Supporting Information

A Base-promoted Regiodivergent Allylation of N-Acylhydrazones with Morita-Baylis-Hillman Carbonates through Tuning Catalyst

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†Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/x0xx00000x

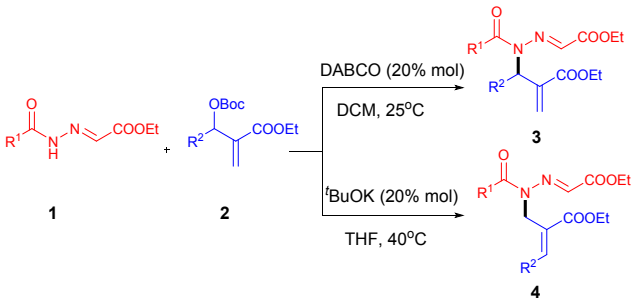
Content

1. General methods

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard. High resolution mass spectra (HRMS) were obtained on a micrOTOF-Q Ⅱ HRMS/MS instrument (Bruker) with the technique of electrospray ionization. The optically active Morita-Baylis-Hillman carbonate **2d** were prepared according to reported procedures.[1]

2. Experimental section

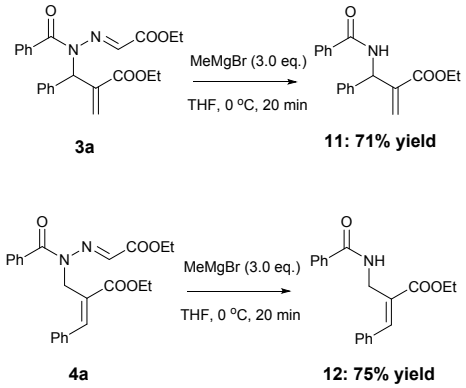
2.1 Typical procedure for the allylation reaction of **3** or **4**.



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with N-Acylhydrazones **1** (0.15 mmol,), MBH carbonates **2** (0.15 mmol), DABCO (0.03 mmol, 3.4 mg) or ^{t}BuOK (0.03 mmol, 3.4 mg). Freshly distilled DCM (3 mL) or THF (3 mL) was added into the mixture with a syringe. The mixture was stirred at corresponding temperature until completion (monitored by TLC). The solvent was removed under reduced pressure and the resulted crude residue was purified by column chromatography (silicagel, mixtures of petroleum ether/ethyl acetate, 5:1-15:1, v/v) to

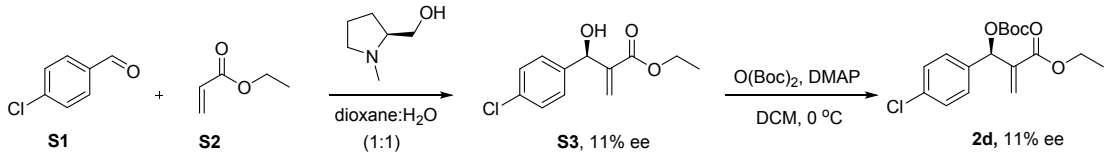
afford the desired product **3** or **4**.

2.2 Typical procedure for the preparations of **11** and **12**.



Under N_2 atmosphere, an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **3a** or **4a** (0.5 mmol, 204 mg). Freshly distilled THF (4 mL) was added into the tube. The mixture was stirred at 0 °C. Diluted Grignard reagent MeMgBr (3.0 eq., 1.5 mL, 0.5 mol/L in THF) was then added dropwise and stirred for 10-20 min. The mixture was stirred at 0 °C until **3a** or **4a** disappeared, as monitored by TLC. Reaction was quenched with saturated ammonium chloride. The aqueous phase were extracted by methylene chloride, dehydrated by anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the resulted crude residue was purified by column chromatography (silicagel, mixtures of petroleum ether/ethyl acetate, 7:1, v/v) to afford the desired product **11** or **12**.

2.3 The optically active Morita-Baylis-Hillman carbonate **2d**



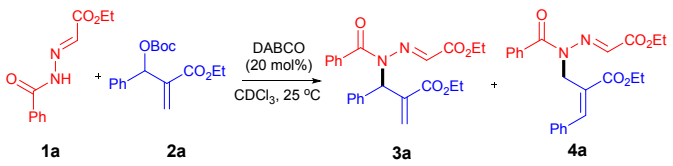
To a cold (0 °C) solution of aldehyde **S1**(1 mmol) in 1,4-dioxane:water (2 mL; 1 :

1, v/v) were added N-methylprolinol (0.5 mmol) and activated alkene **S2** (3 mmol) and the mixture was stirred for 24 h at the same temperature. After completion of the reaction (by TLC), the reaction mixture was partitioned with diethyl ether (2×50 mL) and water (1×60 mL). The organic phase was washed with brine (2×50 mL), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography (silicagel, mixtures of petroleum ether/ethyl acetate, 7:1, v/v) to afford product **S3**.

Then, alcohol **S2** were converted to the corresponding carbonate **3b**: alcohol **S3** (1.0 eq., 1.0 mmol) and $O(Boc)_2$ (1.1 eq., 1.1 mmol) were dissolved in DCM (2.0 mL) and the solution was cooled to 0 °C. Afterward, DMAP (0.10 eq., 0.10 mmol) was added and the reaction mixture stirred at room temperature for 12 h. After 12 h, the reaction mixture was diluted with CH_2Cl_2. The combined organic phase was washed with 4 N aq. HCl solution, saturated aq. $NaHCO_3$ and brine. The organic layer, dried over anhydrous Na_2SO_4, filtered and vacuum at rotary evaporator to obtain an oil. The crude product was purified by chromatography (silicagel, mixtures of petroleum ether/ethyl acetate, 7:1, v/v) to afford **2d**.

3. Mechanism study

3.1 Kinetic profile experiment between **3a** and **4a**



An NMR sample tube was charged with N-Acylhydrazones **1a** (0.15 mmol, 33.1 mg), MBH carbonates **2a** (0.15 mmol, 46.0 mg), DABCO (0.03 mmol, 3.4 mg). $CDCl_3$ (3 mL) was added into the mixture. Shake the mixture well. We used

Mesitylene as the internal standard and NMR to monitor the reaction in real time.

Entry	time(min)	**2a**(%)	**3a**(%)	**4a**(%)
1	0	100	0	0
2	5	96	2	0
3	36	85	10	0
4	62	80	19	0
5	133	58	41	0
6	203	35	63	0
7	270	20	79	0
8	338	11	89	0

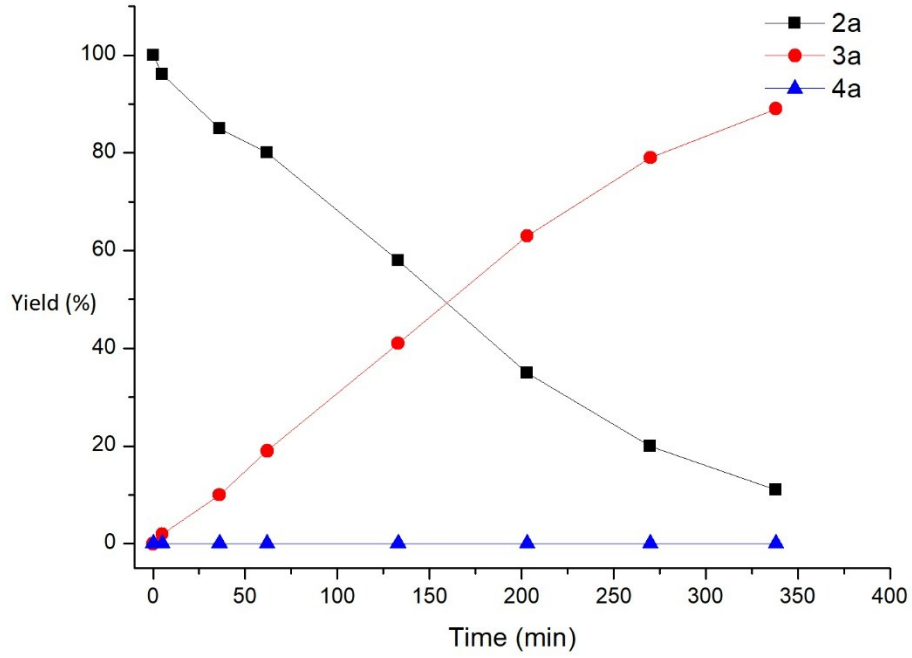
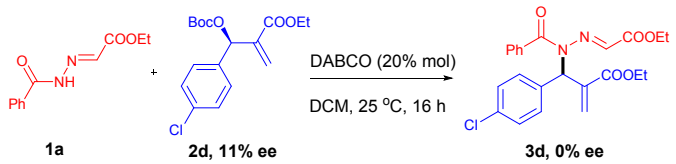


Figure S1. Kinetic reaction profile between **3a** and **4a**

3.2 The relationship between the optical activity of reactants and products

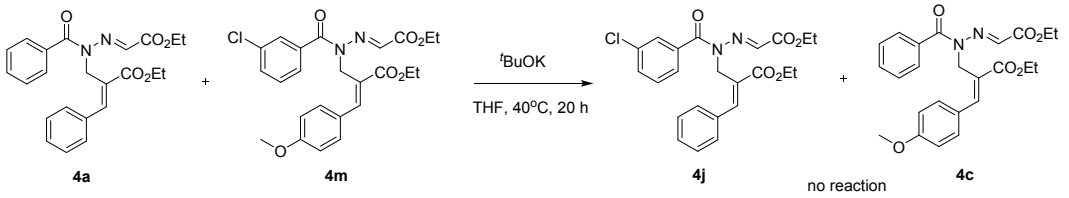


An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with N-Acylhydrazones **1a** (0.15 mmol, 33 mg), MBH carbonates **2d** (0.15 mmol, 51

mg), DABCO (0.03 mmol, 3.4 mg). Freshly distilled DCM (3 mL) was introduced into the mixture with a syringe. The reaction system was stirred at corresponding temperature until completion (monitored by TLC). After removal of the solvent under reduced pressure, the resulted crude residue was purified by column chromatography (silicagel, mixtures of petroleum ether/ethyl acetate, 7:1, v/v) to afford the racemic product **3d**.

3.3 Cross-over experiments

A mixture of isolated products **3a** (0.15 mmol), **3n** (0.15 mmol), DABCO (0.03 mmol, 3.4 mg) was added into an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar. Then freshly distilled DCM (3 mL) was input into the reaction system with a syringe. The mixture was stirred at corresponding temperature to observe the product equilibration (monitored by TLC).



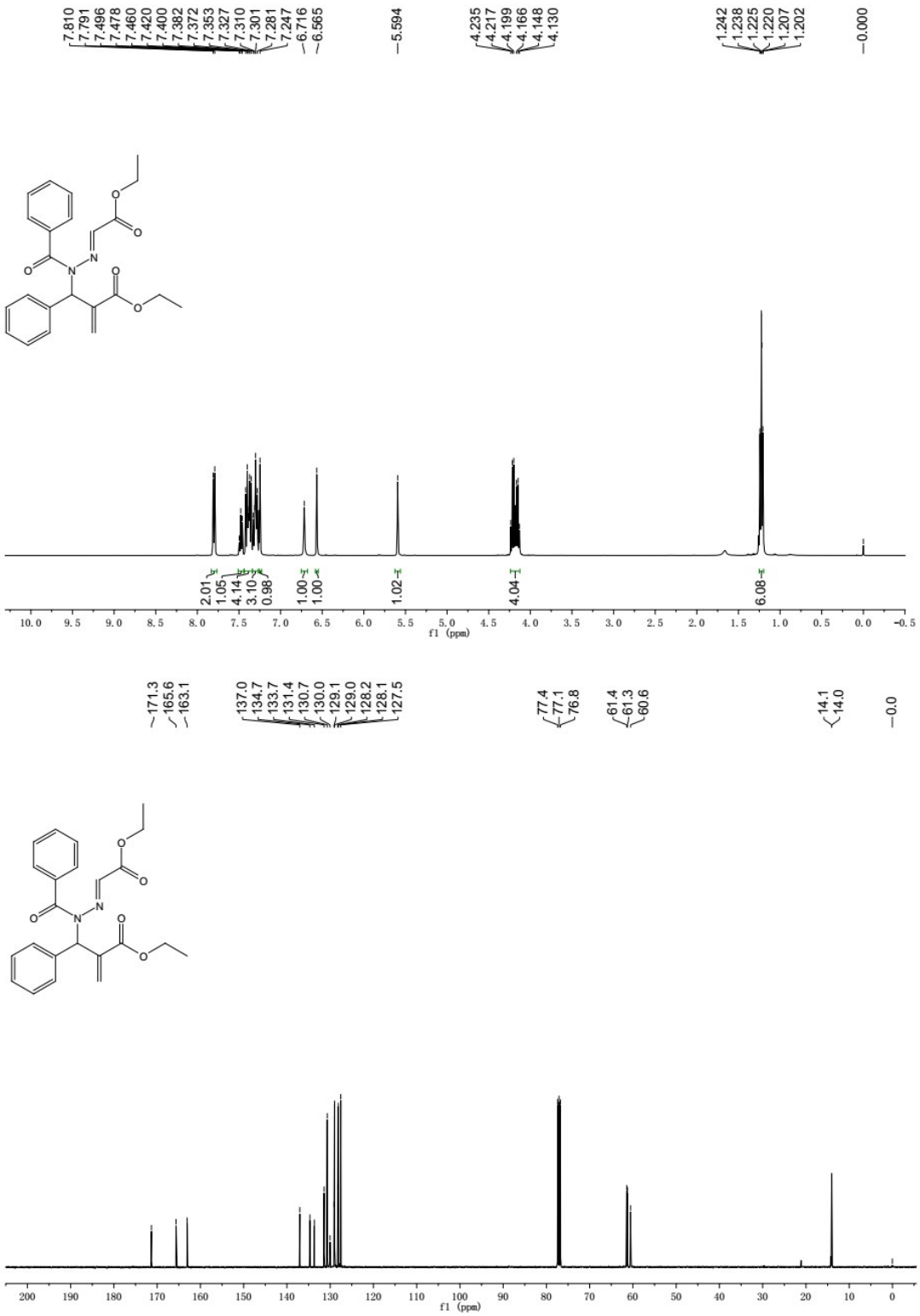
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with isolated products **4a** (0.15 mmol), **4m** (0.15 mmol), ^{t}BuOK (0.03 mmol, 3.4 mg). Freshly distilled THF (3 mL) was added into the mixture with a syringe. The mixture was stirred at corresponding temperature and the product equilibration was monitored by TLC.

4. References

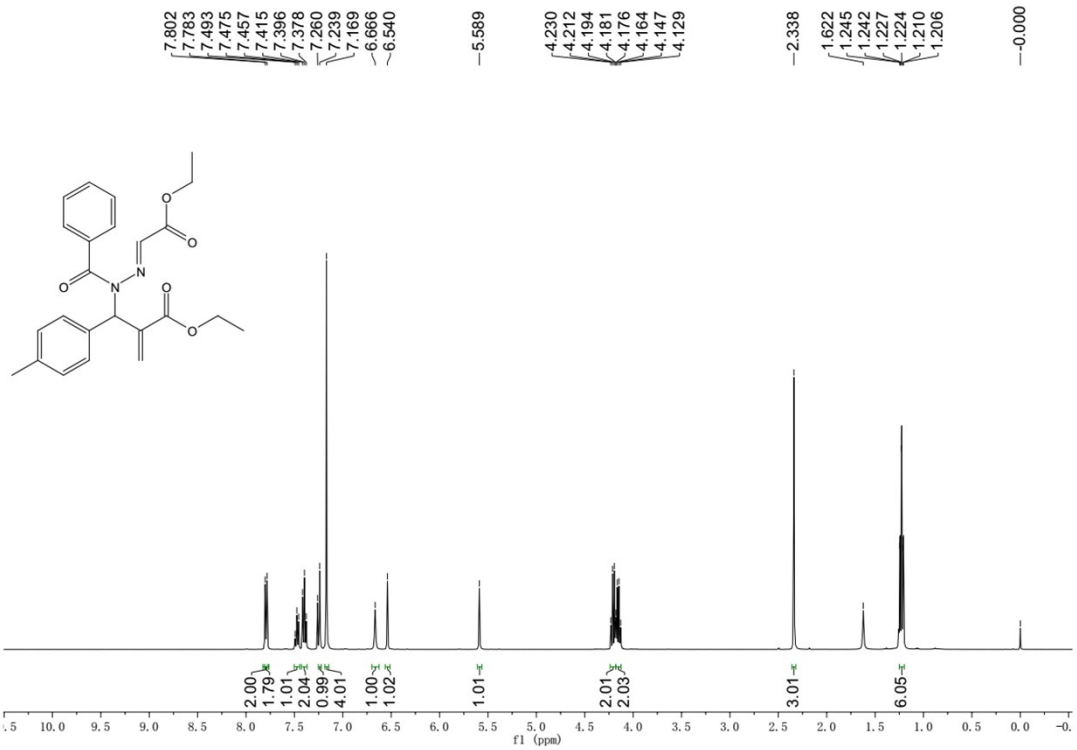
1.P. Radha Krishna, V. Kannan and P. V. Narasimha Reddy, *Adv. Synth. Catal.* 2004, **346**, 603.

5. Copies of ^{1}H and ^{13}C NMR spectra of products

3a



3b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4.212
4.194
4.181
4.176
4.164
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1.622
1.245
1.242
1.227
1.224
1.210
1.206
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2.00
1.79
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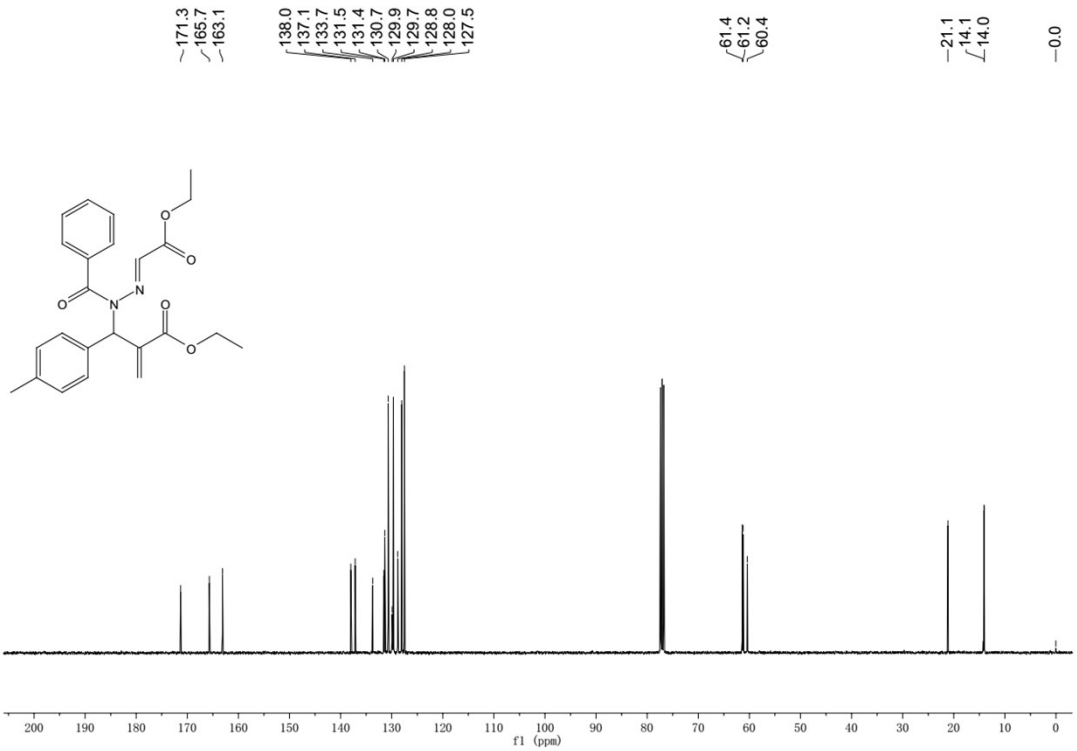
1.01
2.01
2.03
3.01
6.05
f1 (ppm)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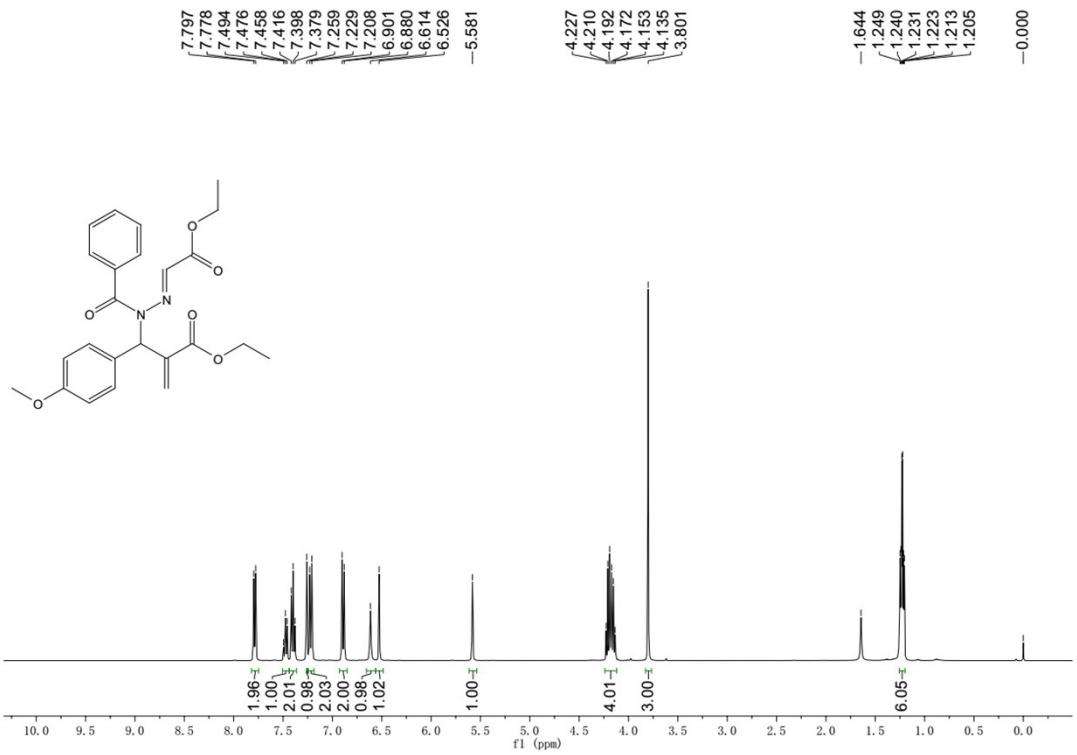
0.0
f1 (ppm)

3c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5.581
4.227
4.210
4.192
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4.135
3.801
1.644
1.249
1.240
1.231
1.223
1.213
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1.96
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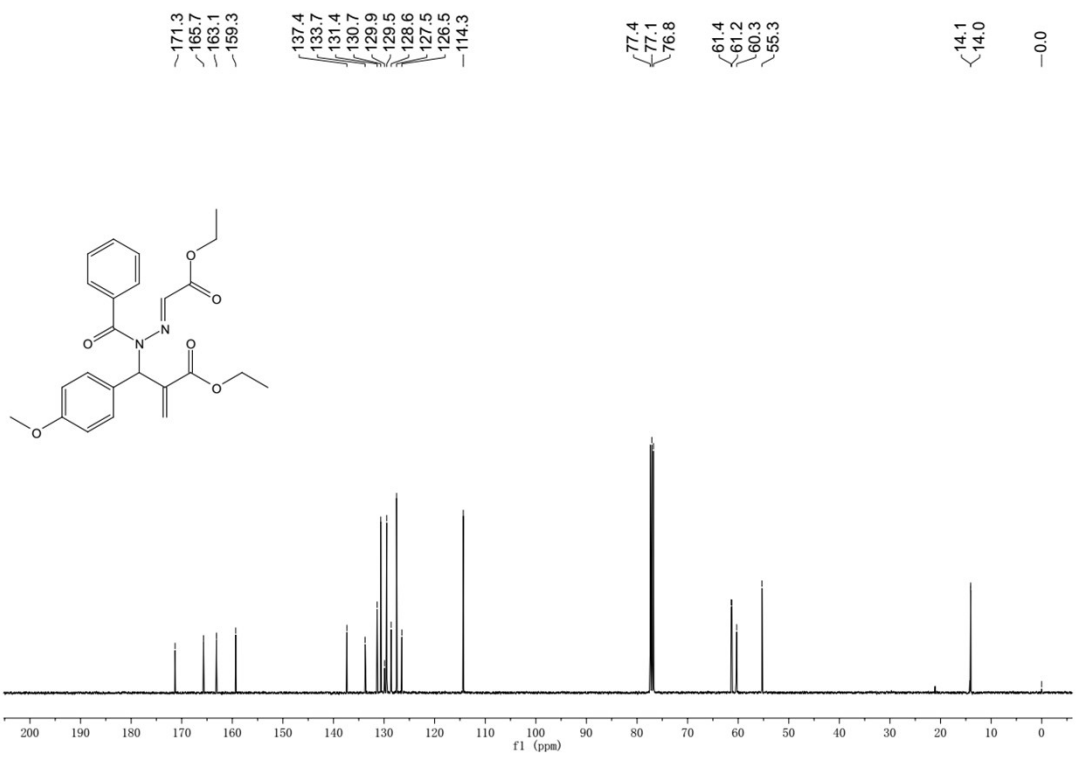
f1 (ppm)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126.5
114.3
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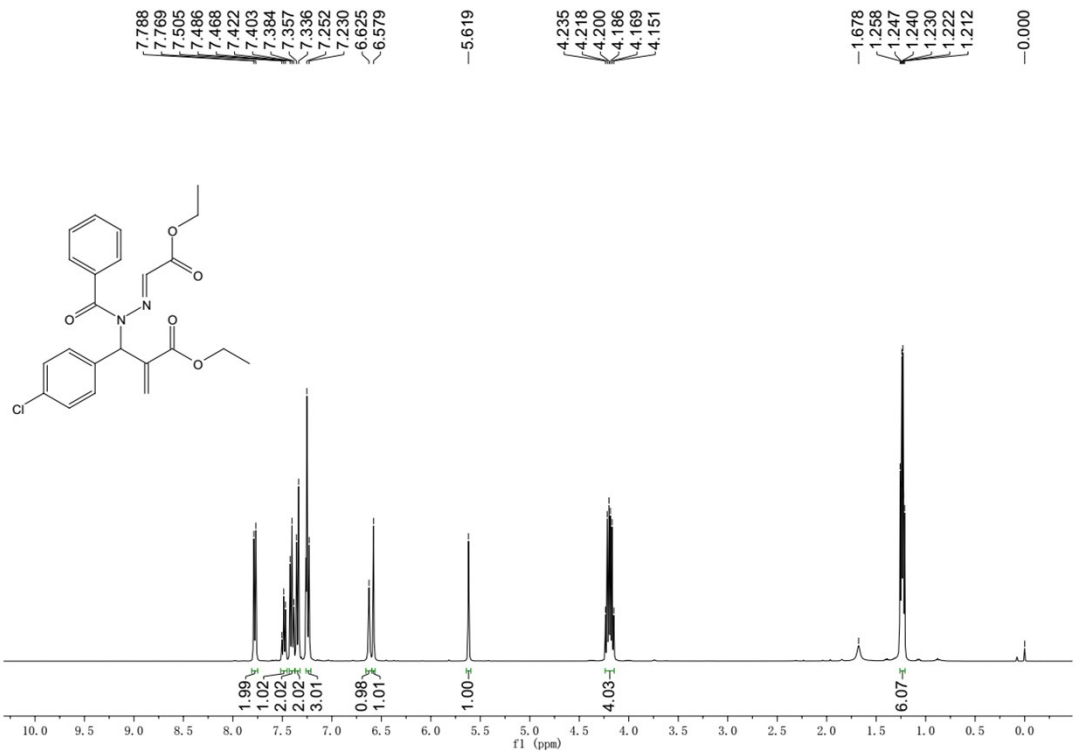
f1 (ppm)

3d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6.579
5.619
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1.258
1.247
1.240
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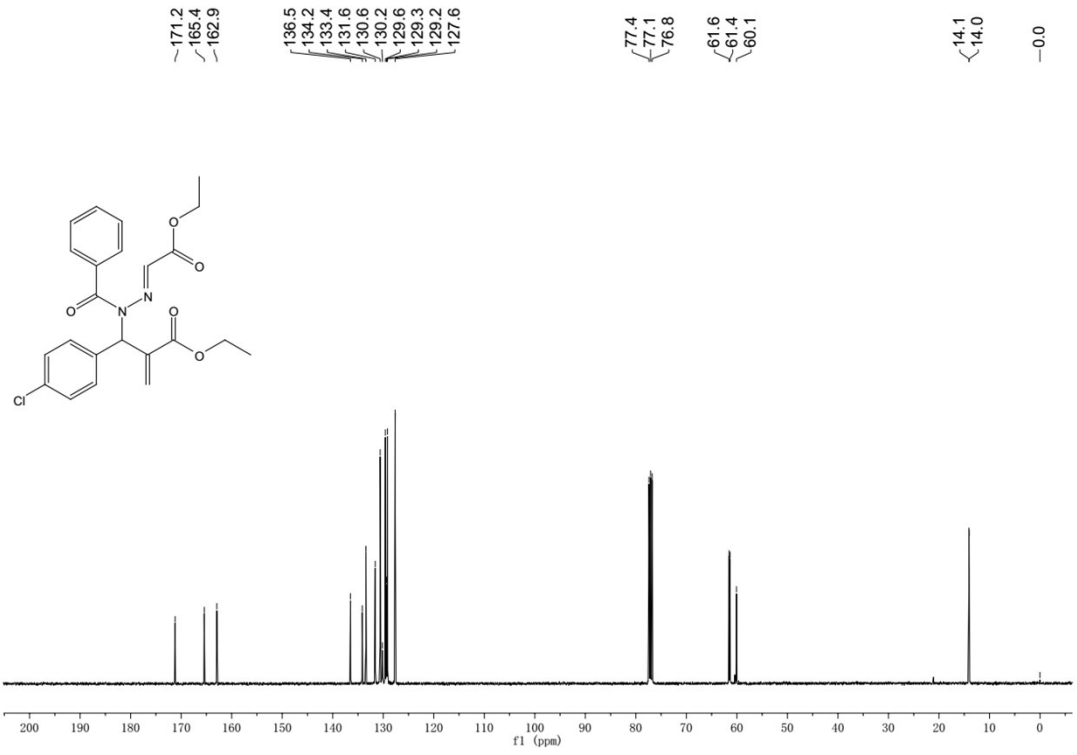
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136.5
134.2
133.4
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130.6
130.2
129.6
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129.2
127.6
77.4
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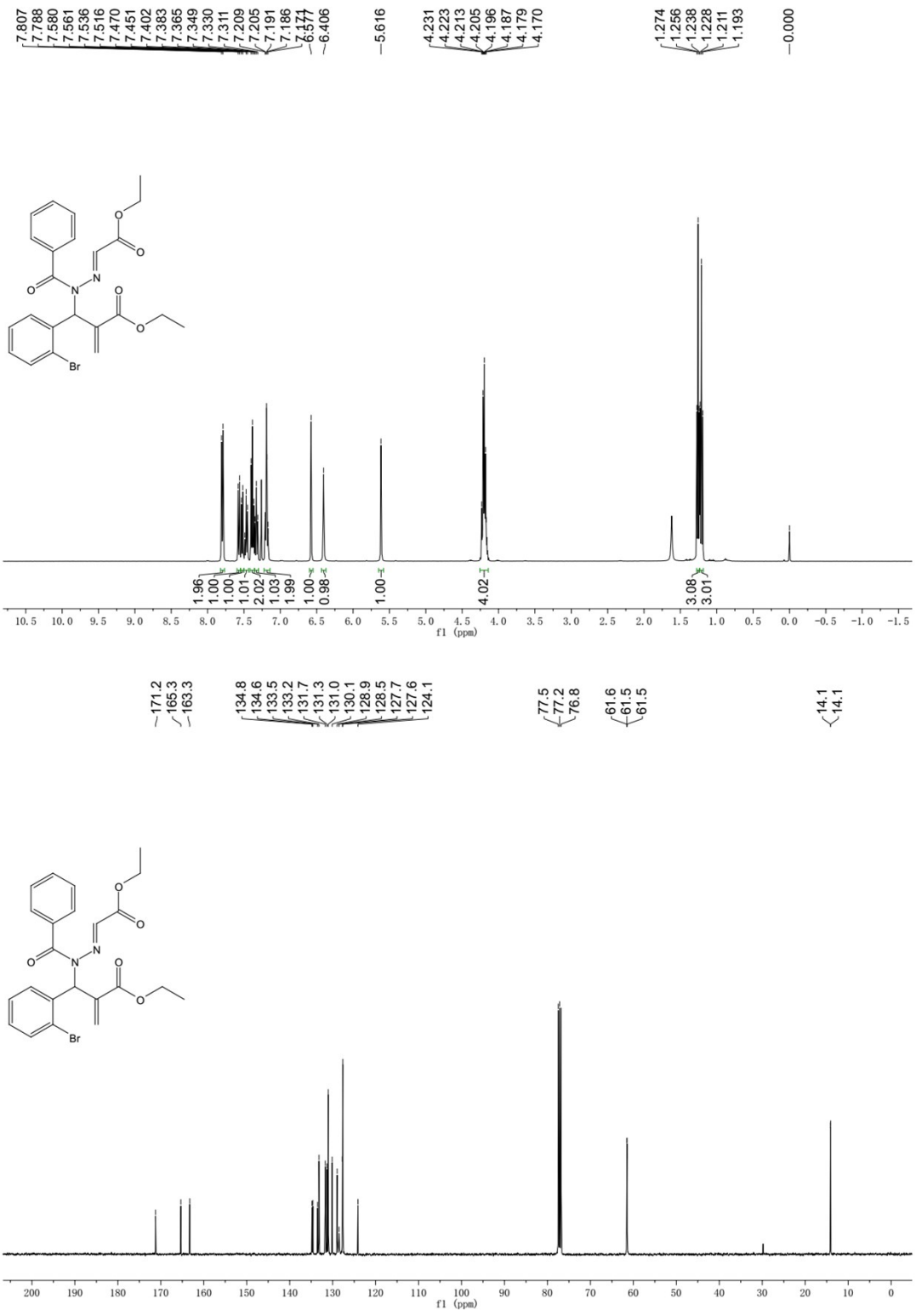
76.8
61.6
61.4
60.1
14.1
14.0
0.0
f1 (ppm)

3e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7.205
7.191
7.186
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6.406
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4.223
4.213
4.205
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4.187
4.179
4.170
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1.238
1.228
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1.00
1.01
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0.98
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f1 (ppm)
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165.3
163.3
134.8
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130.1
128.9
128.5
127.7
127.6
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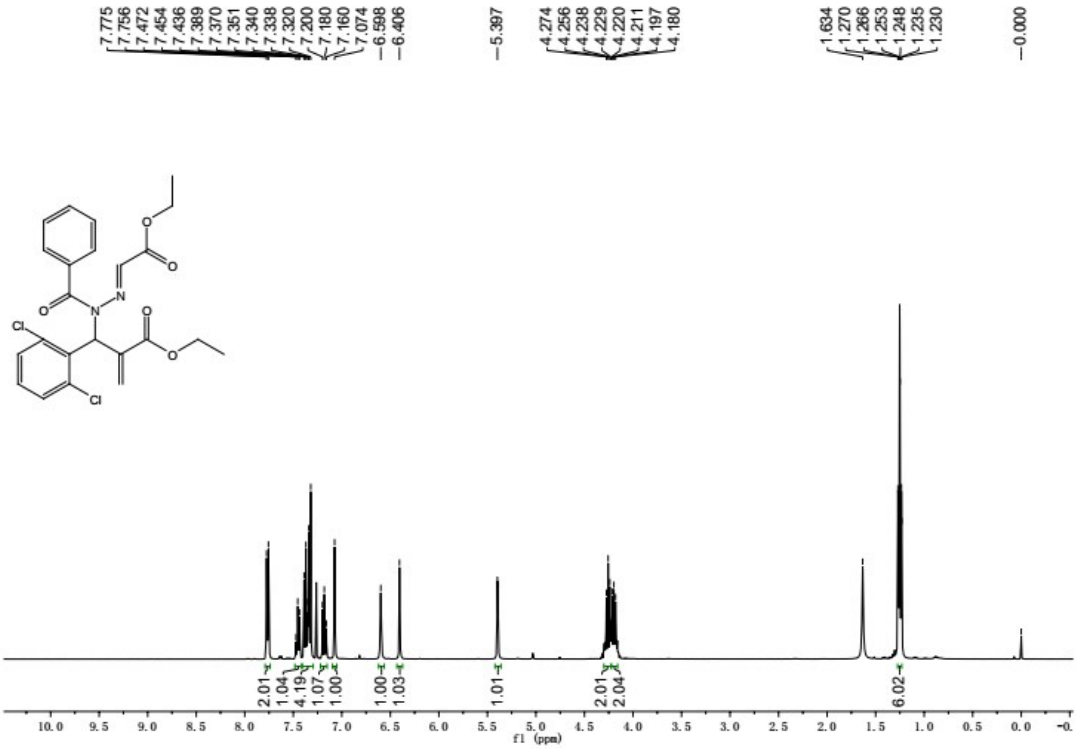
Br
f1 (ppm)

3f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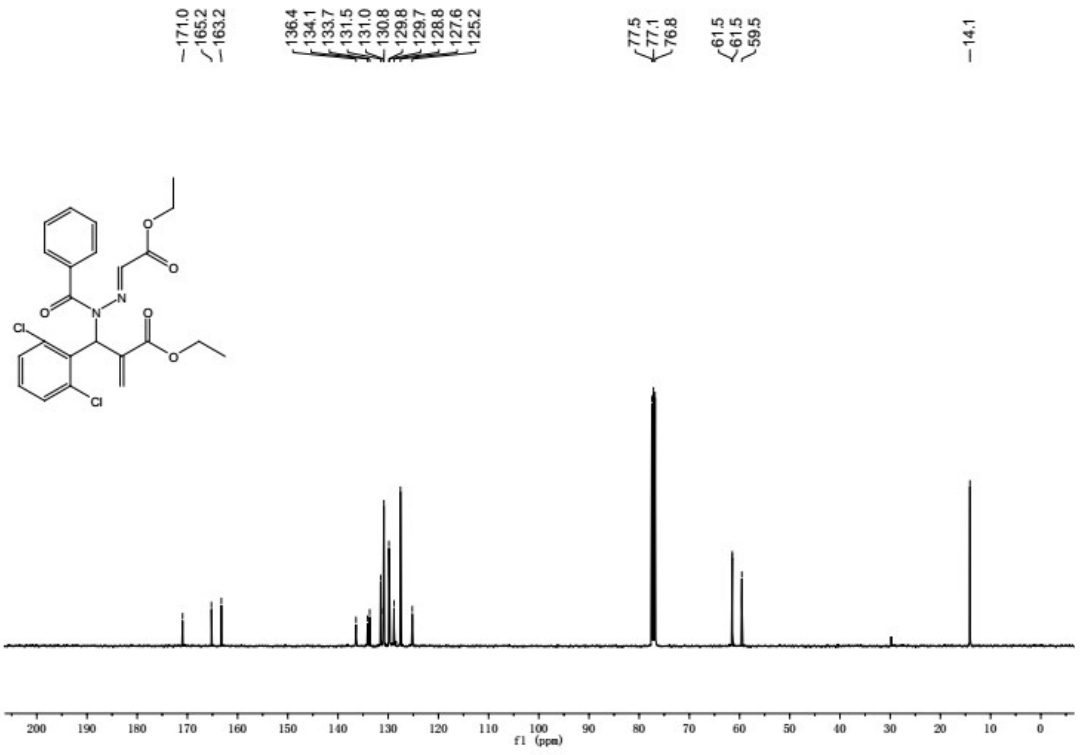
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61.5
59.5
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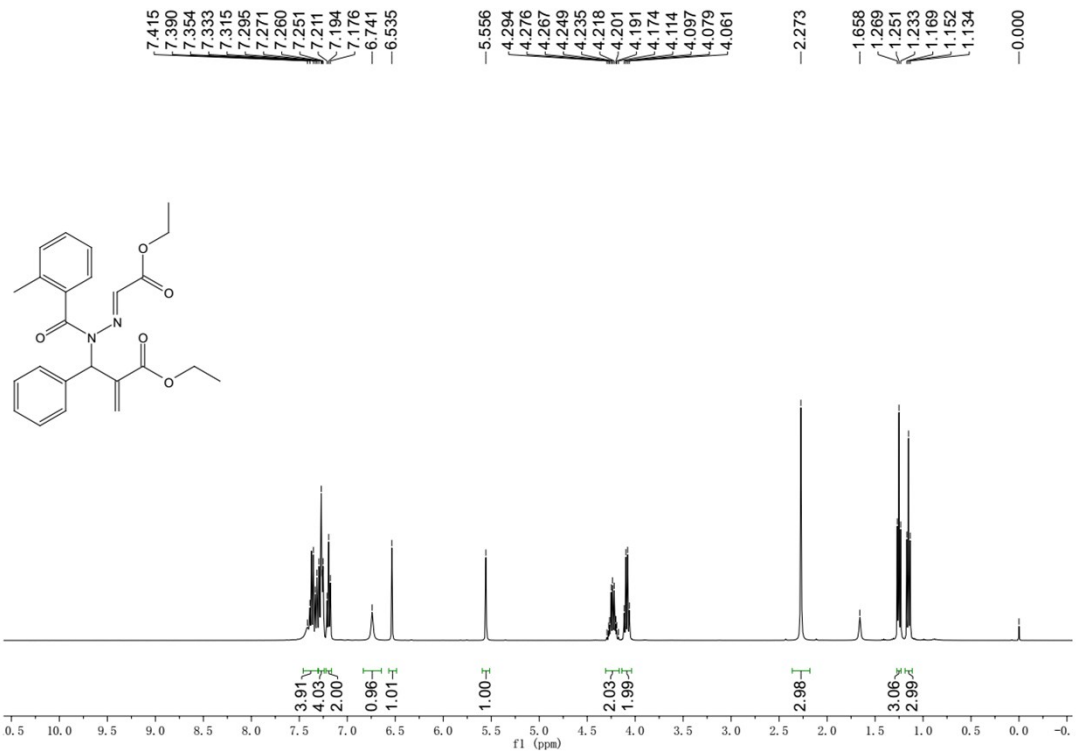
f1 (ppm)

3g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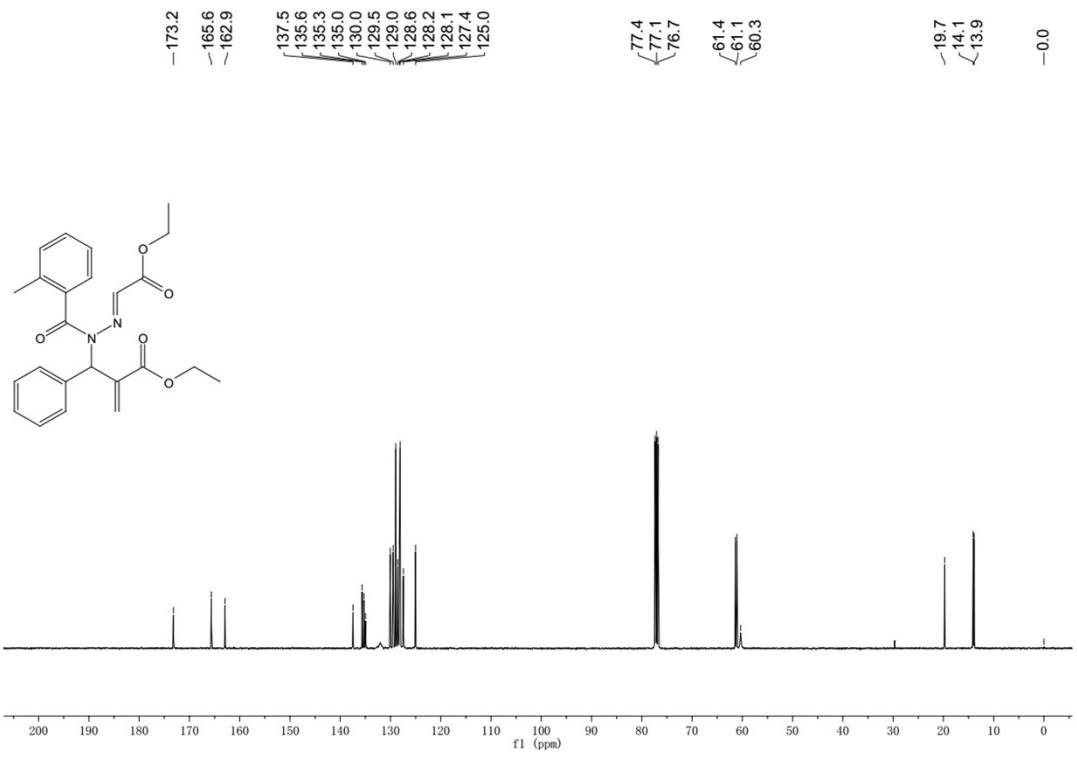
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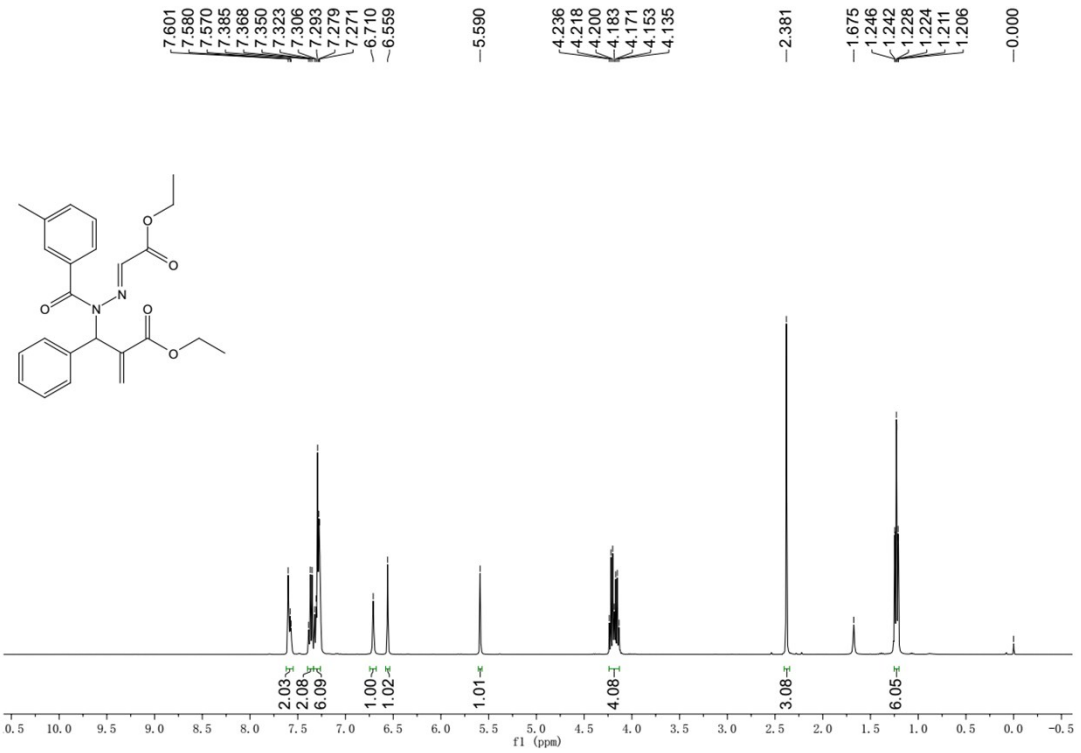
3h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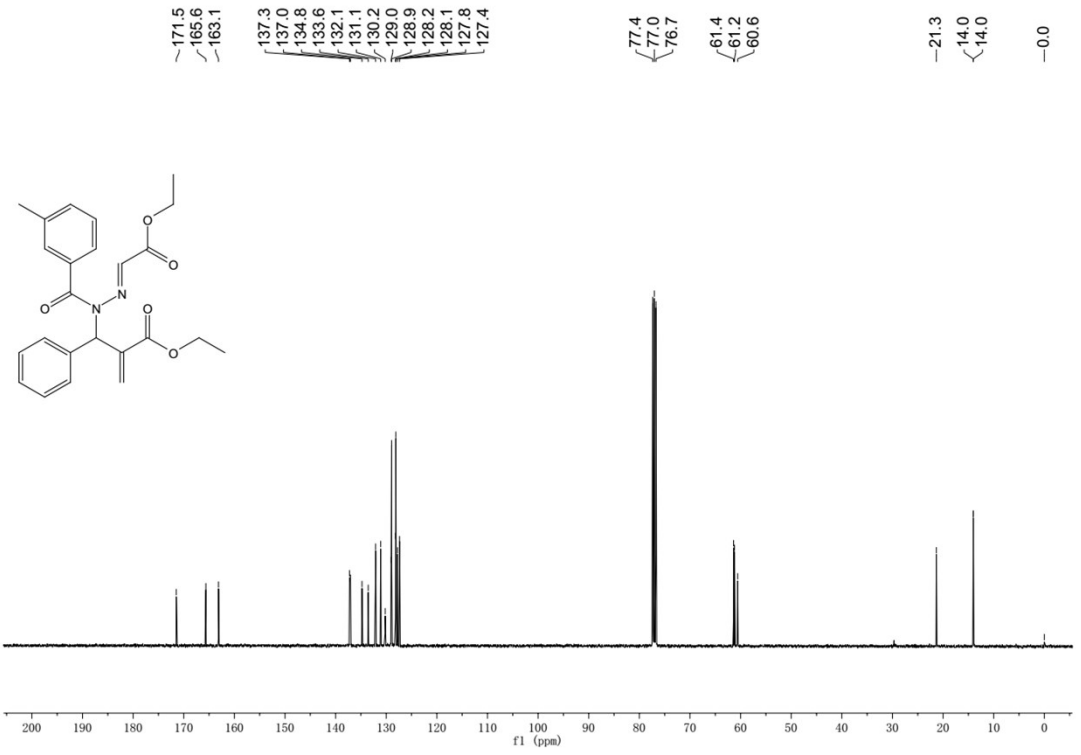
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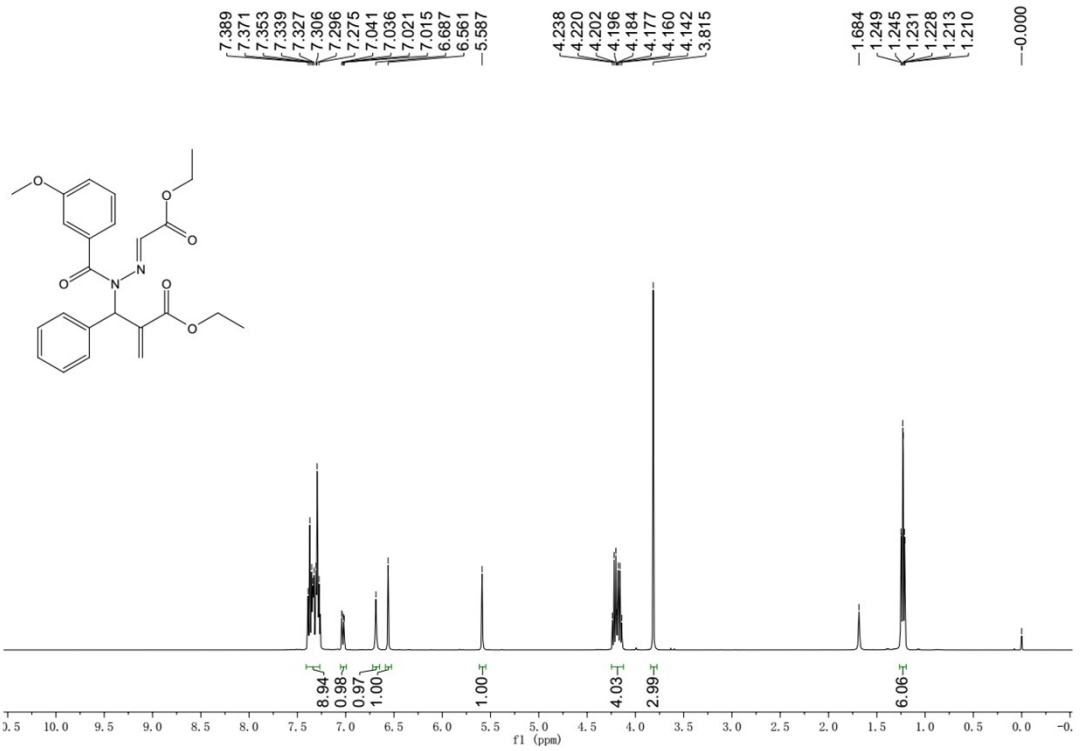
f1 (ppm)

3i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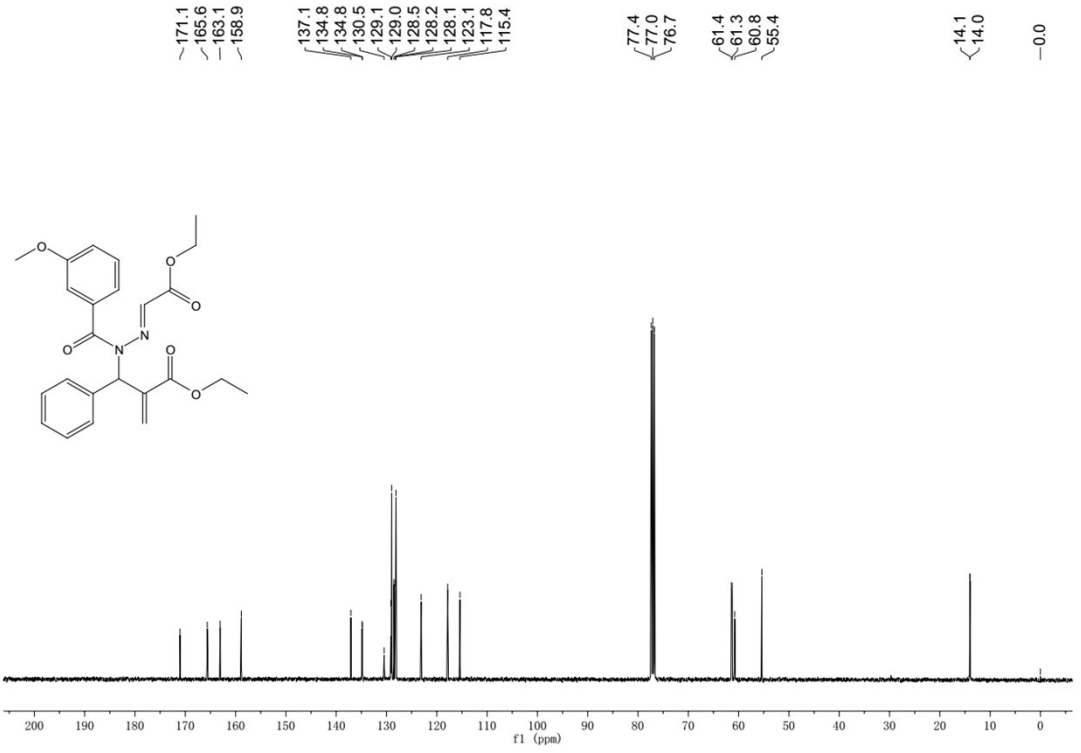
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123.1
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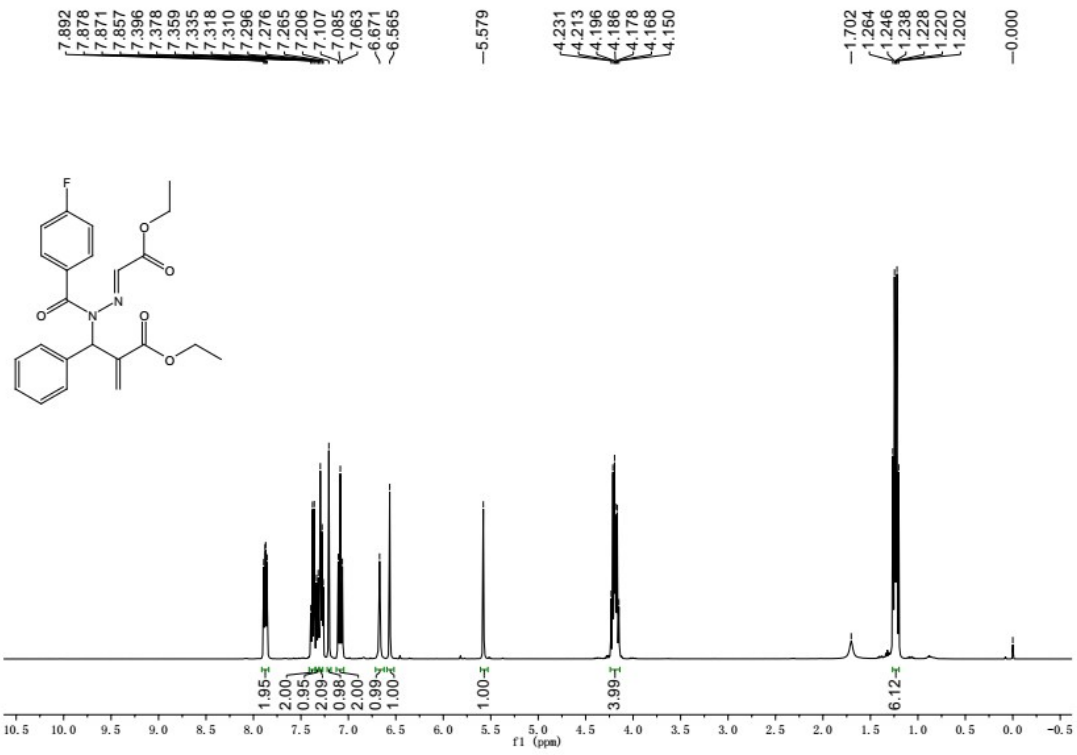
f1 (ppm)

3j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1.228
1.220
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O
N
N
O
O
O
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0.95
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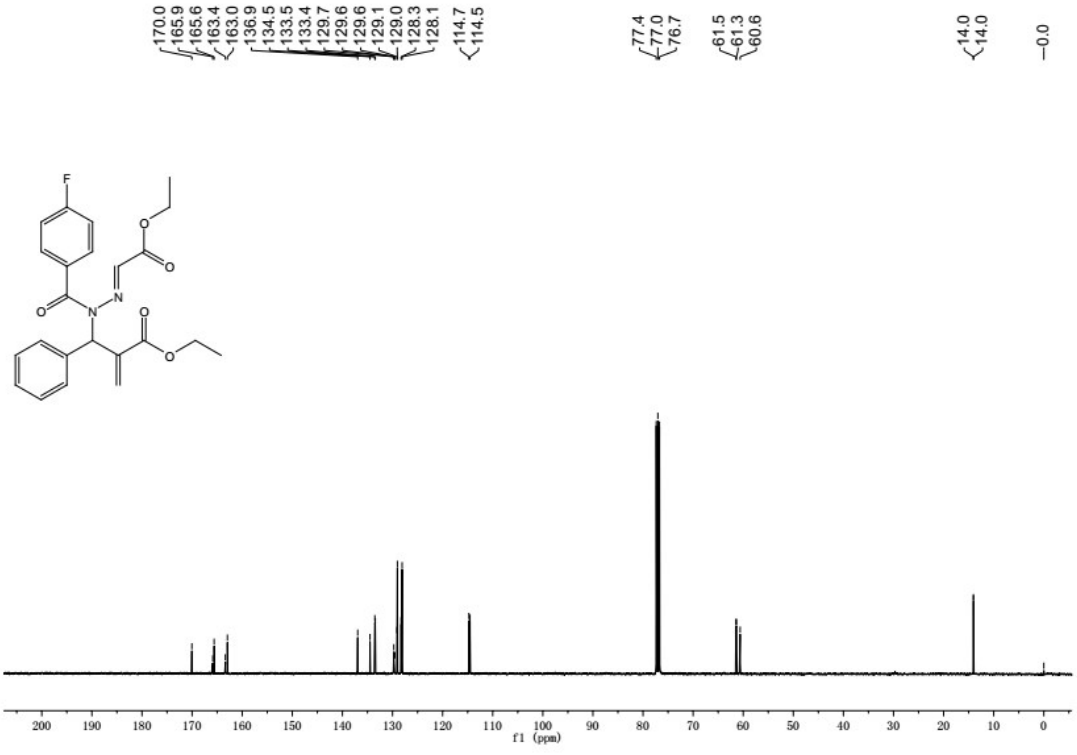
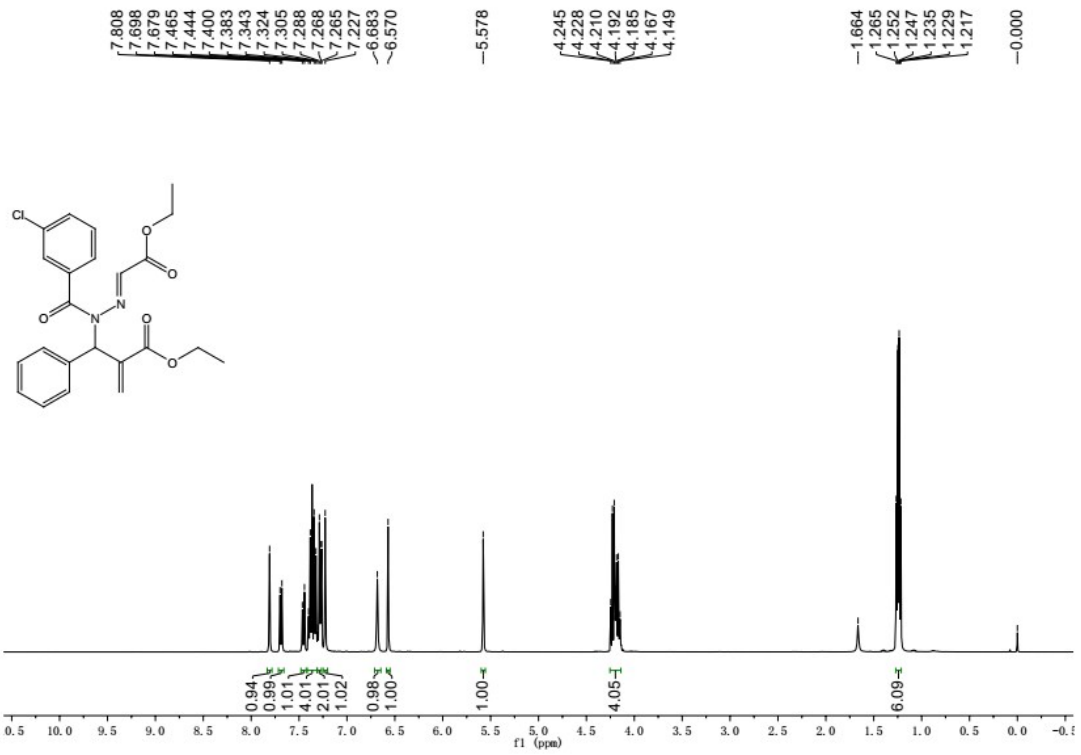
1.00
3.99
6.12
f1 (ppm)


170.0
165.9
165.6
163.4
163.0
136.9
134.5
133.5
133.4
129.7
129.6
129.6
129.1
129.0
128.3
128.1
114.7
114.5
77.4
77.0
76.7
61.5
61.3
60.6
14.0
14.0
0.0
F
O
O
N
N
O
O
O
f1 (ppm)

3k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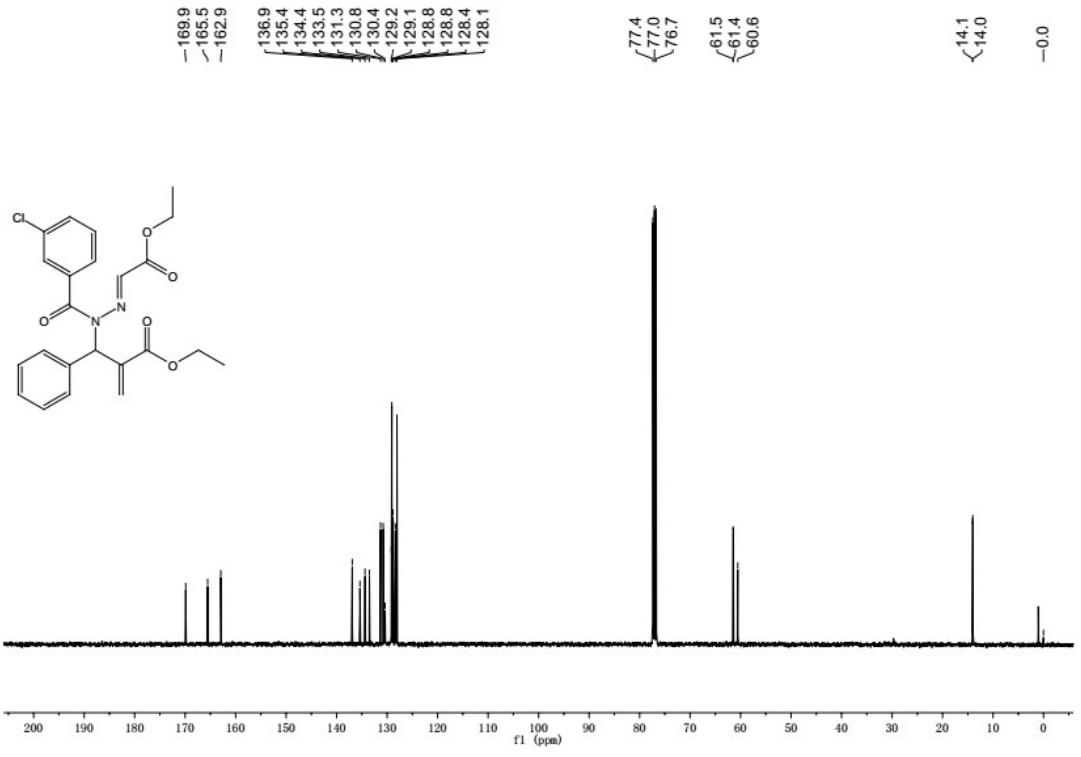
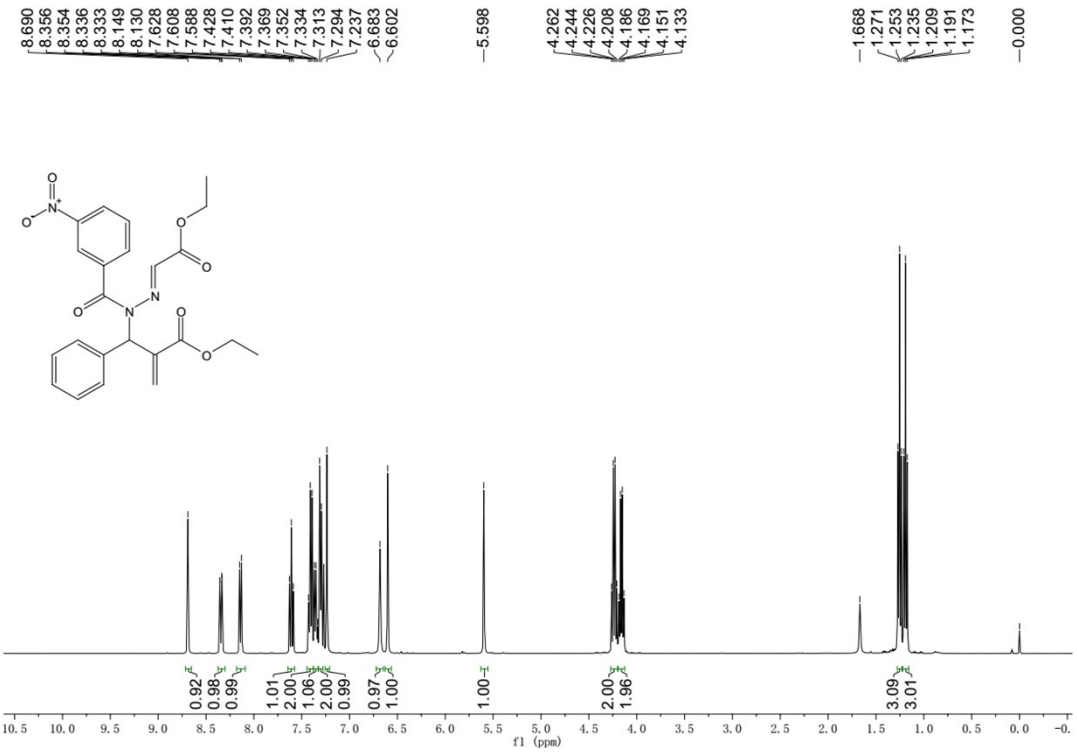
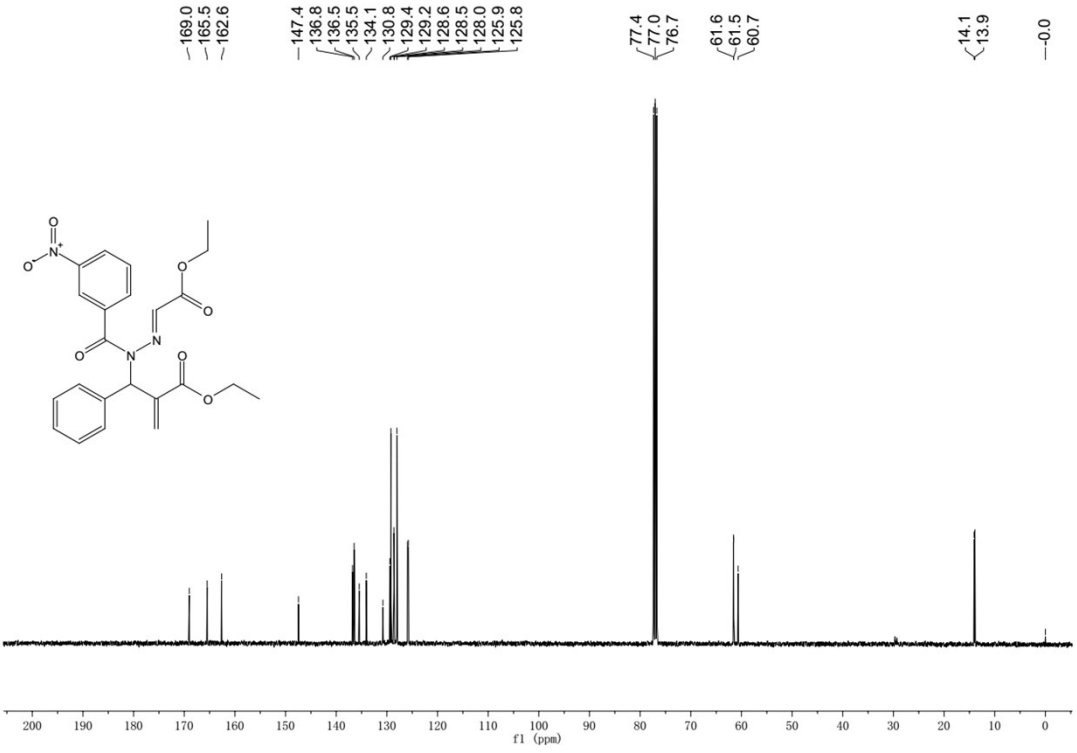
7.698
7.679
7.465
7.444
7.400
7.383
7.343
7.324
7.305
7.288
7.268
7.265
7.227
6.683
6.570
5.578
4.245
4.228
4.210
4.192
4.185
4.167
4.149
1.664
1.265
1.252
1.247
1.235
1.229
1.217
0.000
Cl
O
N
0.94
0.99
1.01
4.01
2.01
1.02
0.98
1.00
1.00
4.05
6.09
f1 (ppm)

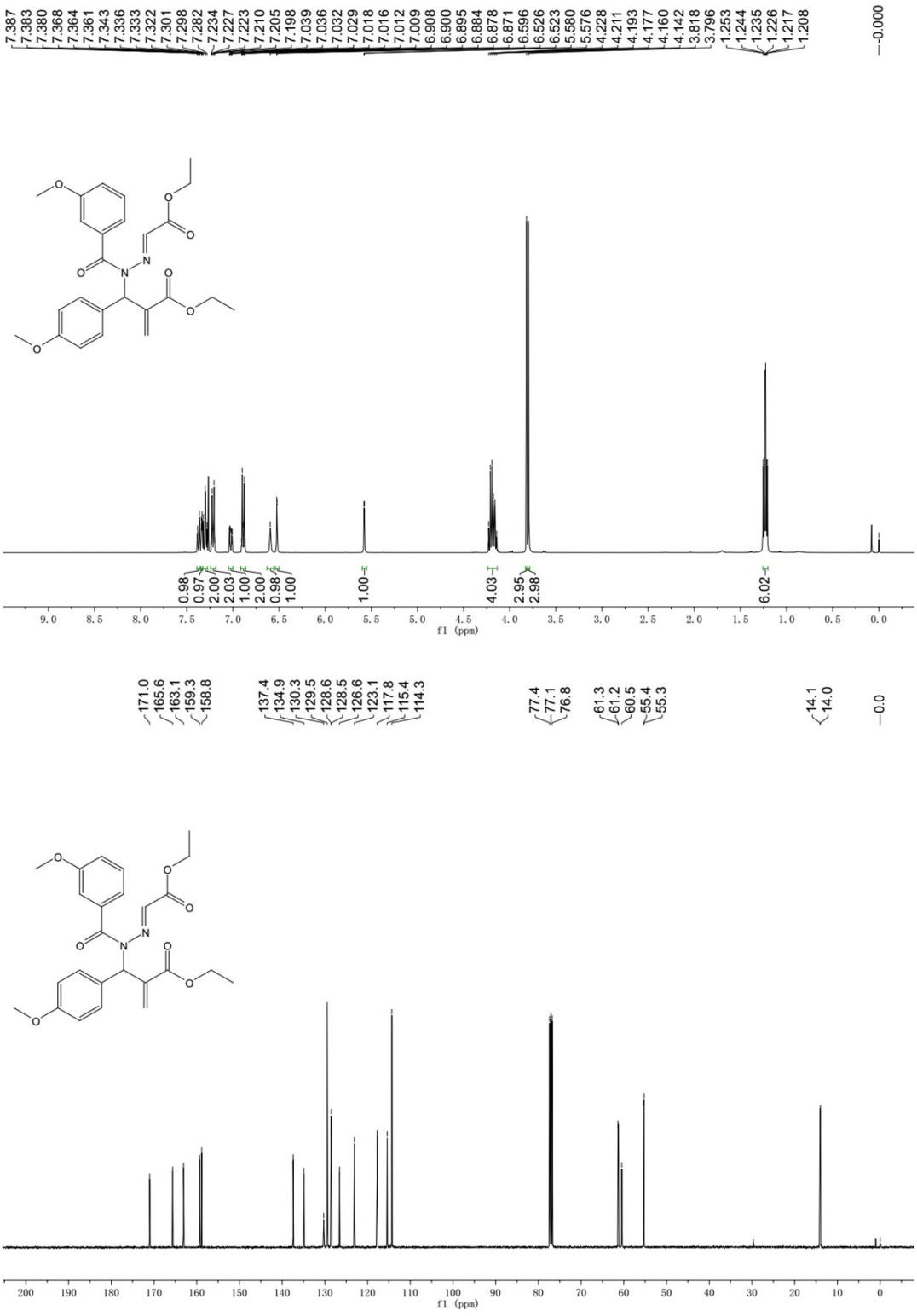

169.9
165.5
162.9
136.9
135.4
134.4
133.5
131.3
130.8
130.4
129.2
129.1
128.8
128.8
128.4
128.1
77.4
77.0
76.7
61.5
61.4
60.6
14.1
14.0
0.0
Cl
O
N
f1 (ppm)

3l


8.690
8.356
8.354
8.336
8.333
8.149
8.130
7.628
7.608
7.588
7.428
7.410
7.392
7.369
7.352
7.334
7.313
7.294
7.237
6.683
6.602
5.598
4.262
4.244
4.226
4.208
4.186
4.169
4.151
4.133
1.668
1.271
1.253
1.235
1.209
1.191
1.173
0.000
0.92
0.98
0.99
1.01
2.00
1.06
2.00
0.99
0.97
1.00
1.00
2.00
1.96
3.09
3.01
f1 (ppm)


169.0
165.5
162.6
147.4
136.8
136.5
135.5
134.1
130.8
129.4
129.2
128.6
128.5
128.0
125.9
125.8
77.4
77.0
76.7
61.6
61.5
60.7
14.1
13.9
0.0
f1 (ppm)

3m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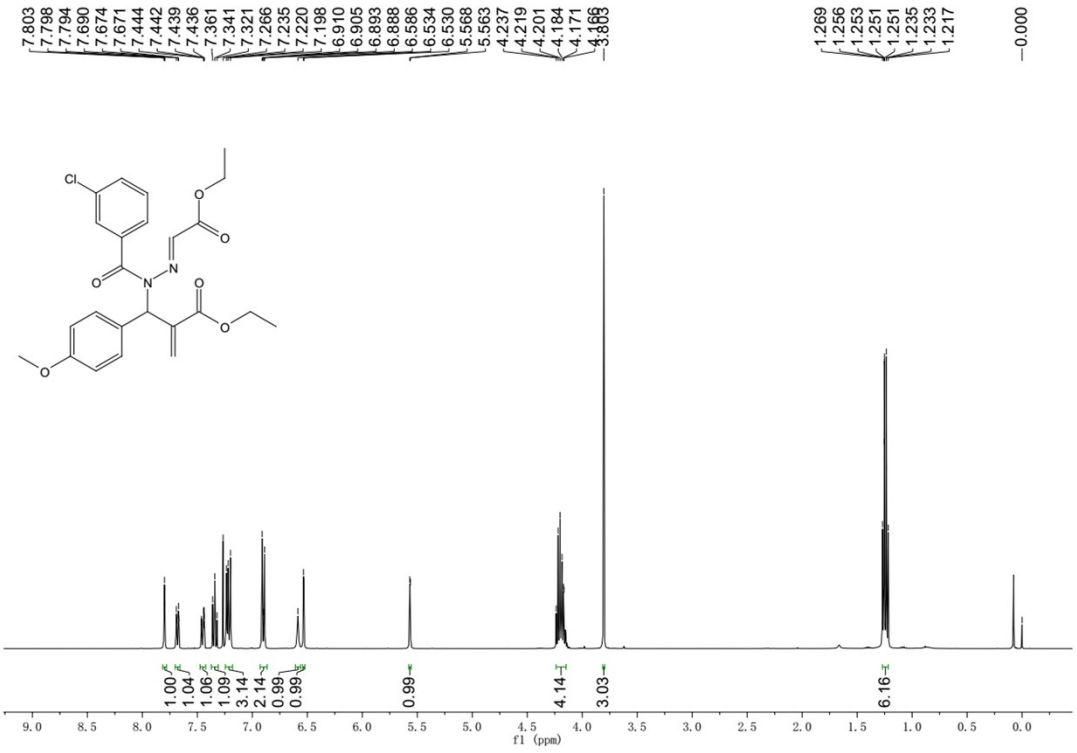
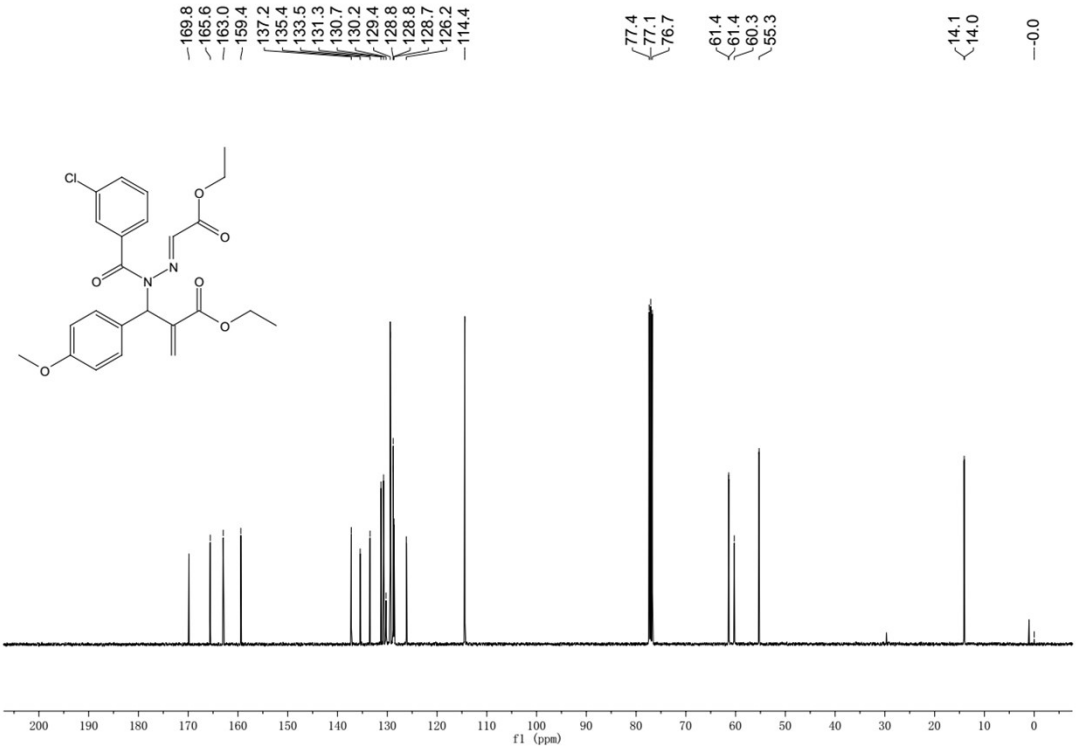
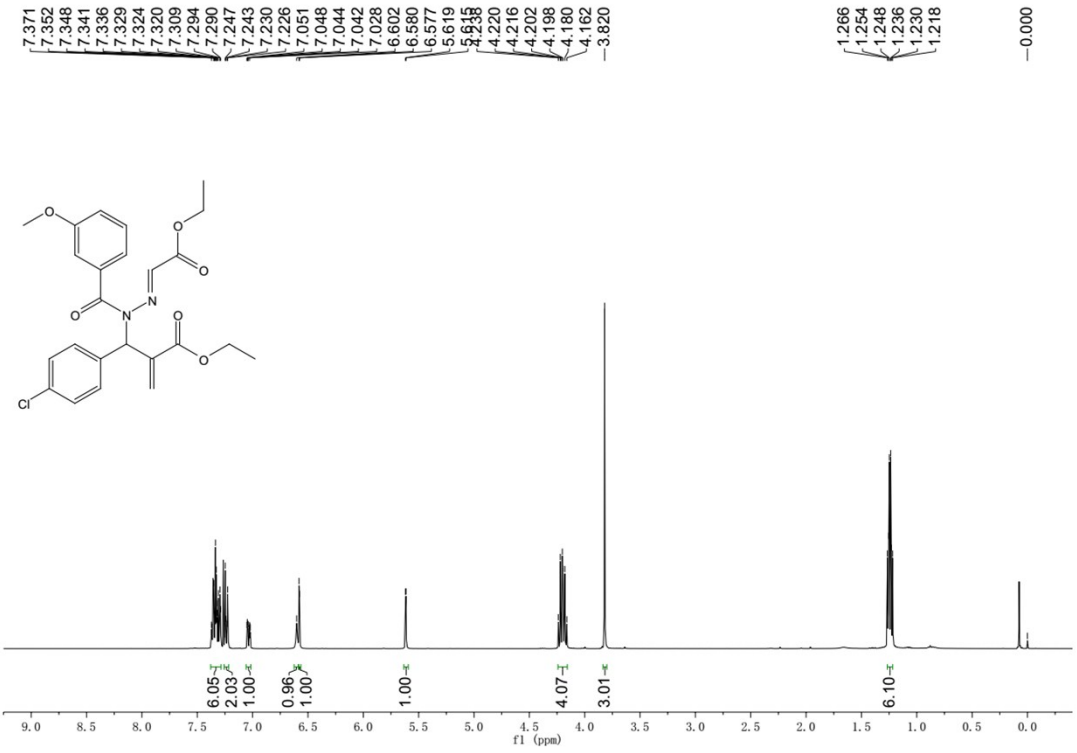
7.383
7.380
7.368
7.364
7.361
7.343
7.336
7.333
7.322
7.301
7.298
7.282
7.234
7.227
7.223
7.210
7.205
7.198
7.039
7.036
7.032
7.029
7.018
7.016
7.012
7.009
6.908
6.900
6.895
6.884
6.878
6.871
6.596
6.526
6.523
5.580
5.576
4.228
4.211
4.193
4.177
4.160
4.142
3.818
3.796
1.253
1.244
1.235
1.226
1.217
1.208
0.000
0.98
0.97
2.00
2.03
1.00
2.00
0.98
1.00
1.00
4.03
2.95
2.98
6.02
f1 (ppm)
171.0
165.6
163.1
159.3
158.8
137.4
134.9
130.3
129.5
128.6
128.5
126.6
123.1
117.8
115.4
114.3
77.4
77.1
76.8
61.3
61.2
60.5
55.4
55.3
14.1
14.0
0.0
f1 (ppm)

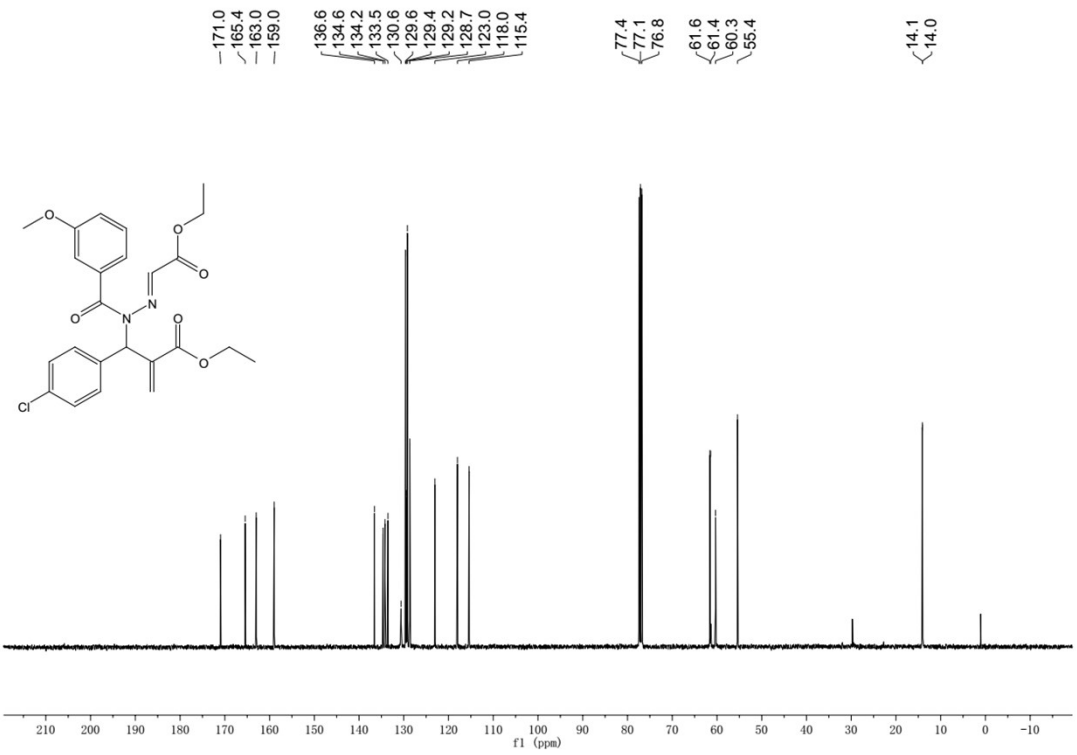
3n


7.803
7.798
7.794
7.690
7.674
7.671
7.444
7.442
7.439
7.436
7.361
7.341
7.321
7.266
7.235
7.220
7.198
6.910
6.905
6.893
6.888
6.586
6.534
6.530
5.568
5.563
4.237
4.219
4.201
4.184
4.171
4.166
3.803
1.269
1.256
1.253
1.251
1.251
1.235
1.233
1.217
0.000
Cl
O
O
N
N
O
O
O
O
1.00
1.04
1.06
1.09
3.14
2.14
0.99
0.99
0.99
4.14
3.03
6.16
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)

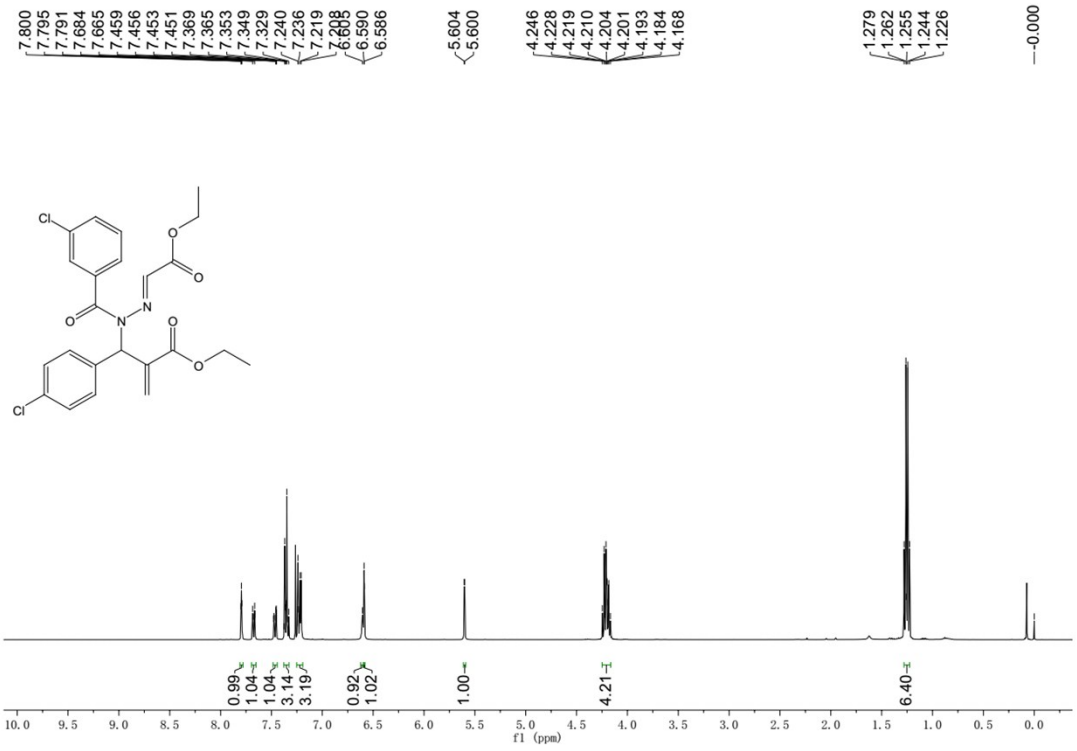

169.8
165.6
163.0
159.4
137.2
135.4
133.5
131.3
130.7
130.2
129.4
128.8
128.8
128.7
126.2
114.4
77.4
77.1
76.7
61.4
61.4
60.3
55.3
14.1
14.0
0.0
Cl
O
O
N
N
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

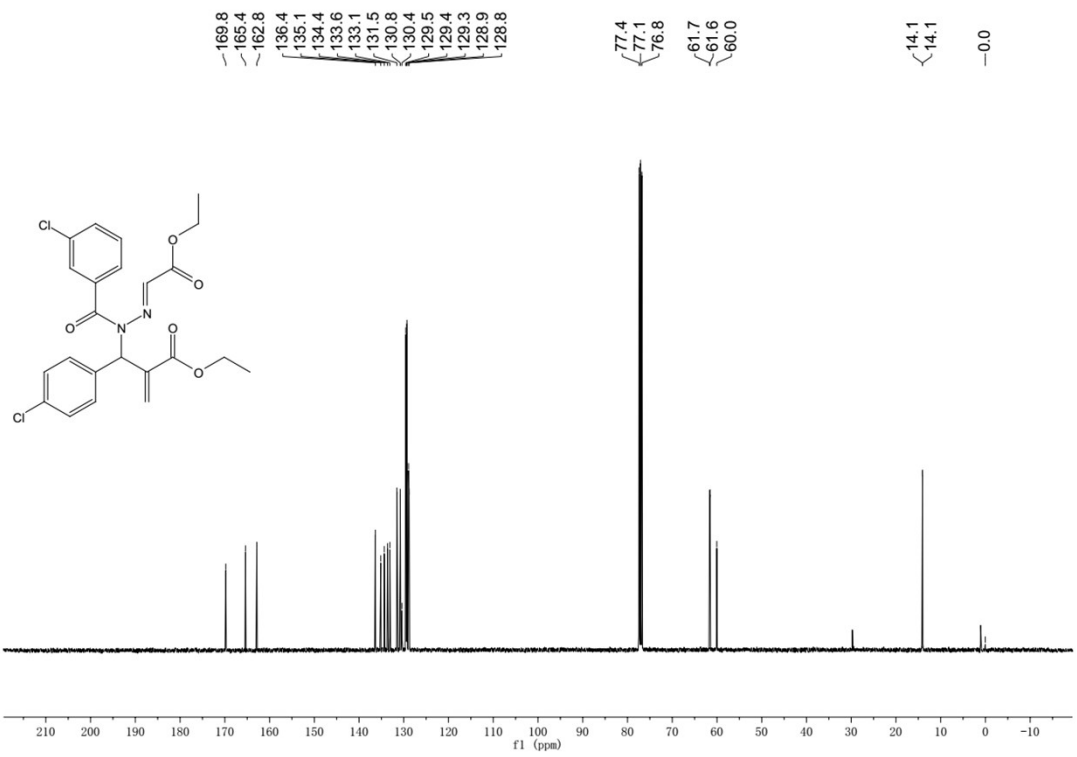
3o


7.371
7.352
7.348
7.341
7.336
7.329
7.324
7.320
7.309
7.294
7.290
7.247
7.243
7.230
7.226
7.051
7.048
7.044
7.042
7.028
6.602
6.580
6.577
5.619
4.238
4.220
4.216
4.202
4.198
4.180
4.162
3.820
1.266
1.254
1.248
1.236
1.230
1.218
0.000
6.05
2.03
1.00
0.96
1.00
1.00
4.07
3.01
6.10
f1 (ppm)

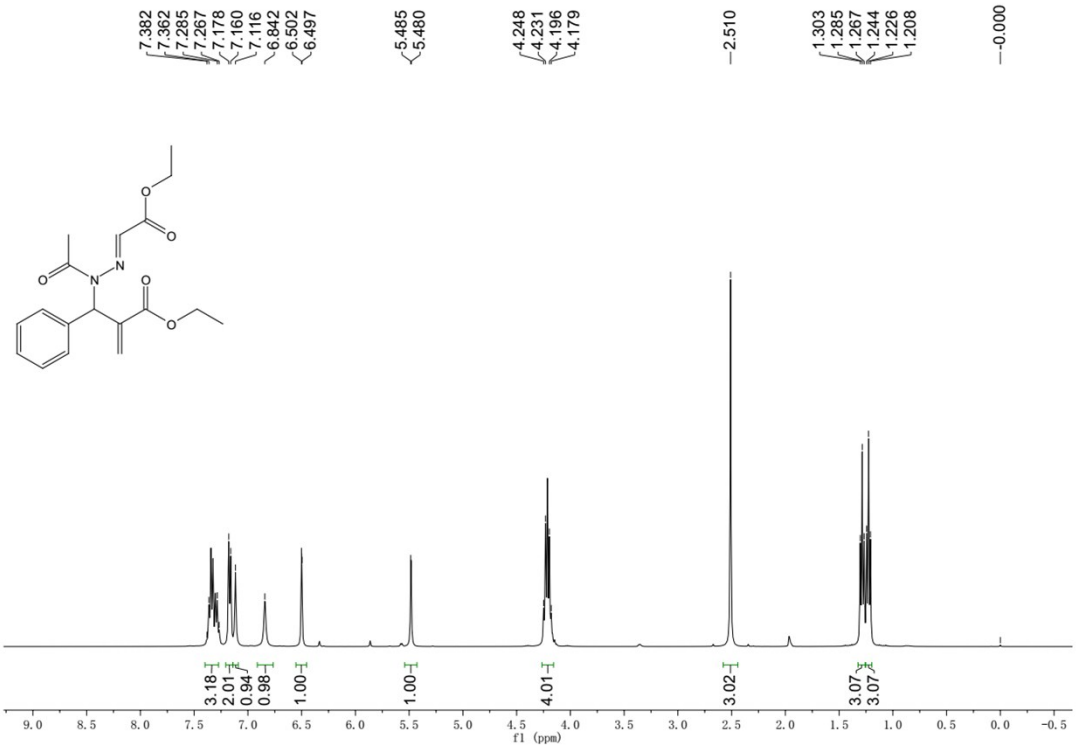

171.0
165.4
163.0
159.0
136.6
134.6
134.2
133.5
130.6
129.6
129.4
129.2
128.7
123.0
118.0
115.4
77.4
77.1
76.8
61.6
61.4
60.3
55.4
14.1
14.0
f1 (ppm)

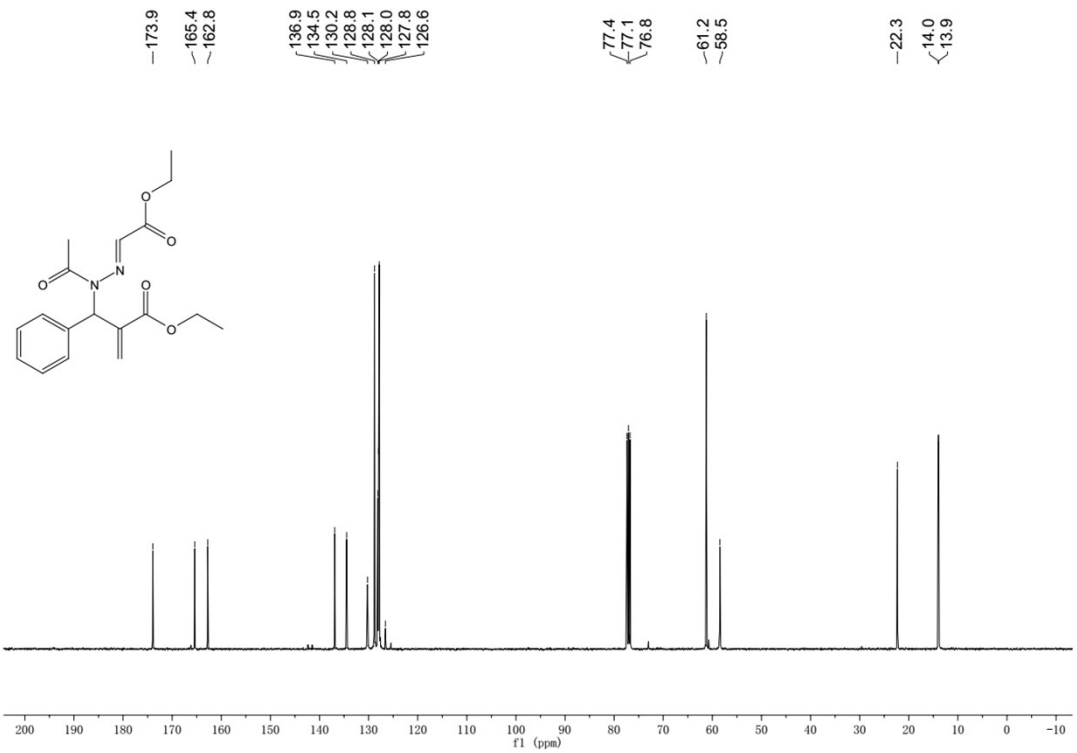
3p


7.800
7.795
7.791
7.684
7.665
7.459
7.456
7.453
7.451
7.369
7.365
7.353
7.349
7.329
7.240
7.236
7.219
6.590
6.586
5.604
5.600
4.246
4.228
4.219
4.210
4.204
4.201
4.193
4.184
4.168
1.279
1.262
1.255
1.244
1.226
0.000
Cl
O
N
0.99
1.04
1.04
3.14
3.19
0.92
1.02
1.00
4.21
6.40
f1 (ppm)

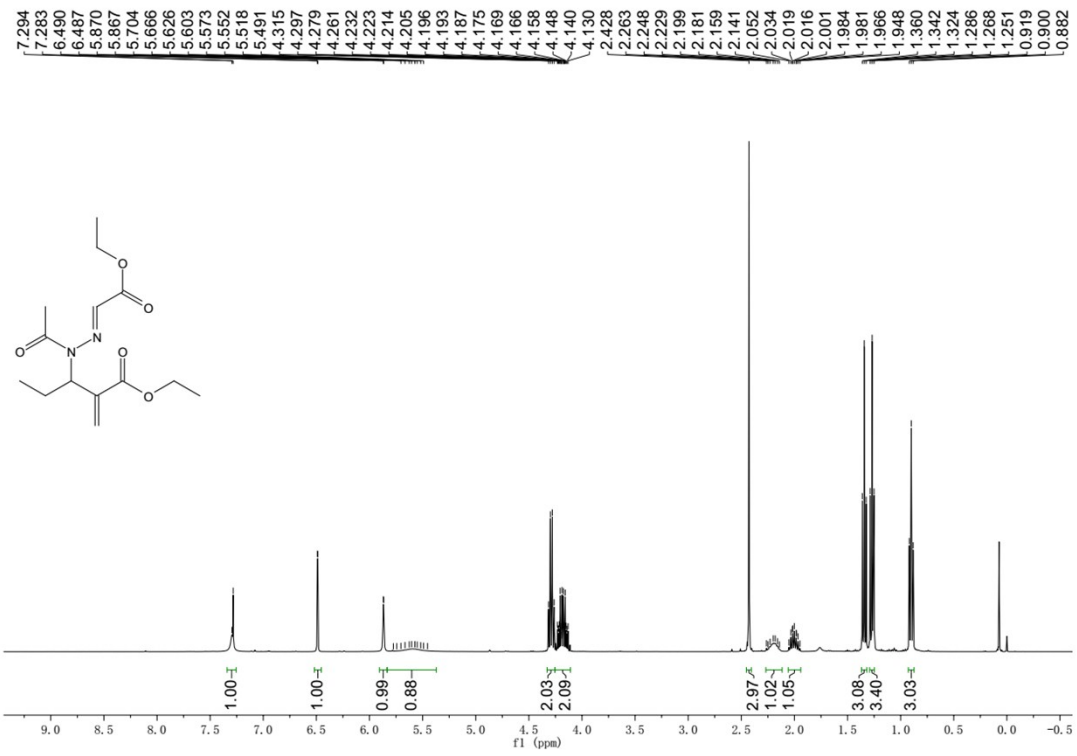

169.8
165.4
162.8
136.4
135.1
134.4
133.6
133.1
131.5
130.8
130.4
129.5
129.4
129.3
128.9
128.8
77.4
77.1
76.8
61.7
61.6
60.0
14.1
14.1
0.0
Cl
O
N
f1 (ppm)

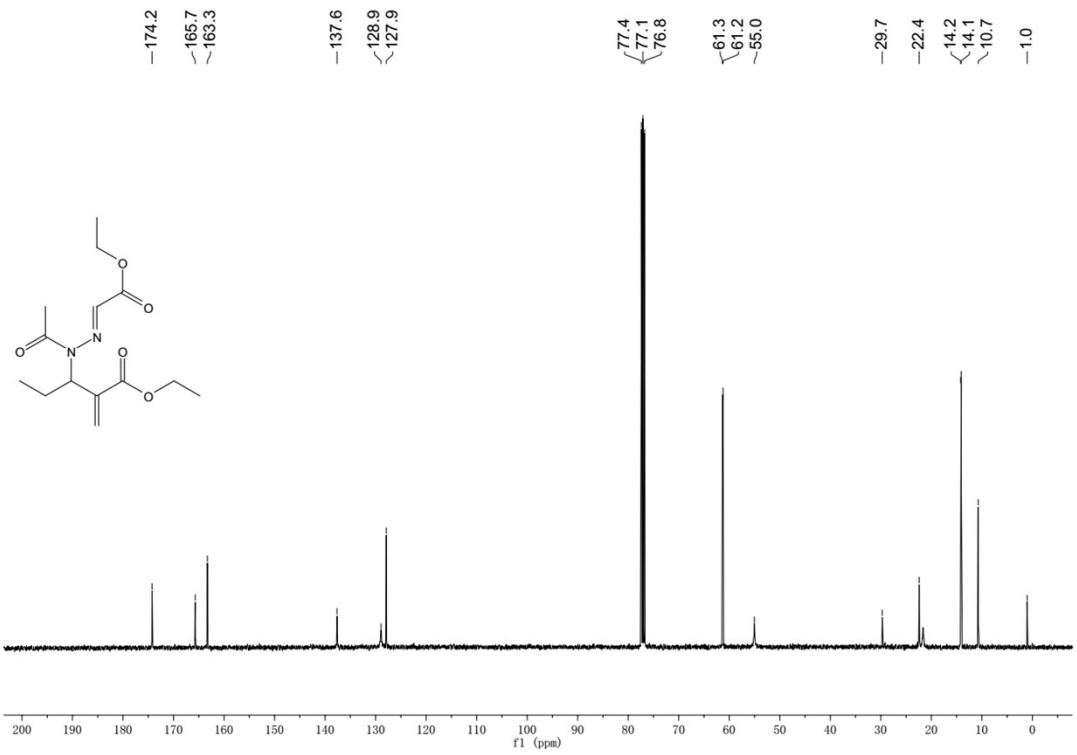
3q


7.382
7.362
7.285
7.267
7.178
7.160
7.116
6.842
6.502
6.497
5.485
5.480
4.248
4.231
4.196
4.179
2.510
1.303
1.285
1.267
1.244
1.226
1.208
0.000
3.18
2.01
0.94
0.98
1.00
1.00
4.01
3.02
3.07
3.07
f1 (ppm)

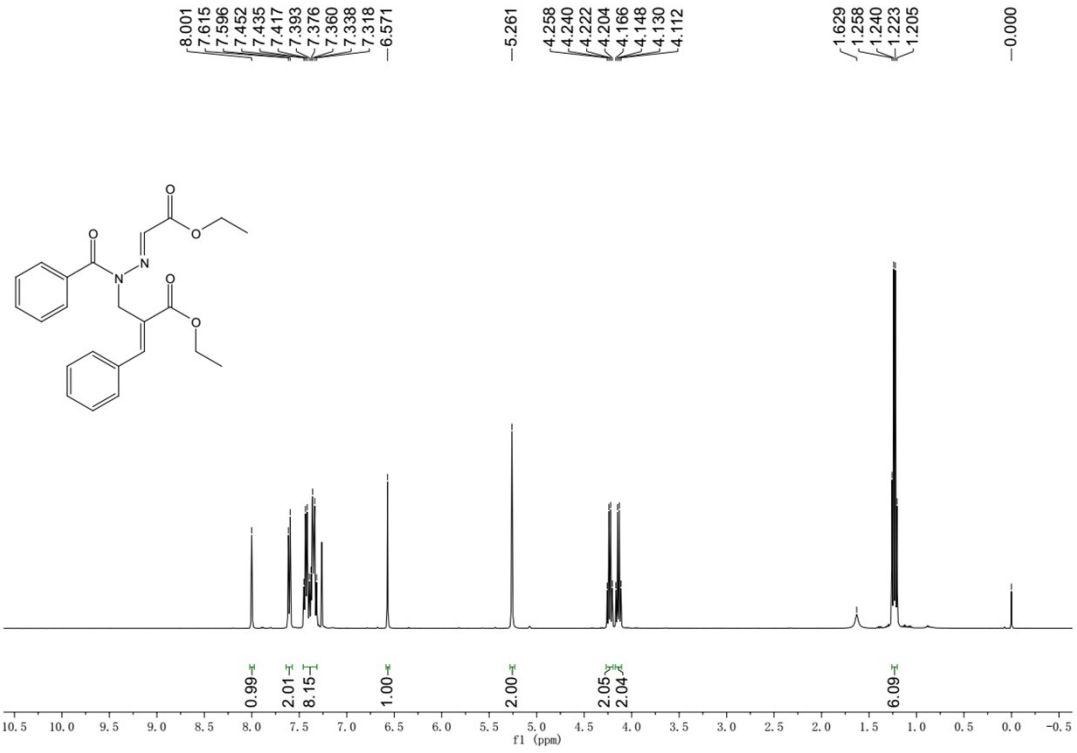

173.9
165.4
162.8
136.9
134.5
130.2
128.8
128.1
128.0
127.8
126.6
77.4
77.1
76.8
61.2
58.5
22.3
14.0
13.9
f1 (ppm)

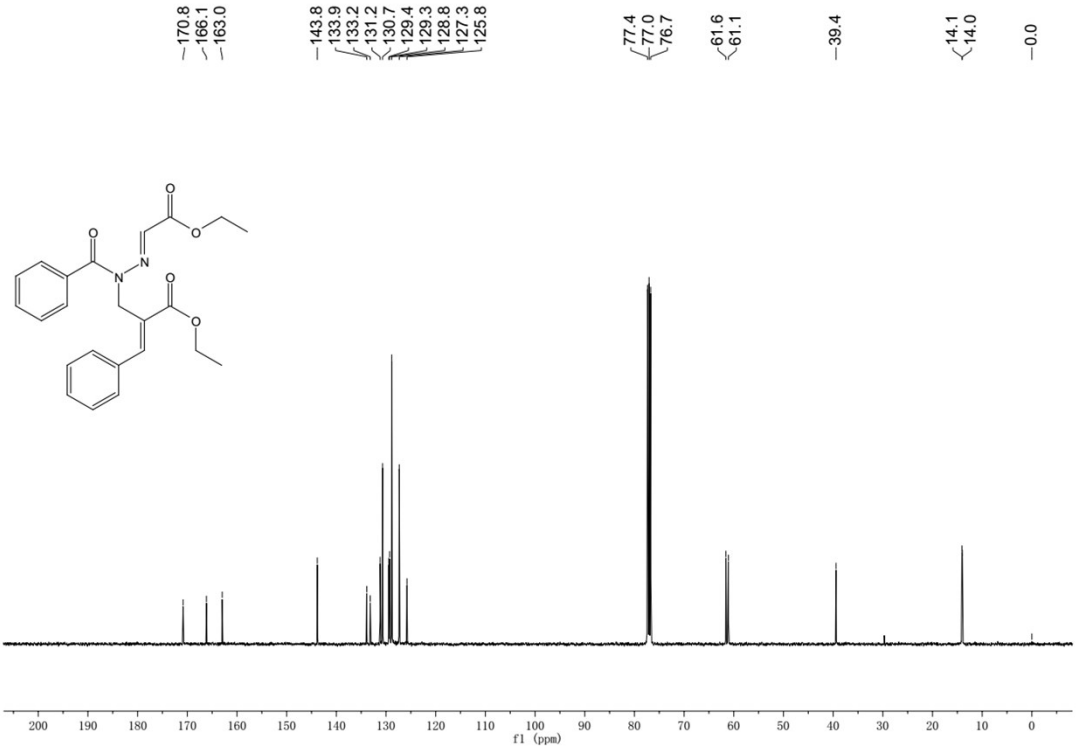
3r


7.294
7.283
6.490
6.487
5.870
5.867
5.704
5.666
5.626
5.603
5.573
5.552
5.518
5.491
4.315
4.297
4.279
4.261
4.232
4.223
4.214
4.205
4.196
4.193
4.187
4.175
4.169
4.166
4.158
4.148
4.140
4.130
2.428
2.263
2.248
2.229
2.199
2.181
2.159
2.141
2.052
2.034
2.019
2.016
2.001
1.984
1.981
1.966
1.948
1.360
1.342
1.324
1.286
1.268
1.251
0.919
0.900
0.882
1.00
1.00
0.99
0.88
2.03
2.09
2.97
1.02
1.05
3.08
3.40
3.03
f1 (ppm)

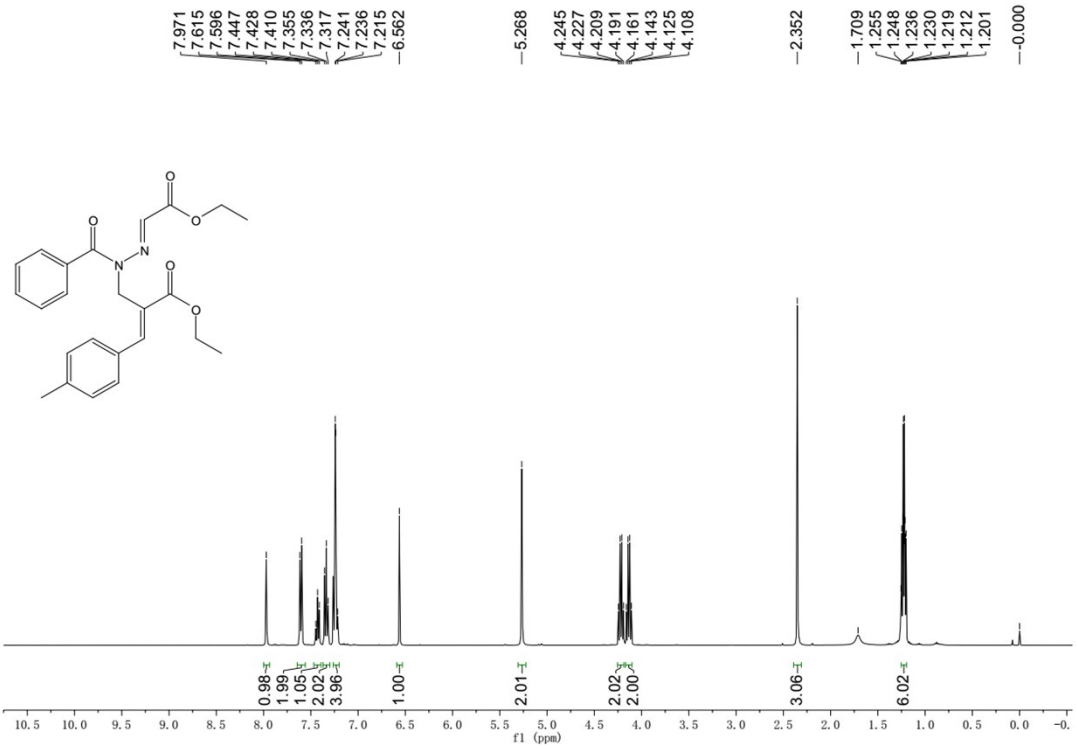

174.2
165.7
163.3
137.6
128.9
127.9
77.4
77.1
76.8
61.3
61.2
55.0
29.7
22.4
14.2
14.1
10.7
1.0
f1 (ppm)

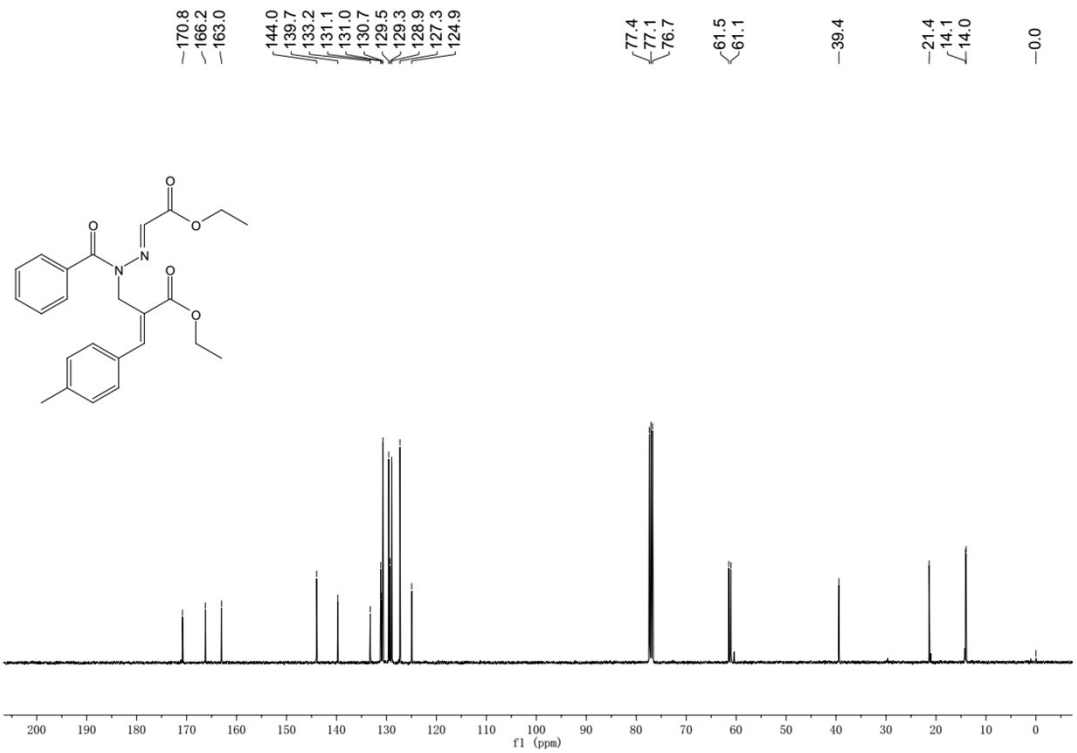
4a


8.001
7.615
7.596
7.452
7.435
7.417
7.393
7.376
7.360
7.338
7.318
6.571
5.261
4.258
4.240
4.222
4.204
4.166
4.148
4.130
4.112
1.629
1.258
1.240
1.223
1.205
0.000
0.99
2.01
8.15
1.00
2.00
2.05
2.04
6.09
f1 (ppm)

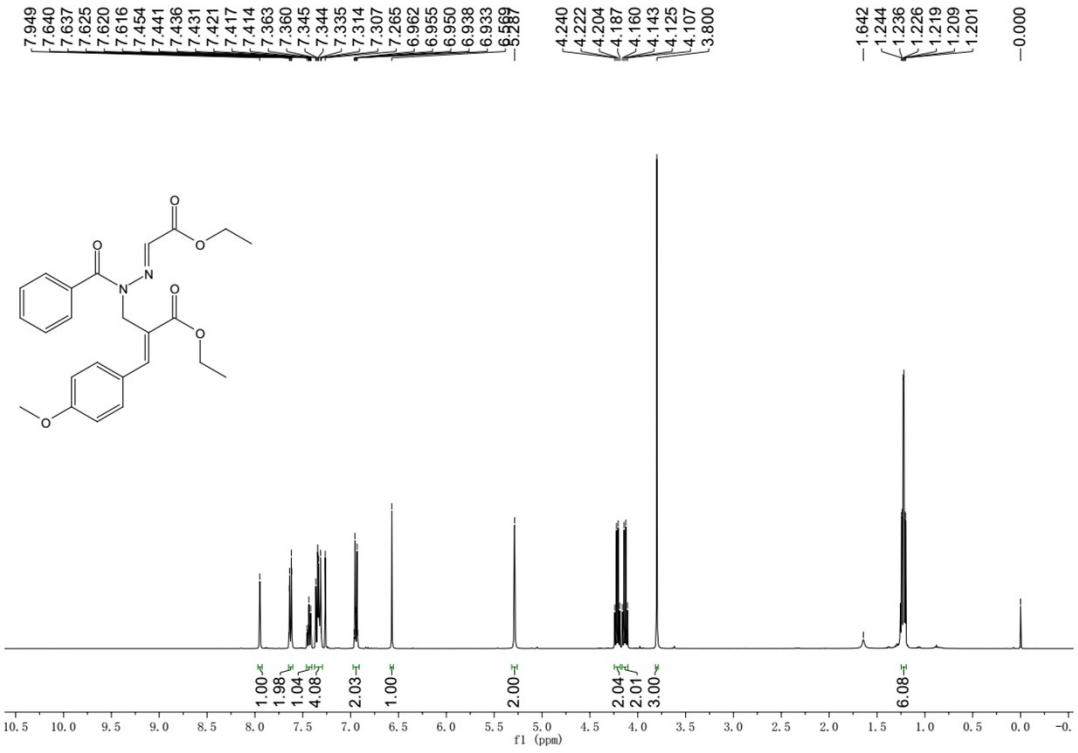

170.8
166.1
163.0
143.8
133.9
133.2
131.2
130.7
129.4
129.3
128.8
127.3
125.8
77.4
77.0
76.7
61.6
61.1
39.4
14.1
14.0
0.0
f1 (ppm)

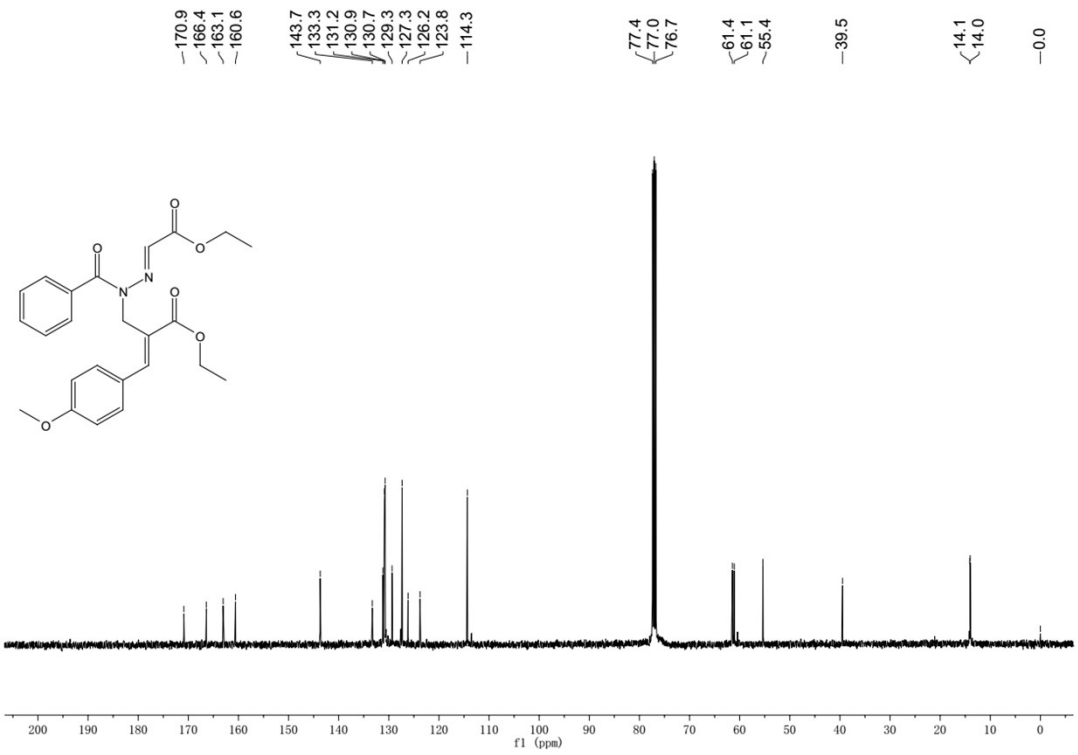
4b


7.971
7.615
7.596
7.447
7.428
7.410
7.355
7.336
7.317
7.241
7.236
7.215
6.562
5.268
4.245
4.227
4.209
4.191
4.161
4.143
4.125
4.108
2.352
1.709
1.255
1.248
1.236
1.230
1.219
1.212
1.201
0.000
0.98
1.99
1.05
2.02
3.96
1.00
2.01
2.02
2.00
3.06
6.02
f1 (ppm)

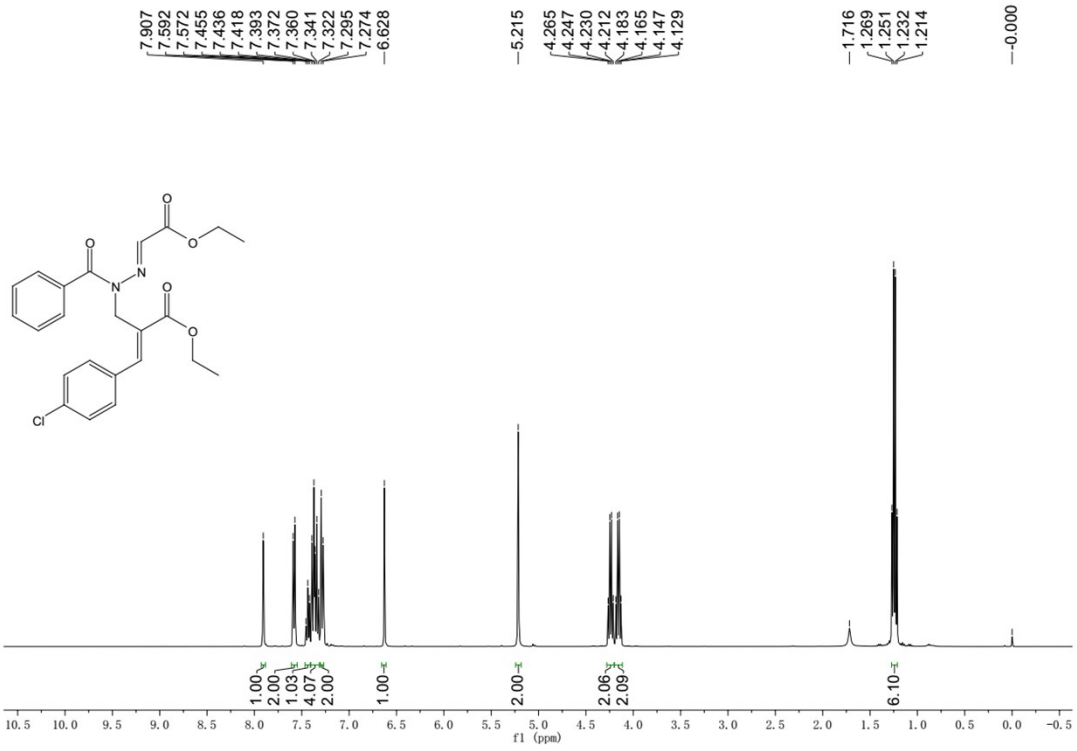

170.8
166.2
163.0
144.0
139.7
133.2
131.1
131.0
130.7
129.5
129.3
128.9
127.3
124.9
77.4
77.1
76.7
61.5
61.1
39.4
21.4
14.1
14.0
0.0
f1 (ppm)

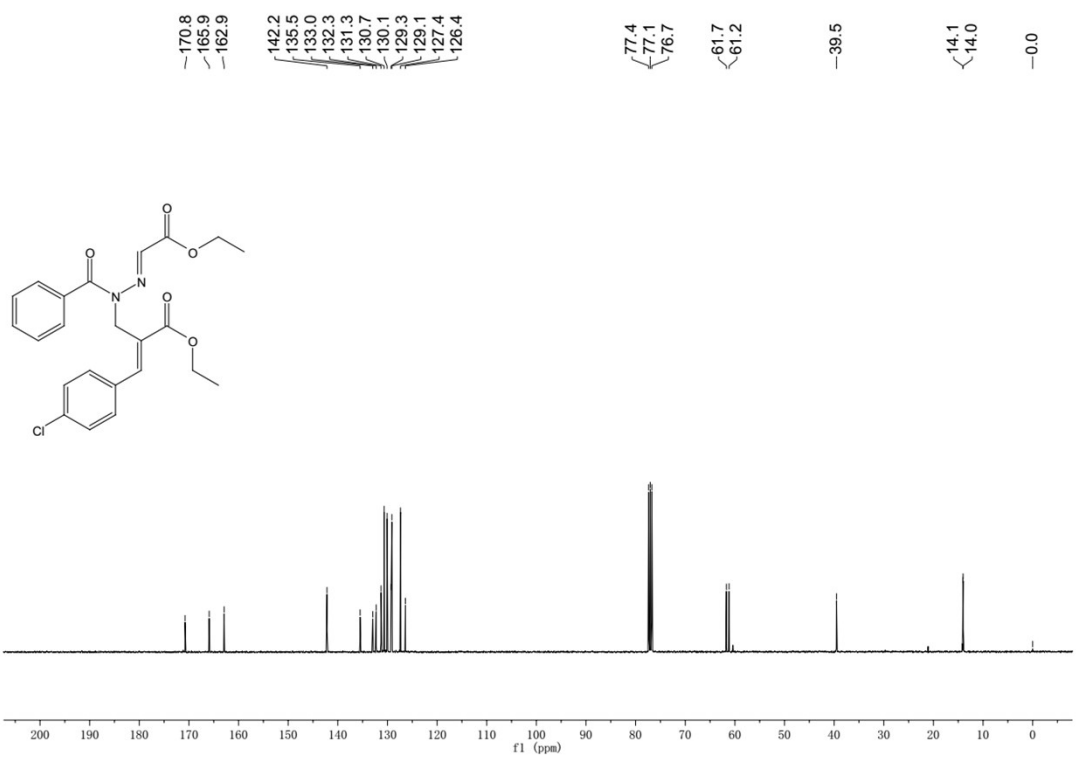
4c


7.949
7.640
7.637
7.625
7.620
7.616
7.454
7.441
7.436
7.431
7.421
7.417
7.414
7.363
7.360
7.345
7.344
7.335
7.314
7.307
7.265
6.962
6.955
6.950
6.938
6.933
5.287
4.240
4.222
4.204
4.187
4.160
4.143
4.125
4.107
3.800
1.642
1.244
1.236
1.226
1.219
1.209
1.201
0.000
1.00
1.98
1.04
4.08
2.03
1.00
2.00
2.04
2.01
3.00
6.08
f1 (ppm)

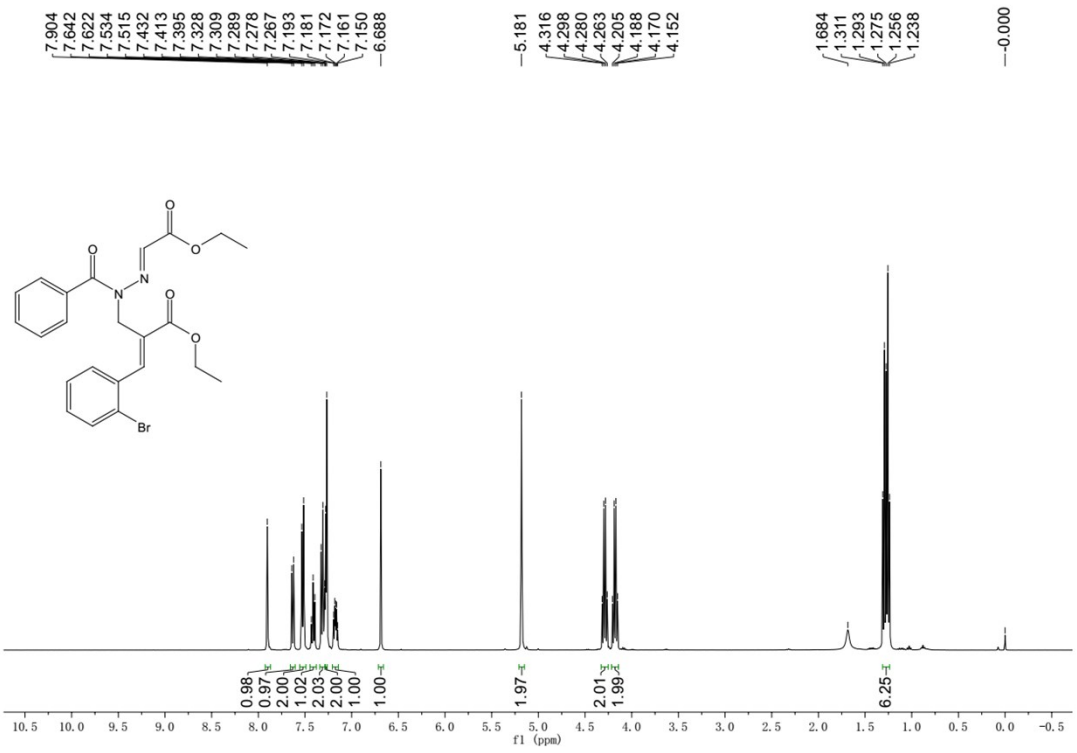

170.9
166.4
163.1
160.6
143.7
133.3
131.2
130.9
130.7
129.3
127.3
126.2
123.8
114.3
77.4
77.0
76.7
61.4
61.1
55.4
39.5
14.1
14.0
0.0
f1 (ppm)

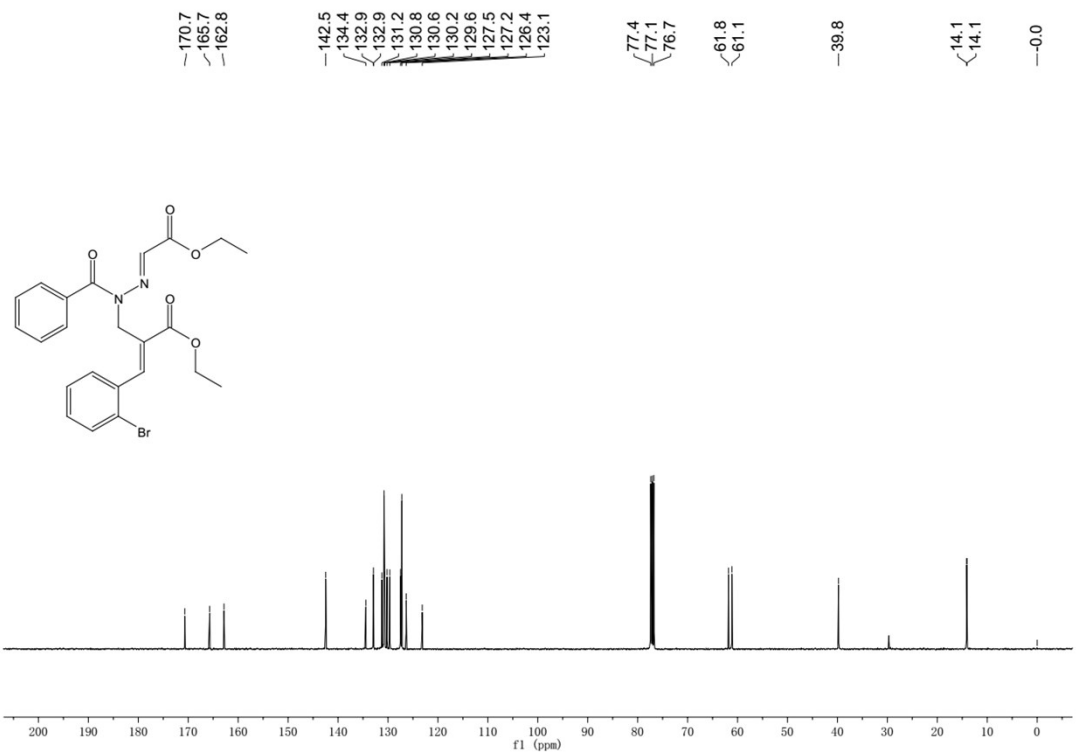
4d


7.907
7.592
7.572
7.455
7.436
7.418
7.393
7.372
7.360
7.341
7.322
7.295
7.274
6.628
5.215
4.265
4.247
4.230
4.212
4.183
4.165
4.147
4.129
1.716
1.269
1.251
1.232
1.214
0.000
Cl
1.00
2.00
1.03
4.07
2.00
1.00
2.00
2.06
2.09
6.10
f1 (ppm)

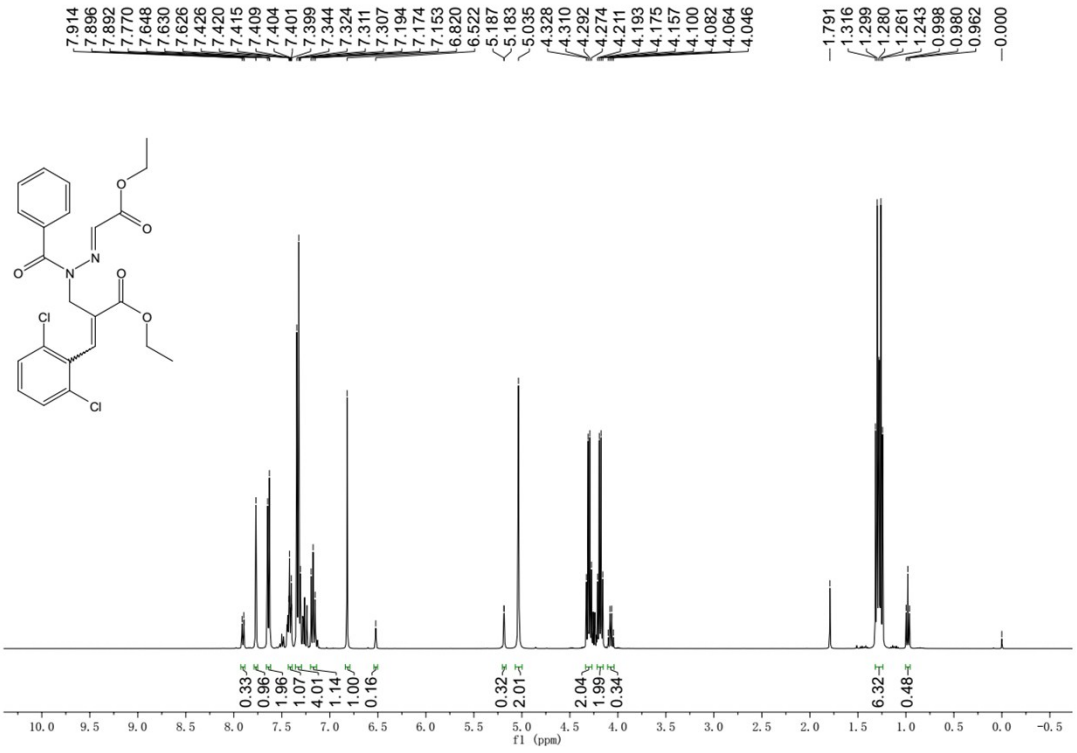

170.8
165.9
162.9
142.2
135.5
133.0
132.3
131.3
130.7
130.1
129.3
129.1
127.4
126.4
77.4
77.1
76.7
61.7
61.2
39.5
14.1
14.0
0.0
Cl
f1 (ppm)

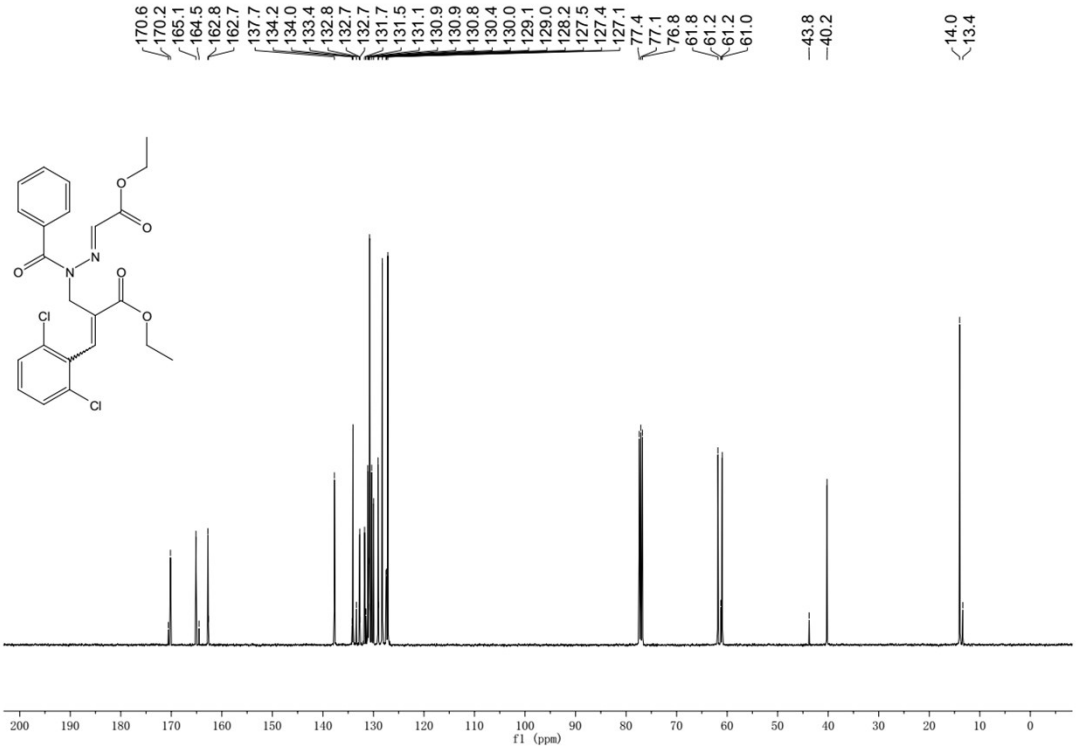
4e


7.904
7.642
7.622
7.534
7.515
7.432
7.413
7.395
7.328
7.309
7.289
7.278
7.267
7.193
7.181
7.172
7.161
7.150
6.688
5.181
4.316
4.298
4.280
4.263
4.205
4.188
4.170
4.152
1.684
1.311
1.293
1.275
1.256
1.238
0.000
Br
0.98
0.97
2.00
1.02
2.03
2.00
1.00
1.00
1.97
2.01
1.99
6.25
f1 (ppm)

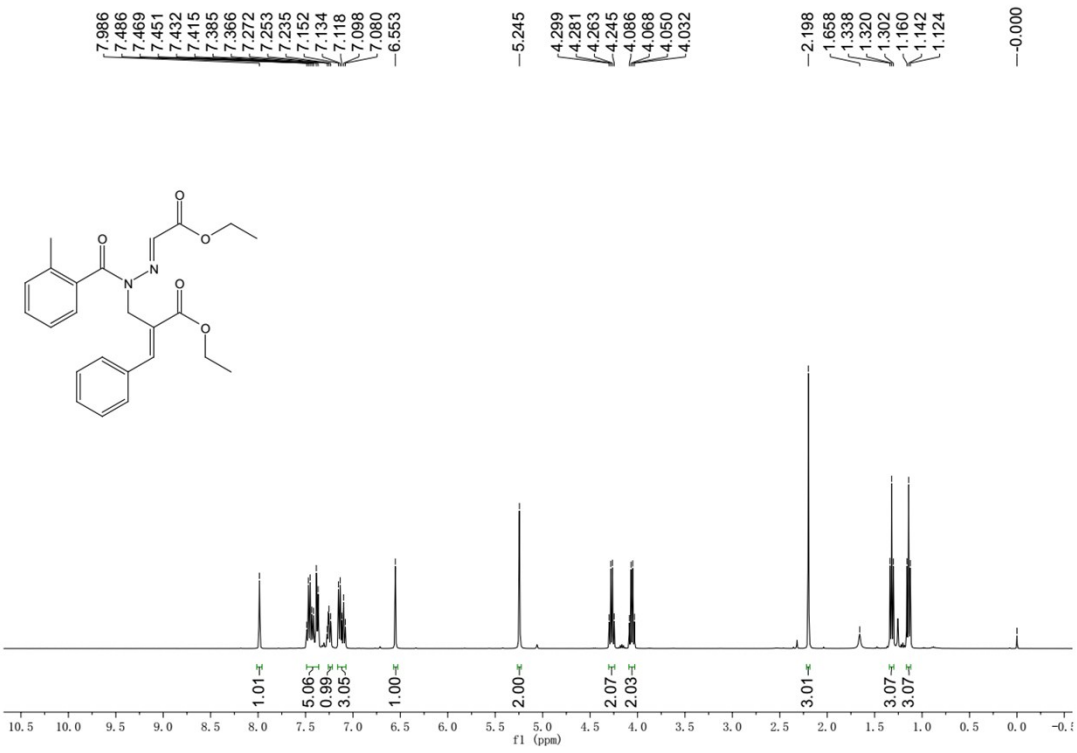

170.7
165.7
162.8
142.5
134.4
132.9
132.9
131.2
130.8
130.6
130.2
129.6
127.5
127.2
126.4
123.1
77.4
77.1
76.7
61.8
61.1
39.8
14.1
14.1
0.0
Br
f1 (ppm)

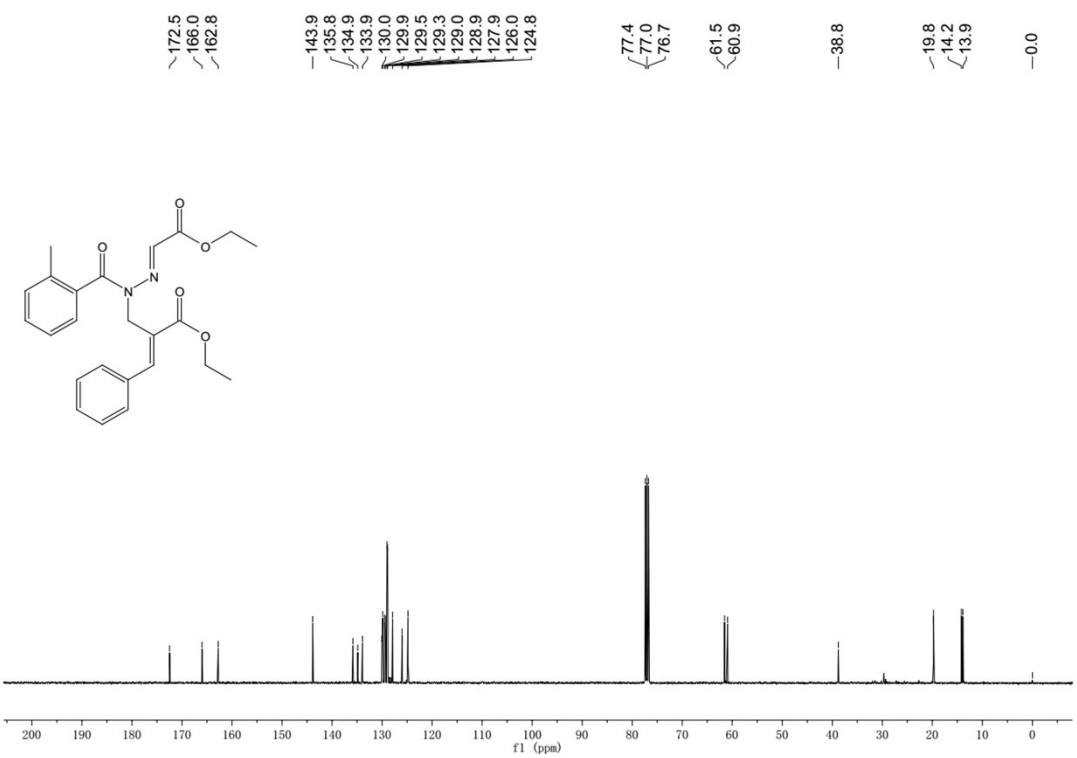
4f


7.914
7.896
7.892
7.770
7.648
7.630
7.626
7.426
7.420
7.415
7.409
7.404
7.401
7.399
7.344
7.324
7.311
7.307
7.194
7.174
7.153
6.820
6.522
5.187
5.183
5.035
4.328
4.310
4.292
4.274
4.211
4.193
4.175
4.157
4.100
4.082
4.064
4.046
1.791
1.316
1.299
1.280
1.261
1.243
0.998
0.980
0.962
0.000
0.33
0.96
1.96
1.07
4.01
1.14
1.00
0.16
0.32
2.01
2.04
1.99
0.34
6.32
0.48
f1 (ppm)

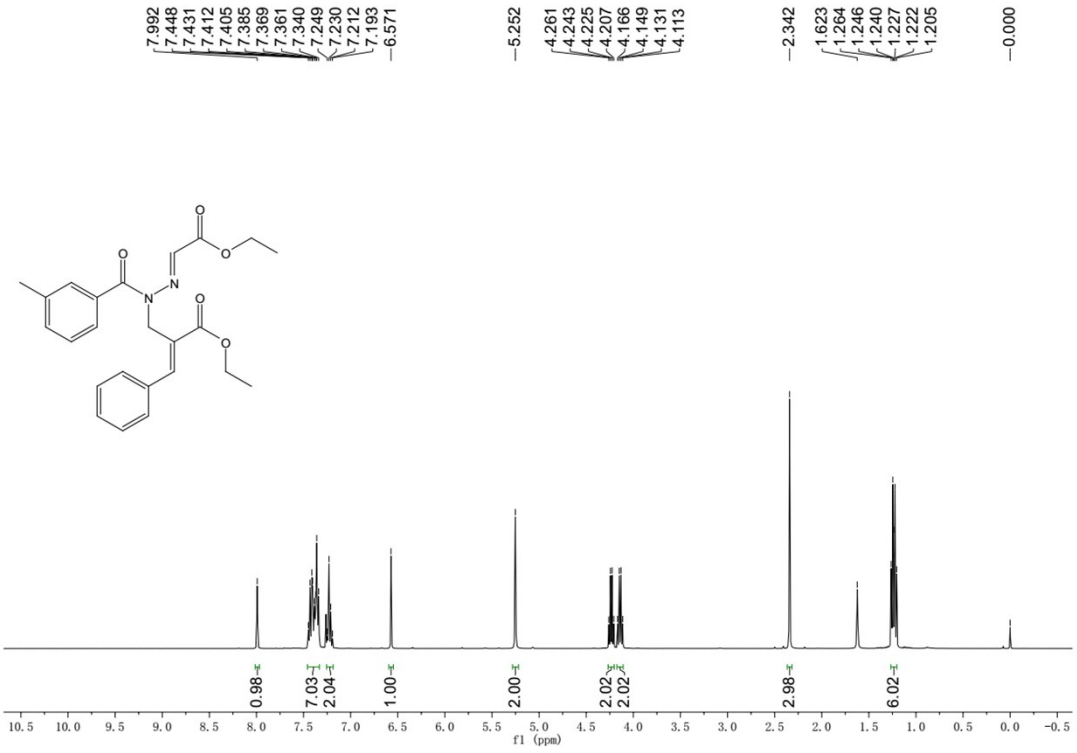

170.6
170.2
165.1
164.5
162.8
162.7
137.7
134.2
134.0
133.4
132.8
132.7
132.7
131.7
131.5
131.1
130.9
130.9
130.8
130.4
130.0
129.1
129.0
128.2
127.5
127.4
127.1
77.4
77.1
76.8
61.8
61.2
61.2
61.0
43.8
40.2
14.0
13.4
f1 (ppm)

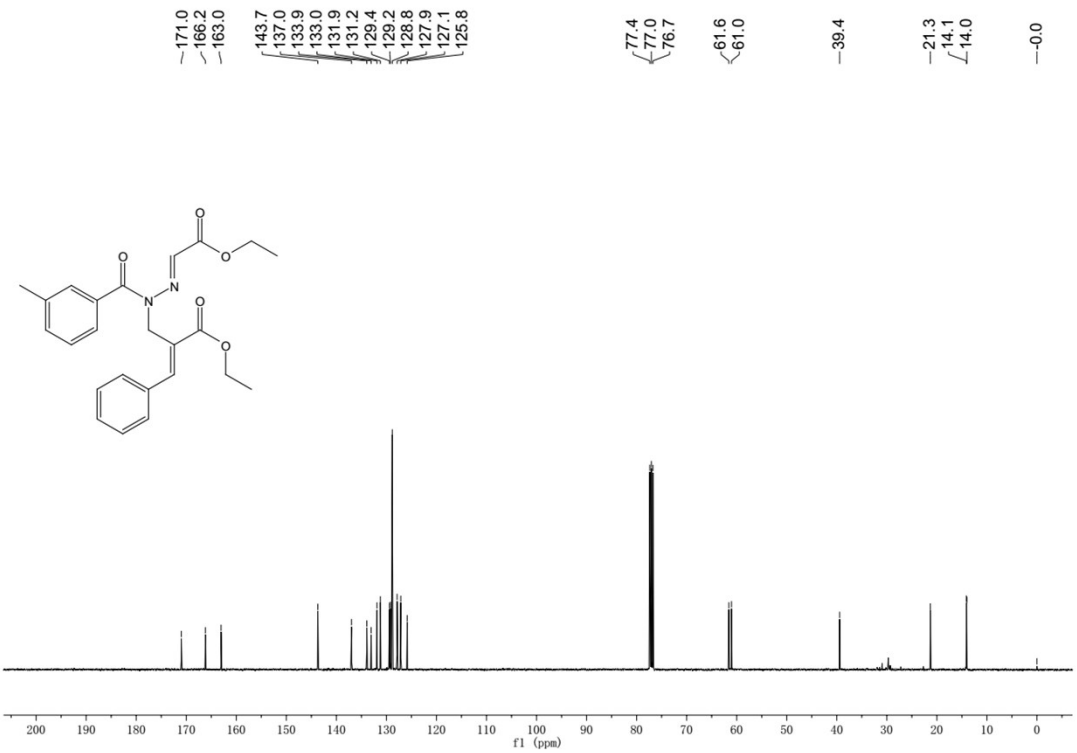
4g


7.986
7.486
7.469
7.451
7.432
7.415
7.385
7.366
7.272
7.253
7.235
7.152
7.134
7.118
7.098
7.080
6.553
5.245
4.299
4.281
4.263
4.245
4.086
4.068
4.050
4.032
2.198
1.658
1.338
1.320
1.302
1.160
1.142
1.124
0.000
1.01
5.06
0.99
3.05
1.00
2.00
2.07
2.03
3.01
3.07
3.07
f1 (ppm)

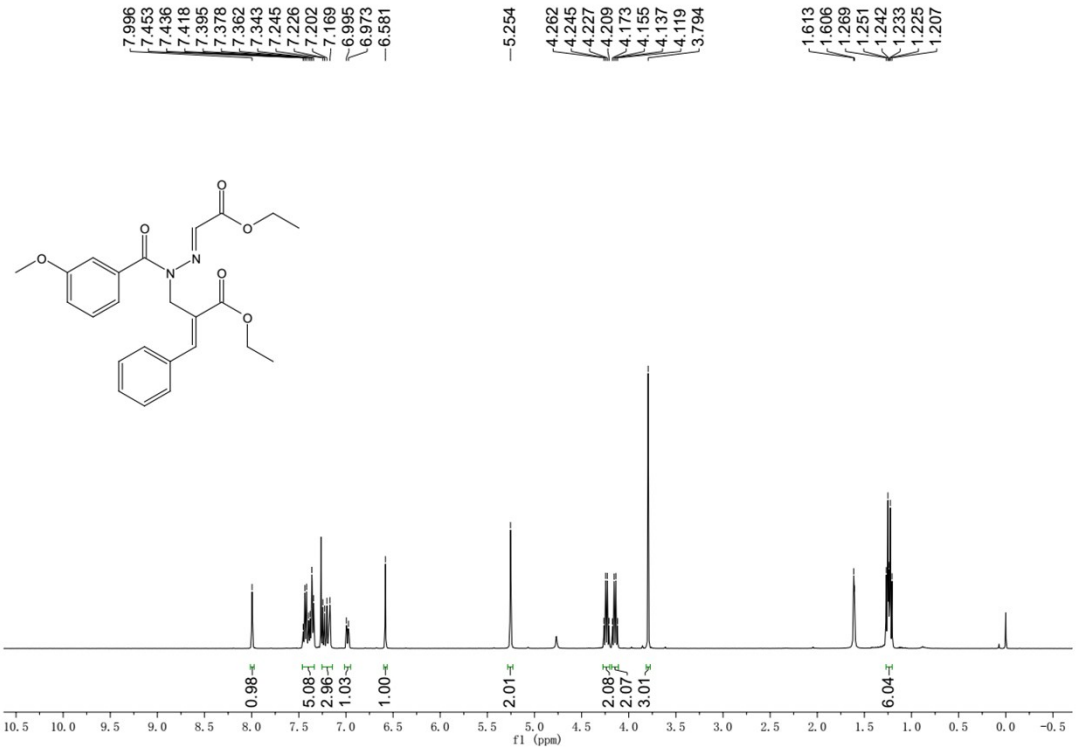

172.5
166.0
162.8
143.9
135.8
134.9
133.9
130.0
129.9
129.5
129.3
129.0
128.9
127.9
126.0
124.8
77.4
77.0
76.7
61.5
60.9
38.8
19.8
14.2
13.9
0.0
f1 (ppm)

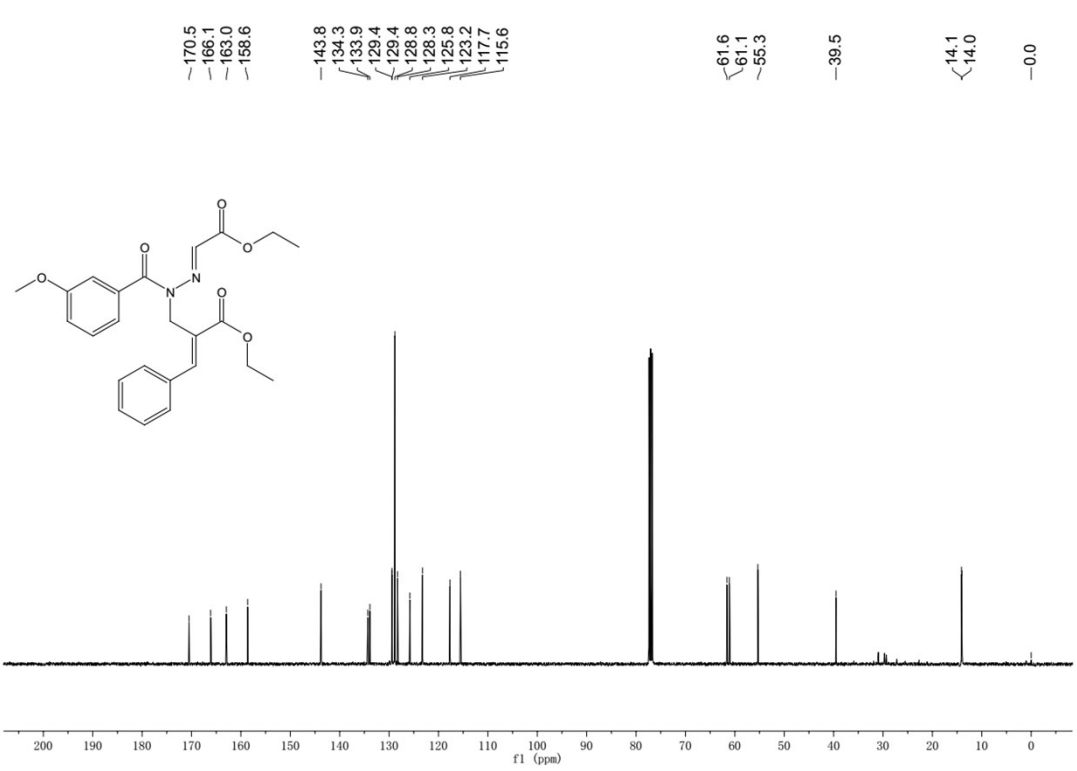
4h


7.992
7.448
7.431
7.412
7.405
7.385
7.369
7.361
7.340
7.249
7.230
7.212
7.193
6.571
5.252
4.261
4.243
4.225
4.207
4.166
4.149
4.131
4.113
2.342
1.623
1.264
1.246
1.240
1.227
1.222
1.205
0.000
0.98
7.03
2.04
1.00
2.00
2.02
2.02
2.98
6.02
f1 (ppm)

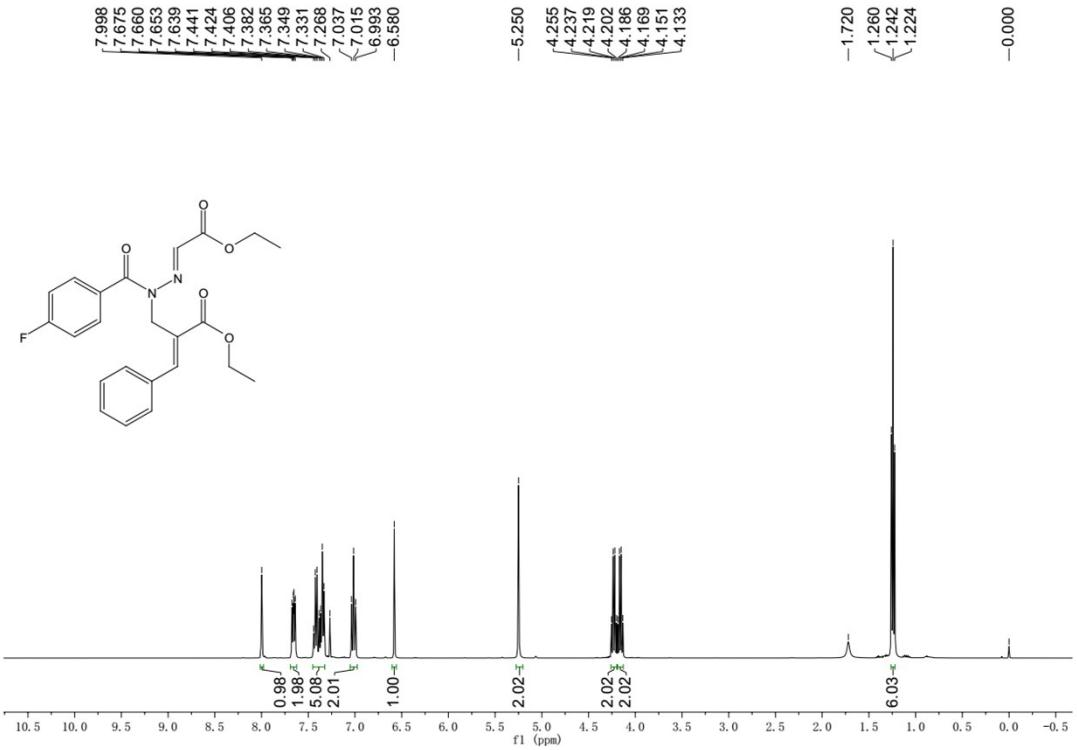

171.0
166.2
163.0
143.7
137.0
133.9
133.0
131.9
131.2
129.4
129.2
128.8
127.9
127.1
125.8
77.4
77.0
76.7
61.6
61.0
39.4
21.3
14.1
14.0
0.0
f1 (ppm)

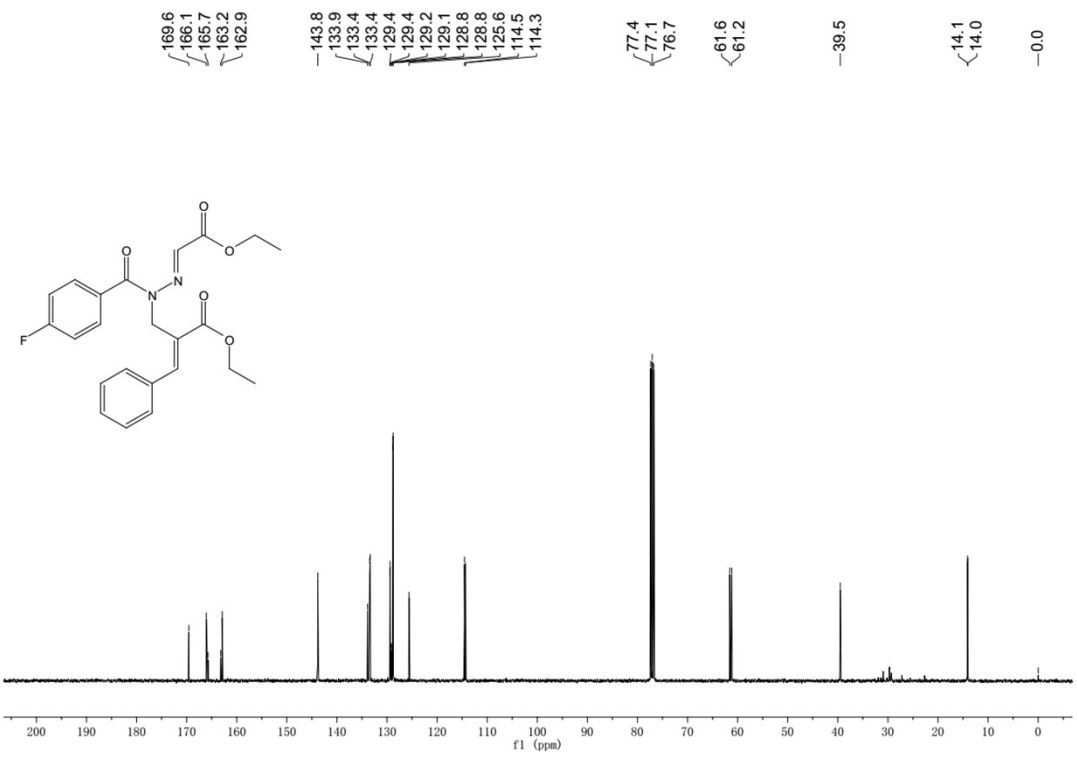
4i


7.996
7.453
7.436
7.418
7.395
7.378
7.362
7.343
7.245
7.226
7.202
7.169
6.995
6.973
6.581
5.254
4.262
4.245
4.227
4.209
4.173
4.155
4.137
4.119
3.794
1.613
1.606
1.269
1.251
1.242
1.233
1.225
1.207
0.98
5.08
2.96
1.03
1.00
2.01
2.08
2.07
3.01
6.04
f1 (ppm)

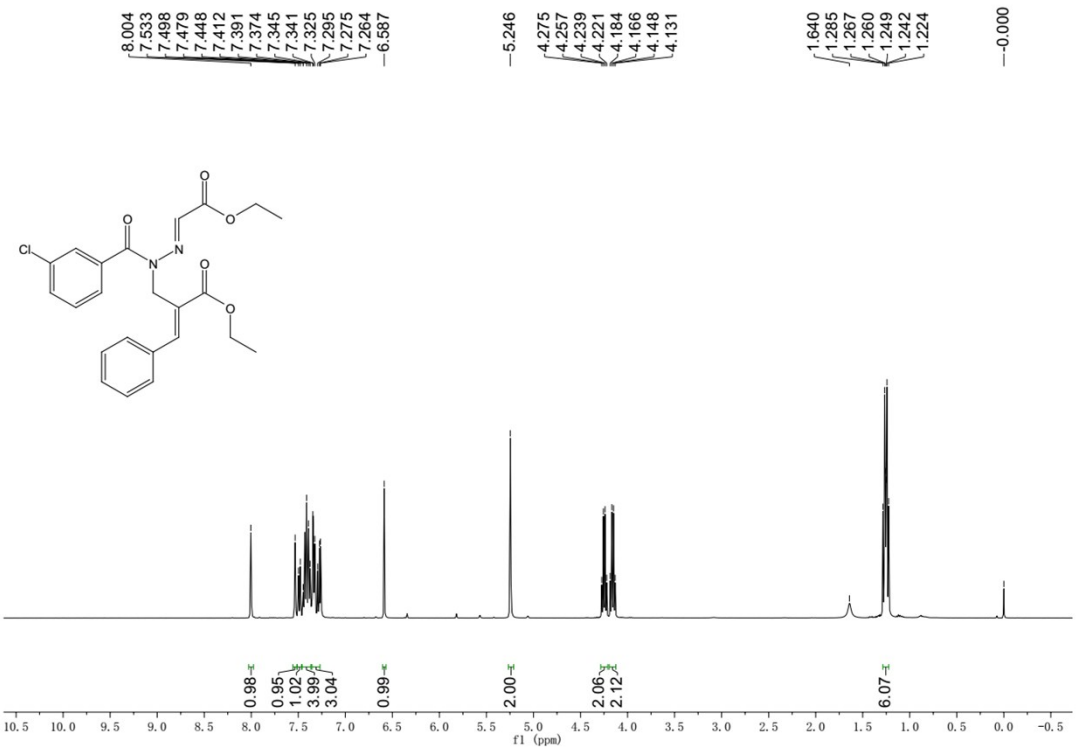

170.5
166.1
163.0
158.6
143.8
134.3
133.9
129.4
129.4
128.8
128.3
125.8
123.2
117.7
115.6
61.6
61.1
55.3
39.5
14.1
14.0
0.0
f1 (ppm)

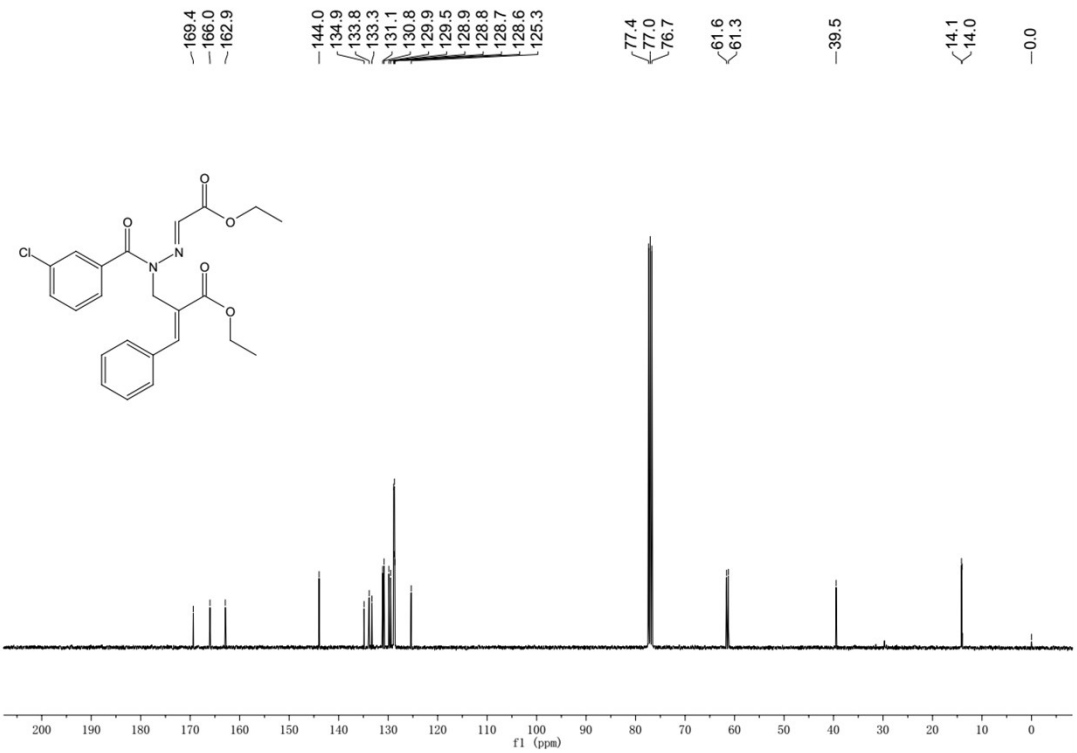
4j


7.998
7.675
7.660
7.653
7.639
7.441
7.424
7.406
7.382
7.365
7.349
7.331
7.268
7.037
7.015
6.993
6.580
5.250
4.255
4.237
4.219
4.202
4.186
4.169
4.151
4.133
1.720
1.260
1.242
1.224
0.000
0.98
1.98
5.08
2.01
1.00
2.02
2.02
2.02
6.03
f1 (ppm)

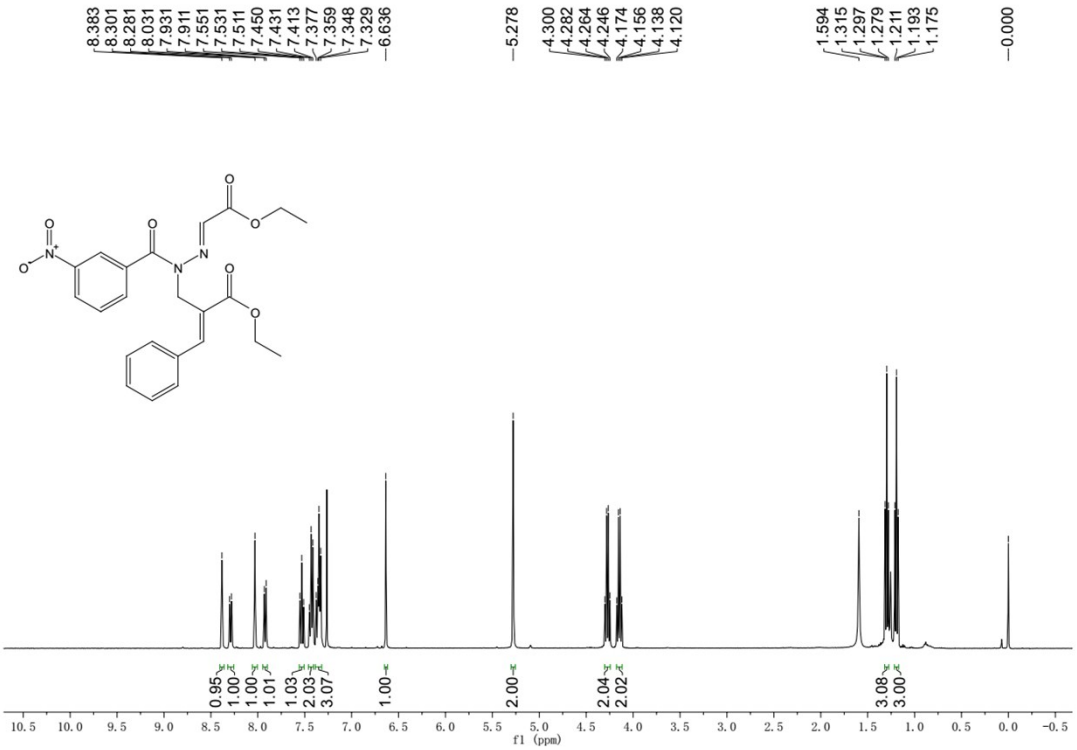

169.6
166.1
165.7
163.2
162.9
143.8
133.9
133.4
133.4
129.4
129.4
129.2
129.1
128.8
128.8
125.6
114.5
114.3
77.4
77.1
76.7
61.6
61.2
39.5
14.1
14.0
0.0
f1 (ppm)

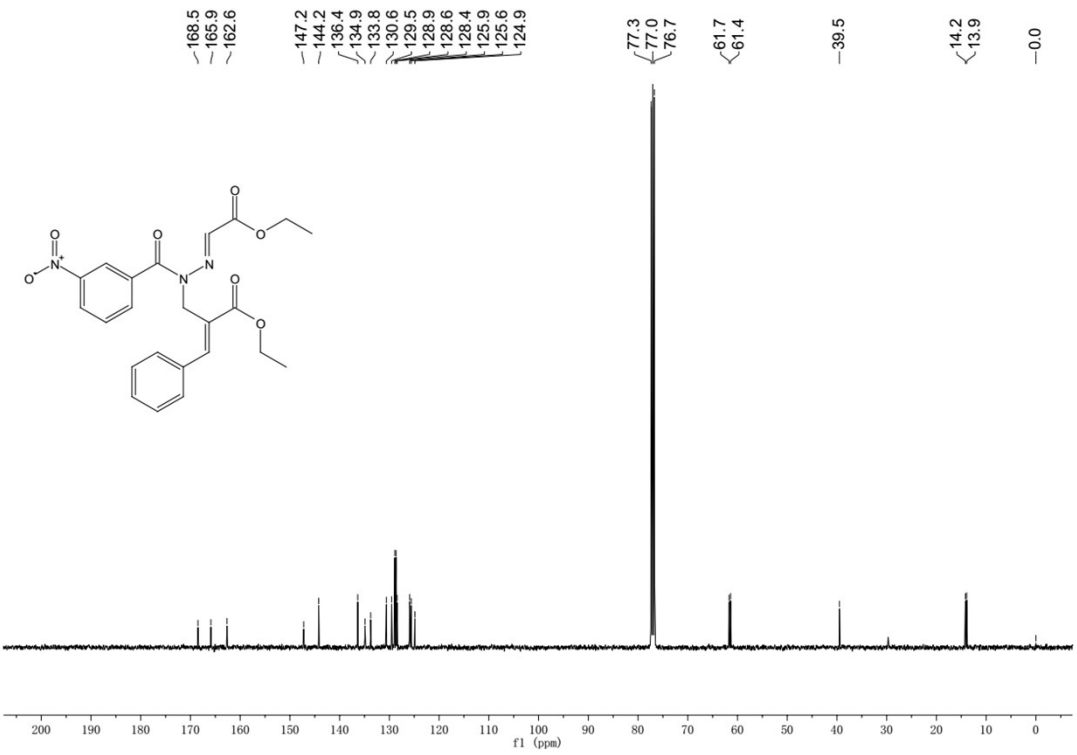
4k


8.004
7.533
7.498
7.479
7.448
7.412
7.391
7.374
7.345
7.341
7.325
7.295
7.275
7.264
6.587
5.246
4.275
4.257
4.239
4.221
4.184
4.166
4.148
4.131
1.640
1.285
1.267
1.260
1.249
1.242
1.224
0.000
Cl
0.98
0.95
1.02
3.99
3.04
0.99
2.00
2.06
2.12
6.07
f1 (ppm)

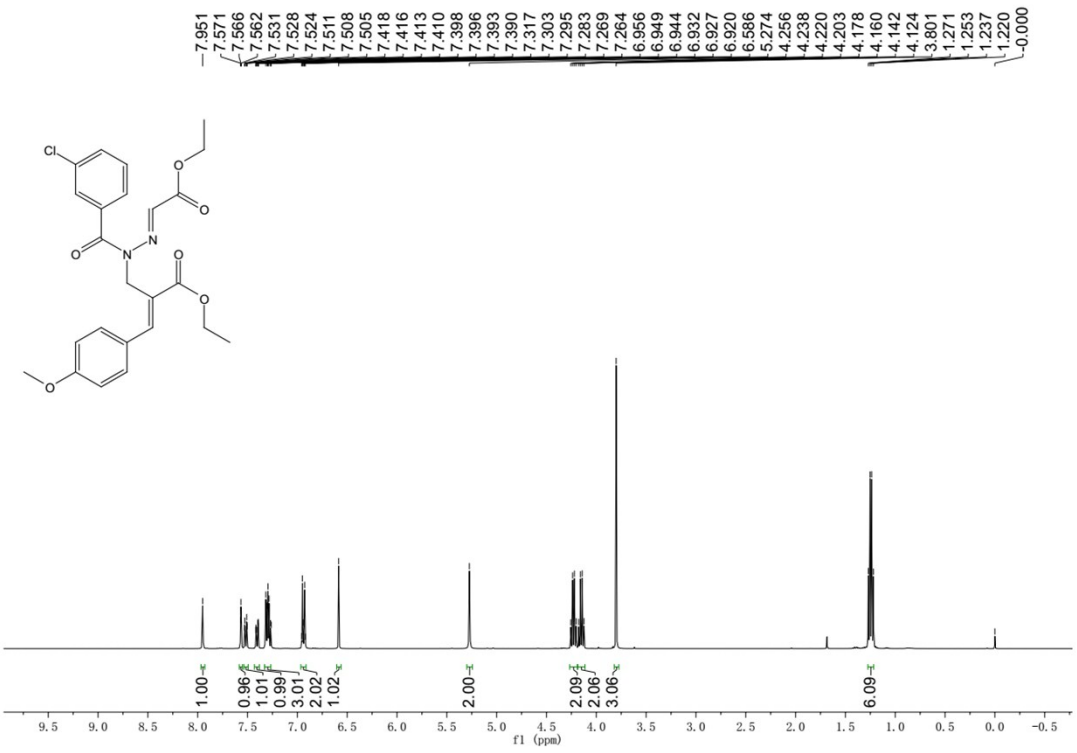

169.4
166.0
162.9
144.0
134.9
133.8
133.3
131.1
130.8
129.9
129.5
128.9
128.8
128.7
128.6
125.3
77.4
77.0
76.7
61.6
61.3
39.5
14.1
14.0
0.0
Cl
f1 (ppm)

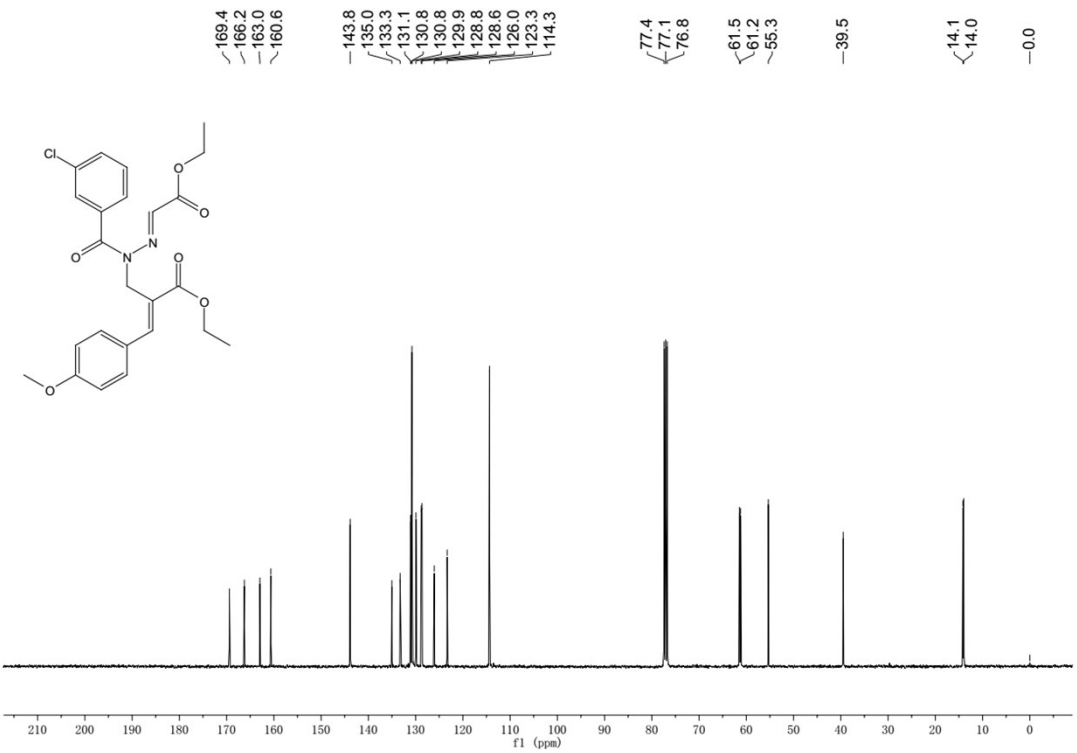
4l


8.383
8.301
8.281
8.031
7.931
7.911
7.551
7.531
7.511
7.450
7.431
7.413
7.377
7.359
7.348
7.329
6.636
5.278
4.300
4.282
4.264
4.246
4.174
4.156
4.138
4.120
1.594
1.315
1.297
1.279
1.211
1.193
1.175
0.000
0.95
1.00
1.00
1.01
1.03
2.03
3.07
1.00
2.00
2.04
2.02
3.08
3.00
f1 (ppm)

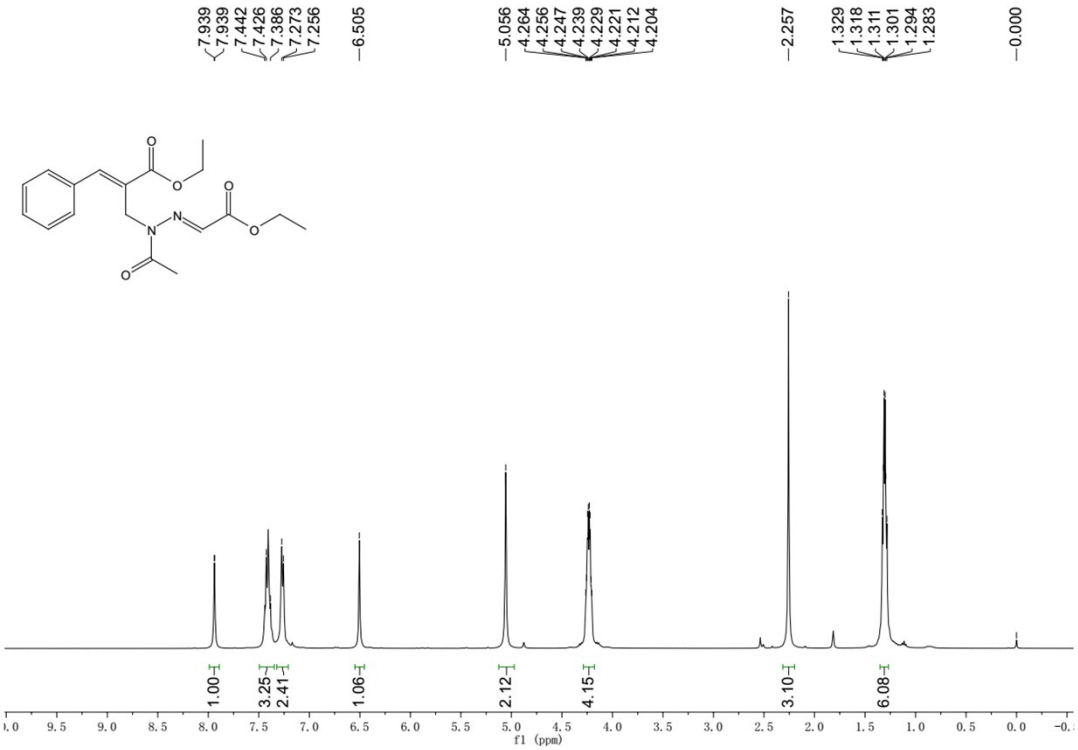

168.5
165.9
162.6
147.2
144.2
136.4
134.9
133.8
130.6
129.5
128.9
128.6
128.4
125.9
125.6
124.9
77.3
77.0
76.7
61.7
61.4
39.5
14.2
13.9
0.0
f1 (ppm)

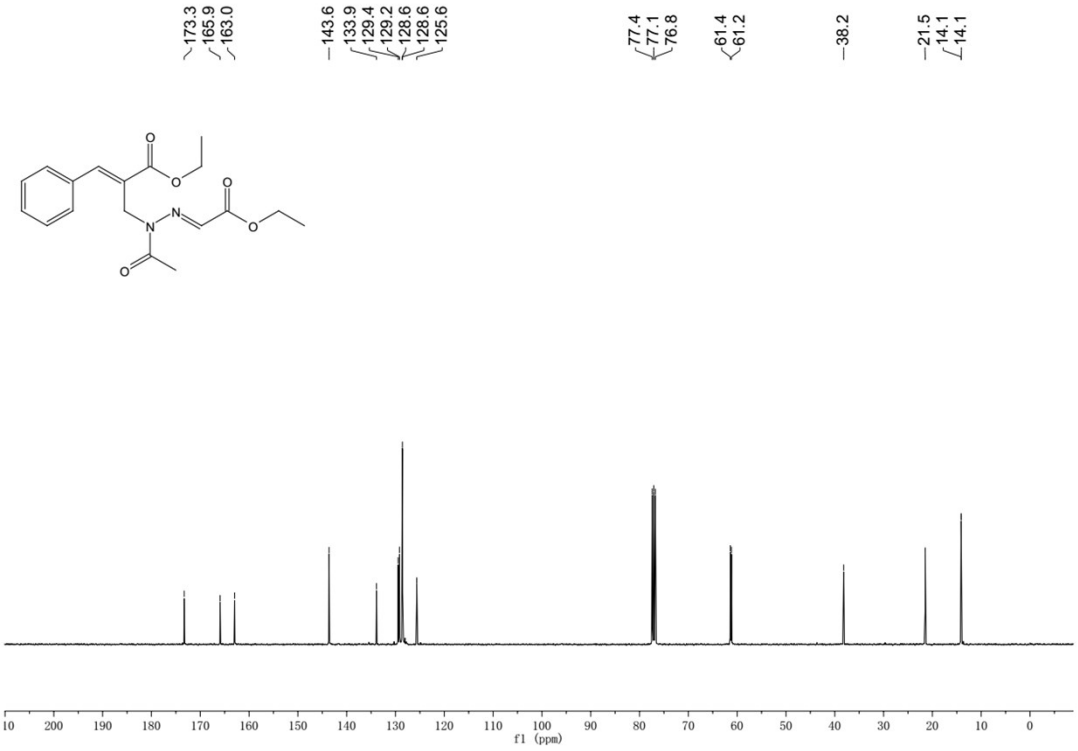
4m


7.951
7.571
7.566
7.562
7.531
7.528
7.524
7.511
7.508
7.505
7.418
7.416
7.413
7.410
7.398
7.396
7.393
7.390
7.317
7.303
7.295
7.283
7.269
7.264
6.956
6.949
6.944
6.932
6.927
6.920
6.586
5.274
4.256
4.238
4.220
4.203
4.178
4.160
4.142
4.124
3.801
1.271
1.253
1.237
1.220
-0.000
Cl
O
O
N
N
O
O
O
O
1.00
0.96
1.01
0.99
3.01
2.02
1.02
2.00
2.09
2.06
3.06
6.09
f1 (ppm)

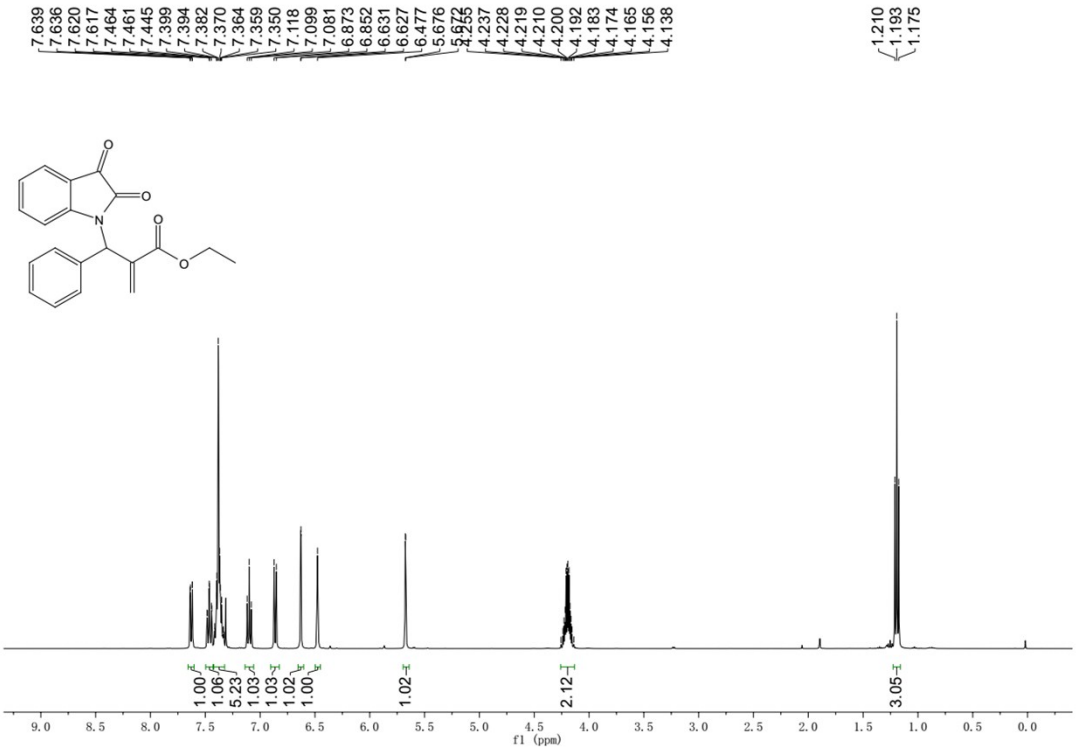

169.4
166.2
163.0
160.6
143.8
135.0
133.3
131.1
130.8
130.8
129.9
128.8
128.6
126.0
123.3
114.3
77.4
77.1
76.8
61.5
61.2
55.3
39.5
14.1
14.0
0.0
Cl
O
O
N
N
O
O
O
O
f1 (ppm)

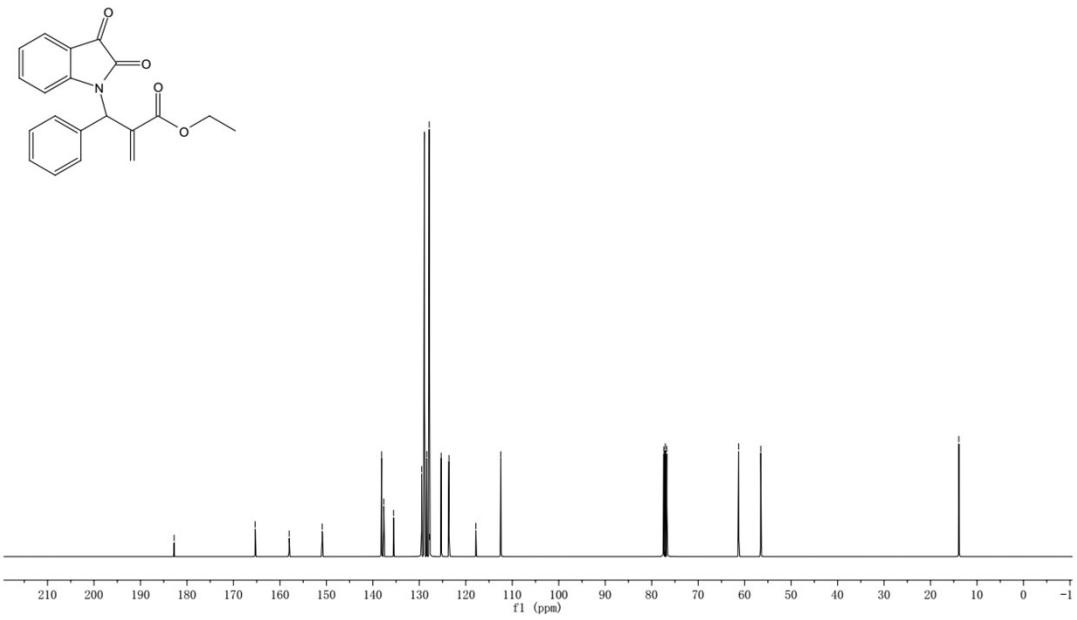
4n


7.939
7.939
7.442
7.426
7.386
7.273
7.256
6.505
5.056
4.264
4.256
4.247
4.239
4.229
4.221
4.212
4.204
2.257
1.329
1.318
1.311
1.301
1.294
1.283
0.000
1.00
3.25
2.41
1.06
2.12
4.15
3.10
6.08
f1 (ppm)

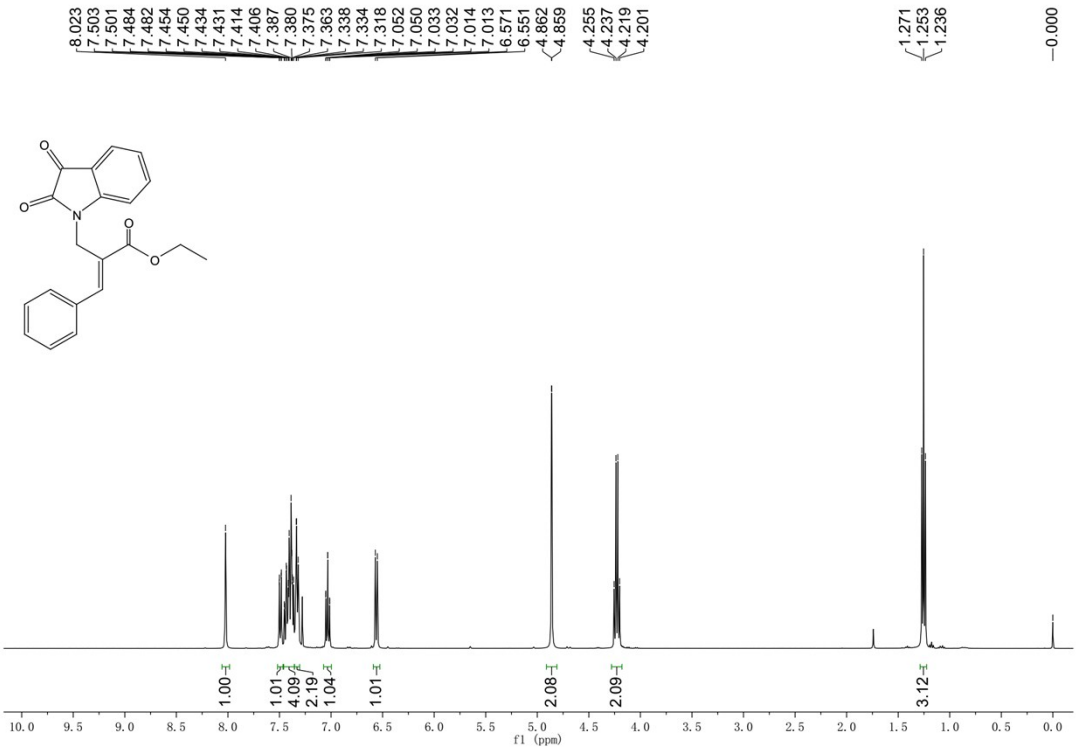

173.3
165.9
163.0
143.6
133.9
129.4
129.2
128.6
128.6
125.6
77.4
77.1
76.8
61.4
61.2
38.2
21.5
14.1
14.1
f1 (ppm)

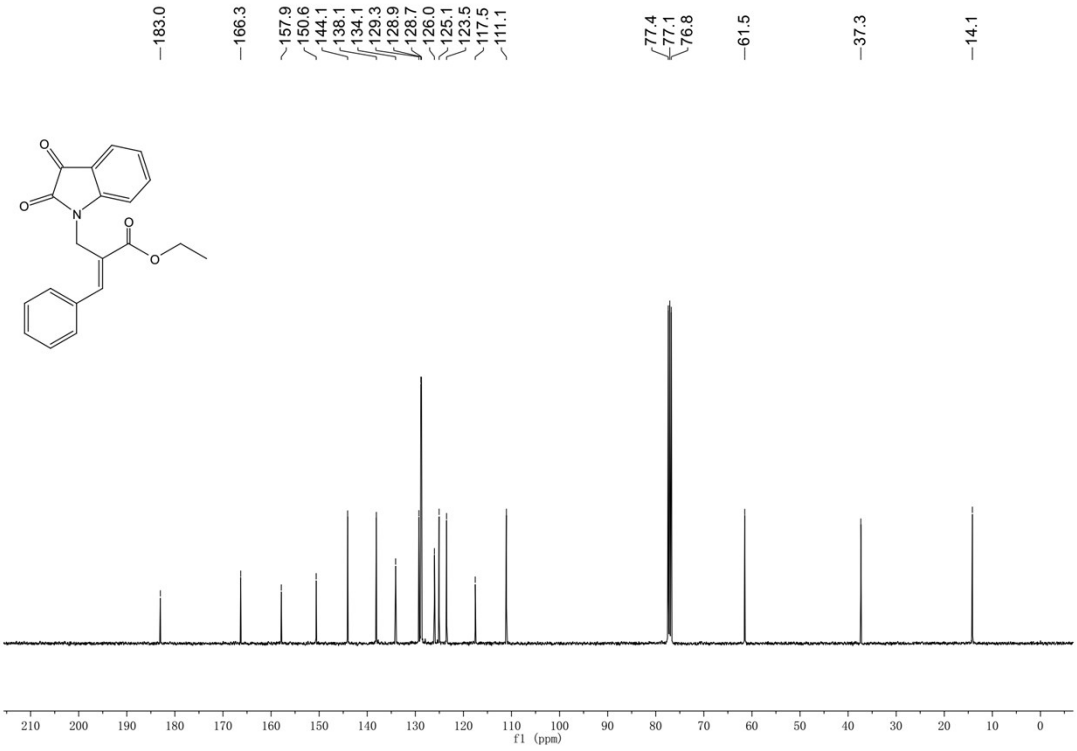
6


7.639
7.636
7.620
7.617
7.464
7.461
7.445
7.399
7.394
7.382
7.370
7.364
7.359
7.350
7.118
7.099
7.081
6.873
6.852
6.631
6.627
6.477
5.676
4.237
4.228
4.219
4.210
4.200
4.192
4.183
4.174
4.165
4.156
4.138
1.210
1.193
1.175
1.00
1.06
5.23
1.03
1.03
1.02
1.00
1.02
2.12
3.05
f1 (ppm)

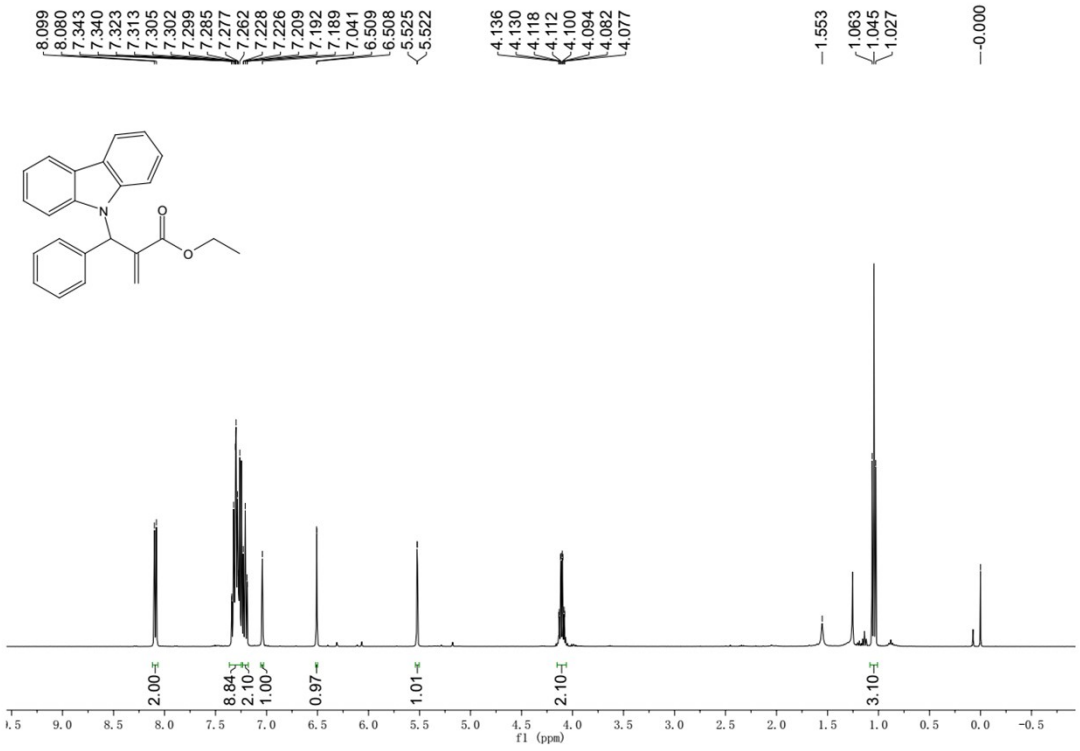

182.8
165.3
158.0
150.9
138.1
137.6
135.5
129.5
128.9
128.4
127.9
127.8
125.3
123.6
117.8
112.5
77.4
77.1
76.8
61.3
56.5
13.9
f1 (ppm)

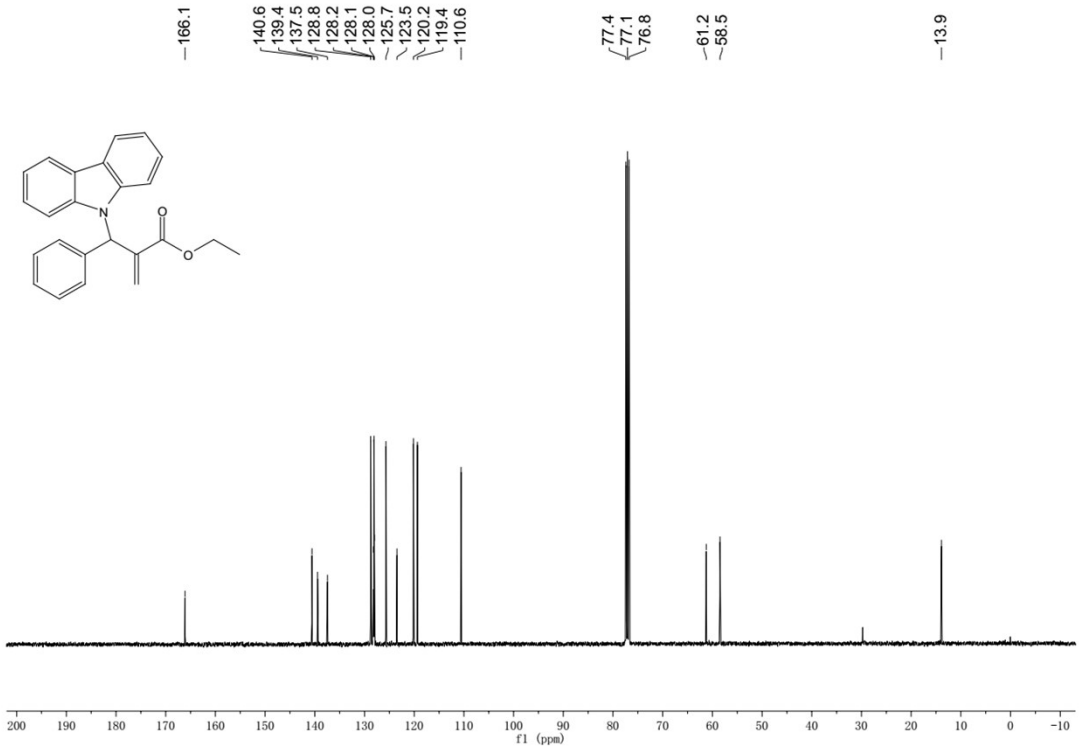
7


8.023
7.503
7.501
7.484
7.482
7.454
7.450
7.434
7.431
7.414
7.406
7.387
7.380
7.375
7.363
7.338
7.334
7.318
7.052
7.050
7.033
7.032
7.014
7.013
6.571
6.551
4.862
4.859
4.255
4.237
4.219
4.201
1.271
1.253
1.236
0.000
1.00
1.01
4.09
2.19
1.04
1.01
2.08
2.09
3.12
f1 (ppm)

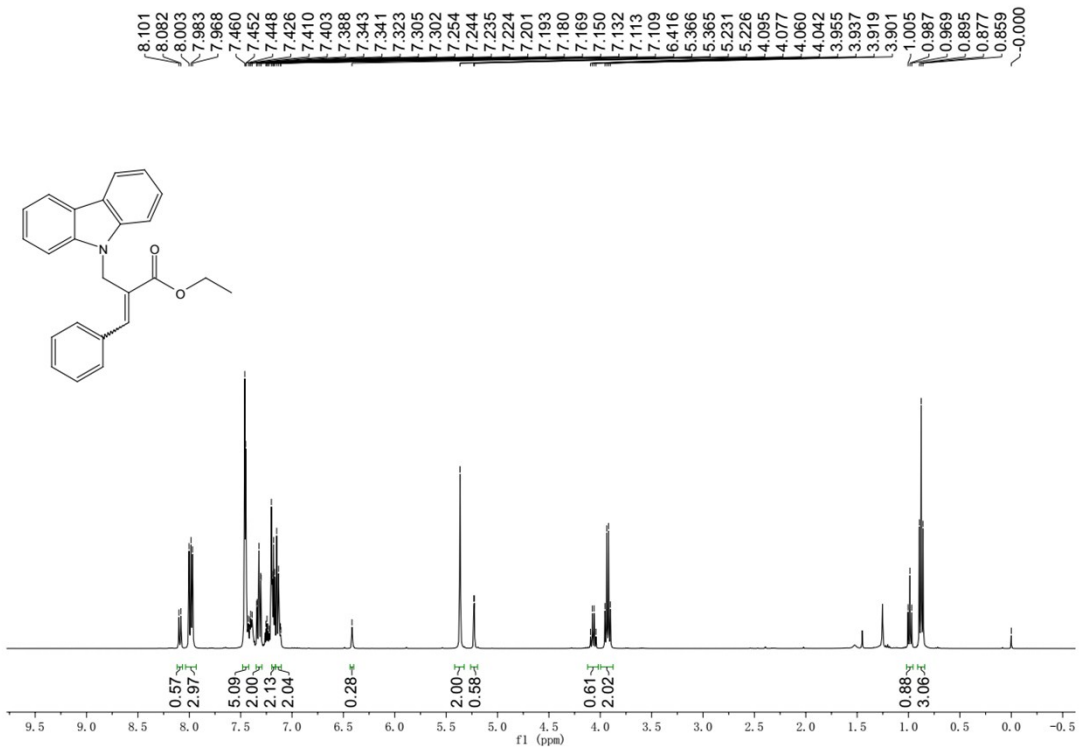

183.0
166.3
157.9
150.6
144.1
138.1
134.1
129.3
128.9
128.7
126.0
125.1
123.5
117.5
111.1
77.4
77.1
76.8
61.5
37.3
14.1
f1 (ppm)

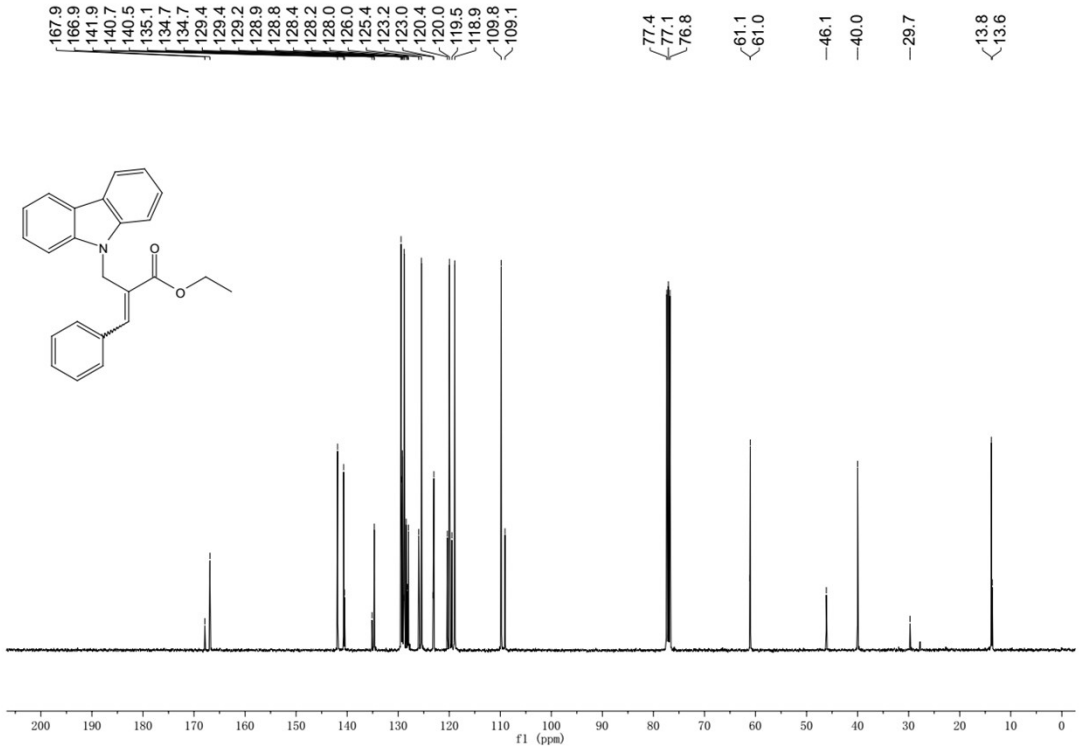
9


8.099
8.080
7.343
7.340
7.323
7.313
7.305
7.302
7.299
7.285
7.277
7.262
7.228
7.226
7.209
7.192
7.189
7.041
6.509
6.508
5.525
5.522
4.136
4.130
4.118
4.112
4.100
4.094
4.082
4.077
1.553
1.063
1.045
1.027
0.000
2.00
8.84
2.10
1.00
0.97
1.01
2.10
3.10
f1 (ppm)

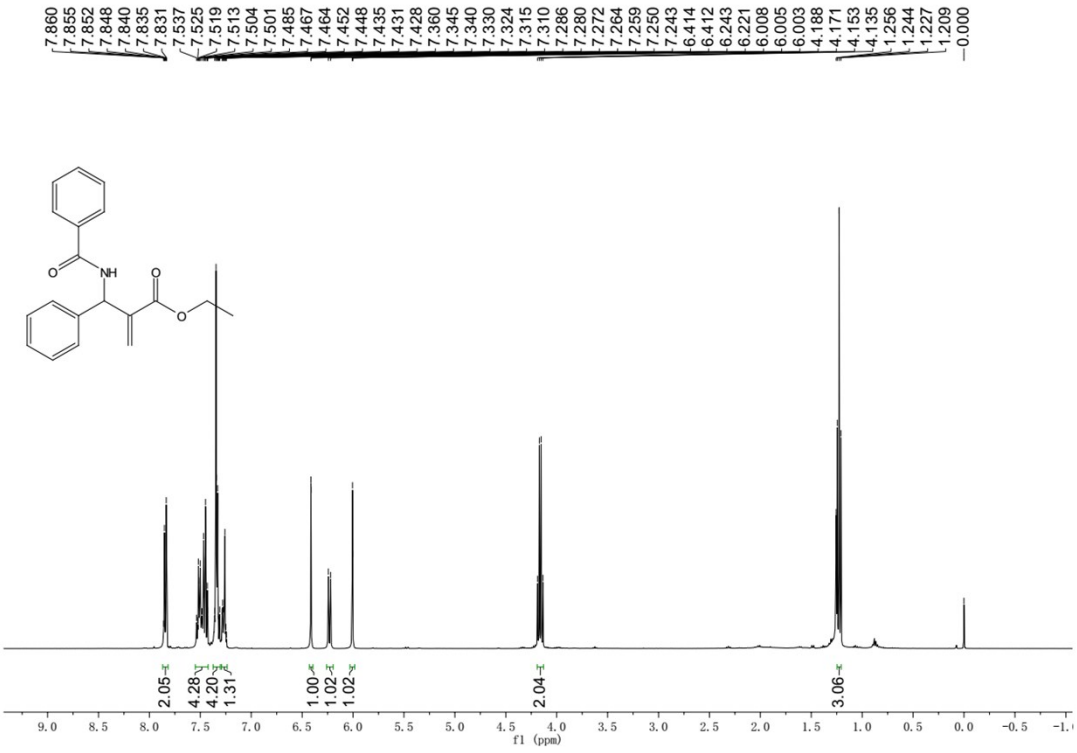

166.1
140.6
139.4
137.5
128.8
128.2
128.1
128.0
125.7
123.5
120.2
119.4
110.6
77.4
77.1
76.8
61.2
58.5
13.9
f1 (ppm)

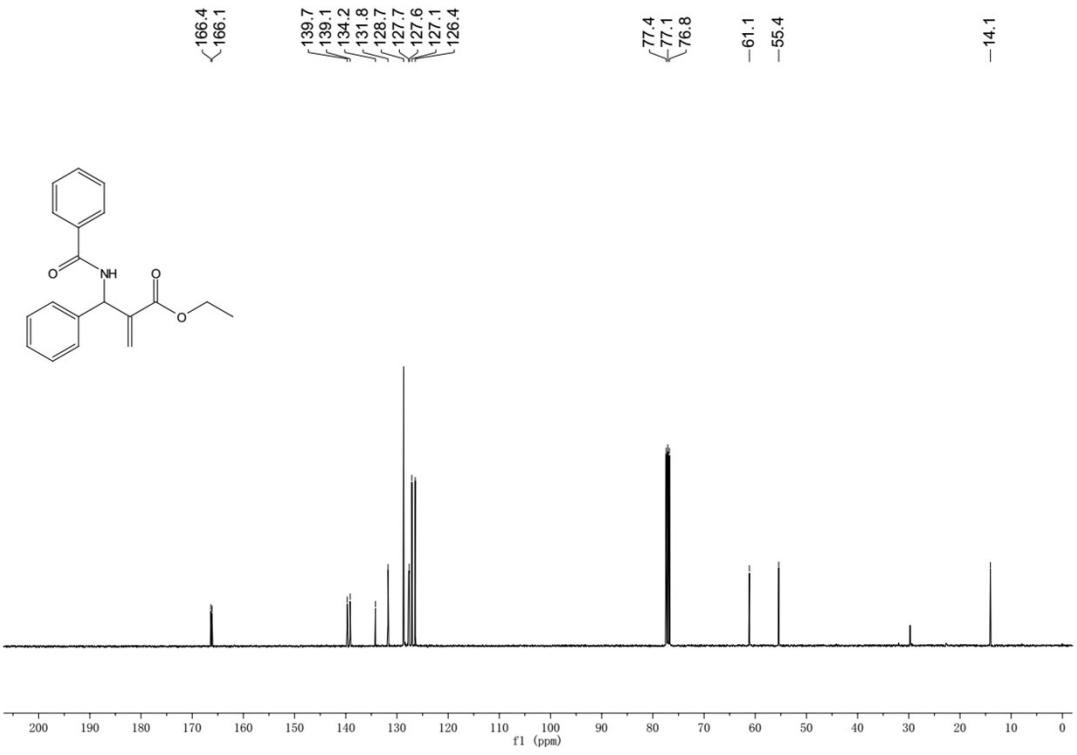
10


8.101
8.082
8.003
7.983
7.968
7.460
7.452
7.448
7.426
7.410
7.403
7.388
7.343
7.341
7.323
7.305
7.302
7.254
7.244
7.235
7.224
7.201
7.193
7.180
7.169
7.150
7.132
7.113
7.109
6.416
5.366
5.365
5.231
5.226
4.095
4.077
4.060
4.042
3.955
3.937
3.919
3.901
1.005
0.987
0.969
0.895
0.877
0.859
-0.000
0.57
2.97
5.09
2.00
2.13
2.04
0.28
2.00
0.58
0.61
2.02
0.88
3.06
f1 (ppm)

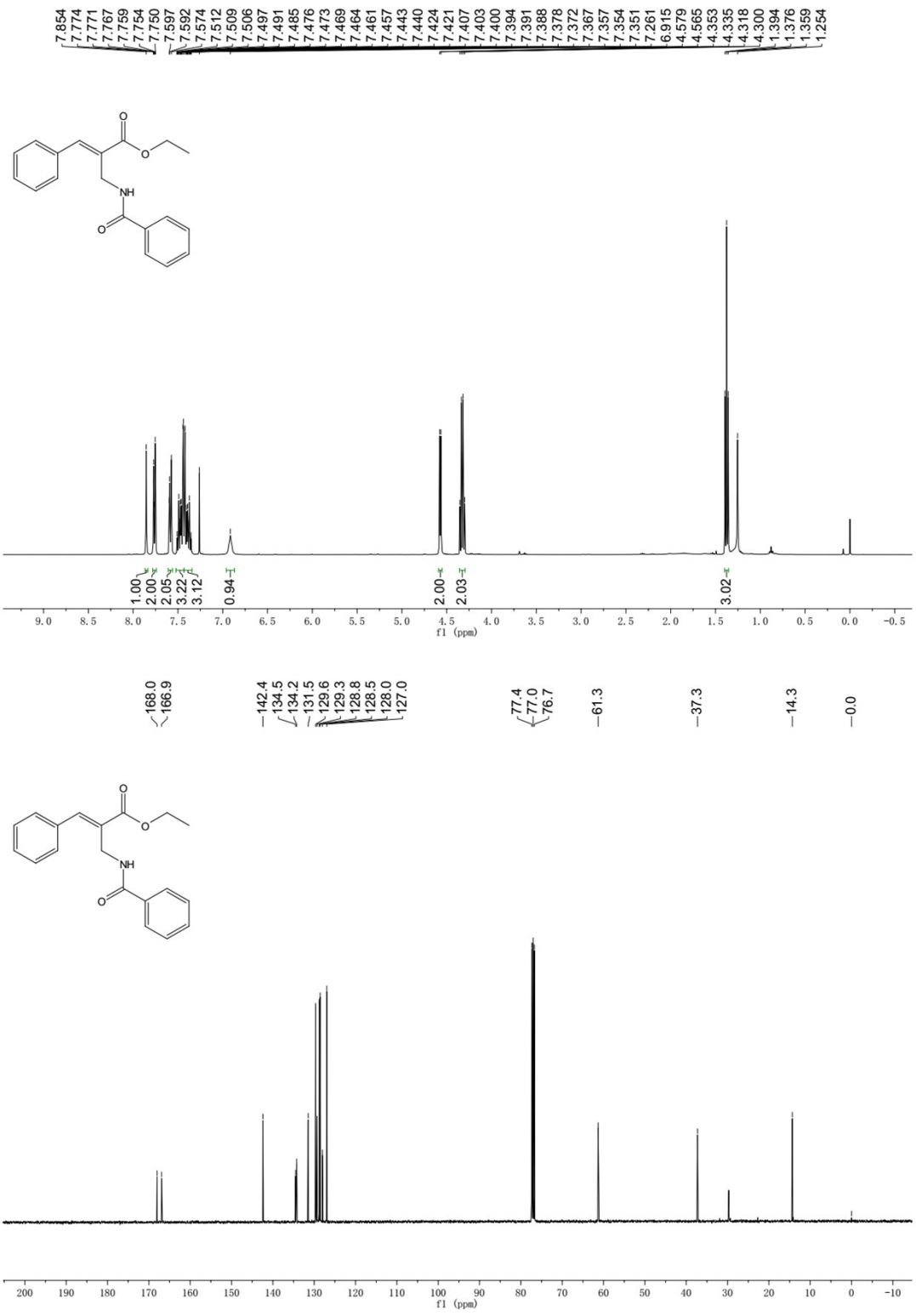

167.9
166.9
141.9
140.7
140.5
135.1
134.7
134.7
129.4
129.4
129.2
128.9
128.8
128.4
128.2
128.0
126.0
125.4
123.2
123.0
120.4
120.0
119.5
118.9
109.8
109.1
77.4
77.1
76.8
61.1
61.0
46.1
40.0
29.7
13.8
13.6
f1 (ppm)

11


7.860
7.855
7.852
7.848
7.840
7.835
7.831
7.537
7.525
7.519
7.513
7.504
7.501
7.485
7.467
7.464
7.452
7.448
7.435
7.431
7.428
7.360
7.345
7.340
7.330
7.324
7.315
7.310
7.286
7.280
7.272
7.264
7.259
7.250
7.243
6.414
6.412
6.243
6.221
6.008
6.005
6.003
4.188
4.171
4.153
4.135
1.256
1.244
1.227
1.209
0.000
NH
O
O
O
2.05
4.28
4.20
1.31
1.00
1.02
1.02
2.04
3.06
f1 (ppm)

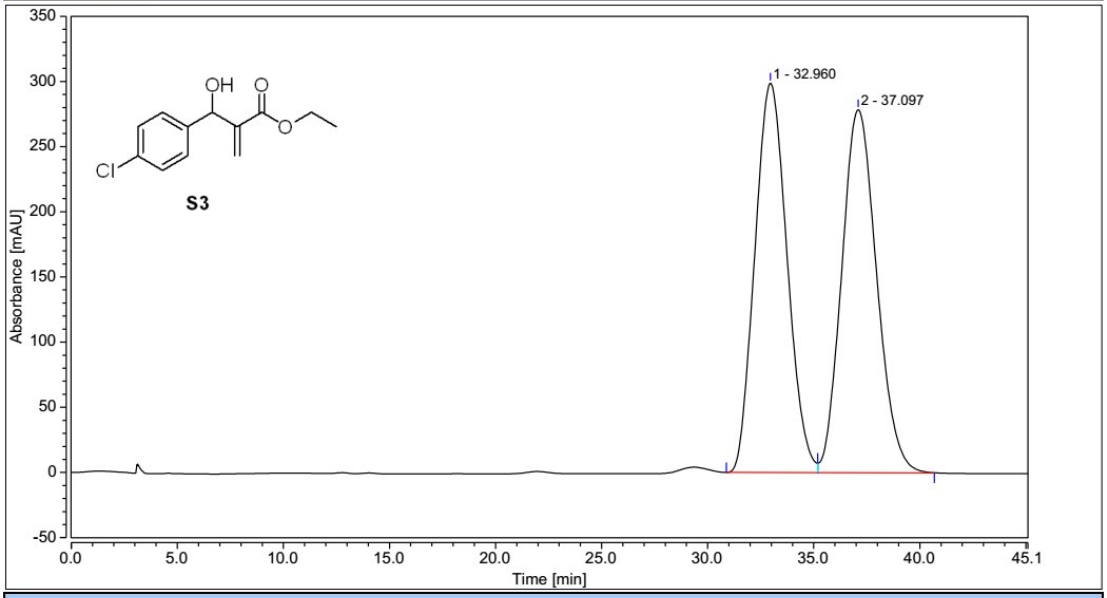

166.4
166.1
139.7
139.1
134.2
131.8
128.7
127.7
127.6
127.1
126.4
77.4
77.1
76.8
61.1
55.4
14.1
NH
O
O
O
f1 (ppm)

12



6. Copies of HPLC Spectra of **S3, 2d and 3d**

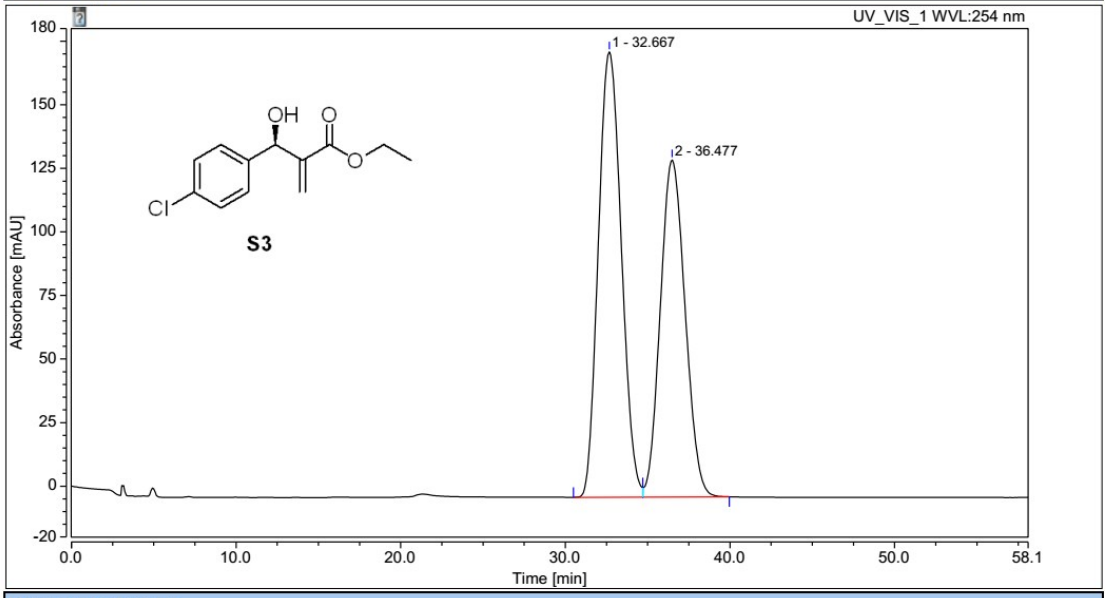
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.960	525.416	298.860	49.70	51.76	n.a.
2		37.097	531.764	278.530	50.30	48.24	n.a.
Total:			**1057.181**	**577.391**	**100.00**	**100.00**	

Chromatogram

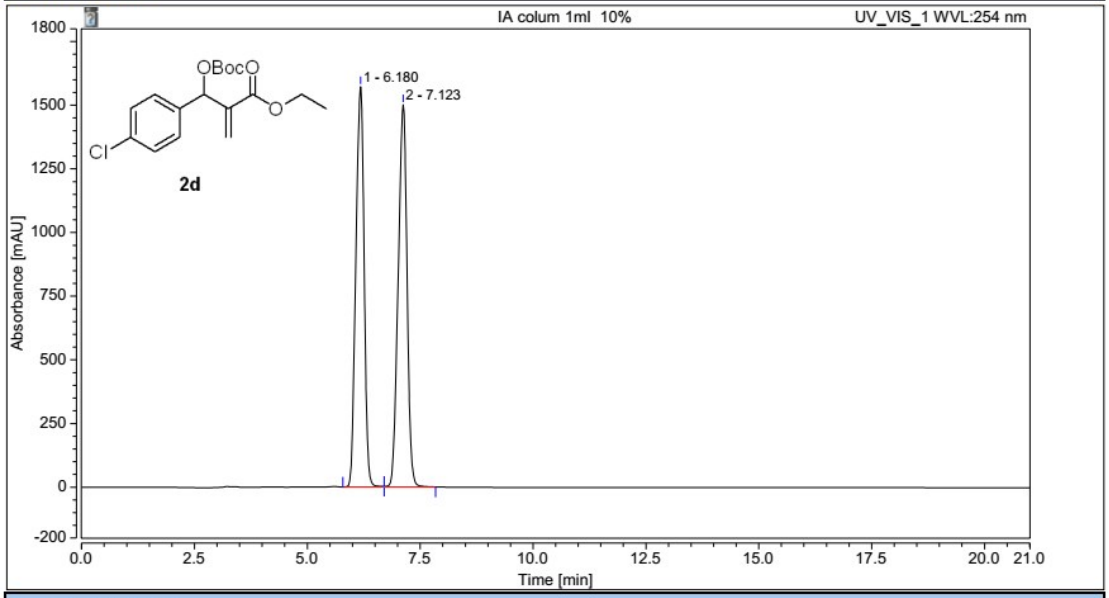


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.667	283.126	175.208	55.04	56.91	n.a.
2		36.477	231.266	132.639	44.96	43.09	n.a.
Total:			**514.392**	**307.848**	**100.00**	**100.00**	

HPLC analysis: 11% ee, [Daicel Chiralpak ODH, n-hexane/2-propanol = 97/3, v = 1.0 mL/min, λ = 254 nm, t (major) = 32.6 min, t (minor) = 36.4 min].

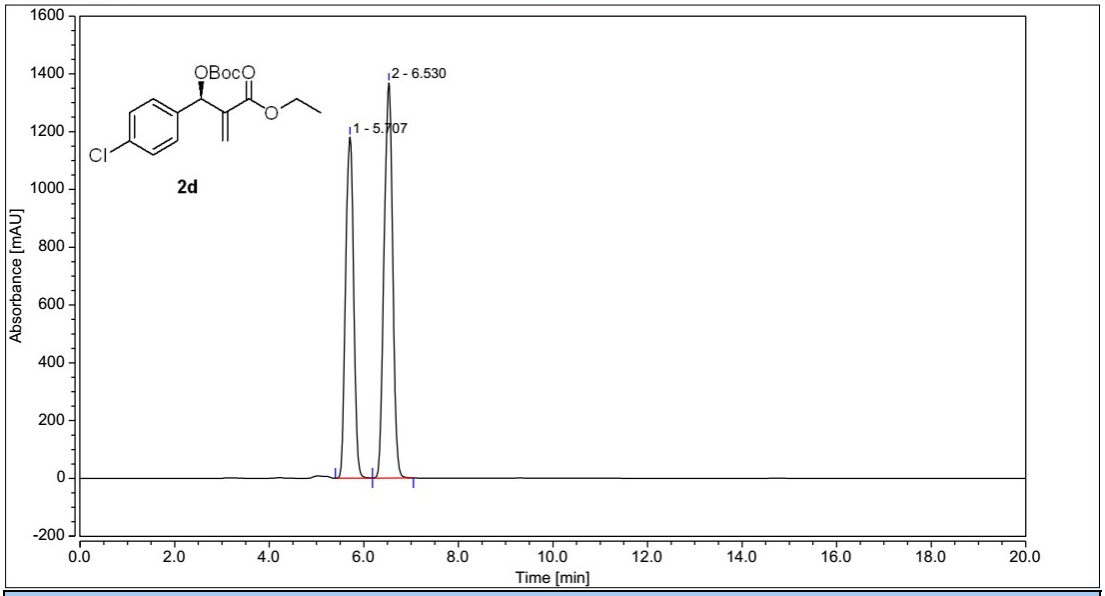
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.180	333.116	1571.837	49.41	51.14	n.a.
2		7.123	341.070	1501.619	50.59	48.86	n.a.
Total:			**674.186**	**3073.456**	**100.00**	**100.00**	

Chromatogram

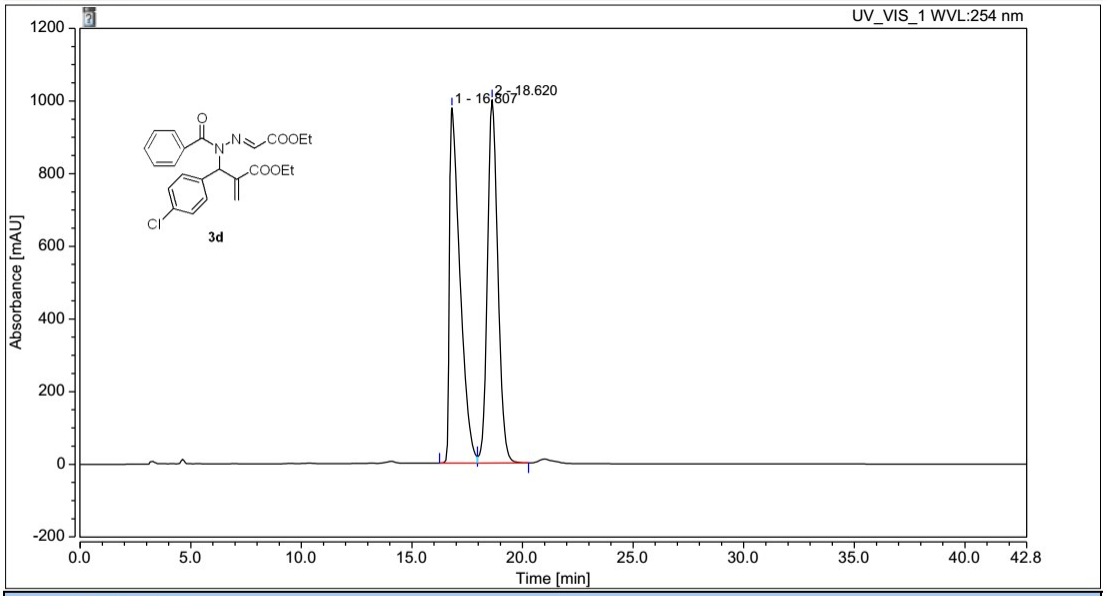


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.707	233.679	1180.211	44.79	46.33	n.a.
2		6.530	288.069	1366.972	55.21	53.67	n.a.
Total:			**521.748**	**2547.184**	**100.00**	**100.00**	

HPLC analysis: 11% ee, [Daicel Chiralpak IA, n-hexane/2-propanol = 90/10, v = 1.0 mL/min, λ = 254 nm, t (major) = 6.3 min, t (minor) = 5.7 min].

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.807	542.428	978.020	49.72	49.44	n.a.
2		18.620	548.456	1000.219	50.28	50.56	n.a.
Total:			**1090.884**	**1978.239**	**100.00**	**100.00**	

HPLC analysis: 0% ee, [Daicel Chiralpak IA, n-hexane/2-propanol = 95/5, v = 1.0 mL/min, λ = 254 nm].