, 52.9.

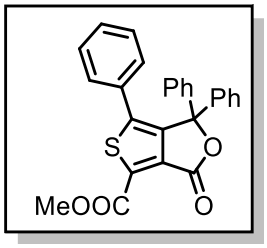
HRMS (ESI-TOF) m/z: $[M+H]^{+\cdot}$ Calcd for $C_{27}H_{21}O_5S$ 457.1104; found 457.1089.



methyl 6-(2-methoxyphenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3g)**

Yield: 22.6 mg, 49%; yellow solid; mp:156-158°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31–7.27 (m, 3H), 7.24–7.22 (m, 4H), 7.16–7.14 (m, 4H), 6.85–6.84 (m, 1H), 6.64–6.61 (m, 1H), 6.40–6.38 (m, 1H), 3.98 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$)**:** δ 160.4, 160.3, 157.0, 151.3, 139.7, 137.7, 133.4, 132.0, 132.0, 131.3, 128.5, 128.0, 127.9, 120.0, 118.5, 110.7, 89.7, 55.3, 52.8.

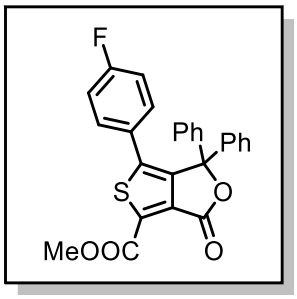
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}O_5S$ 457.1104; found 457.1091.



methyl 3-oxo-1,1,6-triphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3h)**

Yield: 16.5 mg, 39%; yellow solid; mp:133-135°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.33 (m, 2H), 7.32 – 7.26 (m, 5H), 7.22 – 7.17 (m, 6H), 6.95-6.85 (m, 2H), 4.00 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.2, 160.1, 160.1, 159.9, 150.5, 150.1, 140.0, 139.5, 139.3, 130.7, 130.6, 130.4, 129.5, 129.1, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.0, 128.0, 89.7, 89.6, 53.1, 53.0.

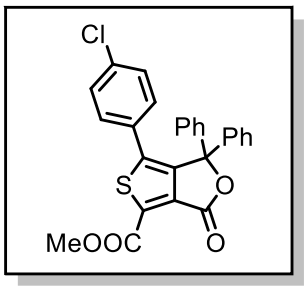
HRMS (ESI-TOF) m/z: [M+H]+ Calcd for $C_{26}H_{19}O_4S$ 427.0999; found 427.0988.



methyl 6-(4-fluorophenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3i)**

Yield: 24.7 mg, 56%; yellow solid; mp:138-140°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.33 (m, 2H), 7.31–7.24 (m, 4H), 7.20–7.14 (m, 4H), 6.93–6.87 (m, 4H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (C-F, d, $^{1}J_{C\text{-}F}$= 250.0 Hz), 160.2, 159.9, 150.4, 140.3, 139.4, 134.6, 131.5, 131.2 (C-F, d, $^{3}J_{C\text{-}F}$= 8.0 Hz), 129.0, 128.4, 128.0, 126.8, 126.7, 116.0 (C-F, d, $^{2}J_{C\text{-}F}$= 22.0 Hz), 89.6, 54.0. ^{19}F NMR (565 MHz, $CDCl_3$): δ -110.2.

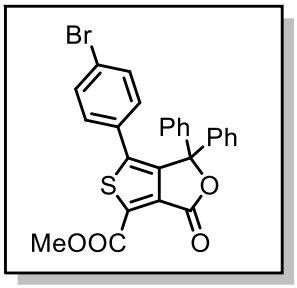
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{18}FO_4S$ 445.0904; found 445.0892.



methyl 6-(4-chlorophenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3j)**

Yield: 20.5 mg, 45%; yellow solid; mp:138-140°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.33 (m, 2H), 7.32-7.30 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.20 (m, 2H), 7.20 – 7.16 (m, 4H), 6.88 – 6.85 (m, 2H), 4.00 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.1, 159.9, 150.5, 140.0, 139.3, 135.9, 134.7, 131.7, 130.4, 129.1, 129.1, 129.0, 128.4, 128.4, 128.1, 128.0, 126.0, 89.6, 53.1.

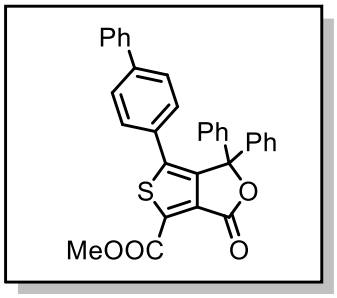
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{18}ClO_4S$ 461.0609; found 461.0598.



methyl 6-(4-bromophenyl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3k)**

Yield: 25.0 mg, 50%; yellow solid; mp:88-86°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.34 (m, 2H), 7.33–7.30 (m, 3H), 7.29–7.27 (m, 3H), 7.21–7.18 (m, 4H), 6.80–6.78 (m, 2H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 159.8, 150.5, 140.0, 139.3, 132.0, 131.7, 130.6, 129.6, 129.0, 128.5, 128.0, 124.2, 89.6, 53.3, 53.1

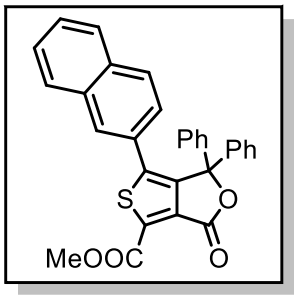
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{18}BrO_4S$ 505.0104; found 505.0094.



methyl 6-([1,1'-biphenyl]-4-yl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3l)**

Yield: 20.9 mg, 42%; yellow solid; mp:99-100°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55–7.54 (m, 2H), 7.44-7.42 (m, 4H), 7.38–7.33 (m, 3H), 7.31-7.29 (m, 4H), 7.27-7.25 (m, 4H), 7.03 (d, J=7.8Hz 2H), 4.01 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.3, 160.1, 150.2, 142.2, 141.4, 139.5, 139.4, 134.8, 131.2, 129.6, 129.5, 128.9, 128.9, 128.4, 128.1, 128.0, 127.3, 126.9, 89.8, 53.0.

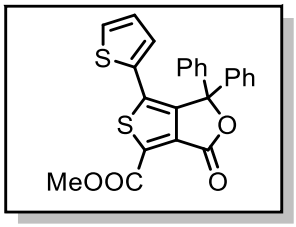
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{23}O_4S$ 503.1312; found 503.1302.



methyl(6-(naphthalen-2-yl)-3-oxo-1,1-diphenyl-1H,3H-thieno[3,4-c]furan-4-carbonyl)oxonium **(3m)**

Yield: 25.4 mg, 53%; yellow solid; mp:165-167°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.71 (m, 2H), 7.52–7.47 (m, 1H), 7.45–7.40 (m, 2H), 7.37–7.33 (m, 2H), 7.30–7.28 (m, 3H), 7.26–7.23 (m, 5H), 7.21–7.16 (m, 2H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 160.1, 150.4, 141.8, 139.6, 134.8, 133.2, 132.6, 131.5, 129.1, 128.9, 128.7, 128.4, 128.4, 128.1, 128.1, 127.7, 127.4, 126.9, 125.9, 89.7, 53.0.

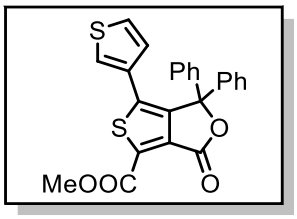
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{21}O_4S$ 477.1155; found 477.1147.



methyl 3-oxo-1,1-diphenyl-6-(thiophen-2-yl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3n)**

Yield: 25.2mg, 58%; yellow solid; mp:144-146°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 3H), 7.29–7.27 (m, 3H), 7.22–7.17 (m, 6H), 6.96–6.93 (m, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 160.0, 150.1, 141.6, 139.5, 134.6, 131.3, 130.7, 129.5, 129.1, 128.9, 128.7, 128.4, 128.3, 128.2, 128.0, 89.7, 53.0.

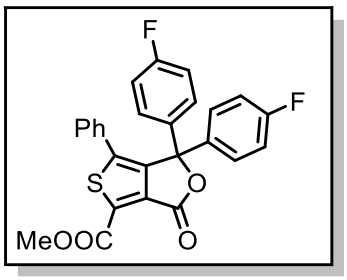
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}O_4S_2$ 433.0563; found 433.0552.



***methyl 3-oxo-1,1-diphenyl-6-(thiophen-3-yl)-1H,3H-thieno[3,4-c]furan-4-carboxylate* (3o)**

Yield: 6.90 mg, 16%; yellow solid; mp:87-89°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.35 (m, 1H), 7.34–7.32 (m, 2H), 7.31–7.30 (m, 2H), 7.30–7.27 (m, 4H), 7.26–7.23 (m, 2H), 6.90– 6.76 (m, 2H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 160.0, 149.8, 139.0, 136.3, 134.8, 130.9, 130.3, 129.0, 128.4, 128.1, 127.5, 127.0, 125.9, 89.6, 53.0.

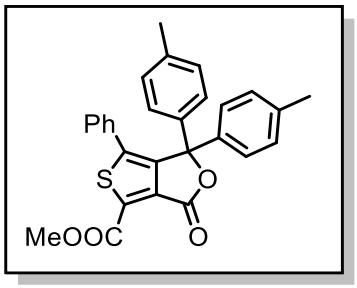
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{17}O_4S_2$ 433.0563; found 433.0555.



***methyl 1,1-bis(4-fluorophenyl)-3-oxo-6-phenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate* (3p)**

Yield: 25.4 mg,55%; yellow solid; mp:94-96°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.33 (m, 2H), 7.27–7.22 (m, 3H), 7.20–7.15 (m, 4H), 7.00–6.95 (m, 6H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, (C-F, d, $^{1}J_{C\text{-}F}$= 302.0 Hz), 160.1, 159.6, 149.7, 141.6, 135.4, 135.3, 134.2, 131.7, 130.4, 129.9 (C-F, d, $^{3}J_{C\text{-}F}$= 9.0 Hz), 129.8, 129.1, 128.9, 115.7 (C-F, d, $^{2}J_{C\text{-}F}$= 22.0 Hz), 88.6, 53.0. ^{19}F NMR (565 MHz, $CDCl_3$): δ -111.9.

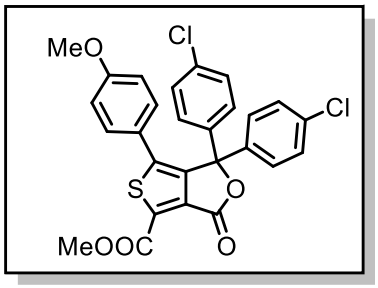
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{17}F_2O_4S$ 463.0810; found 463.0799.



methyl 3-oxo-6-phenyl-1,1-di-p-tolyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3q)**

Yield: 33.6 mg, 74%; yellow solid; mp:184-186°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.28 (m, 1H), 7.22–7.18 (m, 2H), 7.10–7.05 (m, 8H), 7.01– 6.98 (m, 2H), 3.99 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.2, 150.4, 141.4, 138.7, 136.6, 134.8, 131.0, 130.8, 129.4, 129.1, 128.9, 128.7, 128.0, 89.8, 52.9, 21.1.

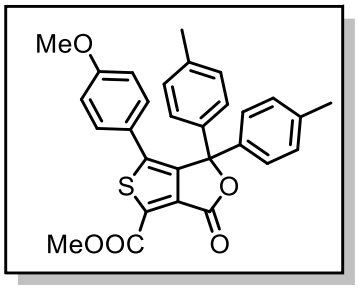
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{23}O_4S$ 455.1312; found 455.1301.



Methyl 1,1-bis(4-chlorophenyl)-6-(4-methoxyphenyl)-3-oxo-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3r)**

Yield: 24.2 mg, 46%; yellow solid; mp:169-171°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.27 (m, 2H), 7.26 (m, 2H), 7.15-7.13 (m, 4H), 6.92-6.89 (m, 2H), 6.76-6.74 (m, 2H), 4.00 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 160.1, 159.6, 148.5, 142.0, 137.8, 135.2, 130.4, 129.3, 128.6, 114.4, 88.3, 55.4, 53.0.

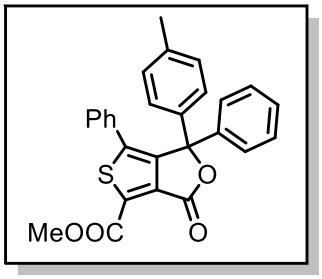
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{19}Cl_2O_5S$ 525.0325; found 525.0315.



methyl 6-(4-methoxyphenyl)-3-oxo-1,1-di-p-tolyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3s)**

Yield: 35.7 mg, 74%; yellow solid; mp:192-194°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–7.01 (m, 4H), 6.99-6.97 (m, 4H), 6.88–6.84 (m, 2H), 6.63–6.61 (m, 2H), 3.88 (s, 3H), 3.67 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 160.3, 160.2, 149.6, 141.6, 138.6, 136.5, 134.9, 130.4, 130.0, 128.9, 127.9, 123.1, 114.1, 89.7, 55.2, 52.8, 21.0.

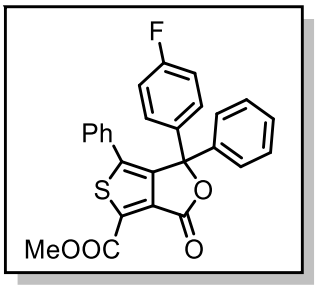
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}O_5S$ 485.1417; found 485.1405.



methyl 3-oxo-1,6-diphenyl-1-(p-tolyl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3t)**

Yield: 21.6 mg, 49%; yellow solid; mp:148-150°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.24 (m, 4H), 7.22-7.18 (m, 4H), 7.09 (s, 4H), 6.99-6.96 (m, 2H), 4.00 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.1, 150.3, 141.5, 139.6, 138.8, 136.5, 134.7, 131.2, 130.8, 129.5, 129.1, 129.0, 128.8, 128.7, 128.2, 128.0, 89.8, 52.9, 21.1.

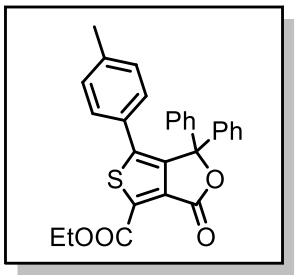
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}O_4S$ 441.1155; found 441.1144.



Methyl 1-(4-fluorophenyl)-3-oxo-1,6-diphenyl-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3u)**

Yield: 21.2 mg, 48%; yellow solid; mp:159-161°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.31 (m, 2H), 7.30-7.26 (m, 2H), 7.24 – 7.21 (m, 2H), 7.20–7.17 (m, 4H), 7.00–6.94 (m, 4H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, (C-F, d, $^{1}J_{C-F}$= 248 Hz), 160.2, 159.8, 149.9, 141.6, 139.4, 135.4, 135.4, 134.4, 131.5, 130.6, 130.0, (C-F, d, $^{3}J_{C-F}$= 8.0 Hz), 129.7, 129.1, 129.0, 128.8, 128.4, 127.9, 115.3, (C-F, d, $^{2}J_{C-F}$= 22.0 Hz), 89.1, 53.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4.

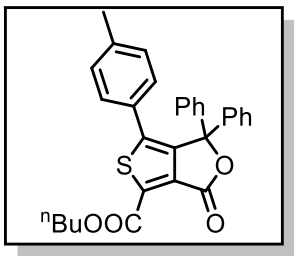
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{17}FO_4SNa$ 467.0724; found 467.0721.



ethyl 3-oxo-1,1-diphenyl-6-(p-tolyl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3y)**

Yield: 11.6 mg, 26%; yellow solid; mp:158-160°C; column chromatography (eluent: PE: EA = 10:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34–7.31 (m, 2H), 7.29–7.26 (m, 4H), 7.23–7.21 (m, 4H), 7.00–6.99 (d, J=8.4 Hz, 2H), 6.84–6.82 (m, 2H), 4.45 (q, J=7.2 Hz, 2H), 2.30 (s, 3H), 1.44 (t, J=7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.1, 159.8, 149.8, 141.7, 139.7, 139.6, 134.6, 131.4, 129.5, 128.9, 128.8, 128.3, 128.1, 127.9, 89.6, 62.2, 21.2, 14.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{23}O_4S$ 455.1312; found 455.1301.

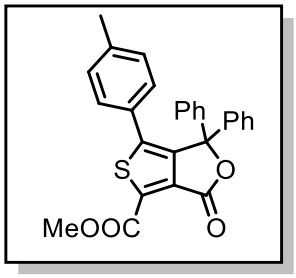


butyl 3-oxo-1,1-diphenyl-6-(p-tolyl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3z)**

Yield: 22.1 mg, 46%; yellow solid; mp:76-78°C; column chromatography (eluent: PE: EA = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.30 – 7.26 (m, 4H), 7.24 – 7.21 (m, 4H), 6.99 (d, J = 7.9 Hz, 2H), 6.86 – 6.81 (m, 2H), 4.39 (t, J = 6.6 Hz, 2H), 2.30 (s, 3H), 1.81-1.76 (m, 2H), 1.54-1.48 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ 160.1, 159.9, 149.8, 141.7, 139.7, 139.6, 134.5, 131.4, 129.5, 128.9, 128.8, 128.3, 128.1, 127.9, 89.6, 66.0, 30.6, 21.2, 19.1, 13.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}O_4S$ 483.1625; found 483.1614.



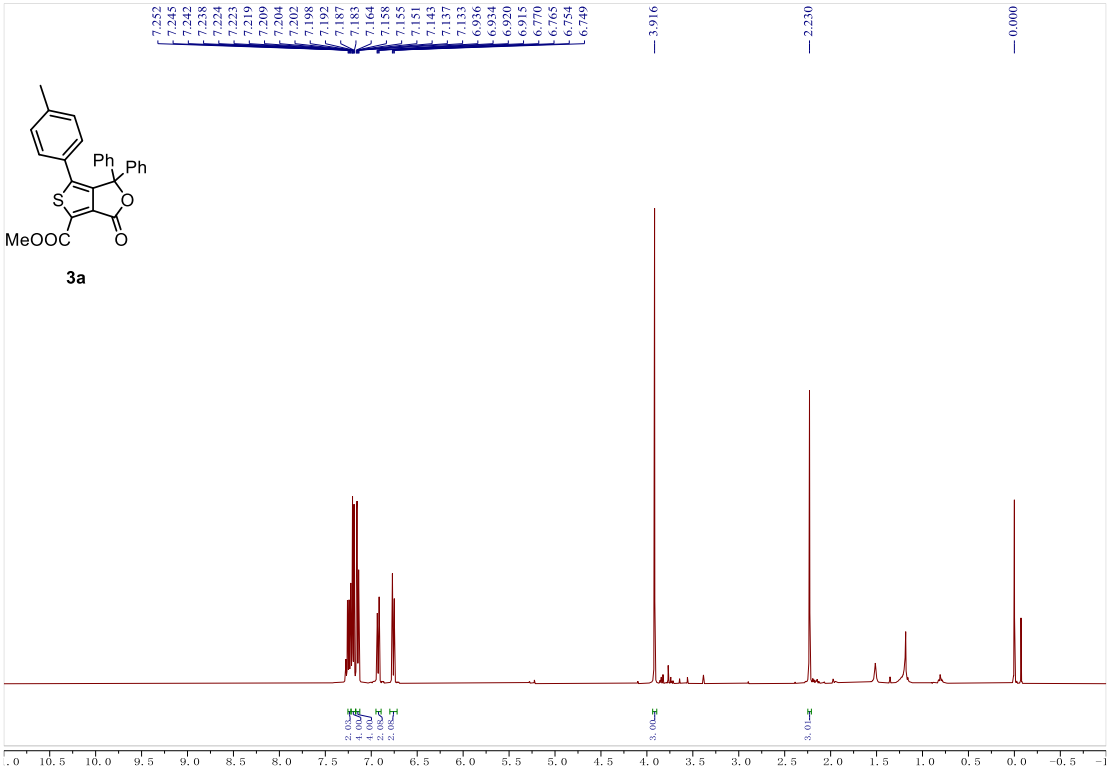
methyl 3-oxo-1,1-diphenyl-6-(p-tolyl)-1H,3H-thieno[3,4-c]furan-4-carboxylate **(3a^b)**

Yield: 6.62 mg, 15%; yellow solid; mp:145-147°C; column chromatography (eluent: PE: EA = 10:1, v/v).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.30 (m, 3H), 7.30–7.26 (m, 3H), 7.24–7.20 (m, 4H), 7.01–6.98 (m, 2H), 6.84 –6.82 (m, 2H), 3.99 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 160.1, 149.8, 142.0, 139.8, 139.5, 134.6, 130.8, 129.5, 128.9, 128.8, 128.3, 128.1, 127.8, 89.7, 52.9, 21.2.

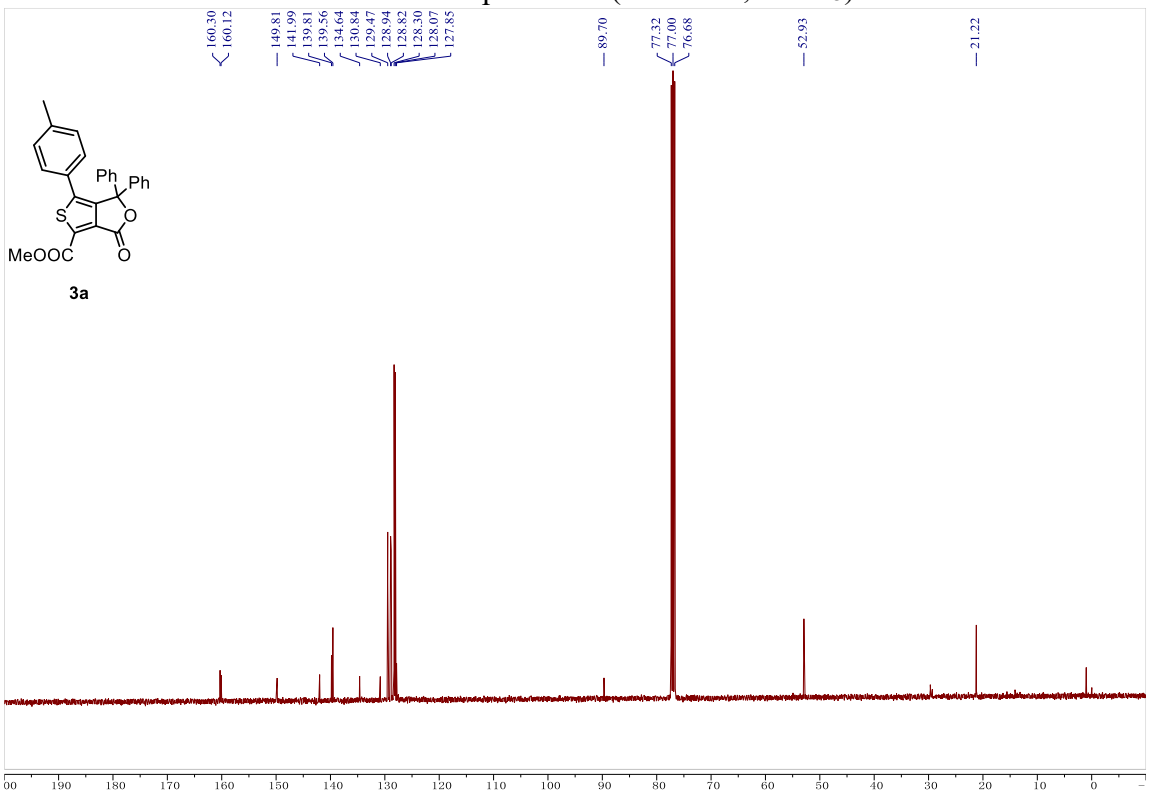
HRMS (ESI-TOF) m/z: $[M+H]^+$, Calcd for $C_{27}H_{21}O_4S$ 441.1155; found 441.1145.

NMR spectra for compounds 3a-3a[b]

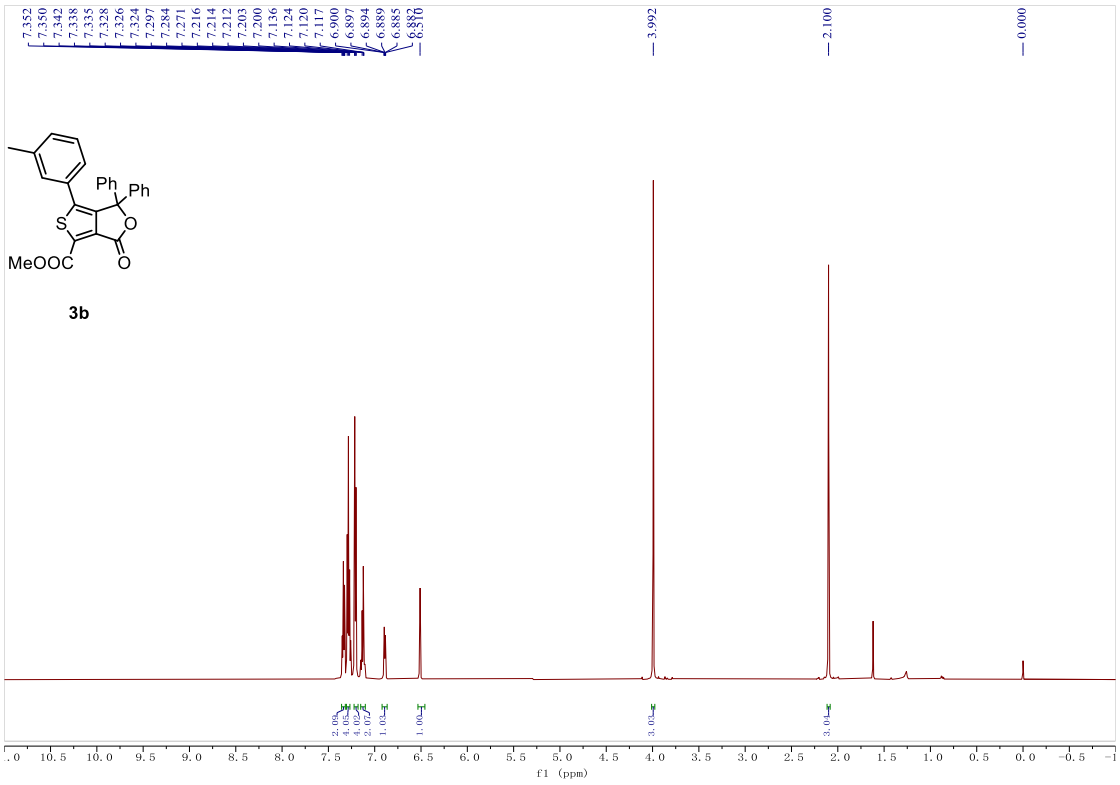
^{1}H NMR of compound **3a** (400 MHz, $CDCl_3$)



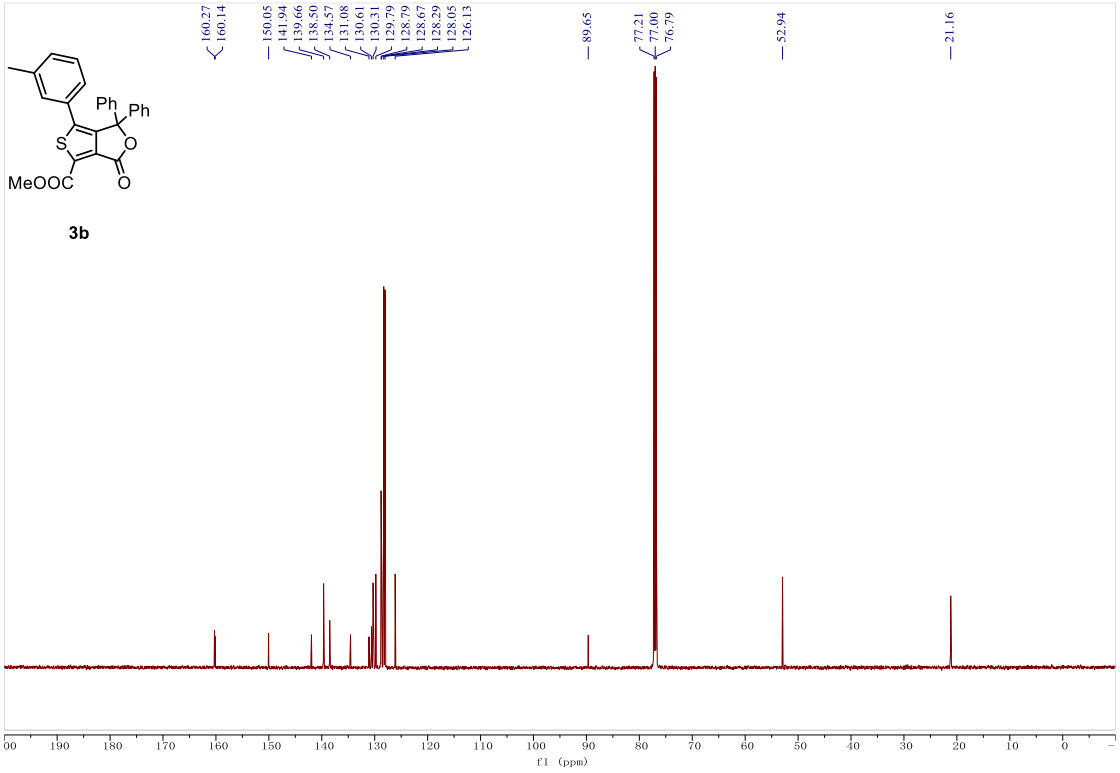
^{13}C NMR of compound **3a** (100 MHz, $CDCl_3$)



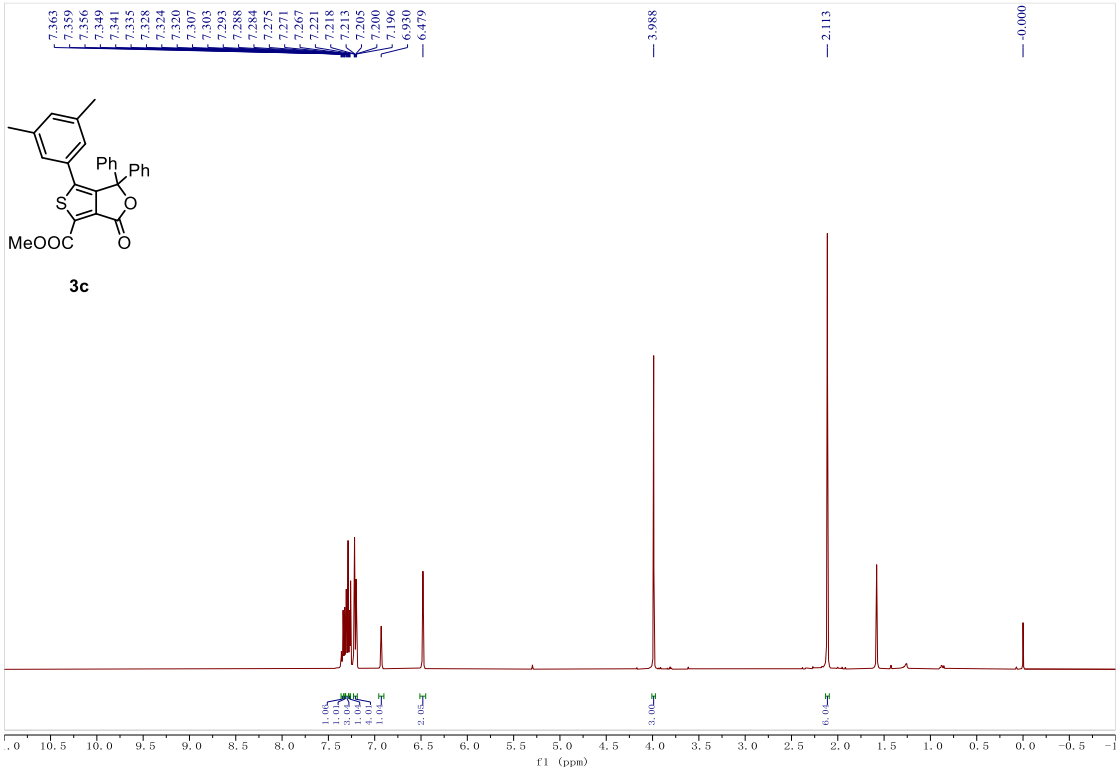
^{1}H NMR of compound **3b** (600 MHz, $CDCl_3$)



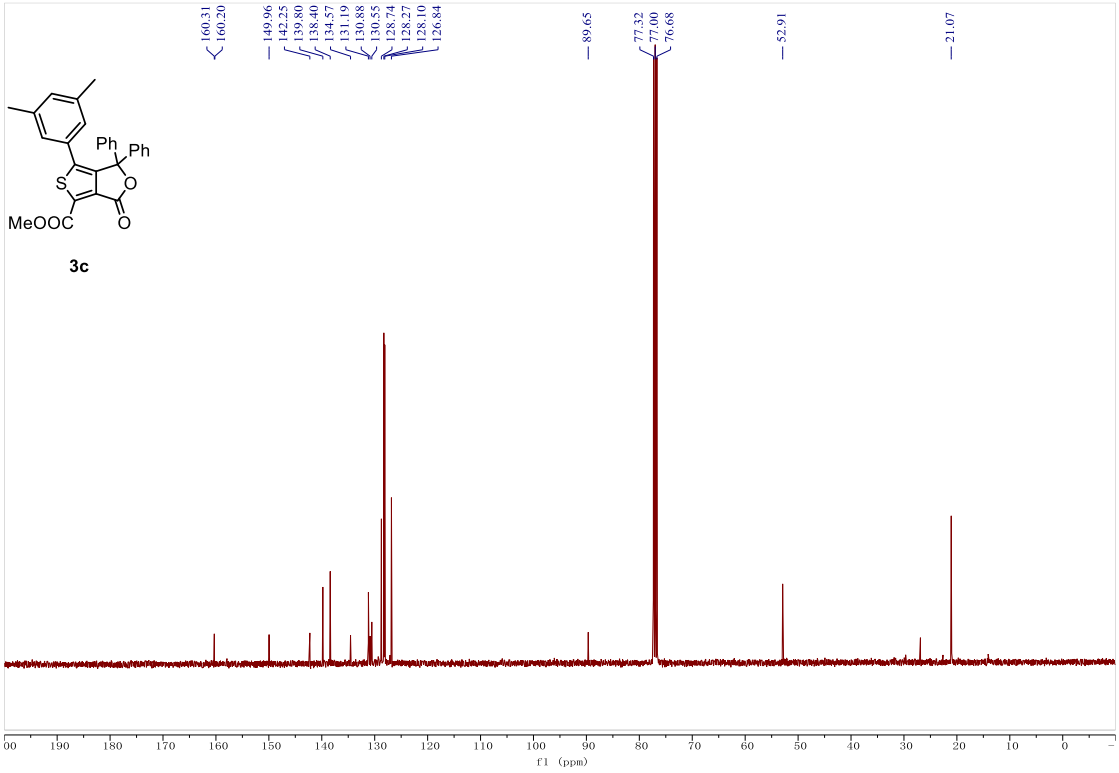
^{13}C NMR of compound **3b** (150 MHz, $CDCl_3$)



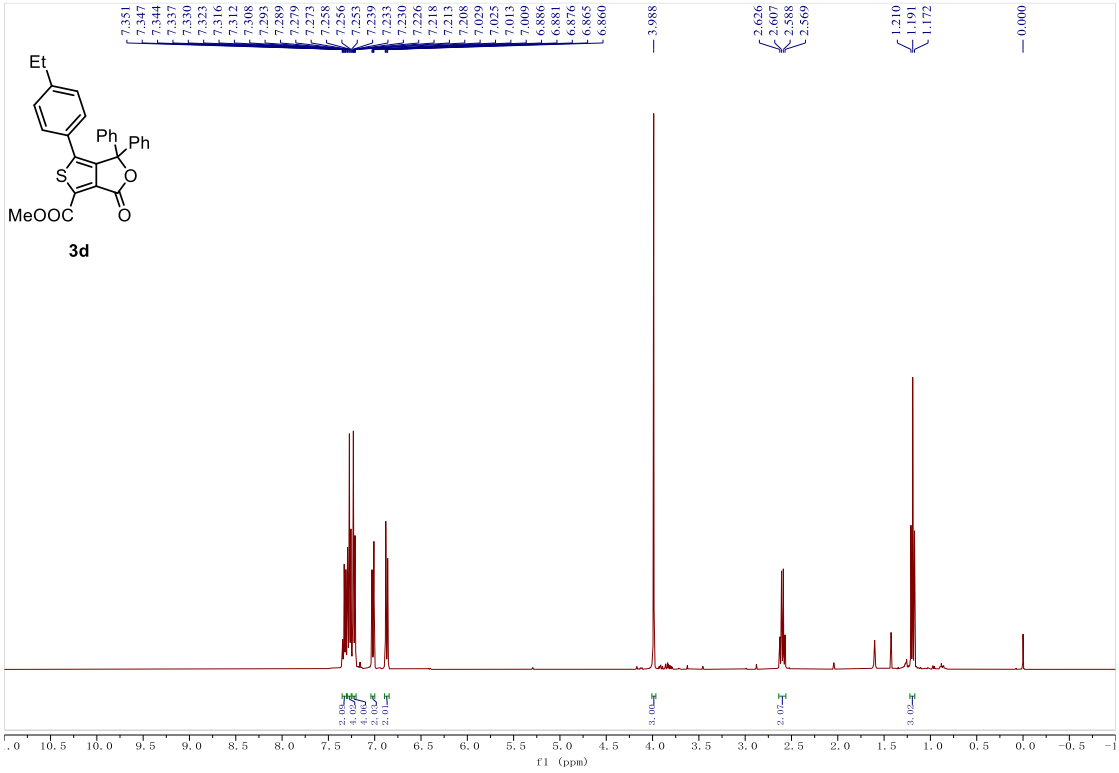
^{1}H NMR of compound **3c** (400 MHz, $CDCl_3$)



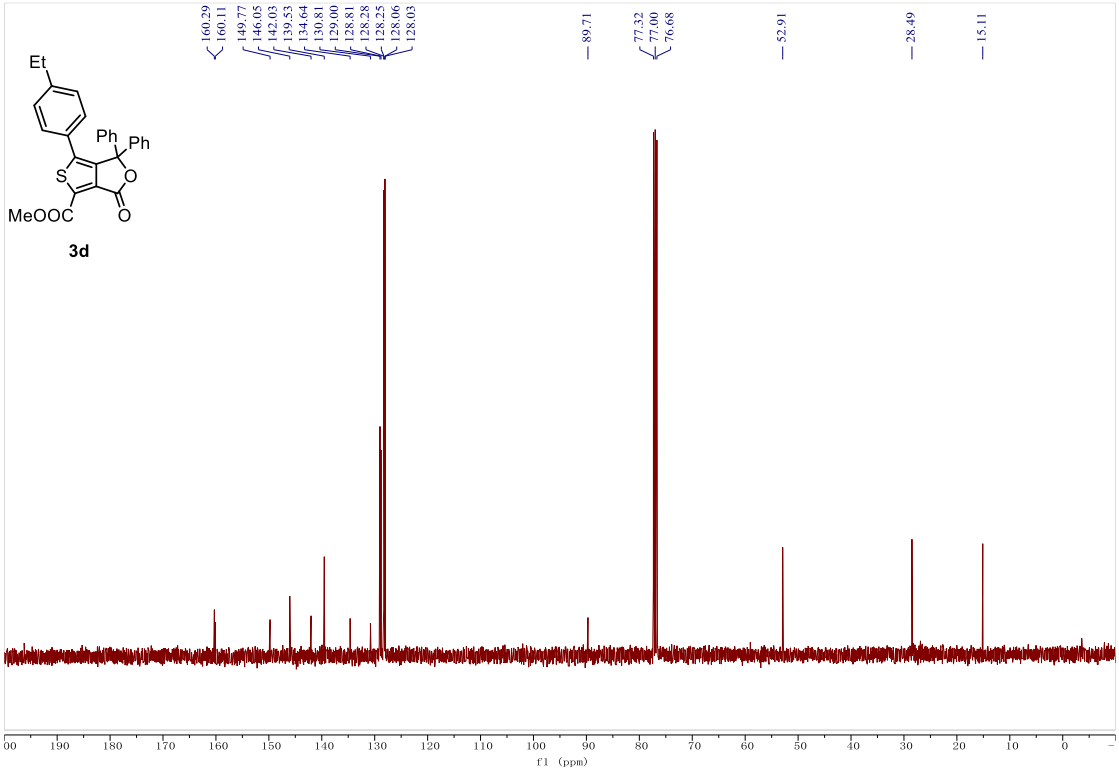
^{13}C NMR of compound **3c** (100 MHz, $CDCl_3$)



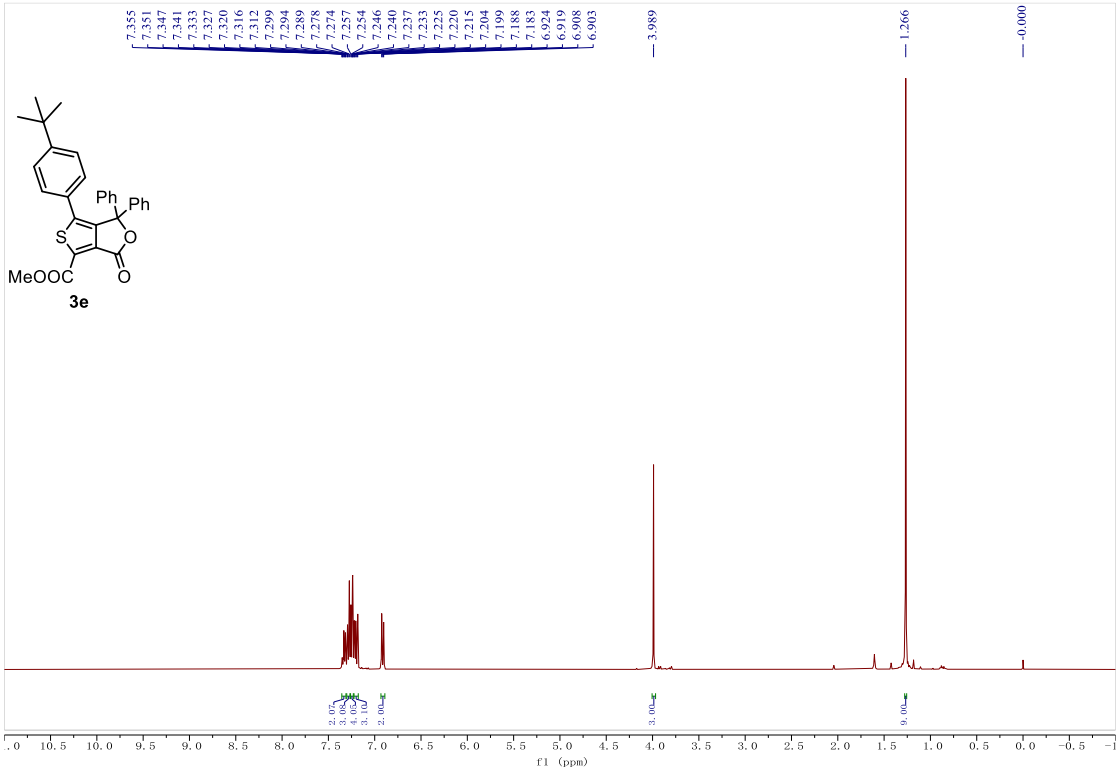
^{1}H NMR of compound **3d** (400 MHz, $CDCl_3$)



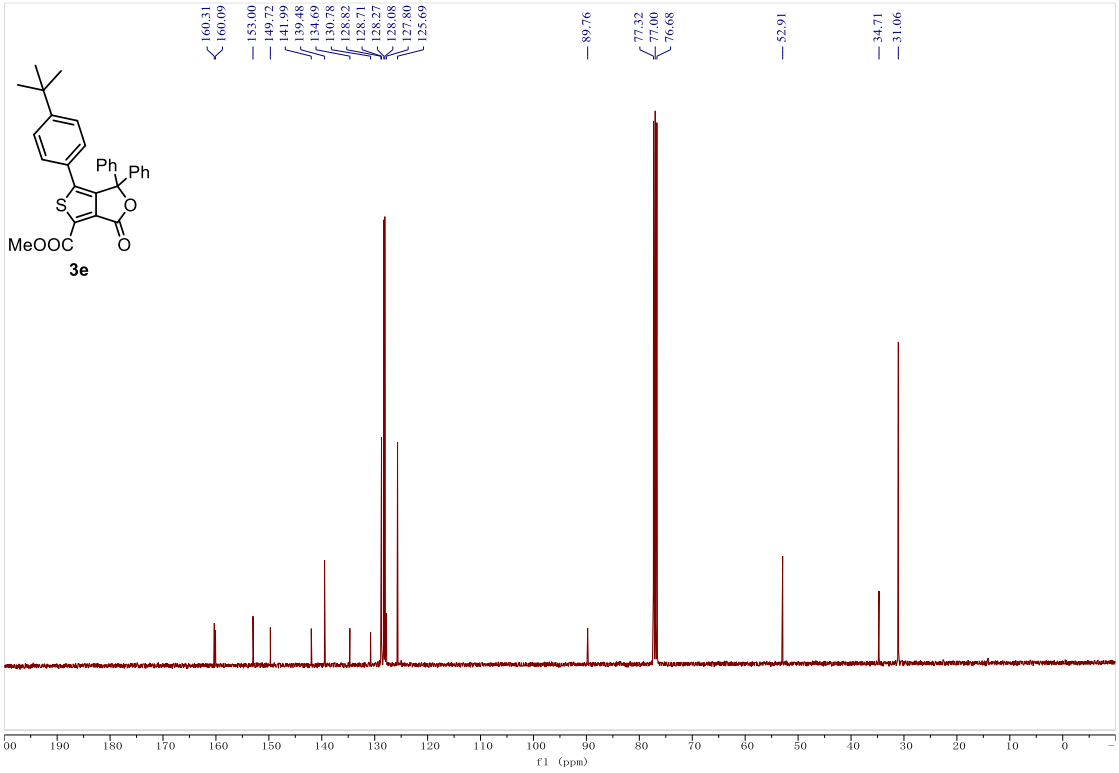
^{13}C NMR of compound **3d** (100 MHz, $CDCl_3$)



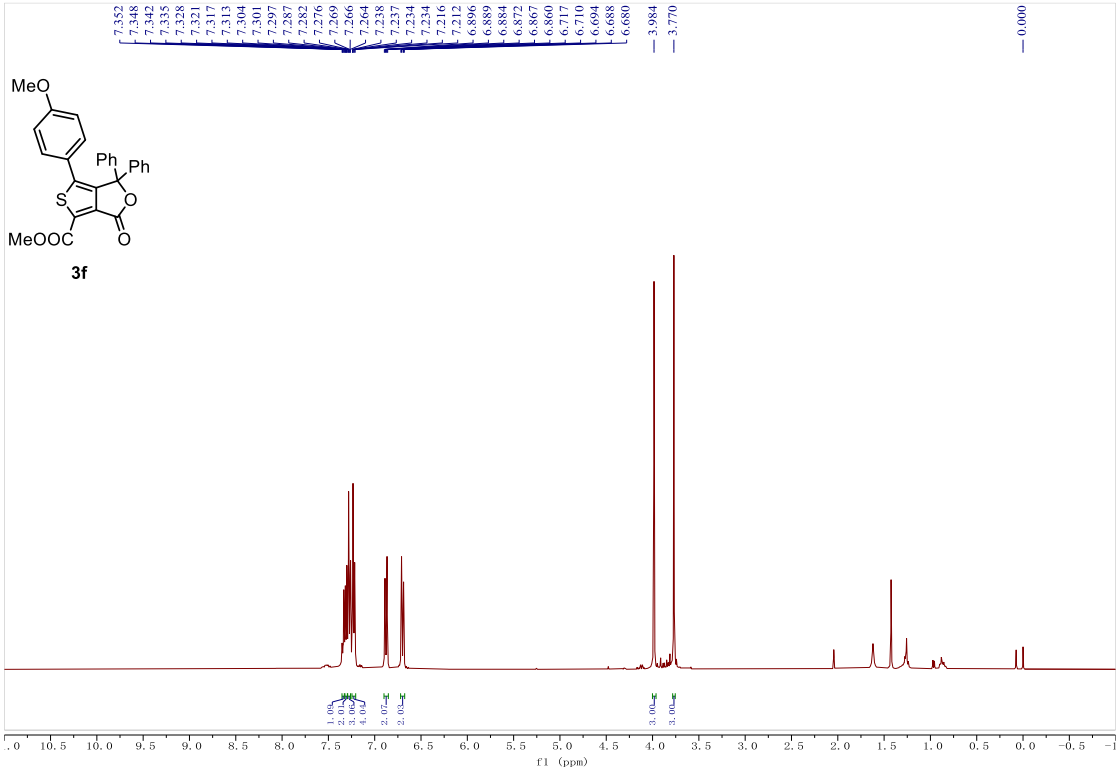
^{1}H NMR of compound **3e** (400 MHz, $CDCl_3$)



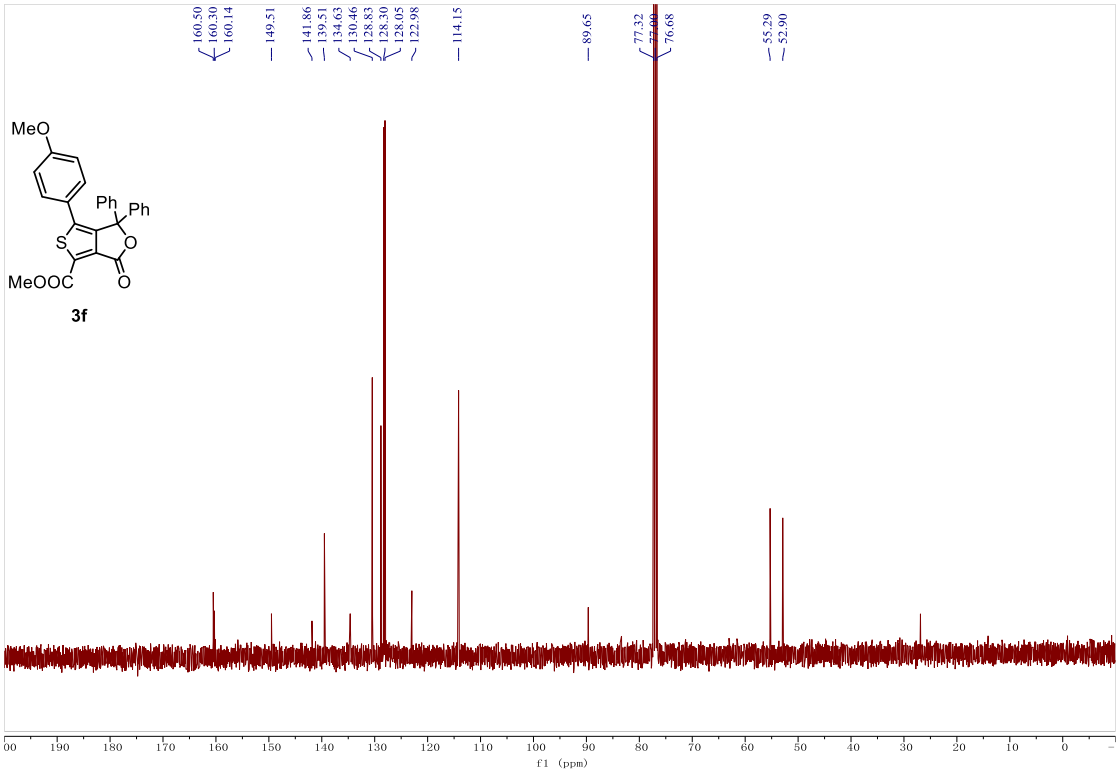
^{13}C NMR of compound **3e** (100 MHz, $CDCl_3$)



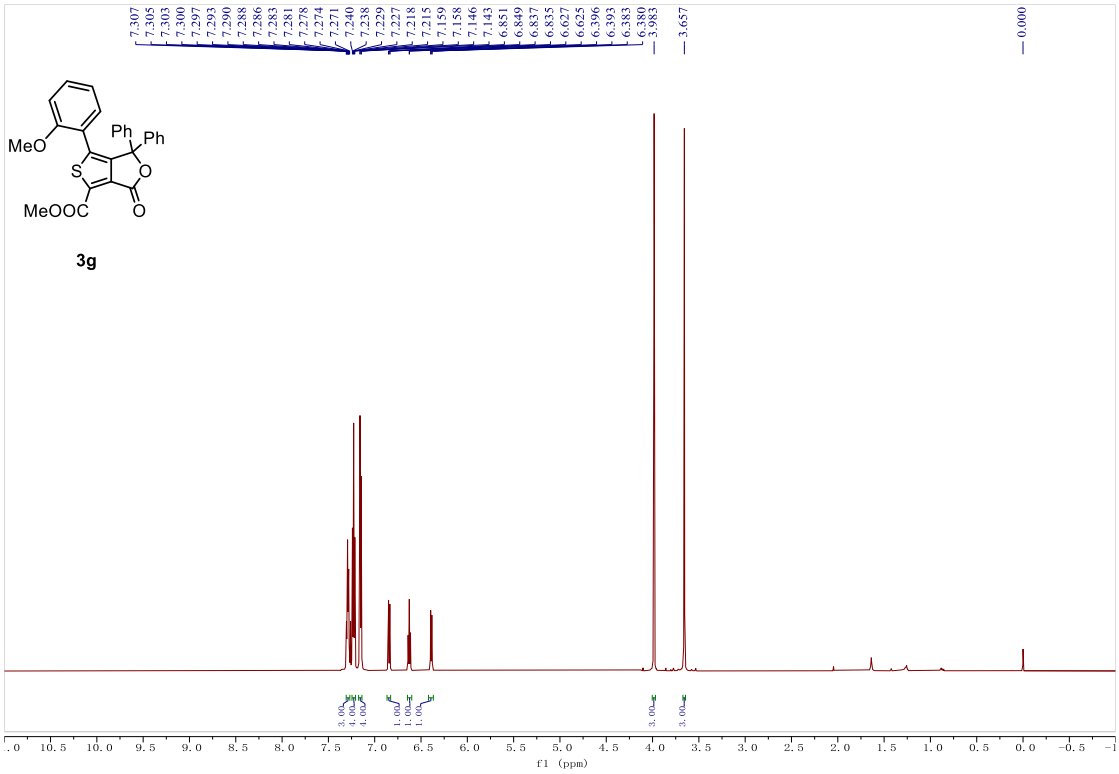
^{1}H NMR of compound **3f** (400 MHz, $CDCl_3$)



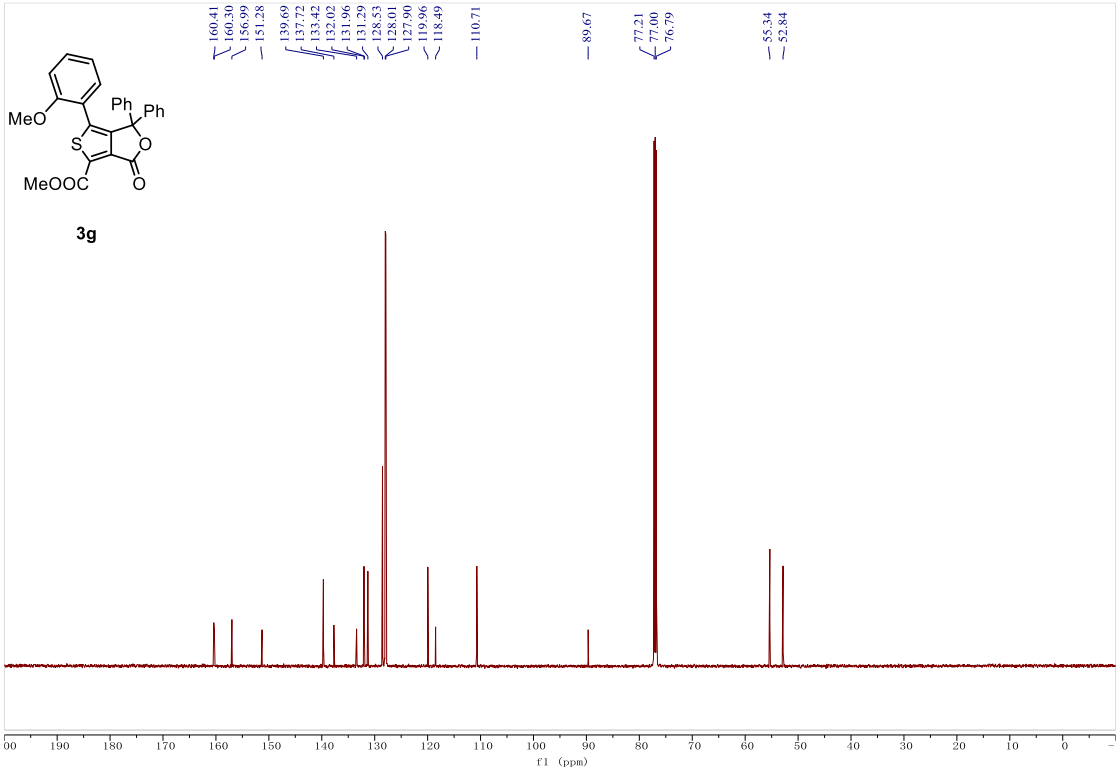
^{13}C NMR of compound **3f** (100 MHz, $CDCl_3$)



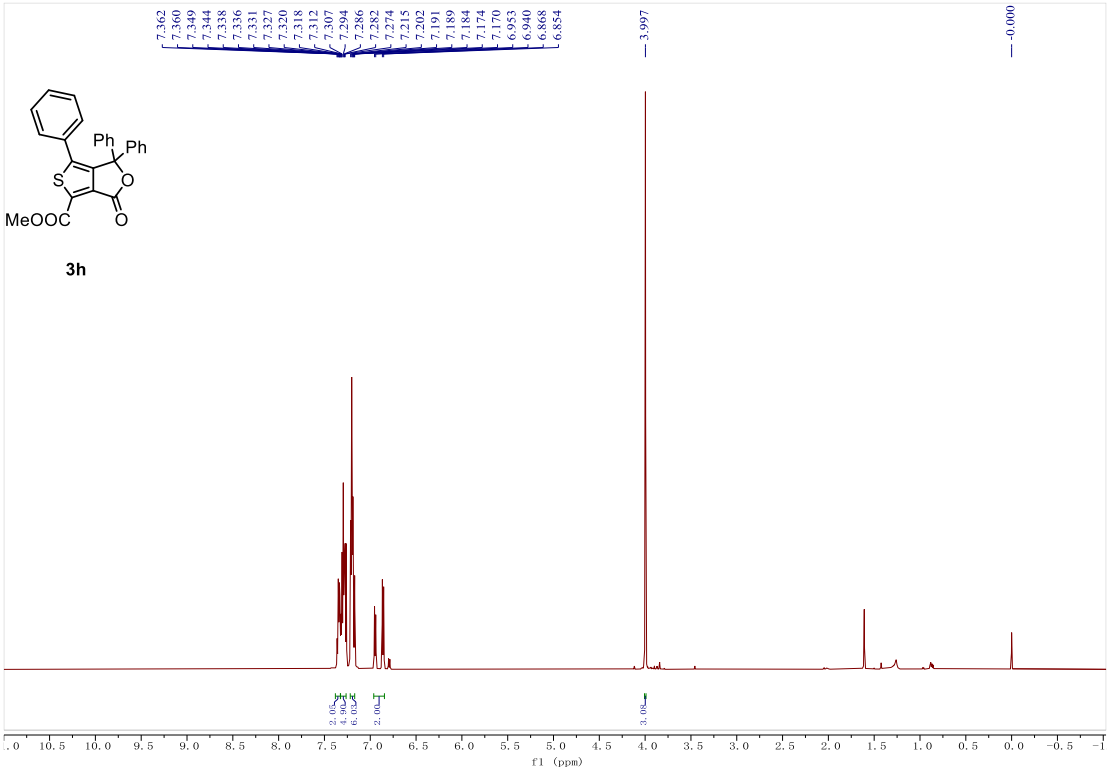
^{1}H NMR of compound **3g** (600 MHz, $CDCl_3$)



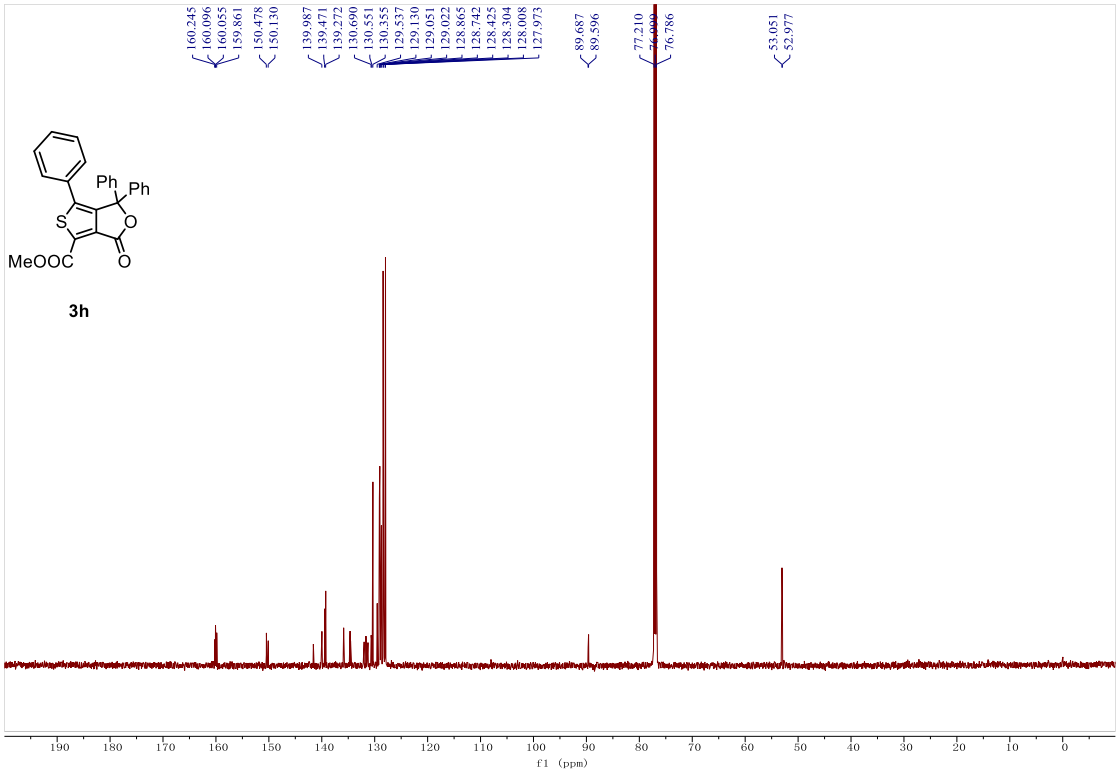
^{13}C NMR of compound **3g** (150 MHz, $CDCl_3$)



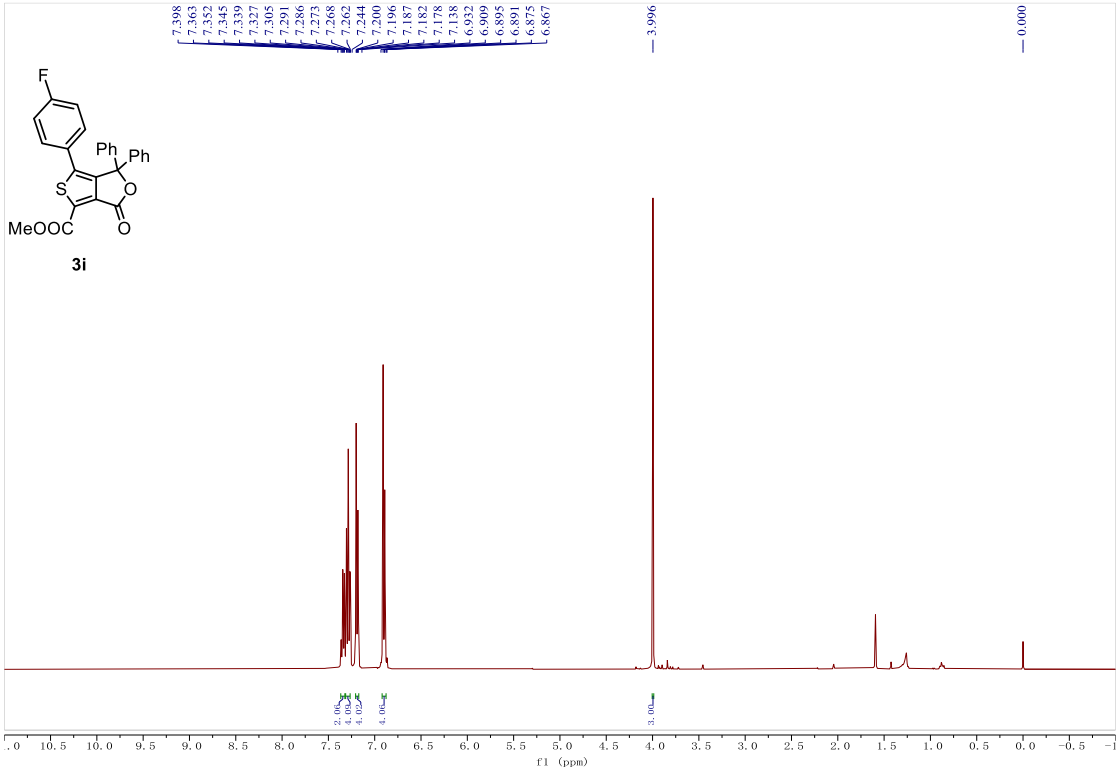
^{1}H NMR of compound **3h** (600 MHz, $CDCl_3$)



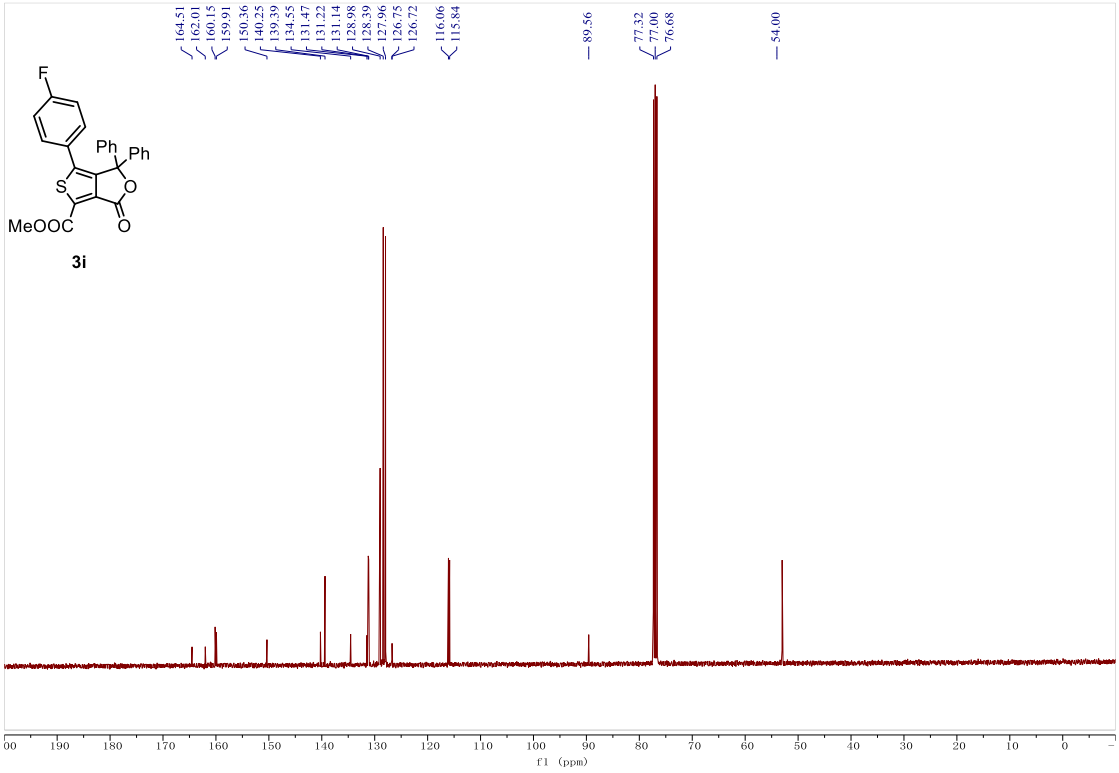
^{13}C NMR of compound **3h** (150 MHz, $CDCl_3$)



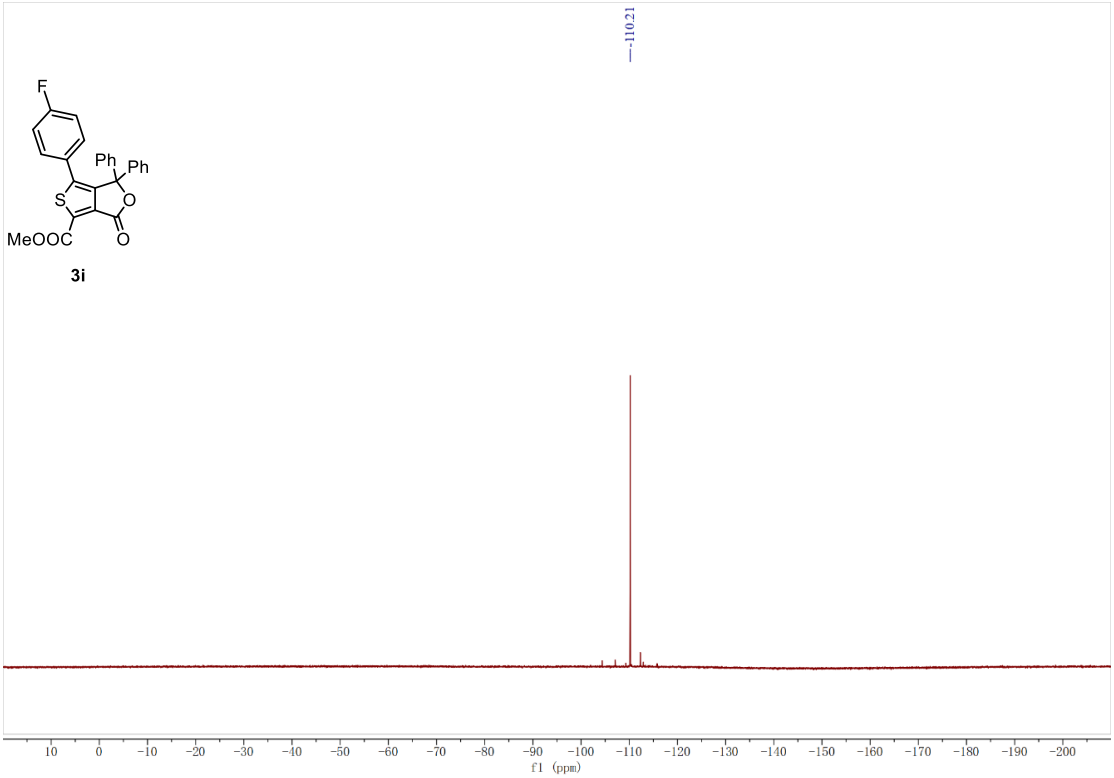
^{1}H NMR of compound **3i** (400 MHz, $CDCl_3$)



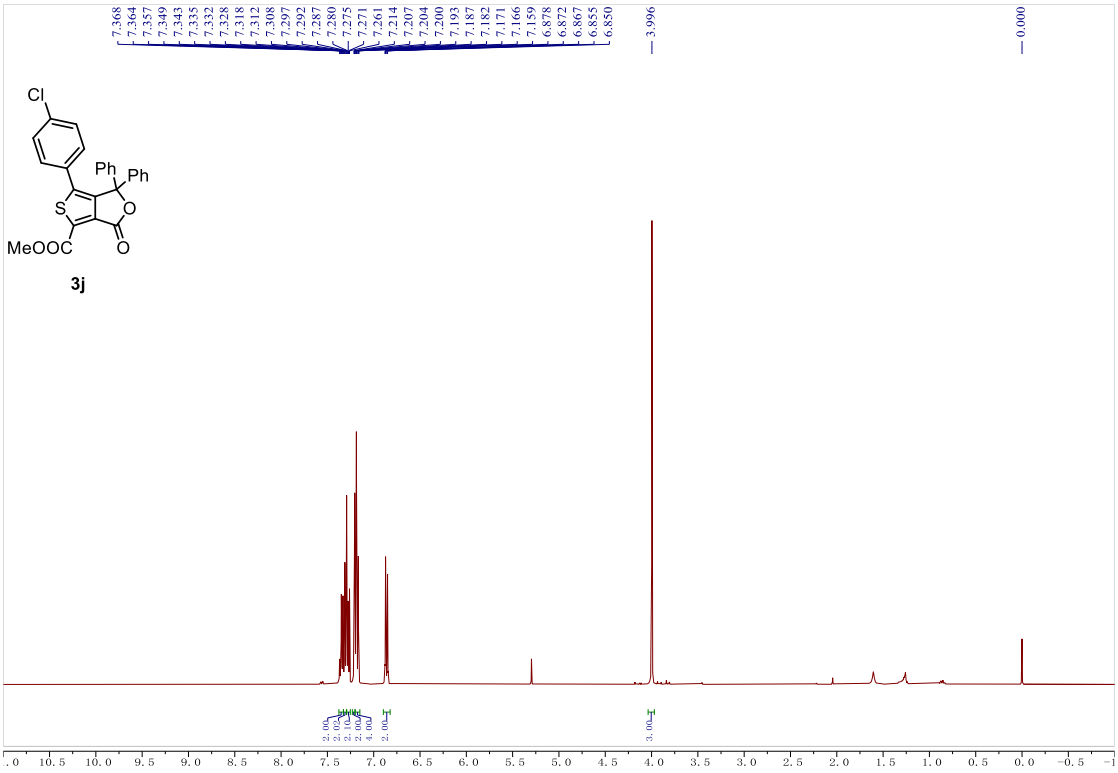
^{13}C NMR of compound **3i** (100 MHz, $CDCl_3$)



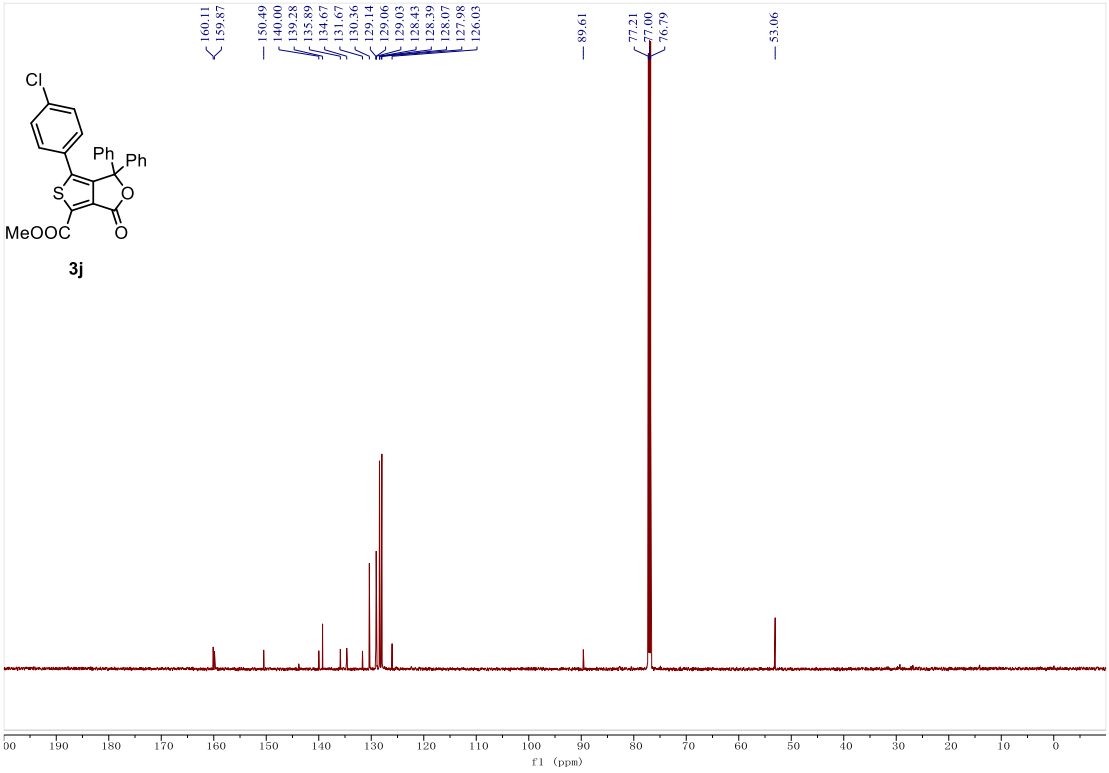
^{19}F NMR of compound **3i** (565 MHz, $CDCl_3$)



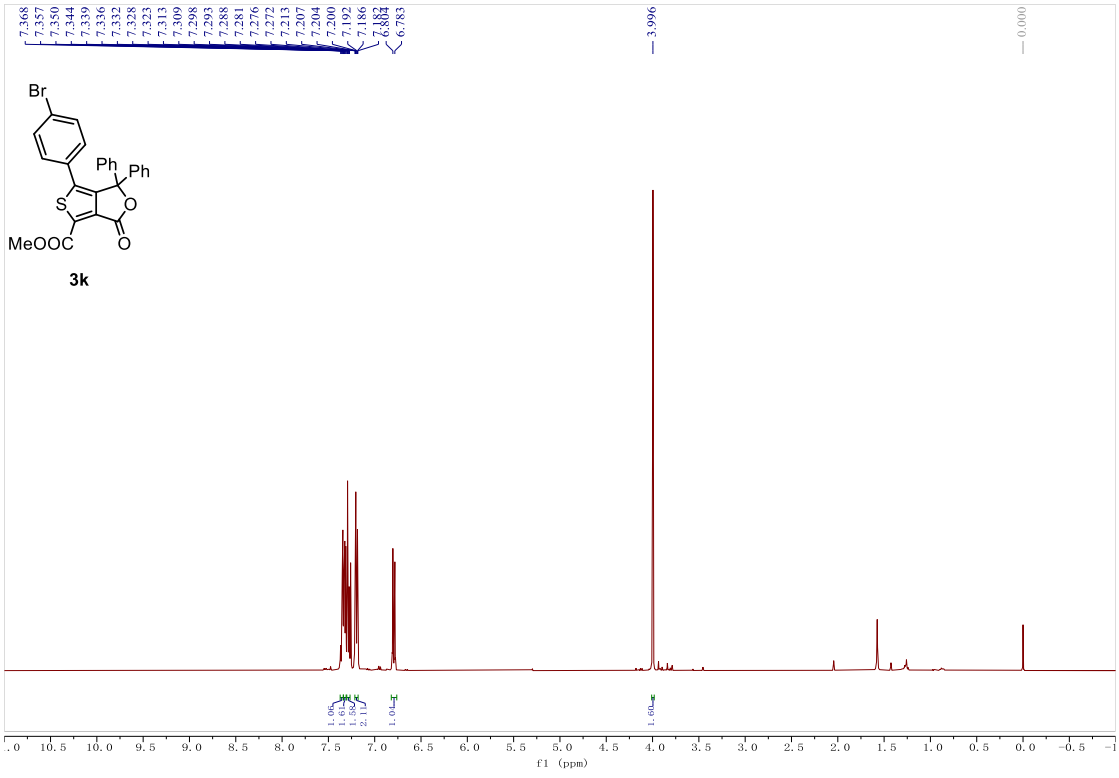
^{1}H NMR of compound **3j** (400 MHz, $CDCl_3$)



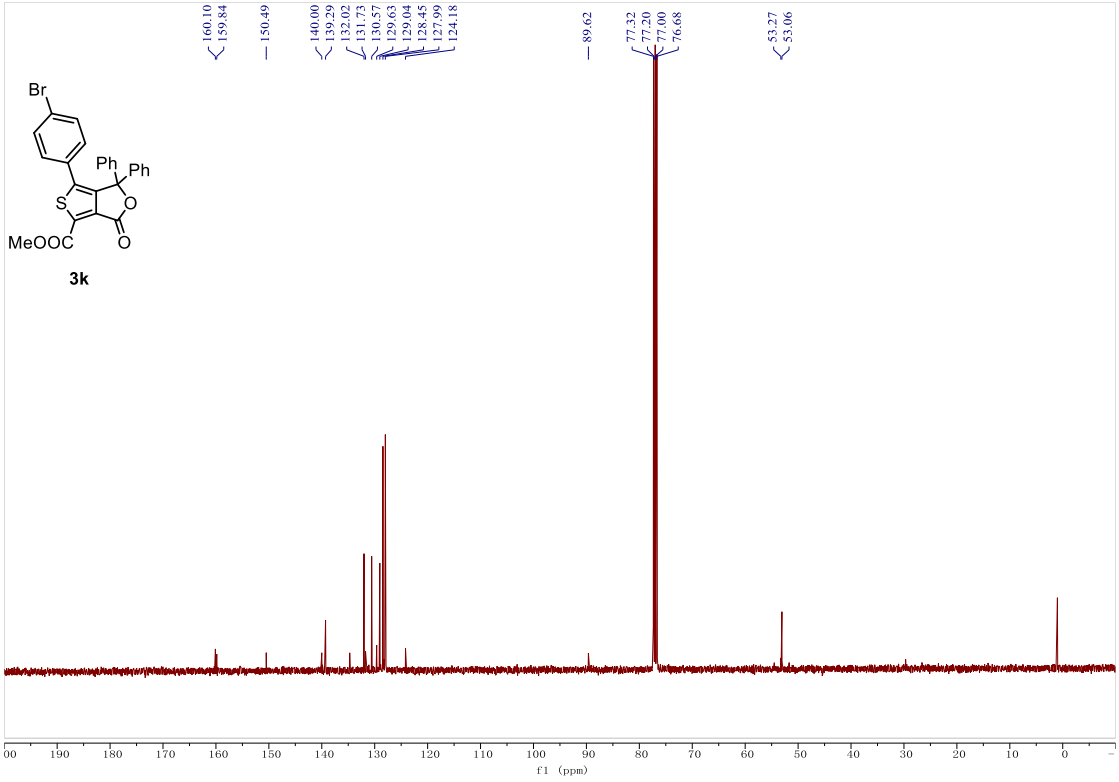
^{13}C NMR of compound **3j** (150 MHz, $CDCl_3$)



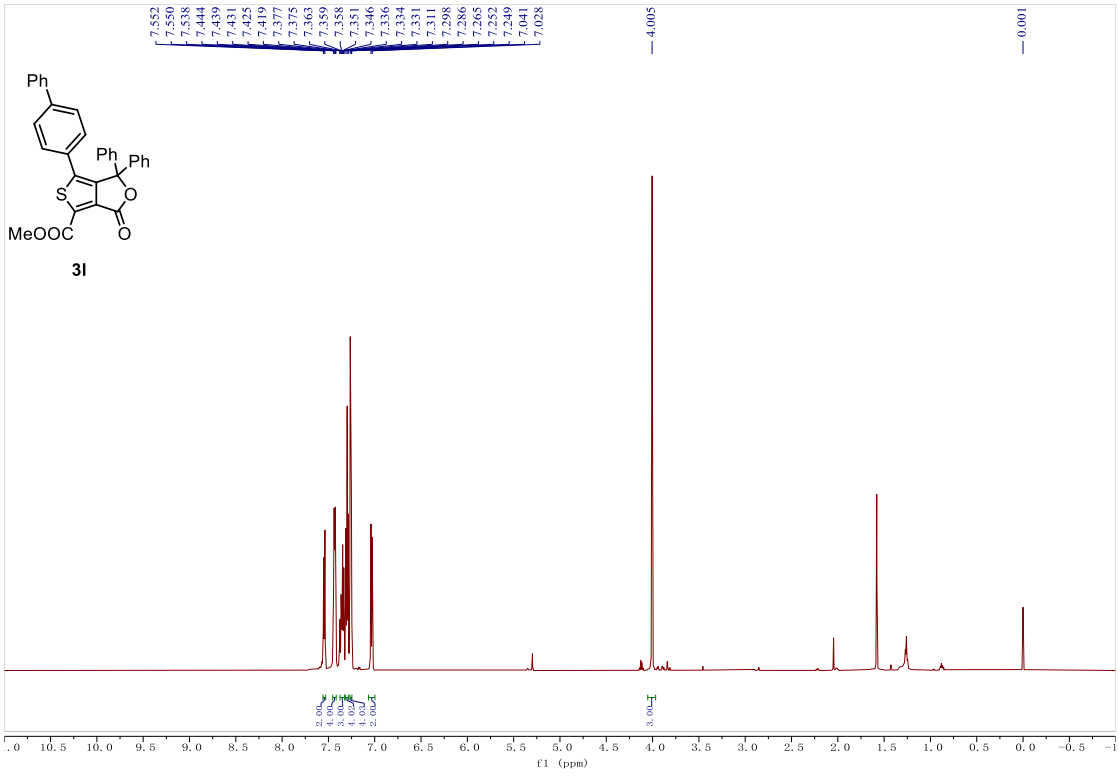
^{1}H NMR of compound **3k** (400 MHz, $CDCl_3$)



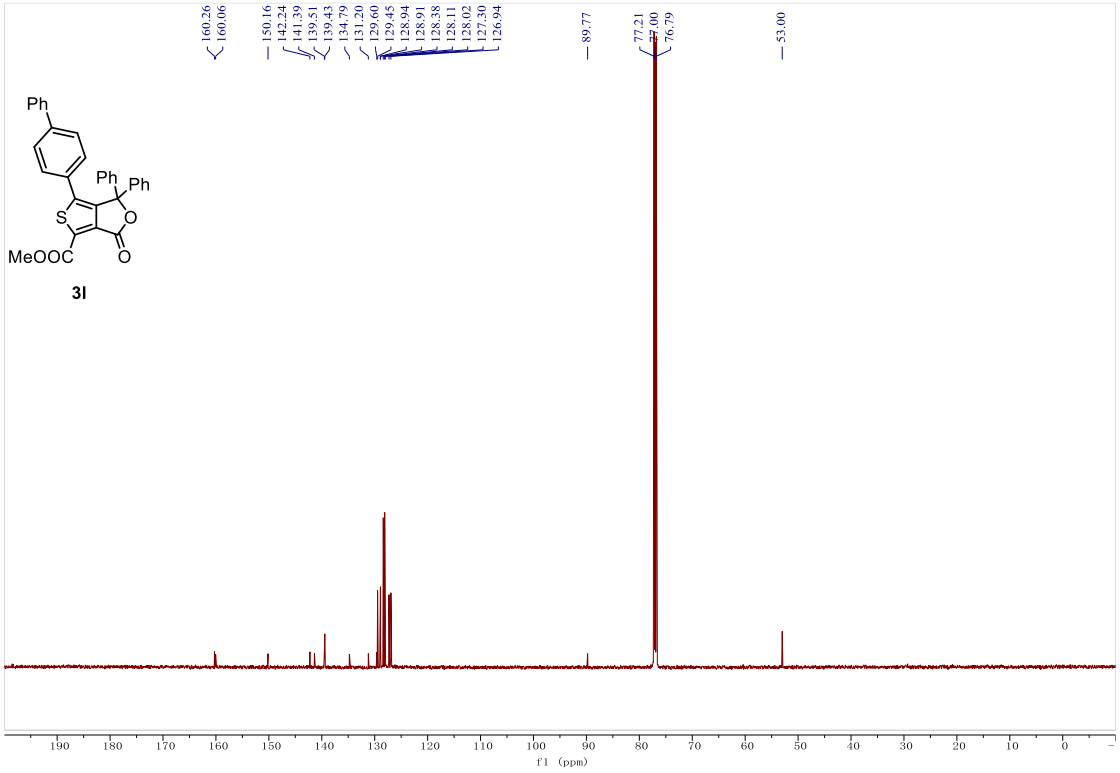
^{13}C NMR of compound **3k** (100 MHz, $CDCl_3$)



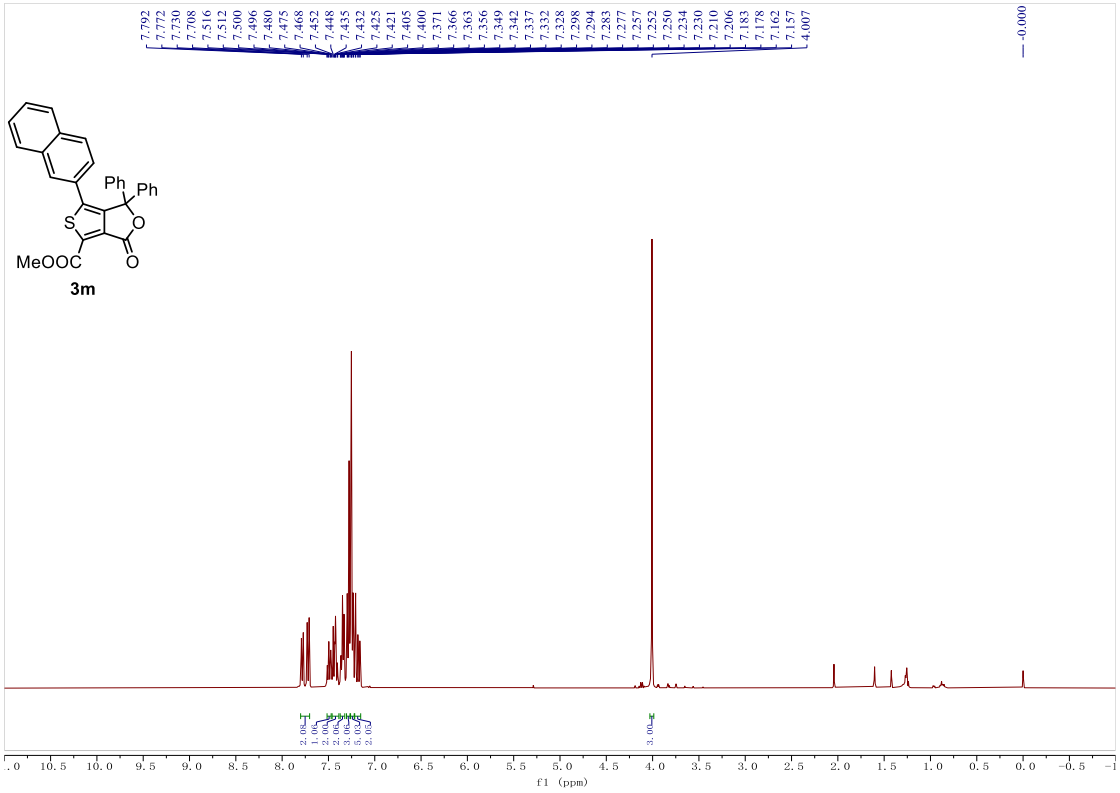
^{1}H NMR of compound **3l** (600 MHz, $CDCl_3$)



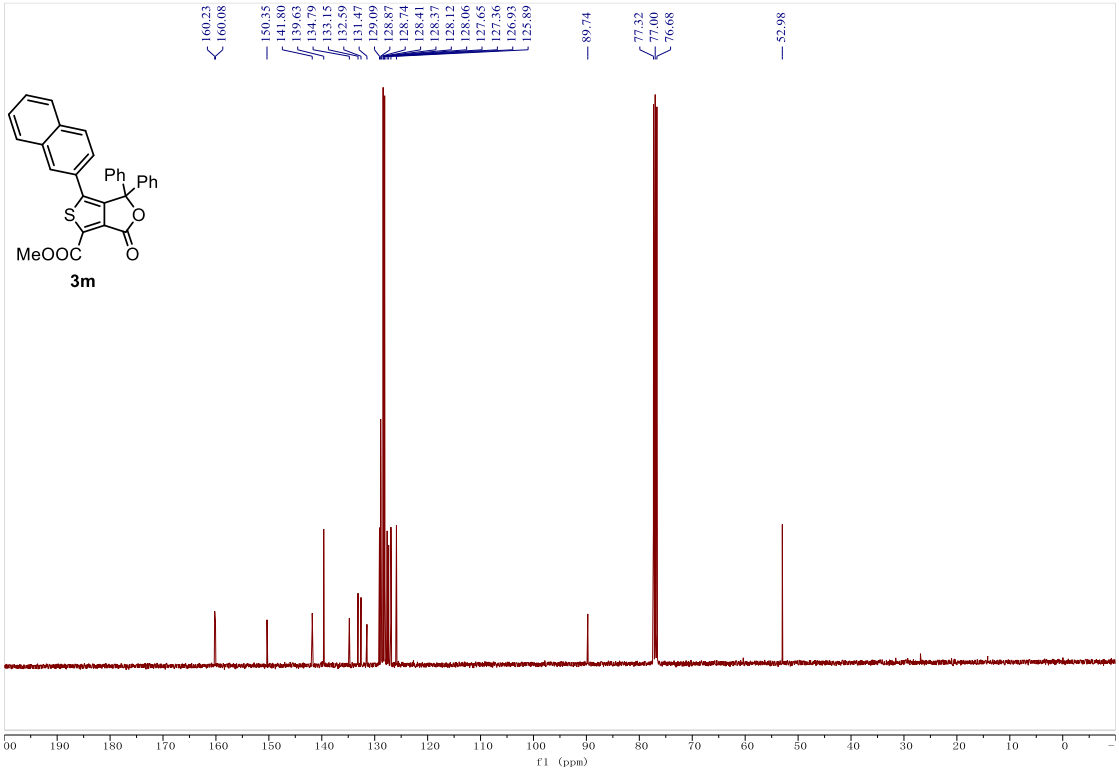
^{13}C NMR of compound **3l** (150 MHz, $CDCl_3$)



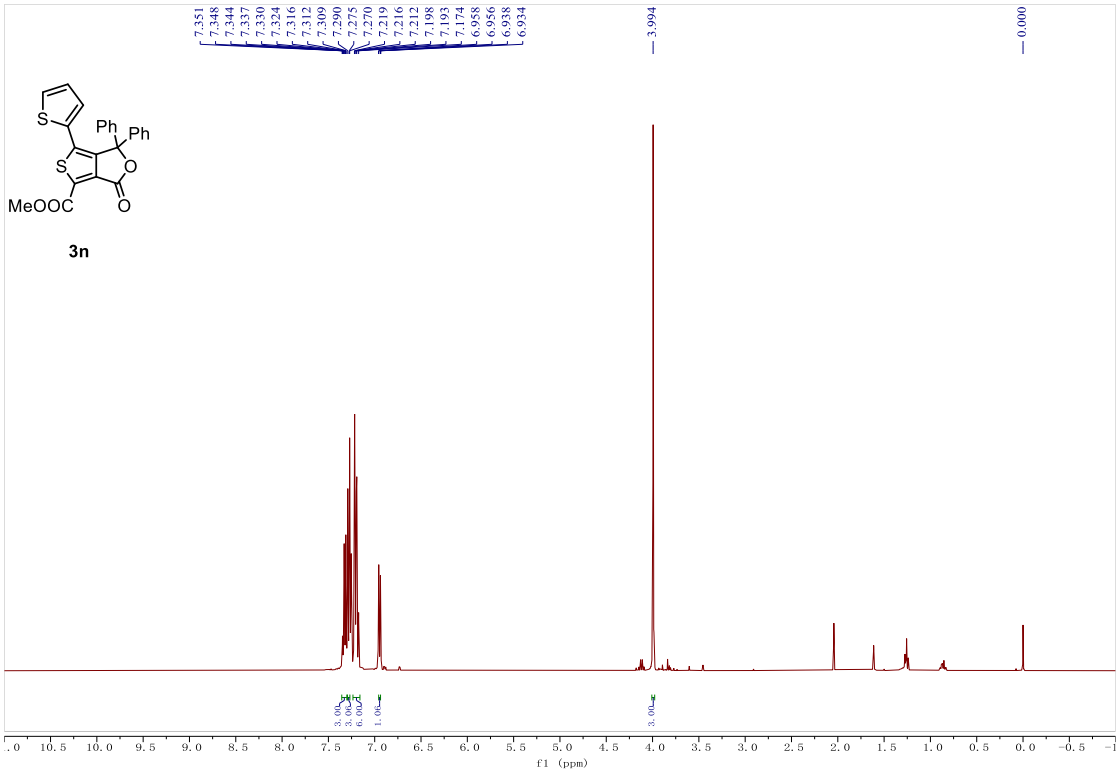
^{1}H NMR of compound **3m** (400 MHz, $CDCl_3$)



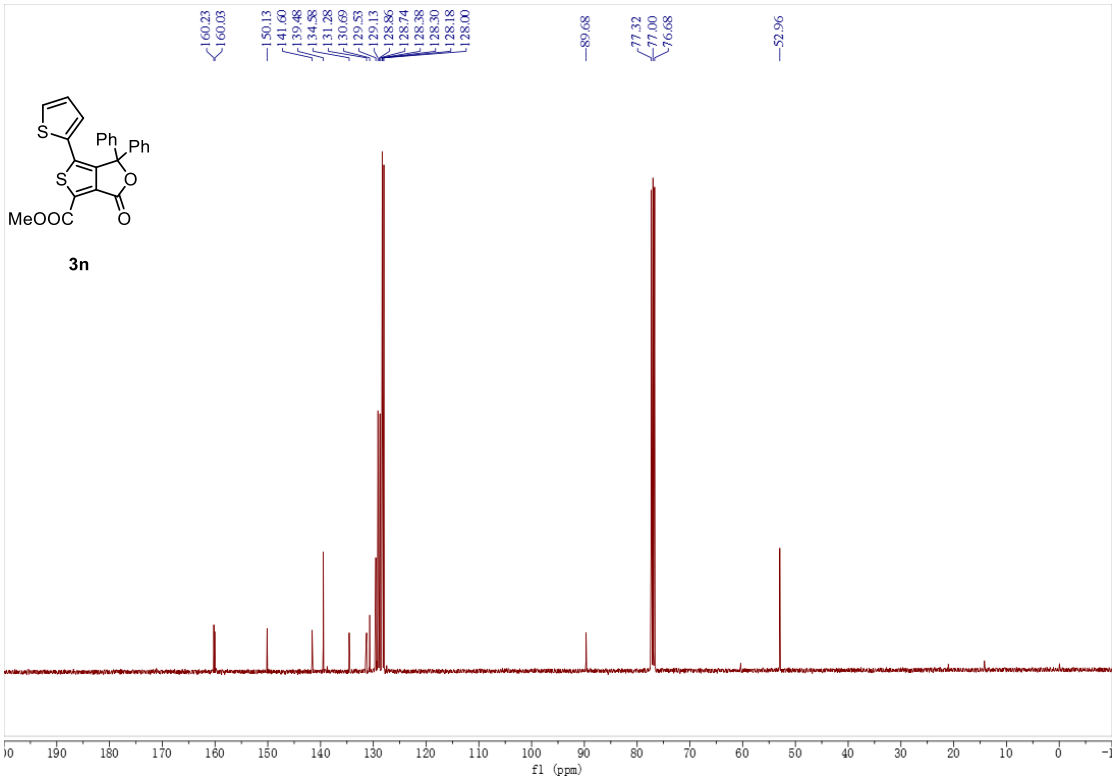
^{13}C NMR of compound **3m** (100 MHz, $CDCl_3$)



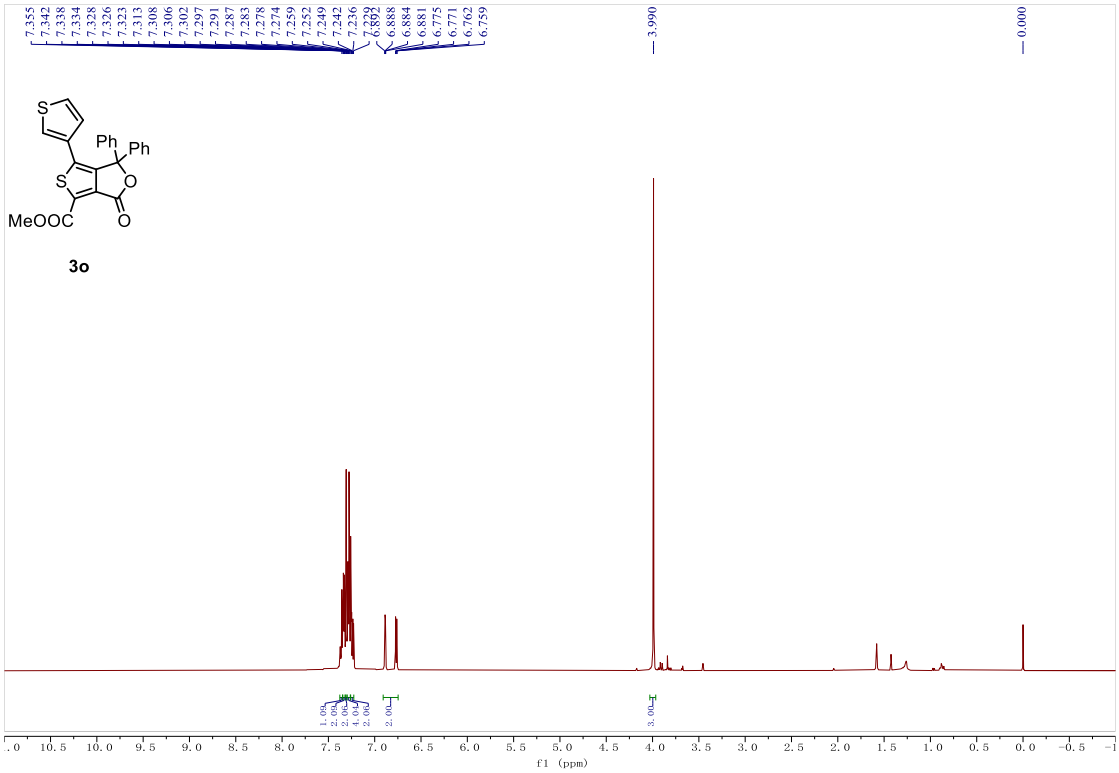
^{1}H NMR of compound **3n** (400 MHz, $CDCl_3$)



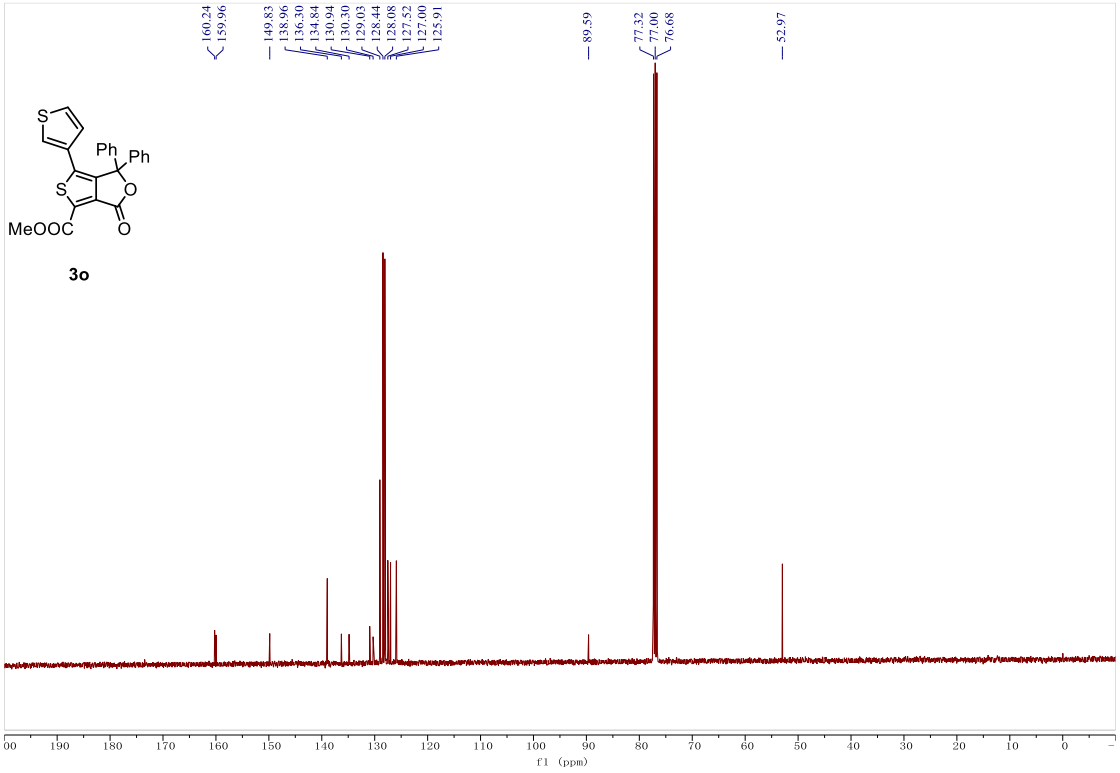
^{13}C NMR of compound **3n** (100 MHz, $CDCl_3$)



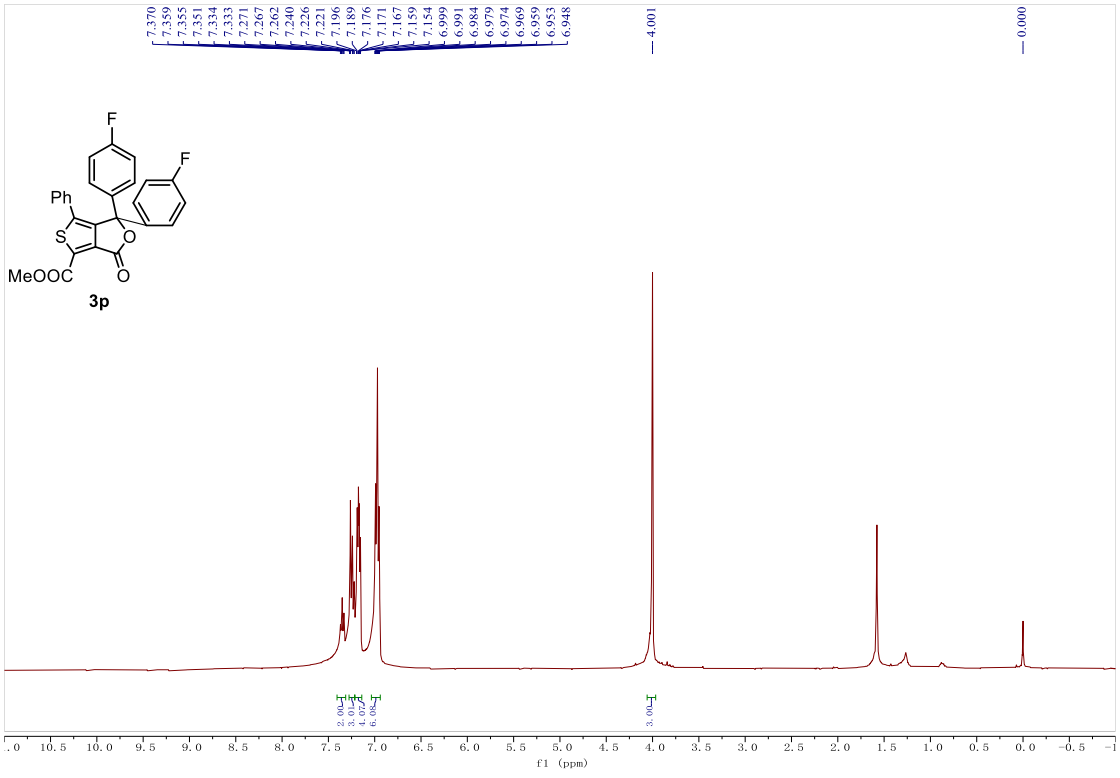
^{1}H NMR of compound **3o** (400 MHz, $CDCl_3$)



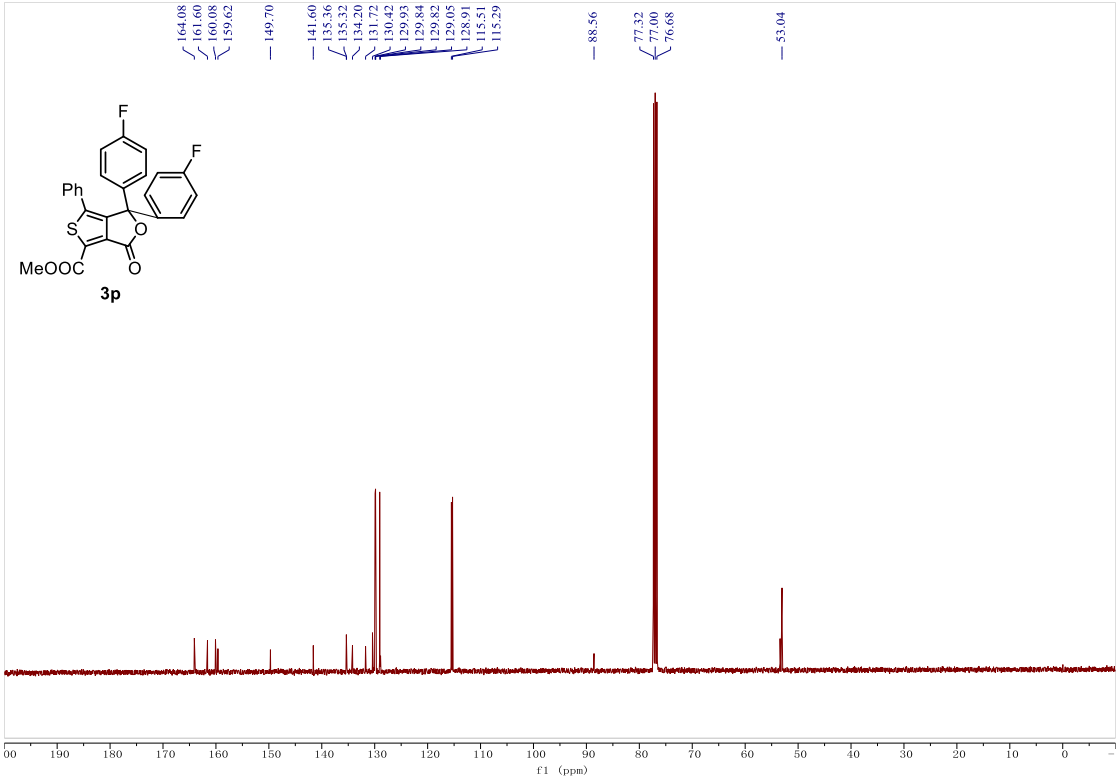
^{13}C NMR of compound **3o** (100 MHz, $CDCl_3$)



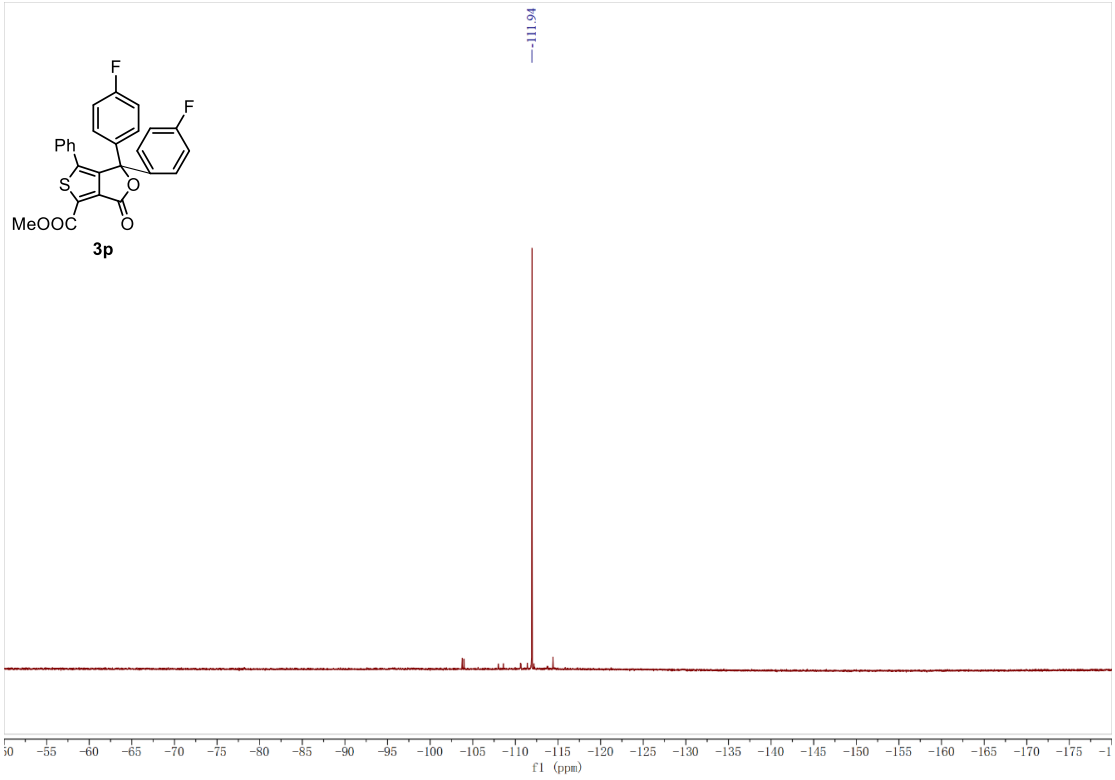
^{1}H NMR of compound **3p** (400 MHz, $CDCl_3$)



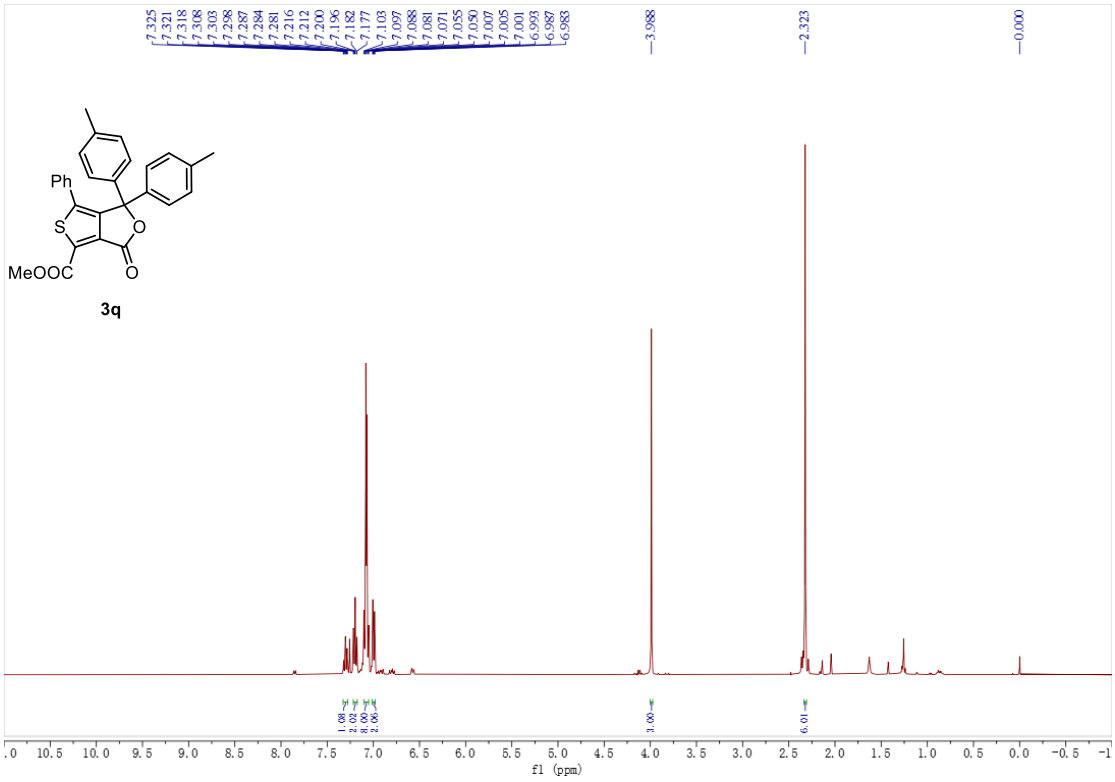
^{13}C NMR of compound **3p** (100 MHz, $CDCl_3$)



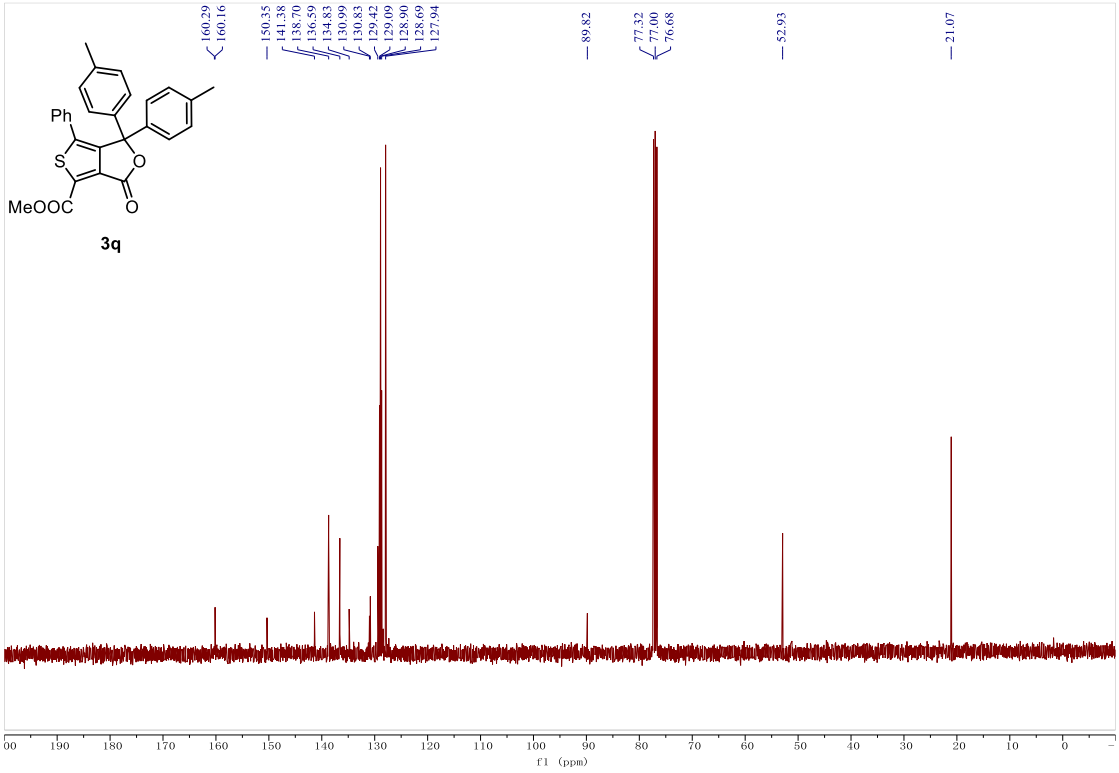
^{19}F NMR of compound **3p** (565 MHz, $CDCl_3$)



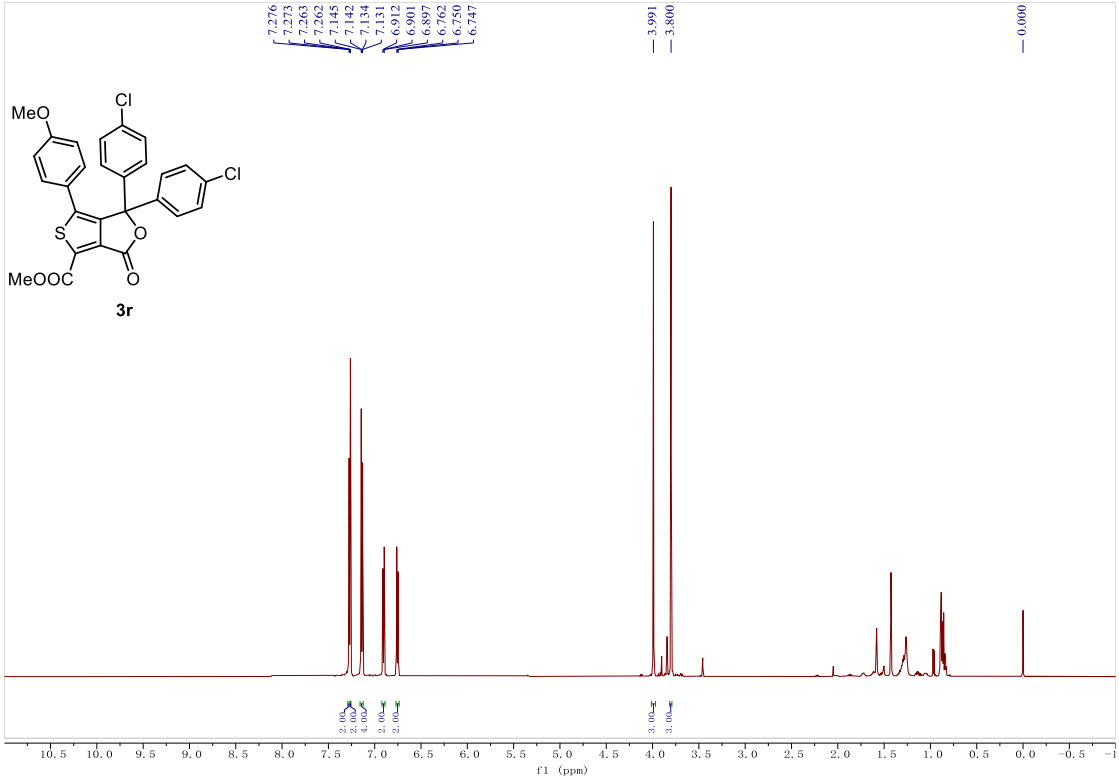
^{1}H NMR of compound **3q** (400 MHz, $CDCl_3$)



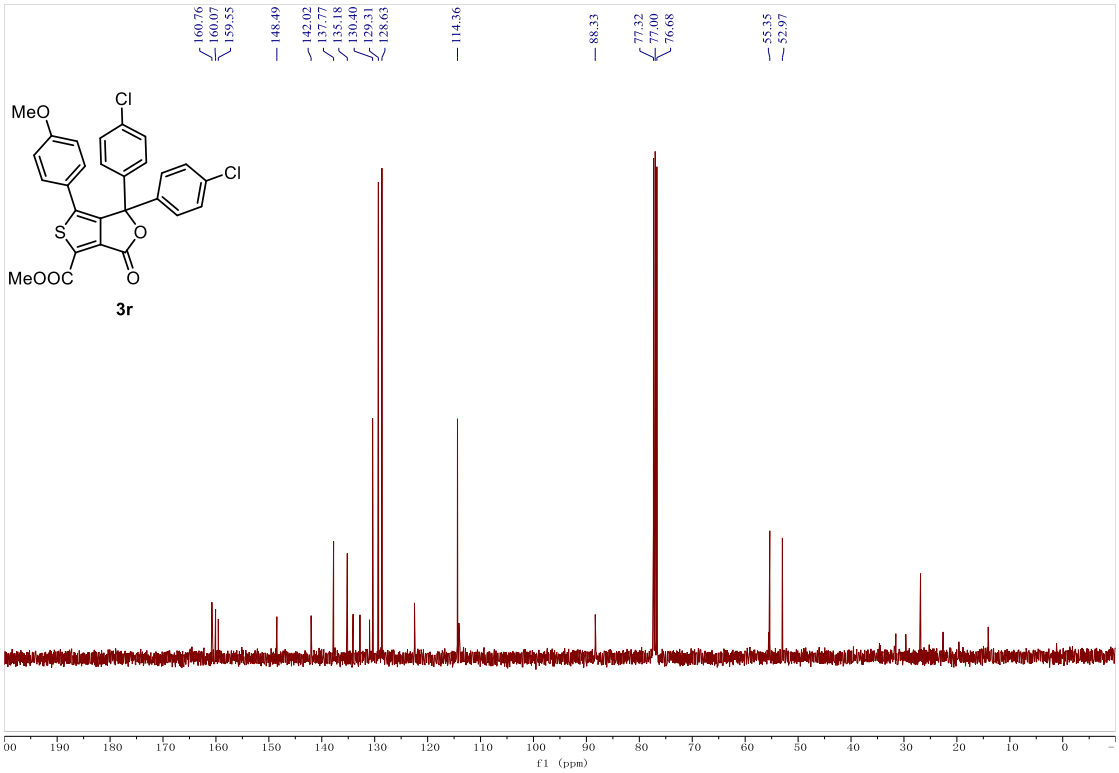
^{13}C NMR of compound **3q** (100 MHz, $CDCl_3$)



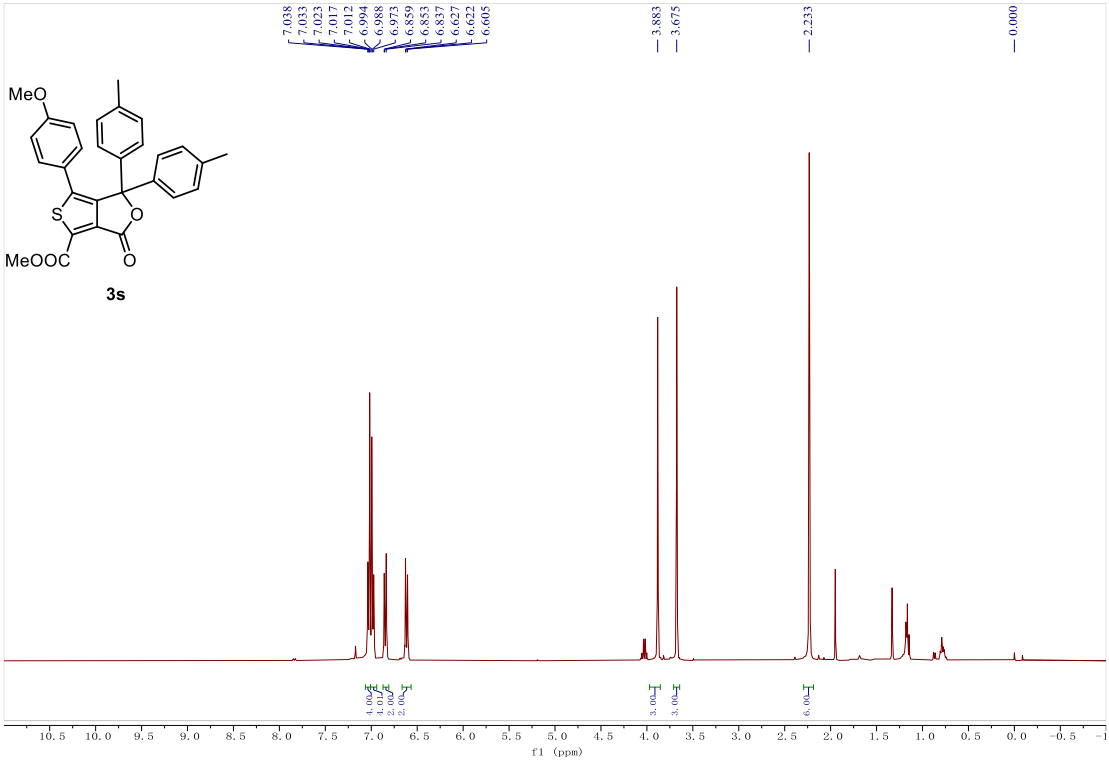
^{1}H NMR of compound **3r** (600 MHz, $CDCl_3$)



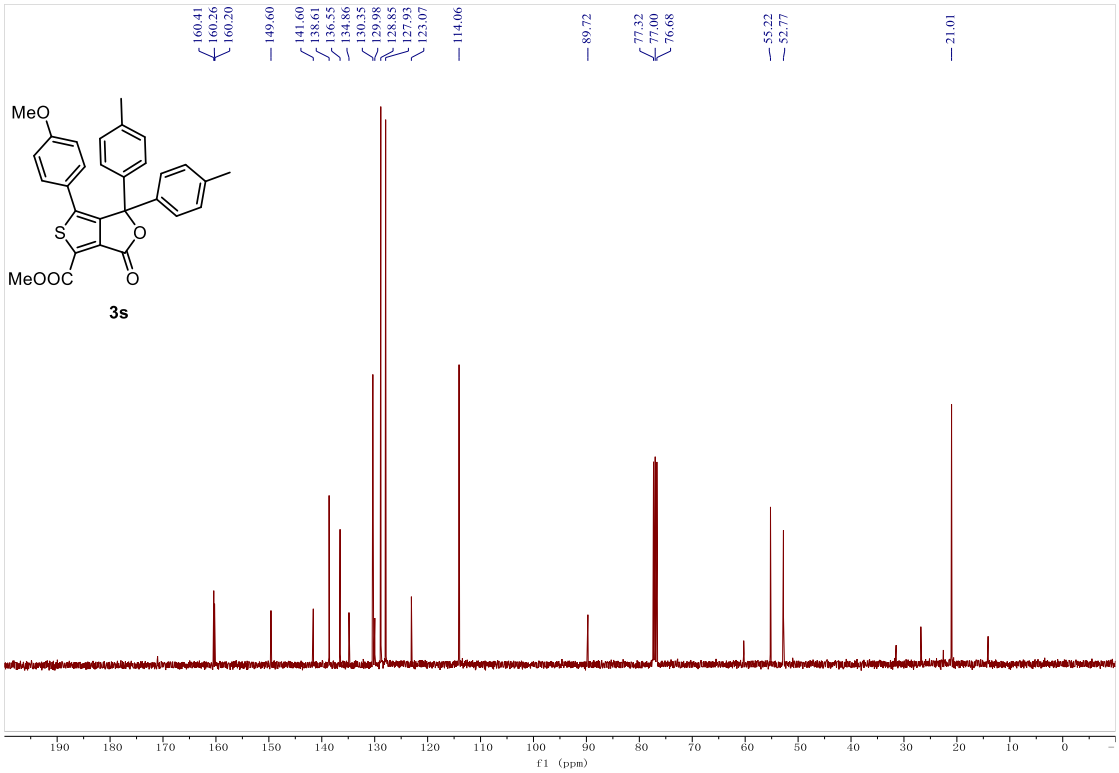
^{13}C NMR of compound **3r** (100 MHz, $CDCl_3$)



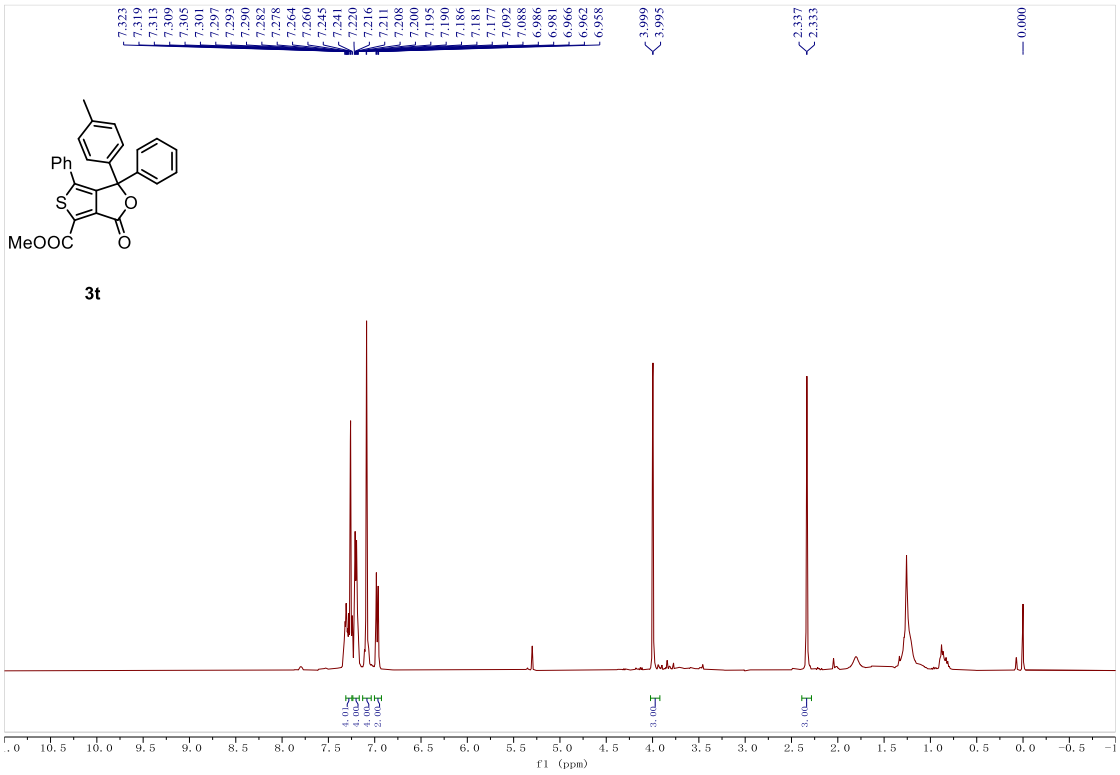
^{1}H NMR of compound **3s** (400 MHz, $CDCl_3$)



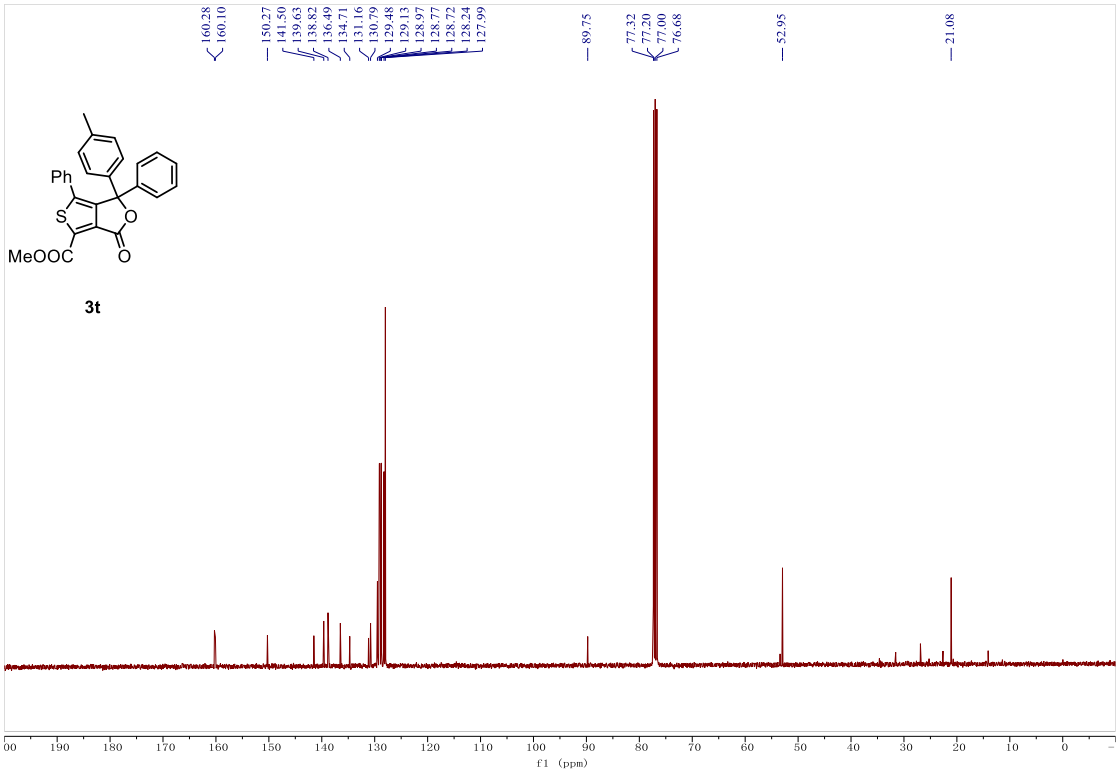
^{13}C NMR of compound **3s** (100 MHz, $CDCl_3$)



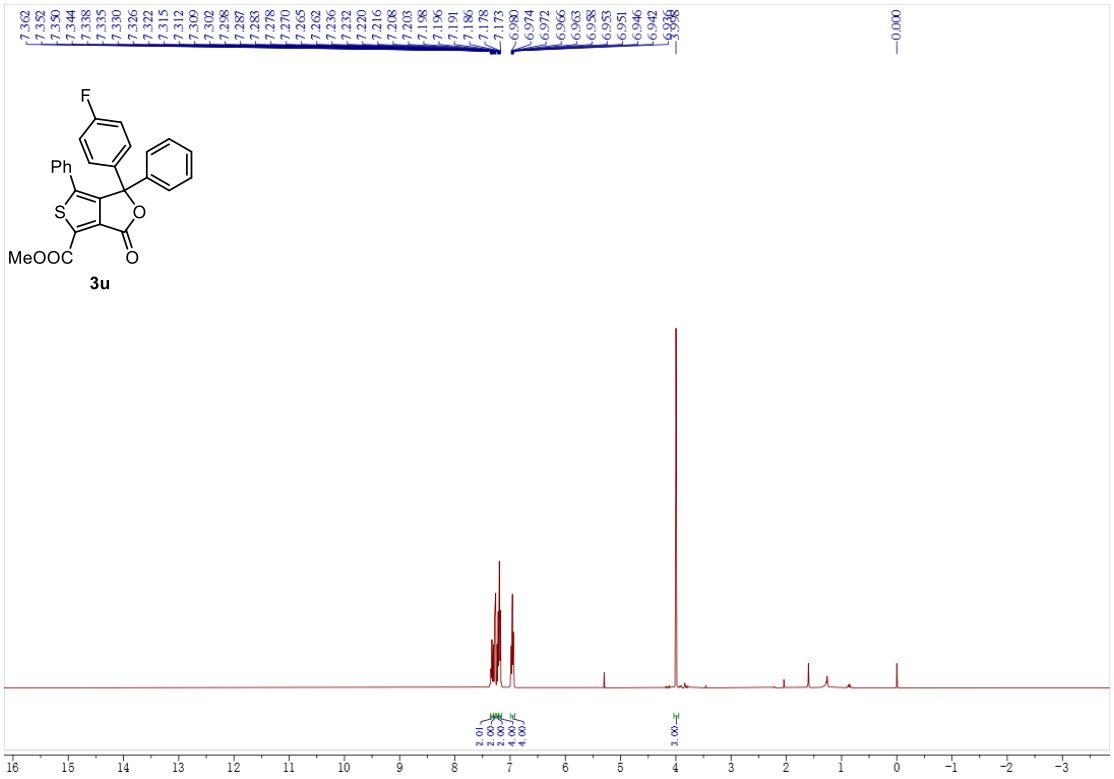
^{1}H NMR of compound **3t** (400 MHz, $CDCl_3$)



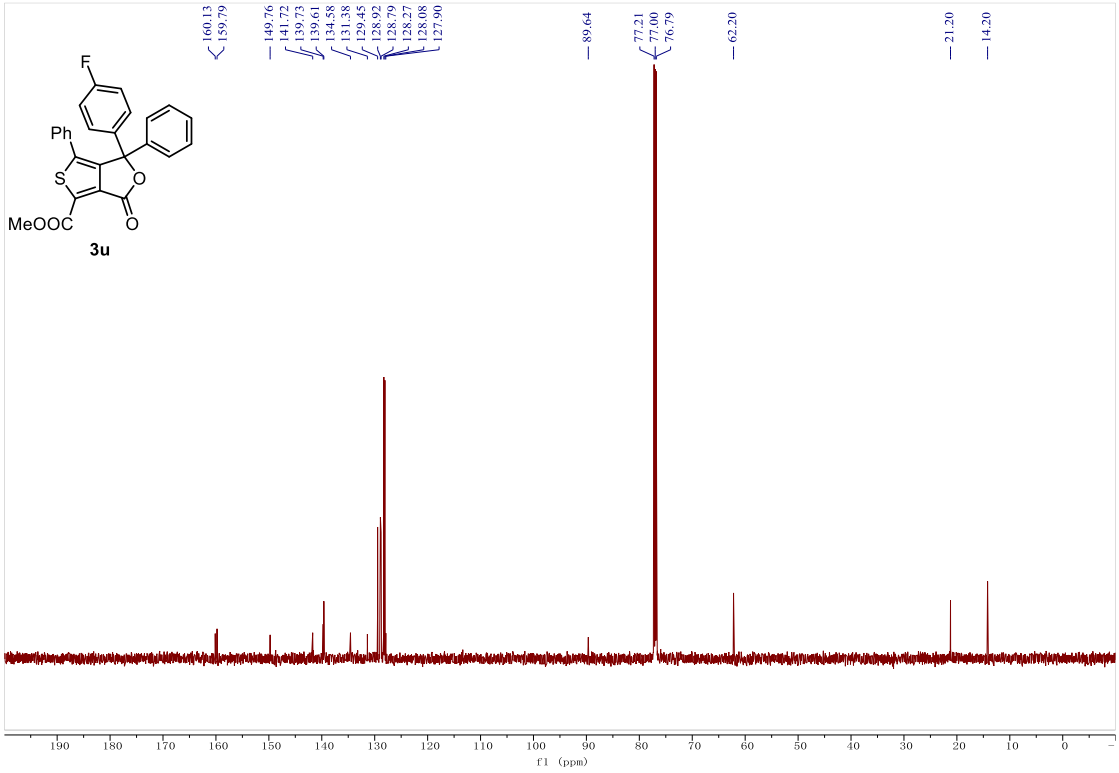
^{13}C NMR of compound **3t** (100 MHz, $CDCl_3$)



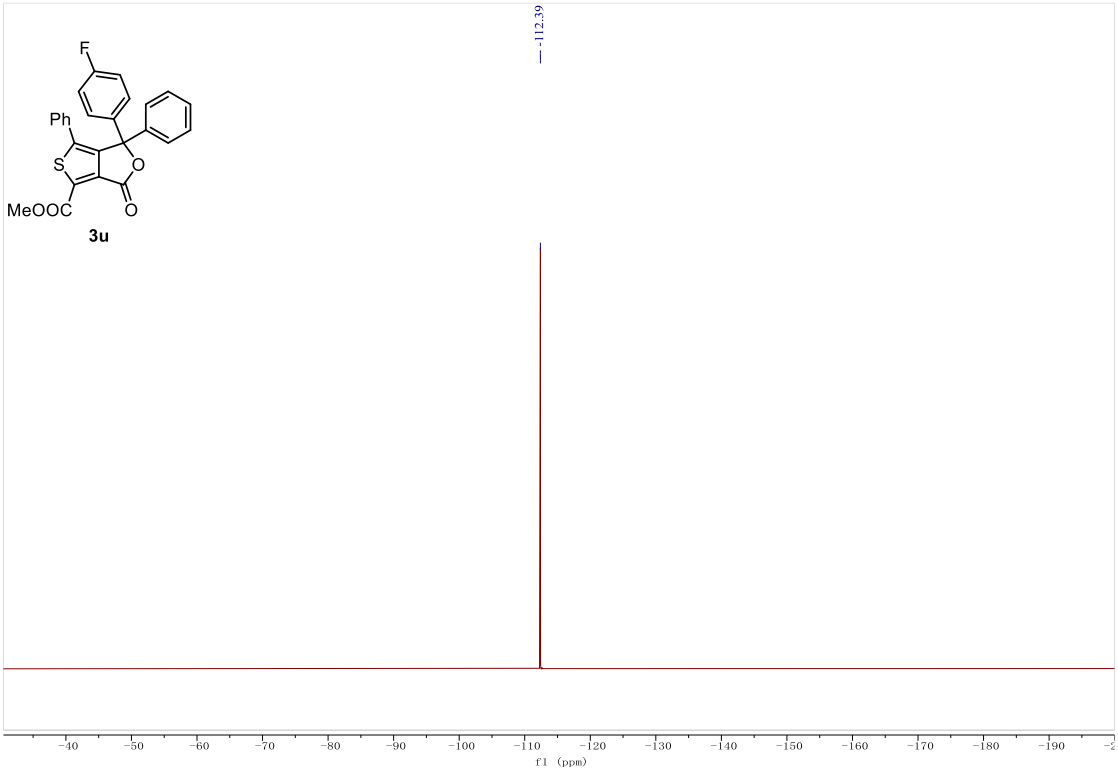
^{1}H NMR of compound **3u** (400 MHz, $CDCl_3$)



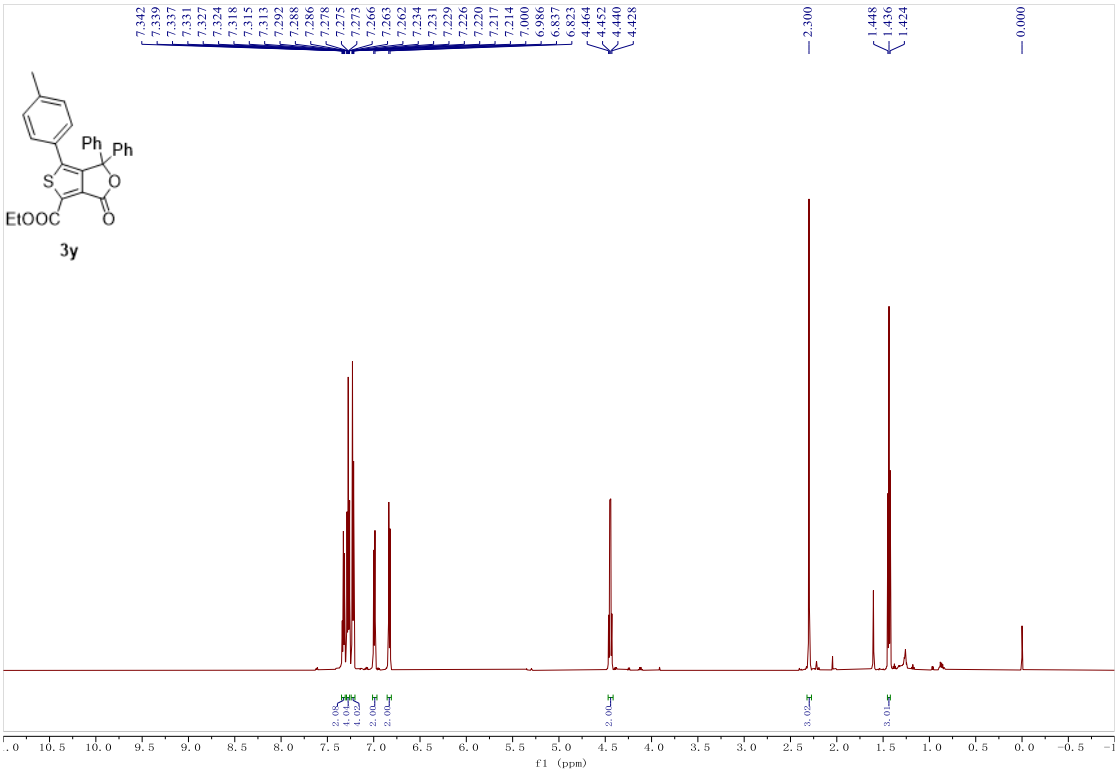
^{13}C NMR of compound **3u** (100 MHz, $CDCl_3$)



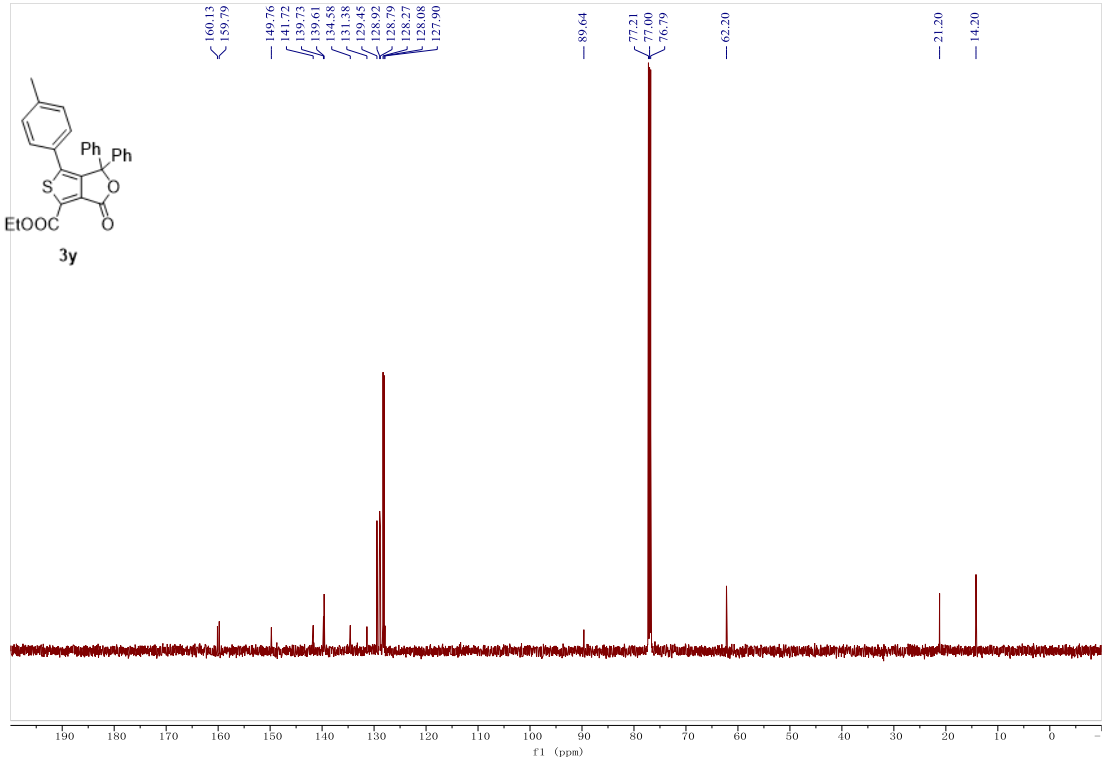
^{19}F NMR of compound **3u** (565 MHz, $CDCl_3$)



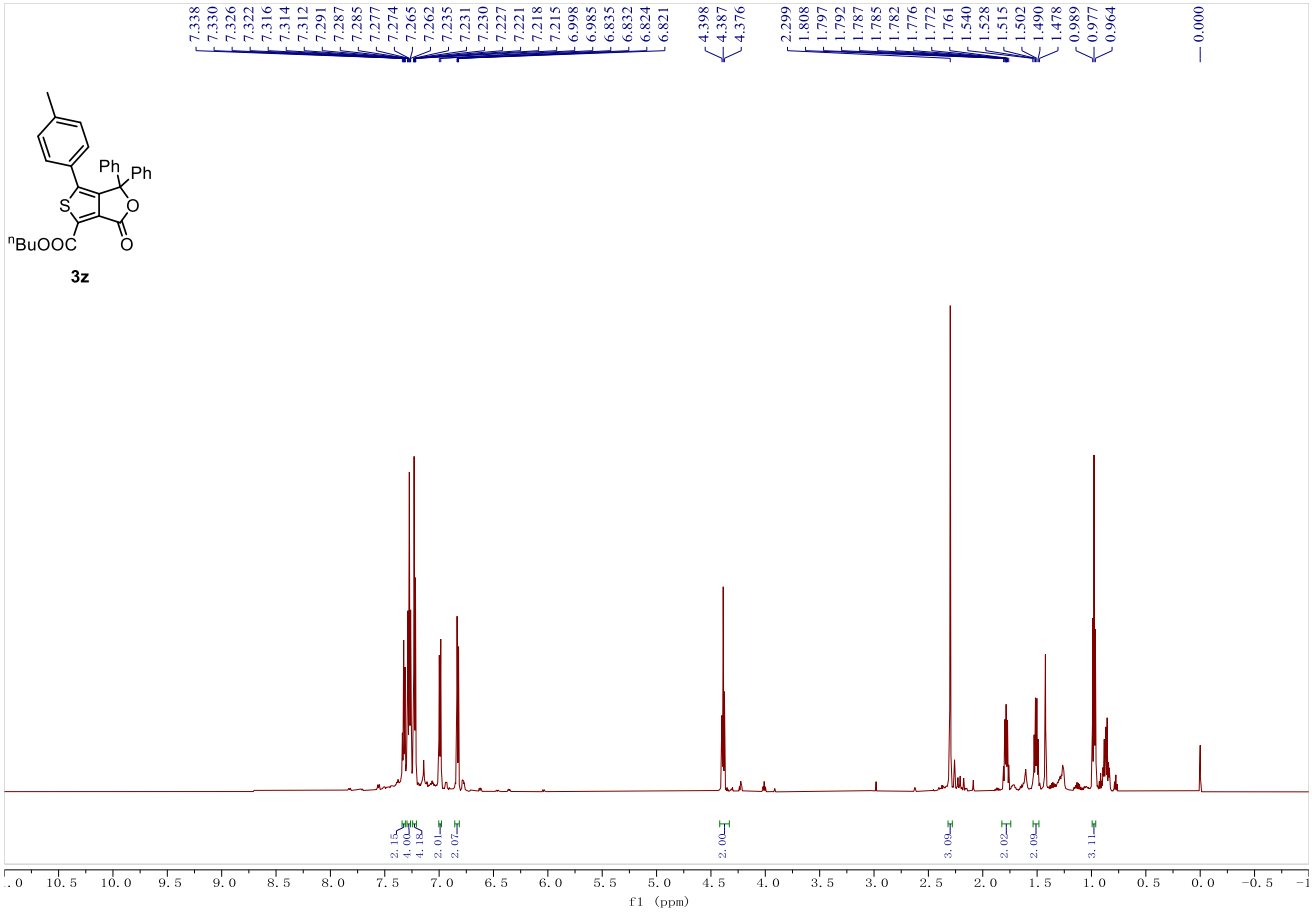
^{1}H NMR of compound **3y** (100 MHz, $CDCl_3$)



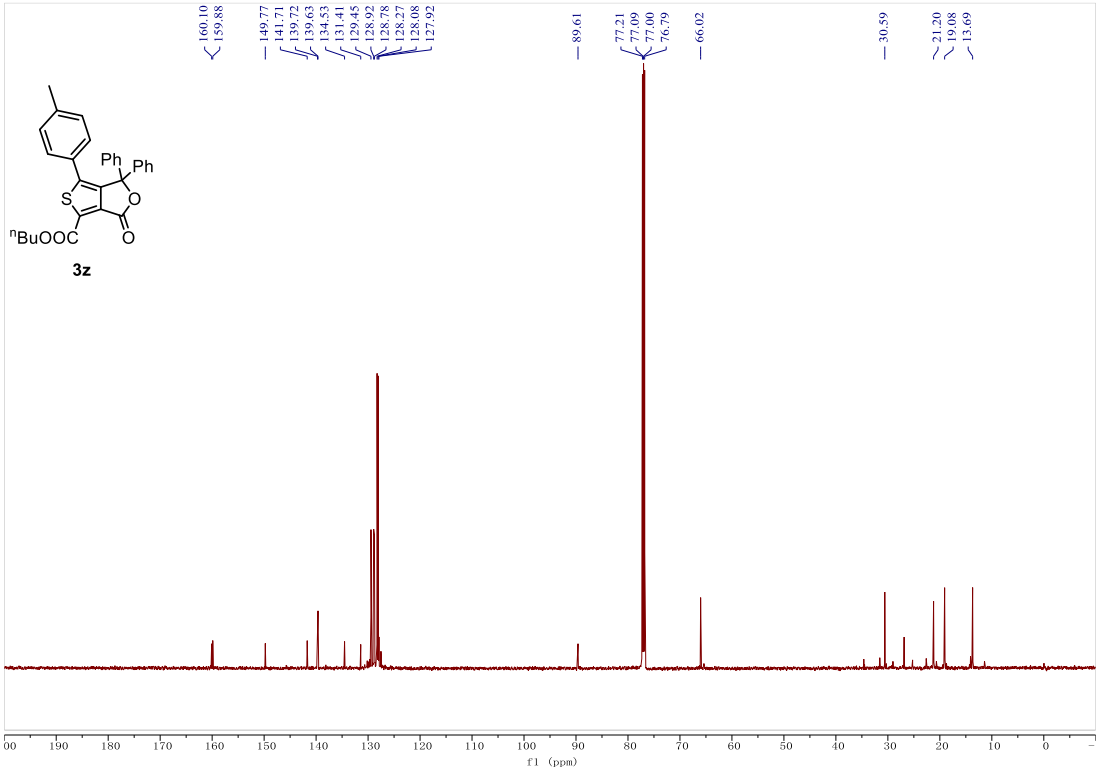
^{13}C NMR of compound **3y** (150 MHz, $CDCl_3$)



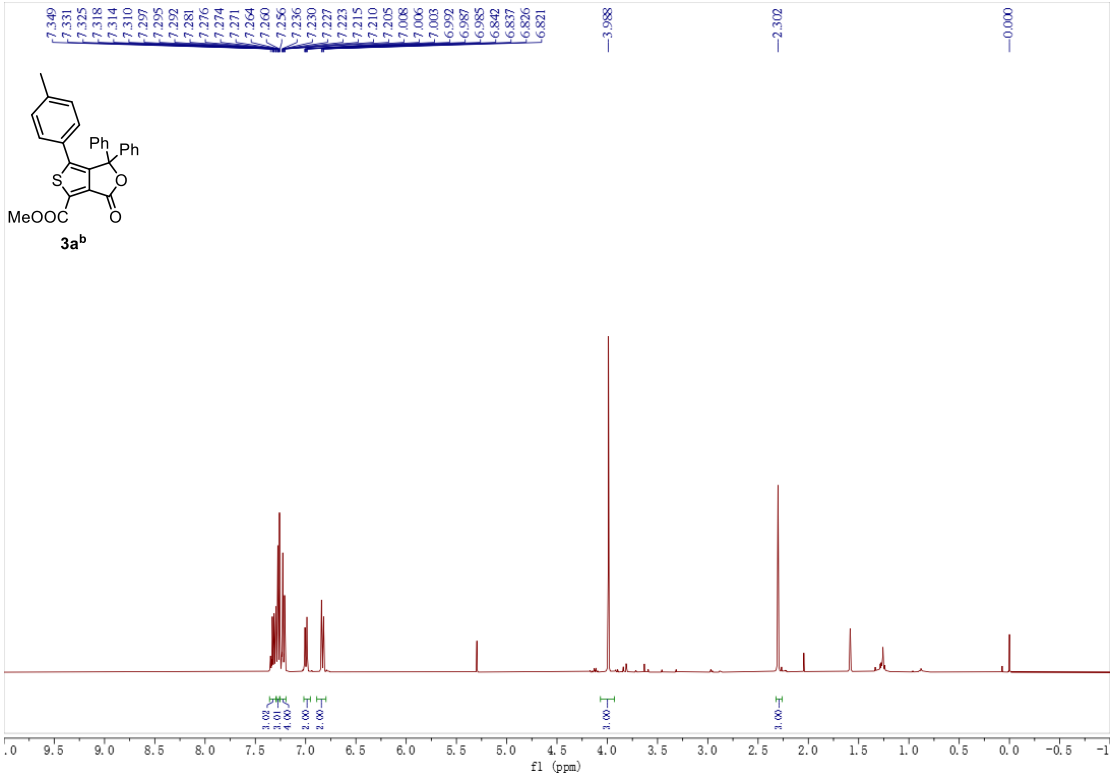
^{1}H NMR of compound **3z** (600 MHz, $CDCl_3$)



^{13}C NMR of compound **3z** (150 MHz, $CDCl_3$)



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



^{13}C NMR of compound **3a^{b}** (100 MHz, $CDCl_3$)