Electronic Supplementary Information

Enantioselective aza-Friedel-Crafts Alkylation of Aniline Derivatives with Cyclic N-Sulfonyl α-Ketiminoesters: The Effect of Catalyst Confinement and The Rationale Behind the High Enantioselectivity

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CONTENTS

1. Experimental Section

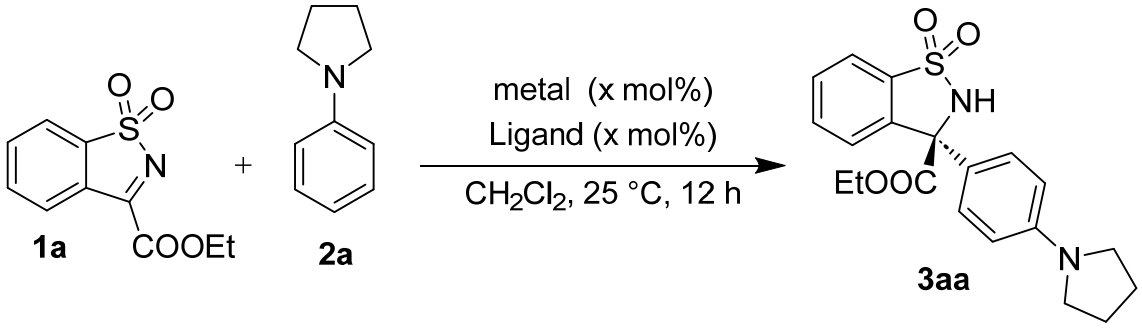
1.1. General Information

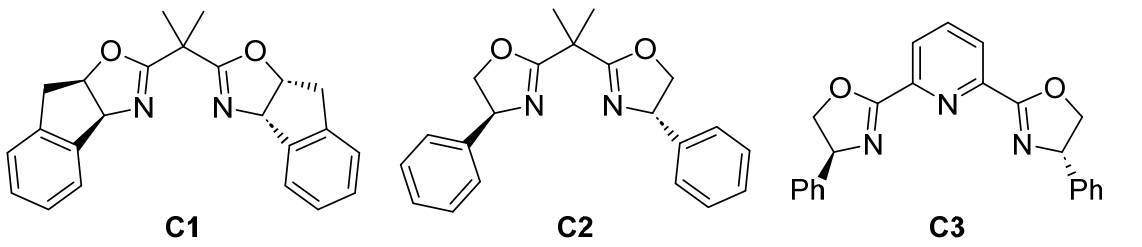
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on 400 MHz nuclear magnetic resonance spectrometer with tetramethylsilane (TMS) as the internal standard. High performance liquid chromatography experiments were performed with Daicel chiral column (AD-H, OD-H, IA, IB, IC, OB-H etc.). Specific rotations were measured with an automatic polarimeter. High-resolution mass spectra (HRMS) were obtained with Varian 7.0T Fourier transform ion cyclotron resonance mass spectrometer. The solvents (such as petroleum ether, ethyl acetate, dichloromethane, etc.) are analytical grade. The room temperature was 25 °C; the silica gel used for column chromatography was 200-300 mesh. Unless otherwise noted, commercial reagents were used as received. All solvents were handled in accordance with standard procedures.

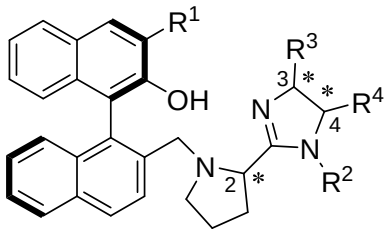
Ligands **C1-C3** are commercially available. Preparation of chiral ligands **L1-L13** have been reported previously.[1]

1.2. Optimization of Reaction Conditions

Table S1. Enantioselective Friedel-Crafts reaction of 1-phenylpyrrolidine **2a** with α-ketiminoester **1a**.[a]







(R_a,S_2)-**L1**: R^1 = H, R^2 = Ts, R^3 = H, R^4 = H
(R_a,S_2,S_3)-**L2**: R^1 = H, R^2 = Ts, R^3 = *i*-Pr, R^4 = H
(R_a,S_2,S_3)-**L3**: R^1 = H, R^2 = Ts, R^3 = *t*-Bu, R^4 = H
(R_a,S_2,S_3,S_4)-**L4**: R^1 = H, R^2 = Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,R_3,R_4)-**L5**: R^1 = H, R^2 = Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,S_3,S_4)-**L6**: R^1 = Cl, R^2 = Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,S_3,S_4)-**L7**: R^1 = I, R^2 = Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,S_3,S_4)-**L8**: R^1 = CF_3, R^2= Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,R_3,R_4)-**L9**: R^1 = Cl, R^2 = Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,R_3,R_4)-**L10**: R^1 = CF_3, R^2 = Ts, R^3 = Ph, R^4 = Ph
(R_a,S_2,S_3)-**L11**: R^1 = Cl, R^2 = Ts, R^3 = *t*-Bu, R^4 = H
(R_a,S_2,S_3)-**L12**: R^1 = Cl, R^2 = Ns, R^3 = *t*-Bu, R^4 = H
(R_a,S_2,S_3)-**L13**: R^1 = Cl, R^2 = Bs, R^3 = *t*-Bu, R^4 = H

Entry	Ligand	Metal	x (mol%)	Yield (%)[b]	ee (%)[c]	Config.[d]
1	C1	$Cu(OTf)_2$	10	30	27	R
2	C2	$Cu(OTf)_2$	10	40	71	S
3	C3	$Cu(OTf)_2$	10	Trace	-	-
4	L1	$Cu(OTf)_2$	10	98	65	R
5	L2	$Cu(OTf)_2$	10	92	90	R
6	L3	$Cu(OTf)_2$	10	86	81	R
7	L4	$Cu(OTf)_2$	10	85	95	R
8	L5	$Cu(OTf)_2$	10	85	72	S
9	L6	$Cu(OTf)_2$	10	95	>99	R
10	L7	$Cu(OTf)_2$	10	94	>99	R
11	L8	$Cu(OTf)_2$	10	97	>99	R
12	L9	$Cu(OTf)_2$	10	93	40	R
13	L10	$Cu(OTf)_2$	10	88	38	R
14	L11	$Cu(OTf)_2$	10	90	50	R
15	L12	$Cu(OTf)_2$	10	80	40	R
16	L13	$Cu(OTf)_2$	10	95	47	R
17	L8	$Cu(ClO_4)_2 \cdot 6H_2O$	10	95	99	R
18	L8	$Zn(OTf)_2$	10	90	69	R
19	L8	$Sc(OTf)_3$	10	30	5	R
20	L8	$Ni(OTf)_2$	10	98	>99	R
21	L8	$Ni(ClO_4)_2 \cdot 6H_2O$	10	90	99	R
22[e]	L8	$Ni(OTf)_2$	10	89	99	R
23[f]	L8	$Ni(OTf)_2$	10	90	99	R

24[g]	L8	$Ni(OTf)_2$	10	none	-	-
25	L8	$Cu(OTf)_2$	5	93	>99	R
26	L8	$Ni(OTf)_2$	5	95	>99	R
27	L8	$Cu(OTf)_2$	1	91	>99	R
28	L8	$Ni(OTf)_2$	1	94	>99	R
29[h]	L8	$Cu(OTf)_2$	0.5	61	88	R
30[h]	L8	$Ni(OTf)_2$	0.5	94	>99	R
31[h]	L8	$Ni(OTf)_2$	0.1	94	>99	R
32[h]	L8	$Ni(OTf)_2$	0.05	71	80	R

[a] Unless otherwise noted, all reactions were performed with **1a** (0.15 mmol), **2a** (0.18 mmol), ligand (10 mol%) and $Cu(OTf)_2$ (10 mol%) in dry CH_2Cl_2 (1.5 mL) at 25 °C for 12 h. [b] Isolated yield. [c] Determined by HPLC on chiral stationary phases. [d] The absolute configuration of **3a** was deduced based on the absolute configuration of **3ah** which was assigned by single crystal X-ray diffraction experiment. [e] THF as solvent. [f] Toluene as solvent. [g] Methanol as solvent. [h] Reaction time = 24 h.

1.3. General Procedures for Enantioselective aza-Friedel-Crafts Reaction of Anilines with Cyclic N-Sulfonyl α-Ketiminoesters

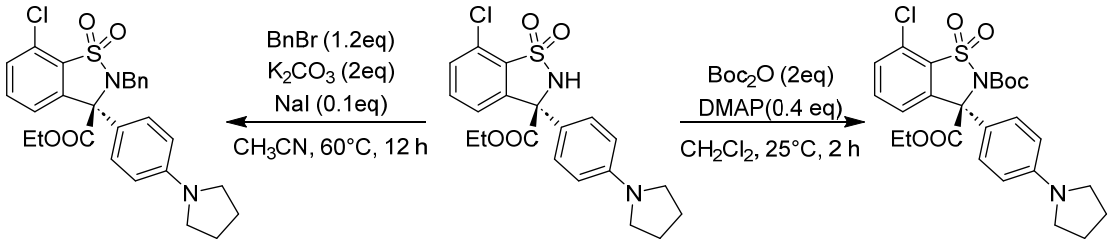
Preparation of the Chiral Catalyst

Binaphthyl-proline-imidazoline chiral ligand **L8** (23.9 mg, 0.03 mmol), $Ni(OTf)_2$ (10.7 mg, 0.03 mmol) were stirred in a dry reaction tube in CH_2Cl_2 (2.0 mL, accessed by pipette) at room temperature, and then the solution was stored in a cool and dry place as stock solution.

General Procedure for the Operation

Cyclic *N*-sulfonyl α-ketiminoester **1** (0.15 mmol) and anilines **2** (0.18 mmol) were stirred in a dry reaction tube in CH_2Cl_2 (1.5 mL) at 25 °C, 10 μl (0.1 mol%) or 50 μl (0.5 mol%) of dichloromethane solution of the catalyst was then added to the reaction mixture with a mechanical pipette. The reaction mixture was stirred for 24 h at 25 °C and the reaction was monitored with TLC. After the consumption of ketimine **1**, the reaction mixture was directly purified with flash chromatography (petroleum ether : ethyl acetate = 5:1) on silica gel to give the desired product.

1.4. Transformation of Product 3



5
97 yeild%, >99 ee%

3ah
99 ee%

4
96 yeild%, >99 ee%

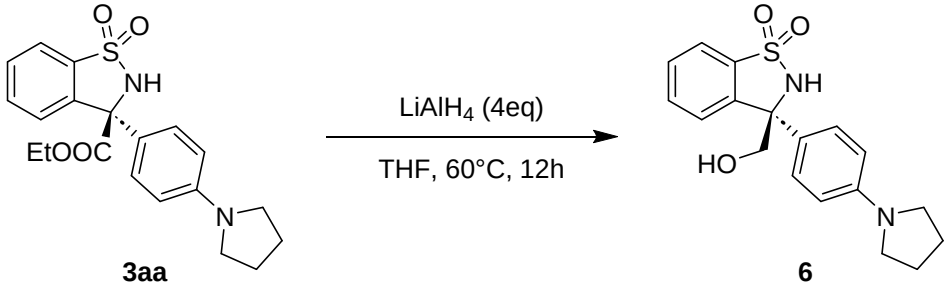
*Synthesis of Compound **4***

Boc_2O (104 mg, 0.48 mmol) was slowly added to a mixture of **3ah** (120 mg, 0.24 mmol) and DMAP (11.6 mg, 0.09 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred for 2 h at room temperature. The organic layer were washed with water, brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified with silica gel column chromatography (petroleum ether : ethyl acetate = 5: 1) to give product **4.**

*Synthesis of Compound **5***

BrBn (49 mg, 0.29 mmol) was added to a mixture of **3ah** (120 mg, 0.24 mmol), potassium carbonate (66 mg, 0.48 mmol) and NaI (3.6 mg, 0.02 mmol) in CH_3CN (20 mL). The mixture was stirred for 12 h at 60 °C. After the reaction was completed, 50 mL of EtOAc was added to the reaction mixture and the organic layer was washed with water, brine, dried with Na_2SO_4, filtered and was concentrated *in vacuo*. The crude product was purified with silica gel column chromatography (petroleum ether: ethyl acetate = 2: 1) to give product **5**.

*Synthesis of Compound **6***



3aa
99 ee%

6
72 yeild%, >99 ee%

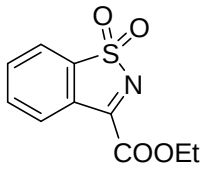
Compound **3aa** (100 mg, 0.26 mmol) was dissolved in 30 mL of dry THF at 0 °C, and $LiAlH_4$ (39 mg, 1.04 mmol) was added in batches in 30 min. The resulting mixture was refluxed for 12 h. The mixture was quenched with $Na_2SO_4 \cdot 10H_2O$ at 0 °C, and the solid was removed by filtration through celite. The filtrate was concentrated *in vacuo* and the residue

was purified by column chromatography (silica gel, petroleum ether : ethyl acetate 1:1) to give product **6**.

2. Preparation of Cyclic N-Sulfonyl α-Ketiminoesters 1.

General experimental details for the preparation of substrates **1** have been reported previously.[2]

Ethyl benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1a**)

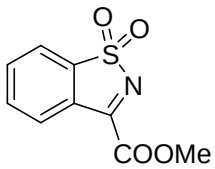


1a

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 6.7 Hz, 1H), 7.95 (d, *J* = 6.4 Hz, 1H), 7.82 – 7.74 (m, 2H), 4.55 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.6, 160.3, 140.5, 134.5, 134.3, 128.5, 127.8, 123.1, 64.0, 14.2.

Methyl benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1b**)

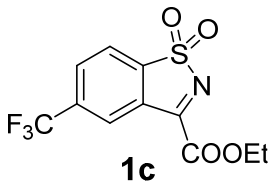


1b

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 – 8.29 (m, 1H), 7.97 – 7.94 (m, 1H), 7.81 – 7.77 (m, 2H), 4.10 (s, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.0, 160.0, 140.3, 134.5, 134.4, 128.3, 127.8, 123.2, 54.2.

Ethyl 5-(trifluoromethyl)benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1c**)



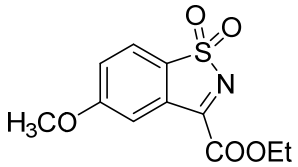
1c

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.09 (t, *J* = 5.4 Hz, 2H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.2, 158.7, 143.4, 136.8 (q, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 131.4 (q, $^{3}J_{C\text{-}F}$= 3.4 Hz), 129.2, 125.1 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 123.7, 122.7 (q, $^{1}J_{C\text{-}F}$= 273.6 Hz), 64.4, 14.1.

^{19}F NMR (Chloroform-*d*) δ -62.9.

Ethyl 5-methoxybenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1d**)

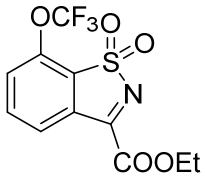


1d

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 2.3 Hz, 1H), 7.23 – 7.20 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 164.5, 160.6, 159.7, 131.5, 130.8, 124.3, 119.4, 112.6, 63.9, 56.4, 14.1.

Ethyl 7-(trifluoromethoxy)benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1e**)



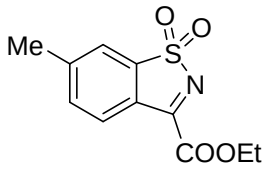
1e

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 7.7 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.2, 158.8, 145.2 (q, $^{3}J_{C\text{-}F}$ = 2.2 Hz), 137.1, 124.6 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz), 131.0, 125.2, 120.2 (q, $^{1}J_{C\text{-}F}$= 263.3 Hz), 64.2, 14.1.

^{19}F NMR (Chloroform-*d*) δ -57.2.

Ethyl 6-methylbenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1f**)

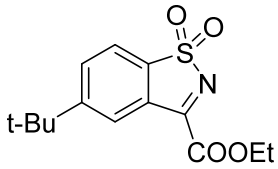


1f

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.9 Hz, 1H), 7.74 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.7, 146.4, 140.4, 135.0, 127.4, 126.1, 123.8, 63.9, 22.0, 14.1.

Ethyl 5-(tert-butyl)benzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1g**)

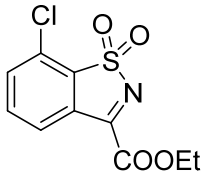


1g

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.79 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.39 (s, 9H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.5, 159.2, 137.5, 131.4, 128.9, 63.8, 35.9, 31.2, 14.1.

Ethyl 7-chlorobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1h**)

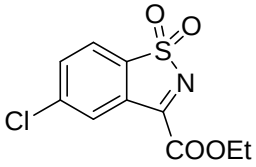


1h

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.18 (m, 1H), 7.73 – 7.68 (m, 2H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.2, 158.9, 137.7, 135.9, 134.9, 131.2, 130.5, 125.9, 64.2, 14.1.

Ethyl 5-chlorobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**1i**)

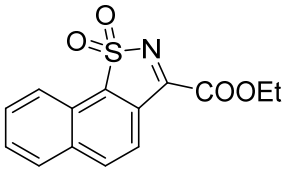


1i

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.74 (m, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.2, 158.9, 141.1, 138.5, 134.1, 130.1, 127.9, 123.9, 64.2, 14.1.

Ethyl naphtho[2,1-*d*]isothiazole-3-carboxylate 1,1-dioxide (**1j**)

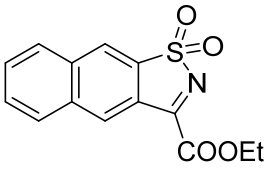


1j

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.1 Hz, 1H), 8.23 – 8.14 (m, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.73 (m, 2H), 4.57 (q, 2H), 1.51 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.9, 160.8, 138.3, 135.3, 130.4, 130.2, 128.9, 124.7, 121.4, 64.0, 14.2.

Ethyl naphtho[2,3-*d*]isothiazole-3-carboxylate 1,1-dioxide (**1k**)



1k

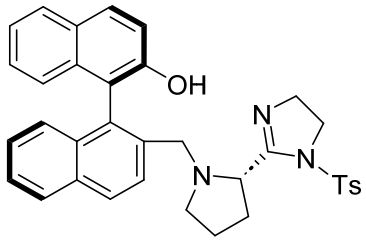
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 8.38 (s, 1H), 8.10 – 8.02 (m, 2H), 7.82 – 7.73 (m, 2H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.7, 160.2, 134.9, 134.6, 134.2, 131.3, 131.2, 131.0, 130.0, 129.8, 124.5, 63.8, 14.1.

Preparation of Chiral Ligands

Ligands **C1-C3** are commercially available, and were purchased from Bidepharm Shanghai. Preparation of chiral ligands **L1-L13** have been developed in our group and has been reported previously.[1]

(R_a,*S*)-2'-((2-(1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol **(L1)**



L1

White solid (0.58 g, 59% yield). m. p. = 95-97 °C; (silica gel, petroleum ether: ethyl acetate = 5: 1).

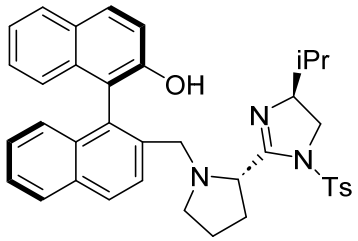
$[\alpha]_D^{20}$ **+247.42** (*c* = 0.30, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.49 (s, 1H), 7.84 – 7.71 (m, 4H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.12 (dd, *J* = 12.9, 7.4 Hz, 3H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.60 (dd, *J* = 15.7, 8.4 Hz, 2H), 3.76 – 3.67 (m, 1H), 3.63 (d, *J* = 12.1 Hz, 1H), 3.55 – 3.44 (m, 1H), 3.27 (q, *J* = 9.6 Hz, 1H), 3.00 (dd, *J* = 13.5, 8.5 Hz, 2H), 2.42 (s, 4H), 2.25 – 2.13 (m, 2H), 2.00 – 1.88 (m, 1H), 1.70 – 1.47 (m, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.1, 155.1, 145.2, 138.2, 136.4, 135.2, 133.9, 133.7, 133.0, 130.2, 129.4, 128.6, 127.9, 127.5, 127.3, 127.3, 127.0, 126.4, 126.1, 125.8, 124.0, 122.5, 120.8, 118.2, 61.9, 59.2, 56.0, 50.4, 48.5, 33.1, 23.6, 21.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{34}N_3O_3S$ 576.2315, found 576.2318.

(R_a,S_2,S_3)-2'-((2-(4-isopropyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol **(L2)**



L2

White solid (0.75 g, 61% yield); m. p. = 172-174 °C; (silica gel, petroleum ether : ethyl acetate = 5: 1).

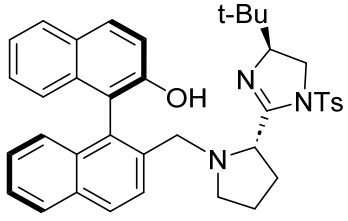
$[\alpha]_D^{20}$ **+134.17** (*c* = 0.80, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.93 – 7.78 (m, 4H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.30 (m, 5H), 7.26 – 7.18 (m, 1H), 7.15 (d, *J* = 3.7 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 8.3 Hz, 1H), 3.99 – 3.82 (m, 1H), 3.79 – 3.57 (m, 2H), 3.23 – 2.98 (m, 2H), 2.99 – 2.83 (m, 1H), 2.60 – 2.42 (m, 4H), 2.39 – 2.24 (m, 2H), 1.86 – 1.70 (m, 2H), 1.68 – 1.53 (m, 1H), 0.27 (d, *J* = 6.7 Hz, 3H), 0.15 (d, *J* = 6.4 Hz, 3H), -0.05 – -0.30 (m, 1H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.8, 154.8, 145.1, 138.2, 136.1, 134.8, 134.3, 134.0, 133.4, 130.2, 129.5, 128.7, 128.0, 127.7, 127.4, 127.4, 127.0, 126.8, 126.2, 126.1, 125.7, 124.4, 122.7, 121.1, 118.8, 70.1, 62.7, 59.6, 56.1, 53.0, 33.6, 32.7, 23.7, 21.8, 19.5, 18.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{38}H_{40}N_3O_3S$ 618.2785, found 618.2788.

(R_a,S_2,S_3)-2'-((2-(4-(tert-butyl)-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol **(L3)**



L3

White solid (0.64 g, 53% yield); m. p. =114-116 °C; (silica gel, petroleum ether: ethyl acetate = 5: 1).

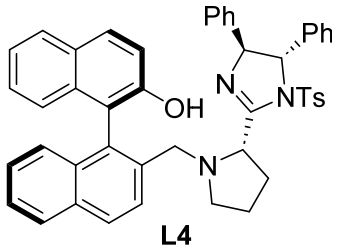
$[\alpha]_D^{20}$ **- 35.26** (*c* = 0.70, CH_2Cl_2);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 3H), 7.43 – 7.38 (m, 1H), 7.35 – 7.29 (m, 2H), 7.22 – 7.13 (m, 3H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.36 (d, *J* = 8.3 Hz, 1H), 3.65 (d, *J* = 9.8 Hz, 3H), 3.57 (t, *J* = 9.6 Hz, 1H), 3.12 (t, *J* = 9.0 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.59 (q, *J* = 7.9 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.37 (s, 3H), 2.02 – 1.95 (m, 1H), 1.90 – 1.81 (m, 1H), 1.77 – 1.70 (m, 1H), 0.29 (s, 9H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 159.7, 154.3, 144.7, 137.3, 134.8, 134.2, 134.1, 133.5, 130.0, 129.7, 129.1, 128.2, 128.1, 127.8, 127.3, 127.2, 126.7, 126.2, 126.2, 125.6, 125.0, 123.0, 121.6, 120.3, 73.6, 62.6, 58.8, 54.0, 49.2, 32.8, 32.7, 27.0, 25.4, 23.2, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{39}H_{42}N_3O_3S$ 632.2941, found 632.2948.

(R_a,S_2,S_3,S_4)-2'-((2-(4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol **(L4)**



L4

White solid (0.80 g, 57% yield); m. p. = 118-120 °C; (silica gel, petroleum ether: ethyl acetate = 8: 1).

$[\alpha]_D^{20}$ **-62.68** (*c* = 0.56, CH_2Cl_2).

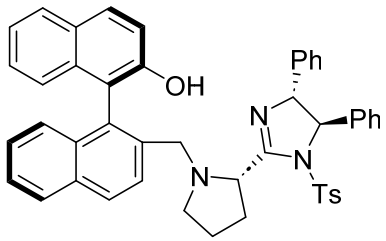
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.90 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.32 (t, *J* = 8.4 Hz, 4H), 7.16 (t, *J* = 9.2 Hz, 6H), 7.09 (d, *J* = 8.5 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.63 (t, *J* = 6.5 Hz, 4H), 6.11 (d, *J* = 7.6 Hz, 2H), 4.80 (d, *J* = 5.5 Hz, 1H), 4.65 (d, *J* = 8.8 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 3.84 (d, *J* = 12.4 Hz, 1H), 3.72 (d, *J* = 12.5 Hz, 1H), 2.91 (d, *J* = 9.5 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.41 – 2.31 (m, 1H), 2.25 (s, 3H), 2.07 (d, *J* = 8.1 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.82 – 1.76 (m, 1H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 161.9, 154.2, 144.5, 141.9, 140.5, 135.2,

134.2, 133.9, 133.4, 132.2, 132.1, 129.8, 129.2, 129.0, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 127.6, 127.3, 127.1, 126.9, 126.4, 126.4, 126.2, 125.7, 125.6, 125.1, 123.0, 121.8, 71.9, 62.9, 58.5, 53.6, 32.3, 26.9, 23.3, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{47}H_{42}N_3O_3S$ 728.2941, found 728.2947.

(R_a,S_2,R_3,R_4)-2'-((2-(4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol **(L5)**



L5

White solid (0.73 g, 53% yield); m. p. = 106-108 °C; (silica gel, petroleum ether : ethyl acetate = 8: 1).

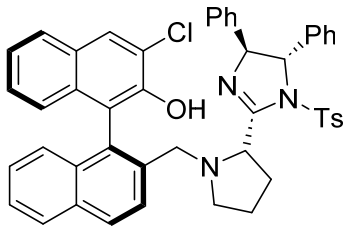
$[\alpha]_D^{20}$ **+126.44** (*c* = 0.60, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.07 (s, 1H), 7.80 – 7.69 (m, 3H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.20 – 7.13 (m, 3H), 7.12 – 7.03 (m, 9H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 7.4 Hz, 2H), 6.62 (dd, *J* = 6.0, 3.0 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 1H), 4.65 (d, *J* = 7.8 Hz, 1H), 4.12 (d, *J* = 7.7 Hz, 1H), 3.85 (d, *J* = 7.7 Hz, 1H), 3.74 (d, *J* = 12.4 Hz, 1H), 3.38 (d, *J* = 12.4 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 1H), 2.54 – 2.37 (m, 2H), 2.27 (s, 3H), 2.08 – 1.97 (m, 1H), 1.96 – 1.85 (m, 1H), 1.71 – 1.62 (m, 1H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.3, 154.8, 144.3, 140.9, 138.9, 137.9, 136.6, 135.0, 134.1, 133.9, 133.1, 129.5, 129.4, 128.9, 128.7, 128.4, 128.1, 128.1, 128.0, 127.7, 127.6, 127.6, 127.3, 126.8, 126.5, 126.1, 126.0, 125.9, 124.5, 122.8, 121.6, 119.4, 76.1, 72.9, 62.8, 59.0, 55.2, 34.3, 23.8, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{47}H_{42}N_3O_3S$ 728.2941, found 728.2949.

(R_a,S_2,S_3,S_4)-3-chloro-2'-((2-((4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol (**L6**)



L6

White solid (1.79 g, 62% yield); m. p. =178-180 °C; (silica gel, petroleum ether : ethyl acetate = 4:1).

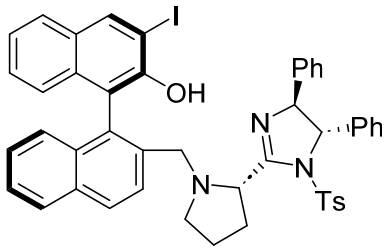
$[\alpha]_D^{20}$ **-33.80** (c = 1.00, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.19 – 7.08 (m, 7H), 7.07 – 7.01 (m, 5H), 6.99 – 6.94 (m, 1H), 6.90 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 7.1 Hz, 2H), 6.66 – 6.58 (m, 2H), 6.53 (d, J = 8.5 Hz, 1H), 4.67 (d, J = 7.5 Hz, 1H), 4.14 – 3.99 (m, 1H), 3.87 (d, J = 7.5 Hz, 1H), 3.69 (d, J = 12.6 Hz, 1H), 3.36 (d, J = 12.6 Hz, 1H), 2.63 – 2.32 (m, 3H), 2.23 (s, 3H), 1.96 (s, 2H), 1.66 (d, J = 6.5 Hz, 1H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.1 , 151.0 , 144.4 , 140.7 , 139.1 , 137.7 , 136.4, 134.5, 133.5, 133.0, 132.6, 129.5 , 128.7 , 128.5 , 128.3 , 128.3 , 128.2 , 127.9 , 127.7 , 127.6 , 127.5 , 127.2 , 127.1 , 126.6 , 126.5 , 126.2 , 126.0 , 125.9 , 124.4 , 123.7 , 75.9 , 72.7 , 62.7 , 58.6 , 55.0 , 34.2 , 23.6 , 21.6 .

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{47}H_{41}ClN_3O_3S^+$ 762.2252; Found 762.2547.

(R_a,S_2,S_3,S_4)-2'-((2-(4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-3-iodo-[1,1'-binaphthalen]-2-ol (**L7**)



L7

White solid (1.44 g, 58% yield); m. p. = 205-207 °C; (silica gel, petroleum ether: ethyl acetate = 6: 1).

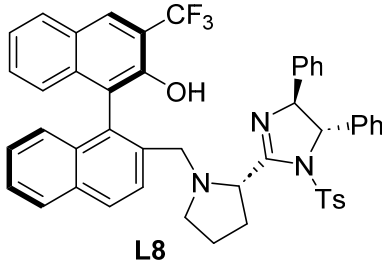
$[\alpha]_D^{20}$ **- 30.11** (c = 1.00, $CHCl_3$) .

^1H NMR (400 MHz, Chloroform-*d*) δ 11.38 (s, 1H), 8.47 (s, 1H), 7.78 – 7.69 (m, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.16 (m, 6H), 7.09 – 7.01 (m, 4H), 7.01 – 6.94 (m, 3H), 6.92 – 6.86 (m, 1H), 6.67 (t, *J* = 7.5 Hz, 3H), 6.38 (d, *J* = 7.8 Hz, 2H), 6.11 (d, *J* = 7.5 Hz, 2H), 4.72 (d, *J* = 5.5 Hz, 1H), 4.63 – 4.46 (m, 2H), 3.83 (d, *J* = 12.5 Hz, 1H), 3.57 (d, *J* = 12.5 Hz, 1H), 2.91 – 2.75 (m, 1H), 2.61 (q, *J* = 7.8 Hz, 1H), 2.49 – 2.33 (m, 1H), 2.05 (s, 4H), 1.95 – 1.81 (m, 1H), 1.80 – 1.67 (m, 1H).

^{13}C {^1H} NMR (100 MHz, Chloroform-*d*) δ 160.6, 152.8, 144.6, 142.0, 140.7, 139.0, 136.2, 135.2, 134.3, 134.1, 133.5, 133.4, 130.5, 129.8, 129.1, 128.4, 128.1, 127.7, 127.3, 127.2, 127.1, 126.8, 126.6, 126.5, 126.4, 126.2, 125.8, 125.7, 125.4, 123.8, 121.6, 94.0, 71.6, 62.4, 57.6, 52.1, 31.9, 25.1, 22.9, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{47}H_{41}IN_3O_3S^+$ 854.1908; Found 854.1902.

(*R_a*,*S_2*,*S_3*,*S_4*)-2'-((2-(4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-3-(trifluoromethyl)-[1,1'-binaphthalen]-2-ol (**L8**)



L8

White solid (1.97 g, 66% yield); m. p.= 105-107 °C; (silica gel, petroleum ether: ethyl acetate = 5: 1).

$[\alpha]_D^{20}$ **- 58.95** (c = 1.00, $CHCl_3$).

^1H NMR (400 MHz, Chloroform-*d*) δ 11.20 (s, 1H), 8.24 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 8.2 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.23 – 7.17 (m, 2H), 7.08 (d, *J* = 7.0 Hz, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.90 (m, 2H), 6.73 – 6.68 (m, 3H), 6.49 (d, *J* = 7.9 Hz, 2H), 6.17 (d, *J* = 7.6 Hz, 2H), 4.74 (d, *J* = 5.5 Hz, 1H), 4.60 – 4.54 (m, 2H), 3.84 (d, *J* = 12.4 Hz, 1H), 3.60 (d, *J* = 12.4 Hz, 1H), 2.86 – 2.80 (m, 1H), 2.60 (q, *J* = 7.5 Hz,

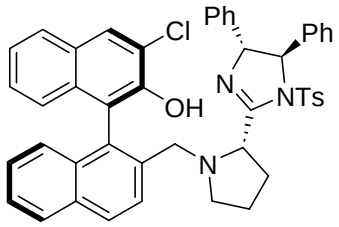
1H), 2.34 – 2.27 (m, 1H), 2.11 (s, 3H), 2.02 – 1.85 (m, 2H), 1.85 – 1.57 (m, 2H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.9, 151.9, 144.6, 142.0, 140.7, 136.7, 135.8, 135.5, 133.5, 133.5, 129.8, 129.4, 129.1, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1 (q, $^{3}J_{C\text{-}F}$= 5.7 Hz), 127.8, 127.4, 127.3, 127.2, 126.7, 126.6, 126.4, 125.9, 125.8, 125.3, 124.3 (q, $^{1}J_{C\text{-}F}$ = 272.6 Hz), 124.2, 122.6 (q, $^{2}J_{C\text{-}F}$= 29.7 Hz), 77.6, 71.7, 62.5, 57.9, 52.5, 31.8, 22.8, 21.4.

^{19}F NMR (Chloroform-*d*) δ -62.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{48}H_{41}F_3N_3O_3S^+$ 796.2816; Found 796.2810.

(R_a,S_2,R_3,R_4)-3-chloro-2'-((2-(4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-[1,1'-binaphthalen]-2-ol **(L9)**



L9

White solid (1.47 g, 56% yield); m. p. = 130-132 °C; (silica gel, petroleum ether: ethyl acetate = 5: 1).

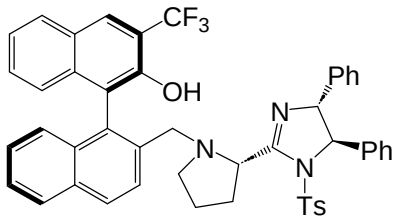
$[\alpha]_D^{20}$ + 299.10 (c = 1.20, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.02 (s, 1H), 7.91 (s, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.18 – 7.08 (m, 7H), 7.07 – 7.01 (m, 5H), 6.99 – 6.94 (m, 1H), 6.90 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 7.1 Hz, 2H), 6.66 – 6.58 (m, 2H), 6.53 (d, J = 8.5 Hz, 1H), 4.67 (d, J = 7.5 Hz, 1H), 4.14 – 3.99 (m, 1H), 3.87 (d, J = 7.5 Hz, 1H), 3.69 (d, J = 12.6 Hz, 1H), 3.36 (d, J = 12.6 Hz, 1H), 2.63 – 2.32 (m, 3H), 2.23 (s, 3H), 2.02 – 1.85 (m, 2H), 1.72 – 1.58 (m, 1H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.1, 151.0, 144.4, 140.7, 139.1, 137.7, 129.5, 128.7, 128.5, 128.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.2, 127.1, 126.6, 126.5, 126.2, 126.0, 125.9, 124.4, 123.7, 75.9, 72.7, 62.7, 58.6, 55.0, 34.2, 23.6, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{47}H_{41}ClN_3O_3S^+$ 762.2552, found 762.2548.

(R_a,S_2,R_3,R_4)-2'-((2-(4,5-diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-3-(trifluoromethyl)-[1,1'-binaphthalen]-2-ol (**L10)**



L10

White solid (1.43 g, 61% yield); m. p. = 120-122 °C; (silica gel, petroleum ether : ethyl acetate = 5: 1).

$[\alpha]_D^{20}$ + 77.80 (c = 1.30, $CHCl_3$).

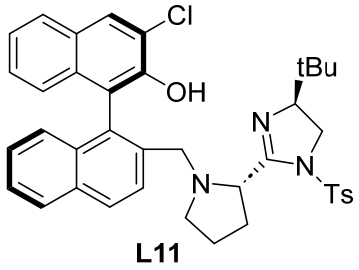
^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.43 (s, 1H), 8.25 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.24 – 7.13 (m, 11H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.97 – 6.90 (m, 4H), 6.82 – 6.78 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 4.80 (d, *J* = 7.1 Hz, 1H), 4.27 – 4.16 (m, 2H), 3.81 (d, *J* = 12.4 Hz, 1H), 3.49 (d, *J* = 12.3 Hz, 1H), 2.63 – 2.46 (m, 3H), 2.33 (s, 3H), 2.04 (d, *J* = 8.7 Hz, 2H), 1.78 – 1.71 (m, 1H).

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.6, 152.1, 144.3, 141.1, 139.3, 137.3, 135.6, 134.1, 133.6, 133.1, 129.4, 129.1, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9 (q, $^3J_{C\text{-}F}$ = 5.7 Hz) 127.6, 127.4, 127.2, 127.1, 126.7, 126.5, 126.0, 125.8, 125.6, 124.3 (q, $^1J_{C\text{-}F}$ = 273.3 Hz) 122.9, 122.6, 122.1 (q, $^2J_{C\text{-}F}$ = 29.5 Hz) 121.9, 75.6, 72.7, 62.4, 58.5, 54.4, 33.8, 23.2, 21.5.

^{19}F NMR (Chloroform-*d*) δ -62.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{48}H_{41}F_3N_3O_3S^+$ 796.2816; Found 796.2820.

(*R_a*,*S_2*,*S_3*)-2'-((2-(4-(tert-butyl)-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-3-chloro-[1,1'-binaphthalen]-2-ol **(L11)**



L11

White solid (0.91 g, 70% yield); m. p. = 198-200 °C; (silica gel, petroleum ether : ethyl acetate = 5: 1).

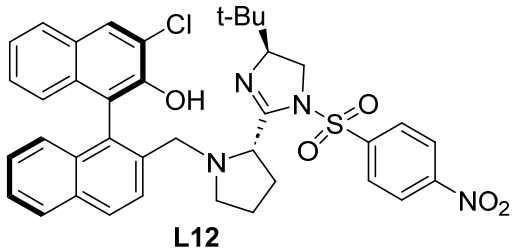
$[\alpha]_D^{20}$ **+ 27.66** (*c* = 0.98, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.88 (s, 1H), 8.05 (s, 1H), 7.89 – 7.66 (m, 3H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.27 (d, *J* = 7.9 Hz, 1H), 3.66 – 3.51 (m, 4H), 3.09 (t, *J* = 7.5 Hz, 1H), 2.76 – 2.62 (m, 1H), 2.55 (q, *J* = 8.0 Hz, 1H), 2.48 – 2.29 (m, 4H), 1.97 – 1.88 (m, 1H), 1.88 – 1.78 (m, 1H), 1.77 – 1.68 (m, 1H), 0.24 (s, 9H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 159.7, 150.8, 144.7, 137.2, 135.0, 134.0, 134.0, 133.6, 132.9, 130.0, 128.9, 128.6, 128.5, 127.9, 127.4, 127.3, 127.0, 126.7, 126.5, 126.3, 125.9, 125.1, 123.9, 122.6, 73.6, 62.7, 59.0, 54.2, 49.2, 33.0, 32.7, 29.8, 25.5, 23.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{39}H_{41}ClN_3O_3S$ 666.2552, found 666.2557.

(*R_a*,*S_2*,*S_3*)-2'-((2-(4-(tert-butyl)-1-((4-nitrophenyl)sulfonyl)-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-3-chloro-[1,1'-binaphthalen]-2-ol **(L12)**



L12

White solid (0.72 g, 68% yield); m. p. = 101-103 °C; (silica gel, petroleum ether: ethyl acetate = 5: 1).

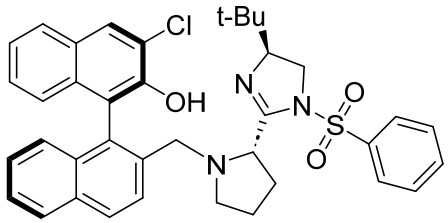
$[\alpha]_D^{20}$ **-5.93** (*c* = 0.30, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.61 (s, 1H), 7.99 (s, 1H), 7.86 – 7.69 (m, 5H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.25 (m, 3H), 7.16 – 7.05 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 4.25 (d, *J* = 8.7 Hz, 1H), 3.66 – 3.45 (m, 4H), 3.05 – 2.94 (m, 1H), 2.86 – 2.74 (m, 1H), 2.65 – 2.54 (m, 1H), 2.45 – 2.31 (m, 1H), 1.90 – 1.68 (m, 3H), 0.25 (s, 9H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 157.9, 150.5, 150.3, 143.3, 136.5, 133.9, 133.8, 133.6, 132.7, 129.0, 128.9, 128.7, 128.5, 128.0, 127.3, 127.0, 126.7, 126.7, 126.7, 126.1, 125.2, 124.6, 124.5, 123.0, 73.9, 62.2, 58.6, 53.2, 49.0, 33.1, 32.1, 25.4, 23.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{38}H_{38}ClN_4O_5S$ 697.2246, found 697.2248.

(R_a,S_2,S_3)-2'-((2-(4-(tert-butyl)-1-(phenylsulfonyl)-4,5-dihydro-1*H*-imidazol-2-yl)pyrrolidin-1-yl)methyl)-3-chloro-[1,1'-binaphthalen]-2-ol **(L13)**



L13

White solid (0.96 g, 72% yield); m. p. = 115-117 °C; (silica gel, petroleum ether: ethyl acetate = 6: 1).

$[\alpha]_D^{20}$ **+29.41** (*c* = 0.75, CH_2Cl_2).

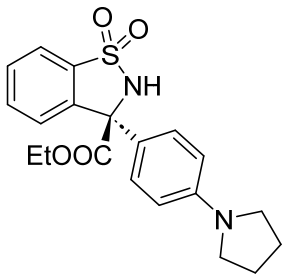
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 7.88 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 8.3 Hz, 3H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.18 – 7.10 (m, 3H), 7.09 – 7.05 (m, 1H), 7.03 – 6.98 (m, 1H), 6.95 – 6.89 (m, 2H), 6.43 (d, *J* = 8.5 Hz, 1H), 4.11 – 4.05 (m, 1H), 3.48 – 3.37 (m, 4H), 2.94 (t, *J* = 8.2 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.39 – 2.31 (m, 1H), 2.29 – 2.19 (m, 1H), 1.81 – 1.73 (m, 1H), 1.69 – 1.60 (m, 1H), 1.57 – 1.50 (m, 1H), 0.01 (s, 9H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.0, 150.6, 137.9, 137.4, 133.9, 133.9, 133.7, 133.5, 132.7, 129.5, 128.6, 128.5, 127.8, 127.4, 127.2, 127.1, 126.7, 126.6, 126.5, 126.3, 125.8, 124.9, 123.9, 122.4, 73.5, 63.0, 59.3, 54.6, 49.2, 33.0, 32.9, 25.3, 23.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{38}H_{39}ClN_3O_3S$ 652.2395, found 652.2398.

3. Characterization and ee Values of the Products

(*R*)-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3aa**)



3aa

54 mg, colorless oil, **93% yield, >99% ee** (silica gel, petroleum ether : ethyl acetate=5: 1).

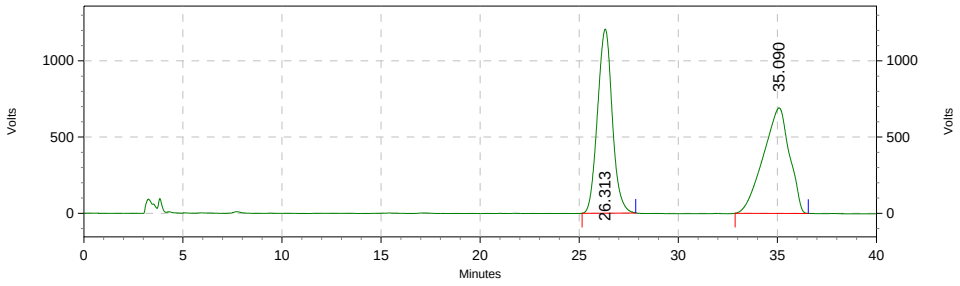
$[\alpha]_D^{20}$ + 21.74 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.68 (m, 2H), 7.66 – 7.47 (m, 2H), 7.24 – 7.09 (m, 2H), 6.55 – 6.38 (m, 2H), 5.92 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.31 – 3.17 (m, 4H), 2.04 – 1.90 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H).

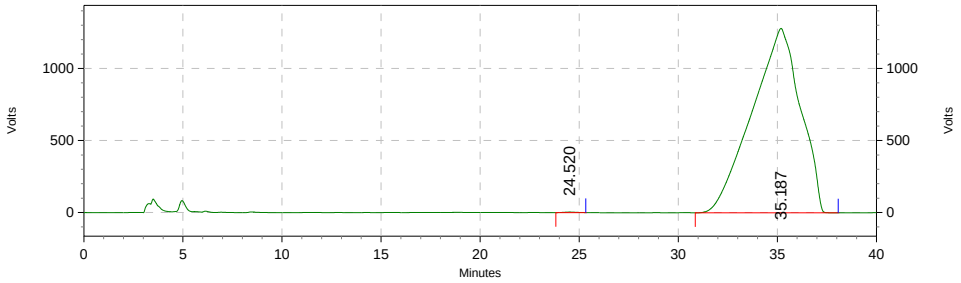
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 148.0, 138.4, 135.5, 133.0, 130.2, 127.5, 127.5, 125.1, 121.0, 111.6, 71.2, 63.5, 47.6, 25.5, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_4S^+$ 387.1374; Found 387.1368.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 24.5 min for (*S*)-isomer and t_R = 35.2 min for (*R*)-isomer.

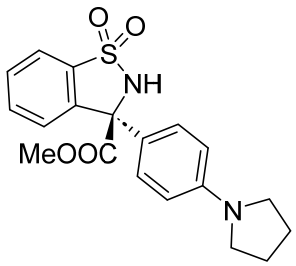


Peaks	Ret. Time	Area	Area%
1	26.313	62330737	49.536
2	35.090	63498451	50.464



Peaks	Ret. Time	Area	Area%
1	24.520	168729	0.078
2	35.187	217291335	99.922

(*R*)-Methyl-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ab**)



3ab

77 mg, yellow oil, **94% yield, >99% ee** (silica gel, petroleum ether : ethyl acetate=5:1).

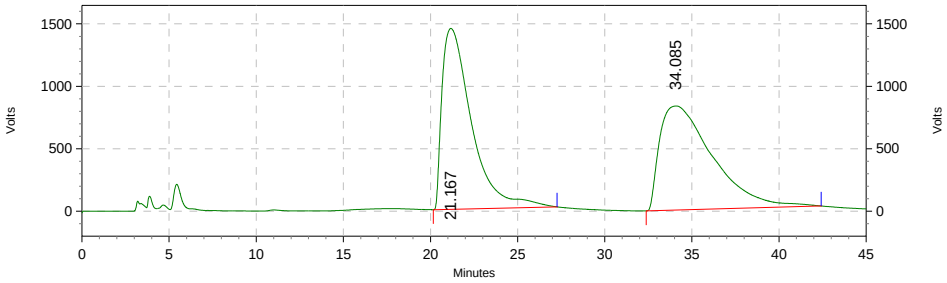
$[\alpha]_D^{20}$ + 53.56 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.75 (m, 1H), 7.73 – 7.69 (m, 1H), 7.65 – 7.61 (m, 1H), 7.60 – 7.55 (m, 1H), 7.16 – 7.15 (m, 1H), 7.14 – 7.12 (m, 1H), 6.50 – 6.48 (m, 1H), 6.47 – 6.46 (m, 1H), 5.90 (s, 1H), 3.87 (s, 3H), 3.24 (t, J = 6.6 Hz, 4H), 1.99 – 1.95 (m, 4H).

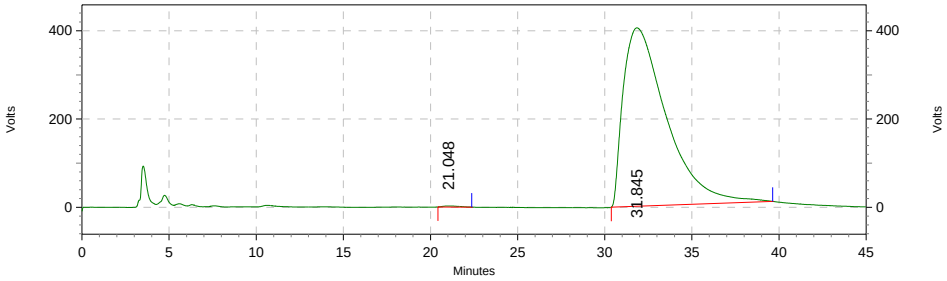
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.4, 148.1, 138.2, 135.5, 133.1, 130.3, 127.6, 127.5, 124.8, 121.1, 111.6, 71.3, 54.1, 47.6, 25.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_4S^+$ 373.1217; Found 373.1211.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 21.0 min for (*S*)-isomer and t_R = 31.8 min for (*R*)-isomer.

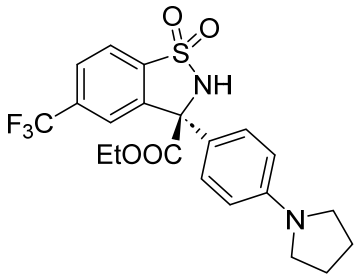


Peaks	Ret. Time	Area	Area%
1	21.167	170953440	49.251
2	34.085	176152146	50.749



Peaks	Ret. Time	Area	Area%
1	21.048	152971	0.219
2	31.845	69695834	99.781

(*R*)-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)-5-(trifluoromethyl)-2,3-dihydrobenzo[*d*] isothiazole-3-carboxylate 1,1-dioxide (**3ac**)



3ac

63 mg, red oil, **93% yield, >99% ee** (silica gel, petroleum ether : ethyl acetate=5:1).

$[\alpha]_D^{20}$ + 15.91 (c = 1.00, $CHCl_3$).

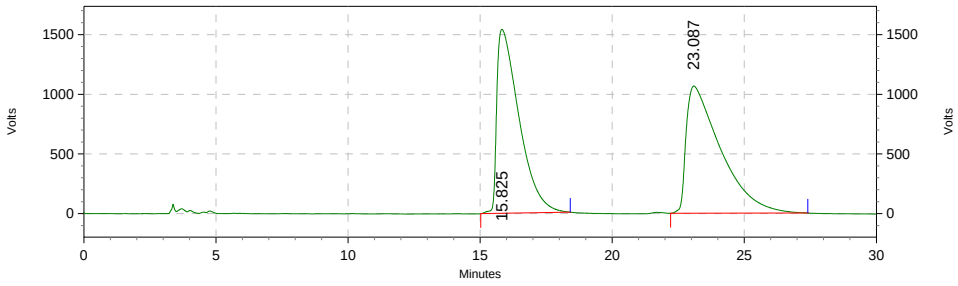
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.9 Hz, 2H), 6.05 (s, 1H), 4.40 – 4.33 (m, 2H), 3.26 (t, J = 6.5 Hz, 4H), 2.01 – 1.96 (m, 4H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.2 , 148.3 , 139.6 , 138.7, 135.2 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 127.5 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 127.4 , 125.0 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 124.0 , 123.2 (q, $^{1}J_{C\text{-}F}$ = 273.1 Hz), 122.0 , 111.8 , 71.2 , 63.9 , 47.6 , 25.6 , 14.1 .

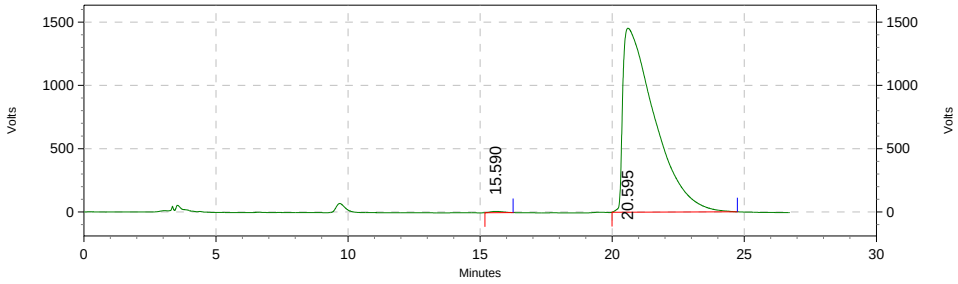
^{19}F NMR (Chloroform-*d*) δ -62.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}F_3N_2O_4S^+$ 455.1247; Found 455.1241.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IB, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 15.6 min for (*S*)-isomer and t_R = 20.6 min for (*R*)-isomer.

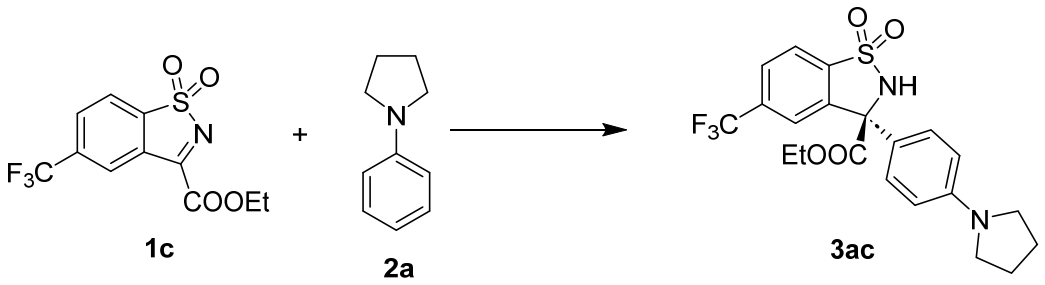


Peaks	Ret. Time	Area	Area%
1	15.825	90184701	48.199
2	23.087	96925005	51.801

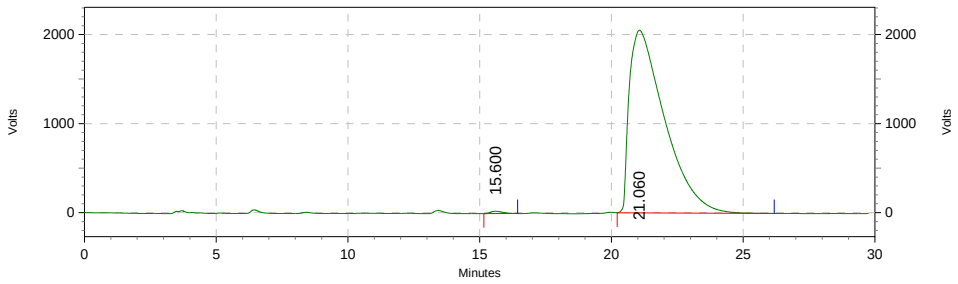


Peaks	Ret. Time	Area	Area%
1	15.590	329019	0.269
2	20.595	121760623	99.731

Control experiments to study the effect of water on the course of the reaction:

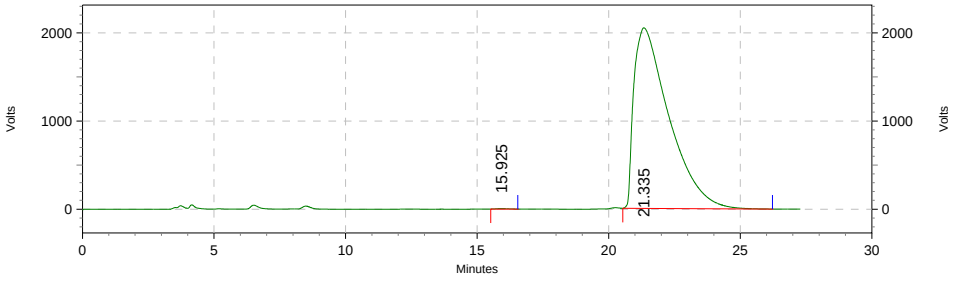


a) Reaction carried out for 5 h with 5% of catalyst:



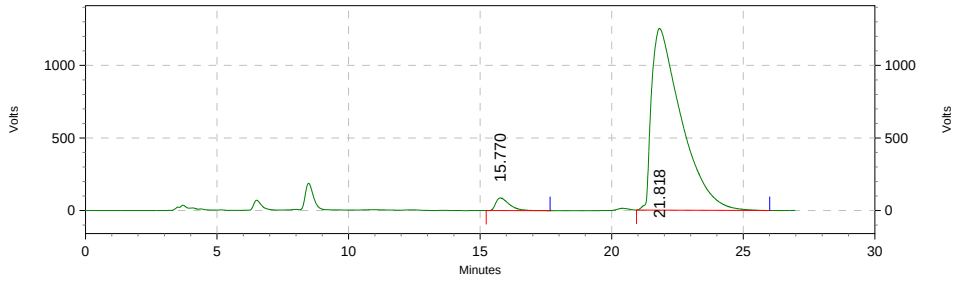
Peaks	Ret. Time	Area	Area%
1	15.600	852034	0.445
2	21.060	190673711	99.555

b) Reaction carried out for 5 h with 5% of catalyst. Molecular sieves (4 Å) were added to the reaction mixture:



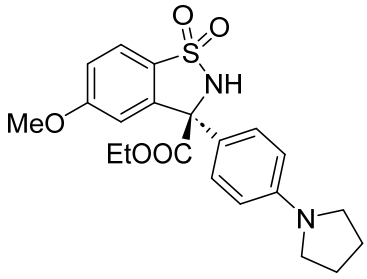
Peaks	Ret. Time	Area	Area%
1	15.925	158993	0.084
2	21.335	189861771	99.916

c) Reaction carried out for 5 h with 5% of catalyst. Wet CH_2Cl_2 was used as the solvent:



Peaks	Ret. Time	Area	Area%
1	15.770	3089247	3.042
2	21.818	98464366	96.958

(*R*)-Ethyl-5-methoxy-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ad**)



3ad

59 mg，yellow oil , **95% yield, 99% ee** (silica gel, petroleum ether : ethyl acetate=5:1).

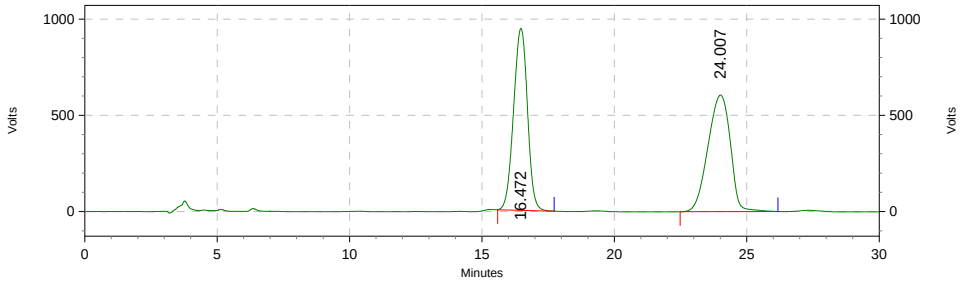
$[\alpha]_D^{20}$ + 92.72 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, J = 8.6 Hz, 1H), 7.16 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 1.8 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.49 (d, J = 8.7 Hz, 2H), 5.88 (s, 1H), 4.38 – 4.32 (m, 2H), 3.84 (s, 3H), 3.25 (t, J = 6.3 Hz, 4H), 1.98 (t, J = 6.4 Hz, 4H), 1.32 (t, J = 7.1 Hz, 3H).

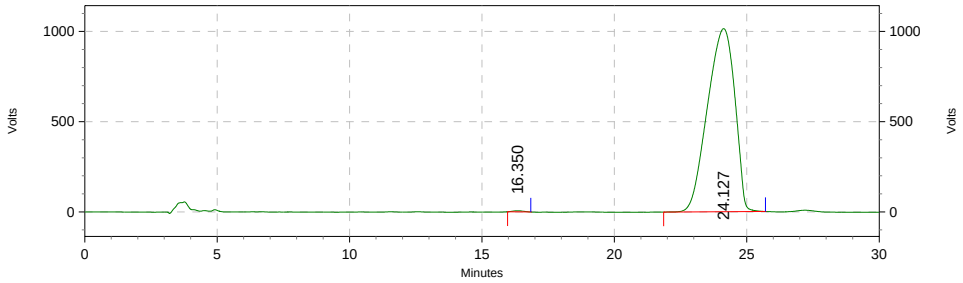
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 163.5, 148.0, 141.0, 127.8, 127.5, 125.2 122.5, 117.2, 111.7, 111.6, 71.0, 63.5, 56.0, 47.6, 25.6, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{25}N_2O_5S^+$ 417.1479; Found 417.1473.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 16.4 min for (*S*)-isomer and t_R = 24.1 min for (*R*)-isomer.

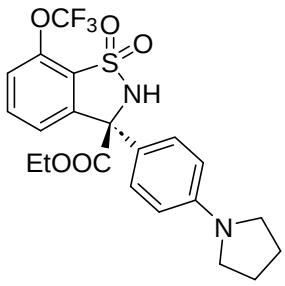


Peaks	Ret. Time	Area	Area%
1	16.472	34382122	49.184
2	24.007	35523672	50.816



Peaks	Ret. Time	Area	Area%
1	16.350	177553	0.243
2	24.127	72974654	99.757

(*R*)-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)-7-(trifluoromethoxy)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ae**)



3ae

53 mg, yellow solid, **93% yield, >99% ee** (silica gel, petroleum ether: ethyl acetate=5:1).

$[\alpha]_D^{20}$ -6.73 (c = 1.00, $CHCl_3$); m.p. = 118-120 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.31 (s, 1H), 7.08 (d, J =

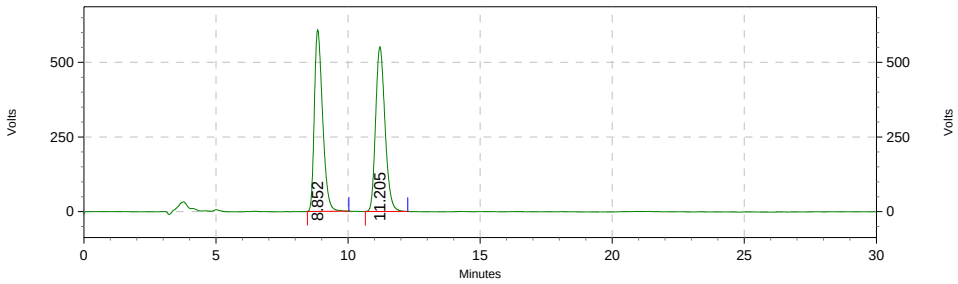
8.8 Hz, 2H), 6.39 (d, J = 8.8 Hz, 2H), 5.99 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.15 (t, J = 6.3 Hz, 4H), 1.88 (t, J = 6.4 Hz, 4H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.3, 148.1, 143.3, 141.7, 134.9, 127.5, 127.4, 125.2, 124.2, 120.3 (q, J_{C-F} = 261.8 Hz), 119.9, 111.6, 70.7, 63.8, 47.5, 25.5, 14.0.

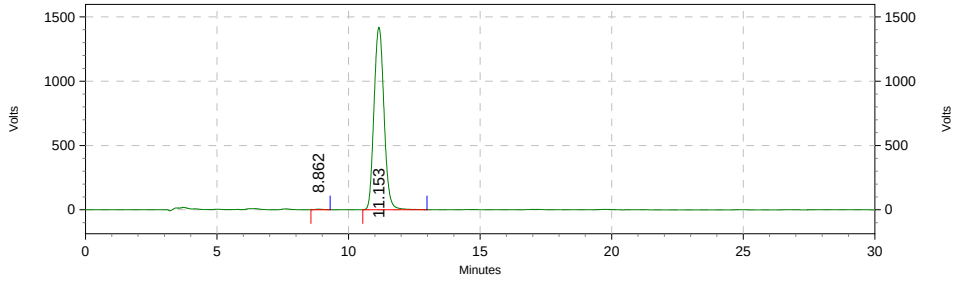
^{19}F NMR (Chloroform-*d*) δ -57.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}F_3N_2O_5S^+$ 471.1197; Found 471.1195.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 8.9 min for (*S*)-isomer and t_R = 11.1 min for (*R*)-isomer.

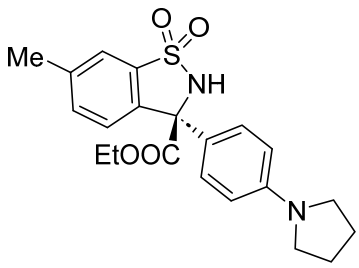


Peaks	Ret. Time	Area	Area%
1	8.852	13167909	49.133
2	11.205	13632638	50.867



Peaks	Ret. Time	Area	Area%
1	8.862	96639	0.258
2	11.153	37412102	99.742

(*R*)-Ethyl-6-methyl-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3af**)



3af

57 mg, yellow oil, **95% yield, 99% ee** (silica gel, petroleum ether: ethyl acetate=5:1).

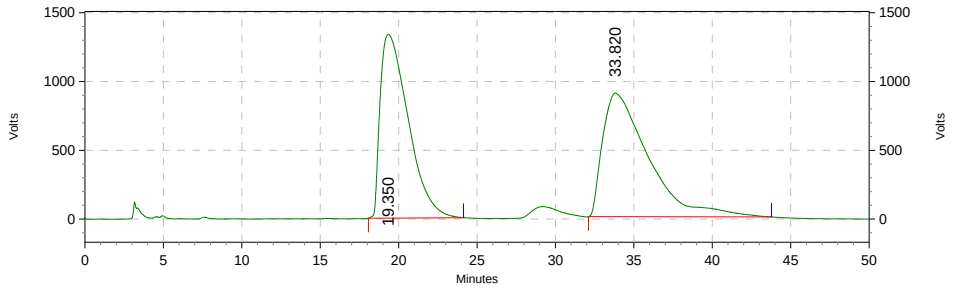
$[\alpha]_D^{20}$ + 29.66 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.07 (d, J = 8.8 Hz, 2H), 6.40 (d, J = 8.8 Hz, 2H), 5.83 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.17 (t, J = 6.5 Hz, 4H), 2.38 (s, 2H), 1.92 – 1.88 (m, 4H), 1.22 (t, J = 7.1 Hz, 3H).

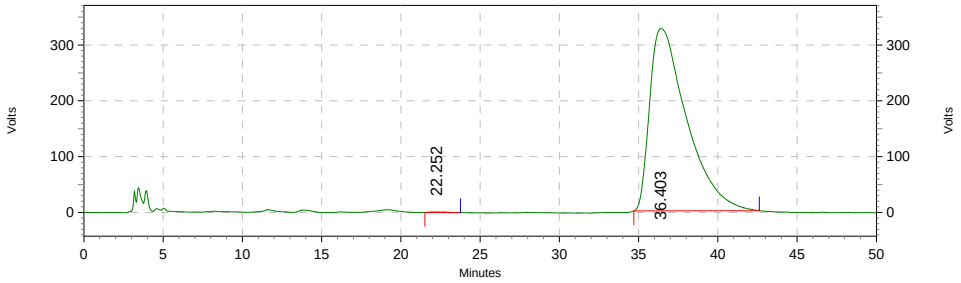
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.1, 148.0, 141.0, 135.6, 134.2, 129.6, 127.5, 127.2, 121.0, 111.6, 71.1, 63.5, 47.6, 25.6, 21.3, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{25}N_2O_4S^+$ 401.1530; Found 401.1526.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel OD-H, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 22.3 min for (*S*)-isomer and t_R = 36.4 min for (*R*)-isomer.

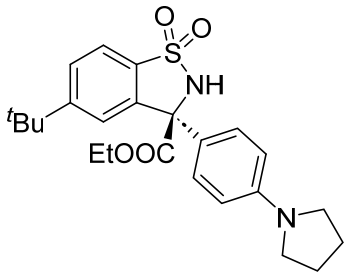


Peaks	Ret. Time	Area	Area%
1	19.350	165382562	47.636
2	33.820	181796058	52.364



Peaks	Ret. Time	Area	Area%
1	22.252	81945	0.154
2	36.403	52980241	99.846

(*R*)-Ethyl-5-(tert-butyl)-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ag**)



3ag

59 mg, yellow oil, **89% yield**, **>99% ee** (silica gel, petroleum ether: ethyl acetate=5:1).

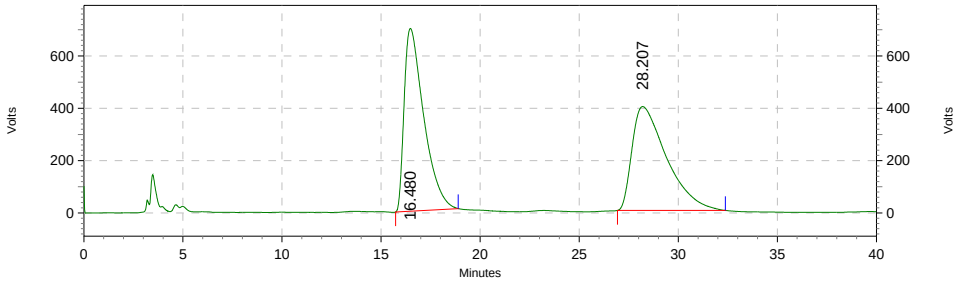
$[\alpha]_D^{20}$ + 85.136 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 1.6 Hz, 1H), 7.69 (d, J = 0.4 Hz, 1H), 7.63 (d, J = 1.6 Hz, 1H), 7.16 – 7.12 (m, 2H), 6.51 – 6.47 (m, 2H), 5.96 (s, 1H), 4.41 – 4.35 (m, 1H), 4.31 – 4.25 (m, 1H), 3.25 (t, J = 6.6 Hz, 4H), 1.99 – 1.95 (m, 4H), 1.34 (s, 9H), 1.30 (t, J = 7.1 Hz, 3H).

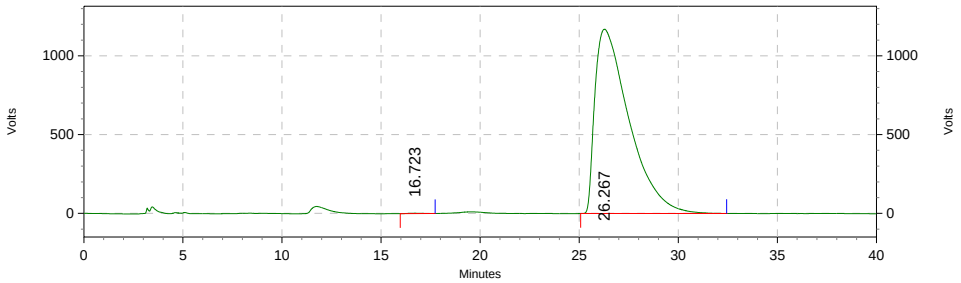
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.1, 157.2, 147.9, 138.2, 133.1, 127.8, 127.5, 125.3, 124.3, 120.6, 111.6, 71.4, 63.4, 47.5, 35.5, 31.2, 25.5, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{31}N_2O_4S^+$ 443.2000; Found 443.1996.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel OD-H, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 16.7 min for (*S*)-isomer and t_R = 26.2 min for (*R*)-isomer.

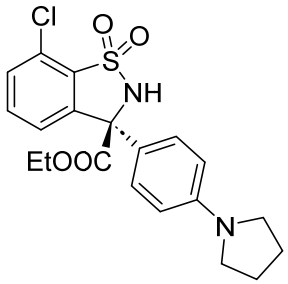


Peaks	Ret. Time	Area	Area%
1	16.480	48028585	50.011
2	28.207	48007182	49.989



Peaks	Ret. Time	Area	Area%
1	16.723	130845	0.093
2	26.267	140175863	99.907

(*R*)-Ethyl-7-chloro-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ah**)



3ah

60 mg, white solid, m.p.= 65-67 °C, **96% yield, 99% ee** (silica gel, petroleum ether: ethyl acetate=5:1). X-ray diffraction experiment confirmed the (*R*)-configuration of the compound (CCDC 2354218, Figure S1).

$[\alpha]_D^{20}$ - 38.46 (c = 1.00, $CHCl_3$).

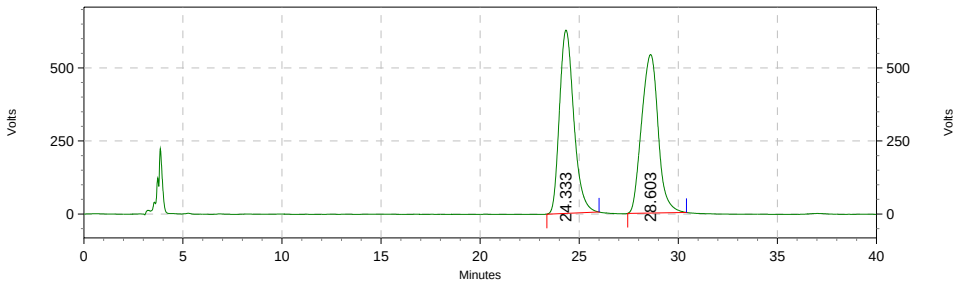
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 7.5 Hz, 1H), 7.58 – 7.46 (m, 2H),

7.16 (d, J = 8.4 Hz, 2H), 6.48 (d, J = 8.4 Hz, 2H), 6.01 (s, 1H), 4.34 (q, J = 7.0 Hz, 2H), 3.26 (s, 4H), 1.98 (s, 4H), 1.31 (t, J = 7.0 Hz, 3H).

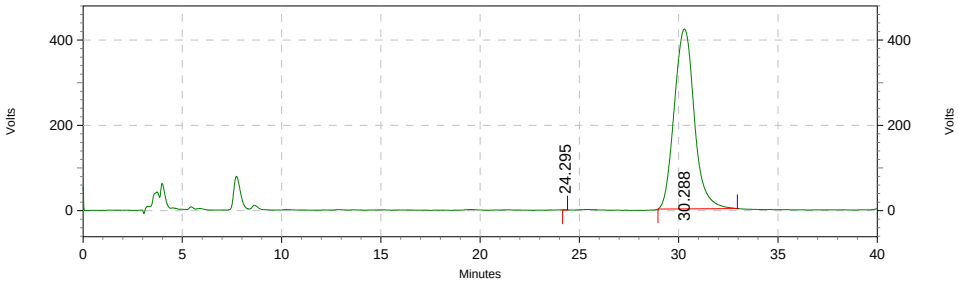
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.4, 148.1, 141.2, 134.1, 133.5, 131.0, 128.6, 127.5, 125.9, 124.5, 111.6, 70.3, 63.8, 47.6, 25.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{27}N_2O_4S^+$ 421.0984; Found 421.0978.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 24.3 min for (*S*)-isomer and t_R = 30.3 min for (*R*)-isomer.



Peaks	Ret. Time	Area	Area%
1	24.333	31470835	49.921
2	28.603	31570063	50.079



Peaks	Ret. Time	Area	Area%
1	24.295	779	0.003
2	30.288	29571283	99.997

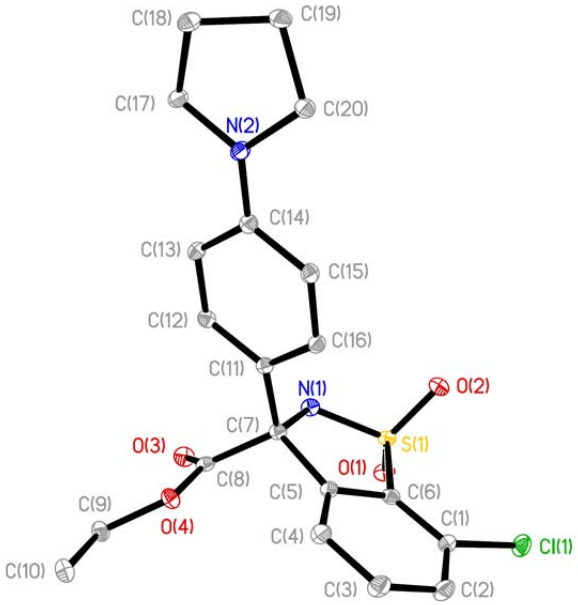
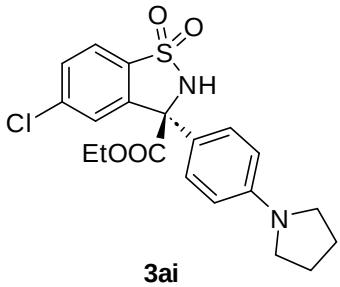


Figure S1. ORTEP Drawing of **3ah** with thermal ellipsoids at 30% of probability (CCDC 2354218). Hydrogen atoms were omitted for clarity.

(*R*)-Ethyl-5-chloro-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ai**)



3ai

59 mg, ccolourless oil, **94% yield, 99% ee** (silica gel, petroleum ether: ethyl acetate=5:1).

$[\alpha]_D^{20}$ + 38.46 (c = 1.00, $CHCl_3$).

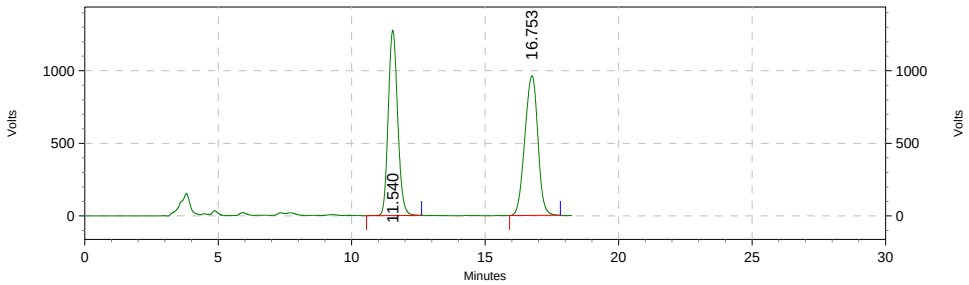
^{1}HNMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 2H), 7.55 – 7.52 (m, 1H), 7.17 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 5.96 (s, 1H), 4.39 – 4.33 (m, 2H), 3.26 (t, J = 6.5 Hz, 4H), 2.01 – 1.96 (m, 4H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.3, 148.2, 140.5, 139.5, 133.9, 130.8, 127.7, 127.4, 124.3, 122.3, 111.7, 70.8, 63.8, 47.6, 25.6, 14.1.

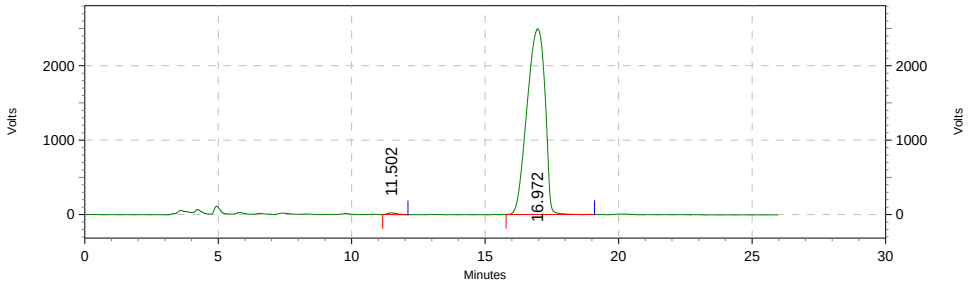
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{22}ClN_2O_4S^+$ 421.0984; Found 421.0979.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA,

hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 11.5 min for (*S*)-isomer and t_R = 16.9 min for (*R*)-isomer.

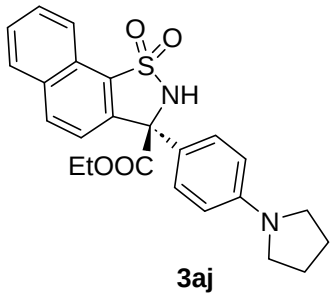


Peaks	Ret. Time	Area	Area%
1	11.540	31314926	48.978
2	16.753	32621987	51.022



Peaks	Ret. Time	Area	Area%
1	11.502	538527	0.461
2	16.972	116371389	99.539

(*R*)-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydronaphtho[2,1-*d*]isothiazole-3-carboxylate 1,1-dioxide (**3aj**)



3aj

59 mg, white solid, m. p. = 208-210 °C. **90% yield, 99% ee** (silica gel, petroleum ether : ethyl acetate=5:1).

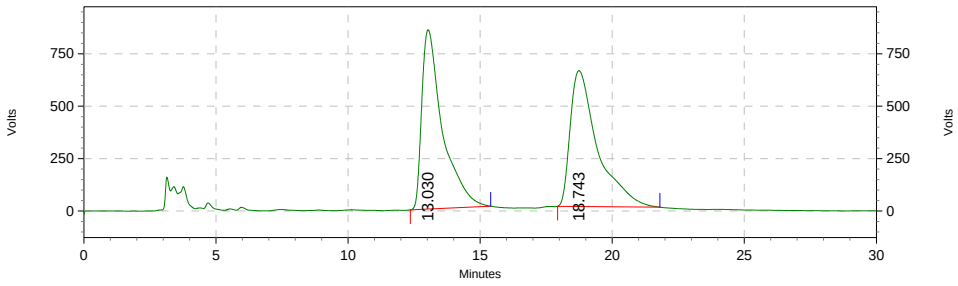
$[\alpha]_D^{20}$ **-29.79** (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.74 – 7.61 (m, 3H), 7.16 (d, J = 8.7 Hz, 2H), 6.47 (d, J = 8.8 Hz, 2H), 6.07 (s, 1H), 4.40 – 4.31 (m, 2H), 3.26 – 3.20 (m, 4H), 2.00 – 1.93 (m, 4H), 1.32 (t, J = 7.1 Hz, 3H).

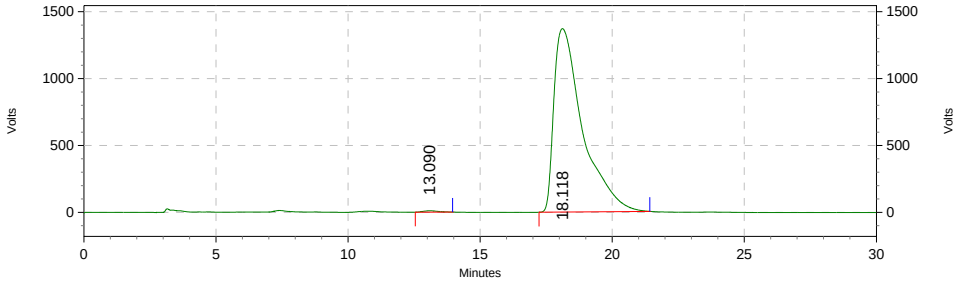
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 148.0, 137.4, 133.9, 133.7, 130.7, 129.1, 128.5, 128.2, 127.6, 125.1, 123.3, 123.2, 111.6, 71.2, 63.6, 47.5, 25.5, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{27}N_2O_4S^+$ 437.1530; Found 437.1522.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel OD-H, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 13.0 min for (*S*)-isomer and t_R = 18.7 min for (*R*)-isomer.

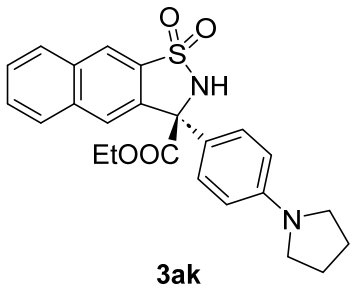


Peaks	Ret. Time	Area	Area%
1	13.030	46352705	49.976
2	18.743	26518911	50.024



Peaks	Ret. Time	Area	Area%
1	13.030	237243	0.565
2	18.743	103725301	99.435

(*R*)-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydronaphtho[2,3-*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ak**)



3ak

56 mg, white solid , m. p. = 200-202 °C, 85% yield, 99% ee (silica gel, petroleum ether: ethyl acetate=5:1).

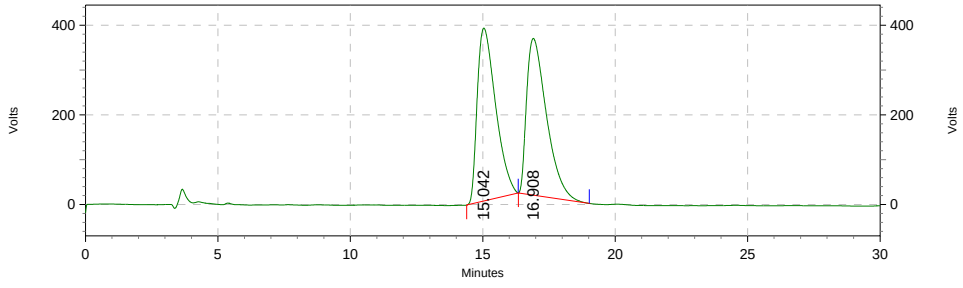
$[\alpha]_D^{20}$ **+105.39** (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 8.18 (s, 1H), 8.02 – 7.97 (m, 1H), 7.94 – 7.89 (m, 1H), 7.66 – 7.59 (m, 2H), 7.24 (d, J = 8.6 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 6.04 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.28 – 3.22 (m, 4H), 2.00 – 1.94 (m, 4H), 1.33 (t, J = 7.1 Hz, 3H).

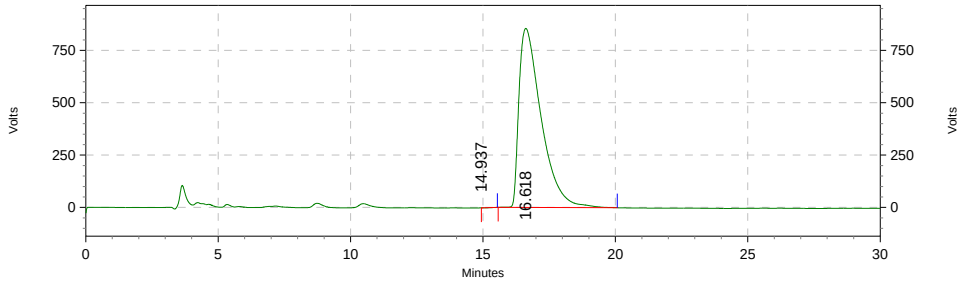
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.1, 148.0, 135.2, 134.3, 133.7, 133.1, 129.3, 128.9, 128.1, 127.7, 127.1,125.4, 121.6, 111.6, 71.1, 63.6, 47.6, 25.6, 14.2.

HRMS **(ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{25}N_2O_4S^+$ 437.1530; Found 437.1525.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IB, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 14.9 min for (*S*)-isomer and t_R = 16.6 min for (*R*)-isomer.

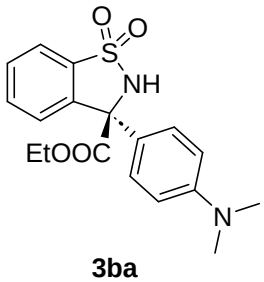


Peaks	Ret. Time	Area	Area%
1	15.042	18611850	50.415
2	16.908	18305261	49.585



Peaks	Ret. Time	Area	Area%
1	14.937	8024	0.016
2	16.618	49879571	99.984

(*R*)-Ethyl-3-(4-(dimethylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ba**)



3ba

40 mg, red oil, **85% yield, 99% ee**, (silica gel, petroleum ether: ethyl acetate=5:1).

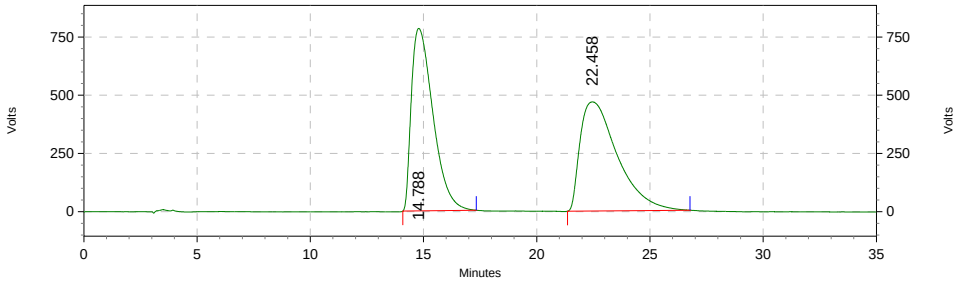
$[\alpha]_D^{20}$ + 20.62 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.60 (m, 2H), 7.59 – 7.42 (m, 2H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 5.93 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.83 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H).

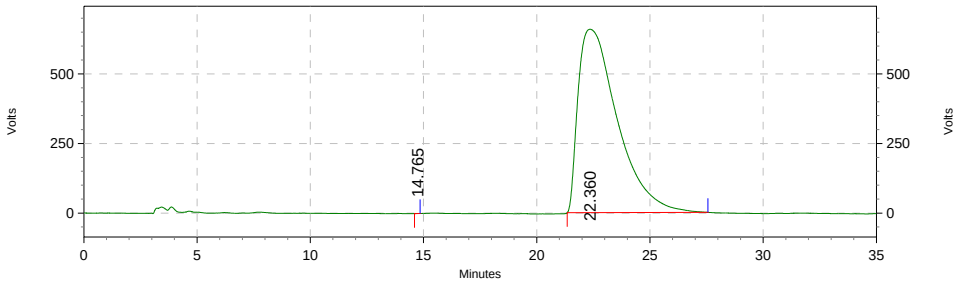
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.8, 150.7, 138.4, 135.6, 133.1, 130.3, 127.5, 127.5, 126.2, 121.2, 112.3, 71.1, 63.7, 40.4, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_2O_4S^+$ 361.1217; Found 361.1226.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 14.8 min for (*S*)-isomer and t_R = 22.4 min for (*R*)-isomer.

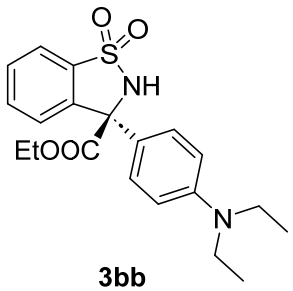


Peaks	Ret. Time	Area	Area%
1	14.788	51998696	49.217
2	22.458	53652141	50.783



Peaks	Ret. Time	Area	Area%
1	14.765	884	0.001
2	22.360	79376075	99.999

(*R*)-Ethyl-3-(4-(diethylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bb**)



3bb

49 mg, yellow oil, **83% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate=5:1).

$[\alpha]_D^{20}$ + 22.46 (c = 1.00, $CHCl_3$).

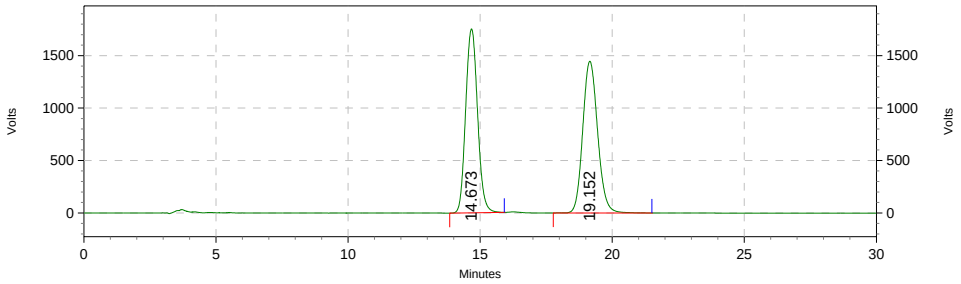
^{1}H NMR (400 MHz, Chloroform-*d*) δ7.76 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 5.99 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.32 (q, *J* = 7.0 Hz, 4H), 1.31

(t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.0 Hz, 6H).

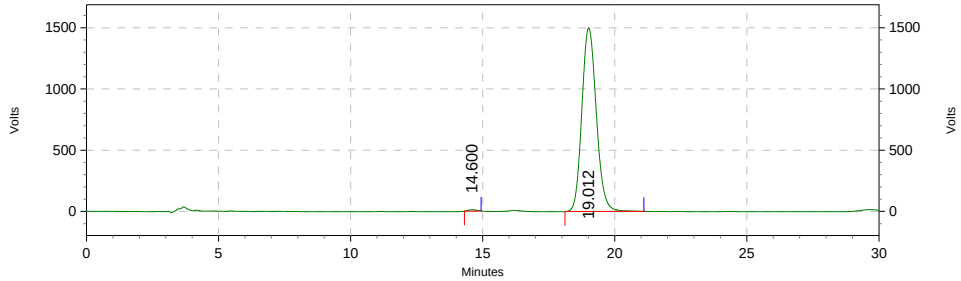
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 147.9, 138.2, 135.4, 133.0, 130.2, 127.6, 127.5, 124.8, 120.9, 111.3, 71.1, 63.5, 44.2, 14.0, 12.5.

HRMS **(ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_4S^+$ 389.1530; Found 389.1525.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 14.6 min for (*S*)-isomer and t_R = 19.0 min for (*R*)-isomer.

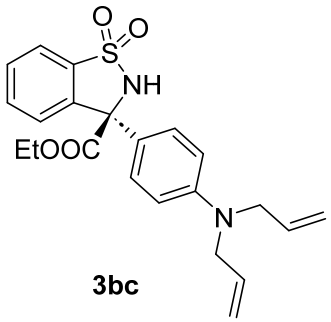


Peaks	Ret. Time	Area	Area%
1	14.673	54888120	49.224
2	19.152	56618501	50.776



Peaks	Ret. Time	Area	Area%
1	14.600	244471	0.427
2	19.012	57051854	99.573

(*R*)-Ethyl-3-(4-(diallylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bc**)



3bc

56 mg, red oil, **91% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate=5:1).

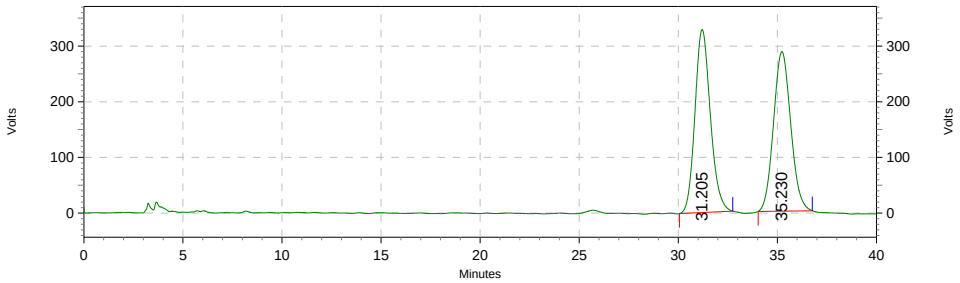
$[\alpha]_D^{20}$ + 18.47 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ7.64 (t, *J* = 6.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 2H), 5.92 (s, 1H), 5.75 – 5.65 (m, 2H), 5.08 – 5.00 (m, 4H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 4.7 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 3H).

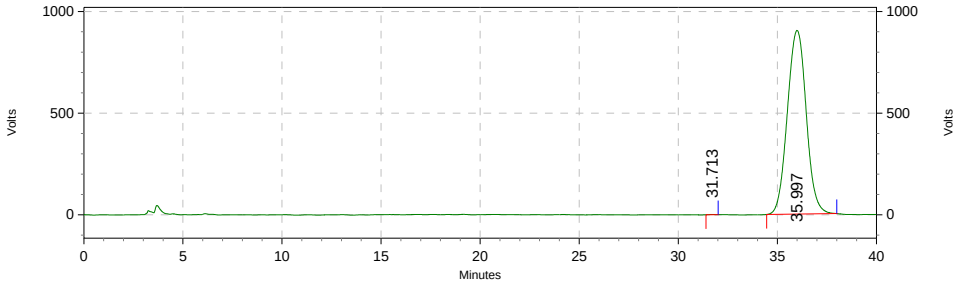
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.6, 148.8, 138.1, 135.3, 133.4, 133.0, 130.2, 127.4, 125.9, 120.8, 116.1, 112.0, 70.9, 63.5, 52.6, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_4S^+$413.1530; Found 413.1525.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 31.7min for (*S*)-isomer and t_R = 36.0 min for (*R*)-isomer.

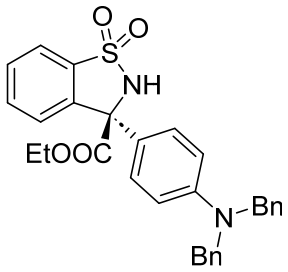


Peaks	Ret. Time	Area	Area%
1	31.205	17785495	50.696
2	35.230	17297431	49.304



Peaks	Ret. Time	Area	Area%
1	31.713	19930	0.033
2	35.997	59688467	99.967

(*R*)-Ethyl-3-(4-(dibenzylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bd**)



3bd

69 mg, yellow oil, **90% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

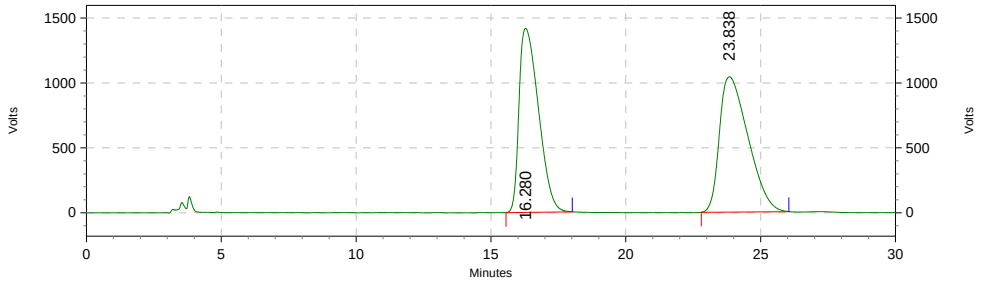
$[\alpha]_D^{20}$ + 10.64 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ7.62 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 4H), 7.16 – 7.06 (m, 6H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 5.86 (s, 1H), 4.52 (s, 4H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).

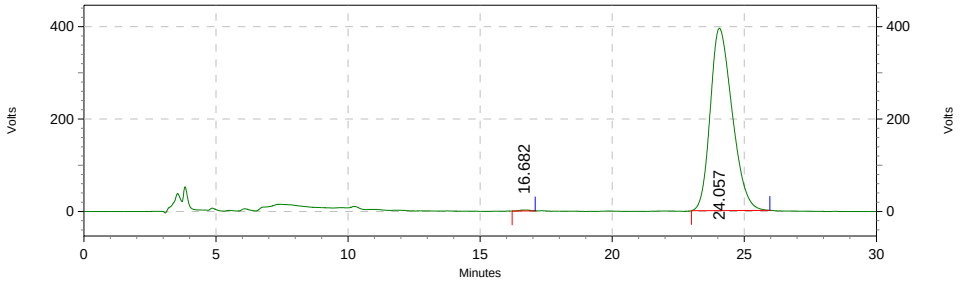
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.6, 149.3, 138.0, 135.3, 133.0, 130.2, 128.7, 127.5, 127.4, 127.0, 126.5, 120.9, 112.3, 70.9, 63.5, 54.2, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{29}N_2O_4S^+$ 513.1843; Found 513.1839.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 16.7 min for (*S*)-isomer and t_R = 24.1 min for (*R*)-isomer.

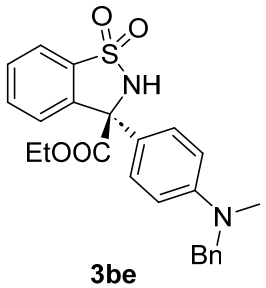


Peaks	Ret. Time	Area	Area%
1	16.280	70970837	48.042
2	23.838	76754298	51.958



Peaks	Ret. Time	Area	Area%
1	16.682	55207	0.242
2	24.057	22757216	99.758

(*R*)-Ethyl-3-(4-(benzyl(methyl)amino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3be**)



3be

63 mg, red oil, **96% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

$[\alpha]_D^{20}$ + 11.75 (c = 1.00, $CHCl_3$).

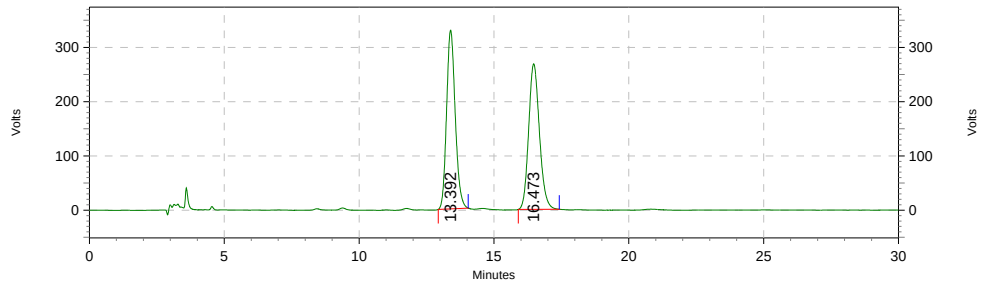
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 2H), 7.64 – 7.54 (m, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.25 – 7.15 (m, 5H), 6.65 (d, J = 8.6 Hz, 2H), 5.94 (s, 1H), 4.51 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.02 (s, 3H), 1.30 (t, J

= 7.1 Hz, 3H).

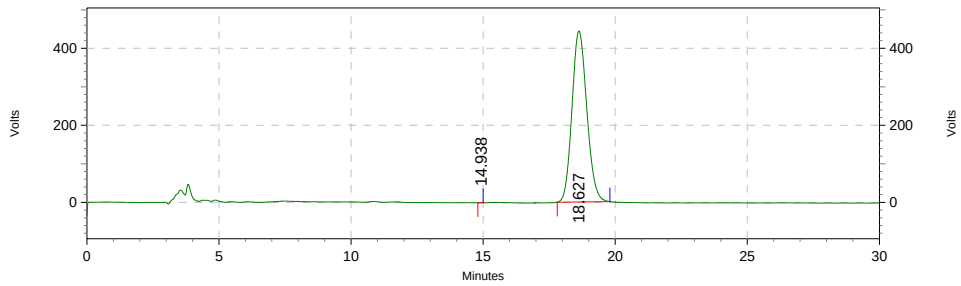
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.7, 149.8, 138.5, 138.2, 135.5, 133.1, 130.3, 128.7, 127.5, 127.5, 127.1, 126.6, 126.2, 121.1, 112.1, 71.1, 63.6, 56.4, 38.7, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{26}N_2O_4S^+$ 437.1530; Found 437.1526.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 14.9 min for (*S*)-isomer and t_R = 18.6 min for (*R*)-isomer.

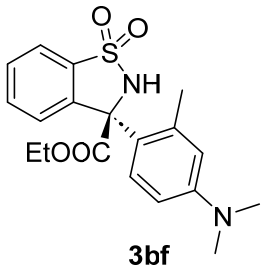


Peaks	Ret. Time	Area	Area%
1	13.392	7335557	49.612
2	16.473	7450185	50.388



Peaks	Ret. Time	Area	Area%
1	14.938	247	0.001
2	18.627	17317079	99.999

(*R*)-Ethyl-3-(4-(dimethylamino)-2-methylphenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bf**)



3bf

45 mg, red oil, **79% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

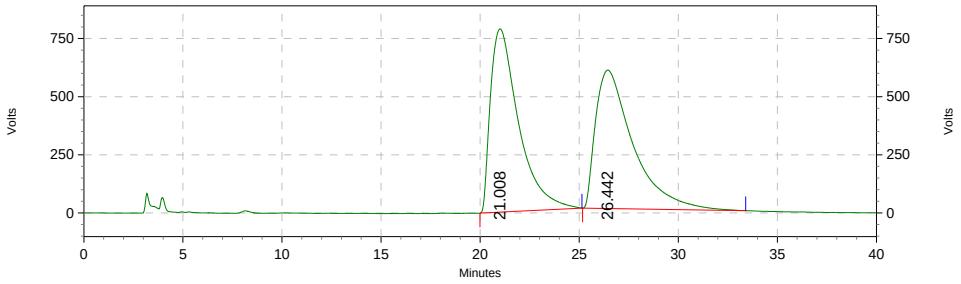
$[\alpha]_D^{20}$ + 62.53 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ7.82 (d, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 14.3 Hz, 3H), 6.55 (d, *J* = 7.0 Hz, 2H), 6.35 (d, *J* = 8.4 Hz, 1H), 6.10 (s, 1H), 4.42 – 4.28 (m, 2H), 2.92 (s, 6H), 2.22 (s, 3H), 1.29 (s, 3H).

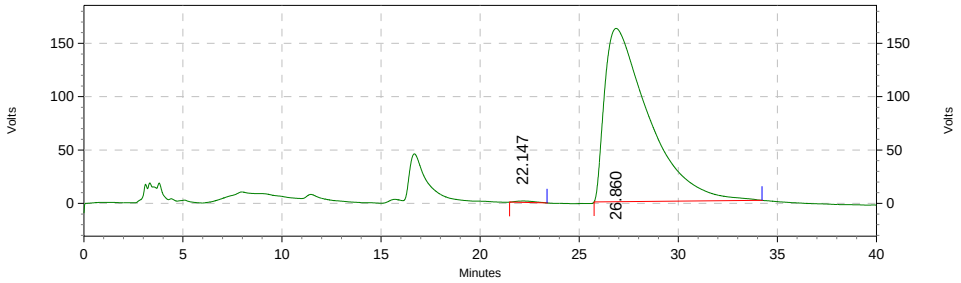
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 150.6, 138.8, 138.0, 137.1, 132.9, 130.6, 128.9, 127.1, 124.4, 121.5, 116.0, 108.9, 71.6, 63.9, 40.2, 20.7, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_2O_4S^+$ 375.1374; Found 375.1368.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 22.1 min for (*S*)-isomer and t_R = 26.9 min for (*R*)-isomer.

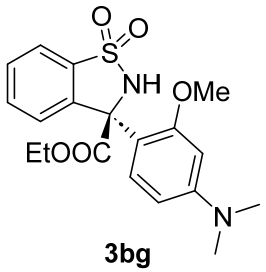


Peaks	Ret. Time	Area	Area%
1	21.008	77746141	49.821
2	26.442	78305102	50.179



Peaks	Ret. Time	Area	Area%
1	22.147	89419	0.354
2	26.860	25170488	99.646

(*R*)-Ethyl-3-(4-(dimethylamino)-2-methoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bg**)



3bg

50 mg, yellow oil, **86% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

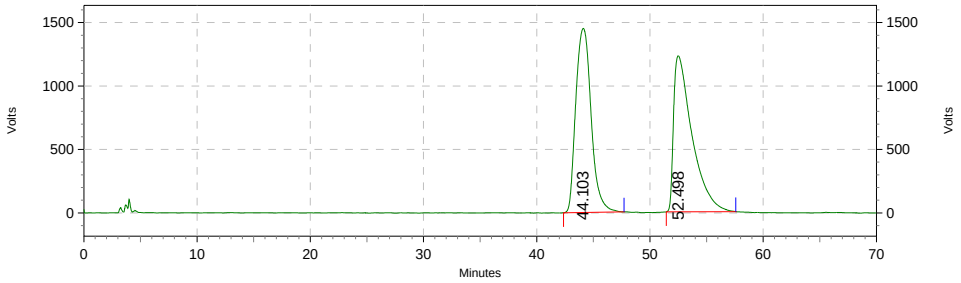
$[\alpha]_D^{20}$ + 169.32 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 7.2 Hz, 1H), 7.71 – 7.61 (m, 3H), 6.48 (d, J = 8.6 Hz, 1H), 6.23 (d, J = 2.1 Hz, 1H), 6.16 (s, 1H), 6.11 – 6.07 (m, 1H), 4.31 – 4.24 (m, 2H), 3.83 (s, 3H), 2.94 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H).

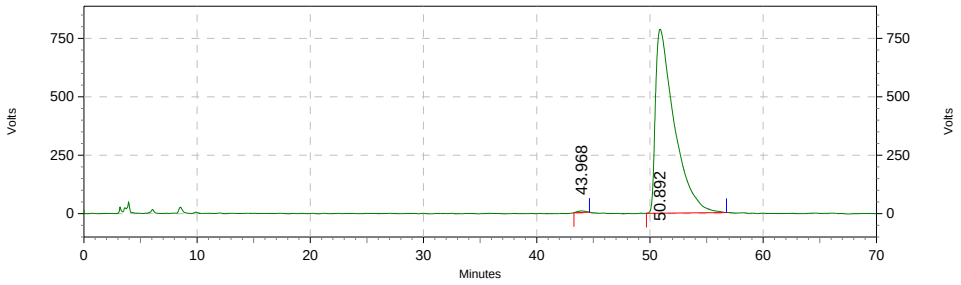
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.1, 158.0, 152.4, 137.1, 132.9, 130.6, 128.4, 127.0, 121.7, 103.8, 95.9, 69.2, 63.3, 55.4, 40.5, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{23}N_2O_5S^+$ 391.1323; Found 391.1319.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 44.0 min for (*S*)-isomer and t_R = 50.9 min for (*R*)-isomer.

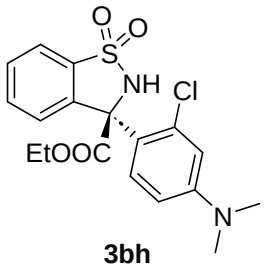


Peaks	Ret. Time	Area	Area%
1	44.103	136457581	49.536
2	52.498	139012829	50.464



Peaks	Ret. Time	Area	Area%
1	43.968	322341	0.353
2	50.892	90941898	99.647

(*R*)-Ethyl-3-(2-chloro-4-(dimethylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bh**)



3bh

30 mg, yellow oil, **50% yield, 98% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

$[\alpha]_D^{20}$ + 42.09 (c = 1.00, $CHCl_3$).

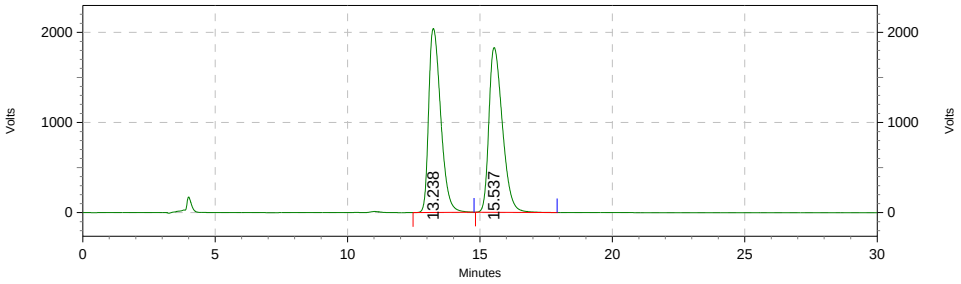
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.0 Hz, 1H), 7.71 – 7.65 (m, 3H), 6.72 (d, *J* = 2.1 Hz, 1H), 6.52 (d, *J* = 8.8 Hz, 1H), 6.36 – 6.32 (m, 1H), 6.28 (s, 1H), 4.38 – 4.29 (m, 2H), 2.91 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.3, 151.3, 137.4, 137.3, 134.8, 133.0,

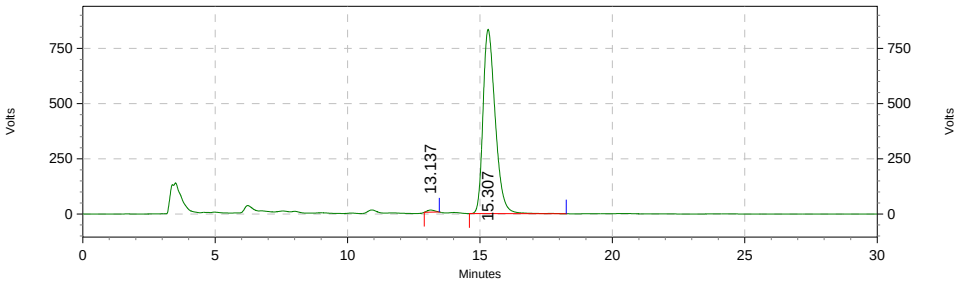
131.0, 129.6, 126.7, 123.8, 121.8, 113.9, 109.6, 70.6, 64.1, 40.1, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}ClN_2O_4S^+$ 395.0827; Found 395.0825.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 13.1 min for (*S*)-isomer and t_R = 15.3 min for (*R*)-isomer.

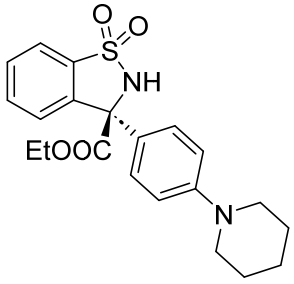


Peaks	Ret. Time	Area	Area%
1	13.238	64340294	49.828
2	15.537	64785739	50.172



Peaks	Ret. Time	Area	Area%
1	13.137	194755	0.723
2	15.307	26759602	99.277

(*R*)-Ethyl-3-(4-(piperidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bi**)



3bi

51 mg, yellow oil, **85% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

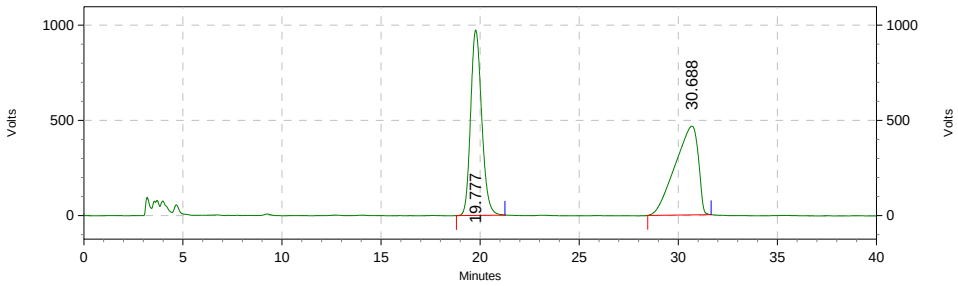
$[\alpha]_D^{20}$ + 22.40 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (t, *J* = 6.7 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.14 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 5.2 Hz, 4H), 1.68 – 1.60 (m, 4H), 1.55 (q, *J* = 5.7 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

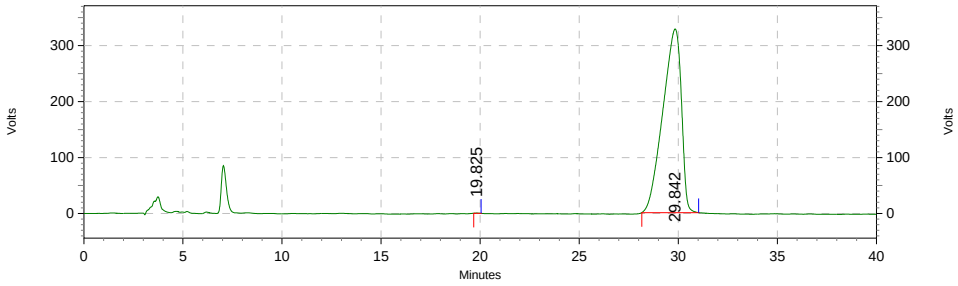
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.5, 151.9, 137.9, 135.2, 133.0, 130.2, 128.2, 127.2, 120.9, 115.6, 70.8, 63.5, 49.6, 25.5, 24.2, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}N_2O_4S^+$ 401.1530; Found 401.1527.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 19.8 min for (*S*)-isomer and t_R = 29.8 min for (*R*)-isomer.

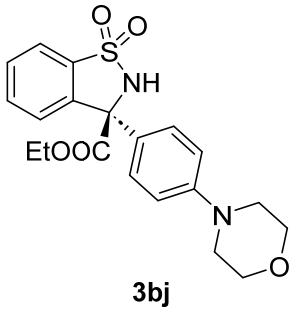


Peaks	Ret. Time	Area	Area%
1	19.777	37774854	49.905
2	30.688	37918567	50.095



Peaks	Ret. Time	Area	Area%
1	19.825	4760	0.022
2	29.842	21317035	99.978

(*R*)-Ethyl-3-(4-morpholinophenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bj**)



3bj

58 mg, white solid, m.p.=63-65 °C, **79% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

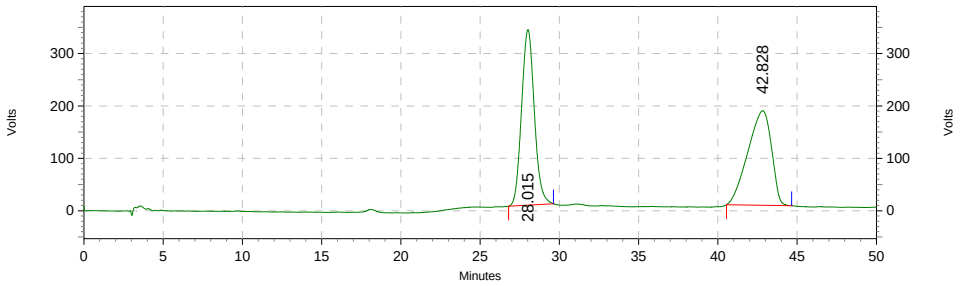
$[\alpha]_D^{20}$ + 25.13 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.69 (m, 2H), 7.68 – 7.53 (m, 2H), 7.26 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.14 (s, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.82 (t, J = 4.8 Hz, 4H), 3.14 (t, J = 4.8 Hz, 4H), 1.31 (t, J = 7.1 Hz, 3H).

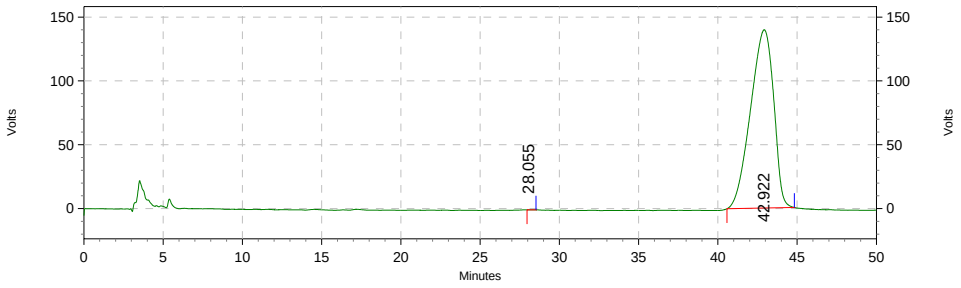
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.5, 151.4, 137.9, 133.1, 130.4, 129.6, 127.5, 127.3, 121.1, 115.3, 70.8, 66.7, 63.7, 48.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_5S^+$ 403.1323; Found 403.1316.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 28.1 min for (*S*)-isomer and t_R = 42.9 min for (*R*)-isomer.

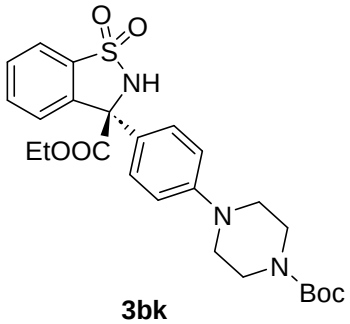


Peaks	Ret. Time	Area	Area%
1	28.015	18728811	50.122
2	42.828	18637945	49.878



Peaks	Ret. Time	Area	Area%
1	28.055	540	0.004
2	42.922	14177370	99.996

(*R*)-Ethyl-3-(4-(4-(tert-butoxycarbonyl)piperazin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bk**)



3bk

65 mg, yellow oil, **86% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

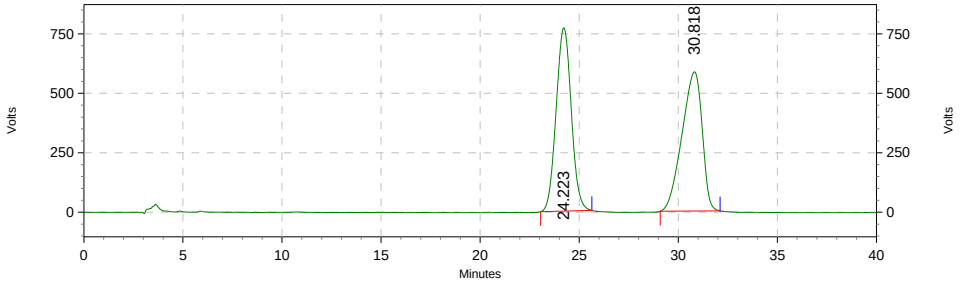
$[\alpha]_D^{20}$ + 22.40 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.20 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.49 – 3.41 (m, 4H), 3.07 – 2.98 (m, 4H), 1.38 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 3H).

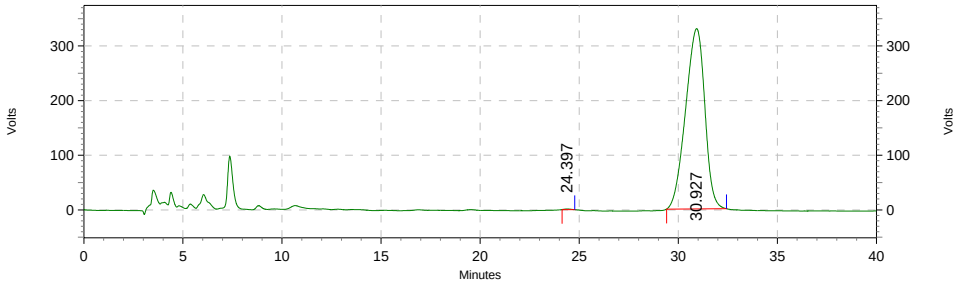
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.3, 154.6, 151.1, 137.7, 135.3, 133.0, 130.3, 129.6, 127.3, 127.2, 120.9, 115.9, 79.9, 70.6, 63.6, 48.4, 28.3, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{31}N_3O_6SNa^+$ 524.1826; Found 524.1821.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 24.4 min for (*S*)-isomer and t_R = 30.9 min for (*R*)-isomer.

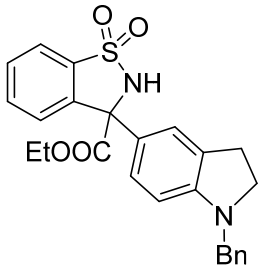


Peaks	Ret. Time	Area	Area%
1	24.223	41010470	49.790
2	30.818	41356703	50.210



Peaks	Ret. Time	Area	Area%
1	24.397	25527	0.115
2	30.927	22197900	99.885

(*R*)-Ethyl-3-(1-benzylindolin-4-yl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bl**)



3bl

49 mg, yellow oil, **83% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

$[\alpha]_D^{20}$ + 20.01 (c = 1.00, $CHCl_3$).

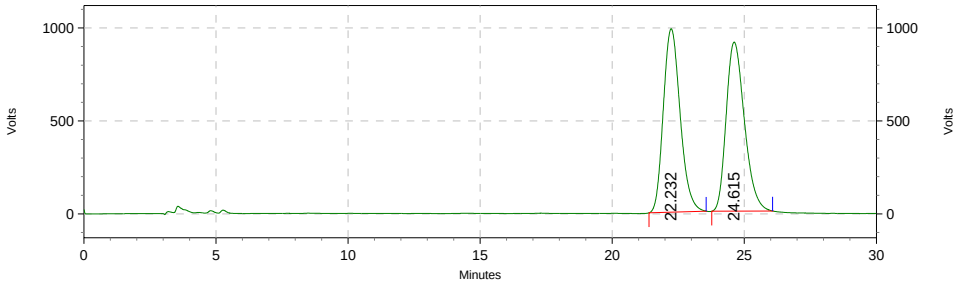
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (t, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.22 (m, 5H), 7.03 – 6.95 (m, 2H), 6.36 (d, *J* = 8.3 Hz, 1H), 5.99 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.22 (s,

2H), 3.34 (t, J = 8.4 Hz, 2H), 2.91 (t, J = 8.4 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H).

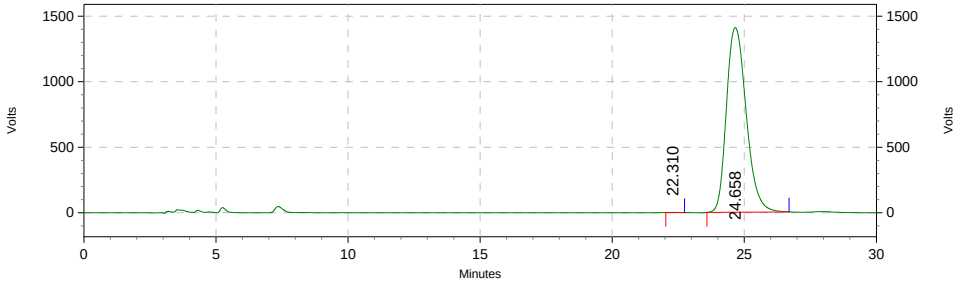
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 152.9, 138.1, 137.9, 133.1, 130.9, 130.3, 128.5, 127.7, 127.6, 127.5, 127.2, 125.9, 122.7, 121.0, 106.1, 71.3, 63.6, 53.4, 53.0, 28.3, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}N_2O_4S^+$ 449.1530; Found 449.1523.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 22.3 min for (*S*)-isomer and t_R = 24.7 min for (*R*)-isomer.

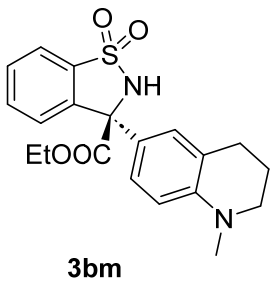


Peaks	Ret. Time	Area	Area%
1	22.232	43673377	50.010
2	24.615	43656129	49.990



Peaks	Ret. Time	Area	Area%
1	22.310	25422	0.035
2	24.658	73328602	99.965

(*R*)-Ethyl-3-(1-methyl-1,2,3,4-tetrahydroquinolin-8-yl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bm**)



3bm

49 mg, light red oil, **88% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

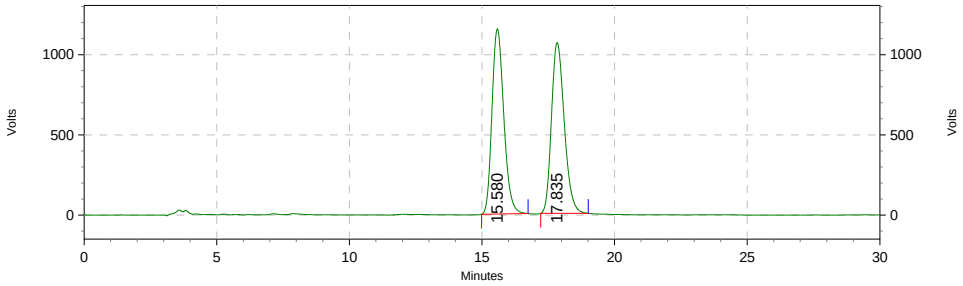
$[\alpha]_D^{20}$ + 21.01 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.69 (m, 2H), 7.66 – 7.52 (m, 2H), 6.98 (d, J = 7.8 Hz, 1H), 6.87 (s, 1H), 6.52 – 6.42 (m, 1H), 6.02 (s, 1H), 4.38 – 4.27 (m, 2H), 3.26 – 3.14 (m, 2H), 2.84 (s, 3H), 2.70 – 2.62 (m, 2H), 1.96 – 1.85 (m, 2H), 1.34 – 1.25 (m, 3H).

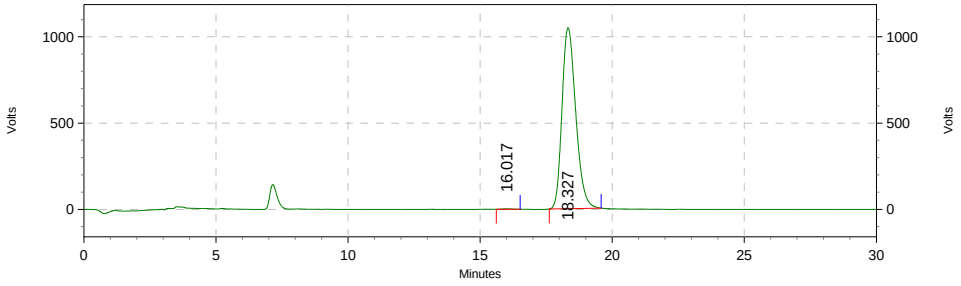
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 146.9, 138.1, 135.3, 133.0, 130.2, 127.5, 126.7, 125.5, 125.2, 122.9, 120.9, 110.3, 63.5, 50.9, 38.8, 27.9, 22.0, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_4S^+$ 387.1374; Found 387.1366.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 16.0 min for (*S*)-isomer and t_R = 18.3 min for (*R*)-isomer.

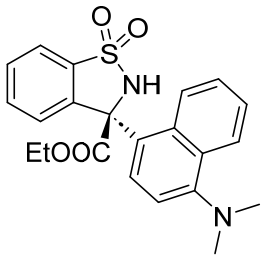


Peaks	Ret. Time	Area	Area%
1	15.580	35721592	50.024
2	17.835	35687362	49.976



Peaks	Ret. Time	Area	Area%
1	16.017	73575	0.194
2	18.327	37860717	99.806

(*R*)-Ethyl-3-(5-(dimethylamino)naphthalen-1-yl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bn**)



3bn

31 mg, white solid, m. p. = 190-192 ºC, **50% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

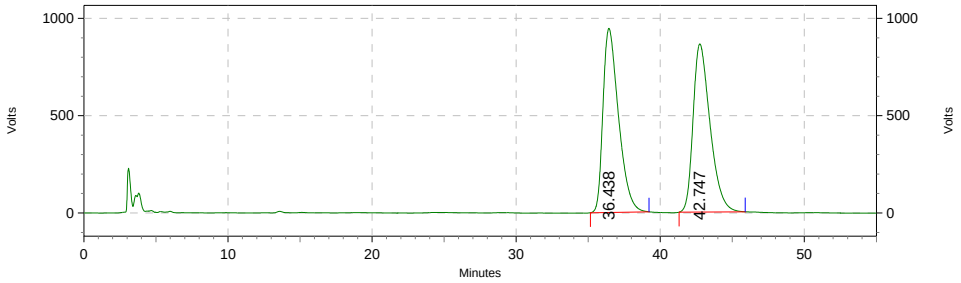
$[\alpha]_D^{20}$ + 136.16 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.78 – 7.71 (m, 2H), 7.68 – 7.52 (m, 3H), 7.38 (s, 2H), 6.70 (s, 2H), 6.26 (s, 1H), 4.21 – 4.06 (m, 2H), 2.73 (s, 6H), 0.97 (t, J = 8.2 Hz, 3H).

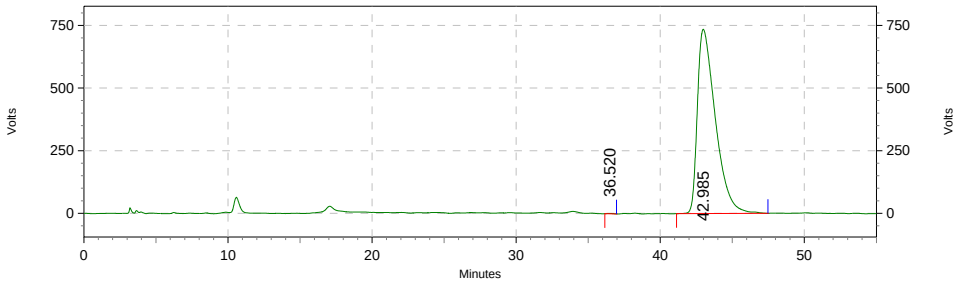
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.4, 152.4, 138.2, 137.3, 133.0, 132.1, 130.9, 129.5, 128.2, 127.1, 126.8, 126.7, 125.4, 125.1, 123.8, 121.8, 112.2, 71.2, 64.0, 45.0, 13.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{23}N_2O_4S^+$ 411.1374; Found 411.1368.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 36.5 min for (*S*)-isomer and t_R = 43.0 min for (*R*)-isomer.

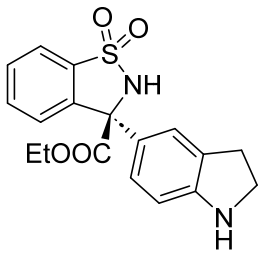


Peaks	Ret. Time	Area	Area%
1	36.438	70911291	50.079
2	42.747	70686526	49.921



Peaks	Ret. Time	Area	Area%
1	36.520	33597	0.053
2	42.985	63824147	99.947

(*R*)-Ethyl-3-(indolin-4-yl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bo**)



3bo

49 mg, yellow oil, **87% yield, 93% ee**; (silica gel, petroleum ether: ethyl acetate = 2:1).

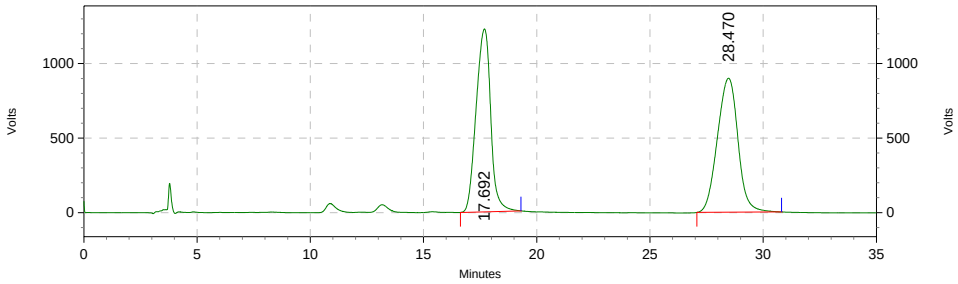
$[\alpha]_D^{20}$ + 17.19 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.01 (s, 1H), 6.95 – 6.88 (m, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.52 (t, *J* = 8.4 Hz, 2H), 2.93 (t, *J* = 8.4 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

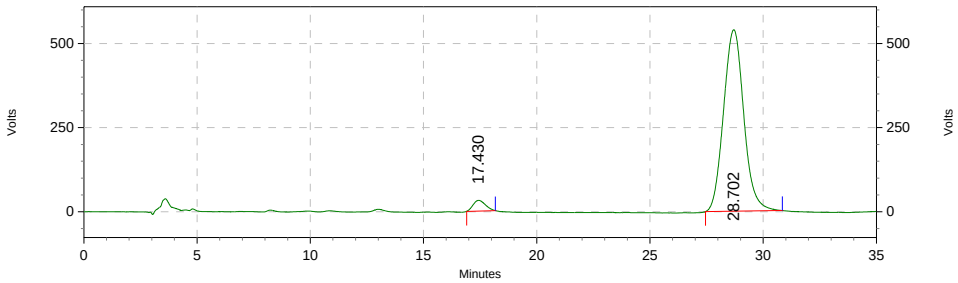
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.8, 152.2, 138.2, 135.5, 133.1, 130.4, 129.6, 128.8, 127.6, 125.9, 122.9, 121.1, 108.9, 71.4, 63.7, 47.5, 29.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}N_2O_4S^+$ 359.1061; Found 359.1058.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 17.4 min for (*S*)-isomer and t_R = 28.7 min for (*R*)-isomer.

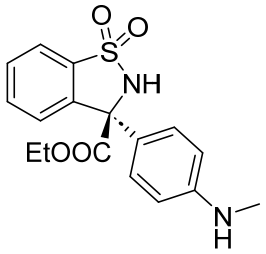


Peaks	Ret. Time	Area	Area%
1	17.692	54789265	49.160
2	28.470	56662640	50.840



Peaks	Ret. Time	Area	Area%
1	17.430	1196758	3.454
2	28.702	33454826	96.546

(*R*)-Ethyl-3-(4-(methylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bp**)



3bp

47 mg, yellow oil, **90% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

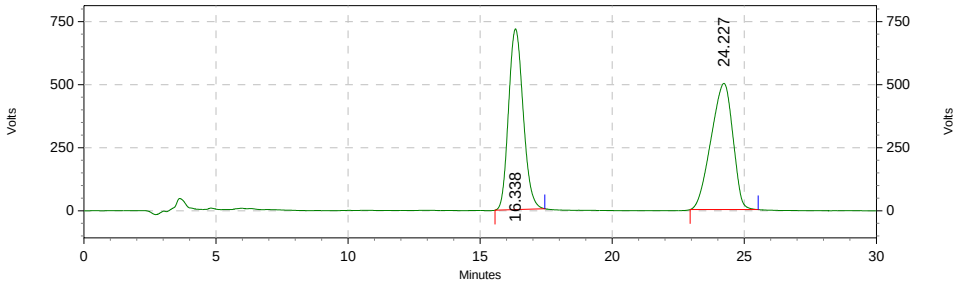
$[\alpha]_D^{20}$ + 16.75 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.39 (d, J = 8.5 Hz, 2H), 6.01 (s, 1H), 4.21 (q, J = 6.9 Hz, 2H), 3.58 (s, 1H), 2.64 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H).

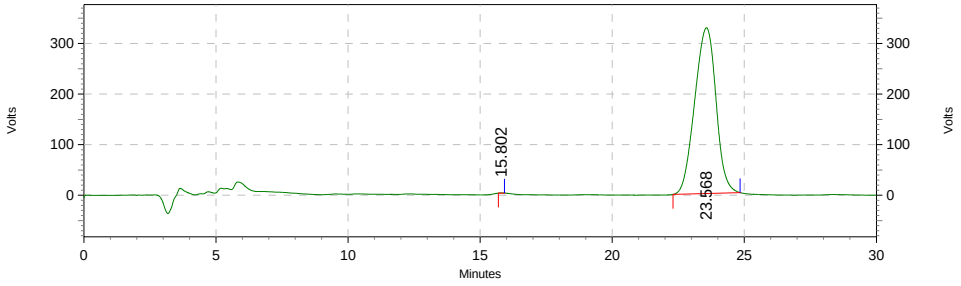
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.7, 149.6, 138.1, 135.3, 133.1, 130.3, 127.5, 126.8, 121.0, 112.3, 71.1, 63.6, 30.4, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}N_2O_4S^+$ 347.1061; Found 347.1056.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 15.8 min for (*S*)-isomer and t_R = 23.6 min for (*R*)-isomer.

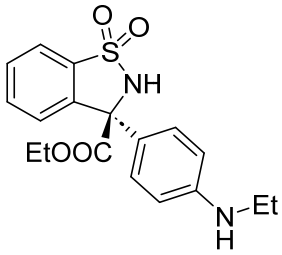


Peaks	Ret. Time	Area	Area%
1	16.338	27471200	48.927
2	24.227	28675659	51.073



Peaks	Ret. Time	Area	Area%
1	15.802	2809	0.015
2	23.568	18333258	99.985

(*R*)-Ethyl-3-(4-(ethylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bq**)



3bq

45 mg, yellow oil, **84% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

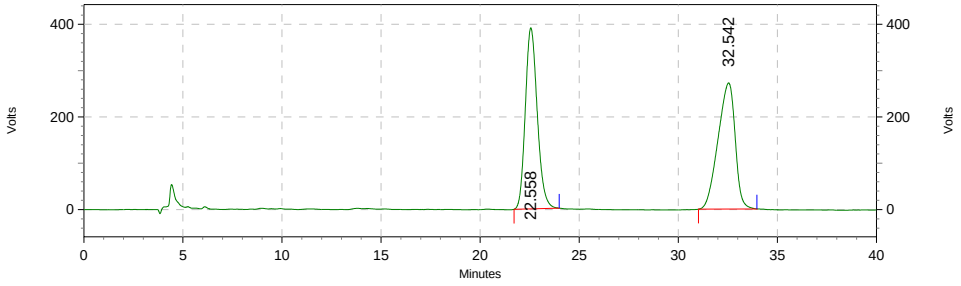
$[\alpha]_D^{20}$ + 22.11 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 6.39 (d, J = 8.6 Hz, 2H), 6.01 (s, 1H), 4.21 (q, J = 6.9 Hz, 2H), 2.98 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H).

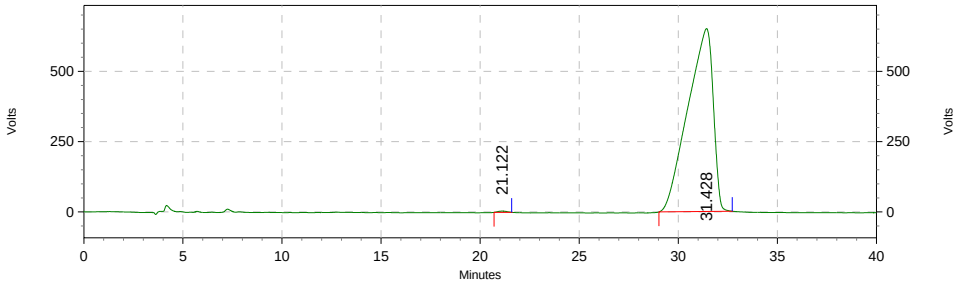
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.6, 148.7, 138.0, 135.2, 133.0, 130.2, 127.4, 126.6, 120.8, 112.4, 71.0, 63.5, 38.1, 14.6, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}N_2O_4S^+$ 361.1217; Found 361.1212.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 21.1 min for (*S*)-isomer and t_R = 31.4 min for (*R*)-isomer.

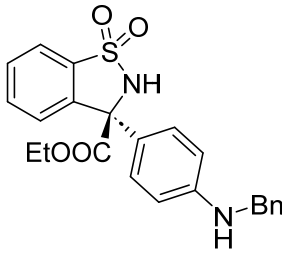


Peaks	Ret. Time	Area	Area%
1	22.558	16362673	50.009
2	32.542	16357086	49.991



Peaks	Ret. Time	Area	Area%
1	21.122	132701	0.228
2	31.428	57943226	99.772

(*R*)-Ethyl-3-(4-(benzylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3br**)



3br

57 mg, yellow oil, **90% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

$[\alpha]_D^{20}$ + 15.55 (c = 1.00, $CHCl_3$).

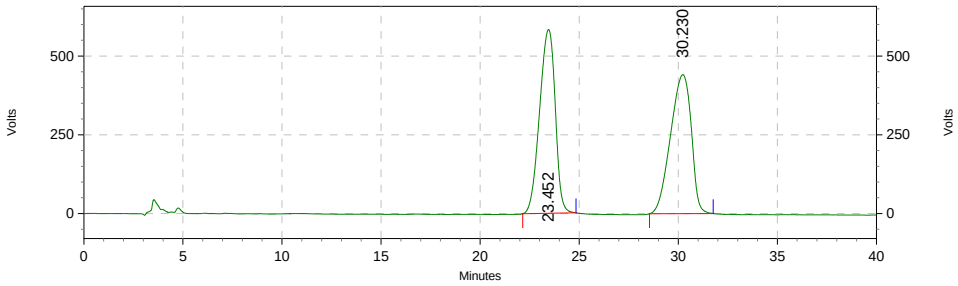
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 4.1 Hz, 3H), 7.15 – 7.10 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 8.5 Hz, 2H), 5.92 (s, 1H), 4.18

(q, J = 7.3 Hz, 2H), 4.14 (s, 2H), 1.16 (t, J = 7.1 Hz, 3H).

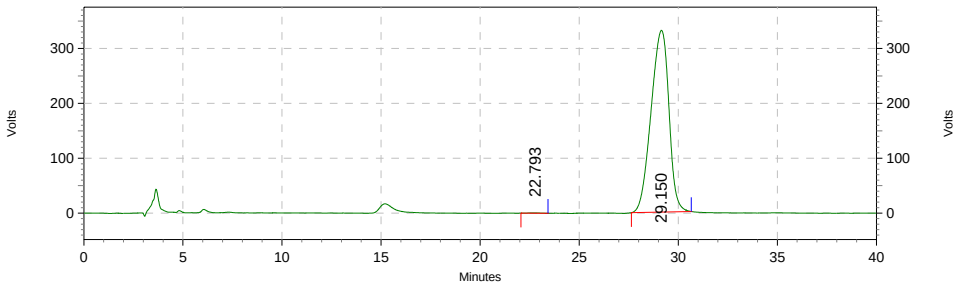
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.6, 148.4, 139.0, 138.0, 135.2, 133.0, 130.2, 128.6, 127.5, 127.4, 127.3, 127.2, 127.0, 120.9, 112.6, 71.0, 63.5, 47.8, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_4S^+$ 423.1374; Found 423.1368.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 22.8 min for (*S*)-isomer and t_R = 29.2 min for (*R*)-isomer.

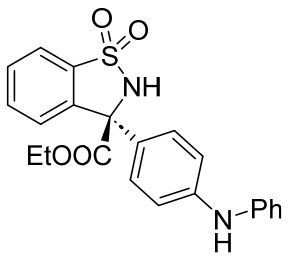


Peaks	Ret. Time	Area	Area%
1	23.452	32019782	49.911
2	30.230	32133906	50.089



Peaks	Ret. Time	Area	Area%
1	22.793	22303	0.107
2	29.150	20726737	99.893

(*R*)-Ethyl-3-(4-(phenylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bs**)



3bs

45 mg, yellow oil, **73% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

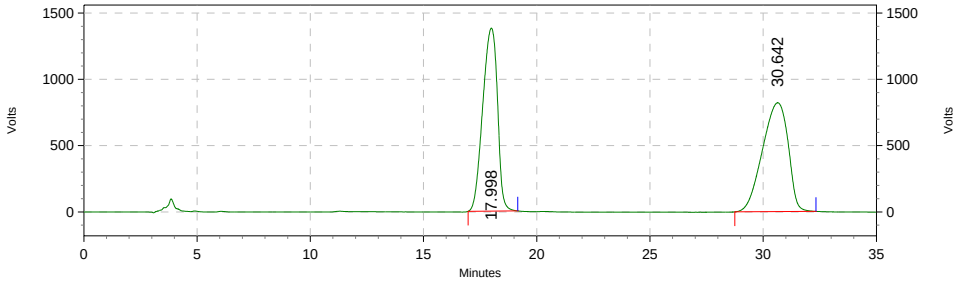
$[\alpha]_D^{20}$ + 15.32 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.20 – 7.03 (m, 5H), 6.93 (d, J = 7.8 Hz, 2H), 6.85 – 6.79 (m, 3H), 6.03 (s, 1H), 5.92 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H).

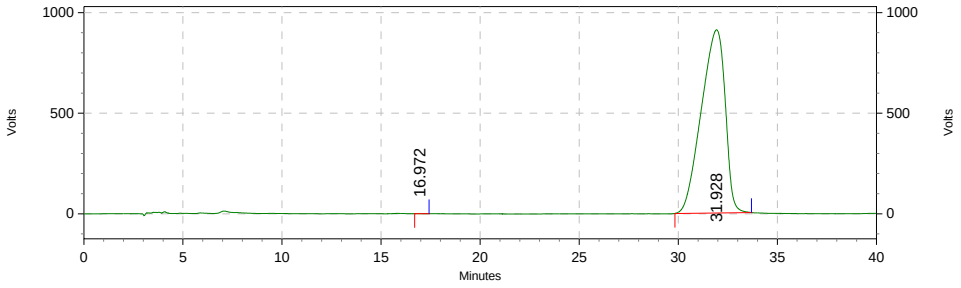
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.5, 144.1, 142.0, 137.7, 135.3, 133.2, 130.4, 130.0, 129.3, 127.5, 127.3, 121.7, 121.1, 118.8, 116.5, 70.9, 63.8, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}N_2O_4S^+$ 409.1217; Found 409.1211.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel IA, hexane/i-PrOH =70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 17.0 min for (*S*)-isomer and t_R = 31.9 min for (*R*)-isomer.

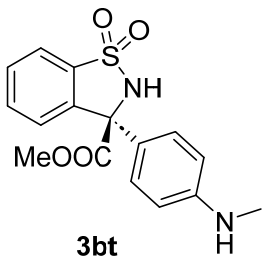


Peaks	Ret. Time	Area	Area%
1	17.998	62634330	49.146
2	30.642	64811500	50.854



Peaks	Ret. Time	Area	Area%
1	16.972	8518	0.011
2	31.928	76298196	99.989

(*R*)-methyl-3-(4-(methylamino)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3bt**)



3bt

46 mg, yellow oil, **93% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 3:1).

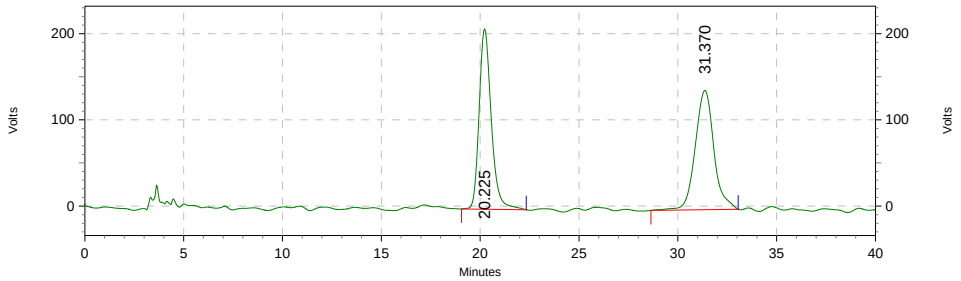
$[\alpha]_D^{20}$ + 41.75 (c = 1.60, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.45 (d, *J* = 8.3 Hz, 2H), 5.88 (s, 1H), 3.79 (s, 3H), 2.71 (s, 3H).

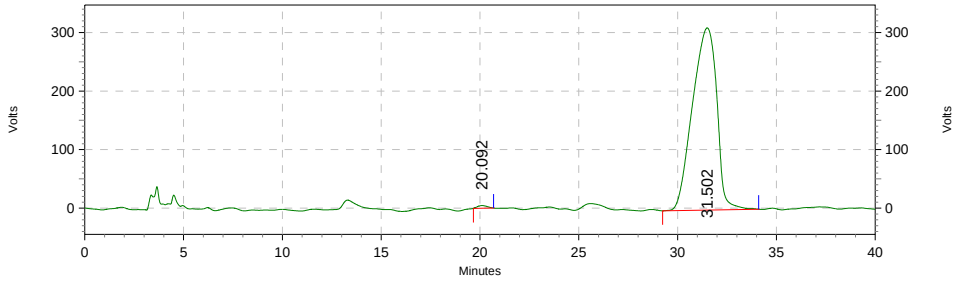
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.3, 149.7, 138.0, 135.4, 133.2, 130.4, 127.6, 127.5, 126.9, 121.1, 112.4, 71.2, 54.2, 30.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}N_2O_4S^+$ 333.0904; Found 333.0908.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 21.0 min for (*S*)-isomer and $_{tR}$ = 31.5 min for (*R*)-isomer.

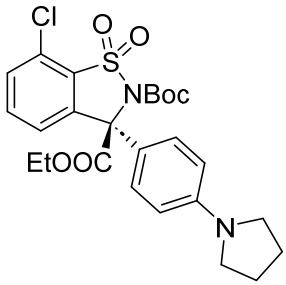


Peaks	Ret. Time	Area	Area%
1	20.225	8968765	49.679
2	31.370	9084779	50.321



Peaks	Ret. Time	Area	Area%
1	20.092	159246	0.595
2	31.502	26593352	99.405

(*R*)-2-(tert-butyl) 3-ethyl -7-chloro-3-(4-(pyrrolidin-1-yl)phenyl)benzo[*d*]isothiazole-2,3(3*H*)-dicarboxylate 1,1-dioxide (**4**)



4

120 mg, white solid, m. p.= 186-188, °C, **96% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 5:1).

$[\alpha]_D^{20}$ **- 90.33** (c = 1.00, $CHCl_3$).

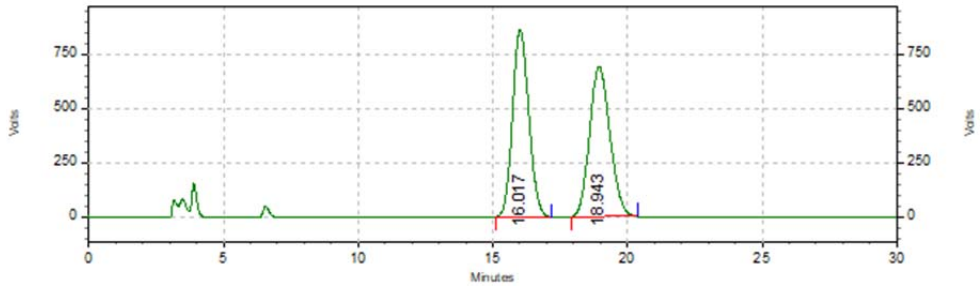
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 4.3 Hz, 2H), 7.38 – 7.27 (m, 3H), 6.44 (d, *J* = 8.8 Hz, 2H), 4.39 – 4.30 (m, 1H), 4.17 – 4.10 (m, 1H), 3.26

(d, J = 6.5 Hz, 4H), 2.01 – 1.91 (m, 4H), 1.49 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H).

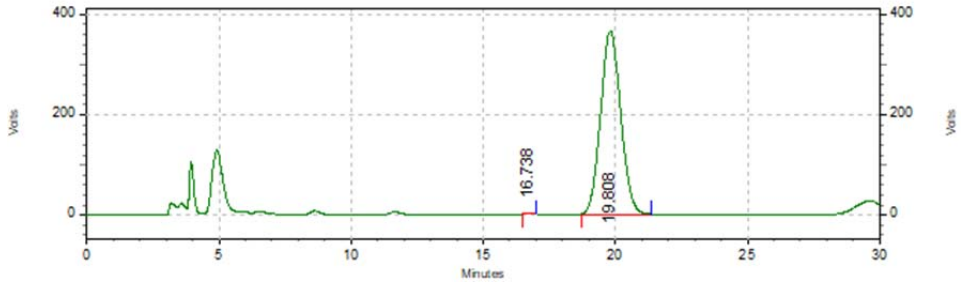
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 167.6, 148.4, 147.5, 138.5, 134.8, 131.2, 129.3, 128.7, 124.2, 110.8, 85.1, 71.6, 63.0, 47.5, 28.1, 25.5, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{30}ClN_2O_6S^+$ 521.1508; Found 521.1502.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 16.7 min for (*S*)-isomer and t_R = 19.8 min for (*R*)-isomer.

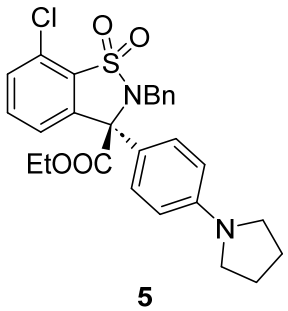


Peaks	Ret. Time	Area	Area%
1	16.017	36014219	49.843
2	18.943	36241475	50.157



Peaks	Ret. Time	Area	Area%
1	16.738	19161	0.099
2	19.808	19250366	99.901

(*R*)-Ethyl-2-benzyl-7-chloro-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**5**)



5

118 mg, colorless oil, **97% yield, 99% ee**; (silica gel, petroleum ether: ethyl acetate = 3:1).

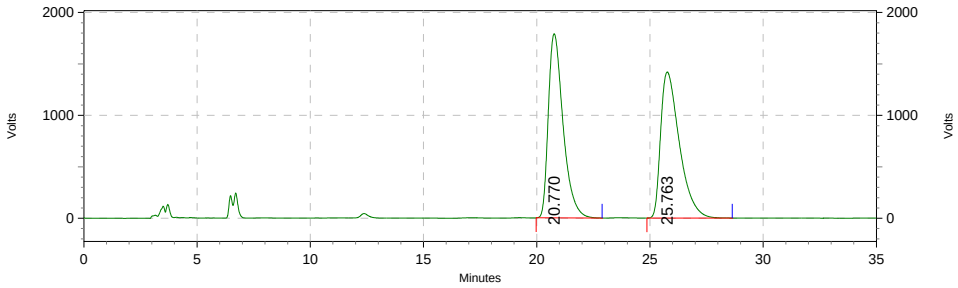
$[\alpha]_D^{20}$ -41.55 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 4.4 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.20 – 7.15 (m, 2H), 7.13 – 7.03 (m, 3H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 8.8 Hz, 2H), 4.37 (q, 2H), 4.11 – 4.00 (m, 2H), 3.22 – 3.10 (m, 4H), 1.95 – 1.85 (m, 4H), 1.06 (t, *J* = 7.1 Hz, 3H).

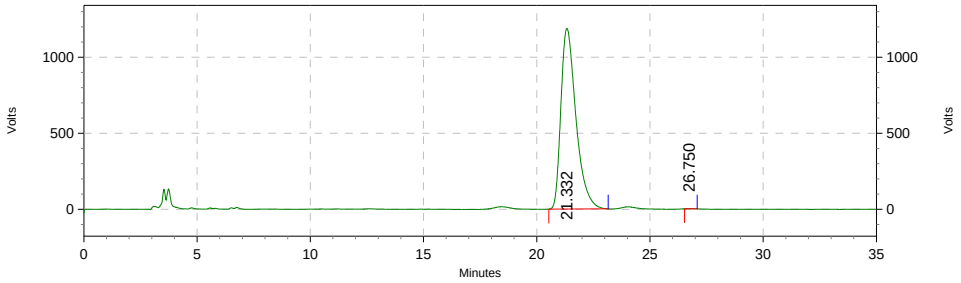
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 168.9, 148.0, 141.1, 136.5, 133.7, 131.9, 130.5, 129.5, 128.7, 127.9, 127.1, 125.6, 121.7, 111.4, 74.4, 62.6, 47.5, 45.5, 25.5, 13.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}ClN_2O_4S^+$ 511.1453; Found 511.1447.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 21.3 min for (*S*)-isomer and $_{tR}$ = 26.8 min for (*R*)-isomer.

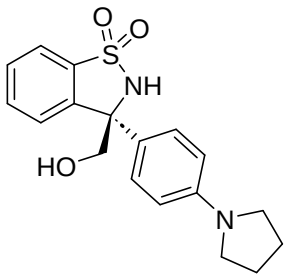


Peaks	Ret. Time	Area	Area%
1	20.770	81027215	49.859
2	25.763	81484600	50.141



Peaks	Ret. Time	Area	Area%
1	21.332	54888970	99.951
2	26.750	26667	0.049

(*R*)-3-(hydroxymethyl)-3-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (**6**)



6

65 mg, colorless oil, **72% yield, 99% ee**, (silica gel, petroleum ether : ethyl acetate=2:1).

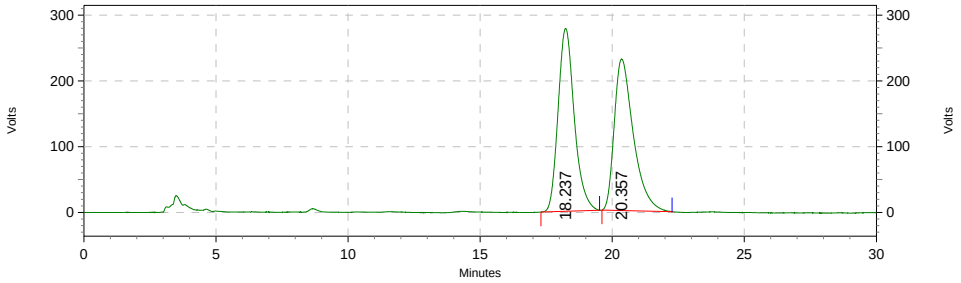
$[\alpha]_D^{20}$ -2.58 (c = 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.20 (t, *J* = 8.9 Hz, 4H), 6.43 (d, *J* = 8.2 Hz, 2H), 5.20 (s, 1H), 4.16 (d, *J* = 11.8 Hz, 1H), 4.02 (d, *J* = 11.6 Hz, 1H), 3.16 (t, *J* = 6.2 Hz, 4H), 1.90 (t, *J* = 6.2 Hz, 4H).

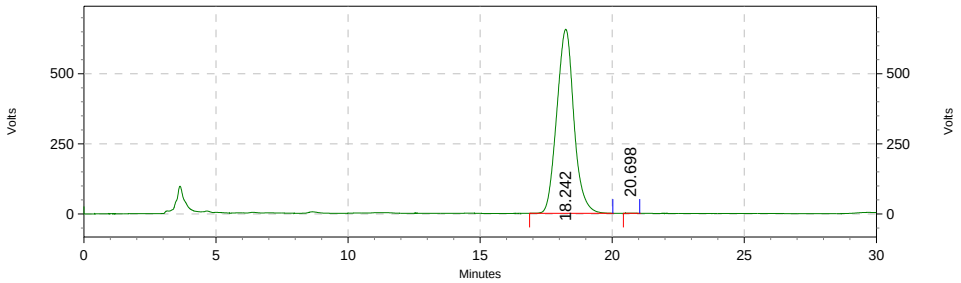
^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 141.8, 135.9 , 133.5 , 129.6, 129.6 , 129.6 , 128.0 , 125.1 , 121.4 , 70.0 , 67.5 , 25.3 .

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}ClN_2O_4S^+$ 345.1268; Found 345.1265.

HPLC The ee value was determined by chiral HPLC analysis (Chiralcel AD-H, hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 220 nm). Retention times: t_R = 18.2 min for (*S*)-isomer and t_R = 20.7 min for (*R*)-isomer.



Peaks	Ret. Time	Area	Area%
1	18.237	11848421	50.561
2	20.357	11585621	49.439



Peaks	Ret. Time	Area	Area%
1	18.242	29513781	99.974
2	20.698	7738	0.026

4. Studies on Reaction Mechanism

5.1. DFT Studies on the Reaction Mechanism

Calculations were performed to get mechanistic insights into the reactions. Ligand **L6** was used for the study to reduce the cost of the calculation. N-Methylaniline (**2p**) was used as the arylamine model, and methyl ester (**1b**) was used as the electrophile model (Figure S2).

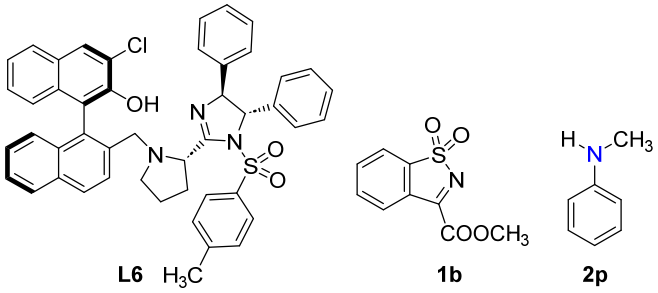


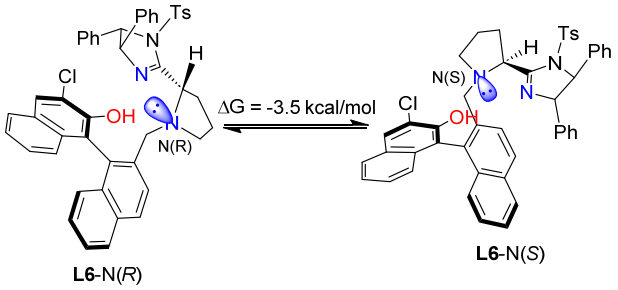
Figure S2. Structures used for the calculation.

The calculations were performed on a Linux platform with Gaussian G09 D01 package.[3] The structures of intermediates/transition states were optimized at M06L level of theory[4] with 6-31G(d) basis set for light atoms[5] and SDD for nickel.[6] Single point energies were calculated at M06L level of theory with 6-311G(d) basis set for light atoms[5d, 5f, g, 7] and LANL2TZ for nickel.[8] Implicit solvation model SMD[9] was used with dichloromethane as the solvent.

The optimized structures for the chiral ligand and the reaction intermediates were confirmed by the absence of imaginary frequency. The transition state geometries were confirmed by the presence of a single imaginary frequency in the Hessian matrix, and the reaction paths were checked by intrinsic reaction coordinate (IRC) calculations.

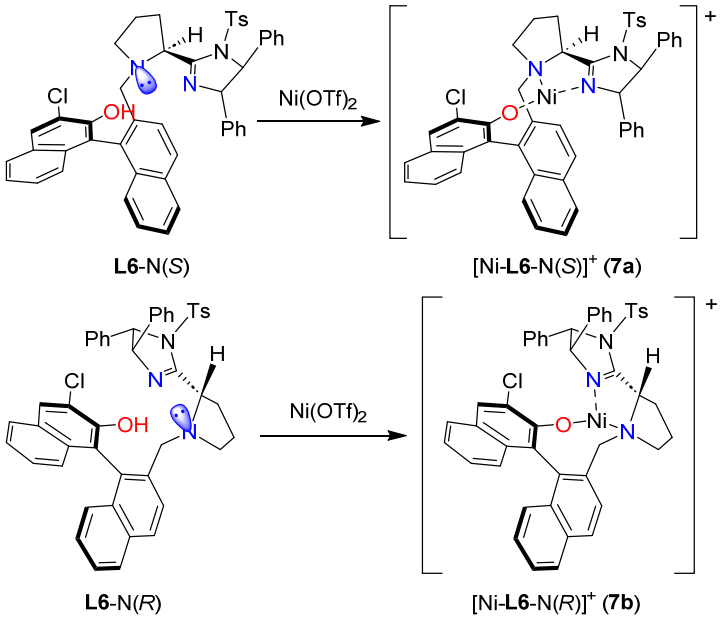
At first, the structure of the chiral ligand was optimized. In our previous study, we found that the nitrogen atom of the proline moiety in the ligand may adopt either an (*R*)- (donated as **L6**-N(*R*)) or (*S*)-configuration (donated as **L6**-N(*S*)) depending on the structures of the functional groups attached to the proline moiety.

Comparison of the energies of the optimized structures of **L6**-N(*R*) and **L6**-N(*S*) suggested that **L6**-N(*S*) was the favored structure in dichloromethane (ΔG = -3.5 kcal/mol) (Scheme S1). This is in agreement with our previous X-ray diffraction study on the structure of similar chiral ligand.[1a]



Scheme S1. Equilibrium between **L6**-N(*R*) and **L6**-N(*S*)

Coordination of $Ni(OTf)_2$ to **L6**-N(*S*) produced nickel complex [**L6**-N(*S*)-Ni]$^+$ (**7a**) which would act as the catalyst in the reaction. This is a favored process especially in the presence of a base. Coordination of $Ni(OTf)_2$ to **L6**-N(*R*) to give [Ni-**L6**-N(*R*)]$^+$ (**7b**) was also considered. But [Ni-**L6**-N(*S*)]$^+$ (**7a**) was favored over [Ni-**L6**-N(*R*)]$^+$ (**7b**) (ΔG = -20.7 kcal/mol).



Scheme S2. Formation of the nickel complexes.

The interaction of **1b** with catalyst **7a** was then studied to account for the high enantioselectivity of the reactions. Coordination of the imine nitrogen atom in electrophile **1b** to the nickel atom in the catalyst produced key intermediate **8**. This process led to the activation of the electrophile **1b**, and aromatic substitution of **2p** happened at the position para- to the N-methylamino group, yielding the corresponding Friedel-Crafts product in high ee.

Different types of interactions could be expected when **1b** coordinated to **7a** with its imine nitrogen atom. In catalyst **7a**, the naphthyl group from binaphthyl moiety and one phenyl

group from the imidazoline moiety formed a narrow slot which allowed the entrance of **1b** from a special direction such that the benzene ring of **1b** was generally parallel to the phenyl group to avoid the steric repulsion between the two groups. When electrophile **1b** entered the narrow slot, the ester group (either ethoxycarbonyl or methoxycarbonyl group) could be located either inside (**8a**) or outside the slot (**8b**). In intermediate **8a**, the *Re*-face of the ketimine C=N bond was covered by the phenyl group, and the activated electrophile used its *Si*-face to react with **2q**, leading to product with (*R*)-configuration. Similarly, reaction of the *Re*-face of **8b** with **2q** provided product with (*S*)-configuration (Figure S3).

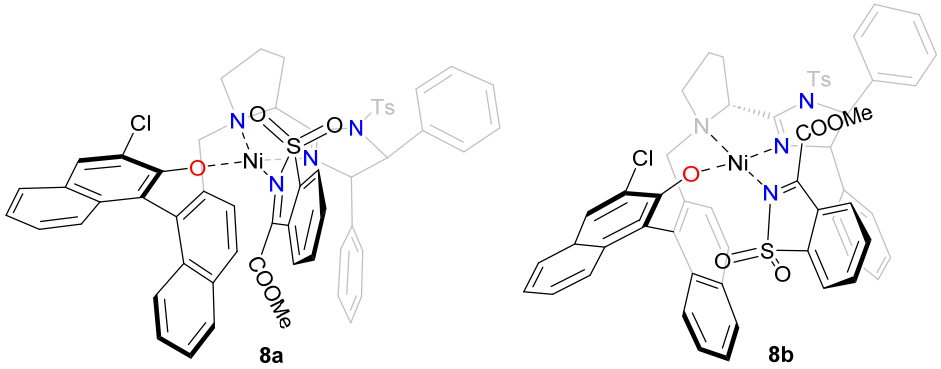
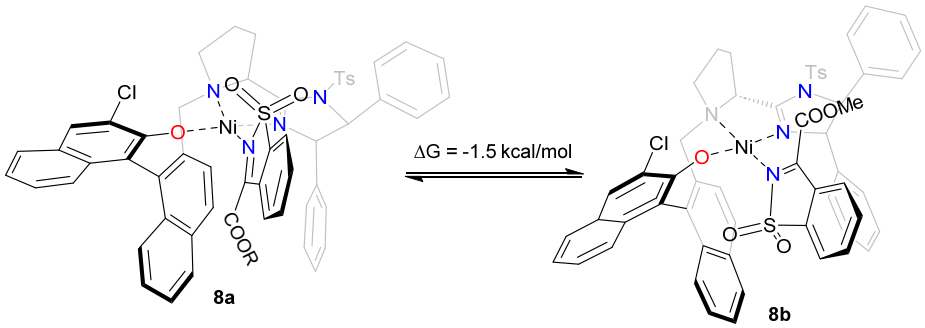


Figure S3. Activation of the electrophile **2p** by the catalyst.

These structures were optimized. Preliminary results suggested that both **8a** and **8b** were present in the reaction system. To our surprise, **8b** was favored over **8a** (ΔG = -1.5 kcal/mol) (Scheme S3). This result indicated that the thermodynamic properties of the key intermediates **8a** and **8b** could not account for the high stereoselectivity of the reaction.



Scheme S3. Equilibrium between the key reaction intermediates **8a** and **8b**.

Preliminary calculations on the **8a**/**8b** suggested that Friedel-Crafts alkylation of **2p** could happen on both intermediates. The transition states for the Friedel-Crafts reaction of **2p** with both **8a** and **8b** were then proposed and optimized (Figures S4 and S6). The structures of the

transition states were confirmed with the presence of single imaginary frequency, and were checked with IRC calculations (Figures S5 and S7).

Calculation results at this stage suggested that reaction between **8b** and **2p** was favored over the reaction between **8a** and **2p** and the diference for the energy of **9a** and **9b** ($\Delta\Delta G^{\neq}$ = 1.6 kcal/mol). It seemed at this stage that, both the kinetic and thermodynamic issues favored the reaction between **8b** and **2p**, and the product should be obtained with (*S*)-configuration rather than the experimentally observed (*R*)-configuration.

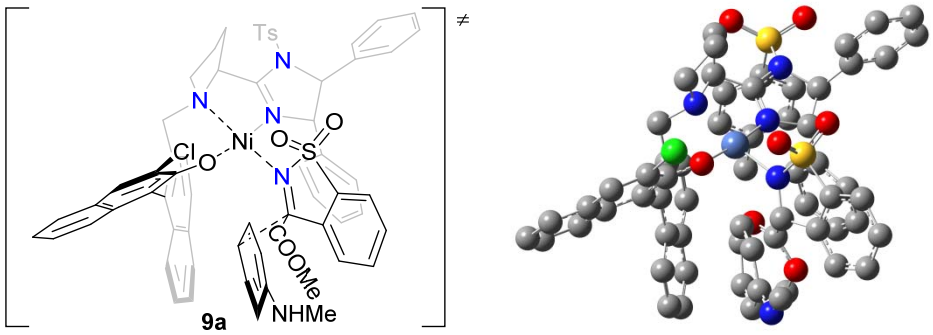


Figure 4. Optimized structure and model for transition state of *Si*-attack (**9a**).

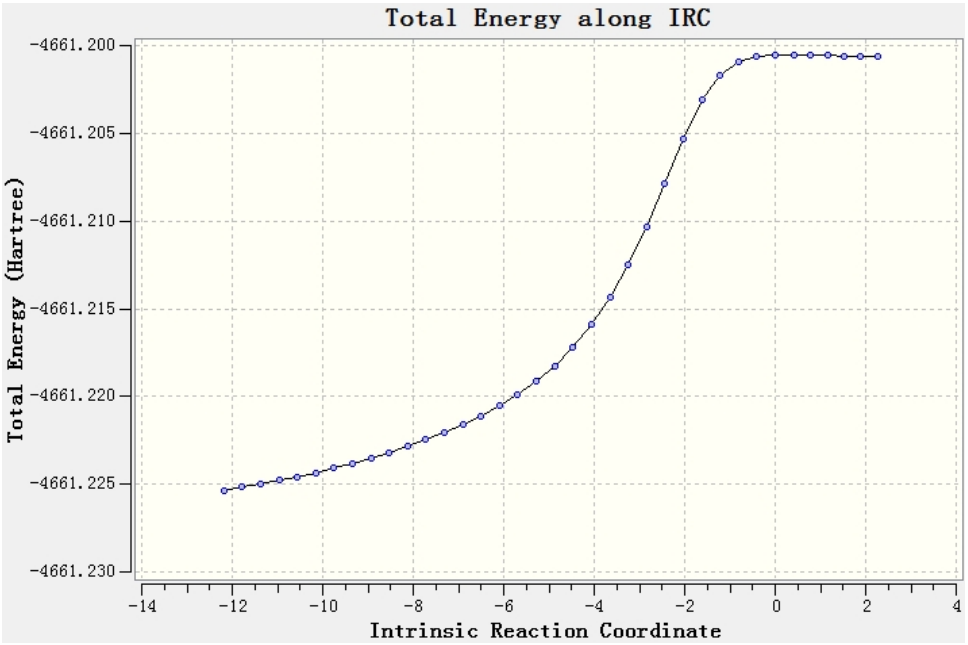


Figure S5. IRC check for transition state **9a**.

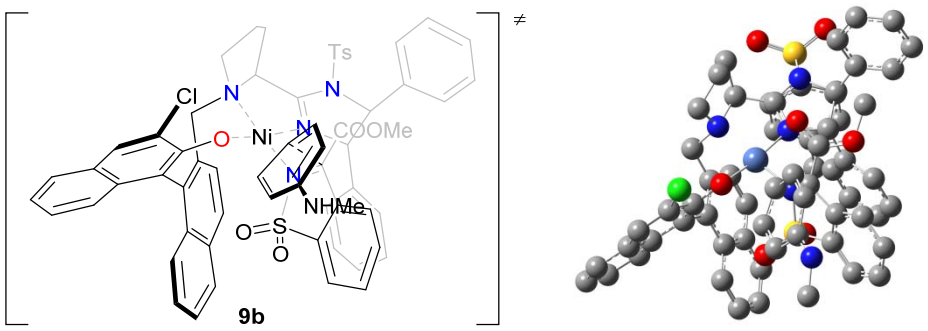


Figure S6. Optimized structure and model for transition state of *Re*-attack (**9b**).

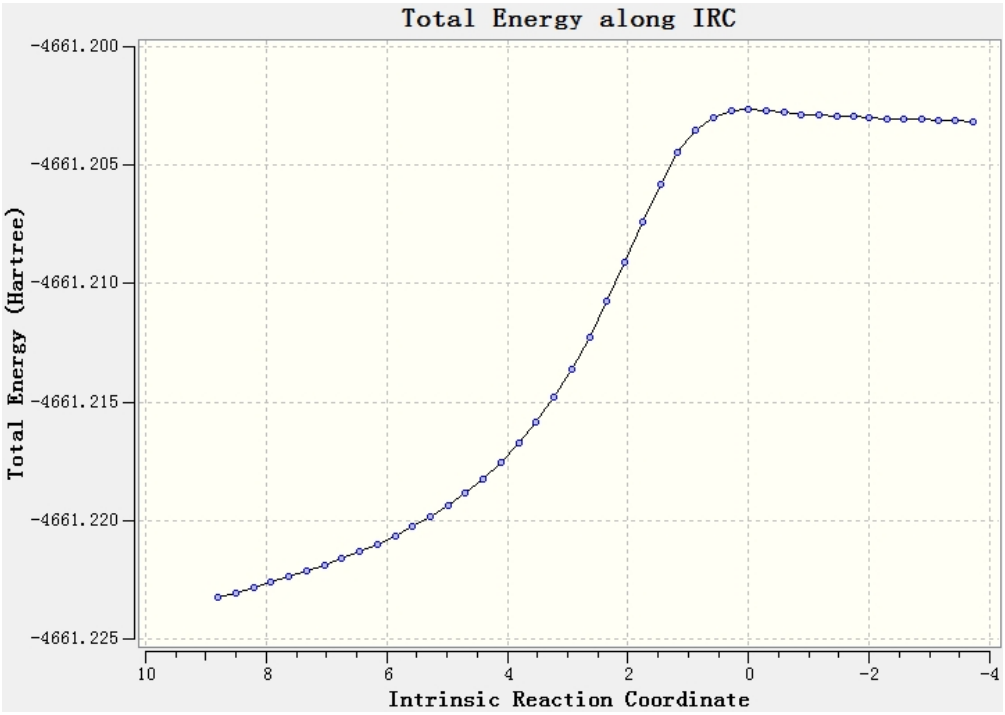


Figure S7. IRC check for transition state **9b**.

As the activation energy difference between the two transition state structures could not account for the high enantioselectivity of the reaction, it seemed to be necessary to investigate the reactions in details.

In general, a Friedel-Crafts reaction would involve the electrophilic attack of an electrophile on the aryl ring and temporarily open one of the C=C double bonds in the aryl ring to give the reaction intermediate. Next, aromatization of the intermediate via proton abstraction provided the corresponding aromatic electrophilic substitution product. In most reactions, electrophilic attack of the catalyst-controlled electrophile on the aryl ring was considered a rate determining step. Enantiofacial selection could be expected when the electrophile selectively interacted with the chiral catalyst with one of its prochiral faces.

However, in the current reaction between a relatively less reaction ketimine such as **1b** with relatively less reactive arylamine such as **2p**, the enantiofacial selection seemed not to be the only governing factor leading to the experimental results, and it was very necessary to establish the links between the activation of the electrophiles and the formation of the product. Further computation results showed that the energies of the Friedel-Crafts intermediates were very closed to the energies of the transition states, and were higher than the sums of energies of **8a** and **2p** (ΔG = 19.3 kcal/mol) or **8b** and **2p** (ΔG = 18.9 kcal/mol). These results suggested that the equilibria favored the starting materials **8** and **2p** rather than the Friedel-Crafts intermediates **10** (Figure S8) if no special measures were taken to shift the equilibria to the product side.

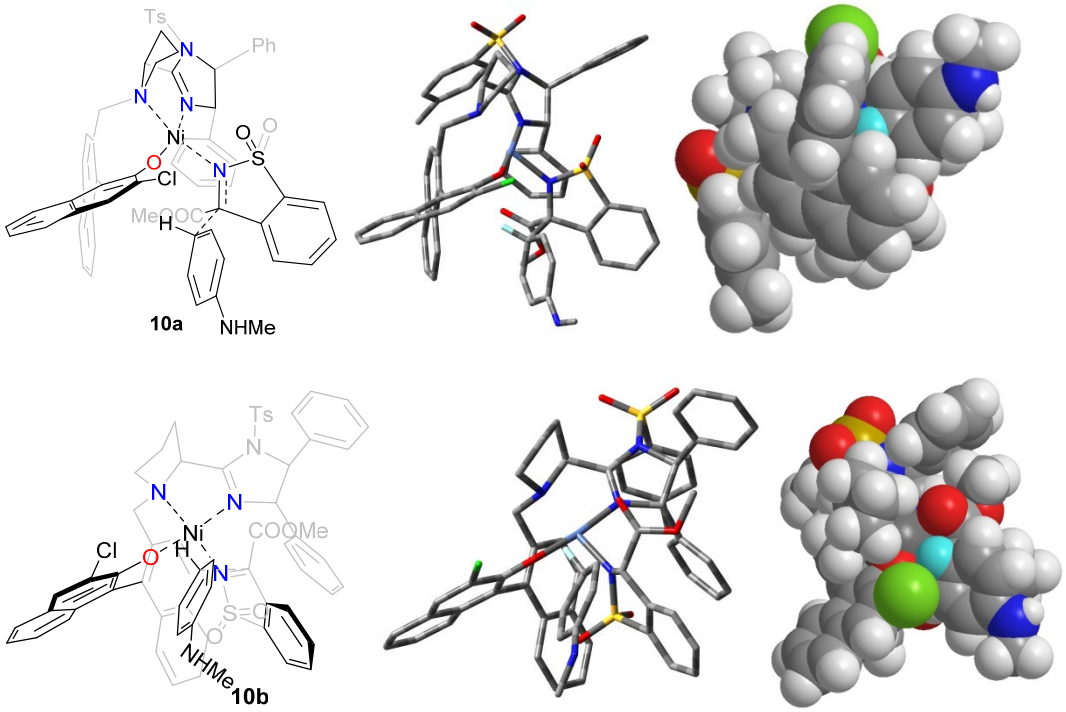


Figure S8. Structures and models for Friedel-Crafts intermediates. (a) **10a**: intermediate for *Si*-attack. (b) **10b**: intermediate for *Re*-attack.

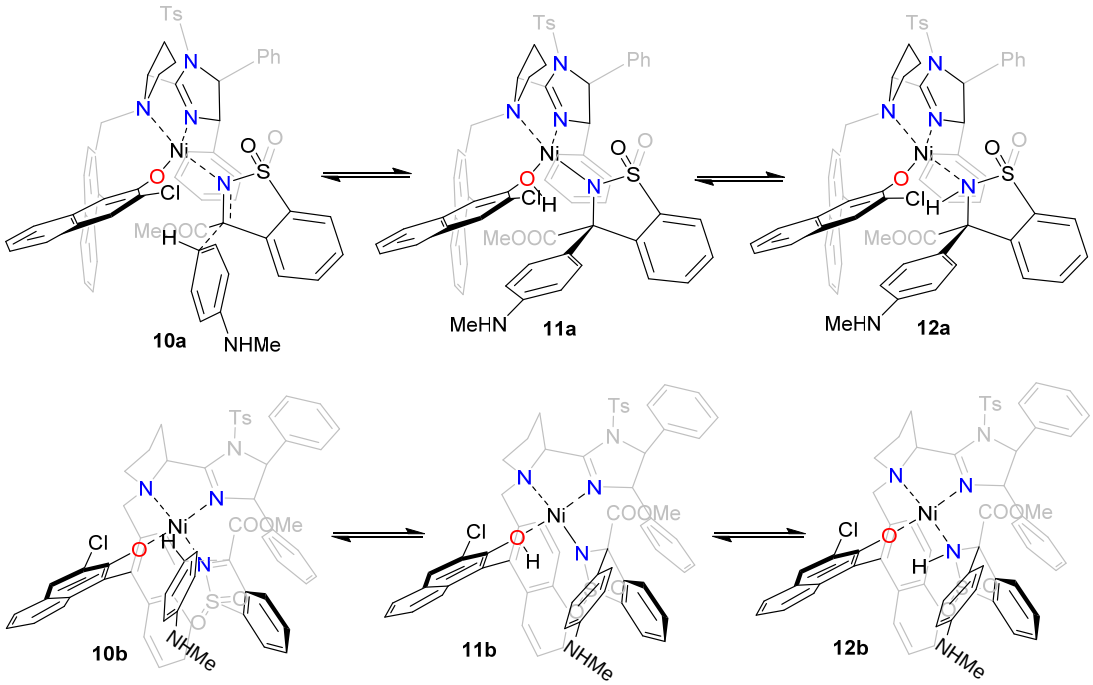
Carefully examining the space filling models of the Friedel-Crafts intermediates **10a** and **10b** suggested that the hydrogen atoms to be abstracted (colored in cyan) in these intermediates were hidden inside the cavities formed by the naphthyl ring, the arylamine ring and the chlorine atom in the chiral ligand. Especially in intermediate **10a**, the hydrogen atom was located deep inside the cavity. The information suggested that aromatization of the intermediates via proton abstraction in the presence of a base was difficult and was less

likely.[10] There must exist other possible ways for the aromatization of the intermediates and/or for the departure of the proton.

Direct departure of the Friedel-Crafts intermediates from the catalyst seemed to be unlikely. Potential energy scan results suggested that the intermediates may decompose to **1b** and **2p** upon increasing the distance between the Friedel-Crafts intermediate and the catalyst. This was also in good agreement with the results that the equilibrium favored the starting material rather than the Friedel-Crafts intermediate and that the reaction between **1b** and **2p** could not happen in the absence of a catalyst.

Different modes for proton departure were then proposed. Further potential energy scan results suggested that direct migration of the proton from the aminoaryl ring to the nitrogen atom seemed to be less likely for either intermediate **10a** or **10b** due to the high energy barriers.

A two-step formation of the product was then proposed. At first, the proton was temporarily transferred from the aminoaryl ring (**10a**/**10b**) to the naphtholate oxygen in the chiral ligand to give intermediates **11a** and **11b**, and another proton transfer from the naphthol group to the nitrogen atom gave intermediates **12a**/**12b** which were ready for the departure of the products and the coordination of another molecule of ketimine **1b** (Scheme S4).



Scheme S4. Possible proton transfers in intermediate **10**.

DFT calculations were carried out to test the feasibility of the proposed reaction pathways. At first, transition state TS-1 for conversion of **10a** to **11a** was optimized and the structure was checked with IRC calculations. Structure of intermediate **11a** was also optimized (Figure S9).

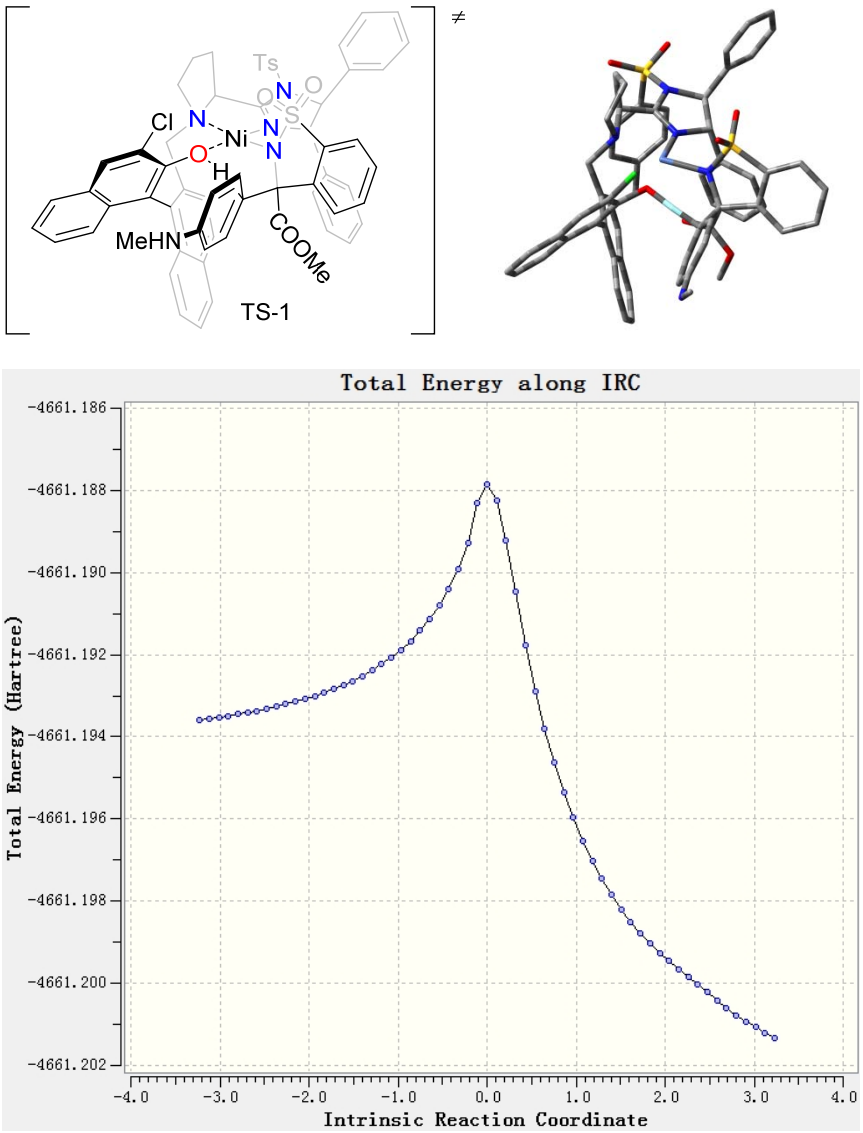
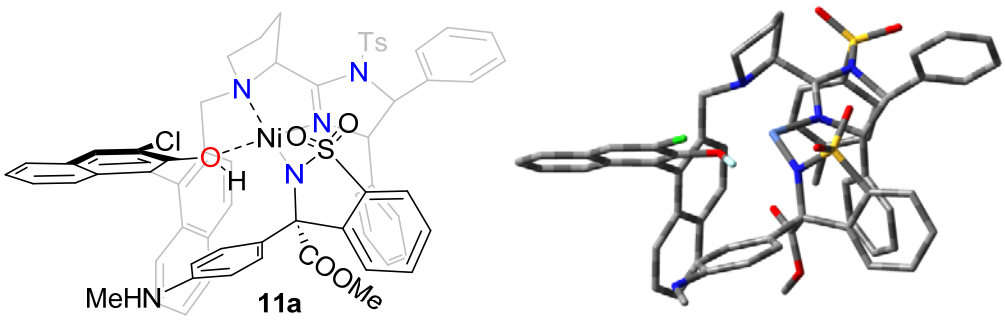
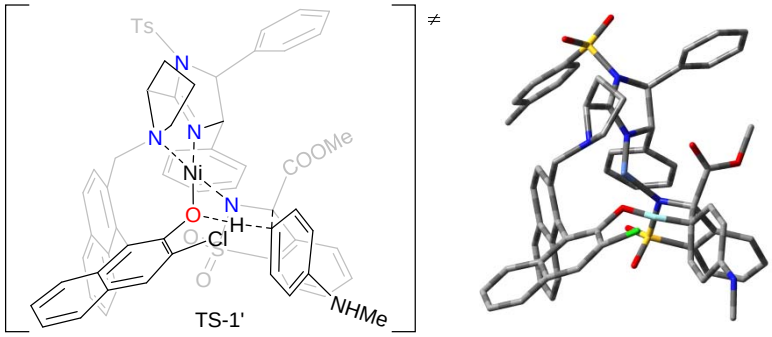


Figure S9. Transition state for proton transfer from aminoaryl ring in **10a** to naphtholate oxygen in the chiral ligand. (a) Optimized transition state **TS-1**. (b) Model for **TS-1**. (c) IRC result for **TS-1**.



Similarly, transition state TS-1' for conversion of **10b** to **11b** was optimized and the structure was checked with IRC calculations. Structure of intermediate **11b** was also optimized (Figure S10).



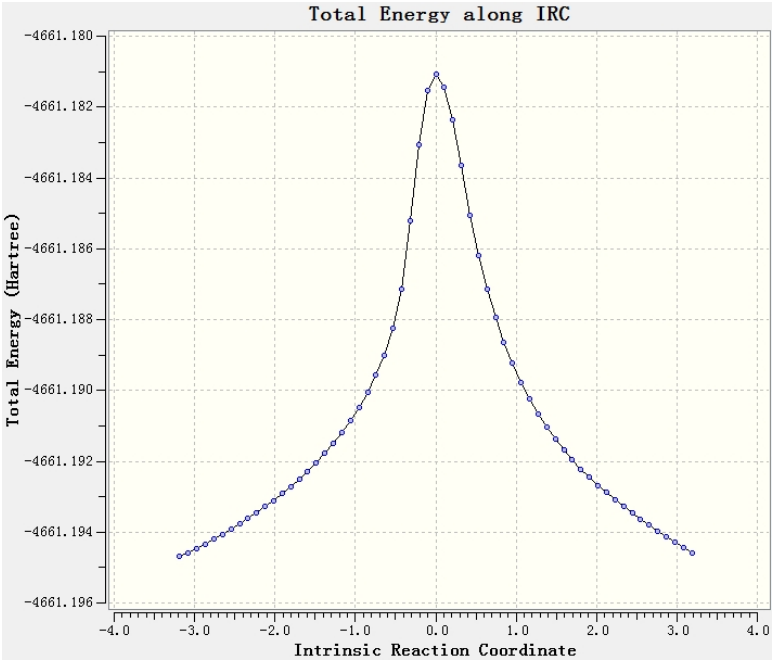
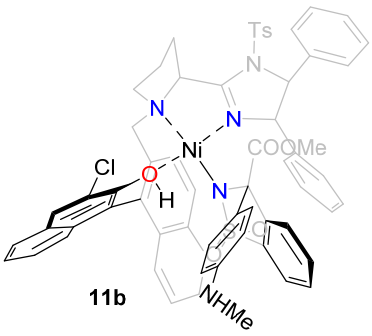
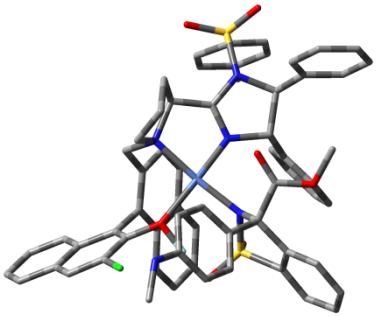


Figure S10. Transition state for proton transfer from aminoaryl ring in **10b** to naphthol oxygen in the chiral ligand. (a) Optimized transition state **TS-1'**. (b) Model for **TS-1'**. (c) IRC result for **TS-1'**.

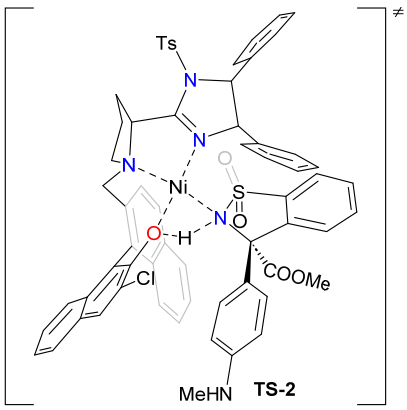


11b

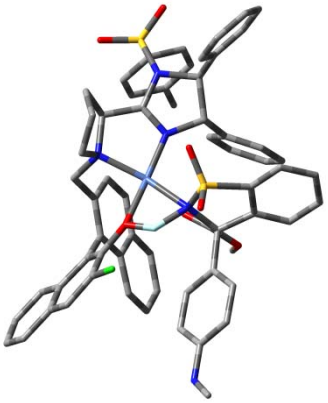


Proton migration processes from naphthol oxygen (**11a**/**11b**) to sulfonamide nitrogen (**12a**/**12b**) were also studied.

Transition state TS-2 for conversion of **11a** to **12a** was optimized and the structure was checked with IRC calculations (Figure S11). Structure of intermediate **12a** was also optimized .



TS-2



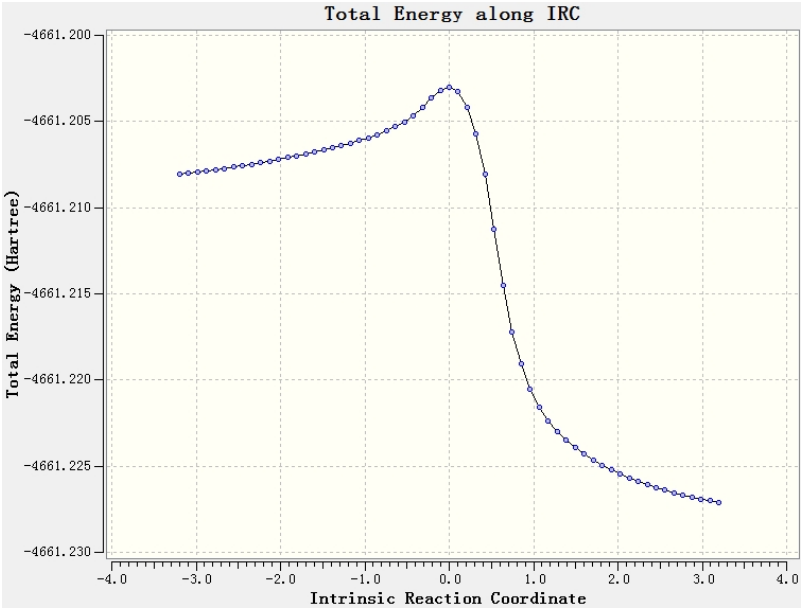
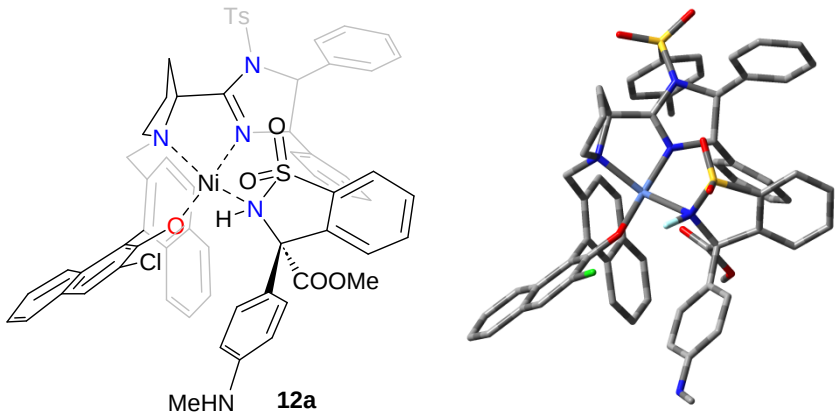
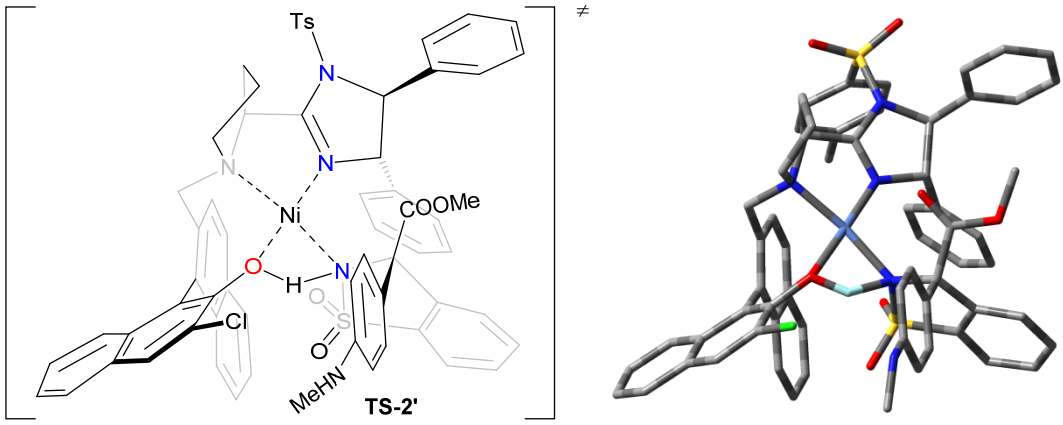


Figure S11. Transition state for proton transfer from naphthol oxygen in **11a** to sulfonamide nitrogen. (a) Optimized transition state **TS-2**. (b) Model for **TS-2**. (c) IRC result for **TS-2**.



Transition state **TS-2'**for reaction of **11b** to **12b** was optimized and the structure was checked with IRC calculations (Figure S12).. Structure of intermediate **12b** was also optimized.



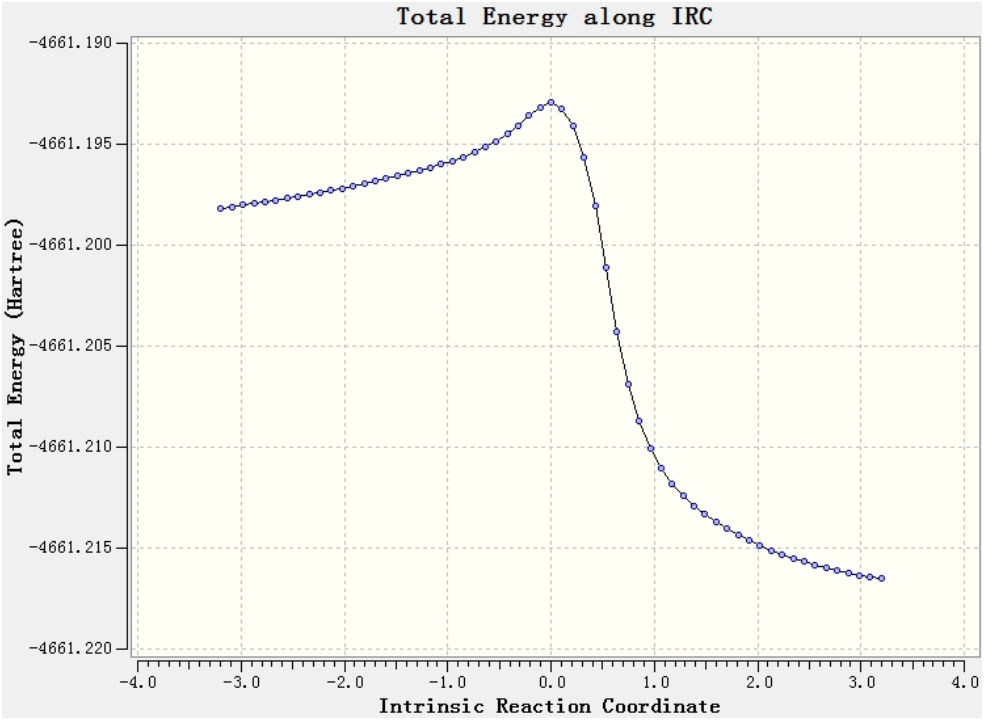
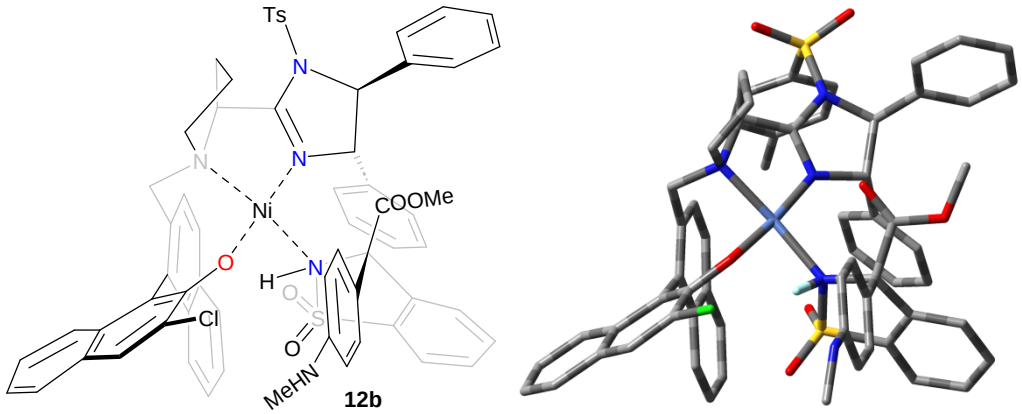


Figure S12. Transition state for proton transfer from naphthol oxygen in **11b** to sulfonamide nitrogen. (a) Optimized transition state **TS-2'**. (b) Model for **TS-2'**. (c) IRC result for **TS-2'**.



Based on these preliminary results, energy profiles for Friedel-Crafts alkylation of **2p** with **8** could be established (Table S2, Figure S13).

Table S2. Relative Energies for Intermediates and Transition States (ΔG, kcal/mol)

Intermediates/ Transition States	ΔG (kcal/mol)	Intermediates/ Transition States	ΔG (kcal/mol)
7a + 1a +2p	0	7a + 1a +2p	0
8a + 2p	-15.4	8b + 2p	-17.0
9a	4.2	9b	2.5
10a	3.9	10b	1.9

TS-1	10.5	TS-1'	14.6
11a	-2.9	11b	4.1
TS-2	1.0	TS-2'	7.2
12a	-17.4	12b	-7.0

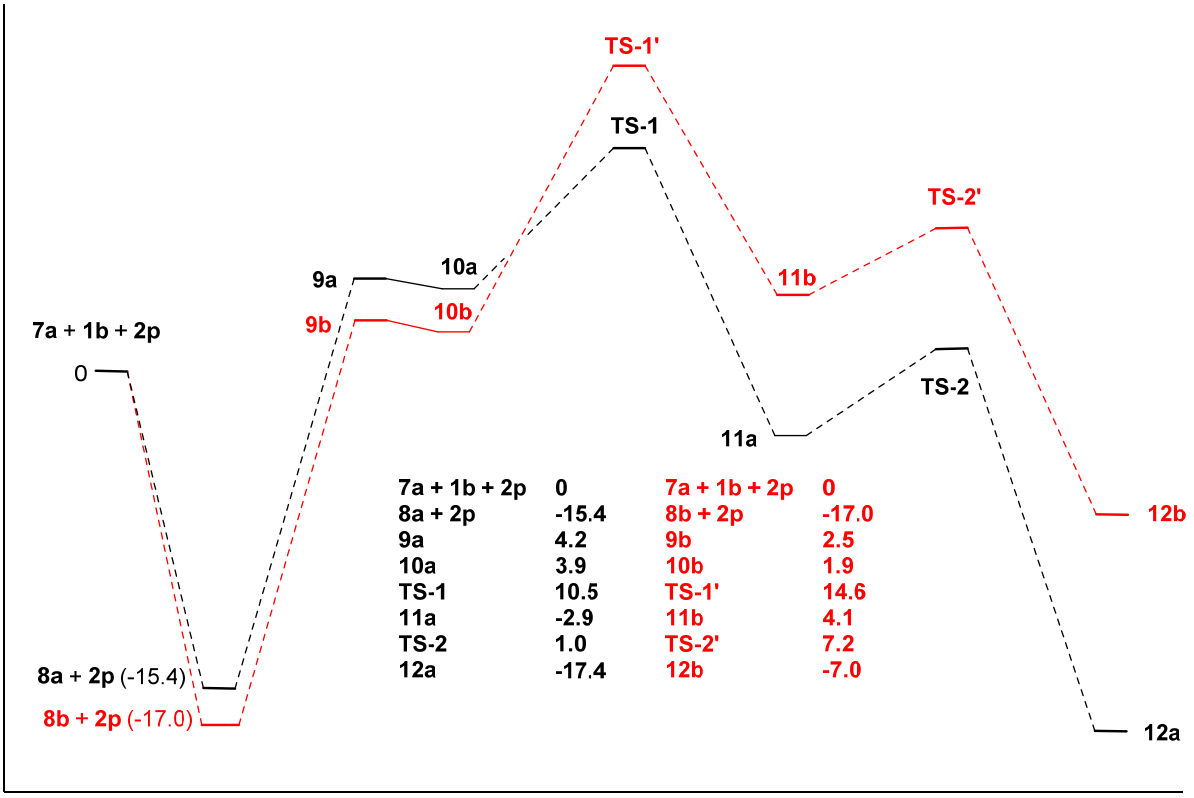
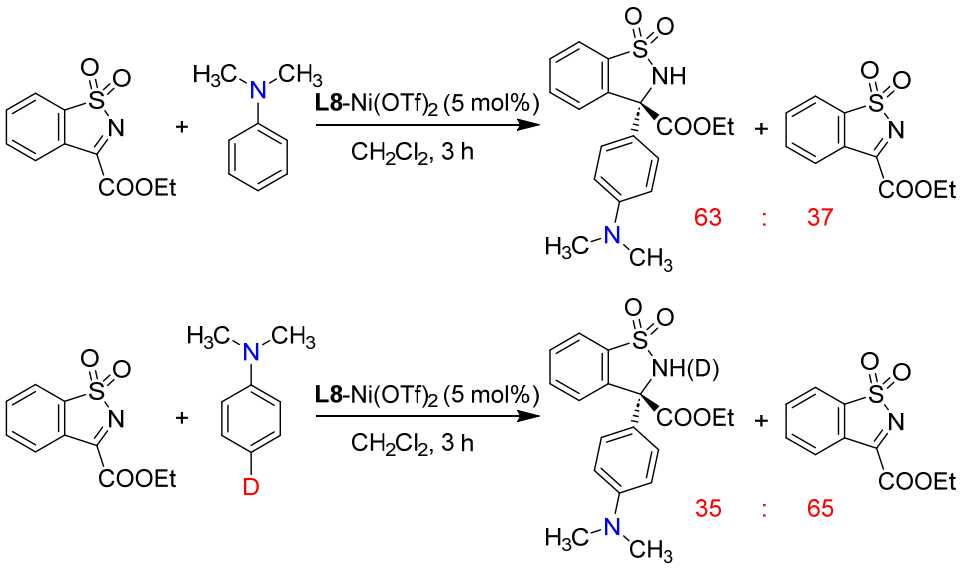


Figure S13. Energy profiles for nickel complex (**7b**)-catalyzed enantioselective Friedel-Crafts reaction of **2p** with **1b**.

The preliminary results suggested that the key factor governing the enantioselectivity of the reaction would be the aromatization of **10** in which the protons transfer from aminoaryl group in **10a** or **10b** to the naphtholate oxygen to form the aromatized intermediate **11a** or **11b**. While the process for transformation from **10a** to **11a** was possible at room temperature (the total activation energy is 25.9 kcal/mol), transformation from **10b** to **11b** proceeded relatively slowly due to a higher energy barrier (the total activation energy was 31.6 kcal/mol). The second proton transfer from the naphthol hydroxyl group to the sulfonamide nitrogen to give intermediate **12** was a fast step and was not rate-determining. In other word, the aromatization of the Friedel-Crafts intermediate **10** is the rate determining step of the reaction, and the formation of intermediate **11a** is a favored process over the formation of intermediate **11b**.

To test if this assumption was reasonable, control experiments were carried out using *N*,*N*-dimethylaniline and 4-deuterated N,N-dimethylaniline as the aromatic compounds and **1a** as the model electrophile.

The reactions were carried out side-by-side under identical optimized conditions, and were quenched after the reaction mixtures were stirred for 3 hours. NMR analysis of the crude products suggested the presence of isotope effect (Scheme S5).



Scheme S5. Isotope effect study using *N*,*N*-dimethylaniline and 4-deuterated *N*,*N*-dimethylaniline as the arylamines.

Further, deuterated product was detected in HRMS analysis although the relative abundance was low due to the possible proton exchange during the handling of the sample (Figure S14). This results suggested that it was reasonable to believe that the amide proton came from the para-hydrogen of the aromatic amine.

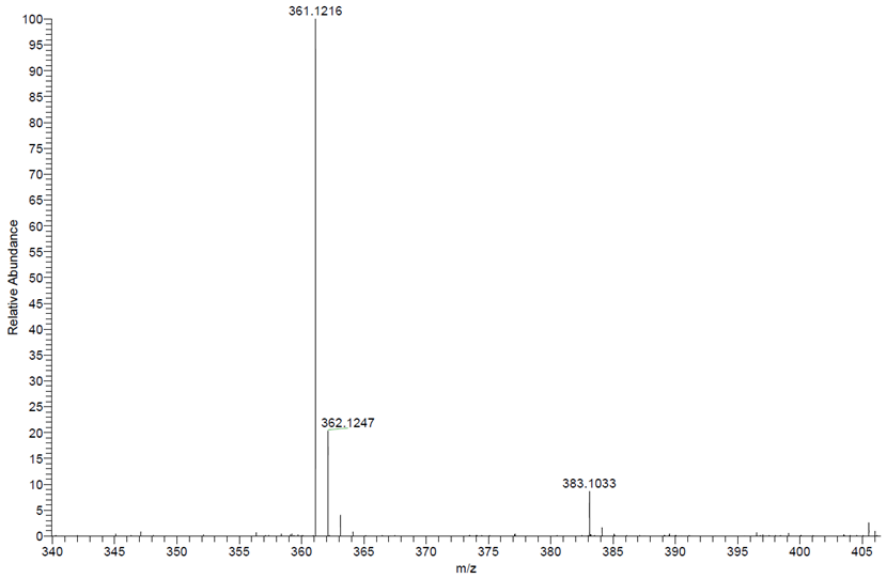
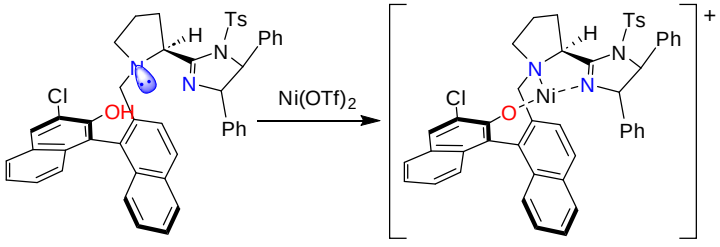
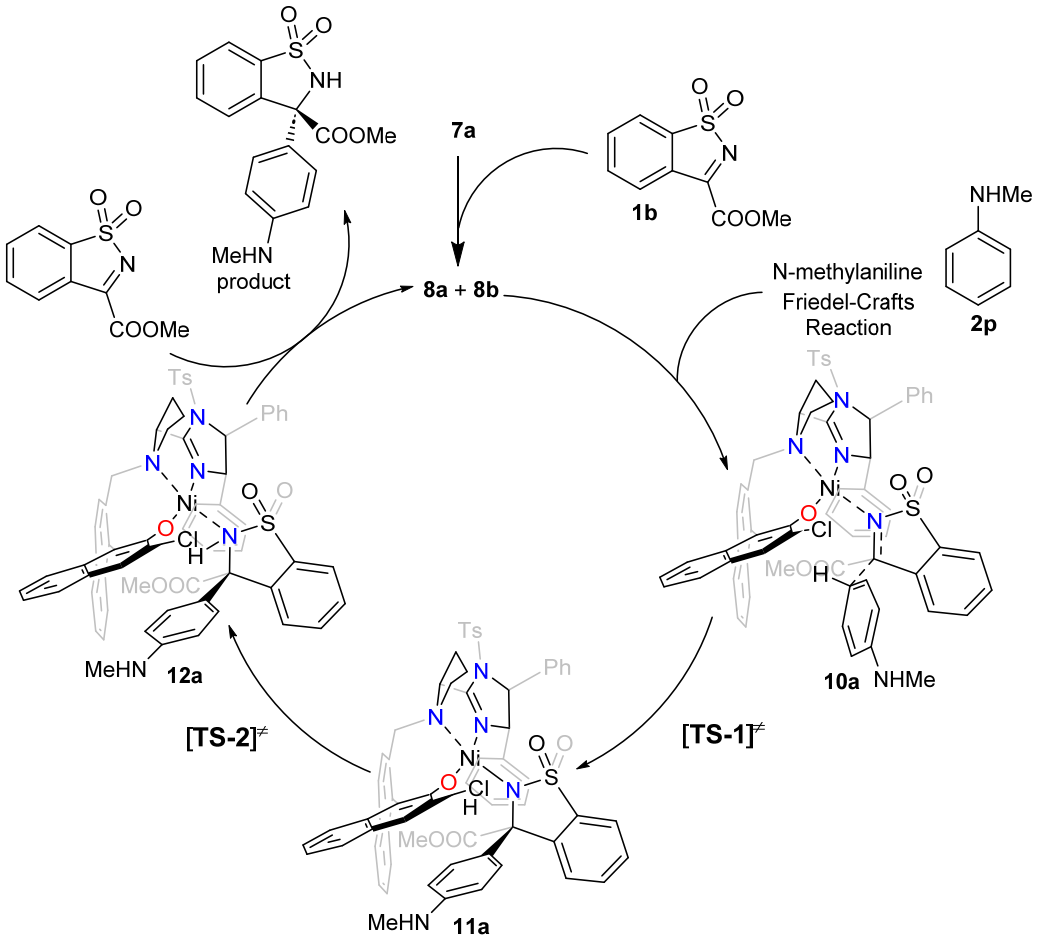


Figure S14. HRMS analysis of the reaction product between **1a** and 4-deuterated *N*,*N*-dimethylaniline.

On the basis of these findings, a tentative reaction mechanism was proposed and was shown in Scheme S6. Reaction between chiral ligand **L6**-N(*S*) and $Ni(OTf)_2$ provided complex **7a** as the catalyst of the reaction. Complexation of the electrophile **2b** to **7a** provided the intermediate **8a** or **8b** in which C=N double bond was activated upon coordination to the central metal. Electrophilic attack of **8a** or **8b** on **2p** via transition state **9a** or **9b** provided the key intermediates **10a** or **10b**. Proton transfer from the aminoaryl ring in **10a** to the naphtholate then occurred, providing intermediate **11a** which was transformed to intermediate **12a** via another proton transfer. Coordination of another molecule of **1b** released the (*R*)-product and provided another molecule of **8**, thus completing the catalytic circle. Formation of intermediate **10b** was kinetically favored. However, subsequent aromatization of this intermediate to **11b** was difficult due to the high energy barrier. Therefore, formation of the (*S*)-product was not the predominant path.



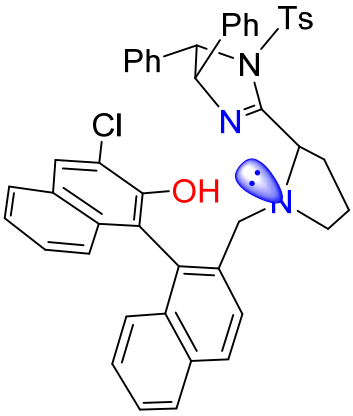
L6-N(*S*) [Ni-**L6**-N(*S*)]$^+$ (**7a**)



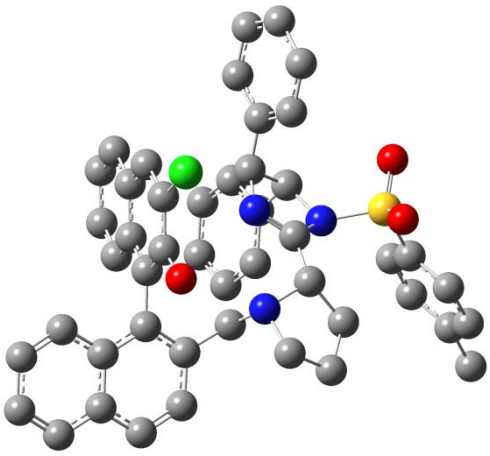
Scheme S6. Catalytic circle for **L8**-Ni(OTf)$_2$-catalyzed enantioselective Friedel-Crafts reaction of **2p** with **1b**.

5.2. Optimized Structures of Chiral Ligand L6

Structure of **L6**-N(*R*)



L6-N(*R*)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.225481	-0.823842	-1.624579
2	6	0	4.015266	-0.377283	-1.144343
3	6	0	3.524776	-0.806223	0.116254
4	6	0	4.327255	-1.715414	0.880191
5	6	0	5.567861	-2.155358	0.357472
6	6	0	6.010876	-1.721779	-0.869988
7	1	0	5.580883	-0.481049	-2.594906
8	1	0	3.419935	0.316921	-1.735457
9	6	0	2.269098	-0.363394	0.642631
10	6	0	3.860883	-2.148916	2.142818
11	1	0	6.164381	-2.847235	0.952079
12	1	0	6.965363	-2.068387	-1.262116
13	6	0	2.653253	-1.710506	2.626243
14	6	0	1.839775	-0.818968	1.885861
15	1	0	4.475744	-2.837189	2.722489
16	1	0	2.298068	-2.048155	3.600562
17	6	0	1.449835	0.600042	-0.147913
18	6	0	1.505963	2.001617	0.100342

19	6	0	0.632441	0.109696	-1.157426
20	6	0	2.255459	2.556826	1.169284
21	6	0	0.764862	2.895768	-0.738482
22	6	0	-0.104060	1.010958	-1.967991
23	6	0	2.269589	3.914933	1.397099
24	1	0	2.818083	1.890822	1.822753
25	6	0	0.817495	4.289383	-0.491493
26	6	0	-0.033006	2.366229	-1.778258
27	6	0	1.549870	4.793597	0.559097
28	1	0	2.842094	4.315269	2.232676
29	1	0	0.248702	4.951869	-1.144147
30	1	0	-0.616382	3.038499	-2.405062
31	1	0	1.570971	5.865357	0.750545
32	8	0	0.505318	-1.209095	-1.421674
33	6	0	0.520897	-0.384953	2.459572
34	1	0	0.395954	0.694169	2.317165
35	1	0	0.527206	-0.572125	3.550316
36	6	0	-0.651957	-2.480283	2.124384
37	6	0	-1.917191	-0.611608	2.350085
38	6	0	-1.204580	-2.579903	3.558278
39	1	0	0.338567	-2.930874	1.998118
40	1	0	-1.333345	-2.970202	1.415917
41	6	0	-2.021920	-1.288402	3.732688
42	1	0	-2.683227	-1.063322	1.700883
43	1	0	-1.814687	-3.479874	3.691419
44	1	0	-0.392213	-2.636095	4.292826
45	1	0	-3.062567	-1.487518	3.999436
46	1	0	-1.604135	-0.642972	4.517969
47	7	0	-0.614689	-1.048793	1.783471
48	1	0	0.910543	-1.699001	-0.681640
49	6	0	-2.092467	0.876228	2.265072
50	7	0	-1.590966	1.569322	1.316102
51	6	0	-2.350768	3.049033	3.036425

52	1	0	-3.222414	3.696984	3.164496
53	6	0	-1.897908	2.976166	1.540860
54	1	0	-0.971466	3.556241	1.437077
55	16	0	-4.306416	1.273666	3.830173
56	8	0	-4.757461	0.100495	3.085994
57	8	0	-5.069391	2.519474	3.787302
58	6	0	-4.078716	0.826392	5.530881
59	6	0	-4.560009	-0.393440	5.994936
60	6	0	-3.451719	1.730380	6.390592
61	6	0	-4.392788	-0.716061	7.338865
62	1	0	-5.053071	-1.082026	5.312187
63	6	0	-3.288752	1.388180	7.724132
64	6	0	-3.753288	0.160217	8.220603
65	1	0	-4.764192	-1.670719	7.708965
66	7	0	-2.726714	1.640250	3.294598
67	1	0	-3.087399	2.687357	6.019305
68	6	0	-3.561544	-0.194392	9.660977
69	1	0	-2.496227	-0.238515	9.921803
70	1	0	-4.011483	0.557493	10.321496
71	1	0	-4.006463	-1.165270	9.902397
72	1	0	-2.793200	2.085631	8.398694
73	17	0	-1.142557	0.358243	-3.209672
74	6	0	-2.903798	3.504211	0.546562
75	6	0	-2.913714	4.870512	0.243893
76	6	0	-3.846739	2.671214	-0.061062
77	6	0	-3.855894	5.397474	-0.634527
78	1	0	-2.166121	5.522891	0.698949
79	6	0	-4.790087	3.197649	-0.941822
80	1	0	-3.832593	1.600126	0.139734
81	6	0	-4.800374	4.560603	-1.228131
82	1	0	-3.849009	6.462379	-0.862143
83	1	0	-5.518130	2.536106	-1.408683
84	1	0	-5.536772	4.969637	-1.917876

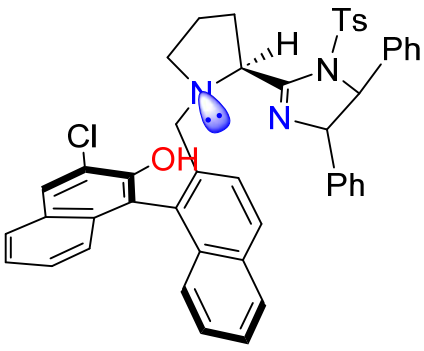
85	6	0	-1.218602	3.500420	3.928317
86	6	0	-0.914612	4.865694	3.983779
87	6	0	-0.412205	2.601840	4.630459
88	6	0	0.172269	5.321747	4.723267
89	1	0	-1.539843	5.575978	3.440532
90	6	0	0.679318	3.056738	5.368232
91	1	0	-0.651353	1.538664	4.607875
92	6	0	0.975817	4.416688	5.416654
93	1	0	0.392163	6.387601	4.760216
94	1	0	1.298173	2.342400	5.909621
95	1	0	1.827206	4.770982	5.995347

Number of imaginary frequency: 0

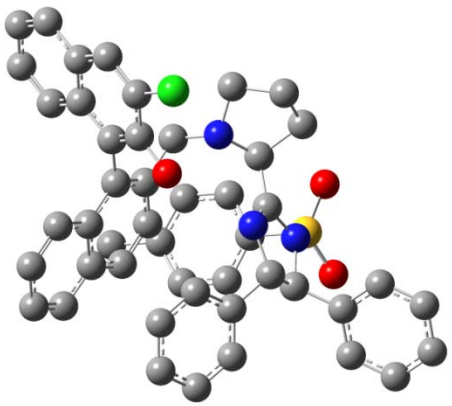
Energy:

Sum of electronic and zero-point Energies=	-3062.846131
Sum of electronic and thermal Energies=	-3062.801450
Sum of electronic and thermal Enthalpies=	-3062.800506
Sum of electronic and thermal Free Energies=	-3062.922790

Structure of **L6**-N(*S*)



L6-N(*S*)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.786908	13.467724	20.185868
2	1	0	2.025240	13.629023	22.176617
3	6	0	2.225045	12.972314	21.332704

4	6	0	3.061753	12.645456	19.060621
5	6	0	1.907307	11.598384	21.418904
6	8	0	3.646481	13.127267	17.943620
7	6	0	2.732960	11.297674	19.105077
8	6	0	1.340600	11.046028	22.593813
9	6	0	2.166431	10.750480	20.292363
10	6	0	2.973772	10.443552	17.908530
11	1	0	1.151039	11.707073	23.439154
12	6	0	1.036968	9.707033	22.667243
13	6	0	1.837814	9.374285	20.404869
14	6	0	4.267549	9.879649	17.690189
15	6	0	1.934875	10.162150	17.029909
16	1	0	0.604084	9.292281	23.575632
17	6	0	1.290072	8.867349	21.561071
18	1	0	2.029407	8.716636	19.558305
19	6	0	5.355337	10.117070	18.570135
20	6	0	4.484303	9.026838	16.559305
21	6	0	2.176704	9.338489	15.905126
22	6	0	0.546045	10.714507	17.252450
23	1	0	1.050206	7.807197	21.623723
24	1	0	5.203544	10.763624	19.433794
25	6	0	6.585469	9.538960	18.352154
26	6	0	5.761954	8.447151	16.364345
27	6	0	3.411883	8.787910	15.667084
28	1	0	1.346712	9.136882	15.226434
29	7	0	0.365401	12.067841	16.743358
30	1	0	-0.191463	10.024452	16.795110
31	1	0	0.327435	10.733768	18.327103
32	1	0	7.404725	9.732787	19.042867
33	6	0	6.793067	8.693545	17.240718
34	1	0	5.912199	7.804998	15.495818
35	1	0	3.582428	8.155611	14.794183
36	6	0	-0.449217	12.951538	17.571436

37	6	0	-0.133755	12.148173	15.370553
38	1	0	7.770501	8.241867	17.078949
39	1	0	0.095677	13.211682	18.489964
40	1	0	-1.410522	12.487025	17.874781
41	6	0	-0.695953	14.122576	16.644329
42	6	0	-1.023496	13.415891	15.332116
43	1	0	-0.748786	11.261713	15.140741
44	6	0	0.979971	12.224421	14.358876
45	1	0	0.225579	14.712502	16.547099
46	1	0	-1.498296	14.786151	16.983345
47	1	0	-0.847013	14.028718	14.441665
48	1	0	-2.076440	13.112805	15.311742
49	7	0	2.161470	12.632899	14.615208
50	7	0	0.733660	11.949530	12.988539
51	6	0	2.931230	12.649042	13.373742
52	16	0	-0.519939	10.980037	12.371069
53	6	0	2.034004	12.018469	12.266332
54	1	0	3.080932	13.710508	13.111039
55	8	0	-1.767444	11.517155	12.903641
56	8	0	-0.271597	10.919073	10.935834
57	6	0	-0.288835	9.350683	13.035570
58	1	0	2.373403	10.996518	12.035818
59	6	0	-1.143671	8.882837	14.032853
60	6	0	0.752860	8.555236	12.550944
61	1	0	-1.971283	9.500955	14.374760
62	6	0	-0.932627	7.615908	14.566526
63	6	0	0.950828	7.295943	13.101151
64	1	0	1.388637	8.910742	11.741617
65	6	0	0.123369	6.811221	14.124579
66	1	0	1.763384	6.671673	12.730624
67	1	0	3.763805	14.090659	18.024319
68	1	0	-1.600458	7.244853	15.343140
69	6	0	0.390427	5.478979	14.747154

70	1	0	0.734905	4.746471	14.008590
71	1	0	1.182676	5.560109	15.505107
72	1	0	-0.496440	5.076640	15.247999
73	17	0	3.171031	15.174234	20.064387
74	6	0	4.297230	12.024106	13.550526
75	6	0	4.928478	12.088105	14.797800
76	6	0	4.973311	11.422282	12.485327
77	6	0	6.205521	11.564278	14.972203
78	1	0	4.399104	12.530064	15.640009
79	6	0	6.248424	10.886874	12.663571
80	1	0	4.506319	11.370472	11.501057
81	6	0	6.869888	10.956862	13.907785
82	1	0	6.674567	11.612937	15.954804
83	1	0	6.755522	10.413931	11.823715
84	1	0	7.862997	10.532479	14.050651
85	6	0	1.971926	12.836545	11.004198
86	6	0	2.467114	12.328495	9.802583
87	6	0	1.454384	14.135240	11.028426
88	6	0	2.454509	13.104342	8.645154
89	1	0	2.855036	11.308768	9.775958
90	6	0	1.432309	14.909137	9.872253
91	1	0	1.056741	14.540182	11.959624
92	6	0	1.935840	14.396640	8.676856
93	1	0	2.843389	12.694270	7.714566
94	1	0	1.020991	15.916830	9.904616
95	1	0	1.920572	15.002625	7.772657

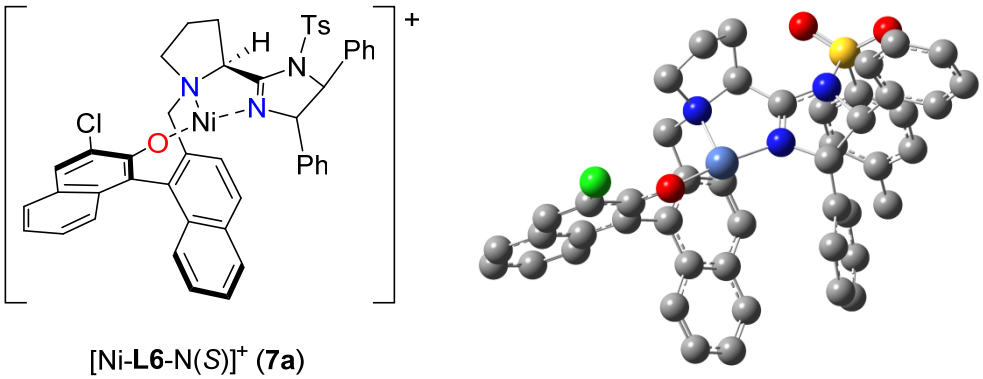
Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-3062.851690
Sum of electronic and thermal Energies=	-3062.806710
Sum of electronic and thermal Enthalpies=	-3062.805766
Sum of electronic and thermal Free Energies=	-3062.928402

5.3 Optimized Structures of the Catalyst, Transition States and the Reaction Intermediates

Optimized Structure of [**L6**-N(*S*)-Ni]$^+$ (**7a**)



[Ni-**L6**-N(*S*)]$^+$ (**7a**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.234124	13.635732	20.449426
2	1	0	2.029385	13.813048	22.566267
3	6	0	2.130112	13.138931	21.718302
4	6	0	2.393090	12.788939	19.302458
5	6	0	2.139570	11.739794	21.936313
6	8	0	2.526571	13.355774	18.123577
7	6	0	2.425264	11.399930	19.504416
8	6	0	2.004975	11.202579	23.237200
9	6	0	2.276643	10.857284	20.815121
10	6	0	2.592077	10.479050	18.347619
11	1	0	1.905155	11.891890	24.075092
12	6	0	1.996713	9.841183	23.441091
13	6	0	2.253825	9.459067	21.063657
14	6	0	3.834474	9.790654	18.172827
15	6	0	1.541729	10.229665	17.464692
16	1	0	1.890933	9.438337	24.446370
17	6	0	2.119124	8.966458	22.342037
18	1	0	2.340565	8.768935	20.226358
19	6	0	4.966568	10.060696	18.983636
20	6	0	3.956910	8.805202	17.140901

21	6	0	1.675384	9.241176	16.460101
22	6	0	0.272983	11.025852	17.550786
23	1	0	2.103903	7.890455	22.505795
24	1	0	4.891128	10.817463	19.762377
25	6	0	6.152204	9.389680	18.789453
26	6	0	5.185609	8.119603	16.980019
27	6	0	2.844553	8.540028	16.306426
28	1	0	0.821404	9.037731	15.812312
29	7	0	0.270742	12.198413	16.603072
30	1	0	-0.616729	10.421086	17.330061
31	1	0	0.146898	11.448752	18.551682
32	1	0	7.011957	9.620275	19.415693
33	6	0	6.263741	8.405675	17.784519
34	1	0	5.262276	7.367044	16.195231
35	1	0	2.939327	7.774773	15.534876
36	6	0	-0.587480	13.312119	17.134835
37	6	0	-0.289208	11.878053	15.217032
38	1	0	7.206220	7.878989	17.645123
39	1	0	-0.020025	13.872072	17.882805
40	1	0	-1.463075	12.858684	17.622425
41	6	0	-1.000637	14.074113	15.902686
42	6	0	-1.370711	12.943187	14.953613
43	1	0	-0.703577	10.863348	15.231481
44	6	0	0.833703	11.972677	14.241627
45	1	0	-0.157831	14.664333	15.515316
46	1	0	-1.833306	14.755598	16.096130
47	1	0	-1.404305	13.234665	13.900507
48	1	0	-2.350622	12.529465	15.214692
49	7	0	2.001725	12.346828	14.660082
50	7	0	0.746347	11.853446	12.879052
51	6	0	2.955978	12.439982	13.538607
52	16	0	-0.338834	10.824289	12.014886
53	6	0	2.069755	12.187394	12.277568

54	1	0	3.335299	13.469006	13.516987
55	8	0	-1.511587	10.711821	12.870159
56	8	0	-0.387345	11.395914	10.681178
57	1	0	2.439137	11.306767	11.736163
58	6	0	4.111545	11.488297	13.731888
59	6	0	5.327564	11.967981	14.225584
60	6	0	3.983493	10.125361	13.446534
61	6	0	6.403730	11.103807	14.416128
62	1	0	5.433981	13.030321	14.447556
63	6	0	5.063454	9.265072	13.617077
64	1	0	3.033617	9.728706	13.085566
65	6	0	6.276688	9.752956	14.100588
66	1	0	7.347279	11.490573	14.796097
67	1	0	4.955701	8.207157	13.376858
68	1	0	7.119069	9.077177	14.239180
69	6	0	1.993216	13.357131	11.337867
70	6	0	2.714024	13.325515	10.143240
71	6	0	1.252839	14.496635	11.665311
72	6	0	2.701722	14.423352	9.286076
73	1	0	3.287523	12.433961	9.886653
74	6	0	1.235206	15.590251	10.805981
75	1	0	0.680598	14.521298	12.593450
76	6	0	1.961385	15.556398	9.615528
77	1	0	3.265384	14.390053	8.355536
78	1	0	0.651050	16.471630	11.063984
79	1	0	1.946357	16.412590	8.943707
80	6	0	0.515837	9.286093	11.959269
81	6	0	0.360824	8.384389	13.014173
82	6	0	1.415460	9.041332	10.919611
83	6	0	1.131678	7.230987	13.026915
84	1	0	-0.363106	8.580894	13.803266
85	6	0	2.182147	7.882762	10.956740
86	1	0	1.510455	9.747826	10.096956

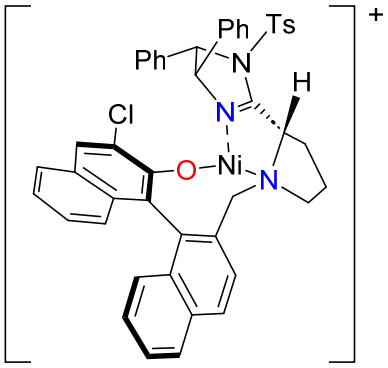
87	6	0	2.062160	6.967486	12.010072
88	1	0	1.011945	6.516637	13.840879
89	1	0	2.892333	7.687152	10.154921
90	6	0	2.892707	5.725638	12.048752
91	1	0	3.198222	5.478817	13.072487
92	1	0	2.325552	4.863335	11.673088
93	1	0	3.791640	5.818403	11.430469
94	17	0	2.201233	15.361037	20.188746
95	28	0	2.136423	12.773562	16.465156

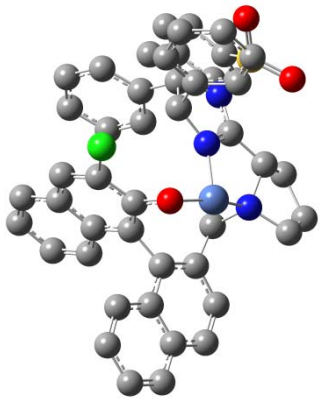
Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-3231.540254
Sum of electronic and thermal Energies=	-3231.494923
Sum of electronic and thermal Enthalpies=	-3231.493979
Sum of electronic and thermal Free Energies=	-3231.616390

Optimized Structure of [**L6**-N(*R*)-Ni]$^+$ (**7b**)





[Ni-**L6**-N(*R*)]$^+$ (**7b**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.624156	-0.244272	-2.115579
2	6	0	3.577003	0.165011	-1.320170
3	6	0	3.184444	-0.583904	-0.181432
4	6	0	3.919969	-1.773520	0.123038
5	6	0	4.994508	-2.165835	-0.710021

6	6	0	5.341593	-1.418584	-1.811720
7	1	0	4.898672	0.345849	-2.987721
8	1	0	3.037189	1.073709	-1.577415
9	6	0	2.085037	-0.182476	0.657331
10	6	0	3.575931	-2.515094	1.276341
11	1	0	5.540765	-3.074185	-0.458351
12	1	0	6.168592	-1.729296	-2.447246
13	6	0	2.512769	-2.135176	2.052989
14	6	0	1.727669	-0.993790	1.740469
15	1	0	4.170266	-3.388735	1.540435
16	1	0	2.268138	-2.701777	2.951061
17	6	0	1.558806	1.198881	0.399299
18	6	0	2.236188	2.296541	1.008587
19	6	0	0.589708	1.423541	-0.594772
20	6	0	3.196251	2.125642	2.041077
21	6	0	1.957256	3.631789	0.564624
22	6	0	0.390360	2.766182	-1.053303
23	6	0	3.826204	3.208948	2.611657
24	1	0	3.431839	1.121344	2.389652
25	6	0	2.618308	4.722893	1.174437
26	6	0	1.042541	3.833046	-0.496501
27	6	0	3.536559	4.519859	2.179890
28	1	0	4.556460	3.052026	3.403444
29	1	0	2.387818	5.729392	0.826019
30	1	0	0.859338	4.842155	-0.860937
31	1	0	4.037904	5.367219	2.643468
32	8	0	-0.138476	0.438580	-1.098598
33	6	0	0.528407	-0.732890	2.618815
34	1	0	0.262525	0.329979	2.655676
35	1	0	0.727327	-1.074681	3.642547
36	6	0	-0.587484	-2.934795	2.392644
37	6	0	-1.965658	-1.158002	2.764889
38	6	0	-0.940121	-2.980835	3.891338

39	1	0	0.395112	-3.333732	2.139921
40	1	0	-1.332928	-3.451113	1.779870
41	6	0	-1.747813	-1.688867	4.173979
42	1	0	-2.711334	-1.808967	2.281939
43	1	0	-1.524313	-3.877672	4.115851
44	1	0	-0.034763	-3.021290	4.506333
45	1	0	-2.692086	-1.893063	4.676641
46	1	0	-1.185893	-0.975266	4.788349
47	7	0	-0.674312	-1.486656	2.055519
48	6	0	-2.332198	0.217653	2.330620
49	7	0	-1.887180	0.569027	1.154647
50	6	0	-2.919599	2.437699	2.148701
51	1	0	-3.892579	2.929898	2.048112
52	6	0	-2.466272	1.863296	0.771176
53	1	0	-1.686765	2.508944	0.351124
54	16	0	-4.398072	1.006027	4.037017
55	8	0	-4.452196	-0.414697	4.342639
56	8	0	-5.514493	1.702553	3.417218
57	7	0	-3.080824	1.187021	2.933494
58	6	0	-1.921103	3.364158	2.800357
59	6	0	-1.956889	4.724666	2.479300
60	6	0	-0.959967	2.903031	3.703640
61	6	0	-1.046101	5.607914	3.051382
62	1	0	-2.712229	5.093391	1.784460
63	6	0	-0.051367	3.787576	4.280232
64	1	0	-0.938260	1.849607	3.982044
65	6	0	-0.092791	5.141835	3.955989
66	1	0	-1.087327	6.665541	2.797676
67	1	0	0.687544	3.415845	4.988708
68	1	0	0.617421	5.833425	4.405689
69	6	0	-3.598149	1.711900	-0.216451
70	6	0	-3.961824	2.818867	-0.990901
71	6	0	-4.341367	0.534263	-0.323420

72	6	0	-5.046677	2.749533	-1.858027
73	1	0	-3.382911	3.739629	-0.915141
74	6	0	-5.425965	0.463224	-1.196204
75	1	0	-4.073643	-0.337942	0.272029
76	6	0	-5.781469	1.569081	-1.963655
77	1	0	-5.315680	3.617325	-2.457365
78	1	0	-5.995405	-0.461345	-1.272639
79	1	0	-6.628551	1.512377	-2.644837
80	6	0	-3.820360	1.933194	5.415032
81	6	0	-3.995993	3.318292	5.412813
82	6	0	-3.105869	1.288063	6.423575
83	6	0	-3.422015	4.063577	6.432361
84	1	0	-4.568813	3.802855	4.624455
85	6	0	-2.547841	2.054322	7.438568
86	1	0	-2.999698	0.205383	6.415827
87	6	0	-2.680055	3.449311	7.451265
88	1	0	-3.547940	5.145420	6.439087
89	1	0	-1.996313	1.563121	8.238599
90	6	0	-2.014192	4.270791	8.506187
91	1	0	-1.770816	3.676321	9.392864
92	1	0	-1.072346	4.690874	8.125955
93	1	0	-2.635053	5.119355	8.814351
94	28	0	-0.620932	-0.583773	0.338588
95	17	0	-0.724620	3.017672	-2.368057

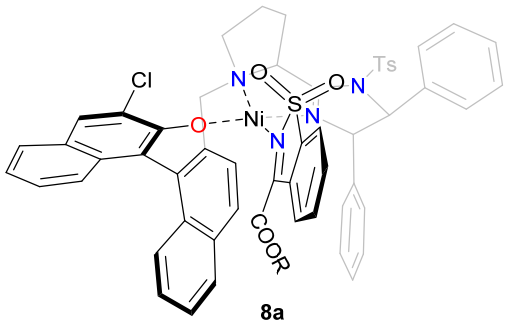
Number of imaginary frequency: 0

Energies:

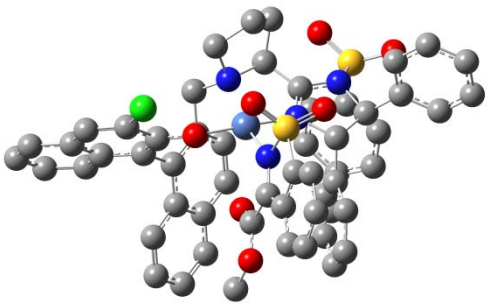
Sum of electronic and zero-point Energies=	-3231.506952
Sum of electronic and thermal Energies=	-3231.461777
Sum of electronic and thermal Enthalpies=	-3231.460833
Sum of electronic and thermal Free Energies=	-3231.583386

Optimized Structures of Key Intermediates **8**

Optimized Structure of **8a**



8a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.471564	13.382124	20.240459
2	1	0	2.343340	13.596279	22.358702
3	6	0	2.392364	12.906146	21.518568
4	6	0	2.560159	12.530869	19.080342
5	6	0	2.346389	11.512879	21.756271
6	8	0	2.694797	13.130427	17.924750
7	6	0	2.552035	11.139189	19.311349
8	6	0	2.214414	11.000270	23.068164
9	6	0	2.405435	10.620184	20.637650
10	6	0	2.575365	10.197245	18.163478
11	1	0	2.178529	11.706752	23.897584
12	6	0	2.121143	9.645753	23.292929
13	6	0	2.284321	9.230109	20.910157
14	6	0	3.659088	9.274735	17.986192
15	6	0	1.498037	10.152706	17.282499
16	1	0	2.016188	9.260492	24.305334
17	6	0	2.147800	8.759269	22.197393
18	1	0	2.290618	8.522370	20.084132
19	6	0	4.795353	9.262728	18.833326
20	6	0	3.611015	8.324159	16.916322
21	6	0	1.469207	9.204894	16.231695
22	6	0	0.339220	11.083920	17.451350

23	1	0	2.054844	7.687821	22.368299
24	1	0	4.863237	9.995168	19.635844
25	6	0	5.809282	8.347604	18.655542
26	6	0	4.672243	7.400907	16.753460
27	6	0	2.495129	8.316107	16.047389
28	1	0	0.597825	9.174001	15.577695
29	7	0	0.371041	12.234290	16.488648
30	1	0	-0.623839	10.570438	17.320515
31	1	0	0.340719	11.520466	18.452847
32	1	0	6.669037	8.357284	19.323781
33	6	0	5.748787	7.403241	17.608858
34	1	0	4.612034	6.682032	15.935475
35	1	0	2.459765	7.584358	15.239383
36	6	0	-0.354226	13.422273	17.071269
37	6	0	-0.350387	11.920776	15.179862
38	1	0	6.554437	6.682520	17.479885
39	1	0	0.349517	13.998859	17.678778
40	1	0	-1.154885	13.042165	17.721653
41	6	0	-0.940442	14.135597	15.880368
42	6	0	-1.470117	12.970151	15.060039
43	1	0	-0.751945	10.903049	15.219616
44	6	0	0.634670	12.049927	14.074129
45	1	0	-0.161735	14.688979	15.334619
46	1	0	-1.720908	14.845266	16.168430
47	1	0	-1.693019	13.209727	14.016582
48	1	0	-2.383329	12.566875	15.512641
49	7	0	1.830396	12.481190	14.334109
50	7	0	0.369322	11.899239	12.737413
51	6	0	2.607007	12.627938	13.084732
52	16	0	-0.758384	10.774796	12.052289
53	6	0	1.592488	12.243867	11.960932
54	1	0	2.871926	13.685829	12.988307
55	8	0	-1.846061	10.691820	13.015904

56	8	0	-0.946840	11.254163	10.694640
57	1	0	1.952280	11.338201	11.453840
58	6	0	3.858407	11.795071	13.074420
59	6	0	5.104869	12.404424	12.919895
60	6	0	3.784183	10.403872	13.186672
61	6	0	6.267739	11.635084	12.896593
62	1	0	5.158099	13.491133	12.827511
63	6	0	4.941700	9.633099	13.151090
64	1	0	2.808316	9.924837	13.302436
65	6	0	6.186453	10.248141	13.010434
66	1	0	7.236888	12.119469	12.784531
67	1	0	4.875255	8.548661	13.235721
68	1	0	7.092580	9.645324	12.987241
69	6	0	1.350660	13.327221	10.949872
70	6	0	1.899420	13.208433	9.672360
71	6	0	0.623629	14.473673	11.283185
72	6	0	1.725427	14.223471	8.734578
73	1	0	2.463991	12.311853	9.413153
74	6	0	0.443038	15.483830	10.344157
75	1	0	0.194226	14.571181	12.281199
76	6	0	0.994401	15.361082	9.068412
77	1	0	2.154344	14.120476	7.739534
78	1	0	-0.130906	16.370296	10.607472
79	1	0	0.850793	16.151645	8.334237
80	6	0	0.127401	9.252174	12.014572
81	6	0	-0.023972	8.346284	13.067033
82	6	0	1.017399	9.004657	10.967182
83	6	0	0.749700	7.194547	13.075360
84	1	0	-0.756083	8.533495	13.850591
85	6	0	1.795549	7.853379	11.006343
86	1	0	1.086983	9.694057	10.127857
87	6	0	1.686921	6.940324	12.061882
88	1	0	0.627510	6.475620	13.884943

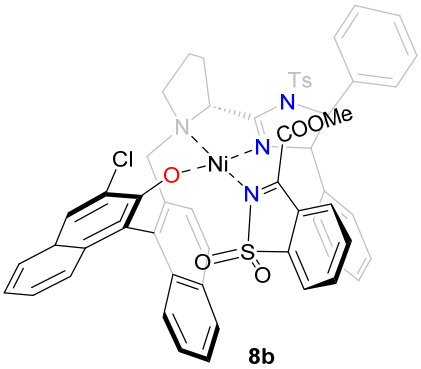
89	1	0	2.499360	7.656721	10.199117
90	6	0	2.540400	5.714526	12.113691
91	1	0	3.102567	5.663187	13.055682
92	1	0	1.932259	4.802306	12.065802
93	1	0	3.258788	5.684699	11.288279
94	17	0	2.481090	15.110422	19.978668
95	28	0	2.235309	12.819010	16.136412
96	6	0	5.905086	14.920032	15.480703
97	6	0	5.128154	16.058073	15.227357
98	6	0	5.659779	17.294862	14.927336
99	6	0	7.054667	17.389431	14.879298
100	6	0	7.853227	16.272682	15.119979
101	6	0	7.295550	15.029661	15.418095
102	6	0	5.052897	13.759715	15.750596
103	1	0	5.028183	18.158518	14.733960
104	1	0	7.516652	18.346717	14.650377
105	1	0	8.934893	16.368593	15.072728
106	1	0	7.931718	14.170614	15.598944
107	16	0	3.414865	15.629903	15.328834
108	8	0	2.767913	15.681336	14.023586
109	8	0	2.752209	16.206915	16.485505
110	6	0	5.481635	12.357295	16.079495
111	8	0	4.681923	11.457123	16.209819
112	8	0	6.800651	12.263603	16.205045
113	6	0	7.297625	10.946904	16.520471
114	1	0	6.822835	10.201775	15.876865
115	1	0	8.372315	10.993158	16.344272
116	1	0	7.086619	10.723153	17.569939
117	7	0	3.770242	13.949511	15.686154

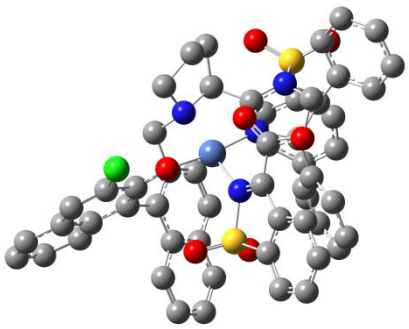
Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-4332.478286
Sum of electronic and thermal Energies=	-4332.419199
Sum of electronic and thermal Enthalpies=	-4332.418255
Sum of electronic and thermal Free Energies=	-4332.568530

Optimized Structure of **8b**





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.207376	13.507484	20.283853
2	1	0	2.263454	13.681965	22.409014
3	6	0	2.295194	13.010187	21.553348
4	6	0	2.246322	12.681153	19.107248
5	6	0	2.413192	11.616173	21.761722
6	8	0	2.122483	13.305816	17.962614
7	6	0	2.418727	11.298224	19.300014
8	6	0	2.468591	11.074415	23.067796
9	6	0	2.460429	10.750022	20.622069
10	6	0	2.525619	10.386346	18.131784
11	1	0	2.438479	11.761516	23.913607
12	6	0	2.552423	9.715667	23.268783
13	6	0	2.525030	9.352305	20.872275
14	6	0	3.728430	9.632046	17.917975
15	6	0	1.449662	10.201258	17.261644
16	1	0	2.594320	9.308645	24.277272
17	6	0	2.570052	8.852287	22.154808

18	1	0	2.531291	8.661661	20.031686
19	6	0	4.883321	9.796836	18.725395
20	6	0	3.790659	8.681387	16.848667
21	6	0	1.530151	9.253633	16.212956
22	6	0	0.193248	11.002158	17.426139
23	1	0	2.615866	7.775094	22.308040
24	1	0	4.869010	10.538373	19.520099
25	6	0	6.023140	9.061165	18.497929
26	6	0	4.978075	7.937387	16.640244
27	6	0	2.664910	8.511636	16.010745
28	1	0	0.661135	9.102890	15.571188
29	7	0	0.123332	12.147066	16.456337
30	1	0	-0.709546	10.390856	17.287717
31	1	0	0.145616	11.441251	18.425761
32	1	0	6.897388	9.213471	19.128789
33	6	0	6.073845	8.117501	17.449993
34	1	0	5.002611	7.219806	15.819336
35	1	0	2.711485	7.773329	15.209402
36	6	0	-0.710170	13.273820	17.014359
37	6	0	-0.530541	11.765199	15.136838
38	1	0	6.982252	7.541569	17.281259
39	1	0	-0.062403	13.921510	17.610893
40	1	0	-1.473439	12.831810	17.669826
41	6	0	-1.353461	13.909223	15.807388
42	6	0	-1.751435	12.689150	14.994758
43	1	0	-0.824649	10.710370	15.166139
44	6	0	0.463695	12.002658	14.056088
45	1	0	-0.628148	14.531089	15.264372
46	1	0	-2.205606	14.538166	16.079979
47	1	0	-1.982504	12.897697	13.947472
48	1	0	-2.622453	12.194819	15.439592
49	7	0	1.639779	12.467665	14.352229
50	7	0	0.211329	11.919800	12.710307

51	6	0	2.410283	12.719115	13.118370
52	16	0	-0.771116	10.717032	11.940175
53	6	0	1.363565	12.490568	11.978834
54	1	0	2.699341	13.776255	13.099882
55	8	0	-1.903585	10.521575	12.832450
56	8	0	-0.912630	11.214571	10.582958
57	1	0	1.752411	11.742589	11.274645
58	6	0	3.654684	11.885113	13.005359
59	6	0	4.878550	12.505330	12.747000
60	6	0	3.590460	10.491537	13.084718
61	6	0	6.033314	11.745229	12.582333
62	1	0	4.916749	13.594173	12.664314
63	6	0	4.742437	9.731266	12.908109
64	1	0	2.629771	10.005704	13.273604
65	6	0	5.964965	10.356372	12.664025
66	1	0	6.984988	12.239487	12.392162
67	1	0	4.690818	8.644183	12.959460
68	1	0	6.864770	9.757993	12.532749
69	6	0	1.010355	13.762617	11.249783
70	6	0	1.945539	14.296171	10.356065
71	6	0	-0.180694	14.451480	11.484998
72	6	0	1.687365	15.494965	9.698871
73	1	0	2.876940	13.760173	10.168025
74	6	0	-0.437993	15.652581	10.825245
75	1	0	-0.918850	14.037055	12.170720
76	6	0	0.493114	16.176660	9.931916
77	1	0	2.417135	15.894094	8.996796
78	1	0	-1.374220	16.176869	11.009173
79	1	0	0.287300	17.111220	9.413011
80	6	0	0.227942	9.267676	11.940126
81	6	0	0.100339	8.363048	12.997121
82	6	0	1.160992	9.070291	10.921028
83	6	0	0.936366	7.256988	13.035130

84	1	0	-0.657772	8.518296	13.762800
85	6	0	1.992435	7.958069	10.984433
86	1	0	1.226985	9.767940	10.088252
87	6	0	1.902847	7.042818	12.040204
88	1	0	0.837454	6.540624	13.850270
89	1	0	2.729787	7.797607	10.199482
90	6	0	2.812437	5.859197	12.113539
91	1	0	3.325520	5.809989	13.082981
92	1	0	2.252409	4.920682	12.011959
93	1	0	3.572869	5.882464	11.326413
94	17	0	2.040840	15.234554	20.052357
95	28	0	1.975979	12.801950	16.175492
96	6	0	5.469522	14.998812	15.250975
97	6	0	6.240771	13.998456	15.852819
98	6	0	7.619014	14.029129	15.900065
99	6	0	8.249239	15.129789	15.308914
100	6	0	7.503891	16.146820	14.714254
101	6	0	6.110930	16.098124	14.677588
102	6	0	4.046276	14.672660	15.320634
103	1	0	8.193103	13.236099	16.372824
104	1	0	9.334727	15.190003	15.319414
105	1	0	8.015586	16.994850	14.266301
106	1	0	5.544971	16.894734	14.205980
107	16	0	5.174894	12.763940	16.544432
108	8	0	5.119685	12.877332	17.992081
109	8	0	5.308453	11.473689	15.895829
110	6	0	2.918198	15.504093	14.779016
111	8	0	1.792493	15.451960	15.229867
112	8	0	3.315618	16.243054	13.749483
113	6	0	2.277446	17.034267	13.127001
114	1	0	1.884123	17.758097	13.845699
115	1	0	2.763370	17.539006	12.293063
116	1	0	1.472715	16.380778	12.775607

117	7	0	3.724827	13.550234	15.891408

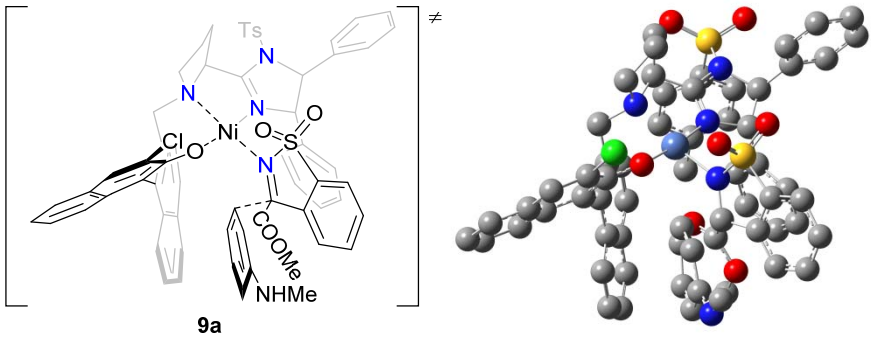
Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-4332.481336
Sum of electronic and thermal Energies=	-4332.422391
Sum of electronic and thermal Enthalpies=	-4332.421447
Sum of electronic and thermal Free Energies=	-4332.571015

Optimized transition states for Friedel-Crafts reaction of **2p**

Structure for transition state **9a**



9a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.156152	13.662224	20.175049
2	1	0	1.955059	13.957778	22.277493
3	6	0	2.117744	13.242156	21.473885
4	6	0	2.383947	12.775433	19.062095
5	6	0	2.263515	11.869936	21.781504
6	8	0	2.470133	13.329605	17.880751
7	6	0	2.545631	11.406789	19.361245
8	6	0	2.194445	11.415180	23.118544
9	6	0	2.451613	10.936947	20.710804
10	6	0	2.734073	10.437643	18.252172
11	1	0	2.056349	12.153859	23.908105
12	6	0	2.288314	10.074928	23.416188

13	6	0	2.518676	9.559760	21.057328
14	6	0	3.934898	9.662559	18.156147
15	6	0	1.721775	10.233321	17.316120
16	1	0	2.232898	9.733505	24.448081
17	6	0	2.441287	9.143911	22.368748
18	1	0	2.627040	8.816268	20.270384
19	6	0	5.036059	9.864998	19.026289
20	6	0	4.052150	8.653448	17.146809
21	6	0	1.871787	9.259040	16.300424
22	6	0	0.443779	11.011244	17.399929
23	1	0	2.493717	8.080238	22.596628
24	1	0	4.975143	10.646780	19.781815
25	6	0	6.173883	9.095090	18.929451
26	6	0	5.228879	7.869453	17.080148
27	6	0	2.996047	8.478031	16.222206
28	1	0	1.057692	9.121626	15.586374
29	7	0	0.397012	12.173818	16.449883
30	1	0	-0.427355	10.373665	17.195892
31	1	0	0.315889	11.423026	18.403819
32	1	0	7.004904	9.271351	19.611213
33	6	0	6.268927	8.076573	17.957046
34	1	0	5.298422	7.102773	16.307686
35	1	0	3.092822	7.715235	15.447989
36	6	0	-0.385998	13.314427	17.047874
37	6	0	-0.316101	11.839508	15.149696
38	1	0	7.169206	7.467289	17.896212
39	1	0	0.283255	13.911339	17.671587
40	1	0	-1.180308	12.887277	17.676886
41	6	0	-0.983658	14.024841	15.863013
42	6	0	-1.469793	12.853575	15.026624
43	1	0	-0.681389	10.806428	15.193439
44	6	0	0.660924	11.994577	14.041650
45	1	0	-0.213867	14.604917	15.332613

46	1	0	-1.786483	14.709118	16.151860
47	1	0	-1.689195	13.097002	13.983876
48	1	0	-2.374794	12.418591	15.465939
49	7	0	1.877846	12.375173	14.284498
50	7	0	0.337976	11.921908	12.706861
51	6	0	2.605814	12.567638	13.010592
52	16	0	-0.772090	10.791219	12.015779
53	6	0	1.529819	12.316555	11.905536
54	1	0	2.918275	13.614850	12.982928
55	8	0	-1.865196	10.681296	12.970900
56	8	0	-0.965620	11.267531	10.656901
57	1	0	1.833143	11.460764	11.287037
58	6	0	3.804745	11.678479	12.840011
59	6	0	5.038727	12.242334	12.514244
60	6	0	3.679564	10.286403	12.891809
61	6	0	6.131882	11.427899	12.223277
62	1	0	5.134396	13.328598	12.476631
63	6	0	4.770290	9.471977	12.606472
64	1	0	2.715169	9.840588	13.149722
65	6	0	5.996425	10.042026	12.260157
66	1	0	7.090592	11.878259	11.969725
67	1	0	4.668617	8.387635	12.649930
68	1	0	6.848460	9.404698	12.028559
69	6	0	1.247400	13.501173	11.026669
70	6	0	1.520155	13.441524	9.660028
71	6	0	0.737333	14.682287	11.574395
72	6	0	1.285713	14.548044	8.846322
73	1	0	1.914210	12.518616	9.232917
74	6	0	0.497760	15.785494	10.762541
75	1	0	0.535392	14.735492	12.644645
76	6	0	0.771729	15.720014	9.396132
77	1	0	1.499891	14.491832	7.780503
78	1	0	0.098049	16.700386	11.196343

79	1	0	0.582283	16.583905	8.761468
80	6	0	0.134078	9.281390	11.981003
81	6	0	0.127712	8.465389	13.114234
82	6	0	0.908019	8.967097	10.863409
83	6	0	0.912196	7.320940	13.120935
84	1	0	-0.491551	8.722253	13.972181
85	6	0	1.688936	7.817298	10.893130
86	1	0	0.891207	9.609260	9.984983
87	6	0	1.706445	6.980287	12.015280
88	1	0	0.908143	6.674264	13.997940
89	1	0	2.299255	7.563465	10.027834
90	6	0	2.545476	5.743609	12.038569
91	1	0	3.048381	5.617230	13.004936
92	1	0	1.928766	4.847900	11.886226
93	1	0	3.306310	5.755407	11.251221
94	17	0	1.906862	15.361156	19.831056
95	28	0	2.269184	12.805774	16.087815
96	6	0	6.145023	14.618313	15.569392
97	6	0	5.397641	15.732868	15.197900
98	6	0	5.959765	16.950976	14.847311
99	6	0	7.349367	17.046653	14.865838
100	6	0	8.123164	15.939818	15.217073
101	6	0	7.536479	14.724600	15.573155
102	6	0	5.256792	13.492741	16.036618
103	1	0	5.336946	17.798707	14.568293
104	1	0	7.831316	17.984333	14.597313
105	1	0	9.208288	16.021992	15.214466
106	1	0	8.157819	13.877084	15.842051
107	16	0	3.674528	15.359300	15.308880
108	8	0	3.004493	15.496186	14.006932
109	8	0	3.054228	16.122208	16.402631
110	6	0	5.609321	12.051994	15.717709
111	8	0	4.802016	11.153263	15.785506

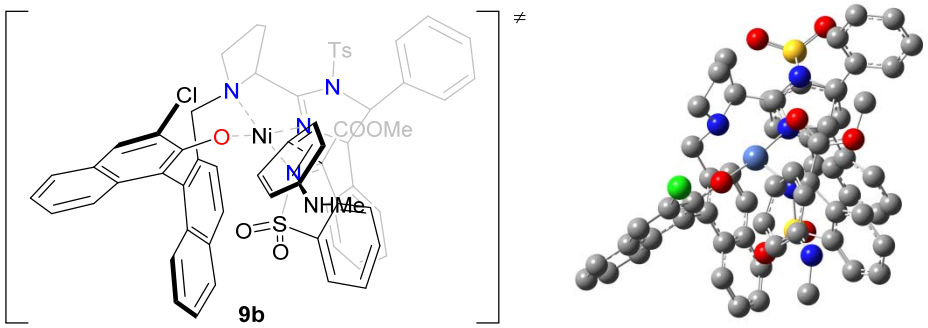
112	8	0	6.912572	11.897943	15.456689
113	6	0	7.367073	10.536585	15.378354
114	1	0	6.702477	9.941960	14.748255
115	1	0	8.368921	10.585682	14.949527
116	1	0	7.401262	10.105433	16.385318
117	7	0	3.926439	13.755257	15.653098
118	6	0	6.799121	12.984665	18.211155
119	6	0	5.098084	14.751967	18.311293
120	6	0	7.716252	13.832765	18.739604
121	1	0	7.073884	11.943797	18.043887
122	6	0	6.013120	15.618831	18.815317
123	1	0	4.068349	15.069472	18.166041
124	6	0	7.368264	15.199961	18.997902
125	1	0	8.724688	13.498352	18.978968
126	1	0	5.721331	16.628416	19.095515
127	7	0	8.303555	16.046617	19.415864
128	1	0	9.244964	15.686000	19.527107
129	6	0	8.097291	17.457930	19.665543
130	1	0	7.364831	17.611735	20.465600
131	1	0	9.048009	17.896260	19.969381
132	1	0	7.743574	17.961956	18.758431
133	6	0	5.459916	13.424192	17.838775
134	1	0	4.689862	12.664571	18.013977

Imaginary frequency: -106.5 cm^{-1}.

Energies:

Sum of electronic and zero-point Energies=	-4659.262738
Sum of electronic and thermal Energies=	-4659.196626
Sum of electronic and thermal Enthalpies=	-4659.195682
Sum of electronic and thermal Free Energies=	-4659.360039

Structure for transition state **9b**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.062330	13.698051	20.137697
2	1	0	2.002726	13.921220	22.258444
3	6	0	2.148596	13.239896	21.422122
4	6	0	2.250866	12.864573	18.978324
5	6	0	2.396950	11.871039	21.669189
6	8	0	2.155475	13.455485	17.814115
7	6	0	2.522698	11.501702	19.216554
8	6	0	2.456110	11.366956	22.990094
9	6	0	2.558056	10.988076	20.552586
10	6	0	2.701906	10.564795	18.077447
11	1	0	2.337902	12.069306	23.815501
12	6	0	2.647369	10.025584	23.228941
13	6	0	2.724618	9.605546	20.842009
14	6	0	3.946665	9.878770	17.885425
15	6	0	1.636971	10.286791	17.219750
16	1	0	2.690526	9.646774	24.248361
17	6	0	2.769682	9.141166	22.138000
18	1	0	2.812739	8.896489	20.021926
19	6	0	5.080194	10.119483	18.703202
20	6	0	4.070969	8.912611	16.836599
21	6	0	1.779512	9.328349	16.188589
22	6	0	0.320148	10.980310	17.396433

23	1	0	2.897343	8.074934	22.319686
24	1	0	5.012733	10.870000	19.486229
25	6	0	6.261572	9.445080	18.501094
26	6	0	5.300702	8.234129	16.651851
27	6	0	2.959714	8.656751	16.000273
28	1	0	0.923608	9.111141	15.547109
29	7	0	0.135754	12.119452	16.435425
30	1	0	-0.523941	10.287652	17.266465
31	1	0	0.244246	11.404654	18.400794
32	1	0	7.118995	9.655739	19.138262
33	6	0	6.377154	8.491822	17.467018
34	1	0	5.373939	7.502156	15.846831
35	1	0	3.055717	7.914481	15.206669
36	6	0	-0.736409	13.188158	17.036521
37	6	0	-0.562179	11.695503	15.156286
38	1	0	7.318798	7.966195	17.316277
39	1	0	-0.107546	13.859204	17.627871
40	1	0	-1.463174	12.699802	17.701746
41	6	0	-1.439656	13.810186	15.856010
42	6	0	-1.815958	12.580904	15.045992
43	1	0	-0.825960	10.632469	15.219395
44	6	0	0.375141	11.931216	14.025933
45	1	0	-0.751679	14.457725	15.294899
46	1	0	-2.305651	14.407004	16.156359
47	1	0	-2.076496	12.788554	14.005291
48	1	0	-2.662308	12.059084	15.506683
49	7	0	1.551545	12.431637	14.246218
50	7	0	0.043966	11.812137	12.695112
51	6	0	2.241660	12.675969	12.965333
52	16	0	-0.934408	10.557484	12.020776
53	6	0	1.156324	12.351835	11.882856
54	1	0	2.481128	13.743346	12.907980
55	8	0	-2.023898	10.364768	12.966675

56	8	0	-1.151873	10.990026	10.650676
57	1	0	1.537258	11.561717	11.221162
58	6	0	3.506707	11.885500	12.792881
59	6	0	4.668098	12.530289	12.365429
60	6	0	3.516288	10.501458	12.980062
61	6	0	5.829965	11.801137	12.127531
62	1	0	4.653918	13.612290	12.216815
63	6	0	4.679061	9.773363	12.750504
64	1	0	2.606913	9.995886	13.314748
65	6	0	5.837102	10.421924	12.322533
66	1	0	6.732320	12.312079	11.794408
67	1	0	4.685463	8.694866	12.909791
68	1	0	6.745780	9.850383	12.140334
69	6	0	0.741565	13.547599	11.067408
70	6	0	1.555435	13.947637	10.002791
71	6	0	-0.388781	14.303378	11.386306
72	6	0	1.243420	15.088107	9.268014
73	1	0	2.435129	13.355872	9.747049
74	6	0	-0.699254	15.445228	10.650516
75	1	0	-1.036257	13.988842	12.204661
76	6	0	0.115742	15.841834	9.592224
77	1	0	1.878867	15.385062	8.435376
78	1	0	-1.585373	16.024420	10.904305
79	1	0	-0.131743	16.731054	9.015269
80	6	0	0.111995	9.139611	12.034569
81	6	0	0.098997	8.307759	13.156187
82	6	0	0.987217	8.912877	10.971250
83	6	0	0.982397	7.239138	13.208643
84	1	0	-0.606088	8.487144	13.966070
85	6	0	1.867936	7.840392	11.048789
86	1	0	0.971379	9.558731	10.095693
87	6	0	1.885388	6.993087	12.163400
88	1	0	0.974163	6.581266	14.077270

89	1	0	2.560424	7.657187	10.228492
90	6	0	2.835322	5.842000	12.238549
91	1	0	3.313341	5.778431	13.223898
92	1	0	2.311806	4.889107	12.084255
93	1	0	3.620059	5.913917	11.478772
94	17	0	1.682308	15.389996	19.874217
95	28	0	1.949237	12.884217	16.042836
96	6	0	5.307979	15.297510	15.075825
97	6	0	6.085327	14.201060	15.439456
98	6	0	7.467130	14.179375	15.336340
99	6	0	8.092906	15.322222	14.840083
100	6	0	7.335921	16.433986	14.467882
101	6	0	5.944788	16.434585	14.579663
102	6	0	3.854150	15.061403	15.373121
103	1	0	8.039659	13.300660	15.626798
104	1	0	9.175703	15.343489	14.737746
105	1	0	7.835891	17.317378	14.075220
106	1	0	5.373899	17.304920	14.271438
107	16	0	5.043118	12.944998	16.128482
108	8	0	5.213327	12.965855	17.587478
109	8	0	5.168174	11.647640	15.471227
110	6	0	2.791769	15.582612	14.423871
111	8	0	1.600615	15.462143	14.634434
112	8	0	3.318792	16.175578	13.352374
113	6	0	2.360920	16.691354	12.405381
114	1	0	1.804415	17.521466	12.851234
115	1	0	2.950390	17.036191	11.556060
116	1	0	1.668118	15.900224	12.108021
117	7	0	3.642035	13.701585	15.616110
118	6	0	3.388969	17.512681	16.392595
119	6	0	4.400314	15.845765	17.872442
120	6	0	4.374081	18.394535	16.702512
121	1	0	2.570929	17.835201	15.748280

122	6	0	5.414086	16.705200	18.166785
123	1	0	4.344055	14.879028	18.363572
124	6	0	5.461654	17.989359	17.543703
125	1	0	4.363956	19.412267	16.315619
126	1	0	6.172300	16.436827	18.898004
127	7	0	6.486851	18.817457	17.739438
128	1	0	6.447994	19.727872	17.294977
129	6	0	7.666191	18.504386	18.517239
130	1	0	8.135414	17.584399	18.149647
131	1	0	8.374593	19.327389	18.417898
132	1	0	7.421093	18.375671	19.578002
133	6	0	3.424060	16.132994	16.844215
134	1	0	2.449693	15.664014	17.006002

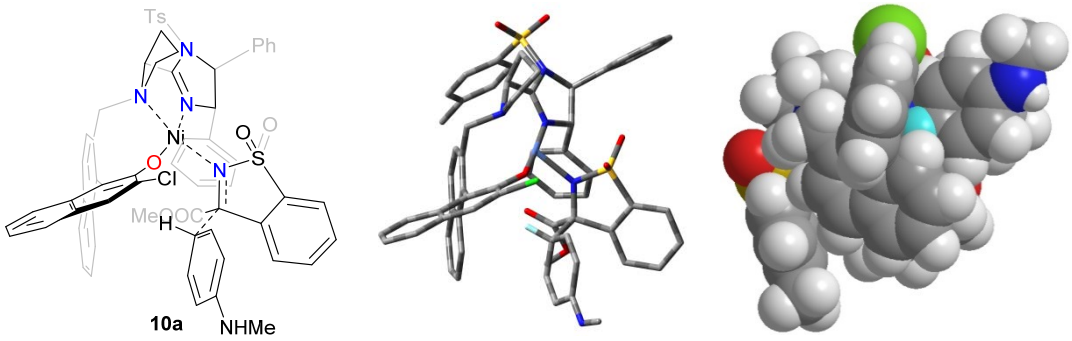
Imaginary frequency: -196.9 cm^{-1}.

Energies:

Sum of electronic and zero-point Energies=	-4659.266338
Sum of electronic and thermal Energies=	-4659.200123
Sum of electronic and thermal Enthalpies=	-4659.199179
Sum of electronic and thermal Free Energies=	-4659.362677

Optimized Structures for Intermediates **10a** and **10b**

Optimized Structures for Intermediate **10a**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	2.253626	13.784315	20.130999
2	1	0	2.107430	14.096459	22.235693
3	6	0	2.254761	13.375283	21.434002
4	6	0	2.455244	12.888829	19.020144
5	6	0	2.420772	12.006950	21.749098
6	8	0	2.497444	13.432861	17.832036
7	6	0	2.632018	11.523783	19.325501
8	6	0	2.393225	11.563318	23.091294
9	6	0	2.585977	11.065869	20.681571
10	6	0	2.779228	10.541249	18.221320
11	1	0	2.269638	12.307389	23.878242
12	6	0	2.506537	10.226537	23.397908
13	6	0	2.676316	9.692606	21.038045
14	6	0	3.981105	9.774473	18.081388
15	6	0	1.727838	10.316910	17.333077
16	1	0	2.481415	9.893996	24.433810
17	6	0	2.639636	9.287726	22.354805
18	1	0	2.770013	8.942900	20.255130
19	6	0	5.121227	10.002557	18.892822
20	6	0	4.064852	8.759253	17.074845
21	6	0	1.833689	9.317514	16.336444
22	6	0	0.464106	11.116272	17.432538
23	1	0	2.708058	8.226576	22.590164
24	1	0	5.080482	10.782581	19.651980
25	6	0	6.274104	9.268222	18.726522
26	6	0	5.257896	8.010178	16.938177
27	6	0	2.962118	8.548105	16.215367
28	1	0	0.986131	9.155705	15.668295
29	7	0	0.418560	12.256005	16.455793
30	1	0	-0.422518	10.489865	17.263399
31	1	0	0.367544	11.554479	18.428994
32	1	0	7.139298	9.471497	19.356529
33	6	0	6.344395	8.256158	17.745395

34	1	0	5.302805	7.241505	16.165864
35	1	0	3.029623	7.771329	15.452284
36	6	0	-0.348734	13.416490	17.033069
37	6	0	-0.307523	11.899846	15.171149
38	1	0	7.260308	7.679612	17.625133
39	1	0	0.327214	14.013620	17.649132
40	1	0	-1.151739	13.011318	17.666005
41	6	0	-0.930422	14.116813	15.834098
42	6	0	-1.434566	12.940731	15.015521
43	1	0	-0.706136	10.881761	15.250996
44	6	0	0.666609	11.991856	14.053167
45	1	0	-0.148383	14.673532	15.296759
46	1	0	-1.721814	14.820288	16.108030
47	1	0	-1.635148	13.169864	13.965649
48	1	0	-2.355598	12.536790	15.450811
49	7	0	1.893418	12.356464	14.271683
50	7	0	0.326396	11.886321	12.724053
51	6	0	2.608749	12.498174	12.983835
52	16	0	-0.813860	10.758545	12.079901
53	6	0	1.514167	12.235238	11.898251
54	1	0	2.939158	13.538735	12.924315
55	8	0	-1.888636	10.684429	13.059155
56	8	0	-1.028210	11.209245	10.715289
57	1	0	1.797686	11.355773	11.304129
58	6	0	3.785805	11.581630	12.804179
59	6	0	4.997325	12.106461	12.350975
60	6	0	3.652257	10.196798	12.948199
61	6	0	6.057523	11.260809	12.030344
62	1	0	5.100580	13.186484	12.235842
63	6	0	4.713862	9.351859	12.641473
64	1	0	2.706629	9.778744	13.301211
65	6	0	5.915504	9.882001	12.169858
66	1	0	6.996832	11.680729	11.673678

67	1	0	4.607339	8.274311	12.768306
68	1	0	6.744240	9.220452	11.921727
69	6	0	1.251426	13.396957	10.983787
70	6	0	1.571575	13.305733	9.628823
71	6	0	0.728160	14.591729	11.486873
72	6	0	1.372806	14.395322	8.783488
73	1	0	1.974482	12.371453	9.236080
74	6	0	0.525348	15.678430	10.643495
75	1	0	0.489097	14.669847	12.547613
76	6	0	0.848529	15.582354	9.289678
77	1	0	1.623888	14.314648	7.727332
78	1	0	0.117538	16.604992	11.043526
79	1	0	0.689587	16.433582	8.629956
80	6	0	0.067585	9.233912	12.056090
81	6	0	0.063553	8.432466	13.199571
82	6	0	0.820564	8.892666	10.932093
83	6	0	0.829893	7.275750	13.210081
84	1	0	-0.540990	8.708931	14.061704
85	6	0	1.584825	7.732085	10.966258
86	1	0	0.800149	9.523434	10.045639
87	6	0	1.605370	6.909777	12.099280
88	1	0	0.826997	6.639742	14.094840
89	1	0	2.180272	7.458768	10.096562
90	6	0	2.427475	5.662006	12.128378
91	1	0	2.922772	5.529855	13.097853
92	1	0	1.799677	4.774665	11.972184
93	1	0	3.192934	5.663189	11.345352
94	17	0	1.980201	15.477485	19.777044
95	28	0	2.301711	12.859939	16.056277
96	6	0	6.163005	14.708230	15.480675
97	6	0	5.386356	15.759081	15.007754
98	6	0	5.918216	16.956324	14.546925
99	6	0	7.302637	17.095082	14.567307

100	6	0	8.104735	16.058257	15.049030
101	6	0	7.549058	14.866316	15.512046
102	6	0	5.314506	13.557936	15.997011
103	1	0	5.272991	17.753521	14.182319
104	1	0	7.759712	18.014367	14.207318
105	1	0	9.186131	16.178956	15.062041
106	1	0	8.194510	14.072440	15.876393
107	16	0	3.673104	15.356483	15.168345
108	8	0	2.958521	15.446628	13.883745
109	8	0	3.077521	16.175106	16.241311
110	6	0	5.713913	12.141214	15.581659
111	8	0	4.966206	11.198985	15.710407
112	8	0	6.990684	12.066288	15.186295
113	6	0	7.534407	10.742171	15.048680
114	1	0	6.781729	10.049539	14.669669
115	1	0	8.370144	10.829662	14.352845
116	1	0	7.896328	10.403873	16.026875
117	7	0	3.955953	13.785475	15.564885
118	6	0	6.788369	12.994127	18.083671
119	6	0	5.080392	14.774464	18.231339
120	6	0	7.588273	13.693413	18.917957
121	1	0	7.118273	12.013190	17.743515
122	6	0	5.881262	15.480225	19.062883
123	1	0	4.104870	15.168028	17.953753
124	6	0	7.173030	14.975193	19.418294
125	1	0	8.552521	13.301019	19.236682
126	1	0	5.550674	16.433054	19.468845
127	7	0	7.992023	15.658764	20.201617
128	1	0	8.893653	15.240367	20.408714
129	6	0	7.718830	16.958434	20.783194
130	1	0	6.846928	16.913705	21.444342
131	1	0	8.589214	17.260905	21.365195
132	1	0	7.535981	17.702614	20.001048

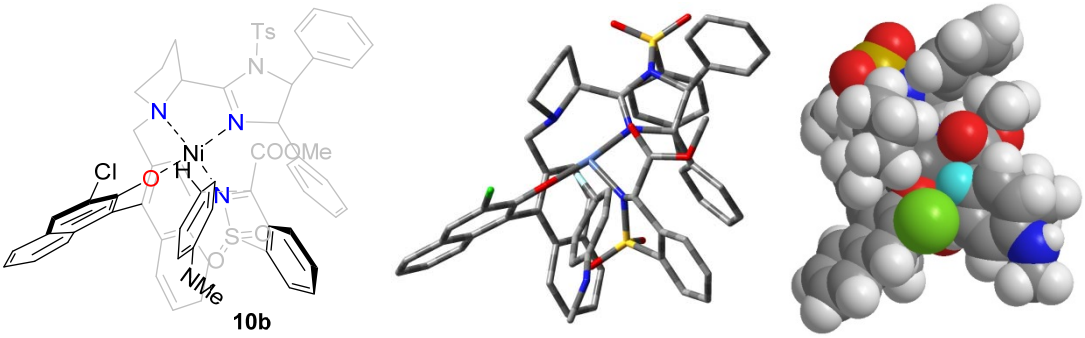
133	6	0	5.471188	13.486544	17.636530
134	1	0	4.707609	12.721109	17.864111

Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-4659.263071
Sum of electronic and thermal Energies=	-4659.196692
Sum of electronic and thermal Enthalpies=	-4659.195748
Sum of electronic and thermal Free Energies=	-4659.360464

Optimized Structures for Intermediate **10b**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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3	6	0	2.250843	13.287586	21.356596
4	6	0	2.349493	12.899390	18.915067
5	6	0	2.510780	11.921732	21.609138
6	8	0	2.254262	13.484628	17.748611
7	6	0	2.625296	11.538298	19.158166
8	6	0	2.577525	11.425728	22.932743
9	6	0	2.672289	11.032836	20.496792
10	6	0	2.782234	10.597049	18.019386
11	1	0	2.457455	12.132164	23.754374
12	6	0	2.777203	10.086970	23.178858
13	6	0	2.849058	9.653209	20.794068
14	6	0	4.019476	9.904694	17.805753

15	6	0	1.700495	10.324108	17.181296
16	1	0	2.825468	9.714351	24.200318
17	6	0	2.901711	9.197003	22.092689
18	1	0	2.939656	8.939409	19.978482
19	6	0	5.169850	10.145207	18.598965
20	6	0	4.118872	8.934356	16.757950
21	6	0	1.819123	9.362516	16.150353
22	6	0	0.392883	11.030560	17.373391
23	1	0	3.037217	8.132748	22.280217
24	1	0	5.120358	10.899356	19.380053
25	6	0	6.345592	9.468663	18.372939
26	6	0	5.342405	8.251832	16.549825
27	6	0	2.990692	8.681321	15.943955
28	1	0	0.951414	9.152172	15.522942
29	7	0	0.208101	12.167517	16.410506
30	1	0	-0.459255	10.345372	17.257735
31	1	0	0.334218	11.458950	18.377219
32	1	0	7.217431	9.680654	18.989767
33	6	0	6.437056	8.511786	17.339721
34	1	0	5.396857	7.516715	15.746215
35	1	0	3.068185	7.936628	15.150556
36	6	0	-0.641429	13.249694	17.018493
37	6	0	-0.514205	11.746324	15.145932
38	1	0	7.374577	7.984548	17.170115
39	1	0	0.003982	13.914271	17.599213
40	1	0	-1.367184	12.775082	17.694852
41	6	0	-1.350647	13.876792	15.844394
42	6	0	-1.757414	12.649148	15.047441
43	1	0	-0.793726	10.688085	15.219907
44	6	0	0.408612	11.961162	14.000257
45	1	0	-0.660210	14.510228	15.269721
46	1	0	-2.202570	14.489529	16.153022
47	1	0	-2.030542	12.853197	14.009182

48	1	0	-2.604181	12.142208	15.523932
49	7	0	1.595108	12.450342	14.193286
50	7	0	0.050110	11.831763	12.676926
51	6	0	2.262991	12.668173	12.895572
52	16	0	-0.960613	10.588307	12.032456
53	6	0	1.152221	12.348493	11.836948
54	1	0	2.520912	13.729710	12.826788
55	8	0	-2.033126	10.416386	13.001650
56	8	0	-1.201970	11.015158	10.664426
57	1	0	1.510053	11.545746	11.177550
58	6	0	3.504181	11.848253	12.688437
59	6	0	4.649724	12.452192	12.168887
60	6	0	3.494021	10.469667	12.911628
61	6	0	5.778172	11.688989	11.880880
62	1	0	4.650946	13.528862	11.984888
63	6	0	4.624045	9.707972	12.632415
64	1	0	2.596559	9.994880	13.316516
65	6	0	5.767526	10.316054	12.115600
66	1	0	6.667960	12.167960	11.474341
67	1	0	4.616238	8.633853	12.818571
68	1	0	6.649770	9.718051	11.893332
69	6	0	0.737628	13.537744	11.013639
70	6	0	1.525798	13.902057	9.917290
71	6	0	-0.363449	14.325349	11.357315
72	6	0	1.219990	15.041985	9.178817
73	1	0	2.382790	13.285488	9.643441
74	6	0	-0.668783	15.465191	10.616667
75	1	0	-0.993763	14.036918	12.198281
76	6	0	0.123256	15.828822	9.529291
77	1	0	1.836445	15.313344	8.323545
78	1	0	-1.532751	16.068762	10.889190
79	1	0	-0.119355	16.717522	8.949459
80	6	0	0.063290	9.153829	12.031429

81	6	0	0.063652	8.329374	13.158544
82	6	0	0.903780	8.901940	10.946146
83	6	0	0.927035	7.243916	13.195059
84	1	0	-0.614336	8.530072	13.986195
85	6	0	1.763894	7.811472	11.006962
86	1	0	0.876665	9.542070	10.066732
87	6	0	1.794643	6.971431	12.126479
88	1	0	0.929682	6.592637	14.068620
89	1	0	2.428057	7.607397	10.168420
90	6	0	2.725750	5.803944	12.186504
91	1	0	3.251591	5.758990	13.148539
92	1	0	2.179004	4.857097	12.085594
93	1	0	3.473618	5.840429	11.387937
94	17	0	1.759931	15.424943	19.794677
95	28	0	2.030784	12.913966	15.982299
96	6	0	5.386582	15.346121	14.997910
97	6	0	6.138893	14.200120	15.225309
98	6	0	7.503516	14.127449	14.984045
99	6	0	8.131344	15.267452	14.488341
100	6	0	7.397707	16.434241	14.262349
101	6	0	6.027184	16.485713	14.515247
102	6	0	3.924499	15.153884	15.360858
103	1	0	8.056991	13.208372	15.168422
104	1	0	9.197794	15.247600	14.273569
105	1	0	7.899739	17.316664	13.870108
106	1	0	5.469013	17.395713	14.308597
107	16	0	5.105071	12.952814	15.942406
108	8	0	5.379095	12.945148	17.391219
109	8	0	5.190556	11.654247	15.276214
110	6	0	2.902308	15.631369	14.323778
111	8	0	1.703491	15.581316	14.522137
112	8	0	3.465427	16.102035	13.211592
113	6	0	2.545015	16.576931	12.208505

114	1	0	2.002953	17.450852	12.583198
115	1	0	3.163860	16.845951	11.352325
116	1	0	1.835314	15.788976	11.945852
117	7	0	3.713393	13.731995	15.507405
118	6	0	3.510077	17.489094	16.359910
119	6	0	4.408002	15.726544	17.832156
120	6	0	4.326407	18.393030	16.942503
121	1	0	2.808390	17.827856	15.596915
122	6	0	5.243928	16.624074	18.408217
123	1	0	4.379693	14.703518	18.192605
124	6	0	5.257343	17.981740	17.958177
125	1	0	4.297710	19.444805	16.663188
126	1	0	5.881539	16.327577	19.237093
127	7	0	6.088981	18.877229	18.469334
128	1	0	6.030417	19.824907	18.109845
129	6	0	7.080154	18.619808	19.494925
130	1	0	7.799999	17.866710	19.157654
131	1	0	7.608982	19.550430	19.700715
132	1	0	6.603899	18.269050	20.416604
133	6	0	3.540364	16.052003	16.692866
134	1	0	2.523152	15.677751	16.891003

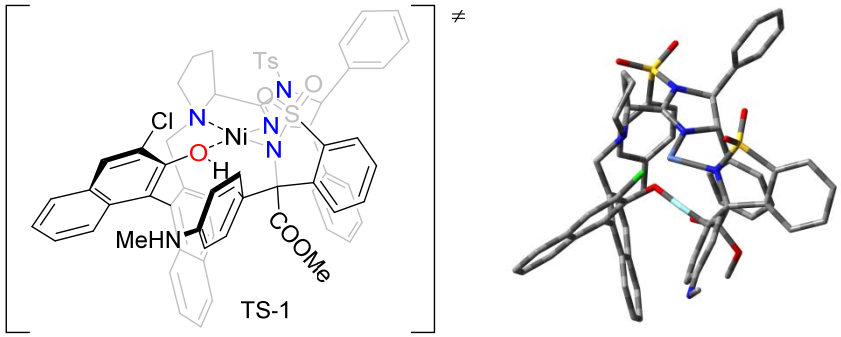
Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-4659.266427
Sum of electronic and thermal Energies=	-4659.199879
Sum of electronic and thermal Enthalpies=	-4659.198935
Sum of electronic and thermal Free Energies=	-4659.363650

Proton departure from Aminoaryl Ring to Naphtholate

TS-1



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4	6	0	2.785730	12.838042	18.964781
5	6	0	2.466227	12.057141	21.670302
6	8	0	3.013062	13.320433	17.726294
7	6	0	2.859172	11.483230	19.293976
8	6	0	2.309832	11.652068	23.017611
9	6	0	2.664773	11.071595	20.651253
10	6	0	3.068598	10.474523	18.222355
11	1	0	2.165276	12.420363	23.776158
12	6	0	2.334608	10.320136	23.359874
13	6	0	2.660138	9.706789	21.039397
14	6	0	4.262604	9.687511	18.182261
15	6	0	2.073792	10.260691	17.273282
16	1	0	2.215015	10.018803	24.398823
17	6	0	2.502836	9.342132	22.357720
18	1	0	2.782788	8.937146	20.280307
19	6	0	5.310901	9.847407	19.123848
20	6	0	4.415009	8.690049	17.166425
21	6	0	2.254011	9.288715	16.260941

22	6	0	0.766615	10.988257	17.369913
23	1	0	2.504708	8.287863	22.627962
24	1	0	5.218351	10.609055	19.895922
25	6	0	6.439662	9.059601	19.076464
26	6	0	5.585276	7.892704	17.146271
27	6	0	3.390249	8.523356	16.204902
28	1	0	1.454533	9.142046	15.532604
29	7	0	0.645283	12.189950	16.470062
30	1	0	-0.069306	10.313780	17.141155
31	1	0	0.614846	11.345661	18.391396
32	1	0	7.228501	9.201455	19.813753
33	6	0	6.578524	8.067208	18.083079
34	1	0	5.683831	7.135632	16.368076
35	1	0	3.515608	7.766355	15.429747
36	6	0	-0.070123	13.309754	17.181393
37	6	0	-0.190275	11.915510	15.228985
38	1	0	7.472024	7.446069	18.058717
39	1	0	0.647916	13.864296	17.792302
40	1	0	-0.830954	12.868931	17.841577
41	6	0	-0.724141	14.097677	16.076305
42	6	0	-1.299714	12.984399	15.214637
43	1	0	-0.606667	10.903540	15.284327
44	6	0	0.694109	12.046888	14.043460
45	1	0	0.025612	14.685641	15.526364
46	1	0	-1.486460	14.785832	16.452152
47	1	0	-1.558281	13.290386	14.196965
48	1	0	-2.201423	12.568958	15.678586
49	7	0	1.910424	12.471423	14.185759
50	7	0	0.291179	11.911825	12.738081
51	6	0	2.559084	12.622188	12.863605
52	16	0	-0.866216	10.770072	12.169668
53	6	0	1.424481	12.290300	11.843730
54	1	0	2.837835	13.674891	12.771915

55	8	0	-1.888451	10.706412	13.204956
56	8	0	-1.150728	11.199710	10.811510
57	1	0	1.707690	11.409298	11.250371
58	6	0	3.776803	11.758713	12.692044
59	6	0	5.014576	12.345841	12.427140
60	6	0	3.675649	10.365218	12.733544
61	6	0	6.137322	11.552583	12.198445
62	1	0	5.093211	13.433645	12.395281
63	6	0	4.792343	9.569948	12.496238
64	1	0	2.706772	9.901828	12.938986
65	6	0	6.025946	10.163577	12.225345
66	1	0	7.100584	12.022964	12.003867
67	1	0	4.701913	8.483929	12.521506
68	1	0	6.901025	9.542942	12.038336
69	6	0	1.055708	13.424105	10.930443
70	6	0	1.222670	13.299126	9.550991
71	6	0	0.564962	14.622294	11.458184
72	6	0	0.906736	14.360299	8.705287
73	1	0	1.599518	12.362026	9.139913
74	6	0	0.245070	15.680266	10.614553
75	1	0	0.447684	14.727432	12.536990
76	6	0	0.415789	15.550974	9.235692
77	1	0	1.038921	14.253883	7.630061
78	1	0	-0.136737	16.609850	11.032793
79	1	0	0.164912	16.380058	8.576334
80	6	0	0.031955	9.254284	12.122848
81	6	0	0.091843	8.463311	13.272025
82	6	0	0.750831	8.920149	10.973974
83	6	0	0.888846	7.326927	13.263636
84	1	0	-0.485299	8.730282	14.156198
85	6	0	1.548868	7.781840	10.990709
86	1	0	0.681664	9.540730	10.082913
87	6	0	1.634918	6.972144	12.129713

88	1	0	0.933298	6.698776	14.152815
89	1	0	2.118968	7.516041	10.101760
90	6	0	2.491584	5.747490	12.137344
91	1	0	3.000937	5.617465	13.099289
92	1	0	1.886783	4.844852	11.977239
93	1	0	3.247202	5.776845	11.345582
94	17	0	2.403565	15.471567	19.559994
95	28	0	2.436514	12.931534	15.926434
96	6	0	6.154861	14.788051	15.015550
97	6	0	5.369828	15.783846	14.440966
98	6	0	5.897274	16.842343	13.714148
99	6	0	7.280596	16.892783	13.560672
100	6	0	8.089140	15.919028	14.150783
101	6	0	7.540246	14.870951	14.889848
102	6	0	5.312872	13.779496	15.789571
103	1	0	5.249805	17.600129	13.276933
104	1	0	7.732595	17.699340	12.987235
105	1	0	9.169508	15.976923	14.033864
106	1	0	8.185574	14.128234	15.350583
107	16	0	3.668209	15.508228	14.856991
108	8	0	2.782402	15.570309	13.682240
109	8	0	3.283965	16.426439	15.948001
110	6	0	5.636642	12.301452	15.561200
111	8	0	4.802481	11.428590	15.667910
112	8	0	6.942783	12.084667	15.378607
113	6	0	7.348176	10.705979	15.418848
114	1	0	6.697615	10.087757	14.794991
115	1	0	8.372692	10.690277	15.044142
116	1	0	7.316155	10.348170	16.455241
117	7	0	3.940192	13.960751	15.299508
118	6	0	6.173355	13.033773	18.157052
119	6	0	5.609350	15.373262	17.815557
120	6	0	6.744433	13.339934	19.359114

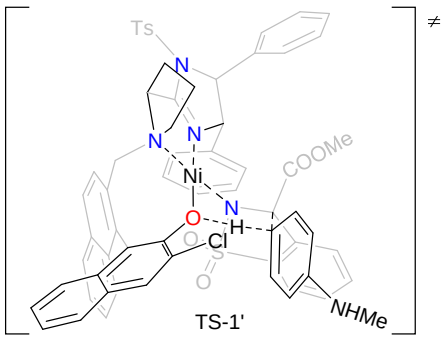
121	1	0	6.161833	11.988010	17.852197
122	6	0	6.183725	15.692915	19.014572
123	1	0	5.161789	16.167728	17.221616
124	6	0	6.769254	14.683373	19.826560
125	1	0	7.193752	12.559346	19.972443
126	1	0	6.201609	16.728049	19.346459
127	7	0	7.334956	14.971254	21.007416
128	1	0	7.749772	14.206888	21.525568
129	6	0	7.420231	16.294919	21.579758
130	1	0	6.425294	16.745098	21.680937
131	1	0	7.867176	16.214075	22.571453
132	1	0	8.043023	16.959663	20.967986
133	6	0	5.489593	14.015600	17.349176
134	1	0	4.238022	13.731984	17.637244

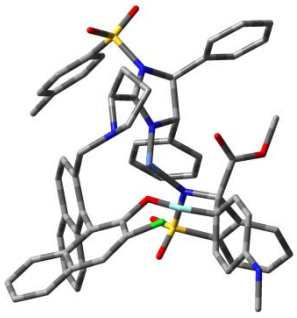
Imaginary frequency: -1527.7 cm^{-1}.

Energies:

Sum of electronic and zero-point Energies=	-4659.253403
Sum of electronic and thermal Energies=	-4659.187261
Sum of electronic and thermal Enthalpies=	-4659.186317
Sum of electronic and thermal Free Energies=	-4659.349944

TS-1'





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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2	1	0	2.590193	14.266219	22.047531
3	6	0	2.702015	13.570660	21.218474
4	6	0	2.706362	13.145140	18.802831
5	6	0	2.931984	12.204419	21.475946
6	8	0	2.556165	13.700118	17.575679
7	6	0	2.913596	11.778839	19.026367
8	6	0	3.036831	11.728547	22.806075
9	6	0	2.990080	11.290195	20.375629
10	6	0	2.901507	10.785151	17.915424
11	1	0	2.996502	12.454028	23.618077
12	6	0	3.167148	10.385777	23.065224
13	6	0	3.091236	9.907220	20.689398
14	6	0	4.041182	9.950597	17.663817
15	6	0	1.720703	10.552263	17.206545
16	1	0	3.242679	10.026651	24.089704
17	6	0	3.180173	9.471387	21.992009
18	1	0	3.093846	9.173550	19.887957
19	6	0	5.265393	10.098345	18.363661
20	6	0	3.951653	8.908075	16.687108
21	6	0	1.654672	9.511382	16.249585
22	6	0	0.496249	11.393420	17.427010
23	1	0	3.254410	8.404241	22.194296
24	1	0	5.360922	10.899600	19.091043
25	6	0	6.334239	9.269740	18.113397
26	6	0	5.072633	8.077556	16.442694
27	6	0	2.738425	8.713615	15.990586
28	1	0	0.714026	9.337323	15.726340
29	7	0	0.350058	12.436980	16.362479
30	1	0	-0.418673	10.784343	17.439783
31	1	0	0.546734	11.923554	18.381224
32	1	0	7.264294	9.408630	18.662195
33	6	0	6.241909	8.249691	17.142473
34	1	0	4.980987	7.294919	15.688963

35	1	0	2.676406	7.911682	15.253873
36	6	0	-0.393743	13.639807	16.876959
37	6	0	-0.435951	11.945644	15.160768
38	1	0	7.097921	7.605439	16.949245
39	1	0	0.319342	14.321702	17.349388
40	1	0	-1.111678	13.298112	17.636587
41	6	0	-1.114269	14.185820	15.669900
42	6	0	-1.624924	12.912786	15.017031
43	1	0	-0.779244	10.920532	15.339958
44	6	0	0.470326	12.001180	13.978885
45	1	0	-0.411218	14.714406	15.012183
46	1	0	-1.916106	14.876874	15.945626
47	1	0	-1.932195	13.031066	13.975229
48	1	0	-2.478548	12.508700	15.573172
49	7	0	1.701182	12.388472	14.118030
50	7	0	0.070120	11.845546	12.671231
51	6	0	2.345135	12.531335	12.798328
52	16	0	-1.031107	10.642276	12.104257
53	6	0	1.176056	12.277986	11.785043
54	1	0	2.673780	13.572456	12.712294
55	8	0	-2.066812	10.555019	13.123855
56	8	0	-1.306960	11.045510	10.735727
57	1	0	1.451523	11.449517	11.118751
58	6	0	3.527812	11.636354	12.563868
59	6	0	4.688878	12.177591	12.009120
60	6	0	3.454224	10.261486	12.796536
61	6	0	5.771208	11.358239	11.701839
62	1	0	4.739641	13.252283	11.819203
63	6	0	4.540188	9.443307	12.499989
64	1	0	2.545704	9.828032	13.220972
65	6	0	5.699755	9.989765	11.952650
66	1	0	6.673626	11.789552	11.270859
67	1	0	4.484851	8.373384	12.702611

68	1	0	6.547698	9.347893	11.719359
69	6	0	0.812266	13.494723	10.975298
70	6	0	1.596395	13.827190	9.865148
71	6	0	-0.234564	14.340208	11.348790
72	6	0	1.339578	14.991484	9.145831
73	1	0	2.412115	13.167959	9.565552
74	6	0	-0.491547	15.503503	10.627475
75	1	0	-0.863057	14.078737	12.199428
76	6	0	0.296659	15.834926	9.527525
77	1	0	1.952632	15.237878	8.280667
78	1	0	-1.314951	16.150410	10.925382
79	1	0	0.092705	16.742509	8.962113
80	6	0	-0.087671	9.154916	12.103944
81	6	0	-0.082766	8.361746	13.253649
82	6	0	0.696239	8.832915	10.995195
83	6	0	0.729541	7.237686	13.288743
84	1	0	-0.719490	8.617676	14.098424
85	6	0	1.506881	7.705224	11.055262
86	1	0	0.667365	9.450757	10.100001
87	6	0	1.543518	6.896740	12.197585
88	1	0	0.734297	6.609209	14.178855
89	1	0	2.128422	7.448138	10.198911
90	6	0	2.428373	5.693693	12.261592
91	1	0	2.982366	5.653819	13.208222
92	1	0	1.842127	4.767043	12.204382
93	1	0	3.152012	5.678838	11.440169
94	17	0	2.093083	15.666623	19.663110
95	28	0	2.214751	12.958738	15.835562
96	6	0	5.639211	15.182151	14.877812
97	6	0	6.346075	13.990987	14.983532
98	6	0	7.697975	13.885021	14.685545
99	6	0	8.356448	15.038519	14.266532
100	6	0	7.670353	16.253791	14.184257

101	6	0	6.314000	16.338300	14.494675
102	6	0	4.181170	15.032420	15.297771
103	1	0	8.219298	12.933643	14.776938
104	1	0	9.413308	14.995472	14.011581
105	1	0	8.203346	17.149206	13.870281
106	1	0	5.789812	17.290239	14.427165
107	16	0	5.288011	12.762636	15.705847
108	8	0	5.556068	12.779871	17.158640
109	8	0	5.355046	11.454203	15.058178
110	6	0	3.165592	15.546116	14.272422
111	8	0	1.963769	15.405874	14.422816
112	8	0	3.722225	16.095758	13.195369
113	6	0	2.797991	16.516923	12.172340
114	1	0	2.121747	17.283664	12.561851
115	1	0	3.417750	16.919941	11.371028
116	1	0	2.216567	15.661420	11.817573
117	7	0	3.925406	13.572814	15.261345
118	6	0	3.149766	16.961491	16.696347
119	6	0	5.064801	15.780875	17.600947
120	6	0	3.348294	17.974793	17.591287
121	1	0	2.325385	17.059557	15.994054
122	6	0	5.256313	16.774381	18.521862
123	1	0	5.748861	14.934971	17.600133
124	6	0	4.407557	17.912591	18.537369
125	1	0	2.693424	18.844993	17.593336
126	1	0	6.078492	16.703663	19.229770
127	7	0	4.583956	18.912586	19.413737
128	1	0	3.950003	19.699703	19.357949
129	6	0	5.645434	18.973836	20.391466
130	1	0	6.633000	18.962878	19.913553
131	1	0	5.542385	19.901874	20.955370
132	1	0	5.590116	18.131901	21.092869
133	6	0	3.953898	15.763560	16.680811

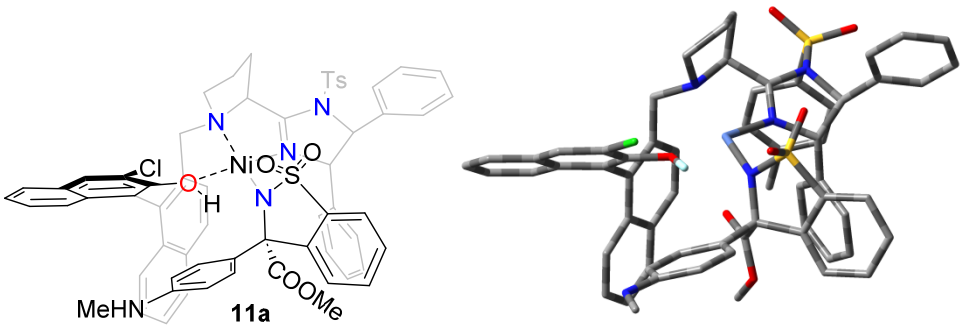
134	1	0	3.197238	14.757652	17.308315

Imaginary frequency: -1444.7 cm^{-1}.

Energies:

Sum of electronic and zero-point Energies=	-4659.247576
Sum of electronic and thermal Energies=	-4659.181554
Sum of electronic and thermal Enthalpies=	-4659.180610
Sum of electronic and thermal Free Energies=	-4659.343373

Optimized Structure of Intermediate **11a**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.566453	1.286968	4.666243
2	1	0	-0.851717	1.580368	6.763007
3	6	0	-0.747813	0.860422	5.954543
4	6	0	-0.417570	0.359100	3.607270
5	6	0	-0.818390	-0.524376	6.231865
6	8	0	-0.240554	0.828455	2.328006
7	6	0	-0.444516	-1.004337	3.833274
8	6	0	-1.030935	-0.989048	7.552921
9	6	0	-0.674349	-1.471239	5.165992
10	6	0	-0.236797	-1.947186	2.700731
11	1	0	-1.137127	-0.254539	8.350099
12	6	0	-1.104457	-2.335311	7.820843
13	6	0	-0.763198	-2.850882	5.479005
14	6	0	0.964481	-2.722961	2.645406

15	6	0	-1.198369	-2.092259	1.706274
16	1	0	-1.268129	-2.681932	8.839281
17	6	0	-0.971330	-3.270540	6.773350
18	1	0	-0.666332	-3.584562	4.681204
19	6	0	2.001783	-2.587433	3.603091
20	6	0	1.140077	-3.671771	1.587993
21	6	0	-0.993970	-3.017297	0.653912
22	6	0	-2.475535	-1.308146	1.758823
23	1	0	-1.036078	-4.335125	6.990461
24	1	0	1.895927	-1.857524	4.403756
25	6	0	3.138141	-3.362595	3.535429
26	6	0	2.314410	-4.462263	1.552797
27	6	0	0.135523	-3.792486	0.598288
28	1	0	-1.766560	-3.119206	-0.111458
29	7	0	-2.530548	-0.160589	0.786802
30	1	0	-3.344428	-1.951875	1.564571
31	1	0	-2.615373	-0.878690	2.753713
32	1	0	3.920291	-3.239749	4.282411
33	6	0	3.293925	-4.317354	2.508904
34	1	0	2.428758	-5.186062	0.745470
35	1	0	0.273110	-4.516984	-0.205386
36	6	0	-3.288866	1.001739	1.387305
37	6	0	-3.269302	-0.501977	-0.497641
38	1	0	4.192442	-4.930453	2.471904
39	1	0	-2.593970	1.636663	1.946659
40	1	0	-4.032566	0.598247	2.088820
41	6	0	-3.972136	1.662625	0.218463
42	6	0	-4.471396	0.455172	-0.555826
43	1	0	-3.573884	-1.554706	-0.472004
44	6	0	-2.336685	-0.260760	-1.631842
45	1	0	-3.252648	2.246184	-0.374380
46	1	0	-4.776117	2.331460	0.538215
47	1	0	-4.771440	0.669681	-1.584314

48	1	0	-5.322671	-0.009235	-0.044334
49	7	0	-1.136615	0.184683	-1.413258
50	7	0	-2.683560	-0.323743	-2.958272
51	6	0	-0.434843	0.414810	-2.693105
52	16	0	-3.725422	-1.521143	-3.647540
53	6	0	-1.536897	0.166988	-3.776546
54	1	0	-0.130676	1.467355	-2.713606
55	8	0	-4.818177	-1.678041	-2.698942
56	8	0	-3.928451	-1.062636	-5.010698
57	1	0	-1.213454	-0.643925	-4.442670
58	6	0	0.761881	-0.475982	-2.892757
59	6	0	1.971086	0.070667	-3.324354
60	6	0	0.651242	-1.863805	-2.749283
61	6	0	3.061714	-0.754661	-3.598010
62	1	0	2.053264	1.150056	-3.457245
63	6	0	1.735637	-2.688463	-3.029250
64	1	0	-0.296972	-2.299348	-2.423960
65	6	0	2.944954	-2.134668	-3.453836
66	1	0	4.001475	-0.316083	-3.930971
67	1	0	1.638326	-3.768407	-2.917558
68	1	0	3.794474	-2.779978	-3.671361
69	6	0	-1.907765	1.373097	-4.589151
70	6	0	-1.624918	1.404567	-5.955128
71	6	0	-2.503754	2.483513	-3.983177
72	6	0	-1.929119	2.534913	-6.710557
73	1	0	-1.168306	0.533643	-6.427032
74	6	0	-2.810503	3.610639	-4.737883
75	1	0	-2.718585	2.465510	-2.914704
76	6	0	-2.522526	3.638905	-6.102817
77	1	0	-1.707342	2.549934	-7.776117
78	1	0	-3.275716	4.470873	-4.259601
79	1	0	-2.764818	4.521576	-6.691965
80	6	0	-2.739335	-2.982106	-3.654333

81	6	0	-2.736571	-3.798288	-2.520949
82	6	0	-1.920354	-3.257737	-4.749963
83	6	0	-1.894392	-4.900741	-2.490682
84	1	0	-3.392046	-3.578044	-1.680107
85	6	0	-1.082711	-4.365805	-4.696279
86	1	0	-1.945323	-2.619636	-5.631287
87	6	0	-1.052026	-5.199930	-3.572280
88	1	0	-1.892219	-5.546936	-1.613271
89	1	0	-0.436523	-4.588441	-5.544011
90	6	0	-0.149534	-6.390399	-3.523597
91	1	0	0.361299	-6.471744	-2.556209
92	1	0	-0.718472	-7.320607	-3.653793
93	1	0	0.608571	-6.357027	-4.312681
94	17	0	-0.481727	2.987123	4.289690
95	28	0	-0.731752	0.584427	0.364073
96	6	0	2.754854	2.376598	-0.954741
97	6	0	1.861069	3.306963	-1.475238
98	6	0	2.166723	4.140016	-2.544334
99	6	0	3.431930	4.019492	-3.113283
100	6	0	4.357819	3.116402	-2.583847
101	6	0	4.035911	2.302902	-1.498386
102	6	0	2.169030	1.579452	0.210858
103	1	0	1.439186	4.854632	-2.924876
104	1	0	3.703124	4.639180	-3.965257
105	1	0	5.348818	3.042504	-3.027634
106	1	0	4.766716	1.604431	-1.099948
107	16	0	0.389779	3.299204	-0.491076
108	8	0	-0.846316	3.221602	-1.284685
109	8	0	0.465629	4.415876	0.463526
110	6	0	2.342613	0.064387	0.059442
111	8	0	1.447675	-0.741585	0.216663
112	8	0	3.618394	-0.258825	-0.147520
113	6	0	3.918964	-1.663634	-0.087232

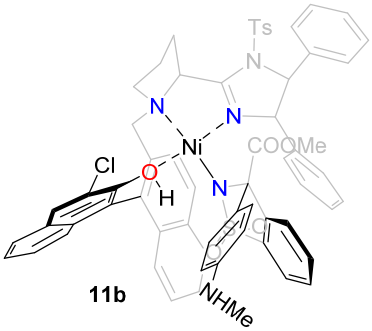
114	1	0	3.190183	-2.238466	-0.663515
115	1	0	4.918692	-1.769357	-0.511223
116	1	0	3.913047	-1.987698	0.959396
117	7	0	0.708662	1.854563	0.221495
118	6	0	2.809091	1.058682	2.630142
119	6	0	3.285246	3.253754	1.797119
120	6	0	3.271667	1.422365	3.882449
121	1	0	2.438393	0.040600	2.493795
122	6	0	3.759405	3.632297	3.047123
123	1	0	3.297966	3.987702	0.992014
124	6	0	3.752224	2.725881	4.124345
125	1	0	3.266003	0.695465	4.695698
126	1	0	4.136224	4.642934	3.187957
127	7	0	4.165872	3.081484	5.385193
128	1	0	4.388683	2.306956	5.996167
129	6	0	4.900108	4.298109	5.631182
130	1	0	4.280028	5.177387	5.417759
131	1	0	5.175426	4.332793	6.687751
132	1	0	5.819662	4.377925	5.028431
133	6	0	2.799021	1.965618	1.557677
134	1	0	0.269640	1.670083	2.286840

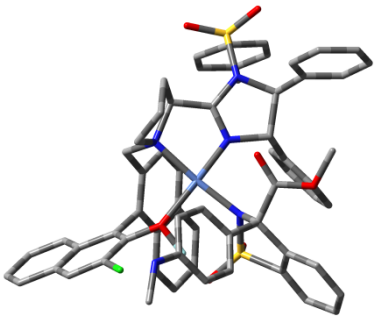
Number of imaginary frequency: 0

Energies:

Sum of electronic and zero-point Energies=	-4659.272072
Sum of electronic and thermal Energies=	-4659.205181
Sum of electronic and thermal Enthalpies=	-4659.204236
Sum of electronic and thermal Free Energies=	-4659.371255

Optimized Structure of Intermediate **11b**





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.288210	13.558908	20.268268
2	1	0	3.360837	13.639075	22.400654
3	6	0	3.275682	13.004204	21.521554
4	6	0	3.188280	12.750716	19.104819
5	6	0	3.149331	11.606137	21.675583
6	8	0	3.204301	13.404020	17.872531
7	6	0	3.121006	11.375283	19.211718
8	6	0	3.104240	11.012552	22.961001
9	6	0	3.069387	10.777169	20.513096
10	6	0	3.054572	10.508788	18.009022
11	1	0	3.168845	11.659504	23.834768
12	6	0	2.974598	9.651086	23.100546
13	6	0	2.928740	9.378377	20.694959
14	6	0	4.166326	9.676429	17.671666
15	6	0	1.887053	10.453186	17.257701
16	1	0	2.938835	9.204109	24.092081
17	6	0	2.883181	8.830618	21.956983
18	1	0	2.851316	8.731333	19.824051
19	6	0	5.393721	9.723757	18.379419
20	6	0	4.048484	8.767823	16.572191
21	6	0	1.781806	9.531078	16.189783
22	6	0	0.743399	11.371031	17.565611
23	1	0	2.772631	7.754329	22.073145
24	1	0	5.503994	10.418041	19.210535

25	6	0	6.452330	8.925934	18.011619
26	6	0	5.154381	7.955346	16.224161
27	6	0	2.828330	8.708998	15.857616
28	1	0	0.842437	9.470046	15.639627
29	7	0	0.676821	12.534032	16.616459
30	1	0	-0.222982	10.850299	17.525716
31	1	0	0.839406	11.792204	18.568987
32	1	0	7.390426	8.986593	18.560230
33	6	0	6.334555	8.033179	16.925532
34	1	0	5.049934	7.265399	15.386754
35	1	0	2.732235	7.995594	15.037961
36	6	0	0.089303	13.748607	17.287084
37	6	0	-0.228353	12.247448	15.430218
38	1	0	7.180382	7.408228	16.645437
39	1	0	0.885957	14.290198	17.808804
40	1	0	-0.646525	13.407104	18.028812
41	6	0	-0.589255	14.497550	16.166623
42	6	0	-1.282064	13.368505	15.420622
43	1	0	-0.692413	11.262915	15.554835
44	6	0	0.615199	12.266142	14.209364
45	1	0	0.152730	14.987498	15.519042
46	1	0	-1.282007	15.259197	16.535893
47	1	0	-1.593624	13.627157	14.405234
48	1	0	-2.168710	13.028161	15.966690
49	7	0	1.869938	12.592829	14.291768
50	7	0	0.156027	12.096248	12.931030
51	6	0	2.475733	12.635187	12.941133
52	16	0	-1.137644	11.044469	12.452574
53	6	0	1.276453	12.309272	11.986917
54	1	0	2.793395	13.662376	12.756856
55	8	0	-2.086168	11.076992	13.556433
56	8	0	-1.474364	11.498545	11.115454
57	1	0	1.487438	11.361565	11.472979

58	6	0	3.645934	11.716175	12.744735
59	6	0	4.876368	12.239740	12.346854
60	6	0	3.493001	10.331879	12.859474
61	6	0	5.945529	11.392266	12.070691
62	1	0	4.990738	13.322273	12.260840
63	6	0	4.561668	9.483281	12.588771
64	1	0	2.523401	9.921150	13.152530
65	6	0	5.790127	10.013019	12.194039
66	1	0	6.902256	11.809221	11.759807
67	1	0	4.436069	8.404538	12.677803
68	1	0	6.624495	9.348595	11.976457
69	6	0	0.998674	13.382242	10.972506
70	6	0	1.675831	13.338335	9.750885
71	6	0	0.146561	14.454069	11.248549
72	6	0	1.507589	14.357686	8.816774
73	1	0	2.335975	12.497993	9.531828
74	6	0	-0.029932	15.465974	10.309097
75	1	0	-0.384817	14.491235	12.199294
76	6	0	0.653730	15.423740	9.094626
77	1	0	2.037450	14.313827	7.866924
78	1	0	-0.701080	16.294491	10.529034
79	1	0	0.514694	16.216450	8.361828
80	6	0	-0.378018	9.456713	12.357978
81	6	0	-0.386681	8.632646	13.485692
82	6	0	0.278083	9.076138	11.185725
83	6	0	0.291607	7.423667	13.438051
84	1	0	-0.935618	8.928894	14.377601
85	6	0	0.953220	7.861104	11.161657
86	1	0	0.250789	9.714876	10.304941
87	6	0	0.982806	7.023898	12.283433
88	1	0	0.285729	6.773286	14.312203
89	1	0	1.471246	7.556460	10.253646
90	6	0	1.728635	5.729192	12.261227

91	1	0	2.482347	5.692014	13.058849
92	1	0	1.055373	4.879708	12.431747
93	1	0	2.238580	5.570433	11.305884
94	17	0	3.470417	15.273843	20.077943
95	28	0	2.500431	13.088684	15.988199
96	6	0	5.819767	15.419616	14.595509
97	6	0	6.555932	14.286678	14.910007
98	6	0	7.907027	14.139249	14.623393
99	6	0	8.542682	15.202418	13.989572
100	6	0	7.833511	16.369692	13.691008
101	6	0	6.478993	16.489746	13.992446
102	6	0	4.354436	15.331111	15.013581
103	1	0	8.440985	13.226539	14.880906
104	1	0	9.597370	15.127599	13.733590
105	1	0	8.345825	17.199071	13.207760
106	1	0	5.940383	17.402244	13.747985
107	16	0	5.515266	13.191805	15.811336
108	8	0	5.741843	13.492596	17.265094
109	8	0	5.636068	11.780947	15.452096
110	6	0	3.387681	15.661550	13.860894
111	8	0	2.178573	15.556627	13.946988
112	8	0	4.017290	16.054680	12.751292
113	6	0	3.175548	16.356427	11.623629
114	1	0	2.367811	17.031717	11.916953
115	1	0	3.831453	16.829007	10.891705
116	1	0	2.760856	15.428877	11.216336
117	7	0	4.123538	13.857740	15.272831
118	6	0	2.712586	16.400519	16.643917
119	6	0	5.013069	17.019411	16.841243
120	6	0	2.376522	17.283791	17.650584
121	1	0	1.927408	15.804658	16.185184
122	6	0	4.695291	17.895714	17.873717
123	1	0	6.058307	16.930468	16.550634

124	6	0	3.362976	18.063855	18.287641
125	1	0	1.339893	17.362516	17.982312
126	1	0	5.492952	18.451625	18.361470
127	7	0	3.005456	18.952555	19.275035
128	1	0	2.098839	18.782360	19.690556
129	6	0	3.987899	19.532803	20.157673
130	1	0	4.667089	20.192274	19.603182
131	1	0	3.473041	20.138842	20.907042
132	1	0	4.601923	18.779412	20.679383
133	6	0	4.034940	16.262121	16.188216
134	1	0	4.156852	13.692920	17.718748

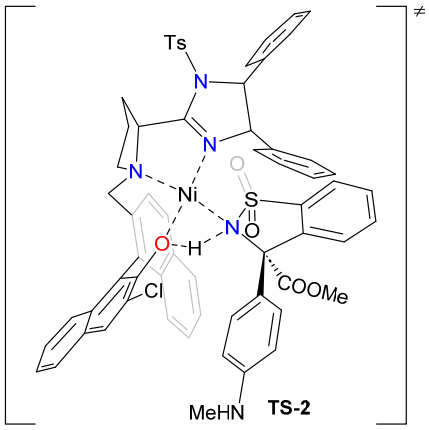
Number of imaginary frequency: 0

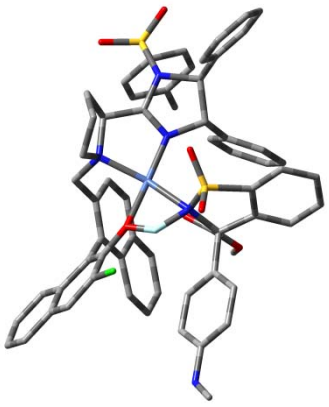
Energies:

Sum of electronic and zero-point Energies=	-4659.264051
Sum of electronic and thermal Energies=	-4659.197923
Sum of electronic and thermal Enthalpies=	-4659.196978
Sum of electronic and thermal Free Energies=	-4659.360169

Proton transfer from naphthol oxygen to sulfonamide nitrogen

TS-2





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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3	6	0	2.622222	13.266001	21.567508
4	6	0	2.618045	12.749656	19.186941
5	6	0	2.579449	11.885309	21.867776
6	8	0	2.561151	13.262145	17.932159
7	6	0	2.642305	11.382790	19.440565
8	6	0	2.539666	11.437375	23.210231
9	6	0	2.570524	10.931568	20.799819
10	6	0	2.784734	10.404481	18.326658
11	1	0	2.553154	12.182367	24.005139
12	6	0	2.478317	10.095371	23.503023
13	6	0	2.491135	9.556962	21.140836
14	6	0	3.977905	9.609263	18.254165
15	6	0	1.793235	10.231377	17.364731
16	1	0	2.447050	9.760798	24.537956
17	6	0	2.444975	9.151353	22.455825
18	1	0	2.459812	8.813180	20.347095
19	6	0	5.051894	9.756198	19.169349
20	6	0	4.111917	8.626862	17.220817
21	6	0	1.960782	9.276588	16.332366
22	6	0	0.520794	11.022237	17.419314
23	1	0	2.380893	8.089977	22.688894
24	1	0	4.989270	10.513066	19.948022
25	6	0	6.169962	8.955238	19.096108
26	6	0	5.270278	7.813399	17.175239
27	6	0	3.081560	8.491704	16.260720
28	1	0	1.163975	9.161347	15.595780
29	7	0	0.454492	12.120414	16.395178
30	1	0	-0.361926	10.381677	17.282953
31	1	0	0.420743	11.506912	18.394044
32	1	0	6.975512	9.089443	19.815897
33	6	0	6.278232	7.963029	18.099907
34	1	0	5.347066	7.065972	16.385035

35	1	0	3.192062	7.748084	15.470326
36	6	0	-0.349200	13.284174	16.933732
37	6	0	-0.223188	11.724655	15.093099
38	1	0	7.162434	7.329763	18.058163
39	1	0	0.316104	13.952306	17.487770
40	1	0	-1.097272	12.878659	17.629262
41	6	0	-1.022250	13.880787	15.725805
42	6	0	-1.456672	12.633157	14.976128
43	1	0	-0.482891	10.658586	15.121380
44	6	0	0.746423	11.988749	13.992681
45	1	0	-0.305044	14.469238	15.136066
46	1	0	-1.857376	14.531169	16.000158
47	1	0	-1.734680	12.809941	13.935115
48	1	0	-2.304573	12.152787	15.478185
49	7	0	1.937506	12.432465	14.261673
50	7	0	0.442616	11.954315	12.654151
51	6	0	2.676867	12.697784	13.012413
52	16	0	-0.545768	10.743547	11.901953
53	6	0	1.611021	12.480480	11.887837
54	1	0	2.982306	13.751171	13.029288
55	8	0	-1.670357	10.542754	12.803501
56	8	0	-0.704601	11.225932	10.541046
57	1	0	1.961735	11.695354	11.205626
58	6	0	3.878041	11.809941	12.825566
59	6	0	5.089523	12.361143	12.407594
60	6	0	3.768166	10.421841	12.964330
61	6	0	6.184477	11.539451	12.141510
62	1	0	5.168413	13.441244	12.276590
63	6	0	4.858072	9.600936	12.693959
64	1	0	2.817125	9.982246	13.275155
65	6	0	6.069750	10.158669	12.282061
66	1	0	7.126343	11.981720	11.819476
67	1	0	4.762610	8.520628	12.804085

68	1	0	6.923198	9.516057	12.072210
69	6	0	1.261984	13.711185	11.102869
70	6	0	1.538551	13.764768	9.736138
71	6	0	0.698153	14.824278	11.734735
72	6	0	1.260302	14.918286	9.006375
73	1	0	1.971074	12.892775	9.243929
74	6	0	0.416617	15.974569	11.005658
75	1	0	0.488246	14.791678	12.803827
76	6	0	0.698464	16.024091	9.639971
77	1	0	1.478279	14.950245	7.940417
78	1	0	-0.024286	16.836085	11.504255
79	1	0	0.476664	16.925056	9.070689
80	6	0	0.463954	9.300389	11.907748
81	6	0	0.411608	8.449084	13.014327
82	6	0	1.345250	9.067365	10.851579
83	6	0	1.263834	7.355178	13.058036
84	1	0	-0.297685	8.634112	13.819811
85	6	0	2.193237	7.968270	10.919952
86	1	0	1.358247	9.728944	9.987307
87	6	0	2.172764	7.102035	12.019429
88	1	0	1.222244	6.678813	13.911430
89	1	0	2.891139	7.780470	10.105428
90	6	0	3.087216	5.921829	12.085042
91	1	0	3.565454	5.835749	13.068684
92	1	0	2.533789	4.986709	11.926502
93	1	0	3.871236	5.973157	11.322673
94	17	0	2.642223	15.380662	19.885567
95	28	0	2.278562	12.796315	16.059197
96	6	0	5.788947	14.641942	14.834026
97	6	0	4.866784	15.554173	14.334565
98	6	0	5.113122	16.359888	13.228879
99	6	0	6.353554	16.236012	12.609551
100	6	0	7.311270	15.354492	13.119392

101	6	0	7.043308	14.560087	14.232250
102	6	0	5.275515	13.854075	16.031110
103	1	0	4.362154	17.057224	12.862380
104	1	0	6.582229	16.838016	11.733016
105	1	0	8.283278	15.280541	12.635781
106	1	0	7.794920	13.873800	14.613559
107	16	0	3.448677	15.594839	15.388856
108	8	0	2.180021	15.470090	14.661348
109	8	0	3.570666	16.719937	16.320632
110	6	0	5.417985	12.339523	15.835638
111	8	0	4.497243	11.553493	15.934049
112	8	0	6.688479	11.999884	15.641532
113	6	0	6.968648	10.588623	15.657897
114	1	0	6.221667	10.041985	15.078522
115	1	0	7.960379	10.479214	15.216827
116	1	0	6.971764	10.240944	16.696670
117	7	0	3.811070	14.132953	16.134472
118	6	0	5.888007	13.342487	18.436589
119	6	0	6.595513	15.451347	17.536704
120	6	0	6.420358	13.676151	19.668180
121	1	0	5.397881	12.371554	18.326170
122	6	0	7.129308	15.803717	18.770317
123	1	0	6.665841	16.162709	16.714554
124	6	0	7.059278	14.919066	19.862958
125	1	0	6.350551	12.976700	20.502154
126	1	0	7.606160	16.774321	18.886502
127	7	0	7.620691	15.216582	21.080315
128	1	0	7.287478	14.657715	21.854450
129	6	0	8.045957	16.553177	21.415774
130	1	0	7.245255	17.302332	21.304435
131	1	0	8.386183	16.561711	22.453725
132	1	0	8.888404	16.864237	20.785367
133	6	0	5.967725	14.219509	17.343239

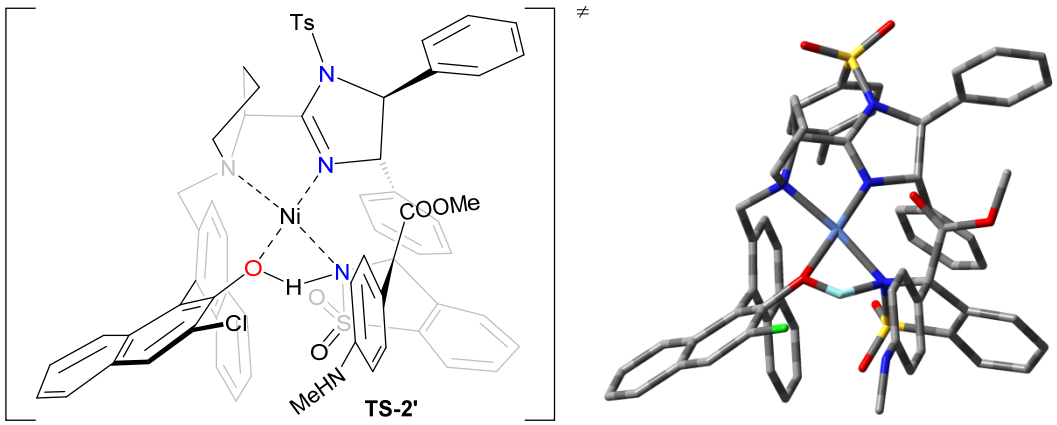
134	1	0	3.336615	13.931936	17.468500

Imaginary frequency: -1243.1 cm^{-1}.

Energies:

Sum of electronic and zero-point Energies=	-4659.267859
Sum of electronic and thermal Energies=	-4659.201785
Sum of electronic and thermal Enthalpies=	-4659.200841
Sum of electronic and thermal Free Energies=	-4659.365057

TS-2'



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.876295	13.721564	20.182092
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3	6	0	3.013042	13.218556	21.448048
4	6	0	2.773657	12.871647	19.045852
5	6	0	3.025954	11.820758	21.653248
6	8	0	2.575920	13.483468	17.839250
7	6	0	2.849346	11.493280	19.201340
8	6	0	3.121126	11.276884	22.957778
9	6	0	2.933839	10.945539	20.524581
10	6	0	2.846506	10.575893	18.030349
11	1	0	3.195392	11.963180	23.800632
12	6	0	3.112749	9.916678	23.155559

13	6	0	2.913216	9.548337	20.770167
14	6	0	4.018277	9.796966	17.751161
15	6	0	1.714180	10.419935	17.234290
16	1	0	3.185268	9.508154	24.161567
17	6	0	2.999937	9.049037	22.050022
18	1	0	2.819240	8.860853	19.932553
19	6	0	5.225589	9.943548	18.479450
20	6	0	3.994553	8.852682	16.675511
21	6	0	1.708625	9.466029	16.187758
22	6	0	0.483235	11.245902	17.462310
23	1	0	2.977527	7.972594	22.209687
24	1	0	5.280208	10.678873	19.278523
25	6	0	6.341301	9.201962	18.163517
26	6	0	5.154827	8.098149	16.380585
27	6	0	2.812905	8.702324	15.915548
28	1	0	0.798512	9.334897	15.602092
29	7	0	0.340172	12.348875	16.452639
30	1	0	-0.431848	10.637773	17.428927
31	1	0	0.515618	11.729292	18.442538
32	1	0	7.260496	9.345246	18.728901
33	6	0	6.309226	8.268084	17.106894
34	1	0	5.113505	7.384998	15.556716
35	1	0	2.795846	7.969034	15.108408
36	6	0	-0.410558	13.515666	17.046278
37	6	0	-0.438861	11.948824	15.210559
38	1	0	7.199023	7.688507	16.867695
39	1	0	0.297156	14.164350	17.570459
40	1	0	-1.127146	13.115042	17.777226
41	6	0	-1.134281	14.138072	15.880962
42	6	0	-1.639949	12.908445	15.148467
43	1	0	-0.759640	10.902735	15.298235
44	6	0	0.473434	12.106314	14.043843
45	1	0	-0.439019	14.713365	15.254414

46	1	0	-1.938564	14.804309	16.205368
47	1	0	-1.961138	13.096302	14.121964
48	1	0	-2.481560	12.455585	15.684965
49	7	0	1.707639	12.477698	14.217241
50	7	0	0.083740	12.008410	12.729599
51	6	0	2.376098	12.633214	12.909933
52	16	0	-1.054509	10.838485	12.119314
53	6	0	1.242220	12.341639	11.869730
54	1	0	2.678818	13.681325	12.820179
55	8	0	-2.104894	10.759261	13.123137
56	8	0	-1.300025	11.281276	10.758194
57	1	0	1.524636	11.446065	11.298708
58	6	0	3.575512	11.752721	12.704657
59	6	0	4.770039	12.310180	12.248603
60	6	0	3.480206	10.367283	12.865268
61	6	0	5.864783	11.495236	11.966858
62	1	0	4.838918	13.392026	12.109688
63	6	0	4.574078	9.554320	12.591297
64	1	0	2.543816	9.924212	13.213474
65	6	0	5.769646	10.117221	12.142707
66	1	0	6.792609	11.938791	11.609205
67	1	0	4.496610	8.475414	12.724930
68	1	0	6.624067	9.479533	11.923219
69	6	0	0.989974	13.476746	10.918206
70	6	0	1.850278	13.602778	9.822705
71	6	0	-0.002001	14.437151	11.126495
72	6	0	1.726976	14.678463	8.949365
73	1	0	2.619293	12.847903	9.654920
74	6	0	-0.133687	15.506278	10.241898
75	1	0	-0.675815	14.343845	11.978250
76	6	0	0.732312	15.633261	9.157141
77	1	0	2.401778	14.765211	8.099729
78	1	0	-0.915272	16.246376	10.404104

79	1	0	0.627276	16.470322	8.469352
80	6	0	-0.143395	9.333033	12.097716
81	6	0	-0.146612	8.528556	13.239644
82	6	0	0.629327	9.008996	10.981215
83	6	0	0.649434	7.392320	13.260498
84	1	0	-0.777129	8.786208	14.088613
85	6	0	1.423570	7.869132	11.027023
86	1	0	0.603729	9.635472	10.092085
87	6	0	1.453633	7.049926	12.162118
88	1	0	0.649737	6.755691	14.144724
89	1	0	2.035523	7.609942	10.164524
90	6	0	2.318293	5.831838	12.208655
91	1	0	2.838642	5.744961	13.170631
92	1	0	1.719319	4.918610	12.094491
93	1	0	3.067105	5.835853	11.410005
94	17	0	2.853937	15.443352	19.924188
95	28	0	2.151411	12.976080	15.980499
96	6	0	5.606540	15.143597	14.687745
97	6	0	6.233579	13.927193	14.913546
98	6	0	7.503221	13.618177	14.435612
99	6	0	8.163306	14.590087	13.693738
100	6	0	7.567193	15.838106	13.482387
101	6	0	6.301808	16.127123	13.981981
102	6	0	4.226359	15.277143	15.322946
103	1	0	7.955723	12.648330	14.634683
104	1	0	9.153515	14.385812	13.292441
105	1	0	8.103951	16.601117	12.922465
106	1	0	5.859120	17.106210	13.821538
107	16	0	5.261192	12.931589	15.990891
108	8	0	5.828202	12.984254	17.345703
109	8	0	4.946898	11.612727	15.446046
110	6	0	3.125239	15.595220	14.301681
111	8	0	1.955481	15.302656	14.468948

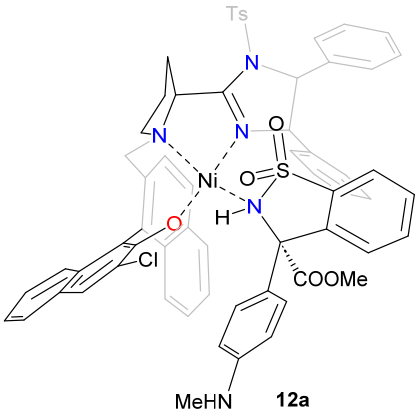
112	8	0	3.585202	16.267214	13.249454
113	6	0	2.617346	16.617530	12.242434
114	1	0	1.725252	17.055874	12.696955
115	1	0	3.118436	17.338854	11.596237
116	1	0	2.349985	15.721320	11.673310
117	7	0	3.902583	13.937062	15.931815
118	6	0	3.046408	17.102996	16.696734
119	6	0	5.352133	16.632964	17.155110
120	6	0	3.040912	18.062116	17.694597
121	1	0	2.121449	16.921953	16.151996
122	6	0	5.357508	17.583395	18.164718
123	1	0	6.268722	16.075302	16.965474
124	6	0	4.198260	18.329619	18.451908
125	1	0	2.128407	18.619493	17.906756
126	1	0	6.267853	17.748922	18.736642
127	7	0	4.179979	19.307459	19.414598
128	1	0	3.259143	19.592817	19.720741
129	6	0	5.230223	19.431142	20.395484
130	1	0	6.181707	19.693482	19.916206
131	1	0	4.971235	20.237111	21.085962
132	1	0	5.387315	18.507683	20.977241
133	6	0	4.205593	16.372681	16.393556
134	1	0	3.440605	13.937649	17.283565

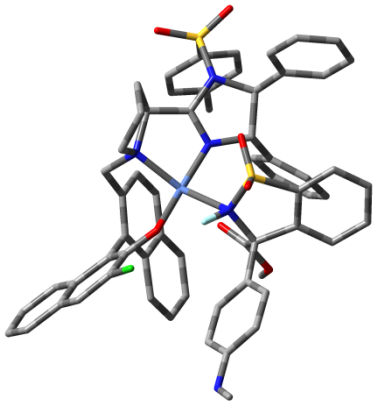
Imaginary frequency: -1253.0 cm^{-1}.

Sum of electronic and zero-point Energies=	-4659.257804
Sum of electronic and thermal Energies=	-4659.191512
Sum of electronic and thermal Enthalpies=	-4659.190568
Sum of electronic and thermal Free Energies=	-4659.355214

Optimized Structures of Intermediates **12a** and **12b**

Optimized Structure of **12a**





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.743055	13.193874	20.374085
2	1	0	2.712144	13.402972	22.498094
3	6	0	2.715597	12.715224	21.654456
4	6	0	2.755953	12.337289	19.221095
5	6	0	2.662443	11.320459	21.890208
6	8	0	2.811192	12.914011	18.044660
7	6	0	2.730120	10.951022	19.442460
8	6	0	2.596043	10.801133	23.204672
9	6	0	2.654539	10.427953	20.769137
10	6	0	2.746284	10.034982	18.272923
11	1	0	2.604857	11.502318	24.039322
12	6	0	2.512348	9.445391	23.426714
13	6	0	2.556529	9.036696	21.037920
14	6	0	3.892950	9.211676	18.020346
15	6	0	1.662553	9.976284	17.396454
16	1	0	2.457854	9.056578	24.441696
17	6	0	2.487652	8.561130	22.328760
18	1	0	2.528323	8.336446	20.204809
19	6	0	5.052101	9.253348	18.837719
20	6	0	3.897196	8.328289	16.891798
21	6	0	1.674043	9.070958	16.307003

22	6	0	0.483899	10.892591	17.559950
23	1	0	2.409797	7.488945	22.502320
24	1	0	5.070260	9.924044	19.694809
25	6	0	6.148919	8.467661	18.559856
26	6	0	5.043000	7.538398	16.629285
27	6	0	2.757951	8.271868	16.055082
28	1	0	0.799632	9.026070	15.657650
29	7	0	0.548446	12.063962	16.610434
30	1	0	-0.471208	10.375490	17.393187
31	1	0	0.462634	11.314243	18.568130
32	1	0	7.026240	8.518069	19.202314
33	6	0	6.148050	7.601689	17.445465
34	1	0	5.027301	6.875269	15.763919
35	1	0	2.757069	7.583399	15.208902
36	6	0	-0.100875	13.282149	17.216527
37	6	0	-0.185946	11.816238	15.290954
38	1	0	7.022337	6.988979	17.233659
39	1	0	0.650152	13.817781	17.803811
40	1	0	-0.897353	12.937473	17.890825
41	6	0	-0.685583	14.031815	16.047015
42	6	0	-1.270240	12.900580	15.217317
43	1	0	-0.616098	10.806603	15.302491
44	6	0	0.817862	11.936061	14.193026
45	1	0	0.097225	14.564302	15.489633
46	1	0	-1.437259	14.760264	16.364087
47	1	0	-1.503814	13.171165	14.184955
48	1	0	-2.187216	12.515514	15.678578
49	7	0	2.069008	12.089619	14.491265
50	7	0	0.532519	12.052097	12.848794
51	6	0	2.860025	12.370982	13.284401
52	16	0	-0.612152	11.002456	12.058181
53	6	0	1.805306	12.318377	12.128301
54	1	0	3.231496	13.399725	13.387424

55	8	0	-1.753464	10.936588	12.958875
56	8	0	-0.700343	11.535736	10.710065
57	1	0	2.036679	11.451310	11.492998
58	6	0	4.021458	11.442831	13.058341
59	6	0	5.255572	11.977179	12.679961
60	6	0	3.866773	10.054934	13.128667
61	6	0	6.326372	11.139994	12.374649
62	1	0	5.369169	13.060512	12.617054
63	6	0	4.937805	9.217734	12.825376
64	1	0	2.902427	9.629356	13.416561
65	6	0	6.168034	9.757051	12.446377
66	1	0	7.283926	11.570247	12.083778
67	1	0	4.811448	8.136789	12.876238
68	1	0	7.001307	9.098692	12.207800
69	6	0	1.769601	13.560428	11.279332
70	6	0	2.780995	13.739169	10.329353
71	6	0	0.797744	14.548401	11.438197
72	6	0	2.818258	14.891025	9.548155
73	1	0	3.537608	12.964506	10.196795
74	6	0	0.832877	15.697701	10.652583
75	1	0	0.008659	14.417347	12.177095
76	6	0	1.840785	15.872775	9.706613
77	1	0	3.605591	15.016077	8.806693
78	1	0	0.065691	16.459242	10.780132
79	1	0	1.861685	16.769842	9.090515
80	6	0	0.204489	9.439887	12.024903
81	6	0	0.064088	8.577697	13.115038
82	6	0	1.034826	9.121031	10.949482
83	6	0	0.782982	7.391153	13.127050
84	1	0	-0.614145	8.829017	13.929189
85	6	0	1.747336	7.928245	10.983886
86	1	0	1.110192	9.792208	10.096498
87	6	0	1.643098	7.051734	12.070854

88	1	0	0.673303	6.707953	13.968895
89	1	0	2.400072	7.672156	10.150770
90	6	0	2.415473	5.772733	12.107592
91	1	0	2.888939	5.617825	13.085226
92	1	0	1.755799	4.911080	11.940670
93	1	0	3.194126	5.746538	11.338297
94	17	0	2.751332	14.923457	20.098815
95	28	0	2.472789	12.321335	16.301326
96	6	0	5.642273	14.968105	14.770180
97	6	0	4.665392	15.686998	14.092383
98	6	0	4.869123	16.264472	12.844850
99	6	0	6.128014	16.119382	12.270874
100	6	0	7.139778	15.437742	12.953578
101	6	0	6.908551	14.855658	14.198420
102	6	0	5.161305	14.345865	16.077055
103	1	0	4.069782	16.802692	12.339420
104	1	0	6.325978	16.548758	11.291394
105	1	0	8.125648	15.349723	12.502246
106	1	0	7.702427	14.319263	14.711698
107	16	0	3.193046	15.821765	15.048551
108	8	0	2.024289	15.356665	14.300126
109	8	0	3.089118	17.119356	15.717734
110	6	0	5.313488	12.818401	15.981960
111	8	0	4.387042	12.008668	16.024404
112	8	0	6.560383	12.434497	15.864054
113	6	0	6.795331	11.004225	15.835780
114	1	0	6.154913	10.532137	15.087498
115	1	0	7.848400	10.895407	15.578257
116	1	0	6.593290	10.592882	16.829436
117	7	0	3.702967	14.619795	16.120345
118	6	0	5.959529	14.026884	18.463789
119	6	0	6.336380	16.154585	17.413327
120	6	0	6.500186	14.503984	19.643283

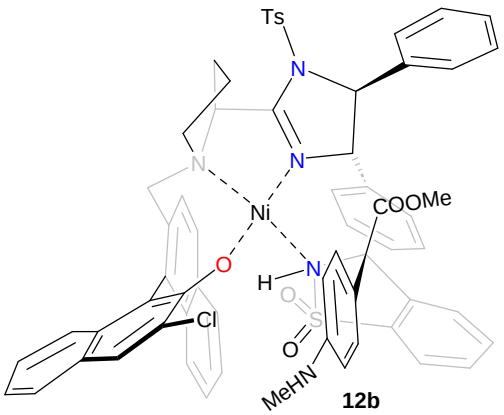
121	1	0	5.582195	13.001938	18.442540
122	6	0	6.871404	16.649715	18.594357
123	1	0	6.274903	16.814579	16.547836
124	6	0	6.967868	15.831031	19.737045
125	1	0	6.548942	13.857492	20.519384
126	1	0	7.217360	17.679860	18.631534
127	7	0	7.530846	16.280750	20.905217
128	1	0	7.316315	15.727598	21.724226
129	6	0	7.758190	17.685062	21.146974
130	1	0	6.845473	18.293108	21.040146
131	1	0	8.140996	17.807554	22.162833
132	1	0	8.511140	18.083702	20.455706
133	6	0	5.872772	14.840085	17.323461
134	1	0	3.362748	14.783973	17.071002

Number of imaginary frequency: 0

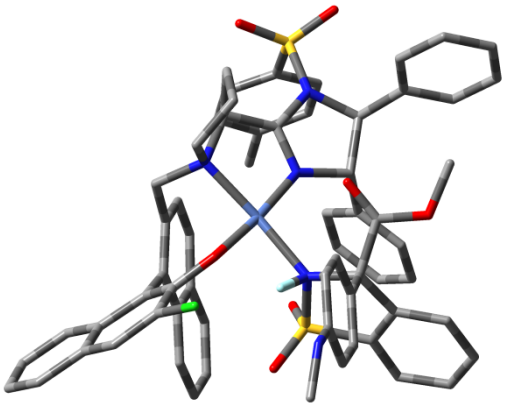
Energies:

Sum of electronic and zero-point Energies=	-4659.297208
Sum of electronic and thermal Energies=	-4659.230911
Sum of electronic and thermal Enthalpies=	-4659.229967
Sum of electronic and thermal Free Energies=	-4659.394419

Optimized Structure of **12b**



12b



Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	2.773577	13.595394	20.212182
2	1	0	3.161299	13.752432	22.303962
3	6	0	3.024322	13.085811	21.454535
4	6	0	2.588847	12.773709	19.047303
5	6	0	3.101096	11.686277	21.641325
6	8	0	2.295949	13.414853	17.933746
7	6	0	2.742194	11.387024	19.201869
8	6	0	3.323963	11.133361	22.924769
9	6	0	2.949072	10.827472	20.505995
10	6	0	2.703178	10.483299	18.023415
11	1	0	3.444610	11.815417	23.766401
12	6	0	3.382158	9.771177	23.108601
13	6	0	2.992852	9.427164	20.740992
14	6	0	3.862494	9.701600	17.696117
15	6	0	1.550849	10.337958	17.252452
16	1	0	3.553249	9.354732	24.099375
17	6	0	3.203105	8.915864	22.002800
18	1	0	2.846727	8.741891	19.909074
19	6	0	5.101534	9.861231	18.367610
20	6	0	3.798786	8.751346	16.627755
21	6	0	1.498994	9.369750	16.220448
22	6	0	0.351298	11.202613	17.491398
23	1	0	3.226777	7.836656	22.145882
24	1	0	5.184153	10.605793	19.155305
25	6	0	6.206237	9.121542	18.012484
26	6	0	4.948330	7.994433	16.294726
27	6	0	2.586097	8.591116	15.919346
28	1	0	0.563067	9.231495	15.678693
29	7	0	0.257864	12.328362	16.500418
30	1	0	-0.587504	10.633112	17.434077
31	1	0	0.396475	11.666784	18.479632
32	1	0	7.148716	9.275341	18.535467

33	6	0	6.131352	8.172928	16.970937
34	1	0	4.873657	7.269283	15.483542
35	1	0	2.531019	7.843279	15.127235
36	6	0	-0.527243	13.477356	17.081930
37	6	0	-0.466663	11.946406	15.223005
38	1	0	7.010786	7.590017	16.702853
39	1	0	0.150149	14.104862	17.665887
40	1	0	-1.284486	13.053711	17.757030
41	6	0	-1.185741	14.128460	15.893870
42	6	0	-1.658460	12.916062	15.112646
43	1	0	-0.805287	10.905939	15.285197
44	6	0	0.486594	12.107933	14.093383
45	1	0	-0.455352	14.711776	15.316113
46	1	0	-2.002727	14.792956	16.189152
47	1	0	-1.923147	13.120694	14.072816
48	1	0	-2.529617	12.459352	15.596166
49	7	0	1.703152	12.519345	14.300642
50	7	0	0.135563	11.983750	12.770419
51	6	0	2.399064	12.670384	13.003276
52	16	0	-0.989235	10.823572	12.123906
53	6	0	1.299303	12.346861	11.936239
54	1	0	2.687577	13.720627	12.896272
55	8	0	-2.049847	10.716683	13.114422
56	8	0	-1.223741	11.297516	10.771056
57	1	0	1.620619	11.459848	11.373437
58	6	0	3.614676	11.804927	12.829278
59	6	0	4.808747	12.370597	12.382520
60	6	0	3.527317	10.418869	12.989852
61	6	0	5.912099	11.562121	12.113430
62	1	0	4.868533	13.451519	12.233804
63	6	0	4.627714	9.611970	12.724831
64	1	0	2.585687	9.974006	13.319667
65	6	0	5.824417	10.183671	12.289738

66	1	0	6.838967	12.009753	11.758525
67	1	0	4.552698	8.531868	12.847584
68	1	0	6.684528	9.551690	12.076136
69	6	0	1.032440	13.471514	10.976549
70	6	0	1.884988	13.598939	9.875622
71	6	0	0.029052	14.420771	11.182246
72	6	0	1.740915	14.663845	8.991843
73	1	0	2.662705	12.852352	9.710552
74	6	0	-0.122938	15.479088	10.288324
75	1	0	-0.638333	14.325314	12.039044
76	6	0	0.734296	15.606618	9.196393
77	1	0	2.408539	14.751222	8.136649
78	1	0	-0.913225	16.210433	10.448375
79	1	0	0.612542	16.434583	8.500403
80	6	0	-0.073248	9.320633	12.071101
81	6	0	-0.148971	8.444641	13.156169
82	6	0	0.766450	9.061589	10.985949
83	6	0	0.652184	7.311820	13.159861
84	1	0	-0.841876	8.641097	13.972126
85	6	0	1.569229	7.927234	11.017563
86	1	0	0.782538	9.731573	10.128661
87	6	0	1.538902	7.046134	12.105170
88	1	0	0.594210	6.619534	13.999445
89	1	0	2.237314	7.722217	10.182547
90	6	0	2.423617	5.842170	12.144313
91	1	0	2.939204	5.755902	13.109342
92	1	0	1.843000	4.918770	12.019356
93	1	0	3.179319	5.868979	11.352589
94	17	0	2.697726	15.329339	19.993845
95	28	0	2.087172	12.991786	16.111810
96	6	0	5.587782	15.132622	14.711255
97	6	0	6.215929	13.949801	15.076164
98	6	0	7.489662	13.585037	14.649818

99	6	0	8.163560	14.469471	13.818664
100	6	0	7.566438	15.679872	13.454323
101	6	0	6.293203	16.022502	13.897926
102	6	0	4.218484	15.372018	15.326552
103	1	0	7.933872	12.640345	14.956189
104	1	0	9.160355	14.222639	13.460934
105	1	0	8.108829	16.374872	12.816950
106	1	0	5.854804	16.975308	13.616671
107	16	0	5.245533	12.994504	16.181218
108	8	0	5.737636	13.076467	17.553987
109	8	0	4.884018	11.704098	15.617997
110	6	0	3.105310	15.645353	14.308667
111	8	0	1.940795	15.356682	14.503268
112	8	0	3.562451	16.293025	13.242815
113	6	0	2.592288	16.636016	12.233711
114	1	0	1.683509	17.035651	12.690036
115	1	0	3.076885	17.385688	11.607714
116	1	0	2.361583	15.742458	11.645664
117	7	0	3.849846	14.080663	16.065223
118	6	0	3.070212	17.234914	16.656364
119	6	0	5.405390	16.826063	17.042736
120	6	0	3.080286	18.221824	17.623933
121	1	0	2.130893	17.016951	16.151496
122	6	0	5.423059	17.801124	18.027594
123	1	0	6.329738	16.288664	16.834744
124	6	0	4.257449	18.530590	18.336534
125	1	0	2.164241	18.766495	17.851567
126	1	0	6.348551	18.000649	18.562648
127	7	0	4.250109	19.525032	19.276197
128	1	0	3.334785	19.818916	19.590519
129	6	0	5.326262	19.697964	20.221638
130	1	0	6.256330	19.971191	19.707932
131	1	0	5.067168	20.513680	20.900170

132	1	0	5.520105	18.792476	20.818677
133	6	0	4.236716	16.522338	16.330711
134	1	0	3.683277	14.348267	17.046689

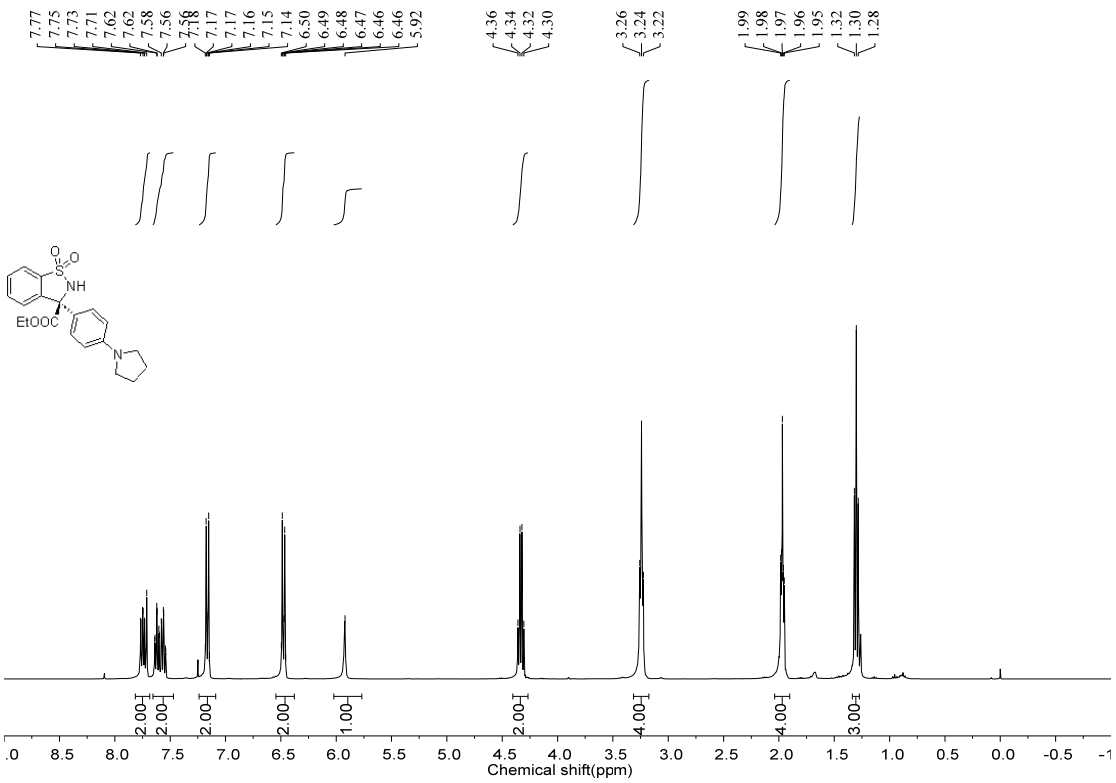
Number of imaginary frequency: 0

Energies:

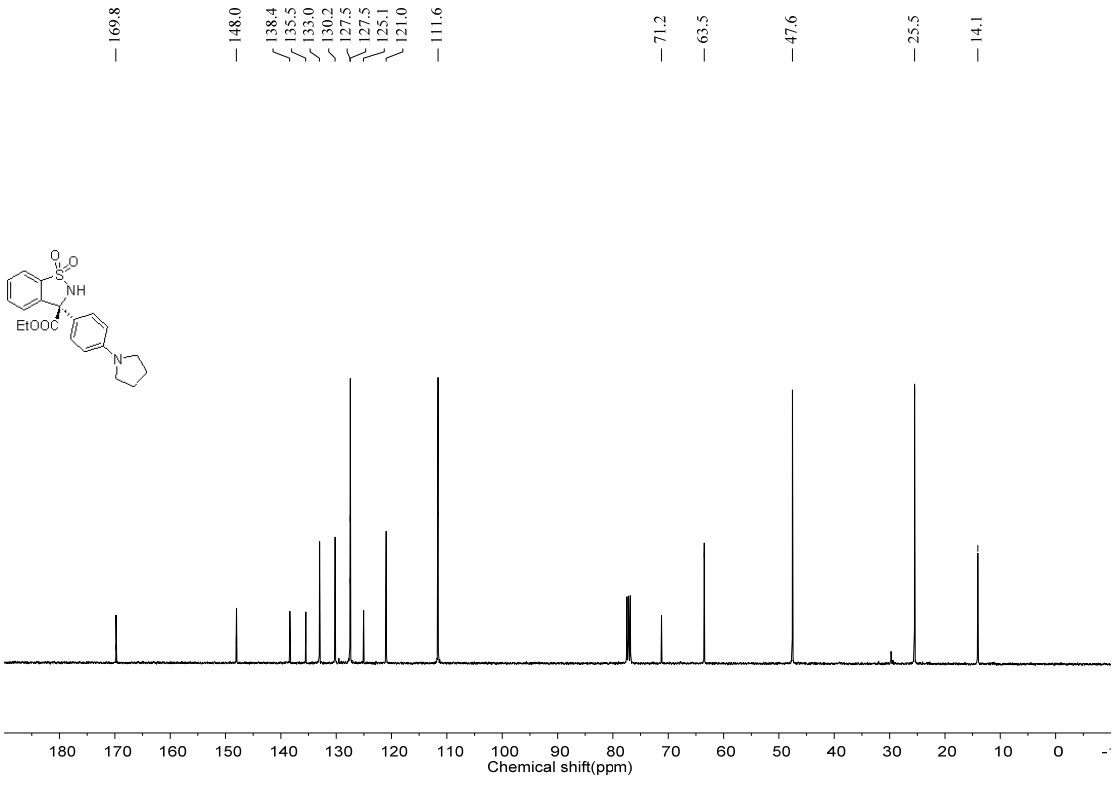
Sum of electronic and zero-point Energies=	-4659.278604
Sum of electronic and thermal Energies=	-4659.211930
Sum of electronic and thermal Enthalpies=	-4659.210986
Sum of electronic and thermal Free Energies=	-4659.377757

5. Copies of NMR Spectra of the Products and Ligands.

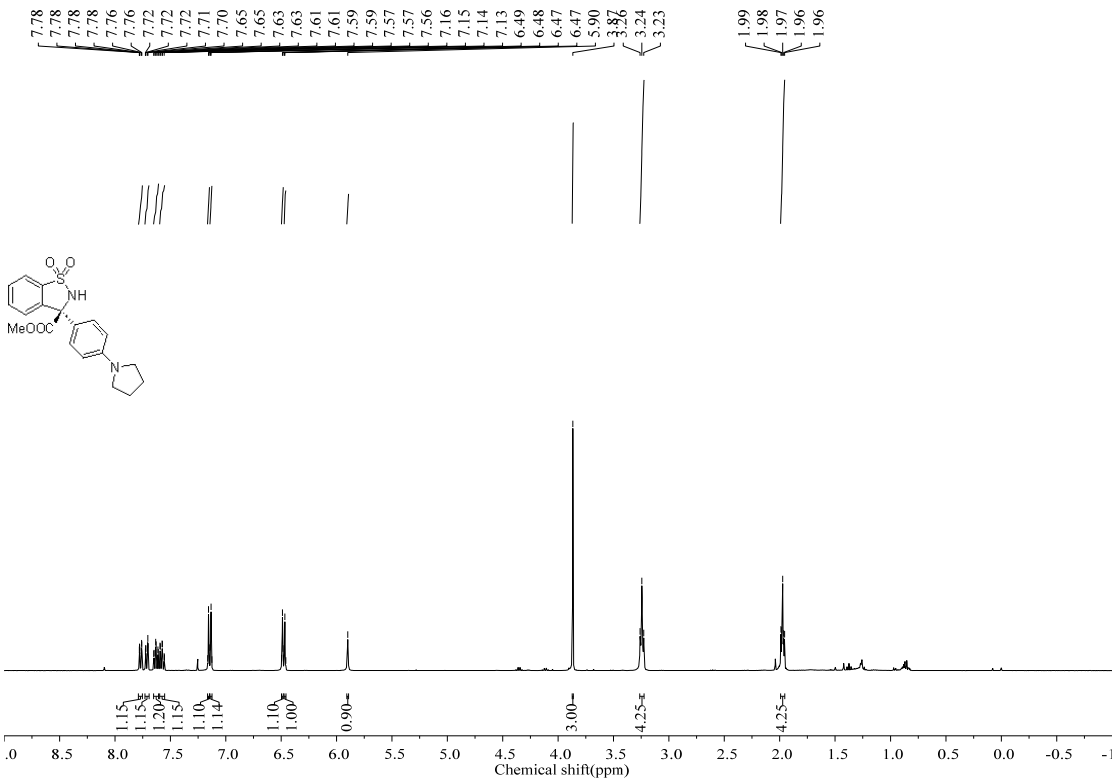
3aa ^{1}H NMR (400 MHz, $CDCl_3$)



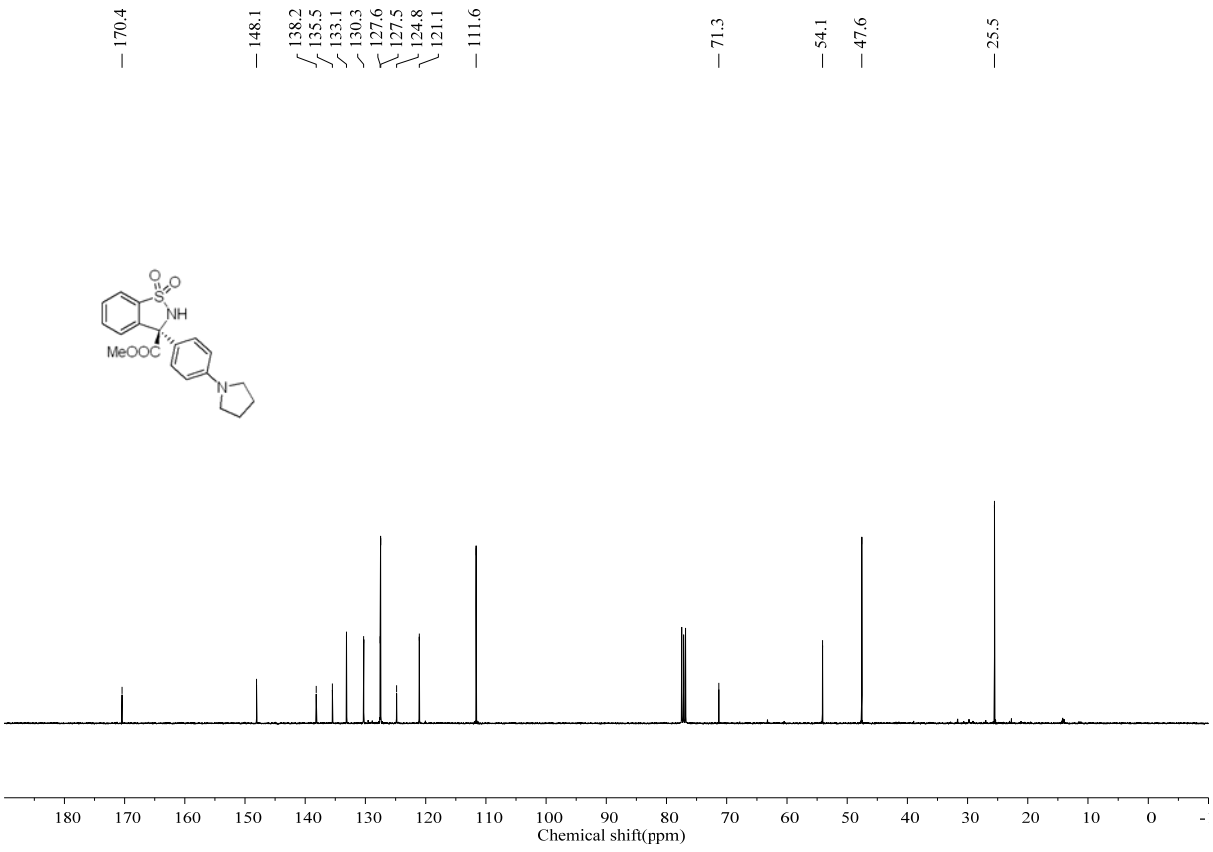
3aa ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



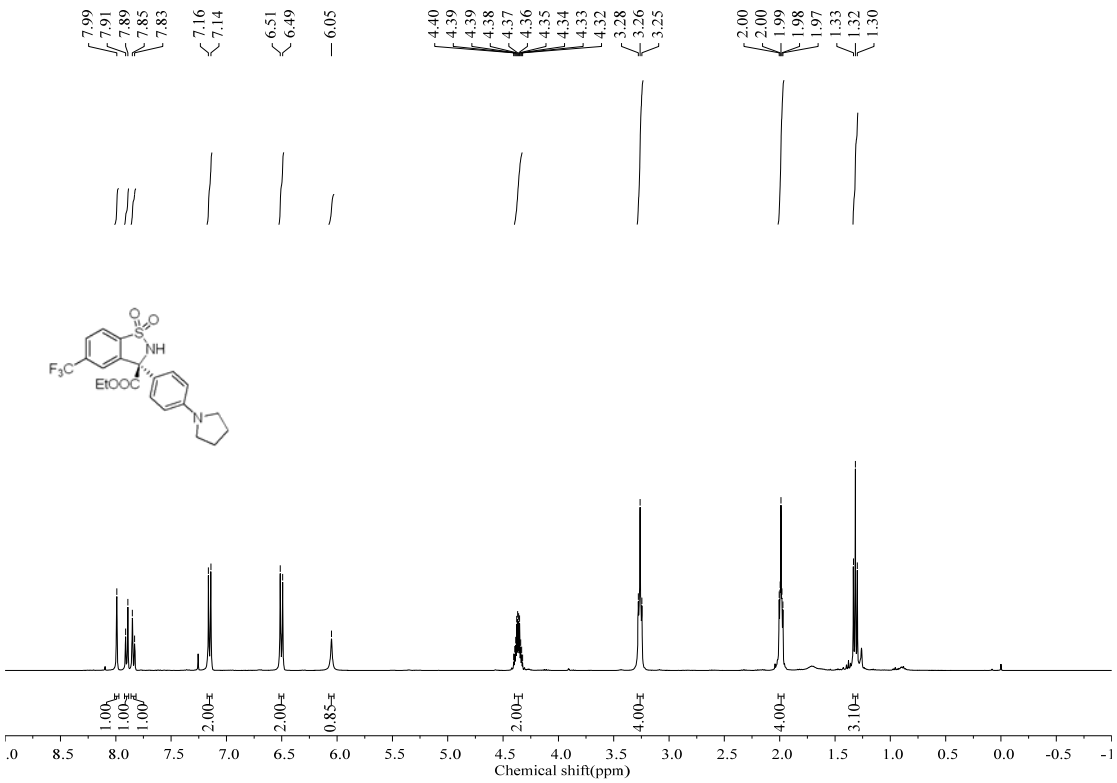
3ab ^{1}H NMR (400 MHz, $CDCl_3$)



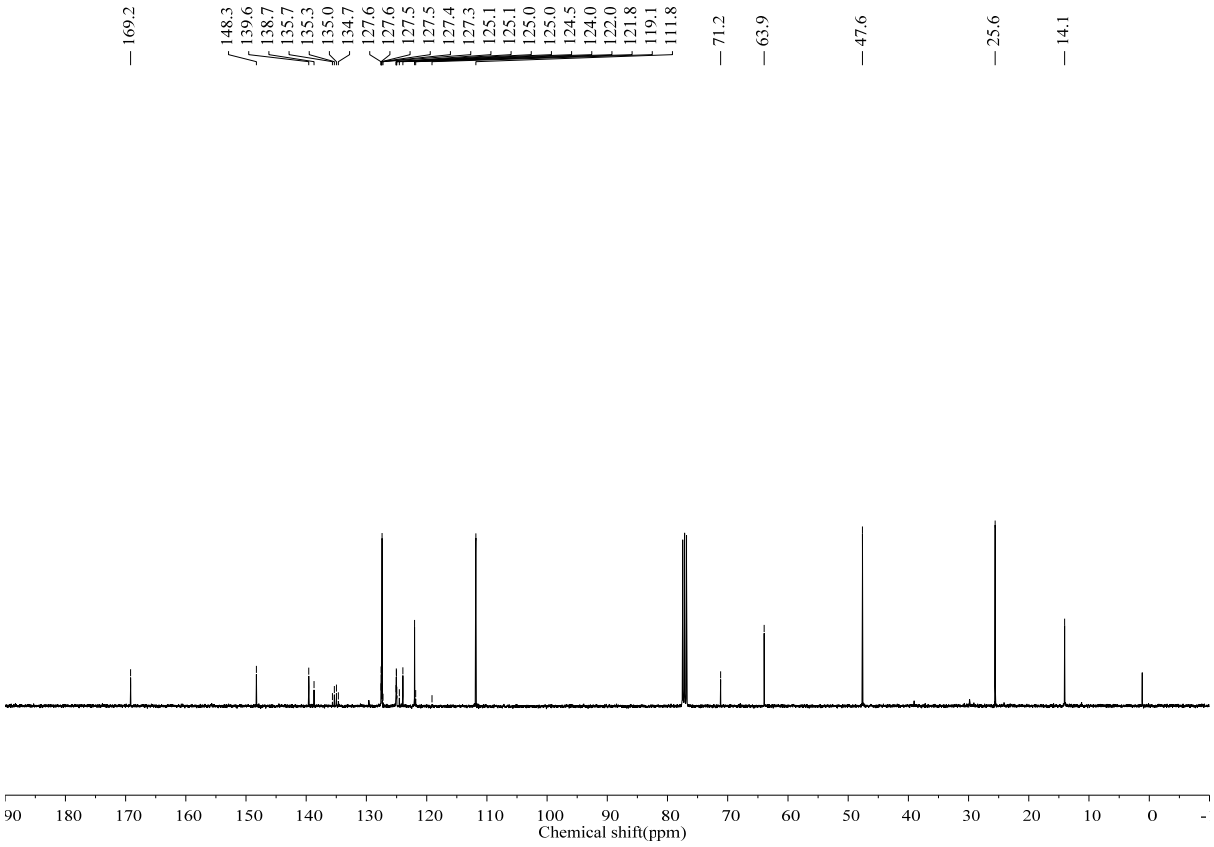
3ab ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



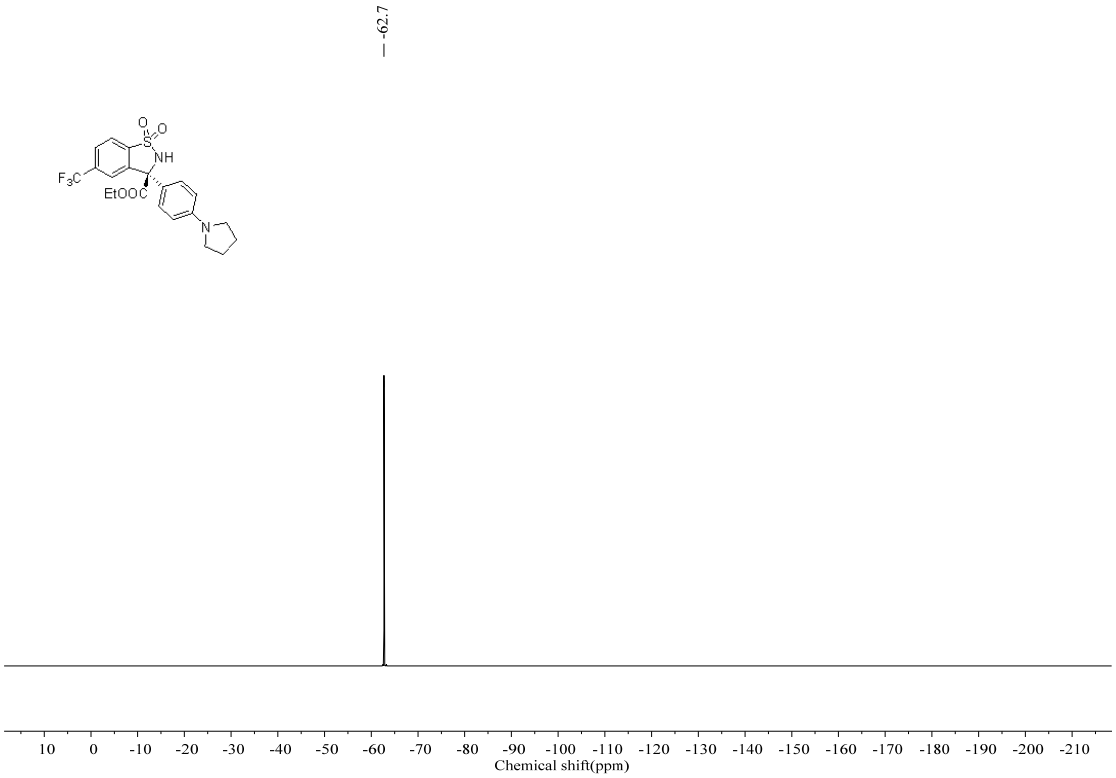
3ac ^{1}H NMR (400 MHz, $CDCl_3$)



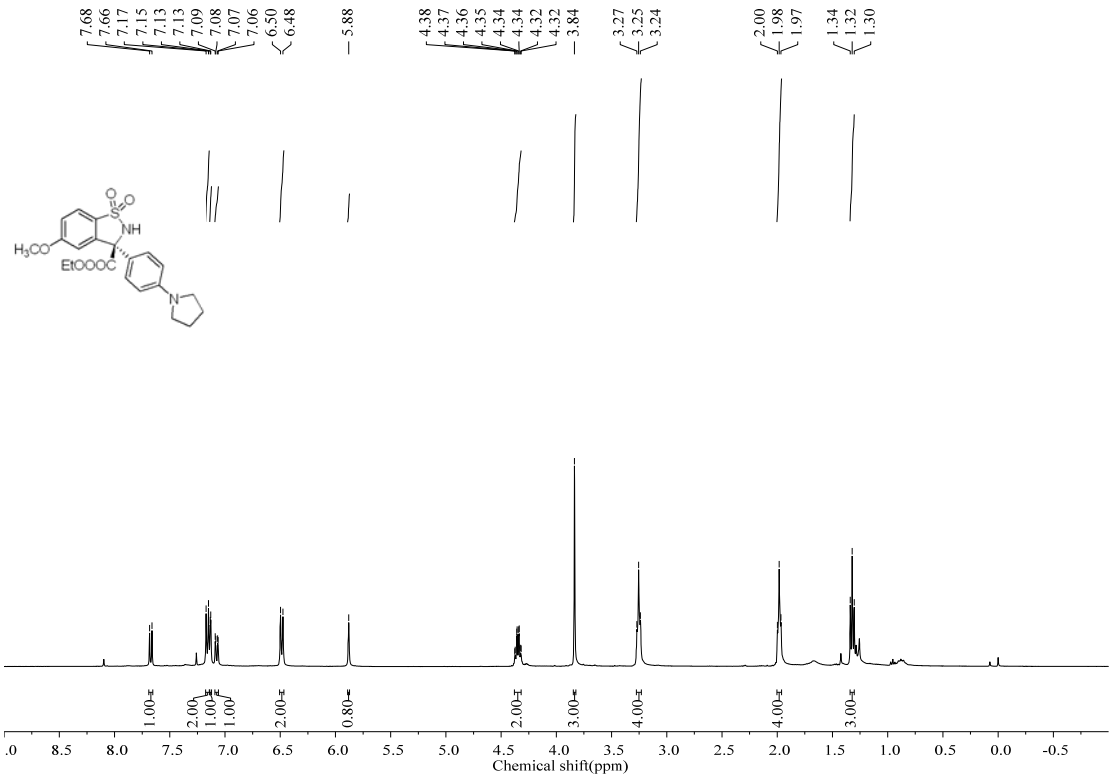
3ac ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



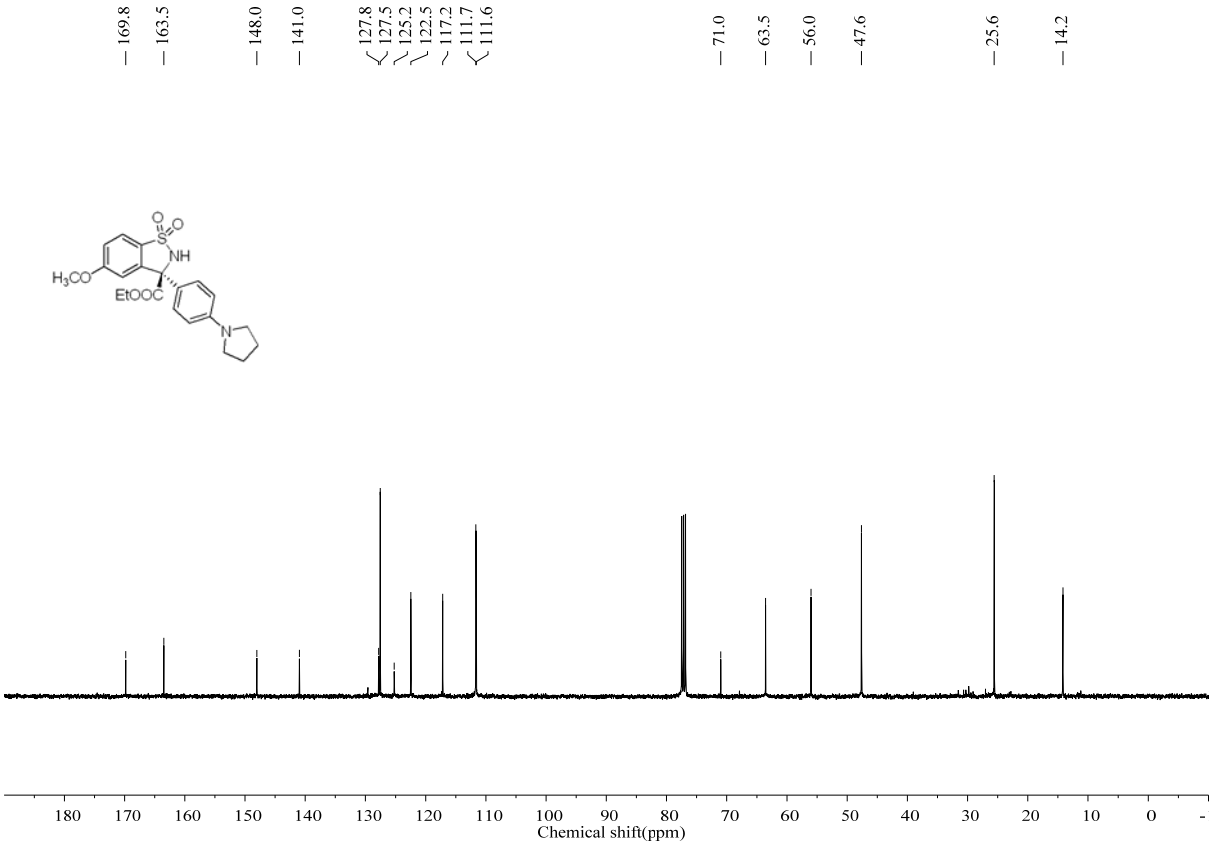
3ac ^{19}F NMR ($CDCl_3$)



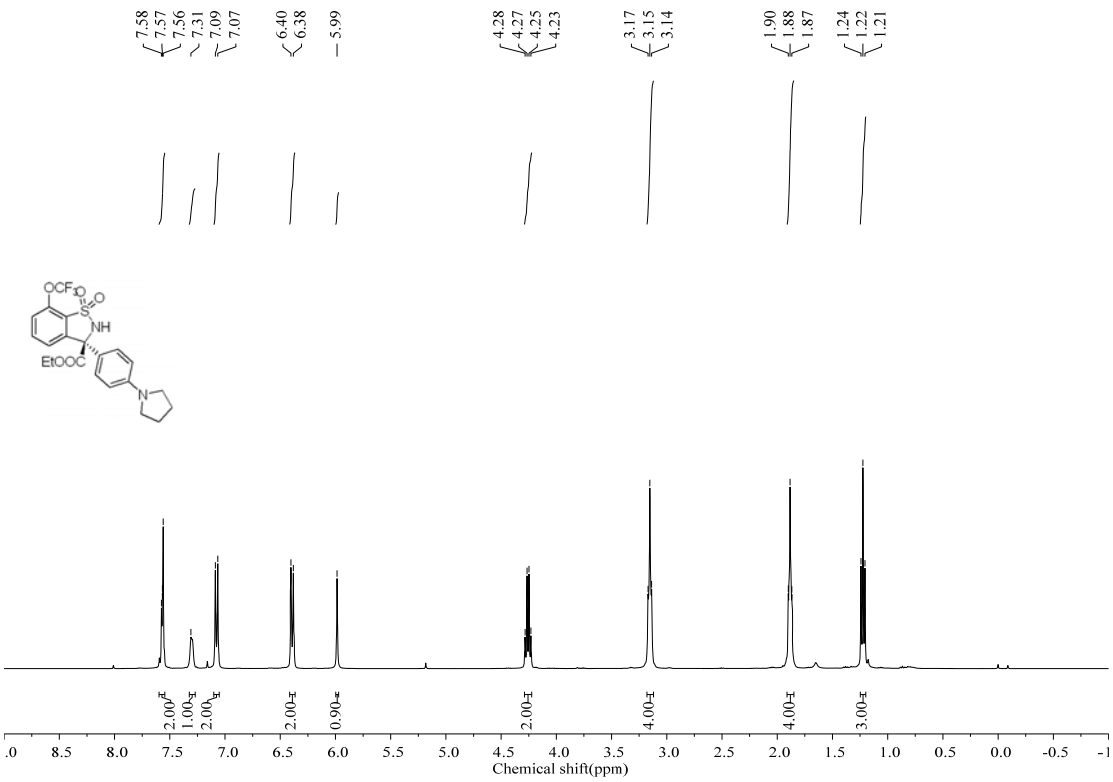
3ad ^{1}H NMR (400 MHz, $CDCl_3$)



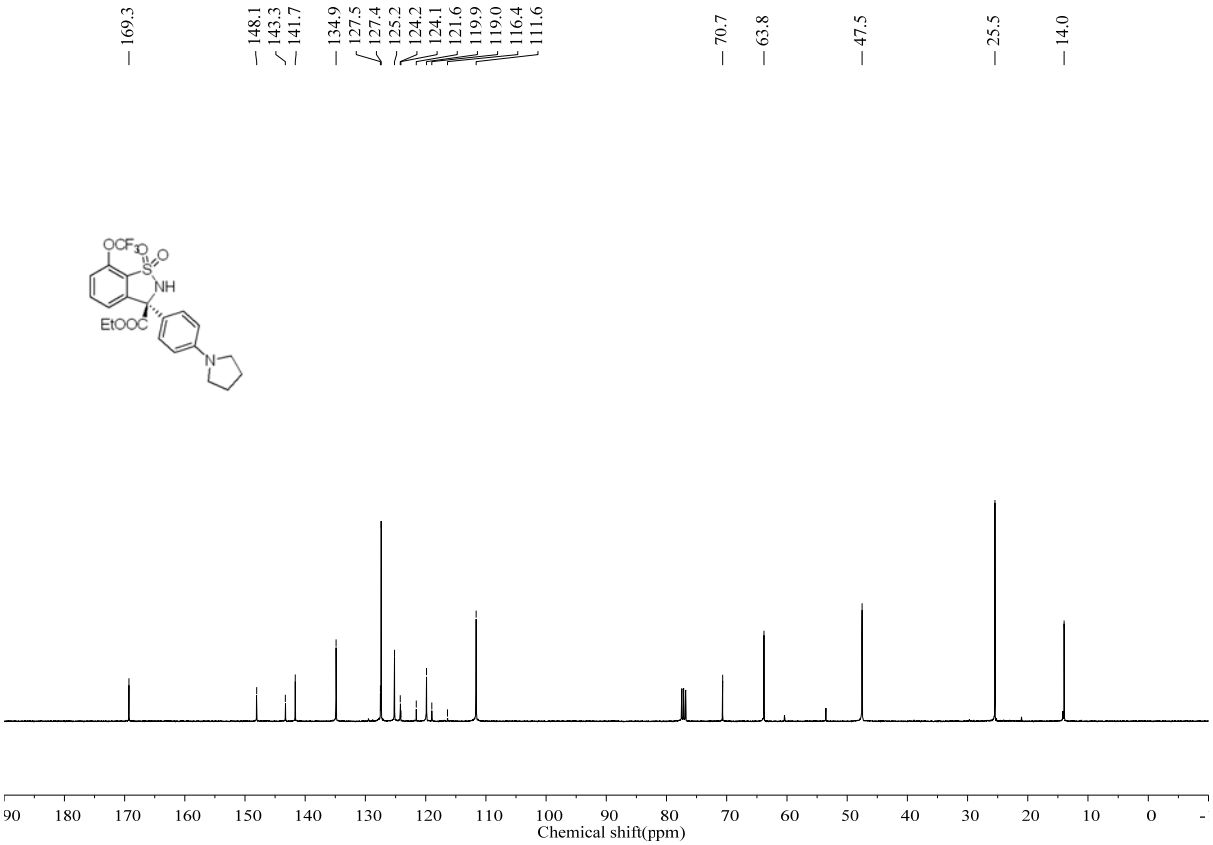
3ad ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



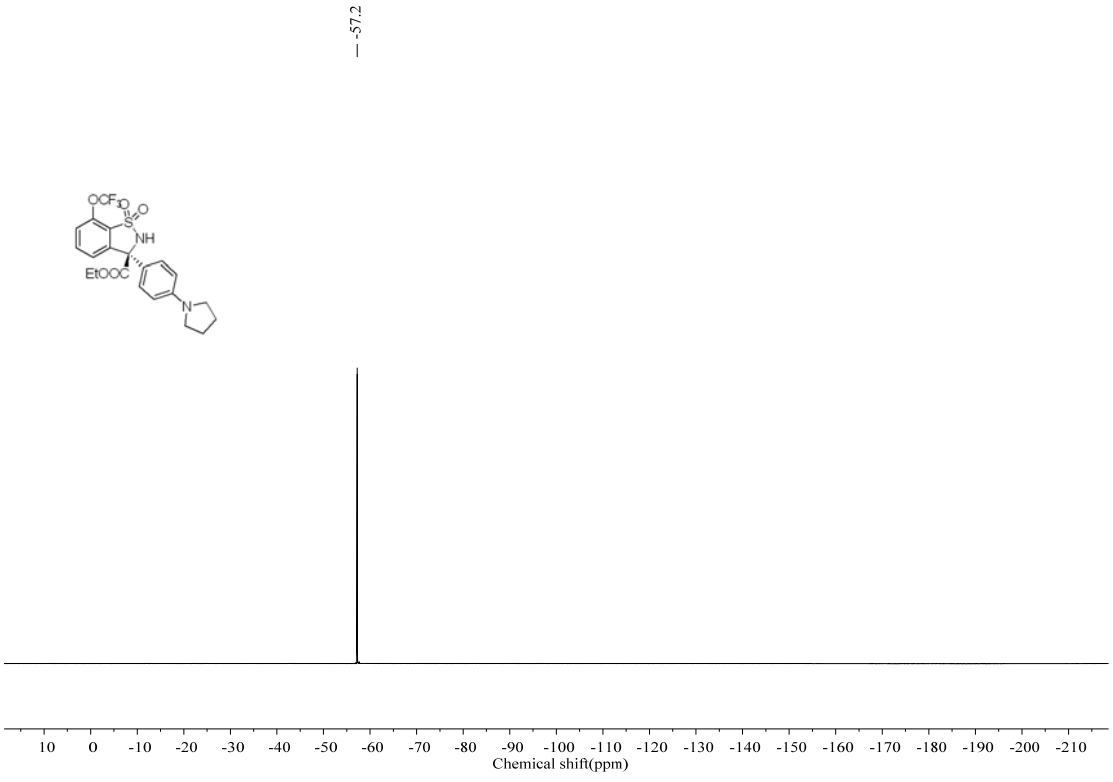
3ae ^{1}H NMR (400 MHz, $CDCl_3$)



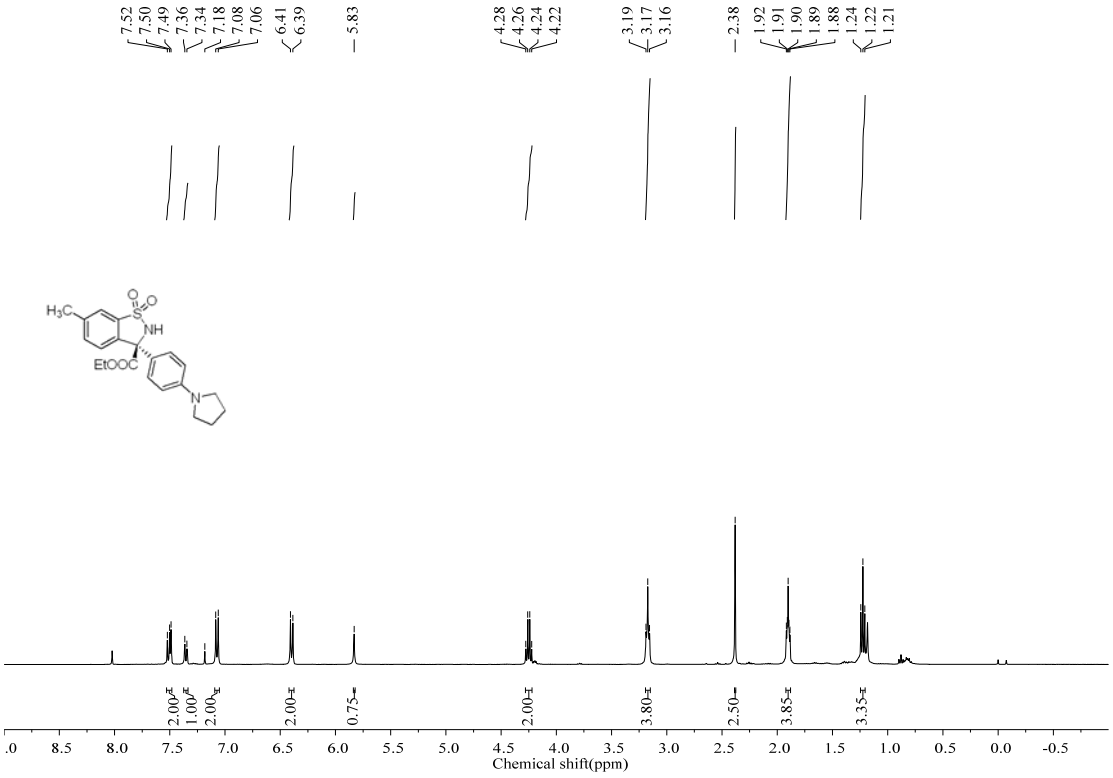
3ae ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



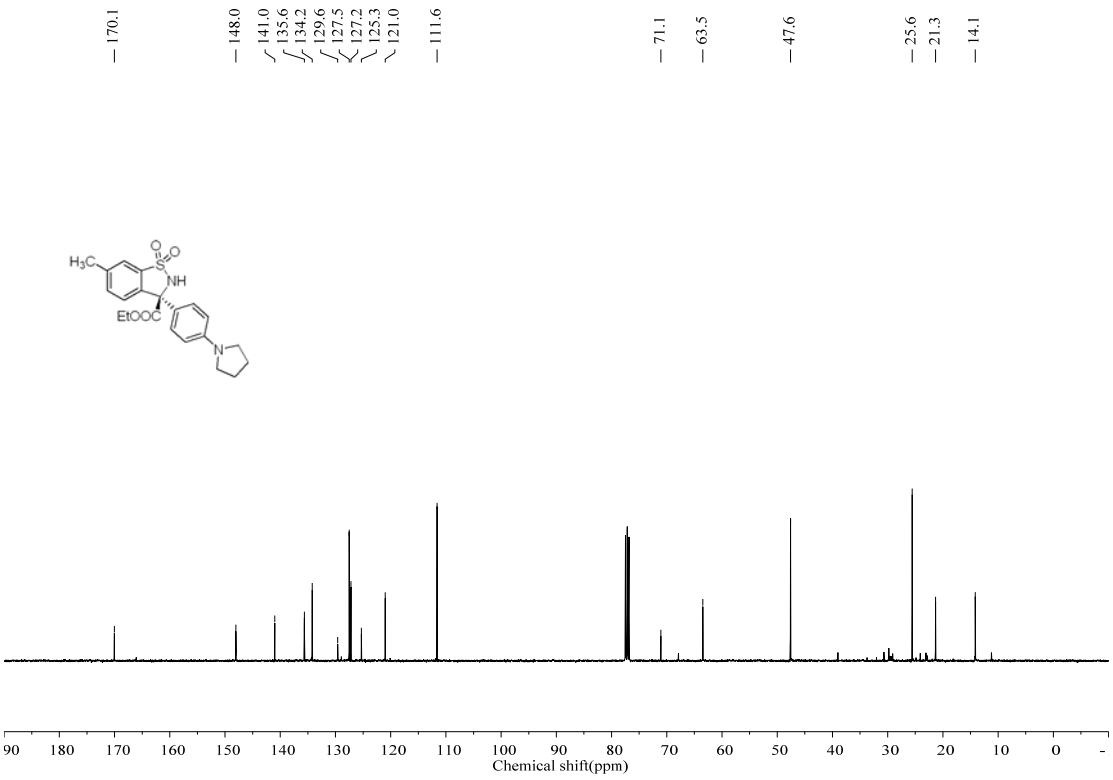
3ae ^{19}F NMR ($CDCl_3$)



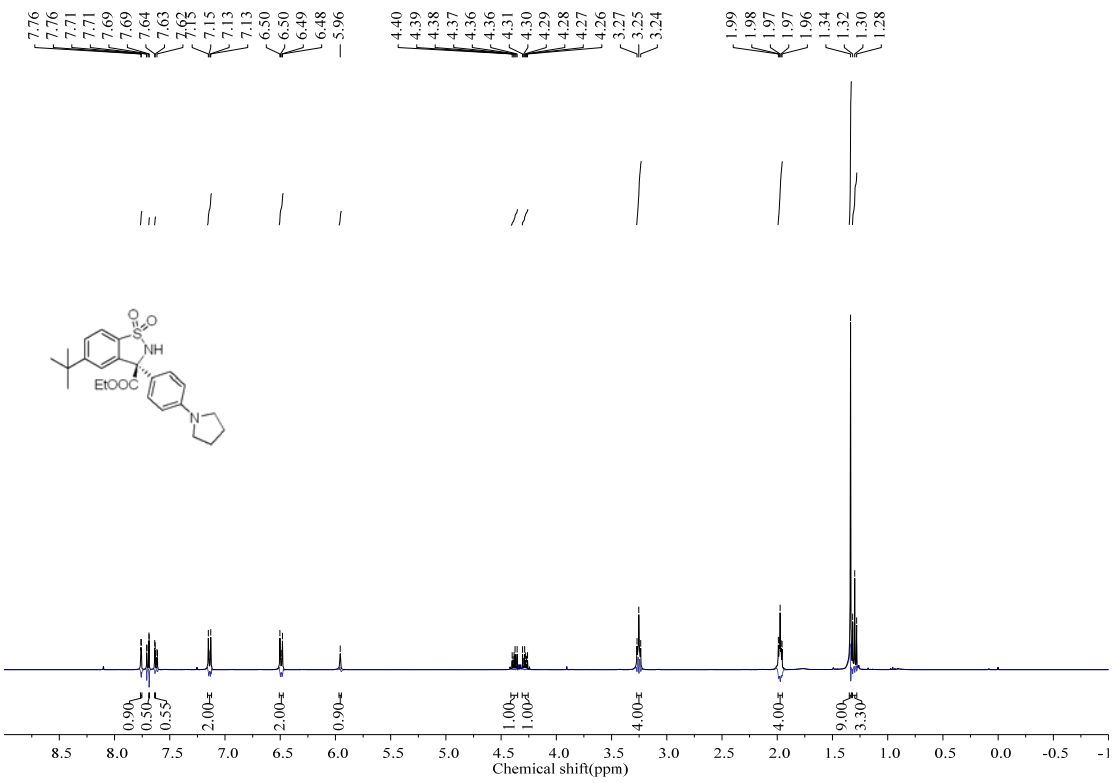
3af ^{1}H NMR (400 MHz, $CDCl_3$)



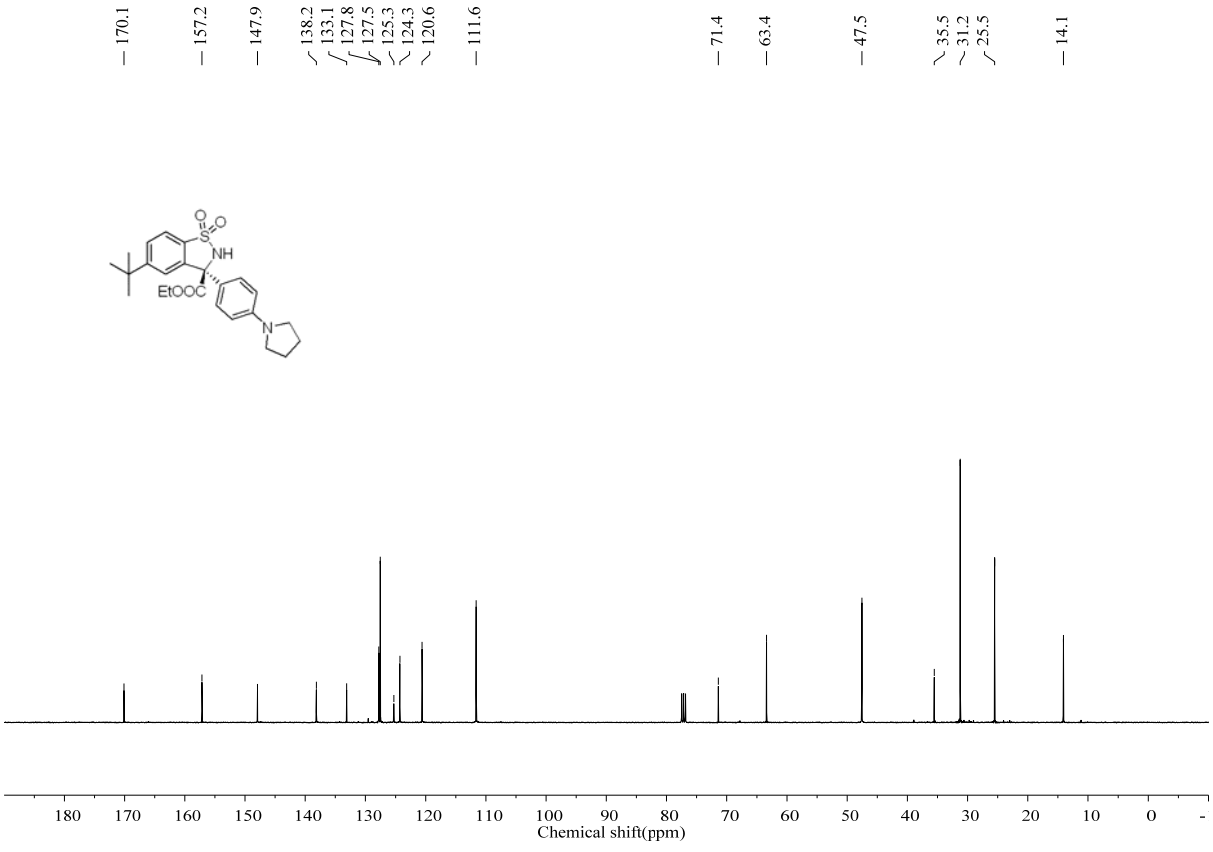
3af ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



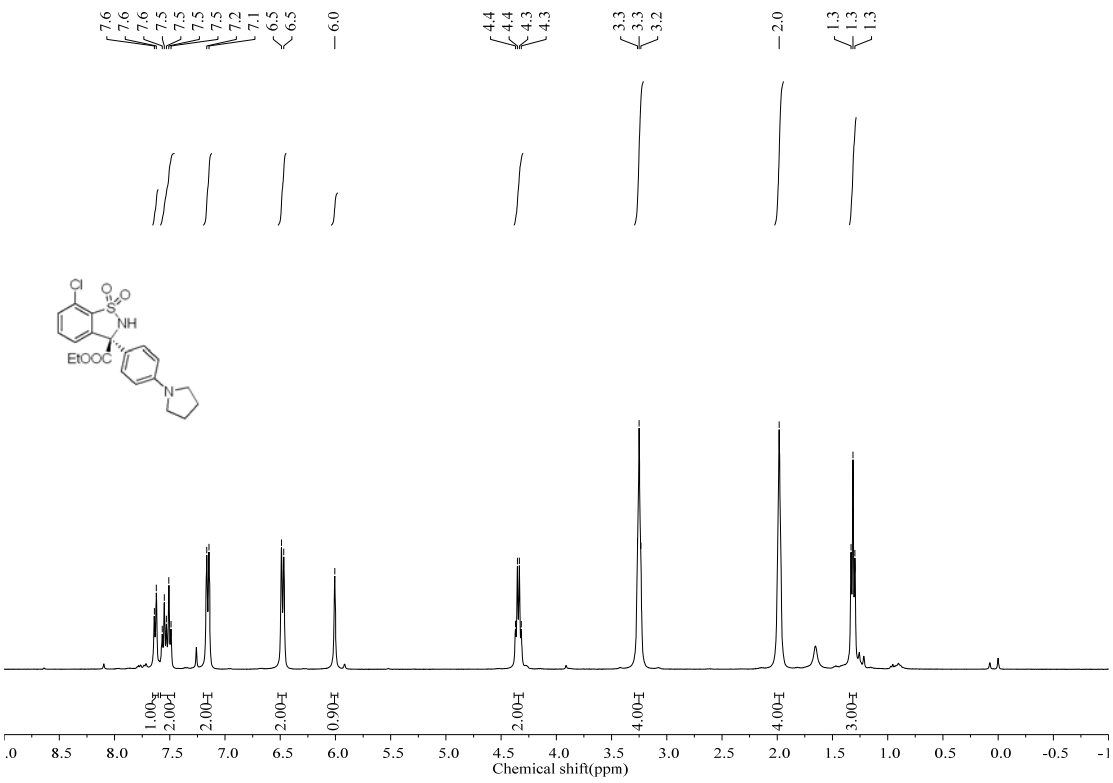
3ag ^{1}H NMR (400 MHz, $CDCl_3$)



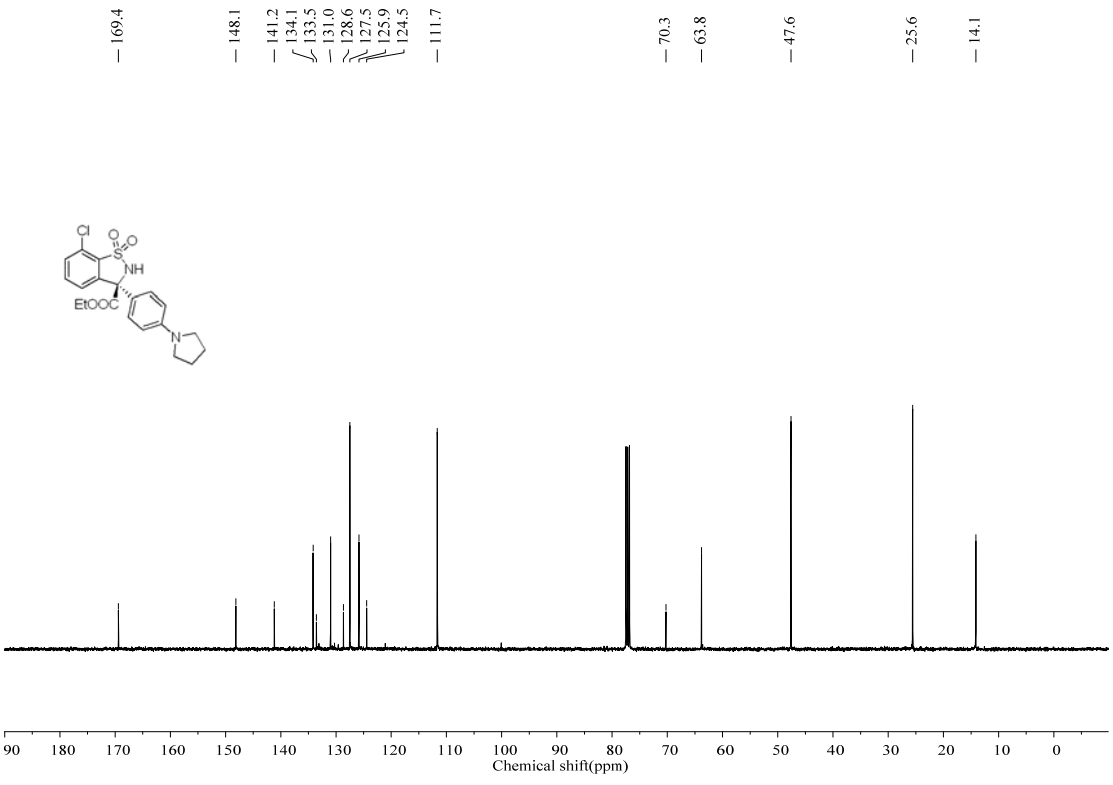
3ag ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



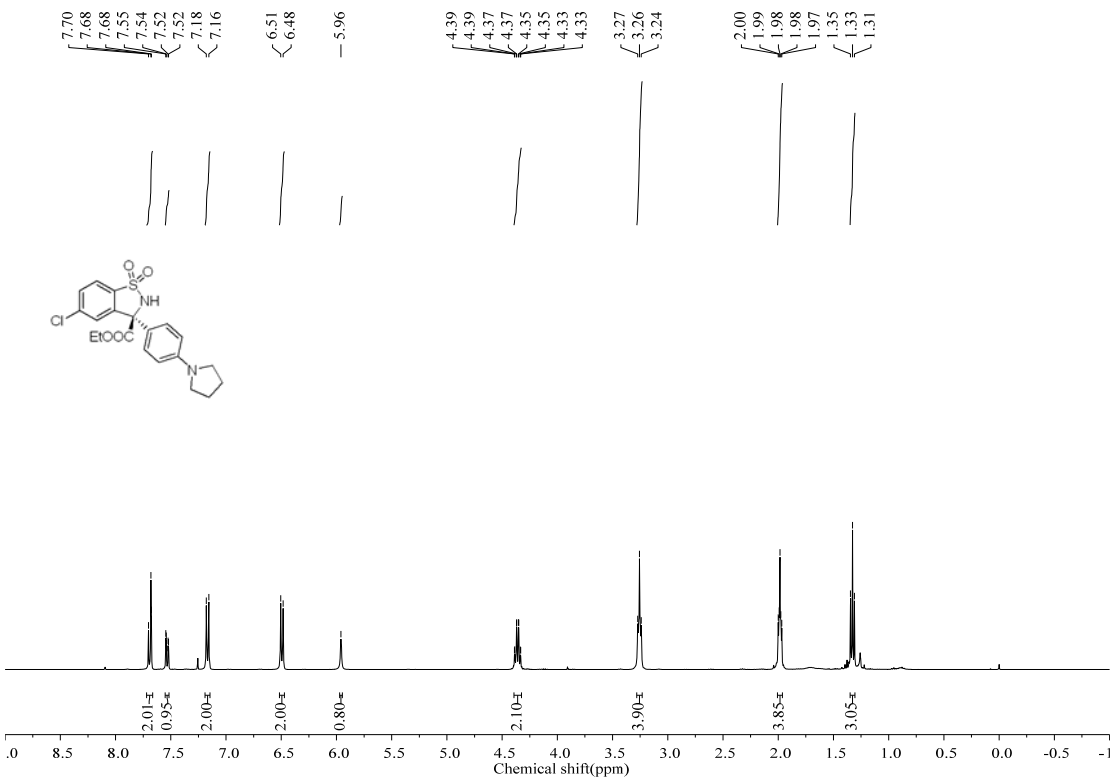
3ah ^{1}H NMR (400 MHz, $CDCl_3$)



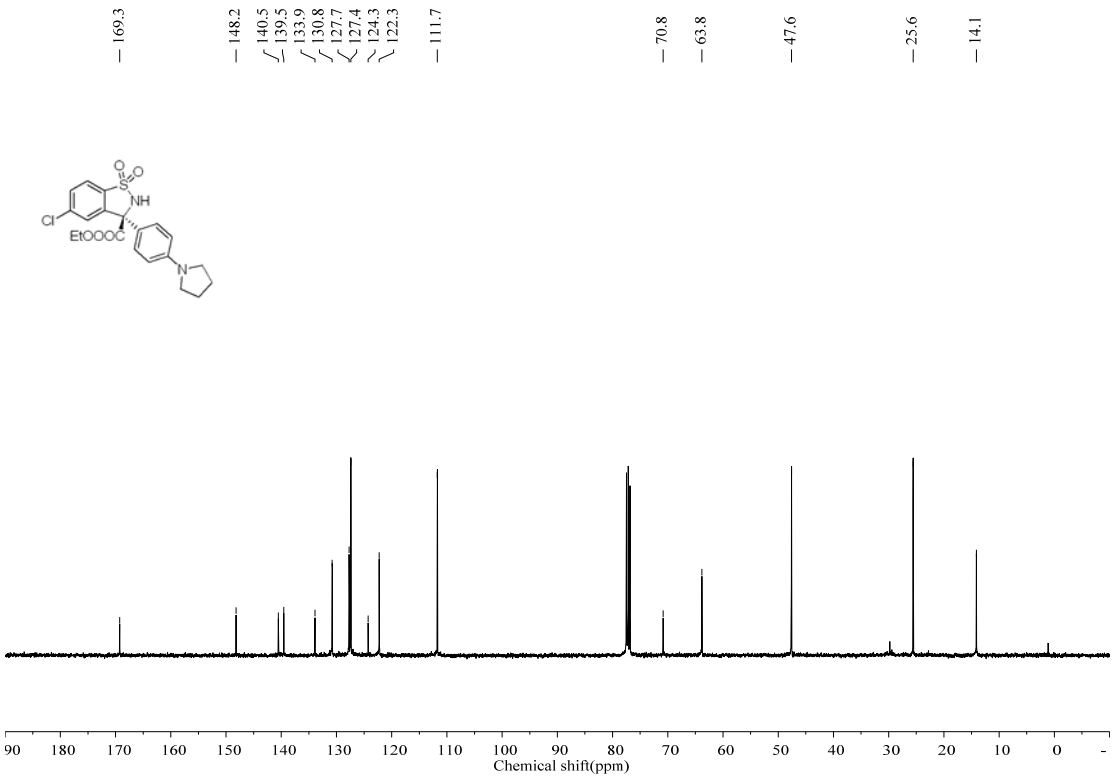
3ah ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



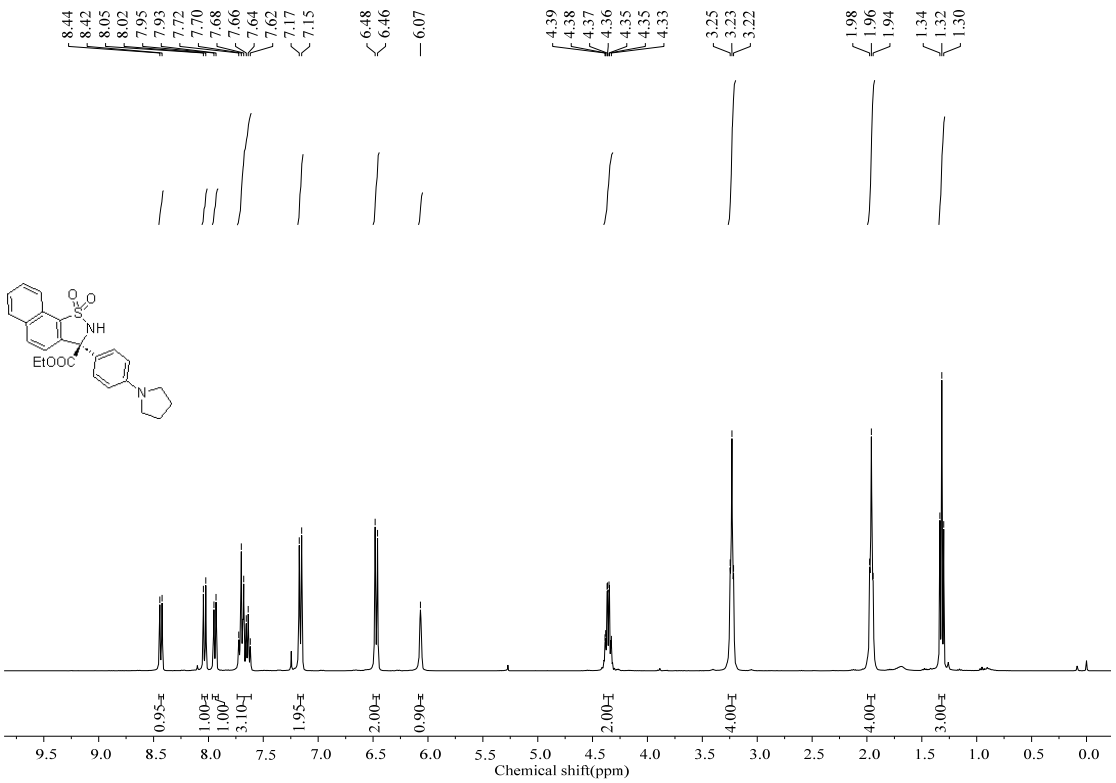
3ai ^{1}H NMR (400 MHz, $CDCl_3$)



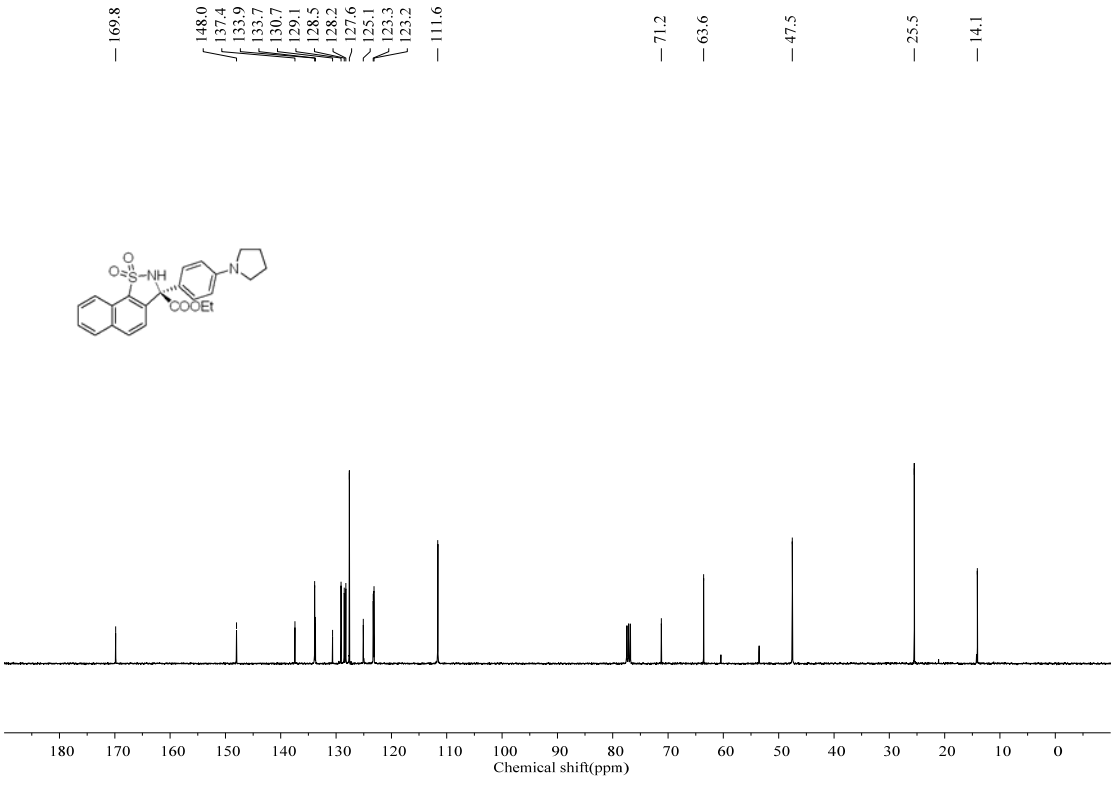
3ai ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



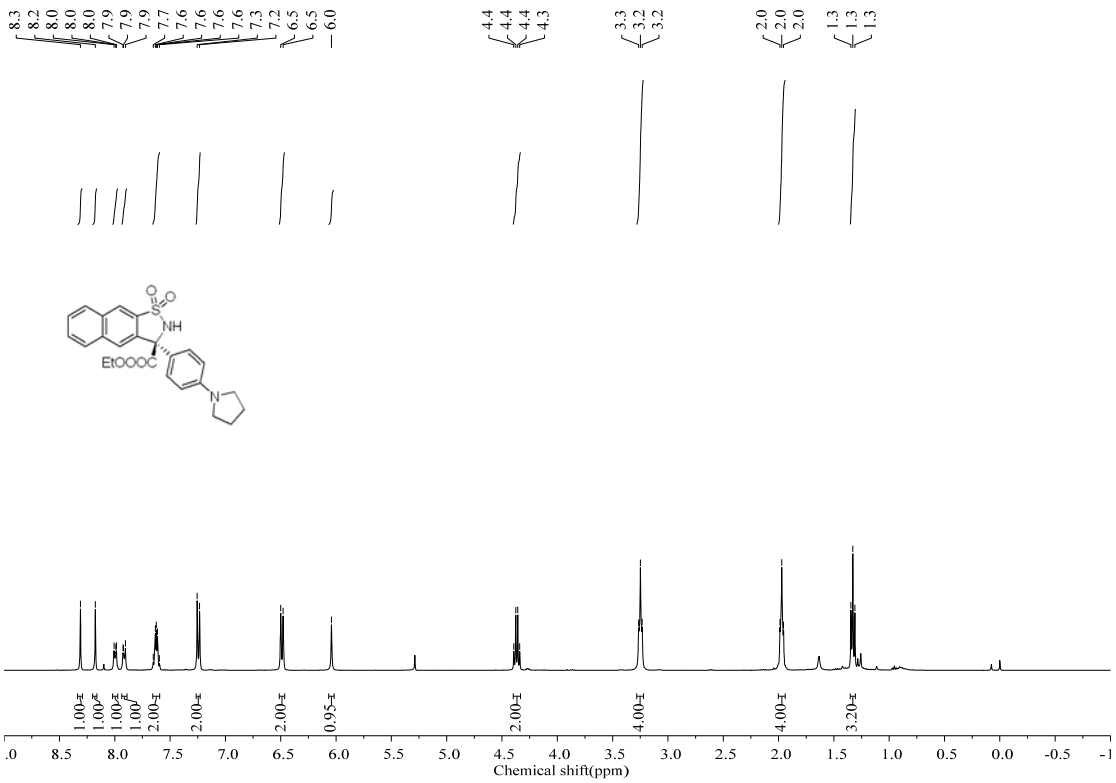
3aj ^{1}H NMR (400 MHz, $CDCl_3$)



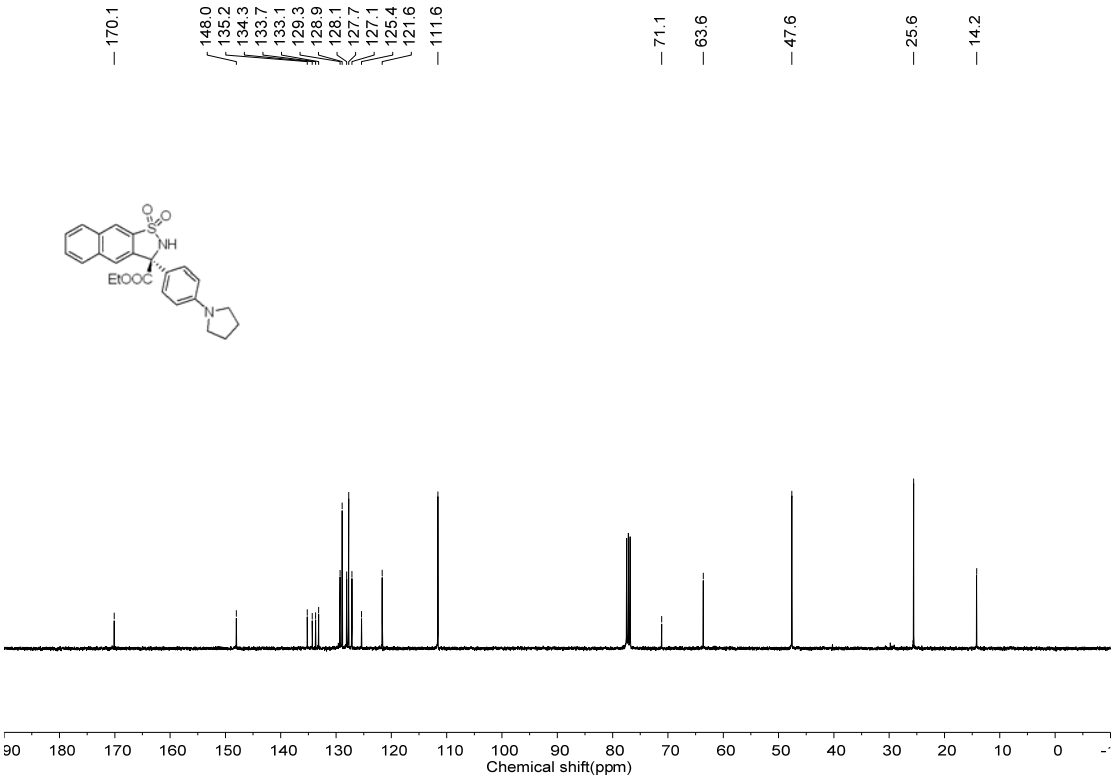
3aj ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



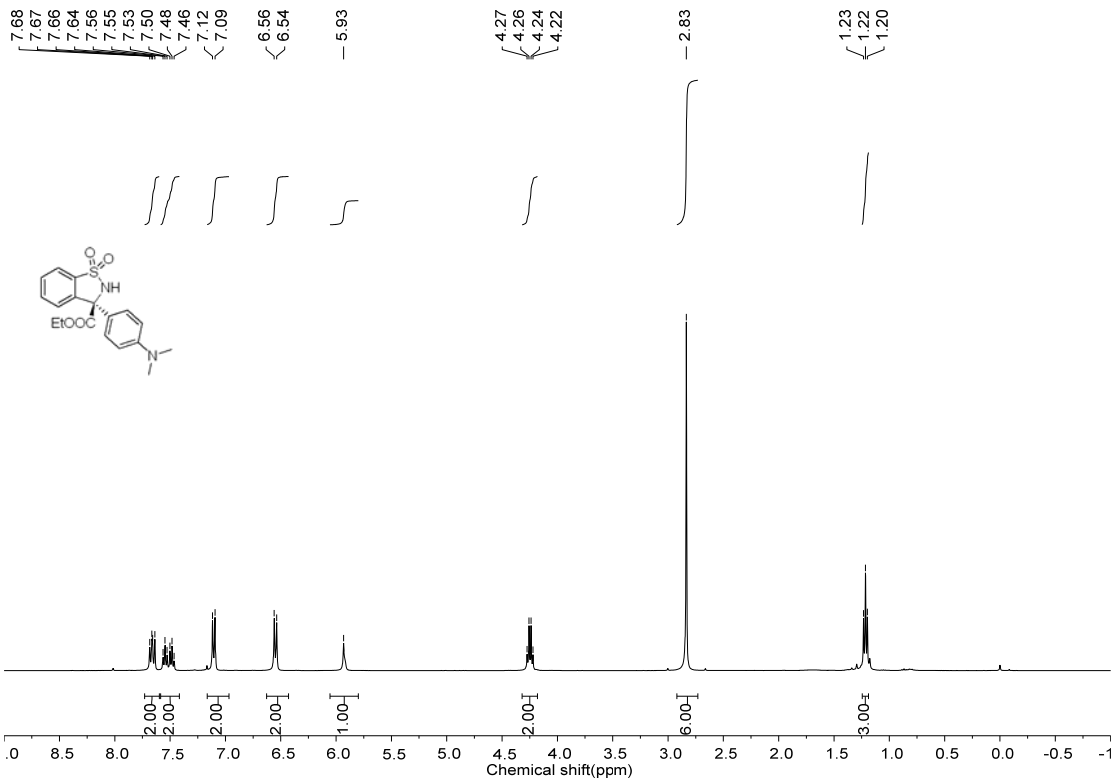
3ak ^{1}H NMR (400 MHz, $CDCl_3$)



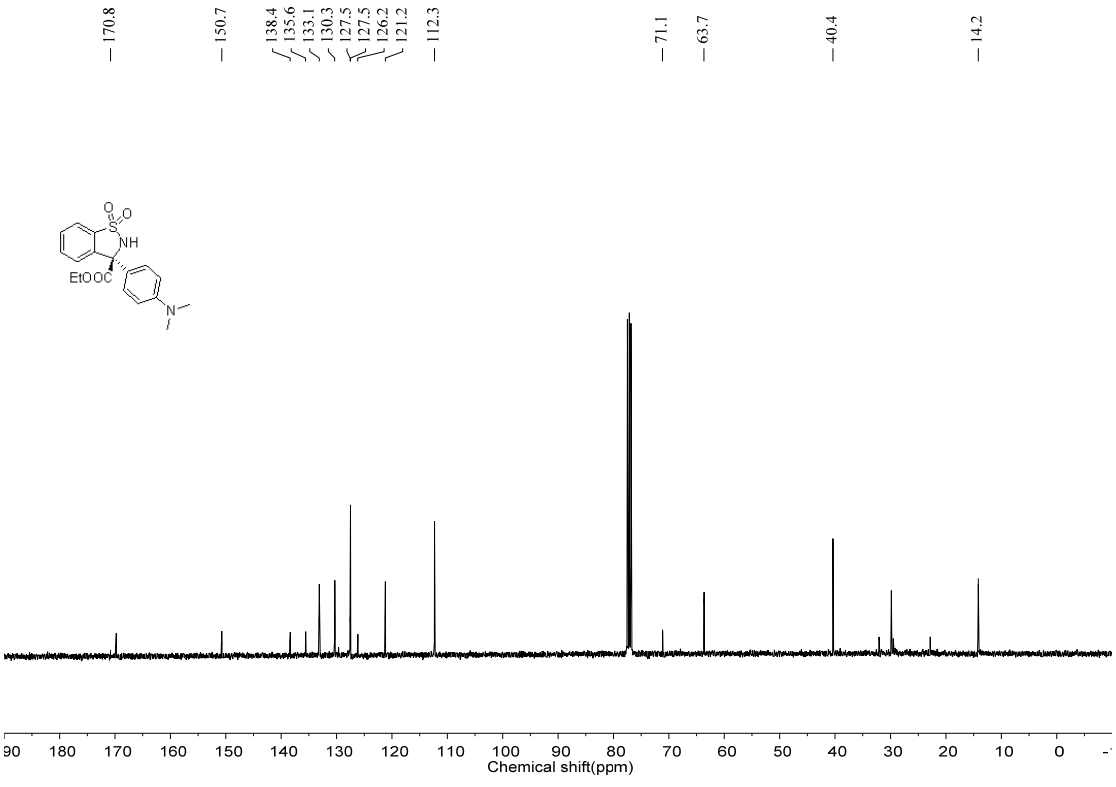
3ak ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



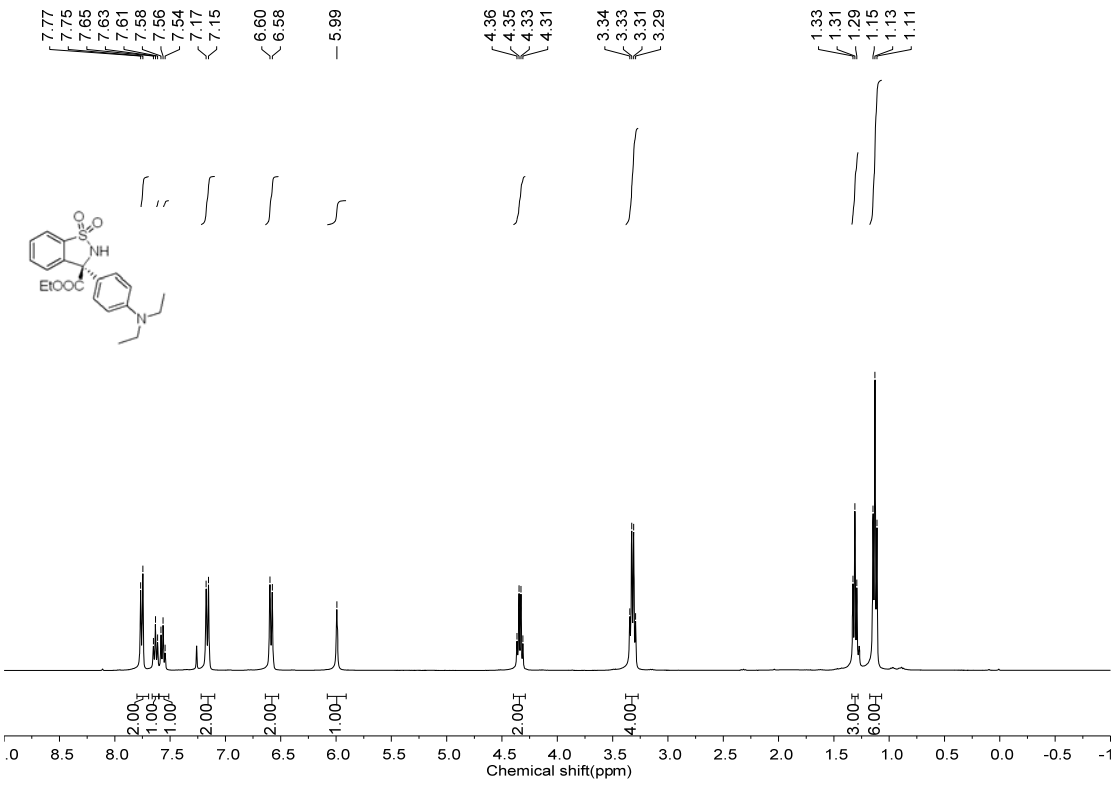
3ba ^{1}H NMR (400 MHz, $CDCl_3$)



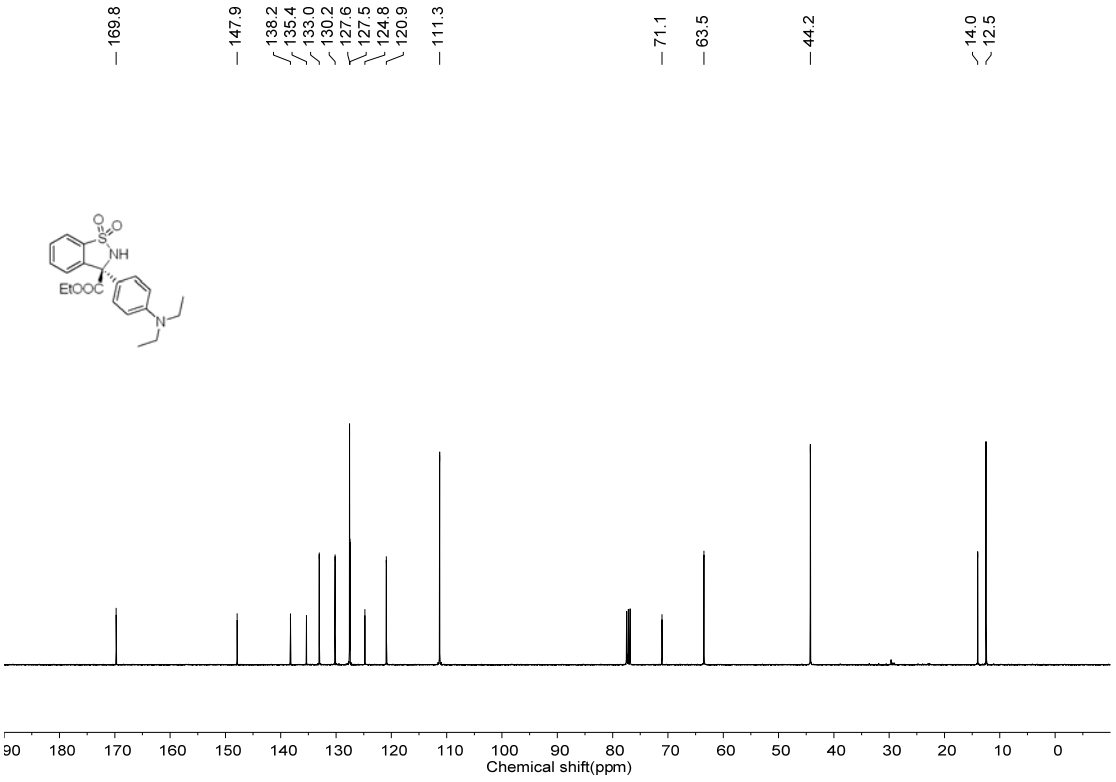
3ba ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



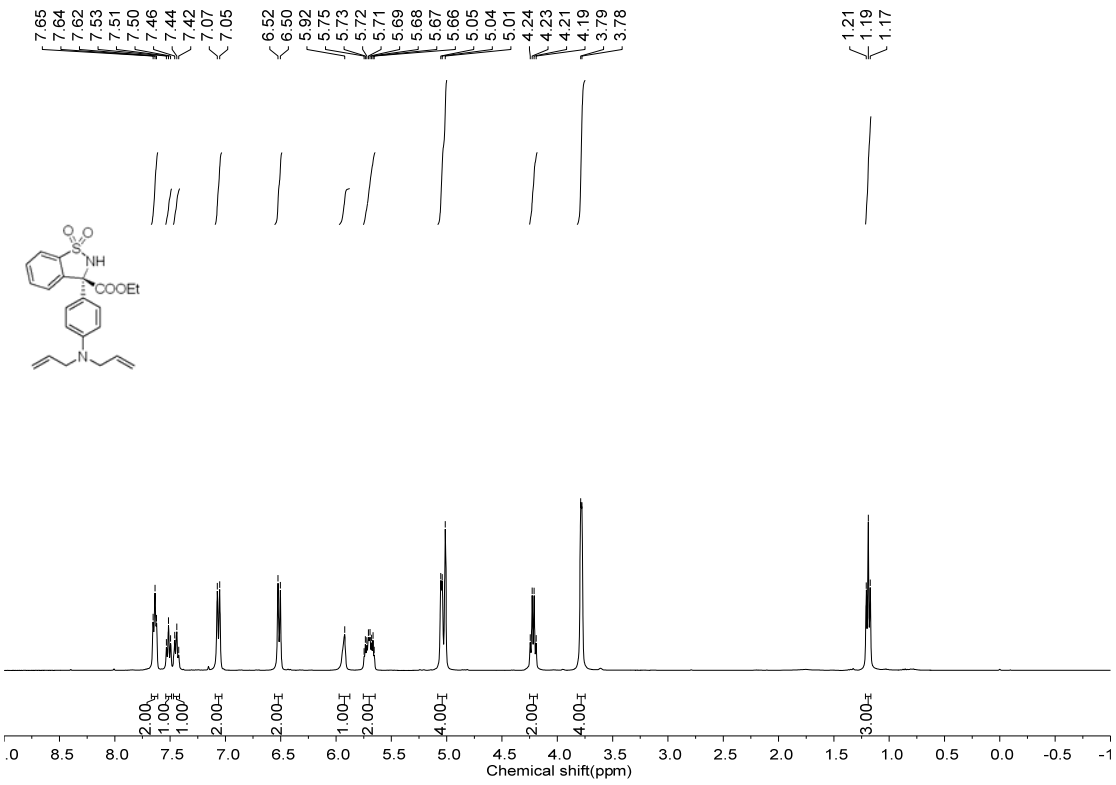
3bb ^{1}H NMR (400 MHz, $CDCl_3$)



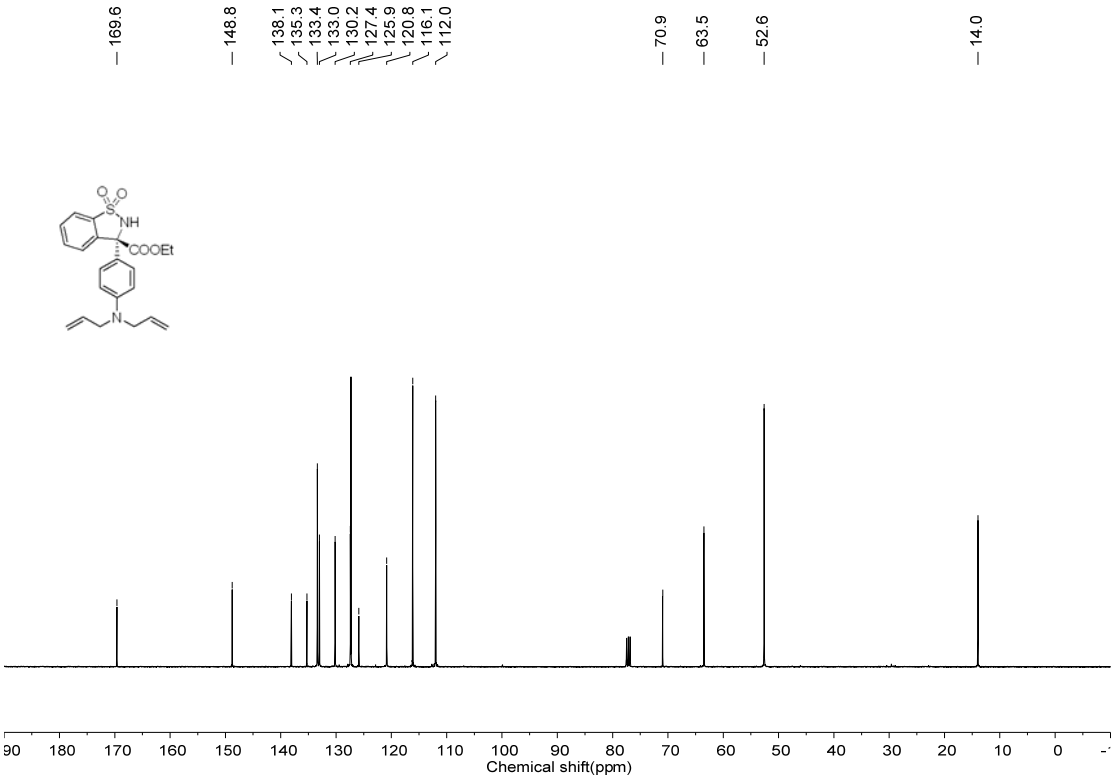
3bb ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



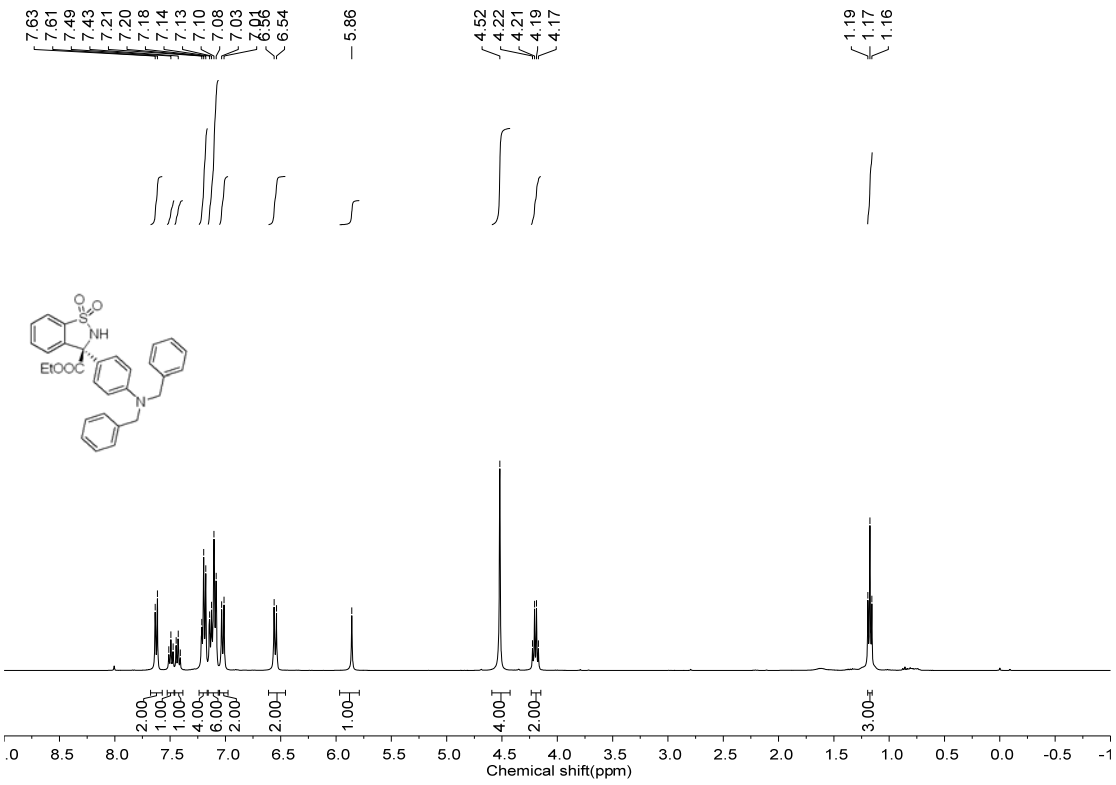
3bc ^{1}H NMR (400 MHz, $CDCl_3$)



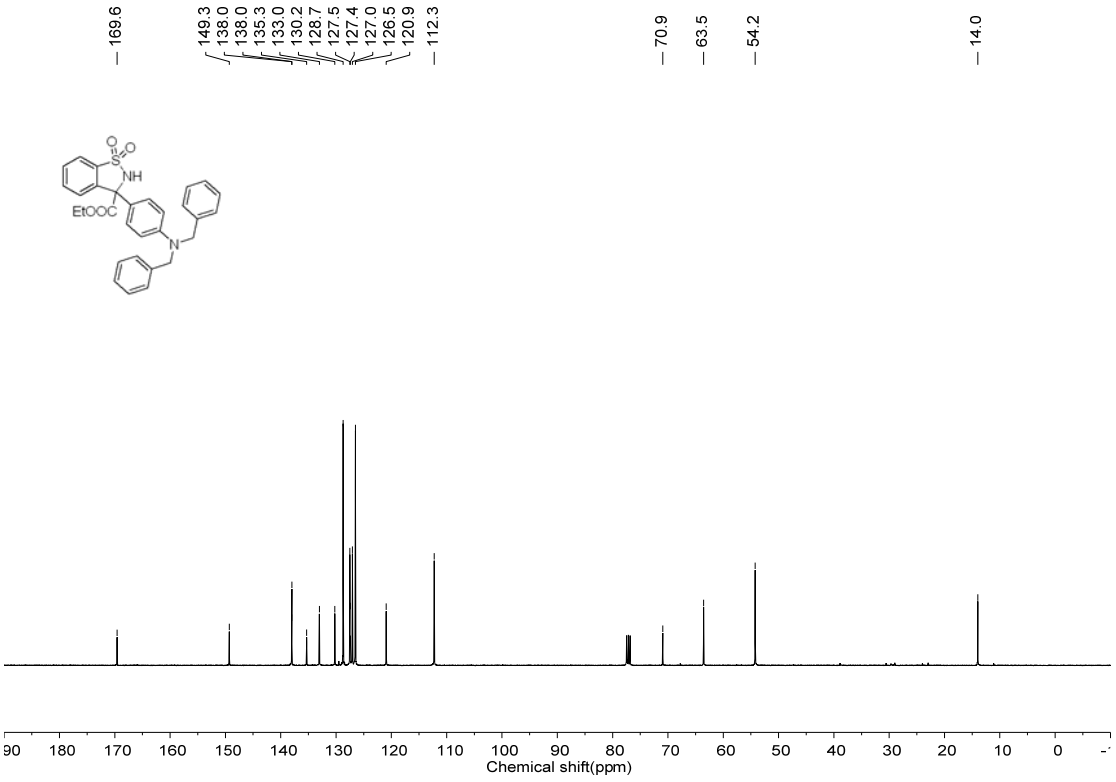
3bc ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



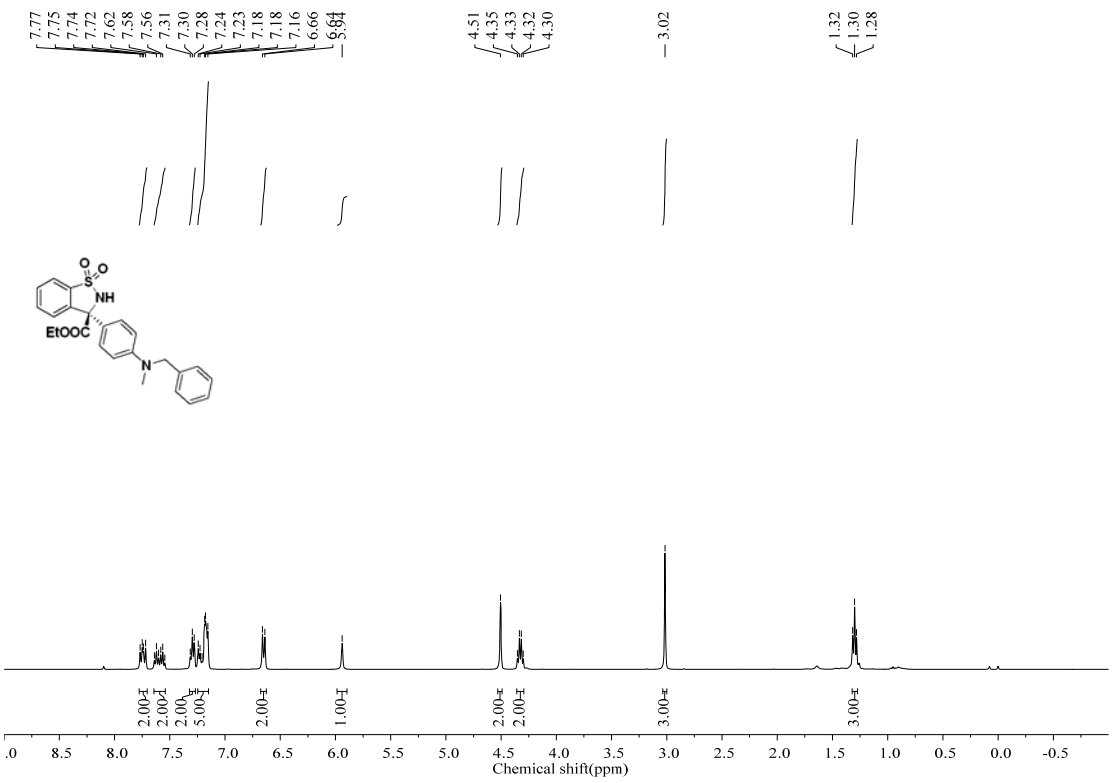
3bd ^{1}H NMR (400 MHz, $CDCl_3$)



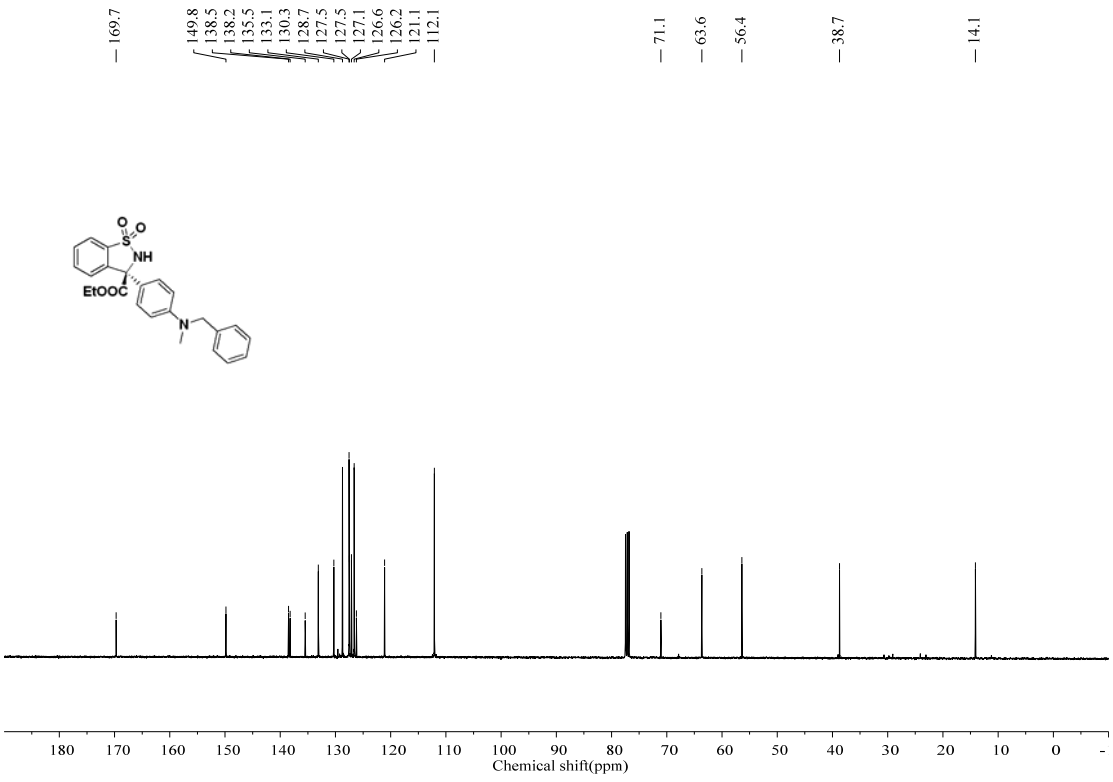
3bd ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



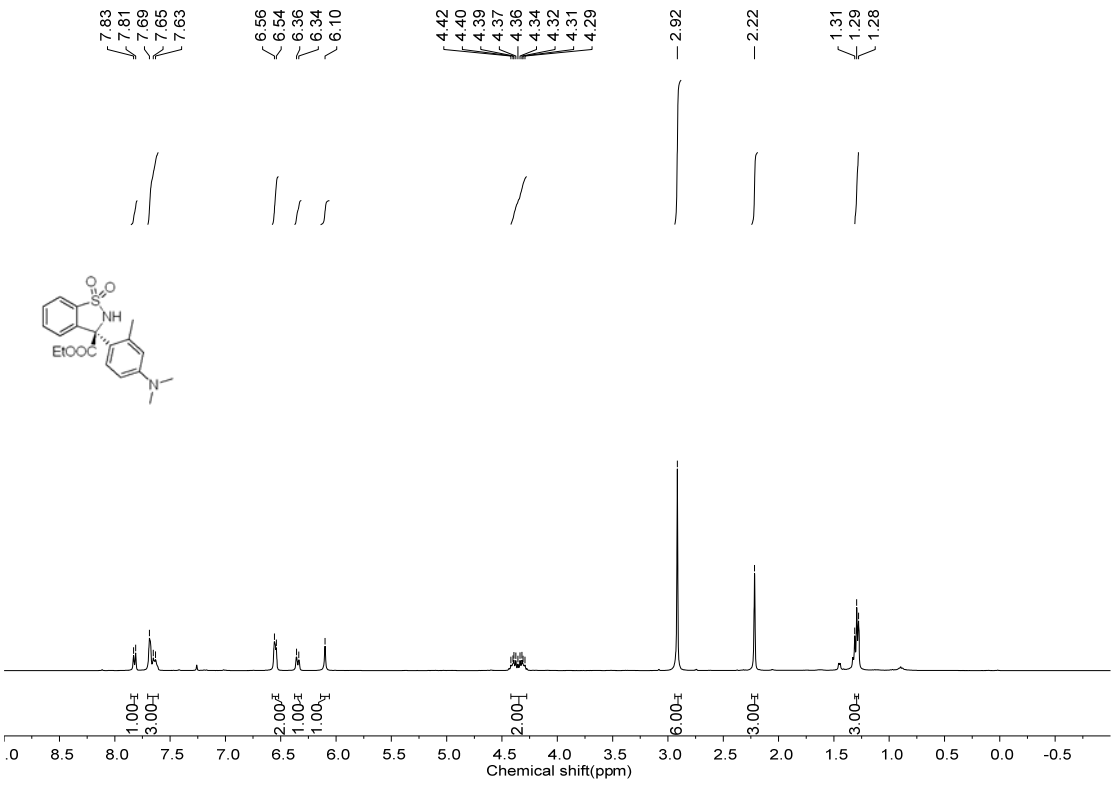
3be ^{1}H NMR (400 MHz, $CDCl_3$)



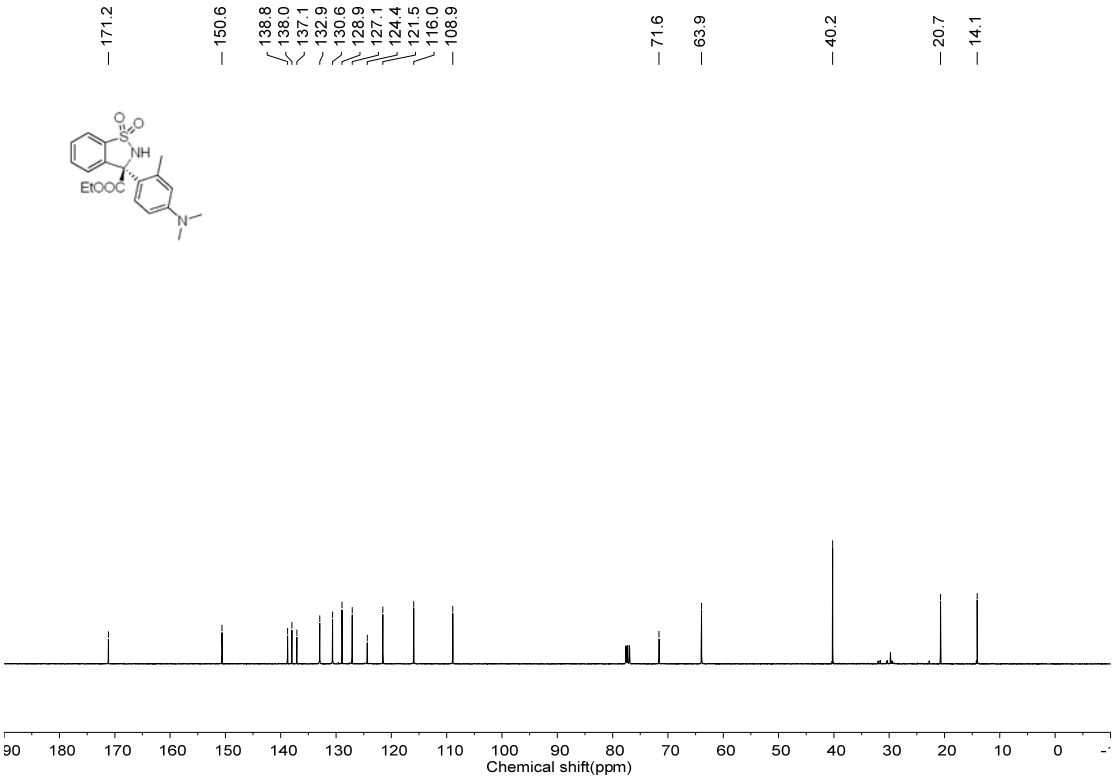
3be ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



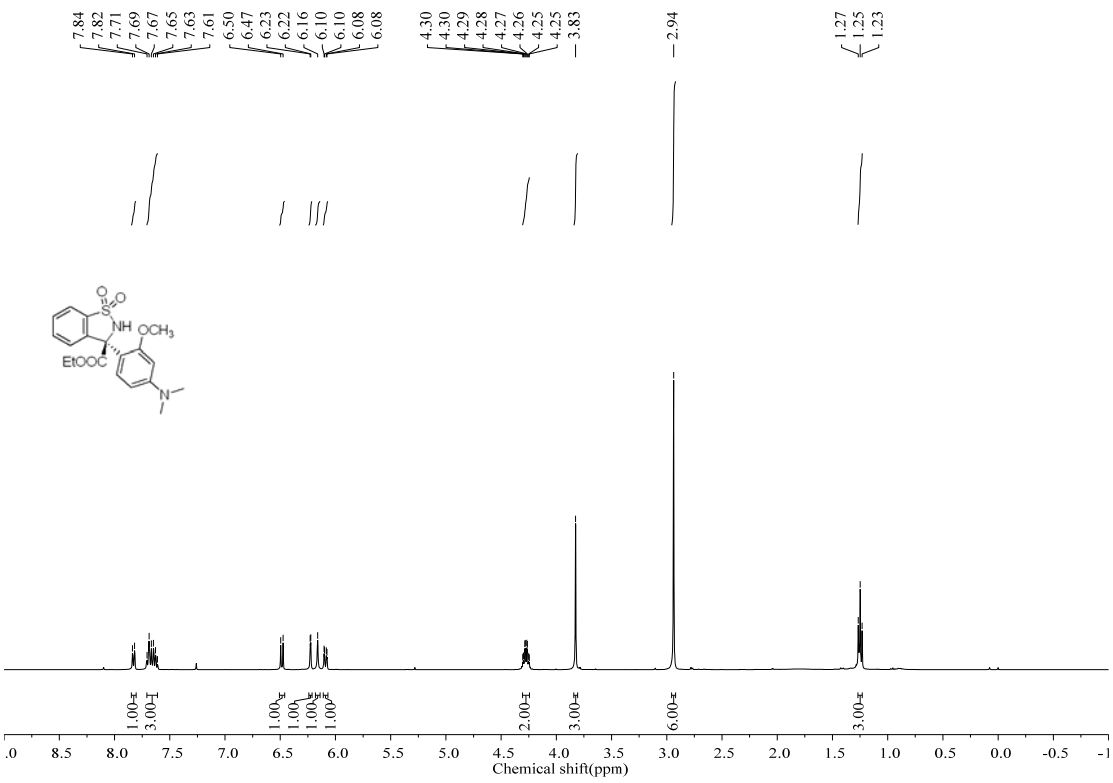
3bf ^{1}H NMR (400 MHz, $CDCl_3$)



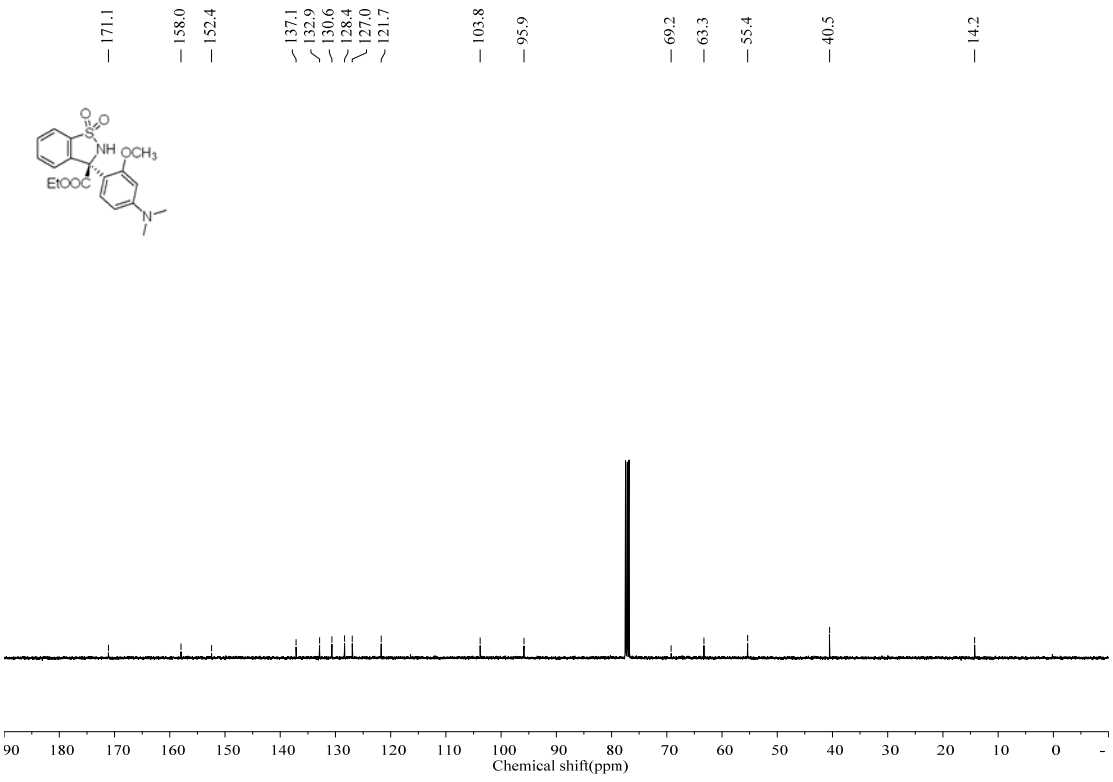
3bf ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



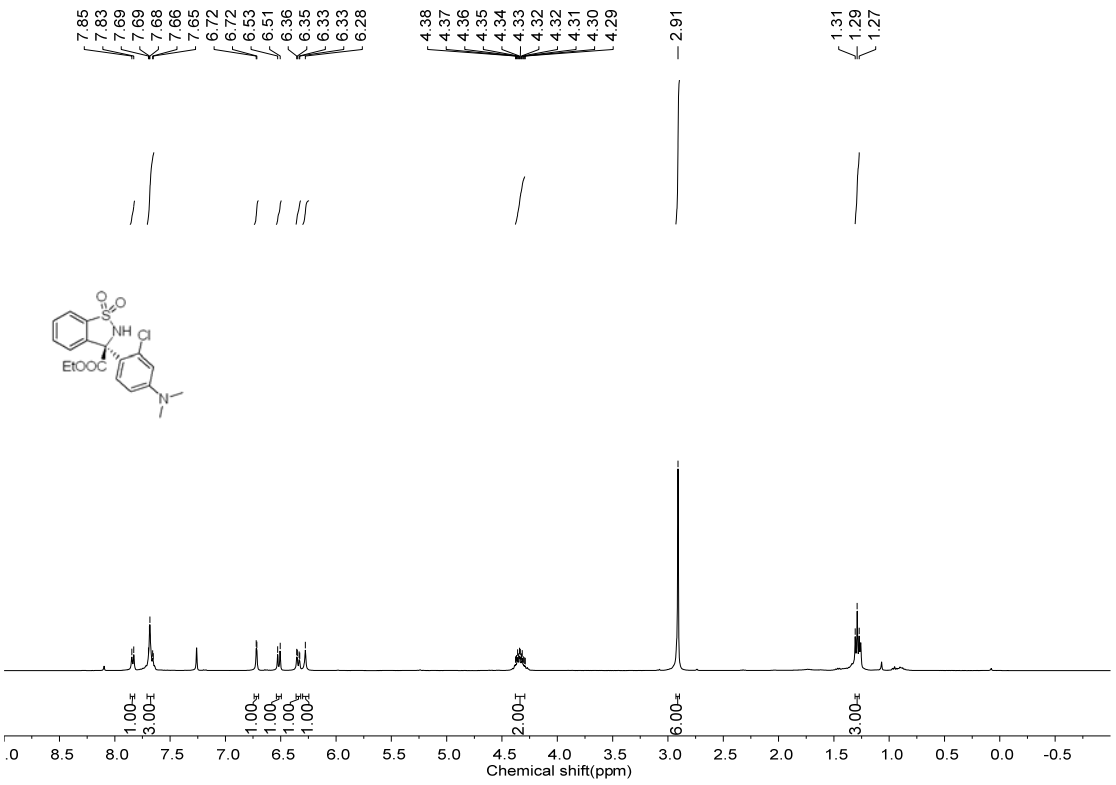
3bg ^{1}H NMR (400 MHz, $CDCl_3$)



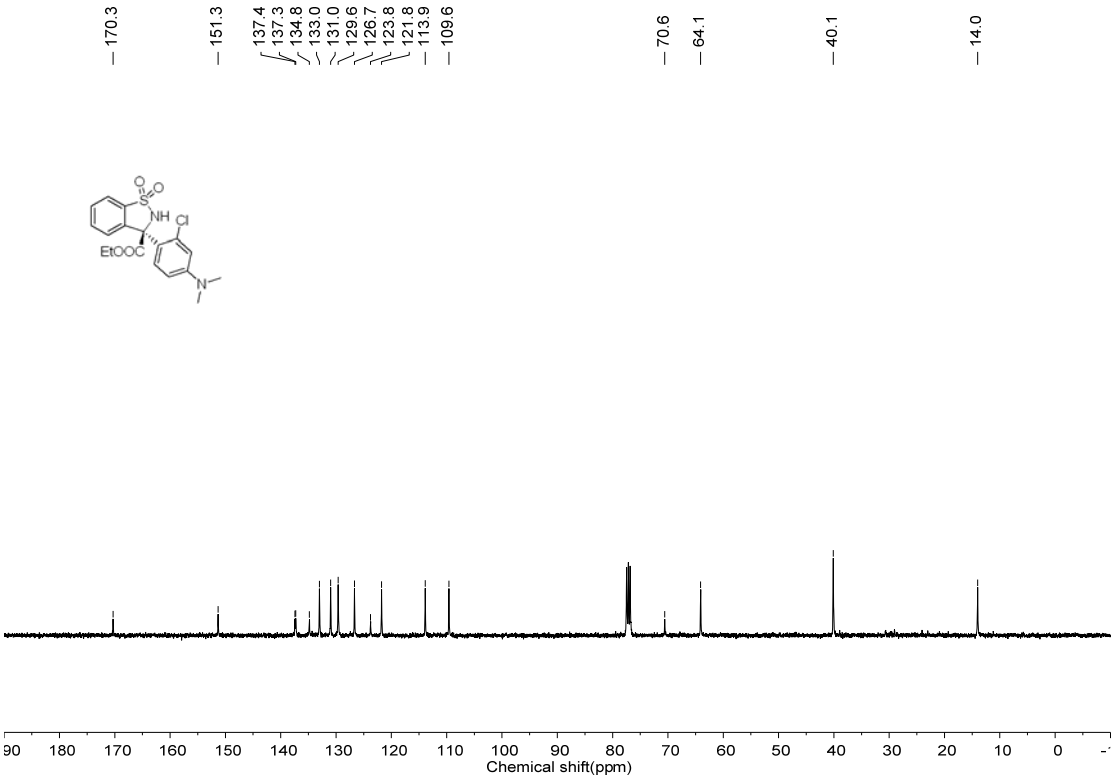
3bg ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



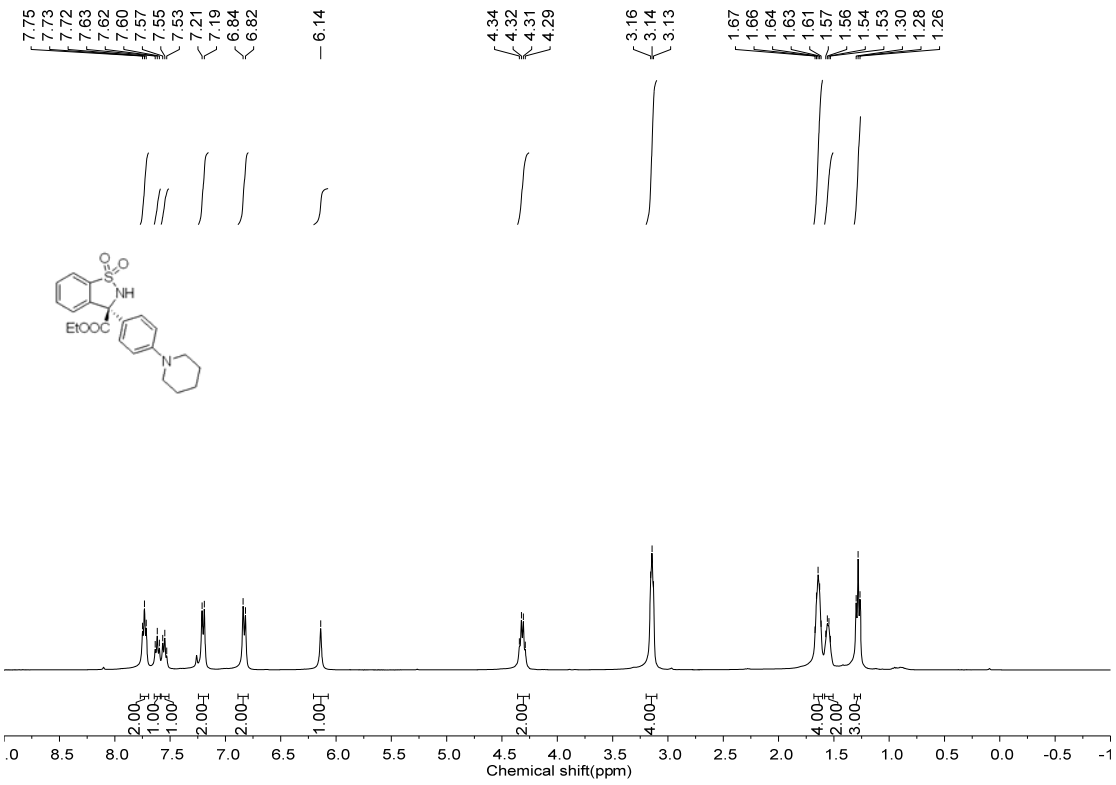
3bh ^{1}H NMR (400 MHz, $CDCl_3$)



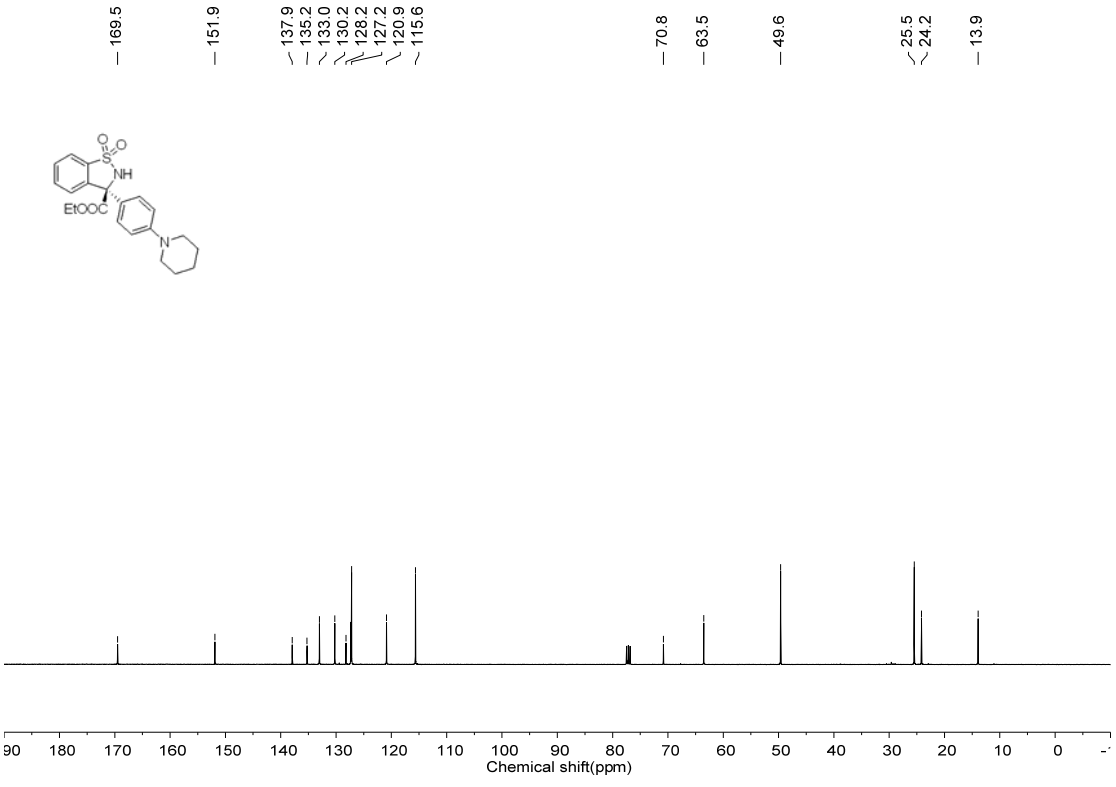
3bh ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



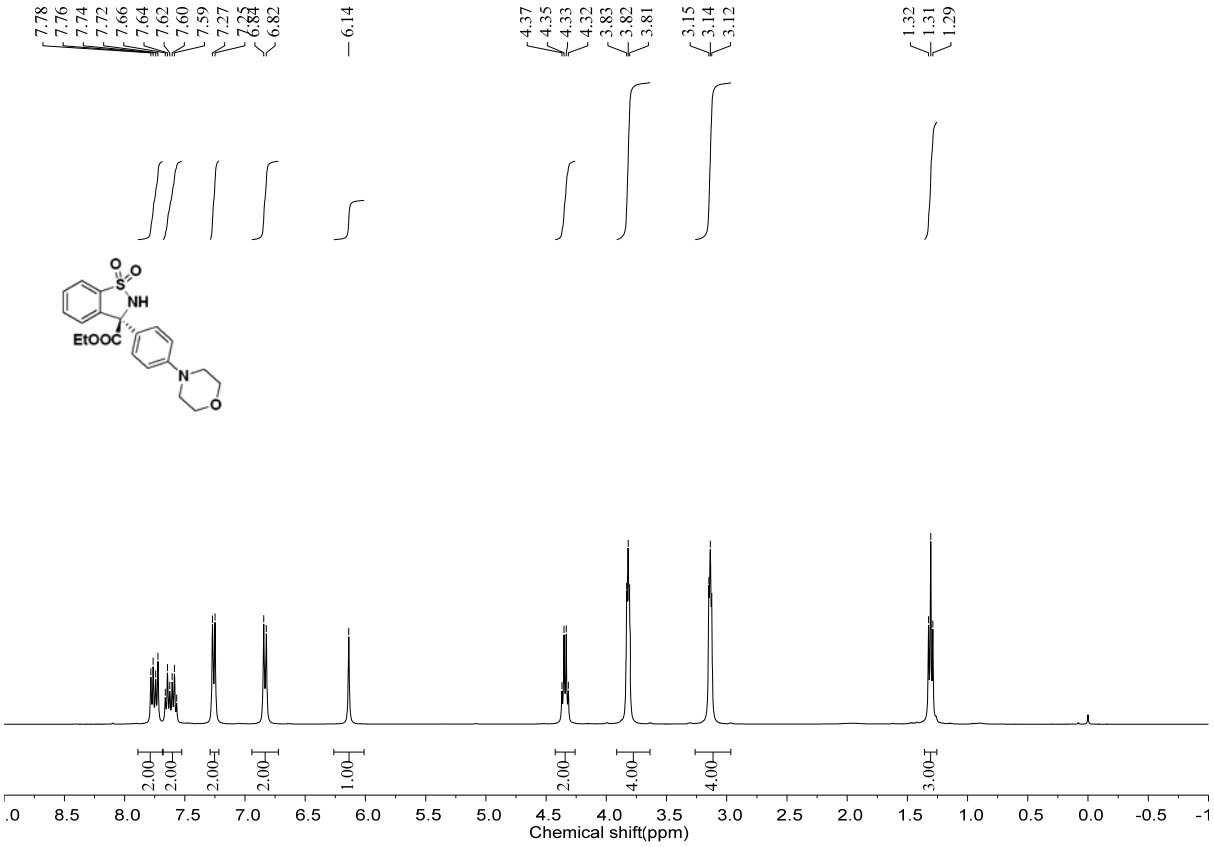
3bi ^{1}H NMR (400 MHz, $CDCl_3$)



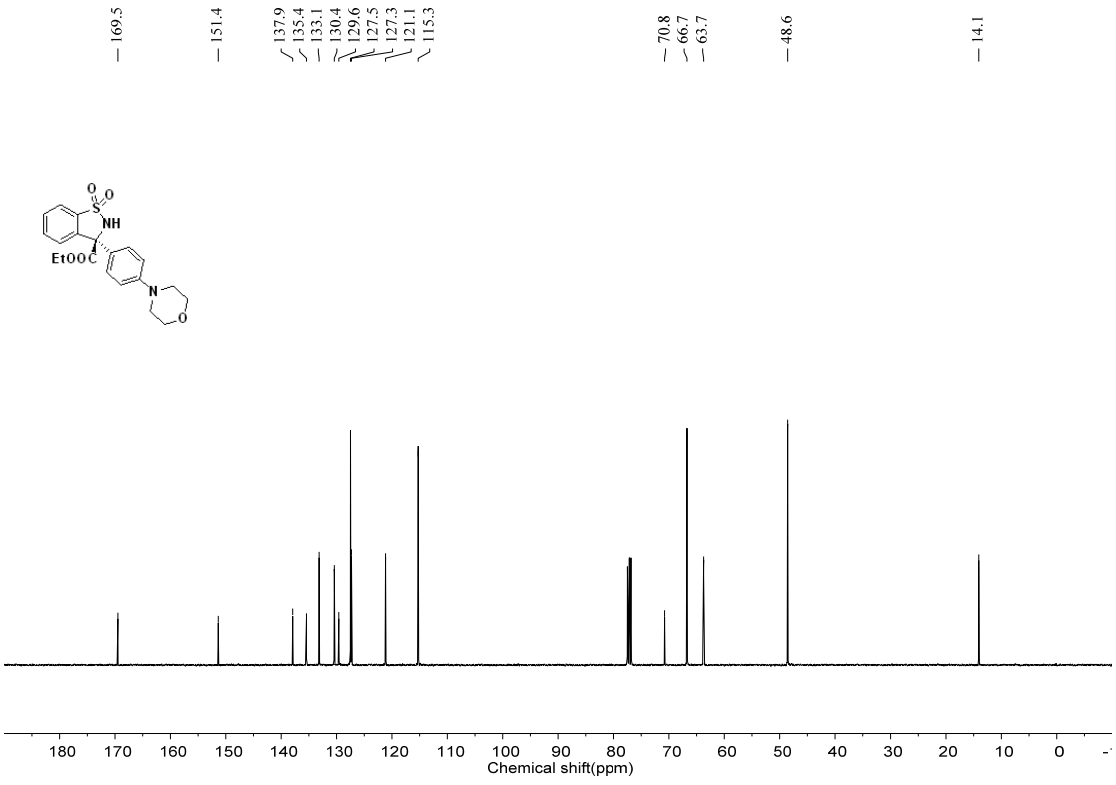
3bi ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



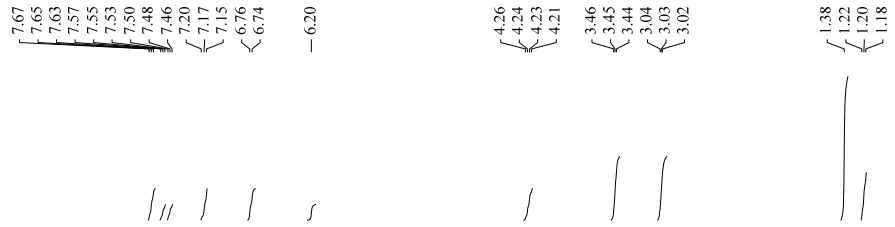
3bj ^{1}H NMR (400 MHz, $CDCl_3$)

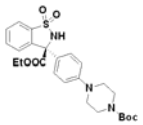


3bj ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

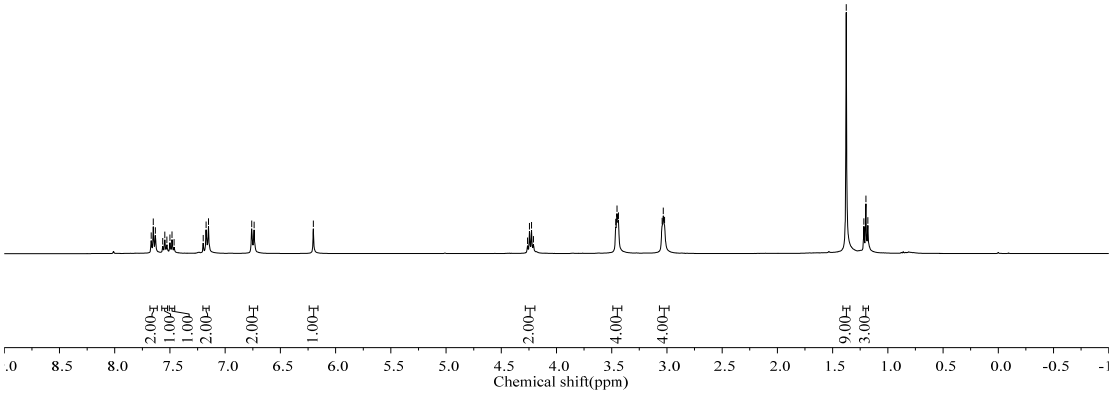


3bk ^{1}H NMR (400 MHz, $CDCl_3$)

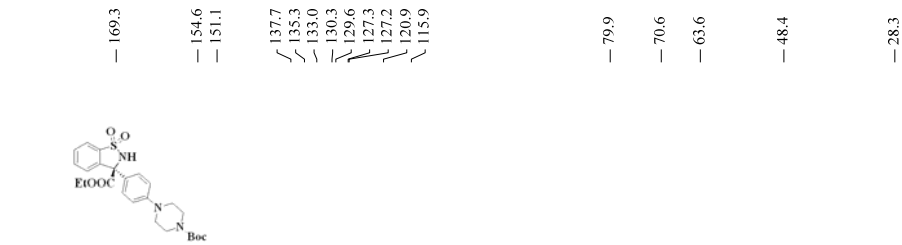


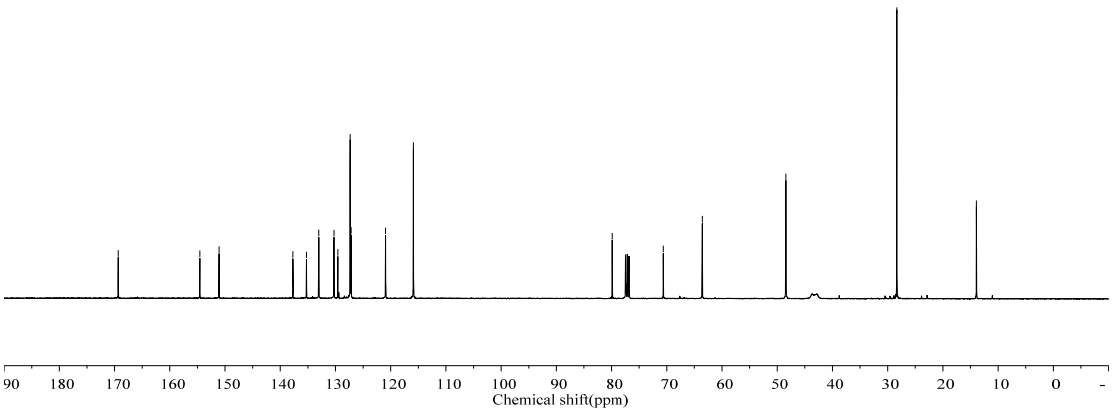


3bs ^{1}H NMR (400 MHz, CDCl3)

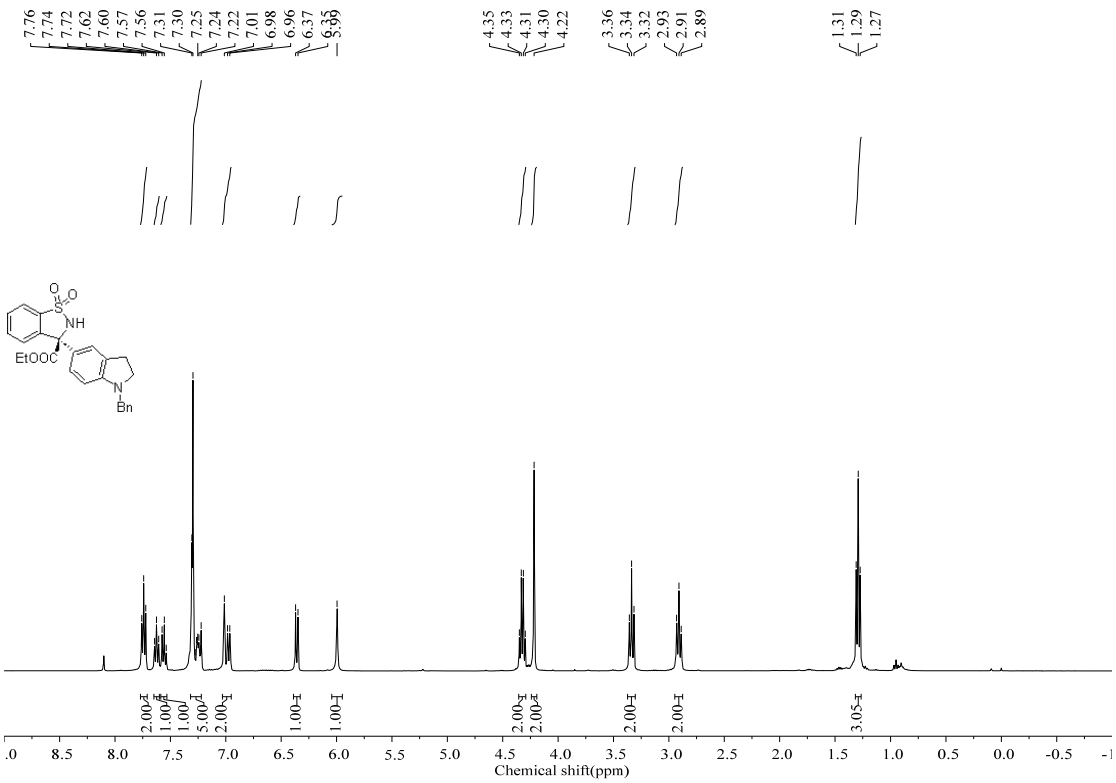


3bk ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

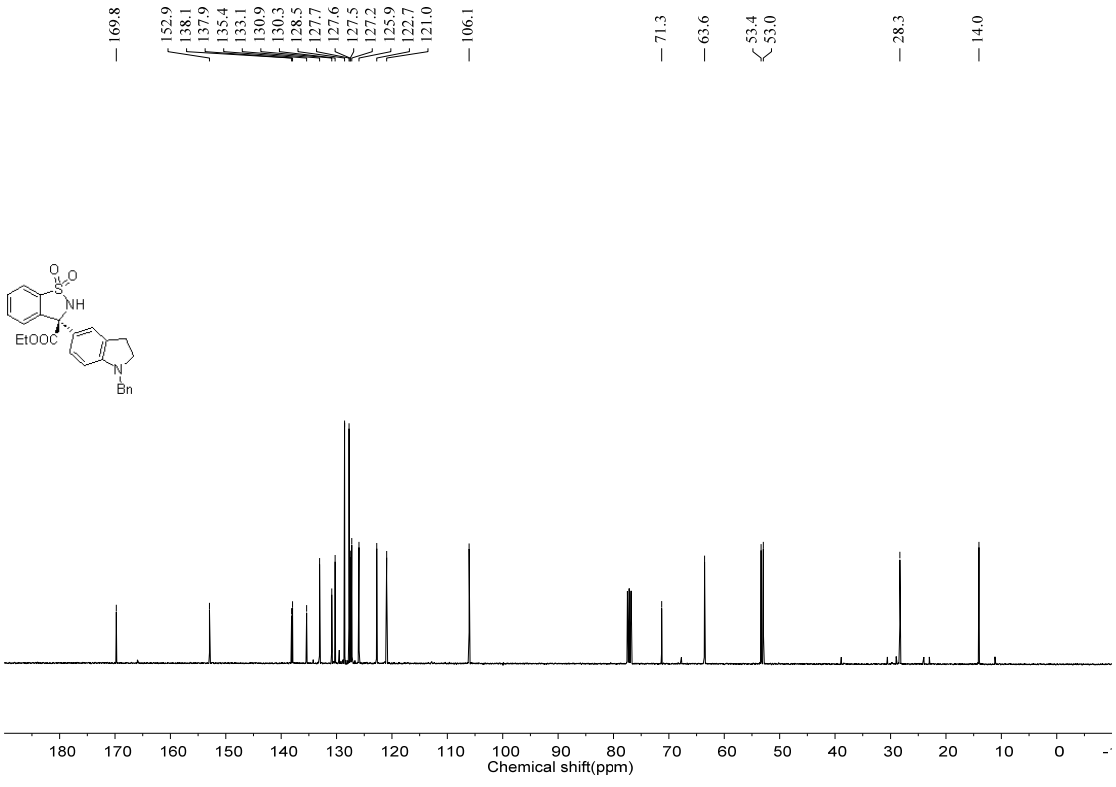




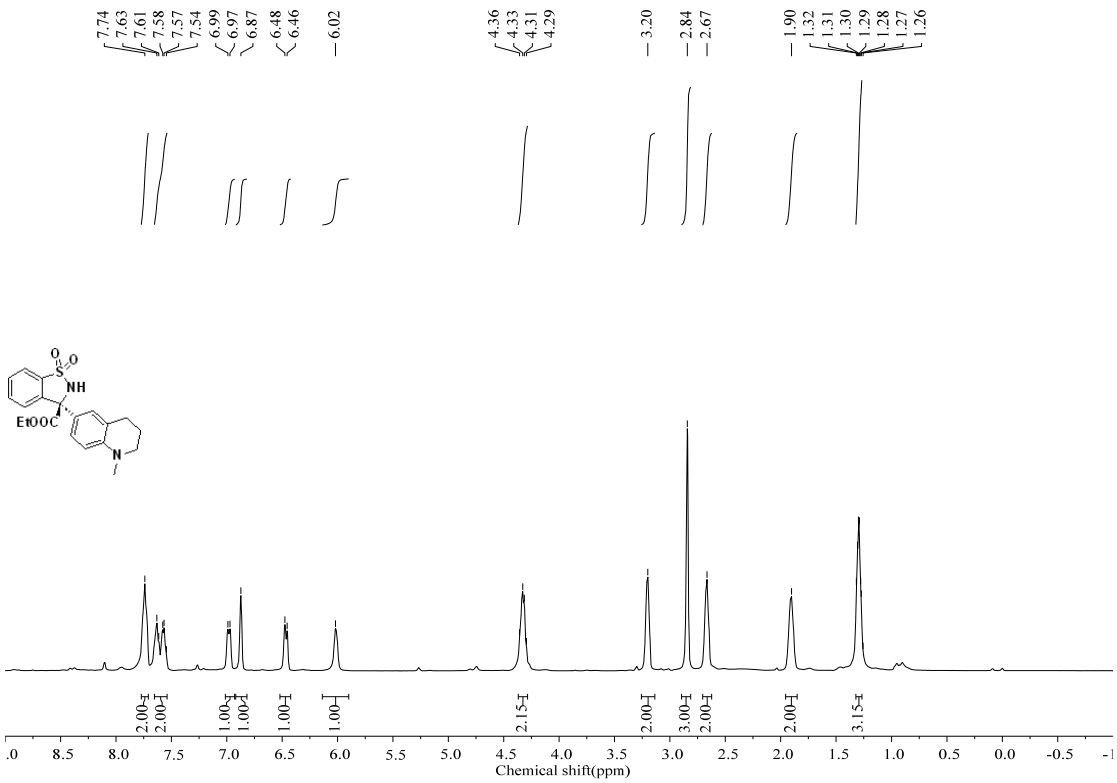
3bl ^{1}H NMR (400 MHz, $CDCl_3$)



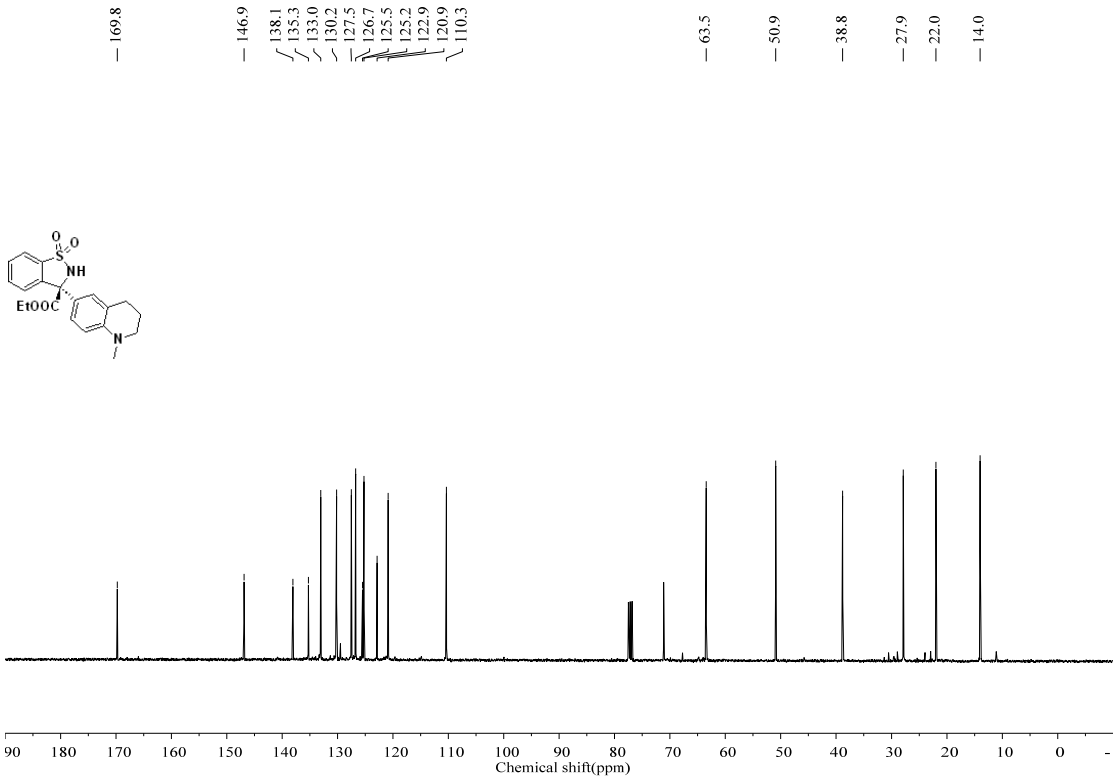
3bl ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



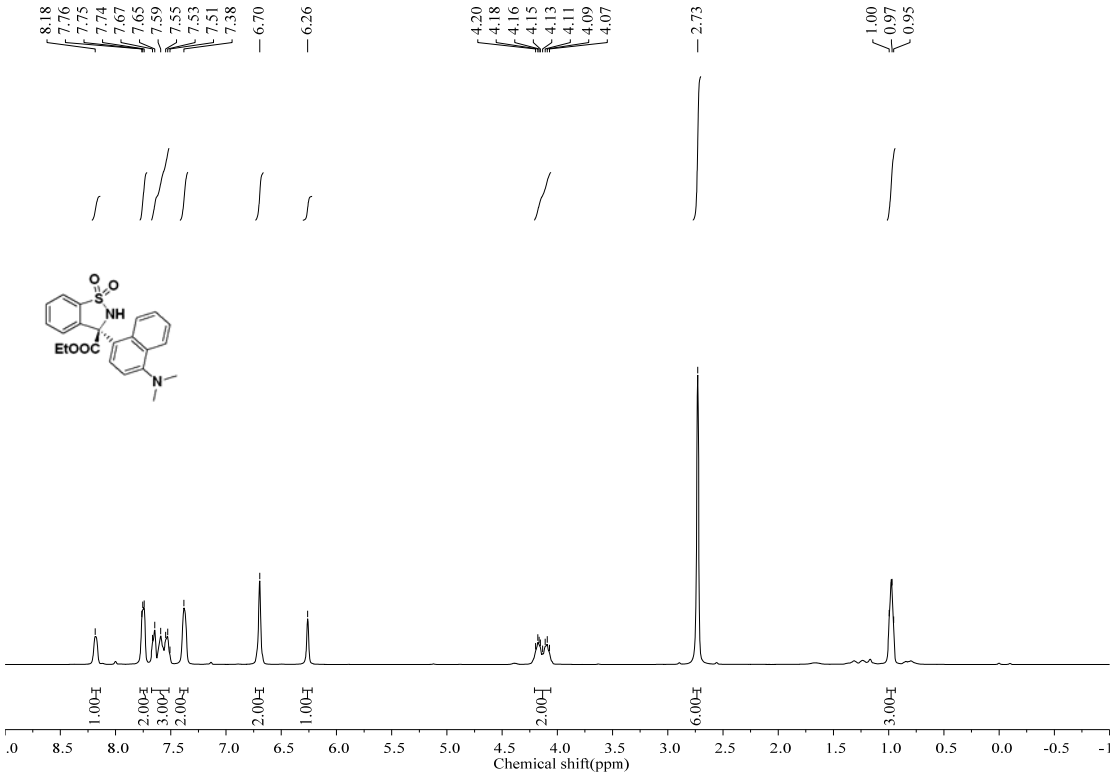
3bm ^{1}H NMR (400 MHz, $CDCl_3$)



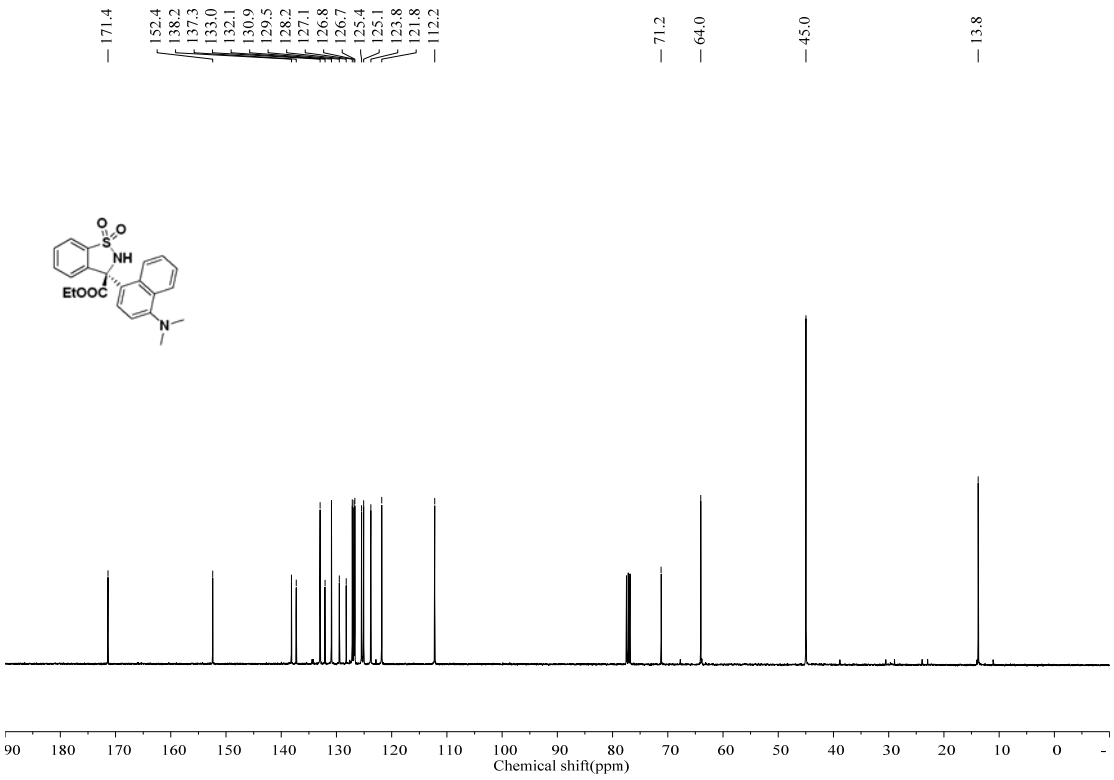
3bm ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



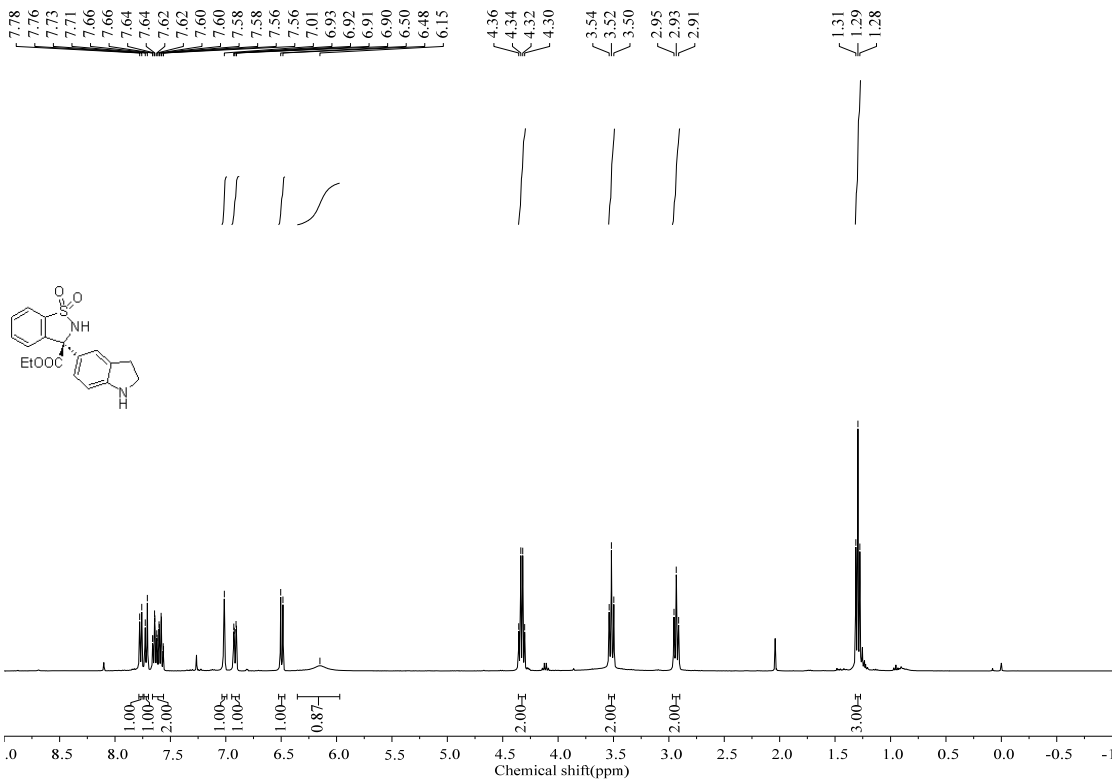
3bn ^{1}H NMR (400 MHz, $CDCl_3$)



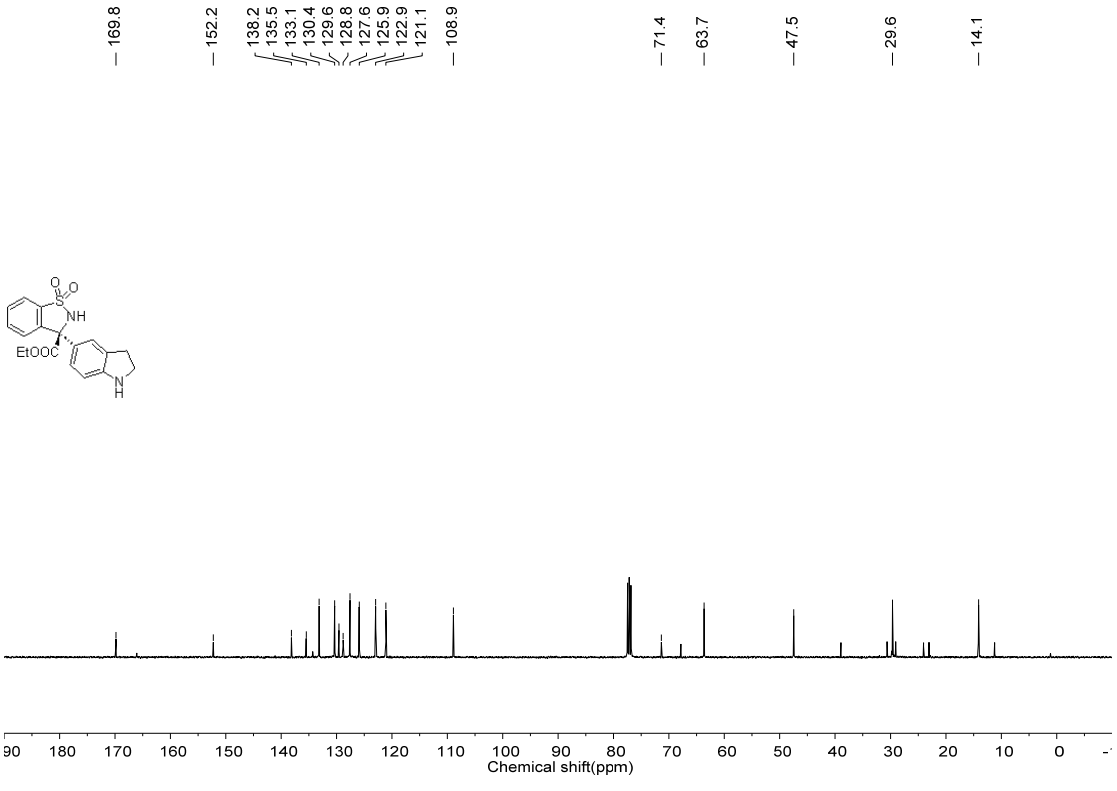
3bn ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



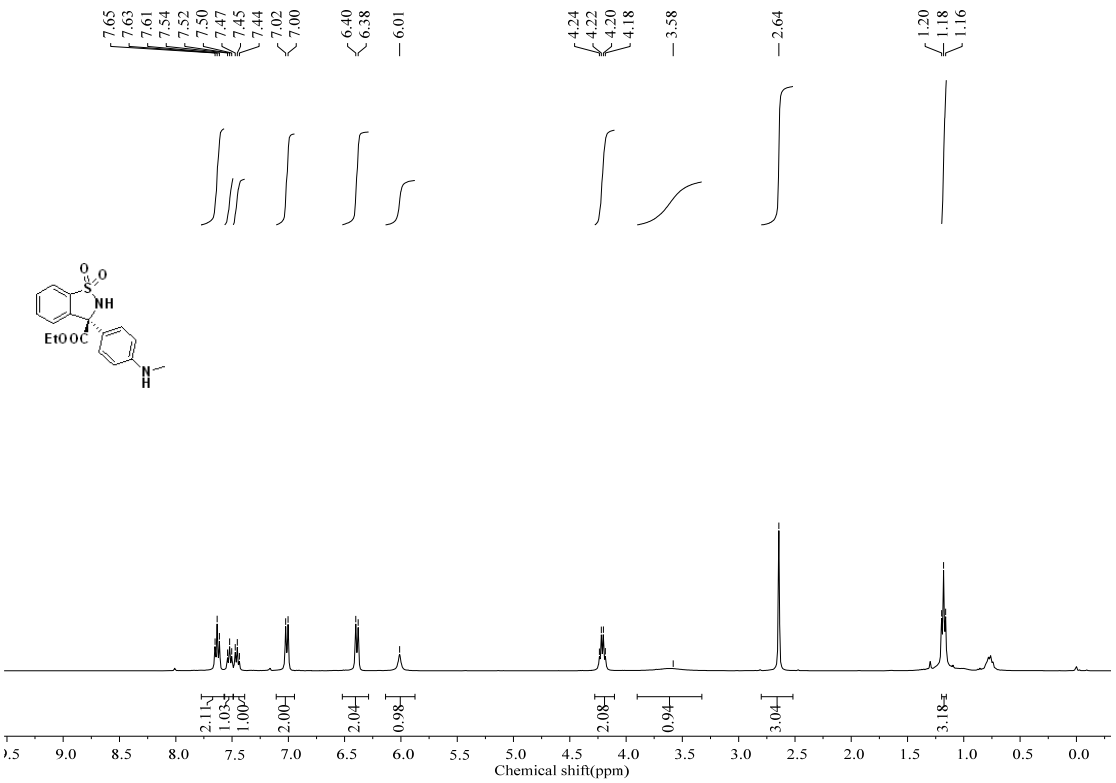
3bo ^{1}H NMR (400 MHz, $CDCl_3$)



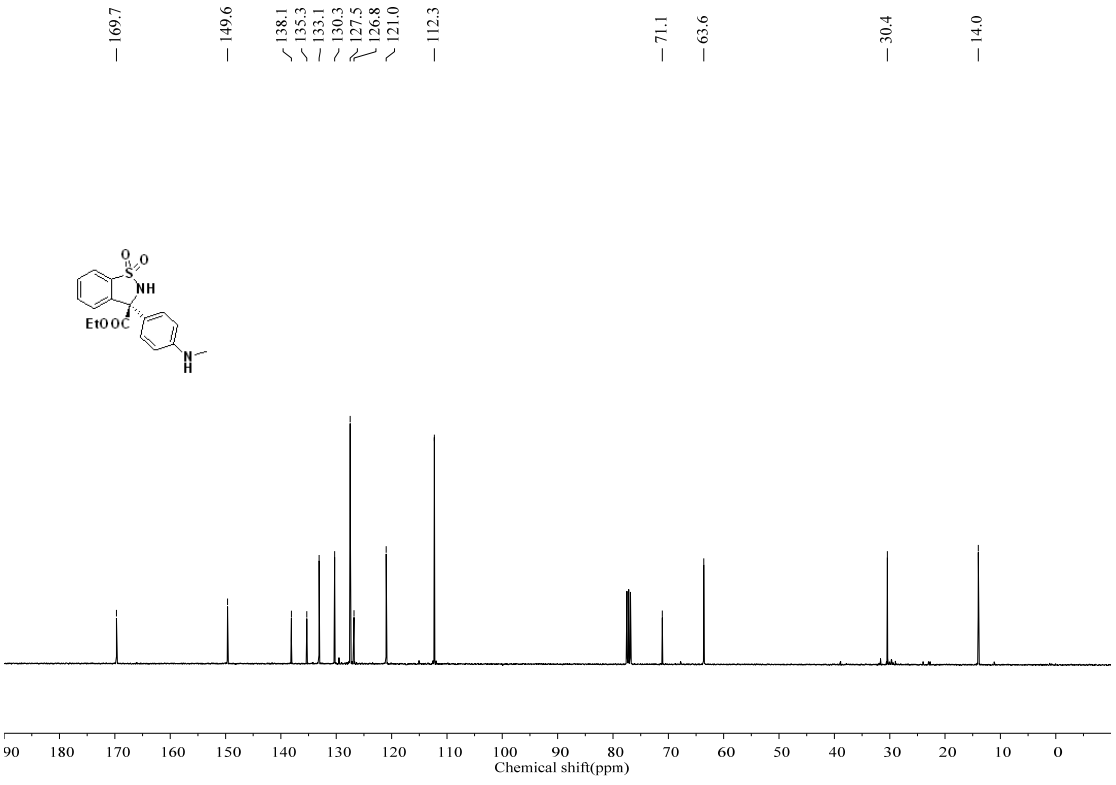
3bo ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



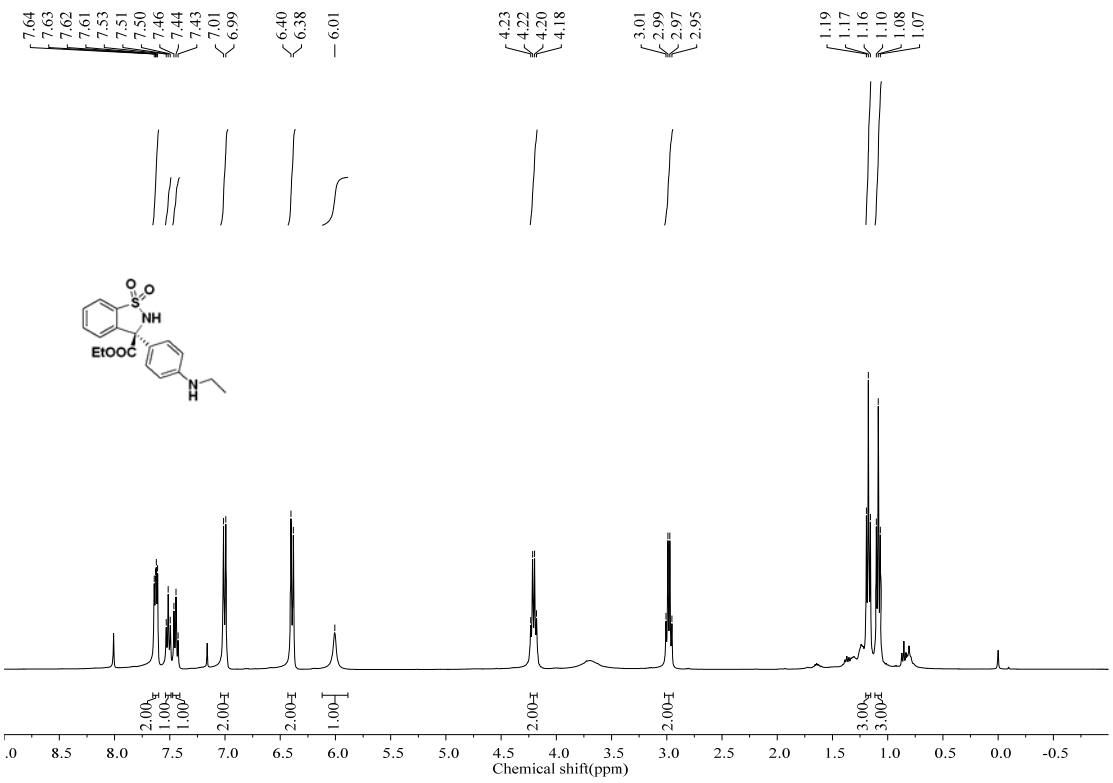
3bp ^{1}H NMR (400 MHz, $CDCl_3$)



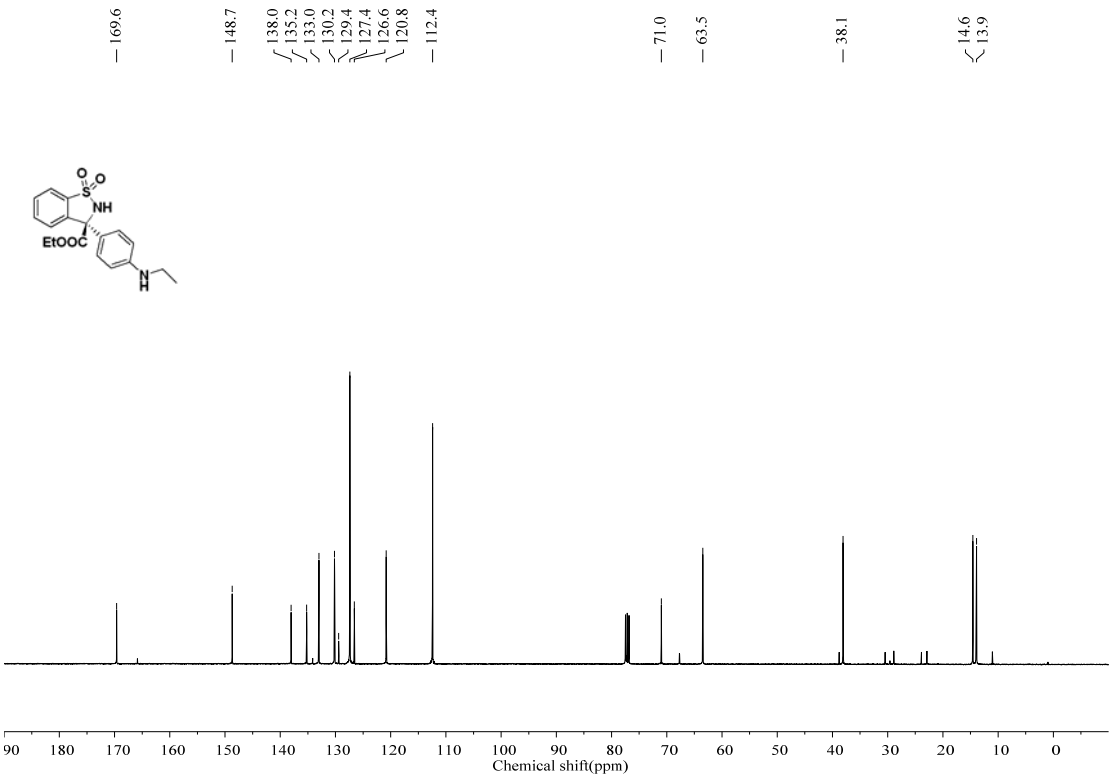
3bp ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



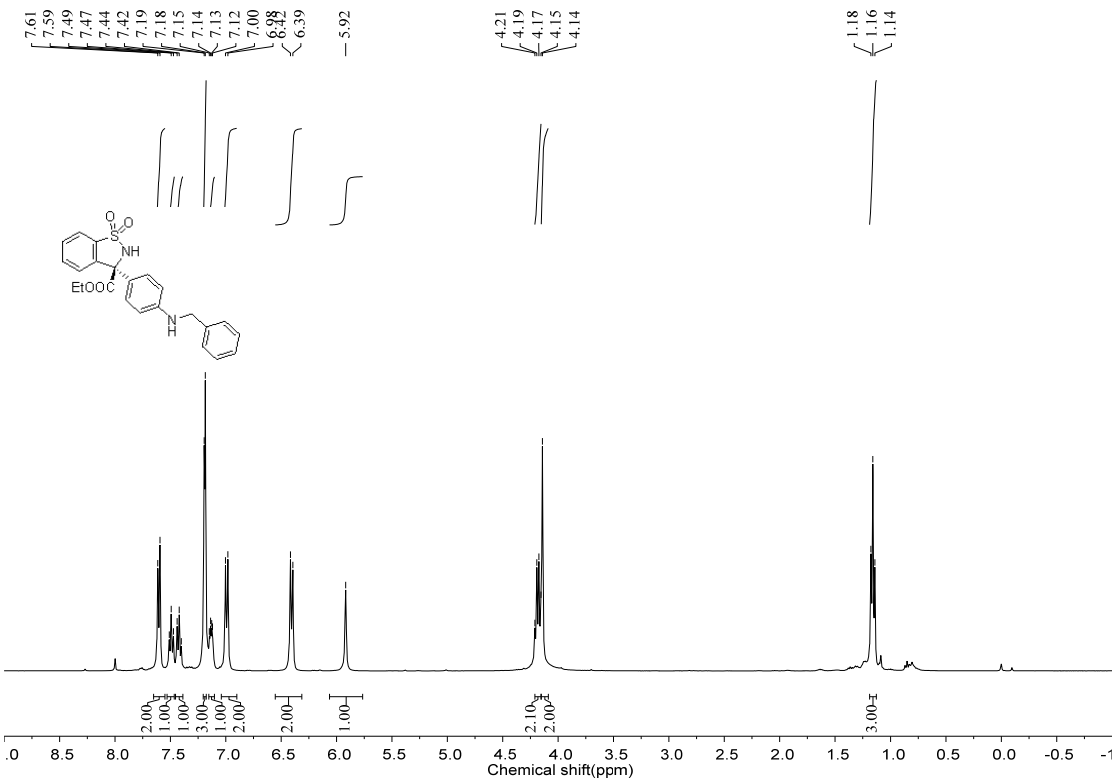
3bq ^{1}H NMR (400 MHz, $CDCl_3$)



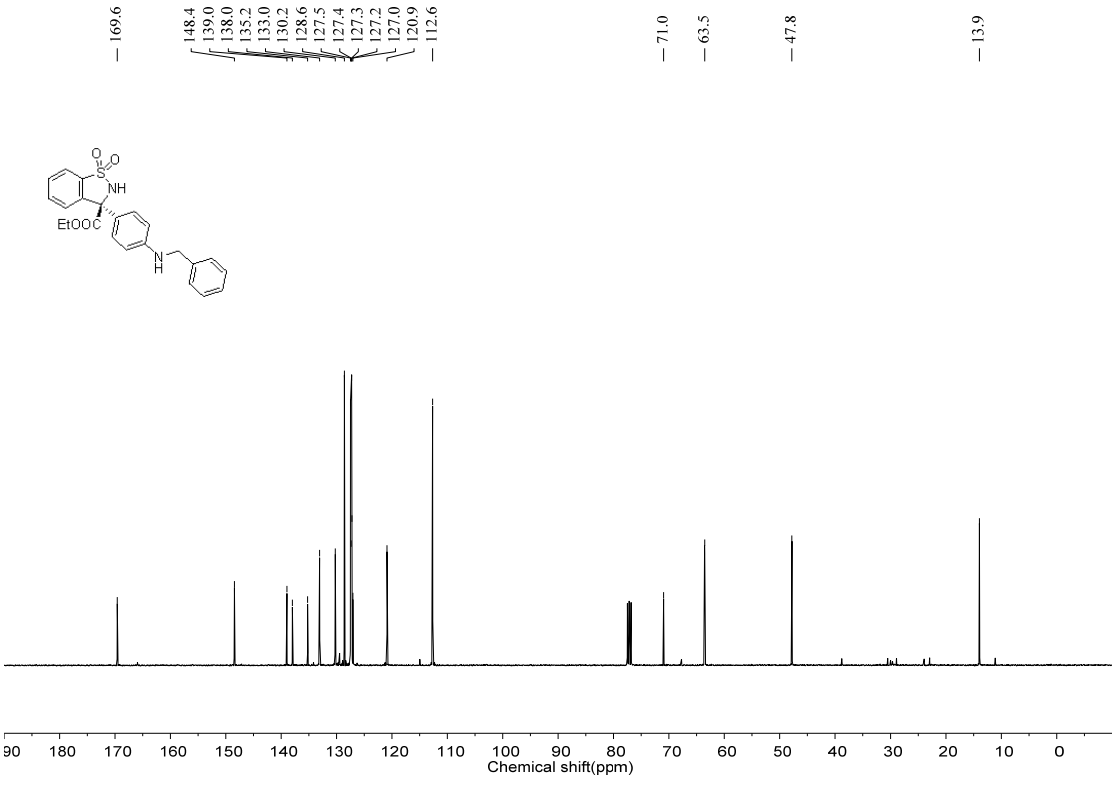
3bq ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



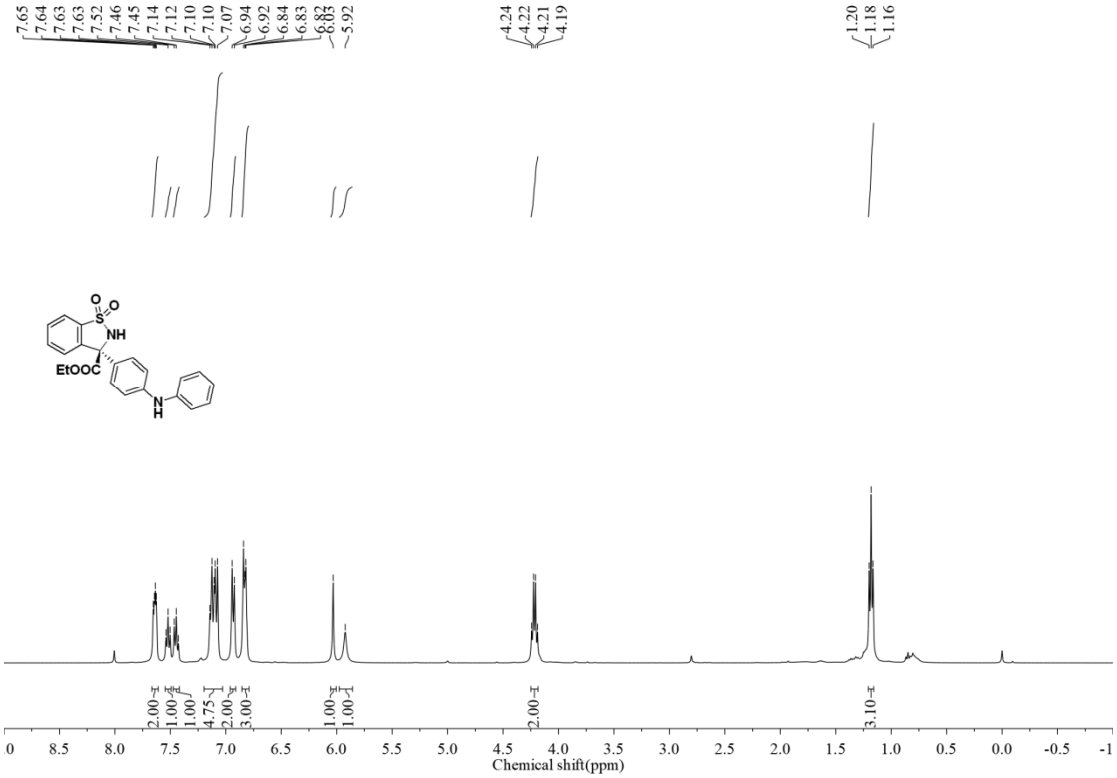
3br ^{1}H NMR (400 MHz, $CDCl_3$)



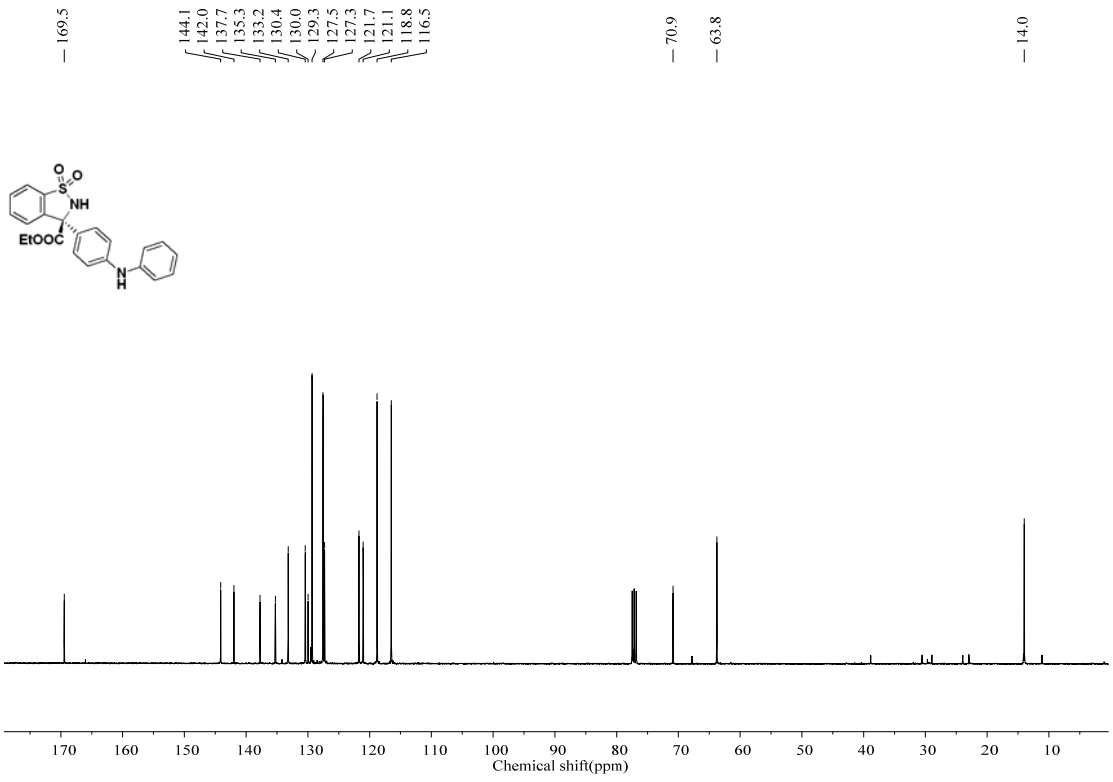
3br ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



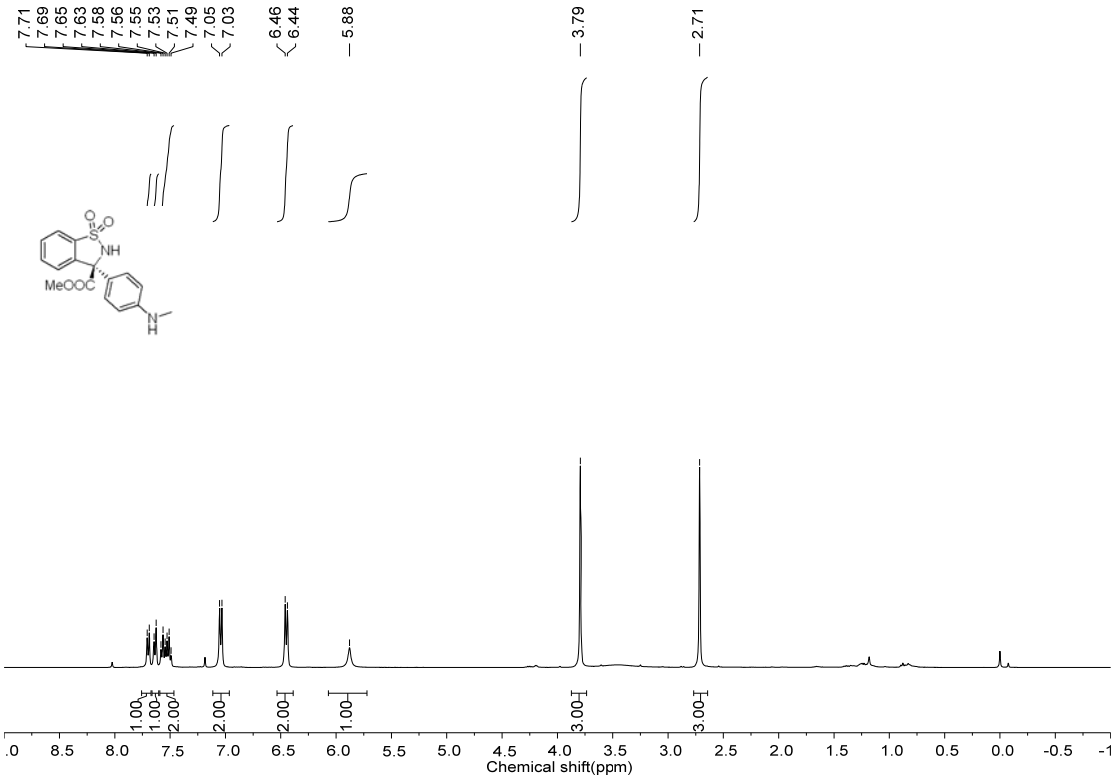
3bs ^{1}H NMR (400 MHz, $CDCl_3$)



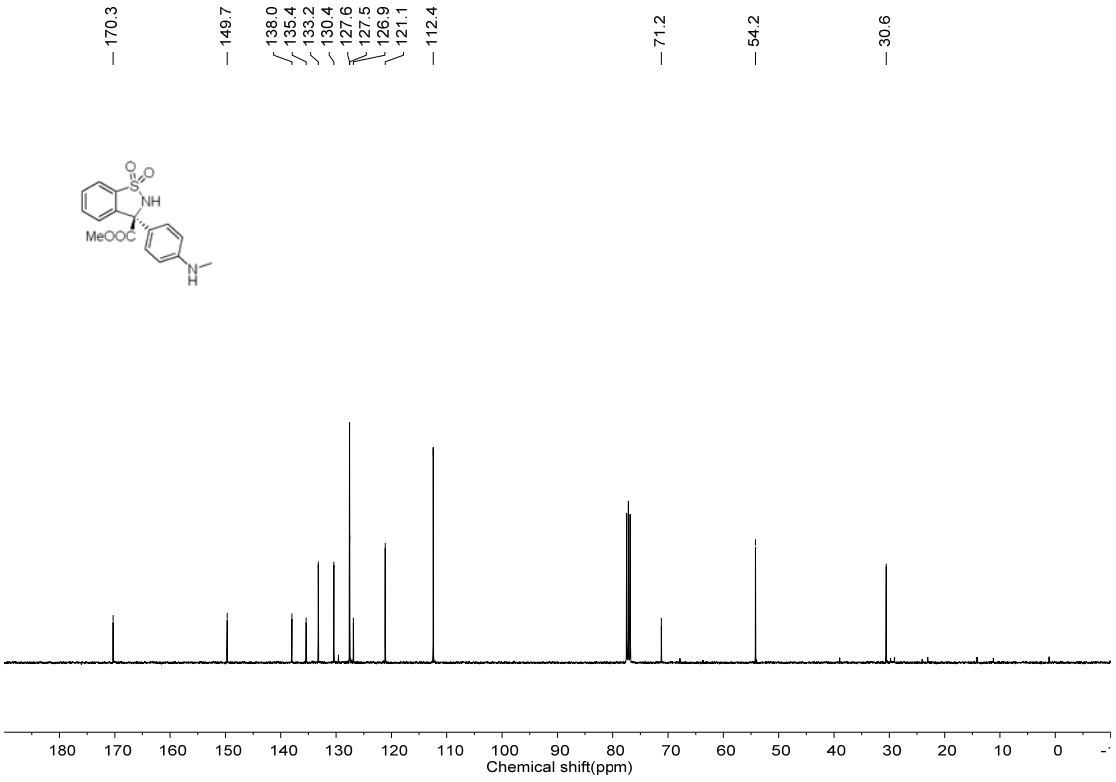
3bs ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



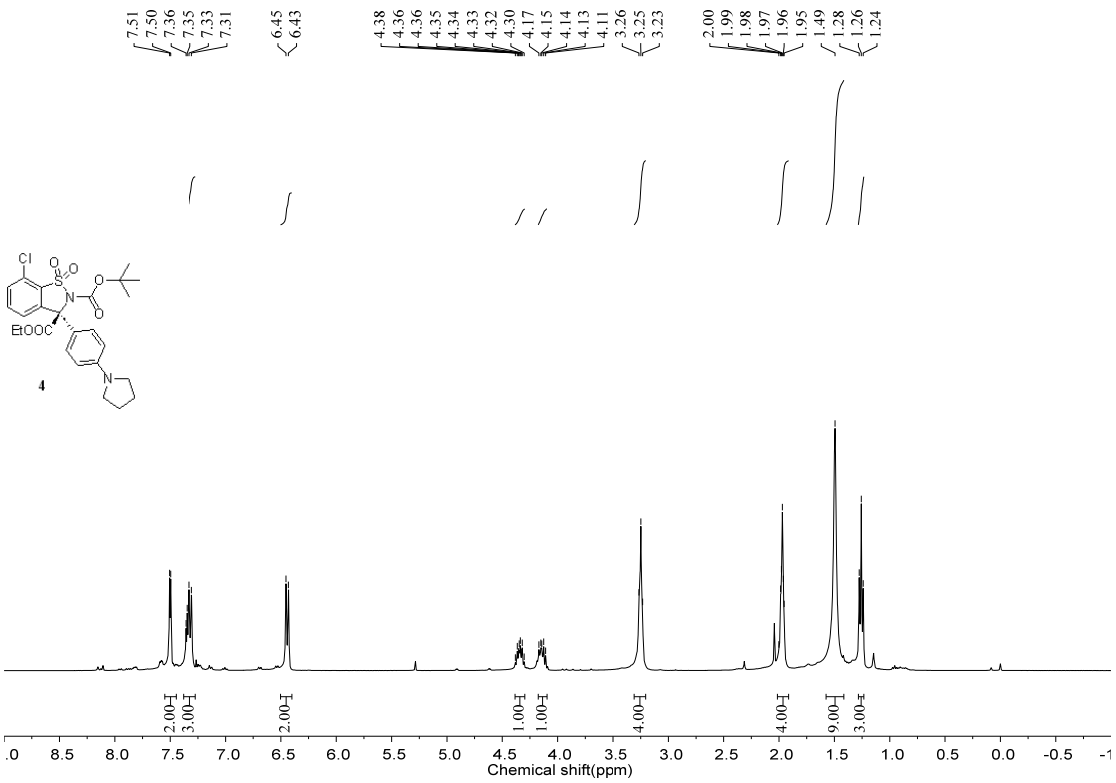
3bt ^{1}H NMR (400 MHz, $CDCl_3$)



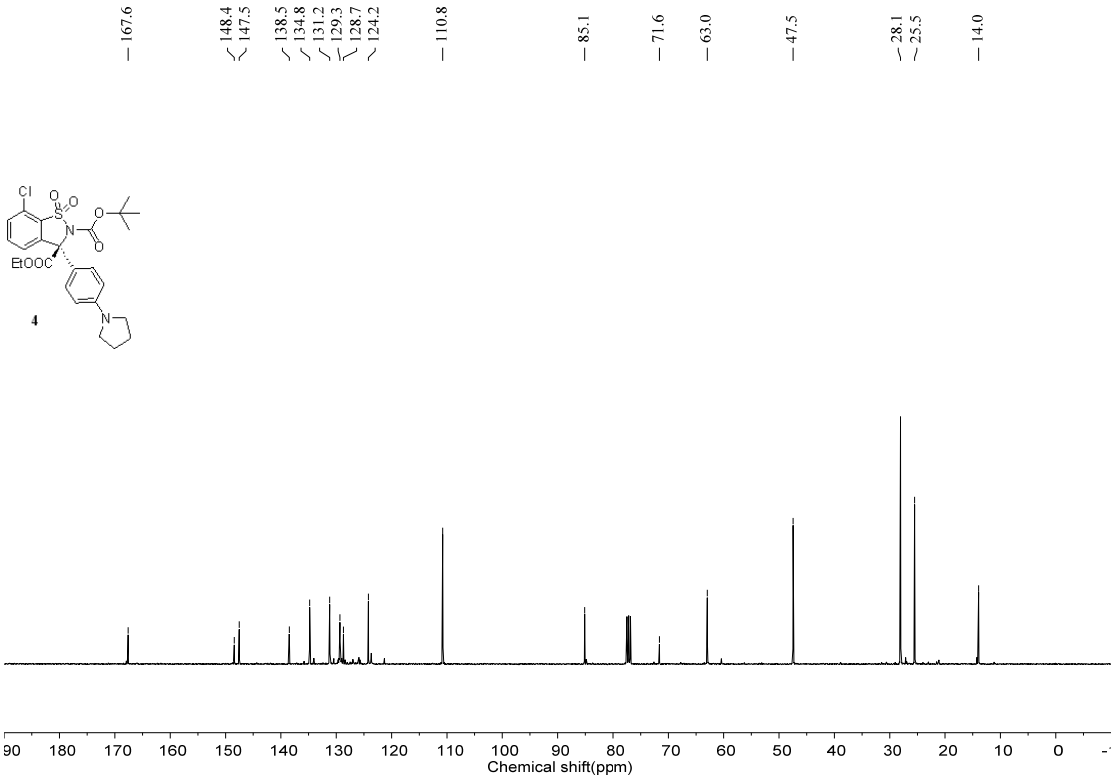
3bt ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



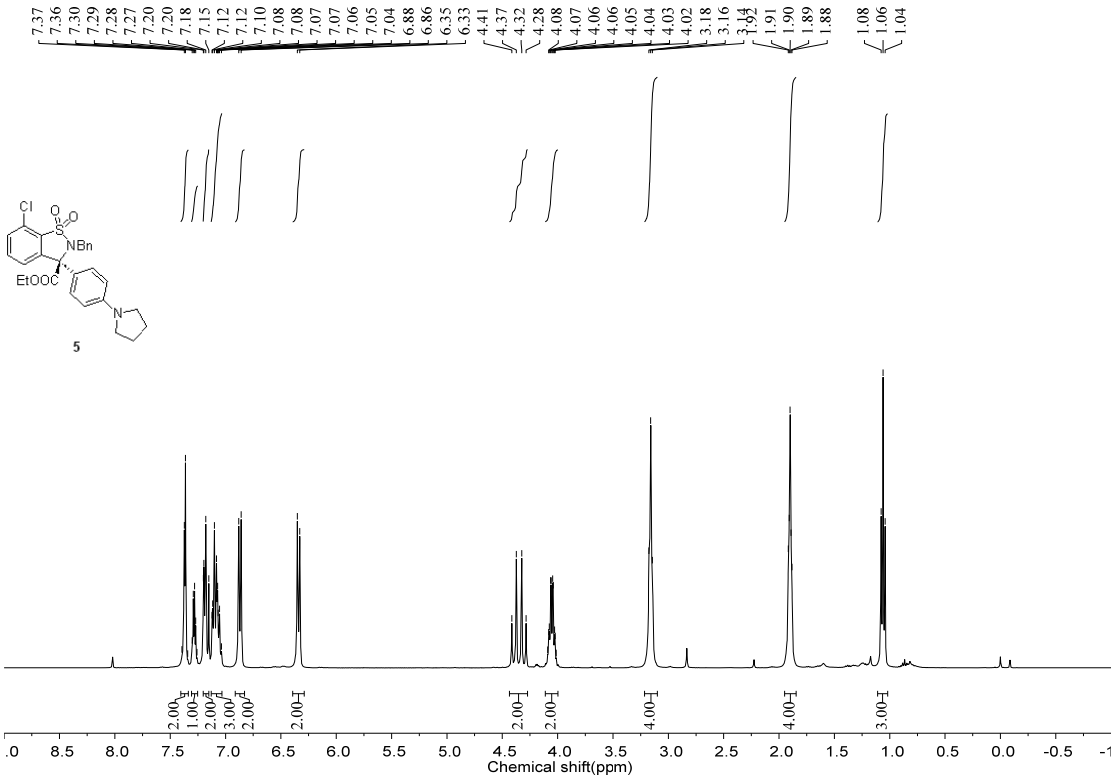
4 ^{1}H NMR (400 MHz, $CDCl_3$)



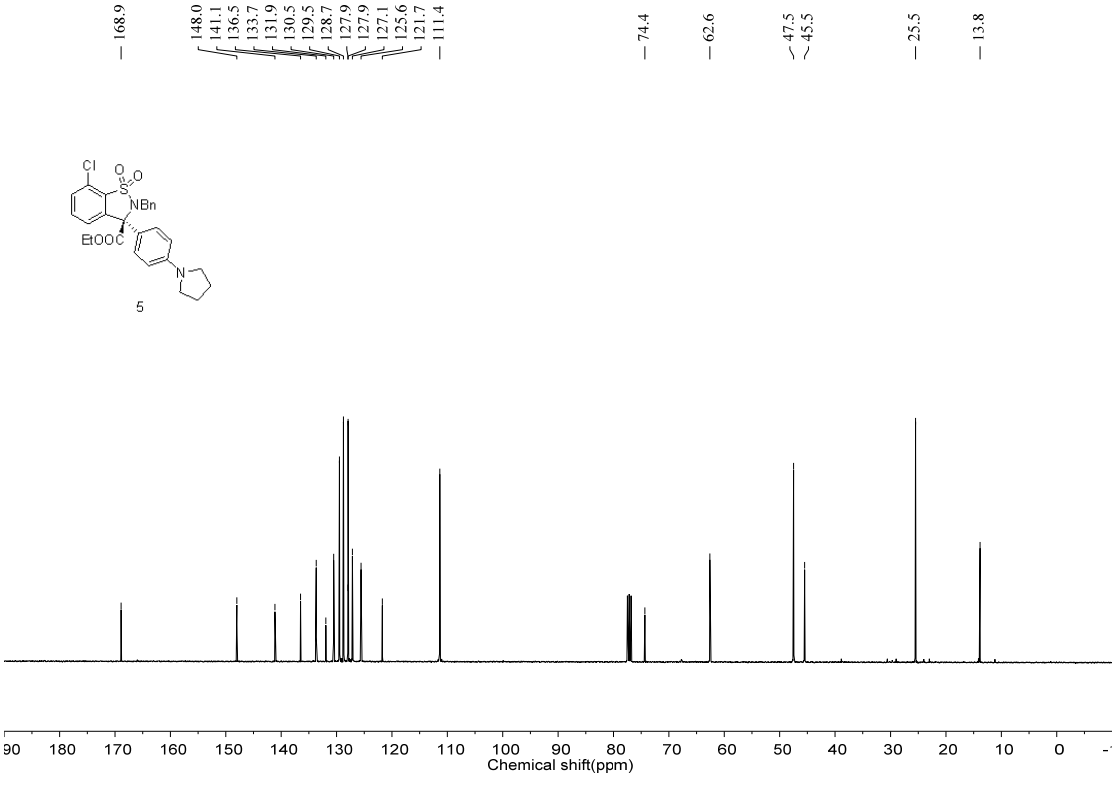
4 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



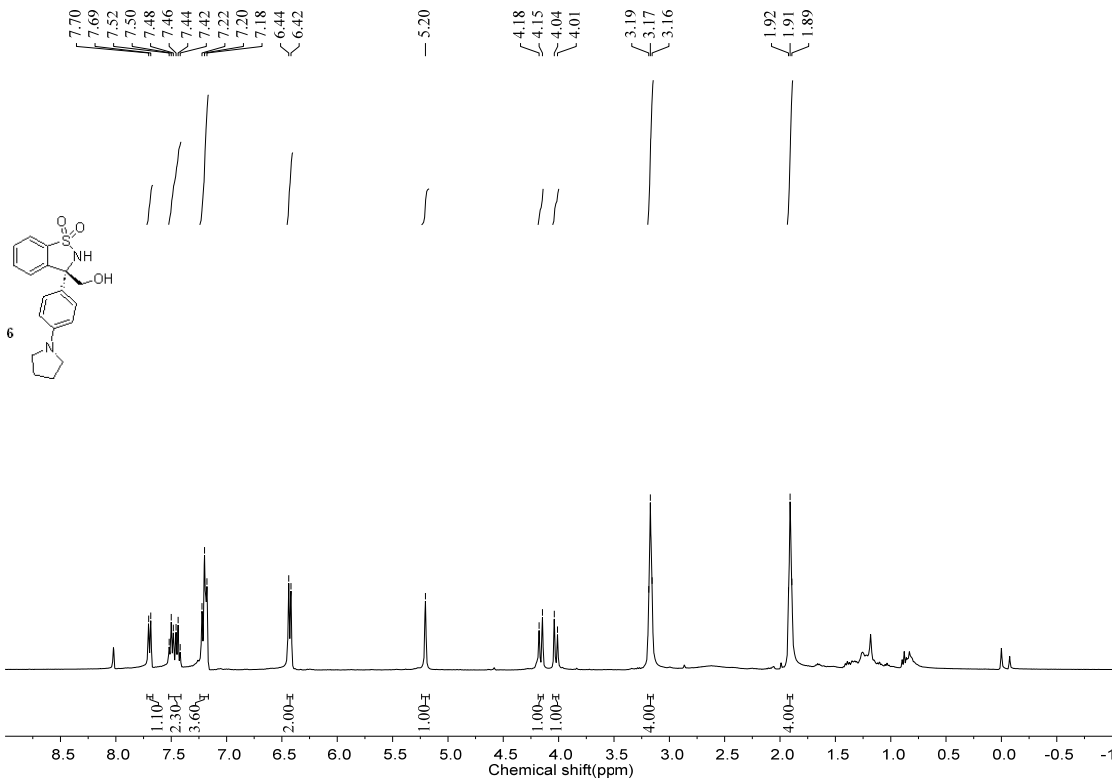
5 ^{1}H NMR (400 MHz, $CDCl_3$)



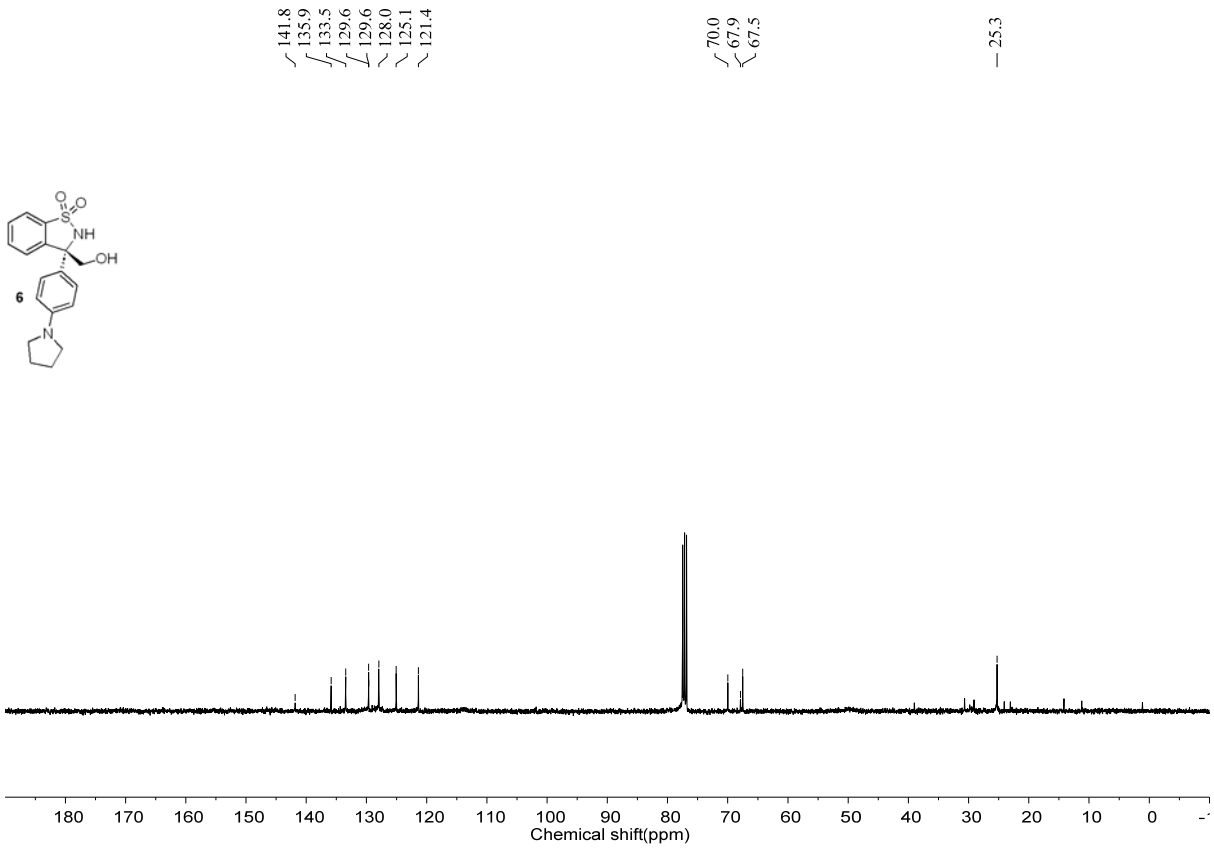
5 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



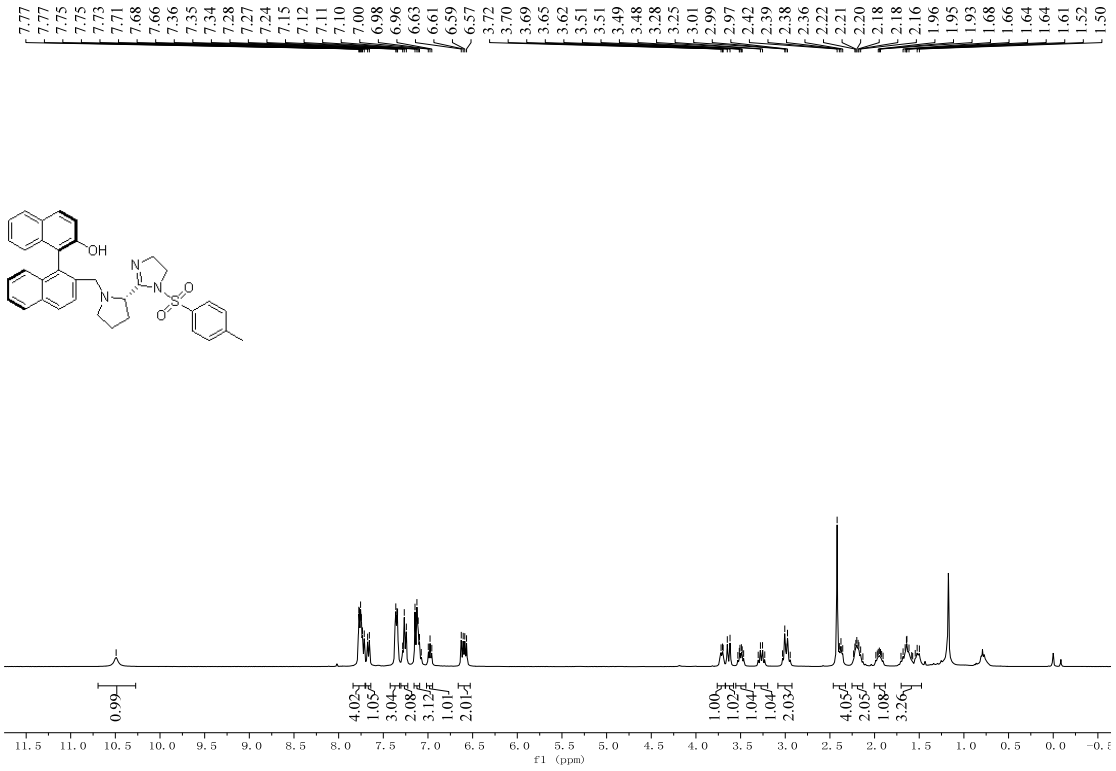
6 ^{1}H NMR (400 MHz, $CDCl_3$)



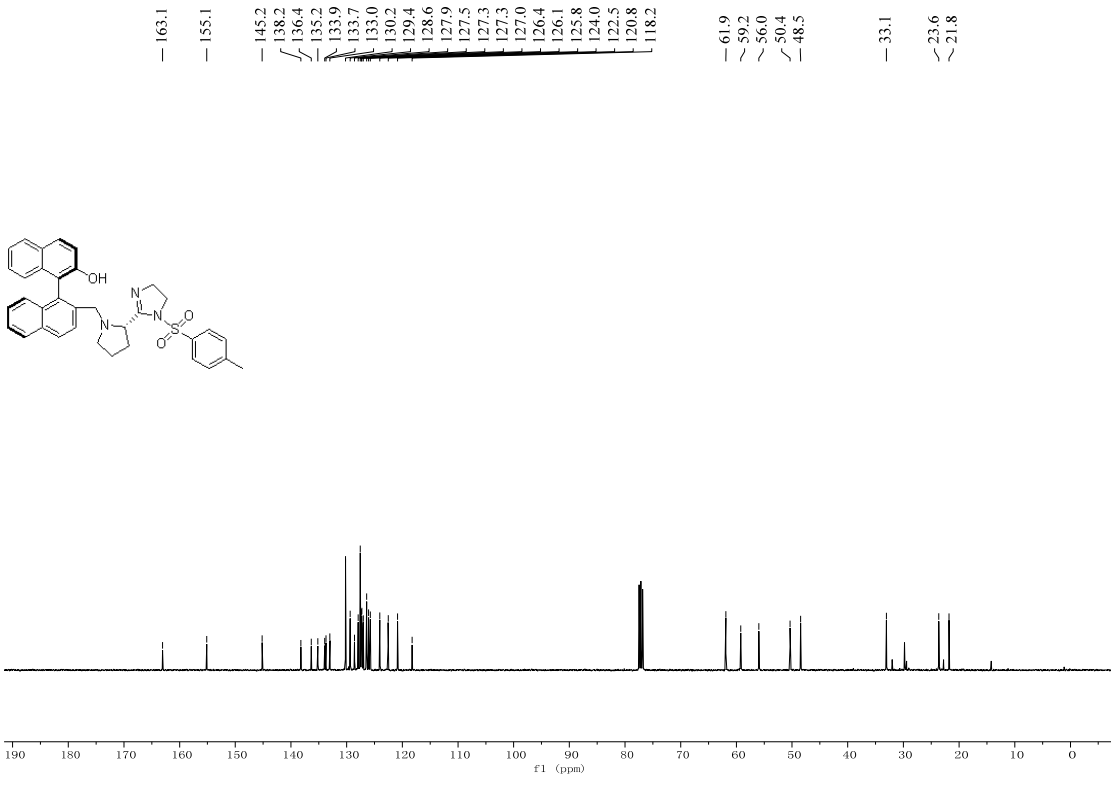
6 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



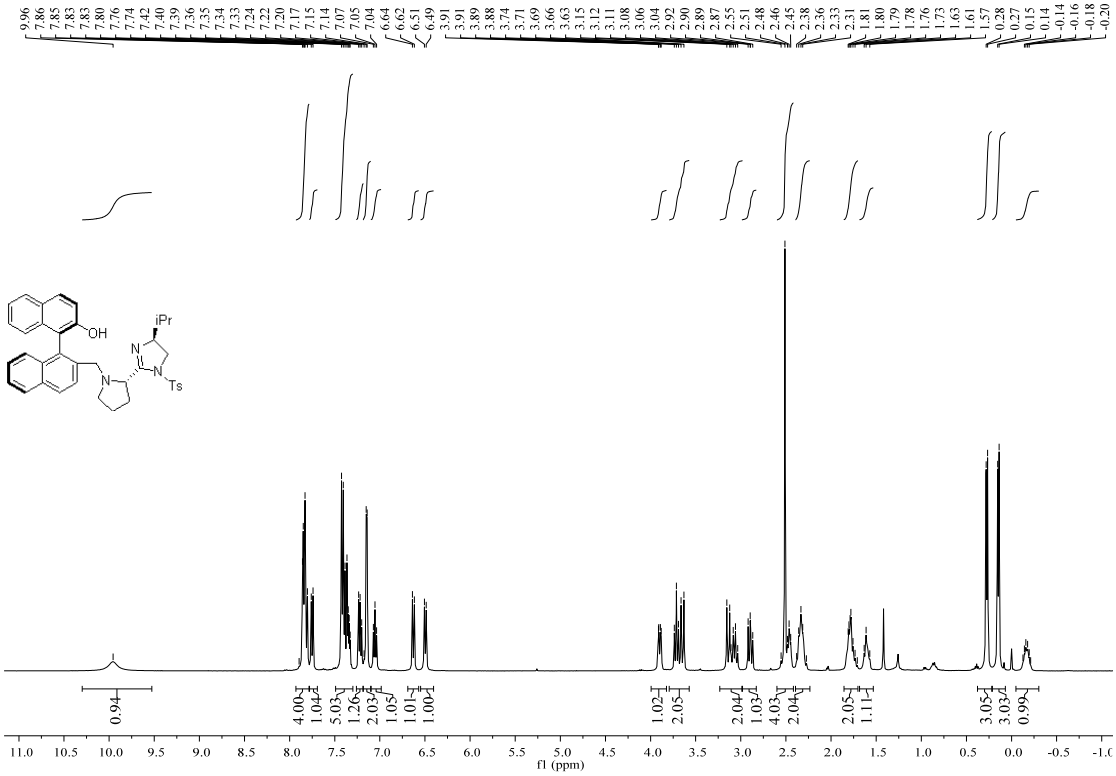
L1 ^{1}H NMR (400 MHz, $CDCl_3$)



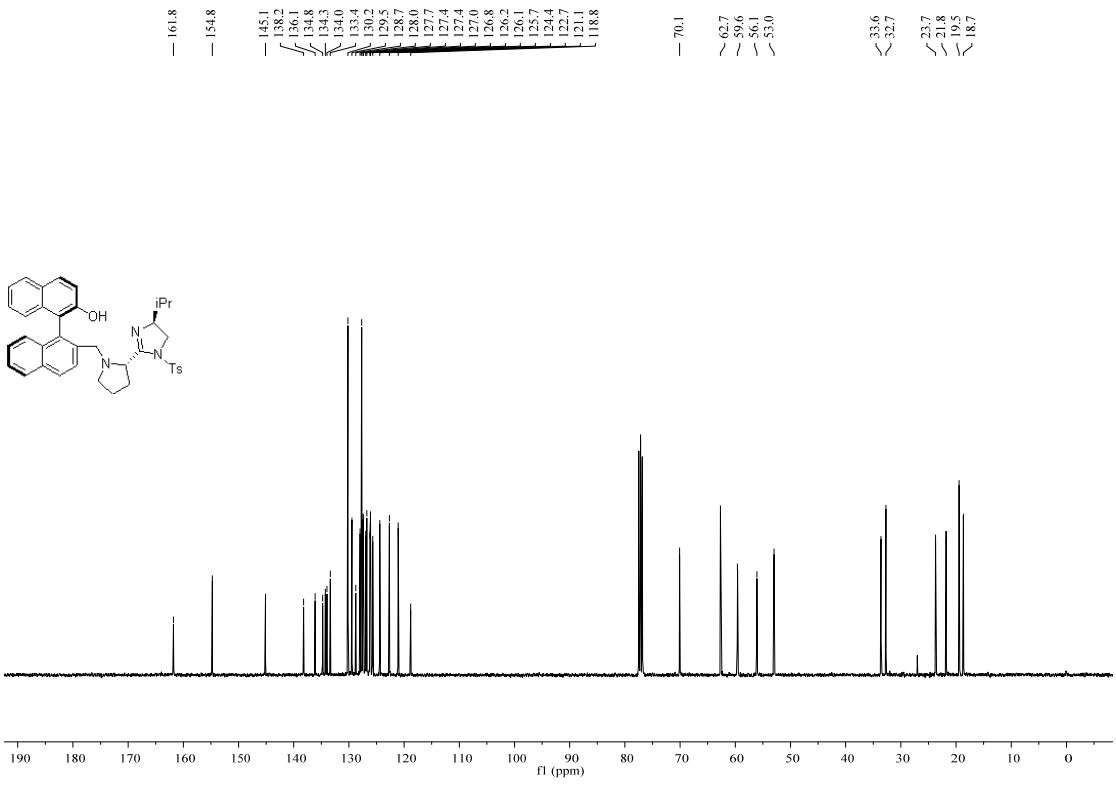
L1 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



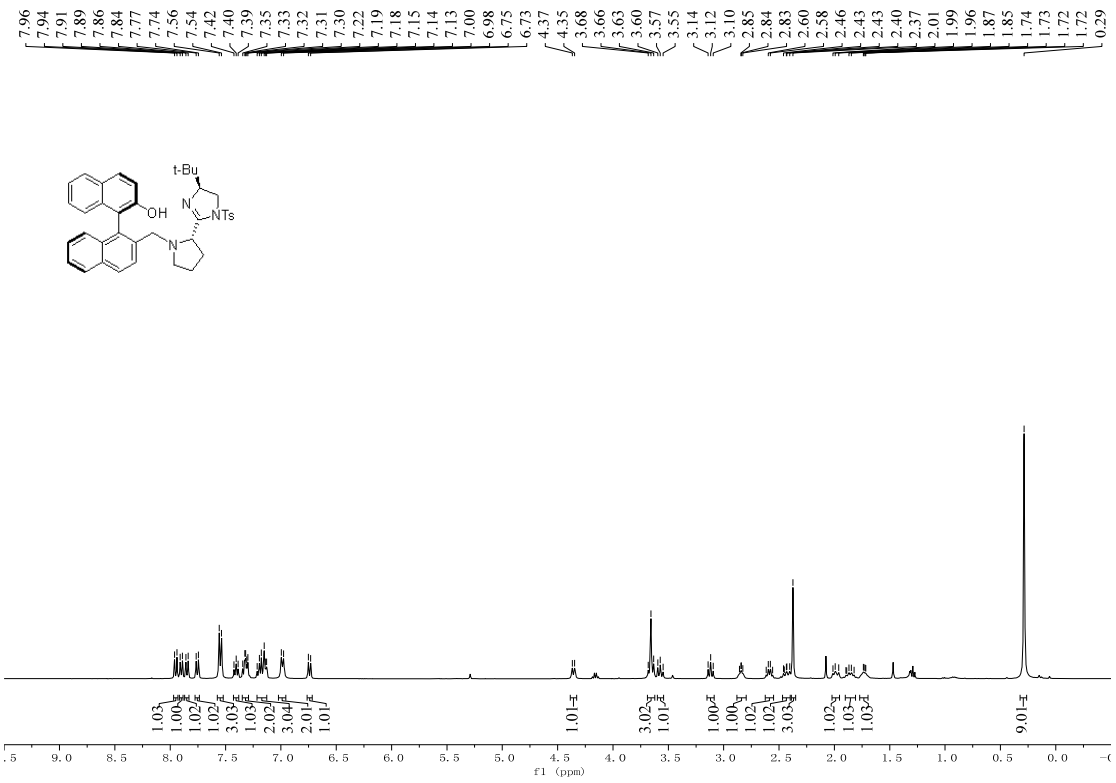
L2 ^{1}H NMR (400 MHz, $CDCl_3$)



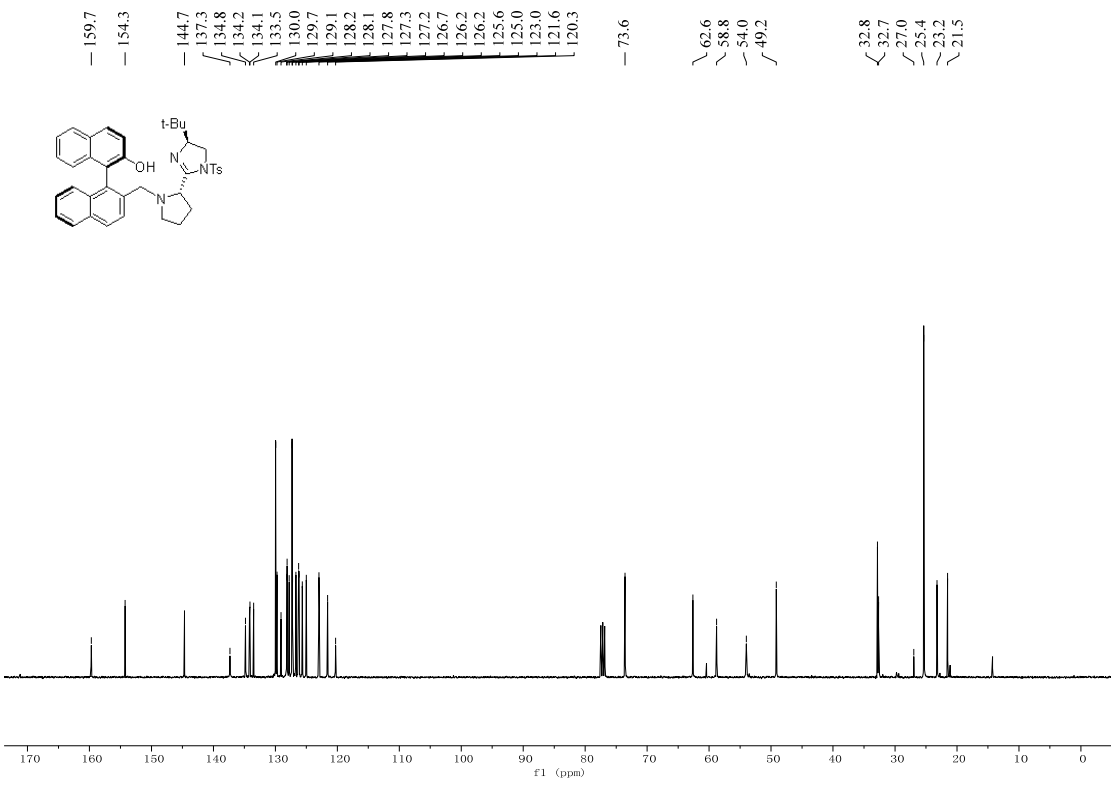
L2 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



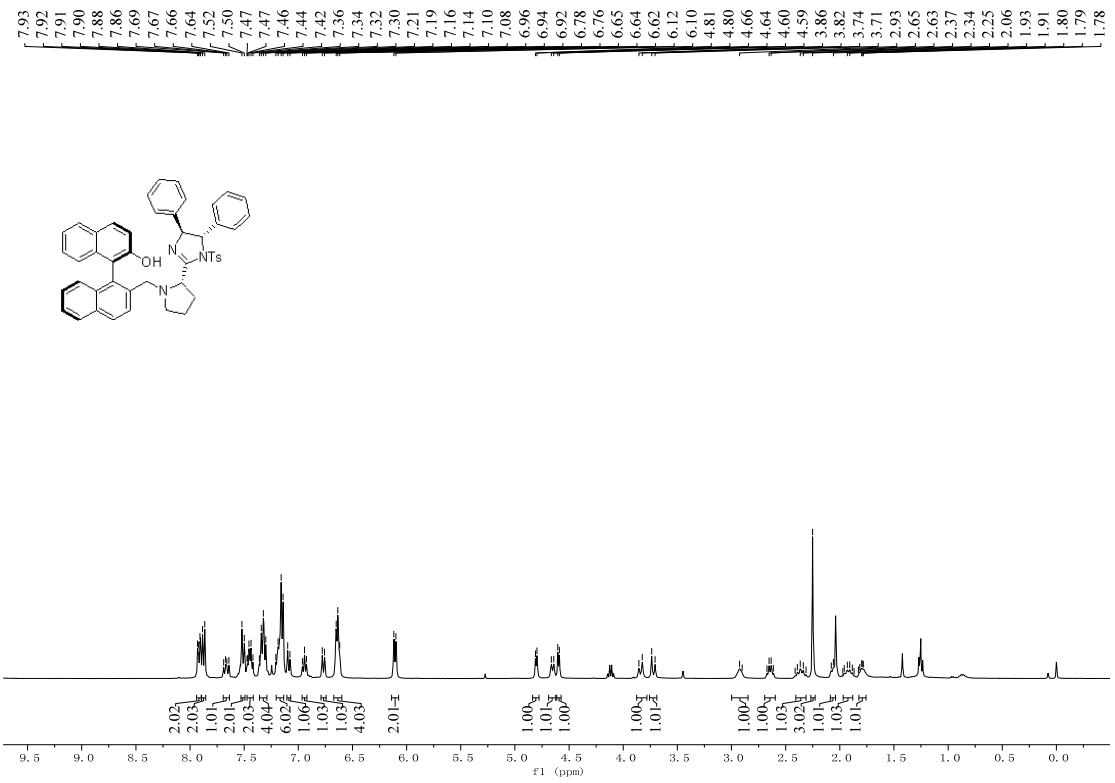
L3 ^{1}H NMR (400 MHz, $CDCl_3$)



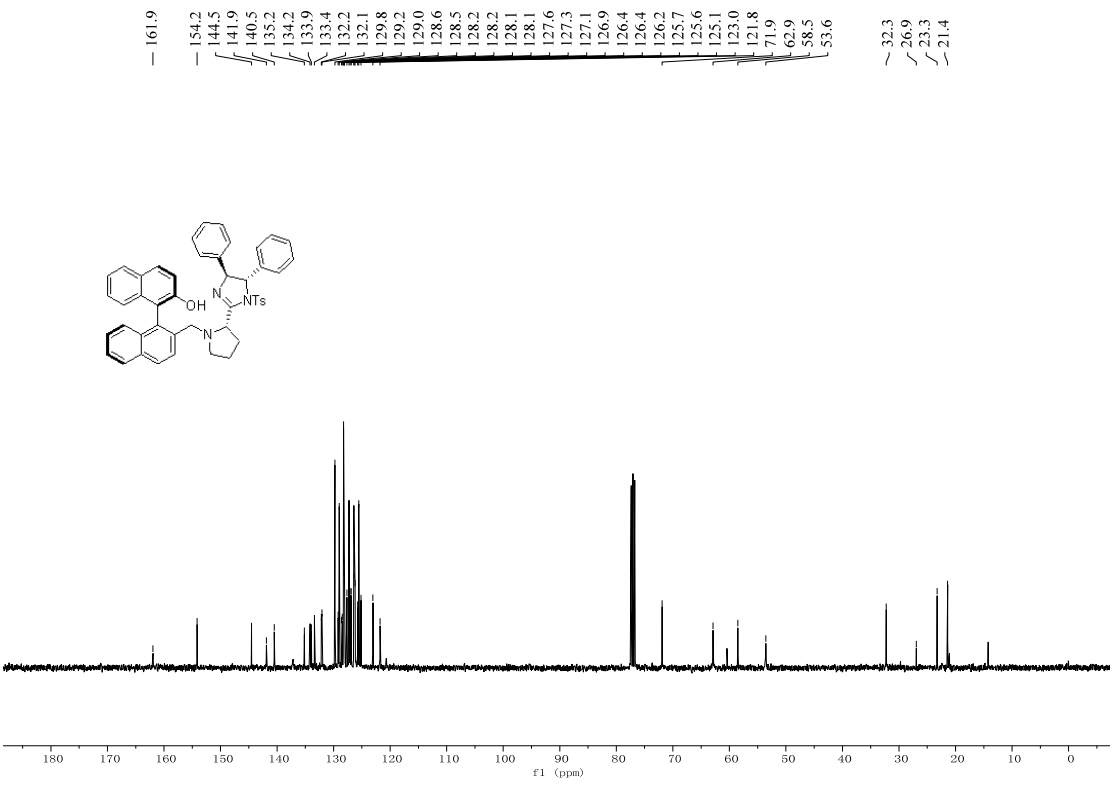
L3 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



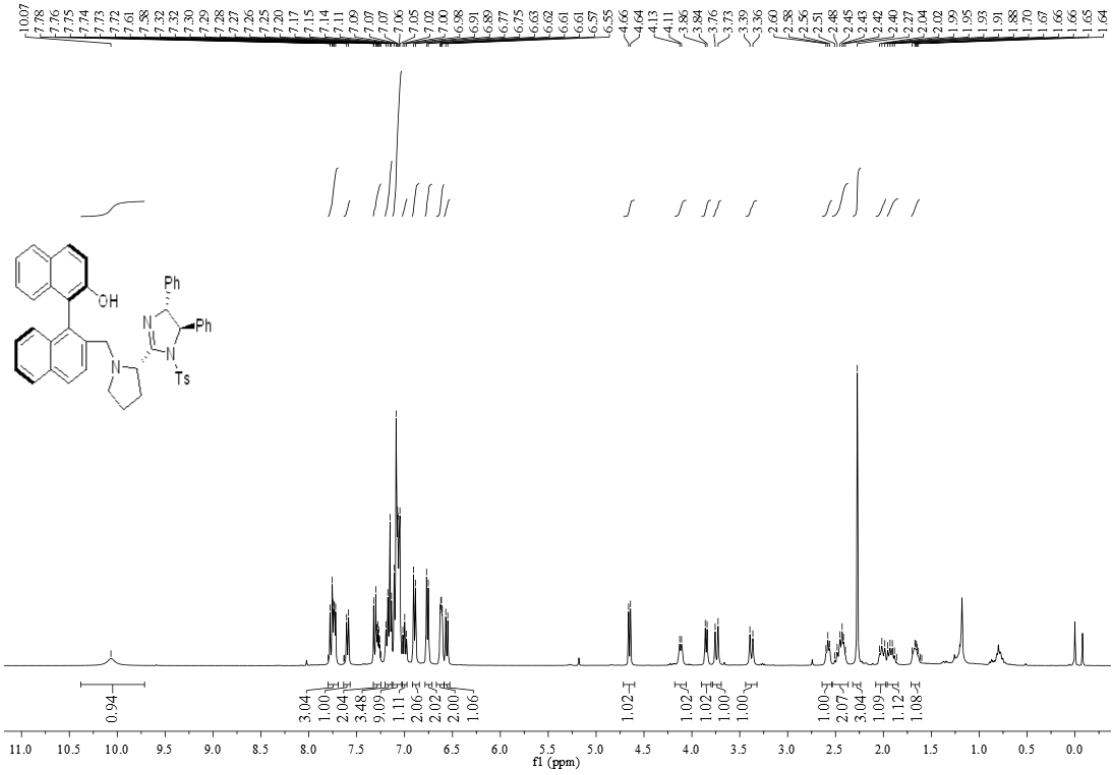
L4 ^{1}H NMR (400 MHz, $CDCl_3$)



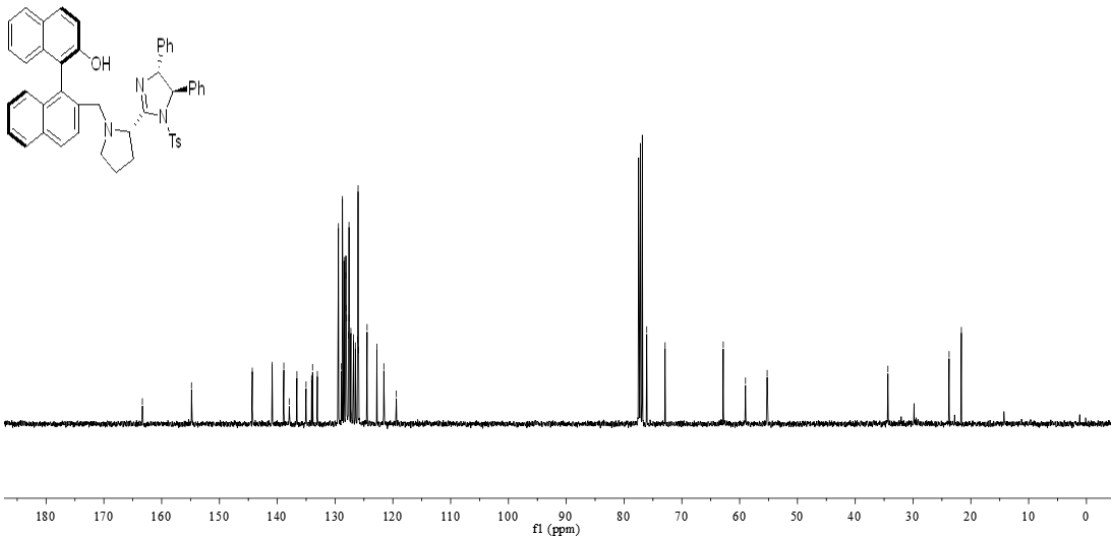
L4 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



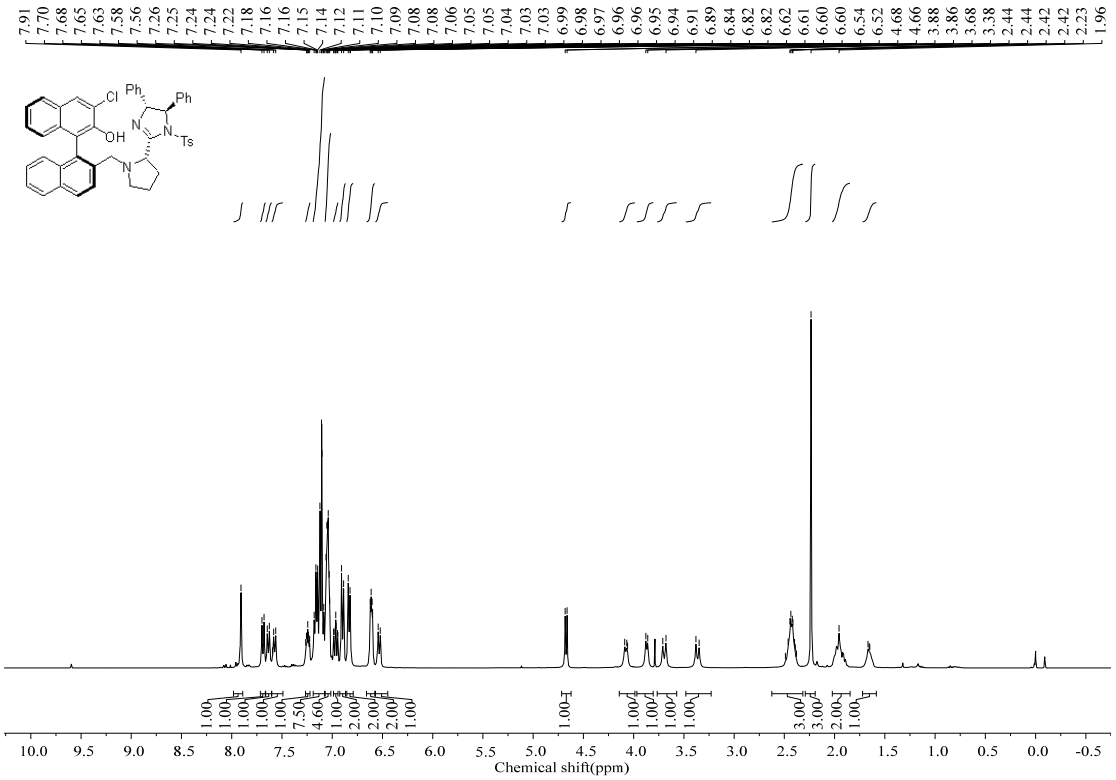
L5 ^{1}H NMR (400 MHz, $CDCl_3$)



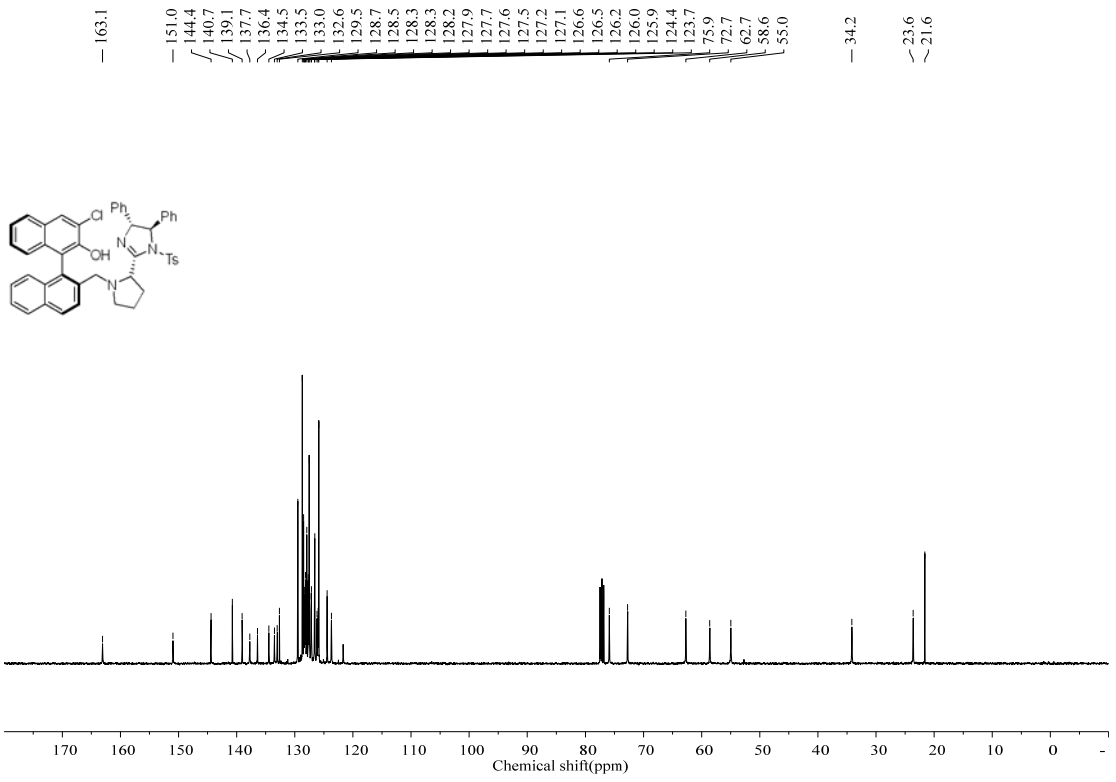
L5 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



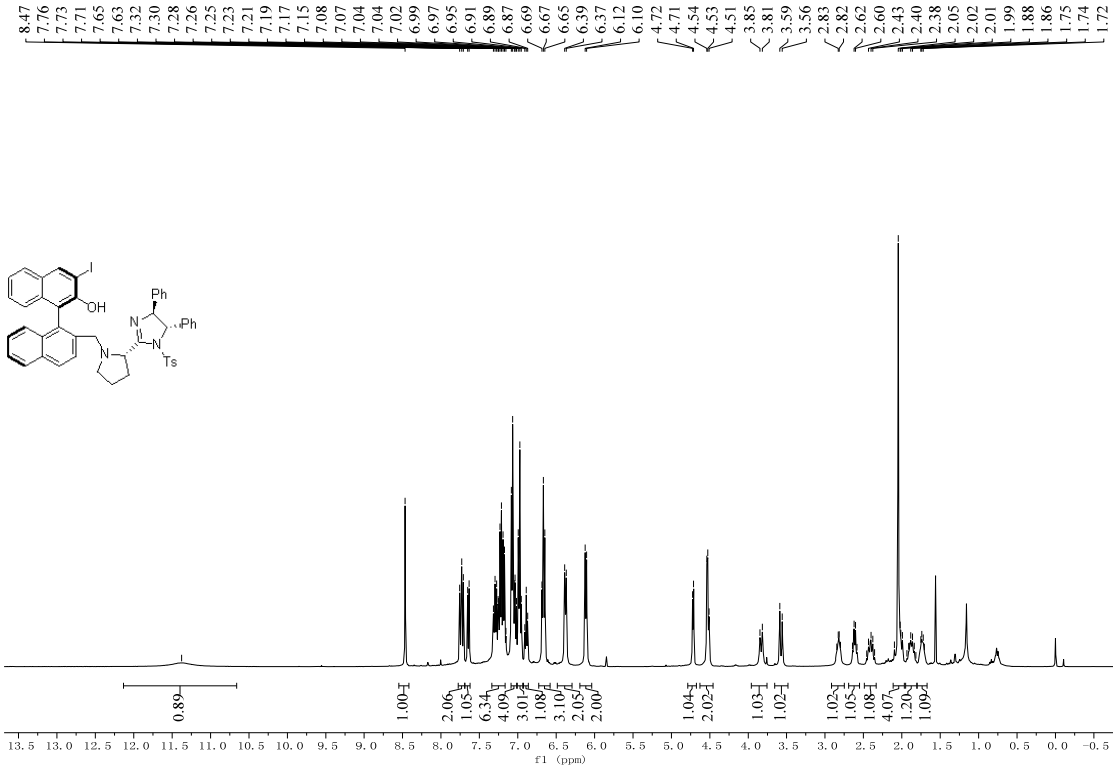
L6 ^{1}H NMR (400 MHz, $CDCl_3$)



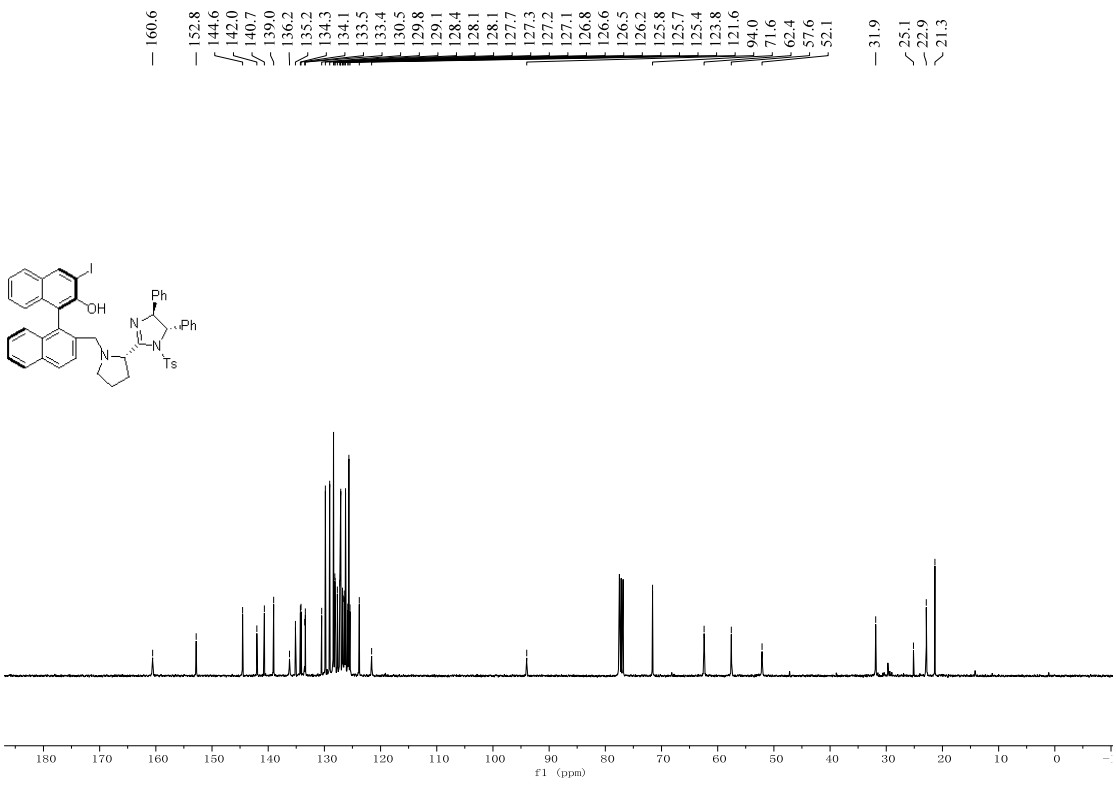
L6 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



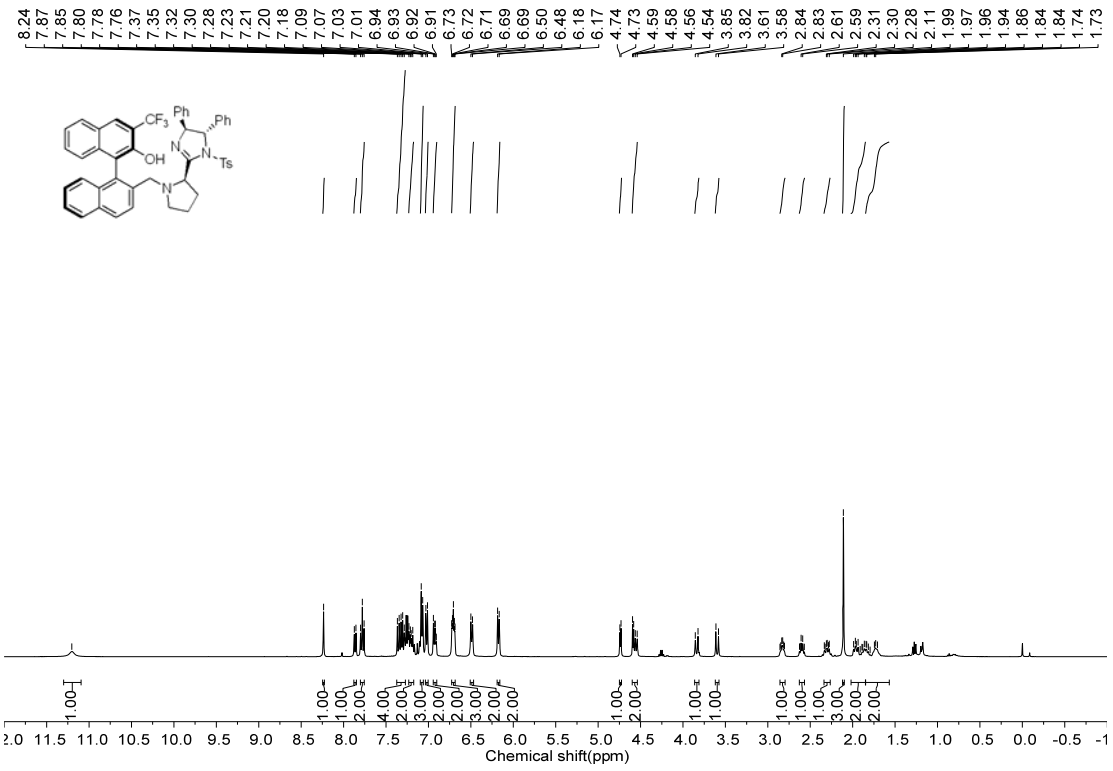
L7 ^{1}H NMR (400 MHz, $CDCl_3$)



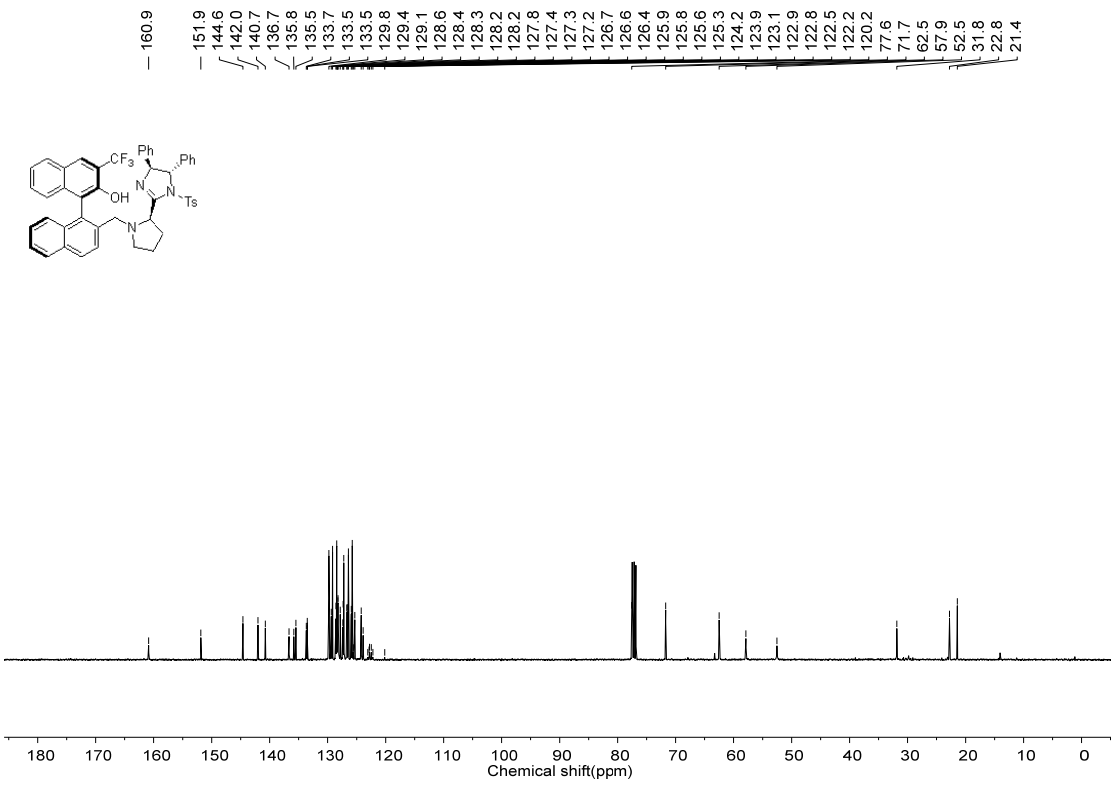
L7 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



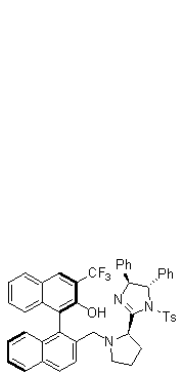
L8 ^{1}H NMR (400 MHz, $CDCl_3$)



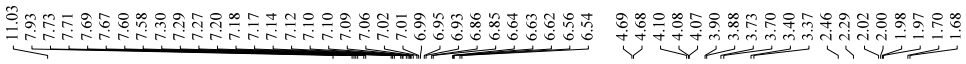
L8 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

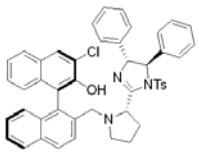


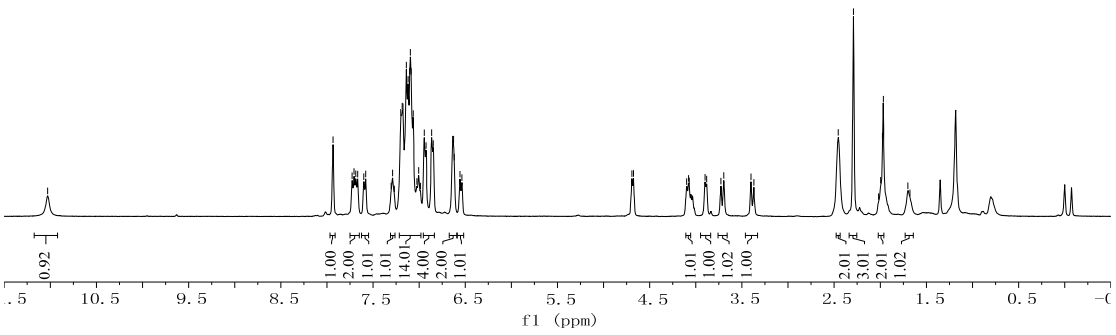
L8 ^{19}F NMR ($CDCl_3$)



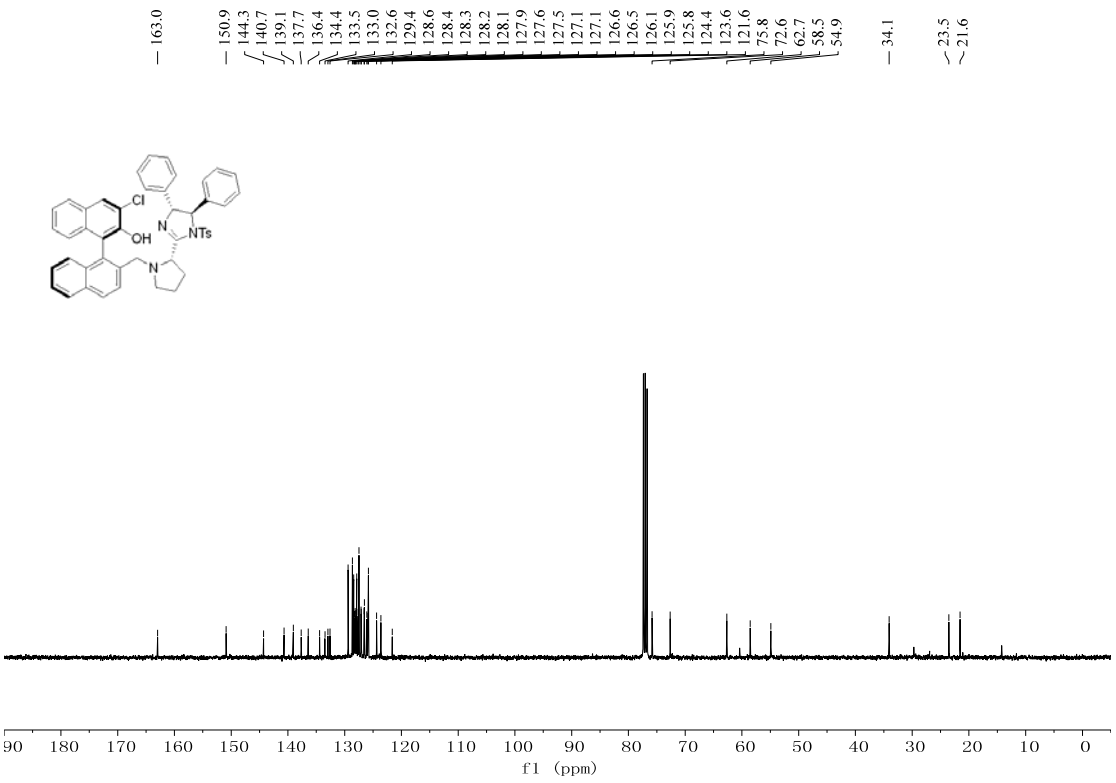
L9 ^{1}H NMR (400 MHz, $CDCl_3$)



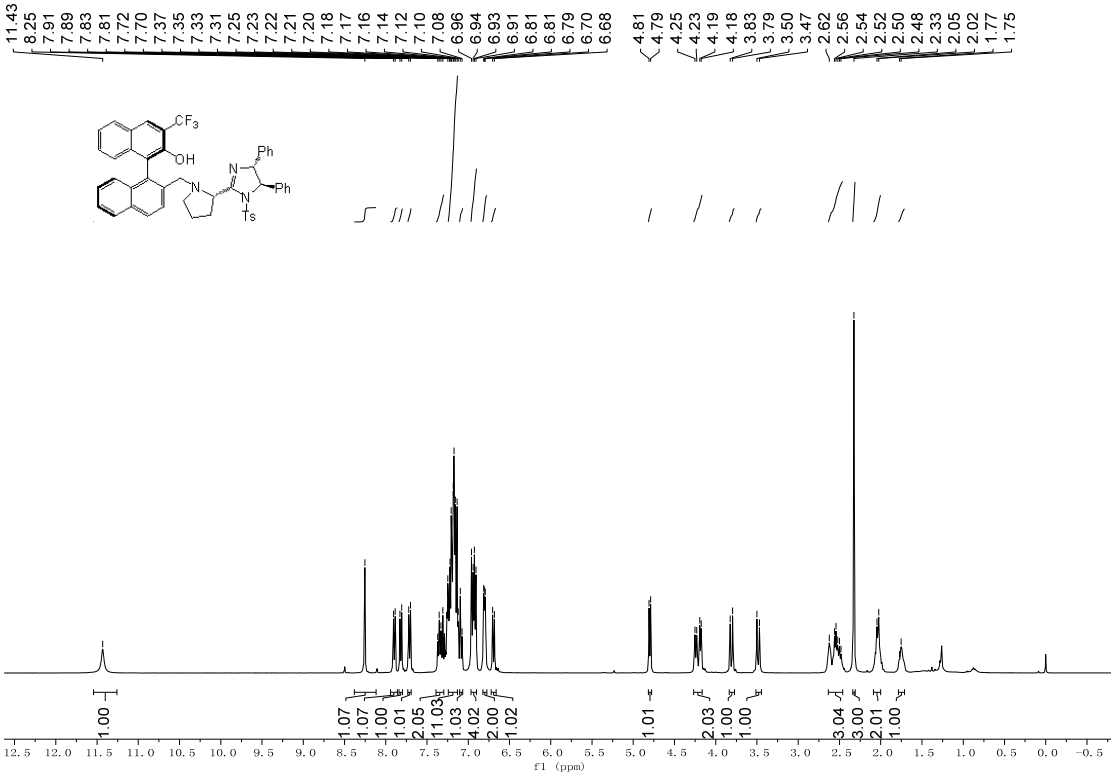




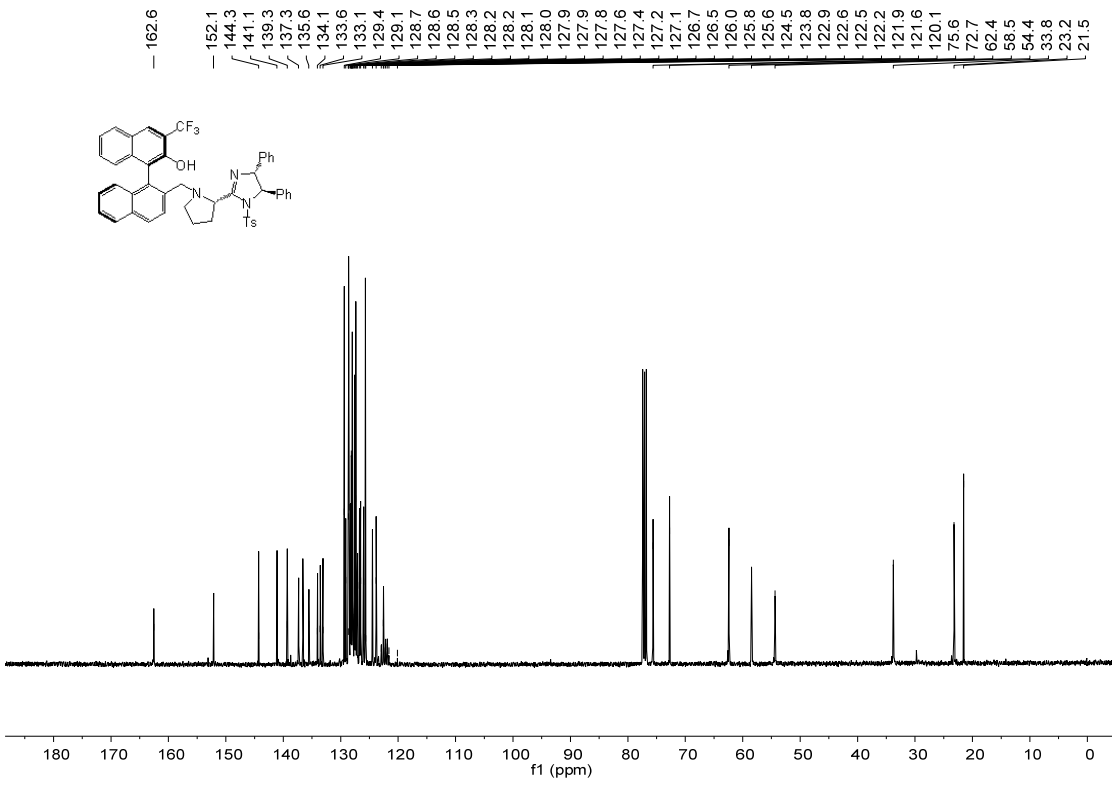
L9 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



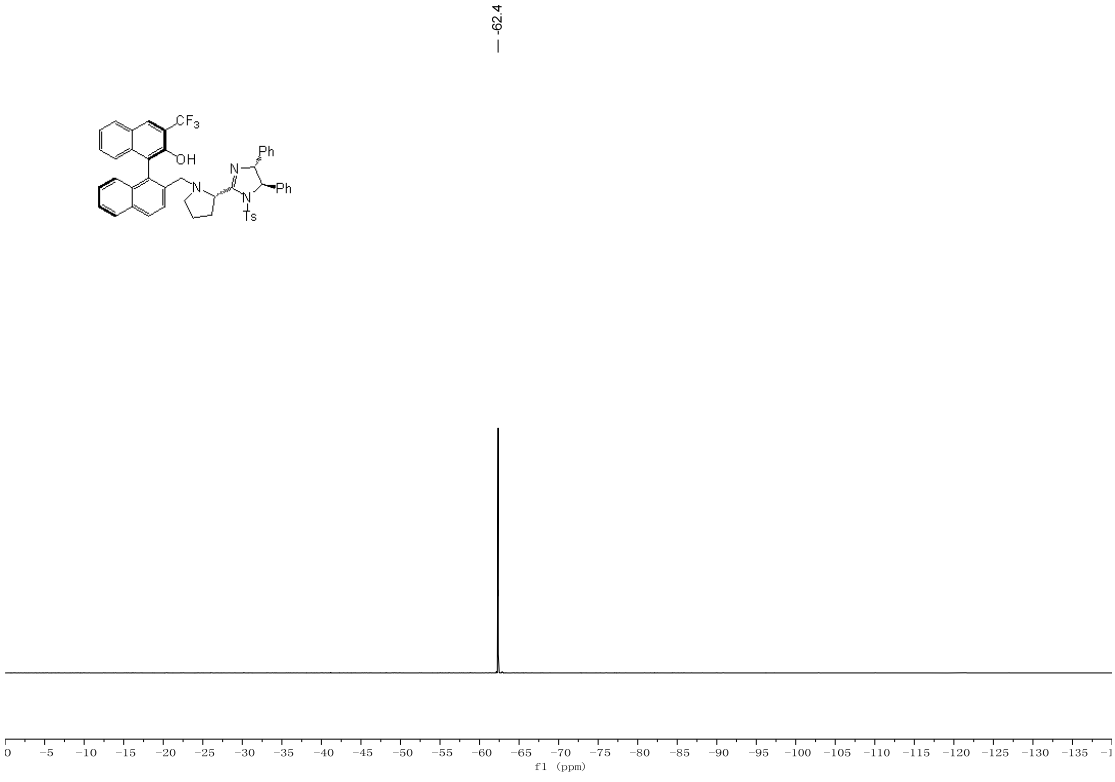
L10 ^{1}H NMR (400 MHz, $CDCl_3$)



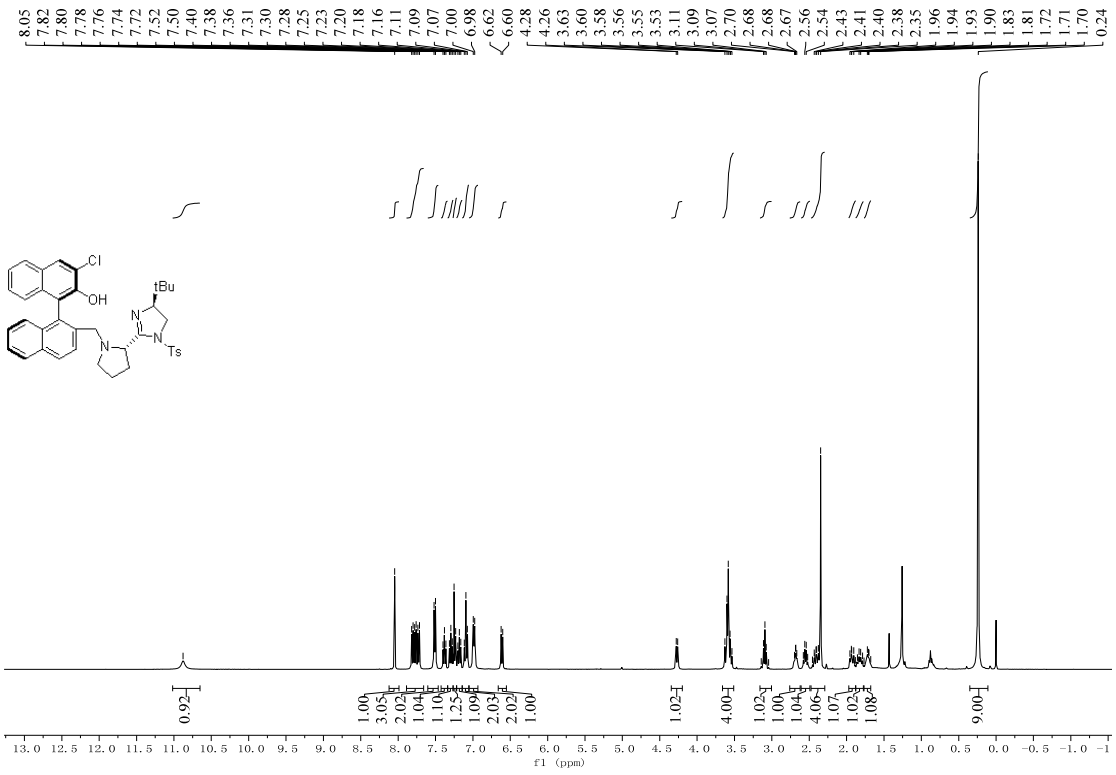
L10 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



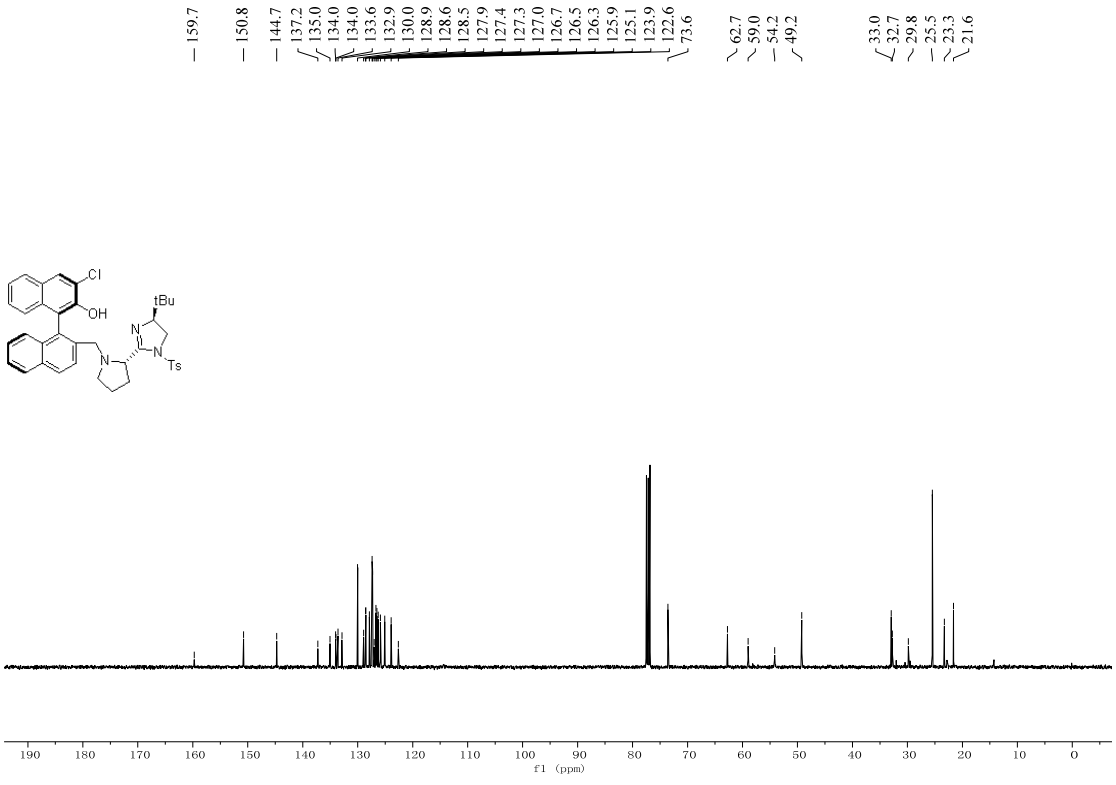
L10 ^{19}F NMR ($CDCl_3$)



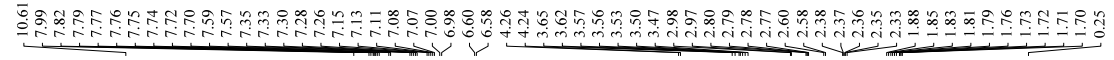
L11 ^{1}H NMR (400 MHz, $CDCl_3$)

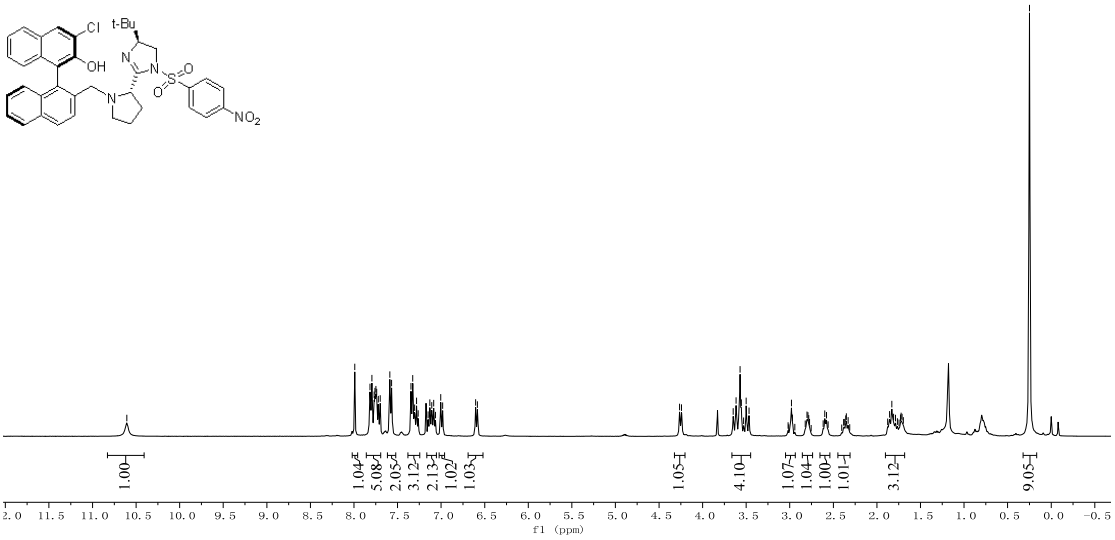


L11 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

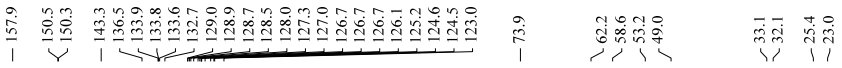


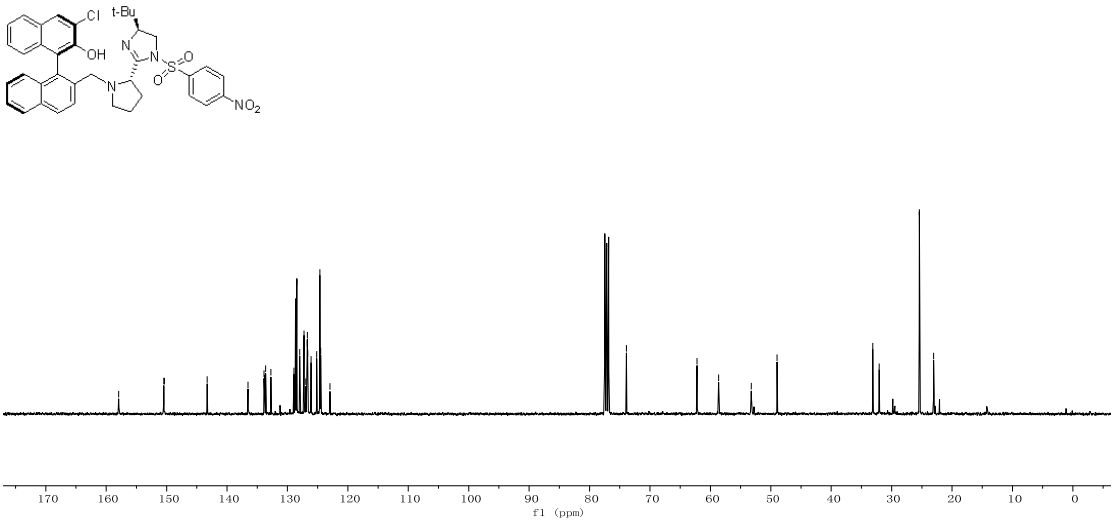
L12 ^{1}H NMR (400 MHz, $CDCl_3$)



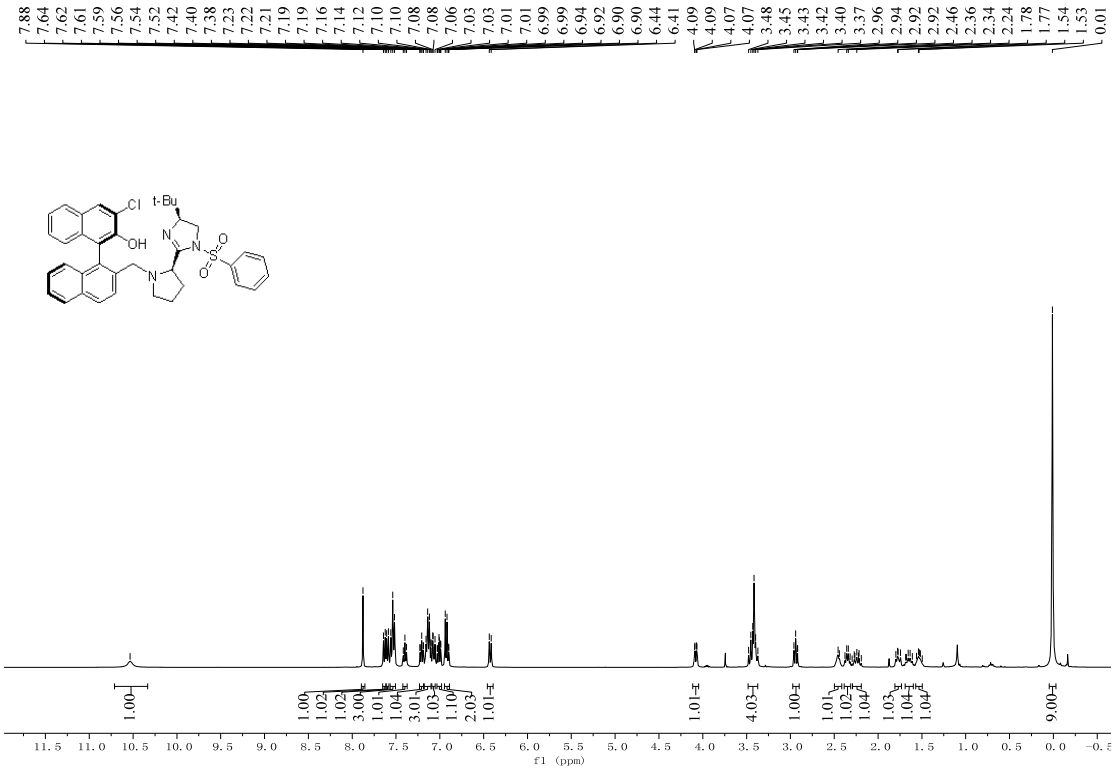


L12 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

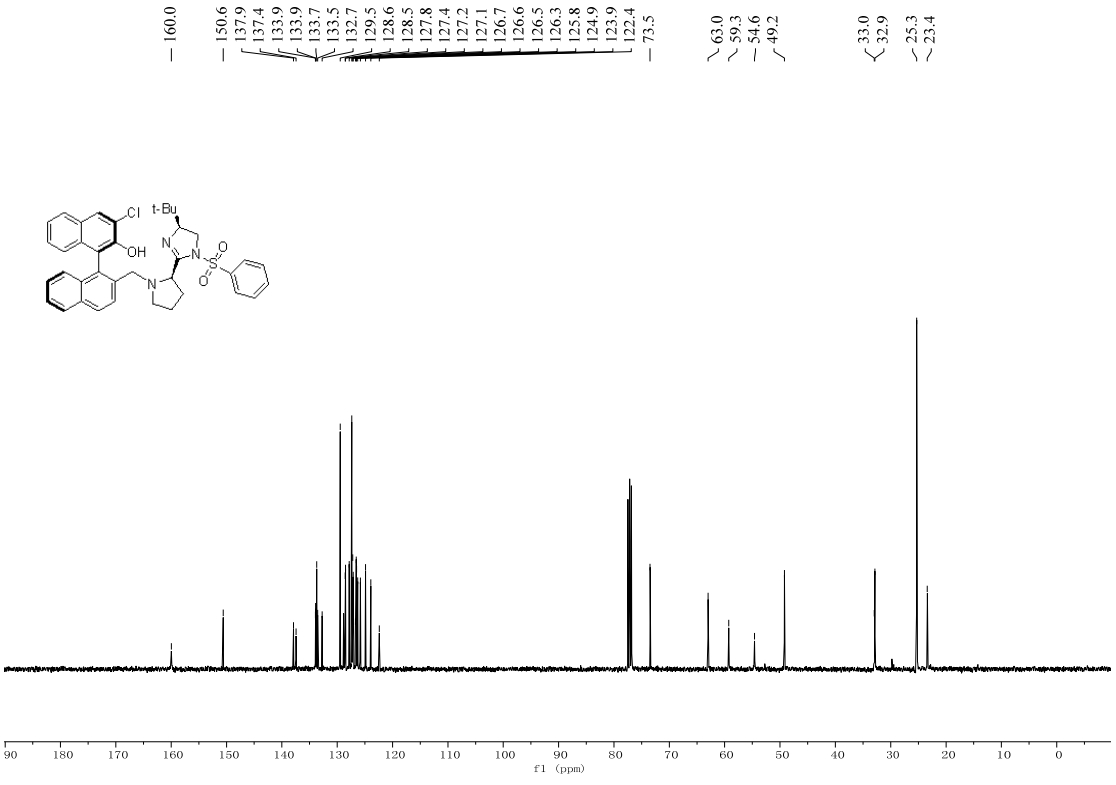




L13 ^{1}H NMR (400 MHz, $CDCl_3$)



L13 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



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