Supporting Information

Substituent-Enabled Oxidative Dehydrogenative Cross-Coupling of 1,4-Naphthoquinones with Alkenes

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[§]These two authors contributed equally to this work.

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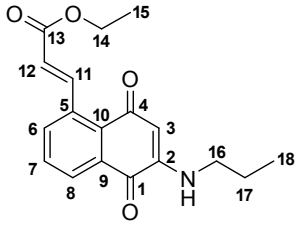
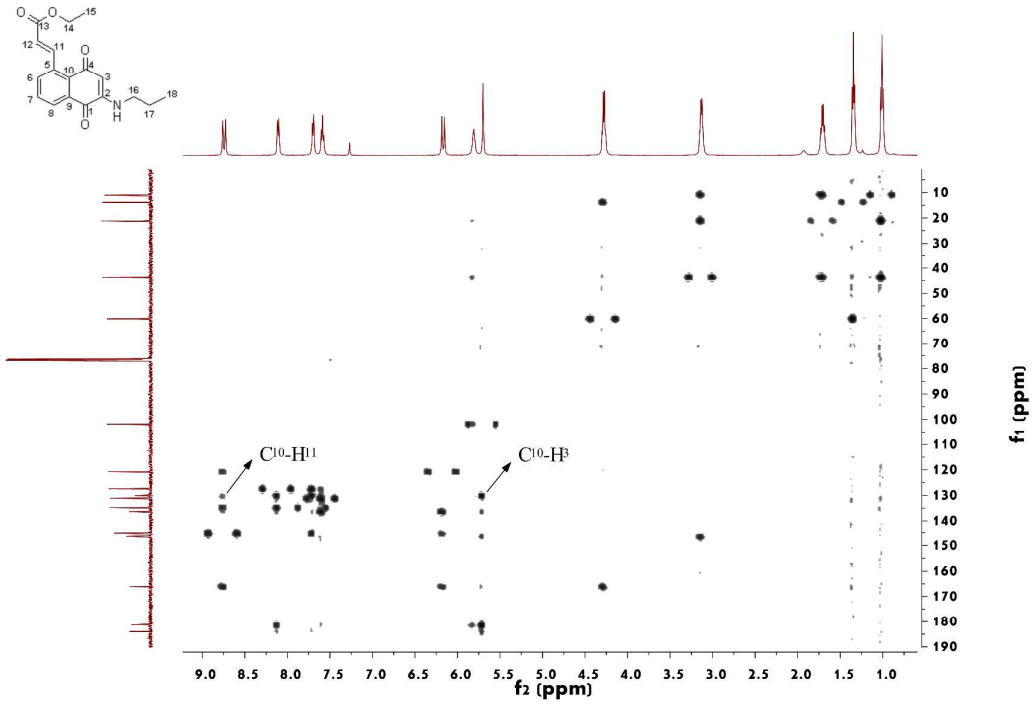
1. HMBC Spectrum of comound 3ba

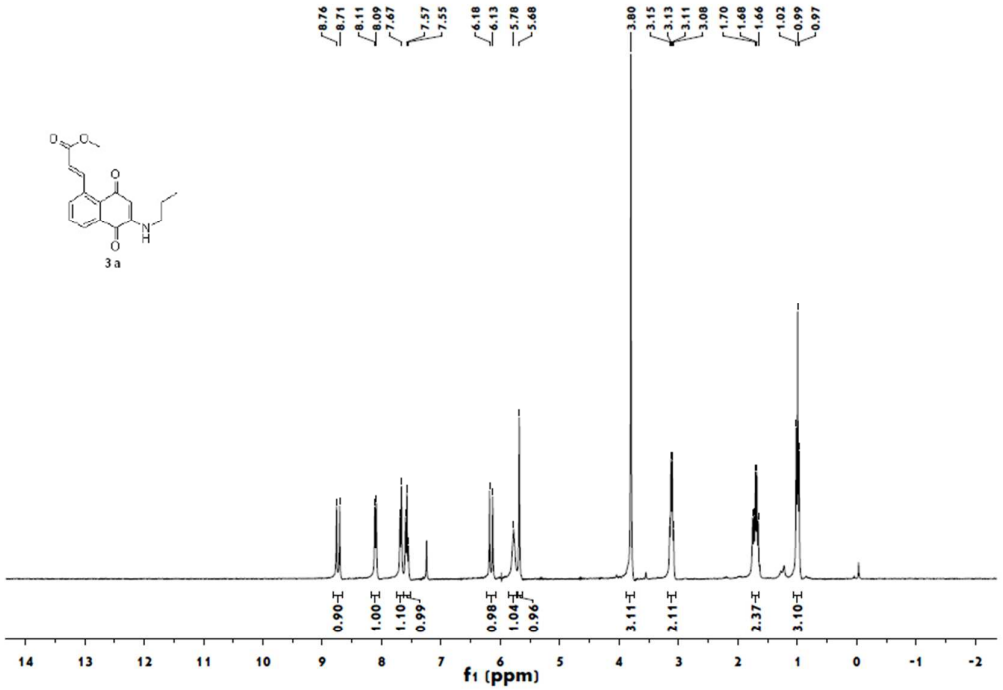


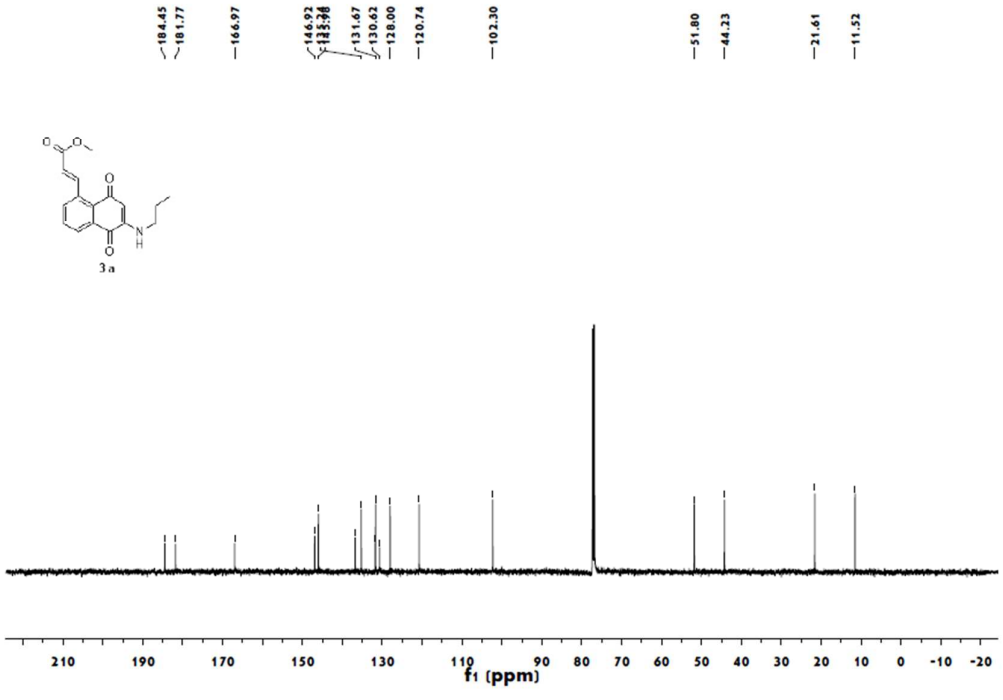
3ba

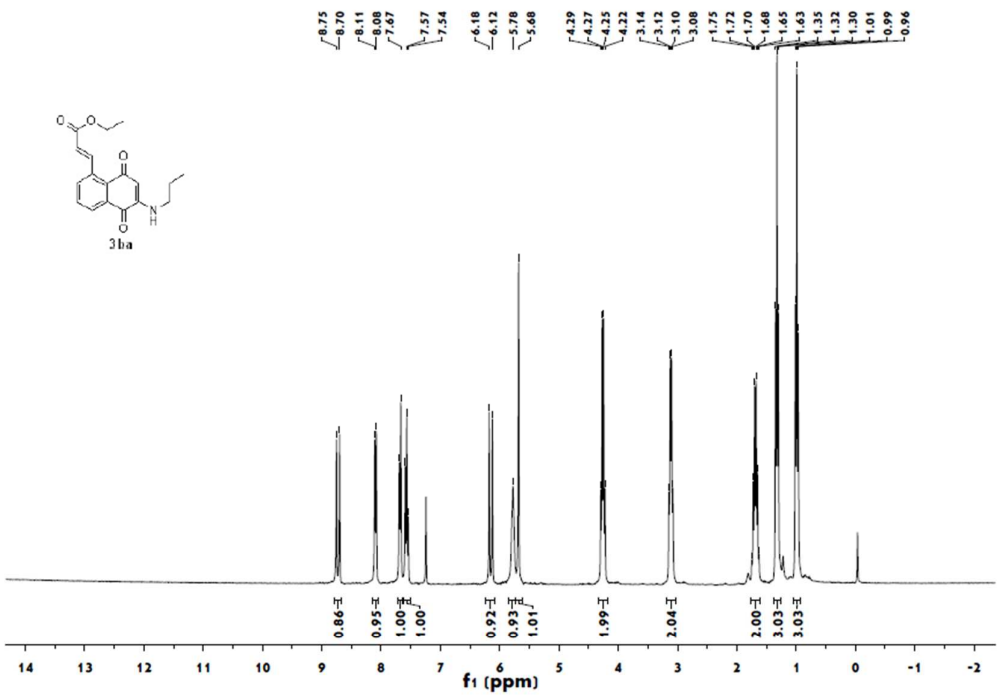


HMBC correlations [δ_C 130.1 (C-10) with δ_H 8.73 (H-11) and δ_C 130.1 (C-10) with δ_H 5.68 (H-3)] placed the alkene group at C-5.

2. NMR Spectra of Products



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3.10
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1.72
1.70
1.68
1.65
1.63
1.35
1.32
1.30
1.01
0.99
0.96
3ba
0.86
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2.00
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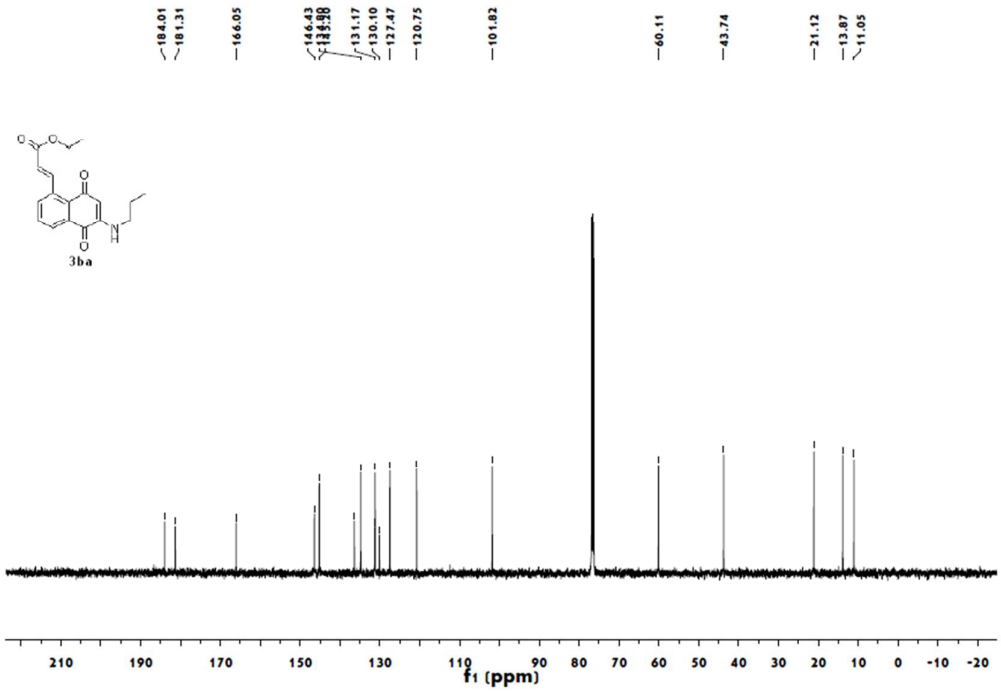
f1 (ppm)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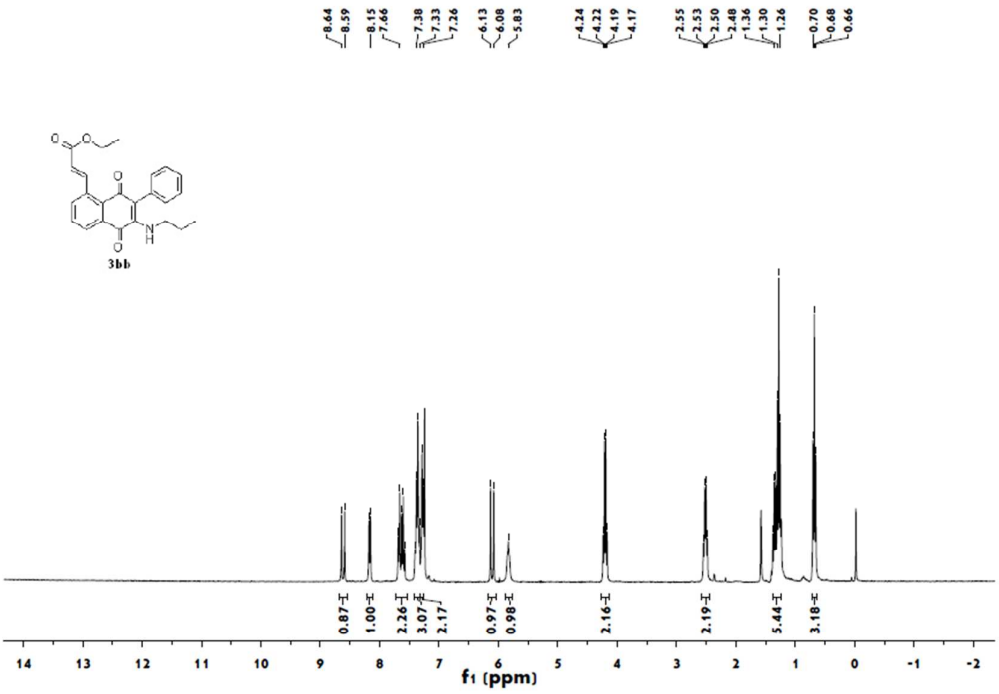
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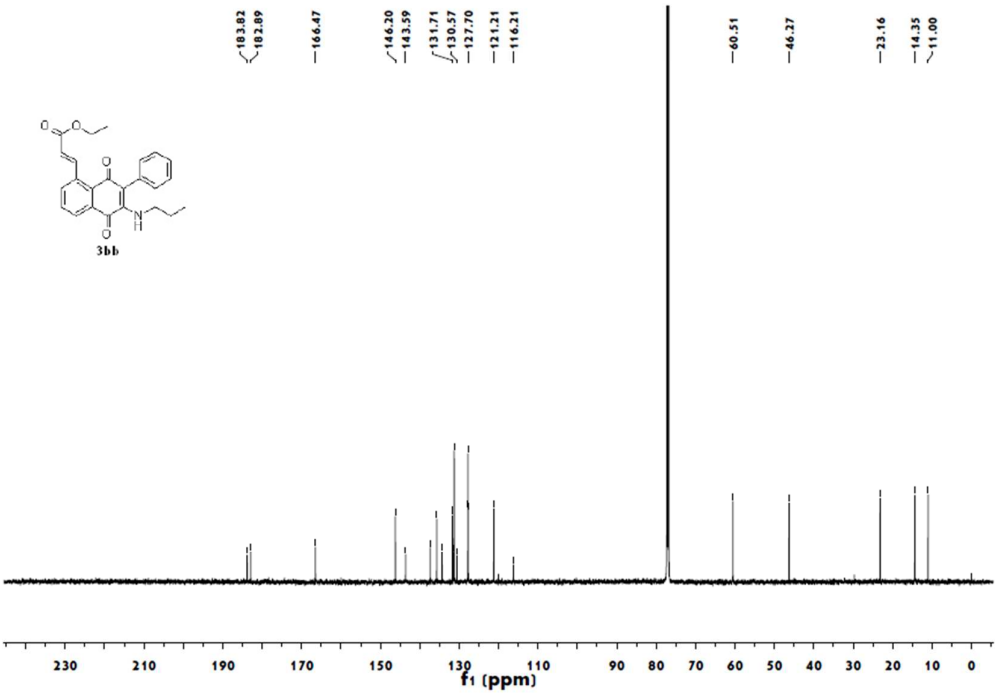
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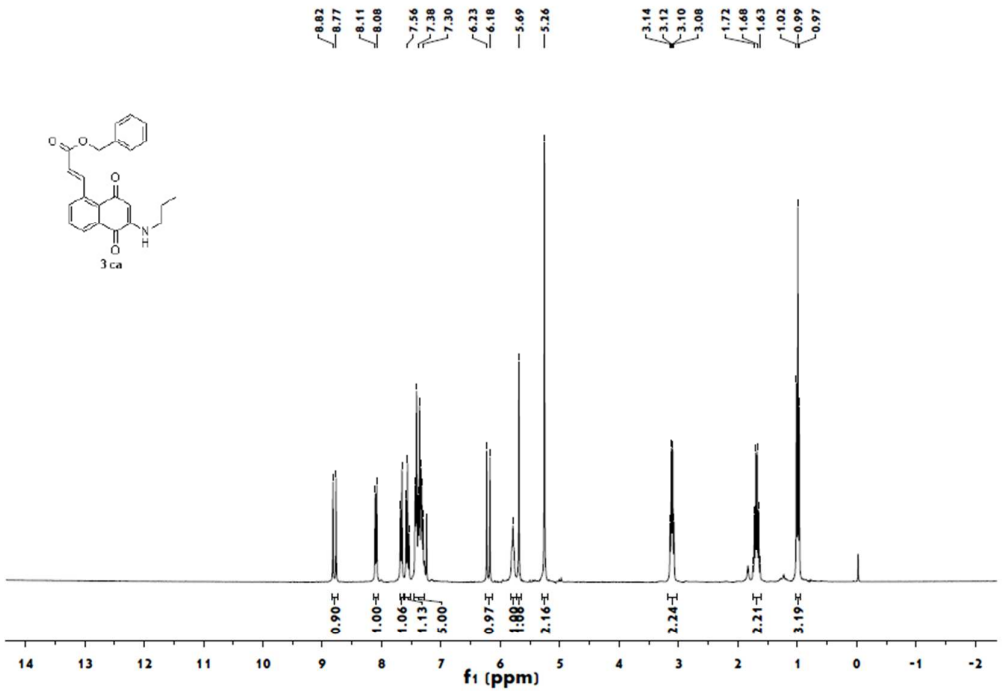
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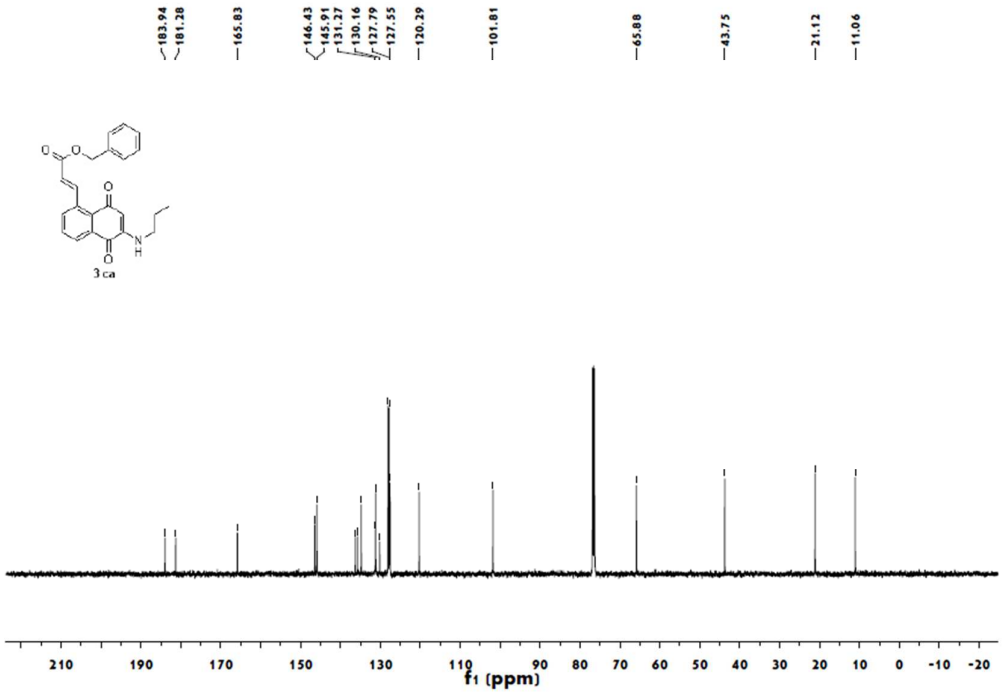
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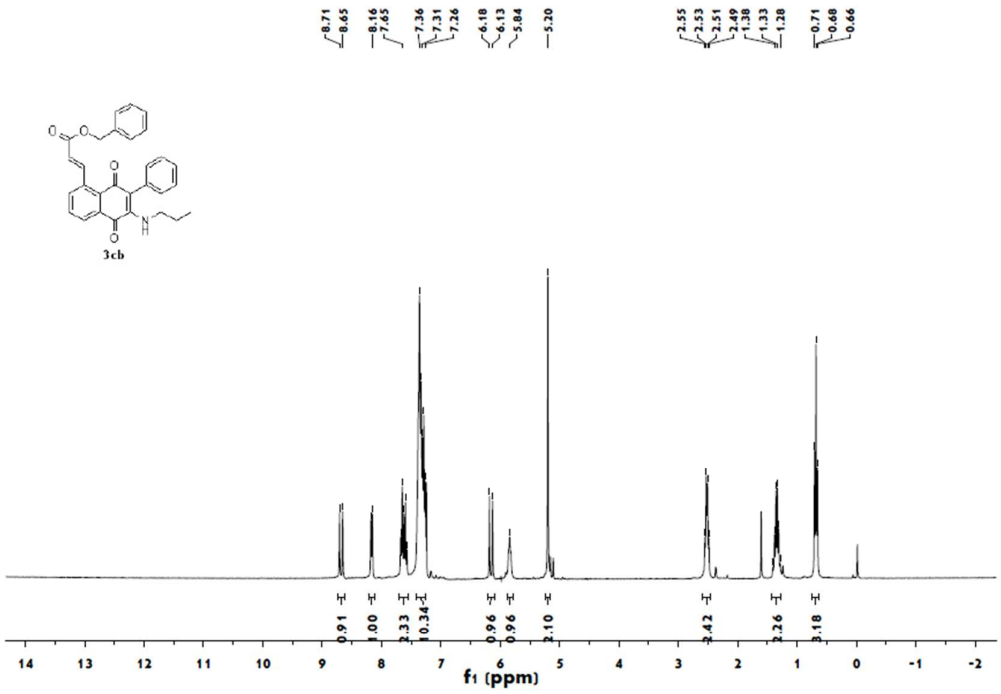
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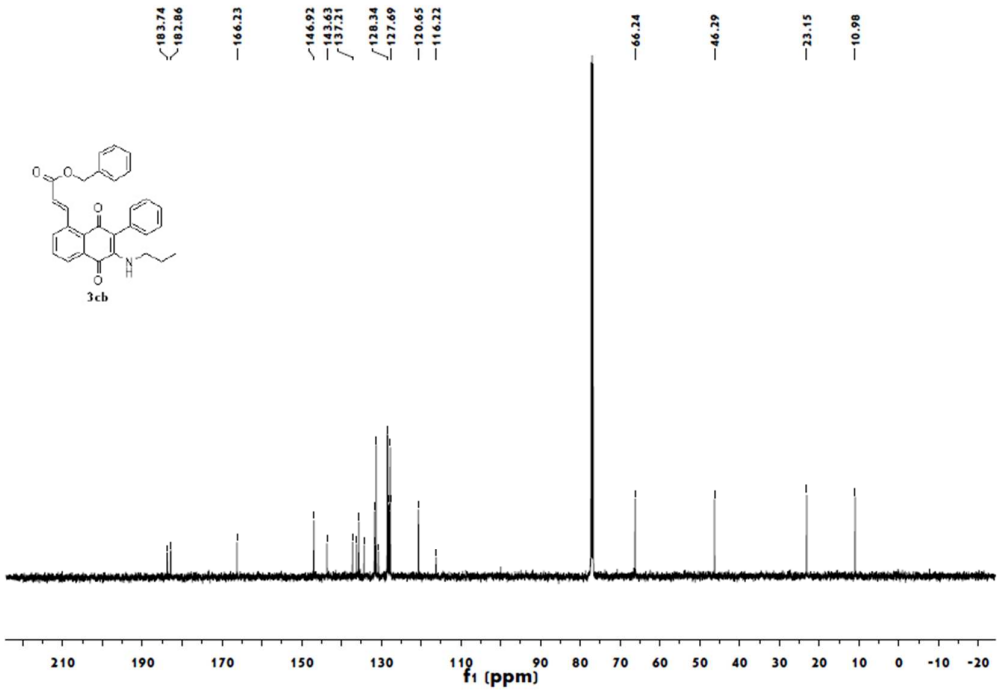
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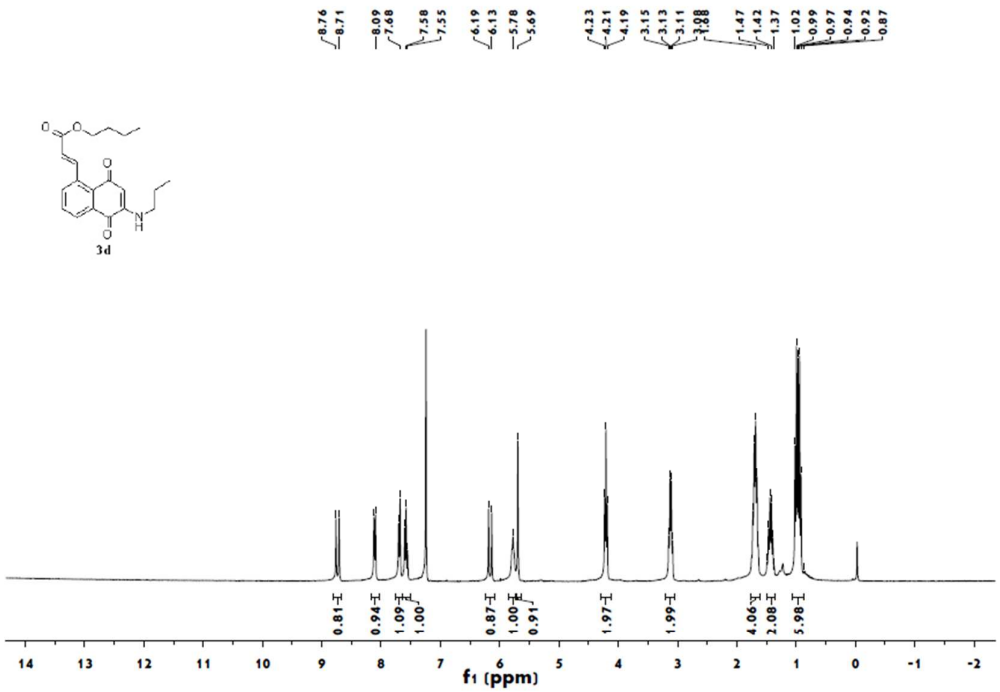
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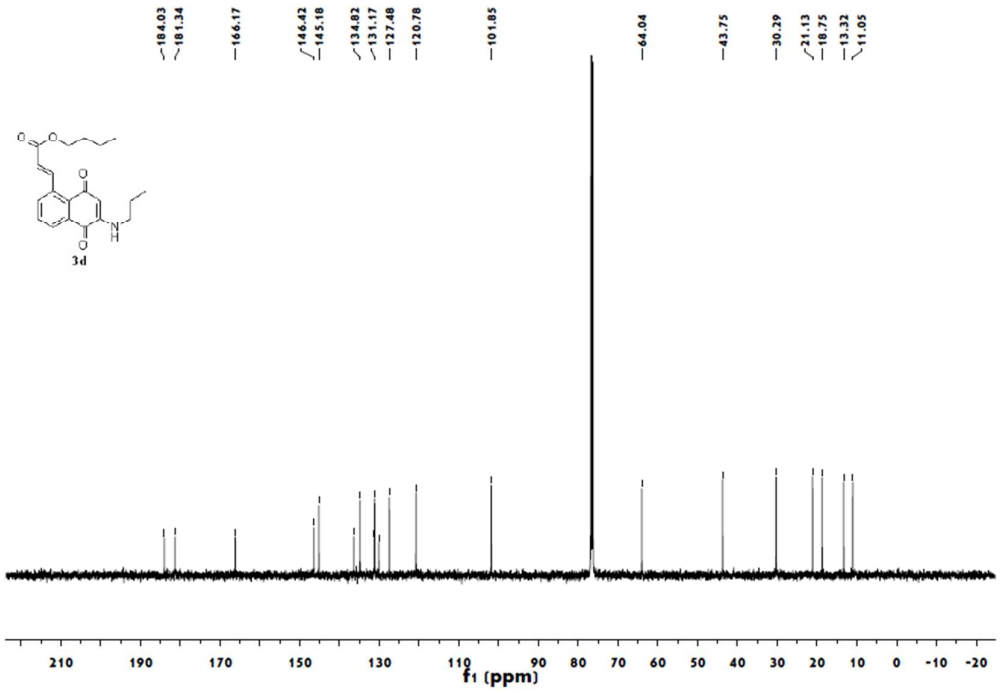
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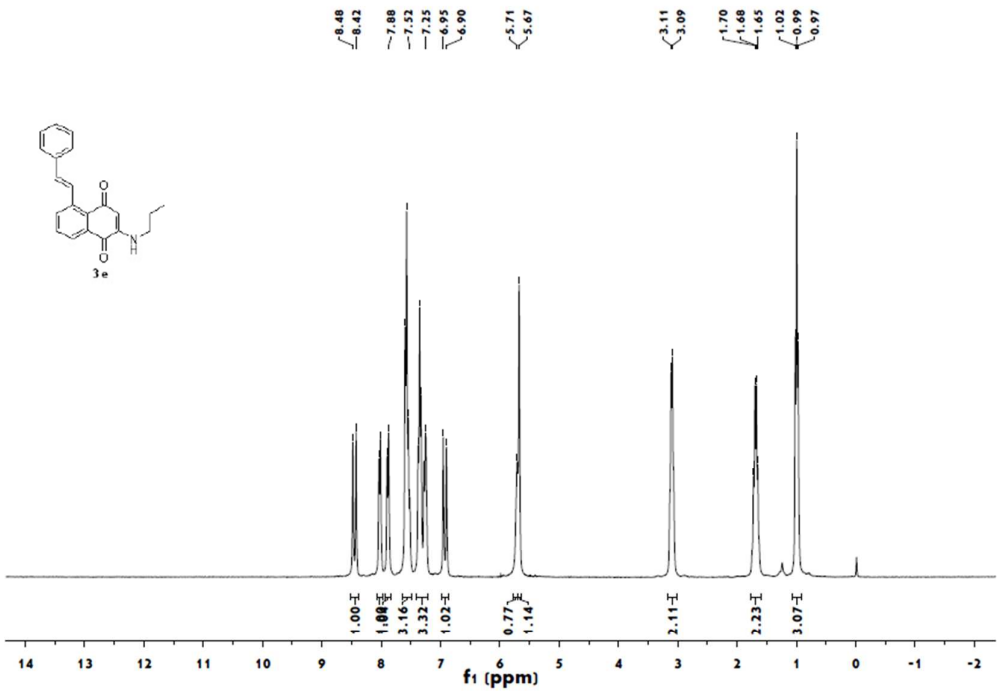
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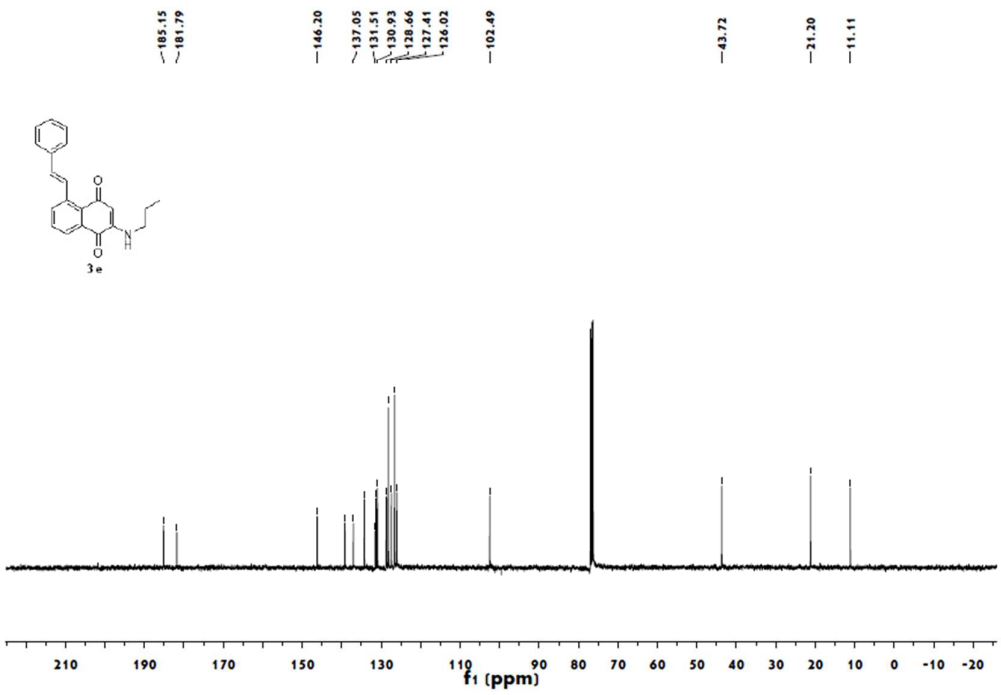
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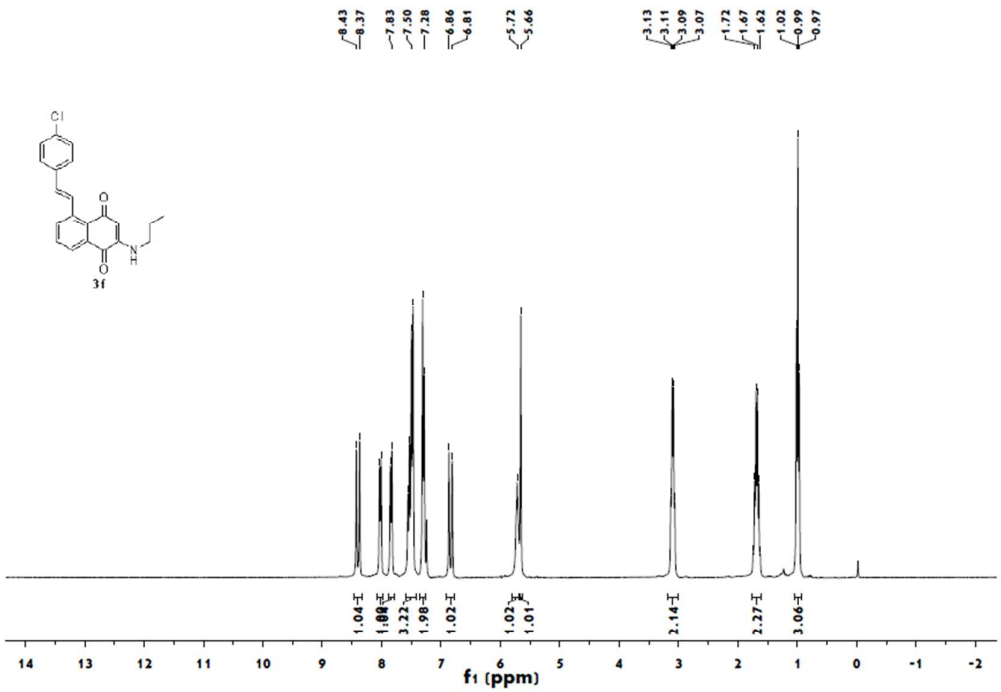
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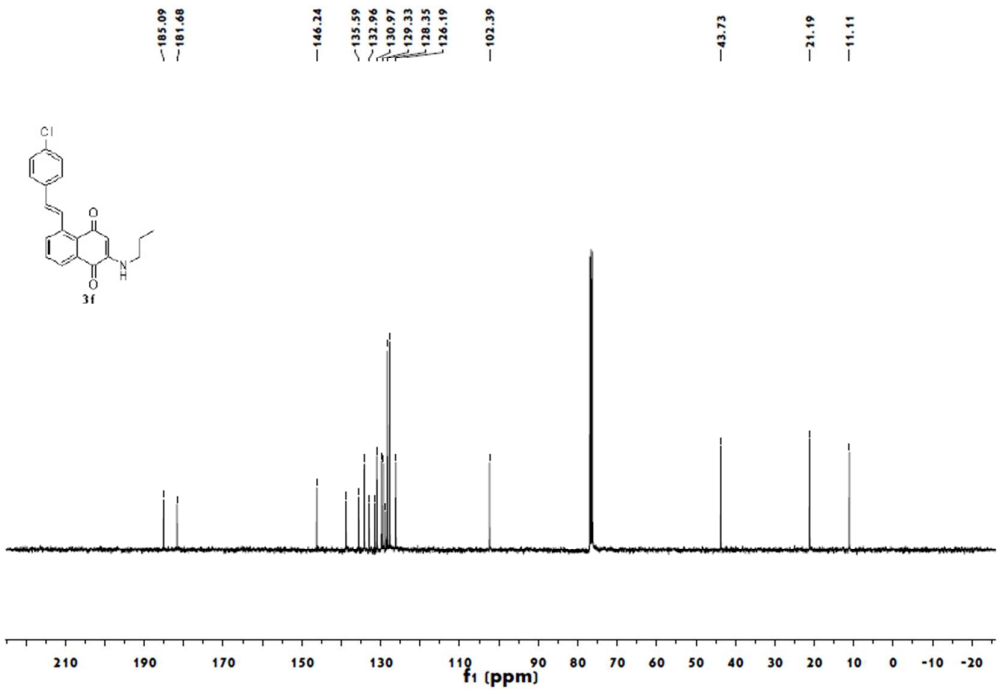
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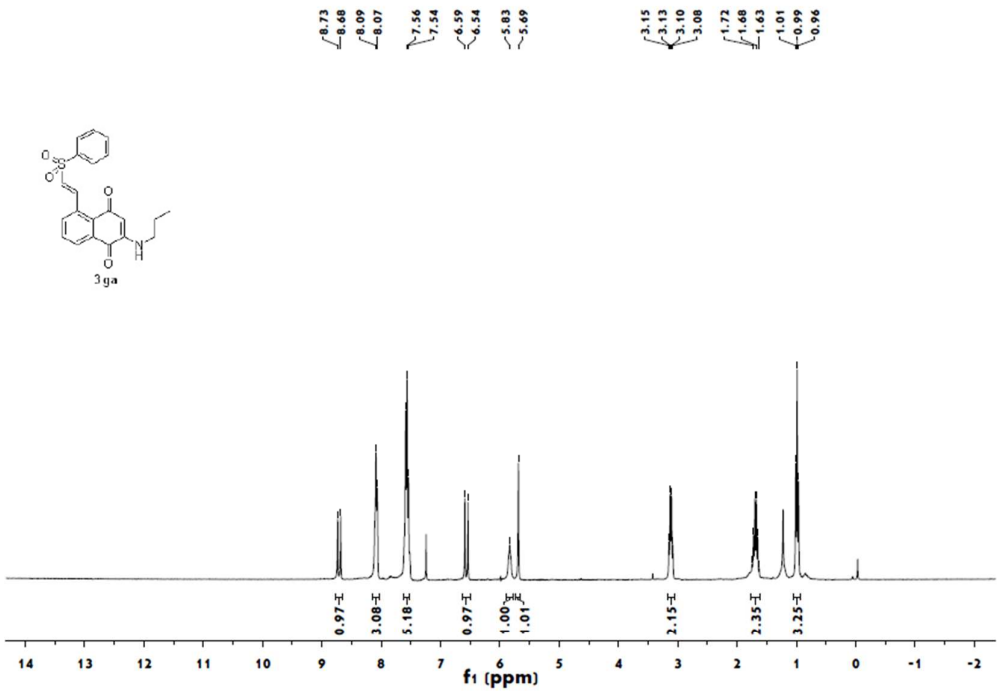
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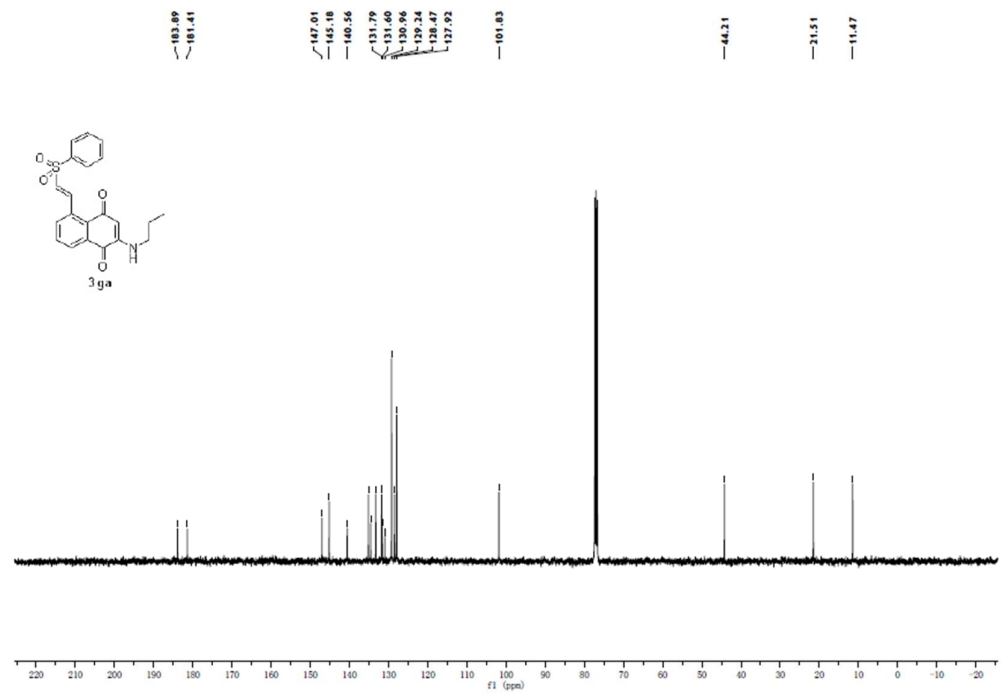
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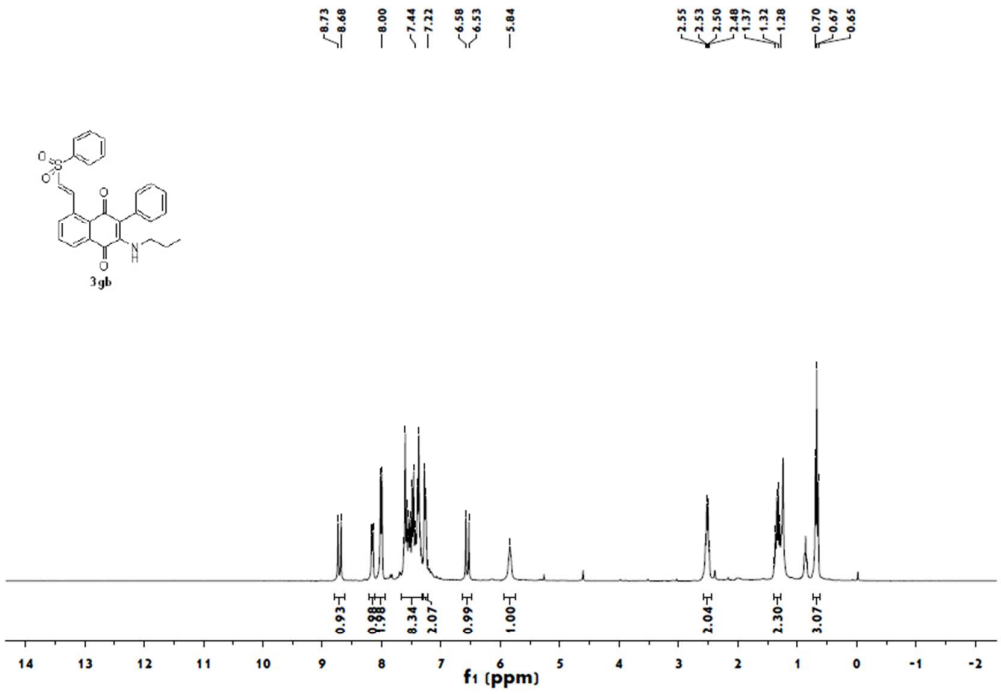
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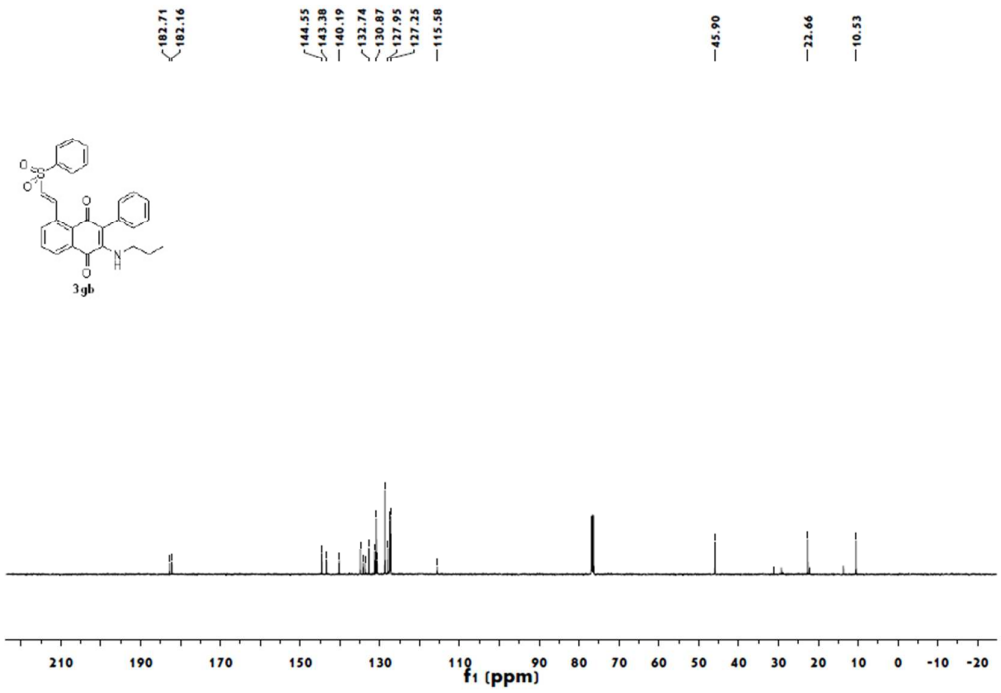
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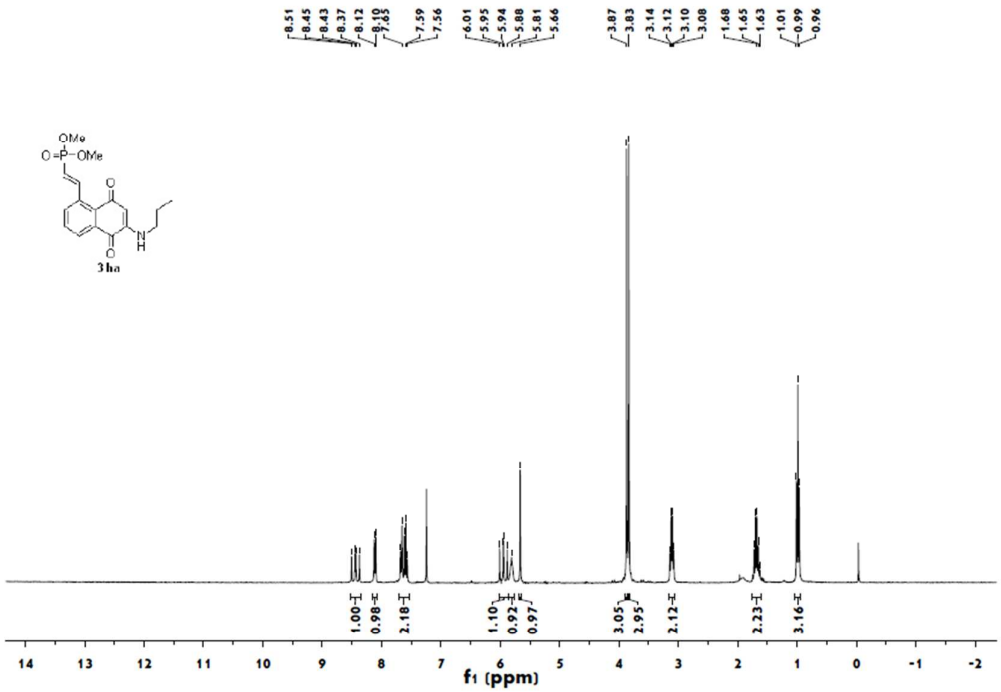
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3.83
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3.12
3.10
3.08
1.68
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1.63
1.01
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0.96
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O=P-OMe
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N
H
O
3ha
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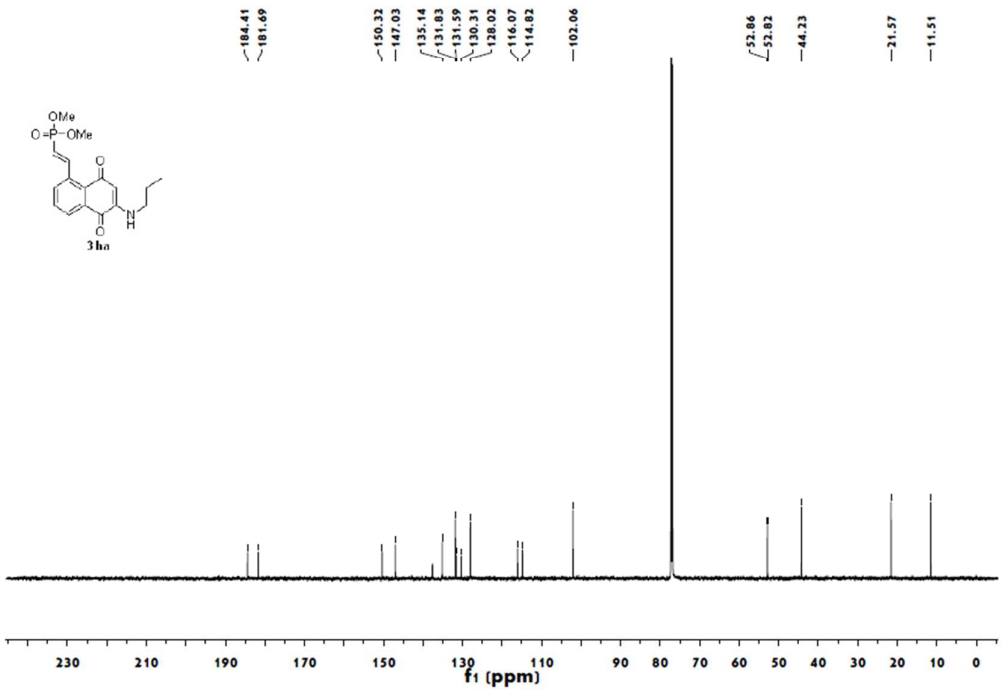
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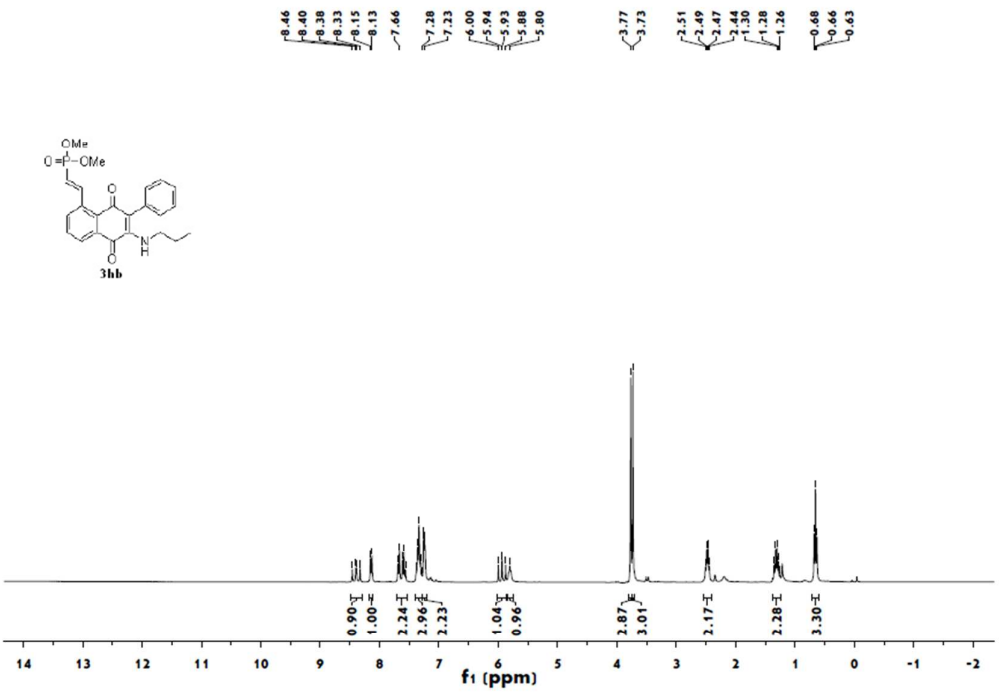
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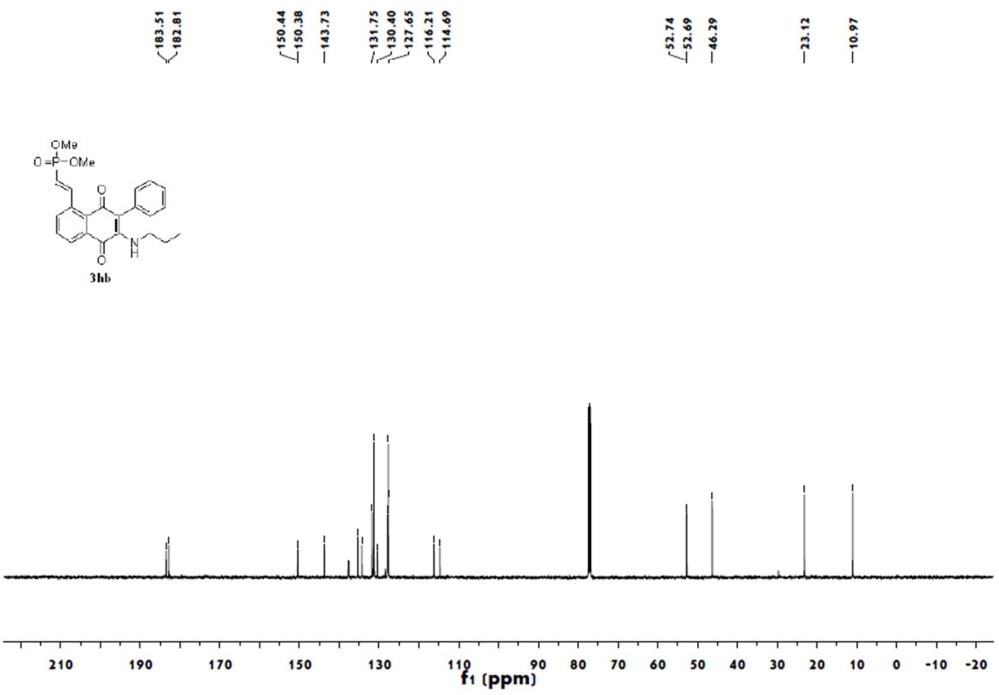
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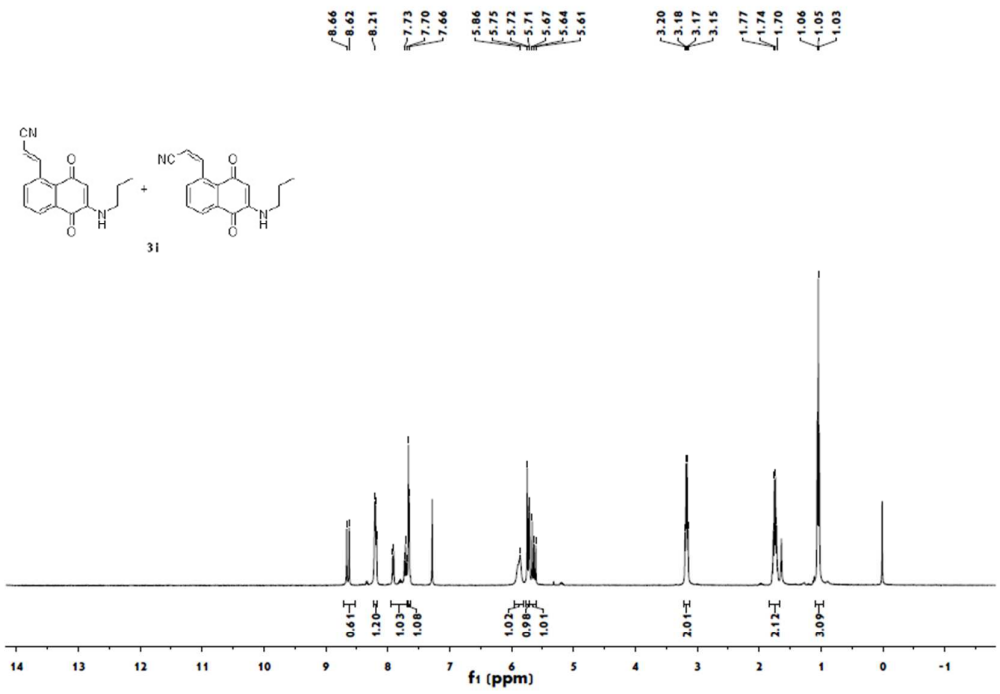
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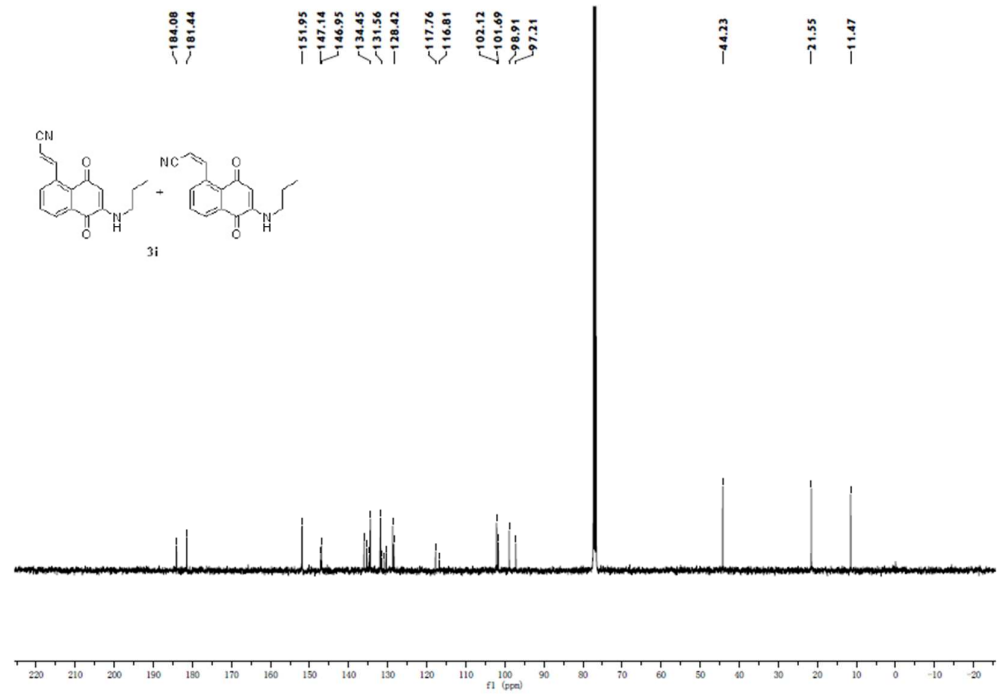
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3i
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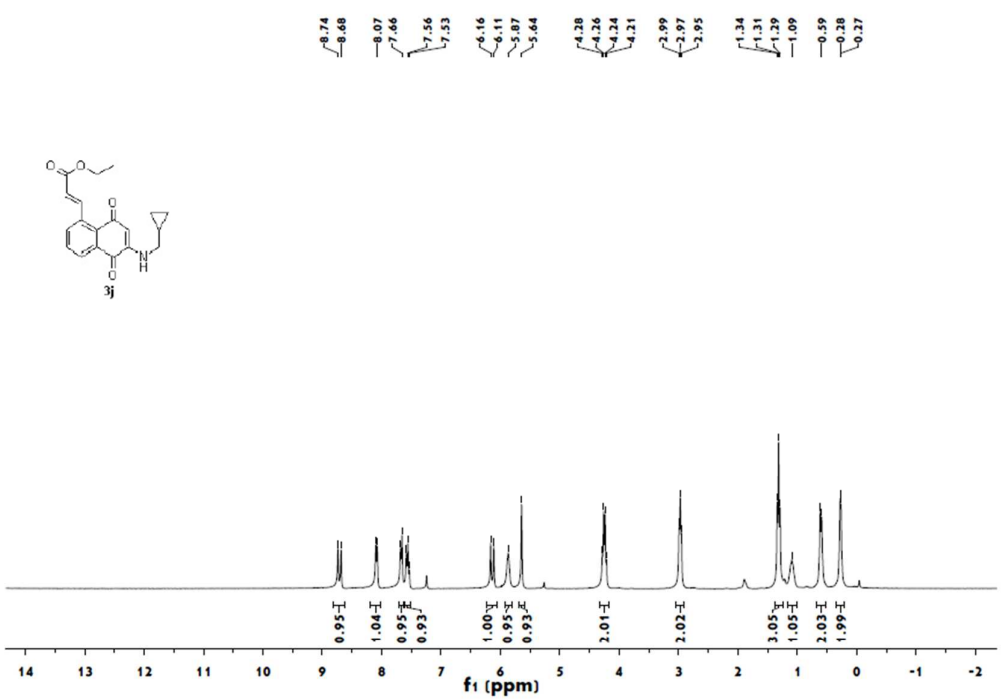
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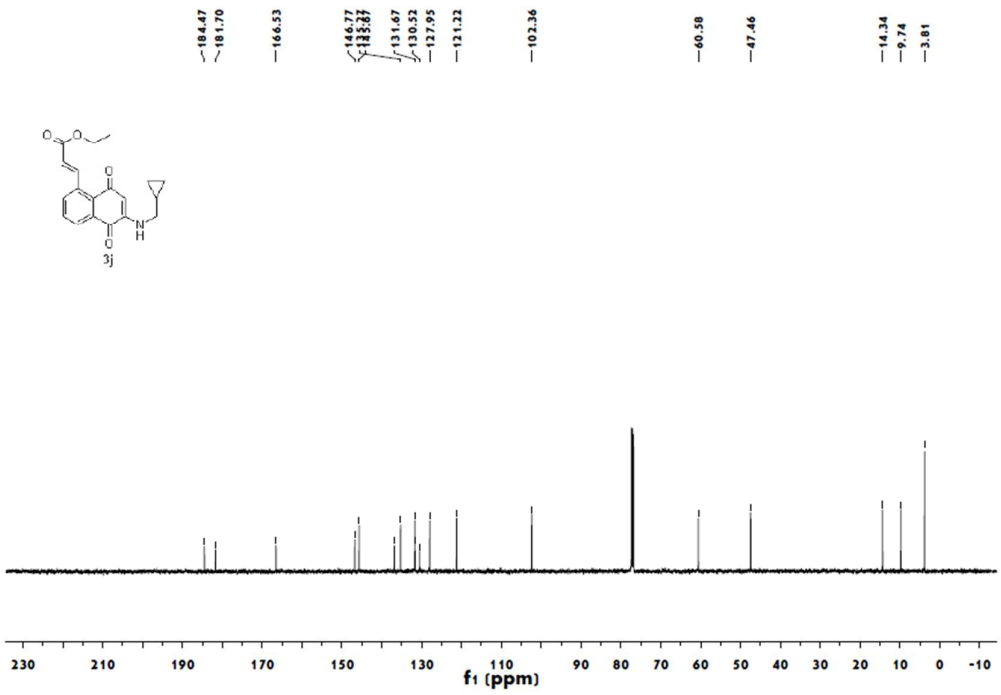
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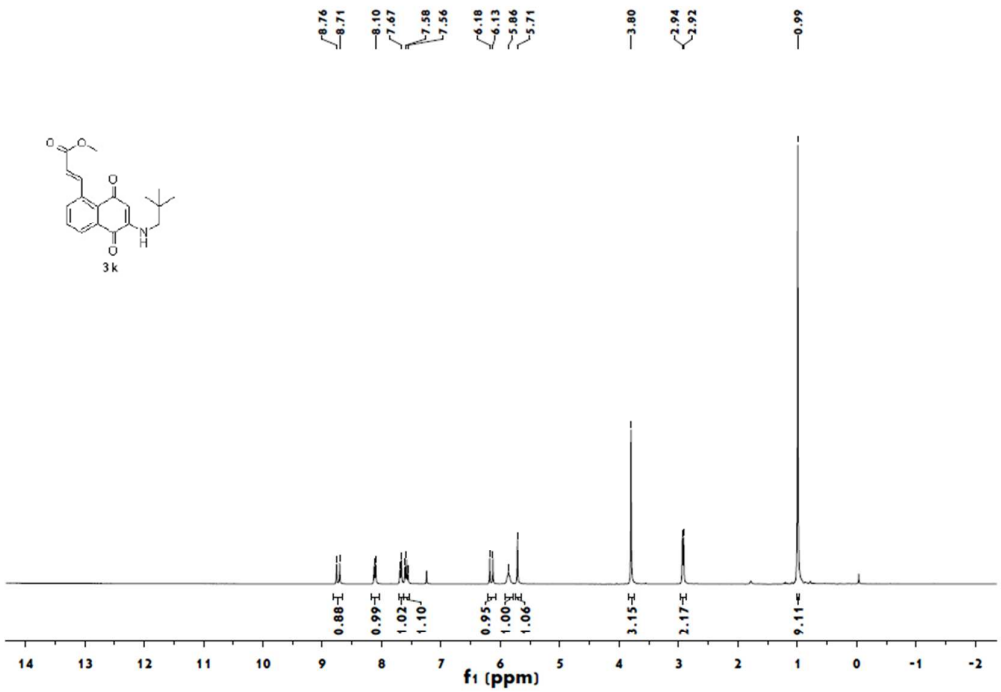
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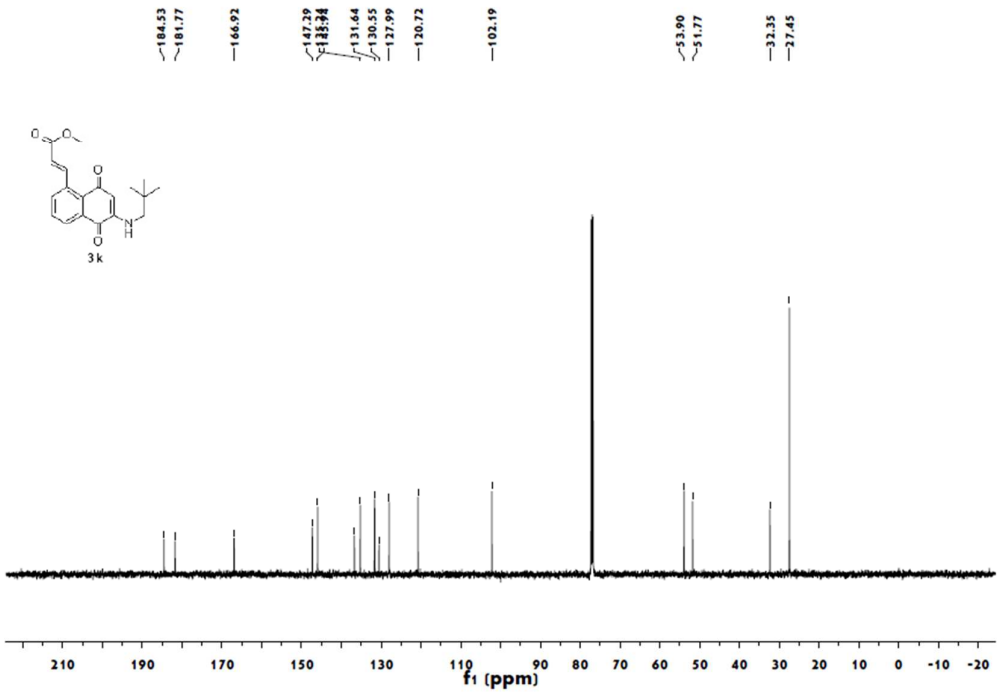
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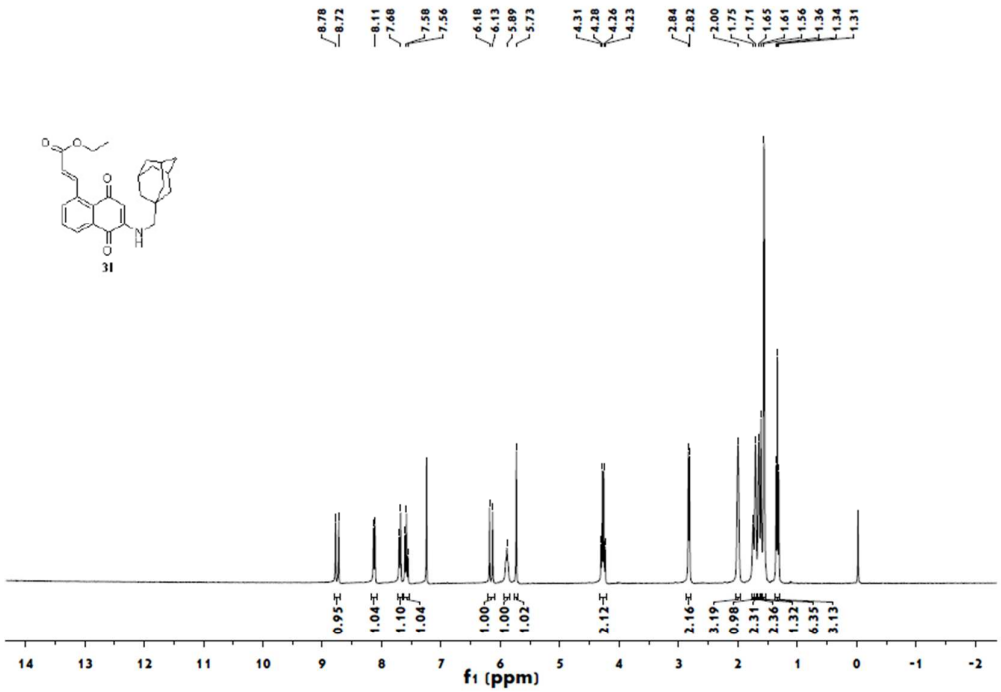
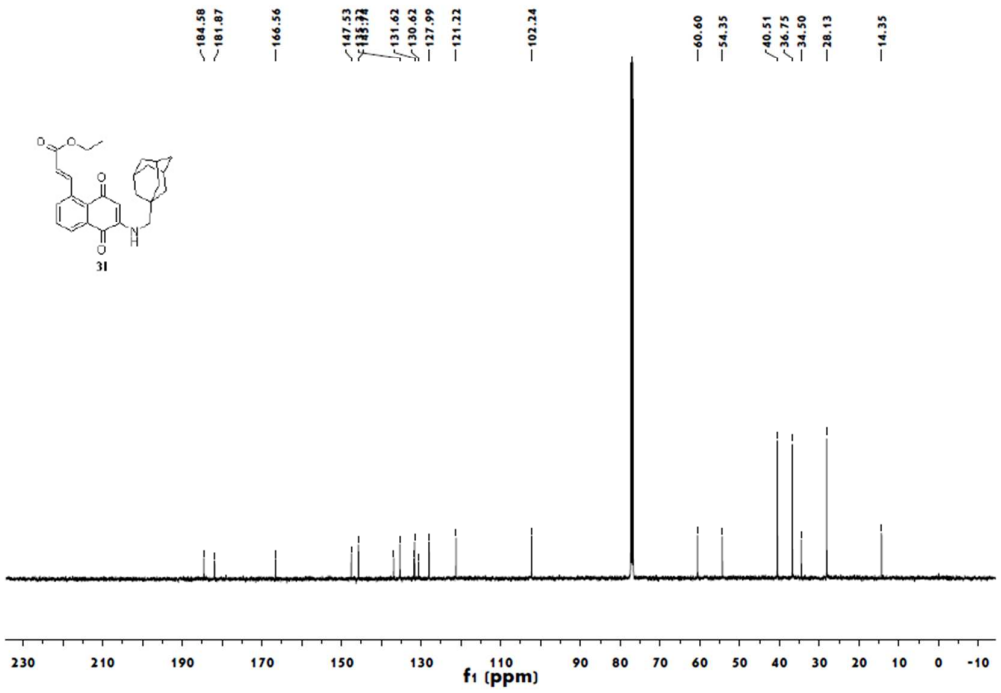
131.64
130.55
127.99
120.72
102.19
53.90
51.77
32.35
27.45
3k
f1 (ppm)


8.78
8.72
8.11
7.68
7.58
7.56
6.18
6.13
5.89
5.73
4.31
4.28
4.26
4.23
2.84
2.82
2.00
1.75
1.71
1.65
1.61
1.56
1.36
1.34
1.31
0.95
1.04
1.10
1.04
1.00
1.00
1.02
2.12
2.16
3.19
0.98
2.31
2.36
1.32
6.35
3.13
31
f1 (ppm)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147.53
131.62
130.62
127.99
121.22
102.24
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54.35
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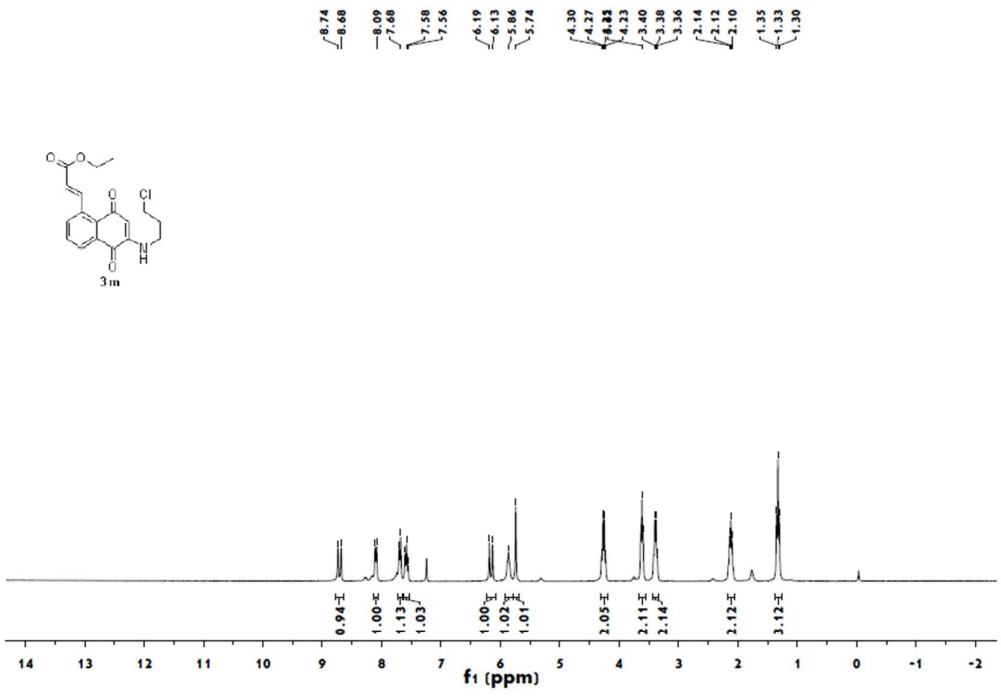
36.75
34.50
28.13
14.35
31
f1 (ppm)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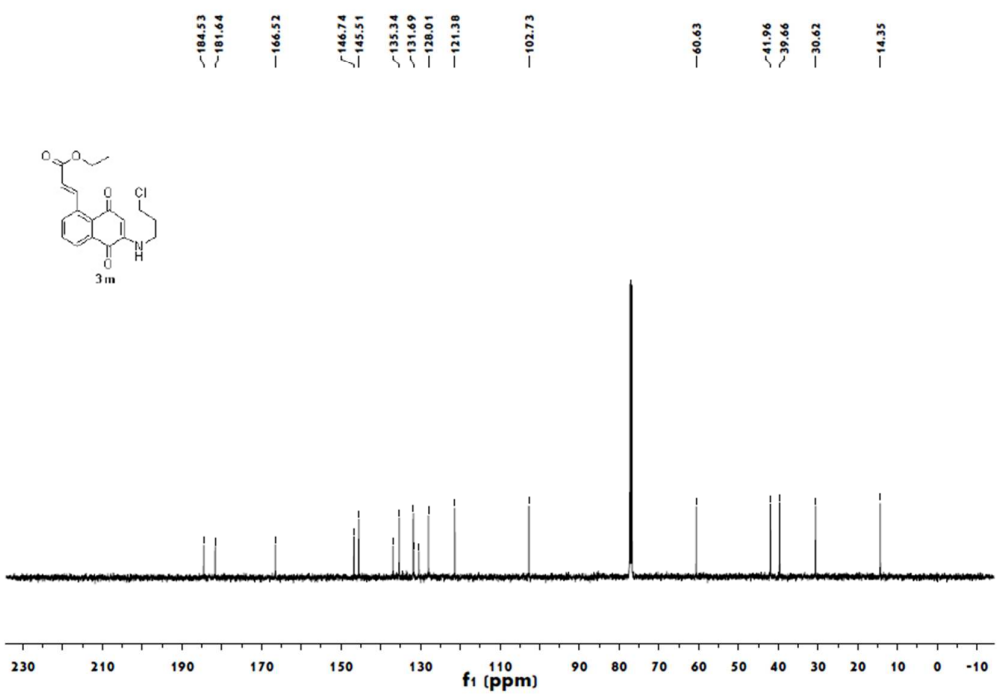
8.09
7.68
7.58
7.56
6.19
6.13
5.86
5.74
4.30
4.27
4.23
3.40
3.38
3.36
2.14
2.12
2.10
1.35
1.33
1.30
O
O
Cl
O
NH
O
3m
0.94
1.00
1.13
1.03
1.00
1.02
1.01
2.05
2.11
2.14
2.12
3.12
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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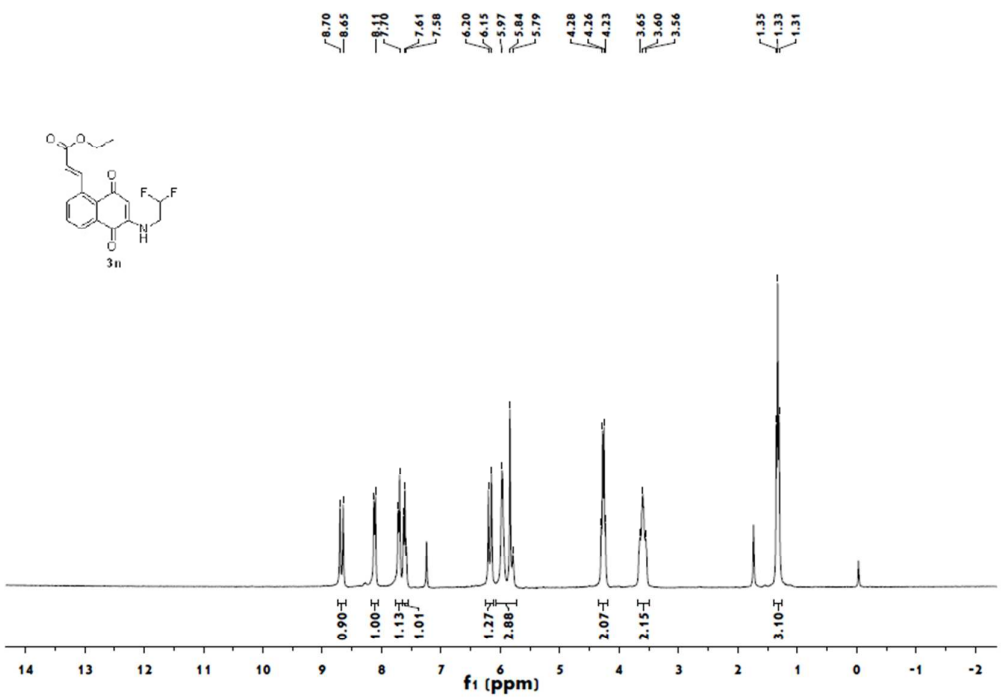
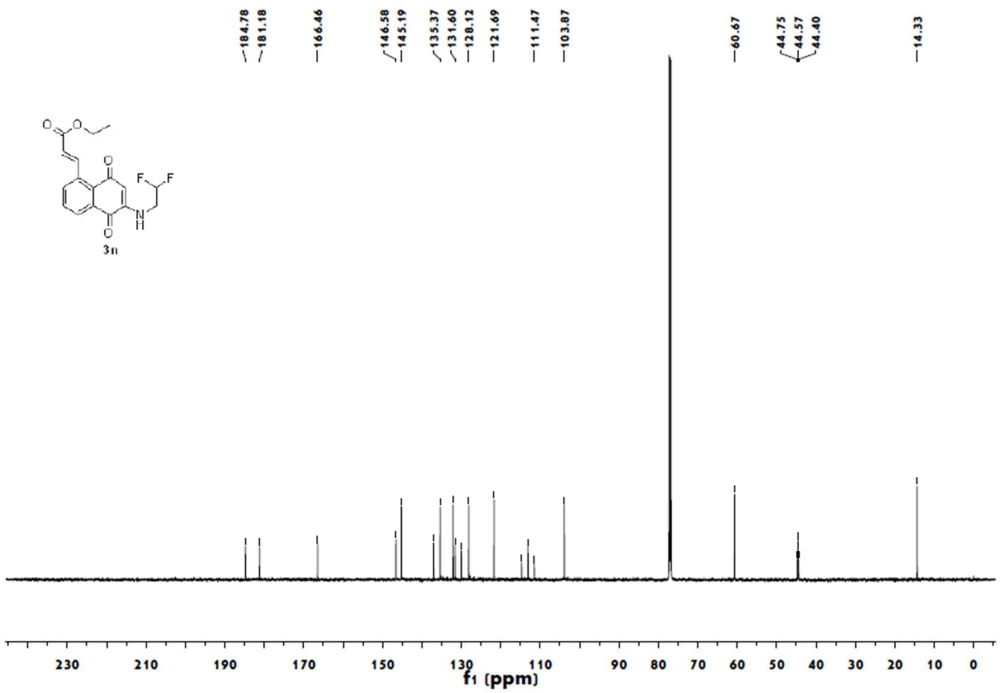
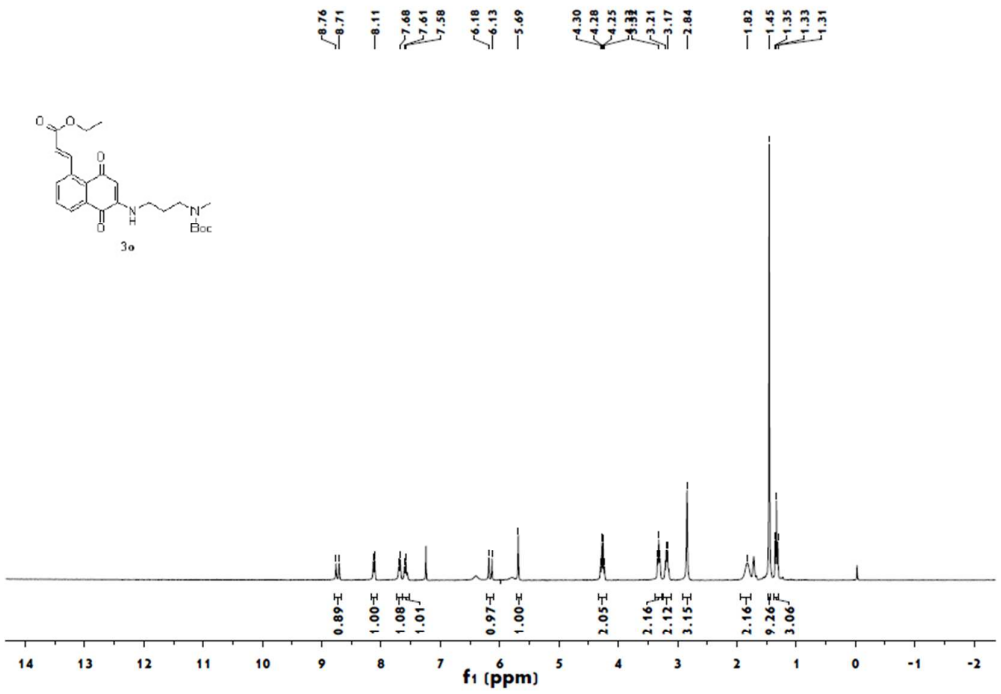
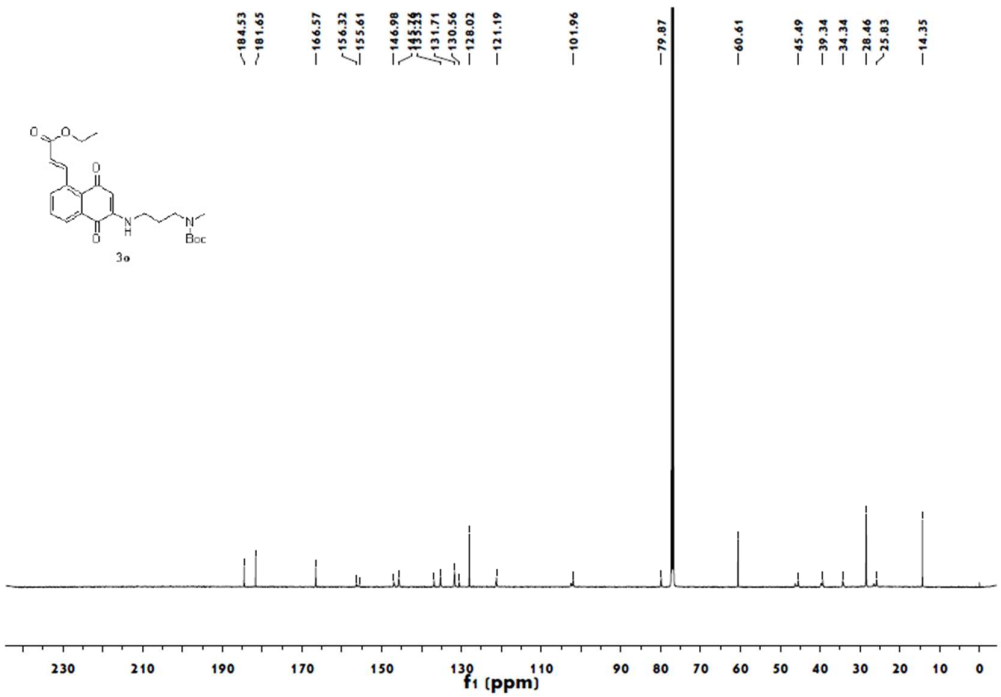
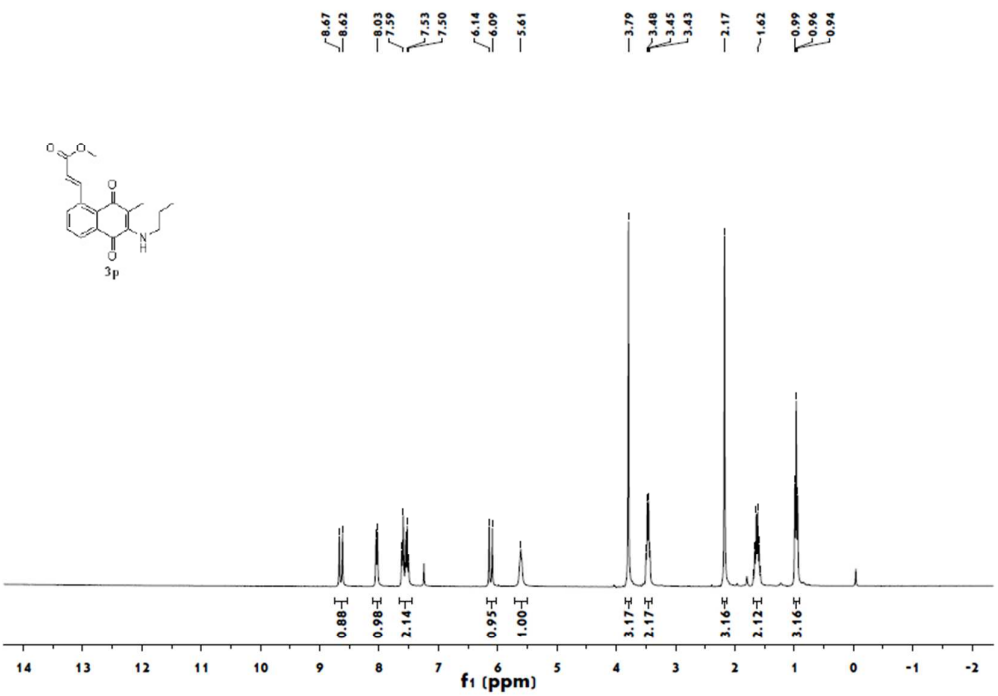
181.64
166.52
146.74
145.51
135.34
131.69
128.01
121.38
102.73
60.63
41.96
39.66
30.62
14.35
O
O
Cl
O
NH
O
3m
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

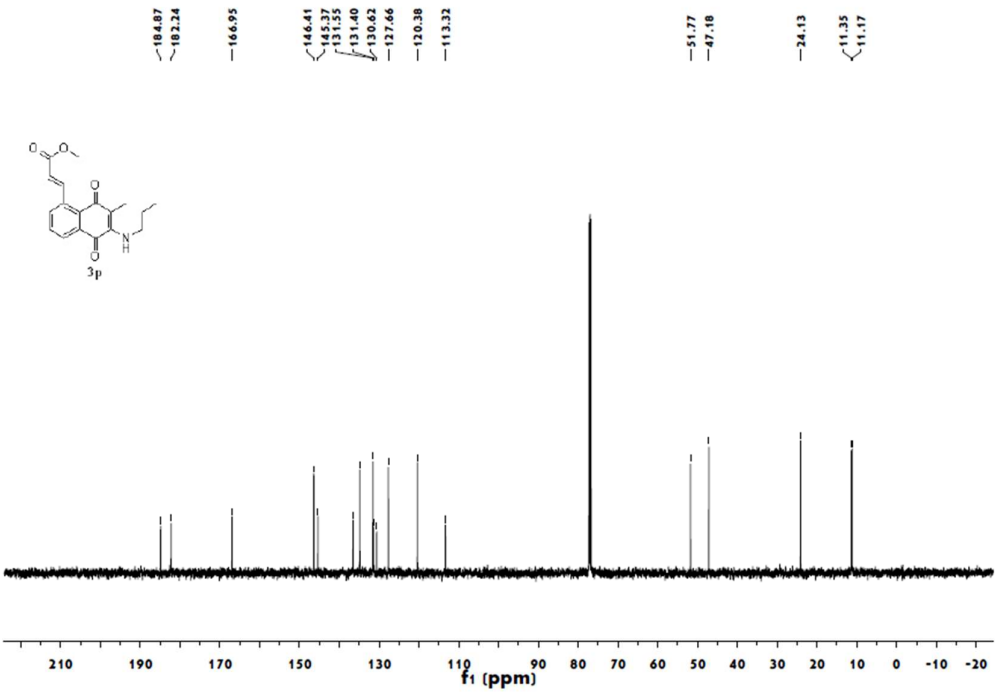

8.70
8.65
7.61
7.58
6.20
6.15
5.97
5.84
5.79
4.28
4.26
4.23
3.65
3.60
3.56
1.35
1.33
1.31
3m
0.90
1.00
1.13
1.01
1.27
2.88
2.07
2.15
3.10
f1 (ppm)

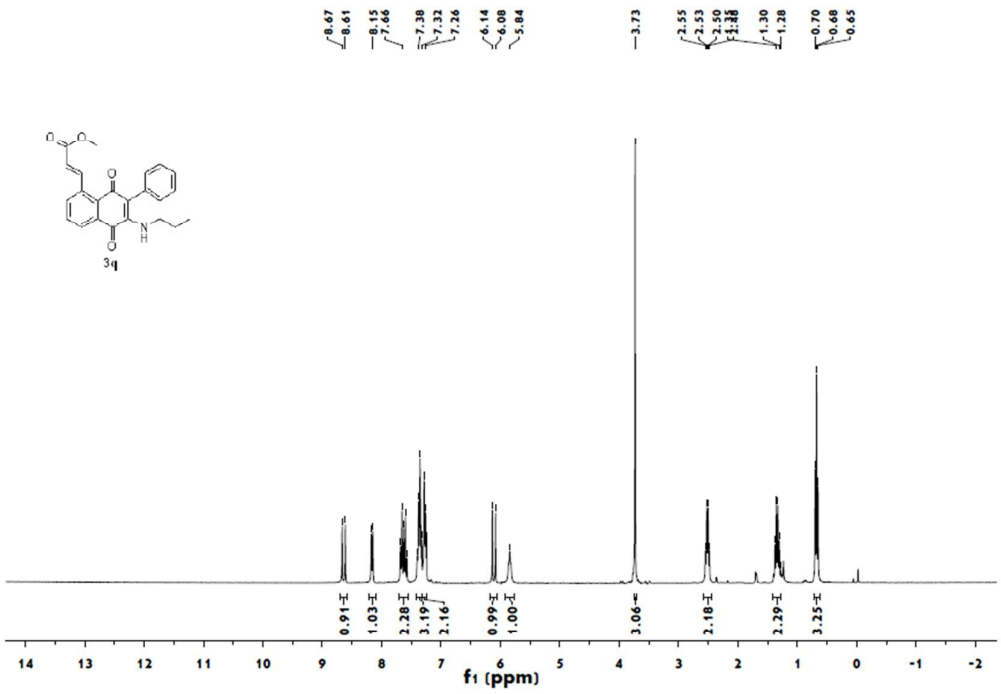

184.78
181.18
166.46
146.58
145.19
135.37
131.60
128.12
121.69
111.47
103.87
60.67
44.75
44.57
44.40
14.33
3m
f1 (ppm)

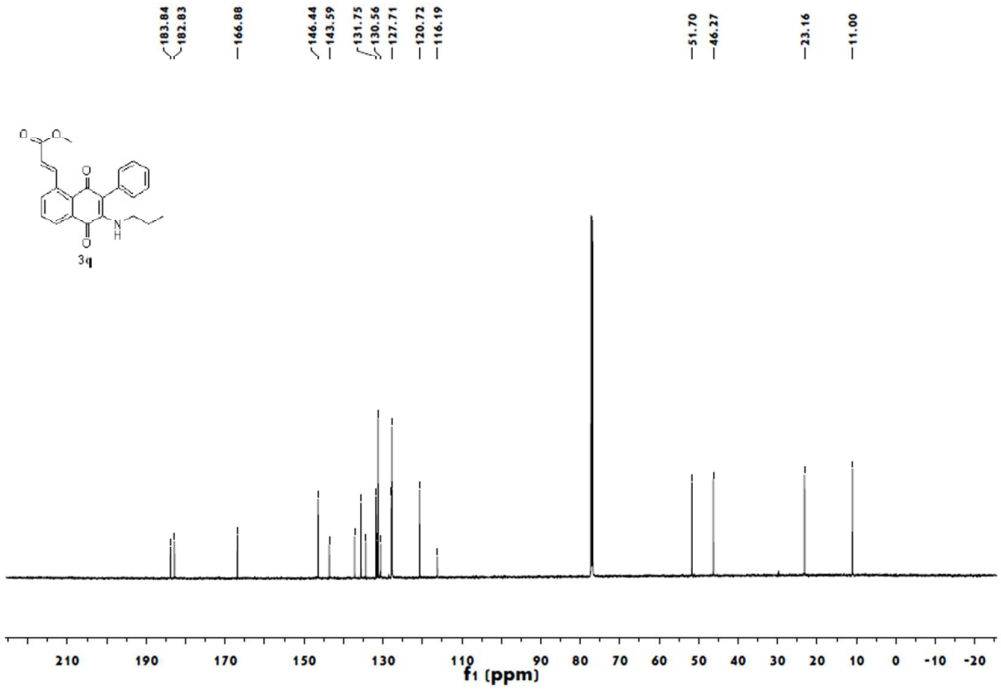

9.76
9.71
8.11
7.68
7.61
7.58
6.18
6.13
5.69
4.30
4.28
4.25
3.21
3.17
2.84
1.82
1.45
1.35
1.33
1.31
0.89
1.00
1.08
1.01
0.97
1.00
2.05
2.16
2.12
3.15
2.16
9.26
3.06
f1 (ppm)
3o

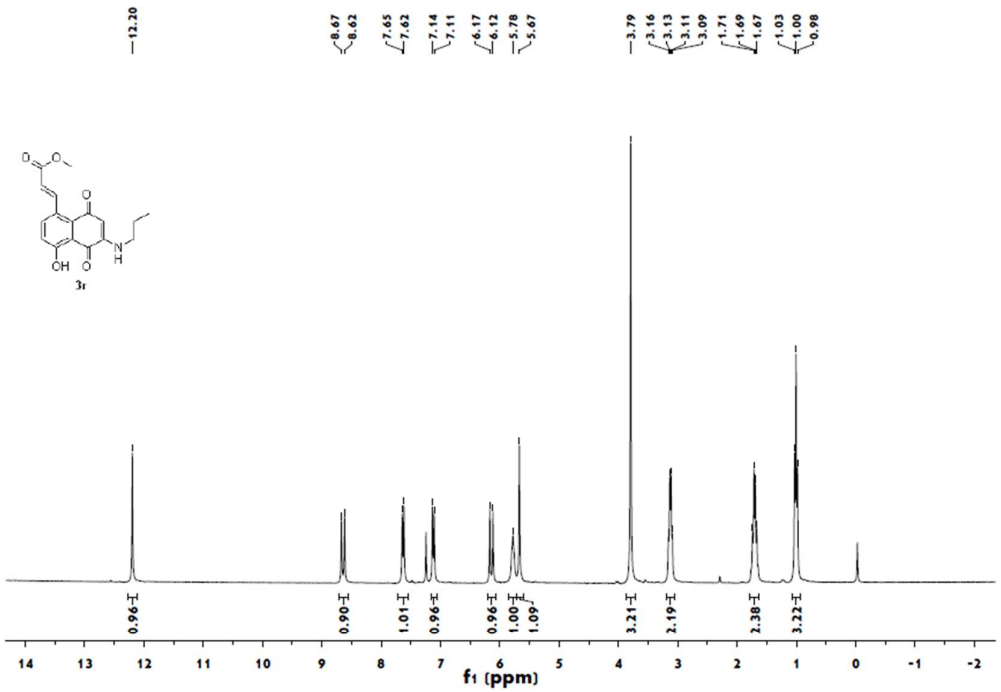

184.53
181.65
166.57
156.32
155.61
146.98
135.26
131.71
130.56
128.02
121.19
101.96
79.87
60.61
45.49
39.34
34.34
28.46
25.83
14.35
f1 (ppm)
3o

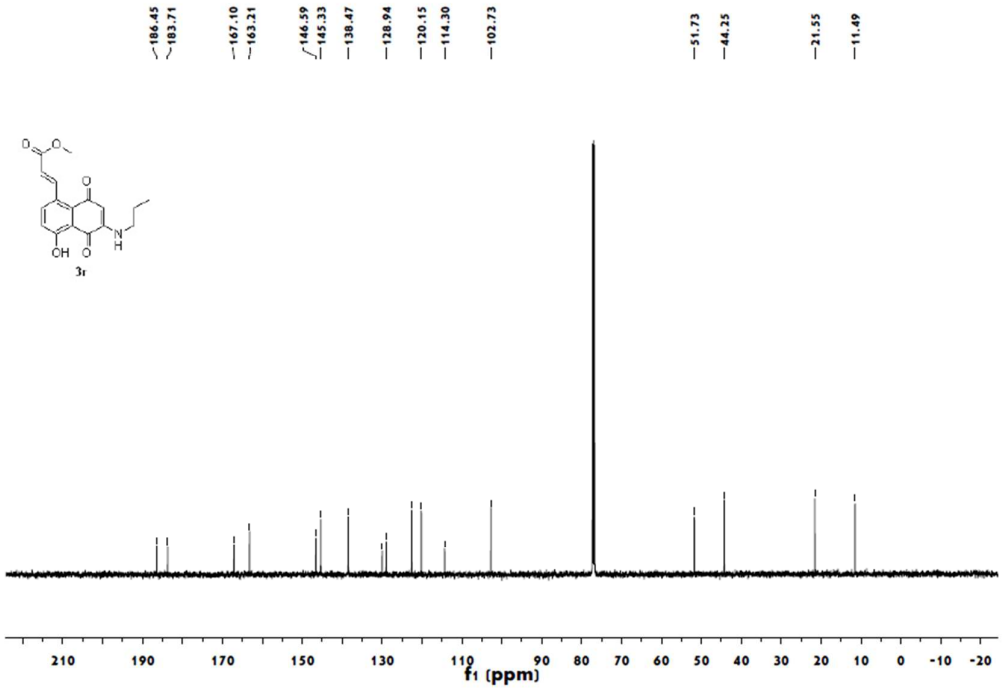

8.67
8.62
8.03
7.59
7.53
7.50
6.14
6.09
5.61
3.79
3.48
3.45
3.43
2.17
1.62
0.99
0.96
0.94
3p
0.88
0.98
2.14
0.95
1.00
3.17
2.17
3.16
2.12
3.16
f1 (ppm)

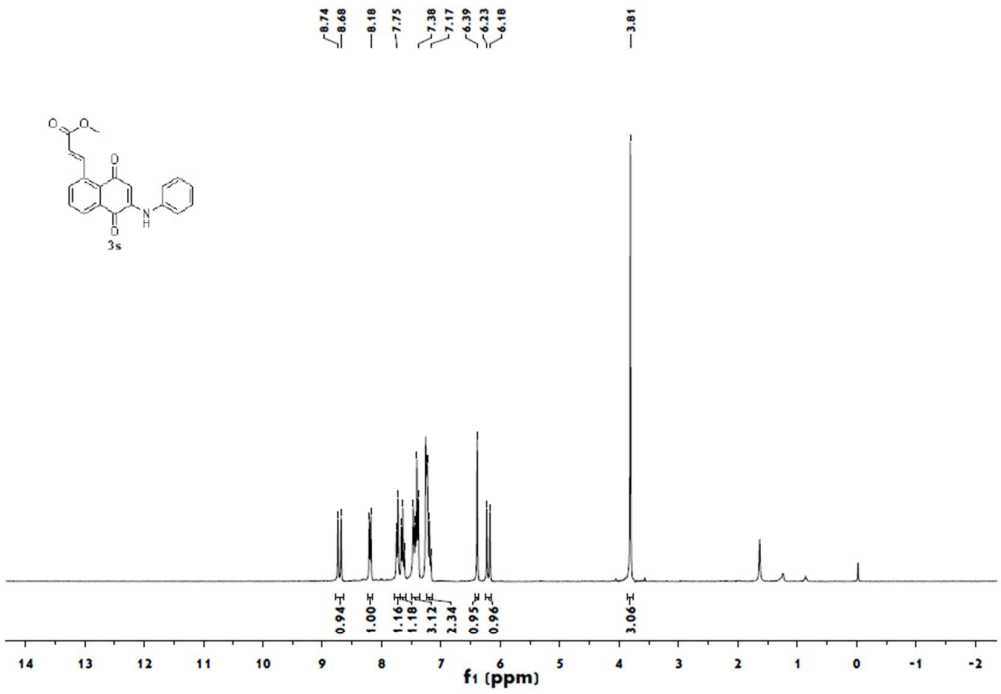

184.87
182.24
166.95
146.41
145.37
131.55
131.40
130.62
127.66
120.38
113.32
51.77
47.18
24.13
11.35
11.17
3p
f1 (ppm)

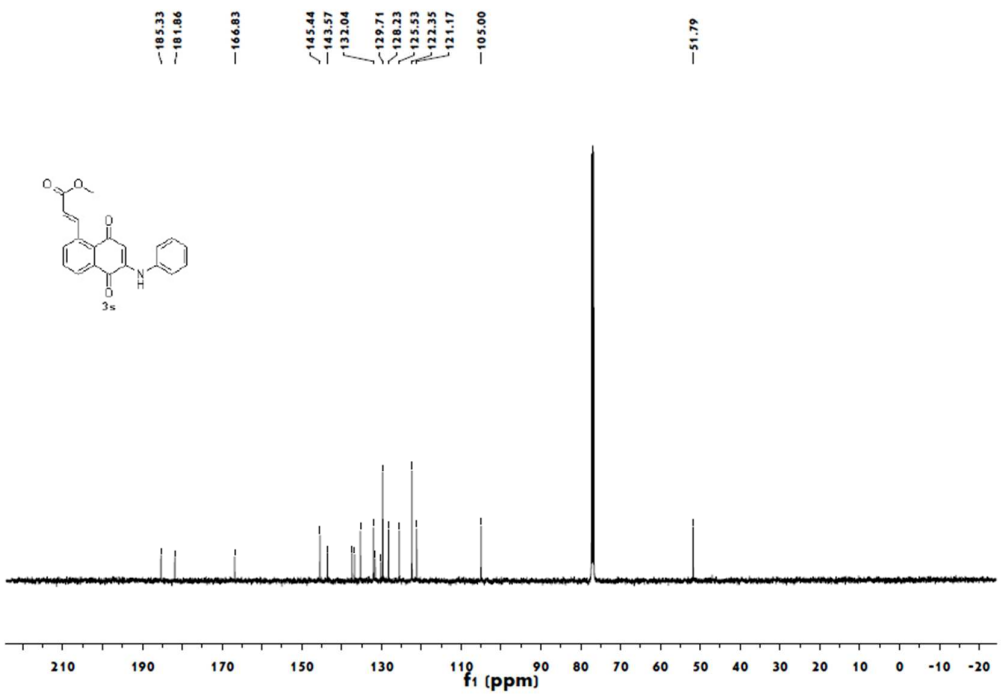

8.67
8.61
8.15
7.66
7.38
7.32
7.26
6.14
6.08
5.84
3.73
2.55
2.53
2.50
1.30
1.28
0.70
0.68
0.65
3q
0.91
1.03
2.28
3.19
2.16
0.99
1.00
3.06
2.18
2.29
3.25
f1 (ppm)

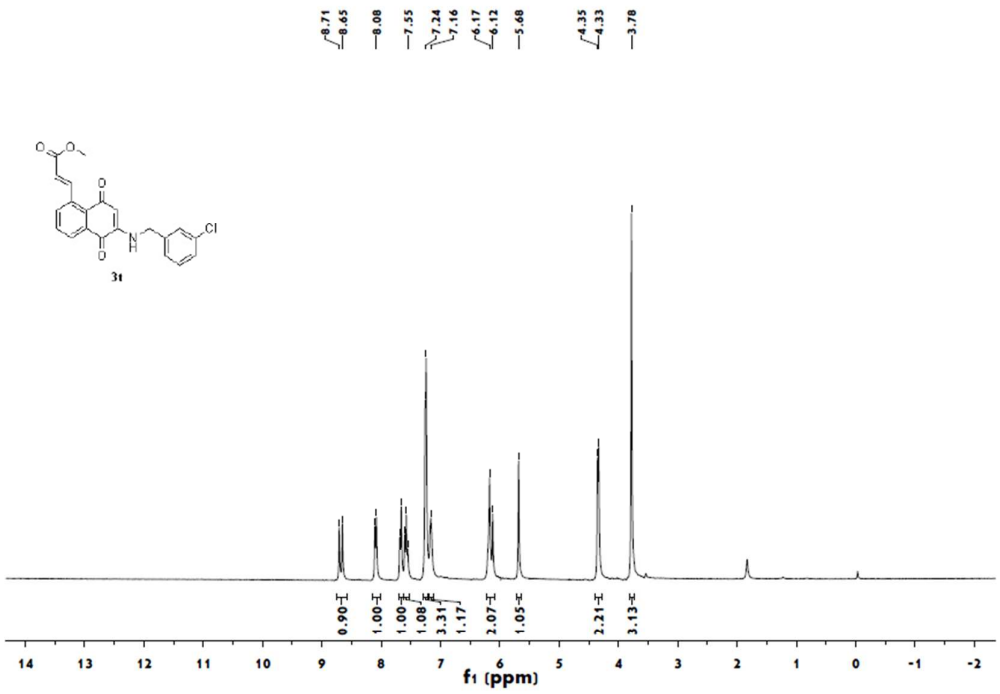

183.84
182.83
166.88
146.44
143.59
131.75
130.56
127.71
120.72
116.19
51.70
46.27
23.16
11.00
3q
f1 (ppm)

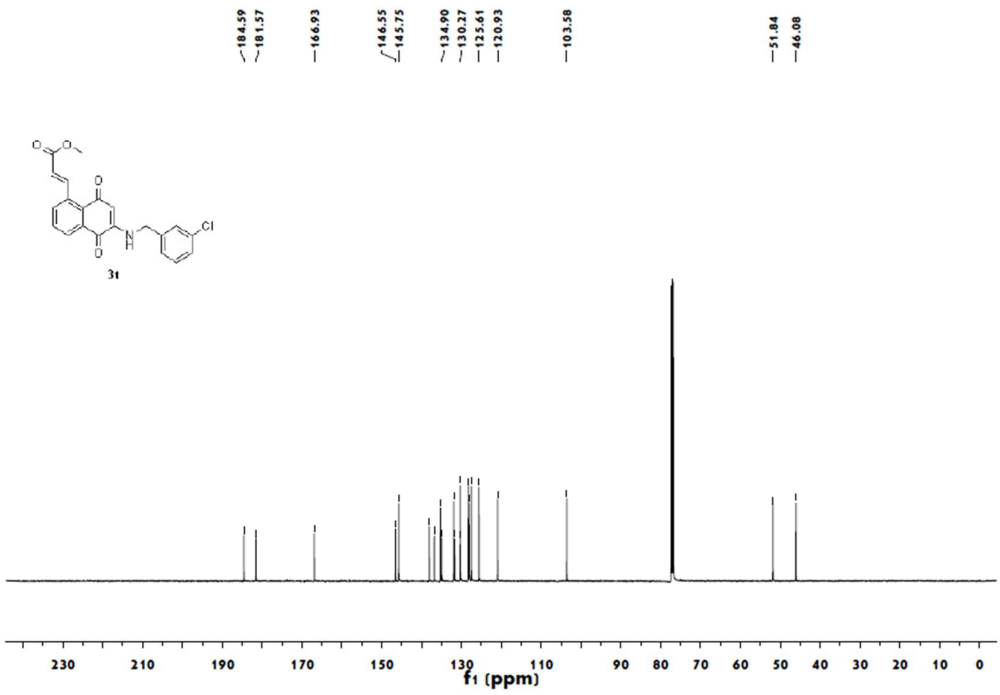

12.20
8.67
8.62
7.65
7.62
7.14
7.11
6.17
6.12
5.78
5.67
3.79
3.16
3.13
3.11
3.09
1.71
1.69
1.67
1.03
1.00
0.98
3r
0.96
0.90
1.01
0.96
0.96
1.00
1.09
3.21
2.19
2.38
3.22
f1 (ppm)


186.45
183.71
167.10
163.21
146.59
145.33
138.47
128.94
120.15
114.30
102.73
51.73
44.25
21.55
11.49
3r
f1 (ppm)


8.74
8.68
8.18
7.75
7.38
7.17
6.39
6.33
6.18
3.81
3s
0.94
1.00
1.16
1.18
3.12
2.34
0.95
0.96
3.06
f1 (ppm)


185.33
181.86
166.83
145.44
143.57
132.04
129.71
128.23
125.53
122.35
121.17
105.00
51.79
3s
f1 (ppm)


9.71
9.65
8.08
7.55
7.24
7.16
6.17
6.12
5.68
4.35
4.33
3.78
3t
0.90
1.00
1.00
1.08
3.31
1.17
2.07
1.05
2.21
3.13
f1 (ppm)


184.59
181.57
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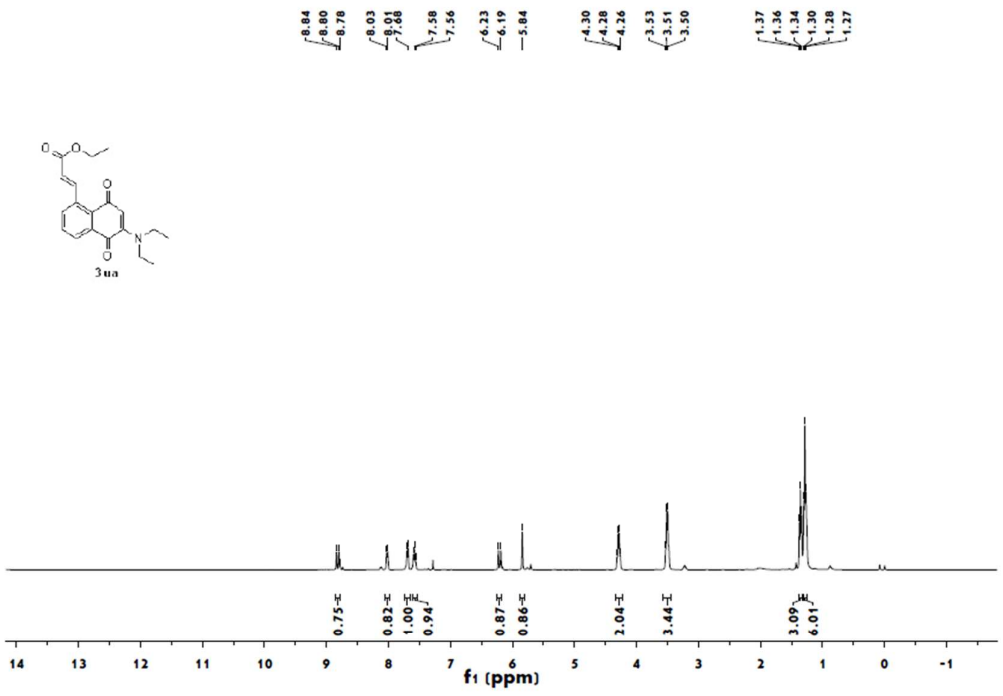
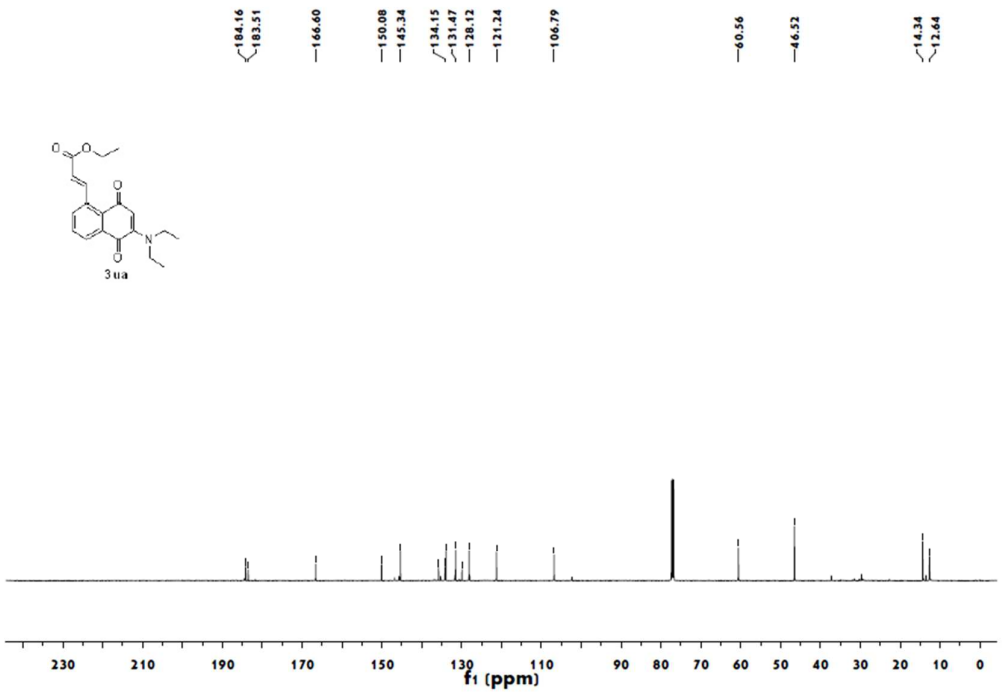
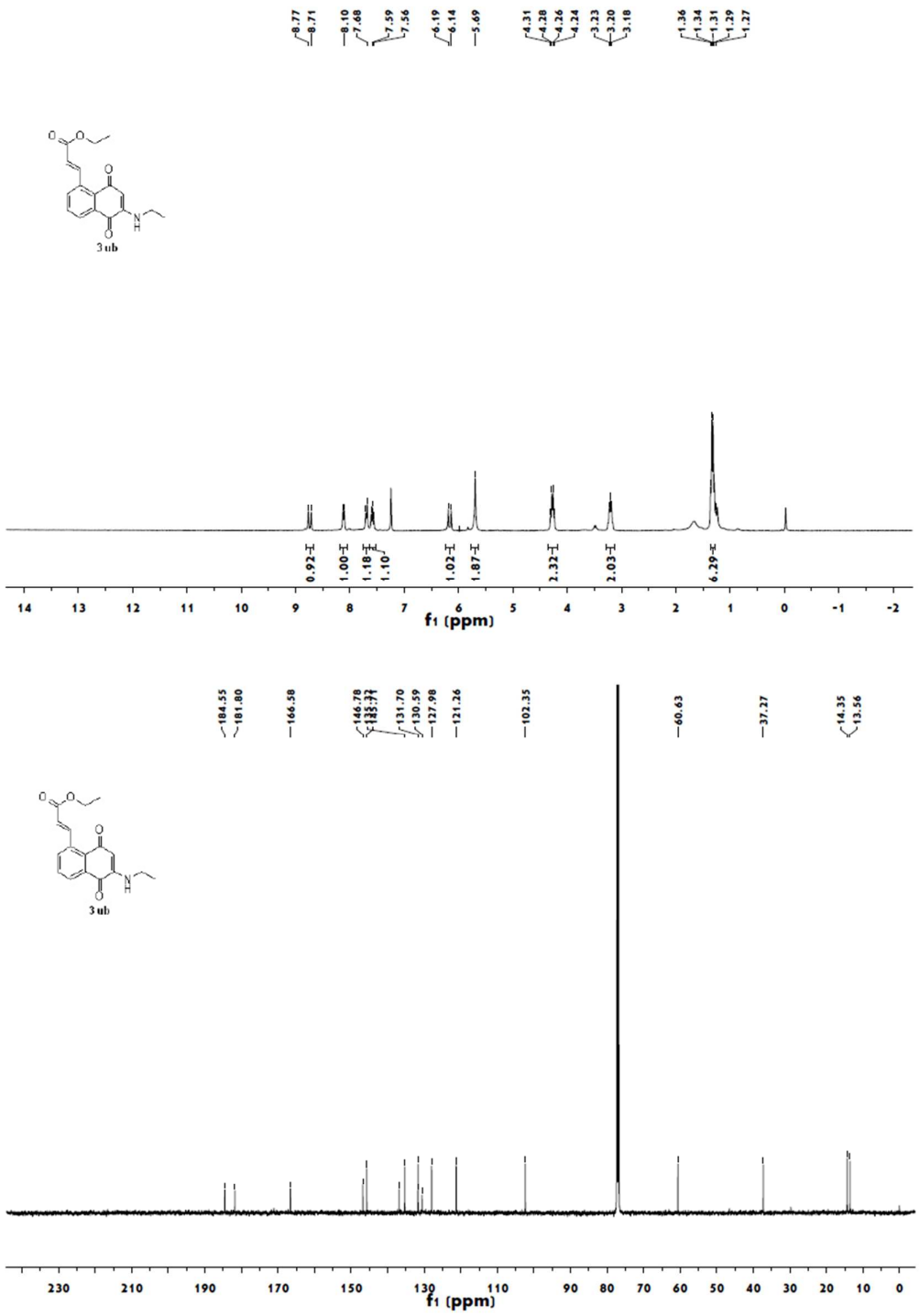
146.55
145.75
134.90
130.27
125.61
120.93
103.58
51.84
46.08
3t
f1 (ppm)

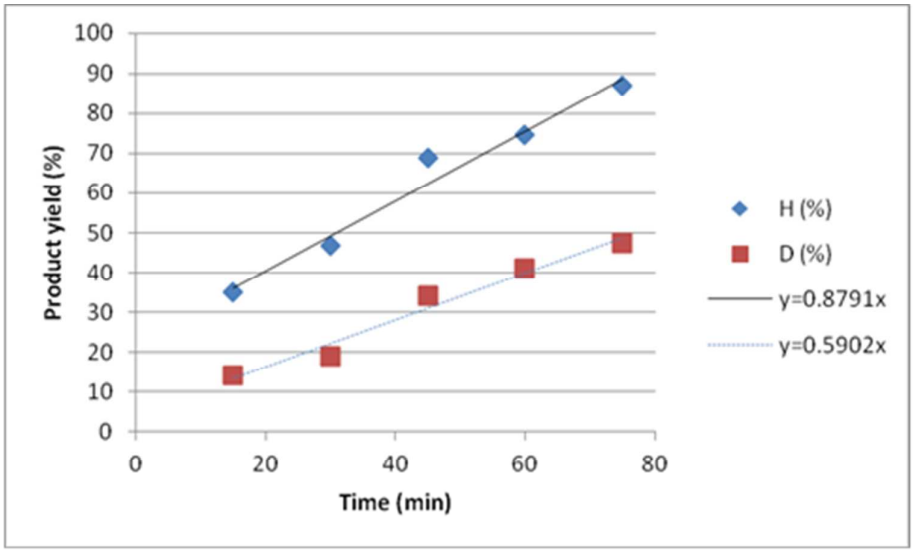

8.84
8.80
8.78
8.03
8.01
8.00
7.58
7.56
6.23
6.19
5.84
4.30
4.28
4.26
3.53
3.51
3.50
1.37
1.36
1.34
1.30
1.28
1.27
3ua
0.75
0.82
1.00
0.94
0.87
0.86
2.04
3.44
3.09
6.01
f1 (ppm)


184.16
183.51
166.60
150.08
145.34
134.15
131.47
128.12
121.24
106.79
60.56
46.52
14.34
12.64
3ua
f1 (ppm)


8.77
8.71
8.10
7.68
7.59
7.56
6.19
6.14
5.69
4.31
4.28
4.26
4.24
3.23
3.20
3.18
1.36
1.34
1.31
1.29
1.27
3ub
0.92
1.00
1.18
1.10
1.02
1.87
2.32
2.03
6.29
f1 (ppm)
184.55
181.80
166.58
146.78
131.70
130.59
127.98
121.26
102.35
60.63
37.27
14.35
13.56
3ub
f1 (ppm)

3. Kinetic isotope effect experiments.

A solution of substrate **1p** or [D_5]-**1p** (0.2 mmol), alkene **2a** (0.4 mmol), [$RhCp^*Cl_2$]$_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), and $Cu(OAc)_2 \cdot H_2O$ (20 mol %) in DCE (1 mL) was stirred in sealed tube at 120 ^oC. A portion of the crude solution (0.1 mL) was taken out every 15 min, concentrated in vacuum, and then subjected to ^{1}H-NMR measurement with 1,2-dibromomethane as the internal standard.



Independent Initial Rate Comparison K_H/K_D for 3p and [D_5]-3p