Supporting Information

Allylic C-S Bond Construction through Metal-Free Direct Nitroalkene Sulfonation

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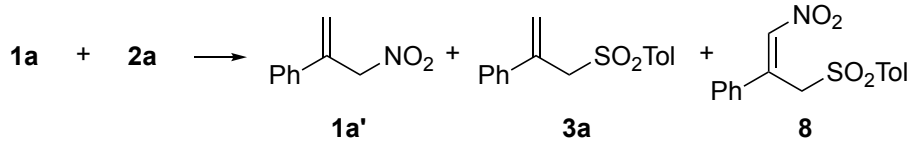
I. Other reactions conditions screening[a]

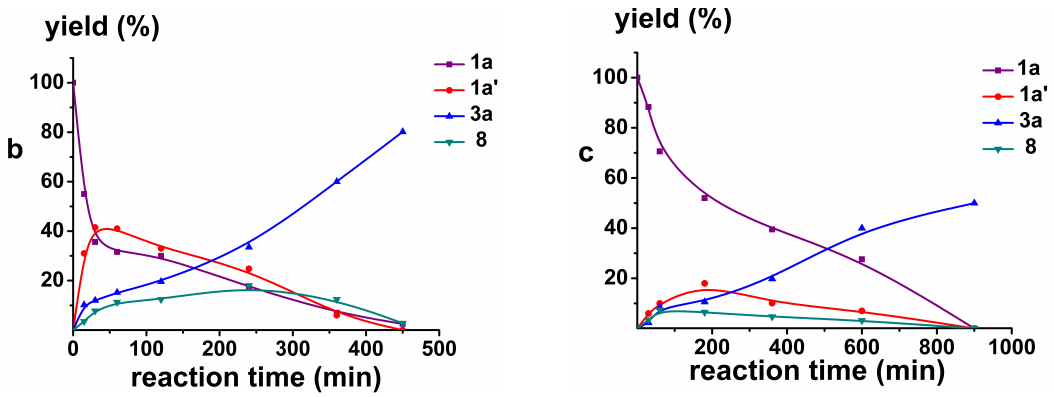
entry	catalyst	additive	solvent	temp (^{o}C)	time (h)	yield(%)[b] 3a	4a
1	$AgNO_3$ (10 %)	$K_2S_2O_8$ (2)	DMF	100	4	15[c]	trace[c]
2	$AgNO_3$ (10 %)	$K_2S_2O_8$ (2)	DMF	100	4	30	trace
3	-	-	DMF	100	4	84	trace
4	-	-	Nitroethane	100	4	10	20
5	-	-	NMP	100	4	74	＜5
6	-	-	toluene	100	4	0	0
7	-	-	n-Butylacetae	100	4	20	0
8	TBAI (10 %)	TBHP (2)	DMSO	100	4	20	trace
9	$CuCl_2$ (10 %)	TBHP (2)	DMSO	100	4	trace	0
10	I_2 (10 %)	$K_2S_2O_8$ (2)	DMSO	80	4	89	trace
11	I_2 (10 %)	DBTP (2)	DMSO	80	4	19	trace
12	I_2 (10 %)	H_2O_2 (2)	DMSO	80	4	50	trace
13	I_2 (10 %)	-	DMSO	80	4	30	0
14	TBAI (20 %)	-	DMSO	100	4	75	0
15	I_2 (10 %)	TBHP (1)	DMSO	80	4	85	trace
16	I_2 (5 %)	TBHP (2)	DMSO	80	4	70	trace

[a]Reaction conditions: **1a** (0.3 mmol, 1 equiv), **2a** (1.5 equiv), catalyst (mol %), oxidant (equiv) in DMSO (3.0 mL), open air.

[b]Isolated yield. [c]Under argon protection.

II. Reaction profile

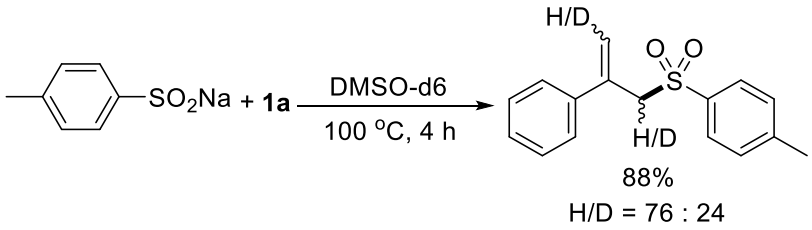


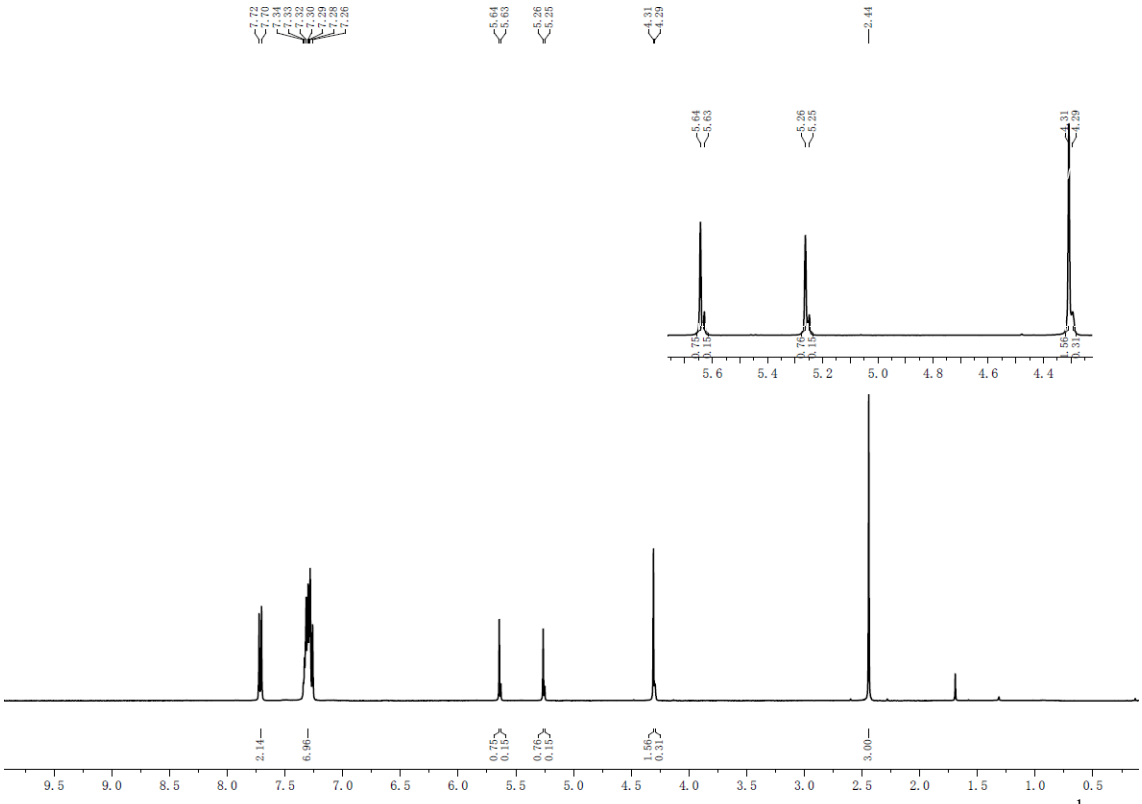


Reaction conditions: nitroolefins (0.3 mmol), sodium sulfinates (0.45 mmol) (b) I_2 (0.03 mmol), DMSO, 80 °C, open air; (c) I_2 (0.3 mmol), DMSO, 80 °C, open air.

The time-dependent reaction profile of the reaction of **1a** with sodium *p*-tolylsulfinate was obtained using ^{1}H NMR. The Lewis base promoted the equilibrium between **1a** and **1a'** occurred within 40 min (condition b). However, 100% I_2 inhibited the formation of allylic compound **1a'** (condition c).

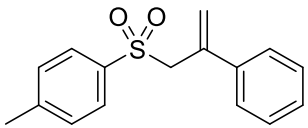
III. Deuterium-Labeling Experiments



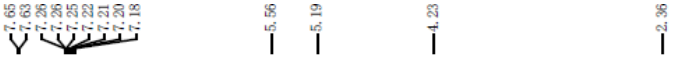


The reaction of **1a** and sodium *p*-tolylsulfinate in DMSO-d6 was also performed, and the ^{1}H NMR spectrum of the corresponding product revealed that D-substituted product formed, the ratio of H and D was 76:24.

IV. NMR spectra data



3a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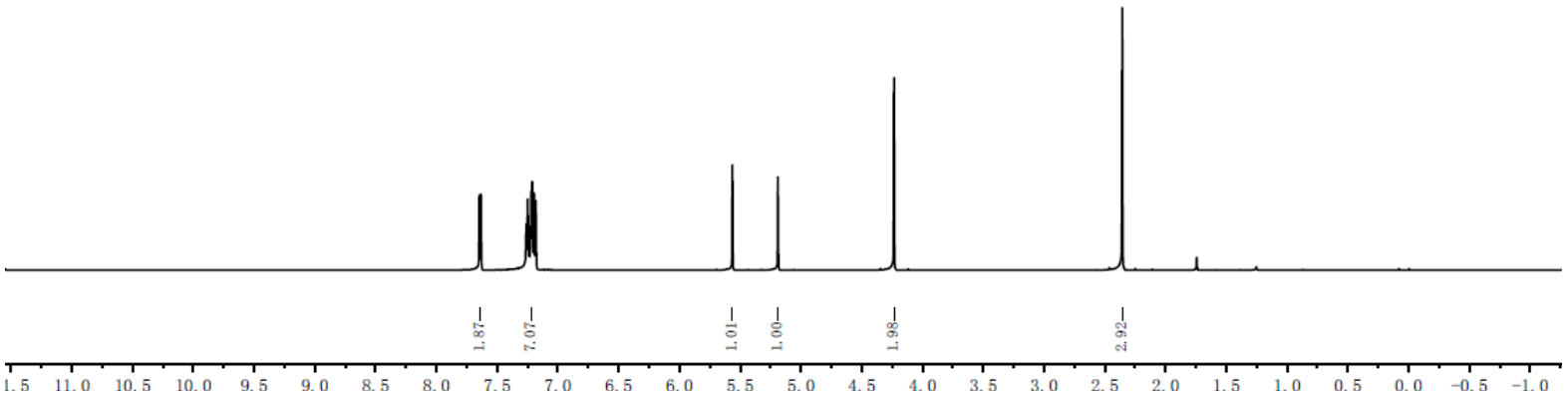
5.19
4.23
2.36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1.00
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2.92
11.5
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
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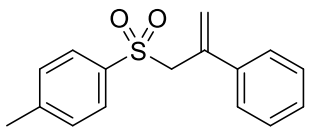
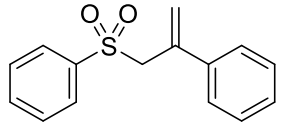

O
O
S

3a

144.45
138.69
136.43
135.27
129.35
128.46
128.18
127.74
126.07
121.55
77.21
77.00
76.79
61.95
21.40
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.78
7.76
7.76
7.54
7.52
7.51
7.42
7.40
7.39
7.25
7.24
7.23
7.23
7.22
7.21
5.57
5.20
4.26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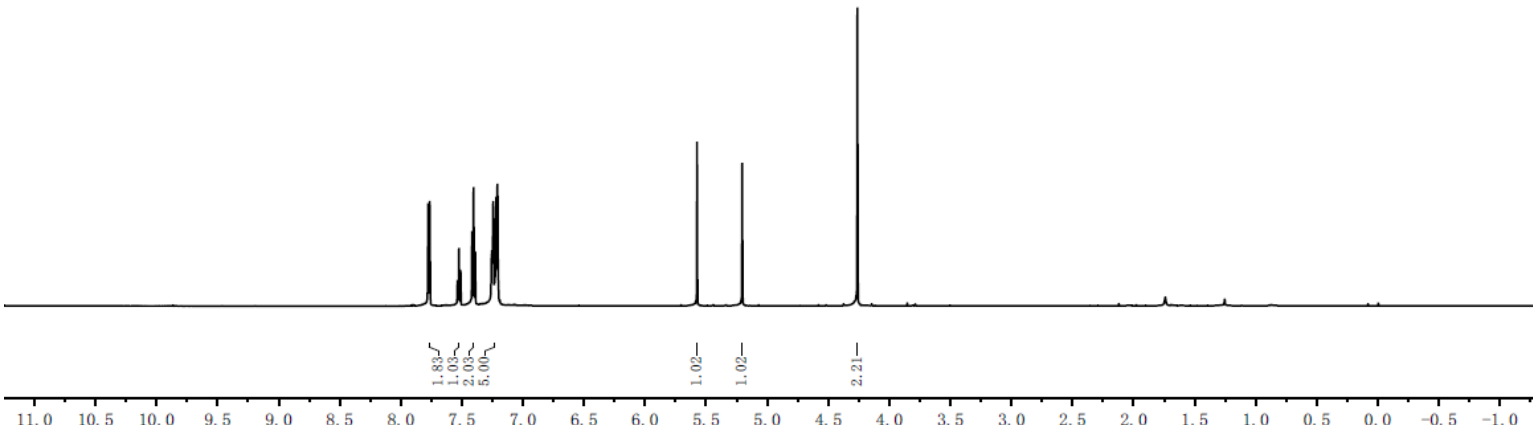
O
S

3b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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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0.5
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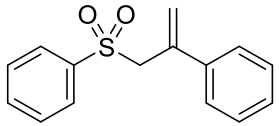
-1.0



3b

138.60
138.25
136.32
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128.75
128.45
128.25
127.89
126.04
121.71
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77.00
76.79
61.88
220
210
200
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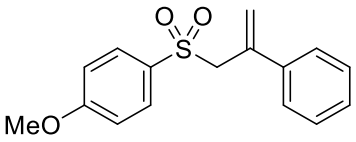
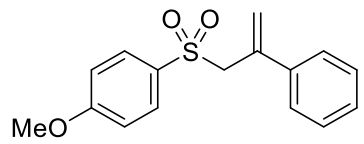

O
O
S
MeO

3c

7.68
7.66
7.26
7.25
7.23
6.85
6.84
5.57
5.19
4.23
3.80
2.08
4.92
2.06
1.01
1.03
2.16
3.27
11.5 11.0 10.5 10.0 9.5 9.0 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 -0.5 -1.0


O
O
S
MeO

3c

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121.56
113.97
77.21
77.00
76.79
62.20
55.55
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20
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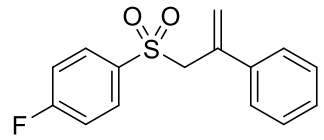
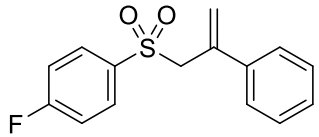

O
O
S
F

3d

7.77
7.76
7.76
7.75
7.23
7.08
7.07
7.05
5.60
5.24
4.28
2.00
5.14
2.00
1.17
1.06
2.18
11.0 10.5 10.0 9.5 9.0 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 -0.5 -1.0


O
O
S
F

3d

166.52
164.82
138.46
136.45
134.34
134.32
131.50
131.44
128.39
128.09
126.09
121.95
116.14
115.99
77.21
77.00
76.79
62.19
220
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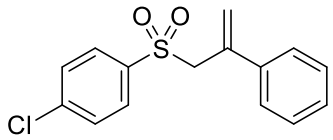
10


O
O
S
Cl

3e


7.67
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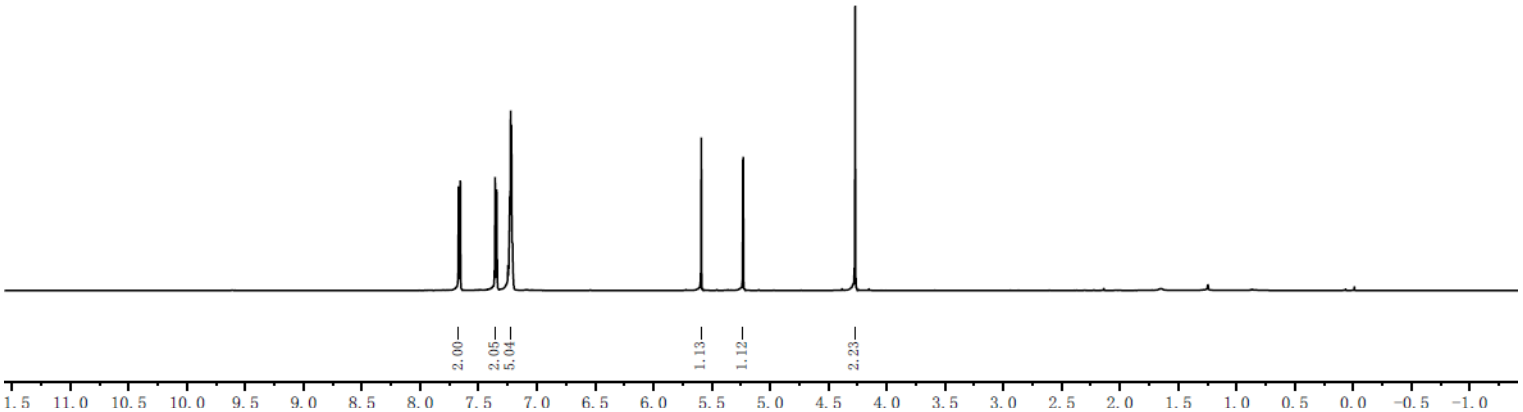
7.22
7.22
7.21
5.59
5.23
4.27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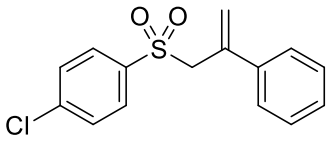
O
O
S
Cl

3e

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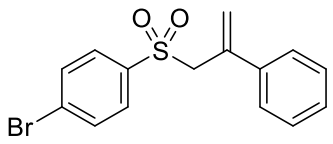
O
O
S
Br

3f

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4.99
1.04
1.03
2.00
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10.5
10.0
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9.0
8.5
8.0
7.5
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6.0
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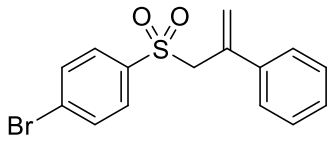
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O
S
Br

3f

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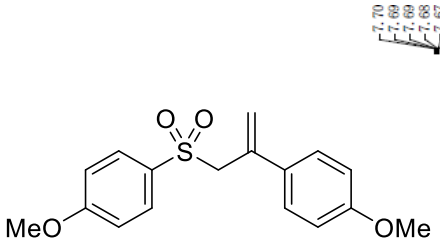
O
O
S
MeO
OMe

3g

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7.69
7.68
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7.20
6.89
6.88
6.88
6.87
6.86
6.79
6.78
6.77
6.76
6.76
5.49
5.45
5.07
4.21
3.83
3.78
1.98
2.01
2.08
2.04
1.00
0.98
2.03
3.23
3.07
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10.0
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9.0
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6.5
6.0
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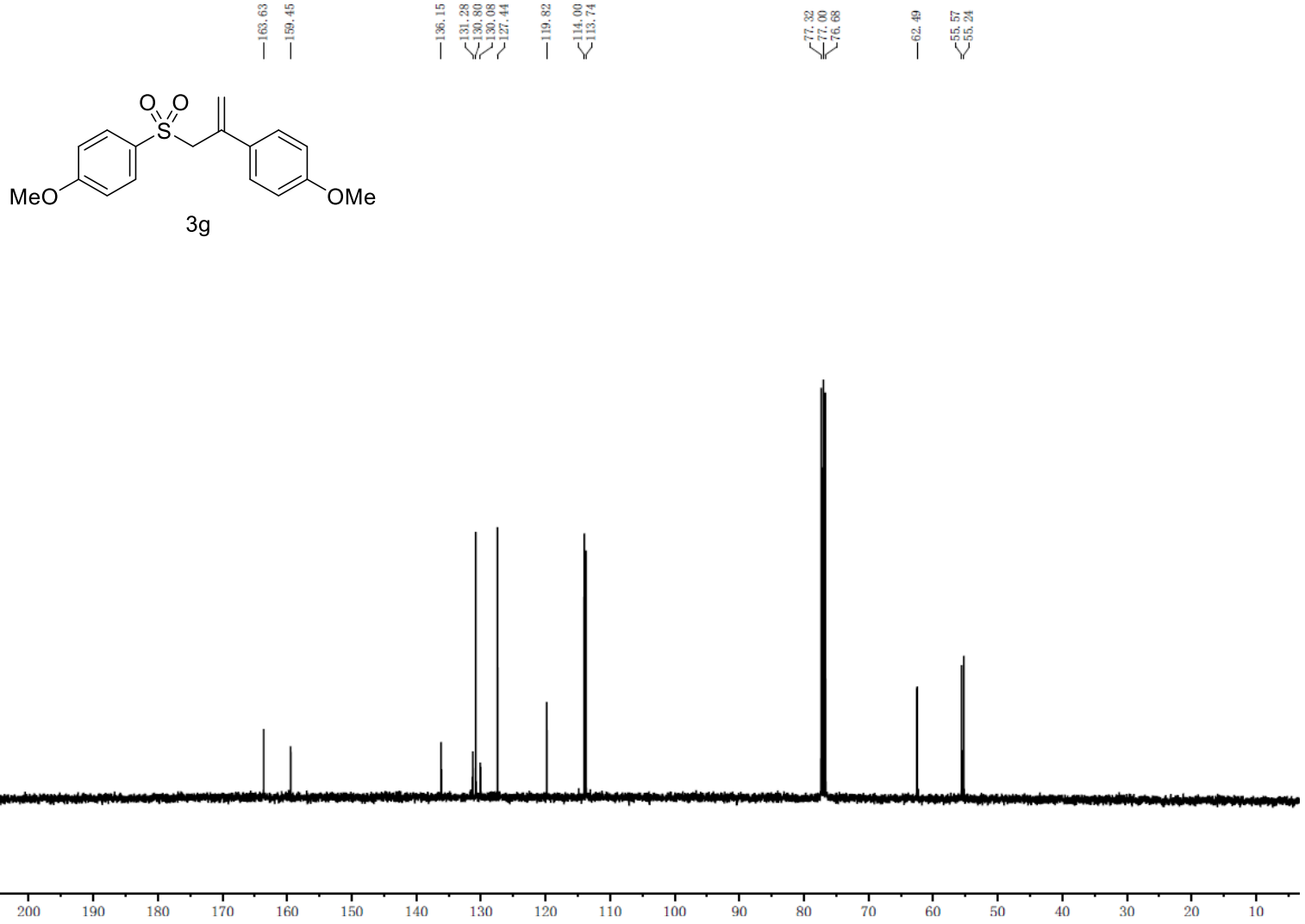
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113.74
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76.68
62.49
55.57
55.24
O
O
S
MeO
OMe
3g
200
190
180
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160
150
140
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120
110
100
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80
70
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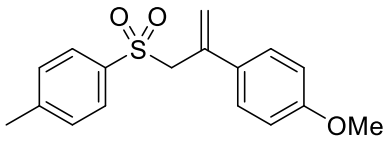
40
30
20
10


O
O
S
OMe

3h

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7.64
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6.75
6.75
6.74
5.48
5.06
4.21
3.77
2.38
1.95
3.95
1.99
1.00
0.99
2.00
3.11
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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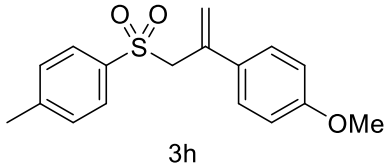

3h

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135.88
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127.37
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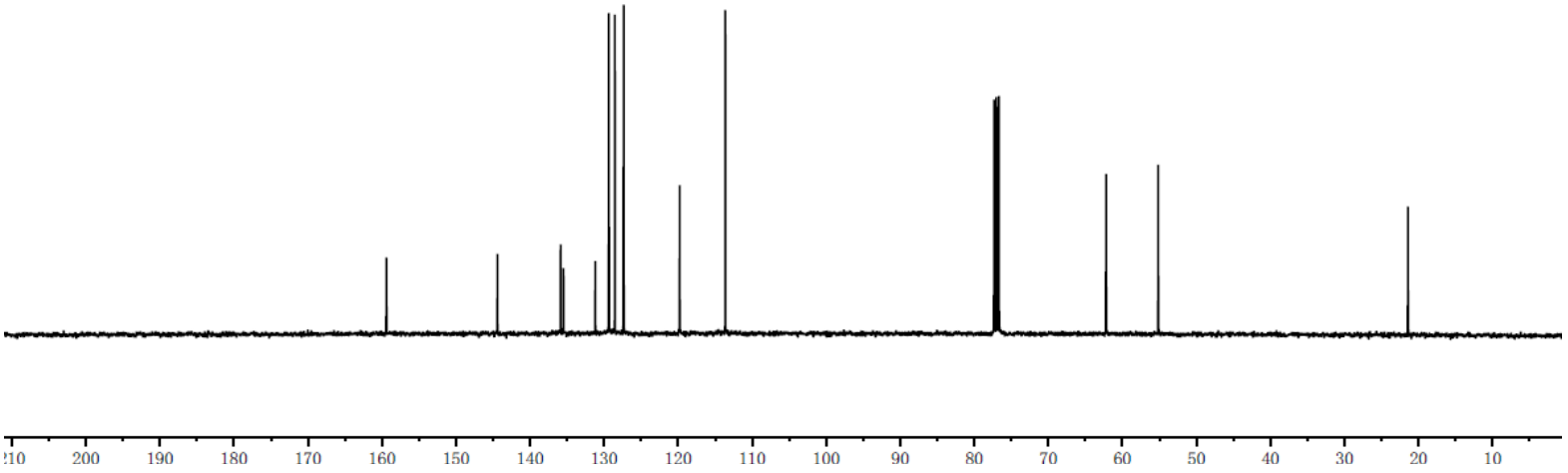

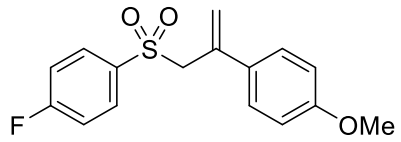
O
O
S
F
OMe

3i

7.78
7.78
7.77
7.77
7.76
7.75
7.75
7.20
7.17
7.11
6.77
6.76
6.76
5.50
5.10
4.25
3.78
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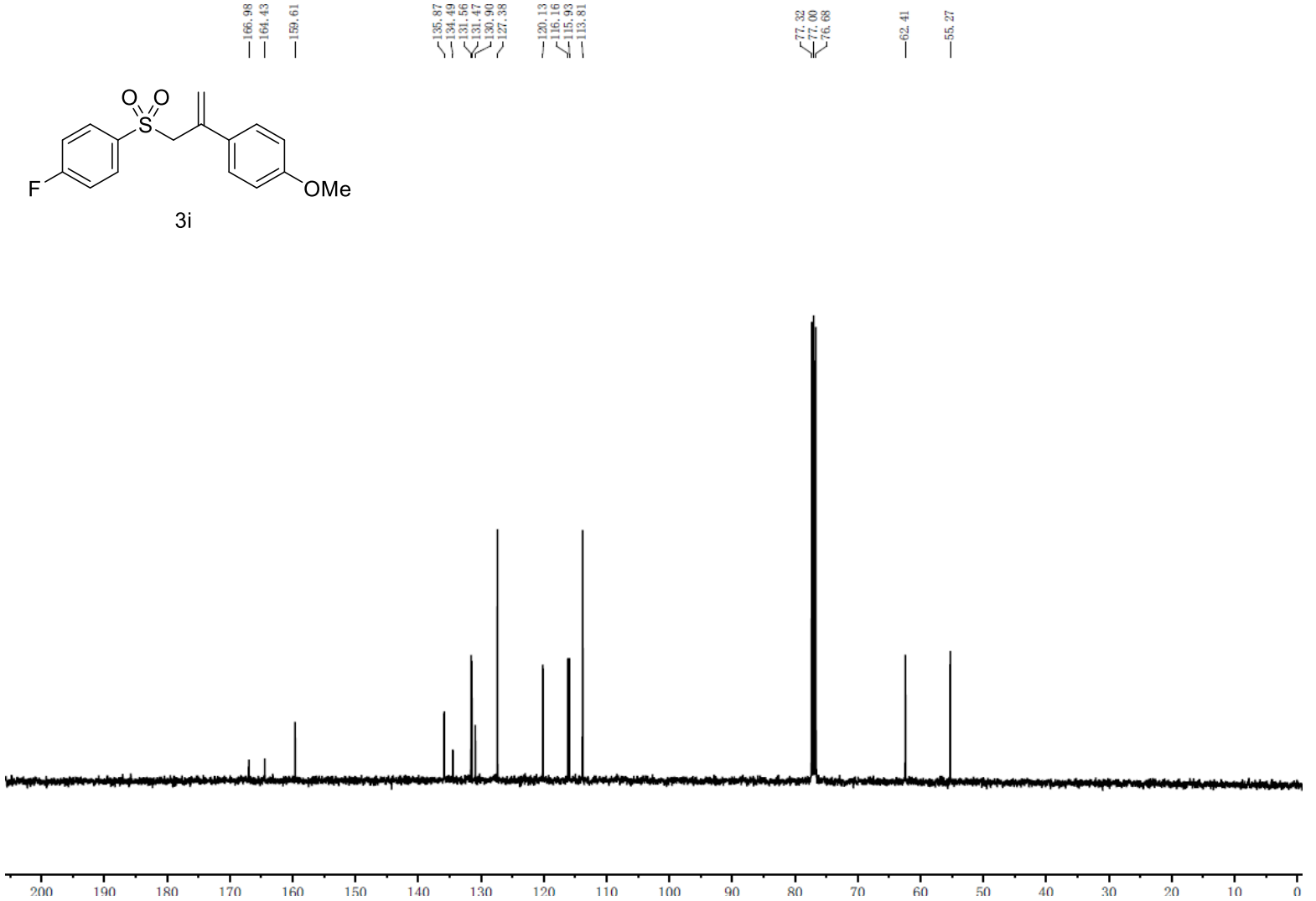
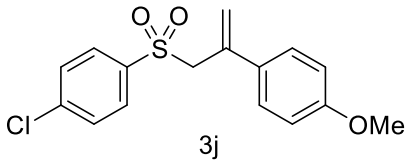
1.99
2.00
1.00
1.01
2.02
3.04


166.98
164.43
159.61
135.87
134.49
131.56
131.47
130.90
127.38
120.13
116.16
115.93
113.81
77.32
77.00
76.68
62.41
55.27
O
O
S
F
OMe
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
O
S
Cl
OMe

3j

7.68
7.66
7.38
7.36
7.17
6.76
6.75
6.75
5.50
5.11
4.24
3.78
1.92
1.93
1.98
1.97
1.00
0.95
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5.5
5.0
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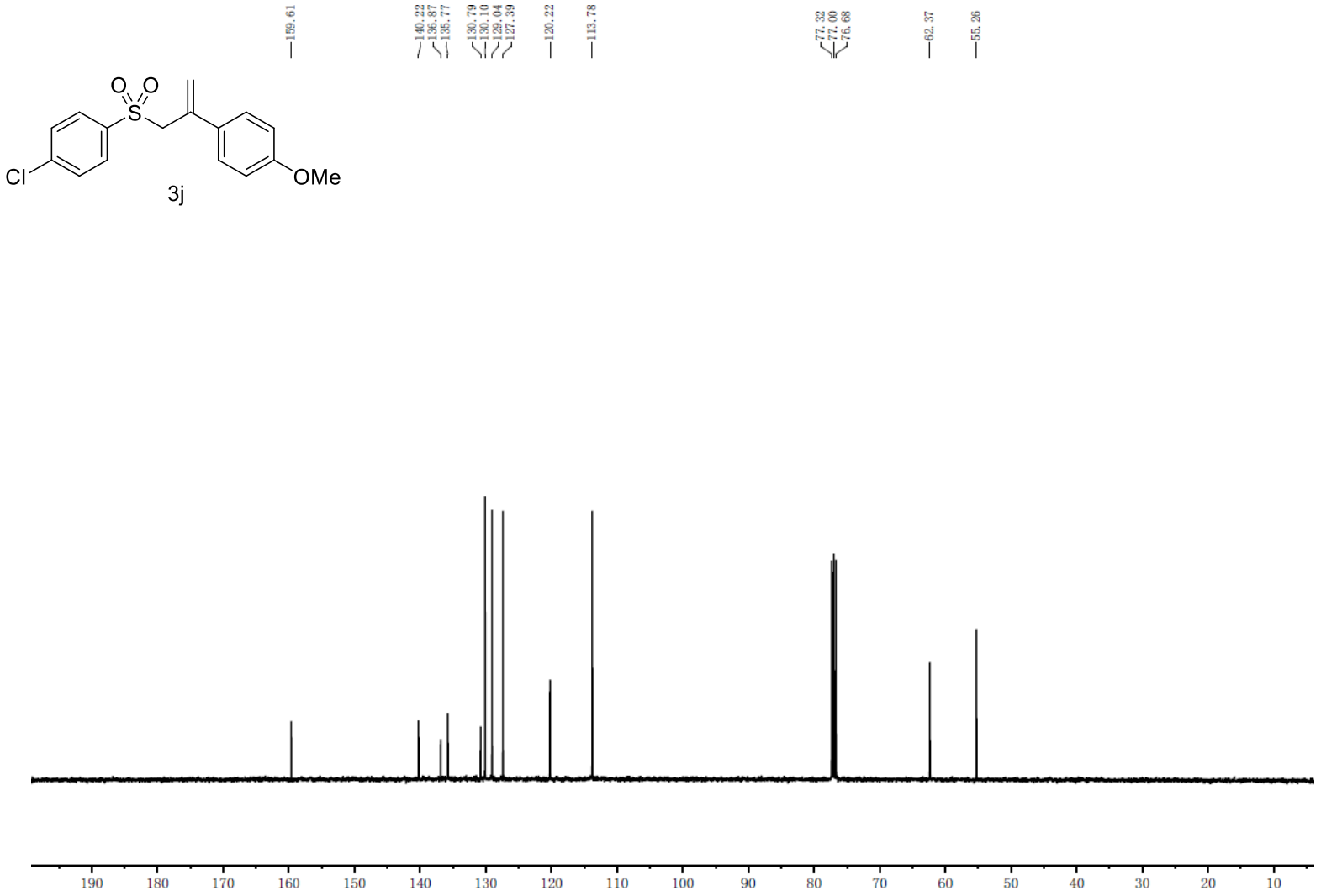
−1.0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77.32
77.00
76.68
62.37
55.26
O
O
S
Cl
OMe
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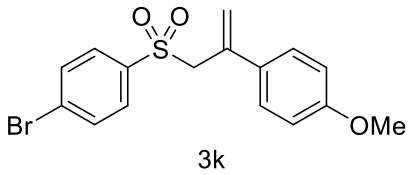
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S
Br
OMe

3k

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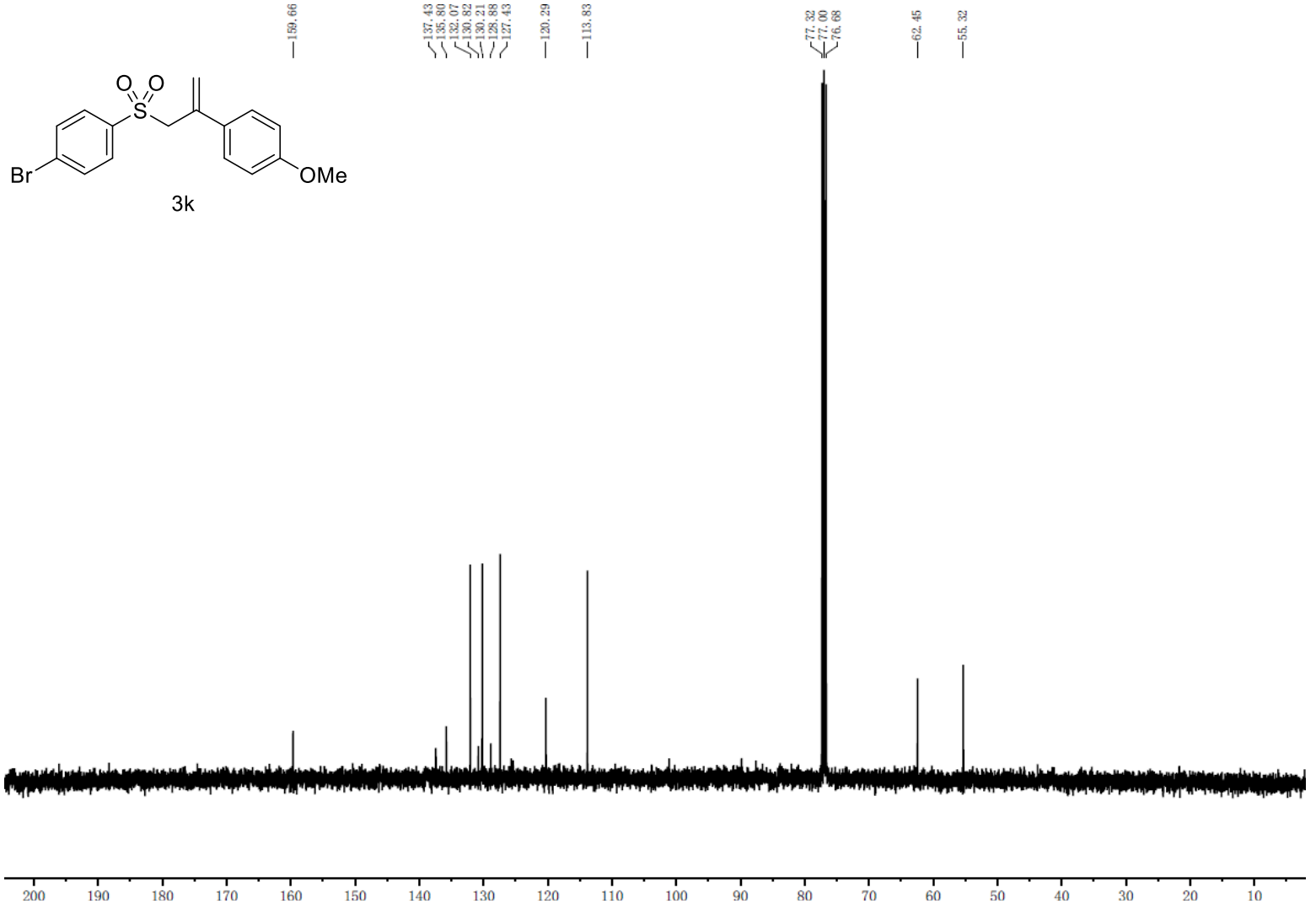
2.04
3.04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127.43
120.29
113.83
77.32
77.00
76.68
62.45
55.32
O
O
S
Br
OMe
3k
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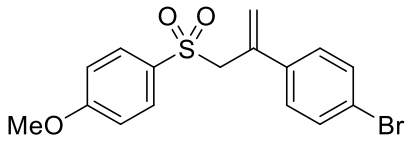
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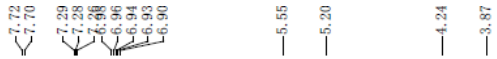
MeO
Br

3l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6.90
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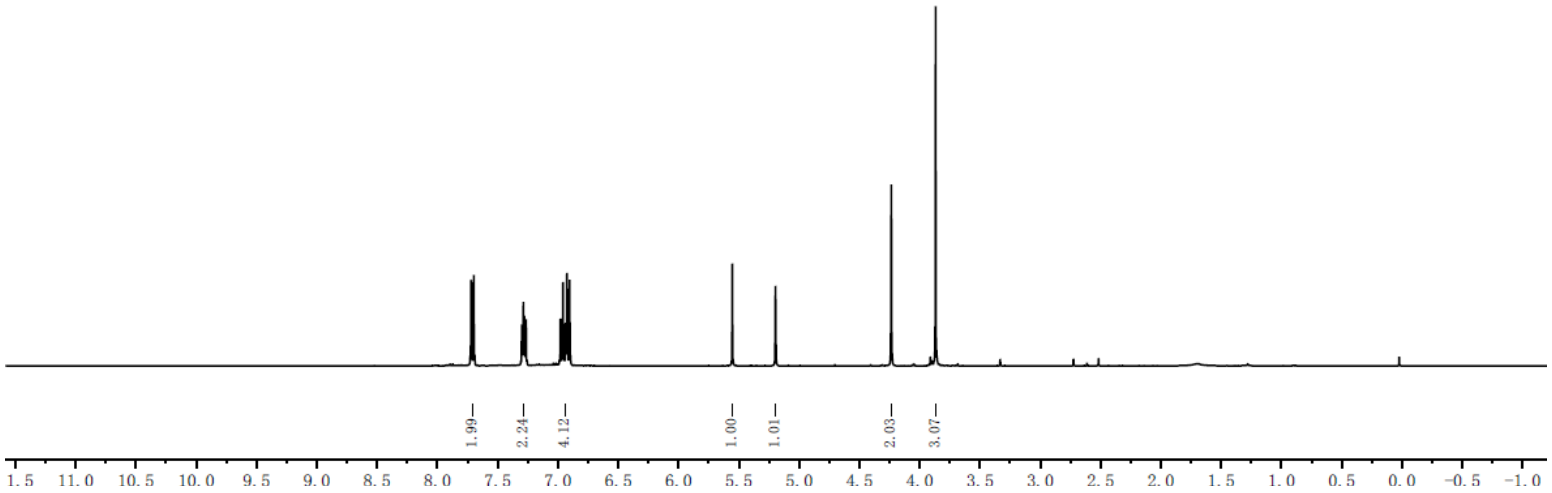
3.87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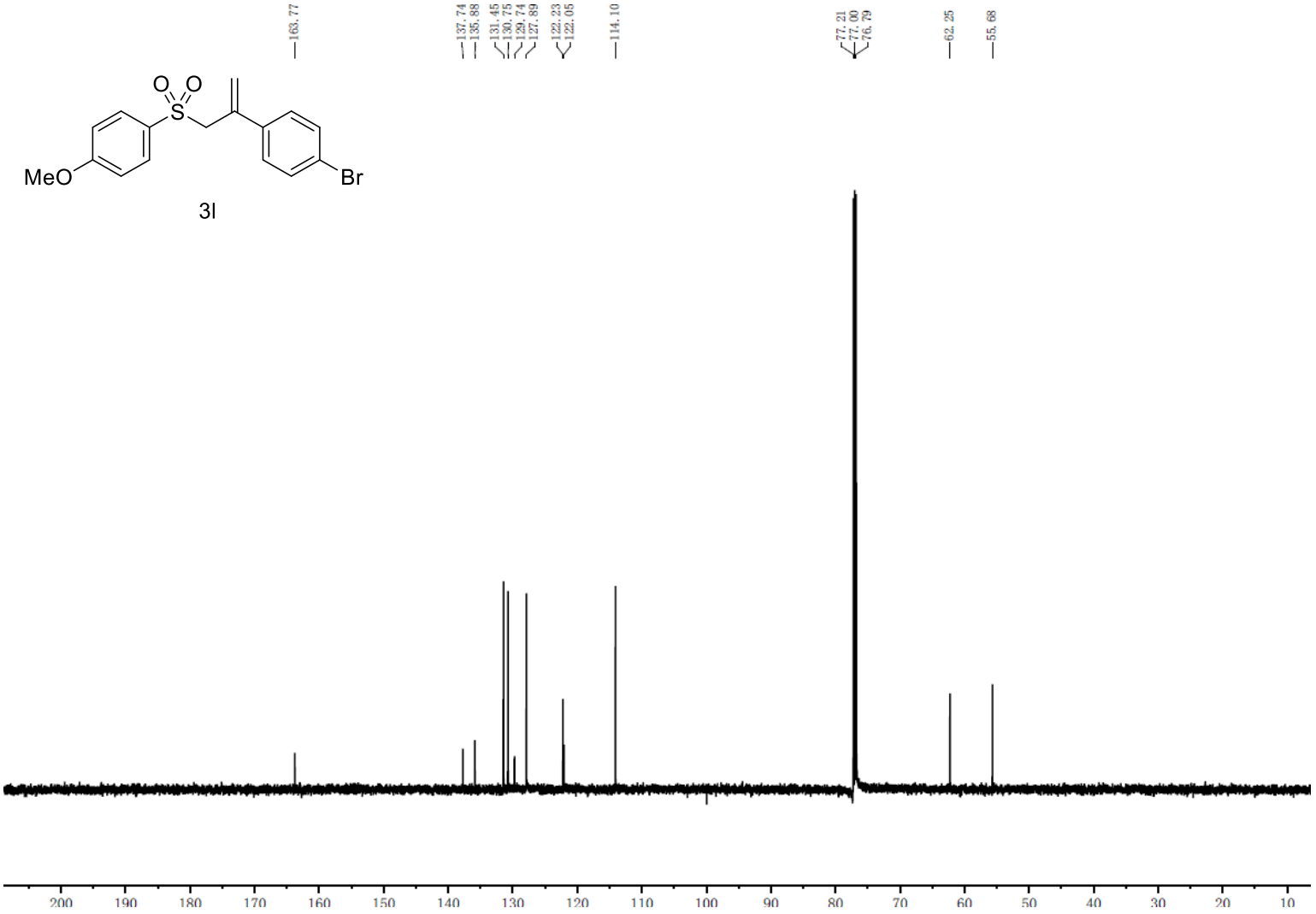
4.12
1.00
1.01
2.03
3.07
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0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122.23
122.05
114.10
77.21
77.00
76.79
62.25
55.68
MeO
Br
3l
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150
140
130
120
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100
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80
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40
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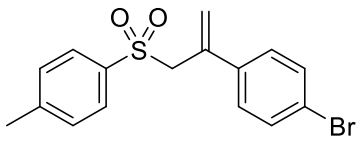
20
10


O
O
S
Br

3m

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7.22
7.14
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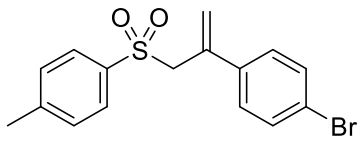
5.57
5.22
4.20
2.41
2.00
1.99
2.01
2.05
1.07
1.06
2.14
3.17
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


O
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S
Br

3m

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122.07
77.21
77.00
76.79
62.03
21.58
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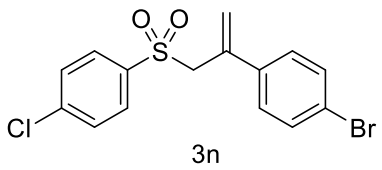
O
O
S
Cl
Br

3n


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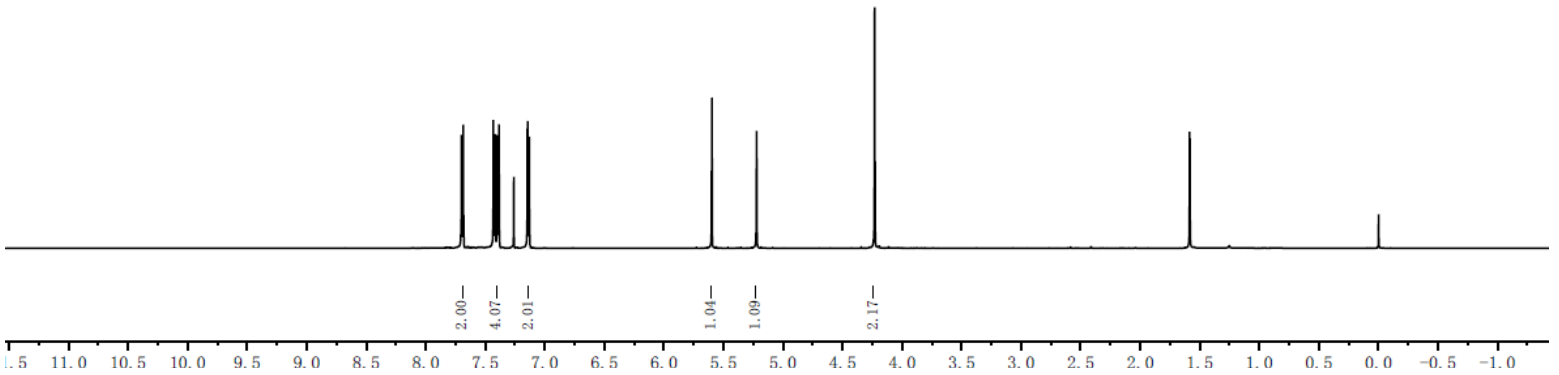
5.60
5.22
4.23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2.17
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10.5
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9.5
9.0
8.5
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7.5
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6.5
6.0
5.5
5.0
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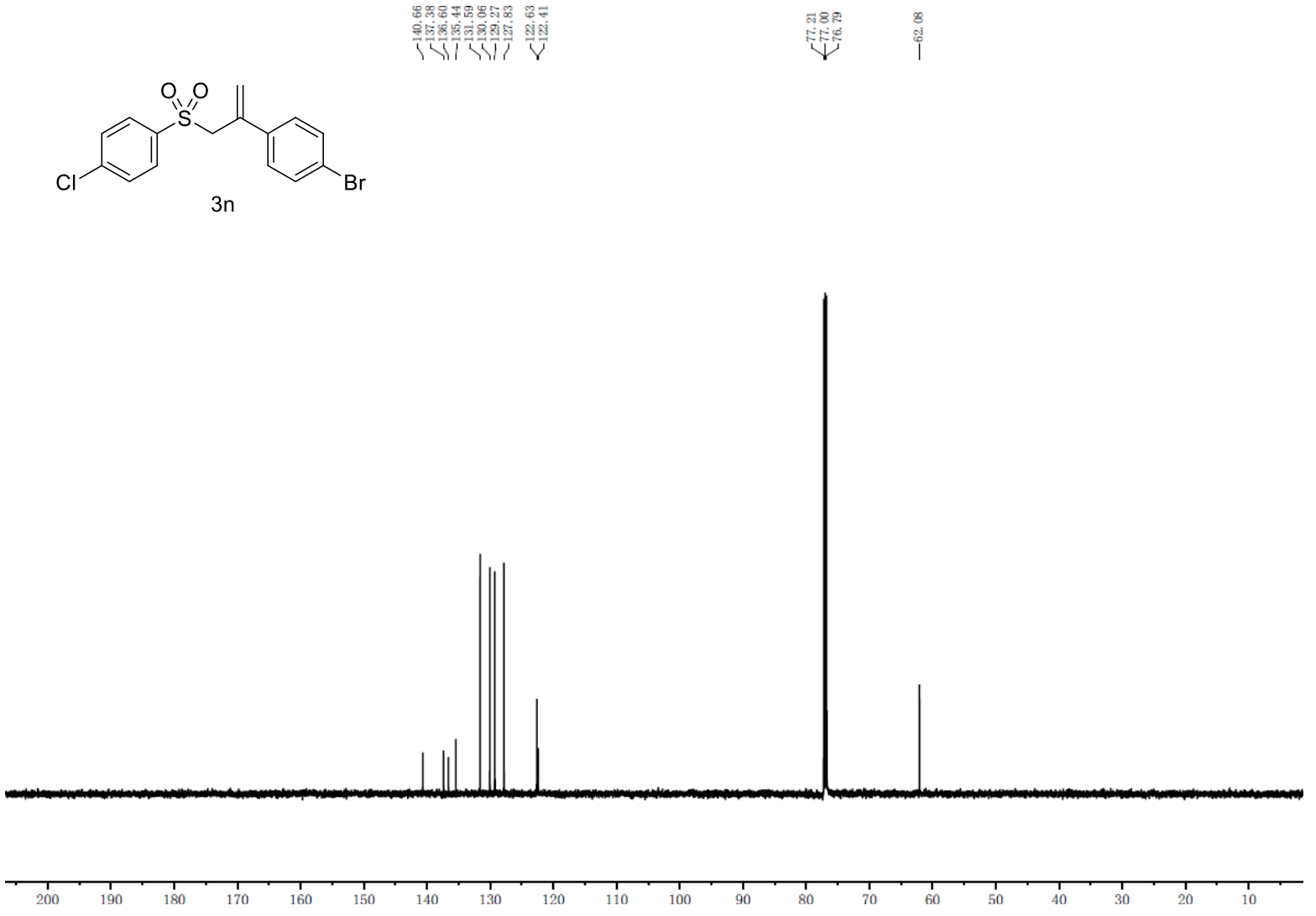
−0.5
−1.0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122.41
77.21
77.00
76.79
62.08
O
O
S
Cl
Br
3n
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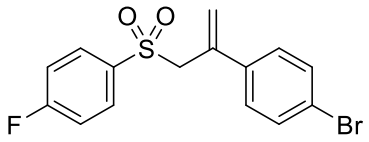
10


O
O
S
F
Br

3o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7.13
7.11
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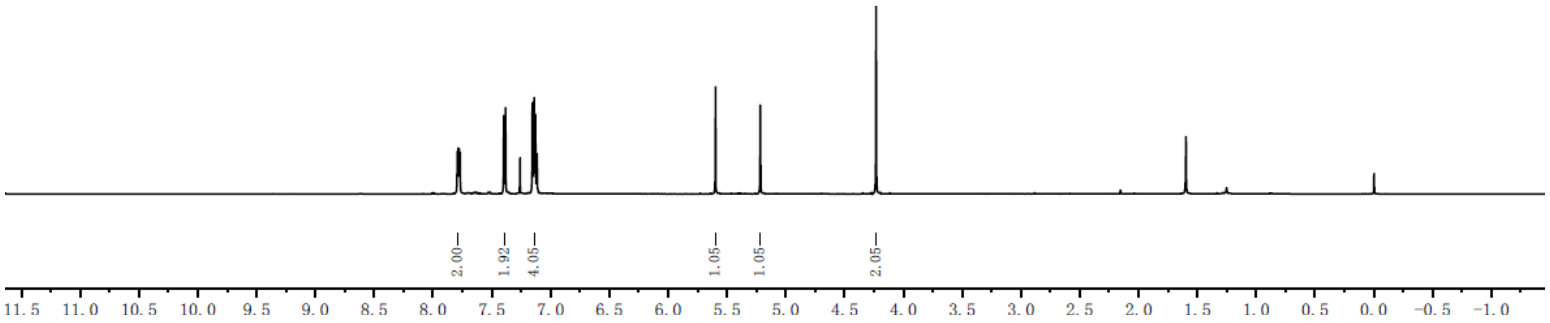
5.22
4.23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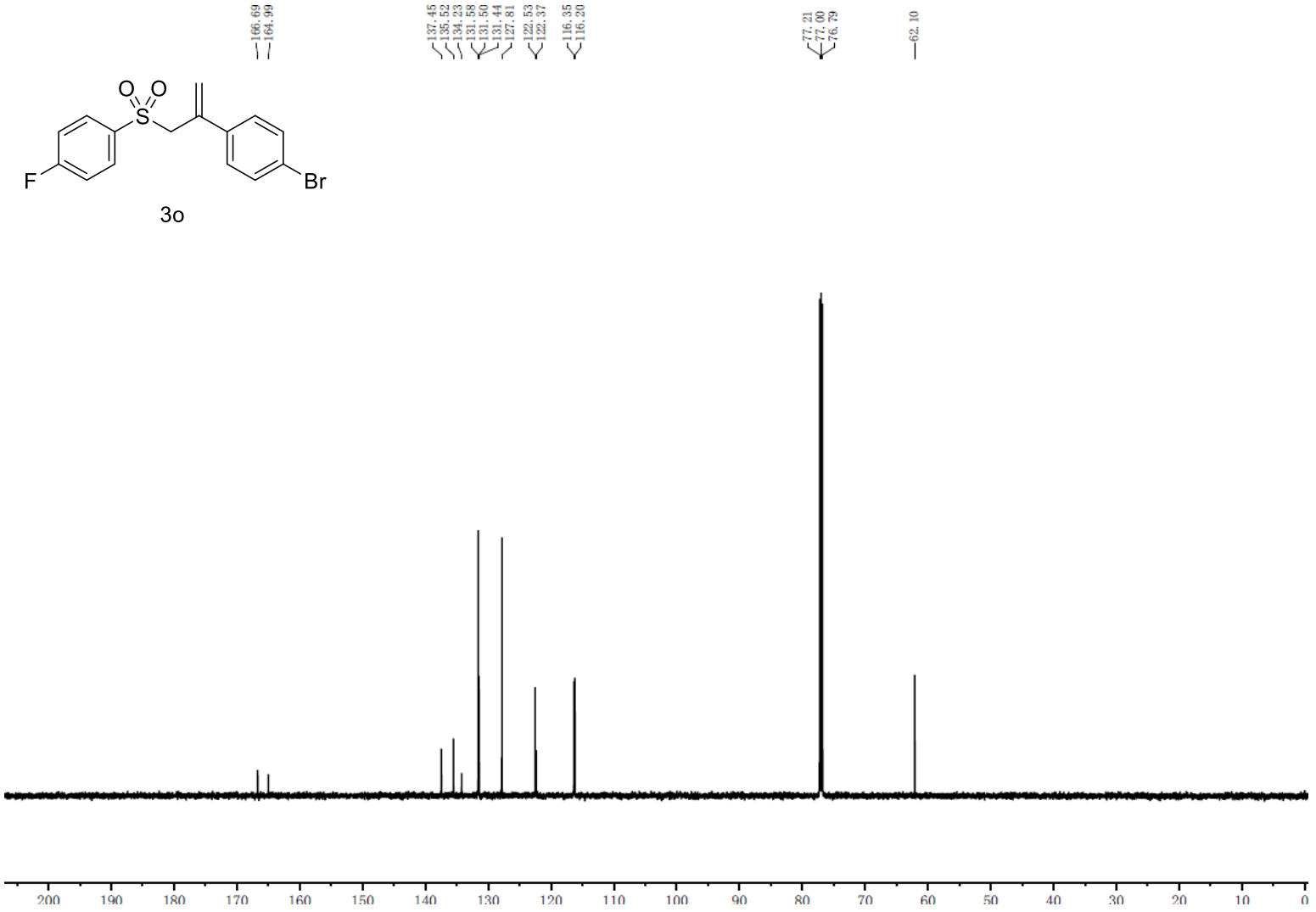
1.92
4.05
1.05
1.05
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0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131.44
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122.53
122.37
116.35
116.20
77.21
77.00
76.79
62.10
O
O
S
F
Br
3o
200
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150
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110
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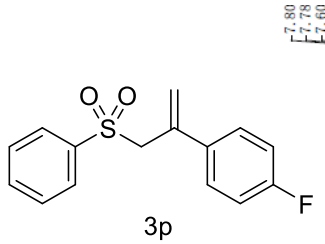
0


O
O
S
F

3p

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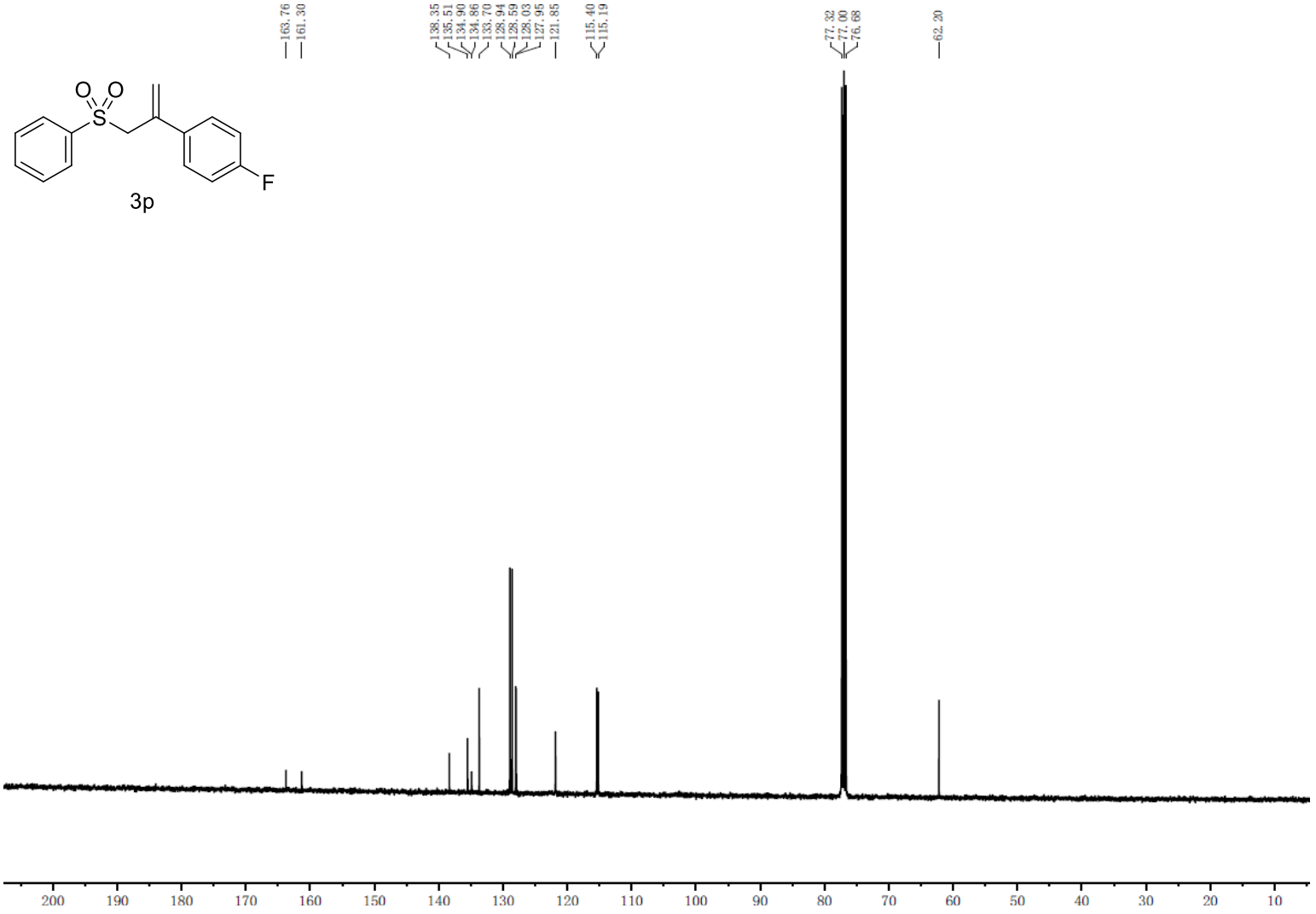
7.26
7.25
7.24
7.23
6.95
6.93
6.91
5.54
5.19
4.24
1.83
0.99
1.96
2.29
1.93
0.89
1.00
1.88
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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115.19
77.32
77.00
76.68
62.20
O
O
S
F
3p
200
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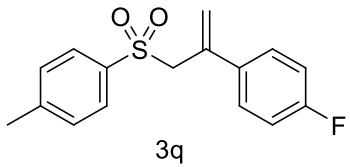
O
O
S
F

3q

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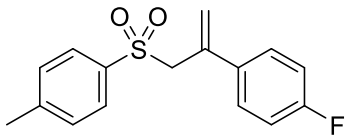
2.92


O
O
S
F

3q

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21.53
10
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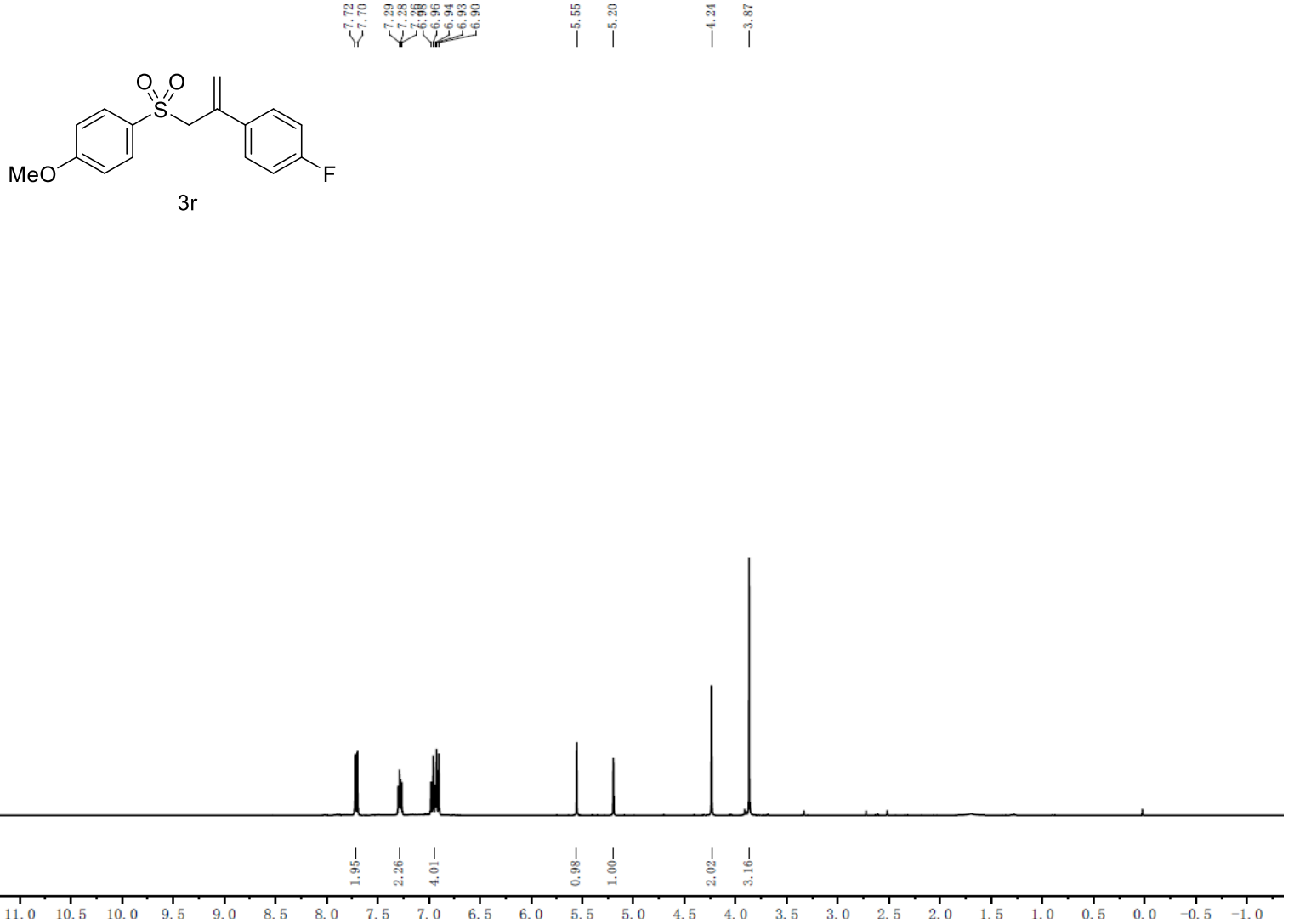
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5.20
4.24
3.87
O
O
S
MeO
F
3r
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2.26
4.01
0.98
1.00
2.02
3.16
11.5
11.0
10.5
10.0
9.5
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8.5
8.0
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7.0
6.5
6.0
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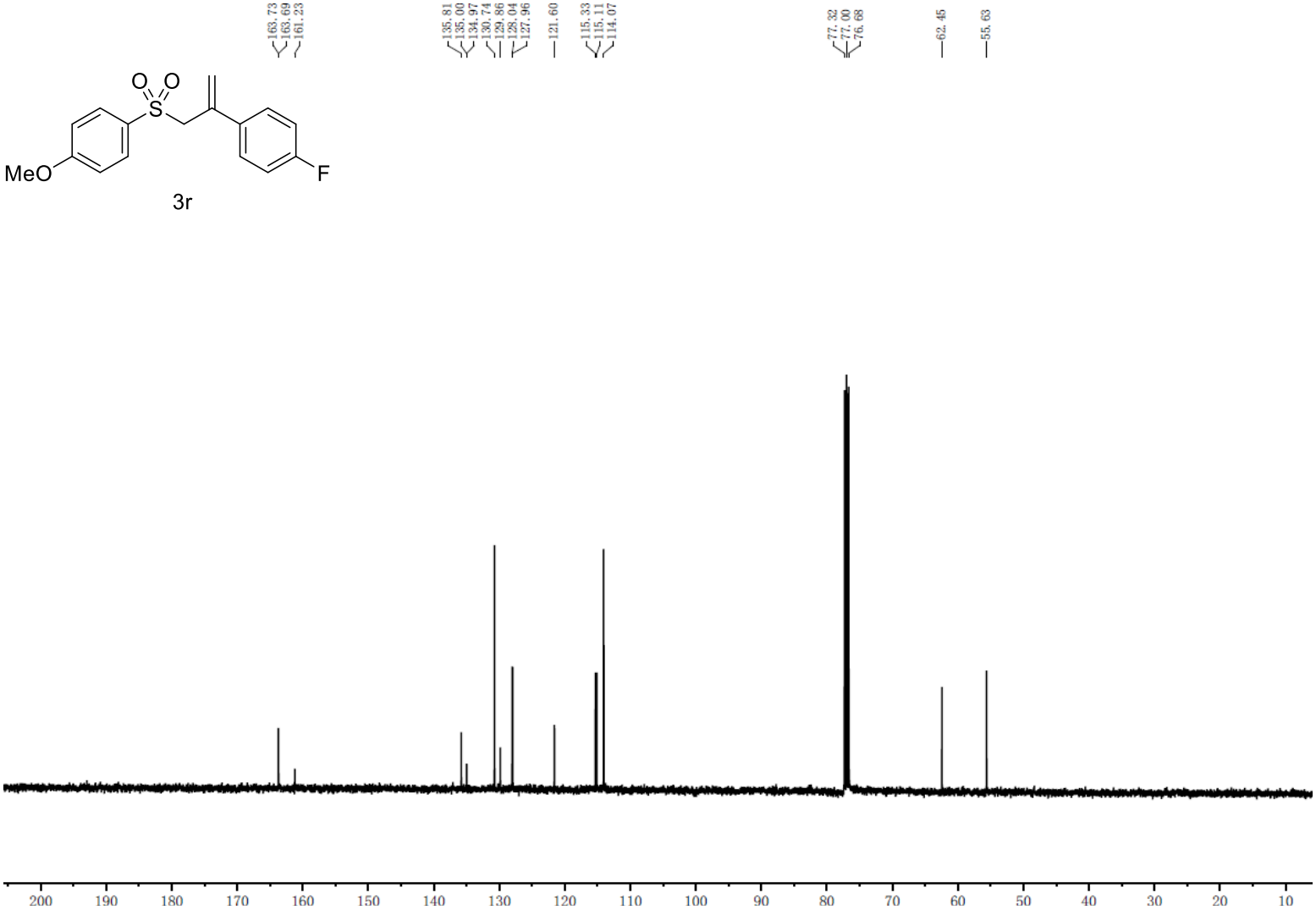
-0.5
-1.0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115.11
114.07
77.32
77.00
76.68
62.45
55.63
O
O
S
MeO
F
3r
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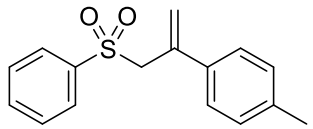

3s

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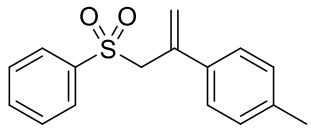
7.18
7.16
7.06
7.04
5.55
5.14
4.26
2.31
1.91
1.00
2.00
1.97
1.96
1.00
1.01
2.03
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0



3s

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21.01
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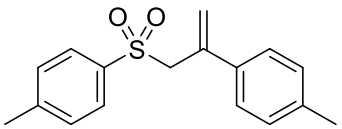

3t

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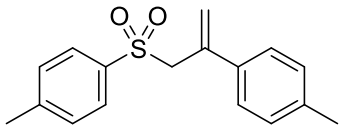
5.12
4.23
2.39
2.31
2.03
4.22
2.04
0.96
1.00
2.17
3.02
3.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5



3t

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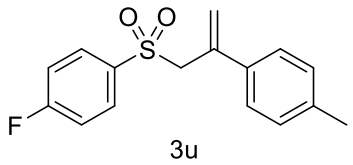
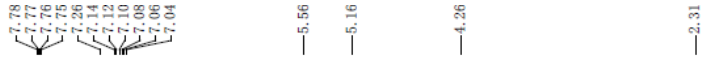

O
O
S
F

3u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7.04
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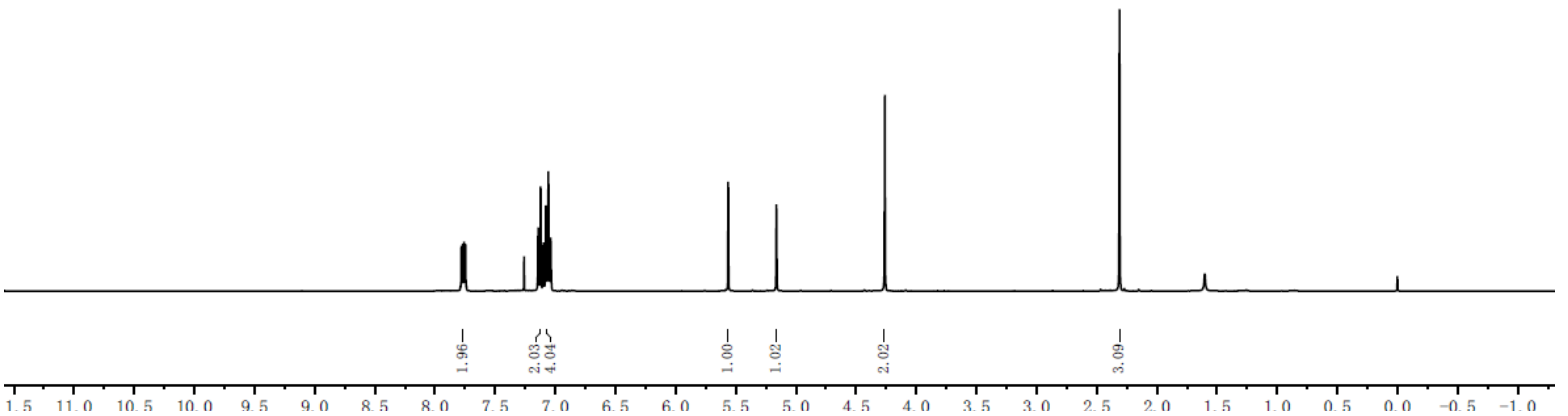
2.31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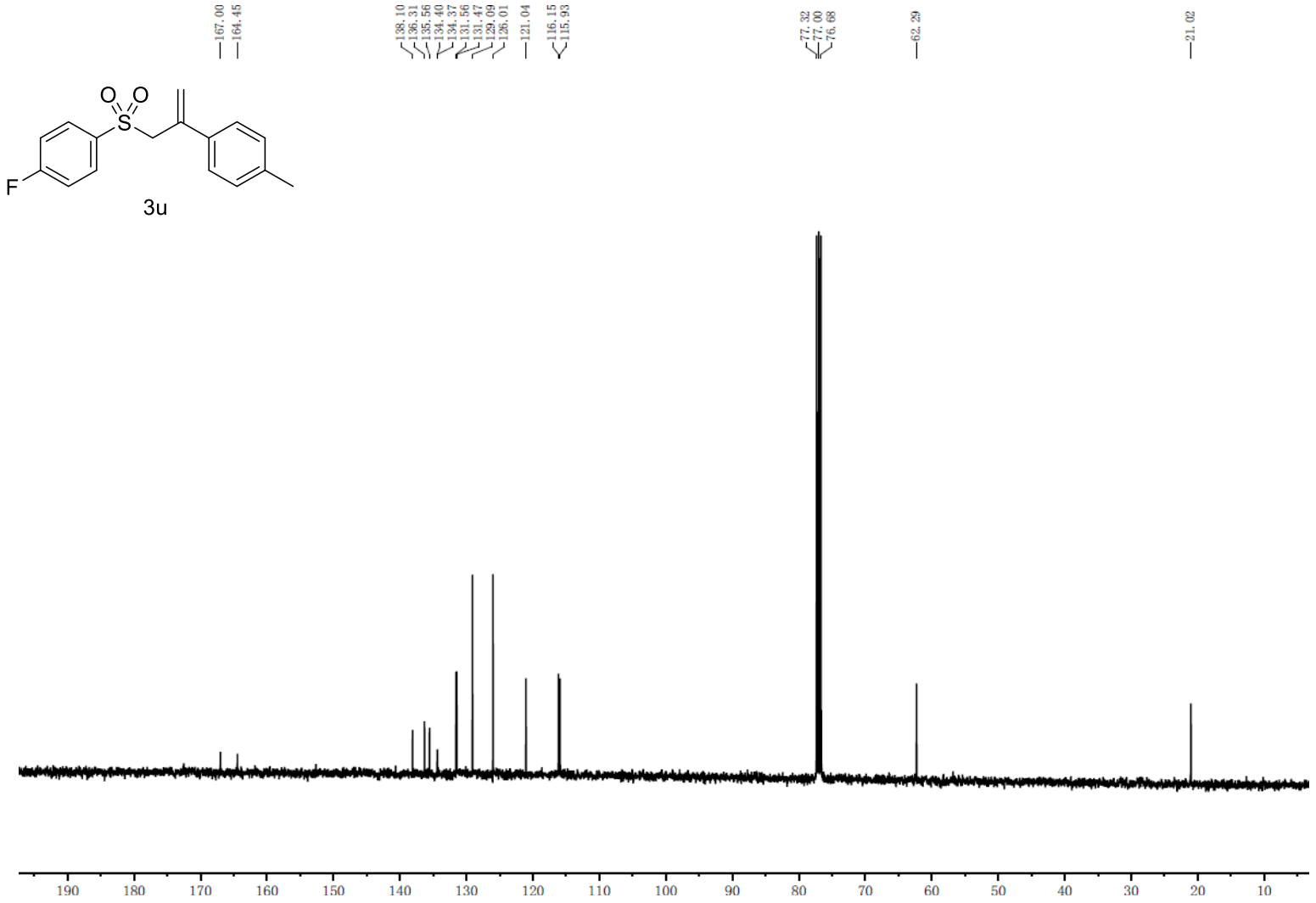
−1.0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121.04
116.15
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77.32
77.00
76.68
62.29
21.02
O
O
S
F
3u
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180
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140
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120
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100
90
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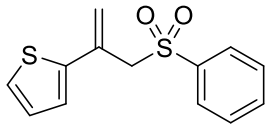
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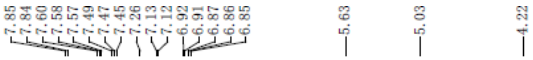
3v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7.47
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6.91
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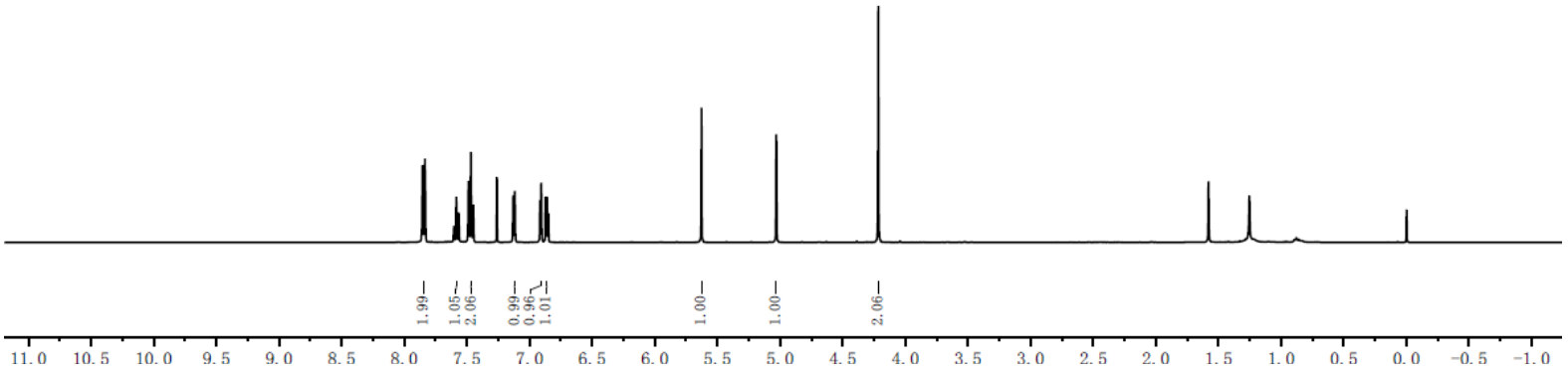
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1.00
2.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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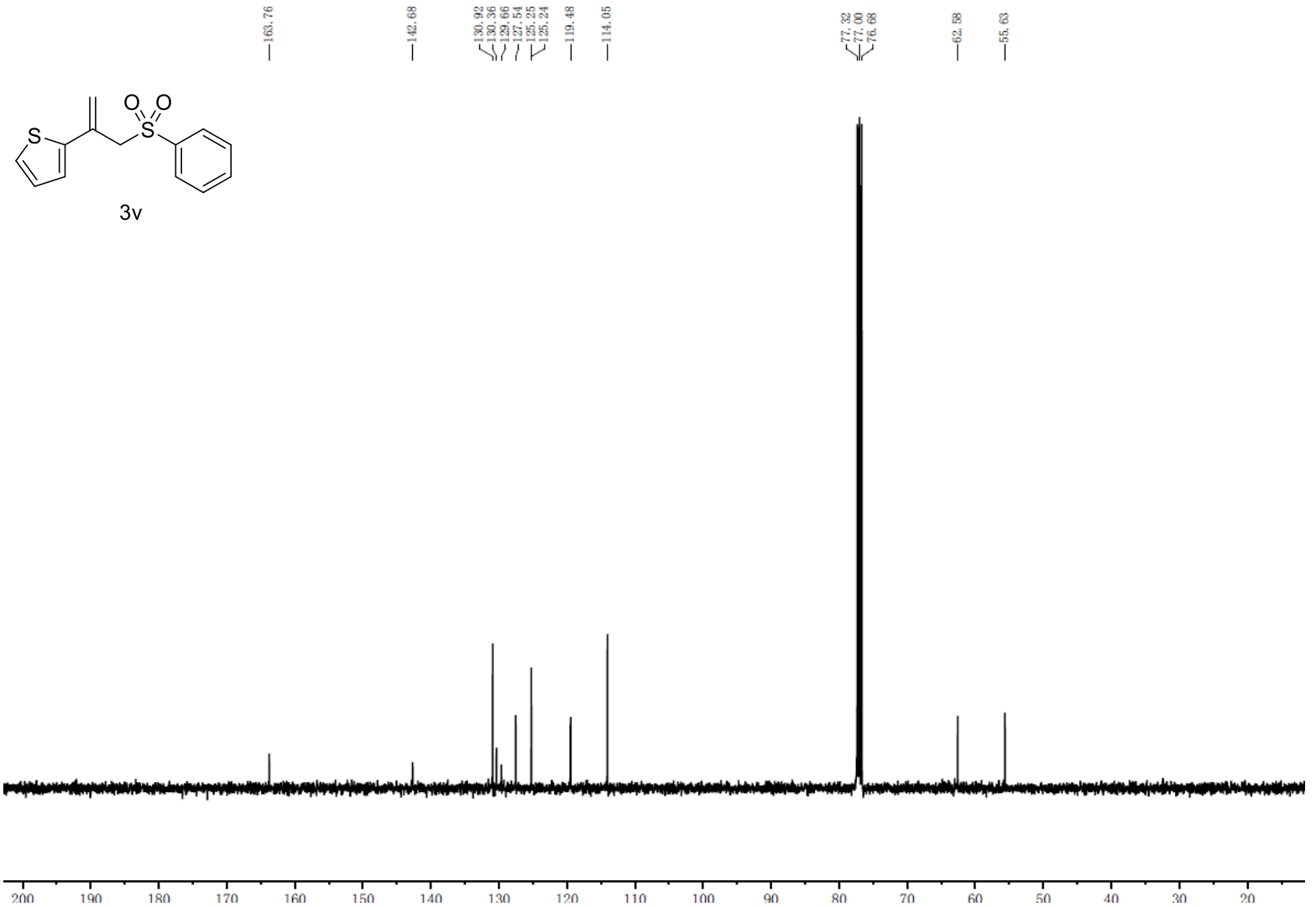
-0.5
-1.0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77.32
77.00
76.68
62.58
55.63
O
O
S
S
3v
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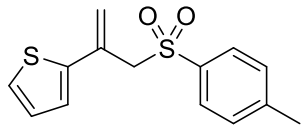
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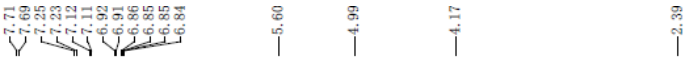
S

3w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6.84
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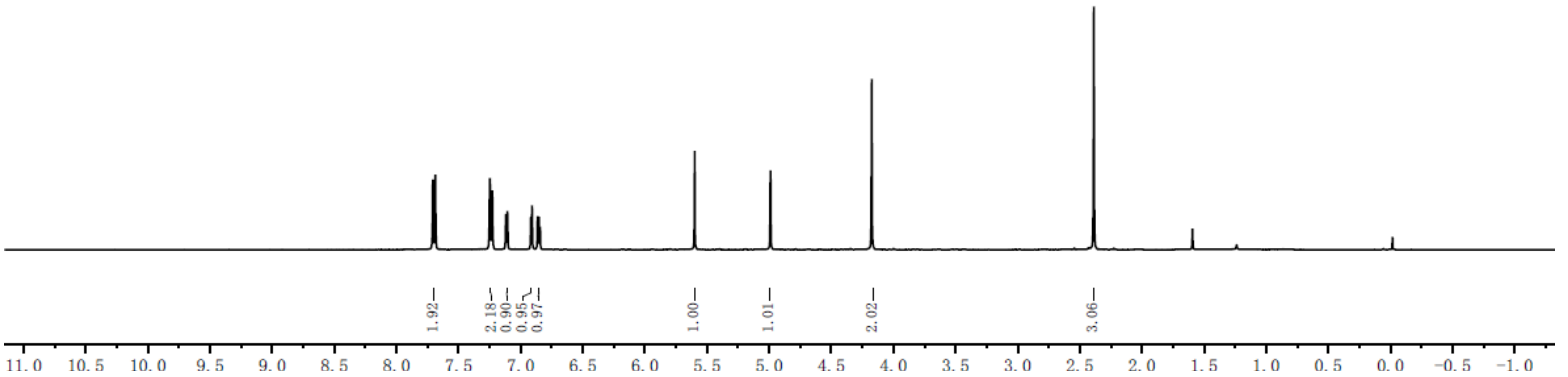
4.17
2.39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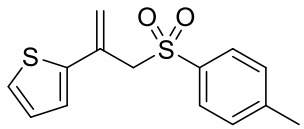
0.97
1.00
1.01
2.02
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


O
O
S
S

3w

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125.27
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119.52
77.32
77.00
76.68
62.38
21.58
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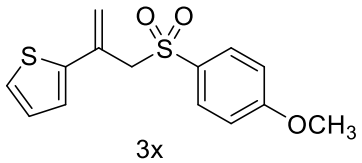
O
O
S
S
OCH3

3x

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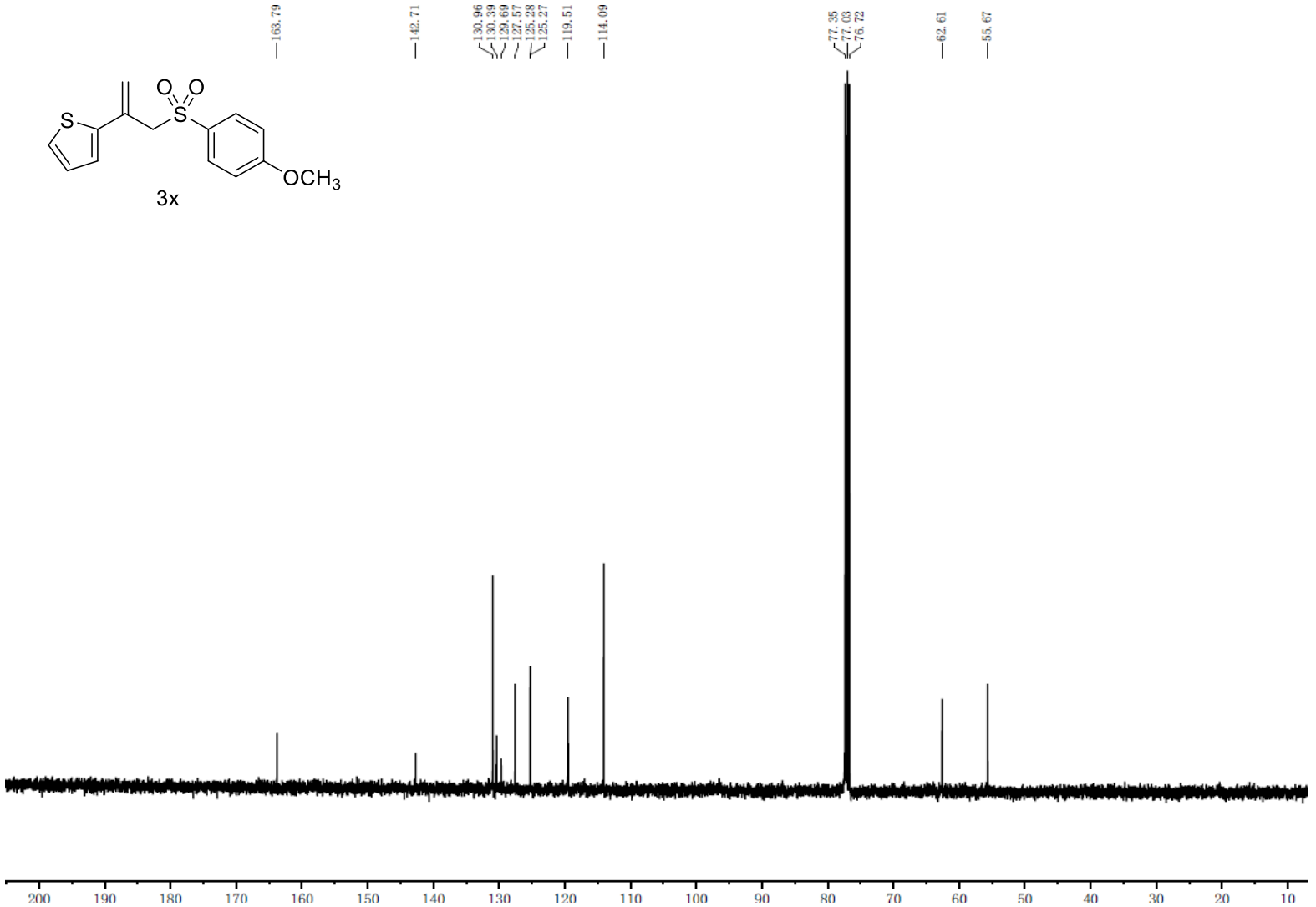
6.92
6.90
6.88
6.87
6.86
5.62
5.01
4.19
3.85
1.97
0.97
4.00
1.00
1.01
1.99
3.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0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77.03
76.72
62.61
55.67
O
O
S
S
OCH3
3x
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80
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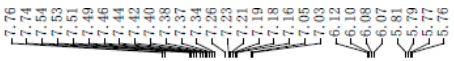
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7.34
7.26
7.23
7.21
7.19
7.18
7.16
7.05
7.03
6.12
6.10
6.08
6.07
5.81
5.79
5.77
5.76
4.37
4.13
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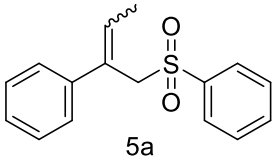
1.66
1.64
1.62



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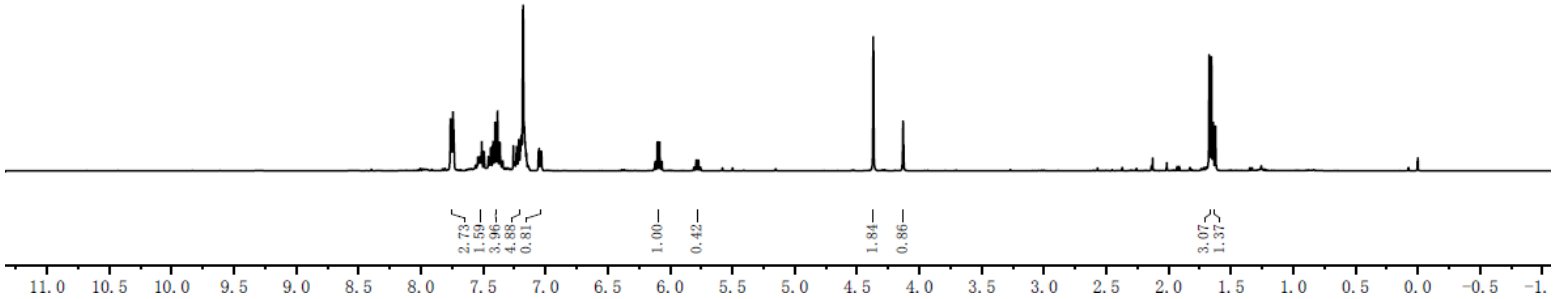
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0.42
1.84
0.86
3.07
1.37
11.0
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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1.0
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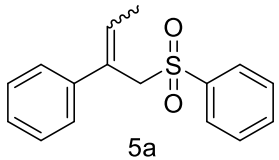
-1.



5a

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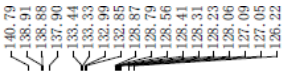
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128.56
128.41
128.31
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127.09
127.05
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77.00
76.68
64.93
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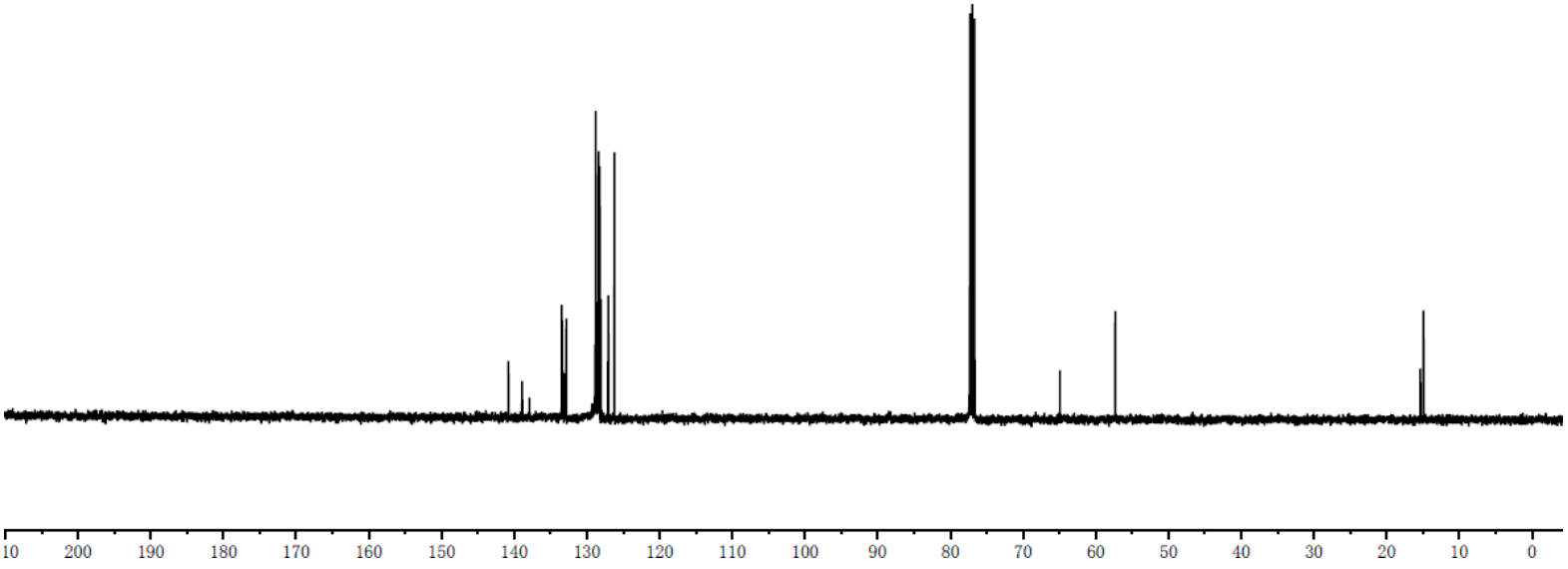
15.34
14.93


10
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100
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50
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30
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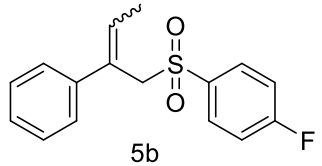
10
0


O
S
O
F

5b

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7.02
6.14
6.12
6.10
6.08
5.84
5.83
5.81
5.79
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4.14
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1.73
1.67
1.65
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8.91
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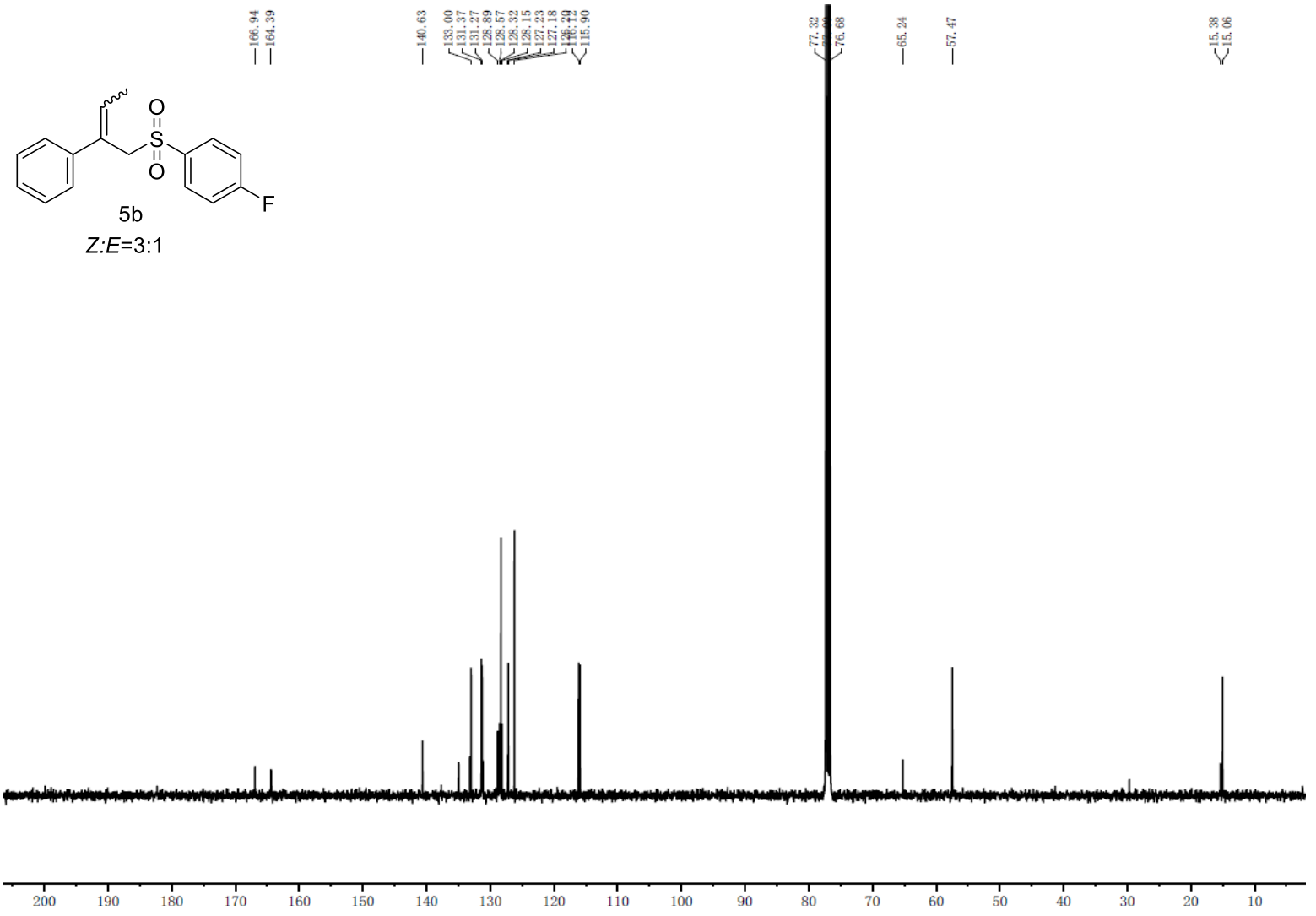
0.28
1.94
0.55
2.94
0.86
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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127.23
127.18
115.90
77.32
76.68
65.24
57.47
15.38
15.06
O
S
O
F
5b
Z:E=3:1
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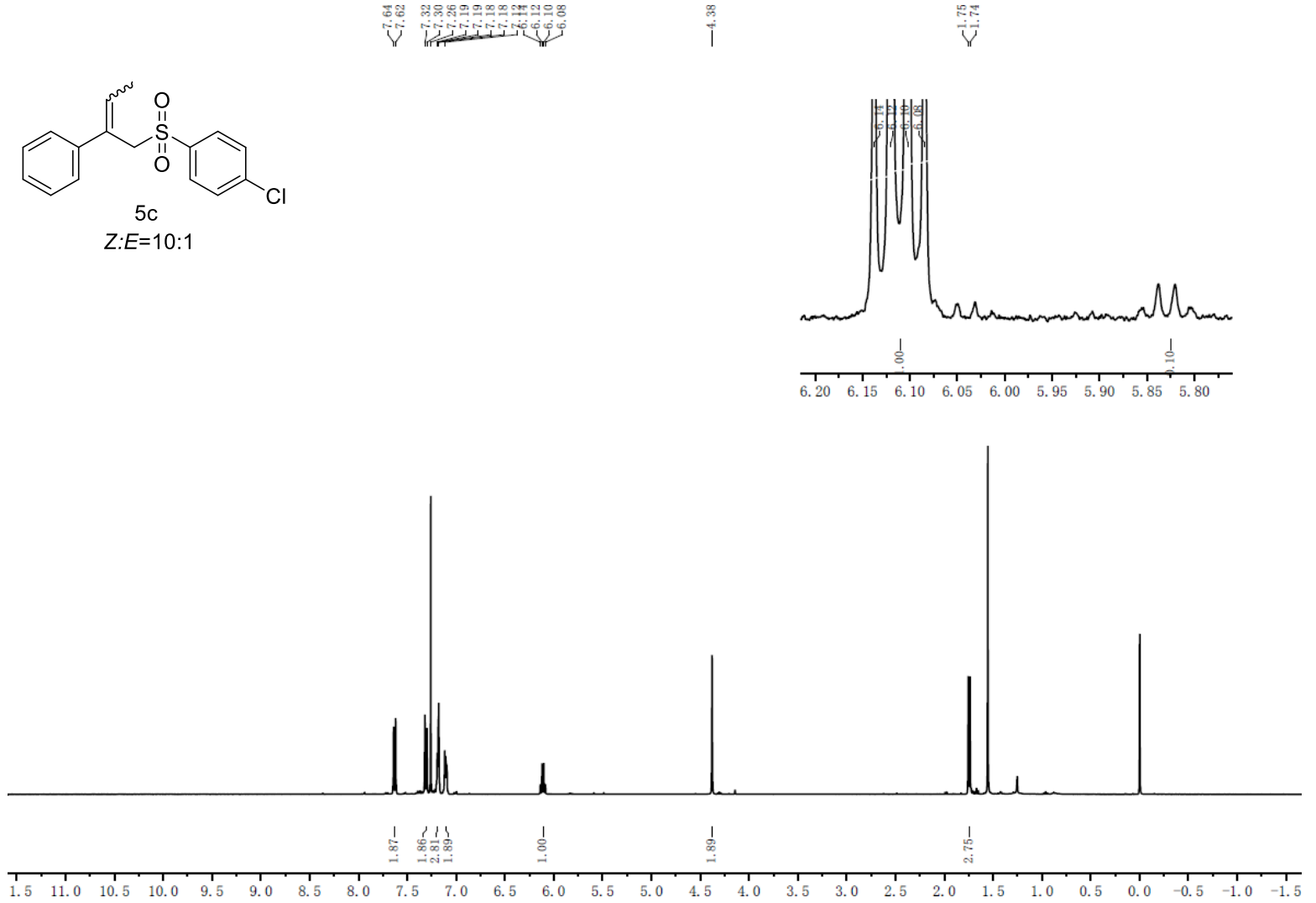
10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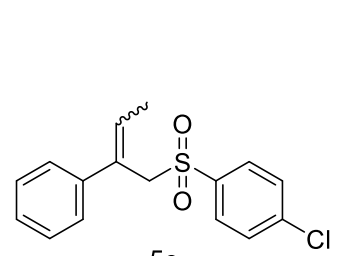
O
S
O
Cl

5c

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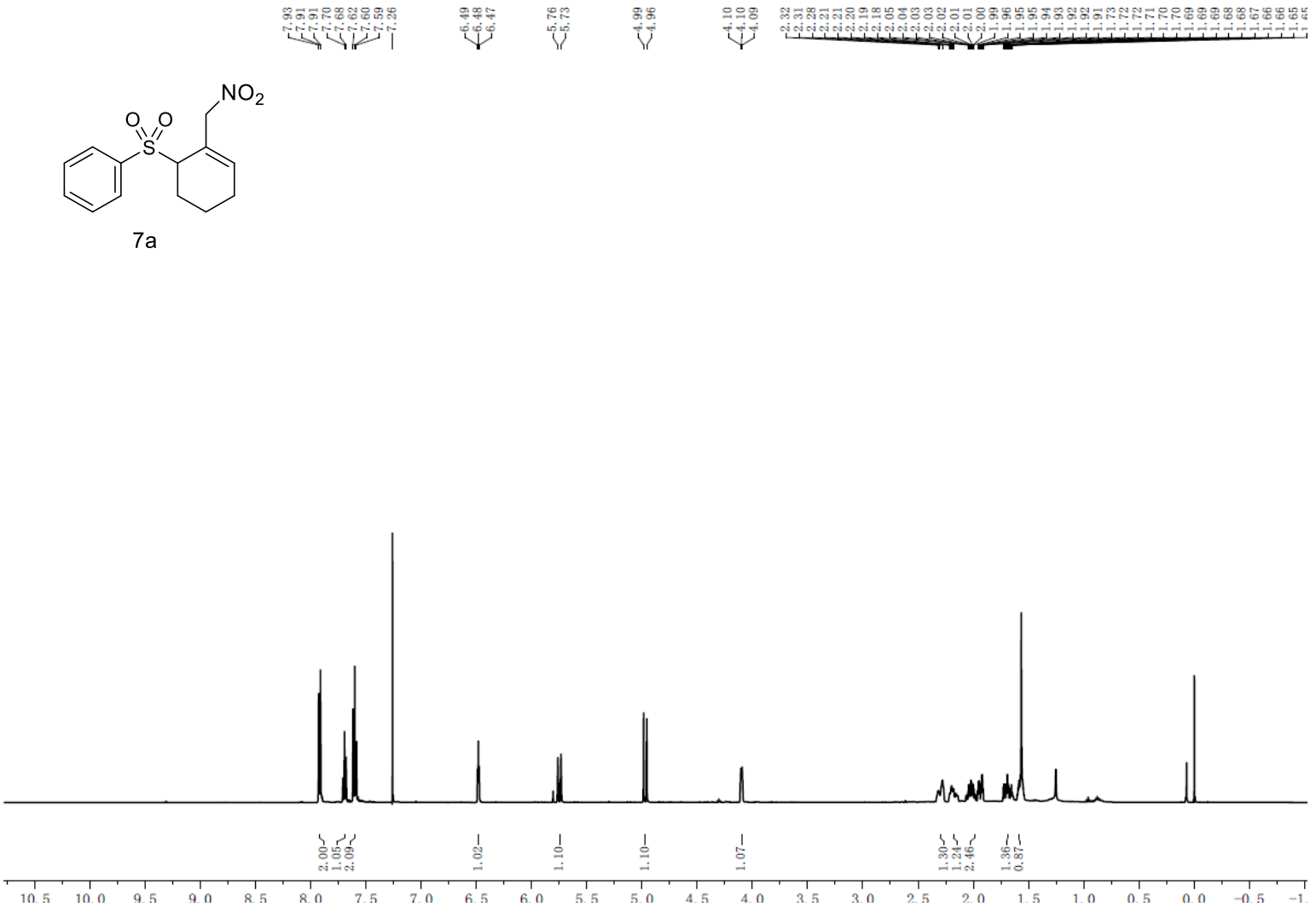
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4.10
4.10
4.09
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2.31
2.28
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2.21
2.20
2.19
2.18
2.05
2.04
2.03
2.03
2.02
2.01
2.01
2.00
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1.95
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O
S
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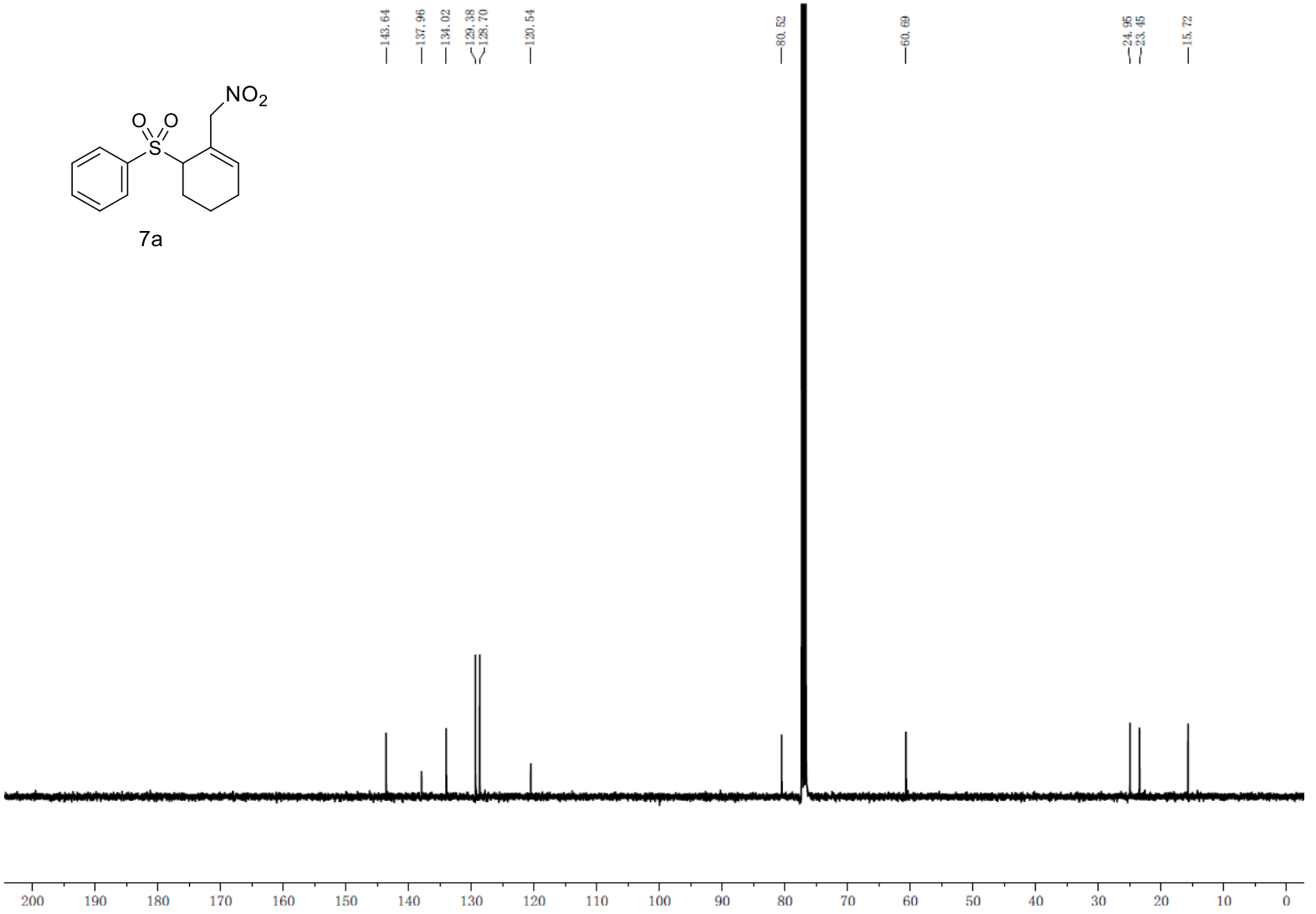
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15.72
NO2
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O
S
7a
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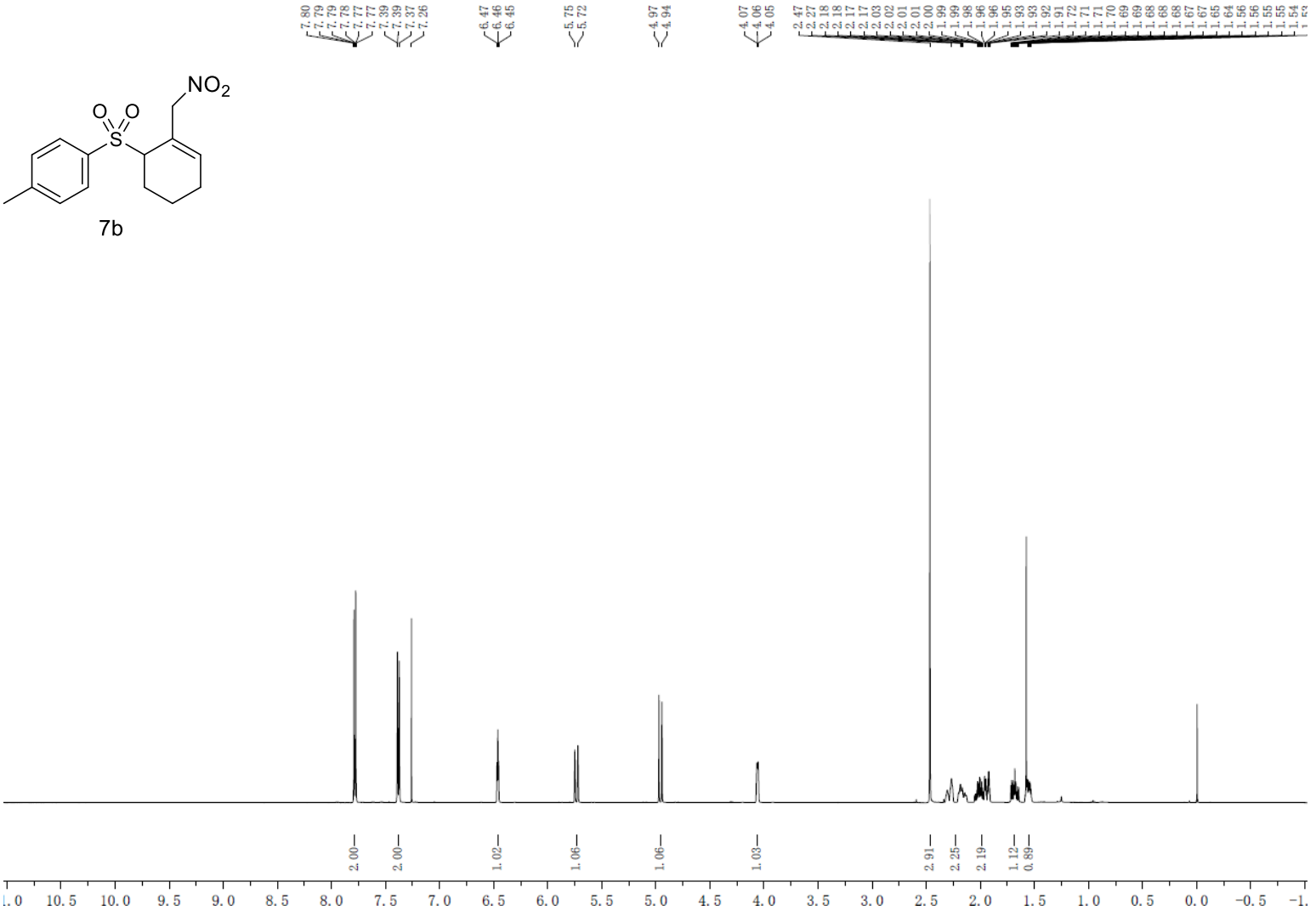
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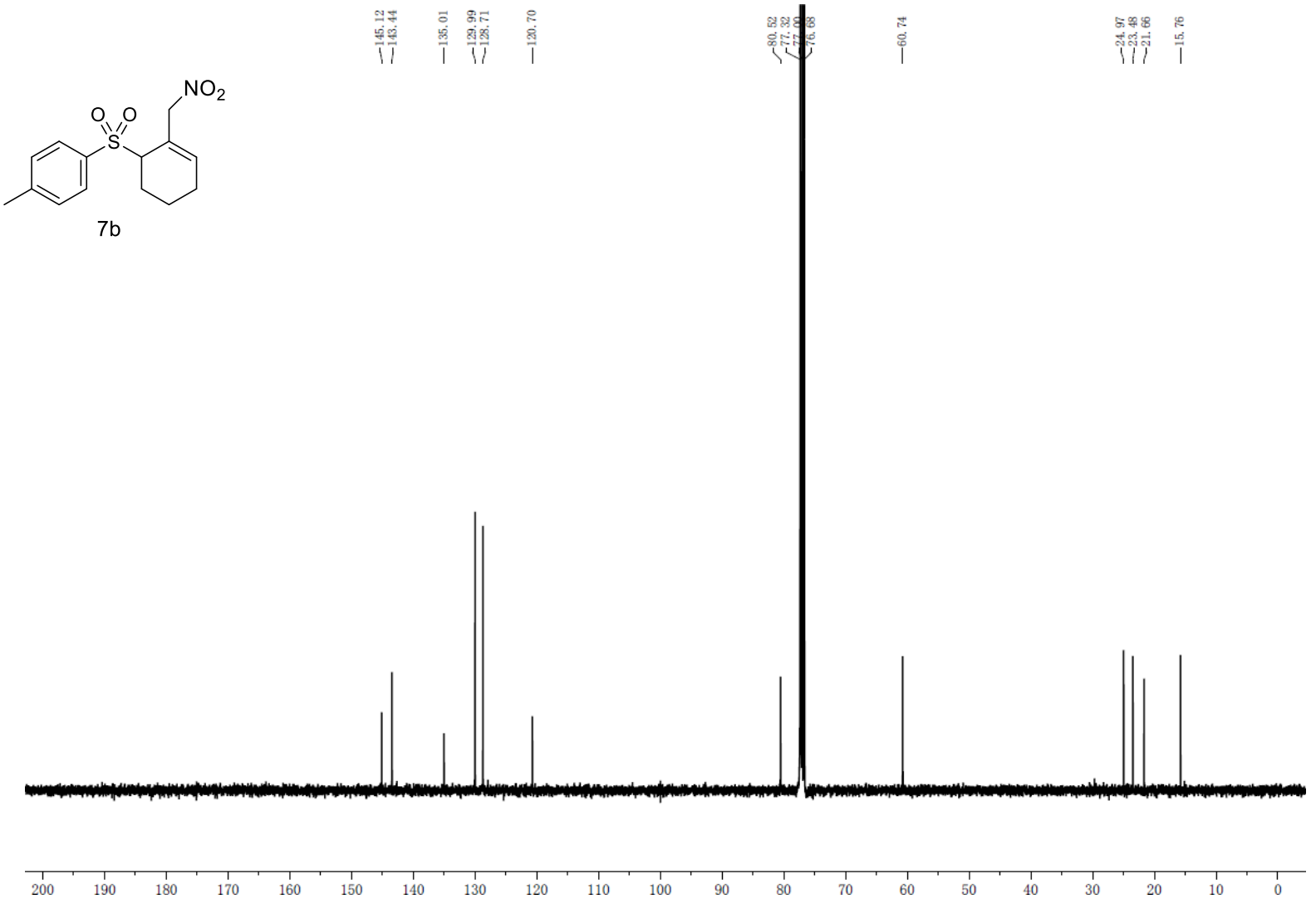
7b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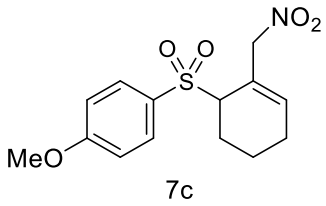
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S
MeO

7c

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4.03
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6.0
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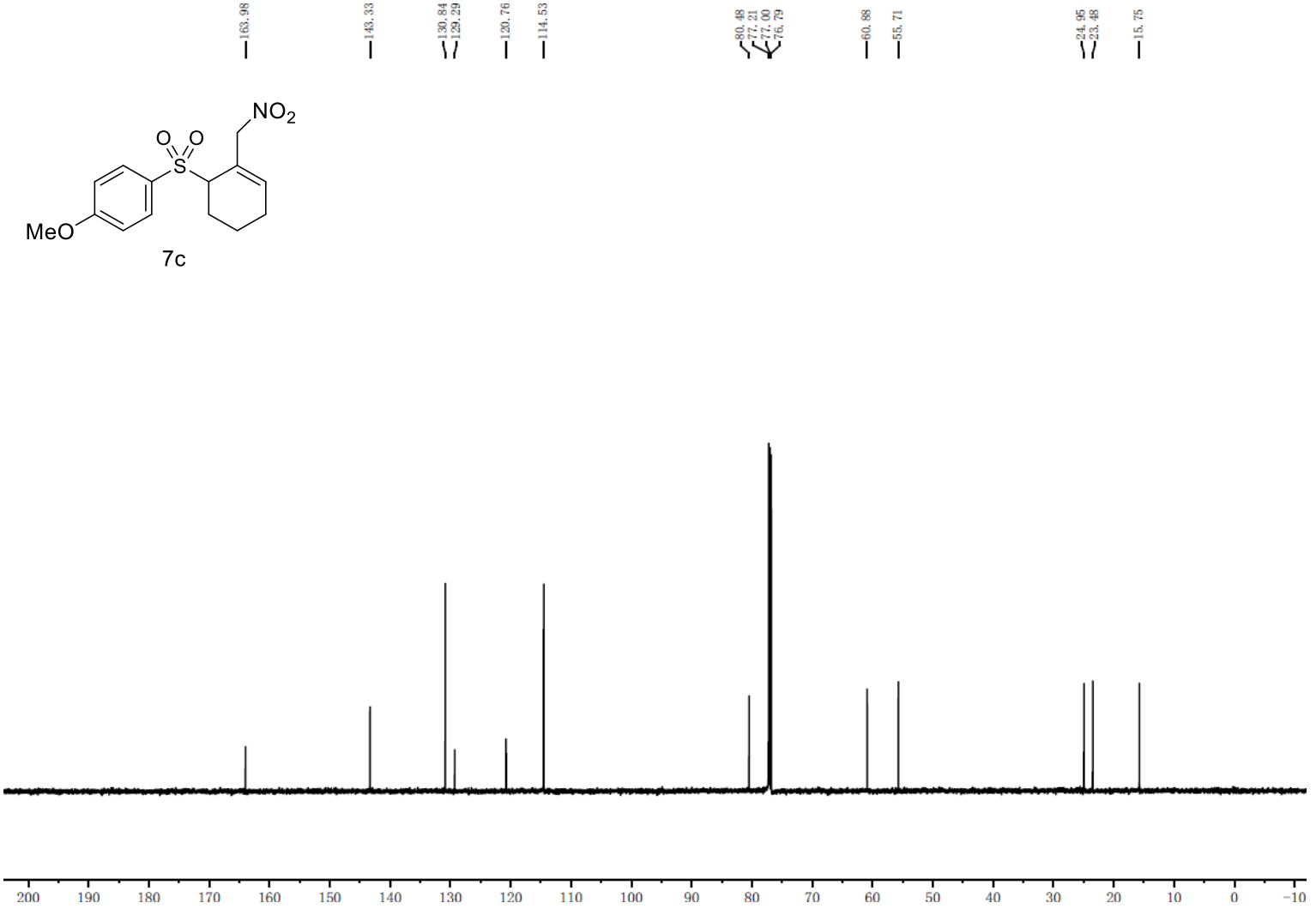
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24.95
23.48
15.75
NO2
O
O
S
MeO
7c
200
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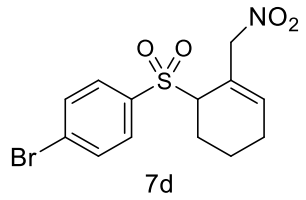
0
−10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O
O
S
Br

7d

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4.09
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2.29
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2.00
2.00
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1.69
1.68
1.60
1.57
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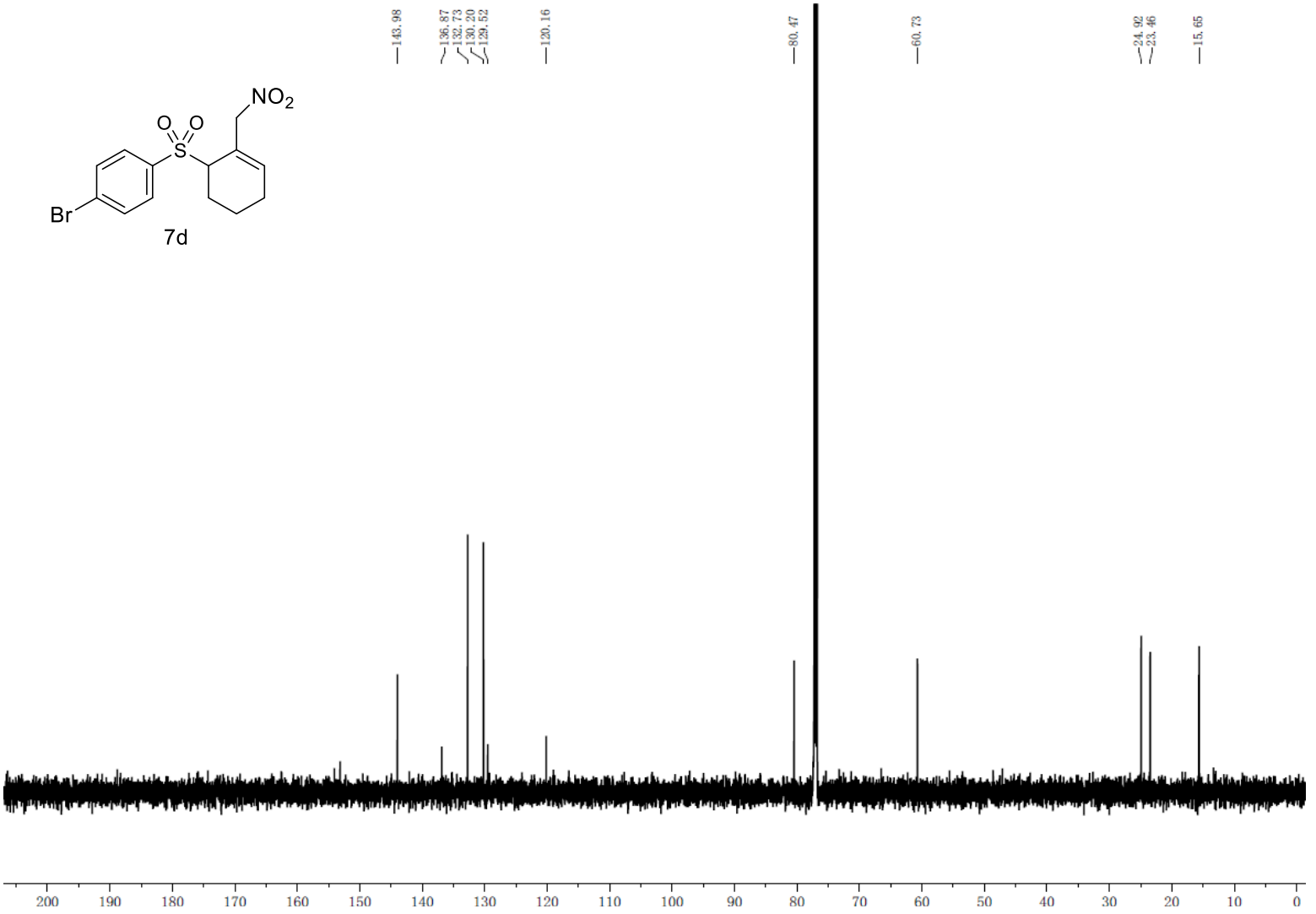
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23.46
15.65
NO2
O
O
S
Br
7d
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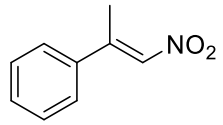
10
0


NO2

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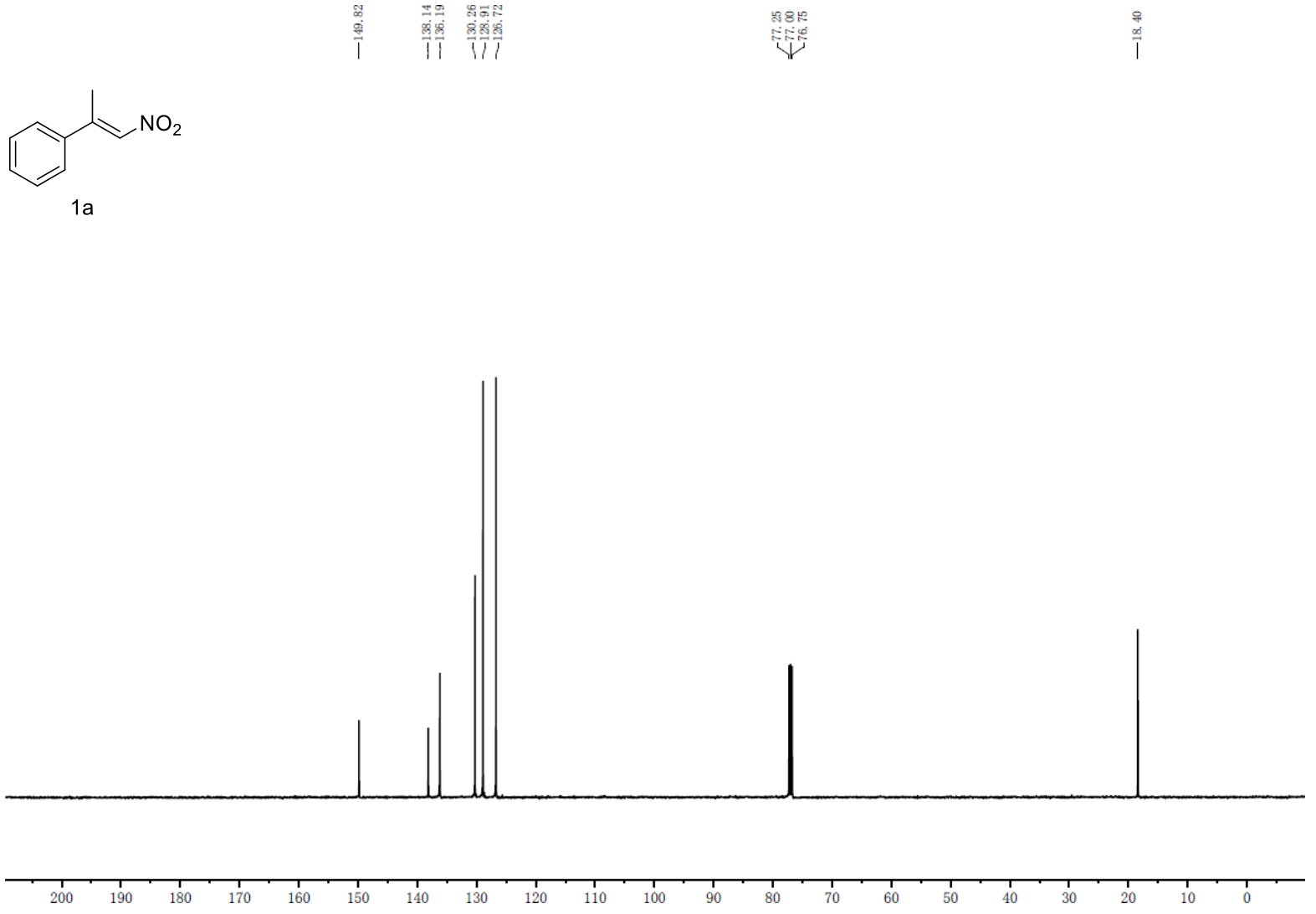
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NO2
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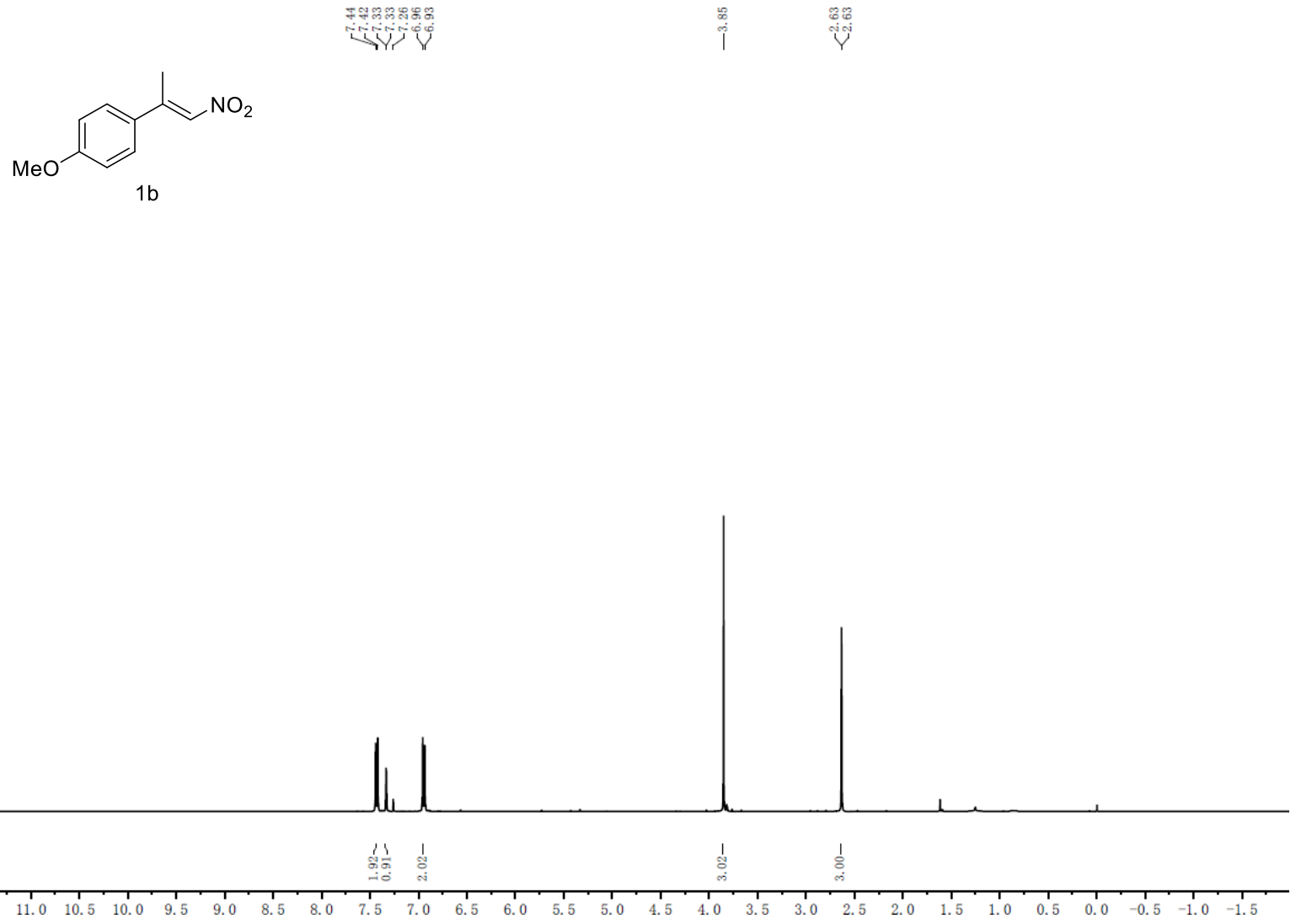
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MeO
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0.91
2.02
3.02
3.00
11.0
10.5
10.0
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7.0
6.5
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5.0
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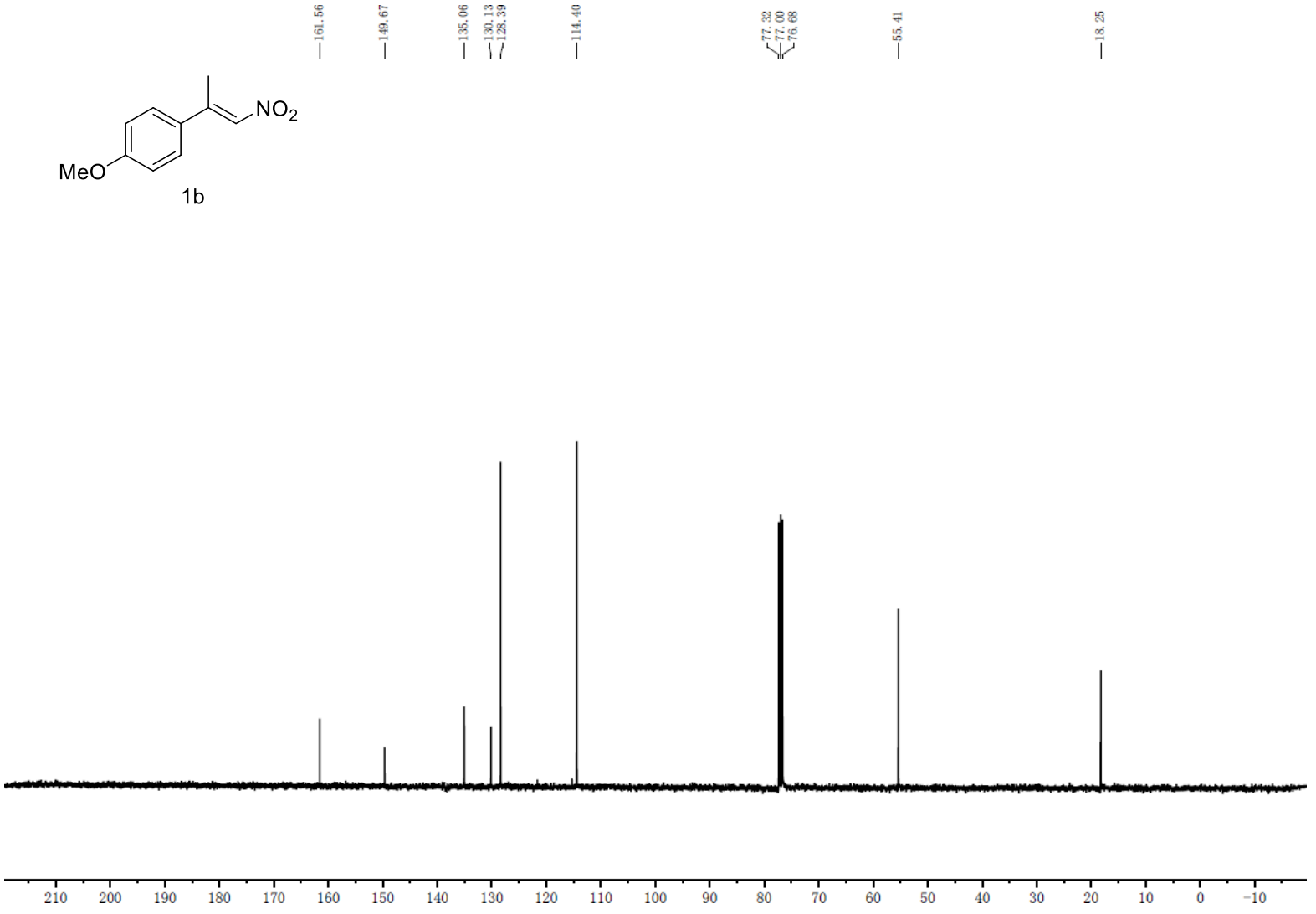
-1.0
-1.5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MeO
1b
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200
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100
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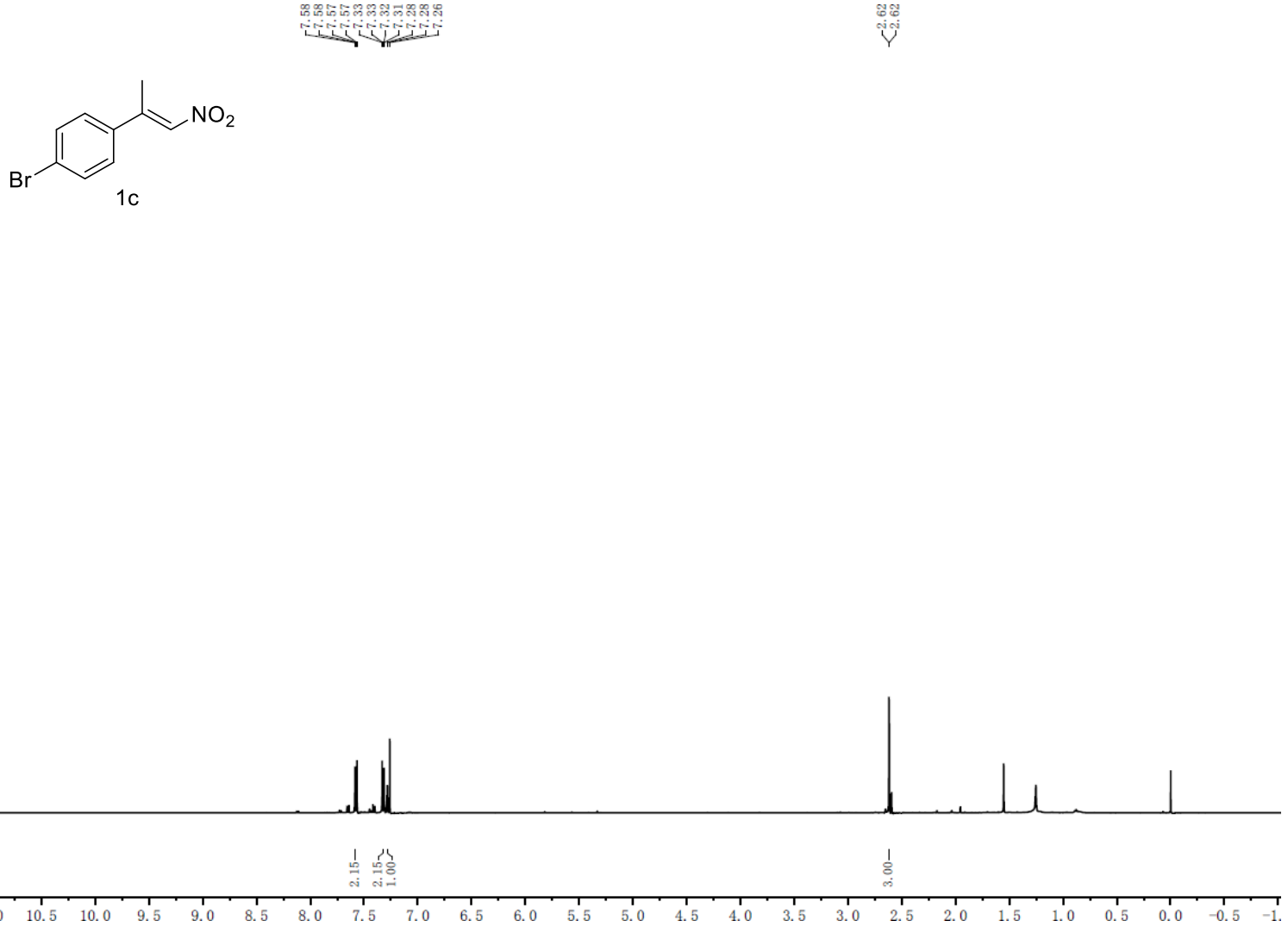
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7.28
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2.62
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Br
1c
2.15
2.15
1.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.5
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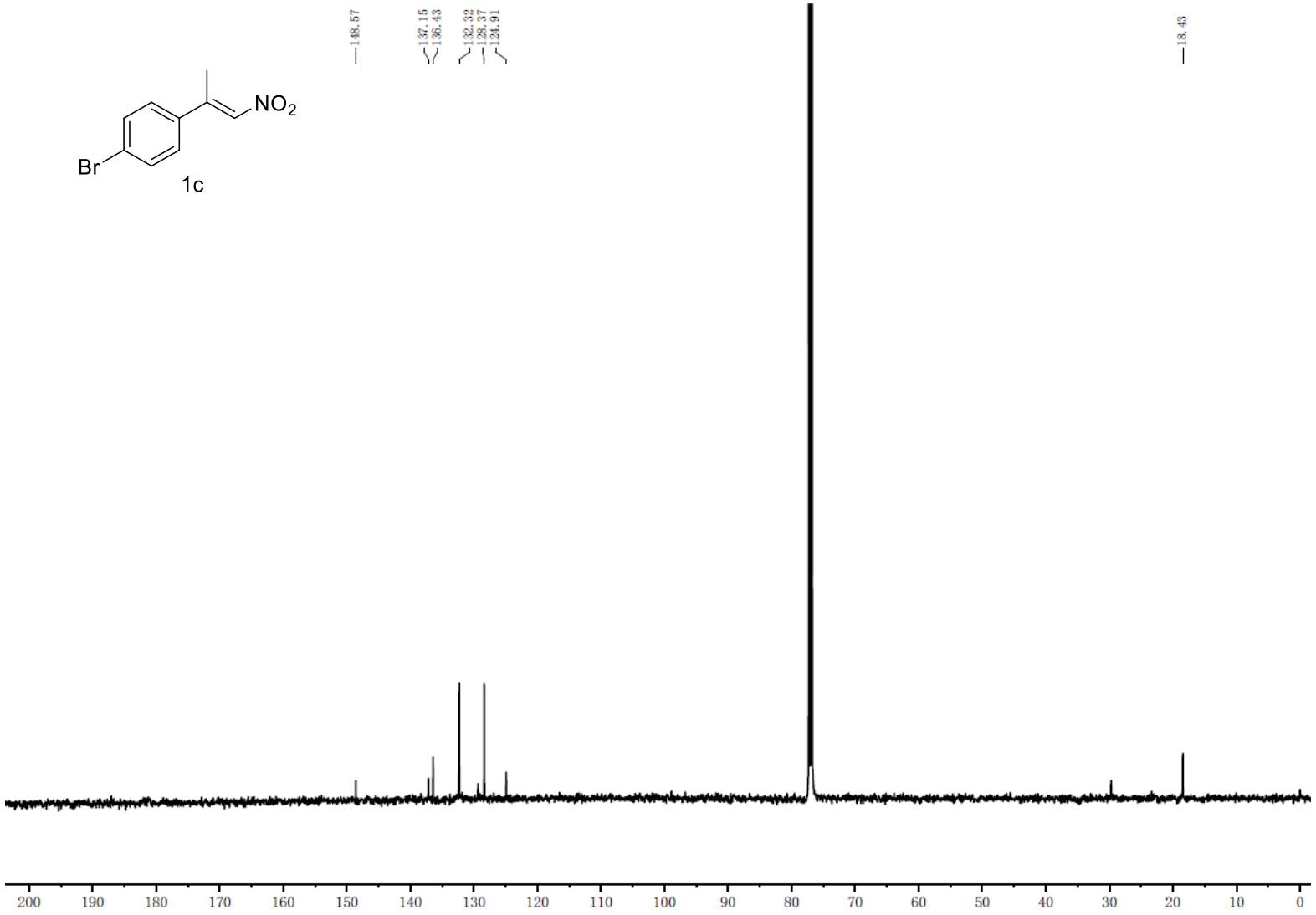
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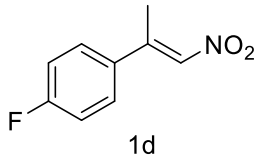
NO2
F

1d

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7.45
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7.26
7.15
7.13
7.12
2.63
2.63
2.33
0.89
2.11
3.00
11.0
10.5
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8.0
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7.0
6.5
6.0
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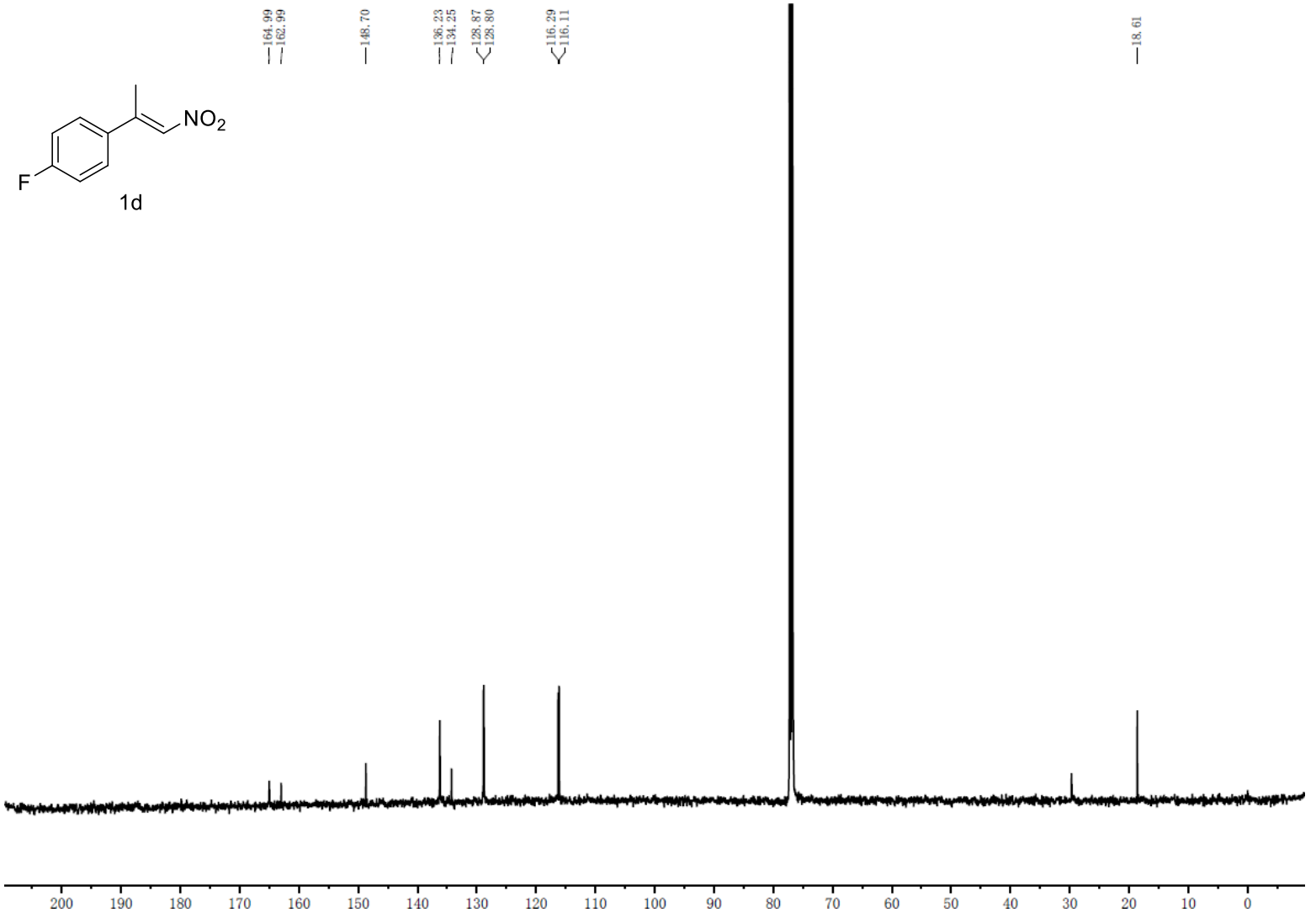
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1d
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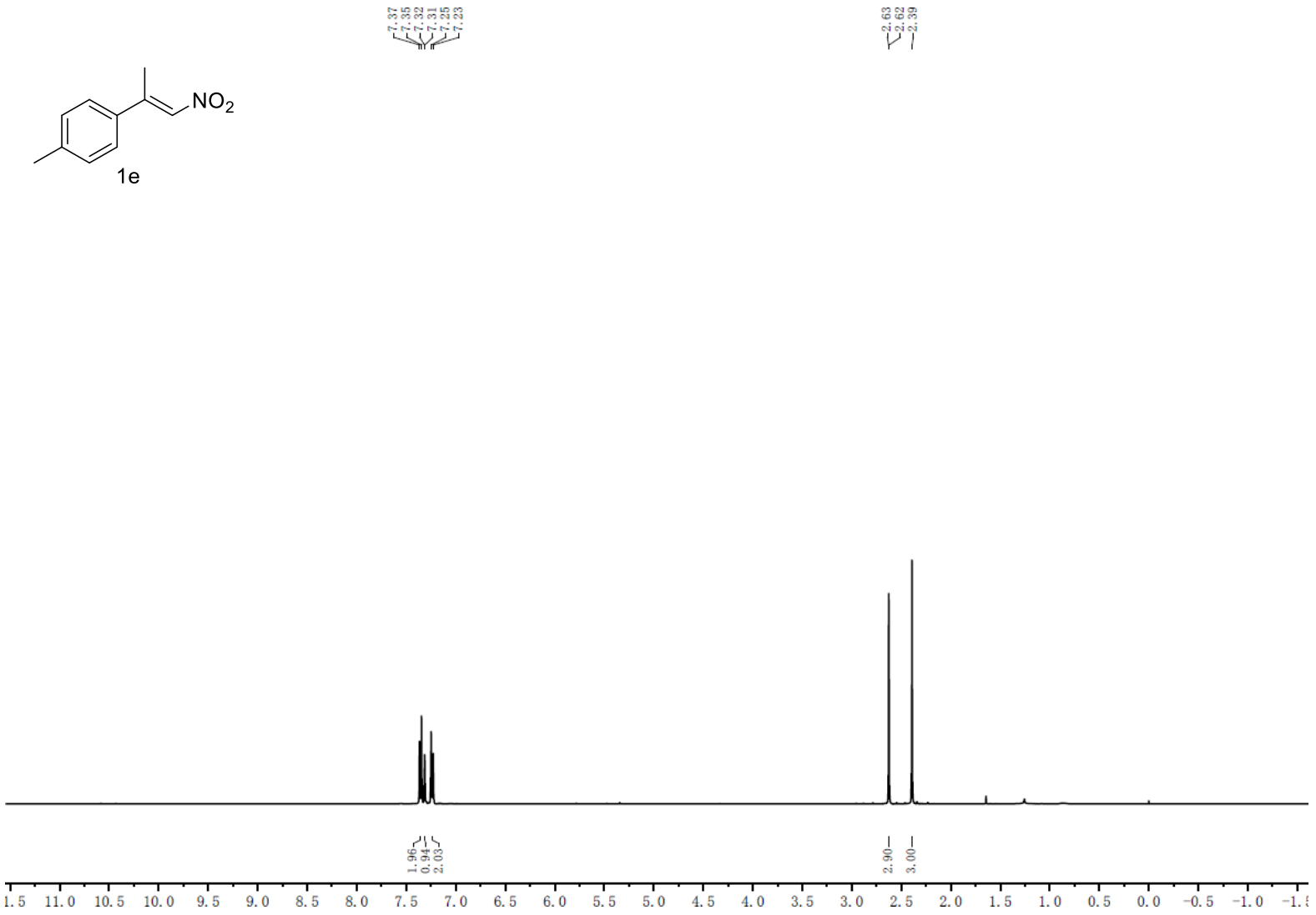
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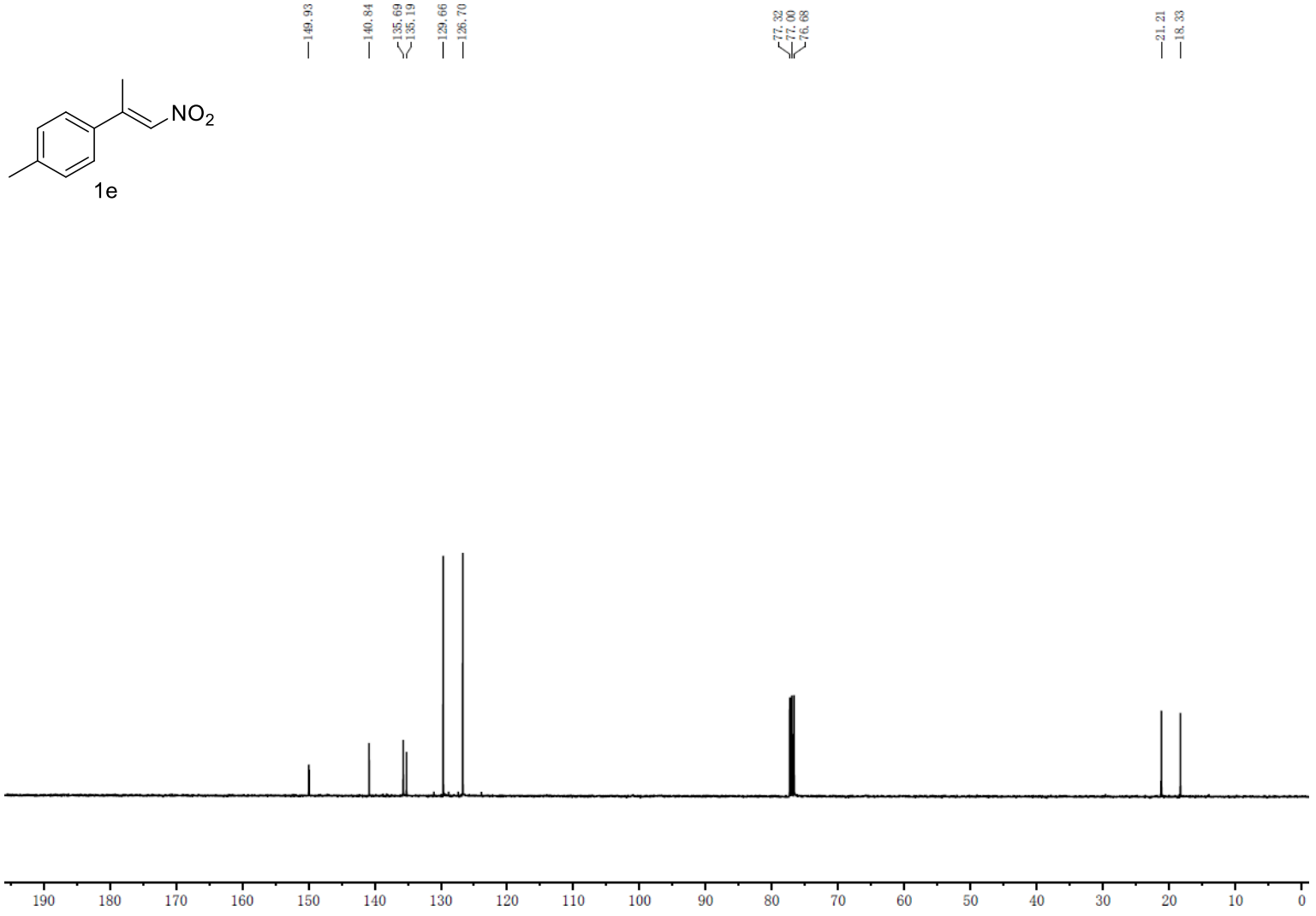
0.94
2.03
2.90
3.00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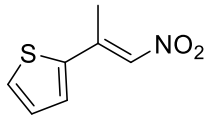
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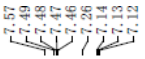
NO2

1f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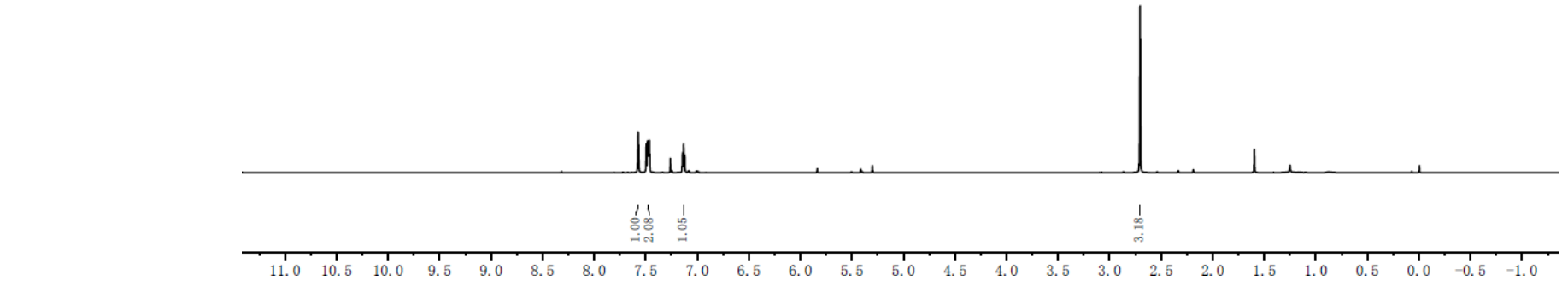
7.26
7.14
7.13
7.12

2.70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9.5
9.0
8.5
8.0
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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1.5
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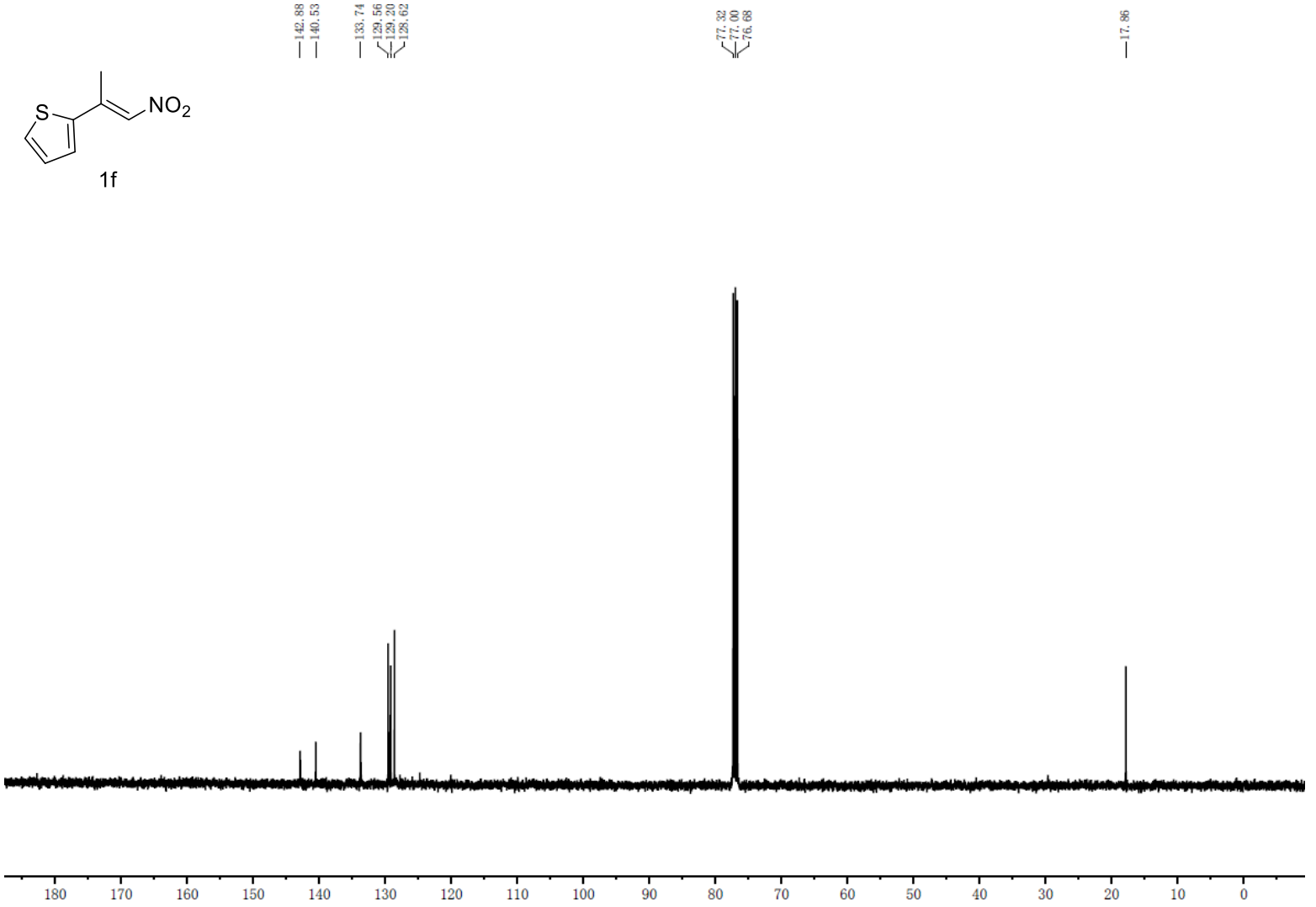
0.5
0.0
-0.5
-1.0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17.86
S
NO2
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150
140
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100
90
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60
50
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30
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10
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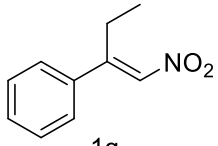
NO2

1g

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3.09
1.20
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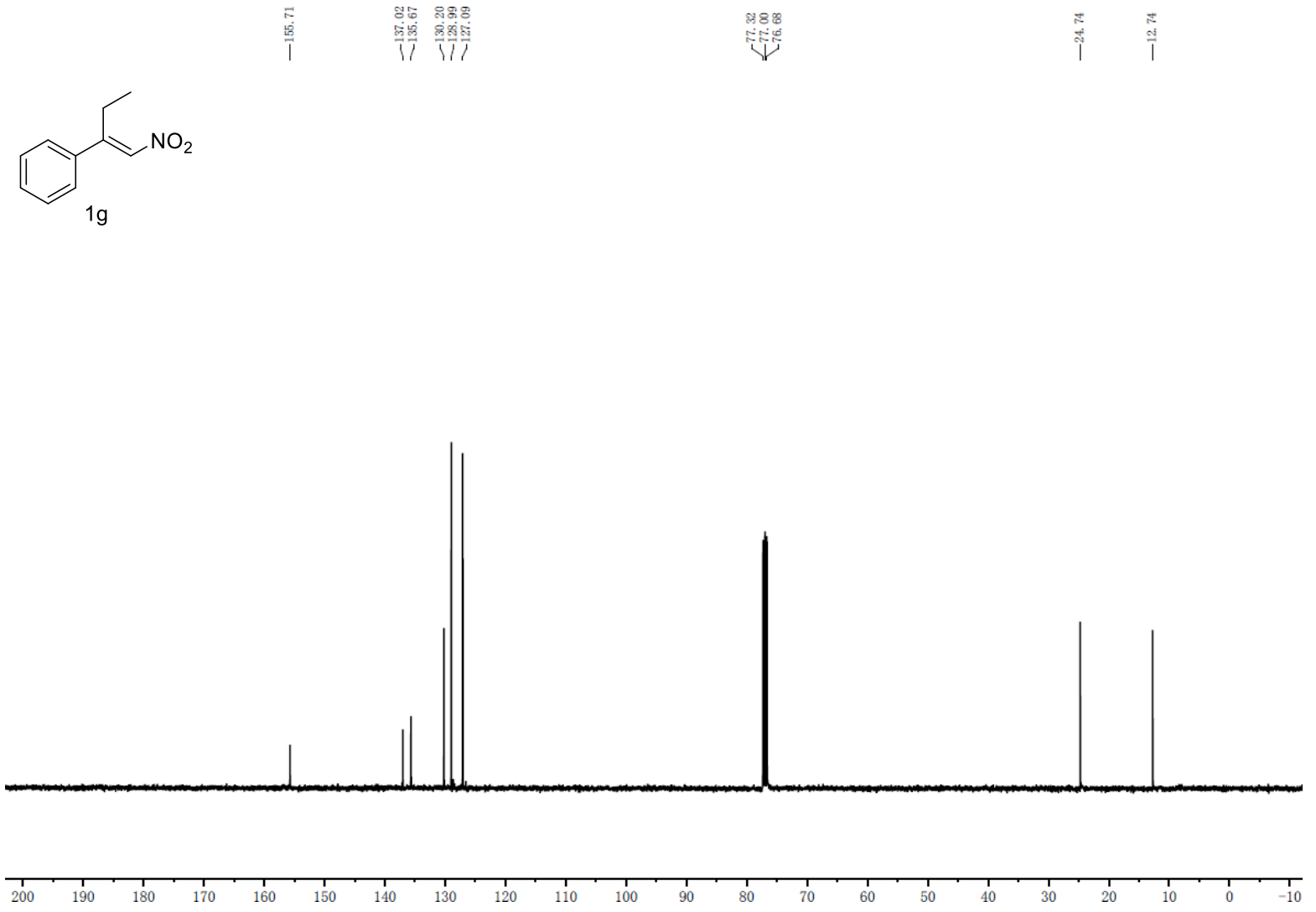
1.17
4.82
0.90
2.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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12.74
NO2
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200
190
180
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150
140
130
120
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100
90
80
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30
20
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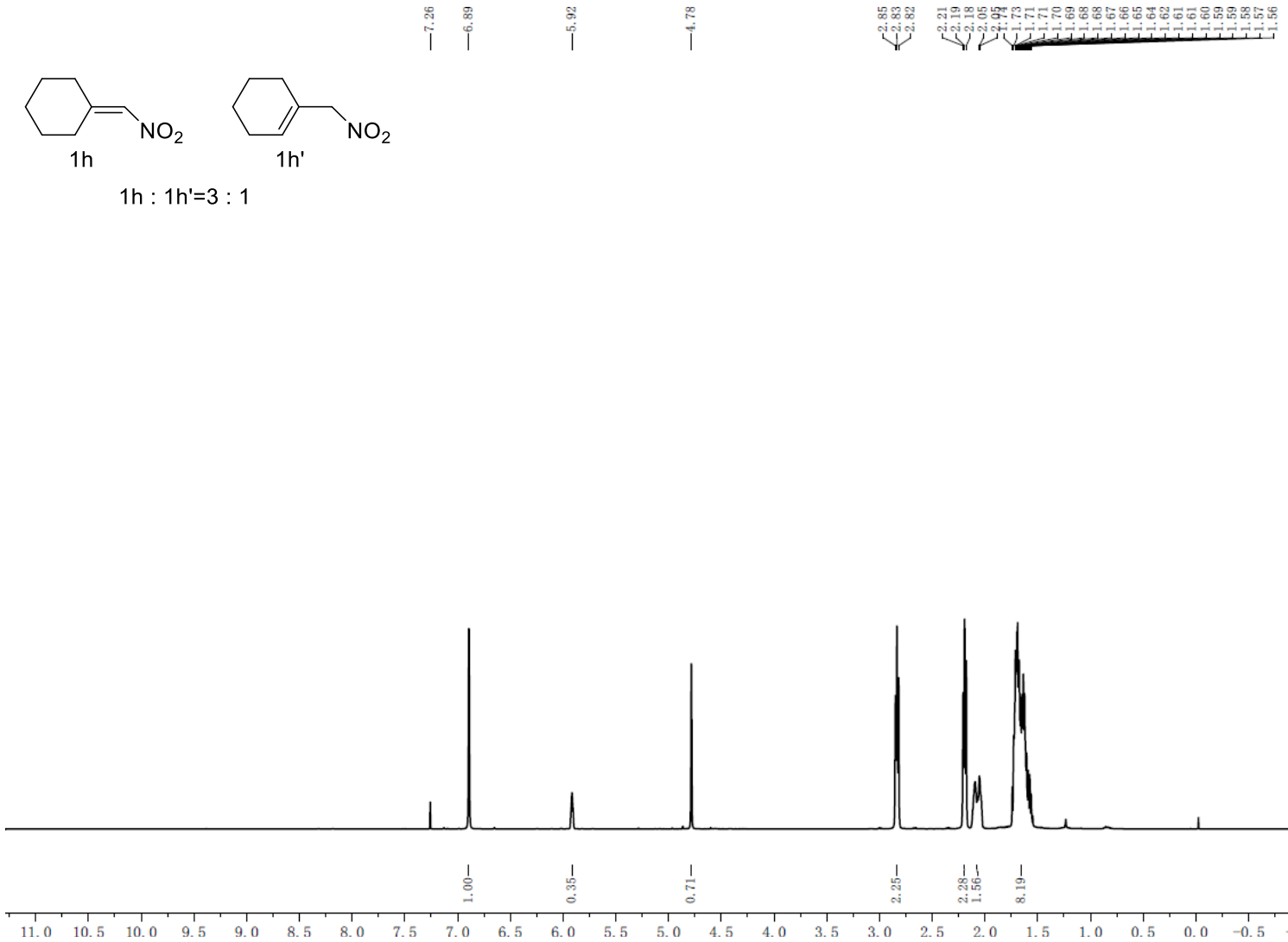
0
−10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2.18
2.05
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1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.62
1.61
1.60
1.59
1.58
1.57
1.56
NO2
1h
NO2
1h'
1h : 1h'=3 : 1
1.00
0.35
0.71
2.25
2.28
1.56
8.19
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9.0
8.5
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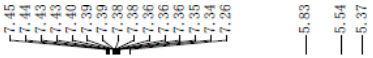
−1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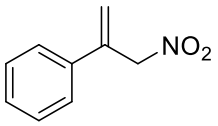
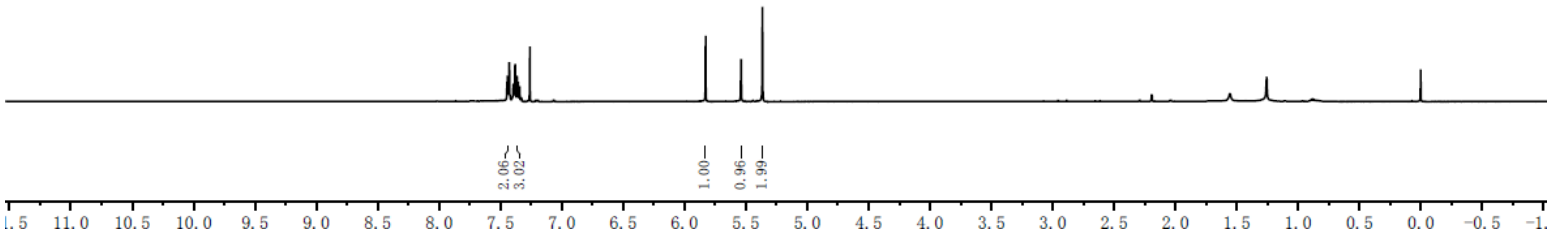
5.37


NO2

1a'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6.5
6.0
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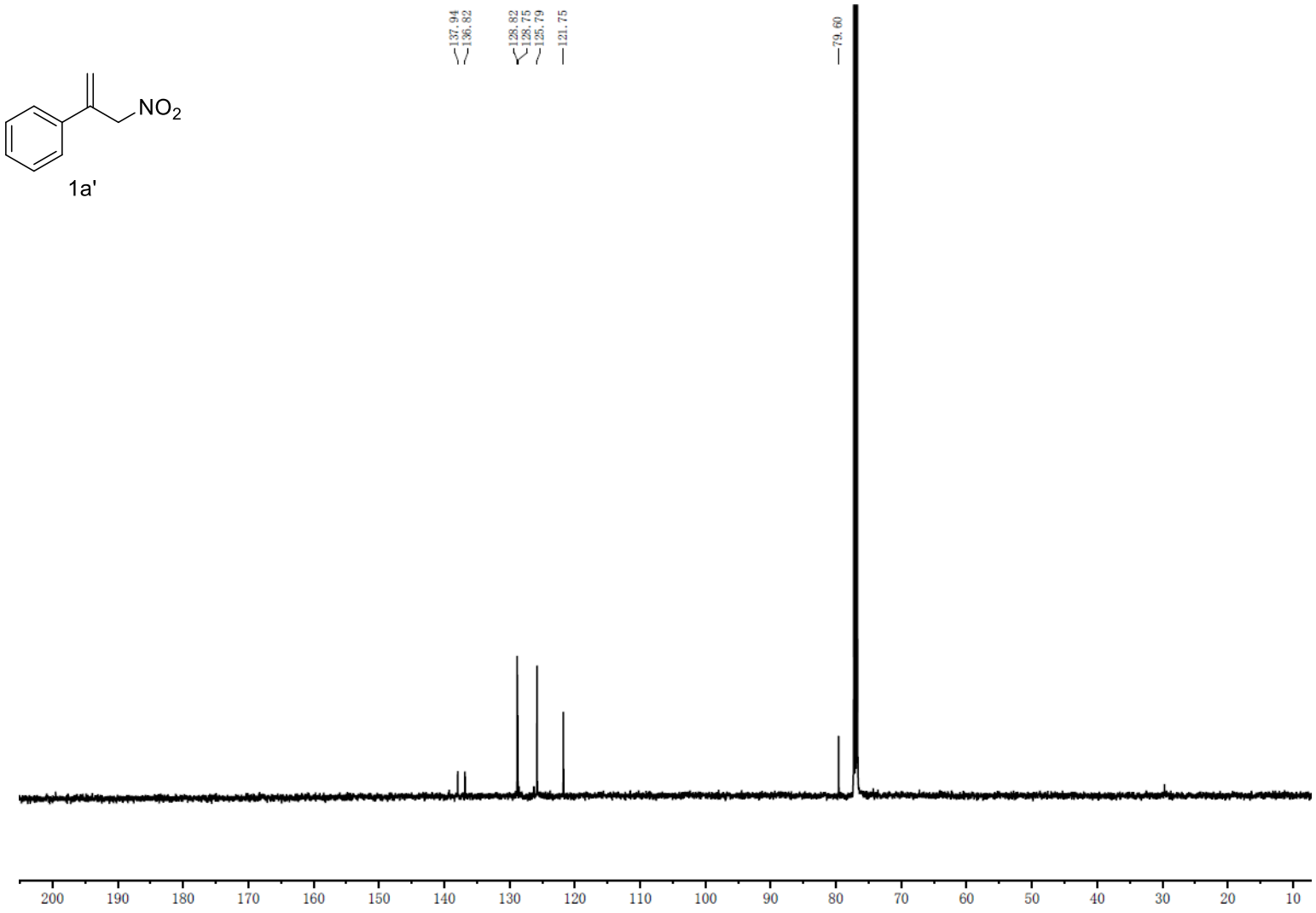
2.0
1.5
1.0
0.5
0.0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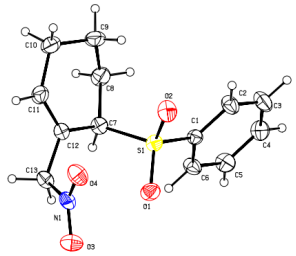
121.75
79.60
NO2
1a'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

V. X-ray diffraction analysis of compounds 7a and 8

The crystallographic data for the single crystal of the complexes **7a** and **8** were collected on a CrysAlis PRO 1.171.39.7a (Rigaku OD, 2015) employing graphite-monochromated MoKα radiation (λ = 0.71072 Å). Empirical absorption corrections were applied using the CrysAlisPro program at 300 K and 293 K respectively. The structure was solved by direct methods and refined by least-squares. Program used to solve structure is SHELXS (Sheldrick, 2008); program used to refine structure is SHELXH (Sheldrick, 2015). Hydrogen atoms of –CH, $–CH_2$, $-CH_3$, groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters.

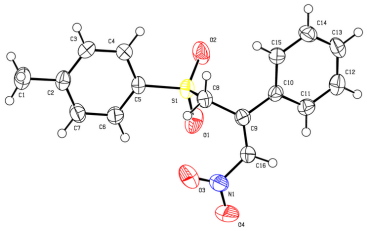
Crystallography data and structure refinement for **7a**. **(**CCDC 1565191) Thermal ellipsoids are shown at 30% probability level.



Empirical formula	$C_{13}H_{15}NO_4S$
Formula weight	281.32
Temperature/K	296(2)
Wavelength/Å	0.71073
Crystal system	monoclinic
a/Å	8.2267(15)
b/Å	12.296(2)
c/Å	13.654(3)
α/°	90
β/°	105.690(3)
γ/°	90
Volume/$Å^3$	1329.7(4)
Z	4
$\rho_{calc}g/cm^3$	1.405
μ/mm^{-1}	0.253
F(000)	592
Crystal size/mm^3	0.23 × 0.1 × 0.1
2Θ range for data collection/°	3.06 to 25.92
Reflections collected	11535
Independent reflections	2140 [R_{int} = 0.0497, R_{sigma} = 0.0514]
Data/restraints/parameters	2140/0/172

Goodness-of-fit on F^2	1.165
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0768, wR_2 = 0.1195

Crystallography data and structure refinement for **8**. **(**CCDC 1565190) Thermal ellipsoids are shown at 30% probability level.



Empirical formula	$C_{16}H_{15}NO_4S$
Formula weight	317.35
Temperature/K	296(2)
Wavelength/Å	0.71073
Crystal system	orthorhombic
a/Å	5.6914(9)
b/Å	7.7326(12)
c/Å	33.904(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1492.1(4)
Z	4
ρ_{calc}g/cm^3	1.413
μ/mm^{-1}	0.235
F(000)	664
Crystal size/mm^3	0.15 × 0.12 × 0.1
2Θ range for data collection/°	2.70 to 30.41
Reflections collected	10718
Independent reflections	2708 [R_{int} = 0.0237, R_{sigma} = 0.0216]
Data/restraints/parameters	2708/0/200
Goodness-of-fit on F^2	1.135
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.0986
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0993