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Asymmetric [4+2] Annulation of 5*H*-Thiazol-4-Ones with a Chiral Dipeptide-Based Brønsted Base Catalyst

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Supporting Information

Table of Contents

1. General information

General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reactions mixtures were stirred in 4 mL sample vial with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed in vacuo under ~30 mmHg and heated with a water bath at 30–40 ^{o}C using rotary evaporator with aspirator. The condenser was cooled with running water at 0 ^{o}C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining $KMnO_4$, ceric molybdate, or anisaldehyde solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained silica gel 200–300 mesh. Columns were packed as slurry of silica gel in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

Instrumentations

Proton nuclear magnetic resonance (^{1}H NMR), carbon NMR (^{13}C NMR), and fluorous (^{19}F NMR) spectra were recorded in $CDCl_3$ otherwise stated. ^{1}H (300 MHz) and ^{13}C (75 MHz) were performed on a 300MHz spectrometer. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26, singlet; ^{13}C NMR: δ 77.0, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *dt* (doublet of triplets), and *br* (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *n*H. The number of carbon atoms (*n*) for a given resonance was indicated by *n*C. HRMS was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in DCM and MeOH (HPLC Grade) unless otherwise stated. Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows; $[\alpha]_{\lambda}^{T^{\circ}C}$ (c = g/100 mL, solvent). Melting points were determined on a melting point apparatus.

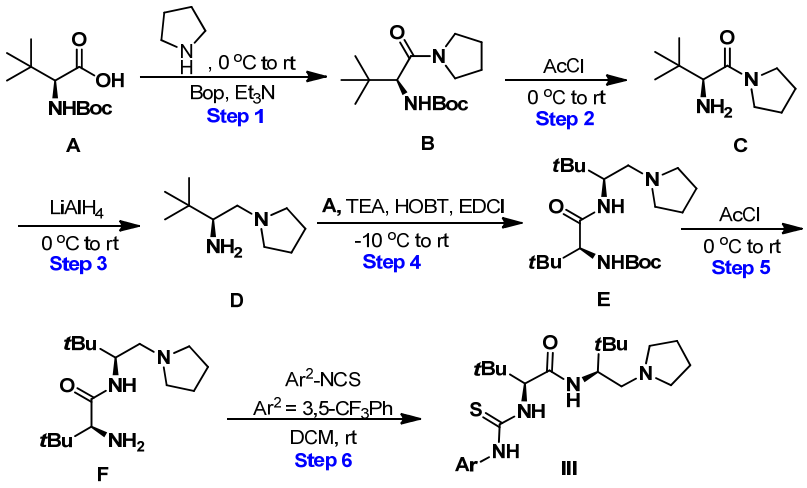
Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 254 nm, 230 nm and 210 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

Materials

All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate

(EtOAc), were distilled. Anhydrous CH_2Cl_2, $CHCl_3$ and DCE were freshly distilled from CaH_2 and stored under N_2 atmosphere. THF, Et_2O and toluene were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a −20 ^oC freezer and light-sensitive compounds were protected with aluminium foil.

2. Synthesis of dipeptide-based III



Step 1: To a solution of crude Boc-protected amino acid **A** (2.31 g, 10 mmol) in THF (15 mL), Et_3N (2.78 mL, 20 mmol) and BOP (5.41 g, 12 mmol) was added at 0 °C. Pyridine (1.16 mL, 13 mmol) was injected after the mixture was stirred for 0.5 hour at 0 °C. Then the reaction mixture was stirred at room temperature for another 8 hours (monitored by TLC). Solvent was removed under reduced pressure and **B** was obtained by flash chromatography (*silica gel*, Hexane/ethyl acetate 10:1–3:1), as a white solid, 2.32 g, 81.6% yield.

Step 2: AcCl (4.6 mL, 65.6 mmol) was added to a solution of **B** (2.32 g, 8.2 mmol) in MeOH (20 mL) 0 °C. The reaction mixture was stirred at room temperature for 8 hours (monitored by TLC). Solvent was removed under reduced pressure and solid **C** (1.51 g, 100%) was obtained for the next step without any purification.

Step 3: $LiAlH_4$ (1.25 g, 32.8 mmol) was added into a solution of **C** (1.51 g, 8.2 mmol) in THF (20 mL) slowly. The mixture was stirred at 0 ºC for about 5.0 minutes then warmed to room temperature and stirred overnight. Subsequently, the reaction was carefully quenched by NaOH aqueous solution (4.0 *N,* 2 mL). The solids were filtered off and washed by THF, and the filtrate was dried over Na_2SO_4. Solvent was removed under reduced pressure and **D** was obtained as yellow oil in 86.5% yield (1.2 g).

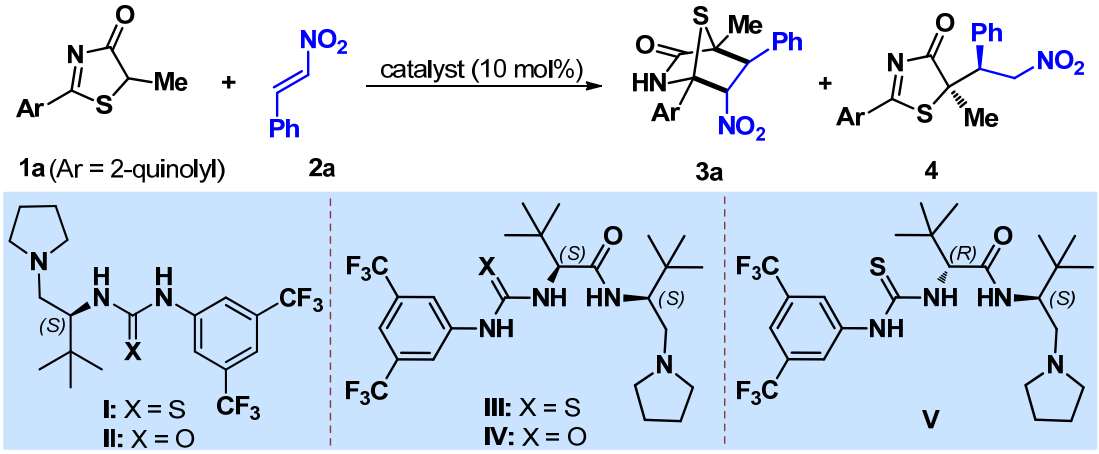
Step 4: To a solution of diamine **D** (0.75 g 4.4 mmol) in THF (25 mL) were added TEA (1.84 ml, 13.2 mmol), Boc-protected amino acid **A** (1.2 g, 5.3 mmol) and HOBt (0.89 g, 6.6 mmol) at −10 °C for 15 min. Then EDCI (1.3 g, 6.6 mmol) was added the mixture, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into water and extracted with AcOEt. The AcOEt layer was washed with water and brine and dried over Na_2SO_4. Filtration and concentration in vacuo and purification by *silica gel* flash column chromatography (AcOEt/n-hexane = 1/5) gave 1.28 g (76%) of **E** as a white solid.

Step 5 AcCl (1.89 mL, 26.7mmol) was added to a solution of **E** (1.28 g, 3.34 mmol) in MeOH (20 mL) 0 °C. The reaction mixture was stirred at room temperature for 8 hours (monitored by TLC). Solvent was removed under reduced pressure and solid **F** (0.95 g, 100%) was obtained for the next step without any purification.

Step 6 (Final step)**:** To a solution of **F** (308.6 mg, 1.09 mmol) in DCM (5 mL) was added 3,5-di(trifluoromethyl)phenyl isothiocyanate (295.2 mg, 1.09 mmol). The resulting solution was stirred for 5 min at 0 ^{o}C. The reaction was concentrated *in vacuo* and the residue was purified by *silica gel* chromatography (*silica gel*, DCM/MeOH 100:1–30:1) to afford product **III** as a white solid in 85% yield (513.1 mg).

3. Optimization of reaction conditions for nitroalkene 2a as acceptor

Table 1 Asymmetric [4+2] cyclization catalyzed by amino acid-derived tertiary amine−(thio)ureas[a]



Entry	Catalyst	Solvent	*T* (°C)	*t* (h)	**3a**:**4**	**3a**			**4**		
						Yield (%)[b]	e.e. (%)[c]	d.r.[d]	Yield (%)[b]	e.e. (%)[c]	d.r.[d]
1	Et_3N	CH_2Cl_2	25	18	trace	trace	n.a.	--	36	n.a.	n.a.
2	**I**	CH_2Cl_2	25	12	1:1	42	0	15:1	45	64	1:1
3	**II**	CH_2Cl_2	25	12	3:1	62	7	9:1	20	3	19:1
4	**III**	CH_2Cl_2	25	12	4:1	73	86	19:1	13	88	12:1
5	**IV**	CH_2Cl_2	25	12	4:1	68	87	8:1	18	87	9:1
6	**III**	THF	25	16	trace	trace	n.a.	n.a.	trace	n.a.	n.a.
7	**III**	toluene	25	16	5:1	84	94	>19:11	8	88	12:1
8	**III**	Et_2O	25	16	4:1	70	92	>19:1	11	96	>19:1
9	**III**	$CHCl_3$	25	16	4.5:1	72	83	>19:1	9	85	>19:1
10	**III**	toluene	10	36	4:1	56	95	>19:1	10	31	3:1
11	**III**	toluene	30	18	4.5:1	78	92	19:1	12	75	19:1
12[e]	**III**	toluene	25	18	5:1	83	95	>19:1	11	88	12:1
13[e]	**V**	toluene	25	18	2.5:1	68	−75	>19:1	17	13	>19:1

[a]The reaction was performed using **1a** (0.05 mmol) and **2a** (0.075 mmol) in 1.0 mL of solvent.

[b]Isolated yield based on **1a** after column chromatography.

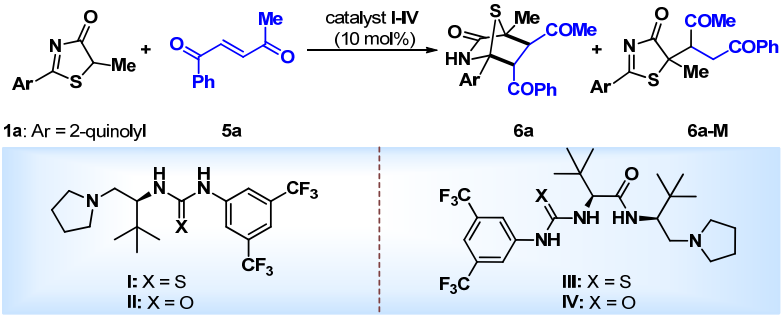
[c]Enantiomeric ratio of product **3a** was determined via chiral phase HPLC analysis.

[d]Determined by crude ^{1}H NMR analysis.

[e]The reaction was performed using **1a** (0.2 mmol) and **2a** (0.4 mmol) in 4.0 mL of solvent.

4. Optimization of reaction conditions for 4-oxo-4-phenylbutenone 5a as acceptor

Table 2 Condition optimization[a]



Entry	Catalyst	Solvent	T (°C)	t (h)	6a		6a-M		
					Yield (%)[b]	e.e. (%)[c]	Yield (%)[b]	e.e. (%)[c]	d.r.[d]
1	Et_3N	CH_2Cl_2	25	96	11	n.a.	72	n.a.	10:1
2	**I**	CH_2Cl_2	25	3	27	62	57	62	>19:1
3	**II**	CH_2Cl_2	25	3	44	54	46	37	>19:1
4	**III**	CH_2Cl_2	25	2.5	85	87	12	32	>19:1
5	**IV**	CH_2Cl_2	25	3	78	68	18	58	19:1
6	**III**	toluene	25	7	54	78	20	73	>19:1
7	**III**	Et_2O	25	7	13	71	5	72	>19:1
8	**III**	$CHCl_3$	25	3.5	82	91	10	50	13:1
9	**III**	DCE	25	5	80	88	13	26/69	11:1
10	**III**	$CHCl_3$	0	18	80	96	17	60/62	13:1
11	**III**	$CHCl_3$	−10	24	86	98	9	69/53	19:1

[a]Reaction conditions: **1a** (0.05 mmol), **5a** (0.075 mmol), solvent (1.0 mL). For product **6a**, all *dr*s are >20:1 determined by crude ^{1}H NMR.

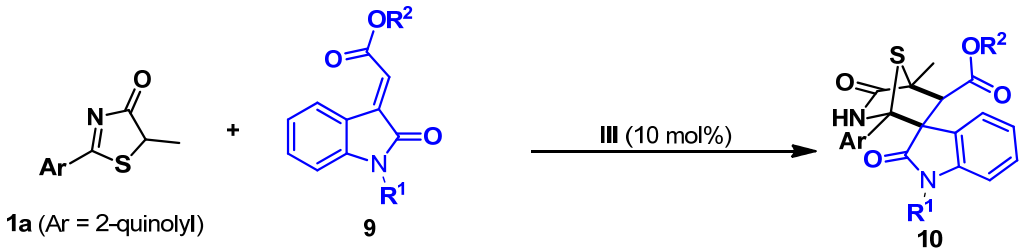
[b]Yield of isolated product.

[c]*Ee* was determined via chiral phase HPLC analysis.

[d]Determined by ^{1}H NMR analysis.

5. Optimization of reaction conditions for methyleneindolinones 9 as acceptor

Table 3 Condition optimization[a]



1a (Ar = 2-quinolyl) 9 10

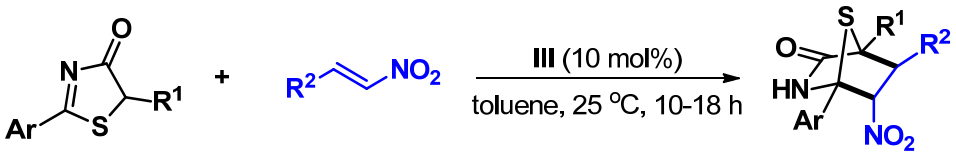
Entry	Solvent	R^1	R^2	*T* (°C)	*t* (h)	**10**	
						Yield (%)[b]	*ee* (%)[c]
1	DCE	Me	Et	25	5	85	73
2	$CHCl_3$	Me	Et	25	5	91	75
3	$CHCl_3$	Me	Et	−10	10	86	85
4	$CHCl_3$	Me	*t*Bu	−10	12	84	80
5	$CHCl_3$	Boc	Et	−10	12	trace	n.a.
6	$CHCl_3$	Bn	Et	−10	12	90	94
7	$CHCl_3$	Bn	Et	−30	24	96	95

[a]Reaction conditions: **1a** (0.05 mmol), **9** (0.075 mmol), solvent (1.0 mL). For product **10**, all *dr*s are >20:1 determined by crude ^{1}H NMR.

[b]Yield of isolated product.

[c]*Ee* was determined via chiral phase HPLC analysis.

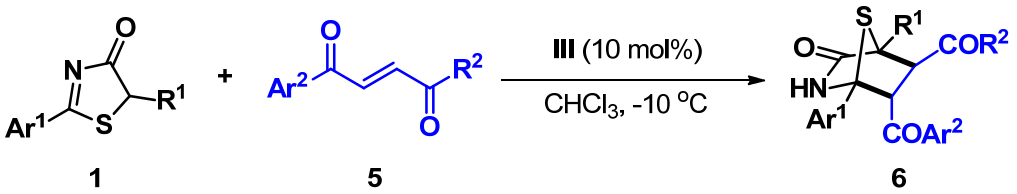
6. General experimental procedure for the [4+2] annulation of 5*H*-thiazol-4-ones 1 with nitroalkenes 2



1 2 3

Nitroalkene **2** (0.4 mmol, 2.0 equiv) and catalyst **III** (11.5 mg, 0.02 mmol, 0.1 equiv) were dissolved in toluene (4.0 mL) and stirred at 25 °C for 15 min. Then 5*H*-thiazol-4-one **1** (0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred at 25 °C and monitored by TLC. Upon complete consumption of 5*H*-thiazol-4-one **1**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with CH_2Cl_2/MeOH (800/1–300/1). Removing the solvent *in vacuo*, afforded products **3a-n**.

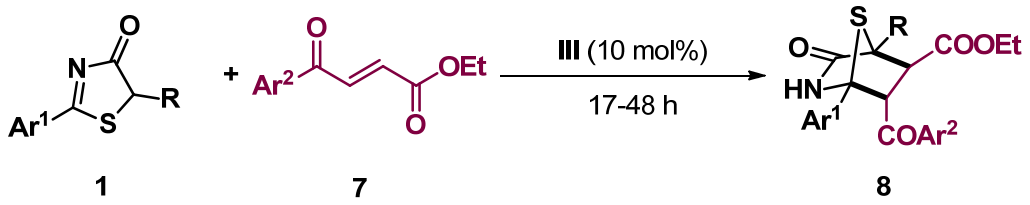
7. General experimental procedure for [4+2] annulation of 5*H*-thiazol-4-ones 1 with 4-oxo-4-arylbutenones 5



1 **5** **6**

4-Oxo-4-arylbutenone **5** (0.3 mmol, 1.5 equiv) and catalyst **III** (11.5 mg, 0.02 mmol, 0.1 equiv) were dissolved in $CHCl_3$ (4.0 mL) and stirred at −10 °C for 15 min. Then 5*H*-thiazol-4-one **1** (0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred at −10 °C and monitored by TLC. Upon complete consumption of 5*H*-thiazol-4-one **1**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with CH_2Cl_2/MeOH (800/1–200/1). Removing the solvent *in vacuo*, afforded products **6a-s**.

8. General experimental procedure for [4+2] annulation of 5*H*-thiazol-4-ones 1 with 4-oxo-4-arylbutenoates 7

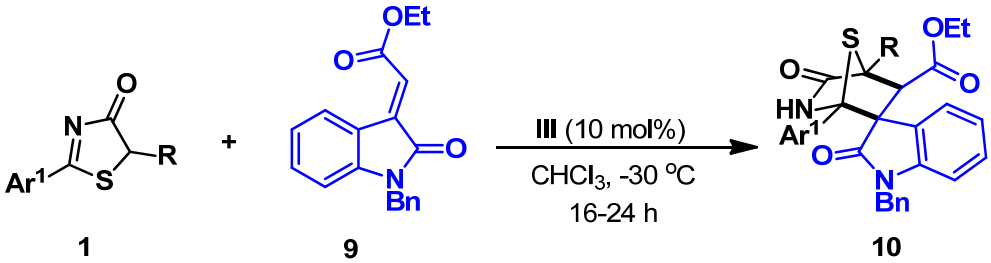


1 **7** **8**

(R = Me): 4-Oxo-4-arylbutenoate **7** (0.3 mmol, 1.5 equiv) and catalyst **III** (11.5 mg, 0.02 mmol, 0.1 equiv) were dissolved in $CHCl_3$ (4.0 mL) and stirred at −30 °C for 15 min. Then 5*H*-thiazol-4-one **1** (0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred at −30 °C and monitored by TLC. Upon complete consumption of 5*H*-thiazol-4-one **1**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with CH_2Cl_2/MeOH (800/1–200/1). Removing the solvent *in vacuo*, afforded products **8a-f** and **8h**.

(R = Ph): 4-Oxo-4-arylbutenoate **7** (0.3 mmol, 1.5 equiv), Li_3PO_4 (0.2 mmol, 1.0 equiv) and catalyst **III** (22.2 mg, 0.04 mmol, 0.2 equiv) were dissolved in $CHCl_3$ (4.0 mL) and stirred at 30 °C for 15 min. Then 5*H*-thiazol-4-one **1** (0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred at 30 °C and monitored by TLC. Upon complete consumption of 5*H*-thiazol-4-one **1**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with CH_2Cl_2/MeOH (800/1–200/1). Removing the solvent *in vacuo*, afforded products **8g**.

9. General experimental procedure for [4+2] annulation of 5*H*-thiazol-4-ones 1 with methyleneindolinones 9

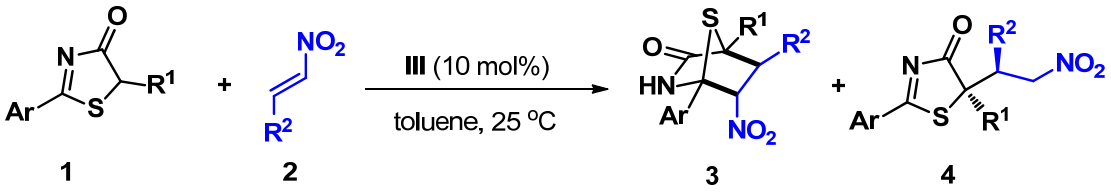


1 **9** **10**

Methyleneindolinones **9** (0.3 mmol, 1.5 equiv) and catalyst **III** (11.5 mg, 0.02 mmol, 0.1 equiv) were dissolved in $CHCl_3$ (4.0 mL) and stirred at −30 °C for 15 min. Then 5*H*-thiazol-4-one **1** (0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred at −30 °C and monitored by TLC. Upon complete consumption of 5*H*-thiazol-4-one **1**, the reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with CH_2Cl_2/MeOH (800/1–200/1). Removing the solvent *in vacuo*, afforded products **10a-n**.

10. Chemoselective results

Table 4 Reactions between **1** and **2** to afford **3** and **4**[a]

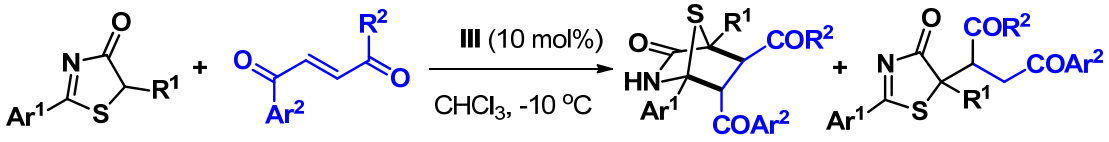


1 2 3 4

Entry	Ar	R^1	R^2	*t* (h)	**3a**	**4**
					Yield (%)[b]	Yield (%)[b]
1	2-quinolyl	Me	Ph	15	83	11
2	2-quinolyl	Me	4-FPh	12	78	16
3	2-quinolyl	Me	4-ClPh	14	89	6
4	2-quinolyl	Me	4-BrPh	13	84	8
5	2-quinolyl	Me	3-ClPh	15	85	9
6	2-quinolyl	Me	2-ClPh	18	82	12
7	2-quinolyl	Me	4-MePh	10	72	20
8	2-quinolyl	Me	3-MePh	13	76	18
9	2-quinolyl	Me	2-MePh	13	82	16
10	2-quinolyl	Me	2-naphthyl	16	88	8
11	2-quinolyl	Me	2-furyl	16	76	18
12	2-quinolyl	Me	cyclohexyl	72	41	51
13	2-quinolyl	Et	Ph	14	55	35
14	4-BrPh	Me	Ph	14	45	52
15	3-pyridyl	Me	Ph	10	76	19

[a]0.2 mmol scale. [b] Isolated yields.

Table 5 Reactions between **1** and **5** to afford **6** and **6-M**[a]

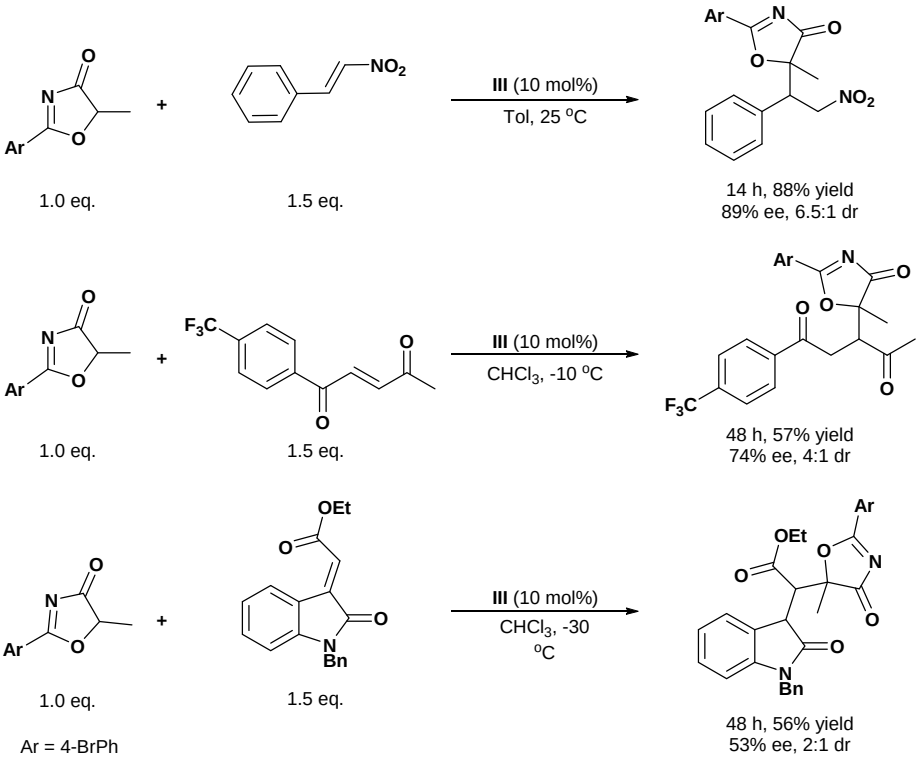


1 **5** **6** **6-M**

entry	Ar^1	R^1	Ar^2	R^2	*t* (h)	**6** yield (%)[b]	**6-M** yield (%)[b]
1	2-quinolyl	Me	Ph	Me	24	86	8
2	2-quinolyl	Me	4-CF_3Ph	Me	10	90	trace
3	2-quinolyl	Me	4-ClPh	Me	8	80	11
4	2-quinolyl	Me	4-BrPh	Me	24	91	trace
5	2-quinolyl	Me	3,4-Cl_2Ph	Me	16	95	trace
6	2-quinolyl	Me	4-MeOPh	Me	48	87	6
7	2-quinolyl	Me	3-MeOPh	Me	24	82	9
8	2-quinolyl	Me	2-MeOPh	Me	66	64	25
9	2-quinolyl	Me	2-BrPh	Me	40	60	28
10	2-quinolyl	Me	2-thienyl	Me	12	98	0
11	2-quinolyl	Me	2-furyl	Me	18	92	trace
12	2-quinolyl	Me	Ph	Et	36	90	5
13	2-pyridyl	Et	Ph	Me	24	87	7
14	3-pyridyl	Me	Ph	Me	24	86	10
15	2-thienyl	Me	Ph	Me	36	70	15
16	2-furyl	Me	Ph	Me	16	75	13
17	4-BrPh	Me	Ph	Me	24	54	42
18	2-quinolyl	Et	Ph	Me	18	72	10
19	2-quinolyl	Bn	Ph	Me	18	90	trace

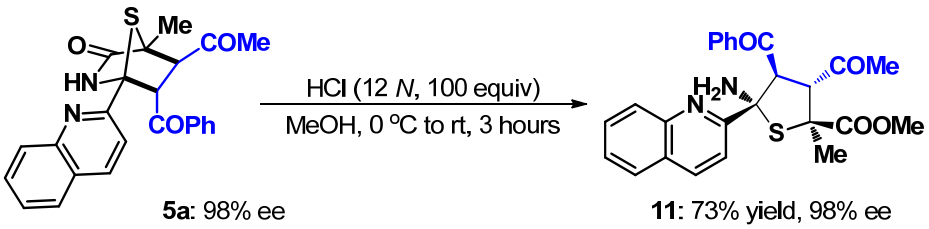
[a]0.2 mmol scale. [b] Isolated yields.

11. Exploration towards reactions between 5*H*-oxazol-4-ones and alkenes



The results indicated that the reactions of 5*H*-oxazol-4-one with a series of activated alkenes under the established reaction conditions only presented conjugate addition adducts, and the corresponding annulation adducts were not observed yet. The moderate yields for 4-oxo-4-arylbutenone and methyleneindolinone as the substrates are produced by the instability of 5*H*-oxazol-4-one in the reactions.

12. Experimental procedure for 5a to 11

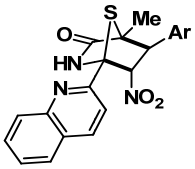


5a: 98% ee

11: 73% yield, 98% ee

The [4+2] annulation adduct **5a** (41.6 mg, 0.1 mmol, 1.0 equiv) was dissolved in MeOH (1.0 mL) and stirred at 0 °C. Then HCl (12 *N*, 0.834 mL, 10.0 mmol, 100.0 equiv) was added. The reaction mixture was stirred at room temperature until the reaction completed (3.0 hours). Evaporation of methanol followed by drying under high vacuo and neutralized by $NaHCO_3$ (aq.) until pH > 7. The mixture was then extracted with EtOAc (3.0 mL x 3), washed with brine, and dried over Na_2SO_4. Concentration was loaded onto a short *silica gel* column, followed by gradient elution with PE/EA (20/1–2/1). Removing the solvent *in vacuo*, afforded products gave the **11** (32.7 mg, 73%).

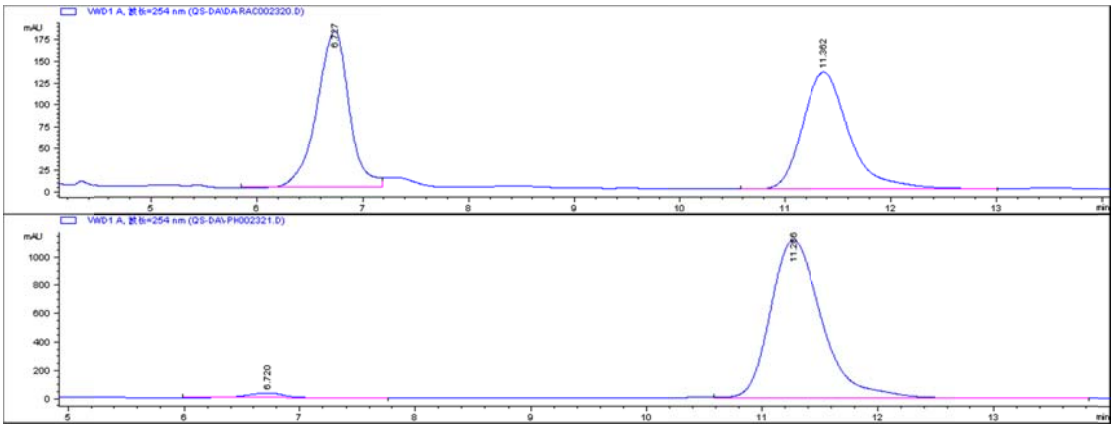
13. Characterization of adducts

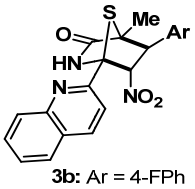


3a: Ar = Ph

White solid, Mp 165.3–166.5 °C; 83% yield; 95% *ee*; $[\alpha]_D^{26}$ –143.0 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.90–7.87 (m, 2H), 7.81–7.73 (m, 2H), 7.68–7.60 (m, 3H), 7.50–7.44 (m, 3H), 6.27 (d, *J* = 4.8 Hz, 1H), 4.04 (d, *J* = 4.8 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.1, 147.0, 138.3, 136.0, 130.6, 129.6, 129.1, 129.0, 128.6, 128.0, 127.9, 127.6, 117.4, 98.6, 76.7, 67.1, 54.8, 13.8; HRMS (ESI) m/z 392.1074 ($M+H^+$), calc. for $C_{21}H_{18}N_3O_3S$ 392.1069.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.7min (minor) and 11.3 min (major).

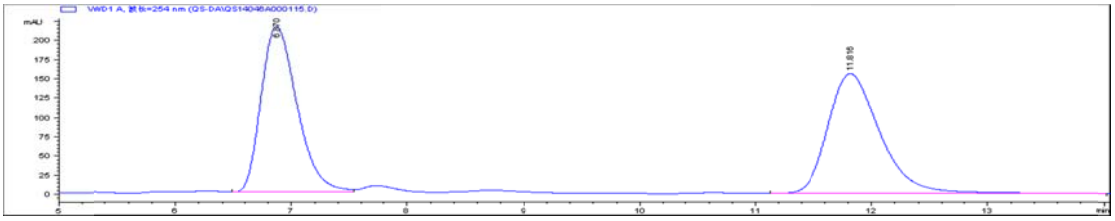


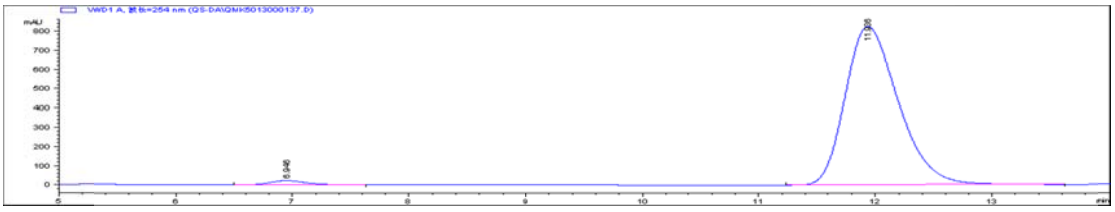


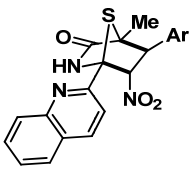
3b: Ar = 4-FPh

White solid, Mp 163.0–165.0 °C; 78% yield; 97% *ee*; $[\alpha]_D^{26}$ –296.6 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.90–7.87 (m, 2H), 7.81–7.72 (m, 2H), 7.68–7.61 (m, 3H), 7.16 (t, *J* = 8.6 Hz, 2H), 6.23 (d, *J* = 4.8 Hz, 1H), 4.01 (d, *J* = 4.8 Hz, 1H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 150.0, 147.1, 138.3, 131.9, 130.6, 130.3, 130.2, 129.6, 128.0, 127.7, 117.4, 116.2, 115.9, 98.6, 76.7, 66.9, 54.3, 13.8; HRMS (ESI) m/z 410.0972 ($M+H^+$), calc. for $C_{21}H_{17}FN_3O_3S$ 410.0975.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.9 min (minor) and 11.9 min (major).



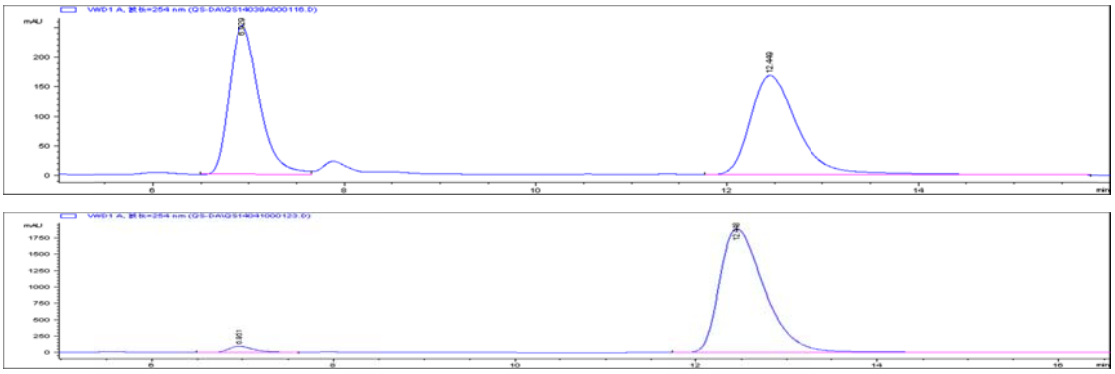


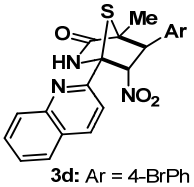


3c: Ar = 4-ClPh

White solid, Mp 97.5–98.6 °C; 89% yield; 94% *ee*; $[\alpha]_D^{18}$ –298.7 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.90–7.85 (m, 2H), 7.81–7.72 (m, 2H), 7.66–7.61 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.26 (s, 2H), 6.22 (d, *J* = 4.8 Hz, 1H), 4.00 (d, *J* = 4.8 Hz, 1H), 1.29 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 150.0, 147.1, 138.3, 135.0, 134.6, 130.6, 129.8, 129.6, 129.3, 128.0, 127.9, 127.7, 117.4, 98.3, 76.8, 66.8, 54.4, 13.8; HRMS (ESI) m/z 426.0683 ($M+H^+$), calc. for $C_{21}H_{17}ClN_3O_3S$ 426.0679.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.0 min (minor) and 12.4 min (major).

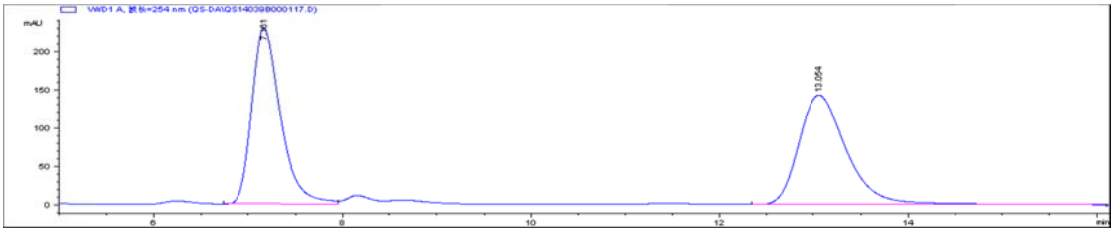


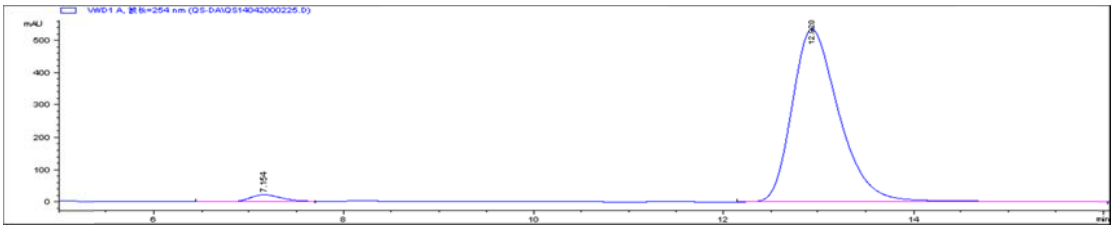


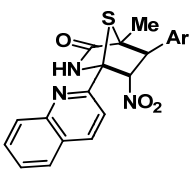
3d: Ar = 4-BrPh

White solid, Mp 95.4–97.1 °C; 84% yield; 96% *ee*; $[\alpha]_D^{21}$ –254.6 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.81–7.72 (m, 2H), 7.66–7.54 (m, 5H), 6.22 (d, *J* = 4.8 Hz, 1H), 3.98 (d, *J* = 4.8 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.0, 147.1, 138.3, 135.1, 132.2, 130.6, 130.2, 129.6, 128.0, 127.9, 127.6, 123.1, 117.4, 98.1, 76.8, 66.7, 54.5, 13.8; HRMS (ESI) m/z 470.0175 ($M+H^+$), calc. for $C_{21}H_{17}BrN_3O_3S$ 470.0174.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.2 min (minor) and 12.9 min (major).



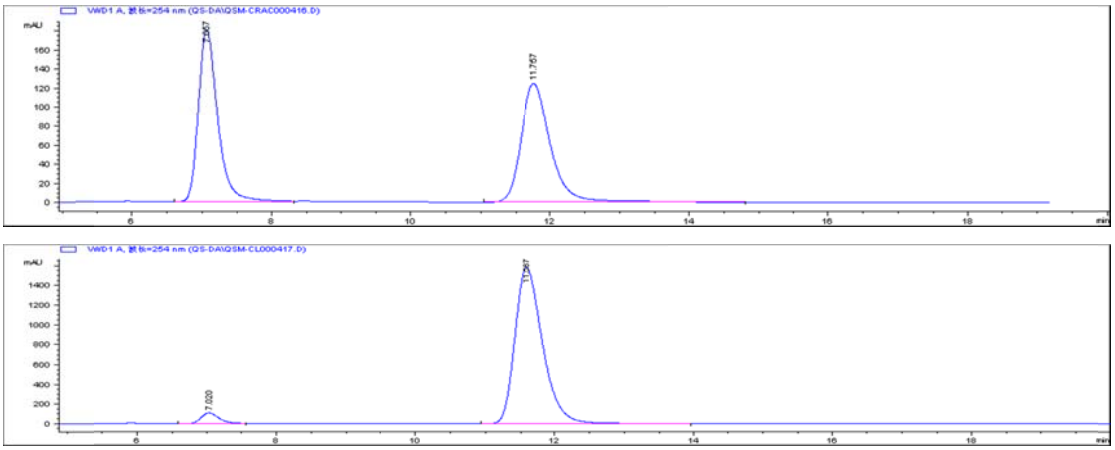


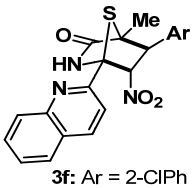


3e: Ar = 3-ClPh

White solid, Mp 163.2–165.8 °C; 85% yield; 92% *ee*; $[\alpha]_D^{26}$ –464.2 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.81–7.73 (m, 3H), 7.66–7.61 (m, 1H), 7.53 –7.51 (m, 1H), 7.45–7.37 (m, 2H), 6.23 (d, *J* = 4.8 Hz, 1H), 4.00 (d, *J* = 4.8 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 150.0, 147.1, 138.3, 138.2, 135.0, 130.6, 130.3, 129.6, 129.2, 128.2, 128.0, 127.9, 127.7, 127.2, 117.4, 98.3, 76.8, 66.8, 54.6, 13.8; HRMS (ESI) m/z 426.0684 ($M+H^+$), calc. for $C_{21}H_{17}ClN_3O_3S$ 426.0679.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.0 min (minor) and 11.6 min (major).

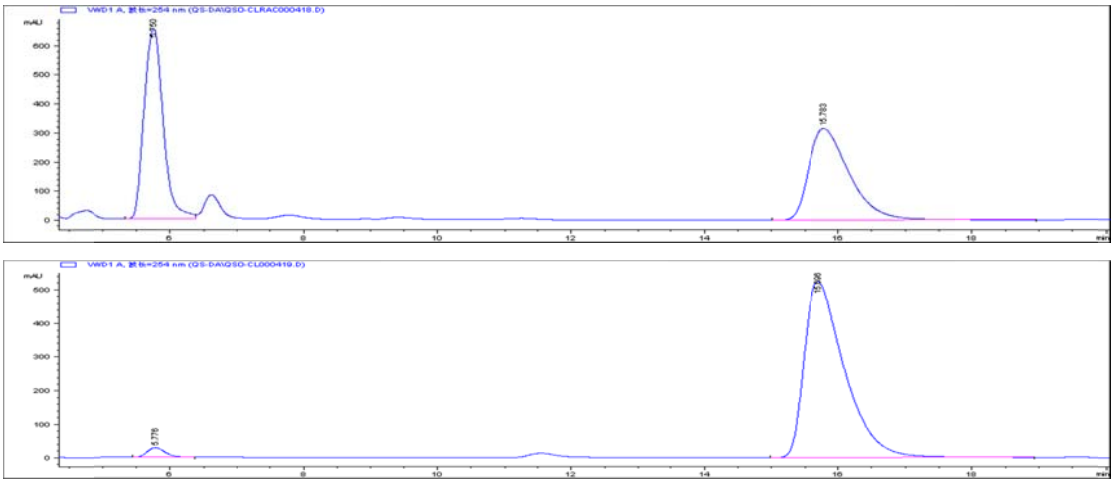


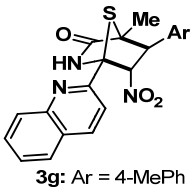


3f: Ar = 2-ClPh

White solid, Mp 184.0–185.6 °C; 82% yield; 95% *ee*; $[\alpha]_D^{26}$ –306.2 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.2 Hz, 1H), 8.10 (dd, *J* = 16.6, 8.2 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 16.6, 7.6 Hz, 3H), 7.68 – 7.59 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.41 (dt, *J* = 16.6, 7.6 Hz, 2H), 6.28 (d, *J* = 4.8 Hz, 1H), 4.89 (d, *J* = 4.8 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 150.1, 147.2, 138.3, 135.9, 133.9, 130.7, 130.2, 130.0, 129.7, 128.1, 128.0, 127.8, 127.7, 127.6, 117.4, 77.0, 98.1, 67.5, 49.7, 12.9; HRMS (ESI) m/z 426.0675 ($M+H^+$), calc. for $C_{21}H_{17}ClN_3O_3S$ 426.0679.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.8 min (minor) and 15.7 min (major).

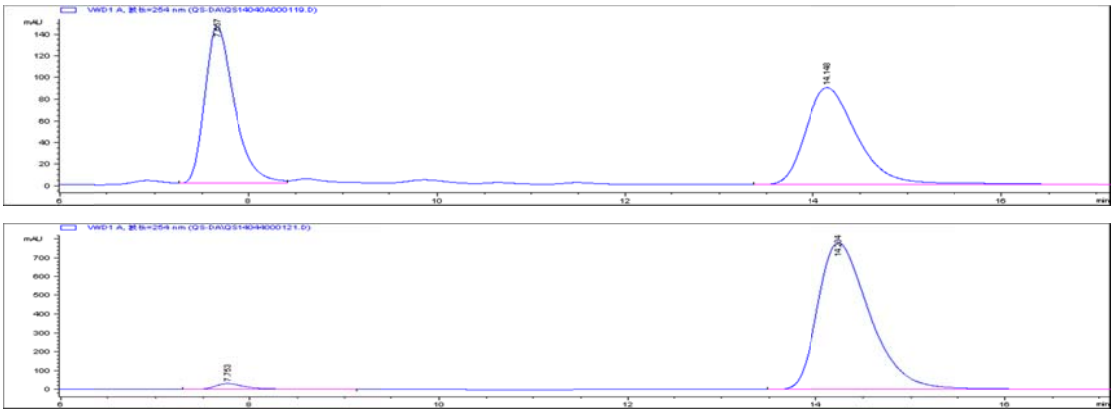


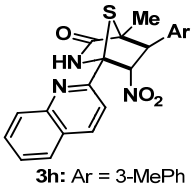


3g: Ar = 4-MePh

White solid, Mp 160.7–161.9 °C; 72% yield; 95% *ee*; $[\alpha]_D^{26}$ –120.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.89–7.77 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.65–7.60 (m, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 6.24 (d, *J* = 4.8 Hz, 1H), 4.00 (d, *J* = 4.8 Hz, 1H), 2.40 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.2, 147.1, 138.8, 138.2, 133.0, 130.6, 129.7, 129.6, 128.4, 128.0, 127.9, 127.7, 117.4, 98.8, 76.7, 67.1, 54.6, 21.2, 13.8; HRMS (ESI) m/z 406.1222 ($M+H^+$), calc. for $C_{22}H_{20}N_3O_3S$ 406.1225.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.8 min (minor) and 14.2 min (major).

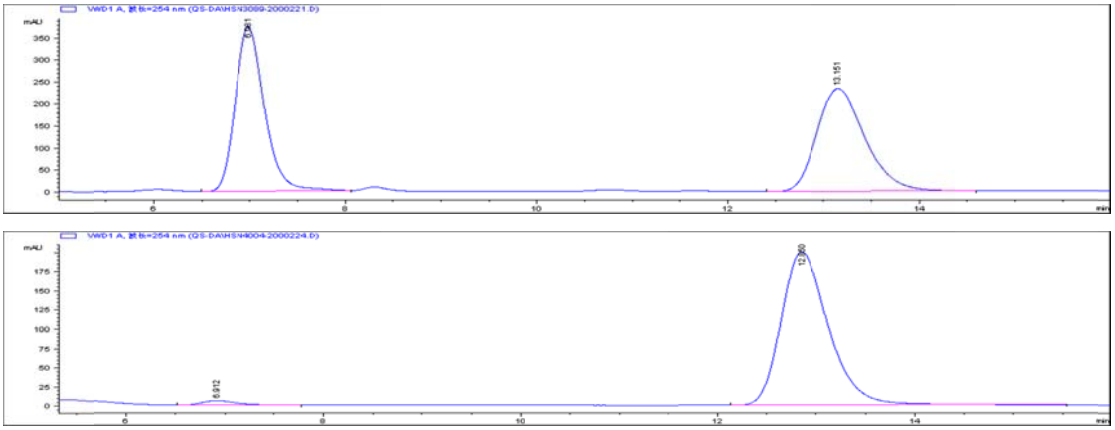


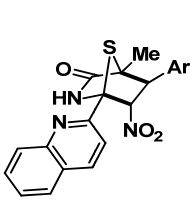


3h: Ar = 3-MePh

White solid, Mp 169.6–170.8 °C; 76% yield; 96% *ee*; $[\alpha]_D^{26}$ –218.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 16.3, 7.8 Hz, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 6.24 (d, *J* = 4.8 Hz, 1H), 3.99 (d, *J* = 4.8 Hz, 1H), 2.43 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.2, 147.1, 138.8, 138.2, 135.9, 130.6, 129.7, 129.6, 129.4, 129.0, 128.0, 127.9, 127.6, 125.5, 117.5, 98.8, 76.7, 67.1, 54.9, 21.6, 13.8; HRMS (ESI) m/z 406.1223 ($M+H^+$), calc. for $C_{22}H_{20}N_3O_3S$ 406.1225.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.9 min (minor) and 12.9 min (major).

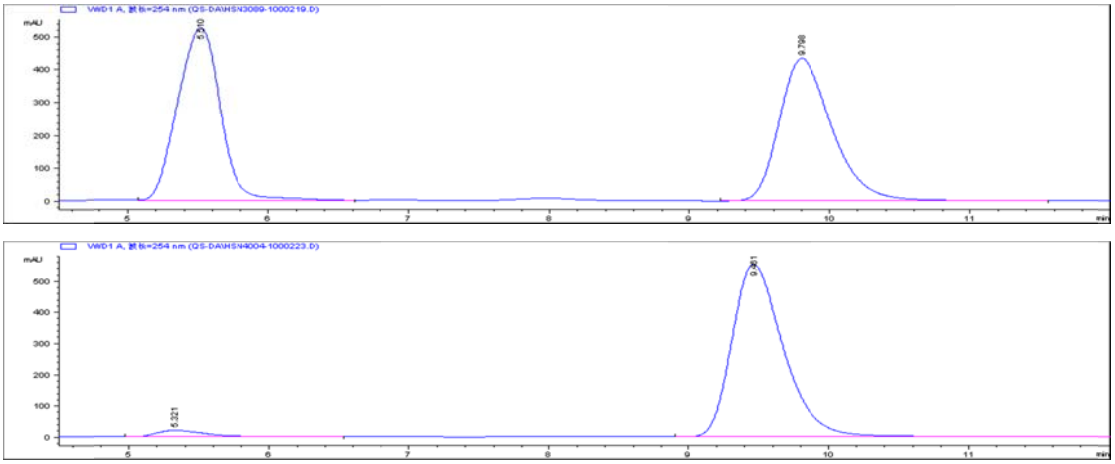


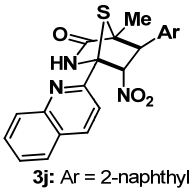


3i: Ar = 2-MePh

White solid, Mp 182.2–183.5 °C; 82% yield; 93% *ee*; $[\alpha]_D^{26}$ –34.6 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.3 Hz, 1H), 8.11–8.06 (m, 2H), 7.96 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.80–7.73 (m, 2H), 7.65–7.60 (m, 1H), 7.38–7.29 (m, 3H), 6.24 (d, *J* = 4.9 Hz, 1H), 4.49 (d, *J* = 4.9 Hz, 1H), 2.40 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 150.2, 147.1, 138.2, 137.8, 134.6, 131.0, 130.6, 129.6, 128.5, 128.0, 127.8, 127.6, 126.9, 125.9, 117.4, 99.6, 76.8, 67.4, 48.9, 20.4, 13.0; HRMS (ESI) m/z 406.1229 ($M+H^+$), calc. for $C_{22}H_{20}N_3O_3S$ 406.1225.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.3 min (minor) and 9.5 min (major).



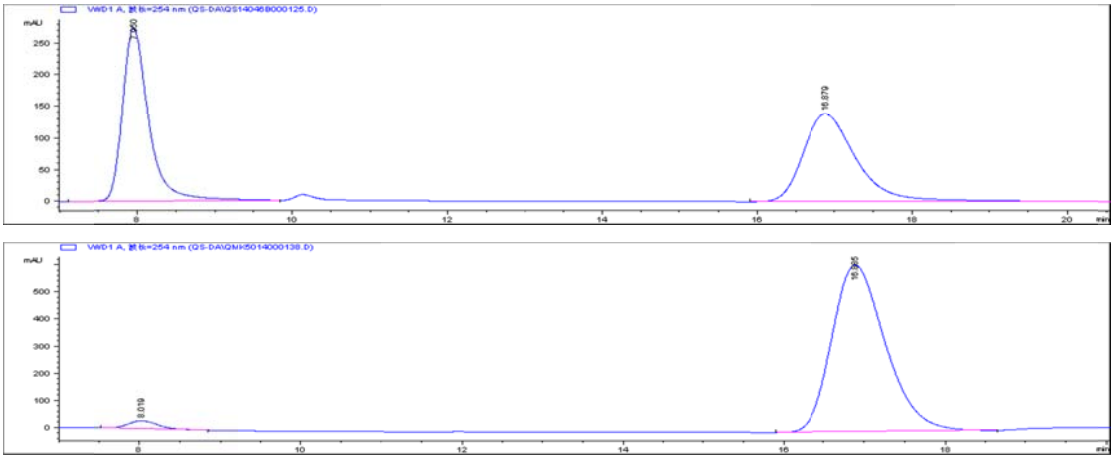


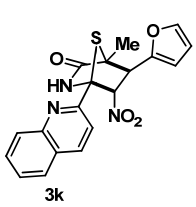
3j: Ar = 2-naphthyl

White solid, Mp 181.4–183.0 °C; 88% yield; 95% *ee*; $[\alpha]_D^{26}$ –384.7 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.1 Hz, 1H), 8.09 (d, *J* = 9.7 Hz, 2H), 7.97–7.85 (m, 6H), 7.79 (t, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.61–7.54 (m, 2H), 6.40 (d, *J* = 4.7 Hz, 1H), 4.20 (d, *J* = 4.7 Hz, 1H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 150.2, 147.1, 138.3, 133.4, 133.3, 130.6, 129.6, 129.0, 128.4,

128.1, 127.9, 127.7, 126.7, 125.5, 117.5, 98.5, 76.8, 67.1, 55.2, 13.9; HRMS (ESI) m/z 442.1231 ($M+H^+$), calc. for $C_{25}H_{20}N_3O_3S$ 442.1225.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.0 min (minor) and 16.9 min (major).

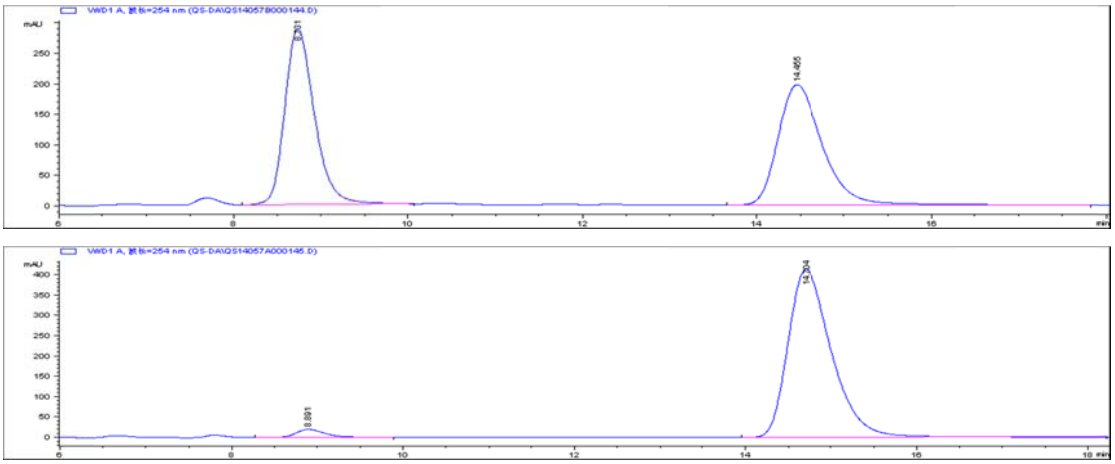


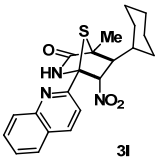


3k

White solid, Mp 156.2–157.9 °C; 76% yield; 94% *ee*; $[\alpha]_D^{26}$ –251.7 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 1H), 6.51 – 6.44 (m, 1H), 6.27 (d, *J* = 4.6 Hz, 1H), 4.27 (d, *J* = 4.6 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 149.9, 149.2, 147.0, 143.4, 138.3, 130.6, 129.6, 128.0, 127.9, 127.6, 117.3, 110.8, 109.9, 96.8, 76.8, 66.4, 49.3, 13.4; HRMS (ESI) m/z 382.0864 ($M+H^+$), calc. for $C_{19}H_{16}N_3O_4S$ 382.0862.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.9 min (minor) and 14.7 min (major).

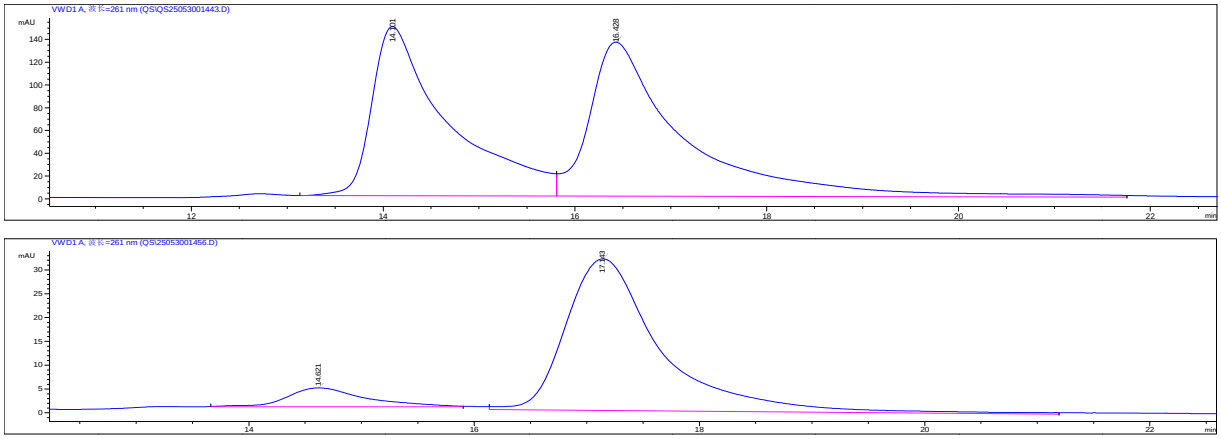


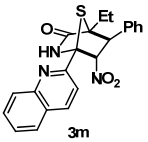


3l

White solid, Mp 94.0–95.6 °C; 41% yield; 82% *ee*; $[\alpha]_D^{26}$ –136.7 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 5.85 (d, *J* = 4.3 Hz, 1H), 2.97 (s, 1H), 2.09–1.78 (m, 5H), 1.70 (s, 3H), 1.37–1.19 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 149.9, 147.0, 138.2, 130.6, 129.6, 128.0, 127.8, 127.6, 117.3, 95.0, 64.5, 52.9, 37.8, 32.0, 28.5, 26.5, 26.2, 26.0, 13.3; HRMS (ESI) m/z 398.1536 ($M+H^+$), calc. for $C_{21}H_{24}N_3O_3S$ 398.1538.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.8 min (minor) and 16.5 min (major).

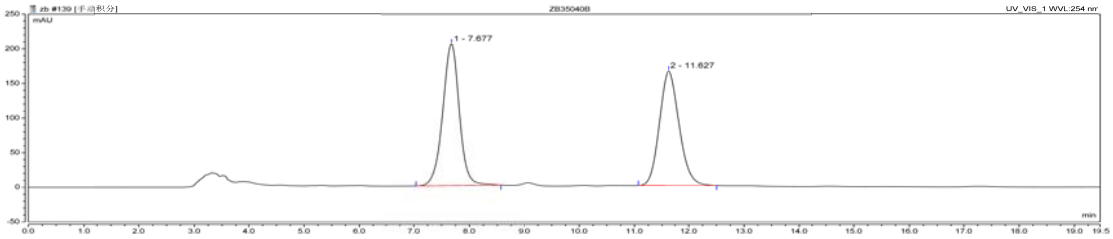


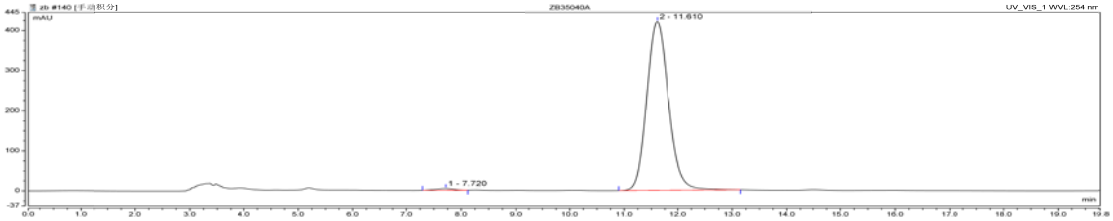


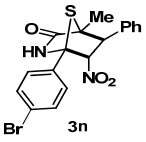
3m

Green solid, Mp 131.8–132.9 °C; 55% yield; 98% *ee*; $[\alpha]_D^{26}$ –201.9 (*c* 1.98, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.90–7.86 (m, 2H), 7.78–7.74 (m, 2H), 7.67–7.59 (m, 3H), 7.45-7.43 (m, 3H), 6.30 (d, *J* = 4.8 Hz, 1H), 4.03 (d, *J* = 4.8 Hz, 1H), 2.08–1.96 (m, 1H), 1.33–1.21 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 150.5, 147.1, 138.2, 136.3, 130.5, 129.6, 129.0, 128.8, 128.0, 127.8, 127.6, 117.6, 98.6, 76.0, 73.6, 55.2, 21.4, 10.9; HRMS (ESI) m/z 406.1228 ($M+H^+$), calc. for $C_{22}H_{20}N_3O_3S$ 406.1225.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.7min (minor) and 11.6 min (major).

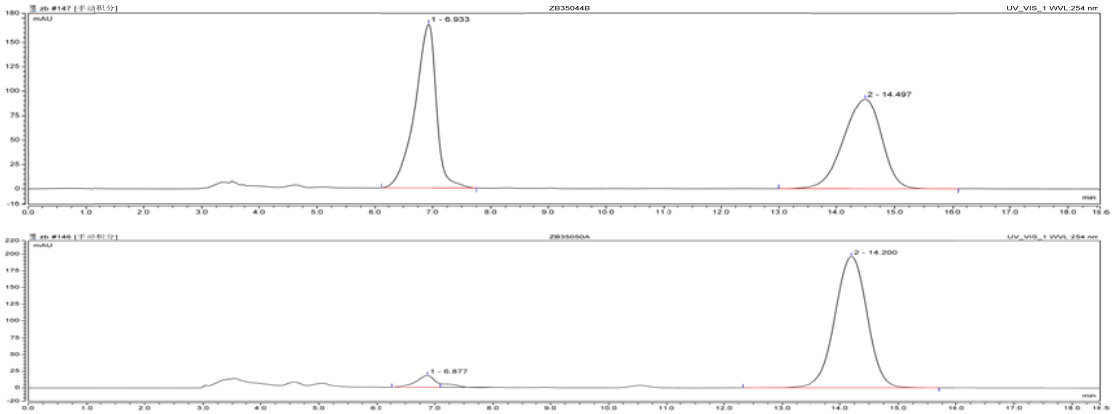


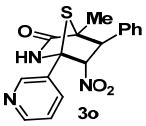




White solid, Mp 165.3–171.9 °C; 45% yield; 90% *ee*; $[\alpha]_D^{26}$ –181.8 (*c* 1.48, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.64–7.57 (m, 4H), 7.50–7.49 (m, 2H), 7.43–7.41 (m, 3H), 5.98 (d, *J* = 4.7 Hz, 1H), 3.90 (d, *J* = 4.7 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 135.6, 132.6, 130.3, 129.1, 128.5, 127.4, 124.3, 98.5, 76.3, 66.1, 56.1, 13.4; HRMS (ESI) m/z 419.0064 ($M+H^+$), calc. for $C_{18}H_{16}BrN_2O_3S$ 419.0065.

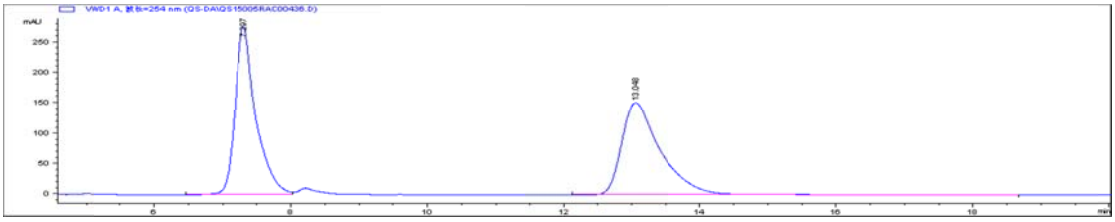
The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.9 min (minor) and 14.2 min (major).

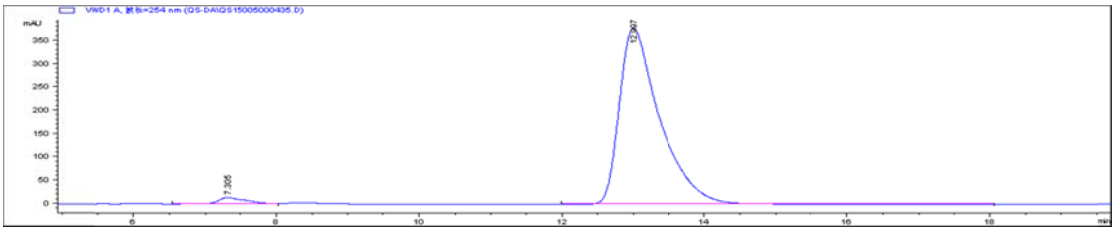


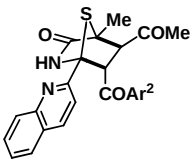


White solid, Mp 136.9–138.1 °C; 76% yield; 95% *ee*; $[\alpha]_D^{27}$ –569.3 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.62–8.61 (m, 1H), 7.89–7.83 (m, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.64–7.61 (m, 2H), 7.45–7.35 (m, 4H), 6.21 (d, *J* = 4.8 Hz, 1H), 3.91 (d, *J* = 4.8 Hz, 1H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4), 150.8, 149.6, 137.7, 136.0, 129.0, 128.9, 128.6, 124.5, 120.8, 98.2, 76.6, 66.6, 55.3, 13.7; HRMS (ESI) m/z 342.0911 ($M+H^+$), calc. for $C_{17}H_{16}N_3O_3S$ 342.0912.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.3 min (minor) and 13.0 min (major).



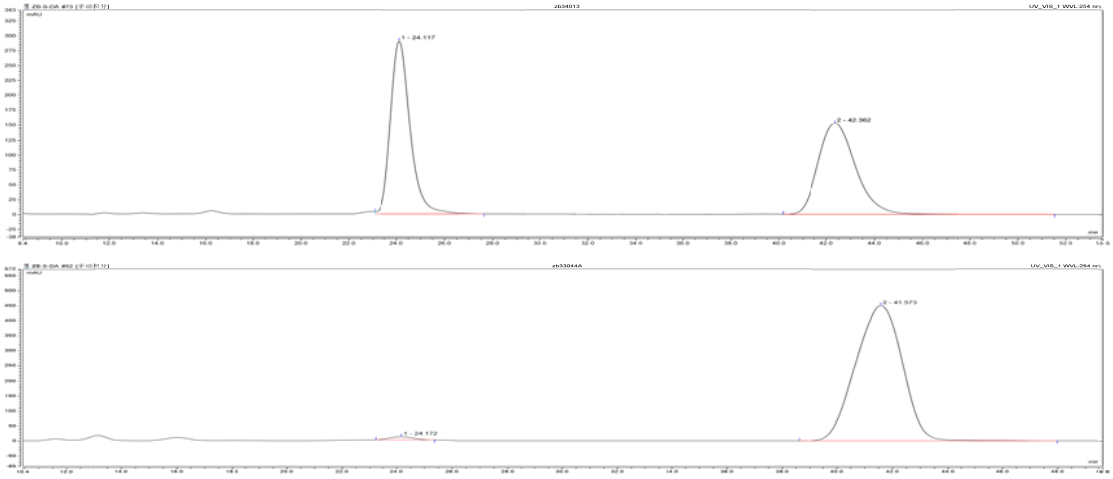


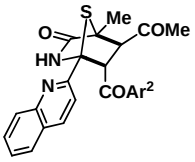


6a: Ar^2 = Ph

White solid, Mp 164.9–165.8 °C; 86% yield; 98% *ee*; $[\alpha]_D^{24}$ –169.6 (*c* 2.37, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.68–7.63 (m, 3H), 7.61–7.56 (m, 2H), 7.48 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 5.70 (d, *J* = 5.4 Hz, 1H), 3.56 (d, *J* = 5.4 Hz, 1H), 2.28 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.9, 198.2, 176.5, 152.2, 146.7, 137.6, 136.9, 133.1, 129.9, 129.2, 128.4, 128.0, 127.5, 127.3, 127.2, 118.2, 79.6, 66.6, 62.0, 58.4, 32.8, 14.4; HRMS (ESI) m/z 417.1277 ($M+H^+$), calc. for $C_{24}H_{21}N_2O_3S$ 417.1273.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.2 min (minor) and 41.6 min (major).

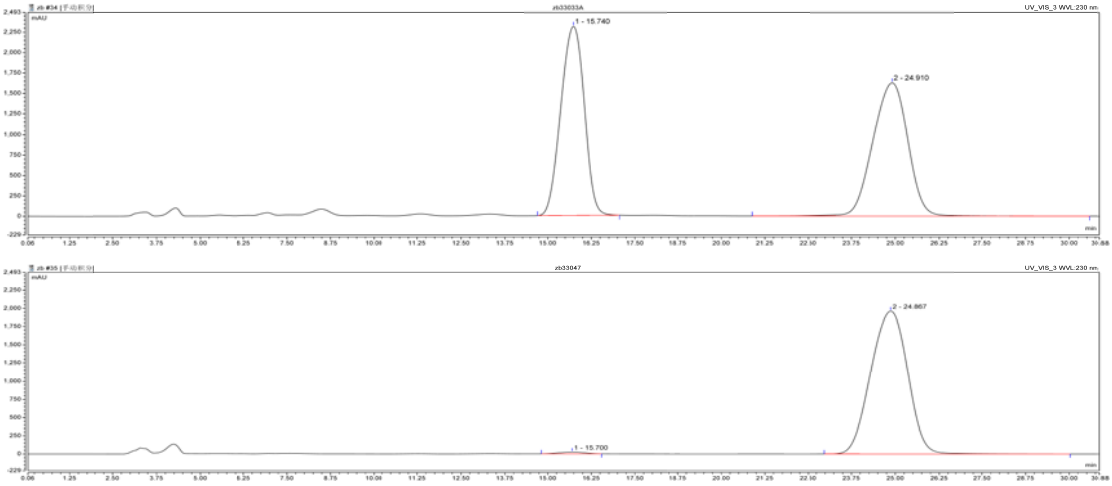


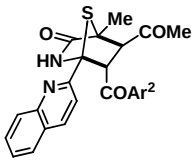


6b: Ar^2 = 4-CF_3Ph

White solid, Mp 181.7–183.6 °C; 90% yield; 98% *ee*; $[\alpha]_D^{25}$ –144.8 (*c* 4.22, ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.71–7.67 (m, 4H), 7.60–7.53 (m, 3H), 7.51–7.46 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.65 (d, *J* = 5.2 Hz, 1H), 3.67 (d, *J* = 5.2 Hz, 1H), 2.32 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 197.2, 176.2, 151.7, 146.5, 139.8, 137.8, 134.2, 133.8, 130.2, 128.8, 128.2, 127.5, 127.4, 125.2, 125.1, 125.0, 121.3, 118.2, 79.7, 66.7, 62.4, 58.2, 32.6, 14.5; HRMS (ESI) m/z 485.1149 ($M+H^+$), calc. for $C_{25}H_{20}F_3N_2O_3S$ 485.1147.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 15.7 min (minor) 24.9 min (major).

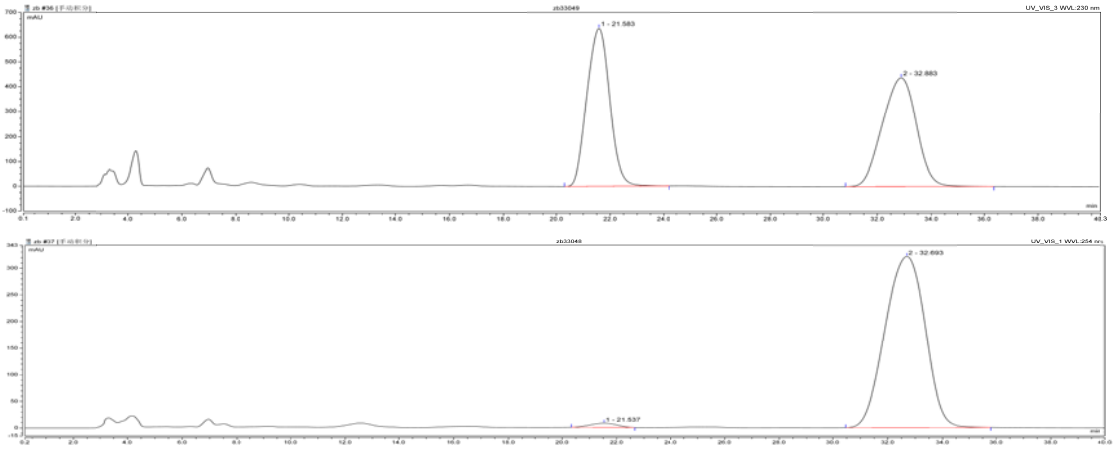


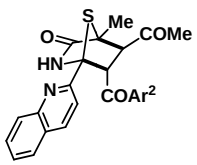


6c: Ar^2 = 4-ClPh

Pale yellow solid, Mp 143.2–145.0 °C; 80% yield; 97% *ee*; $[\alpha]_D^{26}$ –172.8 (*c* 2.92, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 1H), 7.73 (t, *J* = 8.7 Hz, 2H), 7.66–7.58 (m, 4H), 7.52–7.48 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 5.64 (d, *J* = 5.3 Hz, 1H), 3.56 (d, *J* = 5.3 Hz, 1H), 2.30 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 197.0, 176.4, 152.0, 146.7, 139.7, 137.7, 135.3, 130.1, 129.4, 129.1, 128.6, 127.6, 127.4, 118.3, 79.8, 66.7, 61.6, 58.5, 32.7, 14.5; HRMS (ESI) m/z 451.0881 ($M+H^+$), calc. for $C_{24}H_{20}ClN_2O_3S$ 451.0883.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.5 min (minor) and 32.7 min (major).

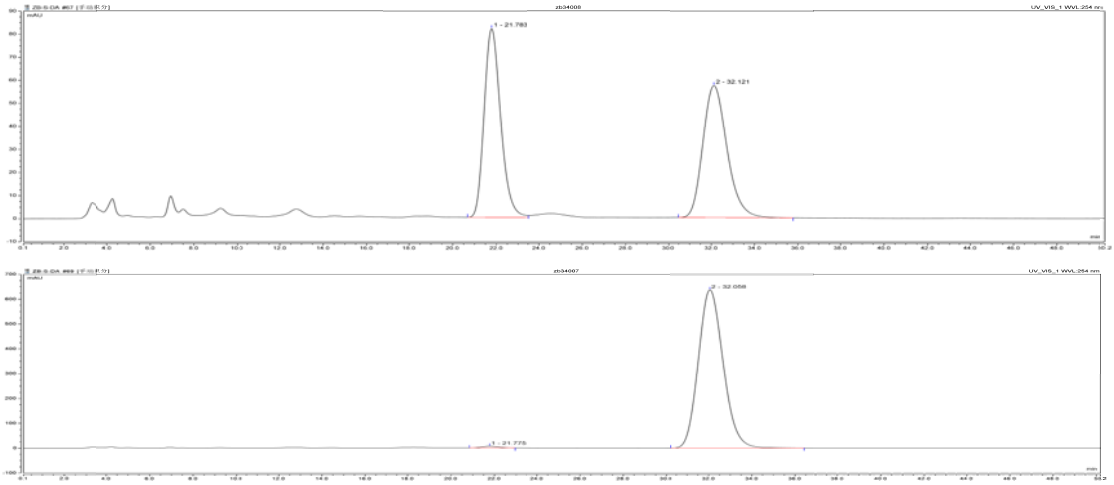


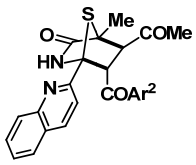


6d: Ar^2 = 4-BrPh

White solid, Mp 175.2–176.5 °C; 91% yield; 99% *ee*; $[\alpha]_D^{26}$ –167.5 (*c* 1.26, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.67–7.60 (m, 2H), 7.54–7.49 (m, 3H), 7.42 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.62 (d, *J* = 5.3 Hz, 1H), 3.57 (d, *J* = 5.3 Hz, 1H), 2.31 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 197.2, 176.4, 151.9, 146.7, 137.8, 135.7, 131.7, 130.2, 129.5, 129.1, 128.4, 127.6, 127.5, 127.4, 118.2, 79.7, 66.7, 61.7, 58.4, 32.8, 14.5; HRMS (ESI) m/z 495.0381 ($M+H^+$), calc. for $C_{24}H_{20}BrN_2O_3S$ 495.0378.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.8min (minor) and 32.0 min (major).

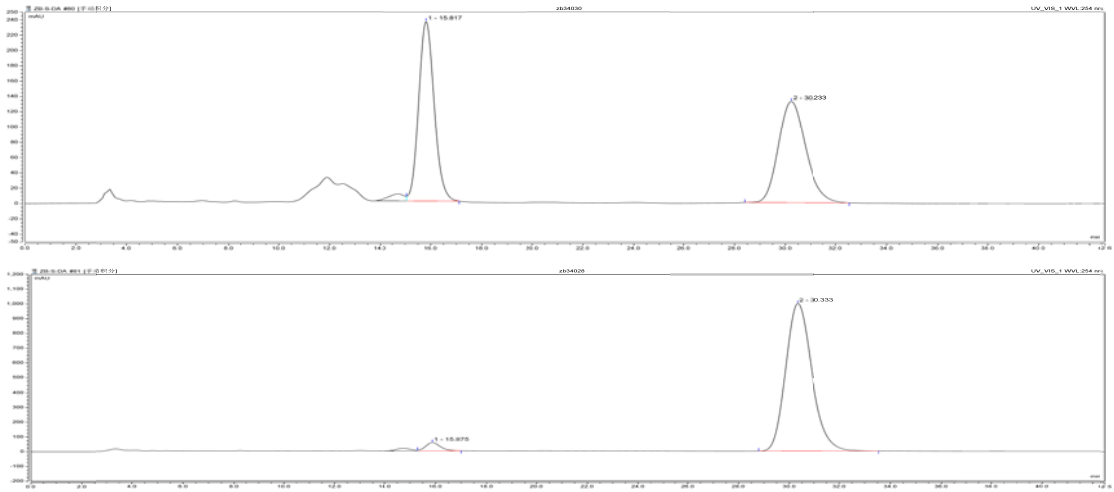


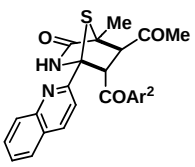


6e: Ar^2 = 3,4-Cl_2Ph

White solid, Mp 176.8–178.7 °C; 95% yield; 94% *ee*; $[\alpha]_D^{25}$ –191.5 (*c* 4.46, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.76–7.68 (m, 3H), 7.62–7.58 (m, 3H), 7.53–7.48 (m, 1H), 7.44 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 5.52 (d, *J* = 5.2 Hz, 1H), 3.69 (d, *J* = 5.2 Hz, 1H), 2.34 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 195.6, 176.2, 151.7, 146.5, 137.8, 137.5, 136.4, 132.8, 130.3, 130.2, 129.8, 128.9, 127.6, 127.5, 127.4, 127.0, 118.2, 79.7, 66.7, 62.2, 58.1, 32.6, 14.5; HRMS (ESI) m/z 485.0494 ($M+H^+$), calc. for $C_{24}H_{19}Cl_2N_2O_3S$ 485.0493.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.9min (minor) and 30.3 min (major).



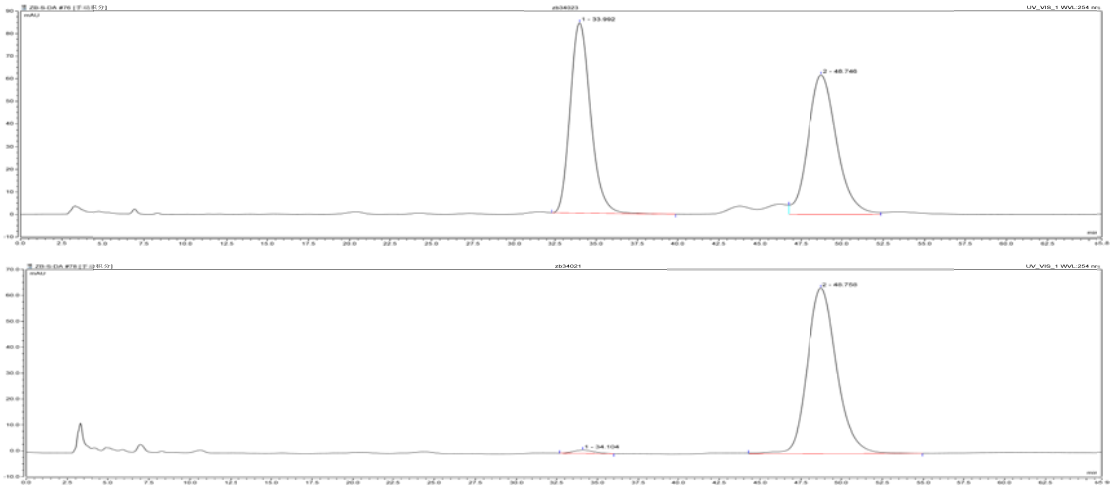


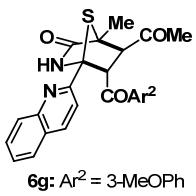
6f: Ar^2 = 4-MeOPh

White solid, Mp 148.5–150.0 °C; 87% yield; 97% *ee*; $[\alpha]_{25D}$ –190.5 (*c* 3.78, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 1H), 7.73 (dd, *J* = 8.7, 5.3 Hz, 3H), 7.65 (t, *J* = 5.3 Hz, 2H), 7.67–7.55 (m, 2H), 7.51–7.46 (m, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 5.64 (d, *J* = 5.4 Hz, 1H), 3.72 (s, 3H), 3.54 (d, *J* = 5.4 Hz, 1H), 2.29 (s,

3H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.1, 196.3, 176.6, 163.6, 152.4, 146.8, 137.5, 130.4, 129.9, 129.8, 129.4, 127.6, 127.3, 127.2, , 118.2, 113.6, 79.7, 66.6, 61.5, 58.7, 55.4, 32.8, 14.4; HRMS (ESI) m/z 447.1377 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_4S$ 447.1379.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 34.1 min (minor) and 48.8 min (major).

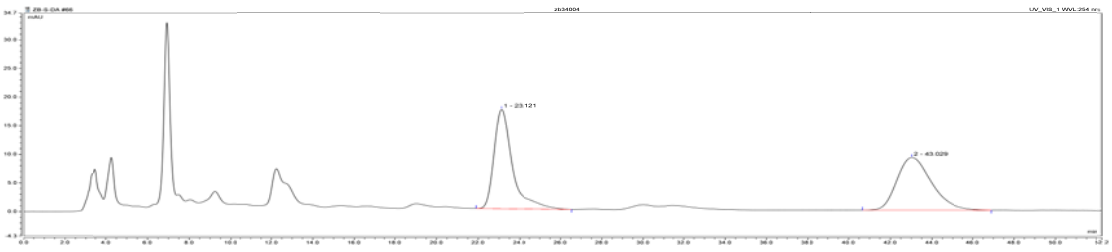


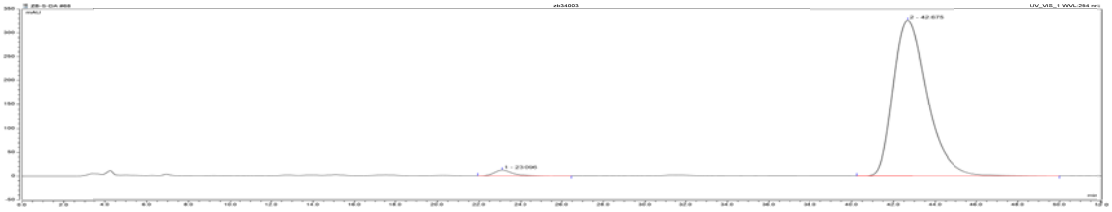


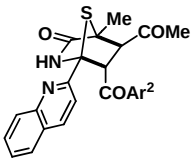
6g: Ar^2 = 3-MeOPh

White solid, Mp 149.1–150.8 °C; 82% yield; 96% *ee*; $[\alpha]_D^{24}$ –192.4 (*c* 1.47, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 8.3 Hz, 3H), 7.62 (dd, *J* = 11.2, 4.6 Hz, 1H), 7.53–7.47 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.14 (dt, *J* = 11.2, 4.6 Hz, 2H), 6.89–6.86 (m, 1H), 5.65 (d, *J* = 5.4 Hz, 1H), 3.72 (s, 3H), 3.55 (d, *J* = 5.4 Hz, 1H), 2.30 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.9, 197.9, 176.4, 159.5, 152.1, 146.8, 138.2, 137.6, 130.0, 129.4, 129.3, 127.6, 127.4, 127.3, 120.6, 119.9, 118.2, 112.0, 79.5, 66.6, 62.5, 58.4, 55.34, 32.9, 14.4; HRMS (ESI) m/z 447.1381 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_4S$ 447.1379.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 23.1 min (minor) and 42.7 min (major).



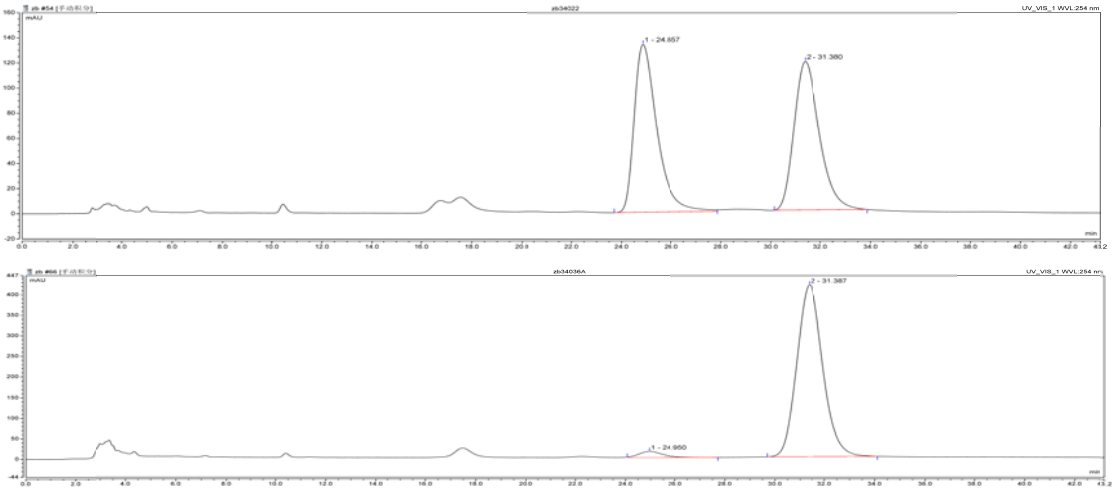


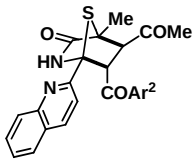


6h: Ar^2 = 2-MeOPh

Weak yellow solid, Mp 132.1–133.8 °C; 64% yield; 94% *ee*; $[\alpha]_D^{26}$ –198.8 (*c* 2.28, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.70–7.62 (m, 3H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.03–6.97 (m, 2H), 6.54–6.46 (m, 2H), 5.52 (d, *J* = 5.2 Hz, 1H), 3.80 (d, *J* = 5.2 Hz, 1H), 3.72 (s, 3H), 2.32 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.0, 199.3, 176.2, 156.8, 151.9, 146.6, 137.0, 132.8, 129.9, 129.7, 129.3, 128.5, 127.4, 127.3, 127.2, 120.3, 117.6, 110.4, 78.8, 68.5, 66.4, 57.1, 55.0, 32.3, 14.0; HRMS (ESI) m/z 447.1383 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_4S$ 447.1379.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 25.0 min (minor) and 31.4 min (major).

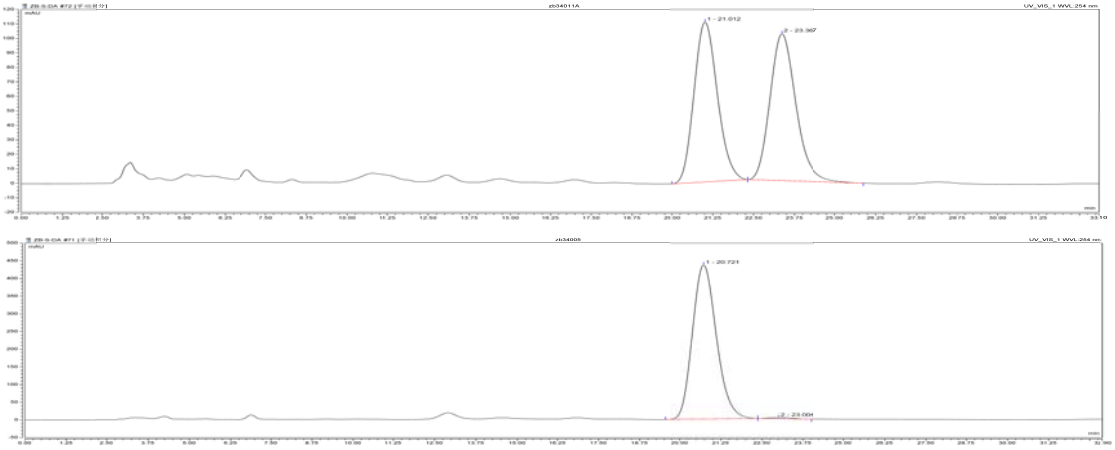


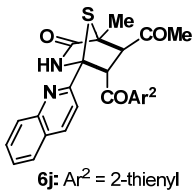


6i: Ar^2 = 2-BrPh

White solid, Mp 151.5–153.0 °C; 60% yield; 99% *ee*; $[\alpha]_D^{25}$ –170.0 (*c* 0.725, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.72 (s, 1H), 7.67–7.62 (m, 2H), 7.54–7.45 (m, 2H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.76–6.65 (m, 2H), 5.44 (d, *J* = 5.1 Hz, 1H), 3.90 (d, *J* = 5.1 Hz, 1H), 2.29 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 198.8, 175.9, 151.4, 146.5, 140.2, 137.5, 132.9, 131.2, 130.2, 129.3, 128.7, 127.5, 127.4, 126.6, 118.6, 117.6, 78.2, 68.2, 66.5, 56.6, 32.6, 14.3; HRMS (ESI) m/z 495.0375 ($M+H^+$), calc. for $C_{24}H_{20}BrN_2O_3S$ 495.0378.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.7 min (major) and 23.0 min (minor).

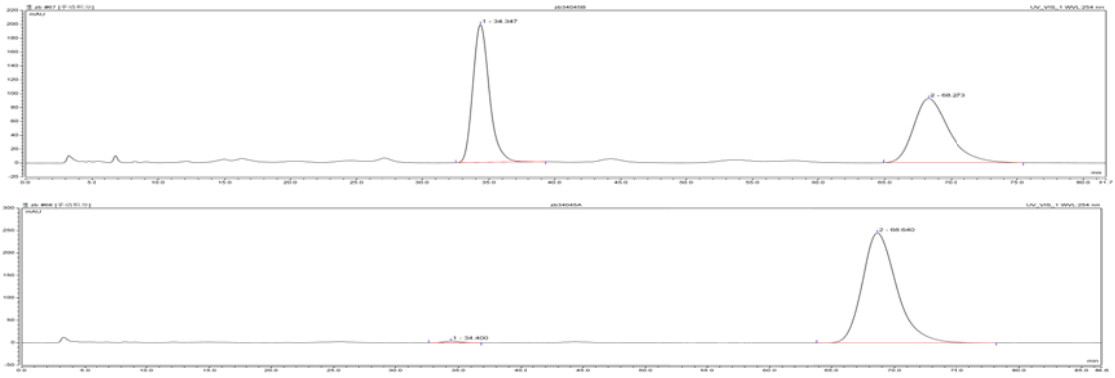


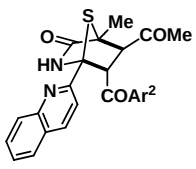


6j: Ar^2 = 2-thienyl

White solid, Mp 179.1–181.0 °C; 98% yield; 99% *ee*; $[\alpha]_D^{26}$ –147.2 (*c* 4.06, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.76–7.73 (m, 3H), 7.65 (s, 1H), 7.63–7.58 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.46–7.44 (m, 2H), 6.89 –6.86 (m, 1H), 5.52 (d, *J* = 5.4 Hz, 1H), 3.65 (d, *J* = 5.4 Hz, 1H), 2.35 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8, 190.2, 176.6, 152.1, 146.8, 144.2, 137.6, 134.7, 132.5, 130.0, 129.3, 128.0, 127.6, 127.4, 127.3, 118.3, 79.8, 66.7, 62.5, 59.0, 32.8, 14.4; HRMS (ESI) m/z 423.0833 ($M+H^+$), calc. for $C_{22}H_{19}N_2O_3S_2$ 423.0837.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 34.4 min (minor) and 68.6 min (major).

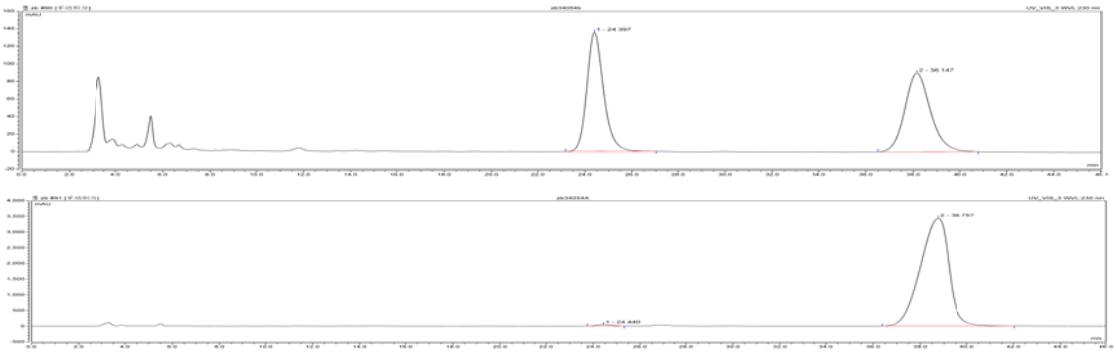


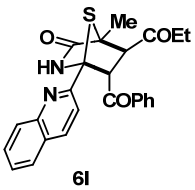


6k: Ar^2 = 2-furyl

White solid, Mp 165.0–166.2 °C; 92% yield; 99% *ee*; $[\alpha]_D^{26}$ –192.1 (*c* 1.36, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.83–7.73 (m, 3H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.27 (s, 1H), 7.03 (d, *J* = 3.6 Hz, 1H), 6.36–6.31 (m, 1H), 5.39 (d, *J* = 5.3 Hz, 1H), 3.64 (d, *J* = 5.3 Hz, 1H), 2.39 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.5, 185.3, 176.3, 152.3, 152.2, 146.9, 146.6, 137.5, 130.0, 129.4, 127.6, 127.4, 127.3, 118.2, 118.1, 112.5, 79.2, 66.3, 62.9, 58.3, 32.2, 14.3; HRMS (ESI) m/z 407.1069 ($M+H^+$), calc. for $C_{22}H_{19}N_2O_4S$ 407.1066.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 24.4 min (minor) and 38.8 min (major).

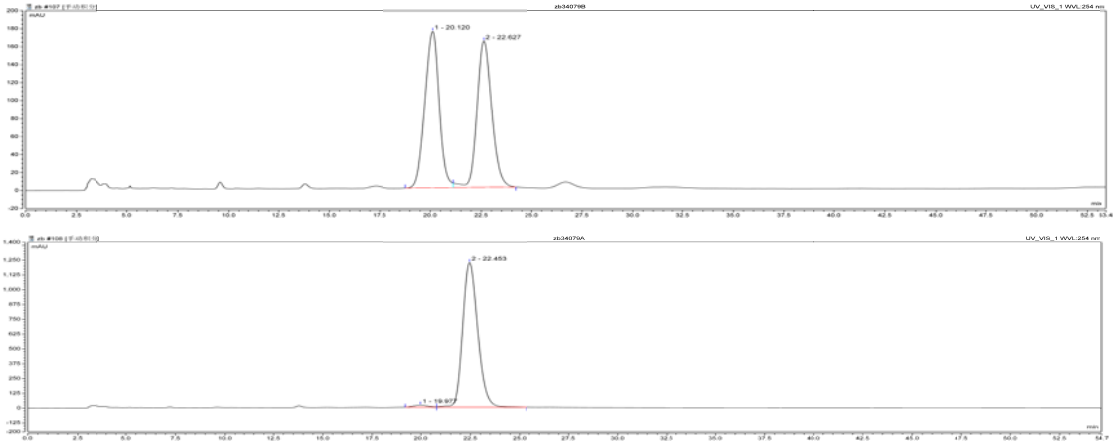


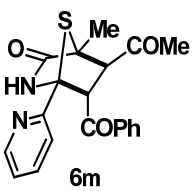


6l

White solid, Mp 158.2–160.0 °C; 90% yield; 97% *ee*; $[\alpha]_D^{20}$ –199.8 (*c* 2.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.74–7.70 (m, 3H), 7.64–7.56 (m, 3H), 7.54–7.46 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 5.69 (d, *J* = 5.5 Hz, 1H), 3.50 (d, *J* = 5.5 Hz, 1H), 2.71–2.60 (m, 1H), 2.35–2.22 (m, 1H), 1.71 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 198.3, 176.6, 152.2, 146.8, 137.6, 136.9, 133.2, 129.9, 129.3, 128.4, 128.0, 127.6, 127.3, 127.2, 118.2, 79.5, 66.8, 62.3, 57.4, 39.2, 14.2, 7.6; HRMS (ESI) m/z 431.1430 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_3S$ 431.1429.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.0 min (minor) and 22.4 min (major).

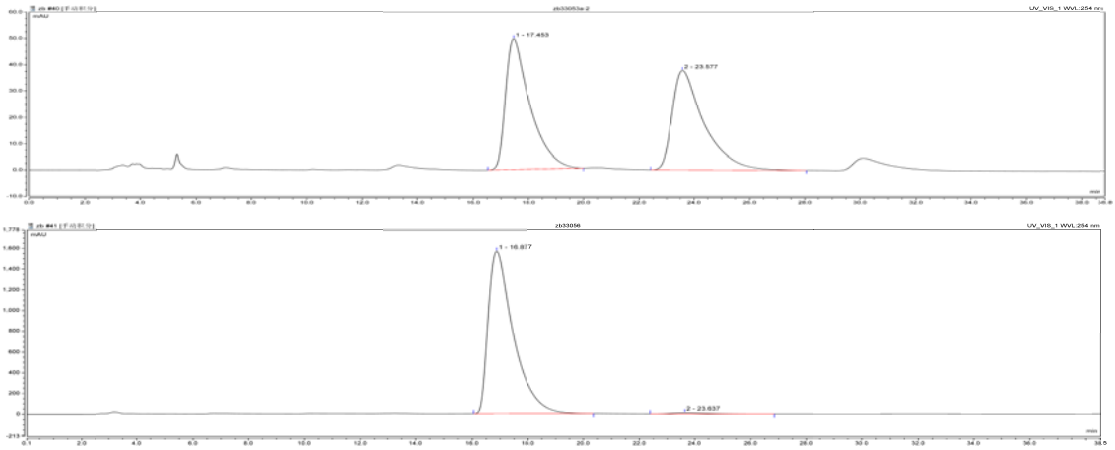


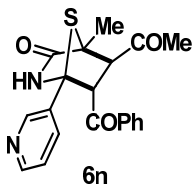


6m

White solid, Mp 138.6–139.1 °C; 87% yield; 98% *ee*; $[\alpha]_D^{23}$ –104.5 (*c* 1.71, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.8 Hz, 1H), 8.54 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.64 – 7.62 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.27 (m, 1H), 5.44 (d, *J* = 5.4 Hz, 1H), 3.35 (d, *J* = 5.4 Hz, 1H), 2.24 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.5, 198.3, 177.1, 150.2, 147.3, 136.0, 134.2, 133.9, 130.2, 129.0, 128.0, 123.5, 76.4, 65.6, 61.6, 59.1, 33.0, 14.2; HRMS (ESI) m/z 367.1119 ($M+H^+$), calc. for $C_{20}H_{19}N_2O_3S$ 367.1116.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 16.9 min (major) and 23.6 min (minor).

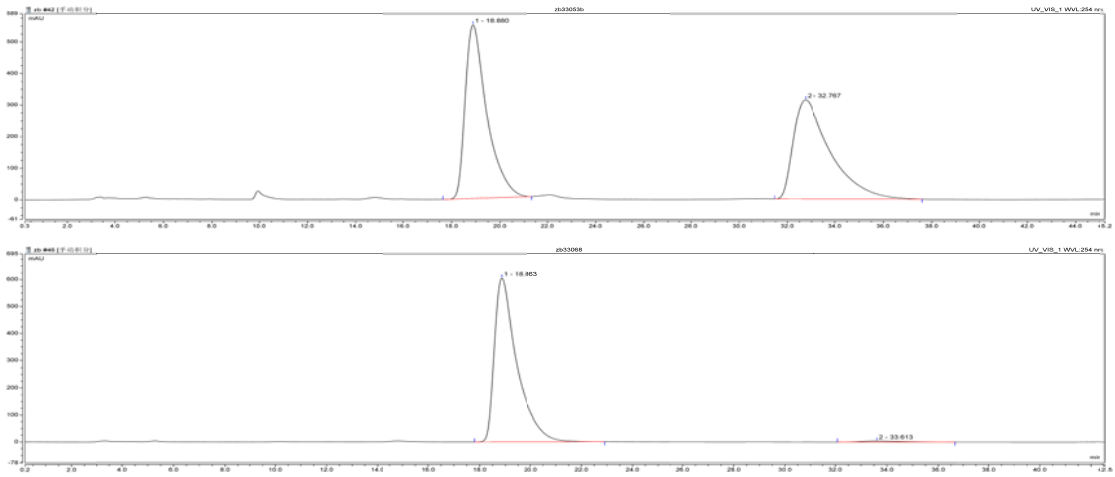


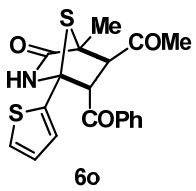


6n

White solid, Mp 120.2–122.1 °C; 86% yield; 98% *ee*; $[\alpha]_D^{24}$ –112.9 (*c* 1.81, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.28–8.27 (m, 1H), 7.67–7.61 (m, 1H), 7.59–7.55 (m, 3H), 7.44–7.38 (m, 1H), 7.28 – 7.23 (m, 3H), 7.10–7.06 (m, 1H), 5.50 (d, *J* = 5.4 Hz, 1H), 3.40 (d, *J* = 5.4 Hz, 1H), 2.19 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.8, 198.0, 176.6, 152.6, 149.1, 137.1, 136.6, 133.5, 128.6, 128.1, 123.7 121.0, 78.9, 66.2, 62.4, 58.6, 32.8, 14.4; HRMS (ESI) m/z 367.1112 ($M+H^+$), calc. for $C_{20}H_{19}N_2O_3S$ 367.1116.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.9 min (major) and 33.6 min (minor).

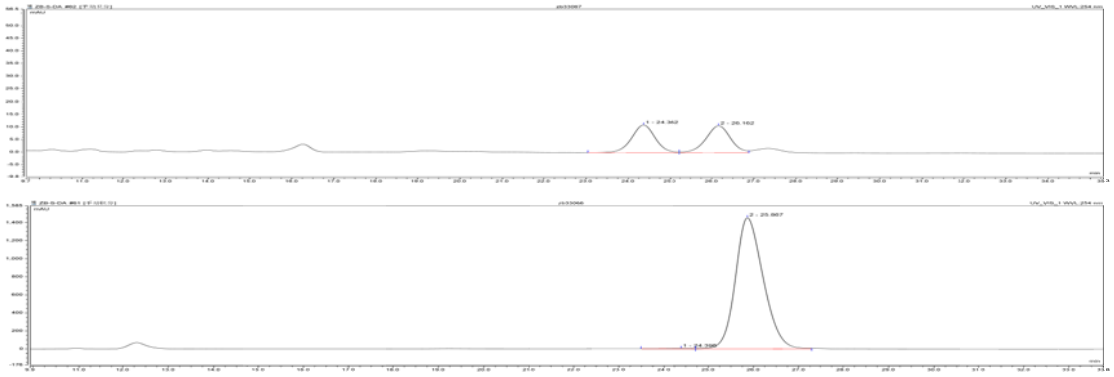


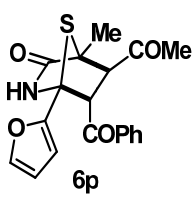


6o

White solid, Mp 134.4–135.6 °C; 70% yield; 99% *ee*; $[\alpha]_D^{25}$ –99.7 (*c* 0.48, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.28 (dd, *J* = 5.1, 2.4 Hz, 1H), 7.11–7.10 (m, 1H), 6.98 (s, 1H), 6.90 (dd, *J* = 5.1, 2.4 Hz, 1H), 5.43 (d, *J* = 5.5 Hz, 1H), 3.26 (d, *J* = 5.5 Hz, 1H), 2.21 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.2, 198.6, 176.7, 136.9, 136.3, 134.2, 129.1, 128.2, 127.2, 126.6, 126.3, 75.3, 66.2, 61.8, 59.8, 32.9, 14.3; HRMS (ESI) m/z 372.0733 ($M+H^+$), calc. for $C_{19}H_{18}NO_3S_2$ 372.0728.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.4 min (minor) and 25.9 min (major).

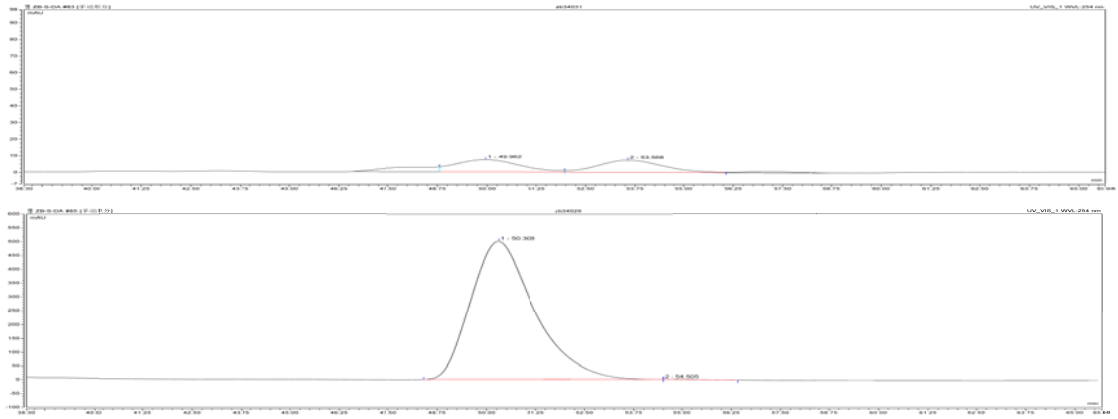


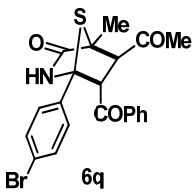


6p

White solid, Mp 155.2–156.7 °C; 75% yield; 99% *ee*; $[\alpha]_D^{26}$ –94.3 (*c* 0.74, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.29 (s, 1H), 6.91 (s, 1H), 6.45 (d, *J* = 3.3 Hz, 1H), 6.32–6.30 (m, 1H), 5.42 (d, *J* = 5.5 Hz, 1H), 3.32 (d, *J* = 5.5 Hz, 1H), 2.22 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 198.1, 176.4, 146.5, 143.0, 136.2, 134.0, 128.9, 128.2, 111.1, 109.0, 72.9, 65.6, 60.8, 58.7, 32.8, 14.3; HRMS (ESI) m/z 356.0958 ($M+H^+$), calc. for $C_{19}H_{18}NO_4S$ 356.0957.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 50.3 min (major) and 54.5 min (minor).

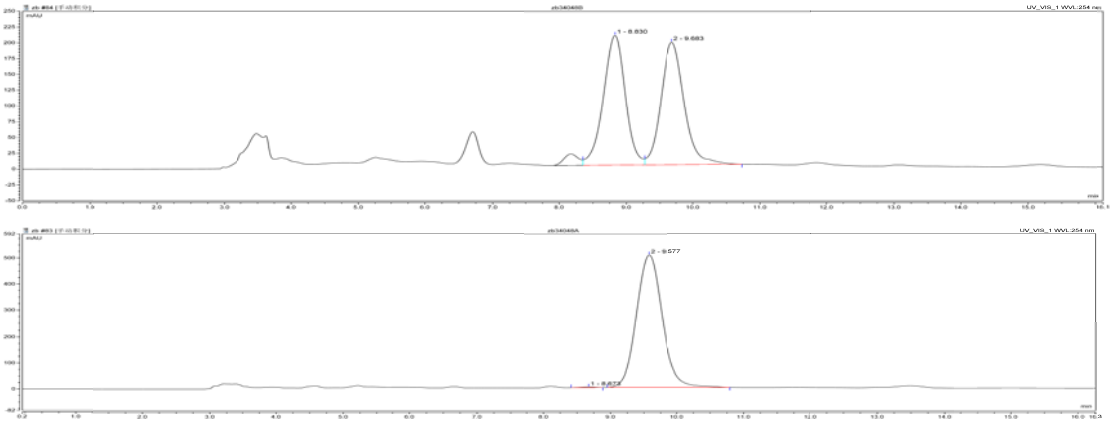


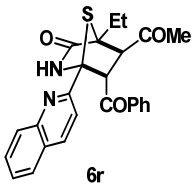


6q

White solid, Mp 140.0–141.8 °C; 54% yield; 99% *ee*; $[\alpha]_D^{20}$ –111.6 (*c* 1.61, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.59–7.54 (m, 1H), 7.48–7.45 (m, 2H), 7.41–7.38 (m, 4H), 7.29 (s, 1H), 5.40 (d, *J* = 5.4 Hz, 1H), 3.31 (d, *J* = 5.4 Hz, 1H), 2.23 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 198.4, 177.2, 136.2, 134.2, 133.0, 132.1, 129.0, 128., 127.6, 123.2, 77.7, 65.7, 61.6, 59.4, 33.04, 14.3; HRMS (ESI) m/z 444.0273 ($M+H^+$), calc. for $C_{21}H_{19}BrNO_3S$ 444.0269.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.7 min (minor) and 9.6 min (major).

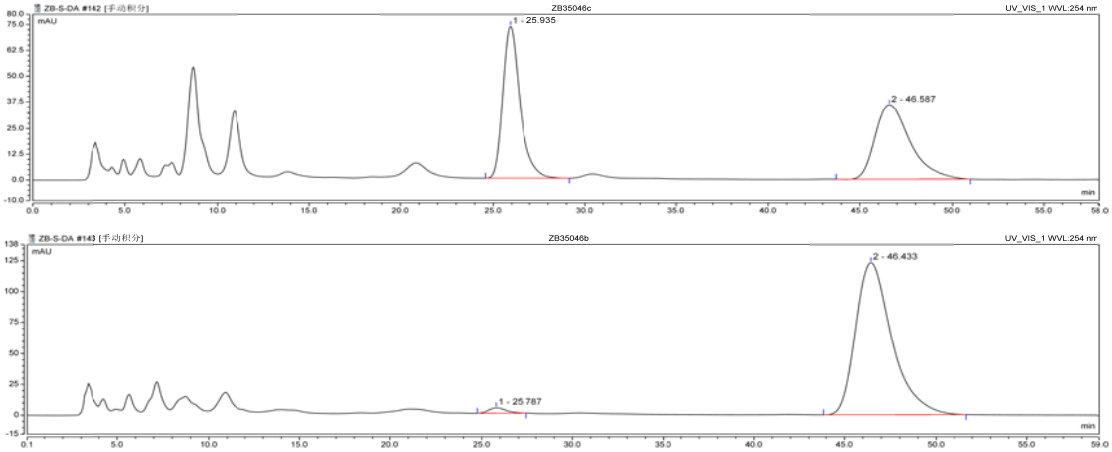


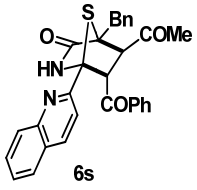


6r

Weak yellow solid, Mp 128.1–129.6 °C; 72% yield; 97% *ee*; $[\alpha]_D^{26}$ –102.5 (*c* 1.06, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.77–7.66 (m, 5H), 7.62–7.56 (m, 1H), 7.52–7.46 (m, 1H), 7.43 (s, 1H), 7.40–7.35 (m, 1H), 7.28–7.23 (m, 1H), 5.70 (d, *J* = 5.5 Hz, 1H), 3.51 (d, *J* = 5.5 Hz, 1H), 2.55–2.42 (m, 1H), 2.27 (s, 3H), 1.92–1.80 (m, 1H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.3, 198.5, 175.8, 152.4, 146.8, 137.6, 137.0, 133.2, 130.0, 129.3, 128.4, 128.1, 127.6, 127.4, 127.3, 118.3, 79.0, 74.0, 61.9, 58.6, 33.2, 22.1, 12.1; HRMS (ESI) m/z 431.1431 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_3S$ 431.1429.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 25.8 min (minor) and 46.4 min (major).



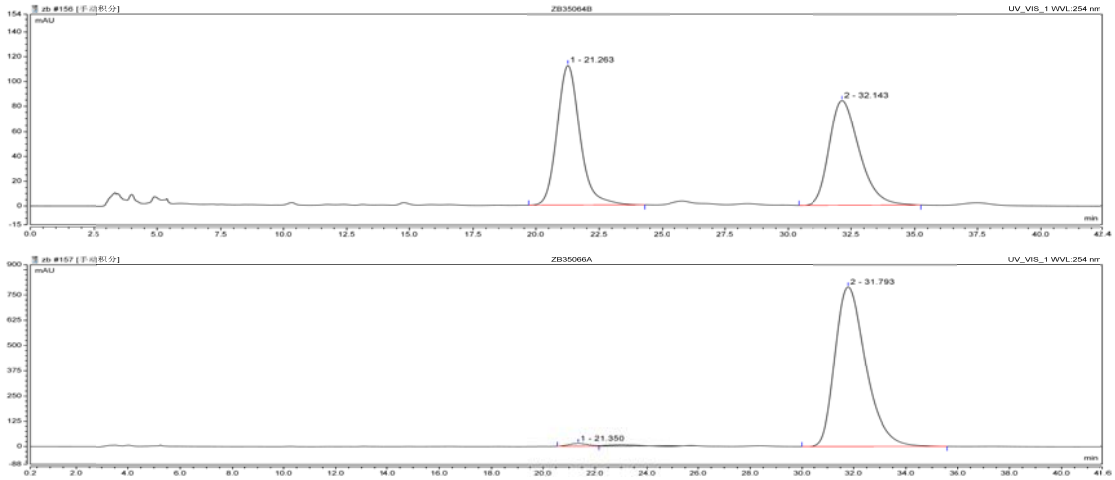


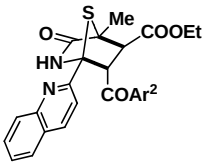
6s

Weak yellow solid, Mp 137.3–138.8 °C; 90% yield; 98% *ee*; $[\alpha]_D^{26}$ –83.3 (*c* 4.68, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.69–7.62 (m, 6H), 7.58–7.53 (m, 1H), 7.48–7.42 (m, 1H), 7.39–7.34 (m, 3H), 7.30–7.22 (m, 5H), 5.66 (d, *J* = 5.6 Hz, 1H), 3.87 (d, *J* = 13.5 Hz, 1H), 3.67 (d, *J* = 5.6 Hz, 1H), 3.02 (d, *J* = 13.5 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.6, 198.1, 175.6,

152.1, 146.6, 137.4, 137.2, 136.9, 133.2, 129.8, 129.1, 128.4, 128.3, 128.0, 127.5, 127.3, 127.2, 118.3, 79.1, 74.1, 62.5, 58.2, 33.8, 33.3; HRMS (ESI) m/z 493.1583 ($M+H^+$), calc. for $C_{30}H_{25}N_2O_3S$ 493.1586.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.4 min (minor) and 31.8 min (major).

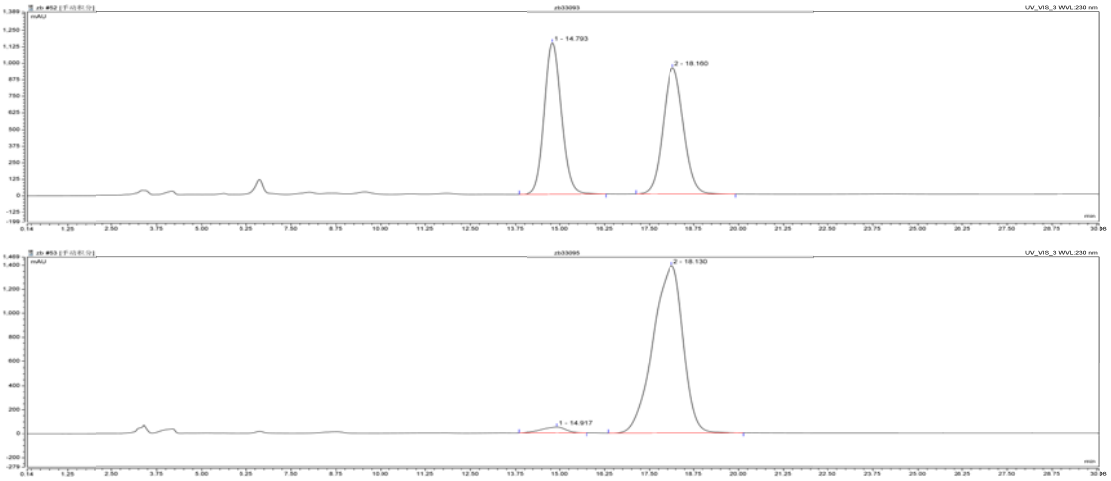


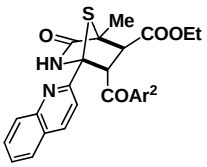


8a: Ar^2 = Ph,

White solid, Mp 141.8–143.2 °C; 87% yield; 95% *ee*; $[\alpha]_D^{26}$ –138.4 (*c* 1.95, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.74–7.66 (m, 5H), 7.62 – 7.56 (m, 1H), 7.52–7.44 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 5.76 (d, *J* = 5.4 Hz, 1H), 4.36–4.22 (m, 2H), 3.34 (d, *J* = 5.4 Hz, 1H), 1.76 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 176.6, 170.6, 152.2, 146.8, 137.6, 137.1, 133.1, 129.9, 129.3, 128.3, 128.1, 127.6, 127.4, 127.3, 118.3, 79.9, 66.5, 62.0, 61.8, 53.3, 14.3, 14.2; HRMS (ESI) m/z 447.1383 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_4S$ 447.1379.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 230 nm; retention time: 14.9 min (minor) and 18.1 min (major).

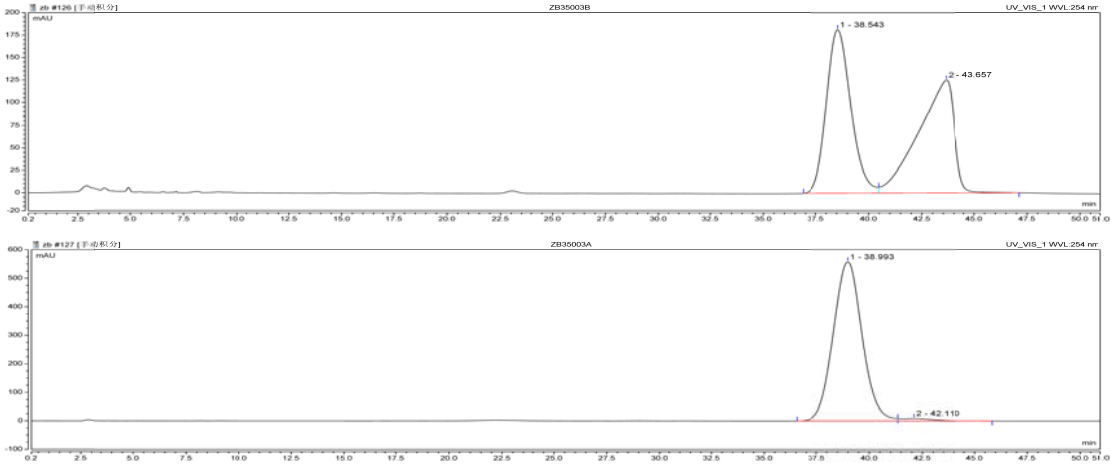


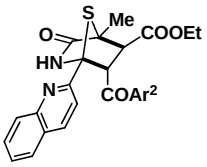


8b: Ar^2 = 4-BrPh

White solid, Mp 157.3–159.0 °C; 97% yield; 97% *ee*; $[\alpha]_D^{20}$ –170.7 (*c* 4.98, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 8.4 Hz, 2H), 7.65–7.57 (m, 5H), 7.53–7.47 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.69 (d, *J* = 5.4 Hz, 1H), 4.36 –4.19 (m, 2H), 3.35 (d, *J* = 5.4 Hz, 1H), 1.75 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 176.61, 170.51, 152.1, 146.7, 137.7, 135.8, 131.5, 130.1, 129.6, 129.1, 128.4, 127.6, 127.4, 118.4, 80.1, 66.6, 61.8, 61.7, 53.2, 14.3, 14.2; HRMS (ESI) m/z 525.0486 ($M+H^+$), calc. for $C_{25}H_{22}BrN_2O_4S$ 525.0484.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.2 mL/min; 25 °C; 254 nm; retention time: 39.0min (major) and 42.1 min (minor).

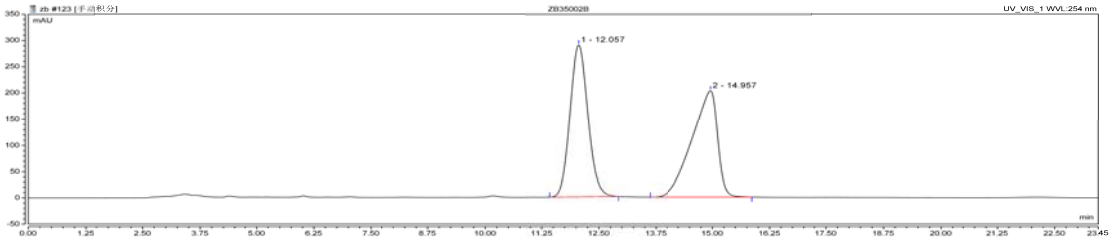


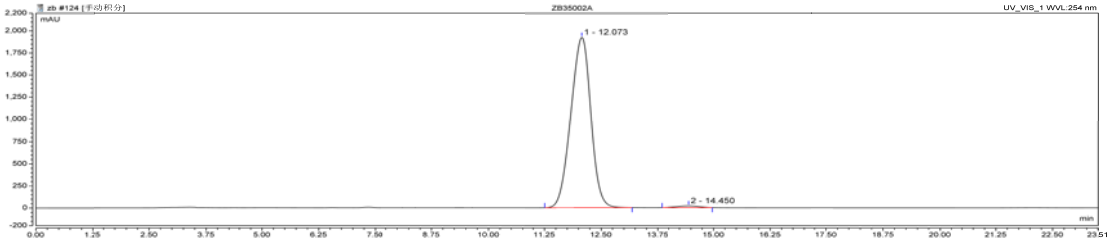


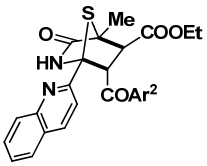
8c: Ar^2 = 3,4-Cl_2Ph

White solid, Mp 155.4–156.5 °C; 96% yield; 98% *ee*; $[\alpha]_D^{20}$ –124.7 (*c* 2.76, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.78–7.74 (m, 1H), 7.72–7.70 (m, 1H), 7.63 (d, *J* = 3.6 Hz, 2H), 7.58–7.49 (m, 3H), 7.27–7.24 (m, 1H), 5.59 (d, *J* = 5.2 Hz, 1H), 4.30 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.43 (d, *J* = 5.2 Hz, 1H), 1.77 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 176.5, 170.4, 151.8, 146.6, 137.8, 137.6, 136.6, 132.9, 130.3, 130.2, 130.0, 129.0, 127.6, 127.5, 127.1, 118.3, 80.0, 66.6, 62.4, 62.0, 52.9, 14.3, 14.2; HRMS (ESI) m/z 515.0602 ($M+H^+$), calc. for $C_{25}H_{21}Cl_2N_2O_4S$ 515.0599.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 12.1 min (major) and 14.4 min (minor).



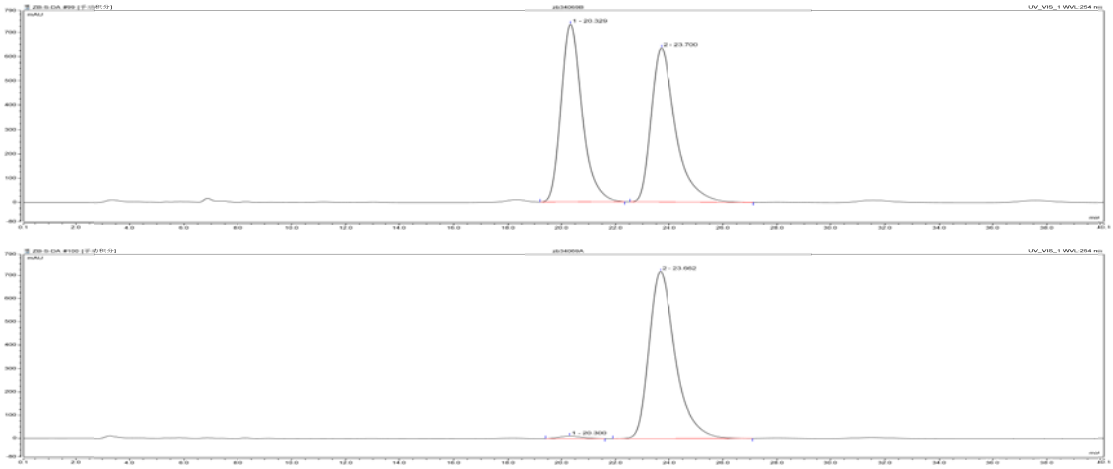


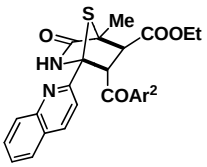


8d: Ar^2 = 4-MeOPh

Weak yellow solid, Mp 122.2–124.0 °C; 90% yield; 98% *ee*; $[\alpha]_D^{26}$ –173.9 (*c* 4.61, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 1H), 7.75–7.71 (m, 5H), 7.62–7.57 (m, 1H), 7.2–7.46 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.71 (d, *J* = 5.4 Hz, 1H), 4.37–4.20 (m, 2H), 3.74 (s, 3H), 3.32 (d, *J* = 5.4 Hz, 1H), 1.75 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 176.7, 170.7, 163.5, 152.4, 146.8, 137.5, 130.6, 130.0, 129.9, 129.4, 127.6, 127.3, 127.2, 118.3, 113.5, 80.0, 66.5, 61.7, 61.5, 55.4, 53.5, 14.3, 14.2; HRMS (ESI) m/z 477.1481 ($M+H^+$), calc. for $C_{26}H_{25}N_2O_5S$ 477.1484.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.3 min (minor) and 23.7 min (major).

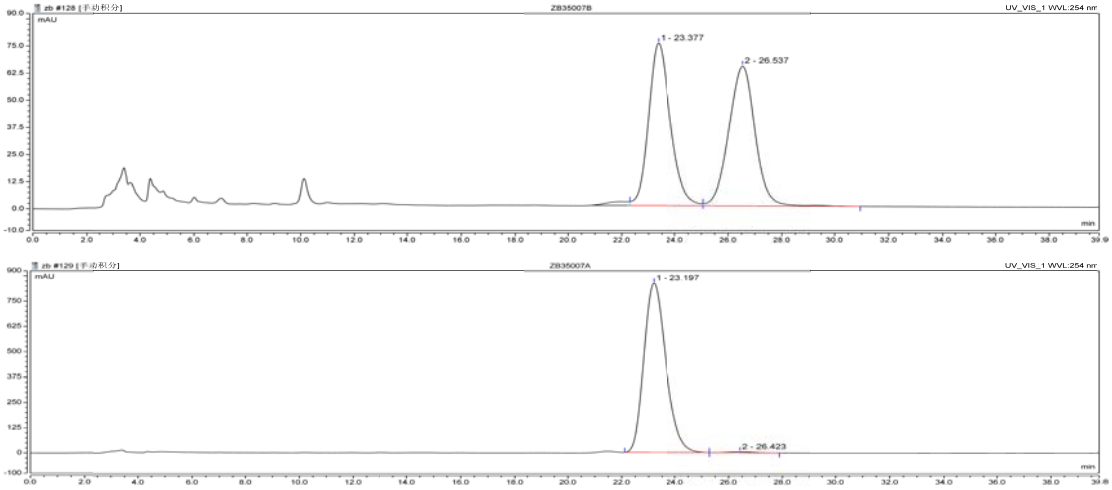


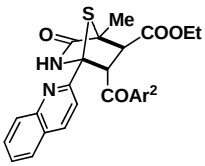


8e: Ar^2 = 2-thienyl

White solid, Mp 137.5–138.7 °C; 97% yield; 99% *ee*; $[\alpha]_D^{26}$ –132.0 (*c* 4.67, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.74–7.71 (m, 3H), 7.62–7.55 (m, 3H), 7.51–7.46 (m, 2H), 6.90–6.87 (m, 1H), 5.57 (d, *J* = 5.3 Hz, 1H), 4.37–4.20 (m, 2H), 3.41 (d, *J* = 5.3 Hz, 1H), 1.76 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{113}C NMR (75 MHz, $CDCl_3$) δ 190.0, 176.6, 170.5, 152.1, 146.8, 144.3, 137.6, 134.7, 132.6, 129.9, 129.3, 127.9, 127.6, 127.4, 127.3, 118.2, 80.0, 66.5, 62.7, 61.8, 53.6, 14.2,(two peaks); HRMS (ESI) m/z 453.0940 ($M+H^+$), calc. for $C_{23}H_{21}N_2O_4S_2$ 453.0943.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 23.2 min (major) and 26.4 min (minor).

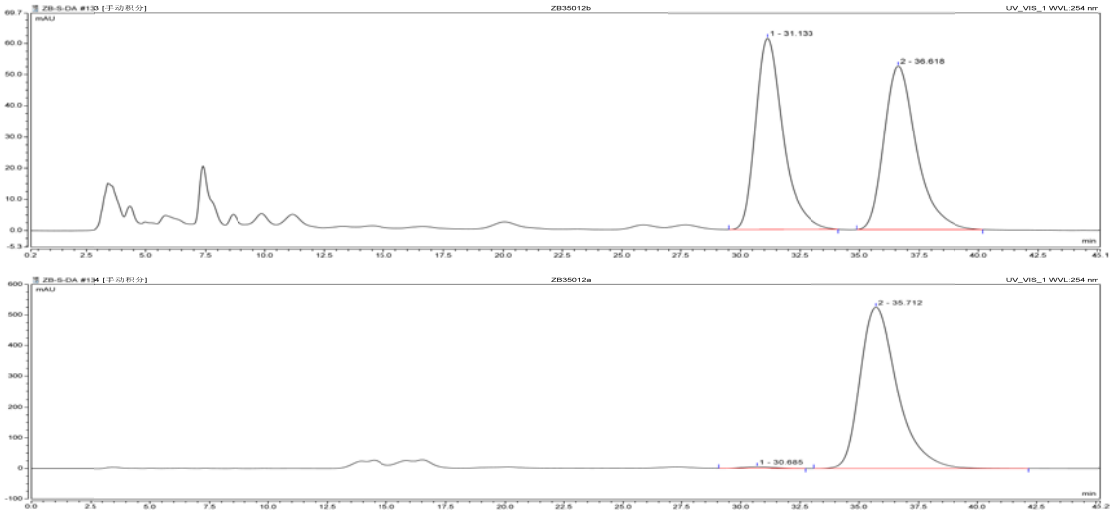


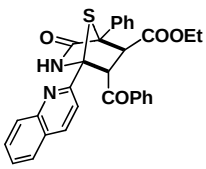


8f: Ar^2 = 2-furyl

White solid, Mp 141.8–143.1 °C; 96% yield; 98% *ee*; $[\alpha]_D^{26}$ –186.1 (*c* 4.29, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 7.79–7.73 (m, 3H), 7.65–7.60 (m, 1H), 7.54–7.49 (m, 2H), 7.25 (s, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.29 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.45 (d, *J* = 5.2 Hz, 1H), 4.38–4.22 (m, 2H), 3.46 (d, *J* = 5.2 Hz, 1H), 1.76 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.0, 176.3, 170.5, 152.3, 152.2, 146.8, 146.6, 137.4, 130.0, 129.4, 127.6, 128.4, 127.3, 118.2, 112.3, 79.5, 66.3, 63.1, 61.7, 53.0, 14.2; HRMS (ESI) m/z 437.1175 ($M+H^+$), calc. for $C_{23}H_{21}N_2O_5S$ 437.1171.

The *ee* was determined by HPLC analysis. CHIRALPAK IA (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 30.7 min (minor) and 35.7 min (major).



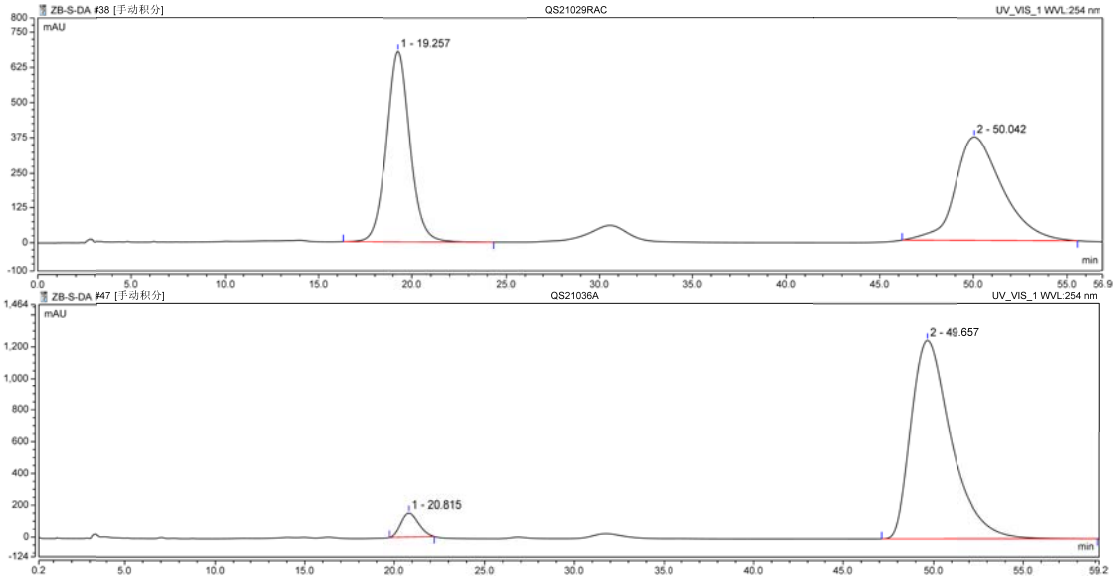


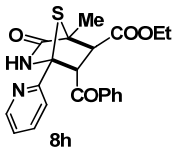
8g

Pale yellow solid, Mp 158.4–160.1 °C; 67% yield; 90% *ee*; $[\alpha]_D^{28}$ –205.7 (*c* 1.50, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.78–7.70 (m, 4H), 7.64–7.49 (m, 5H), 7.43–7.35 (m, 4H), 7.28 (s, 1H), 7.23 (s, 1H), 5.86 (d, *J* = 5.4 Hz, 1H), 3.80 (d, *J* = 5.4 Hz, 1H), 3.82–3.62 (m, 2H), 0.74 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 174.5, 170.1, 152.1,

146.8, 137.7, 137.0, 133.2, 131.4, 130.0, 129.3, 128.7, 128.6, 128.4, 128.2, 128.0, 127.6, 127.4, 118.3, 78.4, 74.3, 62.5, 61.3, 54.7, 13.4; HRMS (ESI) m/z 509.1538 ($M+H^+$), calc. for $C_{30}H_{25}N_2O_4S$ 509.1535.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 60/40; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.3 min (minor) and 50.0 min (major).

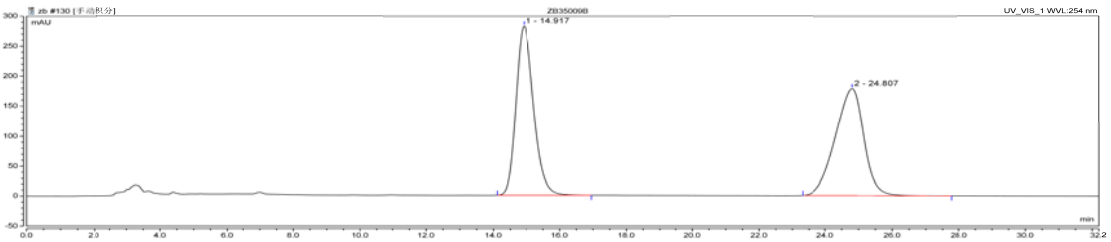


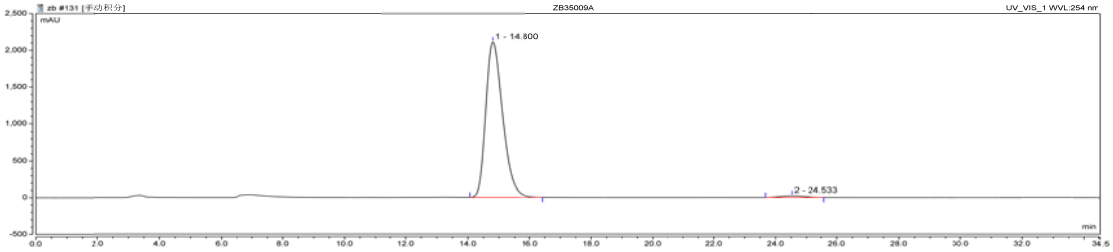


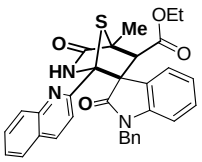
8h

White solid, Mp 125.5–126.8 °C; 95% yield; 97% *ee*; $[\alpha]_D^{26}$ –134.7 (*c* 3.72, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.0 Hz, 1H), 8.54–8.52 (m, 1H), 7.95 (s, 1H), 7.88–7.84 (m, 1H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.35–7.24 (m, 3H), 7.24 (s, 0H), 5.43 (d, *J* = 5.4 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.22 (d, *J* = 5.4 Hz, 1H), 1.68 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 177.3, 170.5, 150.1, 147.2, 136.1, 134.0, 133.9, 130.2, 128.8, 128.2, 123.5, 76.7, 65.4, 62.0, 54.0, 14.2; HRMS (ESI) m/z 397.1221 ($M+H^+$), calc. for $C_{21}H_{21}N_2O_4S$ 397.1222.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.8 min (major) and 24.5 min (minor).



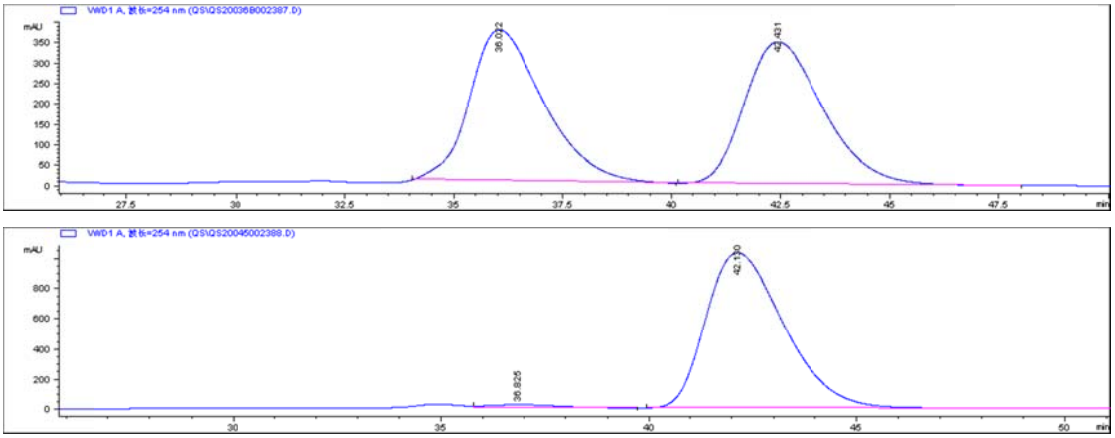


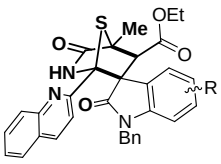


10a

Pale yellow solid, Mp 102.2–103.8 °C; 96% yield; 95% *ee*; $[\alpha]_D^{24}$ –348.8 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.95–7.91 (m, 3H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.74–7.68 (m, 2H), 7.58–7.52 (m, 1H), 7.05–6.88 (m, 4H), 6.84–6.75 (m, 4H), 6.25–6.23 (m, 1H), 4.74 (s, 2H), 3.76 (s, 1H), 3.74–3.51 (m, 2H), 1.98 (s, 3H), 0.53 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 174.2, 167.9, 150.4, 146.6, 143.1, 136.2, 135.0, 130.2, 129.6, 129.4, 128.4, 127.5, 127.4, 127.3, 126.5, 126.4, 126.0, 122.0, 118.9, 108.7, 82.7, 67.8, 63.0, 60.6, 60.2, 44.0, 13.3, 13.1; HRMS (ESI) m/z 550.1803 ($M+H^+$), calc. for $C_{32}H_{28}N_3O_4S$ 550.1801.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 36.8 min (minor) and 42.1min (major).

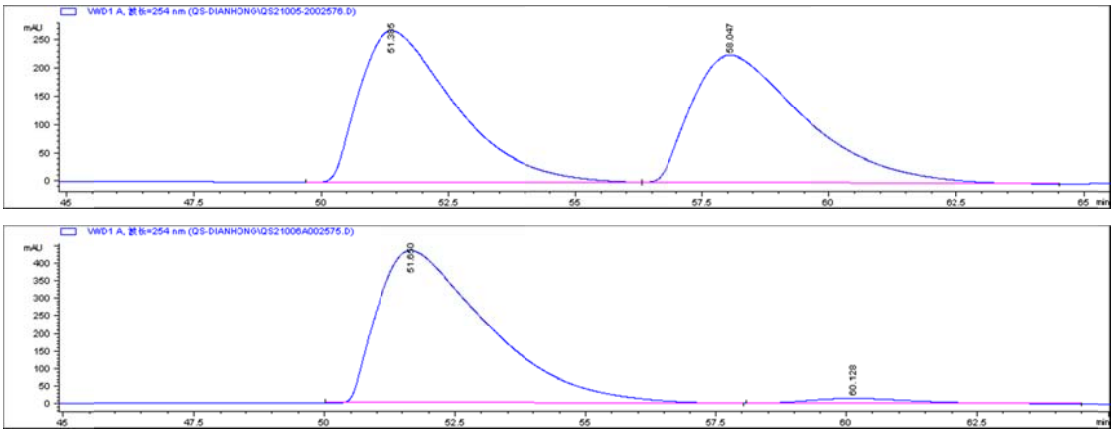


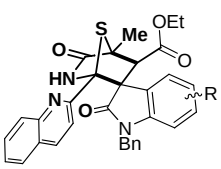


10b: R = 5-F

Pale yellow solid, Mp 130.4–132.2 °C; 98% yield; 94% *ee*; $[\alpha]_D^{24}$ –138.0 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (t, *J* = 9.0 Hz, 3H), 7.77–7.69 (m, 3H), 7.59–7.54 (m, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.88–6.78 (m, 4H), 6.69 (td, *J* = 8.6, 3.5 Hz, 1H), 6.16 (dd, *J* = 8.6, 3.5 Hz, 1H), 4.82 (d, *J* = 15.8 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 3.78–3.60 (m, 3H), 1.97 (s, 3H), 0.59 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 174.1, 167.6, 160.0, 156.8, 150.2, 146.6, 139.1, 139.0, 136.6, 134.7, 130.3, 129.5, 128.4, 127.8, 127.7, 127.6, 127.5, 127.4, 126.5, 118.7, 115.7, 115.4, 114.7, 114.3, 109.2, 109.0, 82.8, 67.8, 62.9, 60.8, 60.2, 44.2, 13.2, 13.1; HRMS (ESI) m/z 590.1529 ($M+Na^+$), calc. for $C_{32}H_{26}FN_3O_4SNa$ 590.1526.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 51.7 min (major) and 60.1 min (minor).

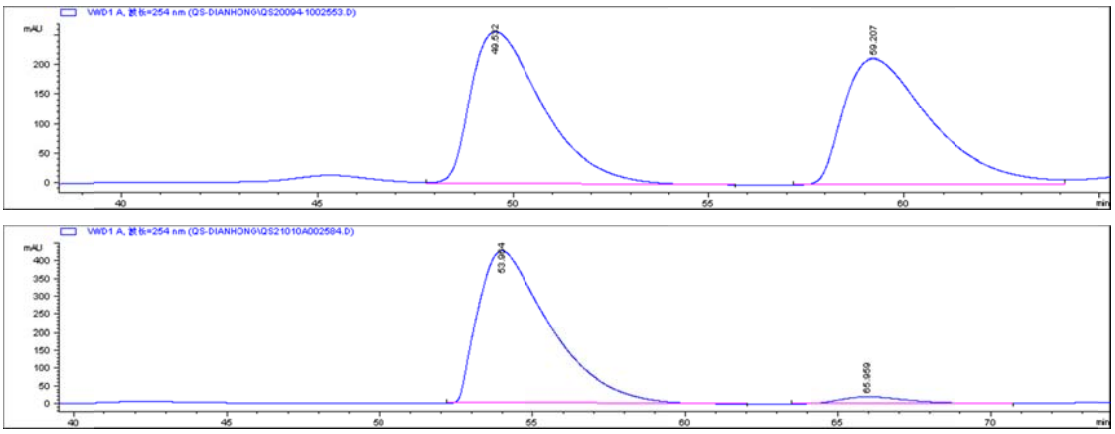


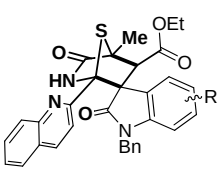


10c: R = 5-Cl

Pale yellow solid, Mp 155.0–156.3 °C; 97% yield; 92% *ee*; $[\alpha]_D^{24}$ –140.5 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.85 (m, 4H), 7.72 (t, *J* = 7.4 Hz, 2H), 7.59–7.54 (m, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.00–6.94 (m, 2H), 6.88–6.78 (m, 4H), 6.17 (d, *J* = 8.3 Hz, 1H), 4.82 (d, *J* = 15.8 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 3.82 – 3.59 (m, 3H), 1.97 (s, 3H), 0.61 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 173.9, 167.6, 150.2, 146.6, 141.6, 136.7, 134.6, 130.4, 129.5, 129.2, 128.5, 127.9, 127.6, 127.5, 126.5, 118.8, 109.6, 82.8, 67.6, 63.0, 60.9, 60.3, 44.1, 13.3, 13.1; HRMS (ESI) m/z 584.1415 ($M+H^+$), calc. for $C_{32}H_{27}ClN_3O_4S$ 584.1411.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 54.0 min (major) and 66.0 min (minor).



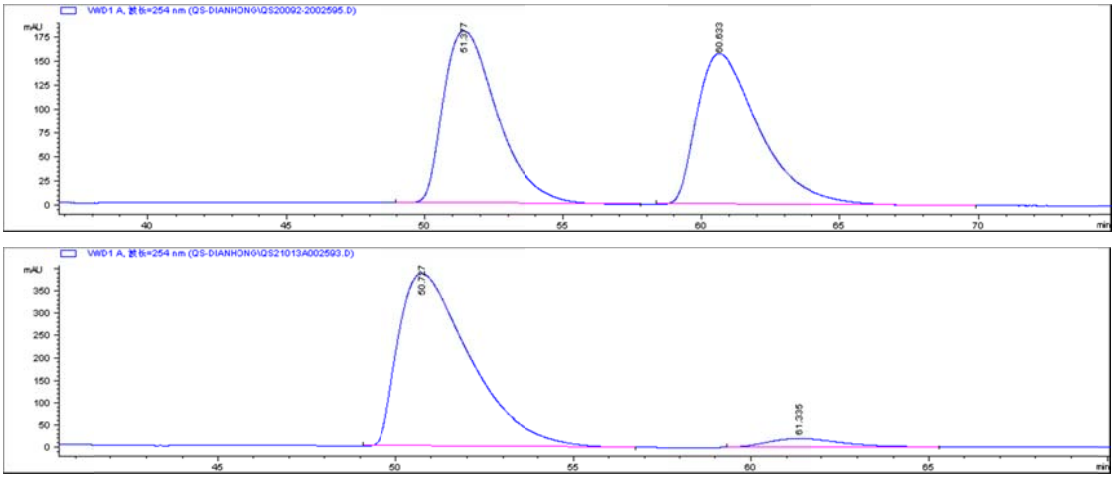


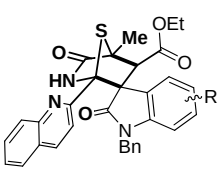
10d: R = 5-Br

Pale yellow solid, Mp 145.3–146.3 °C; 98% yield; 90% *ee*; $[\alpha]_D^{24}$ –86.1 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.6 Hz, 1H), 7.91 (d, *J* = 2.6 Hz, 1H), 7.88 (s, 2H), 7.71 (t, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.12–7.03 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.13 (d, *J* = 8.4 Hz, 1H), 4.81 (d, *J* = 15.9 Hz, 1H), 4.68 (d, *J* = 15.9 Hz, 1H), 3.76–3.66 (m, 3H), 1.97 (s, 3H), 0.60 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 173.8, 167.5, 150.1, 146.6, 142.1, 136.7, 134.5, 132.1, 130.3, 129.4, 129.2, 128.4, 128.2, 127.5, 127.4, 126.5, 118.8, 114.7, 110.0,

67.5, 62.9, 60.9, 60.2, 44.1, 13.3, 13.1; HRMS (ESI) m/z 650.0720 ($M+Na^+$), calc. for $C_{32}H_{26}BrN_3O_4SNa$ 650.0725.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 50.7 min (minor) and 61.3 min (major).

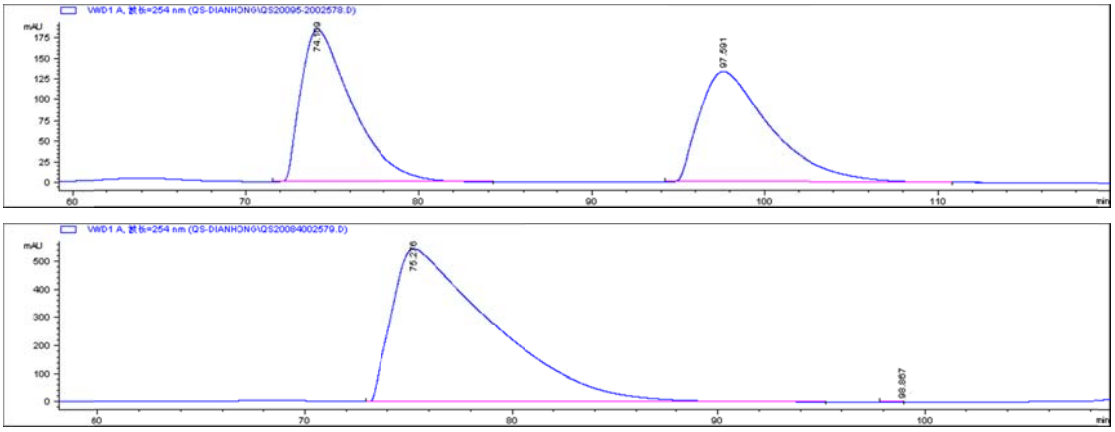


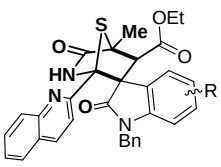


10e: R = 5-Me

Pale yellow solid, Mp 137.5–138.5 °C; 95% yield; >99% *ee*; $[\alpha]_D^{24}$ –431.3 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.73–7.68 (m, 3H), 7.57–7.52 (m, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.80–6.71 (m, 5H), 6.12 (d, *J* = 7.8 Hz, 1H), 4.75 (d, *J* = 16.0 Hz, 1H), 4.69 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 1H), 3.73–3.54 (m, 2H), 2.29 (s, 3H), 1.98 (s, 3H), 0.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 174.2, 168.0, 150.5, 146.6, 140.7, 136.2, 135.1, 131.5, 130.2, 129.6, 128.3, 127.5, 127.4, 127.2, 127.1, 126.5, 126.0, 118.9, 108.5, 82.7, 67.9, 62.9, 60.7, 60.1, 44.0, 21.2, 13.2; HRMS (ESI) m/z 586.1780 ($M+Na^+$), calc. for $C_{33}H_{29}N_3O_4SNa$ 586.1776.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 75.3 min (major) and 98.9 min (minor).

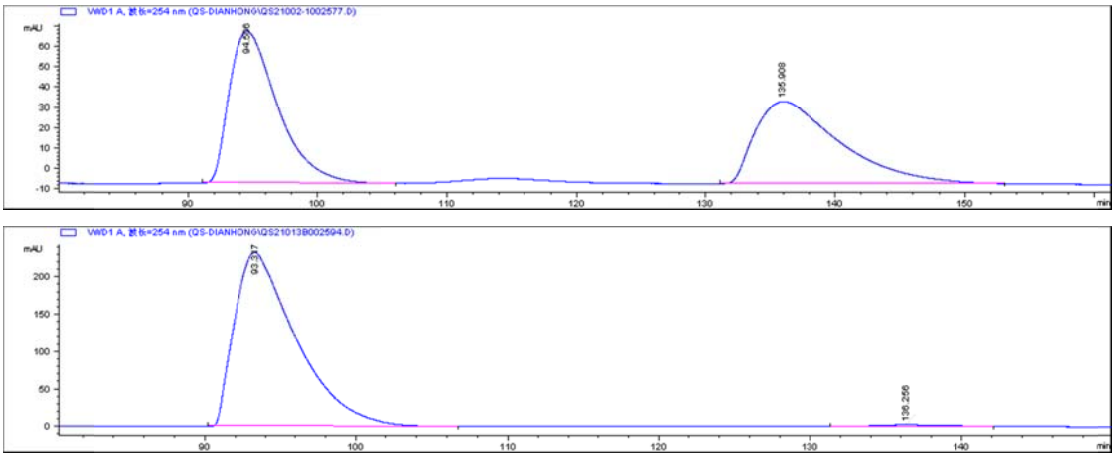


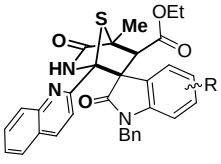


10f: R = 5-OMe

Pale yellow solid, Mp 141.1–142.3 °C; 98% yield; 98% *ee*; $[\alpha]_D^{24}$ –303.4 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.66–7.62 (m, 2H), 7.52–7.46 (m, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.75–6.66 (m, 4H), 6.45 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.06 (d, *J* = 8.5 Hz, 1H), 4.65 (s, 2H), 3.72–3.50 (m, 6H), 1.90 (s, 3H), 0.50 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 173.9, 167.8, 155.2, 150.3, 146.6, 136.5, 136.3, 135.0, 130.2, 129.5, 128.3, 127.5, 127.4, 127.2, 127.1, 126.5, 118.7, 114.2, 113.5, 109.0, 82.7, 68.0, 62.9, 60.6, 60.0, 55.9, 44.0, 13.3, 13.1; HRMS (ESI) m/z 602.1724 ($M+Na^+$), calc. for $C_{33}H_{29}N_3O_5SNa$ 602.1726.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 93.3 min (major) and 136.3 min (minor).

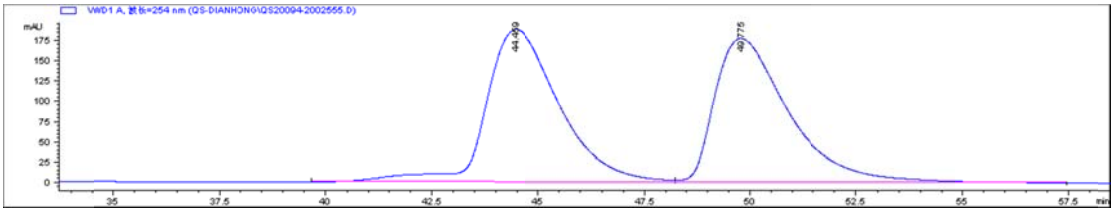


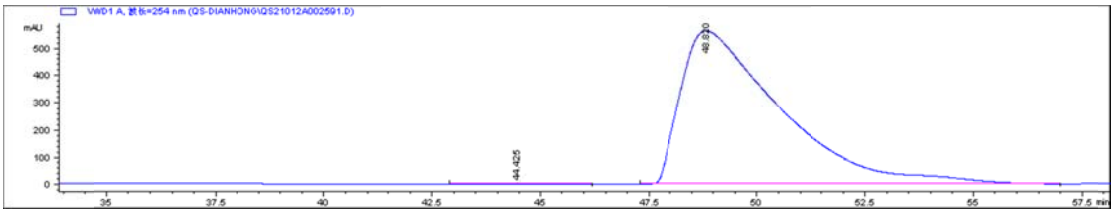


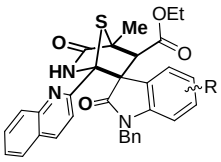
10g: R = 6-Cl

Pale yellow solid, Mp 96.4–96.9 °C; 97% yield; >99% *ee*; $[\alpha]_D^{24}$ –133.7 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.85–7.75 (m, 4H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.52–7.46 (m, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.88–6.71 (m, 6H), 6.19 (s, 1H), 4.73 (d, *J* = 15.9 Hz, 1H), 4.61 (d, *J* = 15.9 Hz, 1H), 3.70–3.41 (m, 3H), 1.88 (s, 3H), 0.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 174.2, 167.6, 150.2, 146.6, 144.2, 136.6, 135.2, 134.4, 130.3, 129.4, 128.5, 127.6, 127.5, 127.4, 127.3, 126.4, 124.4, 121.8, 118.7, 109.1, 82.7, 67.2, 62.8, 60.8, 60.3, 44.1, 13.3, 13.0; HRMS (ESI) m/z 584.1414 ($M+H^+$), calc. for $C_{32}H_{27}ClN_3O_4S$ 584.1411.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 44.4 min (minor) and 48.8 min (major).



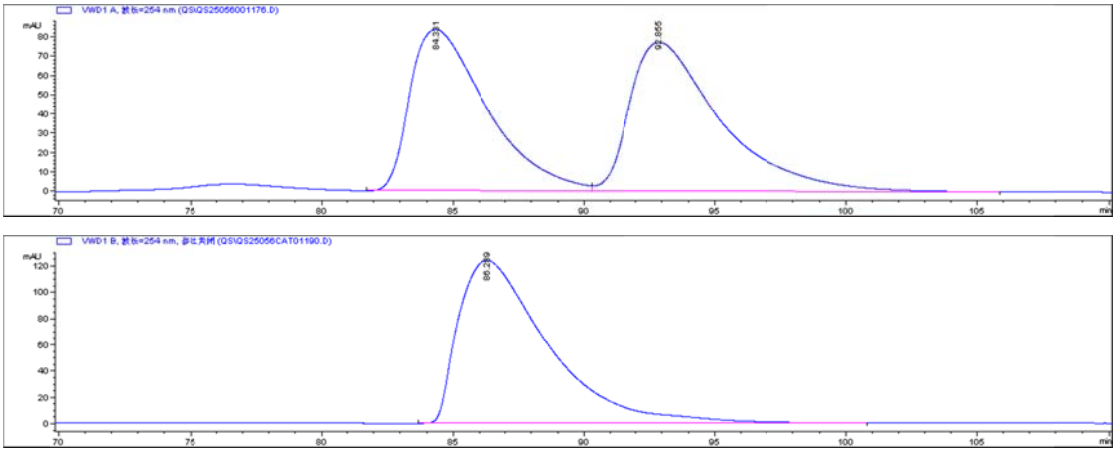


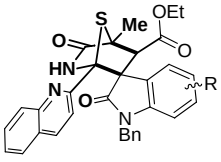


10h: R = 6-OMe

Pale yellow solid, Mp 123.0–124.8 °C; 94% yield; >99% *ee*; $[\alpha]_D^{24}$ –269.5 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.92–7.86 (m, 2H), 7.75 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.67–7.62 (m, 2H), 7.52–7.46 (m, 1H), 6.94 (t, *J* = 7.1 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.73–6.63 (m, 4H), 6.38 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.75 (d, *J* = 2.3 Hz, 1H), 4.68 (d, *J* = 15.9 Hz, 1H), 4.59 (d, *J* = 15.9 Hz, 1H), 3.70–3.48 (m, 6H), 1.89 (s, 3H), 0.54 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 174.6, 168.0, 160.7, 150.5, 146.6, 144.3, 136.3, 134.9, 130.2, 129.6, 128.3, 127.5, 127.4, 127.2, 126.5, 118.9, 117.7, 105.4, 96.7, 82.6, 67.5, 62.8, 60.6, 60.1, 55.2, 44.0, 13.4, 13.1; HRMS (ESI) m/z 602.1730 ($M+Na^+$), calc. for $C_{33}H_{29}N_3O_5SNa$ 602.1726.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 101.9 min (minor) and 110.0 min (major).

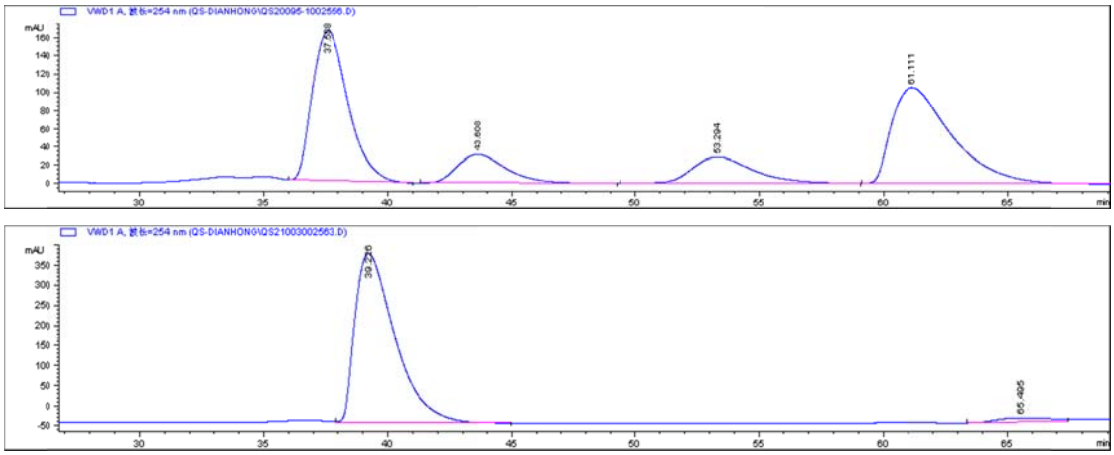


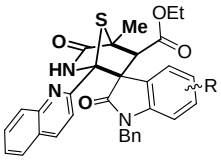


10i: R = 7-Cl

Pale yellow solid, Mp 70.4–72.1 °C; 96% *ee*; $[\alpha]_D^{24}$ –240.4 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.88–7.83 (m, 3H), 7.75–7.68 (m, 3H), 7.57–7.52 (m, 1H), 7.11–7.05 (m, 1H), 7.00–6.75 (m, 7H), 5.06 (d, *J* = 15.5 Hz, 1H), 4.78 (d, *J* = 15.5 Hz, 1H), 3.75 (s, 1H), 3.72–3.51 (m, 2H), 1.96 (s, 3H), 0.55 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 174.2, 167.6, 150.1, 146.6, 136.5, 136.4, 130.3, 129.5, 128.2, 127.5, 127.4, 127.2, 126.7, 122.5, 122.4, 122.3, 122.2, 118.7, 117.6, 117.3, 82.9, 67.6, 62.8, 60.7, 60.6, 45.5, 13.2, 13.1; HRMS (ESI) m/z 606.1233 ($M+Na^+$), calc. for $C_{32}H_{26}ClN_3O_4SNa$ 606.1230.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 39.2 min (major) and 65.5 min (minor).

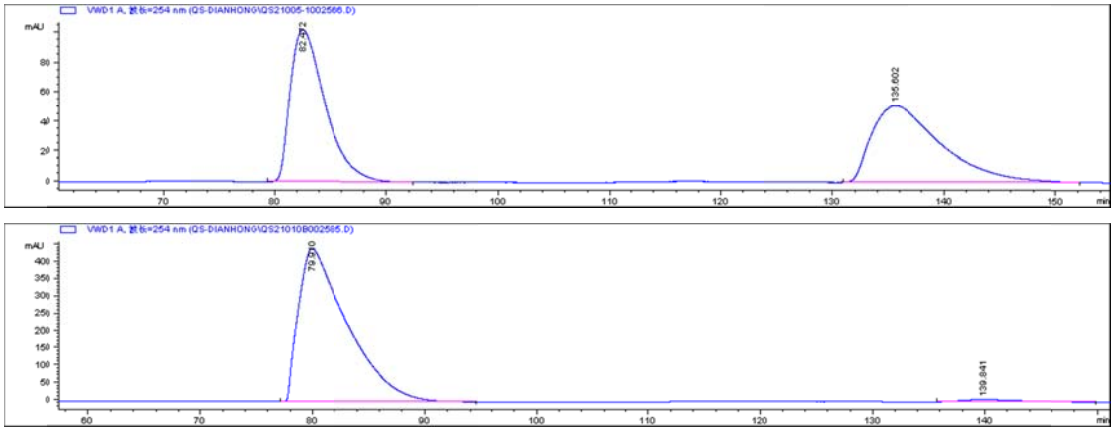


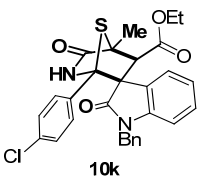


10j: R = 7-Me

Pale yellow solid, Mp 87.0–88.6 °C; 97% yield; 96% *ee*; $[\alpha]_D^{24}$ –281.9 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.90–7.87 (m, 2H), 7.82–7.75 (m, 2H), 7.67–7.63 (m, 2H), 7.52–7.46 (m, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.86–6.77 (m, 4H), 6.71 (d, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 2H), 5.04 (d, *J* = 17.0 Hz, 1H), 4.84 (d, *J* = 17.0 Hz, 1H), 3.74–3.52 (m, 3H), 1.91 (s, 3H), 1.79 (s, 3H), 0.59 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 175.3, 168.0, 150.5, 146.6, 141.2, 137.1, 136.2, 133.4, 130.2, 129.6, 128.5, 127.5, 126.9, 126.6, 125.2, 124.4, 122.0, 119.1, 119.0, 83.0, 67.2, 63.0, 60.7, 60.6, 45.3, 18.6, 13.5, 13.2; HRMS (ESI) m/z 586.1778 ($M+Na^+$), calc. for $C_{33}H_{29}N_3O_4SNa$ 586.1776.

The *ee* was determined by HPLC analysis. CHIRALPAK ID-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 79.9 min (major) and 139.8 min (minor).

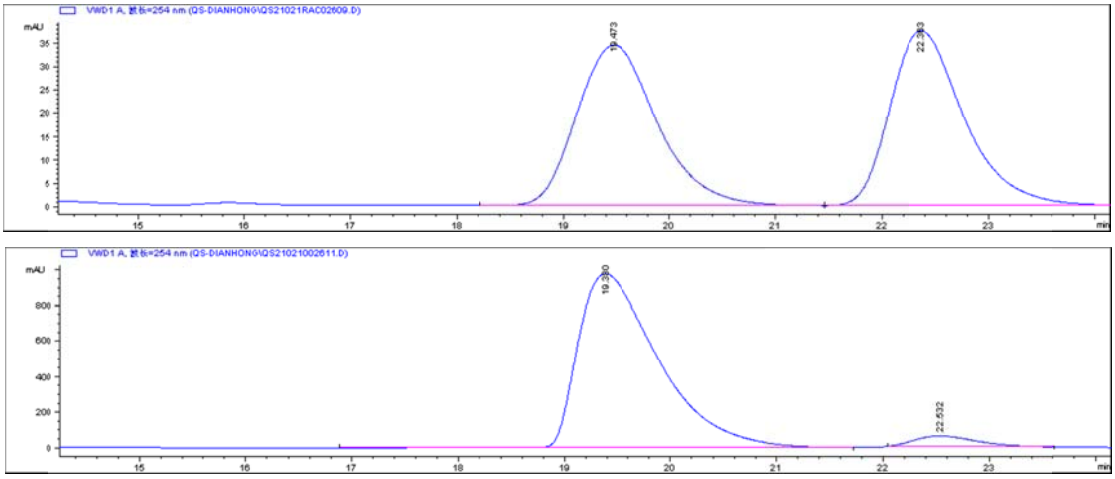


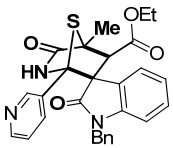


10k

Pale yellow solid, Mp 87.8–89..8 °C; 94% yield; 90% *ee*; $[\alpha]_D^{24}$ –72.5 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.3 Hz, 1H), 7.61 (s, 1H), 7.28–7.25 (m, 3H), 7.08–7.04 (m, 3H), 6.99–6.88 (m, 5H), 6.46 (d, *J* = 7.3 Hz, 1H), 5.03 (d, *J* = 15.7 Hz, 1H), 4.67 (d, *J* = 15.7 Hz, 1H), 3.68–3.45 (m, 3H), 1.92 (s, 3H), 0.47 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 174.8, 167.6, 142.5, 135.0, 134.9, 129.7, 129.4, 128.7, 128.3, 127.8, 127.3, 127.1, 126.6, 126.0, 122.4, 108.8, 82.6, 68.0, 61.3, 60.7, 60.4, 44.0, 13.2, 12.9; HRMS (ESI) m/z 555.1123 ($M+Na^+$), calc. for $C_{29}H_{25}ClN_2O_4SNa$ 555.1121.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.4 min (major) and 22.5 min (minor).

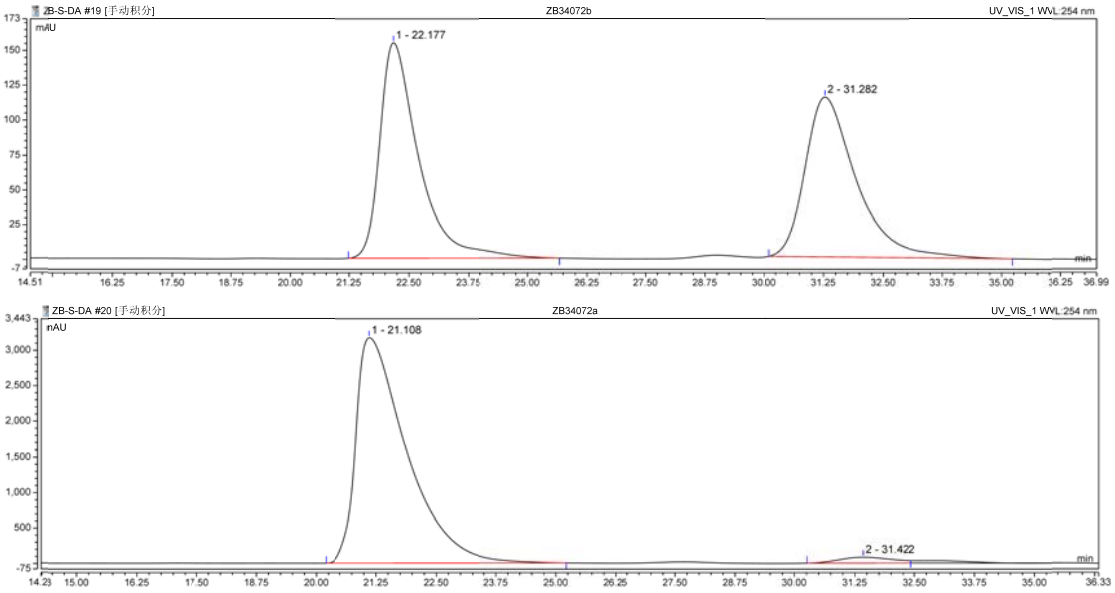


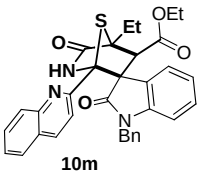


10l

Pale yellow solid, Mp 101.3–102.6 °C; 96% yield; 95% *ee*; $[\alpha]_D^{24}$ –62.0 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 4.2 Hz, 1H), 7.81–7.78 (m, 1H), 7.59 (s, 1H), 7.33 (td, *J* = 7.7, 1.7 Hz, 1H), 7.26–7.22 (m, 3H), 7.12–6.98 (m, 4H), 6.92–6.82 (m, 2H), 6.39 (d, *J* = 7.7 Hz, 1H), 4.89 (d, *J* = 15.7 Hz, 1H), 4.72 (d, *J* = 15.7 Hz, 1H), 3.71–3.49 (m, 3H), 1.94 (s, 3H), 0.50 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 174.4, 167.8, 150.4, 148.5, 142.9, 136.0, 135.3, 129.2, 128.5, 127.5, 127.2, 126.1, 126.0, 123.6, 122.0, 121.6, 108.4, 82.8, 67.3, 62.4, 60.6, 60.3, 44.0, 13.2, 13.1; HRMS (ESI) m/z 522.1466 ($M+Na^+$), calc. for $C_{28}H_{25}N_3O_4SNa$ 522.1463.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.1 min (major) and 31.4 min (minor).

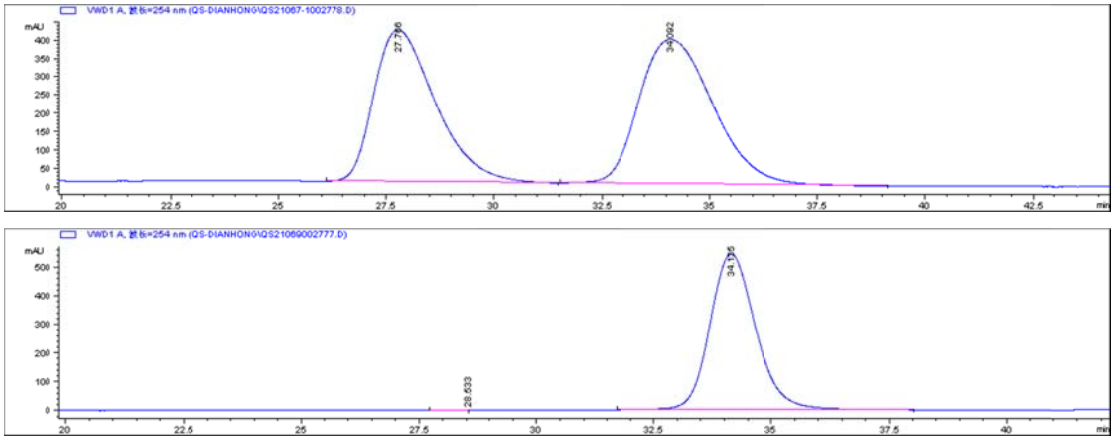


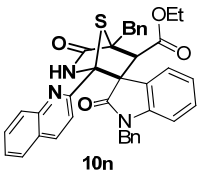


10m

Pale yellow solid, Mp 92.3–94.1 °C; 87% yield; >99% *ee*; $[\alpha]_D^{24}$ –67.8 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.93–7.91 (m, 3H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.79–7.68 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.06–7.04 (m, 1H), 6.98–6.91 (m, 3H), 6.86–6.78 (m, 4H), 6.25–6.22 (m, 1H), 4.79 (d, *J* = 15.8 Hz, 1H), 4.71 (d, *J* = 15.8 Hz, 1H), 3.79 (s, 1H), 3.72–3.49 (m, 2H), 2.60 (dq, *J* = 14.5, 7.2 Hz, 1H), 2.40 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.52 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 174.3, 167.9, 150.6, 146.6, 143.0, 136.2, 135.0, 130.2, 129.5, 129.3, 128.4, 127.5, 127.4, 127.3, 126.6, 125.9, 121.9, 118.9, 108.6, 81.9, 69.4, 67.5, 60.6, 59.4, 44.0, 20.4, 13.2, 12.0; HRMS (ESI) m/z 586.1775 ($M+Na^+$), calc. for $C_{33}H_{29}N_3O_4SNa$ 586.1776.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 28.5 min (minor) and 3401 min (major).

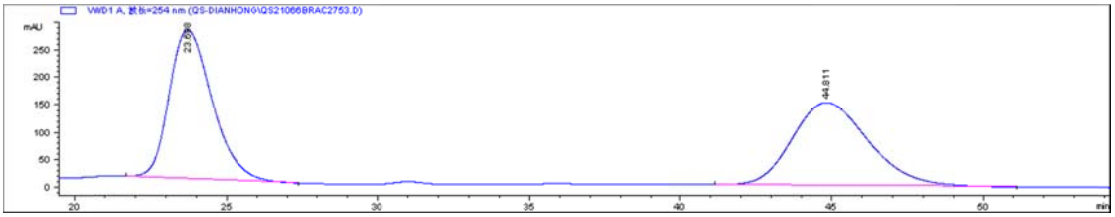


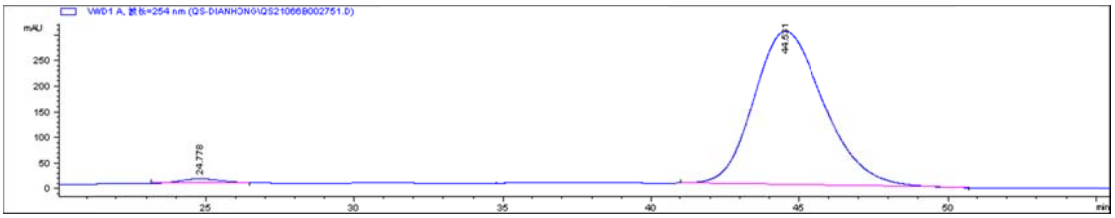


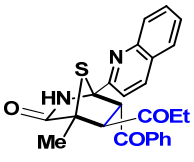
10n

Pale yellow solid, Mp 108.2–109.9 °C; 84% yield; 97% *ee*; $[\alpha]_D^{24}$ –101.0 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.98–7.89 (m, 3H), 7.73–7.64 (m, 3H), 7.58–7.48 (m, 3H), 7.37–7.30 (m, 3H), 7.24–7.22 (m, 1H), 7.06–6.92 (m, 3H), 6.86–6.78 (m, 5H), 6.24–6.21 (m, 1H), 4.79 (d, *J* = 15.9 Hz, 1H), 4.72 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 1H), 3.81 (s, 1H), 3.76–3.53 (m, 2H), 0.54 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 174.1, 168.1, 150.4, 146.5, 143.0, 139.1, 136.0, 135.0, 130.1, 130.0, 129.5, 129.4, 128.4, 128.3, 127.5, 127.3, 126.9, 126.6, 125.8, 122.0, 118.9, 108.7, 81.6, 70.7, 68.1, 60.7, 59.5, 44.0, 31.9, 13.3; HRMS (ESI) m/z 648.1932 ($M+Na^+$), calc. for $C_{38}H_{31}N_3O_4SNa$ 648.1933.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 70/30; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 24.8 min (minor) and 44.5 min (major).



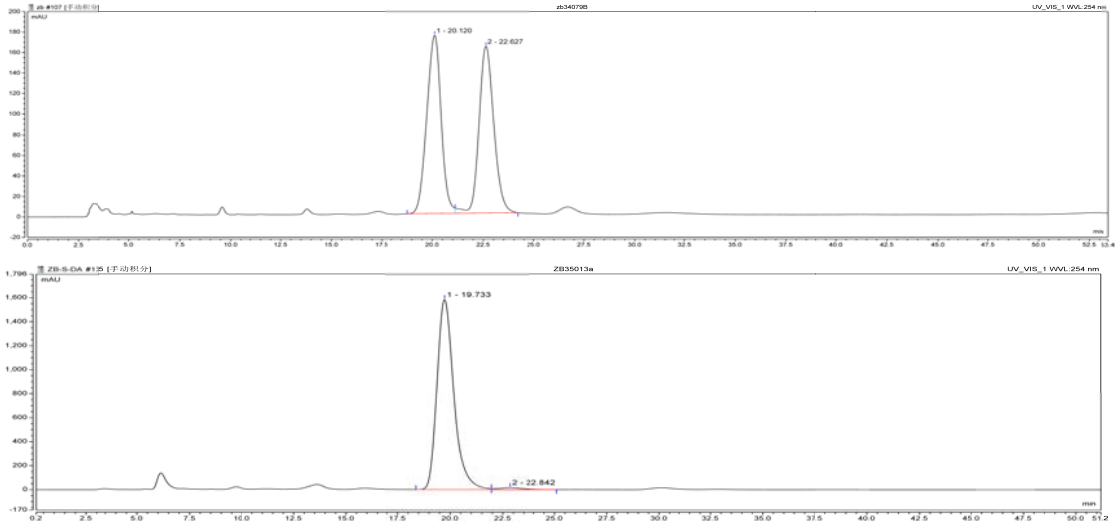


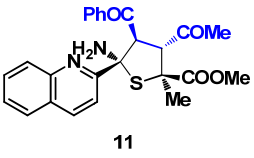


ent-**6l**

White solid, Mp 128.6–129.8 °C; 91% yield; 97% *ee*; $[\alpha]_D^{26}$ +183.4 (*c* 3.44, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.73–7.69 (m, 3H), 7.65–7.56 (m, 4H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 1H), 5.70 (d, *J* = 5.5 Hz, 1H), 3.50 (d, *J* = 5.5 Hz, 1H), 2.66 (dq, *J* = 18.2, 7.2 Hz, 1H), 2.29 (dq, *J* = 18.2, 7.2 Hz, 1H), 1.72 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 198.3, 176.6, 152.2, 146.8, 137.5, 137.0, 133.1, 129.9, 129.3, 128.4, 128.0, 127.6, 127.3, 127.2, 118.2, 79.6, 66.8, 62.3, 57.4, 39.1, 14.2, 7.6; HRMS (ESI) m/z 431.1430 ($M+H^+$), calc. for $C_{25}H_{23}N_2O_3S$ 431.1429.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.7 min (major) and 22.8 min (minor).

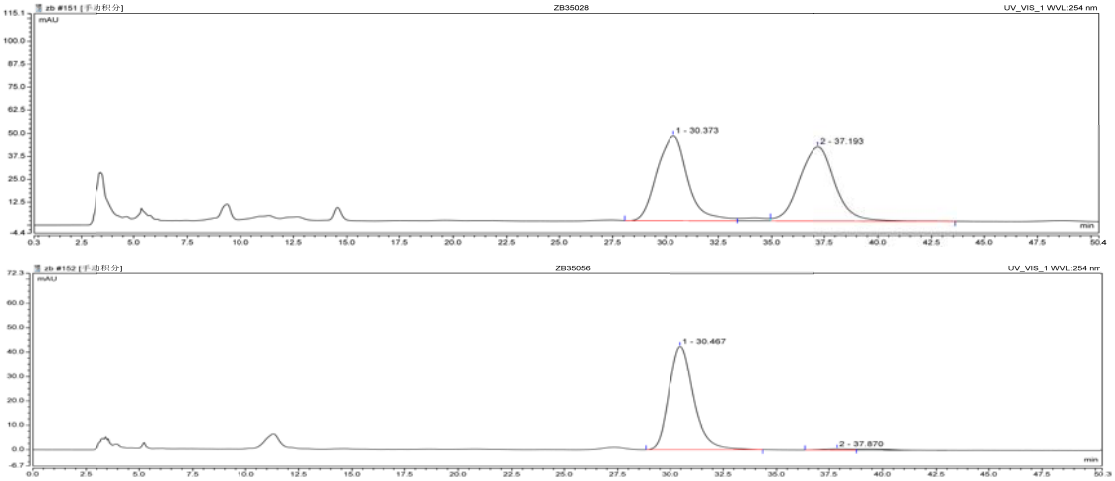


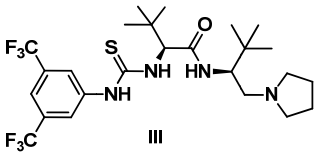


11

Green solid, Mp 121.9–123.0 °C; 73% yield; 98% *ee*; $[\alpha]_D^{26}$ +161.4 (*c* 0.94, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (ddd, *J* = 8.4, 6.3, 1.4 Hz, 1H), 7.46 (ddd, *J* = 8.4, 6.3, 1.4 Hz, 3H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 2H), 5.42 (d, *J* = 12.5 Hz, 1H), 5.25 (d, *J* = 12.5 Hz, 1H), 3.91 (s, 3H), 2.28 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 198.3, 174.0, 158.5, 146.1, 137.5, 136.6, 131.9, 129.5, 129.2, 128.1, 127.4, 127.0, 126.8, 119.3, 77.3, 62.7, 61.9, 55.0, 53.5, 30.9, 23.7; HRMS (ESI) m/z 449.1539 ($M+H^+$), calc. for $C_{25}H_{25}N_2O_4S$ 449.1535.

The *ee* was determined by HPLC analysis. CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 30.5 min (major) and 37.9 min (minor).



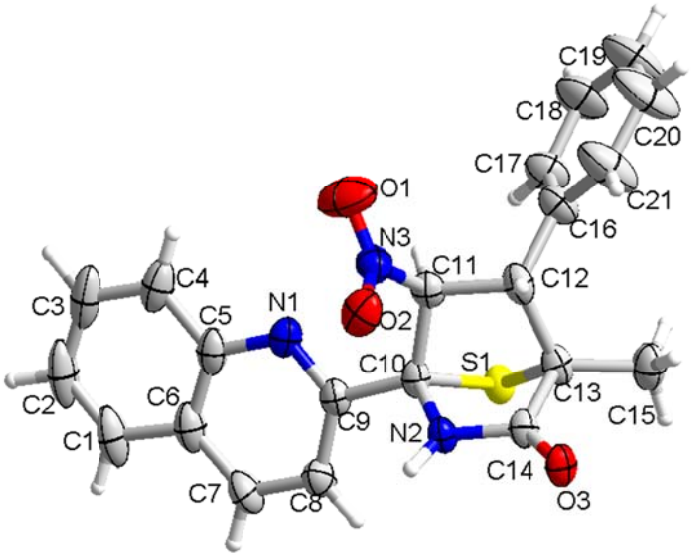


III

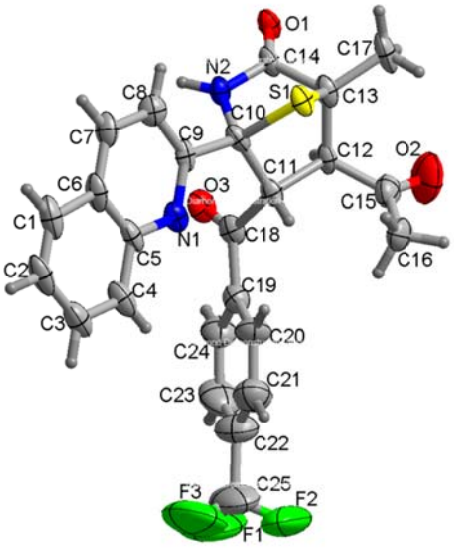
White solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.30 (s, 1H), 4.22 (s, 2H), 2.73 (s, 6H), 1.89 (s, 4H), 1.17 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.0, 172.7, 140.2, 131.6, 131.2, 130.9, 130.7, 130.3, 128.8, 128.4, 124.8, 123.9, 121.2, 117.8, 67.0, 65.6, 55.7, 54.0, 34.7, 33.8, 27.3, 26.6, 23.4; HRMS (ESI) m/z 555.2593 ($M+H^+$), calc. for $C_{25}H_{37}F_6N_4OS$ 555.2592.

14. Determination of the absolute configuration

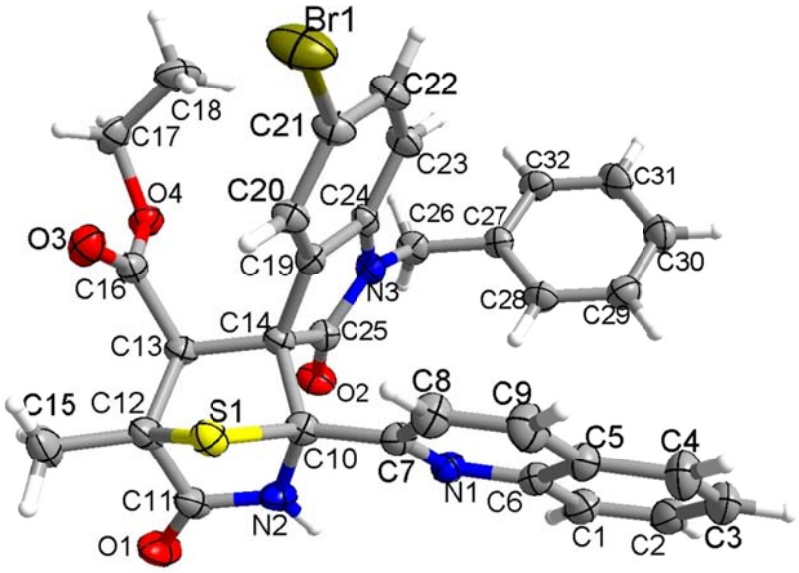
(1) Absolute configurations of the [4+2] annulation adducts **3a-n** are determined by *X*-ray structure analysis of the product **3a** (CCDC 1419583**)**



(2) Absolute configurations of the [4+2] annulation adducts **6a-s** and **9a-h** are determined by *X*-ray structure analysis of the product **6b** (CCDC 1419574)



(3) Absolute configurations of the [4+2] annulation adducts **11a-n** are determined by *X*-ray structure analysis of the product **11d** (CCDC 1463891)


Br1
C22
C18
C21
C17
C23
C32
C31
O4
C20
C24
C26
C27
O3
C19
C30
C16
N3
C28
C29
C14
C25
C13
O2
C8
C9
C15
C12
S1
C5
C4
C10
C7
N1
C6
C11
N2
C1
C2
C3
O1

15. Computational methods

All quantum chemical calculations were carried out with Gaussian 09[1]. All ΔG values are reported relative to the individual free starting materials **1**, **2** and catalyst **III.**

Optimization of minimum and transition state (TS) structures were first carried out with Becke's three parameter[2] and Lee-Yang-Parr's[3] B3LYP density functional using Pople's[4] 6-31G(d,p) basis set under the SMD[5] polarizable continuum solvent model (toluene parameters). It is important to note that Simón and Goodman[6] showed that B3LYP/6-31G(d) is adequate to model a variety of organocatalytic reactions. Subsequently, Houk *et al*[7] applied the dispersion-corrected meta-hybrid M06-2X(D3) approach towards modelling stereoselective intramolecular Aldol reaction and thiourea-amine catalyzed Nazarov cyclization with excellent qualitative agreement to experiment.

The B3LYP/6-31G(d,p) thermal and vibrational corrections from frequency calculations were combined to higher level single-point energies of the optimized geometries. The single-point energies were evaluated with Peverati and Truhlar's screened-exchange density functional MN12-SX under same polarizable continuum solvent model toluene parameters, herein termed MN12-SX/SMD.[8] The newer meta-hybrid non separable gradient MN12-SX functional was assessed to perform better in chemical energetics and thus preferred over M06-2X.[9] In conjunction with the MN12-SX/SMD, the Wiegend and Aldrich's def2-TZVPP triple zeta quality basis set was used.[10] Second order derivative or Hessian of the completed calculations were checked to verify transition state structures having only one negative eigenvalue and none for minimum.

Gibbs free energies in solution were calculated from the geometries, frequencies and improved energies using a thermocycle in which the gas-phase was treated using the standard textbook formulae for an ideal gas under the harmonic oscillator / rigid rotor approximation, and the Gibbs free energies of solvation (in toluene) were then calculated using the SMD continuum solvation model. Corrections were included to consider passage of 1 atm gas into 1M in solution, $\Delta G^{1atm \rightarrow 1M}$ as follows[11]:

$$\Delta G^{1atm \rightarrow 1M} = dN*R*T*\ln(RT/P)$$

where dN is the number of moles of gas change from reactant to product and ln(RT/P) equals to 1.89 at 298 K. We have recently shown that this approach provides an excellent quantitative description of the temperature dependent behavior of solution-phase Diels-Alder reactions.[12]

Electron density topological analyses based on the reduced density gradient was carried out with NCIplot[13] to qualify regions of non-covalent interactions especially hydrogen bonding

(H-bonding) or regions of repulsive interactions. Regions which are attractive have sign of the second density Hessian eigenvalue, $sign(\lambda_2)$, as positive and repulsive as negative. The electron density ρ(r) is set at an isovalue of 0.4 au in the $sign(\lambda_2)\rho$(r) range of -0.4 to 0.4, which corresponds to blue-green-red color scale (see Figure S1). The 3-D molecular graphics for NCIplot were rendered with VMD[14] and graphics inset corresponding to the NCIplot showing key H-bond interactions in figure 3 of the manuscript were rendered with Cylview[15].

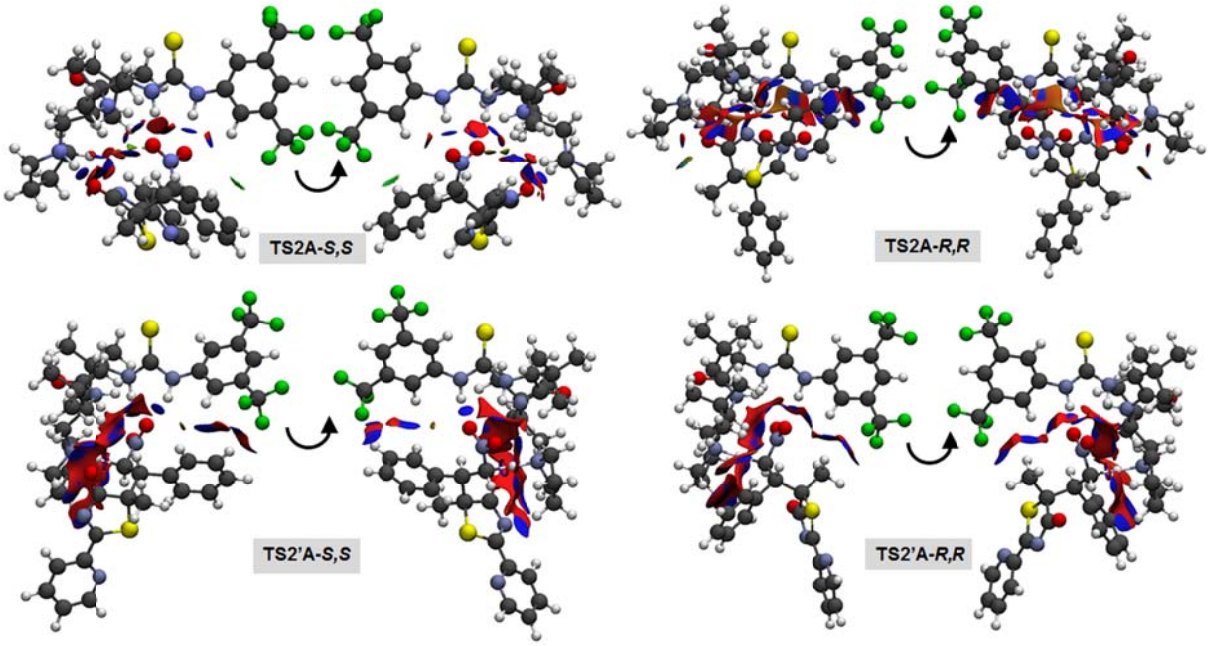


Figure S1. Non-covalent interaction isosurfaces of optimized TS structures of Mannich process (**TS2A-*S,S*** and **TS2A-*R,R***) and the protonation process (**TS2'A-*S,S*** and **TS2'A-*R,R***). Blue-green-red color scale from -0.4 < $sign(\lambda_2)\rho$(r) > 0.4 au, where blue (positive) is favorable and red (negative) is unfavorable interaction. Two images for each TS are flipped horizontally to allow viewing from the front and back sides.

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Molecule	MN12SX E	B3LYP E	$G_{correction}$	$H_{correction}$	ZPE (298K)	G_{sol} (MN12SX)
III	-2265.238831	-2265.933466	0.526197	0.640233	0.60057	-2264.703614
1	-930.478833	-930.724803	0.119136	0.169065	0.157119	-930.359697
2	-513.963184	-514.176050	0.101575	0.146955	0.136956	-513.861609
TS1A-*R,R*	-3709.692433	-3710.841985	0.796699	0.960728	0.899259	-3708.892727
TS1A-*S,S*	-3709.695202	-3710.844099	0.796696	0.961218	0.899614	-3708.895499
TS1B-*R,R*	-3709.69039	-3710.83715	0.797744	0.961166	0.899645	-3708.889639
TS1B-*S,S*	-3709.688422	-3710.838464	0.797171	0.961137	0.899743	-3708.888244
int1A-*R,R*	-3709.705159	-3710.854112	0.799168	0.96316	0.90194	-3708.902984
int1A-*S,S*	-3709.714753	-3710.863604	0.800902	0.963818	0.902572	-3708.910844
int1B-*R,R*	-3709.714366	-3710.860514	0.796381	0.961835	0.899977	-3708.914978
int1B-*S,S*	-3709.713598	-3710.861334	0.798688	0.962503	0.901149	-3708.911903
TS2A-*R,R*	-3709.699503	-3710.843566	0.804677	0.962433	0.902263	-3708.891819
TS2A-*S,S*	-3709.698245	-3710.843839	0.799844	0.962093	0.901234	-3708.895394
int2A-*R,R*	-3709.710927	-3710.853914	0.802751	0.964022	0.903051	-3708.905169
int2A-*S,S*	-3709.71474	-3710.857422	0.800695	0.963549	0.902543	-3708.911038
TS2'A-*R,R*	-3709.690718	-3710.836448	0.795499	0.957718	0.896357	-3708.892212
TS2'A-*S,S*	-3709.693888	-3710.837503	0.798308	0.957859	0.897082	-3708.892573
int2'A-*R,R*	-3709.712573	-3710.860005	0.792608	0.962243	0.899753	-3708.916958
int2'A-*S,S*	-3709.712922	-3710.861514	0.795597	0.962489	0.900231	-3708.914318

*All energy values in hatrees.

Gaussian Archive Files

Catalyst **III**

```
1\1\GINC-R1102\FOpt\RB3LYP\6-31G(d,p)\C25H36F6N4O1S1\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Catalyst III\\0,1\C,1.9345173079,0.1913285951,-1.
2675001586\O,2.7222233811,-0.0115586208,-2.1905041561\C,1.0106971573,1
.4394955675,-1.3269008674\H,0.645363335,1.4648738374,-2.355854527\N,1.
8184572705,-0.5798134111,-0.158914149\H,1.0738800145,-0.3245909597,0.4
718634769\C,2.6492454085,-1.7284155289,0.2519299286\H,2.4689319057,-1.
8051190086,1.3308211293\C,2.1719890722,-3.1040802263,-0.3402051028\C,0
.6437094855,-3.217673919,-0.1766577936\H,0.1121645481,-2.4877299589,-0
.7921152638\H,0.3374482578,-3.0747134033,0.8680231677\H,0.3043017939,-
4.2137057113,-0.4809826574\C,2.5322001042,-3.2642068952,-1.829019438\H
,2.1307405187,-2.4483810422,-2.4337829887\H,2.1251325727,-4.2074545727
,-2.2112858297\H,3.6154797385,-3.2896756892,-1.9864691966\C,2.81628368
24,-4.2514734696,0.4676217447\H,3.9049038954,-4.2836959,0.3649586651\H
,2.4316736996,-5.2156645468,0.1178654957\H,2.5824557205,-4.1737072856,
1.5365026558\C,4.1490892125,-1.4358323091,0.0511560015\H,4.7191826574,
-2.3523108328,0.28289469\H,4.3201618973,-1.1936768557,-0.9978704599\N,
4.636044141,-0.3165031866,0.8549308163\C,5.9845376224,0.1133510513,0.4
62546004\H,5.9653950685,0.5831364452,-0.5257586169\H,6.6786769798,-0.7
486247418,0.4079606765\C,6.4152538149,1.065952585,1.5896537744\H,7.495
9584795,1.0321948572,1.7529615673\H,6.15458027,2.098312689,1.340152949
1\C,4.7481579731,-0.5816959913,2.29408829\H,5.2546508957,-1.5492740071
,2.4818874798\H,3.7634183122,-0.6312522996,2.76944665\C,5.6066390903,0
.582485208,2.8266273613\H,6.2501935688,0.2545677982,3.6478160651\H,4.9
736191167,1.3868462685,3.2125657352\N,-0.1595420705,1.3332697755,-0.45
22302794\H,-0.1028967702,1.8337715807,0.4267243583\C,1.774772315,2.784
504687,-1.0410692578\C,2.8993065031,2.9798408282,-2.0762303819\H,3.382
1201824,3.9488390641,-1.9080383853\H,2.5041851409,2.9749525477,-3.0973
922727\H,3.657526666,2.1990607342,-2.0140345912\C,0.7869700397,3.96061
87813,-1.1910797265\H,1.3215996731,4.9099194184,-1.081037854\H,0.31018
95316,3.9585507434,-2.1772513457\H,-0.0082995073,3.949228743,-0.437976
7755\C,2.3846461119,2.790653866,0.3751985688\H,1.6248830384,2.71510565
84,1.1655085401\H,2.9159442158,3.7325868354,0.5487537325\H,3.094517527
2,1.9693082066,0.5168708945\C,-1.3734823931,0.8308135204,-0.8138098533
\N,-2.3408405425,1.0707516051,0.1409349841\H,-2.1224123162,1.795846689
7,0.8144984513\C,-3.6722429153,0.6197129142,0.2286350453\C,-6.34628870
77,-0.1817627483,0.5763075794\C,-4.5914077565,1.4627833248,0.868164970
7\C,-4.0936174068,-0.6367994761,-0.2249863883\C,-5.4239186959,-1.01734
21487,-0.0527575816\C,-5.9129009696,1.0586266636,1.0424324835\H,-4.277
5860816,2.441848976,1.2154116223\H,-3.3966674364,-1.299884231,-0.71585
38118\H,-7.3795857217,-0.4857340693,0.6915724522\C,-5.8582040808,-2.39
26746795,-0.4905093553\C,-6.8803771074,1.9477472162,1.7772181303\F,-5.
1116366962,-2.8626108081,-1.5100467778\F,-5.7534041112,-3.2895656308,0
.5206549455\F,-7.1495013658,-2.407385535,-0.8895254796\F,-6.9916248115
,1.5939605879,3.080272198\F,-6.4996084107,3.2446310506,1.7564853412\F,
-8.1213692613,1.8803497818,1.2496709851\S,-1.6294862095,0.0131052177,-
2.2613320743\\Version=ES64L-G09RevD.01\State=1-A\HF=-2265.9334657\RMSD
=3.062e-09\RMSF=3.879e-06\Dipole=1.5061837,1.3993149,2.5813559\Quadrup
ole=-5.5669599,10.3516241,-4.7846643,-1.1306324,8.696064,-1.3952121\PG
=C01 [X(C25H36F6N4O1S1)]\\@
```

Nucleophile **1**

```
1\1\GINC-R187\FOpt\RB3LYP\6-31G(d,p)\C9H8N2O1S1\ROOT\08-Dec-2015\0\\#
freq=noraman rb3lyp/6-31g** opt=(maxcyc=200) scf=maxcyc=200 scrf=(smd,
solvent=toluene)\\thialzone\\0,1\C,2.1554781473,0.2865250426,-1.087641
2741\N,0.7608895514,0.2468581964,-1.2569431491\C,0.1370455655,0.142805
6312,-0.1285469919\S,1.0717769464,0.0603537612,1.3773149285\C,2.614494
6534,0.151016418,0.3843888075\O,2.9433634364,0.4184260807,-2.000445150
5\C,3.5631509442,1.2777329633,0.7972476518\H,4.4126237243,1.2886236346
,0.1081342314\H,3.940527843,1.1268027194,1.8118754788\H,3.067386483,2.
2514982769,0.7525850411\C,-1.3338590343,0.088377536,-0.0324464268\C,-4
.0405584073,-0.0352659537,0.2560712795\C,-2.128222856,0.1264854004,-1.
1841882541\C,-3.1607699297,-0.0653097693,1.3431224334\C,-3.5109969468,
0.0627724193,-1.0293982231\H,-1.6581958472,0.2038071719,-2.1574254572\
H,-3.540957238,-0.1406251873,2.3592228336\H,-4.162067137,0.0893912875,
-1.8975925336\H,-5.1115667728,-0.0878153923,0.4216019107\H,3.123020701
8,-0.8148681183,0.477055709\N,-1.8356267876,-0.0062094085,1.2097094748
\\Version=ES64L-G09RevD.01\State=1-A\HF=-930.7248031\RMSD=3.756e-09\RM
SF=1.642e-05\Dipole=-1.6832476,-0.1296111,0.7592088\Quadrupole=11.3769
612,-3.1382543,-8.2387069,0.2600011,8.9690621,0.7530011\PG=C01 [X(C9H8
N2O1S1)]\\@
```

Electrophile **2**

1\1\GINC-R228\FOpt\RB3LYP\6-31G(d,p)\C8H7N1O2\ROOT\08-Dec-2015\0\\# fr
eq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(smd,solv
ent=toluene)\\Nitro-olefin\\0,1\C,-1.2918462576,0.2423683973,0.0001013
845\C,-0.1927246612,-0.5281051296,-0.0004433292\N,1.1237692805,0.06778
88413,0.0004942712\O,1.2422449181,1.2976328932,0.0017773572\O,2.076183
0956,-0.7219065727,-0.0001516785\H,-0.1459416234,-1.6073583437,-0.0015
662802\H,-1.1285640753,1.3171325925,0.0012663455\C,-2.6785138305,-0.20
96379835,-0.0007085052\C,-3.6949747019,0.7642788139,0.0000757672\C,-3.
0475694702,-1.5700876464,-0.0022366964\C,-5.0374804338,0.3940614646,-0
.0006346018\H,-3.4216752009,1.8156329434,0.0012512356\C,-4.3878067081,
-1.9366763516,-0.0029424809\H,-2.2835799191,-2.3407096134,-0.002869839
7\C,-5.386927374,-0.9569120605,-0.0021452073\H,-5.8091603691,1.1576023
494,-0.0000122151\H,-4.6584773182,-2.9879737308,-0.0041181271\H,-6.432
6748107,-1.2489794834,-0.0027037997\\Version=ES64L-G09RevD.01\State=1-
A\HF=-514.1760499\RMSD=5.485e-09\RMSF=2.370e-05\Dipole=-2.5496758,-0.5
367424,-0.0011302\Quadrupole=-6.6220613,5.777527,0.8445344,-2.3985822,
-0.0040124,0.0046836\PG=C01 [X(C8H7N1O2)]\\@

TS1A-*R,R*

1\1\GINC-R2526\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\0
\\# freq=noraman rb3lyp/6-31g** opt=(ts,calcfc,noeigen,maxcyc=200) scf
=maxcyc=200 scrf=(smd,solvent=toluene) iop(1/8=1)\\TS for 1st C-C addi
tion conf. 1: R(elec),R(nuc) (tol opt; cat III)\\0,1\C,-1.2494256521,-
3.3217510012,1.5412784212\O,-1.8428046469,-4.3656027817,1.8276263161\C
,-0.4497597284,-2.559354909,2.6260201828\H,0.2602087816,-3.3012465511,
3.0030594856\N,-1.2451761302,-2.7862125825,0.28985455\H,-0.7808328521,
-1.8954887562,0.1743628054\C,-1.8576129575,-3.3601722141,-0.917472701\
H,-1.8278499219,-2.5357806327,-1.639196206\C,-1.0388791819,-4.51870663
23,-1.5987836517\C,0.4270887284,-4.0672780818,-1.73737922\H,0.90505582
77,-3.9265574591,-0.7649756148\H,0.5059624251,-3.1284151269,-2.2995787
67\H,1.0027685127,-4.8233342217,-2.2814790697\C,-1.0893396649,-5.84796
52111,-0.821879708\H,-0.6607399659,-5.755668468,0.1767218786\H,-0.5232
31928,-6.6112271309,-1.3679756012\H,-2.1121938814,-6.2231834928,-0.707
5903777\C,-1.6028345021,-4.7442357847,-3.0189780114\H,-2.6271332884,-5
.1329777883,-3.0139811842\H,-0.9905264953,-5.4817460953,-3.5476638974\
H,-1.58864617,-3.8229103883,-3.6137670951\C,-3.3356732842,-3.704894339
,-0.6492774884\H,-3.712009638,-4.4685146773,-1.3305665645\H,-3.4422252
642,-4.0690386299,0.3709633969\N,-4.2271605949,-2.5055327939,-0.812865
0749\C,-5.5429373154,-2.638086815,-0.078368513\H,-5.3825345194,-2.3733
92849,0.9675433067\H,-5.8572679963,-3.6833831058,-0.1440380173\C,-6.48
38171309,-1.7168153642,-0.8438946751\H,-7.5322605662,-1.9400666394,-0.
6338491797\H,-6.2844761741,-0.6767711186,-0.570893015\C,-4.5636787147,
-2.1539368045,-2.2613046213\H,-4.1991620575,-2.9499487617,-2.910442450
6\H,-4.0326332534,-1.2325820176,-2.4996800407\C,-6.0908788583,-1.98049
98185,-2.3063102216\H,-6.5659902056,-2.8989378935,-2.6659348678\H,-6.3
808054087,-1.1705739794,-2.9791623775\N,0.355853338,-1.4792963388,2.07
16994486\H,-0.0934681591,-0.5614948431,1.9574385303\C,-1.3503559441,-2
.097985181,3.8385825763\C,-1.6645688365,-3.3266129872,4.7163591637\H,-
2.3136754954,-3.0354634606,5.5504463822\H,-0.7472925285,-3.7501540105,
5.1411523283\H,-2.1625751477,-4.1100490194,4.1428874393\C,-0.573712967
1,-1.0787483301,4.6963719503\H,-1.1349220511,-0.8748932807,5.615190671
2\H,0.4098327327,-1.4626878847,4.9875683658\H,-0.4297618321,-0.1246994
225,4.1820154774\C,-2.6714933697,-1.4628475031,3.3618077972\H,-2.51466
1573,-0.6375496995,2.6615538247\H,-3.225530459,-1.0667376469,4.2204314
766\H,-3.3121451935,-2.2088172023,2.8792439051\C,1.6929735081,-1.56133
09879,1.8353043108\N,2.2268268077,-0.3588225478,1.447331538\H,1.628746
9459,0.4762828542,1.5451807061\C,3.5112711566,-0.0572026143,0.96667182
36\C,5.9927017002,0.7744437113,-0.0865689268\C,4.0027612568,1.23410303
1,1.2250618834\C,4.2722737321,-0.9268916298,0.1762284079\C,5.498010017
3,-0.5020733052,-0.3399626041\C,5.2274126513,1.6371374954,0.7016425452
\H,3.414015762,1.9196975698,1.8230915413\H,3.9072354731,-1.9224584426,
-0.0342573279\H,6.9427620745,1.0925781922,-0.4974455989\C,-2.876719734
7,0.7725079255,-0.7296040773\N,-1.6250849053,0.3985950223,-1.234024007
5\C,-1.1329174248,1.3261053536,-2.0113431405\S,-2.1280474027,2.7583278
343,-2.2627711835\C,-3.2399420224,2.1546194918,-1.0236388251\O,-3.6235
054464,-0.0191930259,-0.1010474722\H,-3.764430723,-1.6346671385,-0.418
089522\C,-4.6985294412,2.5164493832,-1.1077982451\H,-5.2088667029,2.21
57359513,-0.1892084646\H,-5.186176099,1.9939127496,-1.941758526\H,-4.8
53728159,3.5876853737,-1.2503322896\C,0.1664670238,1.2454598213,-2.697
1820778\C,2.5445635579,1.2218132697,-4.0443273747\C,1.0876826223,0.228
0506119,-2.4162892514\C,2.2995974688,0.2225963971,-3.1040007973\C,1.56
44456269,2.1967129969,-4.2518636983\H,0.8586920508,-0.5165441079,-1.66
3879087\H,3.0478925842,-0.5366240461,-2.9002194705\H,1.7240701047,2.99
51738219,-4.9732744165\H,3.4760470658,1.2560520986,-4.5994318758\C,-2.
5294928753,3.1141587213,0.8472111455\C,-1.124120071,3.1270503441,0.886
9131861\N,-0.4195127932,2.0467121519,1.3263483704\O,-1.0295281435,0.98
3573429,1.6635278118\O,0.8454863953,2.1233573491,1.4110303967\H,-0.508

4752287,3.9707213224,0.6163714551\H,-3.0058722822,2.3298805887,1.42725
10525\C,-3.2501971741,4.4047915483,0.8056479118\C,-4.4370828776,4.5504
138315,1.5456047124\C,-2.7831635948,5.5097256585,0.0692621475\C,-5.128
0036836,5.7612003981,1.5618536723\H,-4.8072117657,3.7097503149,2.12585
44666\C,-3.4801878098,6.7156873746,0.0787523428\H,-1.8756749689,5.4237
222575,-0.5195868372\C,-4.6539053112,6.8480186877,0.8257004523\H,-6.03
6795544,5.8547669059,2.1493452473\H,-3.1048998442,7.5562196481,-0.4977
862961\H,-5.1918718219,7.7913940977,0.8346089122\C,6.2338672307,-1.434
5456867,-1.2612432639\C,5.7720975297,3.0034018586,1.0196060122\F,5.597
1646813,-1.5460095147,-2.4611944401\F,6.3189001993,-2.6852967204,-0.76
13922435\F,7.4896759801,-1.0174832422,-1.5273128215\F,6.7265217715,2.9
538694761,1.9800900021\F,6.3508011139,3.5738079731,-0.0642401416\F,4.8
172723195,3.8504130839,1.4577153548\S,2.586894857,-2.9938714215,2.0216
885915\N,0.4031987412,2.2168281812,-3.5976451634\\Version=ES64L-G09Rev
D.01\State=1-A\HF=-3710.8419853\RMSD=2.761e-09\RMSF=2.005e-06\Dipole=-
6.6537827,-0.2097452,-3.366587\Quadrupole=17.2215166,-9.4653241,-7.756
1925,17.5997242,-2.5011595,16.9565079\PG=C01 [X(C42H51F6N7O4S2)]\\@

TS1A-*S,S*

1\1\GINC-R2536\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\08-Dec-2015\0
\\# freq=noraman rb3lyp/6-31g** opt=(ts,calcfc,noeigen,maxcyc=200) scf
=maxcyc=200 scrf=(smd,solvent=toluene)\\TS for 1st C-C addition conf.
2: S(elec),S(nuc) (tol opt; cat III)\\0,1\C,1.0158485385,-3.7267428083
,0.3060019318\O,1.6919049613,-4.7444672011,0.4974735651\C,-0.087709557
2,-3.7157431807,-0.7931549157\H,-0.7778829127,-4.5051658274,-0.4796912
529\N,1.144266676,-2.5895557909,1.0305560215\H,0.5802611237,-1.7901271
804,0.7593720044\C,1.88116759,-2.3739553205,2.2856050266\H,1.934191190
3,-1.2833461682,2.3691135934\C,1.0985704846,-2.8539980721,3.5681699687
\C,-0.3559862141,-2.3533319577,3.4727860153\H,-0.9087437239,-2.8514277
945,2.6729473564\H,-0.401056048,-1.2728681749,3.2925661048\H,-0.884025
6361,-2.5563869678,4.4104911061\C,1.0988316661,-4.3857352958,3.7278514
508\H,0.6636284677,-4.8879510321,2.8614466398\H,0.5135381746,-4.667466
6049,4.61051337\H,2.1089975959,-4.7859991239,3.870016884\C,1.738617494
8,-2.2096779384,4.8174243155\H,2.7448800289,-2.5871574923,5.0277049442
\H,1.1301433599,-2.4299911654,5.7005963717\H,1.7989062279,-1.119109451
2,4.7237250257\C,3.3289579307,-2.8860826674,2.2527207341\H,3.751193894
,-2.7993536314,3.2537440353\H,3.3838708192,-3.923760604,1.9267960742\N
,4.2275927282,-2.0693443254,1.3616521661\C,4.1909800991,-2.4235041906,
-0.1184753797\H,3.5676250685,-1.6716170548,-0.5999864055\H,3.735473156
7,-3.4074906326,-0.2192969817\C,5.6551447134,-2.3790317519,-0.60023585
68\H,6.0364617708,-3.3948033308,-0.7429054896\H,5.746208067,-1.8516043
098,-1.5523438812\C,5.6748553376,-2.1311313829,1.7795831825\H,5.908309
3068,-3.1687579417,2.0369742995\H,5.8110391804,-1.4987015443,2.6585710
228\C,6.4233116267,-1.6770513103,0.5336290935\H,7.4804051956,-1.950283
558,0.569923244\H,6.3537160195,-0.5894397871,0.433769629\N,-0.86802681
05,-2.4855827039,-0.7873886927\H,-0.4253067533,-1.6409368323,-1.144480
7355\C,0.400246091,-4.0776249473,-2.2457853644\C,0.9681811556,-5.50967
11706,-2.284626333\H,1.2431718029,-5.7680533907,-3.3140379016\H,0.2210
608523,-6.2373129148,-1.9490269691\H,1.844829869,-5.6216369471,-1.6468
345077\C,-0.8130105552,-4.0210795775,-3.1973208927\H,-0.5147278109,-4.
3607900948,-4.1952242069\H,-1.6241083035,-4.6699341044,-2.8519630672\H
,-1.2140776345,-3.0088736344,-3.2993884849\C,1.4682169765,-3.084053593
1,-2.7386855655\H,1.1130449172,-2.0475417981,-2.7116333477\H,1.7366368
435,-3.3044352108,-3.7780895646\H,2.3830943587,-3.1496006497,-2.143650
1184\C,-2.1768439596,-2.370147984,-0.4119742043\N,-2.6101064814,-1.075
2918643,-0.5317388515\H,-1.8669355226,-0.409416706,-0.7801451727\C,-3.
8612449162,-0.4629895918,-0.3887406491\C,-6.267337465,1.0098727665,-0.
2117784311\C,-3.8763901475,0.9300696333,-0.6082720042\C,-5.0648560553,
-1.1074372187,-0.0759081033\C,-6.2458591158,-0.362835702,0.0058444885\
C,-5.0614546344,1.6469348686,-0.5207434016\H,-2.9530038511,1.439275484
2,-0.8632700415\H,-5.0719197649,-2.1741077341,0.0976657568\H,-7.192105
1579,1.5691812357,-0.1506475955\C,3.5137247339,1.3120607096,0.71545074
86\N,3.4353428663,0.8601419801,-0.6042412254\C,3.4214319428,1.85641395
44,-1.4490677248\S,3.5225398269,3.4730183392,-0.7633226355\C,3.3542839
932,2.7520146591,0.8449665478\O,3.7098302728,0.5397343035,1.6901447015
\H,3.9496490436,-1.0383955386,1.4430540095\C,3.9253973281,3.4552311098
,2.0434820277\H,3.6249286298,2.9306431336,2.9544919141\H,3.5970322241,
4.4940782489,2.1162480744\H,5.0229880012,3.4497909996,2.0128113058\C,3
.3518579301,1.7113473121,-2.911697518\C,3.2335848972,1.5786909953,-5.6
400166394\C,3.188463704,0.4585707505,-3.516951851\C,3.1291924925,0.398
0648797,-4.9067952571\C,3.3951073638,2.7804742037,-4.9443785616\H,3.10
22940419,-0.4305731663,-2.9051008988\H,2.9978145278,-0.5559111369,-5.4
083186836\H,3.480472593,3.7221685669,-5.4823219439\H,3.1895083823,1.57
62954582,-6.7240823519\C,1.1098952312,2.8023049541,1.1370603145\C,0.46
68257665,2.3323430245,-0.0225953194\N,0.2137412708,1.0044988827,-0.191
8649519\O,0.5792872568,0.161651533,0.6735014765\O,-0.4250486311,0.6232
322782,-1.2393300793\H,0.0888847191,2.9566785211,-0.8167322718\H,1.200

2137909,2.0793048308,1.94125414\C,0.930165457,4.2052586432,1.554847777
9\C,0.8842622772,4.5067868656,2.928511635\C,0.7690736788,5.2591247298,
0.6348467222\C,0.673961038,5.8120604308,3.3696767097\H,0.9985497954,3.
7042826597,3.6516924533\C,0.5677373189,6.5637831889,1.0777399269\H,0.8
094224362,5.0592091585,-0.4303484037\C,0.5167398418,6.846127392,2.4455
062158\H,0.6314944063,6.0205816898,4.4347092484\H,0.4467676066,7.36307
07278,0.3524627115\H,0.3538433451,7.8642772911,2.7864519847\C,-7.51481
15181,-1.1026915143,0.3377486562\C,-5.0508980167,3.1396914384,-0.70595
21086\F,-7.7779092498,-2.0736882391,-0.5676376078\F,-7.4374606391,-1.7
118700056,1.5436233014\F,-8.5930503938,-0.2884046249,0.3719672142\F,-5
.0616597656,3.7925309952,0.4816767995\F,-3.9593678233,3.5680172099,-1.
3774490829\F,-6.1378802626,3.5673785053,-1.3888464933\S,-3.0940101015,
-3.6822484954,0.1404994963\N,3.4535620403,2.8536921205,-3.6145975558\\
Version=ES64L-G09RevD.01\State=1-A\HF=-3710.8440986\RMSD=2.040e-09\RMS
F=5.596e-07\Dipole=6.5299047,0.8539562,-0.1043642\Quadrupole=-9.041444
6,-15.4603478,24.5017925,-26.1317886,3.2768767,3.9374612\PG=C01 [X(C42
H51F6N7O4S2)]\\@

TS1B-*R,R*

1\1\GINC-R3133\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\14-Dec-2015\0
\\# freq=noraman rb3lyp/6-31g** opt=(ts,calcfc,noeigen,maxcyc=200) scf
=maxcyc=200 scrf=(smd,solvent=toluene) iop(1/8=1)\\TS for 1st C-C addi
tion conf. 2: R(elec),R(nuc) (tol opt; cat III)\\0,1\C,-1.0268779147,-
3.5958345421,-0.4230891725\O,-1.5544048367,-4.6817388658,-0.6873851355
\C,-0.0501149664,-3.5001277816,0.7764911213\H,0.6387244583,-4.33796733
66,0.6446746296\N,-1.2641244437,-2.454034009,-1.1227133582\H,-0.776437
5178,-1.6067730031,-0.8472267112\C,-2.1454375587,-2.2998791434,-2.2919
175902\H,-2.3003350157,-1.2178572758,-2.3570236978\C,-1.4976923284,-2.
7057555627,-3.667340745\C,-0.0712856307,-2.1272417023,-3.7330153773\H,
0.6022452581,-2.6270292745,-3.0332904283\H,-0.0566002703,-1.0549405656
,-3.5066449305\H,0.3409480954,-2.2611349594,-4.7386353711\C,-1.4373222
935,-4.2303352898,-3.8786680242\H,-0.8789687049,-4.7290670509,-3.08458
2344\H,-0.9475596136,-4.4515425459,-4.8337026474\H,-2.4344310886,-4.68
37286353,-3.9158049313\C,-2.324736349,-2.0645053265,-4.802055738\H,-3.
3537353899,-2.4380160234,-4.8466466858\H,-1.8661110238,-2.2893435135,-
5.7703705347\H,-2.3651146068,-0.9729718972,-4.7046304428\C,-3.51345765
55,-2.9646355472,-2.040904375\H,-4.0371865055,-3.1700488965,-2.9742300
338\H,-3.3622626565,-3.9026915215,-1.5103477409\N,-4.4377777525,-2.109
9956277,-1.2103532352\C,-5.4320915211,-2.900236137,-0.400841285\H,-4.9
051906024,-3.411007976,0.4063237222\H,-5.8674958245,-3.6466183802,-1.0
716883353\C,-6.4531336816,-1.8574302725,0.0585970593\H,-7.4395191895,-
2.3082838061,0.1852492368\H,-6.1407937884,-1.4301895074,1.0127491339\C
,-5.2899949962,-1.1419237577,-1.9951053348\H,-5.6587510401,-1.67887096
98,-2.8723077857\H,-4.6690530187,-0.3066054827,-2.3175029192\C,-6.4317
320156,-0.7545240228,-1.0383508111\H,-7.3739813091,-0.6971896879,-1.58
79445336\H,-6.2522507934,0.2238639111,-0.5887229946\N,0.7664280183,-2.
2972464947,0.7244383706\H,0.3344015602,-1.4121008421,0.986251783\C,-0.
7637120427,-3.6852918423,2.1682328201\C,-1.2811727611,-5.1308998083,2.
302548465\H,-1.7610433183,-5.2618782356,3.2794718092\H,-0.4607443986,-
5.8538586909,2.2343493817\H,-2.0039724888,-5.3785267136,1.5239266272\C
,0.2717950286,-3.4455984713,3.2845614298\H,-0.1851494403,-3.6381373567
,4.2617666033\H,1.1314448976,-4.1159000098,3.1805780092\H,0.6543505862
,-2.4213509478,3.2867909497\C,-1.9436238993,-2.7074043154,2.3276041389
\H,-1.6652365836,-1.6640113044,2.1554035467\H,-2.3597651447,-2.7776752
082,3.3386780898\H,-2.753445894,-2.9441881172,1.6302223111\C,2.0525229
421,-2.2417135832,0.2724895044\N,2.4137696423,-0.9500332776,-0.0195611
447\H,1.6108238866,-0.3395672393,-0.2303810639\C,3.6550474468,-0.40259
66911,-0.3629220536\C,6.0442659412,0.9331323781,-1.0394814964\C,3.6297
102861,0.7549935673,-1.1574827925\C,4.8889352131,-0.8889351707,0.09277
35392\C,6.0626706436,-0.2192841797,-0.2539909841\C,4.8116260095,1.4159
842794,-1.4795416842\H,2.6764871577,1.1346306782,-1.5093864208\H,4.927
9512469,-1.7709171654,0.7153517315\H,6.9628845072,1.4504885612,-1.2863
01911\C,-0.233318,1.2706287743,0.2570880369\N,-0.3745320886,0.80305303
53,1.568180898\C,-0.5424366178,1.7877194325,2.4112139065\S,-0.54514980
56,3.4098239739,1.7319620933\C,-0.491033217,2.6933514321,0.1163560769\
O,0.0984897971,0.5084669816,-0.6889005446\H,-3.8650631699,-1.502781157
5,-0.5566791805\C,0.1365346888,3.4520498057,-1.0190392383\H,-0.0576703
828,2.9318682403,-1.9610127206\H,1.225787303,3.5100941973,-0.899507471
5\H,-0.2446245144,4.4720055149,-1.1019730478\C,-0.6877303226,1.6396324
353,3.867742865\C,-0.9422987996,1.5087591521,6.587166069\C,-0.65811607
91,0.3833184947,4.4855636584\C,-0.7868529211,0.3236543437,5.8706751625
\C,-0.9583646048,2.7147214738,5.8798444273\H,-0.5383562575,-0.50997825
89,3.8871303326\H,-0.766288361,-0.6346866994,6.3805291538\H,-1.0741930
365,3.6604879708,6.4049981647\H,-1.0470962448,1.5069102992,7.667082192
4\C,-2.6831189544,2.5453816384,-0.418516486\C,-3.420343274,1.992904818
2,0.6415897705\N,-3.5899934534,0.6422670075,0.7687948414\O,-2.99607406
35,-0.1446448323,-0.0570344635\O,-4.3412508298,0.1785158664,1.66185442

05\H,-3.9528979789,2.5653631706,1.3852836669\H,-2.4231194814,1.8554607
836,-1.2146816203\C,-2.9417484917,3.9375780853,-0.8365372228\C,-2.8516
375777,4.2689705493,-2.2010437664\C,-3.3089763165,4.9495690665,0.07119
88035\C,-3.1295141813,5.5600635518,-2.6468766445\H,-2.5701728134,3.500
9239671,-2.9159093445\C,-3.5780376349,6.2410444912,-0.3749577572\H,-3.
3736060112,4.7285001506,1.1310284197\C,-3.4927840914,6.5520733112,-1.7
348234534\H,-3.0605614184,5.7909835502,-3.7059093706\H,-3.8561737414,7
.0083763035,0.3416516395\H,-3.7066060747,7.5596057056,-2.0790651567\C,
7.3842487947,-0.7846445212,0.1943434067\C,4.759651238,2.6283696698,-2.
3677397888\F,7.2892320863,-1.4230648133,1.3814744624\F,7.8736623094,-1
.6823356927,-0.6936744338\F,8.3255297942,0.1784246665,0.3303621142\F,4
.8525051812,2.2985491759,-3.6786883034\F,3.6010880724,3.3162947561,-2.
2253694373\F,5.769626383,3.4889251829,-2.1113743603\S,3.0370559422,-3.
6016942212,0.0595603102\N,-0.8331697299,2.7873673588,4.5548847073\\Ver
sion=ES64L-G09RevD.01\State=1-A\HF=-3710.8371502\RMSD=5.153e-09\RMSF=2
.423e-06\Dipole=-7.0887648,1.0666892,-0.4357827\Quadrupole=-3.4679904,
-19.1018329,22.5698233,20.8968404,19.795618,1.6488922\PG=C01 [X(C42H51
F6N7O4S2)]\\@

TS1B-*S,S*

1\1\GINC-R2649\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\0
\\# freq=noraman rb3lyp/6-31g** opt=(ts,calcfc,noeigen,maxcyc=200) scf
=maxcyc=200 scrf=(smd,solvent=toluene)\\TS for 1st C-C addition conf.
1: S(elec),S(nuc) (tol opt; cat III)\\0,1\C,0.870988939,-3.1308271147,
-1.9638942971\O,1.5060553727,-4.0579824836,-2.4742611134\C,-0.11268449
69,-2.2884894137,-2.8141336201\H,-0.8575332408,-3.0076475245,-3.168435
2361\N,0.9685370738,-2.7937712606,-0.6502250747\H,0.4039754789,-2.0142
659844,-0.3433791896\C,1.7489386406,-3.4880891003,0.3843327377\H,1.773
2521619,-2.7772004739,1.2186612001\C,1.0516306974,-4.7723361692,0.9703
470707\C,-0.3972097314,-4.4109587457,1.3497378509\H,-0.9980853208,-4.1
518585564,0.4749605207\H,-0.4325722578,-3.5661818823,2.0494039652\H,-0
.8800095878,-5.2619519928,1.8412115166\C,1.0369528256,-5.9582329853,-0
.0123650007\H,0.4881153082,-5.7257707663,-0.9258458456\H,0.556864438,-
6.8209408988,0.4634297181\H,2.046107685,-6.2678392044,-0.3042895172\C,
1.7883771185,-5.1948895591,2.259039696\H,2.8133480514,-5.5347590763,2.
0737066854\H,1.261131947,-6.0321053844,2.7279066385\H,1.8240352948,-4.
3818921333,2.9938664213\C,3.2032209281,-3.7050257137,-0.0894383178\H,3
.6330106595,-4.6215319439,0.3162863438\H,3.2275852443,-3.7741668687,-1
.1748322311\N,4.1189182019,-2.5857665212,0.3290695157\C,5.3964428045,-
2.5533385816,-0.4902586478\H,5.2194856784,-1.9353588233,-1.3717734099\
H,5.6122063257,-3.5772980507,-0.8061682646\C,6.4576007396,-2.029799938
5,0.47117995\H,7.4648802319,-2.2910842864,0.1379974495\H,6.3821612944,
-0.9433616426,0.5602135428\C,4.5322167296,-2.6311127974,1.801591314\H,
4.056921206,-3.4903482415,2.2723721937\H,4.1749781737,-1.7050226016,2.
2481757454\C,6.0646620261,-2.6985352144,1.7968237518\H,6.4046816522,-3
.7400266885,1.8147075126\H,6.4841201755,-2.1927260082,2.6694175117\N,-
0.8346693794,-1.3125426033,-2.0126853853\H,-0.3847433036,-0.4091869315
,-1.8325380984\C,0.5622785717,-1.6289005311,-4.0772222758\C,0.89709614
35,-2.720477347,-5.1133923583\H,1.3617521412,-2.2641150228,-5.99524905
17\H,-0.0106555575,-3.2366386322,-5.446738518\H,1.5768455607,-3.469040
0634,-4.7055664891\C,-0.4335908945,-0.6449243208,-4.7247360399\H,-0.02
49664855,-0.2863768518,-5.6760334373\H,-1.3941437369,-1.1263692548,-4.
9373099337\H,-0.624953455,0.2309223259,-4.0983640461\C,1.8469022868,-0
.8716145794,-3.6911633381\H,1.6687654155,-0.1246107306,-2.9109989116\H
,2.2510543148,-0.3468668341,-4.5641375189\H,2.6225944651,-1.555500048,
-3.3322677237\C,-2.1316115364,-1.4246888583,-1.6110196576\N,-2.5496668
177,-0.2932389833,-0.9587489604\H,-1.8238880459,0.4232626958,-0.855155
9244\C,-3.7662625394,0.0050771131,-0.3243040026\C,-6.1162289337,0.7927
326782,1.0125155205\C,-3.7019294376,0.8317444556,0.8067964454\C,-5.018
8517277,-0.417175689,-0.7931335613\C,-6.1731187493,-0.0276816879,-0.11
49468469\C,-4.8686259927,1.2213439664,1.4623241577\H,-2.7334742543,1.1
447786821,1.1834752743\H,-5.0824644567,-1.0480098566,-1.6675941216\H,-
7.0213763819,1.0811627275,1.5329507064\C,0.2766900213,1.8900942027,-0.
2441647281\N,0.3426903813,1.2006512512,0.9703896913\C,0.7533395975,1.9
784636959,1.9335904445\S,1.1057759718,3.6520044781,1.5076269733\C,0.84
45884176,3.2289676686,-0.191223101\O,-0.2231662365,1.3864296945,-1.280
0895161\H,3.6416997041,-1.6554221333,0.1620460893\C,0.344175537,4.2800
44108,-1.1434185684\H,0.3285185315,3.8798378548,-2.1597791171\H,0.9629
473132,5.1798872203,-1.1346860836\H,-0.6829129223,4.5729373475,-0.8906
403317\C,0.895880758,1.5449397039,3.3317457798\C,1.1610472024,0.849485
5255,5.9598126641\C,0.5930508687,0.2303836673,3.711434969\C,0.72995823
15,-0.1172125516,5.0522145426\C,1.4368786531,2.134135704,5.4825711931\
H,0.2521604204,-0.4763756526,2.9640391563\H,0.4998733434,-1.1250213763
,5.3848124068\H,1.7716851195,2.9148009385,6.1622179763\H,1.279277359,0
.6215267588,7.0139883093\C,2.8724385484,2.6236745992,-0.9188022706\C,3
.6220131293,2.0965981128,0.1490024554\N,3.6729656806,0.7687735099,0.44
38439522\O,3.0177088704,-0.0911139929,-0.250675924\O,4.4177410473,0.38

1755755,1.3919390625\H,4.2494969011,2.6909735548,0.7946132476\H,2.4565
24185,1.8934624711,-1.6052129631\C,3.3072108391,3.8913932417,-1.542952
9607\C,3.157855775,4.0520694049,-2.9320757249\C,3.8850718747,4.9441878
408,-0.8085313032\C,3.5838077132,5.2162097995,-3.5698592791\H,2.713608
1223,3.2490196601,-3.5136036005\C,4.3029335148,6.1098337967,-1.4461376
029\H,3.9982539917,4.8568912653,0.2673886314\C,4.1573260336,6.25064386
91,-2.8292340263\H,3.4661652669,5.3144747835,-4.6451380543\H,4.7439789
127,6.9120148998,-0.8615064949\H,4.4868629825,7.1598931811,-3.32322191
17\C,-7.5217377013,-0.4304792079,-0.6499347249\C,-4.779136293,2.150236
7042,2.6424816817\F,-7.4617037506,-1.5346500338,-1.4217439927\F,-8.069
3746519,0.5513786122,-1.4086013285\F,-8.4024907759,-0.6798705635,0.347
1857564\F,-3.6304404704,1.9820357488,3.3359427274\F,-4.8160799961,3.45
02831257,2.2618232882\F,-5.8020898038,1.969648852,3.5078561891\S,-3.07
25411061,-2.8131371949,-1.8566030575\N,1.3093362058,2.4822729131,4.201
6764882\\Version=ES64L-G09RevD.01\State=1-A\HF=-3710.838464\RMSD=2.589
e-09\RMSF=2.336e-06\Dipole=6.1762029,-0.8244549,2.0622529\Quadrupole=-
9.501287,1.4342856,8.0670014,-22.3064793,-0.9742518,-27.6542337\PG=C01
[X(C42H51F6N7O4S2)]\\@

int1A-*R,R*

1\1\GINC-R2851\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Intm 1 after conj. addition conf. 1: R(elec),R(nu
c) (tol opt; cat III)\\0,1\C,-2.0621530958,-3.0715646977,1.6208730863\
O,-2.9578835744,-3.8802330245,1.879925032\C,-1.1865747128,-2.462245921
3,2.7458989095\H,-0.6354107166,-3.315952282,3.1542315496\N,-1.76204462
23,-2.6731369714,0.3524871156\H,-1.0074346945,-2.0061870702,0.26954421
84\C,-2.3302232102,-3.1827379823,-0.9032542177\H,-2.0017715416,-2.4553
17672,-1.6539111422\C,-1.7471817151,-4.561511805,-1.3908953468\C,-0.21
0583612,-4.5005066592,-1.311325126\H,0.1454123931,-4.3939176925,-0.283
7577759\H,0.1896784326,-3.6654411366,-1.8999492096\H,0.2224116764,-5.4
208896982,-1.7167690334\C,-2.251094213,-5.7603191836,-0.5652587272\H,-
1.9689108028,-5.6813973555,0.4854824372\H,-1.8226222545,-6.6859945658,
-0.9655612976\H,-3.3410094569,-5.8635751671,-0.6068796707\C,-2.1398064
719,-4.7644623056,-2.8706426502\H,-3.2185971494,-4.8914246095,-3.01414
34923\H,-1.6633091363,-5.6704825092,-3.2584492372\H,-1.8089320048,-3.9
282234438,-3.4985396187\C,-3.8687039975,-3.1456422987,-0.8409814636\H,
-4.327437378,-3.8566272749,-1.5282322273\H,-4.1892297417,-3.3818123943
,0.1718021191\N,-4.4296111159,-1.7926733079,-1.2004671638\C,-5.8485188
363,-1.5711018156,-0.6747973546\H,-5.7638094642,-0.9415780941,0.211579
7885\H,-6.2560876399,-2.5382001015,-0.3803567173\C,-6.6332210664,-0.91
30437883,-1.8236110145\H,-7.2803487899,-1.652104063,-2.3054161041\H,-7
.2679052324,-0.1019463971,-1.4610075495\C,-4.4698905768,-1.4902513525,
-2.6846803401\H,-4.748898769,-2.4121951124,-3.2011737858\H,-3.47801223
91,-1.1742989362,-3.0084064065\C,-5.5547113751,-0.4258817806,-2.805919
6475\H,-5.9193586158,-0.3392834885,-3.8319371568\H,-5.1603704707,0.545
2301125,-2.4960473072\N,-0.1897690119,-1.5437666345,2.2198233127\H,-0.
5085522723,-0.5883967264,1.9763813859\C,-2.0246394963,-1.8219234984,3.
9201282408\C,-2.6651892999,-2.9439839832,4.7622924207\H,-3.2417030469,
-2.5077405959,5.586447816\H,-1.8980784408,-3.5918705902,5.2024516552\H
,-3.3293630018,-3.567709342,4.1625930641\C,-1.0716686125,-1.0198287217
,4.8300560928\H,-1.6169108039,-0.6726004043,5.71504026\H,-0.2365103223
,-1.6379855735,5.1774632742\H,-0.6551383493,-0.1404432063,4.3310984354
\C,-3.1251852852,-0.8858812028,3.3833351142\H,-2.716247683,-0.10134159
11,2.7385977158\H,-3.6418002012,-0.3979280734,4.2178442179\H,-3.877637
7591,-1.4456556947,2.8170350391\C,1.1379948189,-1.8095681978,2.0952466
605\N,1.8413763231,-0.6815839179,1.7543612749\H,1.3445336288,0.2183721
143,1.9346681676\C,3.1397686963,-0.5132612549,1.2667347385\C,5.6866818
46,0.0838605877,0.1895665449\C,3.6512509495,0.7998359895,1.3036760124\
C,3.9201186035,-1.5214304712,0.6817826618\C,5.1725599634,-1.2093718219
,0.1484877168\C,4.9066044095,1.0827569979,0.7777585452\H,3.0483146417,
1.589380008,1.7403935055\H,3.5520096753,-2.5373096979,0.653329173\H,6.
6646988477,0.3081829841,-0.2162265633\C,-2.2675926586,1.1982118662,-0.
9857913386\N,-1.2475953938,0.4930011785,-1.6294640774\C,-0.3642963563,
1.2859210186,-2.1603192753\S,-0.5964630452,3.0307113468,-1.9889726689\
C,-2.1350949619,2.7444846082,-1.0099533012\O,-3.308930047,0.6702816116
,-0.6003399492\H,-3.8356213459,-1.0362715457,-0.7903097326\C,-3.355842
7296,3.2881678086,-1.7763765476\H,-4.2623279249,3.0903202923,-1.197534
3729\H,-3.4530211014,2.8000005824,-2.7503707789\H,-3.2763768779,4.3635
655574,-1.9393519241\C,0.8213684631,0.7884790807,-2.8701492956\C,3.064
6504146,-0.0434086408,-4.1905300747\C,1.4322638578,1.5301835387,-3.895
1634216\C,1.3942835737,-0.4446179402,-2.5228069659\C,2.5408927679,-0.8
614663694,-3.1867747727\H,1.0075017017,2.4813327364,-4.210526983\H,0.9
612403188,-1.0336104907,-1.7222136352\H,3.042130945,-1.7841626404,-2.9
16207948\H,3.9653386174,-0.3394117564,-4.7238731649\C,-2.0603806566,3.
3548090783,0.4663773807\C,-0.7800306221,3.1365600514,1.2120371926\N,-0
.4117122003,1.93351992,1.5927474015\O,-1.115283137,0.8998201773,1.2154

946235\O,0.6282776783,1.7320780103,2.3369694557\H,-0.1448375946,3.9487
138774,1.5308126542\H,-2.8594222891,2.7960461228,0.9737821088\C,-2.420
1414634,4.8359925837,0.5016780192\C,-3.6486928347,5.248378691,1.033356
7409\C,-1.5371113909,5.817397026,0.0248451566\C,-3.9920886878,6.600691
2401,1.0838008161\H,-4.3386042906,4.502933312,1.4205990285\C,-1.879074
1464,7.1692192827,0.0704337271\H,-0.5693366117,5.5278396255,-0.3754843
866\C,-3.1086931256,7.565961626,0.5998089183\H,-4.9476399705,6.8981823
327,1.5064340071\H,-1.1803936291,7.9129310828,-0.3019467696\H,-3.37234
75704,8.6188163513,0.6394170754\C,5.9319818899,-2.3051673111,-0.546975
4412\C,5.4060231238,2.5021788231,0.7789846789\F,5.3618309285,-2.620233
8307,-1.7446370749\F,5.9561365209,-3.44858107,0.1706406131\F,7.2123130
462,-1.9651679861,-0.808299761\F,5.0656926912,3.1560404923,-0.36021186
28\F,4.9022501518,3.2227971812,1.80397118\F,6.7549652544,2.5627195081,
0.8676059438\S,1.8072722905,-3.3525831511,2.3513130808\N,2.5211634024,
1.1270904743,-4.5522642332\\Version=ES64L-G09RevD.01\State=1-A\HF=-371
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.6588921\Quadrupole=23.1053737,-8.6592515,-14.4461222,7.0969168,15.197
5033,19.669009\PG=C01 [X(C42H51F6N7O4S2)]\\@

int1A-*S,S*

1\1\GINC-R3044\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Intm 1 after conj. addition conf. 2: S(elec),S(nu
c) (tol opt; cat III)\\0,1\C,0.6496699057,-3.7208848616,-0.049112754\O
,1.2504327357,-4.7961857474,0.0921116979\C,-0.3358053849,-3.5331160611
,-1.2370775926\H,-1.0617692344,-4.3429570377,-1.11158297\N,0.789054672
3,-2.6731317852,0.7986482783\H,0.2748097617,-1.8051270962,0.615824133\
C,1.3911028312,-2.6725668421,2.1398201298\H,1.5124621605,-1.606490371,
2.3589808905\C,0.4345515925,-3.2226648974,3.2714676727\C,-0.9761333205
,-2.6419460161,3.0526489197\H,-1.4541357156,-3.0561077177,2.1620905574
\H,-0.9562030454,-1.5521492588,2.9462834819\H,-1.6133192747,-2.8863237
31,3.9091725705\C,0.3502894254,-4.7612614775,3.2860099451\H,0.03989247
89,-5.1617295448,2.3187047686\H,-0.3805565206,-5.084362963,4.035805820
4\H,1.3068263346,-5.2275987922,3.5489358327\C,0.9432633356,-2.72587001
81,4.6428405367\H,1.915029343,-3.1480442768,4.9212937968\H,0.238597611
7,-3.0200228078,5.4276251953\H,1.0272931004,-1.633212429,4.669581013\C
,2.7834525448,-3.3157275977,2.2109995805\H,3.1076755114,-3.3260718947,
3.2513627609\H,2.7820183236,-4.3310397371,1.8193754726\N,3.8483225238,
-2.5435585245,1.4645170518\C,3.9749771888,-2.8593504863,-0.0275348268\
H,3.6440825404,-1.971022516,-0.5647208121\H,3.3123570966,-3.6919280362
,-0.2559445696\C,5.4622020263,-3.1634639986,-0.2618249977\H,5.64160233
85,-4.2427084154,-0.2176732593\H,5.7913372198,-2.8133341607,-1.2427560
266\C,5.2277421462,-2.7260814436,2.0652769374\H,5.3022111592,-3.760257
2022,2.4116241651\H,5.3259378023,-2.0514281064,2.9174099069\C,6.174737
6462,-2.4599124833,0.9027831891\H,7.1759346785,-2.8503367829,1.0990486
916\H,6.2521747695,-1.3835943809,0.7160577436\N,-1.0854144658,-2.29504
1058,-1.1381933246\H,-0.5858063596,-1.4065509412,-1.2779925868\C,0.306
9947281,-3.6971694069,-2.6679173219\C,0.8377790962,-5.1304117372,-2.86
23252833\H,1.2563856464,-5.2346820963,-3.870423711\H,0.0309434608,-5.8
650900851,-2.7619274408\H,1.6071105493,-5.3868838019,-2.1335889489\C,-
0.7878910498,-3.4489026272,-3.725755283\H,-0.3894486682,-3.6615420446,
-4.7242122438\H,-1.6542686097,-4.0981152155,-3.565504614\H,-1.13838041
97,-2.4134008095,-3.7218737089\C,1.4480987269,-2.685906816,-2.88808281
72\H,1.1351268332,-1.6533712094,-2.6946462988\H,1.7949276962,-2.730053
1256,-3.9267027671\H,2.3084261052,-2.9059319038,-2.2497592659\C,-2.418
2712013,-2.1777897038,-0.8901072717\N,-2.786037878,-0.855841941,-0.861
6043828\H,-1.98242304,-0.214323935,-0.9629290557\C,-4.0145048783,-0.20
33354949,-0.7548635275\C,-6.3681882335,1.3593398098,-0.6110030712\C,-3
.9697044385,1.1962274973,-0.9325244549\C,-5.2526201057,-0.8063446371,-
0.4937162093\C,-6.40615675,-0.0184634567,-0.4289406873\C,-5.1285726601
,1.9563511878,-0.8629110462\H,-3.0181447424,1.6747267957,-1.1395309937
\H,-5.3049227745,-1.8767801451,-0.3516834126\H,-7.2722680661,1.9529754
846,-0.566133604\C,3.508273875,1.0940771586,1.0431114765\N,4.263612861
1,0.9562009781,-0.1090500583\C,4.3946851621,2.0975110103,-0.7323981095
\S,3.6393676773,3.528222299,-0.0621192705\C,2.9512487025,2.5042983797,
1.323851441\O,3.303624774,0.1706675796,1.8298651226\H,3.6307293074,-1.
5250895382,1.5449683622\C,3.4967015482,2.9963784586,2.6737496282\H,3.1
401850485,2.330898761,3.4654819157\H,3.1551523278,4.0097219861,2.89045
63562\H,4.5905548082,2.9896790523,2.6840255909\C,5.1601923022,2.237206
6407,-1.9828121387\C,6.5403090886,2.627026213,-4.2997473055\C,5.761438
2906,1.1313322184,-2.5935291752\C,6.4652468189,1.3377314665,-3.7782895
597\C,5.9043782521,3.6679979816,-3.6126807536\H,5.6673995547,0.1502556
277,-2.1448894144\H,6.9443065518,0.5060348234,-4.2850809596\H,5.942877
7155,4.6859990386,-3.992520852\H,7.0775165858,2.831224807,-5.220008577
5\C,1.374612973,2.4296476749,1.2940022879\C,0.8470504726,1.9379976423,
-0.0222170782\N,0.1797544374,0.8022704845,-0.1153827224\O,-0.027303266
7,0.0244020119,0.892468623\O,-0.3106278532,0.4482813696,-1.283682995\H

,0.8960445425,2.5143746406,-0.933805995\H,1.133512701,1.6511543246,2.0
235030052\C,0.7101113111,3.7253307576,1.757421029\C,0.1822813408,3.805
6762698,3.0540322541\C,0.5960637696,4.8480972906,0.923057018\C,-0.4301
909924,4.9736268148,3.5110235781\H,0.2437159906,2.9402357904,3.7083783
605\C,-0.0111864277,6.0184586804,1.3791025809\H,0.9695524775,4.8098018
268,-0.0955127662\C,-0.5250910057,6.0866403259,2.6753434718\H,-0.83756
27898,5.0098576215,4.5174153726\H,-0.0909872571,6.8749244901,0.7157390
416\H,-1.0029256279,6.9963856473,3.0270015153\C,-7.711027503,-0.714482
449,-0.1489262394\C,-5.0588823953,3.451333654,-1.0097321325\F,-7.98587
94496,-1.6592157288,-1.0784256501\F,-7.6942778906,-1.3475359404,1.0478
887438\F,-8.7594590865,0.1395068043,-0.130127902\F,-5.1036122226,4.078
3319087,0.1914201775\F,-3.9258264701,3.8593264491,-1.6215075432\F,-6.1
00082668,3.9328767027,-1.7299471305\S,-3.4456927738,-3.5103334044,-0.6
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evD.01\State=1-A\HF=-3710.8636039\RMSD=5.242e-09\RMSF=8.243e-06\Dipole
=10.2658765,0.7845393,0.7609327\Quadrupole=10.7150398,-23.3844671,12.6
694274,-23.4973925,-14.8085621,-11.2147161\PG=C01 [X(C42H51F6N7O4S2)]\
\@

int1B-*R,R*

1\1\GINC-R2844\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Intm 1 after conj. addition conf. 2: R(elec),R(nu
c) (tol opt; cat III)\\0,1\C,-0.8482079714,-3.4573941896,1.5117919293\
O,-1.2943895085,-4.5078746734,1.9788488913\C,0.0656606131,-2.558769061
3,2.3877130158\H,0.7931964921,-3.2616742064,2.8010172564\N,-1.09136494
53,-3.0383325514,0.2432749805\H,-0.7266842964,-2.1356442285,-0.0232851
949\C,-1.8592977039,-3.7484101155,-0.7943541149\H,-1.9942655573,-2.989
8861666,-1.5712469197\C,-1.0892498804,-4.9207970268,-1.5062518109\C,0.
3385021241,-4.4508076,-1.8419478482\H,0.9441909329,-4.3113316327,-0.94
37513594\H,0.334364192,-3.5057561262,-2.3987457611\H,0.8419624854,-5.1
966537832,-2.4662525116\C,-1.0126355474,-6.2086437013,-0.6641338951\H,
-0.5021434438,-6.044402877,0.2854675075\H,-0.4682940901,-6.9801422932,
-1.2206548884\H,-2.0051661437,-6.6140141203,-0.4381984005\C,-1.8135971
357,-5.2283628269,-2.8351294255\H,-2.8430416736,-5.5733461105,-2.68981
61204\H,-1.2861768023,-6.023280884,-3.3726001728\H,-1.840165978,-4.351
381085,-3.4933256503\C,-3.2605110516,-4.1373187806,-0.2717805669\H,-3.
6452601532,-5.0300094627,-0.7683481255\H,-3.2026271842,-4.3459015198,0
.7949832428\N,-4.2658020349,-3.0452086595,-0.4834791805\C,-5.408641246
2,-3.0719995163,0.491802898\H,-5.053947655,-2.6655712735,1.4376186712\
H,-5.7051289216,-4.117200897,0.6211156353\C,-6.5159775907,-2.227006390
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29392,-1.2563427868,0.3266883249\C,-4.9235933189,-3.0323188982,-1.8332
720129\H,-5.2685265994,-4.0488711206,-2.0483924767\H,-4.1992218597,-2.
7281358567,-2.5901202683\C,-6.0851334811,-2.0549305148,-1.6479913879\H
,-6.8926894375,-2.2628419115,-2.3536373542\H,-5.7345808957,-1.03576729
09,-1.8254586153\N,0.8271770079,-1.5924536936,1.6039771296\H,0.3927771
238,-0.6918718363,1.4277797742\C,-0.6621414784,-1.8628405697,3.5954033
018\C,-1.341265028,-2.9204937724,4.487640684\H,-1.7627107916,-2.427158
568,5.3707531559\H,-0.6257303574,-3.6737105468,4.8335729202\H,-2.14571
91534,-3.4457604068,3.9714599599\C,0.3994637864,-1.1364031909,4.446767
732\H,-0.0753224399,-0.6894789288,5.3271806242\H,1.1736559655,-1.82695
46229,4.7987458903\H,0.8932767364,-0.3309295482,3.8947907765\C,-1.7164
095391,-0.8466930213,3.1205292359\H,-1.2704552986,0.0176840952,2.61453
18943\H,-2.2597252378,-0.4457037593,3.9834178262\H,-2.4605000529,-1.27
78395054,2.445758614\C,2.1162833029,-1.7492773857,1.1845655862\N,2.552
1897624,-0.6462704252,0.4915242174\H,1.8150681911,0.0323588558,0.29063
89016\C,3.7639646443,-0.3364725177,-0.1402453273\C,6.093734659,0.52296
16848,-1.4867609118\C,3.7233616764,0.7478191292,-1.0364624299\C,4.9891
479649,-0.9795259467,0.0845617947\C,6.1294597367,-0.5470759909,-0.5969
76415\C,4.8730875859,1.1692702947,-1.6929239391\H,2.783548098,1.259013
0082,-1.2149660929\H,5.0438119582,-1.8039937348,0.7804315568\H,6.99013
1903,0.8544415669,-1.9952284063\C,-0.2968764985,1.9072342884,0.0846802
039\N,-0.0723374781,2.414501873,1.3528033619\C,-0.665947409,3.56430493
49,1.5208341476\S,-1.6071625878,4.2421042796,0.2032703454\C,-1.1787173
412,2.7697570773,-0.8429538725\O,0.1921714967,0.8504375664,-0.31221083
21\H,-3.766023552,-2.0692252244,-0.4188835204\C,-0.3385336638,3.209762
7799,-2.0538527404\H,-0.0301501418,2.3220086166,-2.614344406\H,0.56169
16913,3.7455182579,-1.7391864539\H,-0.9116737497,3.8593510735,-2.71757
71337\C,-0.5692516699,4.3269566182,2.7764733078\C,-0.4548982371,5.8334
89499,5.0426559208\C,0.1971889938,3.8568729727,3.8490768049\C,0.250598
5832,4.633008797,5.0052559532\C,-1.192340477,6.2155914889,3.9157547984
\H,0.7262778893,2.9152712514,3.7635201618\H,0.8339825416,4.3052851378,
5.8598517257\H,-1.7533408738,7.1471130061,3.9125417209\H,-0.4397318442
,6.467982629,5.9226513114\C,-2.4346944757,1.9173250388,-1.2518044291\C
,-3.195522128,1.4233617571,-0.0552513246\N,-3.5020150274,0.1460398228,
0.0967906293\O,-3.0605362294,-0.7519065978,-0.765998605\O,-4.228089615

7,-0.2650842757,1.067385237\H,-3.6338238521,2.0805003388,0.6817659453\
H,-2.0068941977,1.0295935665,-1.7254680632\C,-3.3213912092,2.610655227
,-2.2879886721\C,-3.2000183383,2.2773371607,-3.6446673695\C,-4.2785958
713,3.5701081057,-1.9233322471\C,-4.0005123455,2.8892831621,-4.6111636
158\H,-2.4754567573,1.5250855799,-3.9454638403\C,-5.0759390123,4.18738
11387,-2.8873606389\H,-4.4134962813,3.828642829,-0.8777982129\C,-4.939
4086953,3.8503789239,-4.2356069505\H,-3.8911189793,2.6121888962,-5.656
0569857\H,-5.8099272555,4.9280933623,-2.5825872024\H,-5.5638401476,4.3
283967306,-4.9848701237\C,7.4191688207,-1.2933746092,-0.3736089156\C,4
.7883669126,2.3001565758,-2.6817798232\F,7.5944506388,-1.6202962024,0.
9259541431\F,7.4549080967,-2.4515002724,-1.0739679\F,8.4974279412,-0.5
717644102,-0.7547228473\F,4.566664319,1.8545794894,-3.9417295039\F,3.7
810697628,3.156716693,-2.3905492852\F,5.9302467984,3.0215851943,-2.721
052126\S,3.013302031,-3.1515788115,1.481316873\N,-1.2516858735,5.48460
4181,2.8040230231\\Version=ES64L-G09RevD.01\State=1-A\HF=-3710.8605137
\RMSD=3.554e-09\RMSF=6.790e-06\Dipole=-4.375349,1.8393436,-0.121126\Qu
adrupole=-19.1380378,4.3575347,14.7805031,27.9974243,14.6659004,36.774
3227\PG=C01 [X(C42H51F6N7O4S2)]\\@

int1B-*S,S*

1\1\GINC-R2992\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Intm 1 after conj. addition conf. 1: S(elec),S(nu
c) (tol opt; cat III)\\0,1\C,2.1923914501,-3.4393816022,-0.7007314637\
O,3.1911352358,-4.1078546386,-0.9822222946\C,1.1835724327,-3.023437169
,-1.8015974682\H,0.6828295464,-3.9545452448,-2.0857808437\N,1.88138073
34,-3.0552387991,0.5619506813\H,1.0566839052,-2.4817241195,0.658966618
4\C,2.6317908187,-3.3480969325,1.7920520376\H,2.1912532466,-2.67183850
3,2.5326433882\C,2.3945092012,-4.7900096504,2.376374905\C,0.8802177839
,-5.0741022258,2.3808767151\H,0.4673111065,-5.1147995901,1.3699639441\
H,0.3274428436,-4.3089263219,2.9397871252\H,0.679671417,-6.0380889634,
2.8602190075\C,3.117617842,-5.8970447122,1.586041763\H,2.7805473658,-5
.9471415079,0.5500807773\H,2.9280094991,-6.8678955801,2.0581404229\H,4
.2030240177,-5.7502948551,1.57067677\C,2.886981808,-4.8138664762,3.839
6134325\H,3.9695316825,-4.6720404358,3.9273464309\H,2.6595281215,-5.78
49906015,4.2913059717\H,2.3916999682,-4.0478569532,4.447988065\C,4.115
7740246,-2.9555352603,1.6277098394\H,4.7638125308,-3.5466159808,2.2770
728762\H,4.4266884352,-3.1222075047,0.5976193911\N,4.3625831515,-1.515
330075,1.9658517924\C,5.6906832331,-1.0166242005,1.4490256047\H,5.5558
773461,-0.7123593642,0.4100226288\H,6.4101361363,-1.8397618382,1.49908
11001\C,6.057649101,0.1111620739,2.4071669645\H,7.1218443306,0.3552714
105,2.3601202669\H,5.4765541033,1.0065665872,2.1717830235\C,4.32003541
56,-1.2103566002,3.4598161424\H,4.2316054235,-2.1489571976,4.007545347
\H,3.4432468432,-0.5851055934,3.6187257483\C,5.6207207062,-0.451325046
5,3.7681926779\H,6.3814981683,-1.1359311755,4.1592042699\H,5.456373361
2,0.3297949499,4.5138381858\N,0.1275617236,-2.1558285298,-1.2834588462
\H,0.347830495,-1.1651914554,-1.2131679947\C,1.8743622738,-2.440399531
8,-3.0937864306\C,2.506416072,-3.5962897394,-3.8962568235\H,3.00757247
73,-3.2003719681,-4.7872836883\H,1.7396073916,-4.3030342455,-4.2344325
965\H,3.2351036998,-4.1438333726,-3.2982503524\C,0.8087609516,-1.77642
99915,-3.9887576543\H,1.2649059986,-1.4868080177,-4.9417901705\H,-0.01
43578609,-2.4633185896,-4.2120973718\H,0.382111097,-0.8735866878,-3.54
23546951\C,2.9601316112,-1.4088593351,-2.7314828314\H,2.5962140539,-0.
648675071,-2.0323497539\H,3.3131208863,-0.9014782357,-3.6365736933\H,3
.822559249,-1.8930595474,-2.2655461988\C,-1.1853490657,-2.522648533,-1
.1440109045\N,-1.9812505063,-1.457845754,-0.8092505045\H,-1.4922451031
,-0.5599475471,-0.7623607257\C,-3.3504827403,-1.3418508291,-0.51871597
38\C,-6.0612379464,-0.8609168545,0.1227585026\C,-3.7686595905,-0.08290
72837,-0.0516070176\C,-4.3091866109,-2.3563964208,-0.673061295\C,-5.64
15355511,-2.1036284832,-0.3486665731\C,-5.1065726586,0.1444914283,0.26
30120522\H,-3.0435767713,0.7179333064,0.0674400597\H,-4.006103816,-3.3
286771819,-1.0314748635\H,-7.0982762143,-0.6822924408,0.3753758323\C,-
0.2485589148,2.0509595122,-0.7662963465\N,-1.16461693,2.6324626292,0.0
930647203\C,-0.9328150418,3.9069092642,0.2521587899\S,0.414517865,4.64
26184958,-0.5995129863\C,0.8229207225,2.9967463229,-1.3509346781\O,-0.
2865877616,0.8657061084,-1.0873357531\H,3.6284366075,-0.8813172099,1.4
637852621\C,0.652017749,3.0617909141,-2.8772975587\H,0.8138727174,2.06
63614384,-3.3011504216\H,1.3690227544,3.7515019384,-3.3259531595\H,-0.
35647715,3.3886830978,-3.1463069045\C,-1.7564603668,4.7627323567,1.122
2154502\C,-3.208110684,6.4468453028,2.696163658\C,-2.8200981946,4.2319
947222,1.8594624665\C,-3.5589608257,5.0996259368,2.6613630236\C,-2.123
5212594,6.8788950664,1.9230527417\H,-3.0496898508,3.1771390755,1.80270
88101\H,-4.3941818036,4.7241378282,3.2439800267\H,-1.8227617918,7.9239
267192,1.9287135859\H,-3.756557087,7.1564707134,3.3068994462\C,2.23252
55448,2.4579806095,-0.9080893565\C,2.3394248545,2.3498621964,0.5837982
298\N,2.66903028,1.2283060432,1.2034658273\O,2.8188612758,0.0982077102
,0.5356749832\O,2.8535132411,1.2090125325,2.4709789368\H,2.2649812111,

3.2079833531,1.2354736995\H,2.2559604287,1.4371899494,-1.2963074062\C,
3.3960200571,3.2212912576,-1.545082783\C,4.0327345097,2.6981008655,-2.
6796698957\C,3.8680781785,4.4347042461,-1.0209002964\C,5.1020818348,3.
3657336153,-3.2792428309\H,3.6920630051,1.7527849324,-3.0930011593\C,4
.9336885449,5.1067522761,-1.6207540533\H,3.4116197961,4.8543069843,-0.
1299727015\C,5.5548633083,4.5756851969,-2.7529642201\H,5.5815887735,2.
9368764079,-4.1548946388\H,5.282929766,6.0448164989,-1.1982910835\H,6.
3872889379,5.0973356231,-3.2164758475\C,-6.6674304492,-3.1830328916,-0
.5772059528\C,-5.498811725,1.4947020827,0.7961809929\F,-6.1437654201,-
4.4210568641,-0.4618082642\F,-7.2126296987,-3.1009086483,-1.8152805171
\F,-7.6926270214,-3.0942095751,0.3022466742\F,-4.9845077939,1.71263515
94,2.0384130481\F,-5.03752411,2.501043054,0.0178432724\F,-6.8349005537
,1.6449125836,0.8976857811\S,-1.7010700684,-4.1240718829,-1.3417897106
\N,-1.4097443433,6.061652061,1.1510847663\\Version=ES64L-G09RevD.01\St
ate=1-A\HF=-3710.8613339\RMSD=6.691e-09\RMSF=4.610e-06\Dipole=3.050112
8,2.5611217,2.221739\Quadrupole=4.6198761,-9.6817639,5.0618879,-30.094
7796,0.0765294,-9.9372846\PG=C01 [X(C42H51F6N7O4S2)]\\@

TS2A-*R,R*

1\1\GINC-R3203\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\0
\\# freq=noraman rb3lyp/6-31g** opt=(ts,calcfc,noeigen,maxcyc=200) # s
cf=maxcyc=200 scrf=(smd,solvent=toluene) iop(1/8=1)\\TS for 2nd C-C bo
nd addition forms DA pdt conf. 1: R(elec),R(nuc) (tol opt; cat III)\\0
,1\C,-0.9463022725,-3.5165523423,0.8638745443\O,-1.354655335,-4.678846
5091,0.9386132137\C,-0.1030651699,-2.9301930948,2.0215598382\H,0.64285
96761,-3.7054159405,2.2146983163\N,-1.2012512582,-2.7074720296,-0.2007
621722\H,-0.9112372324,-1.7391911918,-0.1418203459\C,-1.9113088072,-3.
0845146106,-1.4343816156\H,-2.0897810322,-2.1235231155,-1.9283507357\C
,-1.068219895,-3.9206301746,-2.4689040447\C,0.3095373313,-3.2547911335
,-2.6388578155\H,0.894257276,-3.2861644401,-1.7165570786\H,0.214364333
8,-2.2088198784,-2.9543339257\H,0.8836544735,-3.7779497992,-3.41087852
46\C,-0.8700777428,-5.3920636576,-2.0585338142\H,-0.3168848426,-5.4844
410681,-1.1233637117\H,-0.3107974468,-5.9166650381,-2.8415925379\H,-1.
8222416121,-5.9190232785,-1.9321247645\C,-1.789711254,-3.8719301096,-3
.8344976558\H,-2.7491765449,-4.4007110656,-3.8318199704\H,-1.170150562
7,-4.3556623148,-4.5965984477\H,-1.9672256288,-2.8416294598,-4.1651241
87\C,-3.2801217872,-3.7112839326,-1.0993643144\H,-3.6468317351,-4.3527
112141,-1.9012446754\H,-3.1935470477,-4.3083815852,-0.1930820943\N,-4.
3413254893,-2.6706416634,-0.8688055376\C,-5.5299672819,-3.1912359318,-
0.0971893219\H,-5.2560526643,-3.2696812908,0.9559973682\H,-5.766598472
8,-4.1868466641,-0.4841941653\C,-6.6263301226,-2.1814423916,-0.4097136
626\H,-7.6192410942,-2.574474646,-0.1805530455\H,-6.4671121148,-1.2729
495115,0.1769927873\C,-4.8999698529,-2.027909282,-2.1348356021\H,-4.64
73436516,-2.6655654053,-2.9818880068\H,-4.4044141663,-1.065498863,-2.2
590681486\C,-6.4210396909,-1.9052703969,-1.9108236915\H,-6.9469762611,
-2.6552119328,-2.5090322197\H,-6.7914690087,-0.9229371292,-2.210741659
3\N,0.6443650938,-1.7356256326,1.6464757225\H,0.1913575464,-0.82697685
83,1.7741385667\C,-0.936980717,-2.7311508837,3.346631387\C,-1.27273221
87,-4.1141627063,3.9407172151\H,-1.8498331128,-3.989928608,4.864256143
5\H,-0.3605346222,-4.6681603639,4.1892263548\H,-1.851167246,-4.7251547
305,3.2461322623\C,-0.0826180905,-1.9657159451,4.3772845275\H,-0.61193
72253,-1.9323090557,5.3359180881\H,0.8798356587,-2.4600656606,4.547087
8054\H,0.1156585025,-0.9328408151,4.0780211449\C,-2.2450490447,-1.9600
11647,3.0881098336\H,-2.0789259612,-0.9888138183,2.6157095773\H,-2.767
5582245,-1.7825693187,4.0350210406\H,-2.9227149404,-2.5332919565,2.447
0065165\C,1.9558159802,-1.7352734575,1.2837525787\S,2.8466097545,-3.15
77800035,1.0272132255\N,2.459123432,-0.4698924276,1.1129343287\H,1.791
1340978,0.3109393928,1.119942462\C,3.7450422126,-0.0909497499,0.677549
4282\C,6.2520089252,0.8136021583,-0.2298220513\C,3.8327408562,0.975660
6121,-0.2244972908\C,4.9235810229,-0.6825052178,1.1566603129\C,6.15773
58744,-0.2293666387,0.6951422177\C,5.0784676437,1.4142511597,-0.676475
3066\H,2.9267782225,1.4584352927,-0.5718888932\H,4.8713852867,-1.48778
19874,1.8747115404\H,7.2170970201,1.1500848136,-0.5883654387\C,7.42768
0206,-0.8142136376,1.2527811251\C,5.1271708821,2.49130159,-1.724360646
5\F,4.2113634613,3.4594200653,-1.5029484529\F,6.3369601198,3.085964301
4,-1.7966996453\F,4.8637319567,1.9935197835,-2.9641817336\F,7.23547534
31,-2.020801186,1.8230794593\F,8.3722646523,-0.964875558,0.2943556073\
F,7.9706458715,-0.0110366986,2.2015857931\C,-3.2901728992,0.6189450253
,-0.1604863817\N,-2.1437383378,0.4696812491,-0.8714638232\C,-1.7654261
795,1.6798508457,-1.3463996311\S,-3.1504709226,2.8275908429,-1.5883037
031\C,-3.6960051784,2.0948769833,0.0204972274\O,-3.9502204991,-0.30797
91264,0.3531252444\H,-3.9546327503,-1.8636458301,-0.3041234016\C,-5.16
07551571,2.2894003148,0.3606156438\H,-5.383377079,1.8140429155,1.32039
35992\H,-5.7964843165,1.822259988,-0.3965888414\H,-5.4231150987,3.3467
399944,0.4312816634\C,-0.5753286043,1.8404348397,-2.2100760394\C,1.613
4135953,2.2798587252,-3.7917796475\C,0.419615812,0.8566911144,-2.26969
16993\C,1.5313971928,1.0855450817,-3.0795687935\C,0.5620479644,3.19391

02165,-3.6764459413\H,0.3196964308,-0.0541323718,-1.6937050106\H,2.325
987605,0.3488495534,-3.1413440535\H,0.5855719119,4.1329871891,-4.22518
30752\H,2.4726082023,2.5054075945,-4.413611175\C,-2.6655990769,2.70654
82123,1.0992177877\C,-1.2727101321,2.6818791028,0.5156421694\N,-0.3578
970909,1.7958007058,1.0475465426\O,-0.7681602115,0.7970128299,1.705876
5726\O,0.8690045622,1.937096865,0.7777051567\H,-0.7952799001,3.5882373
041,0.1703379412\H,-2.6885155186,2.0151717358,1.9454928568\C,-3.082207
0062,4.0772331054,1.6175468235\C,-3.6994175447,4.1634858395,2.87460448
31\C,-2.8792938773,5.2636412449,0.8956218446\C,-4.1130376509,5.3910810
493,3.3927063446\H,-3.8531453662,3.2578177793,3.4556345413\C,-3.291519
0127,6.492566081,1.4130838351\H,-2.4018142077,5.2324890721,-0.07774586
02\C,-3.9108676553,6.5622752278,2.661913689\H,-4.586491818,5.430970939
4,4.3696529743\H,-3.1222627373,7.3984424789,0.8378102638\H,-4.22777371
62,7.5204729442,3.0633863003\N,-0.5074039631,2.9882828237,-2.906472808
5\\Version=ES64L-G09RevD.01\State=1-A\HF=-3710.8435663\RMSD=3.960e-09\
RMSF=1.886e-06\Dipole=-6.7126887,-0.3538909,-2.0756578\Quadrupole=9.30
10975,-12.9703199,3.6692224,30.6508612,-2.1779055,16.4546341\PG=C01 [X
(C42H51F6N7O4S2)]\\@

TS2A-*S,S*

1\1\GINC-R3090\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\0
\\# freq=noraman rb3lyp/6-31g** opt=(ts,calcfc,noeigen,maxcyc=200) # s
cf=maxcyc=200 scrf=(smd,solvent=toluene) iop(1/8=1)\\TS for 2nd C-C bo
nd addition forms DA pdt conf. 2: S(elec),S(nuc) (tol opt; cat III)\\0
,1\C,-1.6842813058,-3.5597508977,-0.3209492431\O,-2.5003078676,-4.4576
084508,-0.5528960983\C,-0.5593642772,-3.7779709313,0.7334822151\H,0.02
81910236,-4.6056764881,0.3240005654\N,-1.6733646296,-2.3672239707,-0.9
65562859\H,-0.9688943174,-1.6938766568,-0.6870686911\C,-2.4359650665,-
1.9605845084,-2.1574331101\H,-2.3475050644,-0.8696701893,-2.1631895734
\C,-1.7907753338,-2.4368841194,-3.515924424\C,-0.2733689335,-2.1739568
687,-3.4619952695\H,0.2290206844,-2.8163707076,-2.7350397442\H,-0.0522
667554,-1.1319739441,-3.2027876357\H,0.1751453778,-2.3743088133,-4.440
4438314\C,-2.0383204199,-3.9308809525,-3.7971168226\H,-1.6485847565,-4
.5663888567,-2.9990240463\H,-1.5439850357,-4.2204922367,-4.7311760991\
H,-3.1040293672,-4.157802875,-3.9113177258\C,-2.3751236892,-1.59103286
26,-4.6687406462\H,-3.4384076376,-1.7826719369,-4.8485857092\H,-1.8525
582133,-1.8248869056,-5.6021337108\H,-2.2547198635,-0.5175204204,-4.48
25440061\C,-3.9355714025,-2.2896182966,-2.0741516751\H,-4.3815387596,-
2.1466967651,-3.0582405564\H,-4.1033118695,-3.3157540278,-1.7491690718
\N,-4.6991842473,-1.3790345861,-1.1508913611\C,-4.5536914273,-1.672426
0021,0.326560889\H,-3.6609568753,-1.1565437377,0.6728843242\H,-4.43014
73868,-2.7510723123,0.4294334478\C,-5.8516975273,-1.1545822088,0.98366
49962\H,-6.3282313035,-1.9578171199,1.5512138454\H,-5.6391164446,-0.33
57844838,1.6734712547\C,-6.1815812475,-1.3852069643,-1.4087874606\H,-6
.5011464634,-2.4295853648,-1.4745935896\H,-6.3790568547,-0.8847632702,
-2.3586104953\C,-6.7543359901,-0.6820579359,-0.1823258496\H,-7.8074443
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0008\N,0.3595553889,-2.647629568,0.8093946777\H,0.026782923,-1.8063750
982,1.2702410963\C,-1.0501209779,-4.2207641073,2.1622363321\C,-1.78358
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124\H,-1.1417001432,-6.3470559872,1.6541177852\H,-2.6919691803,-5.5234
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91324\H,0.7146815673,-3.4612104574,3.2447774204\C,-1.9775472622,-3.162
6664843,2.7860130976\H,-1.4866956421,-2.1858474738,2.8709620648\H,-2.2
657689566,-3.4626256063,3.7996489105\H,-2.8982264583,-3.0388553665,2.2
08107421\C,1.6661363911,-2.6464241568,0.4020567105\S,2.4020434616,-3.9
985617229,-0.3000950456\N,2.253269392,-1.427161386,0.6180558507\H,1.60
30892676,-0.6891162001,0.9113445637\C,3.5592886322,-0.9495743145,0.431
1319858\C,6.0996370115,0.2521684802,0.1372065151\C,3.728083939,0.43706
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77\H,2.8710214568,1.0523846315,0.8607110974\H,4.5768656171,-2.79920447
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21,-1.9759835609,-0.4221082008\C,5.137159785,2.4957916963,0.7200713452
\F,5.3517741904,2.7539073775,2.0334058267\F,6.1844353615,3.0201595982,
0.0454115822\F,4.0359997778,3.1942024284,0.3641423528\F,7.1183834463,-
2.2157917237,-1.7550917423\F,8.2843818731,-1.3919046196,-0.1171137097\
F,7.081853543,-3.181586578,0.1879398611\C,-3.3459265277,1.8017076395,-
0.6968436792\N,-3.1513496489,1.3397841352,0.5585642691\C,-2.552071396,
2.3075744125,1.2945919688\S,-2.9523451006,3.9876491297,0.729084142\C,-
2.7214318071,3.1924389418,-0.924911324\O,-3.8906502631,1.1670684305,-1
.6281895335\H,-4.364000415,-0.3779045047,-1.3076421824\C,-3.3004473444
,3.9446137373,-2.1068775454\H,-3.1206180066,3.3793315674,-3.0260763046
\H,-2.8530841459,4.9343651673,-2.2178318799\H,-4.3821477712,4.05810598
,-1.9960703459\C,-2.2806549949,2.1159871208,2.7387362701\C,-1.76167049
08,1.8759586341,5.4127035042\C,-2.3156203656,0.8423816841,3.3186483285

\C,-2.0520892315,0.7263569658,4.681891167\C,-1.7509841831,3.1025179138
,4.7428867858\H,-2.5570627405,-0.0190854195,2.7094914565\H,-2.07408375
54,-0.2460931317,5.1644480317\H,-1.5332275816,4.0223702049,5.281554910
5\H,-1.5491741473,1.8314981551,6.4758056619\C,-1.1319703739,2.92838639
67,-0.9995145314\C,-0.6623965507,2.3978401843,0.3398348287\N,-0.248478
3422,1.0775929985,0.3945693605\O,-0.6062598413,0.2713871413,-0.5000918
6\O,0.3973820479,0.6731160173,1.4157202403\H,-0.0890111965,3.020712905
9,1.0126759834\H,-1.0038824064,2.1332115915,-1.7382059027\C,-0.3351031
739,4.1314159037,-1.4864159433\C,0.126124475,4.1404441443,-2.811265342
3\C,-0.0350247538,5.234143622,-0.671392079\C,0.8567333687,5.2174182057
,-3.3137693977\H,-0.0841729393,3.2897093302,-3.4545652603\C,0.69580804
14,6.3121497723,-1.1728389874\H,-0.3753810966,5.2560506923,0.358147869
4\C,1.1435824383,6.3098701873,-2.4947890478\H,1.2054103679,5.198271560
6,-4.3424225828\H,0.9192728158,7.1544734443,-0.524208666\H,1.716257060
3,7.1482700201,-2.8805733148\N,-2.0006253105,3.2279555903,3.4385121114
\\Version=ES64L-G09RevD.01\State=1-A\HF=-3710.8438388\RMSD=4.158e-09\R
MSF=1.960e-06\Dipole=-5.7341306,0.5692837,0.3092312\Quadrupole=3.95605
43,-26.4885085,22.5324542,26.8575029,4.9977499,-6.3001326\PG=C01 [X(C4
2H51F6N7O4S2)]\\@

int2A-*R,R*

1\1\GINC-R3470\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Diels-Alder product (non protonated) conf. 1: R(e
lec),R(nuc) (tol opt; cat IV)\\0,1\C,-2.0722612703,-2.6687257708,0.830
8610355\O,-2.7343918474,-3.7115192172,0.8399954461\C,-1.1366628525,-2.
3800735104,2.0308335388\H,-0.6815223631,-3.3528843829,2.227764882\N,-2
.1099706586,-1.7690005046,-0.1861897398\H,-1.6319977097,-0.8710363404,
-0.0999868022\C,-2.896623028,-1.9007415533,-1.4233788656\H,-2.82197917
99,-0.9030533635,-1.8691667971\C,-2.3055849945,-2.8753507923,-2.510829
5434\C,-0.7816507208,-2.6744539581,-2.5913523844\H,-0.2772324222,-3.04
17850459,-1.6951201464\H,-0.5145454826,-1.6195291067,-2.7184684091\H,-
0.3779466381,-3.2262075064,-3.4471753214\C,-2.6011034406,-4.3633129924
,-2.2378277361\H,-2.2026499551,-4.6872093145,-1.2759776056\H,-2.147946
6596,-4.9762118709,-3.0253354778\H,-3.6753302168,-4.5804984487,-2.2414
06154\C,-2.9159152758,-2.4861665935,-3.8751878466\H,-4.0050410595,-2.6
027255419,-3.9031302683\H,-2.50908119,-3.1274379044,-4.6639596802\H,-2
.6824000443,-1.4487623661,-4.1428658491\C,-4.3774046179,-2.1749028292,
-1.1009089369\H,-4.9086687656,-2.6087300507,-1.9496027234\H,-4.4350811
652,-2.869454517,-0.2649327499\N,-5.1237336109,-0.9261730476,-0.718777
6312\C,-6.3415920969,-1.194982463,0.1502026118\H,-6.028882819,-1.08847
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018894184\H,-7.8470964113,0.3435434545,0.5721898421\C,-5.6163033915,-0
.0951562505,-1.8779802631\H,-6.0346835822,-0.7759073537,-2.6253071581\
H,-4.7769130511,0.450366029,-2.3099978257\C,-6.6889073075,0.7843119141
,-1.2449462222\H,-7.3515656837,1.2213281869,-1.9952504478\H,-6.2093529
72,1.5909509865,-0.6860086615\N,-0.0413192798,-1.4797453272,1.69861249
77\H,-0.2624687136,-0.4917940309,1.6255385605\C,-1.8730222071,-1.93246
79026,3.3492835037\C,-2.9899248743,-2.9331537589,3.7025266556\H,-3.414
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0998547\H,-3.7989484491,-2.929370999,2.9689998091\C,-0.8411564482,-1.9
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919730421,-2.9242056553,4.6296518653\H,-0.0323126901,-1.2195901383,4.3
173617275\C,-2.4766443427,-0.5217486574,3.2176153009\H,-1.7037729617,0
.2466407909,3.1108544479\H,-3.0431135664,-0.2746352955,4.1227776713\H,
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.4469512973\S,1.7420551173,-3.4729216614,1.4127268316\N,2.0642359426,-
0.7674745027,1.2691015107\H,1.6373336506,0.1246050385,1.5110640964\C,3
.3957609401,-0.6370823802,0.8507817683\C,6.0343166709,-0.1142871538,-0
.0085677001\C,3.9716873648,0.6347091162,1.0259964907\C,4.1526630109,-1
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8058686,-0.3372120626\C,6.271130349,-2.486539438,-0.7797831557\C,5.824
2269196,2.2797337144,0.7000571522\F,5.3060746274,2.9617746592,1.741463
8957\F,7.1682005211,2.2824688347,0.8391602162\F,5.5525139761,3.0084821
185,-0.4170508029\F,6.8669353217,-3.2444732119,0.1706139205\F,5.513341
2197,-3.3215863274,-1.5244819594\F,7.2575110127,-2.0191271638,-1.57993
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86531,-0.3873749331\C,-0.9355072714,2.404830527,-0.7610253902\S,-2.152
5544133,3.7060140082,-1.4953914984\C,-2.9454933622,3.3032351108,0.1412
524855\O,-3.907535053,1.0818637518,0.490869138\H,-4.4836429595,-0.2640
876928,-0.1708007005\C,-4.304773752,3.9197438186,0.3862156298\H,-4.717
457616,3.5412051404,1.3262535011\H,-4.9987733427,3.6505846972,-0.41453
96606\H,-4.249334411,5.0089953027,0.4443762698\C,0.1854242244,2.063548
2354,-1.7153296667\C,2.2777140058,1.5166711873,-3.3949680068\C,-0.0780

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88445\C,2.4418015793,2.1391063291,-2.1602664402\H,-1.0966418441,1.1718
339152,-3.202469759\H,0.8166165149,0.66428175,-4.7406544437\H,3.427935
2511,2.432239575,-1.8092942881\H,3.1365514476,1.3206929917,-4.02835524
47\C,-1.8224510993,3.6461136783,1.2103874301\C,-0.505533888,3.28936252
25,0.463548944\N,0.4881101759,2.6449886958,1.3982411306\O,0.2585803071
,1.5030940563,1.828155674\O,1.4733628173,3.293057848,1.7154167868\H,0.
0299755557,4.1699739408,0.1246680756\H,-1.9590407868,2.9397279889,2.03
5774778\C,-1.8541845478,5.0435152147,1.801141969\C,-2.2546985607,5.208
1113374,3.1347411727\C,-1.5170368435,6.1874366411,1.0604122784\C,-2.31
77418982,6.4749358449,3.7163832992\H,-2.5129970947,4.3329767361,3.7258
952215\C,-1.5821015483,7.4546467805,1.6396729394\H,-1.2086777348,6.088
8085226,0.0245815748\C,-1.9818874773,7.6039156002,2.9691181626\H,-2.62
388245,6.5772082401,4.7536004833\H,-1.3157596298,8.3273706847,1.050208
2336\H,-2.0257208576,8.5912935055,3.4195380598\N,1.4209755719,2.408325
8928,-1.3335413376\\Version=ES64L-G09RevD.01\State=1-A\HF=-3710.853913
7\RMSD=3.316e-09\RMSF=6.677e-06\Dipole=-6.5453333,1.5025983,-2.1238696
\Quadrupole=23.6854392,-32.6630229,8.9775837,15.2527424,3.5125071,12.6
167509\PG=C01 [X(C42H51F6N7O4S2)]\\@

int2A-*S,S*

1\1\GINC-R3505\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\09-Dec-2015\
0\\# freq=noraman rb3lyp/6-31g** opt=maxcyc=200 scf=maxcyc=200 scrf=(s
md,solvent=toluene)\\Diels-Alder product (non protonated) conf. 2: S(e
lec),S(nuc) (tol opt; cat IV)\\0,1\C,-1.4189449435,-3.1930664887,0.238
3783568\O,-2.1800947861,-4.1640017228,0.2879621596\C,-0.192671519,-3.1
149902939,1.193622236\H,0.4240710081,-3.9708664156,0.901475962\N,-1.55
75039246,-2.1687148122,-0.6410257334\H,-0.8504389285,-1.4464897568,-0.
5973461954\C,-2.4384491503,-2.0843466509,-1.8205517089\H,-2.4718007544
,-1.015186766,-2.0534932831\C,-1.8352343178,-2.780064706,-3.101725303\
C,-0.3610191687,-2.3568522452,-3.2547773794\H,0.2692805988,-2.76187619
45,-2.4593955889\H,-0.2494917778,-1.2660229824,-3.2587104182\H,0.03668
64191,-2.7293300351,-4.2044627525\C,-1.9123201226,-4.3166766242,-3.029
2363549\H,-1.3951558695,-4.7110505561,-2.1515176584\H,-1.4459674613,-4
.7543559553,-3.9189308585\H,-2.9460460964,-4.67792702,-2.9958456398\C,
-2.5966346262,-2.2833427962,-4.3504011726\H,-3.6365747899,-2.623689823
8,-4.385480285\H,-2.111268711,-2.6649859714,-5.2546771969\H,-2.5984496
425,-1.1889947134,-4.4135580981\C,-3.8872592431,-2.5221676388,-1.54472
8255\H,-4.4076618911,-2.6000217007,-2.4989125821\H,-3.9244973327,-3.48
45615327,-1.037135668\N,-4.6773302173,-1.5334200928,-0.7368786224\C,-4
.4466581071,-1.5692852748,0.7627009995\H,-3.7046953943,-0.8008965845,0
.982062169\H,-4.0570322677,-2.5543606787,1.0185911815\C,-5.82221494,-1
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,-0.9366471541\H,-6.4143739918,-2.7383785788,-0.8878409331\H,-6.421049
991,-1.2838700648,-1.9225026861\C,-6.7435851189,-0.8954103448,0.235700
741\H,-7.7921678089,-1.14530589,0.4131232882\H,-6.6776351376,0.1777470
881,0.0328489476\N,0.6346125288,-1.9361454859,0.9461051021\H,0.3371887
628,-1.0781270362,1.3970888531\C,-0.5191070827,-3.277410352,2.72653331
38\C,-1.0938226601,-4.6810320979,3.0037886981\H,-1.2555422518,-4.80402
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17565\H,0.6011950031,-3.3505200532,4.5837876205\H,1.5512637573,-3.8499
777413,3.178517122\H,1.2213309112,-2.1354777321,3.4665230226\C,-1.5171
307761,-2.2099819073,3.2114850928\H,-1.1626231018,-1.1871823488,3.0344
394803\H,-1.674209239,-2.306337841,4.2914020853\H,-2.491478325,-2.3183
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23037,-3.3490253314,-0.1593932182\N,2.4589329074,-0.6947882886,0.42048
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54783,1.0595911605,-0.3838218787\C,4.9006951042,-1.0554866612,0.182694
587\C,6.1413730606,-0.5217434537,-0.1651428463\C,5.1241430447,1.576977
2328,-0.7125946609\H,2.9932631202,1.6856711848,-0.4715455969\H,4.82803
52708,-2.0710538778,0.5413663275\H,7.2418999941,1.1928566158,-0.881000
3919\C,7.364445687,-1.3983257981,-0.0986334771\C,5.2538382537,3.020557
3907,-1.118398483\F,5.5811779519,3.8075685533,-0.0651344208\F,6.220412
9392,3.1953556863,-2.0470957798\F,4.105389526,3.5127367437,-1.63190414
06\F,7.6113927207,-2.0029564505,-1.2844165843\F,8.4737903151,-0.688617
3188,0.2124991636\F,7.2412521224,-2.3772864117,0.8231408047\C,-3.61500
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5134\C,-2.4195321457,2.6713235902,0.7134423731\S,-3.4463795068,4.15163
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3517745,0.8844996353,-1.6458624938\H,-4.4322586502,-0.5245945652,-1.07
80719736\C,-4.1085392525,3.5844645296,-2.6343244597\H,-3.9815542251,2.
8783627022,-3.4606703859\H,-3.8171596927,4.579469025,-2.9783627898\H,-
5.1712130165,3.5997696485,-2.3771362616\C,-2.1190968729,2.7798991342,2
.1894840902\C,-1.5617399086,3.1168253947,4.848594727\C,-2.6998838245,1

.9074968906,3.1134648248\C,-2.4144896276,2.0833489251,4.4670175375\C,-
1.0326079612,3.9367018899,3.8501575736\H,-3.3608944051,1.1261351063,2.
7614148704\H,-2.853247378,1.4240369702,5.2104049086\H,-0.3639387343,4.
7559538439,4.1069948025\H,-1.3103610199,3.2896151279,5.8899939439\C,-1
.7120377398,3.0777048358,-1.6635361315\C,-1.1531234466,2.8744161961,-0
.2340962194\N,-0.2820402618,1.6507001104,-0.1207327173\O,-0.4214932058
,0.7149184486,-0.9045074149\O,0.5198205619,1.6227242994,0.8270123518\H
,-0.5312670757,3.6806721179,0.146408348\H,-1.5137482515,2.1741020851,-
2.245551352\C,-1.1013024142,4.241494242,-2.4256902868\C,-0.7827397899,
4.0621294428,-3.7805199896\C,-0.8468863789,5.4938768587,-1.8447956729\
C,-0.2361171935,5.0982607069,-4.5377955872\H,-0.9608591934,3.095869617
3,-4.2457980922\C,-0.2985808664,6.5310607985,-2.6008413379\H,-1.085327
9012,5.6661912422,-0.8009640873\C,0.00813803,6.3392733749,-3.948712316
4\H,0.0050050396,4.9321271056,-5.5838881381\H,-0.1079474323,7.49156629
89,-2.1306574112\H,0.4385052819,7.1476276674,-4.5327530497\N,-1.299699
025,3.780126533,2.5508425336\\Version=ES64L-G09RevD.01\State=1-A\HF=-3
710.8574218\RMSD=6.207e-09\RMSF=3.334e-06\Dipole=-4.5193444,-0.2536463
,0.6928996\Quadrupole=-2.1661381,-21.3549103,23.5210484,30.1793774,1.1
771194,0.4394585\PG=C01 [X(C42H51F6N7O4S2)]\\@

TS2′A-*R,R*

1\1\GINC-R2954\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\07-Mar-2016\0
\\# freq=noraman b3lyp/6-31G(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) s
cf=maxcyc=200 scrf=(smd,solvent=toluene)\\TS for protonation of int1DA
 conf. 1: R(elec),R(nuc) (tol opt; cat III)\\0,1\C,-2.5947187433,-3.64
38747332,0.4112902557\O,-2.4787015037,-4.869440531,0.4636541744\C,-3.8
752612725,-2.9554720028,-0.1560244372\H,-4.5527111448,-2.8265709862,0.
6964598518\N,-1.6399374811,-2.7846082148,0.8570367267\H,-1.8490829565,
-1.797703187,0.8054564987\C,-0.3733175139,-3.0946915189,1.5408528835\H
,0.1437096694,-2.1307257605,1.5455918013\C,-0.5333714327,-3.4808701537
,3.0637095568\C,-1.6087641977,-2.5749288719,3.694731771\H,-2.606537514
5,-2.7817442831,3.2992314819\H,-1.3955048354,-1.5130851939,3.524676207
5\H,-1.6425987357,-2.735054083,4.7775541113\C,-0.9196799917,-4.9568528
842,3.2826180773\H,-1.8372395673,-5.2205150119,2.7536996863\H,-1.07045
40374,-5.1443811724,4.351819013\H,-0.1333151557,-5.6409670183,2.945048
3051\C,0.8009456969,-3.1981743482,3.787962705\H,1.6307666577,-3.802664
8338,3.4071203928\H,0.7026791869,-3.4294285172,4.8537943354\H,1.084291
6427,-2.1423267071,3.7084545363\C,0.5084774123,-4.0840653946,0.7609676
4\H,1.4060746931,-4.2656670014,1.3538789926\H,-0.0113636542,-5.0352839
102,0.6253313825\N,0.9863909513,-3.626038388,-0.5840906582\C,0.0307675
693,-3.8785823964,-1.7151985277\H,-0.7469917749,-3.119933097,-1.710021
5685\H,-0.4277979369,-4.8601251055,-1.5602787747\C,0.8966161078,-3.851
3355423,-2.9838929365\H,0.5294900657,-4.5792124145,-3.7112363026\H,0.8
534848204,-2.8687236609,-3.4596326176\C,2.2108871544,-4.3883292542,-0.
9894929541\H,2.0413131603,-5.4469300079,-0.7561809852\H,3.0671089499,-
4.0363054051,-0.4130660199\C,2.337582177,-4.1708425363,-2.5015369852\H
,2.7545170723,-5.0572178801,-2.9854577406\H,3.0108931753,-3.3376140649
,-2.7138961749\N,-3.5546690054,-1.6038741924,-0.6009100677\H,-2.819917
8755,-1.5160661802,-1.2959411063\C,-4.6494794407,-3.7910956587,-1.2398
526169\C,-5.3140032393,-5.0105113146,-0.5683878438\H,-5.8825222983,-5.
5800157658,-1.3123788245\H,-6.0192685818,-4.691853366,0.2083585296\H,-
4.5762157639,-5.6714510689,-0.1135844174\C,-5.765032847,-2.9131883123,
-1.8418505918\H,-6.3848739482,-3.5192243967,-2.5118239422\H,-6.4144444
031,-2.4955758169,-1.0667809291\H,-5.3632654717,-2.0803218968,-2.42666
81491\C,-3.7206693968,-4.2594491823,-2.3755860856\H,-3.2154351442,-3.4
167114929,-2.8643942835\H,-4.3044891329,-4.7687382441,-3.1502679306\H,
-2.9649920072,-4.9590154091,-2.011533367\C,-4.0497462285,-0.4369360222
,-0.0959800539\N,-3.3564804786,0.6449416208,-0.5834085523\H,-2.4362614
506,0.4186313704,-0.9657948623\C,-3.5258689247,2.0093361707,-0.2815549
439\C,-3.687353188,4.7780519111,0.1850377762\C,-2.3702248837,2.7584976
909,-0.0454824114\C,-4.7733605274,2.6489386888,-0.2839747975\C,-4.8397
28819,4.0198904351,-0.0436283355\C,-2.4542779015,4.1332419648,0.175846
1503\H,-1.4099528193,2.2551076334,-0.0192777456\H,-5.6743261479,2.0848
895259,-0.4797826654\H,-3.7528067156,5.8447061411,0.3588802374\C,3.668
3719064,1.1809680885,-1.8077224695\N,4.9718498138,1.6832392076,-1.7526
890767\C,5.2955058912,2.067287661,-0.5563973997\S,4.1239176086,1.90704
49357,0.7486479887\C,2.9027942582,1.1954367919,-0.4556035823\O,3.14940
3724,0.7828065681,-2.8358240803\H,1.2404135055,-2.3237760661,-0.633321
2537\C,1.7193637129,2.1727412259,-0.5982523987\H,1.0524883159,1.836999
8763,-1.3968034158\H,2.0793240126,3.1683555297,-0.8698731221\H,1.15964
48209,2.2582826227,0.3346688881\C,6.6172836241,2.6395683212,-0.2402501
621\C,9.0295489456,3.6994725756,0.4514746145\C,7.5803326635,2.81050825
76,-1.24151951\C,8.8116782653,3.3523485732,-0.8804673097\H,7.351767157
8,2.5215203351,-2.2604612336\H,9.5861281236,3.5006779615,-1.6265849103
\H,9.9740041339,4.1243018046,0.7752815391\C,2.4635527565,-0.2518420081
,0.0228355306\C,1.4063145835,-0.9010124101,-0.88092\N,0.0802290603,-0.
4476919734,-0.6888144996\O,-0.3089505619,-0.0612445999,0.4393195853\O,

-0.737965889,-0.5422994542,-1.6481360918\H,1.6255614568,-0.8665691755,
-1.9453813024\H,1.9860786594,-0.099700067,0.9939543257\C,3.6542552645,
-1.1855063197,0.2462871515\C,3.9391237392,-1.639416883,1.5427431051\C,
4.4815075829,-1.6203142264,-0.802241389\C,5.010253531,-2.4993233866,1.
7896832937\H,3.321527437,-1.3041883789,2.371777267\C,5.5604145285,-2.4
730025732,-0.5564669005\H,4.2905417215,-1.2994360864,-1.8201654274\C,5
.8285180897,-2.917494779,0.7388498009\H,5.211149613,-2.8311435579,2.80
43244336\H,6.190548779,-2.7890980262,-1.3829760973\H,6.6683897892,-3.5
79601988,0.9281148576\C,-6.182422629,4.6996961458,0.0080307058\C,-1.17
40493805,4.8881346782,0.4050265179\F,-7.1189057736,4.0344513696,-0.701
8396352\F,-6.1250319034,5.9598264632,-0.4831520945\F,-6.646885818,4.80
04669209,1.275766684\F,-0.4723315209,4.3744152743,1.4446655271\F,-0.35
42494644,4.8181294607,-0.6744931401\F,-1.3798088064,6.194396802,0.6656
339562\S,-5.3180386041,-0.3543147033,1.0134430467\N,6.8183443333,2.972
4489882,1.0451976704\C,8.0010799913,3.4903584252,1.3765415968\H,8.1375
098785,3.751995038,2.4232835418\\Version=ES64L-G09RevD.01\State=1-A\HF
=-3710.8364478\RMSD=2.588e-09\RMSF=8.943e-07\Dipole=5.9194107,-2.55729
43,-0.3602981\Quadrupole=9.1534184,-0.0374494,-9.115969,10.6816339,12.
1741268,4.871166\PG=C01 [X(C42H51F6N7O4S2)]\\@

TS2′A-*S,S*

1\1\GINC-R2615\FTS\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\07-Mar-2016\0
\\# freq=noraman b3lyp/6-31G(d,p) opt=(ts,calcfc,noeigen,maxcyc=200) s
cf=maxcyc=200 scrf=(smd,solvent=toluene)\\TS for protonation of int1DA
 conf. 2: S(elec),S(nuc) (tol opt; cat III)\\0,1\C,0.2416416681,3.8266
590114,0.3338847397\O,-0.4729820406,4.8284151799,0.3938936957\C,1.5866
271949,3.8154212678,-0.4578321139\H,2.3346230751,4.230631042,0.2276024
873\N,-0.0439550594,2.6581942131,0.9656795562\H,0.6234781421,1.9104375
727,0.846581504\C,-1.1408520008,2.3347373416,1.8919051784\H,-1.1225816
301,1.2411225553,1.9358628944\C,-0.864132442,2.8018322,3.3719303526\C,
0.5378878713,2.3012942016,3.7751824704\H,1.328275467,2.7552323196,3.17
12609908\H,0.6200757596,1.2122619351,3.6742059476\H,0.7396315824,2.550
3417564,4.8221929151\C,-0.9244248608,4.3309692306,3.5450413093\H,-0.20
49869698,4.847556841,2.9069319023\H,-0.7035761989,4.5919066044,4.58651
58961\H,-1.9167323815,4.7322808502,3.314313515\C,-1.8930602219,2.14435
15099,4.3172238091\H,-2.8965563051,2.5674834774,4.2090027401\H,-1.5926
709042,2.3043954712,5.3583136756\H,-1.9684351447,1.0644365567,4.152570
3104\C,-2.5328416956,2.7254296617,1.3733391607\H,-3.2563437265,2.40126
2659,2.1204581517\H,-2.6143917828,3.8074387081,1.2437648001\N,-2.95336
51941,2.0712091771,0.0911181233\C,-2.4969526554,2.776030499,-1.1562017
524\H,-1.4525466974,2.5545371354,-1.3431323046\H,-2.607698932,3.852469
3296,-0.9931986706\C,-3.4334171251,2.2699687271,-2.2635787641\H,-3.640
9904702,3.0664552977,-2.9821217296\H,-2.9668064383,1.4496499686,-2.814
4537016\C,-4.4452851506,2.1113810312,-0.0477133315\H,-4.7733176969,3.1
306860067,0.1943469491\H,-4.9120727722,1.4238780071,0.6564419541\C,-4.
7114016133,1.7923536148,-1.5222298038\H,-5.6159017707,2.2955385508,-1.
872410126\H,-4.8637660643,0.7192087469,-1.6650151779\N,2.0182479913,2.
4417238261,-0.7091889326\H,1.3960359164,1.8545506772,-1.2642256401\C,1
.6120824474,4.7105719318,-1.7521093082\C,1.5798112317,6.1984999801,-1.
3463520338\H,1.6369021517,6.8287185787,-2.2414561066\H,2.4394864016,6.
449529975,-0.7138484967\H,0.6697426638,6.4464363892,-0.7999882393\C,2.
9299613238,4.4531522987,-2.5101159289\H,3.0128524218,5.1557671511,-3.3
46545259\H,3.801454429,4.5924412635,-1.8639096488\H,2.9772243267,3.441
5469957,-2.924274222\C,0.4322398276,4.3993984956,-2.6907218074\H,0.399
7692563,3.3388580101,-2.9684722511\H,0.5319608647,4.969773858,-3.62098
9623\H,-0.522364105,4.6713356533,-2.2350129467\C,3.1636488621,1.866328
9302,-0.2490795721\N,3.1737422165,0.5062635893,-0.4838494988\H,2.24761
10005,0.0797857559,-0.5287896851\C,4.2403819742,-0.3965938496,-0.34175
52009\C,6.2899312329,-2.3152976797,-0.1280090064\C,3.9553573467,-1.693
2566154,0.1016063306\C,5.5571615537,-0.0681306227,-0.6995630064\C,6.56
33932532,-1.0221340385,-0.5799455952\C,4.9775344172,-2.6400356314,0.20
25604778\H,2.9384050722,-1.9585591098,0.3727673971\H,5.788071393,0.920
7507503,-1.0687417489\H,7.0797282436,-3.0504949219,-0.0424792184\C,-4.
2191726716,-0.9725574426,1.5579297777\N,-5.5153444315,-0.8721738976,1.
036599587\C,-5.6974193112,-1.6795220602,0.0356428924\S,-4.3776420247,-
2.7312214149,-0.4767541984\C,-3.3749015859,-2.1240196442,0.9638338679\
O,-3.790968058,-0.2415045074,2.4321259138\H,-2.489200297,0.8181539741,
-0.011332473\C,-3.3407151614,-3.229846202,2.0431999243\H,-2.8221661639
,-2.8502318759,2.9293490942\H,-2.8218457333,-4.1197577077,1.6847225718
\H,-4.3547869316,-3.5154947334,2.3365366025\C,-6.9747908073,-1.7579287
939,-0.6970138695\C,-9.2856388022,-1.9908596759,-2.1212315831\C,-8.084
4437732,-1.0070422473,-0.2917605163\C,-9.263279865,-1.1327143207,-1.02
36405827\C,-8.1216160372,-2.6961995505,-2.446394984\H,-8.0084293327,-0
.3568215524,0.5717399776\H,-10.1478659924,-0.5708827152,-0.7406062269\
H,-8.1052144742,-3.3742556307,-3.2964340011\H,-10.1833868498,-2.118837
0265,-2.7169367286\C,-1.932594415,-1.648563573,0.6036580254\C,-1.88527
97017,-0.4680884166,-0.3852513119\N,-0.549129281,-0.0645888474,-0.6602

257239\O,0.3292778845,-0.2019290096,0.2308734328\O,-0.2730672322,0.493
8390202,-1.7466659132\H,-2.3717483807,-0.652056211,-1.3429587067\H,-1.
5394108531,-1.2923112662,1.5601946977\C,-1.0456986675,-2.8174755834,0.
1600796269\C,-0.1243014948,-3.3739316886,1.0580425042\C,-1.1161172369,
-3.3515125819,-1.1350485018\C,0.6987258858,-4.4355646283,0.6798860104\
H,-0.0425762834,-2.9617675578,2.0602265891\C,-0.2974934759,-4.41678220
45,-1.5155289312\H,-1.8023353034,-2.9288059808,-1.8627591987\C,0.61478
26304,-4.9605620004,-0.6109903677\H,1.4197258576,-4.8363597462,1.38455
65674\H,-0.3678555149,-4.8134084915,-2.5243409381\H,1.2636529383,-5.77
80073965,-0.9099938065\C,7.9844998754,-0.6451576457,-0.9047759394\C,4.
6328709301,-4.0335525195,0.6531904815\F,8.0527753275,0.3619497269,-1.8
021174016\F,8.6611464071,-0.2388188867,0.1950356111\F,8.6752491924,-1.
6896746665,-1.4190748967\F,3.8553816676,-4.0238158533,1.7645299979\F,3
.938596776,-4.7132662936,-0.2923733846\F,5.7278264283,-4.7681620947,0.
9405141792\S,4.3857613068,2.7100767013,0.5553757723\N,-6.9884074931,-2
.588023179,-1.7534303018\\Version=ES64L-G09RevD.01\State=1-A\HF=-3710.
8375027\RMSD=4.463e-09\RMSF=1.310e-06\Dipole=-7.1561926,-1.0594188,-1.
2302585\Quadrupole=21.5025381,-18.5386161,-2.963922,-5.4132273,13.8453
829,-2.3033073\PG=C01 [X(C42H51F6N7O4S2)]\\@

int2'A-*R,R*

1\1\GINC-R2461\FOpt\RB3LYP\6-31G(d,p)\C42H51F6N7O4S2\ROOT\13-Mar-2016\
0\\# freq=noraman b3lyp/6-31g(d,p) opt=maxcyc=200 scf=maxcyc=200 scrf=
(smd,solvent=toluene) iop(1/8=1)\\Conjugate addition-protonation produ
ct conf. 1: R(elec),R(nuc) (tol opt; cat III)\\0,1\C,-3.402912635,-1.5
754347151,1.0133751139\O,-4.3062359998,-2.2476391766,1.512422864\C,-2.
451760219,-0.7795495548,1.9491885297\H,-2.1826604738,-1.4905608918,2.7
32527785\N,-3.1690745474,-1.461865356,-0.3155553078\H,-2.378173639,-0.
8982389746,-0.5849131666\C,-3.9681308765,-1.9966020314,-1.4331515731\H
,-3.6504217087,-1.388313137,-2.2875148737\C,-3.5950306915,-3.472580153
3,-1.8259710359\C,-2.0602764525,-3.5891117982,-1.9113709724\H,-1.58782
95269,-3.4422709087,-0.9369133204\H,-1.6389953141,-2.85369347,-2.60899
64205\H,-1.7751700445,-4.5834809964,-2.2721119016\C,-4.1238945783,-4.5
096833877,-0.817621334\H,-3.7661679219,-4.3104028782,0.1944993863\H,-3
.7939150154,-5.5142003003,-1.1077891606\H,-5.2183300092,-4.5229765822,
-0.7840860051\C,-4.1697533992,-3.7841621629,-3.2248885893\H,-5.2634584
43,-3.806270664,-3.2359198753\H,-3.8235112502,-4.7679842115,-3.5605536
056\H,-3.8409645151,-3.0488287211,-3.9695282228\C,-5.4746309787,-1.749
0244003,-1.2262035331\H,-6.0205768717,-2.2100298168,-2.0688592594\H,-5
.7924819521,-2.2460903744,-0.3093011419\N,-5.8178222614,-0.3341601731,
-1.1085454687\C,-7.2143732956,-0.1234132511,-0.7128845267\H,-7.3744780
784,-0.4512057734,0.3191667713\H,-7.9068610093,-0.70114722,-1.35760336
61\C,-7.4350785952,1.3832475589,-0.9209842854\H,-8.4707037873,1.605045
7636,-1.1938684866\H,-7.2140706406,1.9320966394,-0.0010658106\C,-5.662
2780942,0.456129082,-2.3351680585\H,-6.1166342587,-0.0623908296,-3.203
3408942\H,-4.6076627238,0.6276617711,-2.5691820766\C,-6.4245653325,1.7
636187381,-2.0395020254\H,-6.9170781006,2.145200958,-2.938408812\H,-5.
7392879998,2.5420983144,-1.6912303315\N,-1.195187167,-0.3925605776,1.3
03891243\H,-1.1962417494,0.4759853664,0.7804484692\C,-3.14464329,0.455
9343395,2.6354853078\C,-4.3108243221,-0.0271851594,3.5203289669\H,-4.7
502132241,0.8304405745,4.0425586241\H,-3.9655502885,-0.739554896,4.277
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int2′A-*S,S*

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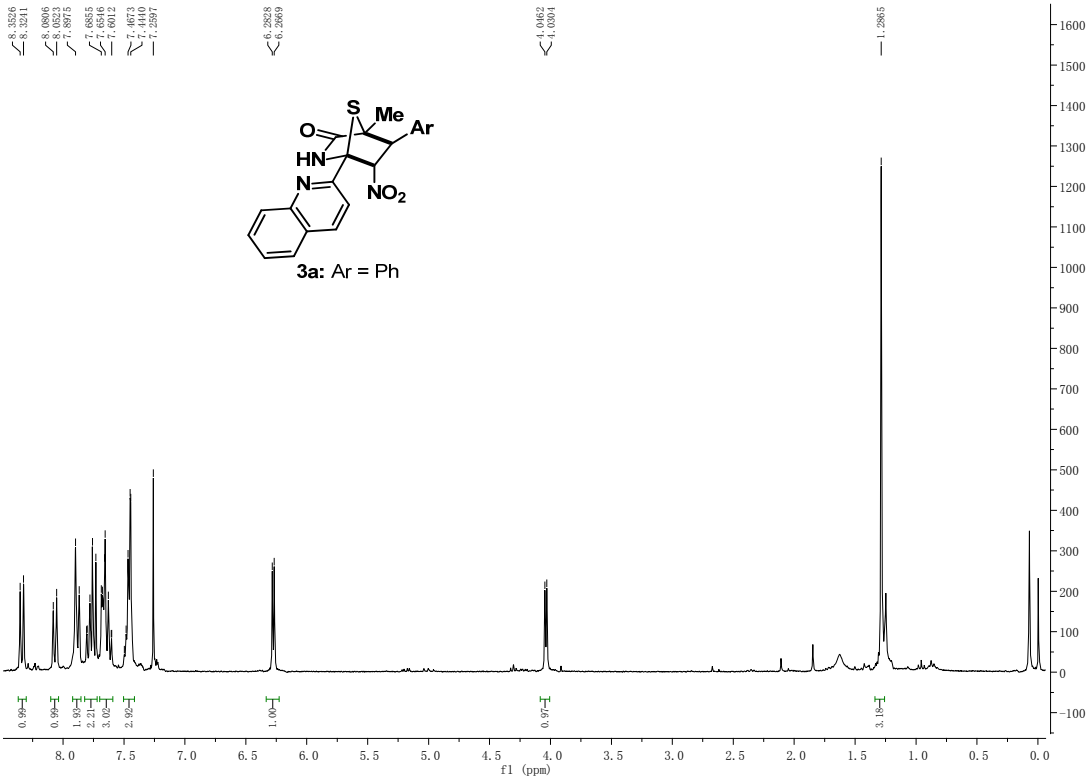
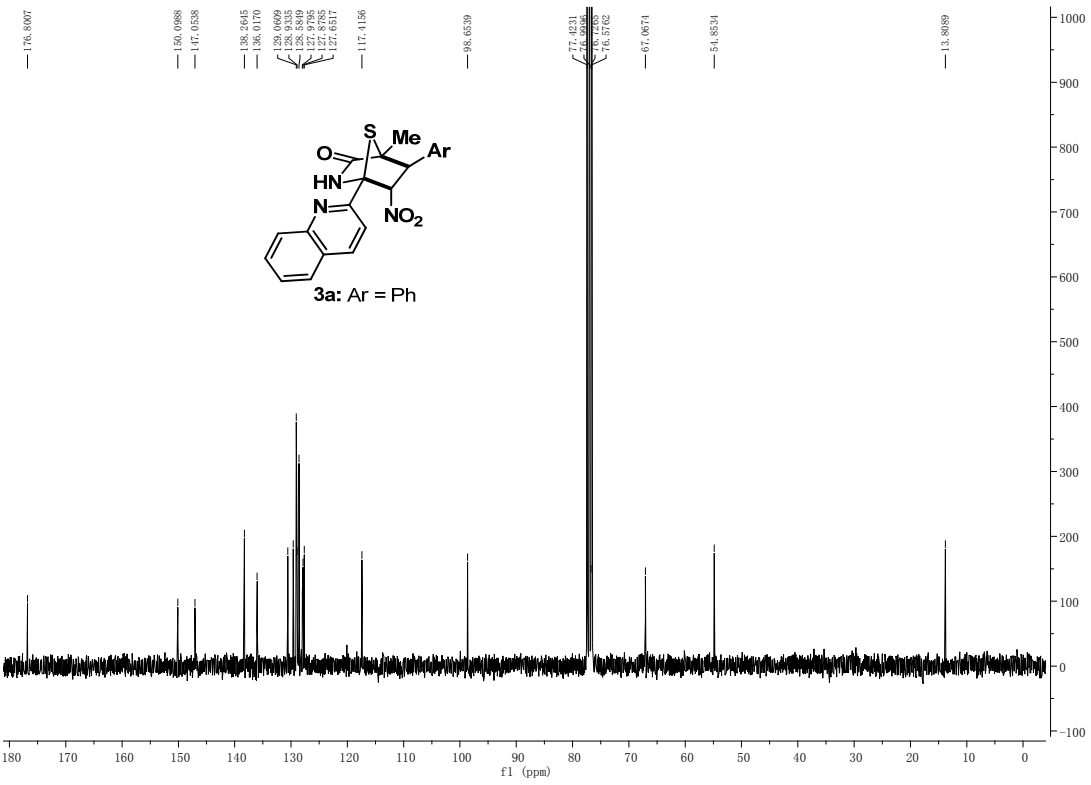
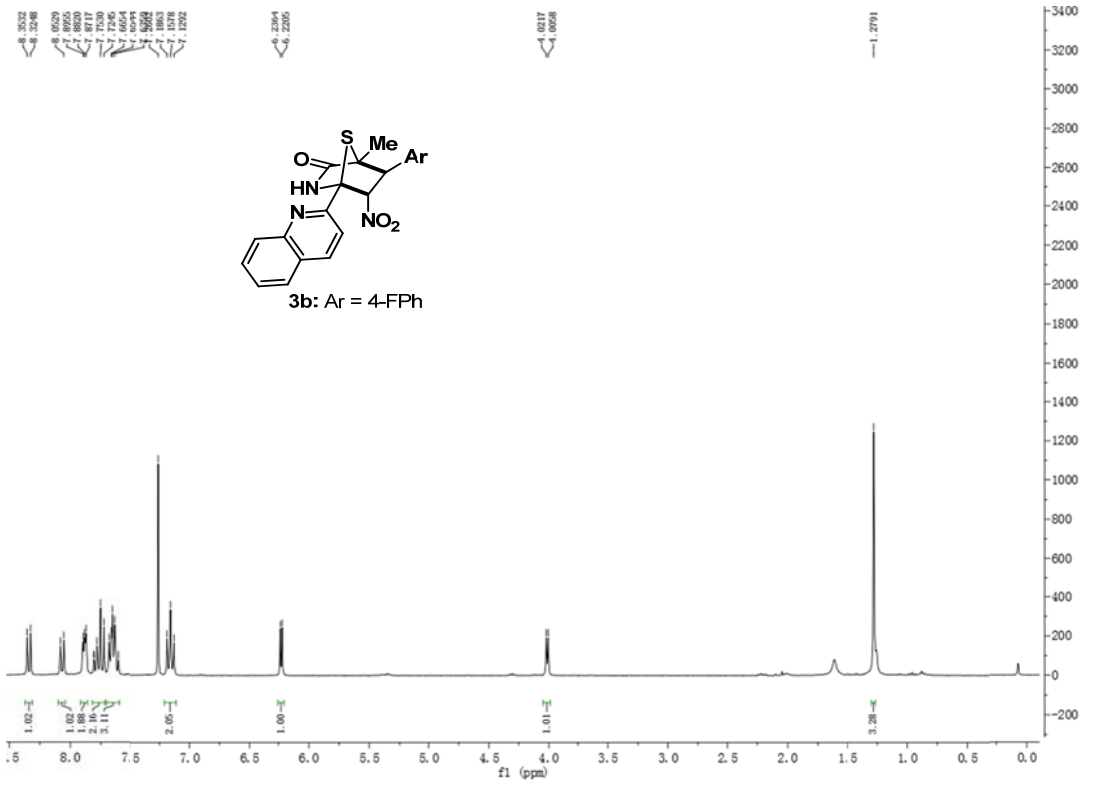
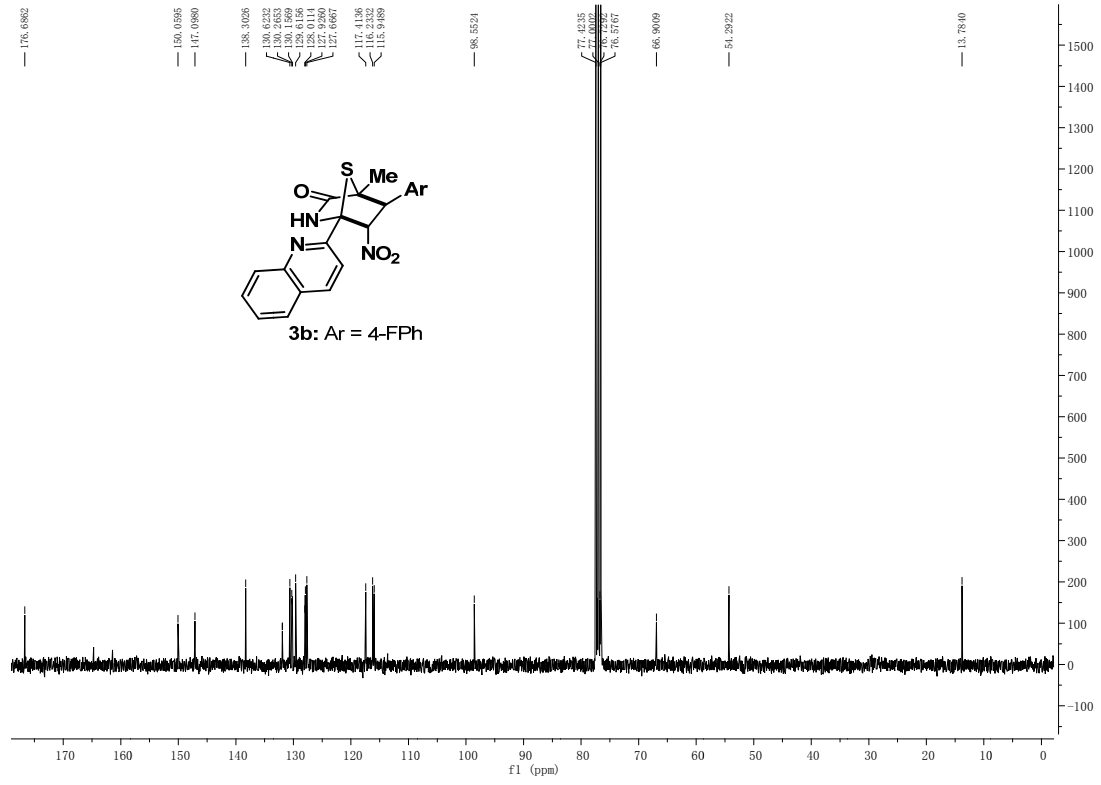
\\@

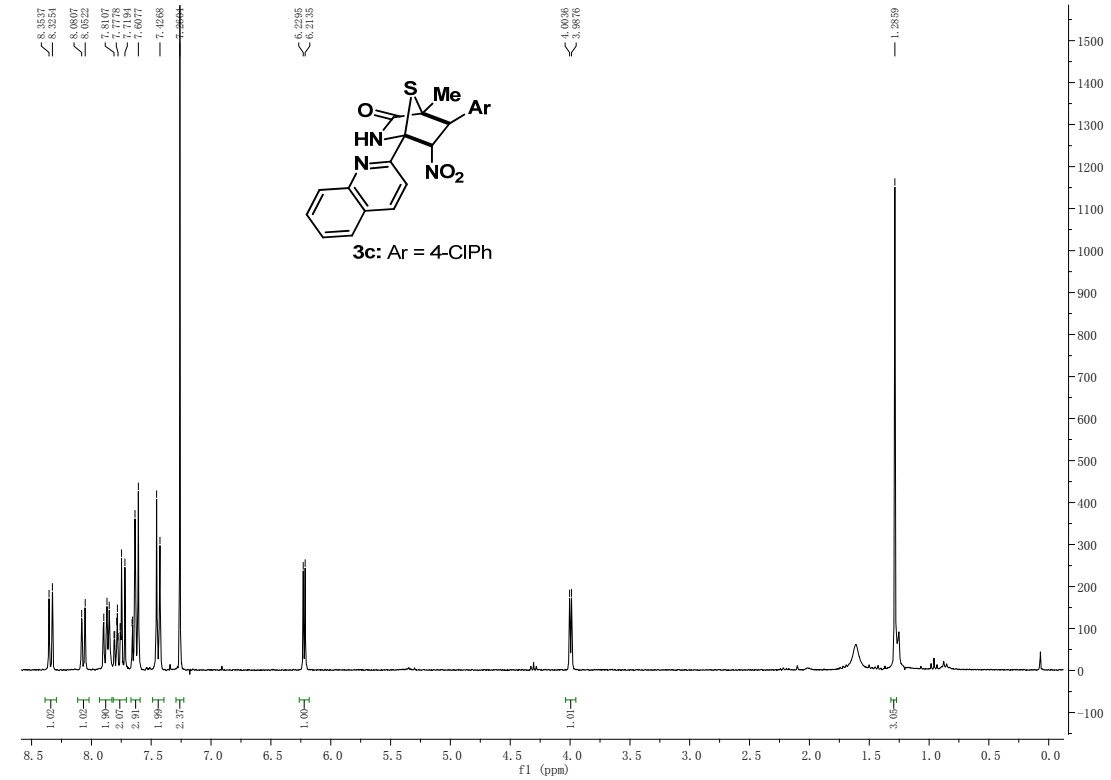
16. Copies of NMR Spectra






S
Me
Ar
O
HN
N
NO2
3b: Ar = 4-FPh
f1 (ppm)


S
Me
Ar
O
HN
N
NO2
3b: Ar = 4-FPh
f1 (ppm)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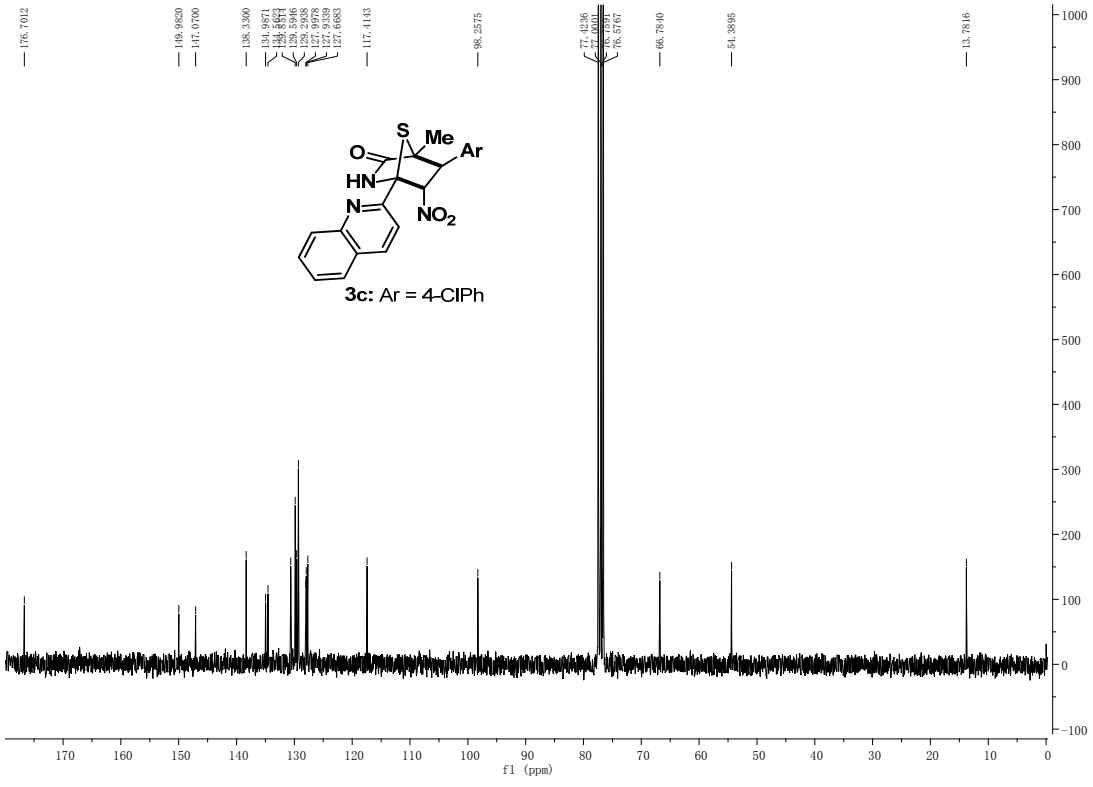
8.0522
7.8107
7.7878
7.7194
7.6977
7.4268
7.2601
6.2295
6.2135
4.0036
3.9876
1.2859
S
Me
Ar
O
HN
N
NO2
3c: Ar = 4-ClPh
1.02
1.02
1.90
2.07
2.91
1.99
2.37
1.00
1.01
3.05
f1 (ppm)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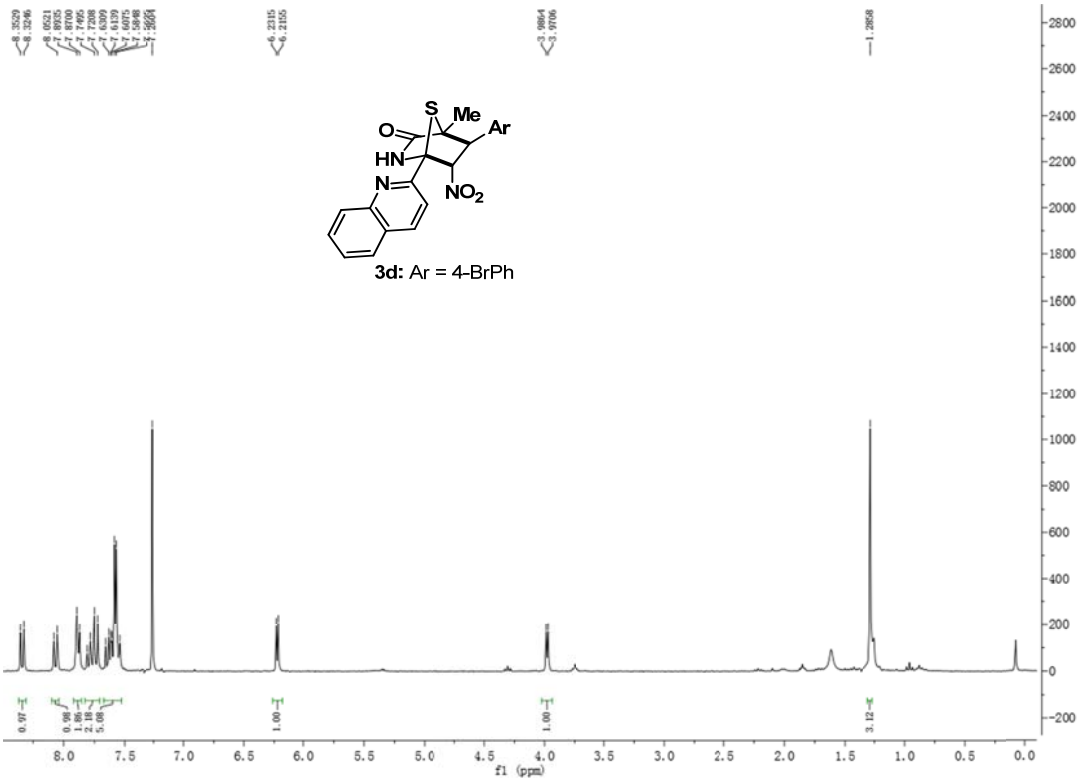
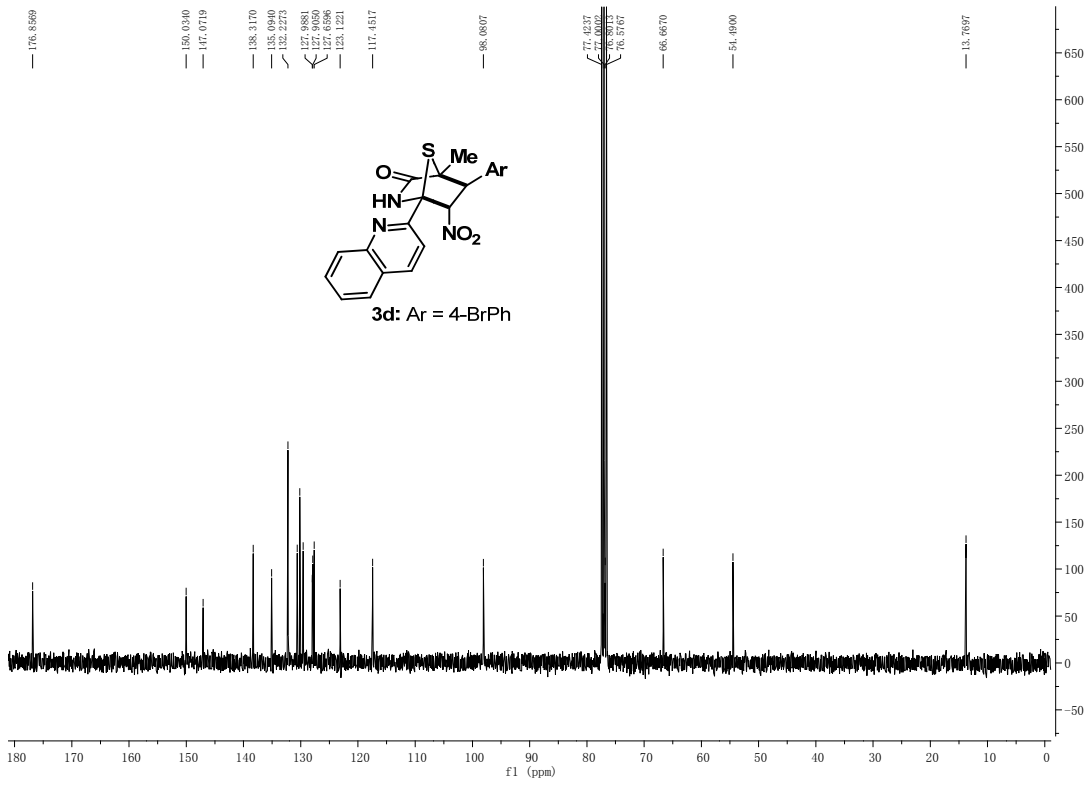
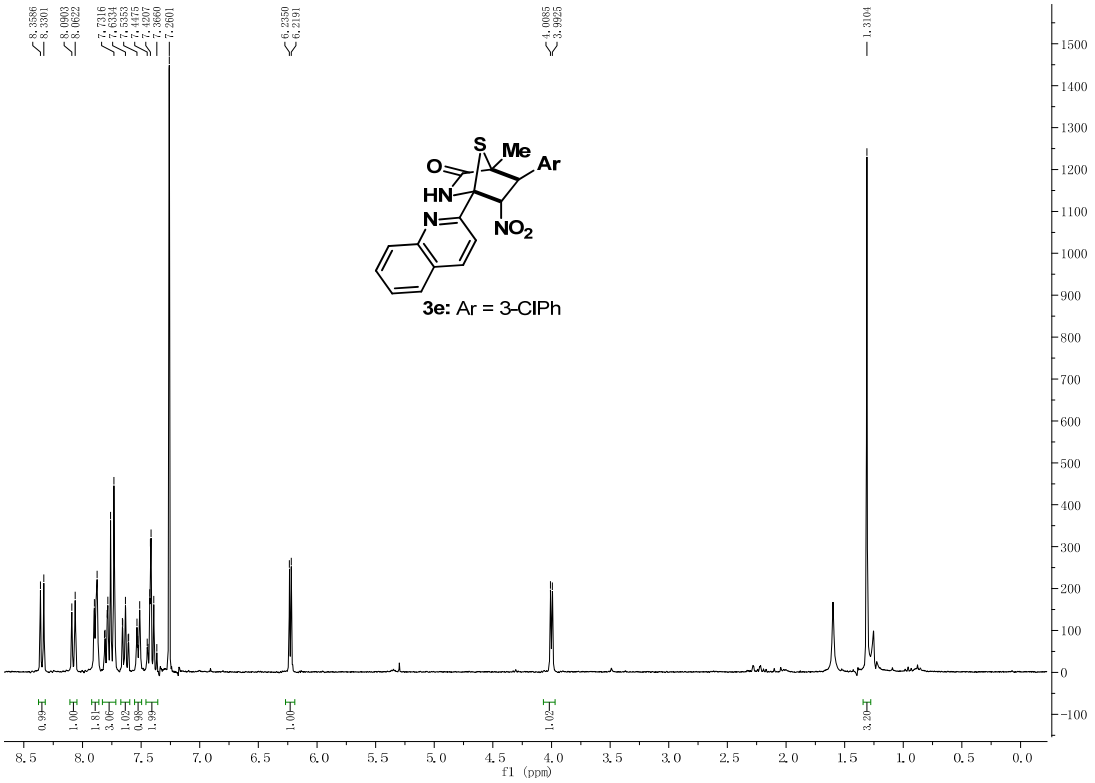
149.9820
147.0700
138.3300
134.9871
129.5946
129.2958
127.9339
127.6683
117.4143
98.2575
77.4236
76.5767
66.7840
54.3895
13.7816
S
Me
Ar
O
HN
N
NO2
3c: Ar = 4-ClPh
f1 (ppm)


S
Me
Ar
O
HN
N
NO2
3d: Ar = 4-BrPh
f1 (ppm)


S
Me
Ar
O
HN
N
NO2
3d: Ar = 4-BrPh
f1 (ppm)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8.3301
8.0903
8.0622
7.7316
7.6534
7.5353
7.4475
7.4207
7.3860
7.2601
6.2350
6.2191
4.0085
3.9925
1.3104
S
Me
Ar
O
HN
N
NO2
3e: Ar = 3-ClPh
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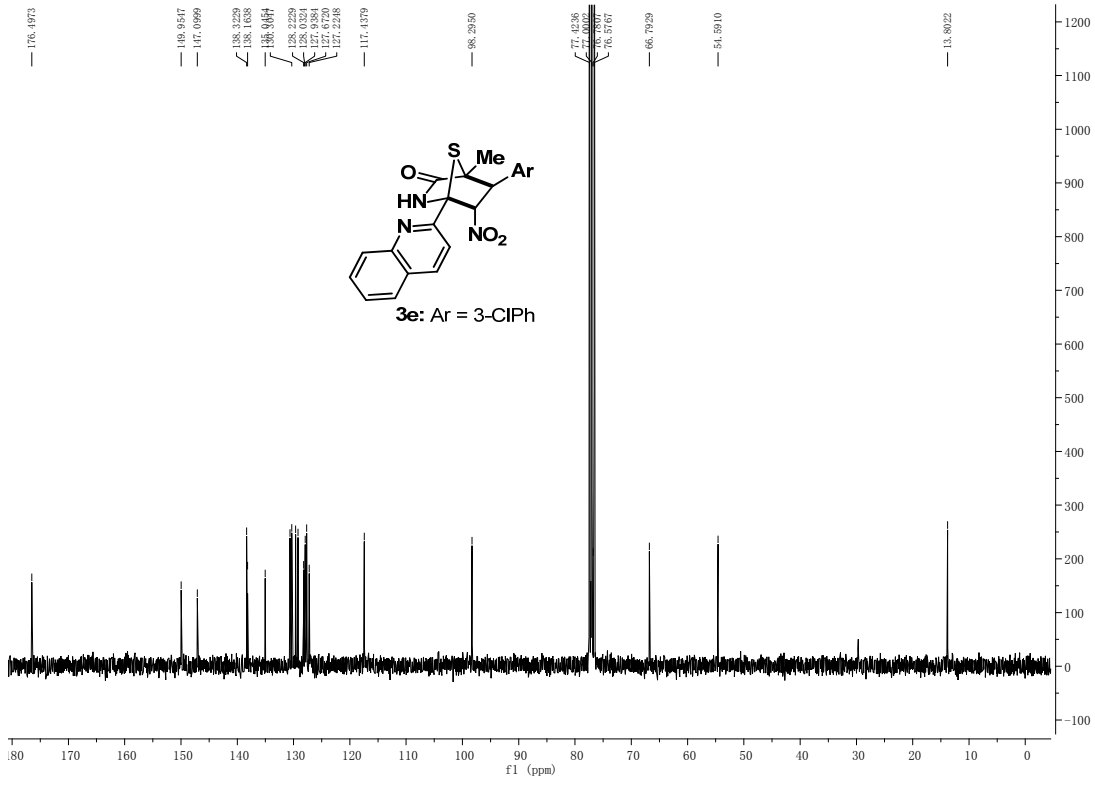
1.00
1.81
3.06
1.02
0.98
1.99
1.00
1.02
3.20
f1 (ppm)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147.0999
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138.1638
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128.0324
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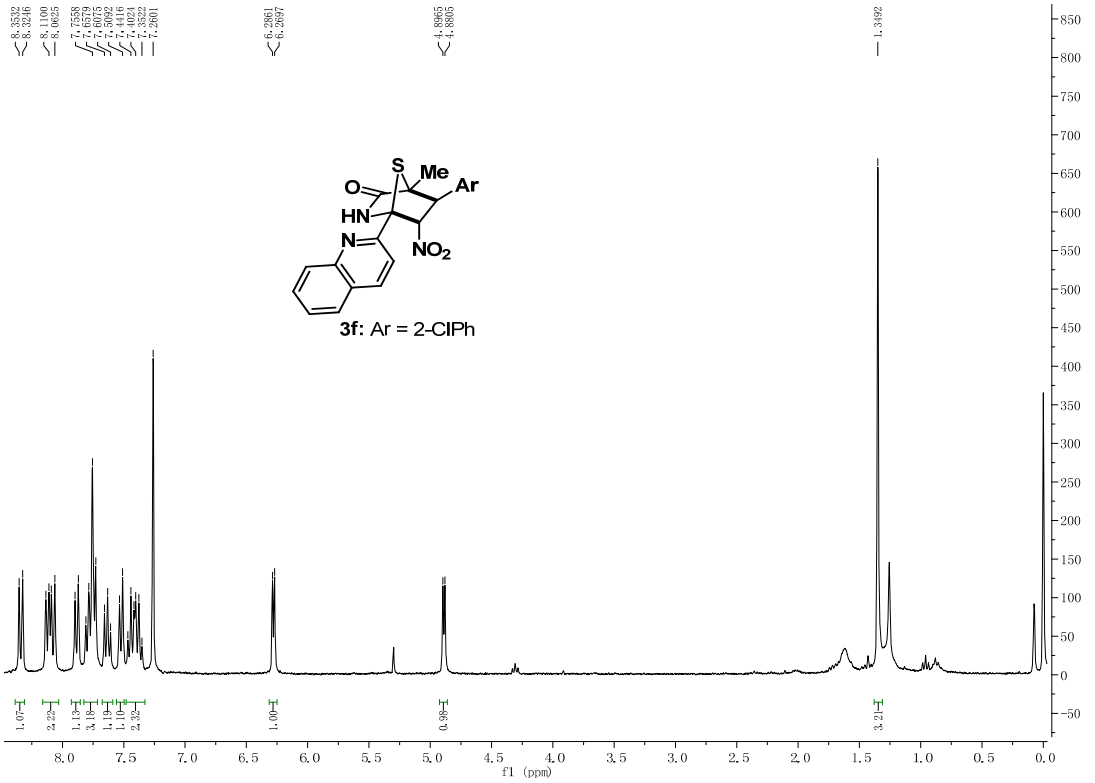
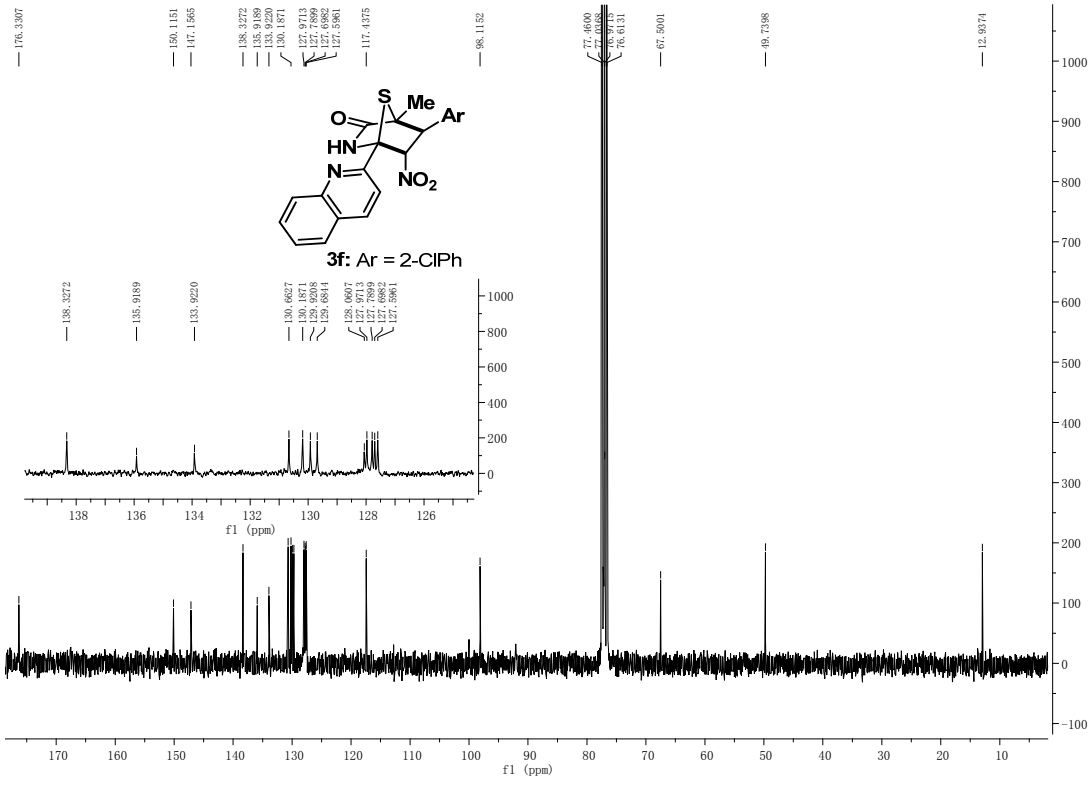
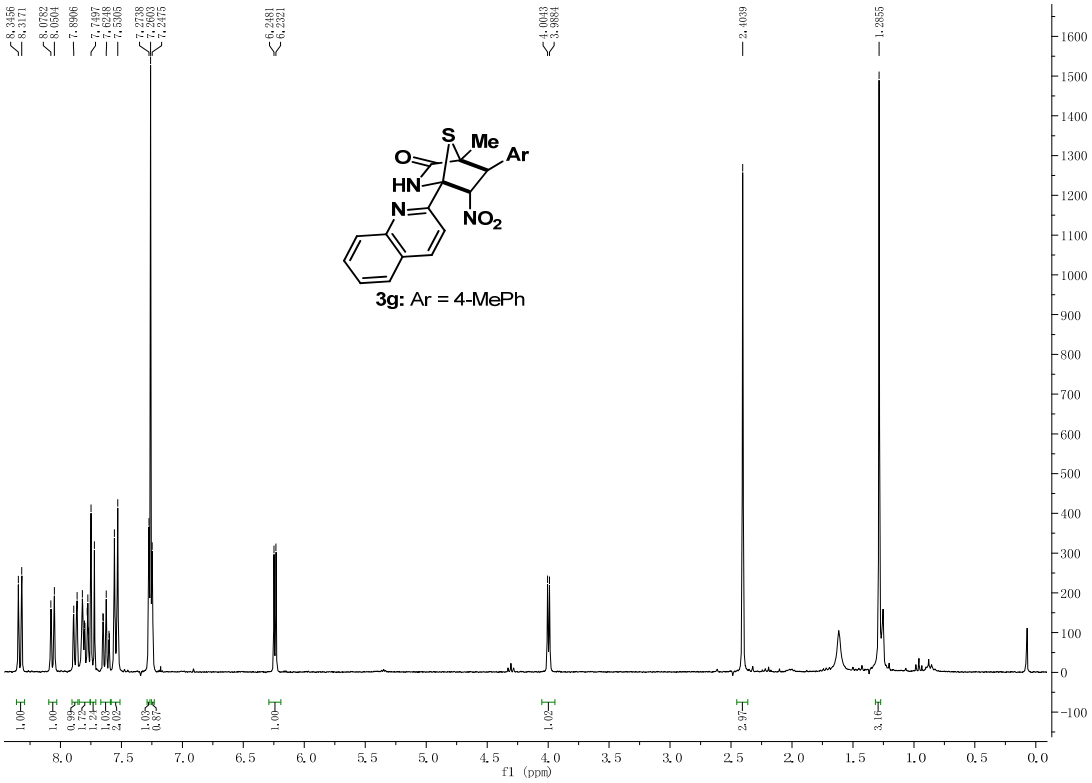
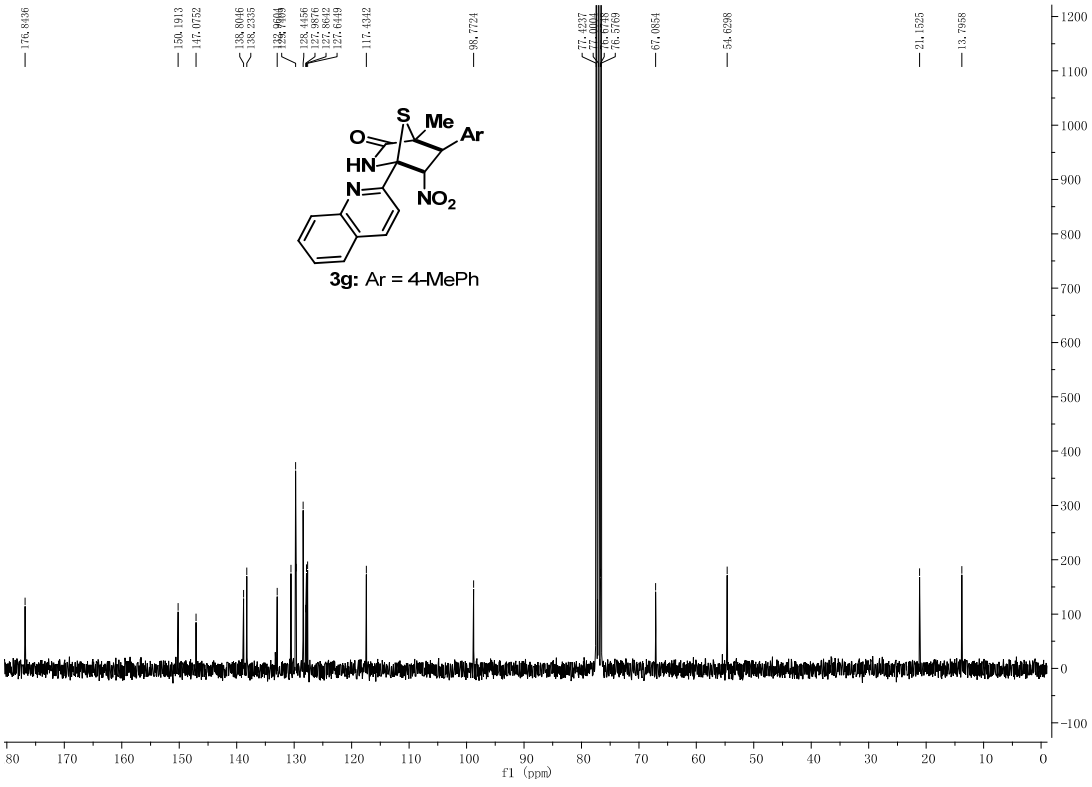
127.6720
127.2248
117.4379
98.2950
77.4236
77.0002
76.5767
66.7929
54.5910
13.8022
S
Me
Ar
O
HN
N
NO2
3e: Ar = 3-ClPh
f1 (ppm)


3f: Ar = 2-ClPh
f1 (ppm)


3f: Ar = 2-ClPh
f1 (ppm)


8.3456
8.3171
8.0782
8.0504
7.8906
7.7497
7.7248
7.6305
7.2738
7.2603
7.2475
6.2481
6.2321
4.0043
3.9884
2.4039
1.2855
S
Me
Ar
O
HN
N
NO2
3g: Ar = 4-MePh
f1 (ppm)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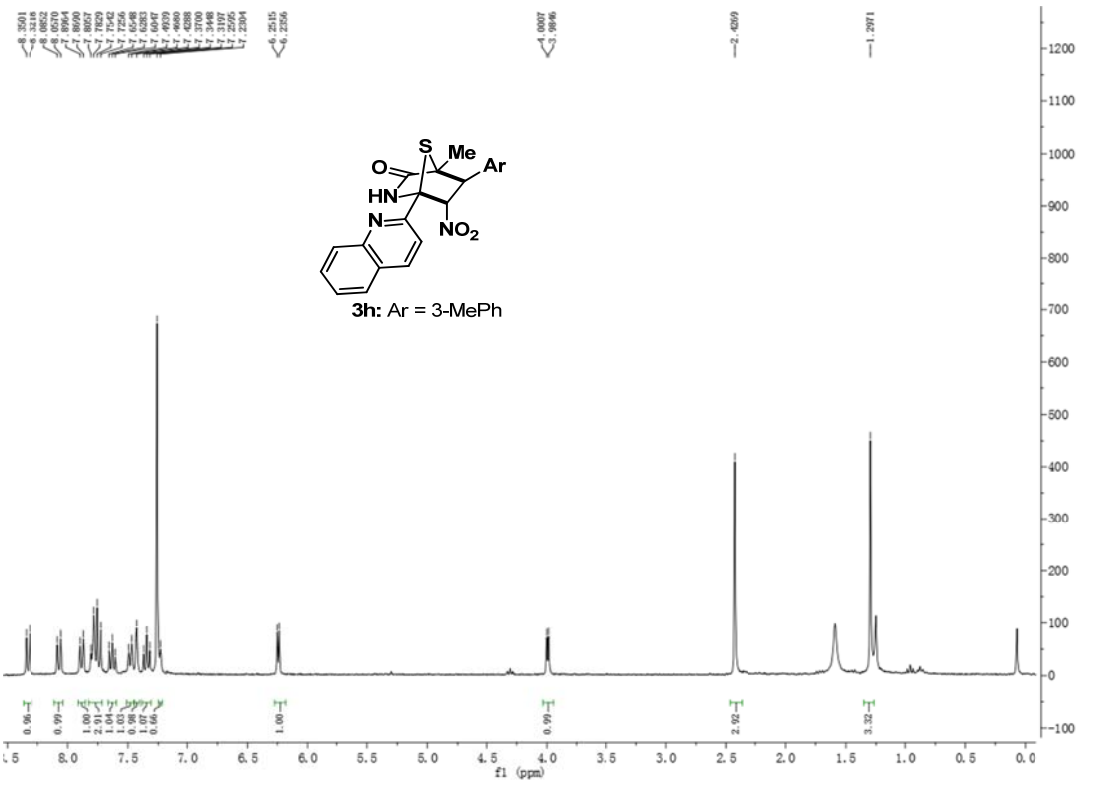
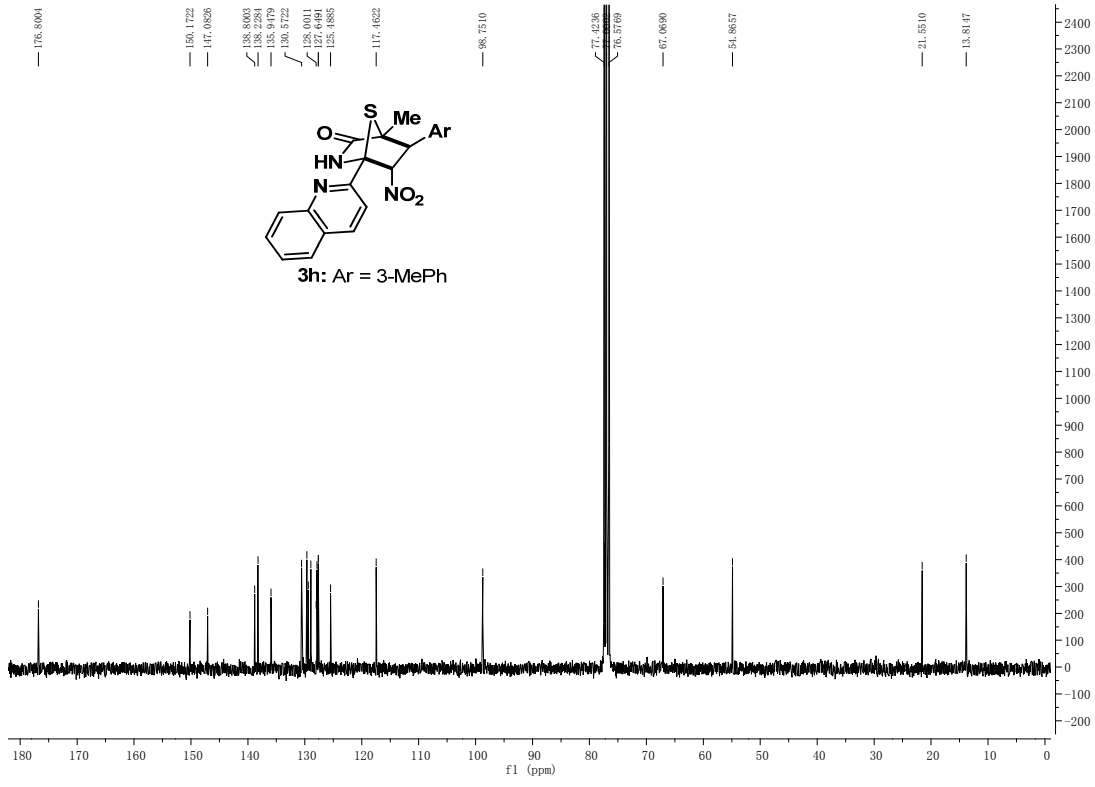
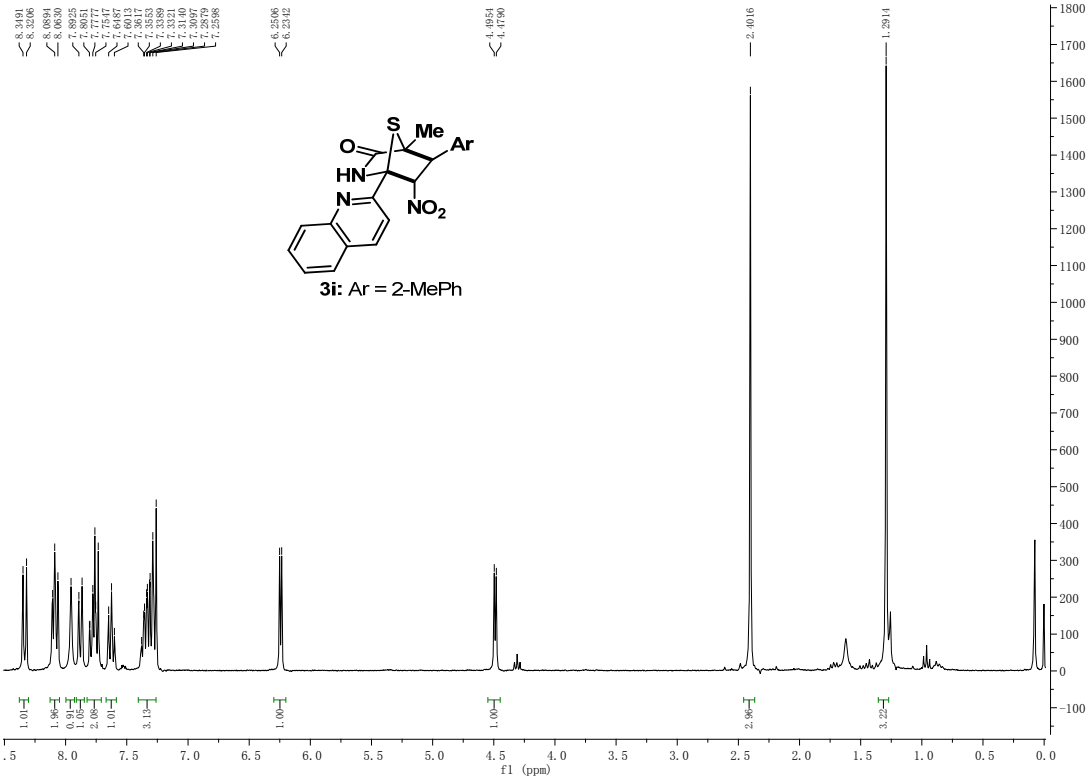
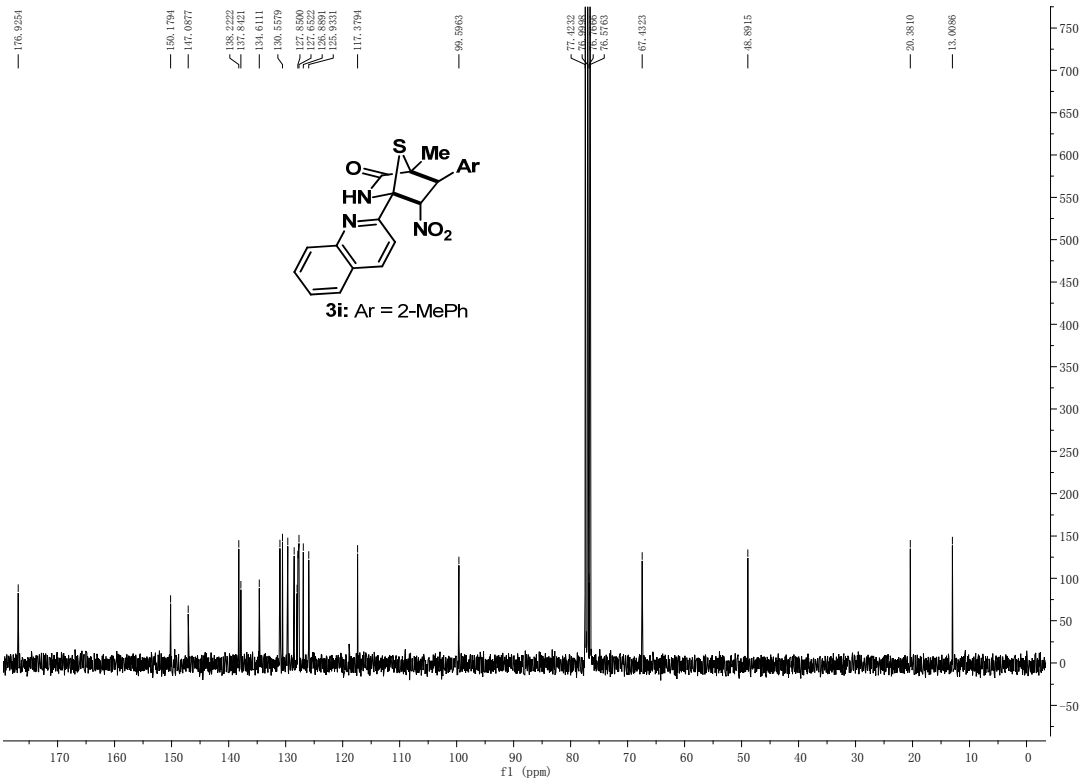
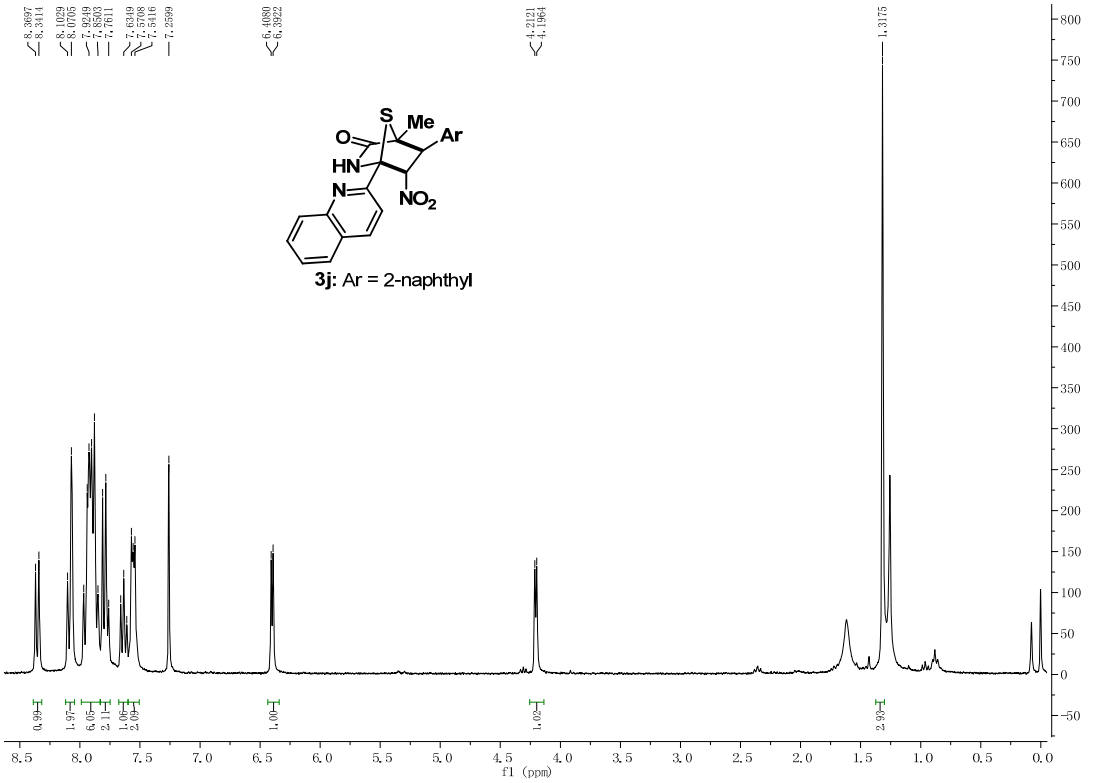
150.1913
147.0752
138.8046
138.2335
128.4456
127.9876
127.8042
127.6449
117.4342
98.7724
77.4237
67.0854
54.6298
21.1525
13.7988
S
Me
Ar
O
HN
N
NO2
3g: Ar = 4-MePh
f1 (ppm)

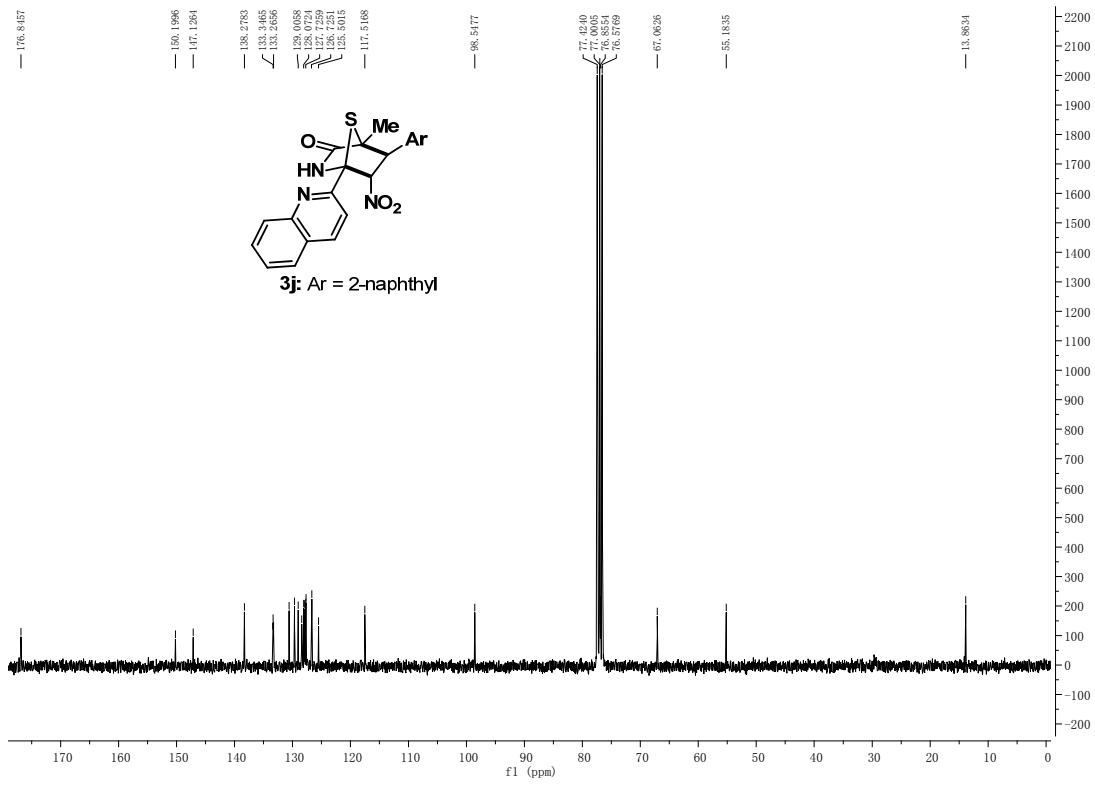

S
Me
Ar
O
HN
N
NO2
3h: Ar = 3-MePh
f1 (ppm)

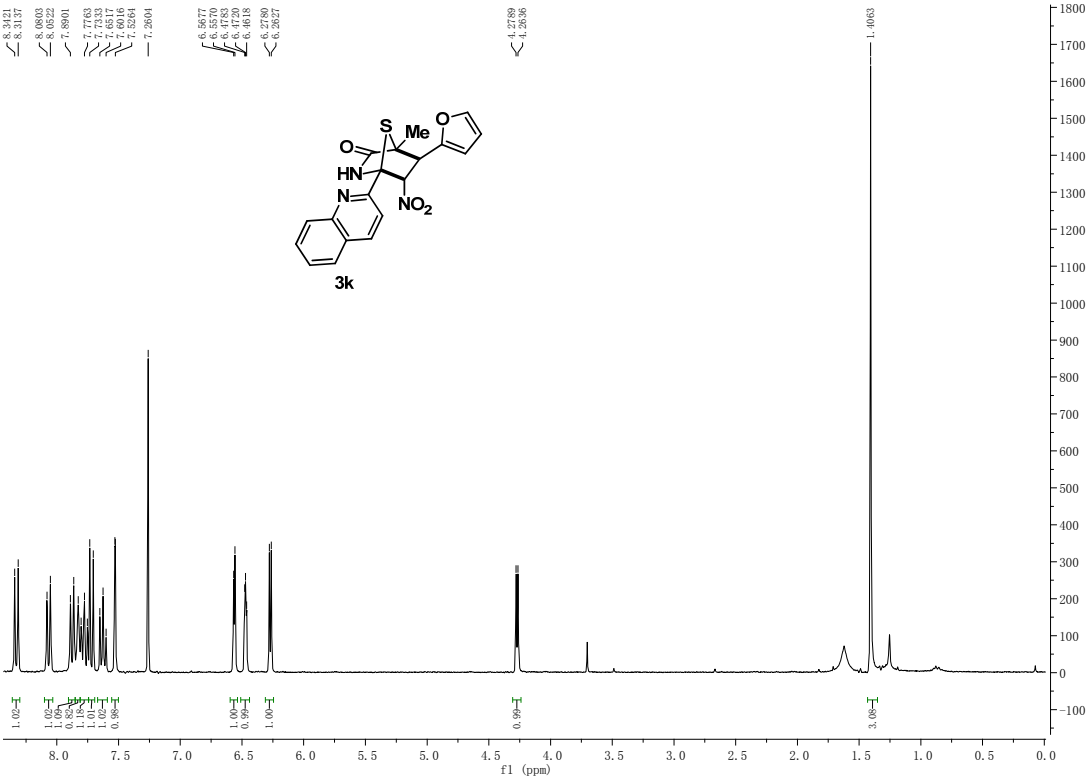

S
Me
Ar
O
HN
N
NO2
3h: Ar = 3-MePh
f1 (ppm)

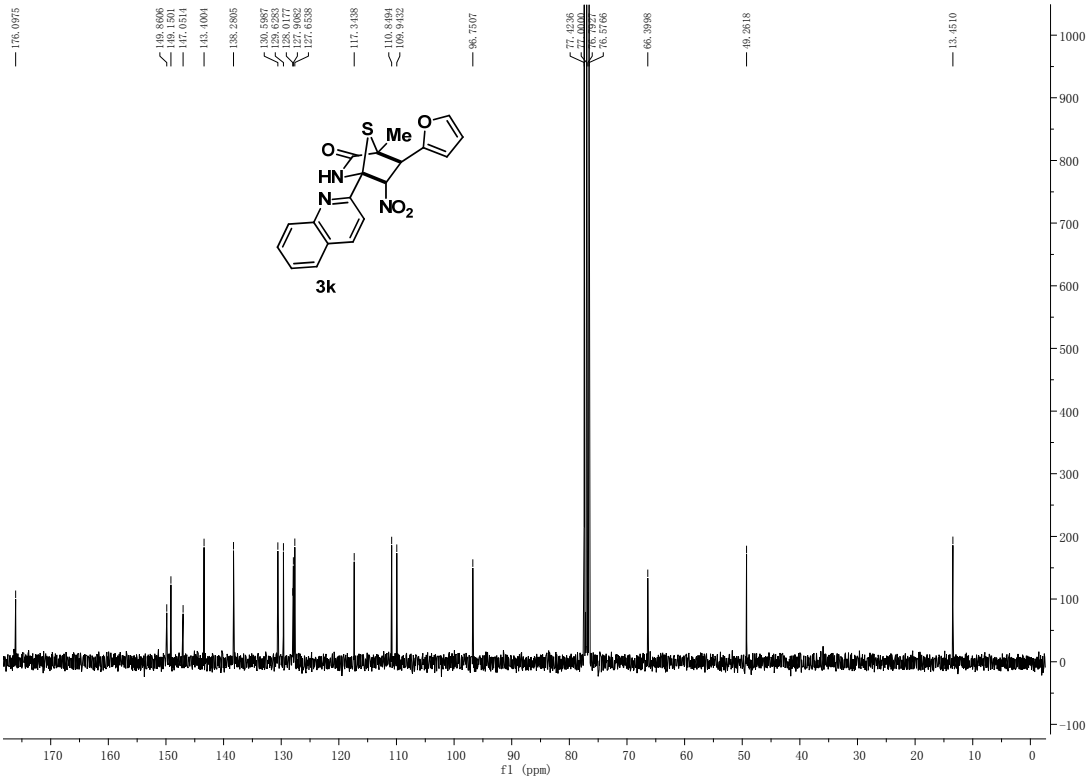

8.3491
8.3206
8.0894
8.0630
7.8925
7.8051
7.7777
7.7547
7.6485
7.6013
7.3617
7.3583
7.3398
7.3321
7.3140
7.3097
7.2879
7.2598
6.2506
6.2342
4.4954
4.4790
2.4016
1.2914
S
Me
Ar
O
HN
N
NO2
3i: Ar = 2-MePh
1.01
1.96
0.91
1.05
2.08
1.01
3.13
1.00
1.00
2.06
3.22
f1 (ppm)

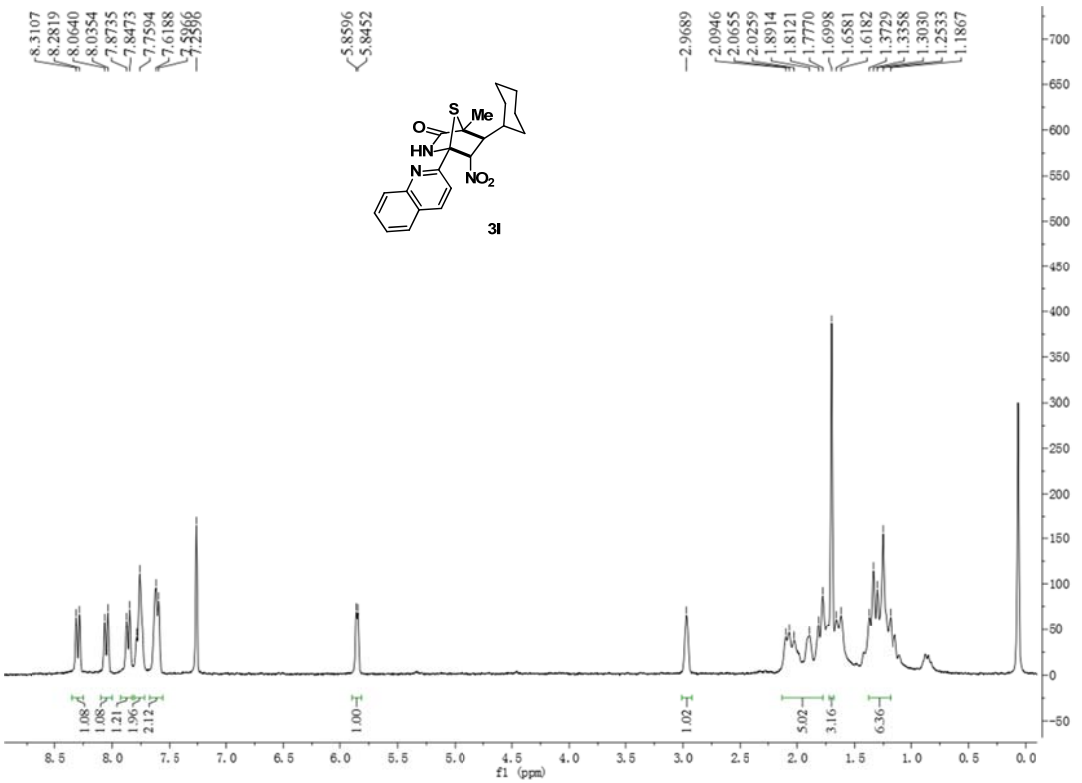

176.9254
150.1794
147.0877
138.2222
137.8421
134.6111
130.5579
127.8500
127.6522
126.8891
125.9331
117.3794
99.6963
77.4232
76.5763
67.4323
48.8915
20.3810
13.6086
S
Me
Ar
O
HN
N
NO2
3i: Ar = 2-MePh
f1 (ppm)

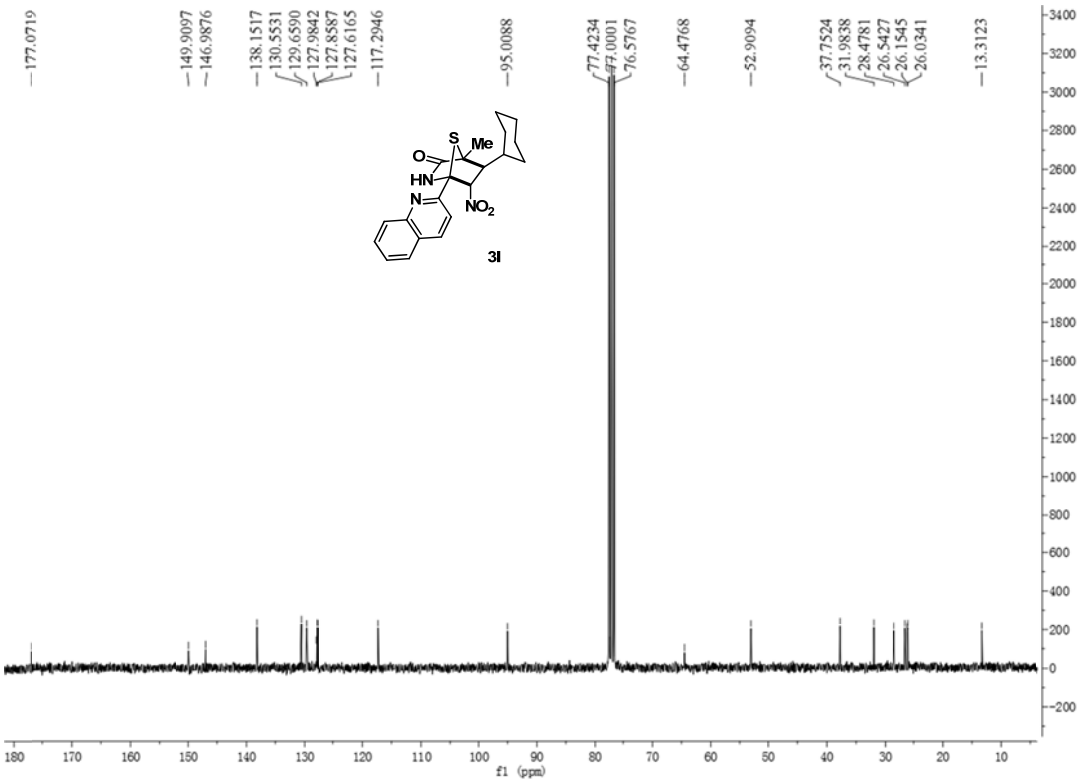

8.3697
8.3414
8.1029
8.0705
7.9249
7.8503
7.7611
7.6349
7.5708
7.5416
7.2599
6.4080
6.3922
4.2121
4.1964
1.3175
S
Me
Ar
O
HN
N
NO2
3j: Ar = 2-naphthyl
0.99
1.97
6.05
2.11
1.06
2.09
1.00
1.02
2.93
f1 (ppm)

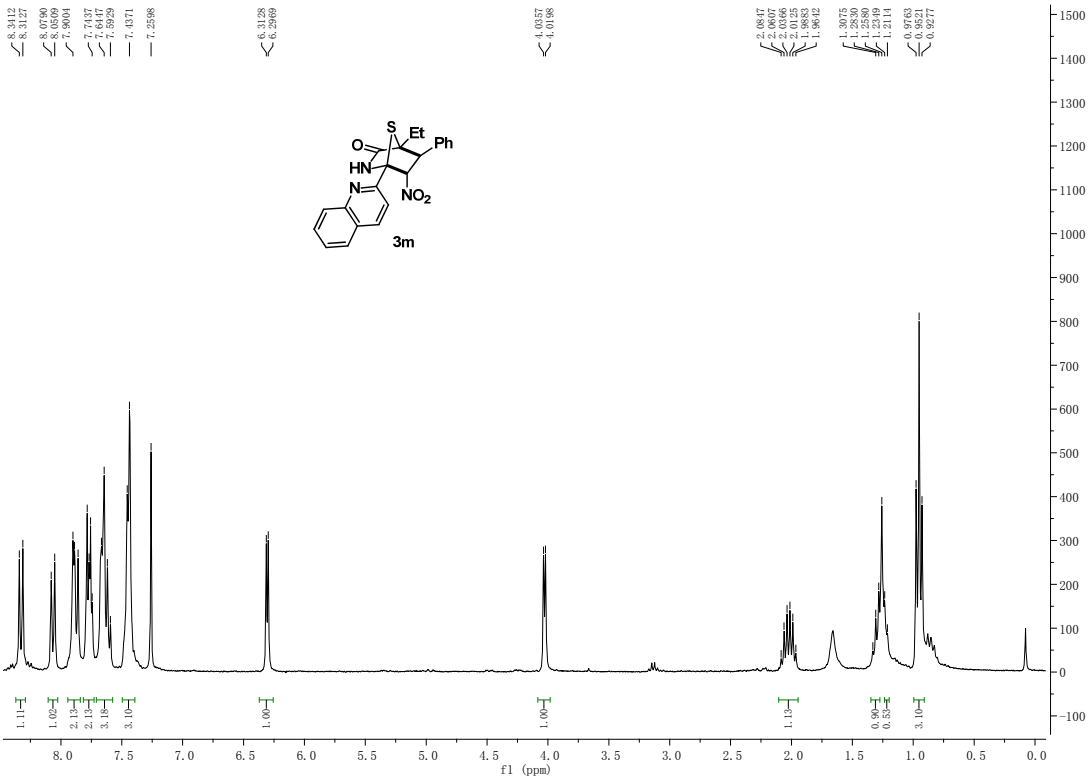

176.8457
150.1996
147.1264
138.2783
133.3465
133.2656
129.0058
128.0724
127.7259
126.7251
125.5015
117.5168
98.5477
77.4240
77.0005
76.8554
76.5769
67.0626
55.1835
13.8634
S
Me
Ar
O
HN
N
NO2
3j: Ar = 2-naphthyl
f1 (ppm)

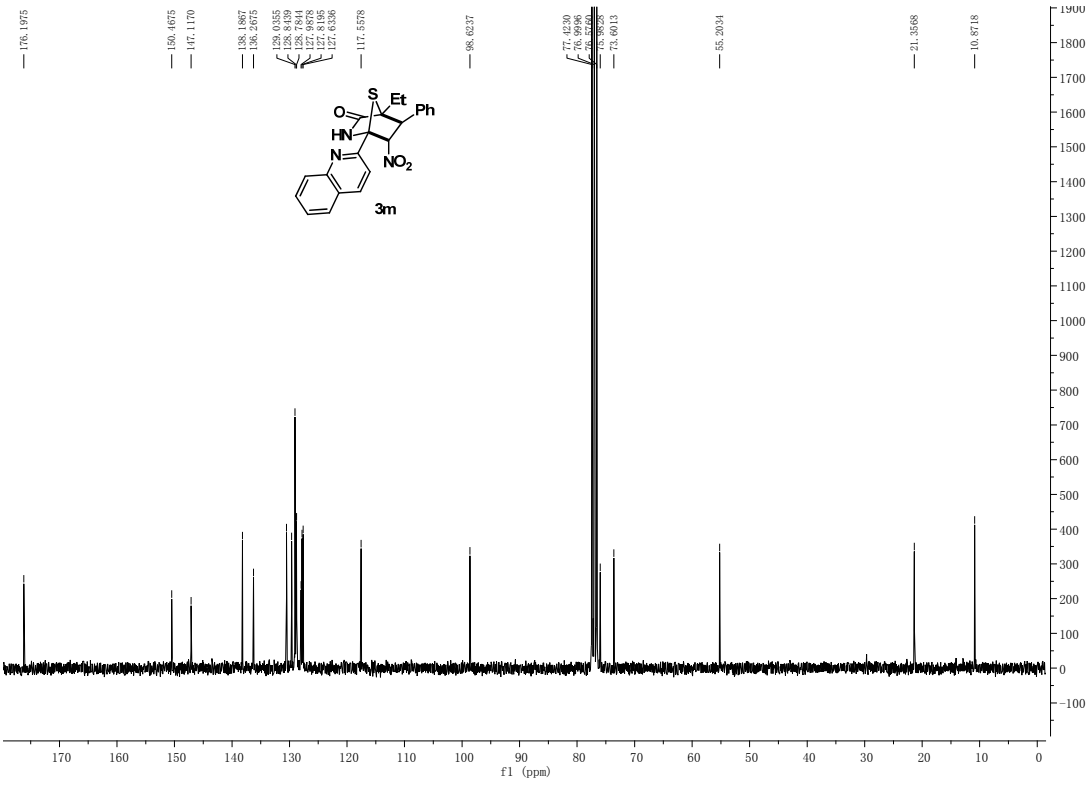

8.3421
8.3137
8.0803
8.0522
7.8901
7.7763
7.7333
7.6517
7.6016
7.5264
7.2604
6.5677
6.5570
6.4783
6.4720
6.4618
6.2780
6.2627
4.2789
4.2636
1.4063
S
Me
O
O
HN
N
NO2
3k
1.02
1.09
0.82
1.18
1.01
1.02
0.98
1.00
0.99
1.00
0.99
3.09
f1 (ppm)

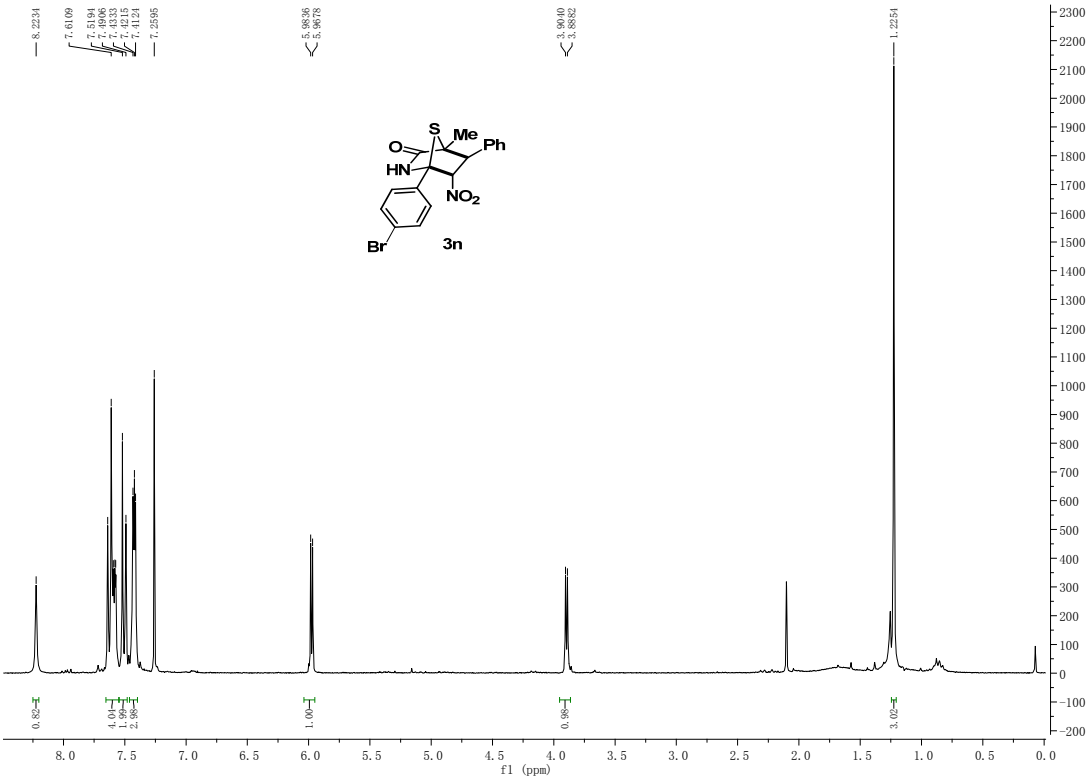

176.0975
149.8606
149.1501
147.0514
143.4004
138.2805
130.5987
129.6283
128.8177
127.9082
127.6538
117.3438
110.8494
109.9432
96.7507
77.4236
76.9999
76.5766
66.3998
49.2618
13.4510
S
Me
O
O
HN
N
NO2
3k
f1 (ppm)

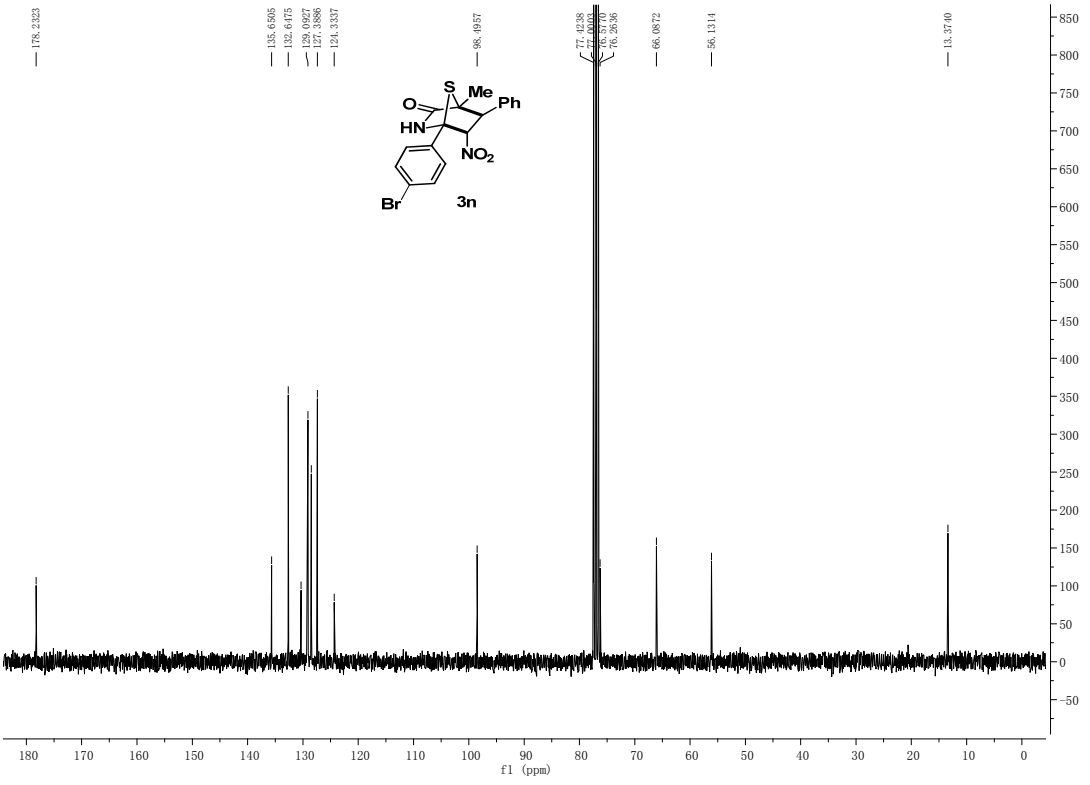

8.3107
8.2819
8.0640
8.0354
7.8735
7.8473
7.7594
7.6188
5.8596
5.8452
2.9689
2.0946
2.0655
2.0259
1.8914
1.8121
1.7770
1.6998
1.6581
1.6182
1.3729
1.3358
1.3030
1.2533
1.1867
S
Me
O
HN
N
NO2
3l
1.08
1.08
1.21
1.96
2.12
1.00
1.02
5.02
3.16
6.36
f1 (ppm)

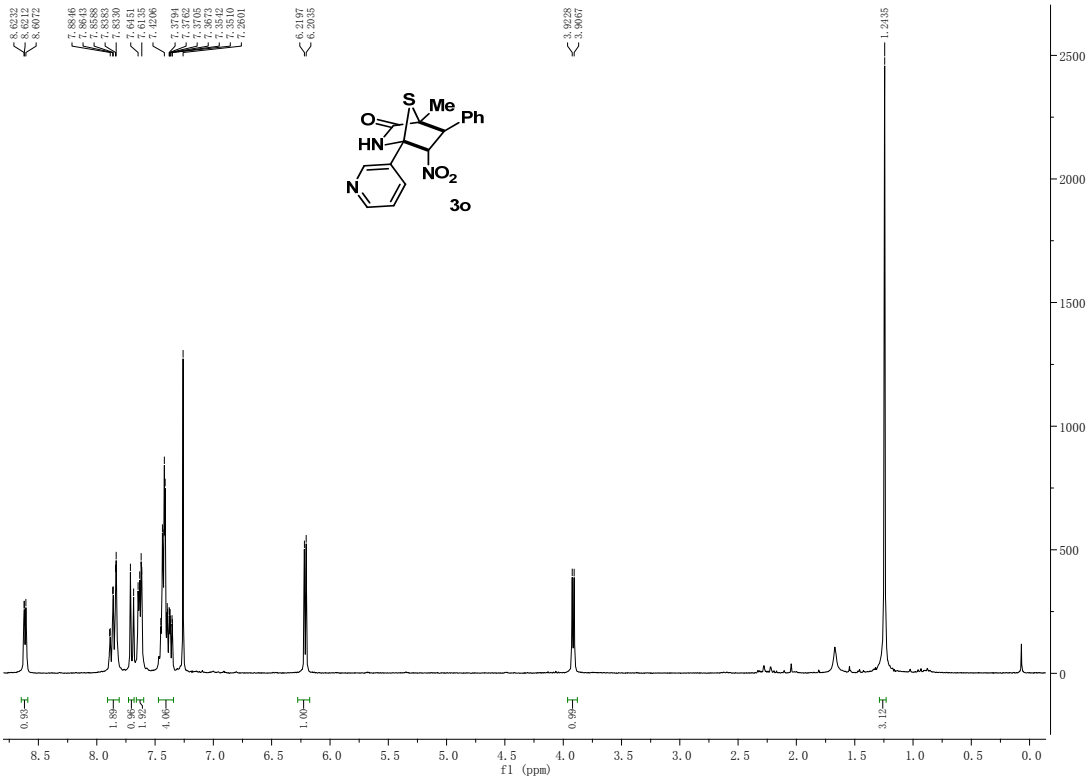

177.0719
149.9097
146.9876
138.1517
130.5531
129.6590
127.9842
127.8587
127.6165
117.2946
95.0088
77.4234
77.0001
76.5767
64.4768
52.9094
37.7524
31.9838
28.4781
26.5427
26.1545
26.0341
13.3123
S
Me
O
HN
N
NO2
3l
f1 (ppm)

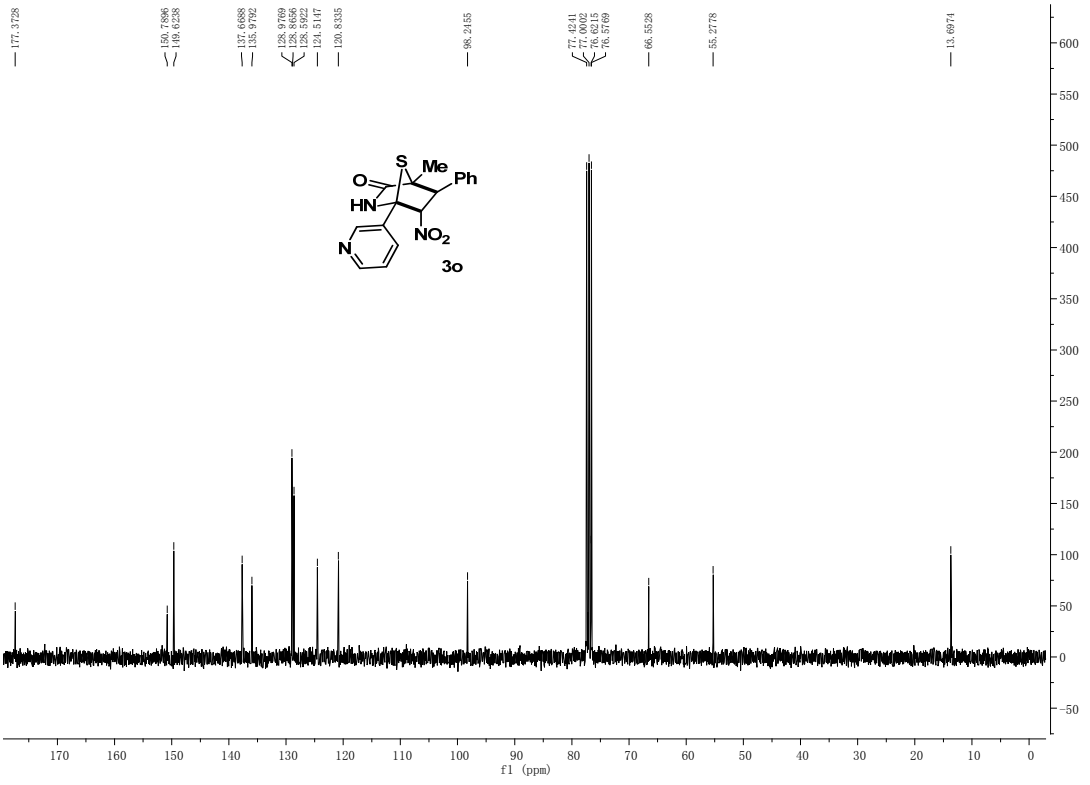

8.3412
8.3127
8.0790
8.0509
7.9004
7.7437
7.6447
7.5929
7.4371
7.2598
6.3128
6.2969
4.0357
4.0198
2.0847
2.0607
2.0366
2.0125
1.9883
1.9642
1.3075
1.2830
1.2580
1.2349
1.2114
0.9763
0.9521
0.9277
S
Et
Ph
O
HN
N
NO2
3m
f1 (ppm)

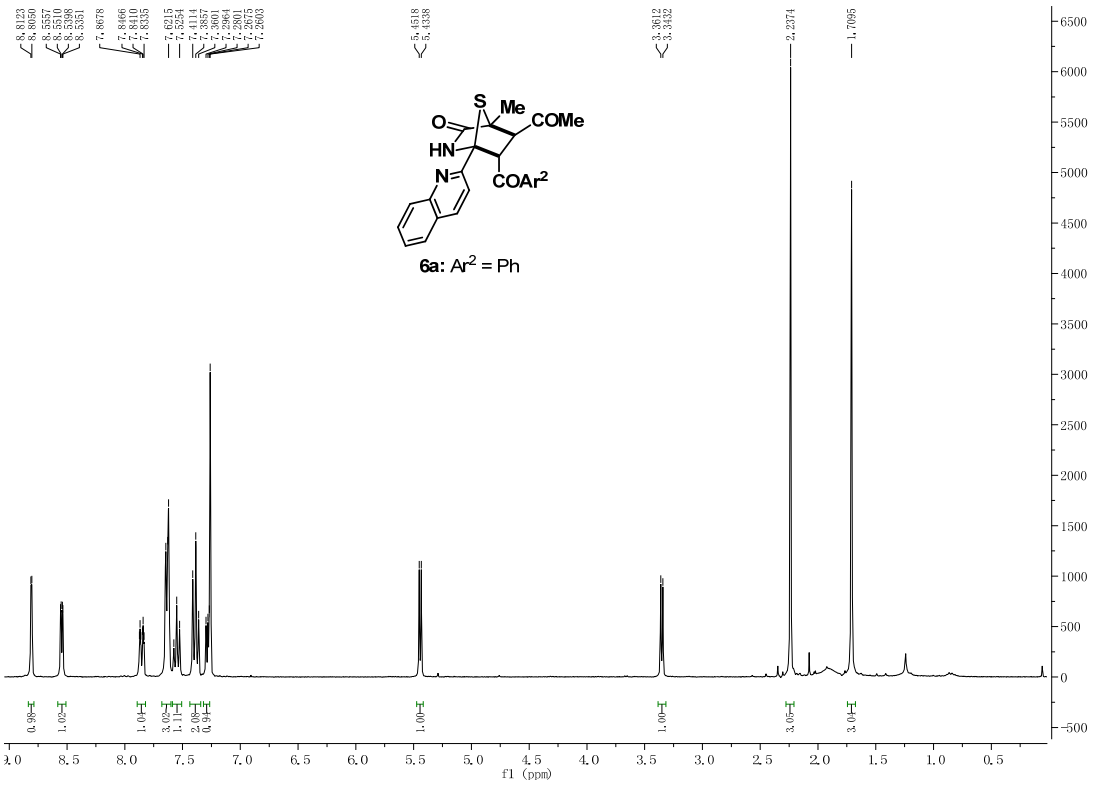

176.1975
150.4675
147.1170
138.1867
136.2675
129.0355
128.8439
128.7944
127.9878
127.8195
127.6336
117.5578
98.6237
77.4230
77.0998
76.7766
76.5760
73.3825
73.6013
55.2034
21.3568
10.8718
S
Et
Ph
O
HN
N
NO2
3m
f1 (ppm)

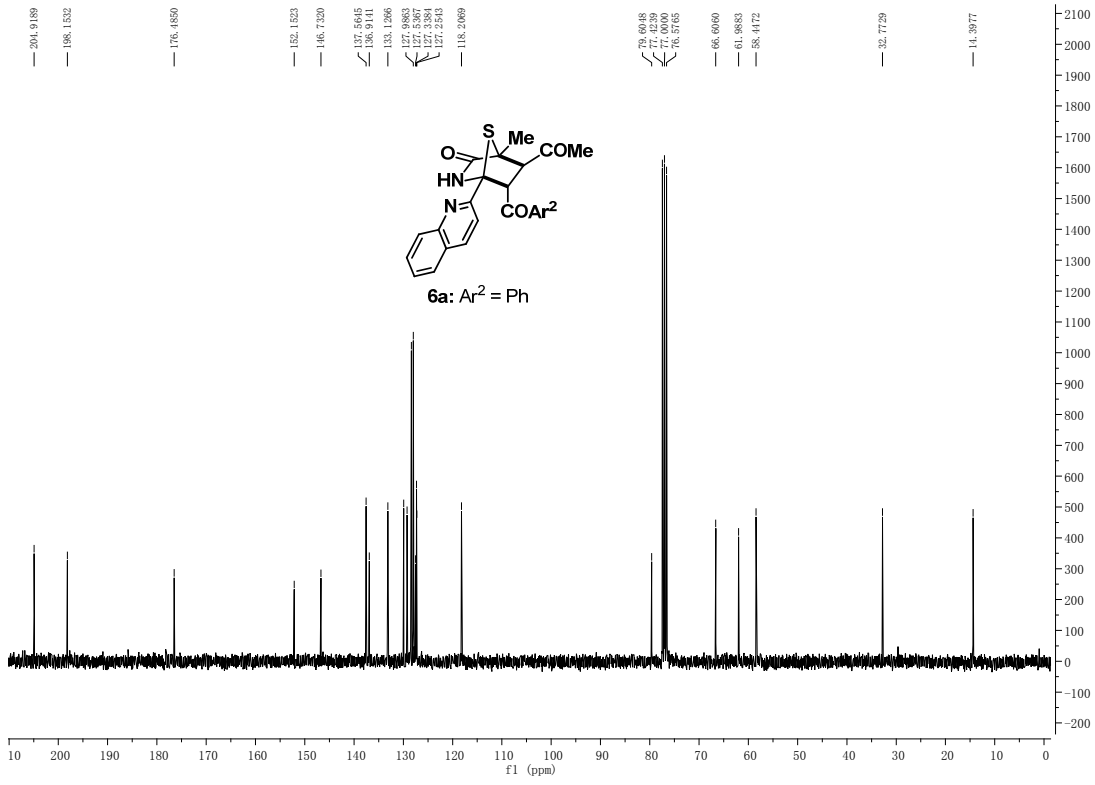

8.2234
7.6109
7.5194
7.4996
7.4333
7.4215
7.4124
7.2595
5.9836
5.9678
3.9040
3.8882
1.2254
S
Me
Ph
O
HN
NO2
Br
3n
0.82
4.01
1.99
2.88
1.00
0.98
3.02
f1 (ppm)

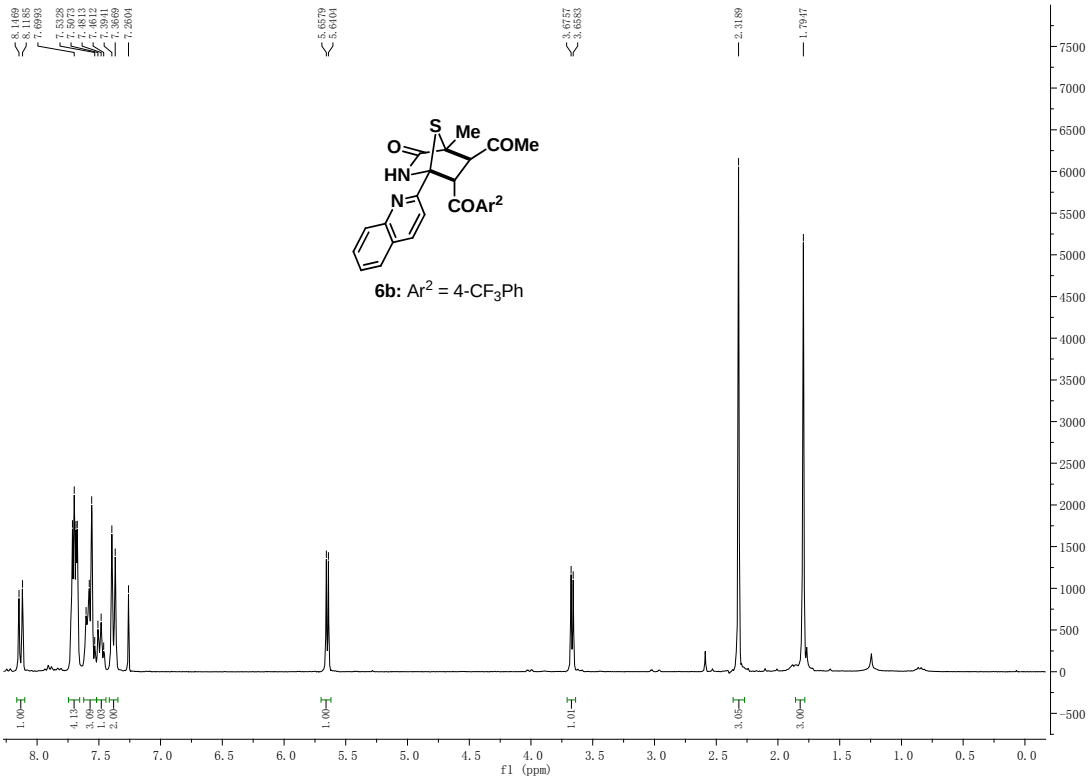

178.2323
135.6505
132.6475
129.0927
127.3886
124.3337
98.4957
77.4238
77.0003
76.5740
76.2636
66.0872
56.1314
13.3740
S
Me
Ph
O
HN
NO2
Br
3n
f1 (ppm)


8.62 32
8.62 12
8.60 72
7.88 46
7.86 43
7.85 88
7.83 53
7.82 30
7.64 51
7.61 35
7.42 06
7.37 94
7.37 62
7.37 05
7.36 73
7.35 42
7.35 10
7.29 01
6.21 97
6.20 35
3.92 28
3.90 67
1.24 35
S
Me
Ph
O
HN
NO2
N
3o
0.93
1.89
0.96
1.92
4.00
1.00
0.89
3.12
f1 (ppm)

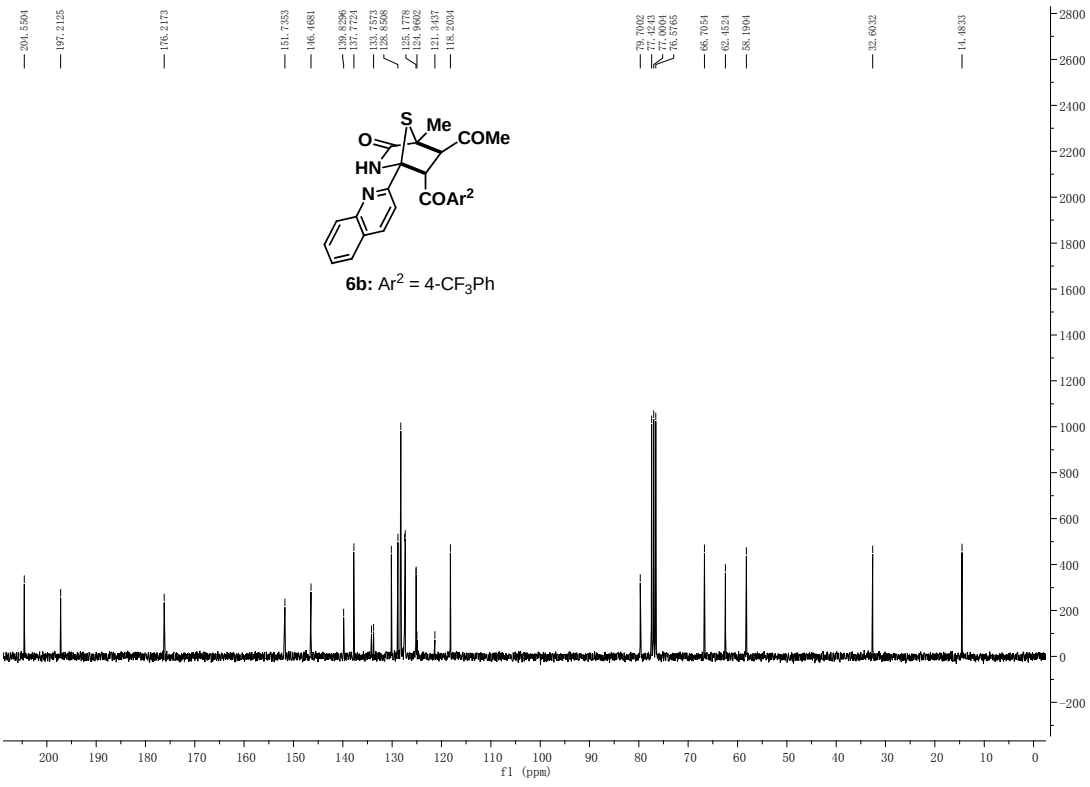

177.3728
150.7896
149.6238
137.6688
135.9792
128.9769
128.8656
128.5922
124.5147
120.8335
98.2455
77.4241
77.0002
76.5763
76.5769
66.5528
55.2778
13.6974
S
Me
Ph
O
HN
NO2
N
3o
f1 (ppm)


8.8123
8.8050
8.5557
8.5510
8.5398
8.5351
7.8678
7.8466
7.8410
7.8335
7.6215
7.5254
7.4144
7.3857
7.3601
7.2964
7.2801
7.2675
7.2603
5.4518
5.4338
3.3612
3.3532
2.2374
1.7095
S
Me
COMe
O
HN
N
COAr2
6a: Ar2 = Ph
0.98
1.02
1.04
3.07
1.17
2.08
0.84
1.00
1.00
3.05
3.04
f1 (ppm)

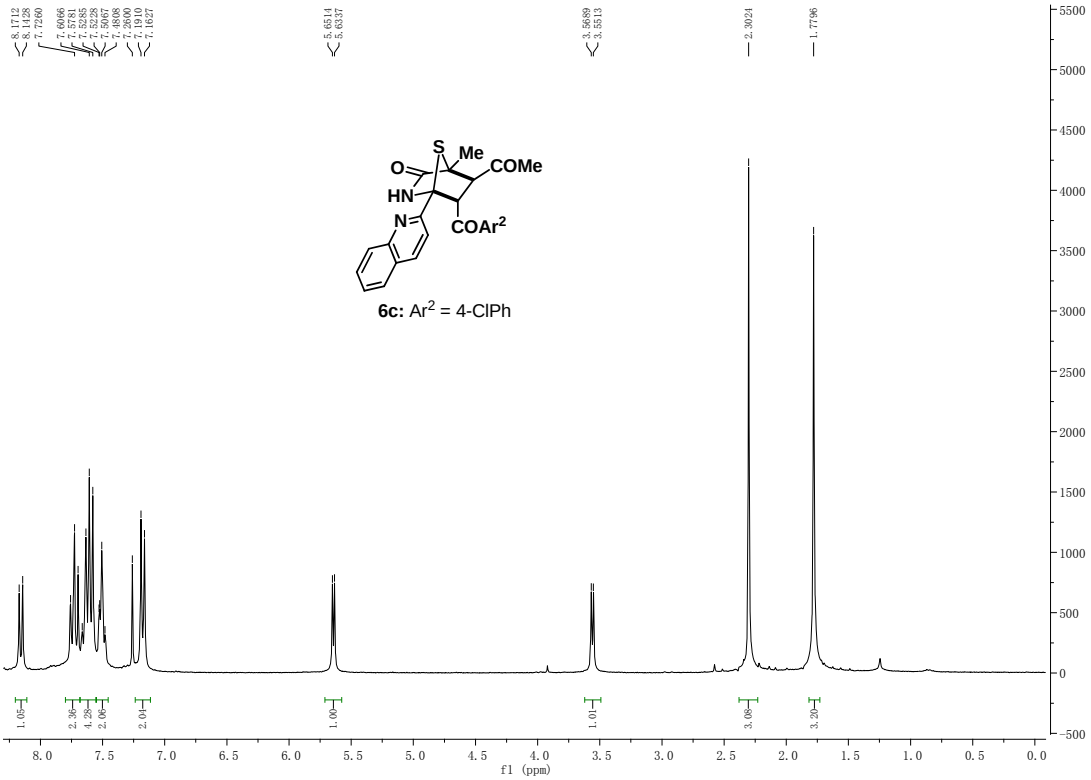

204.9189
198.1532
176.4850
152.1523
146.7320
137.5645
136.9141
133.1266
127.9863
127.5357
127.3384
127.2543
118.2069
79.6048
77.4219
77.0000
76.5765
66.6060
61.8883
58.4472
32.7729
14.3977
S
Me
COMe
O
HN
N
COAr2
6a: Ar2 = Ph
f1 (ppm)

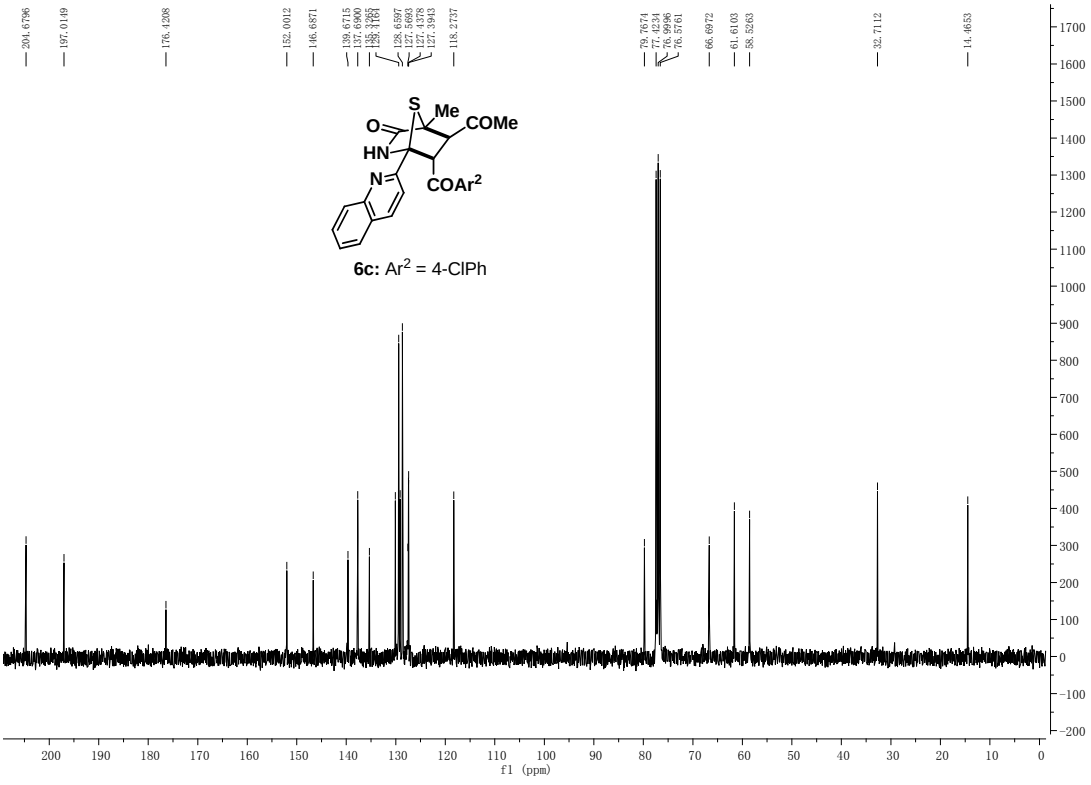


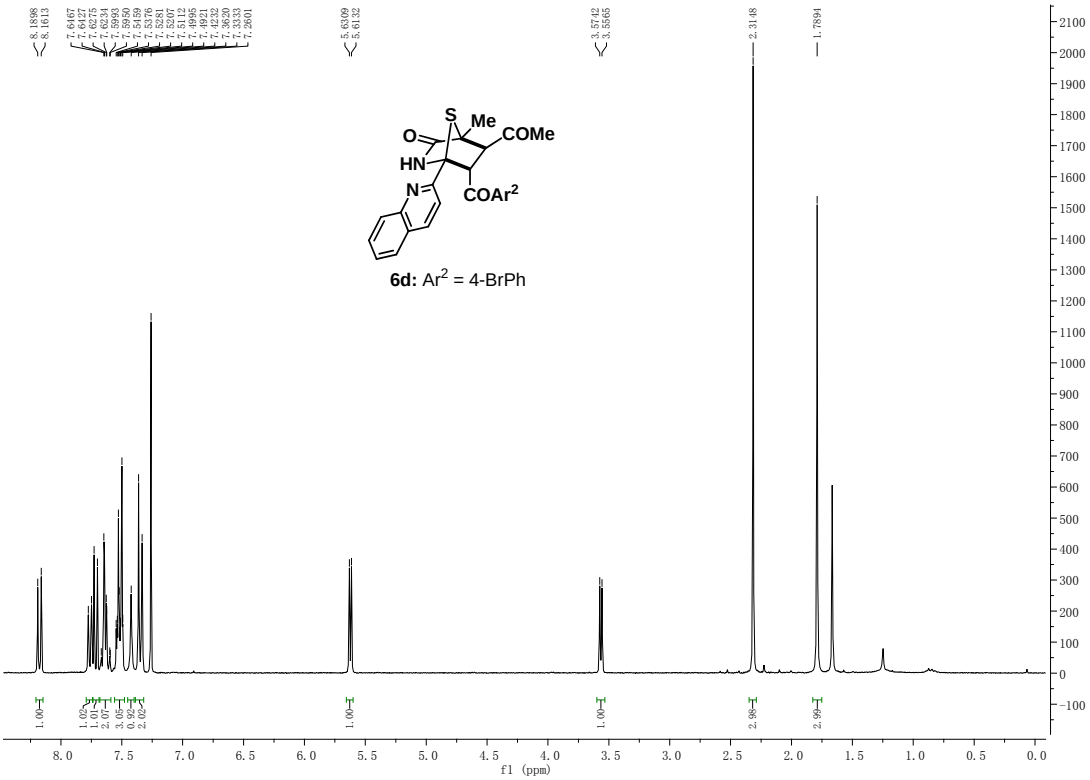
6b: Ar^2 = 4-CF_3Ph



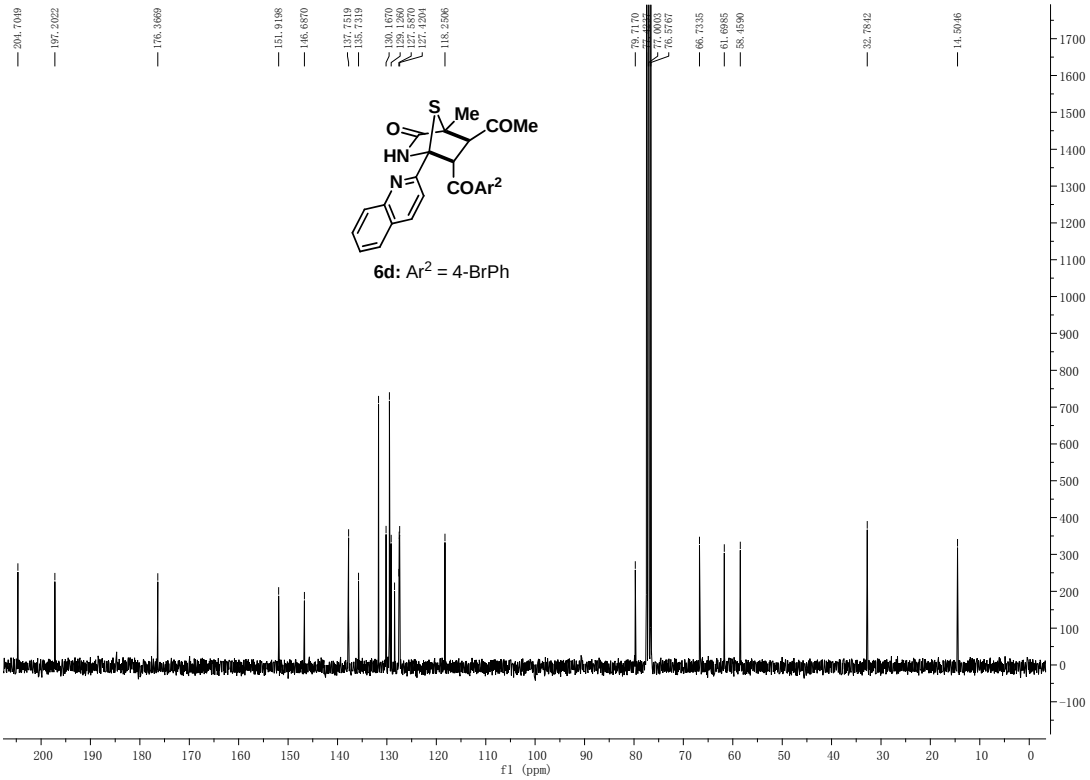
6b: Ar^2 = 4-CF_3Ph


8.1712
8.1428
7.7260
7.6066
7.5781
7.5285
7.5228
7.3867
7.3698
7.2600
7.1910
7.1627
5.6514
5.6337
3.5689
3.5513
2.3024
1.7796
S
Me
COMe
O
HN
N
COAr2
6c: Ar2 = 4-ClPh
1.05
2.36
4.28
2.06
2.01
1.00
1.01
3.08
3.20
f1 (ppm)

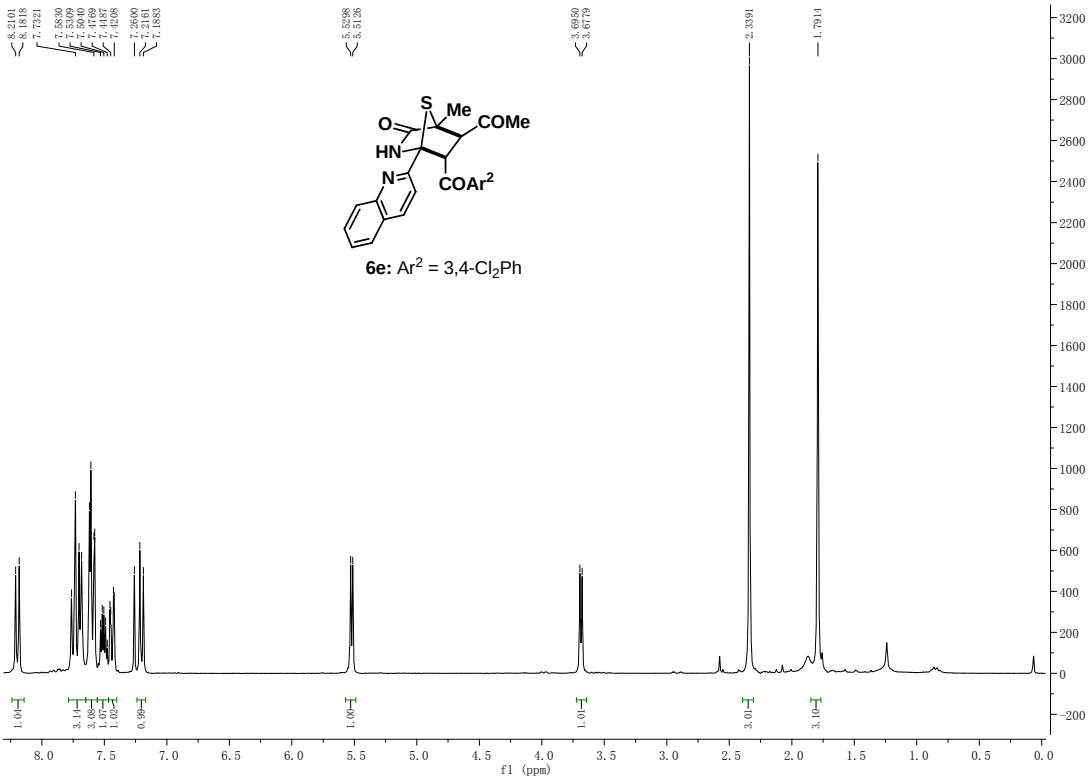

204.6796
197.0149
176.4208
152.0012
146.6871
139.6715
137.6900
135.3265
128.6597
127.5693
127.1378
127.3943
118.2737
79.7674
77.4234
76.9996
76.5761
66.6972
61.6103
58.3263
32.7112
14.4653
S
Me
COMe
O
HN
N
COAr2
6c: Ar2 = 4-ClPh
f1 (ppm)



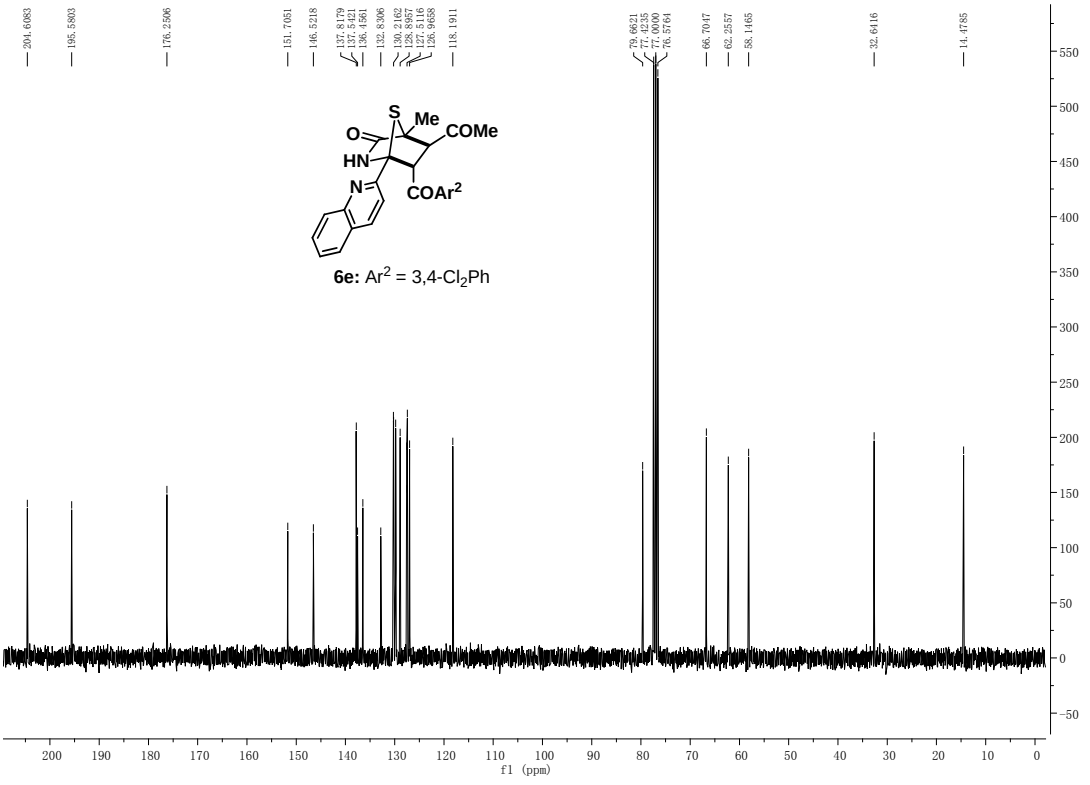
6d: Ar^2 = 4-BrPh



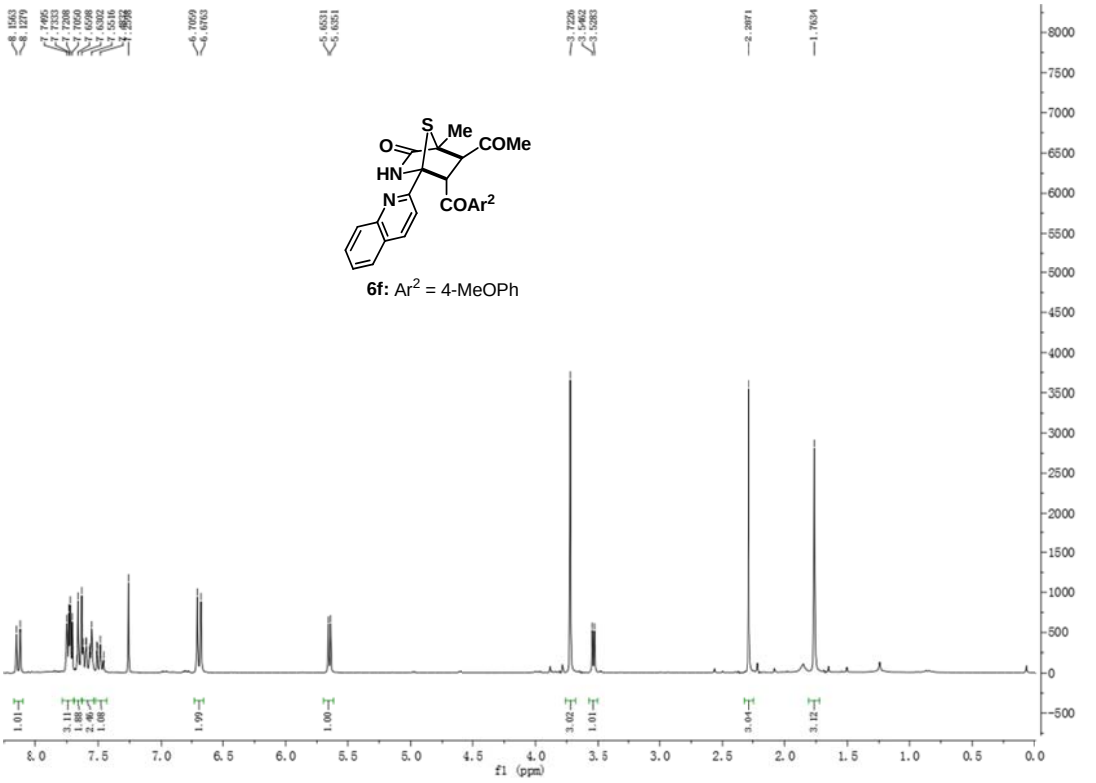
6d: Ar^2 = 4-BrPh



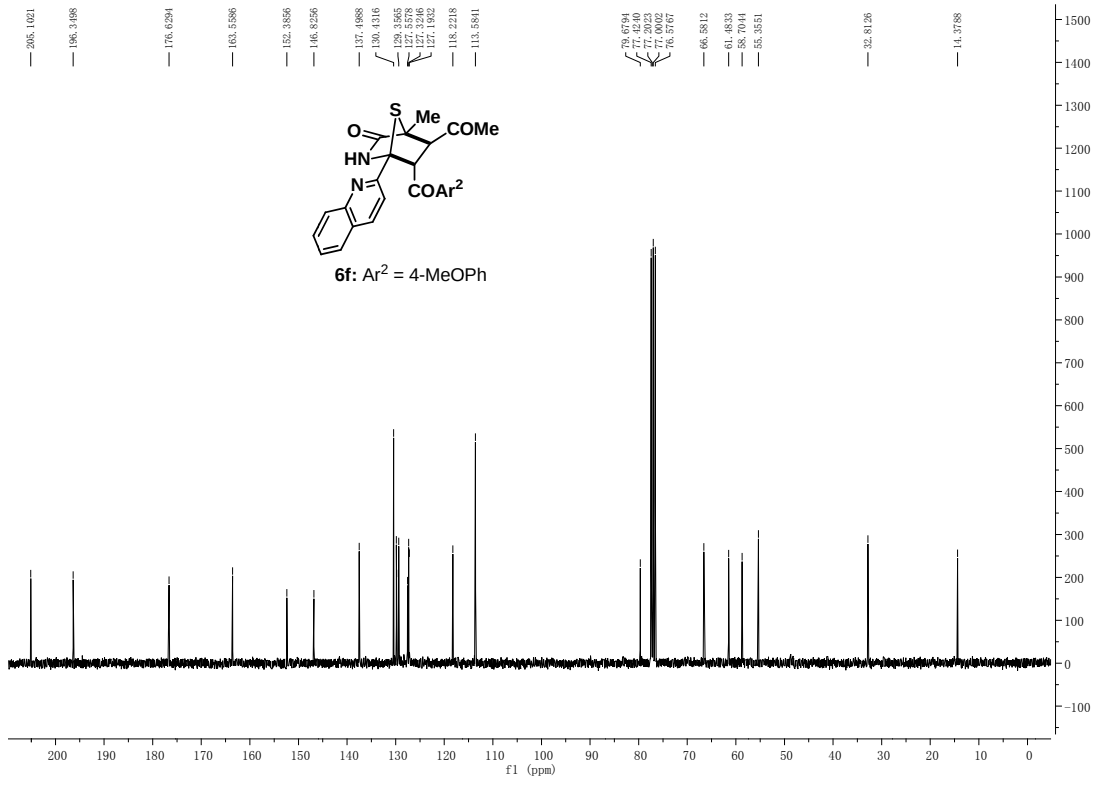
6e: Ar^2 = 3,4-Cl_2Ph



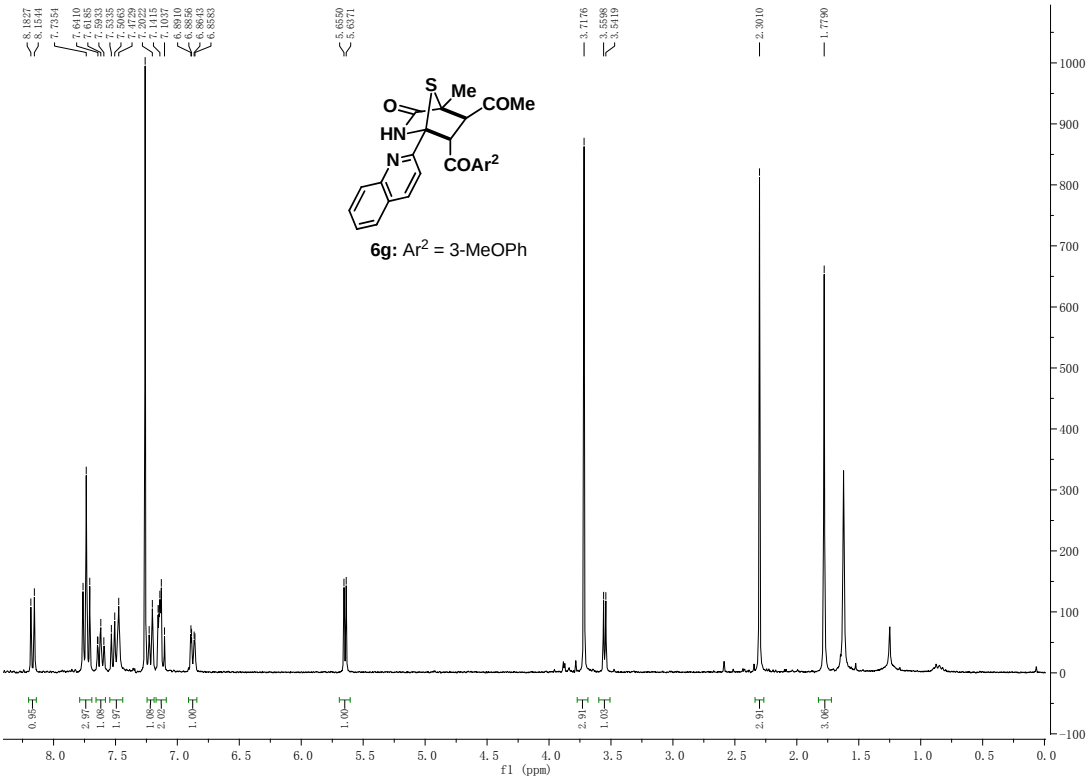
6e: Ar^2 = 3,4-Cl_2Ph

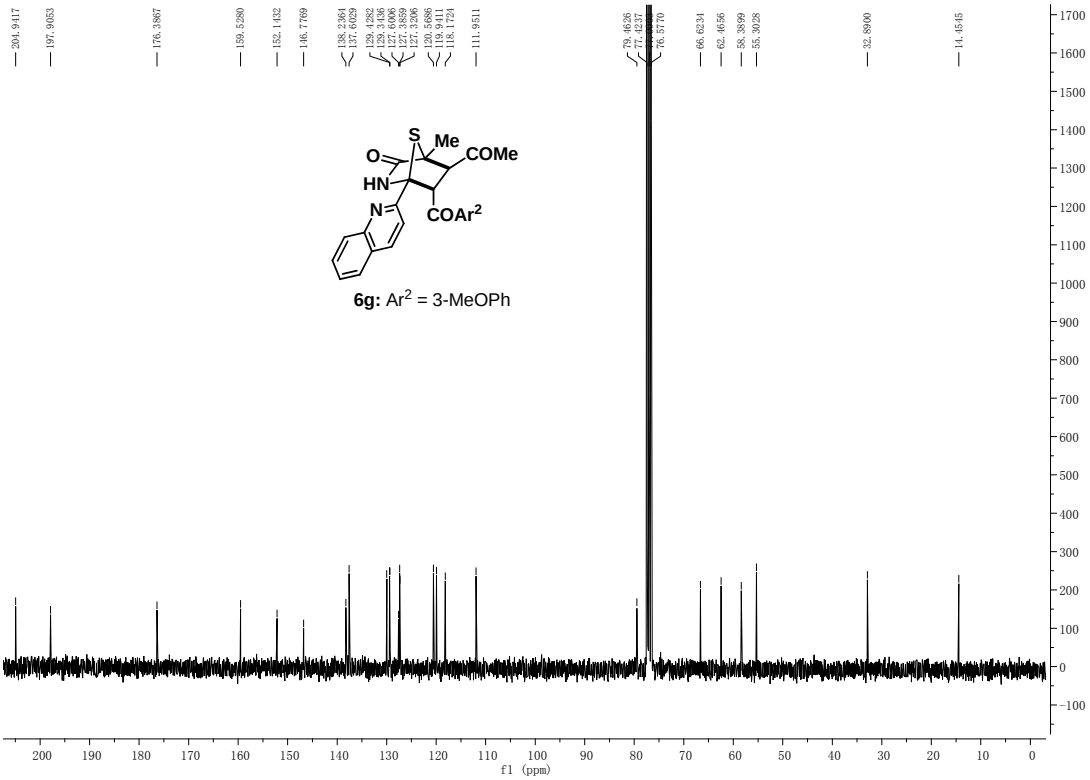


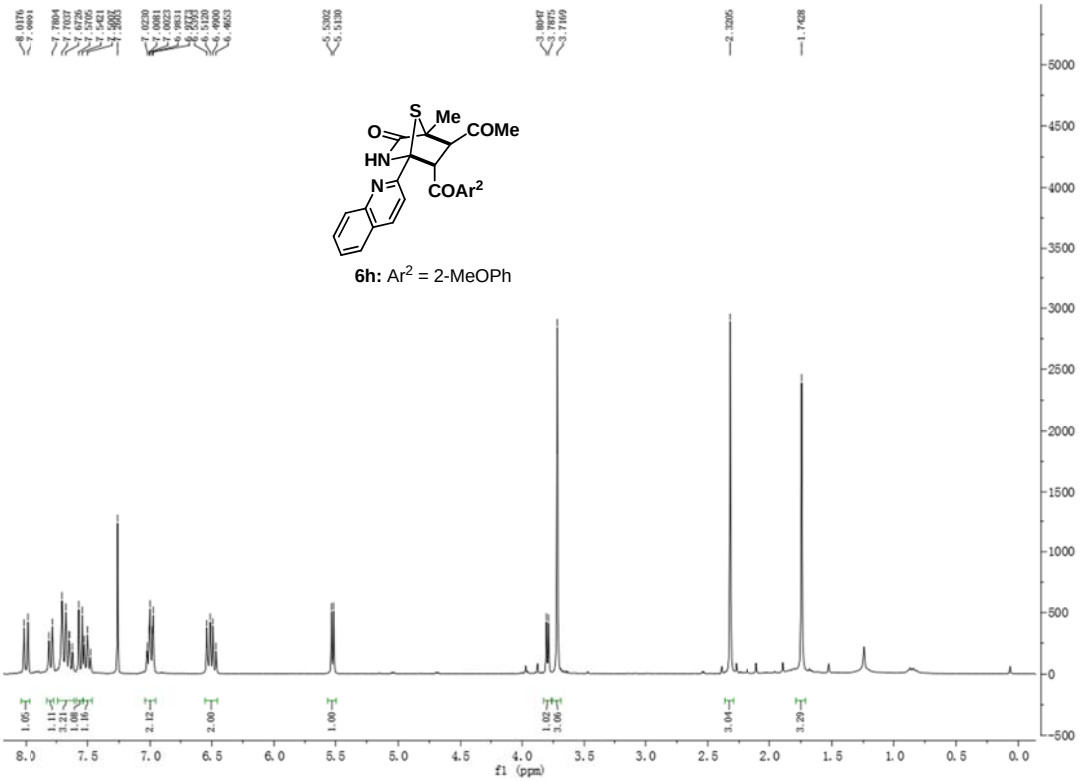
6f: Ar^2 = 4-MeOPh



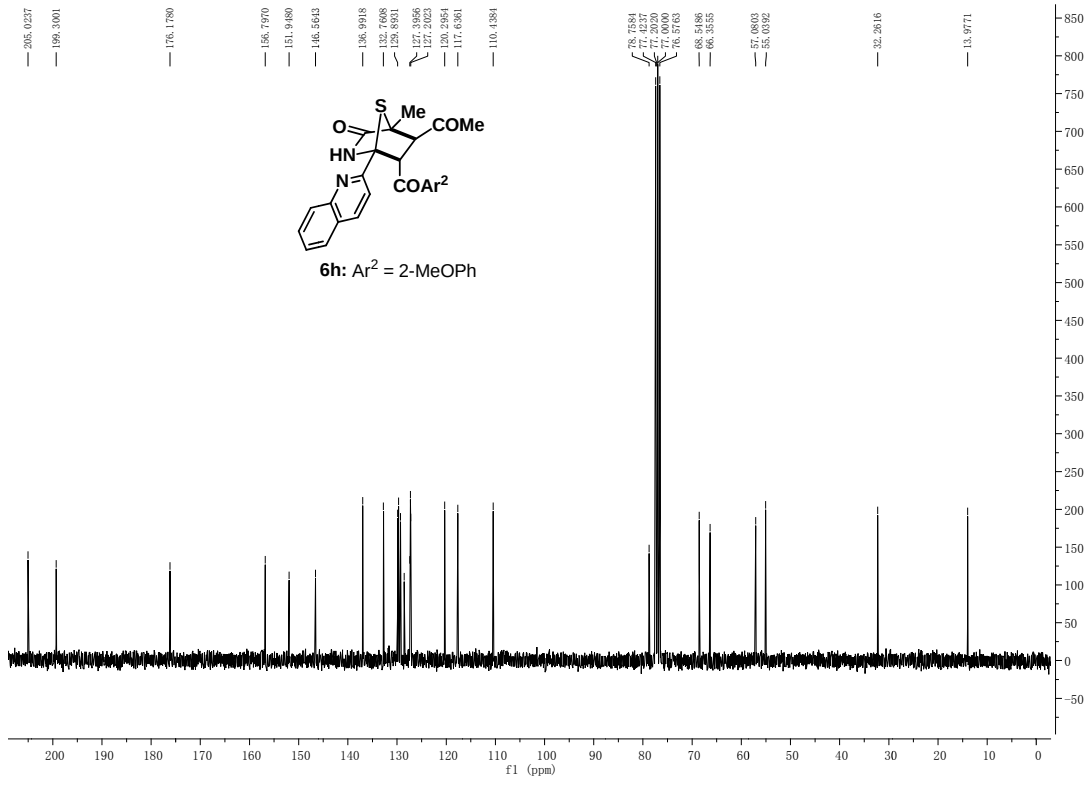
6f: Ar^2 = 4-MeOPh


8.1827
8.1544
7.7354
7.6410
7.6185
7.5933
7.5335
7.5063
7.4759
7.2022
7.1415
7.1037
6.8910
6.8656
6.8614
6.8583
5.6550
5.6371
3.7176
3.5598
3.5419
2.3010
1.7790
S
Me
COMe
O
HN
N
COAr2
6g: Ar2 = 3-MeOPh
0.95
2.97
1.08
1.97
1.08
2.02
1.00
1.00
2.91
1.03
2.91
3.00
f1 (ppm)

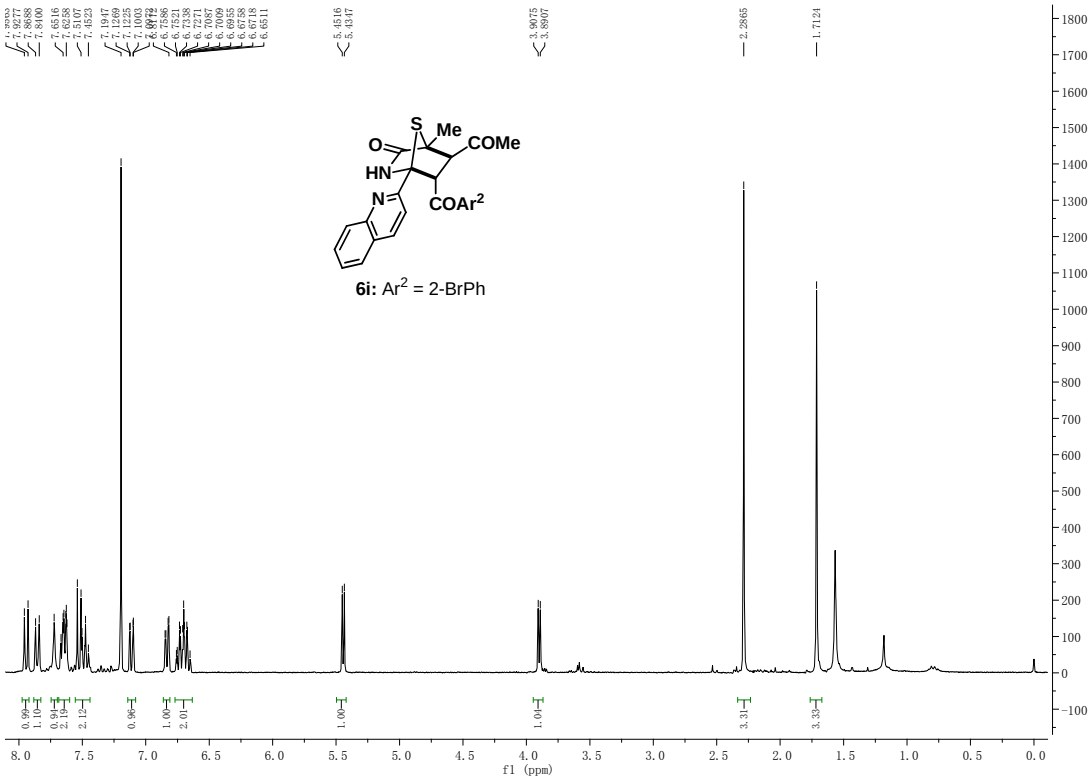

204.9417
197.9053
176.3867
159.5280
152.1432
146.7769
138.2364
137.6029
129.4282
129.3436
127.6006
127.3859
127.3206
120.8686
119.9411
118.1724
111.9511
79.4626
77.4237
76.8770
66.6234
62.4656
58.3899
55.3028
32.8900
14.4545
S
Me
COMe
O
HN
N
COAr2
6g: Ar2 = 3-MeOPh
f1 (ppm)



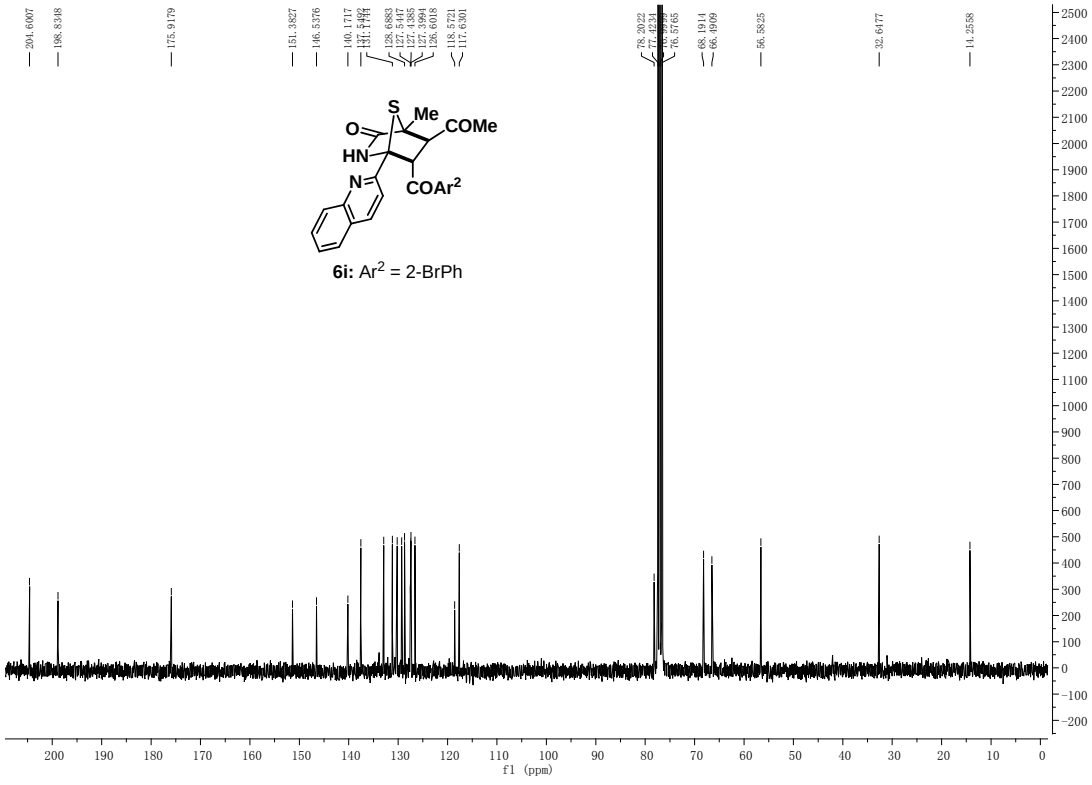
6h: Ar^2 = 2-MeOPh



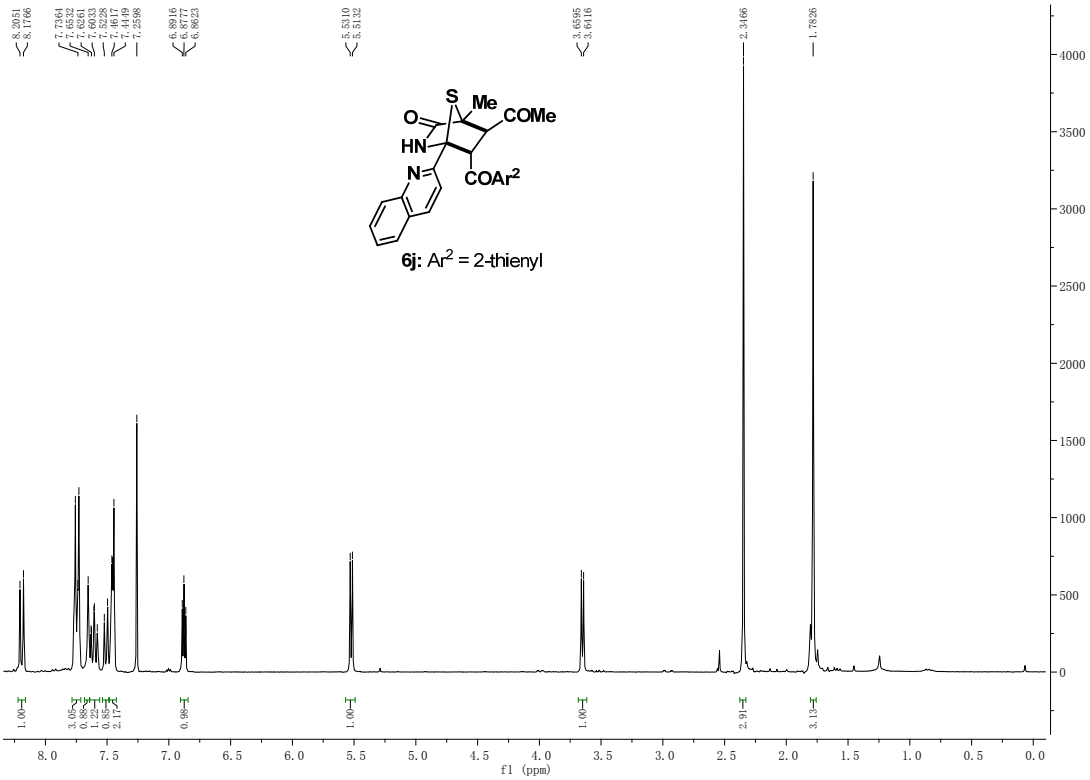
6h: Ar^2 = 2-MeOPh

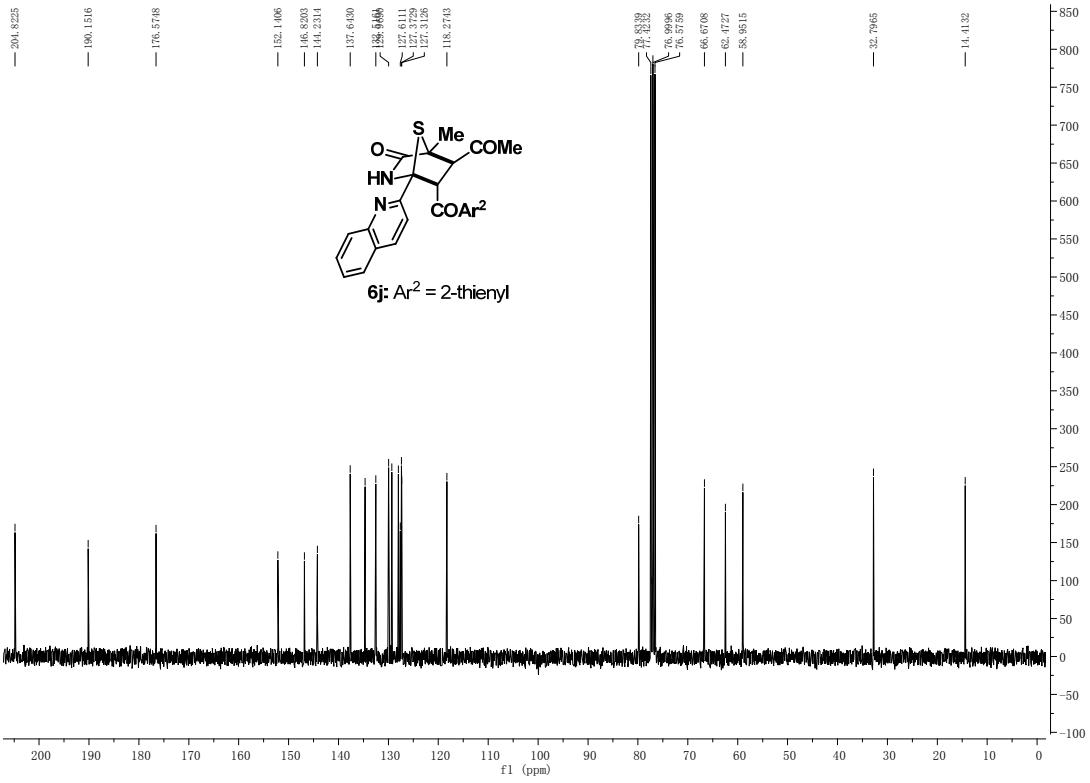


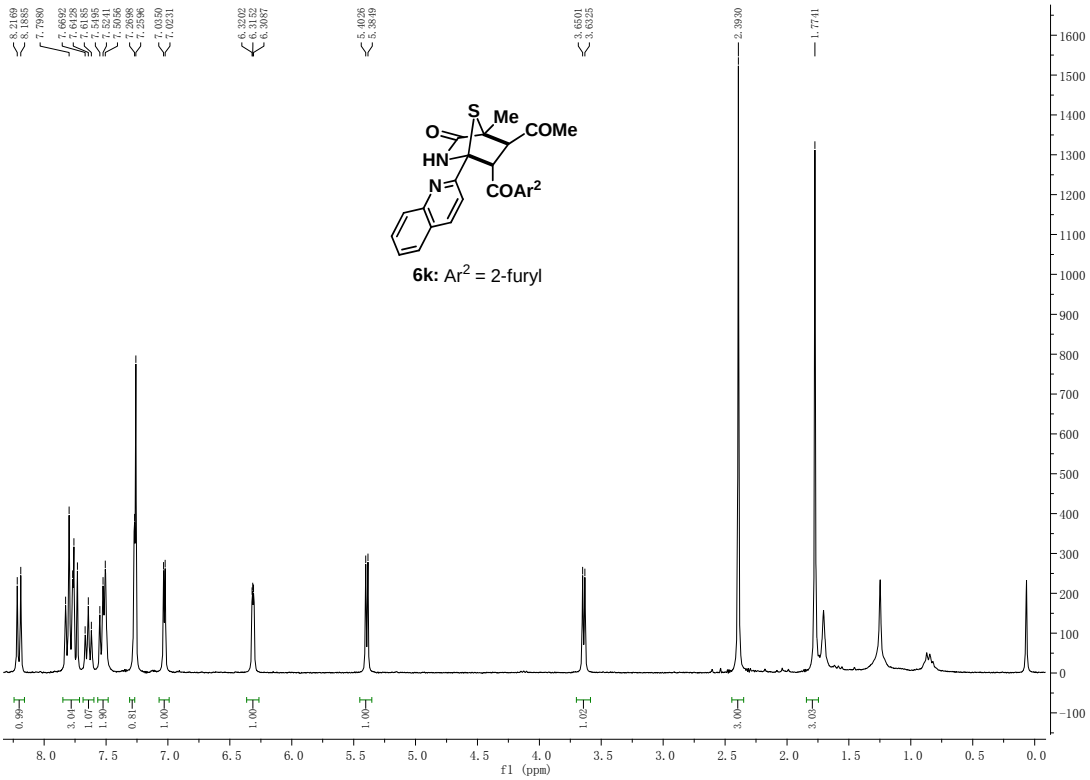
6i: Ar^2 = 2-BrPh



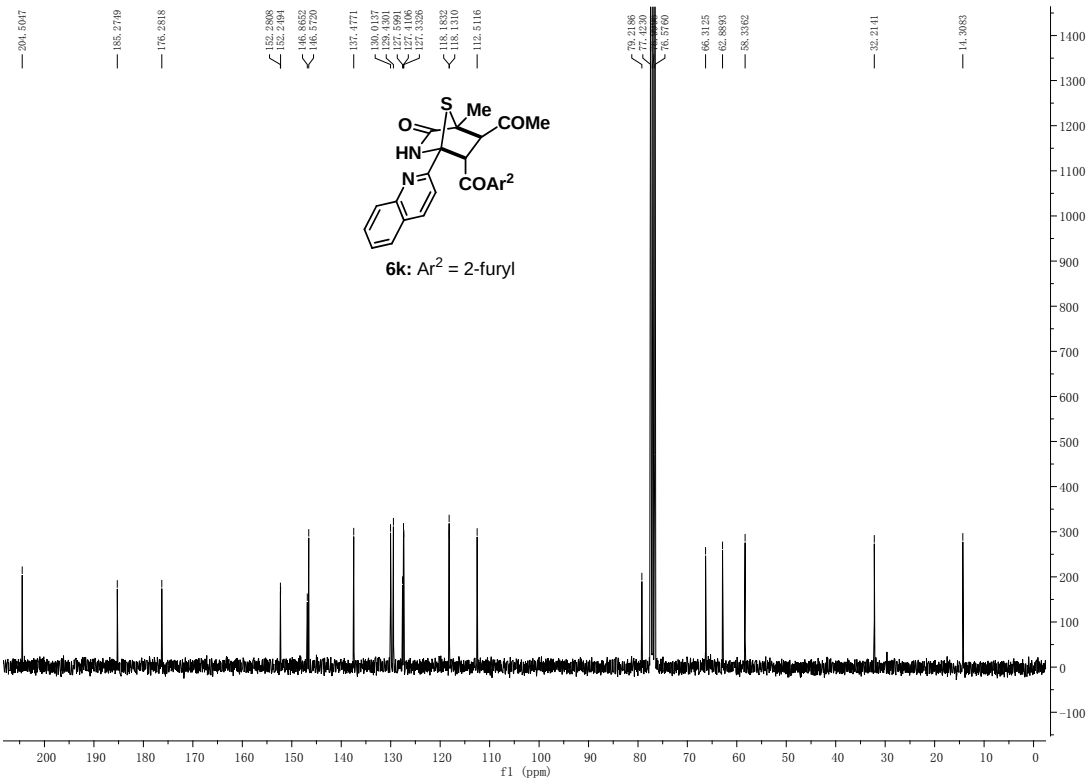
6i: Ar^2 = 2-BrPh


8.2051
8.1766
7.7364
7.6532
7.6261
7.6033
7.5238
7.4617
7.4449
7.2598
6.8916
6.8777
6.8623
5.5310
5.5132
3.6595
3.6416
2.3466
1.7826
S
Me
COMe
O
HN
N
COAr2
6j: Ar2 = 2-thienyl
f1 (ppm)

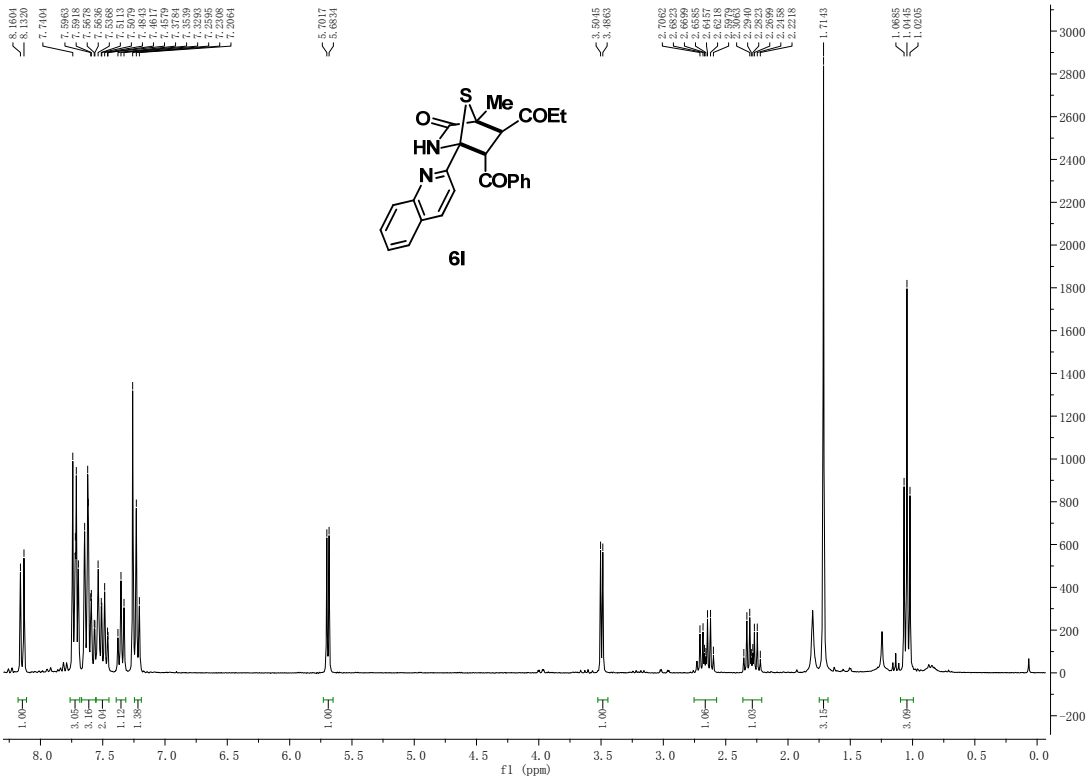

204.8225
190.1516
176.5748
152.1406
146.8203
144.2314
137.6430
127.6111
127.3729
127.3126
118.2743
76.9996
76.5759
66.6708
62.4727
58.9515
32.7965
14.4132
S
Me
COMe
O
HN
N
COAr2
6j: Ar2 = 2-thienyl
f1 (ppm)

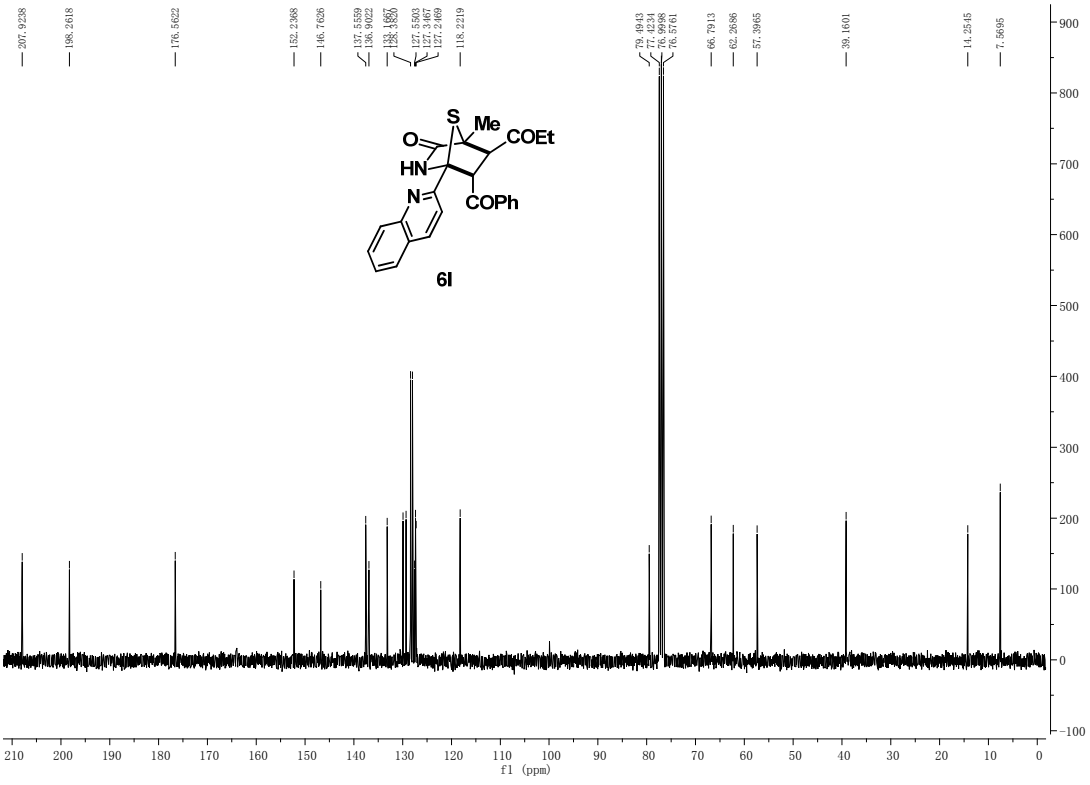


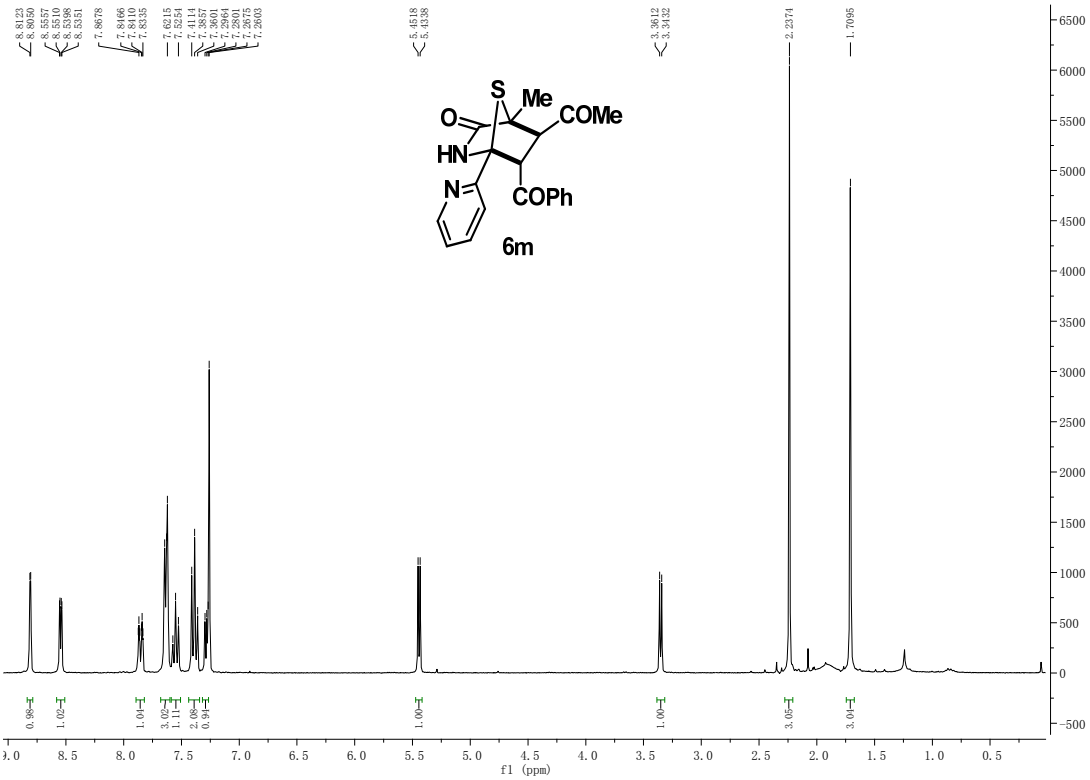
6k: Ar^2 = 2-furyl

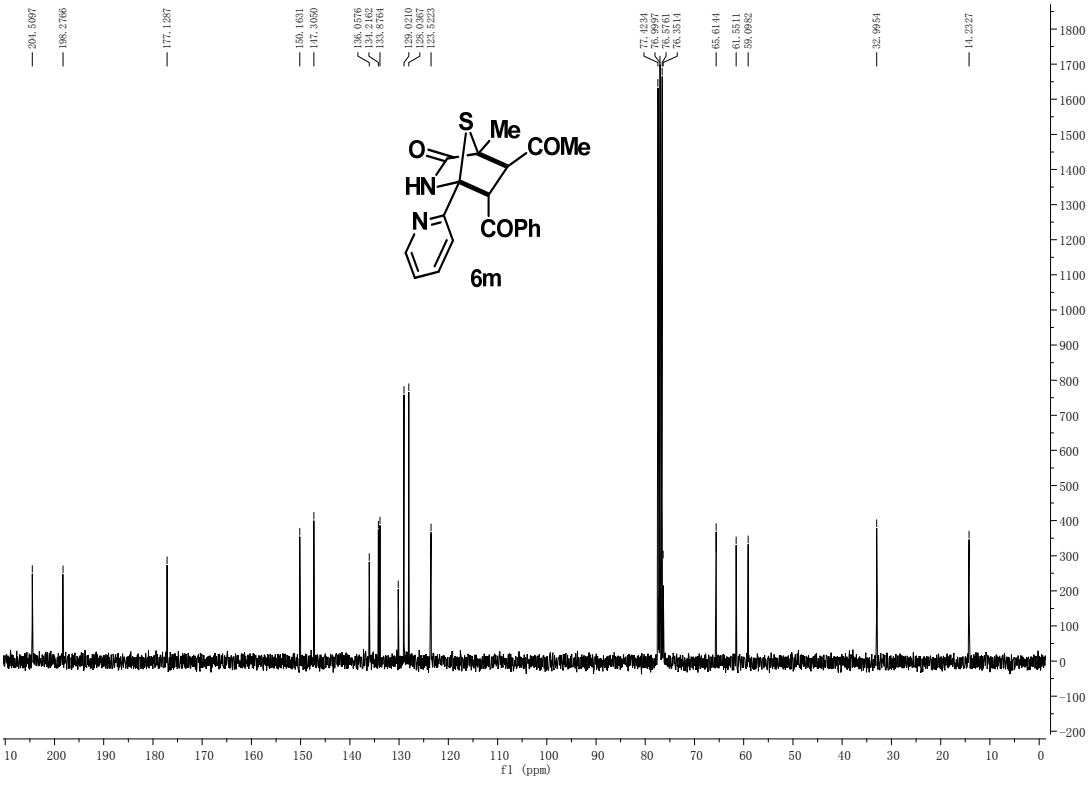


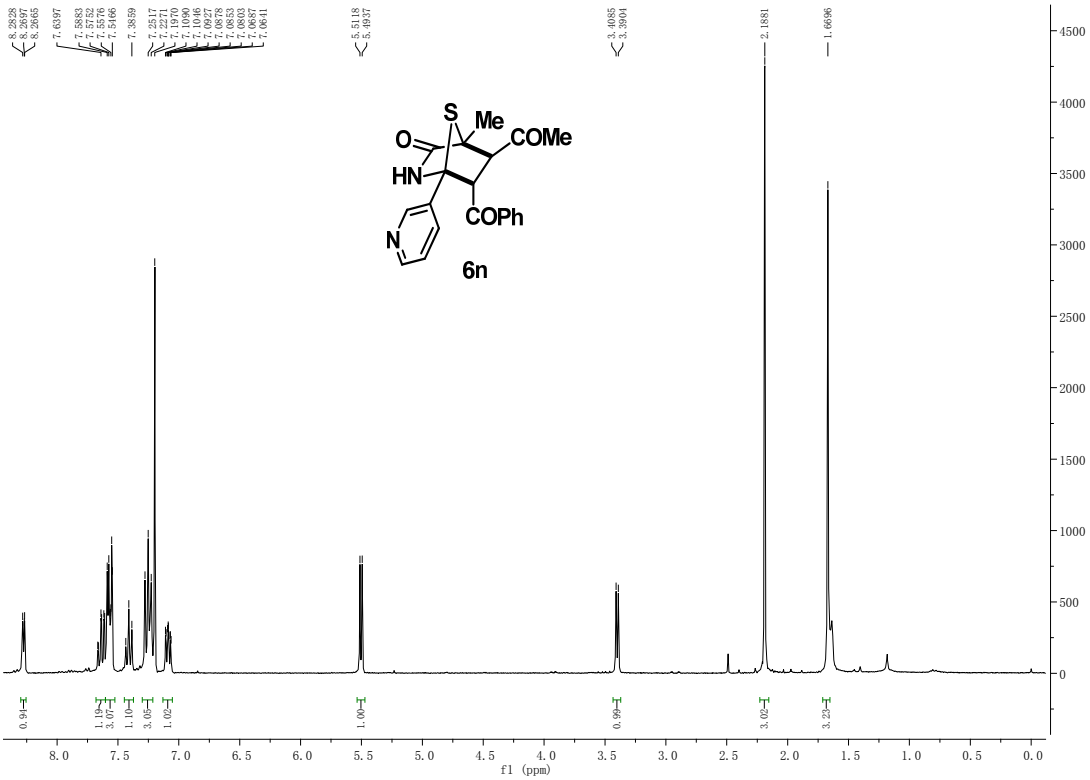
6k: Ar^2 = 2-furyl


S
Me
COEt
O
HN
N
COPh
6l
f1 (ppm)


S
Me
COEt
O
HN
N
COPh
6l
f1 (ppm)


S
Me
COMe
O
HN
N
COPh
6m
f1 (ppm)


S
Me
COMe
O
HN
N
COPh
6m
f1 (ppm)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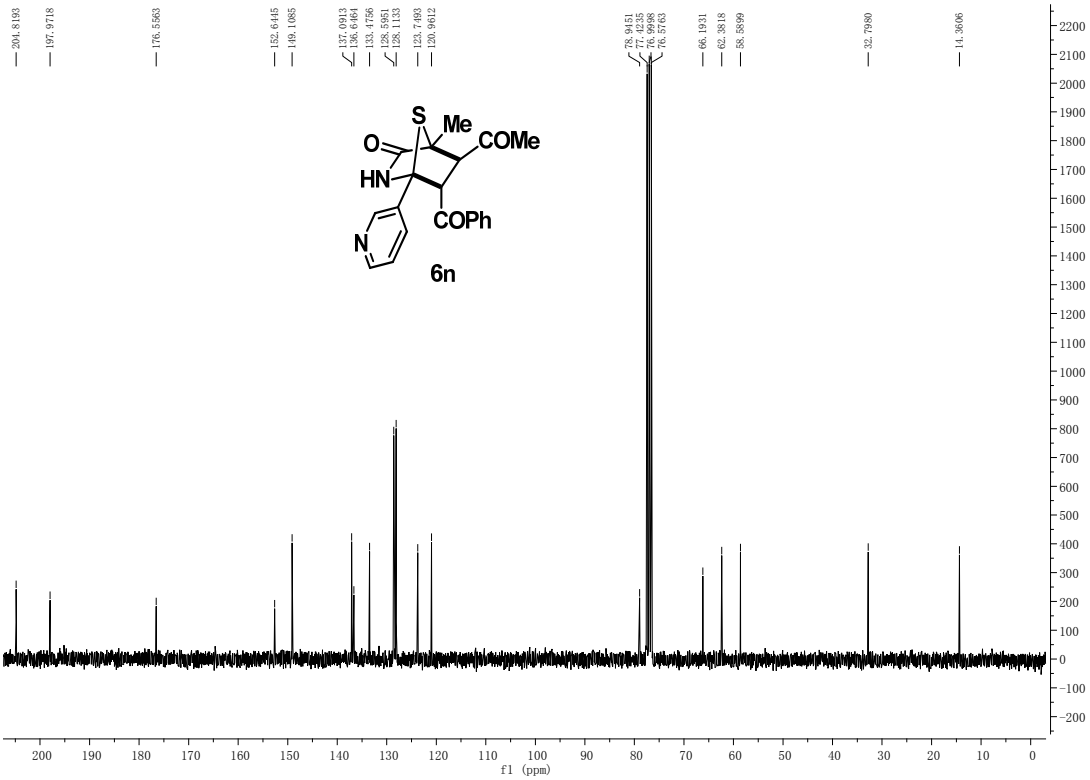
8.2665
7.6397
7.5883
7.5732
7.5576
7.5466
7.3859
7.2517
7.2271
7.1990
7.1696
7.1046
7.0927
7.0878
7.0653
7.0603
7.0687
7.0641
5.5118
5.4937
3.4085
3.3904
2.1881
1.6696
S
Me
COMe
O
HN
COPh
N
6n
0.91
1.19
3.07
1.10
3.05
1.02
1.00
0.99
3.02
3.23
f1 (ppm)


204.8193
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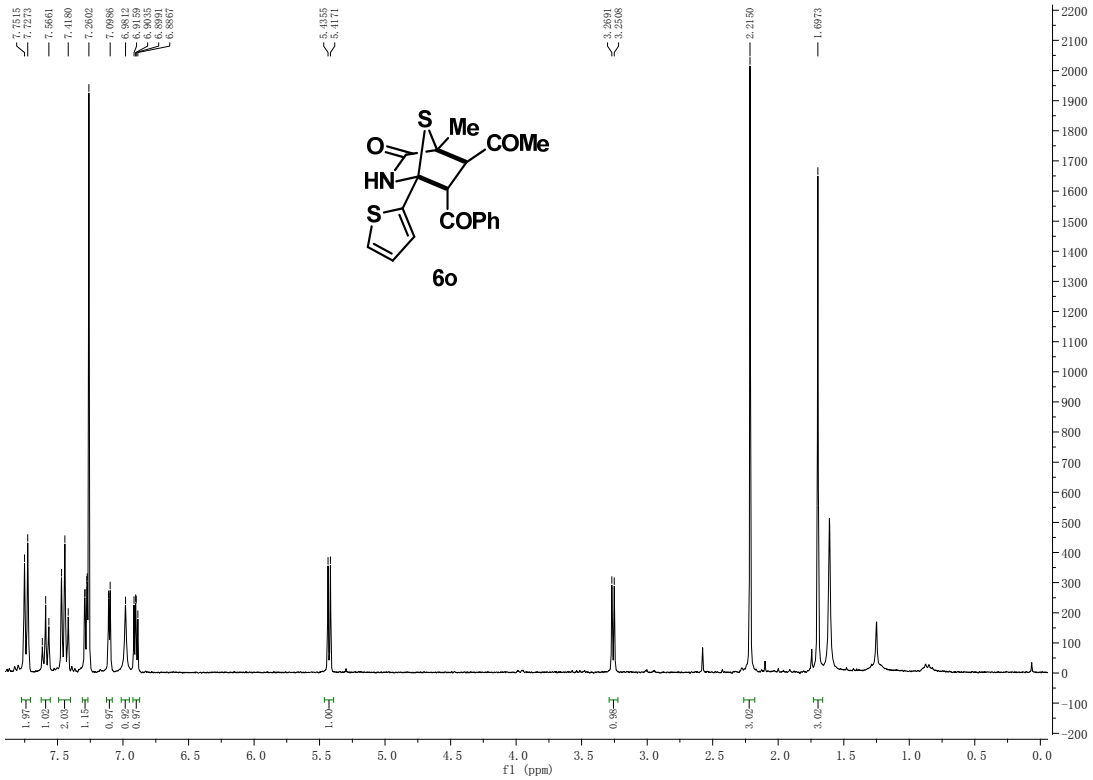
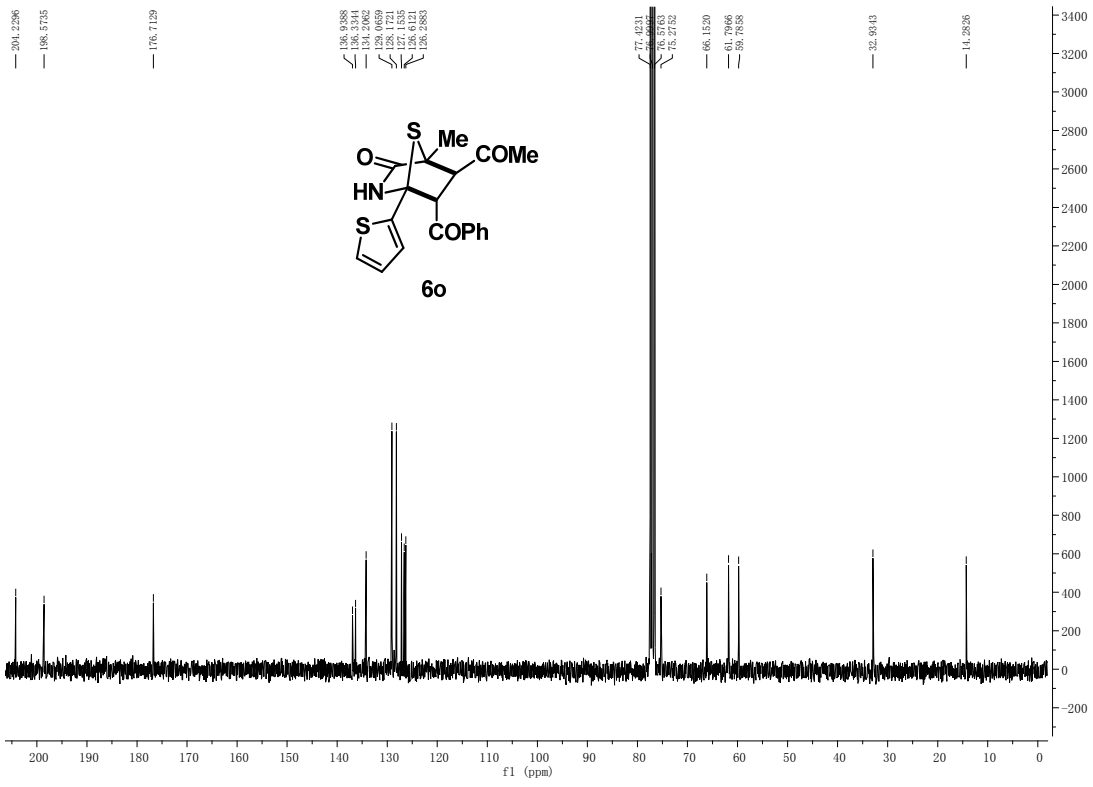
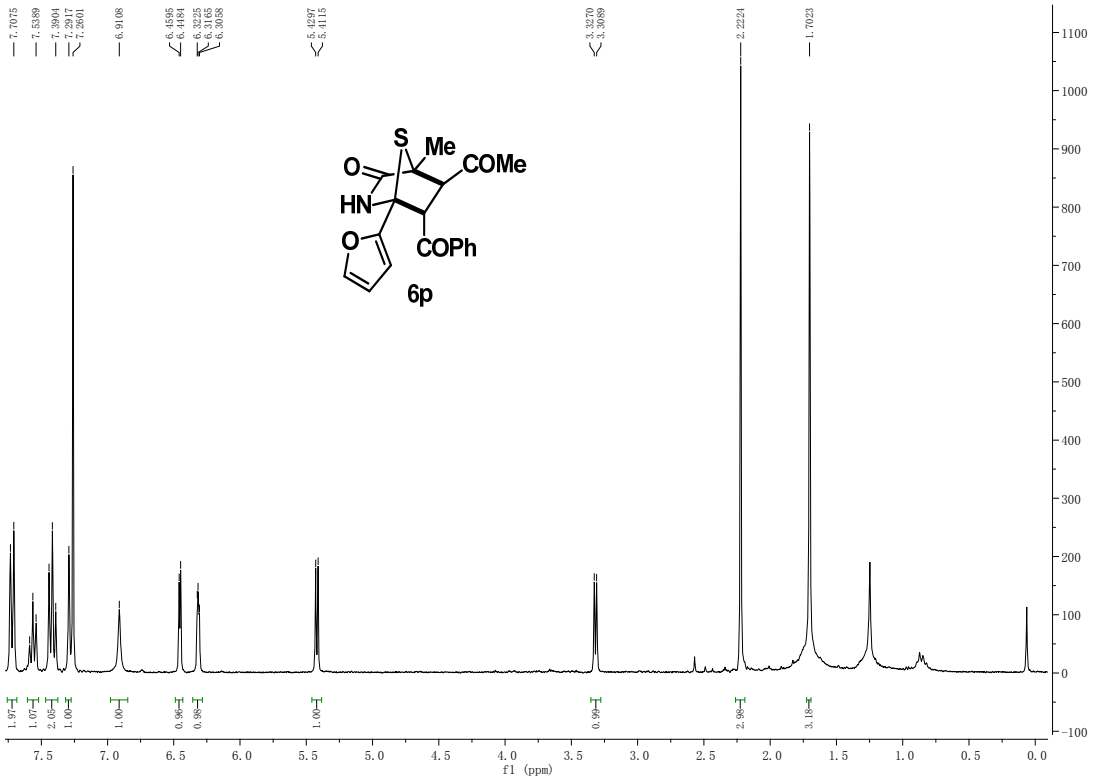
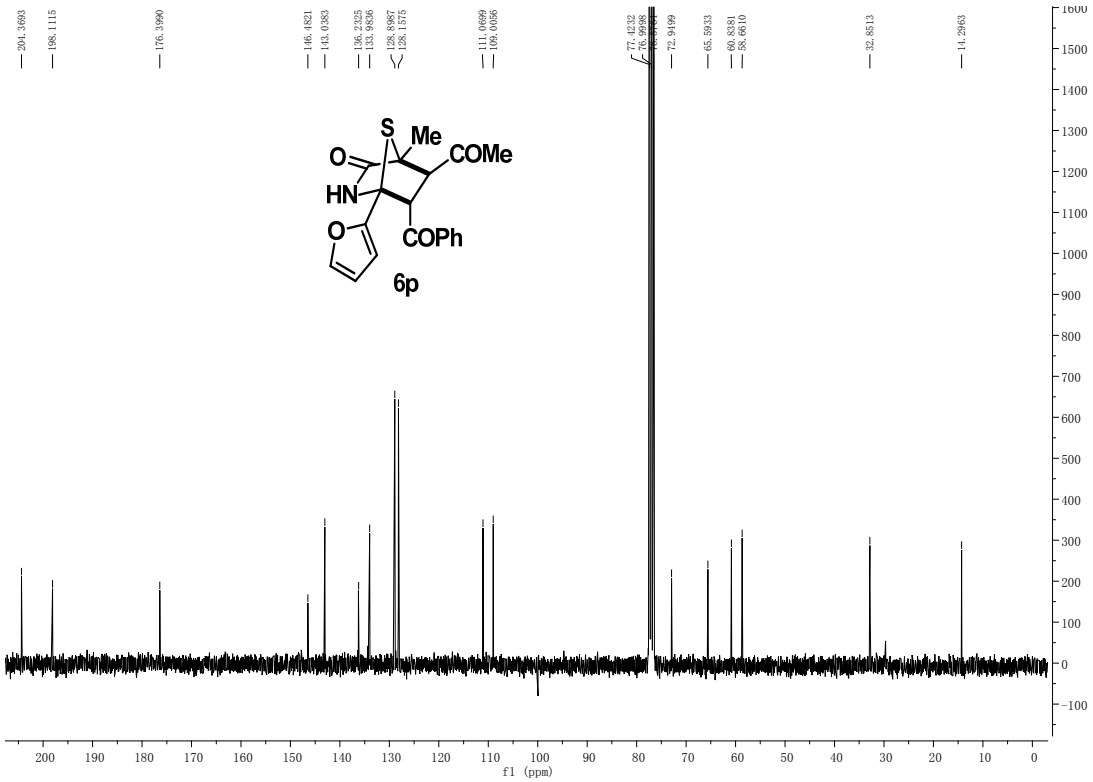
176.5563
152.6445
149.1085
137.0913
136.6464
133.4756
128.5951
128.1153
123.7493
120.9612
78.9151
77.4235
76.8998
76.5762
66.1931
62.3818
58.5899
32.7980
14.3606
S
Me
COMe
O
HN
COPh
N
6n
f1 (ppm)


7.7515
7.7273
7.5661
7.4180
7.2602
7.0986
6.9812
6.9159
6.8935
6.8891
6.8867
5.4355
5.4171
3.2691
3.2508
2.2150
1.6973
S
Me
COMe
O
HN
S
COPh
6o
1.97
1.02
2.03
1.15
0.97
0.92
0.97
1.00
0.98
3.02
3.02
f1 (ppm)


204.2296
186.5735
176.7129
136.9388
136.3344
134.2062
129.0659
128.1721
127.4535
126.6511
126.2883
77.4231
76.5763
75.2752
66.1520
61.7966
59.7838
32.9343
14.2826
S
Me
COMe
O
HN
S
COPh
6o
f1 (ppm)


7.7075
7.5389
7.3904
7.2917
7.2601
6.9108
6.4595
6.4484
6.3225
6.3165
6.3058
5.4297
5.4115
3.3270
3.3089
2.2224
1.7023
S
Me
COMe
O
HN
O
COPh
6p
1.97
1.07
2.05
1.00
1.00
0.96
0.88
1.00
0.99
2.98
3.18
f1 (ppm)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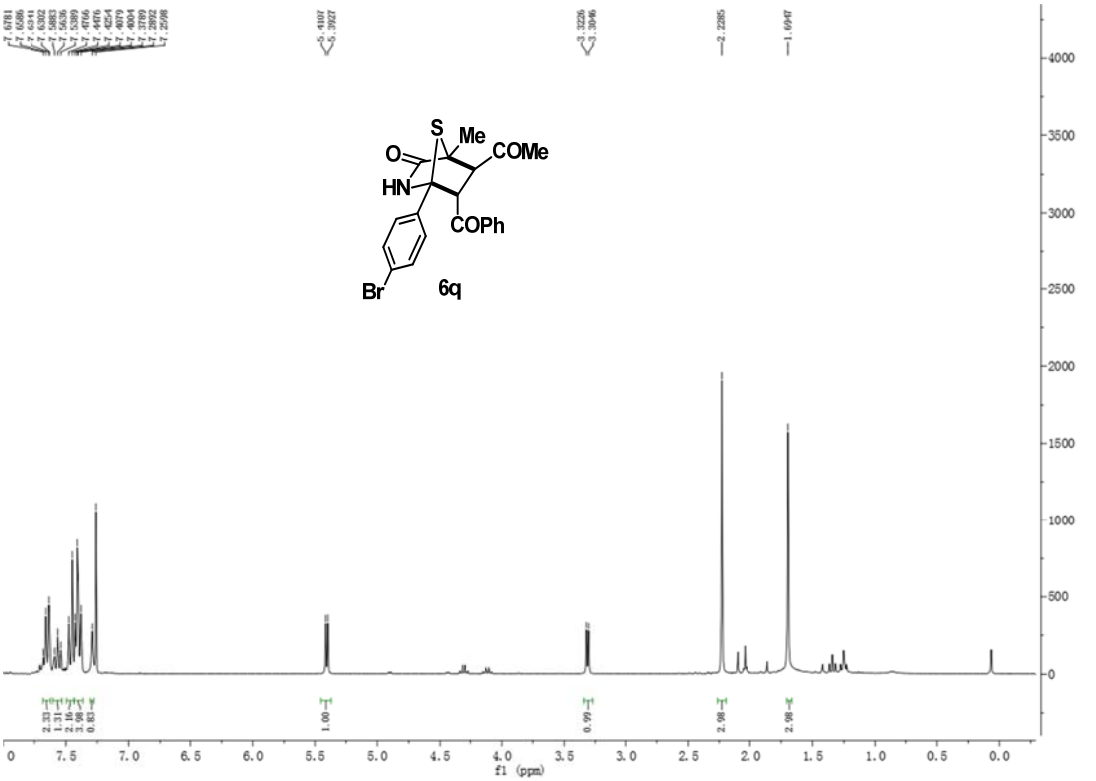
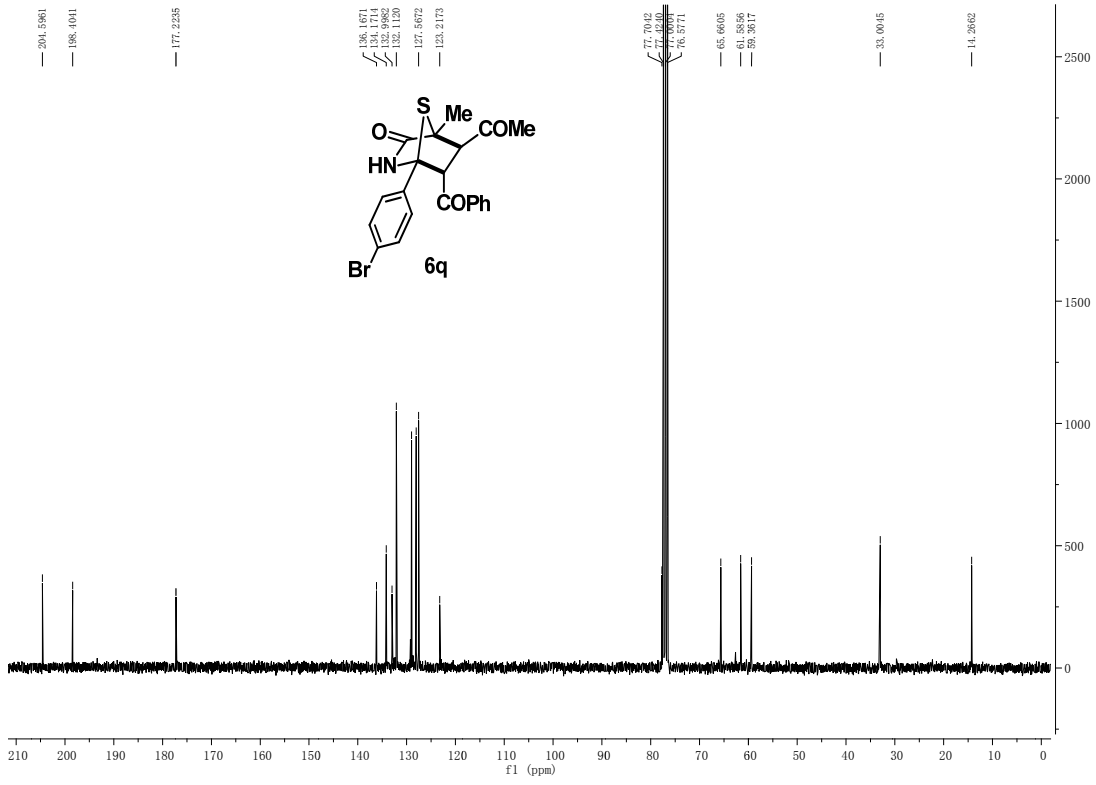
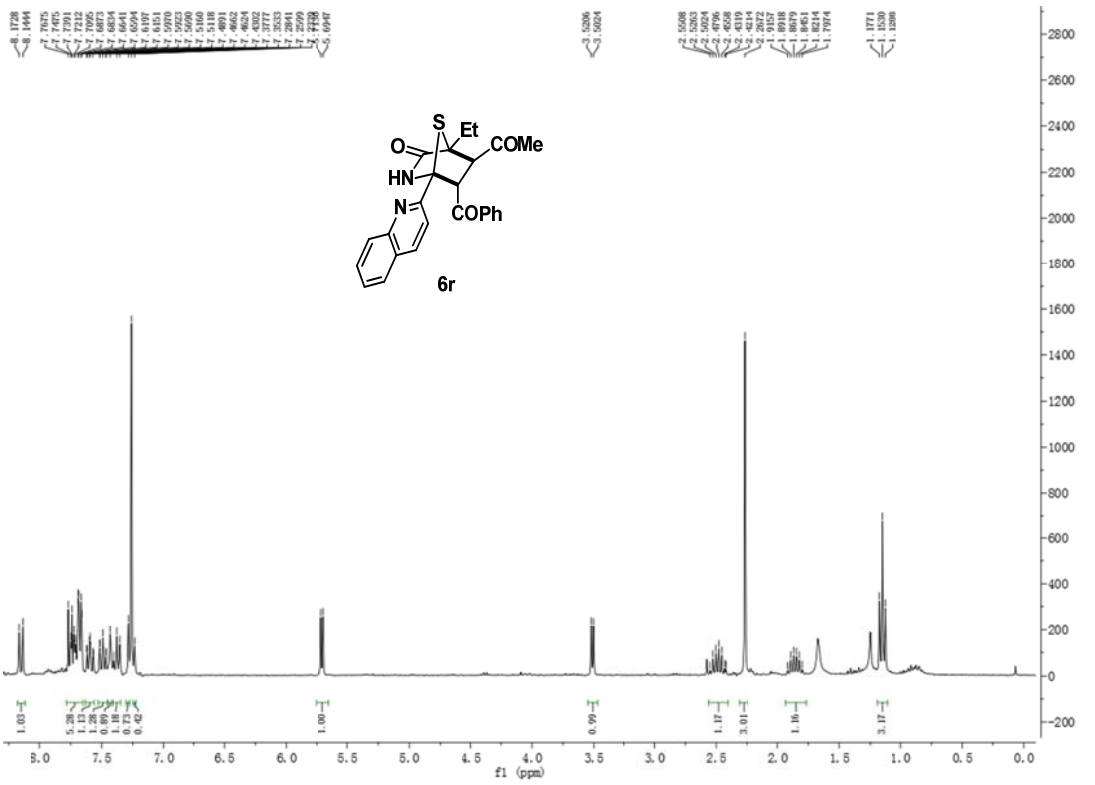
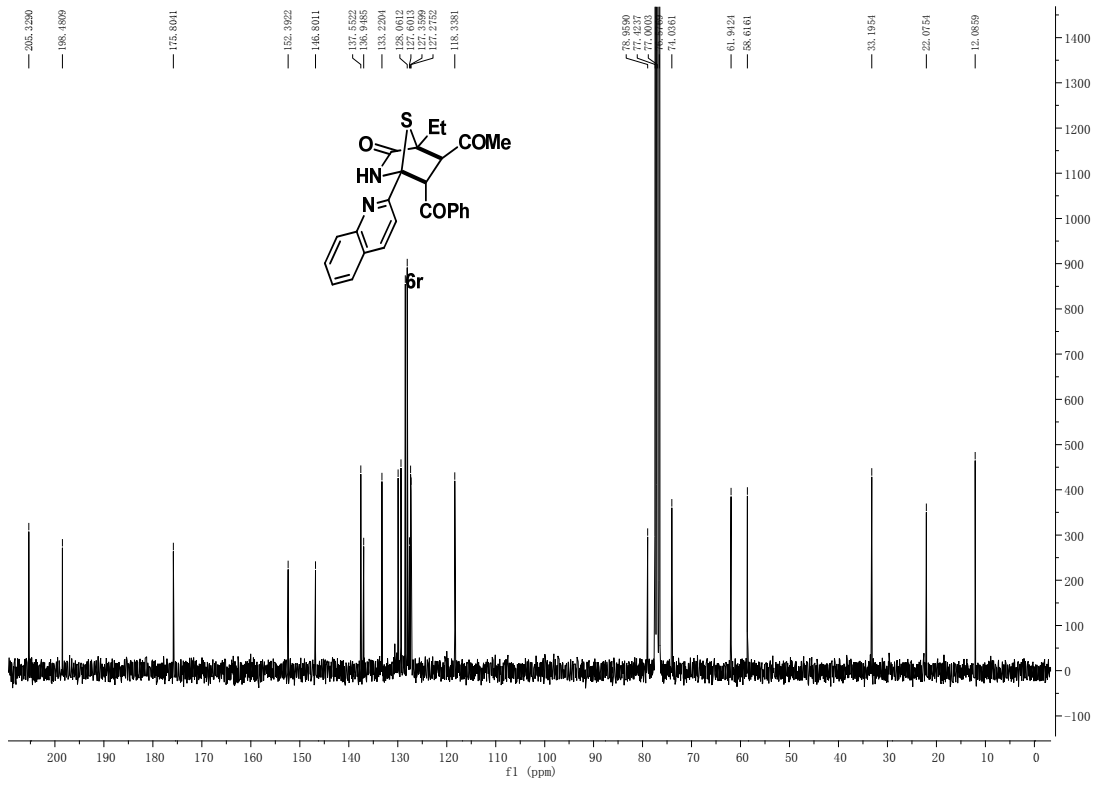
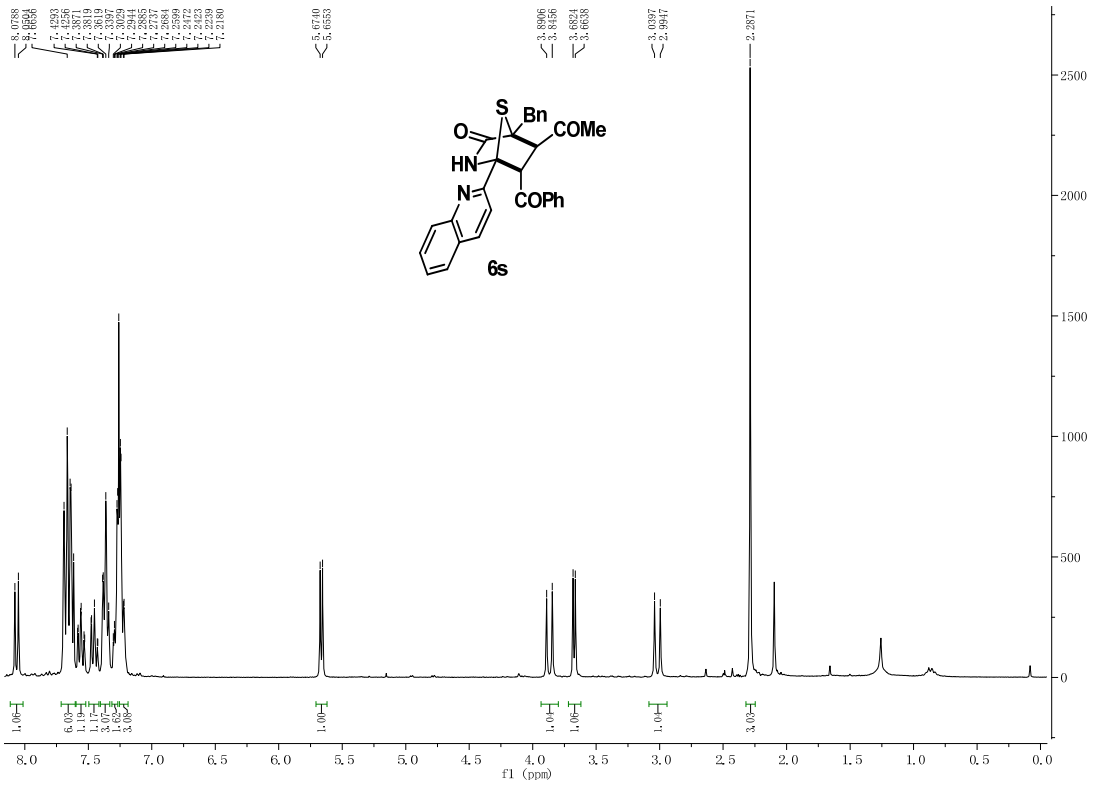
176.3990
146.4821
143.0383
136.2325
133.9836
128.8987
128.1575
111.0699
109.0056
77.4232
76.9998
72.9499
65.5933
60.8381
58.6610
32.8513
14.2963
S
Me
COMe
O
HN
O
COPh
6p
f1 (ppm)

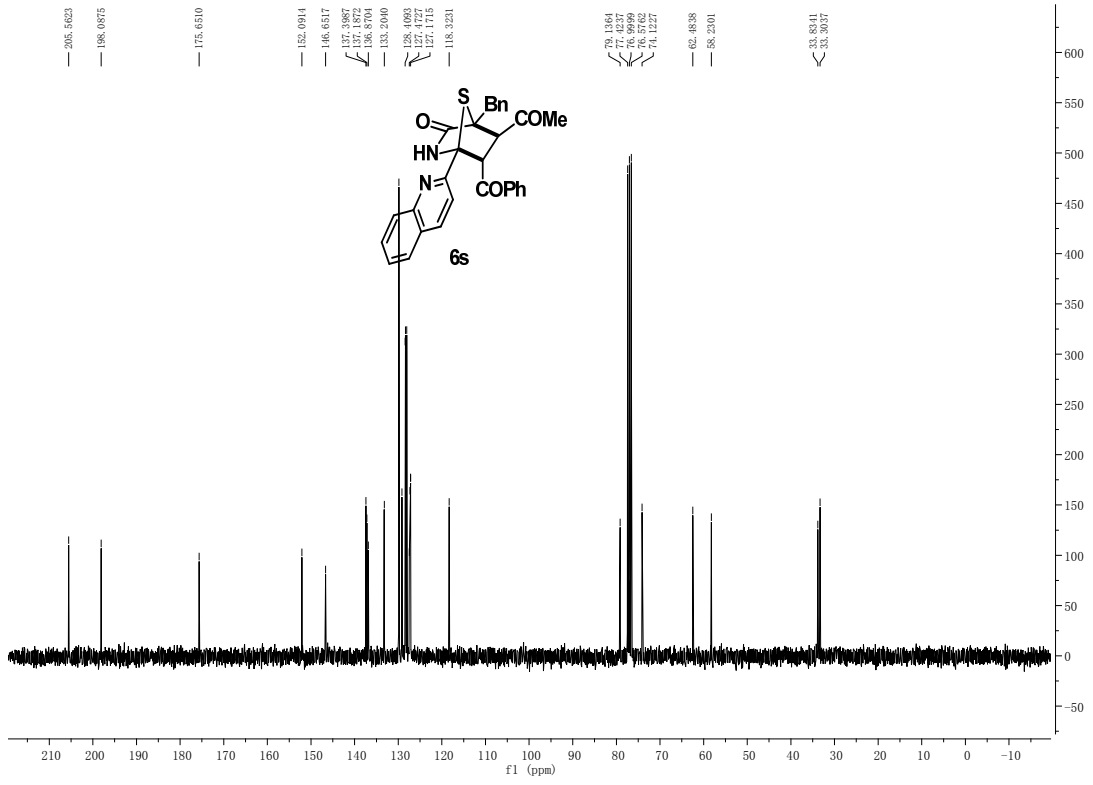

S
Me
COMe
O
HN
COPh
Br
6q
f1 (ppm)

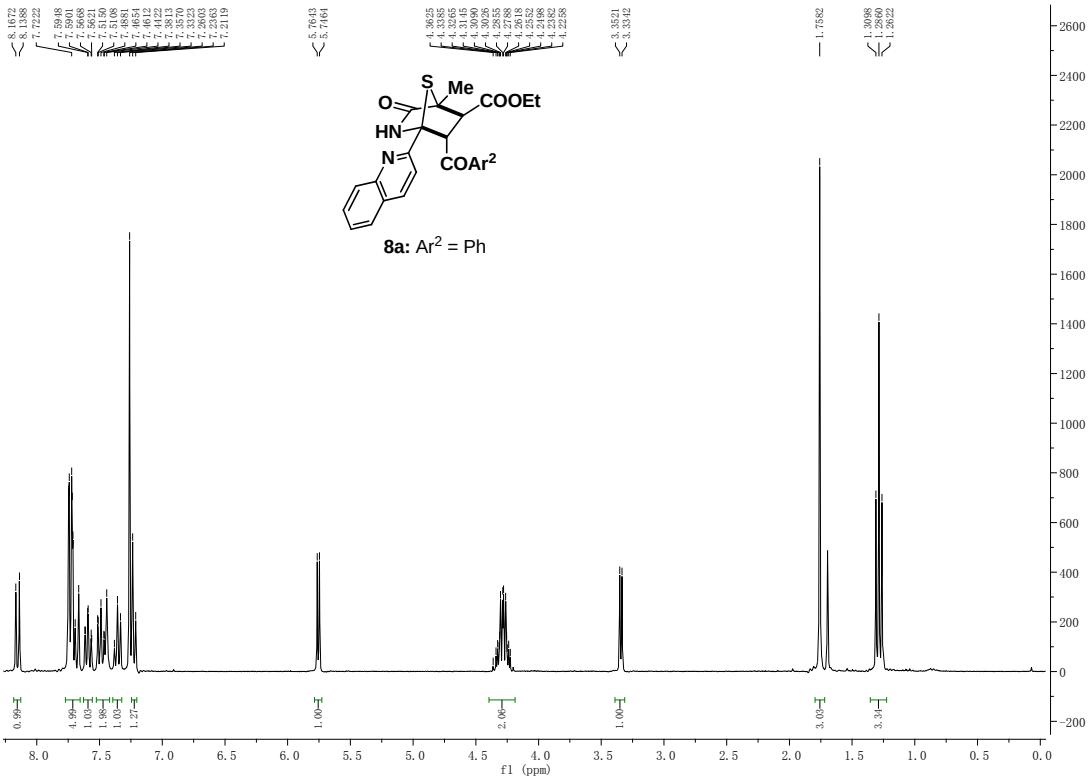

S
Me
COMe
O
HN
COPh
Br
6q
f1 (ppm)

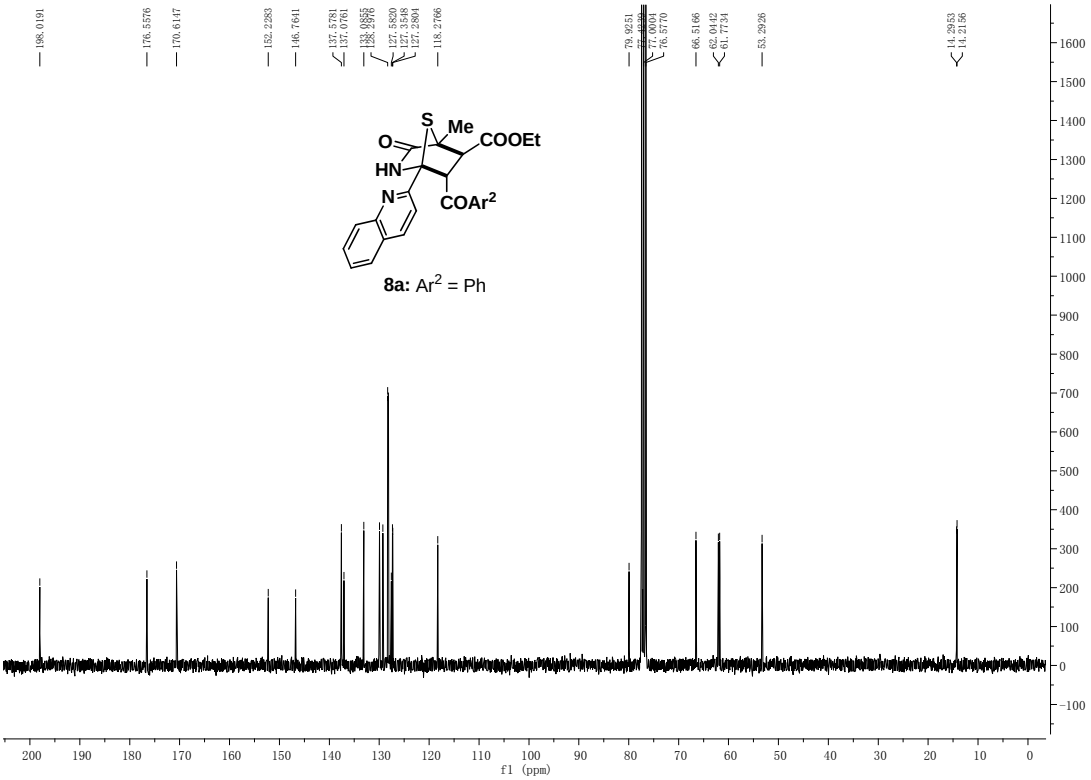

S
Et
COMe
O
HN
N
COPh
6r
f1 (ppm)

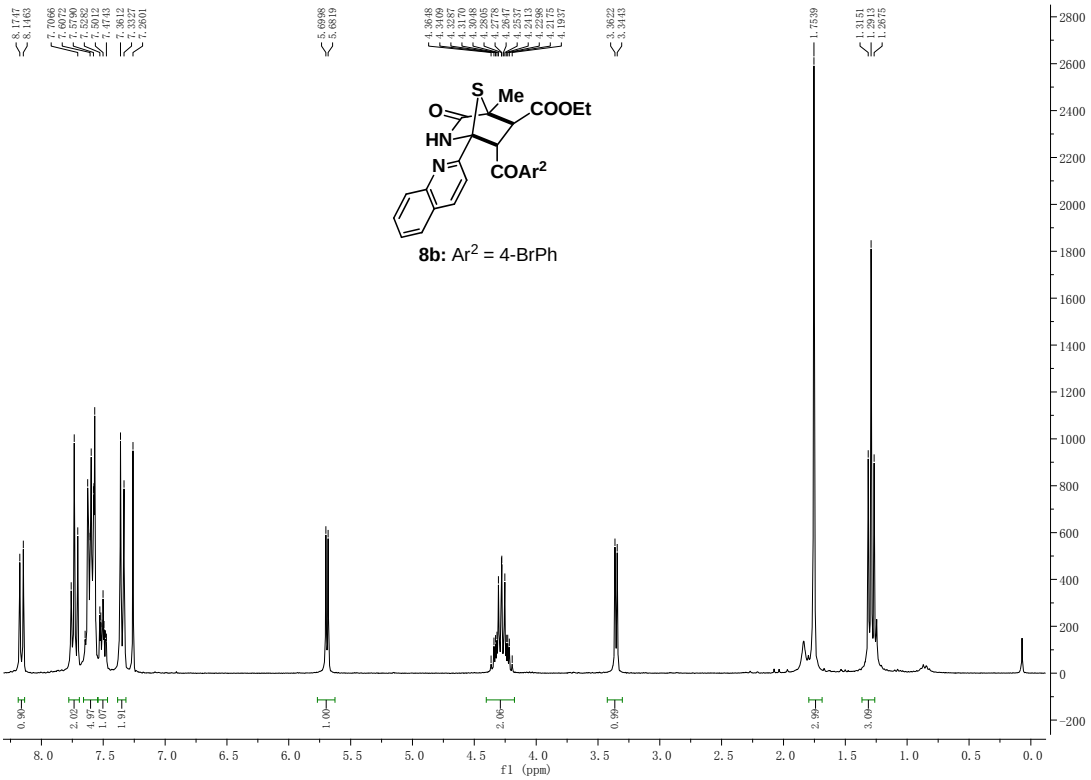

S
Et
COMe
O
HN
N
COPh
6r
f1 (ppm)

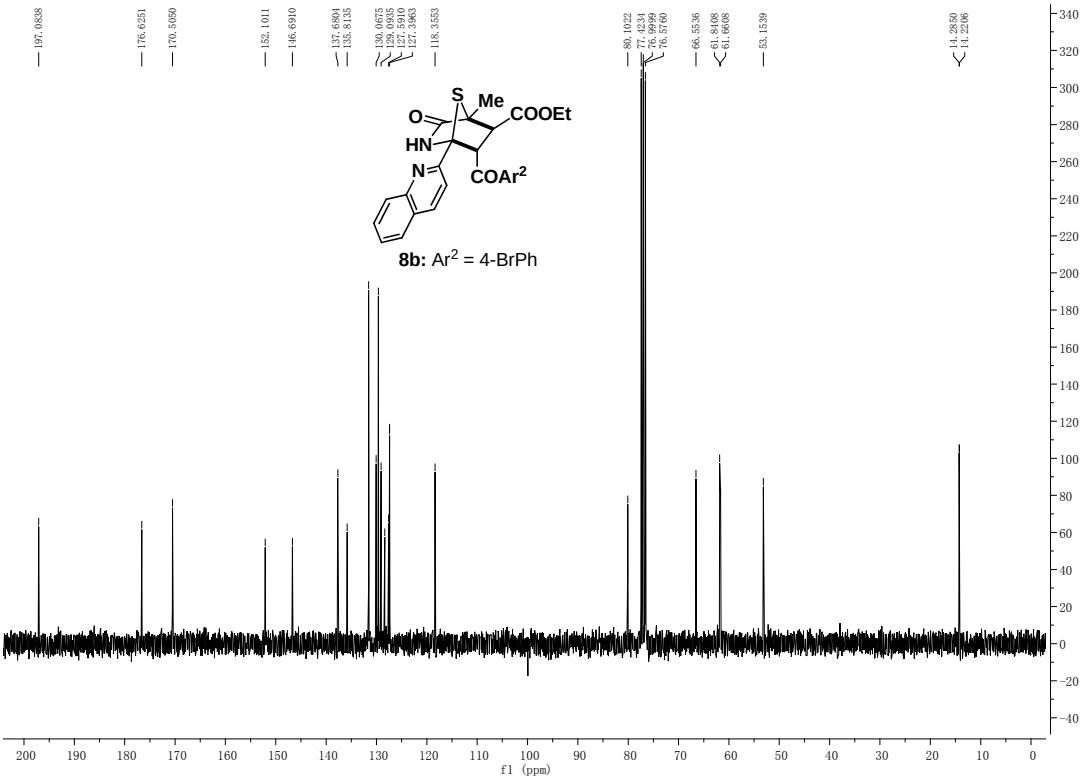

S
Bn
COMe
O
HN
N
COPh
6s
f1 (ppm)

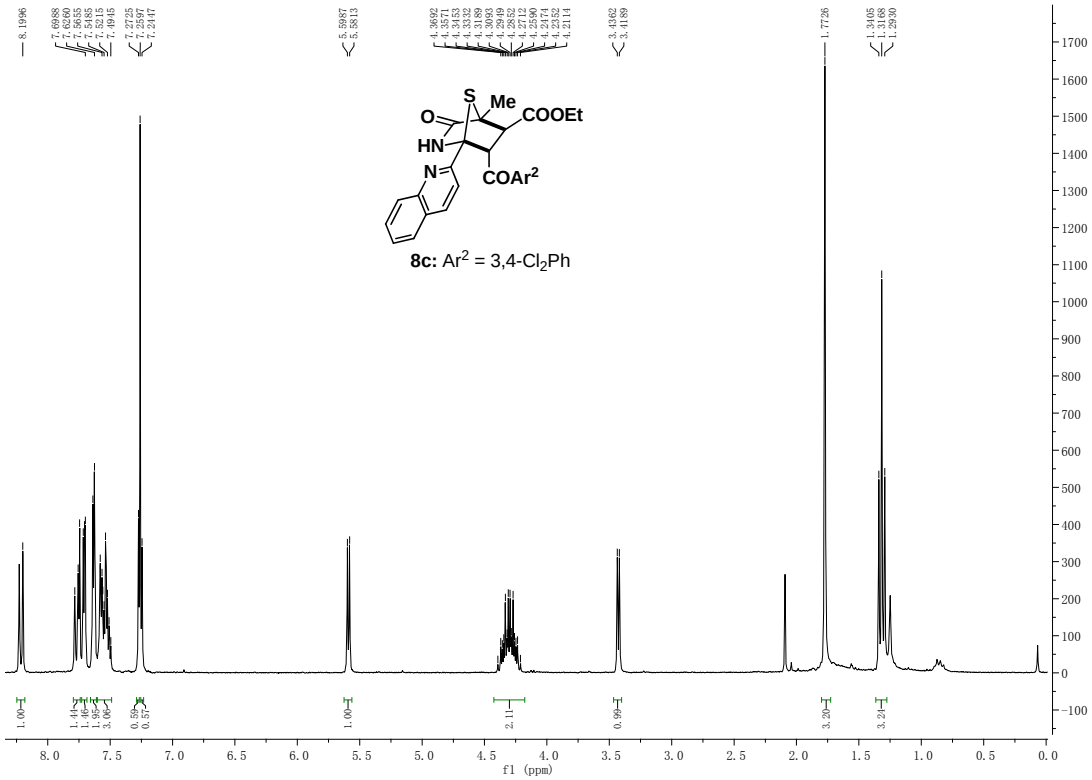

S
Bn
COMe
O
HN
N
COPh
6s
f1 (ppm)


8.1672
8.1388
7.7222
7.5948
7.5901
7.5668
7.5621
7.5159
7.5108
7.4881
7.4654
7.4612
7.4422
7.3813
7.3570
7.3323
7.2963
7.2463
7.2119
5.7643
5.7464
4.3625
4.3385
4.3205
4.3145
4.3090
4.3026
4.2955
4.2788
4.2618
4.2552
4.2498
4.2332
4.2258
3.3521
3.3342
1.7582
1.3098
1.2860
1.2622
S
Me
COOEt
O
HN
N
COAr2
8a: Ar2 = Ph
0.99
4.99
1.03
1.98
1.03
1.27
1.00
2.06
1.00
3.03
3.34
f1 (ppm)

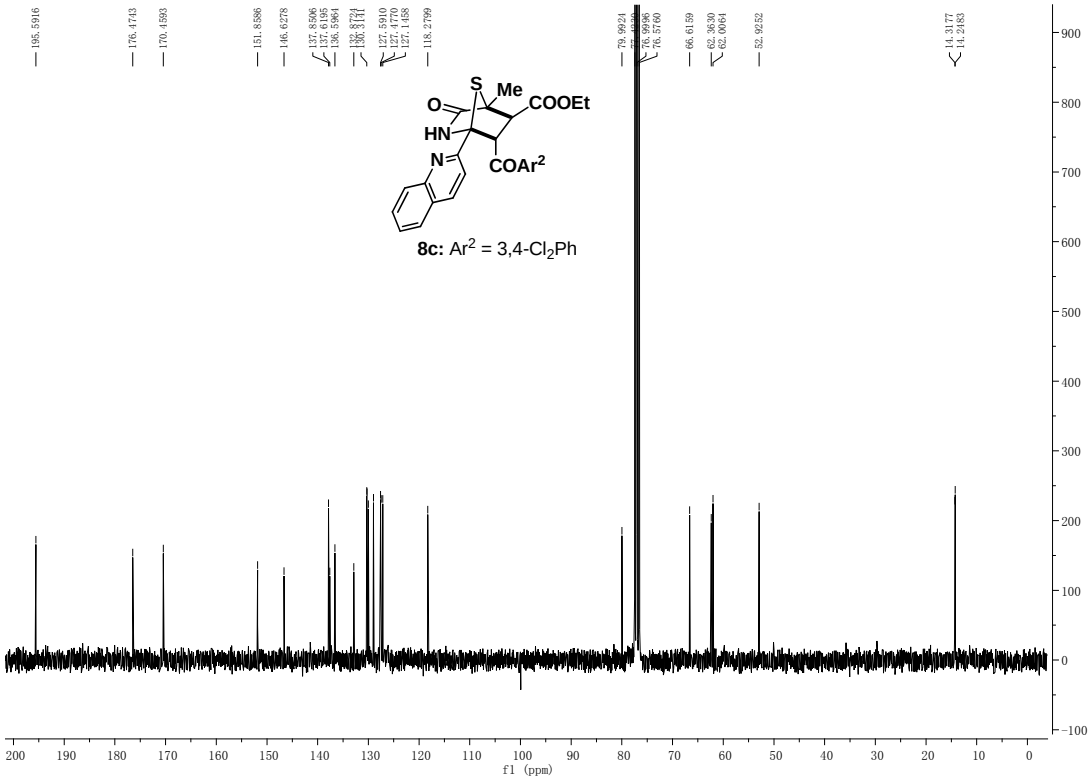

198.0191
176.5576
170.6147
152.2383
146.7641
137.5781
137.0761
133.0855
128.2978
127.5820
127.3548
127.2804
118.2766
79.9251
77.4004
76.5770
66.5166
62.0942
61.7734
53.3926
14.2953
14.2156
S
Me
COOEt
O
HN
N
COAr2
8a: Ar2 = Ph
f1 (ppm)


8.17 47
8.14 63
7.70 66
7.69 72
7.57 96
7.52 82
7.50 12
7.47 43
7.36 12
7.33 27
7.26 01
5.69 98
5.68 19
4.36 48
4.34 09
4.32 87
4.31 70
4.30 48
4.28 05
4.27 78
4.26 47
4.25 37
4.24 13
4.22 98
4.21 75
4.19 37
3.36 22
3.34 13
1.75 39
1.31 51
1.29 13
1.26 75
S
Me
COOEt
O
HN
N
COAr2
8b: Ar2 = 4-BrPh
0.90
2.02
4.07
1.07
1.91
1.00
2.06
0.99
2.69
3.09
f1 (ppm)

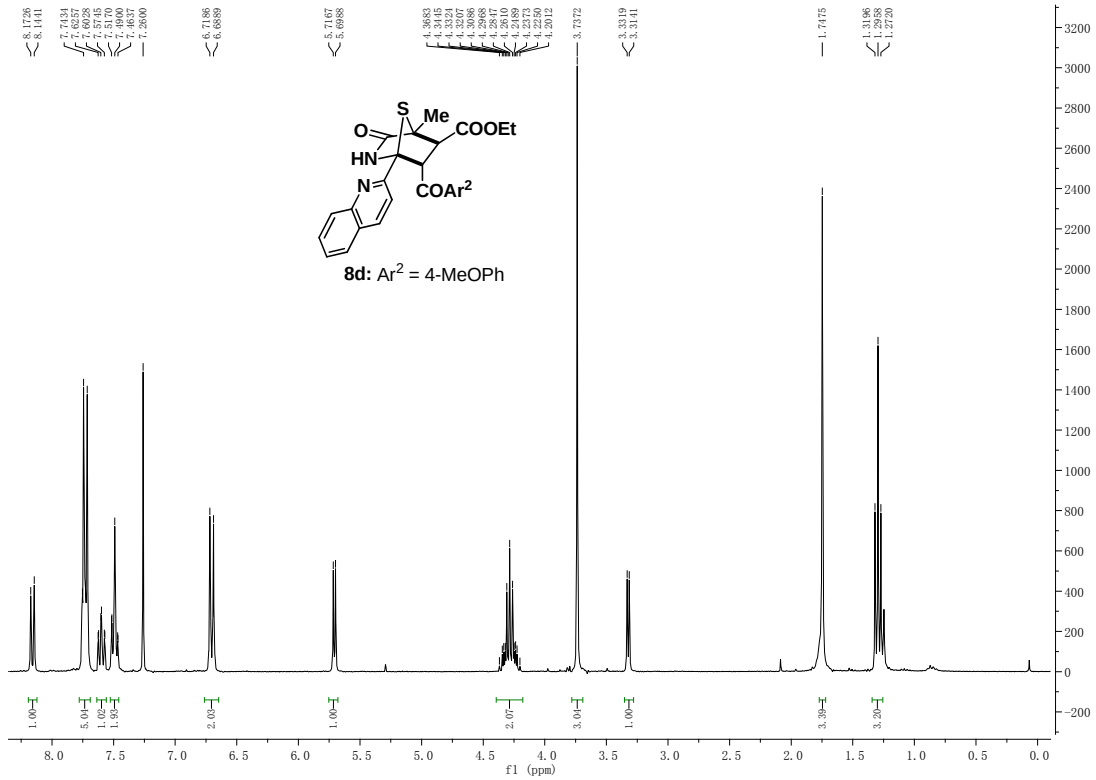

197.0838
176.6251
170.5050
152.1011
146.6910
137.6804
135.8135
130.0675
129.0935
127.5910
127.3963
118.3553
80.1022
77.4234
76.9999
76.5760
66.5536
61.8408
61.6608
53.1539
14.2850
14.2296
S
Me
COOEt
O
HN
N
COAr2
8b: Ar2 = 4-BrPh
f1 (ppm)



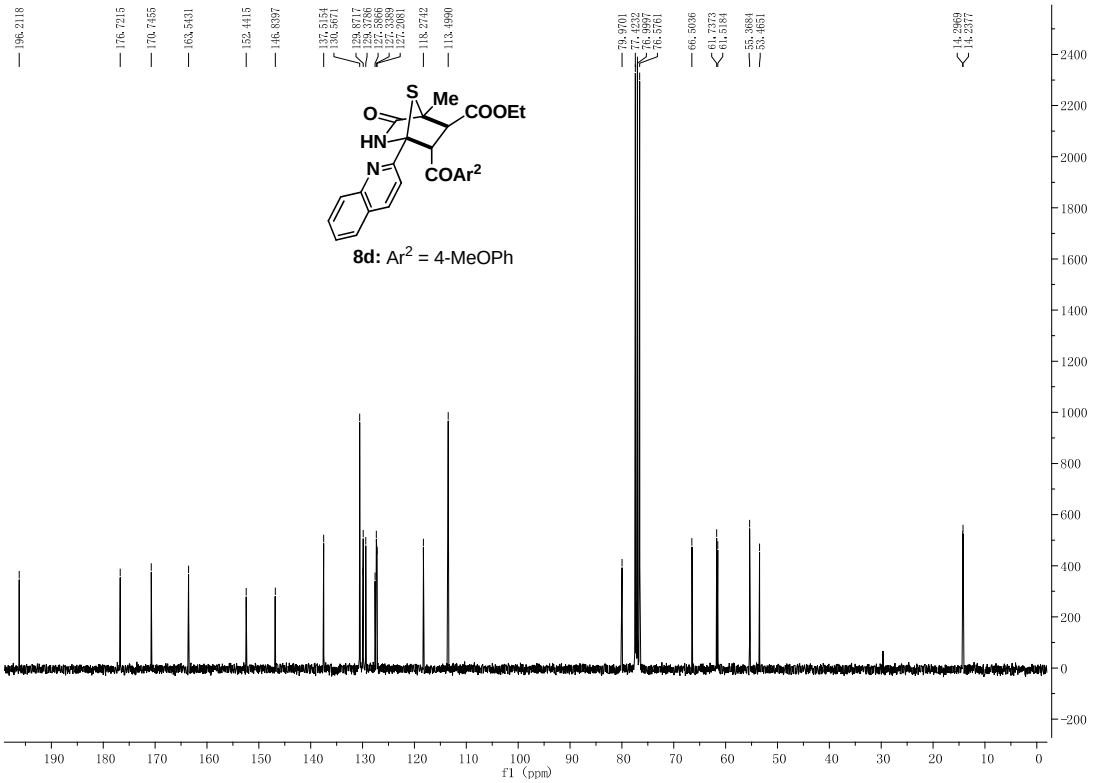
8c: Ar^2 = 3,4-Cl_2Ph



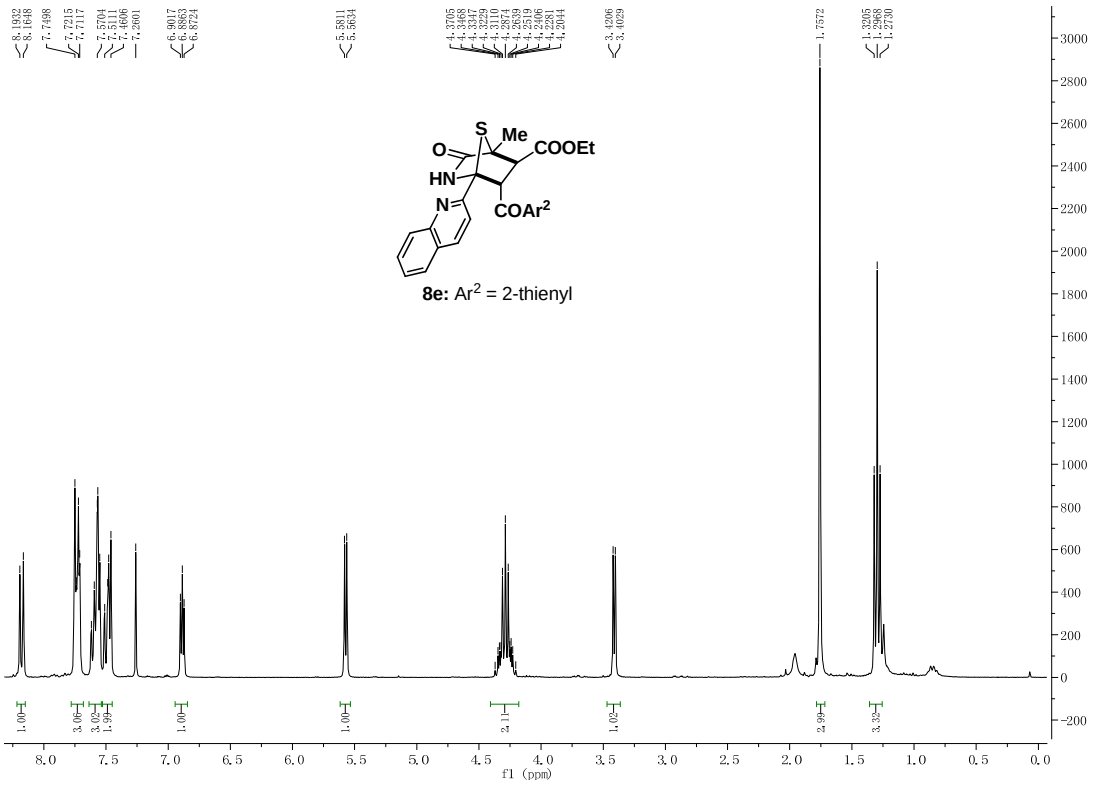
8c: Ar^2 = 3,4-Cl_2Ph



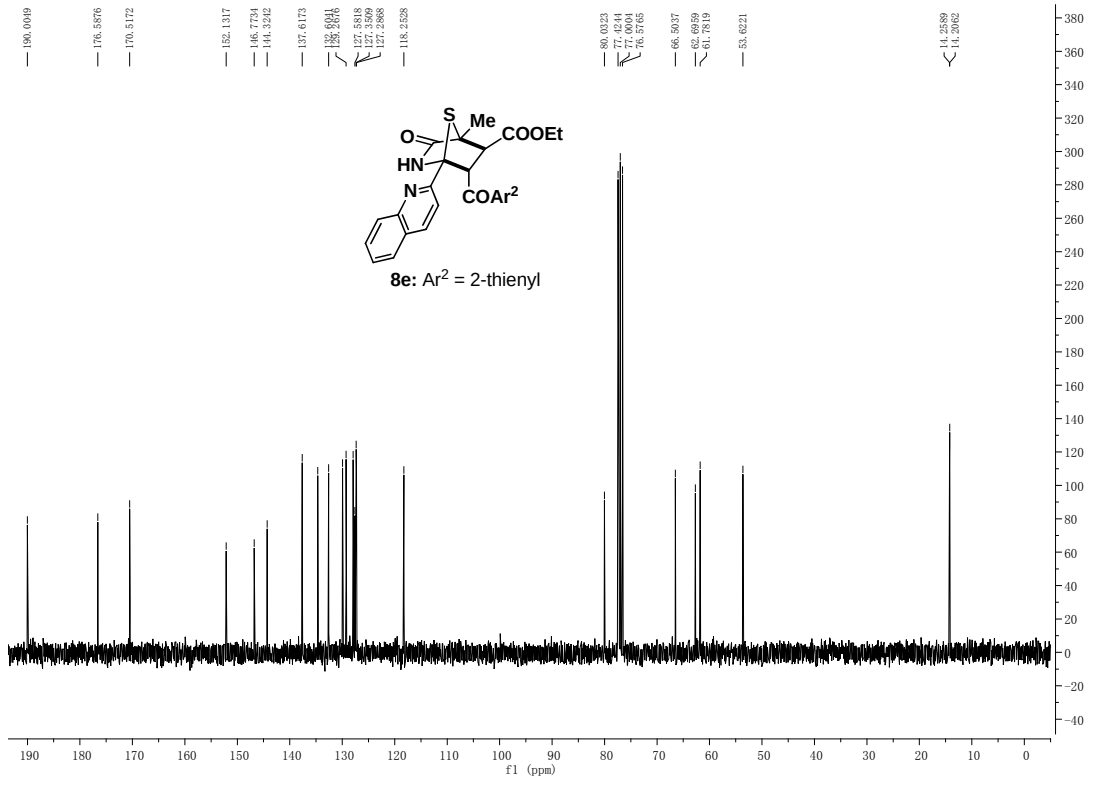
8d: Ar^2 = 4-MeOPh



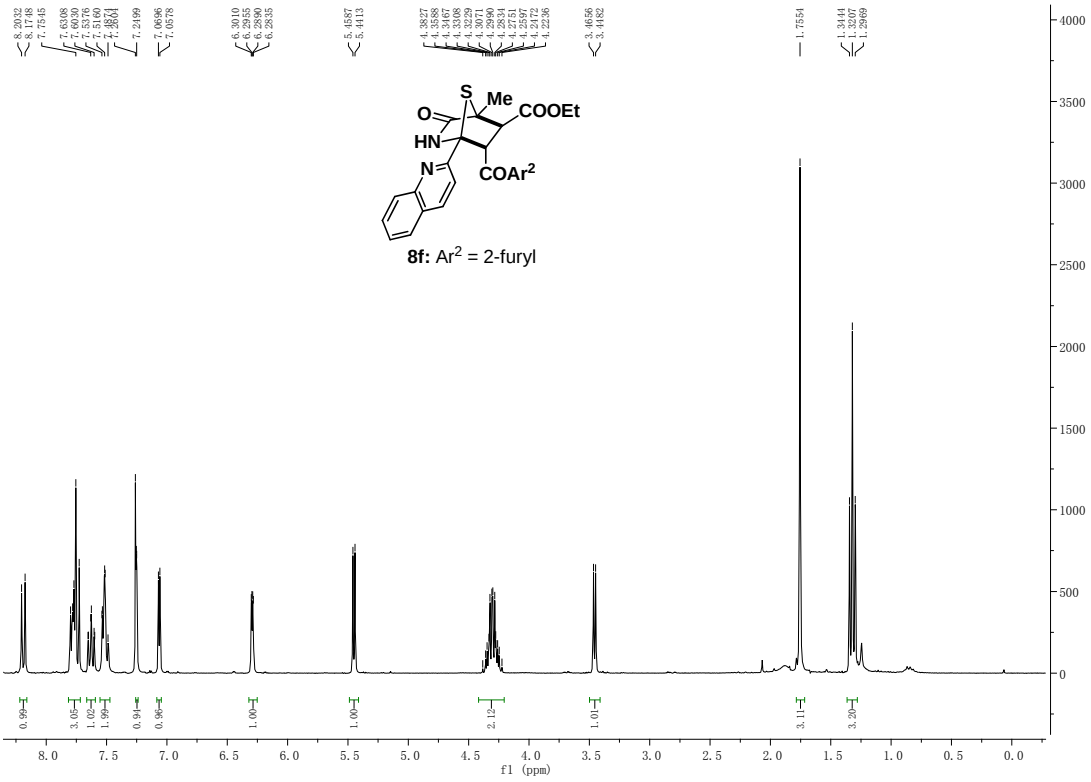
8d: Ar^2 = 4-MeOPh

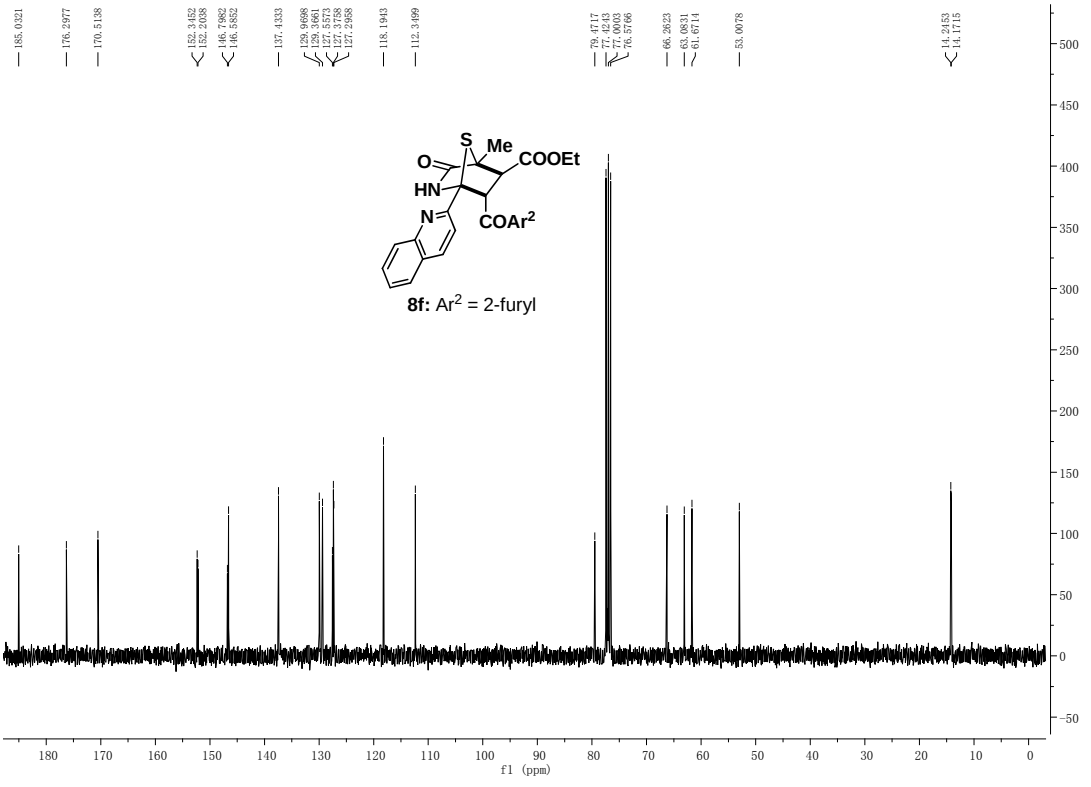


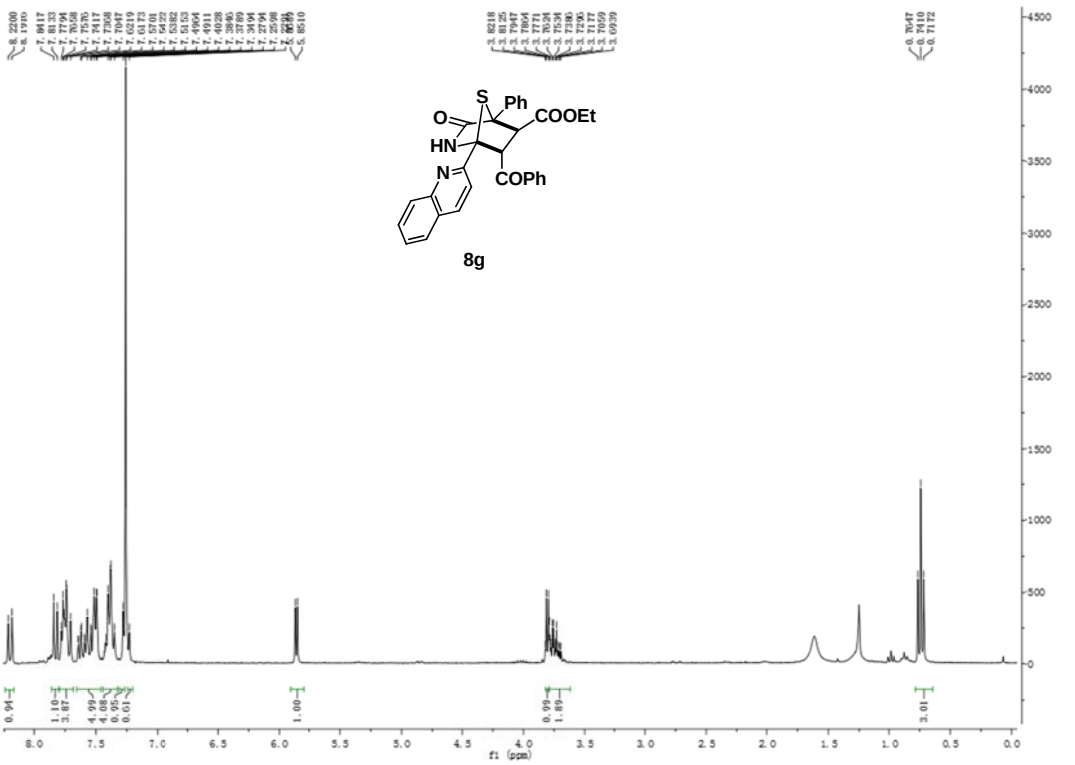
8e: Ar^2 = 2-thienyl



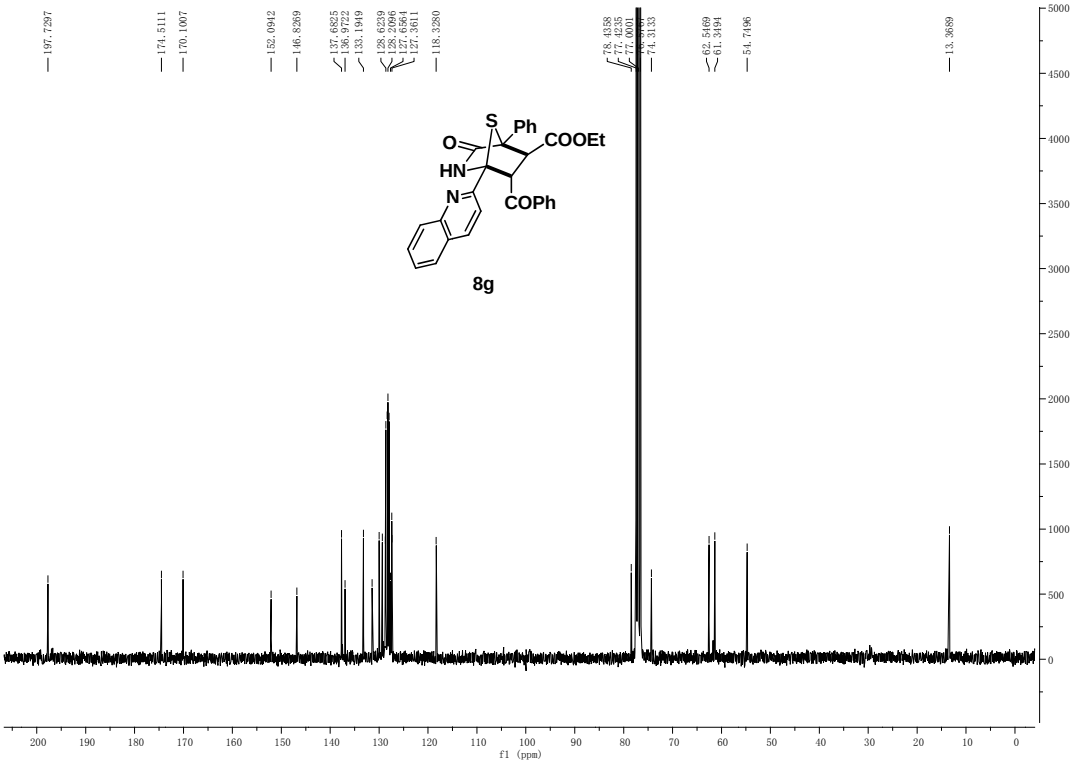
8e: Ar^2 = 2-thienyl


8f: Ar2 = 2-furyl
f1 (ppm)

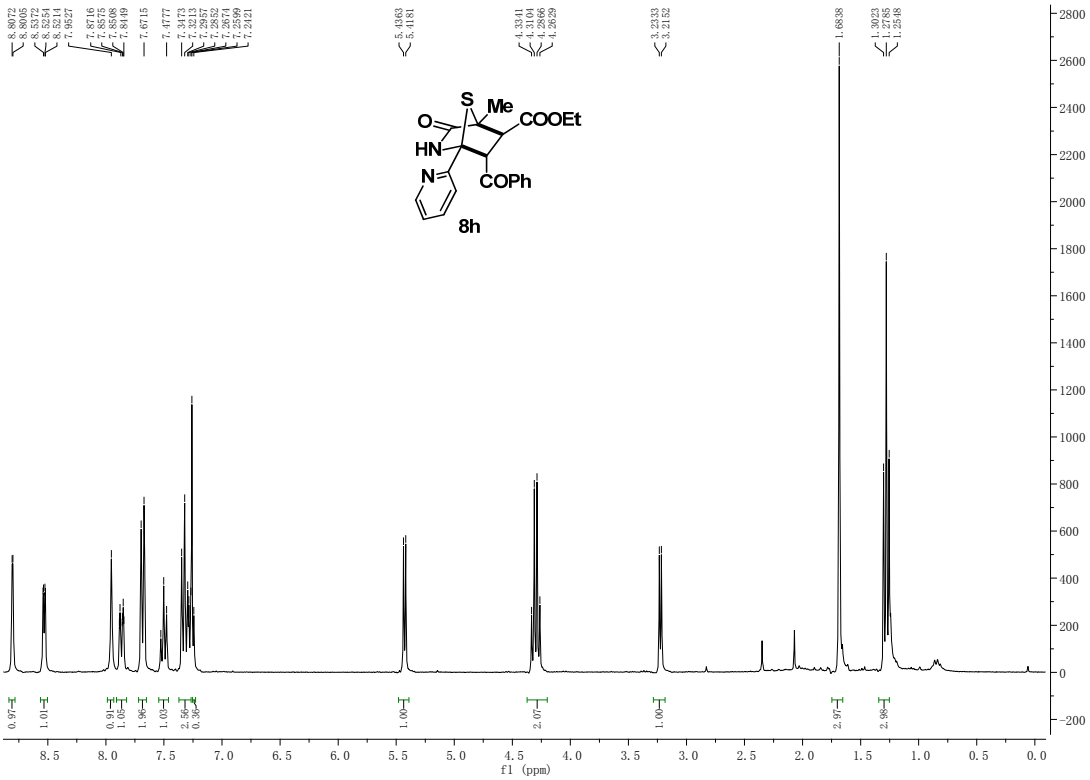

8f: Ar2 = 2-furyl
f1 (ppm)



8g



8g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8.5214
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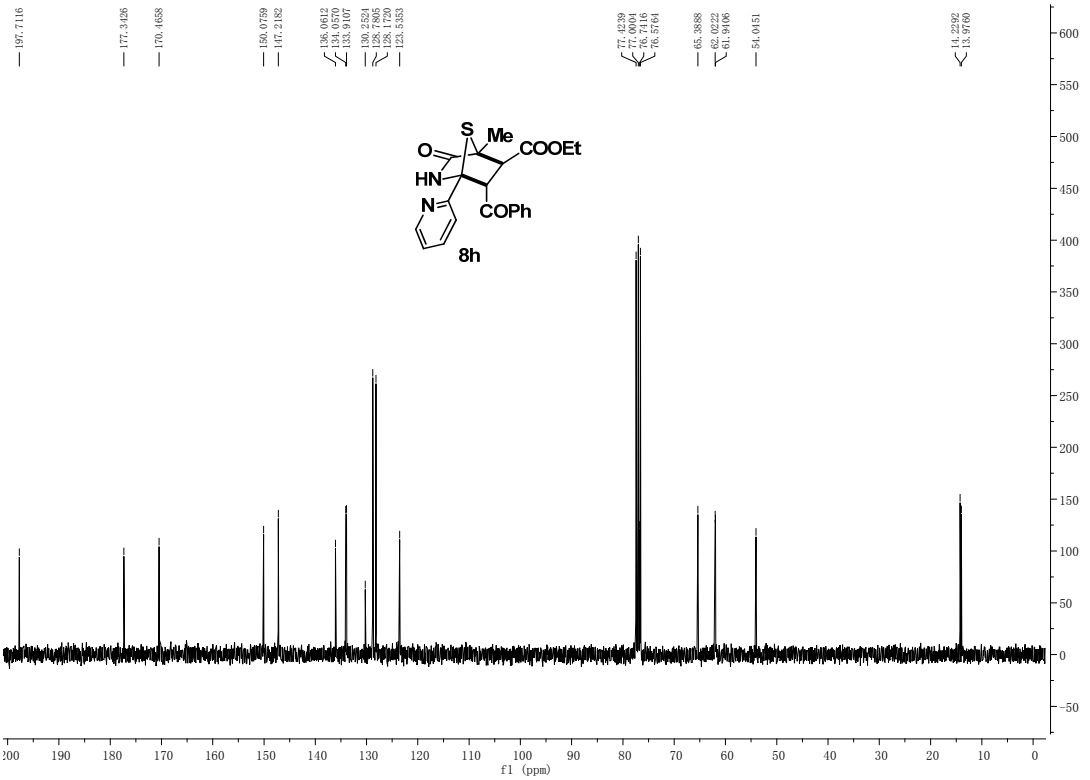
7.8716
7.8575
7.8508
7.8449
7.6715
7.4777
7.3473
7.3213
7.2987
7.2832
7.2674
7.2599
7.2421
5.4363
5.4181
4.3341
4.3104
4.2866
4.2629
3.2333
3.2152
1.6838
1.3023
1.2735
1.2548
S
Me
COOEt
O
HN
N
COPh
8h
0.97
1.01
0.91
1.05
1.98
1.03
2.59
0.36
1.00
2.07
1.00
2.97
2.88
f1 (ppm)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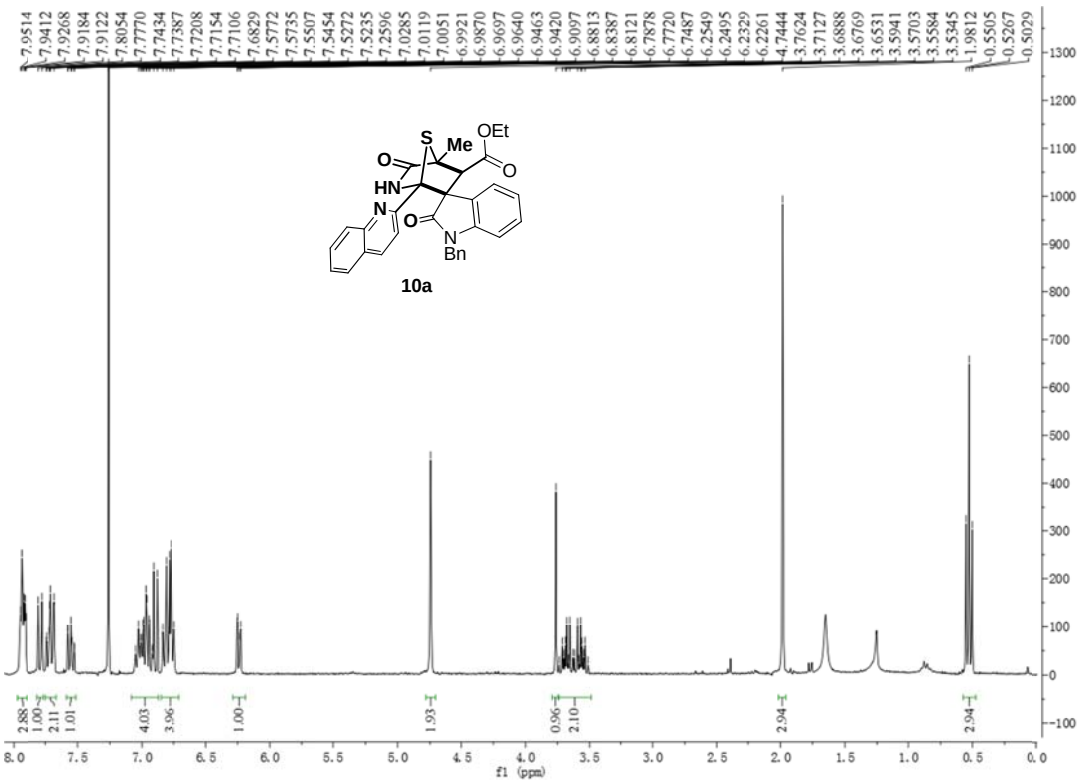
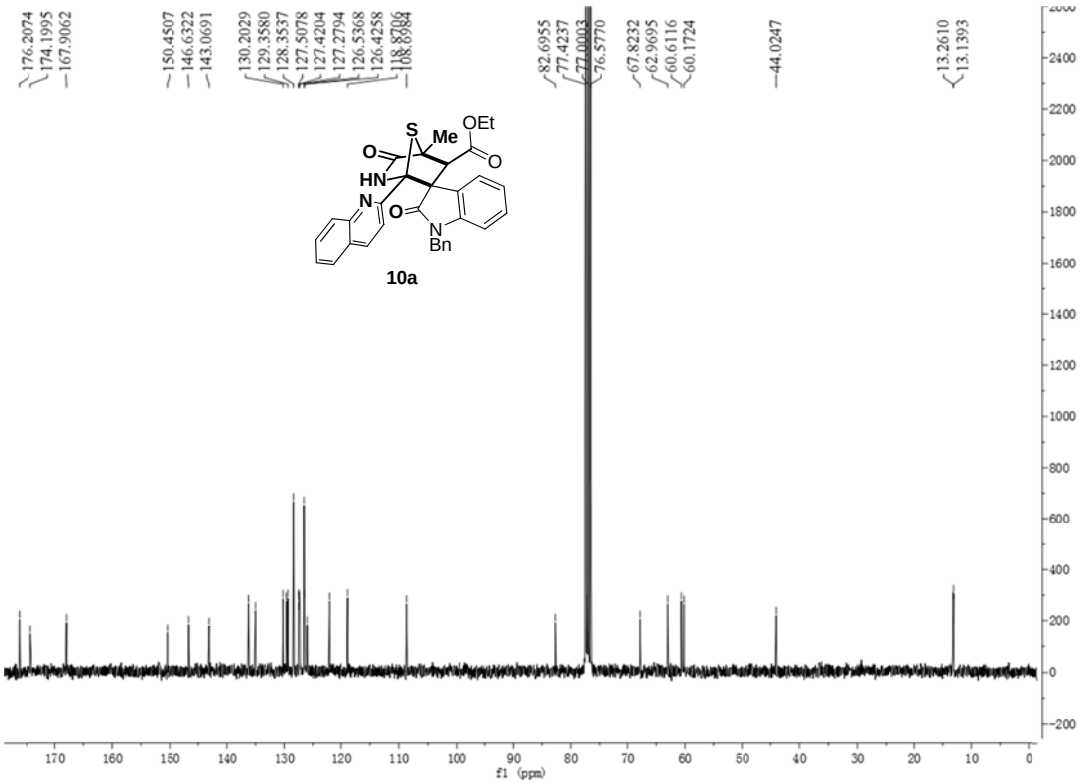
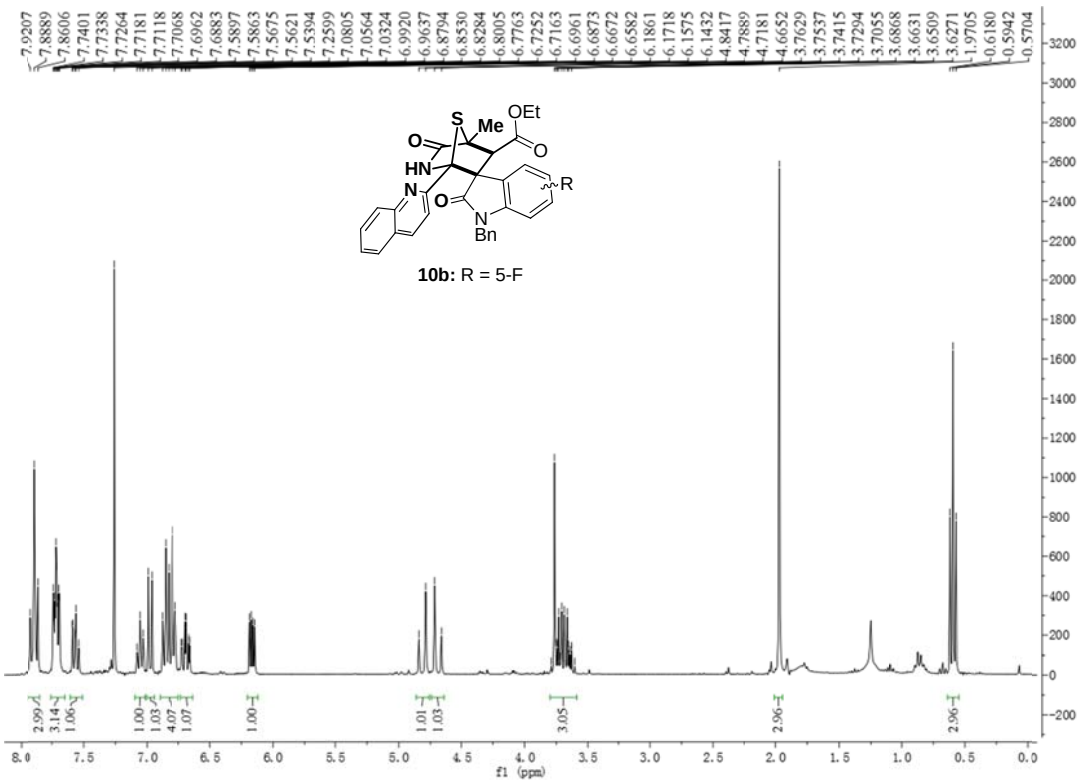
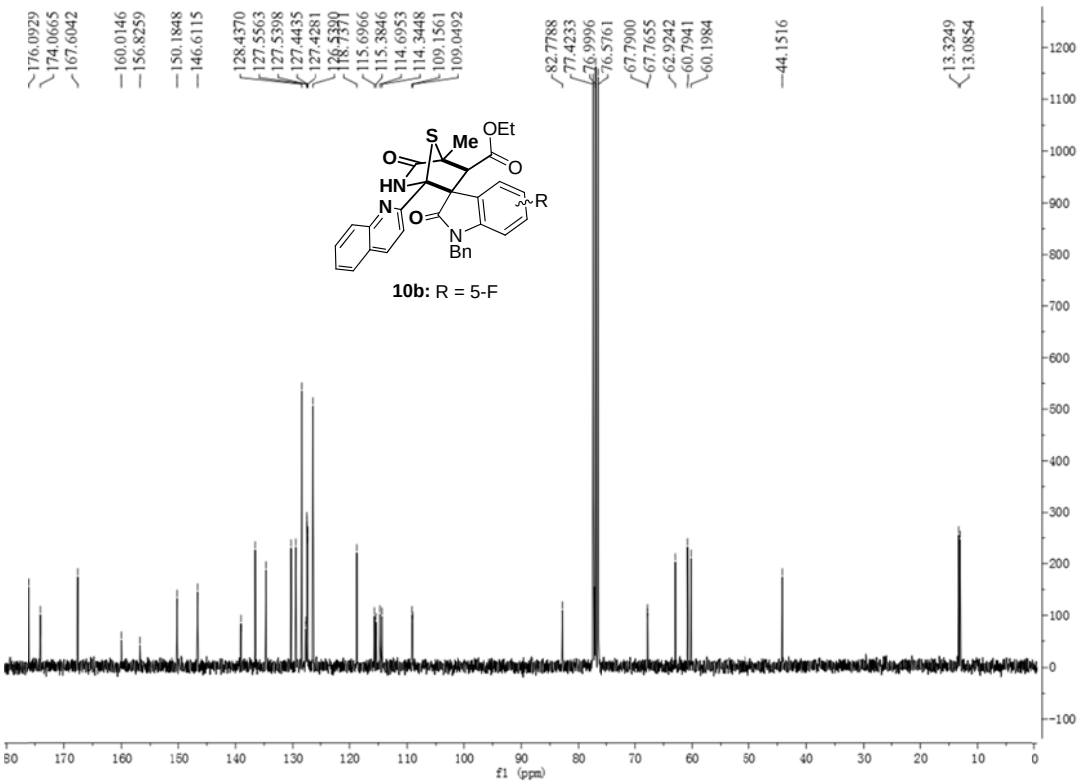
177.3426
170.4658
150.0759
147.2182
136.0612
134.0570
133.9107
130.2524
128.7805
128.1720
123.5353
77.4239
77.0004
76.7416
76.5764
65.3888
62.0222
61.9406
54.0451
14.2292
13.9760
S
Me
COOEt
O
HN
N
COPh
8h
f1 (ppm)


10a

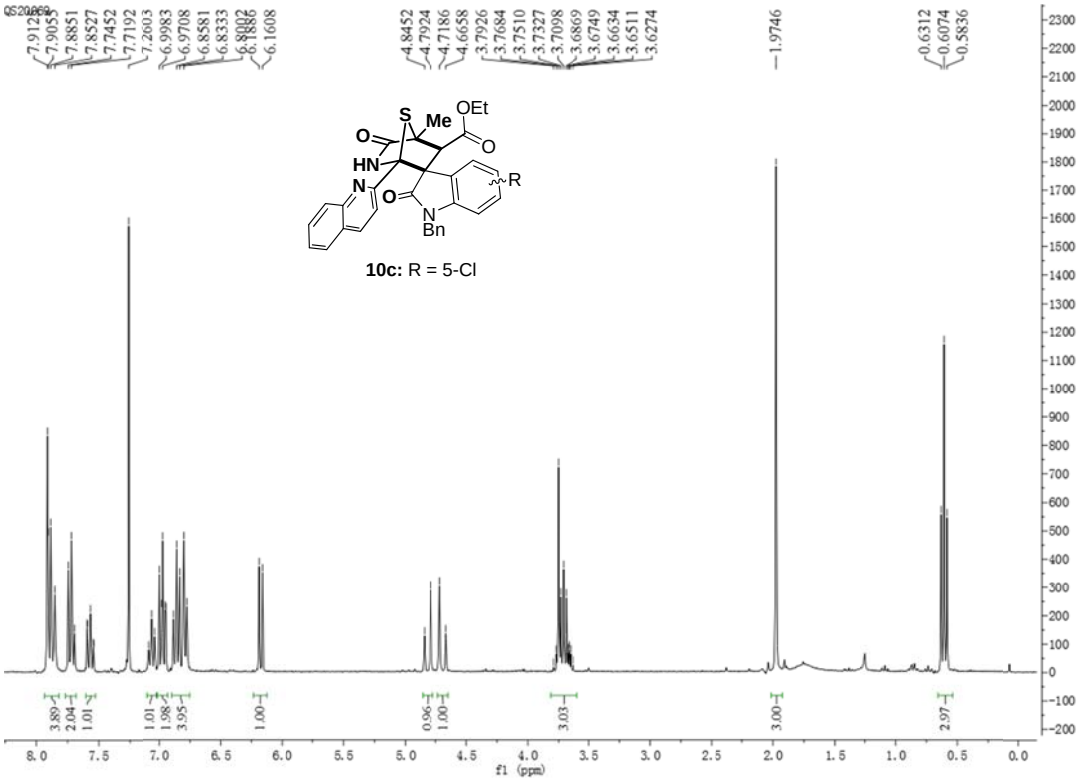

10a



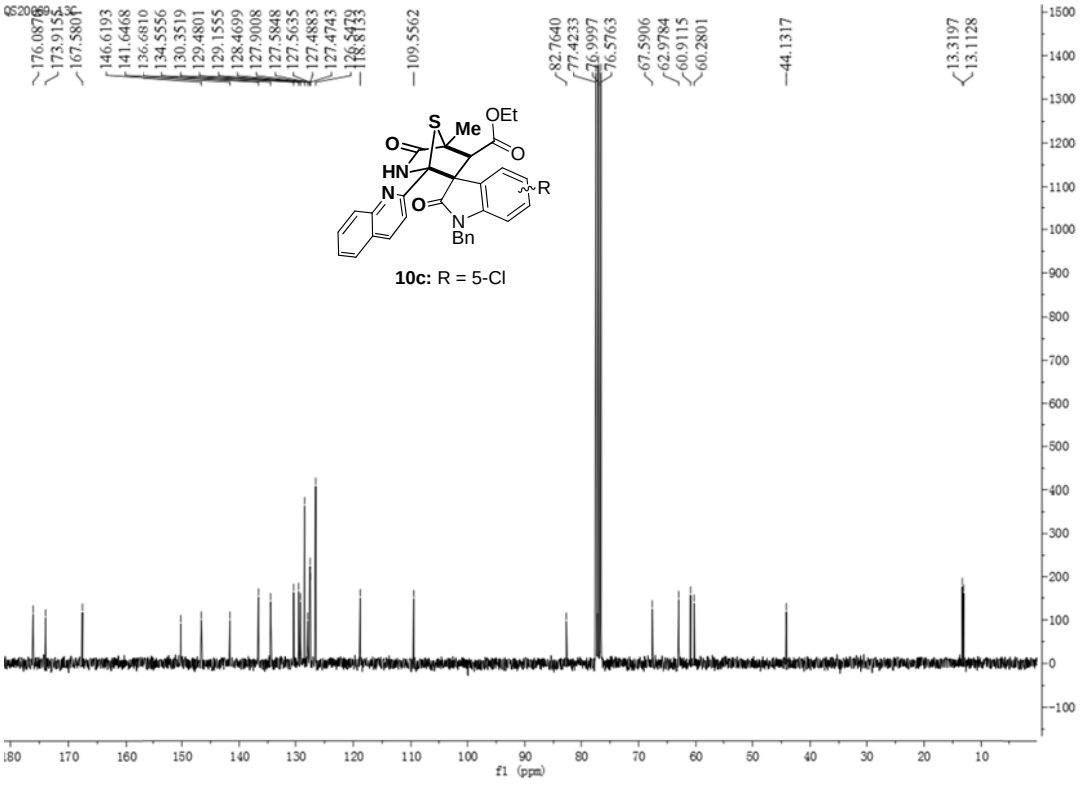
10b: R = 5-F



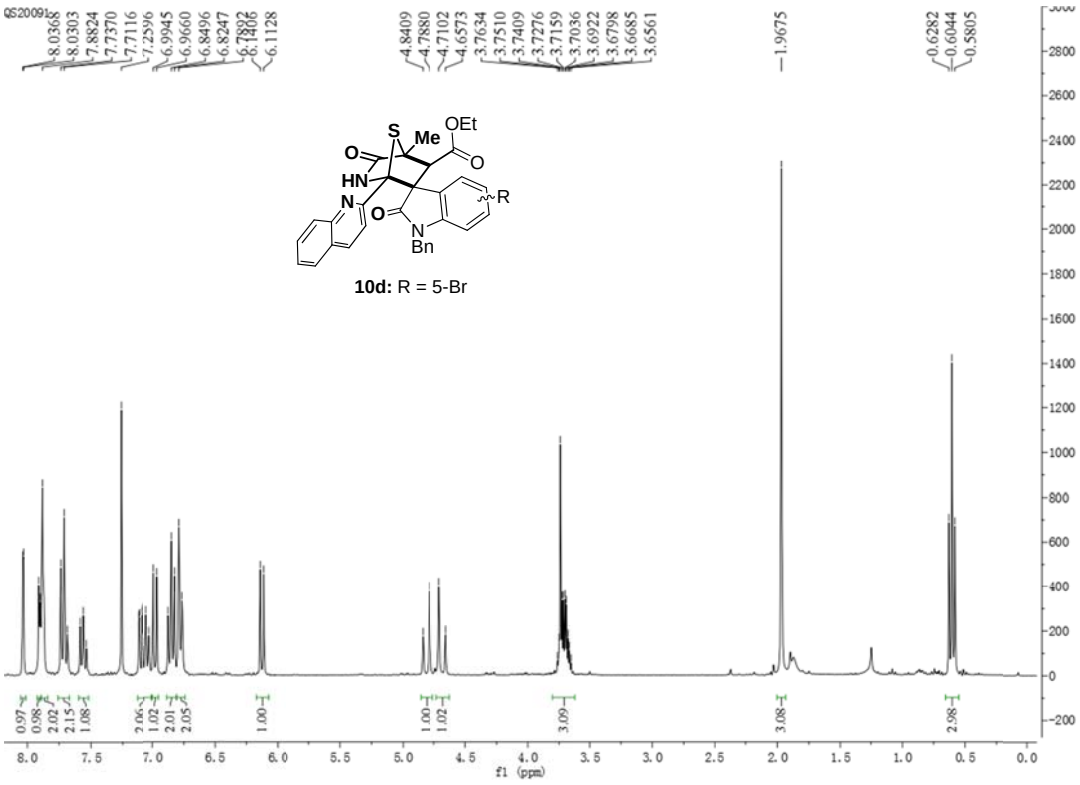
10b: R = 5-F

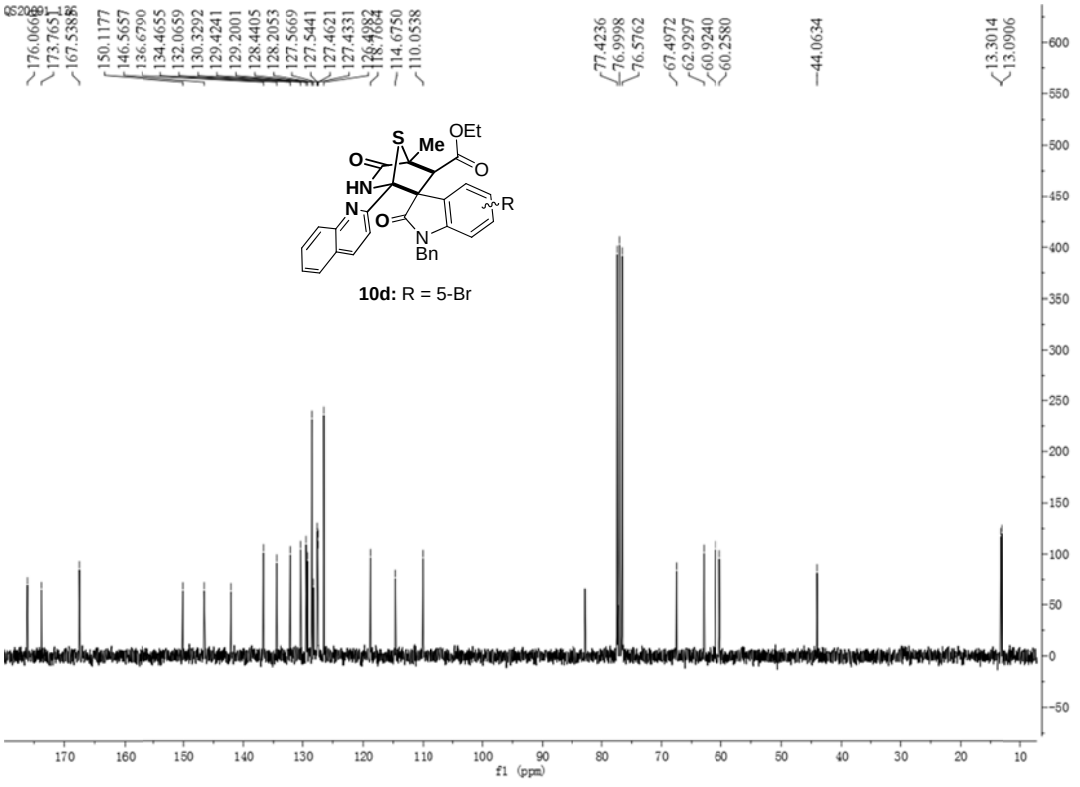


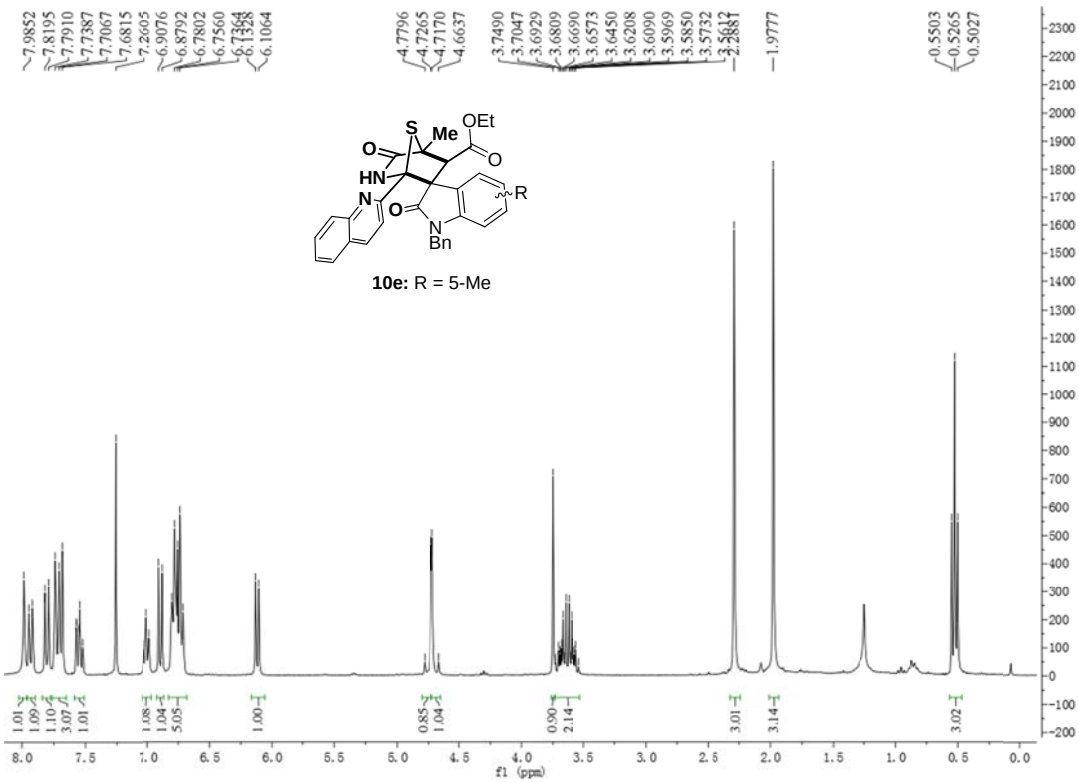
10c: R = 5-Cl

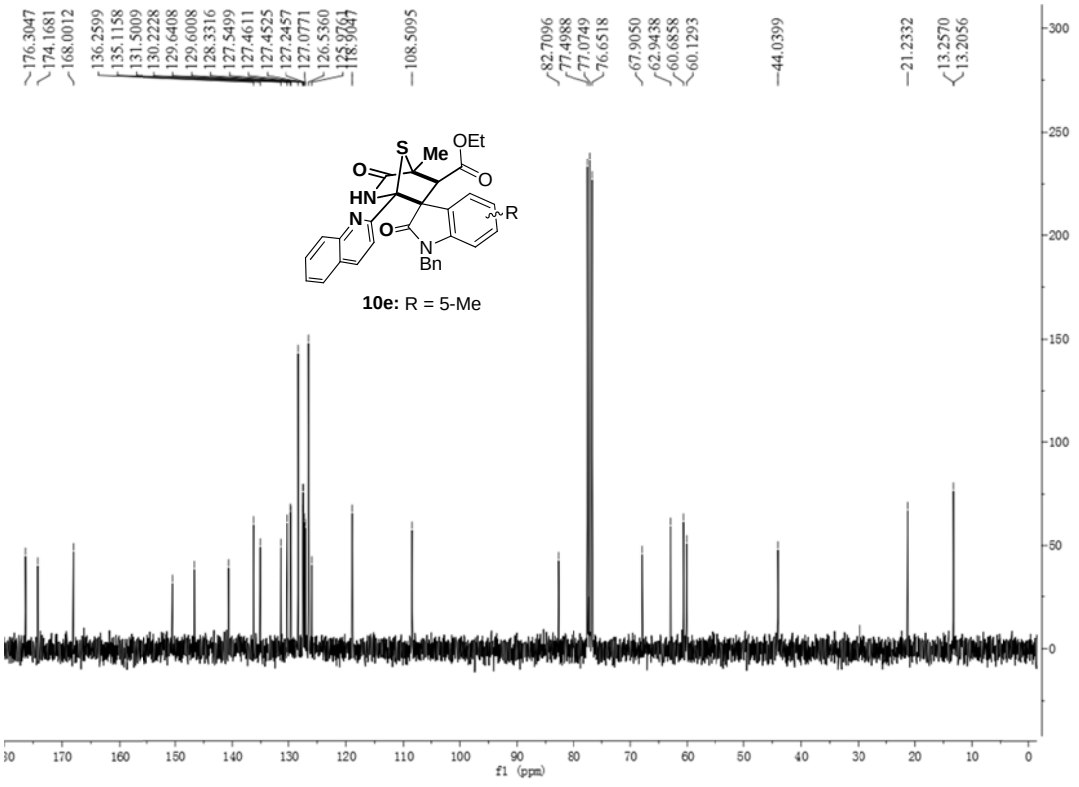


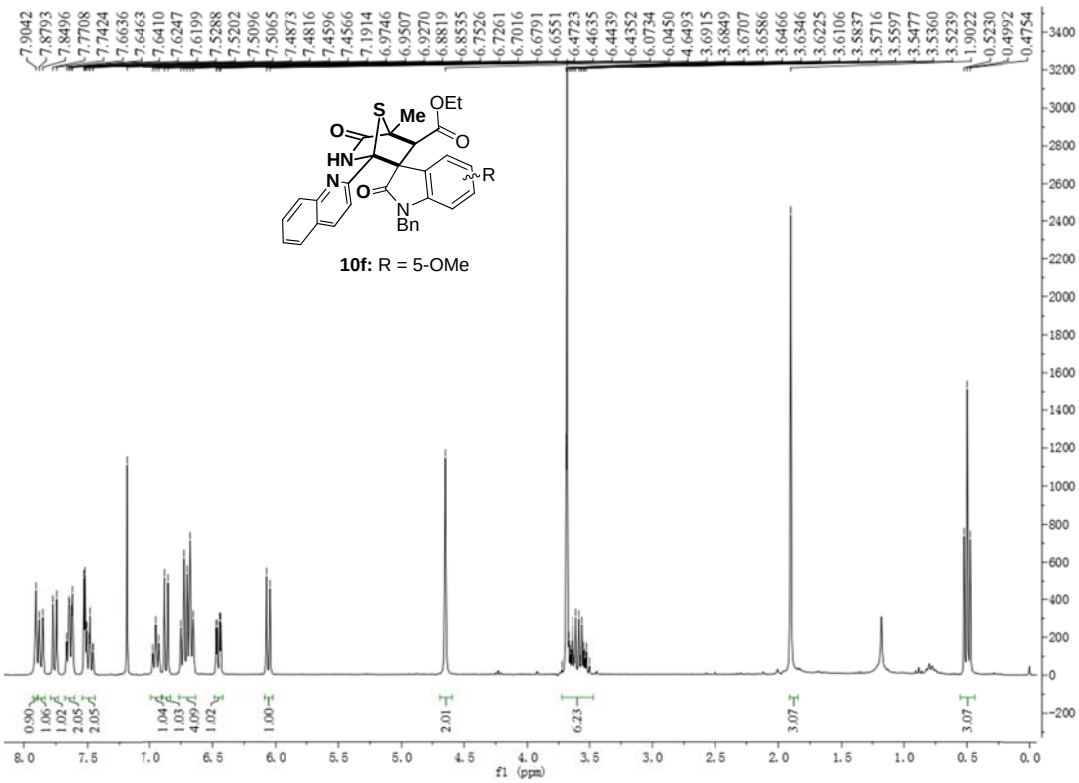
10c: R = 5-Cl


QS20091
8.0368
8.0303
7.8824
7.7370
7.7116
7.2596
6.9945
6.9660
6.8496
6.8247
6.1406
6.1128
4.8409
4.7880
4.7102
4.6573
3.7634
3.7510
3.7409
3.7276
3.7159
3.7036
3.6922
3.6798
3.6685
3.6561
1.9675
0.6282
0.6044
0.5805
S
Me
OEt
O
O
HN
N
O
R
N
Bn
10d: R = 5-Br
f1 (ppm)

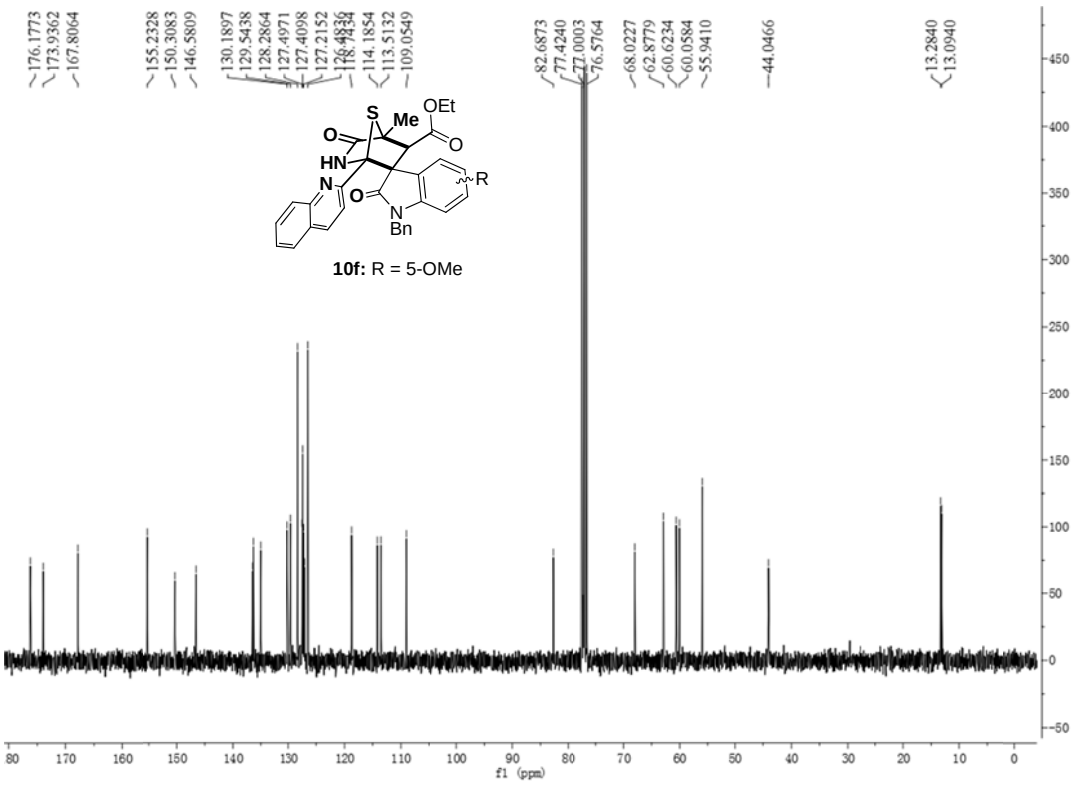

QS20091
176.0666
173.7651
167.5386
150.1177
146.5657
136.6790
134.4655
132.0659
130.3292
129.4241
129.2001
128.4405
128.2053
127.5669
127.5441
127.4621
127.4331
126.4982
118.7664
114.6750
110.0538
77.4236
76.9998
76.5762
67.4972
62.9297
60.9240
60.2580
44.0634
13.3014
13.0906
S
Me
OEt
O
O
HN
N
O
R
N
Bn
10d: R = 5-Br
f1 (ppm)


7.9852
7.8195
7.7910
7.7387
7.7067
7.6815
7.2605
6.9076
6.8792
6.7802
6.7560
6.7364
6.1328
6.1064
4.7796
4.7265
4.7170
4.6637
3.7490
3.7047
3.6929
3.6809
3.6690
3.6573
3.6450
3.6208
3.6090
3.5969
3.5850
3.5732
2.2881
1.9777
0.5503
0.5265
0.5027
S
Me
OEt
O
O
HN
N
O
R
N
Bn
10e: R = 5-Me
f1 (ppm)

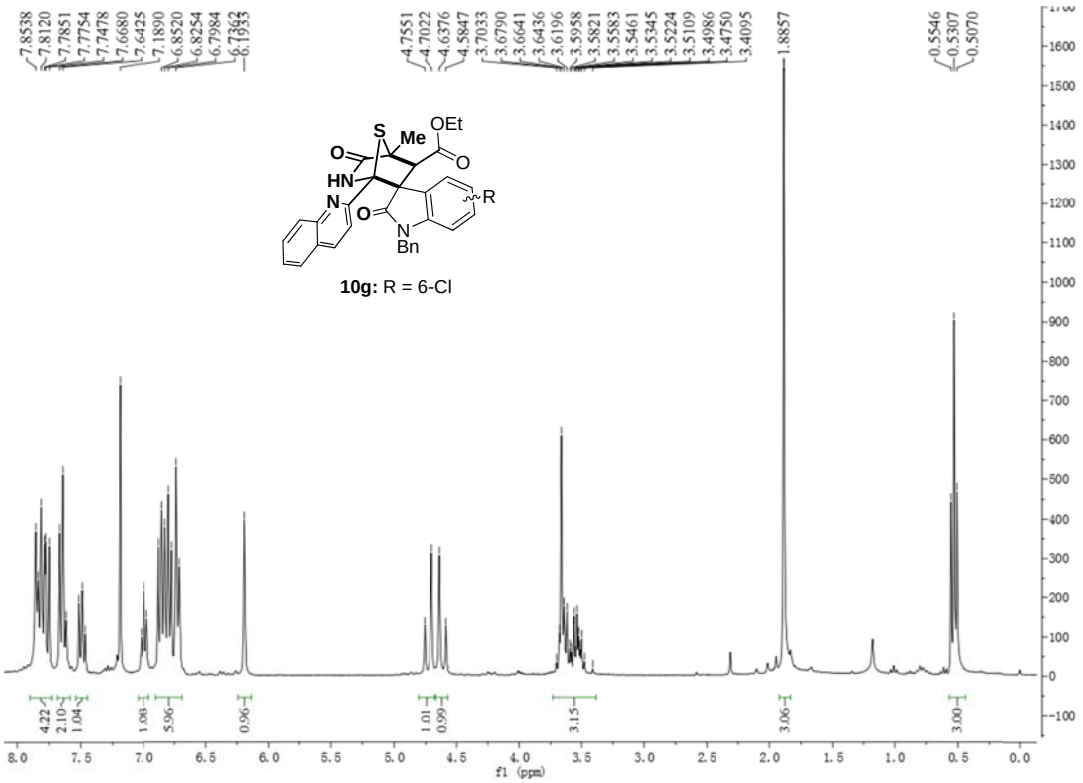

176.3047
174.1681
168.0012
136.2599
135.1158
131.5009
130.2228
129.6408
129.6008
128.3316
127.5499
127.4611
127.4525
127.2457
127.0771
126.5360
125.9761
118.9047
108.5095
82.7096
77.4988
77.0749
76.6518
67.9050
62.9438
60.6858
60.1293
44.0399
21.2332
13.2570
13.2056
S
Me
OEt
O
O
HN
N
O
R
N
Bn
10e: R = 5-Me
f1 (ppm)

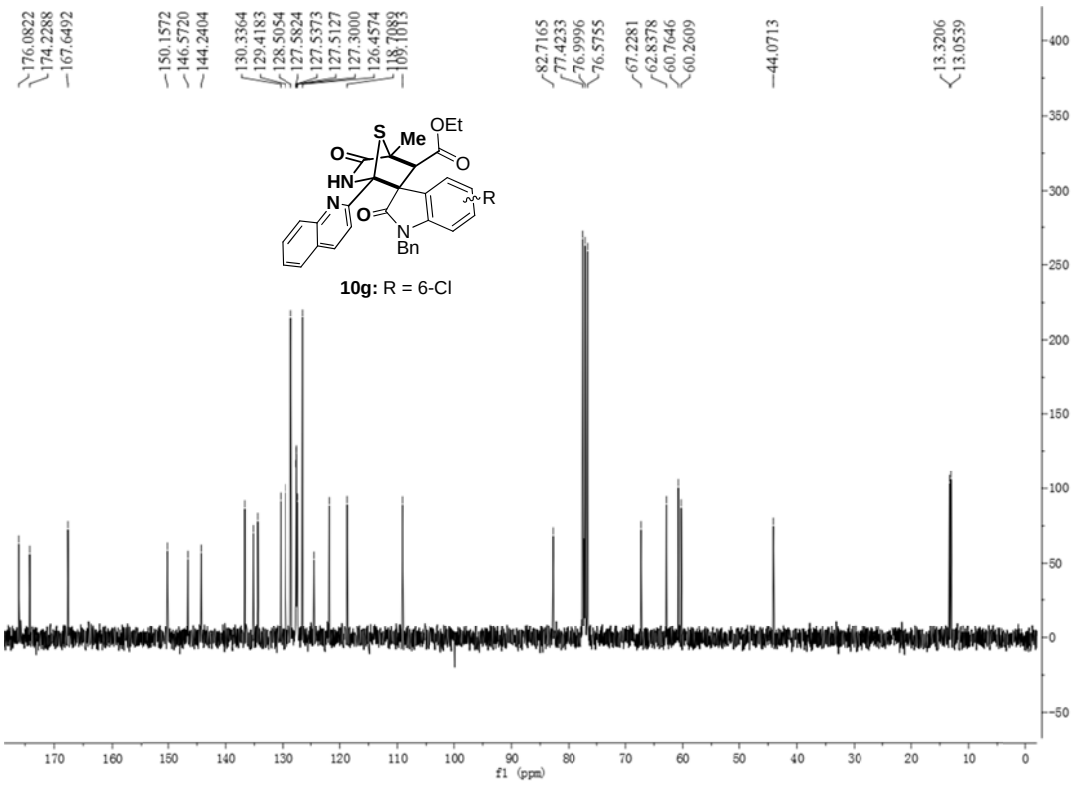


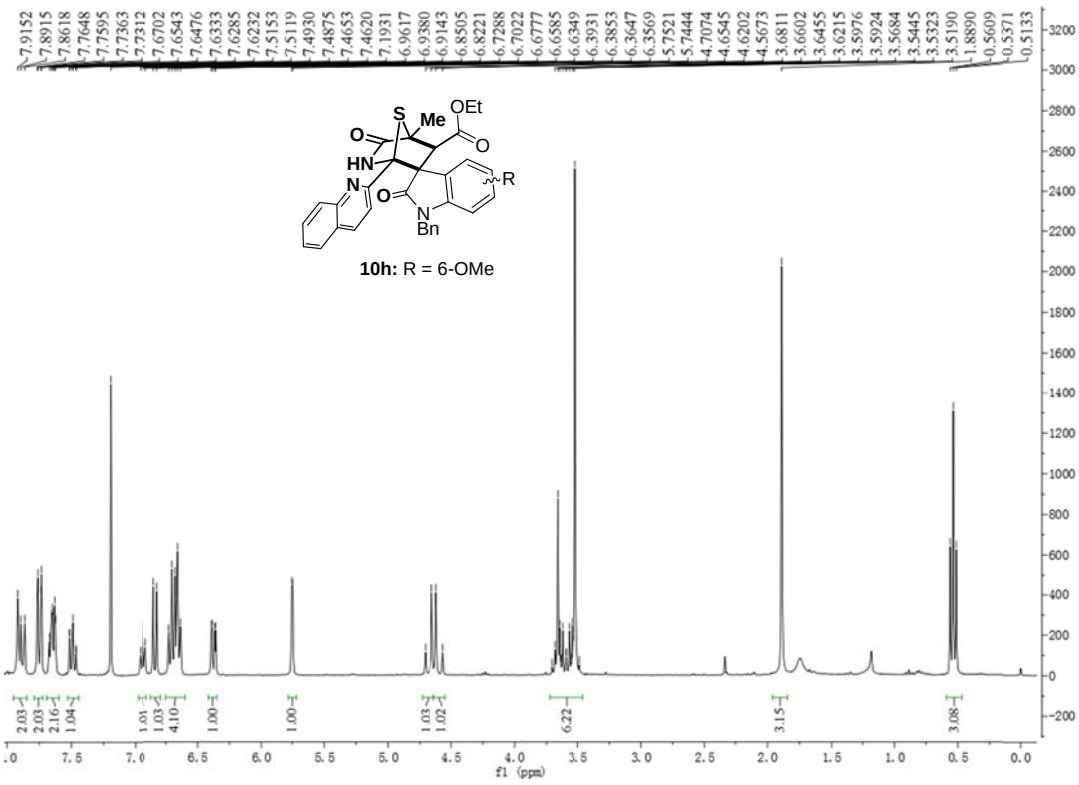
10f: R = 5-OMe



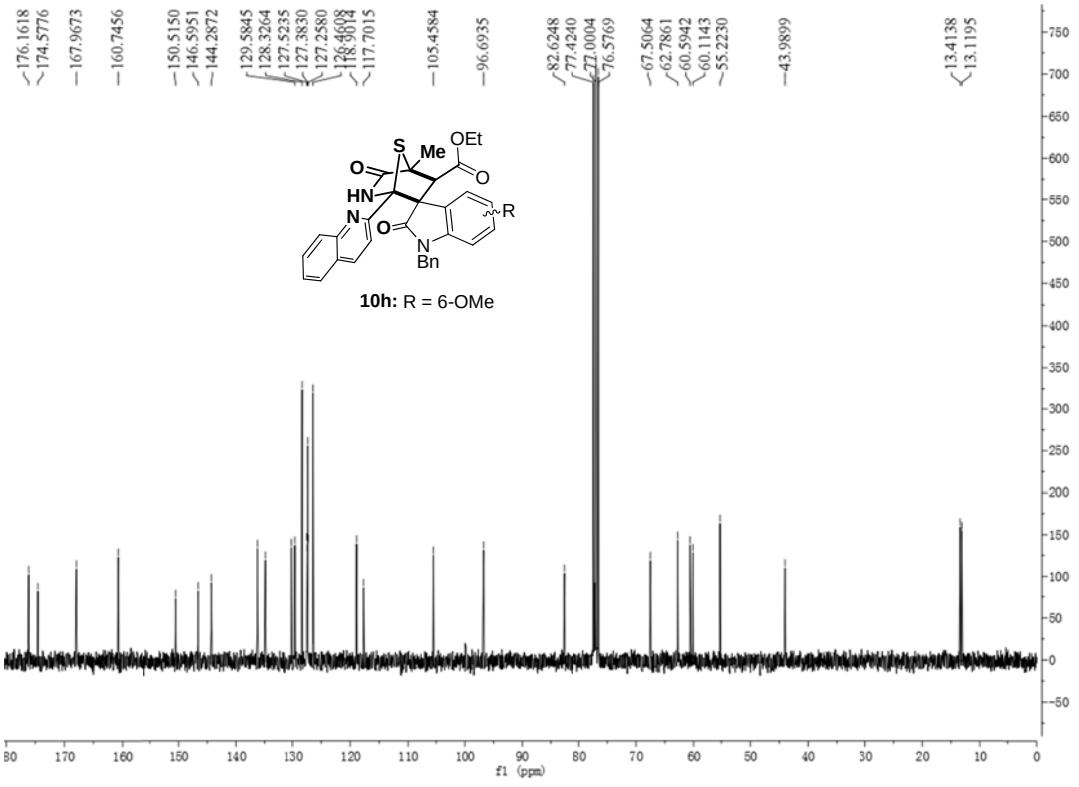
10f: R = 5-OMe


7.8538
7.8120
7.7851
7.7754
7.7478
7.6680
7.6425
7.1890
6.8520
6.8254
6.7984
4.7551
4.7022
4.6376
4.5847
3.7033
3.6790
3.6641
3.6436
3.6196
3.5958
3.5821
3.5583
3.5461
3.5345
3.5224
3.5109
3.4986
3.4750
3.4095
1.8857
0.5546
0.5307
0.5070
S
Me
OEt
O
HN
N
O
R
N
Bn
10g: R = 6-Cl
4.22
2.10
1.04
5.06
0.96
1.01
0.99
3.15
3.06
3.00
f1 (ppm)

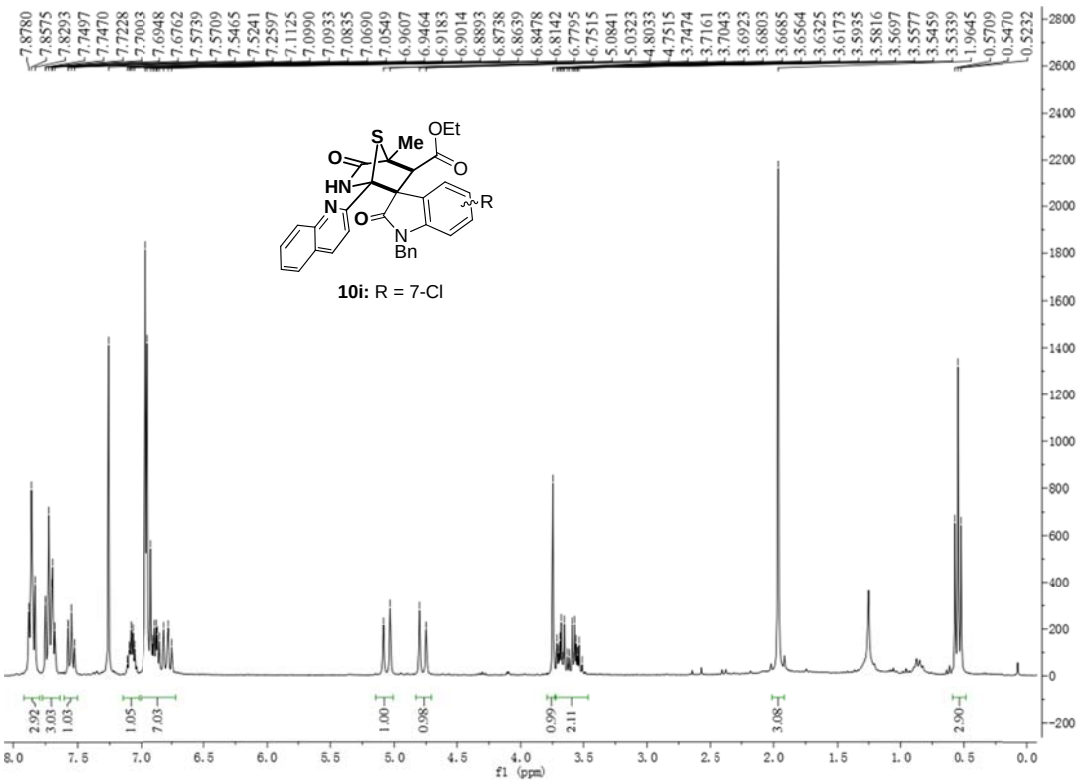

176.0822
174.2288
167.6492
150.1572
146.5720
144.2404
130.3364
129.4183
128.5054
127.5824
127.5373
127.5127
127.3000
126.4574
82.7165
77.4233
76.9996
76.5755
67.2281
62.8378
60.7646
60.2609
44.0713
13.3206
13.0539
S
Me
OEt
O
HN
N
O
R
N
Bn
10g: R = 6-Cl
f1 (ppm)



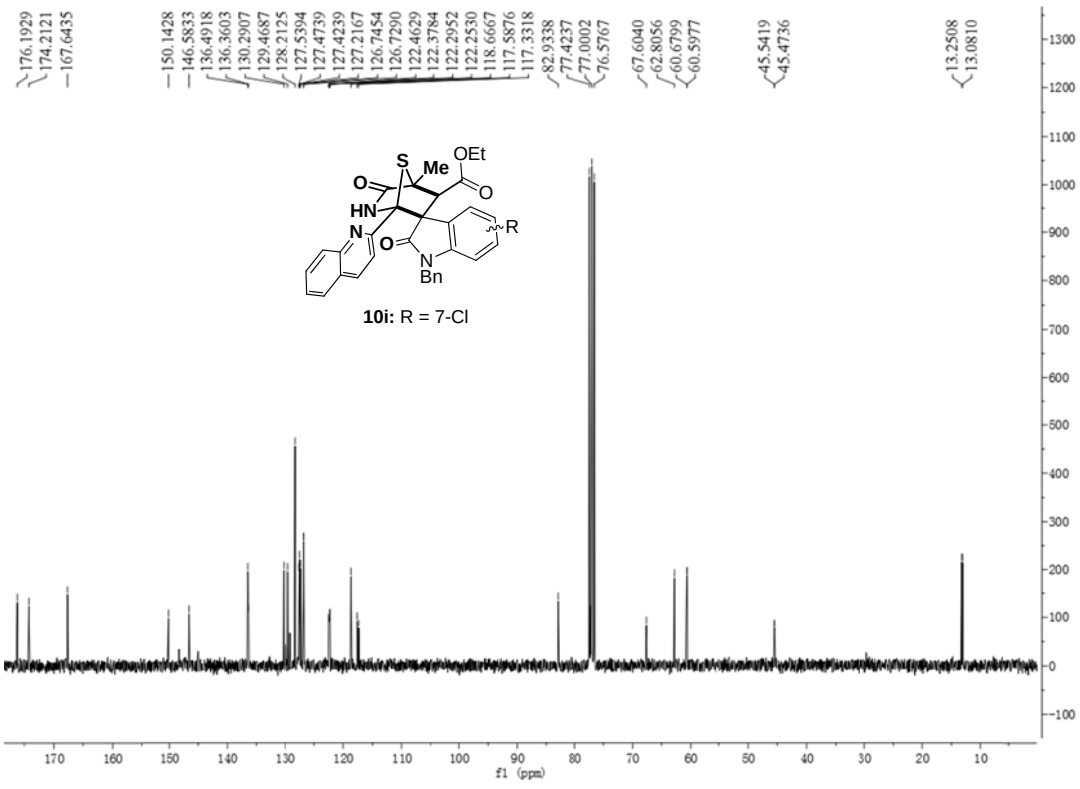
10h: R = 6-OMe



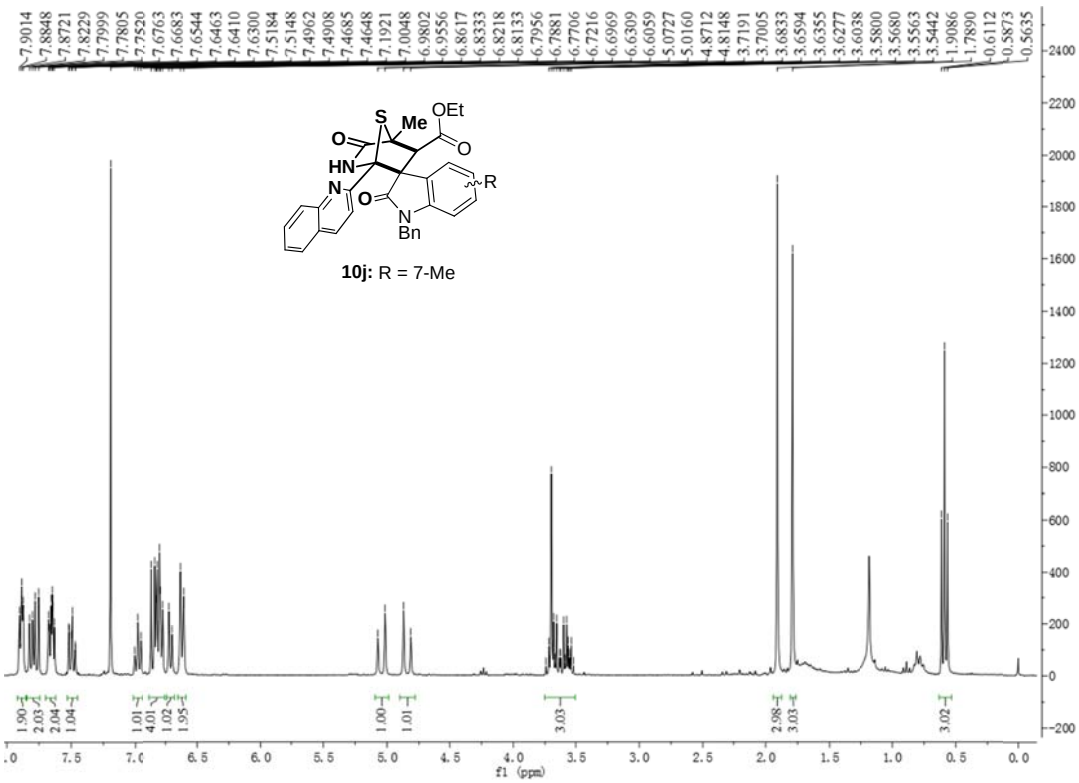
10h: R = 6-OMe



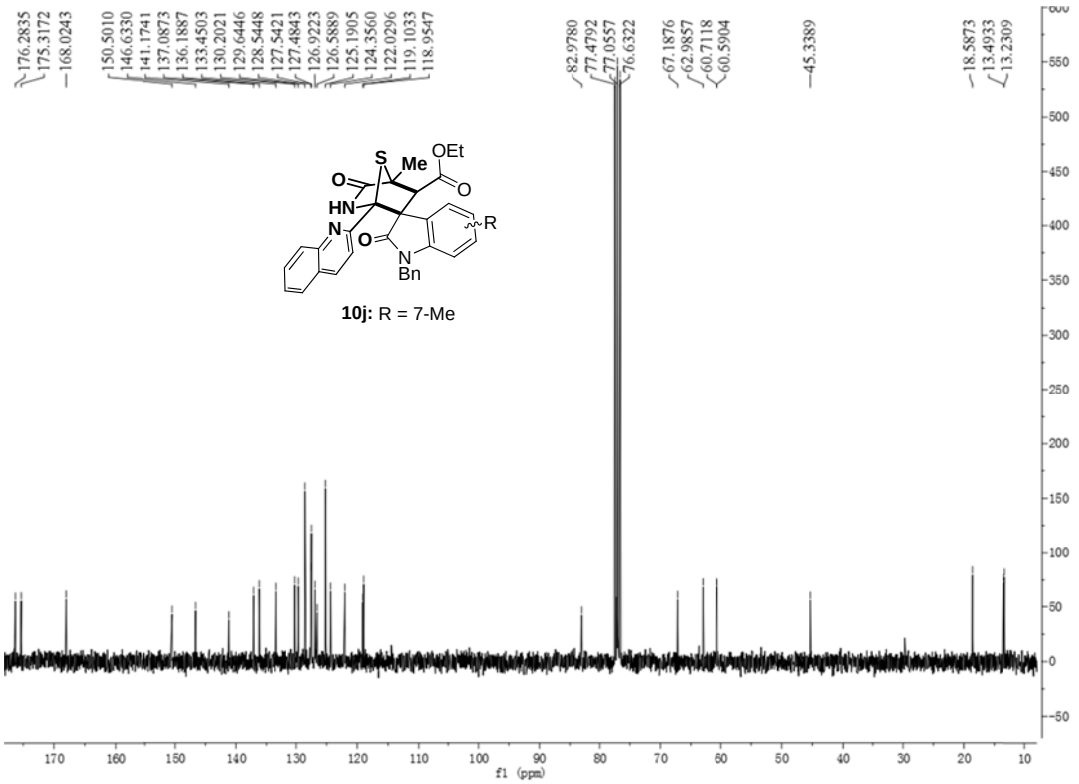
10i: R = 7-Cl



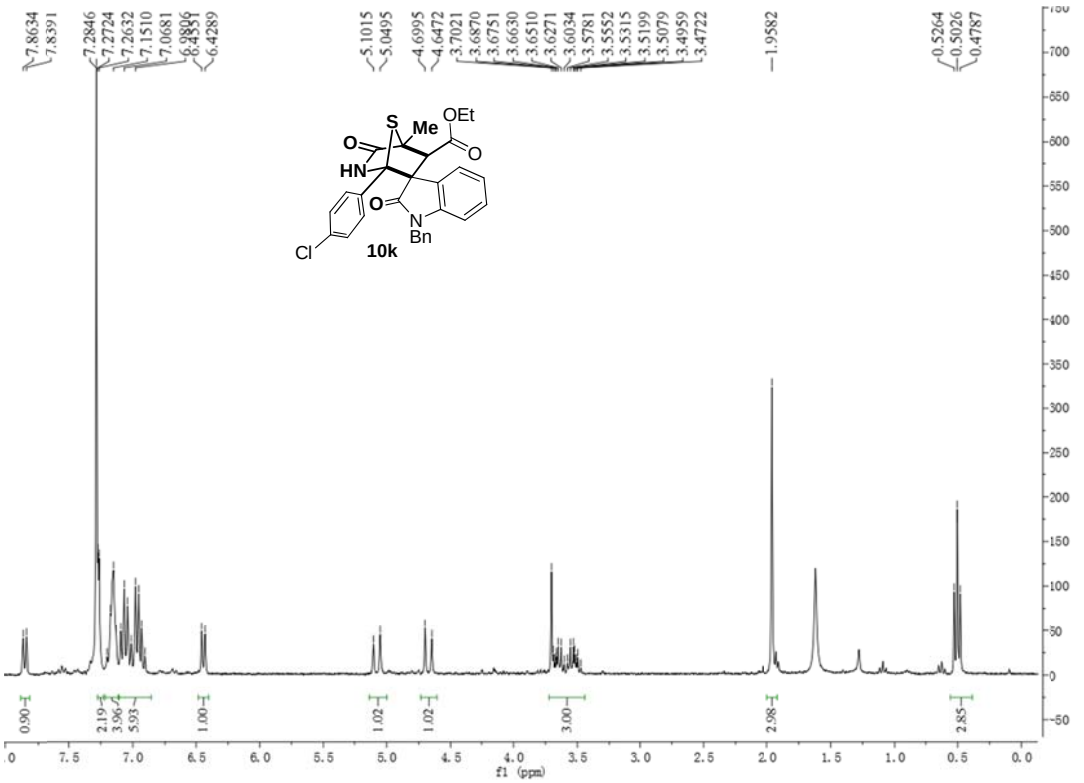
10i: R = 7-Cl

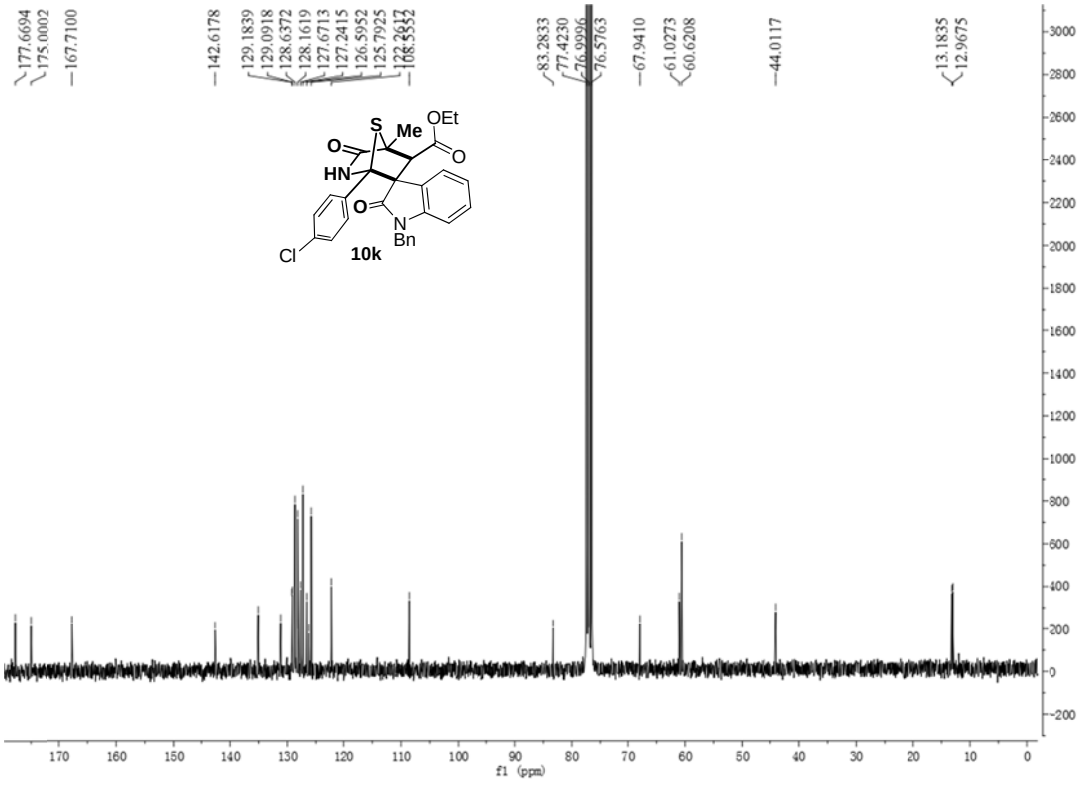


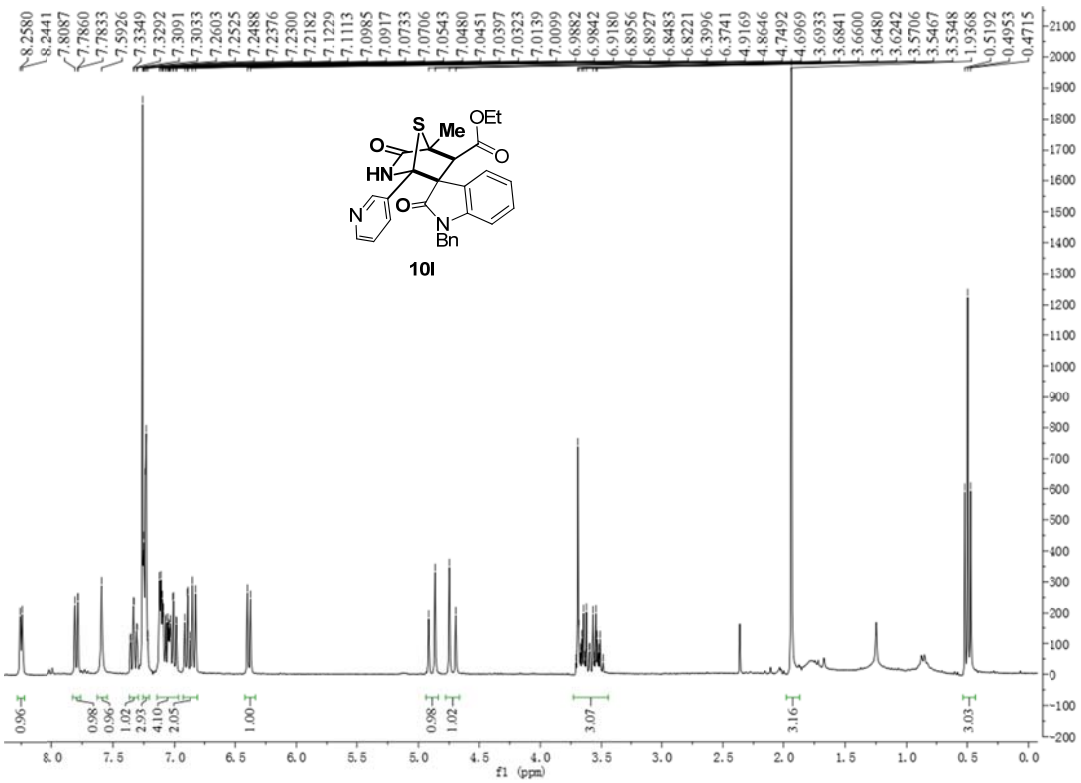
10j: R = 7-Me

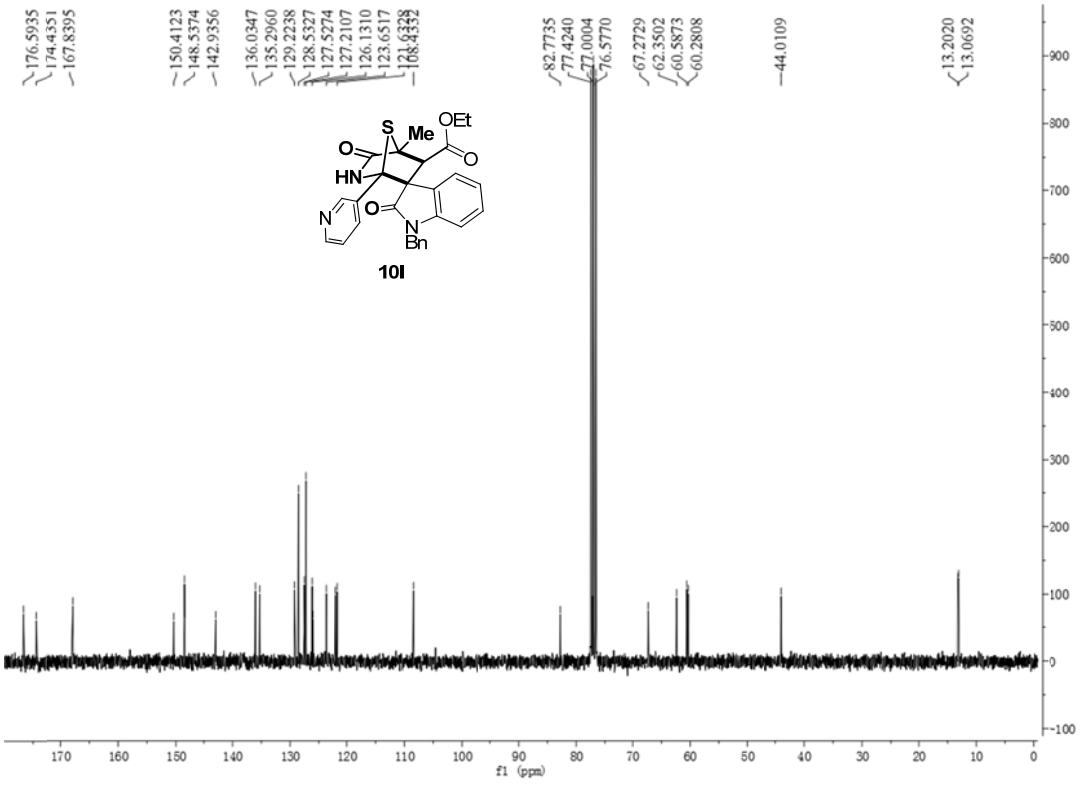


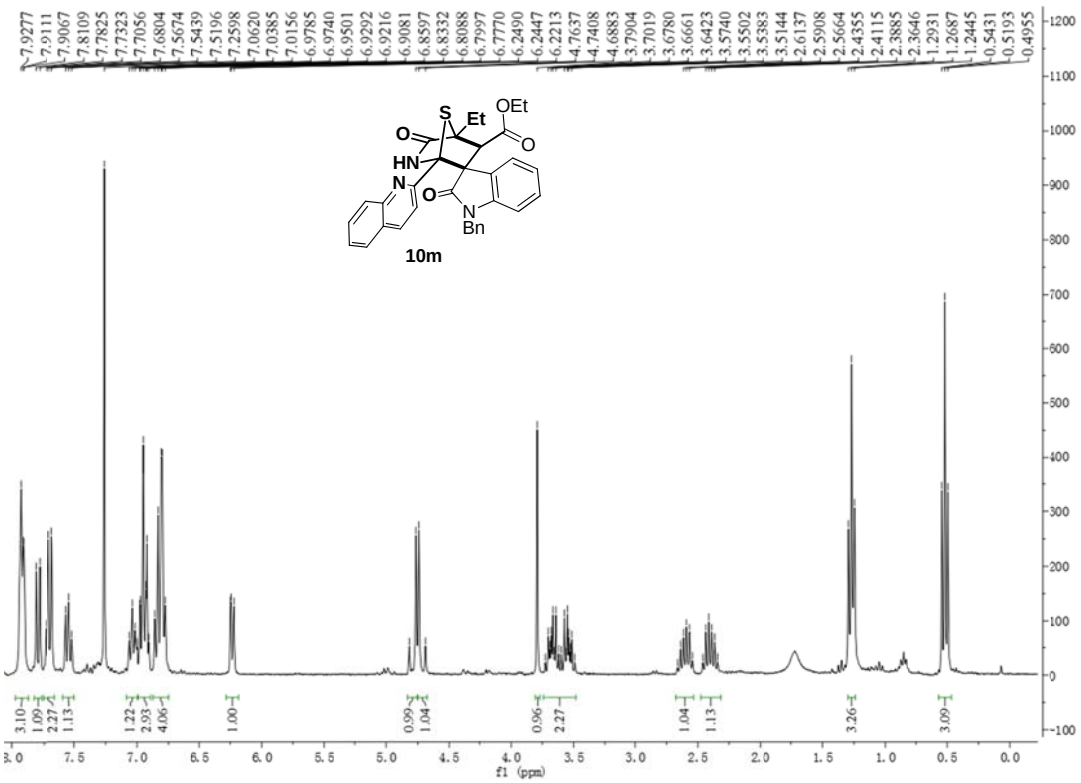
10j: R = 7-Me

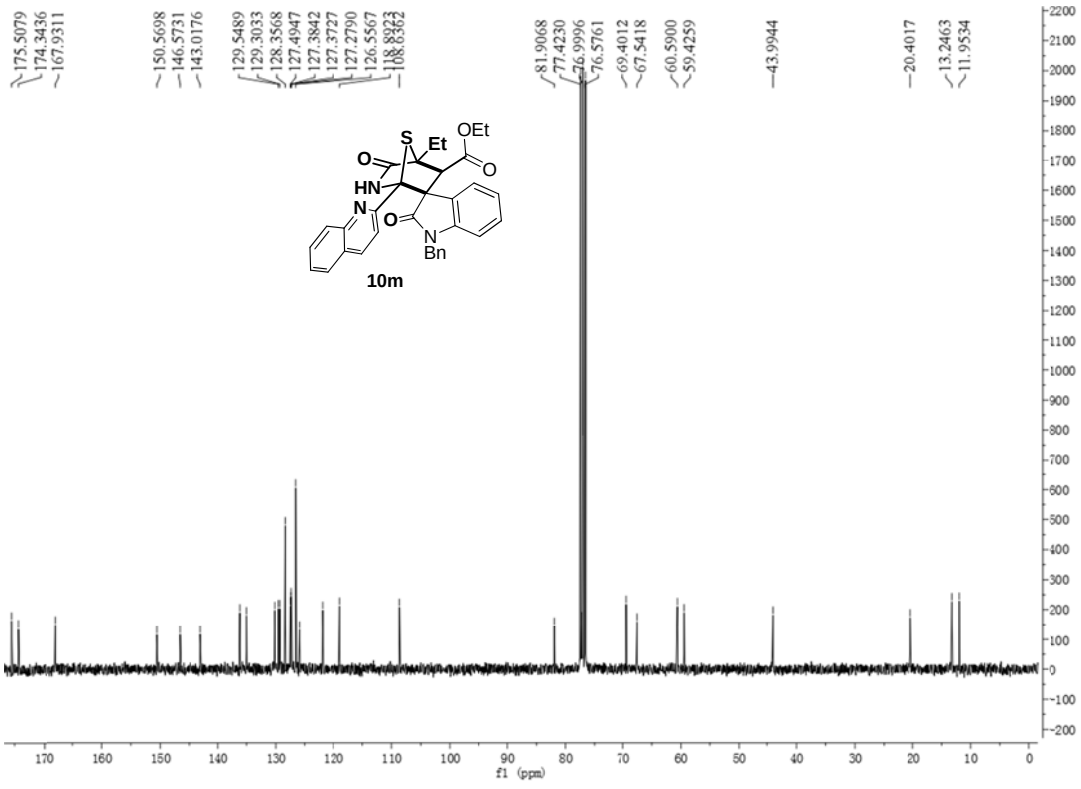

7.8634
7.8391
7.2846
7.2724
7.2632
7.1510
7.0681
6.4551
6.4289
5.1015
5.0495
4.6995
4.6472
3.7021
3.6870
3.6751
3.6630
3.6510
3.6271
3.6034
3.5781
3.5552
3.5315
3.5199
3.5079
3.4959
3.4722
1.9582
0.5264
0.5026
0.4787
S
Me
OEt
O
HN
O
N
Bn
Cl
10k
f1 (ppm)

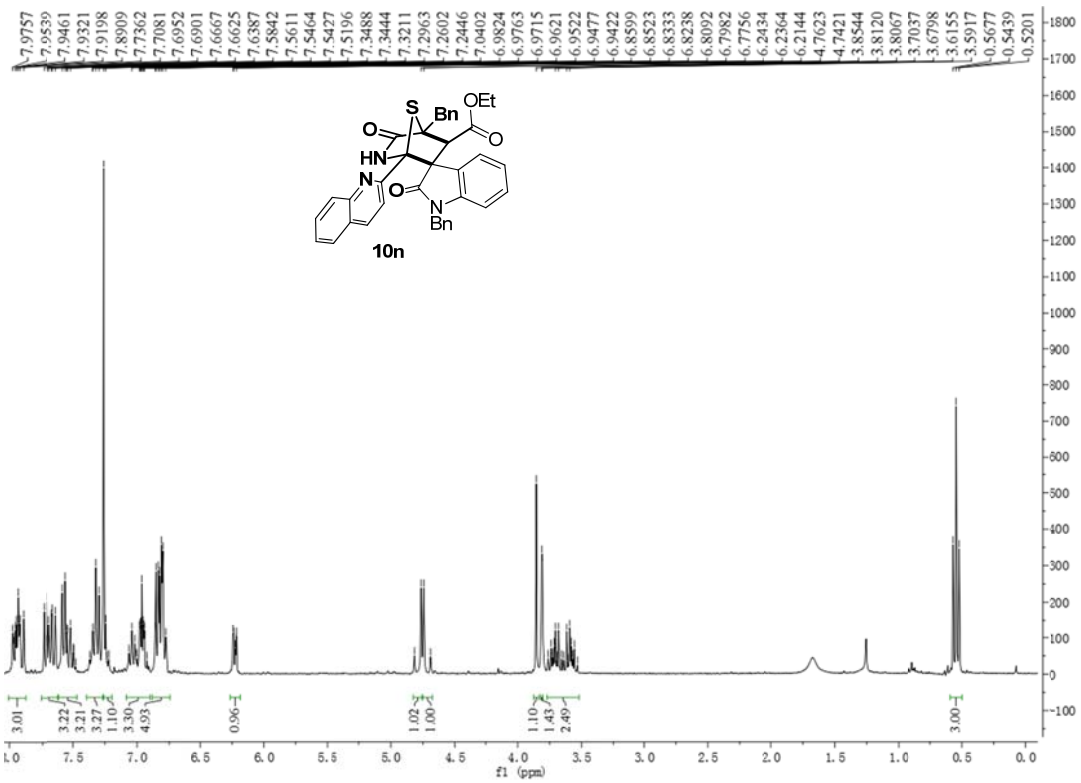

177.6694
175.0002
167.7100
142.6178
129.1839
129.0918
128.6372
128.1619
127.6713
127.2415
126.5952
125.7925
83.2833
77.4230
76.9996
76.5763
67.9410
61.0273
60.6208
44.0117
13.1835
12.9675
S
Me
OEt
O
HN
O
N
Bn
Cl
10k
f1 (ppm)

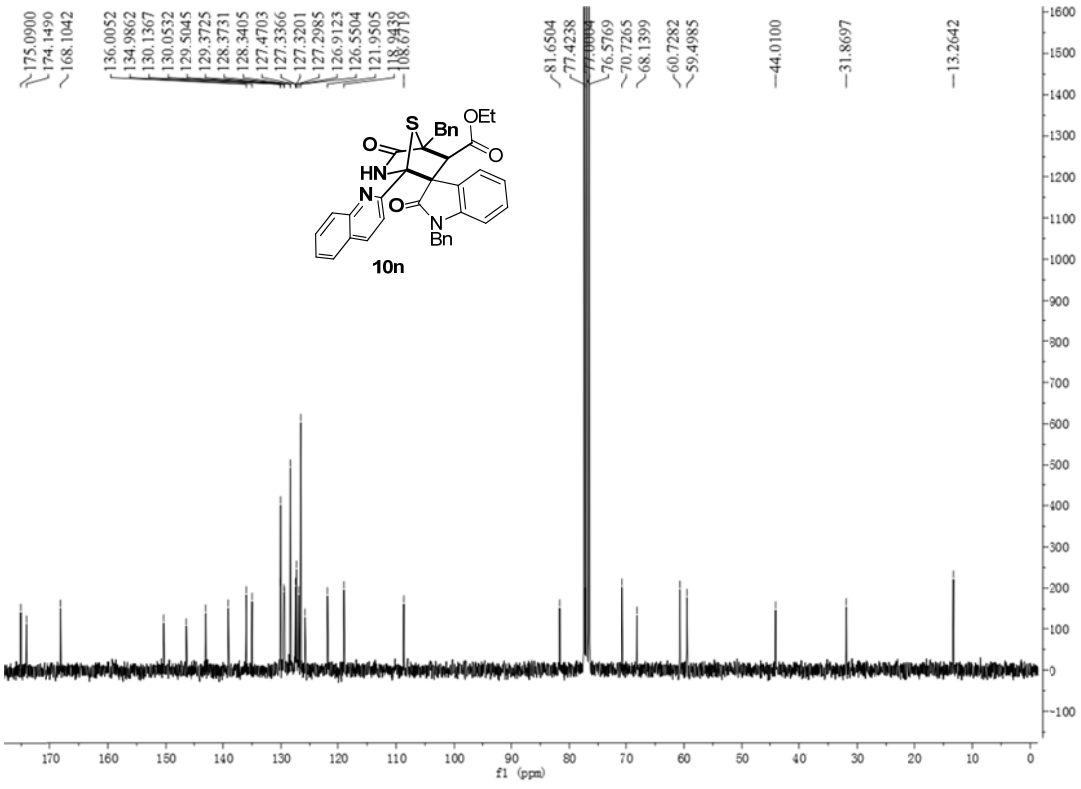

8.2580
8.2441
7.8087
7.7860
7.7833
7.5926
7.3349
7.3292
7.3091
7.3033
7.2603
7.2525
7.2488
7.2376
7.2300
7.2182
7.1229
7.1113
7.0985
7.0917
7.0733
7.0706
7.0543
7.0480
7.0451
7.0397
7.0323
7.0139
7.0099
6.9882
6.9842
6.9180
6.8956
6.8927
6.8483
6.8221
6.3996
6.3741
4.9169
4.8646
4.7492
4.6969
3.6933
3.6841
3.6600
3.6480
3.6242
3.5706
3.5467
3.5348
1.9368
0.5192
0.4953
0.4715
S
Me
OEt
O
HN
O
N
O
N
Bn
10l
0.96
0.98
0.96
1.02
2.93
4.10
2.05
1.00
0.98
1.02
3.07
3.16
3.03
f1 (ppm)

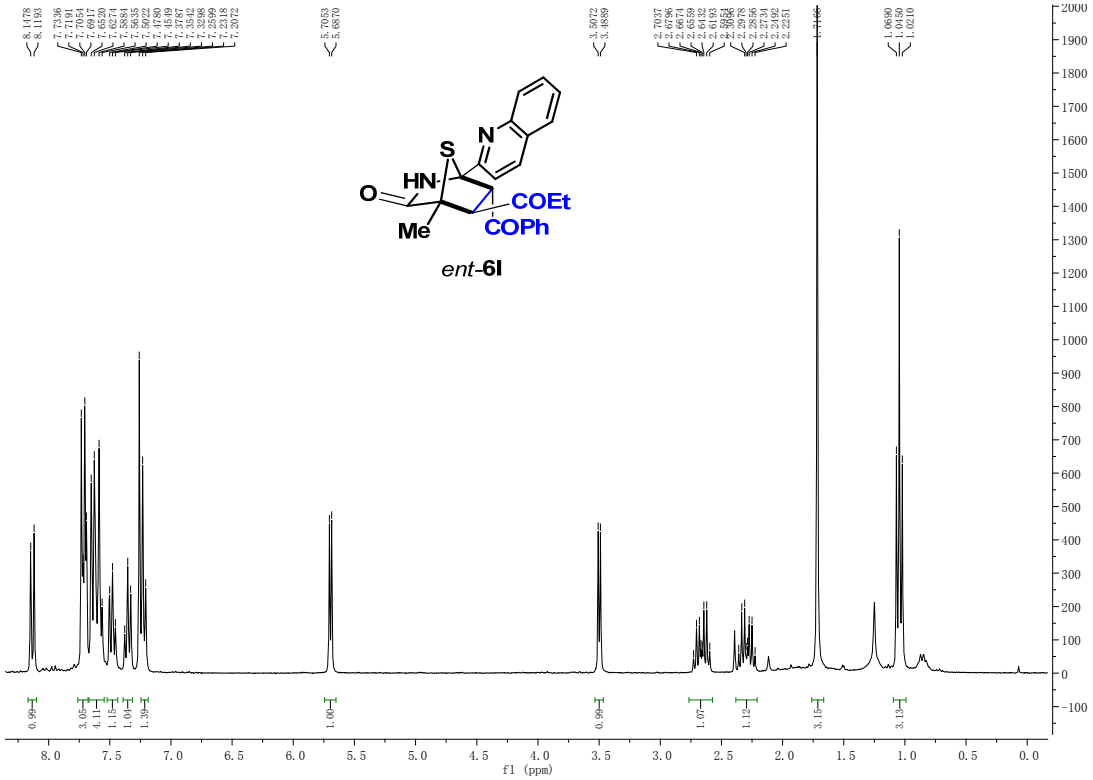

176.5935
174.4351
167.8395
150.4123
148.5374
142.9356
136.0347
135.2960
129.2238
128.5327
127.5274
127.2107
126.1310
123.6517
121.6328
108.4332
82.7735
77.4240
77.0004
76.5770
67.2729
62.3502
60.5873
60.2808
44.0109
13.2020
13.0692
S
Me
OEt
O
HN
O
N
O
N
Bn
10l
f1 (ppm)


10m
f1 (ppm)

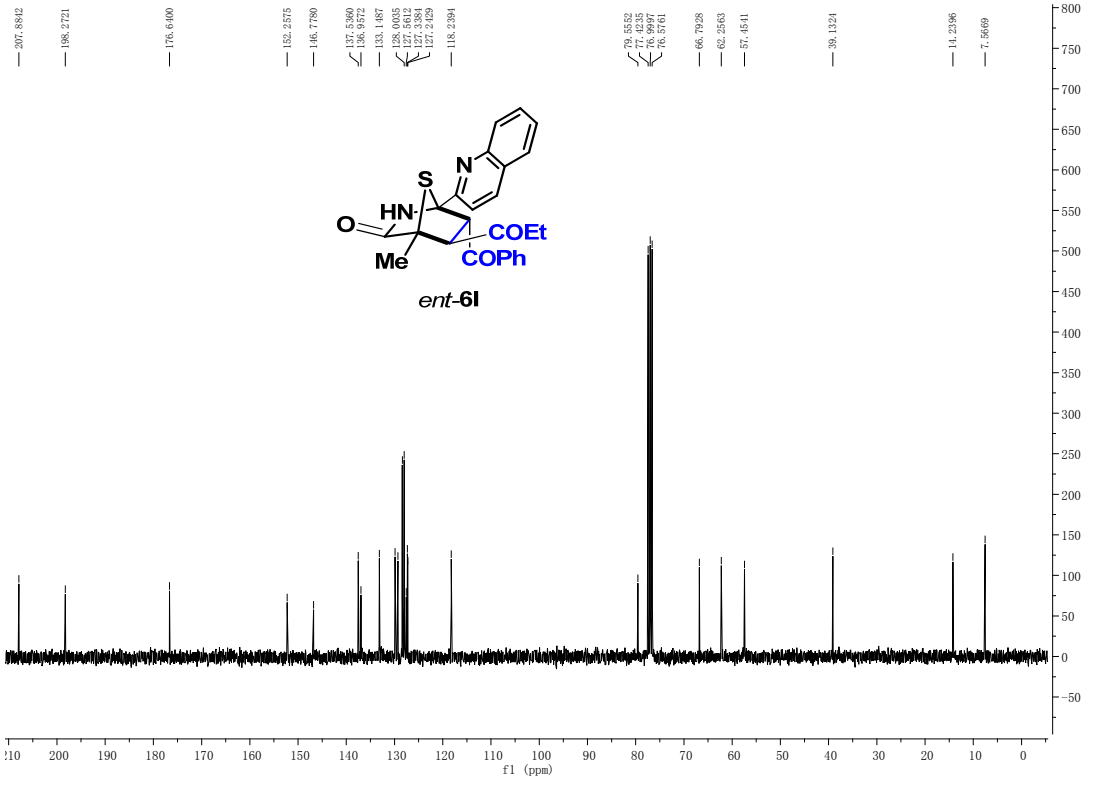

10m
f1 (ppm)


10n

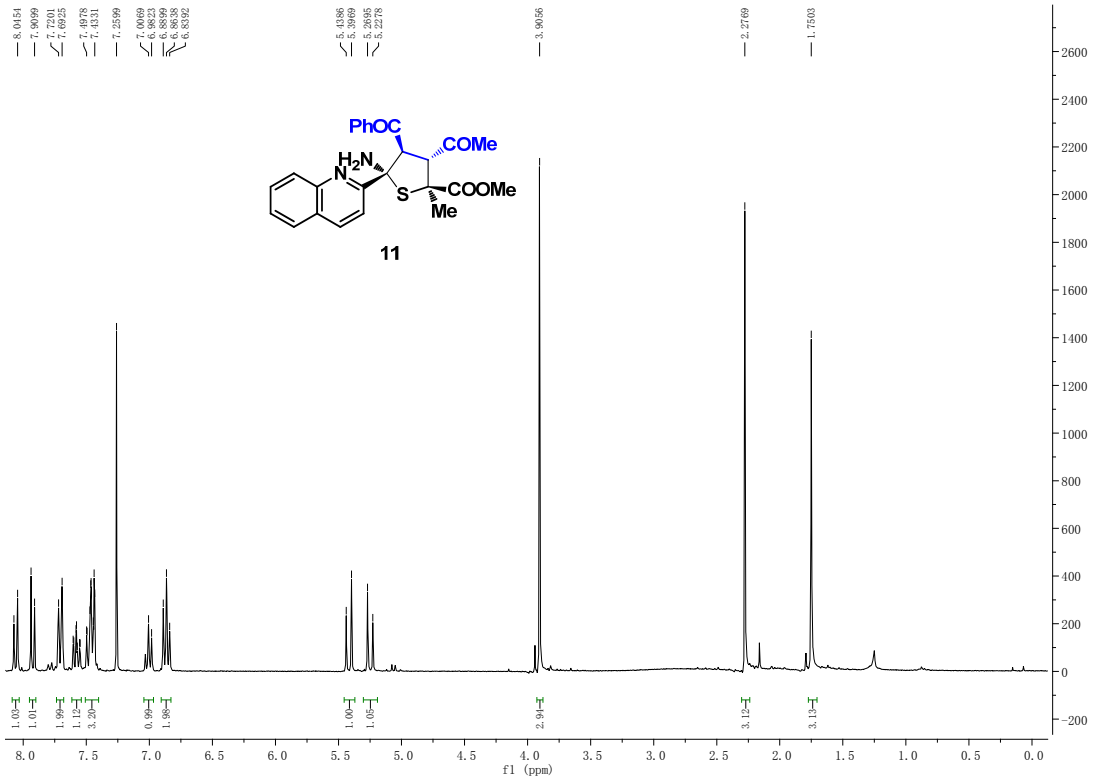

10n

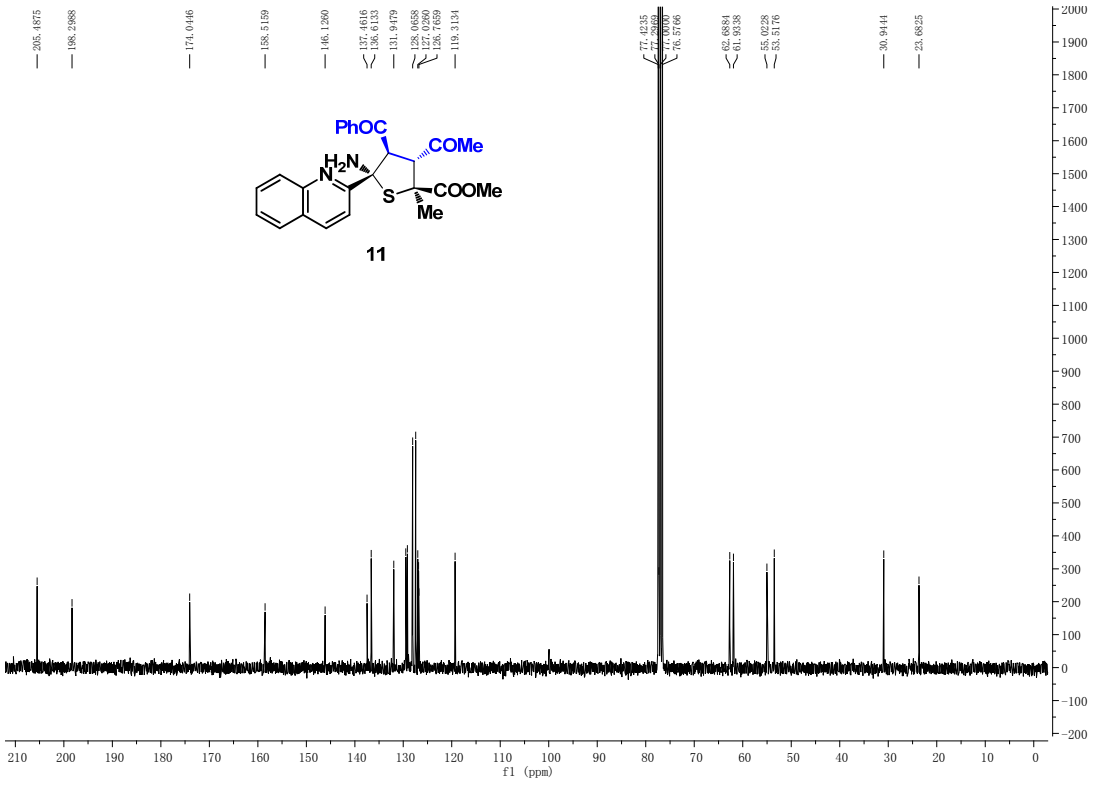


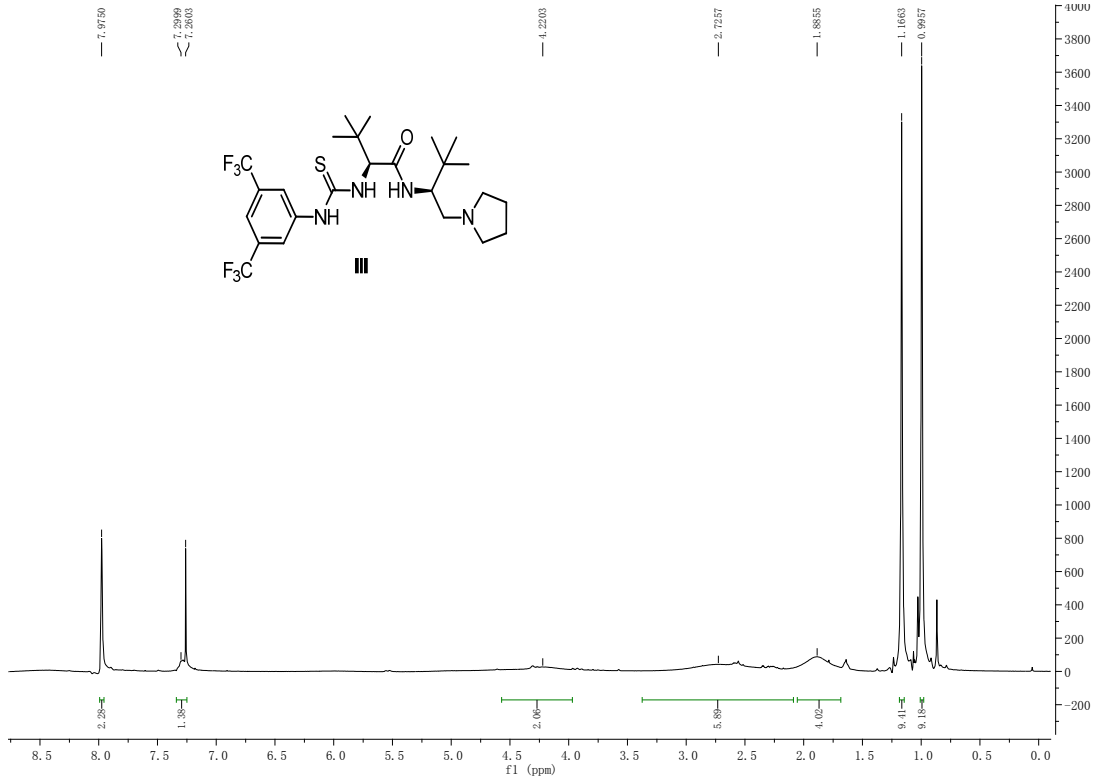
ent-**6l**

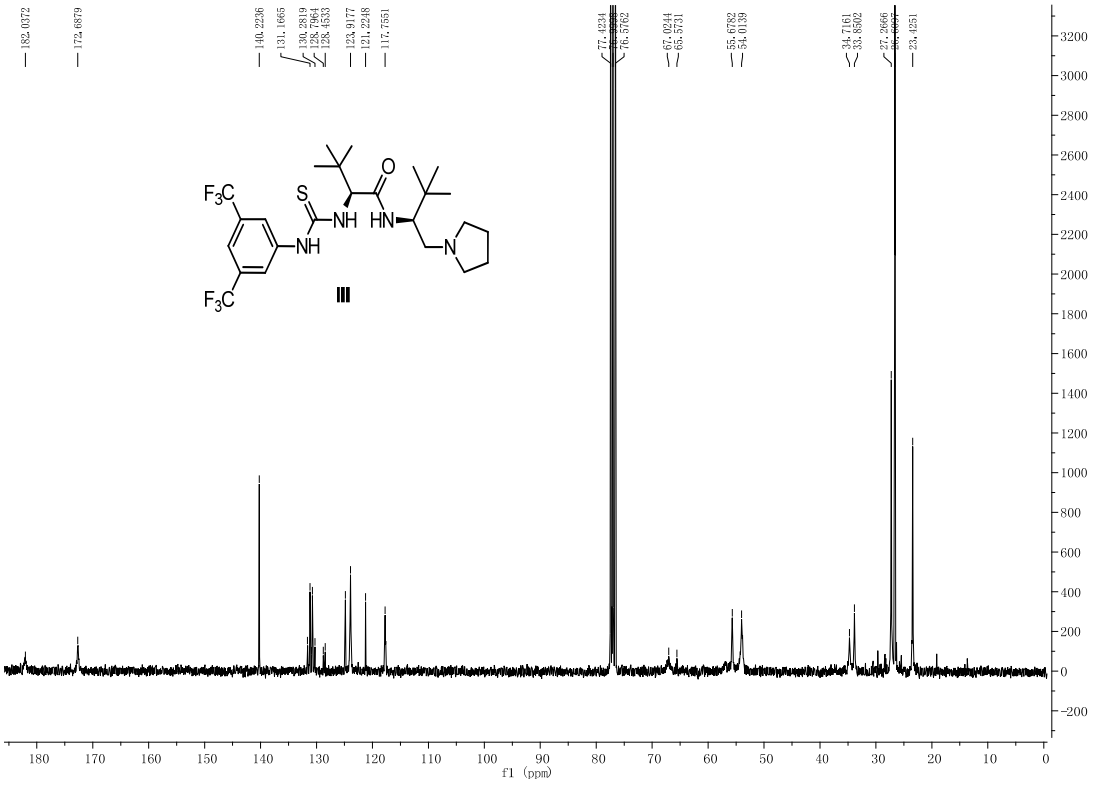


ent-**6l**


8.0454
7.9099
7.7201
7.6925
7.4978
7.4331
7.2599
7.0069
6.9853
6.8899
6.8638
6.8392
5.4386
5.3969
5.2695
5.2278
3.9056
2.2769
1.7503
PhOC
COMe
H2N
N
S
COOMe
Me
11
1.03
1.01
1.99
1.12
3.20
0.99
1.98
1.00
1.05
2.94
3.12
3.13
f1 (ppm)


205.4875
198.2988
174.0446
158.5159
146.1260
137.4616
136.6133
131.9479
128.0658
127.0260
126.7659
119.3134
77.4235
76.5766
62.6884
61.9338
55.0228
53.5176
30.9444
23.6825
PhOC
COMe
H2N
N
S
COOMe
Me
11
f1 (ppm)


7.9750
7.2999
7.2603
4.2203
2.7257
1.8855
1.1663
0.9957
F3C
S
NH
HN
O
N
F3C
III
2.29
1.39
2.06
5.69
4.02
9.41
9.18
f1 (ppm)


182.0372
172.6879
140.2236
131.1665
130.2819
128.7964
128.4533
123.9177
121.2248
117.7551
77.4234
76.5762
67.0244
65.5731
55.6782
54.0109
34.7161
33.8502
27.2666
23.4251
F3C
S
NH
HN
O
N
F3C
III
f1 (ppm)