Catalytic (3 + 2) umpolung annulations of α-thioacyl carbenes with aryl isothiocyanates

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Note added after first publication: This supplementary information file replaces that originally published on 20 June 2022. There were some incorrect structures in the original version, which have been corrected in this updated version. The structure of compound **1x** on page S13 (at the end of Figure S1), page S17 (Scheme S10), page S18, page S33 (at the end of Scheme S11), and page S52 (on the ^{1}H and ^{13}C NMR spectra) has been corrected. The structure for compound **12** on page S132 (on the ^{1}H and ^{13}C NMR spectra) has also been corrected. This does not affect the conclusions in the paper.

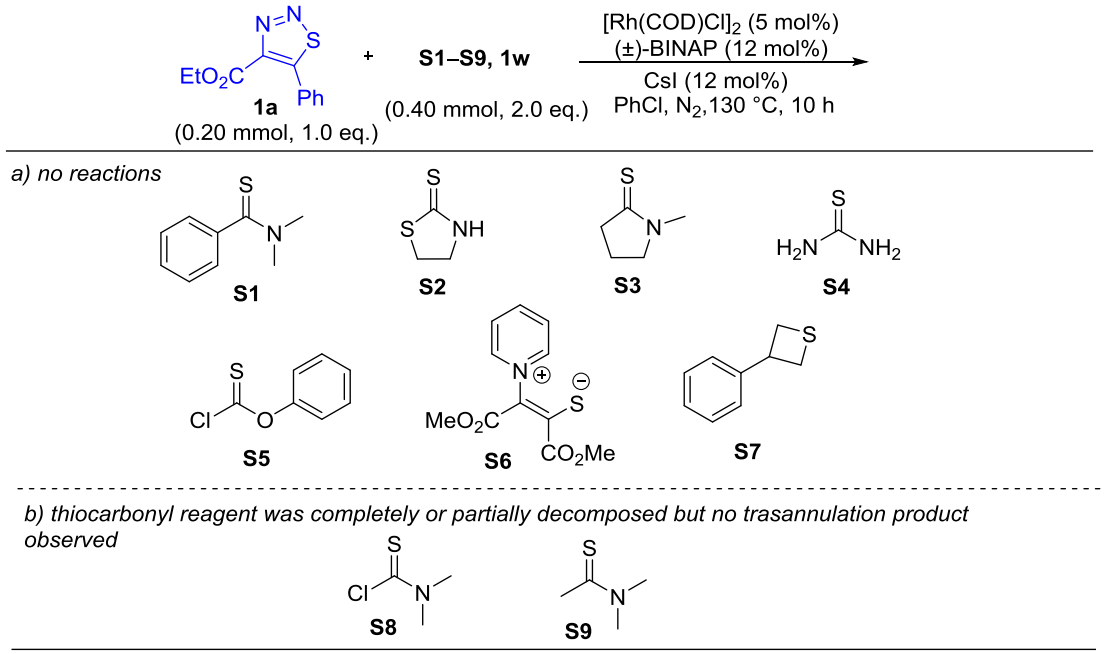
Content

1. General information

Unless otherwise noted, all materials were purchased from commercial suppliers. Chlorobenzene (PhCl) and perchloroethylene (PCE) were refluxed over CaH_2 prior to distillation; toluene (PhMe), xylenes and mesitylene was refluxed over sodium with benzophenone as indicator under nitrogen atmosphere prior to distillation; 1,2-dichlorobenzene (*o*-DCB), cumene, *tert*-butylbenzene (Ph^{t}Bu), and ethylbenzene (PhEt) was dried over anhydrous $CaCl_2$ and then filtered through silica gel. Column chromatography was performed using silica gal (normal phase, 200–300 mesh) from Yantai Xinnuo Chemical Co., Ltd., usually with petroleum ether (PE, bp 60–90 °C) and ethyl acetate (EA) as eluent. Reactions were monitored by thin-layer chromatography (TLC) on G254 silica gal plates (0.2 mm) from Yantai Xinnuo Chemical Co., Ltd. The plates were visualized by UV light. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker 400 MHz spectrometer with $CDCl_3$ as solvents and deuterated solvent residual peak or tetramethylsilane (TMS) as internal standard. Coupling constants (J) are reported in Hertz (Hz), and the chemical shifts (δ) were reported in parts per million (ppm). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), dd (double doublet), td (triple doublet), tt (triple triplet), m (multiplet), and br (broad). HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer or a Thermo scientific Q Exactive spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. X-ray diffraction data were collected on a Rigaku Gemin E diffractometer.

2. Unsuccessful transannulations of 1,2,3-thiadiazoles with thio- or thia- reagents

Scheme S1. Unsuccessful transannulations of 1,2,3-thiadiazole **1a** thio or thia reagents



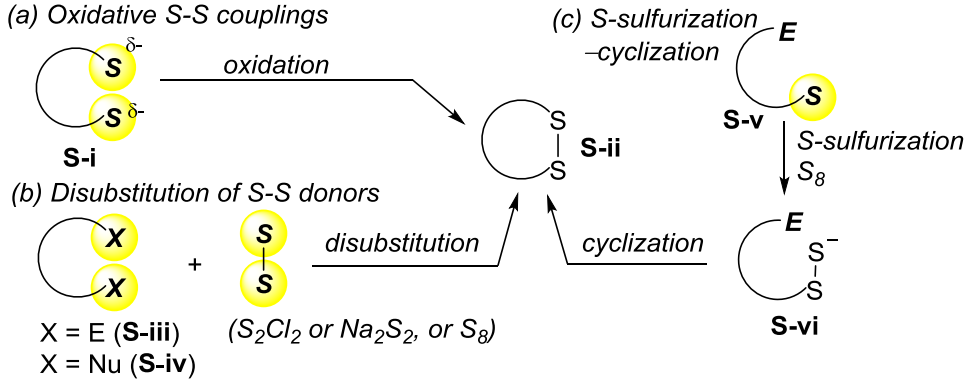
Compounds **S2**, **S4**, **S5**, **S8** and **S9** were purchased from commercial suppliers. *N*,*N*-dimethylbenzothioamide (**S1**) was obtained by Ohwada's procedure.[1] 1-Methylpyrrolidine-2-thione (**S3**) was obtained by Hussaini's procedure.[2] (*Z*)-1,4-dimethoxy-1,4-dioxo-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (**S6**) was obtained by Bazgir's procedure.[3] 3-Phenylthietane (**S7**) was obtained by Tan and Xu's procedure.[4]

3. Previous seminal work on synthesis of 3*H*-1,2-dithiol-3-imines and thiones

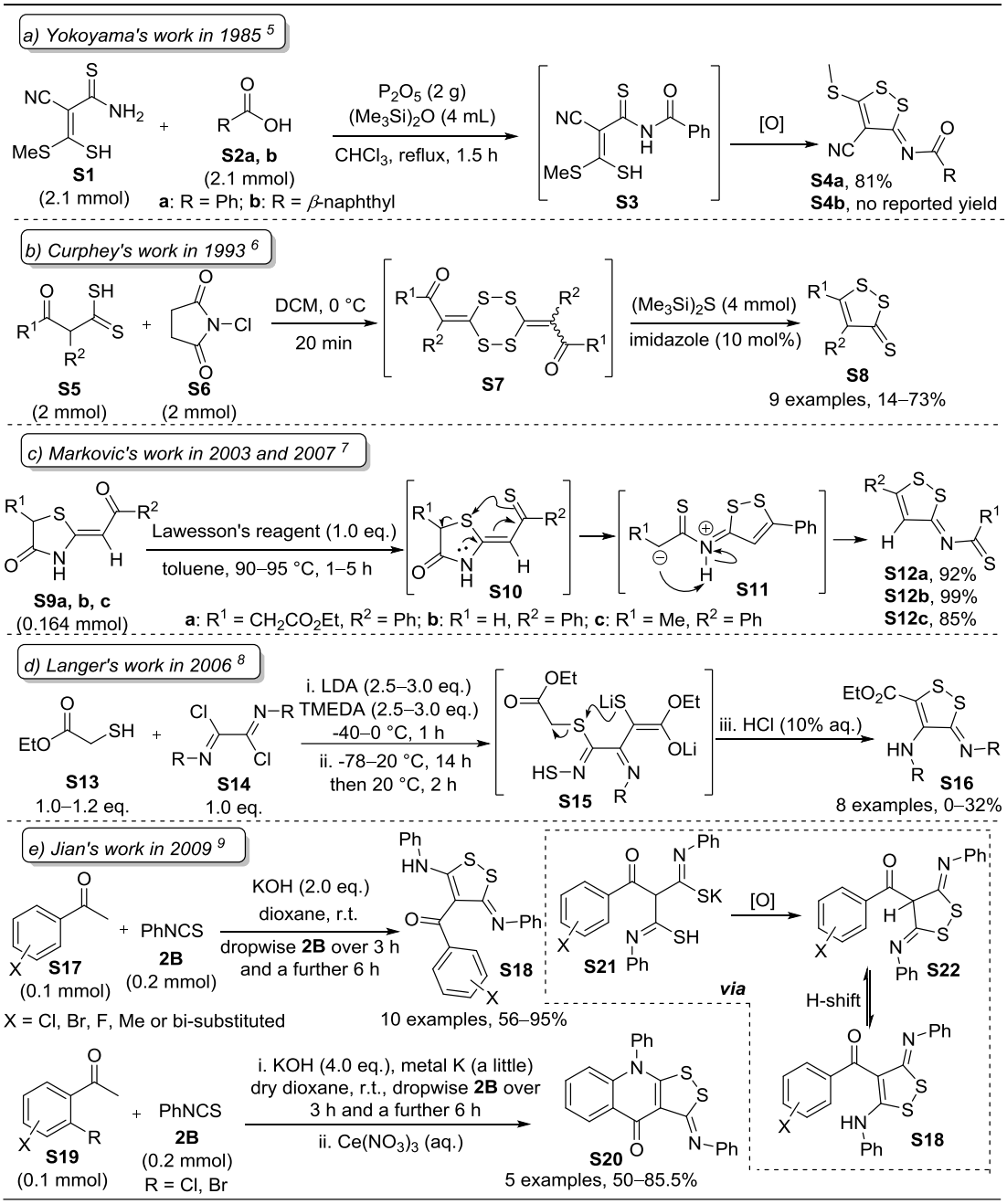
Previous syntheses of 3*H*-1,2-dithiol-3-imines and thiones were highly relied on three strategies (**Scheme S2**): (1) oxidative S–S coupling, [5-9] (2) disubstitution of S–S donors, [10-14] and (3) S-sulfurization–cyclization. [15–19]

In the *oxidative S–S coupling* strategy (**Scheme S2a, Scheme S3**), dithiols or their derivatives (**S-i**) with two nucleophilic sulfur terminals, which are always pre-prepared by several steps, are oxidized to cyclic disulfides (**S-ii**) following ionic or radical mechanisms. In the *disubstitution of S–S donor* strategy (**Scheme S2b, Scheme S4**), the practicable S–S donors include dielectrophilic disulfur dichloride (S_2Cl_2), dinucleophilic sodium disulfide (Na_2S_2), and reactivity-varying elemental sulfur (S_8). Their disubstitutions with electronically matched dinucleophiles (**S-iii**) or dielectrophiles (**S-iv**) give rise to cyclic disulfides (**S-ii**). In the *S-sulfurization–cyclization* strategy (**Scheme S2c, Scheme S5**), sulfur-terminated electrophiles (**S-v**), synthesized through multiple steps, are first sulfurized into disulfide anion (**S-vi**), which subsequently cyclized into cyclic disulfides (**S-ii**). The previously documented methods and strategies are plagued by disadvantages such as low functionality tolerance, unsatisfactorily controlled chemoselectivity, and low atom- and step-economy.

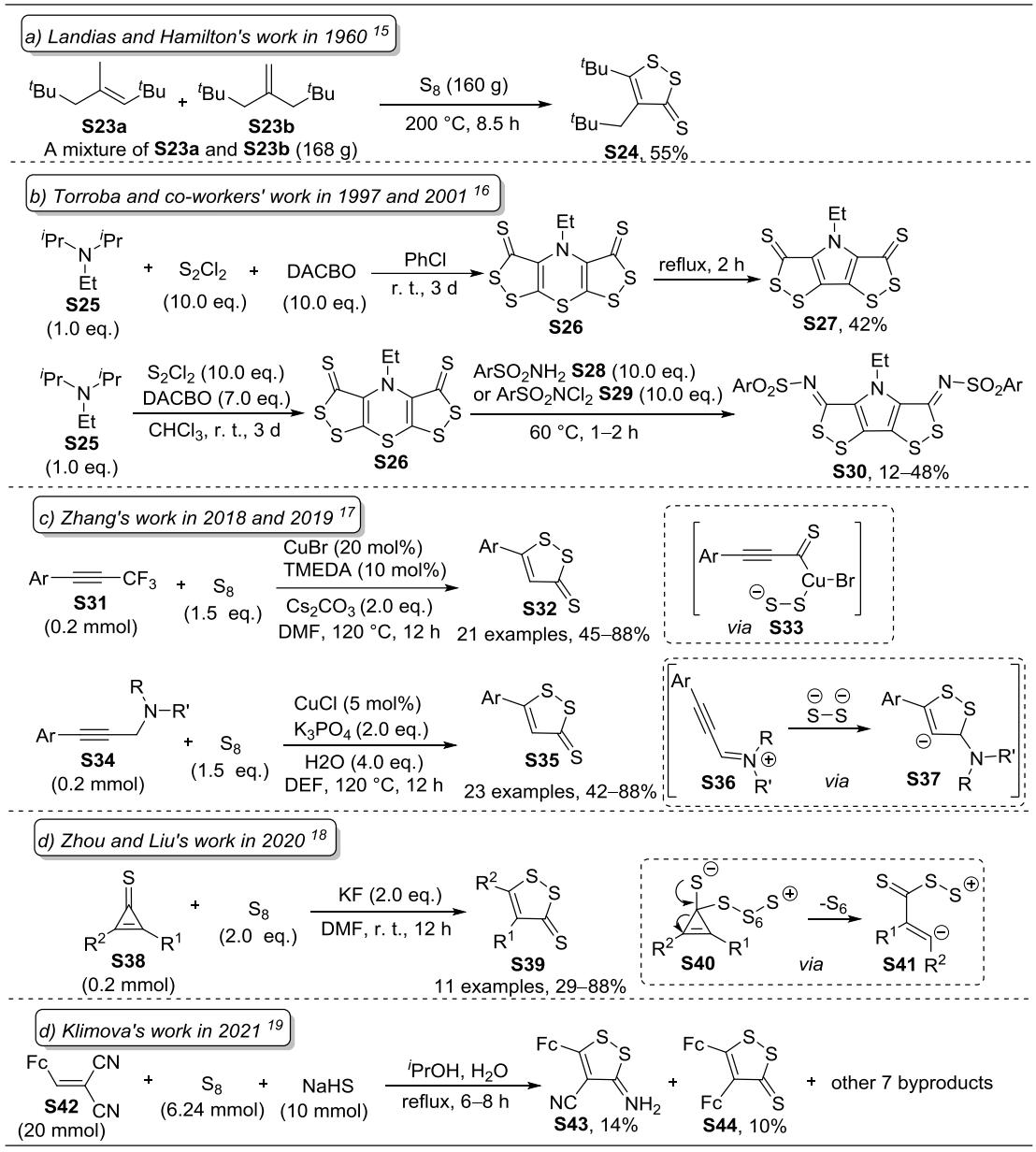
Scheme S2. Strategies for synthesis of 1,2-dithiacycles.



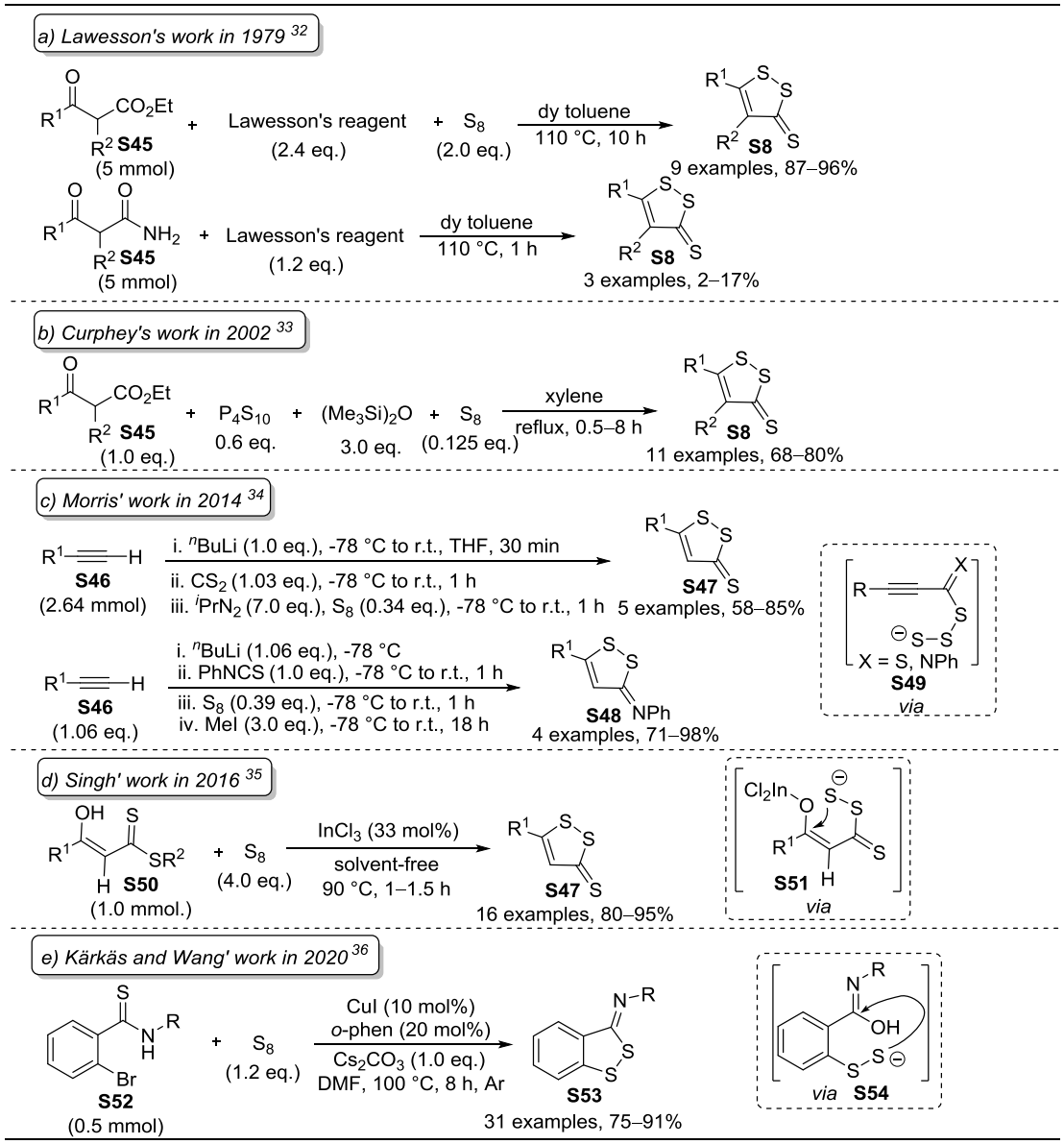
Scheme S3. Seminal work on synthesis of 3*H*-1,2-dithiol-3-imines and thiones featuring *oxidative S-S couplings*



Scheme S4. Seminal work on synthesis of 3*H*-1,2-dithiol-3-imines and thiones featuring *disubstitution of S-S donors*

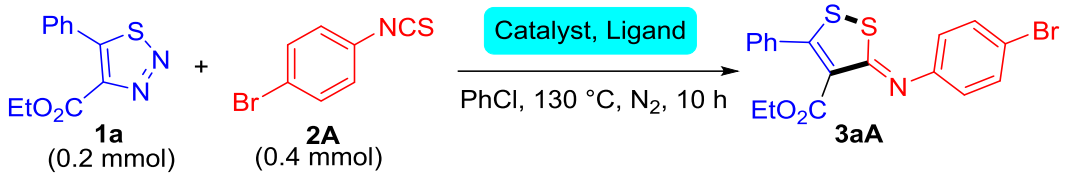


Scheme S5. Seminal work on synthesis of 3*H*-1,2-dithiol-3-imines and thiones featuring *S-sulfurization–cyclization*



4. Optimization studies

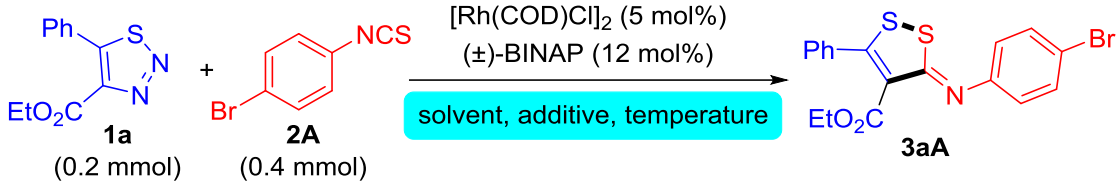
Table S1. Optimization of catalysts and ligands



entry	catalyst (mol%)	ligand (mol%)	yield (%)[b]
1	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	21
2	$[Rh(COD)Cl]_2$ (5)	—	0
3	$[Rh(COD)Cl]_2$ (5)	DPEPhos (12)	9
4	$[Rh(COD)Cl]_2$ (5)	DPPP (12)	13
5	$[Rh(COD)Cl]_2$ (5)	DPPB (12)	18
6	$[Rh(COD)Cl]_2$ (5)	(±)-BINAP (12)	51
7	$[Rh(COD)Cl]_2$ (5)	DPPBz (12)	0
8	$[Rh(COD)Cl]_2$ (5)	DPPPenta (12)	0
9	$[Rh(COD)Cl]_2$ (5)	XantPhos (12)	0
10	$[Rh(COD)Cl]_2$ (5)	PPh_3 (24)	0
11	$Rh(PPh_3)_3Cl$ (10)	(±)-BINAP (12)	34
12	$[Rh^*CpCl_2]_2$ (5)	(±)-BINAP (12)	11
13	$[Rh(CO)_2Cl]_2$ (5)	(±)-BINAP (12)	21
14	$Rh(CO)_2(acac)$ (10)	(±)-BINAP (12)	9
15	$[Ir(COD)Cl]_2$ (5)	(±)-BINAP (12)	0
16	$[Ir^*CpCl_2]_2$ (5)	(±)-BINAP (12)	0
17	$Rh_2(OAc)_4$ (5)	(±)-BINAP (12)	8
18	$Rh_2(Oct)_4$ (5)	(±)-BINAP (12)	10

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2A** (0.4 mmol, 2.0 equiv.), catalyst (5–10 mol%) and ligand (12–24 mol%) were used at 130 °C for 10 h in chlorobenzene (2 mL) under N_2 atmosphere. [b]The yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene (2/3 equiv.) as an internal standard.

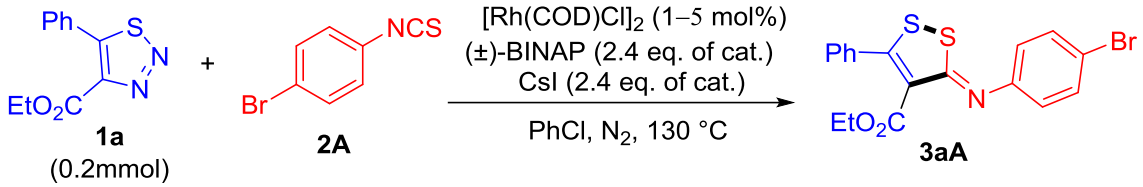
Table S2. Optimization of additives and solvents



entry	additive (mol%)	solvent	Temperature (°C)	yield (%)[b]
1	$AgBF_4$ (12)	PhCl	130	0
2	$AgSbF_6$ (12)	PhCl	130	26
3	CF_3SO_3Ag (12)	PhCl	130	0
4	$(CF_3SO_2)_2NAg$ (12)	PhCl	130	0
5	$NaBAr_F$ (12)	PhCl	130	0
6	CsI (12)	PhCl	130	55
7	NaI (12)	PhCl	130	34
8	KI (12)	PhCl	130	54
9	CsI (24)	PhCl	130	46
10	CsI (36)	PhCl	130	44
11	CsI (48)	PhCl	130	48
12	CsI (12)	toluene	110	32
13	CsI (12)	xylenes	130	47
14	CsI (12)	mesitylene	130	30
15	CsI (12)	PCE	120	51
16	CsI (12)	*o*-DCB	130	44
17	CsI (12)	cumene	130	38
18	CsI (12)	Ph^{t}Bu	130	32
19	CsI (12)	PhEt	130	0

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2A** (0.4 mmol, 2.0 equiv.), $[Rh(COD)Cl]_2$ (5 mol%), (±)-BINAP (12 mol%) and additive (12–48 mol%) were used at 130 °C for 10 h in solvent (2 mL) under N_2 atmosphere. [b]The yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene (2/3 equiv.) as an internal standard.

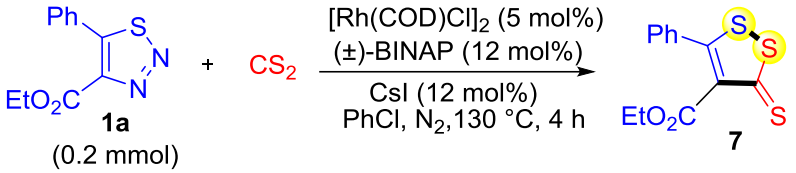
Table S3. Optimization of other conditions



entry	**1a**/**2A**	$[Rh(COD)Cl]_2$ (mol%)	Time	yield (%)[b]
1	1:3	5	10 h	19
2	1:1.5	5	10 h	63
3	1:1.2	5	10 h	84
4	1:1	5	10 h	79
5	1:0.8	5	10 h	99
6	1:0.5	5	10 h	98
7	1:0.8	5	15 min	99 (95[c])
8	1:0.8	2.5	15 min	23
9	1:0.8	1	15 min	0

[a]Reaction conditions: **1a** (0.20 mmol, 1.0 equiv.), **2A** (0.16–0.60 mmol, 0.8–3.0 equiv.), $[Rh(COD)Cl]_2$ (1–5 mol%), (±)-BINAP (2.4–12 mol%) and CsI (2.4–12 mol%) were used at 130 °C in chlorobenzene (2 mL) under N_2 atmosphere. [b]The yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene (2/3 equiv.) as an internal standard. The yields were based on the amount of **1a** in entry 1–4, while yields were based on the amount of **2A** in entry 5–9. [c]Isolated yields after column chromatography.

Table S4. Simple optimization of the transannulation of thiadiazole **1a** and CS_2



entry	CS_2 (equiv.)	yield (%)[b]
1	1.0	6
2	2.0	28
3	4.0	29
4	6.0	42 (44[c])
5	8.0	38
6	10.0	35

[a]Reaction conditions: **1a** (0.20 mmol, 1.0 equiv.), CS_2 (0.20–2.00 mmol, 1.0–10.0 equiv.), $[Rh(COD)Cl]_2$ (5 mol%), (±)-BINAP (12 mol%) and CsI (12 mol%) were used at 130 °C for 4 h in chlorobenzene (2 mL) under N_2 atmosphere. [b]The yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene (2/3 equiv.) as an internal standard. [c]Isolated yields after column chromatography.

5. Experimental procedures for synthesis of thiadiazoles 1

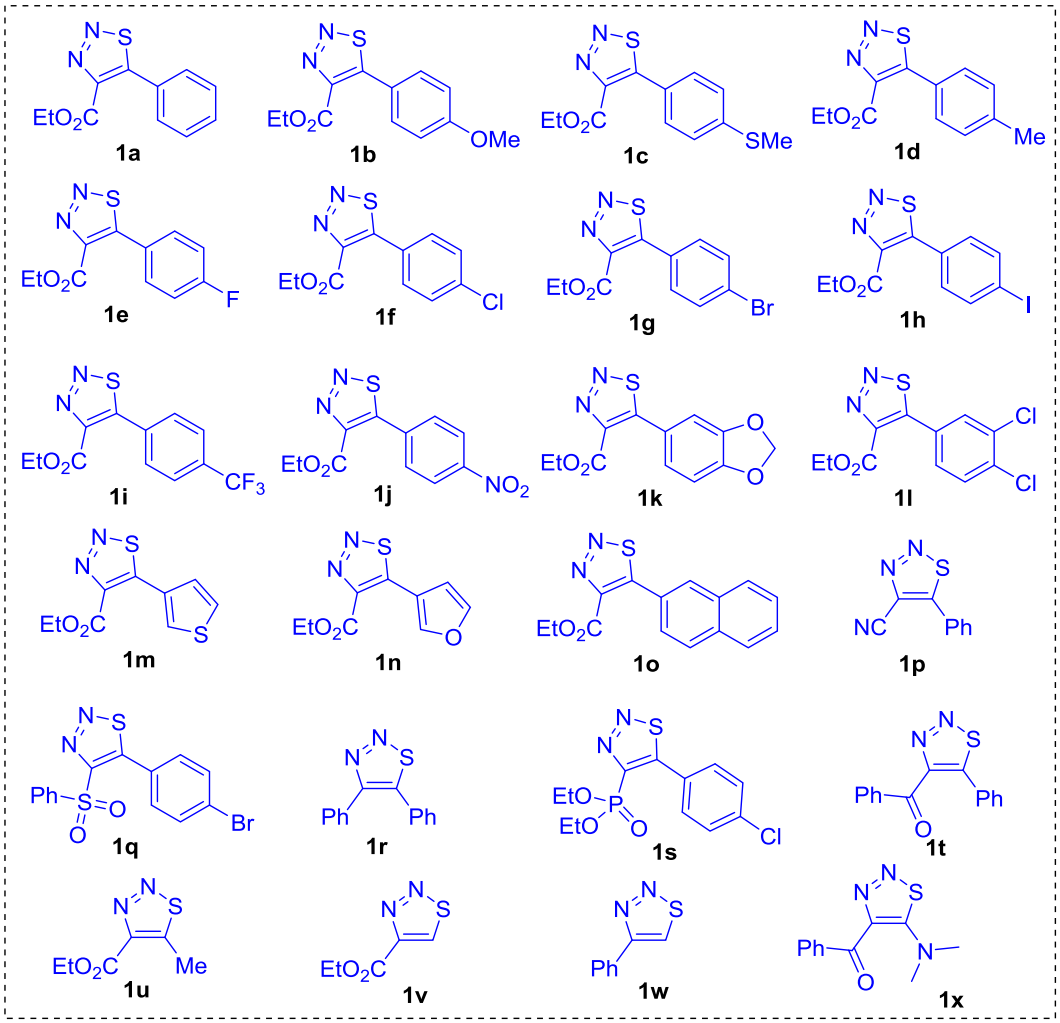
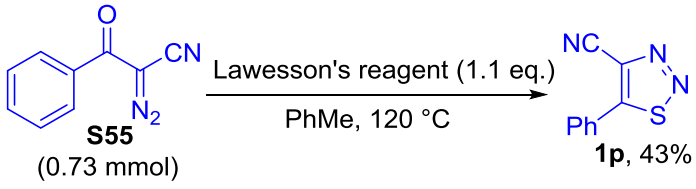


Figure S1. The structural formula and identifier of thiadiazoles used in this article

Except **1p**, **1q**, **1s**, **1t** and **1x**, all the thiadiazoles are known compounds and were synthesized by reported procedures [20] which were summarized in the electronic supplementary information of *ref.20f*.

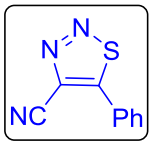
Scheme S6. Synthesis of 5-phenyl-1,2,3-thiadiazole-4-carbonitrile (**1p**)



To a 10 mL-heavy-walled pressure tube equipped with a magnetic stirring bar was added 2-diazo-3-oxo-3-phenylpropanenitrile [21] (**S55**) (125 mg, 0.73 mmol, 1.0 eq.),

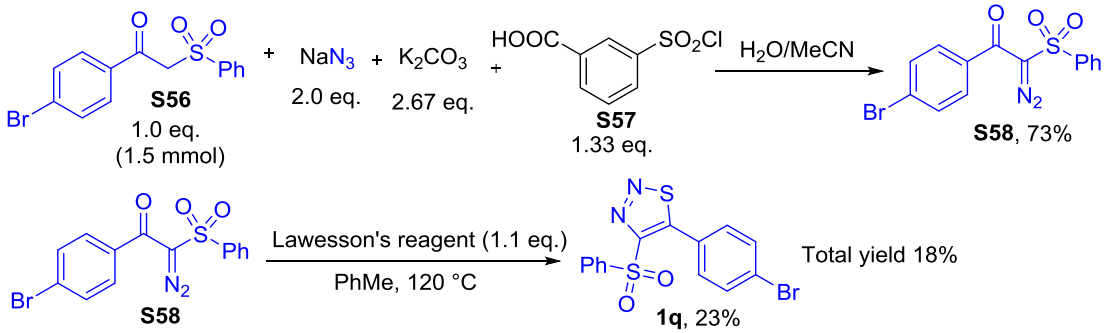
Lawesson's reagent (324 mg, 0.80 mmol, 1.1 eq.) and toluene (4 mL). The tube was sealed and stirred at 120 ºC (oil bath) for 6 h. Then, after cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded the 5-phenyl-1,2,3-thiadiazole-4-carbonitrile (**1p**) in 43% yield.

5-phenyl-1,2,3-thiadiazole-4-carbonitrile (**1p**)



Brownish yellow crystals, 59 mg, yield 43%, mp 52–53 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80–7.77 (m, 2H), 7.64–7.55 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.3, 132.6, 130.5, 130.1, 128.9, 124.5, 112.2. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_9H_6N_3S^+$ 188.0277, found 188.0281.

Scheme S7. Synthesis of 5-(4-bromophenyl)-4-(phenylsulfonyl)-1,2,3-thiadiazole (**1q**)



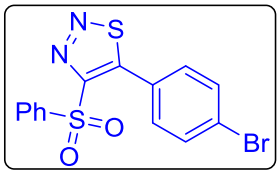
Note: The crude diazo compound **S58** was prepared according to Krasavin's procedure.[21]

To a solution of sodium azide (195 mg, 3 mmol, 2.0 eq.) and potassium carbonate (552 mg, 4 mmol, 2.67 eq.) in water (4 mL) and acetonitrile (2 mL) was added 3-(chlorosulfonyl)benzoic acid (**S57**) (441 mg, 2 mmol, 1.33 eq.) and 1-(4-bromophenyl)-2-(phenylsulfonyl)ethan-1-one [22] (**S56**) (509 mg, 1.5 mmol, 1.0 eq.). The mixture was stirred vigorously at room temperature overnight and then extracted with chloroform (4 mL × 3). The combined organic layers dried over anhydrous calcium chloride. After filteration and removing the solvent in vacuum, the residue was purified by column

chromatography on silica gel afforded the crude product 1-(4-bromophenyl)-2-diazo-2-(phenylsulfonyl)ethan-1-one (**S58**) as yellow solid in 73% yield.

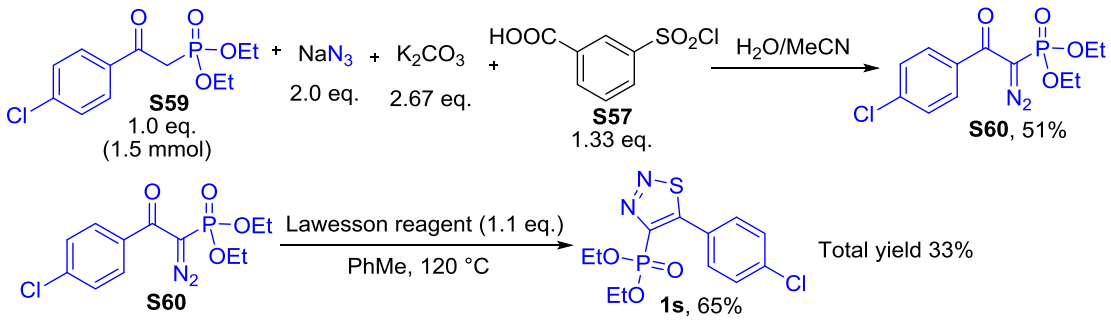
To a 10 mL-heavy-walled pressure tube equipped with a magnetic stirring bar was added crude 1-(4-bromophenyl)-2-diazo-2-(phenylsulfonyl)ethan-1-one (**S58**) (398 mg, 1.09 mmol, 1.0 eq.), Lawesson's reagent (485 mg, 1.2 mmol, 1.1 eq.) and toluene (4 mL). The tube was sealed and stirred at 120 ºC (oil bath) for 6 h. Then, after cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded the 5-(4-bromophenyl)-4-(phenylsulfonyl)-1,2,3-thiadiazole (**1q**) in 23% yield.

5-(4-bromophenyl)-4-(phenylsulfonyl)-1,2,3-thiadiazole (**1q**)



White crystals, 167 mg, yield 18% over two steps, mp 123–125 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (dd, J = 8.5, 1.4 Hz, 2H), 7.70–7.61 (m, 3H), 7.53 (t, J = 7.8 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.9, 156.7, 139.8, 134.6, 132.2, 131.7, 129.4, 128.8, 126.2, 123.2. **HRMS** (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{10}BrN_2O_2S_2^+$ 380.9362, found 380.9358.

Scheme S8. Synthesis of diethyl (5-(4-chlorophenyl)-1,2,3-thiadiazol-4-yl)phosphonate (**1s**)

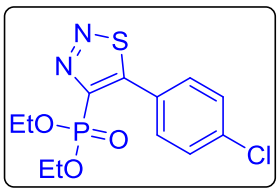


Note: The crude diazo compound **S60** was prepared according to Krasavin's procedure.[21]

To a solution of sodium azide (195 mg, 3 mmol, 2.0 eq.) and potassium carbonate (552 mg, 4 mmol, 2.67 eq.) in water (4 mL) and acetonitrile (2 mL) was added 3-(chlorosulfonyl)benzoic acid (**S57**) (441 mg, 2 mmol, 1.33 eq.) and diethyl (2-(4-chlorophenyl)-2-oxoethyl)phosphonate [23] (**S59**) (436 mg, 1.5 mmol, 1.0 eq.). The mixture was stirred vigorously at room temperature overnight and then extracted with chloroform (4 mL × 3). The combined organic layers dried over anhydrous calcium chloride. After filteration and removing the solvent in vacuum, the residue was purified by column chromatography on silica gel afforded the crude product diethyl (2-(4-chlorophenyl)-1-diazo-2-oxoethyl)phosphonate (**S60**) as light yellow liquid in 51% yield.

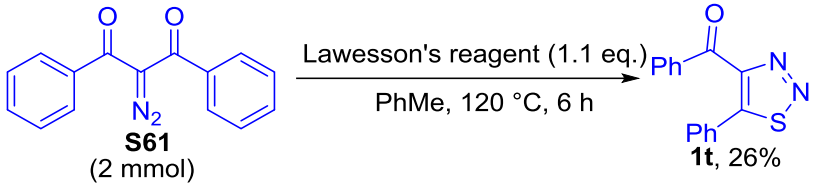
To a 10 mL-heavy-walled pressure tube equipped with a magnetic stirring bar was added crude diethyl (2-(4-chlorophenyl)-1-diazo-2-oxoethyl)phosphonate (**S60**) (240 mg, 0.76 mmol, 1.0 eq.), Lawesson's reagent (340 mg, 0.84 mmol, 1.1 eq.) and toluene (4 mL). The tube was sealed and stirred at 120 ºC (oil bath) for 6 h. Then, after cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded the diethyl (5-(4-chlorophenyl)-1,2,3-thiadiazol-4-yl)phosphonate (**1s**) in 65% yield.

Diethyl (5-(4-chlorophenyl)-1,2,3-thiadiazol-4-yl)phosphonate (**1s**)



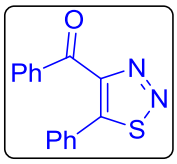
Light brownish red oil, 164 mg, yield 33% over two steps, R_f = 0.60 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 4.29–4.15 (m, 4H), 1.22 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.2 (d, $J_{C\text{-}P}$ = 25.9 Hz), 154.3 (d, $J_{C\text{-}P}$ = 184.5 Hz), 136.9, 131.3, 129.0, 125.1, 64.1 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.0 (d, $J_{C\text{-}P}$ = 7.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 67.84. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{12}H_{14}ClKN_2O_3PS^+$ 370.9783, found 370.9794.

Scheme S9. Synthesis of phenyl(5-phenyl-1,2,3-thiadiazol-4-yl)methanone (**1t**)



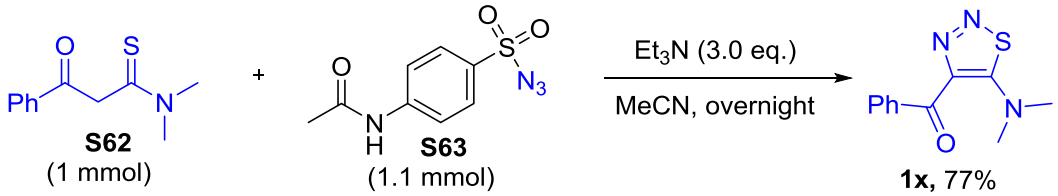
To a 10 mL-heavy-walled pressure tube equipped with a magnetic stirring bar was added 2-diazo-1,3-diphenylpropane-1,3-dione [24] (**S61**) (500 mg, 2.0 mmol, 1.0 eq.), Lawesson's reagent (890 mg, 2.2 mmol, 1.1 eq.) and toluene (6 mL). The tube was sealed and stirred at 120 ºC (oil bath) for 6 h. Then, after cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded the phenyl(5-phenyl-1,2,3-thiadiazol-4-yl)methanone (**1t**) in 26% yield.

Phenyl(5-phenyl-1,2,3-thiadiazol-4-yl)methanone (**1t**)



Tan solid, 136 mg, yield 26%, mp 69–72 ºC, R_f = 0.60 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06–7.99 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.56–7.38 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 187.6, 160.8, 155.0, 136.9, 134.1, 130.8, 130.7, 129.7, 129.1, 128.6, 126.4. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{10}N_2NaOS^+$ 289.0406, found 289.0403.

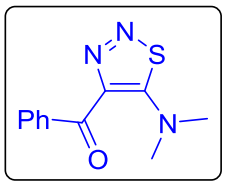
Scheme S10. Synthesis of (5-(dimethylamino)-1,2,3-thiadiazol-4-yl)(phenyl)methanone (**1x**)



To a 25 mL-flask equipped with a magnetic stirring bar was added *N*,*N*-dimethyl-3-oxo-3-phenylpropanethioamide [25] (**S62**) (207 mg, 1.0 mmol, 1.0 eq.), 4-acetamidobenzenesulfonyl azide (**S63**) (264 mg, 1.1 mmol, 1.1 eq.), MeCN (10 mL), and Et_3N (0.46 mL, 3.0 eq.), successively. The flask was sealed and stirred at room

temperature overnight and monitored by TLC. After the reaction completion, filtered through celite and removed the volatiles in vacuum. The residue was purified by column chromatography on silica gel afforded the (4-(dimethylamino)-1,2,3-thiadiazol-5-yl)(phenyl)methanone (**1x**) in 77% yield.

(5-(dimethylamino)-1,2,3-thiadiazol-4-yl)(phenyl)methanone (**1x**)



Yellow crystals, 180 mg, yield 77%, mp 54–55 ºC, R_f = 0.15 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 3.19 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 186.7, 173.0, 141.2, 138.9, 132.9, 130.6, 128.2, 47.2. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{12}N_3OS^+$ 234.0696, found 234.0699.

6. Experimental procedures for synthesis of isothiocyantes 2

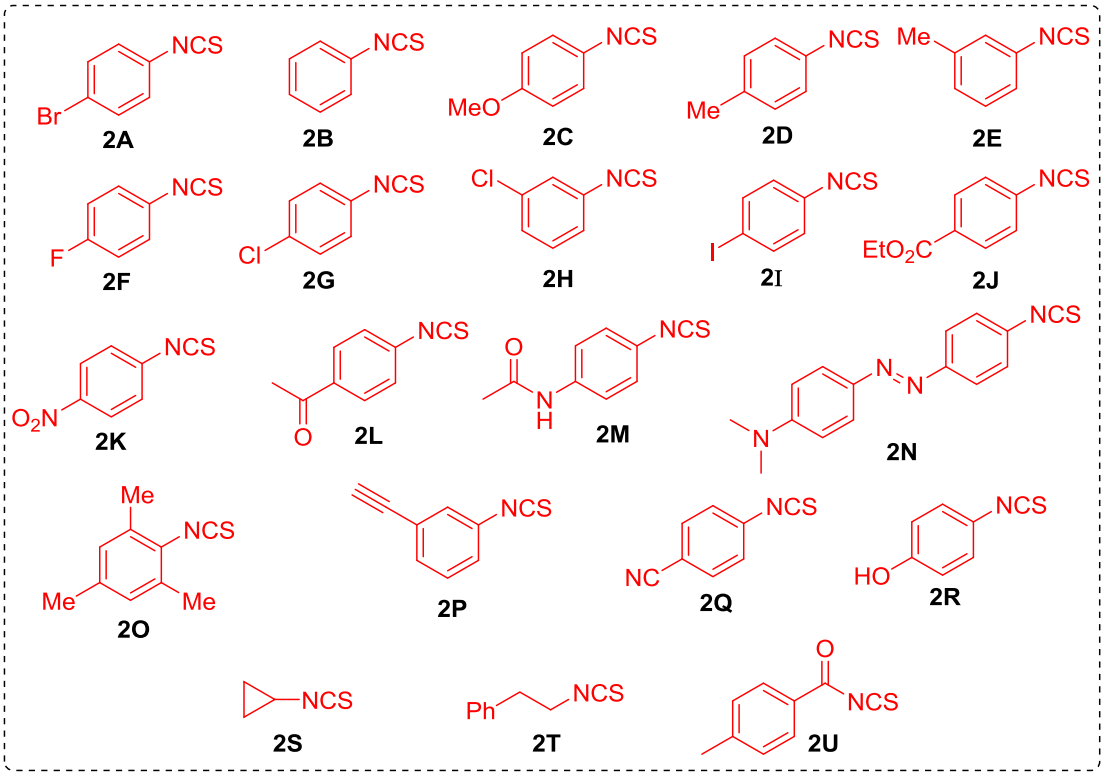


Figure S2. The structural formula and identifier of isothiocyantes used in this article

All the isothiocyantes are known compounds. Isothiocyantes **2K** and **2N** were

purchased from commercial suppliers. Isothiocyantes **2A–2D**, **2G**, **2H**, **2J**, **2O**, **2P**, and **2T** were obtained by our previous procedure. [26] Isothiocyantes **2E**, **2F** and **2Q** were obtained by Lin and Xiao's procedure. [27] Isothiocyante **2I** was obtained by Chen and Sun's procedure. [28] Isothiocyante **2L** was obtained by Zhang's procedure. [29] Isothiocyante **2M** was obtained by Boas' procedure. [30] Isothiocyantes **2R** were obtained by Xu' procedure. [31] Isothiocyante **2S** was obtained by Decker's procedure. [32] Isothiocyante **2U** was obtained by Patel's procedure. [33]

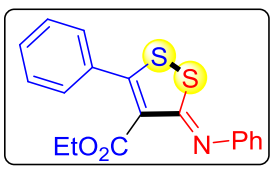
7. Experimental procedure for the reaction of thiadiazoles 1 and isothiocyantes 2

General procedure

An oven-dried 10 mL-reaction tube equipped with a magnetic stirring bar was charged with thiadiazole **1** (0.200 mmol, 1.0 equiv.), isothiocyante **2** (0.16 mmol, 0.800 equiv.), $[Rh(COD)Cl]_2$ (5 mg, 0.010 mmol, 0.05 equiv.), (±)-BINAP (15 mg, 0.024 mmol, 0.12 equiv.) and CsI (6 mg, 0.024 mmol, 0.12 equiv.). The tube was sealed immediately and protected with a nitrogen balloon after evacuation-backfill operations for three times. Then chlorobenzene (2 mL) was injected to the tube via a syringe. The reaction mixture was allowed to stir at 130 °C (pre-heated metal module), and the progress of the reaction was monitored by TLC. When isothiocyante **2** was completely consumed, the reaction mixture was immediately dropped to room temperature and directly subjected to column chromatography on silica gel. Further purified column chromatography on silica gel to afforded the corresponding product **3**.

7.1 Analytic data of products for scope of 1,2,3-thiadiazoles

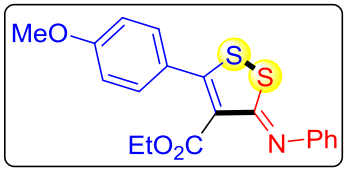
Ethyl (*Z*)-5-phenyl-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3aB**)



Prepared by general procedure and reacted for 5 min. Yellow crystals, 50 mg, yield 92%, mp 98–100 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55–7.36 (m, 7H),

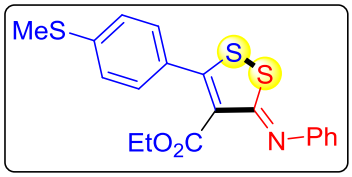
7.16 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.2 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 166.6, 164.2, 161.8, 151.7, 132.3, 131.0, 129.8, 129.1, 127.8, 127.3, 125.2, 112.0, 62.1, 13.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{16}NO_2S_2^+$ 342.0617, found 342.0612.

Ethyl (*Z*)-5-(4-methoxyphenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3bB**)



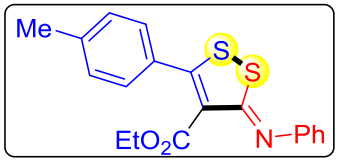
Prepared by general procedure and reacted for 20 h (isothiocyante **2B** was not completely consumed). Yellow crystals, 44 mg, yield 74%, mp 104–106 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.48 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 166.8, 164.6, 161.8, 161.5, 151.7, 129.8, 129.3, 126.3, 125.1, 124.4, 120.0, 114.5, 62.2, 55.6, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{18}NO_3S_2^+$ 372.0723, found 372.0718.

Ethyl (*Z*)-5-(4-(methylthio)phenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3cB**)



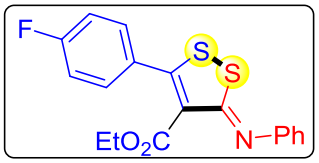
Prepared by general procedure and reacted for 5 min. Yellow crystals, 60 mg, yield 97%, mp 93–95 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.43 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.15 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.08 (dd, J = 8.4, 1.3 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 2.50 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 166.6, 164.3, 161.0, 151.6, 143.2, 129.8, 128.3, 128.0, 126.8, 125.9, 125.2, 119.9, 62.2, 15.1, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{18}NO_2S_3^+$ 388.0494, found 388.0487.

Ethyl (*Z*)-3-(phenylimino)-5-(*p*-tolyl)-3*H*-1,2-dithiole-4-carboxylate (**3dB**)



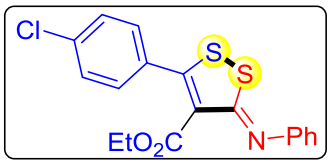
Prepared by general procedure and reacted for 5 min. Yellow crystals, 54 mg, yield 95%, mp 109–111 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42–7.36 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.4 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.8, 164.4, 161.8, 151.7, 141.5, 129.8, 129.3, 127.7, 126.8, 125.2, 112.0, 62.1, 21.6, 13.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{18}NO_2S_2^+$ 356.0773, found 356.0767.

Ethyl (*Z*)-5-(4-fluorophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3eB**)



Prepared by general procedure and reacted for 5 min. Yellow crystals, 54 mg, yield 94%, mp 78–80 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.20–7.06 (m, 5H), 4.22 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.2, 164.2 (d, $J_{C\text{-}F}$ = 252.5 Hz), 163.0, 160.3, 151.5, 130.0 (d, $J_{C\text{-}F}$ = 9.1 Hz), 129.8, 128.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.5, 125.3, 119.9, 116.3 (d, $J_{C\text{-}F}$ = 22.2 Hz), 62.2, 13.9. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -108.38. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}FNO_2S_2^+$ 360.0523, found 360.0517.

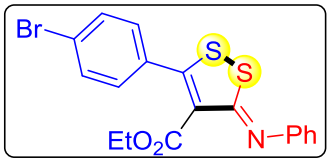
Ethyl (*Z*)-5-(4-chlorophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3fB**)



Prepared by general procedure and reacted for 5 min. Yellow crystals, 60 mg, yield 99%, mp 105–107 ºC, R_f = 0.30 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50–7.35 (m, 6H), 7.16 (tt, J = 7.3, 1.2 Hz, 1H), 7.09 (dd, J = 8.5, 1.2 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.2, 163.9, 160.1, 151.5, 137.2, 130.6, 129.8, 129.4, 129.2, 127.7, 125.3, 119.8, 62.2, 14.0.

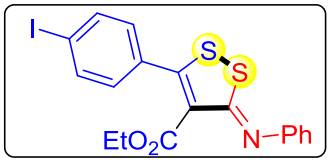
HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}ClNO_2S_2^+$ 376.0227, found 376.0222.

Ethyl (*Z*)-5-(4-bromophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3gB**)



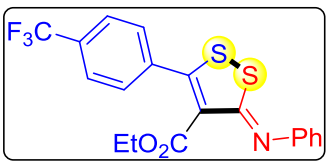
Prepared by general procedure and reacted for 5 min. Yellow crystals, 67 mg, yield 99%, mp 118–120 ºC, R_f = 0.60 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.58 (d, *J* = 8.5 Hz, 2H), 7.41–7.37 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 166.1, 163.9, 160.1, 151.4, 132.3, 131.1, 129.8, 129.3, 127.7, 125.5, 125.4, 119.8, 62.3, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}BrNO_2S_2^+$ 419.9722, found 419.9716.

Ethyl (*Z*)-5-(4-iodophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3hB**)



Prepared by general procedure and reacted for 15 min. Yellow crystals, 69 mg, yield 93%, mp 111–113 ºC, R_f = 0.55 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.78 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 166.1, 163.9, 160.2, 151.4, 138.3, 131.6, 129.8, 129.3, 127.6, 125.3, 119.8, 97.5, 62.3, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}INO_2S_2^+$ 467.9583, found 467.9580.

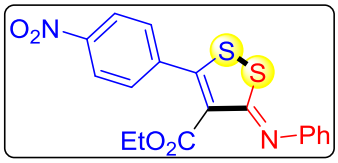
Ethyl (*Z*)-3-(phenylimino)-5-(4-(trifluoromethyl)phenyl)-3*H*-1,2-dithiole-4-carboxylate (**3iB**)



Prepared by general procedure and reacted for 5 min. Yellow crystals, 65 mg, yield 99%, mp 82–84 ºC, R_f = 0.45 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.43–7.38 (m, 2H), 7.17 (tt, *J* = 7.2, 1.2 Hz,

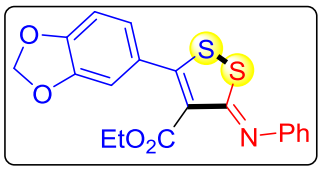
1H), 7.10 (dd, J = 8.4, 1.3 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.10 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.9, 163.6, 159.7, 151.4, 135.8, 132.8 (q, $J_{C\text{-}F}$ = 33.3 Hz), 129.9, 128.4, 126.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.5, 123.6 (q, $J_{C\text{-}F}$ = 273.6 Hz), 119.8, 62.3, 13.9. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.99. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{15}F_3NO_2S_2^+$ 410.0491, found 410.0485.

Ethyl (*Z*)-5-(4-nitrophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3jB**)



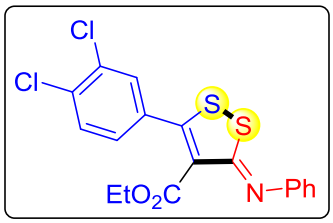
Prepared by general procedure and reacted for 5 min. Yellow crystals, 56 mg, yield 91%, mp 94–96 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.41 (t, J = 7.9 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.3 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.4, 163.4, 158.5, 151.3, 149.1, 138.4, 129.9, 129.2, 129.0, 125.6, 124.2, 119.7, 62.5, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}N_2O_4S_2^+$ 387.0468, found 387.0464.

Ethyl (*Z*)-5-(benzo[*d*][1,3]dioxol-5-yl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3kB**)



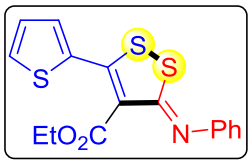
Prepared by general procedure and reacted for 5 min. Yellow crystals, 58 mg, yield 94%, mp 86–88 ºC, R_f = 0.35 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (t, J = 7.8 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.12–7.02 (m, 3H), 7.00 (d, J = 1.8 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.03 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.5, 164.4, 160.9, 151.5, 150.0, 148.3, 129.7, 126.7, 125.7, 125.2, 122.3, 119.9, 108.8, 108.1, 101.9, 62.2, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{16}NO_4S_2^+$ 386.0515, found 387.0507.

Ethyl (*Z*)-5-(3,4-dichlorophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3lB**)



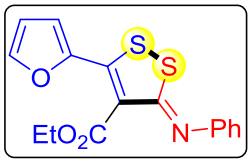
Prepared by general procedure and reacted for 5 min. Yellow crystals, 62 mg, yield 94%, mp 121–123 ºC, R_f = 0.60 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, J = 2.2 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.44–7.32 (m, 3H), 7.17 (tt, J = 7.2, 1.2 Hz, 1H), 7.08 (dd, J = 8.4, 1.2 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.7, 163.6, 158.3, 151.3, 135.4, 133.5, 131.9, 131.1, 129.8, 129.7, 128.3, 127.1, 125.5, 119.8, 62.4, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{14}Cl_2NO_2S_2^+$ 409.9838, found 409.9833.

Ethyl (*Z*)-3-(phenylimino)-5-(thiophen-2-yl)-3*H*-1,2-dithiole-4-carboxylate (**3mB**)



Prepared by general procedure and reacted for 5 min. Yellow crystals, 51 mg, yield 92%, mp 77–79 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (dd, J = 5.1, 1.2 Hz, 1H), 7.43 (dd, J = 3.7, 1.2 Hz, 1H), 7.42–7.35 (m, 2H), 7.16 (tt, J = 7.4, 1.2 Hz, 1H), 7.11 (dd, J = 5.1, 3.8 Hz, 1H), 7.09 (dd, J = 8.4, 1.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.1, 164.5, 152.2, 151.4, 132.6, 130.0, 129.8, 129.4, 128.3, 126.4, 125.3, 120.0, 62.6, 14.1. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{14}NO_2S_3^+$ 348.0181, found 348.0176.

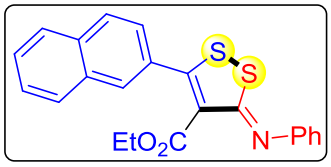
Ethyl (*Z*)-5-(furan-2-yl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3nB**)



Prepared by general procedure and reacted for 15 min. Yellow crystals, 50 mg, yield 94%, mp 62–64 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.8 Hz, 2H), 6.84 (d, J = 3.6 Hz, 1H), 6.55–6.53 (m, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.0, 164.6, 151.6, 146.7, 145.6, 145.4, 129.7, 125.3, 124.6, 120.0,

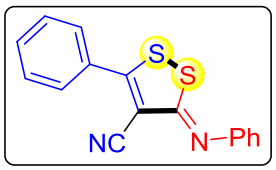
113.1, 112.7, 62.6, 14.2. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{14}NO_3S_2^+$ 332.0410, found 332.0404.

Ethyl (*Z*)-5-(naphthalen-2-yl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3oB**)



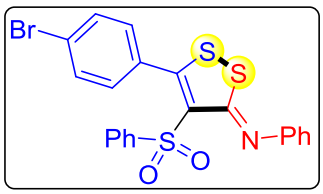
Prepared by general procedure and reacted for 5 min. Yellow crystals, 60 mg, yield 95%, mp 133–135 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, J = 1.8 Hz, 1H), 7.93–7.83 (m, 3H), 7.64–7.52 (m, 3H), 7.41 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.12 (dd, J = 8.4, 1.2 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.7, 164.3, 161.8, 151.7, 134.3, 132.9, 129.9, 129.6, 129.0, 128.7, 128.0, 127.9, 127.3, 125.3, 124.7, 120.0, 62.2, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{22}H_{18}NO_2S_2^+$ 392.0773, found 392.0768.

(*Z*)-5-phenyl-3-(phenylimino)-3*H*-1,2-dithiole-4-carbonitrile (**3pB**)



Prepared by general procedure on 0.1 mmol scale and reacted for 5 min. Yellow crystals, 21 mg, yield 89%, mp 119–120 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.4, 1.2 Hz, 2H), 7.64–7.52 (m, 3H), 7.43 (t, J = 7.8 Hz, 2H), 7.21 (tt, J = 7.6, 1.2 Hz, 1H), 7.11 (dd, J = 8.4, 1.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.4, 164.2, 150.8, 132.8, 130.4, 130.0, 129.7, 127.9, 125.9, 119.8, 114.0, 106.6. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{10}N_2NaS_2^+$ 317.0178, found 317.0173.

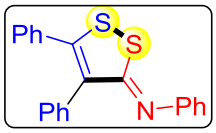
(*Z*)-5-(4-bromophenyl)-*N*-phenyl-4-(phenylsulfonyl)-3*H*-1,2-dithiol-3-imine (**3qB**)



Prepared by general procedure on 0.1 mmol scale and reacted for 20 h (isothiocyante **1B** was not completely consumed). Yellow crystals, 4 mg, yield 10%, mp 246–248 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*), 0.10 (PE/DCM = 1:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.8 Hz, 2H), 7.67–7.61 (m, 3H), 7.51 (t, J

= 7.7 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 169.7, 161.3, 150.6, 140.0, 133.8, 131.8, 130.7, 130.2, 129.9, 129.5, 128.5, 125.9, 125.7, 119.3. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{15}BrNO_2S_3^+$ 487.9443, found 487.9441.

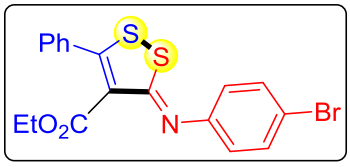
(*Z*)-*N*,4,5-triphenyl-3*H*-1,2-dithiol-3-imine (**3rB**)



Prepared by general procedure and reacted for 20 h (isothiocyante **2B** was not completely consumed). Yellow crystals, 11 mg, yield 20%, mp 159–161 ºC, R_f = 0.60 (PE/EA = 5:1, *v*/*v*), 0.30 (PE/DCM = 1:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.38 (t, *J* = 7.8 Hz, 2H), 7.34–7.20 (m, 10H), (tt, *J* = 7.2, 1.2 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 170.2, 157.1, 152.6, 134.5, 134.0, 132.4, 131.0, 129.8, 129.0, 128.8, 128.4, 128.0, 124.8, 120.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{16}NS_2^+$ 346.0719, found 346.0715.

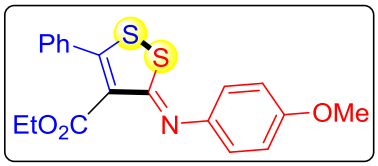
7.2 Analytic data of products for scope of isothiocyantes

Ethyl (*Z*)-3-((4-bromophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aA**)



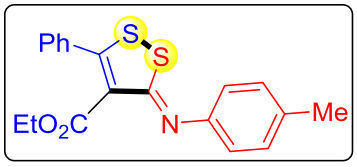
Prepared by general procedure and reacted for 15 min. Yellow crystals, 64 mg, yield 95%, mp 116–118 ºC, R_f = 0.55 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.56–7.39 (m, 7H), 6.98 (d, *J* = 8.6 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 167.2, 164.0, 162.3, 150. 5, 132.9, 132.1, 131.1, 129.1, 127.8, 127.2, 121.9, 118.1, 62.2, 13.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}BrNO_2S_2^+$ 419.9722, found 419.9717.

Ethyl (*Z*)-3-((4-methoxyphenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aC**)



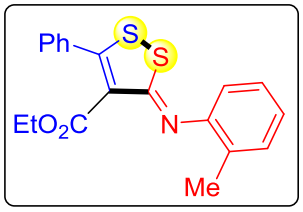
Prepared by general procedure and reacted for 5 min. Orange crystals, 54 mg, yield 91%, mp 88–90 ºC, R_f = 0.40 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (dd, J = 7.9, 1.6 Hz, 2H), 7.48–7.41 (m, 3H), 7.07 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.7, 164.3, 161.0, 157.1, 144.8, 132.3, 130.9, 129.0, 127.8, 127.4, 121.3, 114.8, 62.1, 55.5, 13.9. **HRMS** (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}NO_3S_2^+$ 372.0723, found 372.0717.

Ethyl (*Z*)-5-phenyl-3-(*p*-tolylimino)-3*H*-1,2-dithiole-4-carboxylate (**3aD**)



Prepared by general procedure and reacted for 10 min. Yellow crystals, 50 mg, yield 98%, mp 105–108 ºC, R_f = 0.30 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54–7.49 (m, 2H), 7.48–7.40 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.1, 164.2, 161.3, 149.1, 134.9, 132.3, 130.9, 130.3, 129.0, 127.8, 127.3, 119.8, 62.1, 21.2, 13.9. **HRMS** (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}NO_2S_2^+$ 356.0773, found 356.0768.

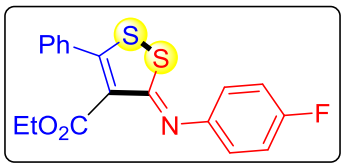
Ethyl (*Z*)-5-phenyl-3-(*o*-tolylimino)-3*H*-1,2-dithiole-4-carboxylate (**3aE**)



Prepared by general procedure and reacted for 20 h (isothiocyante **2E** was not completely consumed). Yellow oil, 17 mg, yield 33%, R_f = 0.30 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (dd, J = 8.0, 1.7 Hz, 2H), 7.52–7.42 (m, 3H), 7.27 (d, J = 3.8 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.08 (td, J = 7.5, 1.3 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.24 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.2, 164.3, 161.5, 150.5, 132.3, 131.2,

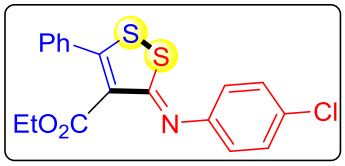
131.0, 129.5, 129.1, 127.9, 127.1, 127.0, 125.3, 118.0, 62.1, 17.7, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{18}NO_2S_2^+$ 356.0773, found 356.0767.

Ethyl (*Z*)-3-((4-fluorophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aF**)



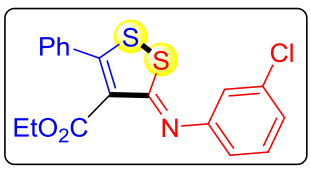
Prepared by general procedure and reacted for 5 min. Yellow oil, 54 mg, yield 94%, R_f = 0.20 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55–7.40 (m, 5H), 7.13–7.02 (m, 4H), 4.20 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.1, 164.1, 162.0, 160.2 (d, $J_{C\text{-}F}$ = 244.4 Hz), 147.7, 132.2, 131.1, 129.1, 127.8, 127.2, 121.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 116.6 (d, $J_{C\text{-}F}$ = 22.2 Hz), 62.2, 13.9. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -117.7. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}FNO_2S_2^+$ 360.0523, found 360.0516.

Ethyl (*Z*)-3-((4-chlorophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aG**)



Prepared by general procedure and reacted for 20 min. Yellow crystals, 57 mg, yield 95%, mp 87–89 ºC, R_f = 0.20 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55–7.41 (m, 5H), 7.35 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.2, 164.0, 162.3, 150.0, 132.1, 131.1, 130.4, 123.0, 129.1, 127.8, 127.3, 121.5, 62.2, 13.9. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{14}ClNNaO_2S_2^+$ 398.0047, found 398.0041.

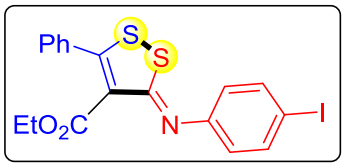
Ethyl (*Z*)-3-((3-chlorophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aH**)



Prepared by general procedure and reacted for 20 min. Yellow oil, 56 mg, yield 93%, R_f = 0.25 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56–7.41 (m, 5H), 7.32 (t, J = 7.9 Hz, 1H), 7.16–7.08 (m, 2H), 6.99 (d, J = 8.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.6, 164.0, 162.5, 152.6,

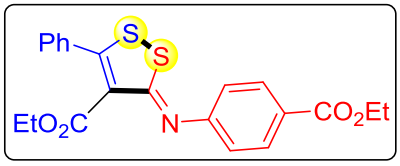
135.3, 132.1, 131.2, 130.9, 129.1, 127.8, 127.3, 125.2, 120.4, 118.2, 62.2, 13.9. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{14}ClNNaO_2S_2^+$ 398.0047, found 398.0044.

Ethyl (*Z*)-3-((4-iodophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aI**)



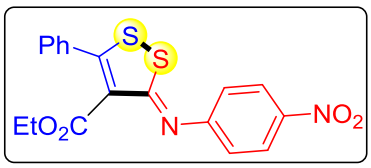
Prepared by general procedure and reacted for 15 min. Yellow crystals, 69 mg, yield 92%, mp 97–99 ºC, R_f = 0.25 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.5 Hz, 2H), 7.56–7.40 (m, 5H), 6.86 (d, J = 8.3 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.06 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.1, 164.0, 162.3, 151.1, 138.8, 132.1, 131.1, 129.1, 127.8, 127.3, 122.2, 89.0, 62.2, 13.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}INO_2S_2^+$ 467.9583, found 467.9581.

Ethyl (*Z*)-3-((4-(ethoxycarbonyl)phenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aJ**)



Prepared by general procedure and reacted for 30 min. Yellow crystals, 62 mg, yield 94%, mp 92–94 ºC, R_f = 0.35 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.5 Hz, 2H), 7.56–7.40 (m, 5H), 7.13 (d, J = 8.6 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.3, 166.3, 163.9, 162.7, 155.4, 132.0, 131.6, 131.1, 129.1, 127.8, 127.2, 127.0, 119.9, 62.2, 60.9, 14.5, 13.8. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{20}NO_4S_2^+$ 414.0828, found 414.0822.

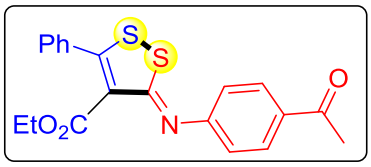
Ethyl (*Z*)-3-((4-nitrophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aK**)



Prepared by general procedure and reacted for 2 h. Yellow crystals, 60 mg, yield 97%, mp 92–94 ºC, R_f = 0.35 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (d, J = 9.0 Hz, 2H), 7.56–7.42 (m, 5H), 7.20 (d, J = 9.0 Hz, 2H), 4.20 (q, J = 7.1

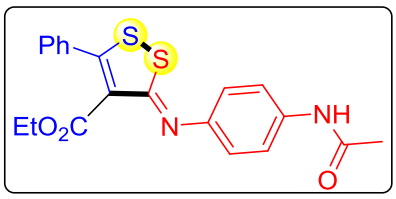
Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.2, 163.8, 163.6, 156.8, 144.6, 131.7, 131.4, 129.2, 127.8, 127.3, 125.9, 120.7, 62.3, 13.8. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{15}N_2O_4S_2^+$ 387.0468, found 387.0462.

Ethyl (*Z*)-3-((4-acetylphenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aL**)



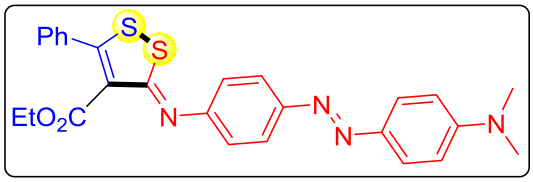
Prepared by general procedure and reacted for 5 min. Yellow viscous oil, 50 mg, yield 81%, R_f = 0.20 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.5 Hz, 2H), 7.56–7.42 (m, 5H), 7.16 (d, J = 8.5 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 2.60 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 197.0, 167.3, 163.8, 162.8, 155.5, 133.9, 131.9, 131.2, 130.5, 129.1, 127.7, 127.2, 120.0, 62.2, 26.6, 13.8. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{18}NO_3S_2^+$ 384.0723, found 384.0731.

Ethyl (*Z*)-3-((4-acetamidophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aM**)



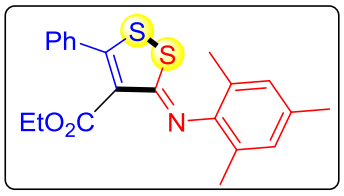
Prepared by general procedure and reacted for 20 h (isothiocyante **2M** was not completely consumed). Yellow crystals, 23 mg, yield 36%, mp 159–160 ºC, R_f = 0.20 (PE/EA = 1:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59–7.36 (m, 7H), 7.23 (br s, 1H), 7.08 (d, J = 8.7 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.18 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.5, 166.5, 164.3, 161.8, 147.6, 135.4, 132.2, 131.0, 129.1, 127.8, 127.3, 121.2, 120.7, 62.2, 24.6, 13.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_3S_2^+$ 399.0832, found 399.0838.

Ethyl (*Z*)-3-((4-((*E*)-(4-(dimethylamino)phenyl)diazenyl)phenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aN**)



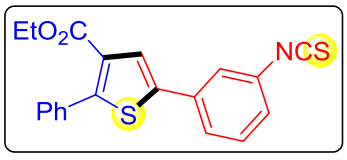
Prepared by general procedure and reacted for 2 h. Red crystals, 63 mg, yield 81%, mp 53–55 ºC, R_f = 0.30 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 9.1 Hz, 2H), 7.57–7.41 (m, 5H), 7.23 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 9.1 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.06 (s, 6H), 1.10 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.6, 164.1, 162.0, 152.44, 152.39, 150.7, 143.9, 132.2, 131.1, 129.1, 127.8, 127.5, 125.0, 123.9, 120.7, 111.6, 62.2, 40.4, 13.9. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{26}H_{24}N_4NaO_2S_2^+$ 511.1233, found 511.1227.

Ethyl (*Z*)-3-(mesitylimino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aO**)



Prepared by general procedure and reacted for 20 h (isothiocyante **2O** was not completely consumed). Yellow oil, 12 mg, yield 20%, R_f = 0.55 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, J = 6.9 Hz, 2H), 7.52–7.41 (m, 3H), 6.90 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 2.17 (s, 6H), 1.11 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.2, 164.2, 162.2, 147.6, 134.1, 132.4, 131.0, 129.4, 129.1, 127.9, 127.0, 125.9, 62.1, 21.0, 17.6, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{22}NO_2S_2^+$ 384.1086, found 384.1082.

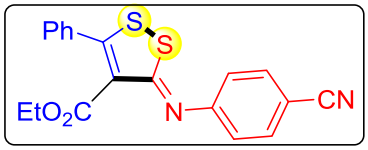
Ethyl 5-(3-isothiocyanatophenyl)-2-phenylthiophene-3-carboxylate (**3aP**)



Prepared by general procedure and reacted for 5 min (isothiocyante **2P** was completely consumed). Yellow crystals, 15 mg, yield 26%, mp 78–80 ºC, R_f = 0.55 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.54–7.50 (m, 3H),

7.48–7.35 (m, 5H), 7.18–7.16 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.1, 150.7, 140.4, 135.2, 133.1, 132.3, 130.4, 129.9, 129.3, 129.0, 128.1, 126.6, 125.1, 124.6, 122.8, 60.9, 14.2. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{15}NNaO_2S_2^+$ 388.0436, found 388.0431.

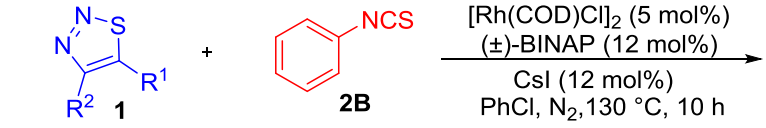
Ethyl (*Z*)-3-((4-cyanophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aQ**)



Prepared by general procedure and reacted for 5 min. Yellow crystals, 50 mg, yield 85%, mp 121–123 ºC, R_f = 0.25 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.6 Hz, 2H), 7.54–7.42 (m, 5H), 7.15 (d, J = 8.5 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.06 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.9, 163.6, 163.4, 155.0, 134.0, 131.7, 131.3, 129.2, 127.7, 127.2, 120.9, 119.1, 108.2, 62.2, 13.8. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{15}N_2O_2S_2^+$ 367.0569, found 367.0565.

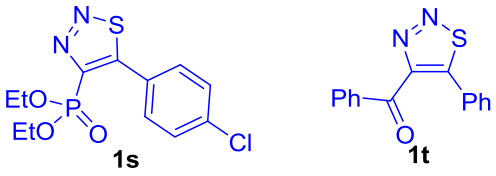
8. Unsuccessful transannulations of 1,2,3-thiadiazoles with isothiocyanates

Scheme S11. Some unsuccessful transannulations of 1,2,3-thiadiazoles (**1**) with isothiocyanatobenzene (**2B**)



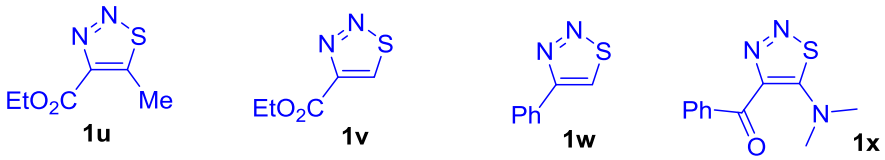
1 (0.20 mmol, 1.0 eq.) + **2B** (0.16 mmol, 0.8 eq.)

a) No reactions between the two reactants



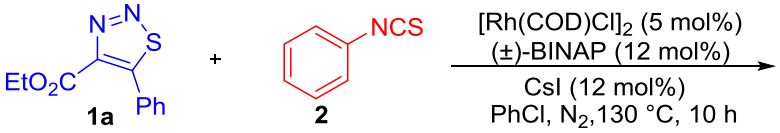
1s **1t**

b) Thiadiazoles were decomposition but no transannulation products observed



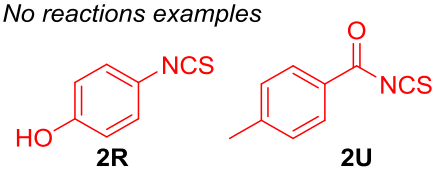
1u **1v** **1w** **1x**

Scheme S12. Some unsuccessful transannulations of 1,2,3-thiadiazole **1a** with isothiocyantes (**2**)



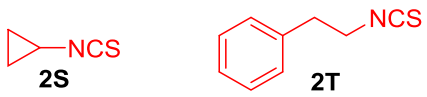
1a (0.20 mmol, 1.0 eq.) + **2** (0.16 mmol, 0.8 eq.)

a) No reactions examples



2R **2U**

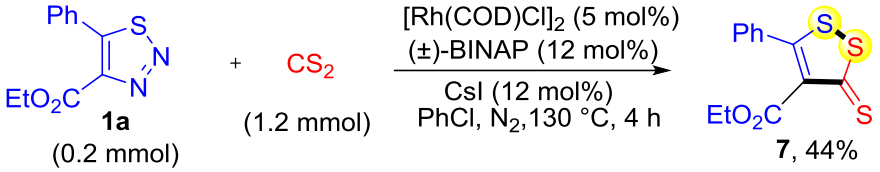
b) Isothiocyantes were decomposition but no 3H-1,2-dithiol-3-imines were isolated



2S **2T**

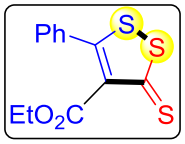
9. Transannulation of thiadiazole 1a with carbon disulfide

Scheme S13. Transannulation of thiadiazole **1a** with carbon disulfide



An oven-dried 10 mL-reaction tube equipped with a magnetic stirring bar was charged with thiadiazole **1a** (47 mg, 0.200 mmol, 1.0 equiv.), carbon disulfide (72 μL, 1.200 mmol, 6.0 equiv.), $[Rh(COD)Cl]_2$ (5 mg, 0.010 mmol, 0.05 equiv.), (±)-BINAP (15 mg, 0.024 mmol, 0.12 equiv.) and CsI (6 mg, 0.024 mmol, 0.12 equiv.). The tube was sealed immediately and protected with N_2 by an evacuation-backfill operations for three times (did not use the balloon). Then chlorobenzene (2 mL) was injected to the tube via a syringe. The reaction mixture was allowed to stir at 130 °C (pre-heated metal module) for 4 h. Then the reaction mixture was dropped to room temperature and directly subjected to column chromatography on silica gel. Further purified by column chromatography on silica gel afforded the corresponding product **7** in 44% yield.

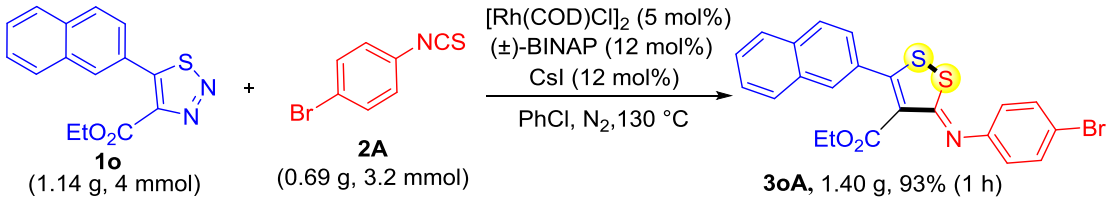
Ethyl 5-phenyl-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**7**) [34]



Orange red crystals, 25 mg, yield 44%, mp 45–46 ºC (no literature reported melting point), R_f = 0.40 (PE/EA = 5:1, *v*/*v*), 0.20 (PE/DCM = 1:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59–7.53 (m, 3H), 7.50–7.46 (m, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 211.4, 172.7, 163.6, 140.9, 132.0, 131.4, 129.5, 127.9, 62.6, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{12}H_{11}O_2S_3^+$ 282.9916, found 282.9919.

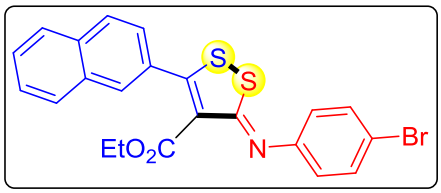
10. Gram scale reaction and product derivatization

Scheme S14. Gram-scale reaction of thiadiazole **1o** and isothiocyante **2A**



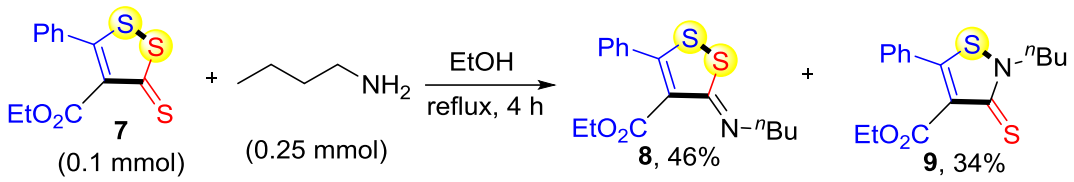
An oven-dried 25 mL-flask equipped with a magnetic stirring bar was charged with thiadiazole **1o** (1.14 g, 4.0 mmol, 1.0 equiv.), isothiocyante **2A** (0.69 g, 3.2 mmol, 0.800 equiv.), $[Rh(COD)Cl]_2$ (98 mg, 0.2 mmol, 0.05 equiv.), (±)-BINAP (298 mg, 0.24 mmol, 0.12 equiv.) and CsI (124 mg, 0.24 mmol, 0.12 equiv.). The flask was sealed immediately and protected with a nitrogen balloon after evacuation-backfill operations for three times. Then chlorobenzene (15 mL) was injected to the tube via a syringe. The reaction mixture was allowed to stir at 130 °C (oil bath), and the progress of the reaction was monitored by TLC (When reacted for 1 h, isothiocyante **2A** was completely consumed). Then, after cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded product **3oA** in 93% yield.

Ethyl (*Z*)-3-((4-bromophenyl)imino)-5-(naphthalen-2-yl)-3*H*-1,2-dithiole-4-carboxylate (**3oA**)



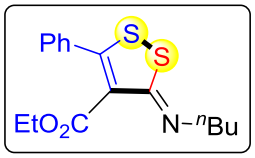
Yellow crystals, 1.40 g, yield 93%, mp 131–133 ºC, R_f = 0.50 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (d, J = 1.8 Hz, 1H), 7.95–7.85 (m, 3H), 7.63–7.55 (m, 3H), 7.52 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.03 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.3, 164.1, 162.4, 150.5, 134.3, 132.9, 129.4, 129.1, 128.7, 128.0, 127.9, 127.4, 127.3, 124.6, 121.9, 118.1, 62.3, 13.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{22}H_{17}BrNO_2S_2^+$ 469.9879, found 469.9875.

Scheme S15. Synthesis of compounds **8** and **9**



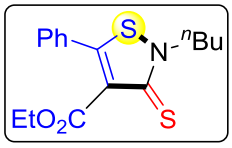
An 10 mL-flask equipped with a magnetic stirring bar was charged with ethyl 5-phenyl-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**7**) (28 mg, 0.1 mmol, 1.0 equiv.), ethanol (2 mL) and *n*-butylamine (25 μL, 0.25 mmol, 2.5 equiv.), successively. The reaction mixture was heated to reflux (oil bath) for 4 h. After cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded product **8** in 46% yield and product **9** in 34% yield.

Ethyl (*Z*)-3-(butylimino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**8**)



Reddish brown oil, 15 mg, yield 46%, R_f = 0.55 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55–7.43 (m, 5H), 4.33 (q, J = 7.1 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 1.88 (quint, J = 7.6 Hz, 2H), 1.48 (sext, J = 7.4 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 184.6, 163.7, 155.0, 131.4, 130.9, 129.5, 128.2, 128.0, 62.4, 48.9, 31.0, 20.0, 14.1, 13.8. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{20}NO_2S_2^+$ 322.0930, found 322.0931.

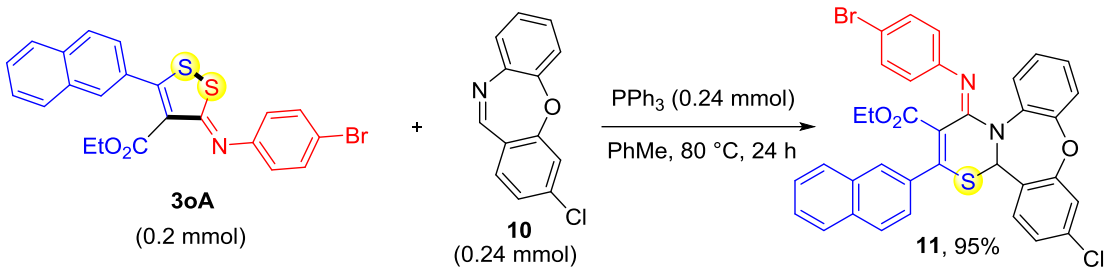
Ethyl 2-butyl-5-phenyl-3-thioxo-2,3-dihydroisothiazole-4-carboxylate (**9**)



Yellow crystals, 11 mg, yield 34%, mp 107–109 ºC, R_f = 0.20 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58–7.46 (m, 3H), 7.31 (dd, J = 7.8, 1.7 Hz, 2H), 4.04 (q, J = 7.1 Hz, 2H), 3.64 (t, J = 7.3 Hz, 2H), 1.73–1.56 (m, 2H), 1.32–1.17 (m, 2H), 0.95 (t, J = 7.1 Hz, 3H), 0.81 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.7, 165.7, 162.4, 130.8, 129.9, 129.0, 128.3, 126.5, 60.8, 49.7, 32.6, 19.5, 13.8, 13.4. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd

for $C_{16}H_{20}NO_2S_2^+$ 322.0930, found 322.937.

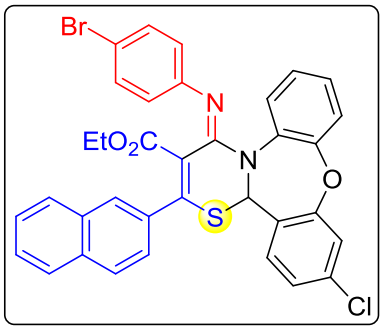
Scheme S12. Synthesis of compound **11**



Note: Compound **11** was synthesized according to Rakitin's procedure. [35]

An oven-dried 10 mL-reaction tube equipped with a magnetic stirring bar was charged with 3*H*-1,2-dithiol-3-imine **3oA** (94 mg, 0.20 mmol, 1.0 equiv.), cyclic imine **10** [36] (55 mg, 0.24 mmol, 1.2 equiv.), triphenylphosphine (63 mg, 0.24 mmol, 1.2 equiv.) and dry toluene (2 mL). The tube was sealed and the mixture was allowed to stir at 80 °C (pre-heated metal module) for 24 h. After cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded polycyclic product **11** in 95% yield.

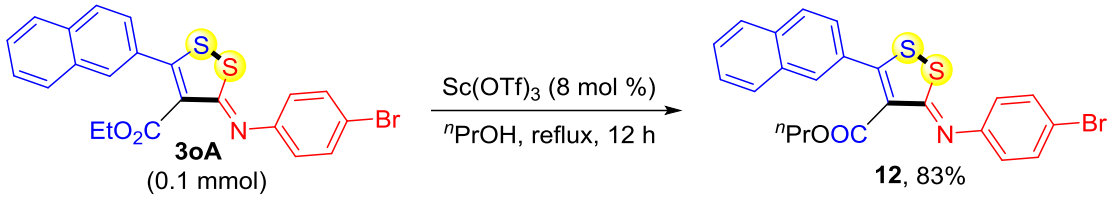
Ethyl 4-((4-bromophenyl)imino)-12-chloro-2-(naphthalen-2-yl)-4*H*,14b*H*-dibenzo[*b*,*f*][1,3]thiazino[3,2-*d*][1,4]oxazepine-3-carboxylate (**11**)



Yellow crystals, 127 mg, yield 95%, mp 167–169 ºC, R_f = 0.45 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.91–7.84 (m, 3H), 7.72 (d, J = 8.5 Hz, 1H), 7.56–7.51 (m, 2H), 7.47 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.25–7.10 (m, 4H), 7.01 (s, 3H), 6.83 (d, J = 8.3 Hz, 2H), 6.60 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 1.00 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.7, 155.9, 153.8, 152.2, 146.6, 135.3, 133.9, 133.8, 132.8, 131.9, 131.2, 130.8, 128.8, 128.7, 128.4, 128.0, 127.9, 127.6, 127.0, 125.8, 125.6, 125.0, 124.7, 123.7, 122.3, 121.8, 121.4, 117.3,

69.3, 61.8, 14.0. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{35}H_{25}BrClN_2O_3S^+$ 667.0452, found 667.0448.

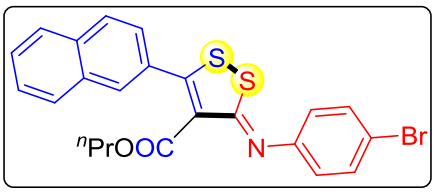
Scheme S13 Synthesis of compound **12**



Note: Compound **12** was synthesized according to Schneider's procedure. [37]

An oven-dried 10 mL-flask equipped with a magnetic stirring bar was charged with 3*H*-1,2-dithiol-3-imine **3oA** (47 mg, 0.10 mmol, 1.0 equiv.), $Sc(OTf)_3$ (4 mg, 0.008 mmol, 0.08 equiv.) and ^{n}PrOH (3 mL). The reaction mixture was heated to reflux (oil bath) overnight. After cooling to room temperature and removing the volatiles in vacuum, the residue was purified by column chromatography on silica gel afforded product **12** in 83% yield.

Propyl (*Z*)-3-((4-bromophenyl)imino)-5-(naphthalen-2-yl)-3*H*-1,2-dithiole-4-carboxylate (**12**)



Yellow crystals, 40 mg, yield 83%, mp 103–105 ºC, R_f = 0.65 (PE/EA = 5:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.95–7.84 (m, 3H), 7.64–7.52 (m, 3H), 7.52 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.10 (t, J = 6.6 Hz, 2H), 1.44 (h, J = 7.1 Hz, 2H), 0.61 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.2, 164.3, 162.3, 150.5, 134.3, 132.9, 129.5, 129.1, 128.7, 128.0, 127.9, 127.5, 127.4, 124.6, 121.9, 118.1, 67.9, 21.7, 10.2. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{19}BrNO_2S_2^+$ 484.0035, found 484.0039.

11. X-Ray crystallographic analysis of 3aA

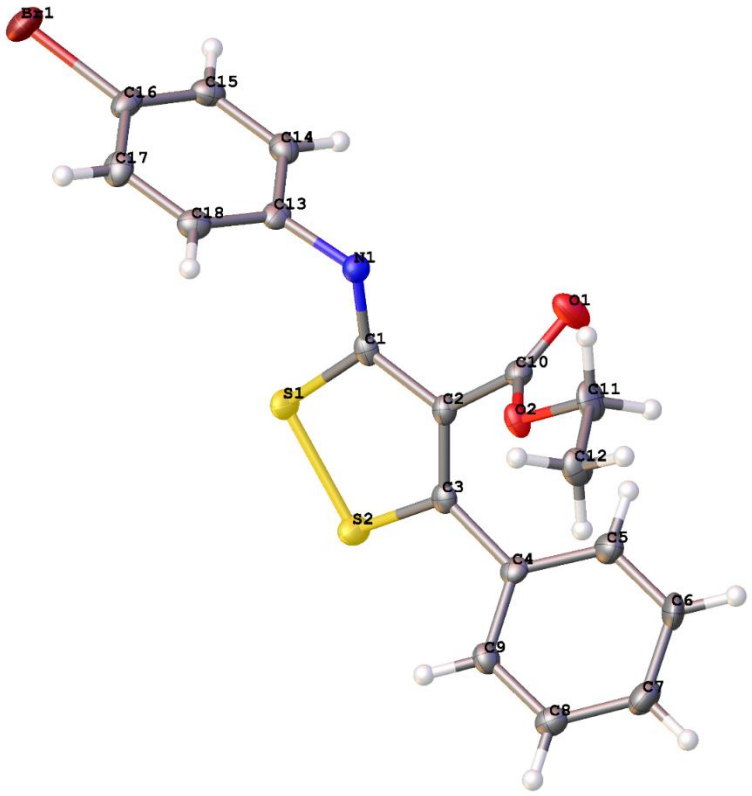


Figure S3. Thermal ellipsoid plot for the crystal structure of **3aA** (at 50% probability level, CCDC No. 2097707 [38])

Experimental

Single crystals of $C_{18}H_{14}BrNO_2S_2$ (**3aA**) were recrystallised from $CDCl_3$ mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal structure determination of 3aA

Crystal Data. $C_{18}H_{14}BrNO_2S_2$, M =420.33, monoclinic, a = 7.3517(4) Å, b = 20.2201(10) Å, c = 11.9402(5) Å, β = 91.625(4)°, U = 1774.23(14) Å3, T = 116.10(10), space group $P2_1/c$ (no. 14), Z = 4, μ(Mo Kα) = 2.562, 7333 reflections measured, 3407 unique (R_{int} = 0.0391) which were used in all calculations. The final *wR(F2)* was 0.0807 (all data).

Table S5: Crystal data and structure refinement for **3aA**

Identification code	**3aA**
Empirical formula	$C_{18}H_{14}BrNO_2S_2$
Formula weight	420.33
Temperature / K	116.10(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å, b / Å, c / Å	7.3517(4), 20.2201(10), 11.9402(5)
α/°, β/°, γ/°	90.00, 91.625(4), 90.00
Volume / Å^3	1774.23(14)
Z	4
ρ_{calc} / mg mm^{-3}	1.574
μ / mm^{-1}	2.562
F(000)	848
Crystal size / mm^3	0.50 × 0.39 × 0.34
2Θ range for data collection	6.74 to 51.98°
Index ranges	$-7 \leq h \leq 8$, $-24 \leq k \leq 23$, $-10 \leq l \leq 14$
Reflections collected	7333
Independent reflections	3407[R(int) = 0.0391 (inf-0.9Å)]
Data/restraints/parameters	3407/0/218
Goodness-of-fit on F^2	1.036
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0421, wR_2 = 0.0741
Final R indexes [all data]	R_1 = 0.0603, wR_2 = 0.0807
Largest diff. peak/hole / e Å^{-3}	0.424/-0.370
Flack Parameters	N
Completeness	0.9973

12. References

1. T. Hori, Y. Otani, M. Kawahata, K. Yamaguchi and T. Ohwada, *J. Org. Chem.*, 2008, **73**, 9102–9108.

2. N. D. Koduri, H. Scott, B. Hileman, J. D. Cox, M. Coffin, L. Glicksberg and S. R. Hussaini, *Org. Lett.*, 2012, **14**, 440–443.

3. L. Moafi, S. Ahadi, H. R. Khavasi and A. Bazgir, *Synthesis*, 2011, **2011**, 1399–1402.

4. T. Zheng, J. Tan, R. Fan, S. Su, B. Liu, C. Tan and K. Xu, *Chem. Commun.*, 2018, **54**, 1303–1306.

5. M. Yokoyama, T. Shiraishi, H. Hatanaka and K. Ogata, *J. Chem. Soc., Chem. Commun.*, 1985, 1704–1705.

6. T. J. Curphey and H. H. Joyner, *Tetrahedron Lett.*, 1993, **34**, 7231–7234.

7. (a) R. Markovic, M. Baranac and S. Jovetic, *Tetrahedron Lett.*, 2003, **44**, 7087–7090; (b) A. Rašović, P. J. Steel, E. Kleinpeter and R. Marković, *Tetrahedron*, 2007, **63**, 1937-1945.

8. E. Bellur, H. Görls and P. Langer, *J. Org. Chem.*, 2006, **71**, 2332–2338.

9. F. Jian, J. Zheng, Y. Li and J. Wang, *Green Chem.*, 2009, **11**, 215–222.

10. P. S. Landis and L. A. Hamilton, *J. Org. Chem.*, 1960, *25*, 1742–1744.

11. (a) C. F. Marcos, C. Polo, O. A. Rakitin, C. W. Rees and T. Torroba, *Chem. Commun.*, 1997, 879–880; (b) S. A. Amelichev, S. Barriga, L. S. Konstantinova, T. B. Markova, O. A. Rakitin, C. W. Rees and T. Torroba, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2409–2412.

12. (a) F. Wei, X.-Q. Shen, X.-H. Zhang and X.-G. Zhang, *Adv. Synth. Catal.*, 2018, **360**, 3911–3915; (b) H.-H. Xu, X.-H. Zhang and X.-G. Zhang, *J. Org. Chem.*, 2019, **84**, 7894–7900.

13. J. Wu, W.-X. Gao, X.-B. Huang, Y.-B. Zhou, M.-C. Liu and H.-Y. Wu, *Org. Lett.*, 2020, **22**, 5555–5560.

14. J. J. Sánchez García, G. Huerta Vargas, M. Flores-Alamo and E. I. Klimova,

Mendeleev Commun., 2021, **31**, 550–551.

15. B. S. Pedersen and S. O. Lawesson, *Tetrahedron*, 1979, **35**, 2433–2437.

16. T. J. Curphey, *J. Org. Chem.*, 2002, **67**, 6461–6473.

17. H. Adams, A. J. Hughes, M. J. Morris and S. I. A. Quenby, *Tetrahedron Lett.*, 2014, **55**, 5283–5285.

18. S. Koley, T. Chanda, S. Samai and M. S. Singh, *J. Org. Chem.*, 2016, **81**, 11594–11602.

19. M.-Q. Huang, T.-J. Li, J.-Q. Liu, A. Shatskiy, M. D. Kärkäs and X.-S. Wang, *Org. Lett.*, 2020, **22**, 3454–3459.

20. (a) D. Kurandina and V. Gevorgyan, *Org. Lett.*, 2016, **18**, 1804–1807; (b) B. Seo, Y. G. Kim and P. H. Lee, *Org. Lett.*, 2016, **18**, 5050–5053; (c) J.-Y. Son, J. Kim, S. H. Han, S. H. Kim and P. H. Lee, *Org. Lett.*, 2016, **18**, 5408–5411; (d) Q. Wu, Z. Dong, J. Xu and Z. Yang, *Org. Biomol. Chem.*, 2021, **19**, 3173–3180; (e) W. He, J. Zhuang, H. Du, Z. Yang and J. Xu, *Org. Biomol. Chem.*, 2017, **15**, 9424–9432; (f) Z. Dong, C. Chen, J. Wang, J. Xu and Z. Yang, *Org. Chem. Front.*, 2021, **8**, 6687–6698.

21. D. Dar'in, G. Kantin and M. Krasavin, *Chem. Commun.*, 2019, **55**, 5239–5242.

22. D. Fu, J. Dong, J. Wang and J. Xu, *Asian J. Org. Chem.*, 2021, **10**, 1756–1764.

23. D. Li and Y. Zhang, *RSC Adv.*, 2014, **4**, 44229–44233.

24. N. Jha, R. P. Singh, P. Saxena and M. Kapur, *Org. Lett.*, 2021, **23**, 8694–8698.

25. L. K. Ransborg, Ł. Albrecht, C. F. Weise, J. R. Bak and K. A. Jørgensen, *Org. Lett.*, 2012, **14**, 724–727.

26. Z. Fu, W. Yuan, N. Chen, Z. Yang and J. Xu, *Green Chem.*, 2018, **20**, 4484–4491.

27. J. Yu, J.-H. Lin and J.-C. Xiao, *Angew. Chem. Int. Ed.*, 2017, **56**, 16669–16673.

28. Z.-Y. Li, H.-Z. Ma, C. Han, H.-T. Xi, Q. Meng, X. Chen and X.-Q. Sun, Synthesis, 2013, **45**, 1667–1674.

29. W. Feng and X.-G. Zhang, *Chem. Commun.*, 2019, **55**, 1144–1147.

30. H. Munch, J. S. Hansen, M. Pittelkow, J. B. Christensen and U. Boas, *Tetrahedron Lett.*, 2008, **49**, 3117–3119.

31. P. Liu, C. Li, J. Zhang and X. Xu, *Synth. Commun.*, 2013, **43**, 3342–3351.

32. D. Dolles, M. Nimczick, M. Scheiner, J. Ramler, P. Stadtmüller, E. Sawatzky, A. Drakopoulos, C. Sotriffer, H.-J. Wittmann, A. Strasser and M. Decker, *ChemMedChem*, 2016, **11**, 1270–1283.

33. A. Dahiya, W. Ali, T. Alam and B. K. Patel, *Org. Biomol. Chem.*, 2018, **16**, 7787–7791.

34. J. L. Charlton, S. M. Loosmore and D. M. McKinnon, *Can. J. Chem.*, 1974, **52**, 3021–3027.

35. V. A. Ogurtsov, Y. V. Karpychev, Y. V. Nelyubina, P. V. Primakov, P. A. Koutentis and O. A. Rakitin, *Eur. J. Org. Chem.*, 2019, **2019**, 4149–4158.

36. Y. Luo and J. Xu, *Org. Lett.*, 2020, **22**, 7780–7785.

37. N. Remme, K. Koschek and C. Schneider, *Synlett*, 2007, **2007**, 491–493.

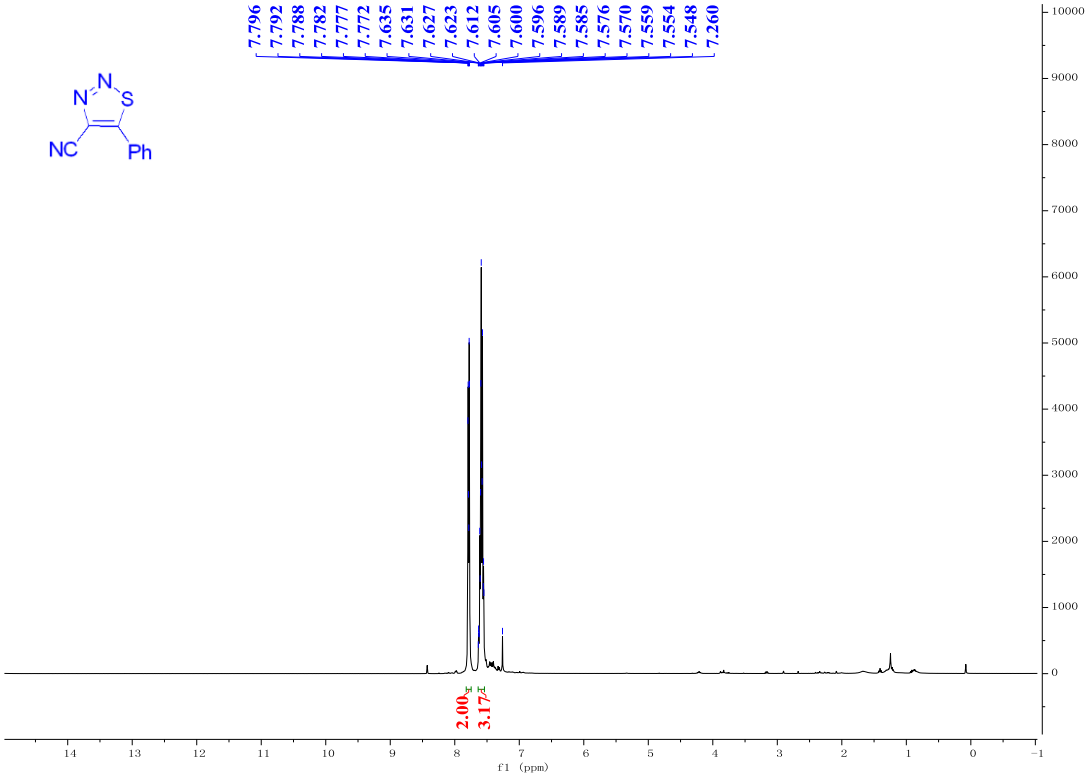
38. CCDC 2097707 (**3aA**) contain the supplementary crystallographlic data for this paper. These data can be obtianed free of charge from The Cambridge Crystallographic Data Centre.

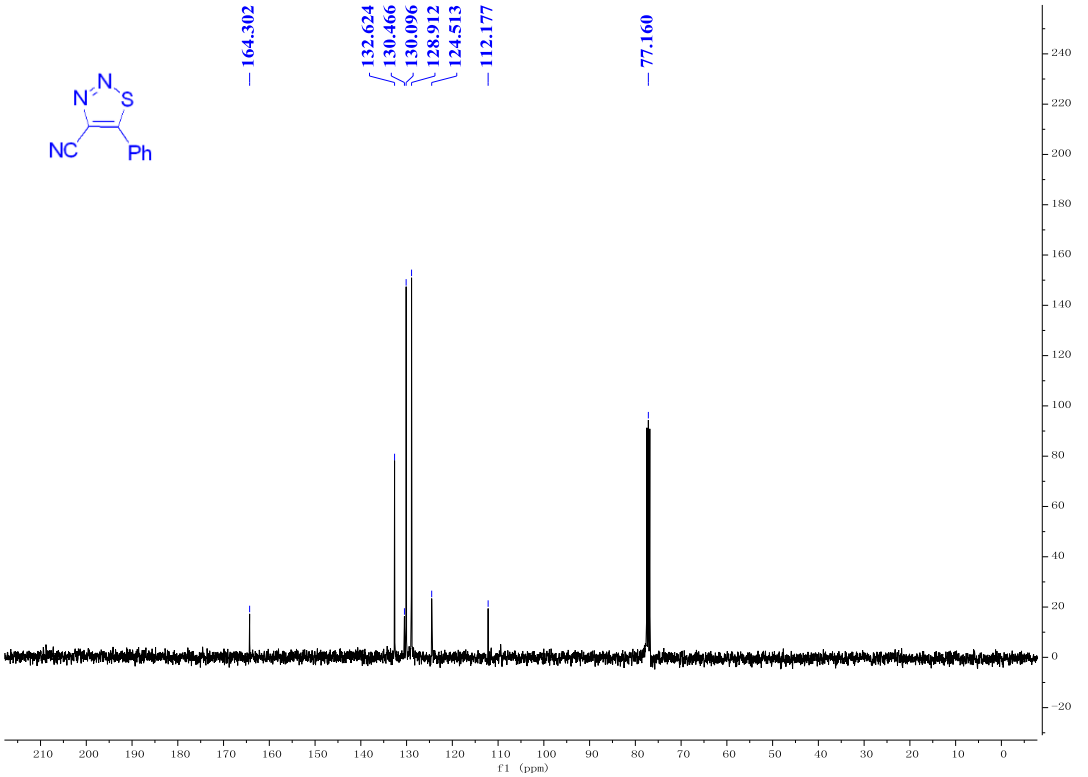
13. Copies of spectra of products and materials

13.1 Copies of spectra of thiadiazoles

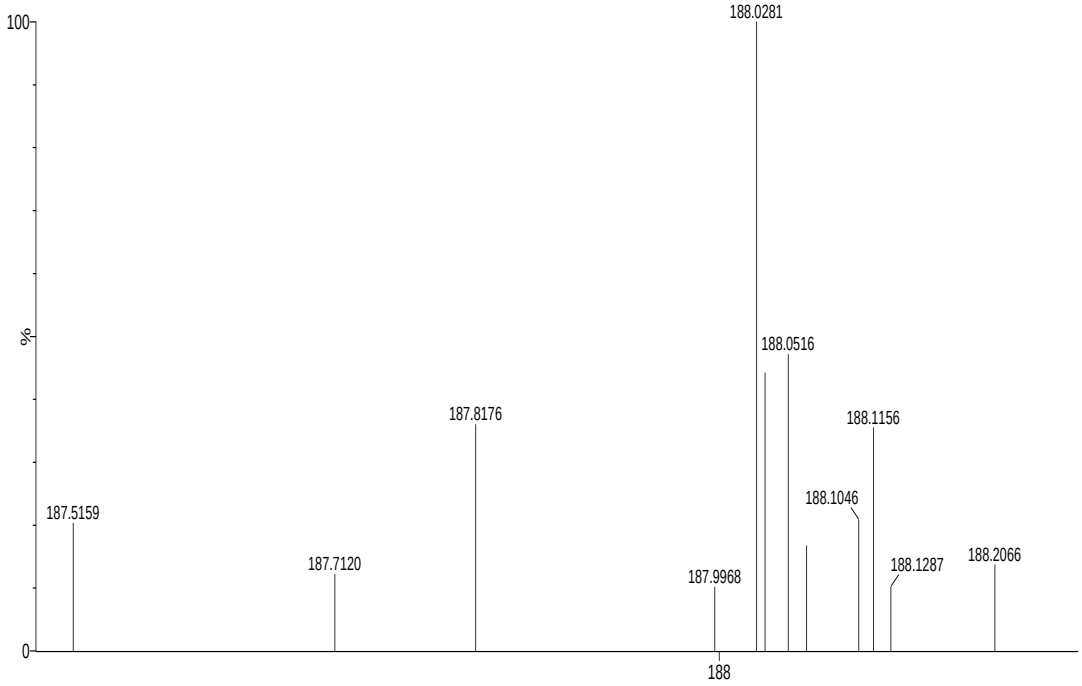
5-phenyl-1,2,3-thiadiazole-4-carbonitrile (**1p**)

^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$)



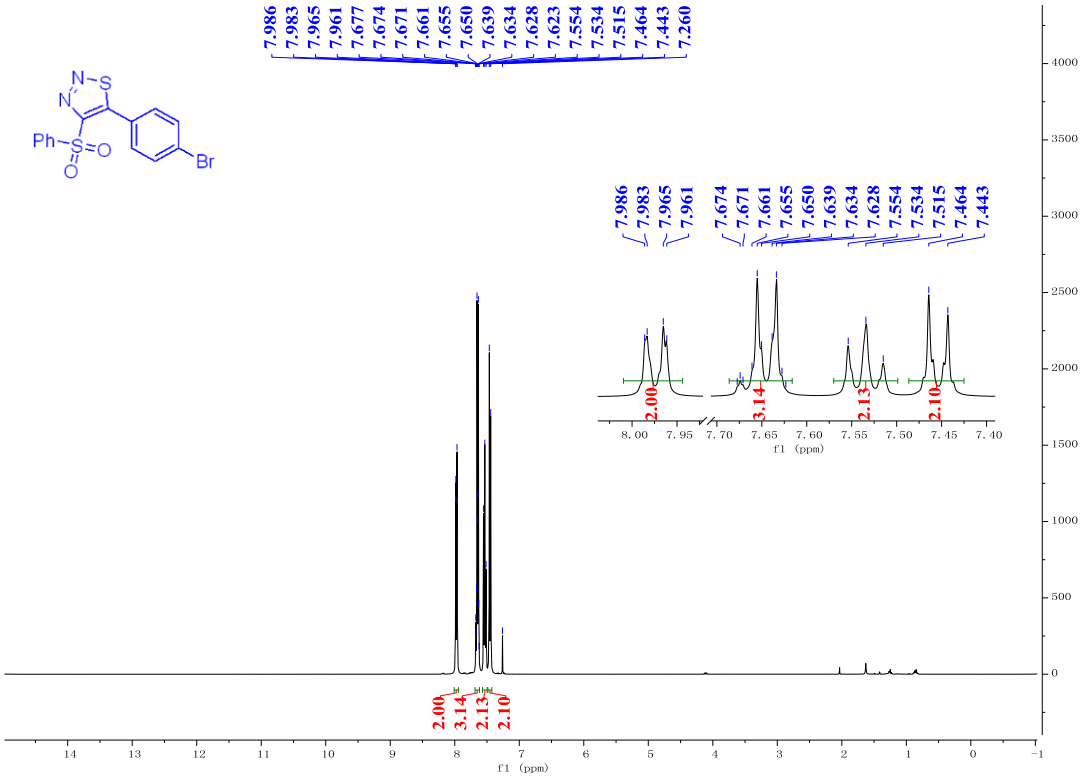


HRMS (ESI)

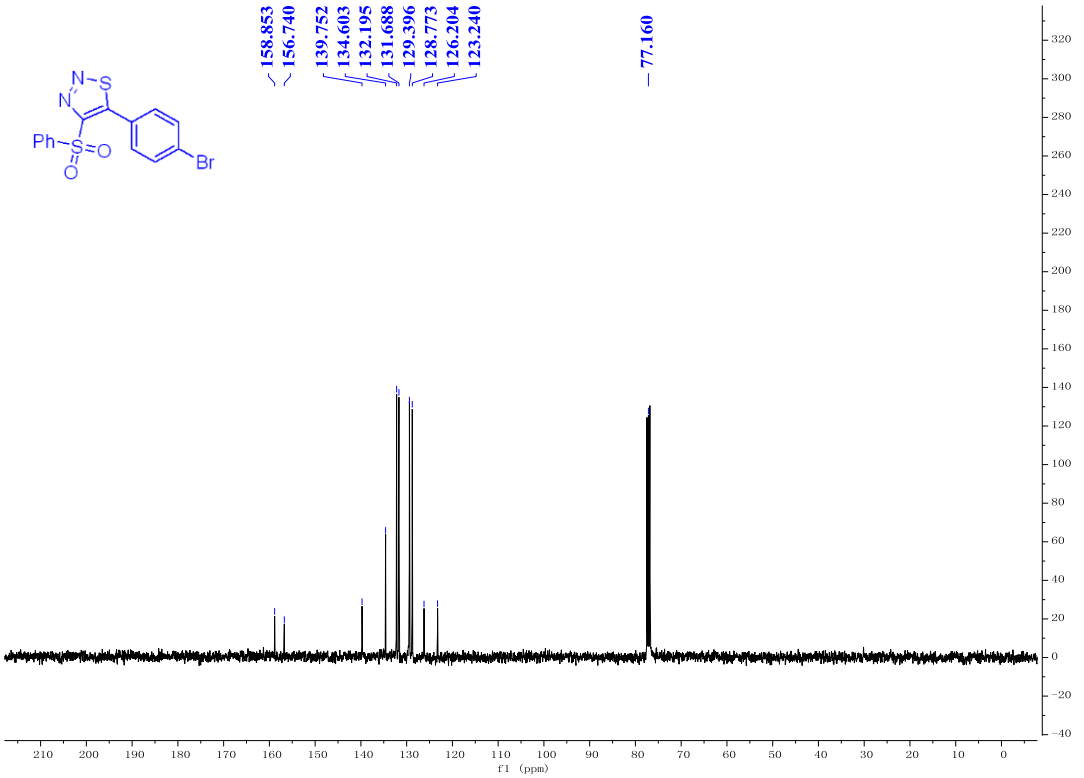

100
%
0
188
188.0281
188.0516
187.8176
188.1156
188.1046
187.5159
187.7120
187.9968
188.1287
188.2066

5-(4-bromophenyl)-4-(phenylsulfonyl)-1,2,3-thiadiazole (**1q**)

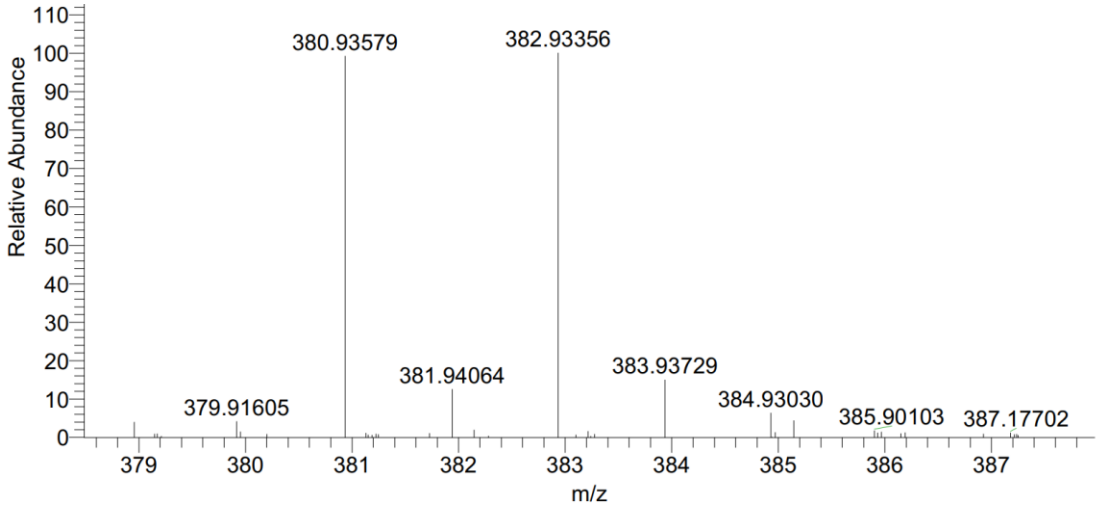
^{1}H NMR (400 MHz, $CDCl_3$)



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

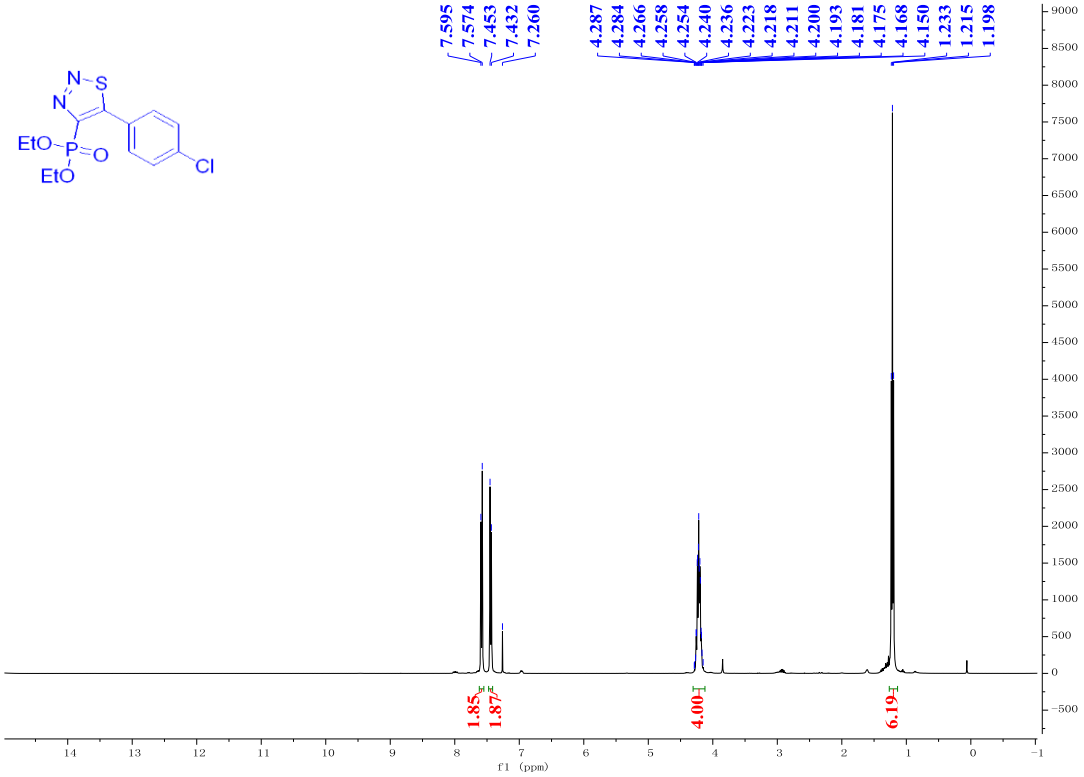


HRMS (ESI)

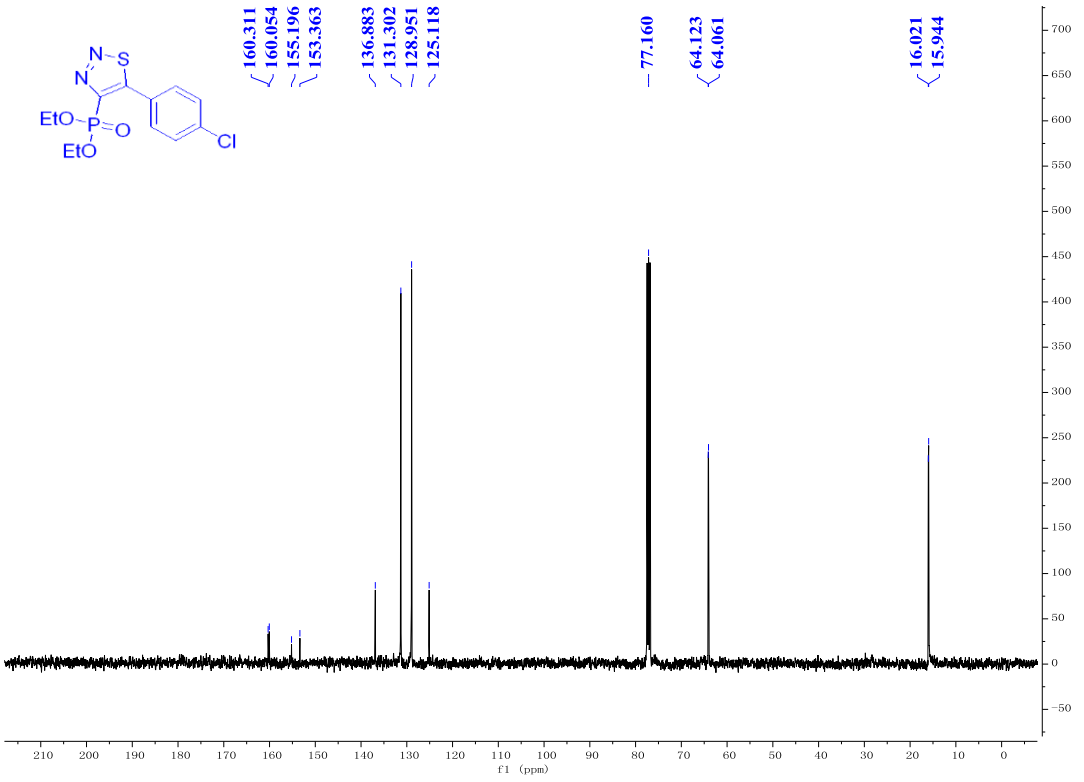

Relative Abundance
110
100
90
80
70
60
50
40
30
20
10
0
380.93579
382.93356
381.94064
383.93729
379.91605
384.93030
385.90103
387.17702
379
380
381
382
383
384
385
386
387
m/z

Diethyl (5-(4-chlorophenyl)-1,2,3-thiadiazol-4-yl)phosphonate (**1s**)

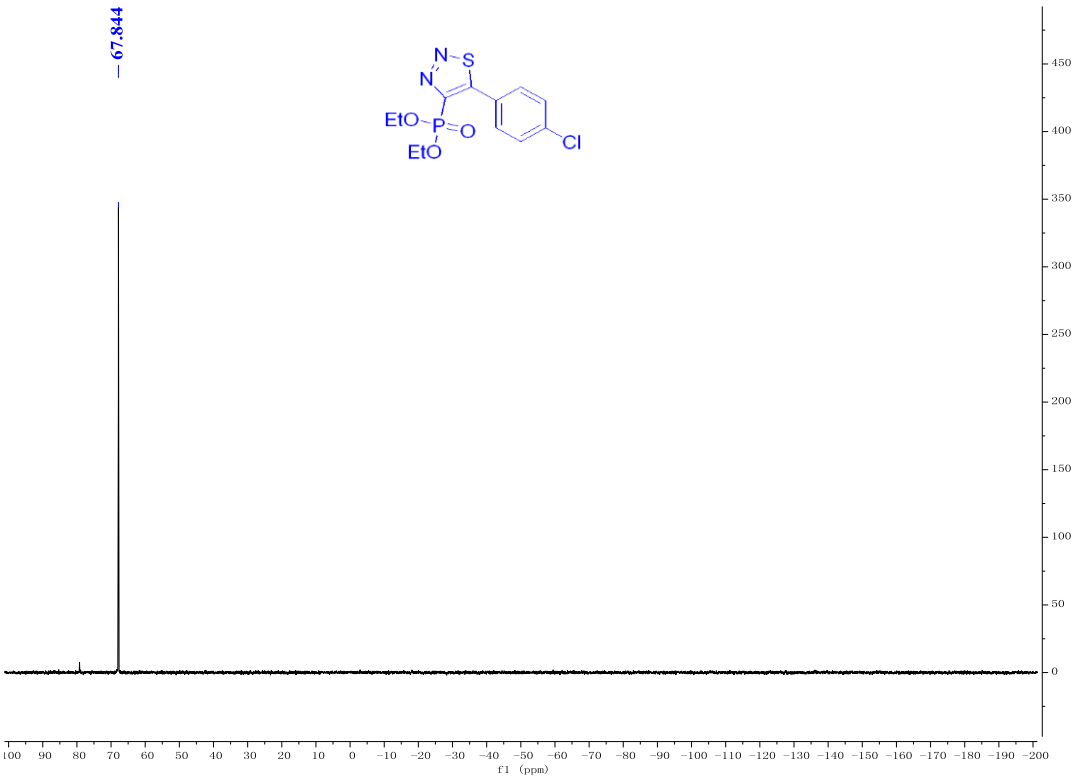
^{1}H NMR (400 MHz, $CDCl_3$)



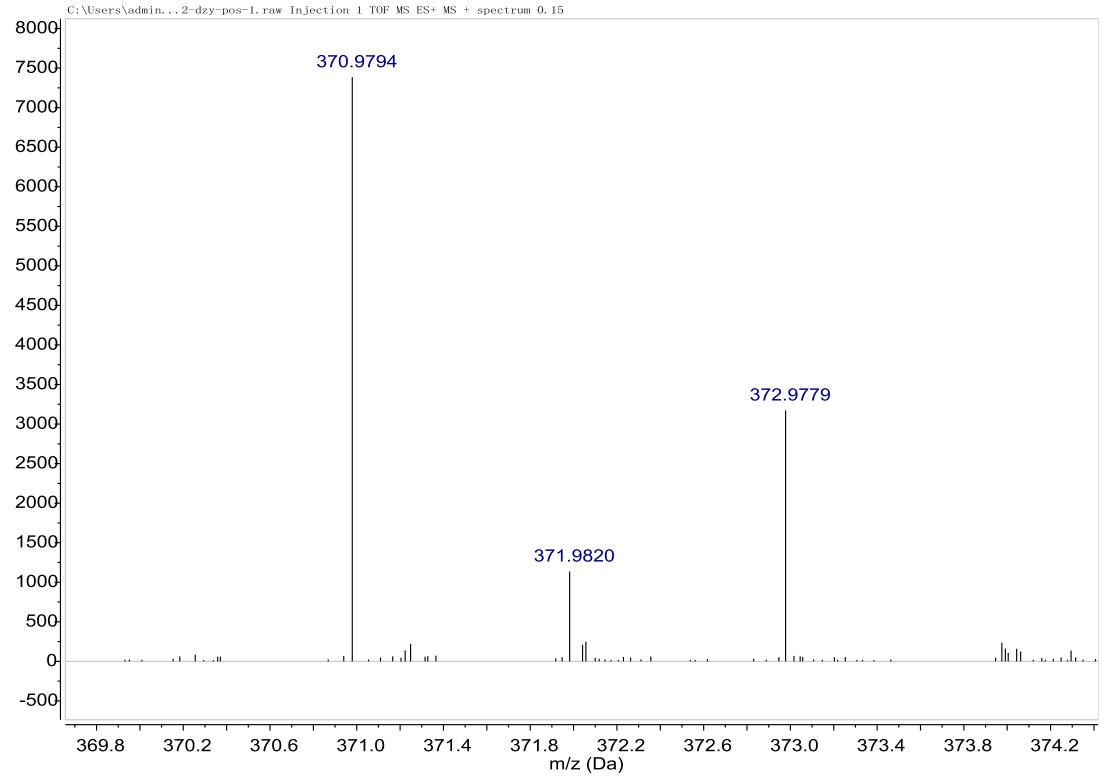
^{13}C NMR (101 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

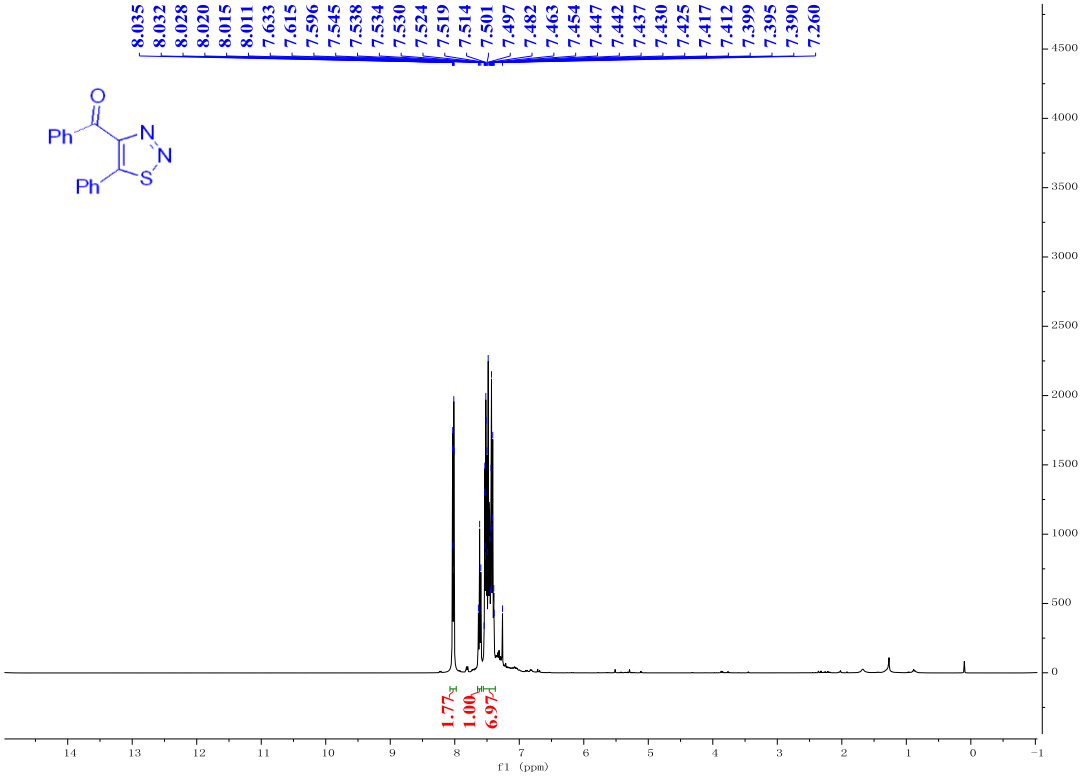


HRMS (ESI)

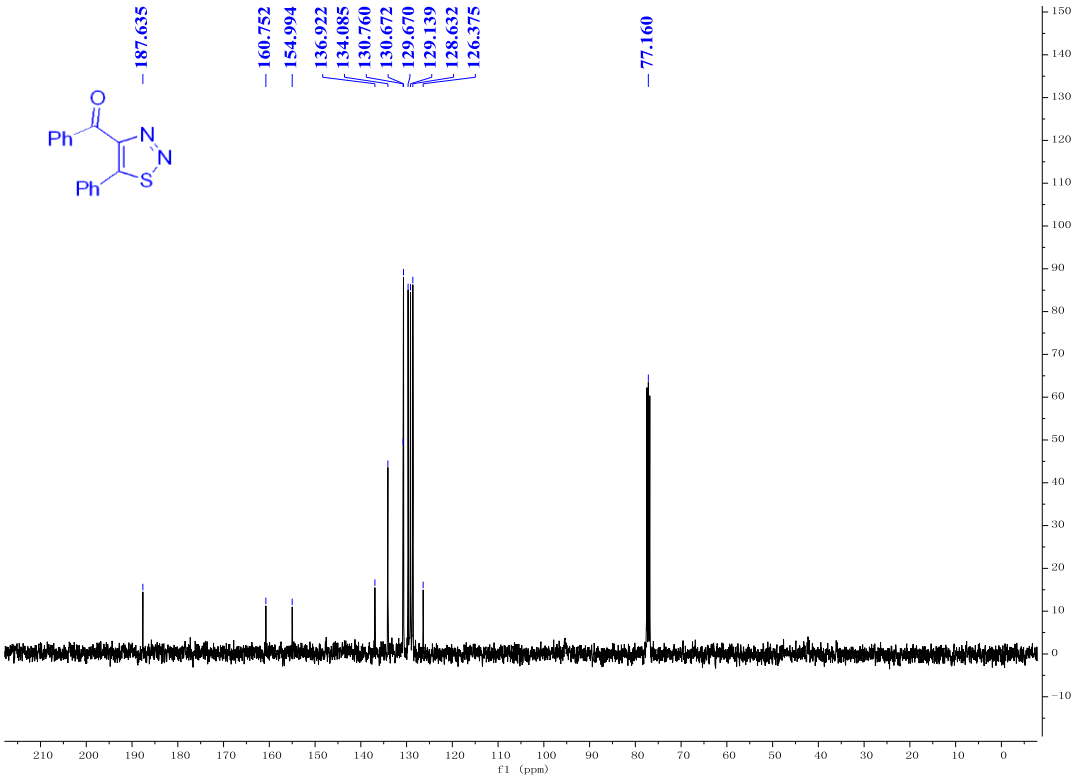


Phenyl(5-phenyl-1,2,3-thiadiazol-4-yl)methanone (**1t**)

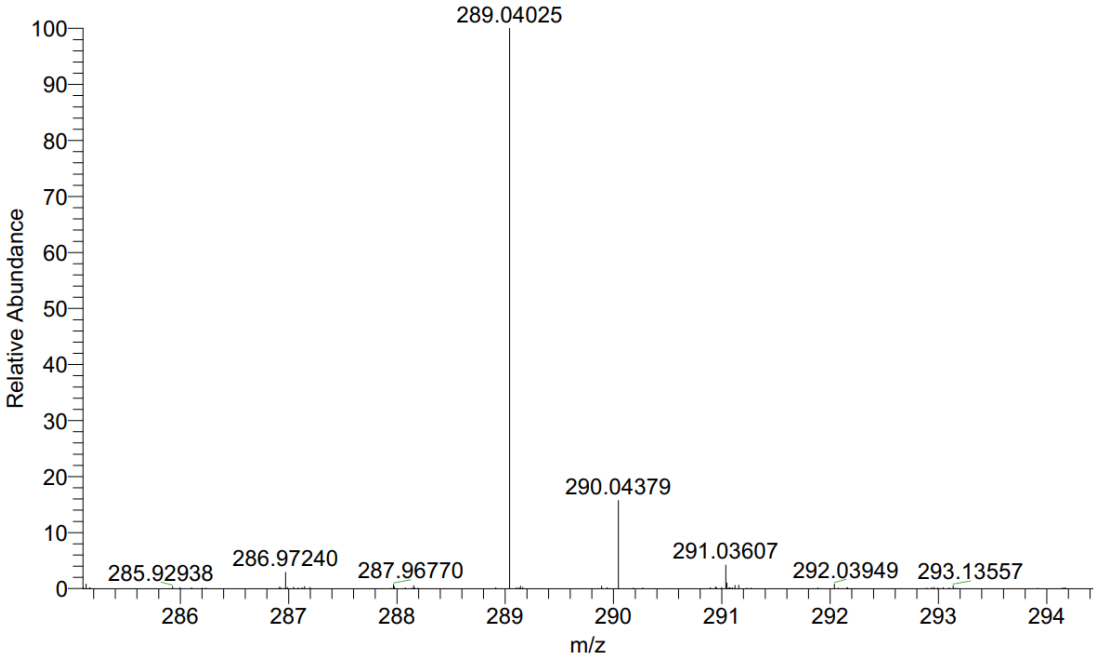
^{1}H NMR (400 MHz, $CDCl_3$)



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

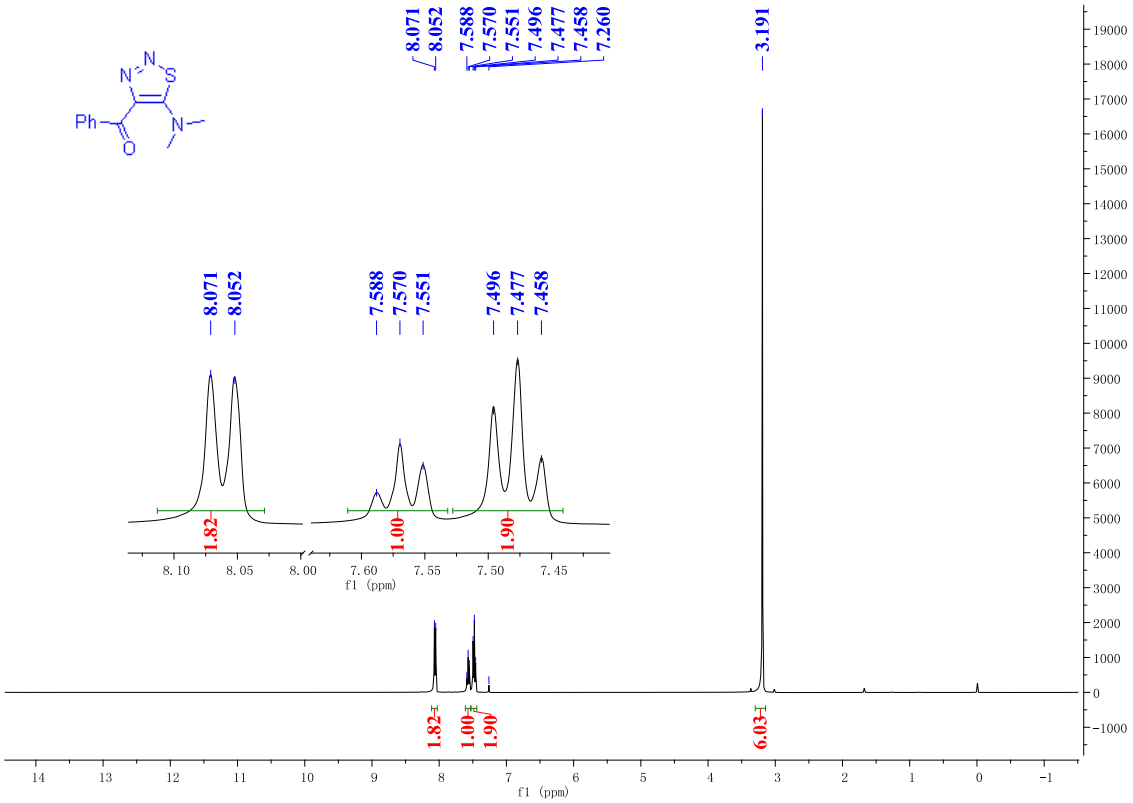


HRMS (ESI)

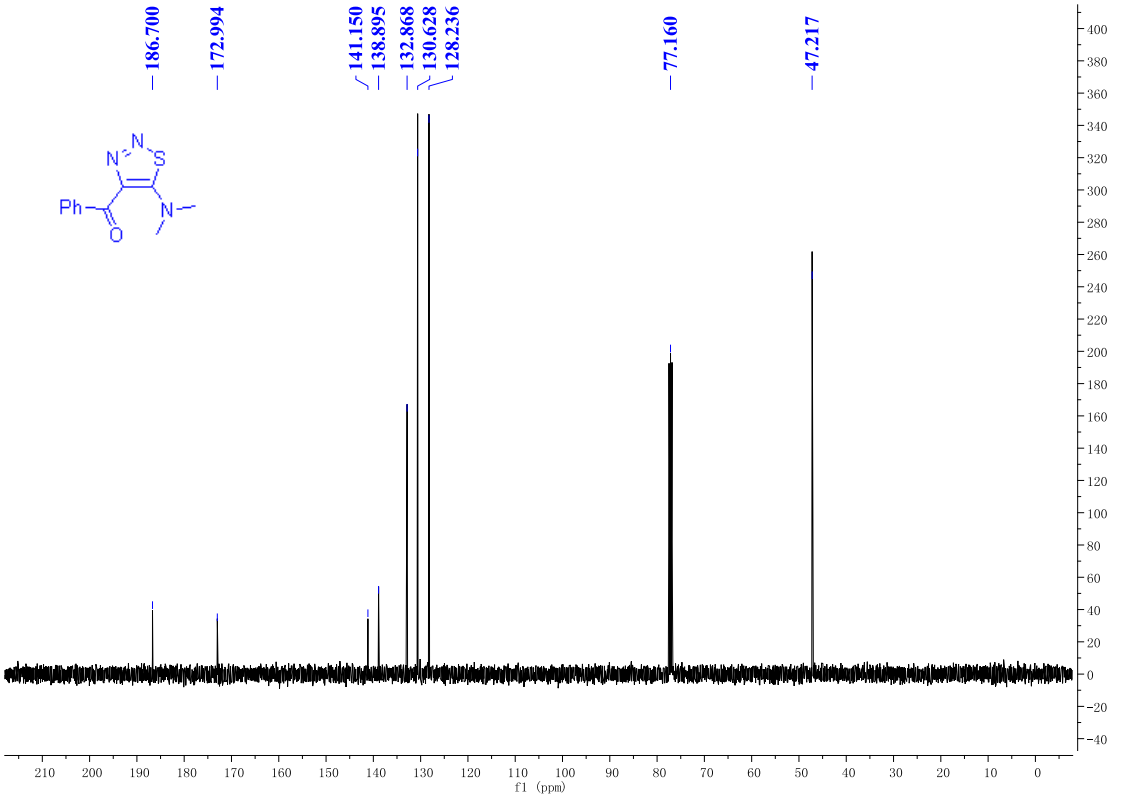

289.04025
290.04379
291.03607
285.92938
286.97240
287.96770
292.03949
293.13557
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
286
287
288
289
290
291
292
293
294

(4-(dimethylamino)-1,2,3-thiadiazol-5-yl)(phenyl)methanone (**1x**)

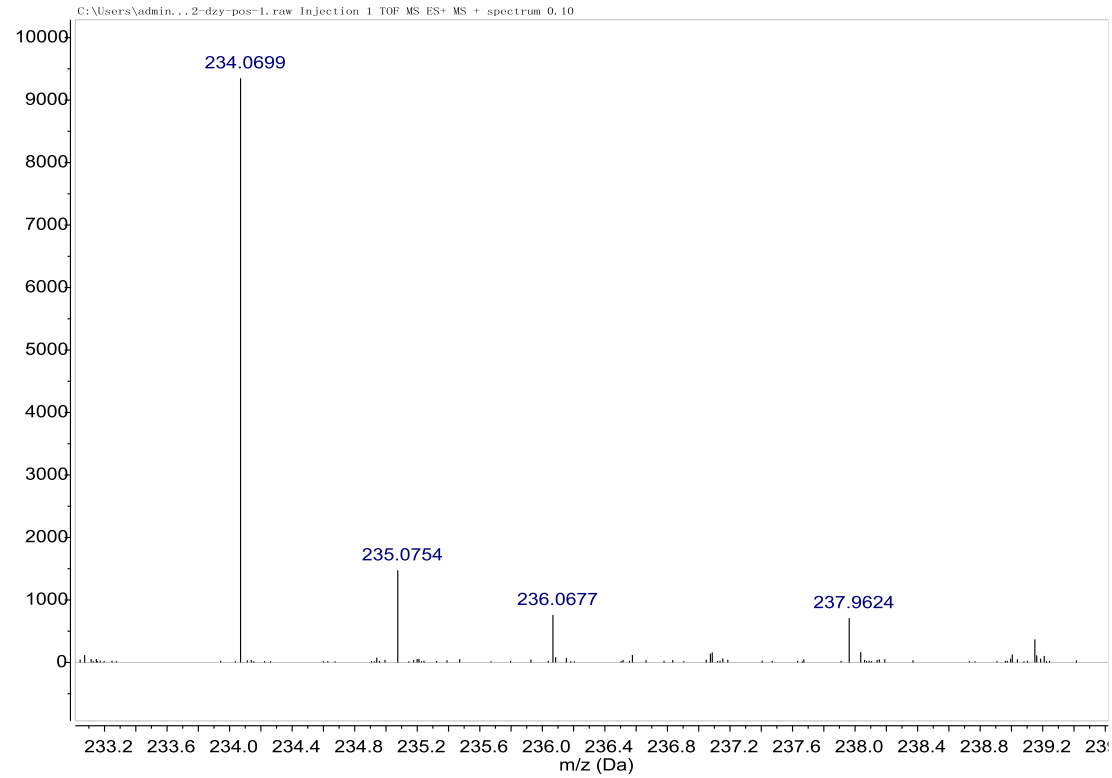
^{1}H NMR (400 MHz, $CDCl_3$)



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



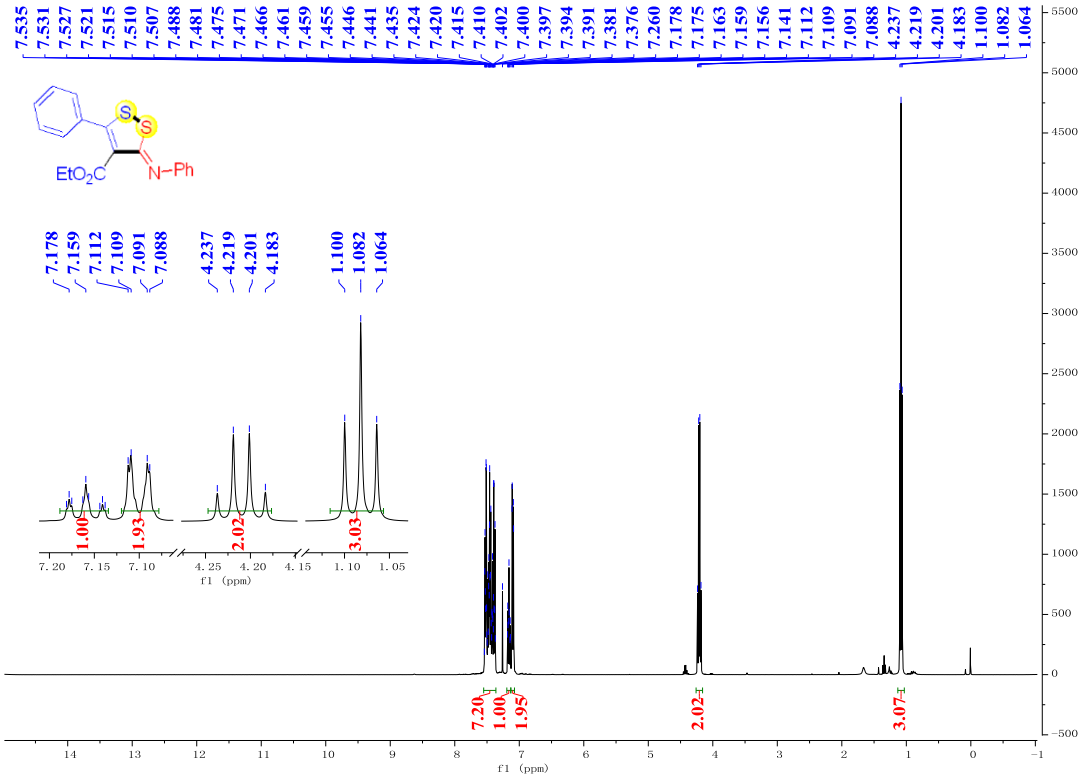
HRMS (ESI)


C:\Users\admin...2-dzy-pos-1.raw Injection 1 TOF MS ES+ MS + spectrum 0.10
234.0699
235.0754
236.0677
237.9624
m/z (Da)

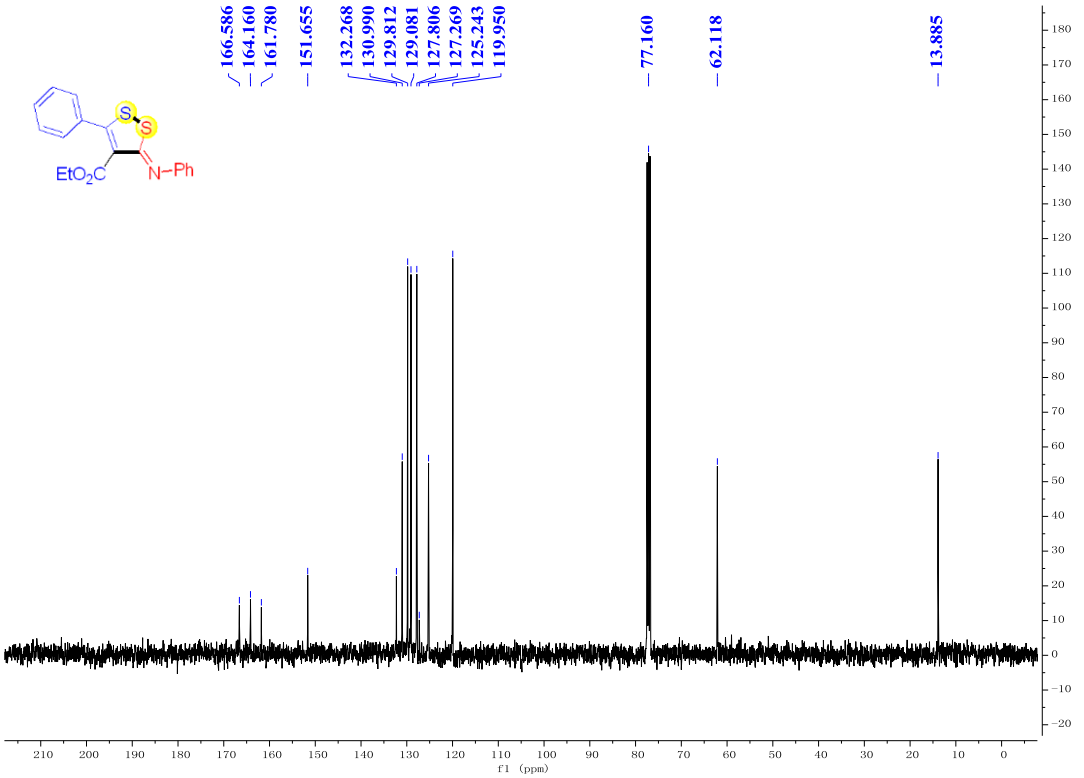
13.2 Copies of spectra of products for scope of 1,2,3-thiadiazoles

Ethyl (*Z*)-5-phenyl-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3aB**)

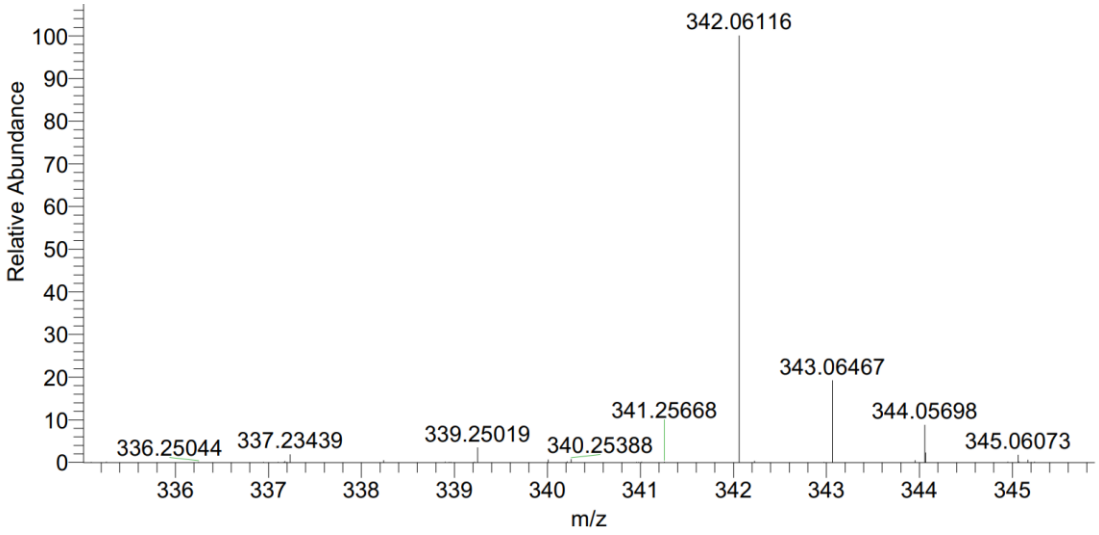
^{1}H NMR (400 MHz, $CDCl_3$)



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

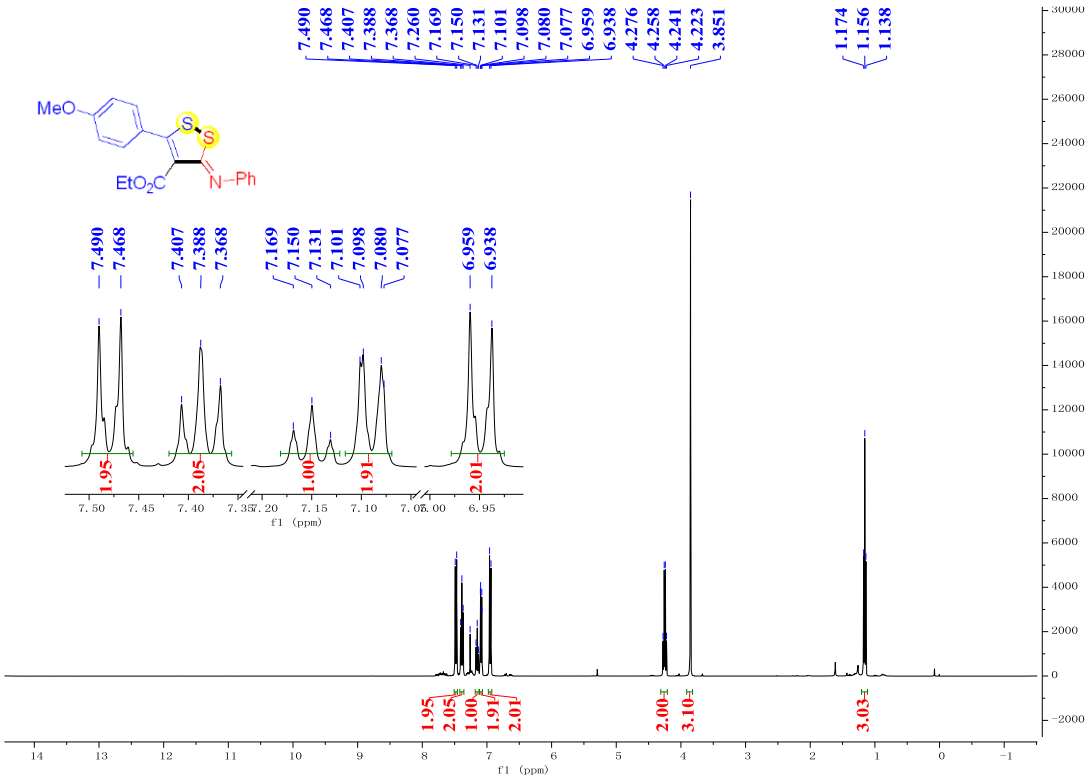


HRMS (ESI)

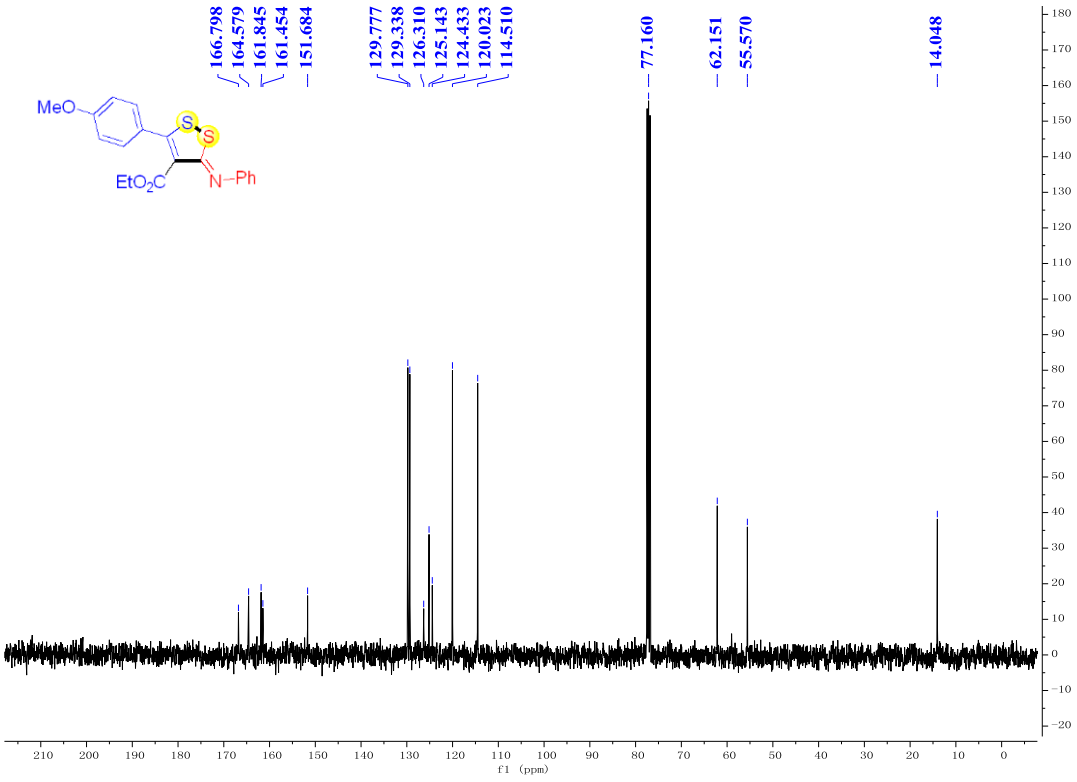

342.06116
343.06467
344.05698
345.06073
341.25668
339.25019
337.23439
336.25044
340.25388
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
336
337
338
339
340
341
342
343
344
345

Ethyl (*Z*)-5-(4-methoxyphenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3bB**)

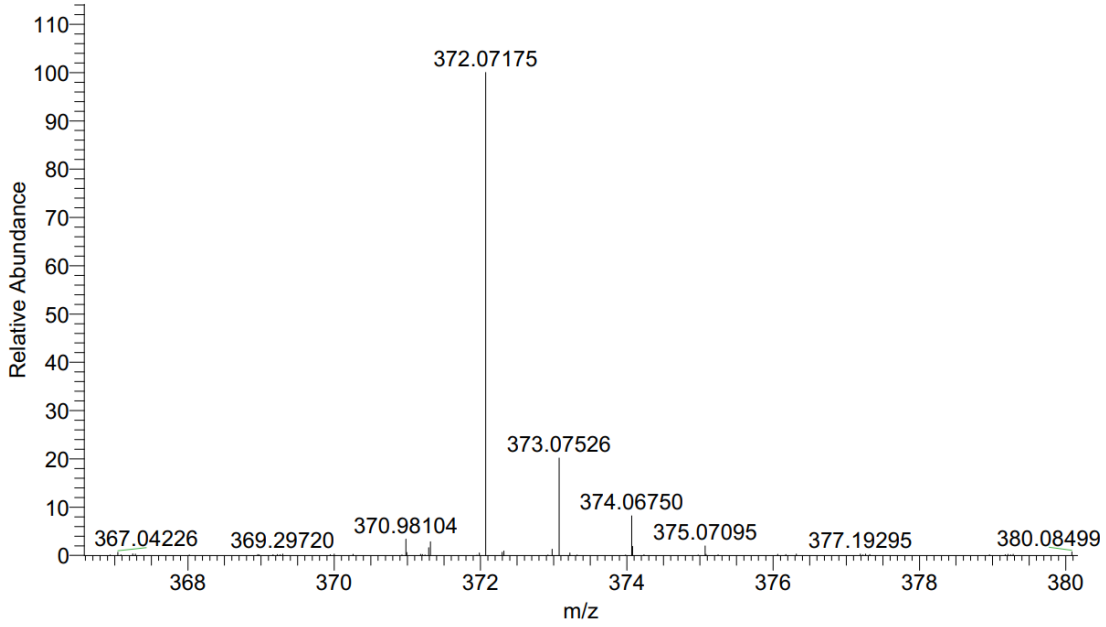
^{1}H NMR (400 MHz, $CDCl_3$)



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

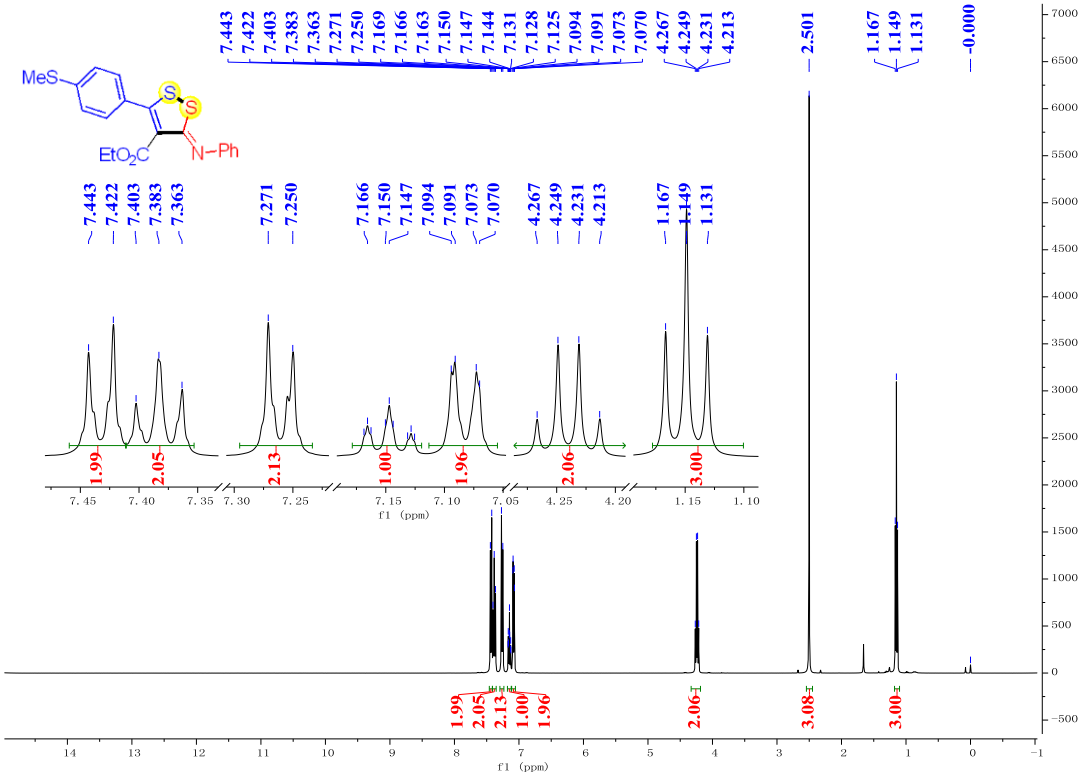


HRMS (ESI)

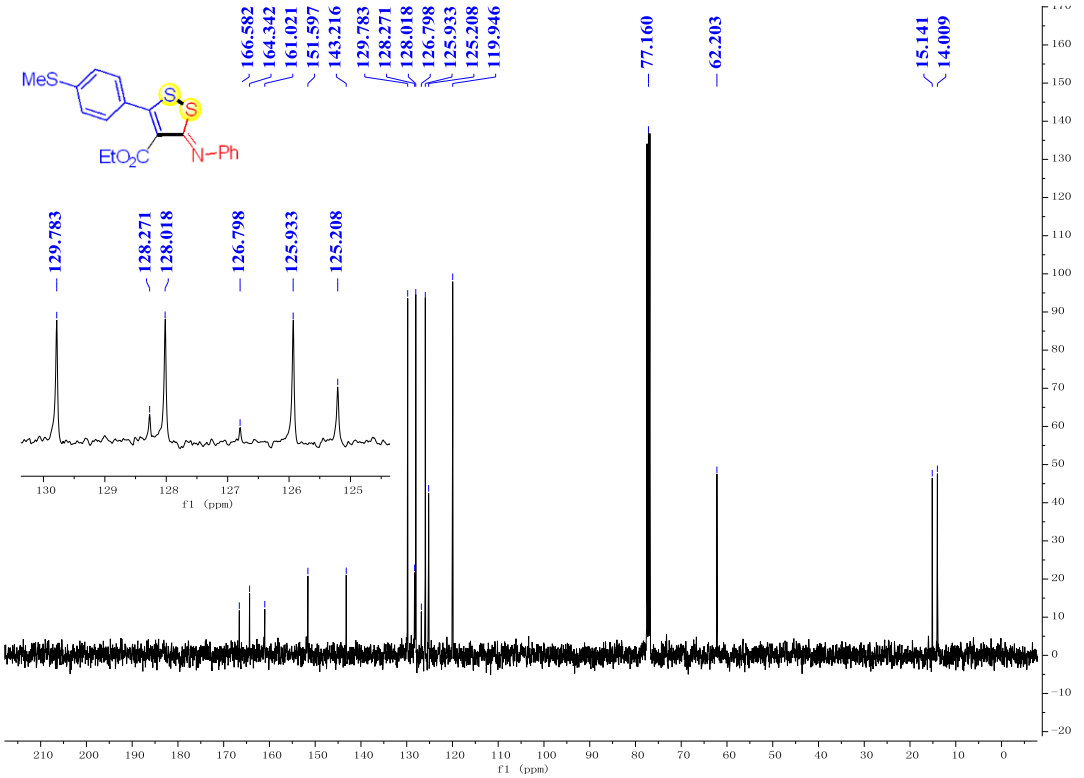

372.07175
373.07526
374.06750
375.07095
367.04226
369.29720
370.98104
377.19295
380.08499
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
100
110
368
370
372
374
376
378
380

Ethyl (*Z*)-5-(4-(methylthio)phenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3cB**)

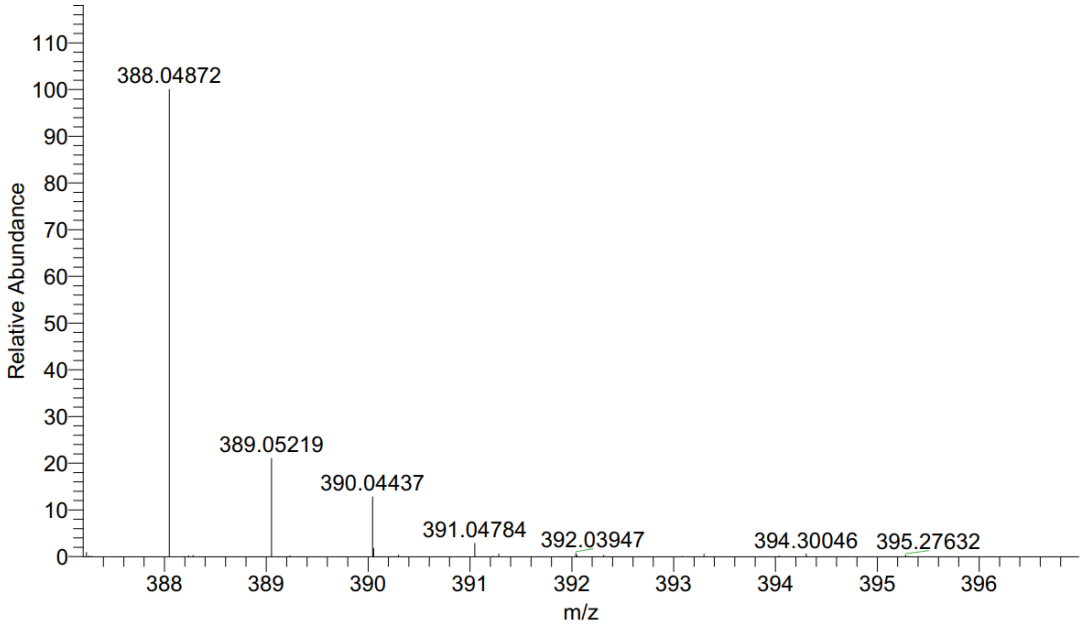
^{1}H NMR (400 MHz, $CDCl_3$)



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

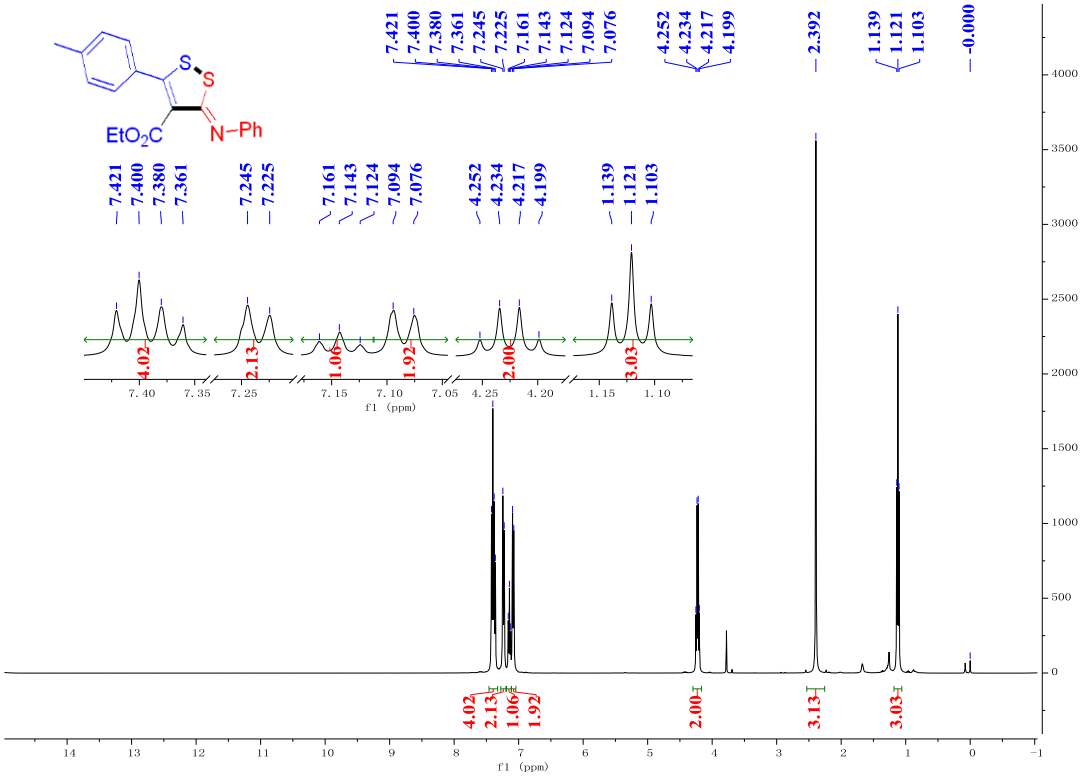


HRMS (ESI)

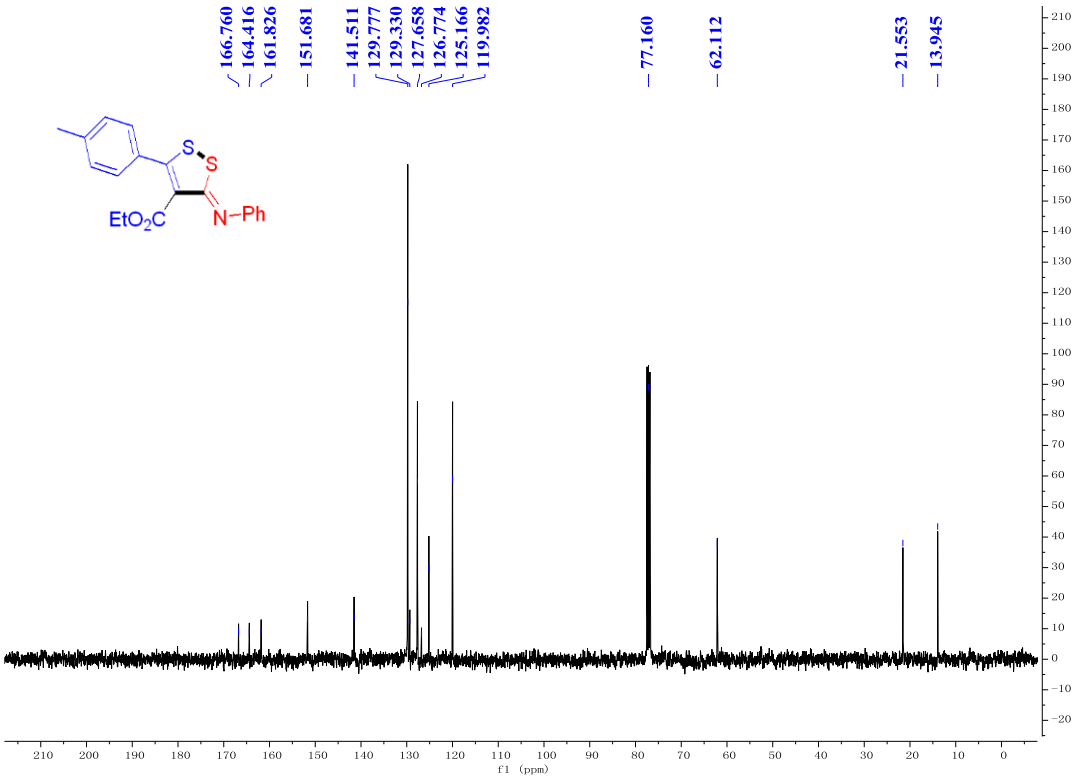

388.04872
389.05219
390.04437
391.04784
392.03947
394.30046
395.27632
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
100
110
388
389
390
391
392
393
394
395
396

Ethyl (*Z*)-3-(phenylimino)-5-(*p*-tolyl)-3*H*-1,2-dithiole-4-carboxylate (**3dB**)

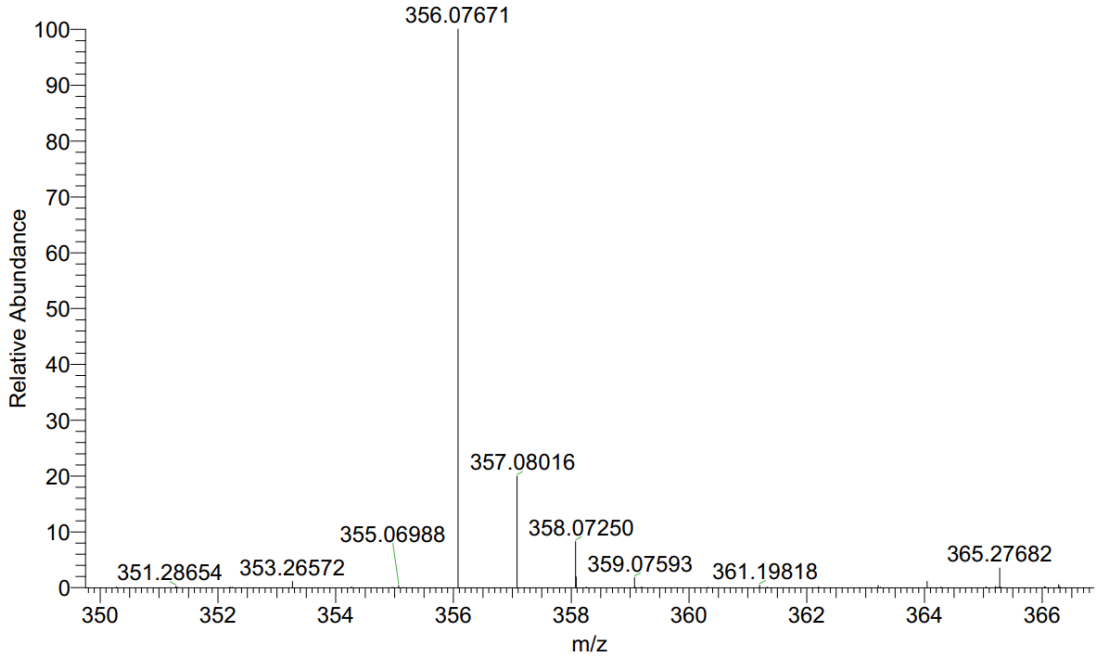
^{1}H NMR (400 MHz, $CDCl_3$)



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

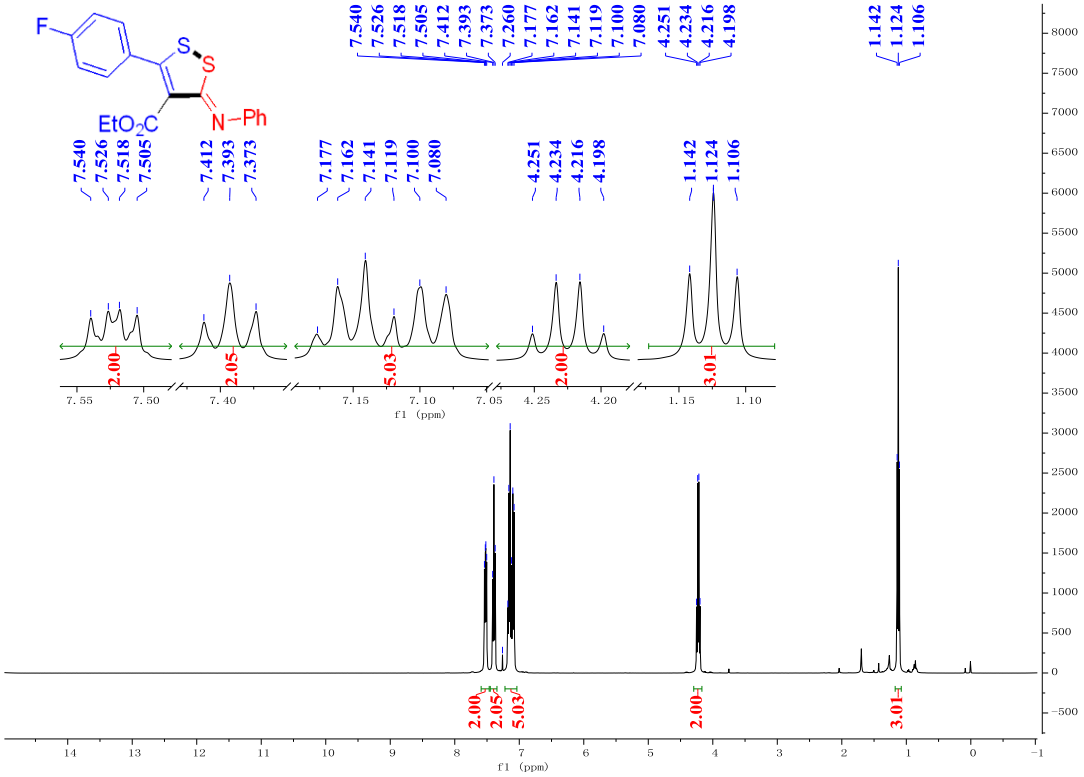


HRMS (ESI)

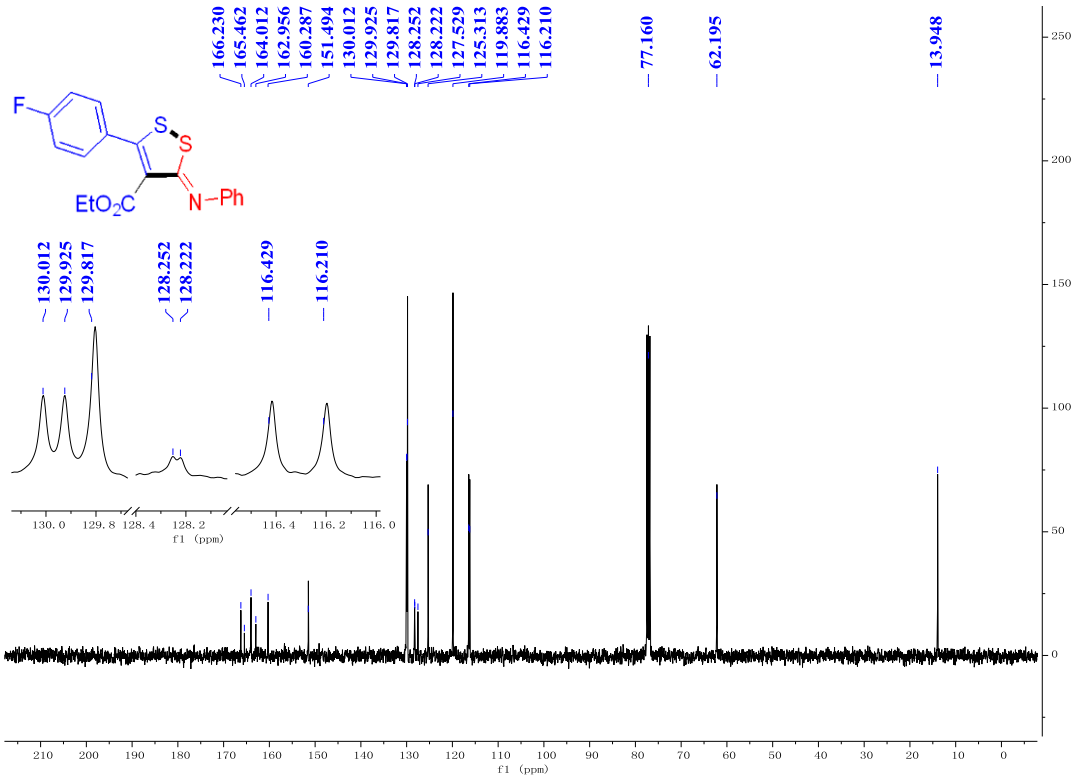

356.07671
357.08016
358.07250
355.06988
359.07593
361.19818
365.27682
351.28654
353.26572
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
350
352
354
356
358
360
362
364
366

Ethyl (*Z*)-5-(4-fluorophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3eB**)

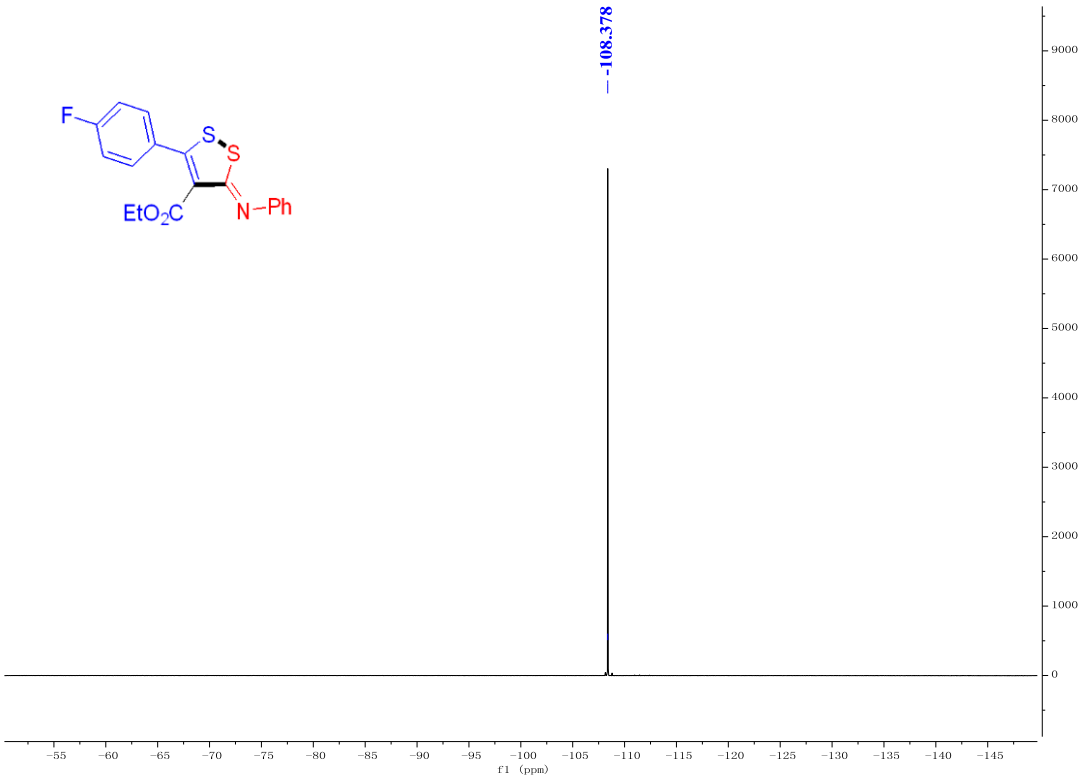
^{1}H NMR (400 MHz, $CDCl_3$)



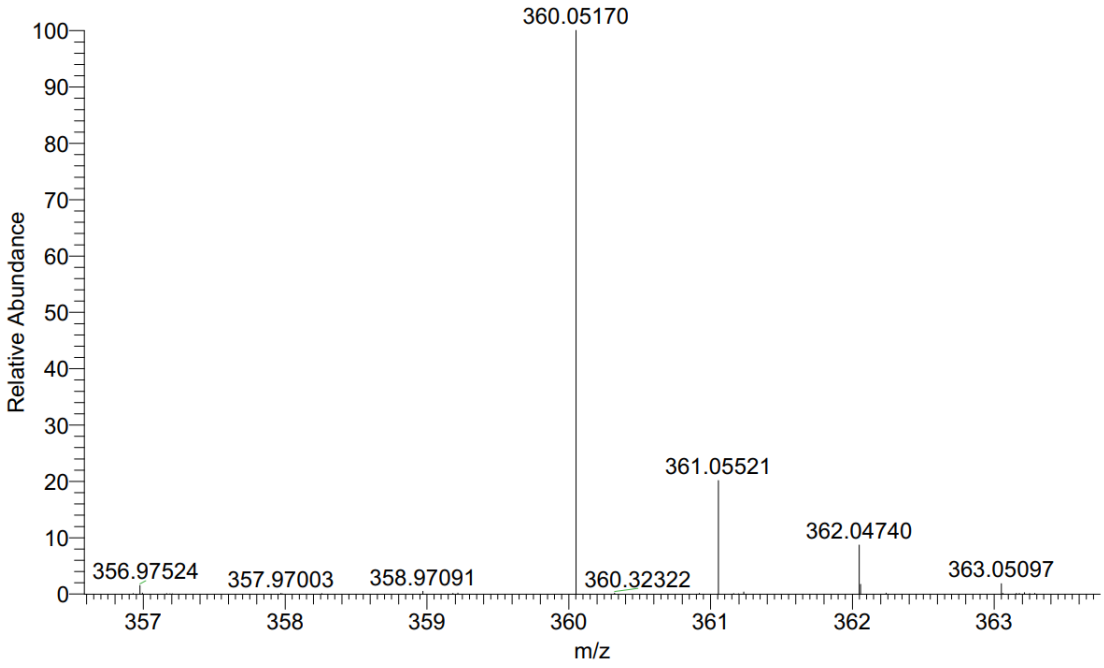
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)

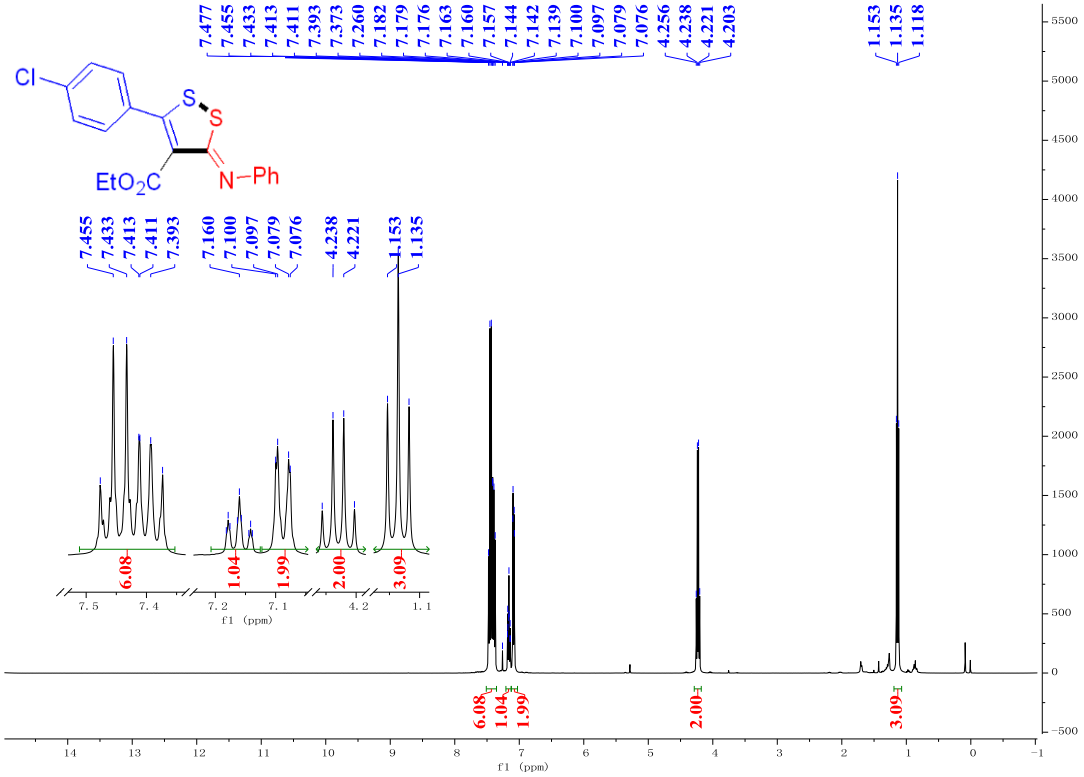


HRMS (ESI)

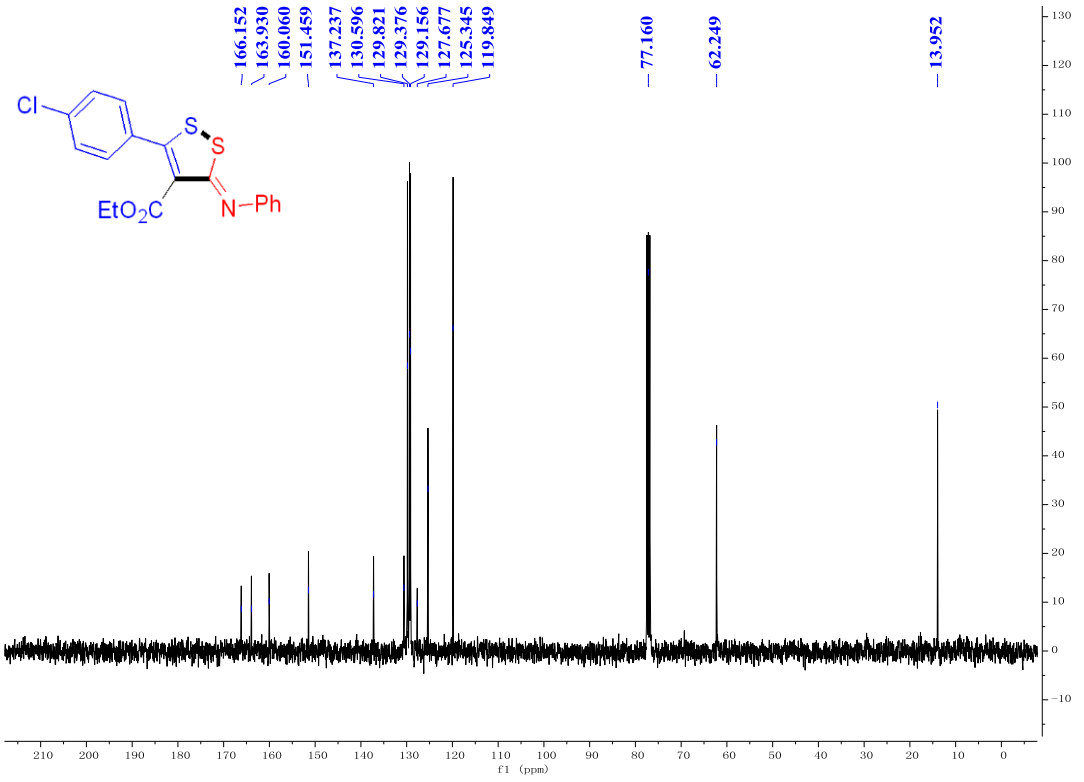


Ethyl (*Z*)-5-(4-chlorophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3fB**)

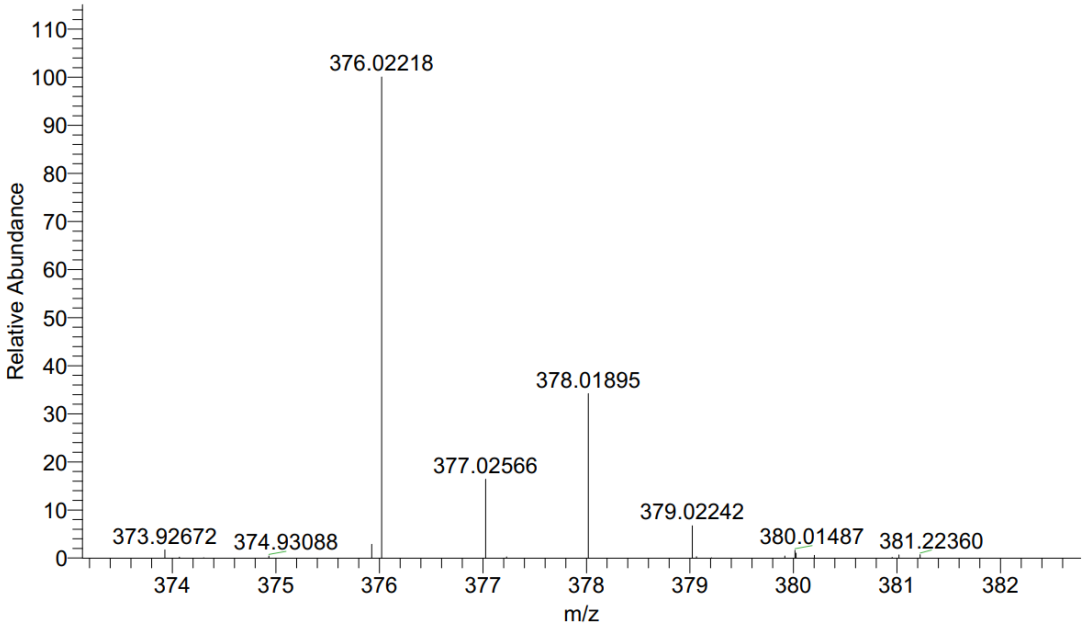
^{1}H NMR (400 MHz, $CDCl_3$)



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

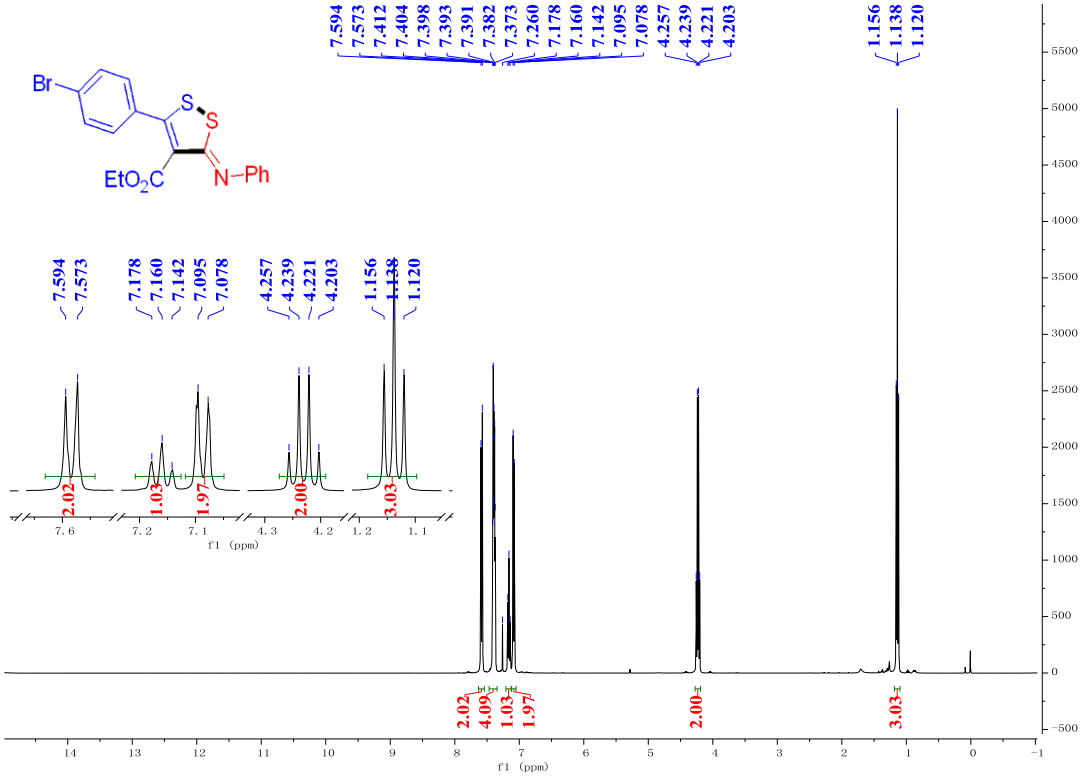


HRMS (ESI)

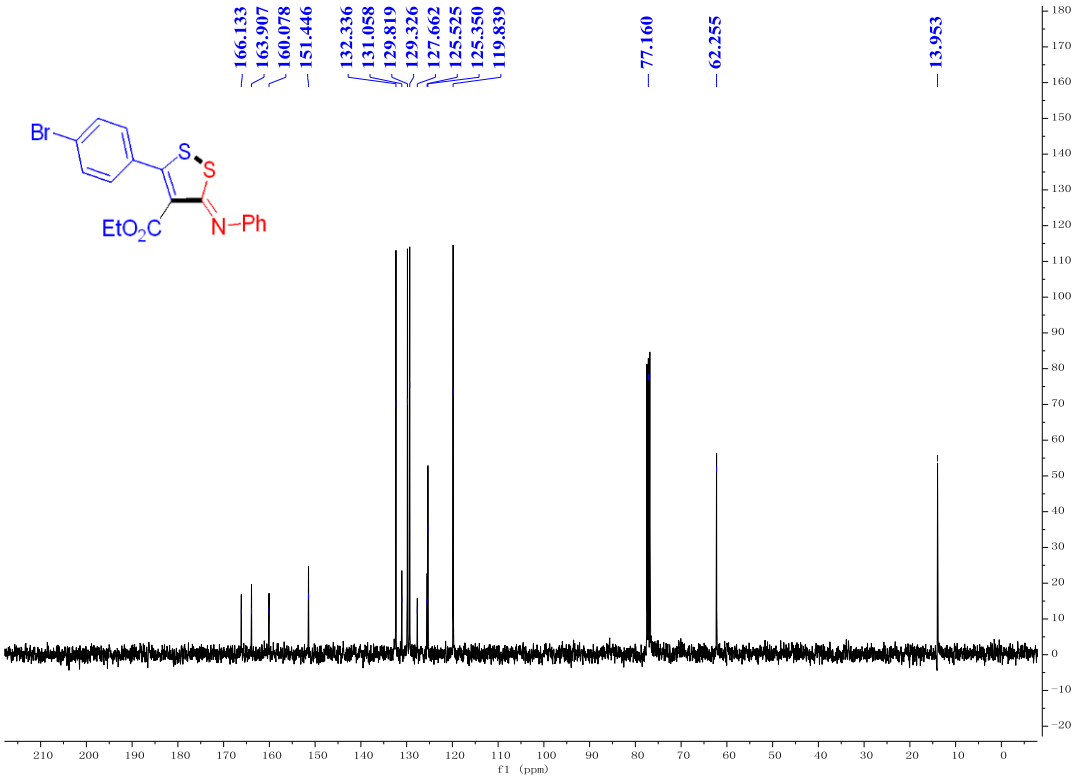

376.02218
378.01895
377.02566
379.02242
373.92672
374.93088
380.01487
381.22360
Relative Abundance
m/z
110
100
90
80
70
60
50
40
30
20
10
0
374
375
376
377
378
379
380
381
382

Ethyl (*Z*)-5-(4-bromophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3gB**)

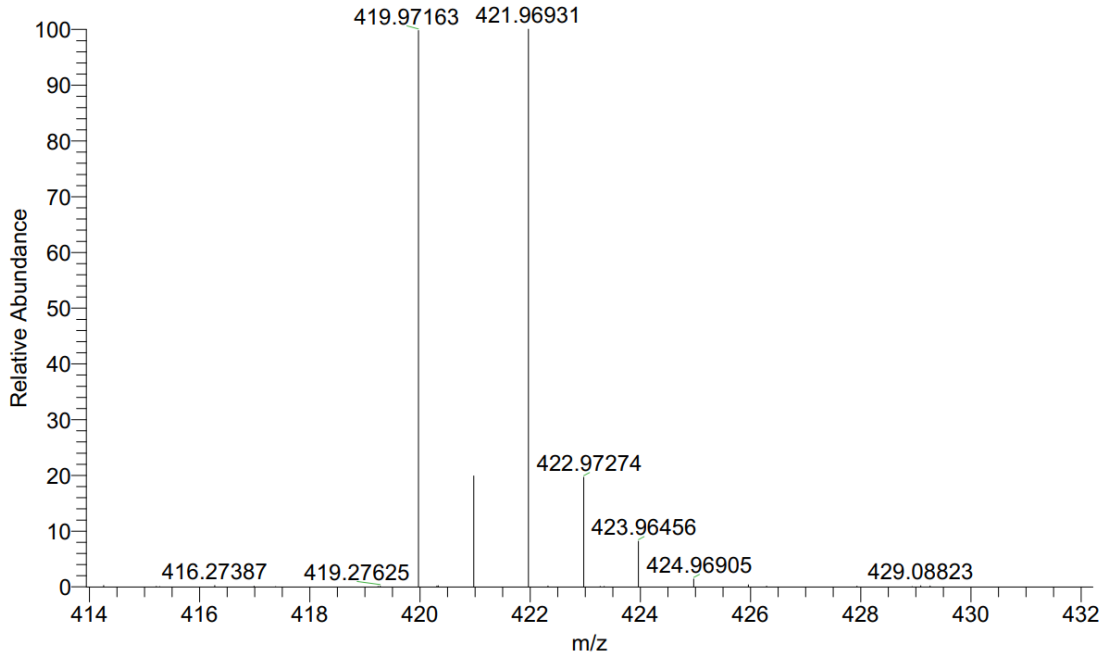
^{1}H NMR (400 MHz, $CDCl_3$)



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

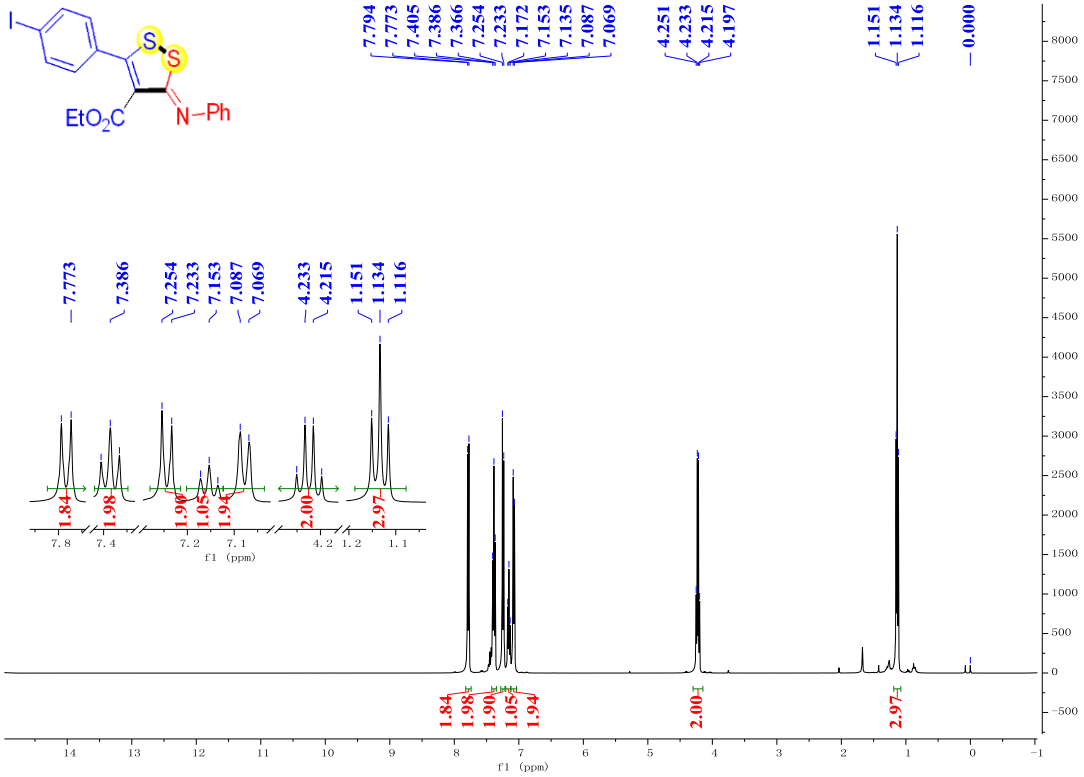


HRMS (ESI)

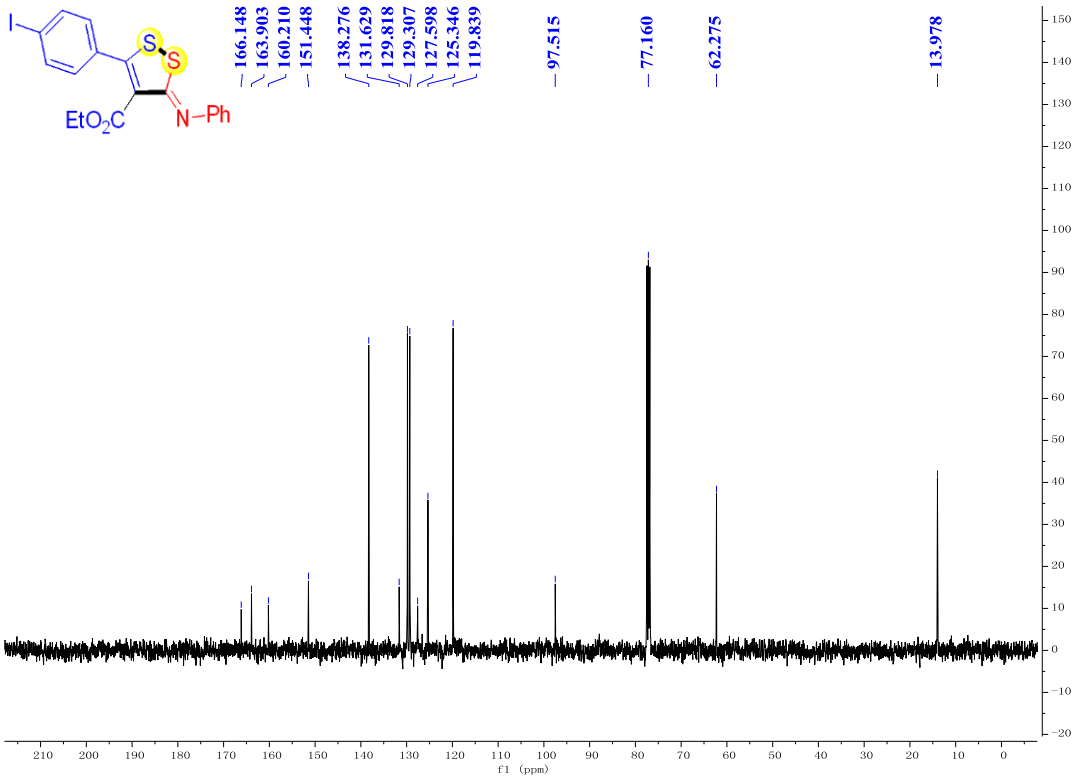

419.97163
421.96931
422.97274
423.96456
424.96905
416.27387
419.27625
429.08823
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
414
416
418
420
422
424
426
428
430
432

Ethyl (*Z*)-5-(4-iodophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3hB**)

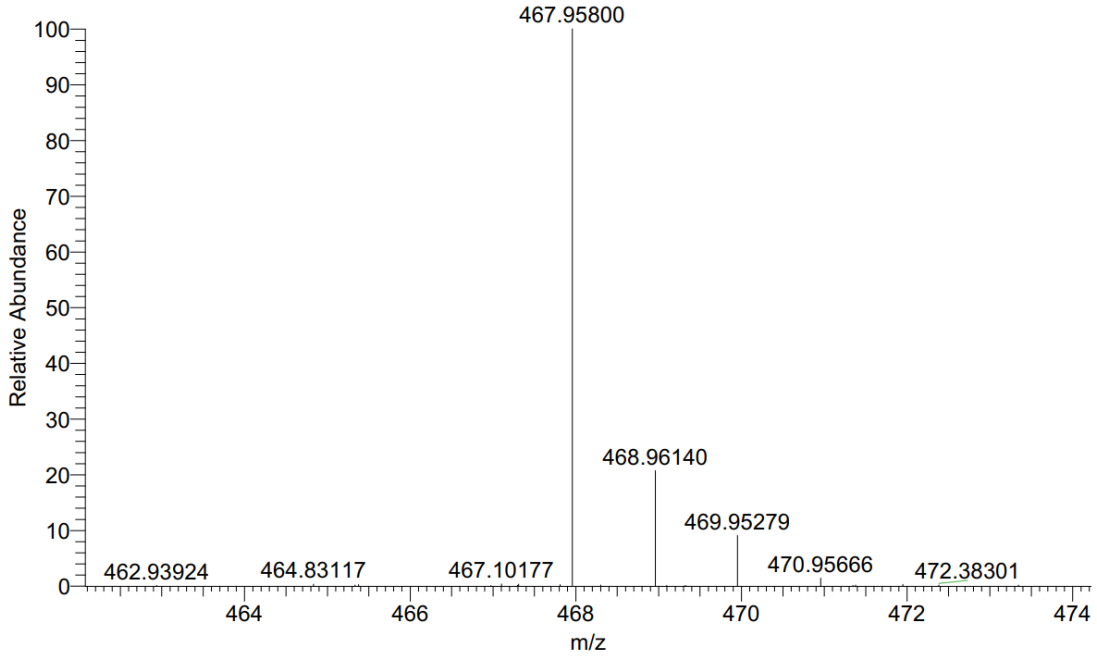
^{1}H NMR (400 MHz, $CDCl_3$)



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

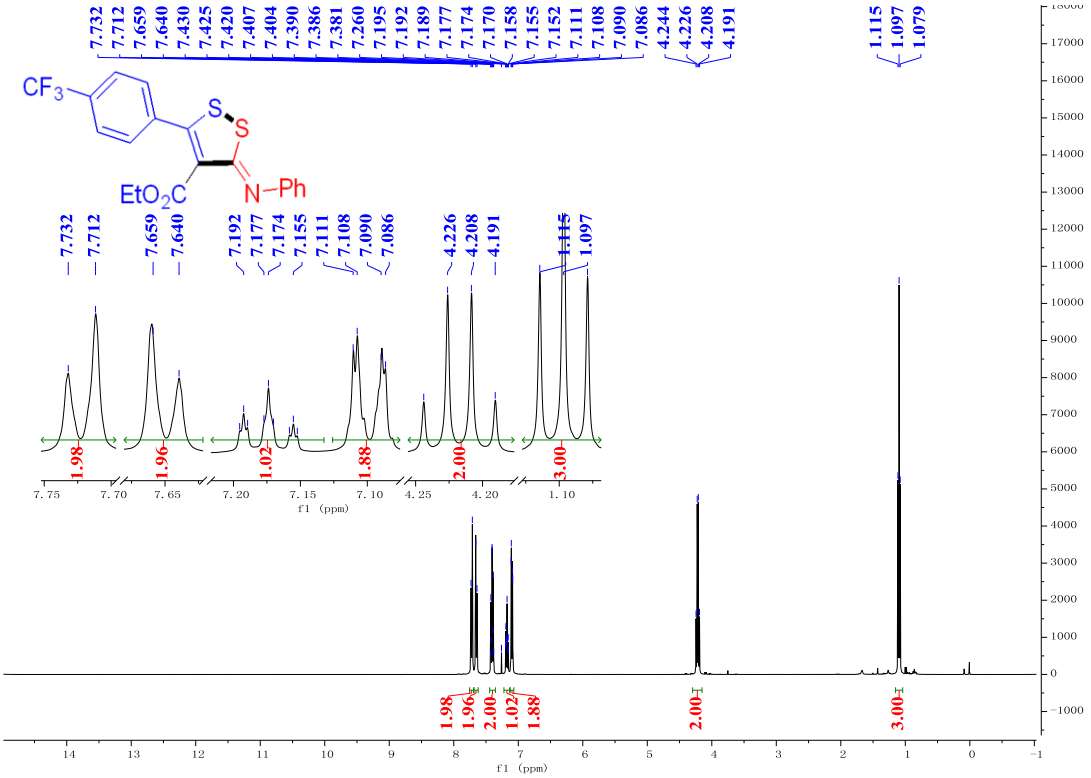


HRMS (ESI)

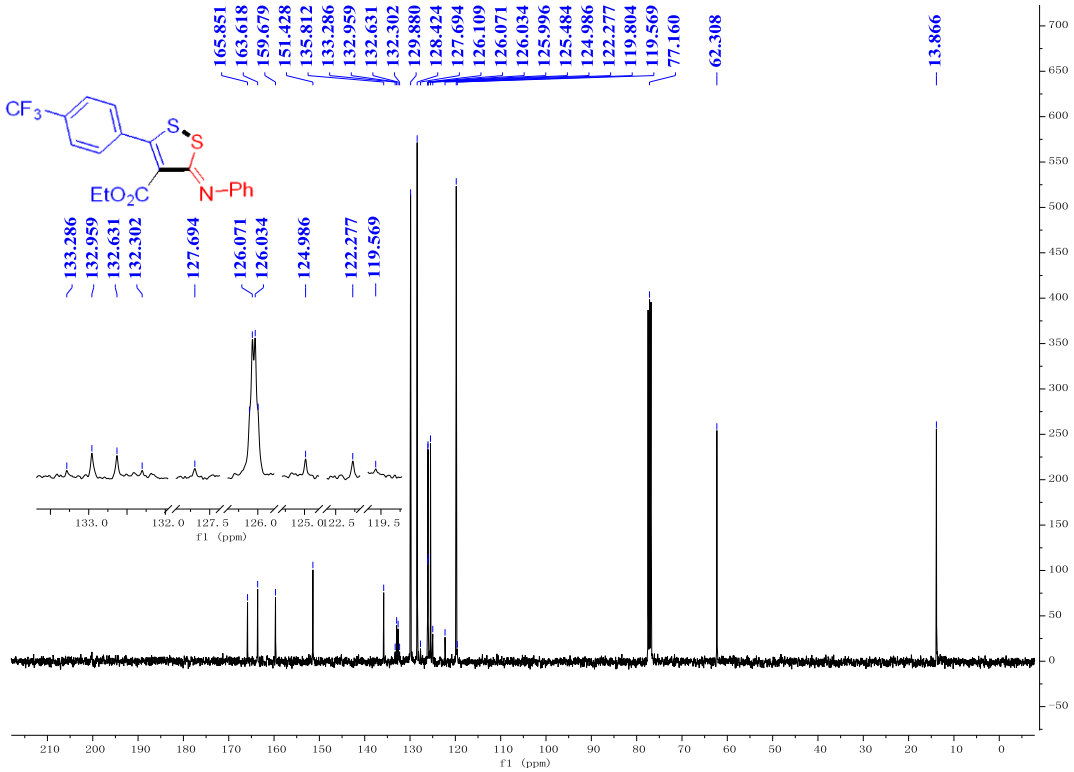

467.95800
468.96140
469.95279
470.95666
472.38301
462.93924
464.83117
467.10177
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
464
466
468
470
472
474

Ethyl (*Z*)-3-(phenylimino)-5-(4-(trifluoromethyl)phenyl)-3*H*-1,2-dithiole-4-carboxylate (**3iB**)

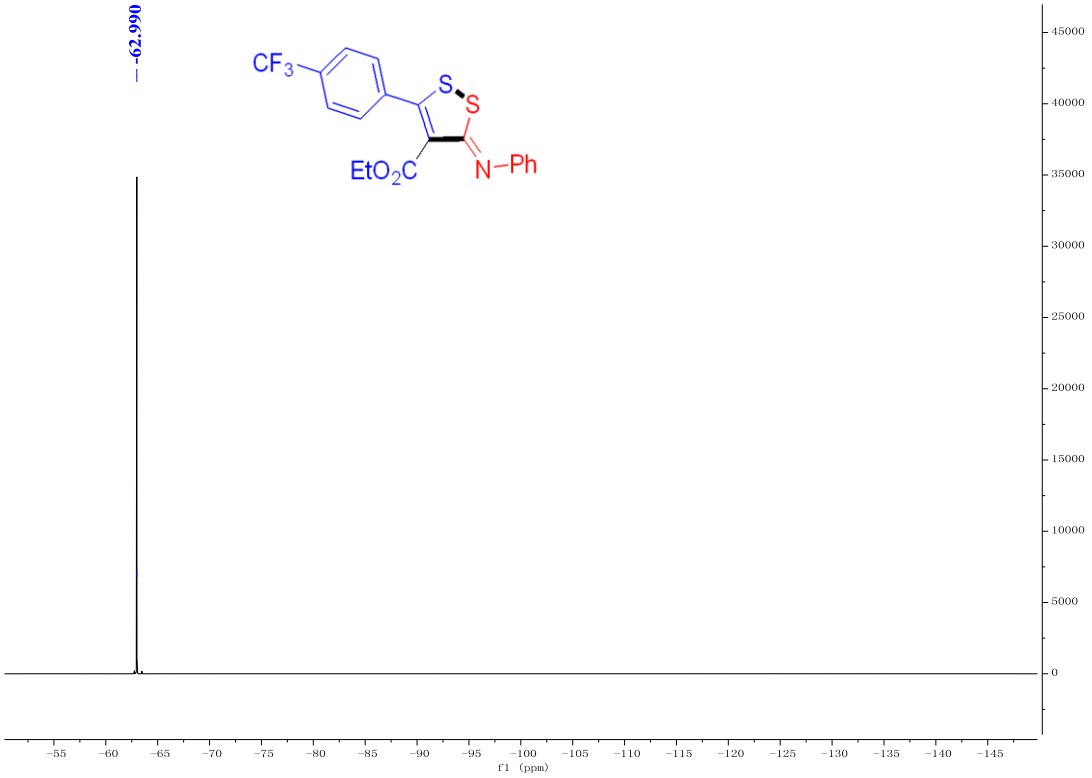
^{1}H NMR (400 MHz, $CDCl_3$)



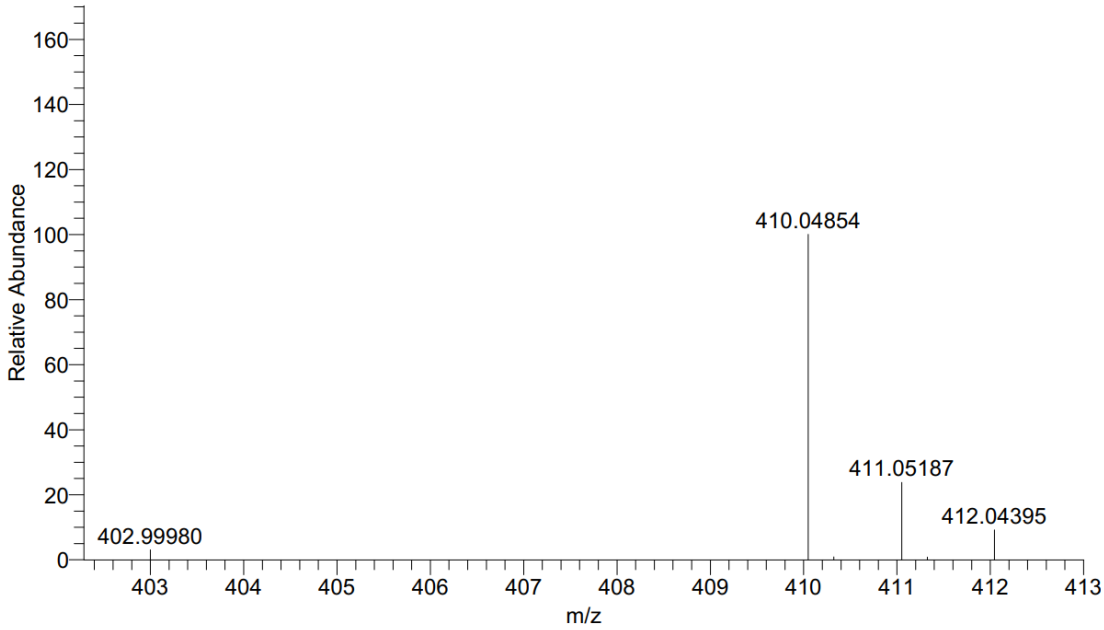
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)

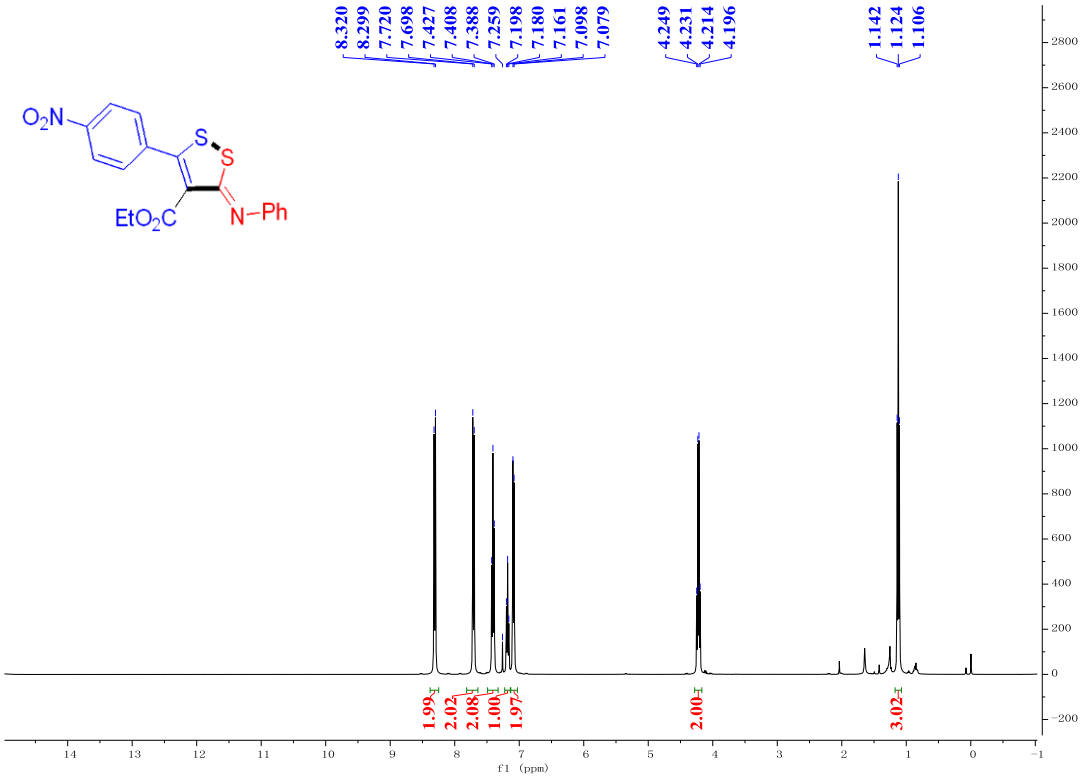


HRMS (ESI)

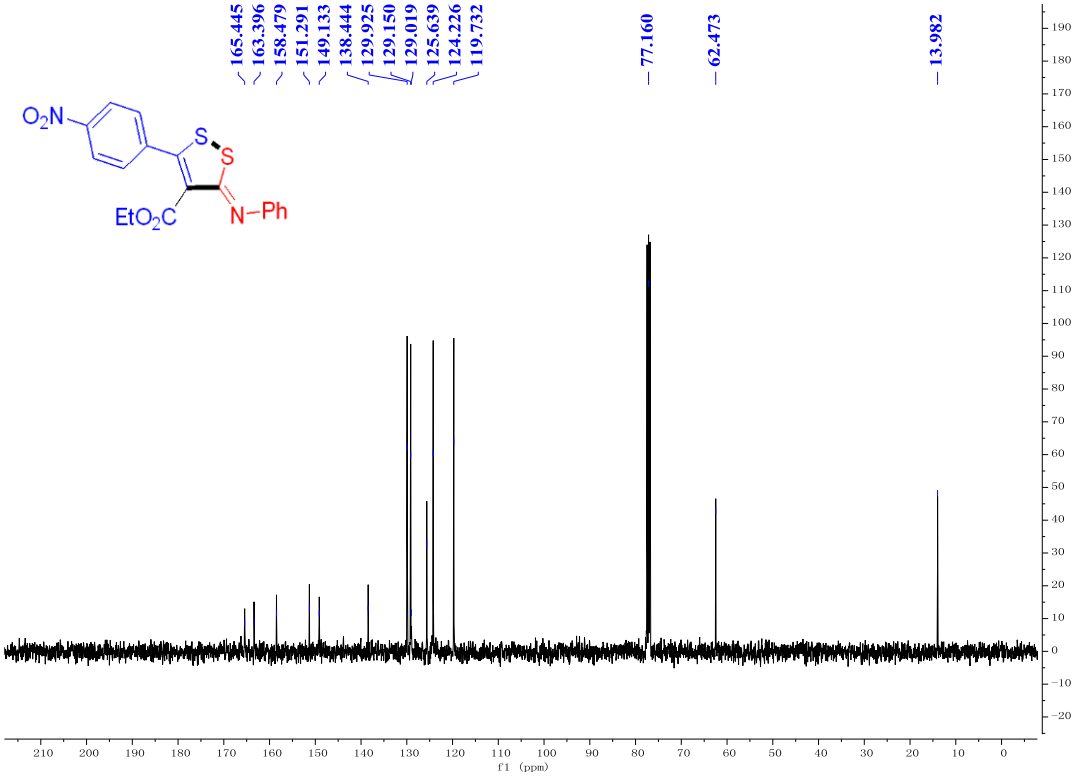


Ethyl (*Z*)-5-(4-nitrophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3jB**)

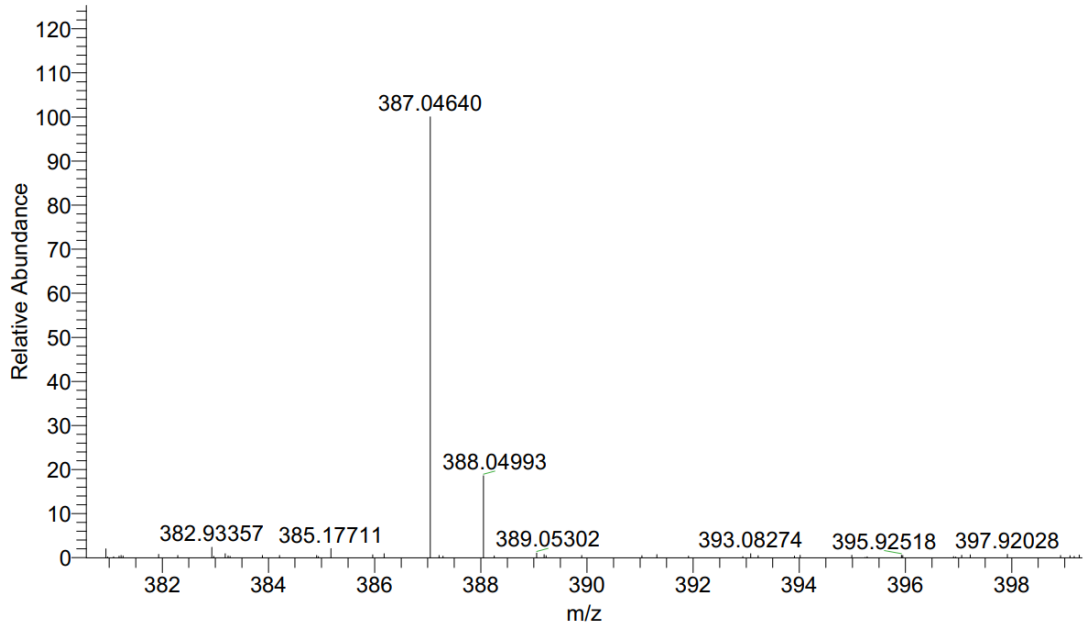
^{1}H NMR (400 MHz, $CDCl_3$)



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

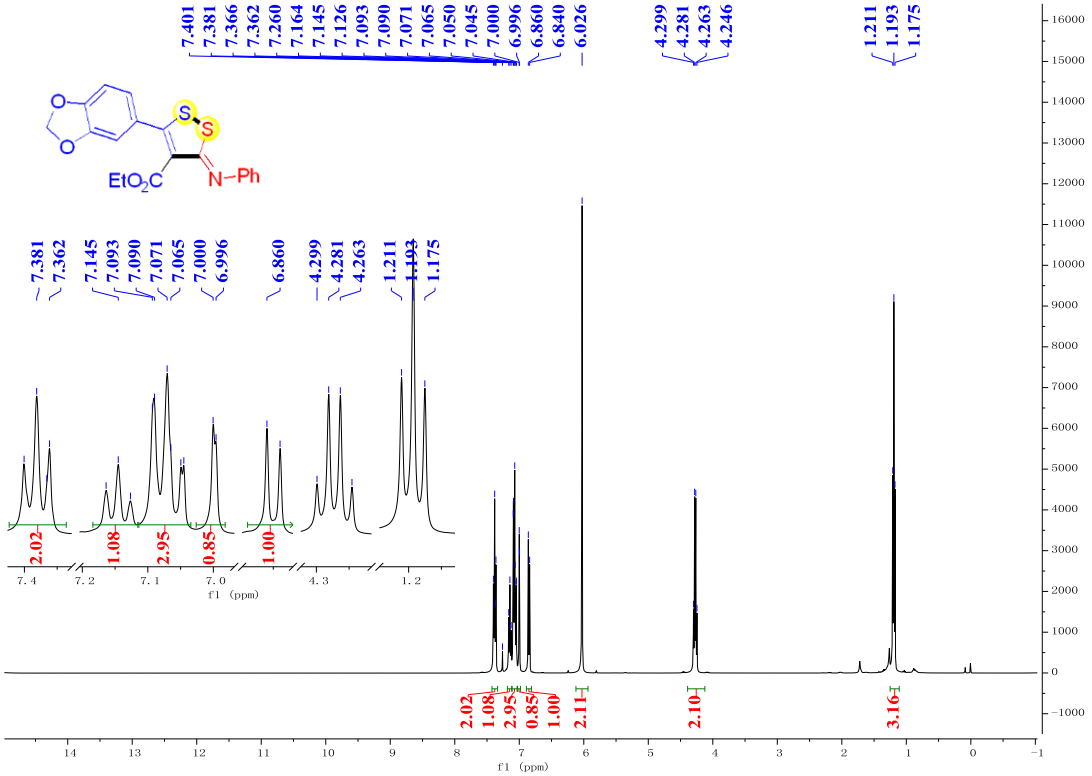


HRMS (ESI)

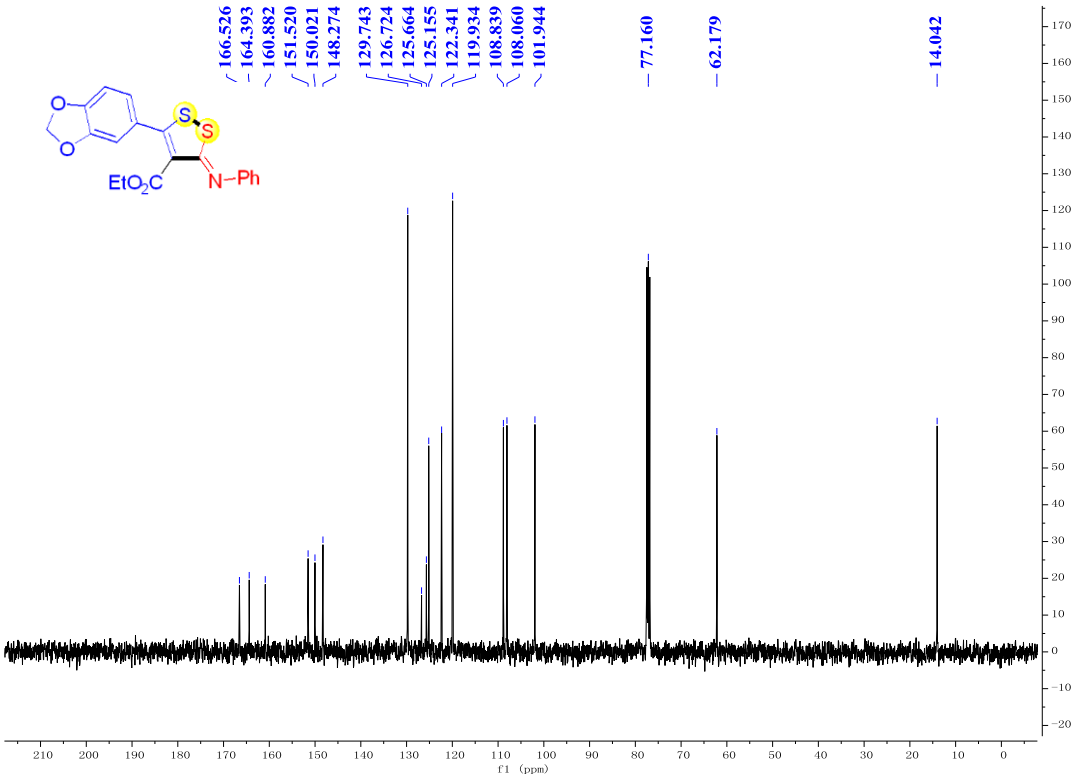

Relative Abundance
m/z
387.04640
388.04993
382.93357
385.17711
389.05302
393.08274
395.92518
397.92028

Ethyl (*Z*)-5-(benzo[*d*][1,3]dioxol-5-yl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3kB**)

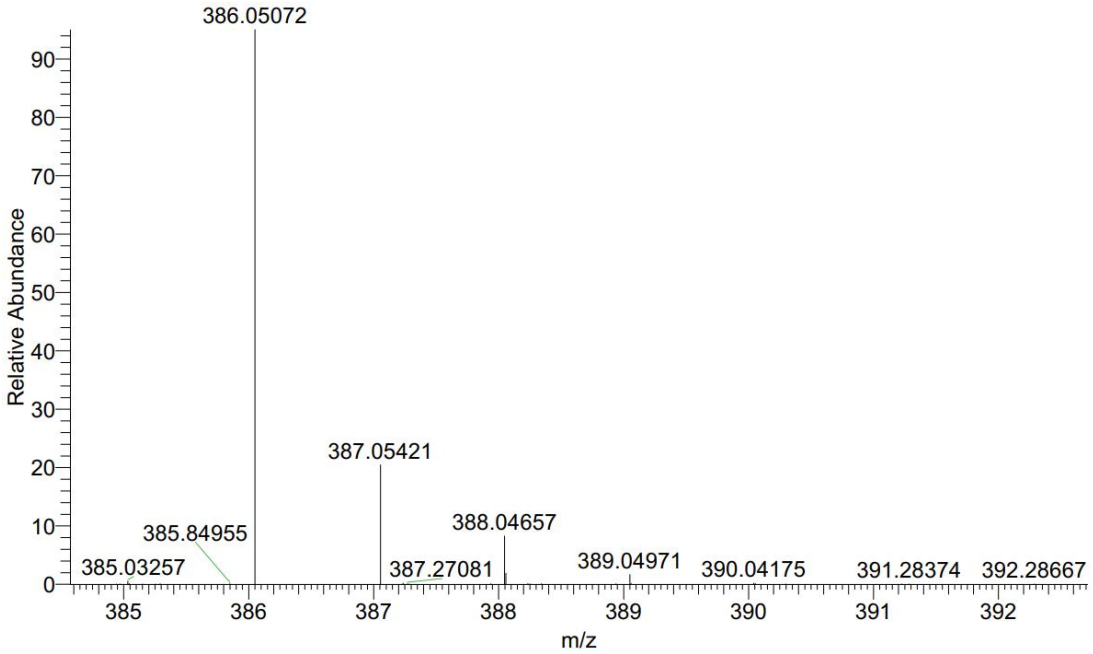
^{1}H NMR (400 MHz, $CDCl_3$)



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

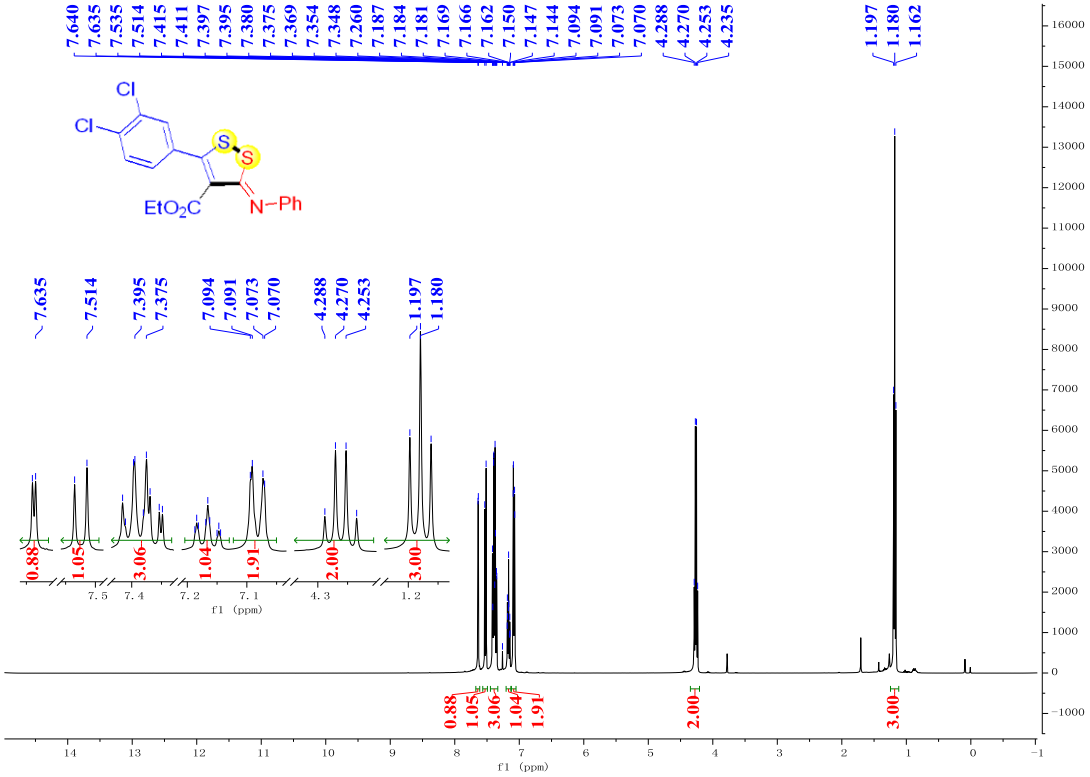


HRMS (ESI)

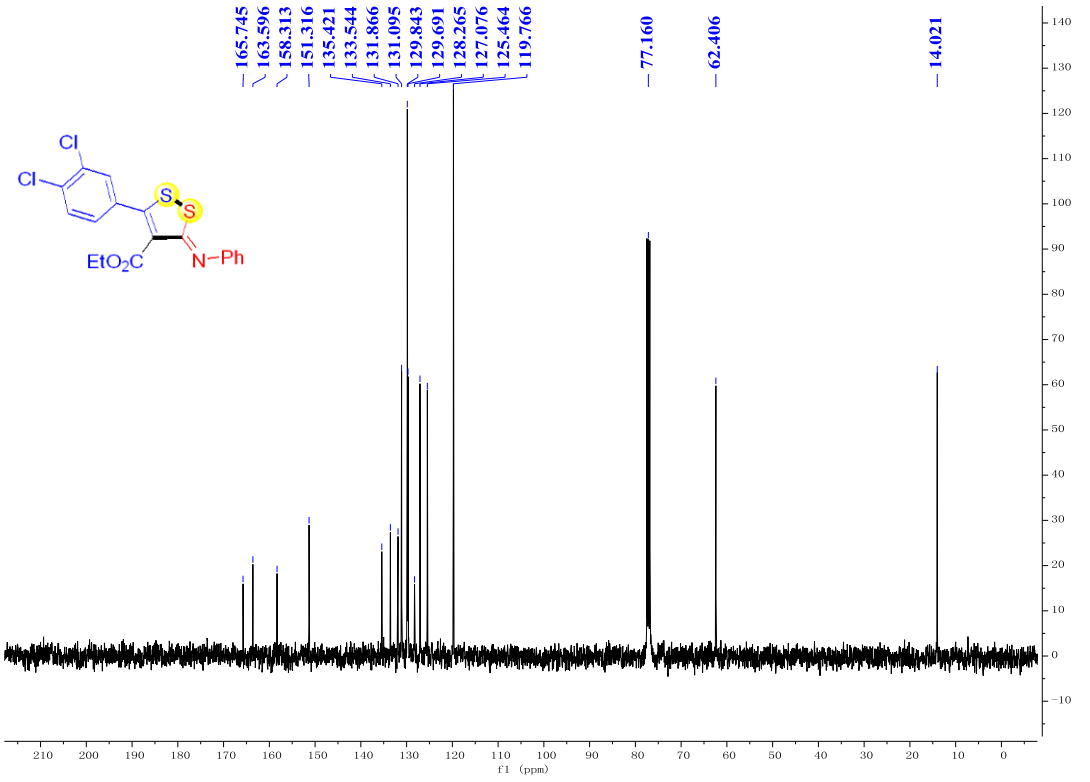

386.05072
387.05421
388.04657
385.84955
385.03257
387.27081
389.04971
390.04175
391.28374
392.28667
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
385
386
387
388
389
390
391
392

Ethyl (*Z*)-5-(3,4-dichlorophenyl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3lB**)

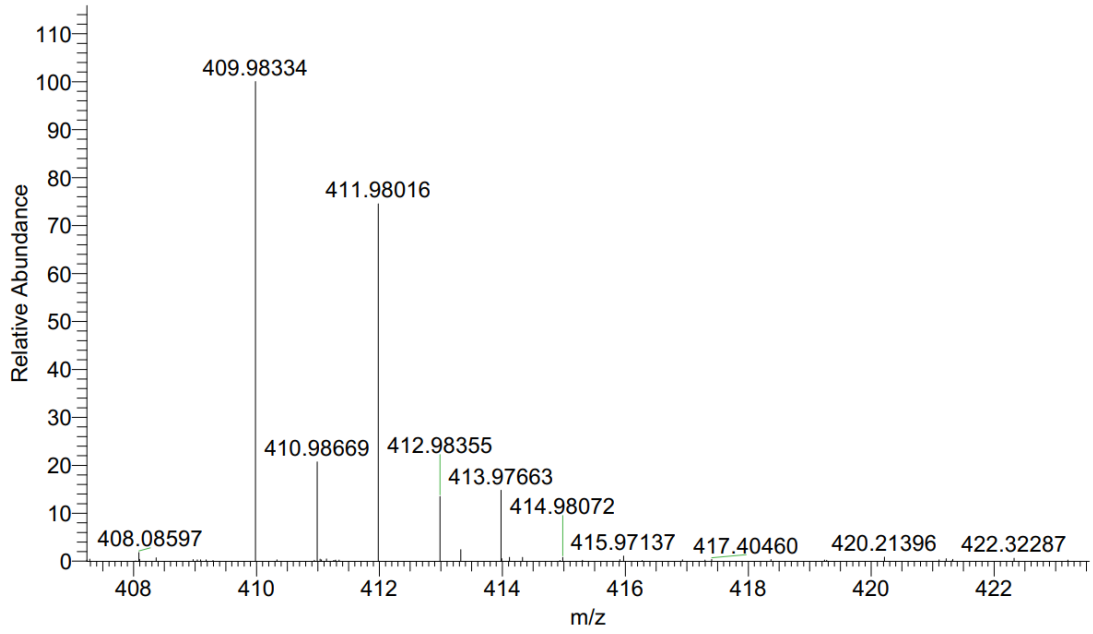
^{1}H NMR (400 MHz, $CDCl_3$)



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

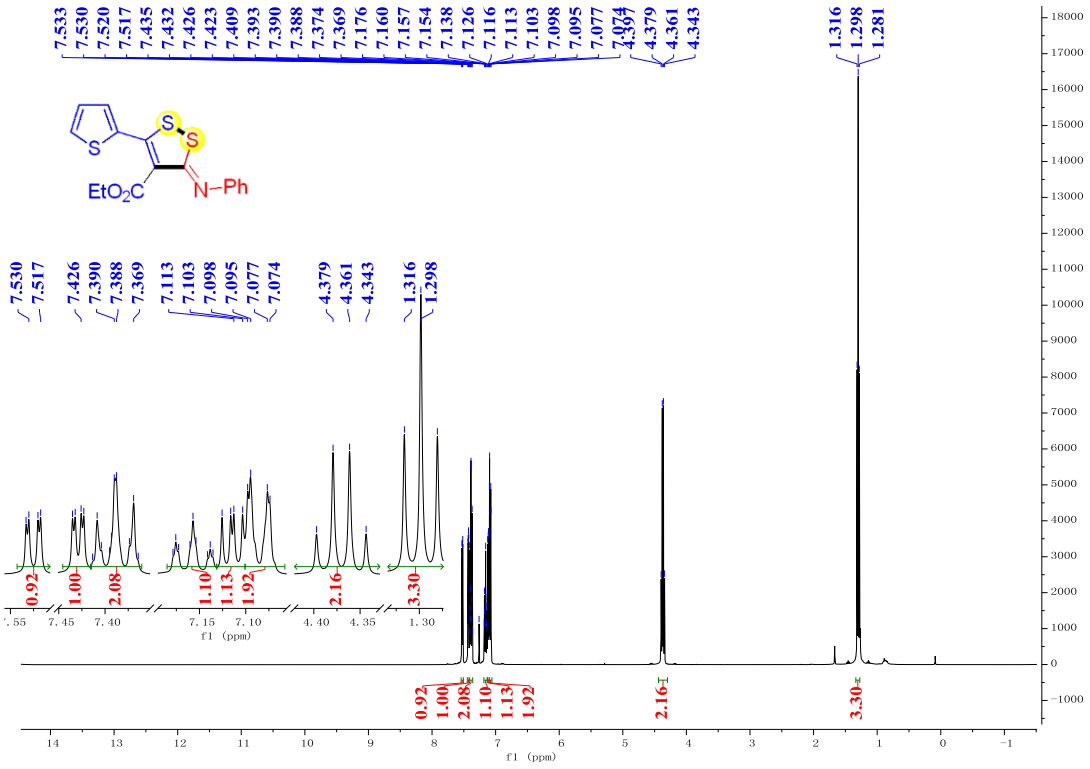


HRMS (ESI)

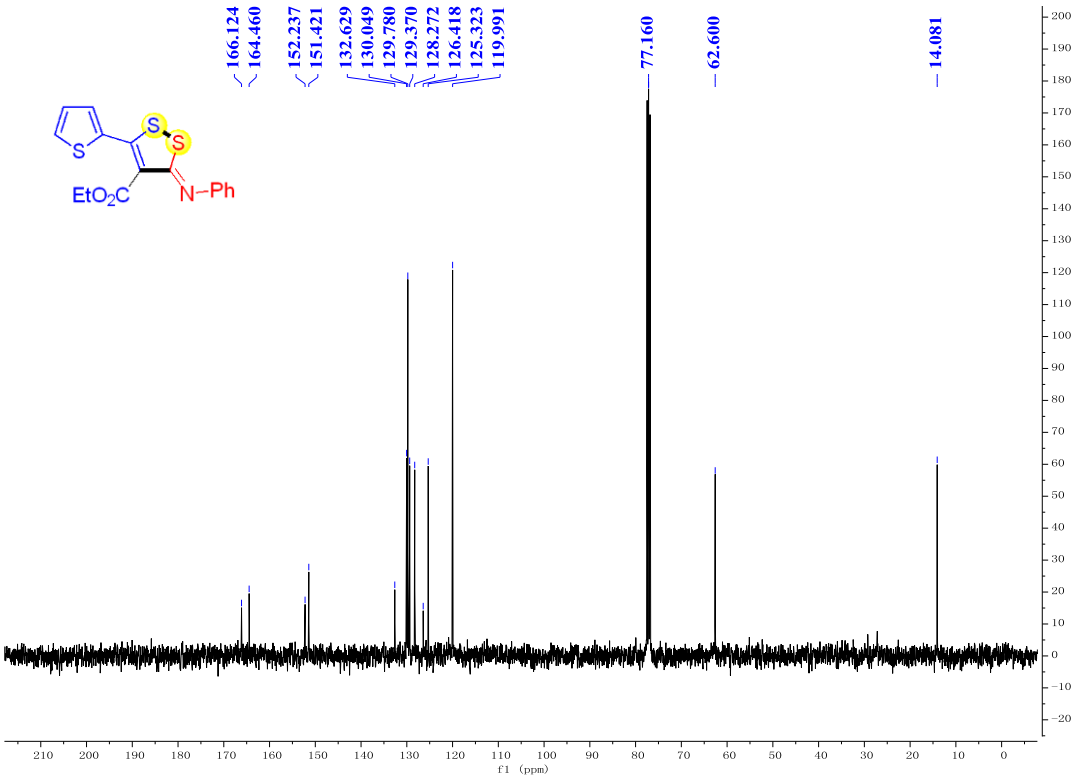

Relative Abundance
m/z
409.98334
411.98016
410.98669
412.98355
413.97663
414.98072
408.08597
415.97137
417.40460
420.21396
422.32287

Ethyl (*Z*)-3-(phenylimino)-5-(thiophen-2-yl)-3*H*-1,2-dithiole-4-carboxylate (**3mB**)

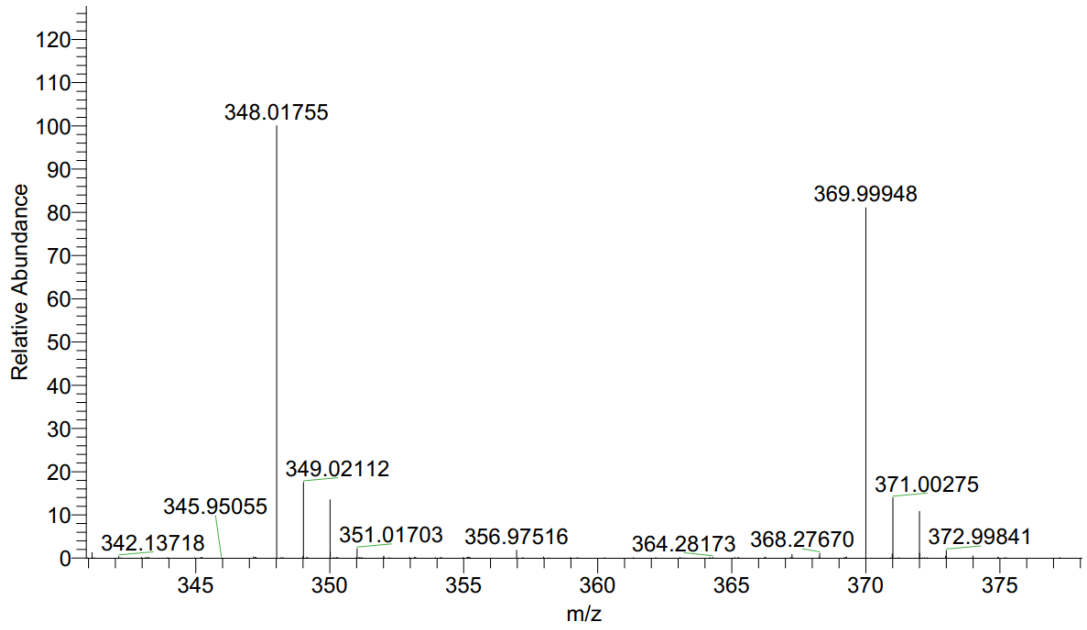
^{1}H NMR (400 MHz, $CDCl_3$)



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

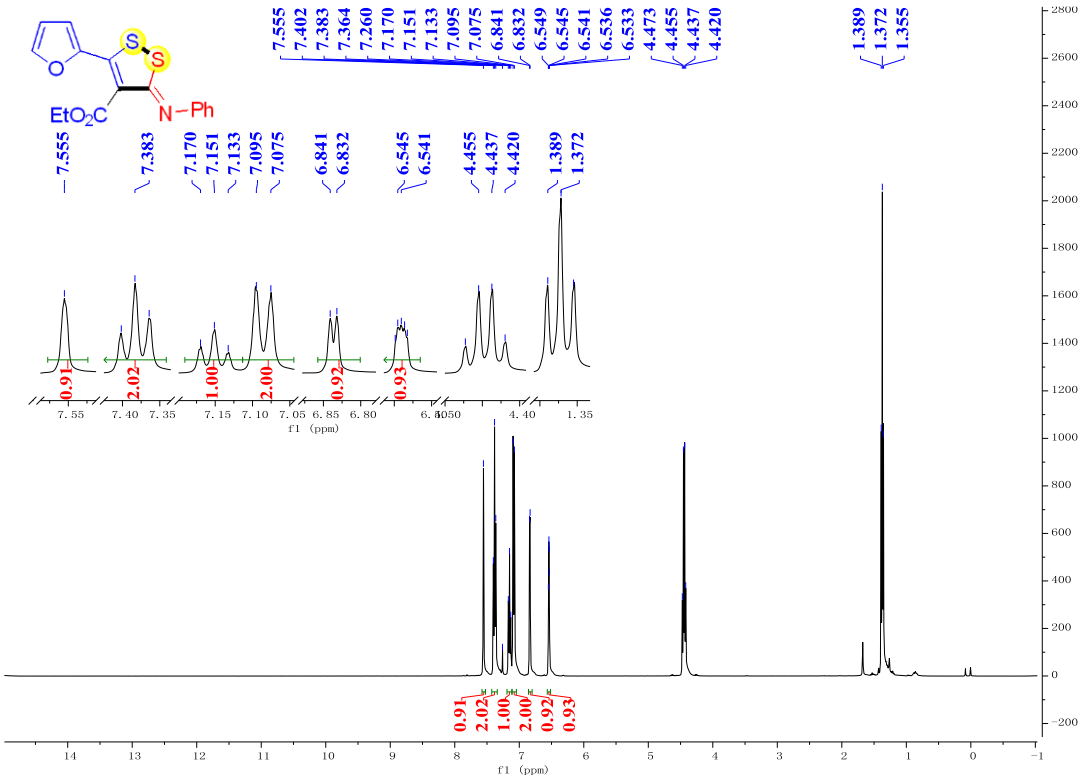


HRMS (ESI)

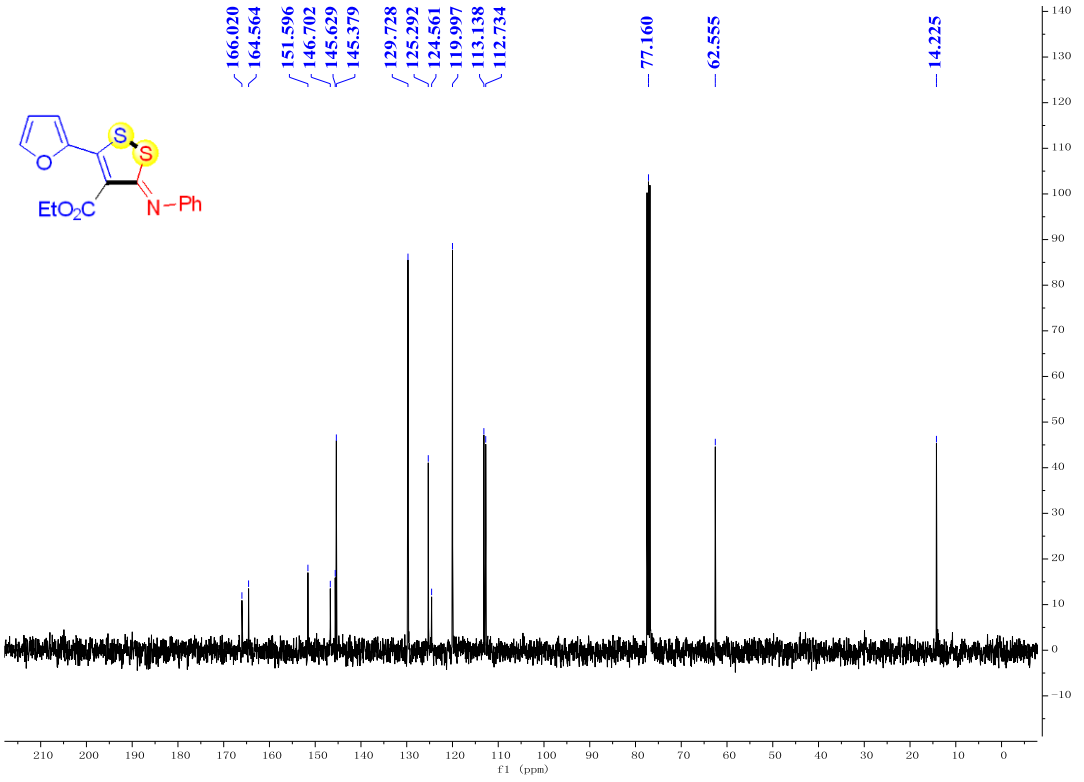

Relative Abundance
m/z
348.01755
369.99948
349.02112
371.00275
345.95055
342.13718
351.01703
356.97516
364.28173
368.27670
372.99841

Ethyl (*Z*)-5-(furan-2-yl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3nB**)

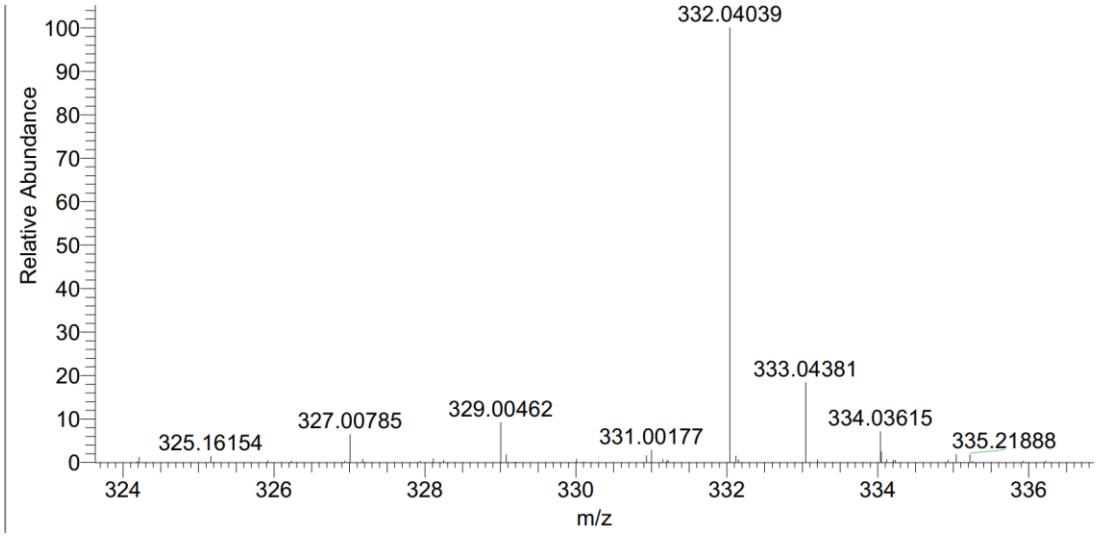
^{1}H NMR (400 MHz, $CDCl_3$)



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

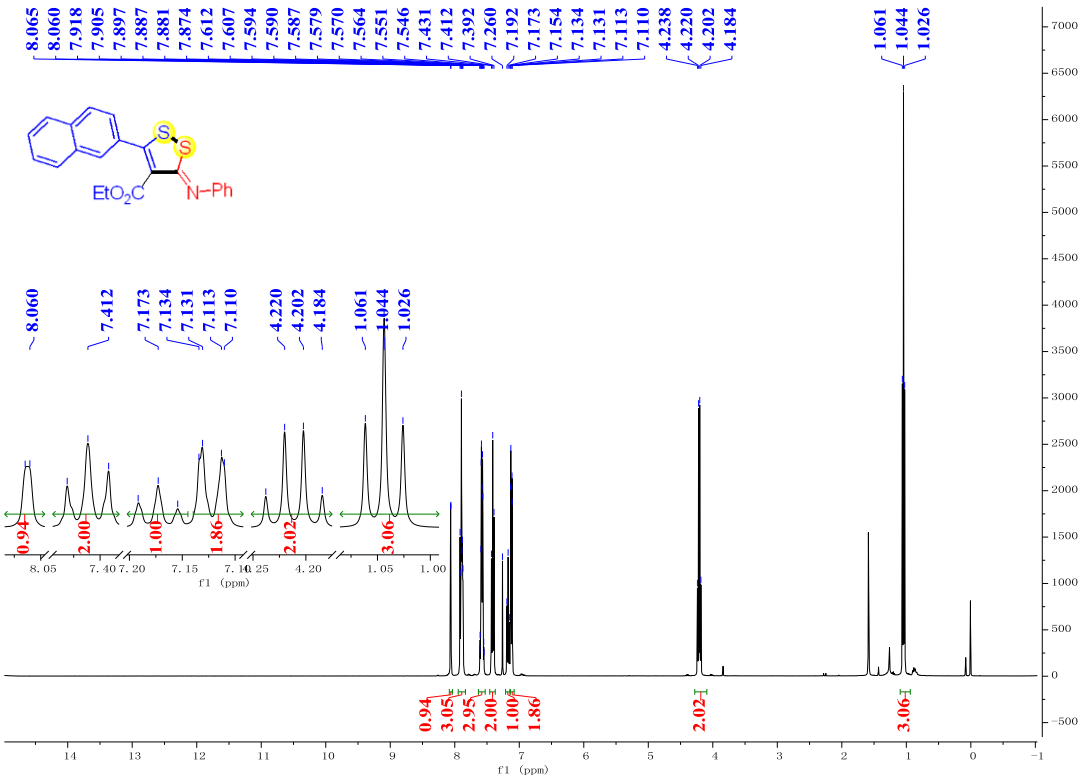


HRMS (ESI)

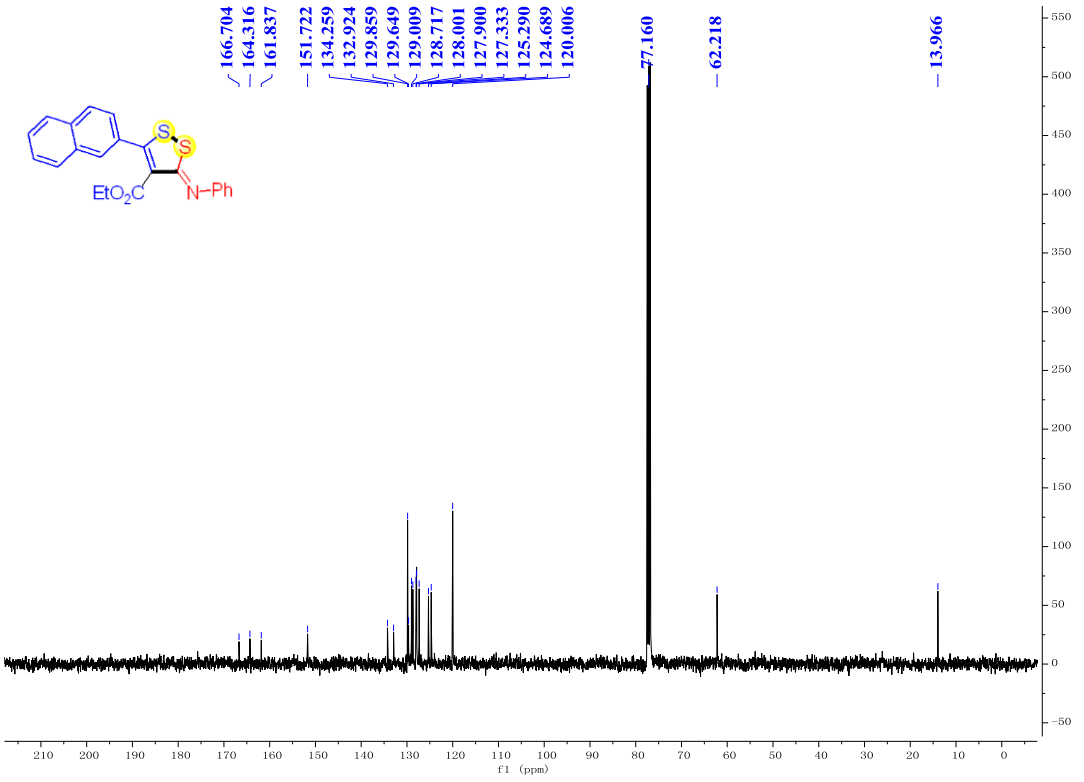

Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
324
326
328
330
332
334
336
332.04039
333.04381
334.03615
335.21888
329.00462
327.00785
331.00177
325.16154

Ethyl (*Z*)-5-(naphthalen-2-yl)-3-(phenylimino)-3*H*-1,2-dithiole-4-carboxylate (**3oB**)

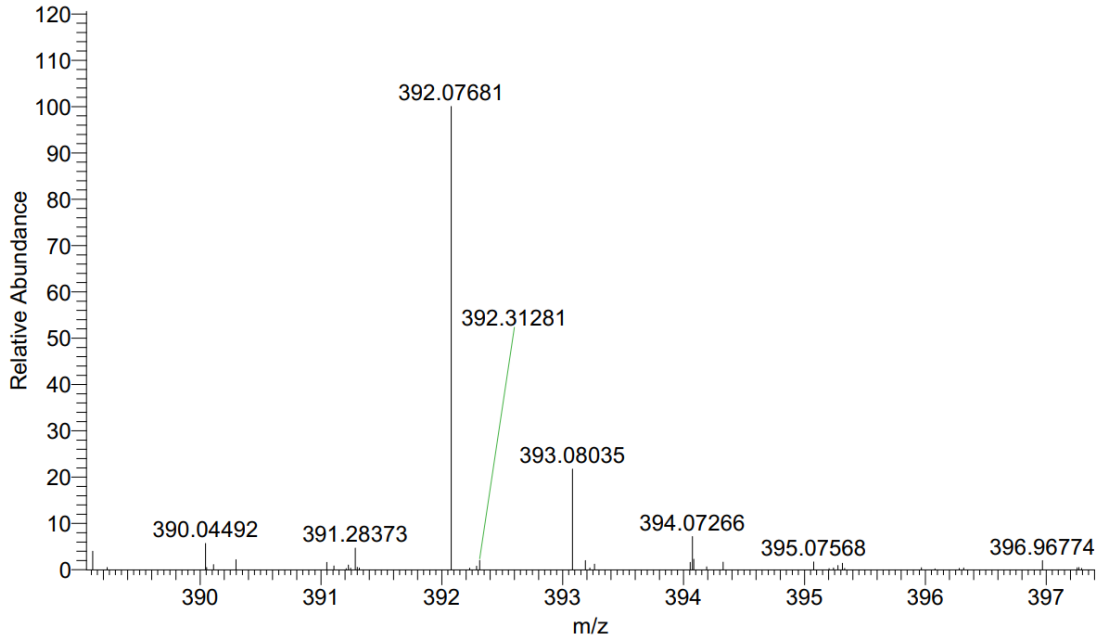
^{1}H NMR (400 MHz, $CDCl_3$)



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

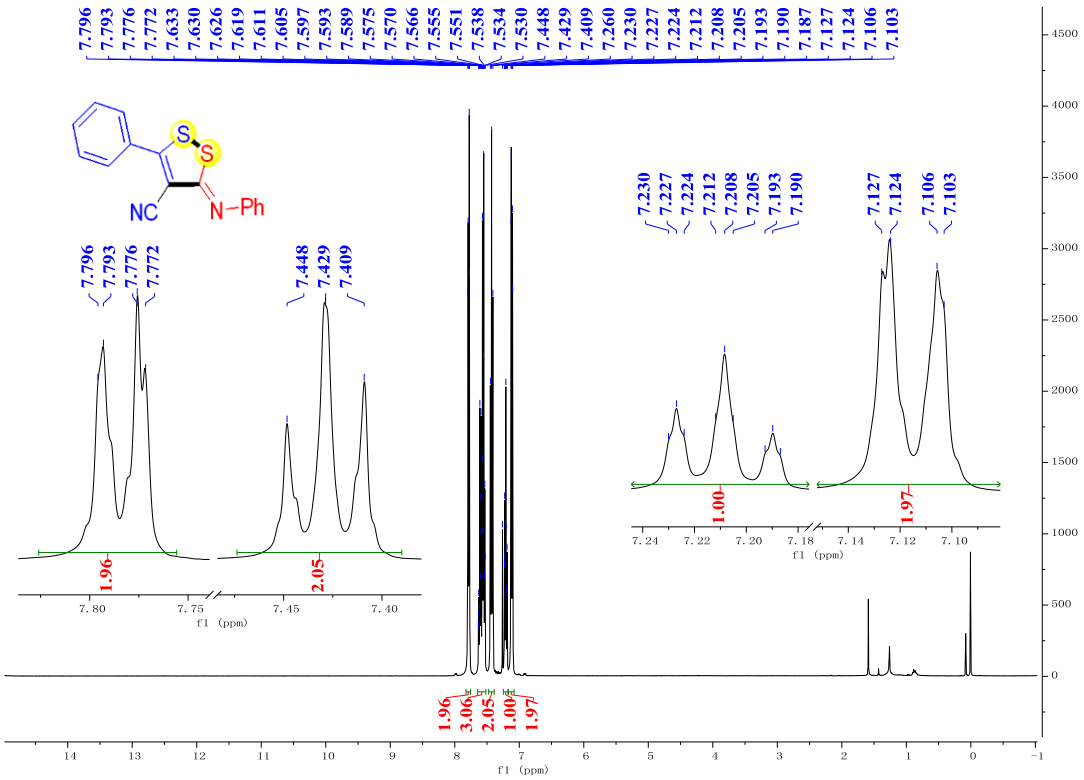


HRMS (ESI)

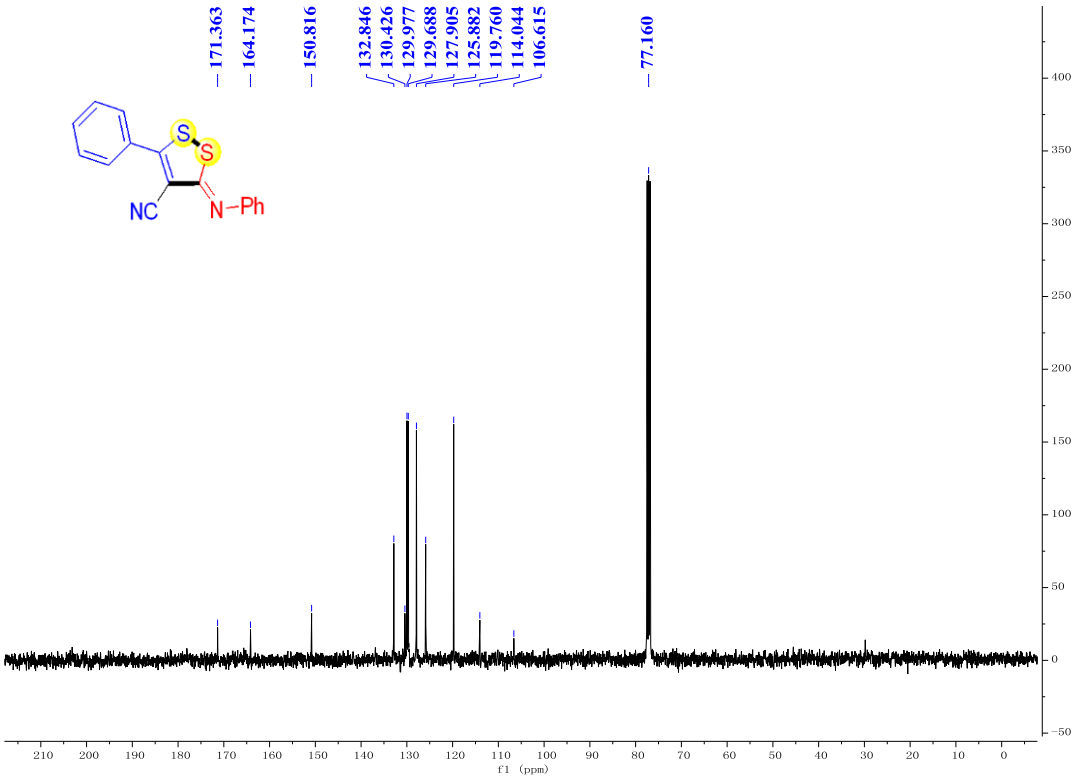

Relative Abundance
m/z
392.07681
392.31281
393.08035
390.04492
391.28373
394.07266
395.07568
396.96774

(*Z*)-5-phenyl-3-(phenylimino)-3*H*-1,2-dithiole-4-carbonitrile (**3pB**)

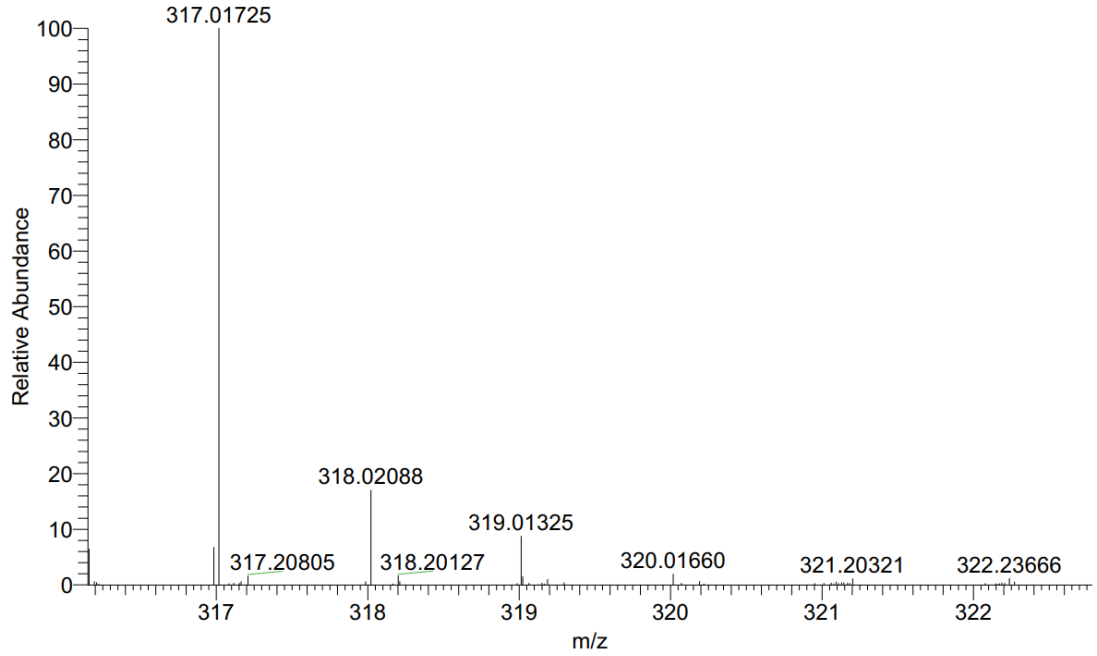
^{1}H NMR (400 MHz, $CDCl_3$)



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

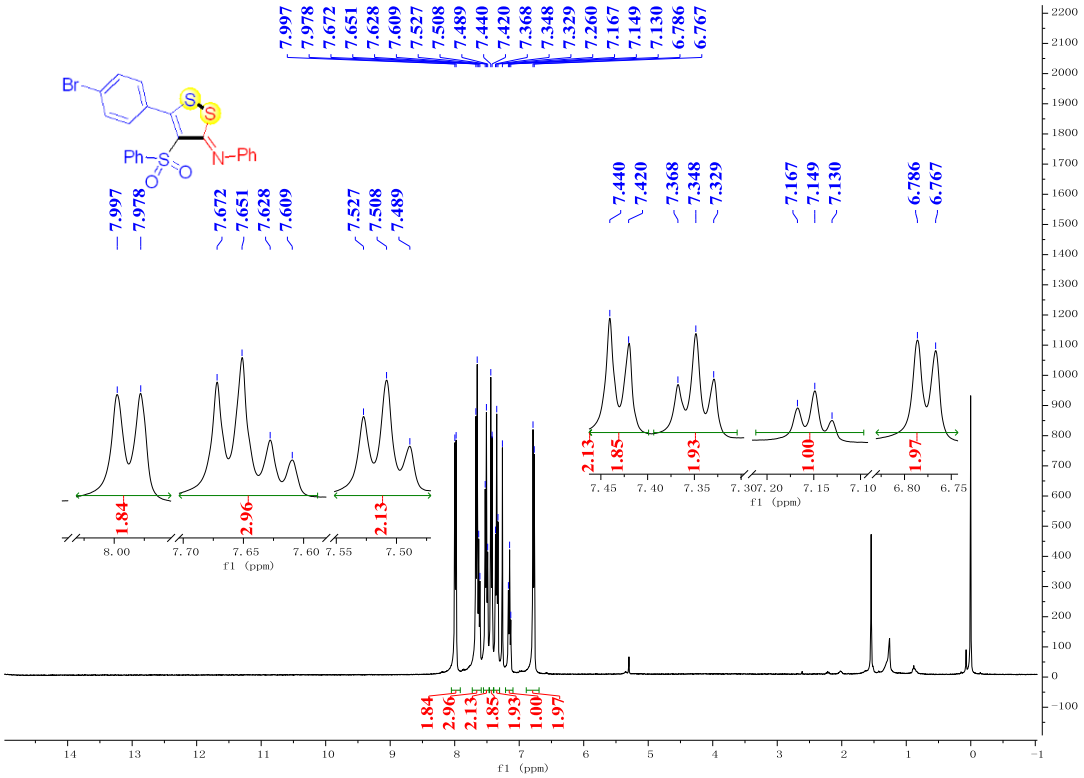


HRMS (ESI)

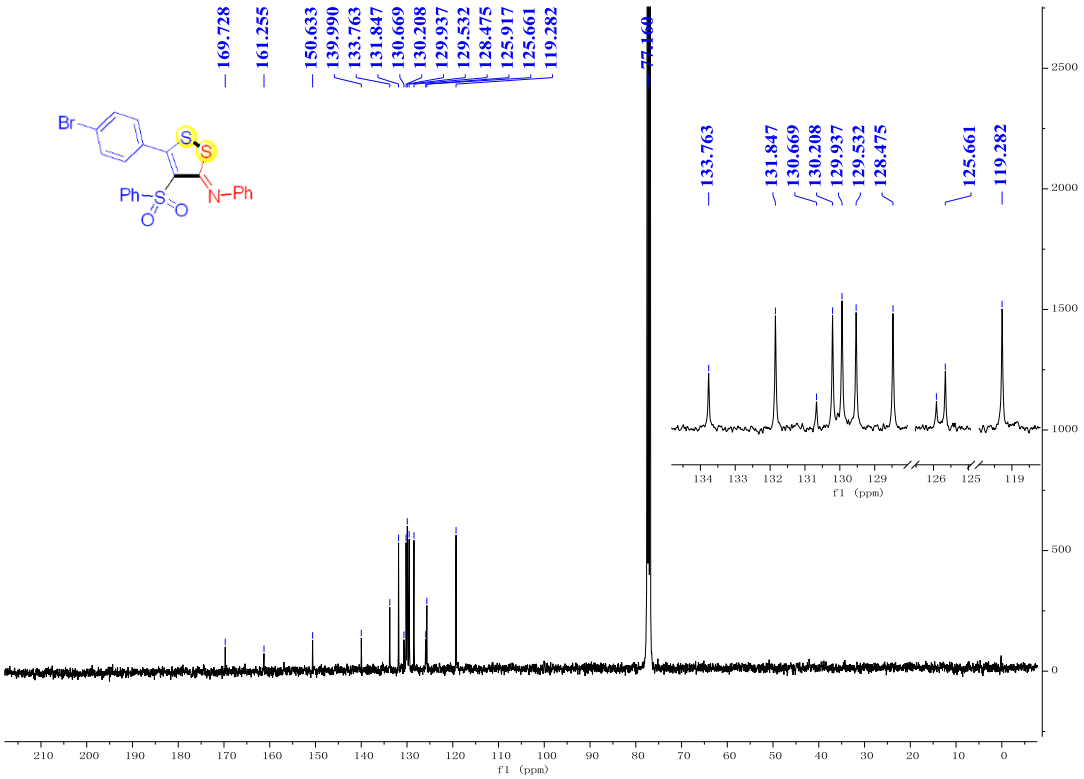

317.01725
318.02088
319.01325
317.20805
318.20127
320.01660
321.20321
322.23666
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
317
318
319
320
321
322

(*Z*)-5-(4-bromophenyl)-*N*-phenyl-4-(phenylsulfonyl)-3*H*-1,2-dithiol-3-imine (**3qB**)

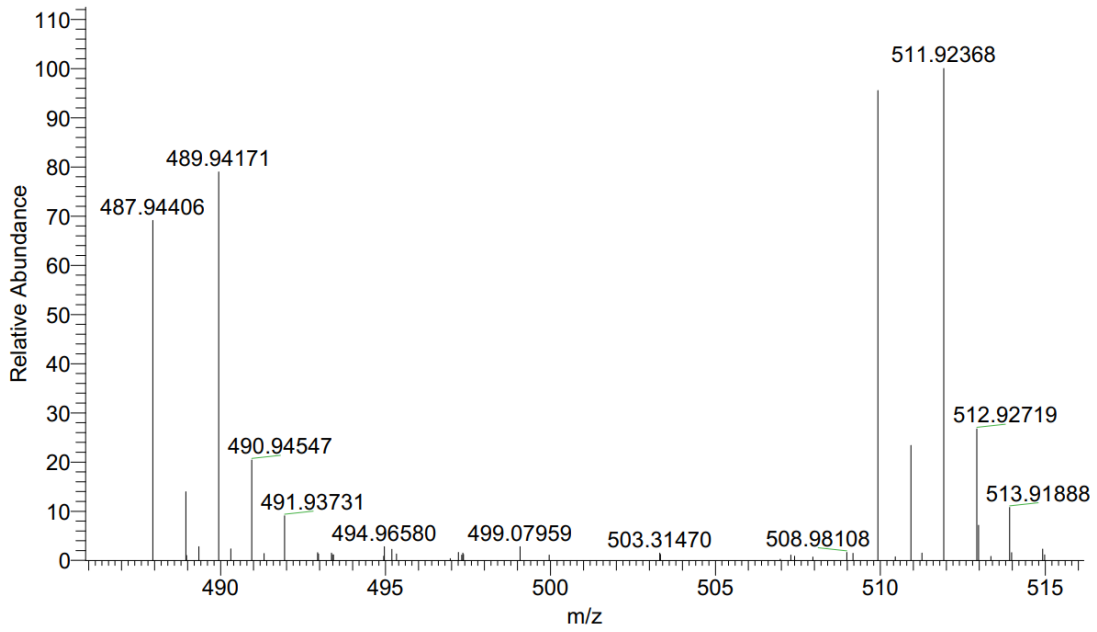
^{1}H NMR (400 MHz, $CDCl_3$)



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

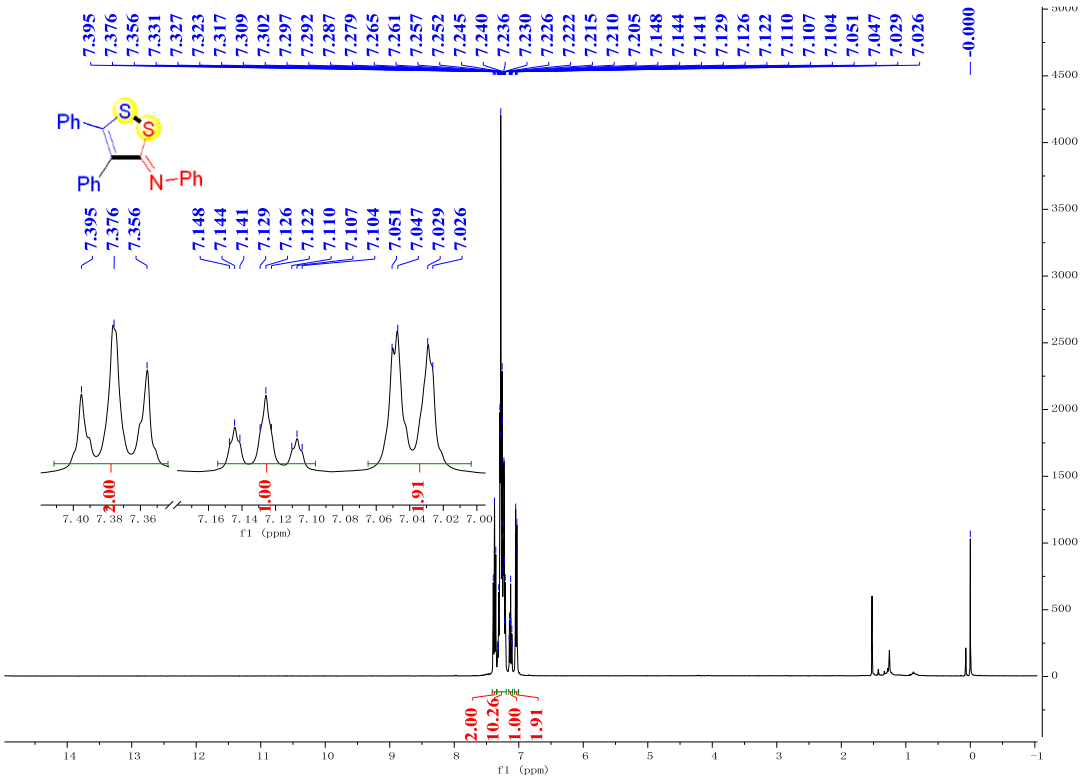


HRMS (ESI)

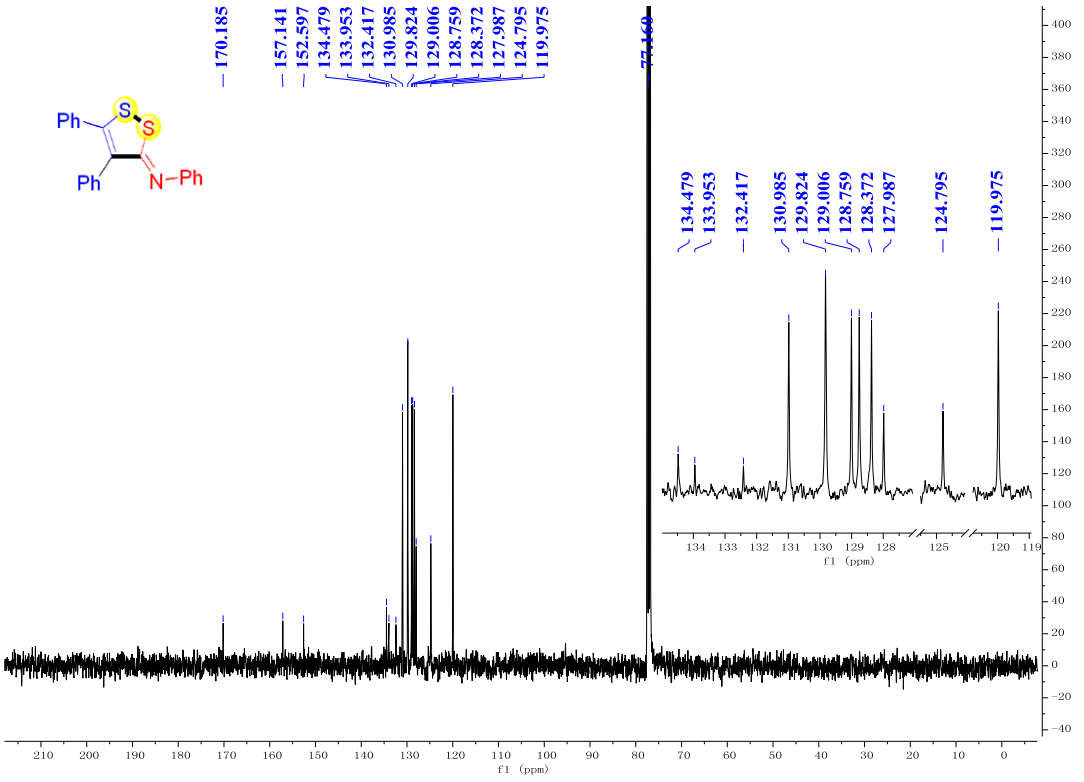

Relative Abundance
m/z
511.92368
489.94171
487.94406
512.92719
490.94547
513.91888
491.93731
494.96580
499.07959
503.31470
508.98108

(*Z*)-*N*,4,5-triphenyl-3*H*-1,2-dithiol-3-imine (**3rB**)

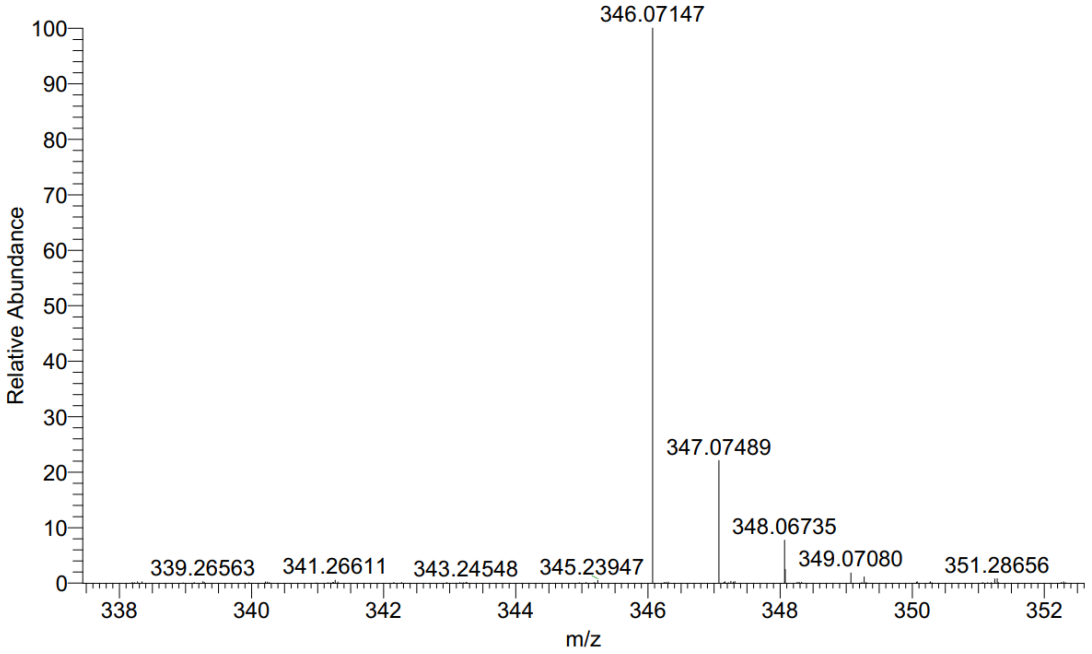
^{1}H NMR (400 MHz, $CDCl_3$)



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



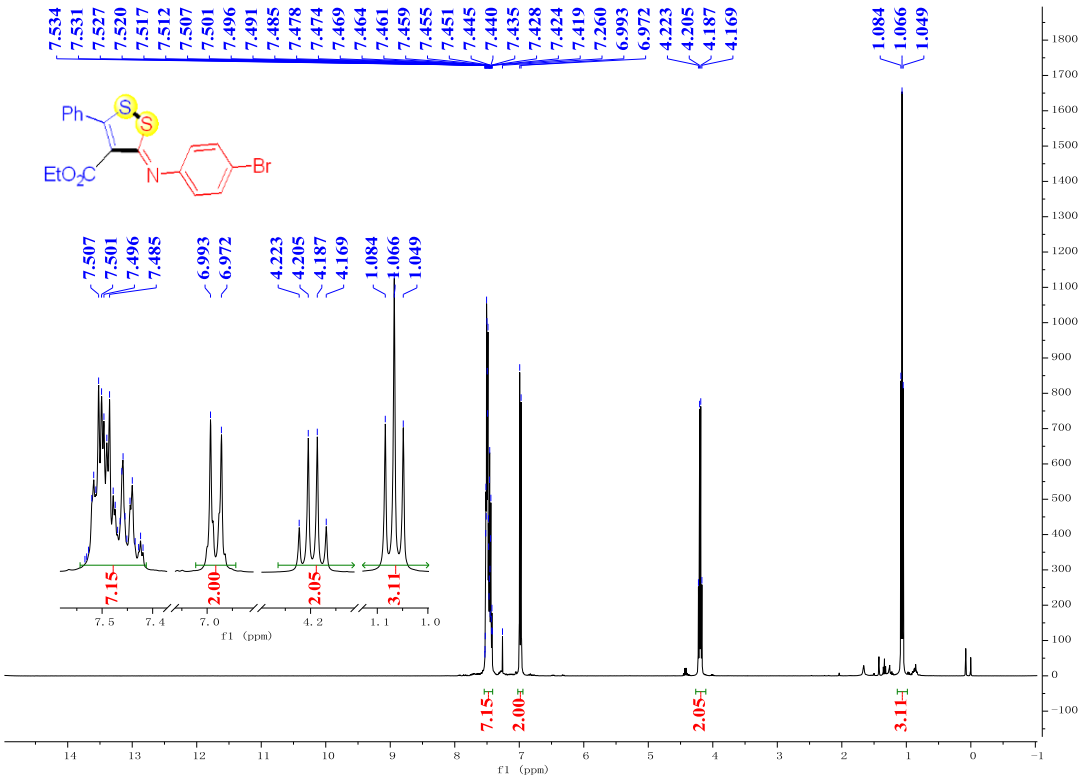
HRMS (ESI)


346.07147
347.07489
348.06735
349.07080
339.26563
341.26611
343.24548
345.23947
351.28656
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
338
340
342
344
346
348
350
352

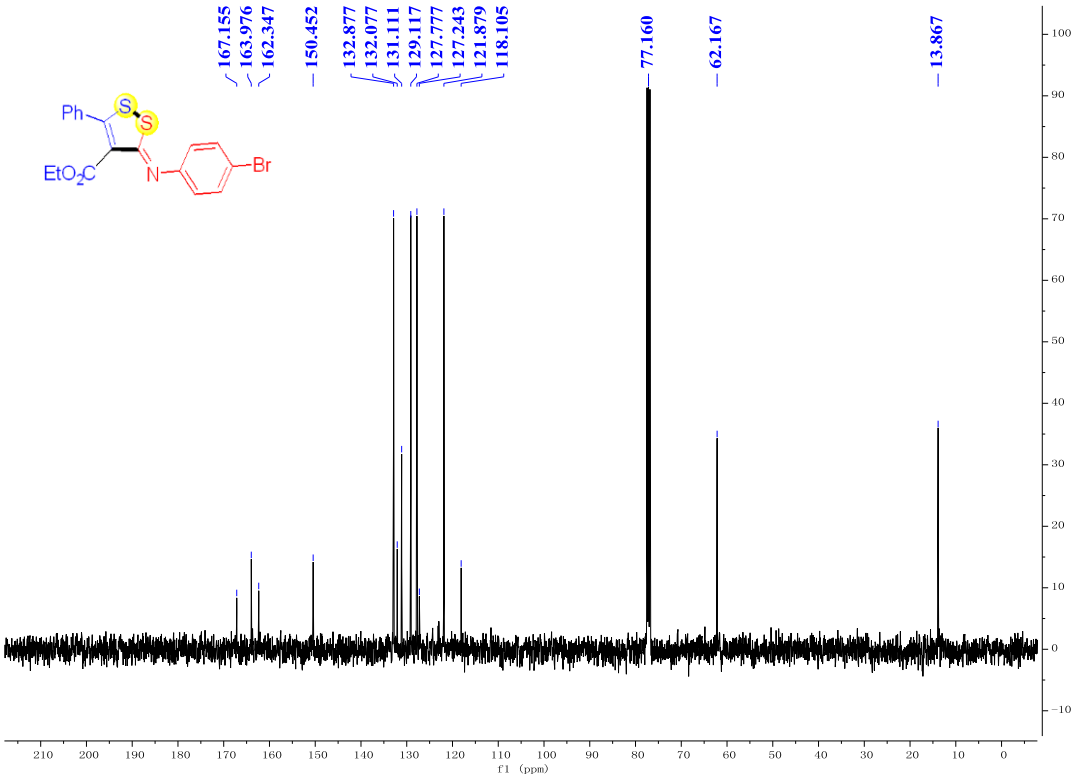
13.3 Copies of spectra of products for scope of isothiocyantes

Ethyl (*Z*)-3-((4-bromophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aA**)

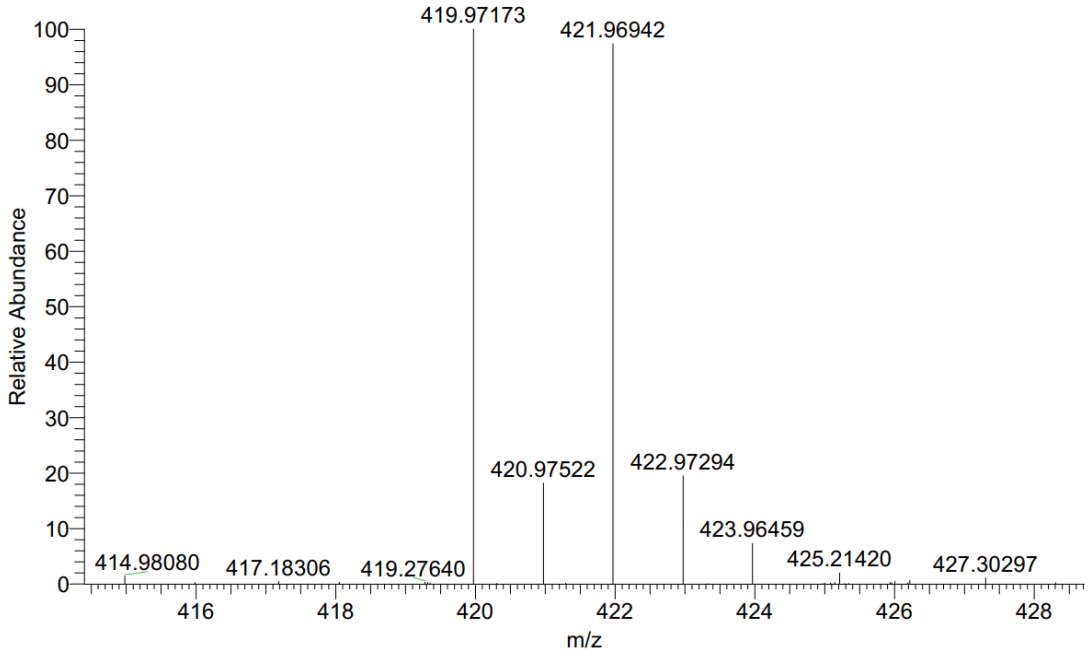
^{1}H NMR (400 MHz, $CDCl_3$)



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

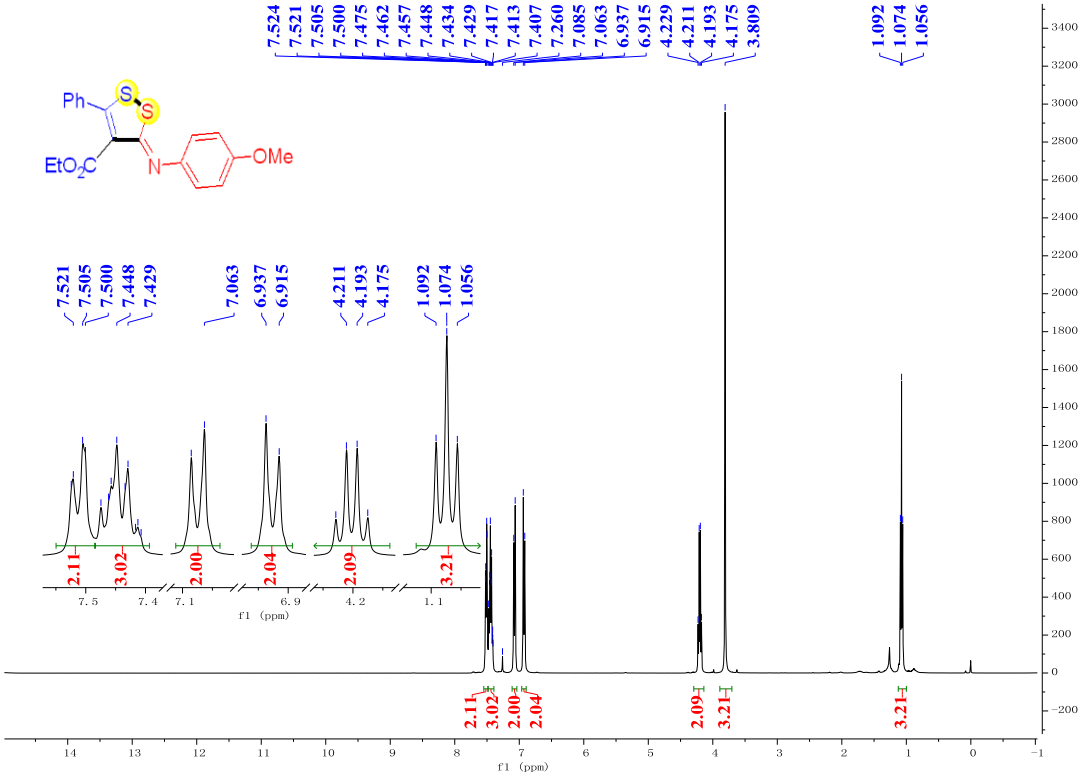


HRMS (ESI)

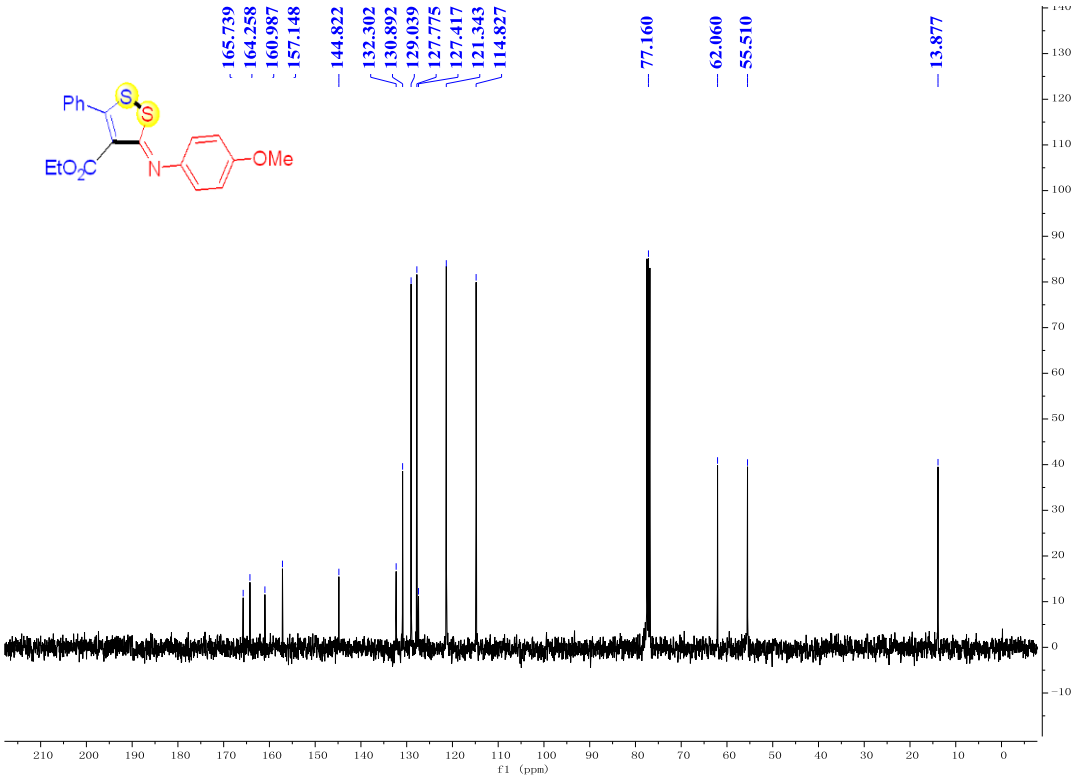

419.97173
421.96942
420.97522
422.97294
423.96459
425.21420
427.30297
414.98080
417.18306
419.27640
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
416
418
420
422
424
426
428

Ethyl (*Z*)-3-((4-methoxyphenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aC**)

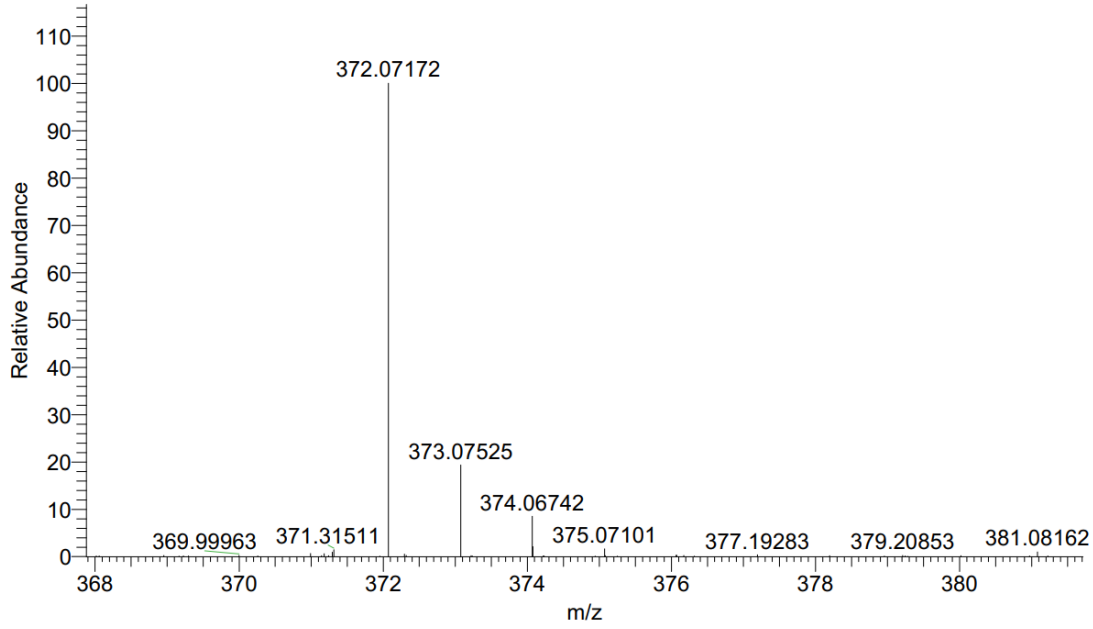
^{1}H NMR (400 MHz, $CDCl_3$)



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

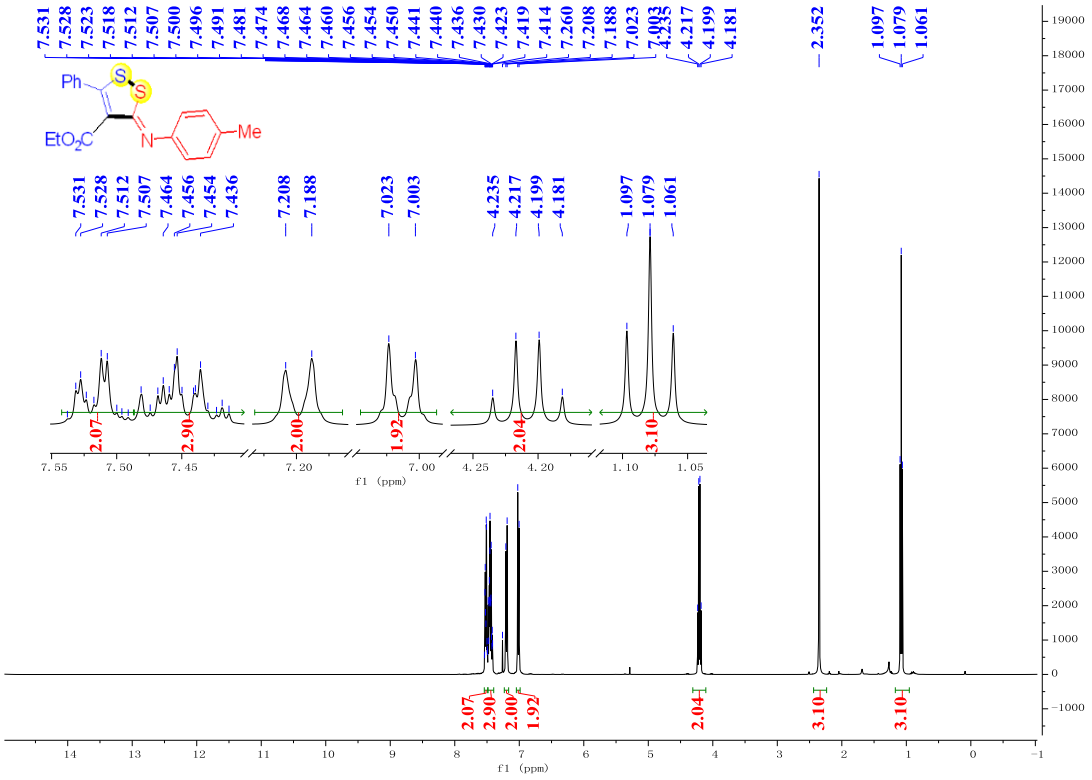


HRMS (ESI)

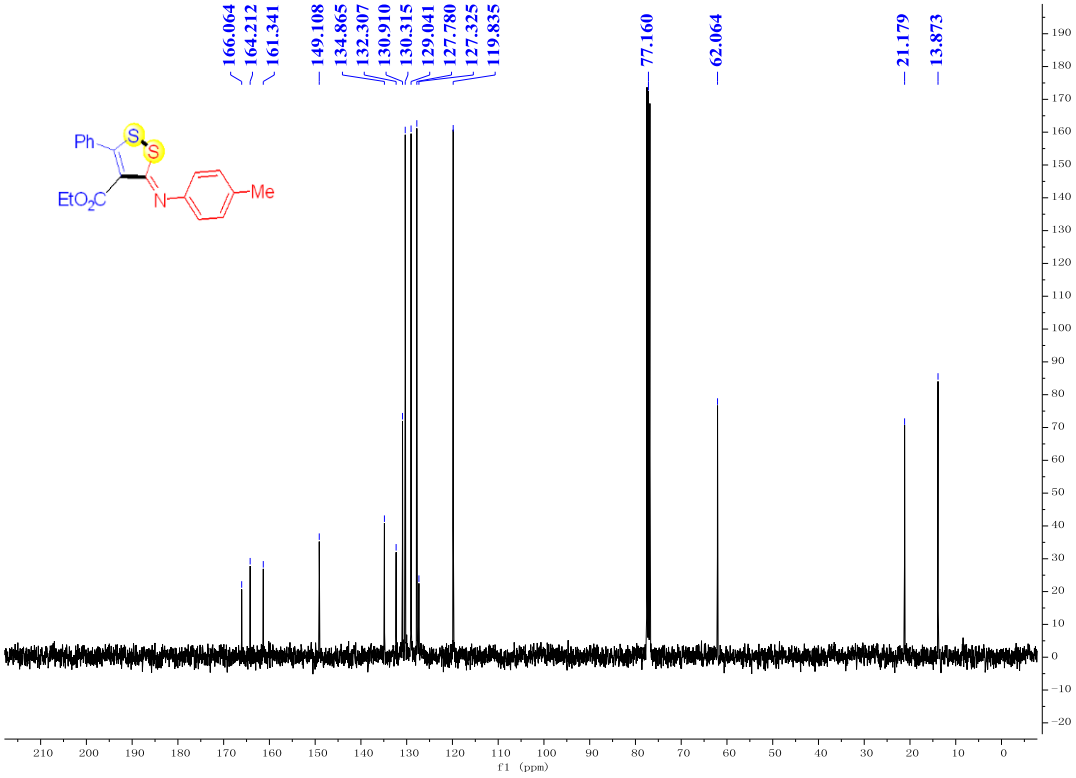

372.07172
373.07525
374.06742
375.07101
369.99963
371.31511
377.19283
379.20853
381.08162
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
100
110
368
370
372
374
376
378
380

Ethyl (*Z*)-5-phenyl-3-(*p*-tolylimino)-3*H*-1,2-dithiole-4-carboxylate (**3aD**)

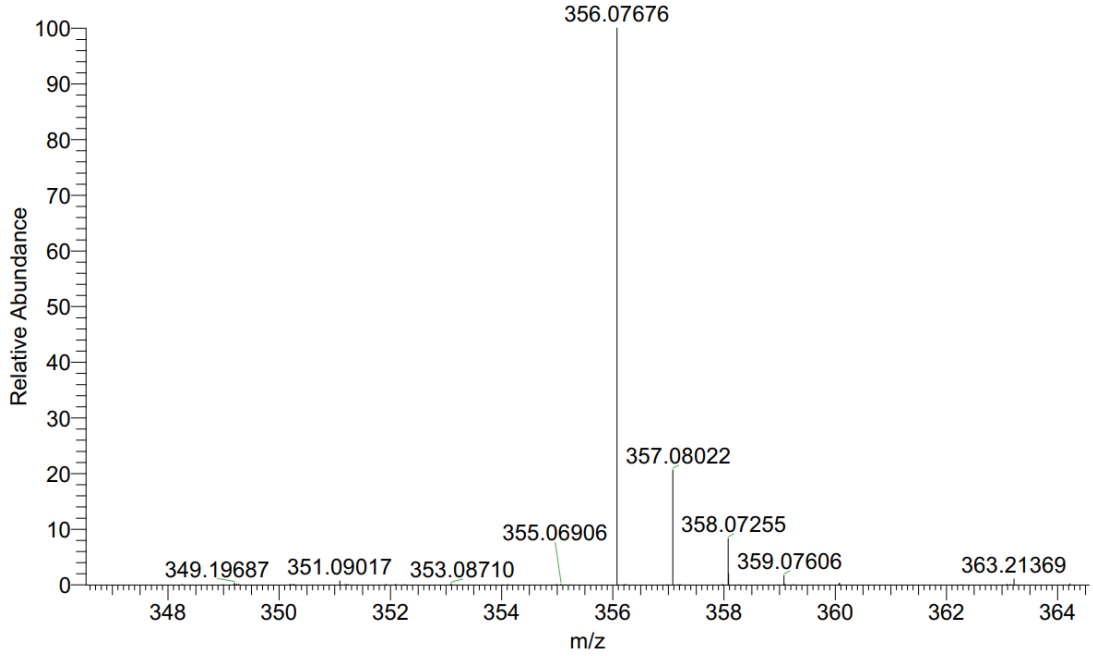
^{1}H NMR (400 MHz, $CDCl_3$)



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

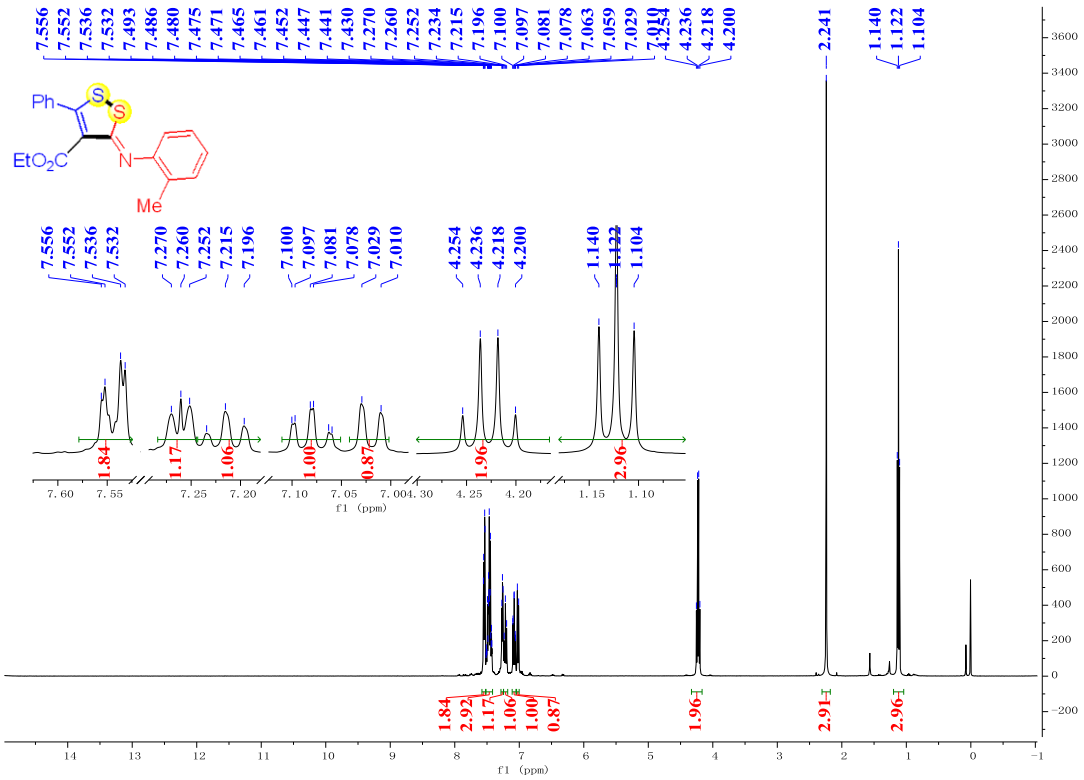


HRMS (ESI)

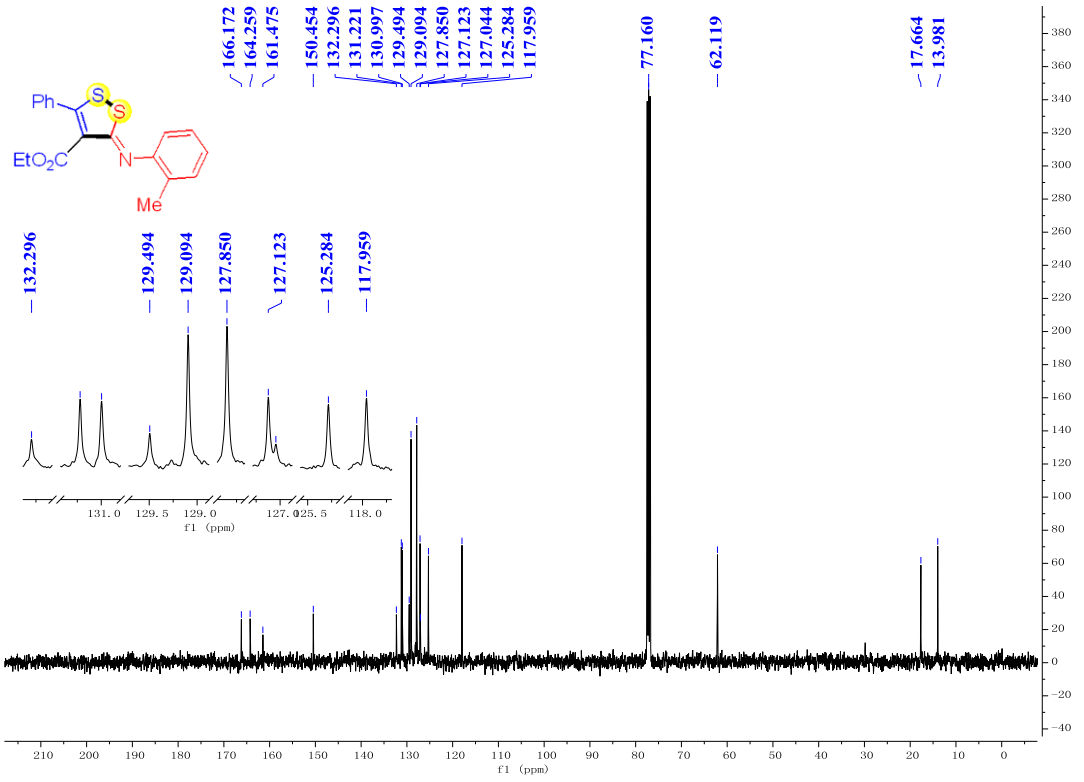

356.07676
357.08022
358.07255
355.06906
359.07606
349.19687
351.09017
353.08710
363.21369
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
348
350
352
354
356
358
360
362
364

Ethyl (*Z*)-5-phenyl-3-(*o*-tolylimino)-3*H*-1,2-dithiole-4-carboxylate (**3aE**)

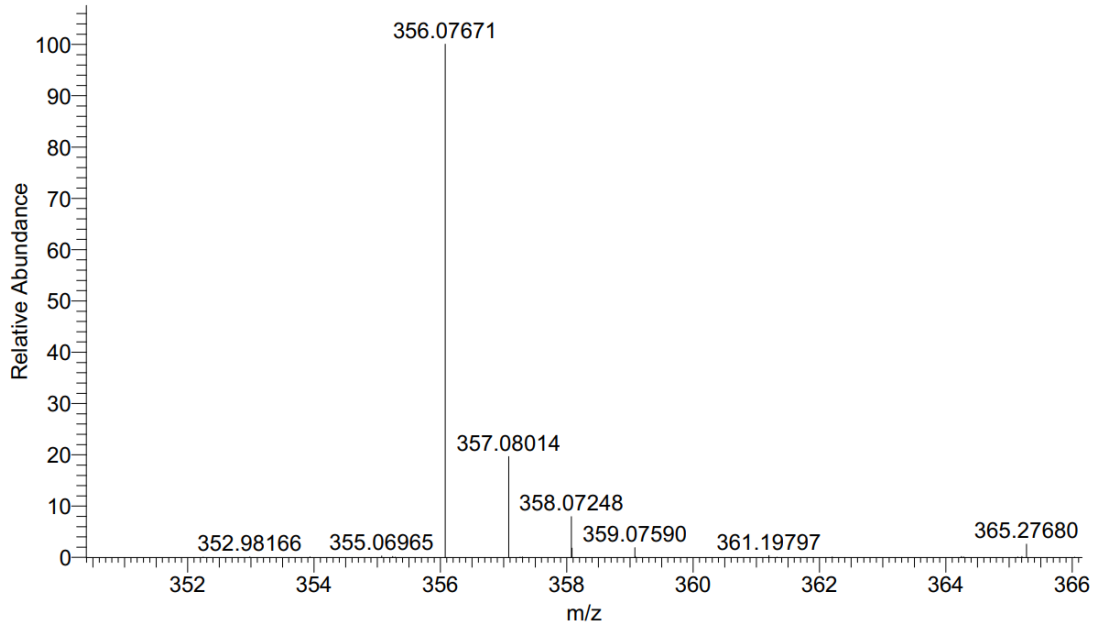
^{1}H NMR (400 MHz, $CDCl_3$)



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

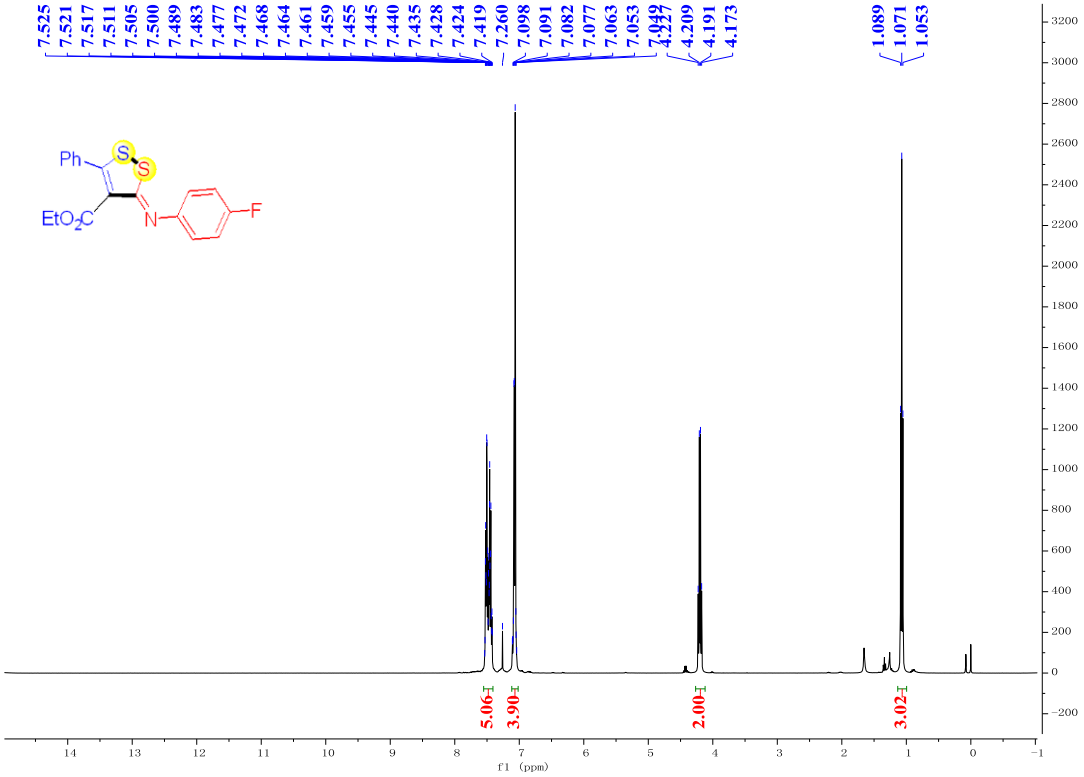


HRMS (ESI)

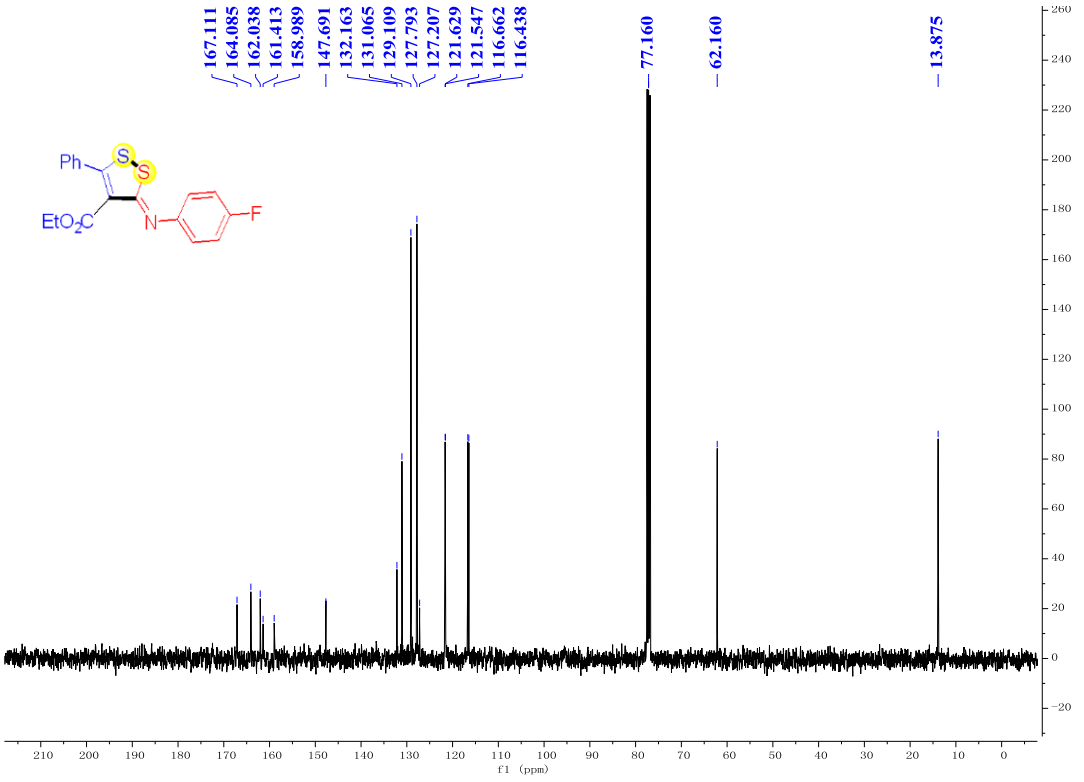

356.07671
357.08014
358.07248
359.07590
352.98166
355.06965
361.19797
365.27680
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
352
354
356
358
360
362
364
366

Ethyl (*Z*)-3-((4-fluorophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aF**)

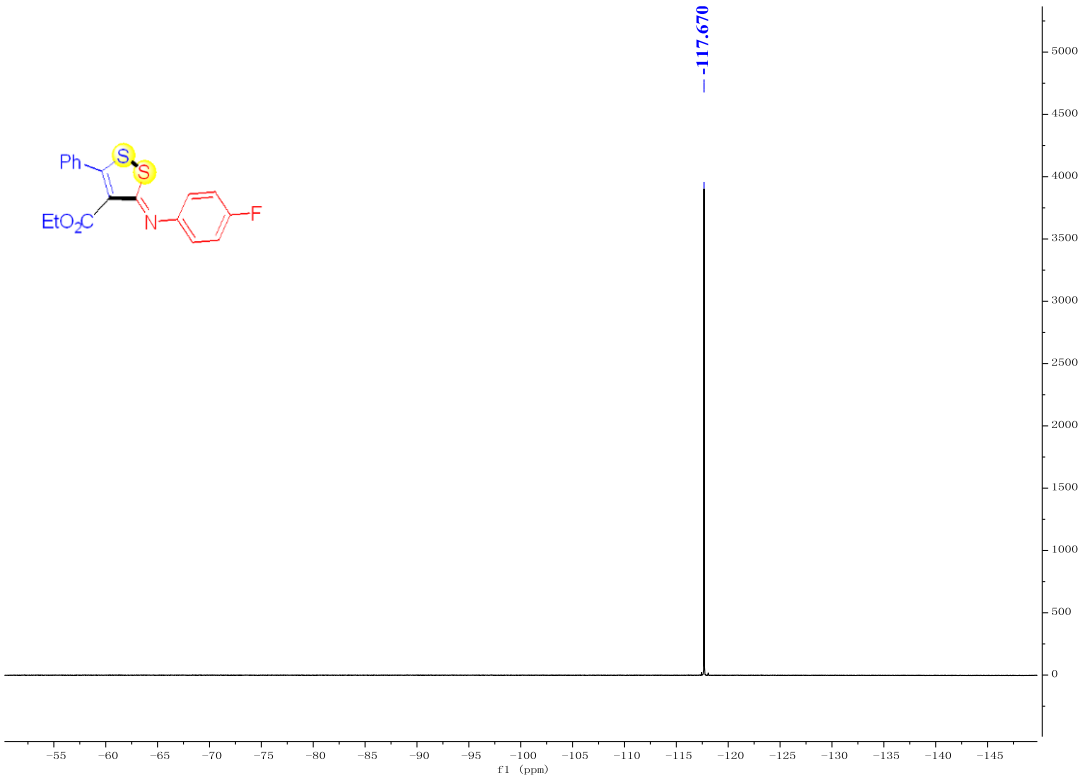
^{1}H NMR (400 MHz, $CDCl_3$)



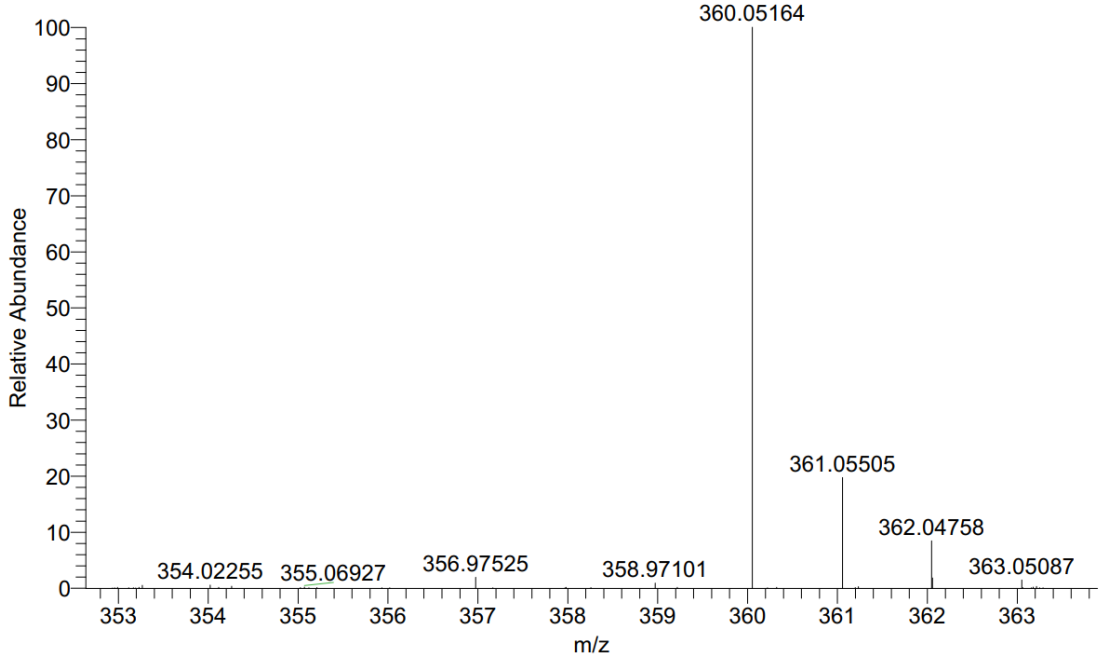
^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)

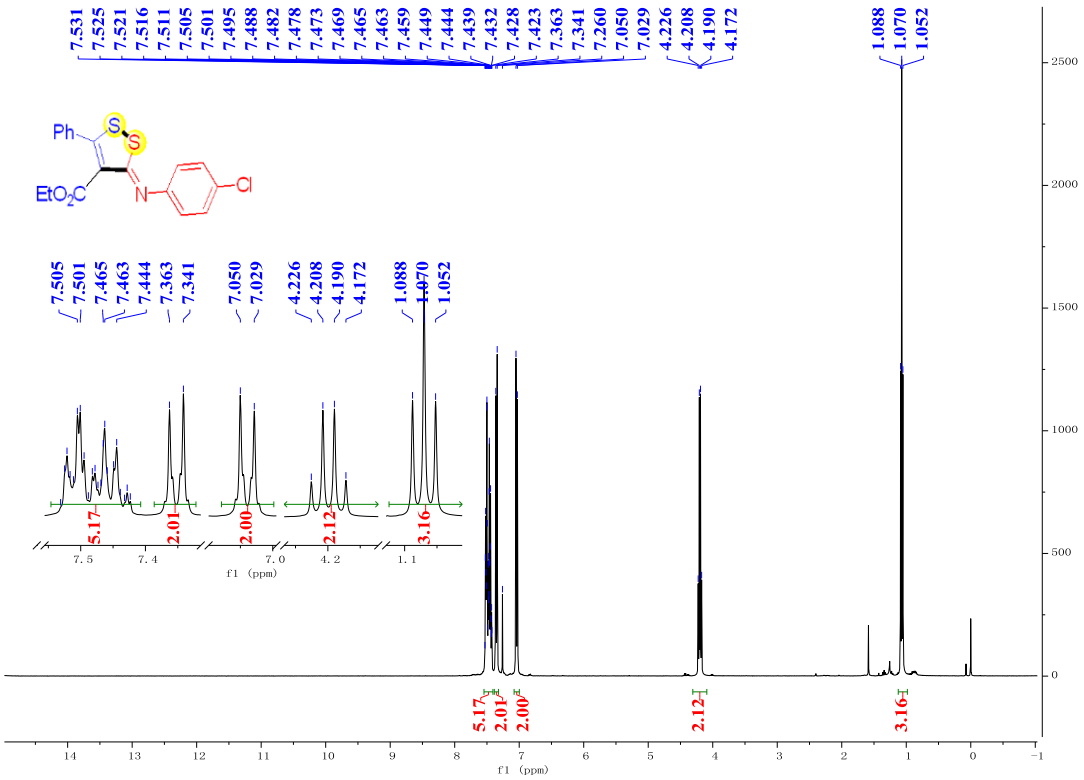


HRMS (ESI)

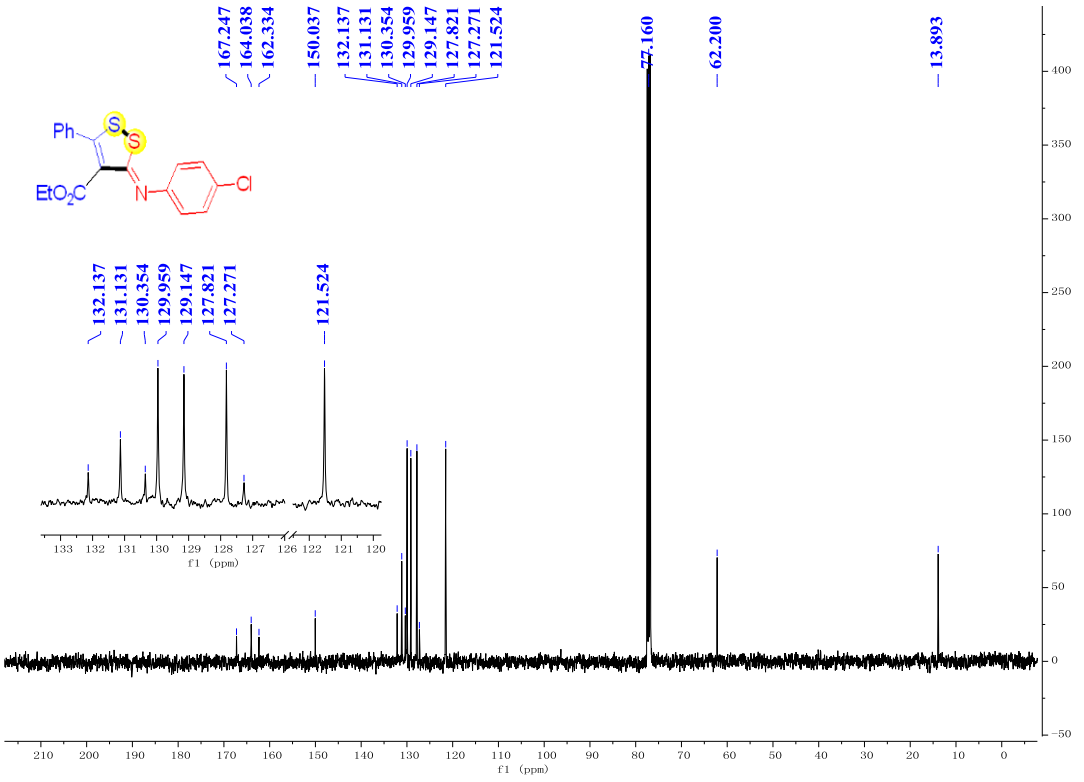


Ethyl (*Z*)-3-((4-chlorophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aG**)

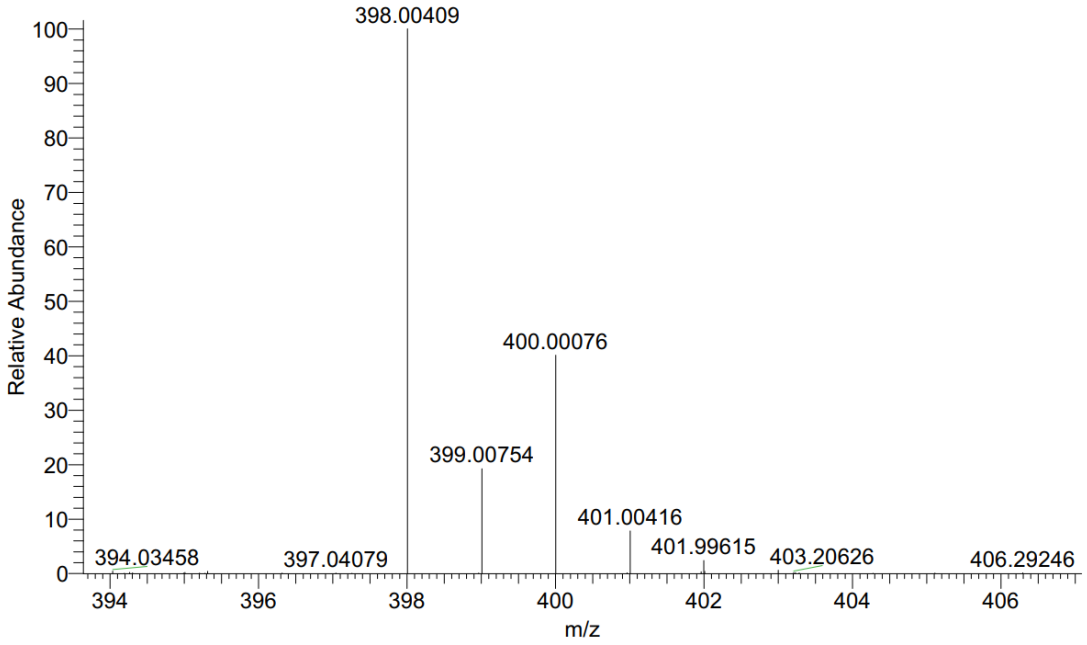
^{1}H NMR (400 MHz, $CDCl_3$)



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

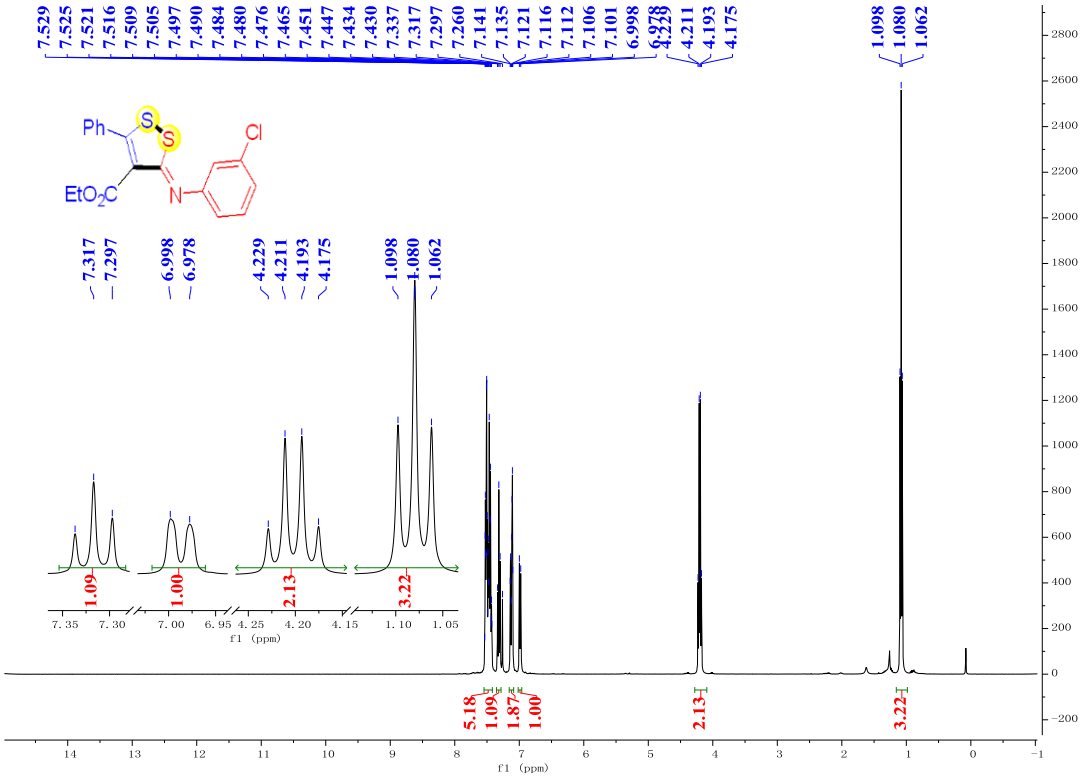


HRMS (ESI)

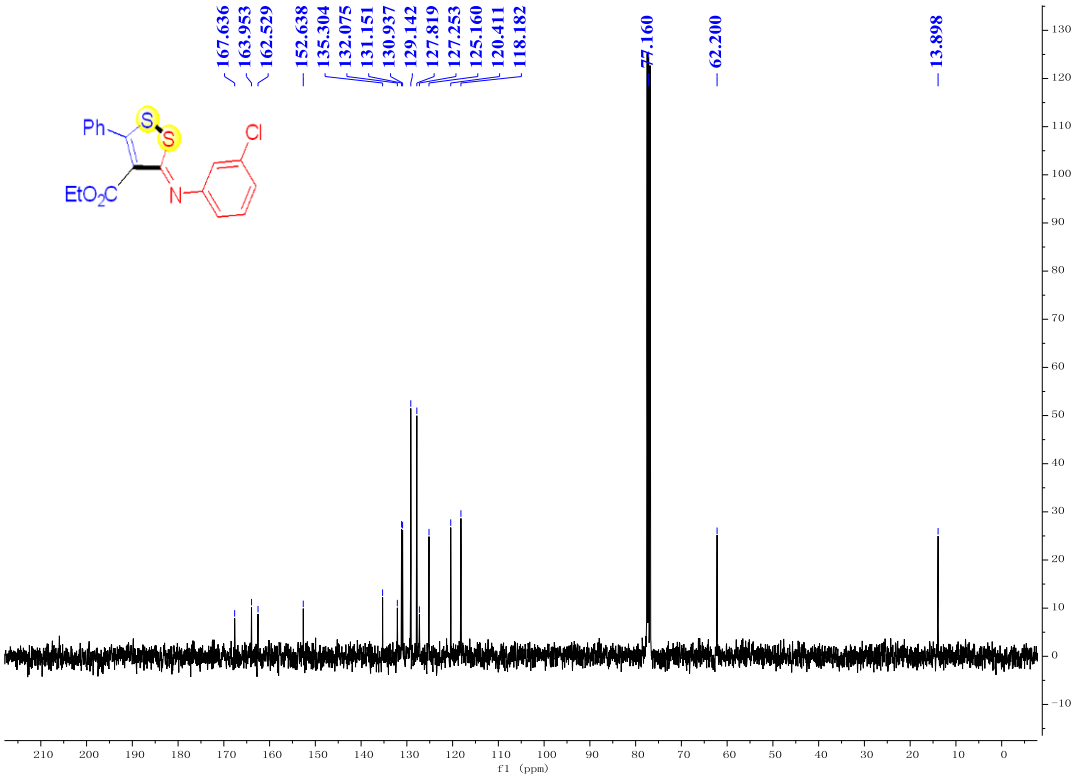

398.00409
400.00076
399.00754
401.00416
401.99615
394.03458
397.04079
403.20626
406.29246
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
394
396
398
400
402
404
406

Ethyl (*Z*)-3-((3-chlorophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aH**)

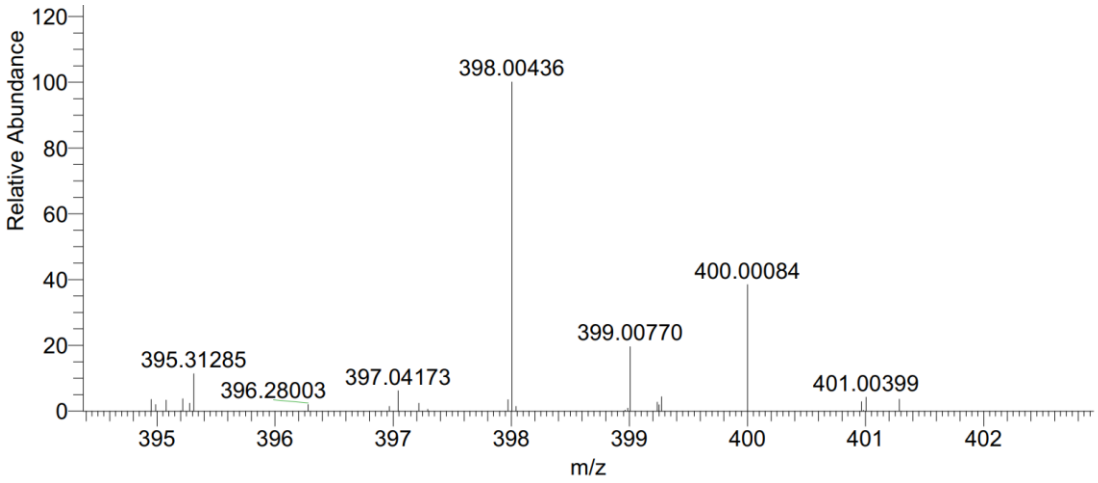
^{1}H NMR (400 MHz, $CDCl_3$)



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

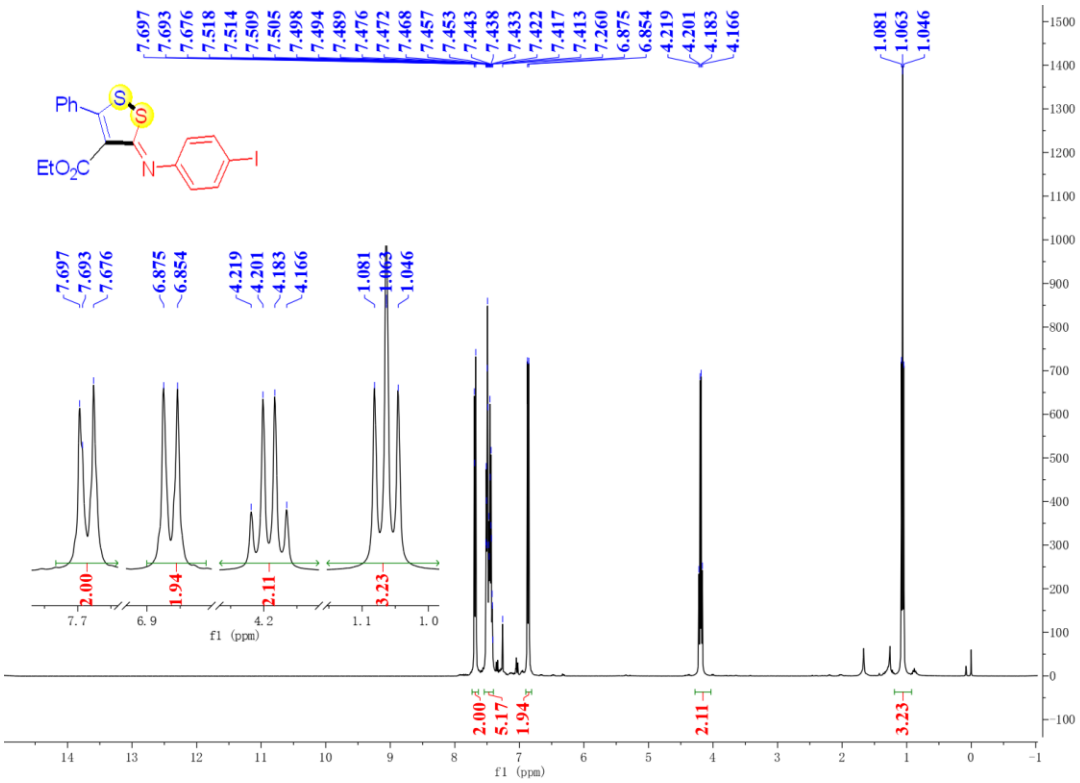


HRMS (ESI)

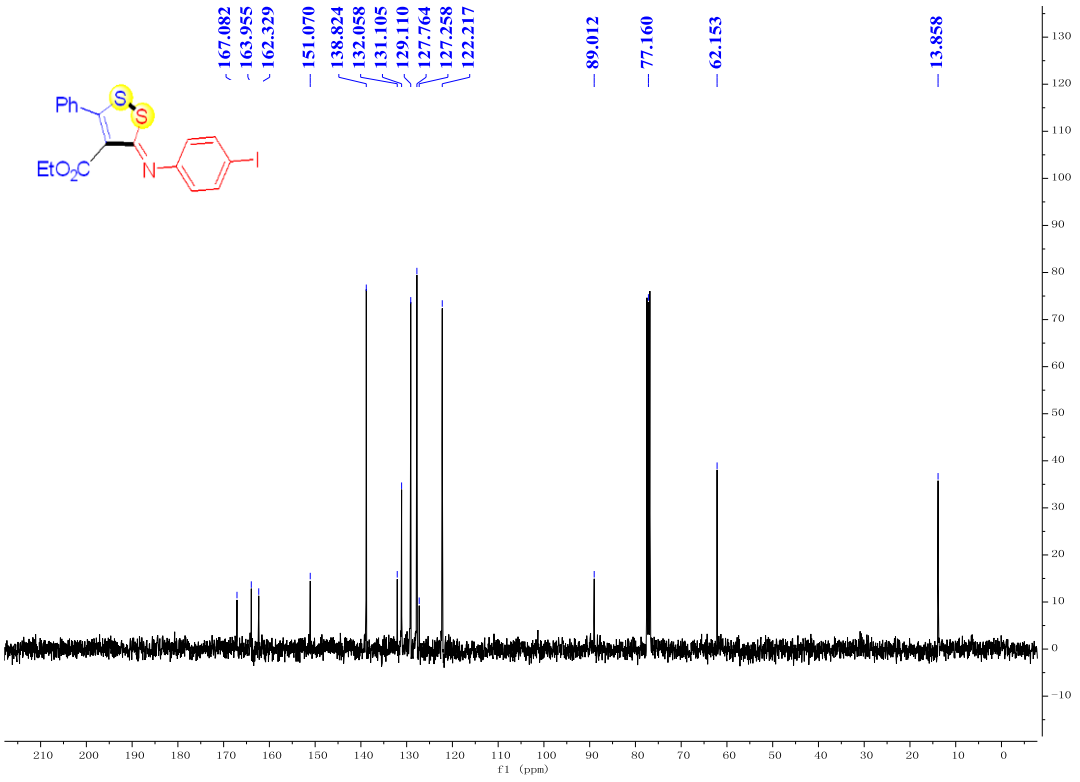

Relative Abundance
120
100
80
60
40
20
0
398.00436
400.00084
399.00770
395.31285
396.28003
397.04173
401.00399
395
396
397
398
399
400
401
402
m/z

Ethyl (*Z*)-3-((4-iodophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aI**)

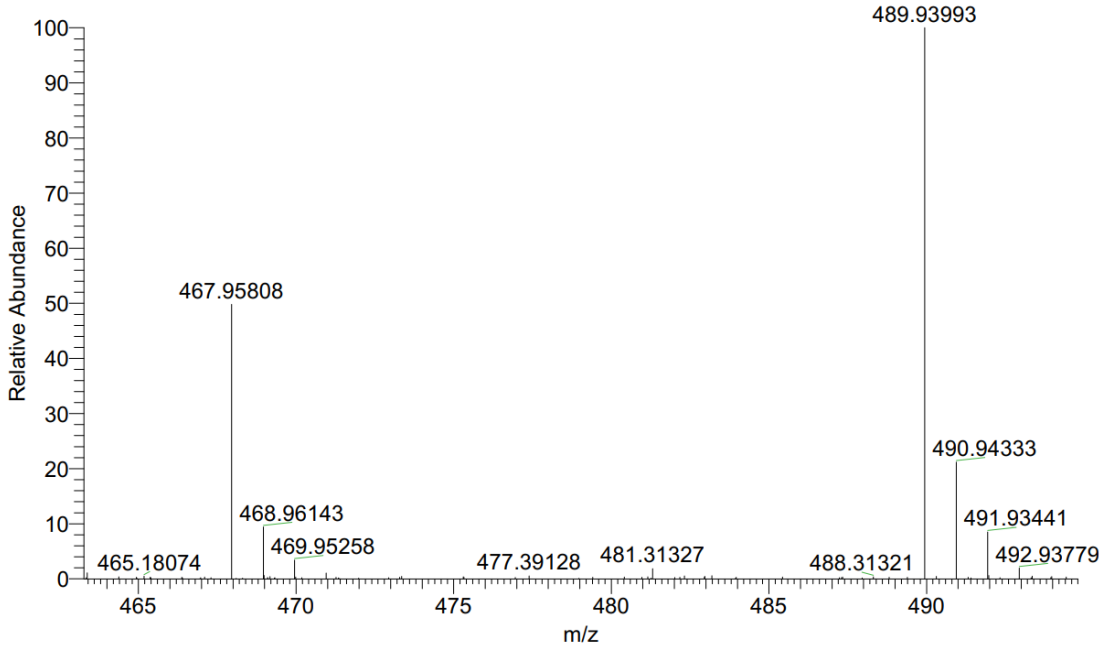
^{1}H NMR (400 MHz, $CDCl_3$)



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

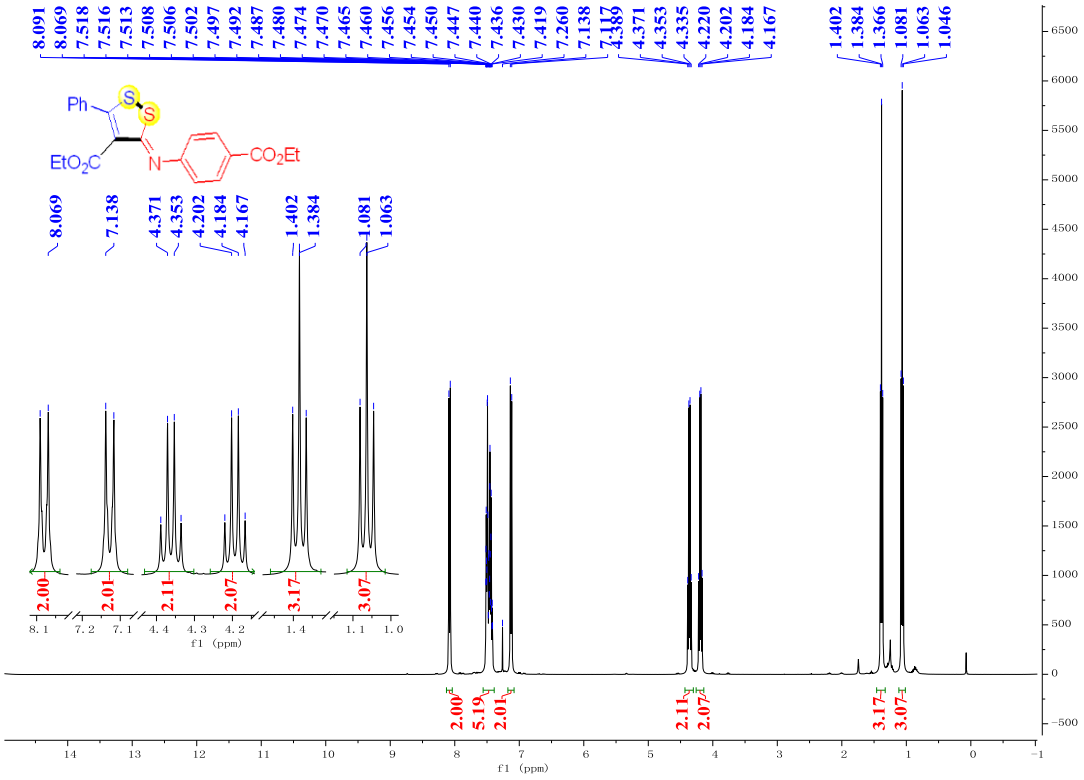


HRMS (ESI)

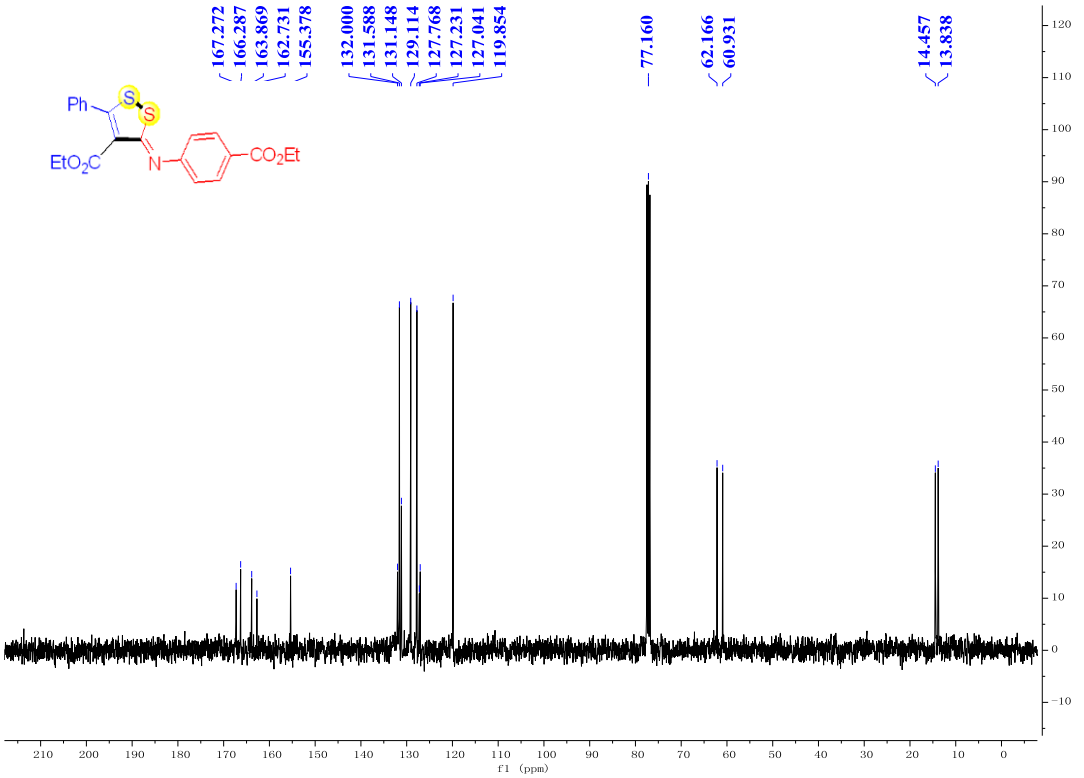

489.93993
467.95808
490.94333
468.96143
491.93441
469.95258
492.93779
465.18074
477.39128
481.31327
488.31321
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
465
470
475
480
485
490

Ethyl (*Z*)-3-((4-(ethoxycarbonyl)phenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aJ**)

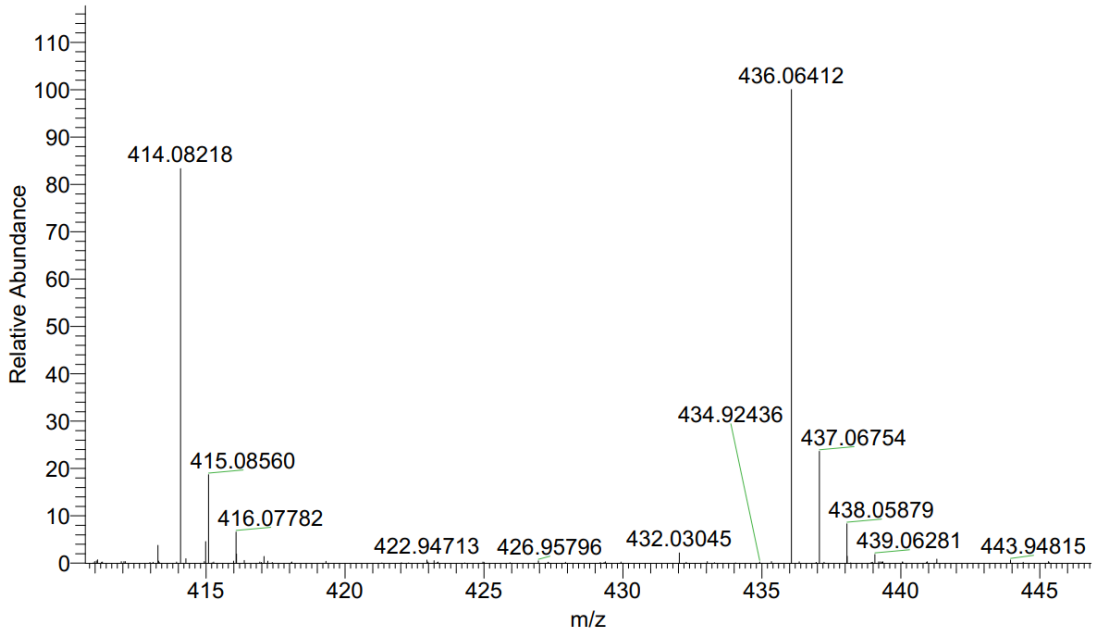
^{1}H NMR (400 MHz, $CDCl_3$)



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

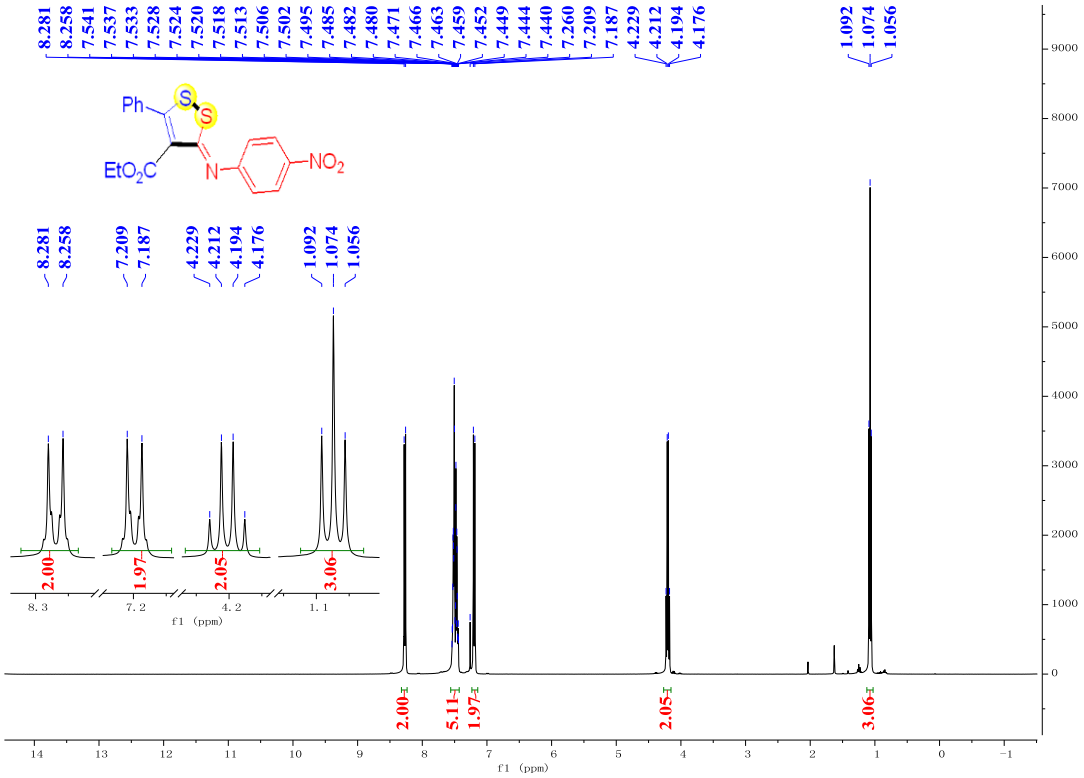


HRMS (ESI)

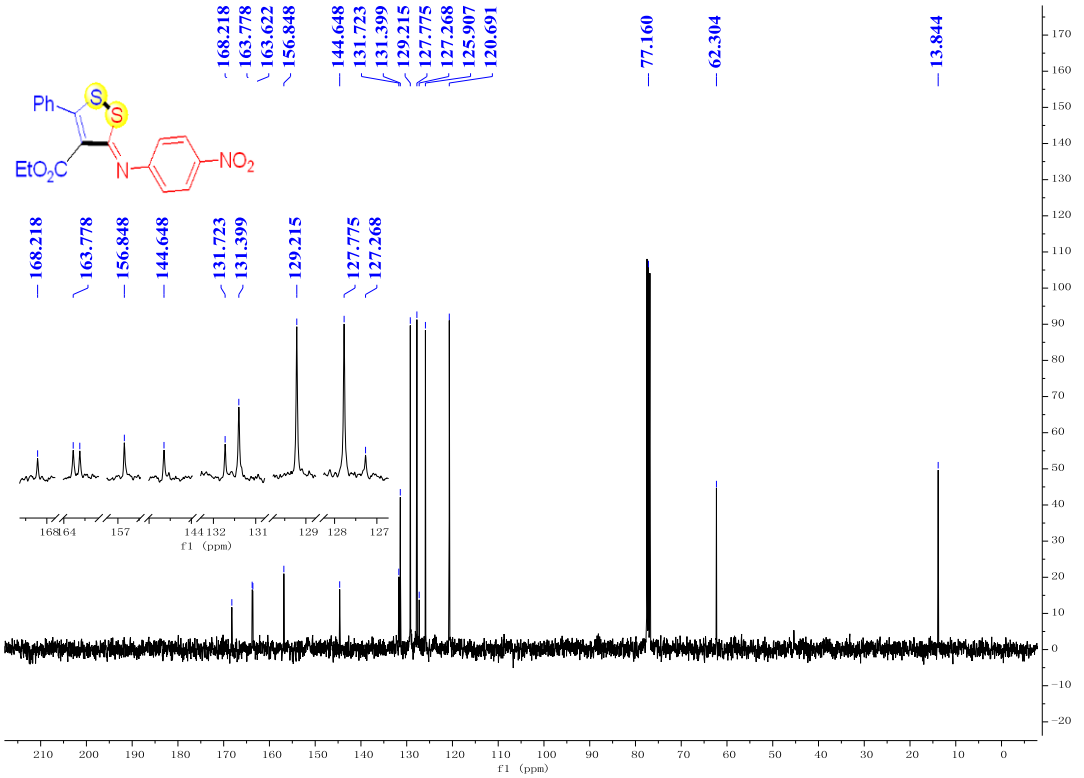

Relative Abundance
m/z
436.06412
414.08218
434.92436
437.06754
415.08560
438.05879
416.07782
439.06281
422.94713
426.95796
432.03045
443.94815

Ethyl (*Z*)-3-((4-nitrophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aK**)

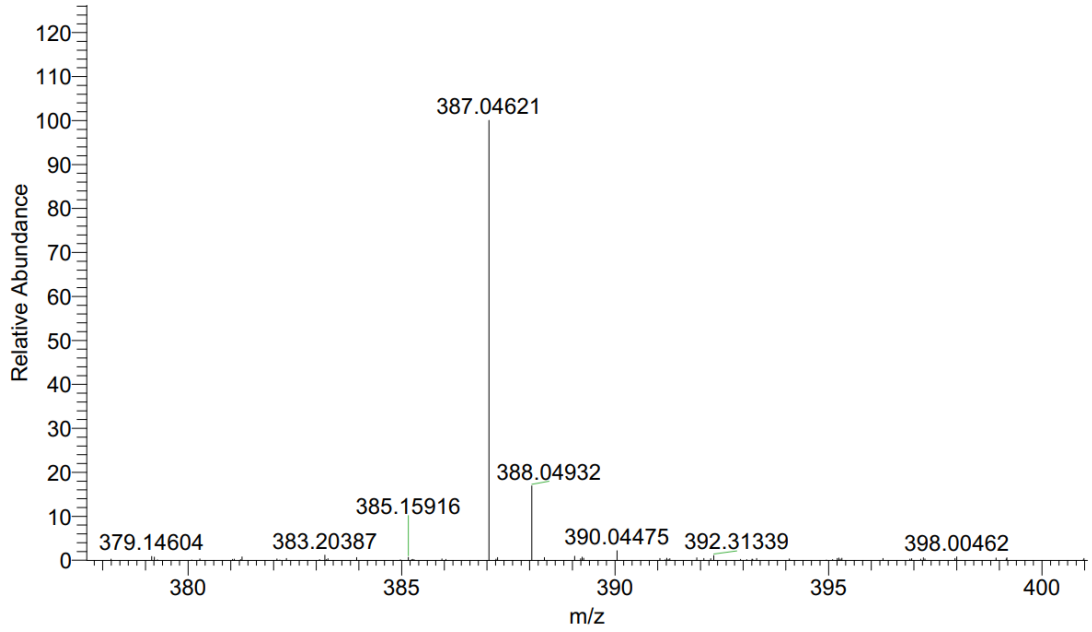
^{1}H NMR (400 MHz, $CDCl_3$)



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

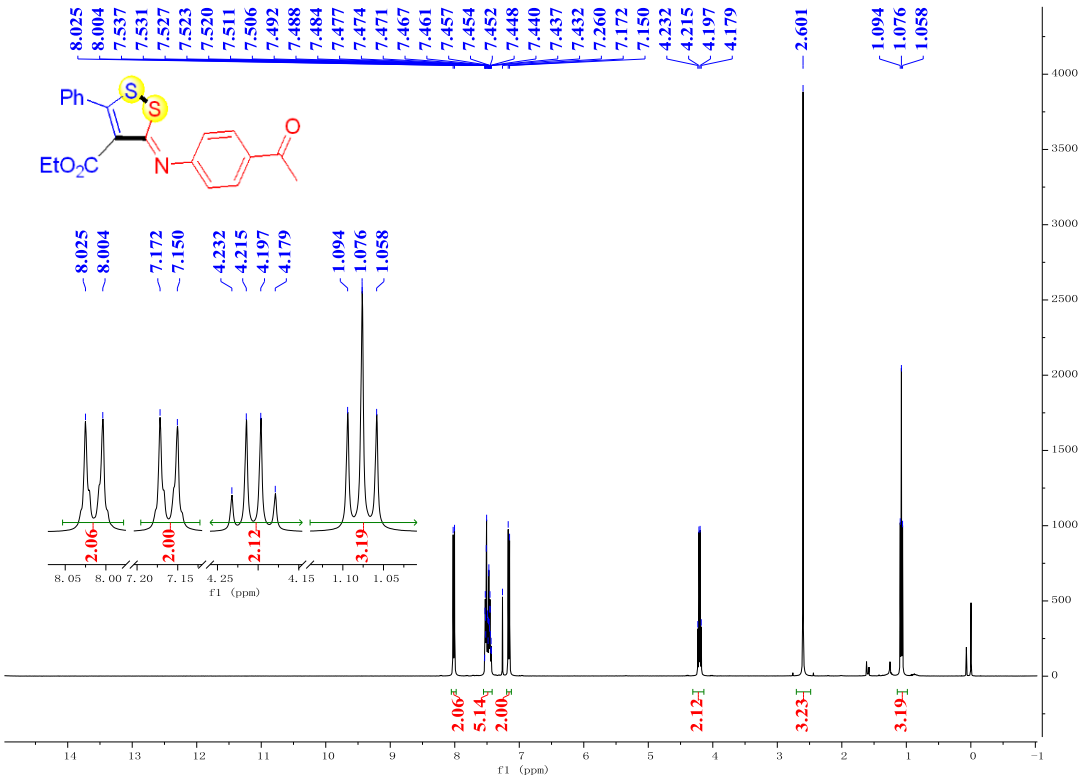


HRMS (ESI)

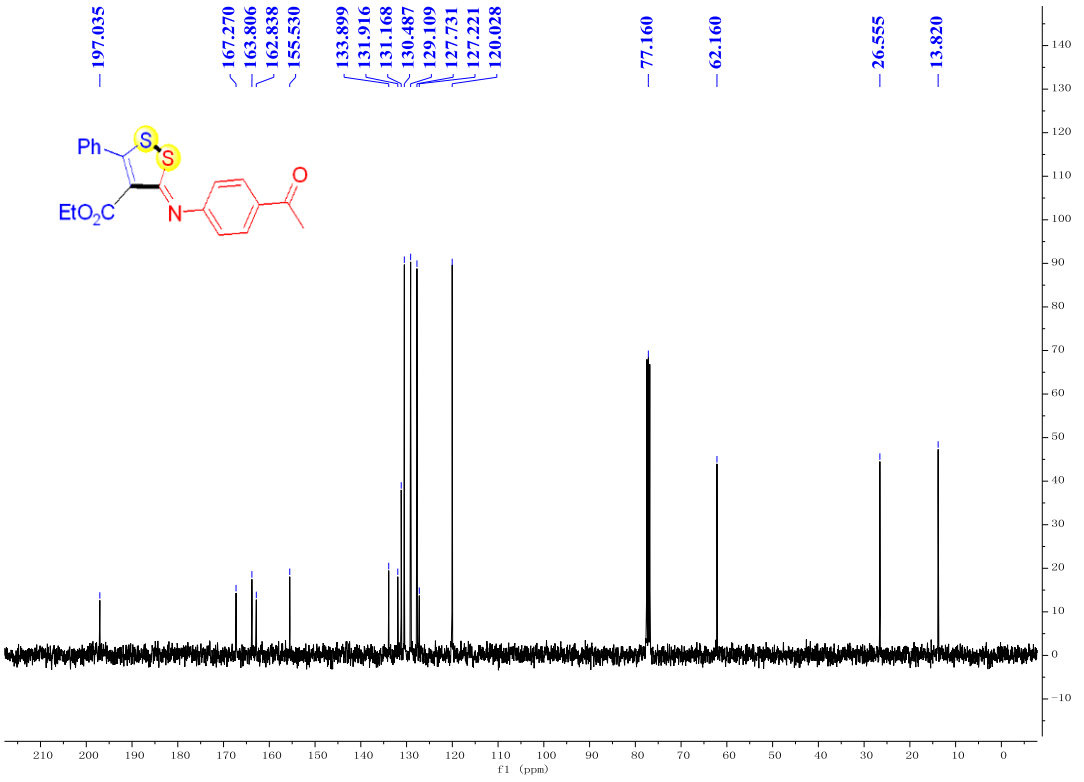

Relative Abundance
m/z
387.04621
388.04932
385.15916
379.14604
383.20387
390.04475
392.31339
398.00462
120
110
100
90
80
70
60
50
40
30
20
10
0
380
385
390
395
400

Ethyl (*Z*)-3-((4-acetylphenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aL**)

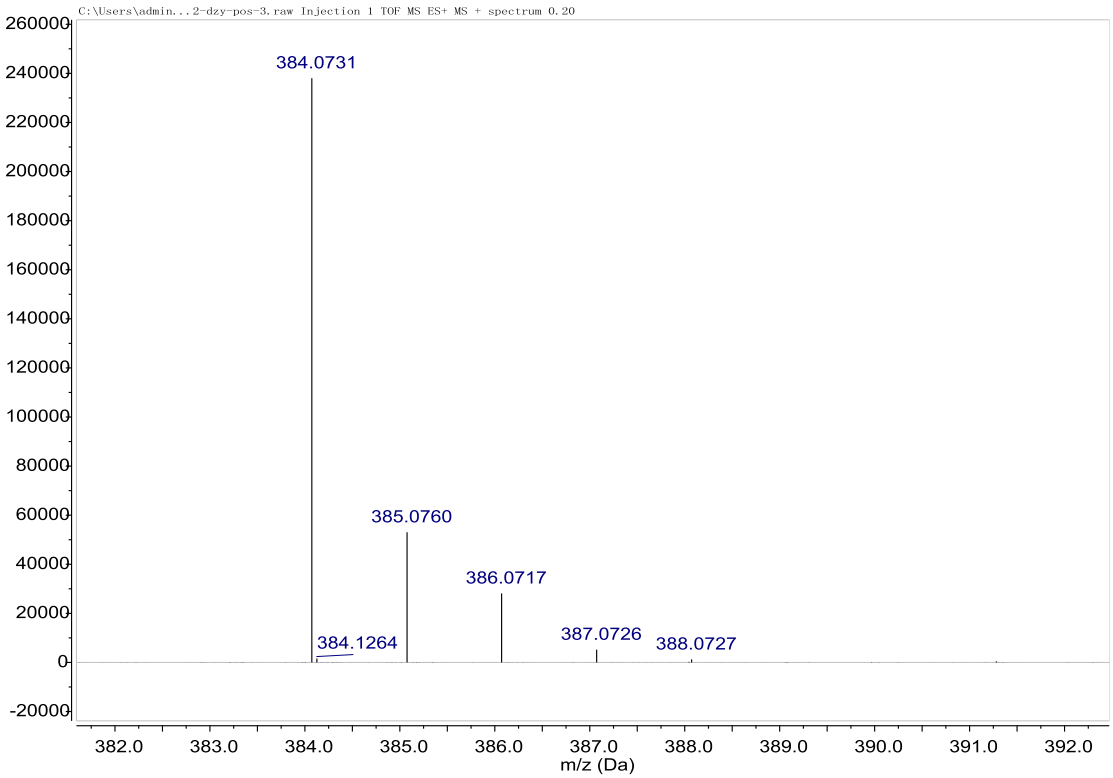
^{1}H NMR (400 MHz, $CDCl_3$)



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

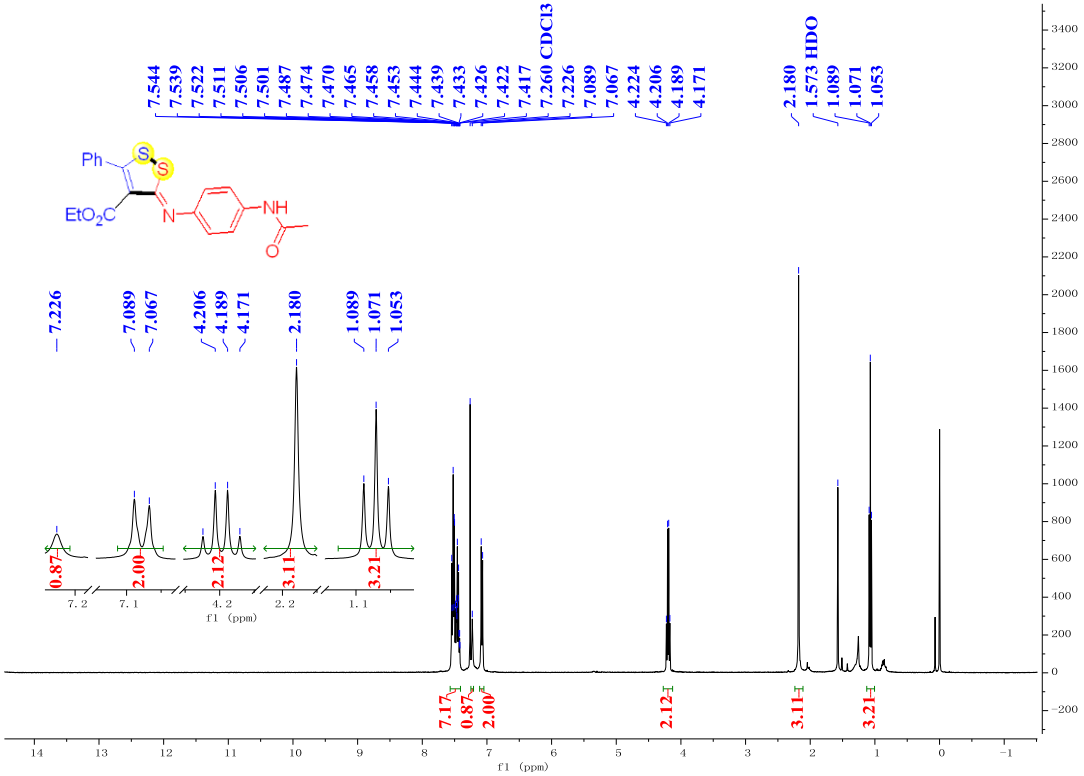


HRMS (ESI)

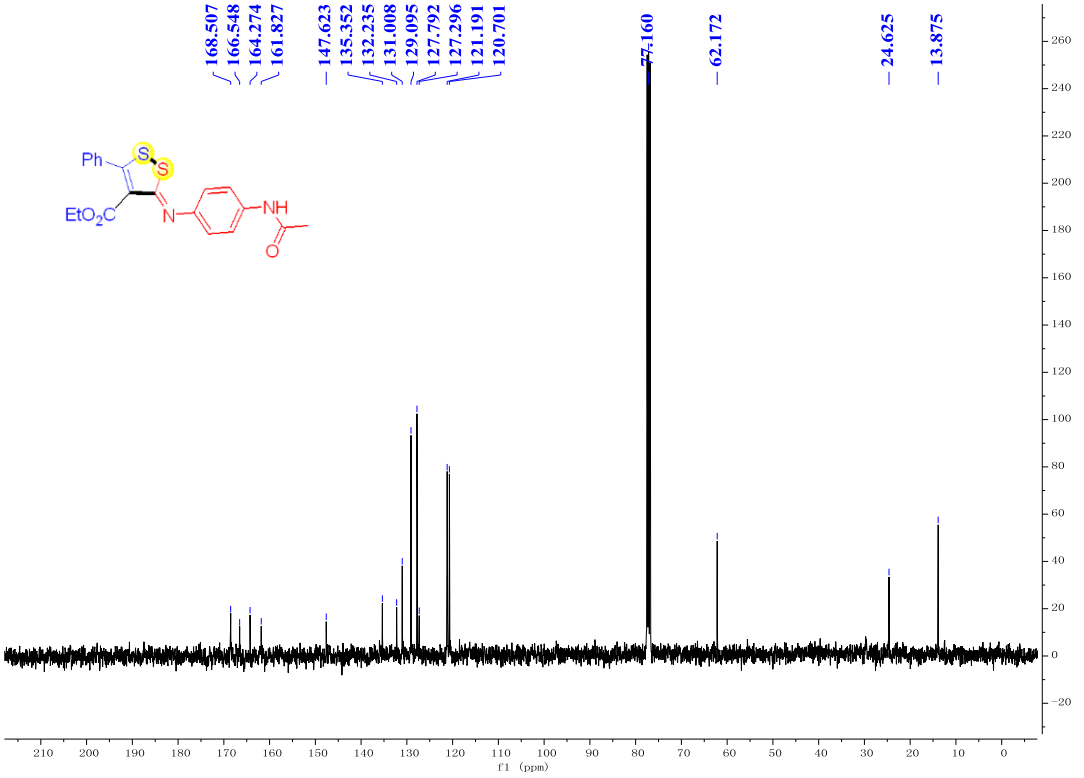

C:\Users\admin...2-dzy-pos-3.raw Injection 1 TOF MS ES+ MS + spectrum 0.20
384.0731
385.0760
386.0717
387.0726
388.0727
384.1264
m/z (Da)

Ethyl (*Z*)-3-((4-acetamidophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aM**)

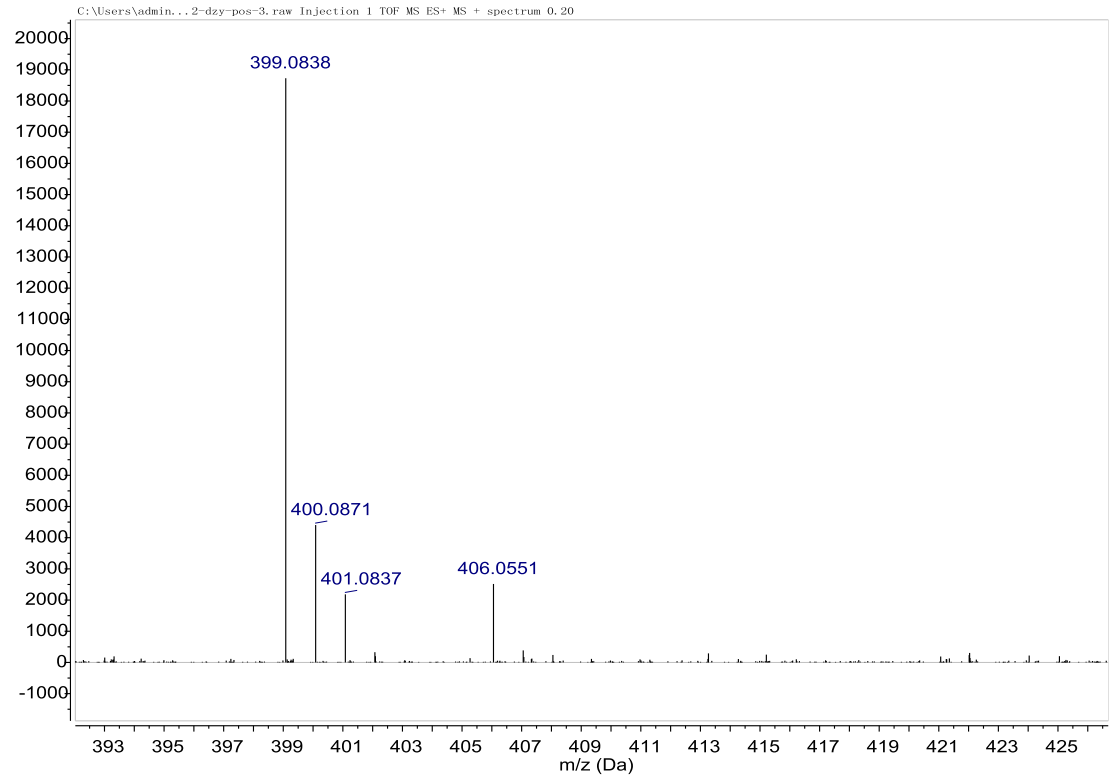
^{1}H NMR (400 MHz, $CDCl_3$)



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

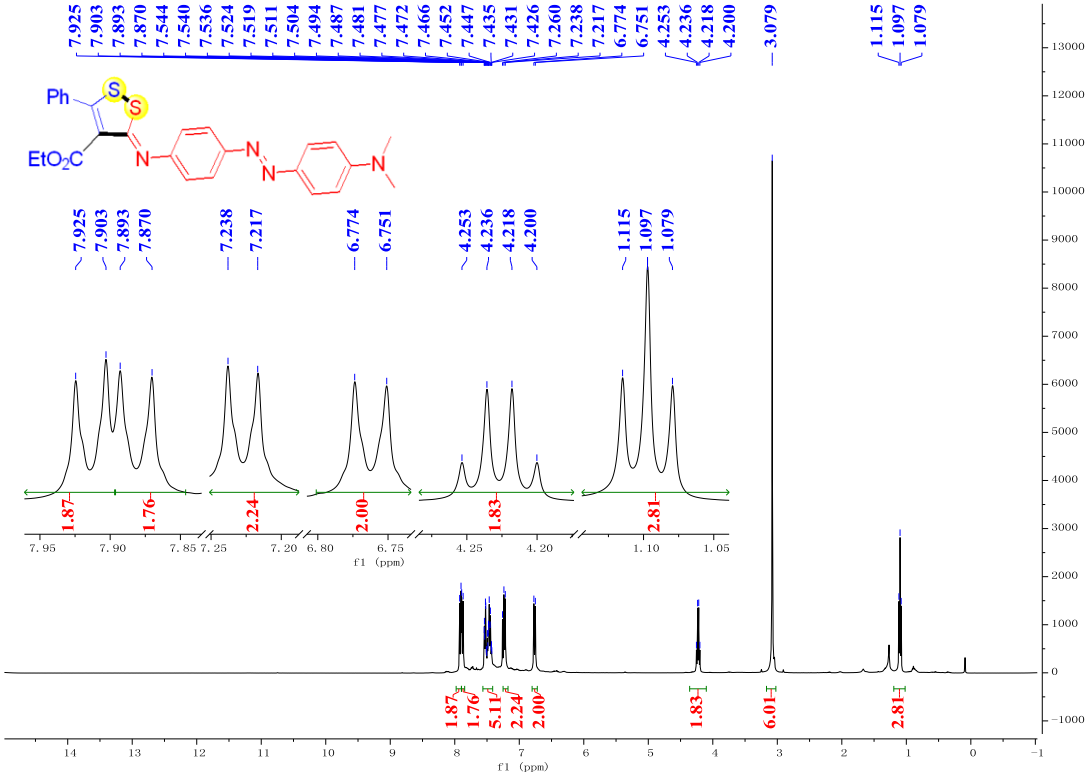


HRMS (ESI)

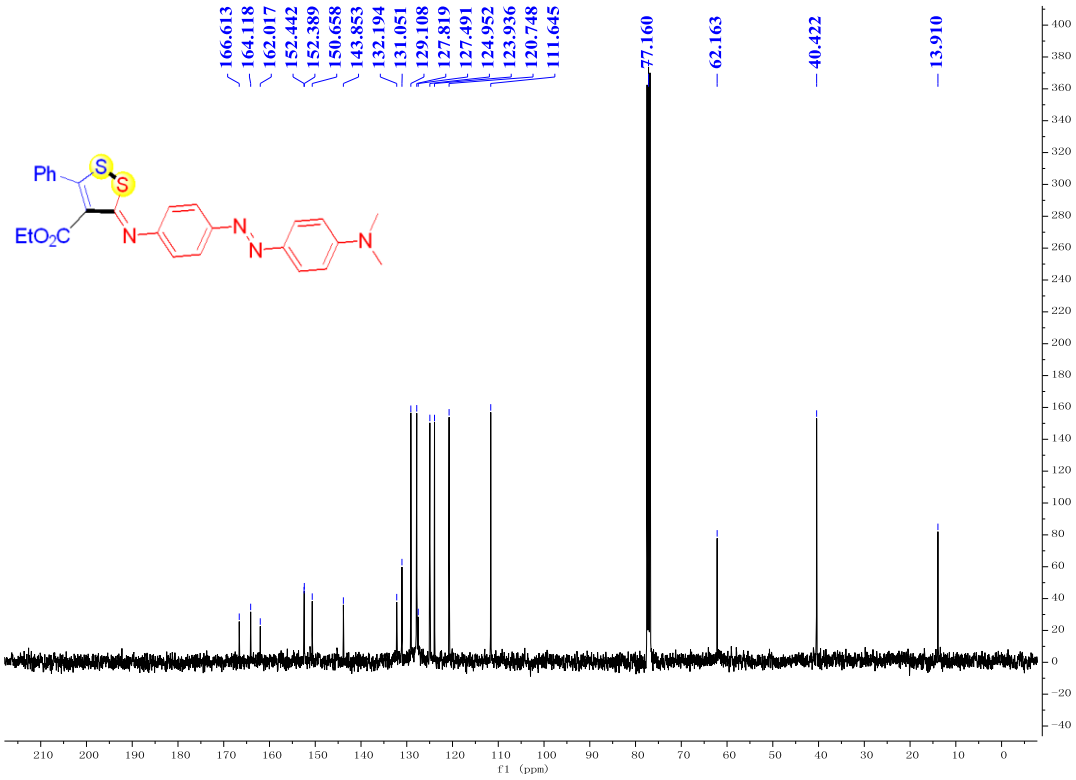

C:\Users\admin...2-dzy-pos-3.raw Injection 1 TOF MS ES+ MS + spectrum 0.20
399.0838
400.0871
401.0837
406.0551
m/z (Da)

Ethyl (*Z*)-3-((4-((*E*)-(4-(dimethylamino)phenyl)diazenyl)phenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aN**)

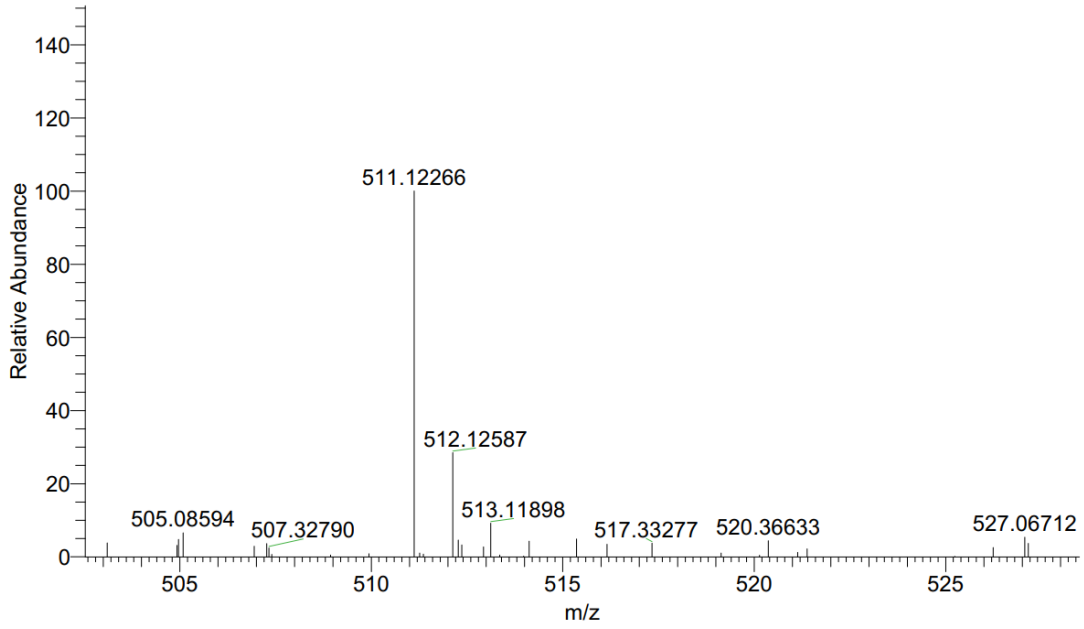
^{1}H NMR (400 MHz, $CDCl_3$)



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

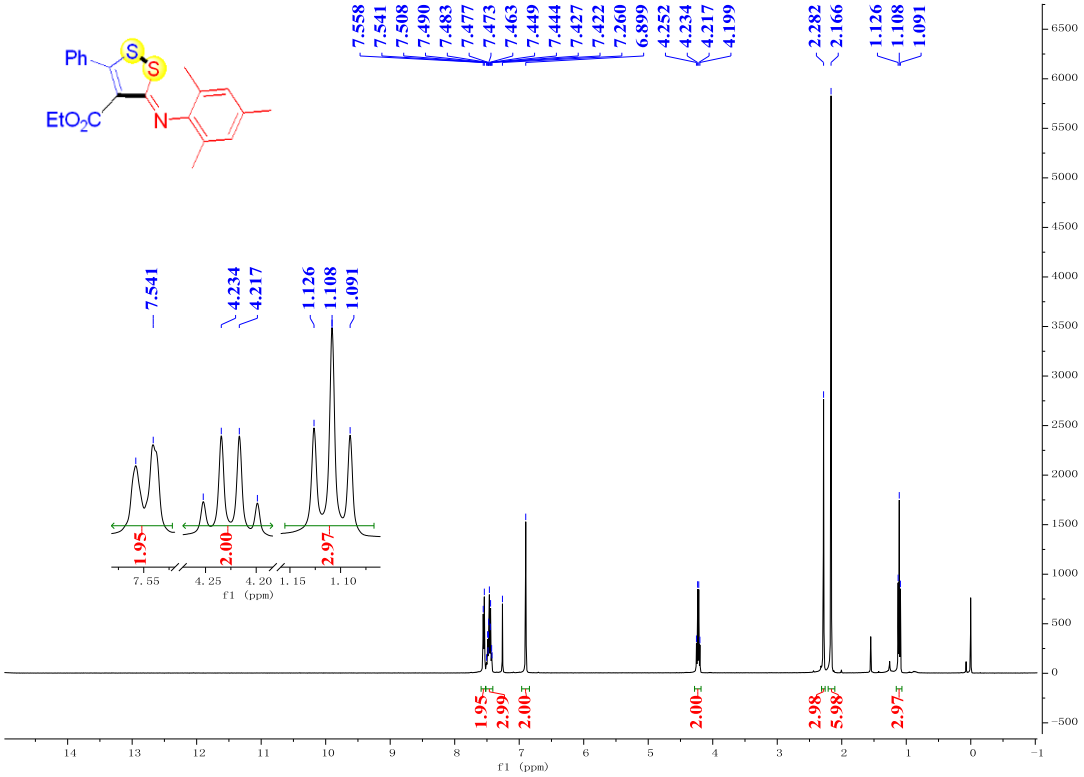


HRMS (ESI)

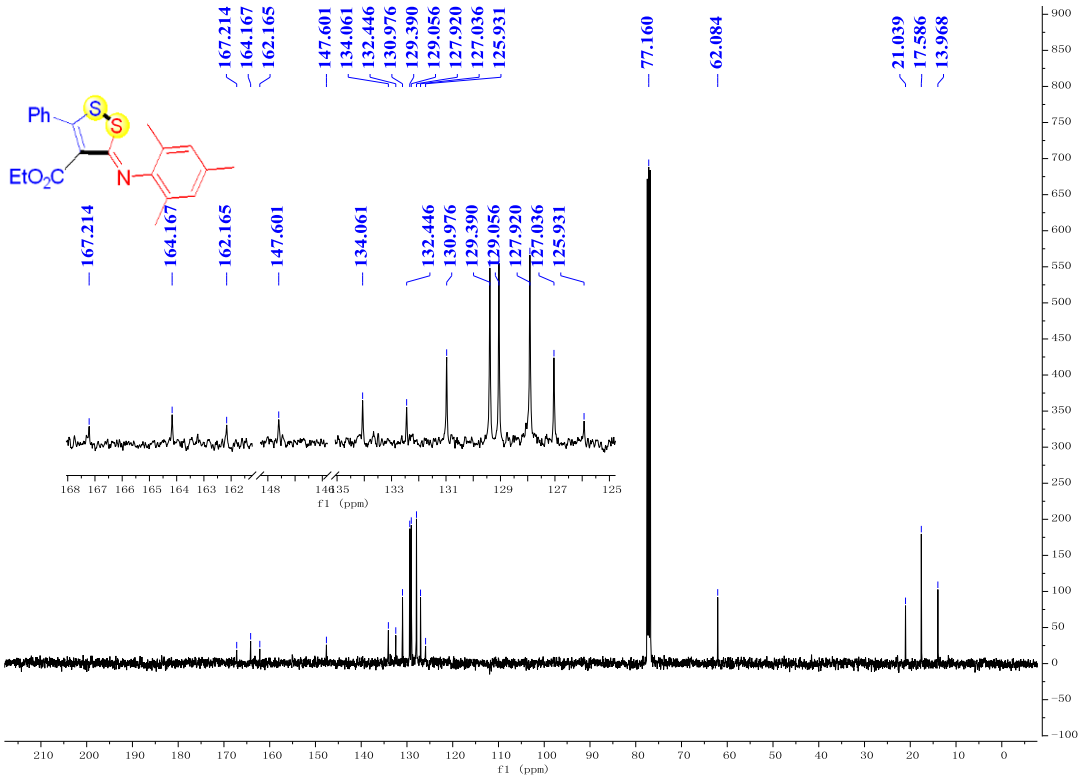

Relative Abundance
m/z
511.12266
512.12587
513.11898
505.08594
507.32790
517.33277
520.36633
527.06712
0
20
40
60
80
100
120
140
505
510
515
520
525

Ethyl (*Z*)-3-(mesitylimino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aO**)

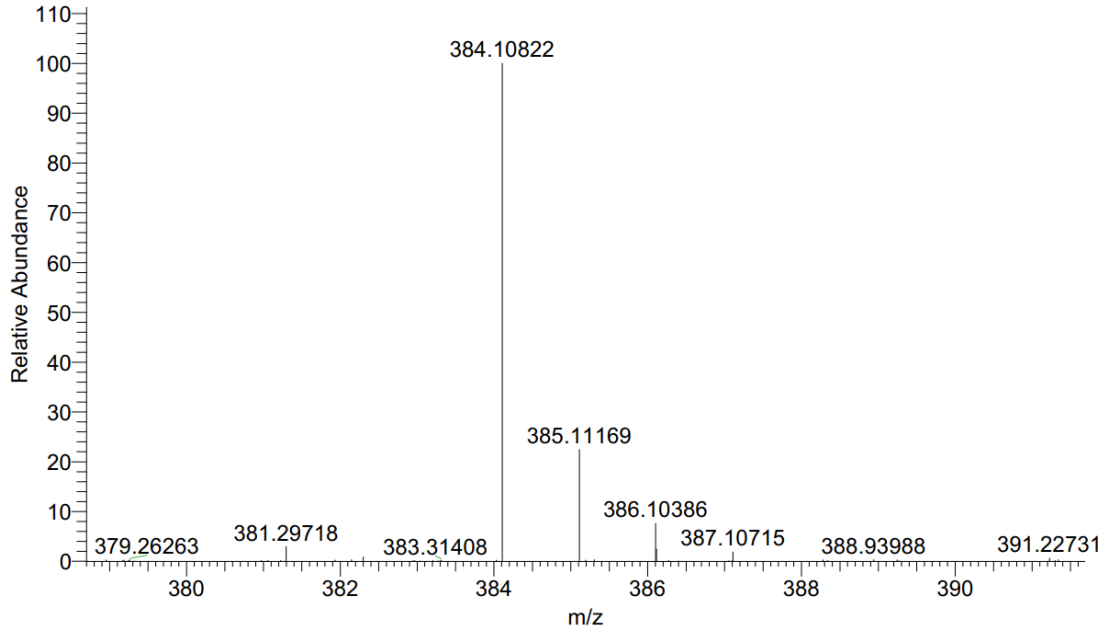
^{1}H NMR (400 MHz, $CDCl_3$)



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

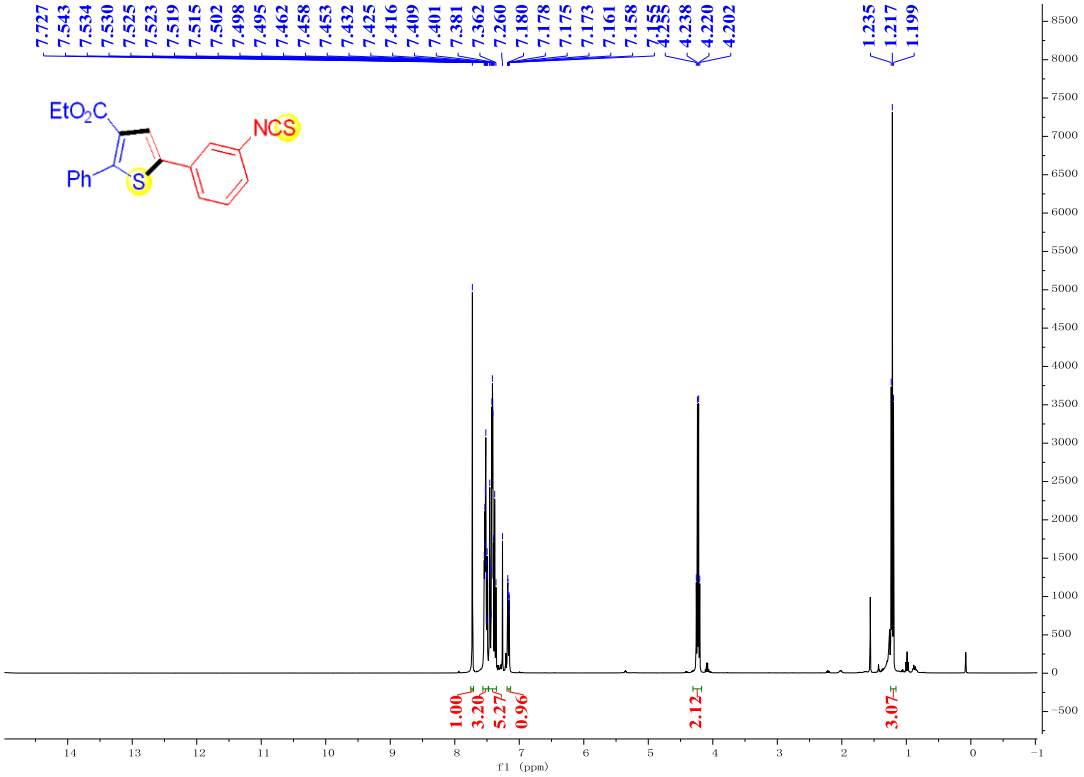


HRMS (ESI)

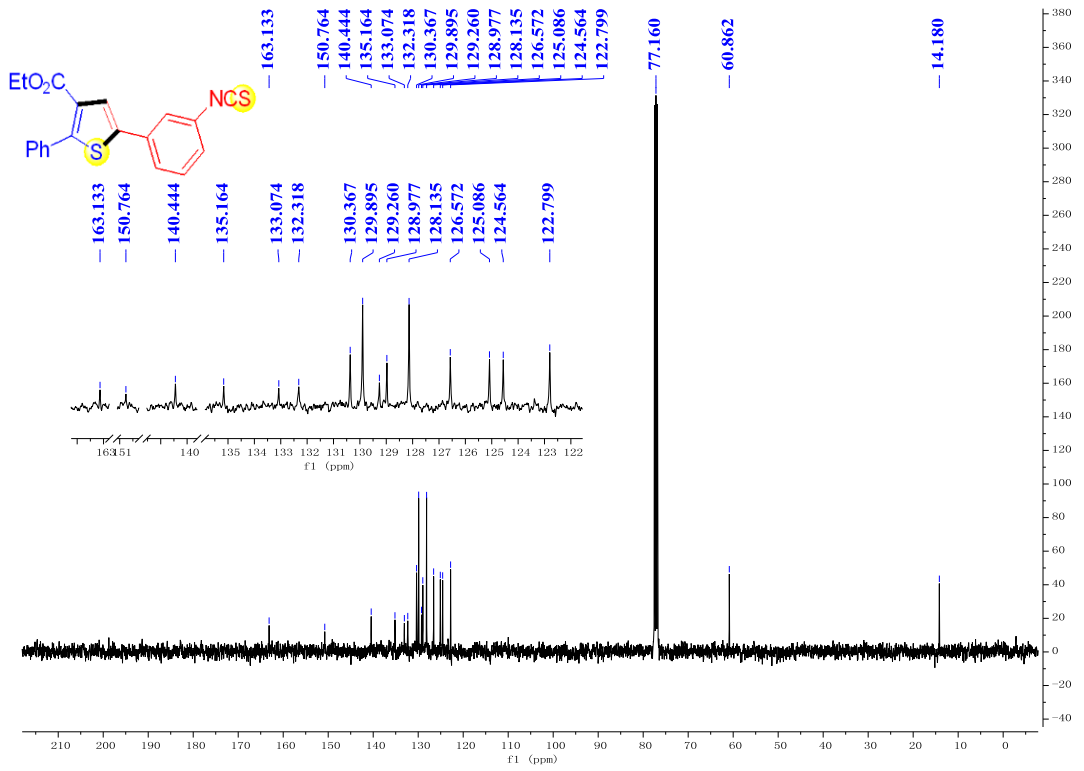

384.10822
385.11169
386.10386
387.10715
379.26263
381.29718
383.31408
388.93988
391.22731
Relative Abundance
m/z
110
100
90
80
70
60
50
40
30
20
10
0
380
382
384
386
388
390

Ethyl 5-(3-isothiocyanatophenyl)-2-phenylthiophene-3-carboxylate (**3aP**)

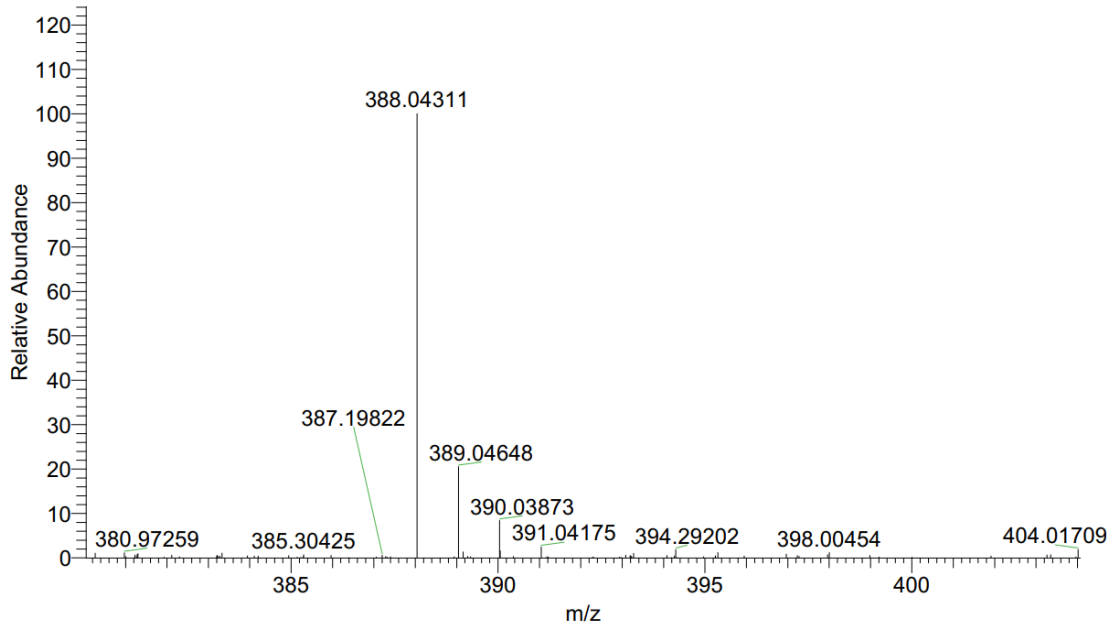
^{1}H NMR (400 MHz, $CDCl_3$)



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

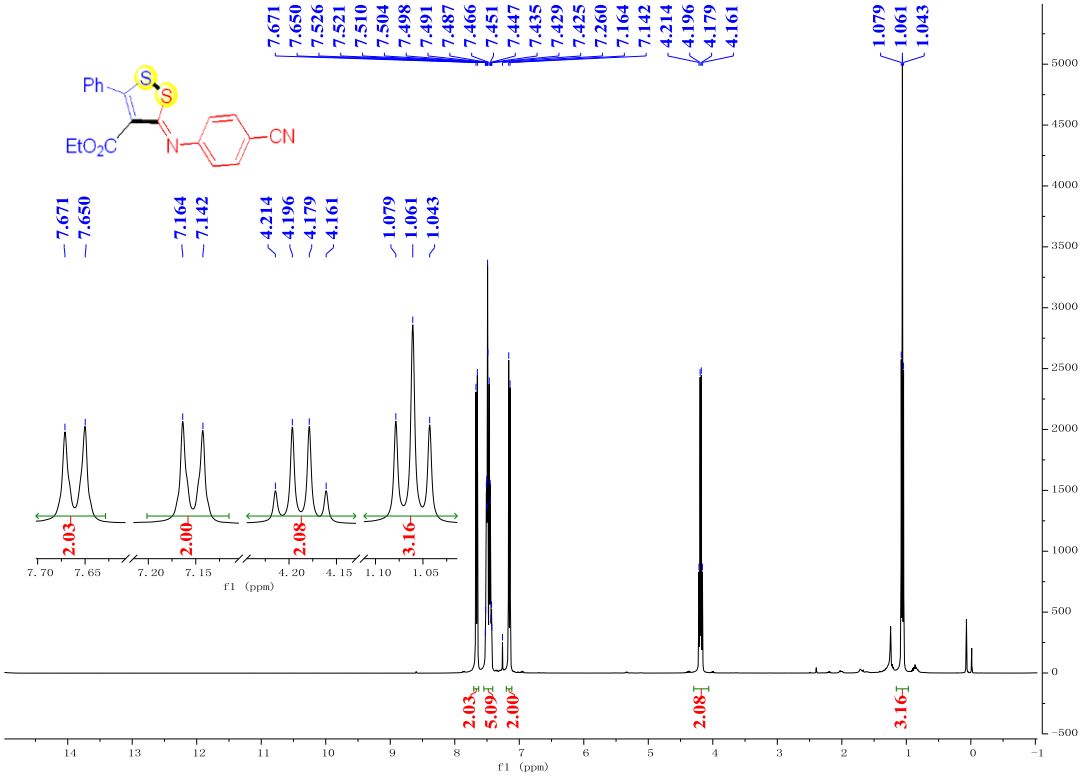


HRMS (ESI)

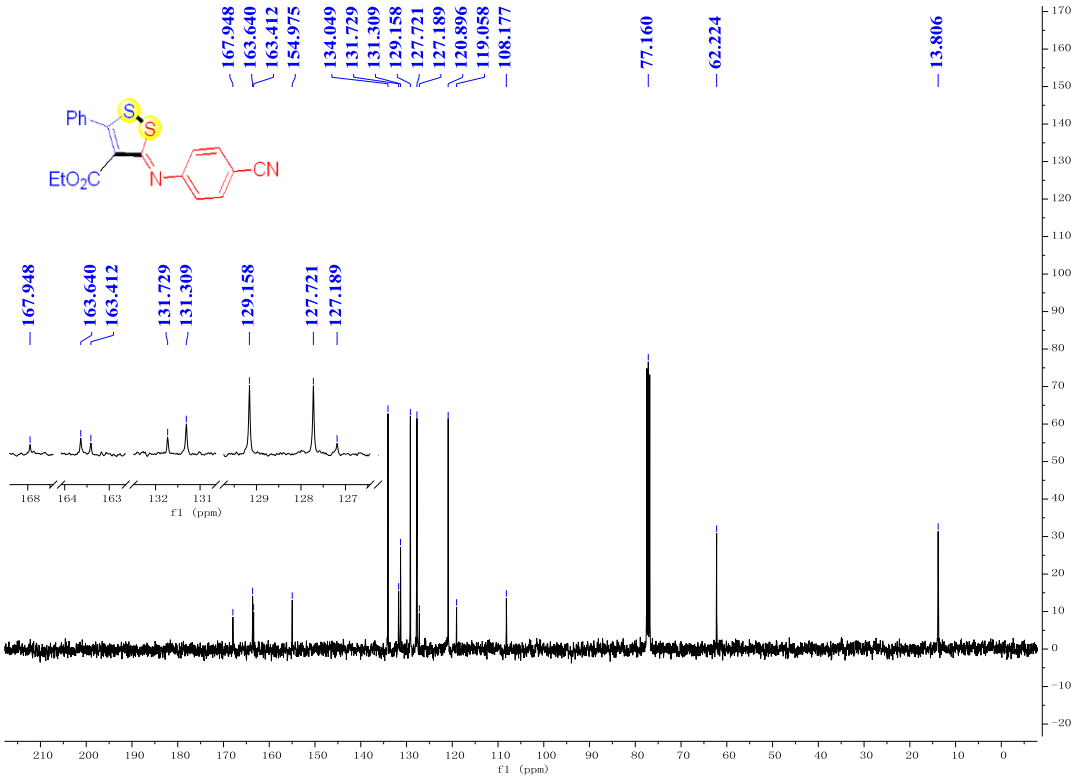

Relative Abundance
m/z
388.04311
387.19822
389.04648
390.03873
391.04175
380.97259
385.30425
394.29202
398.00454
404.01709

Ethyl (*Z*)-3-((4-cyanophenyl)imino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**3aQ**)

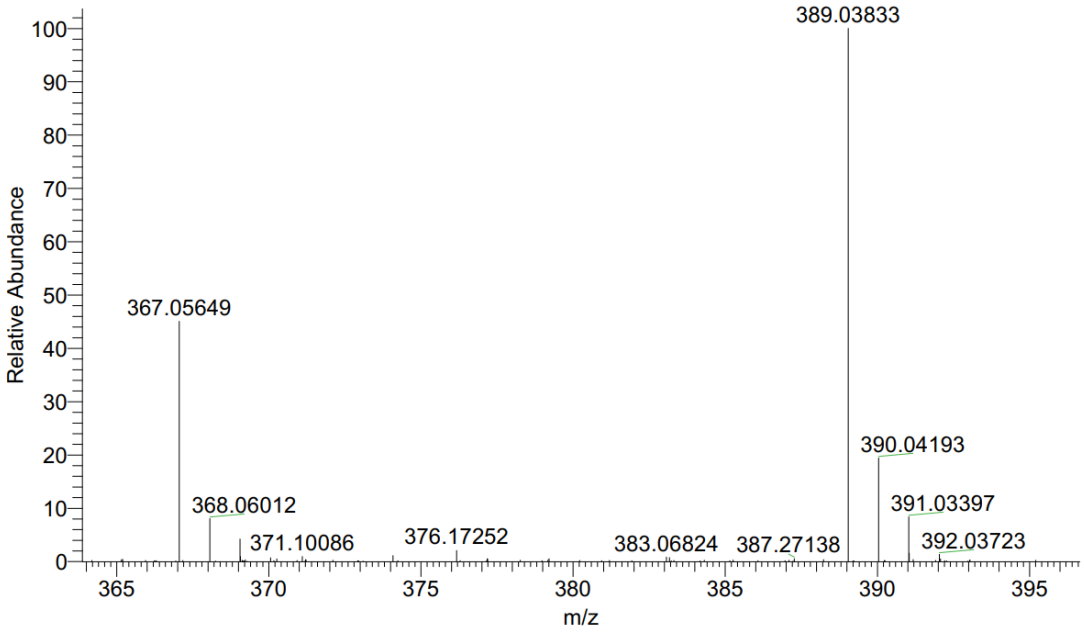
^{1}H NMR (400 MHz, $CDCl_3$)



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



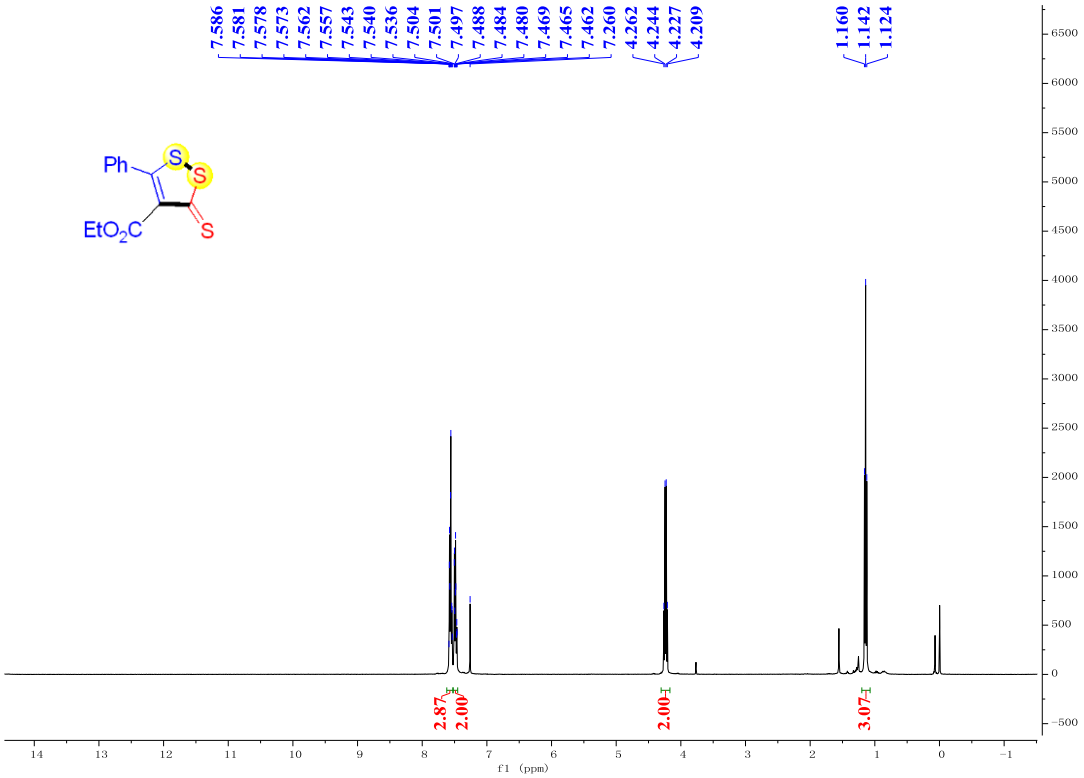
HRMS (ESI)

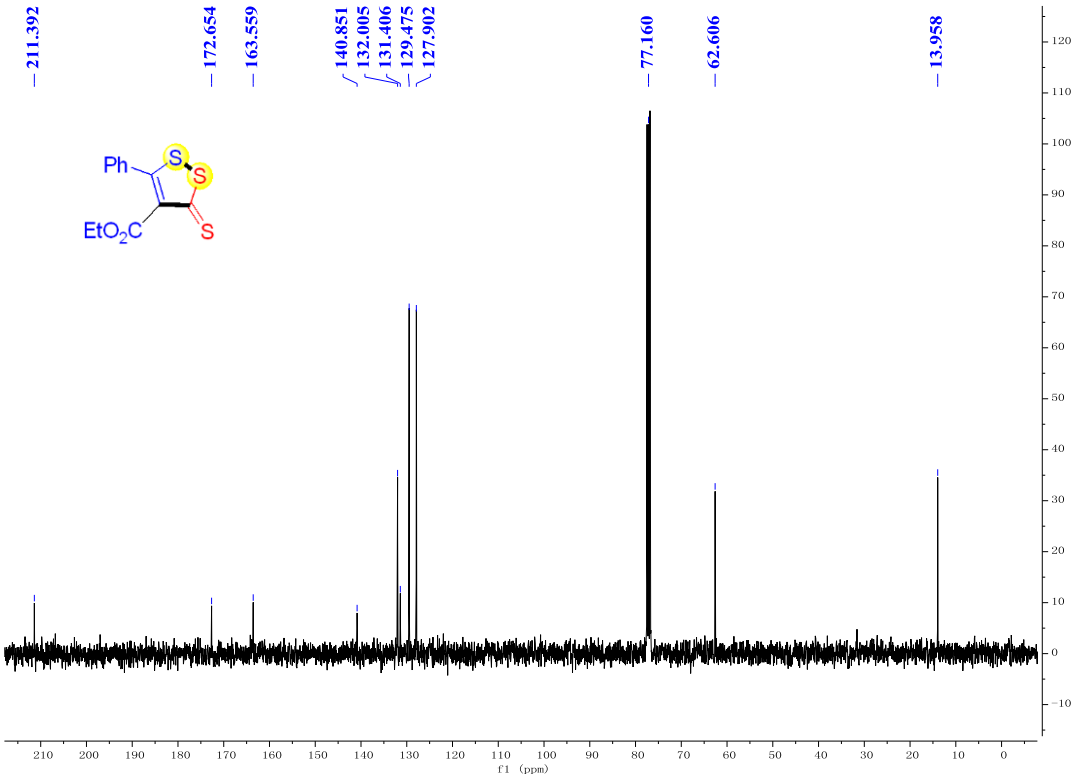

389.03833
367.05649
390.04193
368.06012
391.03397
371.10086
376.17252
383.06824
387.27138
392.03723
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
365
370
375
380
385
390
395

13.4 Copies of spectra of products for reaction with carbon disulfide, gram-scale reaction and product derivatization

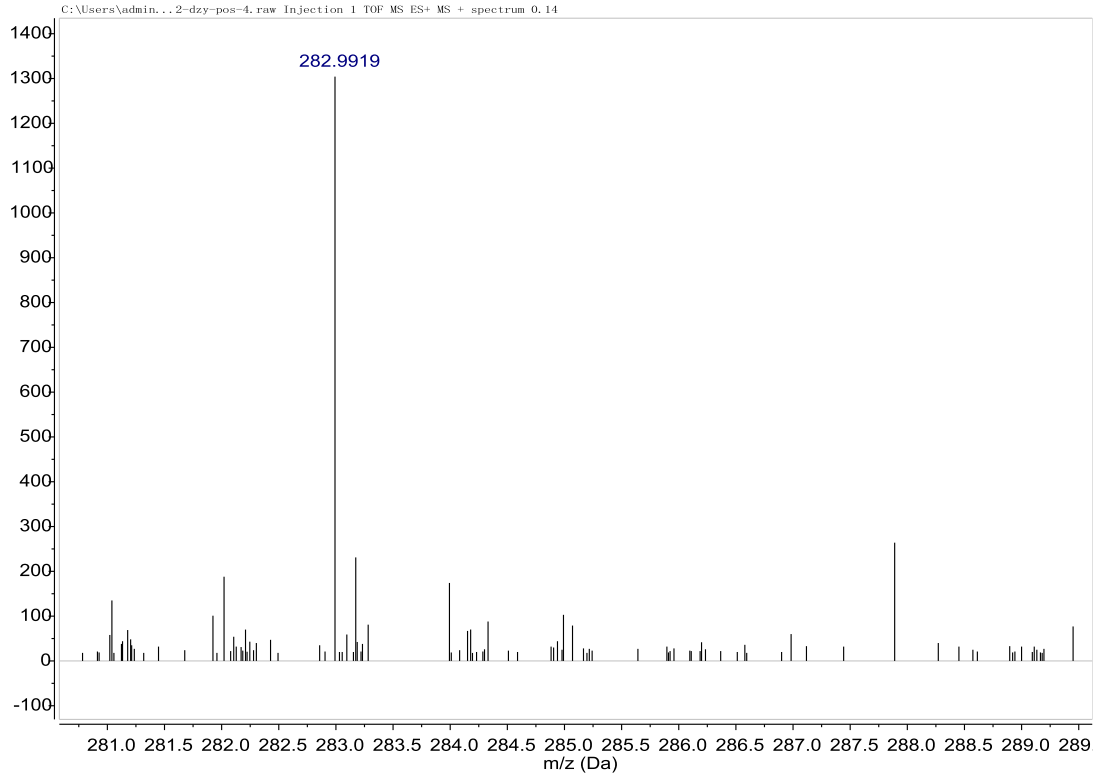
Ethyl 5-phenyl-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**7**)

^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$)



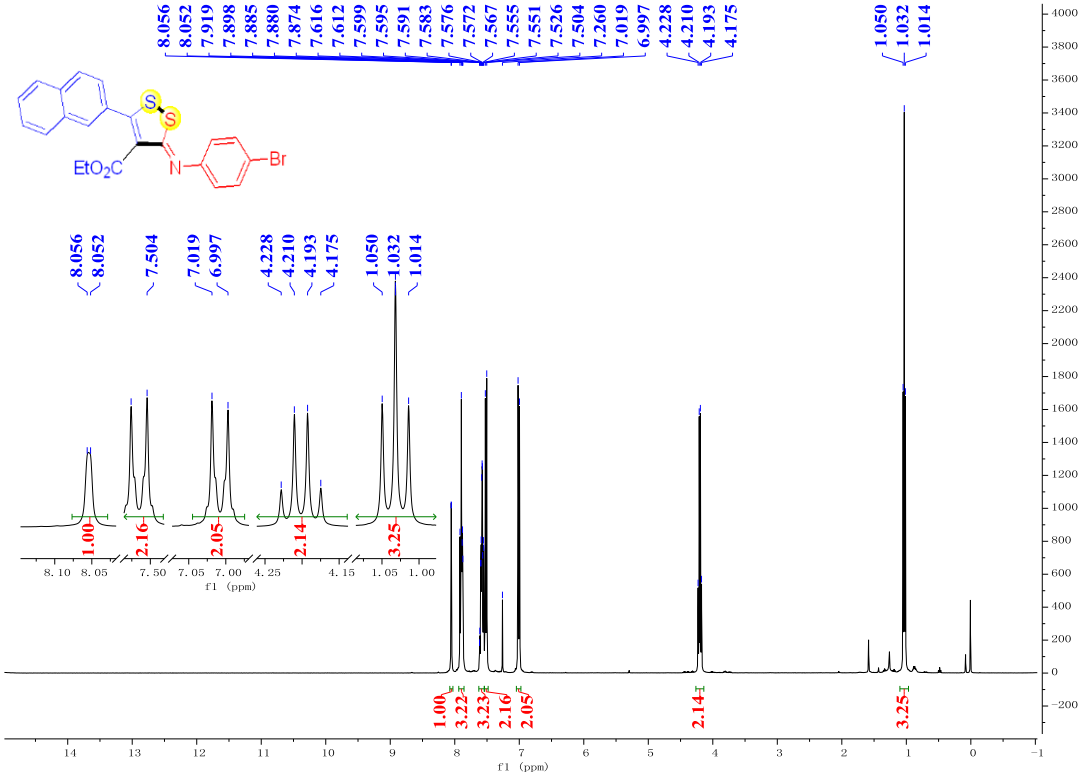


HRMS (ESI)

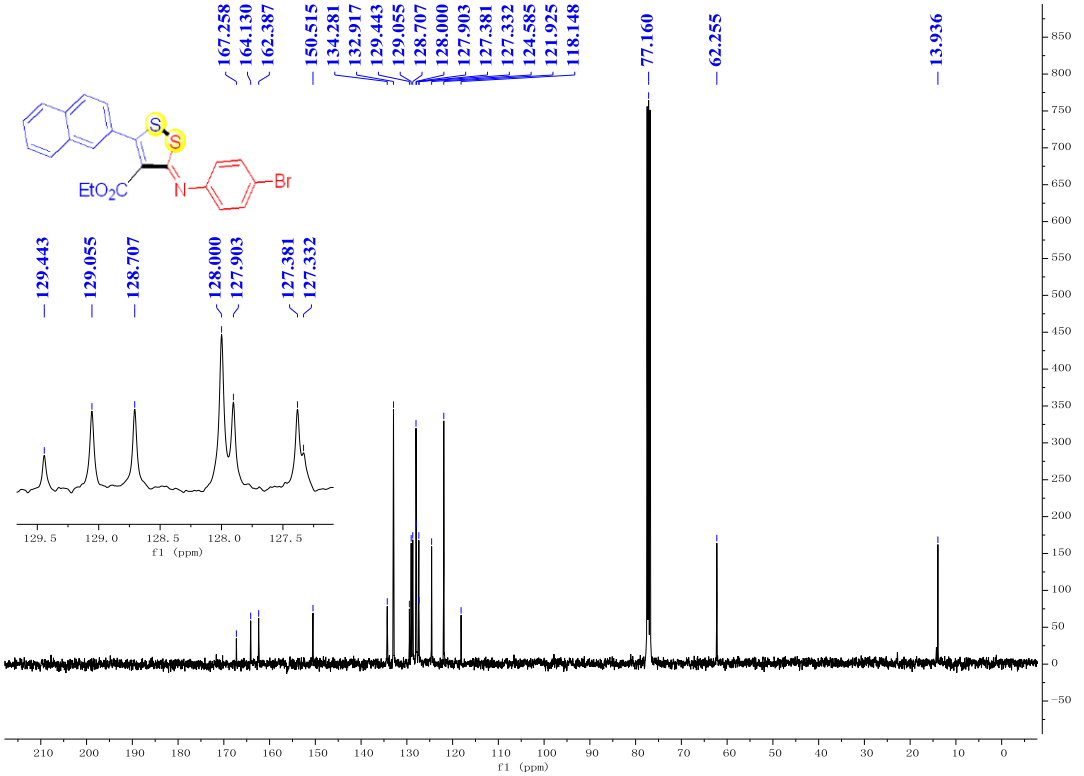

C:\Users\admin...2-dzy-pos-4.raw Injection 1 TOF MS ES+ MS + spectrum 0.14
282.9919
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
281.0 281.5 282.0 282.5 283.0 283.5 284.0 284.5 285.0 285.5 286.0 286.5 287.0 287.5 288.0 288.5 289.0 289
m/z (Da)

Ethyl (*Z*)-3-((4-bromophenyl)imino)-5-(naphthalen-2-yl)-3*H*-1,2-dithiole-4-carboxylate (**3oA**)

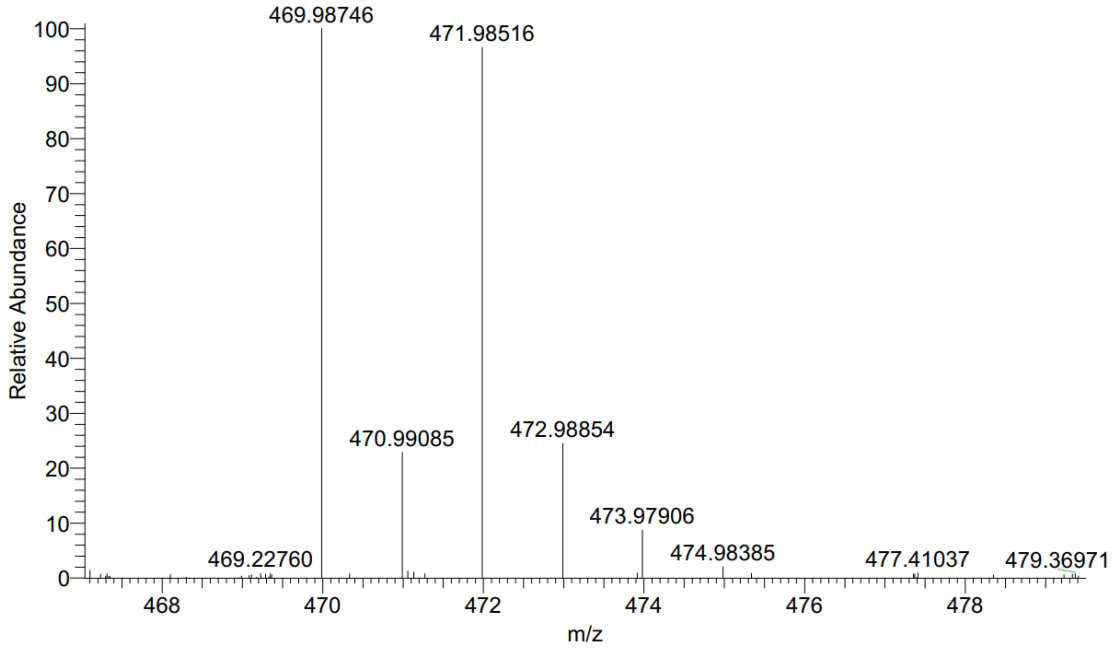
^{1}H NMR (400 MHz, $CDCl_3$)



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

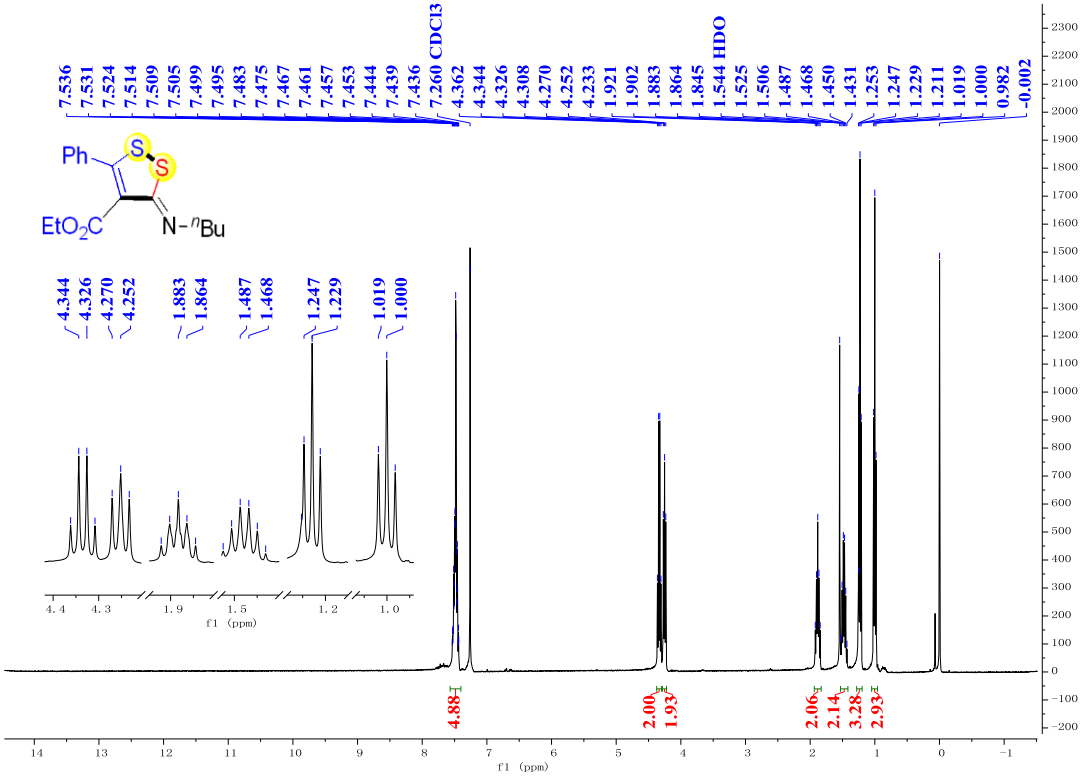


HRMS (ESI)

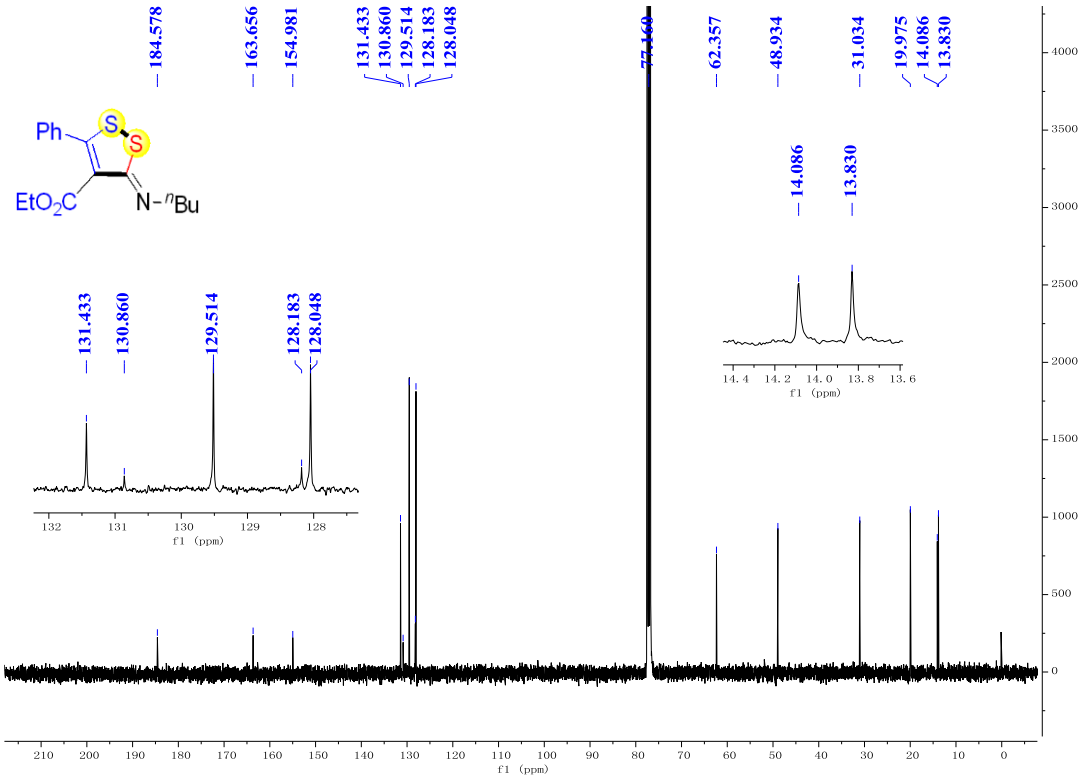

469.98746
471.98516
470.99085
472.98854
473.97906
474.98385
469.22760
477.41037
479.36971
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
468
470
472
474
476
478

Ethyl (*Z*)-3-(butylimino)-5-phenyl-3*H*-1,2-dithiole-4-carboxylate (**8**)

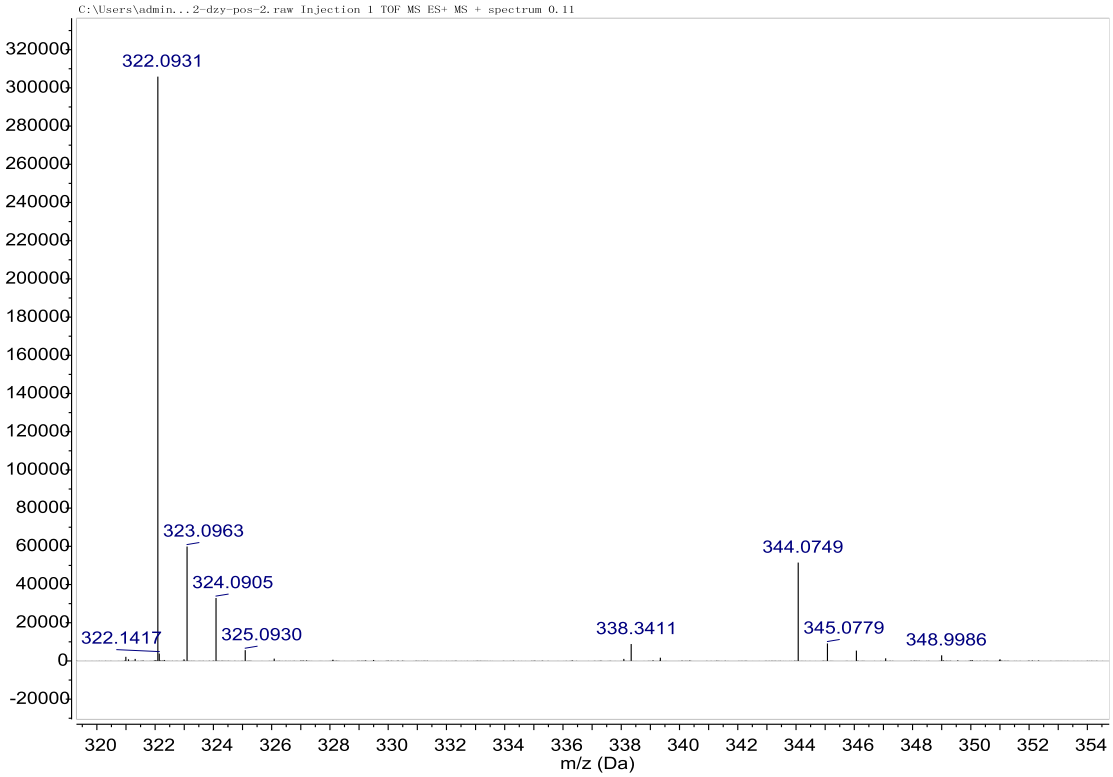
^{1}H NMR (400 MHz, $CDCl_3$)



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

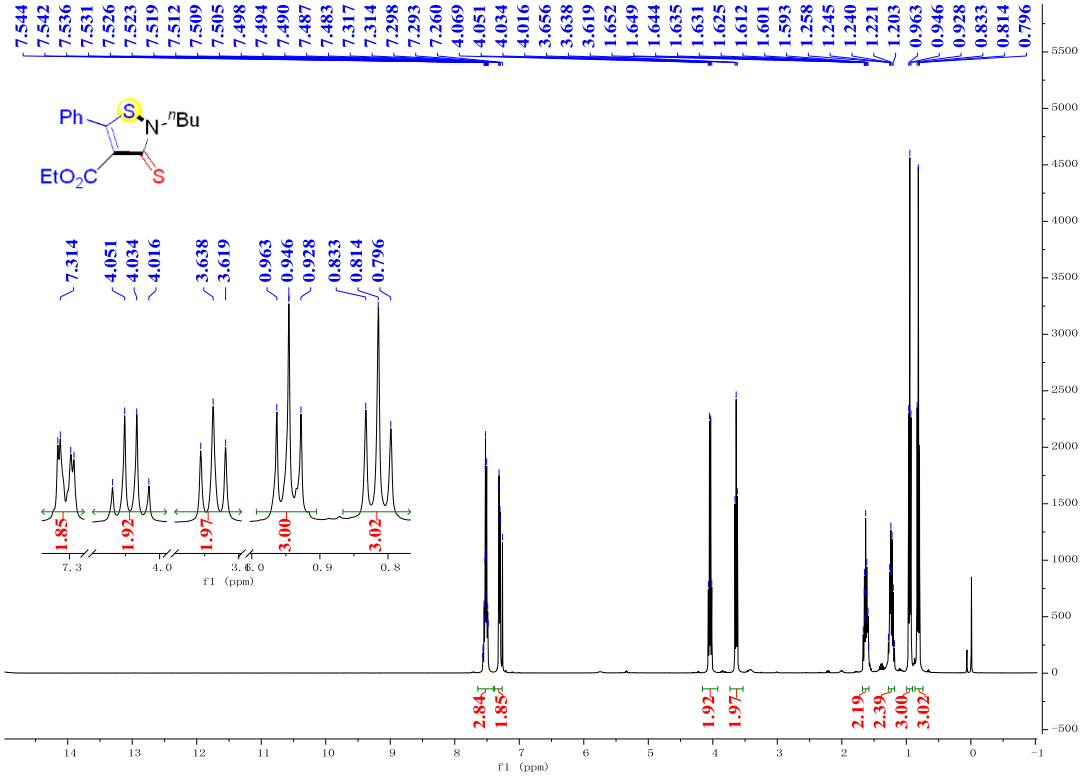


HRMS (ESI)

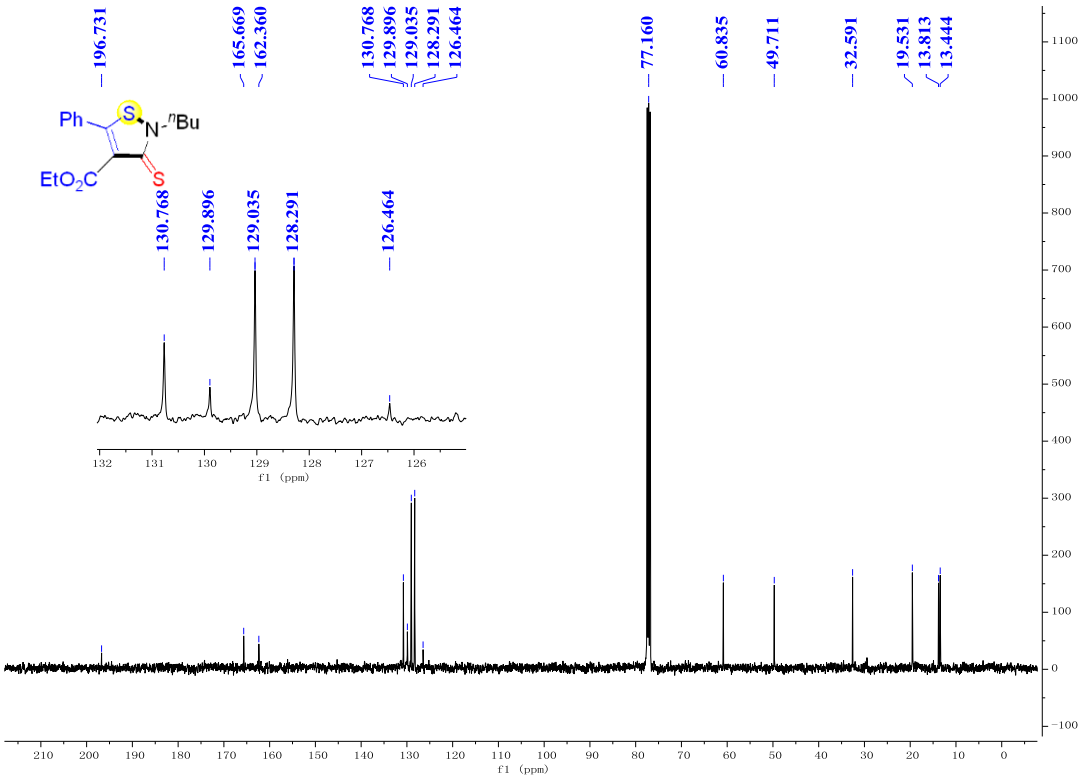

C:\Users\admin...2-dzy-pos-2.raw Injection 1 TOF MS ES+ MS + spectrum 0.11
322.0931
323.0963
324.0905
325.0930
322.1417
338.3411
344.0749
345.0779
348.9986
m/z (Da)

Ethyl 2-butyl-5-phenyl-3-thioxo-2,3-dihydroisothiazole-4-carboxylate (**9**)

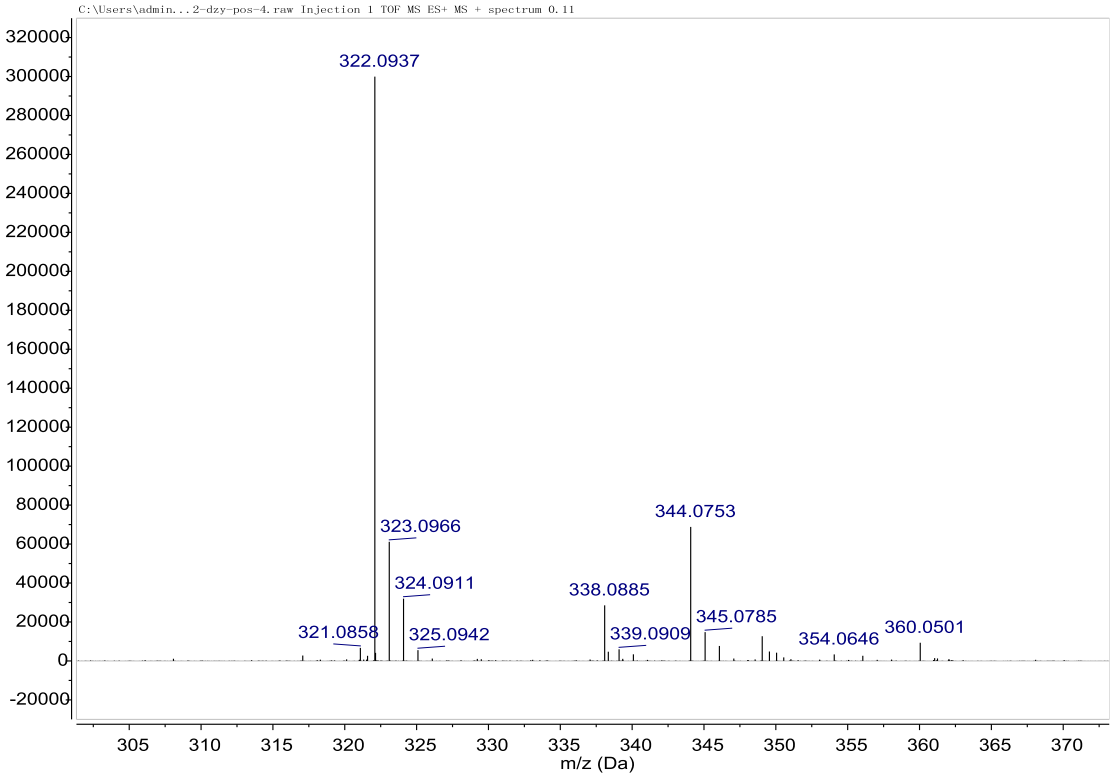
^{1}H NMR (400 MHz, $CDCl_3$)



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

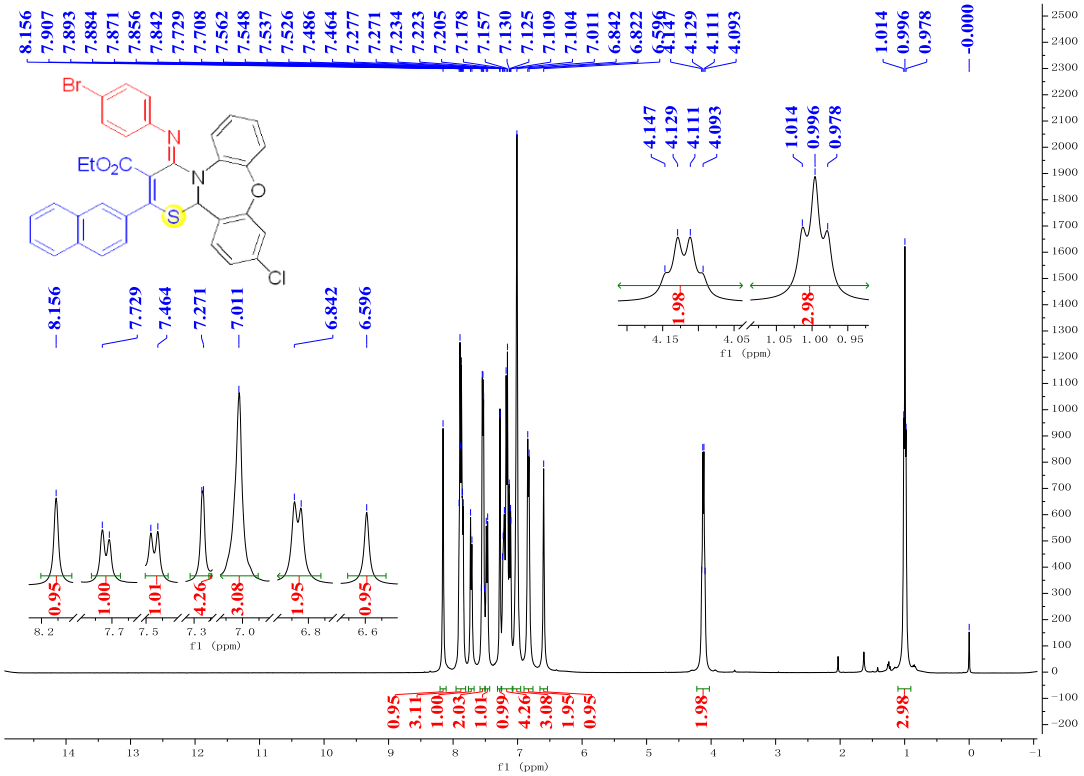


HRMS (ESI)

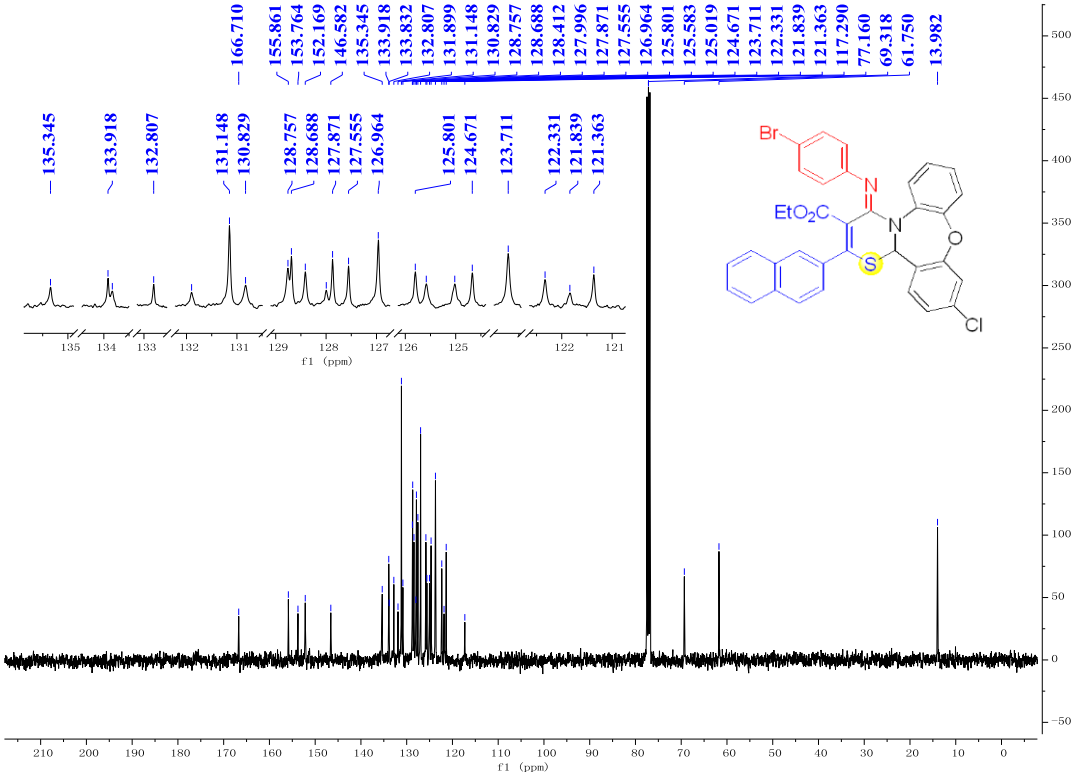

C:\Users\admin...2-dzy-pos-4.raw Injection 1 TOF MS ES+ MS + spectrum 0.11
322.0937
323.0966
324.0911
321.0858
325.0942
338.0885
344.0753
339.0909
345.0785
354.0646
360.0501
m/z (Da)

Ethyl 4-((4-bromophenyl)imino)-12-chloro-2-(naphthalen-2-yl)-4*H*,14b*H*-dibenzo[*b*,*f*][1,3]thiazino[3,2-*d*][1,4]oxazepine-3-carboxylate (**11**)

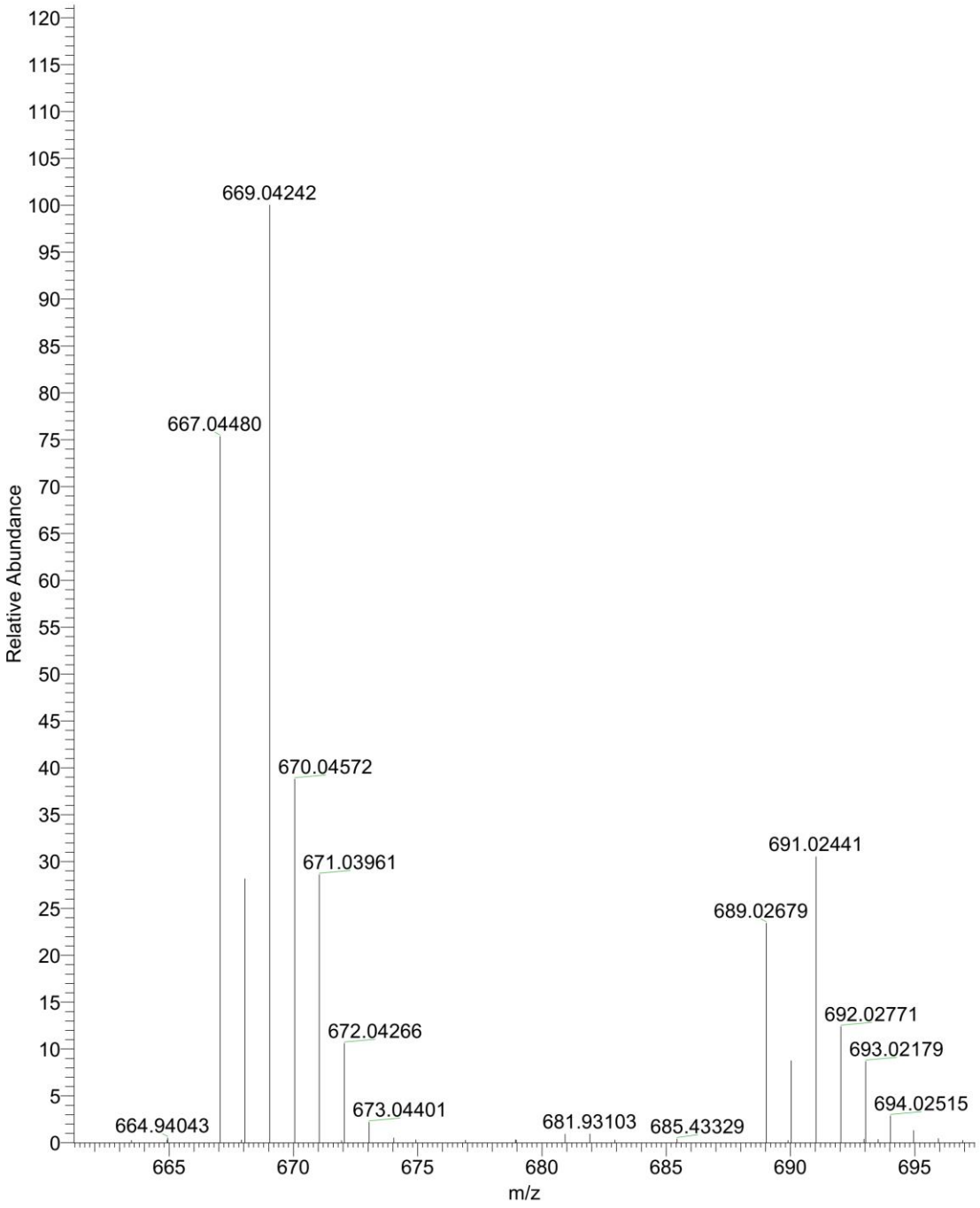
^{1}H NMR (400 MHz, $CDCl_3$)



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

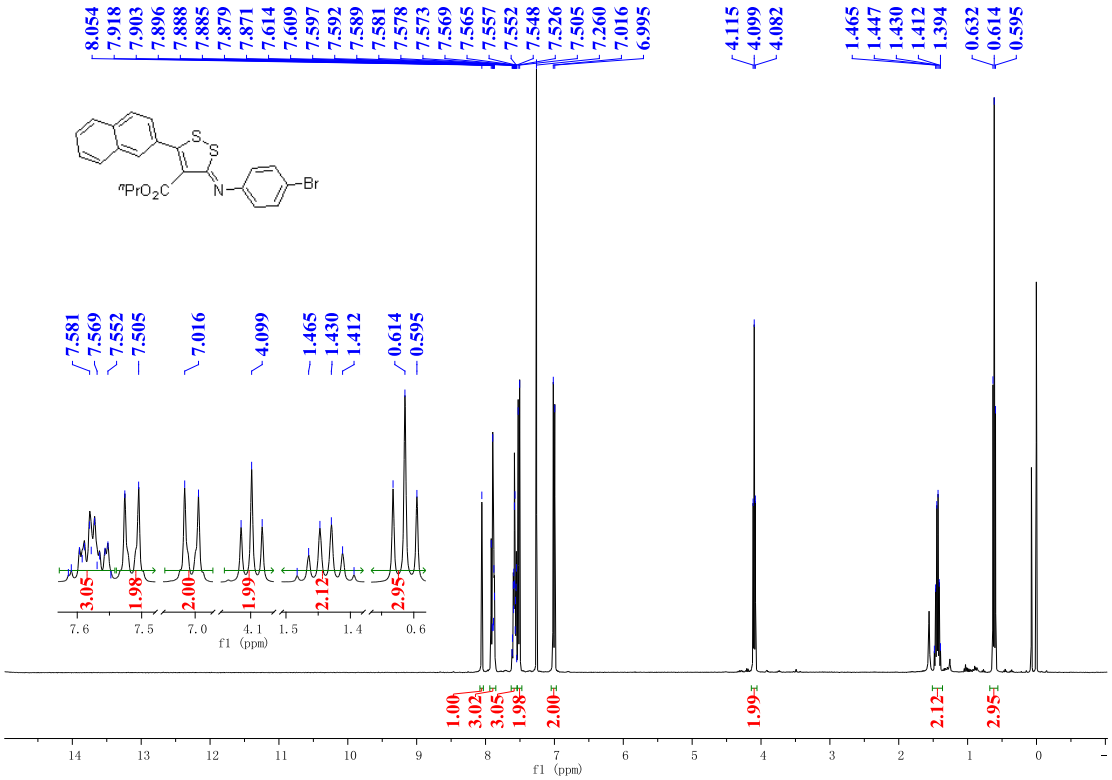


HRMS (ESI)

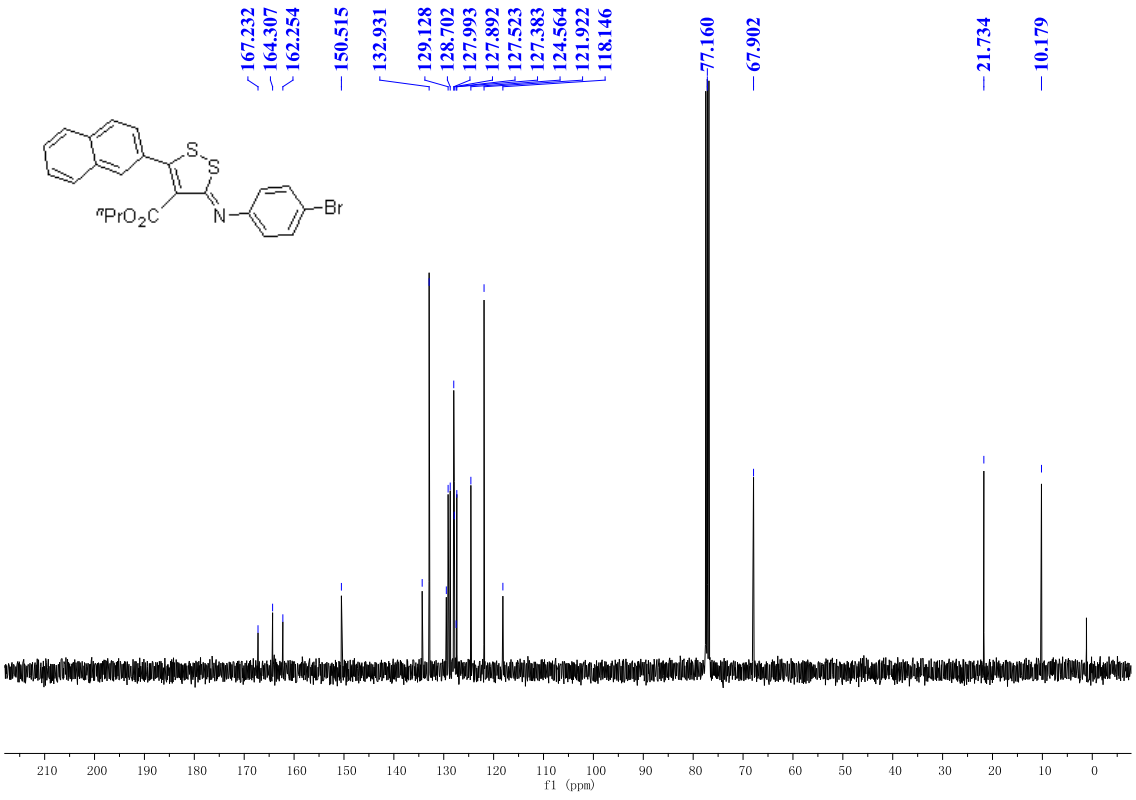

669.04242
667.04480
670.04572
671.03961
672.04266
673.04401
664.94043
681.93103
685.43329
691.02441
689.02679
692.02771
693.02179
694.02515
Relative Abundance
m/z

Propyl (*Z*)-3-((4-bromophenyl)imino)-5-(naphthalen-2-yl)-3*H*-1,2-dithiole-4-carboxylate (**12**)

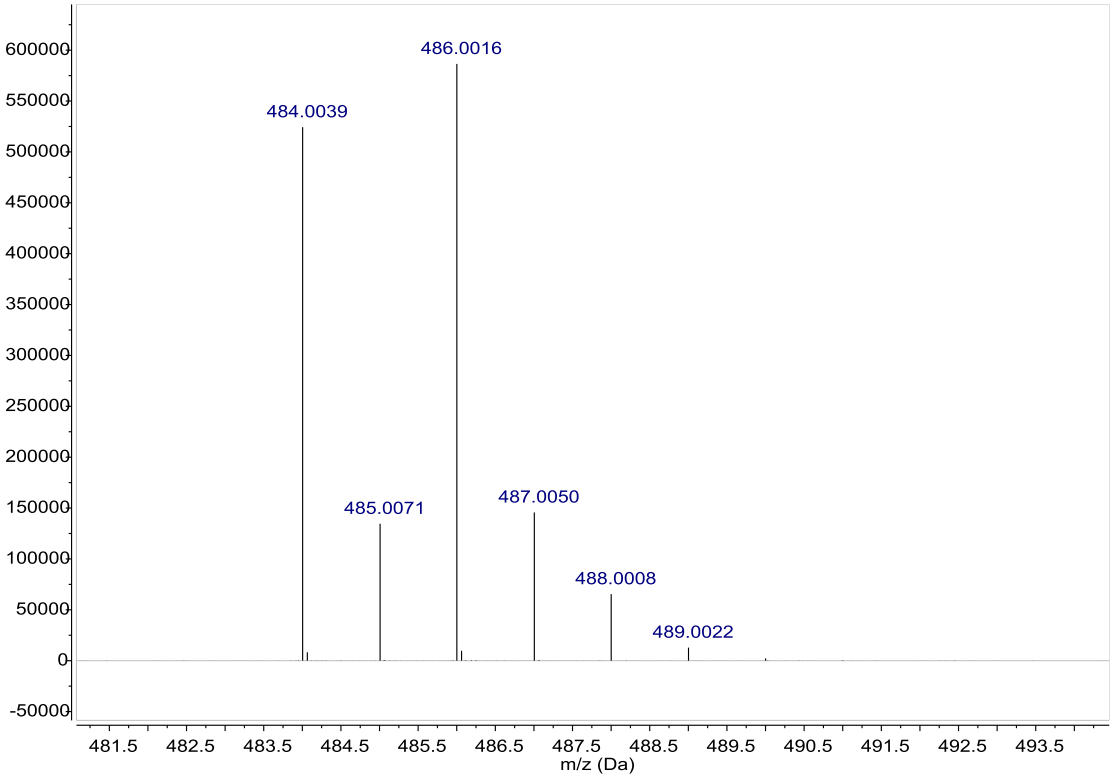
^{1}H NMR (400 MHz, $CDCl_3$)



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



HRMS (ESI)


600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
484.0039
486.0016
485.0071
487.0050
488.0008
489.0022
481.5
482.5
483.5
484.5
485.5
486.5
487.5
488.5
489.5
490.5
491.5
492.5
493.5
m/z (Da)