Chiral Phosphoric Acid-Catalyzed Enantioselective Synthesis of Biphenyl-Bridged *ε*-Sultams via Friedel-Crafts Reactions of Cyclic N-Sulfonylimines with Indolizines

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Supporting Information

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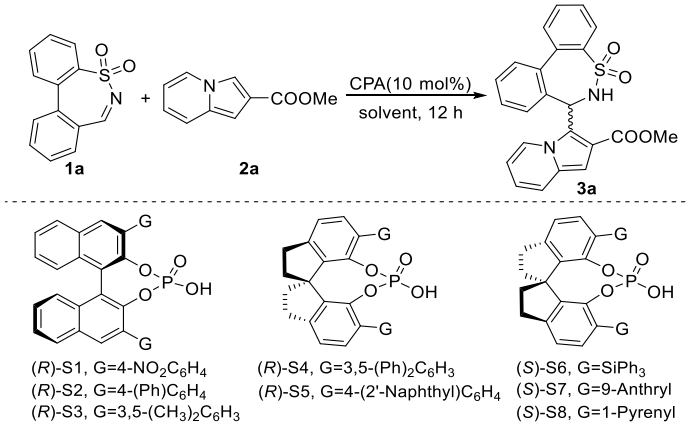
1. General information

The products were purified by column chromatography on silica gel (200-300 mesh). For thin-layer chromatography (TLC) analysis, silica gel plates (HSGF254) were used. Visualization of the developed TLC plates was performed with ultraviolet irradiation 254 nm. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on Bruker DRX-300 or Bruker DRX-400 spectrometers. Chemical shifts (δ) are quoted in ppm relative to TMS (^{1}H). Coupling constants (J) are quoted in Hz. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, m: multiplet, dd: doublet of doublets, qt: quadruplet of triplets, tt: triplet of triplets, tq: triplet of quadruplets, tqt: triplet of quadruplet of triplets. The residual solvent signals were used as references ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). The *ee* values determination was carried out using chiral HPLC with Daicle Chiralpak INA-H, INC-H and ND-H column on Agilent 1200 LC instrument. The solvents were distilled from appropriate drying agents prior to use, unless otherwise noted.

Seven-membered cyclic N-sulfonylimines (**1**)[1], 2-indolizine esters (**2**)[2] and six-membered cyclic N-sulfonylimine (**5**)[3] were prepared according to the literature. The CPAs were purchased from Daicel Chiral technologies (China)CO., LTD and direct used without additional process. The racemic products were prepared by running reactions with a racemic catalyst.

2. More results on the condition optimization

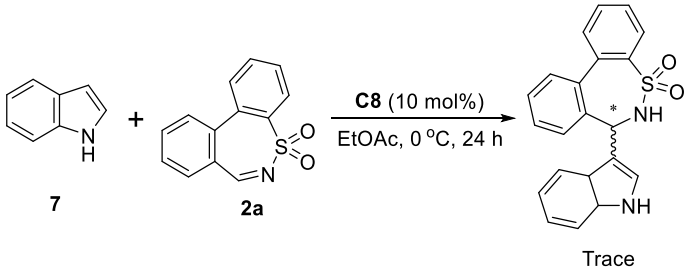
Table S1. Screening for more chiral CPA catalysts and solvents[a,b,c]



Entry	Catalyst	Solvent	Yield(%)[b]	*ee*(%)[c]
1	**S1**	toluene	trace	-
2	**S2**	toluene	8	0
3	**S3**	toluene	trace	-
4	**S4**	toluene	86	80
5	**S5**	toluene	87	71
6	**S6**	toluene	trace	-
7	**S7**	toluene	90	4
8	**S8**	toluene	89	91
9	**C8**	CH_2Cl_2	57	91
10	**C8**	DMF	NR	-
11	**C8**	$PhCF_3$	95	93
12	**C8**	*m*-xylene	96	94
13	**C8**	*p*-xylene	93	94

[a]Unless otherwise noted, reaction was performed with **1a** (0.05 mmol), **2a** (0.06 mmol), catalyst (10 mol%) in solvent (1.0 mL) at r.t. for 12 h. [b]Isolated yields. [c]Determined by HPLC analysis using a chiral column, and the minus *ee* value indicates that the opposite enantiomer was obtained as the major form.

3. Control Experiment.



Scheme S2 The control experiment.

Indole **7** (0.06 mmol, 1.2 equiv.), **C8** (2.8 mg, 0.005 mmol, 10 mol%) and EtOAc (1.0 mL) were added in an oven-dried 5 mL round-bottomed flask. It was allowed to stir for 10 min in air at 0 °C. Then, seven-membered cyclic N-sulfonyl mines **2a** (0.05 mmol, 1.0 equiv.) was added and it was allowed to stir at 0 °C for 24 h. At the end of the reaction, TLC monitoring of the reaction revealed that the reaction produced trace products.

4. Experimental section

Typical procedure for synthesis of **3**: Indolizine **2** (0.06 mmol, 1.2 equiv.), **C8** (2.8 mg, 0.005 mmol, 10 mol%) and EtOAc (1.0 mL) were added in an oven-dried 5 mL round-bottomed flask. It was allowed to stir for 10 min in air at 0 °C. Then, seven-membered cyclic N-sulfonylimines **1** (0.05 mmol, 1.0 equiv.) was added and the mixture was stirred at 0 °C for 12-48 h. The crude product was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 6:1) to afford the product **3**.

(*S*)-Methyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3aa**): white solid (20.1 mg, 96% yield, 99% *ee*); R_f= 0.50 (petroleum ether/ethyl acetate, 3:1); mp: 121.8–132.9 °C. $[\alpha]_D^{25}$ = +176.9 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.75 (d, J = 7.4 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.47 (s, 1H), 7.44 (d, J = 4.3 Hz, 2H), 7.25 – 7.15 (m, 1H), 6.92 (d, J = 3.6 Hz, 1H), 6.88 (d, J = 7.0 Hz, 2H), 6.68 (t, J = 6.9 Hz, 1H), 6.58 (d, J = 7.8 Hz, 1H), 5.36 (s, 1H), 3.67 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 140.3, 138.9, 137.1, 133.7, 133.4, 132.6, 130.8, 130.2, 129.6, 129.1, 128.8, 128.0, 126.4, 125.7, 121.7, 120.3, 119.3, 117.5, 112.6, 101.4, 52.7, 51.6. **HRMS** (ESI) calcd for $C_{23}H_{19}N_2O_4S^+$ *m/z* 419.1060 $[M+H]^+$, found: 419.1071. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 °C, λ = 254 nm 1.0 mL/min): t_1 = 9.38 min (major), t_2 = 13.38 min (minor).

(*S*)-Ethyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ab**): white solid (19.9 mg, 92% yield, 98% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 3:1); mp:189.4–190.6 °C. $[\alpha]_D^{25}$ = +205.7 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.74 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.54 – 7.39 (m, 3H), 7.21 (dt, J = 8.6, 4.3 Hz, 1H), 6.89 (d, J = 14.0 Hz, 3H), 6.68 (t, J = 7.0 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 5.26 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.1, 140.2, 138.9, 137.0, 133.7, 133.4, 132.6, 130.9, 130.2, 129.7, 129.1, 128.8, 128.1, 126.5, 125.8, 121.3, 120.3, 119.3, 119.0, 112.6, 101.6, 60.4, 52.7, 14.2. **HRMS** (ESI) calcd for $C_{24}H_{21}N_2O_4S^+$ *m/z* 433.1216 $[M+H]^+$, found: 433.1226. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 °C, λ = 254 nm, 1.0 mL/min): t_1 = 8.44 min (major), t_2 = 13.50 min (minor).

(*S*)-Benzyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ac**): white solid (23.0 mg, 94% yield, 96% *ee*); R_f= 0.4 (petroleum ether/ethyl acetate, 3:1); mp: 91.7–92.3 °C. $[\alpha]_D^{25}$ = +172.3 (c =1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.76 (d, J = 7.3 Hz, 1H), 8.03 (d, J = 7.7 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.57 (dd, J = 12.5, 7.6 Hz, 2H), 7.46 (d, J = 2.7 Hz, 1H), 7.44 (s, 2H), 7.32 – 7.26 (m, 3H), 7.21 (dq, J = 6.8, 3.3, 2.7 Hz, 3H), 6.95 (s, 1H), 6.90 (t, J = 3.4 Hz, 1H), 6.88 – 6.81 (m, 1H), 6.68 (t, J = 7.0 Hz, 1H), 6.60 (d, J = 7.8 Hz, 1H), 5.30 (s, 1H), 5.13 (q, J = 12.6 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 164.8, 140.3, 138.9, 137.2, 136.0, 133.6, 133.4, 132.7, 130.8, 130.3, 129.6, 129.1, 128.7, 128.6, 128.1, 128.1, 127.8, 126.5, 125.7, 121.6, 120.4, 119.3, 117.7, 112.6, 101.8, 66.0, 52.9. **HRMS** (ESI) calcd for $C_{29}H_{23}N_2O_4S^+$ *m/z* 495.1373 $[M+H]^+$, found: 495.1383. HPLC (Chiralpak INA-H column,

n-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min) t_R = 12.50 min (major), t_R = 20.73 min (minor).

(*S*)-Butyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ad**): white solid (22.3 mg, 97% yield, 99% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 3:1)；mp: 153.2–154.6 ℃. $[\alpha]_D^{25}$ = +250.1 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 6.6 Hz, 3H), 7.20 (dt, *J* = 8.6, 4.4 Hz, 1H), 6.88 (d, *J* = 11.4 Hz, 3H), 6.68 (t, *J* = 6.8 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 5.37 (s, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.51 (p, *J* = 6.8 Hz, 2H), 1.28 (q, *J* = 7.5 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 165.1, 140.2, 138.9, 137.1, 133.6, 133.4, 132.7, 130.8, 130.2, 129.6, 129.1, 128.8, 128.1, 126.5, 125.7, 121.3, 120.2, 119.3, 118.1, 112.5, 101.7, 64.3, 52.8, 30.6, 19.2, 13.8. **HRMS** (ESI) calcd for $C_{26}H_{25}N_2O_4S^+$ *m/z* 461.1529 $[M+H]^+$, found: 461.1553. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 8.00 min (major), t_2 =13.71 min (minor).

(*S*)-Tert-butyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ae**): white solid (22.0 mg, 96% yield, 80% *ee*); R_f= 0.6 (petroleum ether/ethyl acetate, 3:1); mp: 197.0–198.1℃. $[\alpha]_D^{25}$ = +148.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.68 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.61–7.53 (m, 1H), 7.44 (d, *J* = 4.7 Hz, 3H), 7.20 (dt, *J* = 8.7, 4.4 Hz, 1H), 6.93 – 6.78 (m, 3H), 6.67 (d, *J* = 6.9 Hz, 1H), 6.64 – 6.53 (m, 1H), 5.41 (s, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 164.3, 140.2, 138.9, 137.3, 133.5, 133.2, 132.6, 131.0, 130.3, 129.6, 129.1, 128.7, 128.3, 126.5, 125.7, 120.5, 120.1, 120.0, 119.1, 112.3, 102.0, 80.9, 52.8, 28.2. **HRMS** (ESI) calcd for $C_{26}H_{25}N_2O_4S^+$ *m/z* 461.1529 $[M+H]^+$, found: 461.1551. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.82 min (major), t_2 = 8.62 min (minor).

(*S*)-Cyclohexyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3af**): pale yellow solid (23.3 mg, 96% yield, 86% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 3:1); mp: 89.4–90.2 ℃. $[\alpha]_D^{25}$ = +112.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 7.1 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.24 – 7.16 (m, 1H), 6.95 – 6.81 (m, 3H), 6.67 (t, *J* = 7.1 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H), 4.79 (s, 1H), 1.59 (m, 5H), 1.28 (m, 5H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 164.5, 140.2, 138.6, 137.1, 133.6, 133.4, 132.6, 131.0, 130.2, 129.6, 129.1, 128.7, 128.2, 126.5, 125.8, 121.0, 120.2, 119.2, 118.7, 112.5, 101.7, 72.5, 52.8, 31.6, 29.7, 25.4, 23.7. **HRMS** (ESI) calcd for $C_{28}H_{27}N_2O_4S^+$ *m/z* 487.1686 $[M+H]^+$, found: 487.1664. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 8.10 min (major), t_2 = 13.14 min (minor).

(*S*)-2-methoxyethyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ag**): brown solid (22.0 mg, 95% yield, 98% *ee*); R_f= 0.4 (petroleum ether/ethyl acetate, 3:1); mp: 119.7–120.2 ℃. $[\alpha]_D^{25}$ = +199.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 7.3 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 3H), 7.19 (dt, *J* = 8.5, 4.4 Hz, 1H), 6.93 (d, *J* = 4.6 Hz, 2H), 6.86 (t, *J* = 8.4 Hz, 1H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.49 (s, 1H), 4.34 – 4.11 (m, 2H), 3.60 – 3.44 (m, 2H), 3.27 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 165.0, 140.3, 138.9, 137.2, 133.6, 133.3, 132.7, 130.9, 130.3, 129.6, 129.1, 128.8, 128.1, 126.4, 125.7,

121.7, 120.3, 119.3, 117.5, 112.6, 101.8, 70.4, 63.4, 59.0, 52.7. **HRMS** (ESI) calcd for $C_{25}H_{23}N_2O_5S^+$ *m/z* 463.1322 $[M+H]^+$, found: 463.1334. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 10.08 min (major), t_2 = 16.12 min (minor).

(*S*)-Methyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)-8-fluoroindolizine-2-carboxylate (**3ah**): pale yellow solid (21.6 mg, 99% yield, 90% *ee*); R_f= 0.4 (petroleum ether/ethyl acetate, 4:1); mp: 124.7–125.4 ℃. $[\alpha]_D^{25}$ = +124.2 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 6.9 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 4.5 Hz, 2H), 7.31-7.21 (m, 1H), 7.07 (s, 1H), 6.93 (s, 1H), 6.58 (dt, *J* = 23.0, 6.4 Hz, 3H), 5.30 (s, 1H), 3.71 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.1, 154.7 (d, $^1J_{C\text{-}F}$ = 249.0 Hz), 140.3, 138.8, 137.0, 133.8, 132.3, 130.8, 130.3, 129.8, 129.0(d, $^2J_{C\text{-}F}$ = 20.3 Hz), 127.9, 126.4, 125.9, 125.8, 123.8, 123.0, 117.7, 111.8(d, $^3J_{C\text{-}F}$ = 6.8 Hz), 101.5 (d, $^3J_{C\text{-}F}$ = 16.5 Hz), 99.2, 52.6, 51.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.41. **HRMS** (ESI) calcd for $C_{23}H_{18}FN_2O_4S^+$ *m/z* 436.0965 $[M+H]^+$, found: 437.0983. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.93 min (major), t_2 = 10.44 min (minor).

(*S*)-Methyl-7-chloro-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ai**): pale yellow solid (21.5 mg, 95% yield, 94% *ee*); R_f = 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 114.5–115.3 ℃. $[\alpha]_D^{25}$ = +60.4 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.70 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.1 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.54 – 7.36 (m, 3H), 7.25 – 7.17 (m, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.83 (s, 1H), 6.65 (d, *J* = 5.4 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 5.28 (s, 1H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.1, 140.3, 138.8, 137.0, 133.8, 133.1, 132.3, 130.8, 130.4, 129.8, 129.1, 128.8, 127.8, 127.2, 126.0, 125.8, 122.4, 118.6, 118.5, 114.2, 101.3, 52.6, 51.7. **HRMS** (ESI) calcd for $C_{23}H_{17}ClN_2O_4SNa^+$ *m/z* 475.0489 $[M+Na]^+$, found: 475.0507(^{35}Cl), 477.0472(^{37}Cl). HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 7.98 min (major), t_2 = 9.20 min (minor).

(*S*)-Methyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)-6-fluoroindolizine-2-carboxylate (**3aj**): pale yellow solid (21.5 mg, 99% yield, 95% *ee*); R_f= 0.4 (petroleum ether/ethyl acetate, 4:1); mp: 157.6–158.6 ℃. $[\alpha]_D^{25}$ = +175.40 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.4 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.46 (q, *J* = 5.2 Hz, 3H), 7.26-7.18 (m, 1H), 6.95 (s, 1H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 5.29 (s, 1H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.1, 153.1 (d, $^1J_{C\text{-}F}$ = 237.0 Hz,), 140.3, 138.9, 137.1, 133.8, 132.2, 131.2, 130.8, 130.3, 129.8, 129.2, 128.8, 127.8, 125.8, 123.1, 121.1 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 118.3, 113.0, 112.6 (d, $^2J_{C\text{-}F}$ = 26.25 Hz), 103.0, 52.7, 51.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -136.72. **HRMS** (ESI) calcd for $C_{23}H_{17}FN_2O_4SK^+$ *m/z* 475.0524 $[M+K]^+$, found: 475.0516. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.62 min (major), t_2 = 8.01 min (minor).

(*S*)-Methyl-6-chloro-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ak**): pale yellow solid (22.4 mg, 99% yield, 94% *ee*); R_f= 0.4 (petroleum ether/ethyl acetate, 4:1); mp: 142.8–143.6 ℃. $[\alpha]_D^{25}$ = +153.6 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.50 – 7.39 (m, 3H), 7.21 (s, 1H), 6.97 – 6.86 (m, 1H), 6.82 (s, 1H),

6.65 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 3.69 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) δ 165.2, 140.3, 138.8, 137.0, 133.8, 133.1, 132.3, 130.8, 130.4, 129.8, 129.2, 128.9, 127.8, 127.2, 126.0, 125.8, 122.4, 118.6, 118.4, 114.2, 101.3, 52.6, 51.7. **HRMS** (ESI) calcd for $C_{23}H_{17}ClN_2O_4SNa^+$ *m/z* 475.0489 $[M+Na]^+$, found: 475.0487(^{35}Cl), 477.0476(^{37}Cl). HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 9.49 min (major), t_2 = 14.61 min (minor).

(*S*)-Methyl-6-bromo-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3al**): pale yellow solid (24.6 mg, 99% yield, 90% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 169.5–170.9 ℃. **$[\alpha]_D^{25}$** = +161.6 (c = 1.0, $CHCl_3$). **^1H NMR** (300 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.37 (d, *J* = 9.5 Hz, 1H), 6.94 (d, *J* = 9.6 Hz, 2H), 6.88 (d, *J* = 3.5 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.27 (s, 1H), 3.69 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) δ 165.1, 140.5, 138.9, 137.0, 133.8, 132.4, 131.6, 130.8, 130.3, 129.8, 129.3, 128.8, 127.7, 125.9, 125.8, 123.1, 122.3, 120.9, 118.0, 108.1, 103.0, 52.7, 51.7. **HRMS** (ESI) calcd for $C_{23}H_{18}BrN_2O_4S^+$ *m/z* 497.0165 $[M+H]^+$, found: 497.0186(^{79}Br), 499.0176(^{81}Br). HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): $t_{R'}$ = 6.83 min (major), t_1 = 10.37 min (minor).

(*S*)-Methyl-3-(5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)-6-methylindolizine-2-carboxylate (**3am**): pale yellow solid (21.4 mg, 99% yield, 95% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 173.3–174.6 ℃. **$[\alpha]_D^{25}$** = +175.40 (c =0.5, $CHCl_3$). **^1H NMR** (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 4.1 Hz, 2H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.25-7.20 (m, 1H), 6.90 (d, *J* = 3.4 Hz, 1H), 6.84 (s, 1H), 6.74 (d, *J* = 9.2 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 5.28 (s, 1H), 3.68 (s, 3H), 2.27 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) δ 165.6, 140.3, 139.0, 137.2, 133.7, 132.8, 132.3, 130.8, 130.1, 129.6, 129.1, 128.7, 128.1, 125.6, 123.5, 122.8, 122.2, 121.2, 119.7, 117.1, 101.3, 52.7, 51.5, 19.1. **HRMS** (ESI) calcd for $C_{24}H_{21}N_2O_4S^+$ *m/z* 433.1216 $[M+H]^+$, found: 433.1234. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_R = 6.30 min (major), t_R = 10.63 min (minor).

(*S*)-Methyl-3-(9-fluoro-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ba**): pale yellow solid (20.5 mg, 94% yield, 98% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 156.2–157.8 ℃. **$[\alpha]_D^{25}$** = + 177.6 (c = 0.5, $CHCl_3$). **^1H NMR** (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 7.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 18.3, 7.5 Hz, 2H), 7.47 (d, *J* = 9.3 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.89 (q, *J* = 7.2, 6.1 Hz, 3H), 6.72 (t, *J* = 7.1 Hz, 1H), 6.29 (d, *J* = 9.5 Hz, 1H), 5.30 (s, 1H), 3.70 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) δ 165.5, 163.0 (d, $^1J_{C\text{-}F}$ = 247.5 Hz), 138.0, 137.0, 136.3, 135.2, 133.8, 133.6, 131.9 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 130.7, 128.9, 126.1, 125.9, 120.8, 120.5, 119.5, 117.7, 116.5 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 113.0, 101.6, 52.4, 51.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.94. **HRMS** (ESI) calcd for $C_{23}H_{17}FN_2O_4SNa^+$ *m/z* 459.0785 $[M+H]^+$, found: 459.0776. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 8.43 min (major), t_2 = 11.36 min (minor).

(*S*)-Methyl-3-(9-chloro-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ca**): white solid (22.3 mg, 99% yield, 98% *ee*); R_f= 0.4 (petroleum ether/ethyl acetate, 4:1); mp: 157.9–159.6 ℃. **$[\alpha]_D^{25}$** = +208.8 (c = 0.5, $CHCl_3$). **^1H NMR** (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.0 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.1 Hz, 1H), 7.71 – 7.56 (m, 2H), 7.48 (d,

J = 9.4 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 6.3 Hz, 3H), 6.73 (t, *J* = 7.1 Hz, 1H), 6.53 (s, 1H), 5.29 (s, 1H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 138.8, 137.8, 137.0, 135.2, 134.6, 133.8, 133.6, 131.4, 130.6, 129.8, 129.1, 128.3, 126.0, 125.9, 120.6, 120.5, 119.6, 117.8, 113.0, 101.7, 52.4, 51.6 **HRMS** (ESI) calcd for $C_{23}H_{17}ClN_2O_4SNa^+$ *m/z* 475.0489 $[M+Na]^+$, found: 475.0502(^{35}Cl), 477.0486(^{37}Cl). HPLC (Chiralpak ND-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 =10.81 min (major), t_2 = 14.85 min (minor).

(*S*)-Methyl-3-(9-methoxy-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3da**): white solid (22.8 mg, 99% yield, 99% *ee*); R_f = 0.4 (petroleum ether/ethyl acetate, 4:1); mp: 103.0–104.7 ℃. **$[\alpha]_D^{25}$** = +203.6 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.69 (m, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.02 – 6.80 (m, 4H), 6.70 (d, *J* = 6.5 Hz, 1H), 6.14 (d, *J* = 3.1 Hz, 1H), 5.30 (s, 1H), 3.69 (s, 3H), 3.60 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 160.0, 138.8, 136.9, 134.1, 133.7, 133.4, 132.5, 131.5, 130.6, 128.2, 126.4, 125.8, 121.6, 120.3, 119.4, 117.6, 115.4, 113.5, 112.6, 101.5, 55.2, 52.7, 51.5. **HRMS** (ESI) calcd for $C_{24}H_{21}N_2O_5S^+$ *m/z* 449.1165 $[M+H]^+$, found: 449.1173. HPLC (Chiralpak ND-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 230 nm, 1.0 mL/min): t_1 = 8.53 min (major), t_2 = 17.00 min (minor). To determine the absolute configuration of **3da** (99% *ee*), it (20.0 mg) was first dissolved in dichloromethane (1.0 mL) and filtered with a microporous membrane before being added to a 5.0 mL vial. Then, *n*-hexane (2.5 mL) was slowly added dropwise in the solution of **3da**. It was slowly volatilized at room temperature, a single crystal of **3da** was obtained after 3-4 days.

(*S*)-Methyl-3-(9-(benzyloxy)-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ea**): white solid (26.0 mg, 99% yield, 99% *ee*); R_f = 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 117.1–118.6 ℃. **$[\alpha]_D^{25}$** = +105.4 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 9.5 Hz, 3H), 7.21 – 7.12 (m, 2H), 7.01 (d, *J* = 5.7 Hz, 1H), 6.93 – 6.76 (m, 3H), 6.66 (t, *J* = 6.9 Hz, 1H), 6.21 (s, 1H), 5.26 (s, 1H), 4.97 – 4.62 (m, 2H), 3.67 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 159.3, 138.8, 136.9, 136.2, 134.1, 133.7, 133.4, 132.6, 131.5, 130.6, 128.6, 128.2, 128.1, 127.6, 126.3, 125.8, 121.5, 120.3, 119.4, 117.6, 115.6, 115.0, 112.7, 101.6, 70.1, 52.7, 51.5. **HRMS** (ESI) calcd for $C_{30}H_{25}N_2O_5S^+$ *m/z* 525.1478 $[M+H]^+$, found: 525.1498. HPLC (Chiralpak INC-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 20.71 min (major), t_2 = 22.79 min (minor).

(*S*)-Methyl-3-(10-fluoro-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3fa**): white solid (20.5 mg, 95% yield, 98% *ee*); R_f = 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 147.6–148.5 ℃. **$[\alpha]_D^{25}$** = +206.6 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.0 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.17 (d, *J* = 9.1 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 4H), 6.70 (t, *J* = 7.1 Hz, 1H), 6.54 (t, *J* = 7.2 Hz, 1H), 5.26 (s, 1H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 163.1 (d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 142.5 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 137.7, 137.1, 133.9, 133.5, 130.6, 130.0 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 129.3, 128.6, 126.2, 125.9, 121.3, 120.4, 119.4, 117.5 (d, $^{3}J_{C\text{-}F}$ = 6.8 Hz), 117.2, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 112.8, 101.5, 52.1, 51.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.11. **HRMS** (ESI) calcd for $C_{23}H_{18}FN_2O_4S^+$ *m/z* 437.0965 $[M+H]^+$, found: 437.0971. HPLC (Chiralpak INA-H

column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 8.43 min (major), t_2 = 11.36 min (minor).

(*S*)-Methyl-3-(10-chloro-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ga**): white solid (21.4 mg, 95% yield, 98% *ee*); R_f = 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 221.1–222.1℃. $[\alpha]_D^{25}$ = + 273.6 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.4 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.75 (m, 1H), 7.65 (dd, *J* = 17.9, 7.5 Hz, 2H), 7.53 – 7.41 (m, 2H), 7.16 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 3H), 6.70 (t, *J* = 6.6 Hz, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 1H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, CDCl3) δ 165.5, 141.9, 137.5, 137.0, 135.5, 133.9, 133.5, 131.2, 130.7, 130.1, 129.5, 129.4, 129.0, 126.2, 125.9, 121.0, 120.4, 119.5, 117.6, 112.9, 101.5, 52.1, 51.7. **HRMS** (ESI) calcd for $C_{23}H_{17}ClN_2O_4SNa^+$ *m/z* 475.0489 $[M+Na]^+$, found: 475.0496(^{35}Cl), 477.0476(^{37}Cl). HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.21 min (major), t_2 = 8.94 min (minor).

(*S*)-Methyl-3-(10-methoxy-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ha**): white solid (22.7 mg, 99% yield, 95% *ee*); R_f = 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 139.7–141.2 ℃. $[\alpha]_D^{25}$ = +199.4 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 7.3 Hz, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 9.1 Hz, 1H), 6.98 (s, 1H), 6.86 (s, 3H), 6.70 (d, *J* = 9.2 Hz, 2H), 6.47 (d, *J* = 8.8 Hz, 1H), 5.27 (s, 1H), 3.80 (s, 3H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 160.2, 141.6, 138.8, 137.1, 133.7, 133.3, 130.7, 129.3, 128.9, 126.5, 125.8, 124.5, 122.0, 120.3, 119.3, 117.4, 116.3, 113.6, 112.5, 101.4, 55.4, 52.2, 51.5. **HRMS** (ESI) calcd for $C_{24}H_{21}N_2O_5S^+$ *m/z* 449.1167 $[M+H]^+$, found: 449.1152. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 7.86 min (major), t_2 =13.35 min (minor).

(*S*)-Methyl-3-(2-fluoro-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ia**): white solid (21.5 mg, 98% yield, 98% *ee*); R_f = 0.4 (petroleum ether/ethyl acetate, 4:1); mp: 151.9–152.7 ℃. $[\alpha]_D^{25}$ = +252.2 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.3 Hz, 1H), 8.04 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.38 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.26 – 7.17 (m, 2H), 6.95 (d, *J* = 3.3 Hz, 1H), 6.88 (q, *J* = 6.0 Hz, 2H), 6.69 (t, *J* = 6.8 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.33 (s, 1H), 3.71 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.6, 165.5 (d, $^1J_{C\text{-}F}$ = 253.5 Hz), 141.8, 139.2, 133.4, 133.3, 132.6, 130.1, 129.7 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.6 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 128.2, 126.3, 121.4, 120.4, 119.4, 118.1, 117.8, 117.6, 115.7 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 112.7, 101.5, 52.6, 51.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.18. **HRMS** (ESI) calcd for $C_{23}H_{17}FN_2O_4SK^+$ *m/z* 475.0524 $[M+K]^+$, found: 475.0523. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.02 min (major), t_2 = 7.55 min (minor).

(*S*)-Methyl-3-(9,10-dimethoxy-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**3ja**): white solid (22.5 mg, 94% yield, 86% *ee*); R_f = 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 121.6–122.2 ℃. $[\alpha]_D^{25}$ = +132.4 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.76 (t, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.52 (m, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 6.91 (d, *J* = 13.3 Hz, 4H), 6.70 (d, *J* = 7.0 Hz, 1H), 6.03 (s, 1H), 5.32 (s, 1H), 3.90 (s, 3H), 3.70 (s, 3H), 3.39 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.5, 149.6, 149.1, 139.0, 137.2, 133.6, 133.3, 132.7, 130.5, 128.3, 126.4, 125.9, 124.8, 122.0, 120.3, 119.3, 117.6, 113.2, 112.5, 111.5, 101.6, 56.1, 55.6, 52.3, 51.6. **HRMS** (ESI) calcd

for $C_{25}H_{23}N_2O_6S^+$ *m/z* 479.1271 $[M+H]^+$, found: 479.1283. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.21 min (major), t_2 = 8.37 min (minor).

Scale-up reaction: Indolizine **2a** (301.0 mg, 1.2 mmol, 1.2 equiv.), **C8** (56.6 mg, 0.1 mmol, 10 mol%) and EtOAc (20 mL) were added in an oven-dried 50 mL round-bottomed flask. It was allowed to stir in air at 0 °C for 10 min, then seven-membered cyclic N-sulfonylimine **1a** (243.0 mg, 1.0 mmol, 1.0 equiv.) was added and the mixture was stirred at 0 ℃ for 36 h. The solvent was removed and the residue was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 6/1) to afford the product **3aa** (415.0 mg, >99% yield, 98% *ee*) as a white solid.

Synthetic transformations: CH_3I or allyl-bromide (0.5mmol, 5.0 equiv.) and K_2CO_3 (0.2 mmol, 2.0 equiv.) was added to the solution of **3aa** (0.1 mmol, 41.8 mg) in CH_3CN (2.0 mL). The mixture was stirred for 8 h. Then the mixture was diluted with EtOAc (20 mL) and washed with brine (10 mL). The organic layer was dried (Na_2SO_4), filtered through a short pad of silica gel, and concentrated in vacuo. Purification of the residue by column chromatography to gave products **4aa** and **4ab**.

(*S*)-Methyl-3-(6-methyl-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-ca rboxylate (**4aa**): white solid (42.1 mg, 97% yield, 99% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 6:1); mp: 163.0–164.3 ℃. $[\alpha]_D^{25}$ = +183.1 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 9.3 Hz, 1H), 7.41 (d, *J* = 3.9 Hz, 2H), 7.14 (q, *J* = 4.1 Hz, 1H), 6.92 (s, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.69 (t, *J* = 6.9 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 2.9 Hz, 1H), 3.73 (s, 3H), 2.55 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.6, 140.4, 139.3, 134.6, 134.3, 133.1, 133.1, 130.7, 130.1, 129.2, 128.9, 128.4, 127.8, 127.2, 126.2, 122.1, 120.2, 119.3, 118.2, 112.8, 101.3, 60.2, 51.5, 38.0. **HRMS** (ESI) calcd for $C_{24}H_{21}N_2O_4S^+$ *m/z* 433.1216 $[M+H]^+$, found: 433.1234. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 95/5, 25 ℃, λ = 230 nm, 1.0 mL/min): t_1 = 11.67 min (major), t_2 = 12.81 min (minor).

(*S*)-Methyl-3-(6-allyl-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carb oxylate (**4ab**): white solid (44.9 mg, 98% yield, 97% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 6:1); mp: 65.0–66.2 ℃. $[\alpha]_D^{25}$ = +145.3 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.2 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.72 (q, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 3.7 Hz, 2H), 7.20 – 7.10 (m, 1H), 6.92 (s, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.67 (d, *J* = 7.0 Hz, 2H), 6.50 (d, *J* = 7.9 Hz, 1H), 5.45 – 5.25 (m, 1H), 4.74 (d, *J* = 10.2 Hz, 1H), 4.62 (d, *J* = 17.0 Hz, 1H), 3.86 (dd, *J* = 15.7, 6.7 Hz, 1H), 3.72 (s, 3H), 3.28 (dd, *J* = 15.8, 6.8 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.6, 140.3, 138.9, 137.3, 134.4, 133.6, 133.0, 131.0, 130.5, 130.3, 129.2, 129.0, 128.6, 128.0, 126.4, 126.1, 121.8, 120.2, 119.3, 119.1, 118.3, 112.8, 101.3, 57.5, 54.0, 51.5. **HRMS** (ESI) calcd for $C_{26}H_{23}N_2O_4S^+$ *m/z* 459.1373 $[M+H]^+$, found: 459.1382. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 95/5, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 11.39 min (major), t_2 = 13.10 min (minor).

To a stirred solution of **4aa** (0.1 mmol, 43.2 mg) in dry THF (3.0 mL) under a N_2 atmosphere was added $LiAlH_4$ (0.2 mL, 1 M in THF, 0.2 mmol, 2.0 equiv.) via syringe at 0℃. The resultant reaction mixture was stirred 2 h, then it was cooled with ice bath. The mixture was diluted with EtOAc (10 mL) and acidified with aq. 2 M HCl until the aqueous layer became clear. The aqueous layer was separated and extracted with EtOAc (2×15 mL). The combined organic layers were

dried (Na_2SO_4), filtered, and concentrated in vacuo. Purification of the residue by flash chromatography to afforded compound **4ac**.

(*S*)-7-(2-(hydroxymethyl)-indolizin-3-yl)-6-methyl-6,7-dihydrodibenzo[d,f][1,2]thiazepine-5,5-dioxide (**4ac**): blue solid (40.0 mg, 98% yield, 96% *ee*); R_f= 0.3 (petroleum ether/ethyl acetate, 2:1); mp: 208.9–209.9 ℃. $[\alpha]_D^{25}$ = +240.0 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.0 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 3H), 7.16 (dt, *J* = 8.7, 4.5 Hz, 1H), 7.00 – 6.20 (m, 5H), 5.25 (s, 1H), 4.54 (s, 2H), 2.55 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 140.1, 139.1, 135.1, 134.3, 133.8, 133.6, 130.5, 129.9, 129.3, 129.1, 128.6, 128.2, 127.3, 125.7, 119.0, 118.2, 115.8, 111.2, 98.9, 60.9, 57.9, 37.9. **HRMS** (ESI) calcd for $C_{23}H_{21}N_2O_3S^+$ *m/z* 405.1250 $[M+H]^+$, found: 405.1270. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.60 min (major), t_2 = 7.47 min (minor).

To a flame-dried 10 mL Schlenk tube with a stirring bar was added **4aa** (43.2 mg, 0.1 mmol) and NaOH (20 mg, 0.5 mmol, 5.0 equiv.) in 5 mL of mixed solvent (THF/MeOH/H_2O=2/2/1). It was allowed refluxing for 6 h, when the solution was cooled to room temperature, adjusted the pH with 1 M HCl and extracted three times with EtOAc. The organic layer was dried (Na_2SO_4), concentrated in vacuo, and purified by column chromatography to gave product **4ad**.

(*S*)-3-(6-methyl-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylic acid (**4ad**): gray solid (39.5 mg, 94% yield, 97% *ee*); R_f= 0.6 (dichloromethane/ methanol, 20:1); mp: 233.1–233.8 ℃. $[\alpha]_D^{25}$ = + 230.0 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.41 (d, *J* = 4.4 Hz, 2H), 7.15 (dd, *J* = 8.1, 4.4 Hz, 1H), 6.95 (s, 1H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.69 (t, *J* = 6.9 Hz, 1H), 6.43 (d, *J* = 7.9 Hz, 1H), 6.21 (s, 1H), 2.52 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 170.1, 140.3, 139.1, 134.3, 134.3, 133.8, 133.2, 130.6, 130.2, 129.3, 129.0, 128.5, 127.7, 127.3, 126.2, 122.6, 120.4, 119.5, 117.4, 113.2, 102.1, 60.3, 38.0. **HRMS** (ESI) calcd for $C_{23}H_{18}N_2O_4S^+$ *m/z* 419.1060 $[M+H]^+$, found: 419.1069. HPLC (Chiralpak INB-H column, *n*-hexane/*i*-PrOH = 50/50, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 5.53 min (major), t_2 = 7.04 min (minor).

To a flame-dried 10 mL Schlenk tube with a stirring bar was added **4aa** (43.2 mg, 0.1 mmol) in 2.0 mL DMSO. Then, thiophenol (2.0 equiv.), potassium iodide (2.0 equiv.) and tert-butyl hydroperoxide (2.0 equiv.) were sequentially added. The vial was tightly sealed, and reaction was heated to 60 ℃ for 24 h. After cooling to room temperature, distilled water was added (20 mL) and the aqueous phase extracted with EtOAc. The organic layer was dried (Na_2SO_4), concentrated, and purified by column chromatography gave product **4ae**.

(*S*)-Methyl-3-(6-methyl-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)-1-(phenylthio) indolizine-2-carboxylate (**4ae**): yellow solid (45.0 mg, 83% yield, 99% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 6:1); mp: 76.8–77.6 ℃. $[\alpha]_D^{25}$ = +144.1 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.84 – 7.66 (m, 3H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 21.9, 6.7 Hz, 4H), 7.15 (dt, *J* = 8.5, 4.6 Hz, 2H), 7.04 (q, *J* = 7.6, 7.2 Hz, 1H), 6.96 – 6.83 (m, 2H), 6.68 (t, *J* = 6.9 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 6.34 (s, 1H), 3.73 (s, 3H), 2.54 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.6, 140.4, 139.2, 134.6, 134.3, 133.8, 133.1, 130.6, 130.1, 129.2, 128.9, 128.7, 128.4, 127.8, 127.3, 126.2, 122.1, 120.2, 119.3, 118.1, 112.8, 101.3, 60.2, 51.5, 38.0. **HRMS** (ESI) calcd for $C_{30}H_{25}N_2O_4S_2^+$ *m/z* 541.1250 $[M+H]^+$, found: 541.1267. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm,

1.0 mL/min): t_1 = 5.15 min (major), t_2 = 6.21 min (minor).

An oven-dried 10 mL vial equipped with a magnetic stir bar was charged with **4ab** (20.0 mg, 0.044 mmol) and methyl acrylate (7.6 mg, 0.088 mmol). To this vessel, a solution of Hoveyda-Grubbs II (5 mol%) in CH_2Cl_2 (1.0 mL) were added. The resulting solution was stirred for 12 h at room temperature. The reaction media were then concentrated under vacuum and purified by column chromatography to gave product **4af**.

Methyl-(*S*,*E*)-3-(6-(4-methoxy-4-oxobut-2-en-1-yl)-5,5-dioxido-6,7-dihydrodibenzo[d,f][1,2]thiazepin-7-yl)indolizine-2-carboxylate (**4af**): yellow solid (16.0 mg, 72% yield, 97% *ee*); R_f= 0.3 (petroleum ether/ethyl acetate, 4:1); mp: 83.4–84.2 ℃. $[\alpha]_D^{25}$ = +86.0 (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.36 (m, 3H), 7.23 – 7.10 (m, 1H), 7.05 – 6.81 (m, 2H), 6.71 (t, *J* = 6.9 Hz, 1H), 6.63 (s, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 6.40 – 6.14 (m, 1H), 5.24 (d, *J* = 15.6 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.73 (s, 3H), 3.69 – 3.63 (m, 1H), 3.57 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 165.6, 141.2, 140.3, 138.9, 136.6, 133.9, 133.8, 133.2, 130.8, 130.4, 129.3, 129.0, 128.7, 128.0, 126.4, 125.9, 123.0, 121.3, 120.2, 119.4, 118.4, 113.0, 101.6, 58.8, 52.3, 51.5, 51.4. **HRMS** (ESI) calcd for $C_{28}H_{25}N_2O_6S^+$ *m/z* 517.1427 $[M+H]^+$, found: 517.1443. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 80/20, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 8.23 min (major), t_2 = 10.40 min (minor).

(*S*)-Methyl-3-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)indolizine-2-carboxylate (**6a**): white solid (32.2 mg, 90% yield, 84% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp:158.6–159.7℃. $[\alpha]_D^{25}$ = -112.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.78 – 7.61 (m, 1H), 7.49 (d, J = 9.1 Hz, 1H), 7.29 (s, 1H), 7.08 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.2 Hz, 1H), 6.76 (s, 1H), 6.49 (s, 1H), 6.35 (s, 1H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 166.7, 151.4, 132.7, 129.8, 125.8, 125.2, 121.7, 120.9, 119.2, 118.6, 114.1, 103.1, 52.3. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.67 min (major), t_2 = 9.32 min (minor).

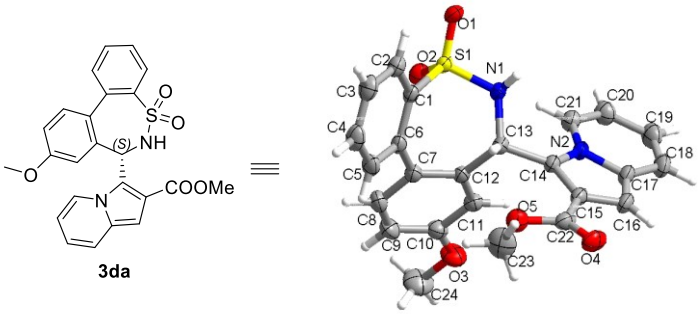
(*S*)-Ethyl-3-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)indolizine-2-carboxylate (**6b**): white solid (31.3 mg, 84% yield, 65% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp:159.4–161.3℃. $[\alpha]_D^{25}$ = -102.9 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.67 (s, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.80 (t, J = 7.8 Hz, 1H), 6.70 (s, 1H), 6.44 (s, 1H), 6.32 (s, 1H), 4.23 – 4.10 (m, 2H), 1.21 (t, J = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 166.2, 151.4, 132.7, 129.8, 125.8, 125.1, 121.7, 120.9, 119.2, 118.6, 114.0, 103.2, 61.4, 52.3, 14.1. (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 6.41 min (major), t_2 = 8.91 min (minor).

(*S*)-Benzyl-3-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)indolizine-2-carboxylate (**6c**): Brown solid (33.0 mg, 74% yield, 99% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 168.9–169.4 ℃. $[\alpha]_D^{25}$ = -109.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.68 (s, 1H), 7.52 (d, J = 9.1 Hz, 1H), 7.47 – 7.23 (m, 6H), 7.13 (d, J = 8.3 Hz, 1H), 7.07 (s, 1H), 6.99 (t, J = 7.7 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 6.80 (s, 1H), 6.56 (s, 1H), 6.41 (s, 1H), 5.24 (s, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 166.2, 151.5, 135.5, 132.7, 129.8, 128.7, 128.4, 128.2, 125.8, 125.1, 121.7, 120.9, 119.3, 118.6, 114.1, 103.3, 66.9, 52.3. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 8.04 min (major), t_2 = 11.34 min (minor).

(*S*)-Butyl-3-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)indolizine-2-carboxylate (**6d**): white solid (29.6 mg, 74% yield, 61% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1); mp: 127.5–129.7℃. $[\alpha]_D^{25}$ = -83.7 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.72 (s, 1H), 7.43 (d, J = 9.0 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 10.1 Hz, 2H), 6.80 (t, J = 7.8 Hz, 1H), 6.71 (s, 1H), 6.43 (s, 1H), 6.30 (s, 1H), 4.11 (s, 2H), 1.62 – 1.53 (m, 2H), 1.38 – 1.24 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 166.4, 151.4, 132.6, 129.8, 125.8, 125.1, 121.7, 120.9, 119.2, 118.6, 114.0, 103.1, 65.2, 52.3, 30.6, 19.1, 13.7. HPLC (Chiralpak INA-H column, *n*-hexane/*i*-PrOH = 70/30, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 5.920 min (major), t_2 = 7.58 min (minor).

(*S*)-Tert-butyl-3-(2,2-dioxido-3,4-dihydrobenzo[e][1,2,3]oxathiazin-4-yl)indolizine-2-carboxylate (**6e**): white solid (33.0 mg, 83% yield, 63% *ee*); R_f= 0.5 (petroleum ether/ethyl acetate, 4:1)；mp: 163.2–164.7℃. $[\alpha]_D^{25}$ = -89.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.64 (s, 1H), 7.47 (d, J = 9.0 Hz, 1H), 7.28 (s, 1H), 7.07 (d, J = 8.2 Hz, 1H), 7.00 – 6.87 (m, 2H), 6.84 (t, J = 7.8 Hz, 1H), 6.74 (s, 1H), 6.58 – 6.25 (m, 2H), 1.39 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 151.56, 132.5, 129.7, 126.0, 124.9, 121.7, 120.8, 119.0, 118.4, 113.7, 103.0, 82.3, 52.3, 28.0. HPLC (Chiralpak INC-H column, *n*-hexane/*i*-PrOH = 90/10, 25 ℃, λ = 254 nm, 1.0 mL/min): t_1 = 18.75 min (minor), t_2 = 22.00 min (major).

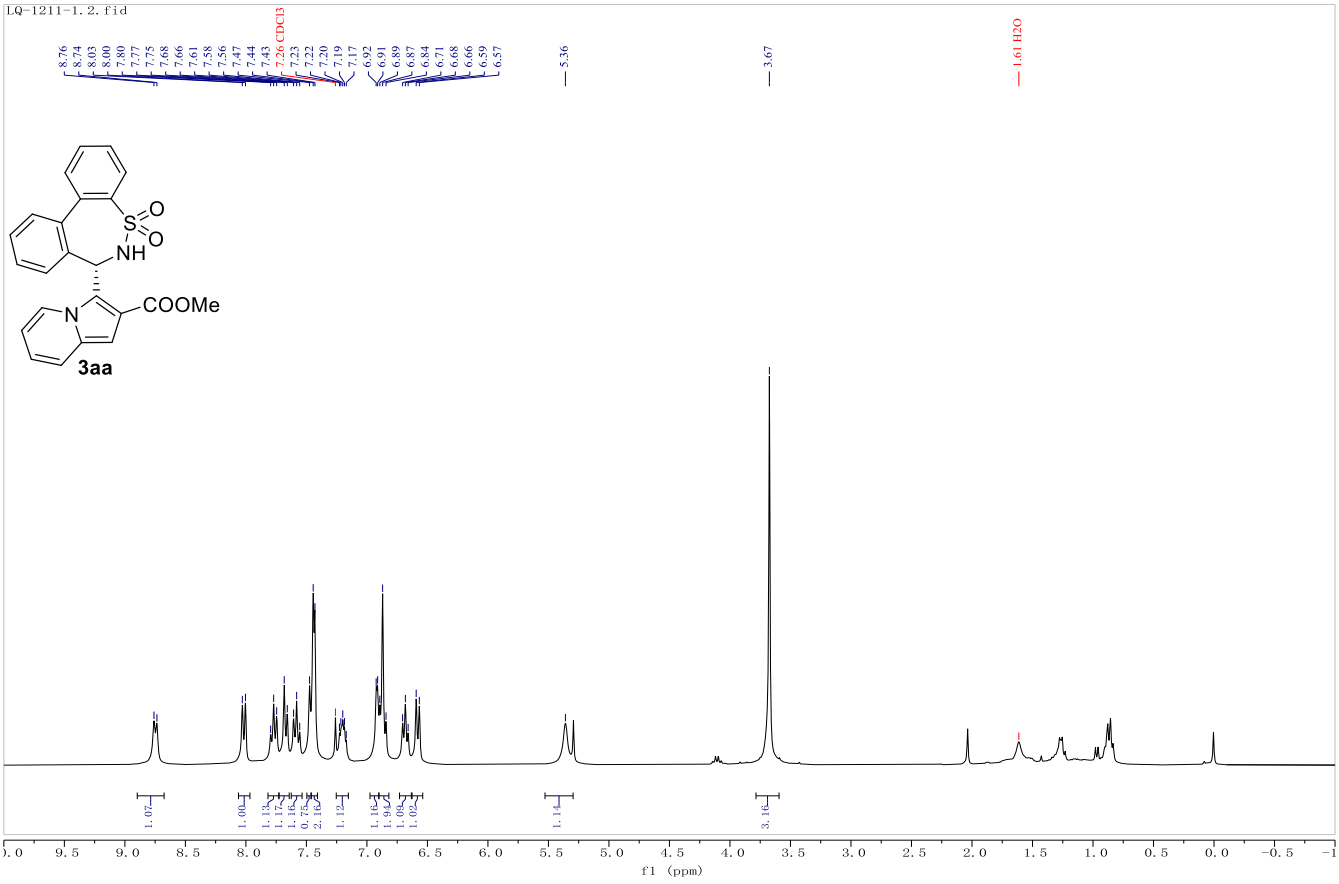
5. X-ray structure for compound 3da



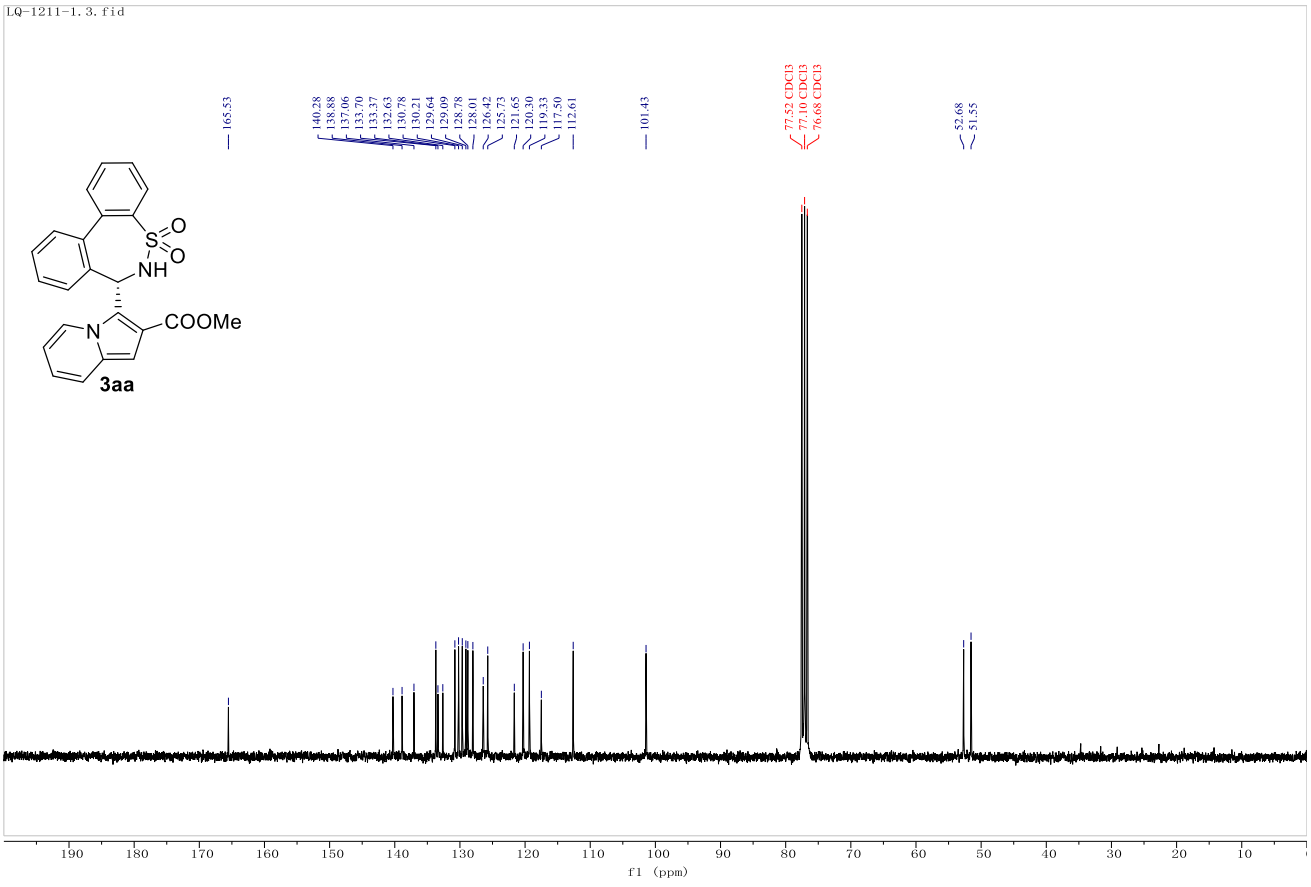
The single crystal of the compound **3da** (CCDC: 2320870) was grown from its solution in dichloromethane and hexane, and one of them is suitable for X-ray diffraction analysis. The correctness of the X-ray data and the structure had been checked by using the Check CIF utility on the submission Web site: http://checkcif.iucr.org.

6. Copy of NMR

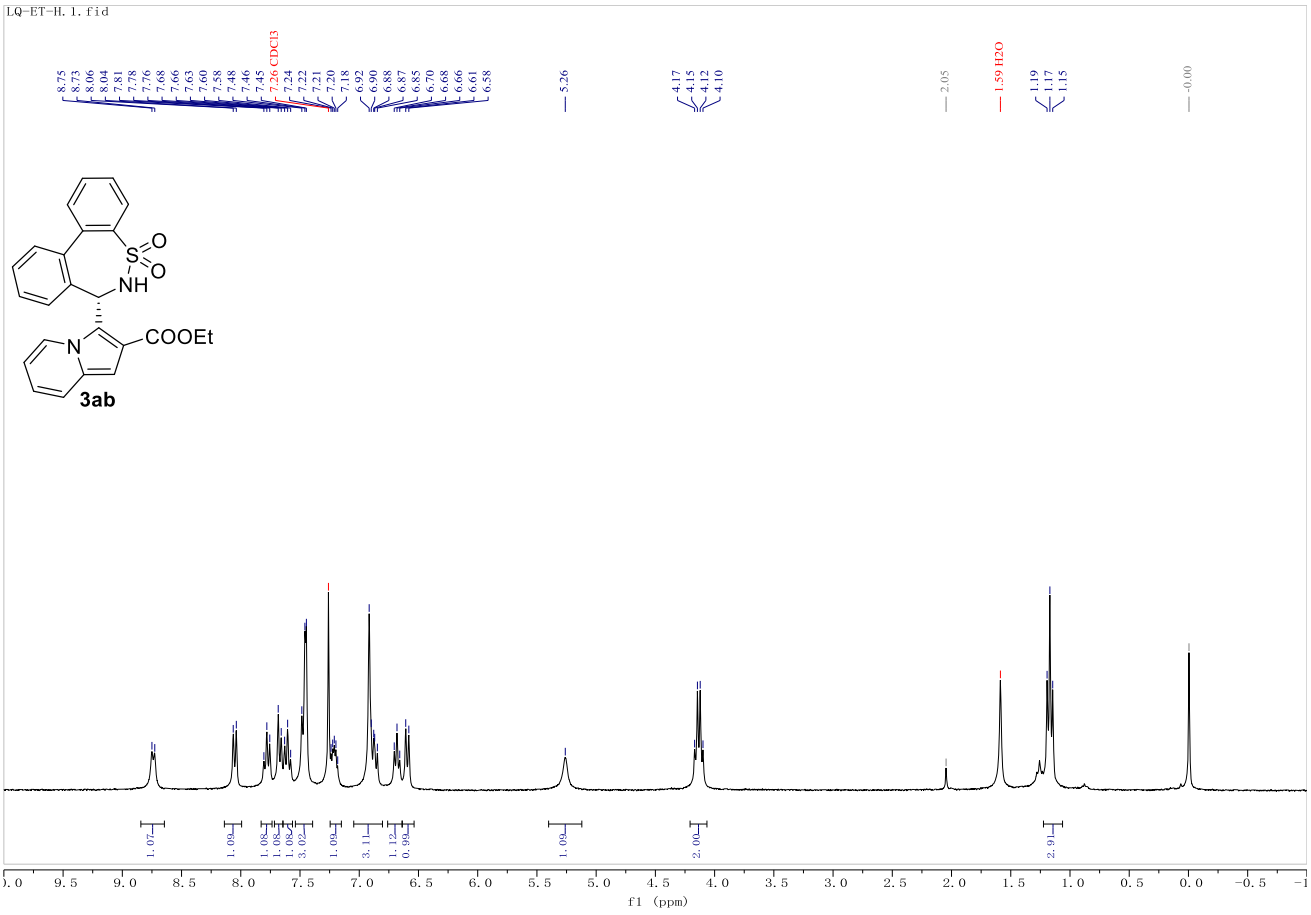
3aa, ^{1}H-NMR in $CDCl_3$



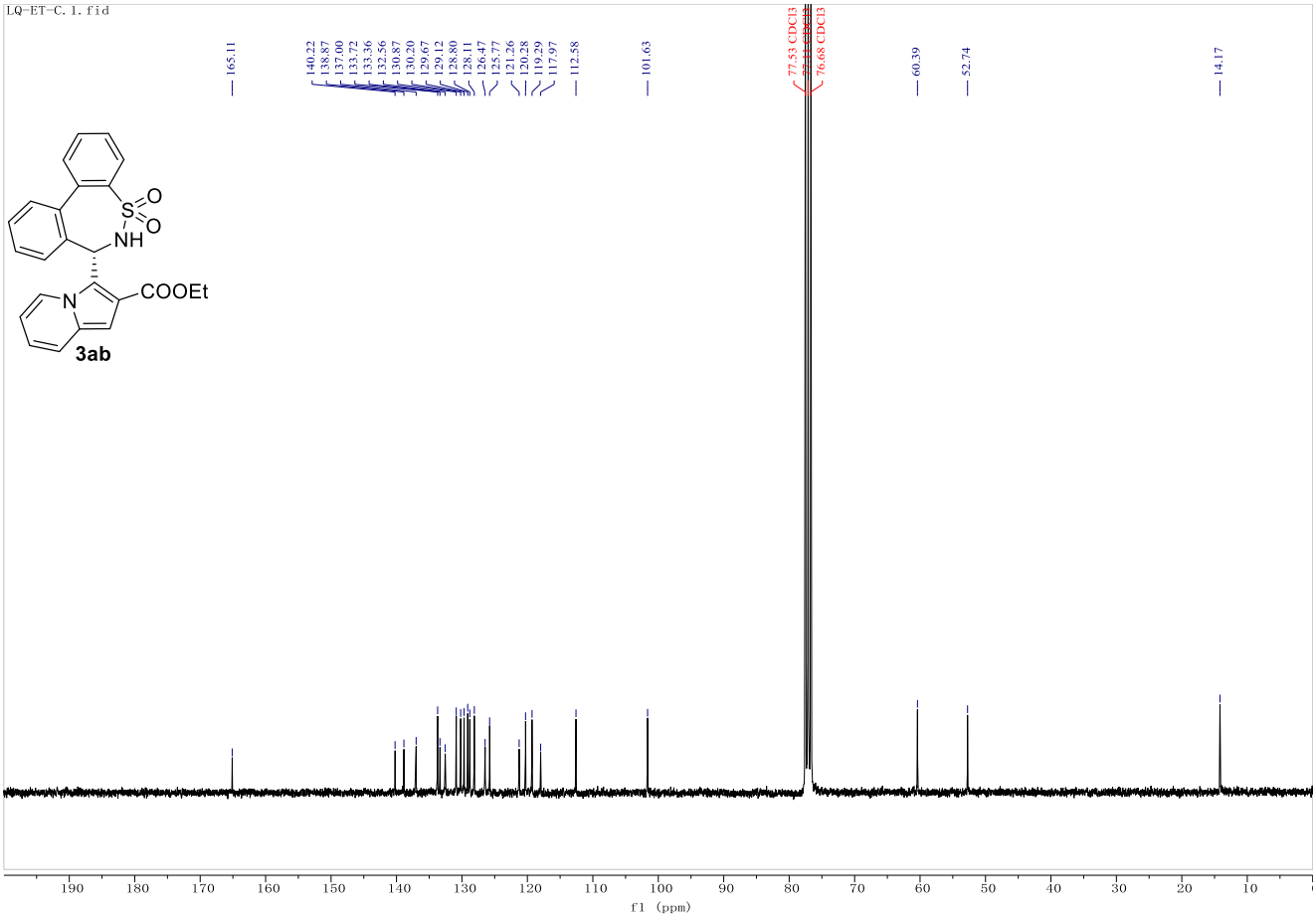
3aa, ^{13}C-NMR in $CDCl_3$



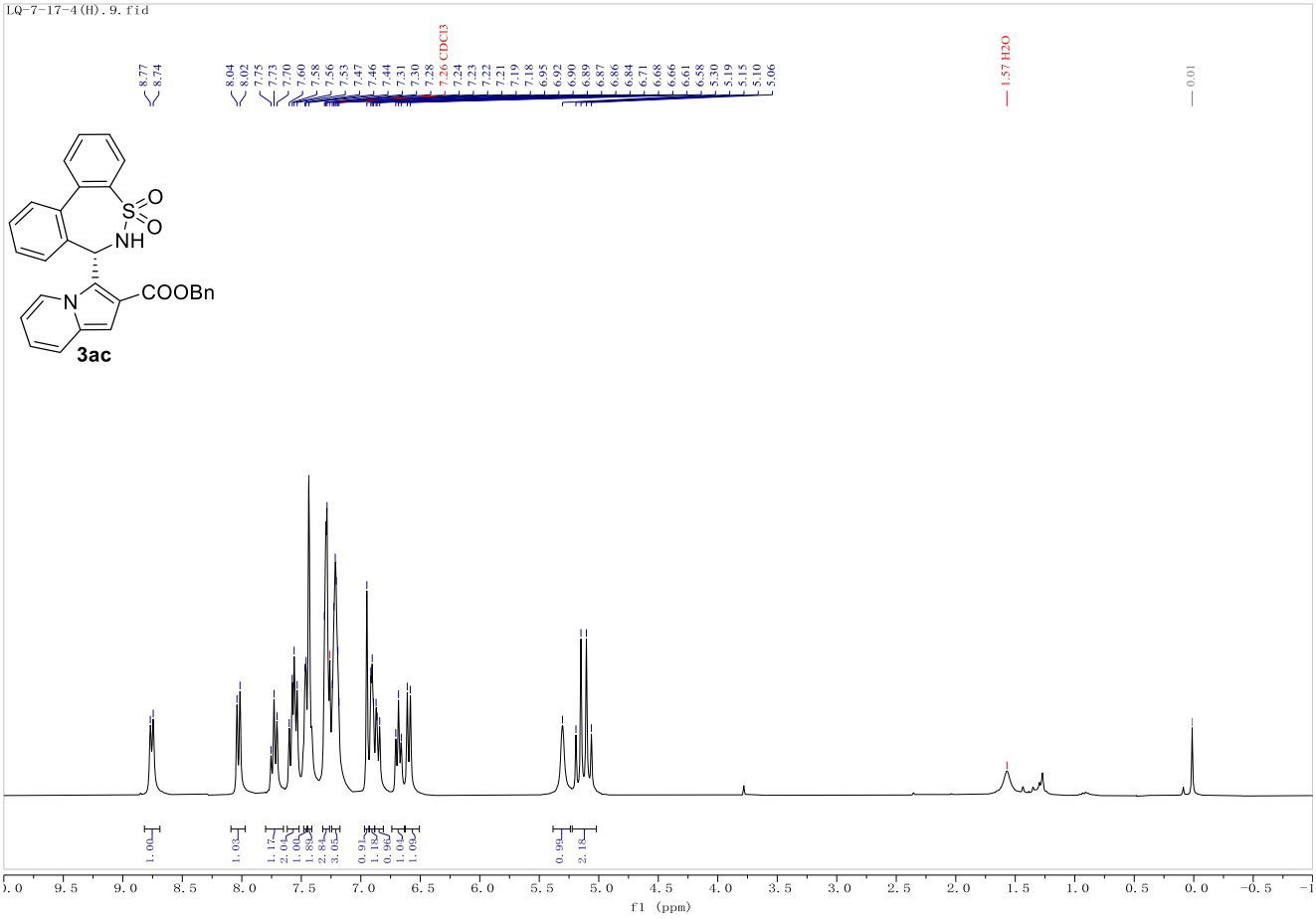
3ab, ^{1}H-NMR in $CDCl_3$



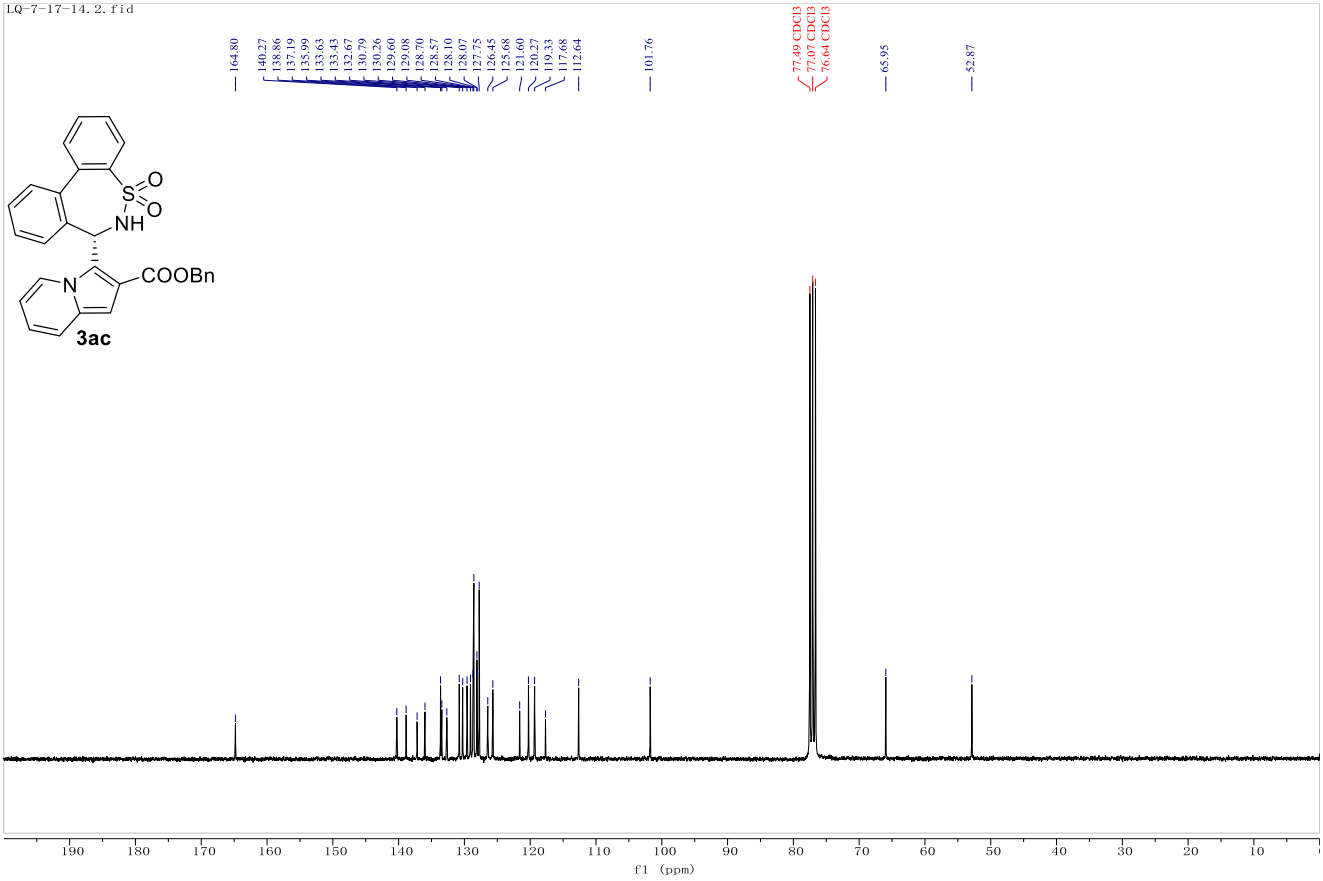
3ab, ^{13}C-NMR in $CDCl_3$



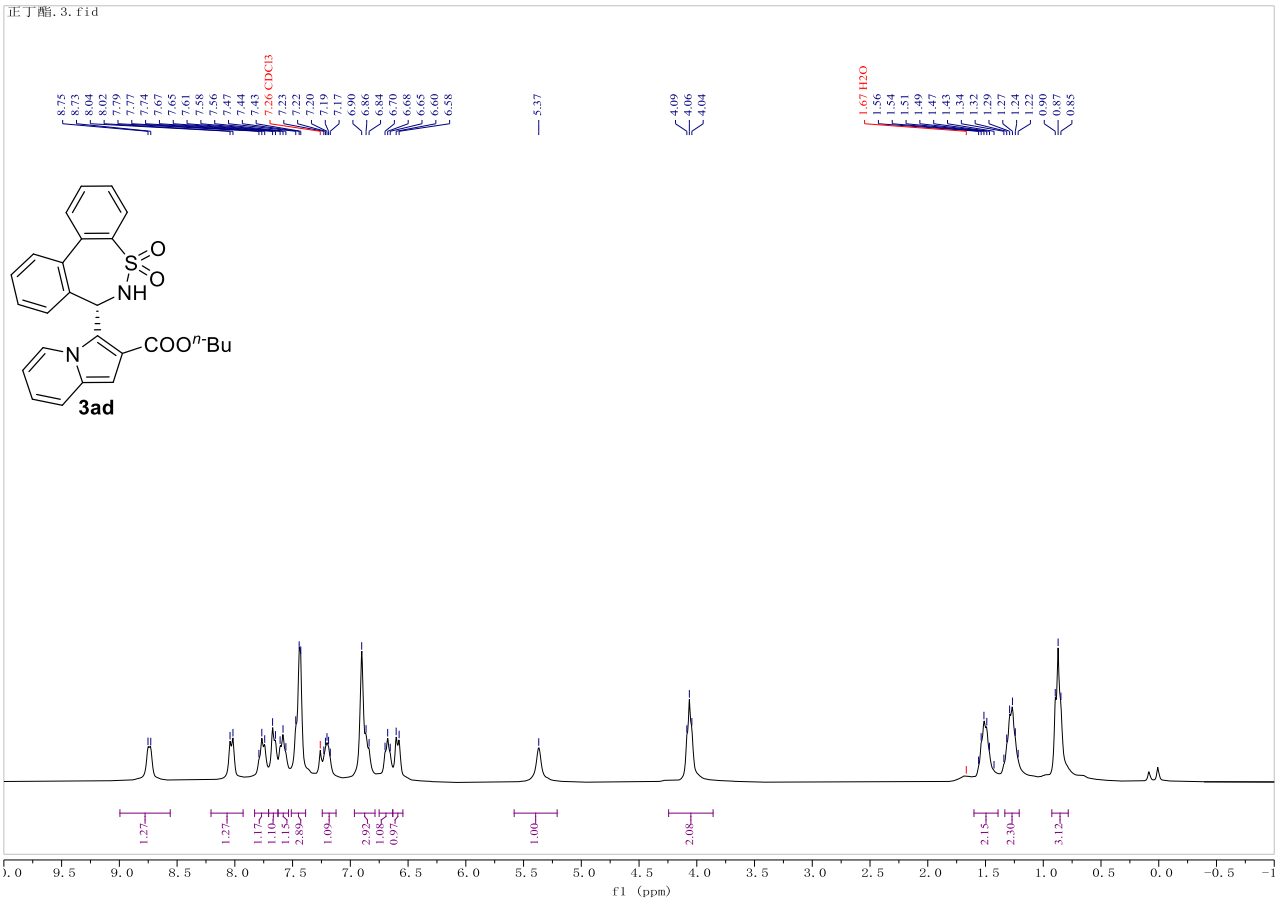
3ac, ^{1}H-NMR in $CDCl_3$



3ac, ^{13}C-NMR in $CDCl_3$



3ad, ^{1}H-NMR in $CDCl_3$



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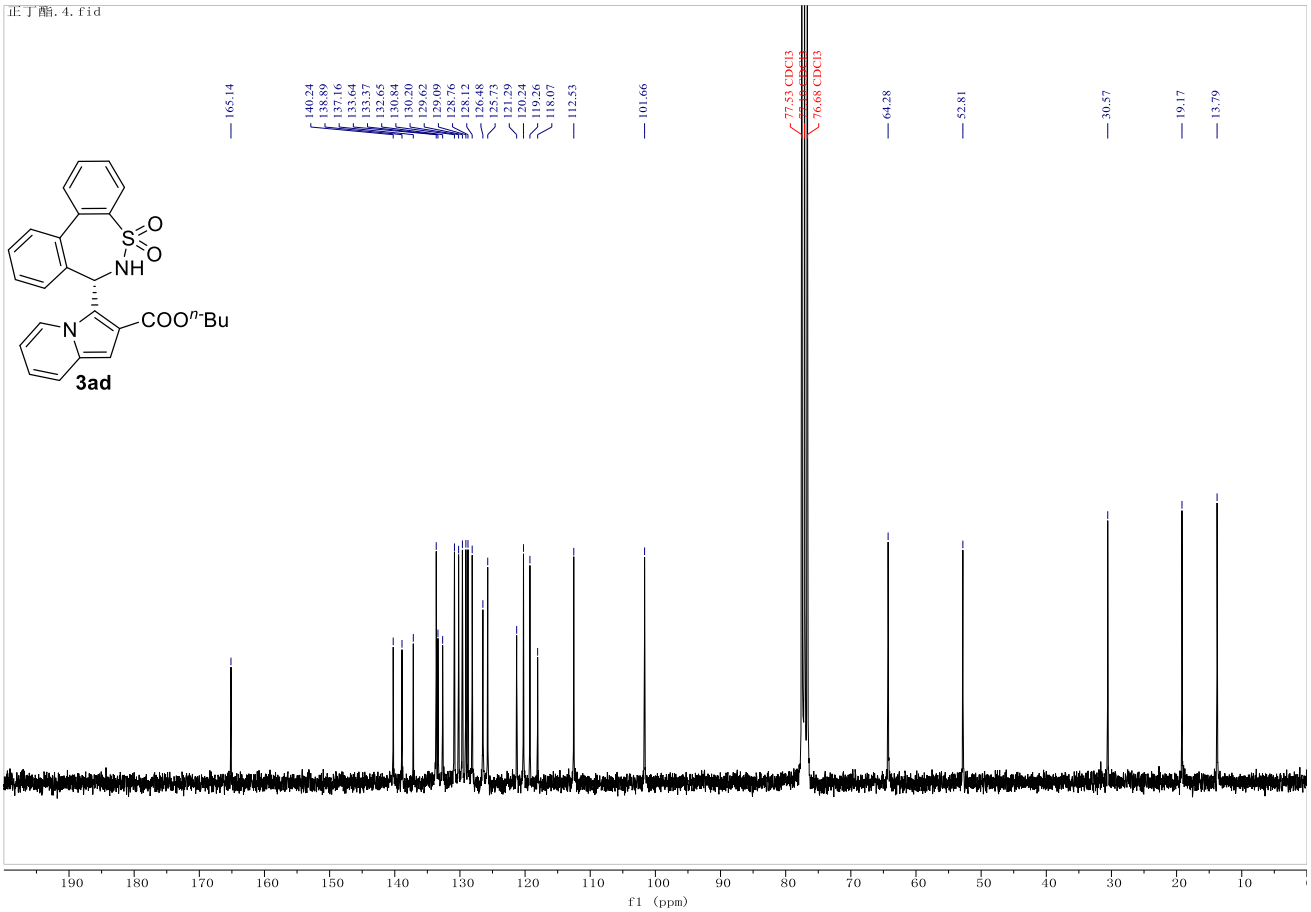
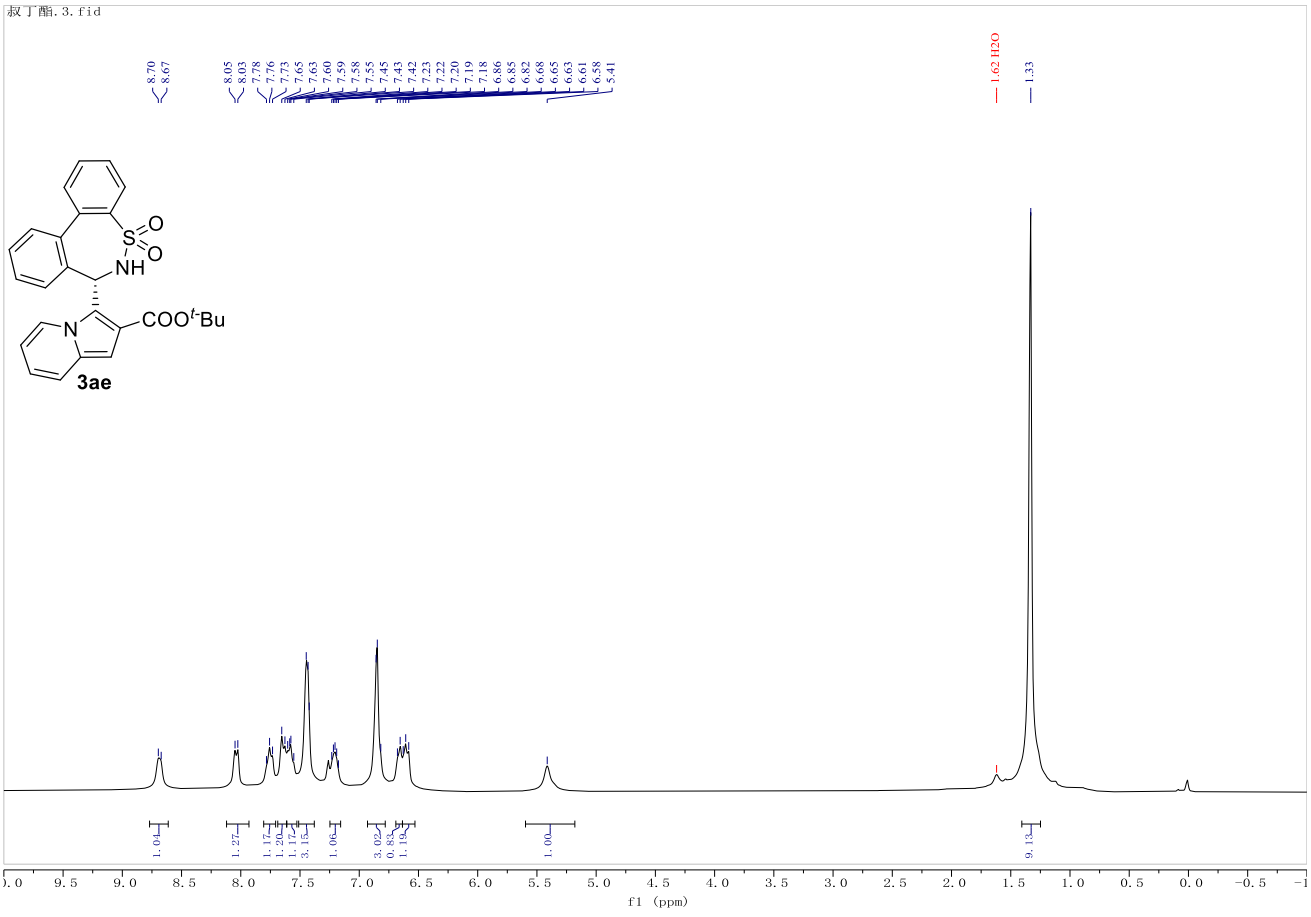
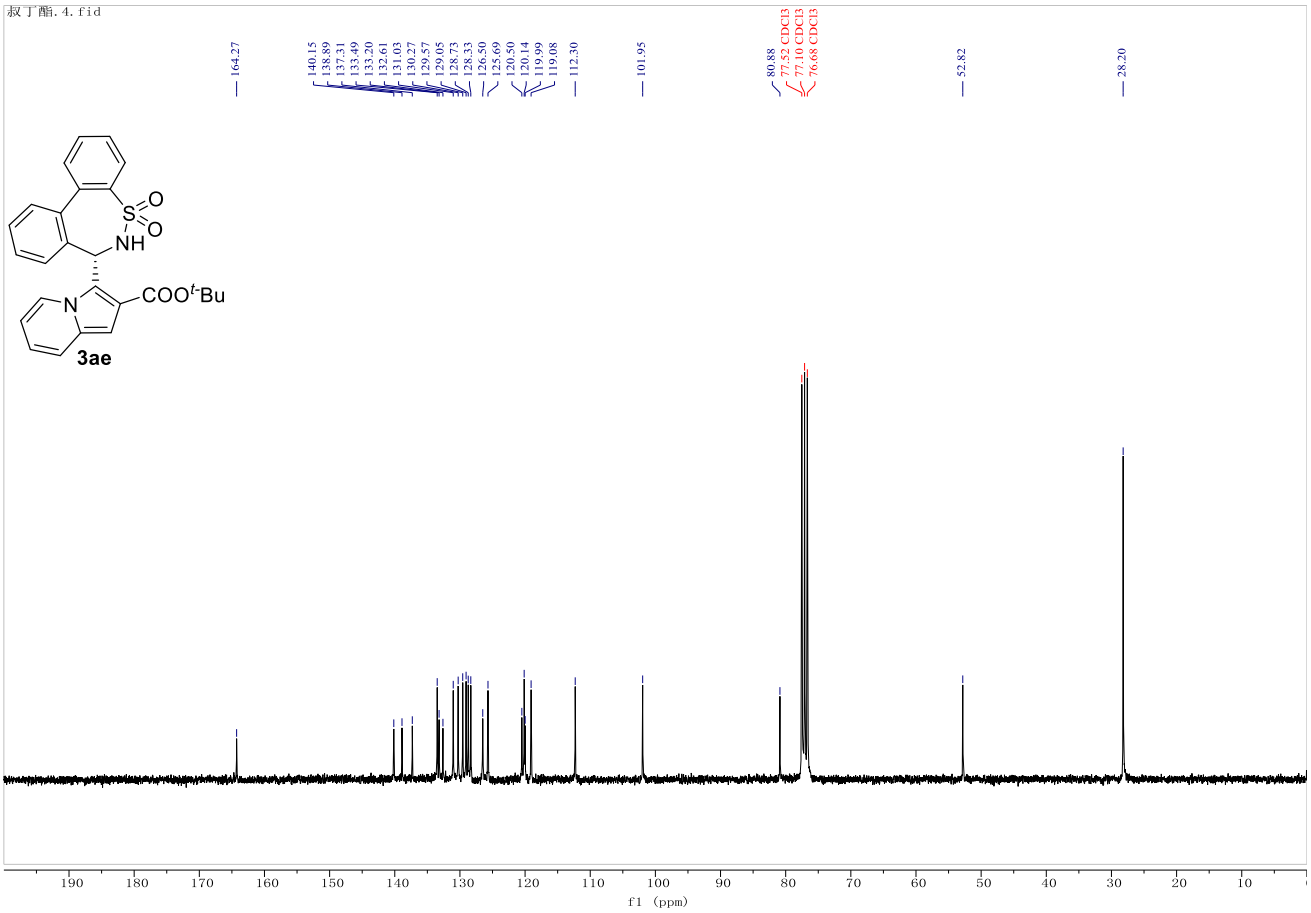


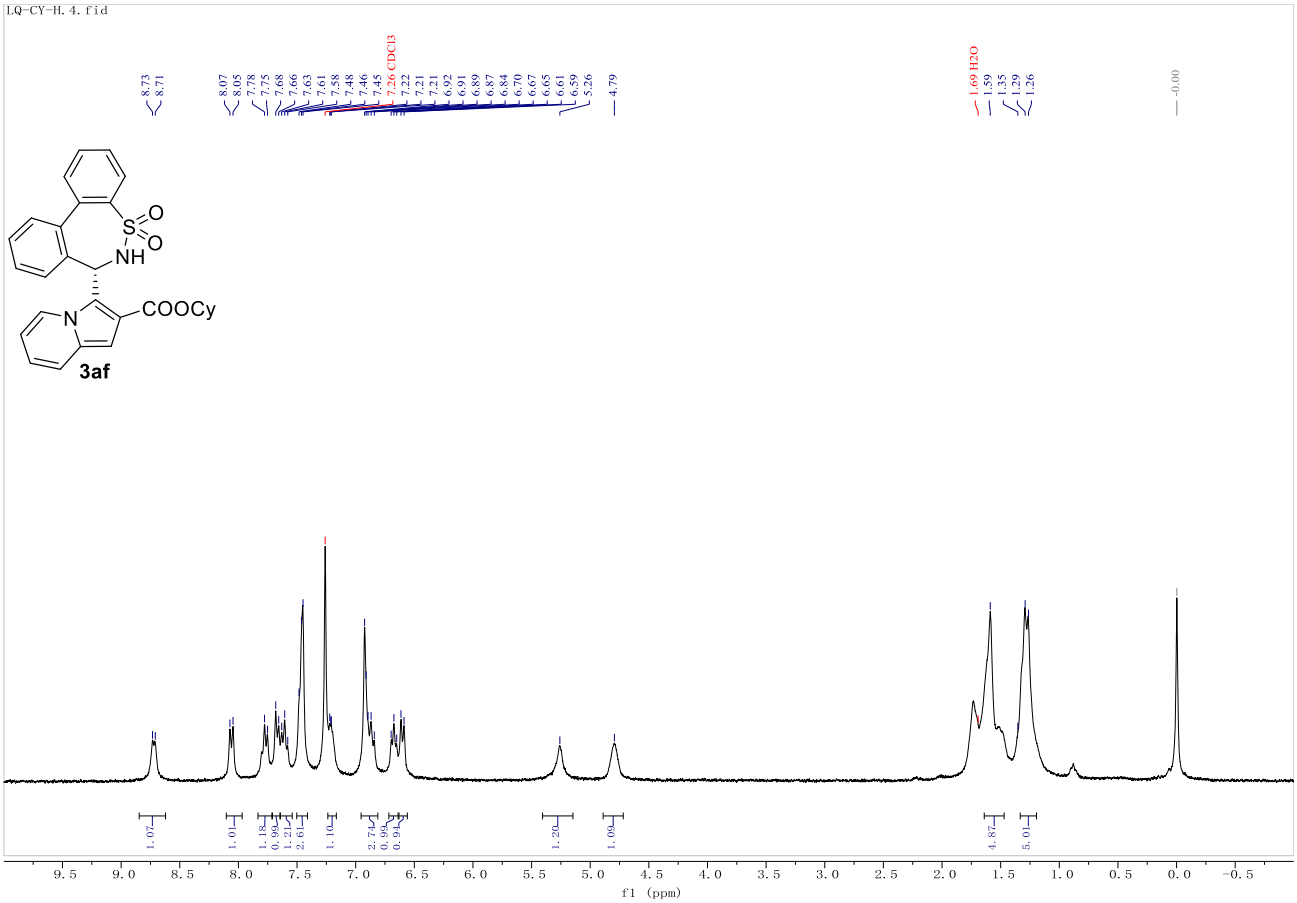
3ae, ^{1}H-NMR in $CDCl_3$



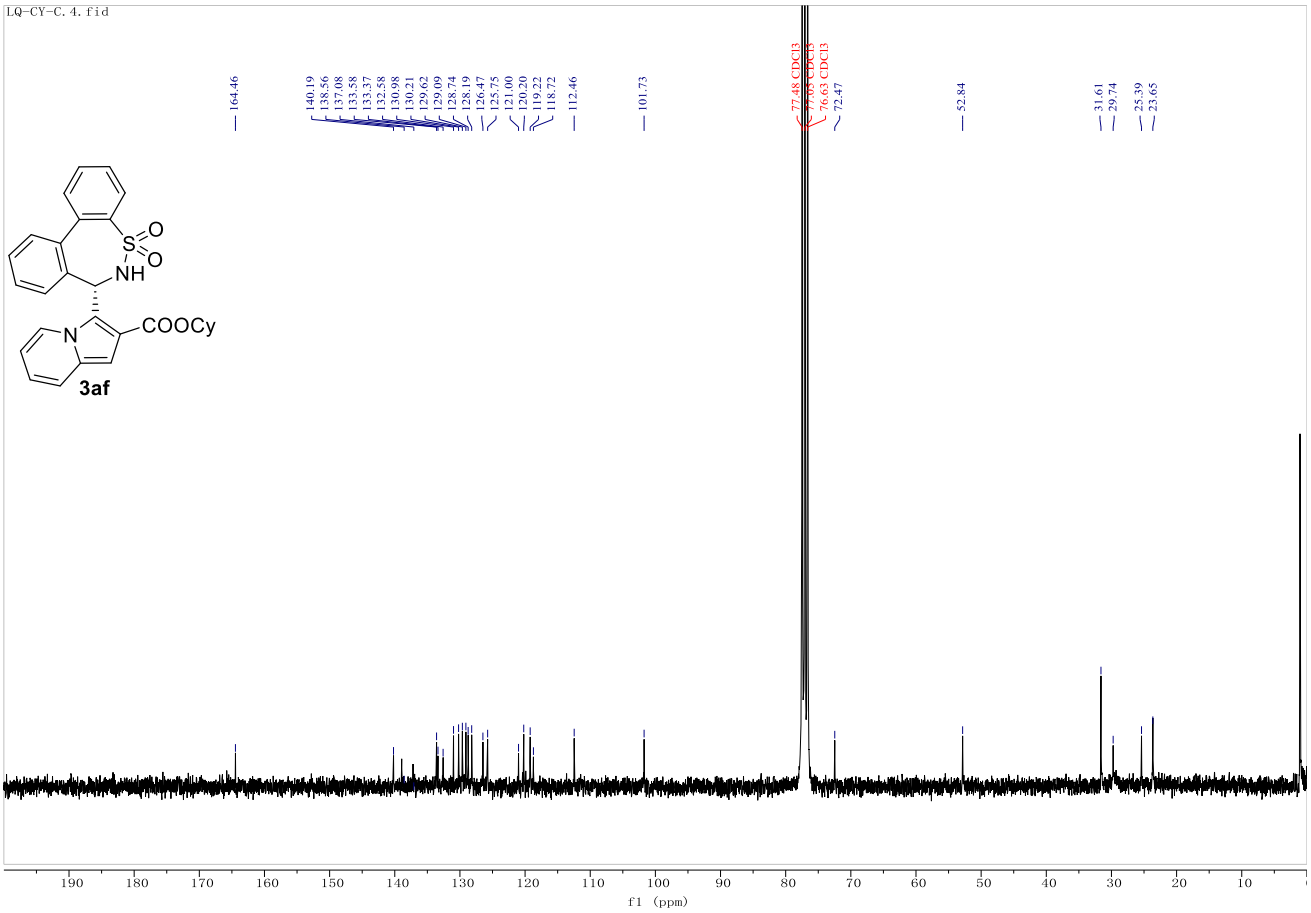
3ae, ^{13}C-NMR in $CDCl_3$



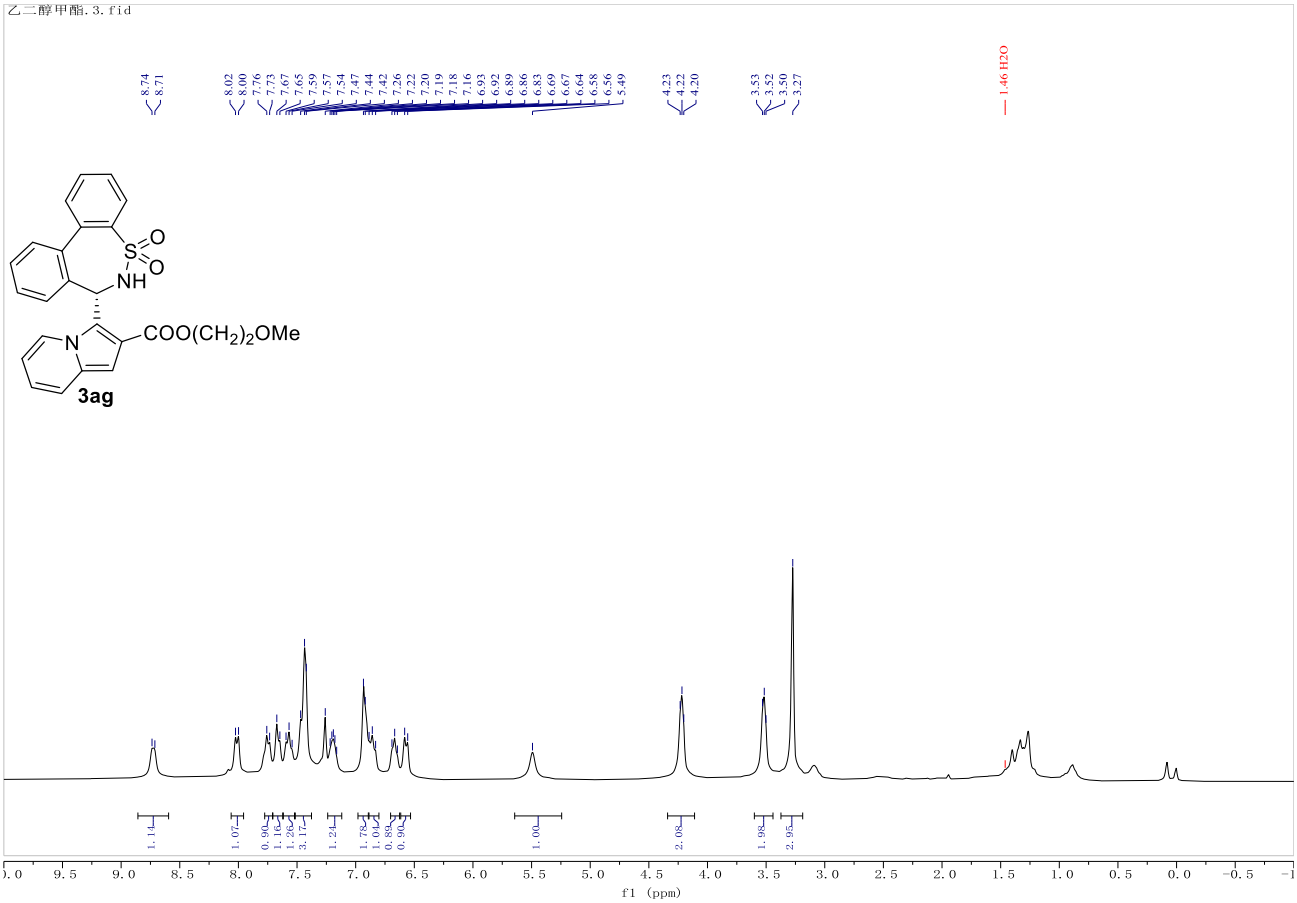
3af, ^{1}H-NMR in $CDCl_3$



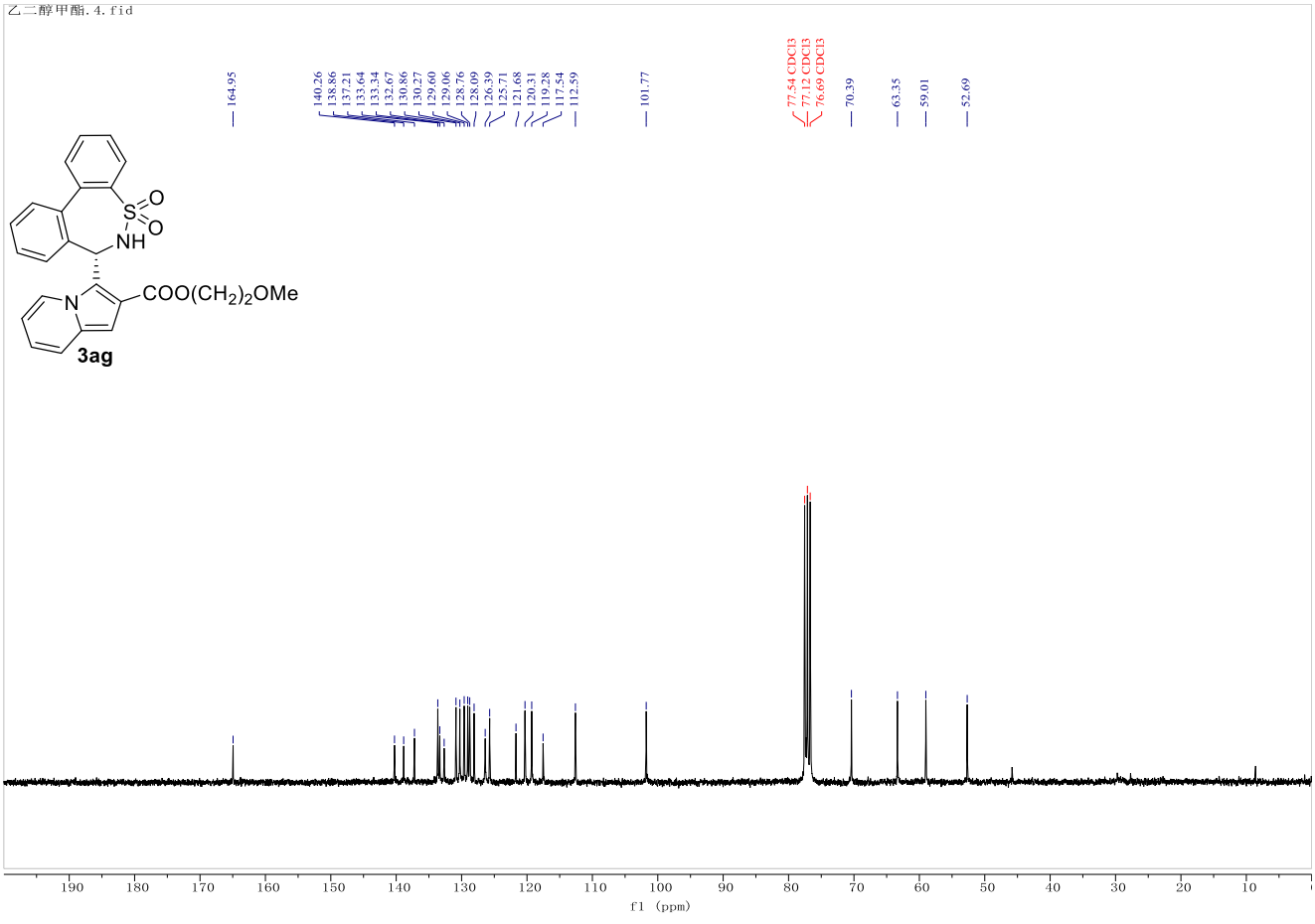
3af, ^{13}C-NMR in $CDCl_3$



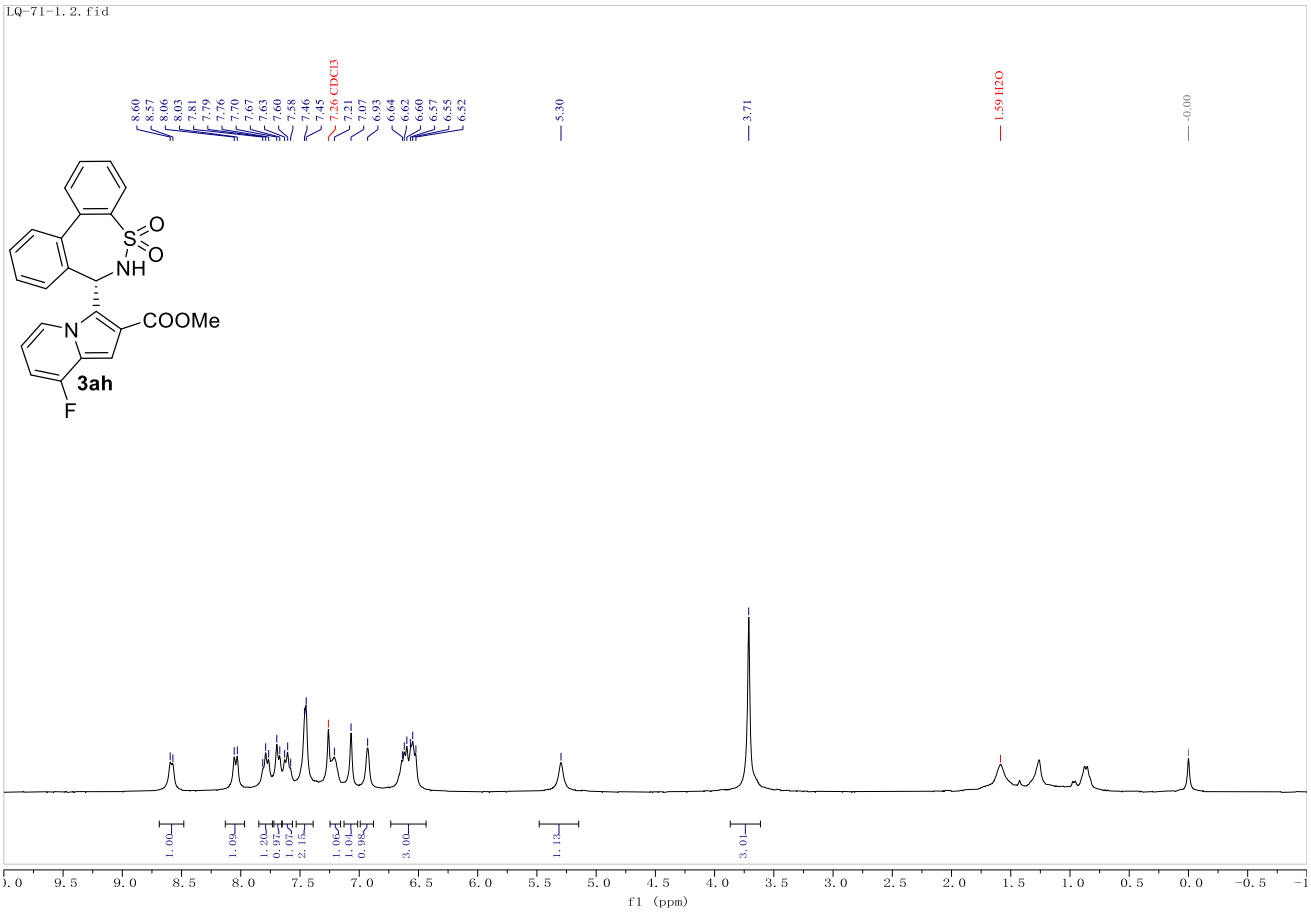
3ag, ^{1}H-NMR in $CDCl_3$



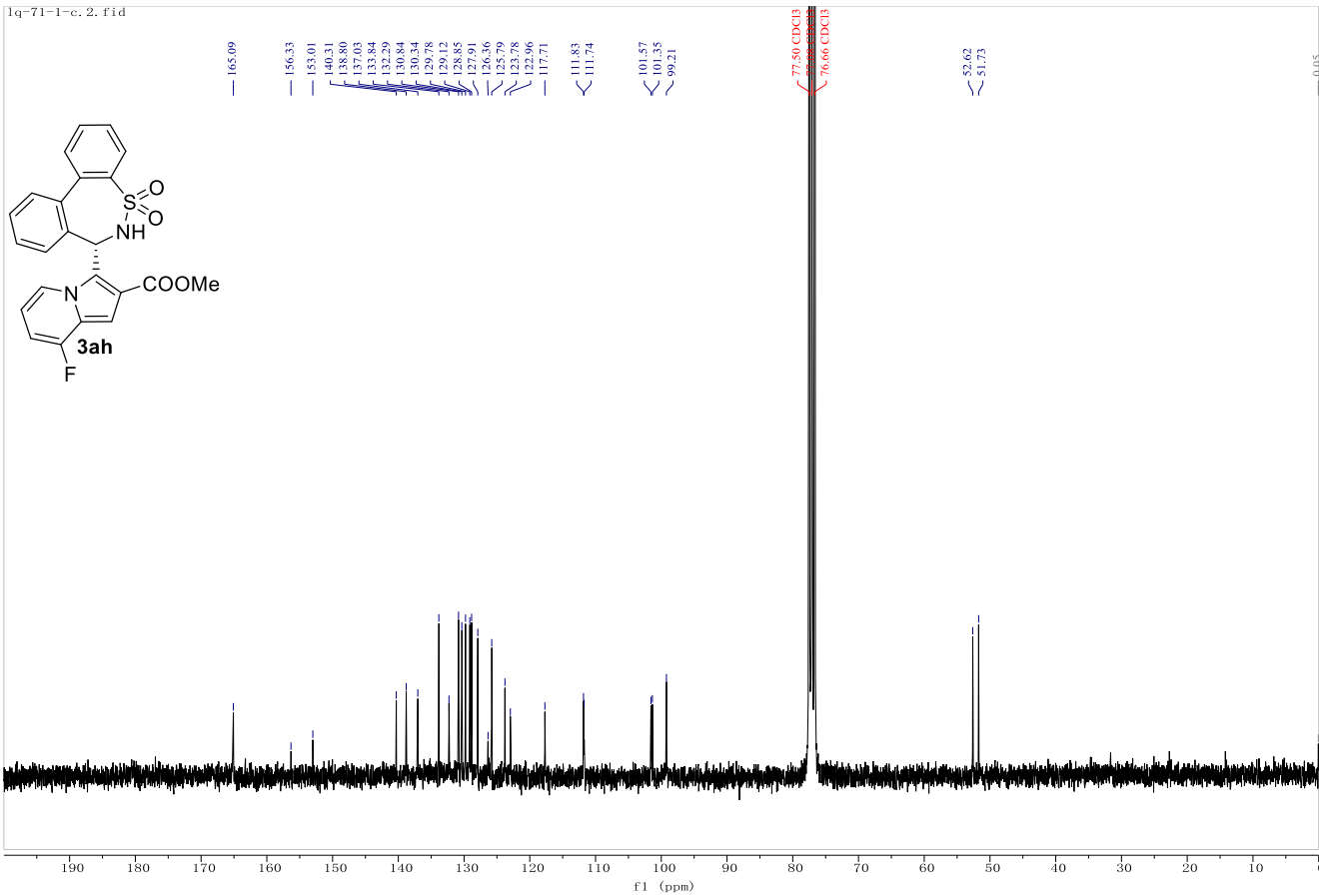
3ag, ^{13}C-NMR in $CDCl_3$



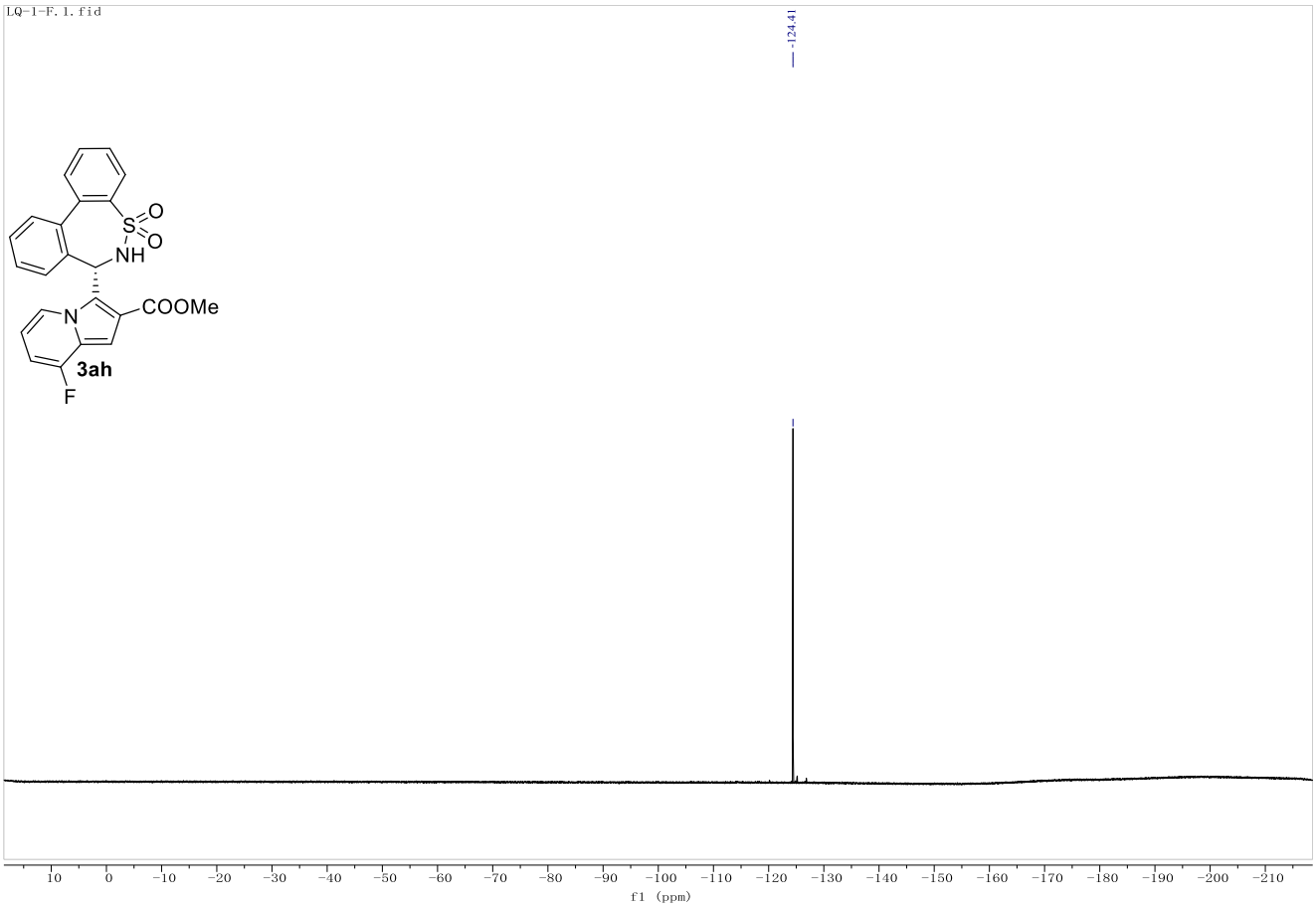
3ah, ^{1}H-NMR in $CDCl_3$



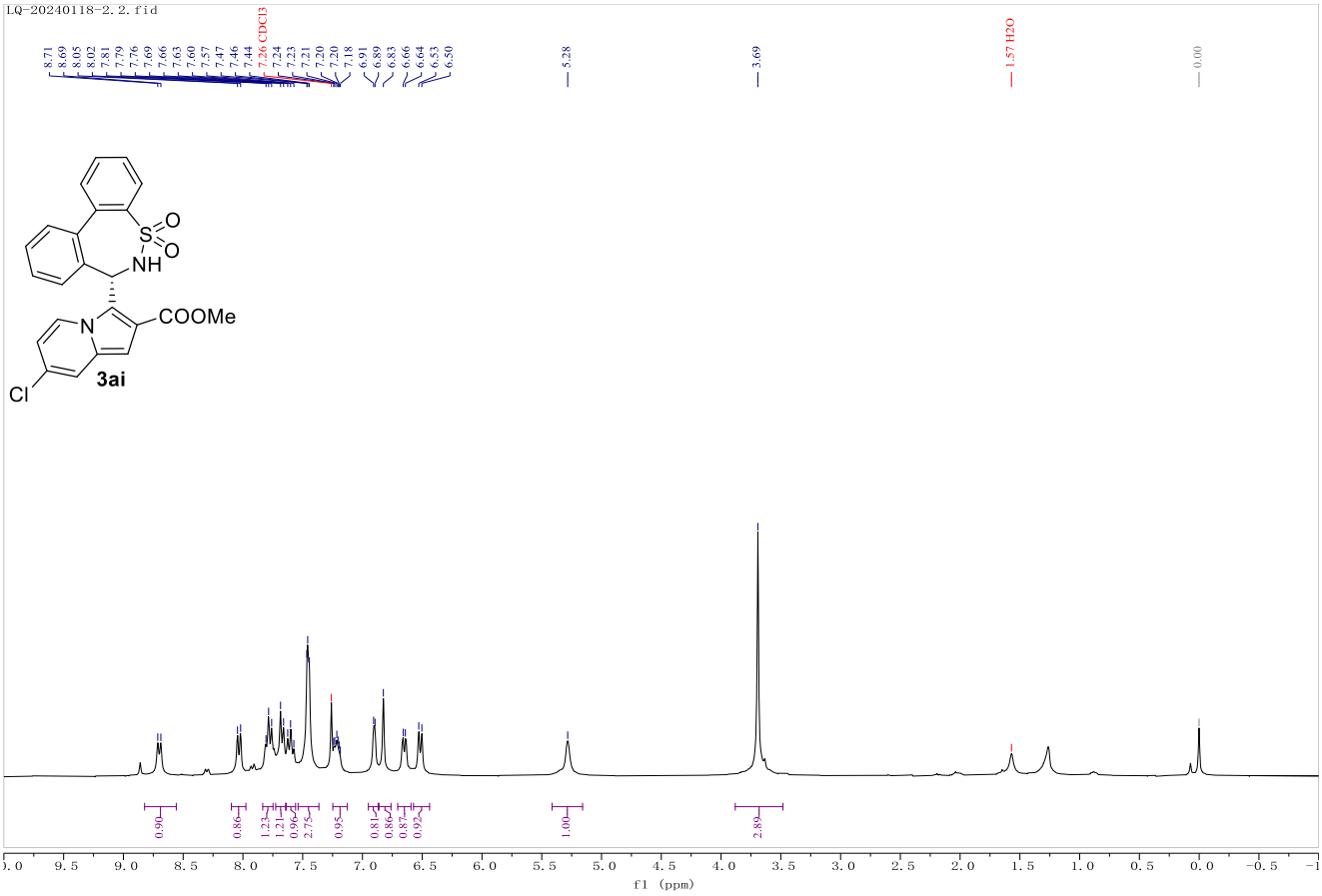
3ah, ^{13}C-NMR in $CDCl_3$



3ah, ^{19}F-NMR in $CDCl_3$



3ai, ^{1}H-NMR in $CDCl_3$



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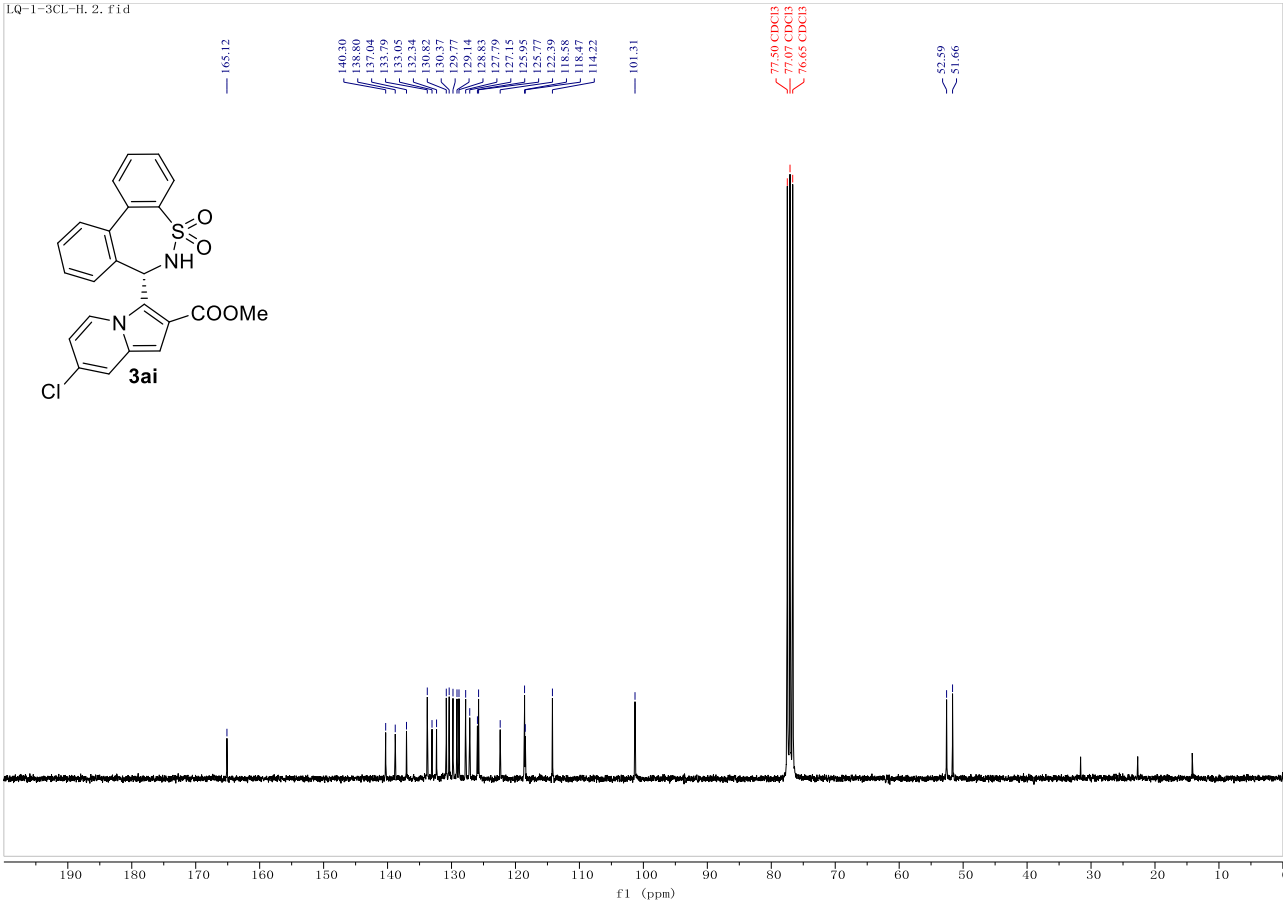

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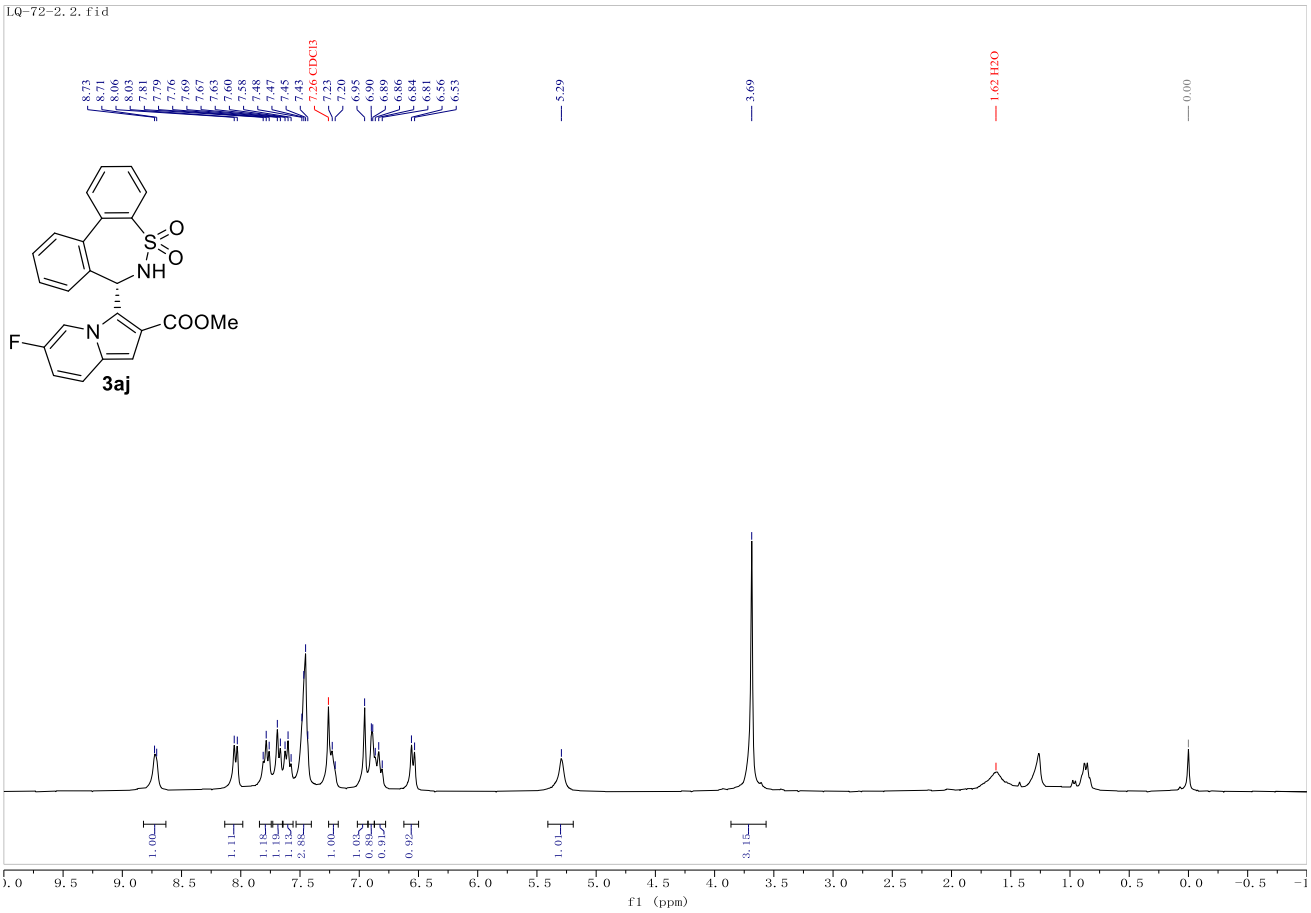
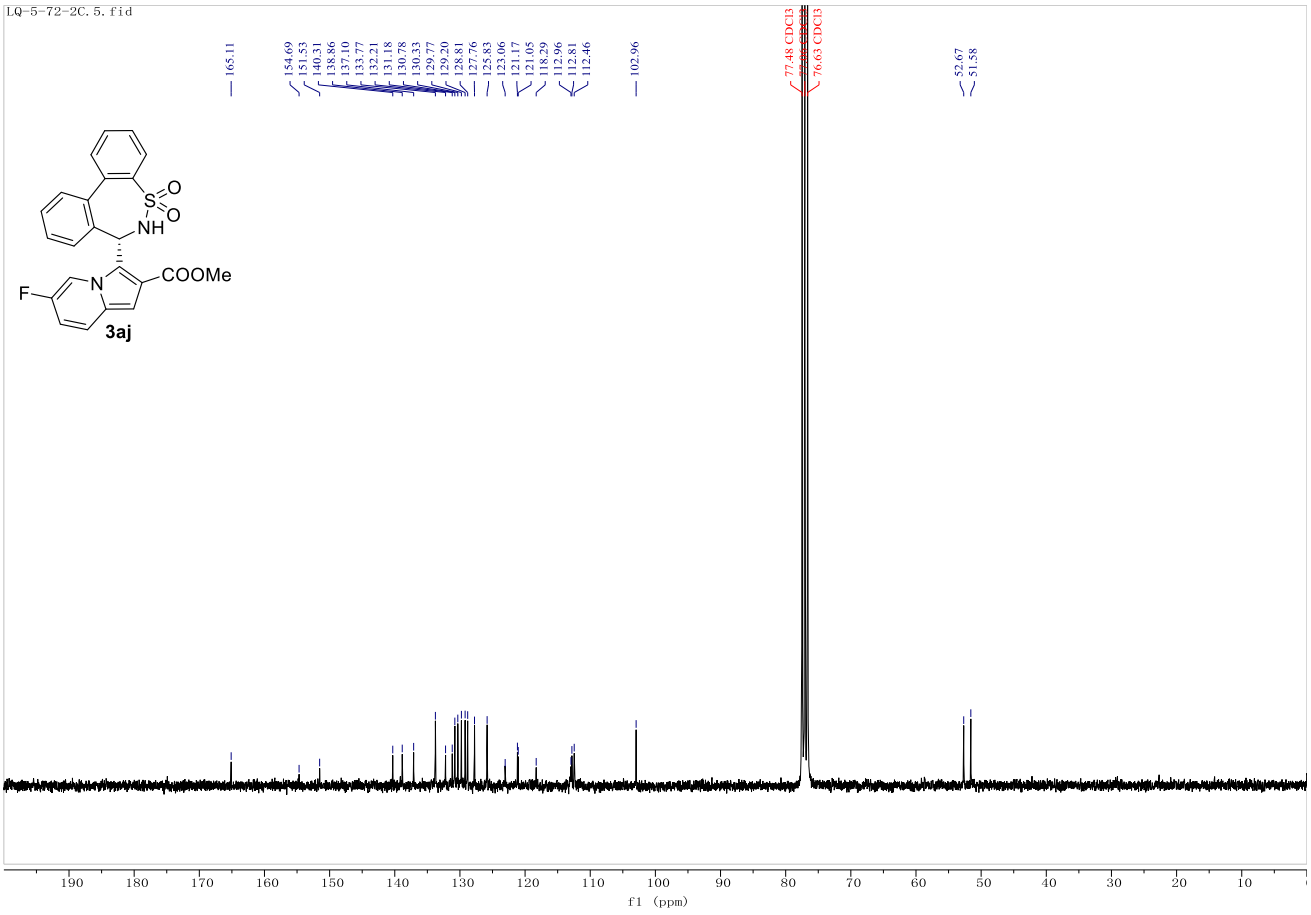
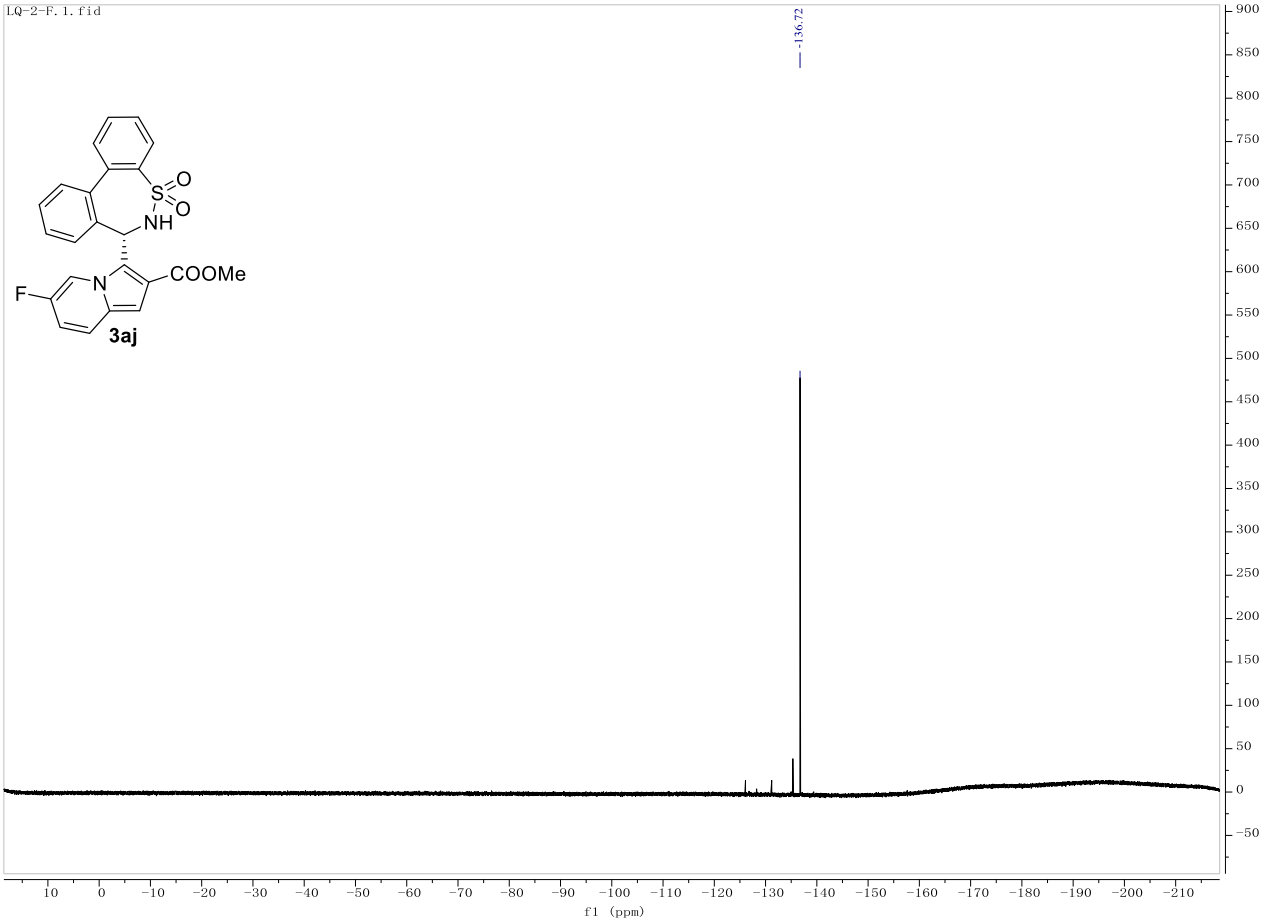


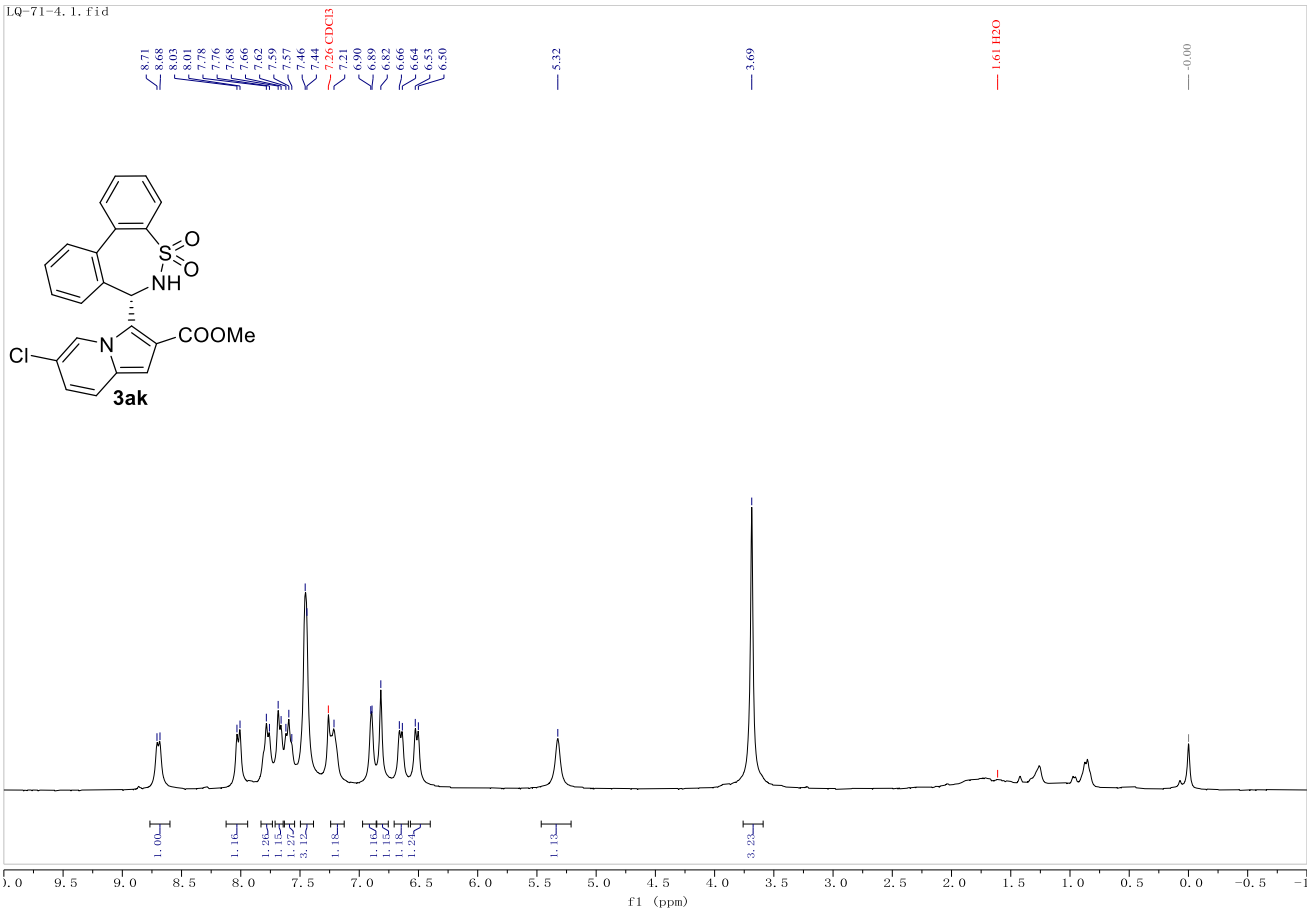
3aj, ^{13}C-NMR in $CDCl_3$



3aj, ^{19}F-NMR in $CDCl_3$



3ak, ^{1}H-NMR in $CDCl_3$



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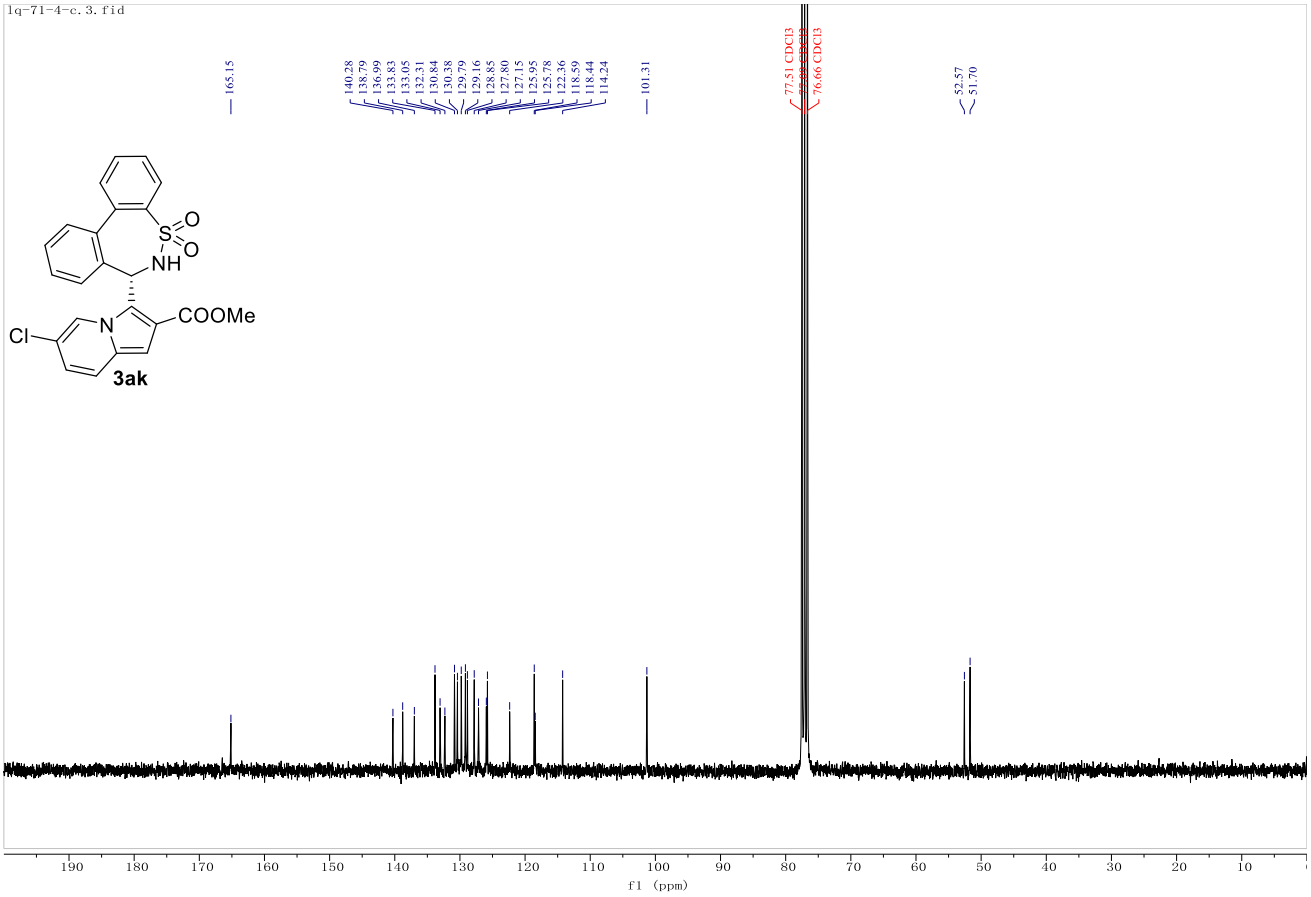

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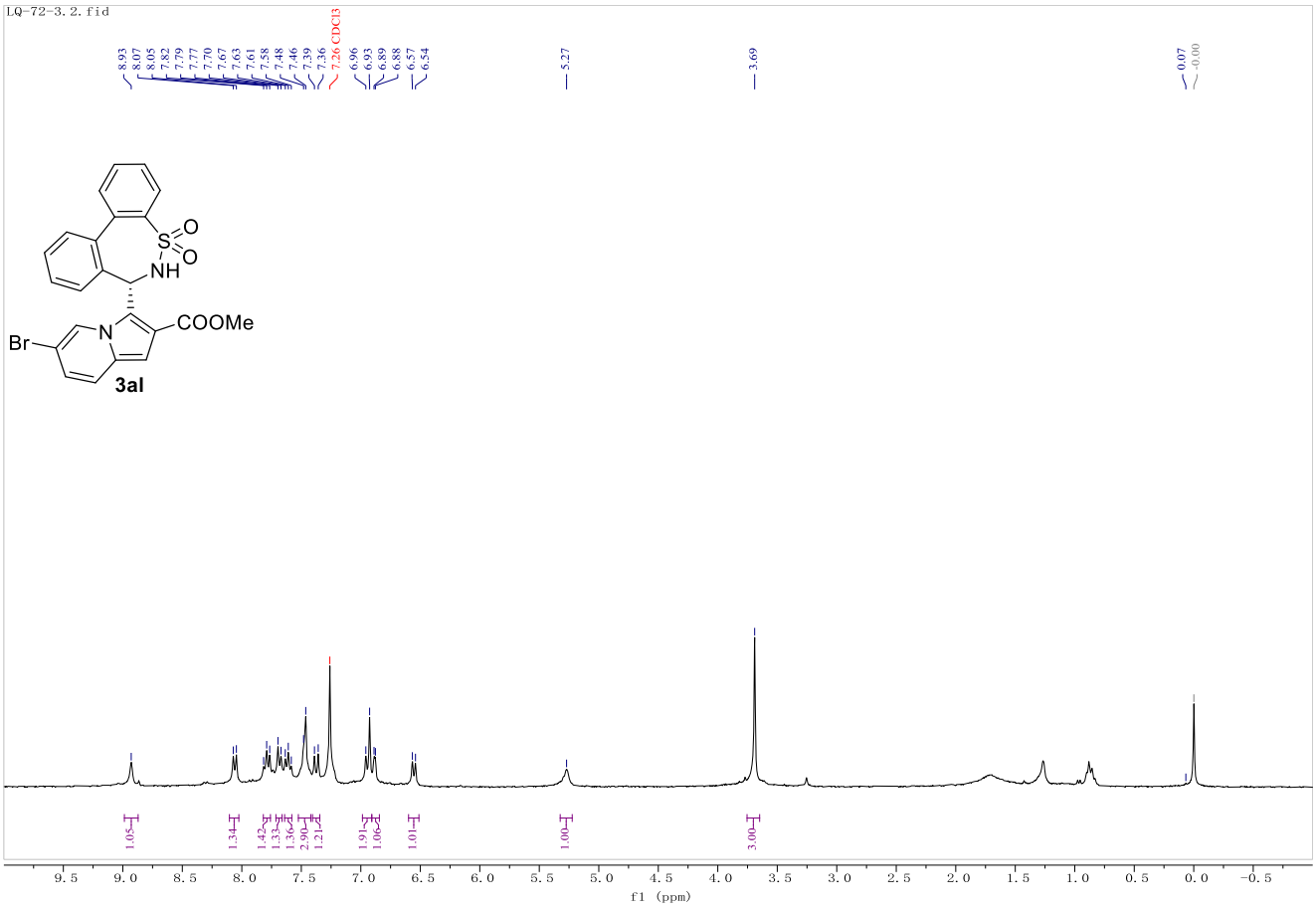
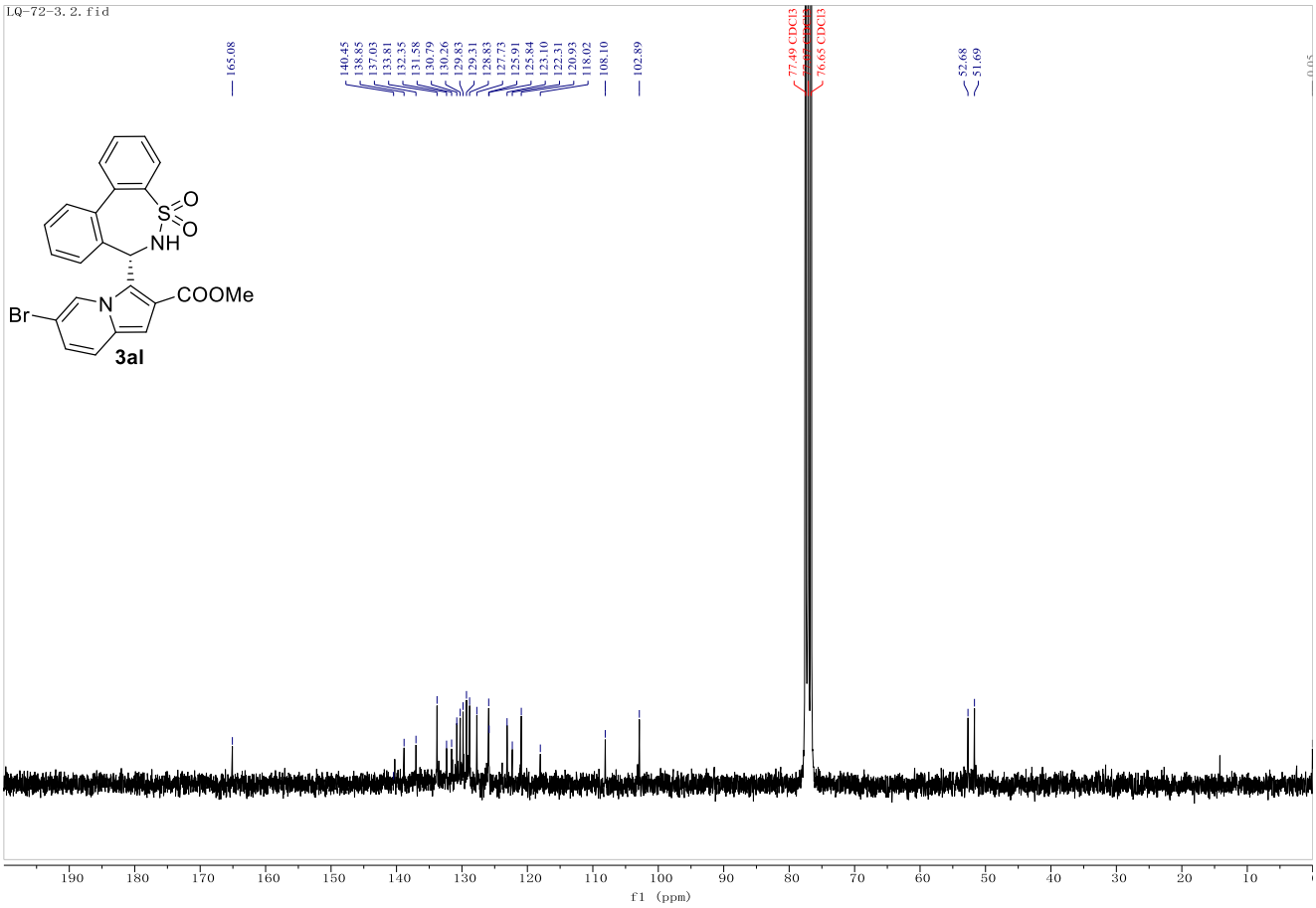
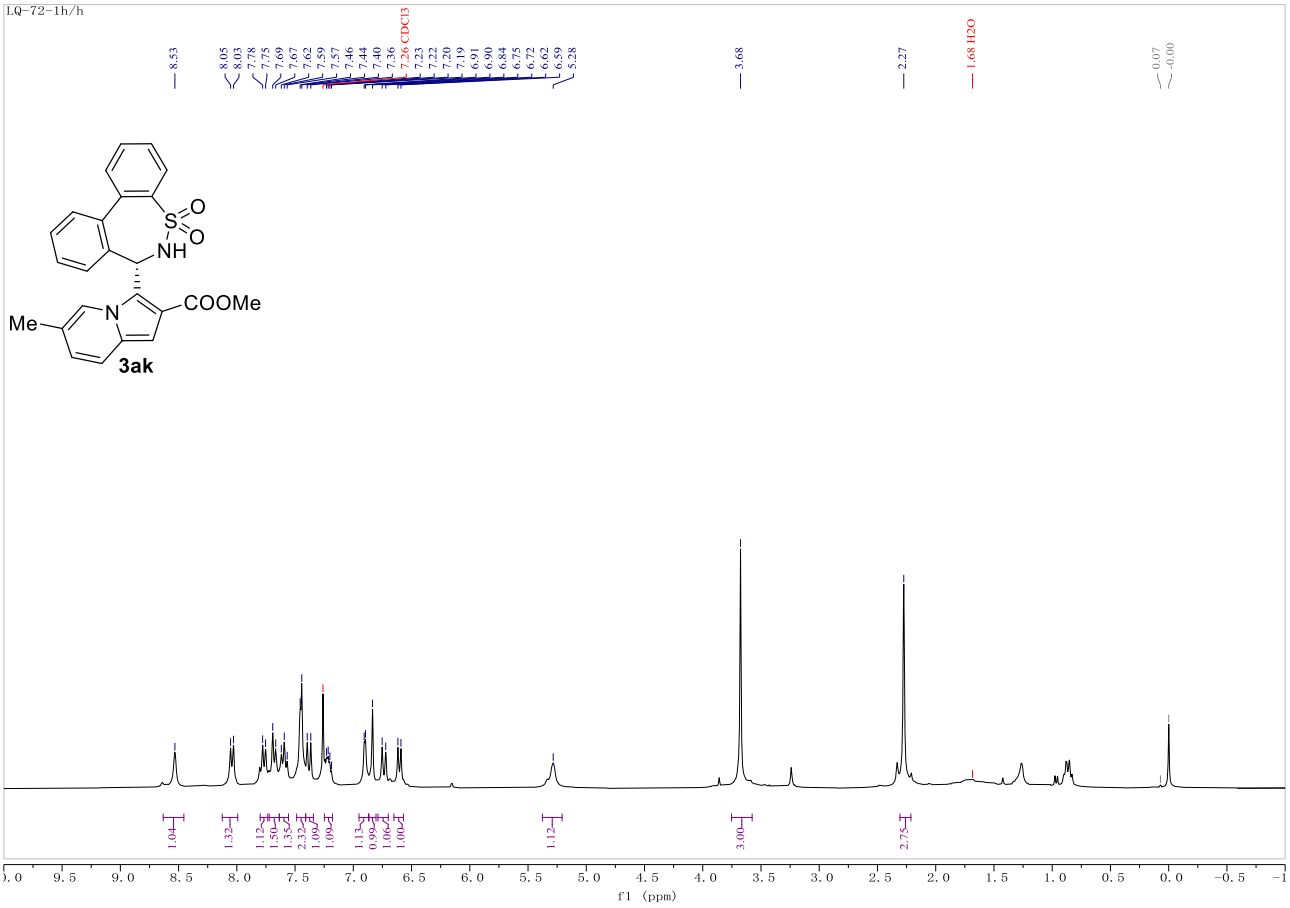


3al, ^{13}C-NMR in $CDCl_3$



3am, ^{1}H-NMR in $CDCl_3$



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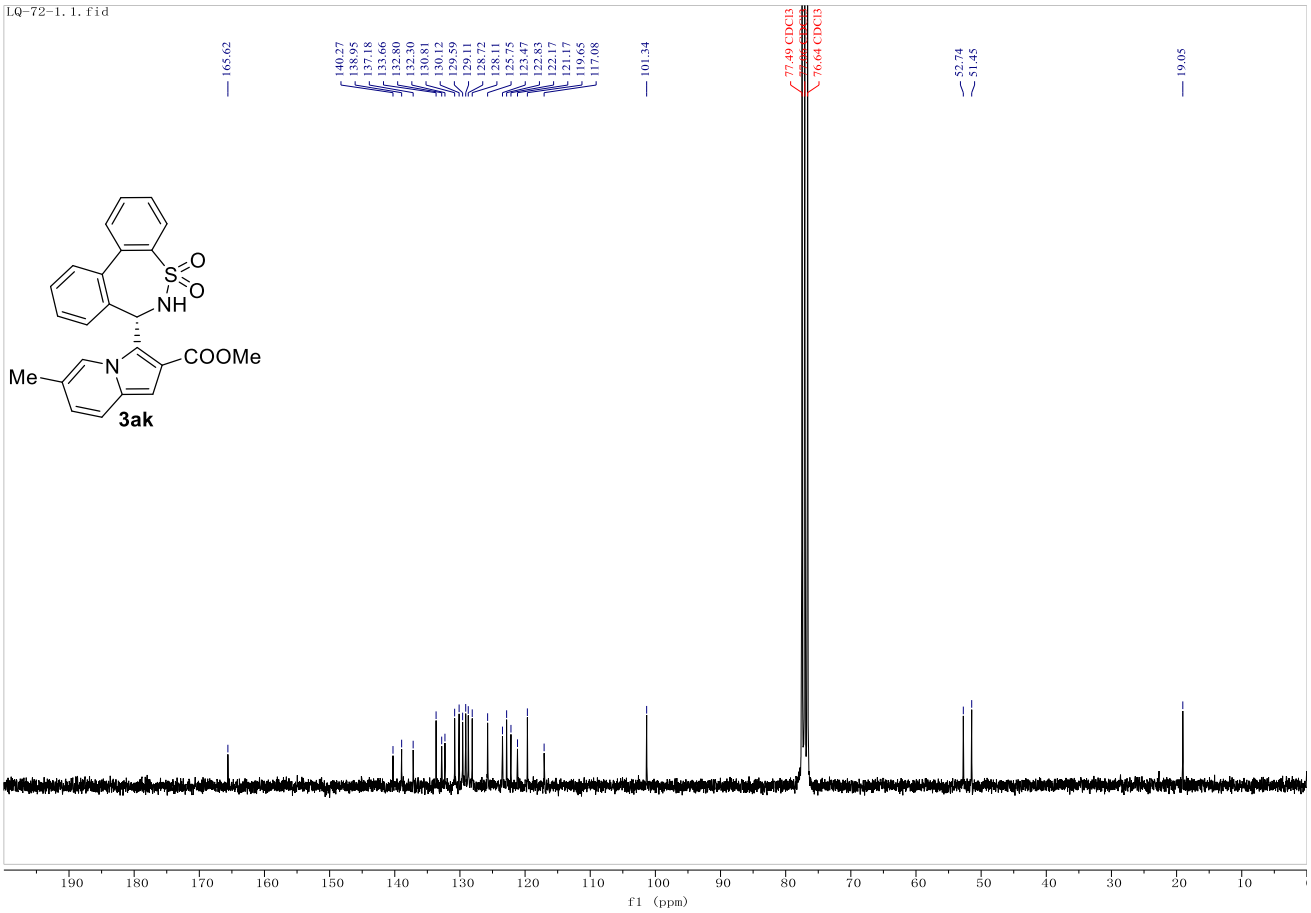
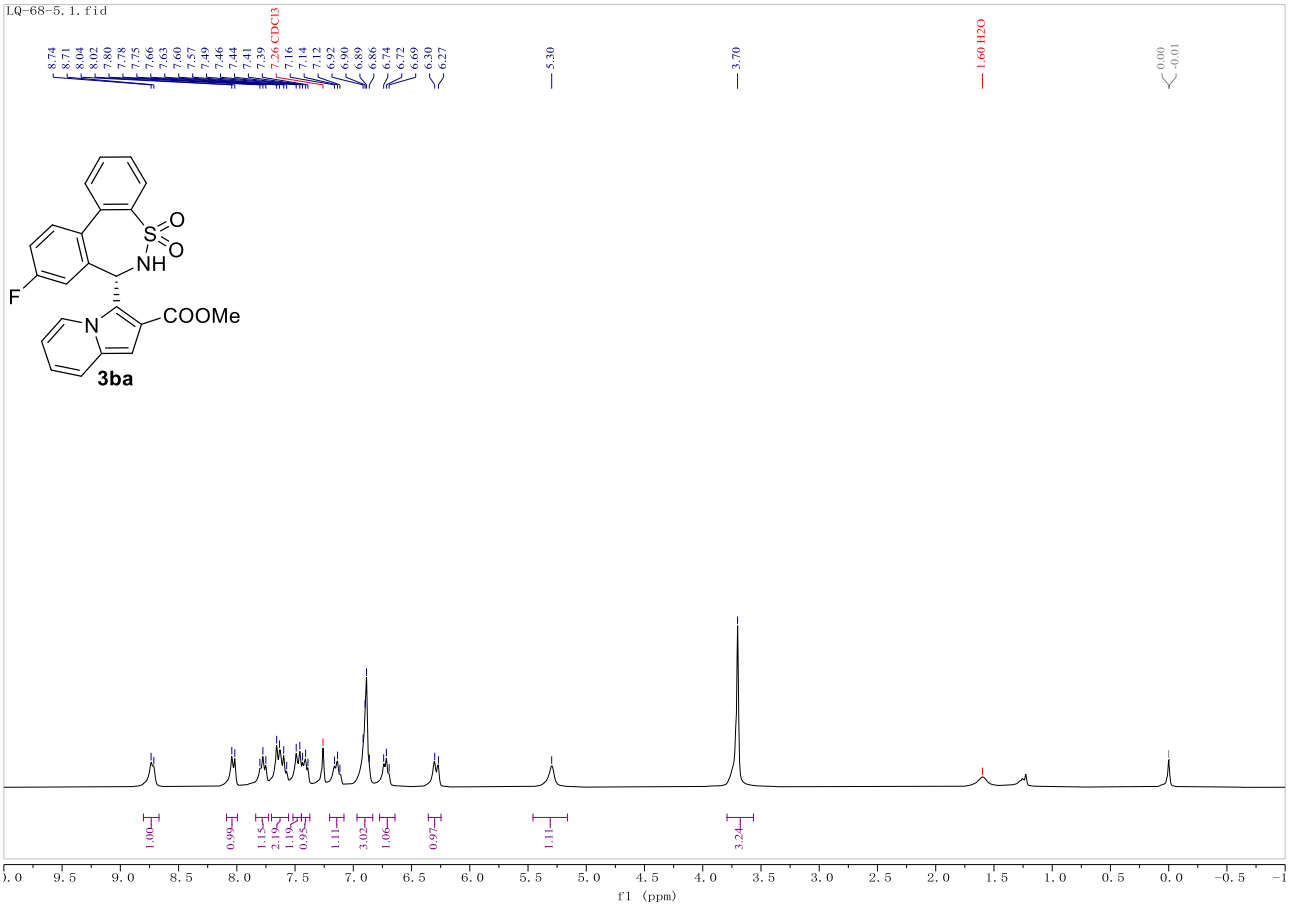
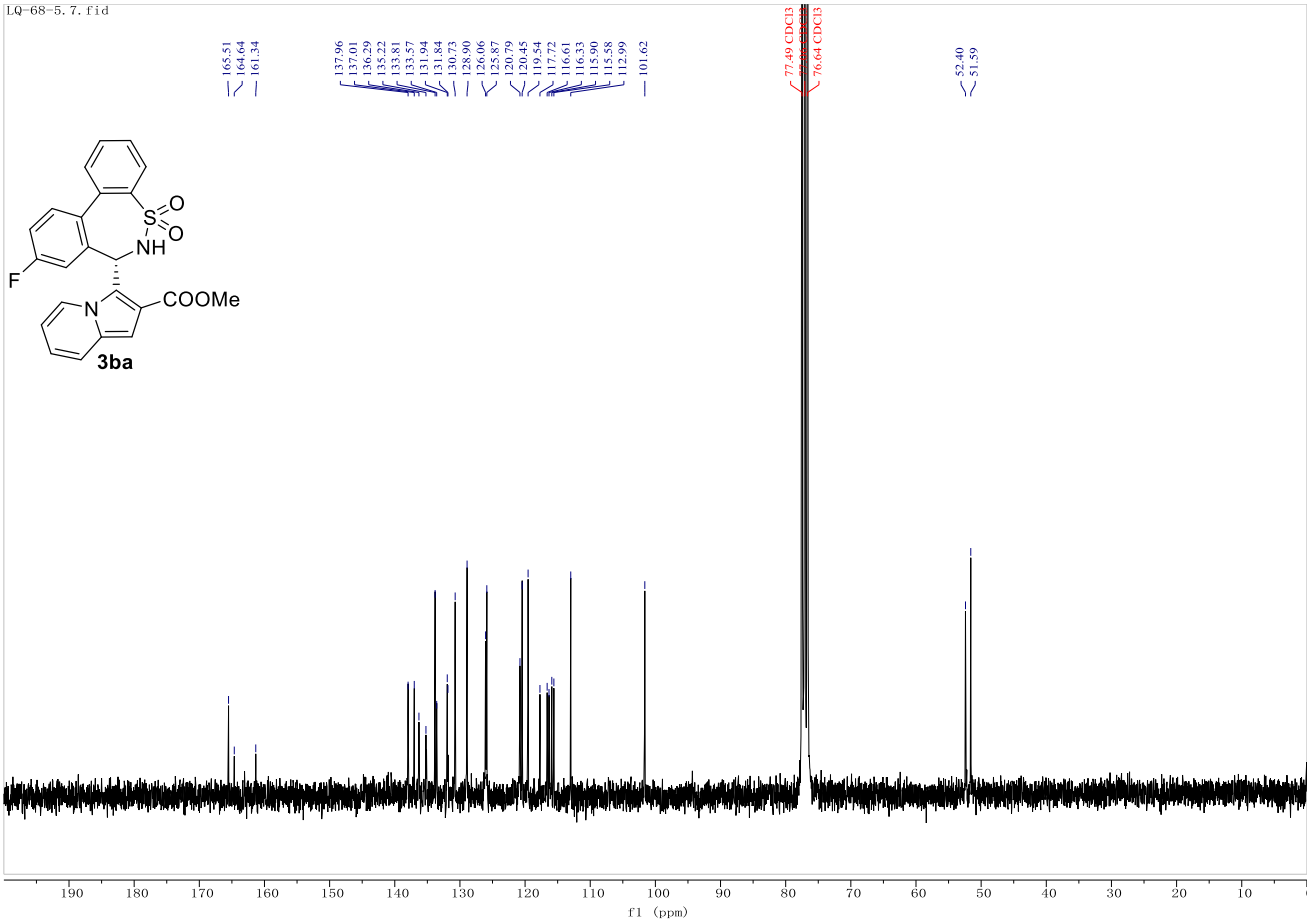


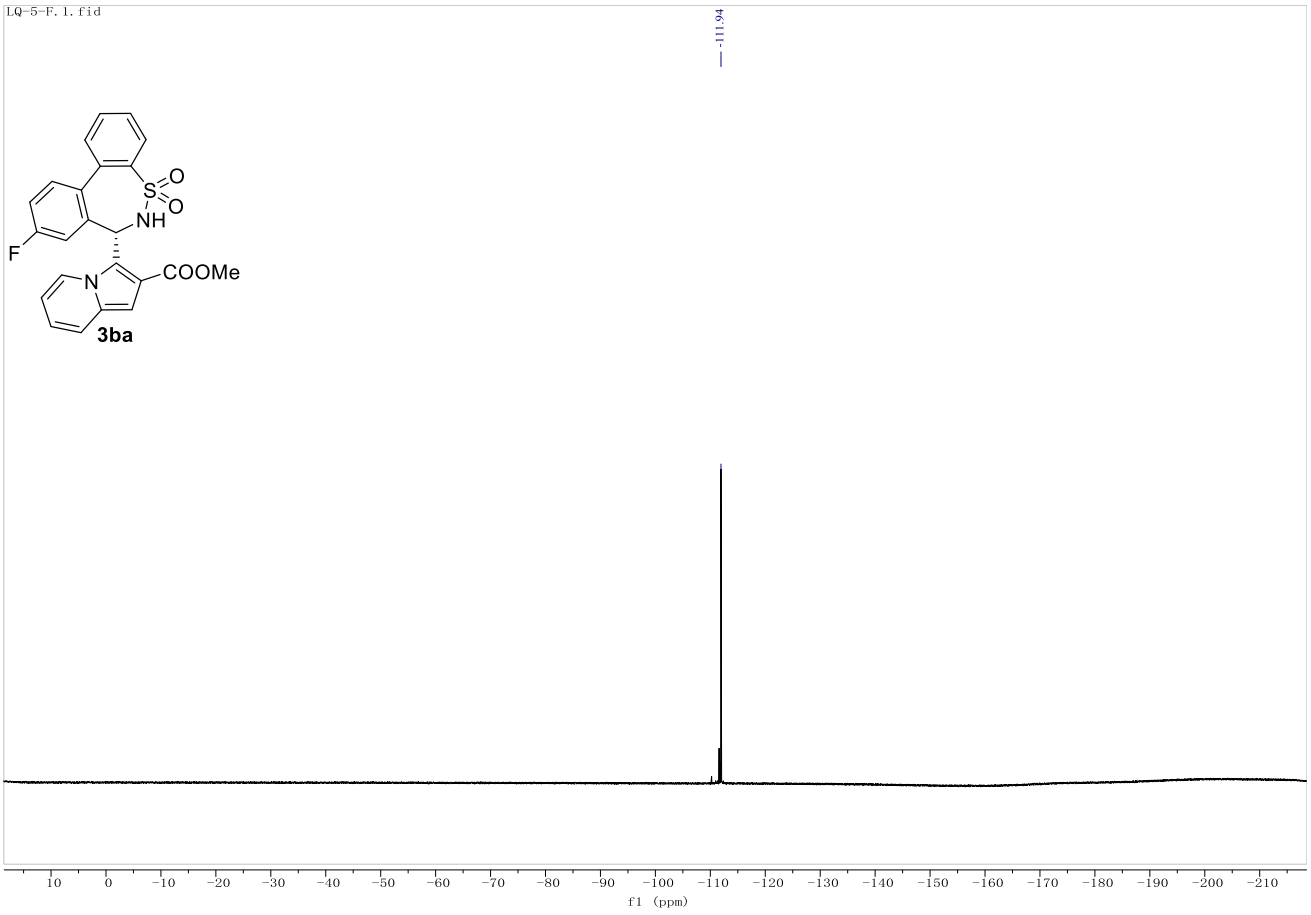
3ba, ^{1}H-NMR in $CDCl_3$



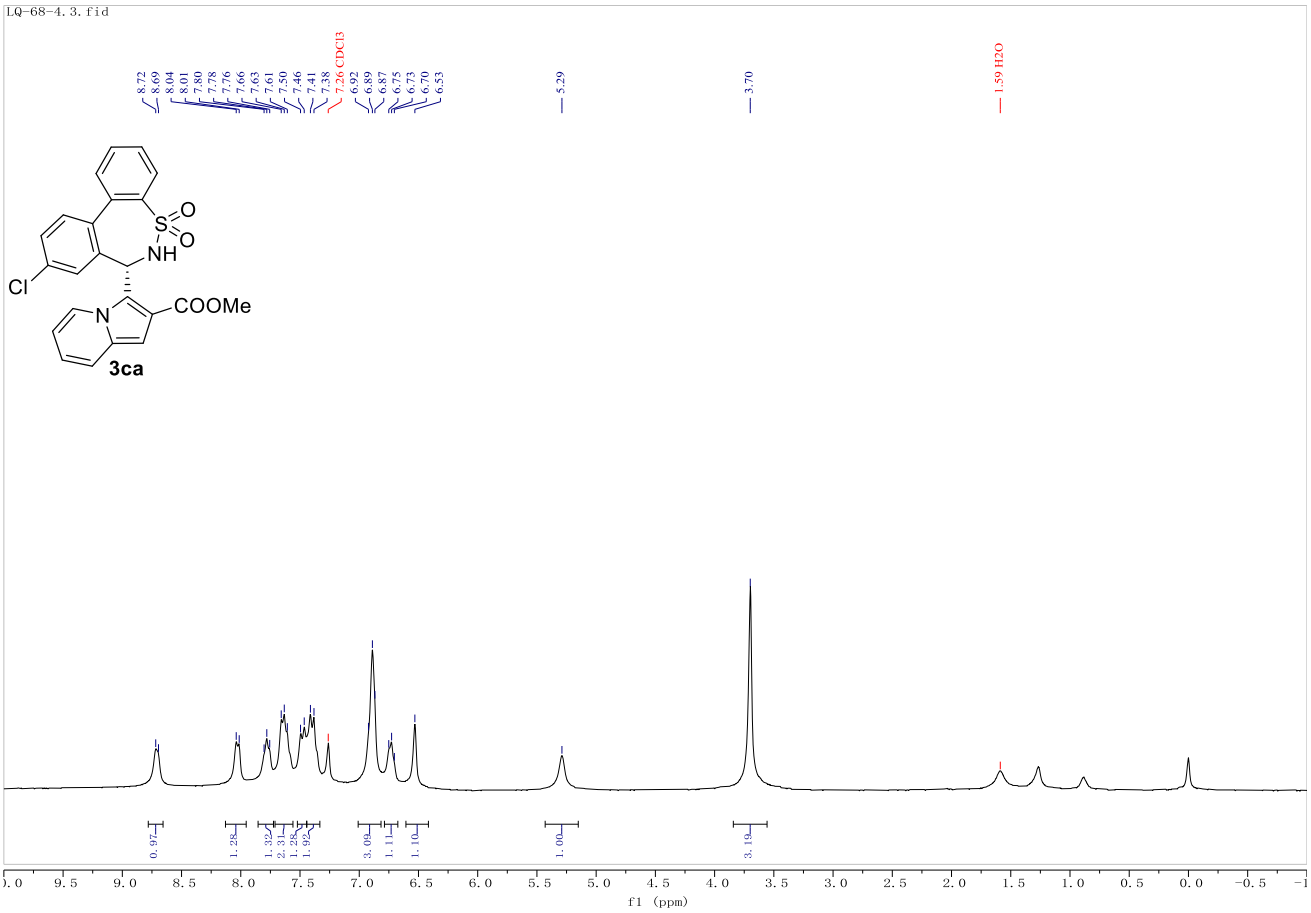
3ba, ^{13}C-NMR in $CDCl_3$



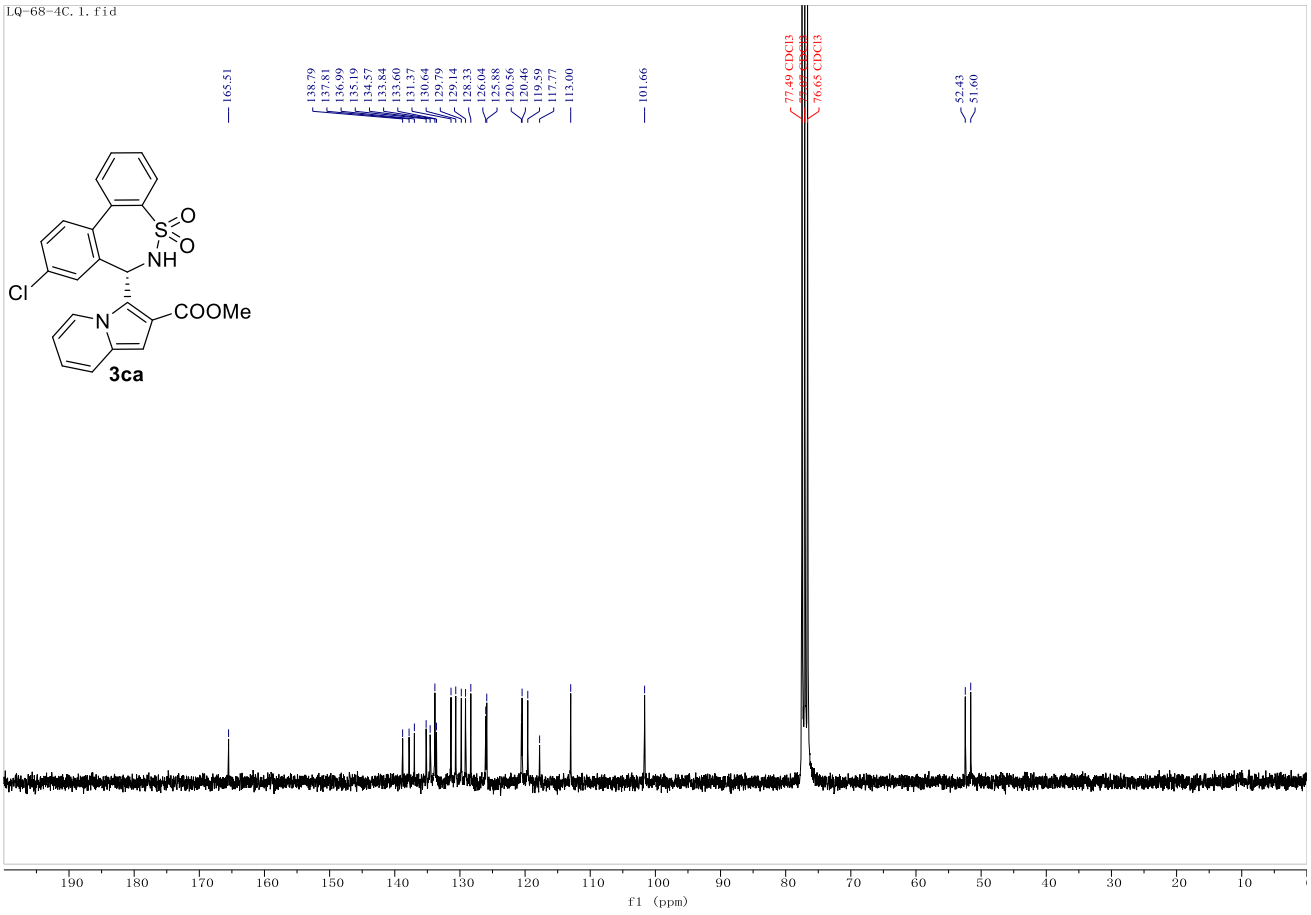
3ba, ^{19}F-NMR in $CDCl_3$



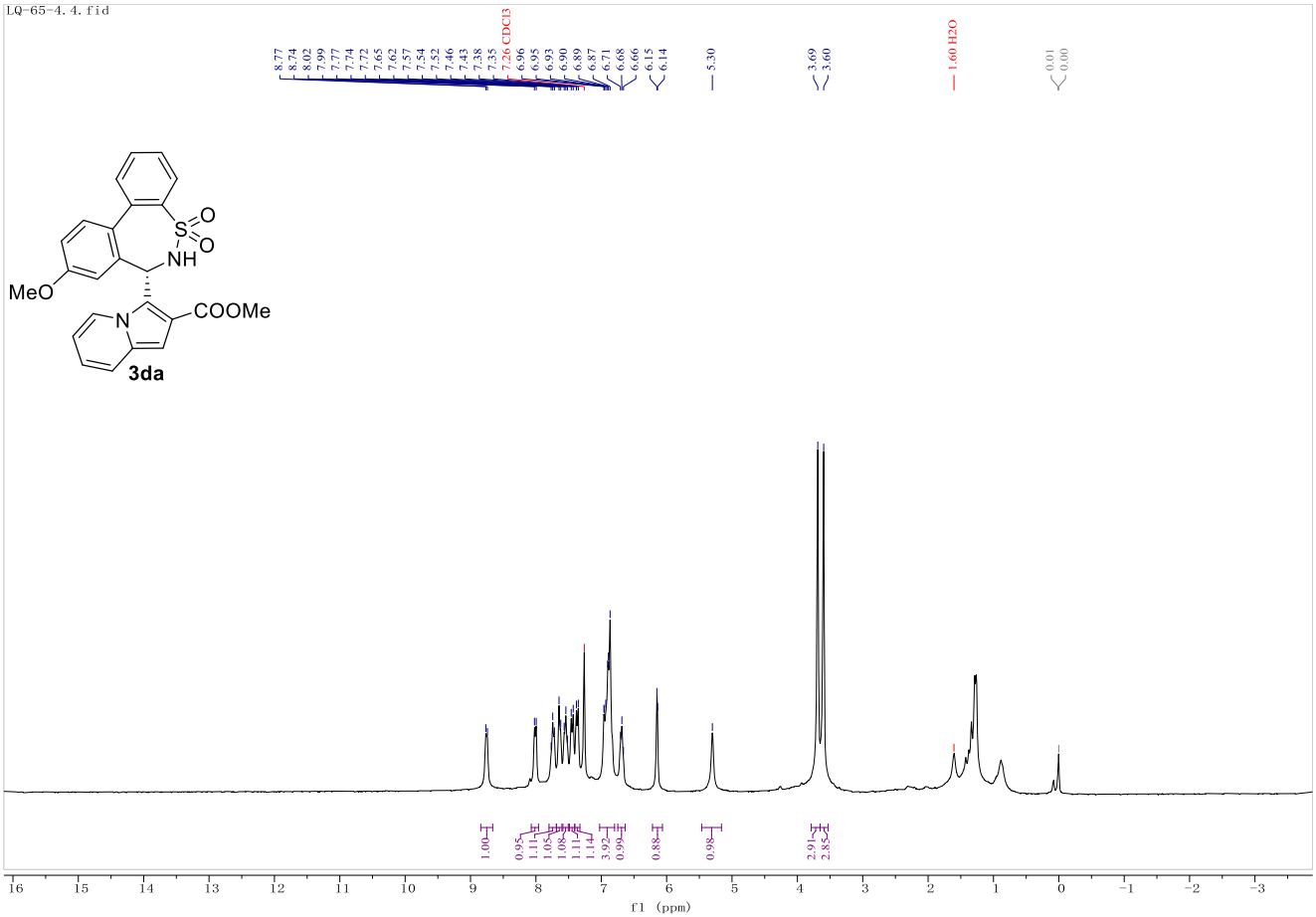
3ca, ^{1}H-NMR in $CDCl_3$



3ca, ^{13}C-NMR in $CDCl_3$



3da, ^{1}H-NMR in $CDCl_3$



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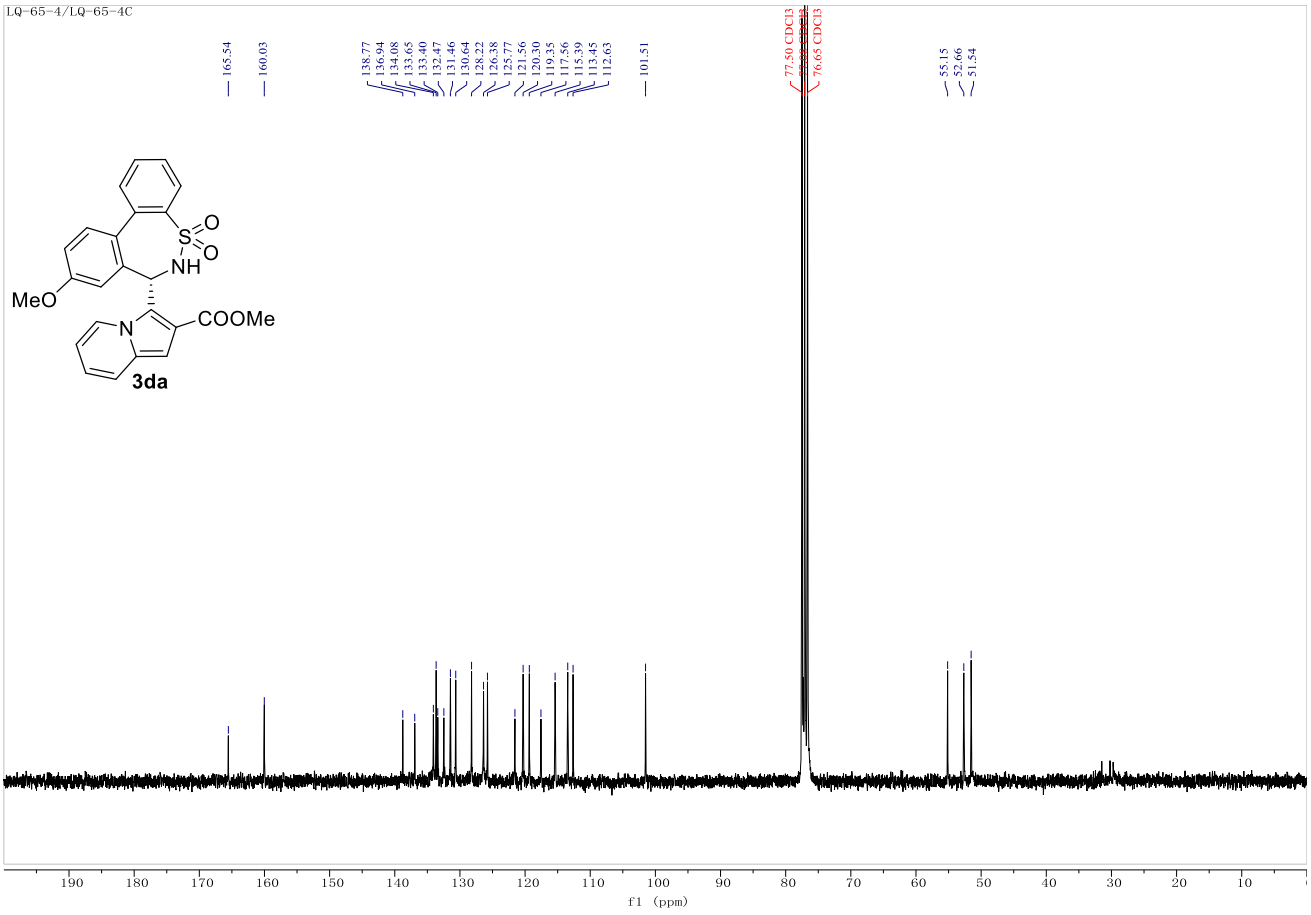

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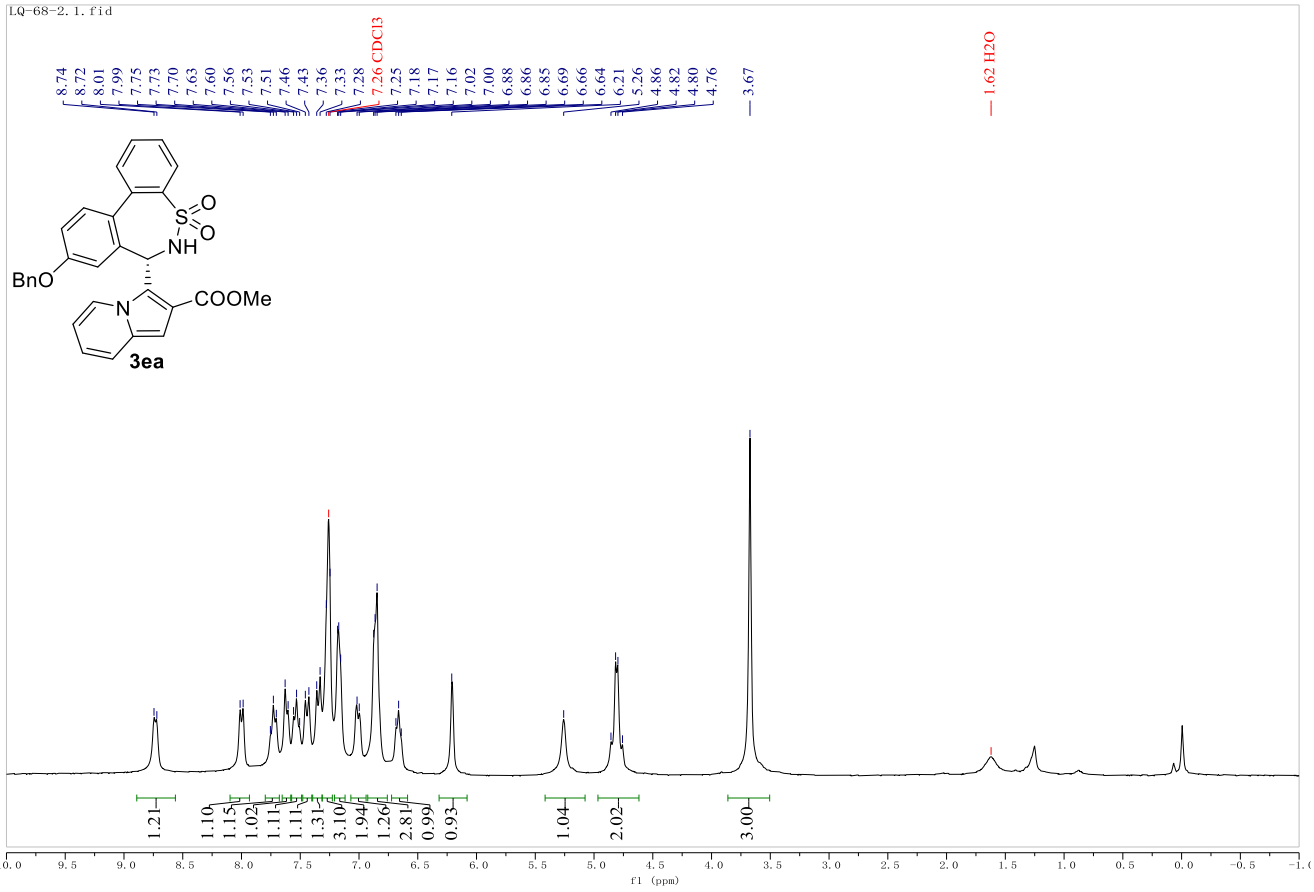
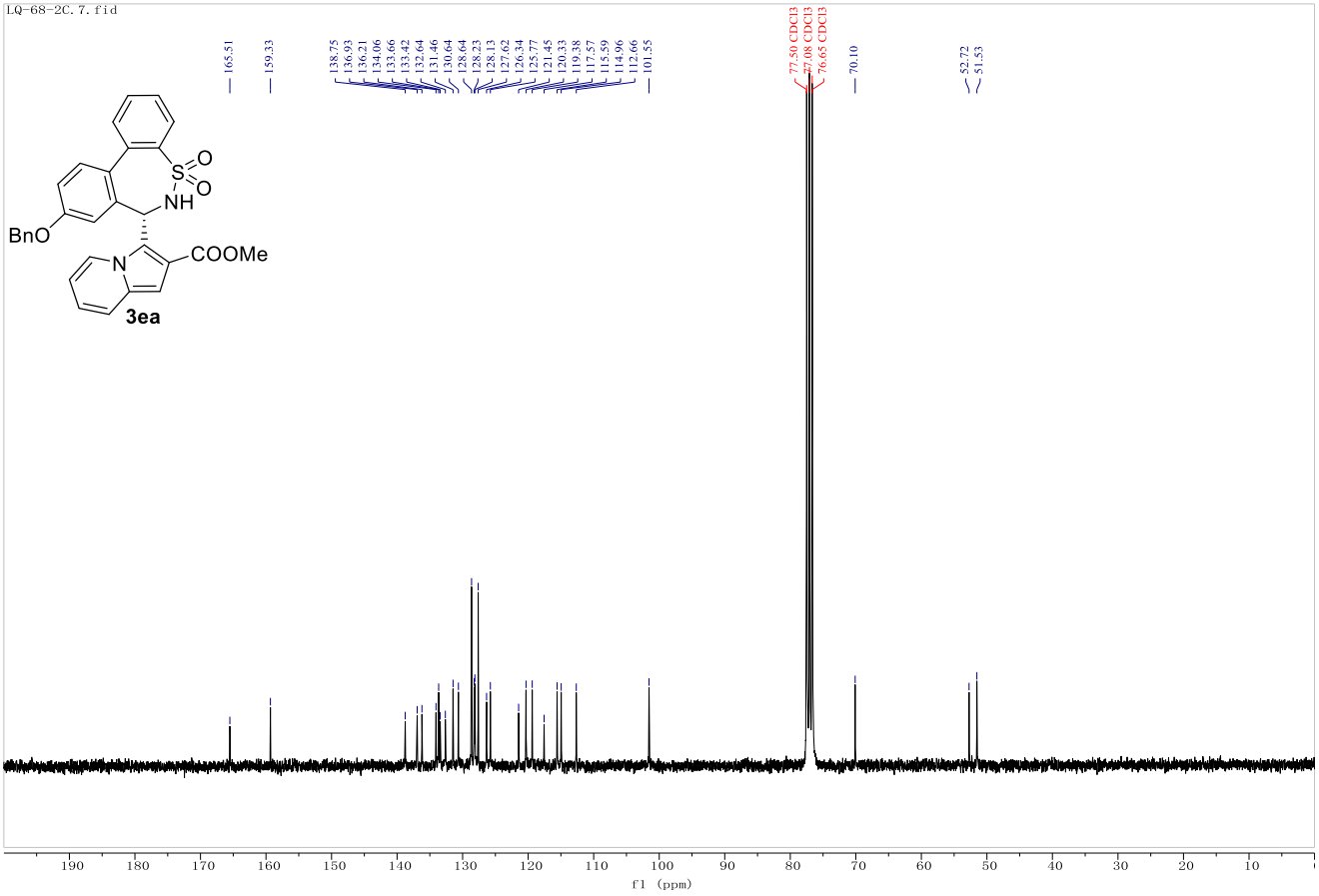
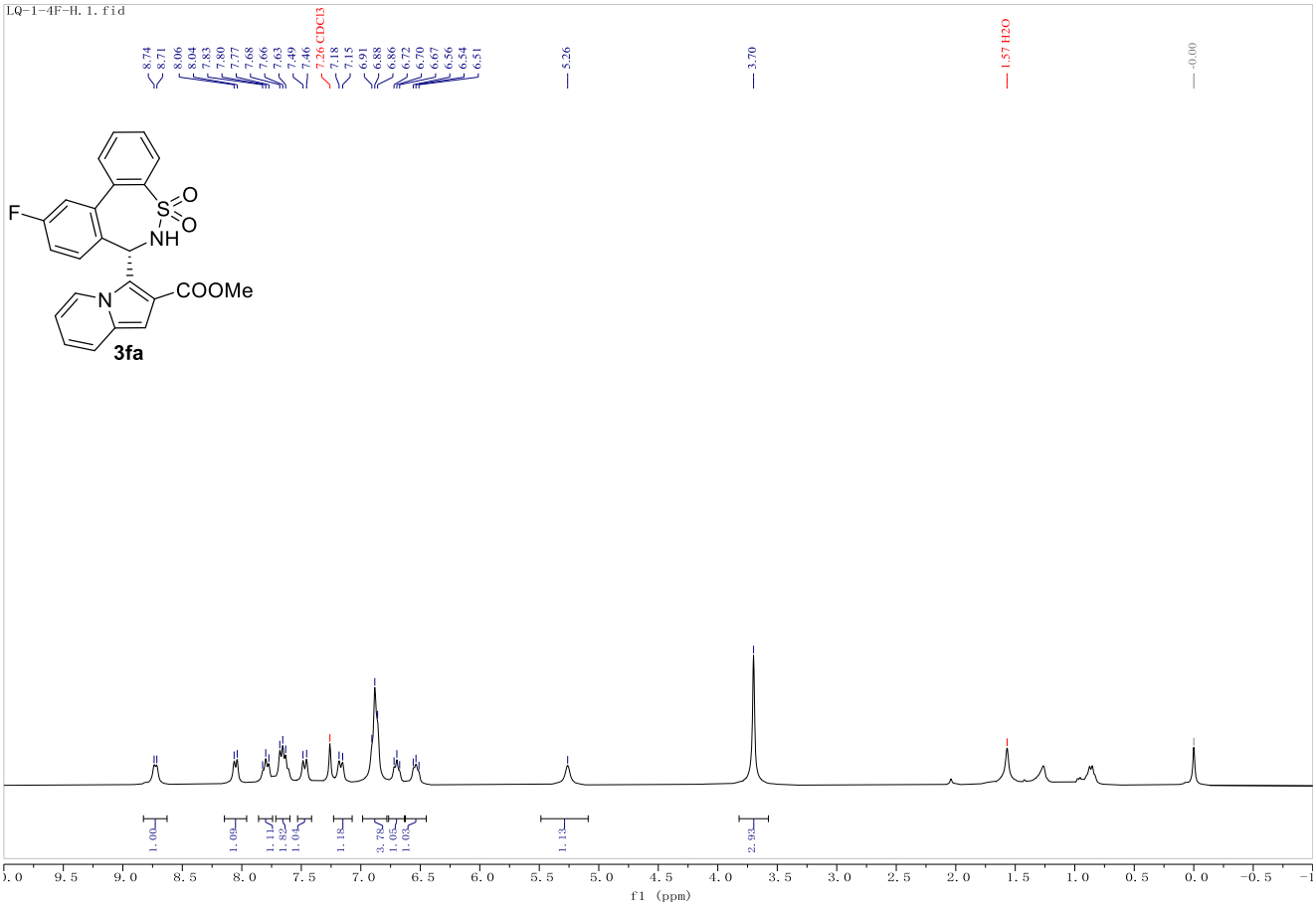


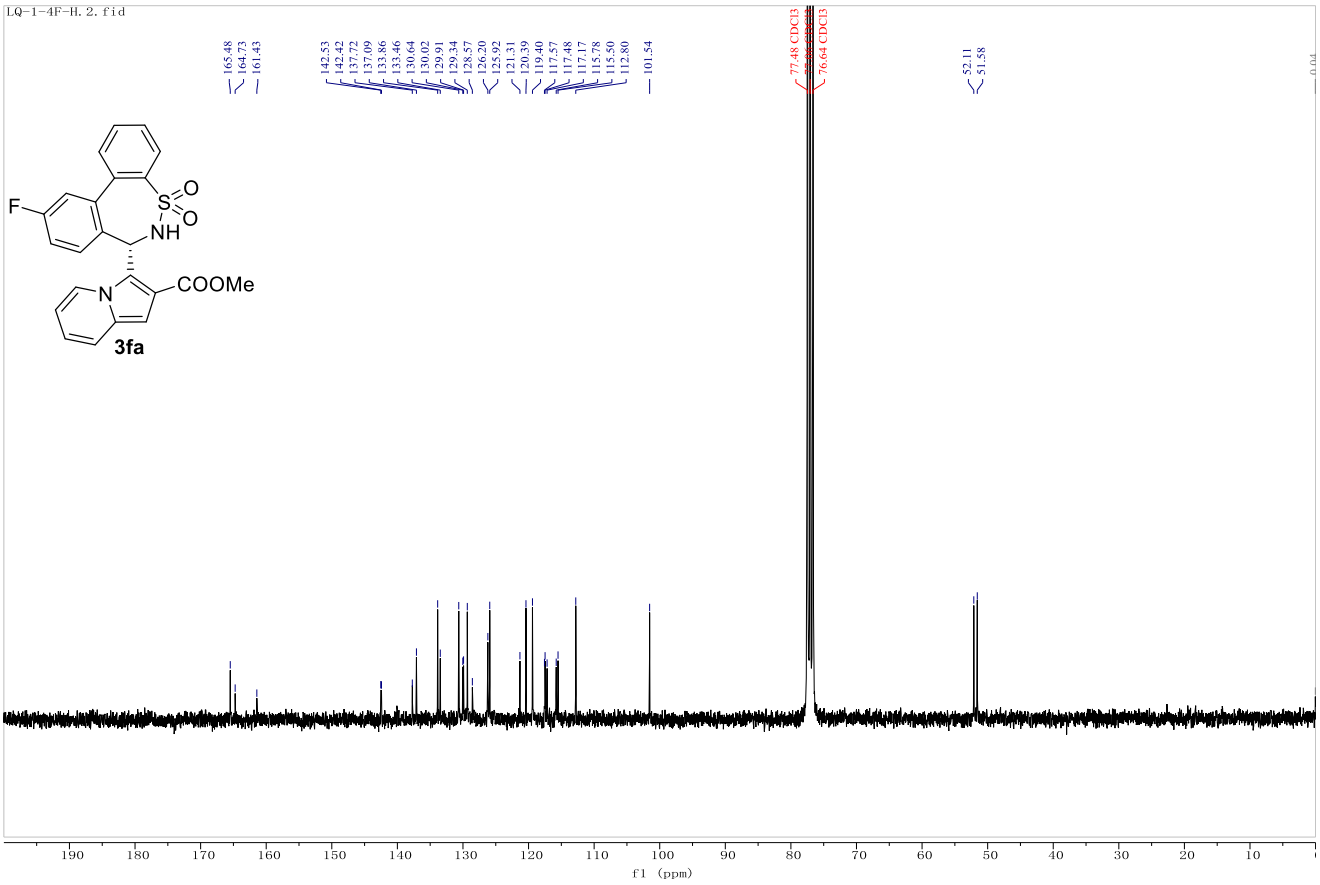
3ea, ^{13}C-NMR in $CDCl_3$



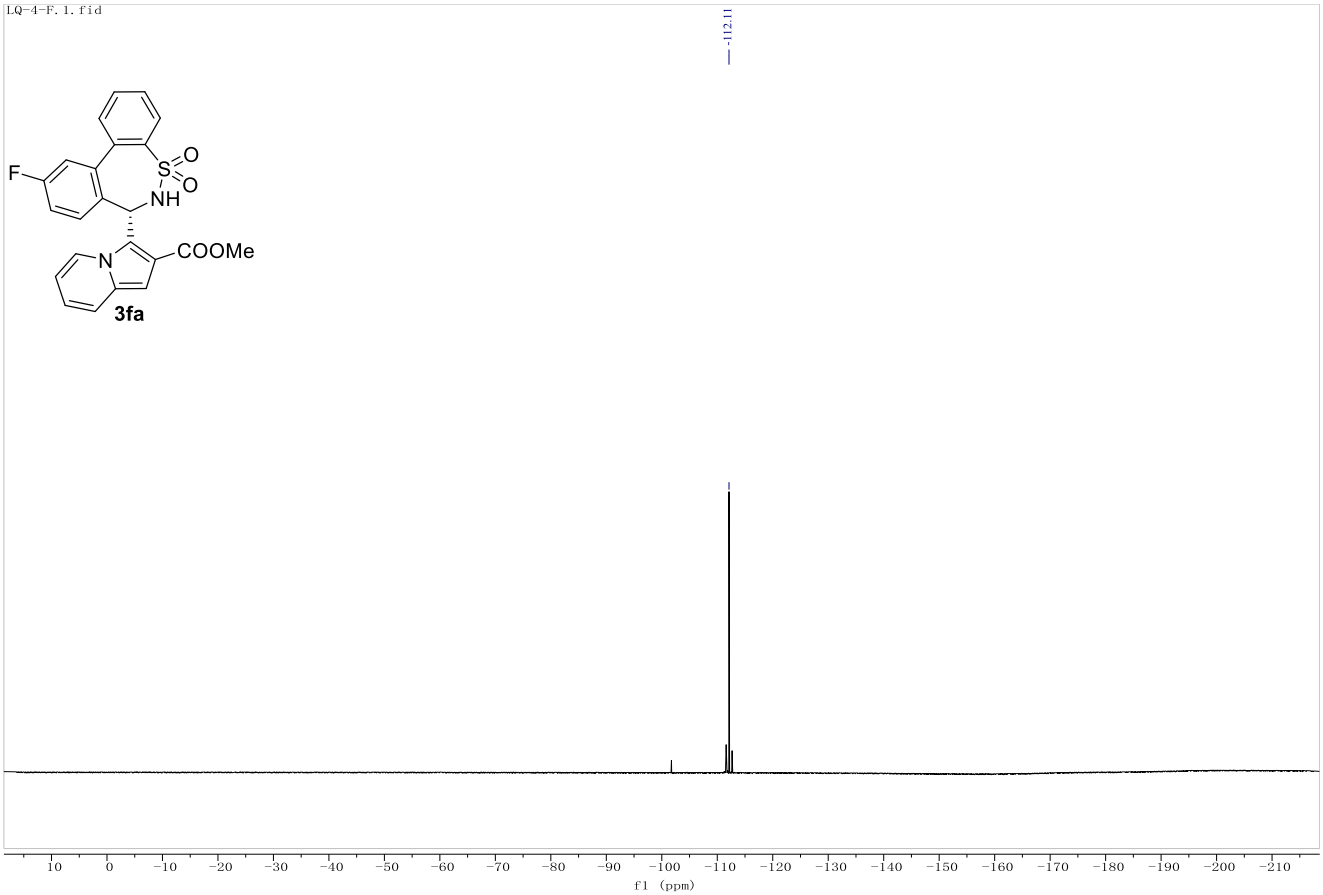
3fa, ^{1}H-NMR in $CDCl_3$



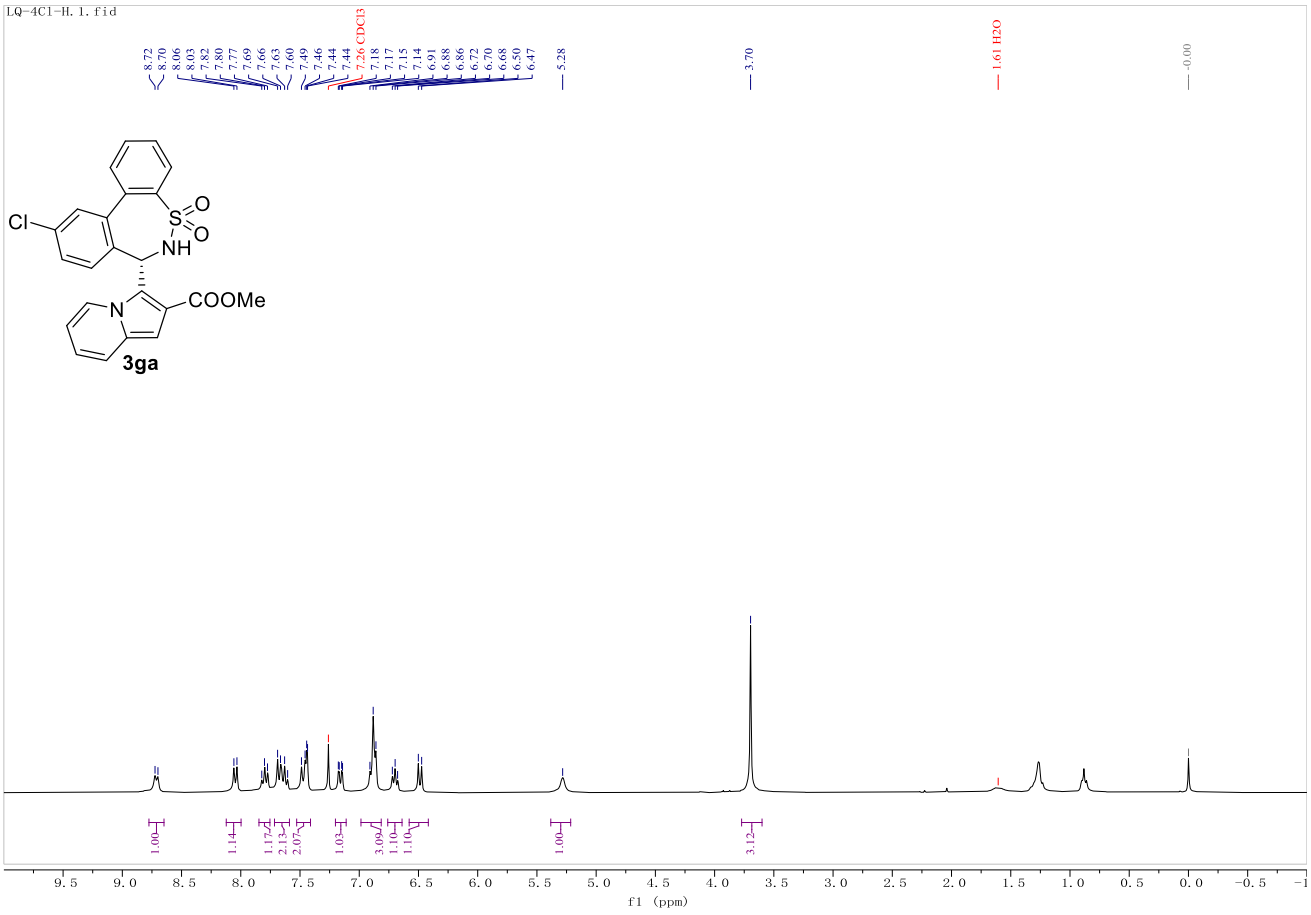
3fa, ^{13}C-NMR in $CDCl_3$



3fa, ^{19}F-NMR in $CDCl_3$



3ga, ^{1}H-NMR in $CDCl_3$



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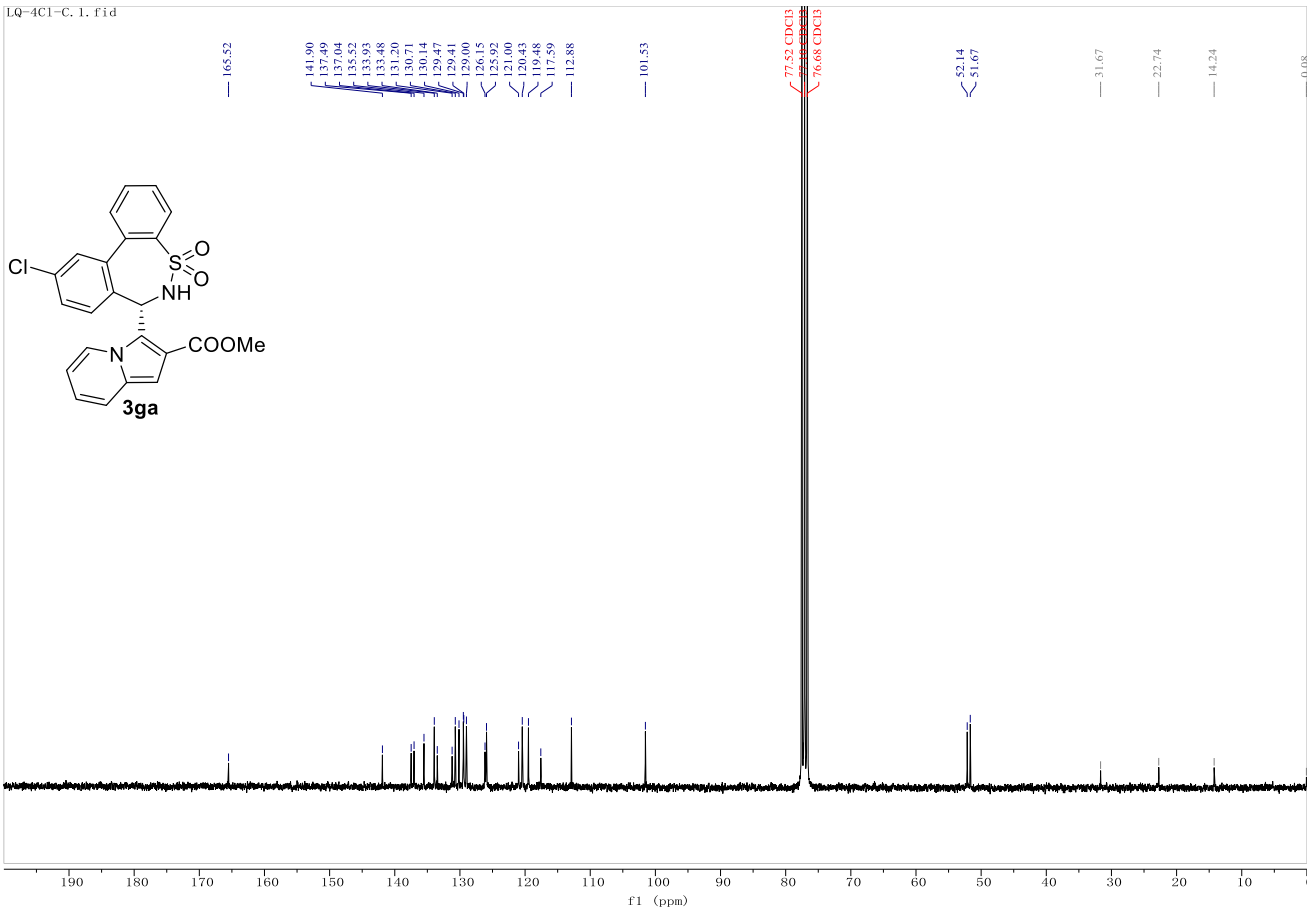
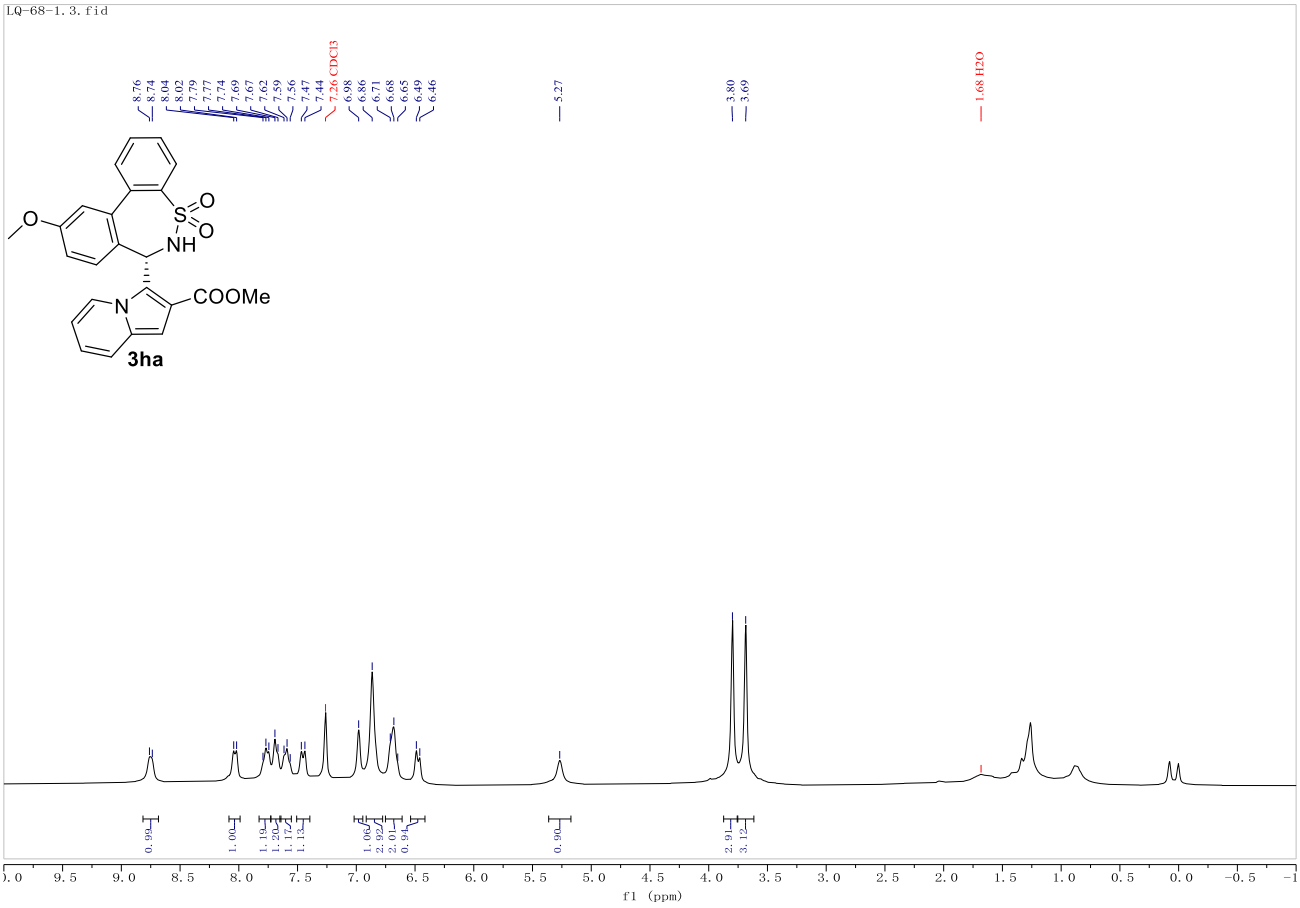


3ha, ^{1}H-NMR in $CDCl_3$



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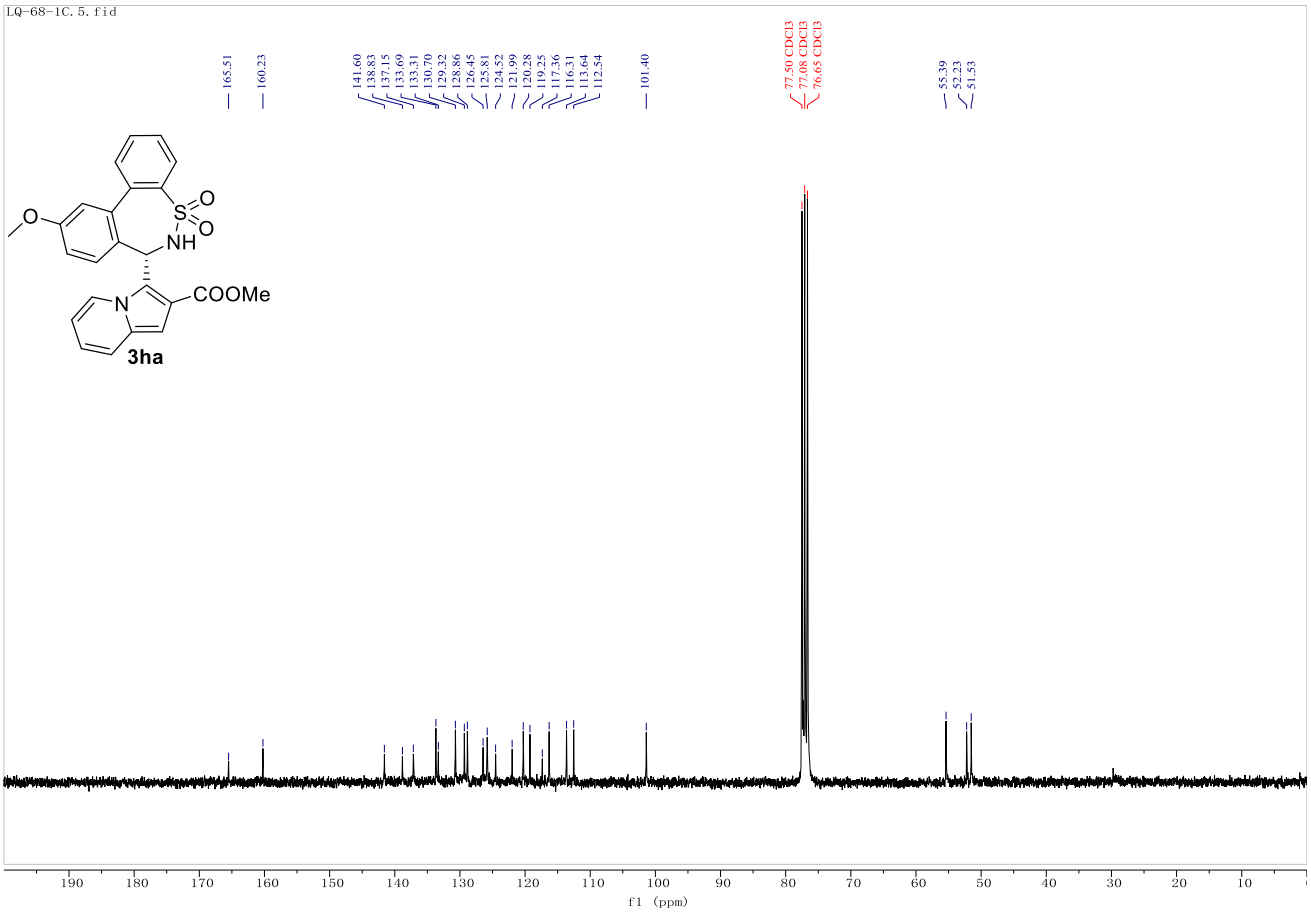
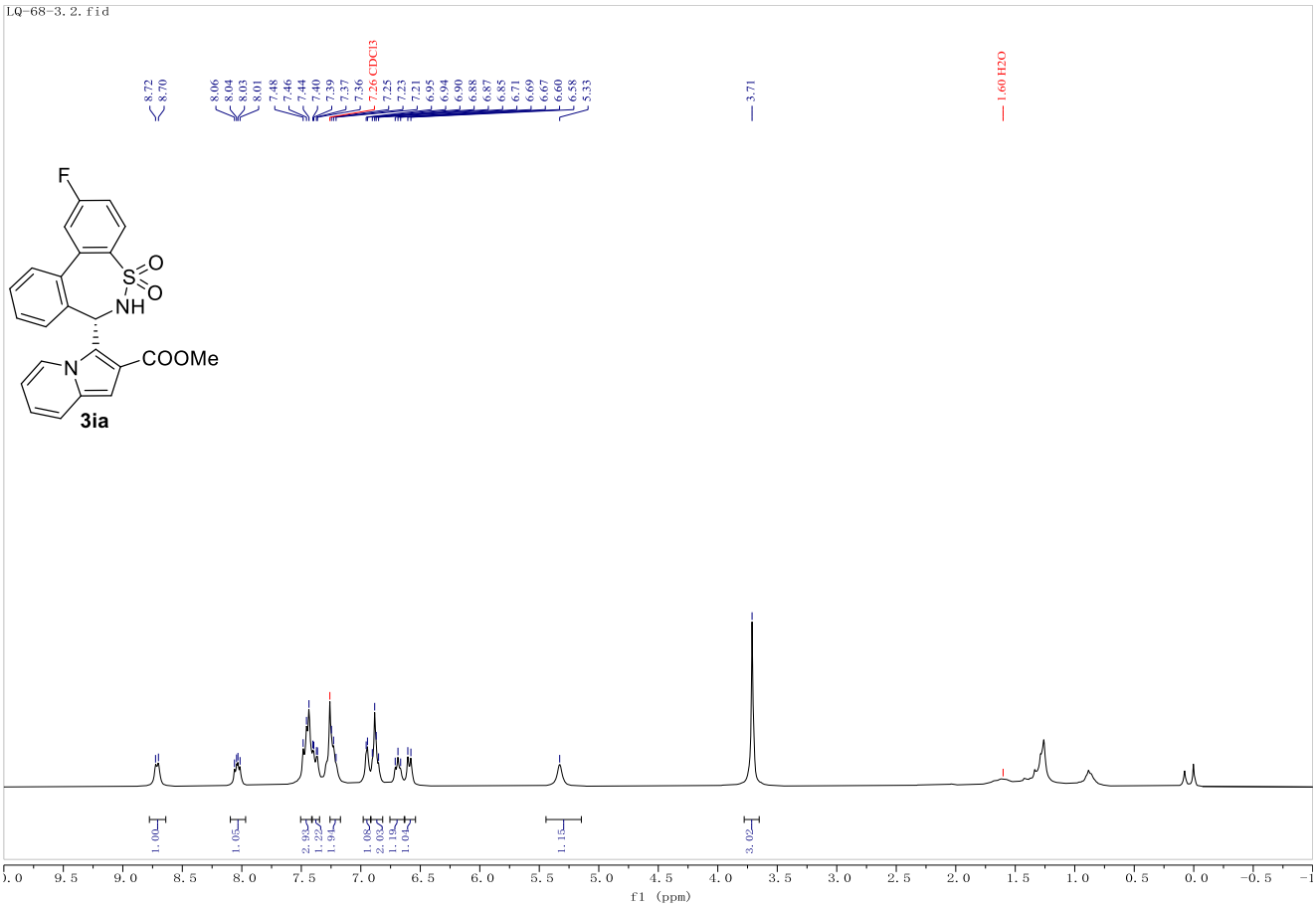
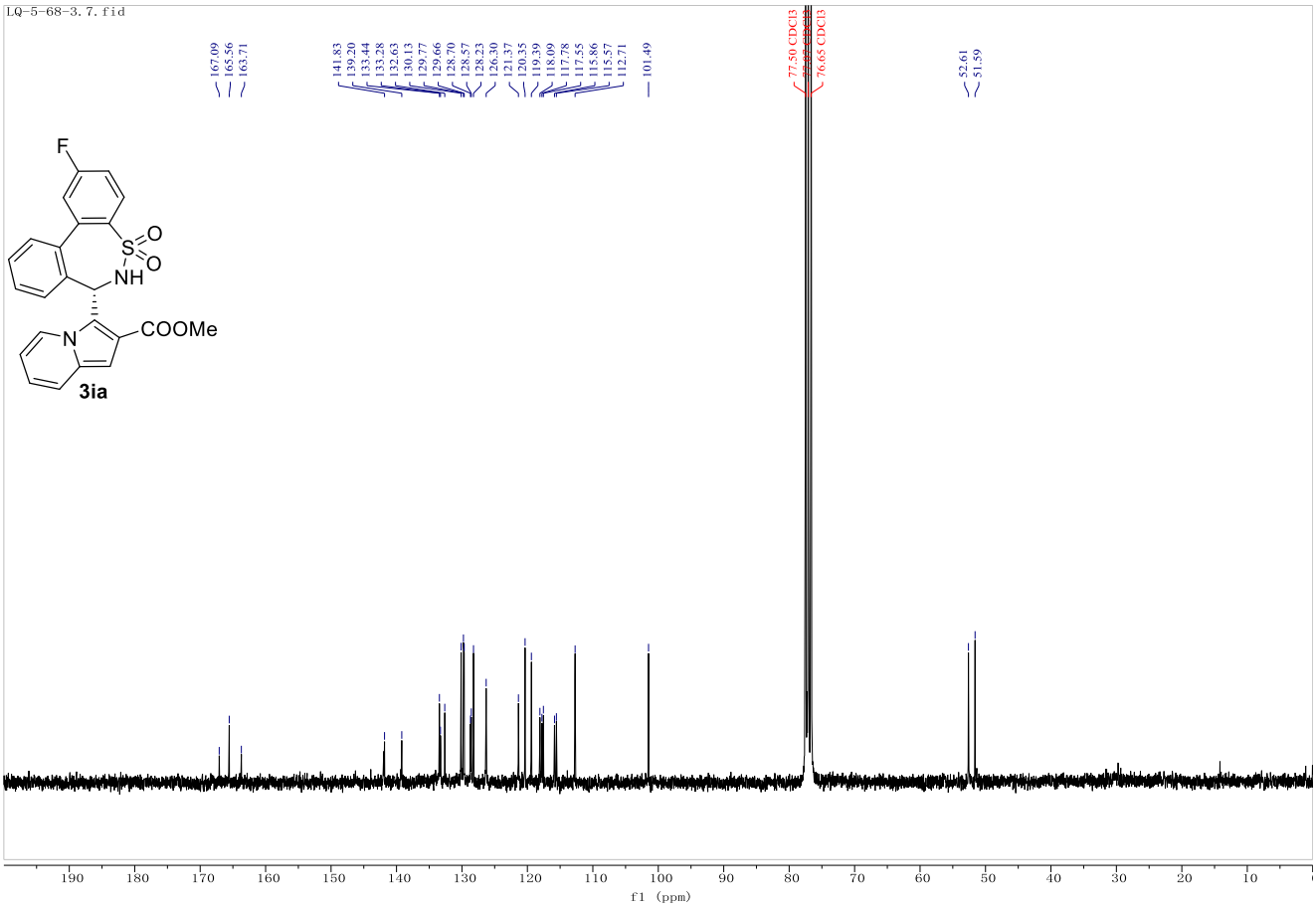


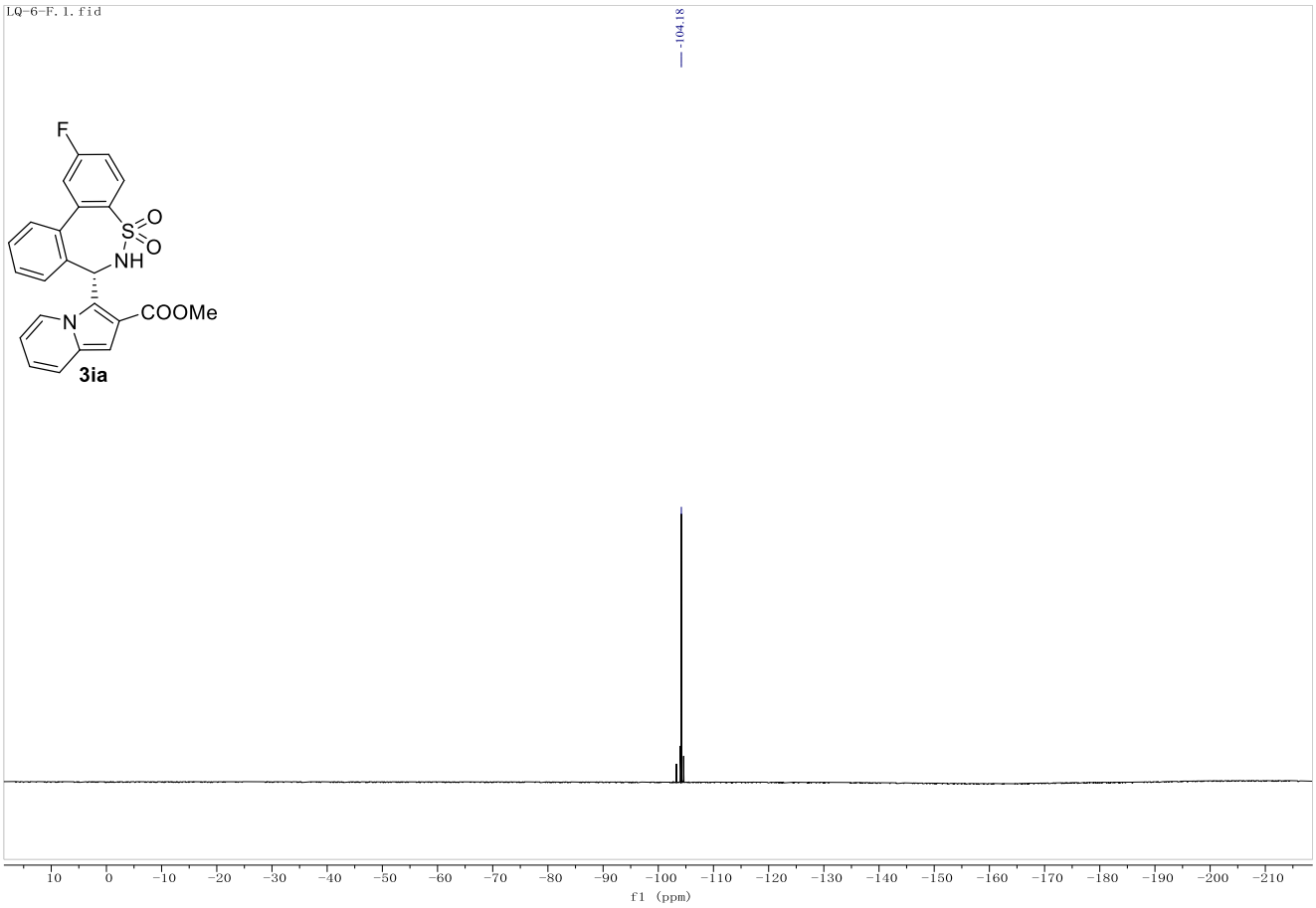
3ia, ^{13}C-NMR in $CDCl_3$



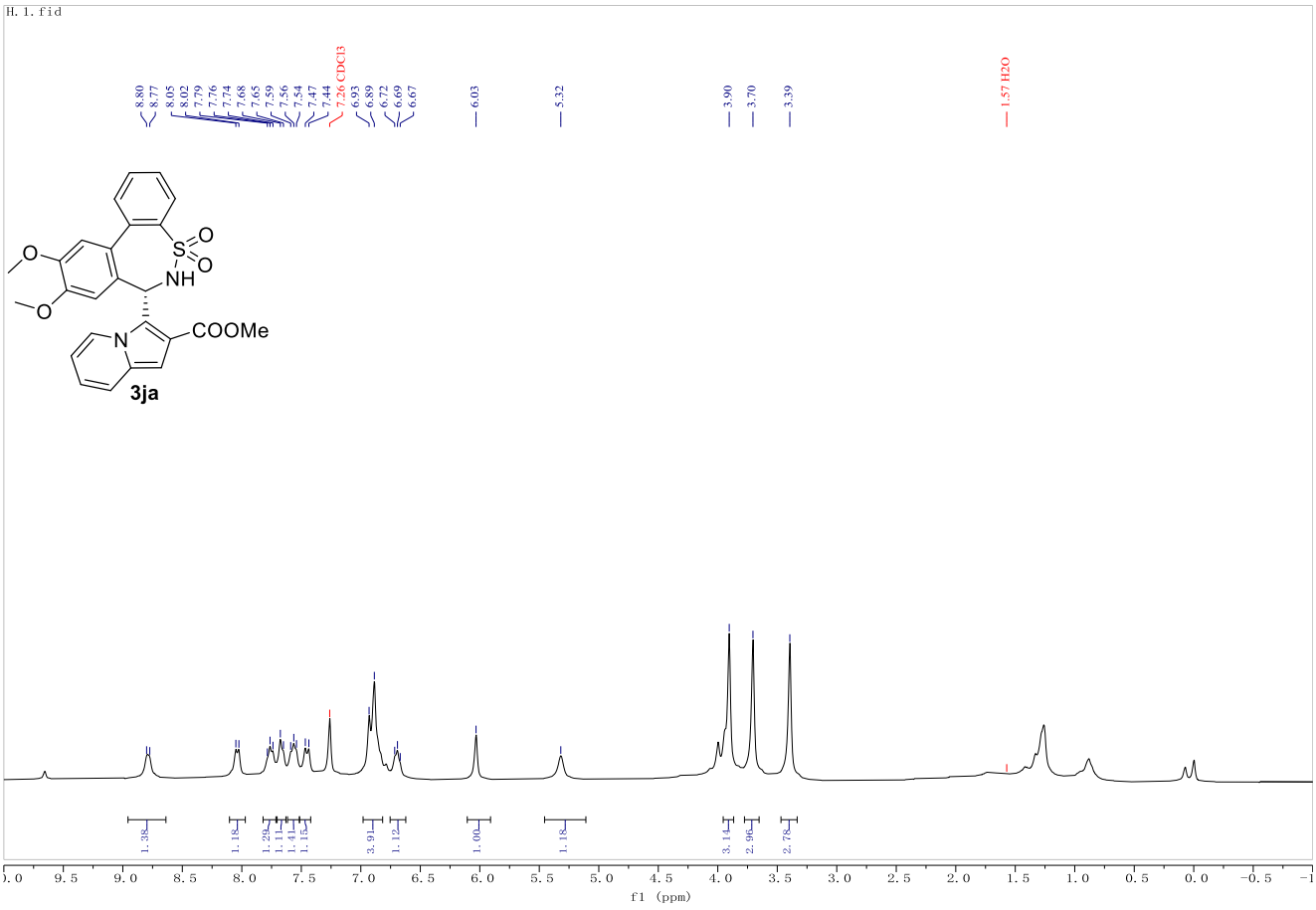
3ia, ^{13}C-NMR in $CDCl_3$



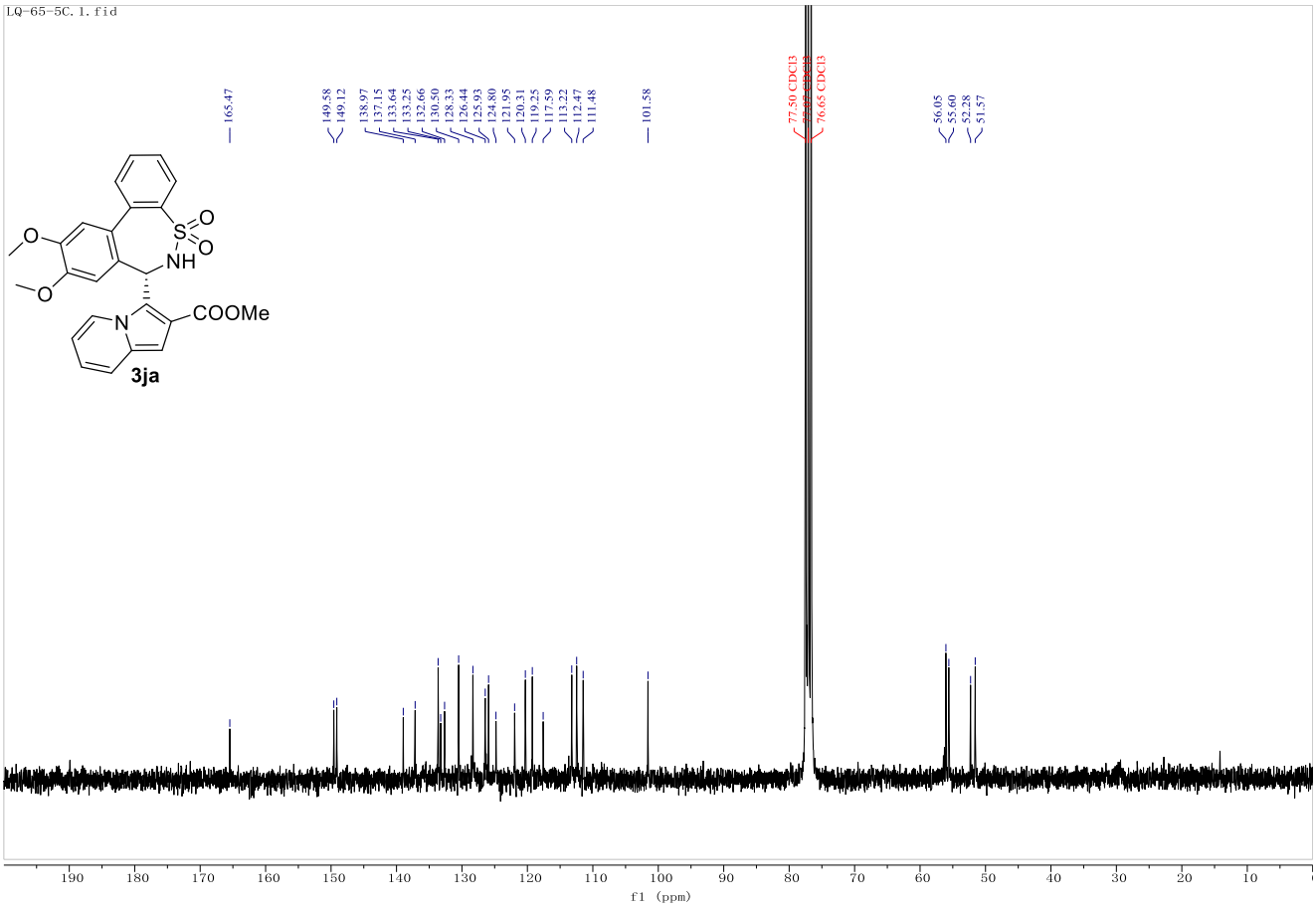
3ia, ^{13}C-NMR in $CDCl_3$



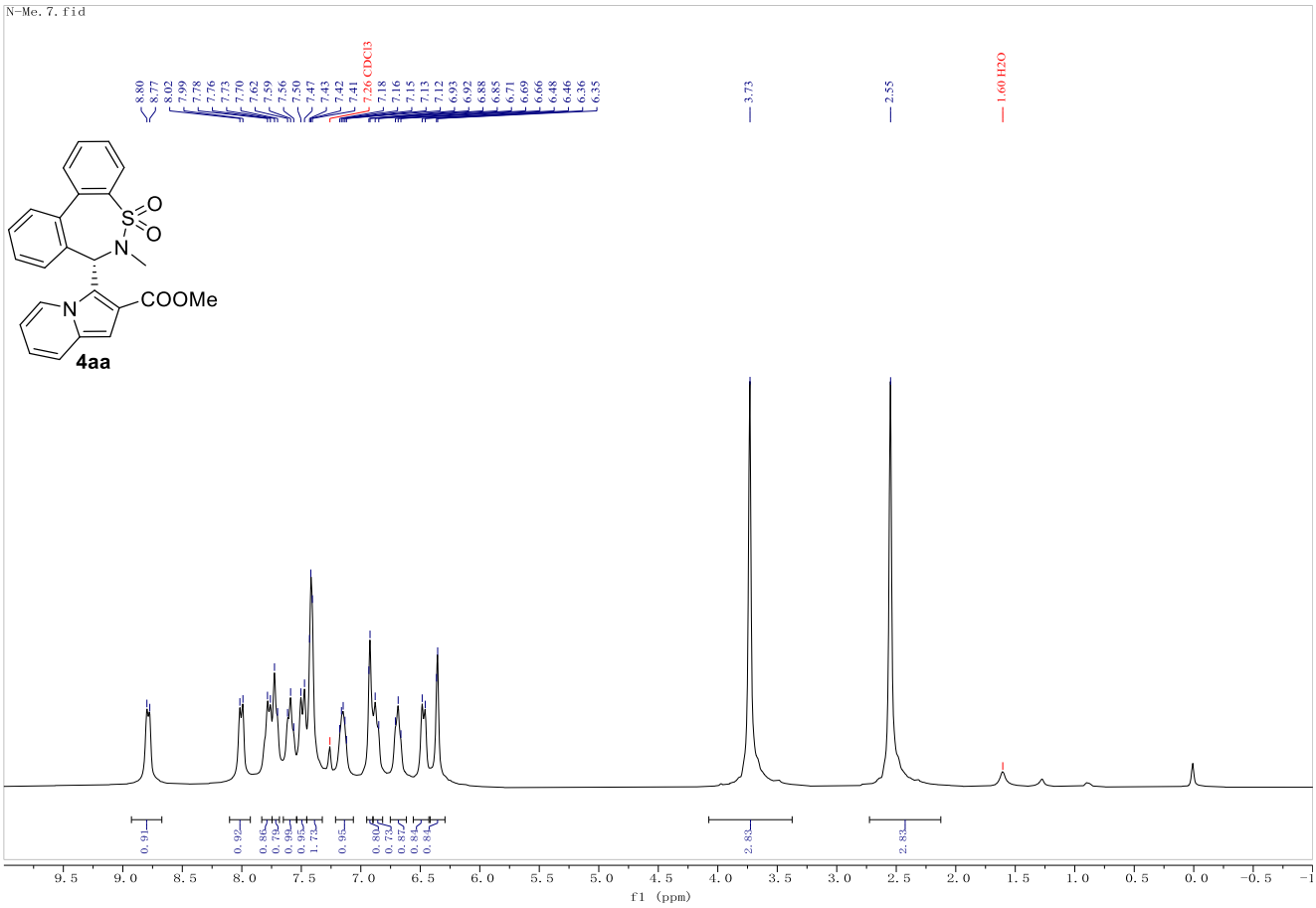
3ja, ^{1}H-NMR in $CDCl_3$



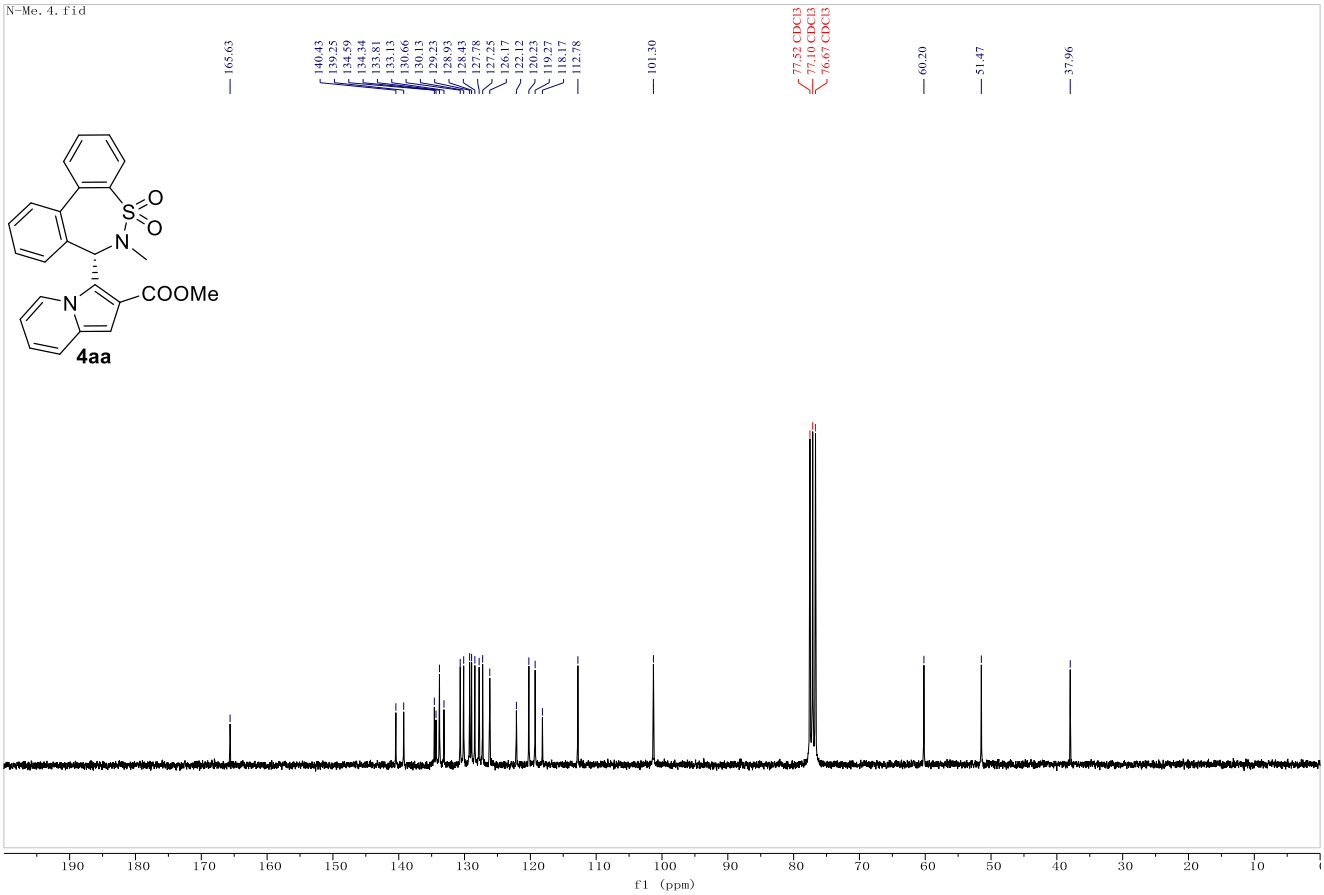
3ja, ^{13}C-NMR in $CDCl_3$



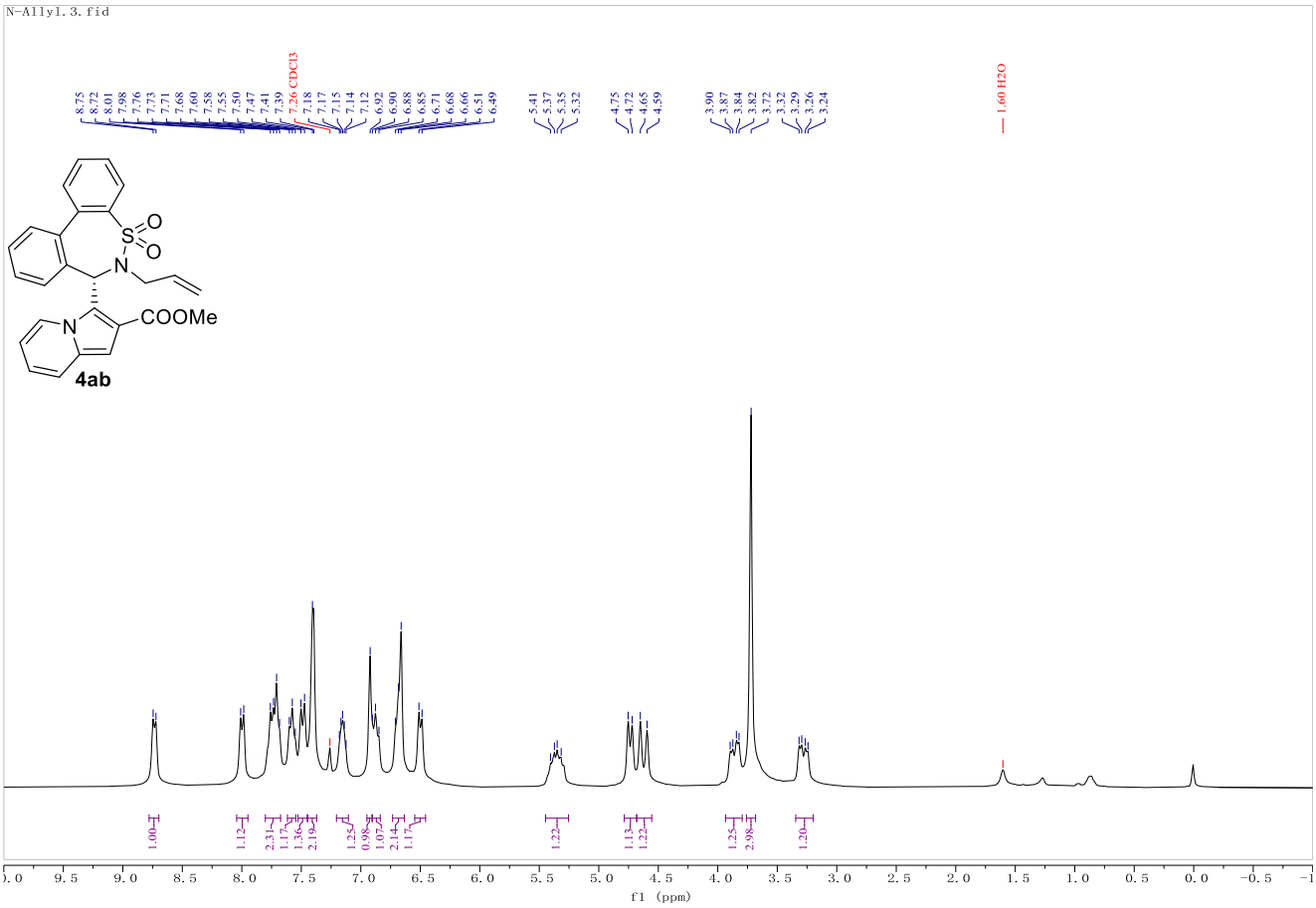
4aa, ^{1}H-NMR in $CDCl_3$



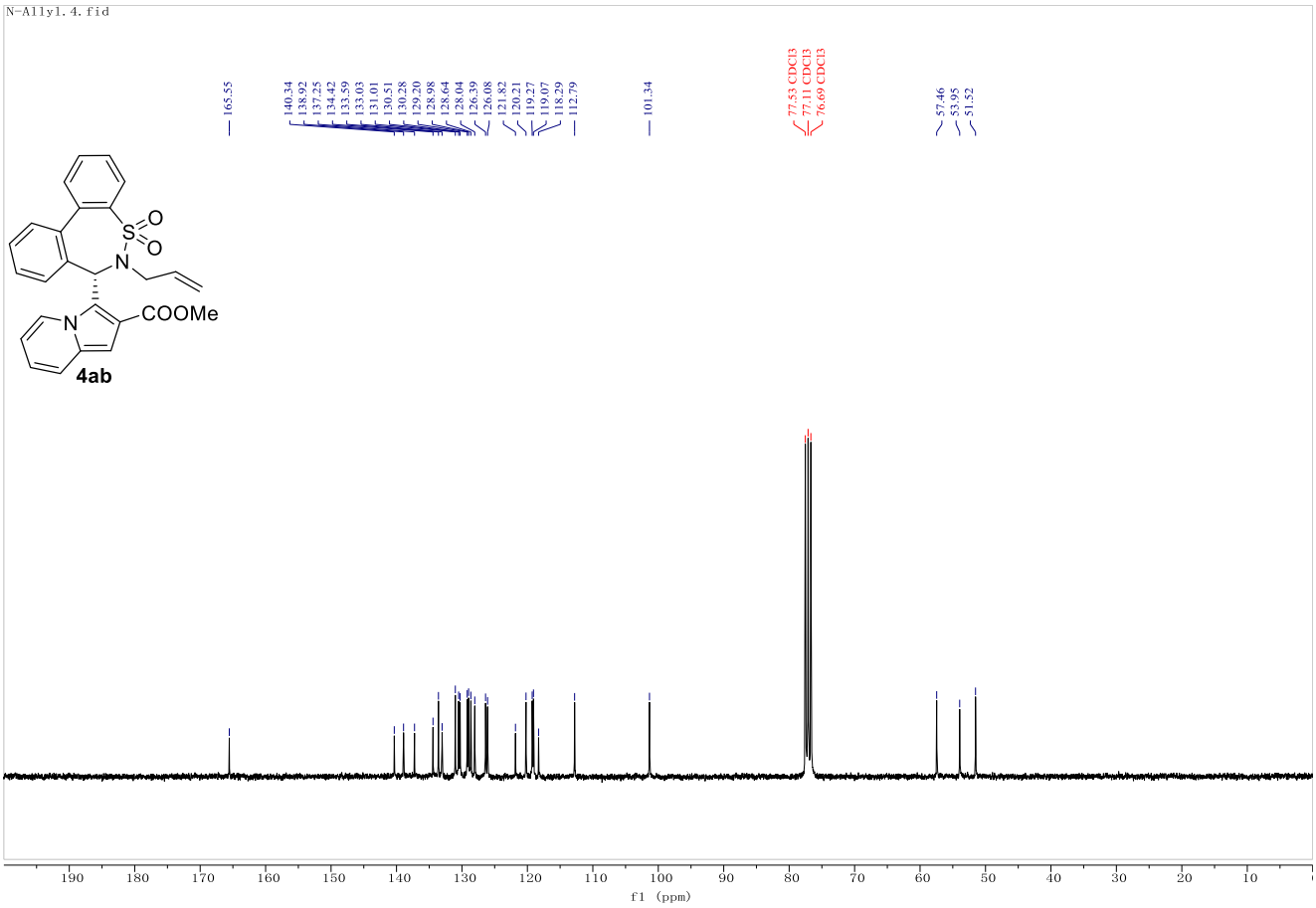
4aa, ^{13}C-NMR in $CDCl_3$



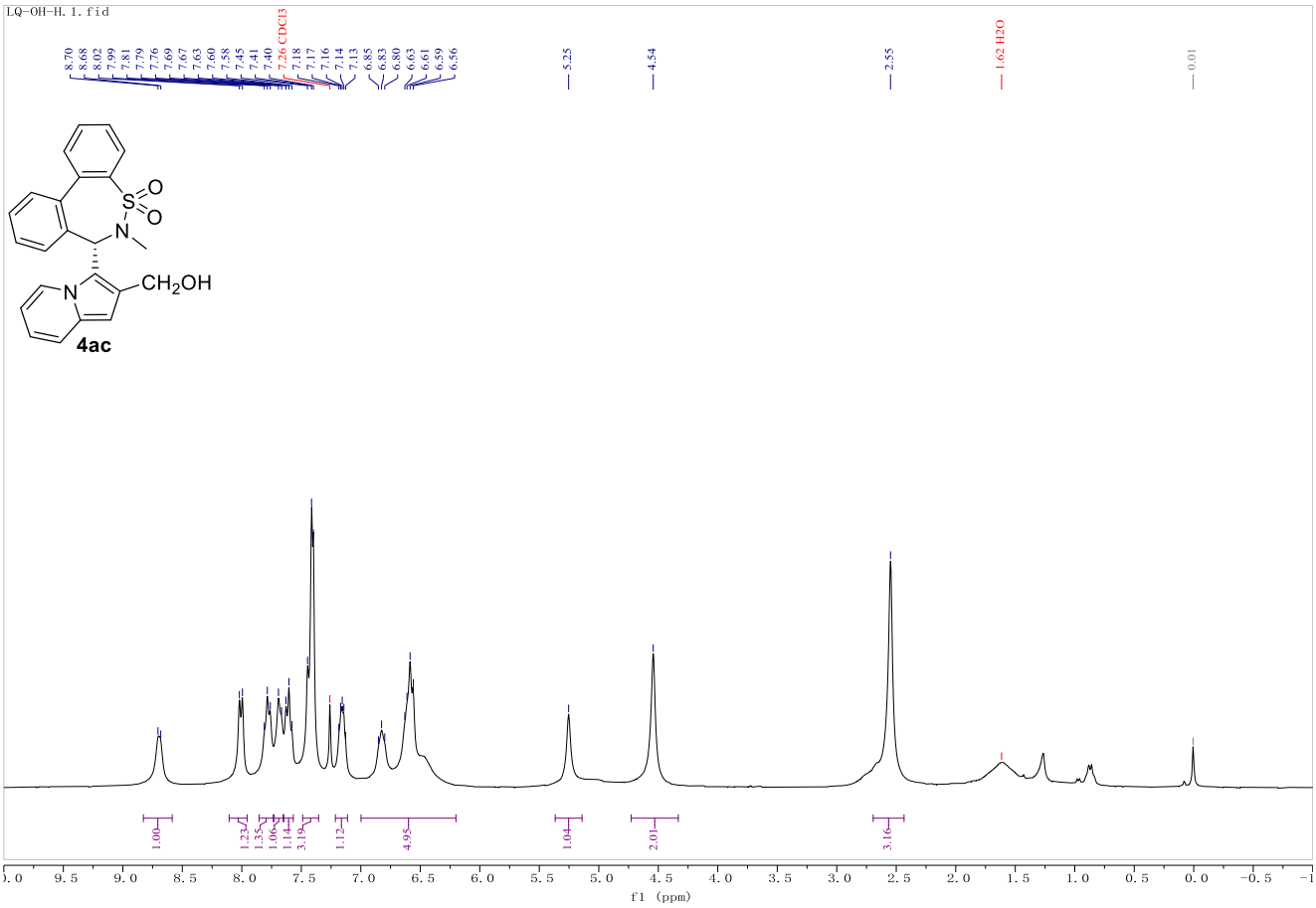
4ab, ^{1}H-NMR in $CDCl_3$



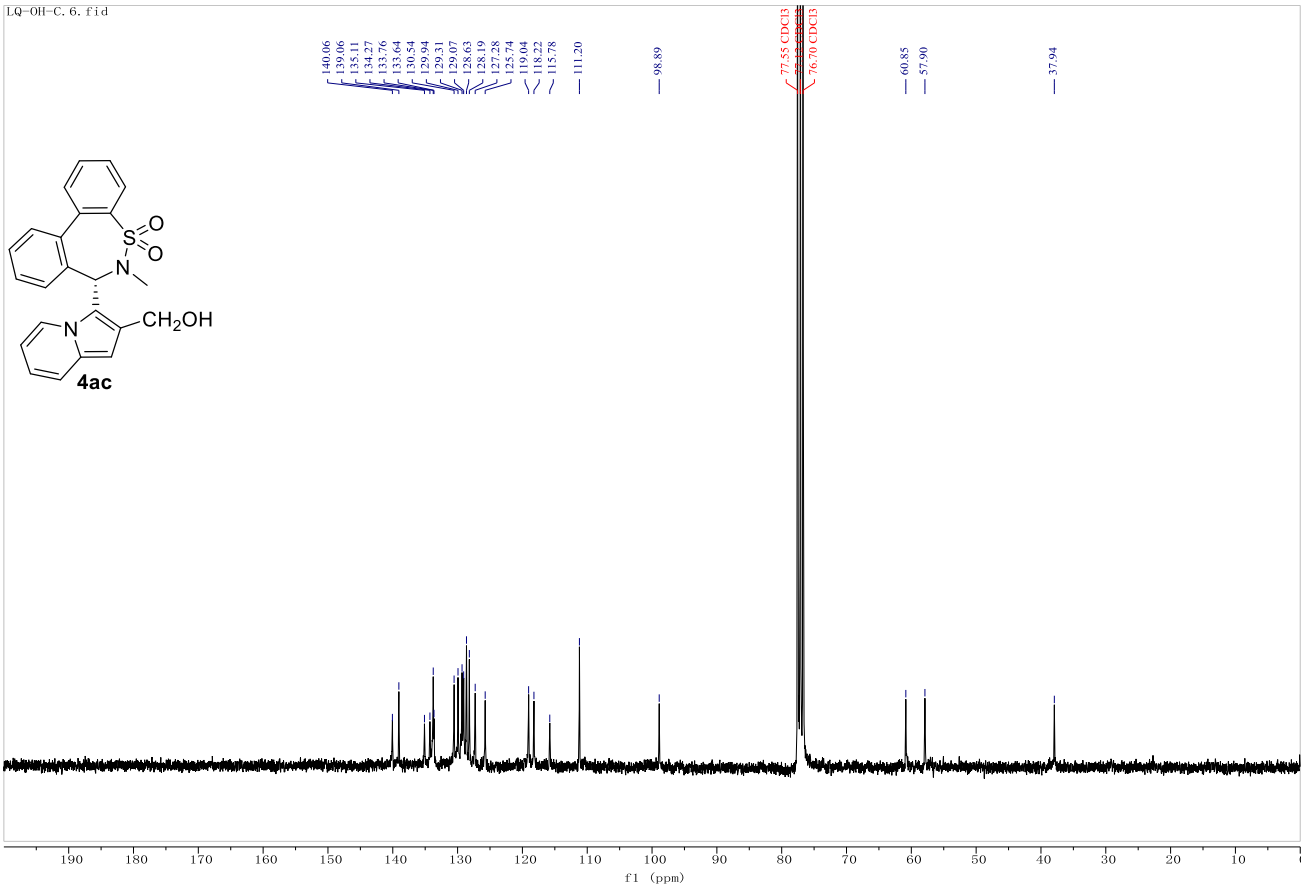
4ab, ^{13}C-NMR in $CDCl_3$



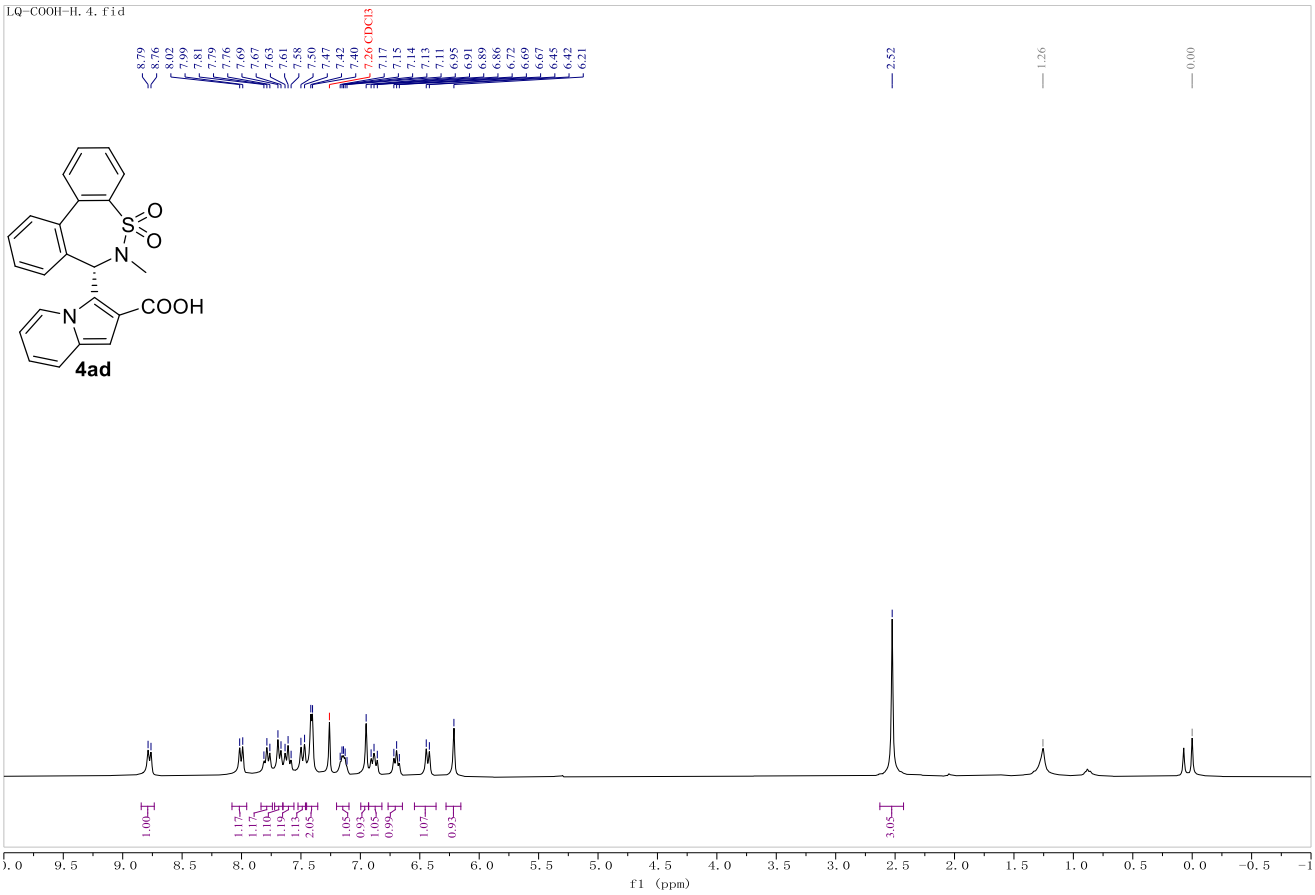
4ac, ^{1}H-NMR in $CDCl_3$



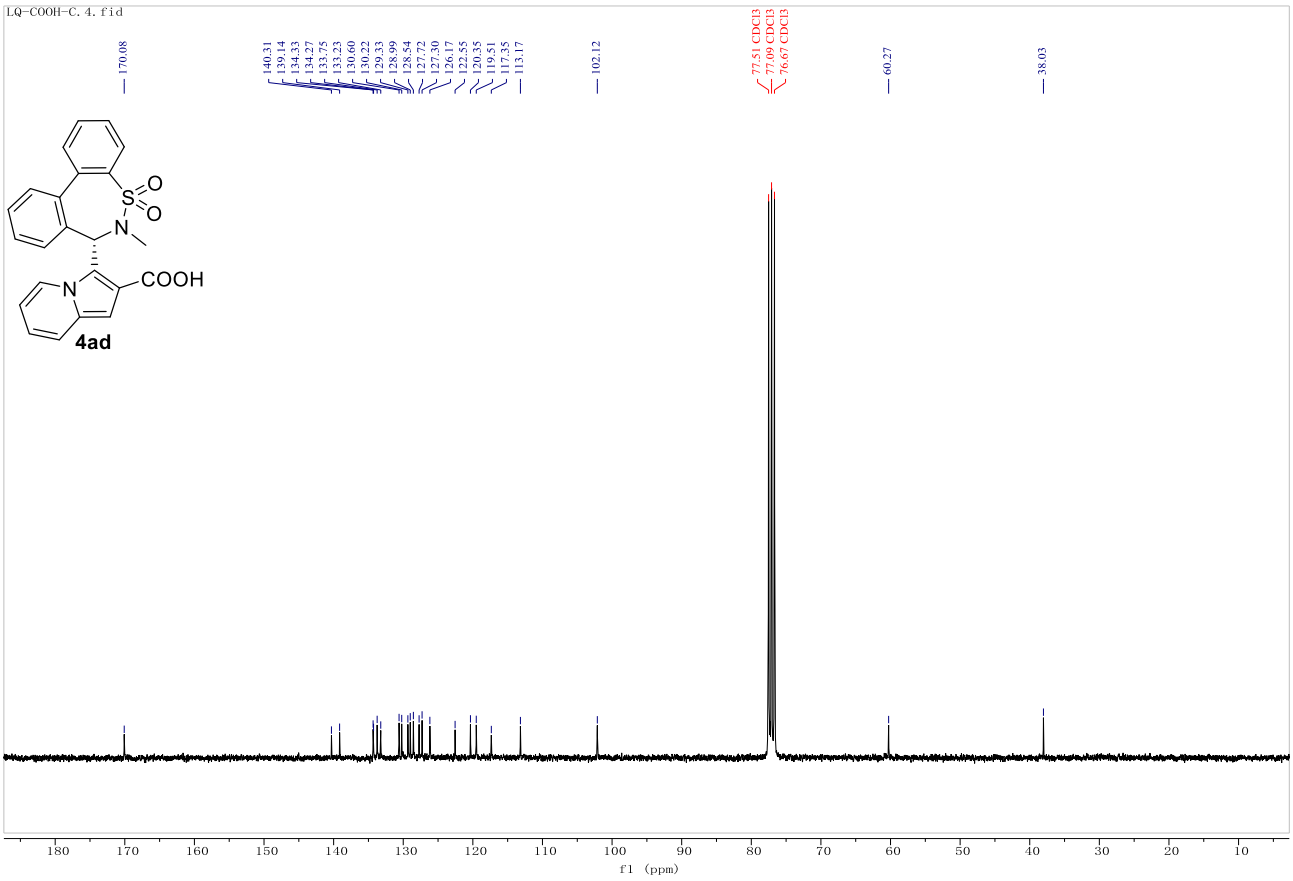
4ac, ^{13}C-NMR in $CDCl_3$



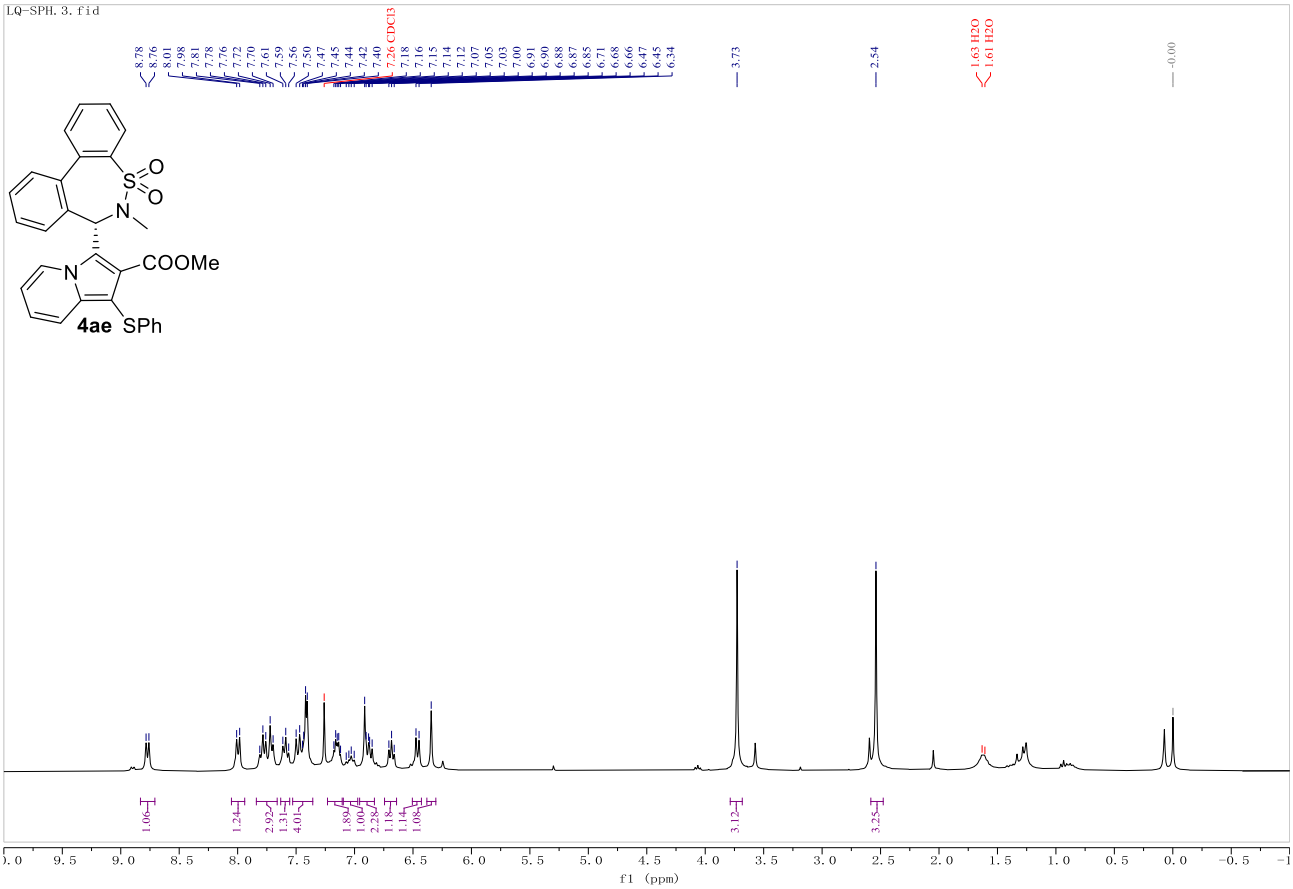
4ad, ^{1}H-NMR in $CDCl_3$



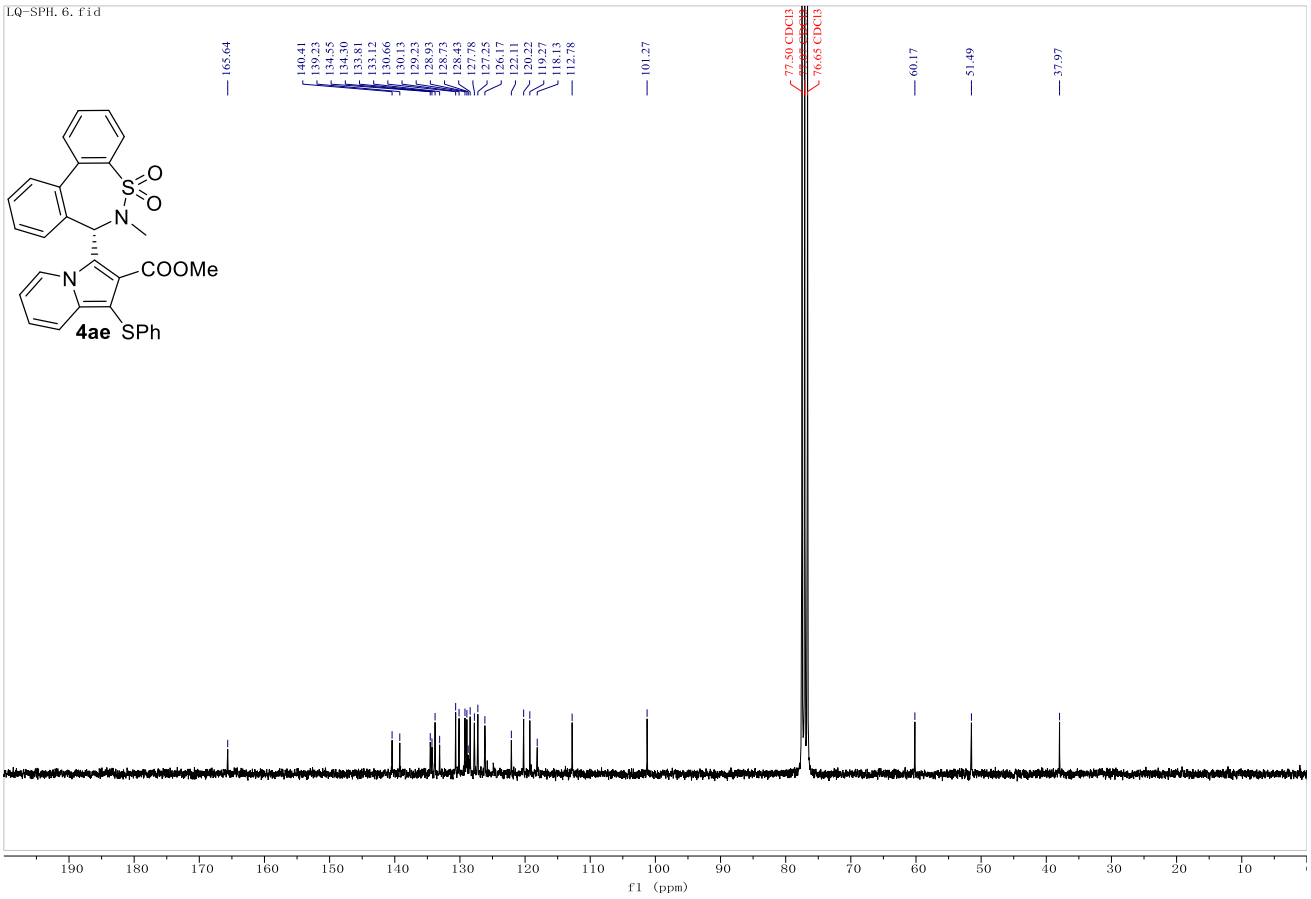
4ad, ^{13}C-NMR in $CDCl_3$



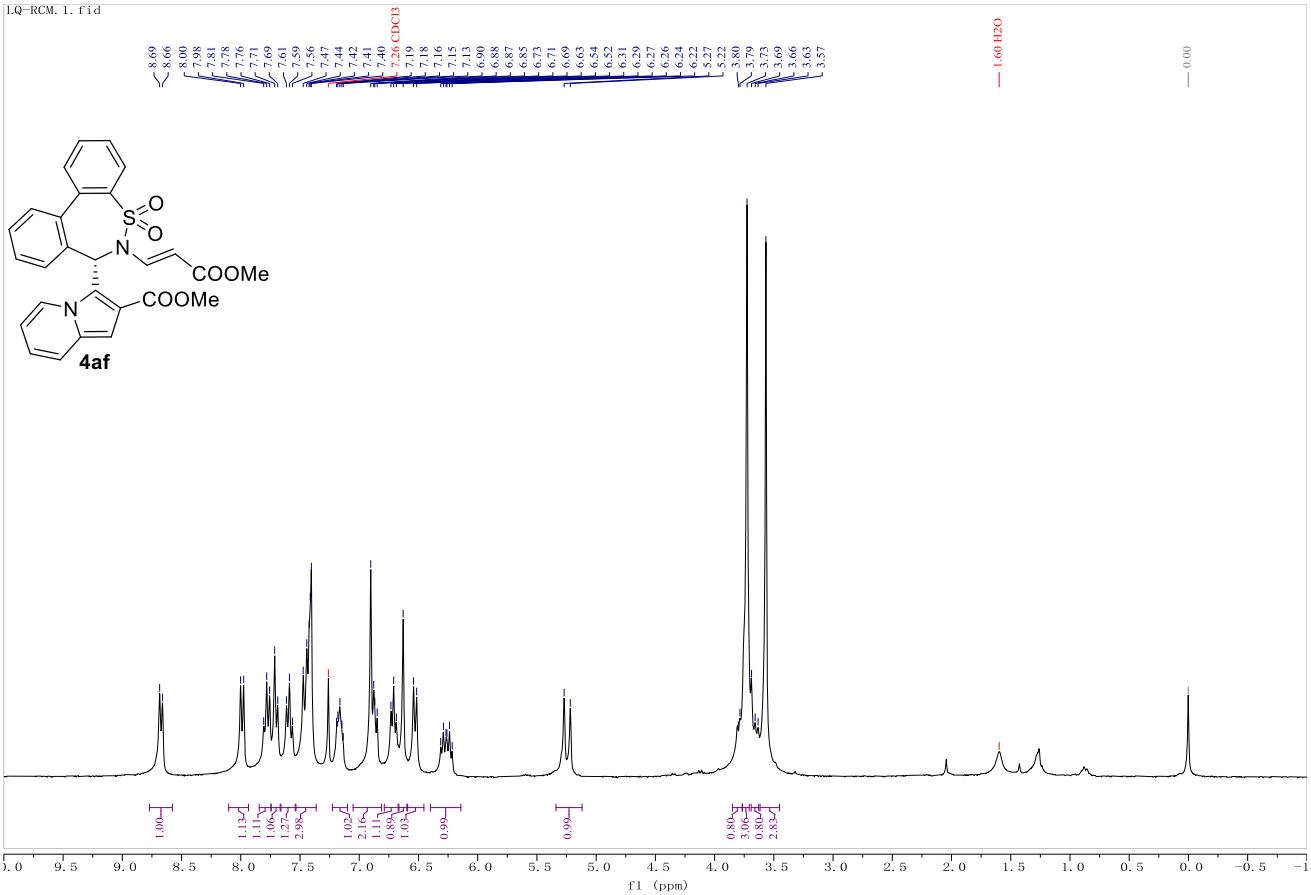
4ae, ^{1}H-NMR in $CDCl_3$



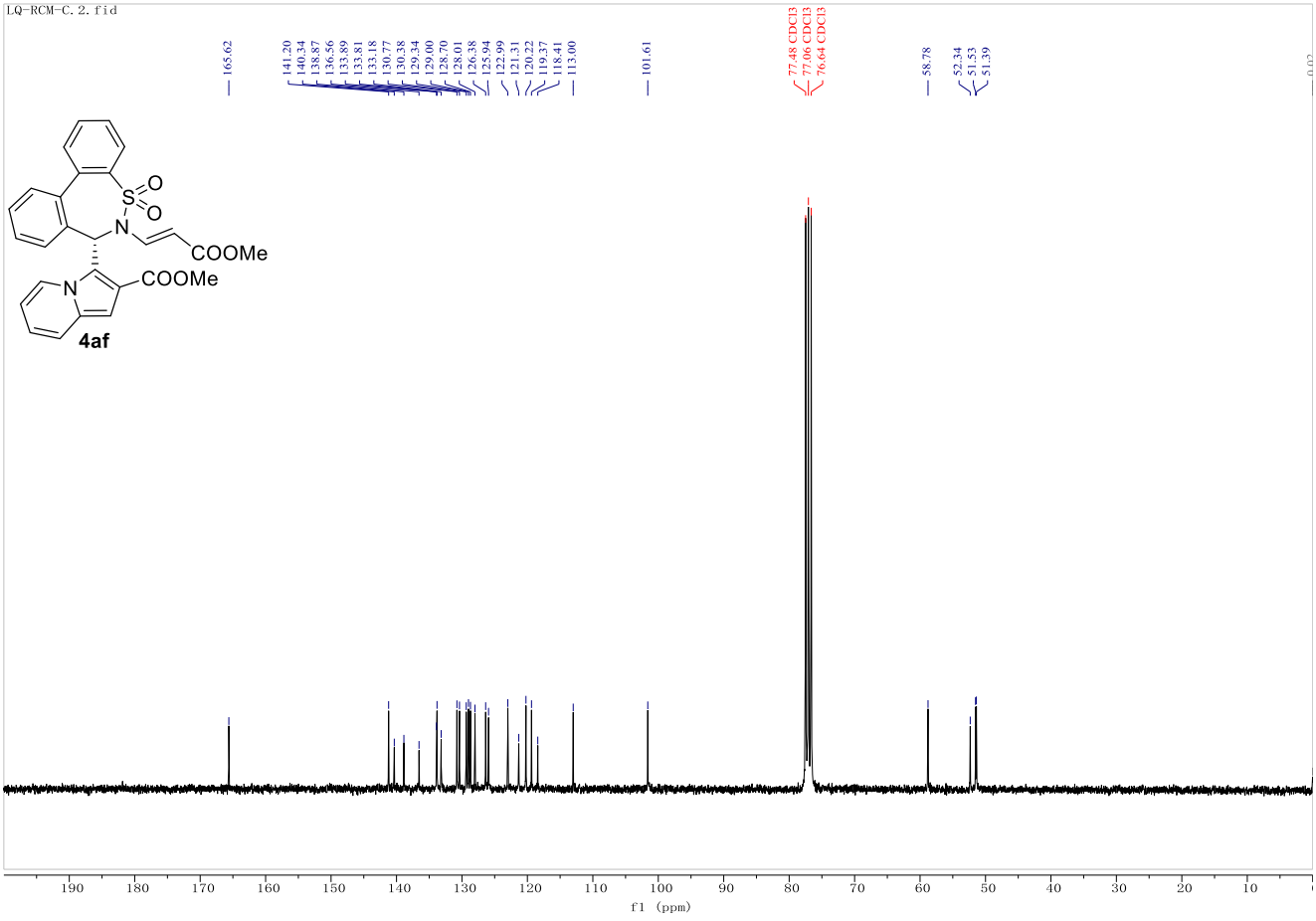
4ae, ^{13}C-NMR in $CDCl_3$



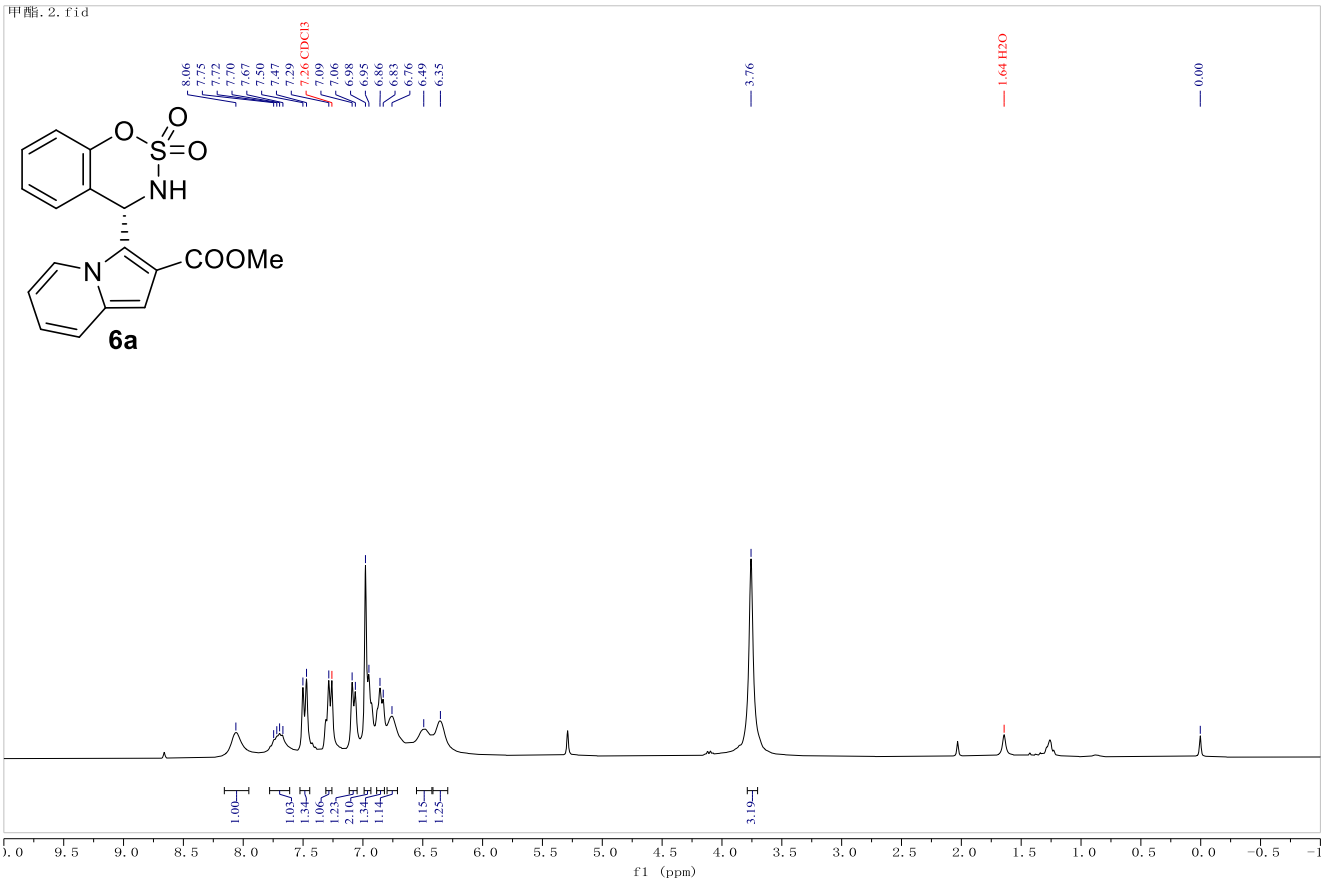
4af, ^{1}H-NMR in $CDCl_3$



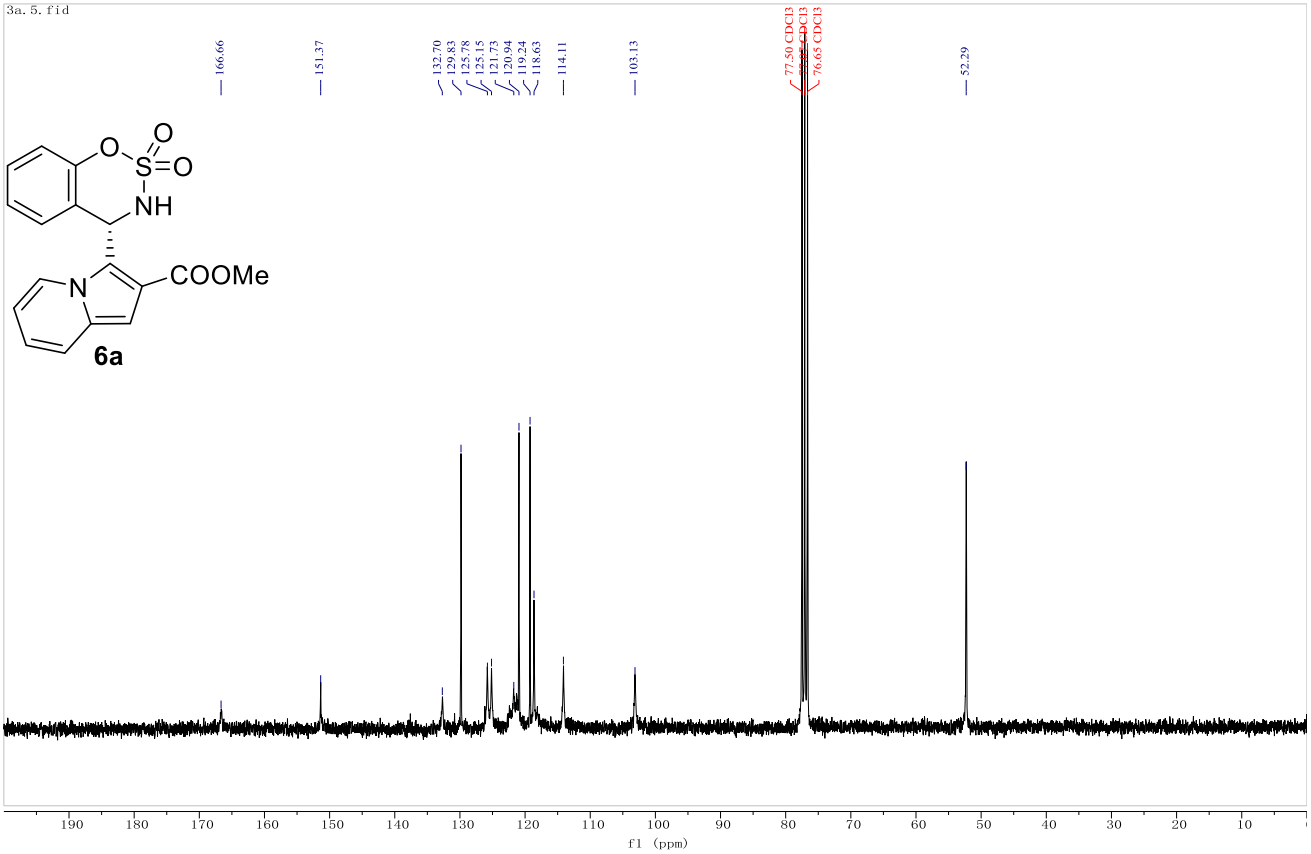
4af, ^{13}C-NMR in $CDCl_3$



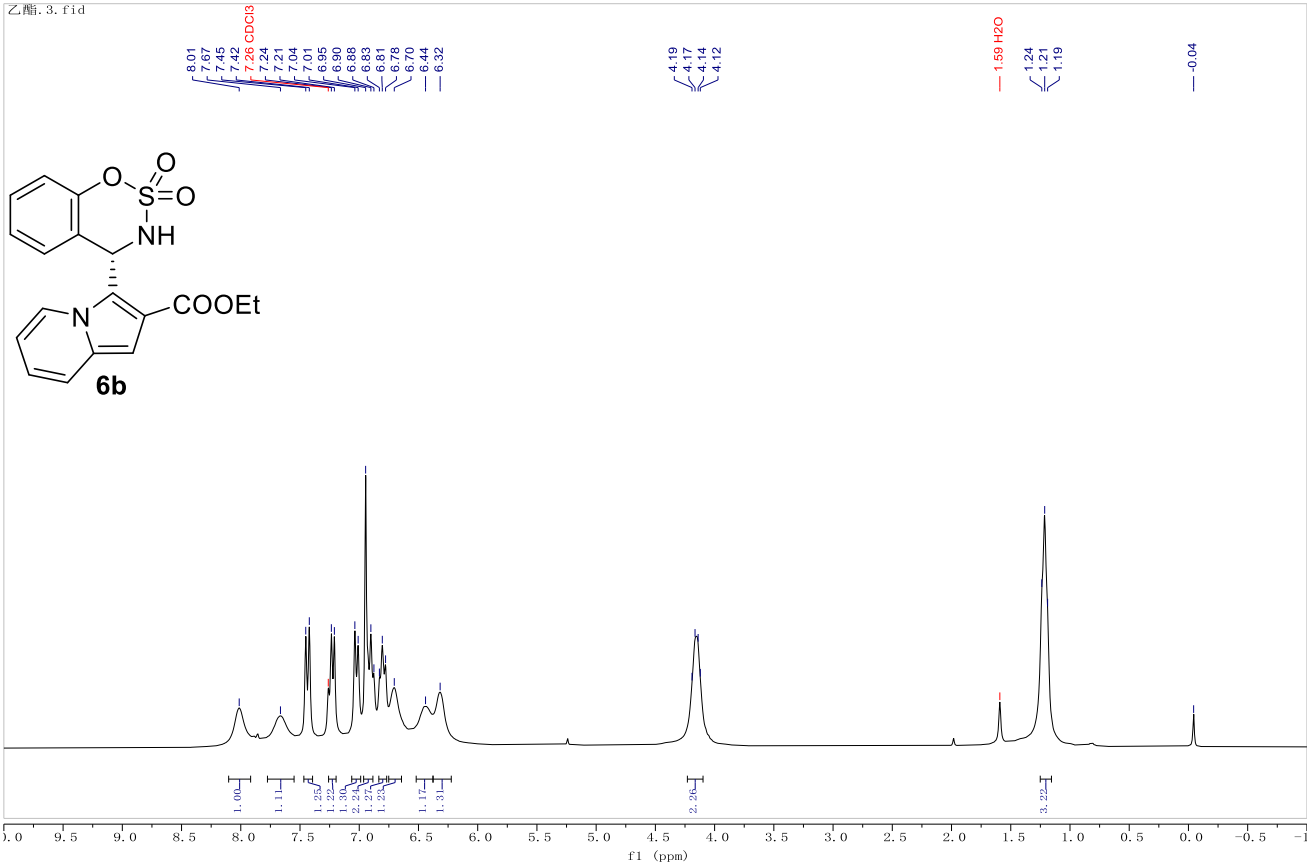
6a, ^{1}H-NMR in $CDCl_3$



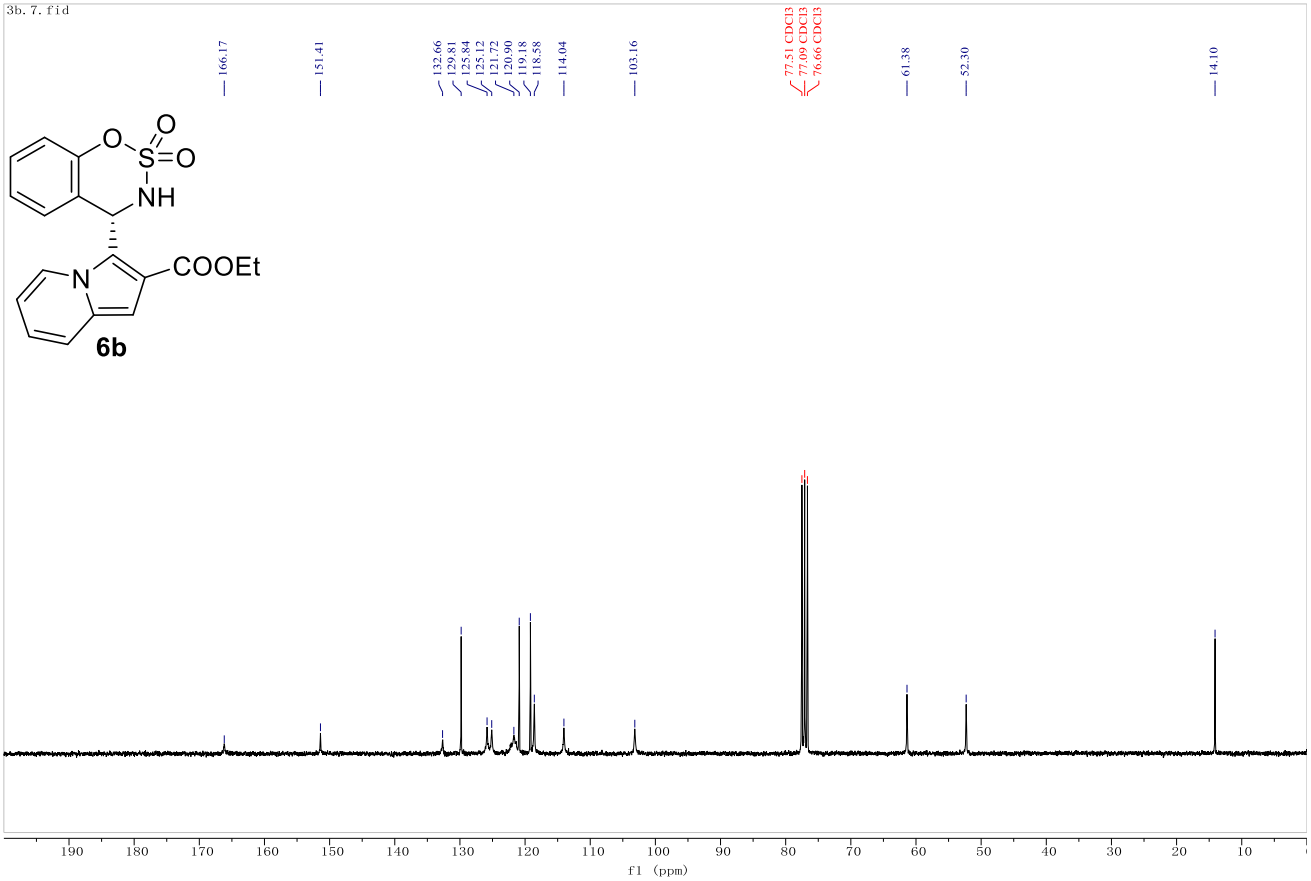
6a, ^{13}C-NMR in $CDCl_3$



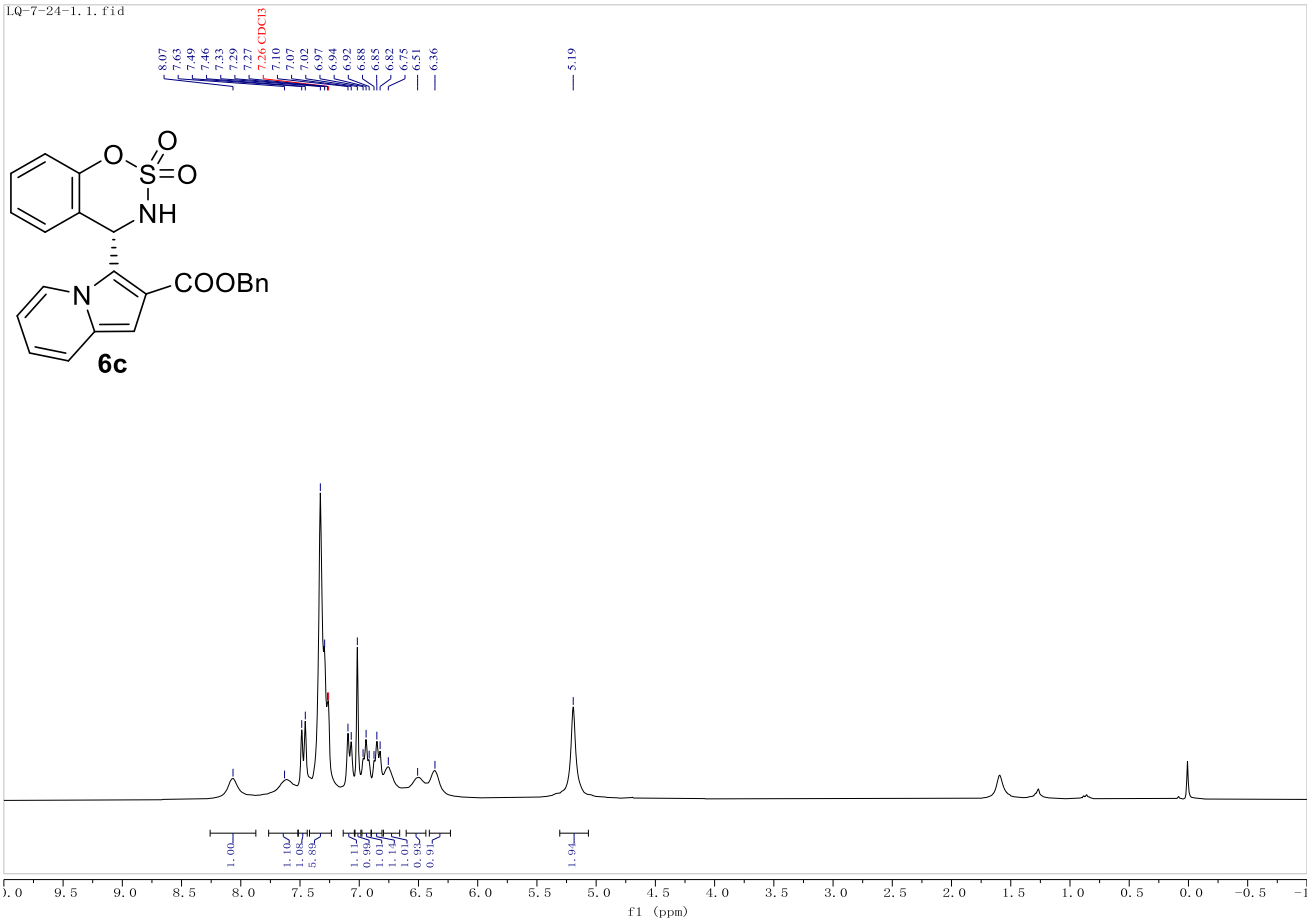
6b, ^{1}H-NMR in $CDCl_3$



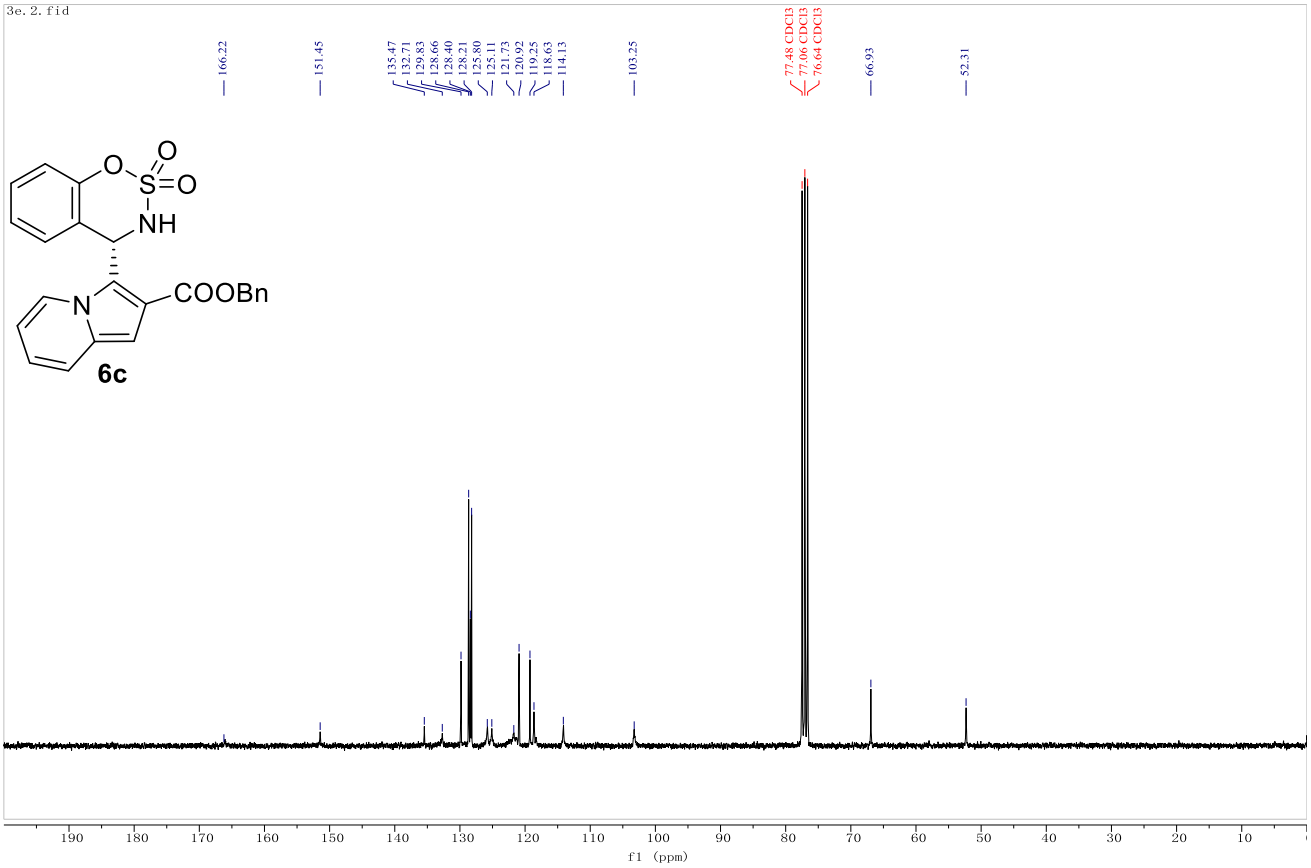
6b, ^{13}C-NMR in $CDCl_3$



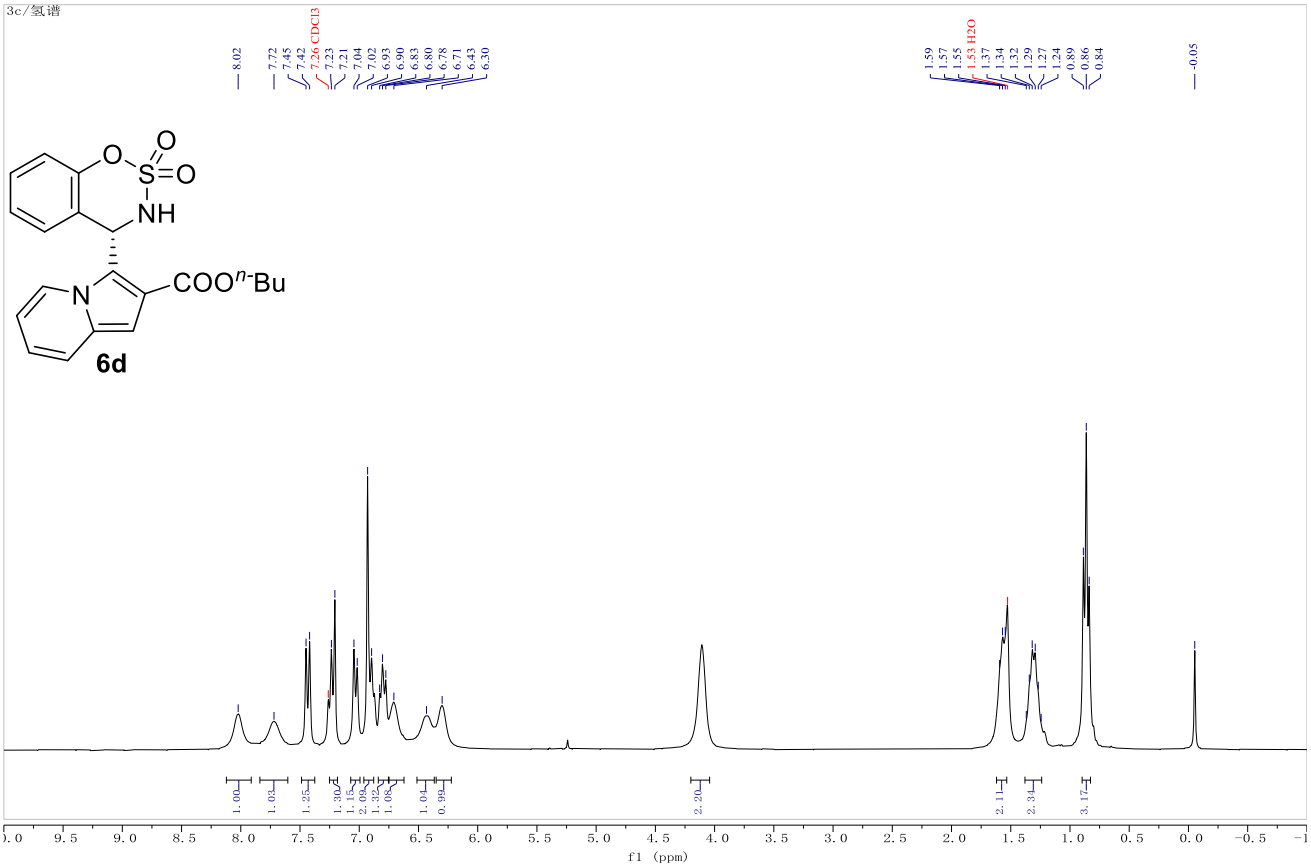
6c, ^{1}H-NMR in $CDCl_3$



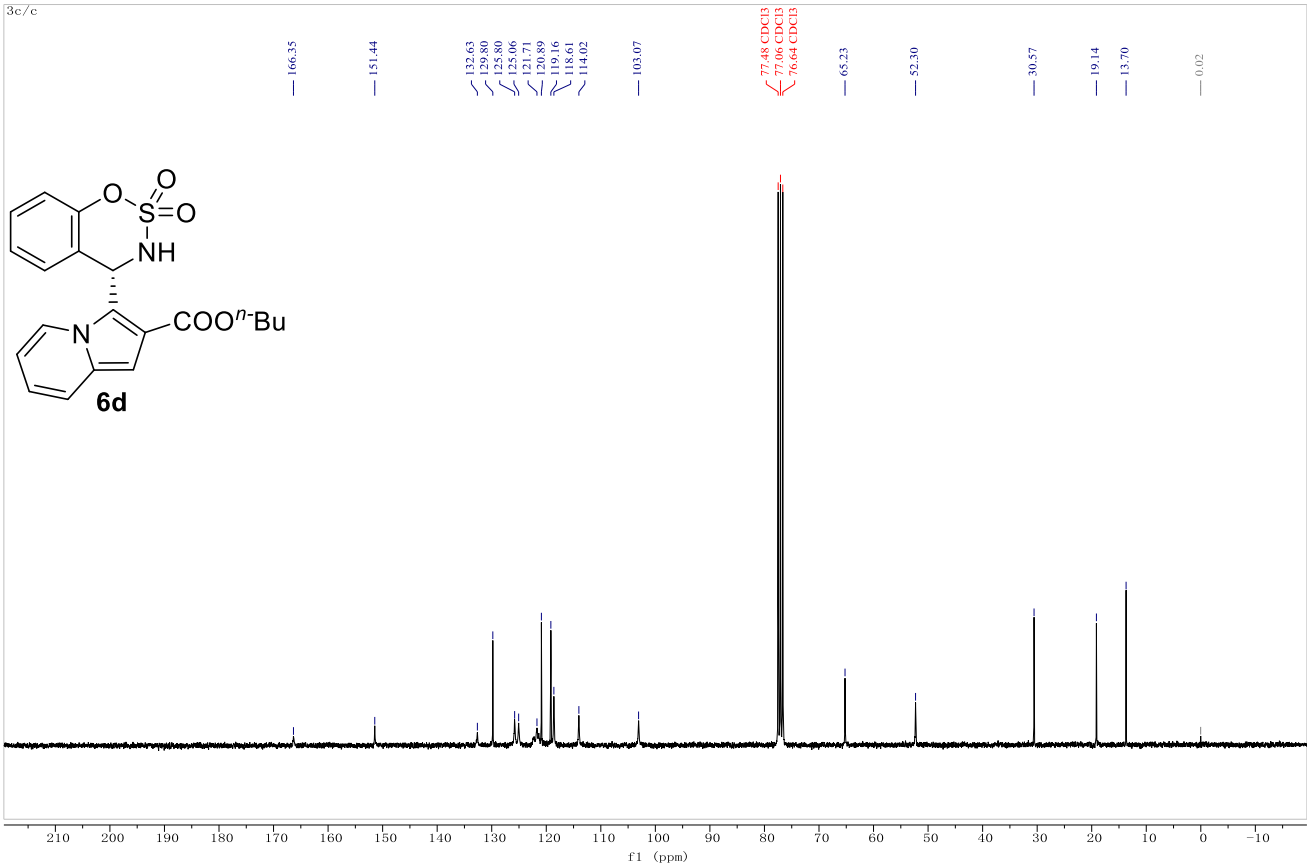
6c, ^{13}C-NMR in $CDCl_3$



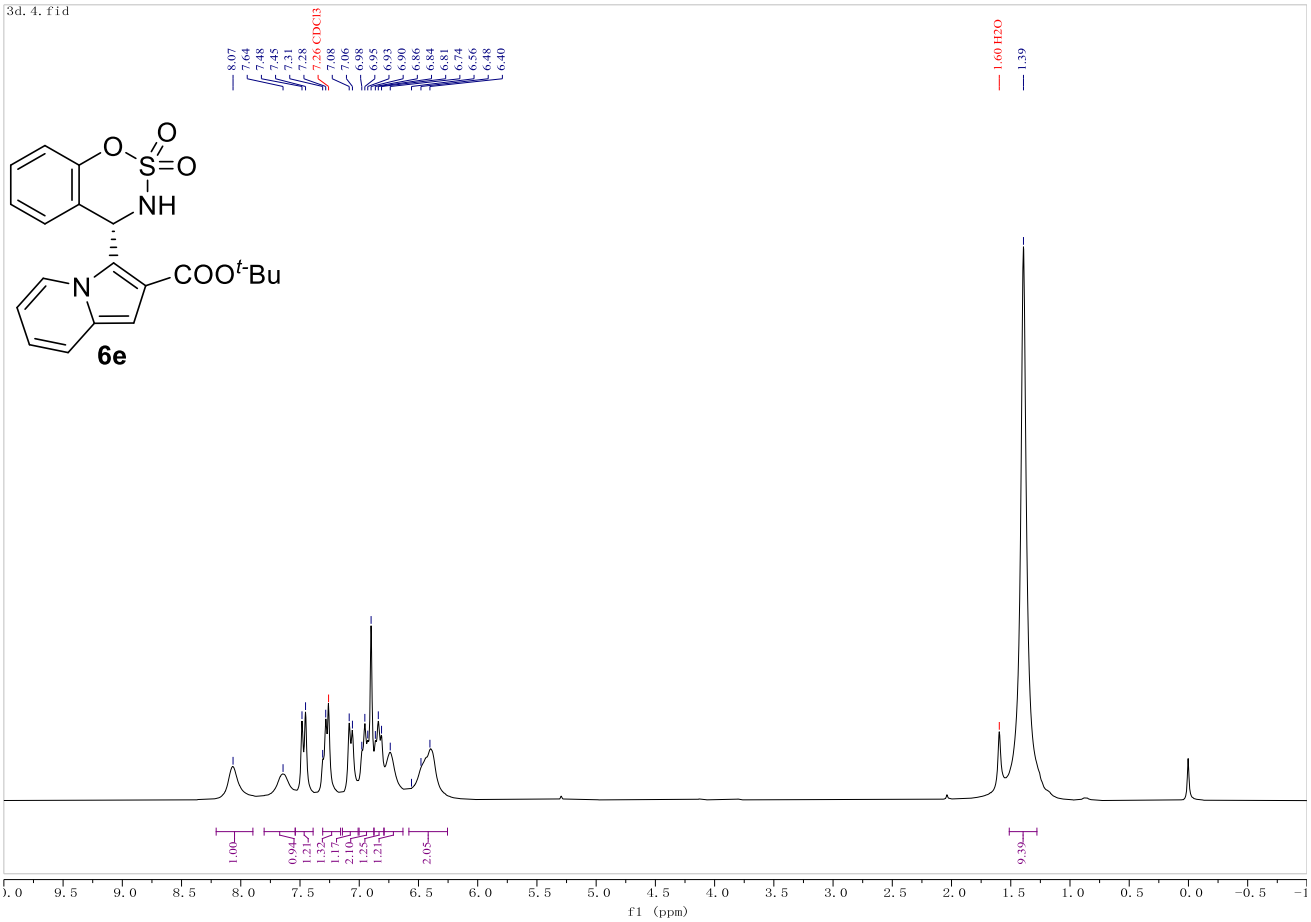
6d, ^{1}H-NMR in $CDCl_3$



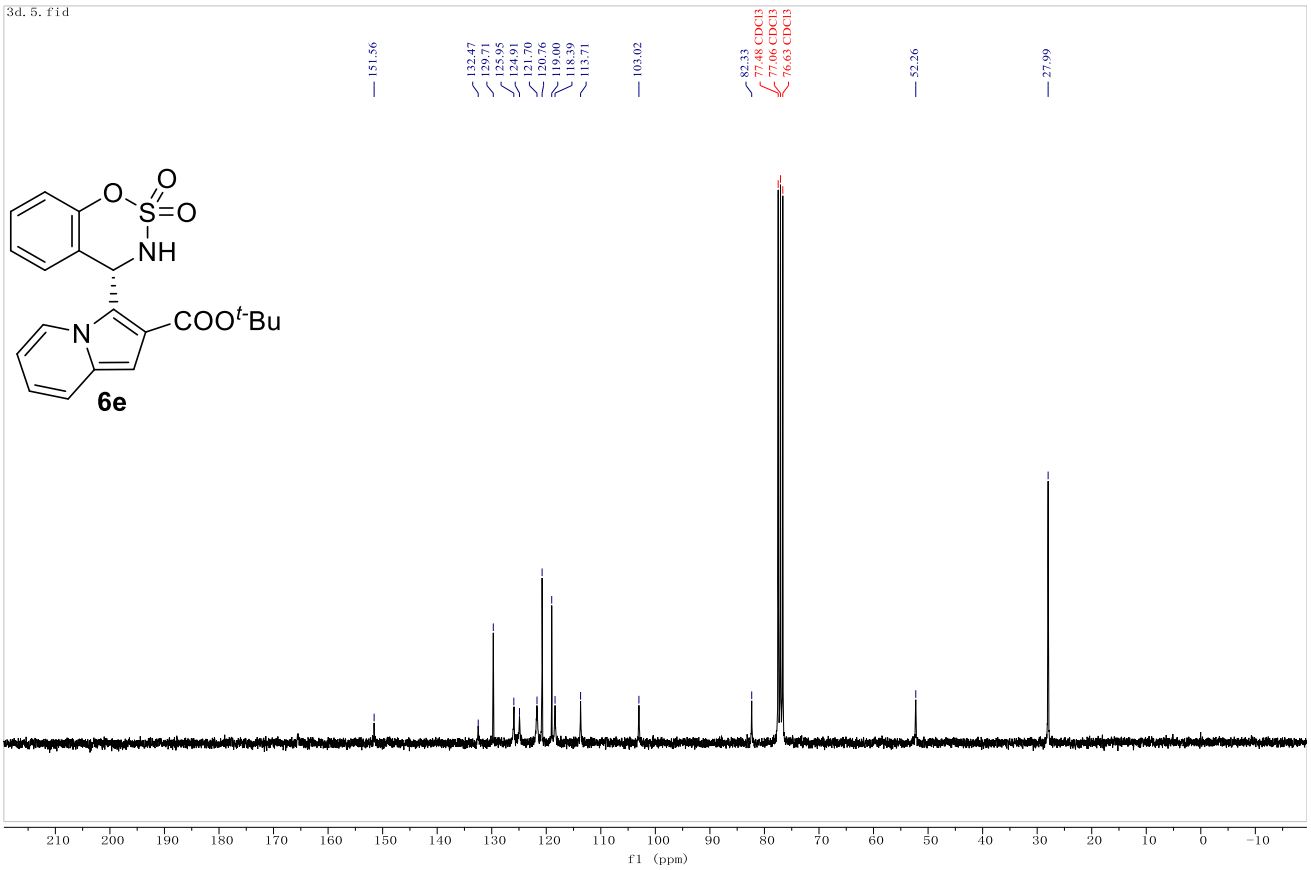
6d, ^{13}C-NMR in $CDCl_3$



6e, ^{1}H-NMR in $CDCl_3$

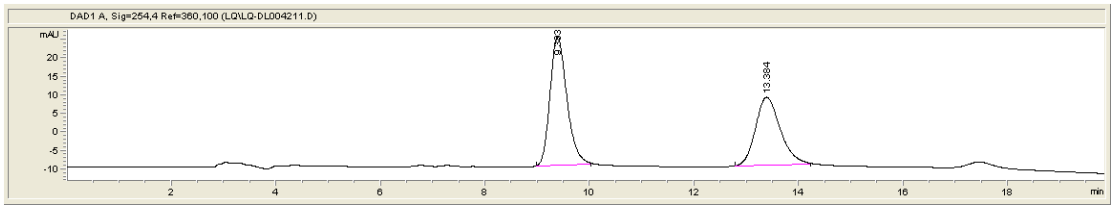


6e, ^{13}C-NMR in $CDCl_3$



7. Copy of HPLC

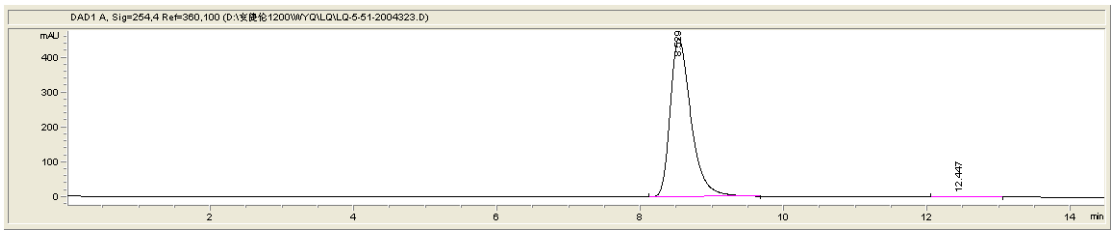
Racemic **3aa**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.383	BB	0.3467	786.93188	34.94194	56.3574
2	13.384	BB	0.5062	609.39136	18.40802	43.6426
总量 :				1396.32324	53.34996	

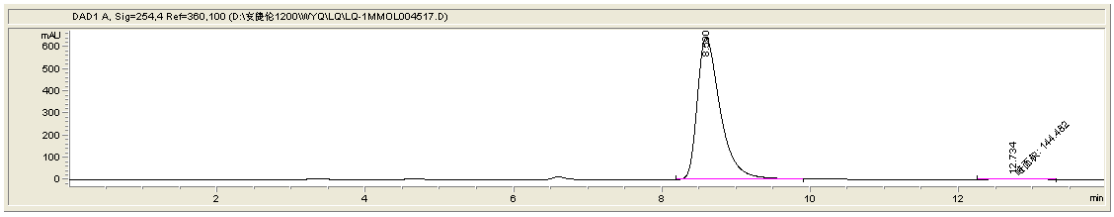
Chiral **3aa**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.529	BB	0.3087	9231.11230	455.05069	99.3979
2	12.447	BB	0.4056	55.91592	1.93250	0.6021
总量 :				9287.02822	456.98319	

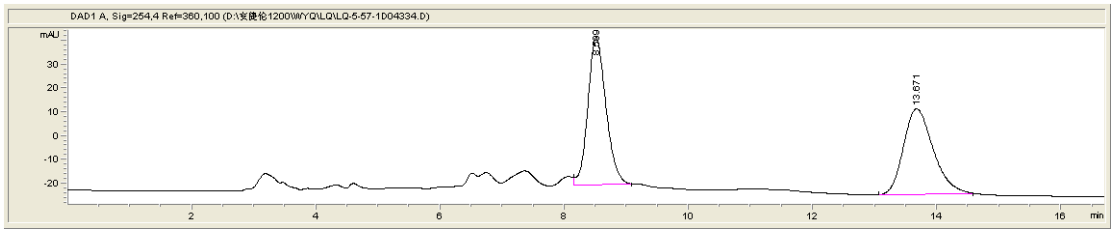
Chiral **3aa (1 mmol)**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.590	BB	0.3246	1.37961e4	642.36749	98.9636
2	12.734	MM	0.4933	144.48209	4.88134	1.0364
总量 :				1.39405e4	647.24883	

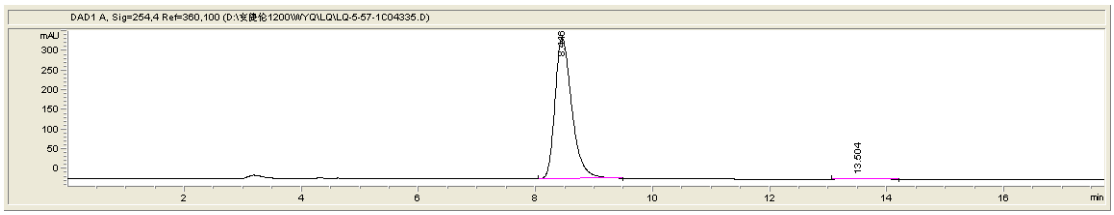
Racemic **3ab**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.509	VB	0.3112	1260.03064	61.96294	51.0495
2	13.671	BB	0.5188	1208.22131	36.06490	48.9505
总量 :				2468.25195	98.02784	

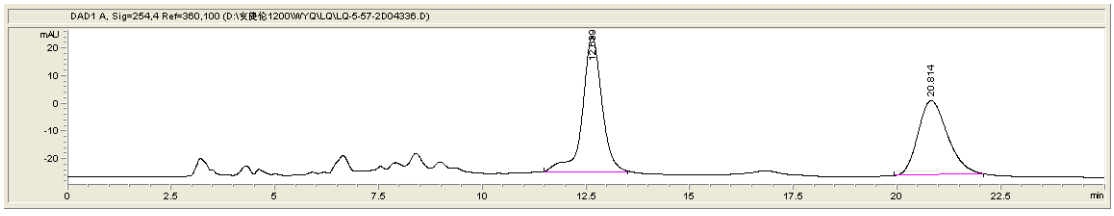
Chiral **3ab**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.446	BB	0.3053	7178.67041	358.99310	98.8873
2	13.504	BB	0.4695	80.77935	2.57870	1.1127
总量 :				7259.44976	361.57180	

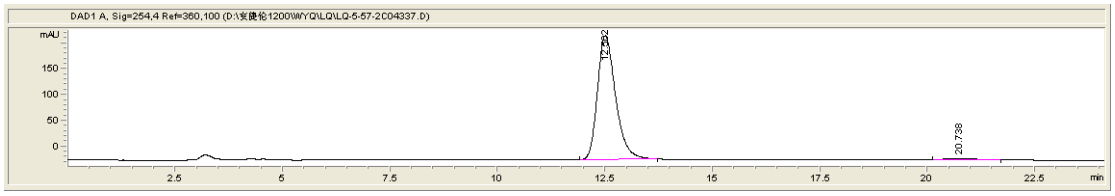
Racemic **3ac**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.639	BB	0.4933	1609.35718	48.98925	54.4552
2	20.814	BB	0.7640	1346.01941	26.98180	45.5448
总量 :				2955.37659	75.97105	

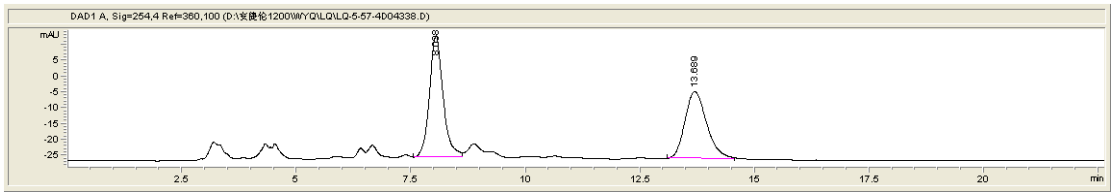
Chiral **3ac**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.502	BB	0.4521	7085.39014	240.21103	97.9414
2	20.738	BB	0.5511	148.92886	3.24693	2.0586
总量 :				7234.31900	243.45796	

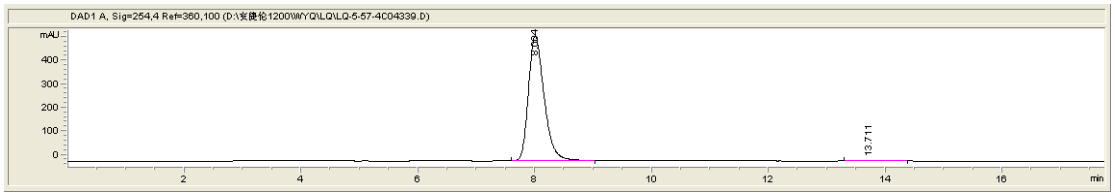
Racemic **3ad**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.038	VB	0.3136	802.31140	38.42495	53.5270
2	13.689	BB	0.5043	696.57843	21.14774	46.4730
总量 :				1498.88983	59.57269	

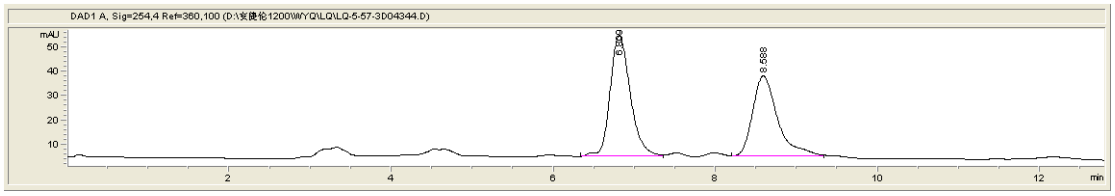
Chiral **3ad**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.004	BB	0.2879	9897.74414	530.02649	99.3288
2	13.711	BB	0.4361	66.88224	2.24130	0.6712
总量 :				9964.62638	532.26779	

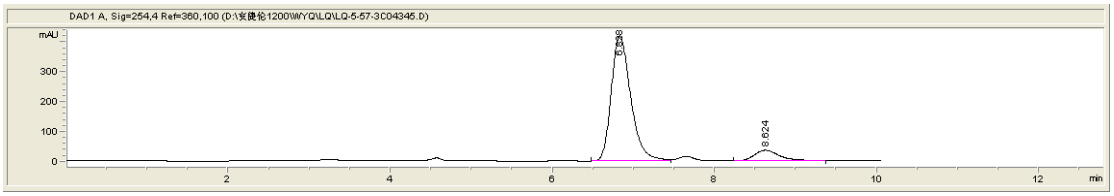
Racemic **3ae**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.809	BB	0.2683	874.59363	49.94981	55.0555
2	8.588	VB	0.3252	713.97498	33.16369	44.9445
总量 :				1588.56860	83.11350	

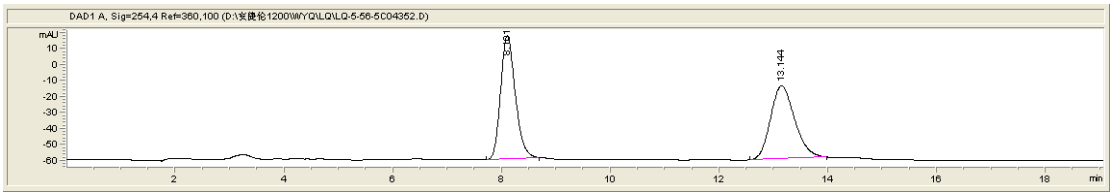
Chiral **3ae**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.828	BV	0.2571	7001.02051	418.71365	89.9897
2	8.624	BB	0.3348	778.78113	35.38276	10.0103
总量 :				7779.80164	454.09642	

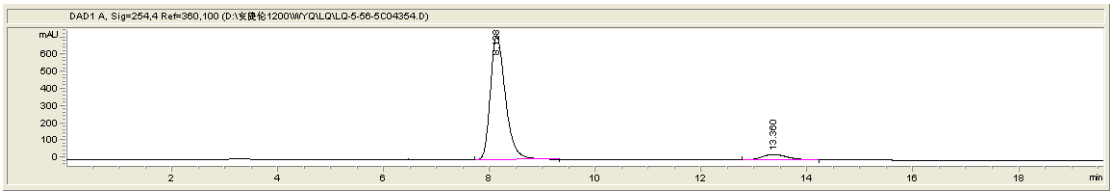
Racemic **3af**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.101	BB	0.2925	1457.75671	77.11700	50.7265
2	13.144	BB	0.4771	1416.00000	45.75404	49.2735
总量 :				2873.75671	122.87104	

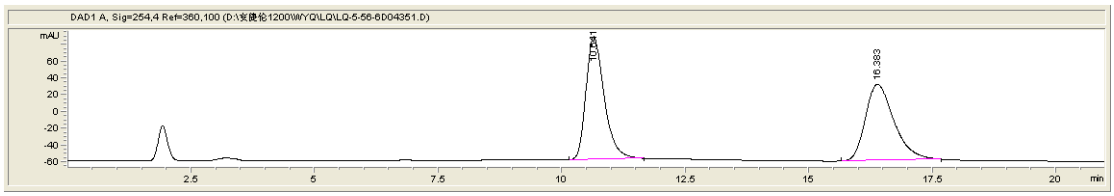
Chiral **3af**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.128	BB	0.3030	1.42978e4	722.19153	93.1522
2	13.360	BB	0.5012	1051.07031	32.17151	6.8478
总量 :				1.53489e4	754.36304	

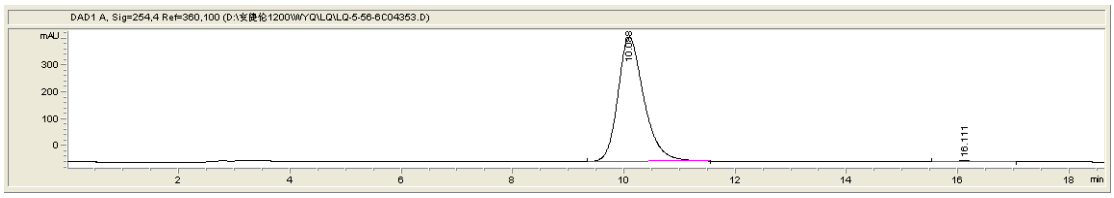
Racemic **3ag**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.641	BB	0.3952	3790.72388	146.81693	50.7014
2	16.383	BB	0.6132	3685.83789	91.26061	49.2986
总量 :				7476.56177	238.07754	

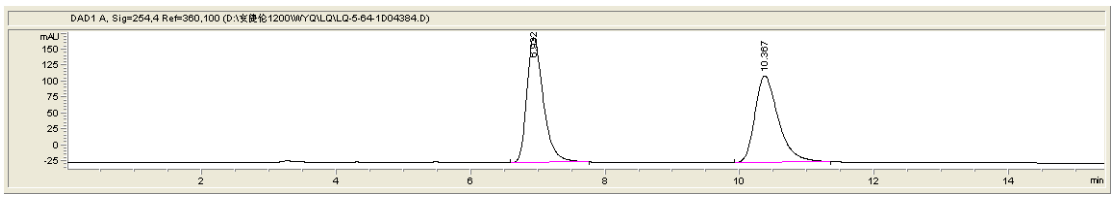
Chiral **3ag**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.088	BB	0.4911	1.50887e4	464.32034	99.0299
2	16.111	BB	0.5380	147.80820	3.42154	0.9701
总量 :				1.52365e4	467.74189	

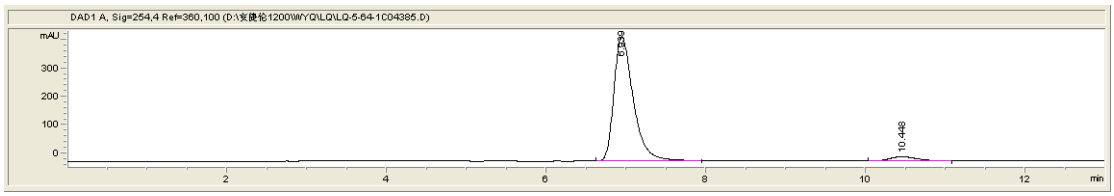
Racemic **3ah**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.932	BB	0.2604	3364.11426	195.81224	50.4133
2	10.367	BB	0.3685	3308.95117	135.69724	49.5867
总量 :				6673.06543	331.50948	

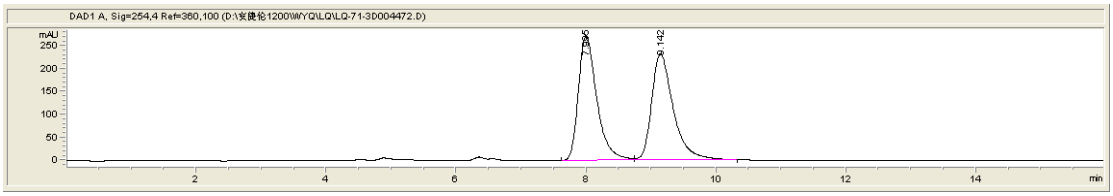
Chiral **3ah**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.939	BB	0.2567	7395.08203	438.67990	95.2050
2	10.448	BB	0.3703	372.45148	15.28143	4.7950
总量 :				7767.53351	453.96133	

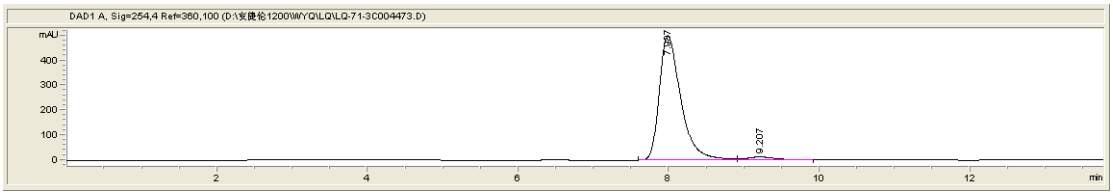
Racemic **3ai**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.995	BV	0.3006	5380.99951	272.28937	49.8555
2	9.142	VB	0.3521	5412.18262	232.02361	50.1445
总量 :				1.07932e4	504.31297	

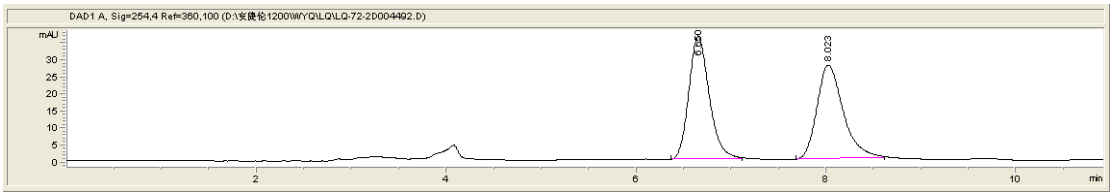
Chiral **3ai**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.987	BB	0.3016	9934.17871	500.42062	96.8221
2	9.207	BB	0.3907	326.05582	12.24522	3.1779
总量 :				1.02602e4	512.66584	

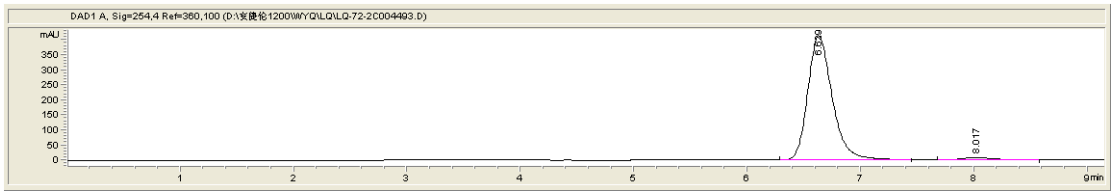
Racemic **3aj**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.650	BB	0.2283	540.01434	36.15530	50.3269
2	8.023	BB	0.2963	532.99866	27.47281	49.6731
总量 :				1073.01300	63.62811	

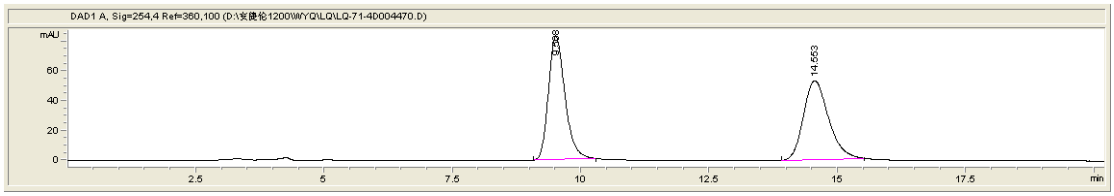
Chiral **3aj**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.629	BB	0.2286	6181.32227	413.14297	97.7464
2	8.017	BB	0.2883	142.51685	7.41406	2.2536
总量 :				6323.83911	420.55704	

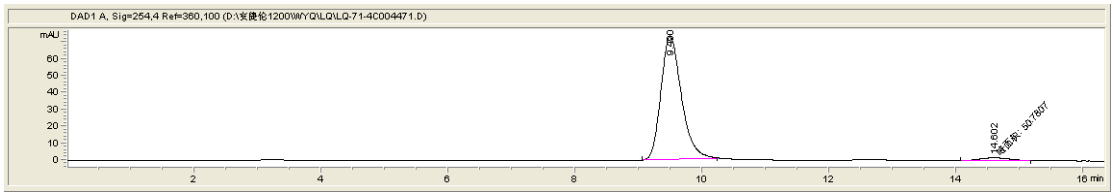
Racemic **3ak**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.508	BB	0.3451	1883.88733	83.53600	50.7887
2	14.553	BB	0.5274	1825.38086	53.32437	49.2113
总量 :				3709.26819	136.86037	

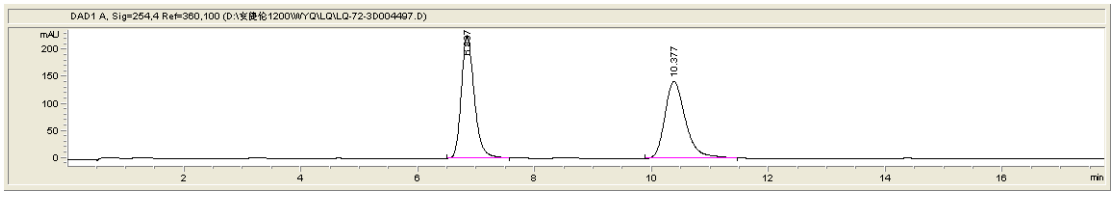
Chiral **3ak**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.490	BB	0.3444	1652.58728	73.46703	97.0188
2	14.602	MM	0.5245	50.78072	1.61367	2.9812
总量 :				1703.36800	75.08069	

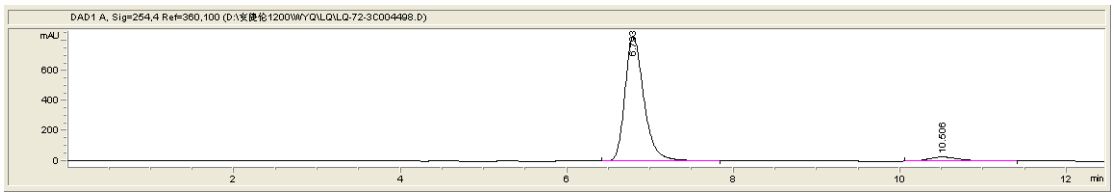
Racemic **3al**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.837	BB	0.2355	3485.34717	226.52129	49.9463
2	10.377	BB	0.3738	3492.84155	142.58202	50.0537
总量 :				6978.18872	369.10330	

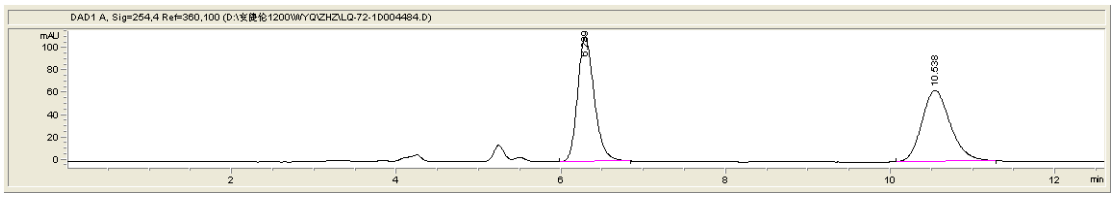
Chiral **3al**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.793	VB	0.2404	1.31209e4	830.26324	94.7499
2	10.506	BB	0.4044	727.02240	26.98153	5.2501
总量 :				1.38479e4	857.24477	

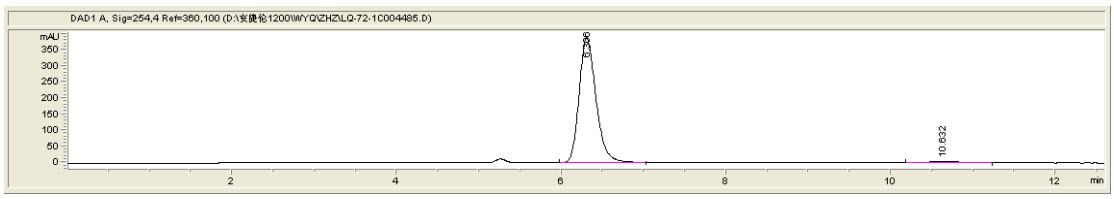
Racemic **3am**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.289	BB	0.2165	1576.10254	111.77472	50.5279
2	10.538	BB	0.3699	1543.16748	63.85543	49.4721
总量 :				3119.27002	175.63015	

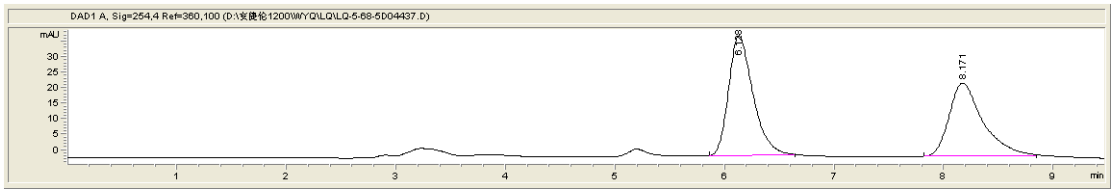
Chiral **3am**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.306	BB	0.2188	5569.03369	389.53912	97.6767
2	10.632	BB	0.3748	132.46118	5.42602	2.3233
总量 :				5701.49487	394.96514	

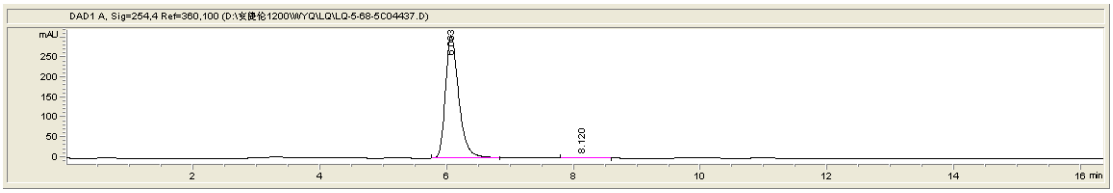
Racemic **3ba**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.128	BB	0.2357	604.31744	38.80529	54.3767
2	8.171	BB	0.3189	507.03662	23.58056	45.6233
总量 :				1111.35406	62.38585	

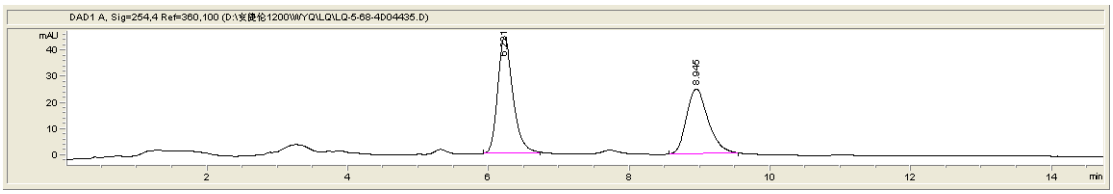
Chiral **3ba**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.063	BB	0.2224	4487.42139	307.21854	99.0418
2	8.120	BB	0.2865	43.41303	2.19780	0.9582
总量 :				4530.83442	309.41633	

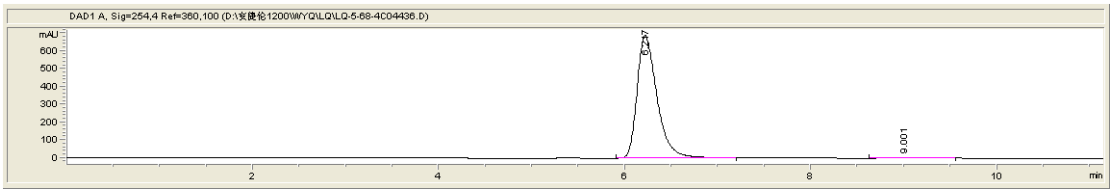
Racemic **3ca**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.221	BB	0.2300	674.24652	44.68898	55.5391
2	8.945	BB	0.3310	539.75604	24.88884	44.4609
总量 :				1214.00256	69.57782	

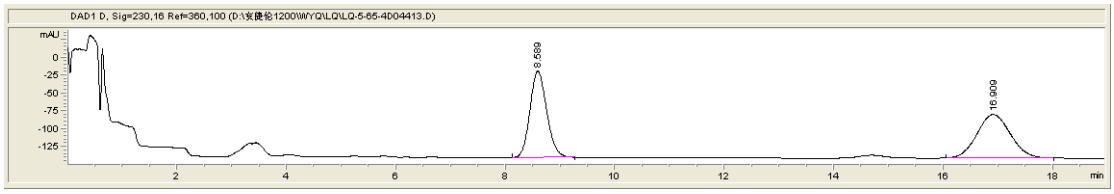
Chiral **3ca**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.217	BB	0.2257	1.02402e4	687.81586	98.9527
2	9.001	BB	0.3309	108.37885	4.80894	1.0473
总量 :				1.03486e4	692.62480	

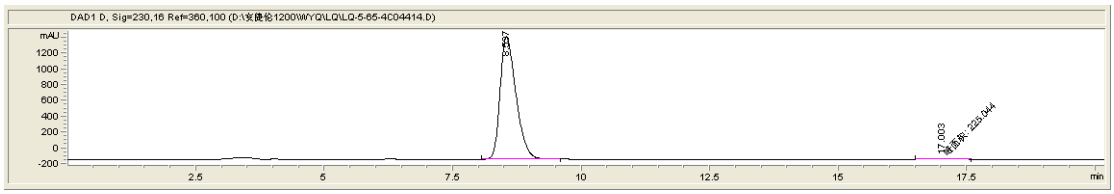
Racemic **3da**:



信号 3: DAD1 D, Sig=230,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.589	BB	0.3293	2588.85742	121.15580	49.9466
2	16.909	BB	0.6617	2594.39453	61.06507	50.0534
总量 :				5183.25195	182.22087	

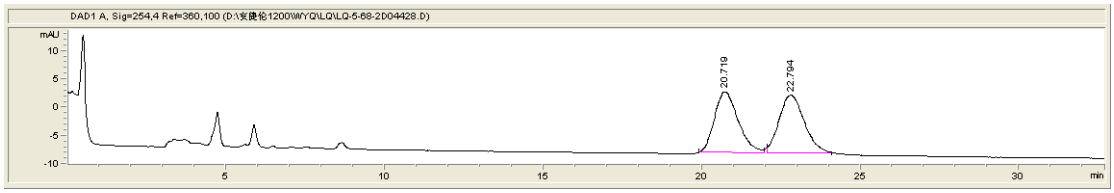
Chiral **3da**:



信号 3: DAD1 D, Sig=230,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.537	BB	0.3307	3.33690e4	1552.64575	99.3301
2	17.003	MM	0.5909	225.04395	6.34727	0.6699
总量 :				3.35941e4	1558.99302	

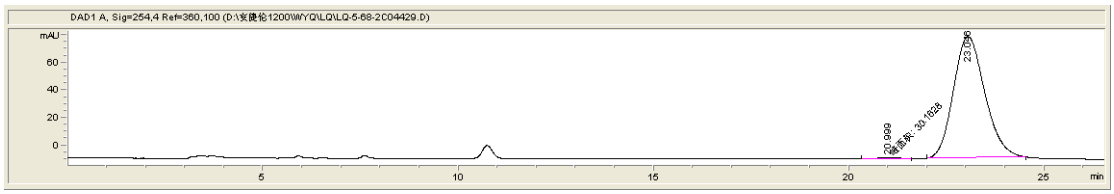
Racemic **3ea**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.719	BB	0.7632	564.15570	10.73407	49.9172
2	22.794	BB	0.7498	566.02826	10.22600	50.0828
总量 :				1130.18396	20.96007	

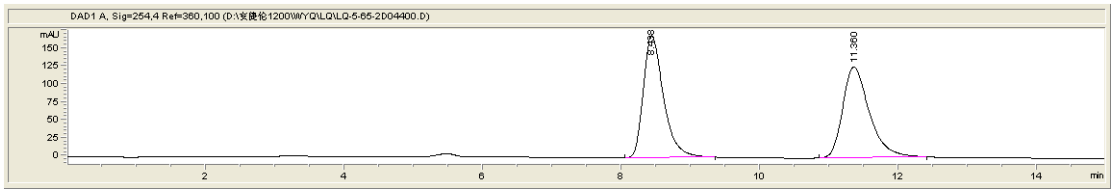
Chiral **3ea**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.999	MM	0.7164	30.16283	7.01717e-1	0.6056
2	23.046	BB	0.8673	4950.74414	88.14051	99.3944
总量 :				4980.90697	88.84223	

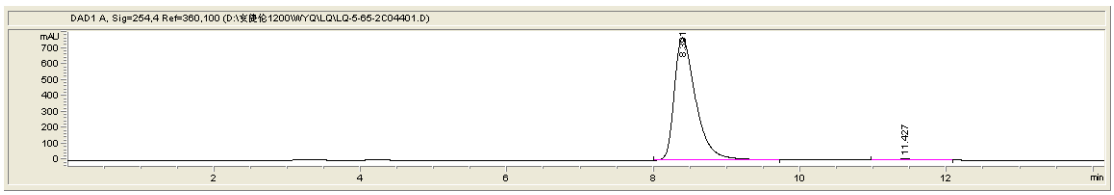
Racemic **3fa**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.438	BB	0.3094	3465.39331	170.29370	50.4103
2	11.360	BB	0.4081	3408.97656	126.61790	49.5897
总量 :				6874.36987	296.91160	

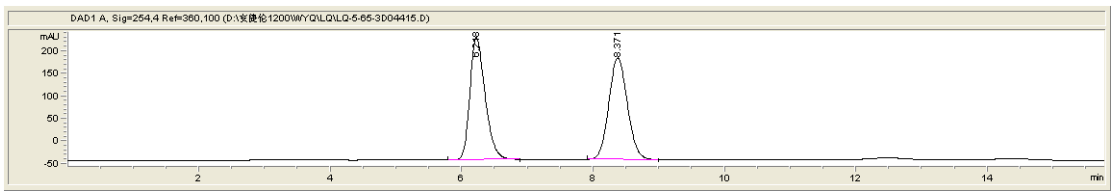
Chiral **3fa**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.391	BB	0.3094	1.56469e4	768.89252	98.9491
2	11.427	BB	0.3936	166.18591	6.30386	1.0509
总量 :				1.58131e4	775.19637	

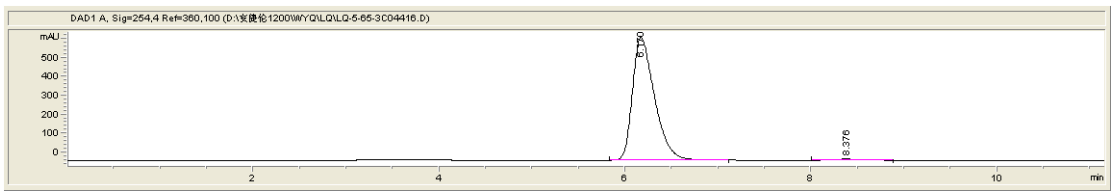
Racemic **3ga**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.218	BB	0.2471	4398.85937	271.38086	49.7551
2	8.371	BB	0.3054	4442.15771	225.92586	50.2449
总量 :				8841.01709	497.30672	

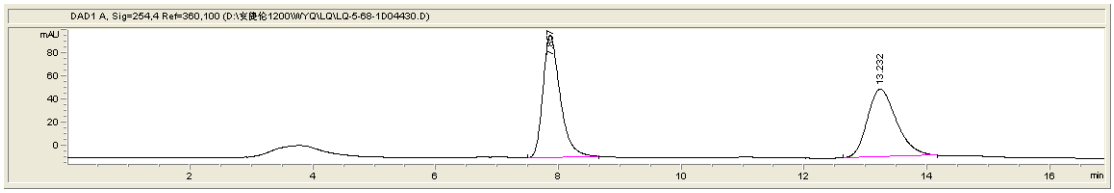
Chiral **3ga**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.170	BB	0.2524	1.06989e4	648.59918	98.9159
2	8.376	BB	0.3124	117.26095	5.78818	1.0841
总量 :				1.08162e4	654.38736	

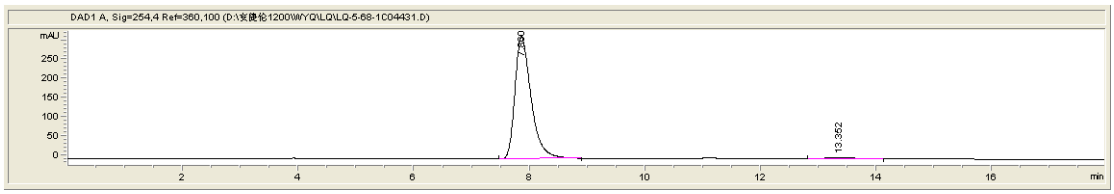
Racemic **3ha**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.857	BB	0.2986	2064.86230	105.37865	51.4612
2	13.232	BB	0.5061	1947.60083	58.84399	48.5388
总量 :				4012.46313	164.22264	

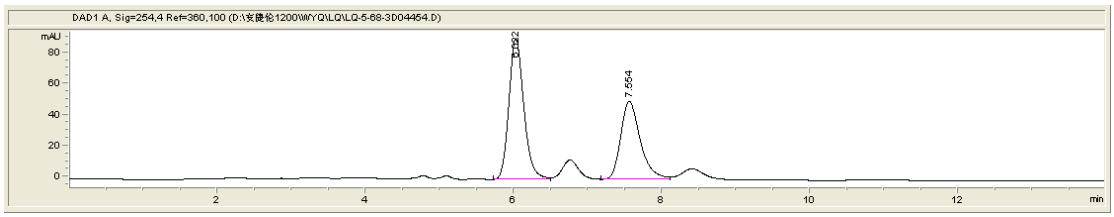
Chiral **3ha**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.860	BB	0.2969	6282.76709	320.22626	97.6480
2	13.352	BB	0.4904	151.32919	4.52270	2.3520
总量 :				6434.09628	324.74896	

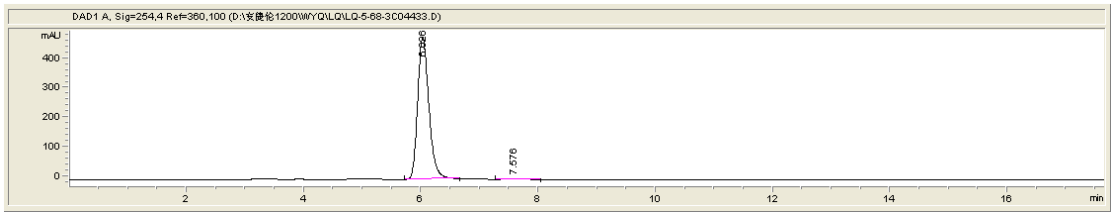
Racemic **3ia**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.022	BB	0.2133	1271.23962	90.81243	57.5364
2	7.554	VV	0.2829	938.21246	50.47276	42.4636
总量 :				2209.45209	141.28519	

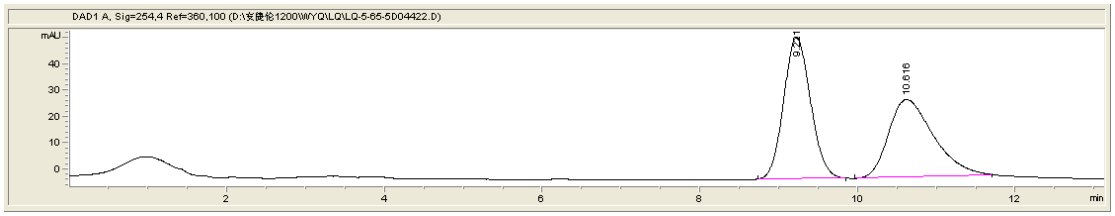
Chiral **3ia**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.026	BB	0.2022	6371.88818	482.14194	99.1338
2	7.576	BB	0.2672	55.67878	3.16487	0.8662
总量 :				6427.56696	485.30681	

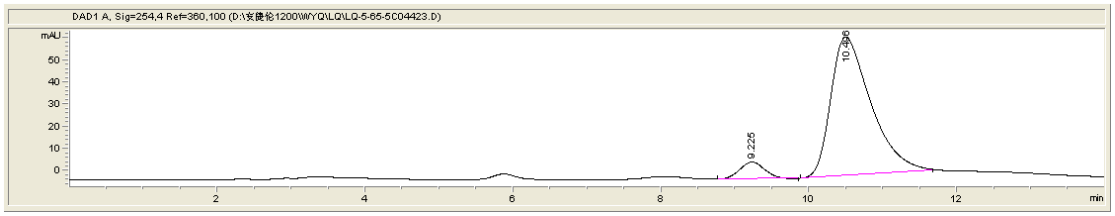
Racemic **3ja**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.221	BB	0.3688	1279.62769	53.93005	51.9491
2	10.616	BB	0.6096	1183.60596	29.65520	48.0509
总量 :				2463.23364	83.58525	

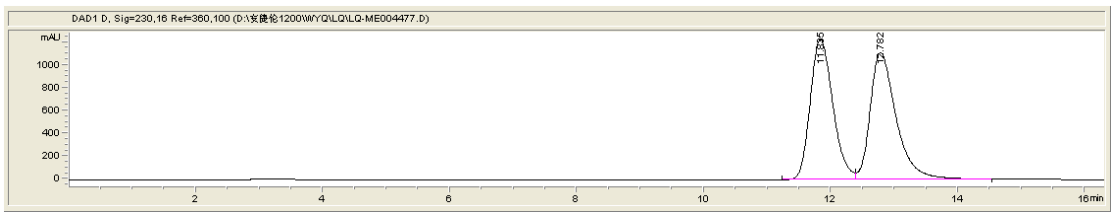
Chiral **3ja**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.225	BB	0.3628	179.41418	7.56083	7.0400
2	10.496	BB	0.5745	2369.08276	62.46379	92.9600
总量 :				2548.49695	70.02463	

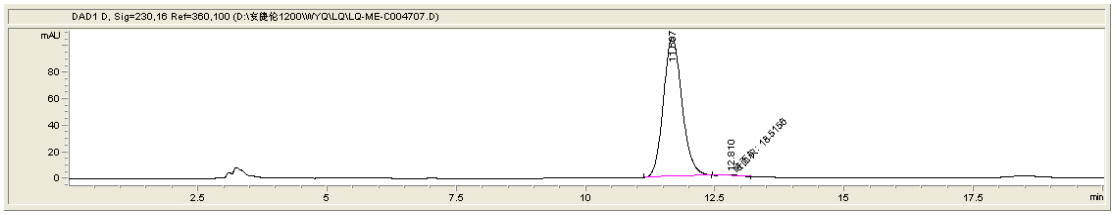
Racemic **4aa**:



信号 3: DAD1 D, Sig=230,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.835	BV	0.3840	3.03833e4	1230.92285	49.0153
2	12.782	VB	0.4318	3.16040e4	1111.12488	50.9847
总量 :				6.19873e4	2342.04773	

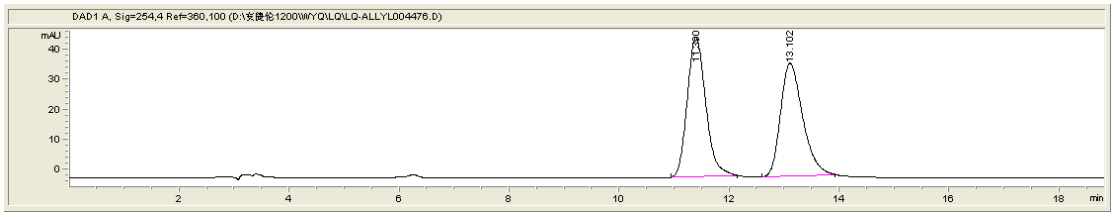
Chiral **4aa**:



信号 3: DAD1 D, Sig=230,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.667	BB	0.3855	2627.81982	105.16831	99.3003
2	12.810	MM	0.3707	18.51560	8.32386e-1	0.6997
总量 :				2646.33542	106.00070	

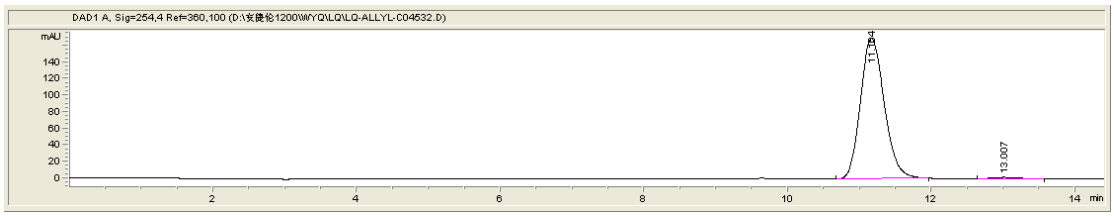
Racemic **4ab**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.390	BB	0.3642	1104.48547	46.66149	50.8154
2	13.102	BB	0.4322	1069.03857	37.76905	49.1846
总量 :				2173.52405	84.43054	

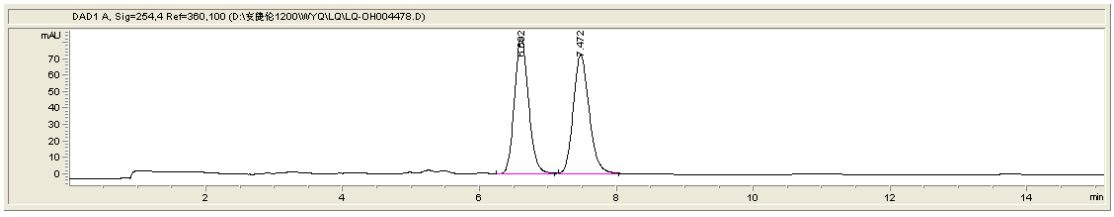
Chiral **4ab**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.164	BB	0.3609	3911.75342	169.70848	98.7262
2	13.007	BB	0.3731	50.46904	1.94265	1.2738
总量 :				3962.22246	171.65113	

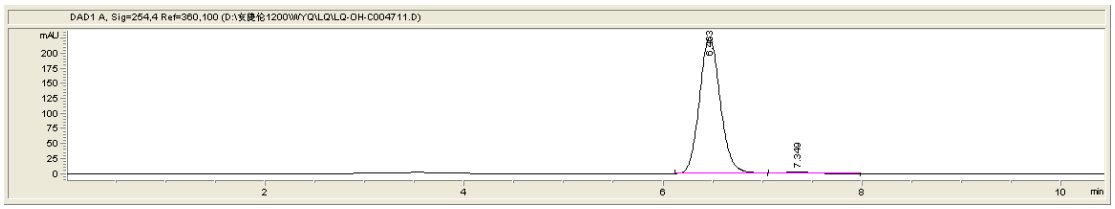
Racemic **4ac**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.602	VB	0.2208	1189.84900	83.20060	50.3480
2	7.472	BB	0.2497	1173.39954	72.16440	49.6520
总量 :				2363.24854	155.36500	

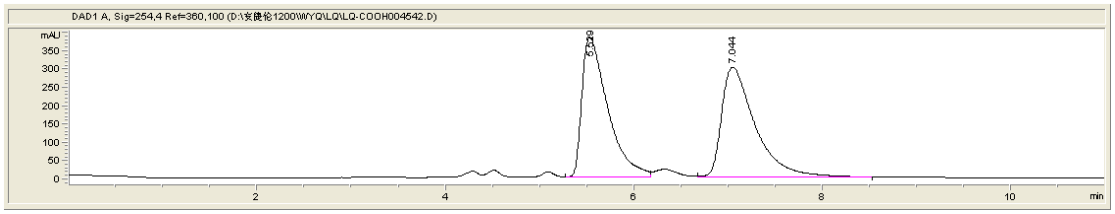
Chiral **4ac**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.463	BB	0.2244	3312.04932	226.71974	98.2277
2	7.349	BB	0.2793	59.75771	3.15078	1.7723
总量 :				3371.80702	229.87052	

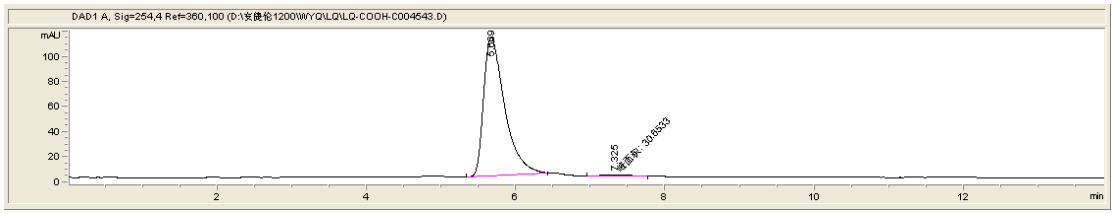
Racemic **4ad**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.529	VV	0.2833	7341.44873	383.49774	49.4718
2	7.044	VB	0.3706	7498.21387	301.07443	50.5282
总量 :				1.48397e4	684.57217	

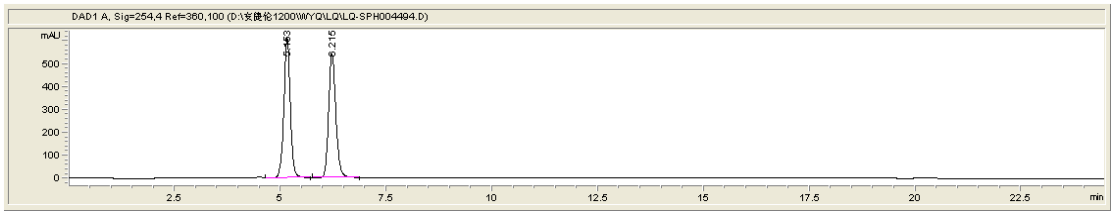
Chiral **4ad**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.669	BB	0.2946	2169.99731	110.75748	98.6071
2	7.325	MM	0.3949	30.65335	1.29367	1.3929
总量 :				2200.65066	112.05115	

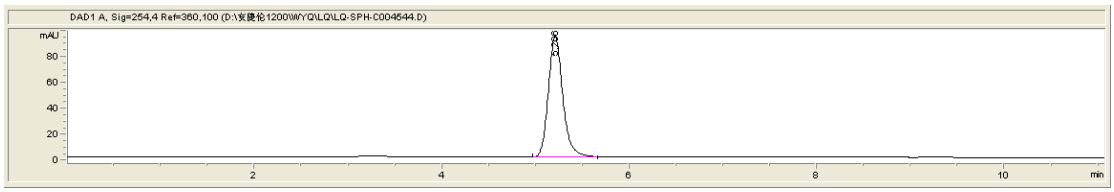
Racemic **4ae**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.153	VB	0.1597	6509.83594	614.13275	50.2314
2	6.215	BB	0.1829	6449.86084	541.91736	49.7686
总量 :				1.29597e4	1156.05011	

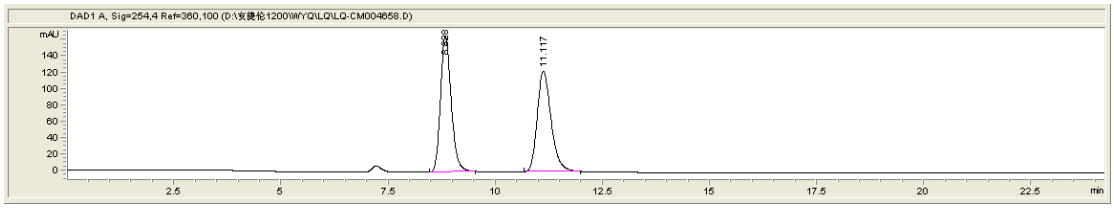
Chiral **4ae**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.206	BB	0.1627	993.83258	92.97012	100.0000
总量 :				993.83258	92.97012	

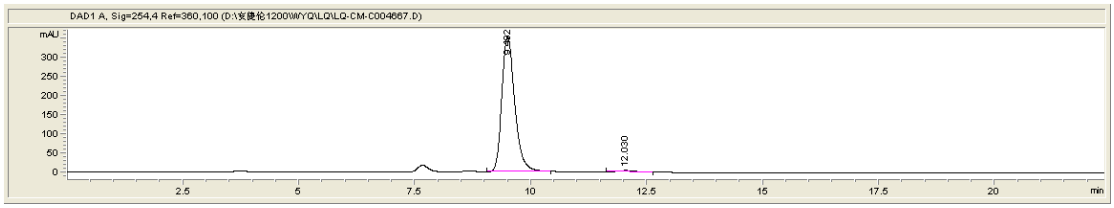
Racemic **4af**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.828	BB	0.2704	2913.14819	166.27229	51.1728
2	11.117	BB	0.3454	2779.61816	123.13933	48.8272
总量 :				5692.76636	289.41162	

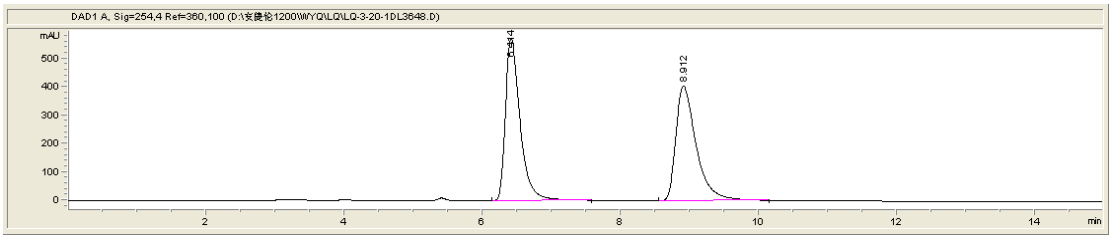
Chiral **4af**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.492	VB	0.2959	6881.46680	355.36636	98.5272
2	12.030	BB	0.3789	102.86619	4.06935	1.4728
总量 :				6984.33298	359.43572	

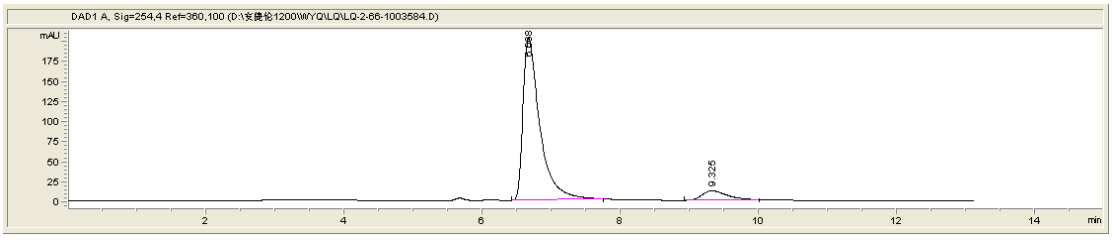
Racemic **6a**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.414	BB	0.2222	8446.17090	572.25580	50.3768
2	8.912	BB	0.3117	8319.82031	404.90045	49.6232
总量 :				1.67660e4	977.15625	

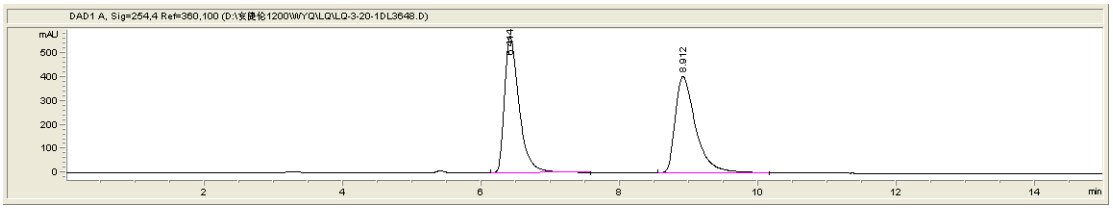
Chiral **6a**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.668	BB	0.2530	3436.63403	201.42960	91.9922
2	9.325	BB	0.3870	299.15582	11.67094	8.0078
总量 :				3735.78986	213.10054	

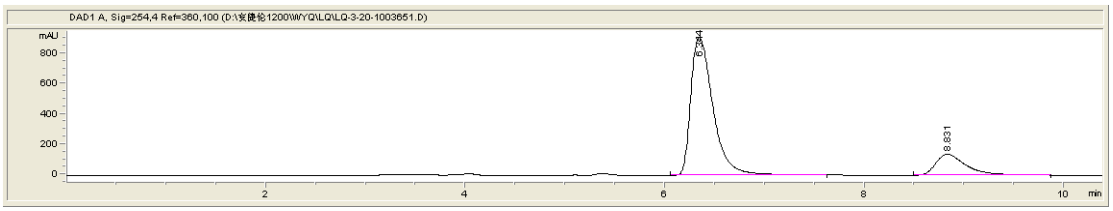
Racemic **6b**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.414	BB	0.2222	8446.17090	572.25580	50.3768
2	8.912	BB	0.3117	8319.82031	404.90045	49.6232
总量 :				1.67660e4	977.15625	

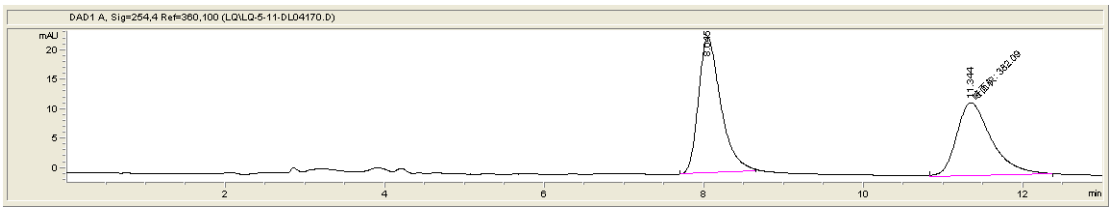
Chiral **6b**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

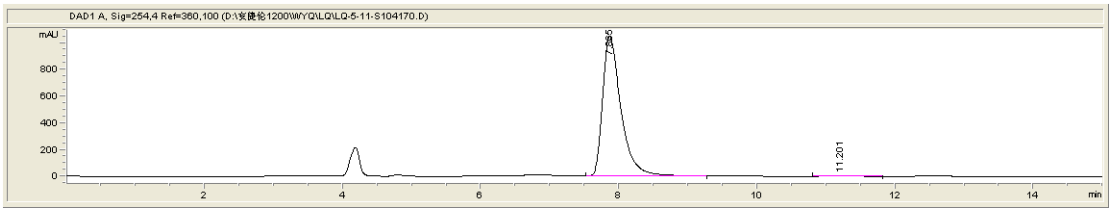
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.344	BB	0.2387	1.40890e4	909.69452	82.7344
2	8.831	BB	0.3210	2940.19141	137.74997	17.2656
总量 :				1.70292e4	1047.44449	

Racemic **6c**:



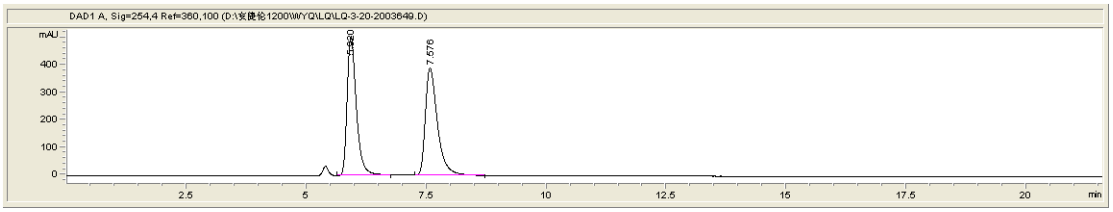
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.045	BB	0.2973	452.87234	23.04215	56.2296
2	11.344	BB	0.4432	352.52563	12.12481	43.7704
总量 :				805.39798	35.16695	

Chiral **6c**:



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.865	VB	0.2799	1.93487e4	1045.77808	99.5922
2	11.201	BB	0.3972	79.23054	2.87783	0.4078
总量 :				1.94279e4	1048.65591	

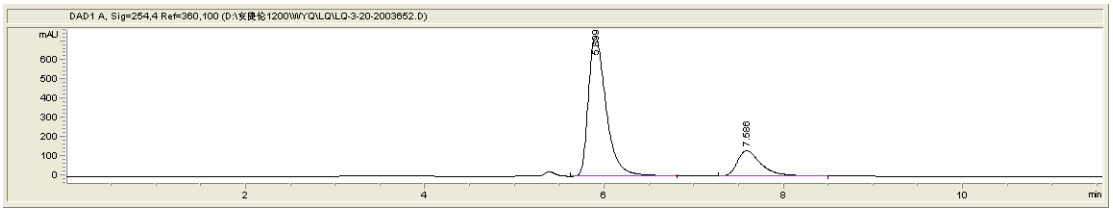
Racemic **6d**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.920	VB	0.2024	6786.58936	506.38809	49.9133
2	7.576	BB	0.2640	6810.15381	389.52136	50.0867
总量 :				1.35967e4	895.90945	

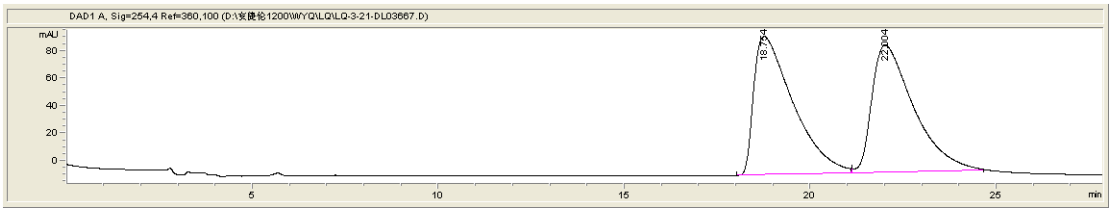
Chiral **6d**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.899	VB	0.2099	1.00028e4	729.90344	80.3806
2	7.586	BB	0.2758	2441.51172	133.24332	19.6194
总量 :				1.24444e4	863.14676	

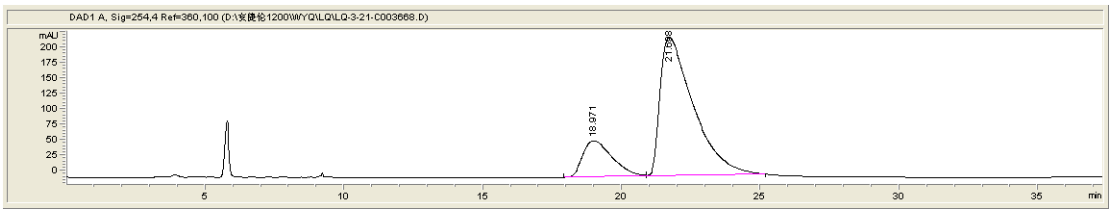
Racemic **6e**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.754	BB	1.0058	7420.65186	100.68619	50.5440
2	22.004	BB	1.0627	7260.91992	92.60964	49.4560
总量 :				1.46816e4	193.29583	

Chiral **6e**:



信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.971	BB	1.0264	4289.25879	58.16071	18.6510
2	21.698	BB	1.1584	1.87082e4	224.00064	81.3490
总量 :				2.29974e4	282.16135	

8. References

[1] Z. B. Zhao, L. Shi, Y. M. Li, F. J. Meng and Y. G. Zhou, Facile synthesis of chiral ε-sultams via an organocatalytic aza-Friedel–Crafts reaction, *Org. Biomol. Chem.*, 2019, **17**, 6364–6368.

[2] X. Song, Y. Fan, Z. Zhu and Q. Ni, Chiral phosphoric acid-catalyzed asymmetric arylation of indolizines: atroposelective access to axially chiral 3-arylindolizines, *Org. Lett.*, 2022, **24**, 2315–2320.

[3] Y. –Q. Wang, X. –Y. Cui, Y. –Y. Ren and Y. Zhang, A highly enantioselective and regioselective organocatalytic direct Mannich reaction of methyl alkyl ketones with cyclic imines benzo[e][1,2,3]oxathiazine 2,2-dioxides, *Org. Biomol. Chem.*, 2014, **12**, 9101–9104.