Supporting Information

Catalyst-Controlled Switchable Reactions of β-Keto Acids to Silyl Glyoxylates

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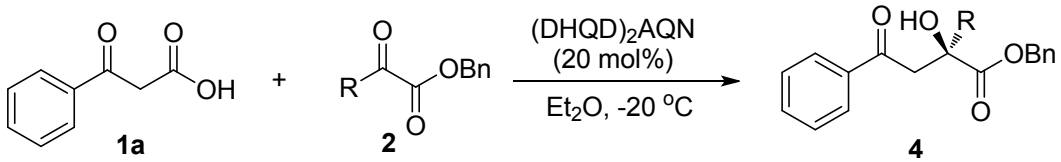
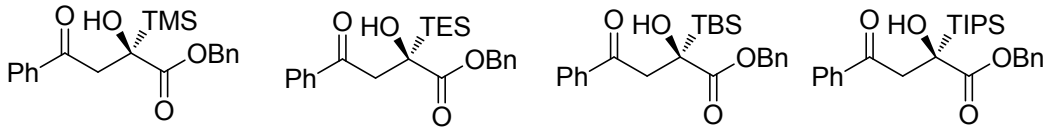
1. Asymmetric decarboxylative addition reaction of β-keto acids to silyl glyoxylate

1.1 General procedure for the asymmetric decarboxylative addition reaction of β-keto acids to silyl glyoxylates

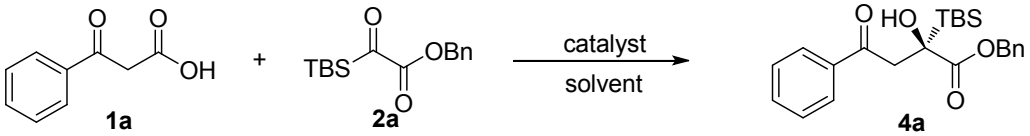
The mixture of *β*-keto acid (**1**, 0.20 mmol) and benzyl 2-(*tert*-butyldimethylsilyl)-2-oxoacetate (**2a**, 0.10 mmol) in solvent (1.0 mL) were added catalyst (20 mol%). After stirring for the indicated time, the mixture was concentrated in vacuo and the residue was purified via flash chromatography to give the desired chiral product **4a**.

1.2 Investigation of silicon substituent effect



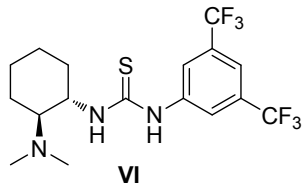


1.3 Investigation of the catalyst effect and solvent effect[a]



Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	**VI**	THF	rt	17	27	11
2	**VII**	THF	rt	17	35	8
3	**VIII**	THF	rt	17	50	-40
4	**XI**	THF	rt	17	46	0
5	**XII**	THF	rt	17	43	2

6	$(DHQD)_2AQN$	THF	rt	24	11	50
7	Cinchonine	THF	rt	1	69	24
8	Quinine	THF	rt	2	36	5
9	$(DHQD)_2AQN$	DCM	rt	18	23	25
10	$(DHQD)_2AQN$	toluene	rt	18	trace	ND
11	$(DHQD)_2AQN$	MeOH	rt	12	32	-24
12	$(DHQD)_2AQN$	EtOH	rt	12	22	-48
13	$(DHQD)_2AQN$	ACN	rt	12	trace	ND
14	$(DHQD)_2AQN$	DMF	rt	12	trace	ND
15	$(DHQD)_2PHAL$	THF	rt	16	13	-43
16	$(DHQD)_2PYR$	THF	rt	16	16	-26
17	$(DHQ)_2PHAL$	THF	rt	16	25	24
18	$(DHQD)_2AQN$	THF	0	16	29	59
19	$(DHQD)_2AQN$	Et_2O	0	16	62	72
20	$(DHQD)_2AQN$	Et_2O	-20	16	45	78
21	$(DHQ)_2AQN$	Et_2O	-20	24	39	64
22	$(DHQD)_2AQN$	THF	-20	16	29	59
23	$(DHQD)_2AQN$	TBME	-20	16	46	73
24	$(DHQD)_2AQN$	EtOAc	-20	16	40	64
25	$(DHQD)_2AQN$	CPME	-20	24	48	70
26	$(DHQD)_2AQN$	DCE	-20	24	trace	ND
27	$(DHQD)_2AQN$	$(i\text{-}Pr)_2O$	-20	24	trace	ND



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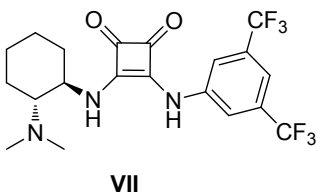

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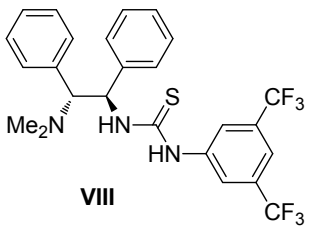

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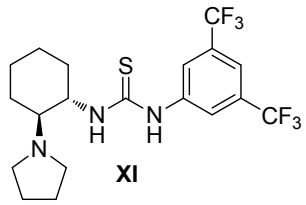

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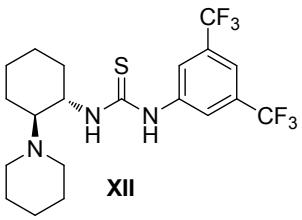
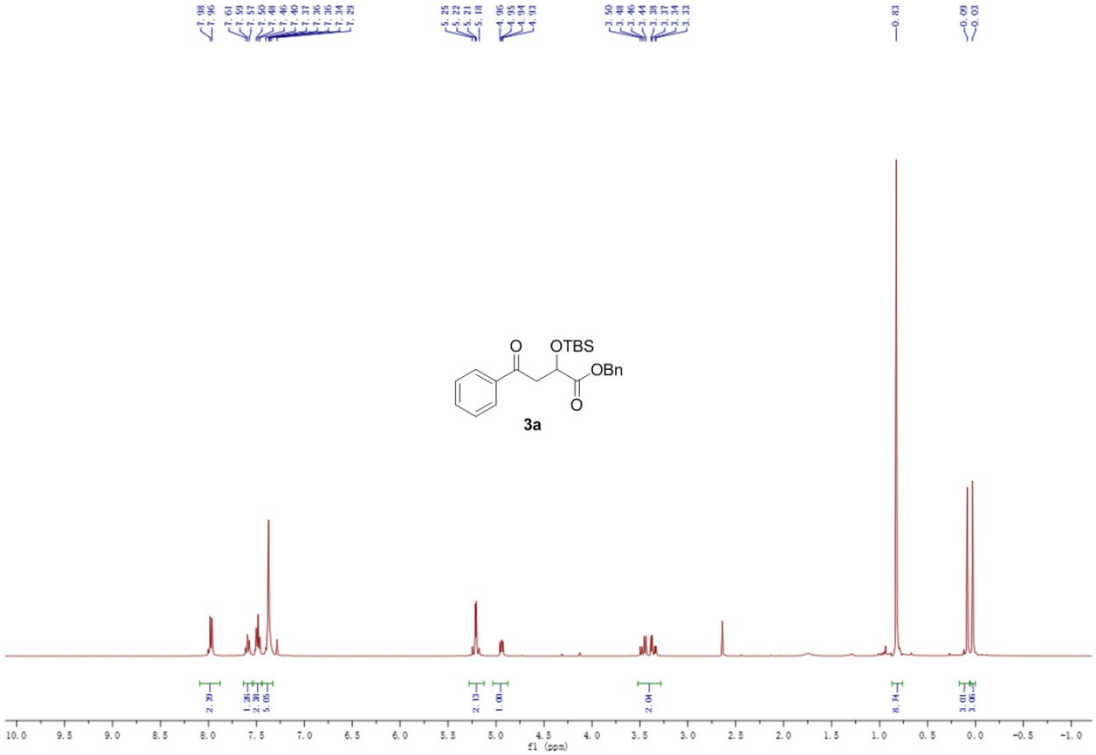
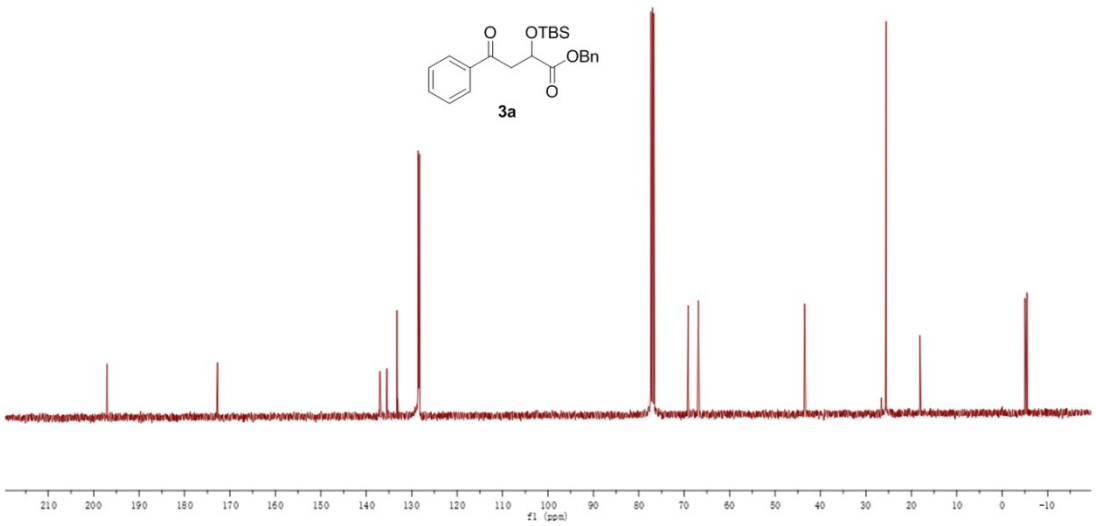


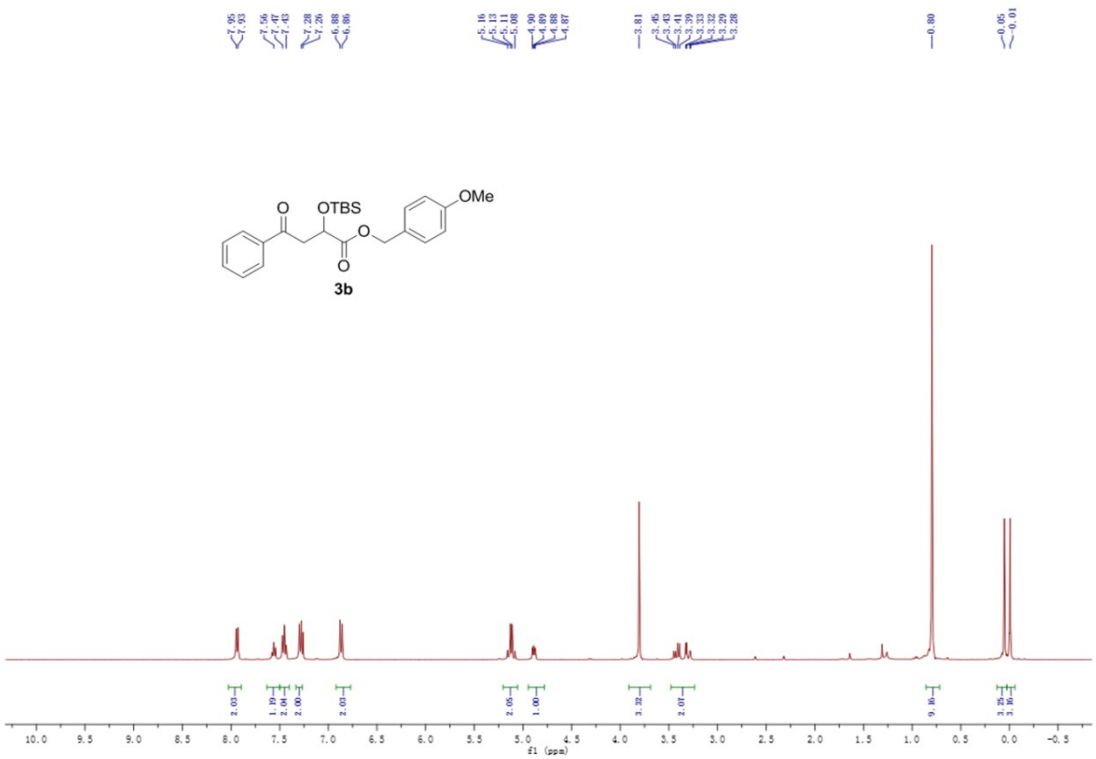
XII

[a] Reactions were performed with 0.2 mmol of **1**, 0.10 mmol of **2a**, and 20 mol% of the catalyst in 1.0 mL of solvent. [b] Isolated yield after purification by column chromatography. [c] Determined by chiral HPLC analysis.

2. ^{1}H and ^{13}C NMR spectra of the products



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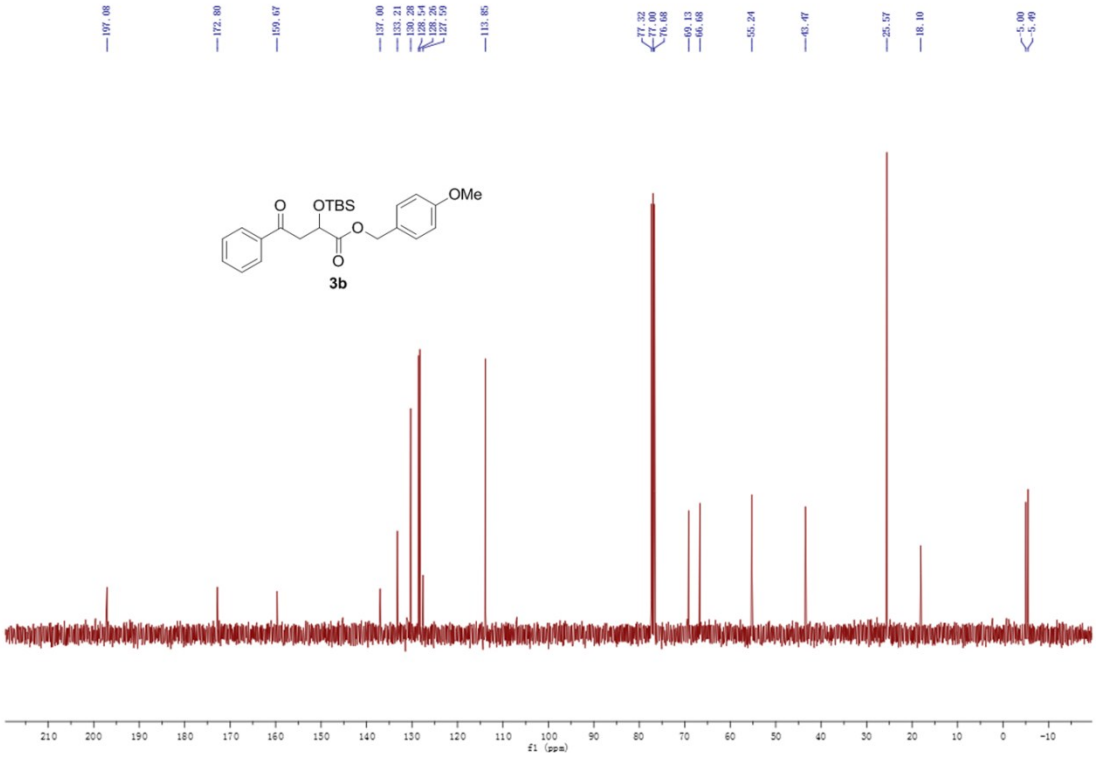
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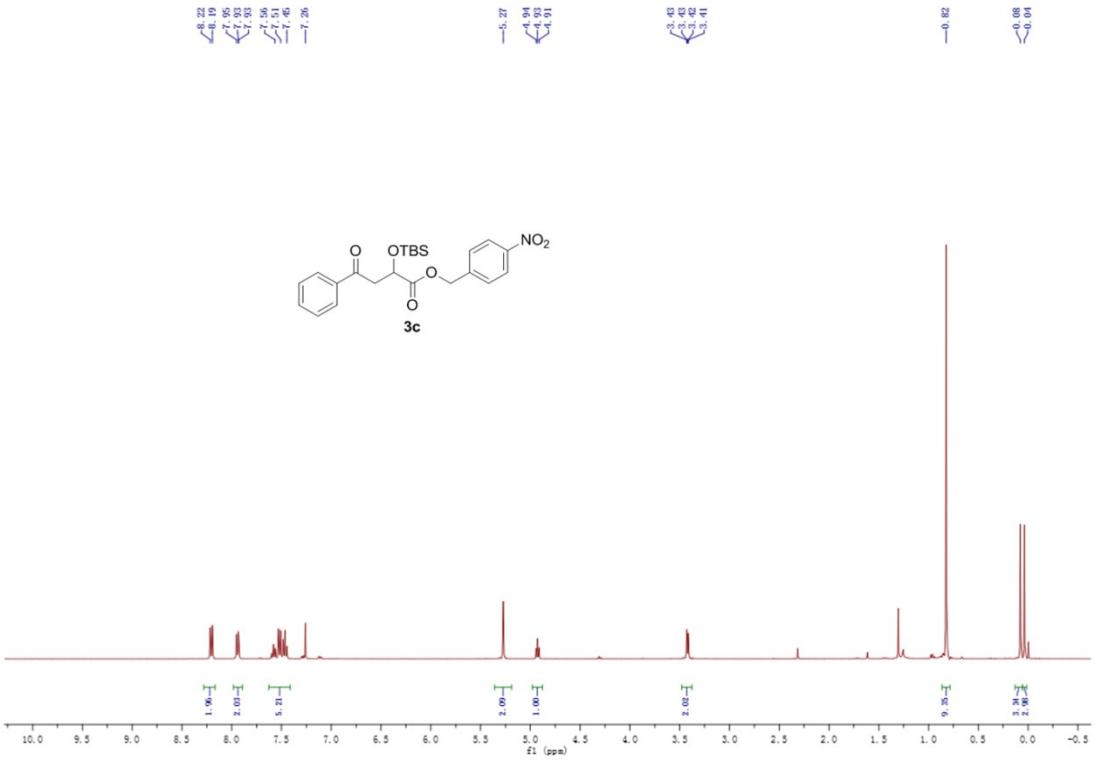
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O
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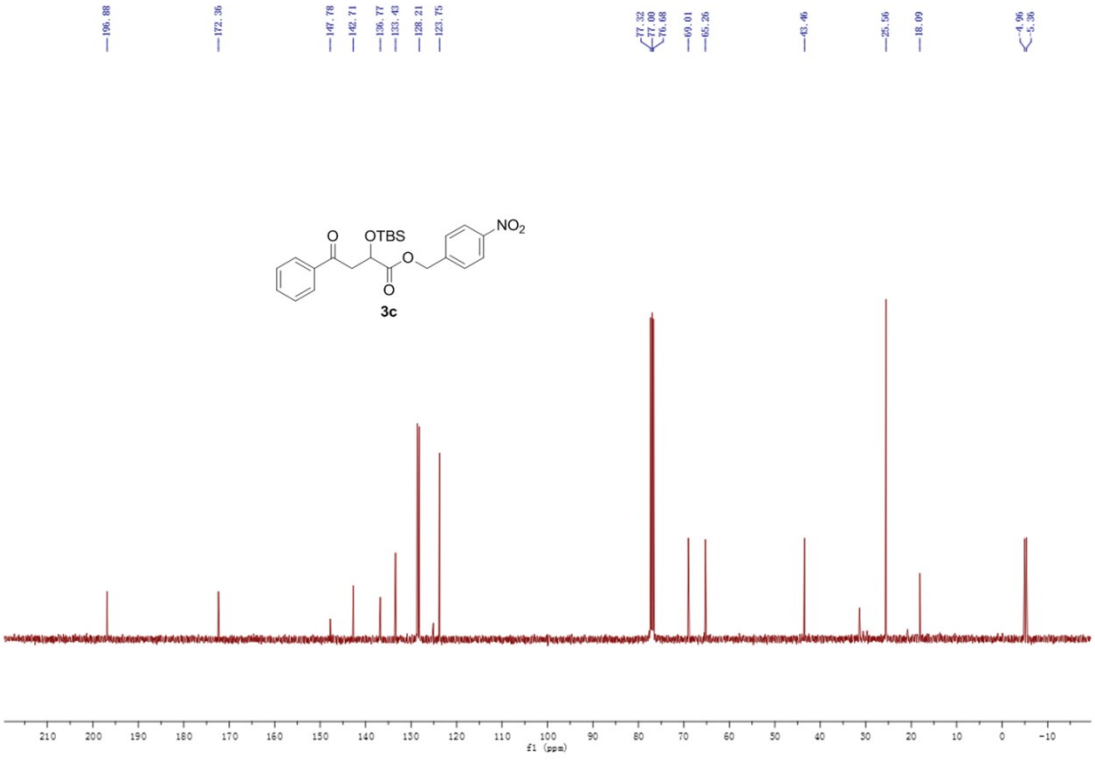
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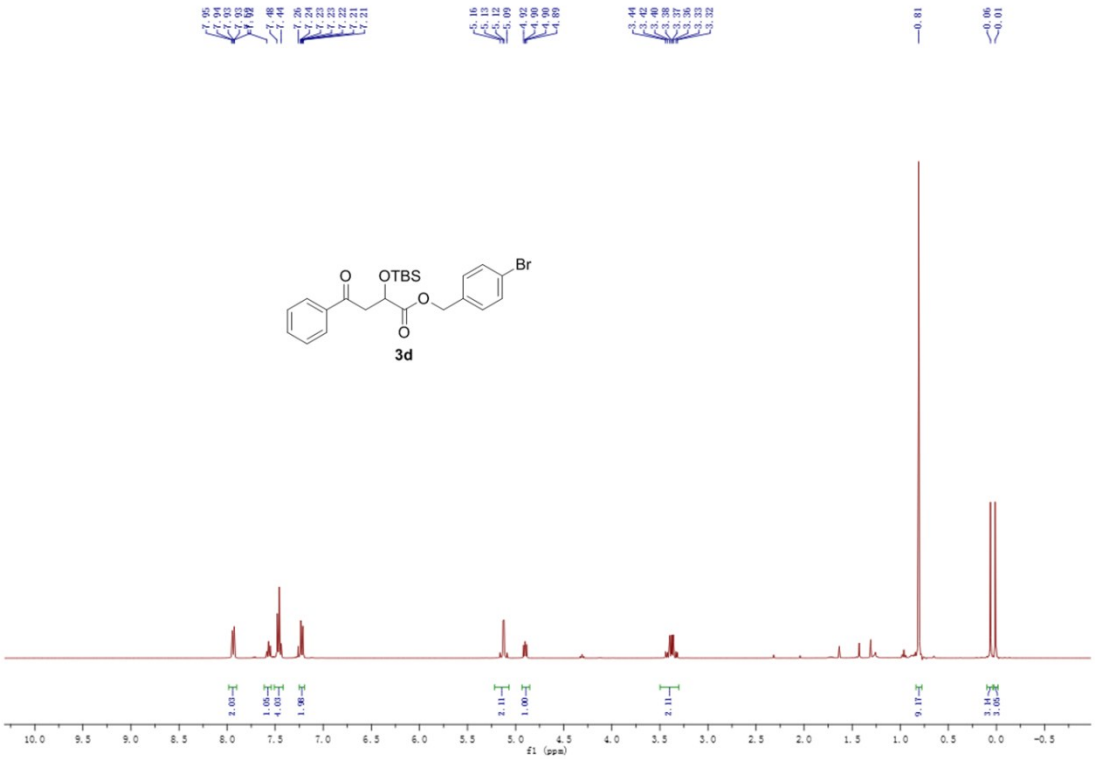
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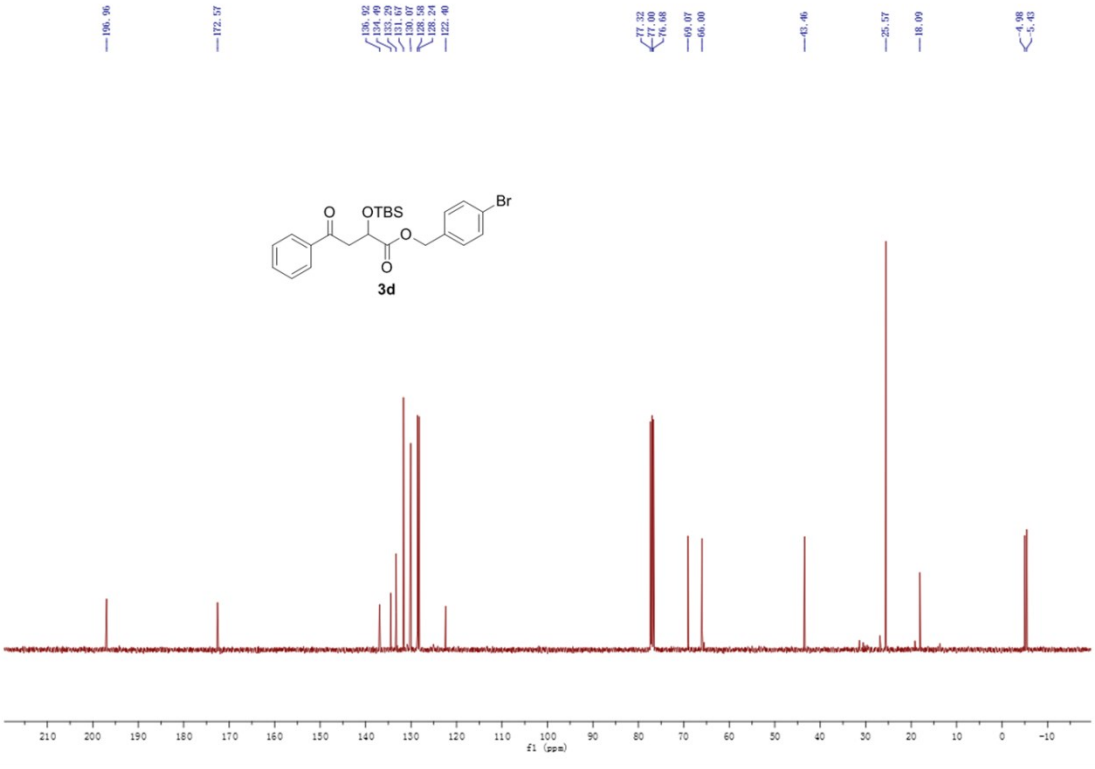
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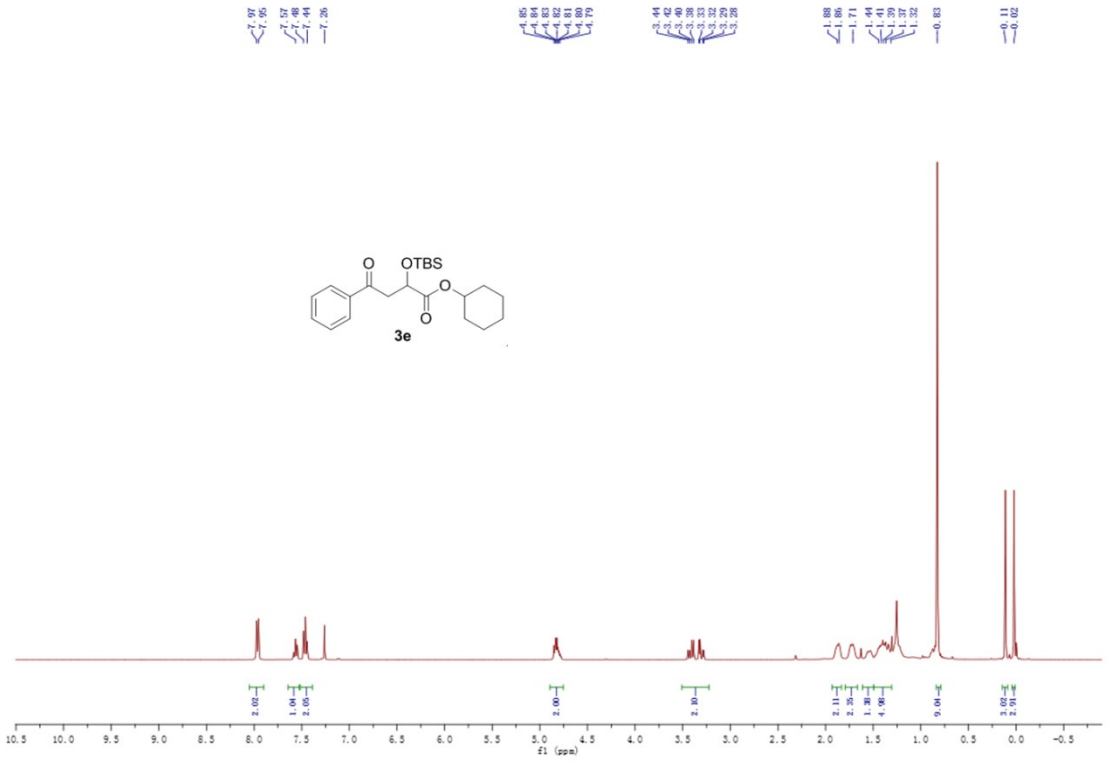
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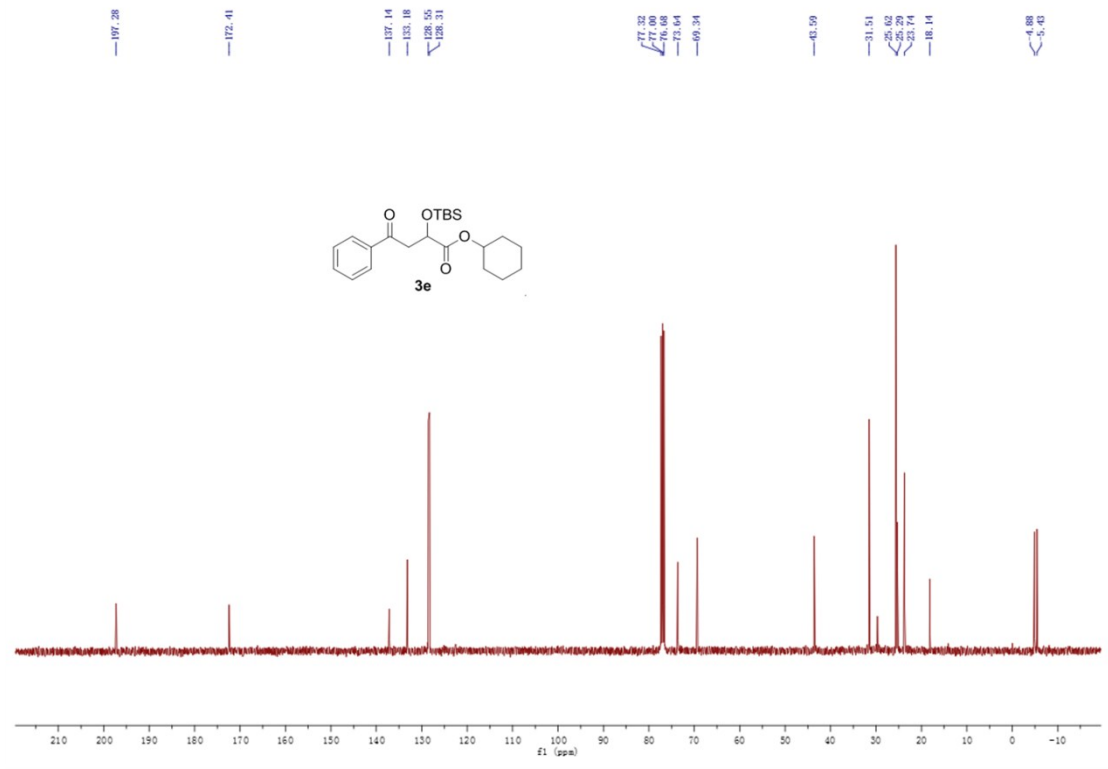
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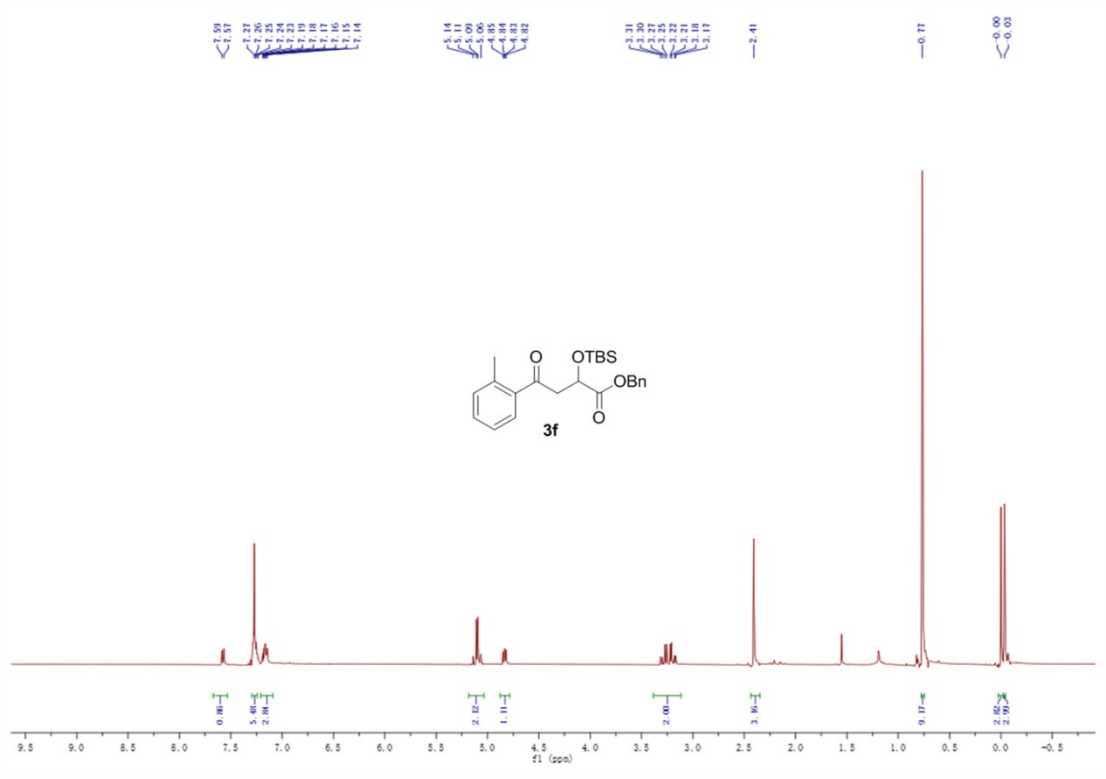
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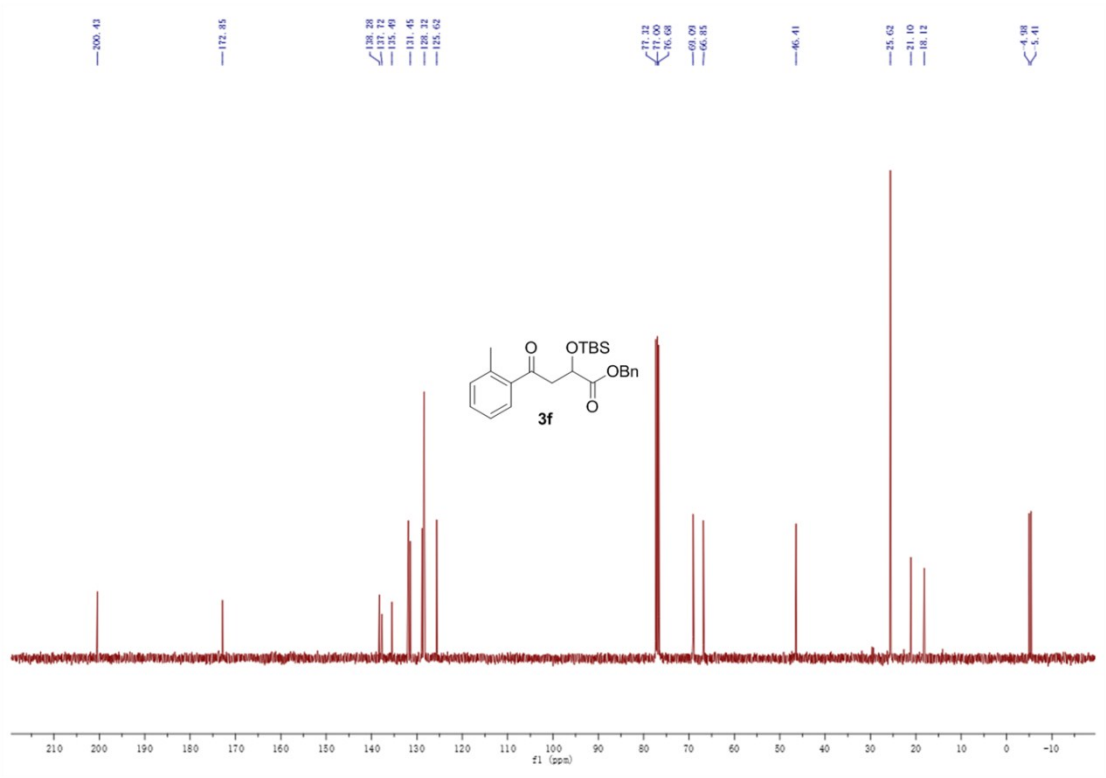
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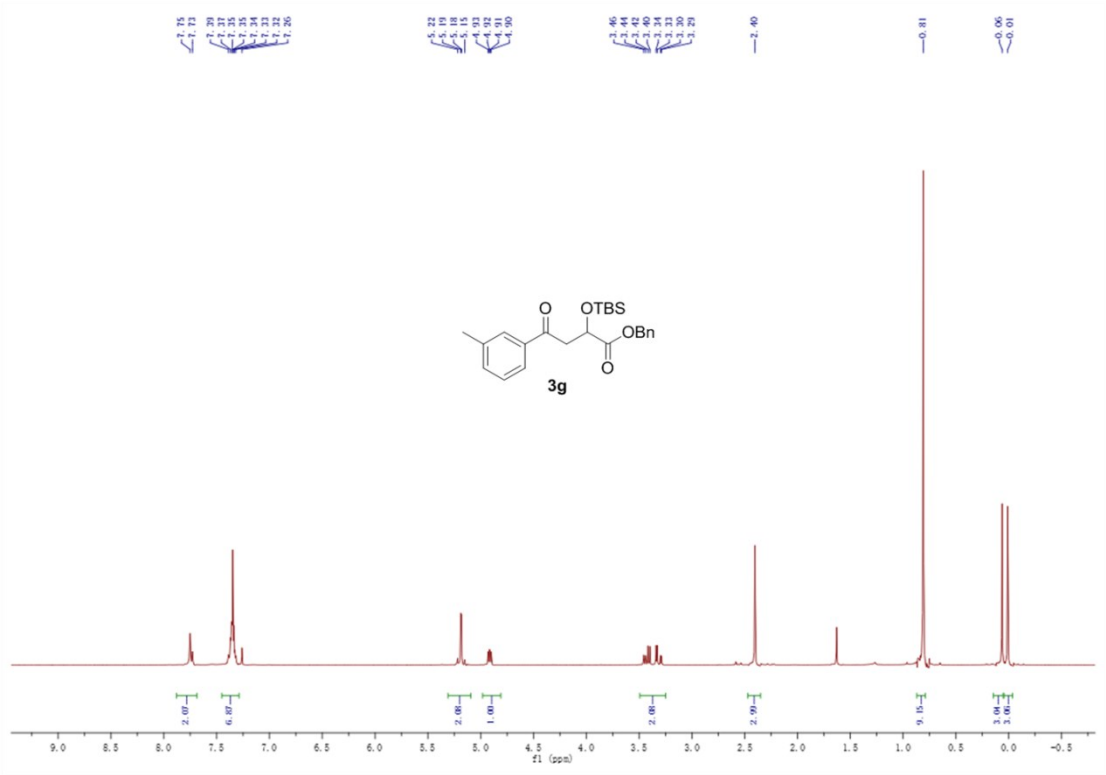
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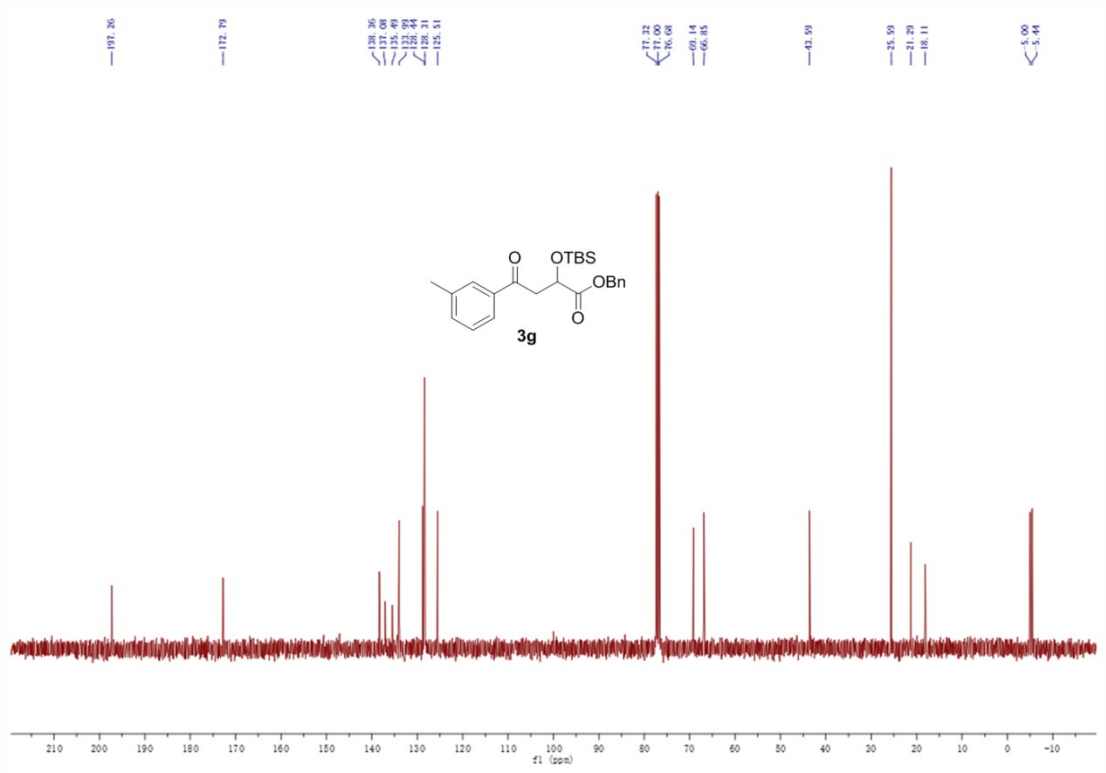
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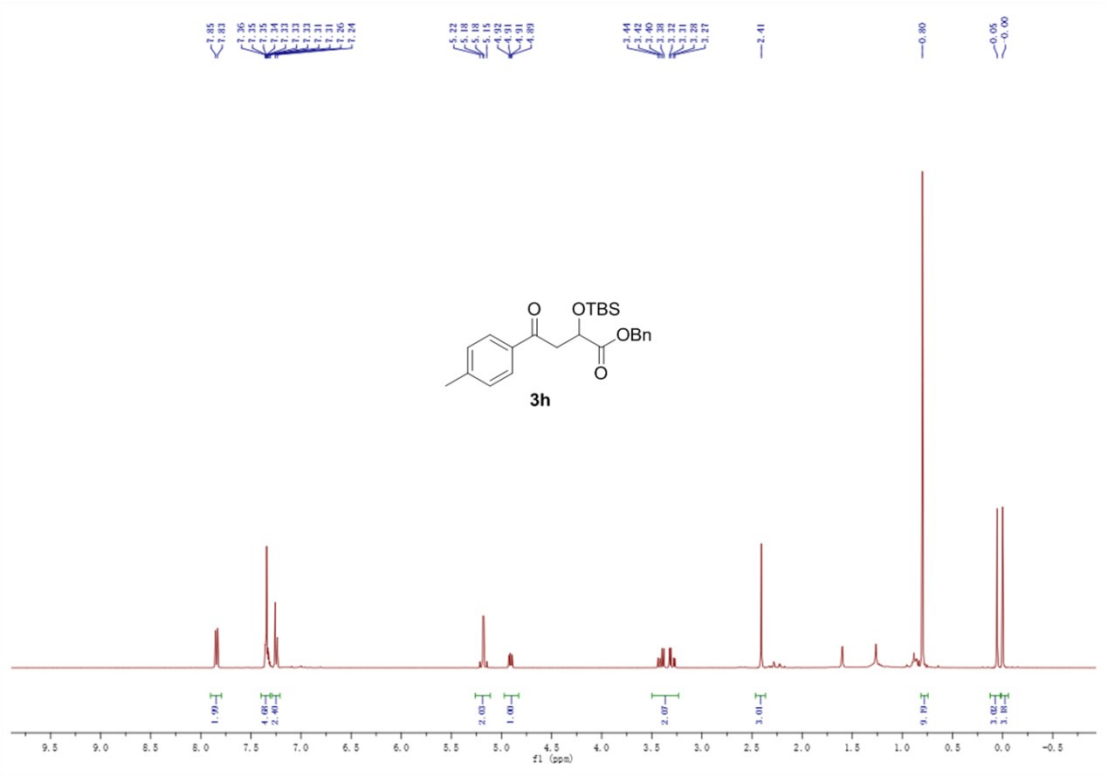
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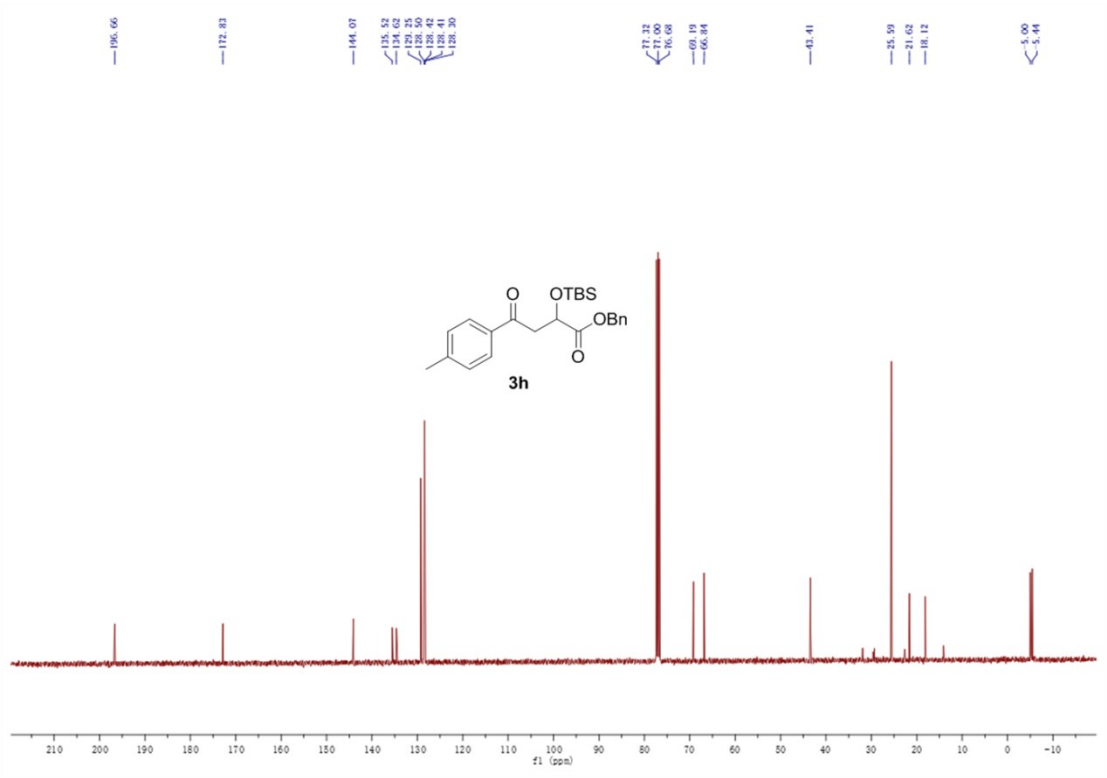
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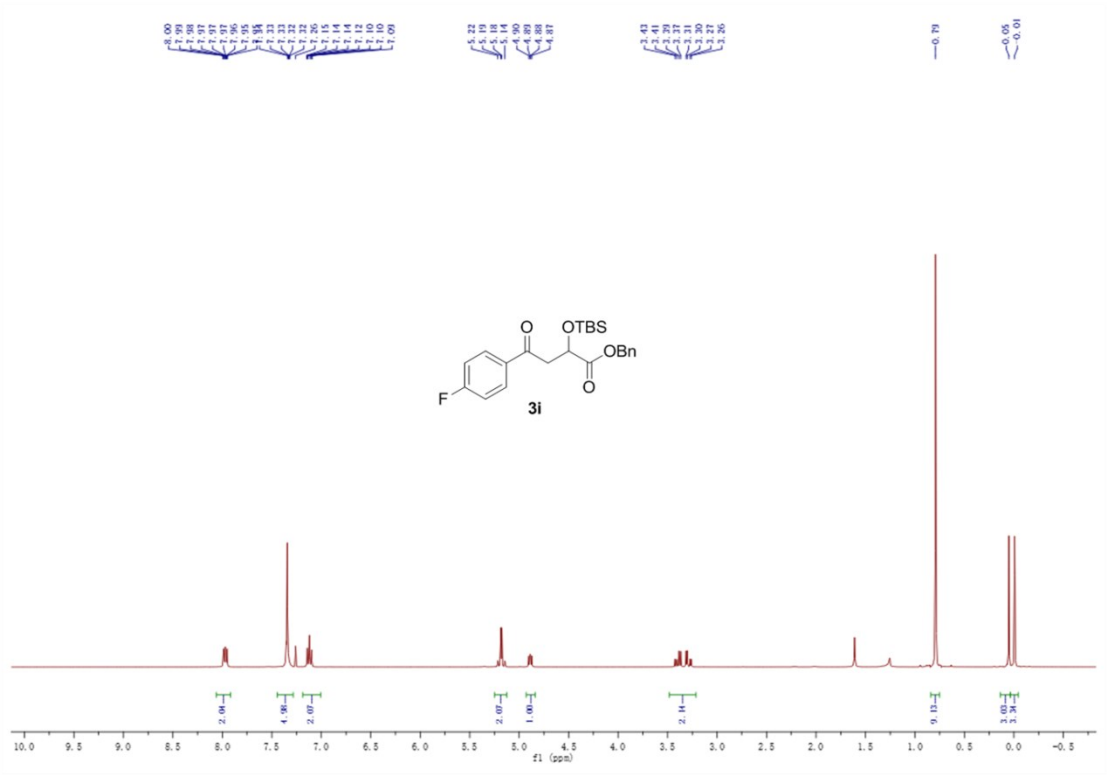
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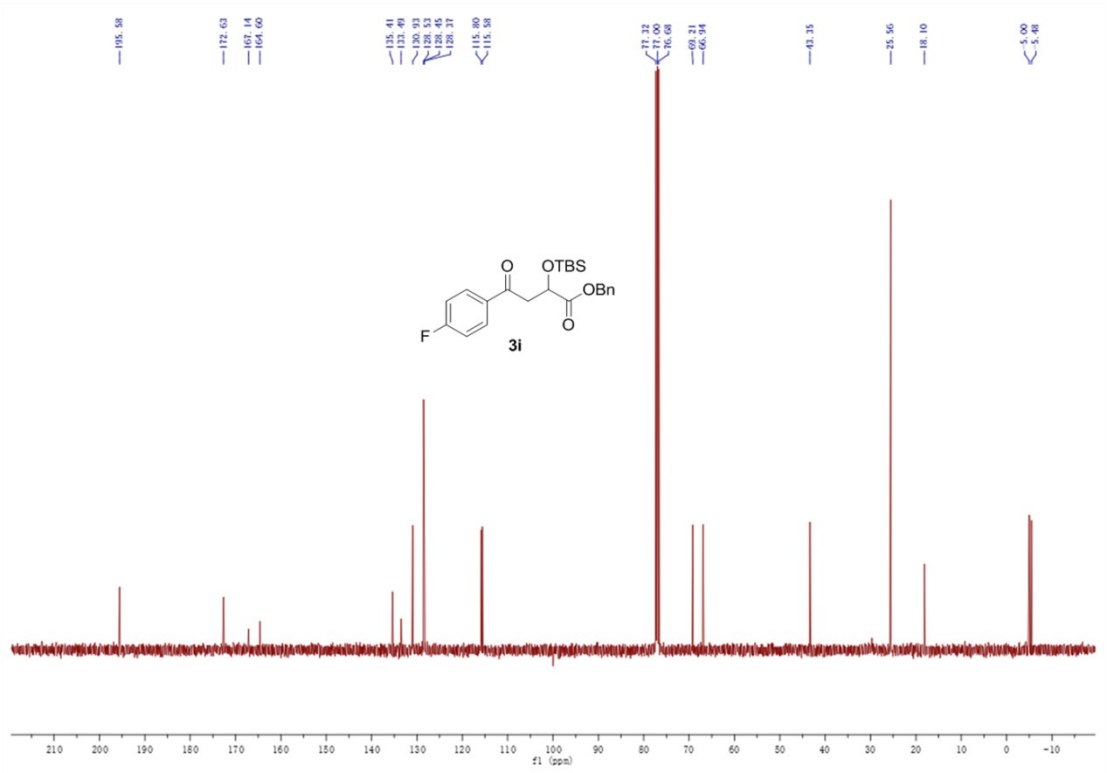
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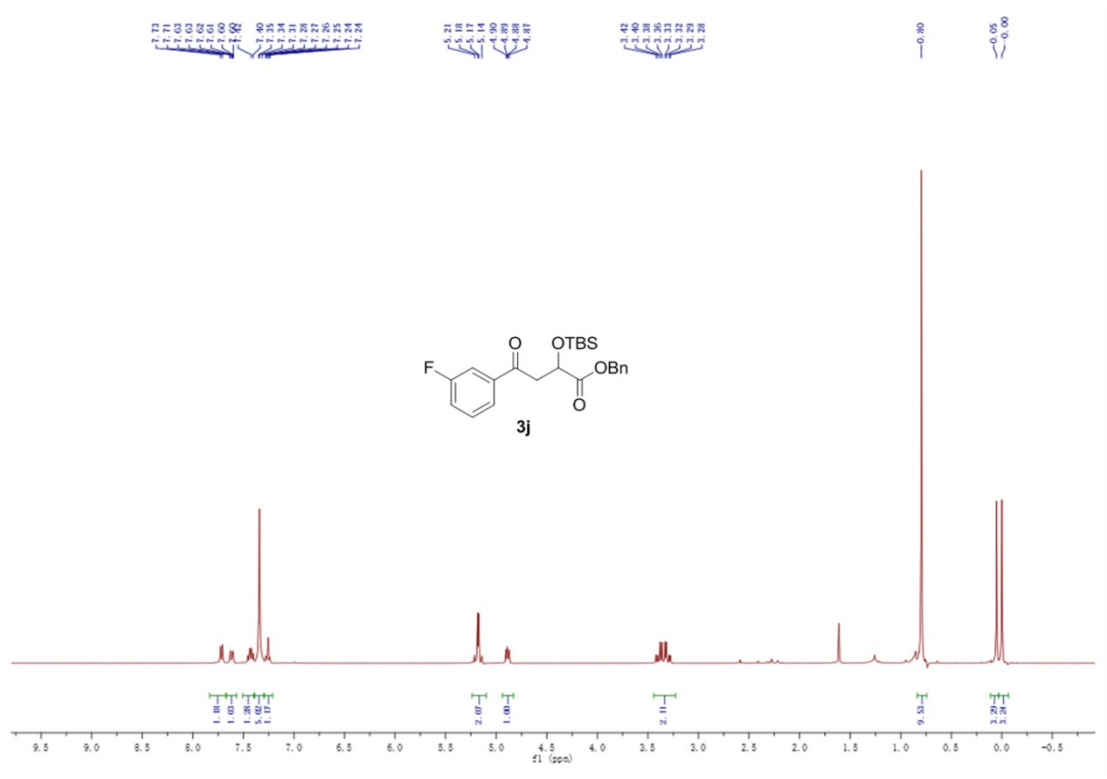
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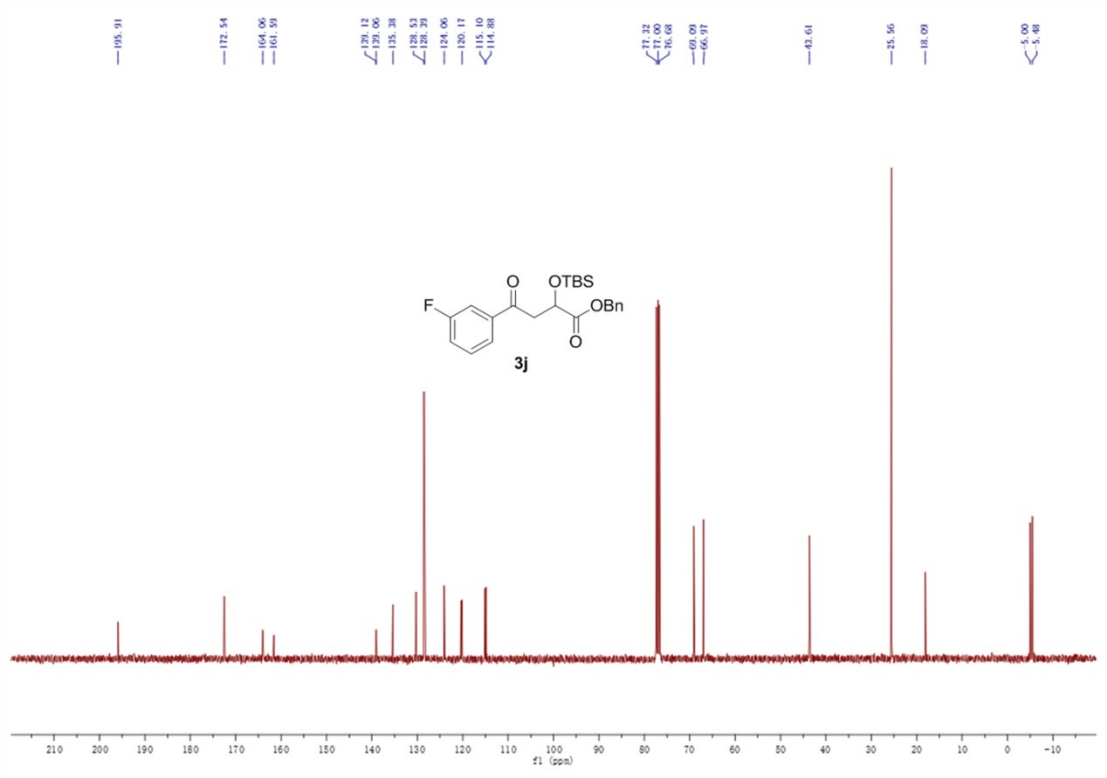
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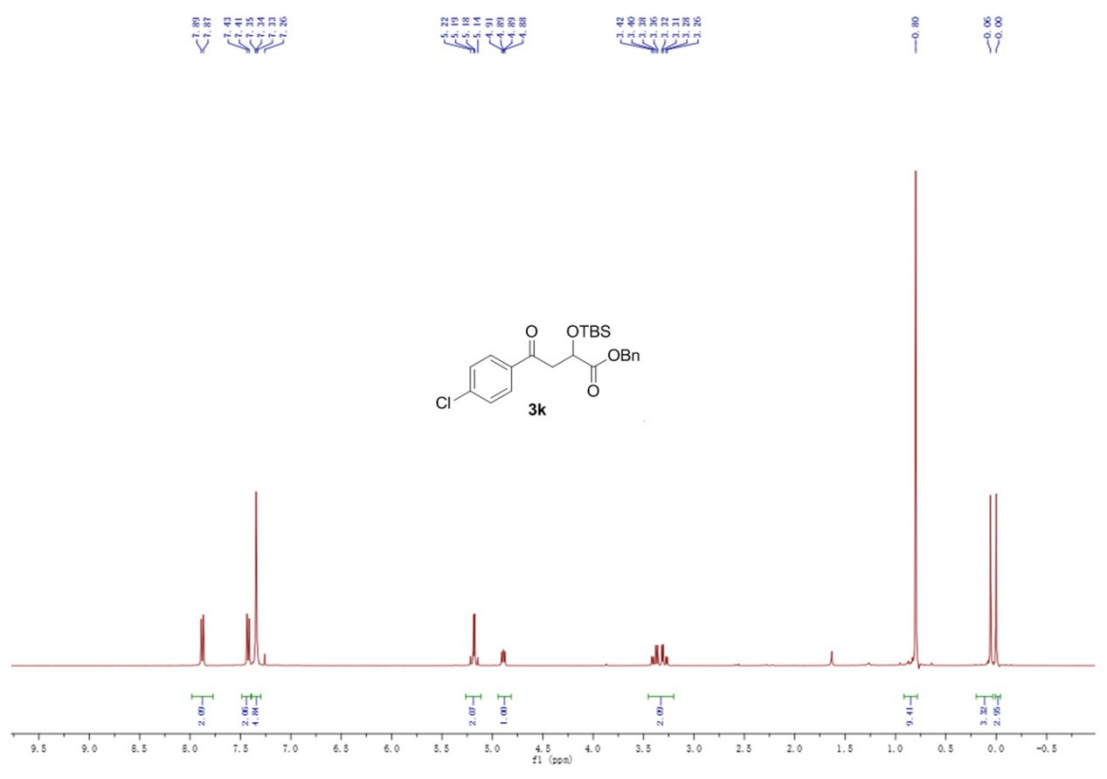
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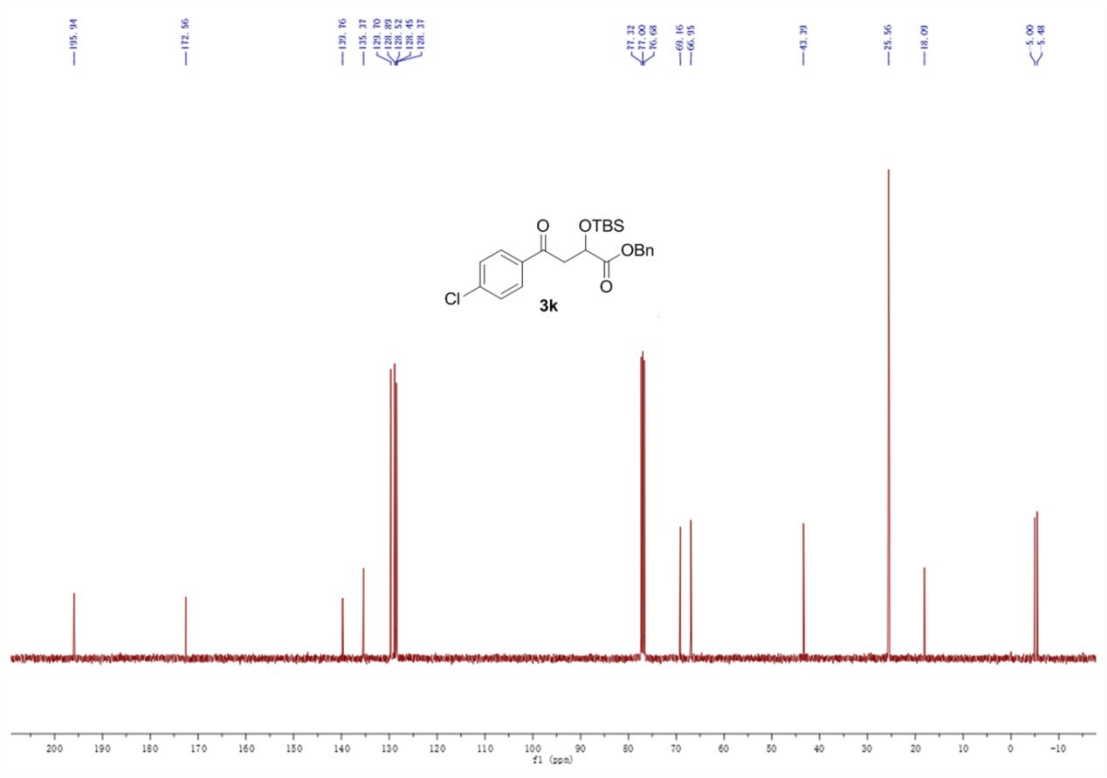
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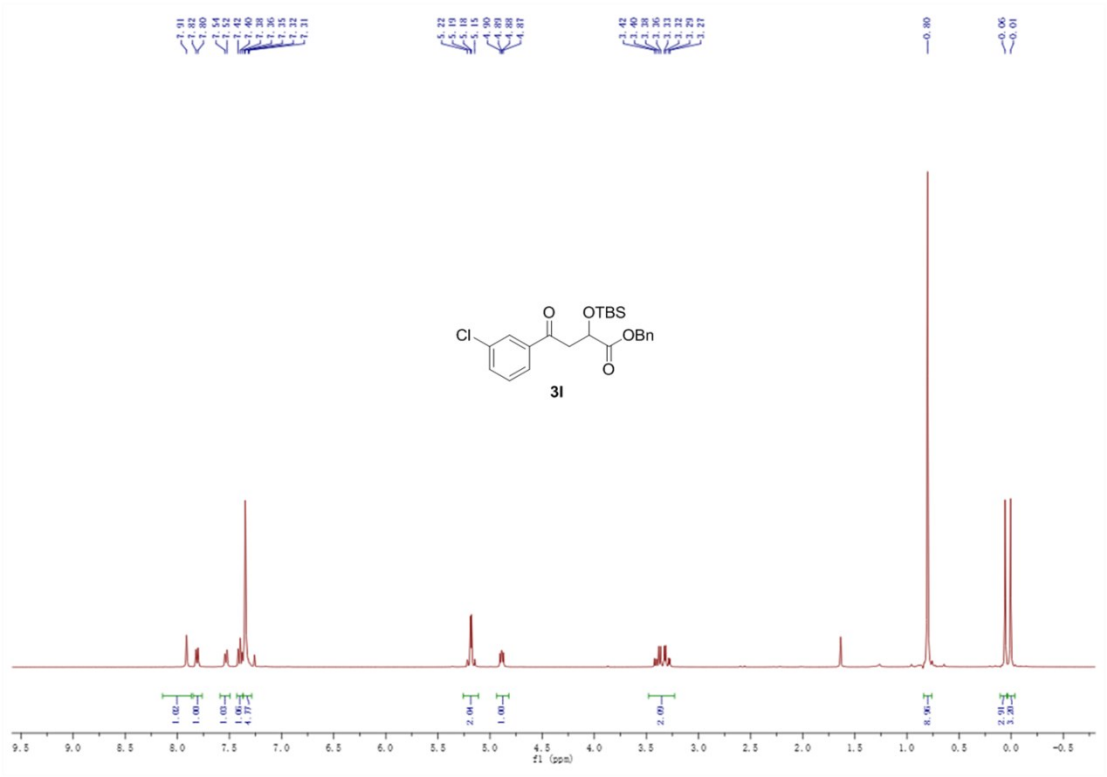
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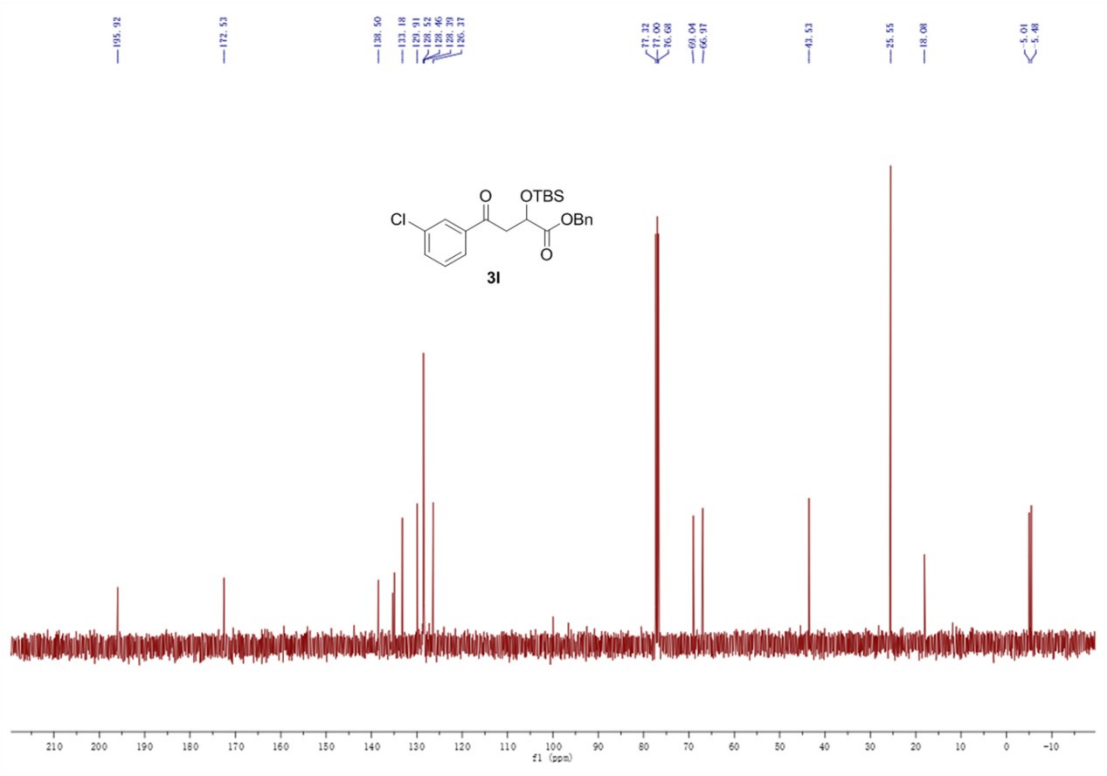
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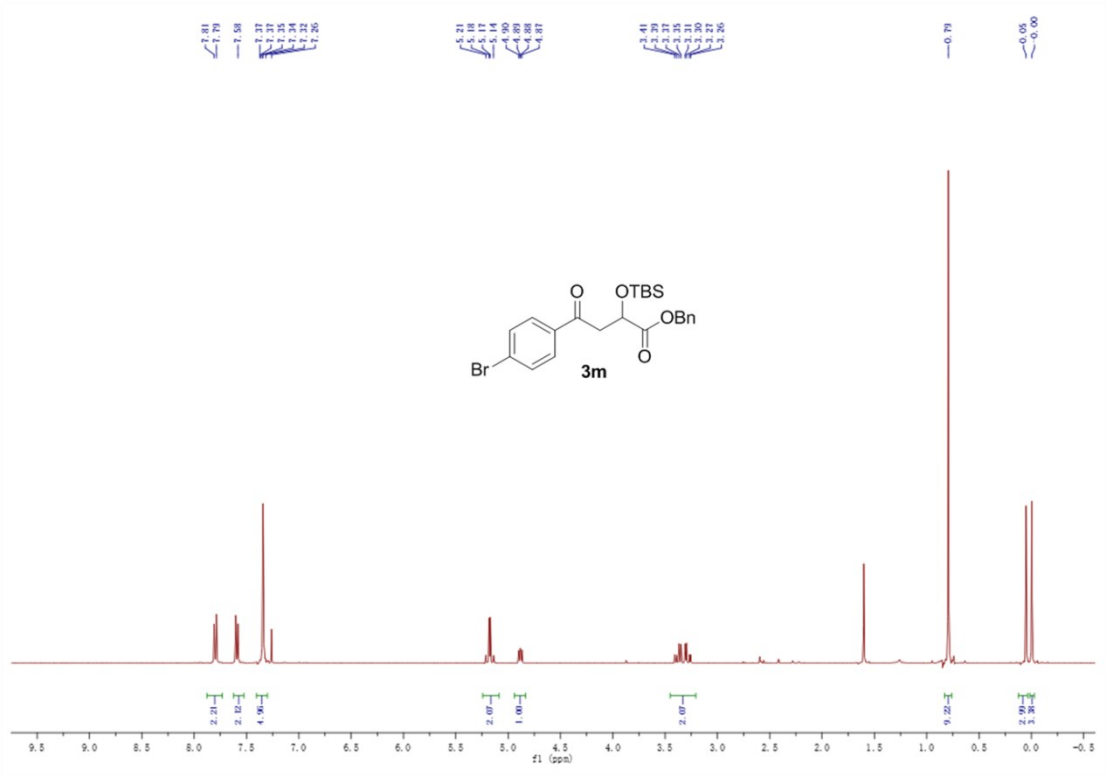
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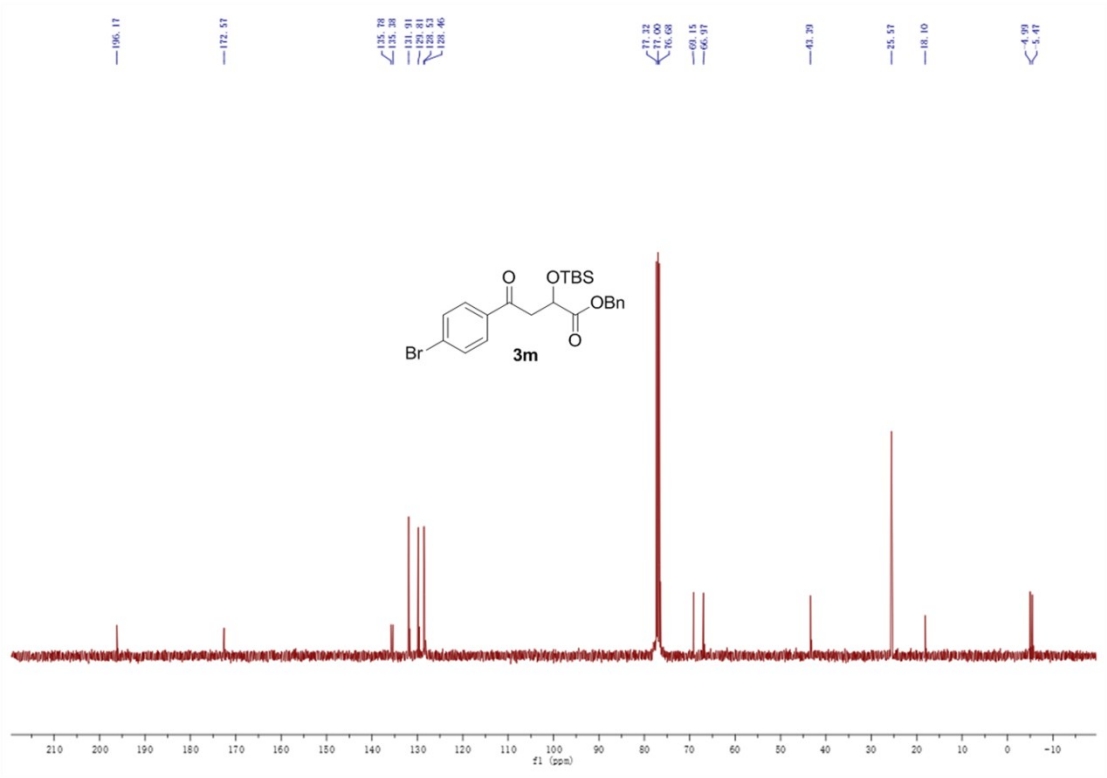
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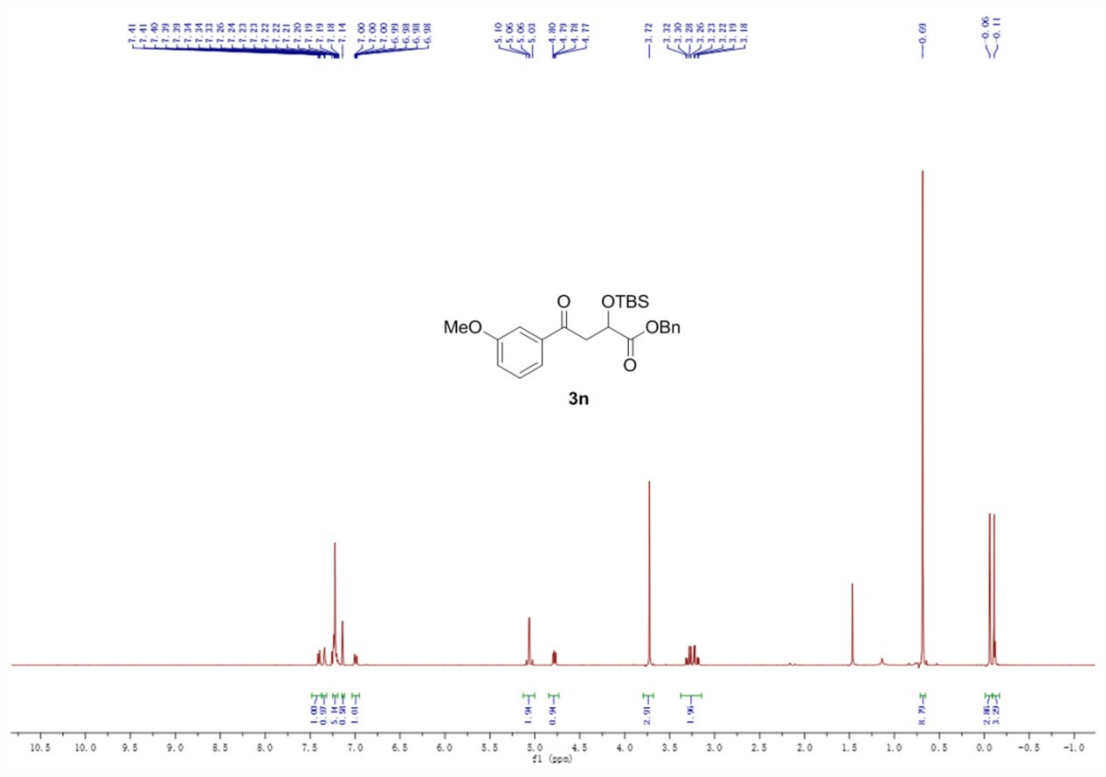
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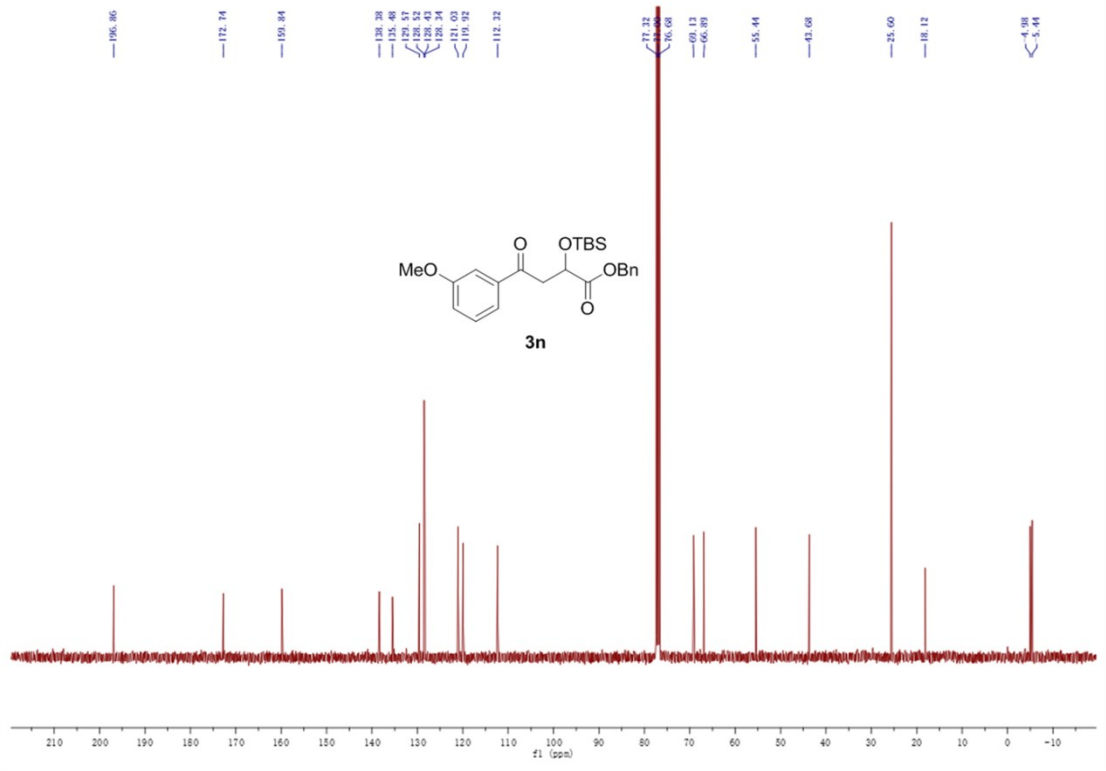
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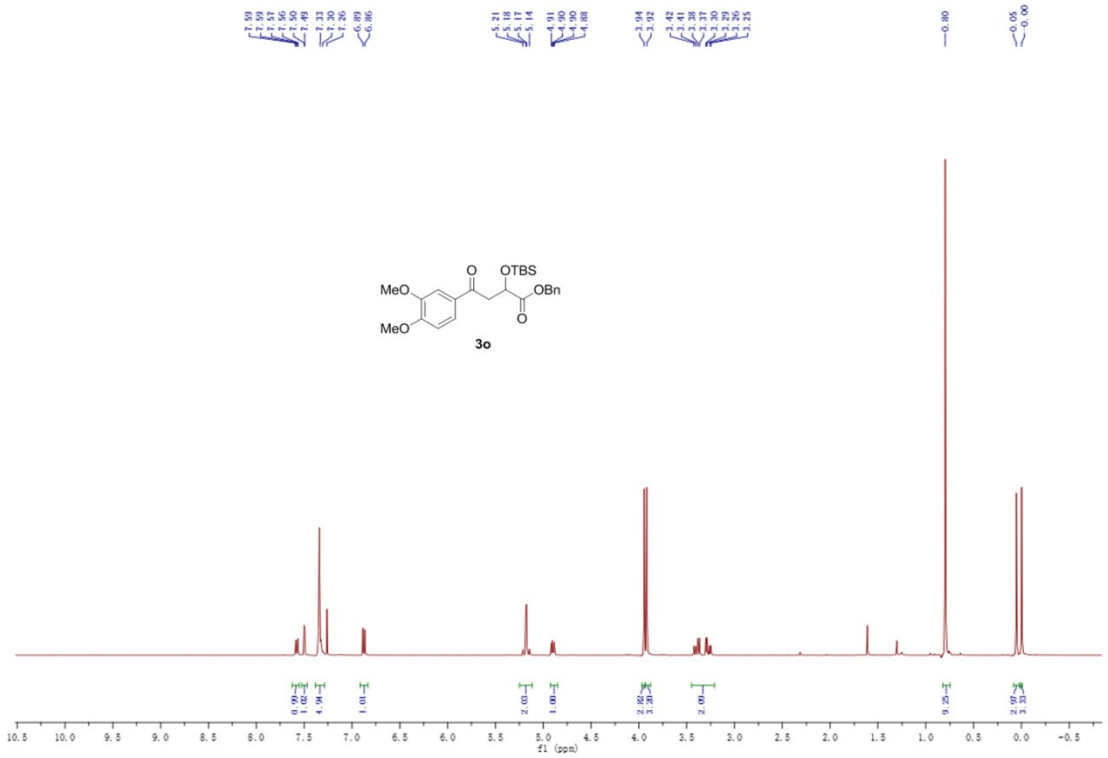
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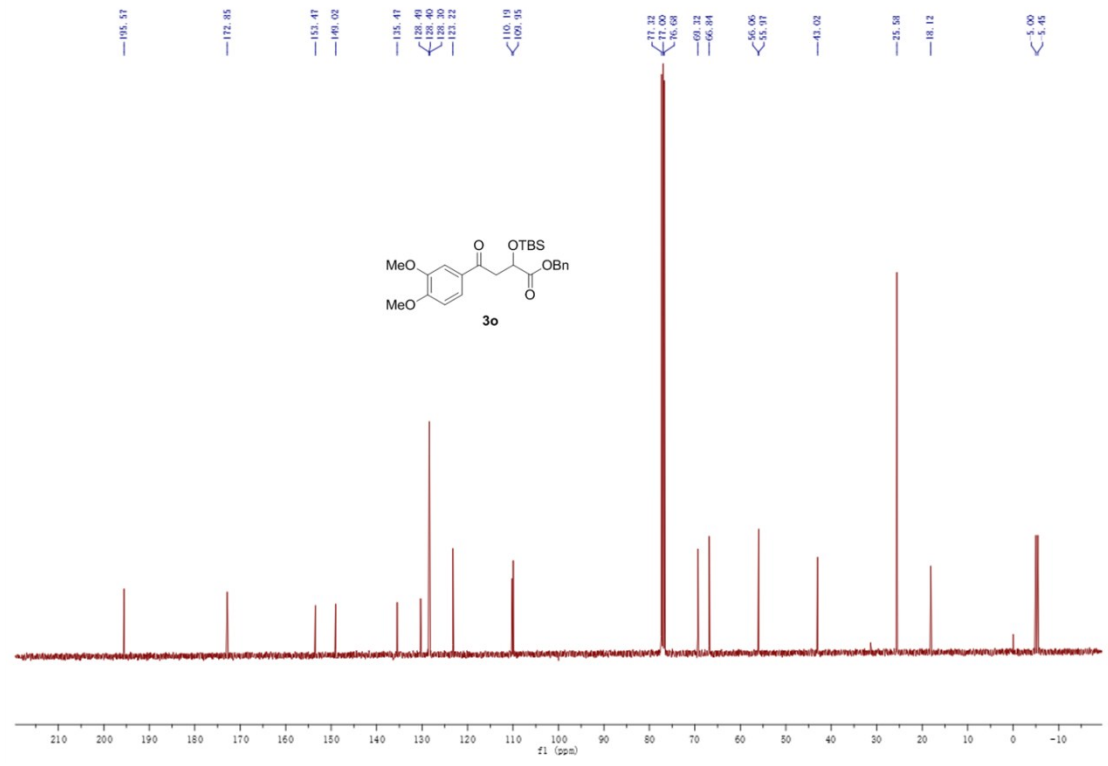
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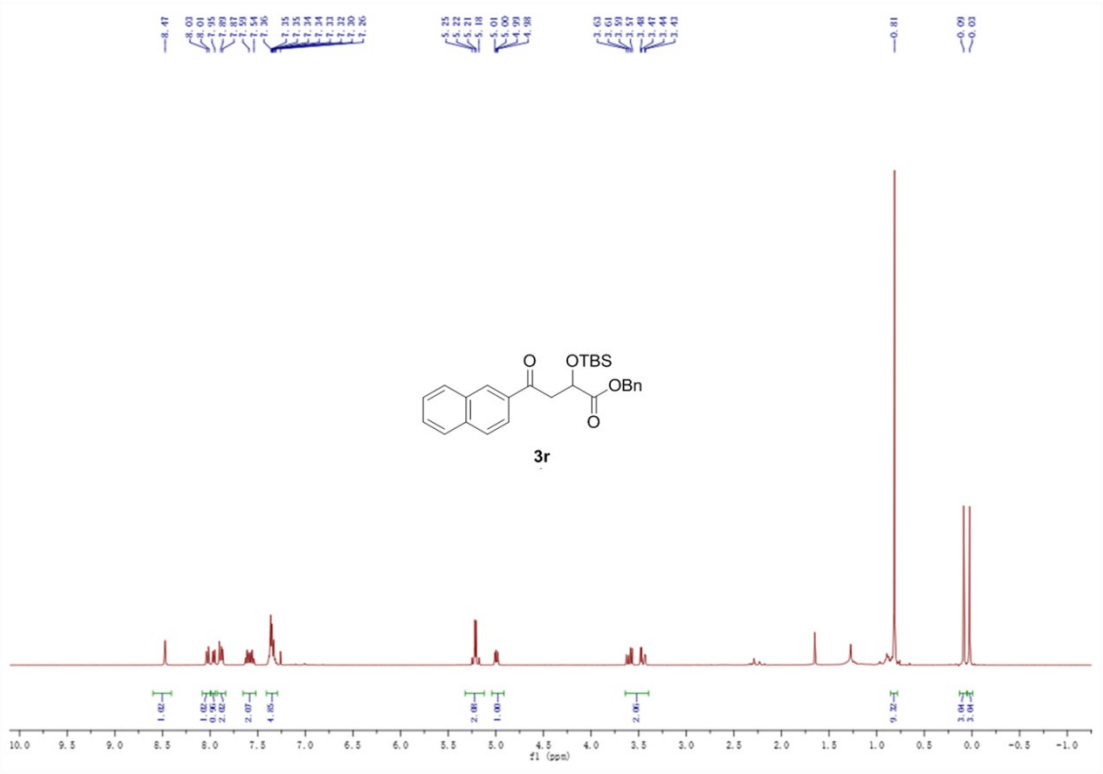
25.58
18.12
5.00
5.45
MeO
MeO
O
OTBS
OBn
O
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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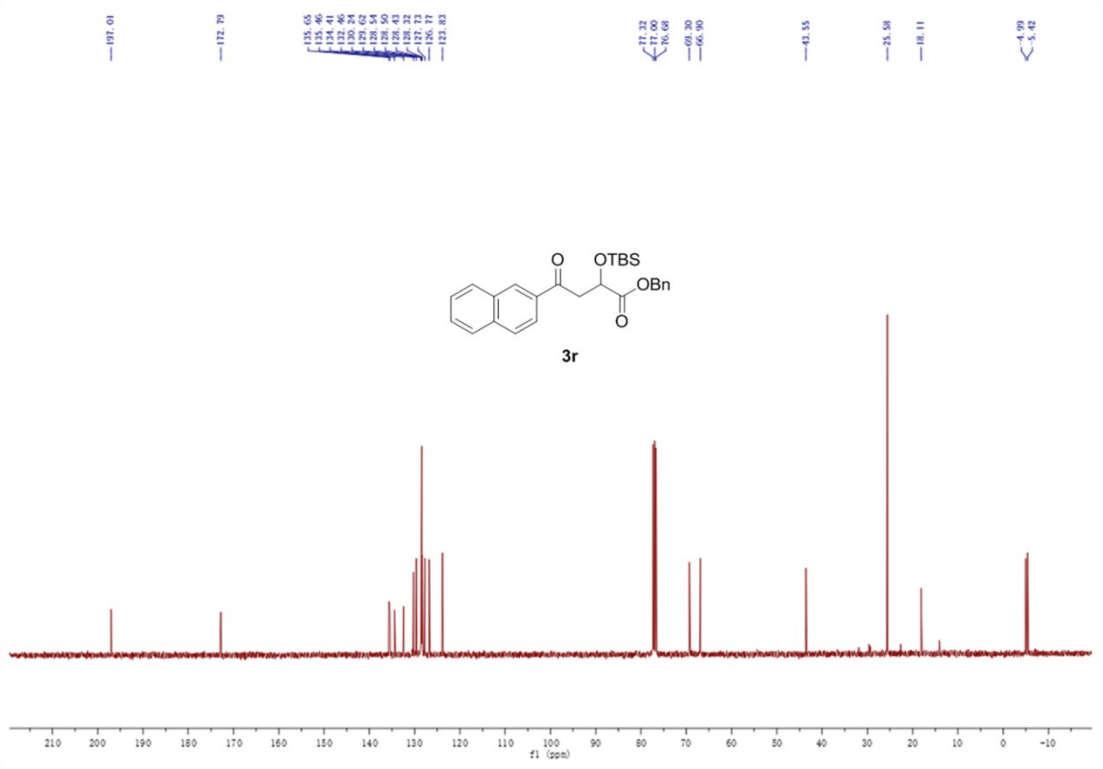
OTBS
OBn
O
3r
f1 (ppm)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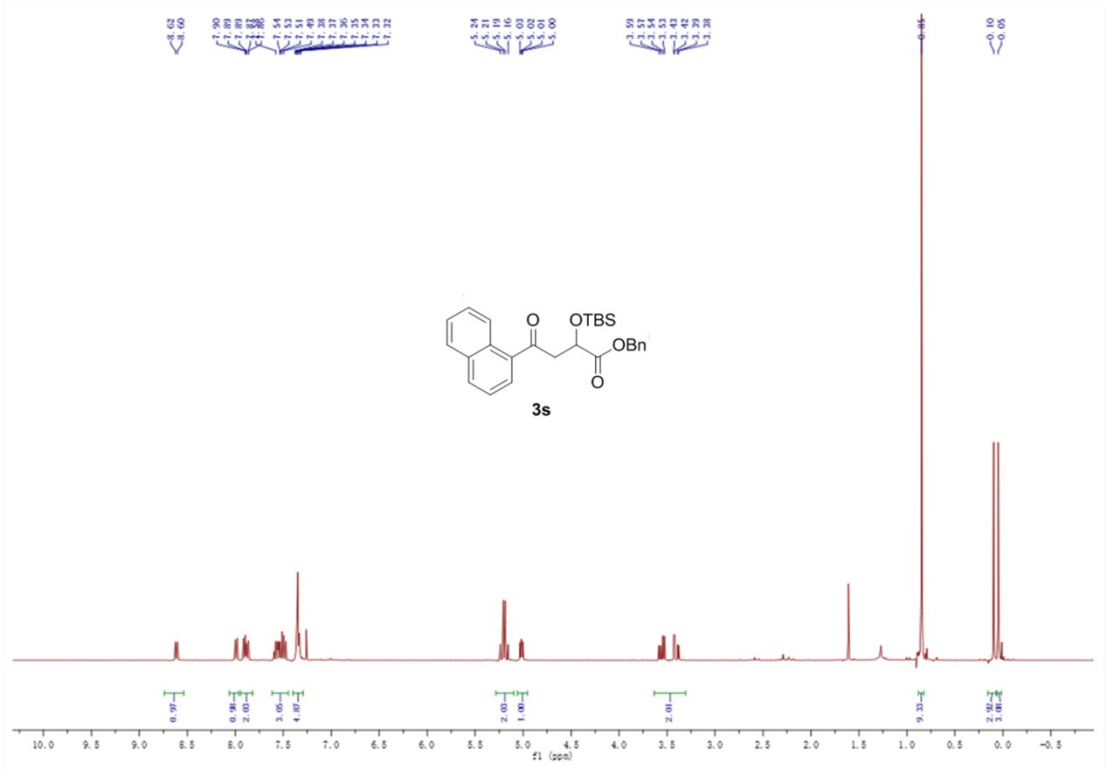
OTBS
OBn
O
3r
f1 (ppm)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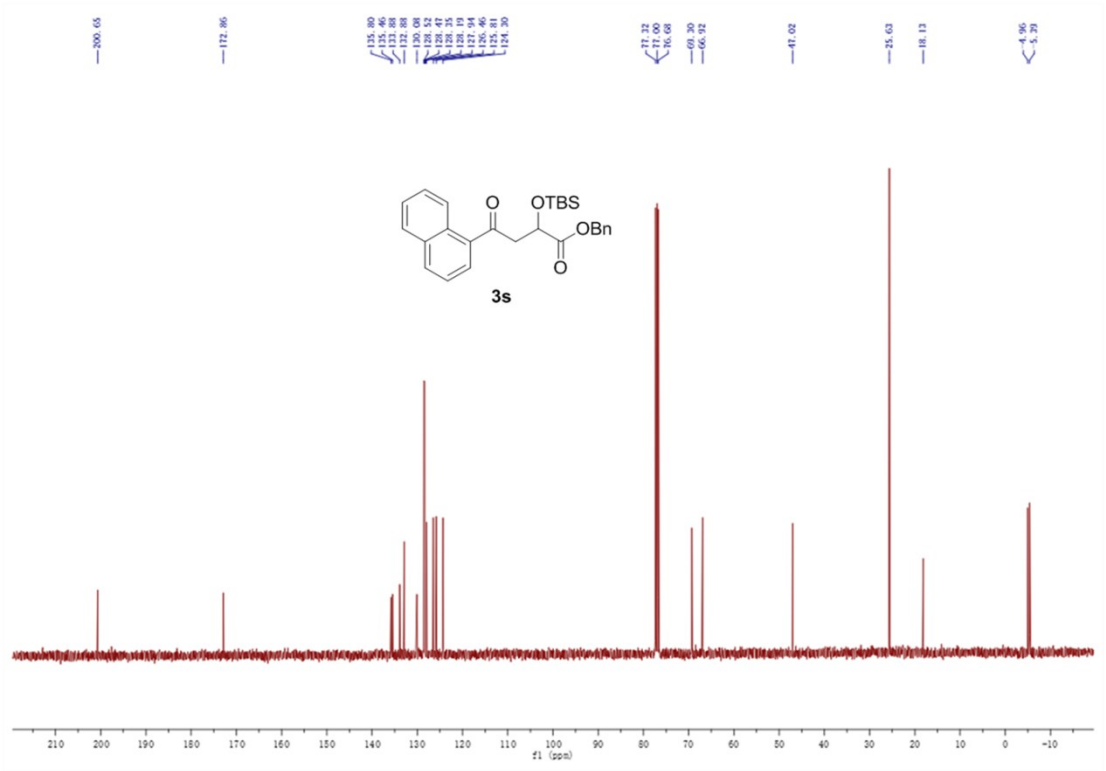
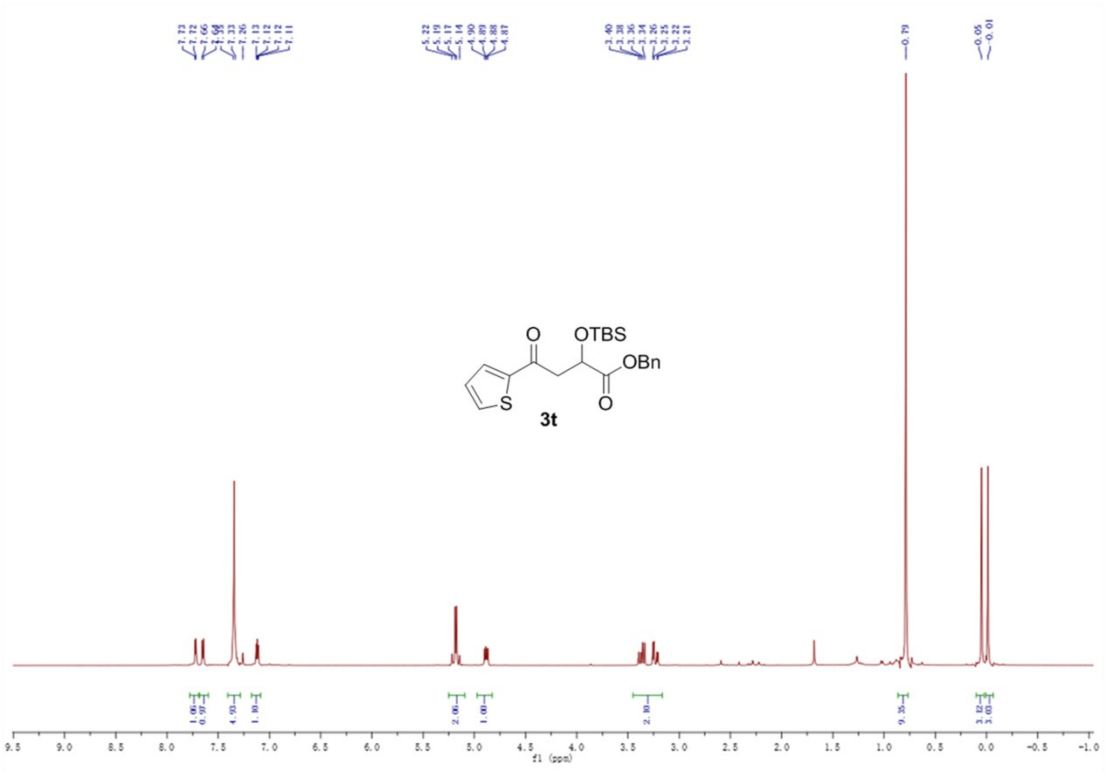
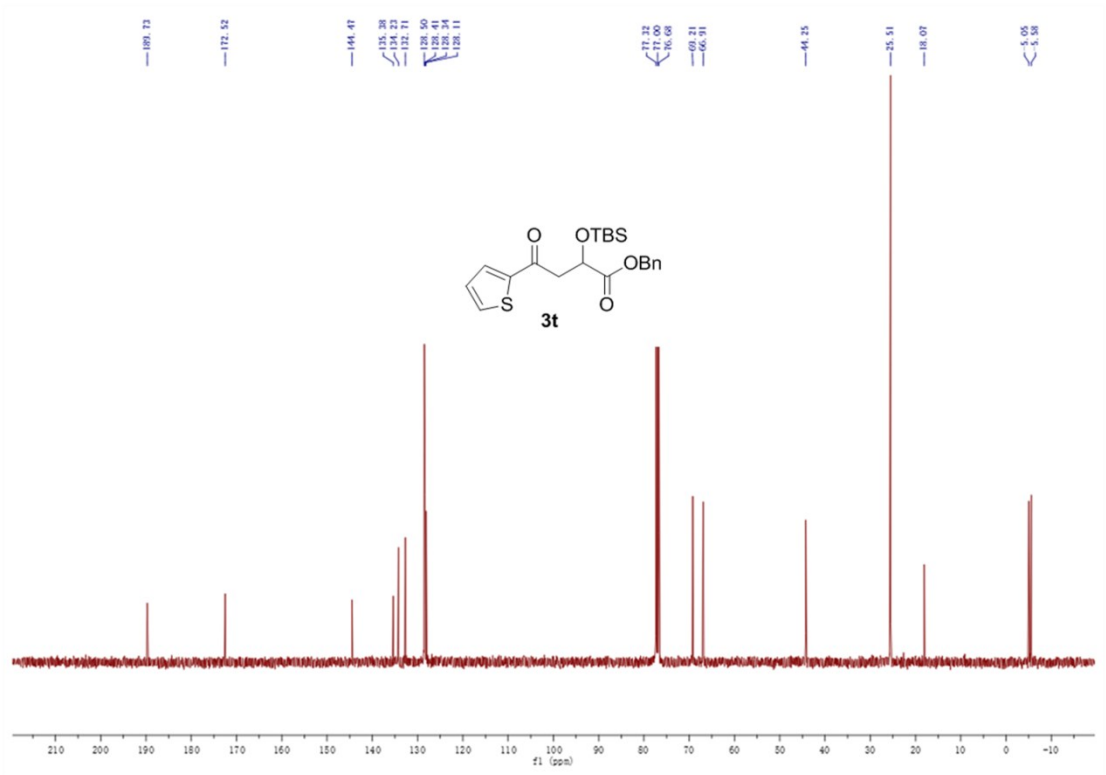
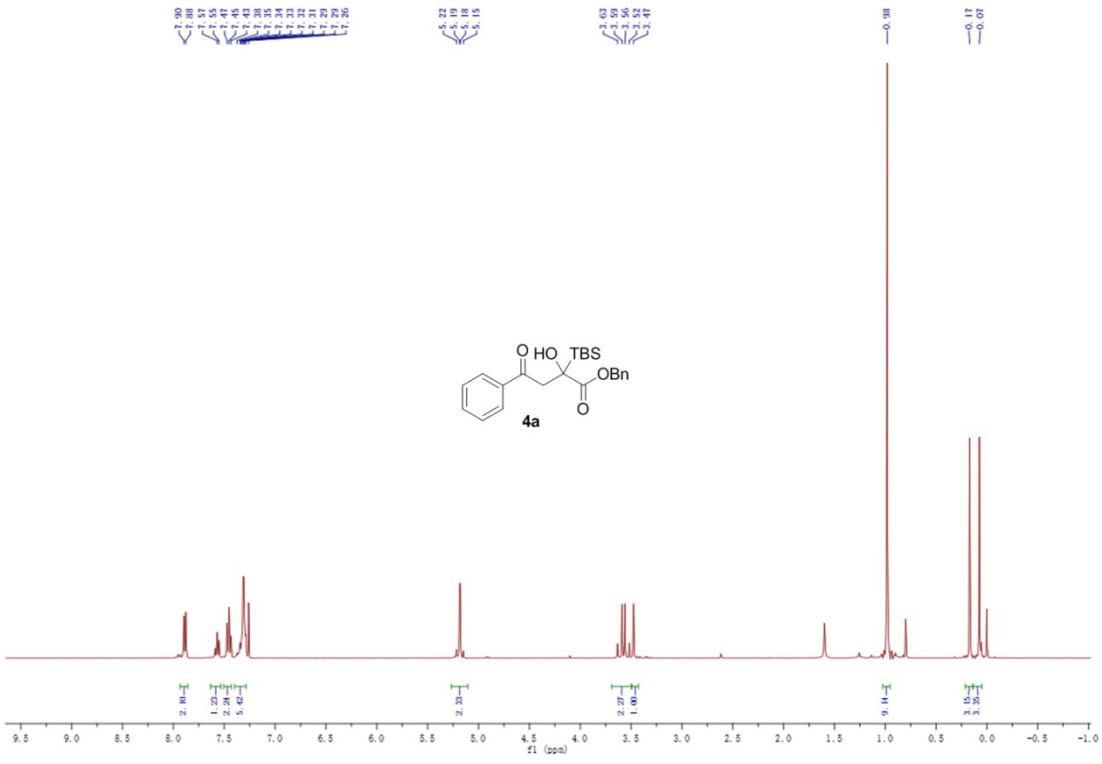
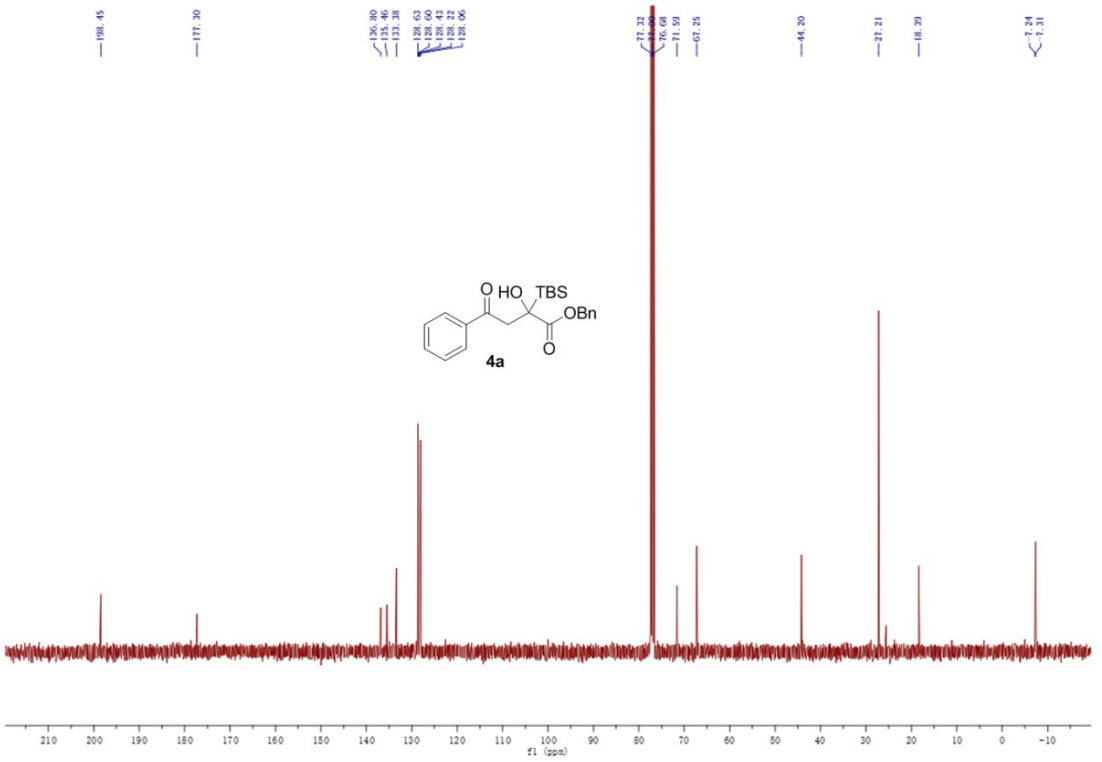
OBn
O
3s


O
OTBS
OBn
O
3s


O
OTBS
OBn
O
S
3t
f1 (ppm)


O
OTBS
OBn
O
S
3t
f1 (ppm)


O HO TBS
OBn
O
4a
f1 (ppm)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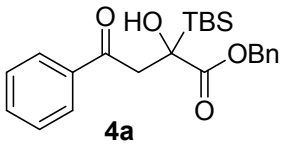
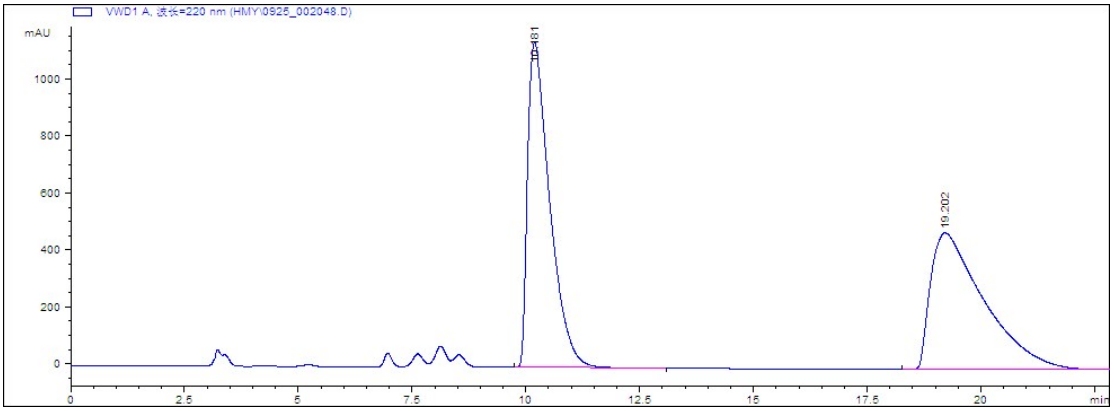
OBn
O
4a
f1 (ppm)



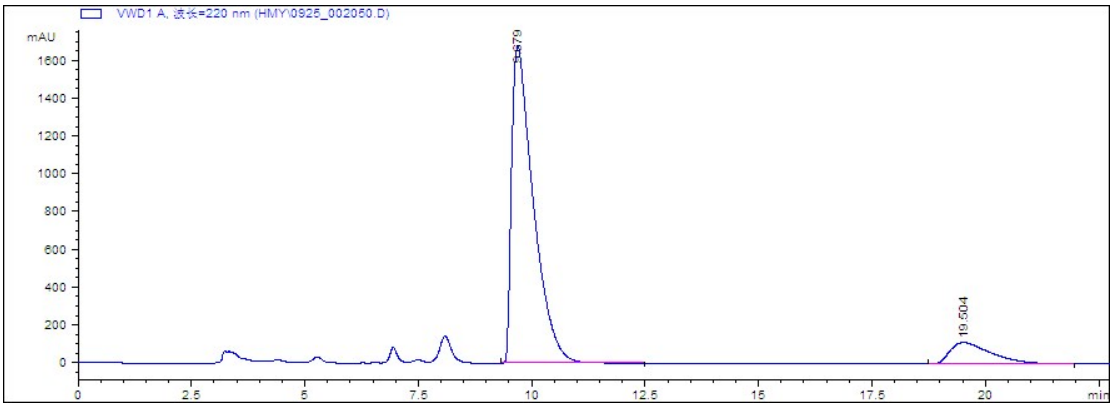
4a

racemic

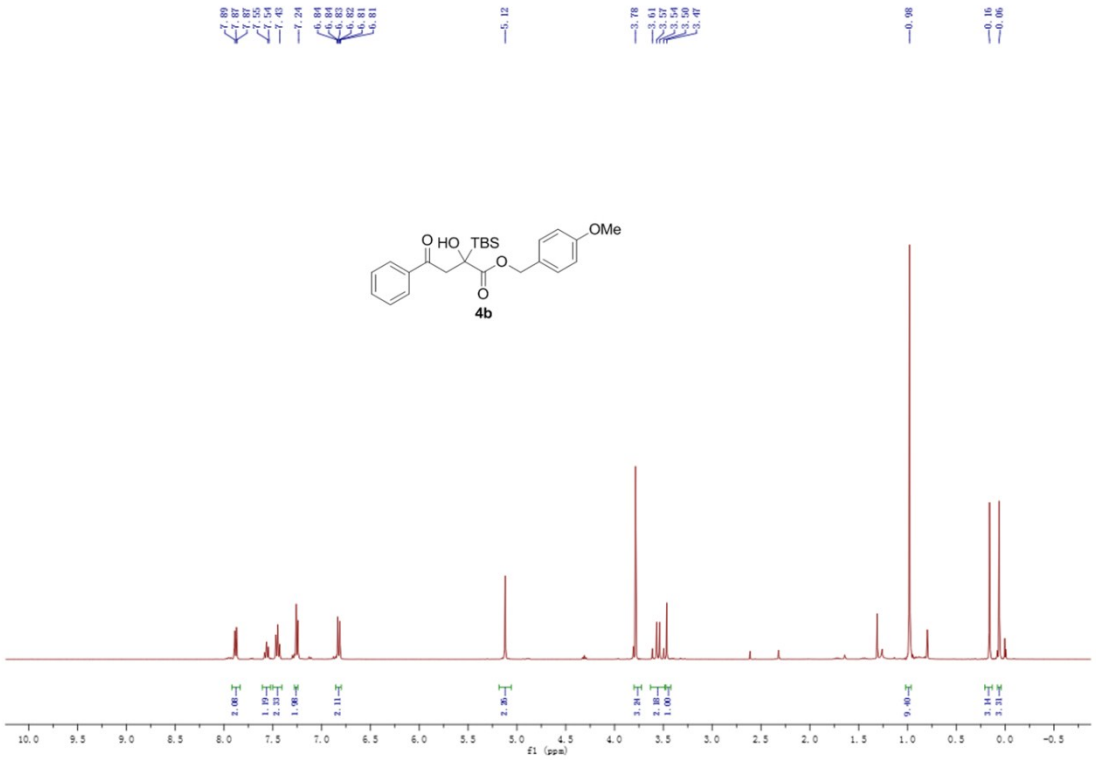


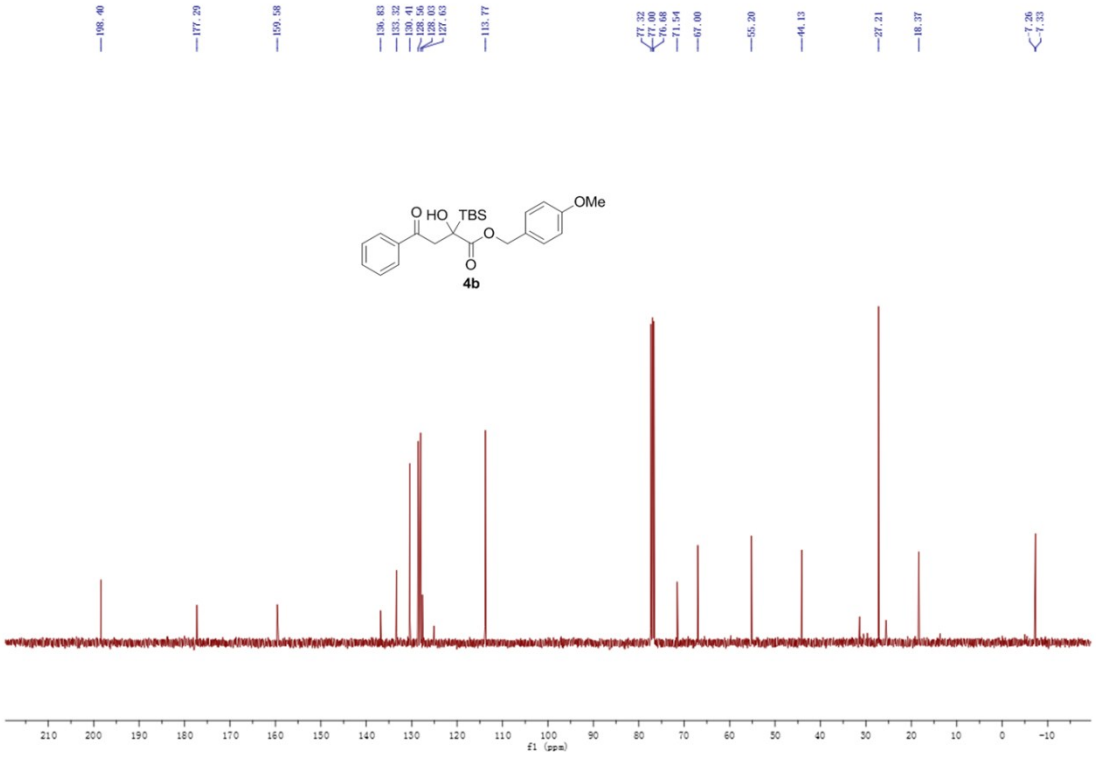
Peak	Retention Time (min)	Area	Height	% Area
1	10.181	38613.4	1141.2	49.696
2	19.202	39085.5	479.5	50.304

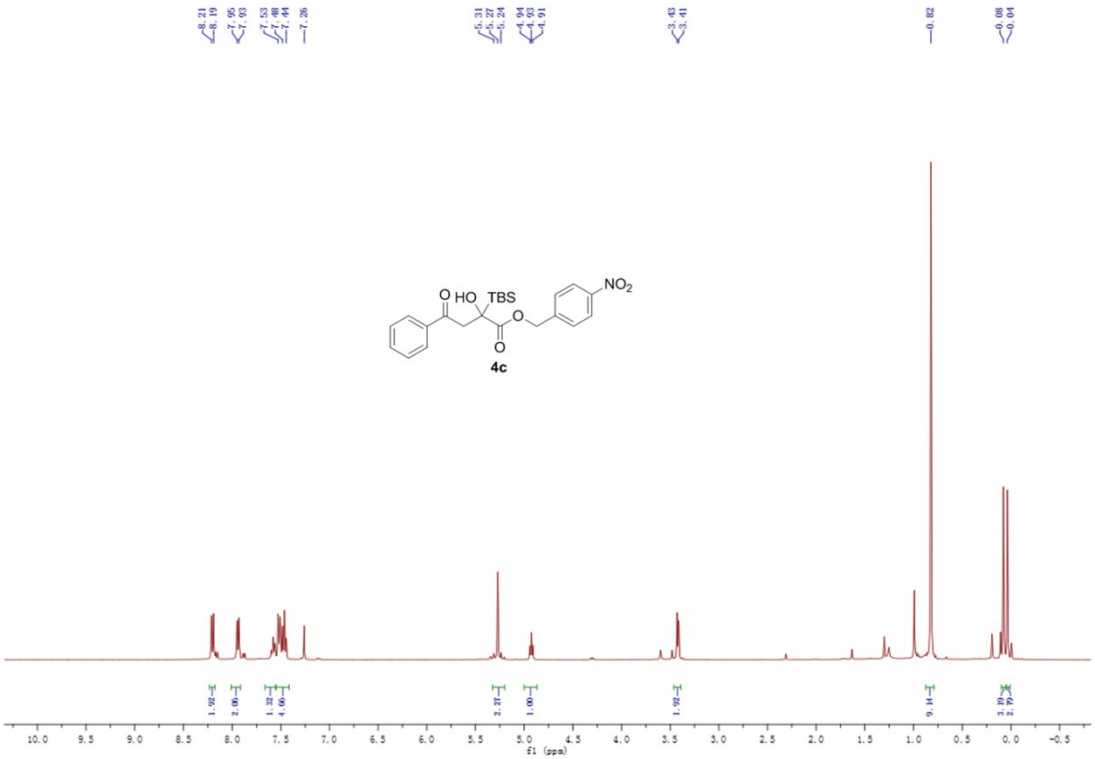
chiral

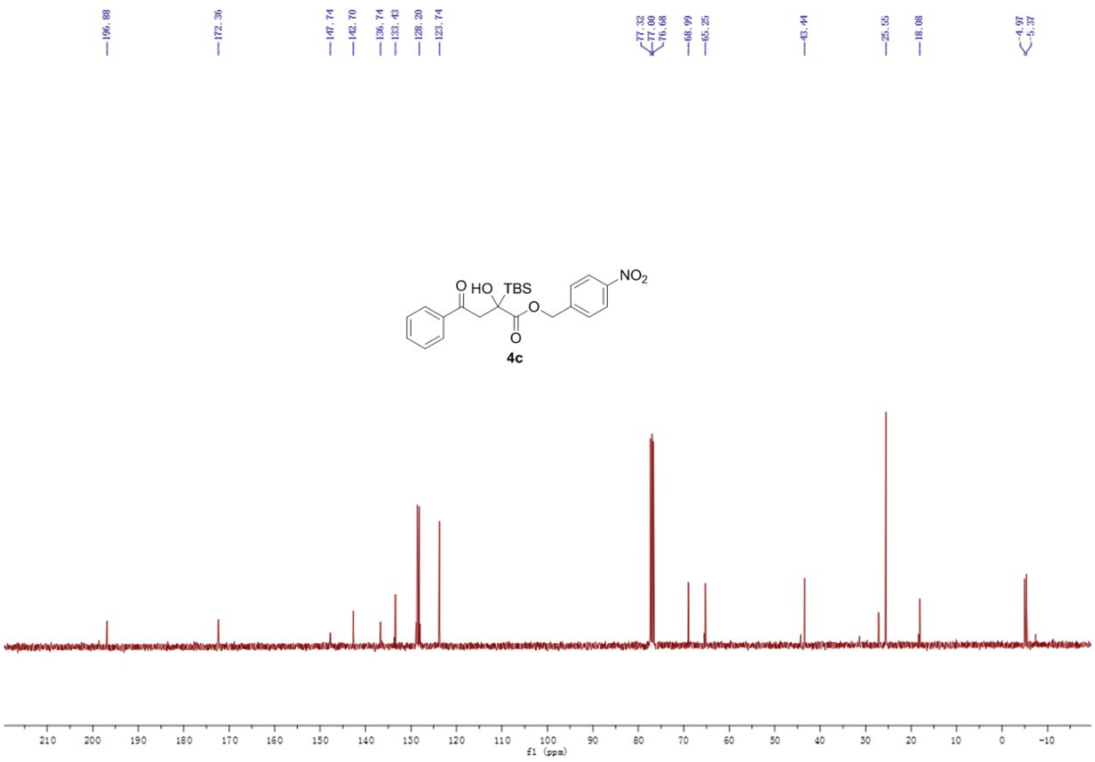


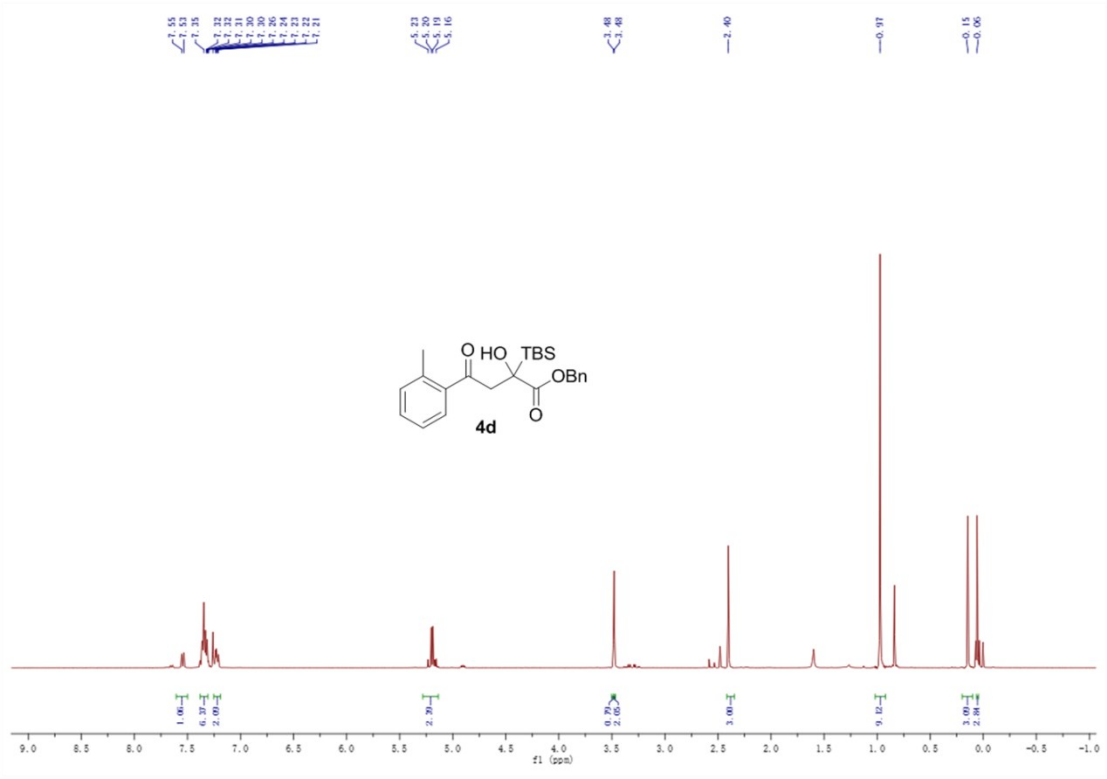
Peak	Retention Time (min)	Area	Height	% Area
1	9.679	56017	1681.9	88.866
2	19.504	7018.3	112.4	11.134

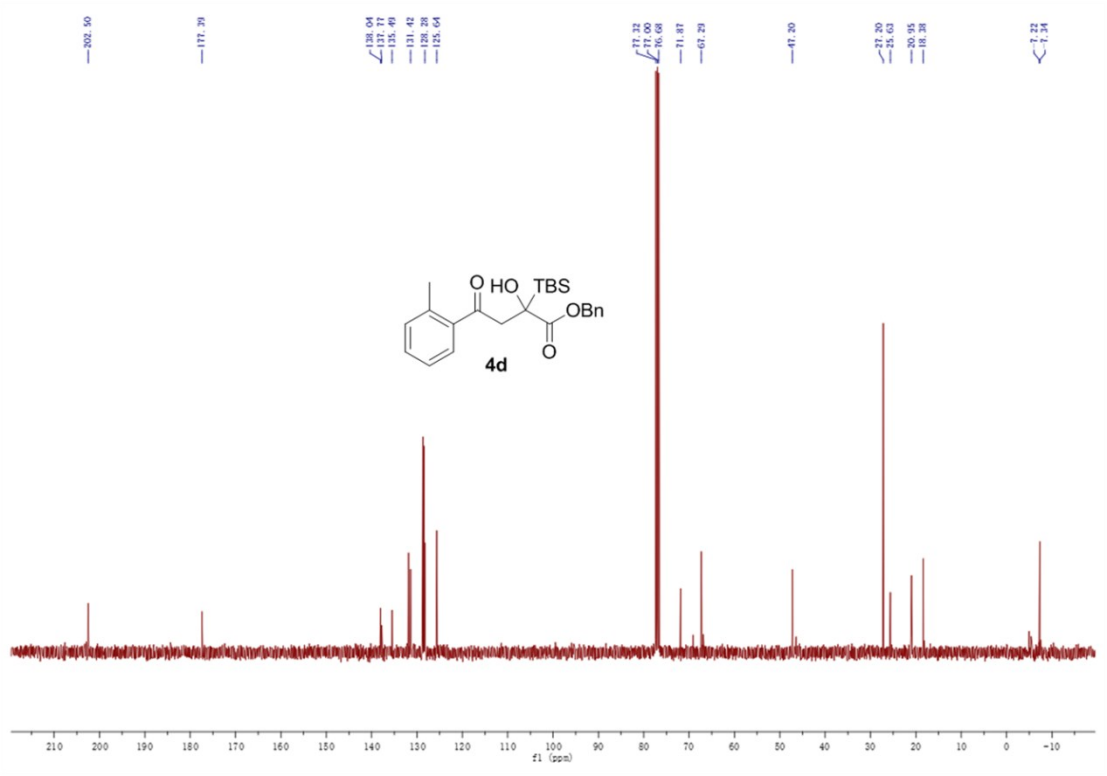

7.89
7.87
7.87
7.55
7.54
7.43
7.24
6.84
6.84
6.83
6.82
6.81
6.81
5.12
3.78
3.61
3.57
3.54
3.50
3.47
0.98
0.16
0.06
O
HO
TBS
O
O
OMe
4b
2.08
1.19
2.33
1.98
2.11
2.26
3.24
2.18
1.00
9.40
3.14
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

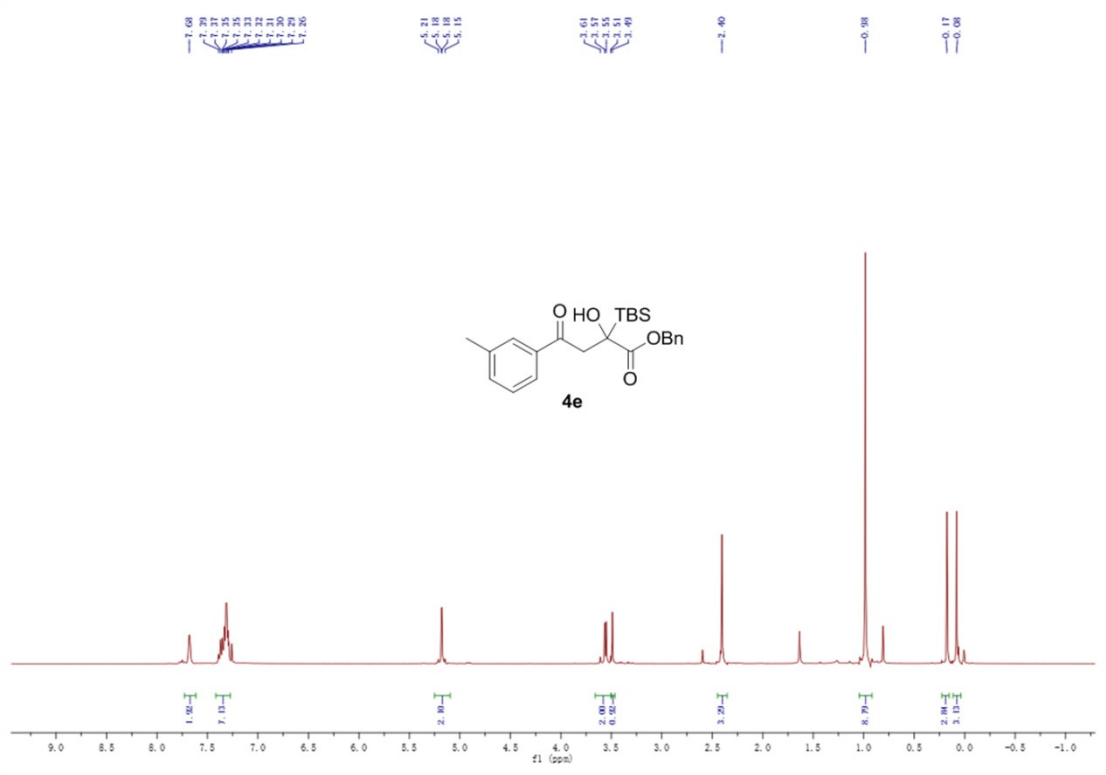

198.40
177.29
159.58
136.83
133.32
130.41
128.56
128.03
127.63
113.77
77.32
77.00
76.68
71.54
67.00
55.20
44.13
27.21
18.37
7.26
7.33
O
HO
TBS
O
O
OMe
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

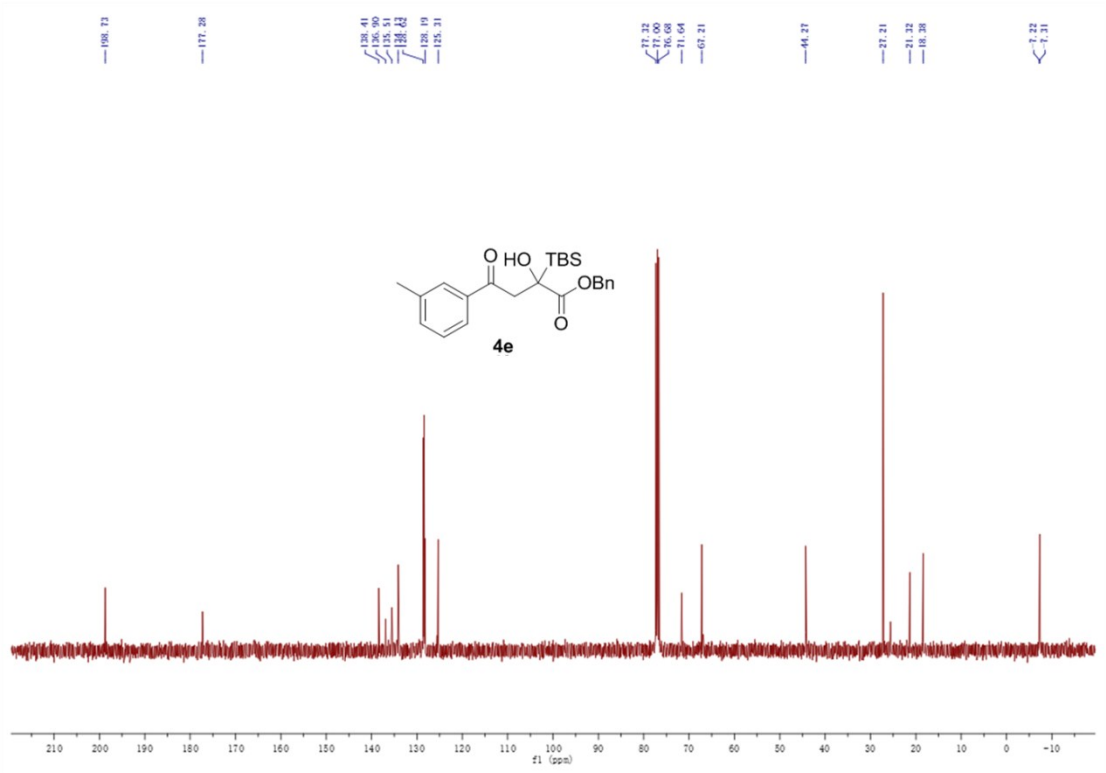

8.21
8.19
7.95
7.93
7.53
7.48
7.44
7.26
5.31
5.27
5.24
4.94
4.93
4.91
3.43
3.41
0.82
0.08
0.04
O HO TBS
O
O
NO2
4c
1.02
2.06
1.22
4.06
2.27
1.00
1.02
9.14
3.19
2.79
f1 (ppm)

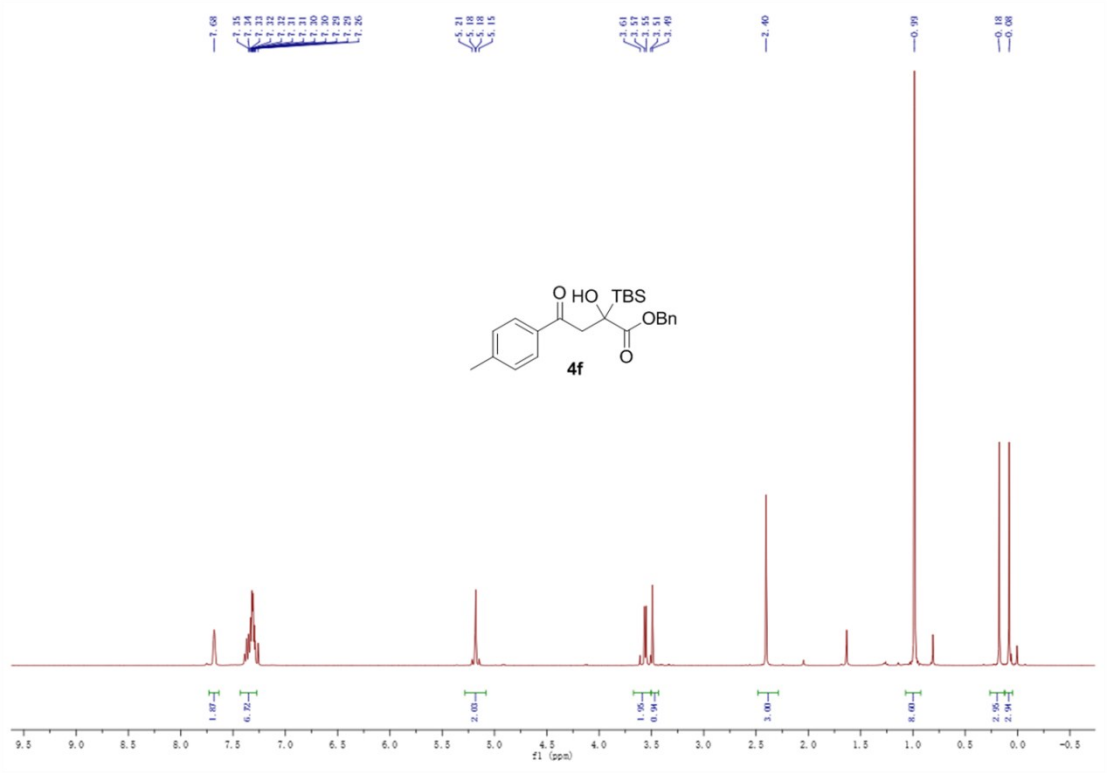

196.88
172.36
147.74
142.70
136.74
133.43
128.20
123.74
77.32
77.00
76.68
68.99
65.25
43.44
25.55
18.08
-4.97
-5.37
O HO TBS
O
O
NO2
4c
f1 (ppm)


O HO TBS
OBn
O
4d
f1 (ppm)


O HO TBS
OBn
O
4d
f1 (ppm)


O HO TBS
OBn
O
4e
f1 (ppm)


O HO TBS
OBn
O
4e
f1 (ppm)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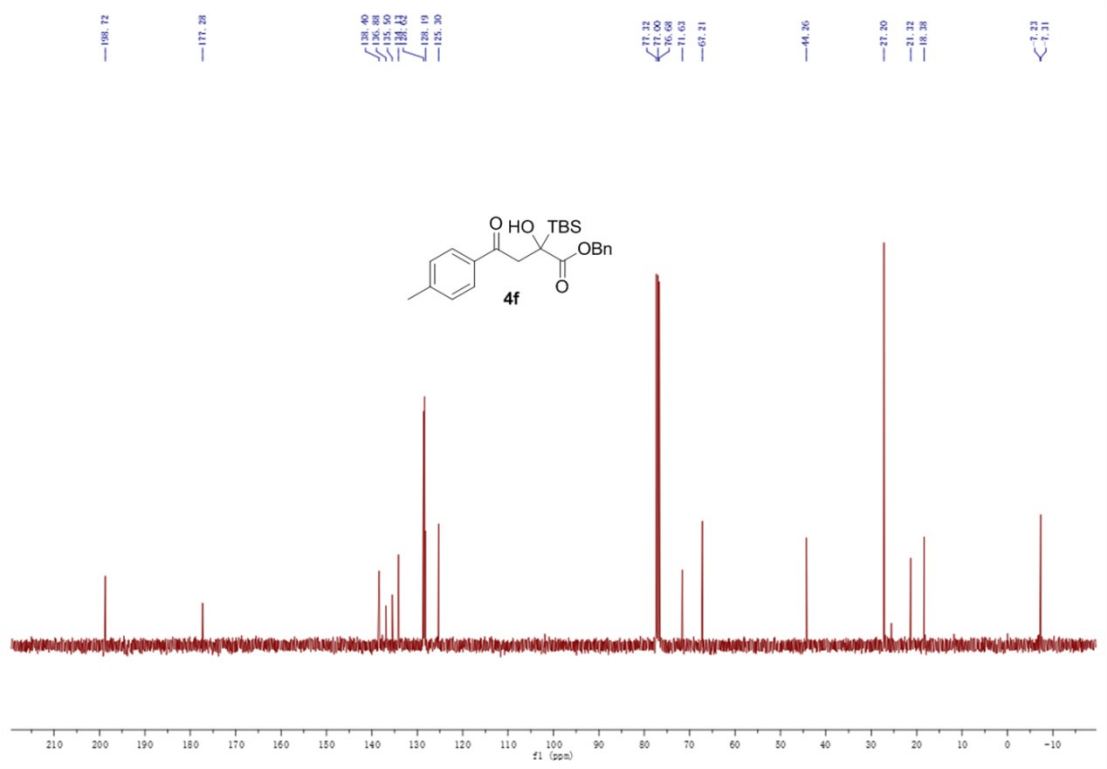
OBn
O
4f
f1 (ppm)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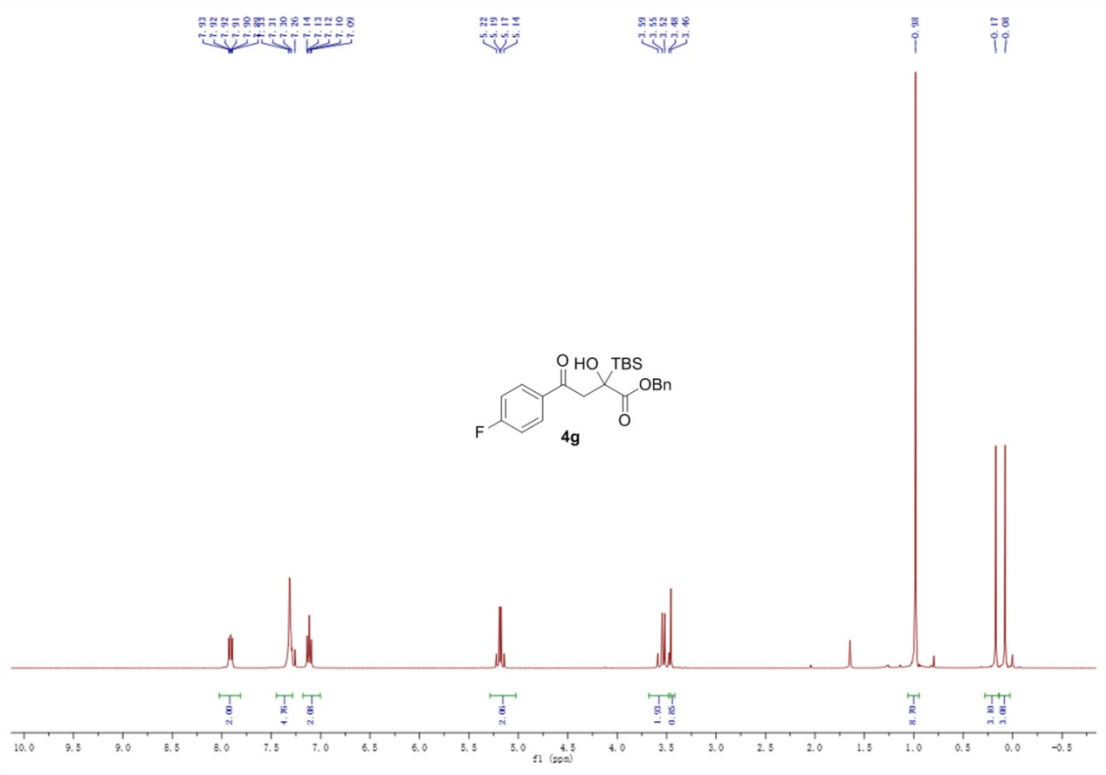
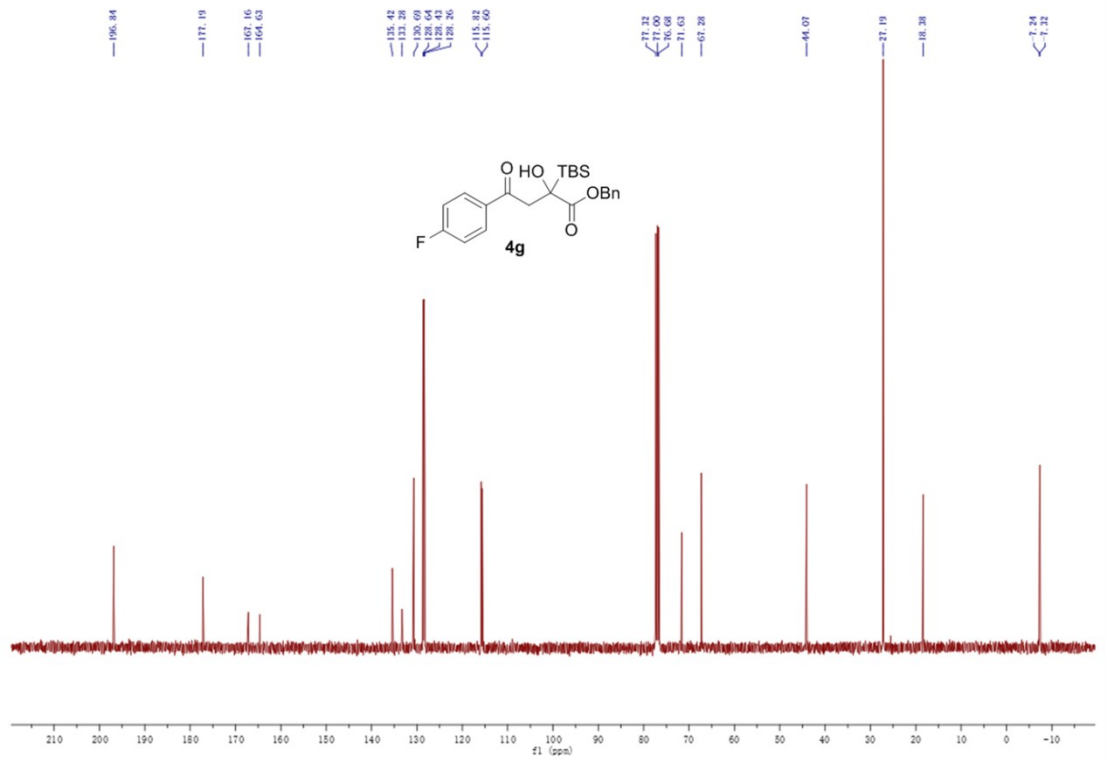
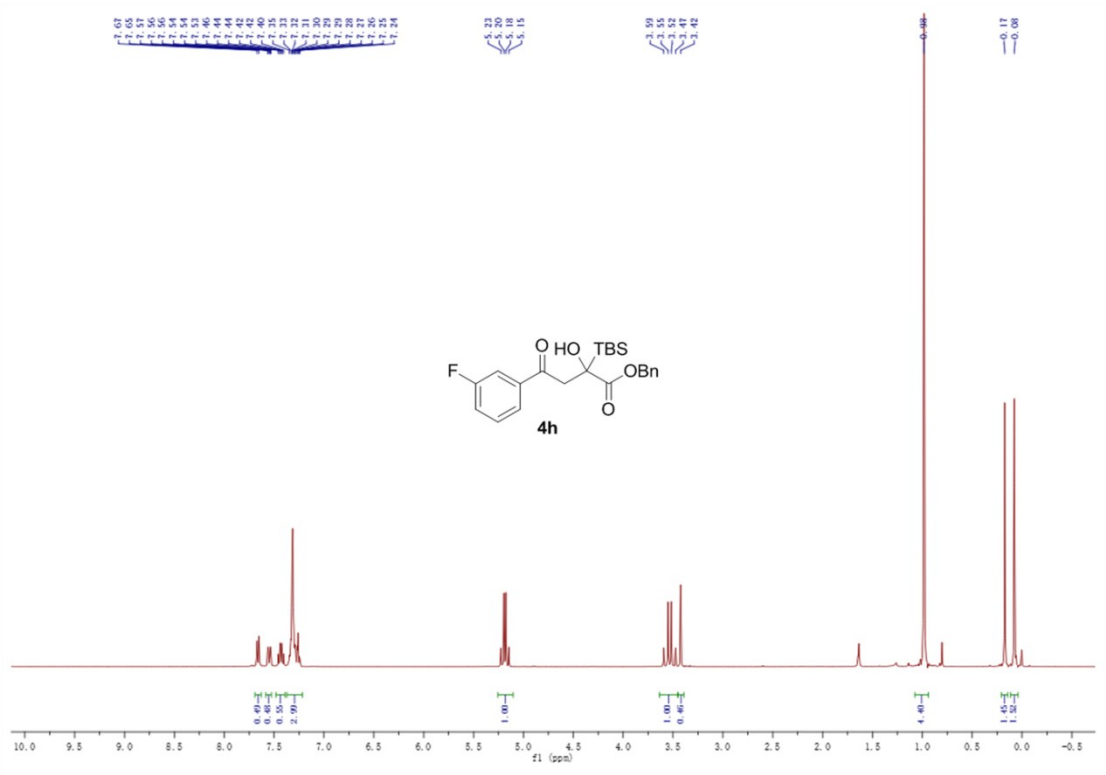
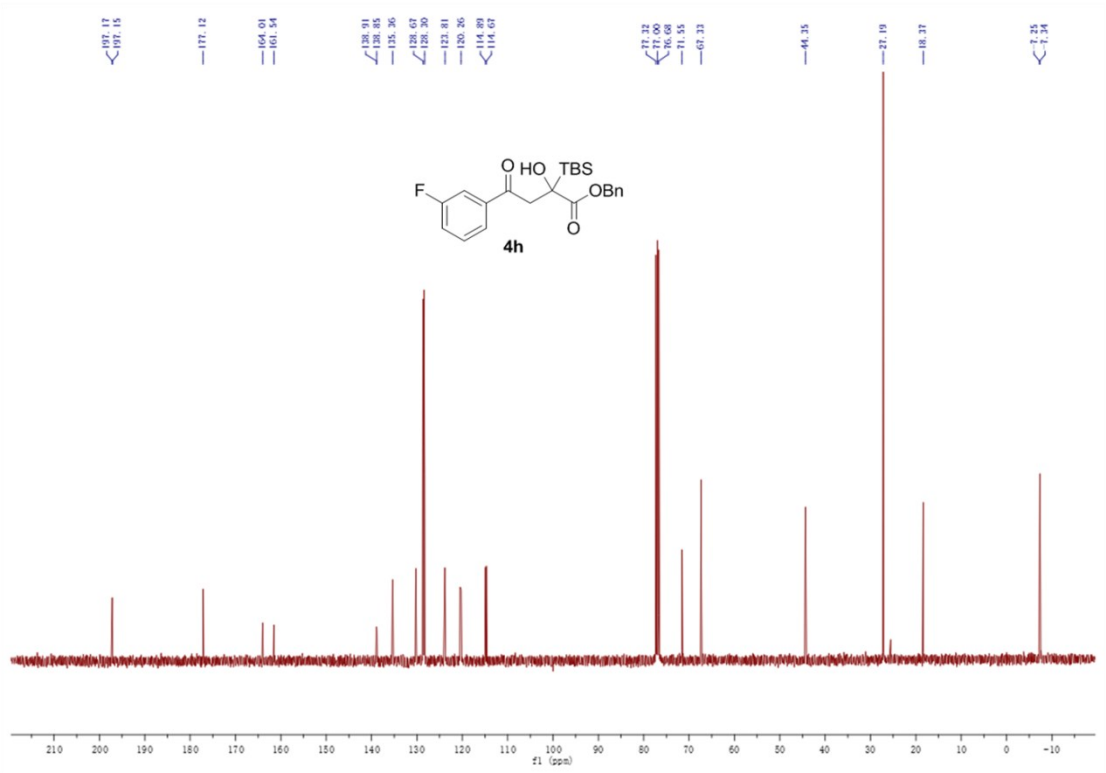
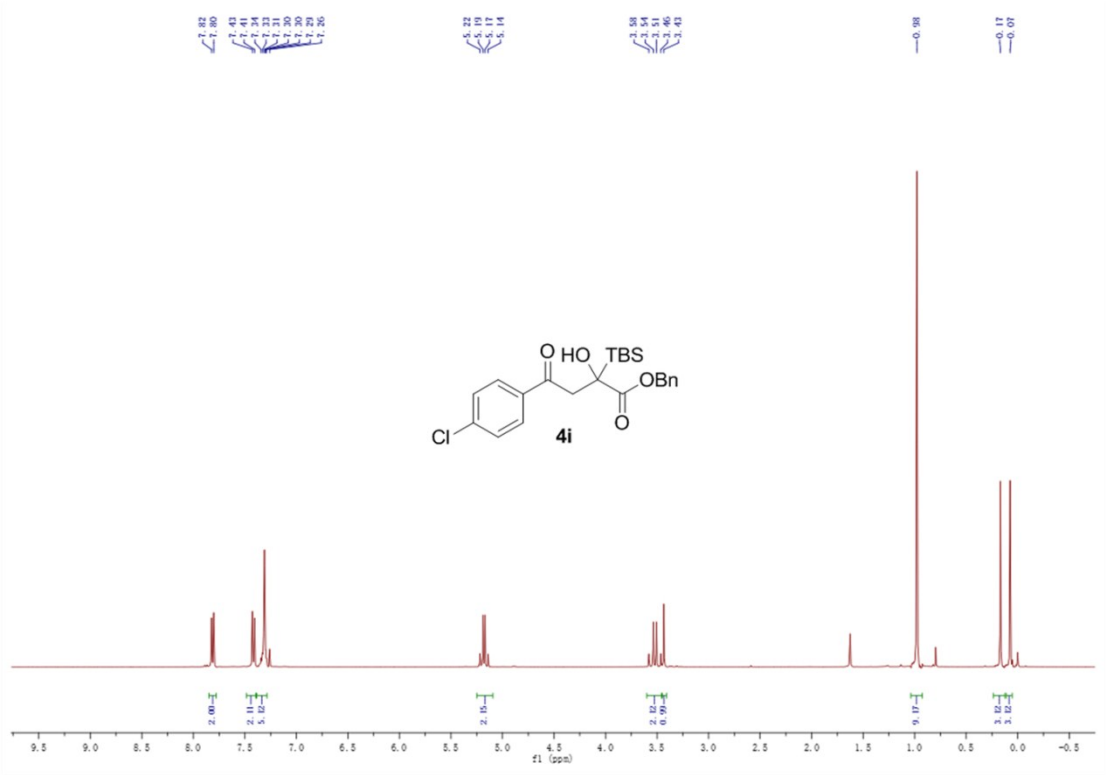
OBn
O
4f
f1 (ppm)

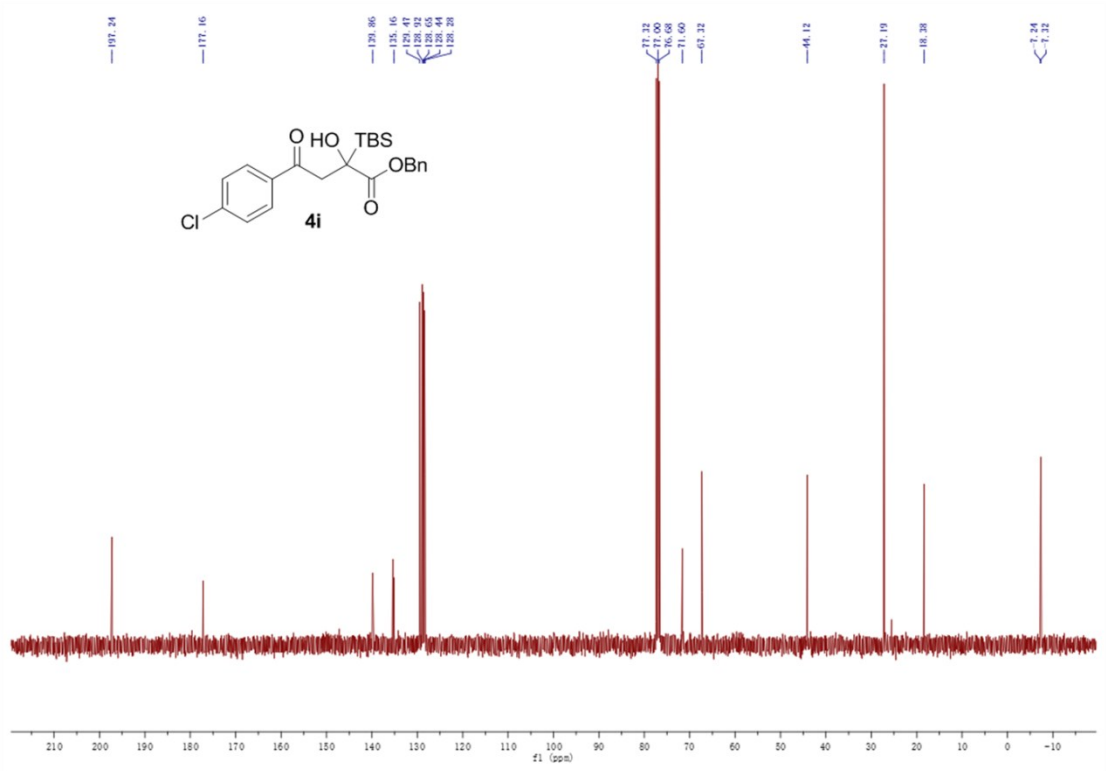

O HO TBS
OBn
O
F
4g
f1 (ppm)


O HO TBS
OBn
O
F
4g
f1 (ppm)


O HO TBS
F
OBn
O
4h
f1 (ppm)


O HO TBS
F
OBn
O
4h
f1 (ppm)


O HO TBS
OBn
O
Cl
4i
f1 (ppm)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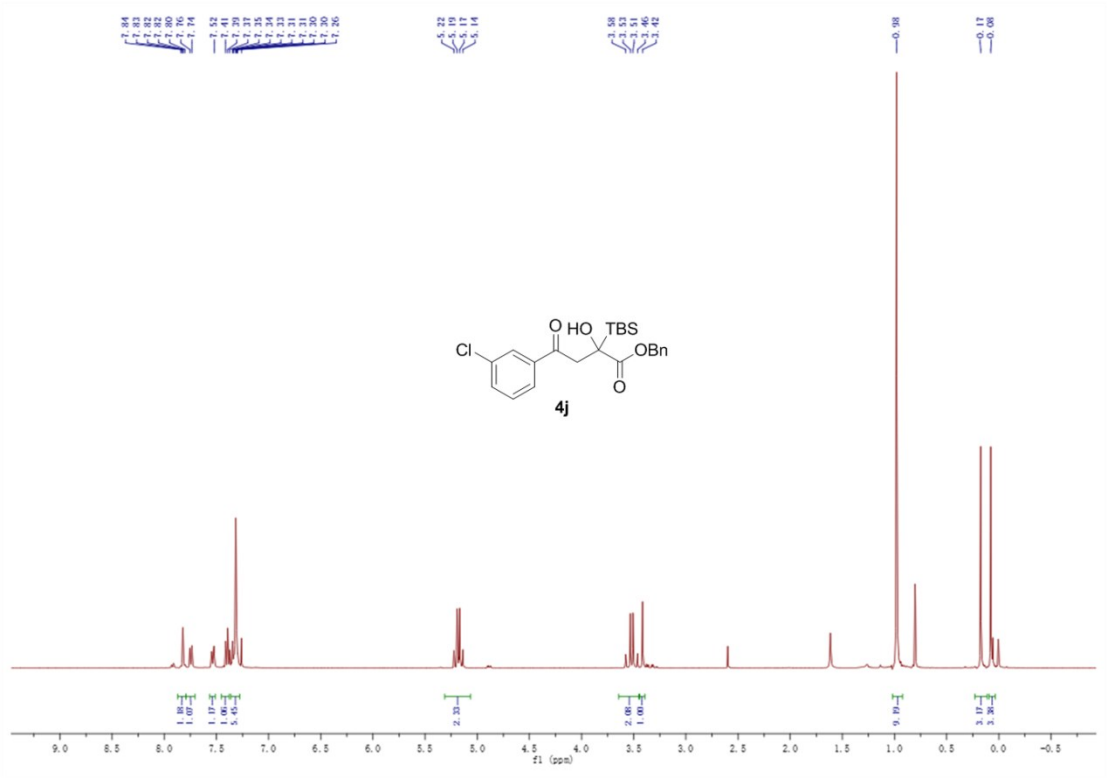
OBn
O
Cl
4i
f1 (ppm)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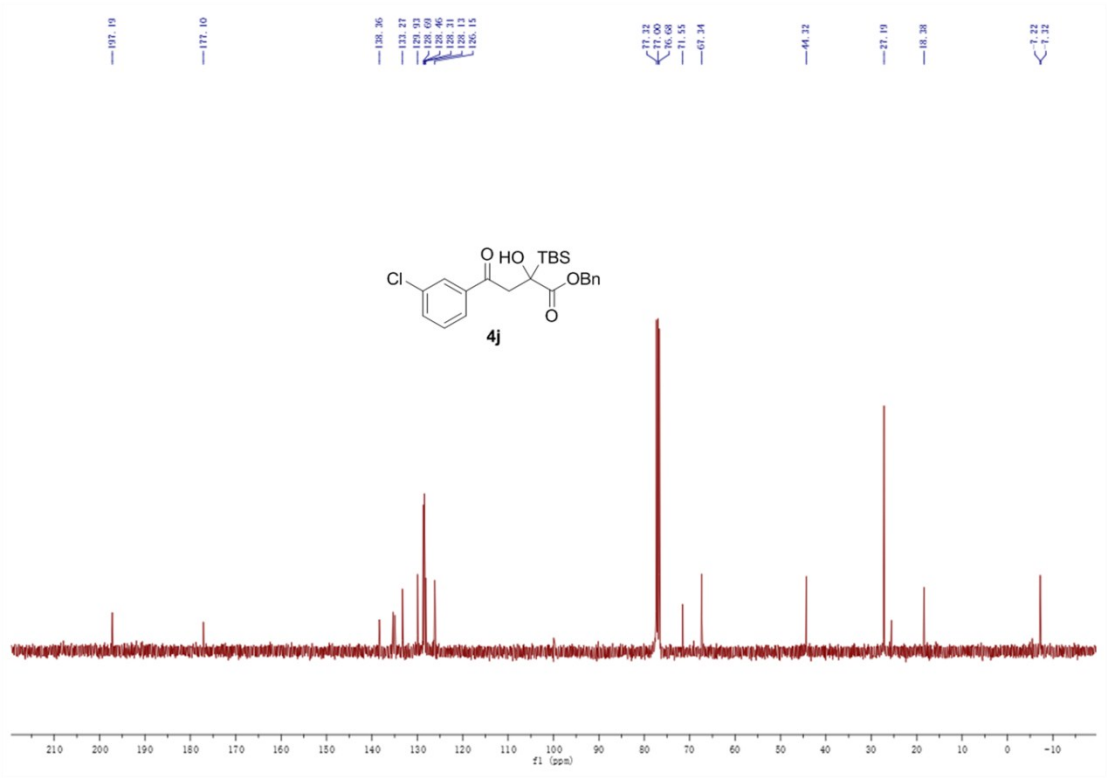
HO
TBS
Cl
OBn
O
4j
f1 (ppm)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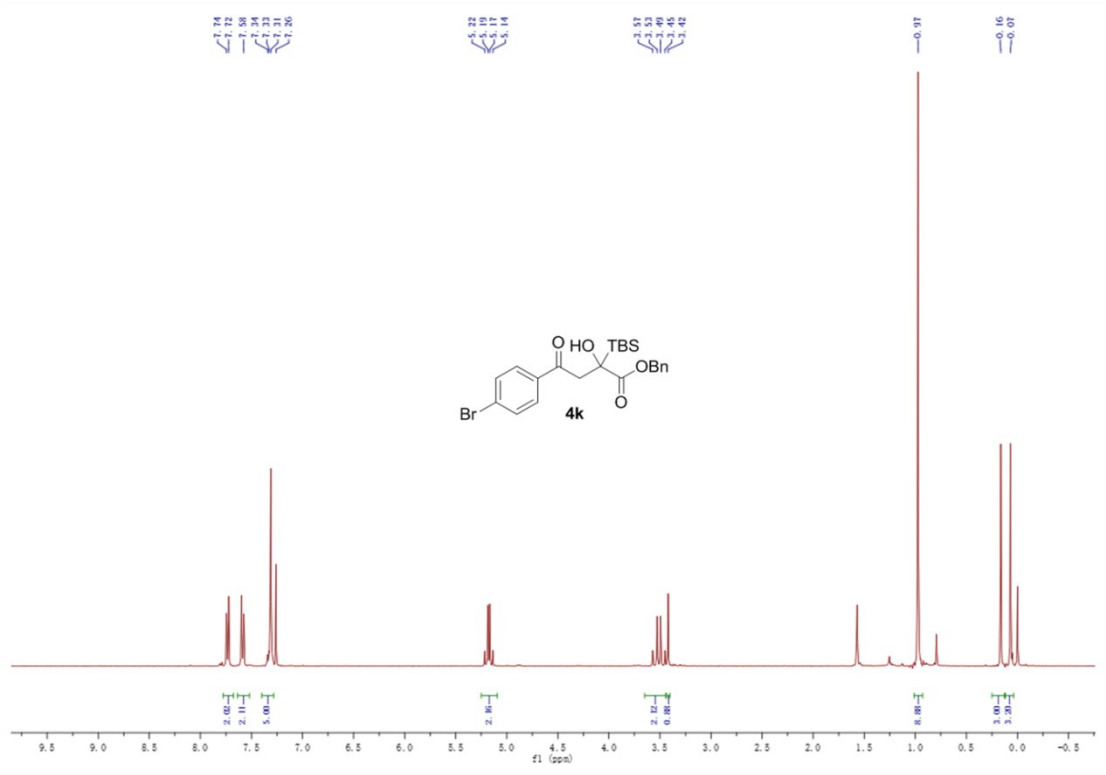
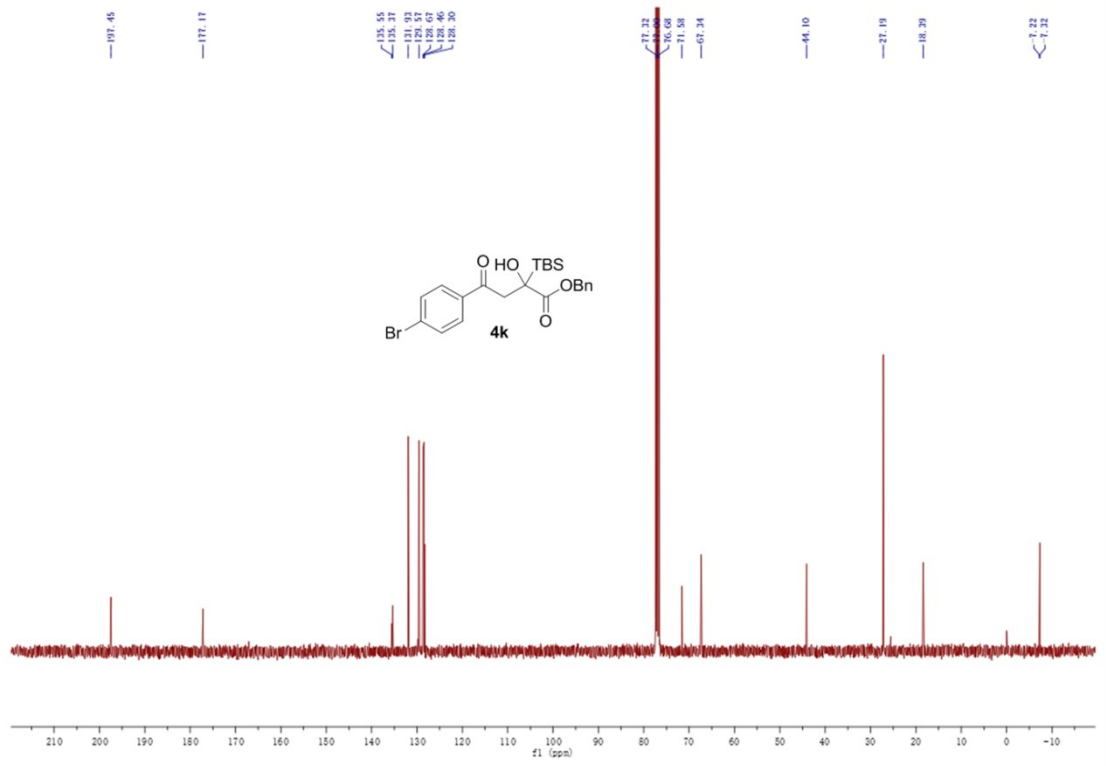
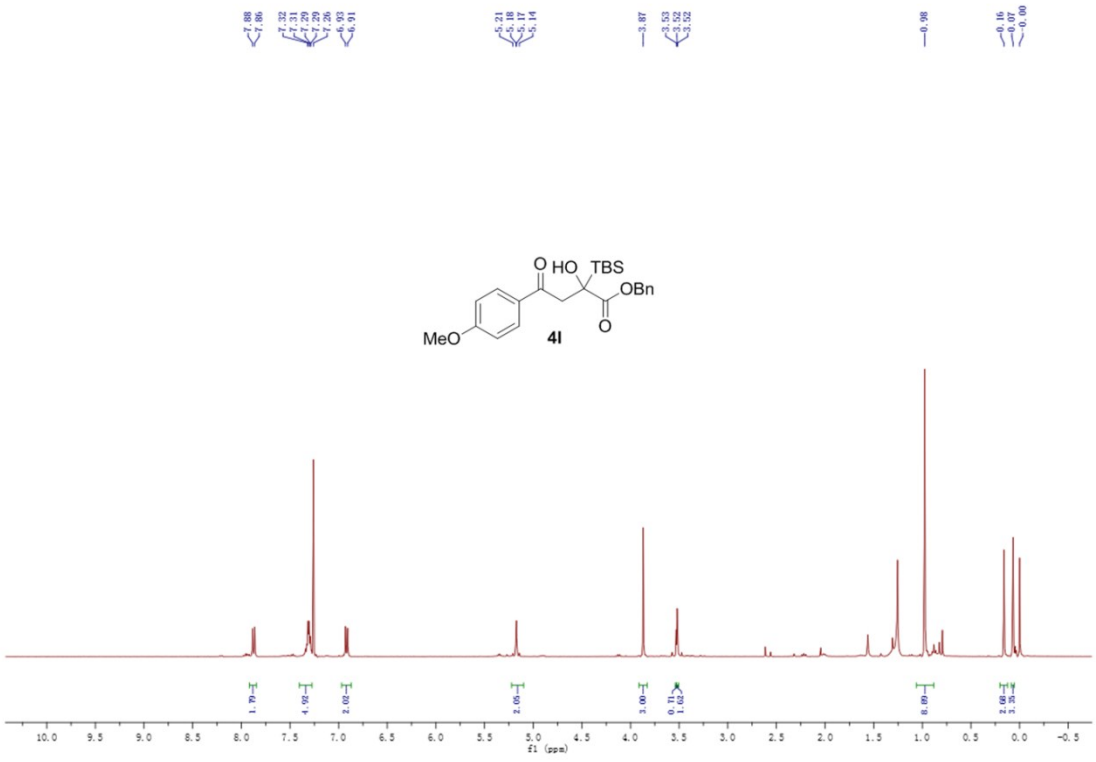
TBS
Cl
OBn
O
4j
f1 (ppm)


O HO TBS
OBn
O
Br
4k
f1 (ppm)


O HO TBS
OBn
O
Br
4k
f1 (ppm)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7.31
7.29
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7.26
6.93
6.91
5.21
5.18
5.17
5.14
3.87
3.53
3.52
3.52
0.98
0.16
0.07
0.00
O
HO
TBS
OBn
O
MeO
4l
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4.92
2.02
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3.00
0.71
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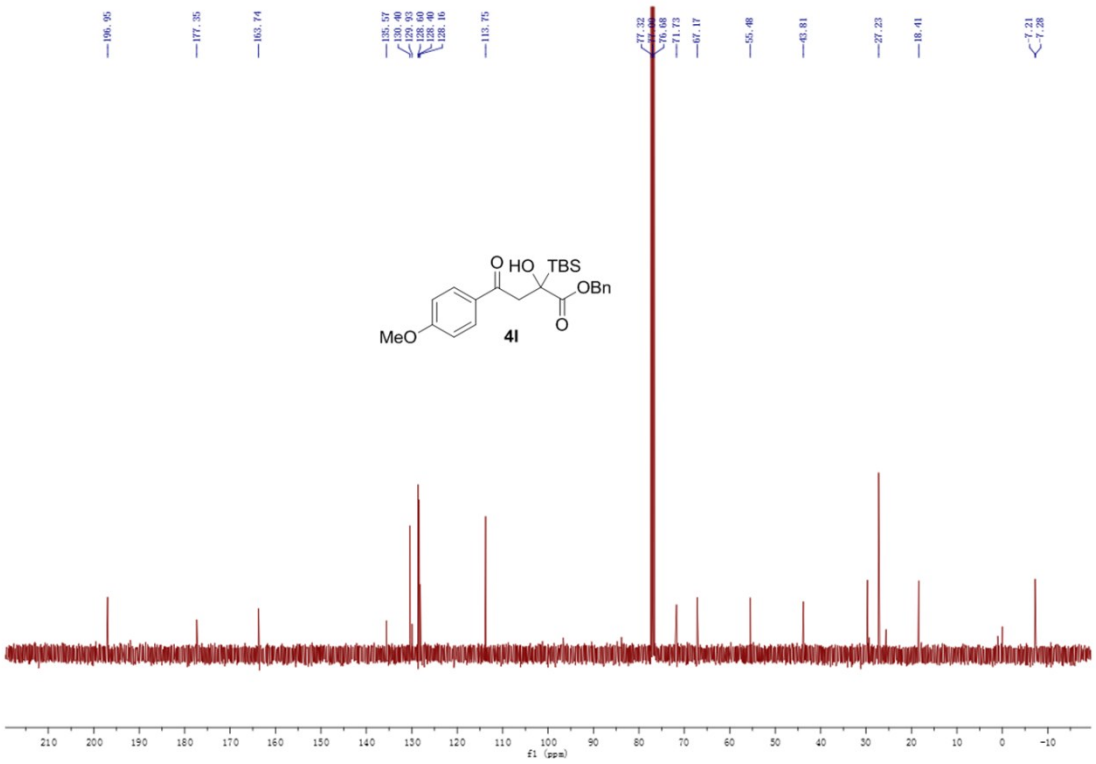
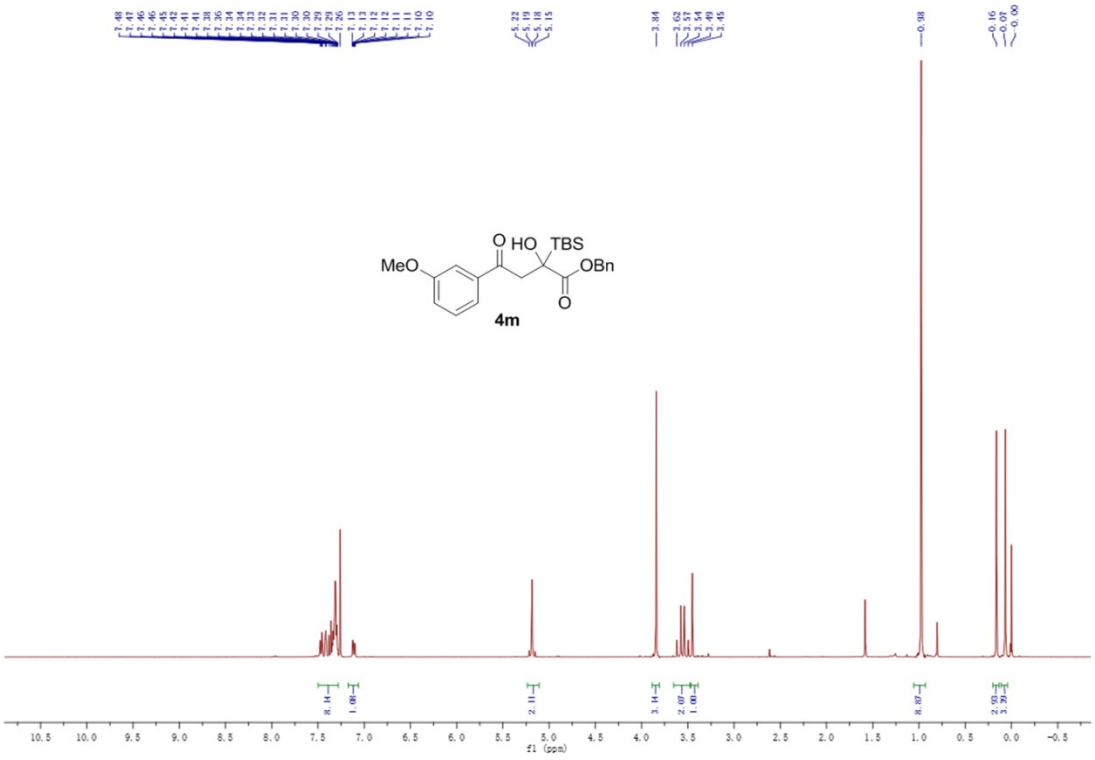
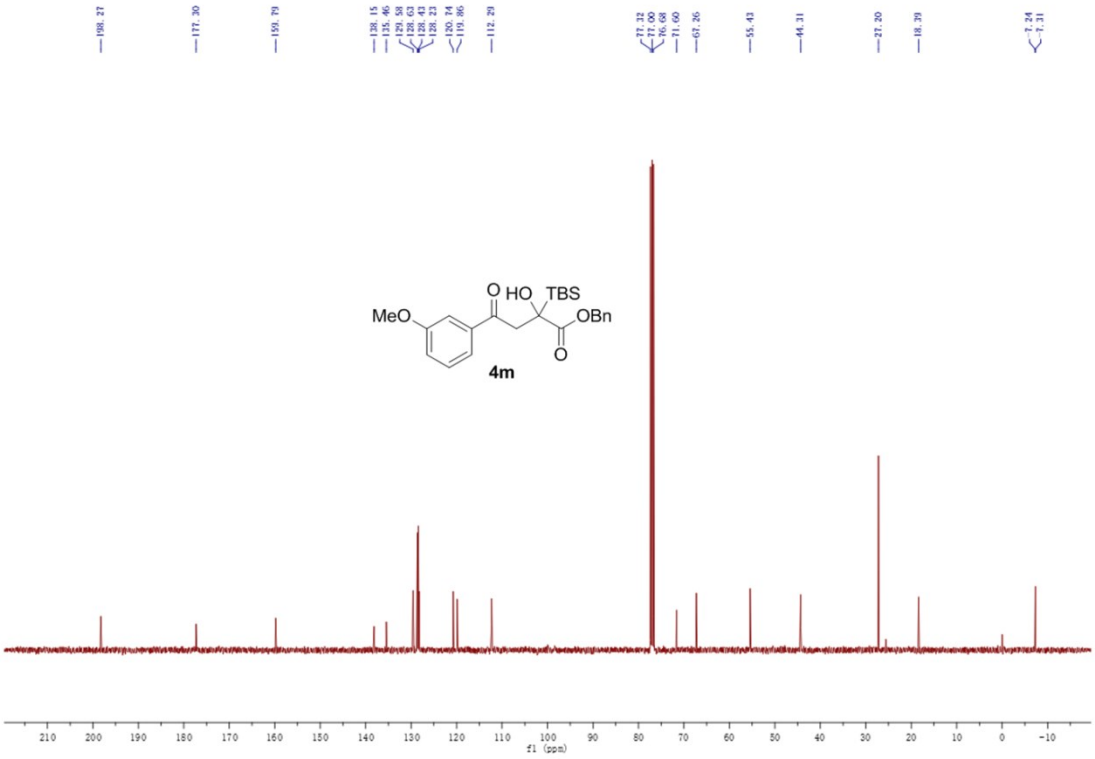
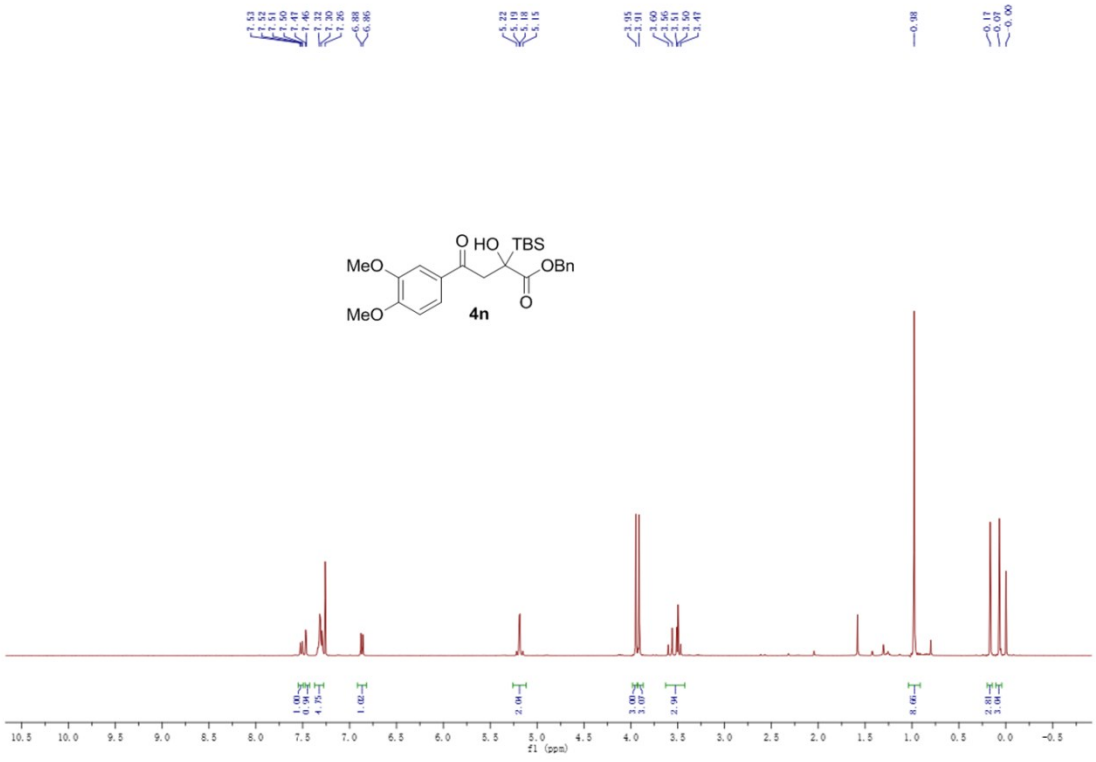
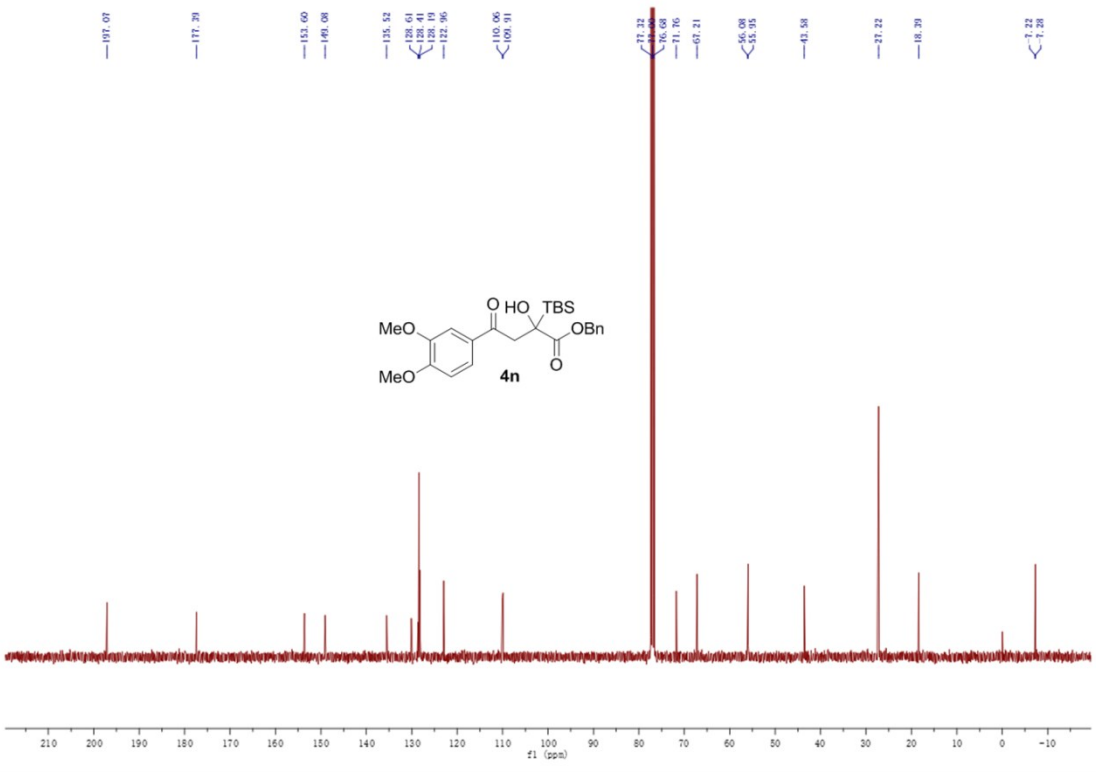
8.89
2.06
3.35
f1 (ppm)

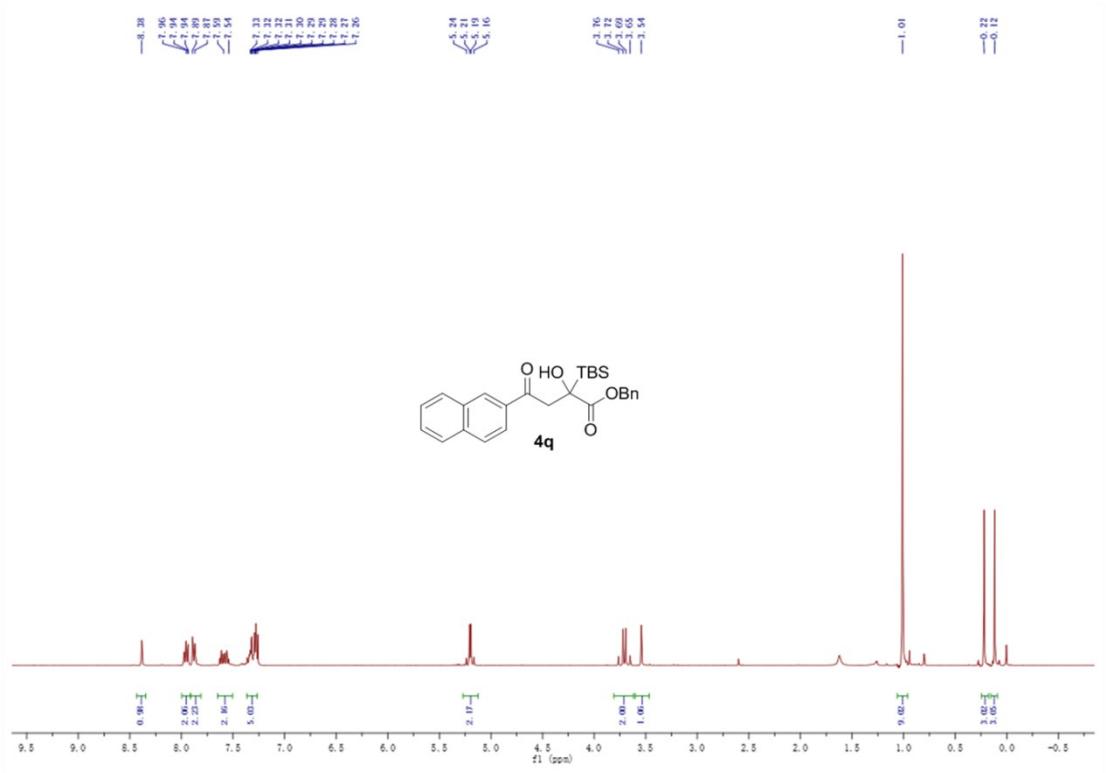

196.95
177.35
163.74
135.57
130.40
129.65
128.60
128.40
128.16
113.75
77.32
77.00
76.68
71.73
67.17
55.48
43.81
27.23
18.41
-7.21
-7.28
O
HO
TBS
OBn
O
MeO
4l
f1 (ppm)

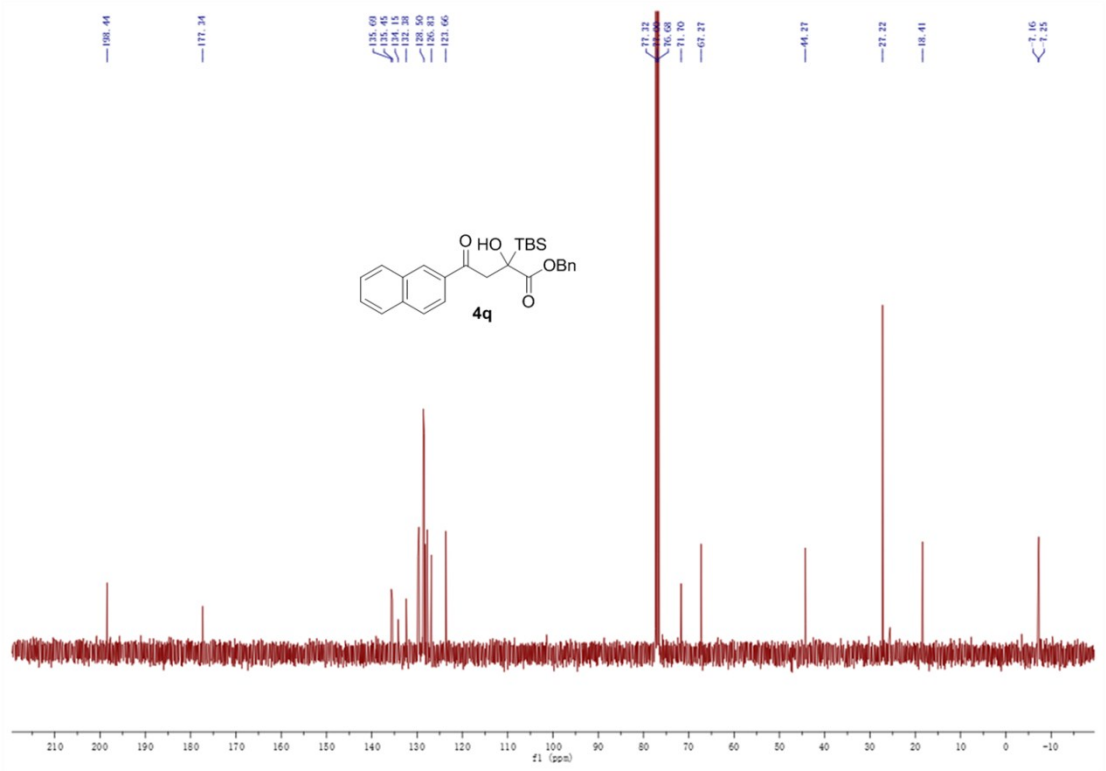

MeO
O
HO
TBS
OBn
O
4m
f1 (ppm)

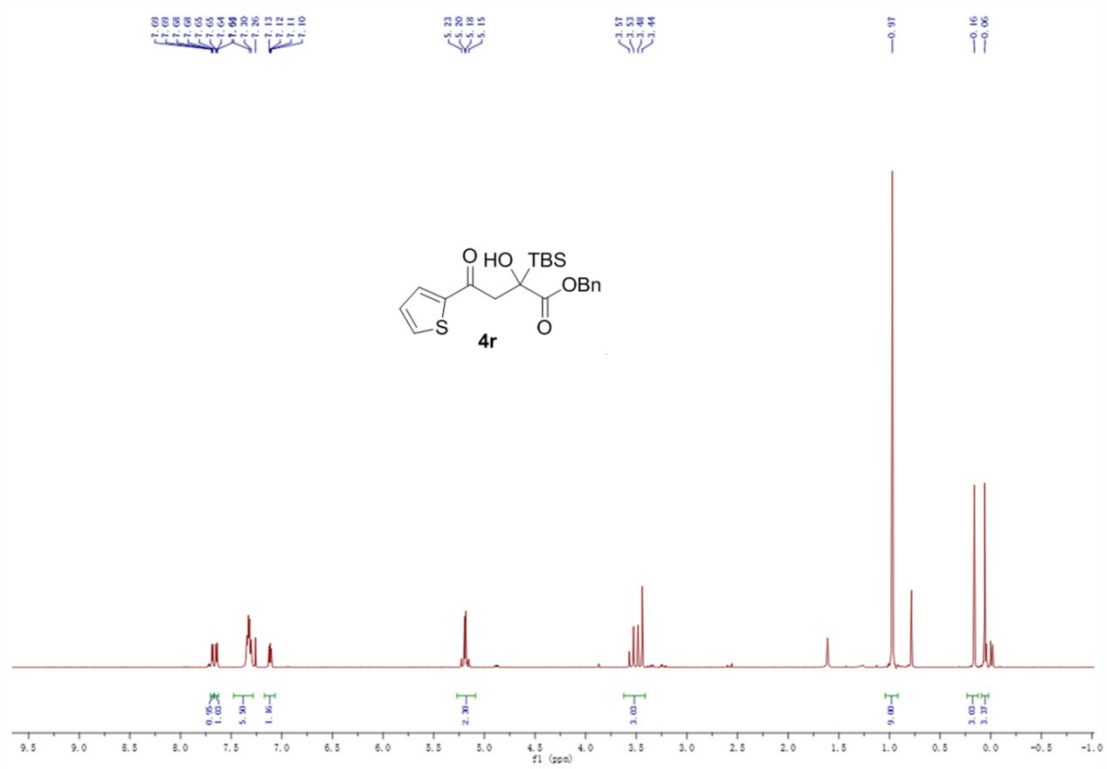

MeO
O
HO
TBS
OBn
O
4m
f1 (ppm)

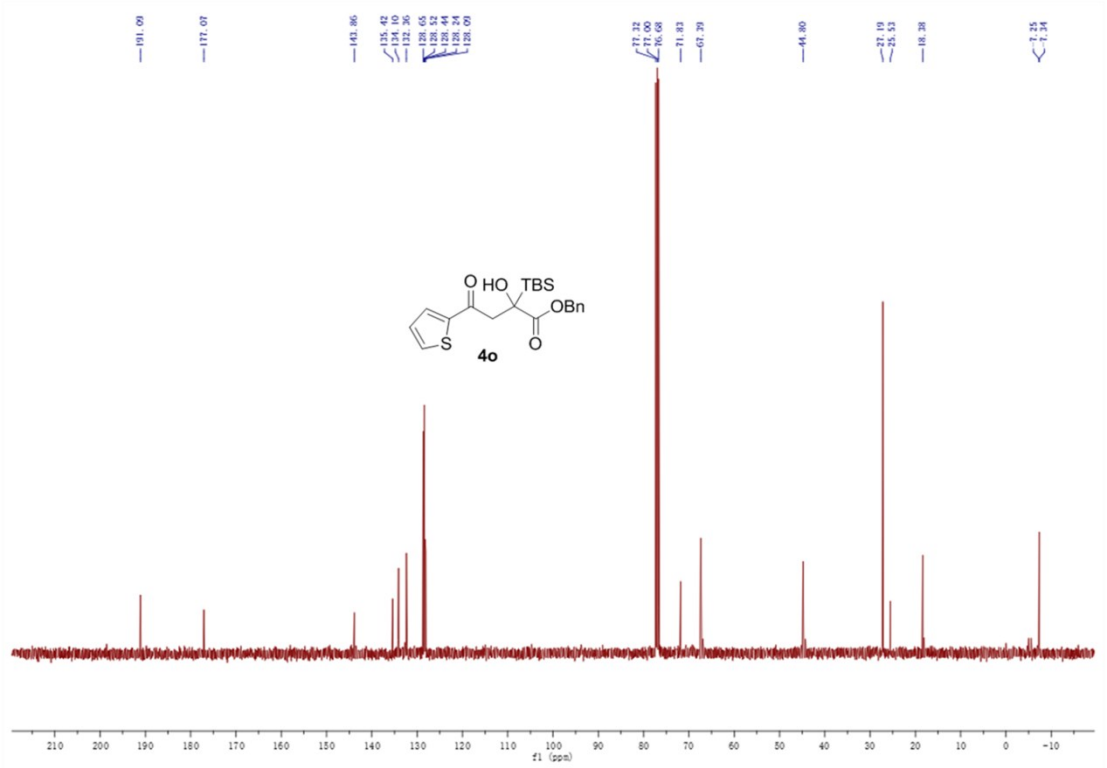

MeO
MeO
O
HO
TBS
OBn
O
4n


MeO
MeO
O
HO
TBS
OBn
O
4n


O HO TBS
OBn
O
4q
f1 (ppm)


O HO TBS
OBn
O
4q
f1 (ppm)


O
HO
TBS
OBn
O
S
4r
f1 (ppm)


O
HO
TBS
OBn
O
S
4o
f1 (ppm)