[*Supporting Information*]

Organobase-Catalyzed Brook Rearrangement of Silyl Glyoxylates

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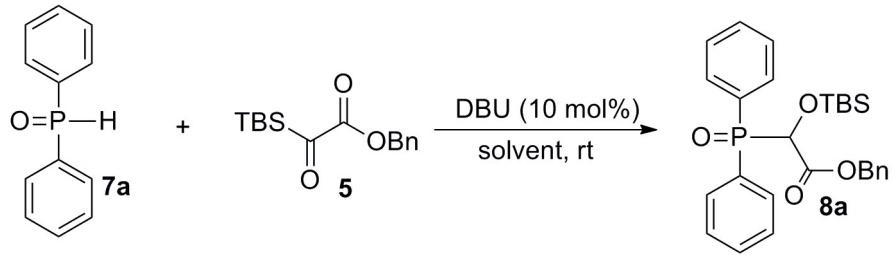
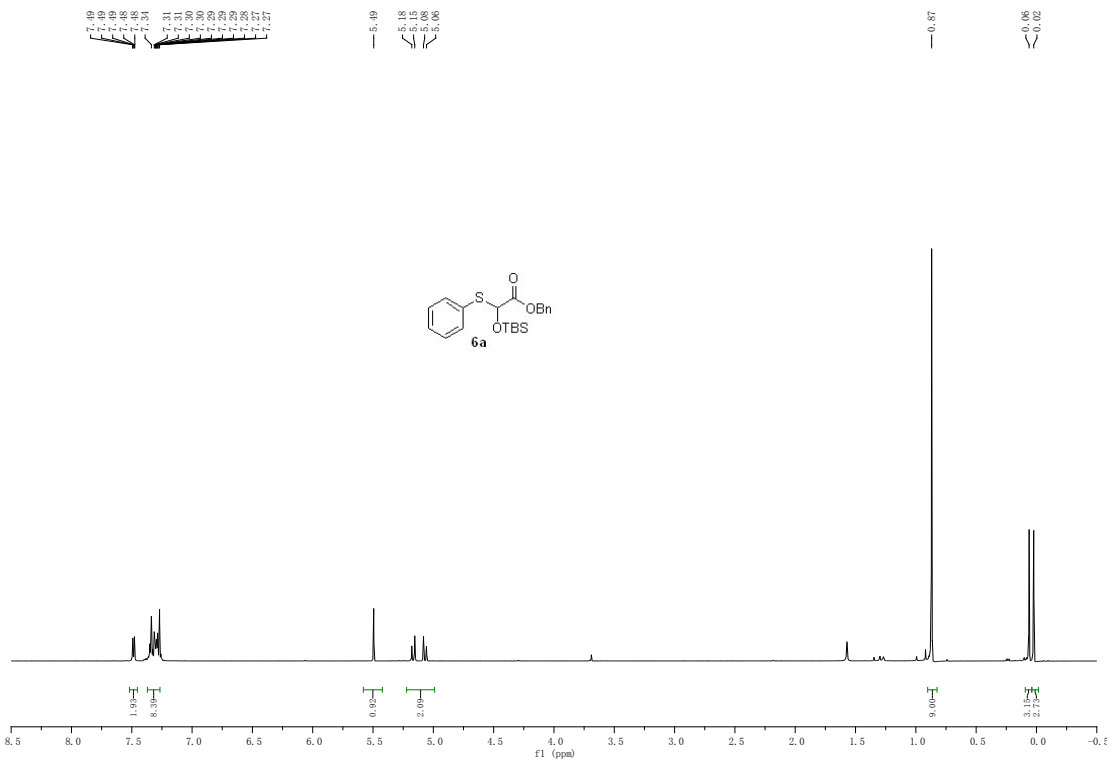
1. Survey of solvent effect[a]

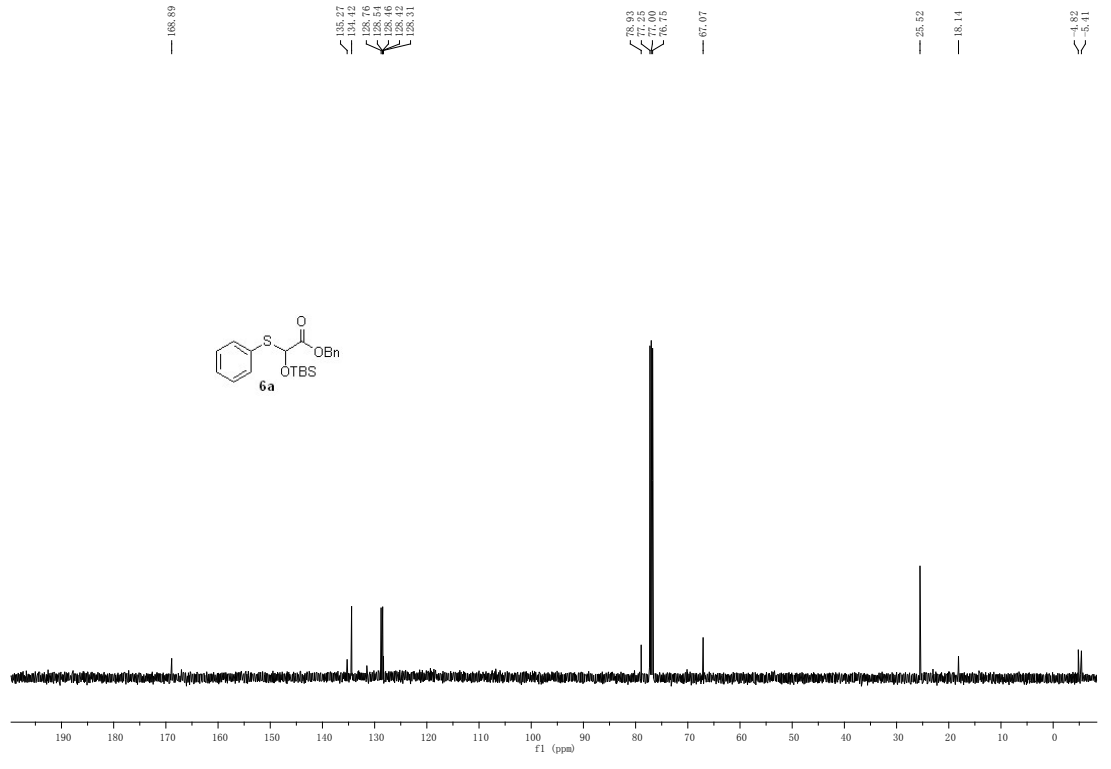


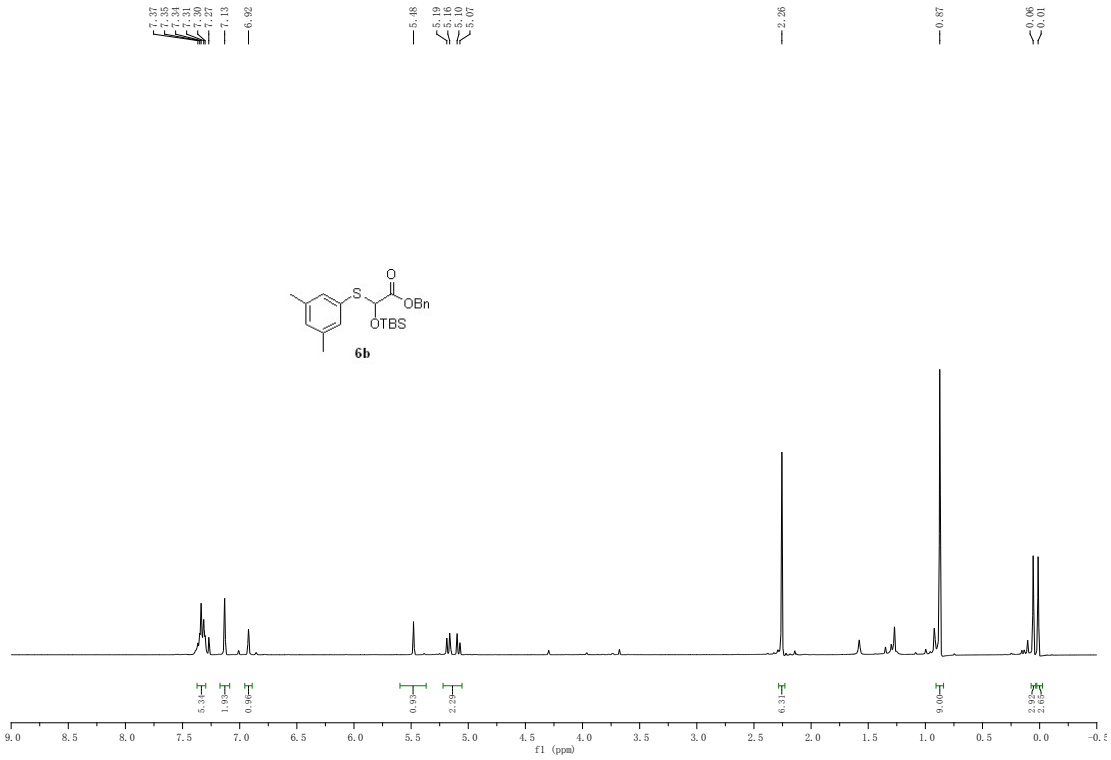
Entry	Solvent	Yield[b]
1	Toluene	53%
2	Acetonitrile	47%
3	THF	36%
4	Dichloroethane	62%
5	Dichloromethane	93%

[a]The experimental condition is: a mixture of secondary phosphine oxides of **7a** (0.043 mmol), silyl glyoxylate **5** (0.036 mmol) and organobase DBU (10 mol %) in 0.71 mL of dry DCM was stirred at room temperature for 10 mins. [b]Isolated yield after purification by flash chromatography.

2. NMR Spectra and HPLC Chromatograms



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OTBS
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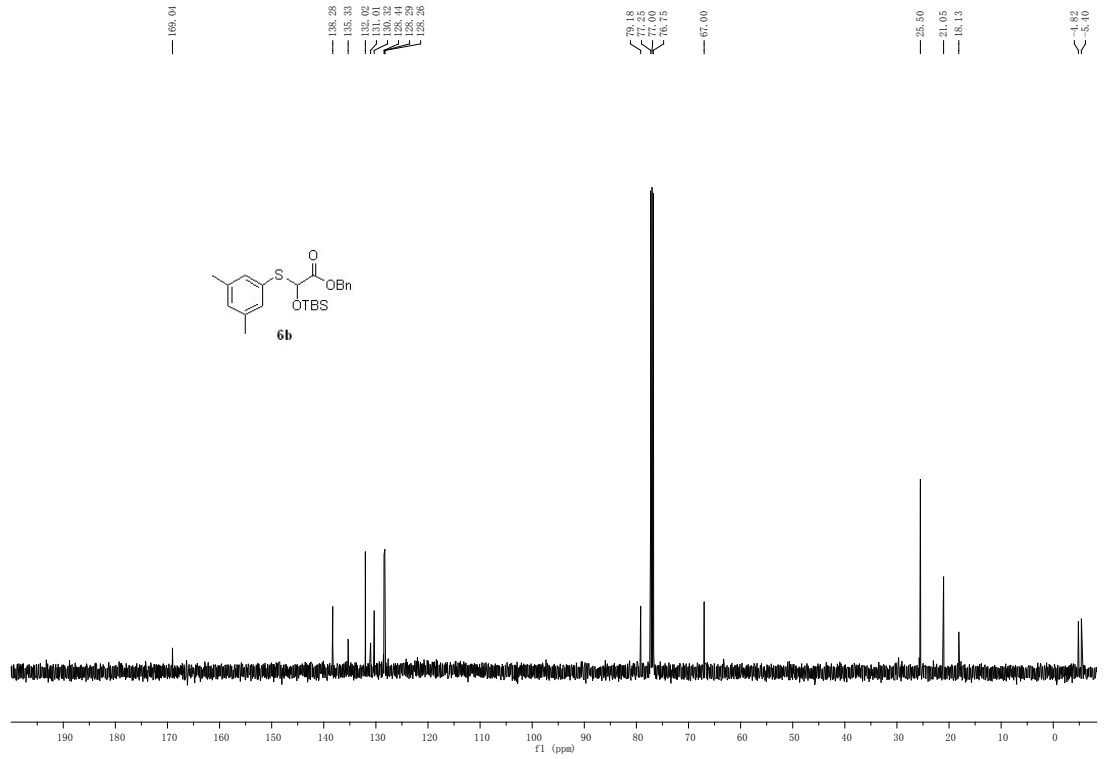
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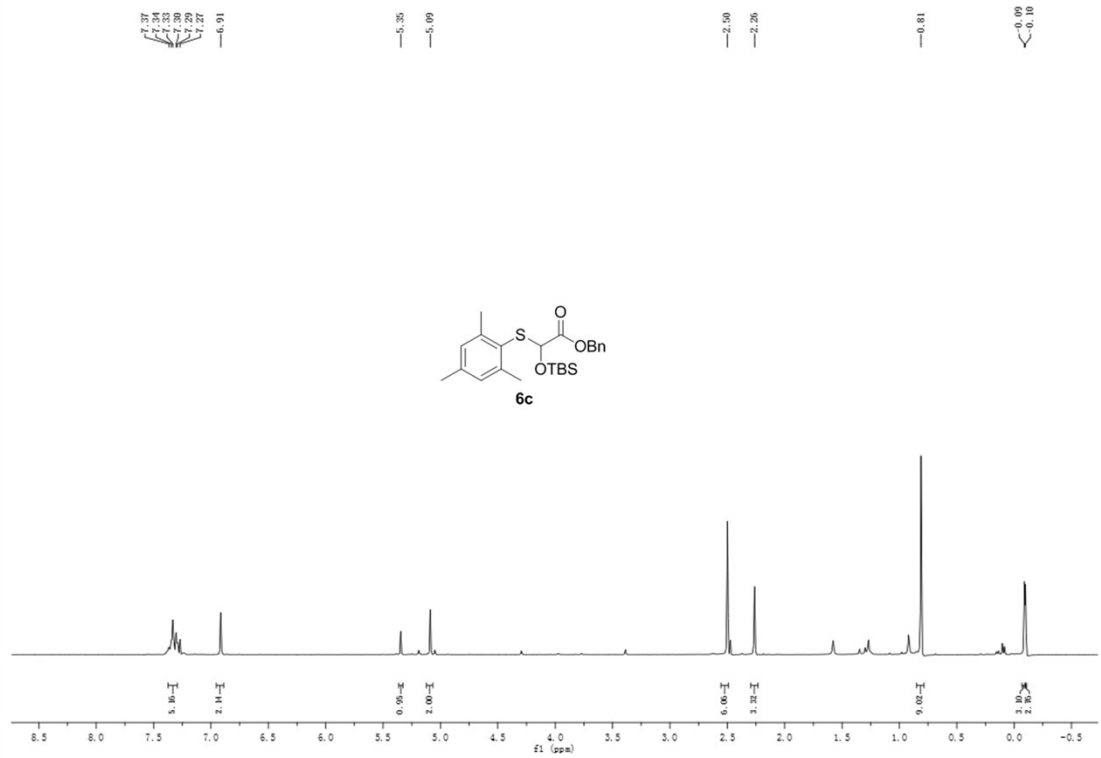
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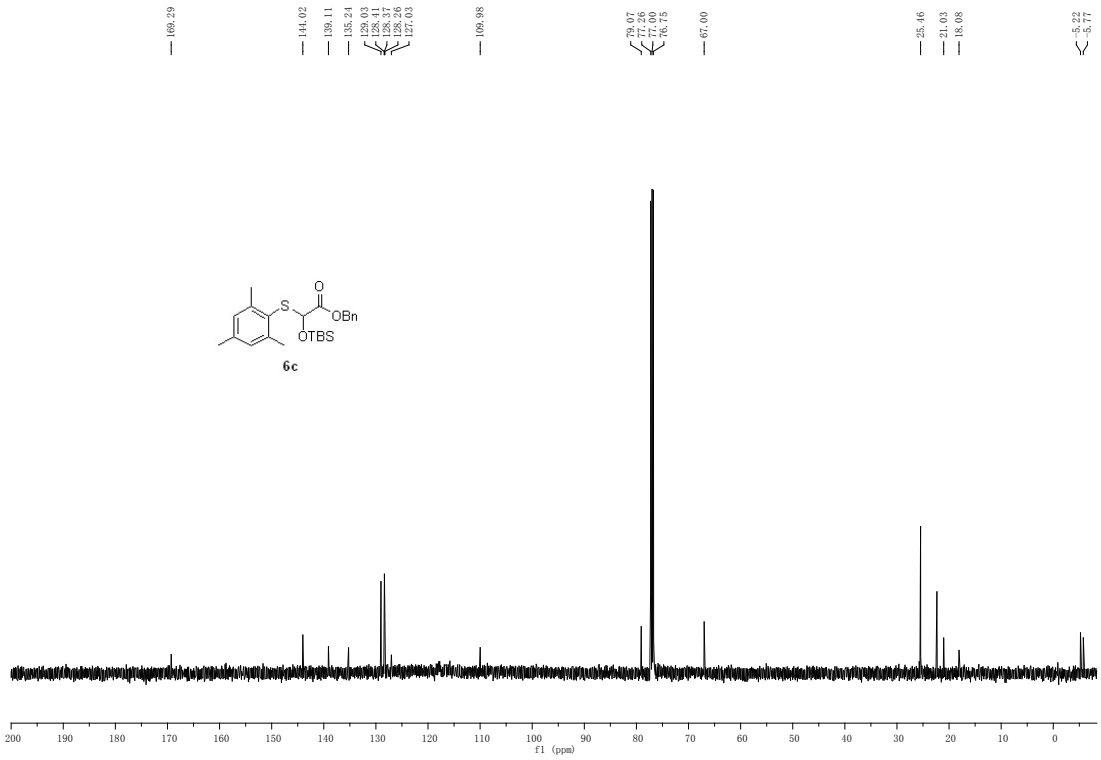
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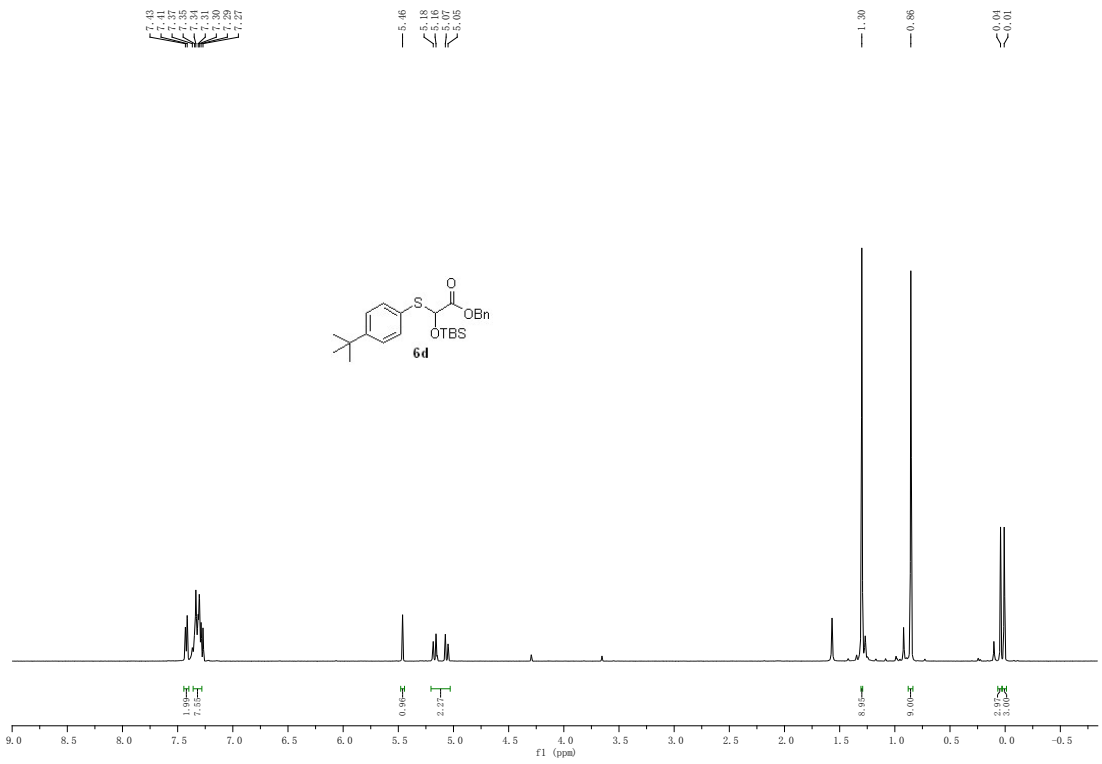
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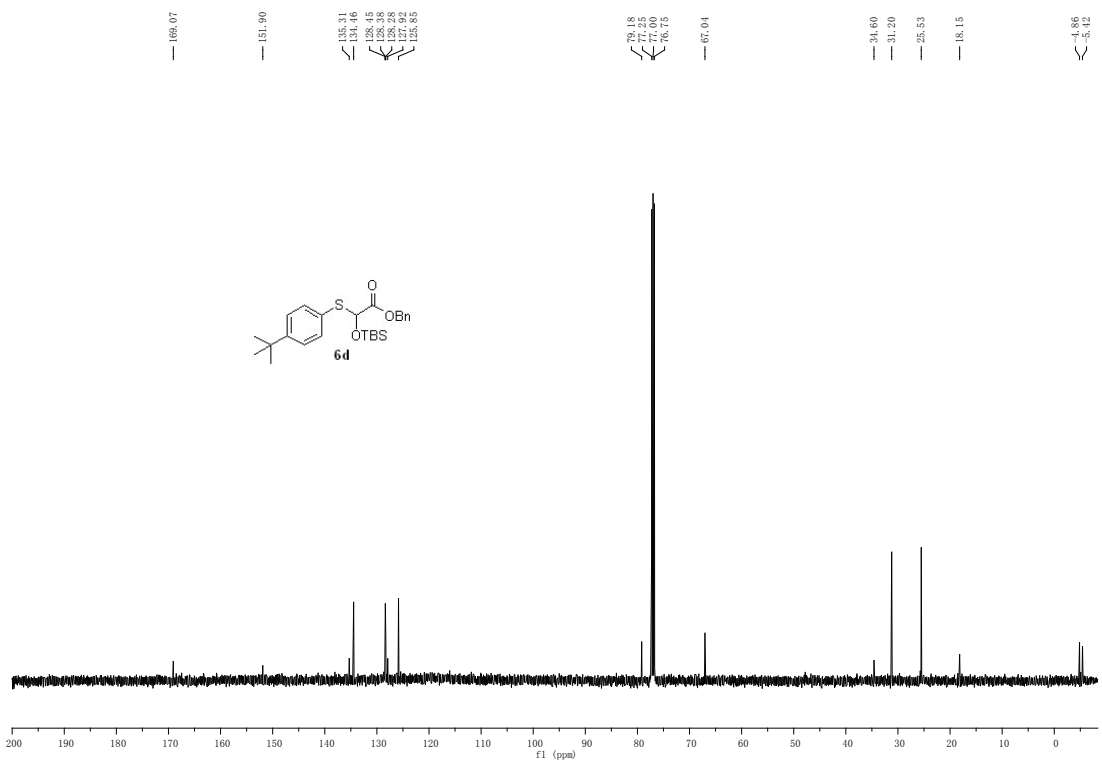
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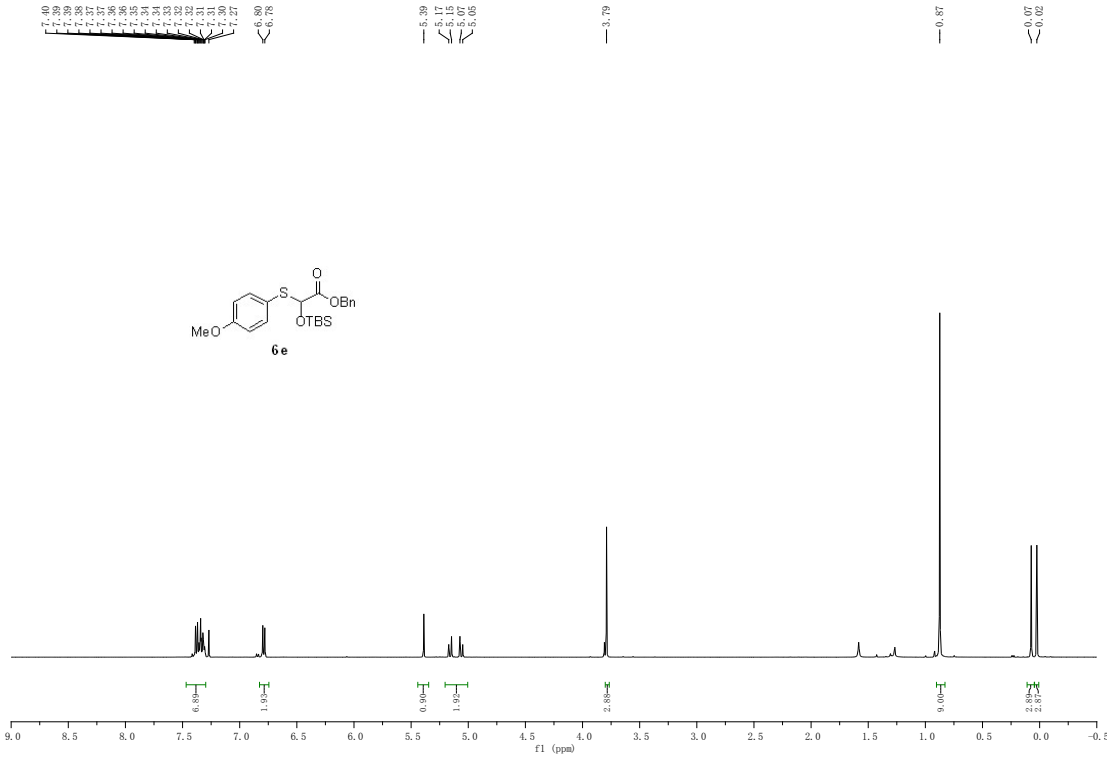
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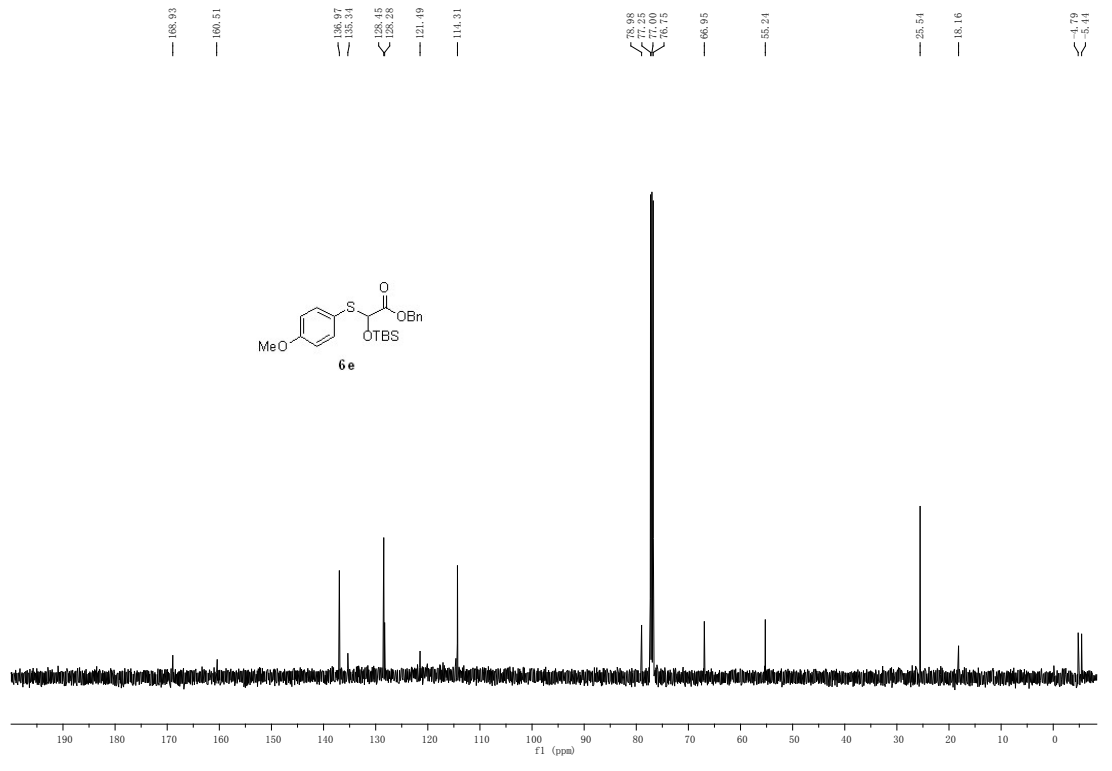
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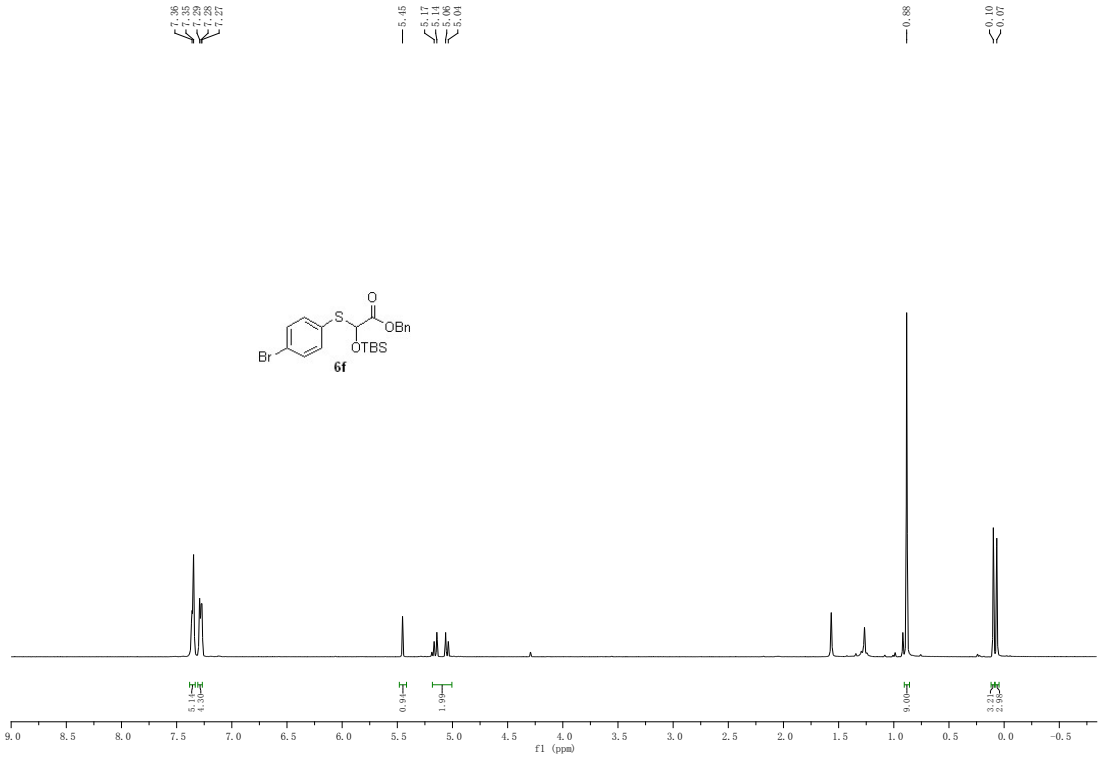
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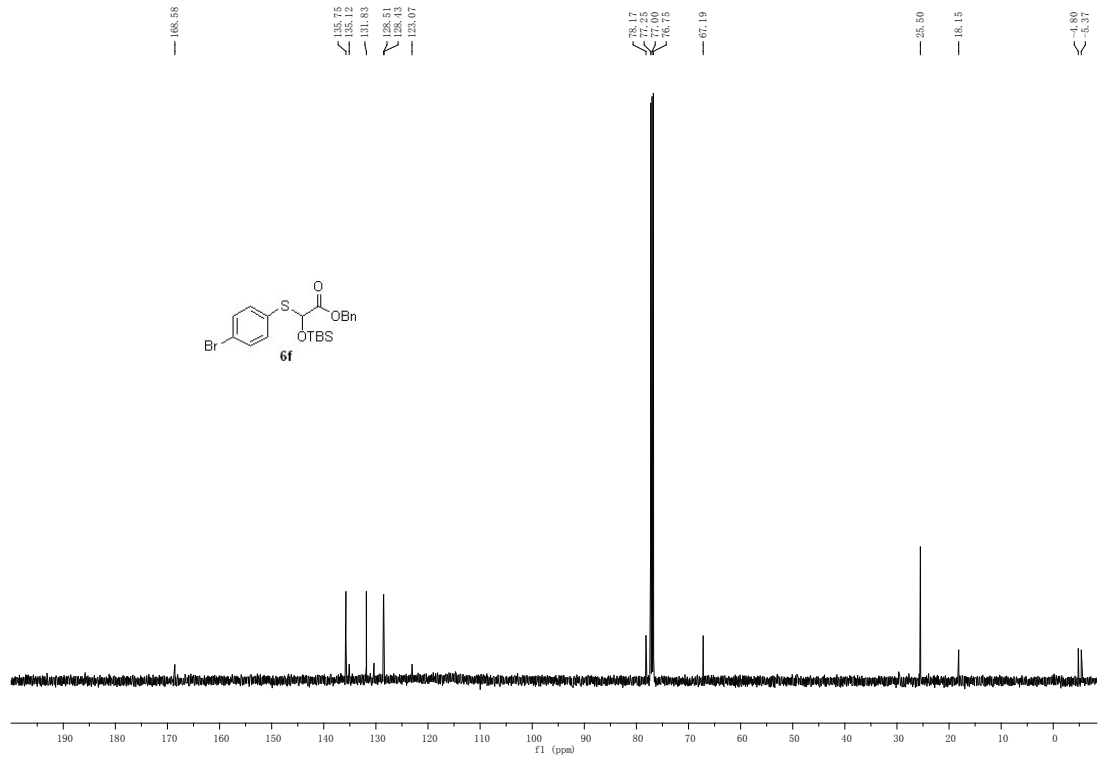
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OTBS
Br
6f
f1 (ppm)


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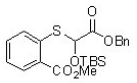
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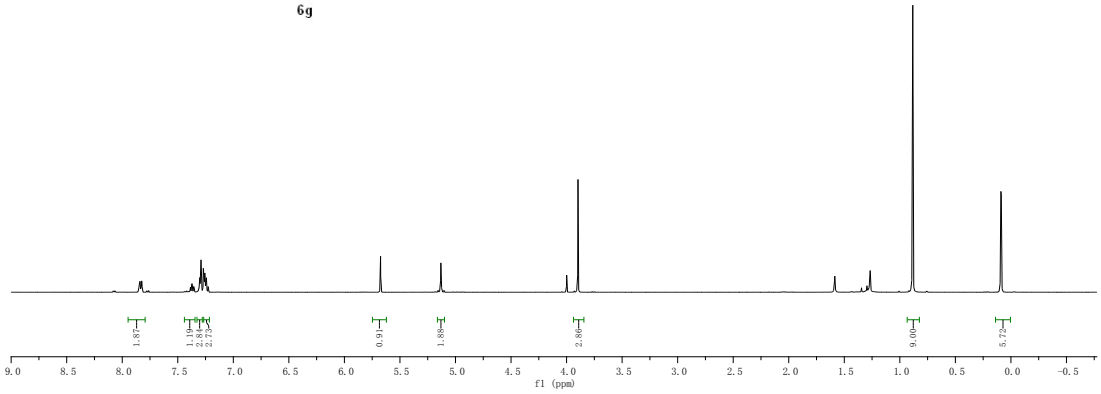
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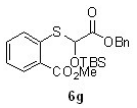
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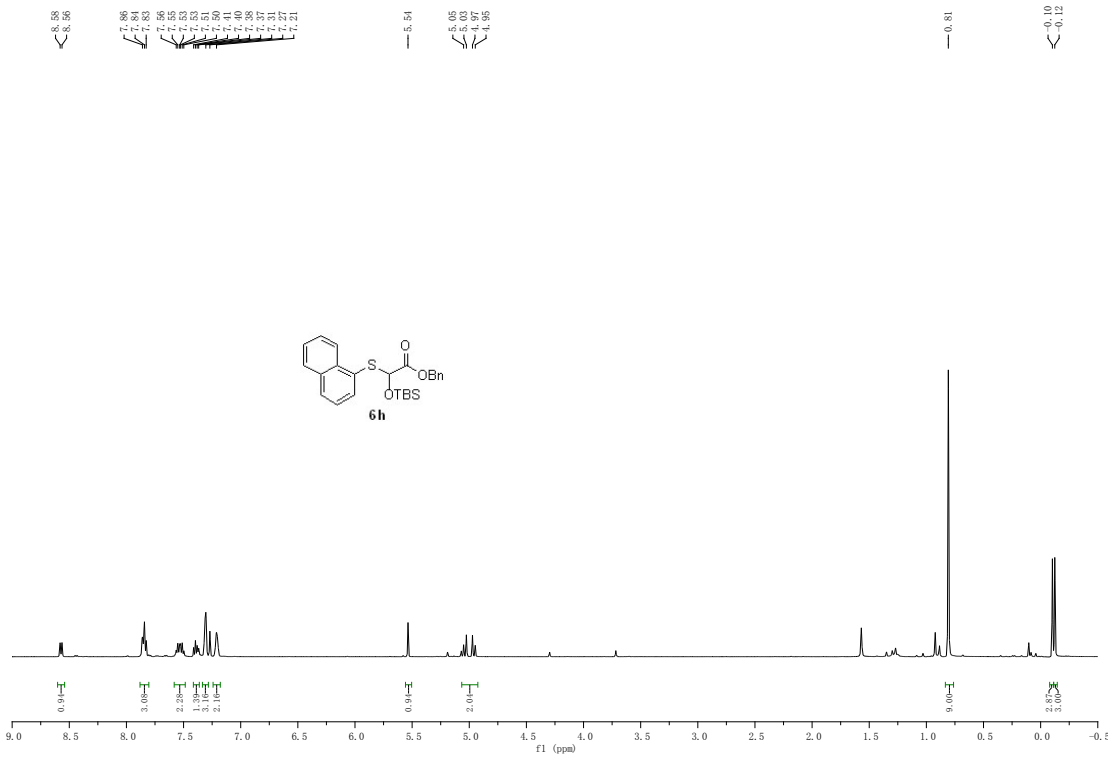
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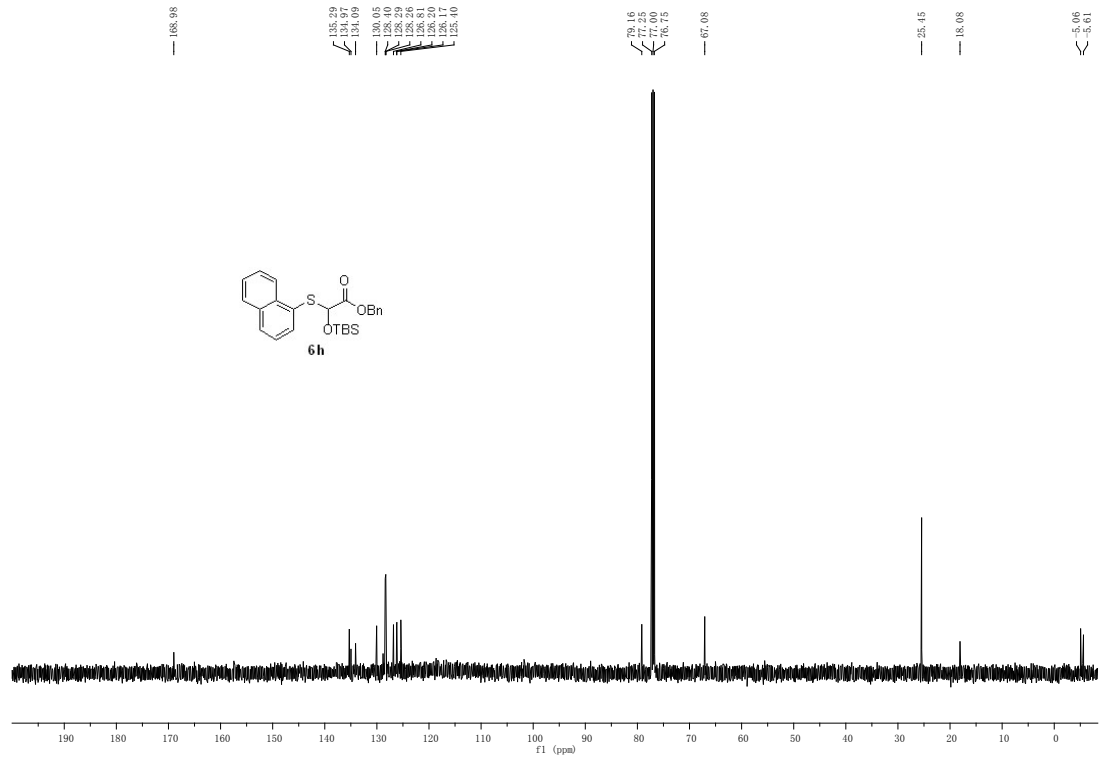
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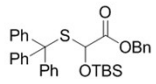
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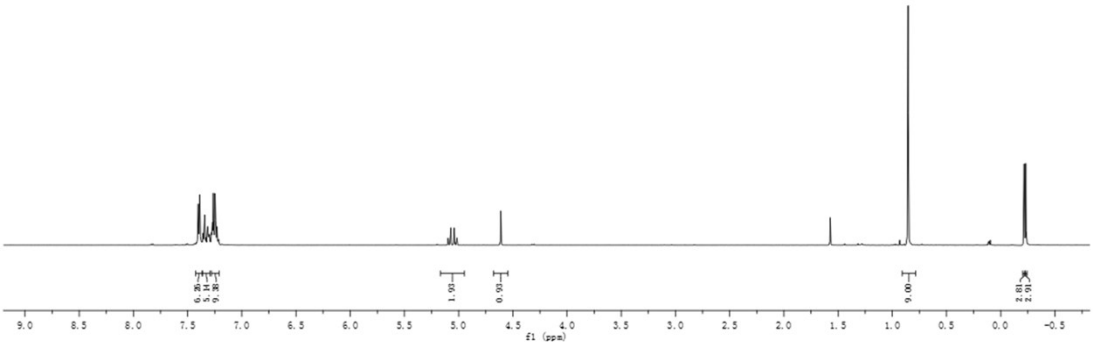
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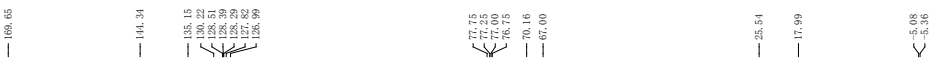

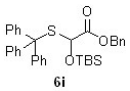
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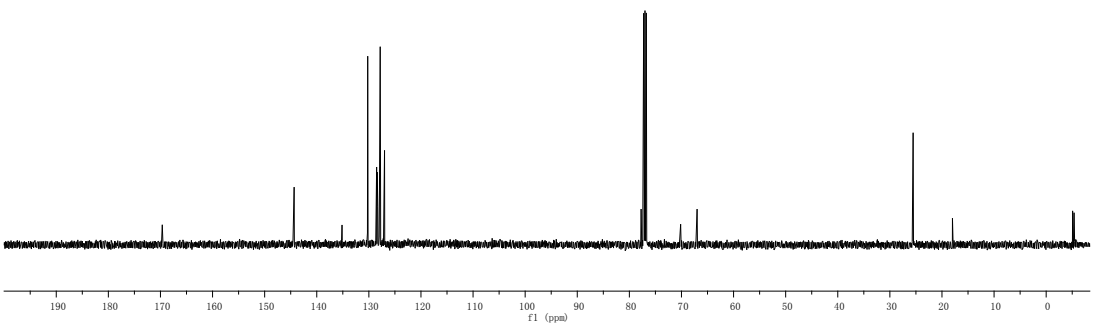
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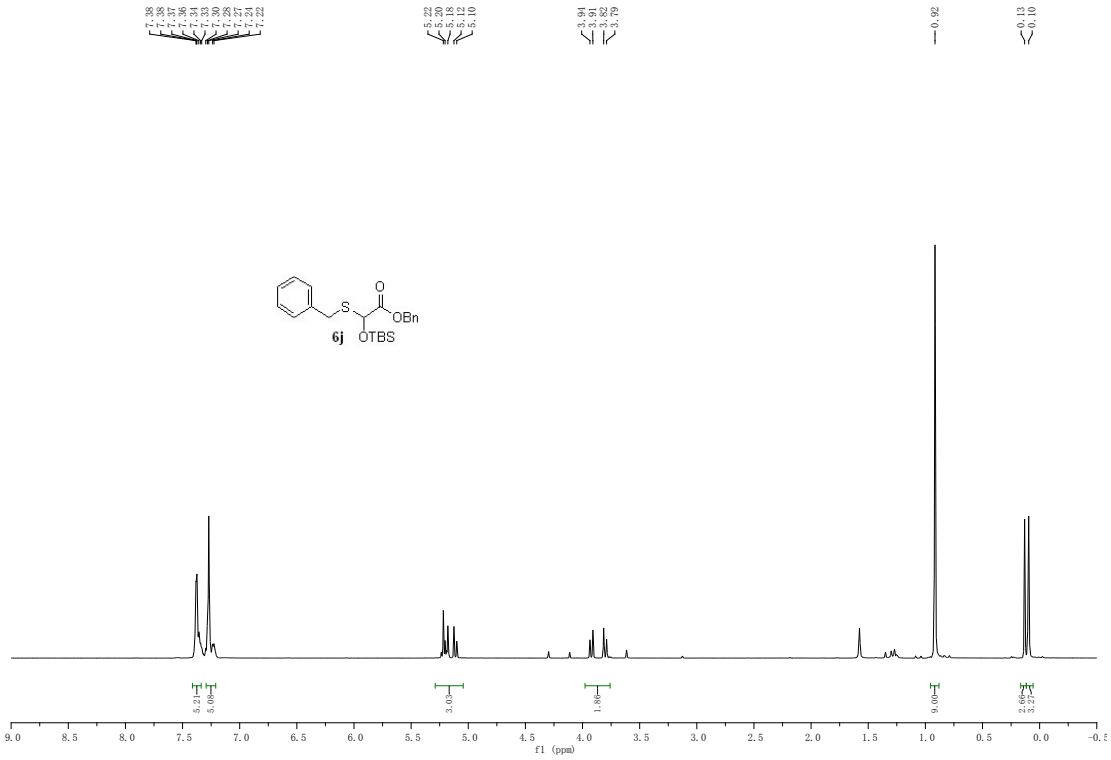
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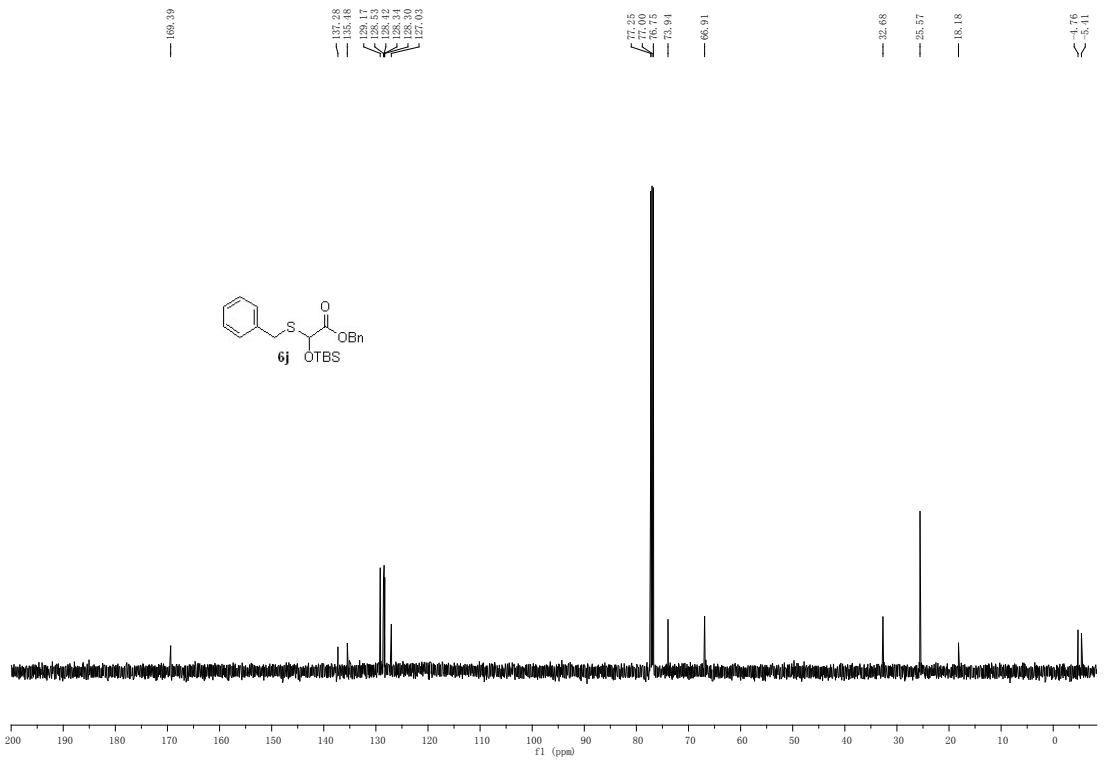
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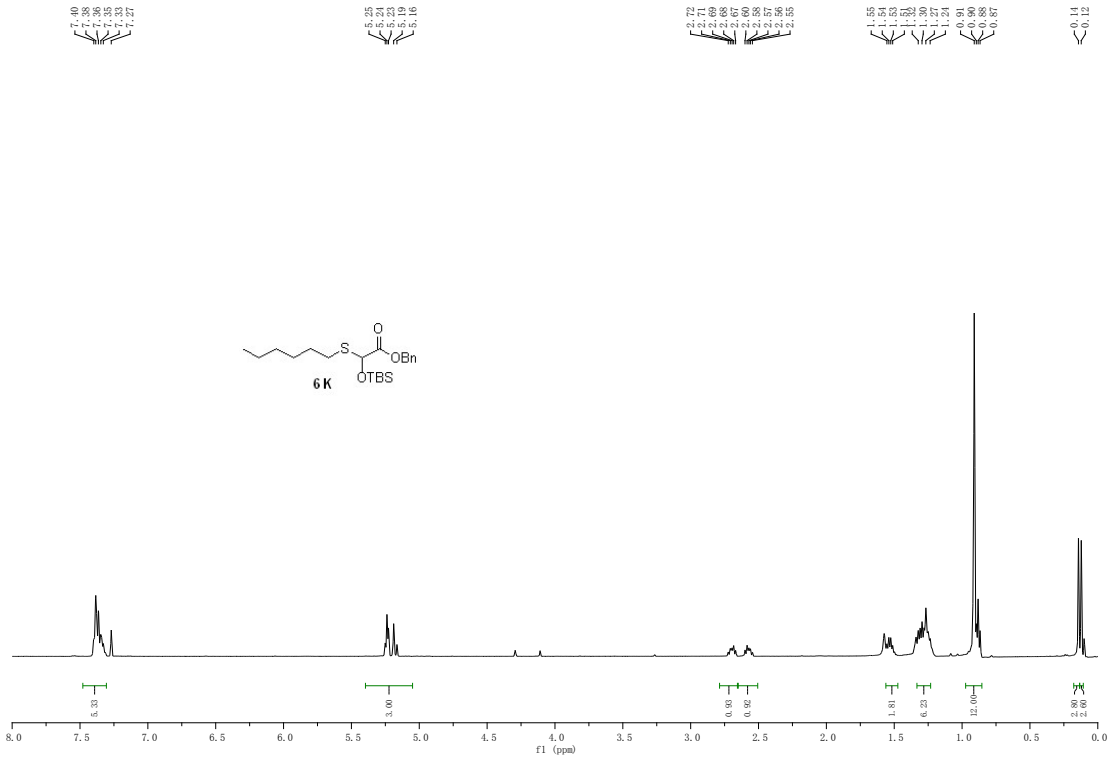
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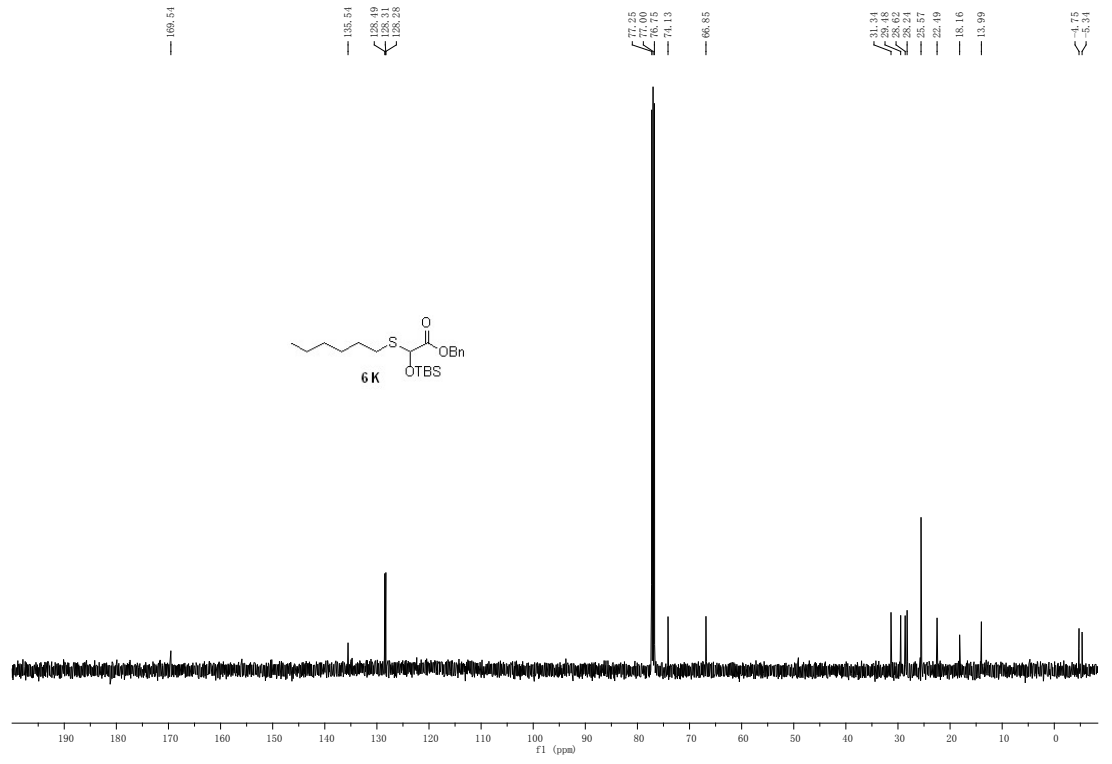
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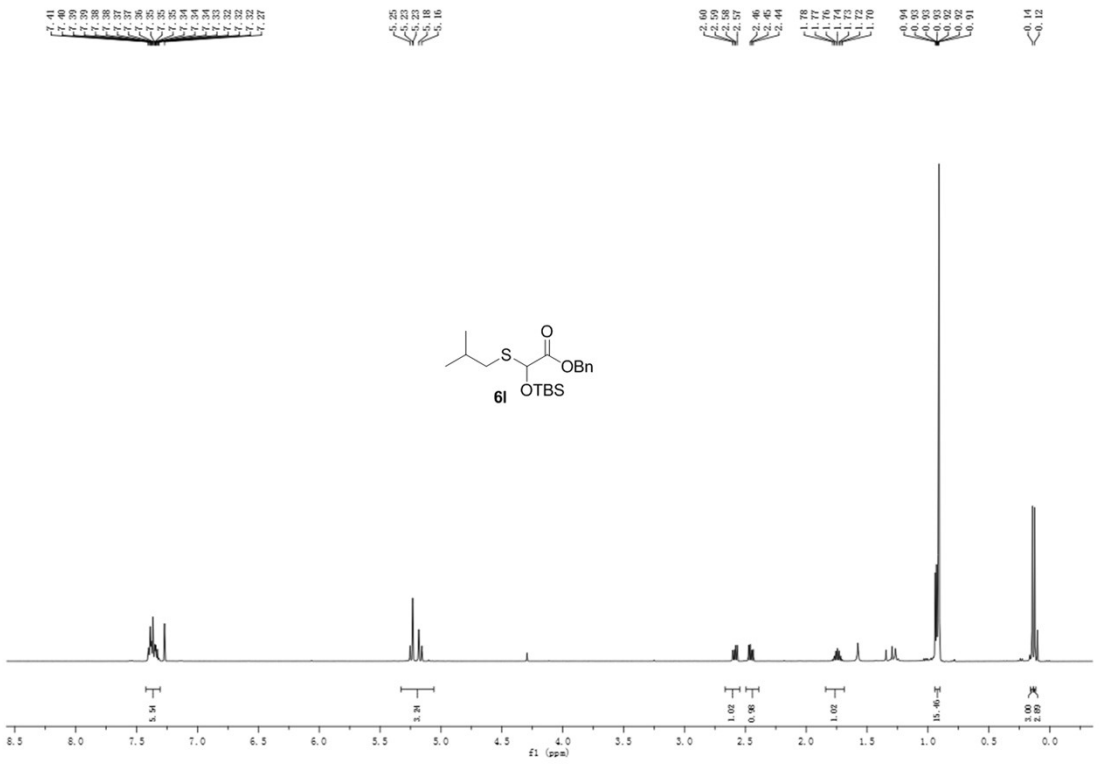
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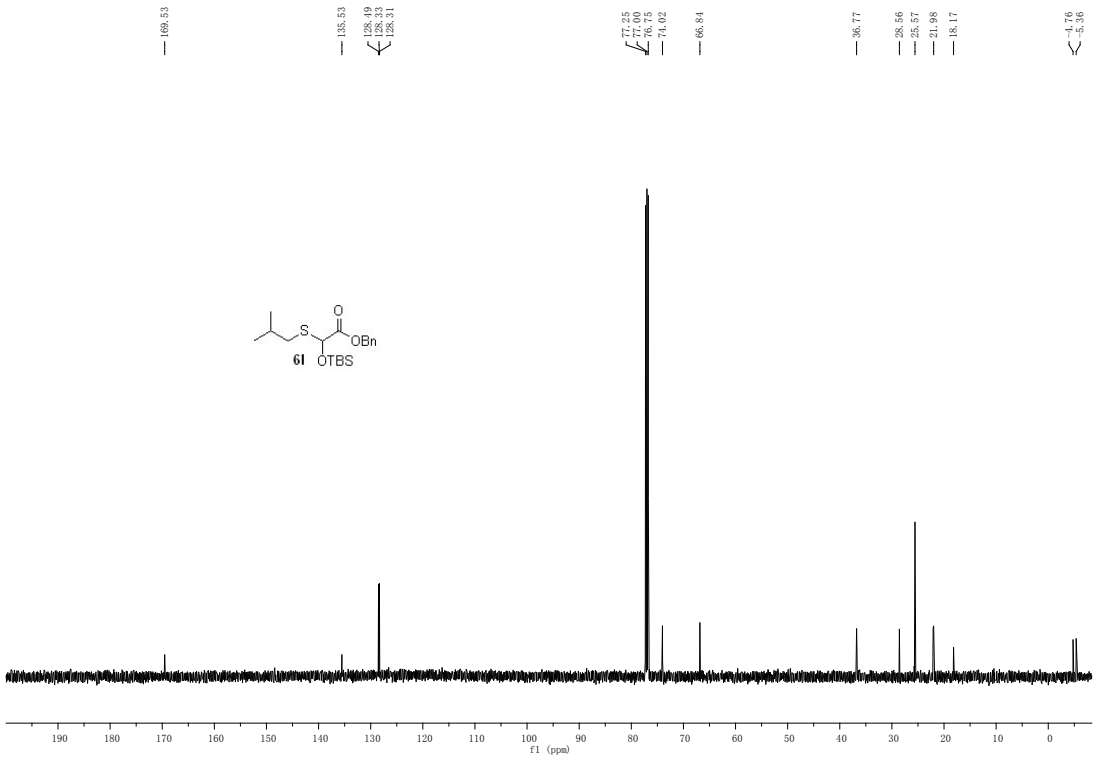
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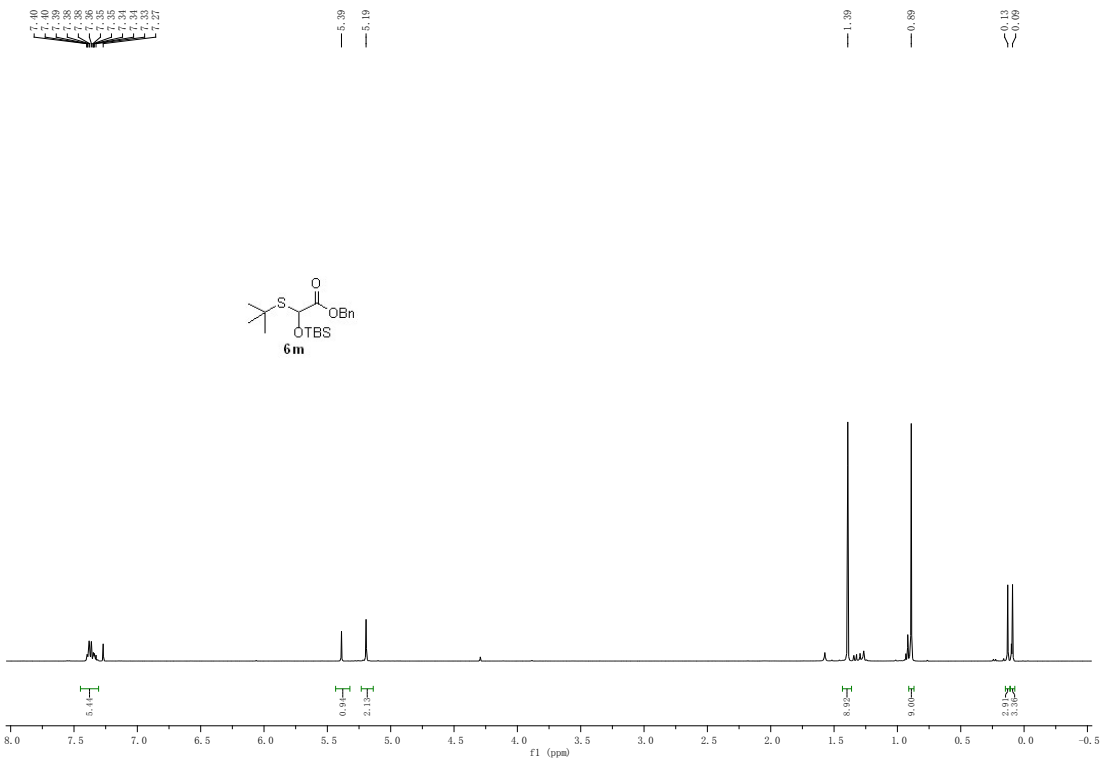
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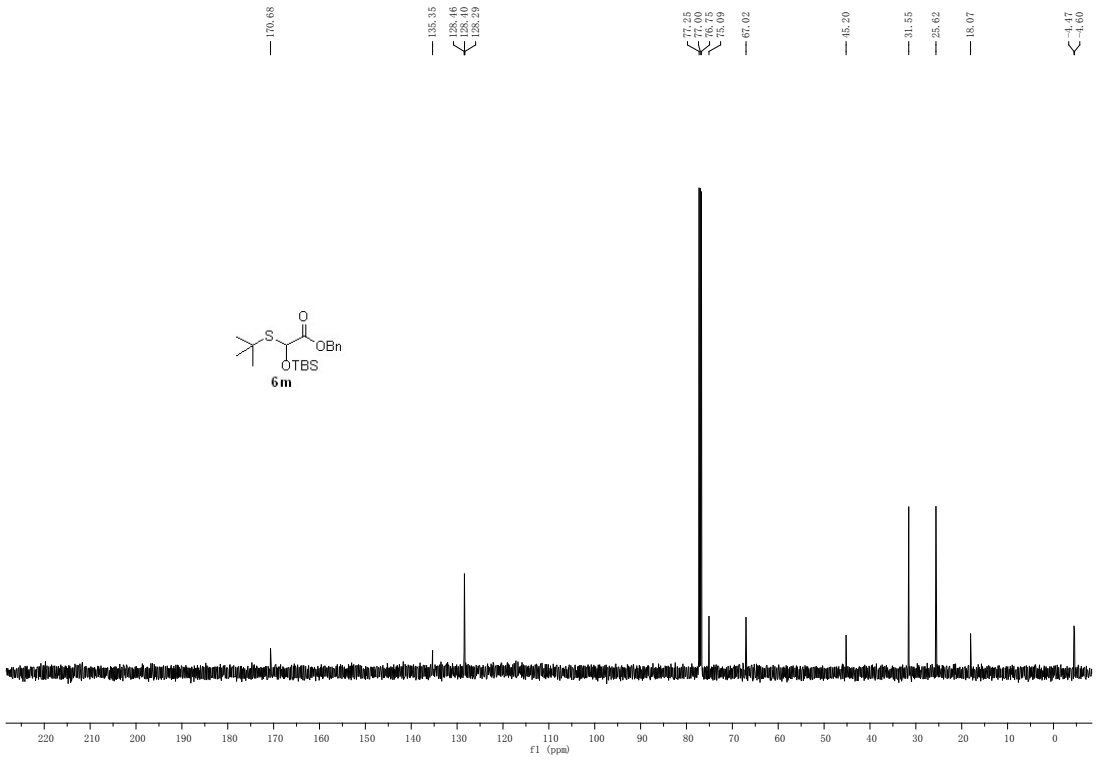
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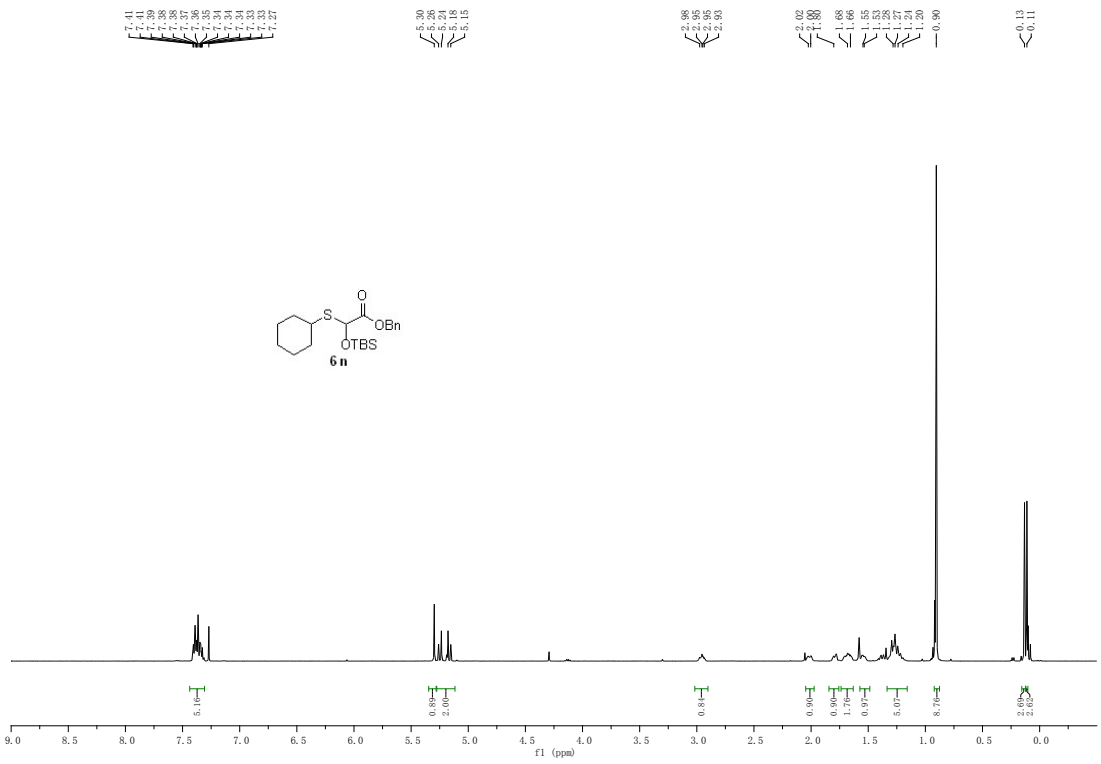
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S
OBn
OTBS
6n
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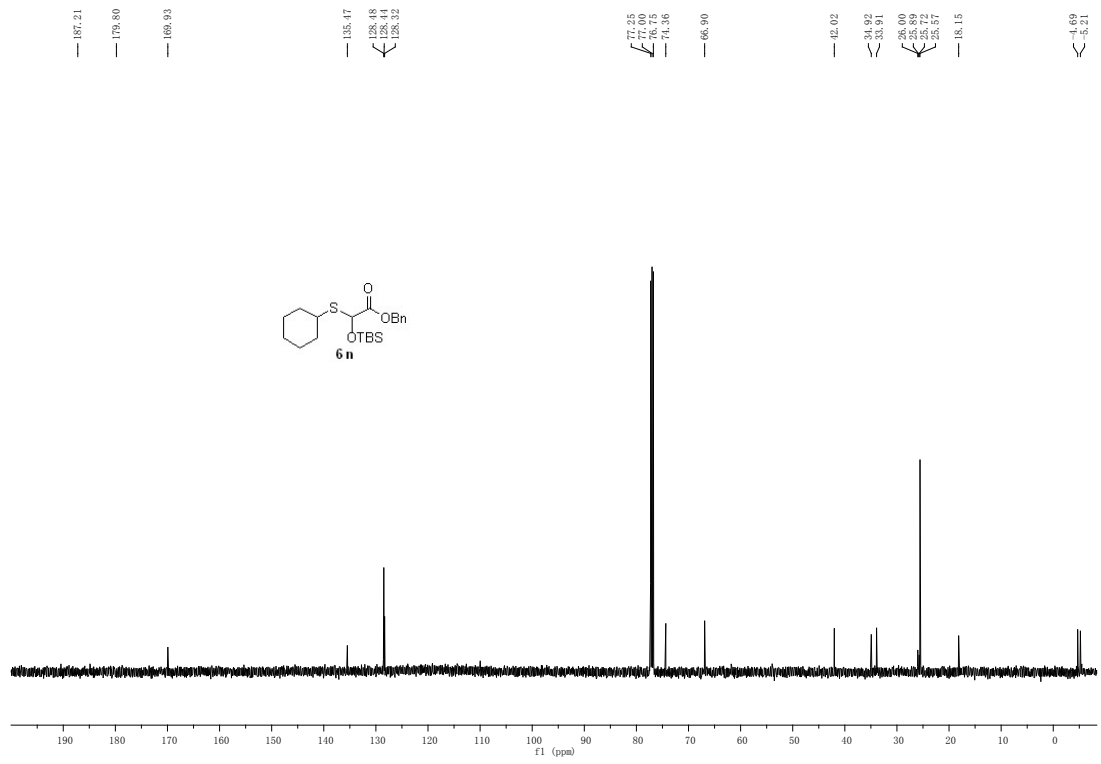
2.69
2.62
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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179.80
169.93
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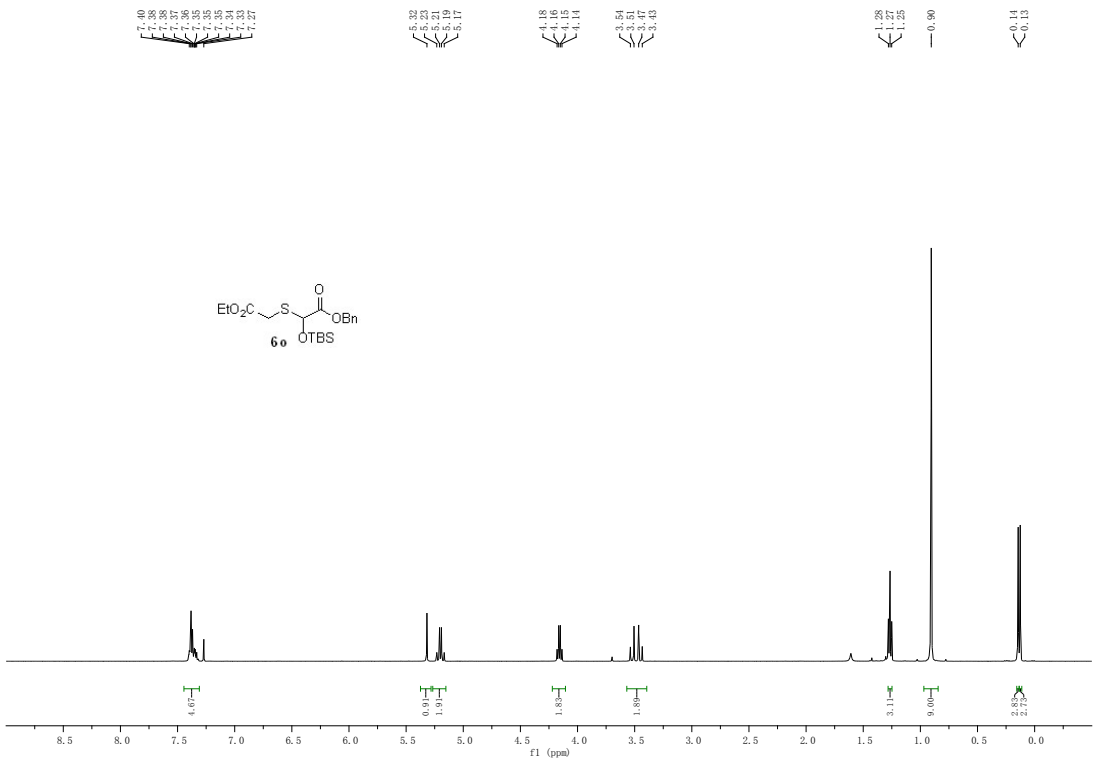
128.44
128.32
77.25
77.00
76.75
74.36
66.90
42.02
34.92
33.91
26.00
25.89
25.72
25.57
18.15
-4.69
-5.21
O
S
OBn
OTBS
6n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.38
7.37
7.36
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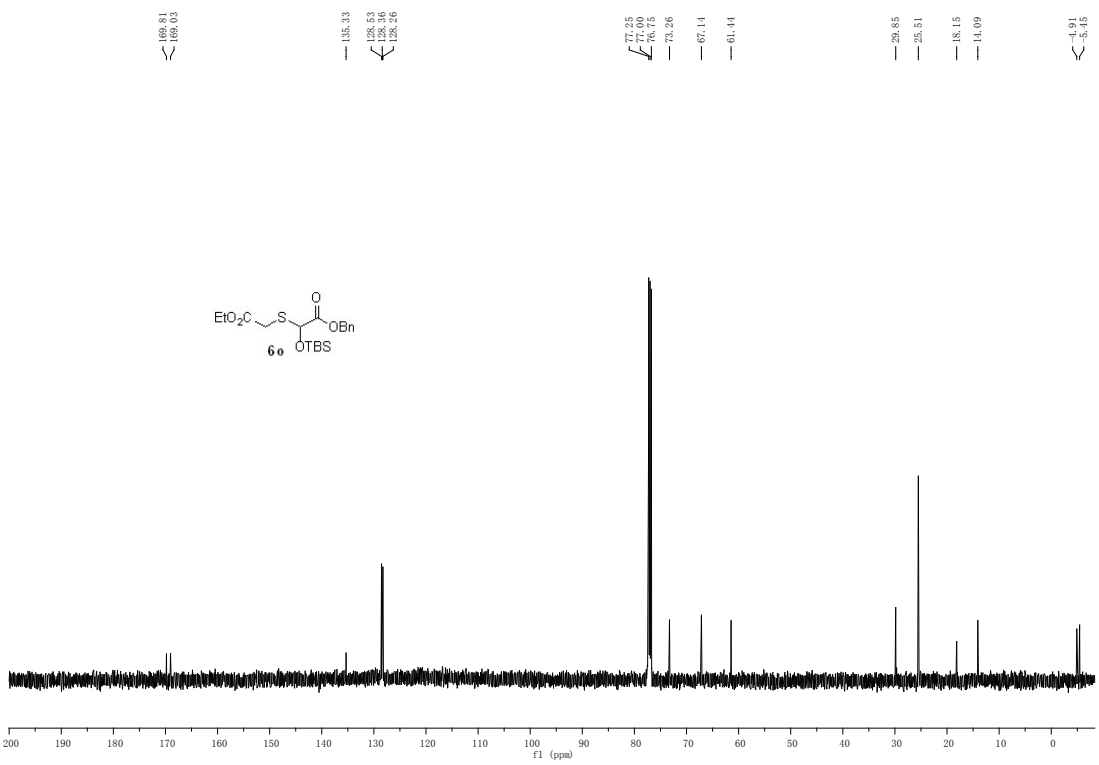
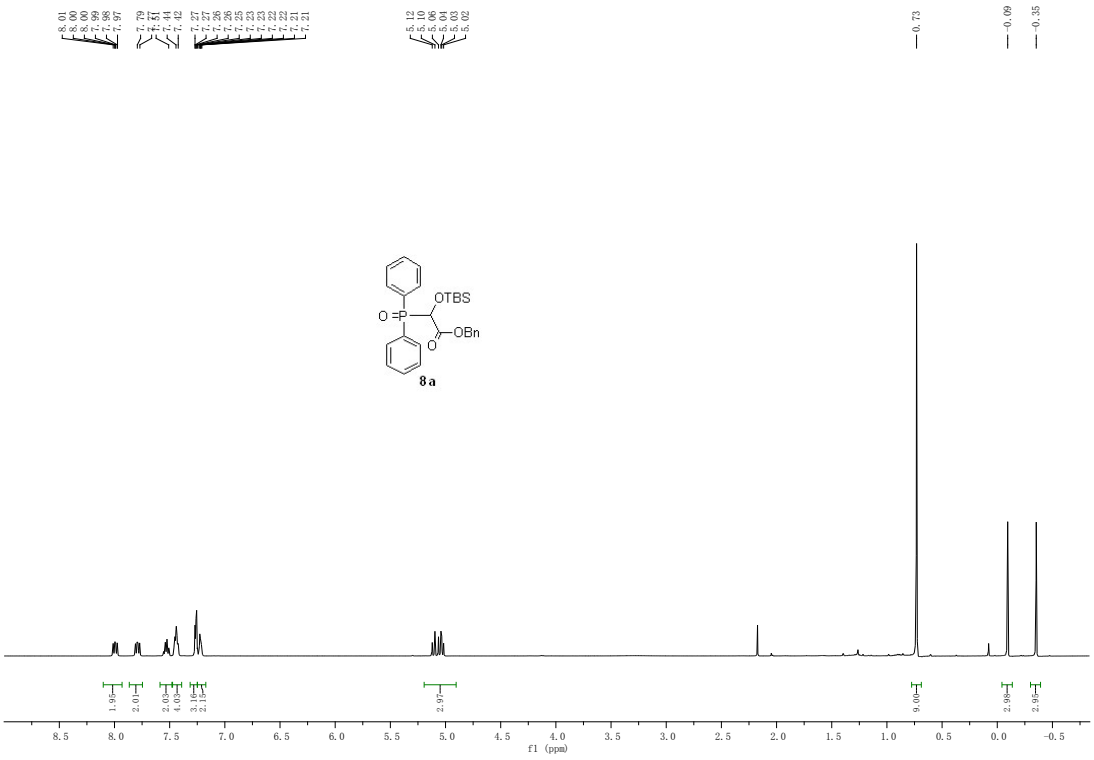
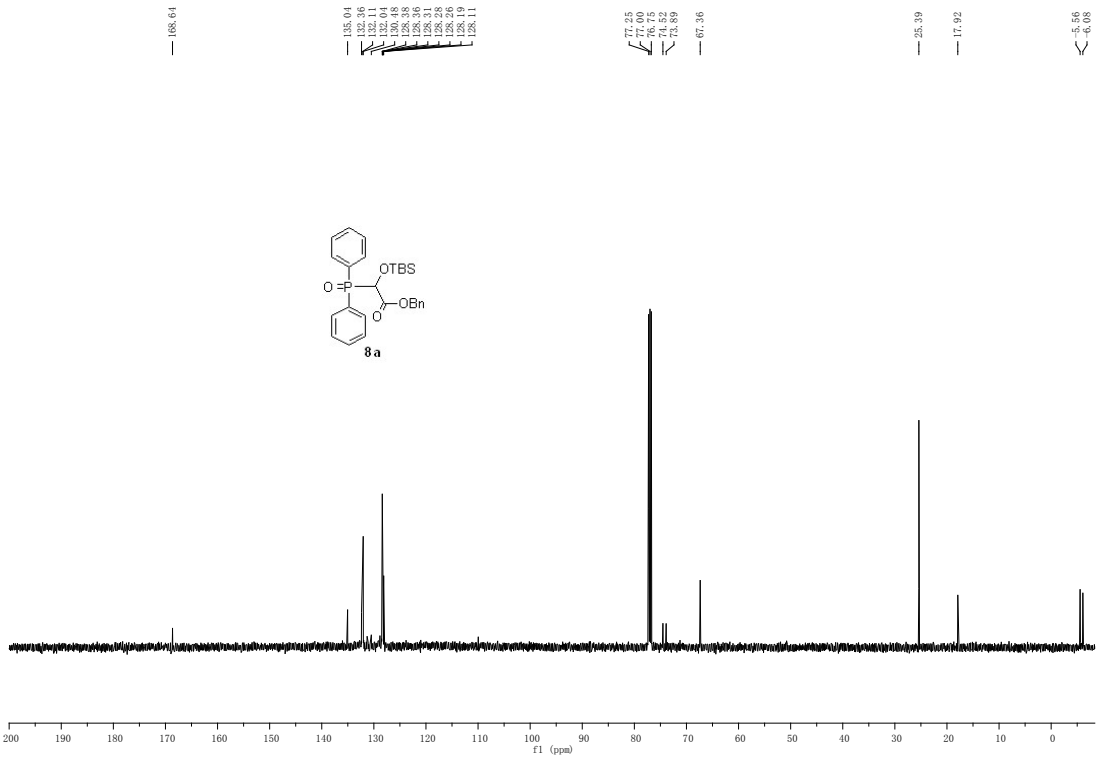
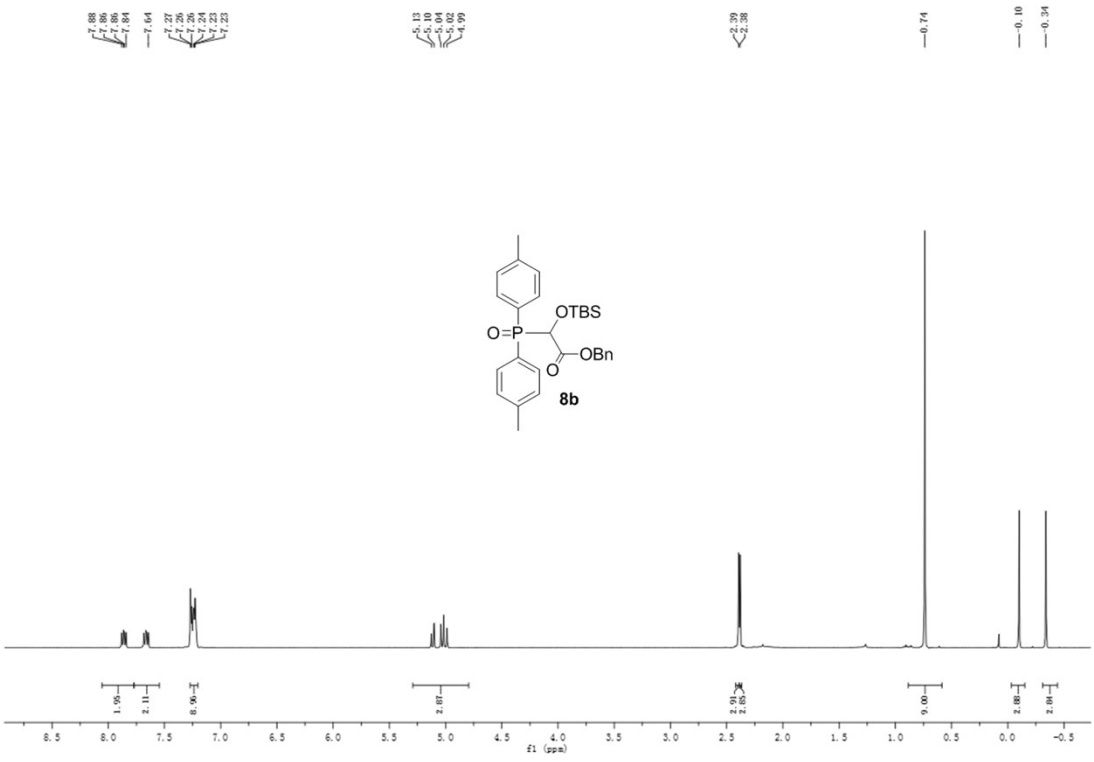
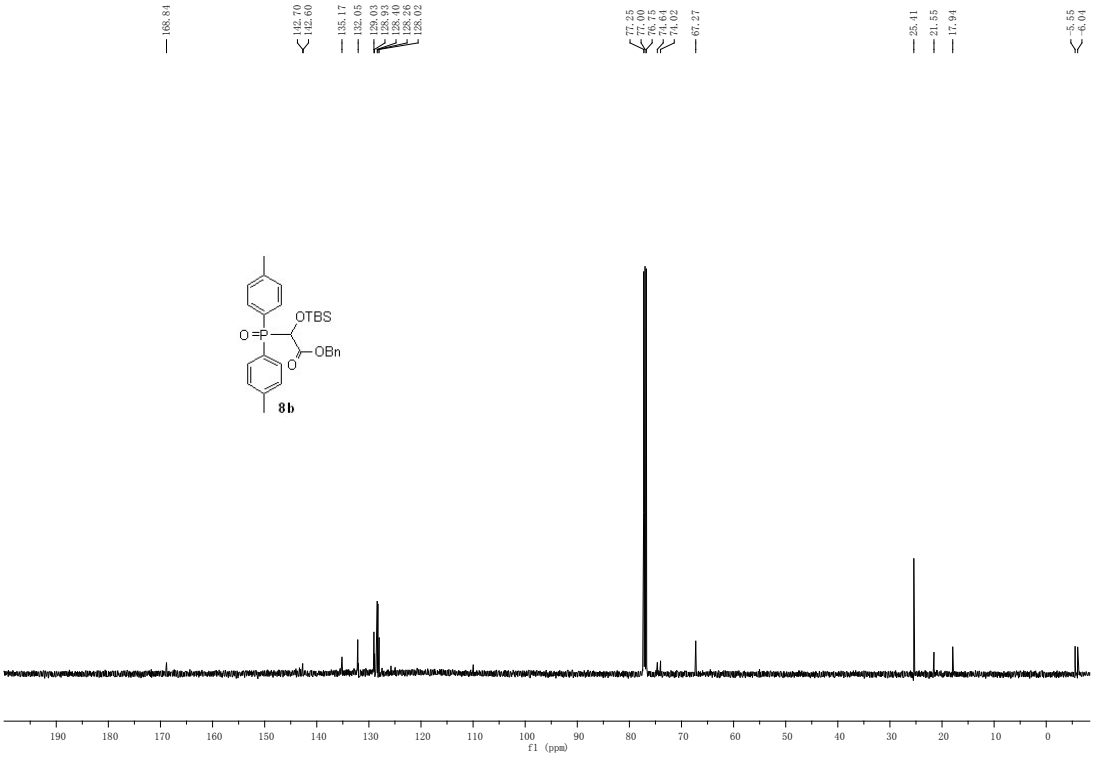
7.35
7.34
7.33
7.27
5.32
5.23
5.21
5.19
5.17
4.18
4.16
4.15
4.14
3.54
3.51
3.47
3.43
1.28
1.27
1.25
0.90
0.14
0.13
EtO2C
S
O
OBn
OTBS
6o
4.67
0.91
1.91
1.83
1.89
3.11
9.00
2.83
2.72
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

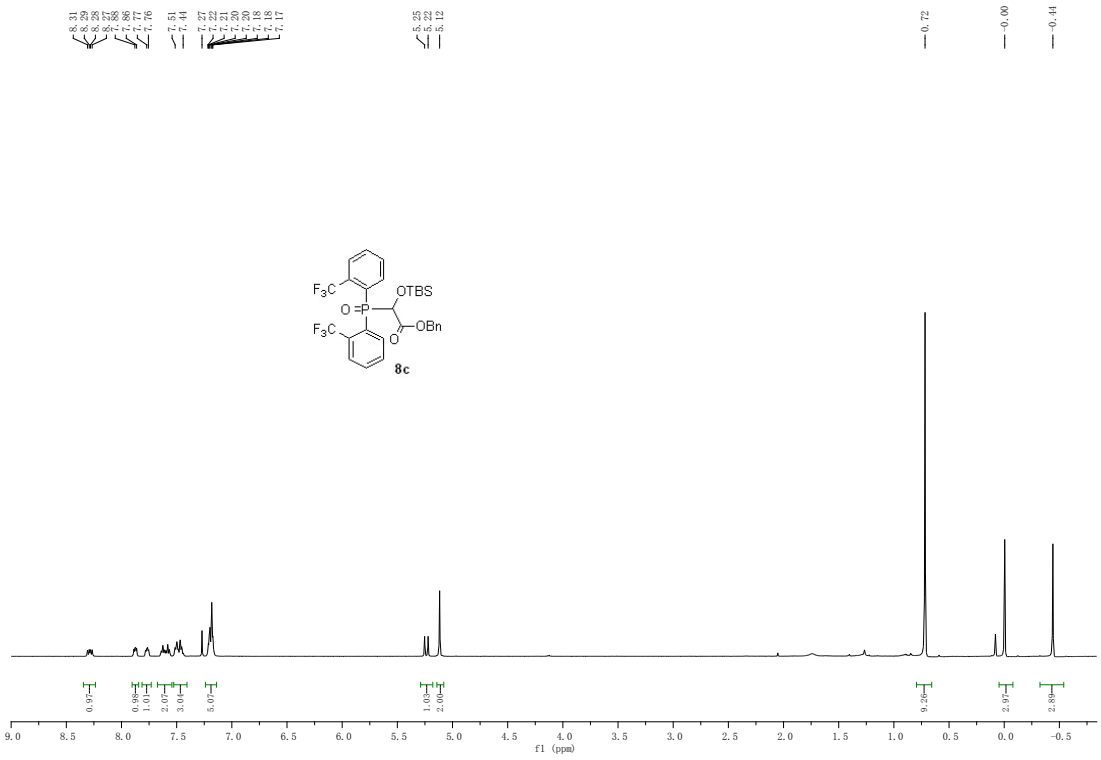

169.81
169.03
135.33
128.53
128.36
128.26
77.25
77.00
76.75
73.26
67.14
61.44
29.85
25.51
18.15
14.09
-4.91
-5.45
EtO2C
S
O
OBn
OTBS
6o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

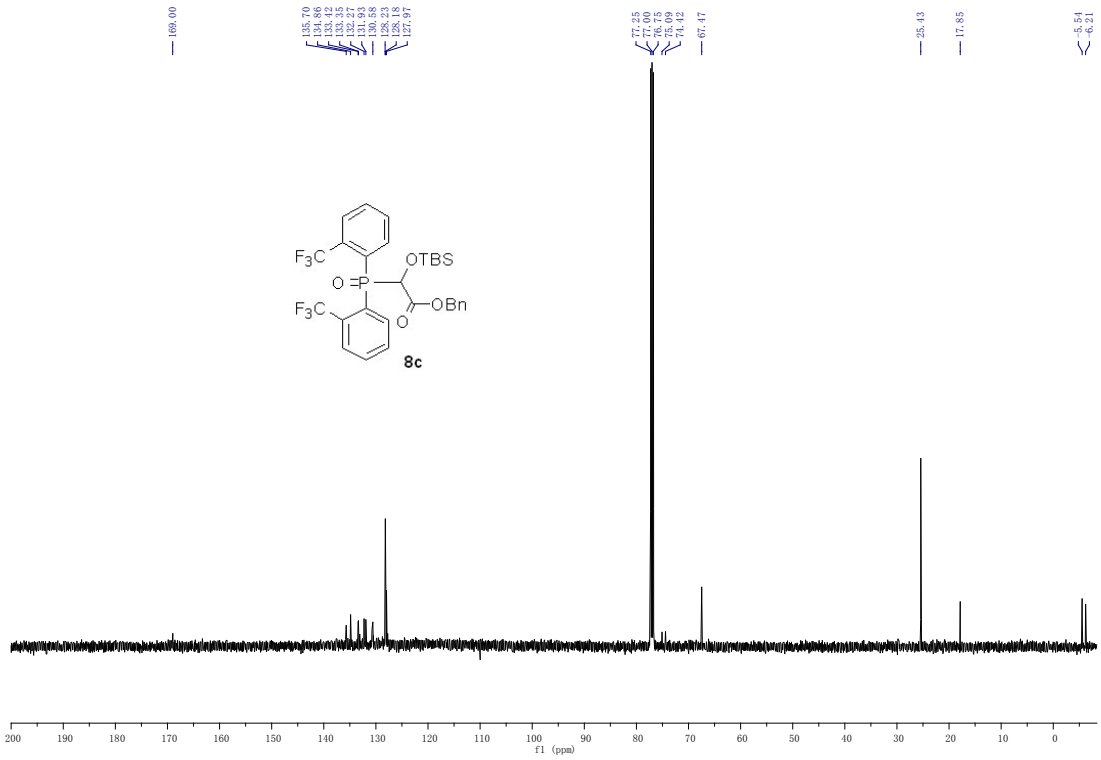

8.01
8.00
8.00
7.99
7.98
7.97
7.79
7.77
7.45
7.44
7.42
7.27
7.27
7.26
7.26
7.25
7.23
7.23
7.22
7.22
7.21
7.21
5.12
5.10
5.06
5.01
5.03
5.02
0.73
-0.09
-0.35
OTBS
O=P
OBn
O
8a
1.95
2.01
2.03
4.03
3.10
2.15
2.97
9.00
2.98
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.64
135.04
133.96
132.11
132.04
130.48
128.38
128.36
128.31
128.28
128.26
128.19
128.11
77.25
77.00
76.75
74.52
73.89
67.36
25.39
17.92
-5.56
-6.68
OTBS
O=P
OBn
O
8a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.88
7.86
7.86
7.84
7.64
7.27
7.26
7.24
7.23
7.23
5.13
5.10
5.04
5.02
4.99
2.39
2.38
0.74
0.10
0.34
OTBS
O=P
O
OBn
8b
1.95
2.11
8.96
2.67
2.91
2.85
9.00
2.08
2.04
f1 (ppm)


168.84
142.70
142.60
135.17
132.05
128.93
128.40
128.26
128.02
77.25
77.00
76.75
74.64
74.02
67.27
25.41
21.55
17.94
-5.55
-6.04
OTBS
O=P
O
OBn
8b
f1 (ppm)


8.31
8.29
8.28
8.27
7.88
7.86
7.77
7.76
7.51
7.44
7.27
7.22
7.21
7.20
7.18
7.17
5.25
5.22
5.12
0.72
-0.00
-0.44
F3C
OTBS
O=P
OBn
F3C
O
8c
0.97
0.98
1.01
2.07
3.04
5.07
1.03
2.00
9.26
2.97
2.89
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
f1 (ppm)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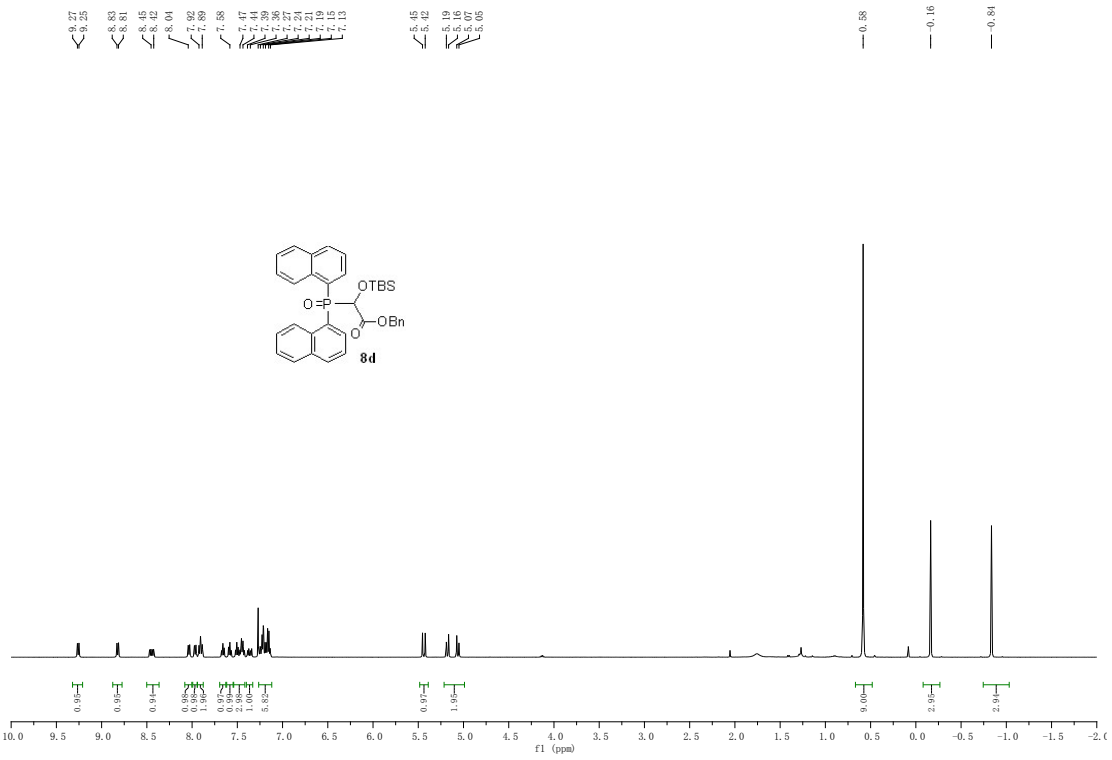
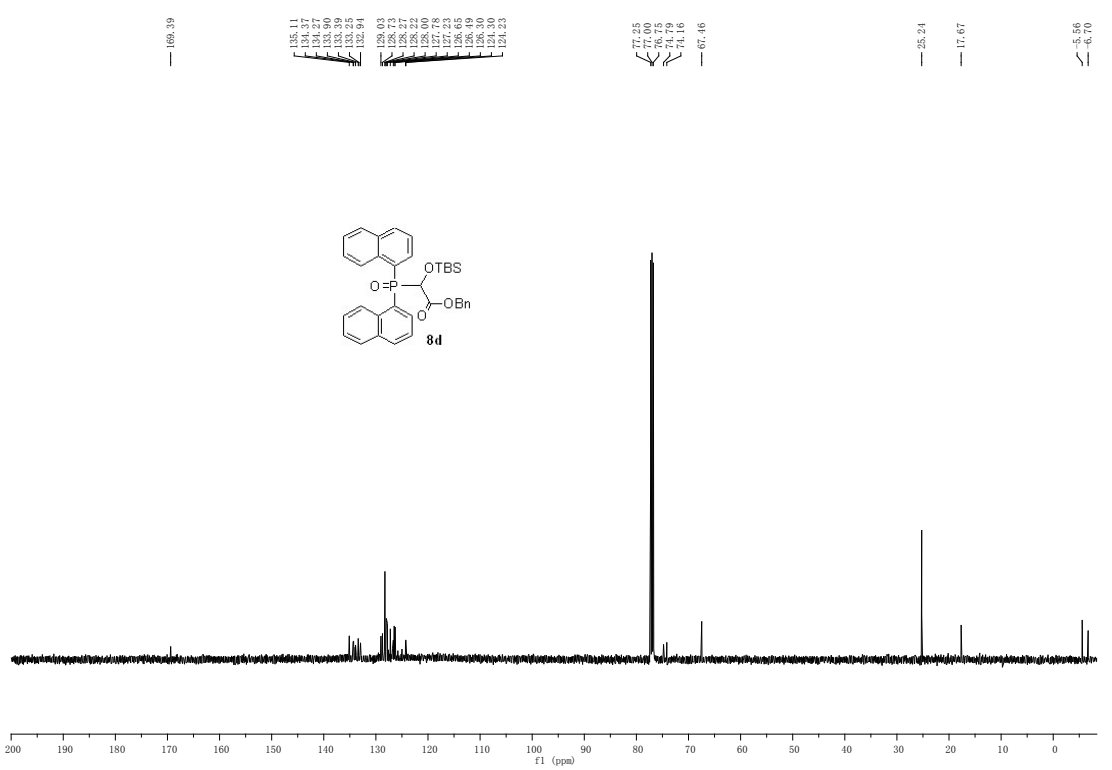
134.86
133.42
133.35
132.27
131.93
130.58
128.23
128.18
127.97
77.25
77.00
76.75
75.09
74.42
67.47
25.43
17.85
-5.54
-6.21
F3C
OTBS
O=P
OBn
F3C
O
8c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.27
9.25
8.83
8.81
8.45
8.42
8.04
7.92
7.89
7.58
7.47
7.44
7.39
7.36
7.27
7.24
7.21
7.19
7.15
7.13
5.45
5.42
5.19
5.16
5.07
5.05
0.58
-0.16
-0.84
OTBS
O=P
OBn
O
8d
f1 (ppm)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133.39
133.25
132.94
129.03
128.73
128.27
128.22
128.00
127.78
127.23
126.65
126.49
126.30
124.30
124.23
77.25
77.00
76.75
74.19
74.16
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25.24
17.67
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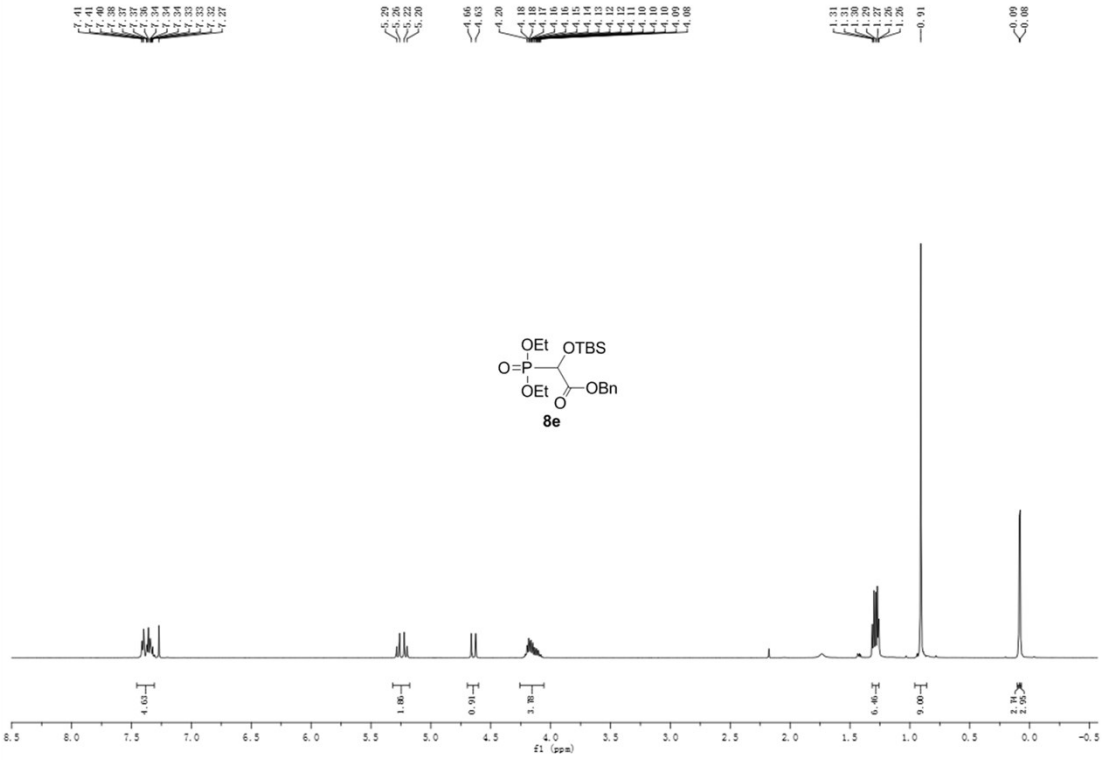
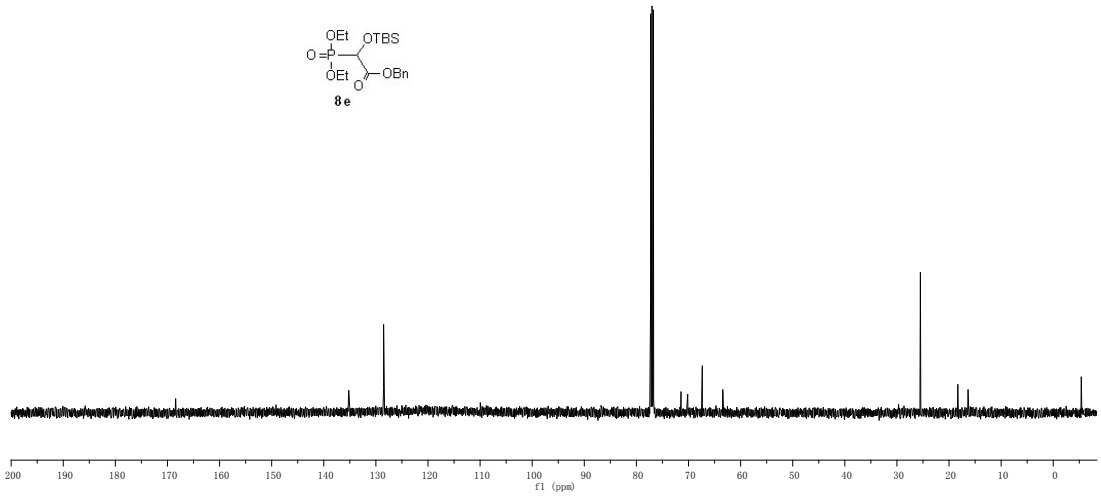
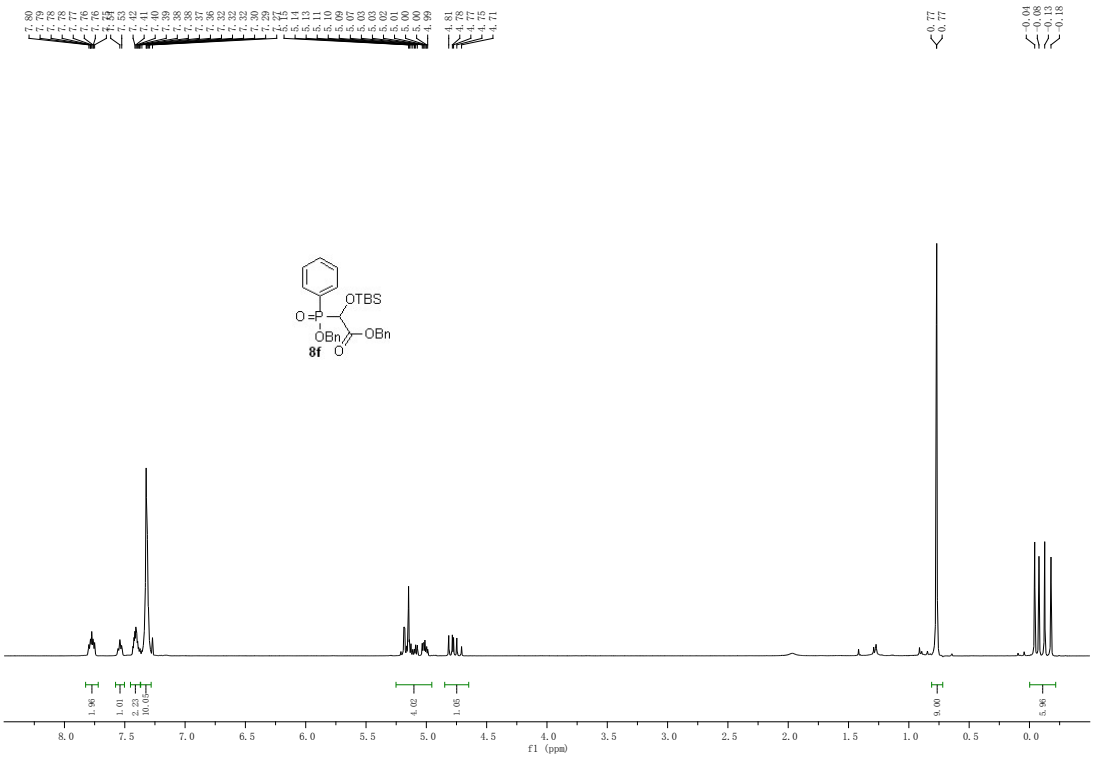
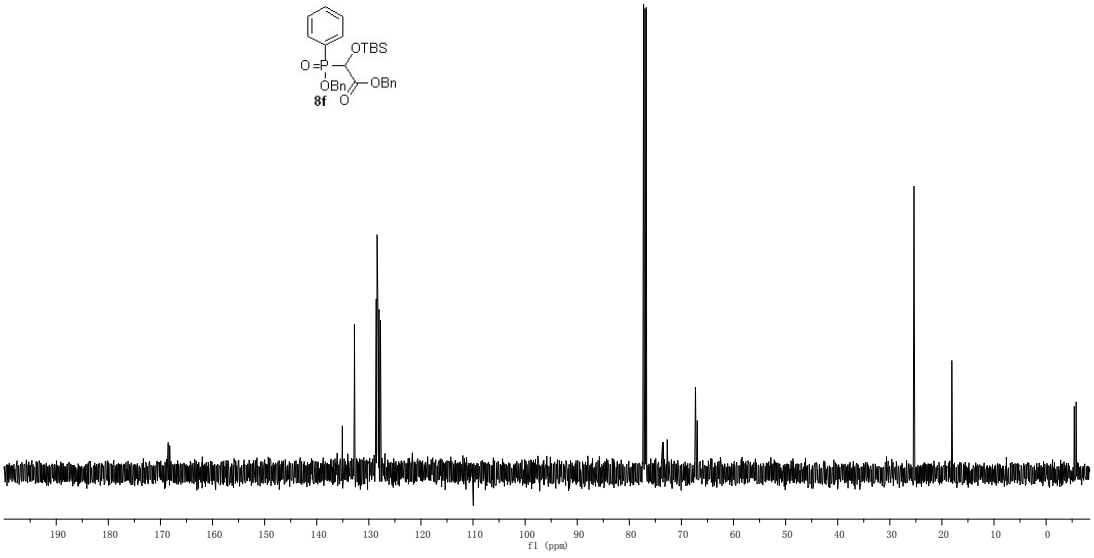
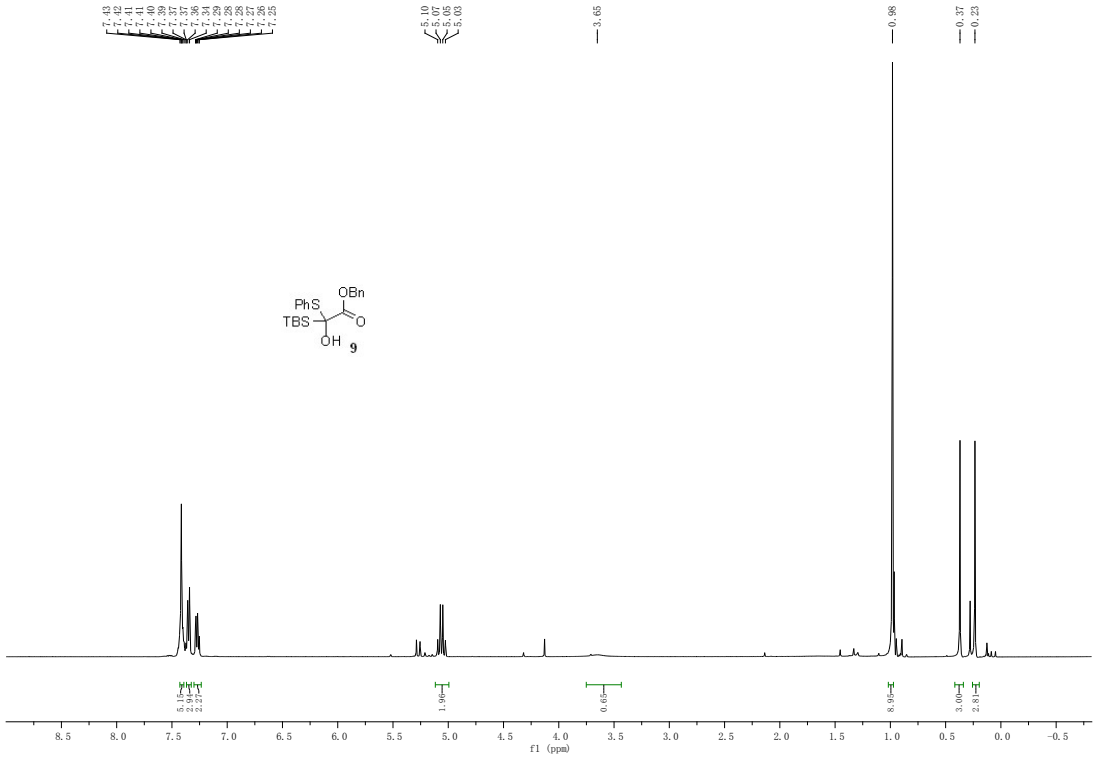
-6.70
OTBS
O=P
OBn
O
8d
f1 (ppm)


OEt
OTBS
O=P
OEt
O
OBn
8e
f1 (ppm)


OEt
OTBS
O=P
OEt
O
OBn
8e
f1 (ppm)


OTBS
OBn
OBn
O
8f
1.96
1.01
2.23
10.05
4.02
1.05
9.00
5.96
f1 (ppm)


OTBS
OBn
OBn
O
8f
f1 (ppm)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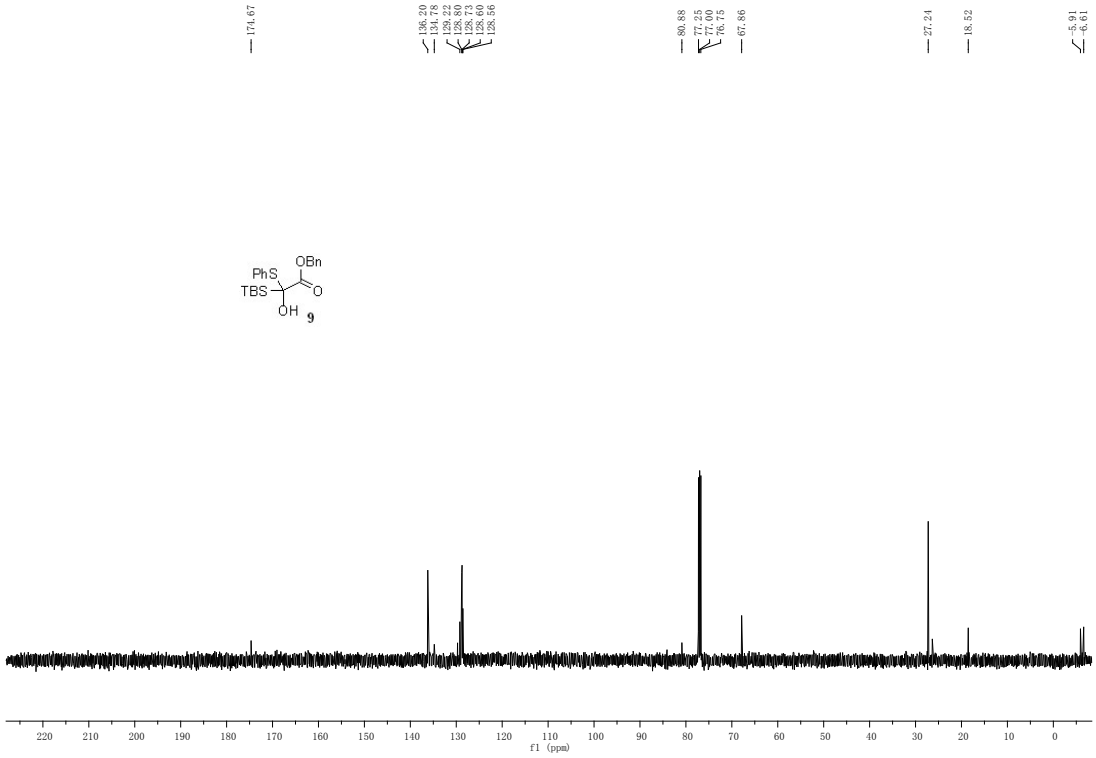
7.36
7.34
7.29
7.28
7.27
7.26
7.25
5.10
5.07
5.05
5.03
3.65
0.98
0.37
0.23
PhS
TBS
OH
OBn
O
9
5.15
2.14
2.27
1.96
0.65
8.95
3.00
2.81
f1 (ppm)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136.20
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128.73
128.60
128.56
80.88
77.25
77.00
76.75
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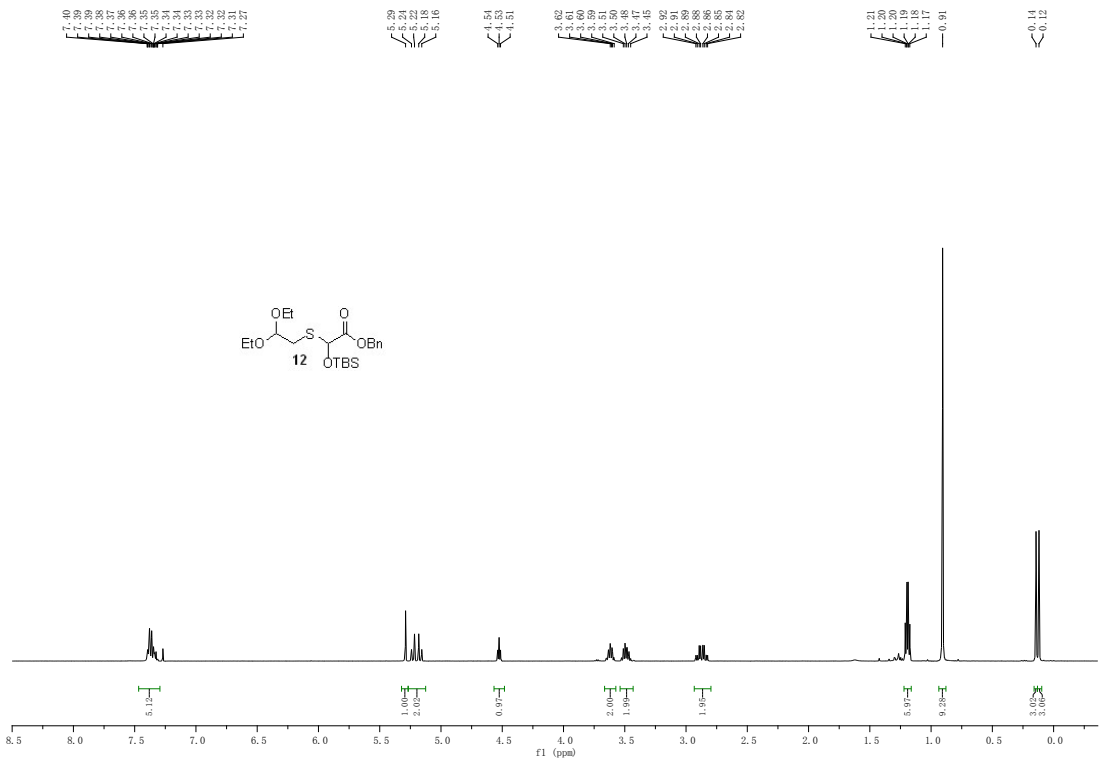
27.24
18.52
-5.91
-6.61
PhS
TBS
OH
OBn
O
9
f1 (ppm)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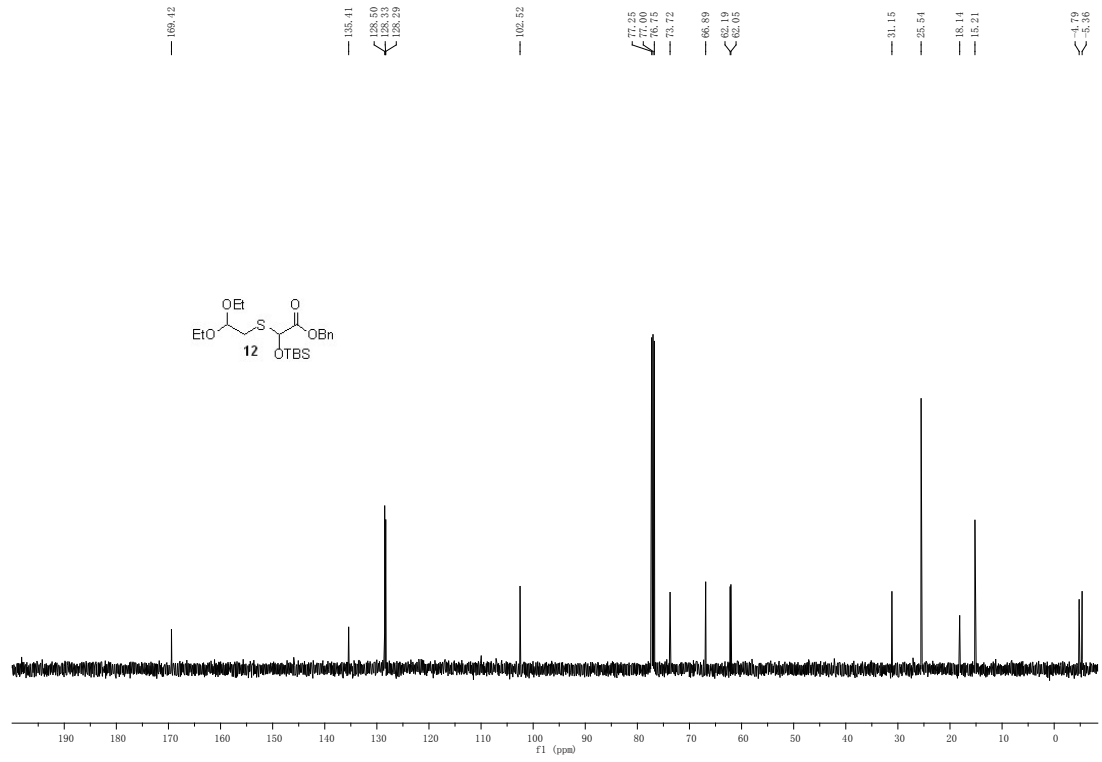
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.27
5.29
5.24
5.22
5.18
5.16
4.54
4.53
4.51
3.62
3.61
3.60
3.59
3.51
3.50
3.48
3.47
3.45
2.92
2.91
2.88
2.86
2.85
2.84
2.82
1.21
1.20
1.19
1.18
1.17
0.91
0.14
0.12
OEt
O
EtO
S
OBn
12
OTBS
5.12
1.00
2.03
0.97
2.00
1.99
1.95
5.97
9.28
3.02
3.00
f1 (ppm)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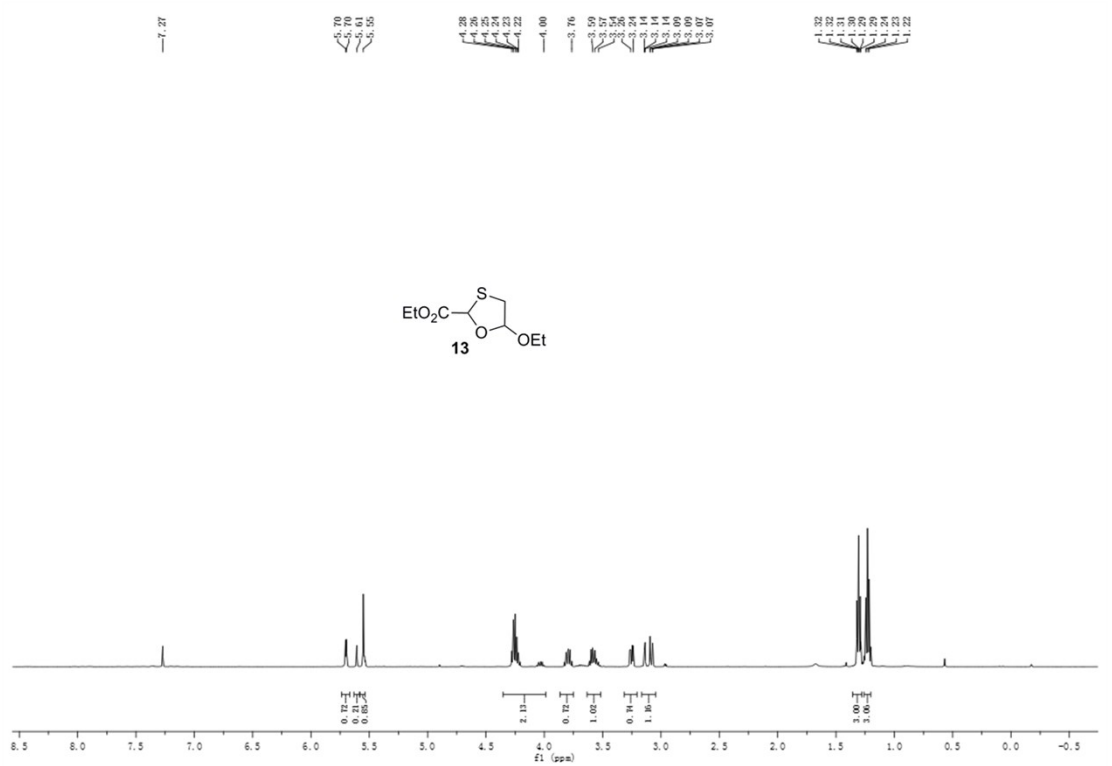
128.50
128.33
128.29
102.52
77.25
77.00
76.75
73.72
66.89
62.19
62.05
31.15
25.54
18.14
15.21
-4.79
-5.36
OEt
O
EtO
S
OBn
12
OTBS
f1 (ppm)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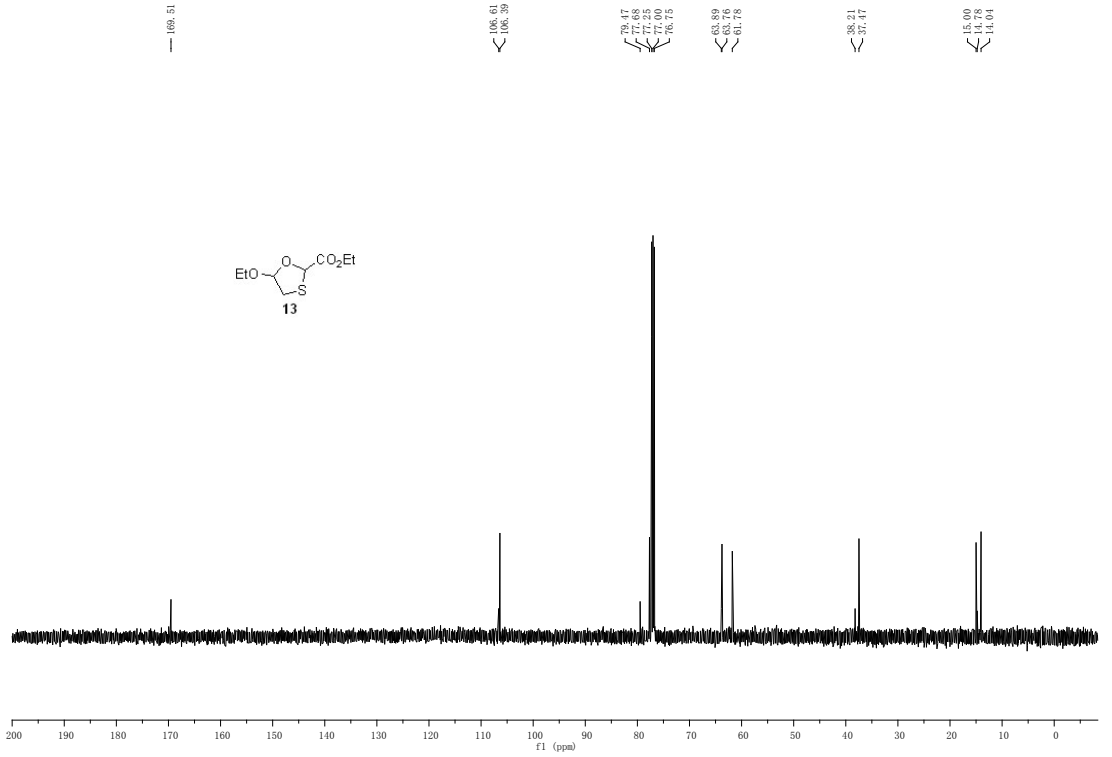
5.70
5.61
5.55
4.28
4.26
4.25
4.24
4.23
4.22
4.00
3.76
3.59
3.57
3.55
3.26
3.24
3.14
3.14
3.09
3.09
3.07
3.07
1.32
1.32
1.31
1.30
1.29
1.29
1.24
1.23
1.22
EtO2C
S
O
OEt
13
0.72
0.21
0.65
2.13
0.72
1.02
0.94
1.16
3.00
3.05
f1 (ppm)


169.51
106.61
106.39
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77.25
77.00
76.75
63.89
63.76
61.78
38.21
37.47
15.00
14.78
14.04
EtO
O
CO2Et
S
13
f1 (ppm)