Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

Sulfonation of Carbonized Xylan-type Hemicellulose: A Renewable and Effective Biomass-based Biocatalyst for the Synthesis of O- and N-Heterocycles

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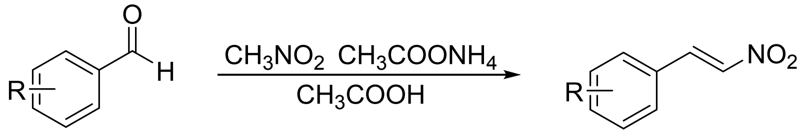
Typical procedure for preparation of nitroolefins[1-3]



A mixture of benzaldehyde (10.0 mmol), nitromethane (12.0 mmol), ammonium acetate (6.0 mmol) and glacial acetic acid (7 mL) were successively charged into a 50 mL pressure flask with a magnetic stirring bar. Then the system was refluxed for 2 h. After the reaction was completed, the reaction mixture was poured into ice-water, and the formed crude product was collected by filtration. Finally, the target product was obtained by column chromatography on silica gel using ethyl acetate/hexane as the eluent. Other nitroolefins were prepared by the same procedure.

References:

(1) X. J. Quan, Z. H. Ren, Y. Y. Wang and Z. H. Guan, *Org. Lett.*, 2014, **16**, 5728.

(2) M. Ganesh and I. N. N. Namboothiri, *Tetrahedron*, 2007, **63**, 11973.

(3) M. C. Yan, Y. J. Jang and C. F. Yao, *Tetrahedron Lett.*, 2001, **42**, 2717.

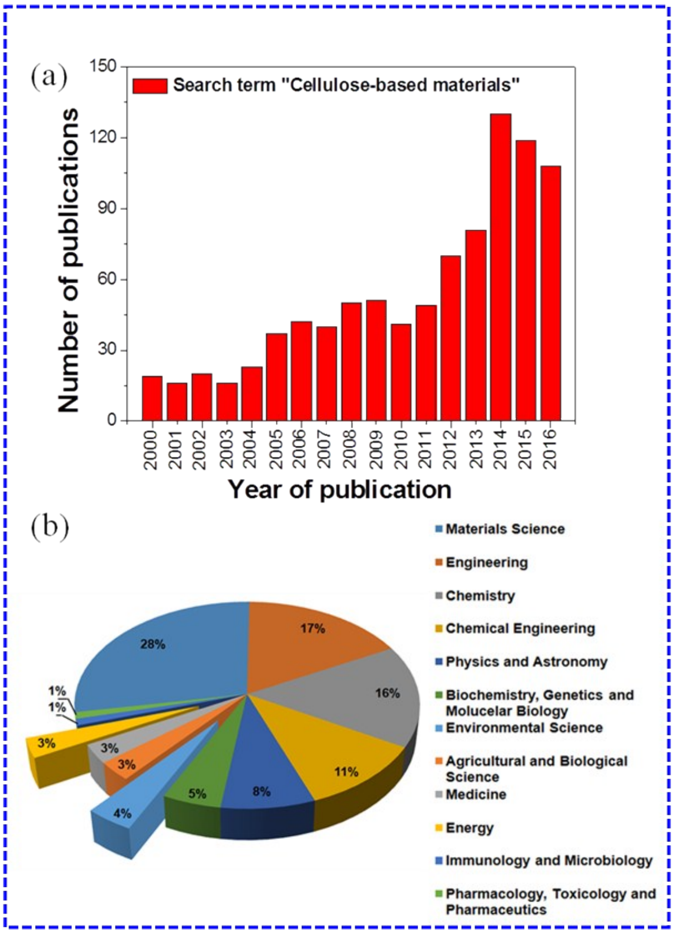


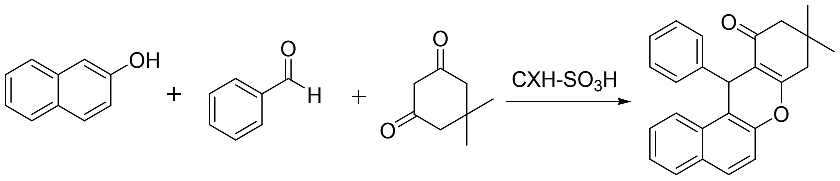
Fig. S1. (a) The annual number of publications on cellulose-based materials and (b) the relevant applications of cellulose-based materials in various fields of research. Reproduced from Ref. (Mohamed et al., 2017 and Gutiérrez et al., 2017)

Table S1 Acid density of sulfonation of carbonized xylan-type hemicellulose and three type lignin

Sample	S content[a] (wt%)	SO_3H density[b] (mmol/g)
CAAL-SO_3H[c]	2.41	0.75
CAL-SO_3H[d]	3.12	0.97
CIL-SO_3H[e]	2.66	0.82
CXH-SO_3H	3.55	1.10

[a]Determined by EA. [b]Calculated from the S content. [c]Sulfonation of carbonized acetic acid lignin. [d]Sulfonation of carbonized alkali lignin. [e]Sulfonation of carbonized industrial lignin.

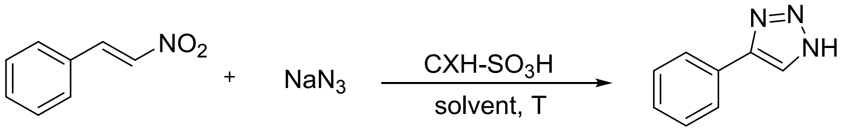
Table S2 Effect of CXH-SO_3H biocatalyst prepared by different raw materials on the one-pot condensation of benzaldehyde with 2-naphthol and dimedone [a]



Entry	Catalyst	Temperature (°C)	Time (h)	Yield (%)[e]
1	CXH-SO_3H-B[b]	90	2	88
2	CXH-SO_3H-E[c]	90	2	88
3	CXH-SO_3H[d]	90	2	88

[a] Typical reaction conditions: benzaldehyde (0.5 mmol), 2-naphthol (0.5 mmol), dimedone (0.6 mmol), 90 °C, and 2 h. [b] The raw materials for the preparetion of CXH-SO_3H-B catalyst is obtained from bamboo. [c] The raw materials for the preparetion of CXH-SO_3H-E catalyst is obtained from eucalyptus. [d] The raw materials for the preparetion of CXH-SO_3H catalyst is obtained from by-product of pulping and papermaking industry. [e] Isolated yield.

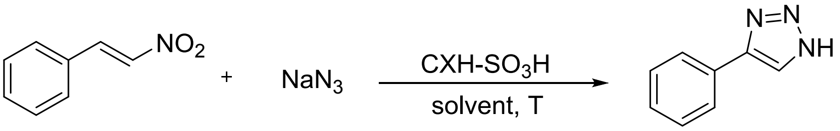
Table S3 Effects of solvent and the dosage of CXH-SO_3H on the synthesis 4-aryl-*NH*-1,2,3-triazoles [a]



Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	1.08	DMSO	60	4	72
2	2.16	DMSO	60	4	89
3	3.24	DMSO	60	4	92
4	4.32	DMSO	60	4	92
5	5.40	DMSO	60	4	94
6	3.24	THF	60	4	16
7	3.24	Toluene	60	4	11
8	3.24	DMF	60	4	83
9	3.24	Ethanol	60	4	34
10	3.24	H_2O	60	4	9

[a] Typical reaction conditions: nitroolefin (0.3 mmol), NaN_3 (0.45 mmol).
[b] Isolated yield.

Table S4 Effects of reaction temperature and reaction time of CXH-SO_3H on the synthesis 4-aryl-*NH*-1,2,3-triazoles [a]

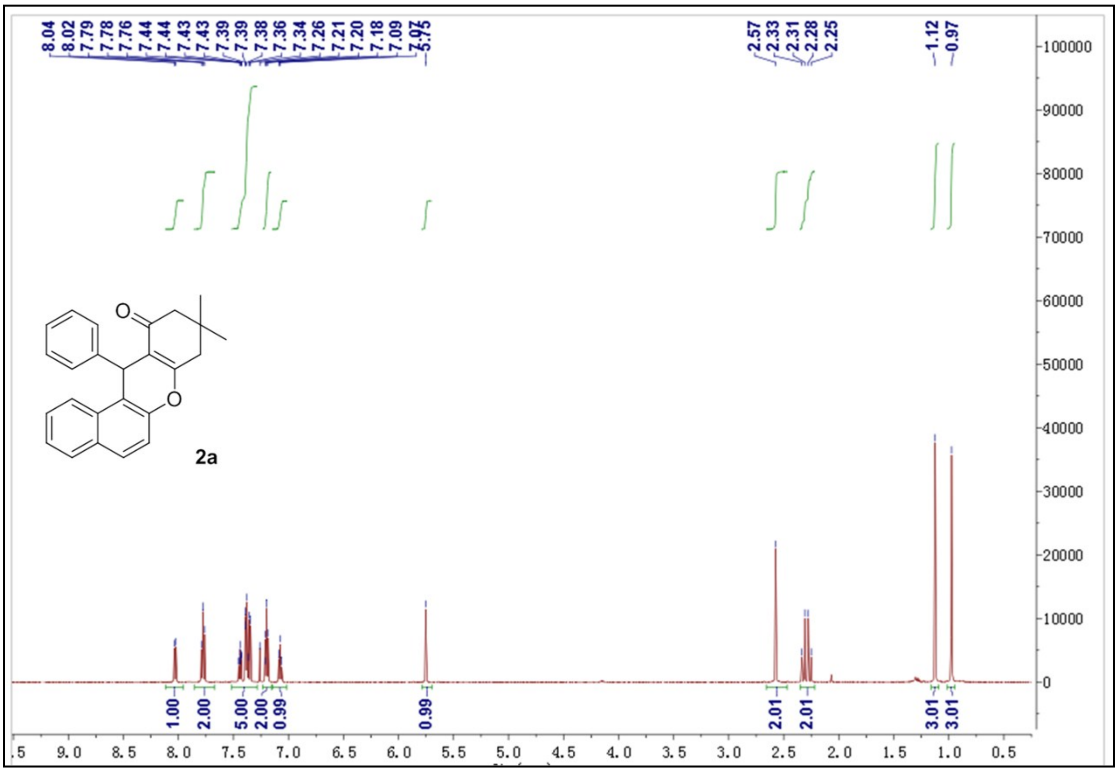


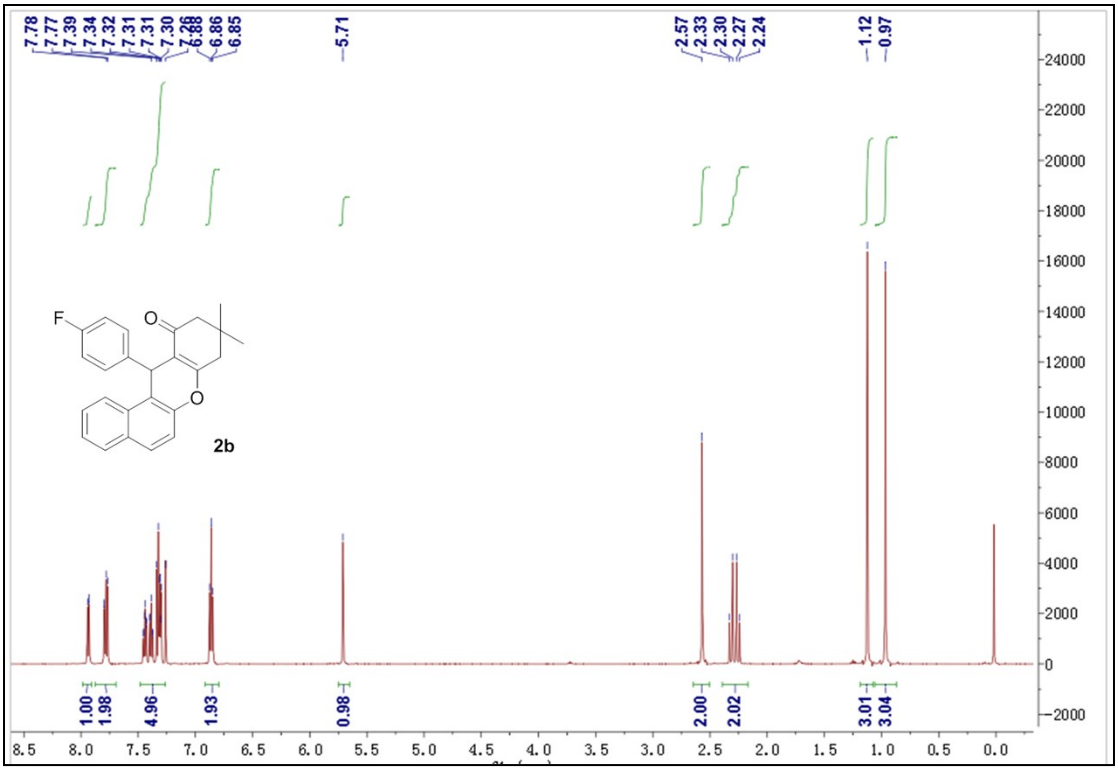
Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	3.24	DMSO	60	2	67
2	3.24	DMSO	60	3	83
3	3.24	DMSO	60	4	92
4	3.24	DMSO	60	5	93
5	3.24	DMSO	60	6	95
6	3.24	DMSO	40	4	82
7	3.24	DMSO	50	4	86
8	3.24	DMSO	80	4	90

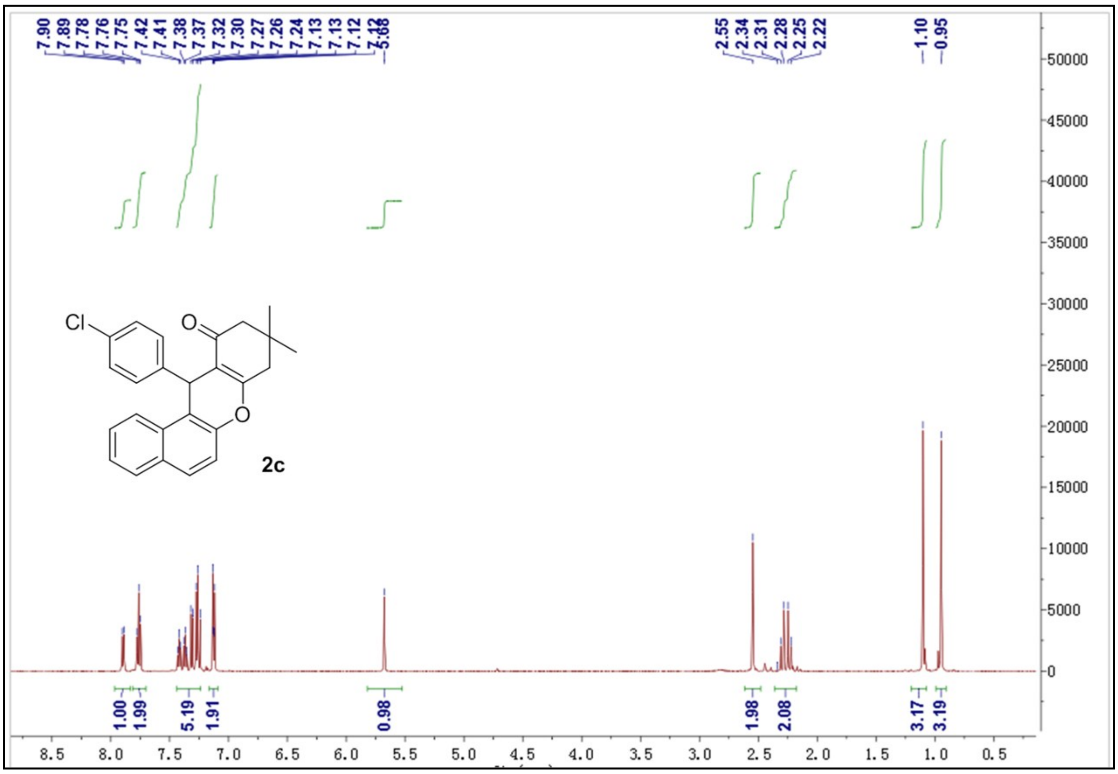
[a] Typical reaction conditions: nitroolefin (0.3 mmol), NaN_3 (0.45 mmol).

[b] Isolated yield.

^{1}H NMR for all compounds



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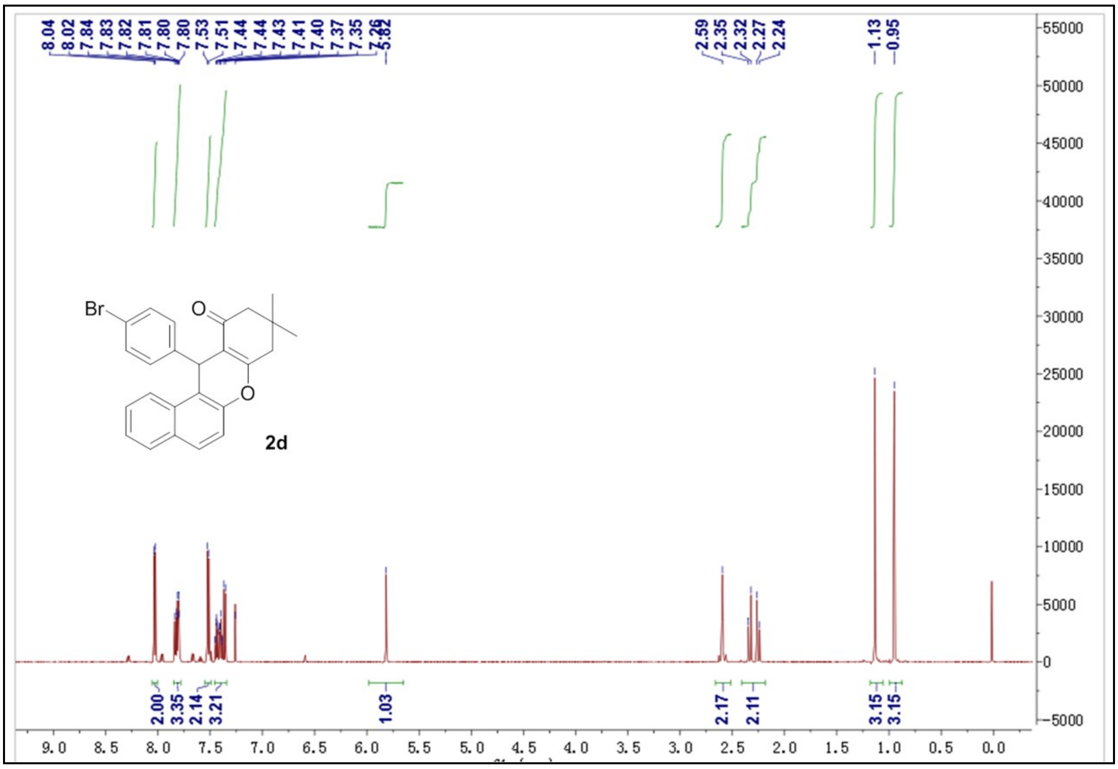
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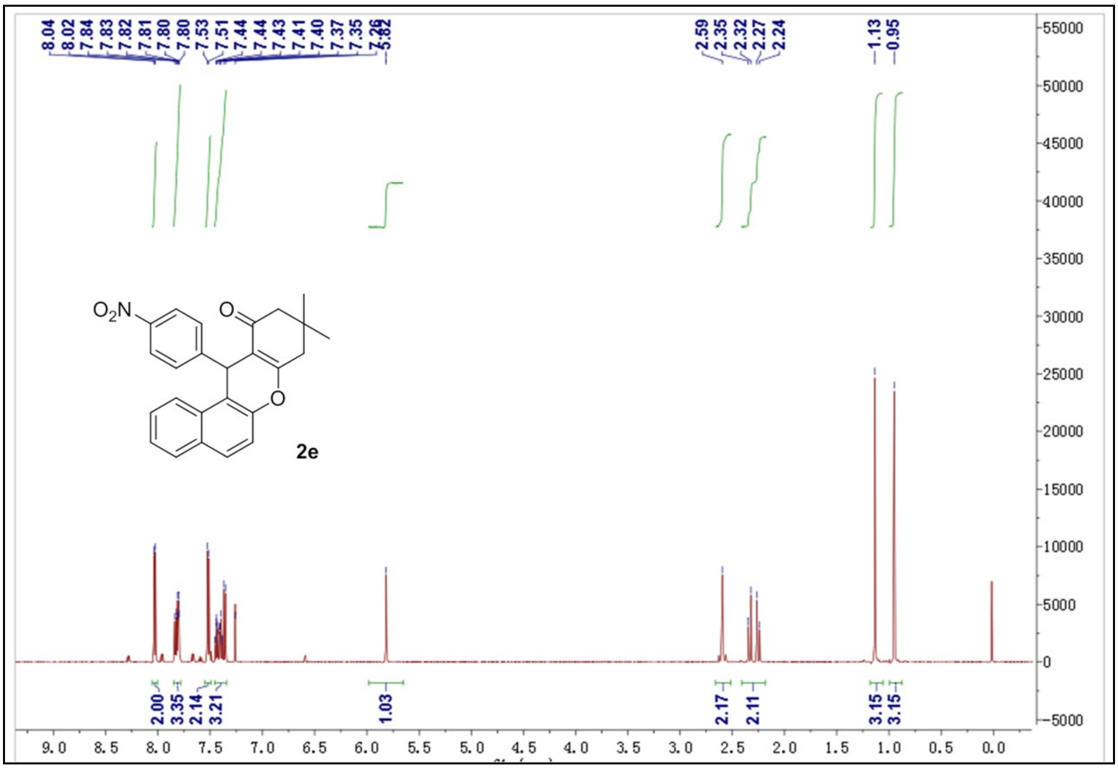
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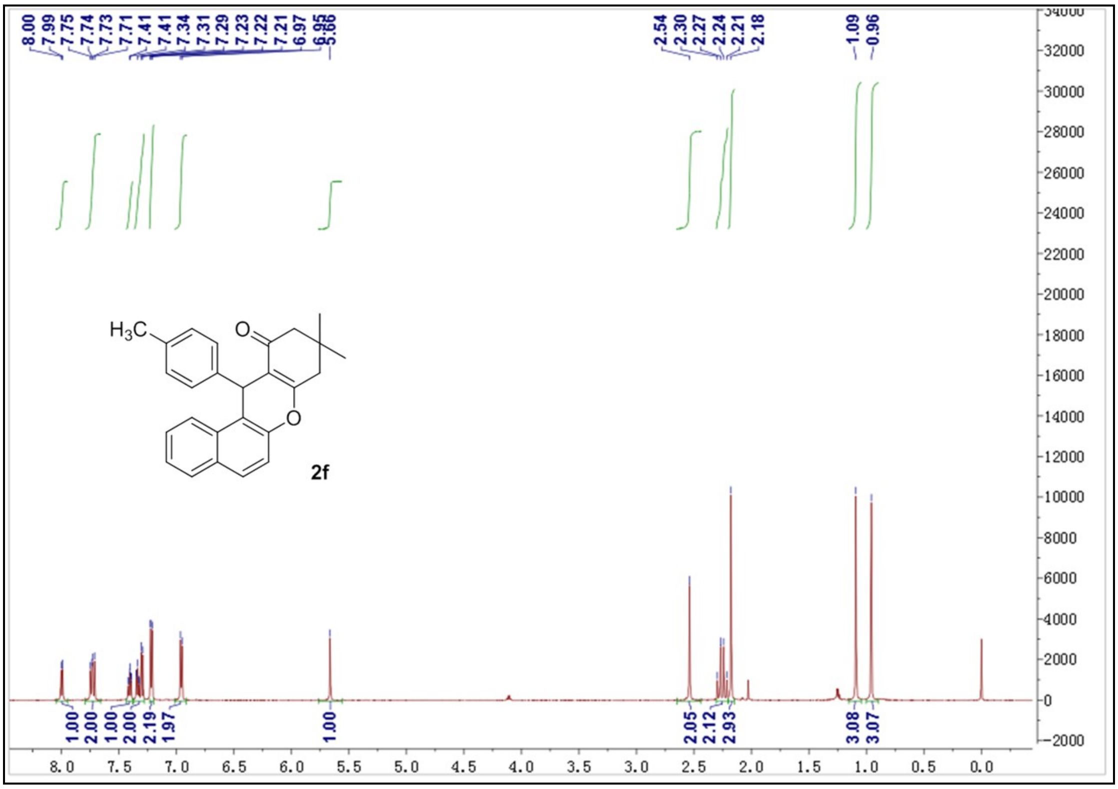
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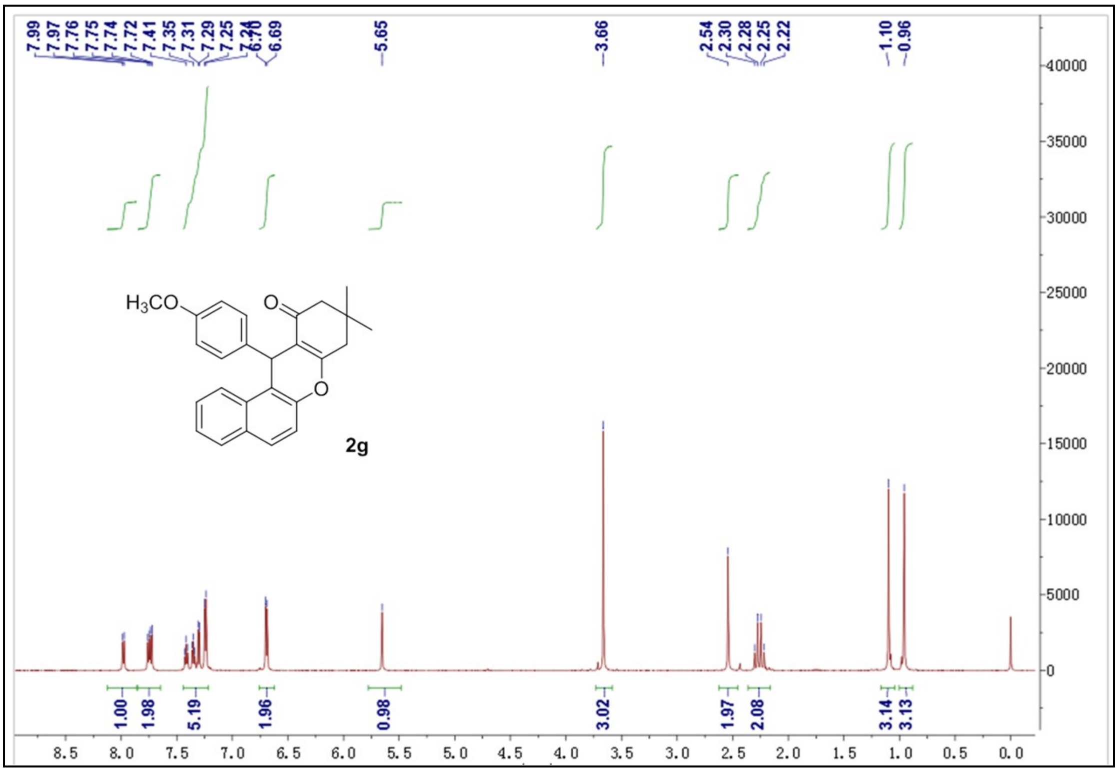

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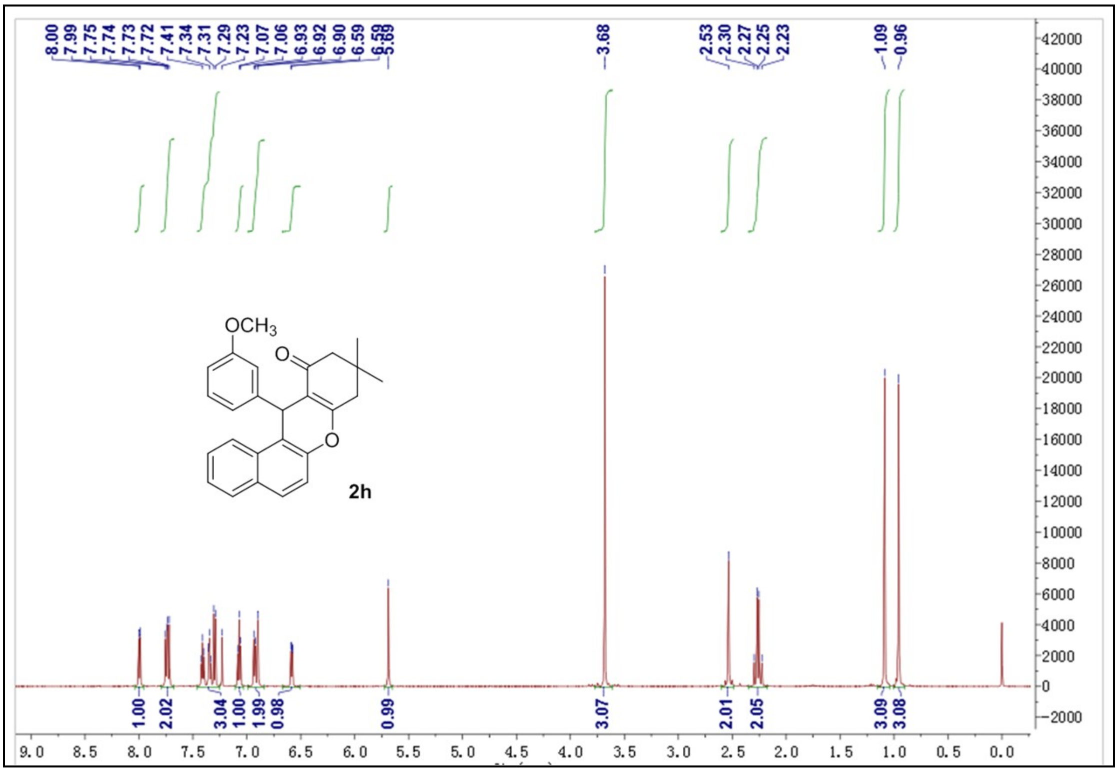

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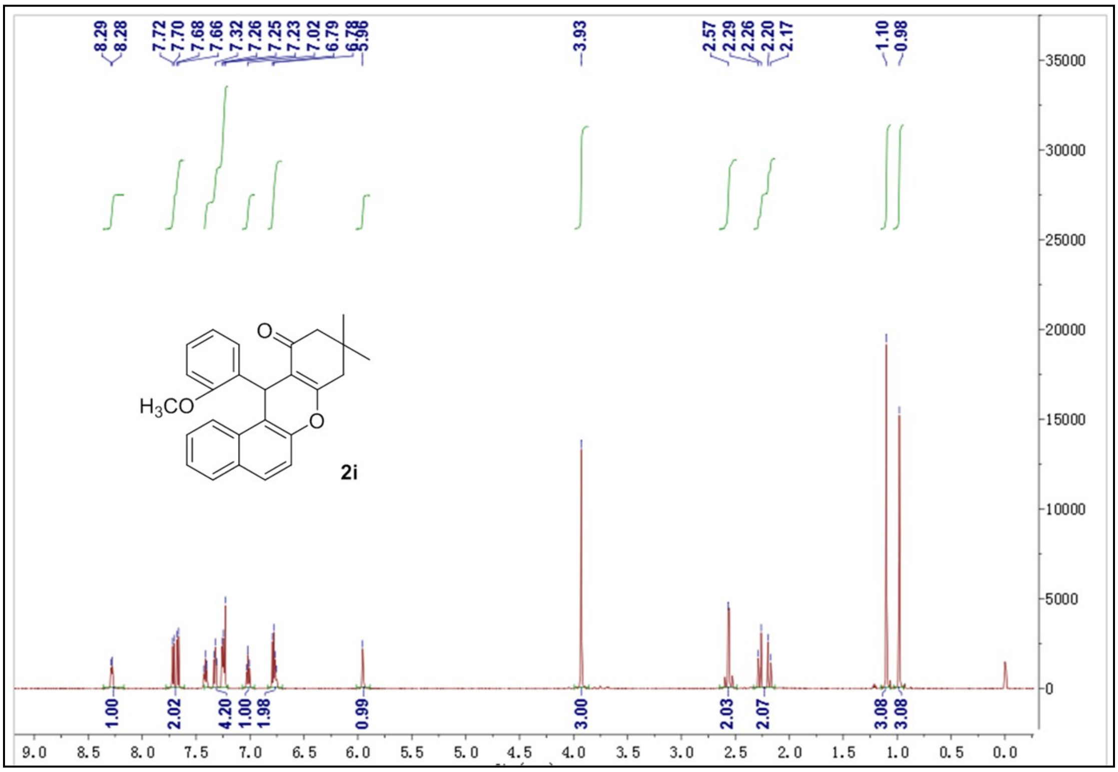
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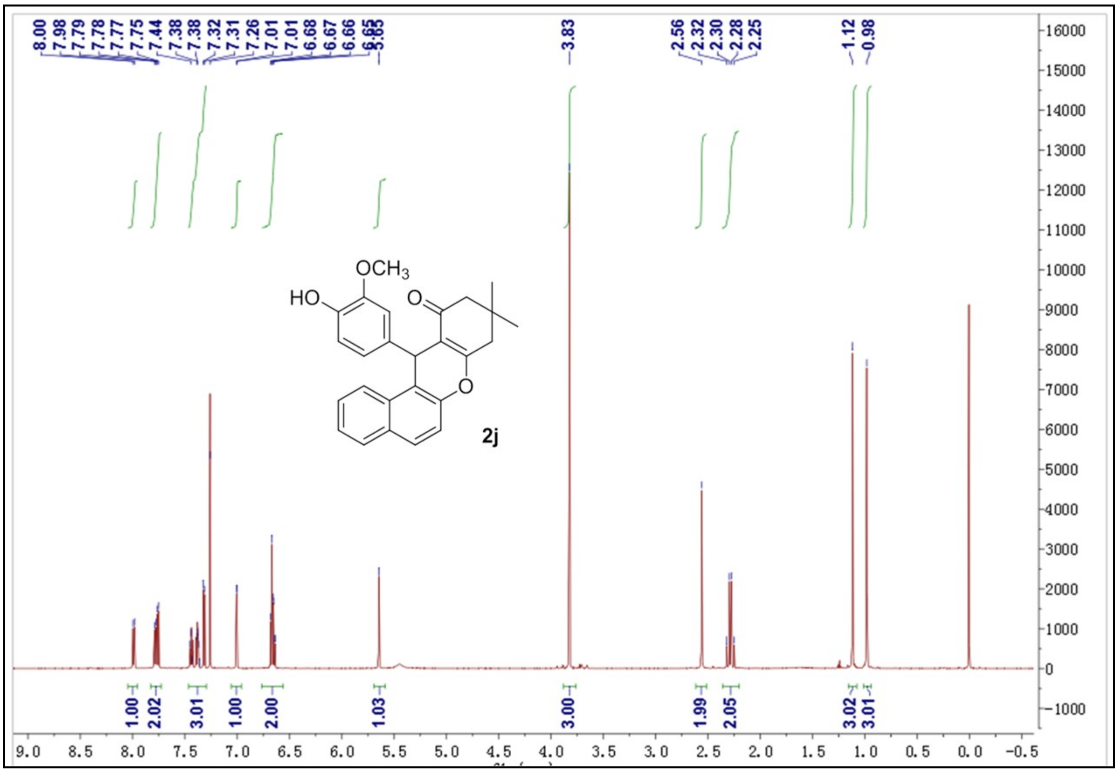
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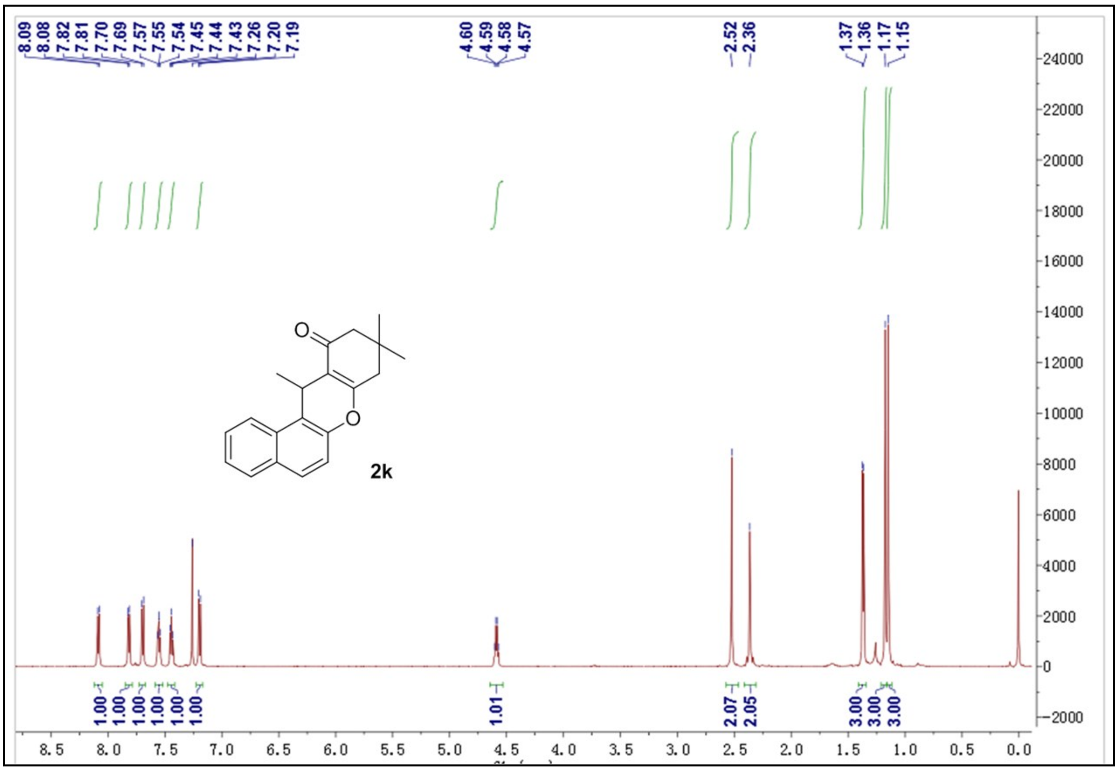
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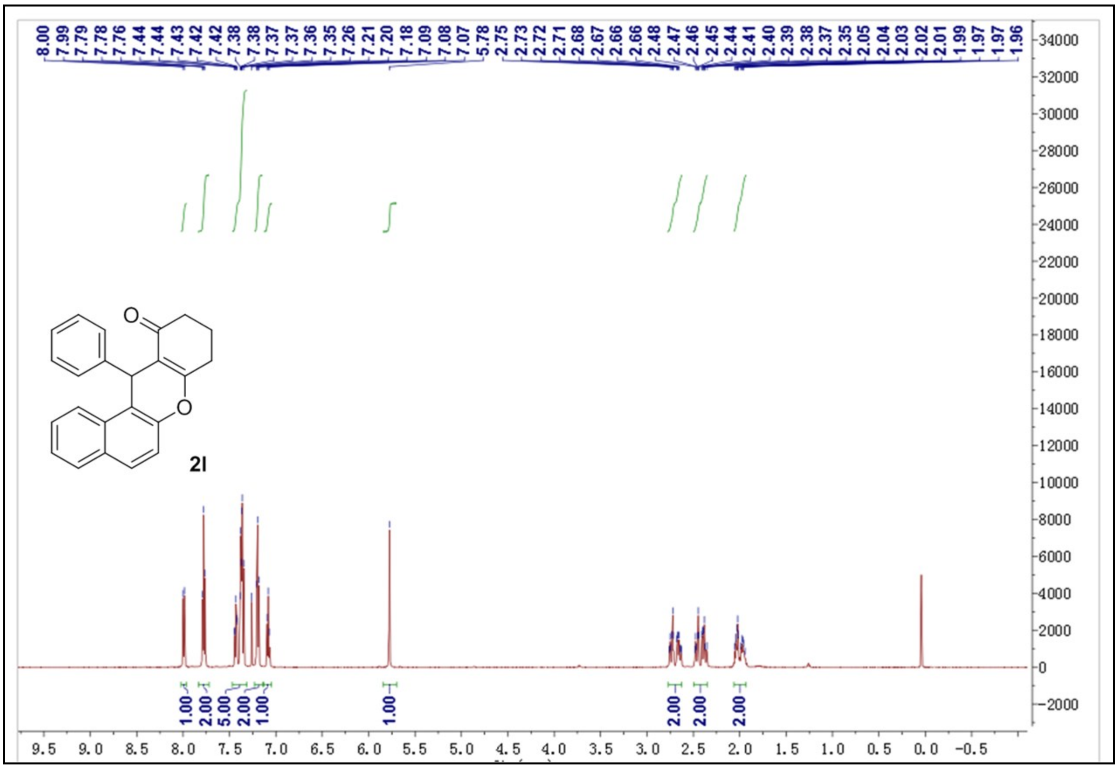
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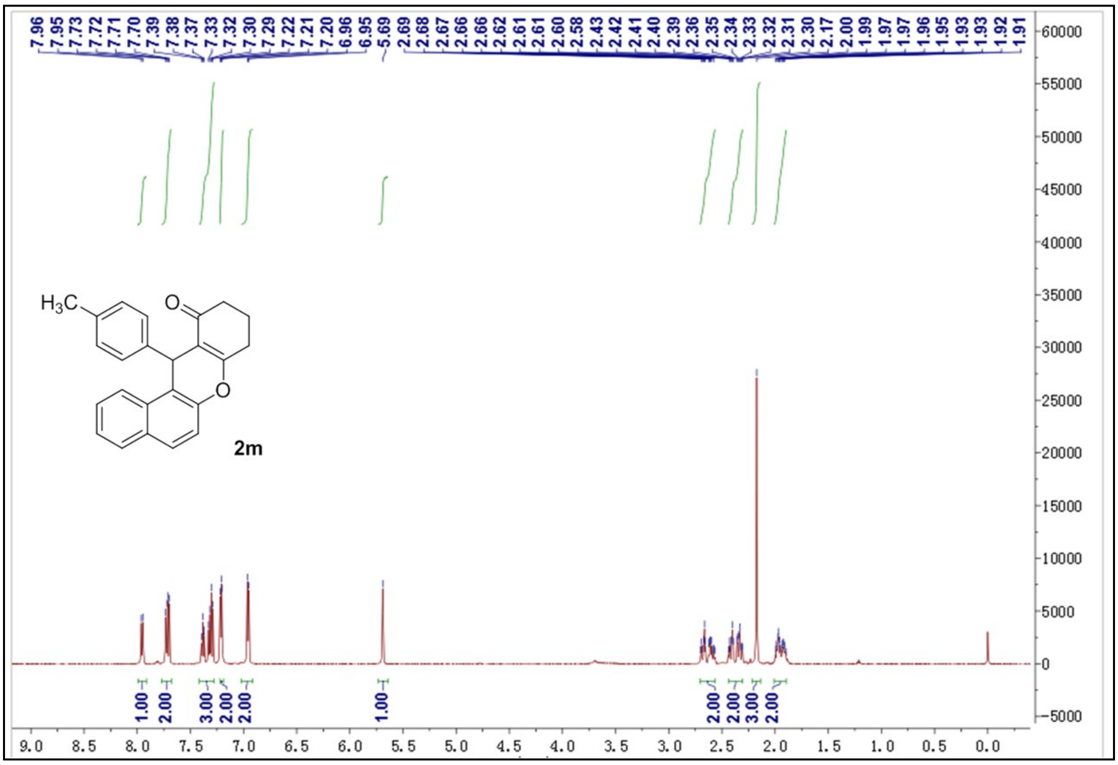
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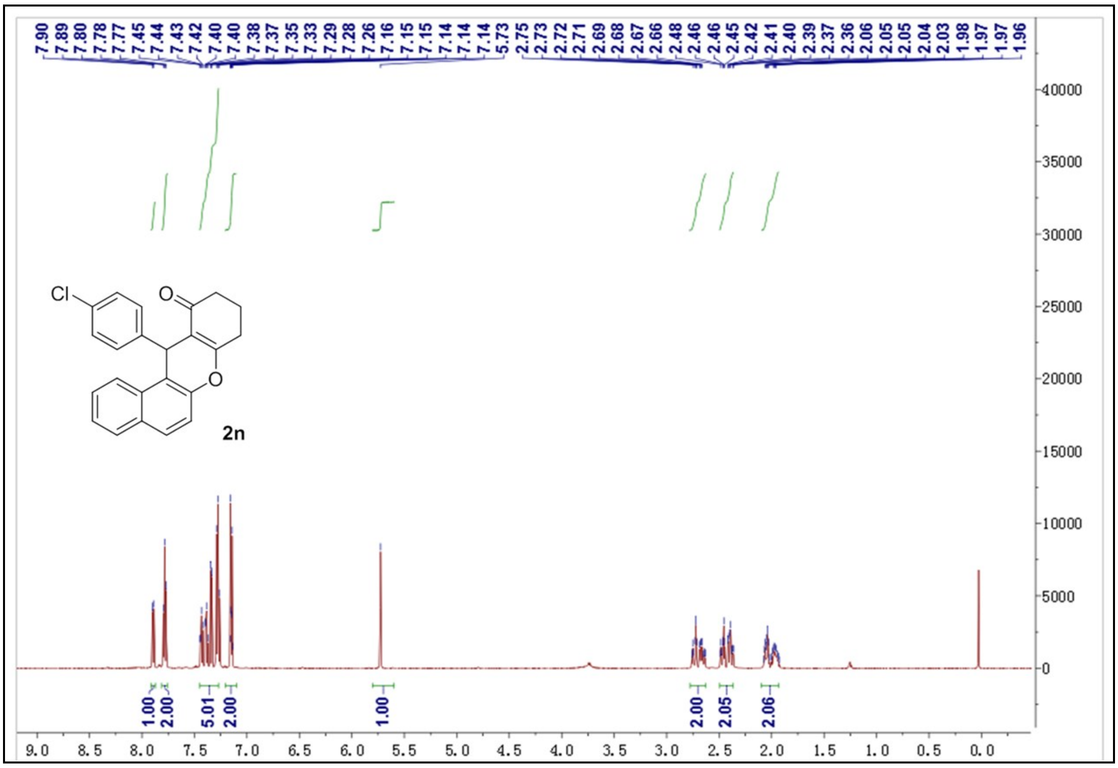
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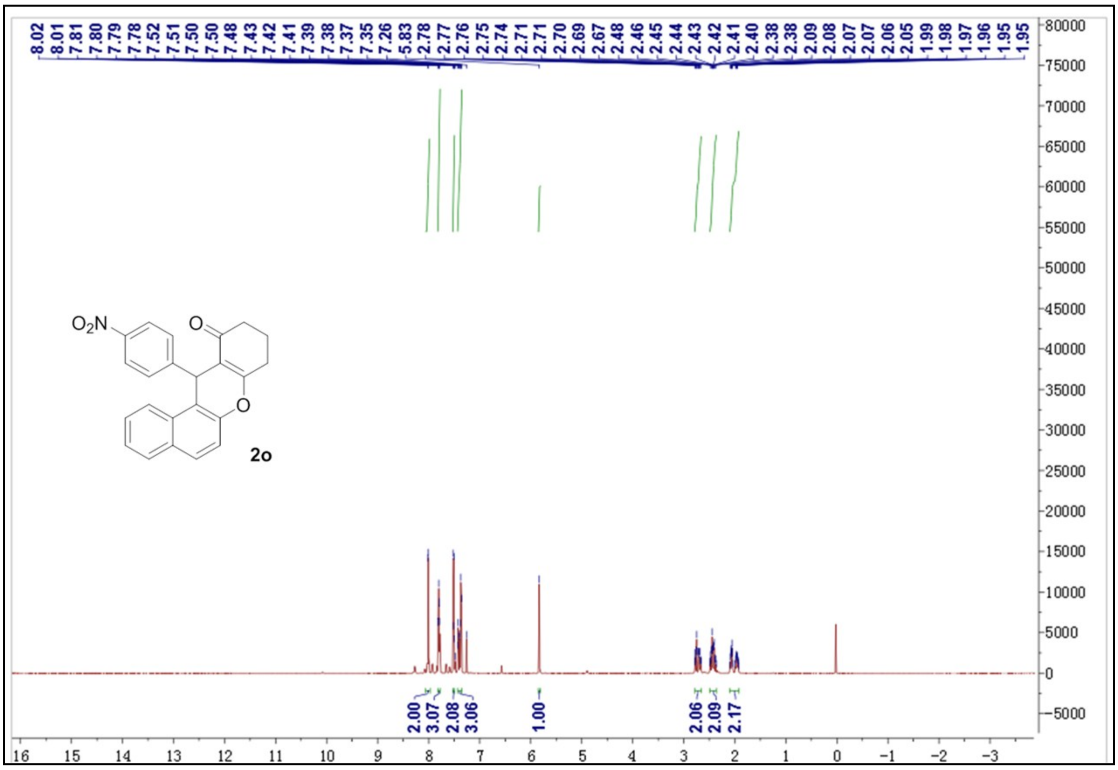
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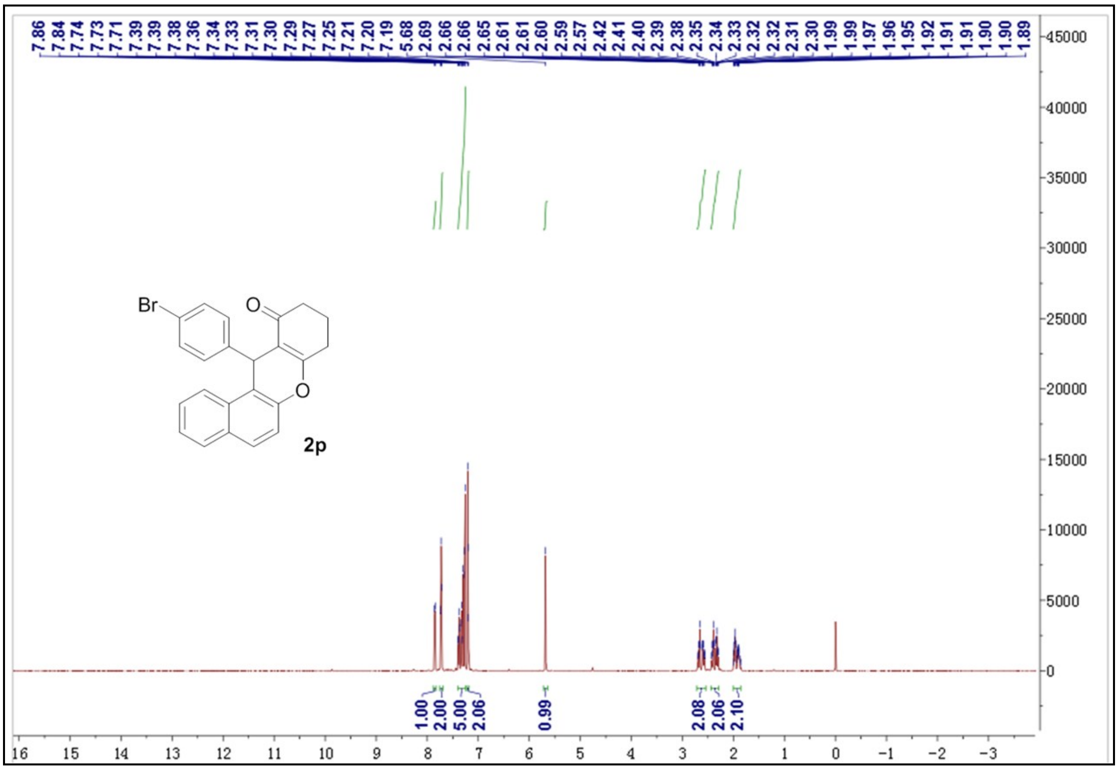
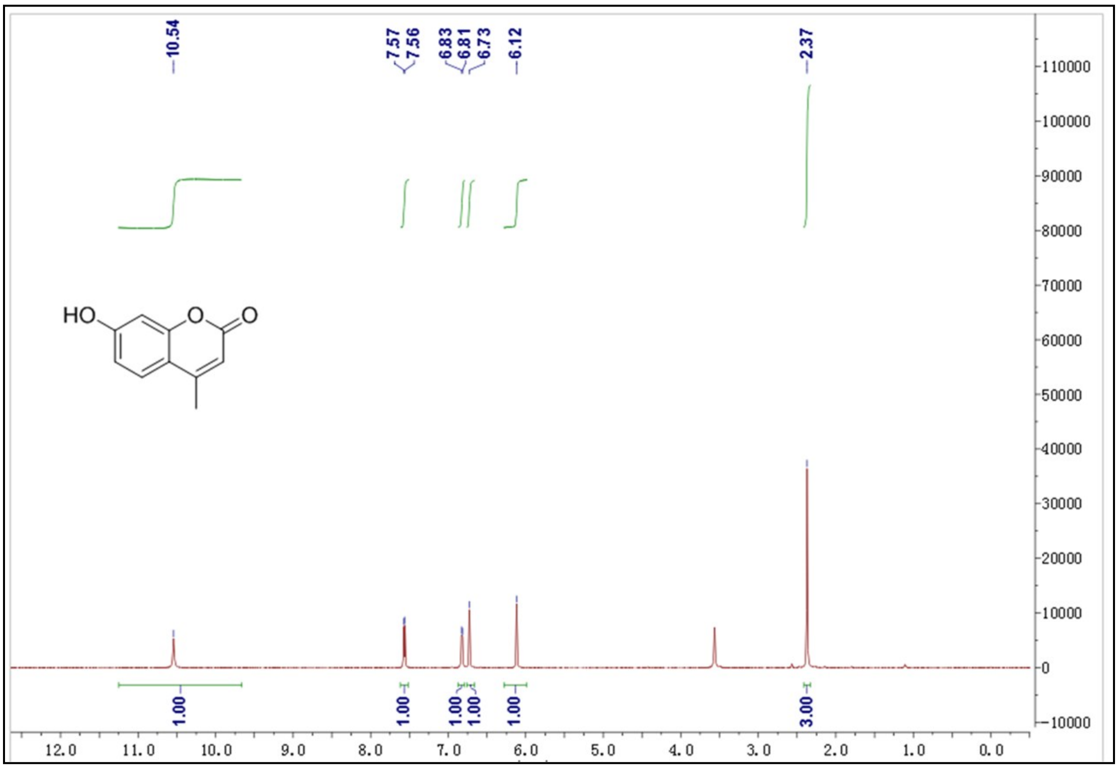
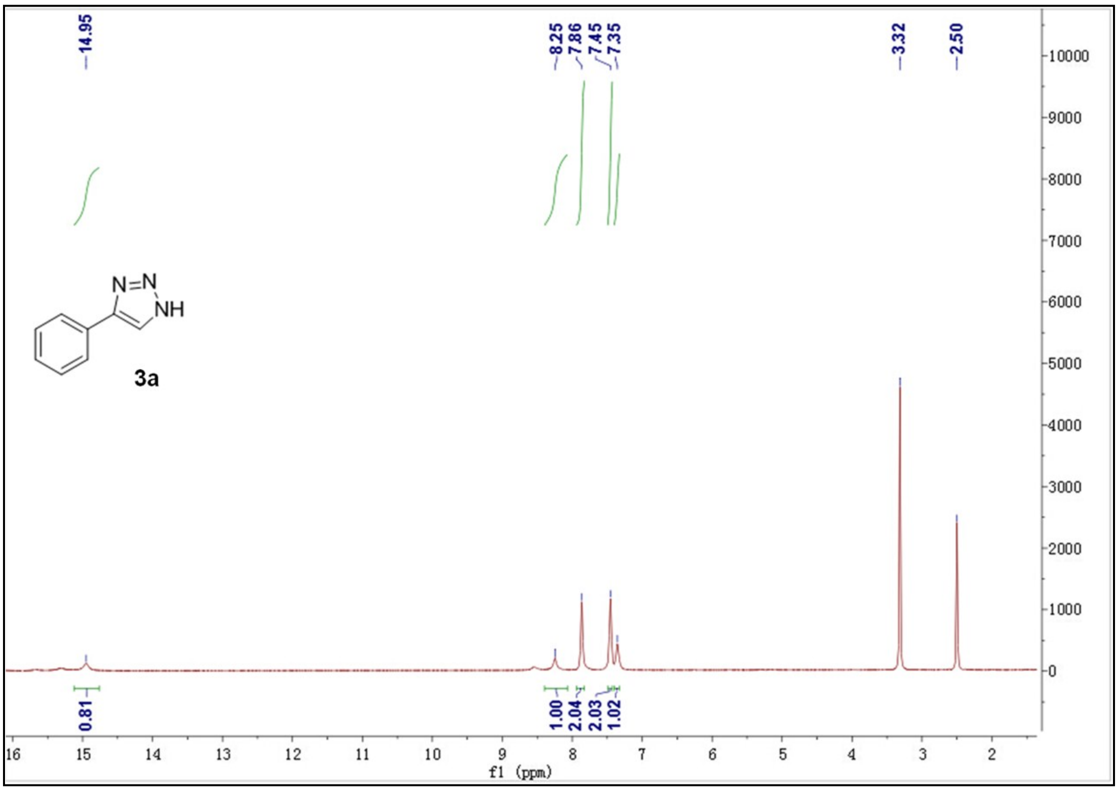
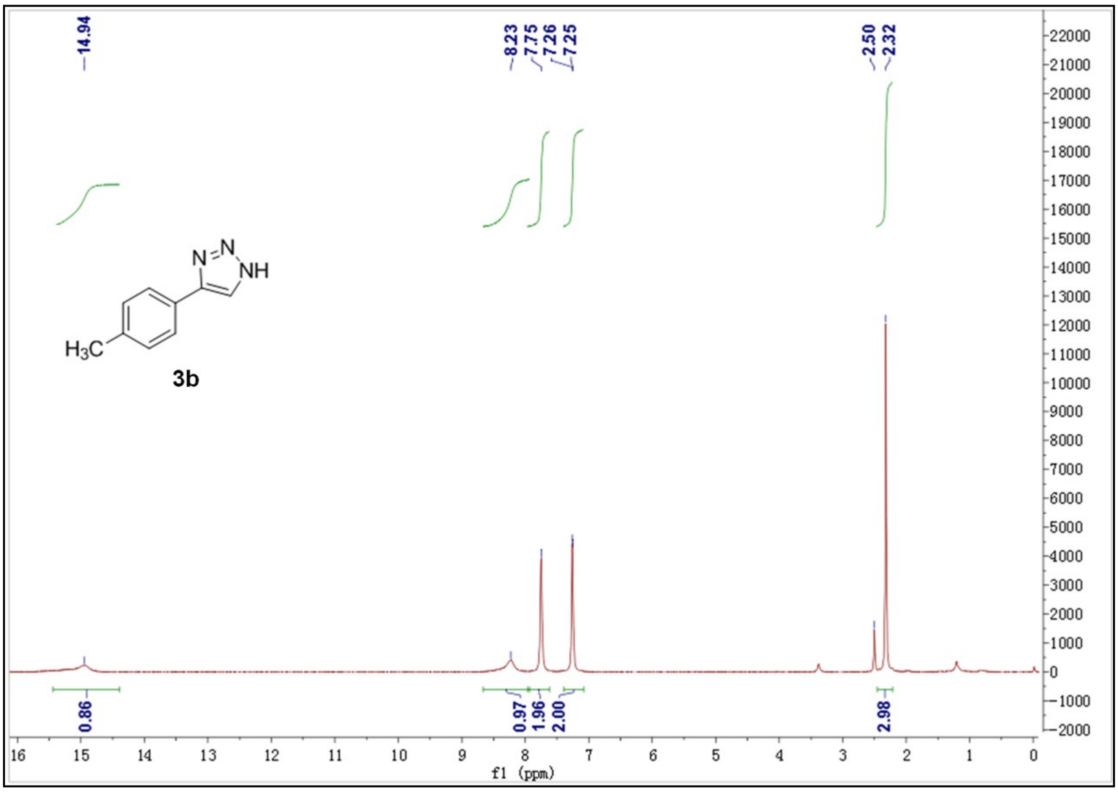

7.86 7.84 7.74 7.73 7.71 7.39 7.39 7.38 7.36 7.34 7.33 7.31 7.30 7.29 7.27 7.25 7.21 7.20 7.19 5.68 2.69 2.66 2.66 2.65 2.61 2.61 2.60 2.59 2.57 2.42 2.41 2.40 2.39 2.38 2.35 2.34 2.33 2.32 2.32 2.31 2.30 1.99 1.97 1.96 1.95 1.92 1.91 1.90 1.90 1.89
Br
O
O
2p
1.00
2.00
5.00
2.06
0.99
2.08
2.06
2.10
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3

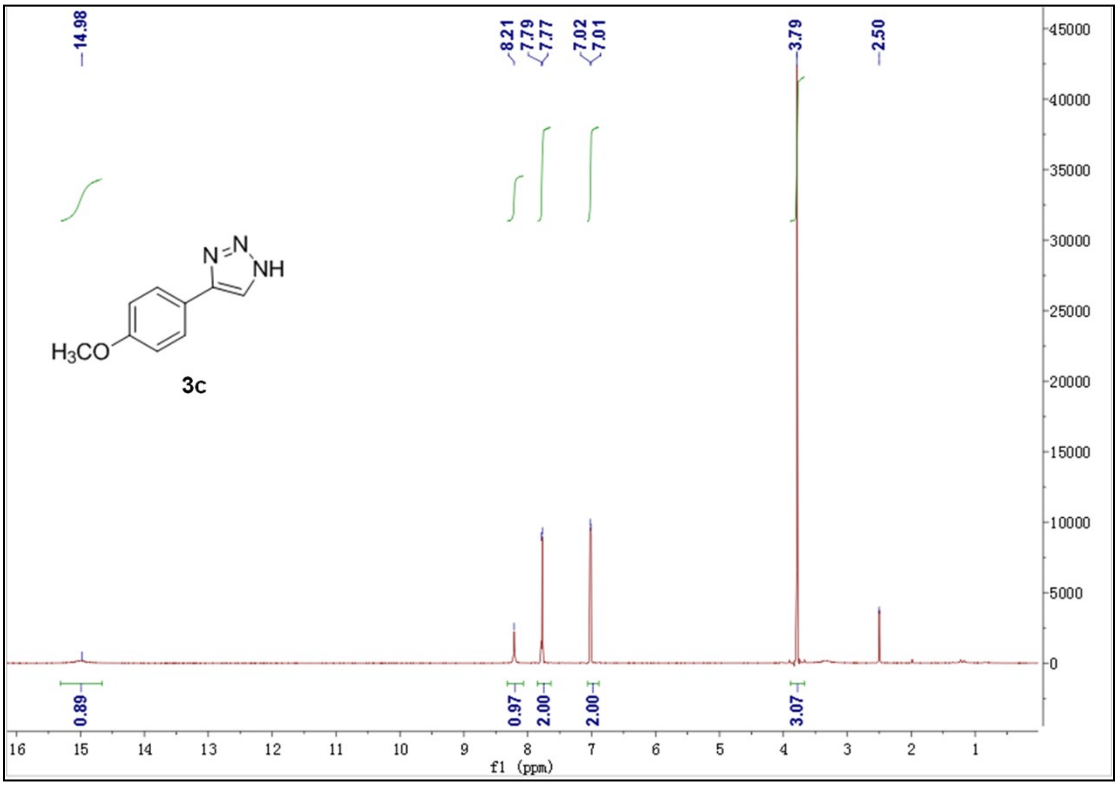

10.54
7.57
7.56
6.83
6.81
6.73
6.12
2.37
HO
O
O
1.00
1.00
1.00
1.00
1.00
3.00
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


14.95
8.25
7.86
7.45
7.35
3.32
2.50
N=N
NH
3a
0.81
1.00
2.04
2.03
1.02
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
f1 (ppm)



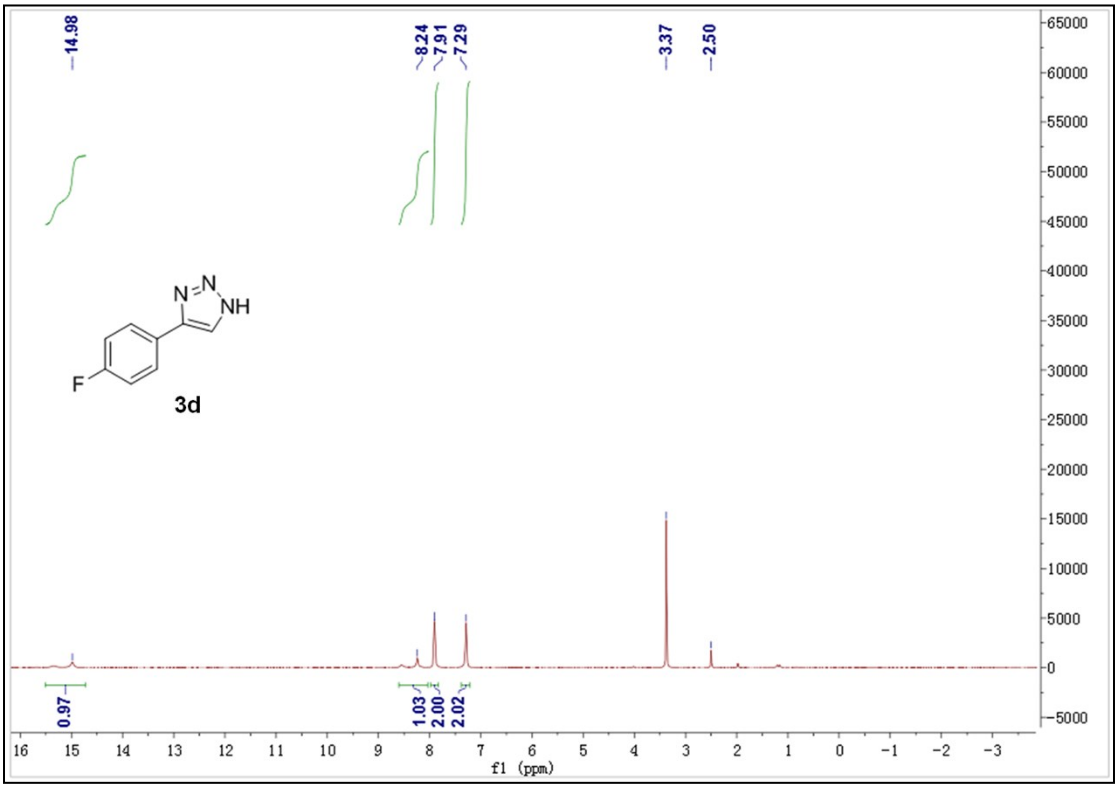
3b

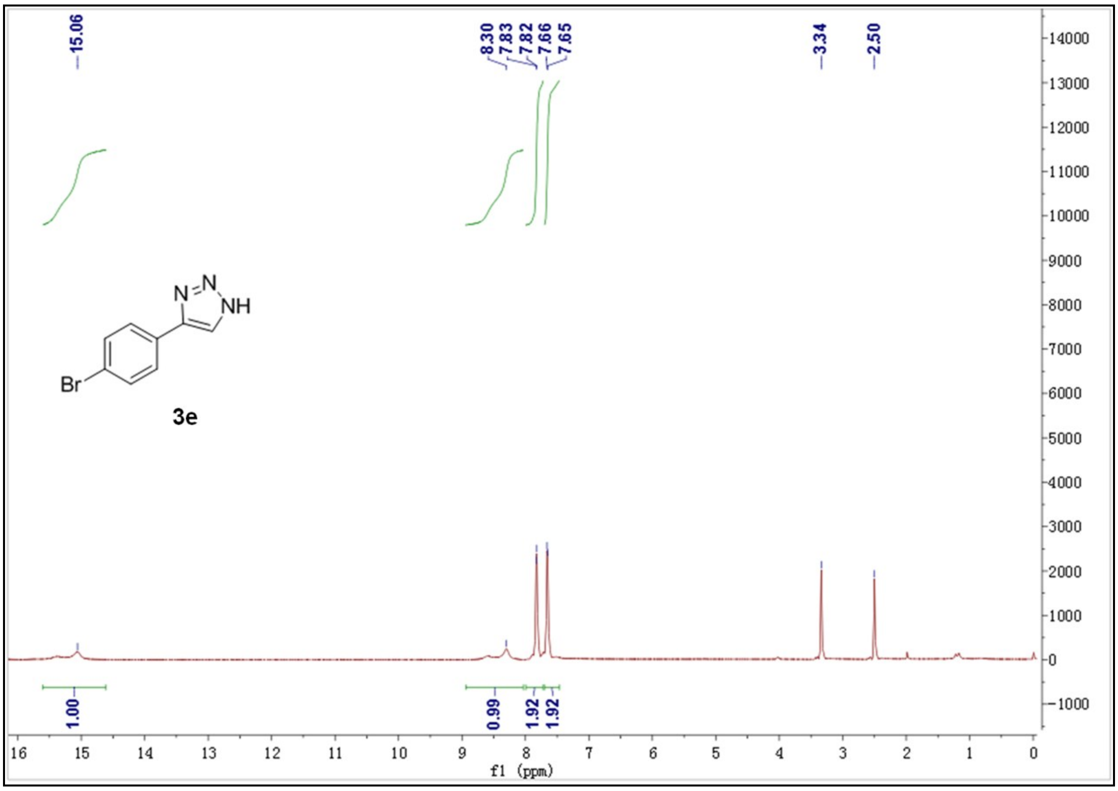
14.94
8.23
7.75
7.26
7.25
2.50
2.32
0.86
0.97
1.96
2.00
2.98
f1 (ppm)
NH
N
N
H_3C

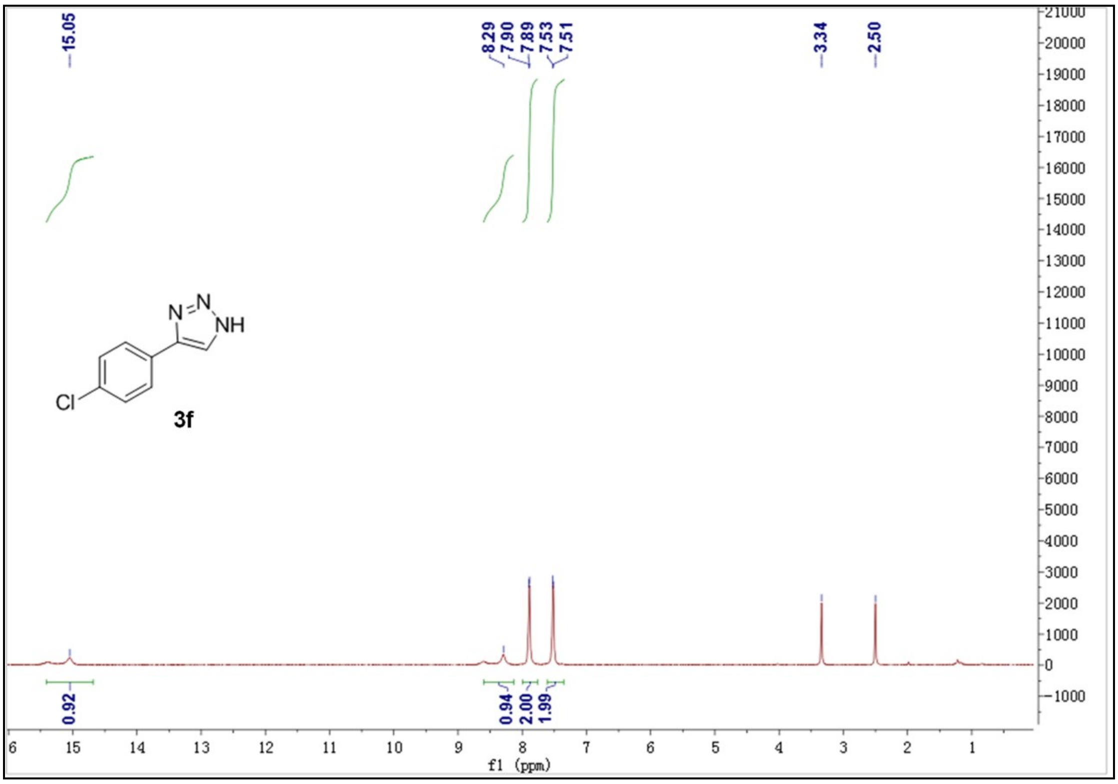


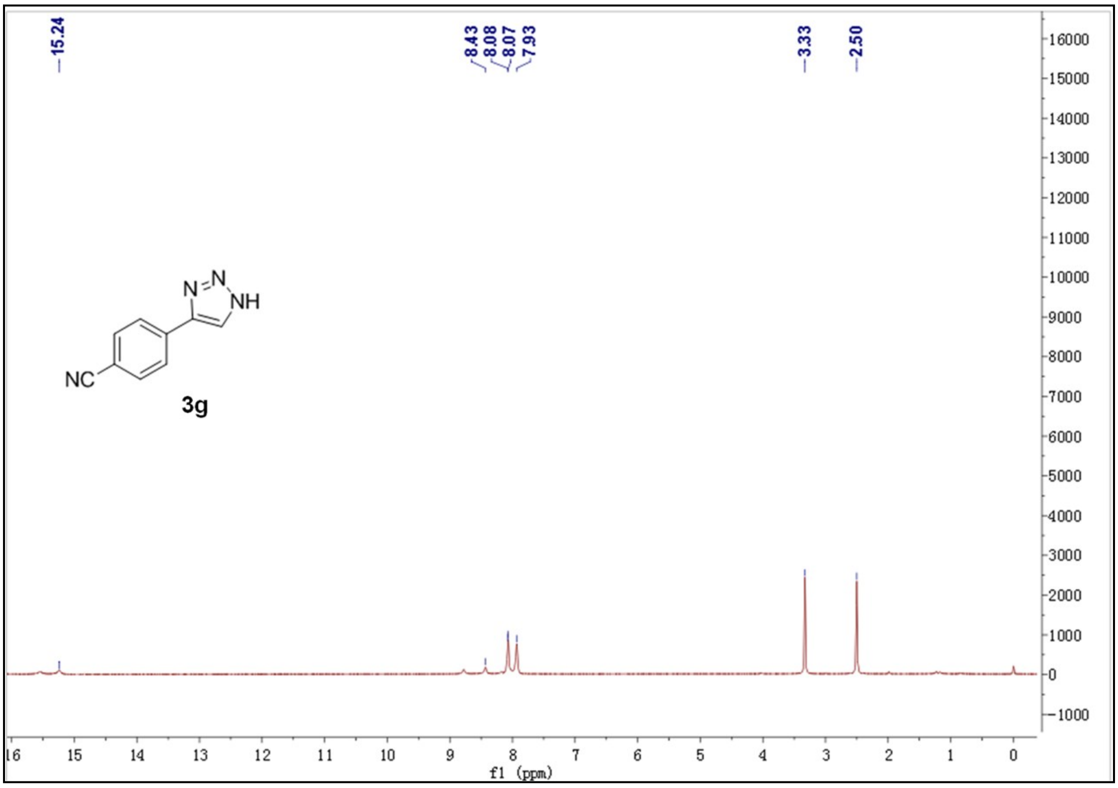
3c

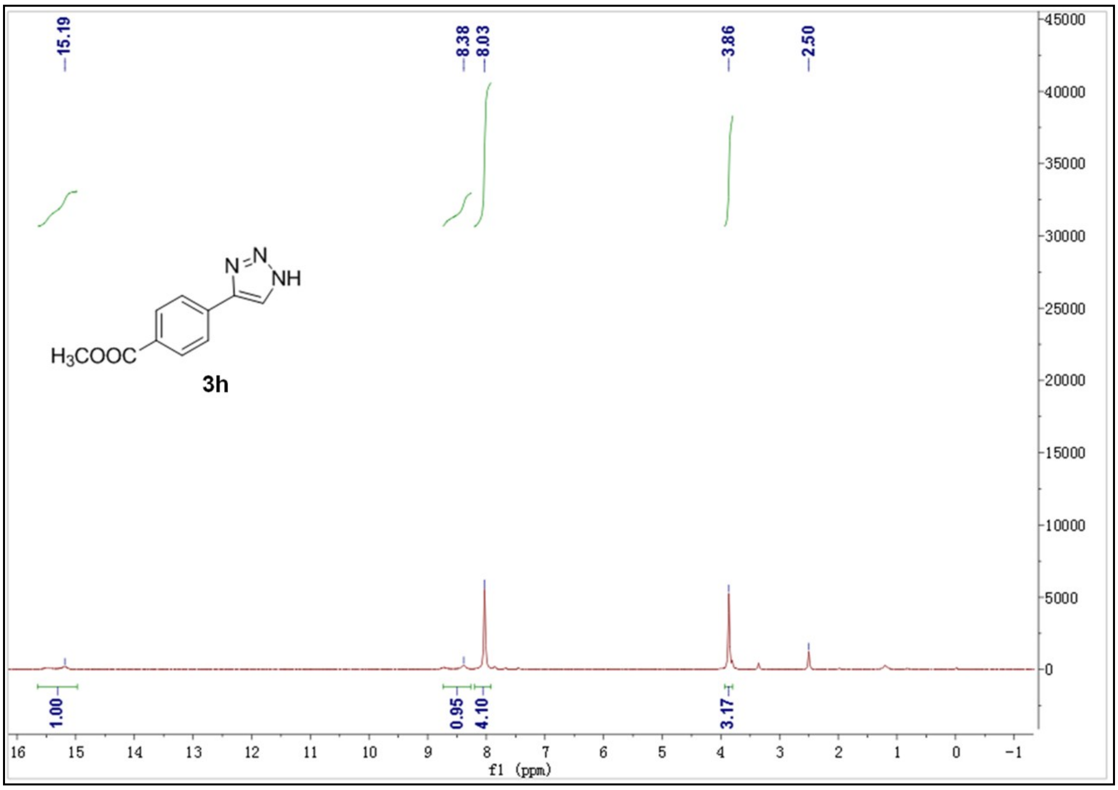
14.98
8.21
7.79
7.77
7.02
7.01
3.79
2.50
0.89
0.97
2.00
2.00
3.07
f1 (ppm)
NH
N
N
H_3CO

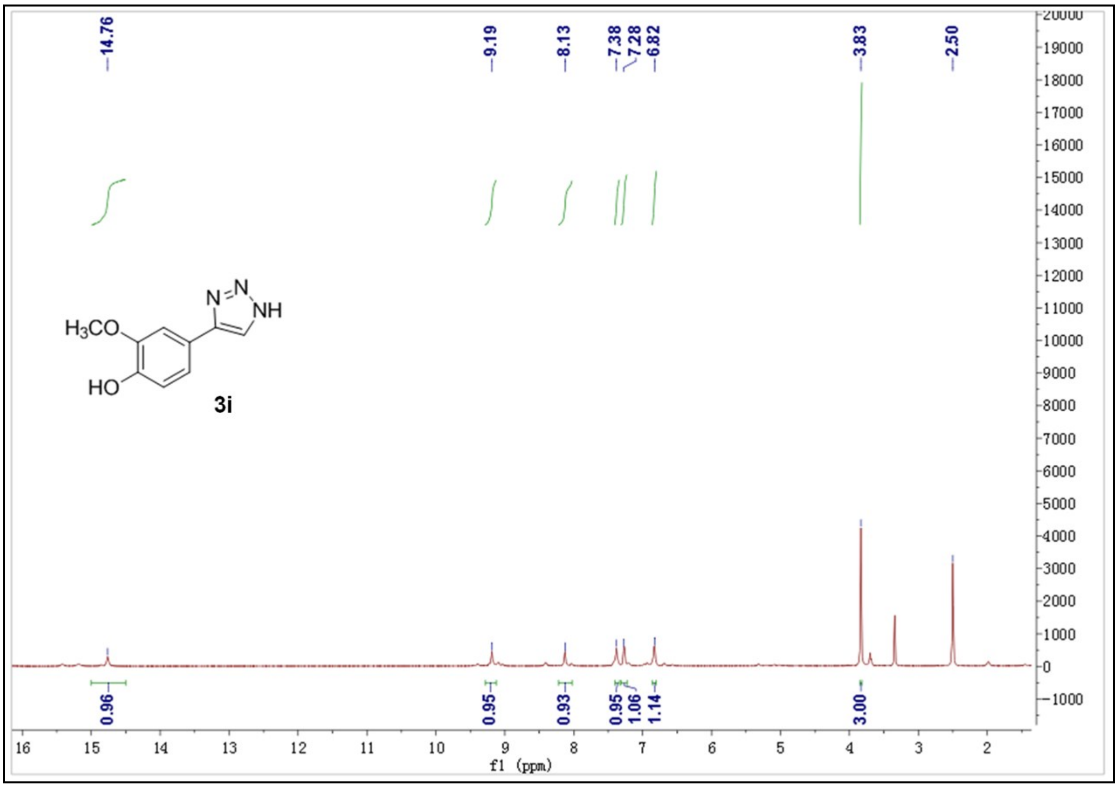

14.98
8.24
7.91
7.29
3.37
2.50
3d
F
N
N
NH
0.97
1.03
2.00
2.02
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 −5000


15.06
8.30
7.83
7.82
7.66
7.65
3.34
2.50
3e
Br
N
N
NH
1.00
0.99
1.92
1.92
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000

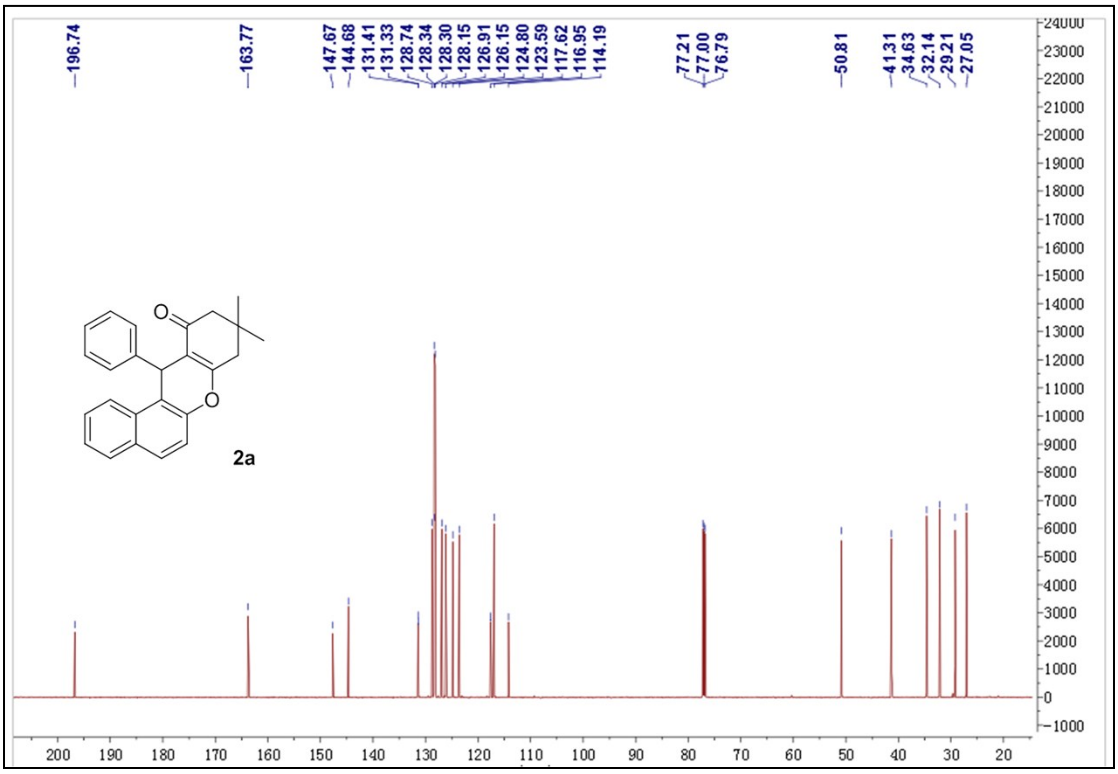

15.05
8.29
7.90
7.89
7.53
7.51
3.34
2.50
N
N
NH
Cl
3f
0.92
0.94
2.00
1.99
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000


15.24
8.43
8.08
8.07
7.93
3.33
2.50
N
N
NH
NC
3g
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000

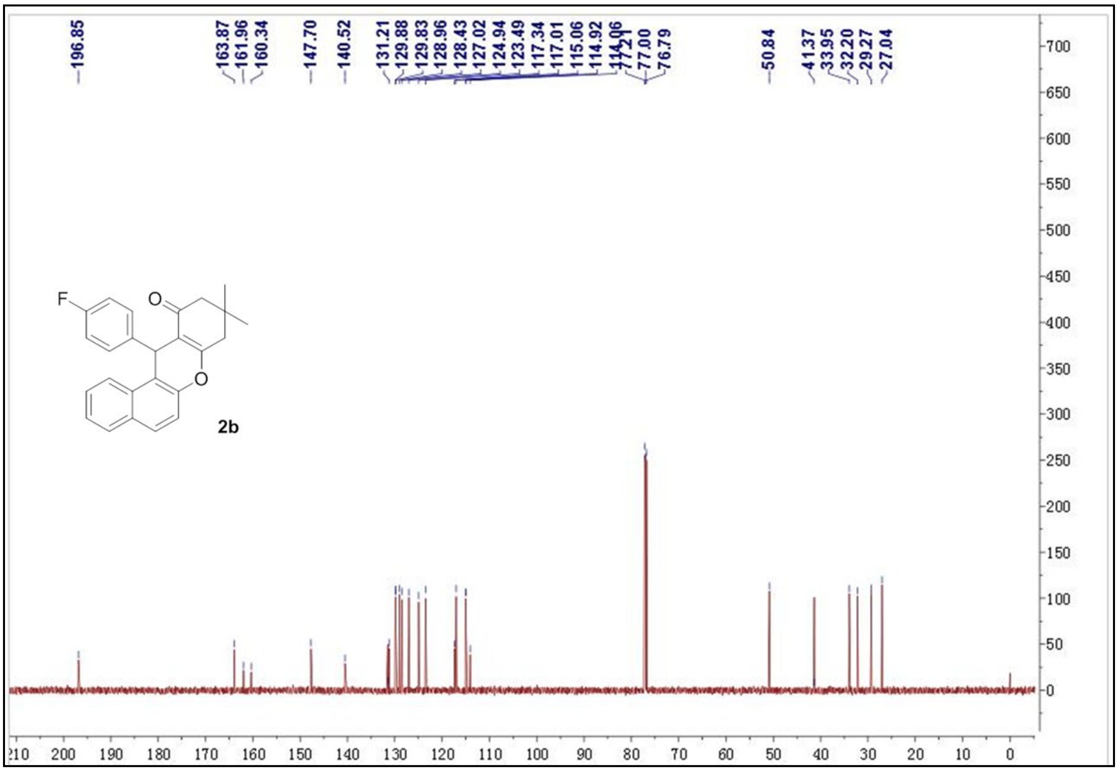

15.19
8.38
8.03
3.86
2.50
H3COOC
N
N
NH
3h
1.00
0.95
4.10
3.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0


14.76
9.19
8.13
7.38
7.28
6.82
3.83
2.50
H3CO
HO
N
N
NH
3i
0.96
0.95
0.93
0.95
1.06
1.14
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2
f1 (ppm)
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

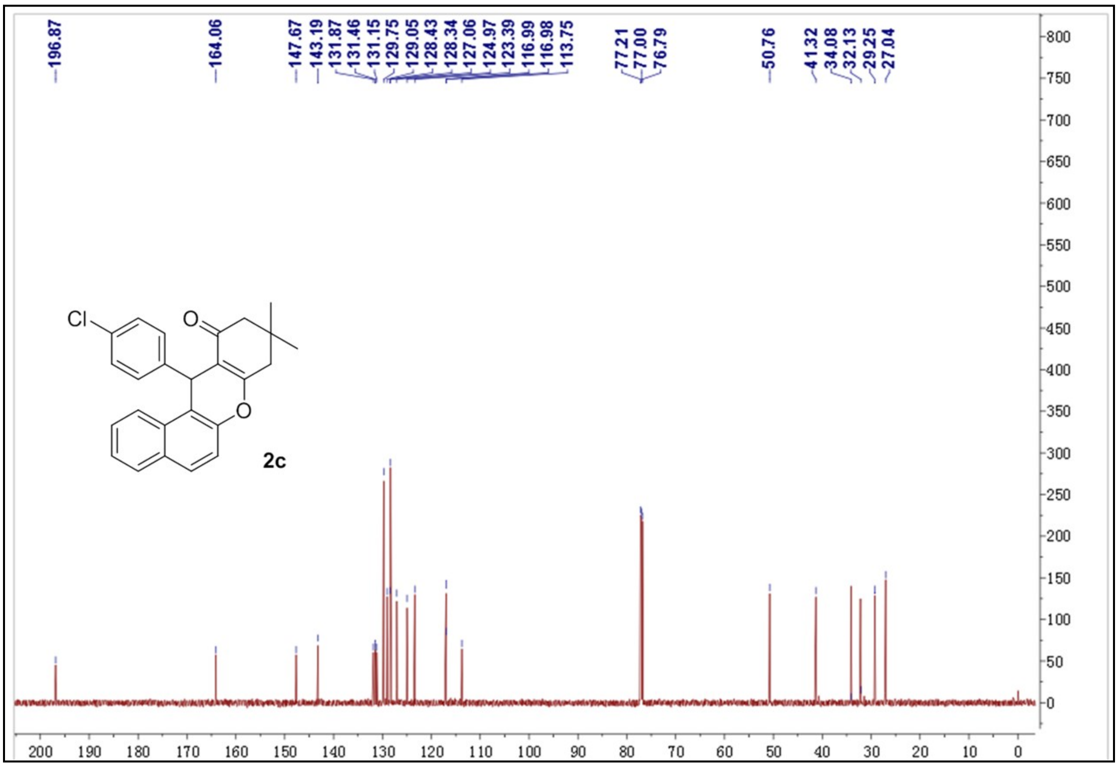
^{13}C NMR for all compounds



2a



2b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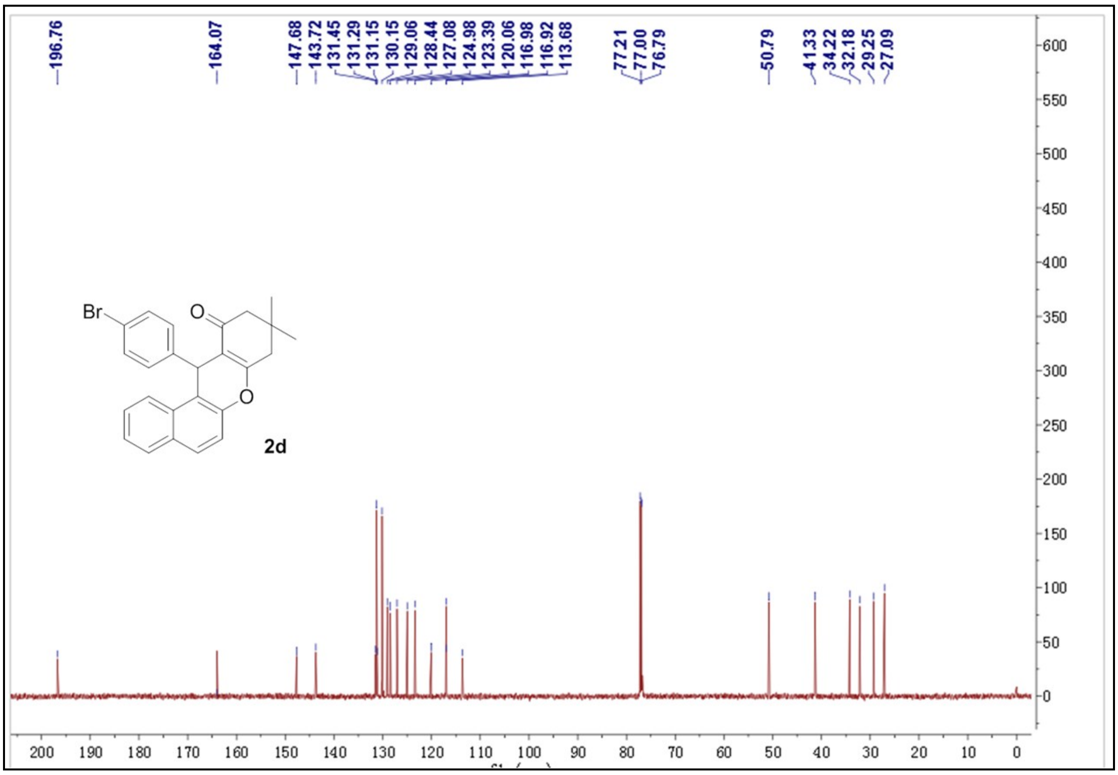
164.06
147.67
143.19
131.87
131.46
131.15
129.75
129.05
128.43
128.34
127.06
124.97
123.39
116.99
116.98
113.75
77.21
77.00
76.79
50.76
41.32
34.08
32.13
29.25
27.04
Cl
O
O
2c
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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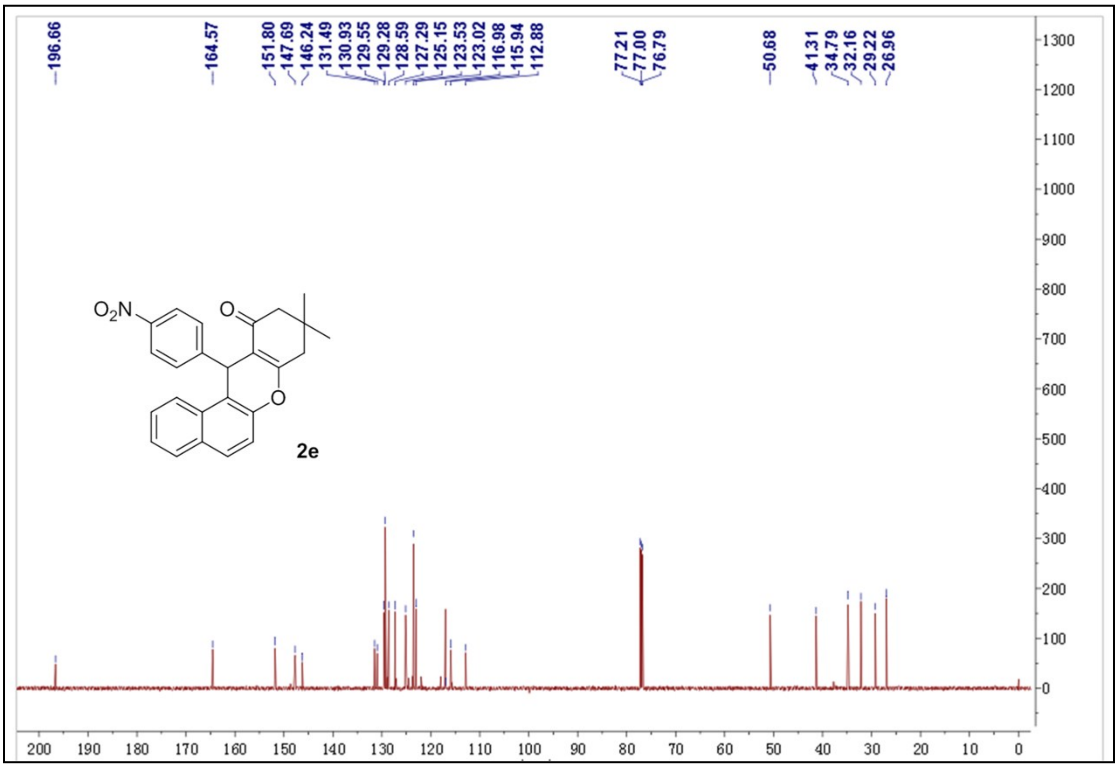
164.07
147.68
143.72
131.45
131.29
131.15
130.15
129.06
128.44
127.08
124.98
123.39
120.06
116.98
116.92
113.68
77.21
77.00
76.79
50.79
41.33
34.22
32.18
29.25
27.09
Br
O
O
2d
600
550
500
450
400
350
300
250
200
150
100
50
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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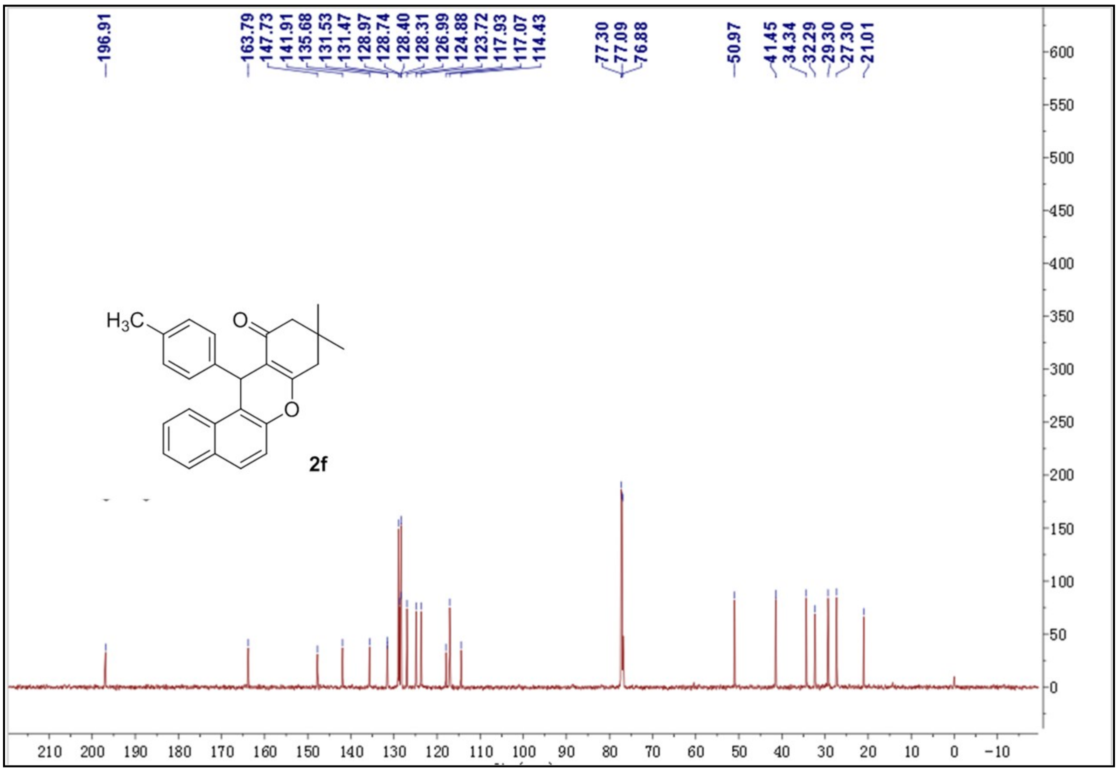
164.57
151.80
147.69
146.24
131.49
130.93
129.55
129.28
128.59
127.29
125.15
123.53
123.02
116.98
115.94
112.88
77.21
77.00
76.79
50.68
41.31
34.79
32.16
29.22
26.96
O_2N
O
O
2e
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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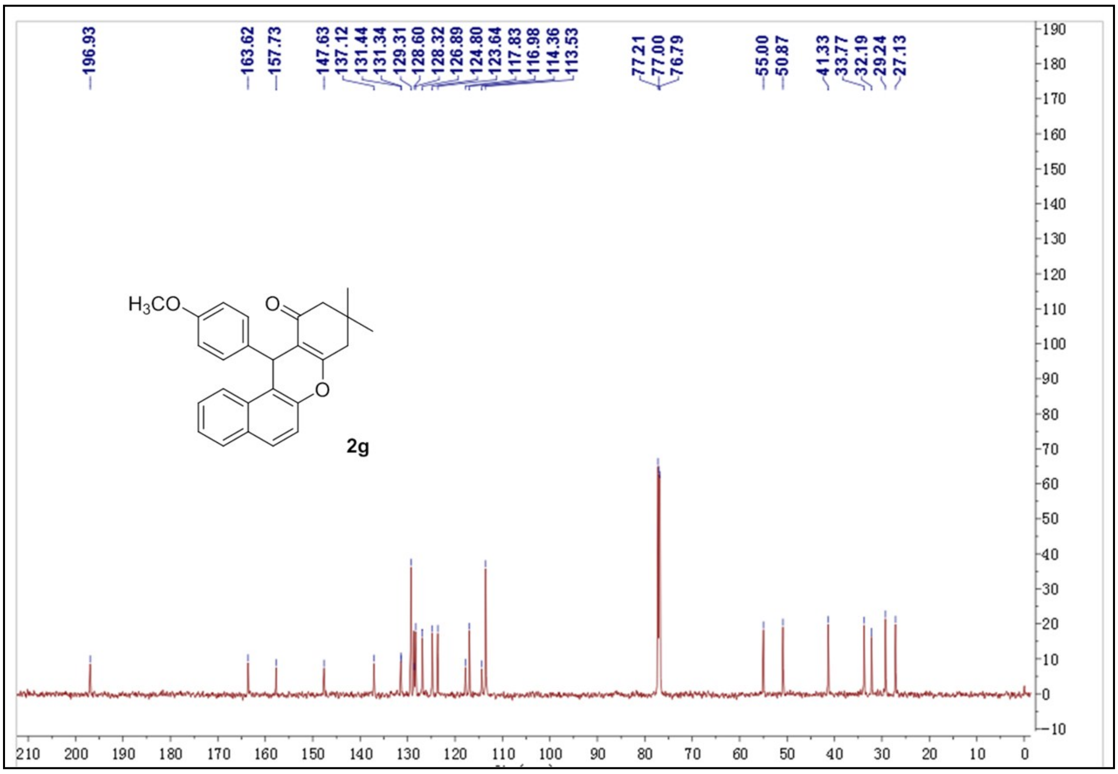
147.73
141.91
135.68
131.53
131.47
128.97
128.74
128.40
128.31
126.99
124.88
123.72
117.93
117.07
114.43
77.30
77.09
76.88
50.97
41.45
34.34
32.29
29.30
27.30
21.01
H_3C
O
O
2f
600
550
500
450
400
350
300
250
200
150
100
50
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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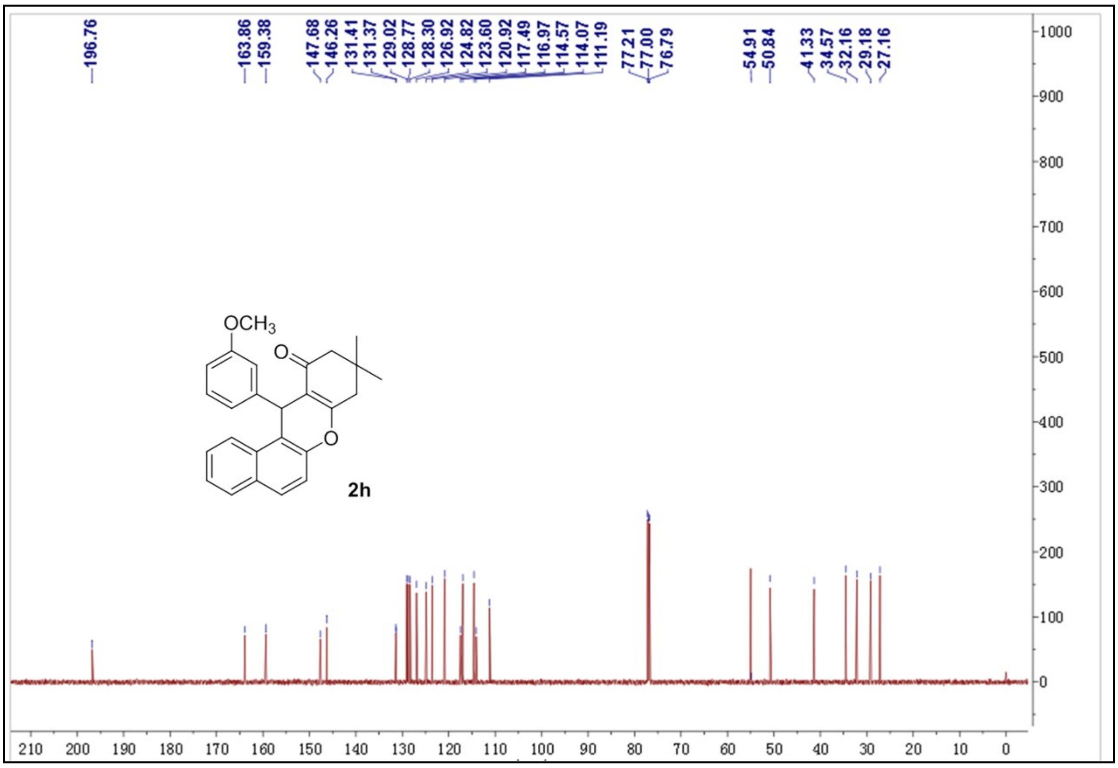
147.63
137.12
131.44
131.34
129.31
128.60
128.32
126.89
124.80
123.64
117.83
116.98
114.36
113.53
77.21
77.00
76.79
55.00
50.87
41.33
33.77
32.19
29.24
27.13
H$_3$CO
O
O
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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159.38
147.68
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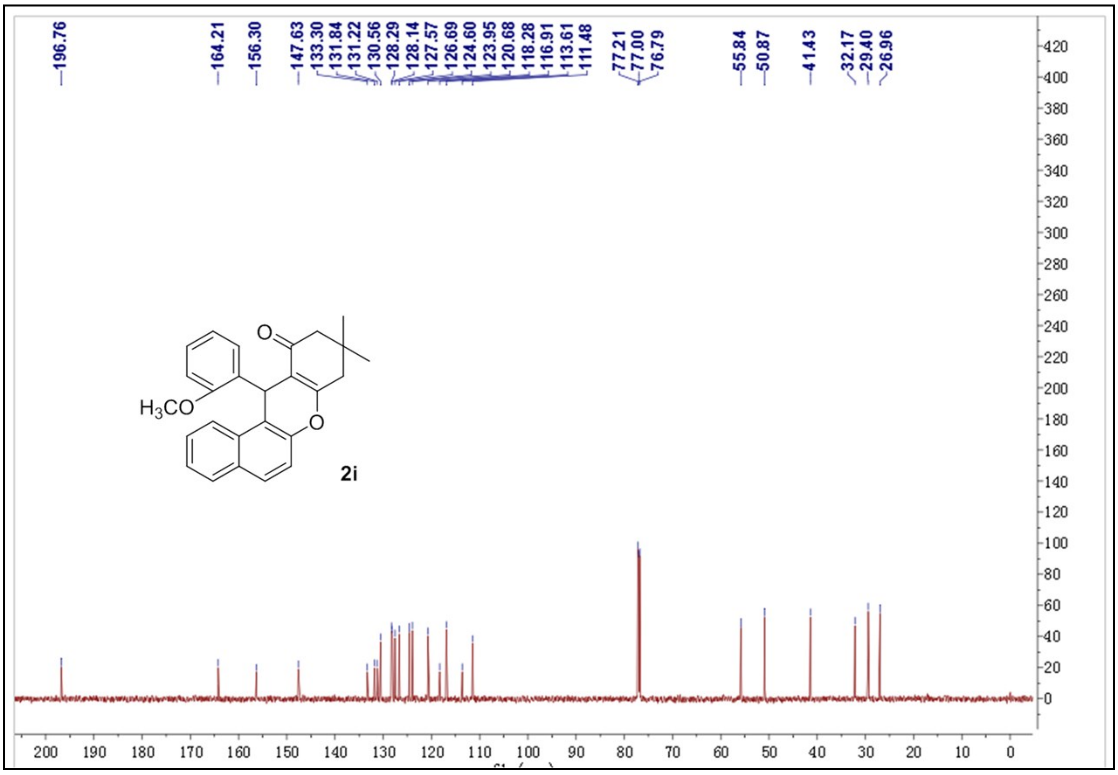
131.41
131.37
129.02
128.77
128.30
126.92
124.82
123.60
120.92
117.49
116.97
114.57
114.07
111.19
77.21
77.00
76.79
54.91
50.84
41.33
34.57
32.16
29.18
27.16
OCH$_3$
O
O
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
1000 900 800 700 600 500 400 300 200 100 0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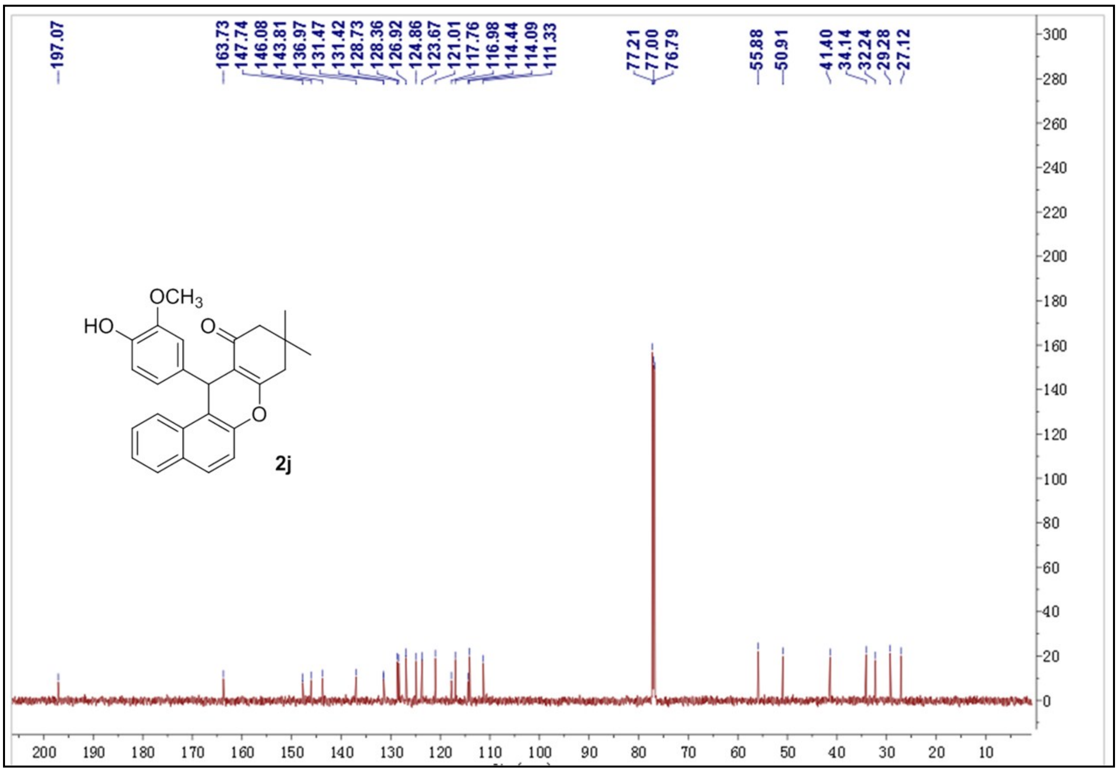
156.30
147.63
133.30
131.84
131.22
130.56
128.29
128.14
127.57
126.69
124.60
123.95
120.68
118.28
116.91
113.61
111.48
77.21
77.00
76.79
55.84
50.87
41.43
32.17
29.40
26.96
H3CO
O
O
2i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0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131.47
131.42
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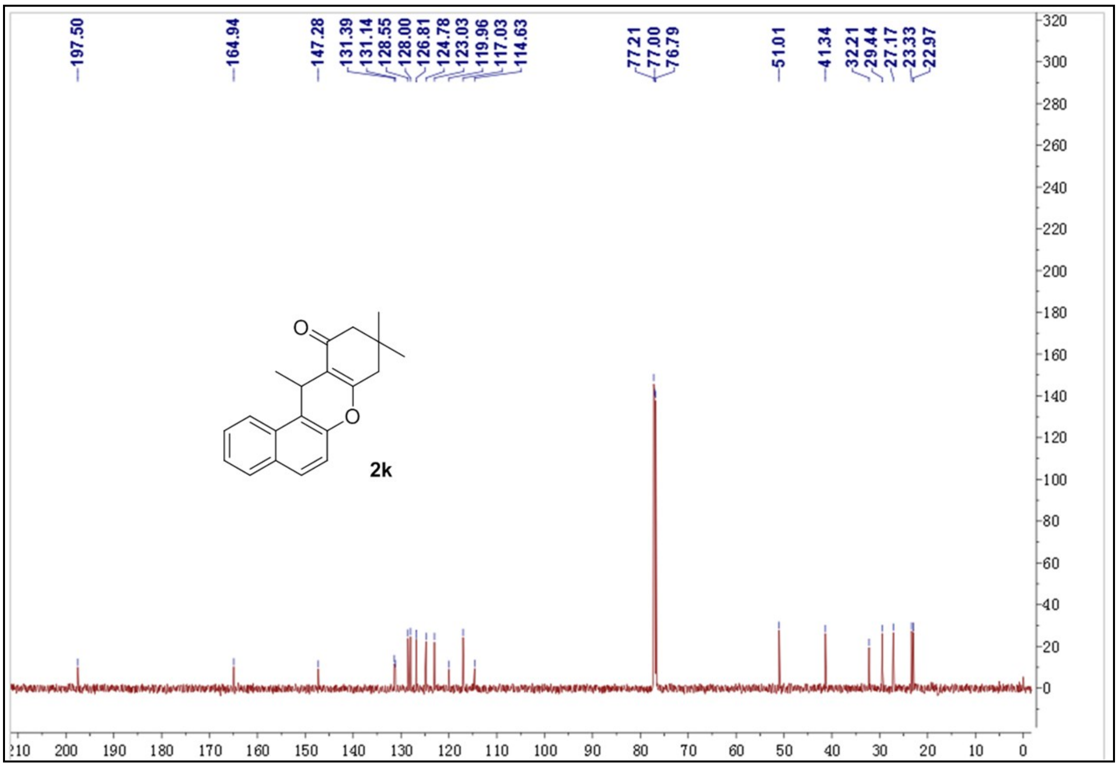
128.36
126.92
124.86
123.67
121.01
117.76
116.98
114.44
114.09
111.33
77.21
77.00
76.79
55.88
50.91
41.40
34.14
32.24
29.28
27.12
OCH3
HO
O
O
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0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131.14
128.55
128.00
126.81
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123.03
119.96
117.03
114.63
77.21
77.00
76.79
51.01
41.34
32.21
29.44
27.17
23.33
22.97
O
O
2k
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
210
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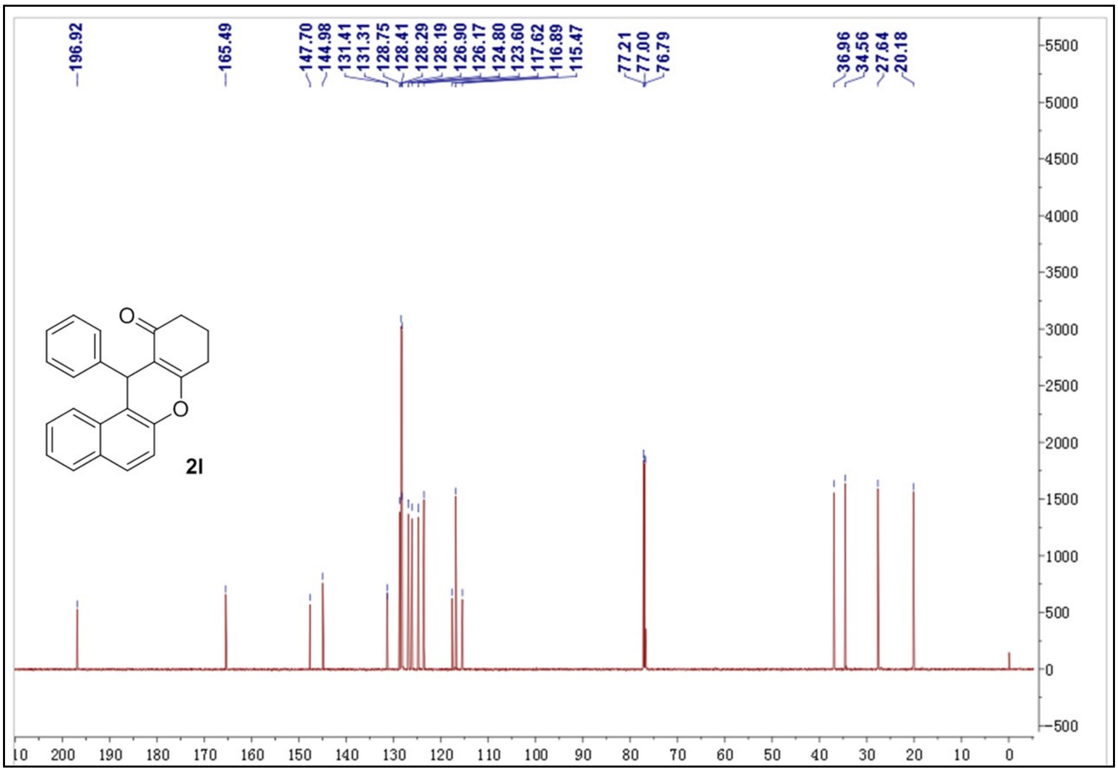
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144.98
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131.31
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128.41
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128.19
126.90
126.17
124.80
123.60
117.62
116.89
115.47
77.21
77.00
76.79
36.96
34.56
27.64
20.18
O
O
2l
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
200
190
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70
60
50
40
30
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10
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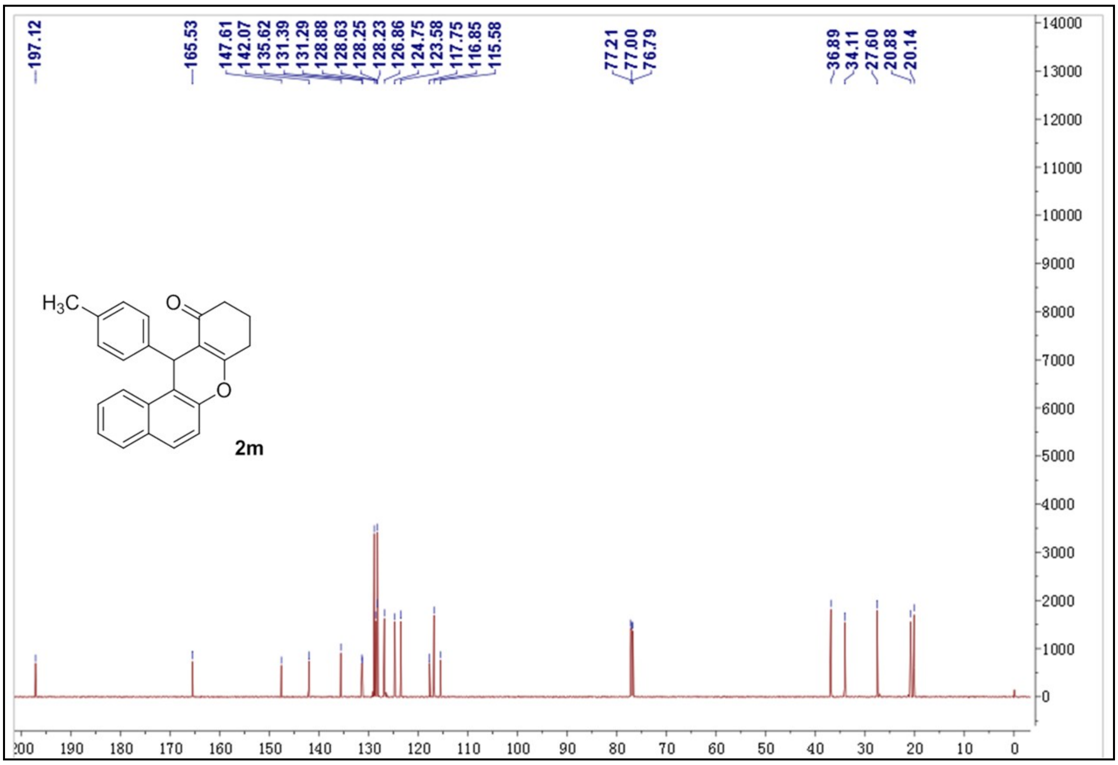
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128.25
128.23
126.86
124.75
123.58
117.75
116.85
115.58
77.21
77.00
76.79
36.89
34.11
27.60
20.88
20.14
H3C
O
O
2m
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
200
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10
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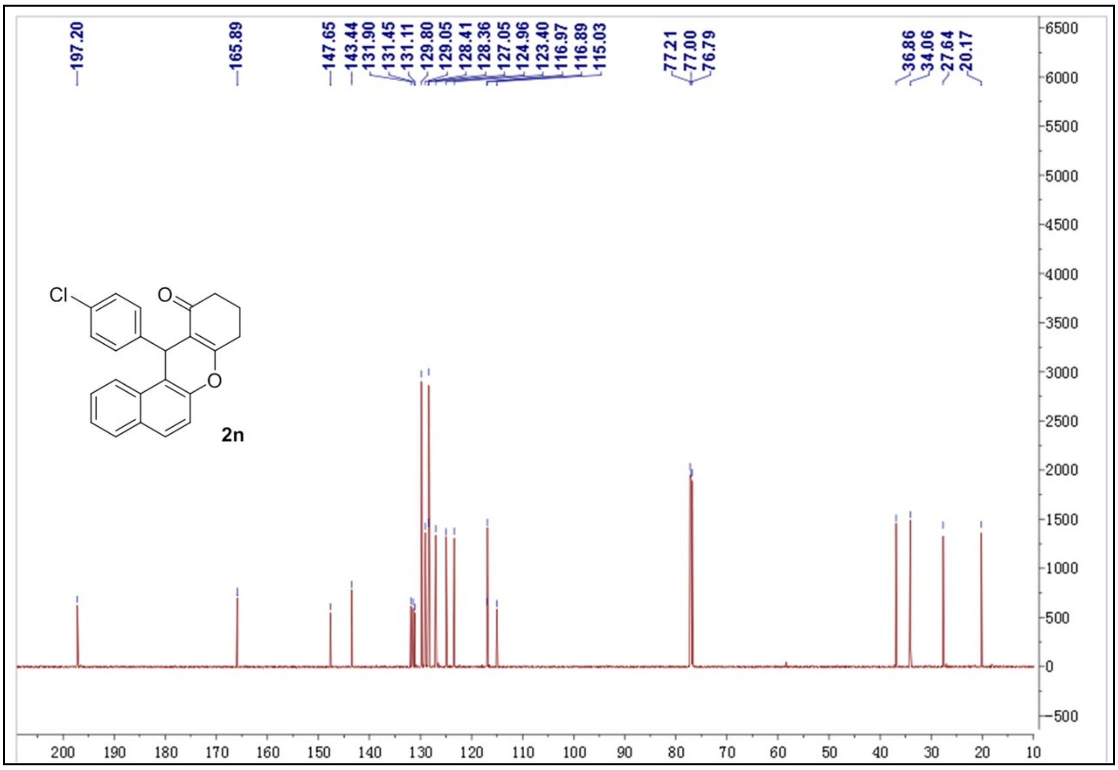
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128.36
127.05
124.96
123.40
116.97
116.89
115.03
77.21
77.00
76.79
36.86
34.06
27.64
20.17
Cl
O
O
2n
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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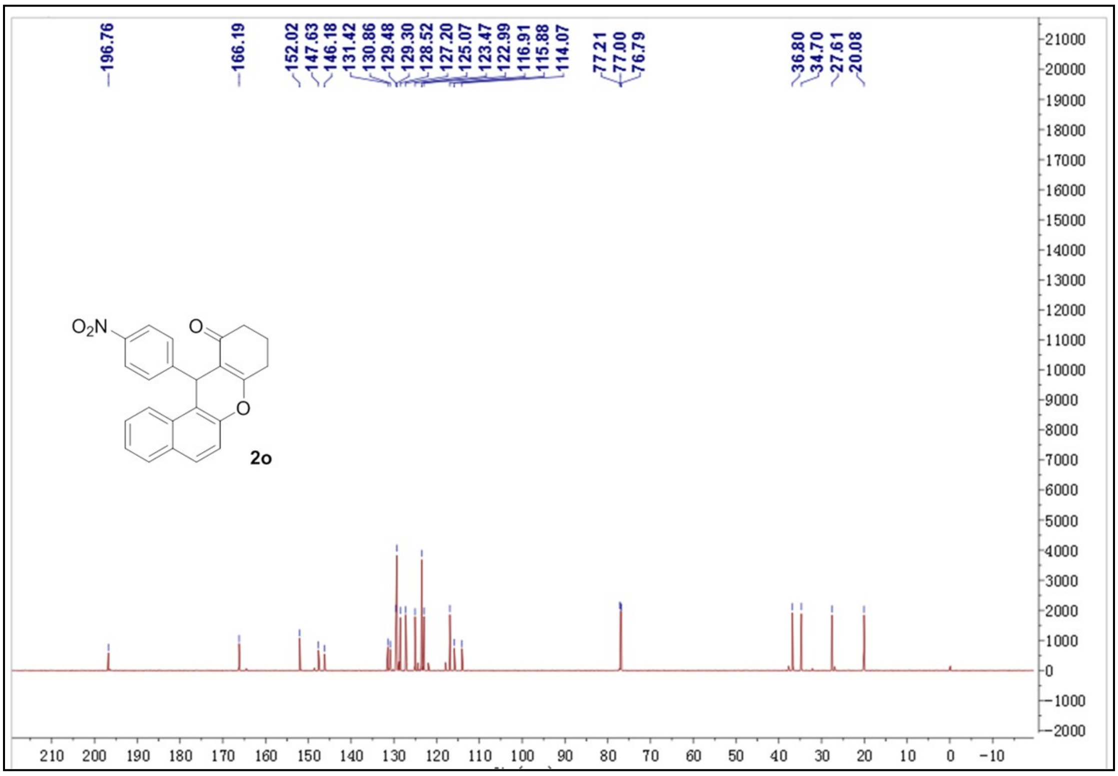
20
10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127.20
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123.47
122.99
116.91
115.88
114.07
77.21
77.00
76.79
36.80
34.70
27.61
20.08
O2N
O
O
2o
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
210
200
190
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30
20
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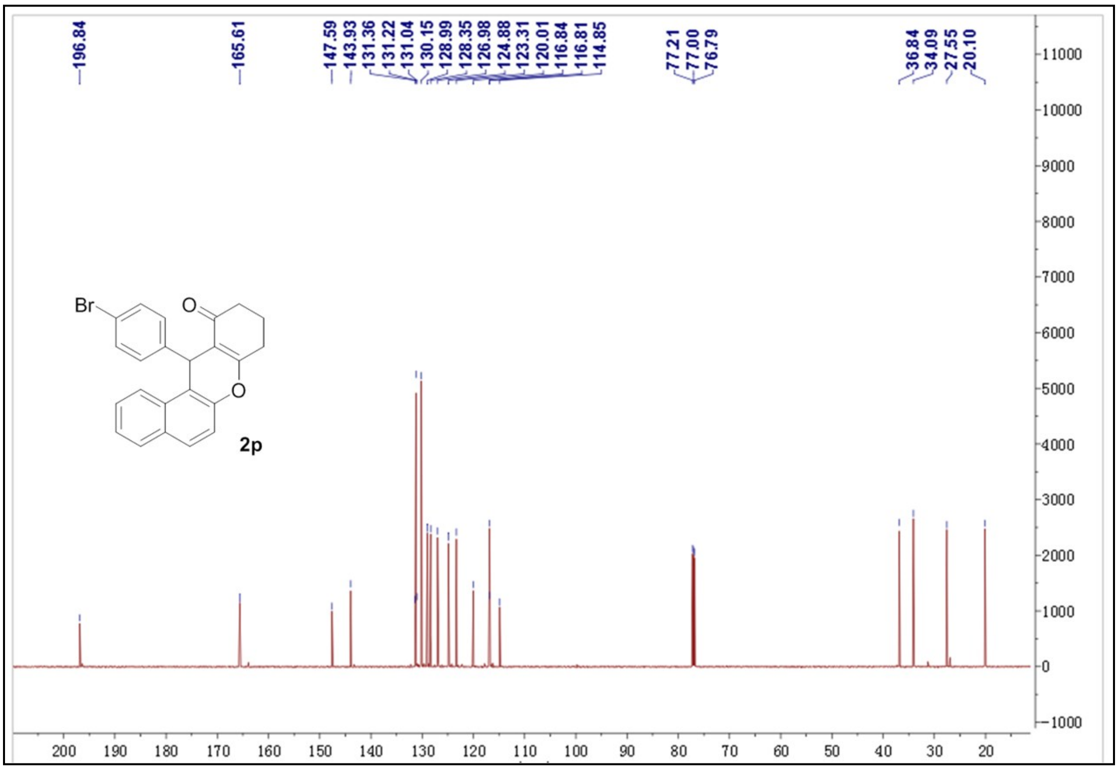
0
−10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124.88
123.31
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116.81
114.85
77.21
77.00
76.79
36.84
34.09
27.55
20.10
Br
O
O
2p
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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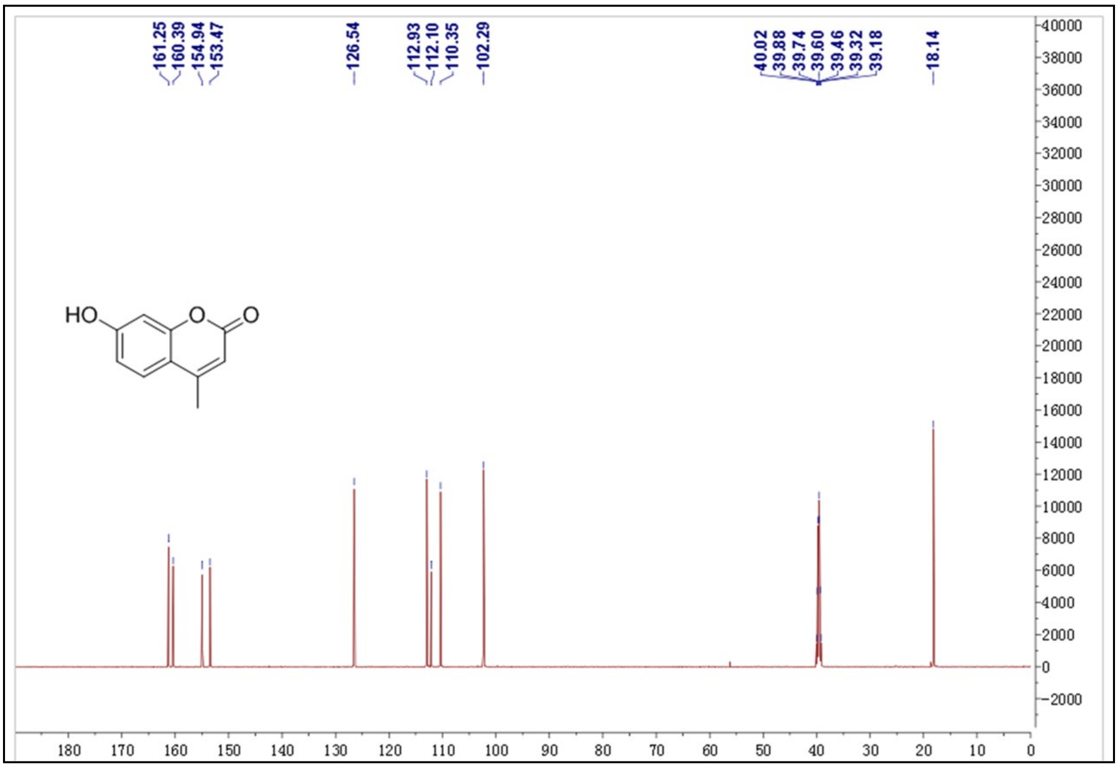
30
20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110.35
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40.02
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39.60
39.46
39.32
39.18
18.14
HO
O
O
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
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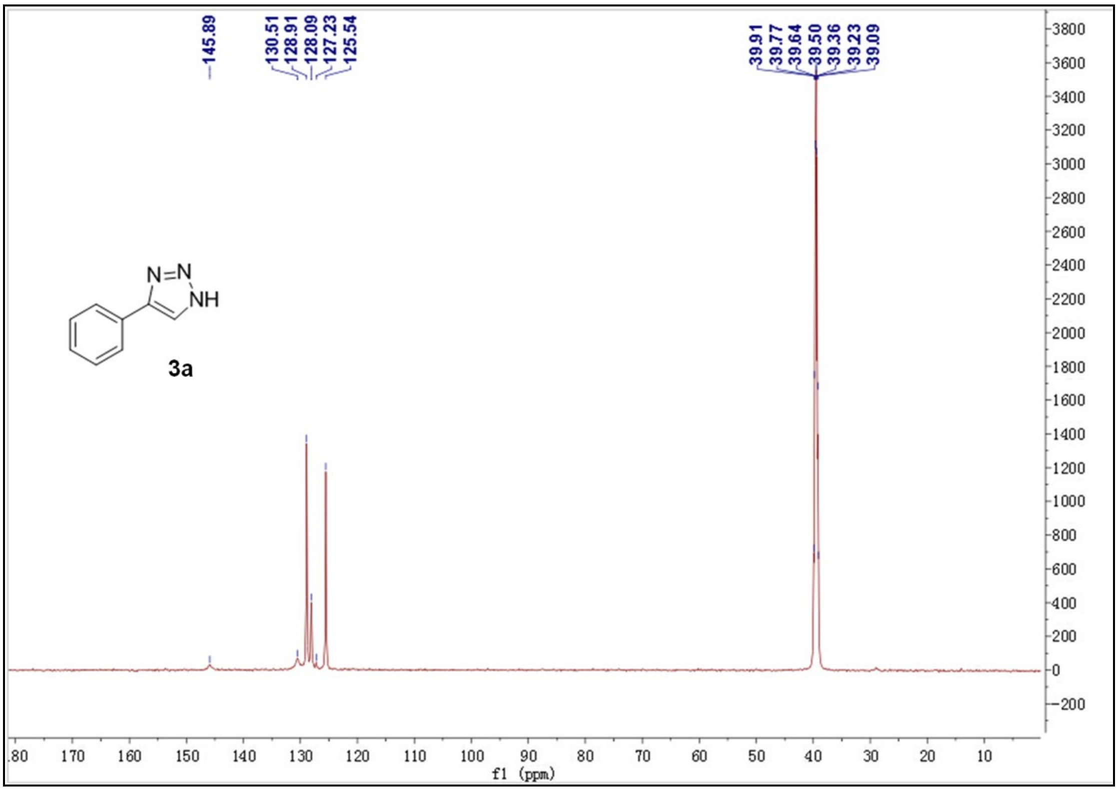
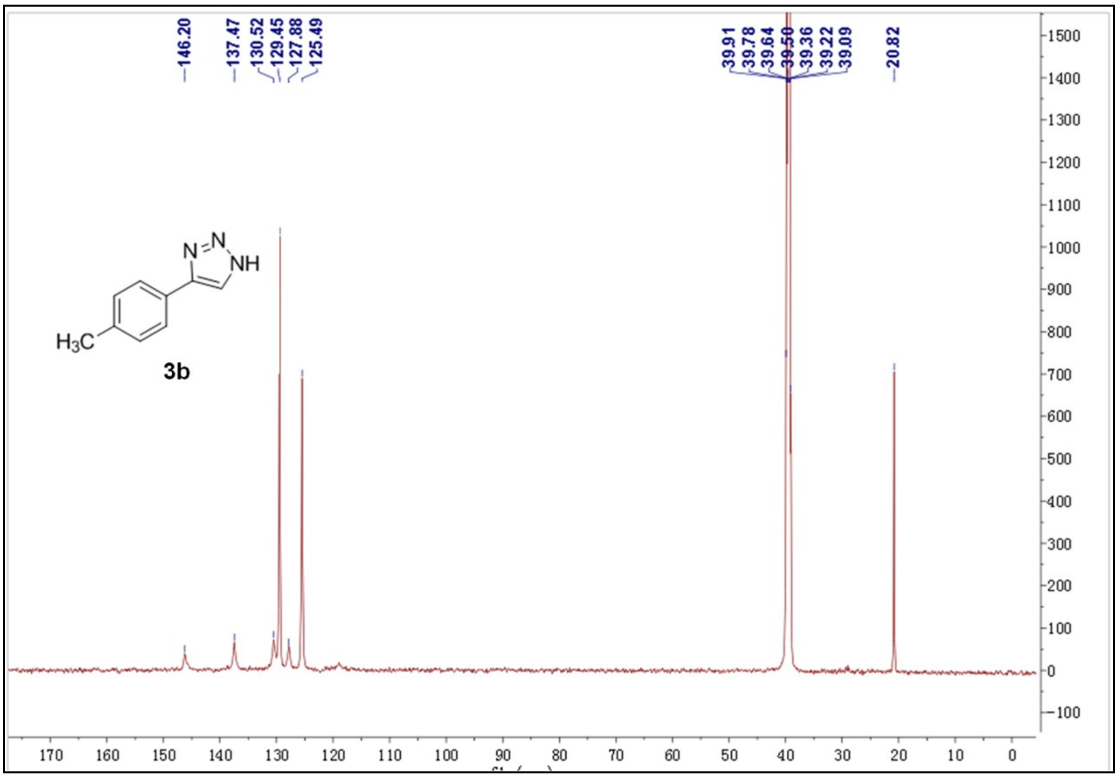
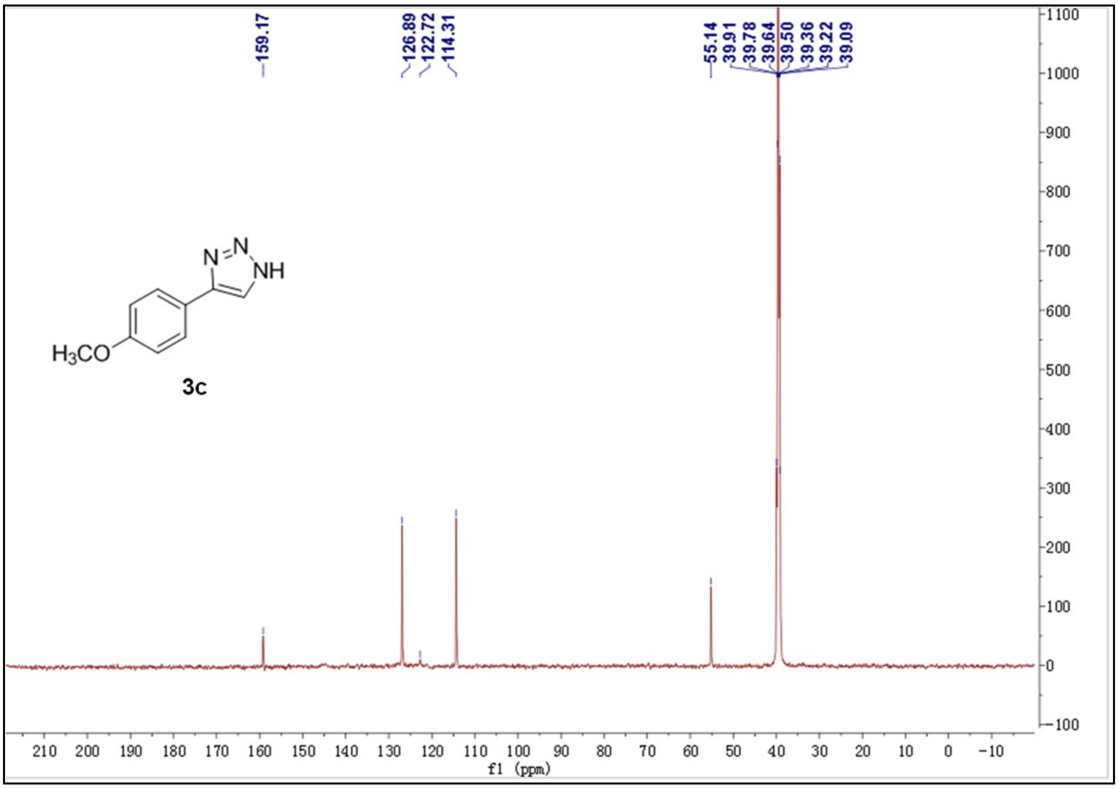
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

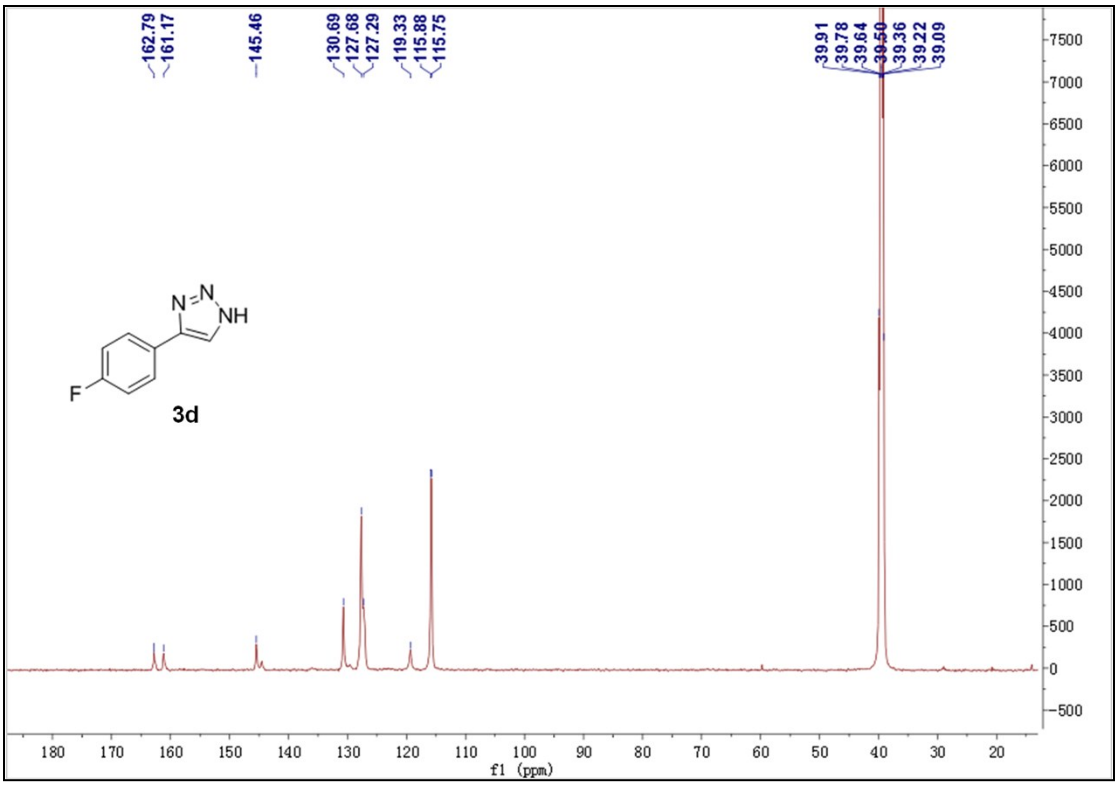

145.89
130.51
128.91
128.09
127.23
125.54
39.91
39.77
39.64
39.50
39.36
39.23
39.09
N=N
NH
3a
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

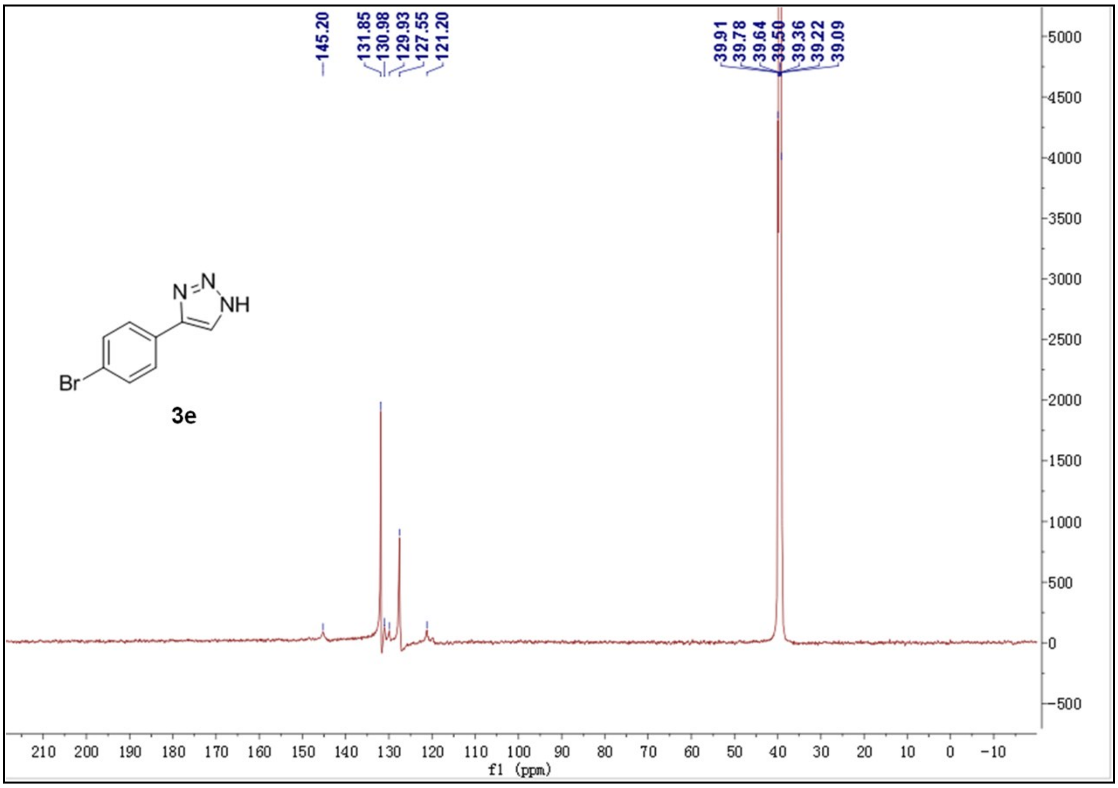


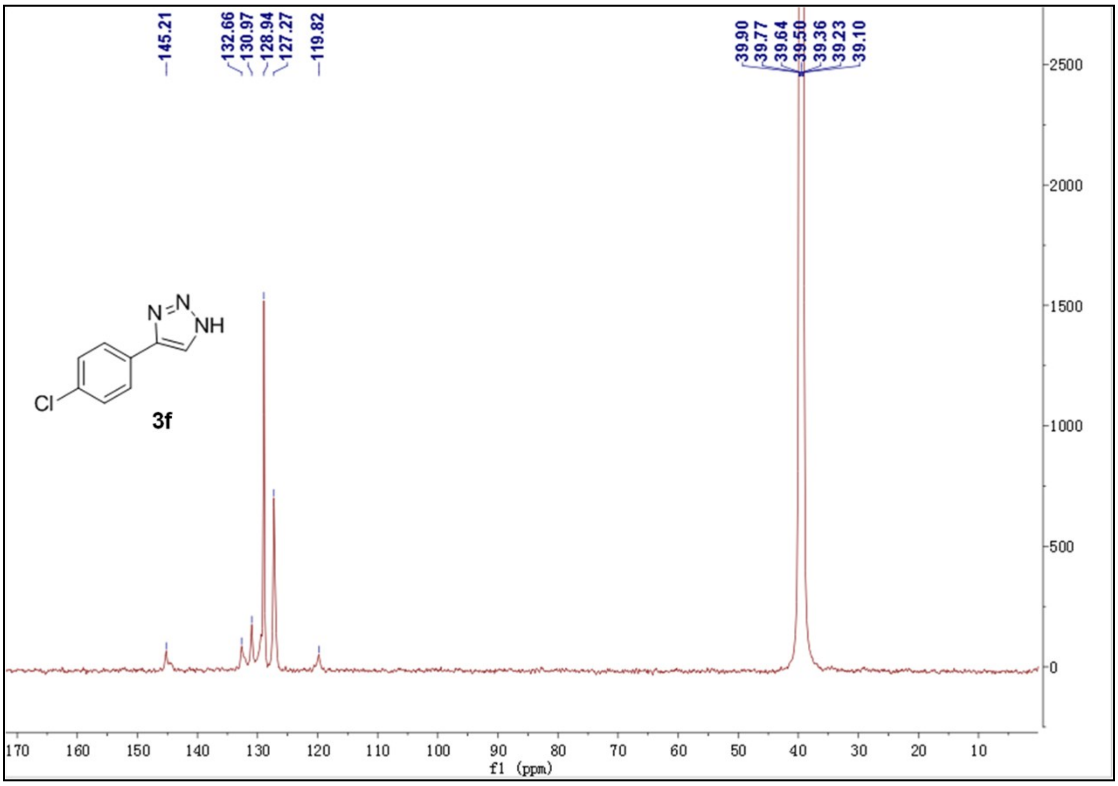
146.20
137.47
130.52
129.45
127.88
125.49
39.91
39.78
39.64
39.50
39.36
39.22
39.09
20.82
N
N
NH
H_3C
3b
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

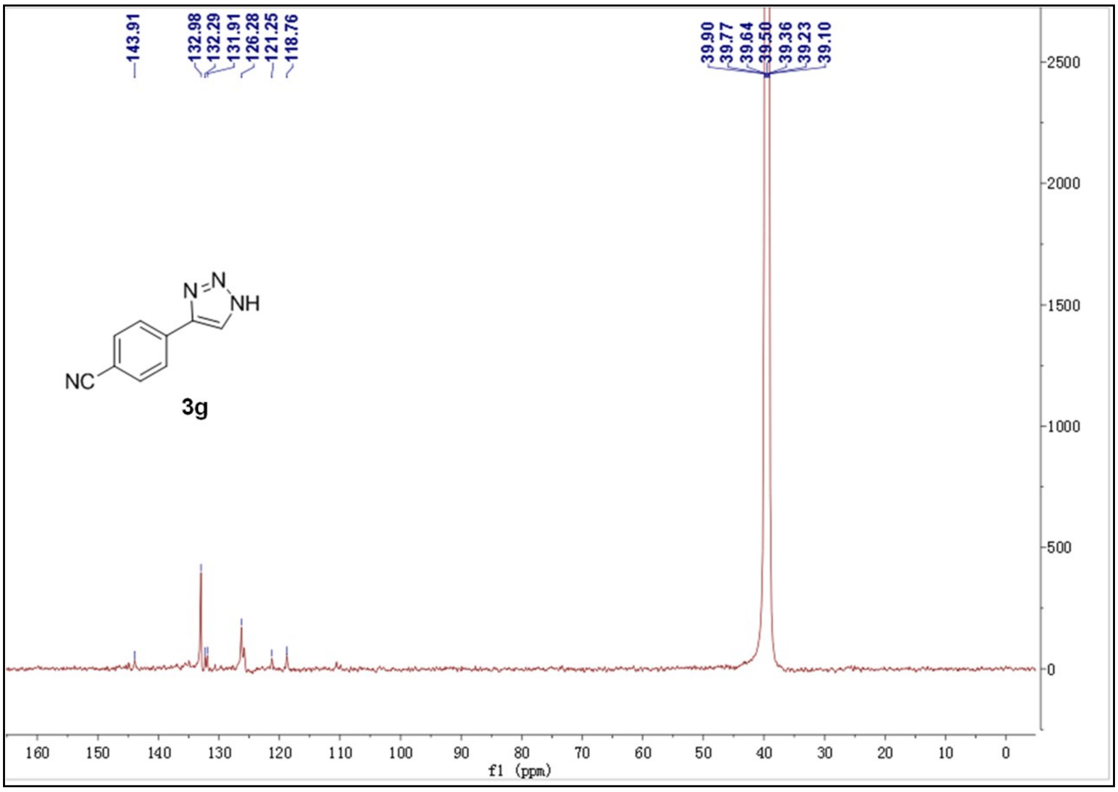


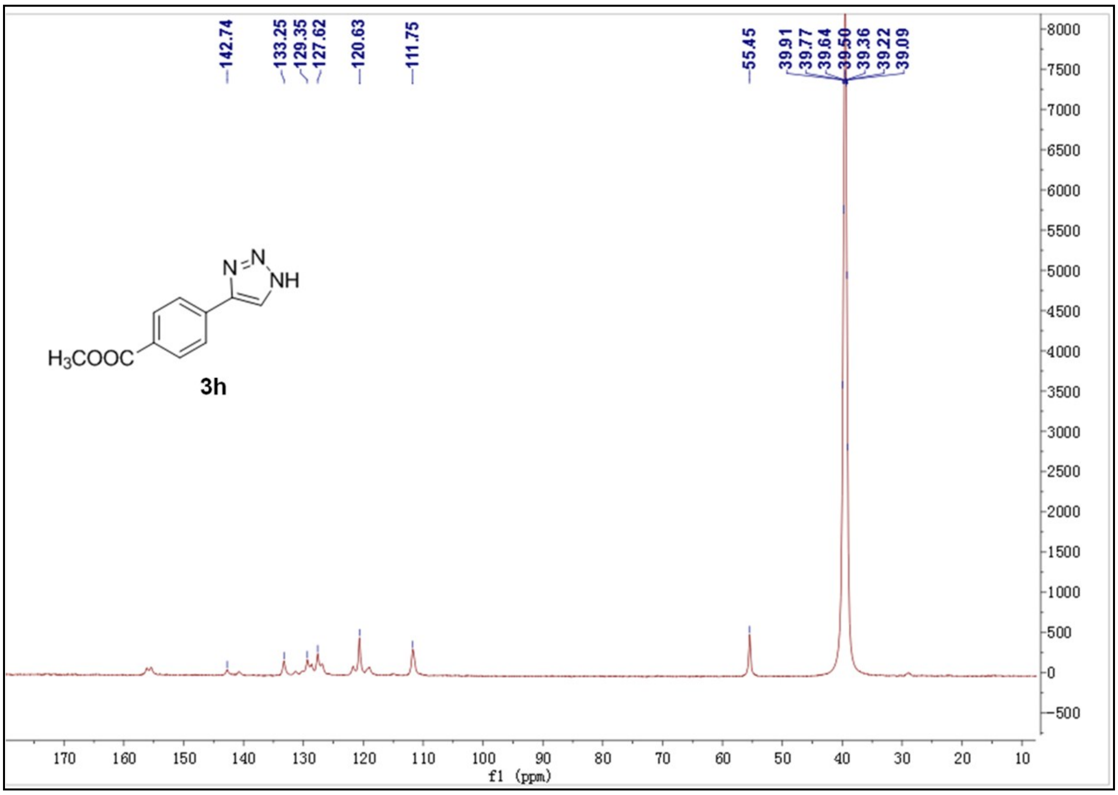
159.17
126.89
122.72
114.31
55.14
39.91
39.78
39.64
39.50
39.36
39.22
39.09
N
N
NH
H_3CO
3c
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


162.79
161.17
145.46
130.69
127.68
127.29
119.33
115.88
115.75
39.91
39.78
39.64
39.50
39.36
39.22
39.09
N
N
NH
F
3d
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

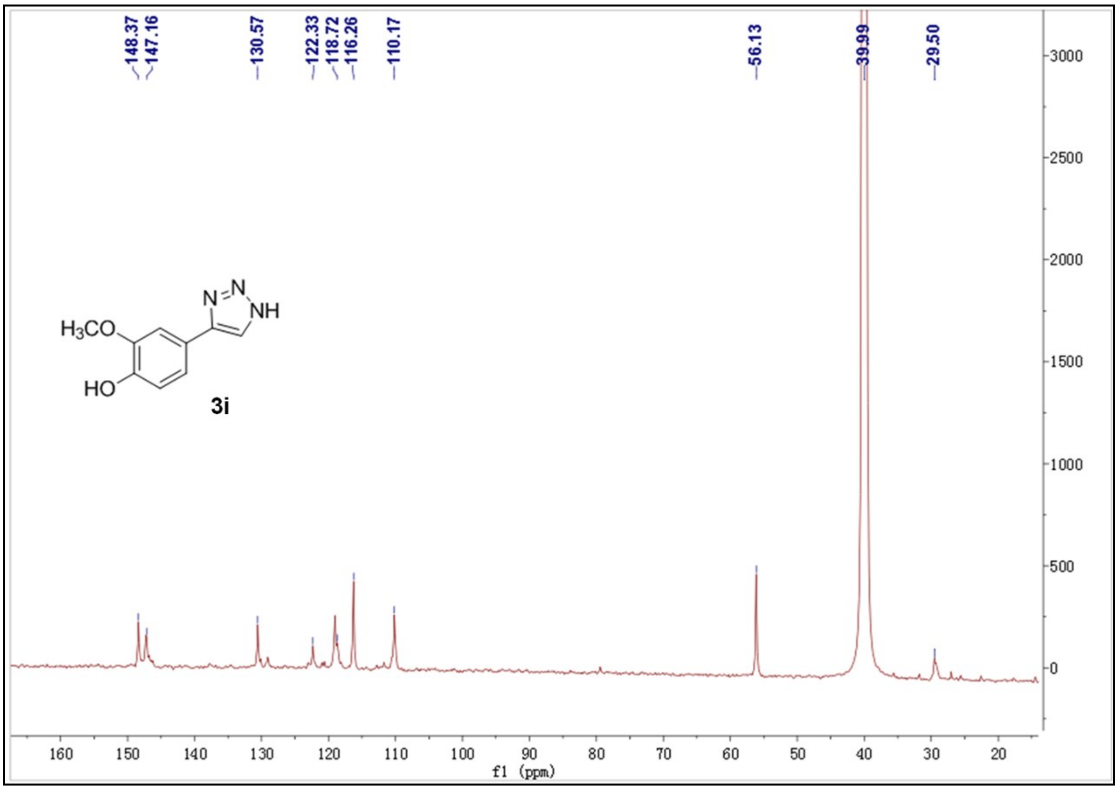

145.20
131.85
130.98
129.93
127.55
121.20
39.91
39.78
39.64
39.50
39.36
39.22
39.09
N
N
NH
Br
3e
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


145.21
132.66
130.97
128.94
127.27
119.82
39.90
39.77
39.64
39.50
39.36
39.23
39.10
N
N
NH
Cl
3f
2500
2000
1500
1000
500
0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


143.91
132.98
132.29
131.91
126.28
121.25
118.76
39.90
39.77
39.64
39.50
39.36
39.23
39.10
N
N
NH
NC
3g
2500
2000
1500
1000
500
0
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


142.74
133.25
129.35
127.62
120.63
111.75
55.45
39.91
39.77
39.64
39.50
39.36
39.22
39.09
N
N
NH
H3COOC
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3h


148.37
147.16
130.57
122.33
118.72
116.26
110.17
56.13
39.99
29.50
N
N
NH
H3CO
HO
3000
2500
2000
1500
1000
500
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

3i