Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

DABCO-catalyzed [3 + 2] Annulation of Sulfamate-derived Cyclic Imines with Isocyanoacetates: Synthesis of Sulfamate-fused 2-Imidazoline

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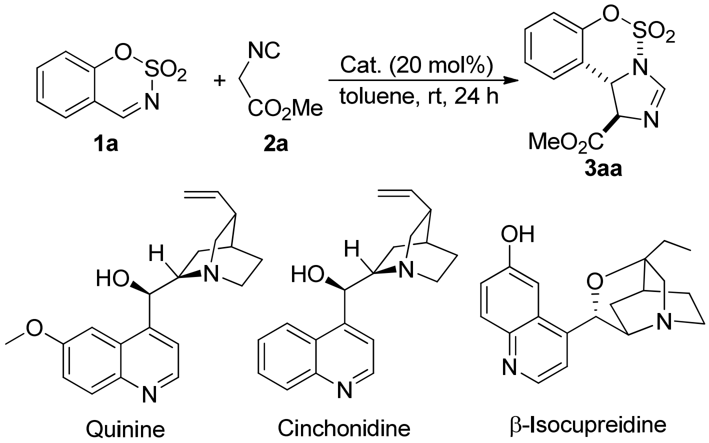
Contents

General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. The solvents employed in the reactions were treated under N_2 atmosphere using the standard procedure. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 300MHz NMR instrument (referenced internally to Me_4Si). Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined by a X-4 digital micro melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724+.

Table S1 Chiral amine-catalyzed [3 + 2] annulation of sulfamate-derived cyclic imine (**1a**) with isocyanoacetate (**2a**)^a



Entry	Cat.	Yield^b (%)	ee^c
1	Quinine	83	0
2	Cinchonidine	91	0
3	β-Isocupreidine	80	0

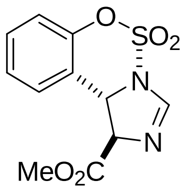
^{a} Unless otherwise indicated, reactions were performed with **1a** (0.2 mmol), **2a** (0.22 mmol) and the catalyst (0.04 mmol) in 2.0 mL of toluene. ^{b} Isolated yields. ^{c} Determined by Chiral HPLC analysis. dr had not been determined.

General Procedure for the Scaled-up Synthesis

Under a N_2 atmosphere, to a stirred solution of cyclic imines **1a** (2 mmol) and DABCO (0.4 mmol) in toluene (20 mL) was added methyl 2-isocyanoacetate **2a** (2.2 mmol) via a syringe in one portion. Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was complete, the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/EtOAc with 1% of Et_3N) to furnish the corresponding product **3aa** (0.429 g) as a white solid (76% yield, 30:1 dr).

General Procedure for Further Transformation of 3aa to the Derivative 4

The mixture of water (22 mg, 1.2 mmol), concentrated HCl solution (37%, 40.6 mg, 0.114 mmol), THF (2 mL), and sulfamate-fused 2-imidazoline **3aa** (56.4 mg, 0.2 mmol) was stirred for 8 h at room temperature. Then, the mixture was purified by column chromatography using EtOAc/MeOH (1:1) as eluent to afford **4** (58.3 mg, 97%yield, 5:1 dr). Diastereomeric ratio was calculated through ^{1}H NMR analysis.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N
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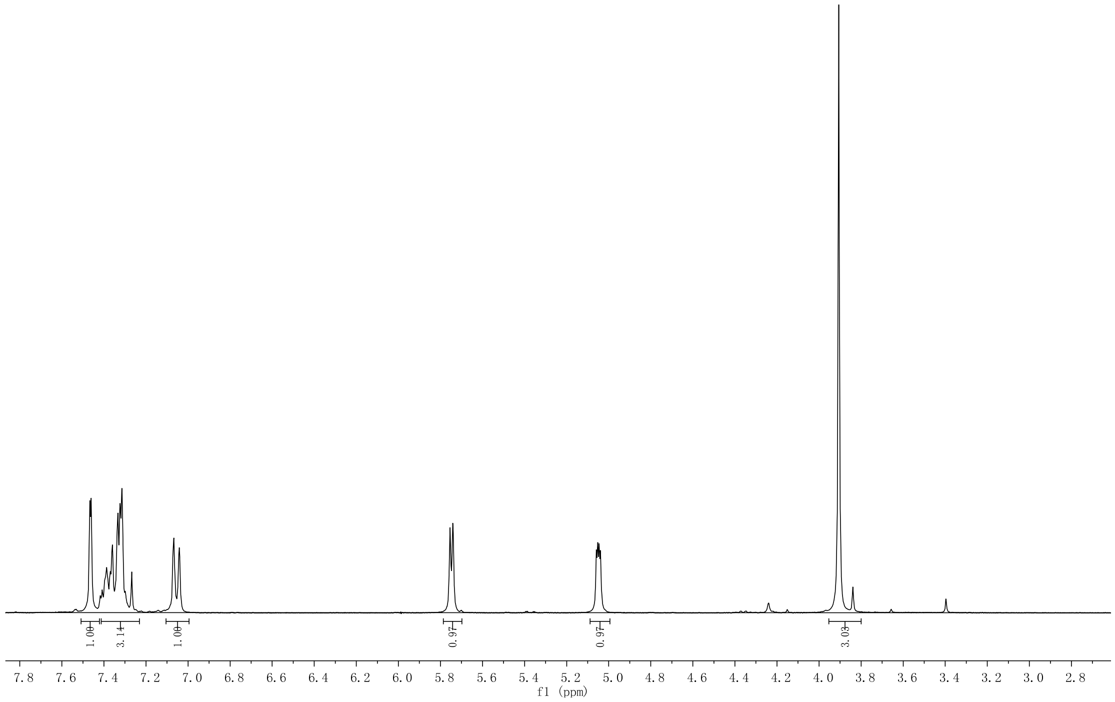
3aa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5.4
5.2
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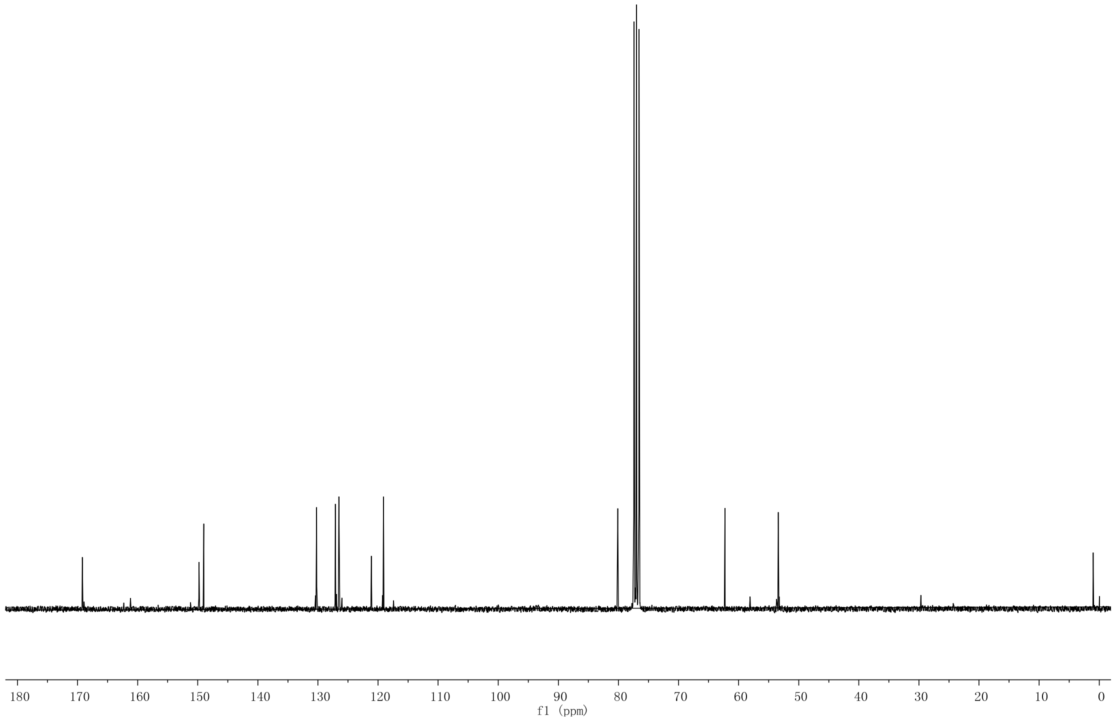
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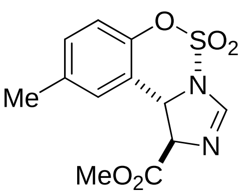
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N
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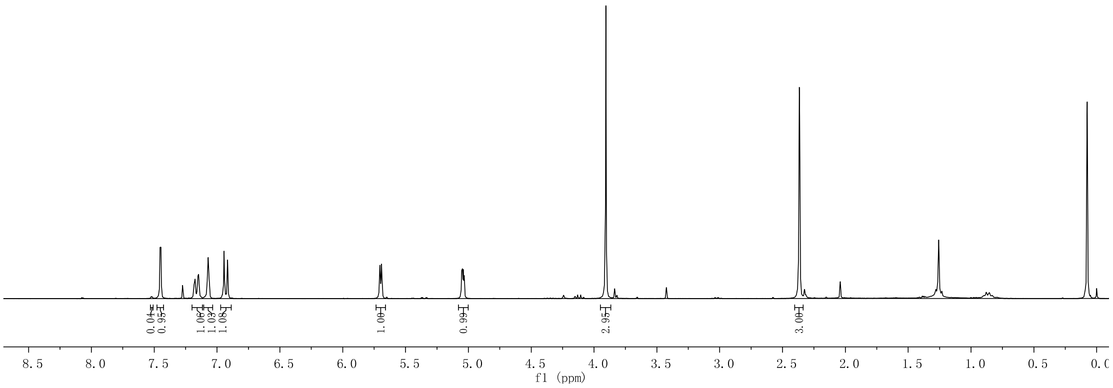
3ba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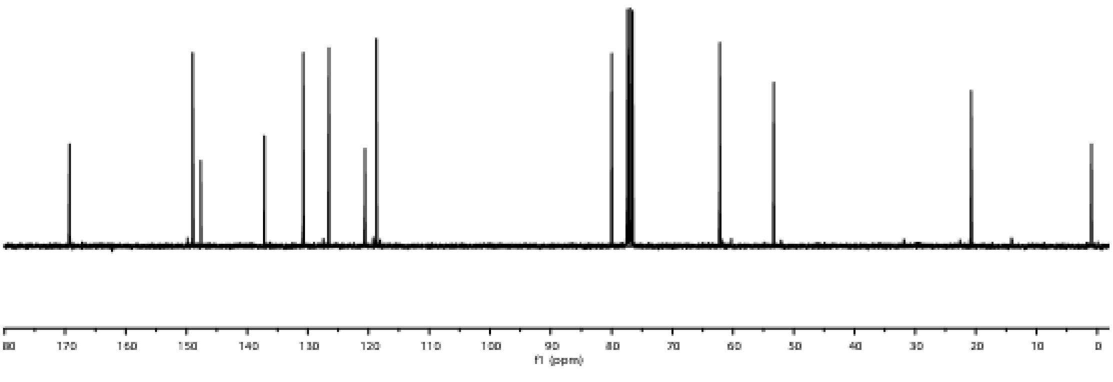
f1 (ppm)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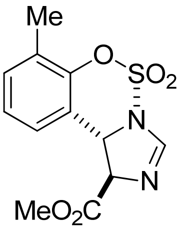
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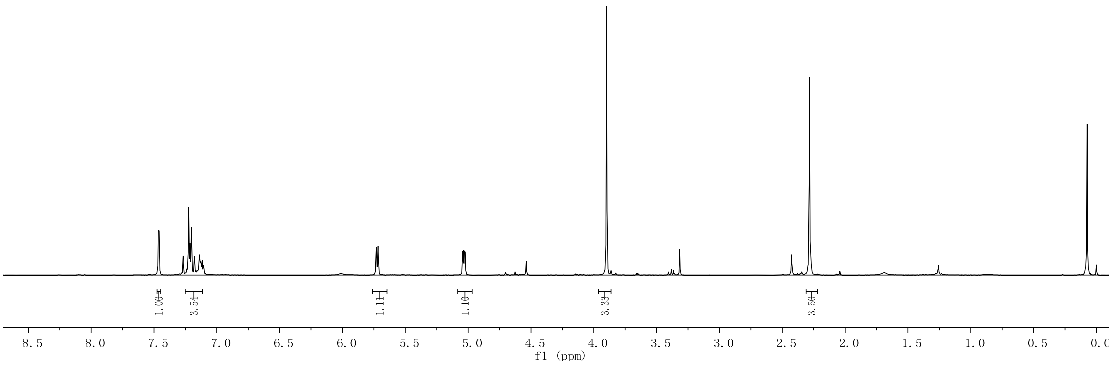
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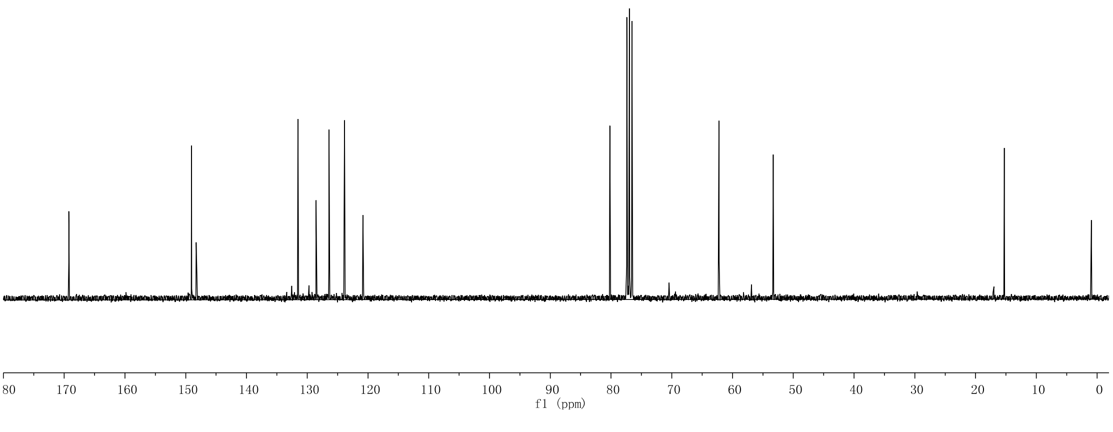
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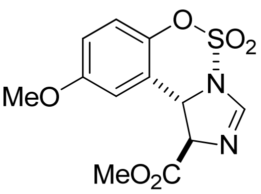
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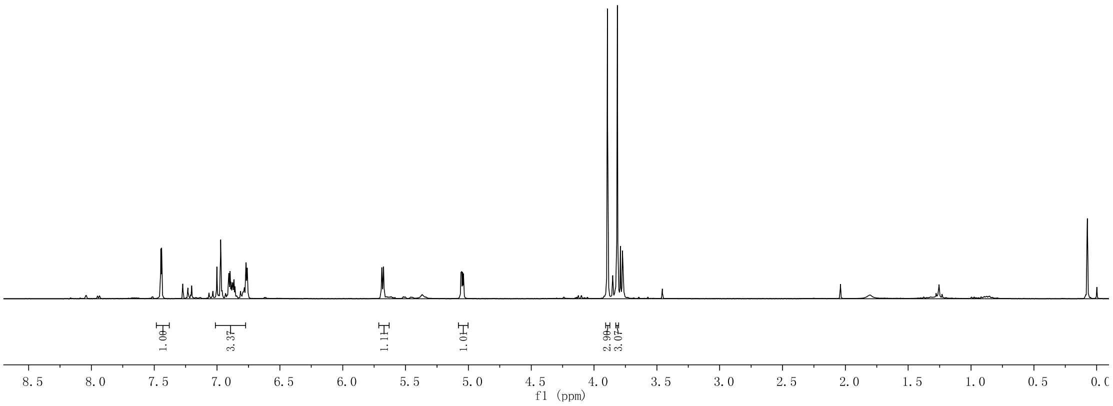
3da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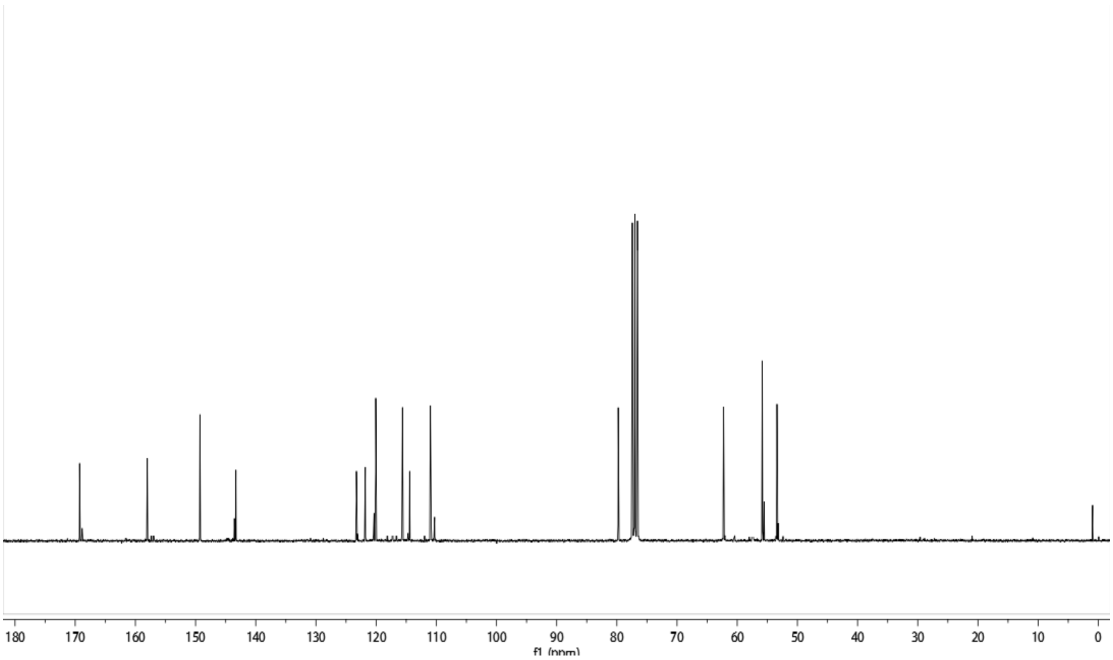
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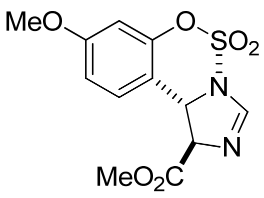
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SO2
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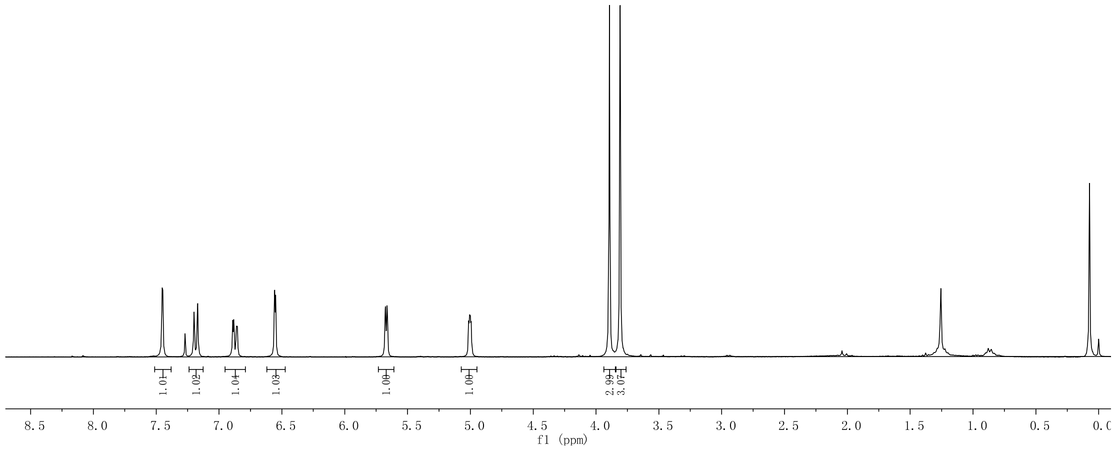
3ea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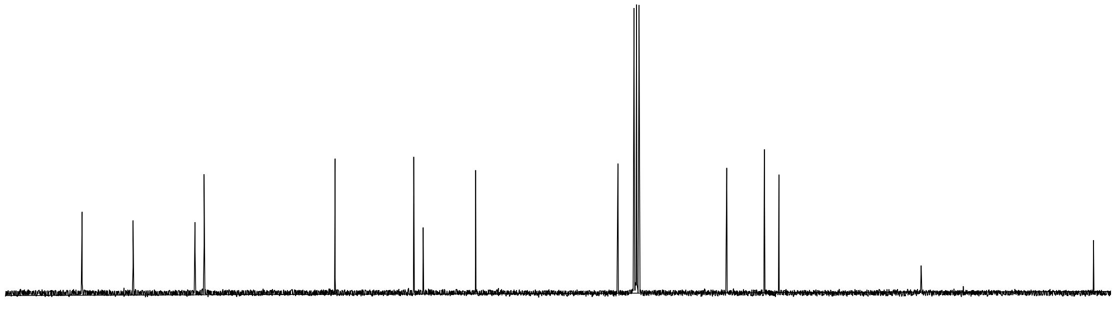
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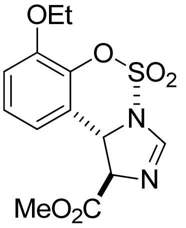
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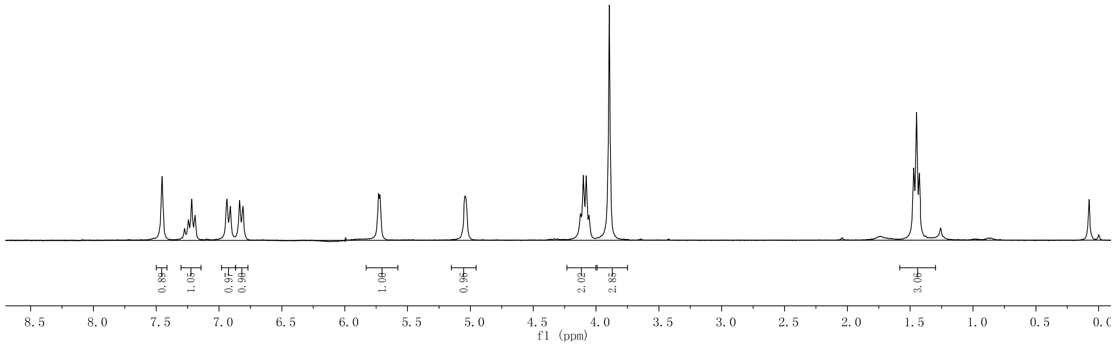
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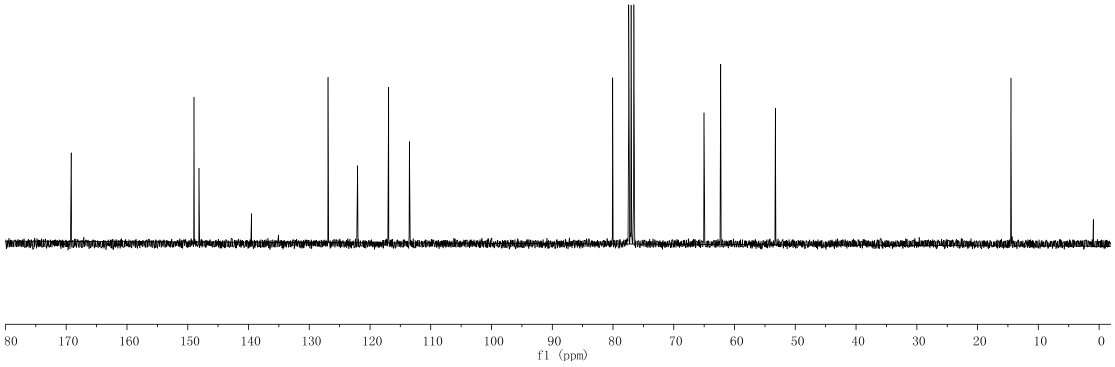
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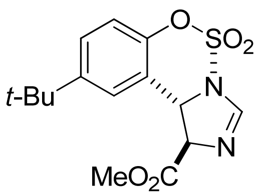
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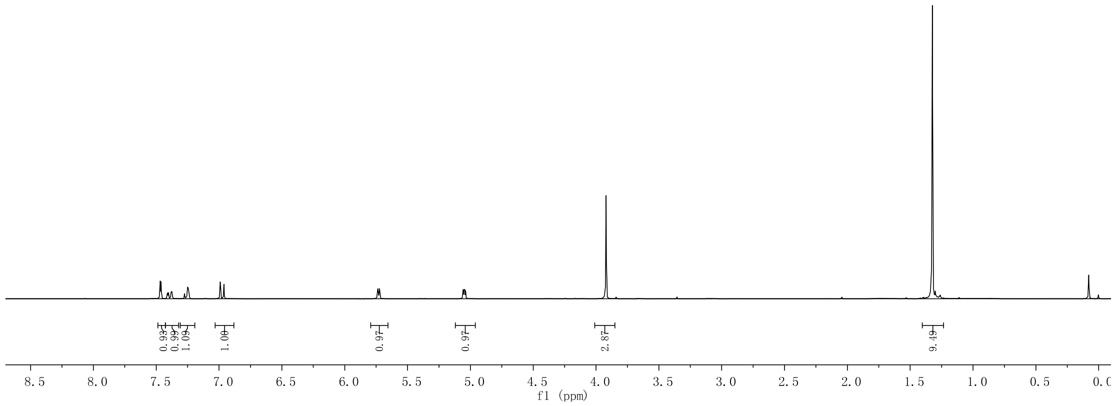
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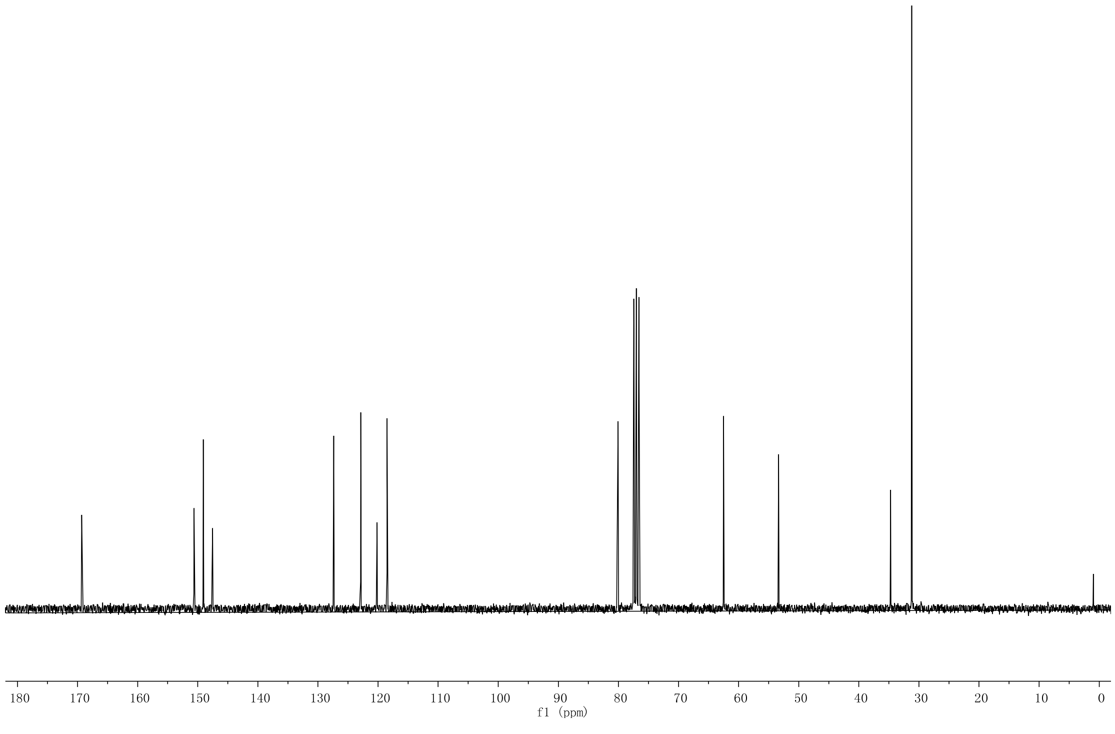
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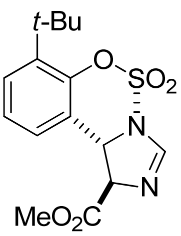

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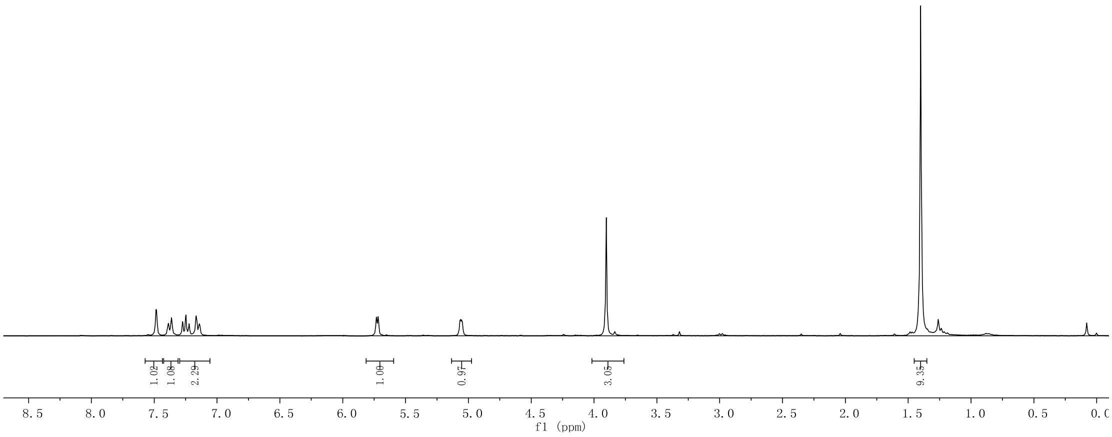

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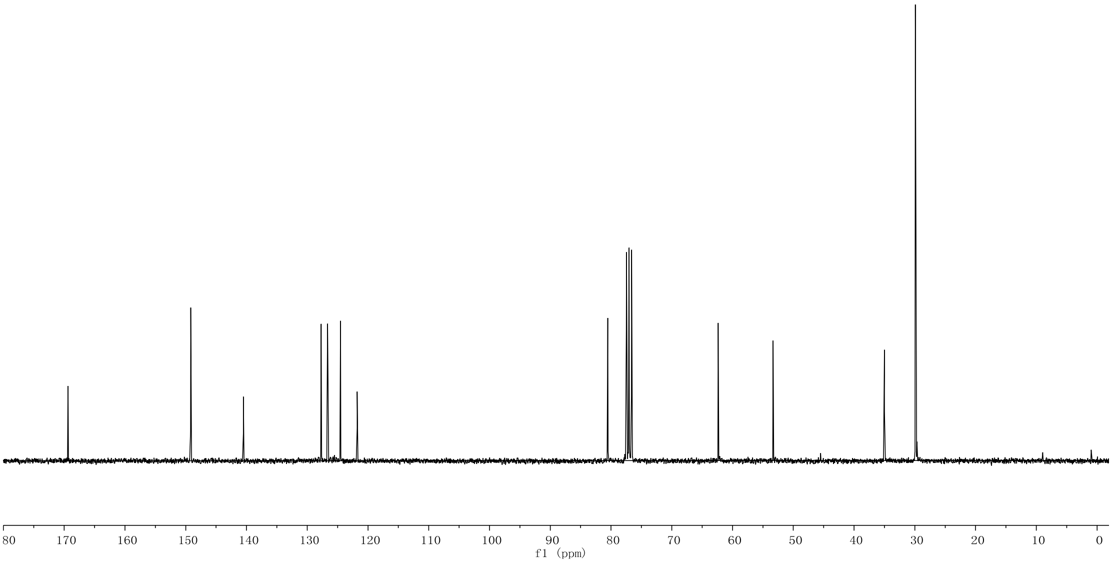

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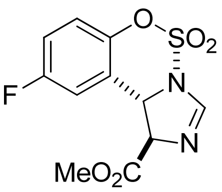
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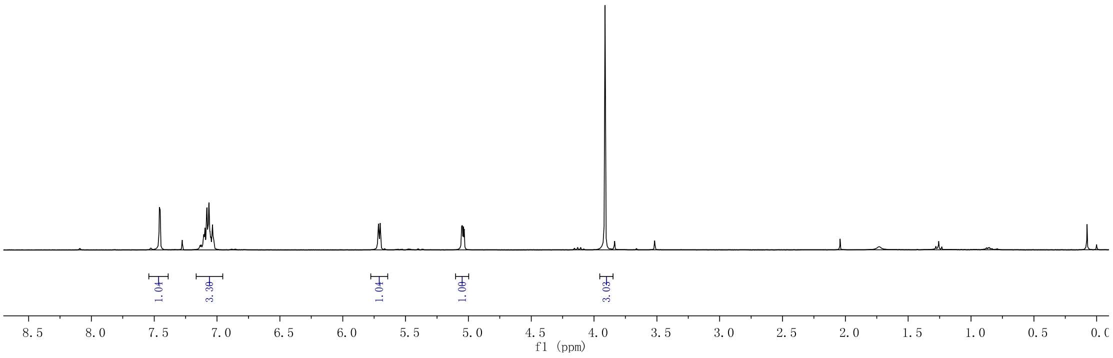
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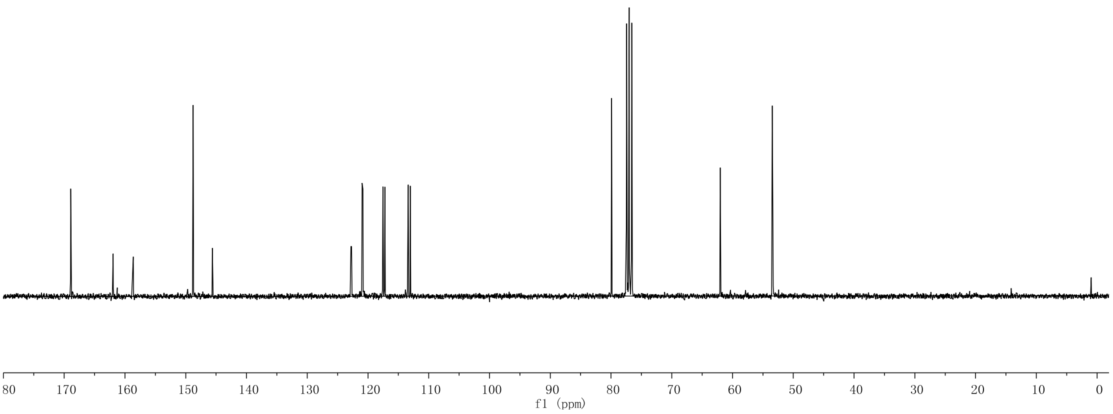
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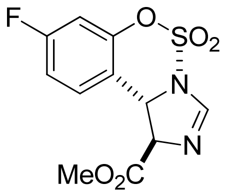
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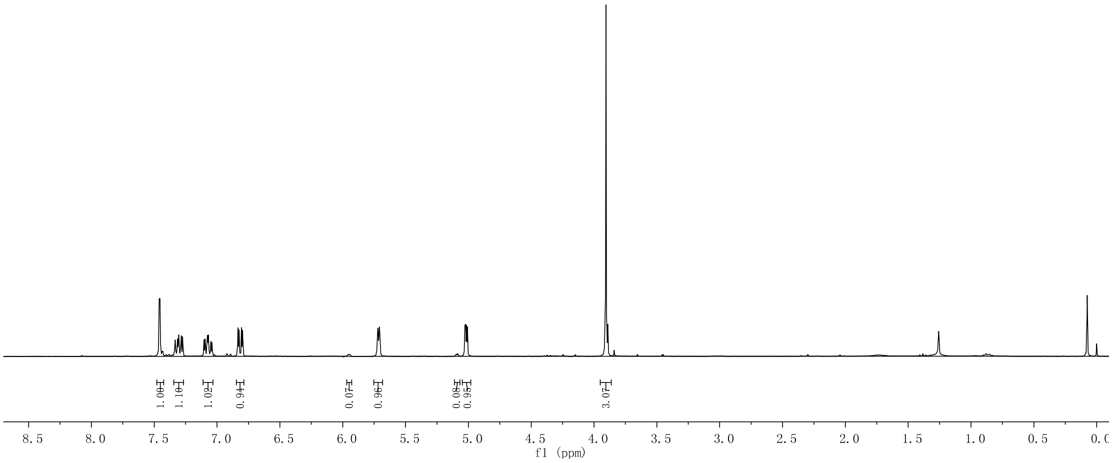
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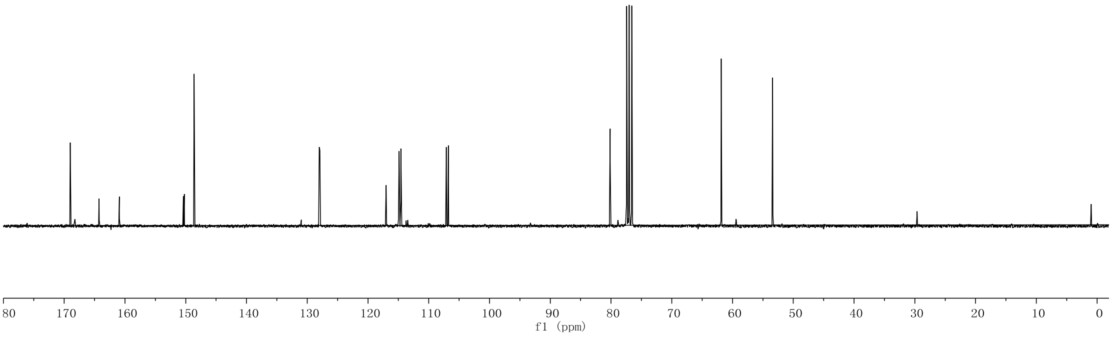
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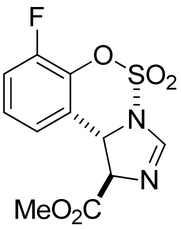
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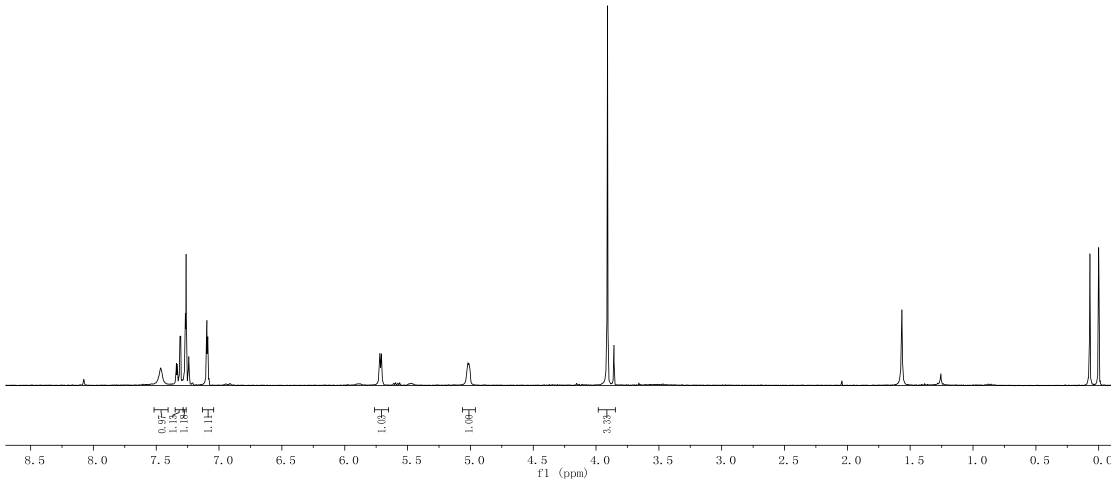
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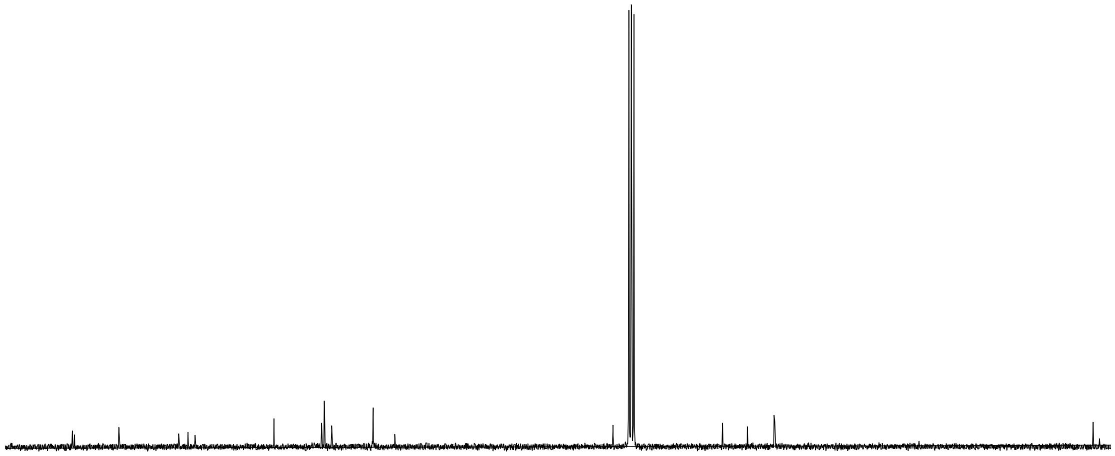

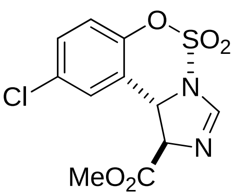
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N
Cl
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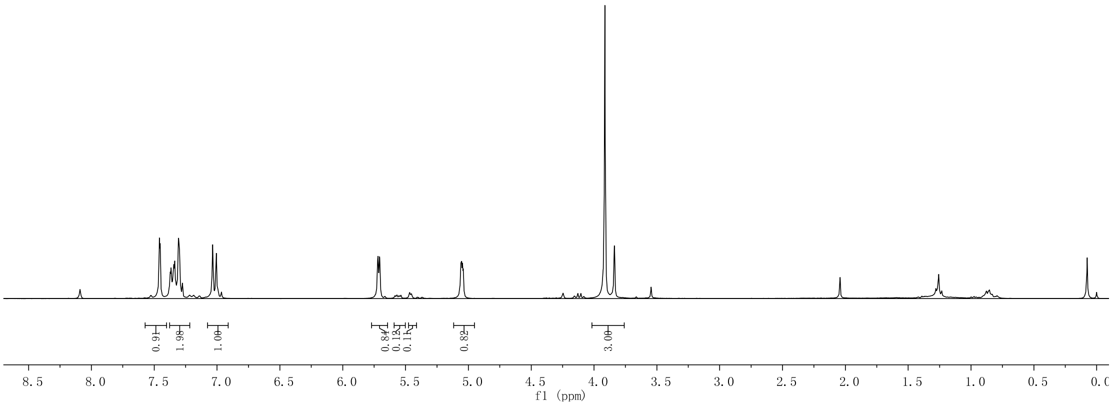
3la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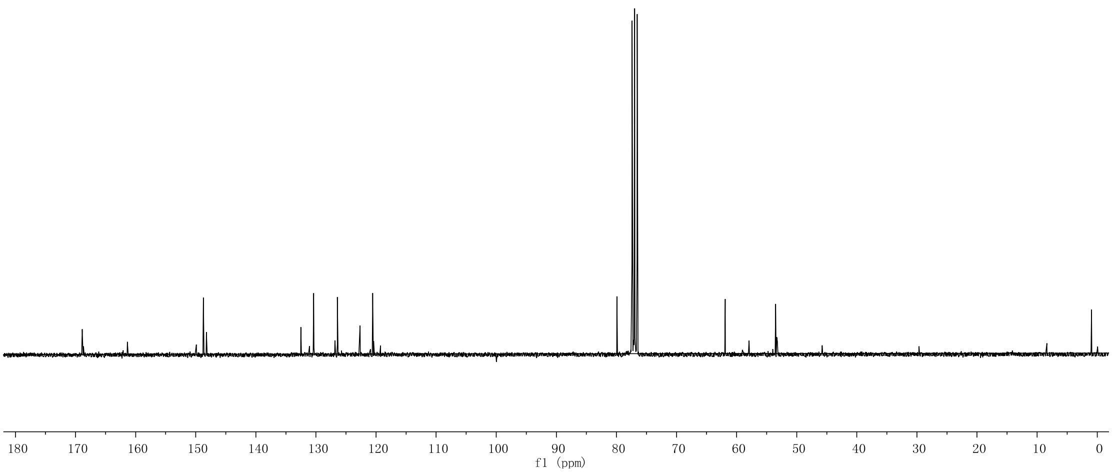
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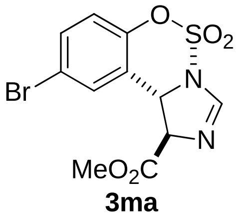
f1 (ppm)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N
Br
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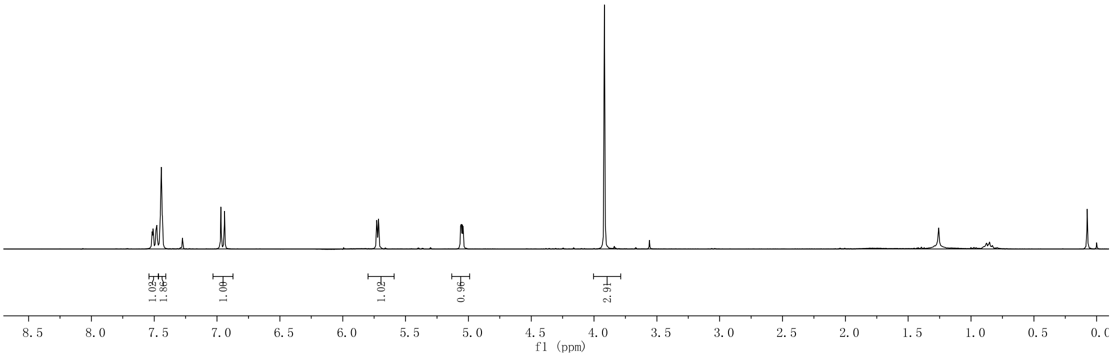
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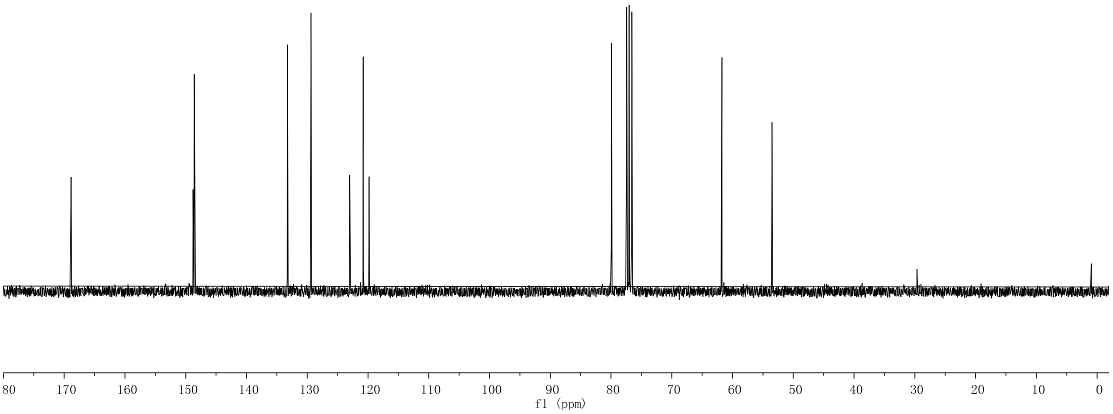
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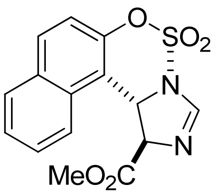
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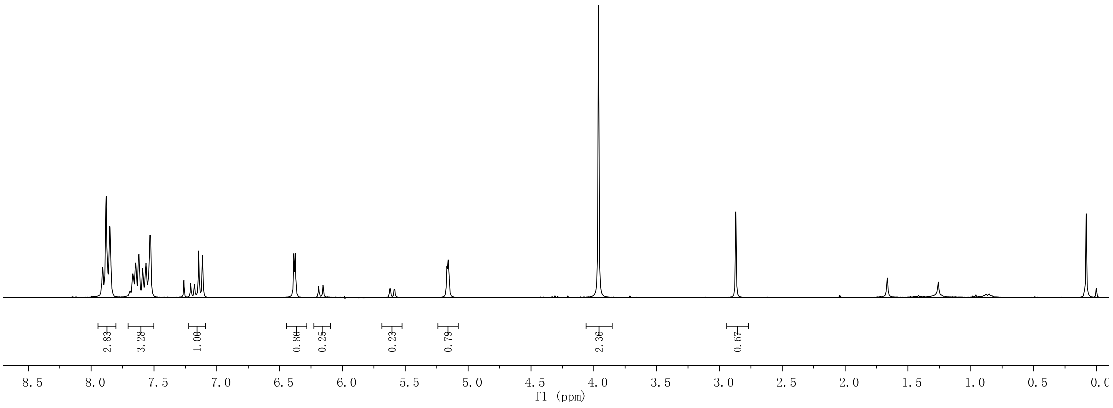
SO2
N
N
MeO2C

3na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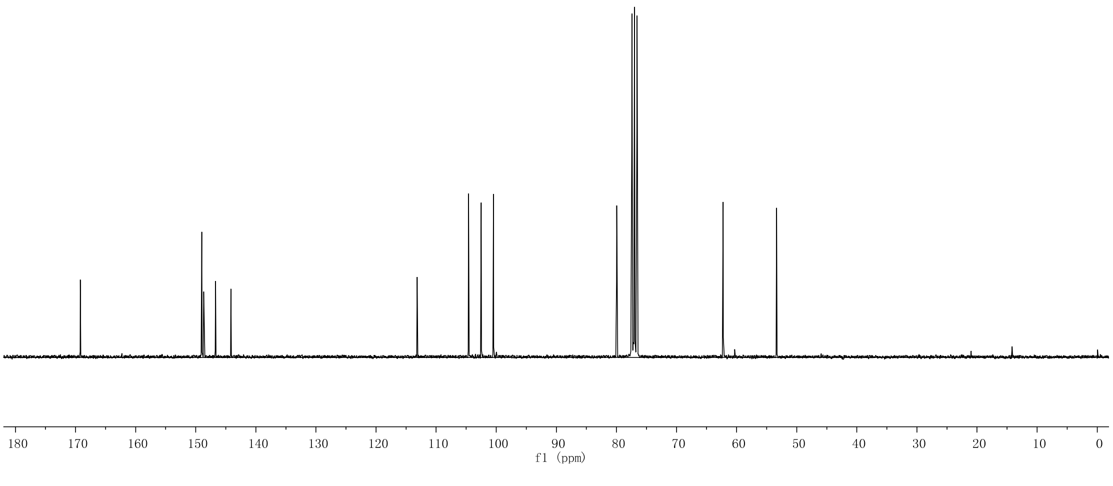
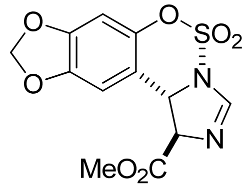
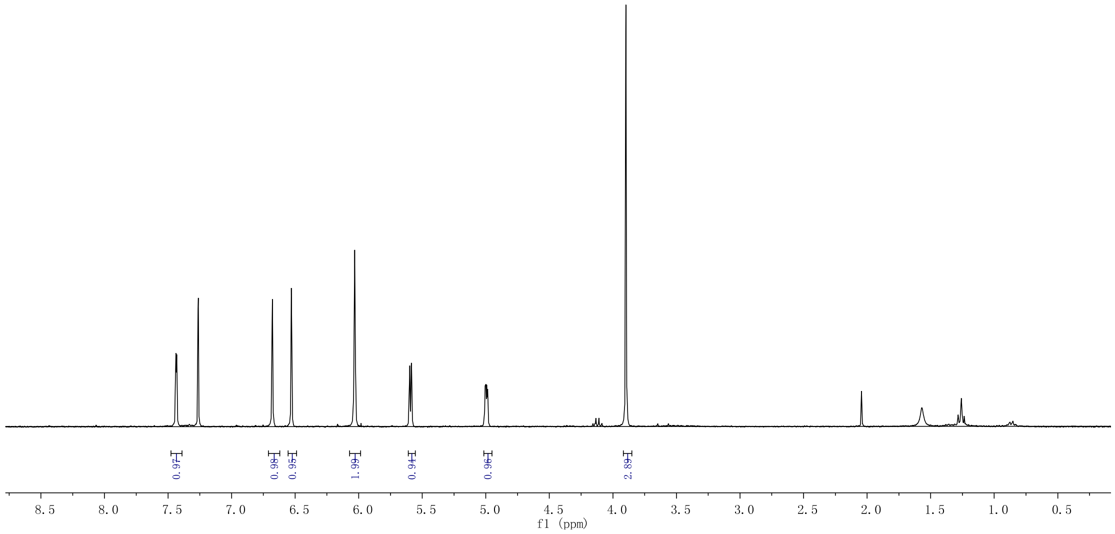
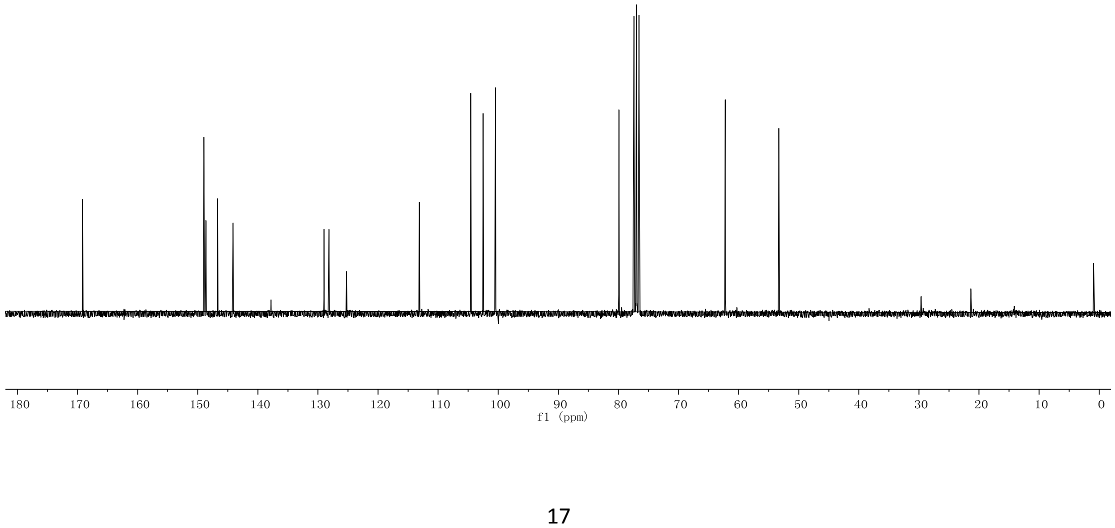
1.00
0.80
0.25
0.23
0.79
2.36
0.67
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

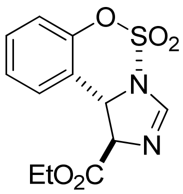

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
SO2
N
N
MeO2C

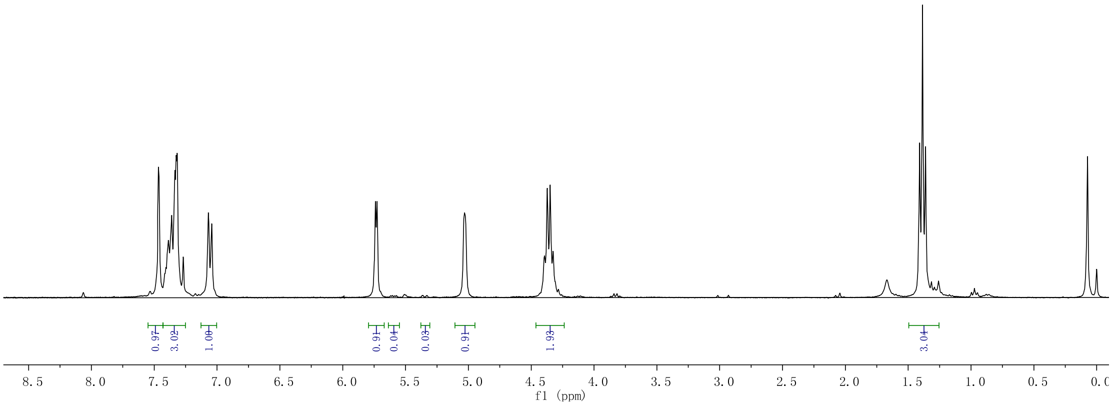
3oa

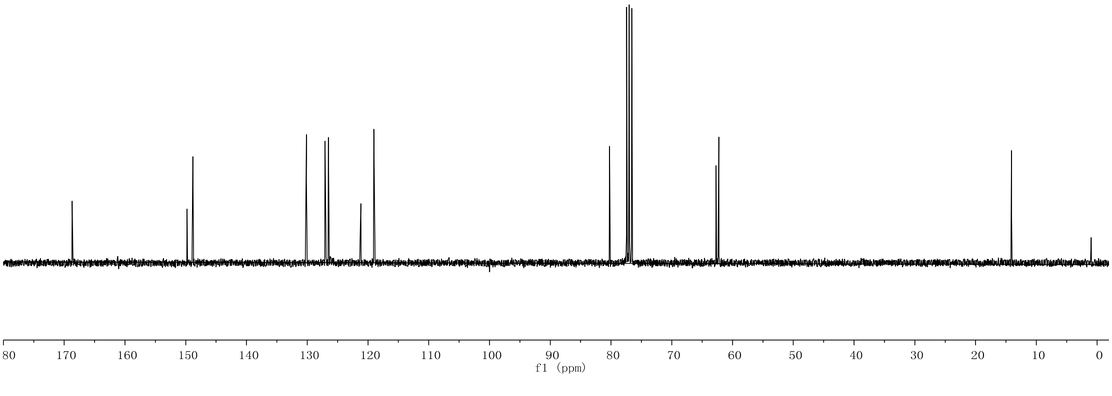

0.97
0.98
0.95
1.99
0.94
0.96
2.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

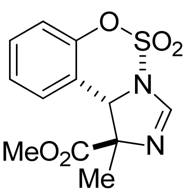

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SO2
N
N
EtO2C

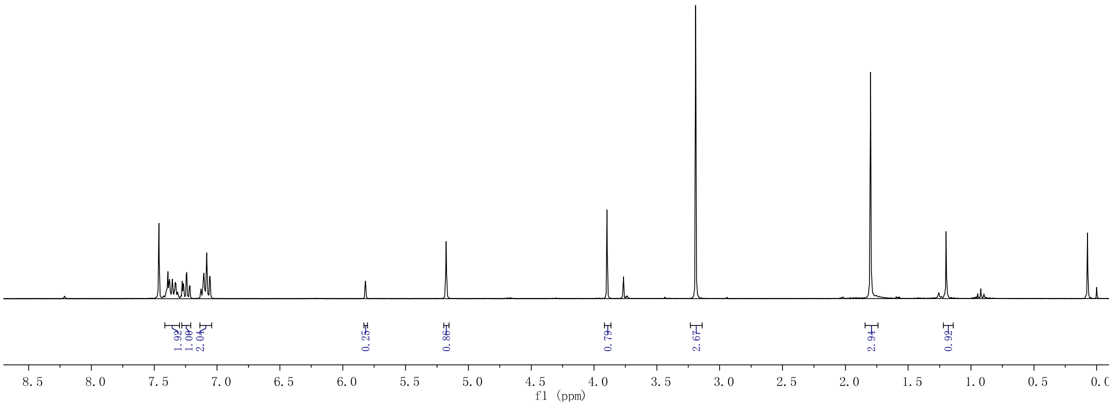
3ab

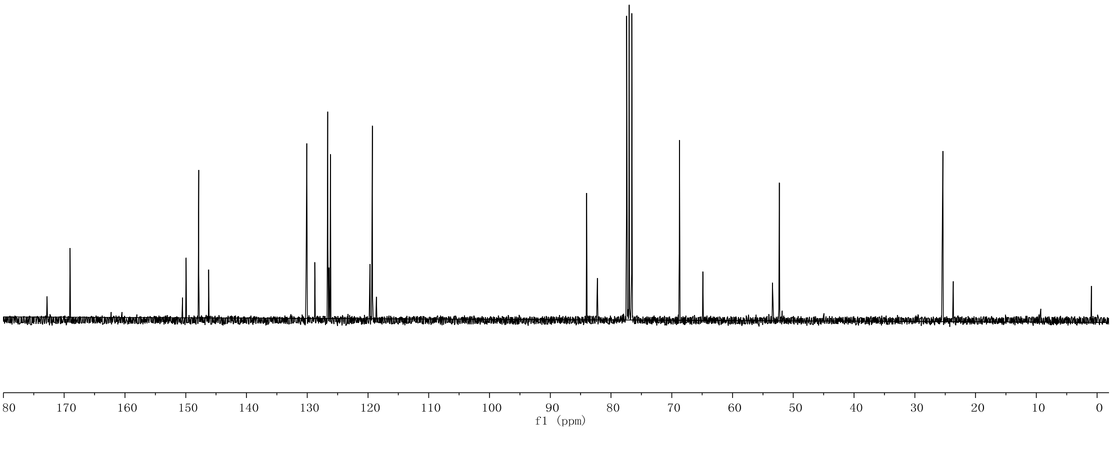

0.97
3.02
1.00
0.91
0.04
0.03
0.91
1.93
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.C
f1 (ppm)

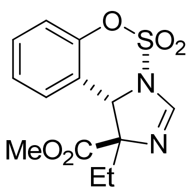

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SO2
N
N
MeO2C
Me

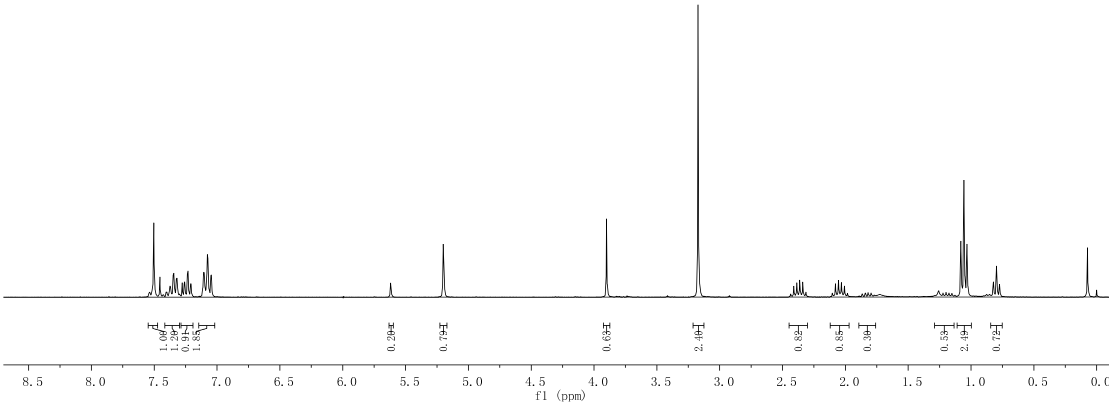
3ac

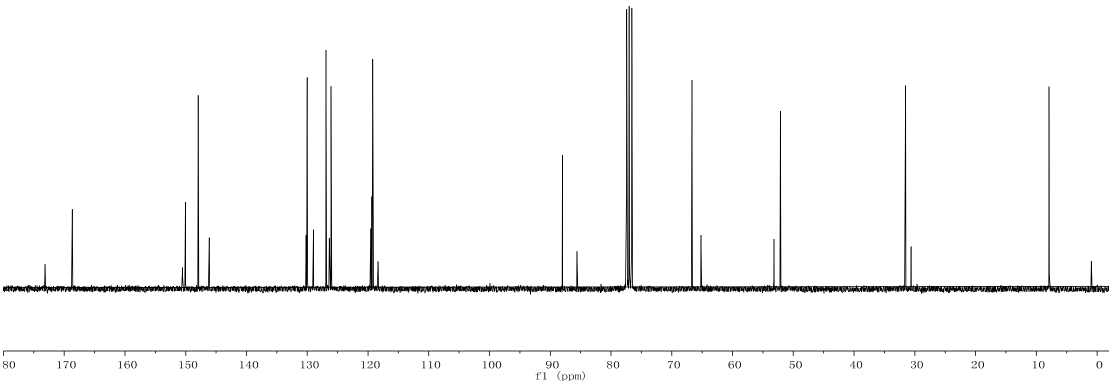

1.92
1.00
2.04
0.25
0.86
0.79
2.67
2.94
0.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

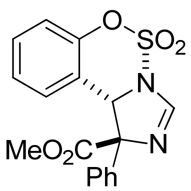

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SO2
N
N
MeO2C
Et

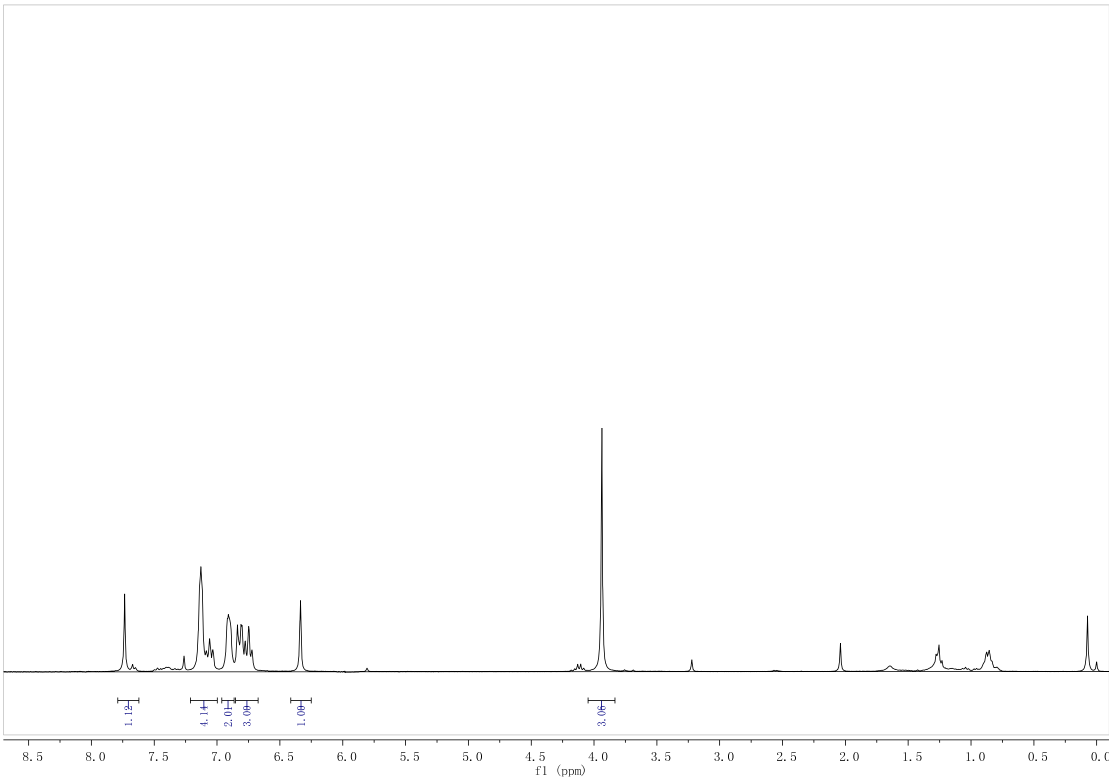
3ad

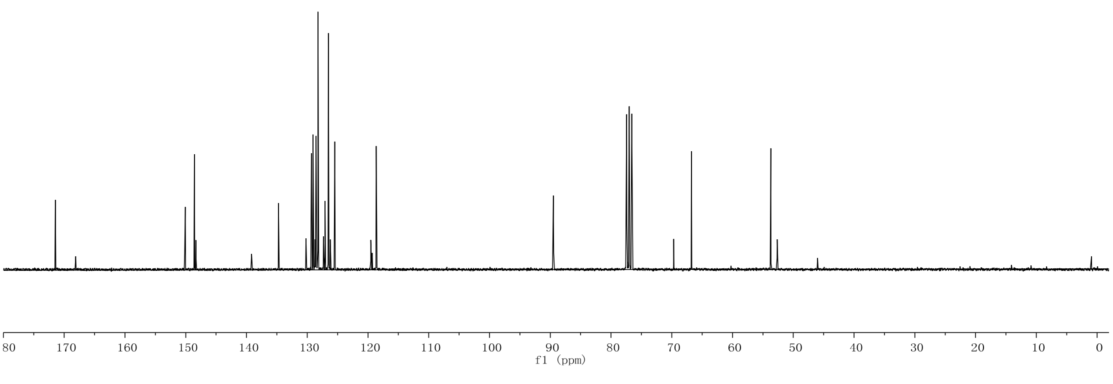

1.00
1.20
0.91
1.85
0.20
0.79
0.63
2.40
0.82
0.85
0.30
0.53
2.49
0.72
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

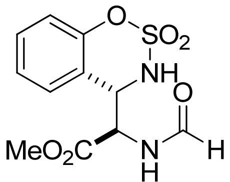

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SO2
N
N
MeO2C
Ph

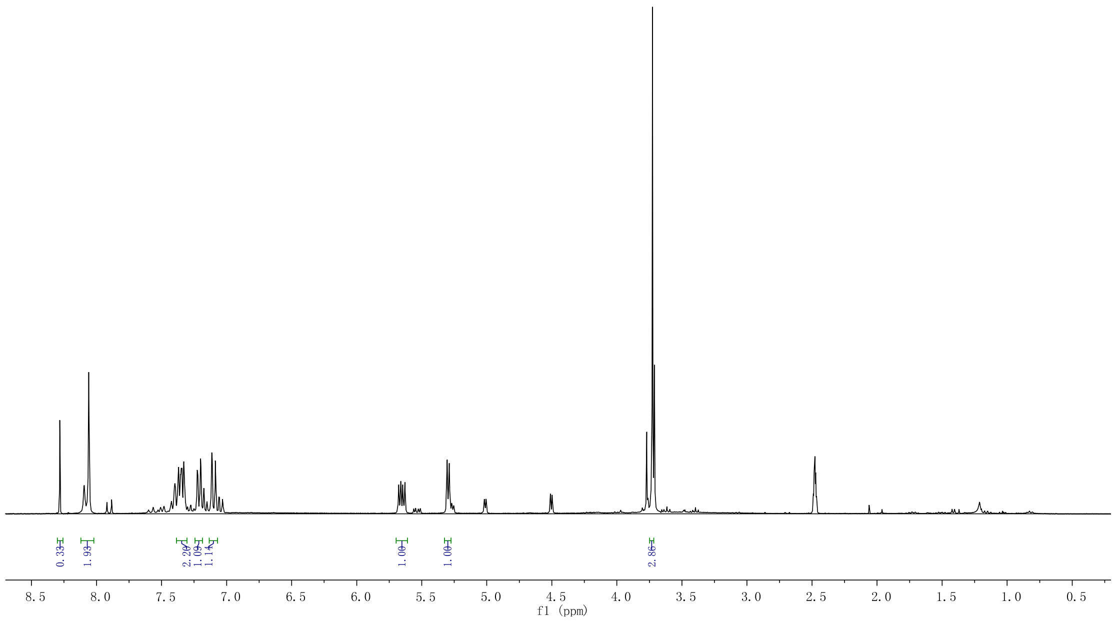
3ae

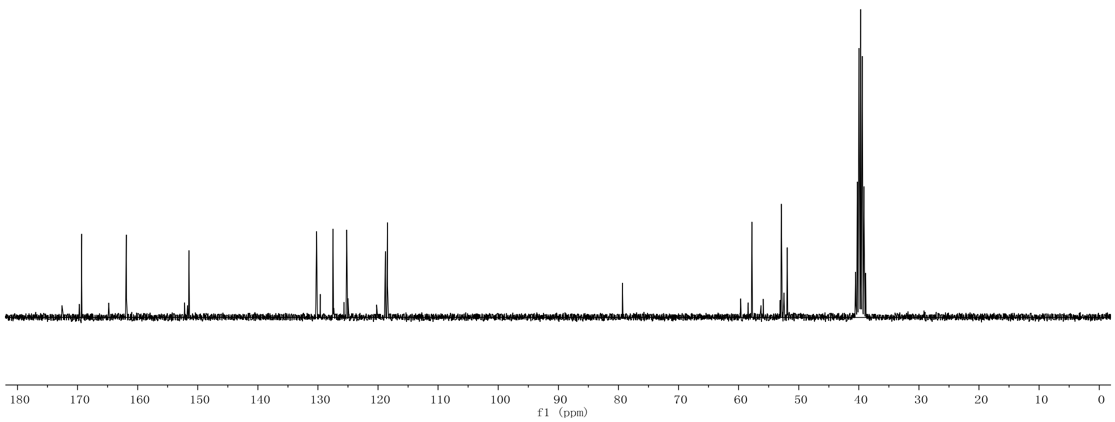

1.12
4.14
2.01
3.00
1.00
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
SO2
NH
O
MeO2C
N
H
H

4


0.33
1.93
2.20
1.09
1.14
1.00
1.00
2.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)