Electronic Supplementary Information

Pd-Catalyzed Diastereoselective [3+2] Cycloaddition of Vinylcyclopropanes with Sulfamate-Derived Cyclic Imines

Qijun Wang, Chang Wang, Wangyu Shi, Yumei Xiao,* and Hongchao Guo*

Department of Applied Chemistry, China Agricultural University, Beijing 100193, P. R. China

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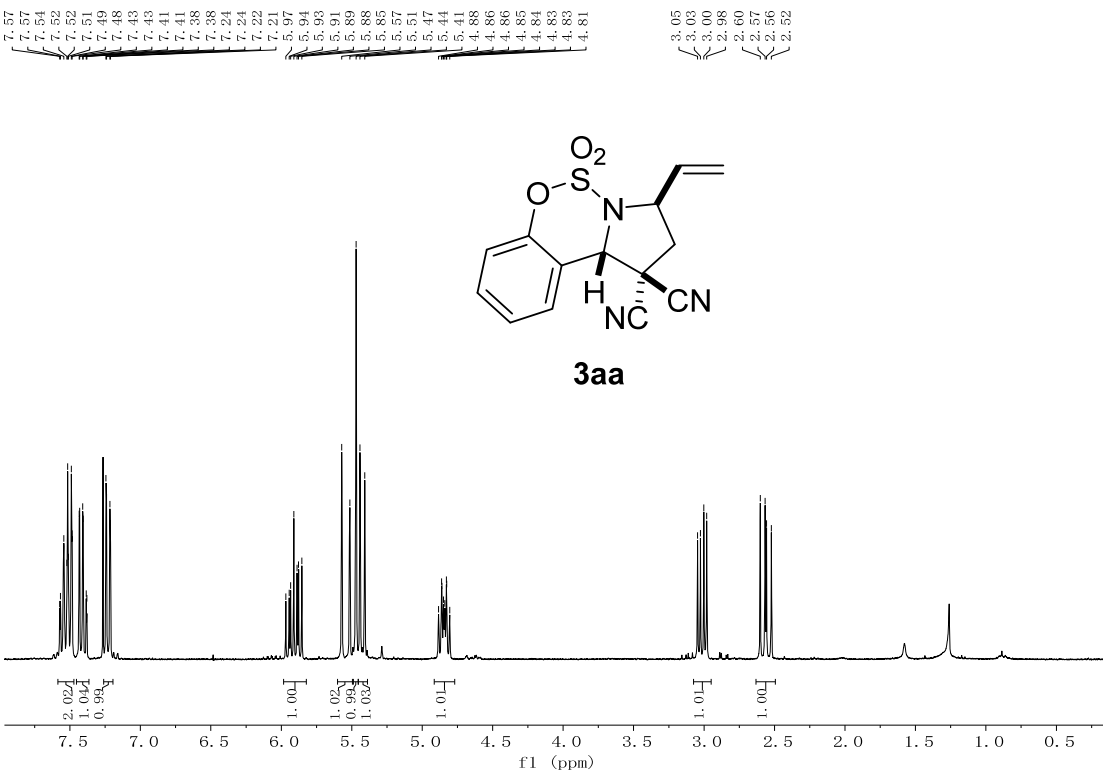
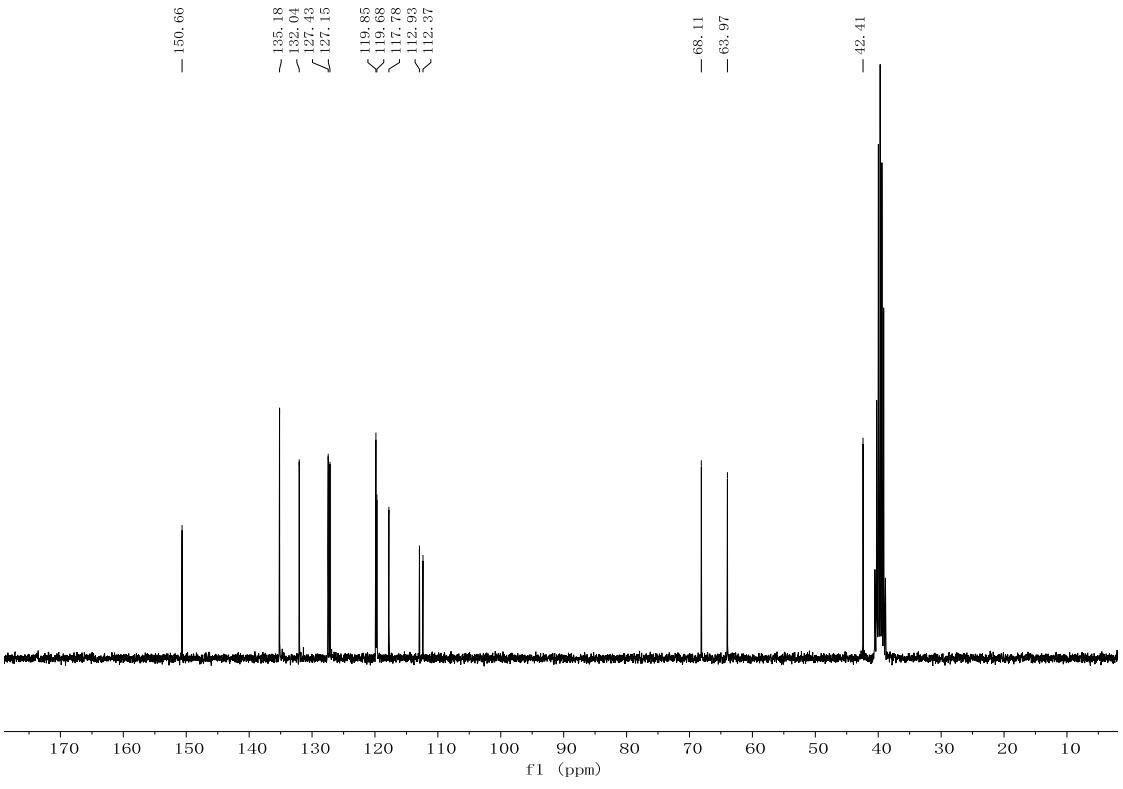
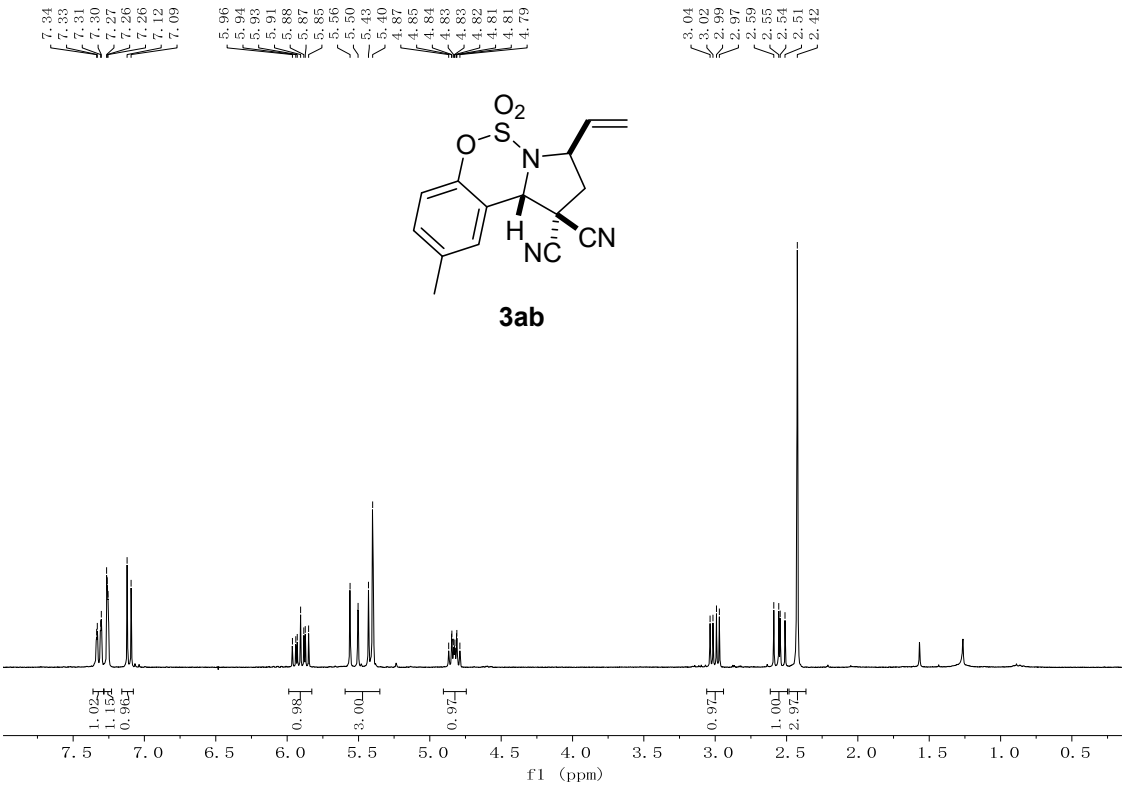
Copies of ^{1}H and ^{13}C NMR Spectra



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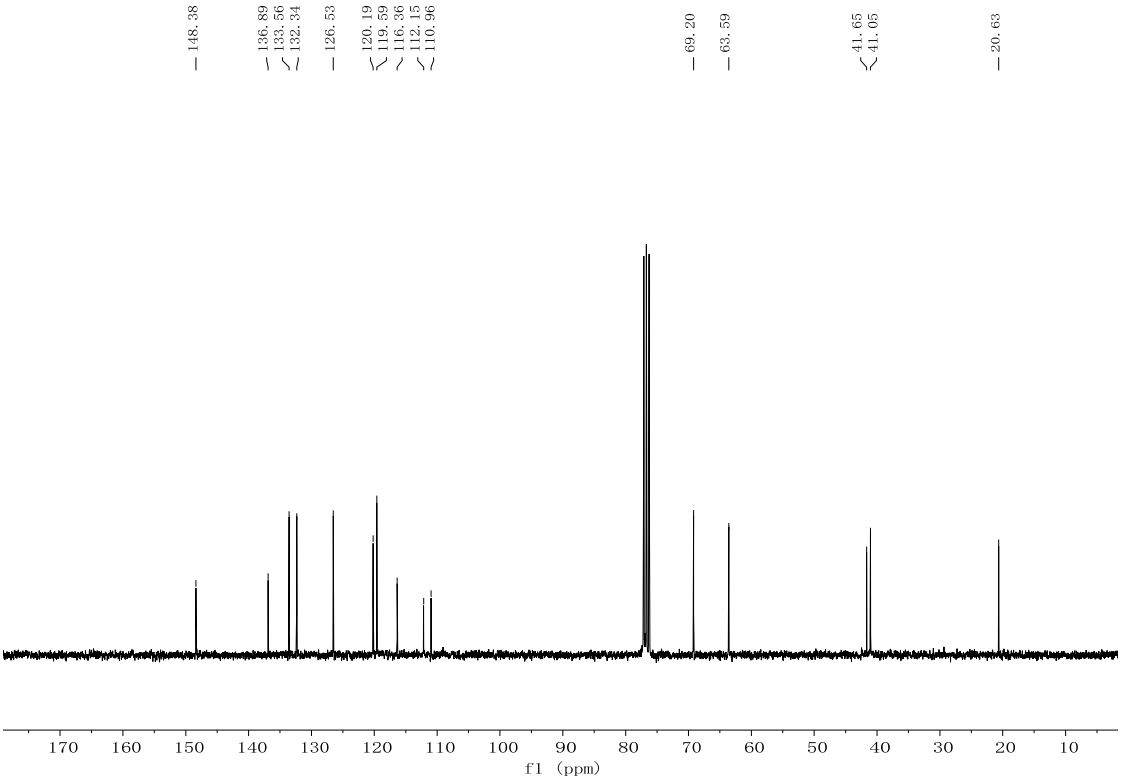
3ab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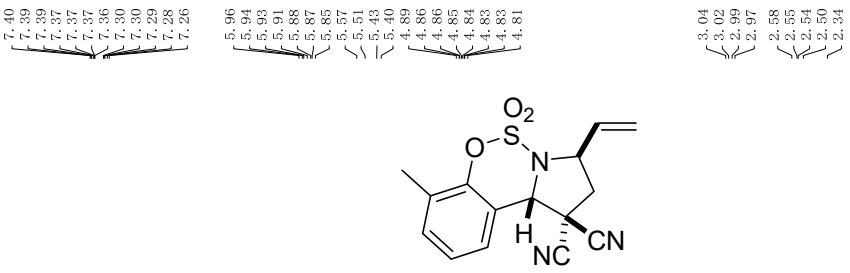
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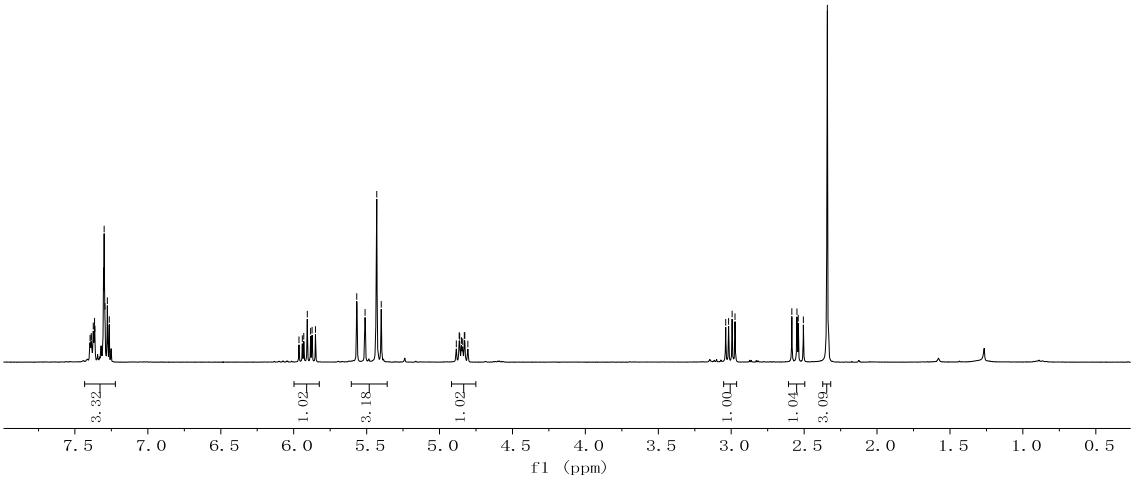
3ac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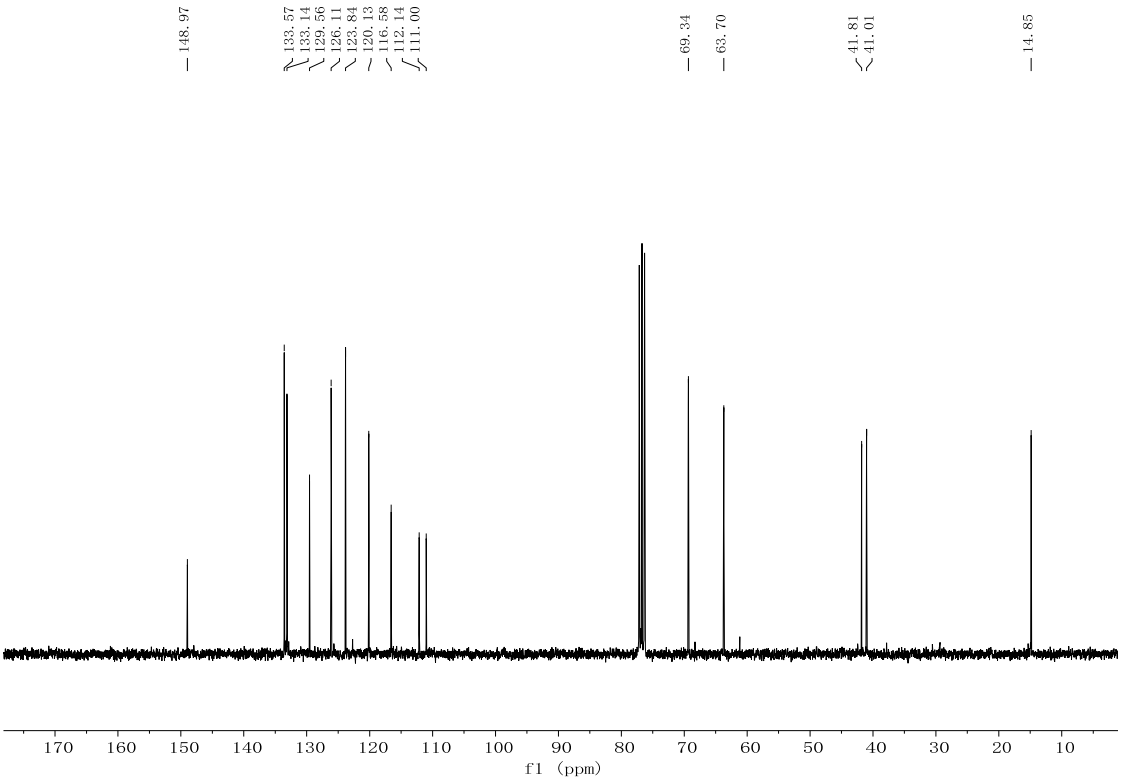
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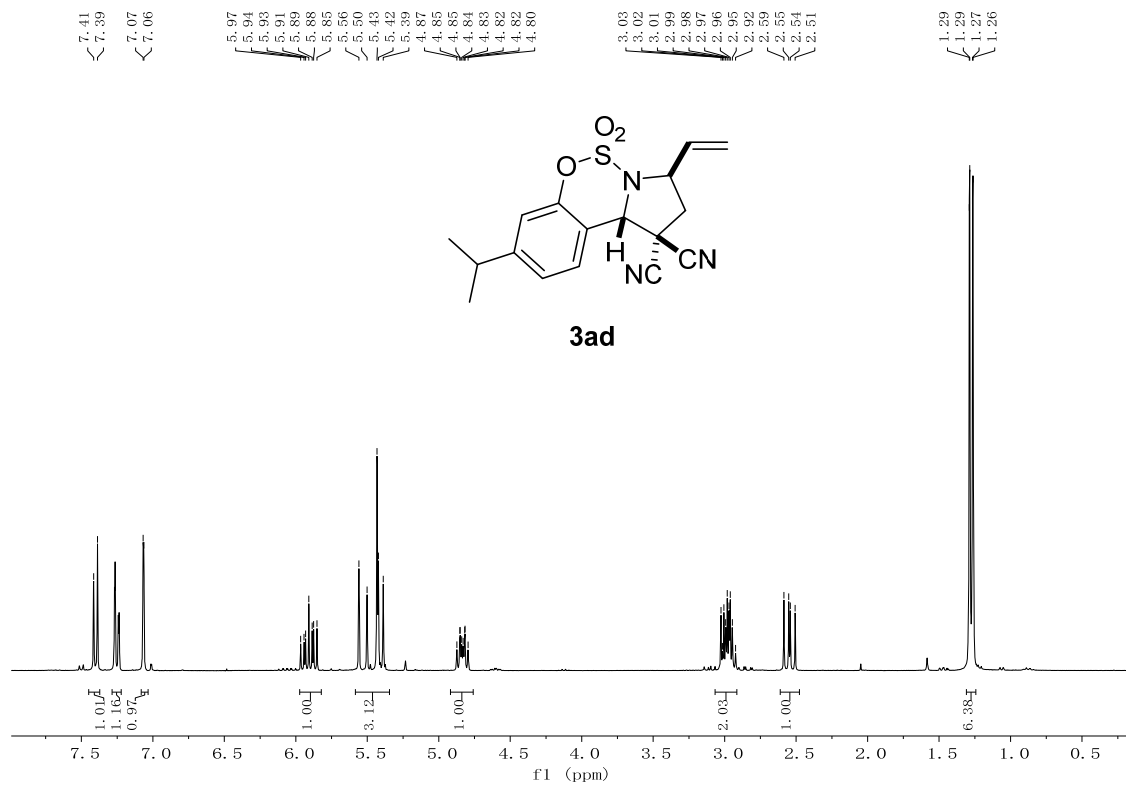
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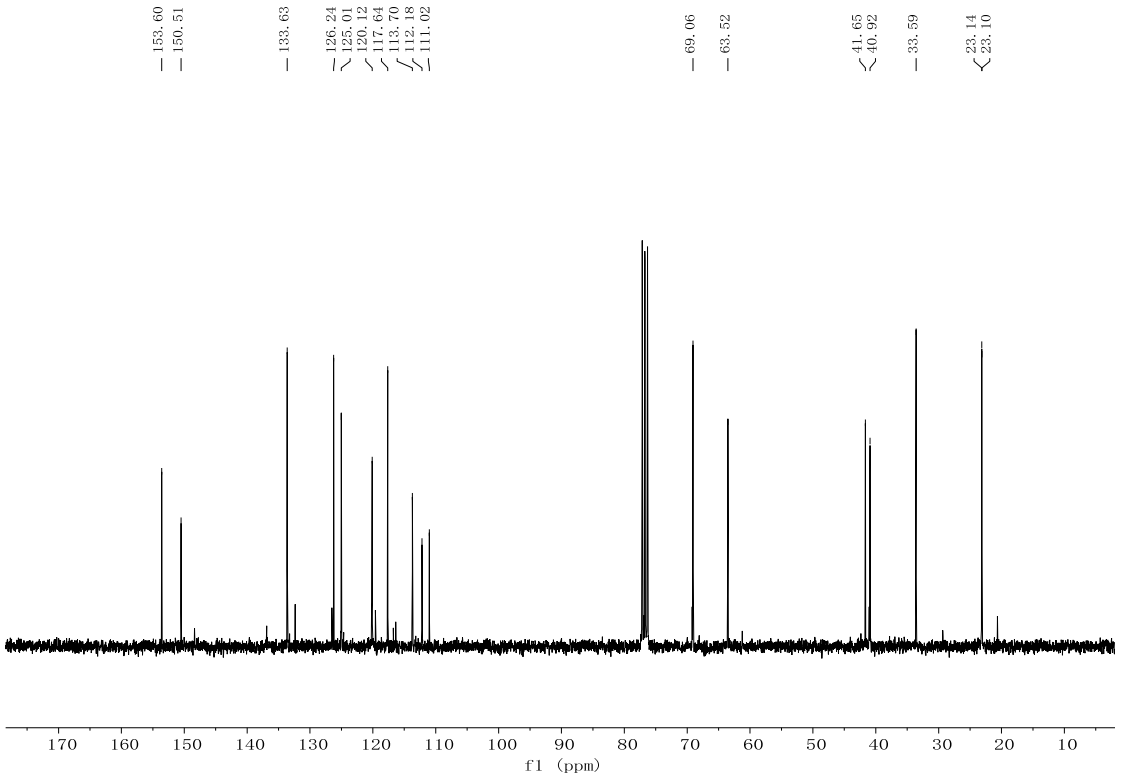
3ad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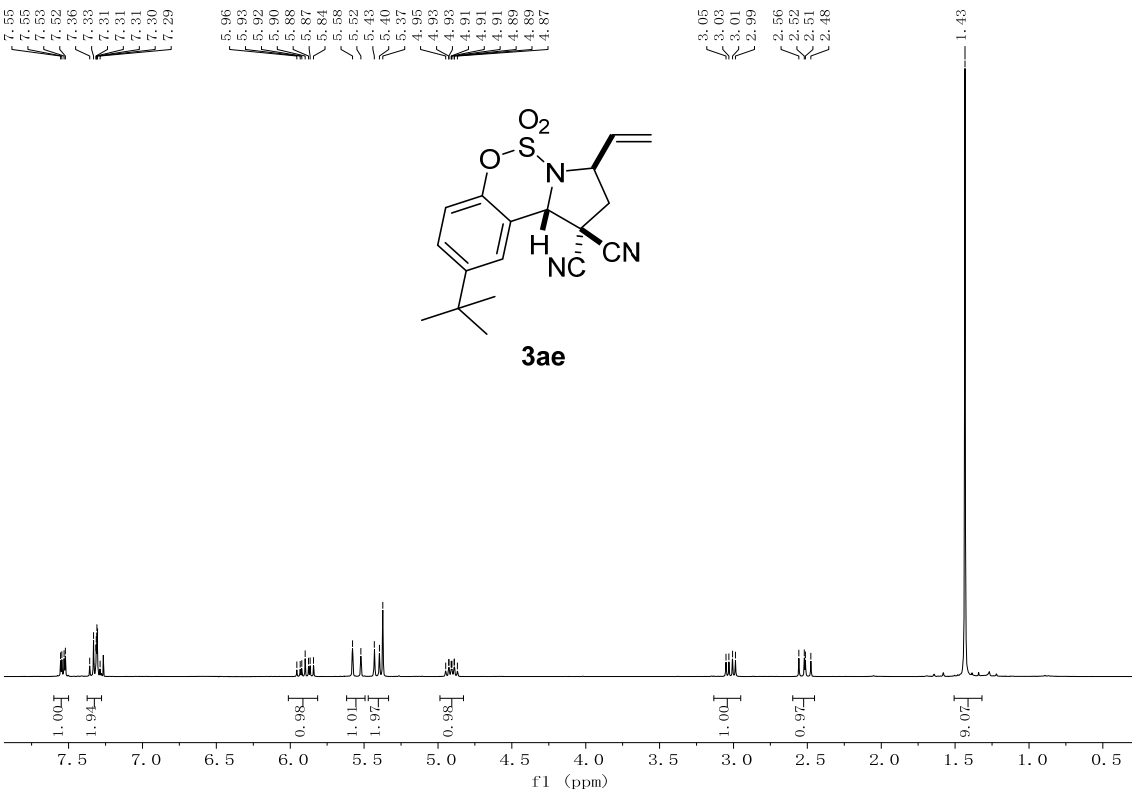
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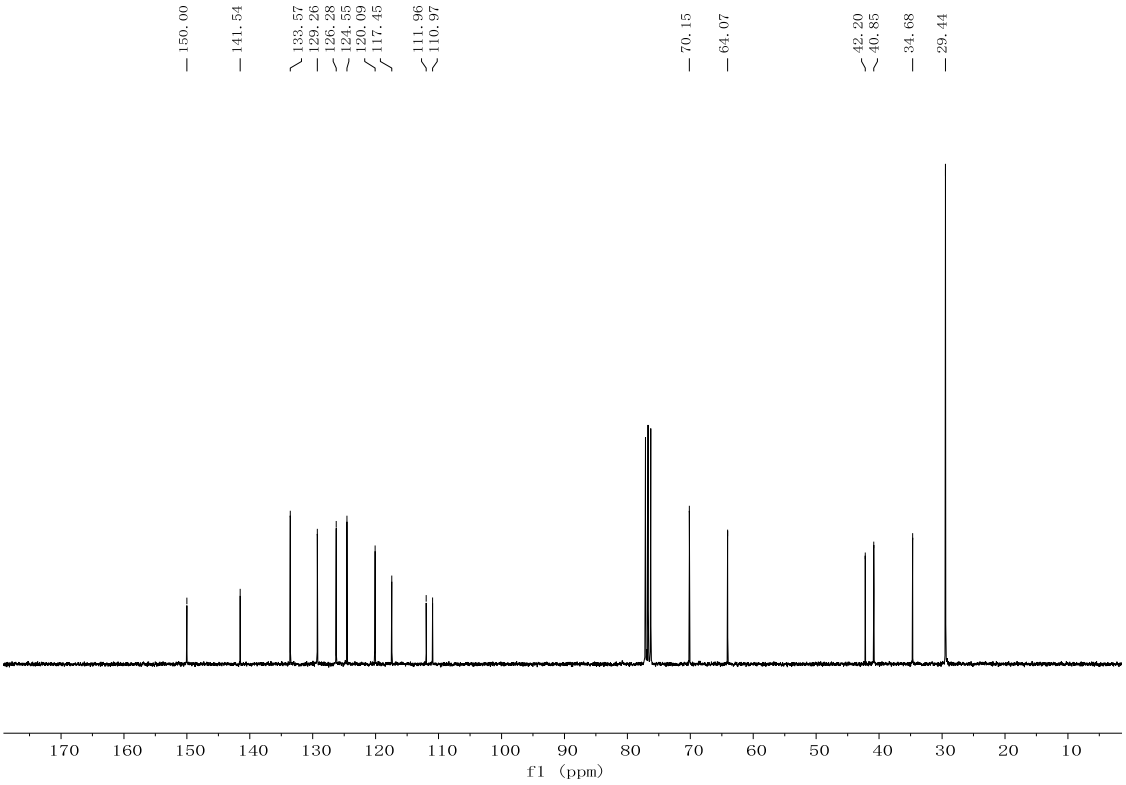
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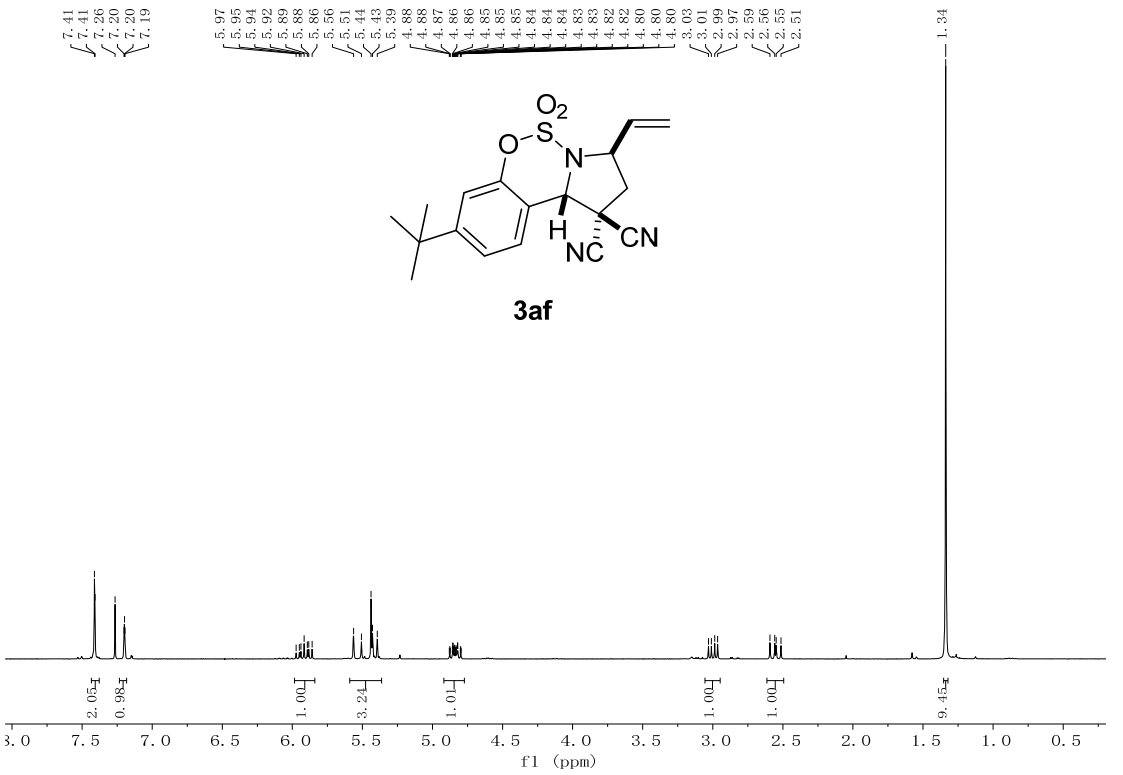
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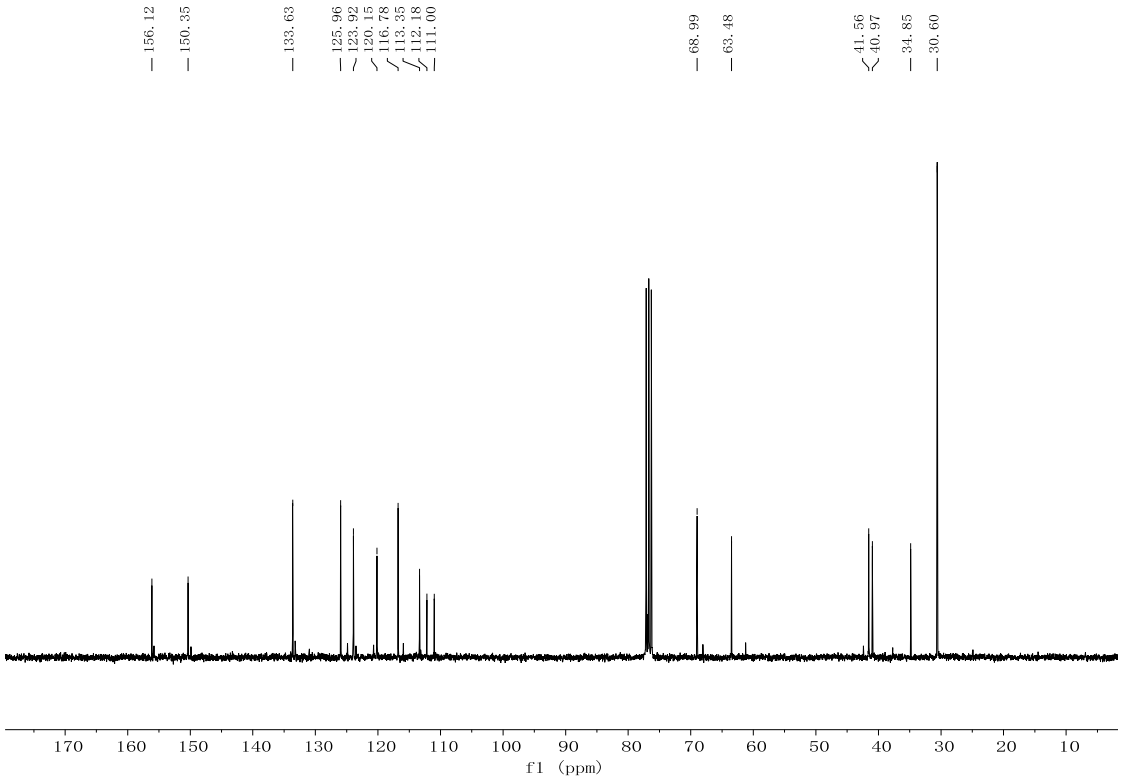
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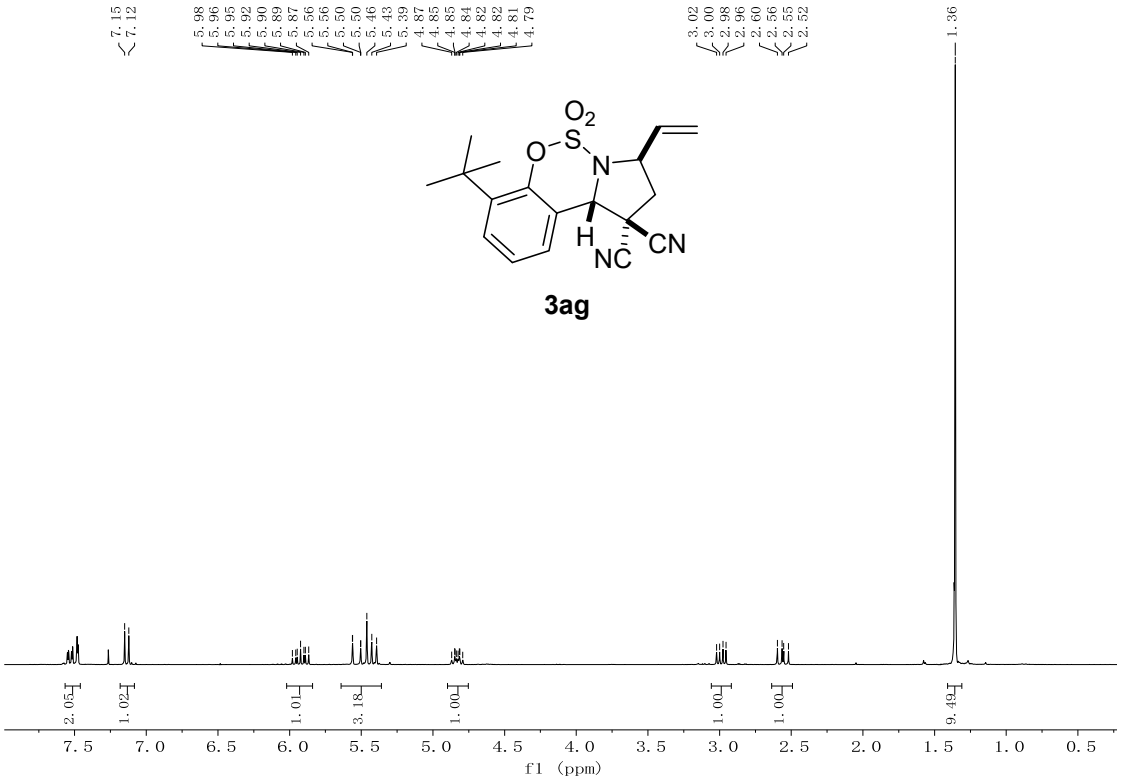
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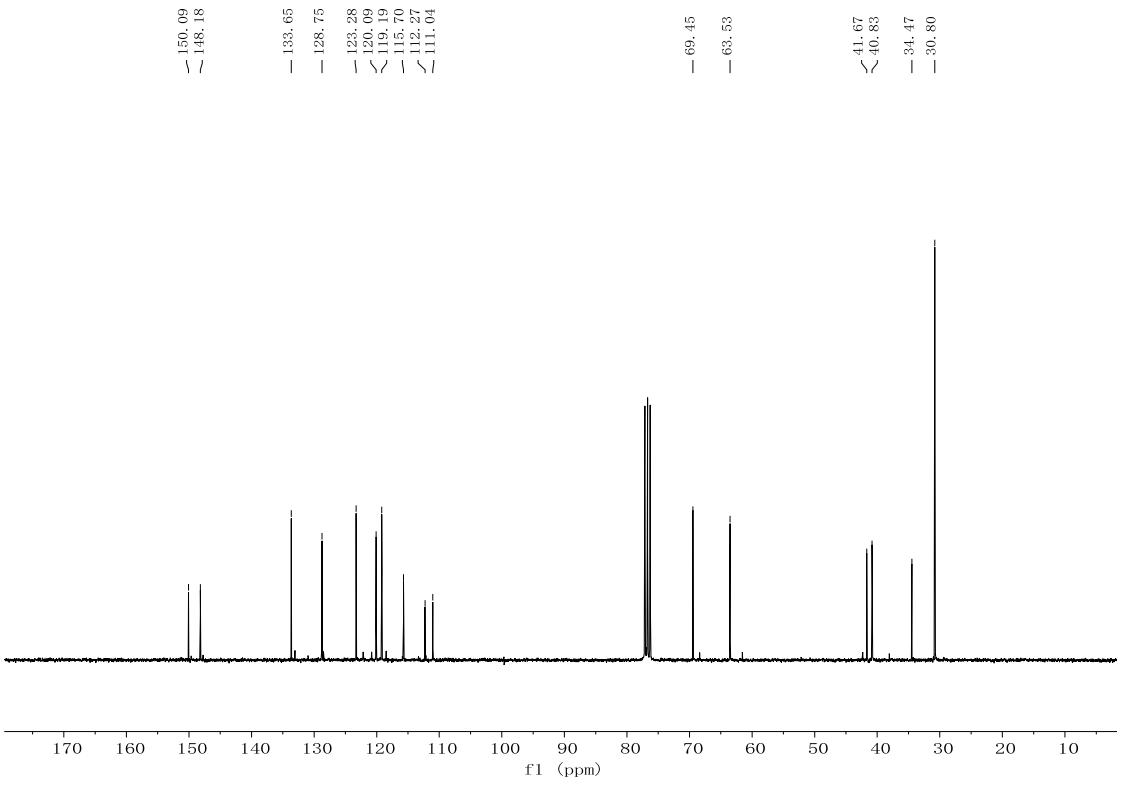
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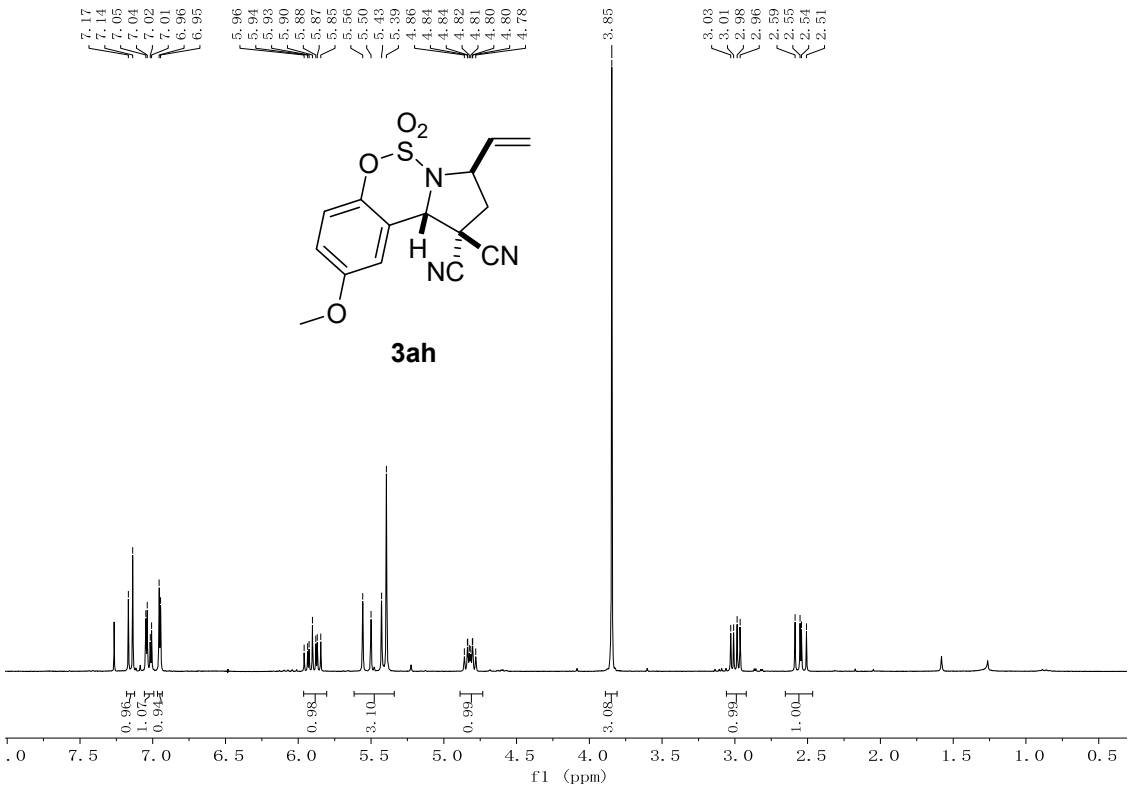
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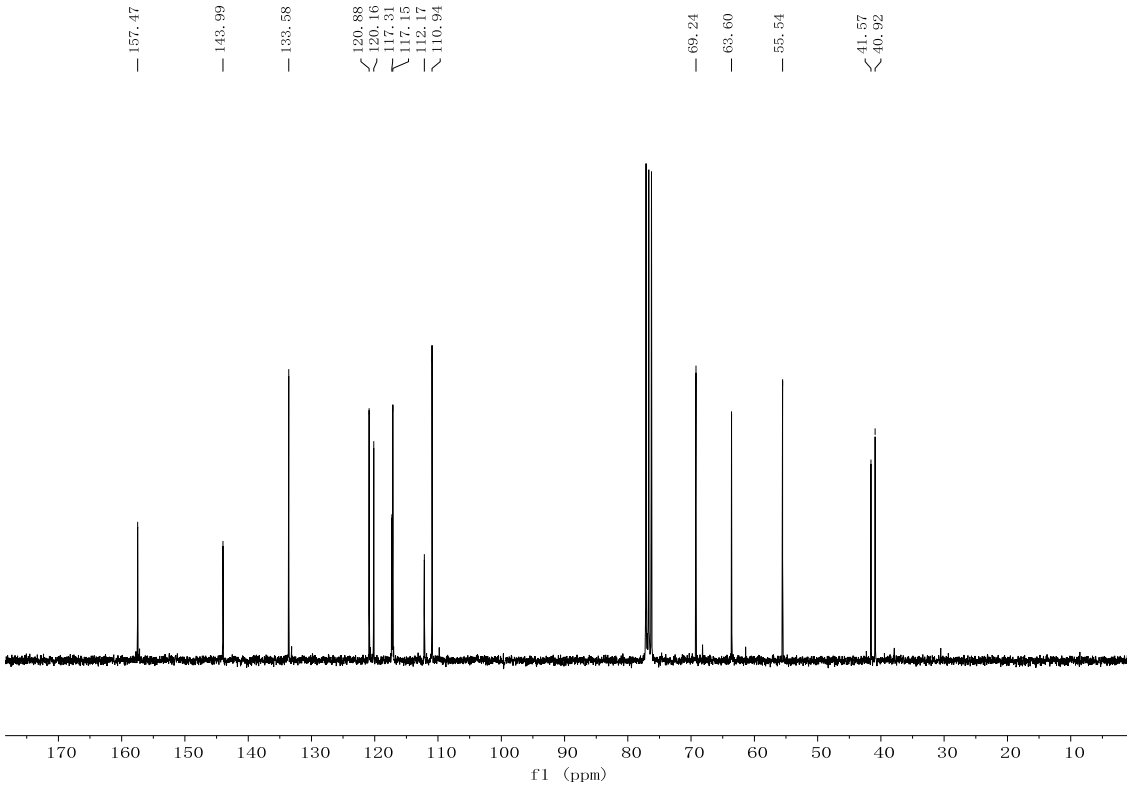
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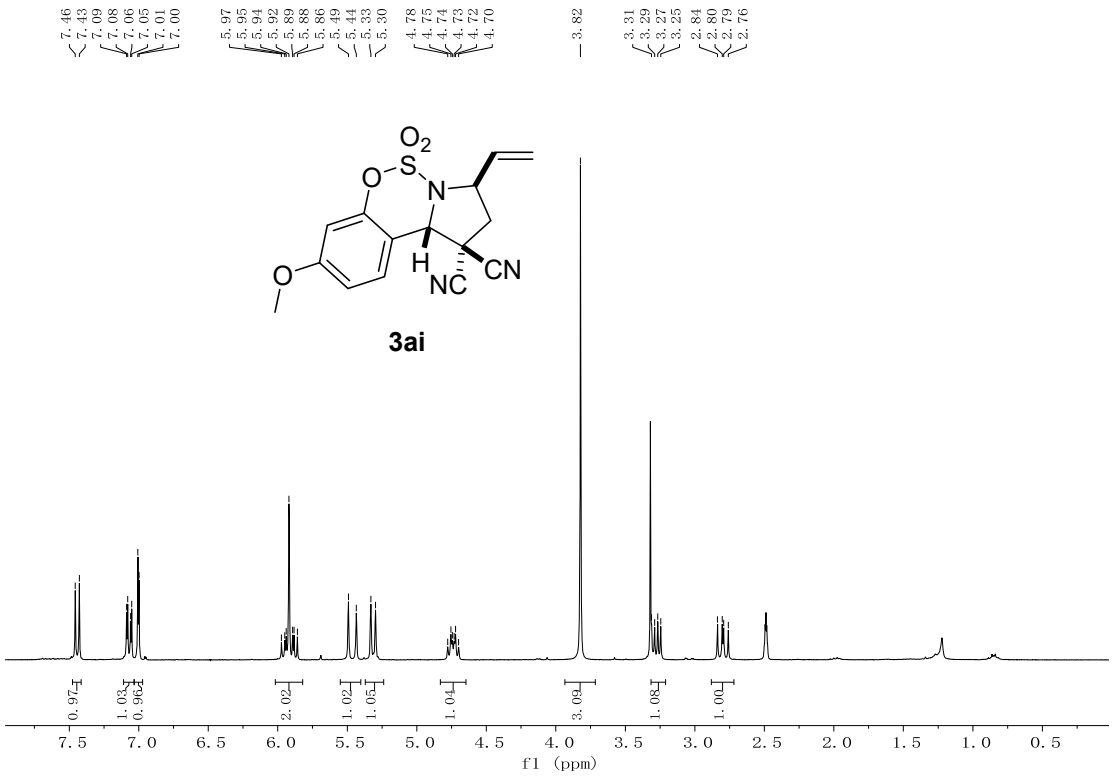
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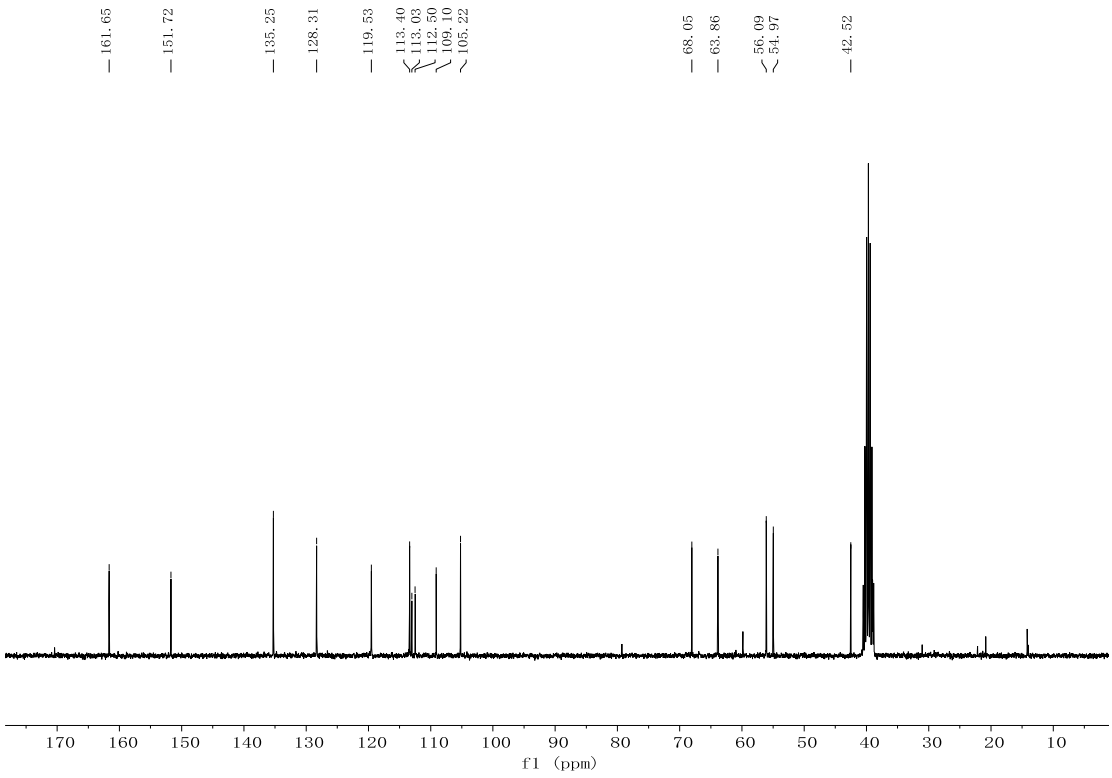
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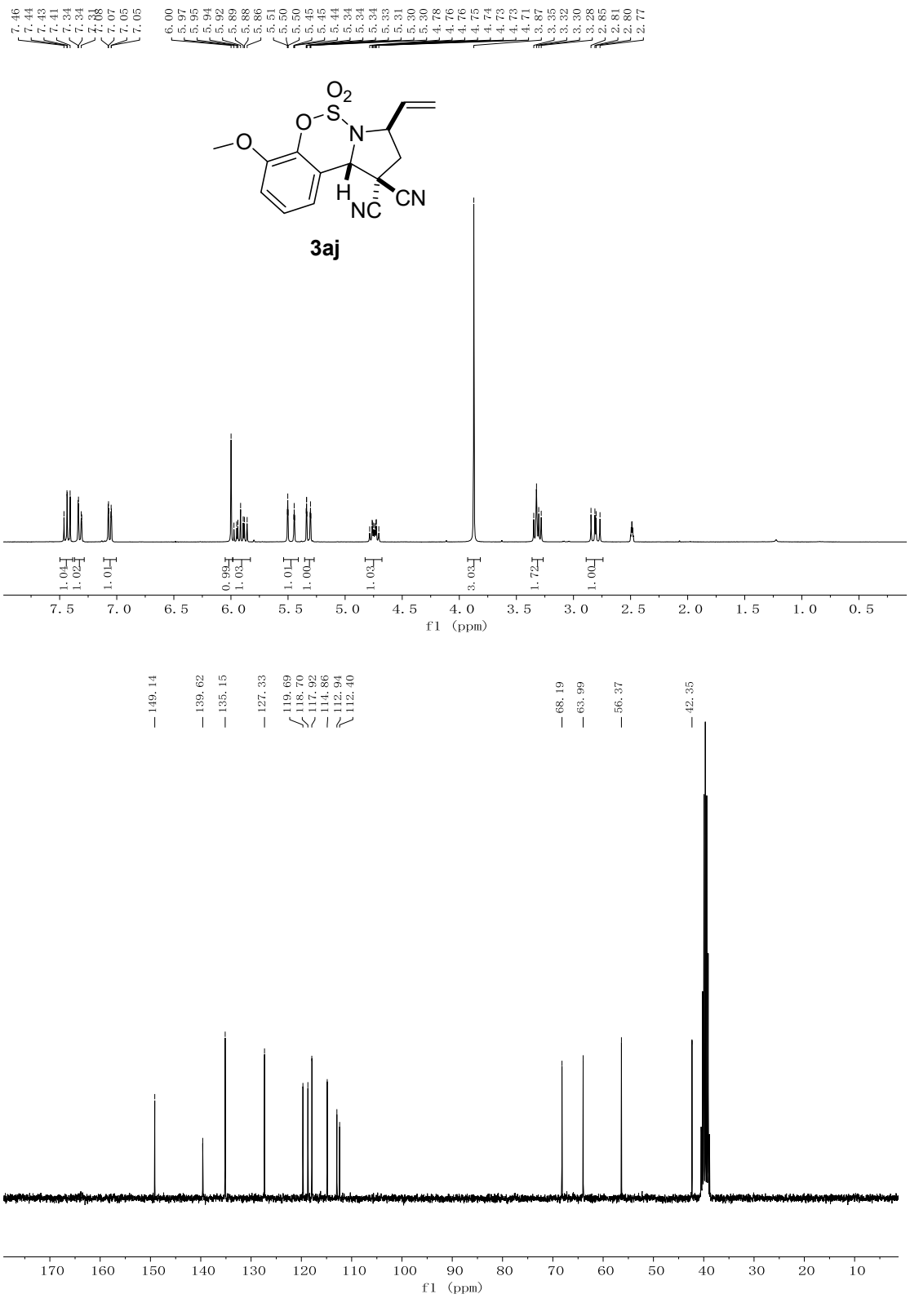
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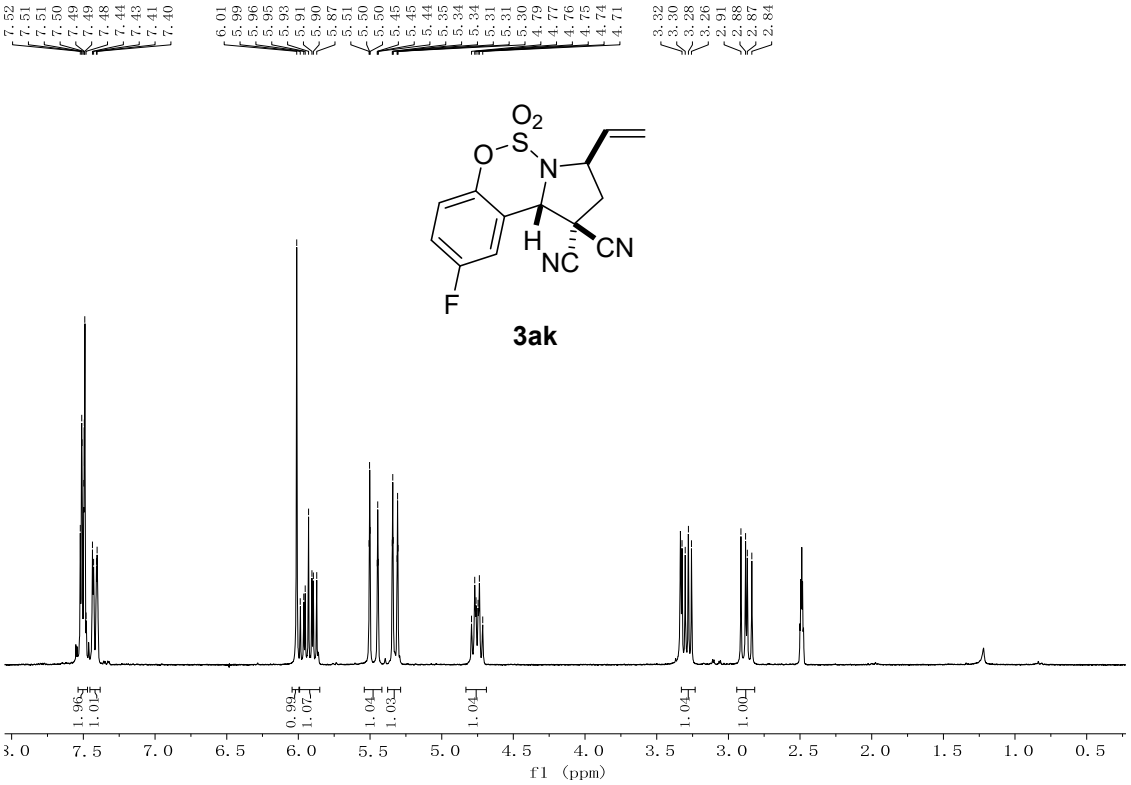
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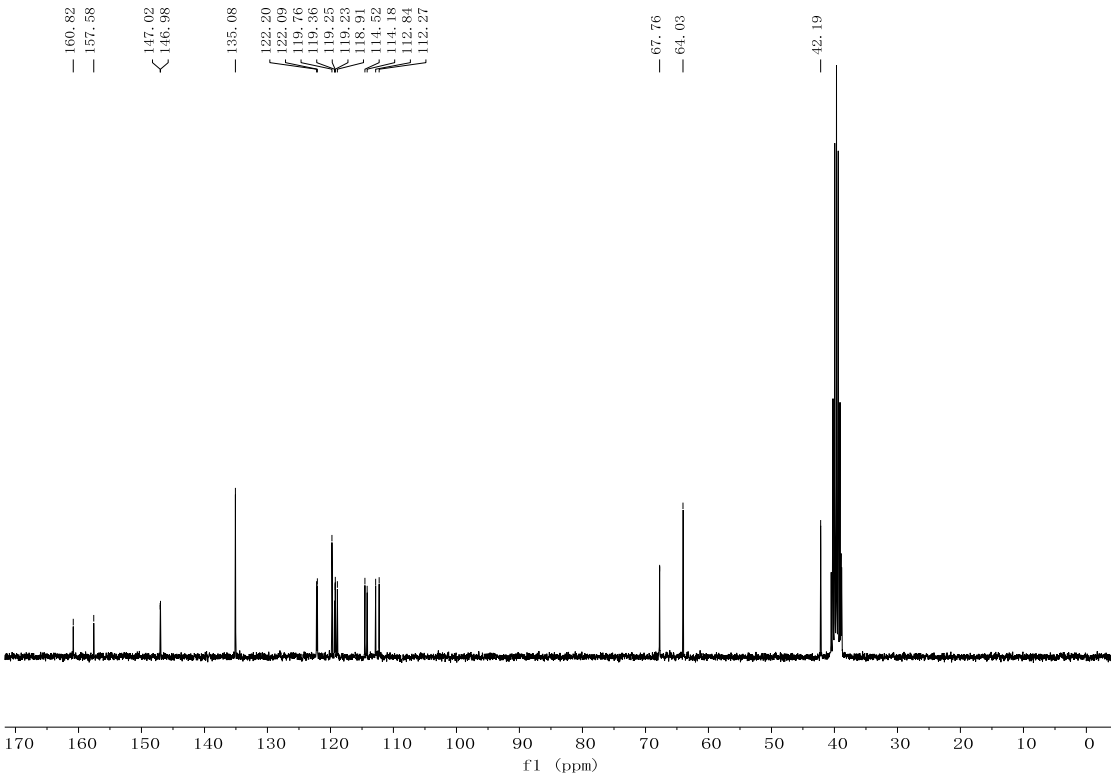
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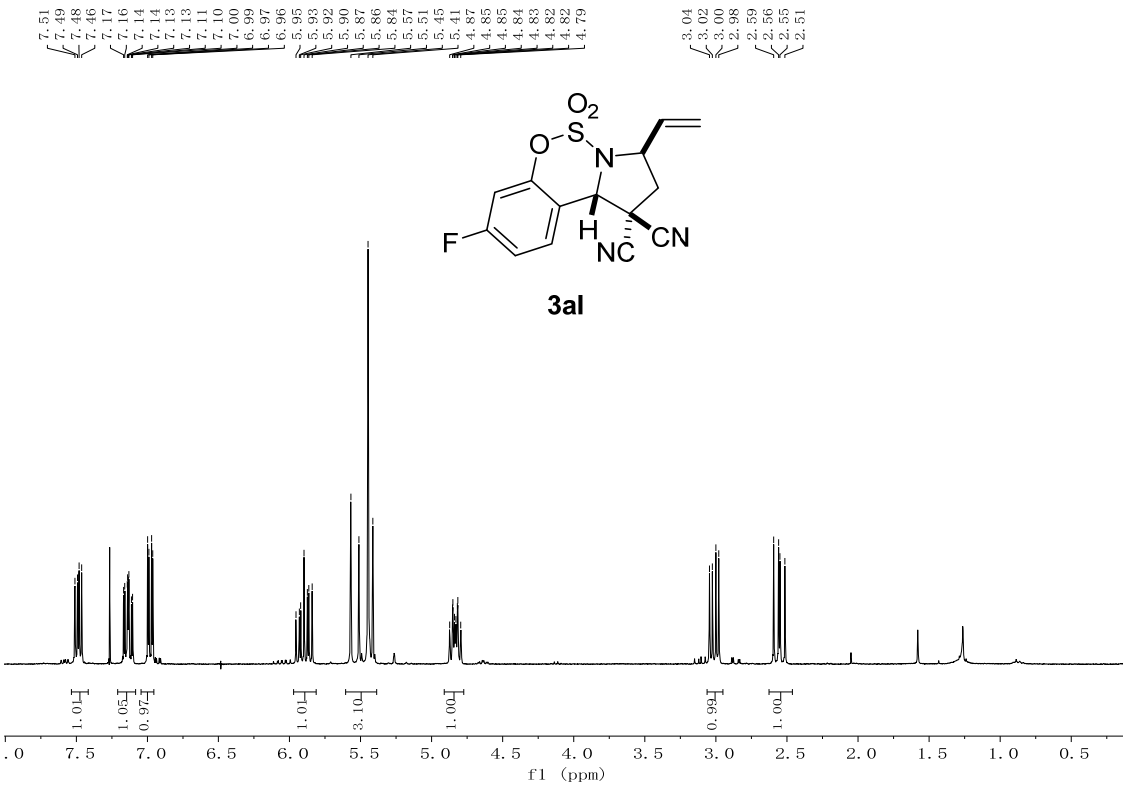
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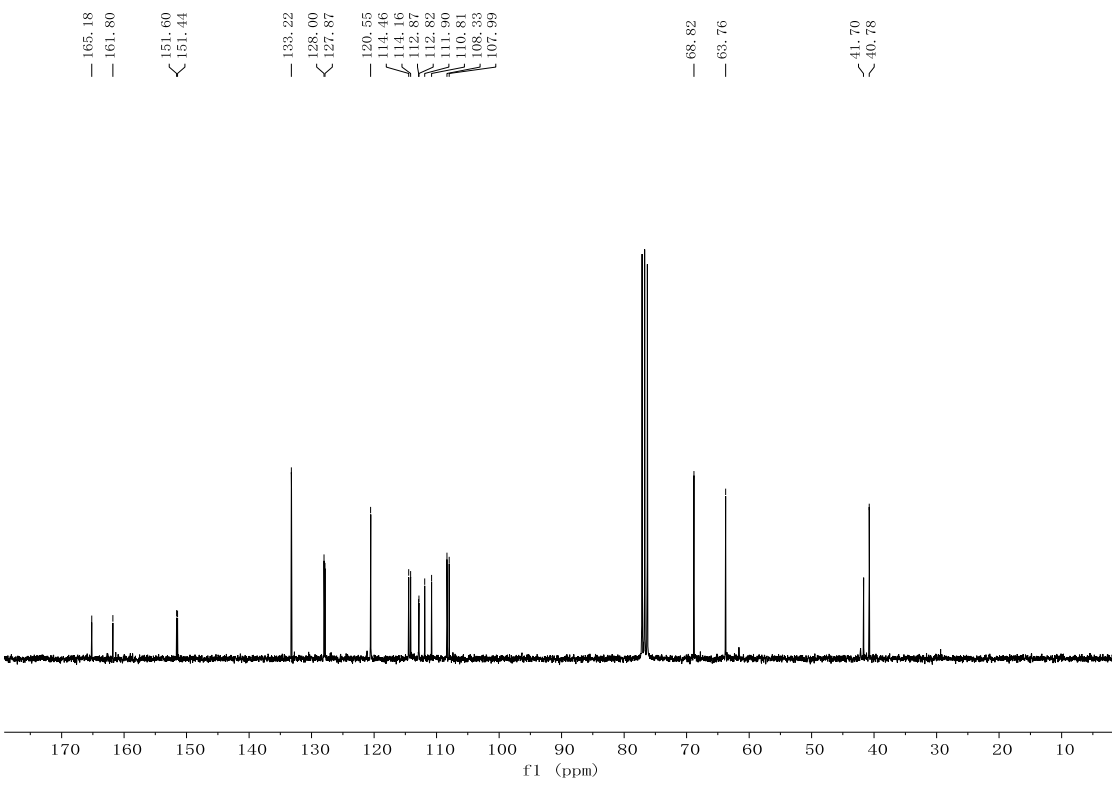
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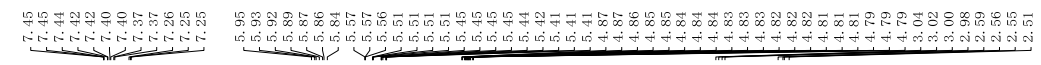
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4.83
4.83
4.82
4.82
4.82
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4.79
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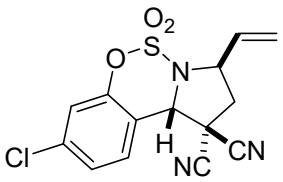
3.02
3.00
2.98
2.59
2.56
2.55
2.51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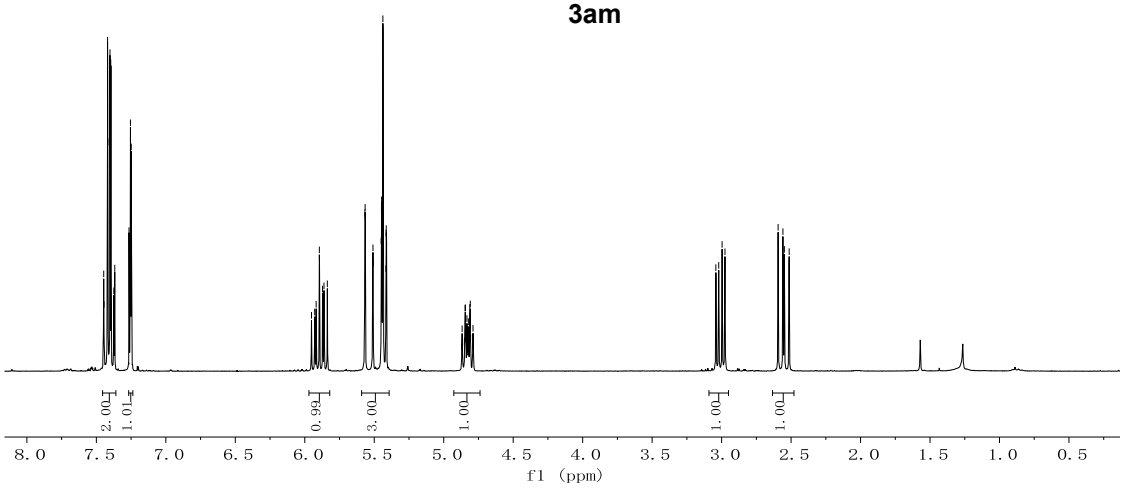
O
S
N
H
NC
CN
Cl

3am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3.0
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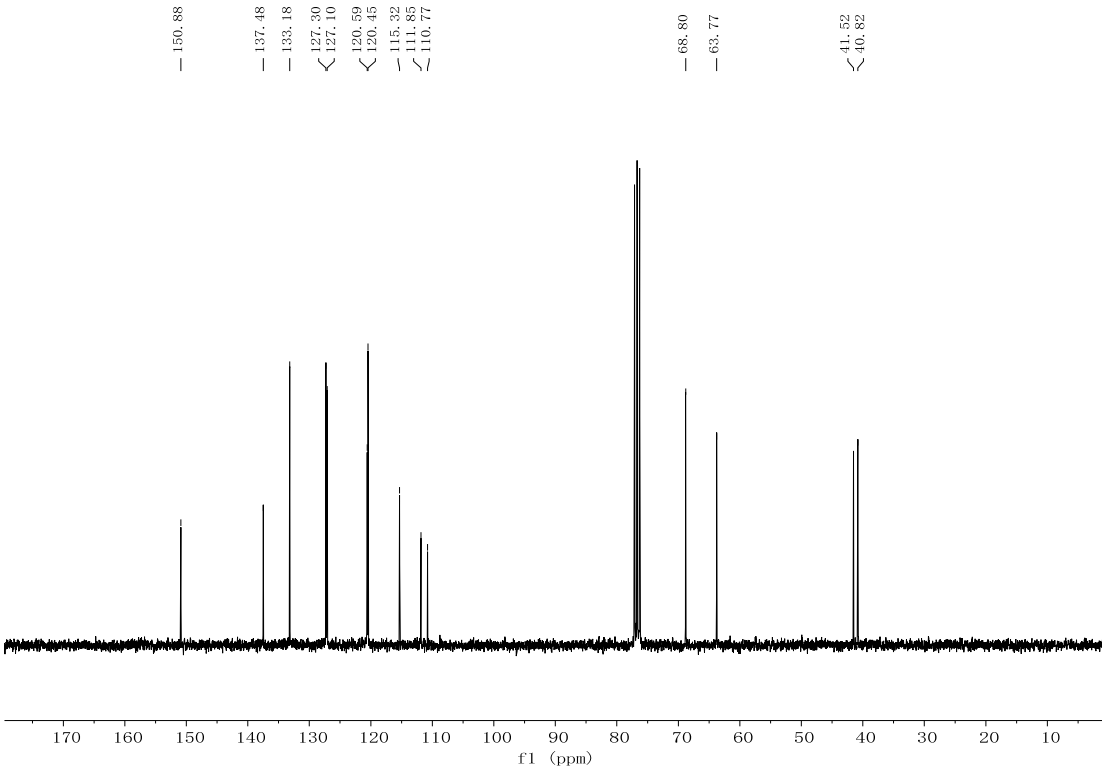
f1 (ppm)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115.32
111.85
110.77
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63.77
41.52
40.82
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140
130
120
110
100
90
80
70
60
50
40
30
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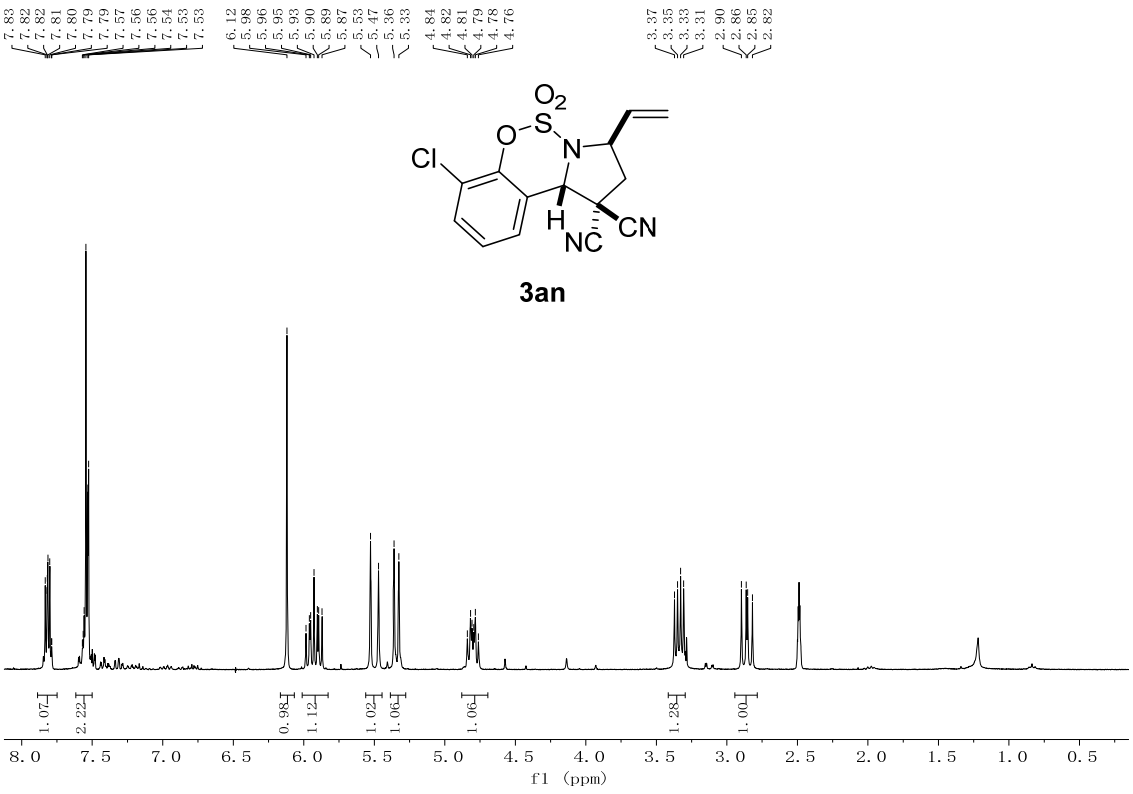
f1 (ppm)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7.56
7.54
7.53
7.53
6.12
5.98
5.96
5.95
5.93
5.90
5.89
5.87
5.53
5.47
5.36
5.33
4.84
4.82
4.81
4.79
4.78
4.76
3.37
3.35
3.33
3.31
2.90
2.86
2.85
2.82
O2
S
O
N
Cl
H
NC
CN
1.07
2.22
0.98
1.12
1.02
1.06
1.06
1.28
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
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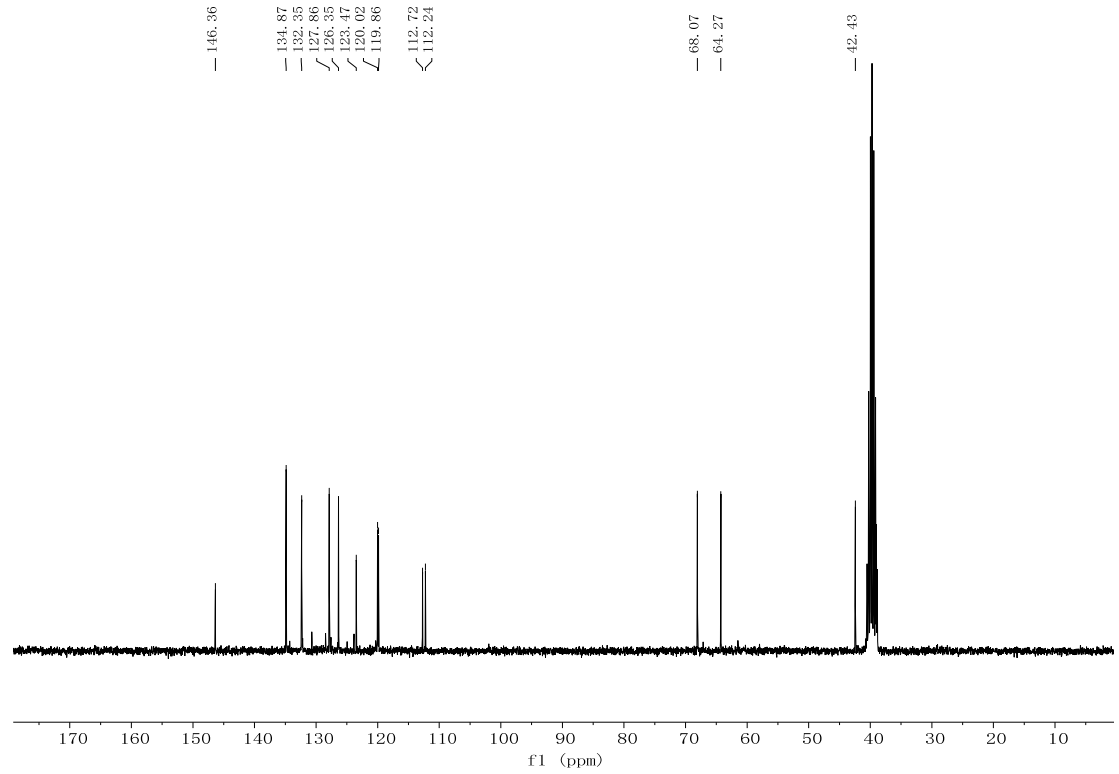
0.5
f1 (ppm)

3an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132.35
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126.35
123.47
120.02
119.86
112.72
112.24
68.07
64.27
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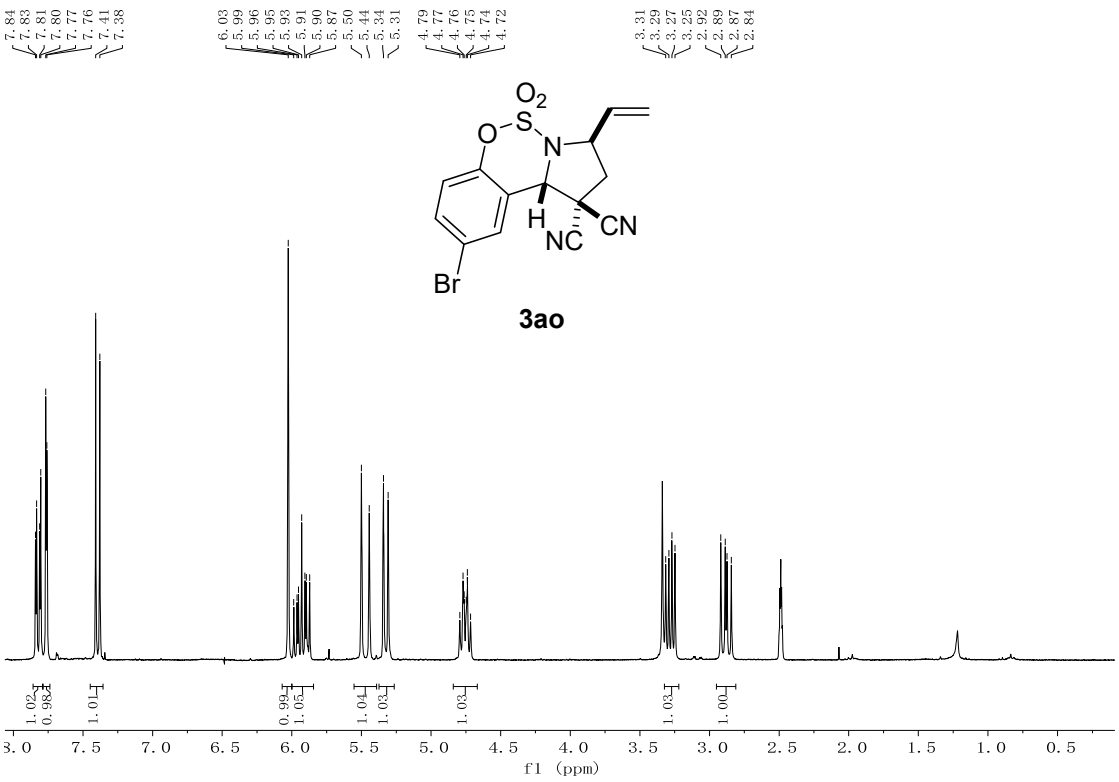
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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5.90
5.87
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4.76
4.75
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2.92
2.89
2.87
2.84
O2
S
O
N
H
NC
CN
Br
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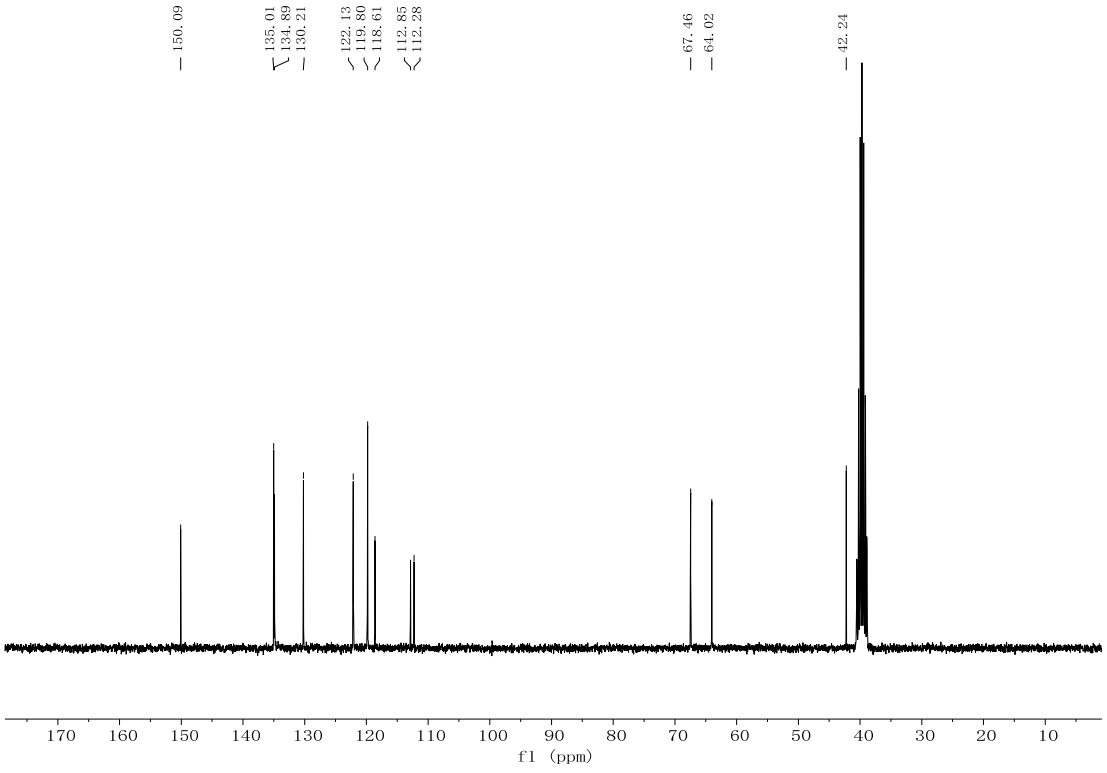
1.04
1.03
1.03
1.03
1.00
f1 (ppm)

3ao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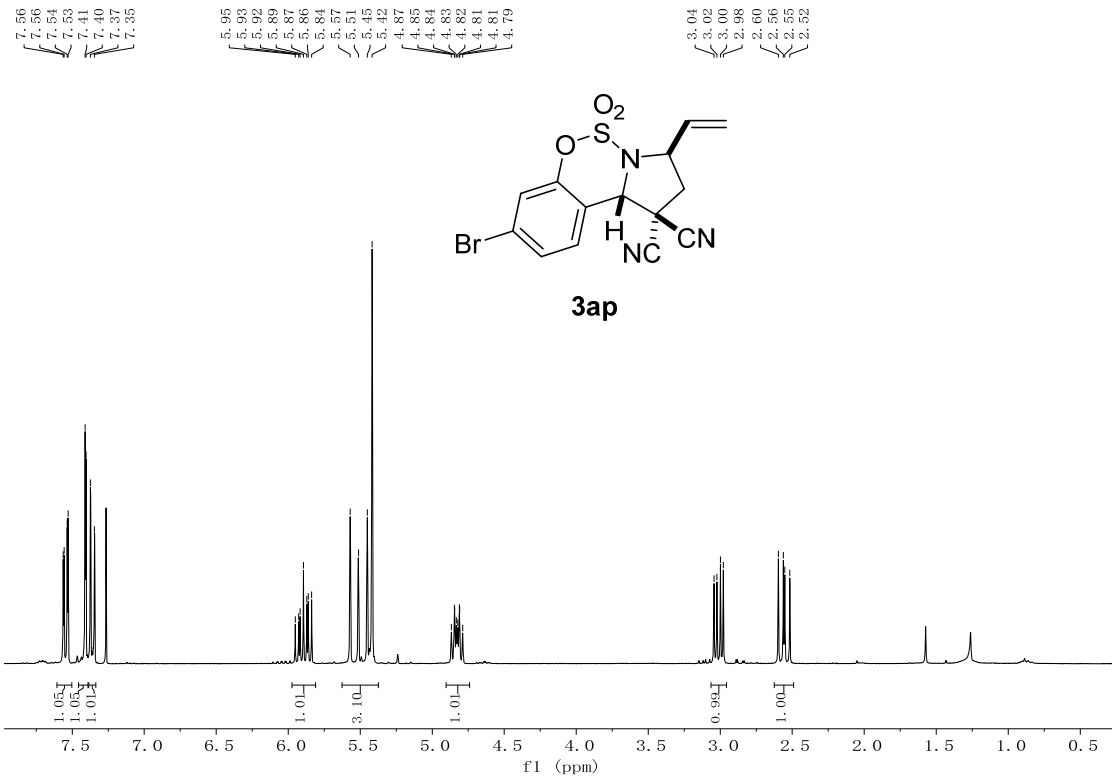
f1 (ppm)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5.92
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5.45
5.42
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4.85
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4.82
4.81
4.81
4.79
3.04
3.02
3.00
2.98
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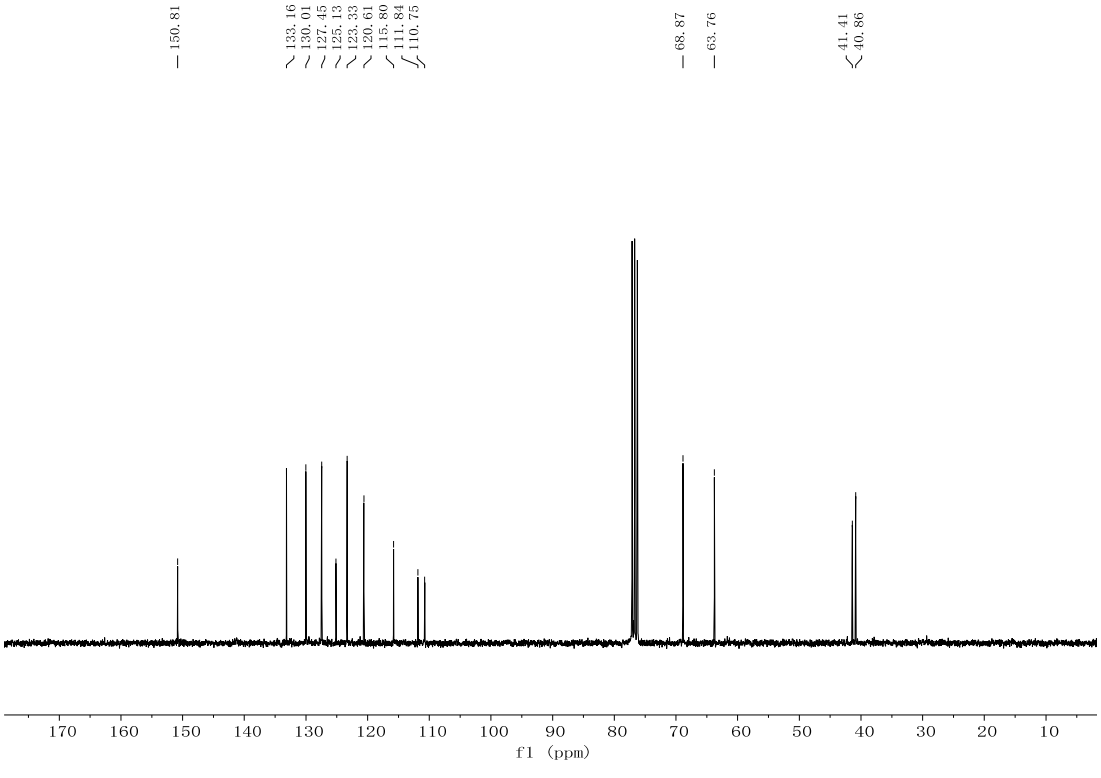
2.56
2.55
2.52
O2
S
O
N
Br
H
NC
CN
3ap
1.05
1.05
1.01
1.01
3.10
1.01
0.99
1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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130.01
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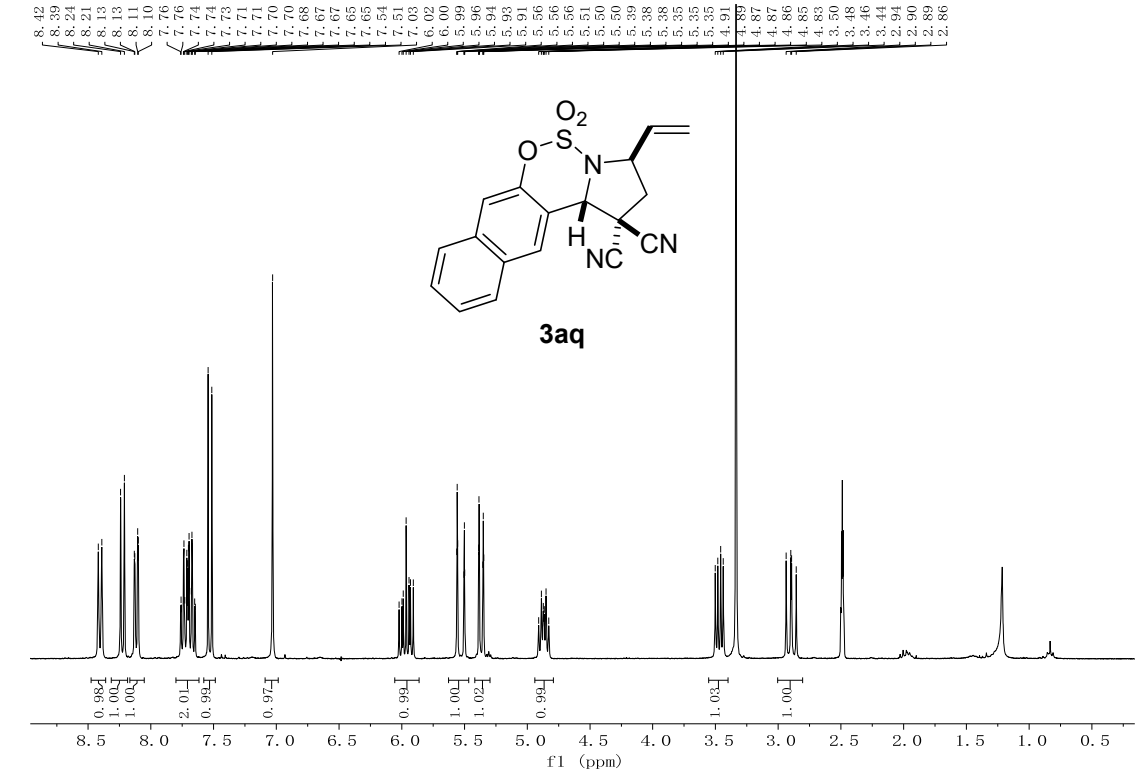
125.13
123.33
120.61
115.80
111.84
110.75
68.87
63.76
41.41
40.86
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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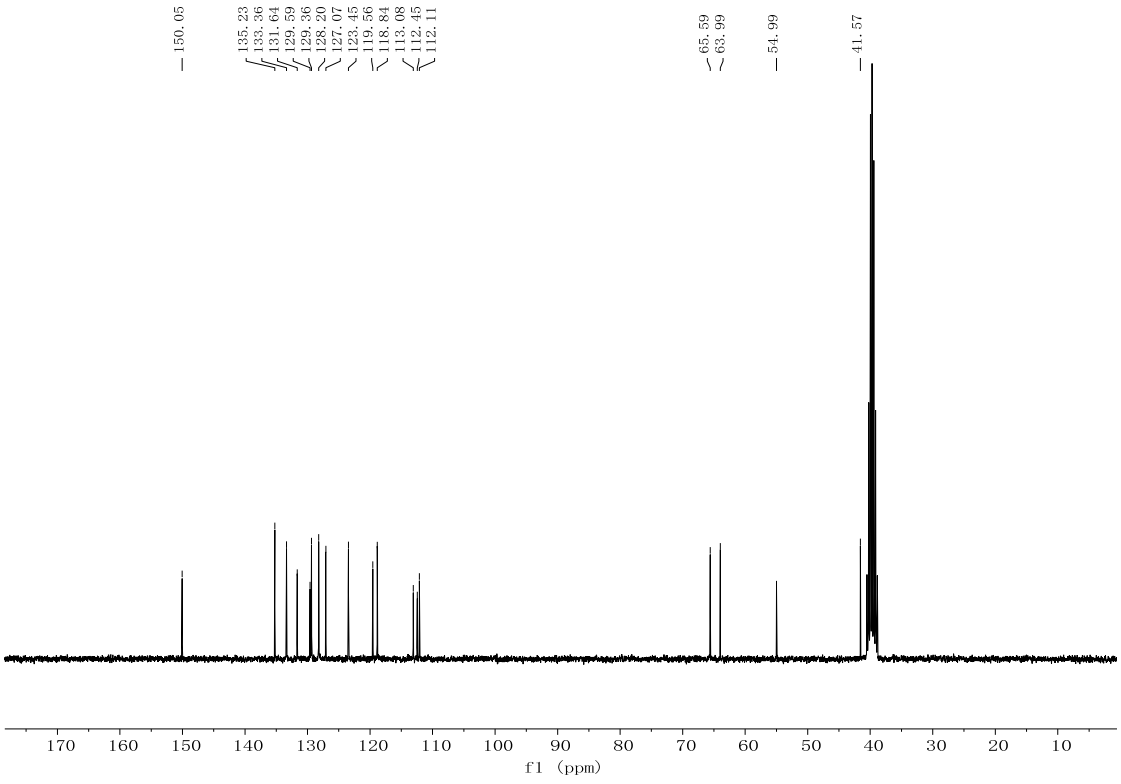
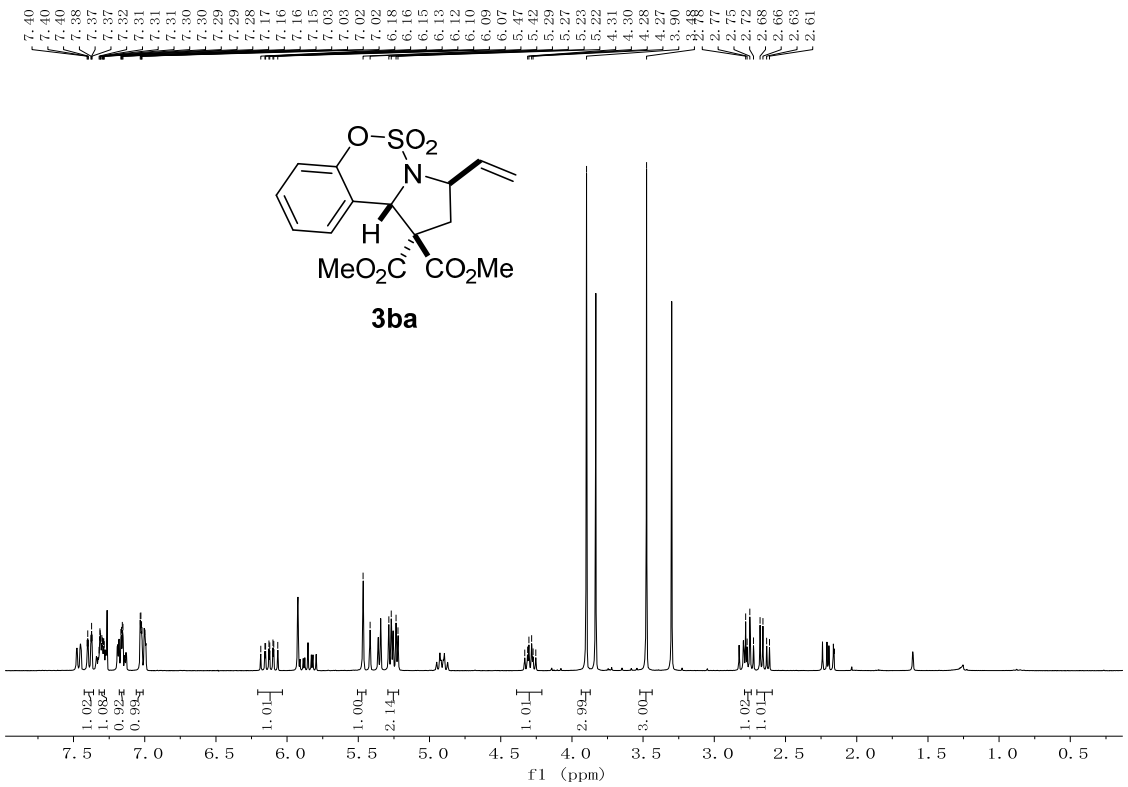
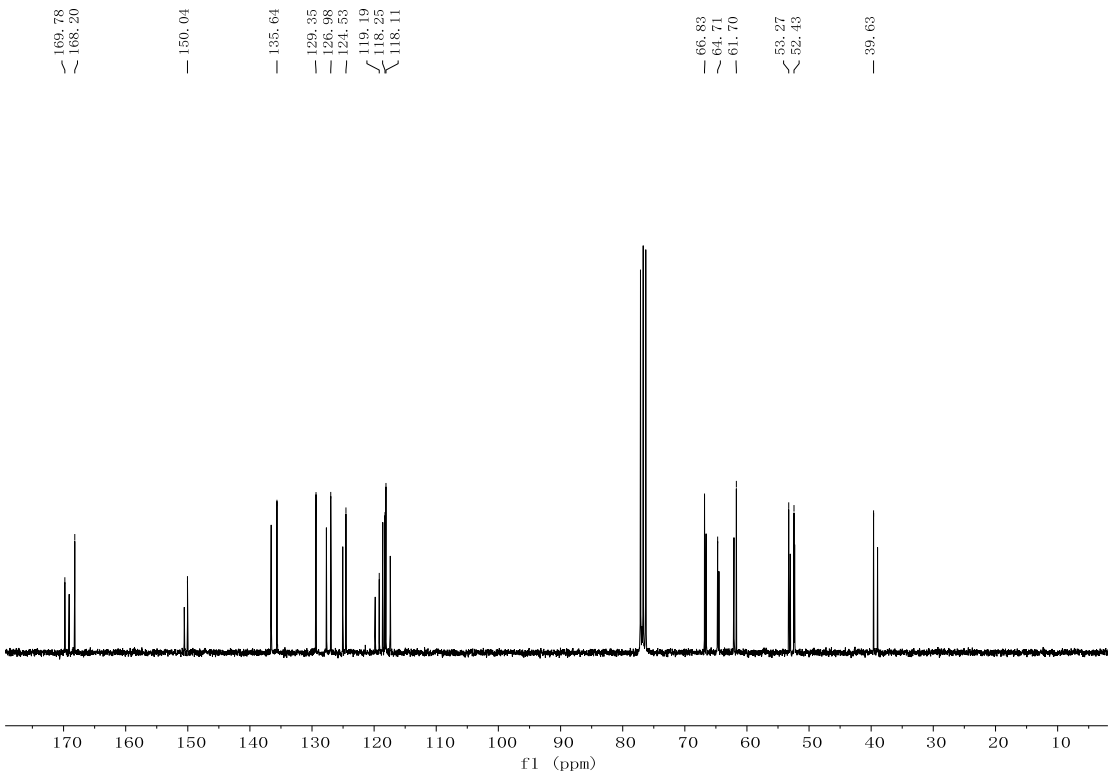
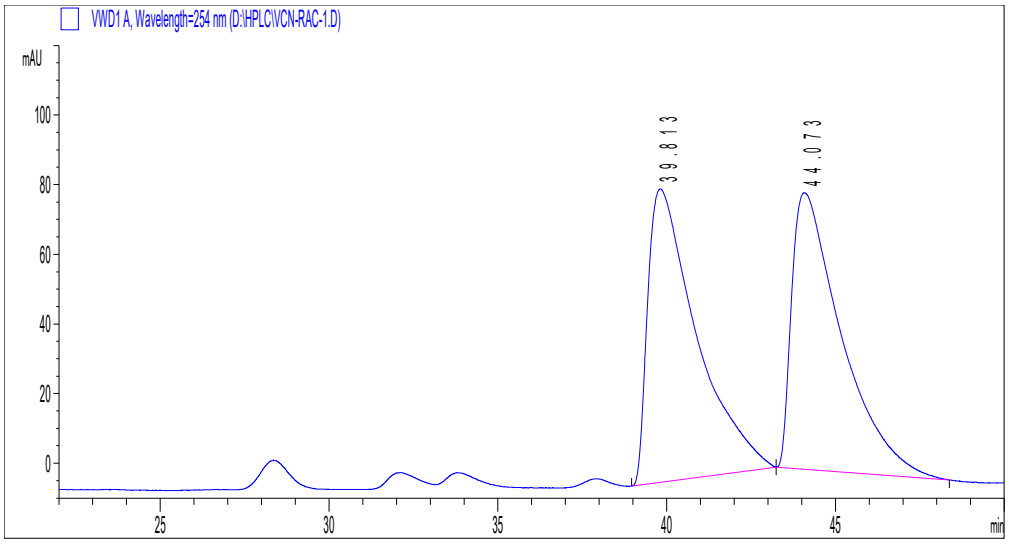
O2
S
O
N
H
NC
CN
3aq
0.98 1.00 1.00 2.01 0.99 0.97 0.99 1.00 1.02 0.99 1.03 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


150.05
135.23 133.36 131.64 129.59 129.36 128.20 127.07 123.45 119.56 118.84 113.08 112.45 112.11
65.59 63.99
54.99
41.57
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.40 7.40 7.40 7.38 7.37 7.37 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.17 7.16 7.16 7.15 7.03 7.03 7.02 7.02 6.18 6.16 6.15 6.13 6.12 6.10 6.09 6.07 5.47 5.42 5.29 5.27 5.23 5.22 4.31 4.30 4.28 4.27 3.90 3.48 2.77 2.75 2.72 2.68 2.66 2.63 2.61
O–SO2
N
H
MeO2C CO2Me
3ba
1.02 1.08 0.92 0.99 1.01 1.00 2.14 1.01 2.99 3.00 1.02 1.01
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)


169.78 168.20 150.04 135.64 129.35 126.98 124.53 119.19 118.25 118.11 66.83 64.71 61.70 53.27 52.43 39.63
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

HPLC Chromatograms of the Racemic Product 3aa



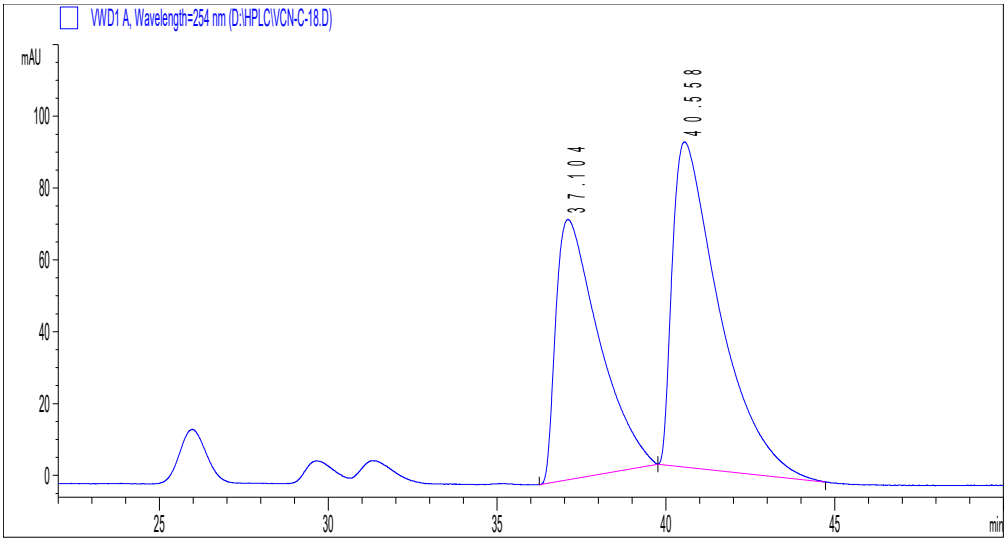
[min] [min] mAU *s [mAU] %

----|-------|----|-------|----------|----------|--------|

1 39.813 BB 1.3289 8427.03125 84.32877 50.9140

2 44.073 BB 1.3472 8124.48291 79.46033 49.0860

HPLC Chromatograms of the Chiral Product 3aa



[min] [min] mAU *s [mAU] %

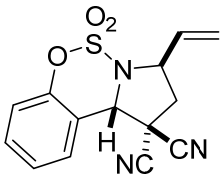
----|-------|----|-------|----------|----------|--------|

1 37.104 BB 1.1770 6444.53760 72.48774 42.3711

2 40.558 BB 1.3119 8765.22168 90.50045 57.6289

X-Ray Crystallographic Data of 3aa.

Crystallographic data for **3aa** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1836267. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3aa

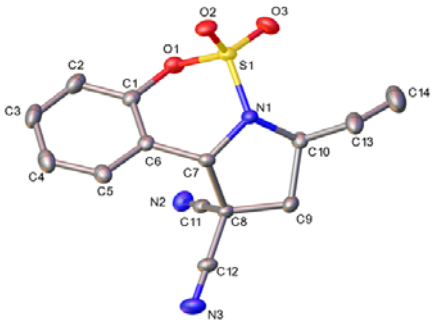


Table S1. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**	
Empirical formula	$C_{14}H_{11}N_3O_3S$	
Formula weight	301.32	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.471(4) Å	a= 90°.
	b = 10.038(3) Å	b= 101.028(5)°.
	c = 13.551(5) Å	g = 90°.
Volume	1398.0(8) $Å^3$	
Z	4	
Density (calculated)	1.432 Mg/m^3	
Absorption coefficient	0.245 mm^{-1}	
F(000)	624	
Crystal size	0.228 × 0.153 × 0.092 mm^3	

Theta range for data collection	2.542 to 27.460°.
Index ranges	-13<=h<=13, -12<=k<=13, -17<=l<=16
Reflections collected	10678
Independent reflections	3175 [R(int) = 0.0486]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.79861
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3175/0/190
Goodness-of-fit on F^2	1.138
Final R indices [I>2sigma(I)]	R_1 = 0.0545, wR_2 = 0.1240
R indices (all data)	R_1 = 0.0595, wR_2 = 0.1274
Extinction coefficient	n/a
Largest diff. peak and hole	0.624 and -0.366 e.Å^{-3}

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	5520(1)	2342(1)	5490(1)	31(1)
C1	6924(2)	2209(2)	4177(2)	30(1)
N1	4497(2)	3183(2)	4673(1)	27(1)
O1	6277(2)	1454(1)	4816(1)	34(1)
O2	6437(2)	3246(2)	6044(1)	38(1)
N2	4389(2)	896(2)	2312(2)	38(1)
C2	8137(2)	1783(3)	4054(2)	43(1)
N3	3809(2)	4975(2)	1410(2)	49(1)
C3	8770(2)	2499(3)	3423(2)	50(1)
O3	4832(2)	1442(2)	5997(1)	47(1)
C4	8212(2)	3636(3)	2944(2)	46(1)

C5	7005(2)	4055(2)	3094(2)	34(1)
C6	6330(2)	3333(2)	3705(1)	26(1)
C7	4979(2)	3751(2)	3804(1)	24(1)
C8	3899(2)	3294(2)	2891(1)	25(1)
C9	2666(2)	3313(2)	3352(2)	31(1)
C10	3102(2)	2730(2)	4406(2)	30(1)
C11	4174(2)	1940(2)	2558(1)	26(1)
C12	3835(2)	4225(2)	2044(2)	33(1)
C13	2306(2)	3292(3)	5119(2)	47(1)
C14	1600(3)	2613(4)	5607(2)	70(1)

Table S3. Bond lengths [Å] and angles [°] for **3aa**.

S1-N1	1.6226(17)
S1-O1	1.5920(16)
S1-O2	1.4260(16)
S1-O3	1.4133(17)
C1-O1	1.417(3)
C1-C2	1.380(3)
C1-C6	1.383(3)
N1-C7	1.481(2)
N1-C10	1.506(3)
N2-C11	1.135(3)
C2-H2	0.9500
C2-C3	1.380(4)
N3-C12	1.139(3)
C3-H3	0.9500
C3-C4	1.385(4)
C4-H4	0.9500

C4-C5	1.383(3)
C5-H5	0.9500
C5-C6	1.391(3)
C6-C7	1.506(3)
C7-H7	1.0000
C7-C8	1.577(3)
C8-C9	1.539(3)
C8-C11	1.477(3)
C8-C12	1.471(3)
C9-H9A	0.9900
C9-H9B	0.9900
C9-C10	1.531(3)
C10-H10	1.0000
C10-C13	1.501(3)
C13-H13	0.9500
C13-C14	1.278(4)
C14-H14A	0.9500
C14-H14B	0.9500
O1-S1-N1	103.65(8)
O2-S1-N1	108.57(10)
O2-S1-O1	107.39(10)
O3-S1-N1	109.48(10)
O3-S1-O1	106.06(10)
O3-S1-O2	120.38(10)
C2-C1-O1	117.8(2)
C2-C1-C6	122.7(2)
C6-C1-O1	119.56(18)
C7-N1-S1	117.49(13)
C7-N1-C10	112.83(15)
C10-N1-S1	119.34(14)

C1-O1-S1	113.59(13)
C1-C2-H2	120.8
C1-C2-C3	118.4(2)
C3-C2-H2	120.8
C2-C3-H3	119.7
C2-C3-C4	120.6(2)
C4-C3-H3	119.7
C3-C4-H4	120.1
C5-C4-C3	119.8(2)
C5-C4-H4	120.1
C4-C5-H5	119.6
C4-C5-C6	120.7(2)
C6-C5-H5	119.6
C1-C6-C5	117.76(19)
C1-C6-C7	122.18(18)
C5-C6-C7	120.02(18)
N1-C7-C6	115.64(16)
N1-C7-H7	108.5
N1-C7-C8	102.11(15)
C6-C7-H7	108.5
C6-C7-C8	113.18(15)
C8-C7-H7	108.5
C9-C8-C7	102.06(15)
C11-C8-C7	110.76(15)
C11-C8-C9	111.28(17)
C12-C8-C7	110.26(16)
C12-C8-C9	113.07(17)
C12-C8-C11	109.25(16)
C8-C9-H9A	110.9
C8-C9-H9B	110.9

H9A-C9-H9B	108.9
C10-C9-C8	104.49(16)
C10-C9-H9A	110.9
C10-C9-H9B	110.9
N1-C10-C9	102.21(16)
N1-C10-H10	110.8
C9-C10-H10	110.8
C13-C10-N1	111.39(17)
C13-C10-C9	110.68(19)
C13-C10-H10	110.8
N2-C11-C8	179.4(2)
N3-C12-C8	177.7(2)
C10-C13-H13	117.3
C14-C13-C10	125.4(3)
C14-C13-H13	117.3
C13-C14-H14A	120.0
C13-C14-H14B	120.0
H14A-C14-H14B	120.0

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3aa**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2hka \times b \times U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	36(1)	33(1)	21(1)	2(1)	-1(1)	1(1)
C1	29(1)	31(1)	28(1)	-6(1)	-1(1)	0(1)
N1	25(1)	33(1)	22(1)	0(1)	1(1)	-2(1)
O1	41(1)	26(1)	32(1)	2(1)	3(1)	5(1)
O2	38(1)	44(1)	27(1)	-6(1)	-8(1)	2(1)

N2	36(1)	34(1)	42(1)	-9(1)	1(1)	0(1)
C2	32(1)	49(1)	43(1)	-11(1)	-2(1)	10(1)
N3	56(1)	47(1)	37(1)	12(1)	-6(1)	-3(1)
C3	27(1)	71(2)	51(2)	-21(1)	8(1)	2(1)
O3	58(1)	51(1)	34(1)	15(1)	10(1)	-4(1)
C4	38(1)	62(2)	42(1)	-14(1)	15(1)	-18(1)
C5	35(1)	39(1)	29(1)	-5(1)	5(1)	-11(1)
C6	25(1)	27(1)	23(1)	-6(1)	0(1)	-4(1)
C7	28(1)	22(1)	20(1)	0(1)	1(1)	0(1)
C8	26(1)	27(1)	21(1)	0(1)	0(1)	3(1)
C9	24(1)	37(1)	28(1)	-4(1)	1(1)	2(1)
C10	26(1)	38(1)	25(1)	-5(1)	2(1)	-7(1)
C11	25(1)	30(1)	21(1)	-1(1)	-2(1)	-2(1)
C12	35(1)	32(1)	27(1)	2(1)	-4(1)	2(1)
C13	36(1)	73(2)	32(1)	-18(1)	8(1)	-8(1)
C14	56(2)	108(3)	52(2)	-15(2)	26(2)	-14(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3aa**.

	x	y	z	U(eq)
H2	8526	1015	4395	51
H3	9597	2211	3316	60
H4	8657	4126	2514	55
H5	6633	4845	2776	41
H7	4957	4745	3851	28
H9A	2339	4234	3388	37
H9B	1970	2762	2951	37
H10	3049	1736	4389	36

H13	2328	4230	5215	56
H14A	1551	1672	5532	84
H14B	1125	3049	6044	84

Table S6. Torsion angles [°] for **3aa**.

S1-N1-C7-C6	7.6(2)
S1-N1-C7-C8	130.95(14)
S1-N1-C10-C9	-155.09(14)
S1-N1-C10-C13	86.7(2)
C1-C2-C3-C4	1.5(4)
C1-C6-C7-N1	19.4(3)
C1-C6-C7-C8	-97.9(2)
N1-S1-O1-C1	58.93(14)
N1-C7-C8-C9	32.95(18)
N1-C7-C8-C11	-85.60(18)
N1-C7-C8-C12	153.35(16)
N1-C10-C13-C14	-126.9(3)
O1-S1-N1-C7	-42.79(16)
O1-S1-N1-C10	99.79(15)
O1-C1-C2-C3	179.19(19)
O1-C1-C6-C5	179.18(17)
O1-C1-C6-C7	-3.2(3)
O2-S1-N1-C7	71.17(16)
O2-S1-N1-C10	-146.25(15)
O2-S1-O1-C1	-55.88(15)
C2-C1-O1-S1	140.67(17)
C2-C1-C6-C5	-0.7(3)
C2-C1-C6-C7	176.94(19)
C2-C3-C4-C5	-0.3(4)

C3-C4-C5-C6	-1.3(3)
O3-S1-N1-C7	-155.61(14)
O3-S1-N1-C10	-13.03(18)
O3-S1-O1-C1	174.21(13)
C4-C5-C6-C1	1.8(3)
C4-C5-C6-C7	-175.86(19)
C5-C6-C7-N1	-163.06(17)
C5-C6-C7-C8	79.6(2)
C6-C1-O1-S1	-39.2(2)
C6-C1-C2-C3	-0.9(3)
C6-C7-C8-C9	157.93(17)
C6-C7-C8-C11	39.4(2)
C6-C7-C8-C12	-81.7(2)
C7-N1-C10-C9	-10.9(2)
C7-N1-C10-C13	-129.1(2)
C7-C8-C9-C10	-40.9(2)
C8-C9-C10-N1	32.0(2)
C8-C9-C10-C13	150.76(18)
C9-C10-C13-C14	120.1(3)
C10-N1-C7-C6	-137.30(17)
C10-N1-C7-C8	-14.0(2)
C11-C8-C9-C10	77.24(19)
C12-C8-C9-C10	-159.35(17)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for **3aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)