Electronic Supplementary Information (ESI) for

One-pot synthesis of thiazino[2,3,4-*hi*]indole derivatives through tandem oxidative coupling/heteroannulation process

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1. General Information.

All one-pot reactions were performed in an over-dried Schlenk tube equipped with a magnetic stir bar under N_2 atmosphere. DMF, DMAc and DMSO were distilled from CaH_2. N-(*o*-Haloaryl) enamines[1] and 2-bromophenylthiols[2] were prepared according to the known literatures. All other reagents were obtained from commercial sources and utilized without further purification, if not stated otherwise. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a 400 or 600 M Hz instrument with TMS as internal standard. Recorded shifts were reported in parts per million (δ) downfield from TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (*J*, Hz) and integration. TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. The chromatographic columns were hand packed with silica gel 60 (160-200 mesh). The unknown key products were additionally confirmed by HRMS. HRMS analyses were carried out using a TOF-MS instrument with an ESI source.

2. General Procedure for the One-Pot Reaction.

An oven-dried Schlenk tube was charged with a magnetic stir bar, N-(*o*-haloaryl) enamine **1** (0.5 mmol), iodine (0.025 mmol, 5 mol%), N-bromosuccinimide (NBS, 0.55 mmol, 1.1 equiv), and K_2CO_3 (0.6 mmol, 1.2 equiv). The tube was evacuated and backfilled with nitrogen (3 times). DMF (1.0 mL) was added to the mixture *via* syringe under nitrogen at room temperature. The reaction mixture was stirred at 100 ºC for 1 h. After that, DBU (2.0 mmol, 4.0 equiv) in DMF (0.5 mL) was added *via* syringe. Under a positive pressure of nitrogen, CuI (0.05 mmol, 10 mol%) and L-proline (0.1 mmol, 20 mol%) was added. Then a solution of *o*-bromophenylthiol (0.6 mmol, 1.2 equiv) in DMF (1.0 mL) was added *via* syringe. The reaction mixture was stirred at 120 ºC for 20-24 h (monitored by TLC). The mixture was cooled to room temperature, diluted with water (20 mL), and extracted with ethyl acetate (20 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, and dried over sodium sulfate. After filtration and removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel with petrol/AcOEt as eluent to give the product.

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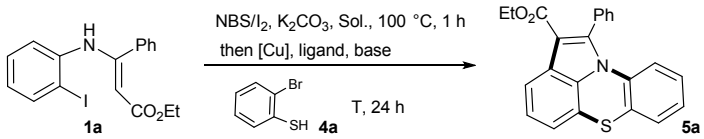
1. J. Maruyama, H. Yamashita, T. Watanabe, S. Arai, and A. Nishida, *Tetrahedron*, 2009, **65**, 1327.

2. C. Mukherjee and E. Biehl，*Heterocycl.*, 2004, **63**, 2309.

3. Optimization of the Reaction Conditions

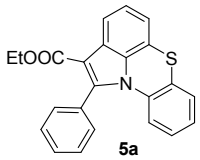
Table S1 Screening of reaction conditions[a]



entry	[Cu]	Ligand	Base	Sol.	T (°C)	Yield (%)[b]
1	CuI	L-proline	K_2CO_3	DMF	90	trace
2	CuI	L-proline	K_2CO_3	DMF	120	15
3	CuI	L-proline	K_2CO_3	DMF	130	15
4	CuI	L-proline	Cs_2CO_3	DMF	120	18
5	CuI	L-proline	K_3PO_4	DMF	120	22
6	CuI	L-proline	*t*-BuONa	DMF	120	30
7	CuI	L-proline	*t*-BuONa	DMSO	120	25
8	CuI	L-proline	*t*-BuONa	DMAc	120	18
9	CuI	L-proline	TEA	DMF	120	trace
10	CuI	L-proline	DABCO	DMF	120	62
11	**CuI**	**L-proline**	**DBU**	**DMF**	**120**	**86**
12	CuI	L-proline	DIPEA[c]	DMF	120	14
13	CuI	L-proline	TMPDA[d]	DMF	120	6
14	CuI	L-proline	TAA[e]	DMF	120	35
15	CuBr	L-proline	DBU	DMF	120	81
16	$Cu(OAc)_2$	L-proline	DBU	DMF	120	trace
17	$Cu(OAc)_2$/CuI	L-proline	DBU	DMF	120	65
18	CuI	1,10-phen	DBU	DMF	120	60
19	CuI	BINOL	DBU	DMF	120	59
20	CuI	DMG[f]	DBU	DMF	120	70
21	CuI	2,2'-bipy	DBU	DMF	120	65

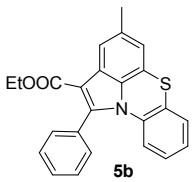
[a] Reaction conditions: enamine **1a** (0.5 mmol), I_2 (0.025 mmol, 5 mol%), NBS (0.55 mmol, 1.1 equiv), K_2CO_3 (0.6 mmol, 1.2 equiv), in solvent (1 mL), under nitrogen, at 100 °C for 1 h. Then Cu source (0.05 mmol, 10 mol%), ligand (0.1 mmol, 20 mol%), base (2.0 mmol, 4 equiv), *o*-bromothiophenol **4a** (0.6 mmol, 1.2 equiv) and solvent (1.5 mL) were added under nitrogen, and the mixture was stirred at the indicated temperature for 24 h. [b] Isolated yield of product **5a**. [c] DIEPA = N,N-diisopropylethylamine. [d] TMPDA = N,N,N',N'-tetramethylpropylenediamine. [e] TAA = triallylamine. [f] DMG = N,N-dimethylglycine.

4. Characterization Data for Products.



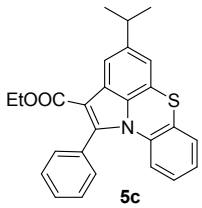
5a

Ethyl 1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5a).White solid (159 mg, 86% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 119 – 121 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.54 (m, 2H), 7.50 – 7.46 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.65 – 6.63 (m, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.4, 144.0, 134.9, 134.7, 132.5, 130.3, 129.4, 128.6, 128.0, 126.8, 126.2, 125.4, 125.2, 123.7, 119.6, 118.7, 117.8, 117.5, 110.4, 59.9, 14.2; HRMS (ESI) calcd. for $C_{23}H_{18}NO_2S$ (M + H^+): 372.1053; found: 372.1053.



5b

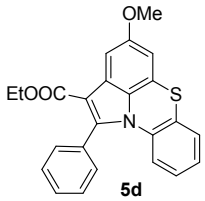
Ethyl 4-methyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5b). White solid (140 mg, 73% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 132 – 133 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.52 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.48 – 7.45 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 6.63 – 6.60 (m, 1H), 6.39 (dd, *J* = 8.4, 0.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 143.8, 135.0, 134.8, 133.1, 132.8, 130.3, 129.3, 128.5, 127.9, 126.6, 126.4, 125.2, 123.7, 119.4, 119.0, 118.3, 117.0, 110.0, 59.8, 21.7, 14.2; HRMS (ESI) calcd. for $C_{24}H_{20}NO_2S$ (M + H^+): 386.1209; found: 386.1207.



5c

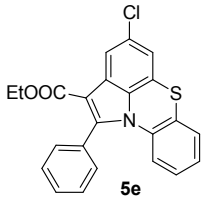
Ethyl 4-isopropyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5c). White solid (167 mg, 81% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 118 – 120 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, *J* = 0.8 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.49 – 7.44 (m, 3H), 7.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.83 (td, *J* = 7.7, 1.0 Hz, 1H), 6.76 (d, *J* = 1.2 Hz, 1H), 6.66 – 6.60 (m, 1H), 6.40 – 6.39 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.29 (d, *J*

= 6.9 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 146.5, 143.9, 134.8, 133.4, 132.8, 130.3, 129.3, 128.6, 127.9, 126.7, 126.4, 125.3, 123.7, 119.4, 117.2, 116.8, 115.8, 110.3, 59.8, 34.5, 24.4, 14.1; HRMS (ESI) calcd. for $C_{26}H_{24}NO_2S$ (M + H^+): 414.1522; found: 414.1521.



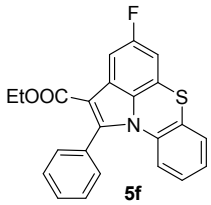
5d

Ethyl 4-methoxy-1-phenylpyrrolo[3,2,1-kl]phenothiazine-2-carboxylate (5d). Yellow solid (140 mg, 70% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 134 – 136 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 5H), 7.27 – 7.25 (m, 1H), 7.08 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.88 (td, *J* = 7.6, 1.0 Hz, 1H), 6.66 (ddd, *J* = 8.7, 7.4, 1.5 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H), 6.43 (dd, *J* = 8.5, 0.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.6, 158.1, 143.9, 134.6, 132.8, 130.3, 129.4, 129.3, 128.6, 127.8, 126.9, 126.7, 125.3, 123.1, 119.4, 118.5, 110.0, 107.6, 100.1, 59.8, 55.7, 14.1; HRMS (ESI) calcd. for $C_{24}H_{20}NO_3S$ (M + H^+): 402.1158; found: 402.1160.



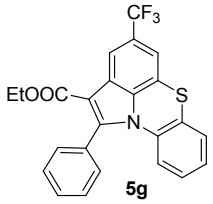
5e

Ethyl 4-chloro-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5e). White solid (163 mg, 80% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 143 – 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.53 – 7.46 (m, 5H), 7.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.88 (td, *J* = 7.7, 1.0 Hz, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 6.67 (ddd, *J* = 8.7, 7.5, 1.5 Hz, 1H), 6.41 (dd, *J* = 8.5, 0.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 144.6, 134.3, 133.0, 132.2, 130.7, 130.2, 129.6, 128.6, 127.9, 127.0, 126.8, 125.6, 122.9, 119.6, 119.3, 118.1, 117.6, 109.9, 60.1, 14.1; HRMS (ESI) calcd. for $C_{23}H_{17}ClNO_2S$ (M + H^+): 406.0663 (^{35}Cl); found: 406.0658.



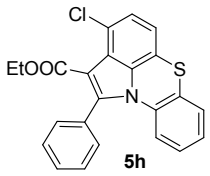
5f

Ethyl 4-fluoro-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5f). White solid (169 mg, 87% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 149 – 150 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.46 (m, 5H), 7.39 (dd, *J* = 9.6, 2.2 Hz, 1H), 7.03 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.87 – 6.84 (m, 1H), 6.67 – 6.63 (m, 1H), 6.59 – 6.56 (m, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.0, 160.9 (d, *J* = 239 Hz), 144.8, 134.3, 132.3, 131.0, 130.2, 129.6, 128.6, 127.8, 127.0, 126.6, 125.6, 122.7, 119.6, 119.2 (d, *J* = 11.1 Hz), 110.2 (d, *J* = 4.2 Hz), 106.3 (d, *J* = 29.6 Hz), 103.9 (d, *J* = 25.7 Hz), 60.0, 14.2; HRMS (ESI) calcd. for $C_{23}H_{17}FNO_2S$ (M + H^+): 390.0959; found: 390.0962.



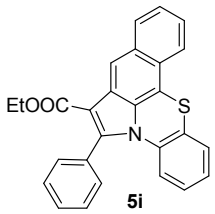
5g

Ethyl 1-phenyl-4-(trifluoromethyl)pyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5g). White solid (180 mg, 82% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 146 – 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.55 – 7.50 (m, 5H), 7.09 – 7.06 (m, 2H), 6.91 (td, *J* = 7.8, 1.0 Hz, 1H), 6.71 – 6.66 (m, 1H), 6.44 (dd, *J* = 8.5, 0.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 145.2, 136.0, 133.0 (d, *J* = 219 Hz), 130.2, 129.8, 128.7, 128.0, 127.8, 127.5, 127.1, 125.9, 125.7, 125.4, 123.0 (d, *J* = 7.5 Hz), 119.7, 119.2, 116.6 (q, *J* = 4.5 Hz), 114.2 (q, *J* = 3.5 Hz), 110.8, 60.2, 14.1; HRMS (ESI) calcd. for $C_{24}H_{17}F_3NO_2S$ (M + H^+): 440.0927; found: 440.0929.



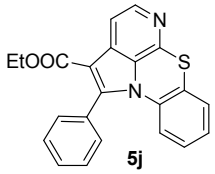
5h

Ethyl 3-chloro-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5h). White solid (127 mg, 63% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 120 – 122 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 2H), 7.48 – 7.45 (m, 3H), 7.12 – 7.08 (m, 2H), 6.92 – 6.89 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.71 (m, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 139.7, 136.5, 134.6, 131.4, 129.6, 129.5, 129.0, 128.0, 127.0, 125.4, 125.3, 123.0, 122.8, 122.7, 119.5, 118.3, 116.8, 114.0, 61.4, 13.9; HRMS (ESI) calcd. for $C_{23}H_{17}ClNO_2S$ (M + H^+): 406.0663 (^{35}Cl); found: 406.0664.



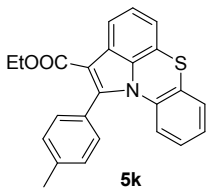
5i

Ethyl 6-phenylbenzo[*c*]pyrrolo[1,2,3-*mn*]phenothiazine-7-carboxylate (5i). Yellow solid. (115 mg, 55% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.5); mp 156 – 158 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 6.3 Hz, 2H), 7.51 – 7.47 (m, 3H), 7.43 – 7.38 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.67 (t, *J* = 7.8 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.4, 147.4, 135.6, 135.1, 132.4, 132.2, 130.3, 129.6, 129.3, 128.6, 128.4, 127.1, 126.1, 125.24, 125.18, 124.8, 124.5, 123.4, 122.6, 119.4, 116.6, 111.6, 109.8, 60.0, 14.2; HRMS (ESI) calcd. for $C_{27}H_{20}NO_2S$ (M + H^+): 422.1209; found: 422.1206.



5j

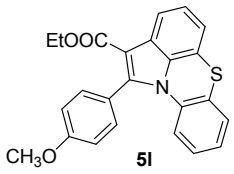
Ethyl 1-phenyl-6-thia-5,10b-diazaaceanthrylene-2-carboxylate (5j). White solid (141 mg, 76% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.5); mp 137 – 139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 5.6 Hz, 1H), 7.60 – 7.50 (m, 6H), 7.17 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.74 – 6.69 (m, 1H), 6.53 (dd, *J* = 8.6, 0.8 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 150.7, 145.2, 143.5, 142.3, 133.2, 131.9, 130.0, 129.9, 129.8, 128.8, 128.5, 126.9, 126.0, 124.1, 119.3, 113.2, 109.8, 60.1, 14.1; HRMS (ESI) calcd. for $C_{22}H_{17}N_2O_2S$ (M + H^+): 373.1005; found: 373.1007.



5k

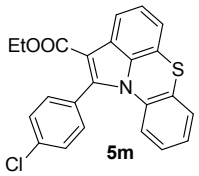
Ethyl 1-(*p*-tolyl)pyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5k). White solid (148 mg, 77% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 119 – 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.70 – 6.66 (m,

1H), 6.49 (dd, *J* = 8.5, 0.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 144.4, 139.4, 134.95, 134.91, 130.2, 129.4, 129.3, 127.9, 126.8, 126.2, 125.3, 125.1, 123.7, 119.7, 118.7, 117.7, 117.5, 110.3, 59.9, 21.6, 14.2; HRMS (ESI) calcd. for $C_{24}H_{20}NO_2S$ (M + H^+): 386.1209; found: 386.1205.



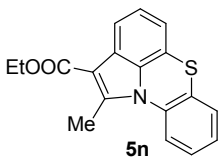
5l

Ethyl 1-(4-methoxyphenyl)pyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5l). White solid (166 mg, 83% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 155 – 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.16 – 7.08 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.91 – 6.85 (m, 2H), 6.75 – 6.69 (m, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 160.4, 144.3, 135.03, 134.99, 131.7, 128.0, 126.8, 126.2, 125.3, 125.1, 124.4, 123.7, 119.7, 118.7, 117.7, 117.5, 114.0, 110.1, 59.9, 55.3, 14.3; HRMS (ESI) calcd. for $C_{24}H_{20}NO_3S$ (M + H^+): 402.1158; found: 402.1162.



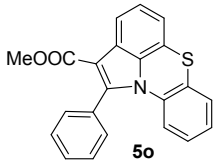
5m

Ethyl 1-(4-chlorophenyl)pyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5m). White solid (135 mg, 67% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 125 – 127 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.48 – 7.45 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.91 (td, *J* = 7.7, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.4, 0.6 Hz, 1H), 6.75 – 6.71 (m, 1H), 6.44 (dd, *J* = 8.5, 0.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.2, 142.5, 135.6, 135.1, 134.5, 131.8, 130.8, 128.9, 128.1, 126.9, 126.1, 125.5, 125.3, 123.8, 119.6, 118.8, 118.0, 117.6, 110.8, 60.1, 14.2; HRMS (ESI) calcd. for $C_{23}H_{17}ClNO_2S$ (M + H^+): 406.0663; found: 406.0665.



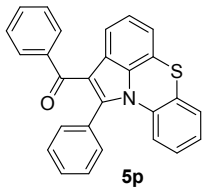
5n

Ethyl 1-methylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5n). White solid (80 mg, 52% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6) ; mp 108 – 110 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.08 – 7.04 (m, 2H), 6.77 (d, *J* = 7.4 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.08 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.6, 143.7, 134.6, 134.4, 128.3, 127.3, 125.8, 125.7, 124.9, 124.3, 118.7, 118.2, 116.9, 116.7, 109.6, 60.0, 16.7, 14.6; HRMS (ESI) calcd. for $C_{18}H_{16}NO_2S$ (M + H^+): 310.0896; found: 310.0899.



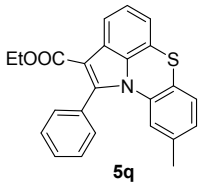
5o

Methyl 1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5o). White solid (141 mg, 79% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.5); mp 149 – 150 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.51 – 7.48 (m, 3H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.88 – 6.85 (m, 2H), 6.66 (ddd, *J* = 8.7, 7.4, 1.5 Hz, 1H), 6.41 – 6.39 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.8, 144.3, 135.0, 134.7, 132.3, 130.3, 129.5, 128.6, 128.0, 126.8, 126.1, 125.4, 125.2, 123.7, 119.7, 118.7, 117.8, 117.6, 110.2, 51.1; HRMS (ESI) calcd. for $C_{22}H_{16}NO_2S$ (M + H^+): 358.0896; found: 358.0893.



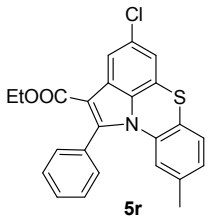
5p

Phenyl(1-phenylpyrrolo[3,2,1-*kl*]phenothiazin-2-yl)methanone (5p). Yellow oil. (155 mg, 77% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.32 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 7.19 – 7.16 (m, 2H), 7.15 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.92 – 6.88 (m, 2H), 6.71 – 6.68 (m, 1H), 6.47 (dd, *J* = 8.5, 0.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.8, 142.3, 138.8, 135.9, 135.0, 132.0, 131.7, 130.3, 129.5, 129.2, 128.7, 128.3, 127.9, 127.1, 126.9, 126.7, 125.4, 125.2, 124.0, 120.0, 118.3, 118.0, 117.9; HRMS (ESI) calcd. for $C_{27}H_{18}NOS$ (M + H^+): 404.1104; found: 404.1100.



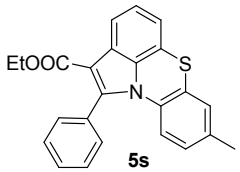
5q

Ethyl 9-methyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5q). White solid (158 mg, 82% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 156 – 158 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.47 (m, 5H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.17 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.82 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.4, 144.0, 136.6, 134.7, 134.3, 132.8, 130.3, 129.2, 128.5, 127.5, 126.2, 126.0, 125.1, 120.7, 119.9, 118.5, 117.8, 117.7, 110.0, 59.9, 21.1, 14.2; HRMS (ESI) calcd. for $C_{24}H_{20}NO_2S$ (M + H^+): 386.1209; found: 386.1206.



5r

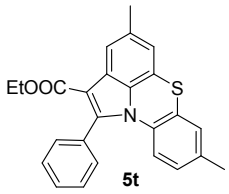
Ethyl 4-chloro-9-methyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5r). White solid (130 mg, 62% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 165 – 167 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 1.8 Hz, 1H), 7.53 – 7.47 (m, 5H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 1.8 Hz, 1H), 6.71 – 6.69 (m, 1H), 6.16 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.81 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.0, 144.6, 136.9, 133.8, 132.8, 132.4, 130.5, 130.2, 129.5, 128.6, 127.5, 126.7, 126.3, 120.7, 119.6, 119.1, 117.9, 117.4, 109.5, 60.0, 21.1, 14.2; HRMS (ESI) calcd. for $C_{24}H_{19}ClNO_2S$ (M + H^+): 420.0820 (^{35}Cl); found: 420.0817.



5s

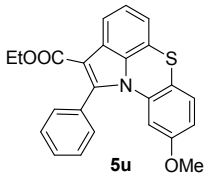
Ethyl 8-methyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5s). White solid (156 mg, 81% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 115 – 117 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.50 – 7.47 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 1.6 Hz, 1H), 6.86 – 6.85 (m, 1H), 6.47 (dd, *J* = 8.6, 1.6

Hz, 1H), 6.29 (d, *J* = 8.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.14 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.4, 143.9, 135.2, 134.6, 132.7, 132.3, 130.3, 129.3, 128.52, 128.51, 128.2, 127.4, 126.1, 125.0, 123.4, 119.4, 118.6, 117.6, 109.9, 59.8, 20.3, 14.2; HRMS (ESI) calcd. for $C_{24}H_{20}NO_2S$ (M + H^+): 386.1209; found: 386.1211.



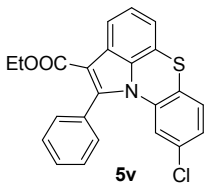
5t

Ethyl 4,8-dimethyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5t). White solid (156 mg, 78% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 132 – 133 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 – 7.55 (m, 1H), 7.53 – 7.51 (m, 2H), 7.49 – 7.46 (m, 3H), 6.88 (d, *J* = 1.4 Hz, 1H), 6.69 (s, 1H), 6.45 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.28 (d, *J* = 8.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.13 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.6, 143.7, 135.1, 134.8, 132.9, 132.8, 132.3, 130.3, 129.2, 128.5, 128.2, 127.3, 126.4, 123.3, 119.2, 118.8, 118.2, 117.1, 109.5, 59.7, 21.7, 20.3, 14.1; HRMS (ESI) calcd. for $C_{25}H_{22}NO_2S$ (M + H^+): 400.1366; found: 400.1367.



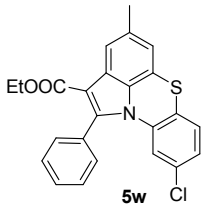
5u

Ethyl 9-methoxy-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5u). Yellow solid (136 mg, 68% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 136 – 137 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.49 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 6.34 (d, *J* = 9.2 Hz, 1H), 6.21 (d, *J* = 7.0 Hz, 1H), 4.21 (q, *J* = 6.9 Hz, 2H), 3.68 (s, 3H), 1.22 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 156.6, 143.7, 134.3, 132.6, 130.3, 129.3, 128.6, 128.1, 126.1, 124.9 (*J* = 10.1 Hz), 120.4, 118.7, 117.5, 117.1, 112.9, 112.0, 109.5, 100.0, 59.8, 55.5, 14.2; HRMS (ESI) calcd. for $C_{24}H_{20}NO_3S$ (M + H^+): 402.1158; found: 402.1166.



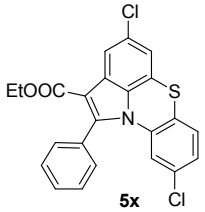
5v

Ethyl 9-chloro-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5v). White solid (174 mg, 86% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 157 – 158 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.53 – 7.47 (m, 5H), 7.05 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.41 (d, *J* = 8.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.9, 144.7, 134.3, 133.0, 132.2, 130.7, 130.2, 129.6, 128.7, 127.9, 127.0, 126.8, 125.6, 122.9, 119.6, 119.3, 118.1, 117.6, 109.8, 60.1, 14.2; HRMS (ESI) calcd. for $C_{23}H_{17}ClNO_2S$ ($M + H^+$): 406.0663 (^{35}Cl); found: 406.0656.



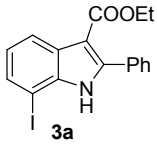
5w

Ethyl 9-chloro-4-methyl-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate (5w). White solid (151 mg, 72% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 176 – 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 6H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.69 (s, 1H), 6.31 (d, *J* = 2.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.3, 143.8, 135.6, 135.3, 132.7, 132.2, 132.1, 130.1, 129.6, 128.8, 128.3, 126.4, 125.1, 122.0, 119.7, 119.2, 118.6, 116.4, 110.4, 59.9, 21.7, 14.1; HRMS (ESI) calcd. for $C_{24}H_{19}ClNO_2S$ ($M + H^+$): 420.0820 (^{35}Cl); found: 420.0817.



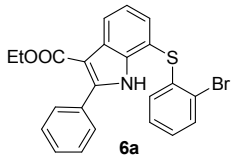
5x

Ethyl 4,9-dichloro-1-phenylpyrrolo[3,2,1-*kl*]phenothiazine-2-carboxylate(5x). White solid (160 mg, 73% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.6); mp 143 – 144 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 1.4 Hz, 1H), 7.58 – 7.50 (m, 5H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.88 – 6.86 (m, 1H), 6.82 – 6.81 (m, 1H), 6.32 (d, *J* = 1.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.7, 144.6, 135.0, 132.6, 132.5, 131.6, 130.9, 130.1, 129.9, 128.9, 128.4, 126.8, 125.5, 121.2, 119.9, 118.7, 118.4, 117.8, 110.3, 60.2, 14.1; HRMS (ESI) calcd. for $C_{23}H_{16}Cl_2NO_2S$ ($M + H^+$): 440.0273 (^{35}Cl); found: 440.0271.



3a

Ethyl 7-iodo-2-phenyl-1H-indole-3-carboxylate (3a). Yellow solid (182 mg, 93% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.5); mp 175 – 176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (b, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.46 (m, 3H), 7.03 (t, *J* = 7.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 144.5, 137.0, 131.8, 131.6, 129.7, 129.6, 128.3, 127.7, 123.7, 122.4, 106.3, 76.1, 59.9, 14.3; HRMS (ESI) calcd. for $C_{17}H_{15}INO_2$ (M + H^+): 392.0142; found: 392.0145.

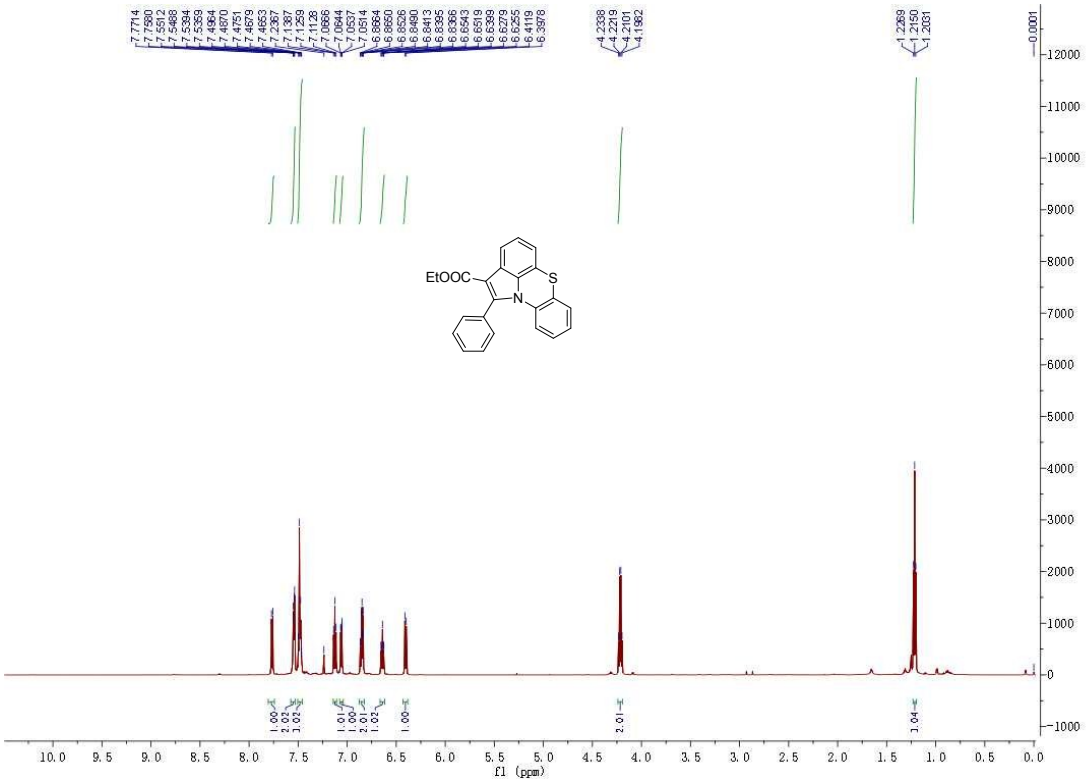


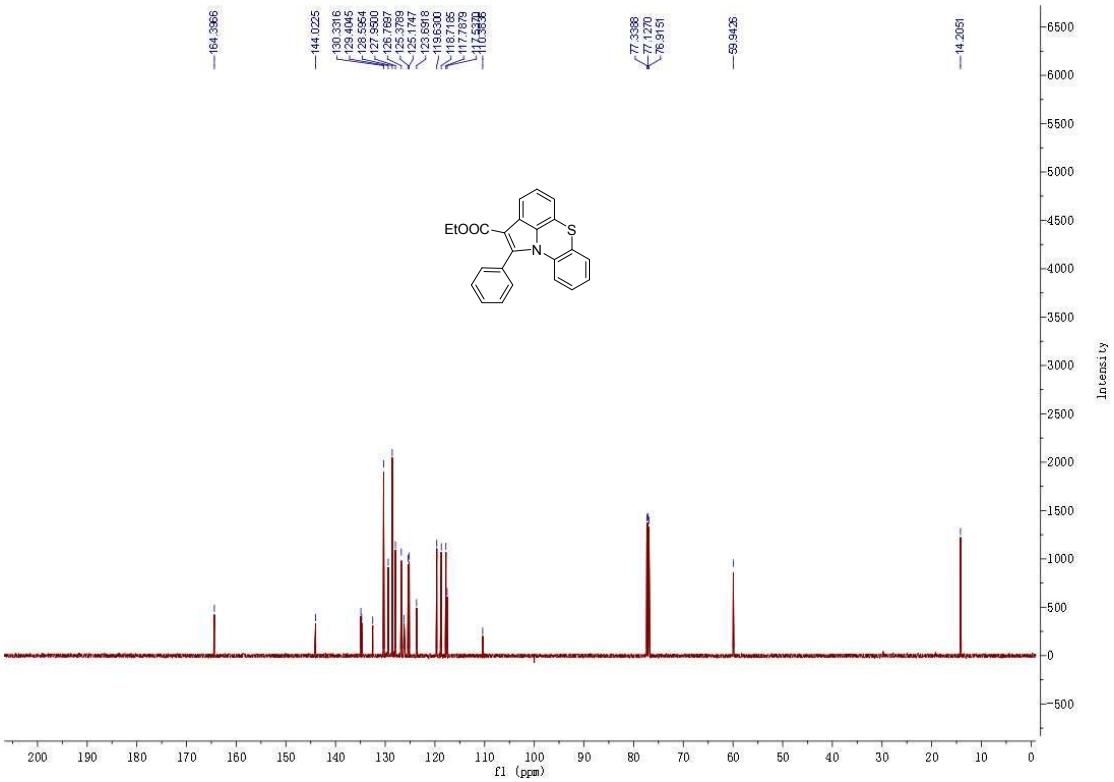
6a

Ethyl 7-((2-bromophenyl)thio)-2-phenyl-1H-indole-3-carboxylate (6a). White solid (97 mg, 43% yield) (petroleum ether/EtOAc = 5:1, R_f = 0.48); mp 189 – 190 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.80 (b, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.53 – 7.51 (m, 2H), 7.44 – 7.42 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.01 (td, *J* = 7.9, 1.2 Hz, 1H), 6.95 (td, *J* = 7.6, 1.5 Hz, 1H), 6.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 144.8, 138.2, 137.3, 133.0, 131.4, 131.3, 129.7, 129.5, 128.5, 128.2, 128.0, 126.9, 126.7, 124.6, 123.3, 120.8, 112.3, 105.8, 60.0, 14.4; HRMS (ESI) calcd. for $C_{23}H_{19}BrNO_2S$ (M + H^+): 452.0314 (^{79}Br); found: 452.0316.

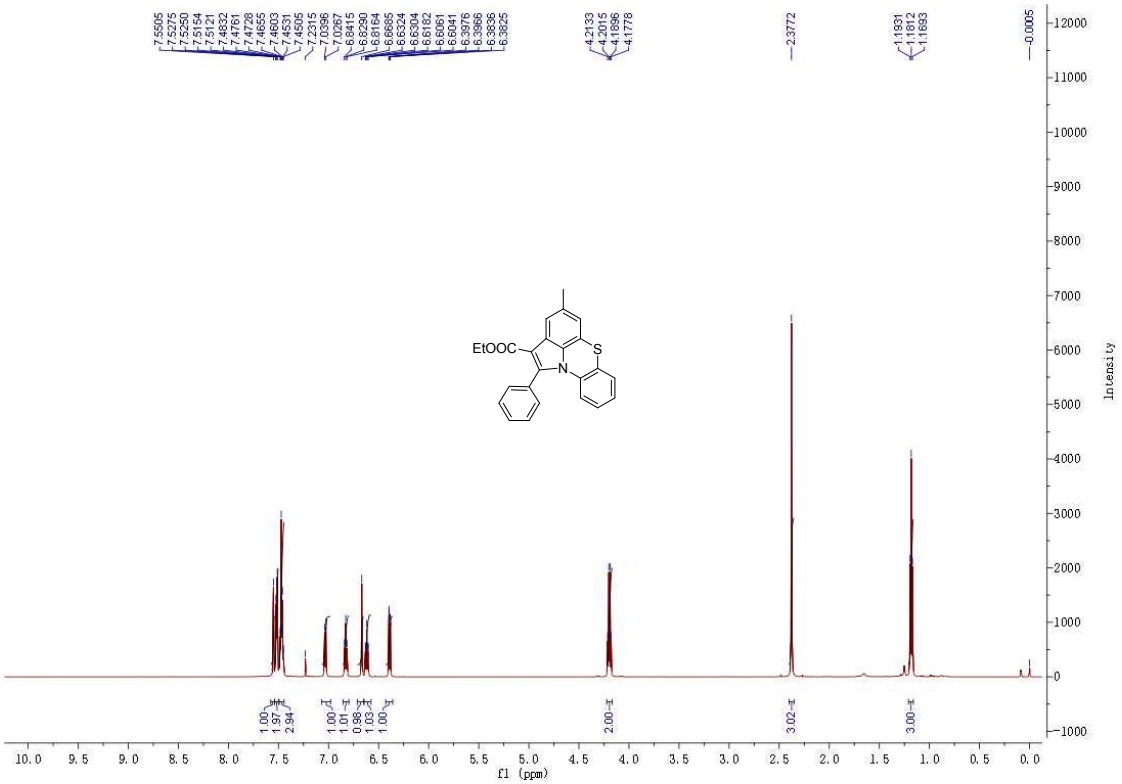
5. Copies of ^{1}H and ^{13}C NMR Spectra for Products 5:

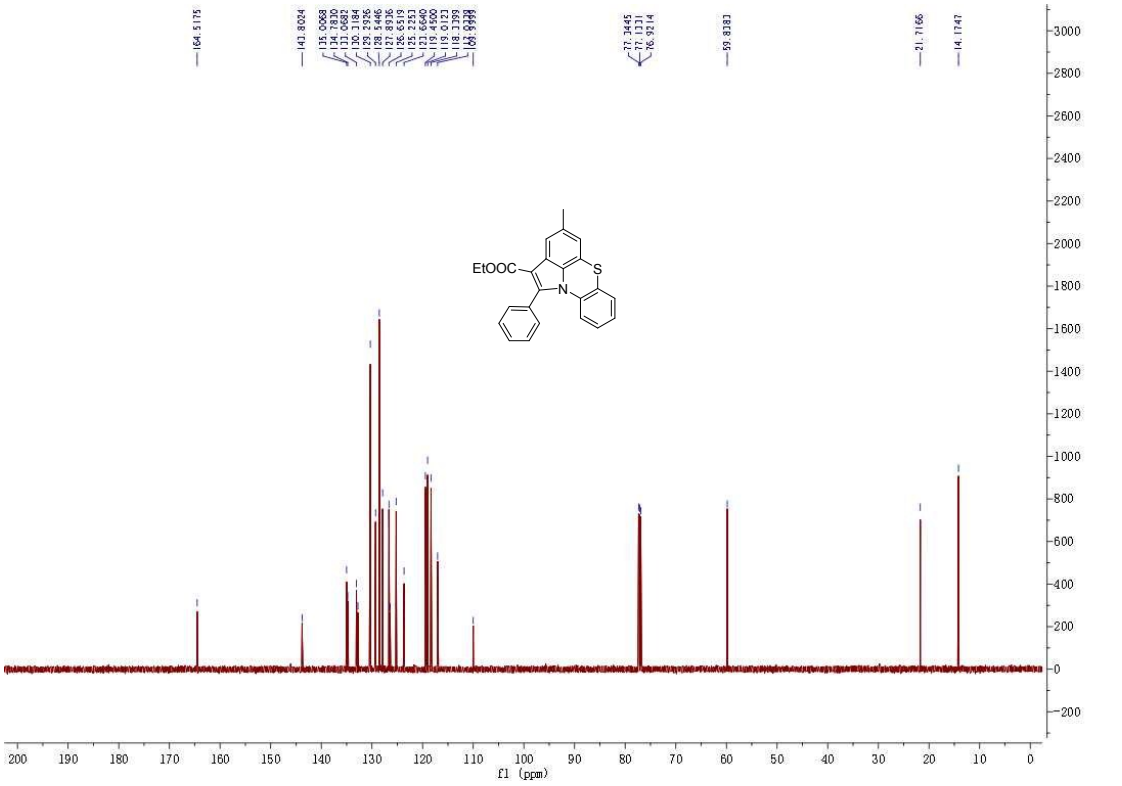
5a:





5b:





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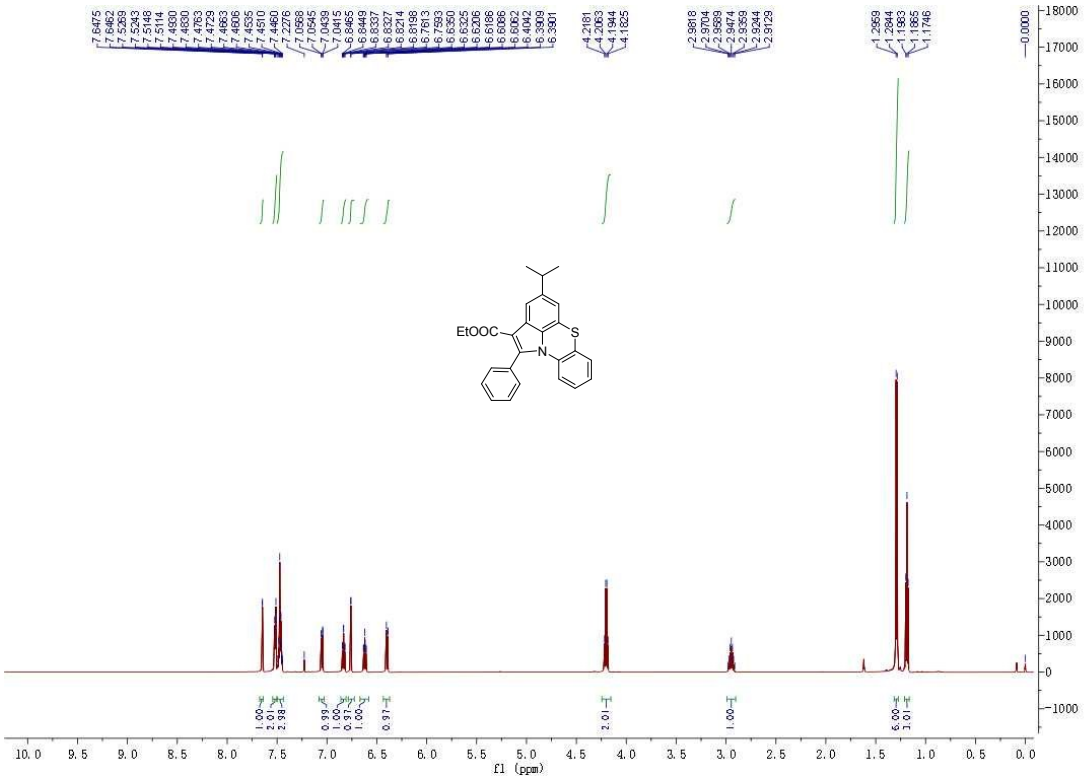

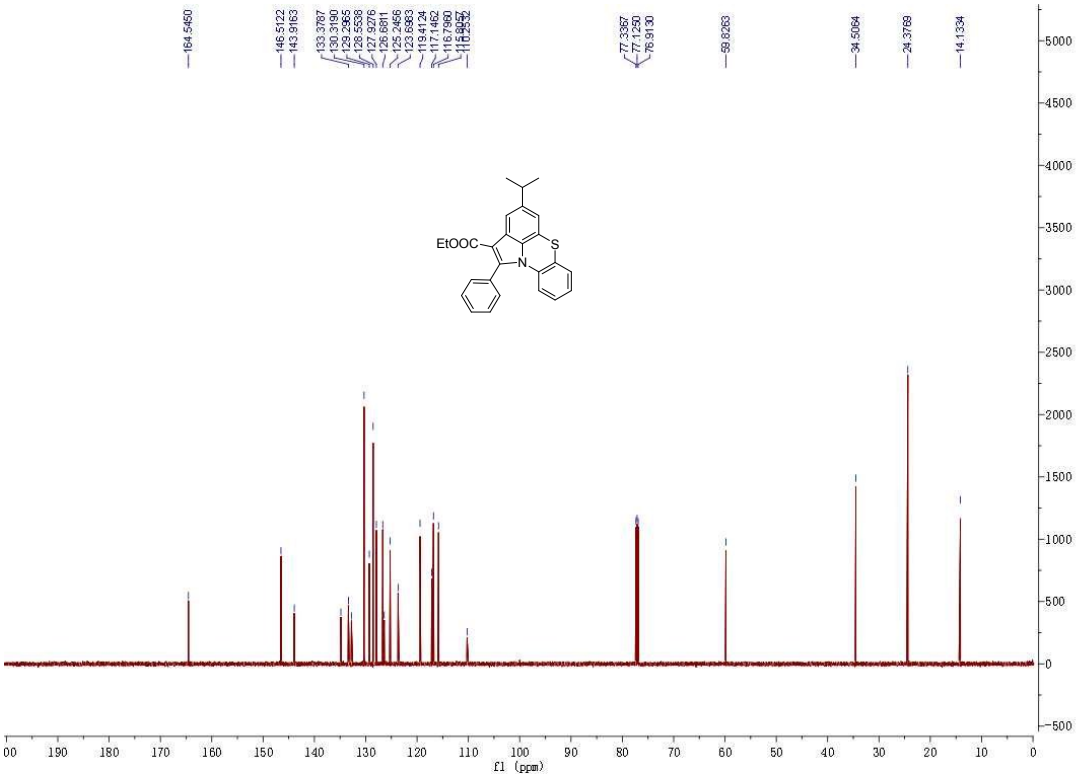

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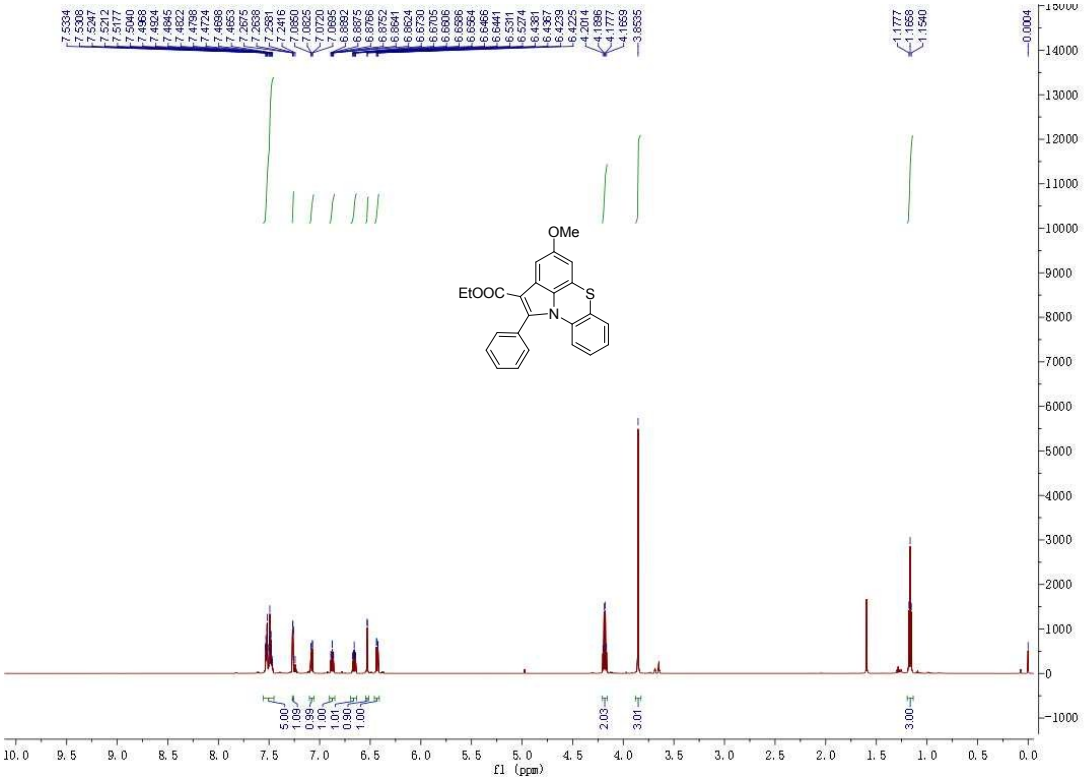

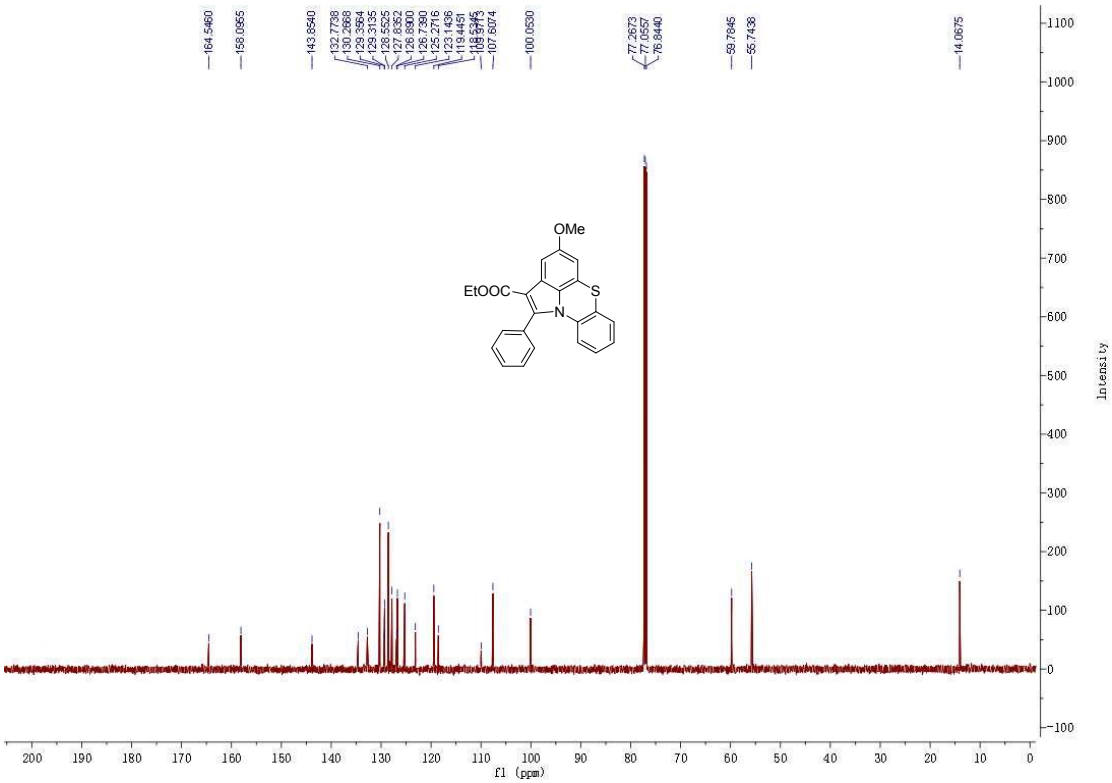

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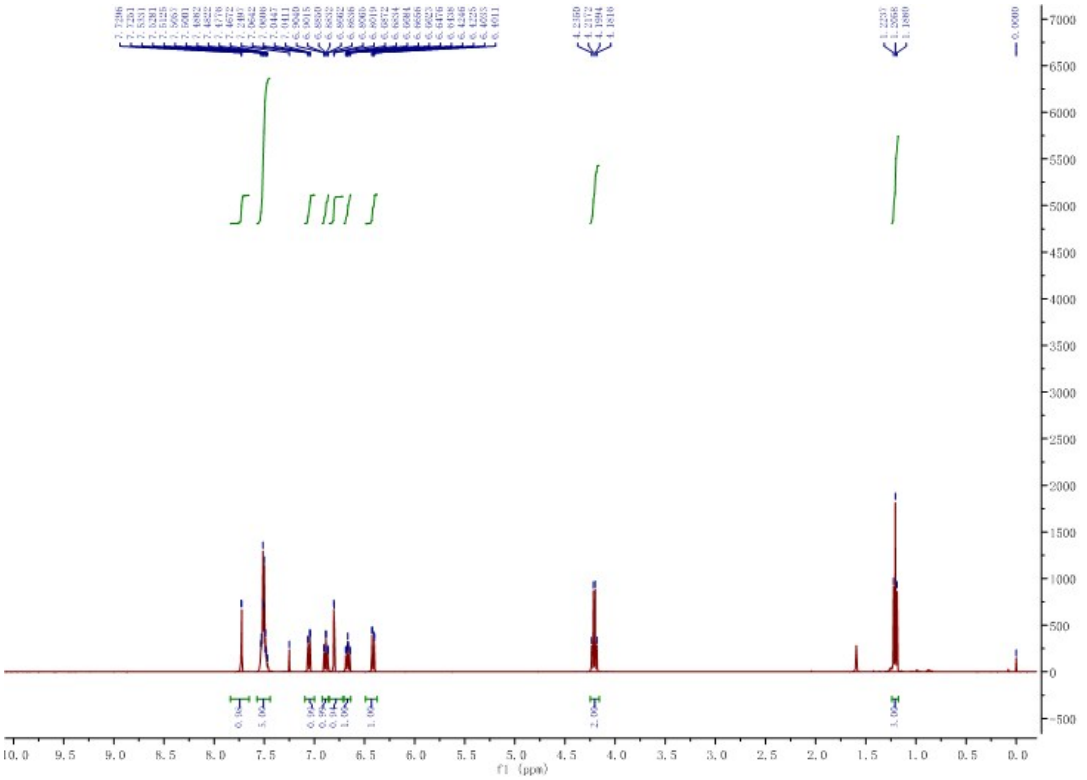

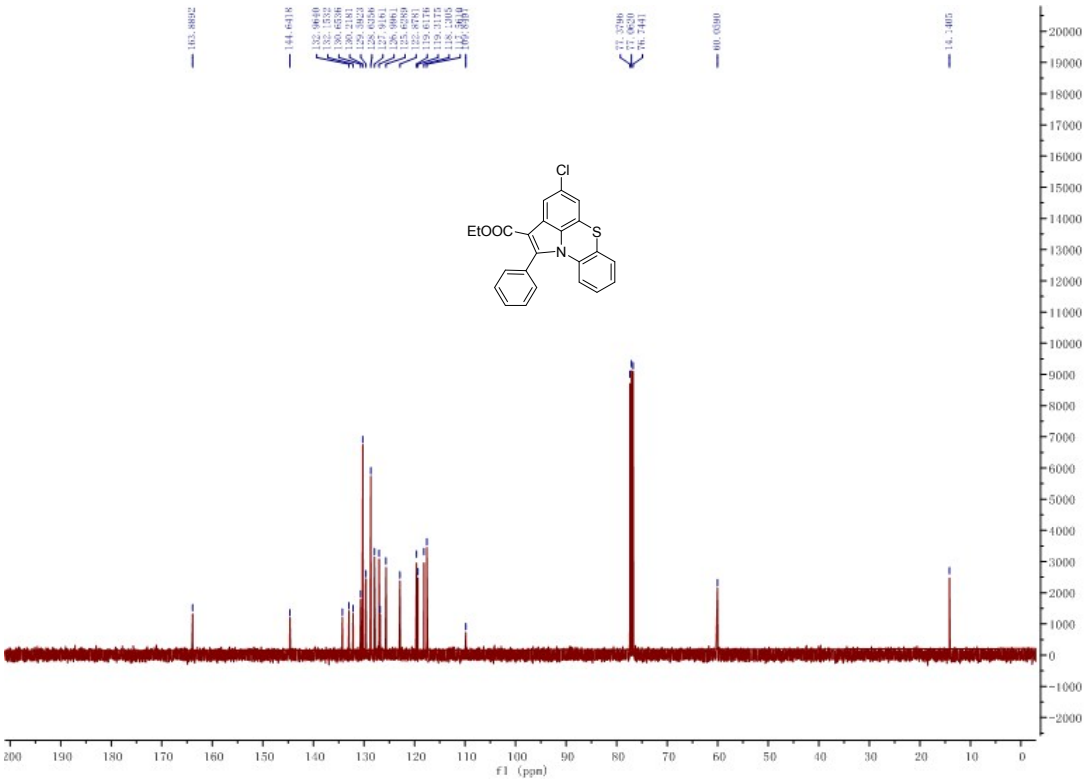

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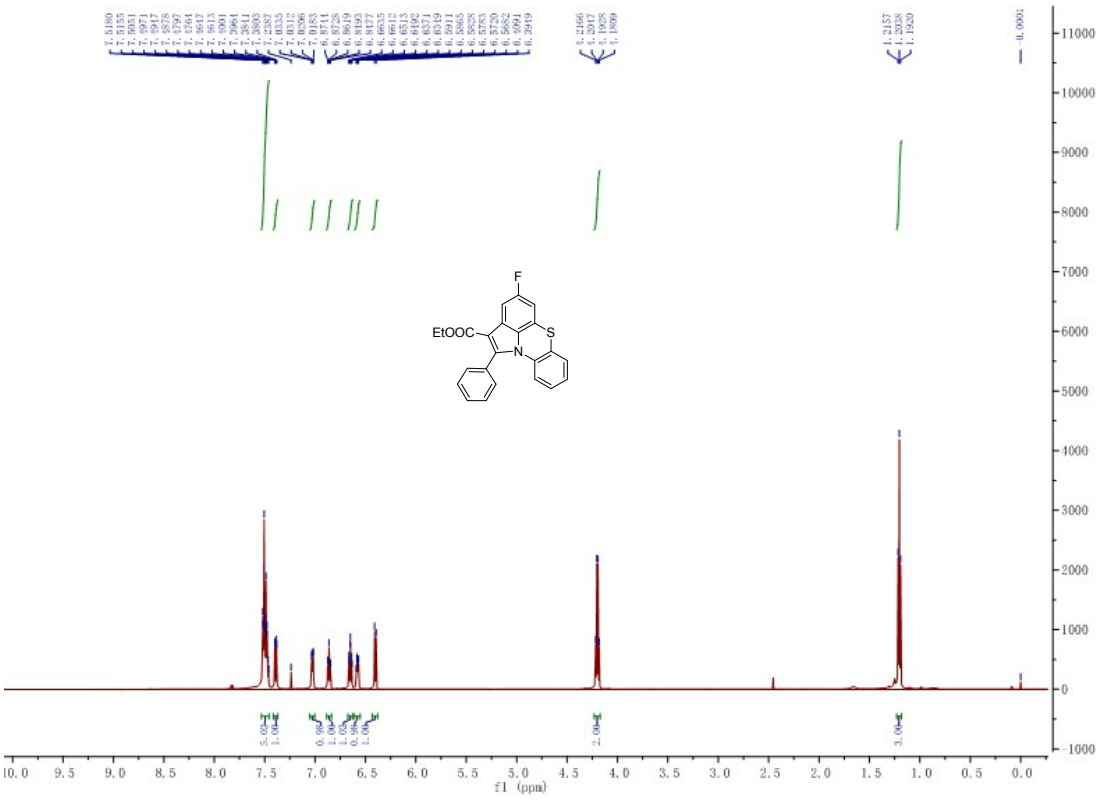

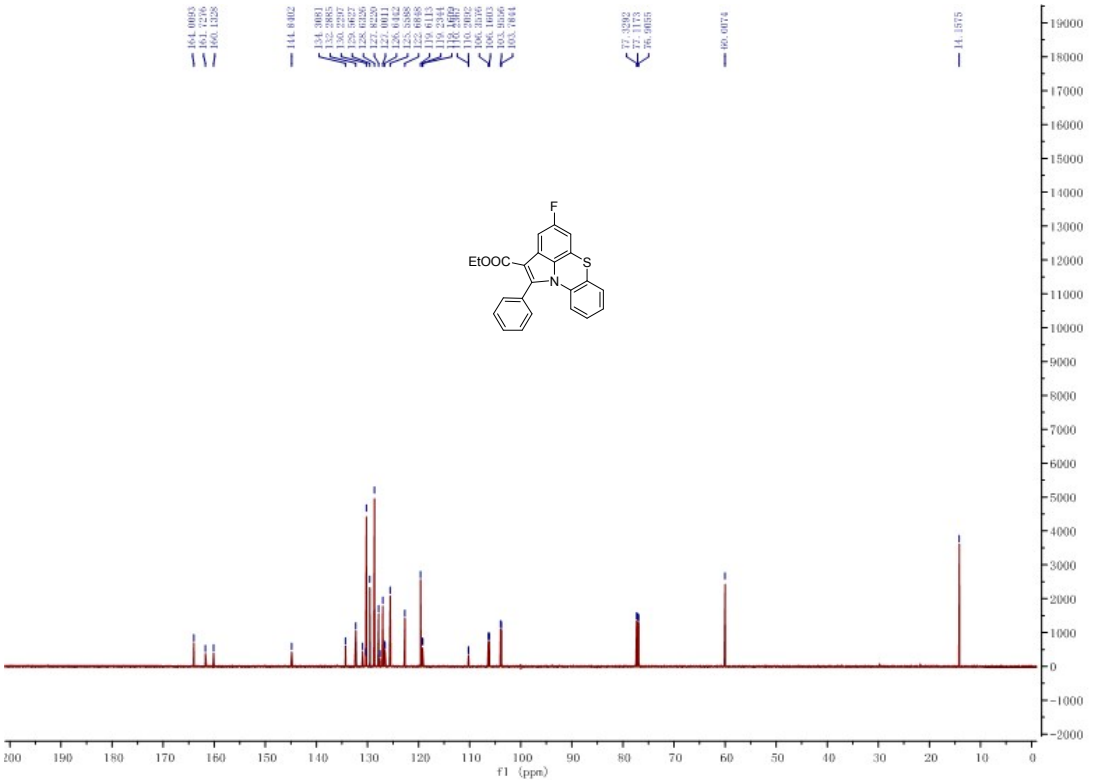

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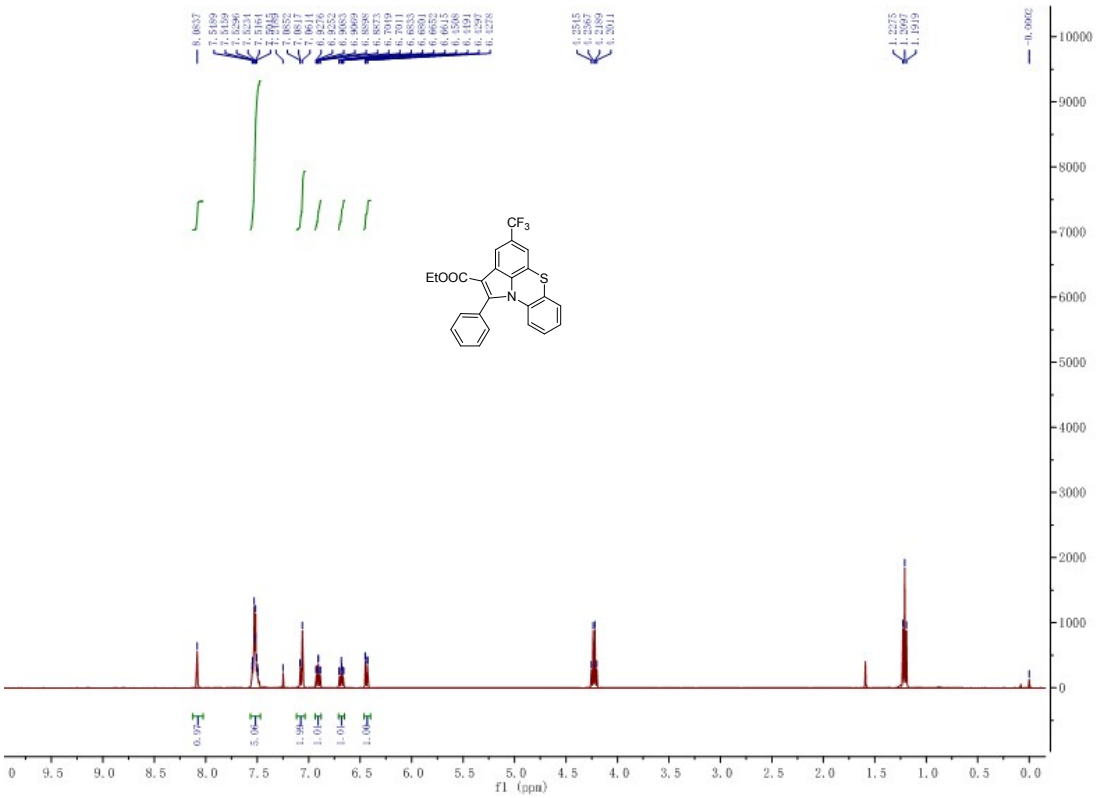

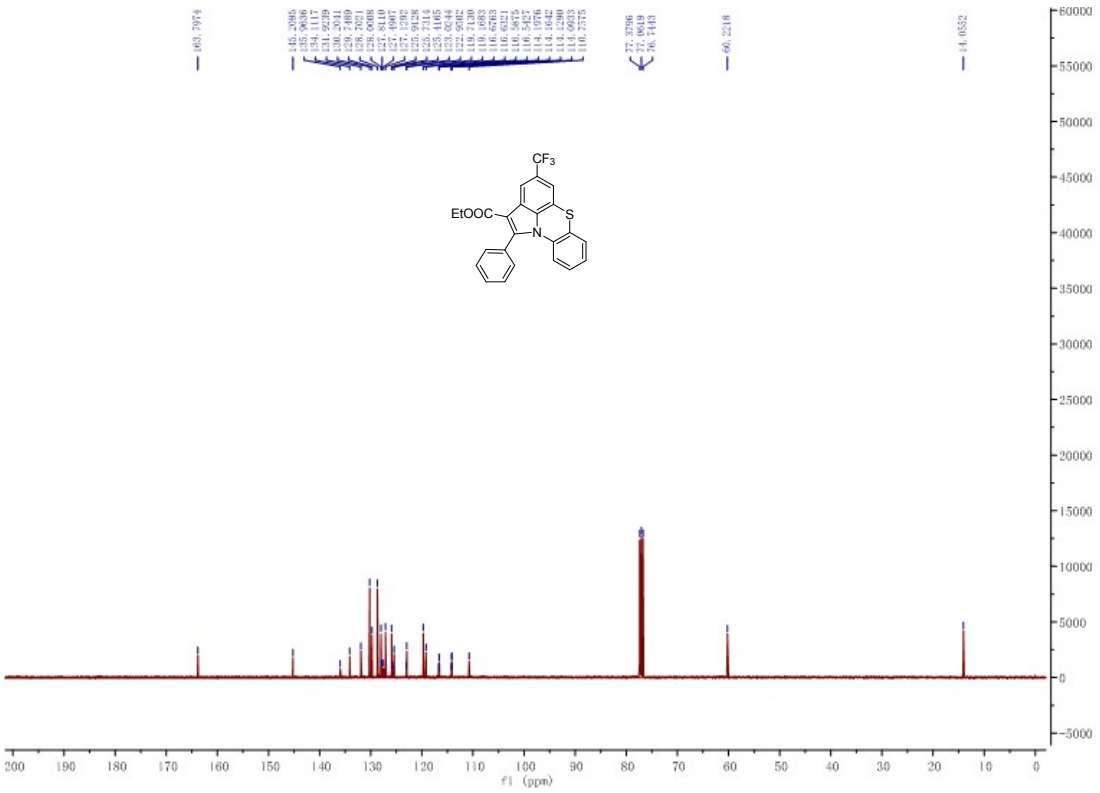

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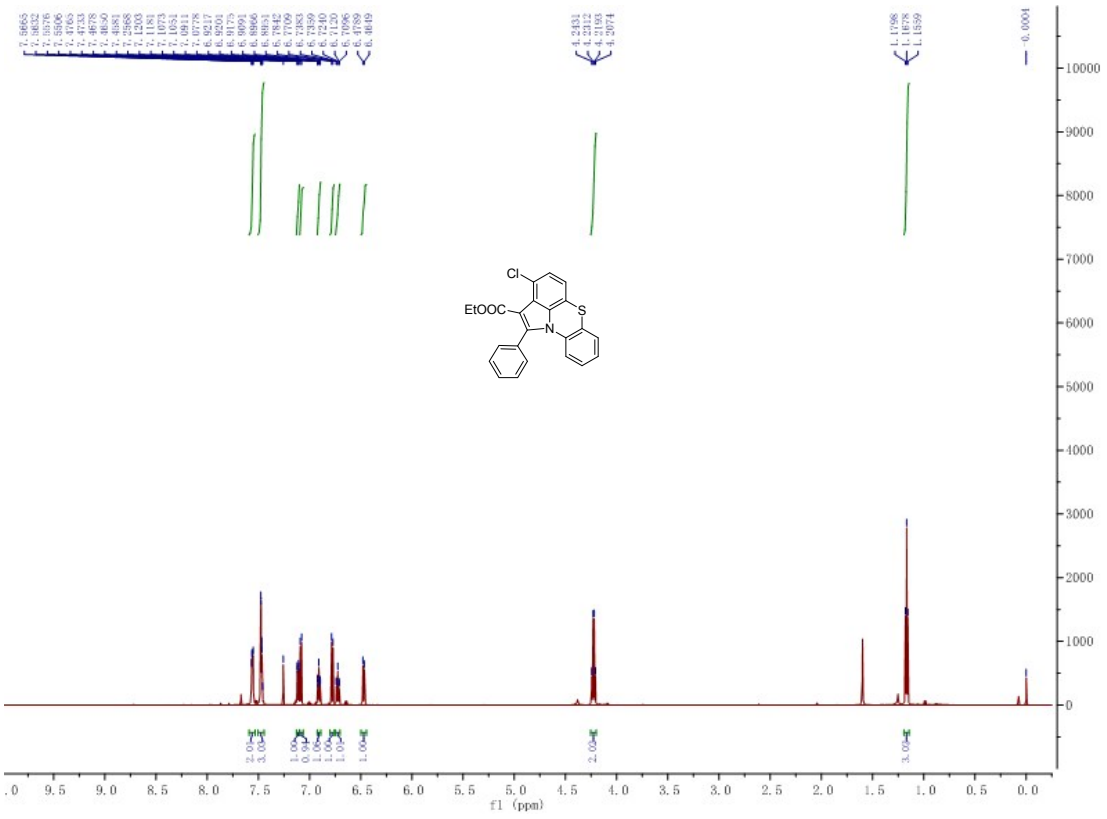

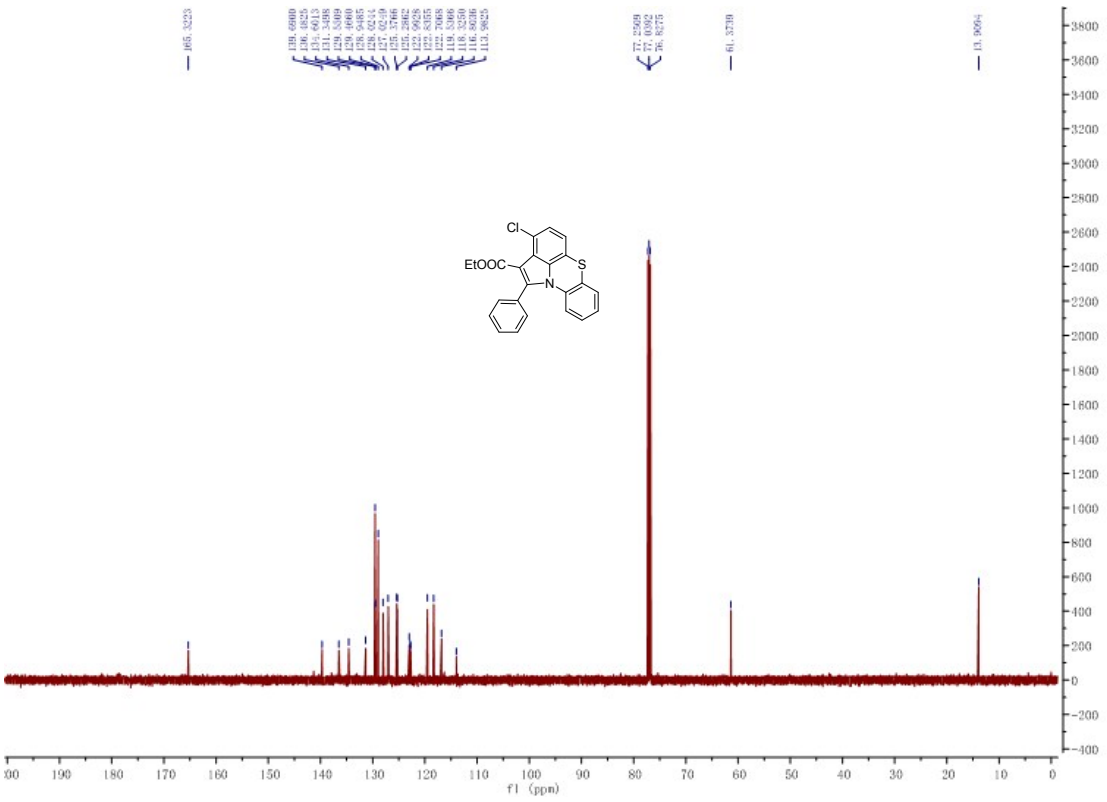

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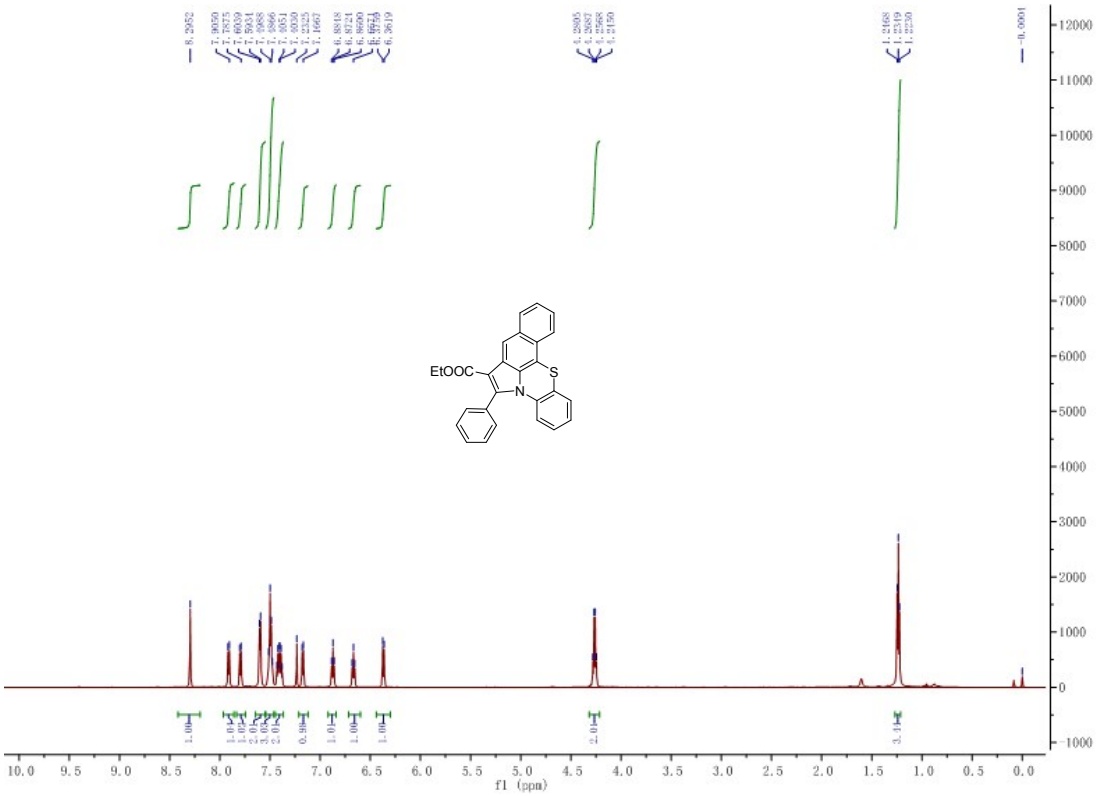

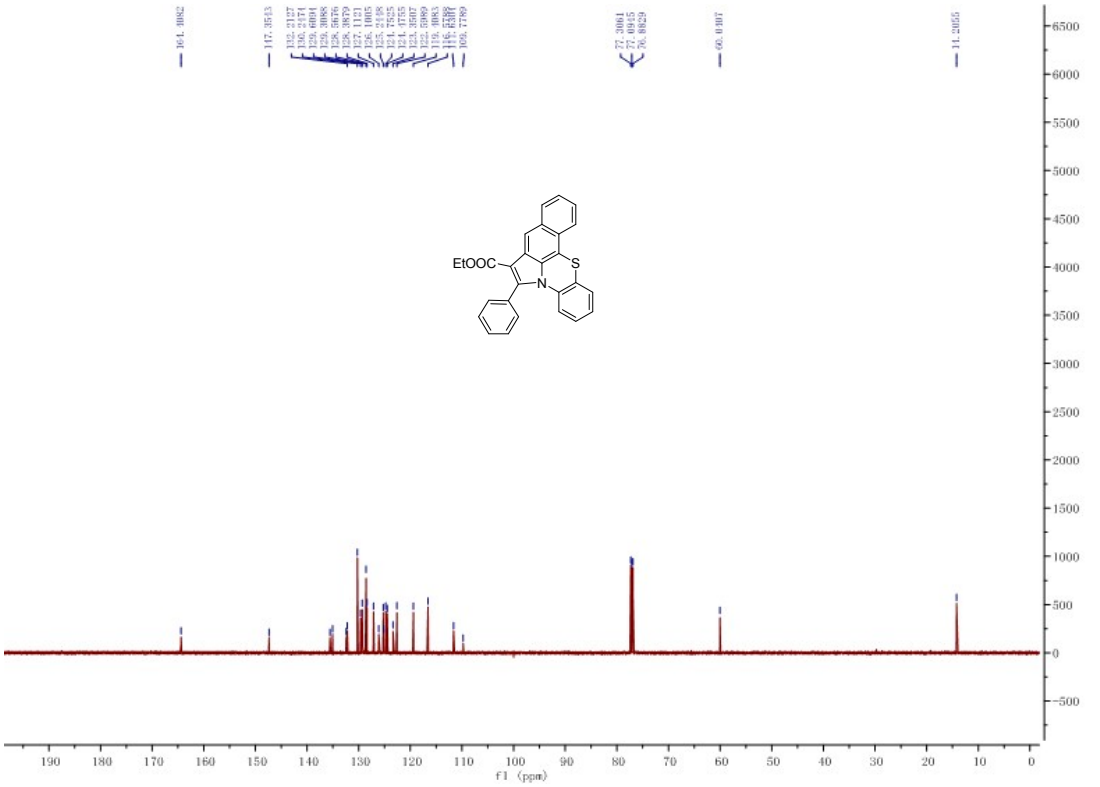

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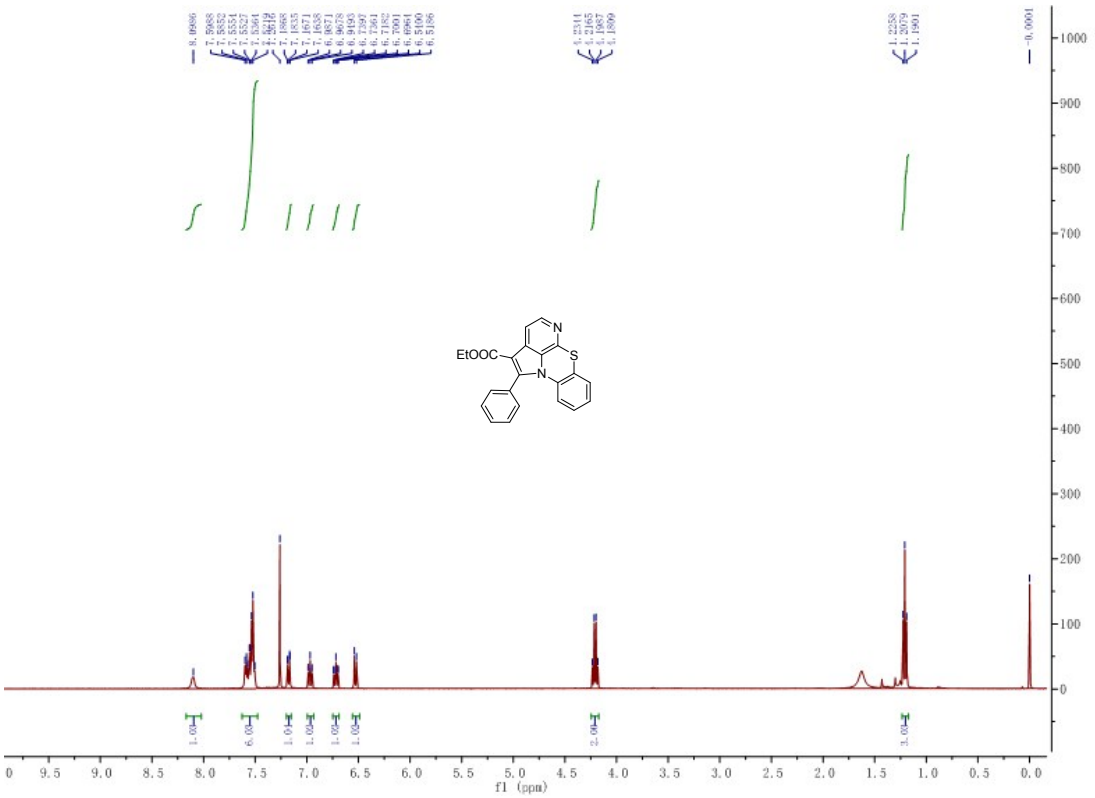

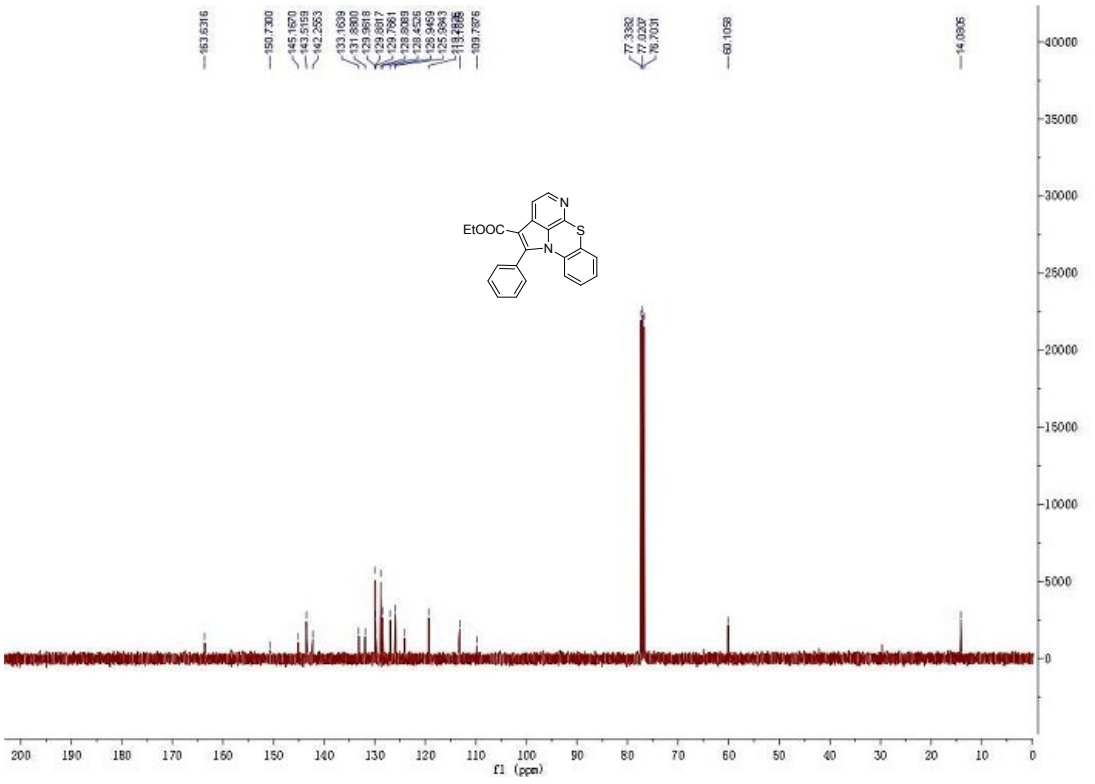

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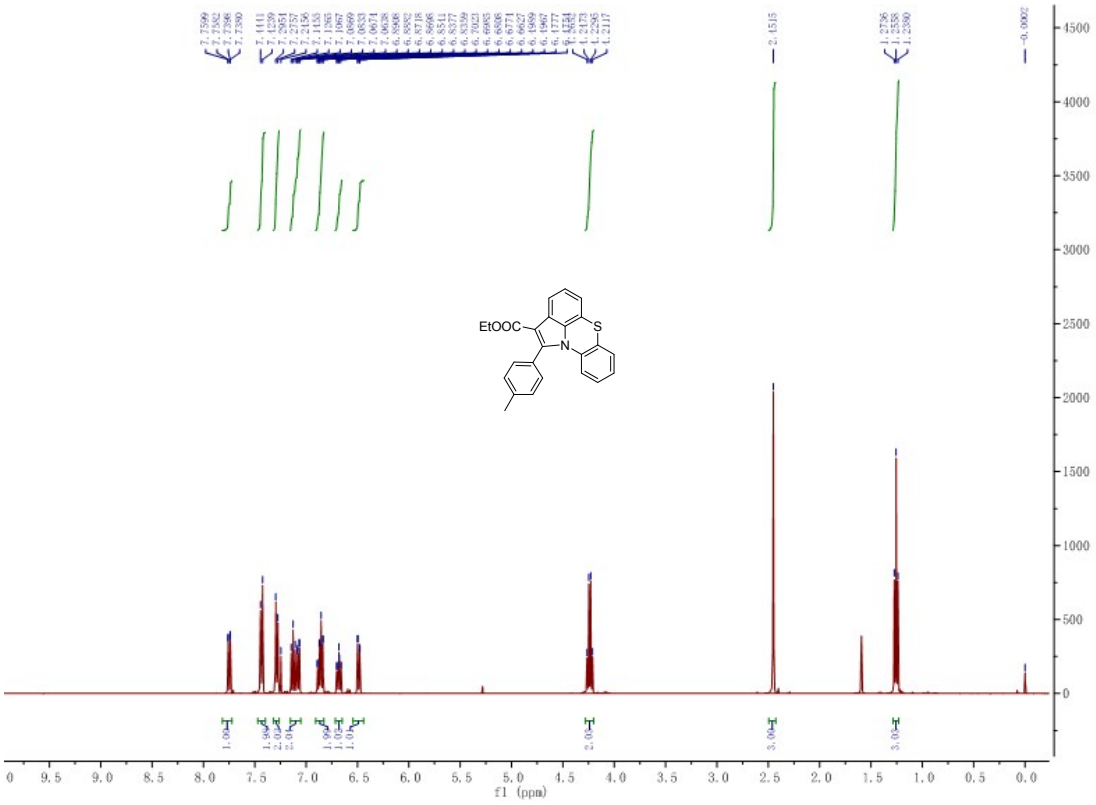

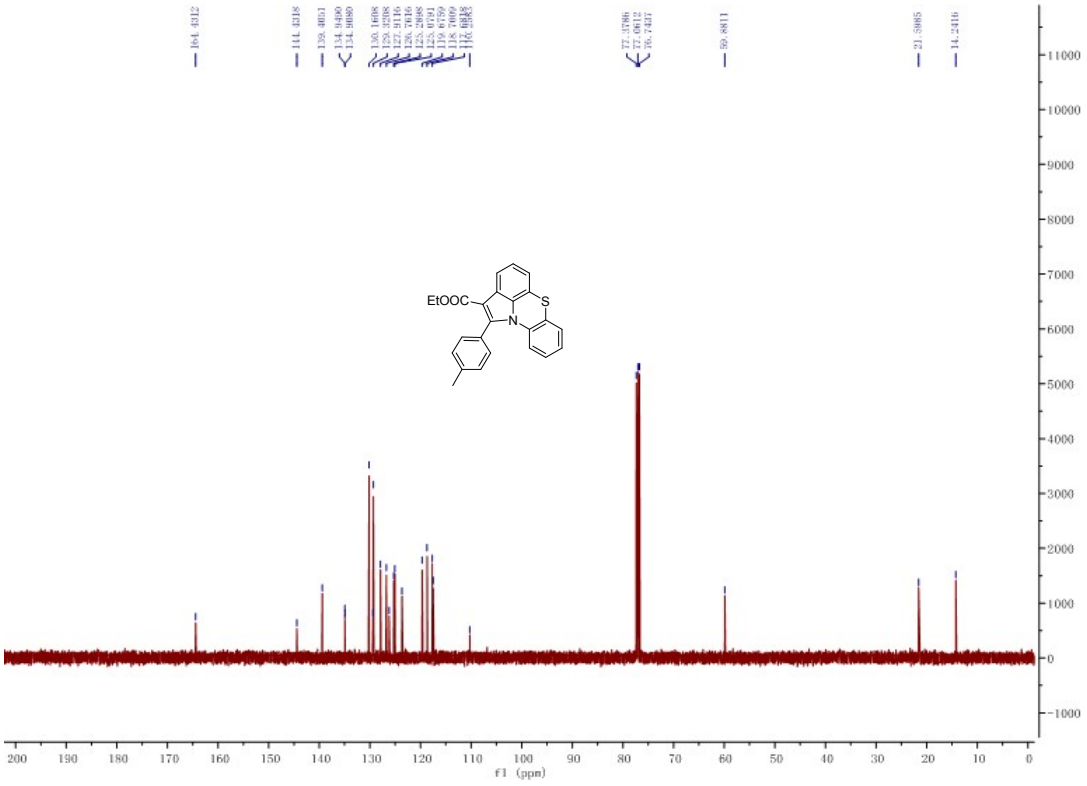

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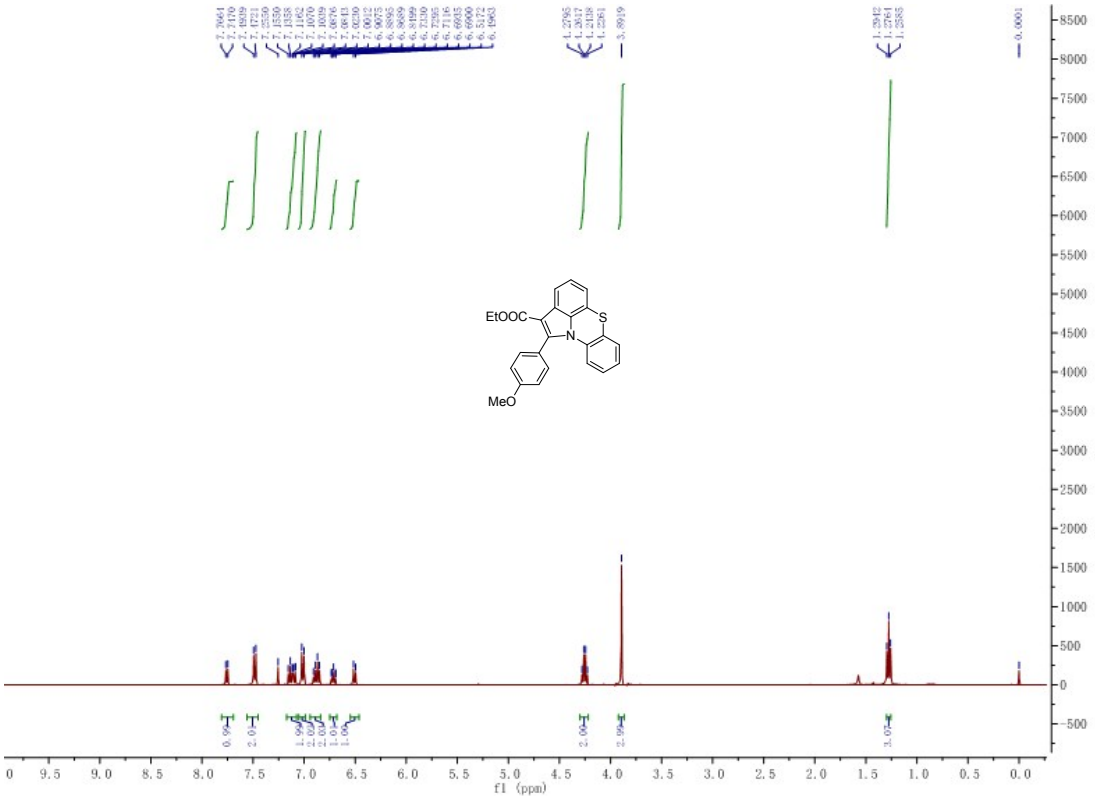

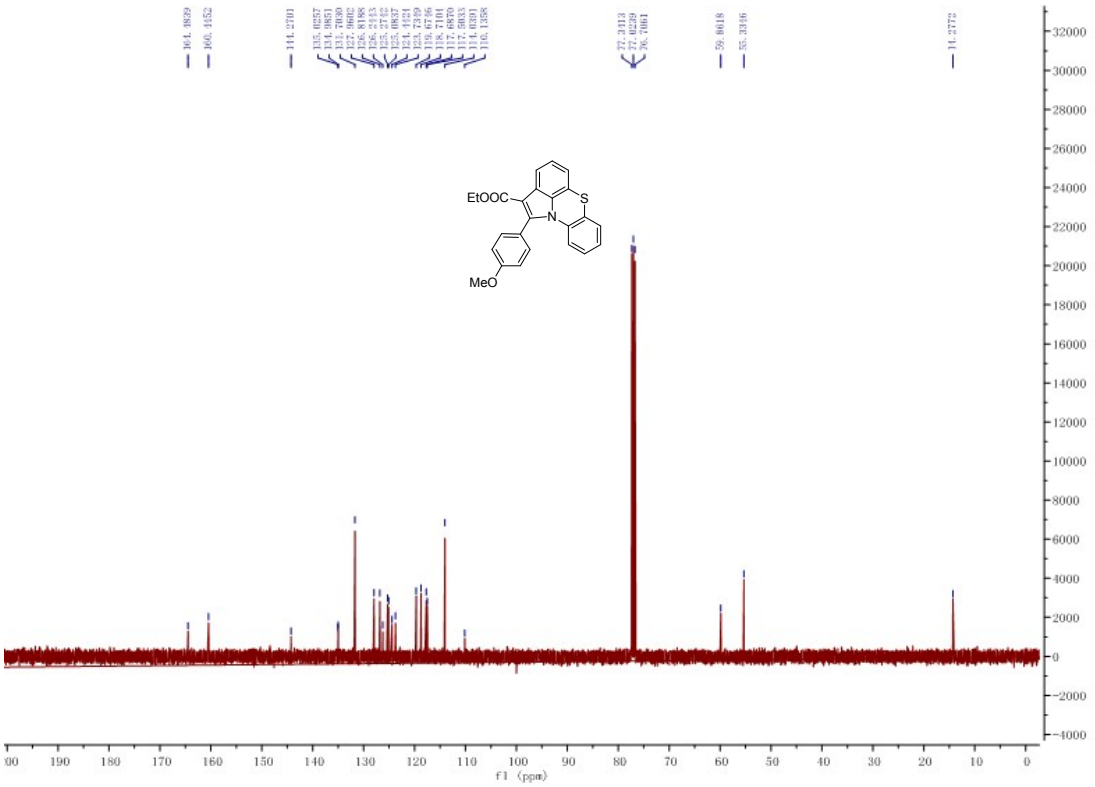

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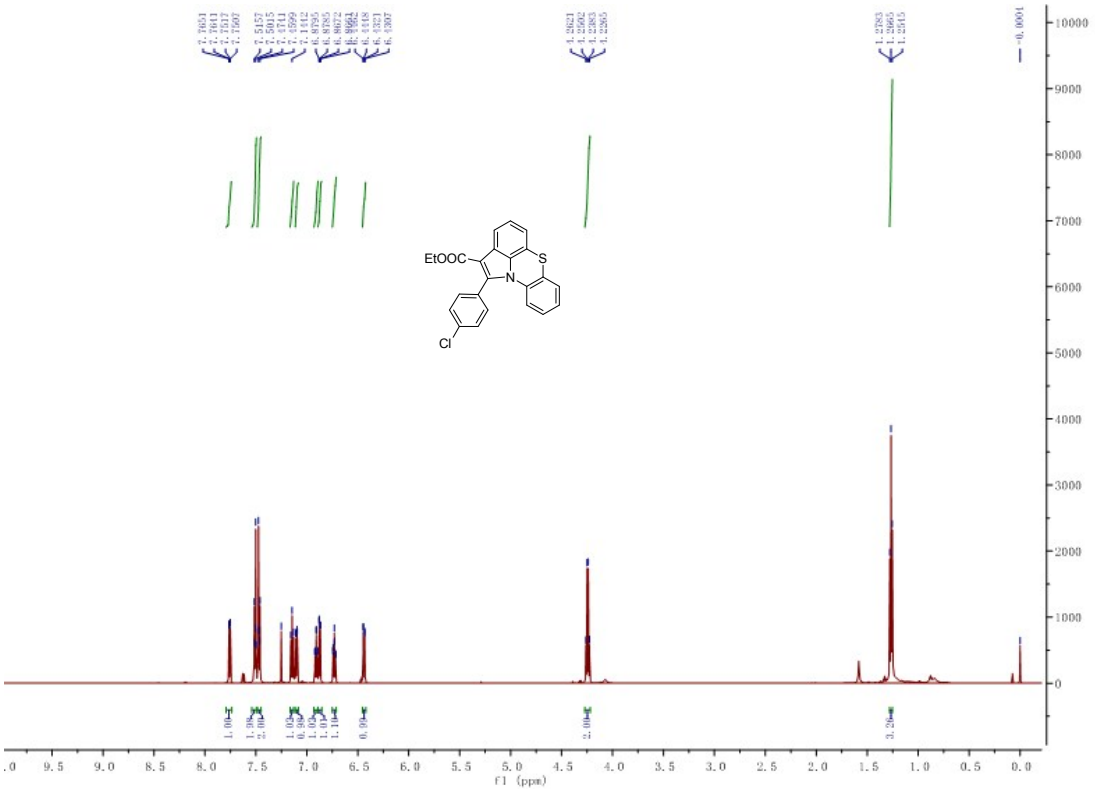

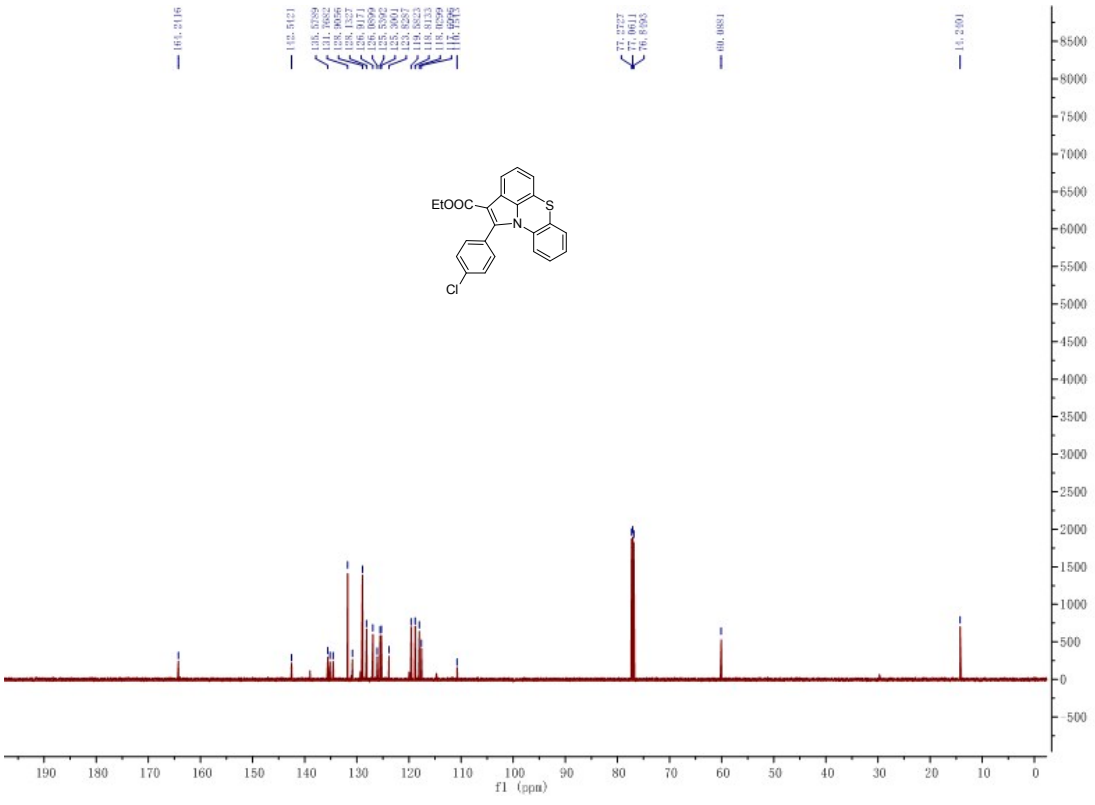

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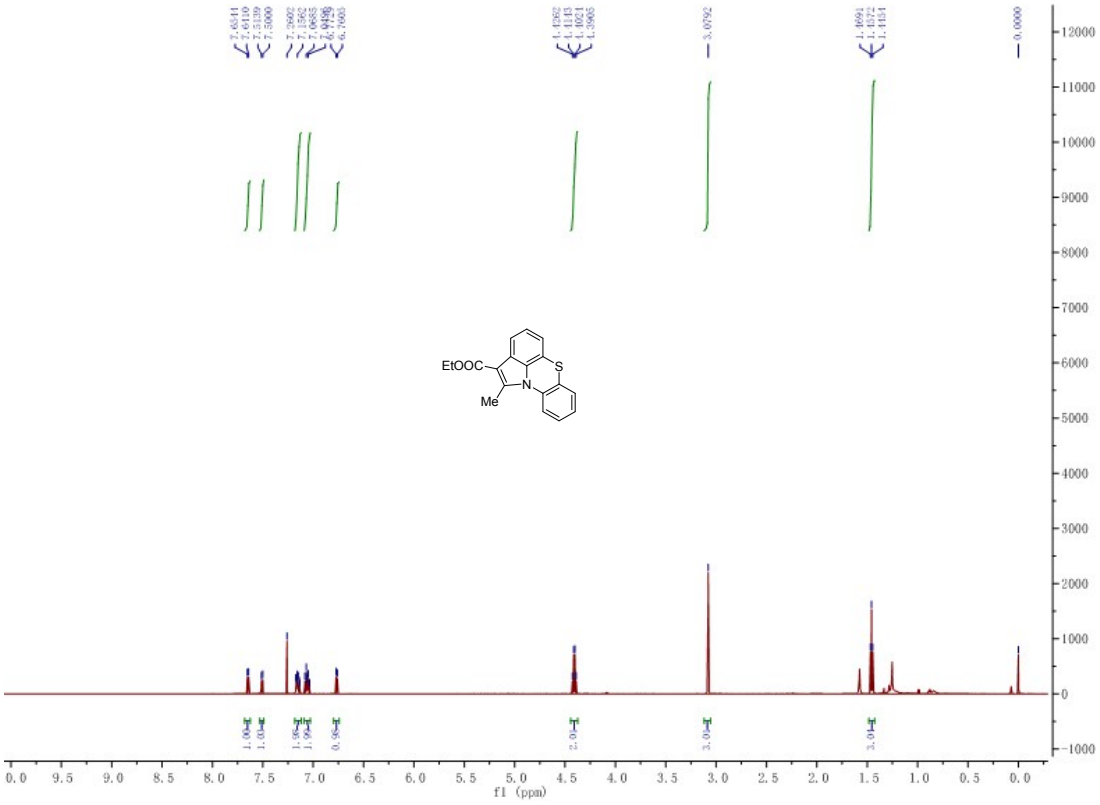

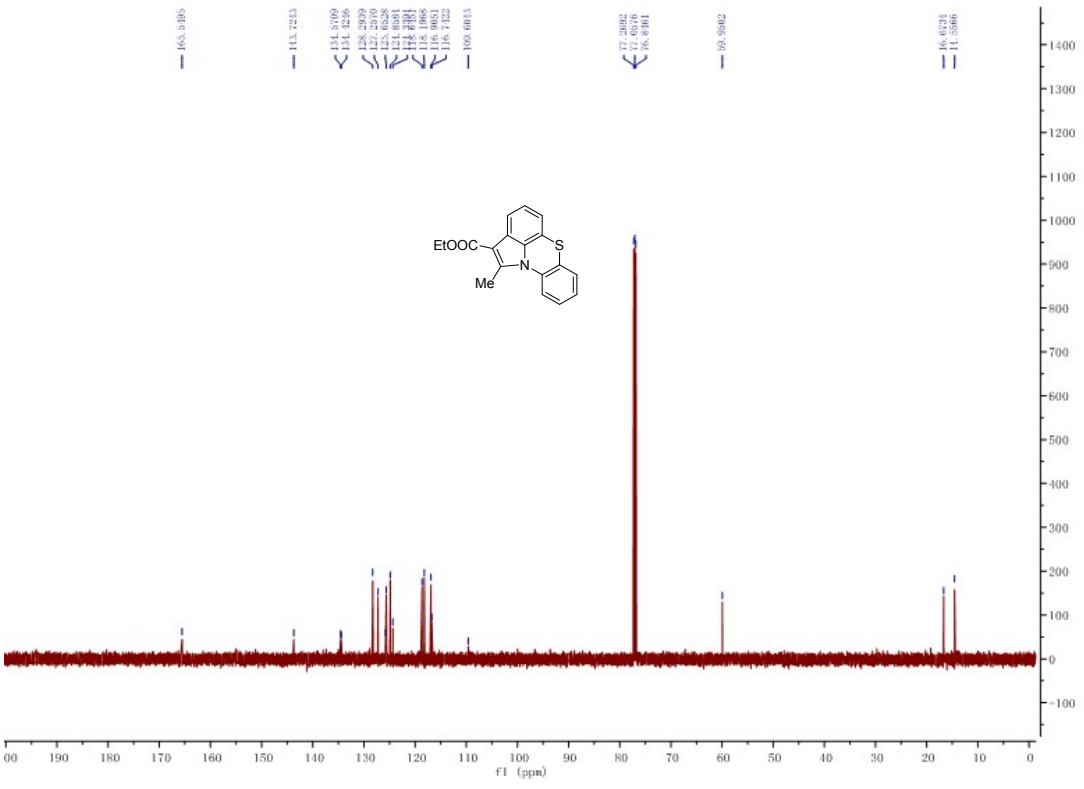

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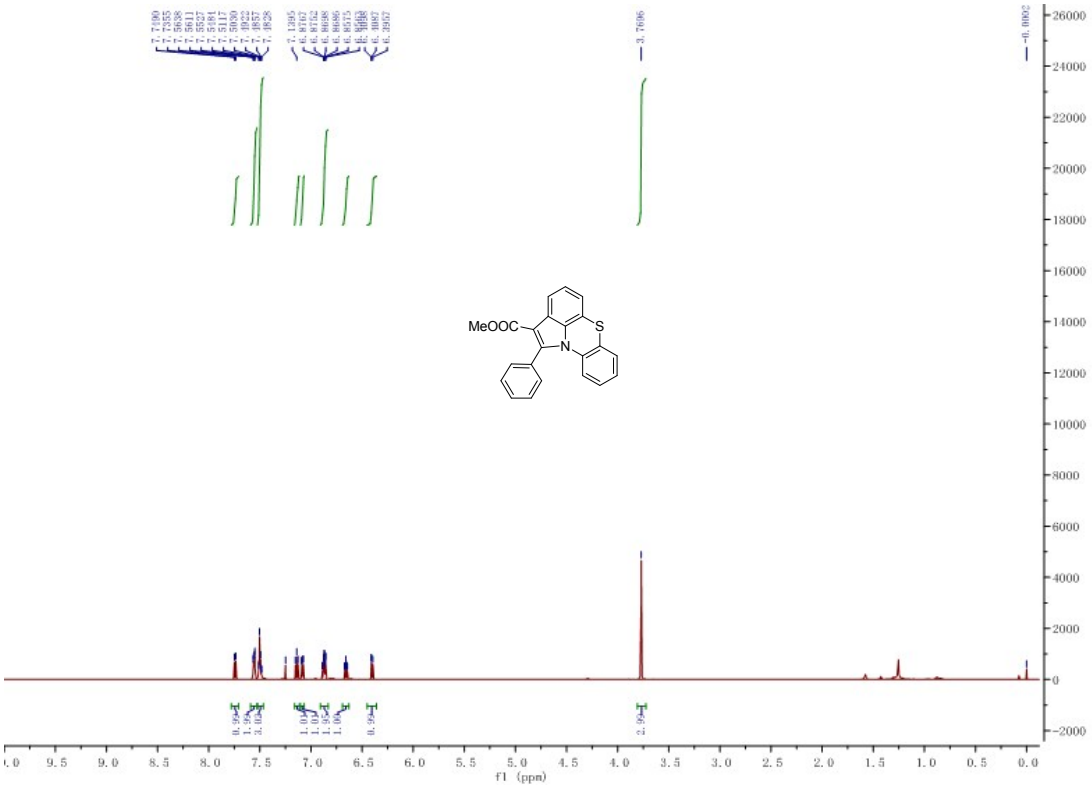

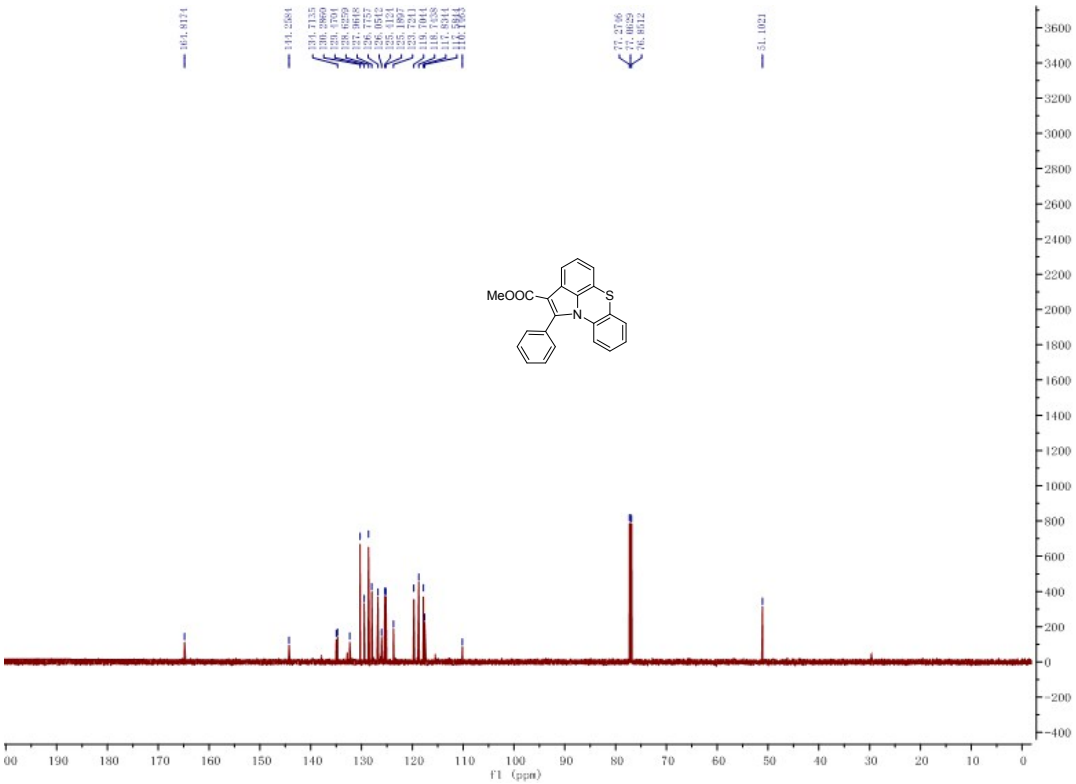

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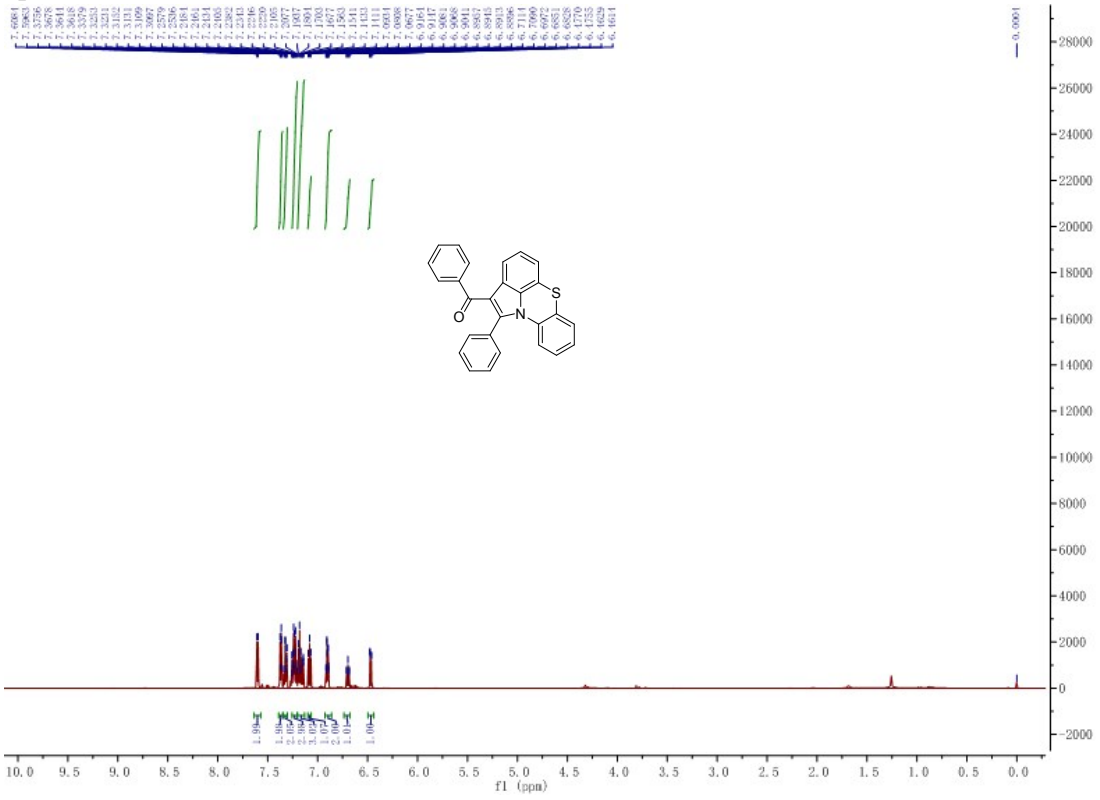
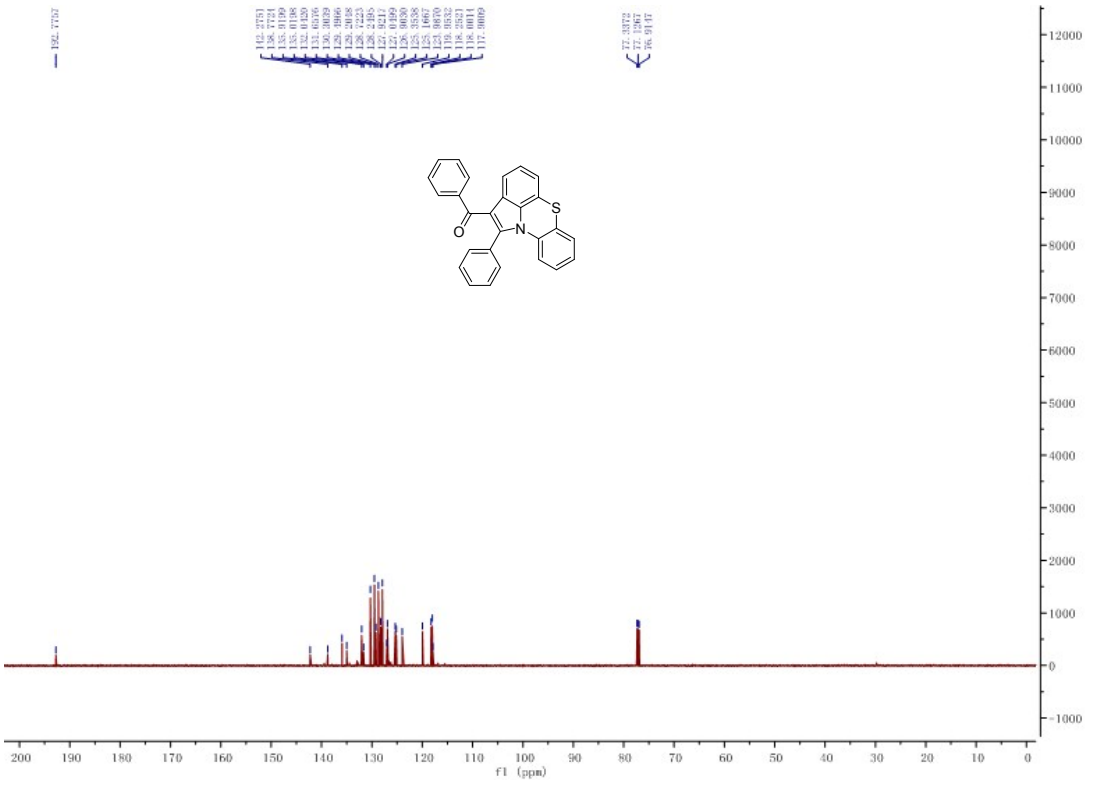
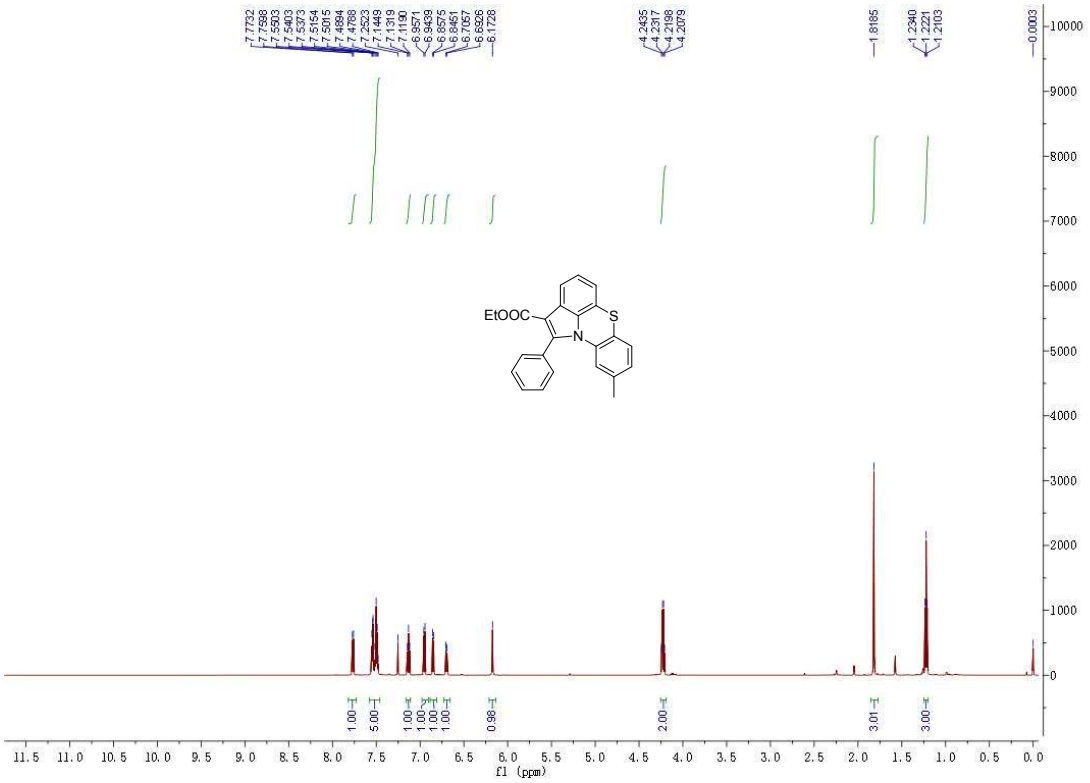




5q: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7.4523
7.1449
7.1319
7.1190
6.9571
6.9439
6.8575
6.8451
6.7057
6.6926
6.1728
4.2435
4.2317
4.2198
4.2079
1.8185
1.2340
1.2221
1.2103
0.0003
EtOOC
S
N
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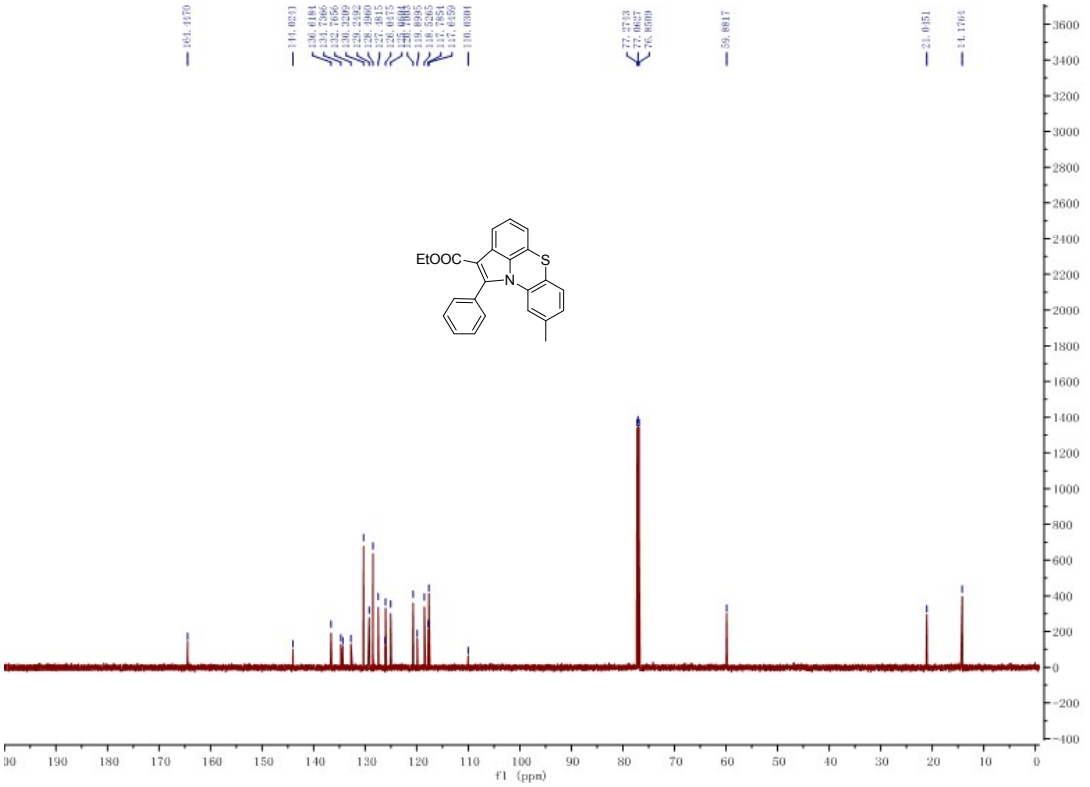
5.00
1.00
1.00
1.00
0.98
2.00
3.01
3.00
f1 (ppm)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134.7966
132.7056
130.3209
129.3292
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127.9815
126.6975
119.8995
118.5265
117.7854
117.6559
110.8384
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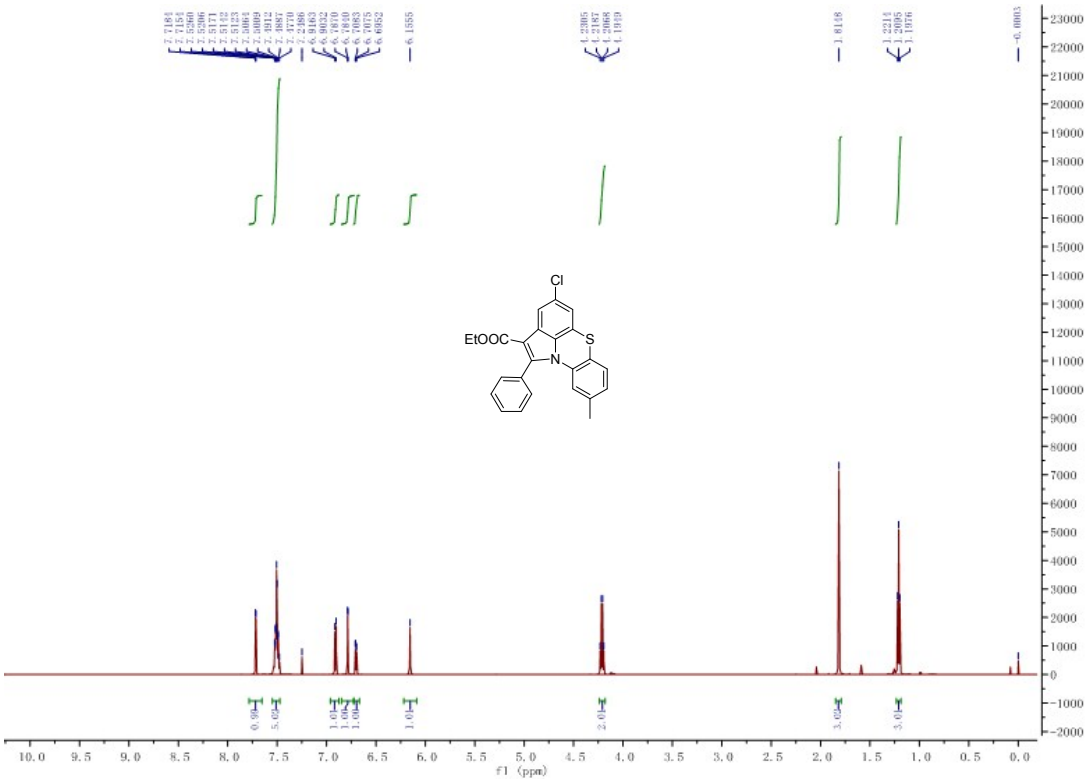
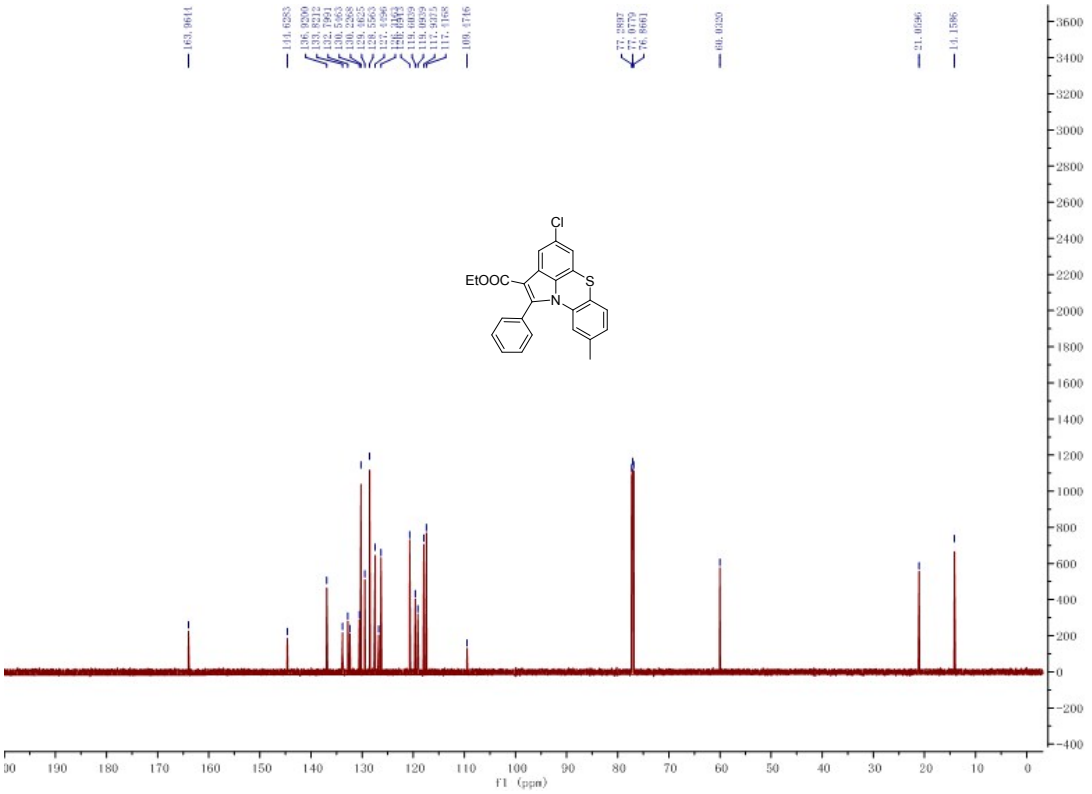
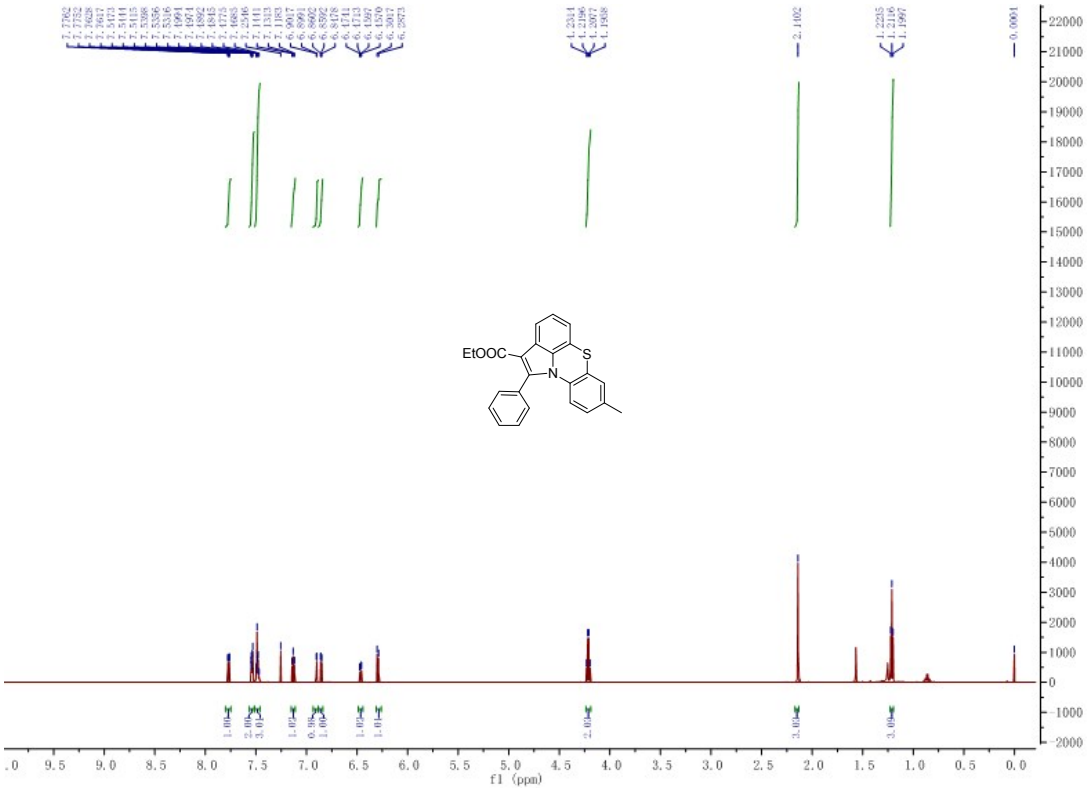
76.8509
59.8817
21.0151
14.1764
EtOOC
S
N
f1 (ppm)

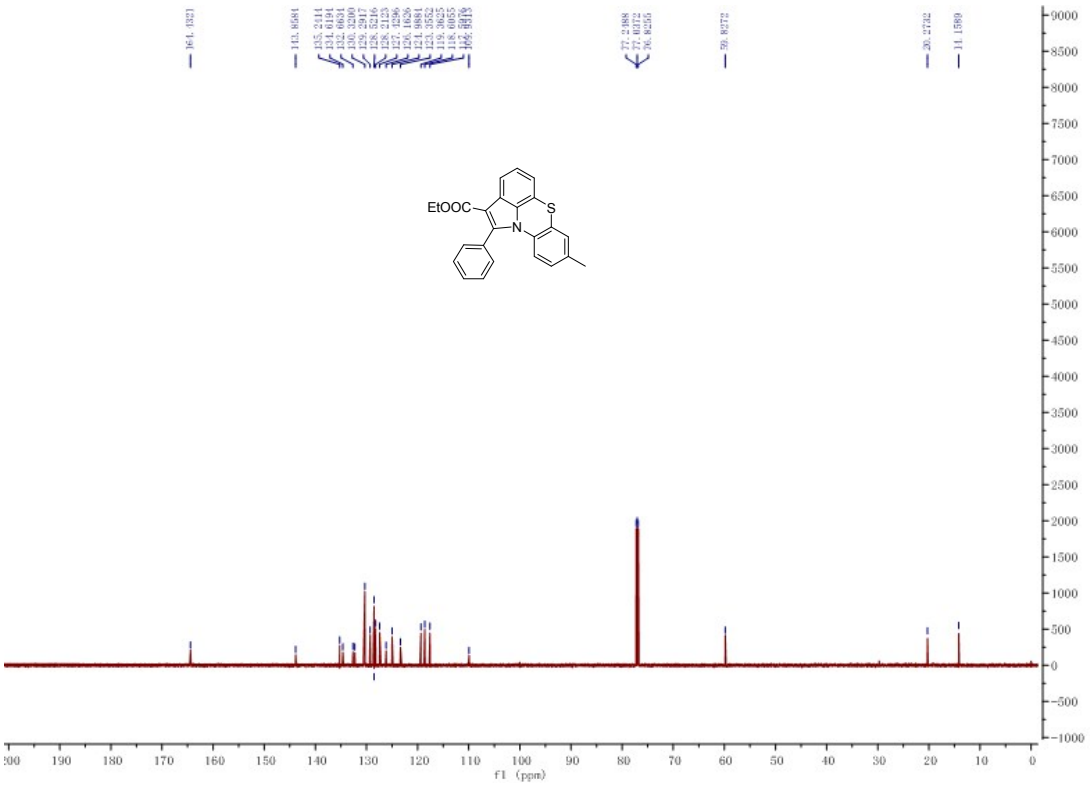
5r:



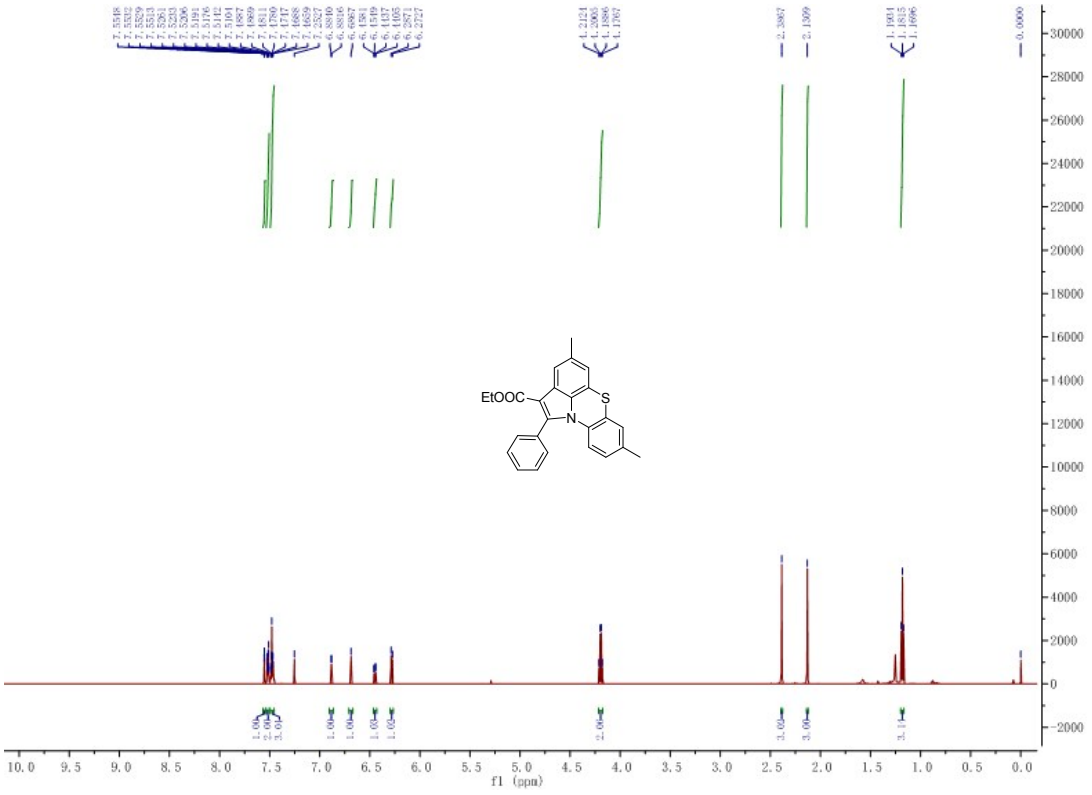


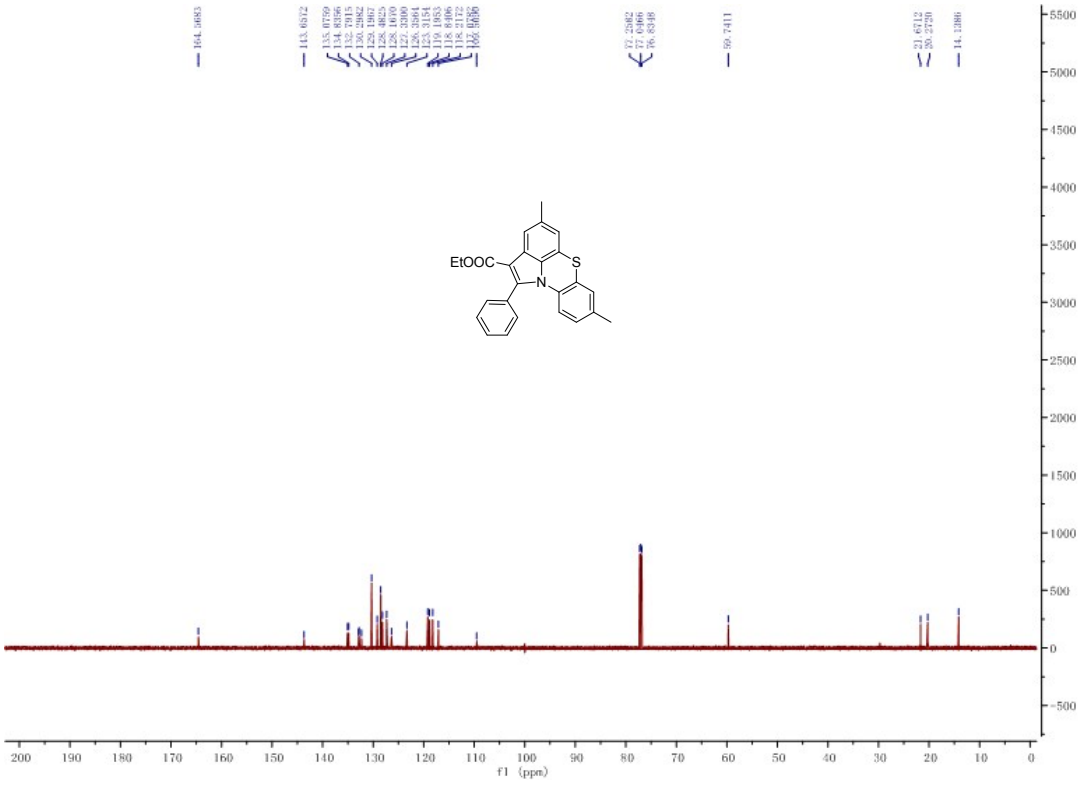
5s:



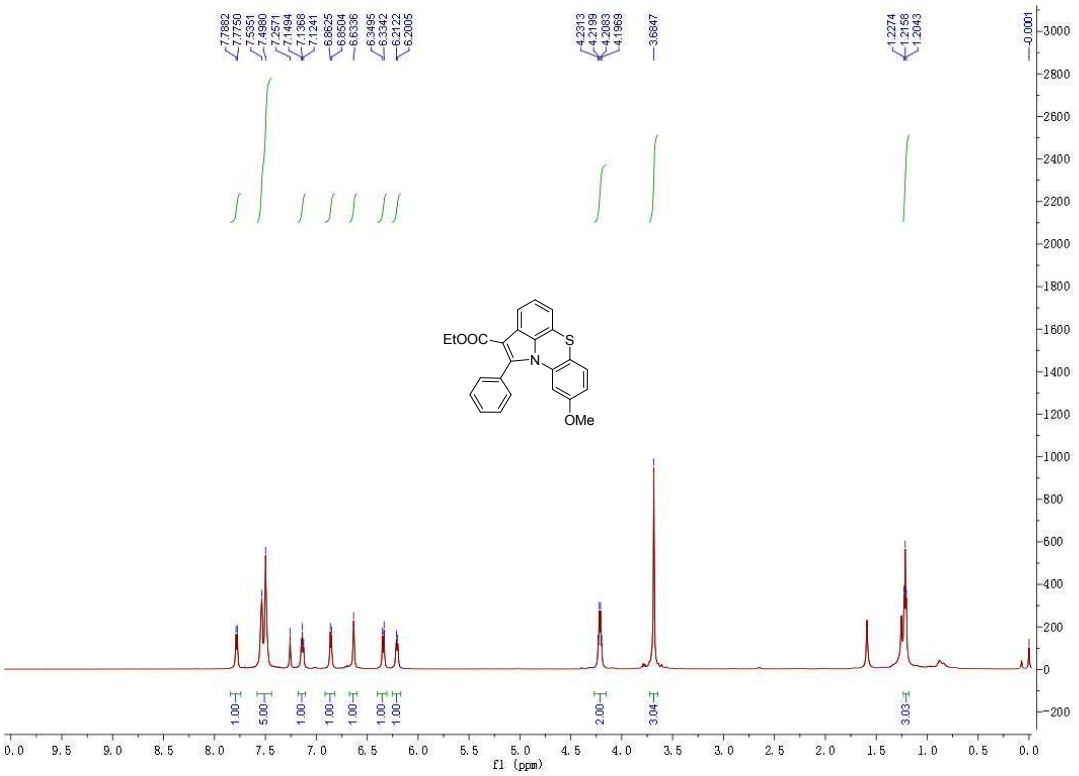


5t:





5u: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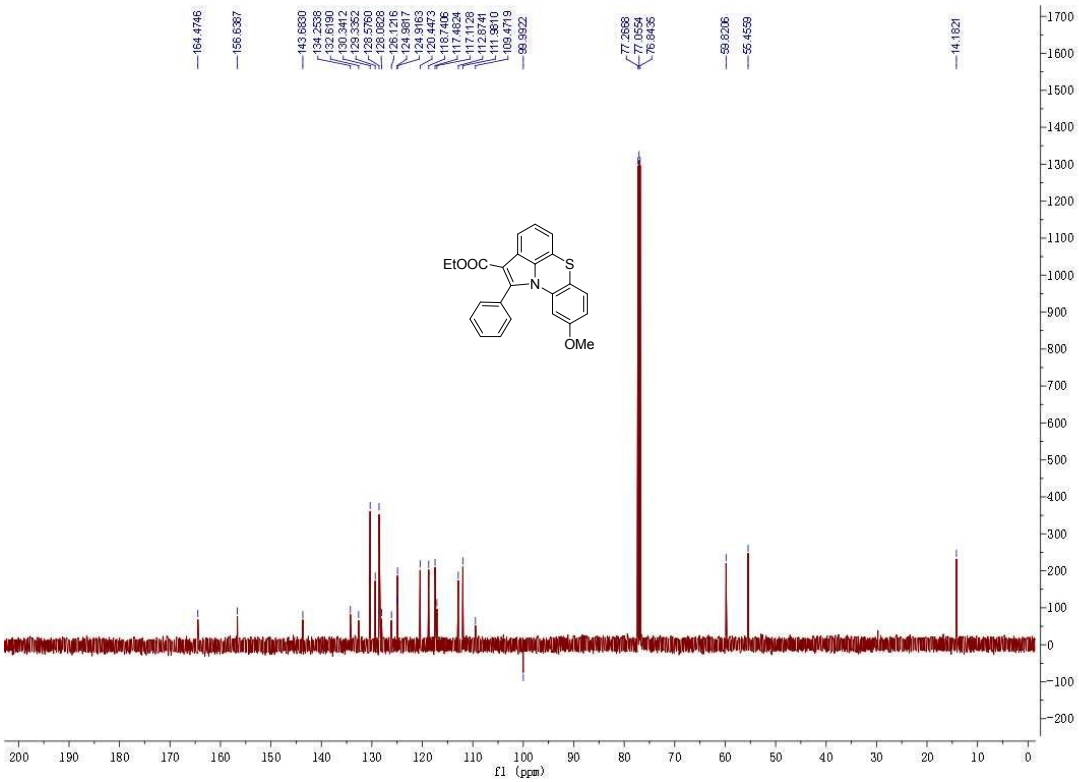
6.3495
6.3342
6.2122
6.2005
4.2313
4.2199
4.2083
4.1969
3.6847
1.2274
1.2158
1.2043
0.0001
EtOOC
S
N
OMe
1.00
5.00
1.00
1.00
1.00
1.00
1.00
2.00
3.04
3.03
f1 (ppm)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143.6830
134.2538
132.6190
130.3412
129.3352
128.5760
128.1028
126.7215
124.9617
124.9163
120.4473
118.7406
117.4824
117.1128
112.8741
111.3810
109.4719
99.9922
77.2668
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59.8206
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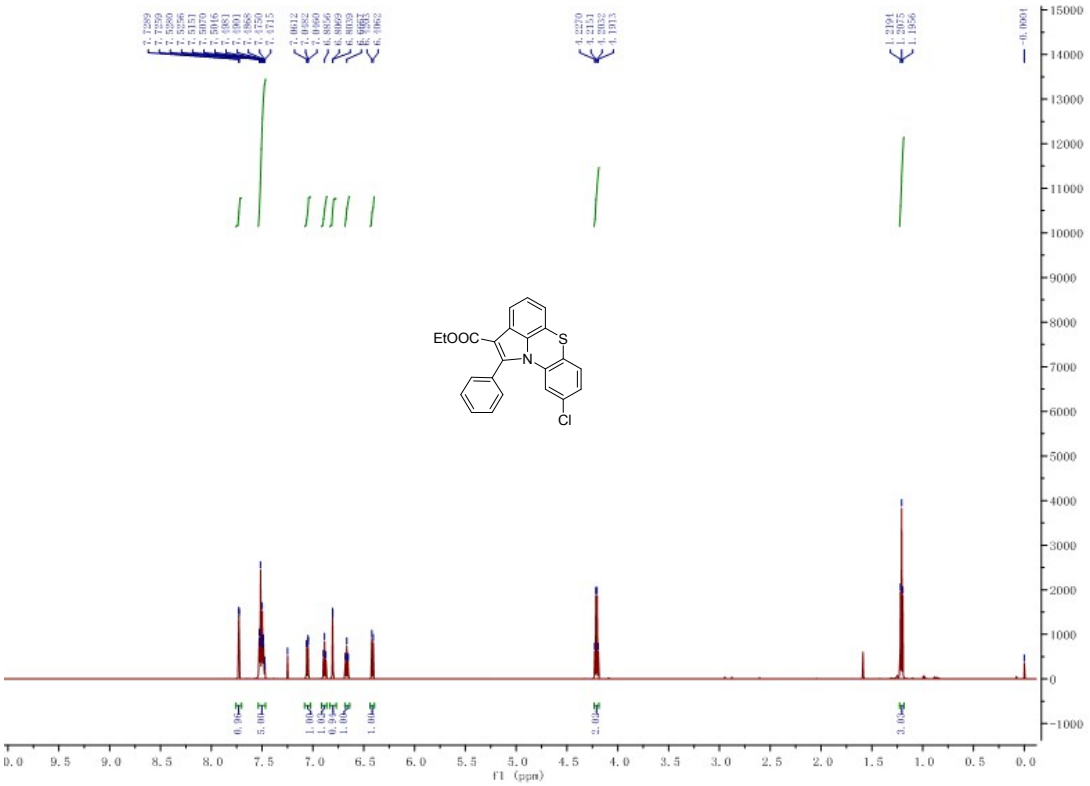
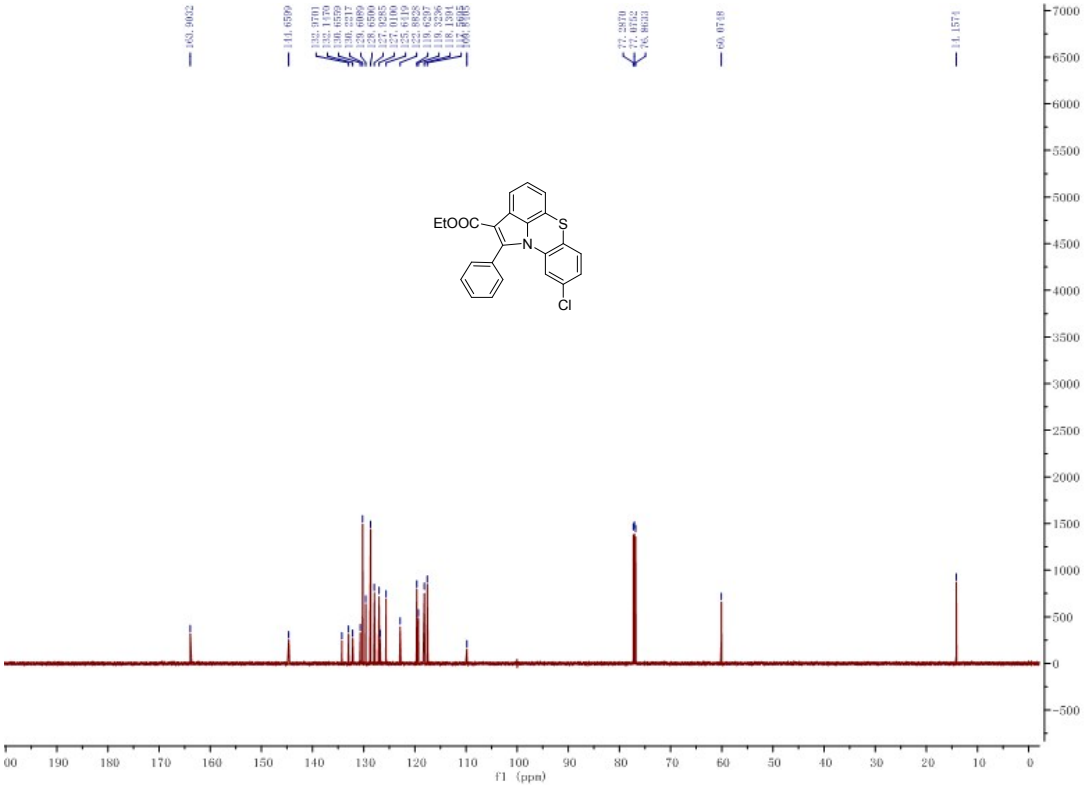
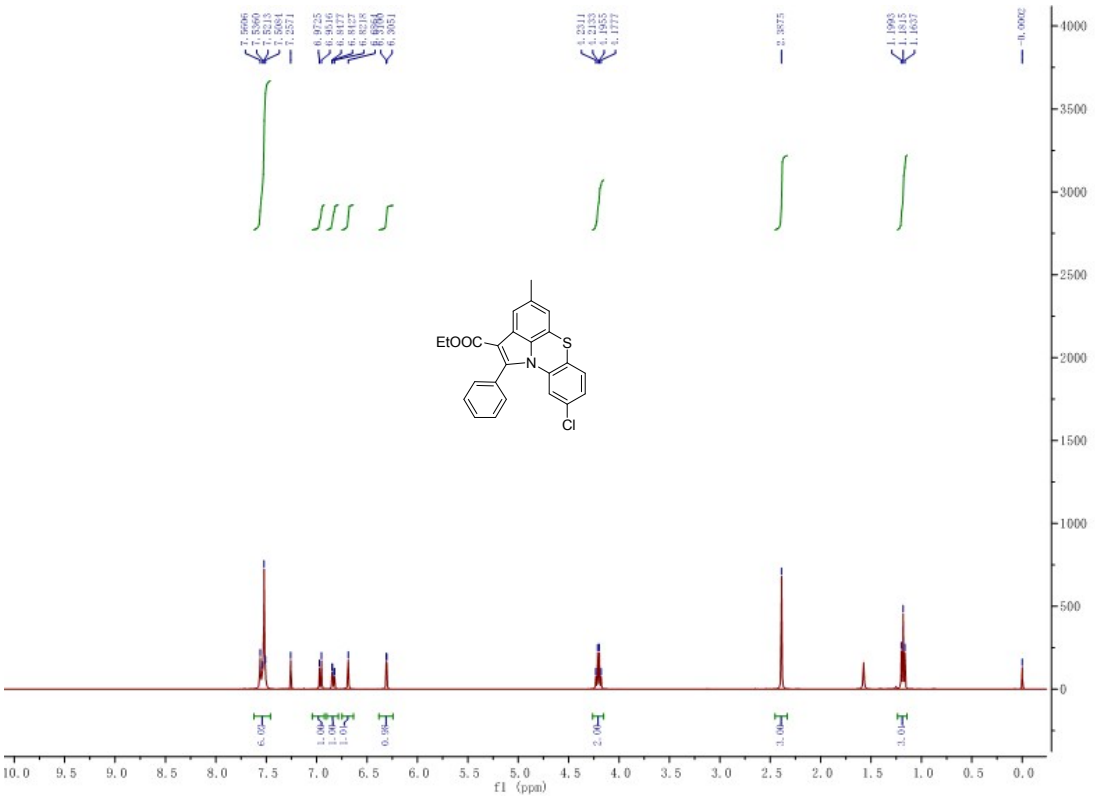
EtOOC
S
N
OMe
f1 (ppm)

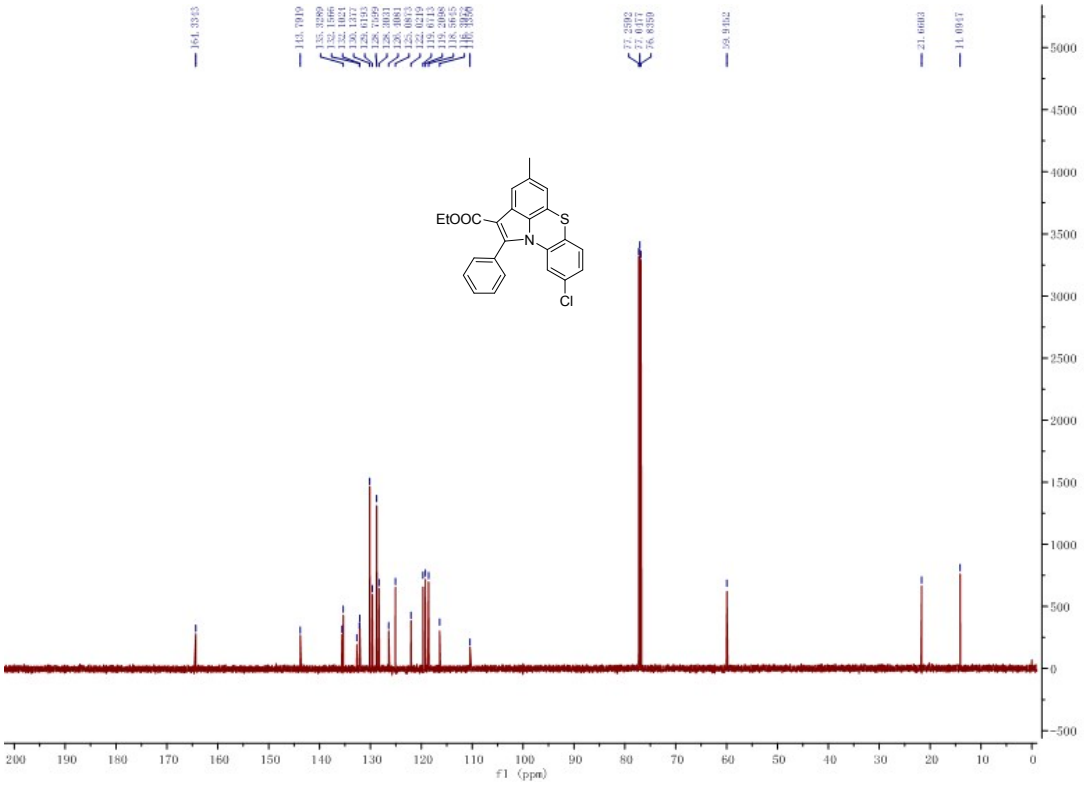
5v:



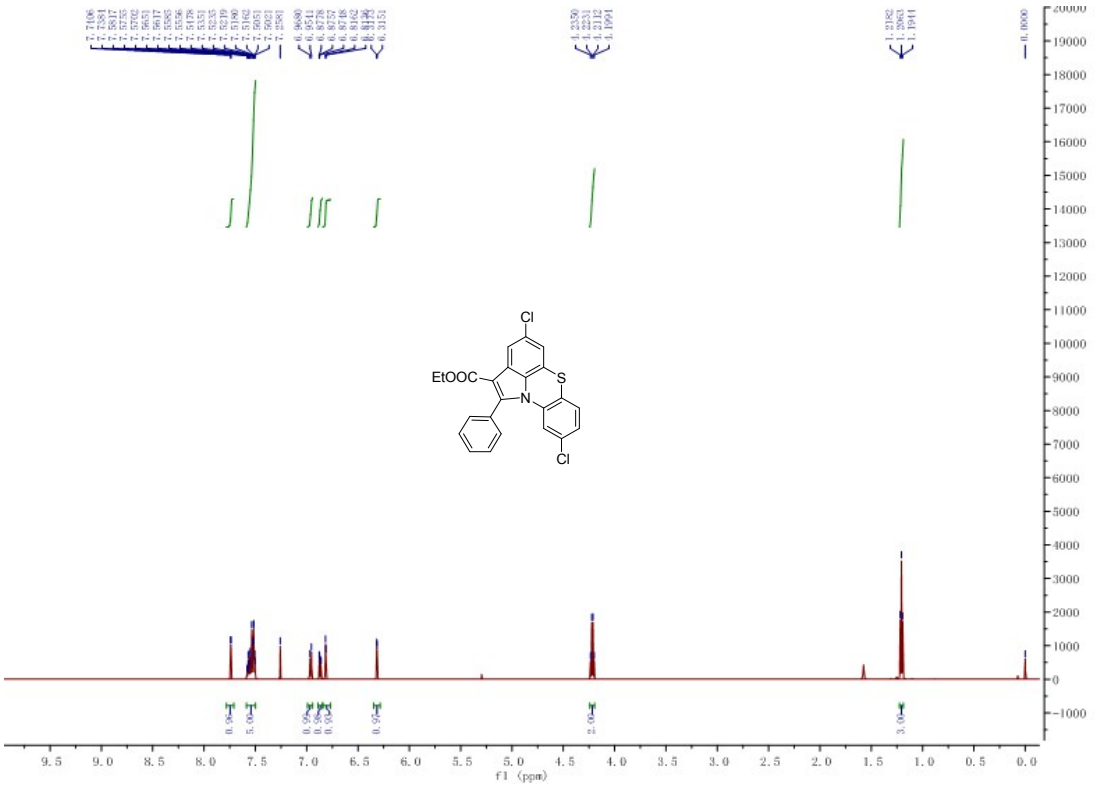


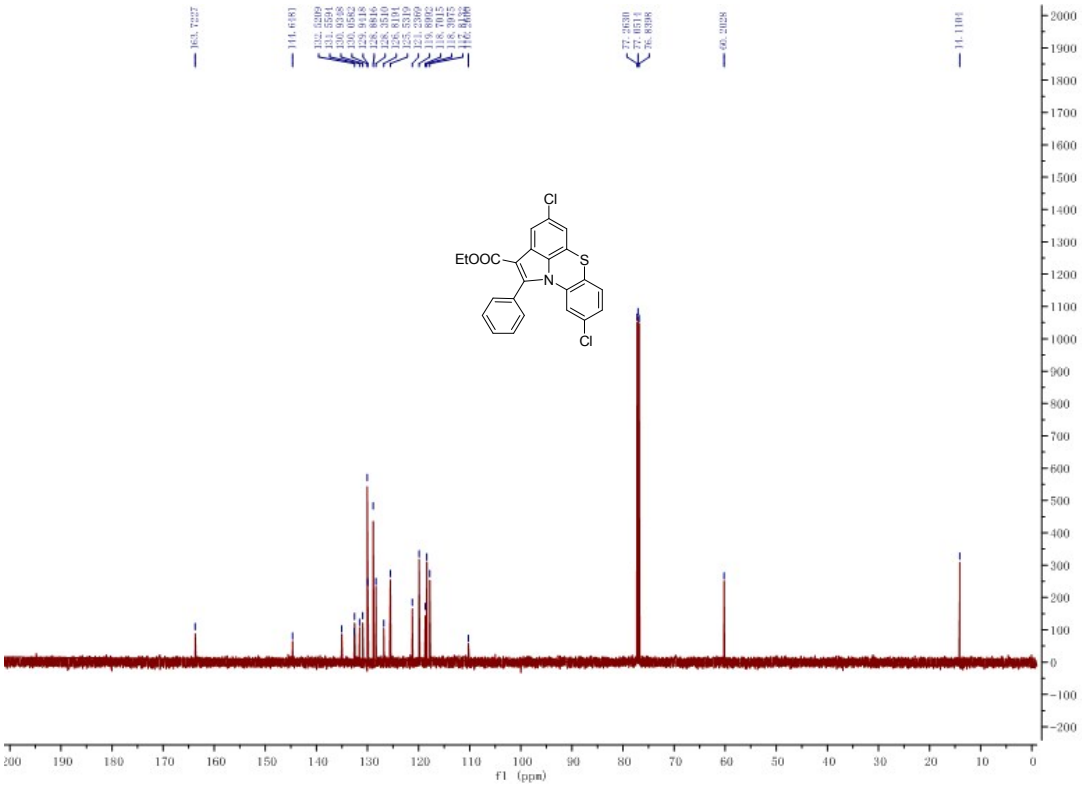
5w:





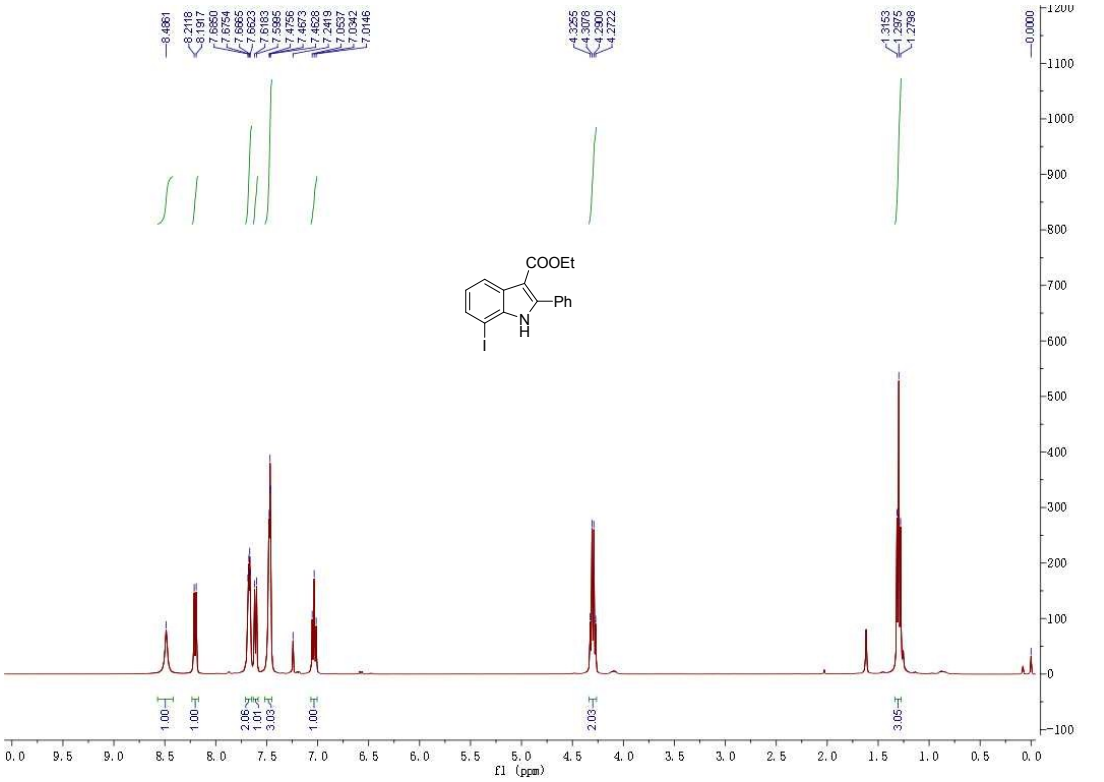
5x:

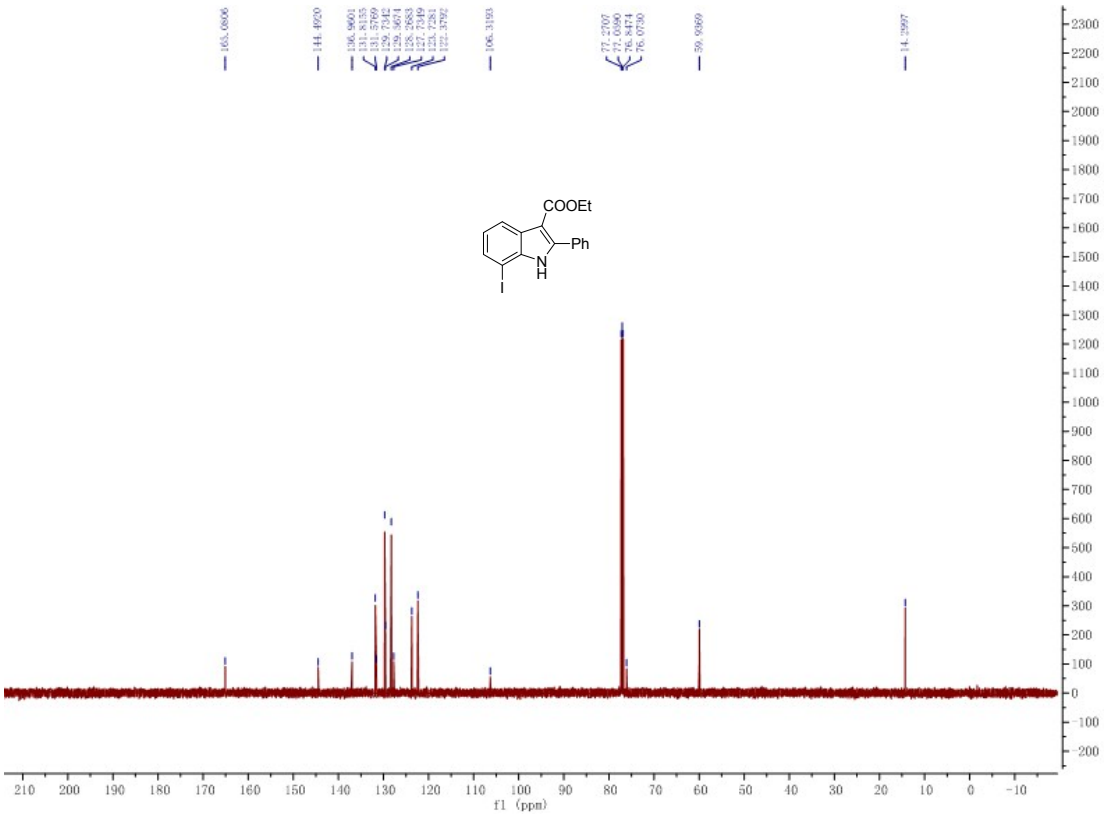




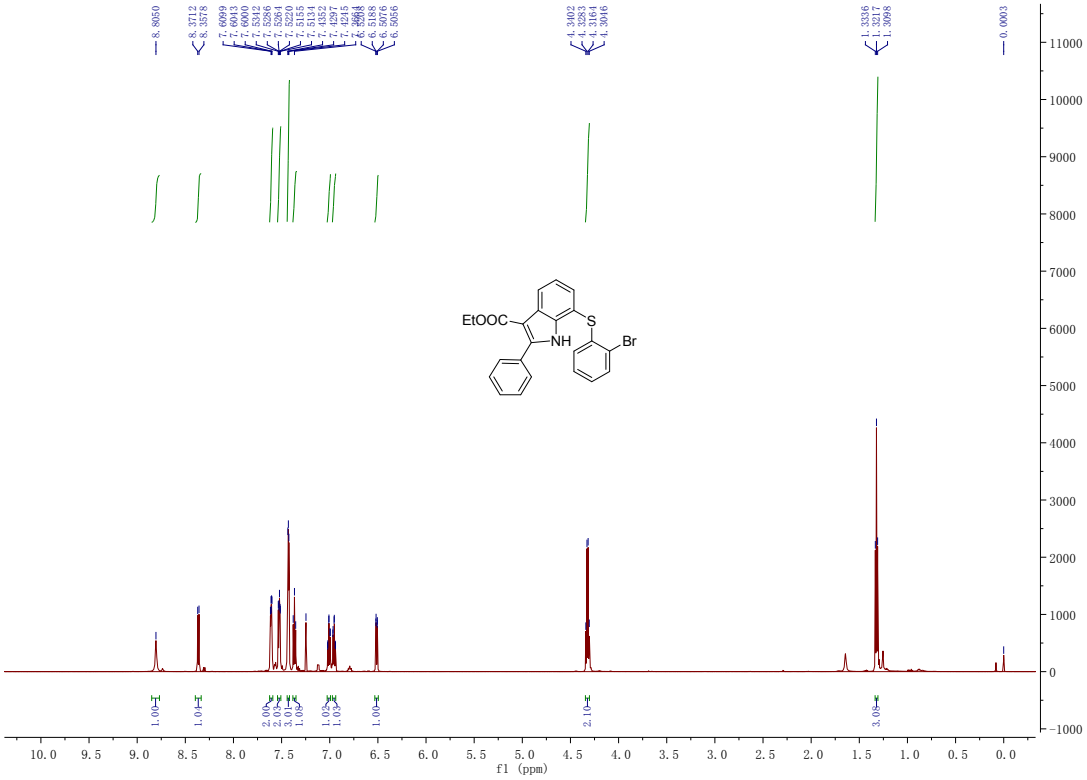
6. Copies of ^{1}H and ^{13}C NMR Spectra for the Intermediates

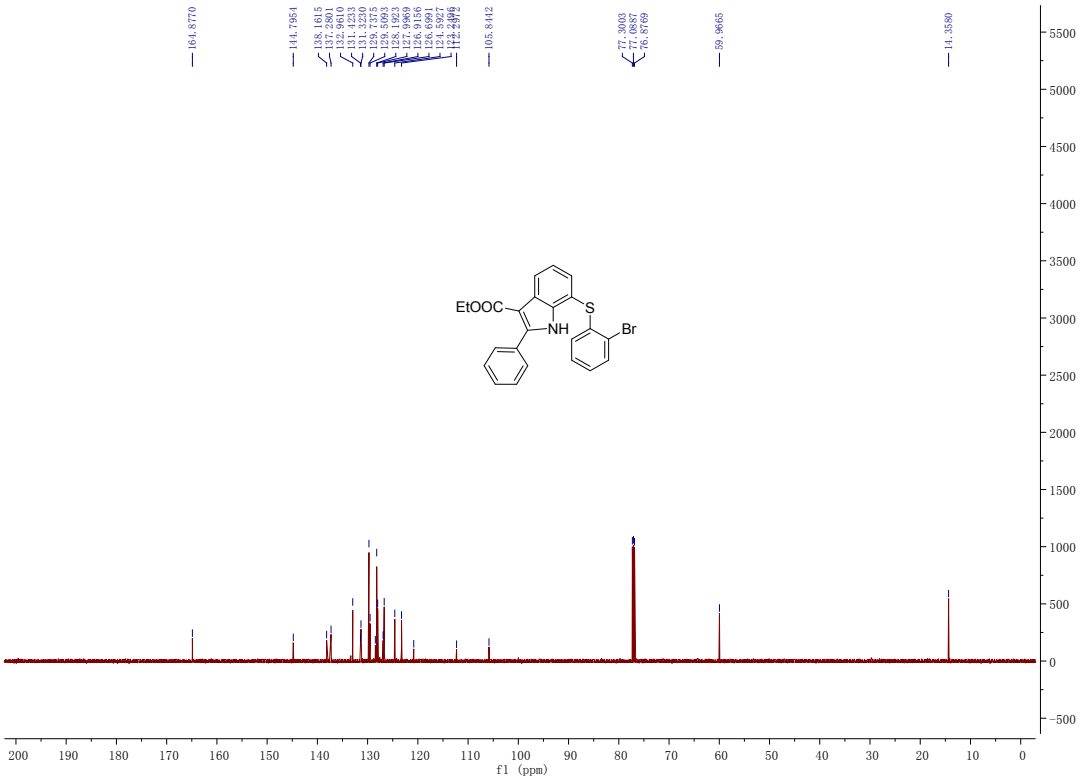
3a:





6a:





7. The X-Ray Crystal Structures of 5r

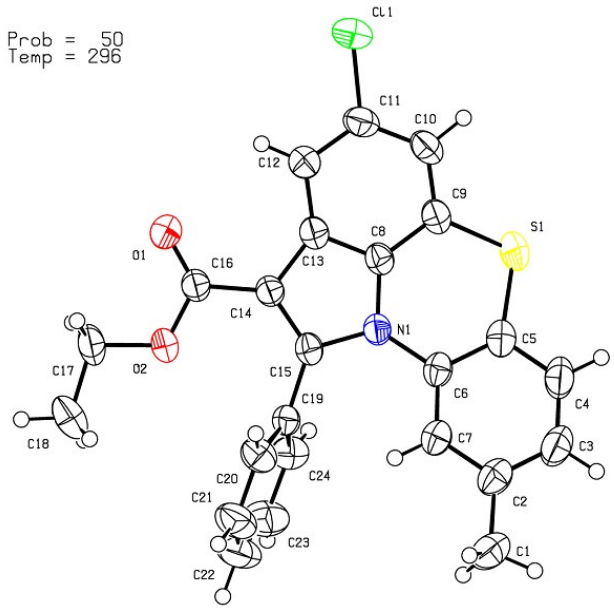


Figure 1. ORTEP diagram of compound 5r.

Important crystal data for 5r:

Bond precision:	C-C = 0.0039 A	Wavelength=0.71073	
Cell:	a=9.5389(3)	b=10.7066(3)	c=11.2370(3)
	alpha=66.541(1)	beta=73.749(2)	gamma=85.725(2)
Temperature:	296 K		
	Calculated	Reported	
Volume	1009.82(5)	1009.82(5)	
Space group	P -1	P-1	
Hall group	-P 1	?	
Moiety formula	$C_{24}H_{18}ClNO_2S$	$C_{24}H_{18}ClNO_2S$	
Sum formula	$C_{24}H_{18}ClNO_2S$	$C_{24}H_{18}ClNO_2S$	
Mr	419.90	419.90	
Dx,g cm^{-3}	1.381	1.381	
Z	2	2	
Mu (mm^{-1})	0.313	0.313	
F000	436.0	436.0	
F000’	436.71		
h,k,l_{max}	12,13,14	12,13,14	
N_{ref}	4710	4662	
T_{min},T_{max}	0.945,0.975	0.922,0.965	

$T_{min'}$ 0.931

Correction method = # Reported T Limits: T_{min}=0.922 T_{max}=0.965

AbsCorr = EMPIRICAL

Data completeness = 0.990 Theta(max)= 27.650

R(reflections)= 0.0577(3340) wR2(reflections)= 0.1567(4662)

S = 1.055 Npar= 262