C-4 benzofuranylation of pyrazolones by a metal-free catalyzed indirect heteroarylation strategy

Wande Zhang, Shah Nawaz, Yue Huang, Wenjing Gong, Xingfu Wei, Jingping Qu and Baomin Wang*

State Key Laboratory of Fine Chemicals, Department of Pharmaceutical Sciences, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China. E-mail: bmwang@dlut.edu.cn

Contents

General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions were carried out in Schlenk tube under a nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{19}F NMR spectra were recorded on a Vaian DL G400 400 MHz and Vaian DL G400 377 MHz respectively, ^{13}C NMR spectra were recorded on a Vaian DL G400 101 MHz. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = double doublet, dt = double triplet, td = triple doublet, coupling constants in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). HRMS (ESI) was determined by an HRMS/MS instrument (LTQ Orbitrap XL^{TM}). The crystal structure of **3aa** was determined by the X-ray analysis.

Pyrazolones and 2-(3-hydroxy-3,3-diarylprop-1-yn-1-yl)phenols were prepared according to the literature procedures.[1,2]

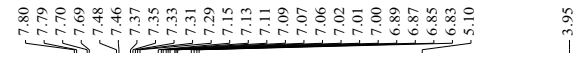
Experimental procedures towards products 3

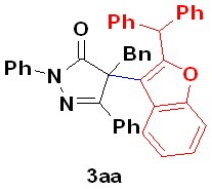
To a stirred solution of pyrazolone **1** (0.36 mmol, 1.2 eq) in toluene (3.0 mL) was added TsOH (0.03 mmol, 0.1 eq) under N_2 at room temperature, and 2-(3-hydroxy-3,3-diarylprop-1-yn-1-yl)phenol **2** was added in batches within 10 minutes after 5 minutes. After the completion of the reaction determined by TLC, the crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 30/1 to 15/1) on neutral alumina to give the product **3**.

References

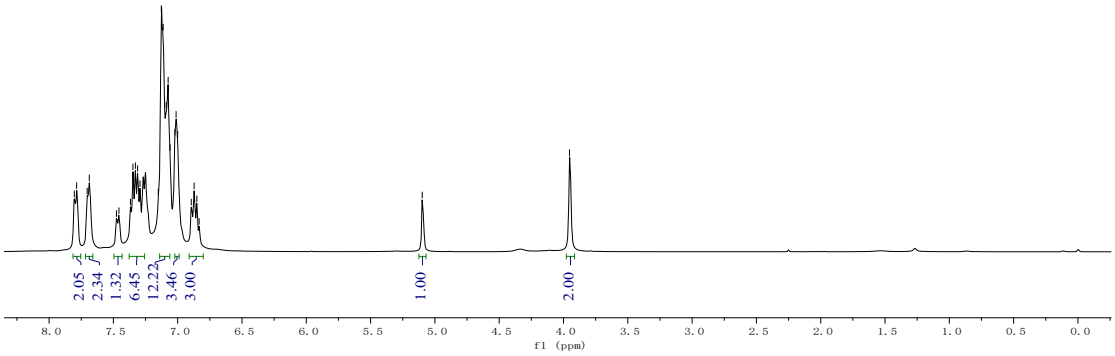
1. (a) M. Kamlar, I. Císařová and J. Veselý, Alkynylation of heterocyclic compounds using hypervalent iodine reagent, *Org. Biomol. Chem.*, 2015, **13**, 2884-2889; (b) X. Sheng, J. Zhang, H. Yang and G. Jiang, Tunable aerobic oxidative hydroxylation/dehydrogenative homocoupling of pyrazol-5-ones under transition-metal-free conditions, *Org. Lett.*, 2017, **19**, 2618-2621.
2. Y. F. Qiu, Y. Y. Ye, X. R. Song, X. Y. Zhu, F. Yang, B. Song, J. Wang, H. L. Hua, Y. T. He, Y. P. Han, X. Y. Liu and Y. M. Liang, Convenient and highly efficient routes to 2H-chromene and 4-chromanone derivatives: Iodine-promoted and *p*-toluenesulfonic acid catalyzed cascade cyclizations of propynols, *Chem. Eur. J.*, 2015, **21**, 3480-3487.

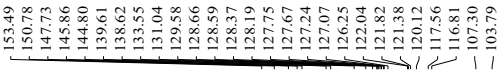
NMR spectra for compounds 3aa-3pa

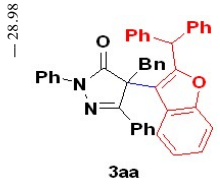




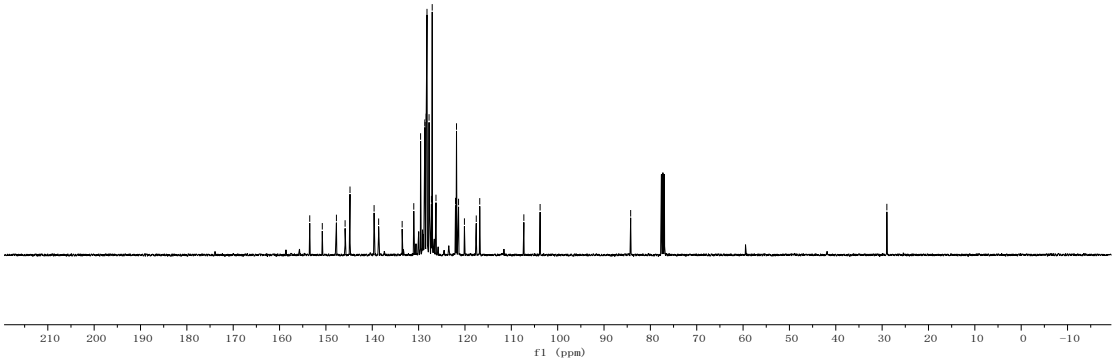
3aa

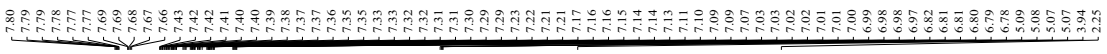


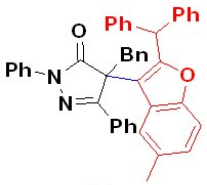




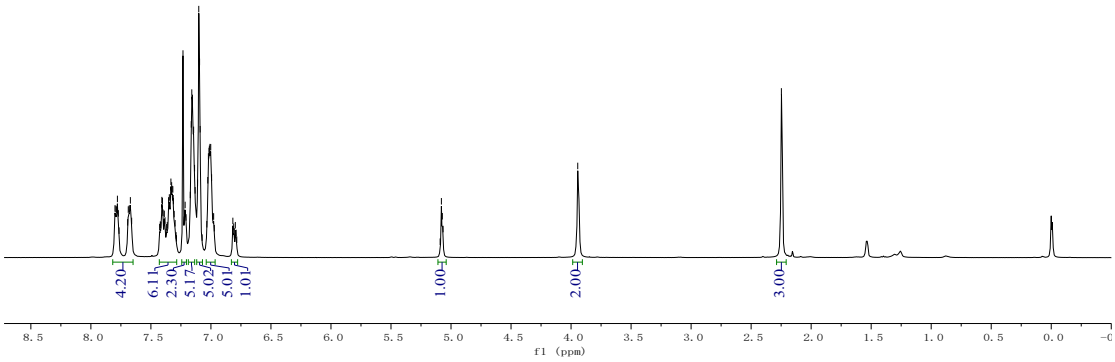
3aa

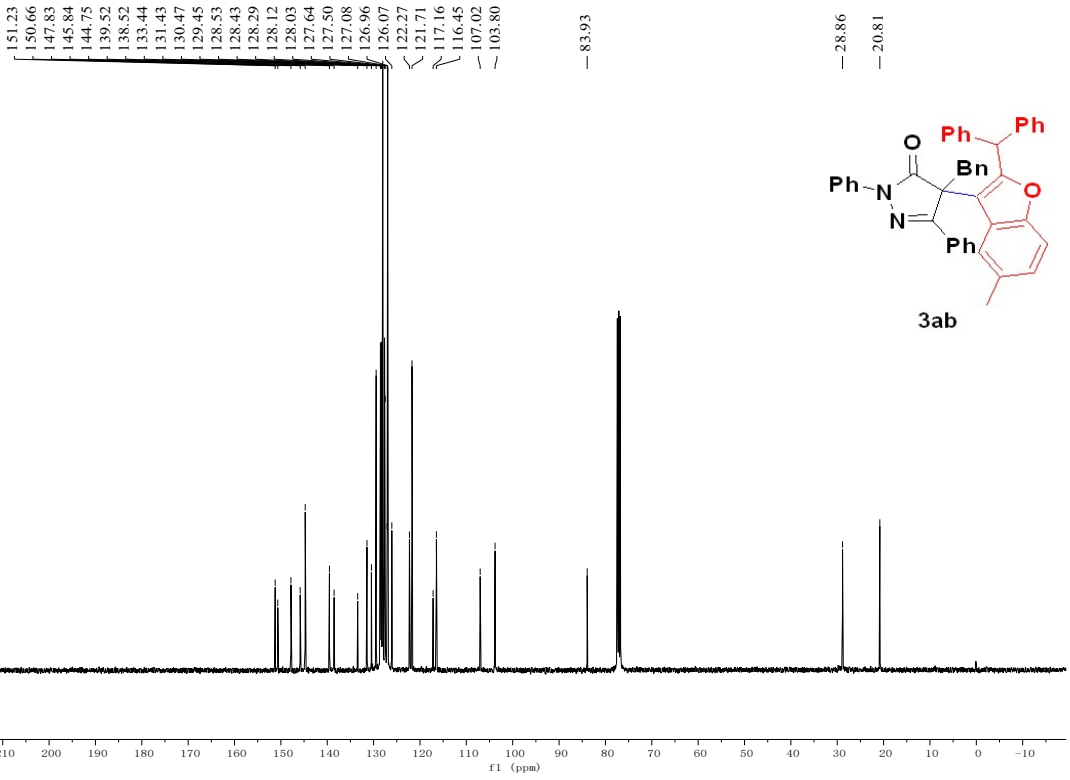



7.80 7.79 7.79 7.78 7.77 7.77 7.69 7.69 7.68 7.67 7.66 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.23 7.22 7.21 7.21 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.11 7.10 7.09 7.09 7.07 7.03 7.02 7.02 7.01 7.01 7.00 6.99 6.98 6.98 6.97 6.82 6.81 6.81 6.80 6.79 6.78 5.09 5.08 5.07 5.07 3.94 2.25


O
Ph
Ph
Bn
Ph
N
N
Ph
O

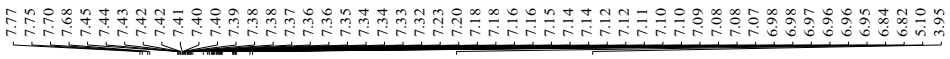
3ab

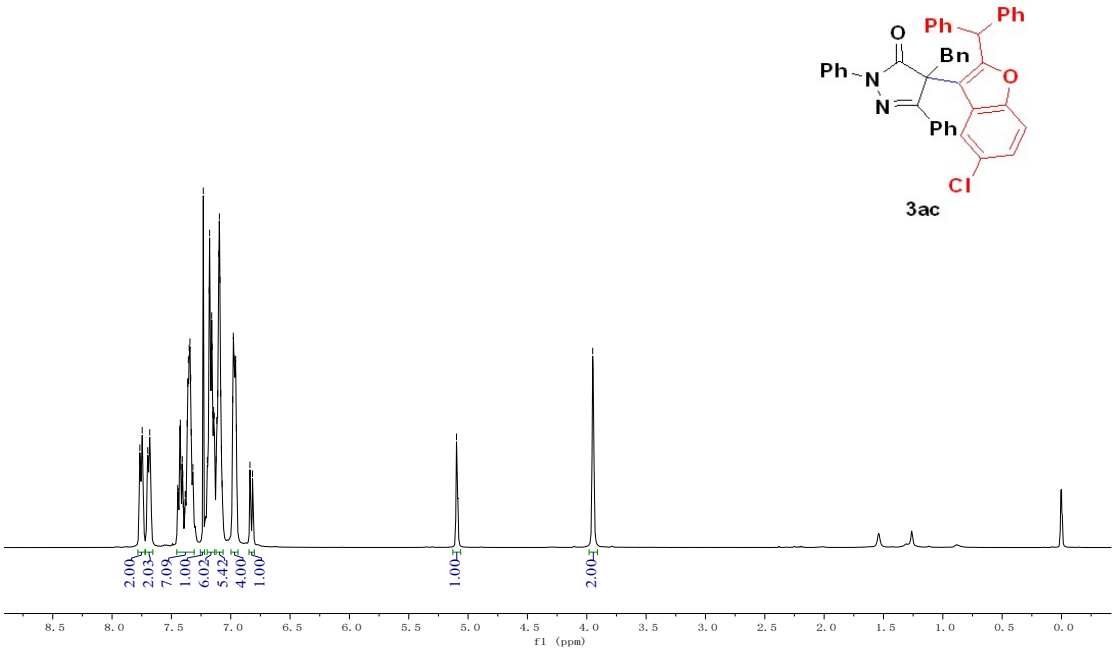

4.20
6.11
2.30
5.17
5.02
5.01
1.01
1.00
2.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

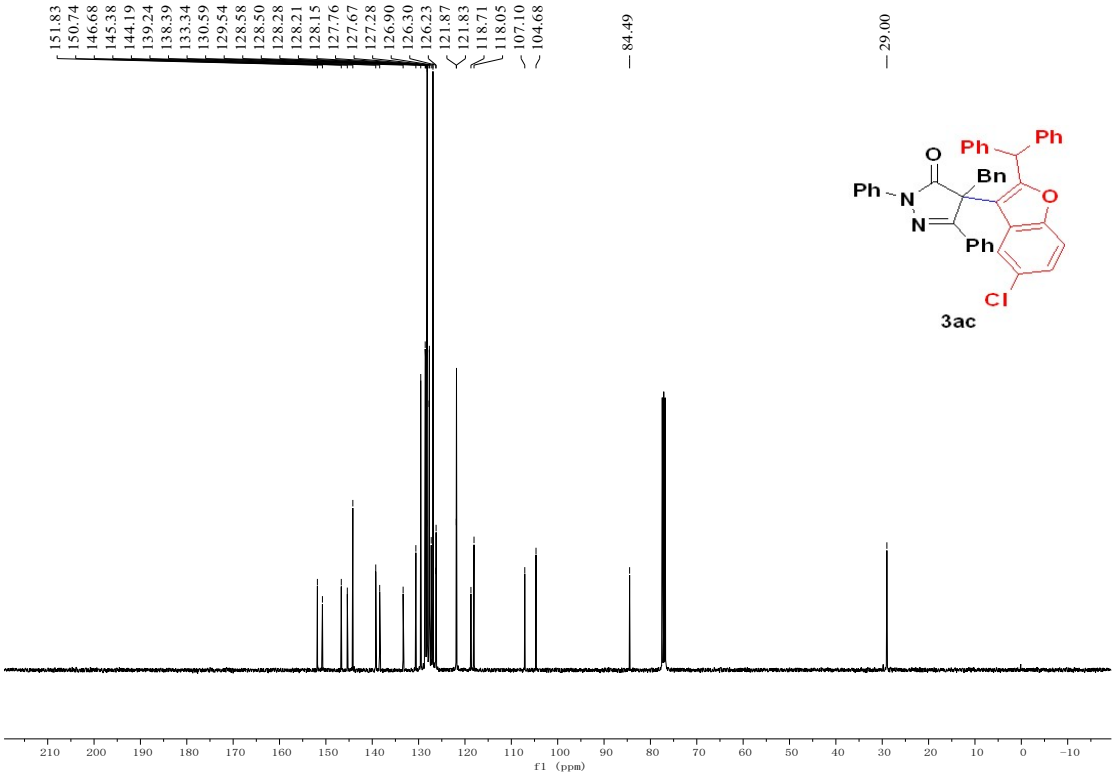

151.23
150.66
147.83
145.84
144.75
139.52
138.52
133.44
131.43
130.47
129.45
128.53
128.43
128.29
128.12
128.03
127.64
127.50
127.08
126.96
126.07
122.27
121.71
117.16
116.45
107.02
103.80
83.93
28.86
20.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

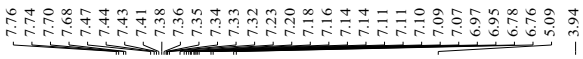
O
Ph
Ph
Bn
Ph
N
N
Ph
O

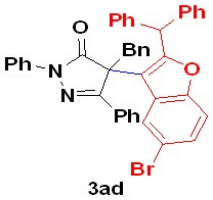
3ab


7.77
7.75
7.70
7.68
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.23
7.20
7.18
7.18
7.16
7.16
7.15
7.14
7.14
7.12
7.12
7.11
7.10
7.10
7.09
7.08
7.08
7.07
6.98
6.98
6.97
6.96
6.96
6.95
6.84
6.82
5.10
3.95

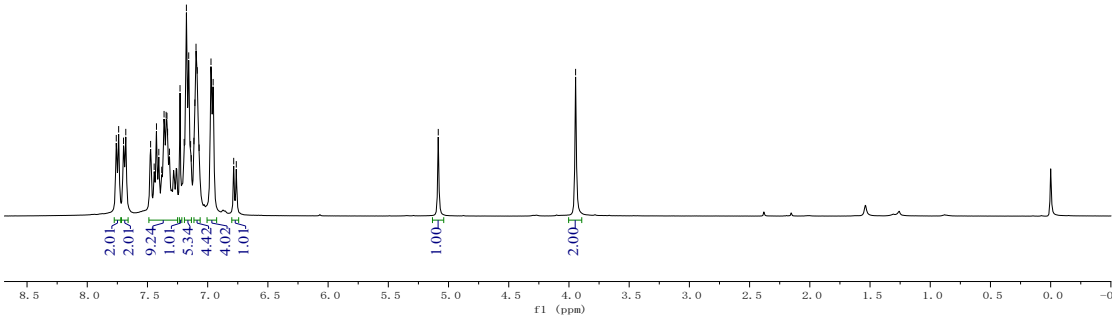

O
Ph
Ph
Bn
Ph
N
N
O
Ph
Cl
3ac
2.00
2.03
7.09
1.00
6.02
5.42
4.00
1.00
1.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

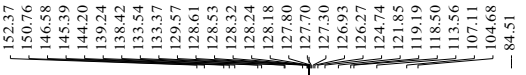

151.83
150.74
146.68
145.38
144.19
139.24
138.39
133.34
130.59
129.54
128.58
128.50
128.28
128.21
128.15
127.76
127.67
127.28
126.90
126.30
126.23
121.87
121.83
118.71
118.05
107.10
104.68
84.49
29.00
O
Ph
Ph
Bn
Ph
N
N
O
Ph
Cl
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.76
7.74
7.70
7.68
7.47
7.44
7.43
7.41
7.38
7.36
7.35
7.34
7.33
7.32
7.23
7.20
7.18
7.16
7.14
7.14
7.11
7.11
7.10
7.09
7.07
6.97
6.95
6.78
6.76
5.09
3.94

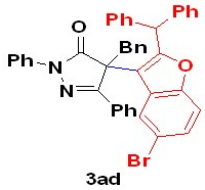

O
Ph
Ph
Bn
Ph
N
N
O
Ph
Br

3ad

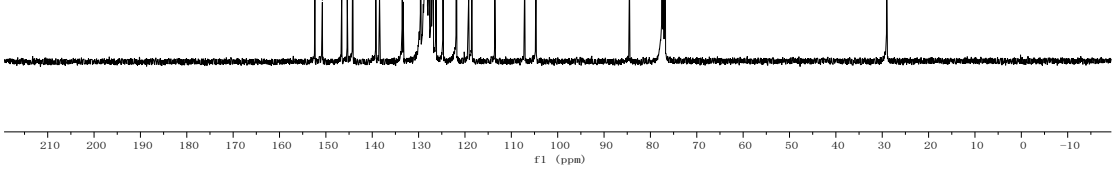

2.01
2.01
9.24
1.01
5.34
4.42
4.02
1.01
1.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

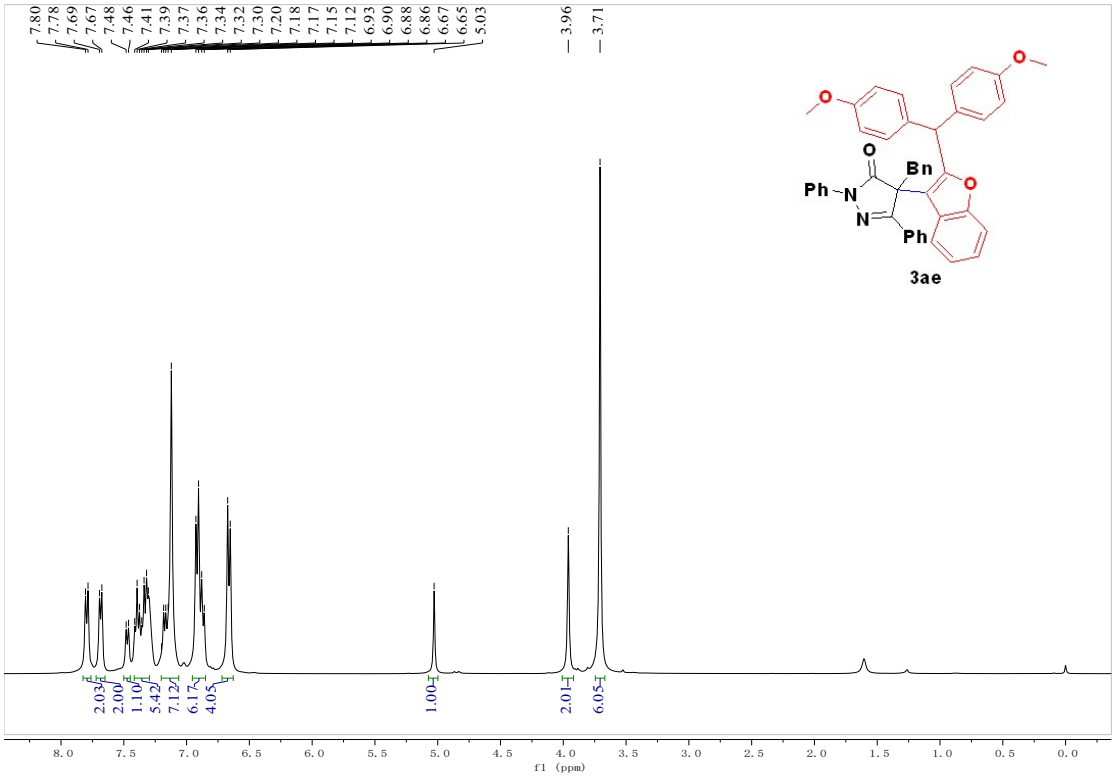

152.37
150.76
146.58
145.39
144.20
139.24
138.42
133.54
133.37
129.57
128.61
128.53
128.32
128.24
128.18
127.80
127.70
127.30
126.93
126.27
124.74
121.85
119.19
118.50
113.56
107.11
104.68
84.51

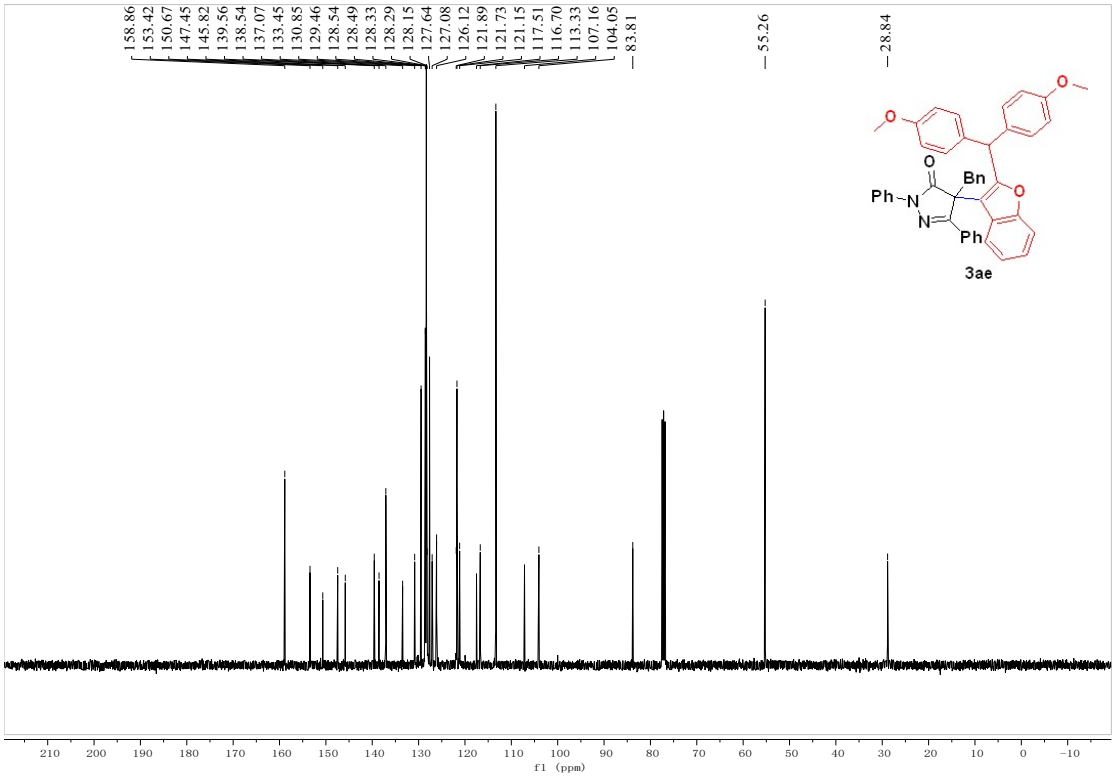

29.05

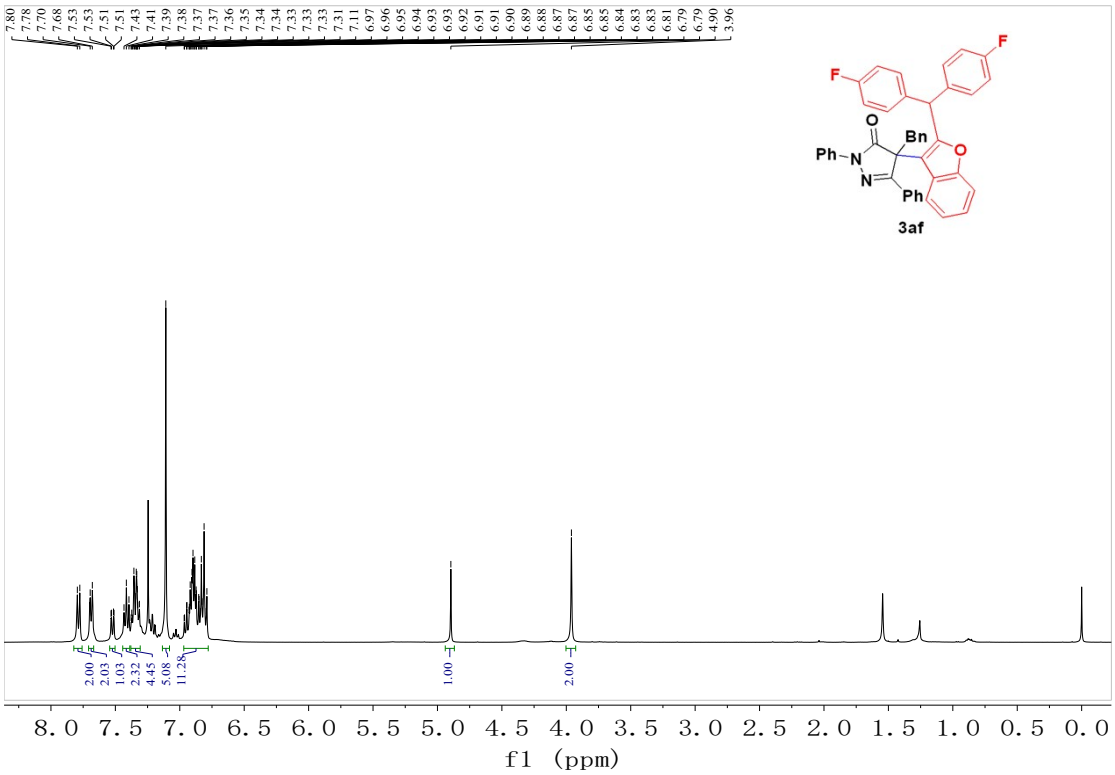

O
Ph
Ph
Bn
Ph
N
N
O
Ph
Br

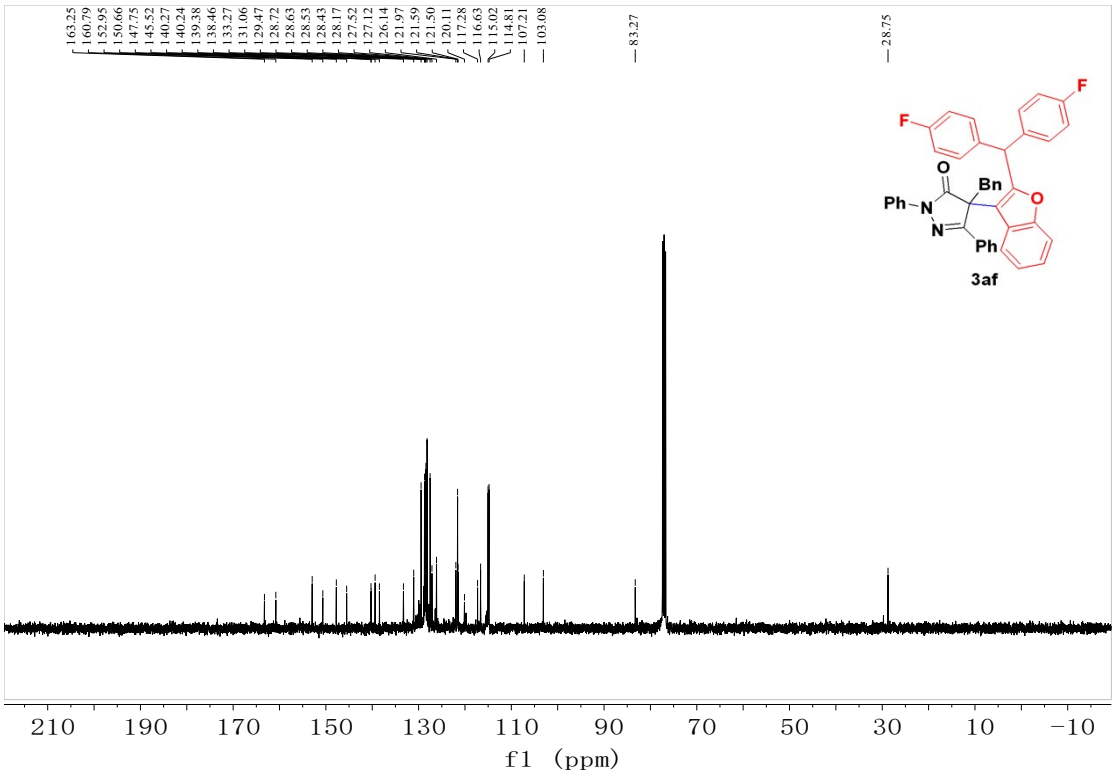
3ad

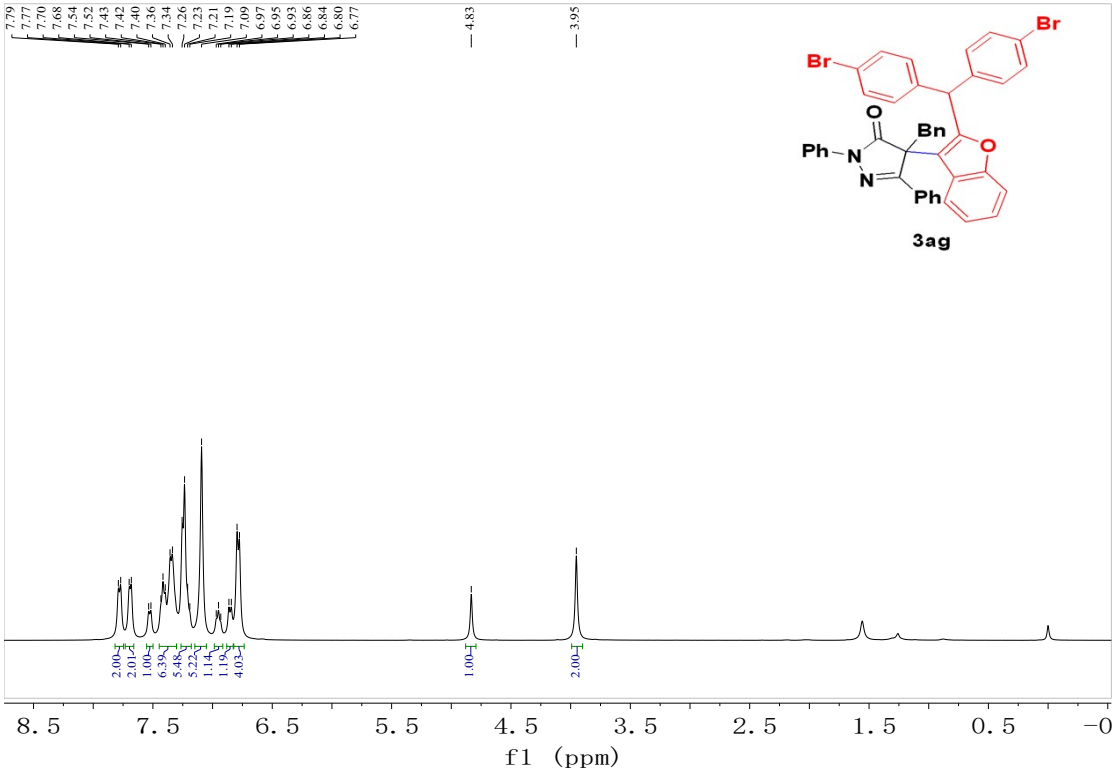

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

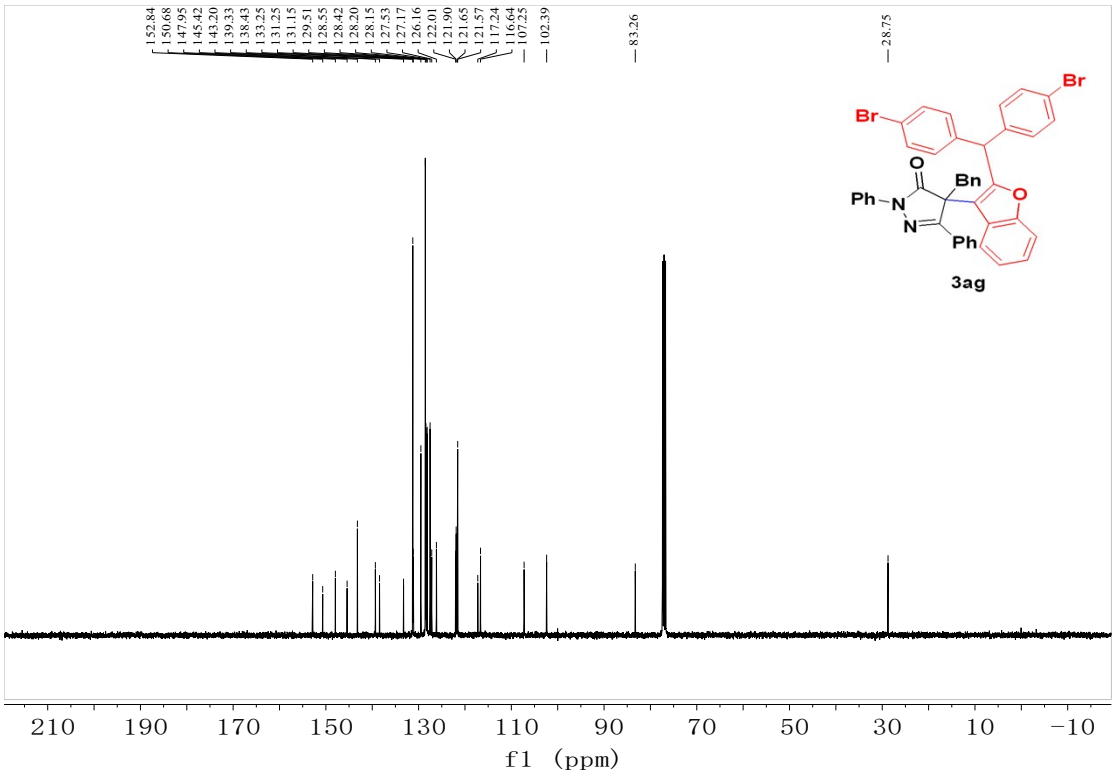

7.80
7.78
7.69
7.67
7.48
7.46
7.41
7.39
7.37
7.36
7.34
7.32
7.30
7.20
7.18
7.17
7.15
7.12
6.93
6.90
6.88
6.86
6.67
6.65
5.03
3.96
3.71
2.03
2.00
1.10
5.42
7.12
6.17
4.05
1.00
2.01
6.05
f1 (ppm)
Ph
N
N
O
Bn
O
Ph
O
O
3ae

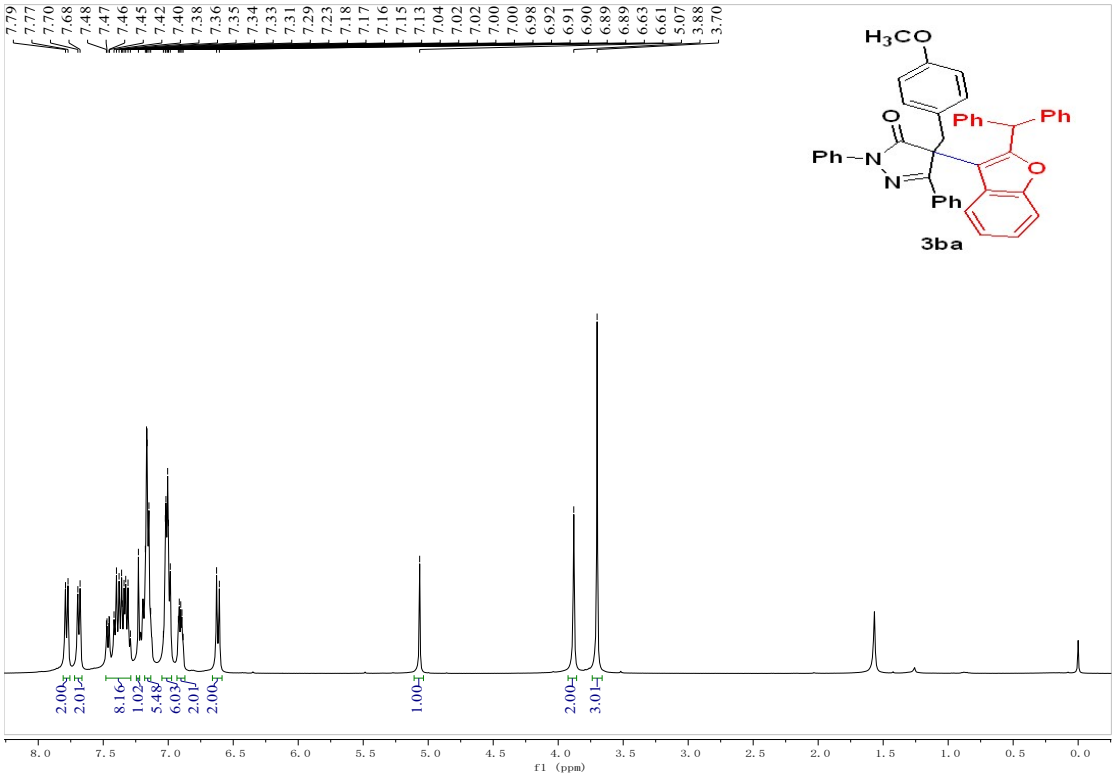

158.86
153.42
150.67
147.45
145.82
139.56
138.54
137.07
133.45
130.85
129.46
128.54
128.49
128.33
128.29
128.15
127.64
127.08
126.12
121.89
121.73
121.15
117.51
116.70
113.33
107.16
104.05
83.81
55.26
28.84
f1 (ppm)
Ph
N
N
O
Bn
O
Ph
O
O
3ae

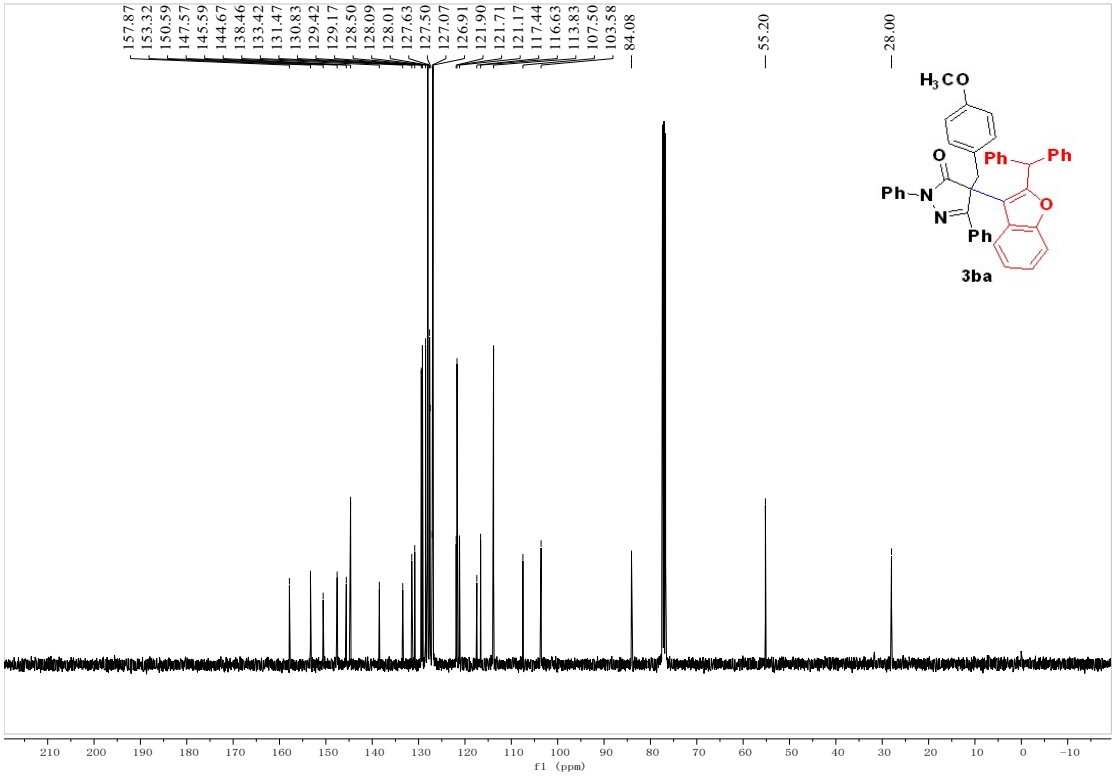

7.80
7.78
7.70
7.68
7.53
7.53
7.51
7.51
7.43
7.41
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.31
7.11
6.97
6.96
6.95
6.94
6.93
6.93
6.92
6.91
6.91
6.90
6.89
6.88
6.87
6.87
6.85
6.85
6.84
6.83
6.83
6.81
6.79
6.79
4.90
3.96
2.00
2.03
1.03
2.32
4.45
5.08
11.28
1.00
2.00
F
F
O
Bn
Ph
N
N
O
Ph
3af
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)

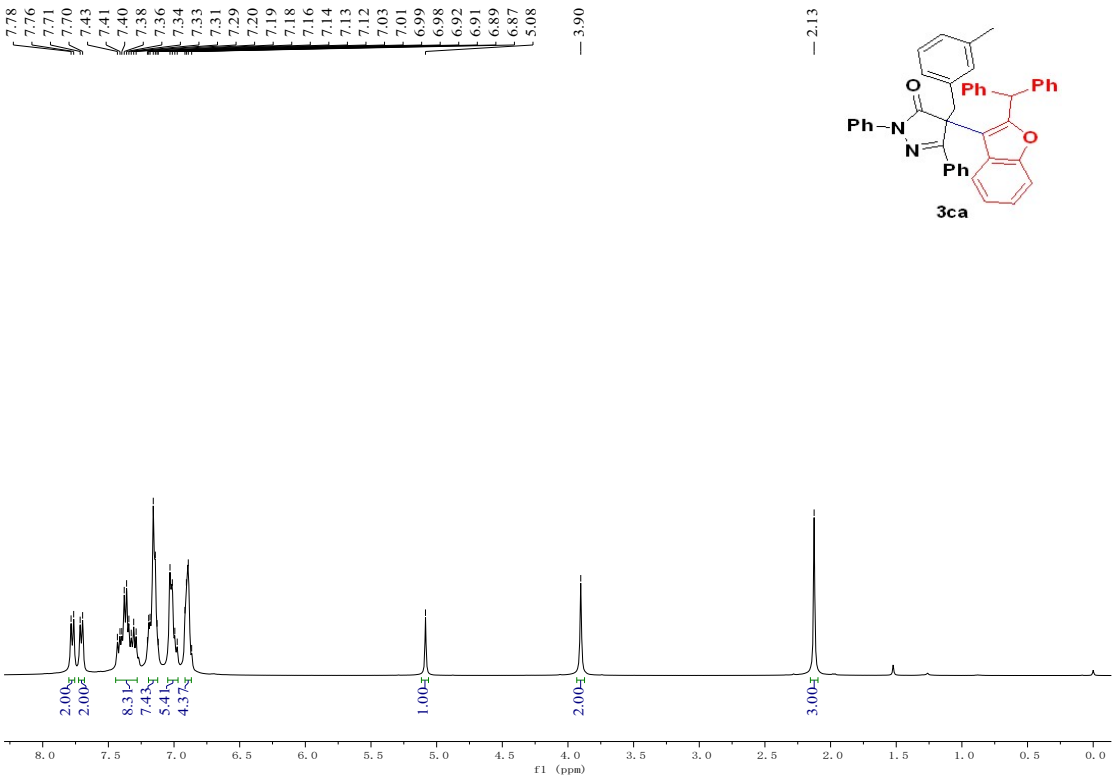

163.25
160.79
152.95
150.66
147.75
145.52
140.27
140.24
139.38
138.46
133.27
131.06
129.47
128.72
128.63
128.53
128.43
128.17
127.52
127.12
126.14
121.97
121.59
121.50
120.11
117.28
116.63
115.02
114.81
107.21
103.08
83.27
28.75
F
F
O
Bn
Ph
N
N
O
Ph
3af
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

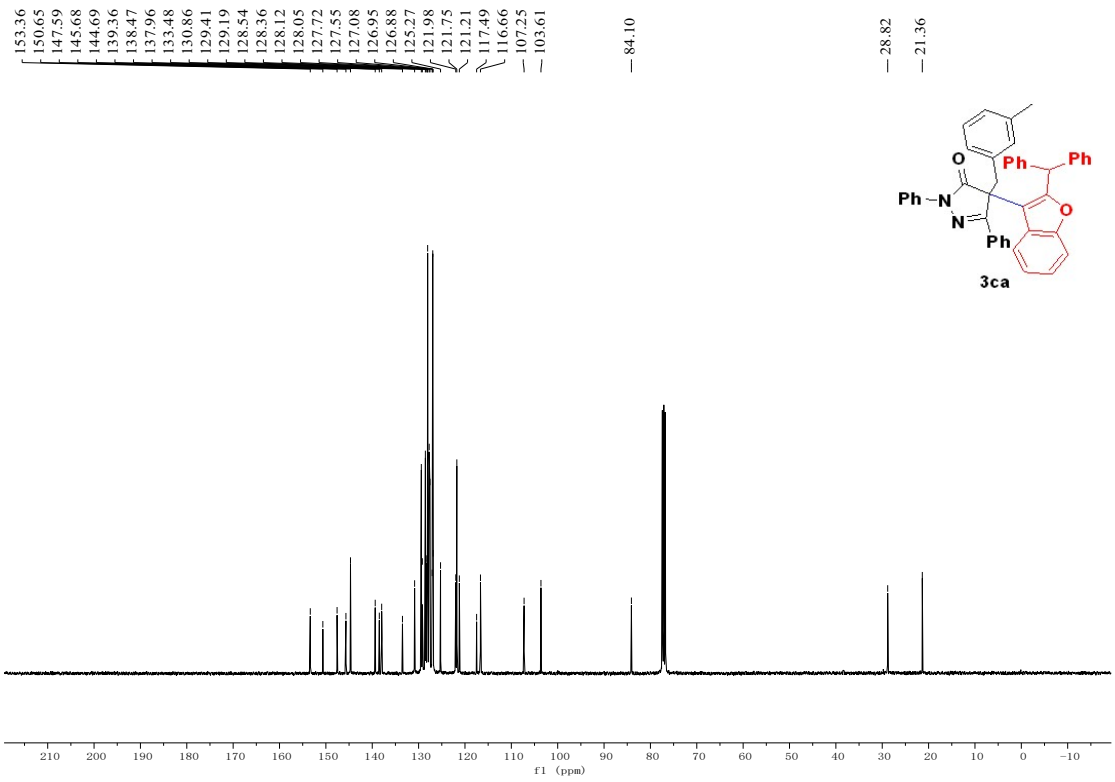

7.79
7.77
7.70
7.68
7.54
7.52
7.43
7.42
7.40
7.36
7.34
7.26
7.23
7.21
7.19
7.09
6.97
6.95
6.93
6.86
6.84
6.80
6.77
4.83
3.95
2.00
2.01
1.00
6.39
5.48
5.22
1.14
1.19
4.03
1.00
2.00
Br
Br
O
Bn
Ph
N
N
O
Ph
3ag
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0
f1 (ppm)

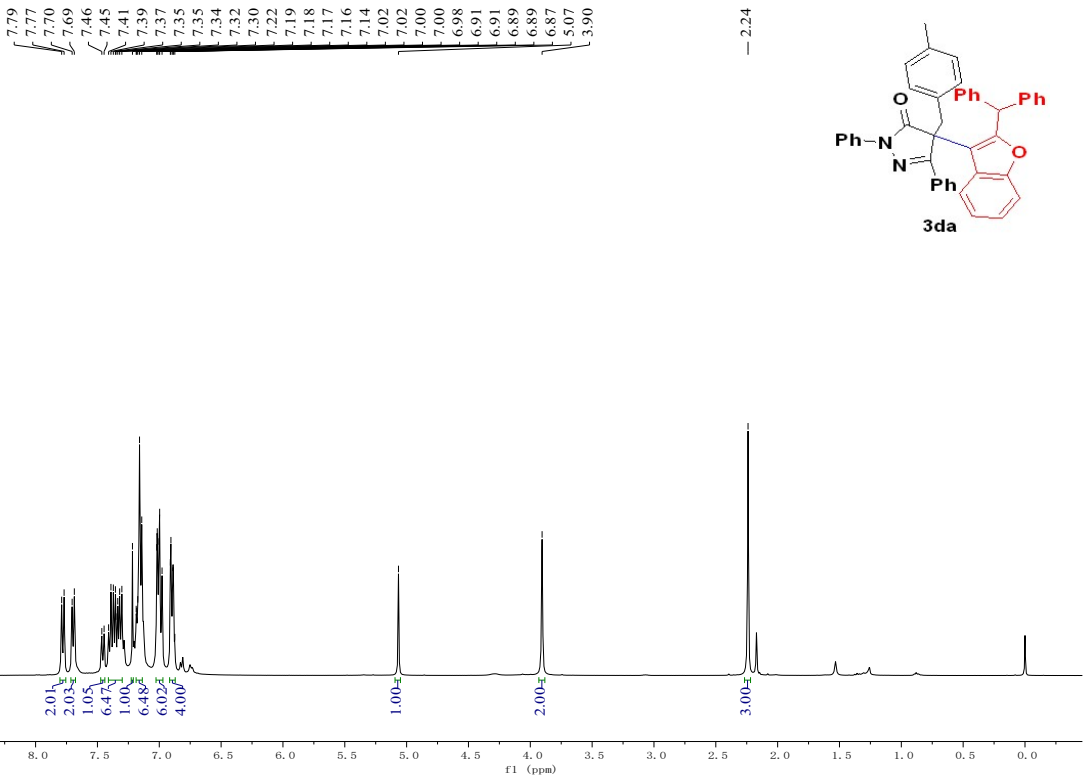

152.84
150.68
147.95
145.42
143.20
139.33
138.43
133.25
131.25
131.15
129.51
128.55
128.42
128.20
128.15
127.53
127.17
126.16
122.01
121.90
121.65
121.57
117.24
116.64
107.25
102.39
83.26
28.75
Br
Br
O
Bn
Ph
N
N
O
Ph
3ag
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)

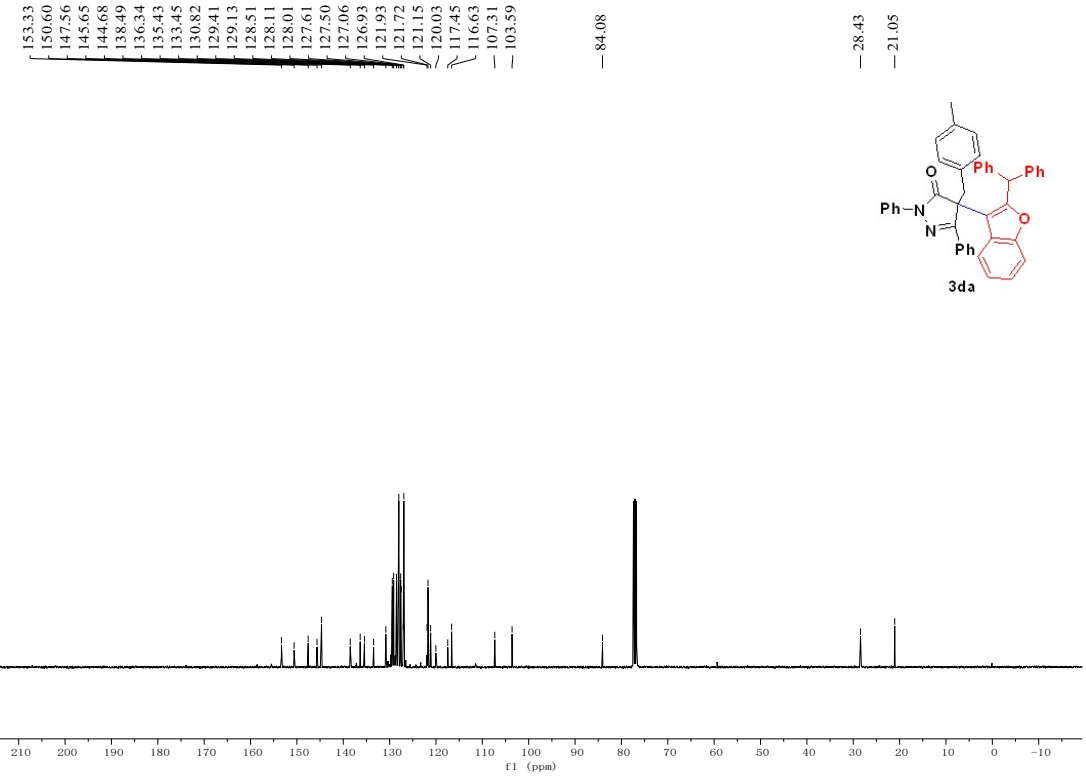

7.79 7.77 7.70 7.68 7.48 7.47 7.46 7.45 7.42 7.40 7.38 7.36 7.35 7.34 7.33 7.31 7.29 7.23 7.18 7.17 7.16 7.15 7.13 7.04 7.02 7.02 7.00 7.00 6.98 6.92 6.91 6.90 6.89 6.89 6.63 6.61 5.07 3.88 3.70
H3CO
Ph
Ph
O
Ph
N
N
Ph
O
3ba
2.00 2.01 8.16 1.02 5.48 6.03 2.01 2.00 1.00 2.00 3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

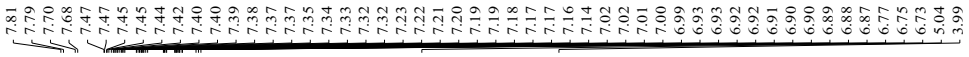

157.87 153.32 150.59 147.57 145.59 144.67 138.46 133.42 131.47 130.83 129.42 129.17 128.50 128.09 128.01 127.63 127.50 127.07 126.91 121.90 121.71 121.17 117.44 116.63 113.83 107.50 103.58 84.08 55.20 28.00
H3CO
Ph
Ph
O
Ph
N
N
Ph
O
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

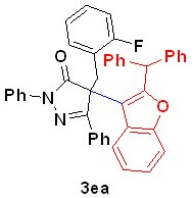

7.78
7.76
7.71
7.70
7.43
7.41
7.40
7.38
7.36
7.34
7.33
7.31
7.29
7.20
7.19
7.18
7.16
7.14
7.13
7.12
7.03
7.01
6.99
6.98
6.92
6.91
6.89
6.87
5.08
3.90
2.13
Ph
Ph
O
Ph–N
N
Ph
O
3ca
2.00
2.00
8.31
7.43
5.41
4.37
1.00
2.00
3.00
f1 (ppm)


153.36
150.65
147.59
145.68
144.69
139.36
138.47
137.96
133.48
130.86
129.41
129.19
128.54
128.36
128.12
128.05
127.72
127.55
127.08
126.95
126.88
125.27
121.98
121.75
121.21
117.49
116.66
107.25
103.61
84.10
28.82
21.36
Ph
Ph
O
Ph–N
N
Ph
O
3ca
f1 (ppm)

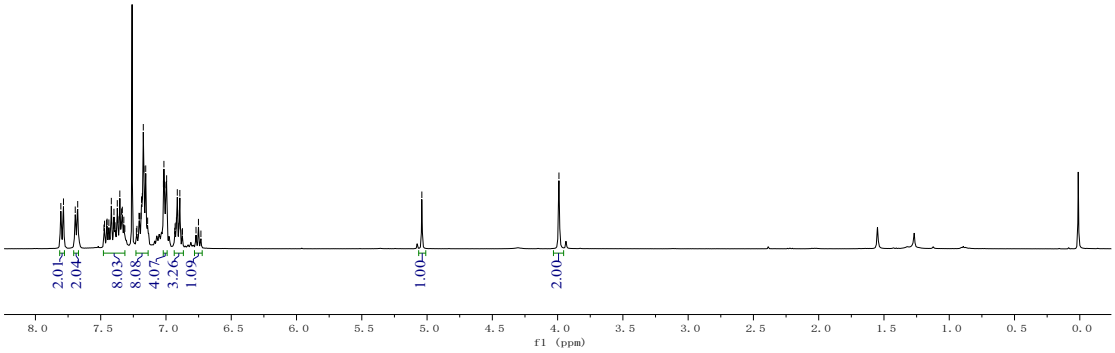

7.79
7.77
7.70
7.69
7.46
7.45
7.41
7.39
7.37
7.35
7.35
7.34
7.32
7.30
7.22
7.19
7.18
7.17
7.16
7.14
7.02
7.02
7.00
7.00
6.98
6.91
6.91
6.89
6.89
6.87
5.07
3.90
2.24
Ph
Ph
O
Ph–N
N
Ph
O
3da
2.01
2.03
1.05
6.47
1.00
6.48
6.02
4.00
1.00
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

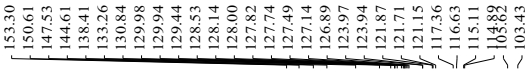

153.33
150.60
147.56
145.65
144.68
138.49
136.34
135.43
133.45
130.82
129.41
129.13
128.51
128.11
128.01
127.61
127.50
127.06
126.93
121.93
121.72
121.15
120.03
117.45
116.63
107.31
103.59
84.08
28.43
21.05
Ph
Ph
O
Ph–N
N
Ph
O
3da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.81
7.79
7.70
7.68
7.47
7.47
7.45
7.45
7.44
7.42
7.40
7.40
7.39
7.38
7.37
7.37
7.35
7.34
7.33
7.32
7.32
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.14
7.02
7.02
7.01
7.00
6.99
6.93
6.93
6.92
6.92
6.91
6.90
6.90
6.89
6.88
6.87
6.77
6.75
6.73
5.04
3.99

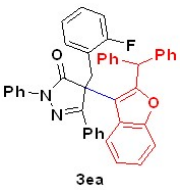

F
Ph
Ph
O
Ph
N
N
O
Ph

3ea

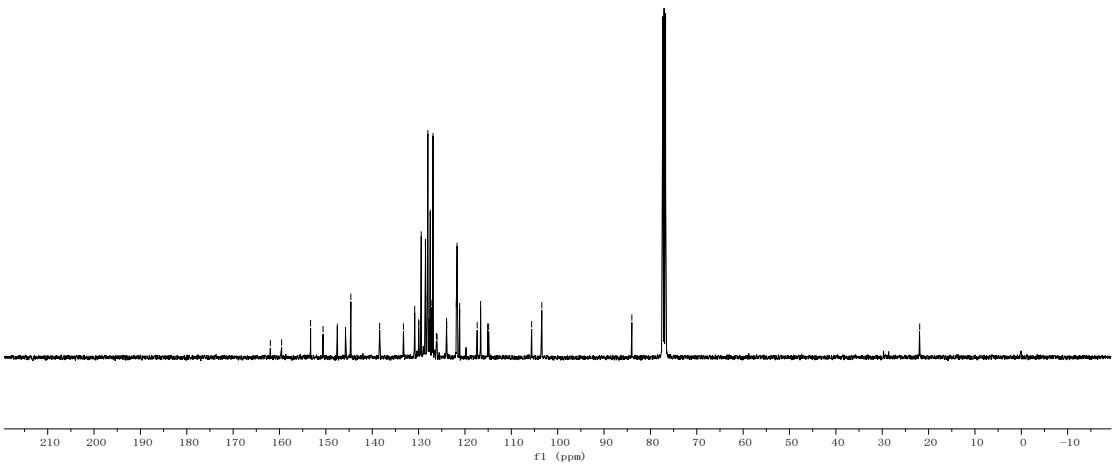

2.01
2.04
8.03
8.08
4.07
3.26
1.09
1.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

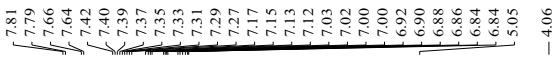

153.30
150.61
147.53
144.61
138.41
133.26
130.84
129.98
129.94
129.44
128.53
128.14
128.00
127.82
127.74
127.49
127.14
126.89
123.97
123.94
121.87
121.71
121.15
117.36
116.63
115.11
114.89
105.82
103.43

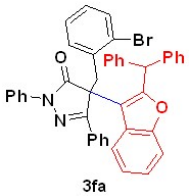

84.01
21.92


F
Ph
Ph
O
Ph
N
N
O
Ph

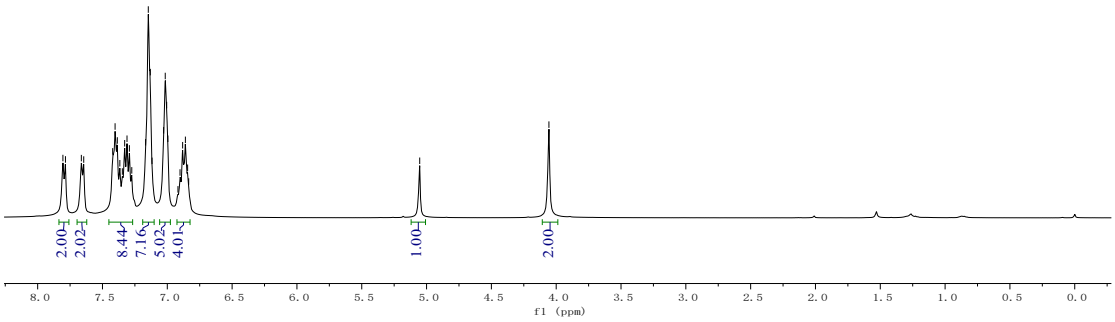
3ea

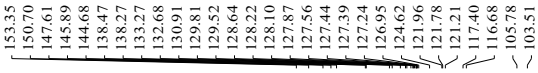

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

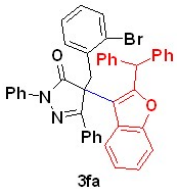

7.81
7.79
7.66
7.64
7.42
7.40
7.39
7.37
7.35
7.33
7.31
7.29
7.27
7.17
7.15
7.13
7.12
7.03
7.02
7.00
7.00
6.92
6.90
6.88
6.86
6.84
6.84
5.05
4.06


Br
Ph
Ph
O
Ph–N
N
O
Ph

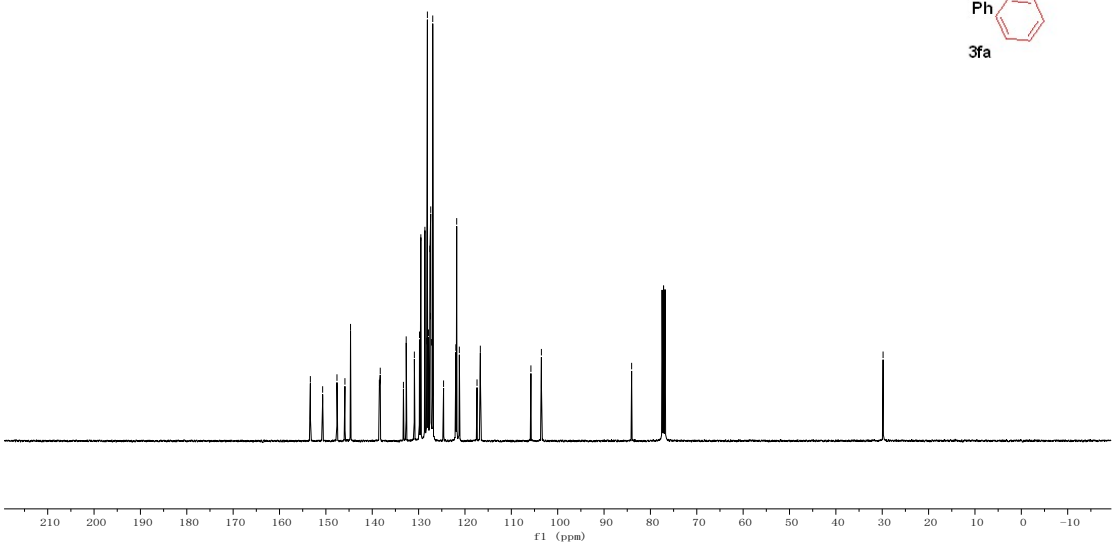
3fa

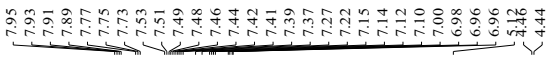

2.00
2.02
8.44
7.16
5.02
4.01
1.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

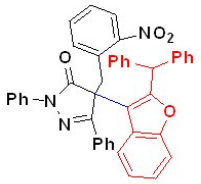

153.35
150.70
147.61
145.89
144.68
138.47
138.27
133.27
132.68
130.91
129.81
129.52
128.64
128.22
128.10
127.87
127.56
127.44
127.39
127.24
126.95
124.62
121.96
121.78
121.21
117.40
116.68
105.78
103.51
84.05
29.82


Br
Ph
Ph
O
Ph–N
N
O
Ph

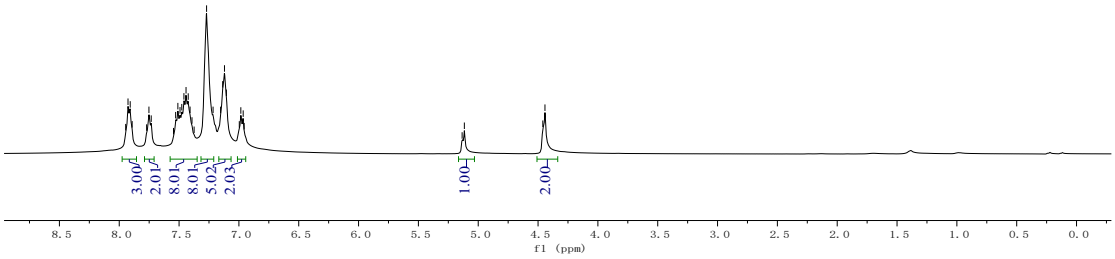
3fa

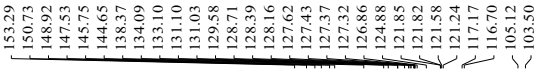

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

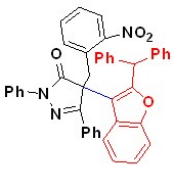

7.95
7.93
7.91
7.89
7.77
7.75
7.73
7.53
7.51
7.49
7.48
7.46
7.44
7.42
7.41
7.39
7.37
7.27
7.22
7.15
7.14
7.12
7.10
7.00
6.98
6.96
6.96
4.46
4.44


NO2
Ph
Ph
O
Ph
N
N
O
Ph

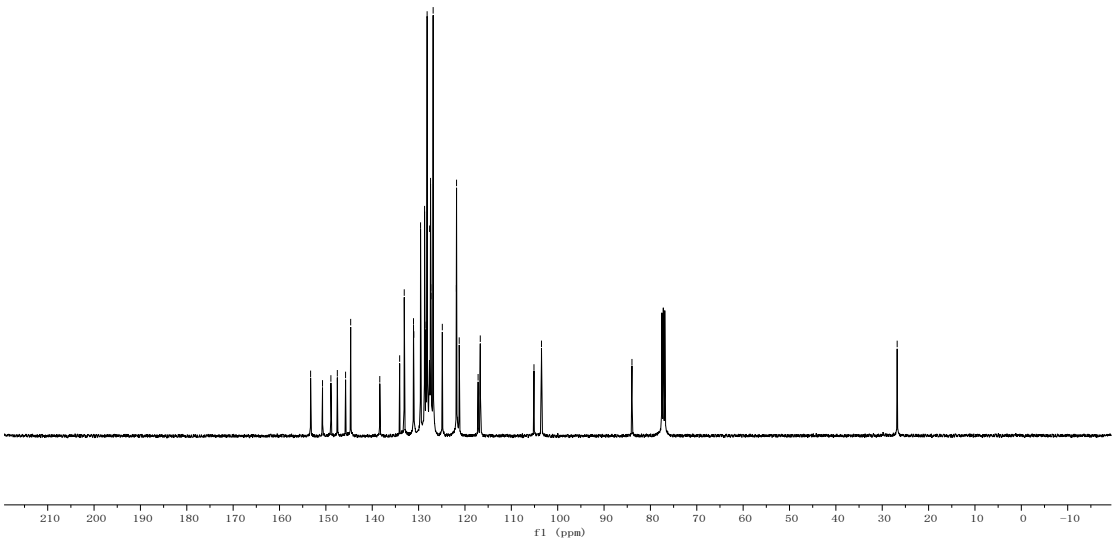
3ga

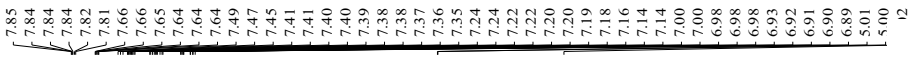

3.00
2.01
8.01
8.01
5.02
2.03
1.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

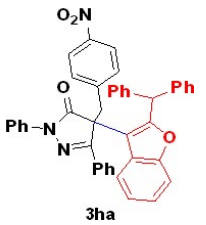

153.29
150.73
148.92
147.53
145.75
144.65
138.37
134.09
133.10
131.10
131.03
129.58
128.71
128.39
128.16
127.62
127.43
127.37
127.32
126.86
124.88
121.85
121.82
121.58
121.24
117.17
116.70
105.12
103.50
83.98
26.78


NO2
Ph
Ph
O
Ph
N
N
O
Ph

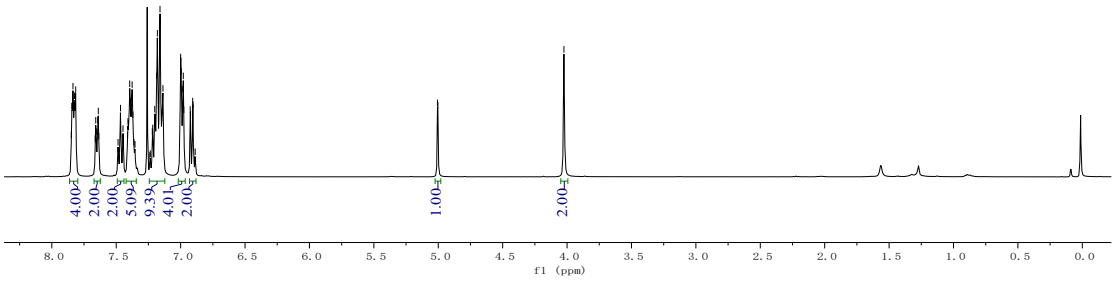
3ga

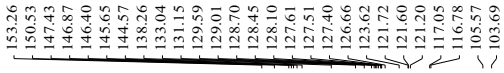

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

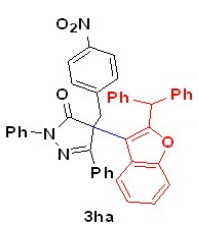



O_2N
O
Ph
Ph
Ph–N
N
O
Ph

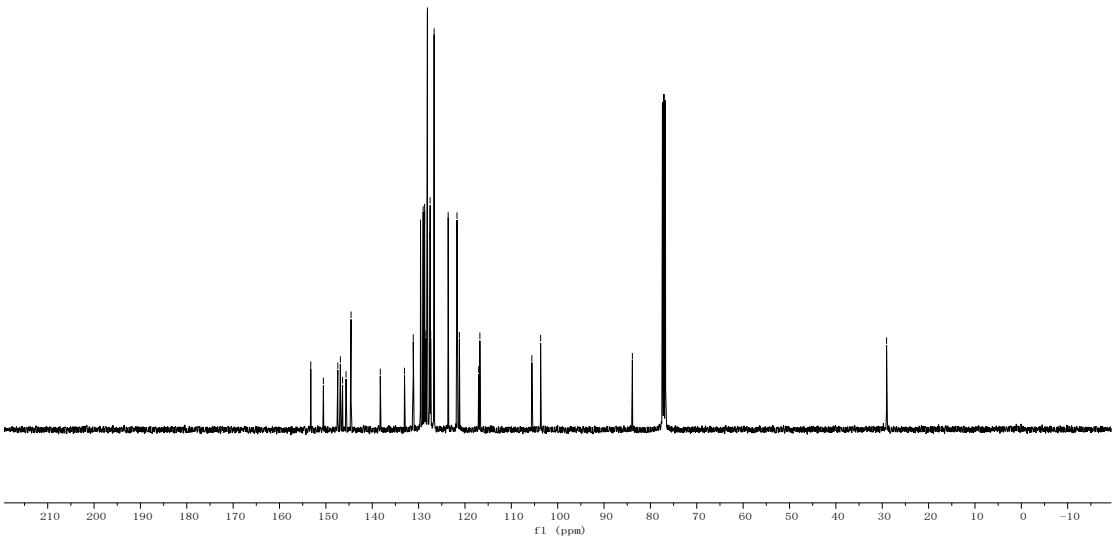
3ha

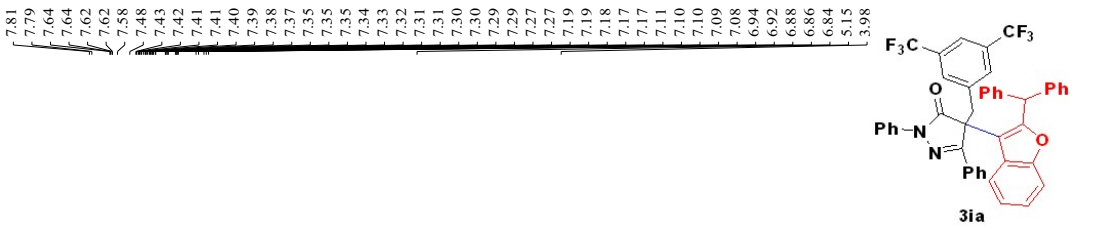

4.00
2.00
2.00
5.09
9.39
4.01
2.00
1.00
2.00
f1 (ppm)

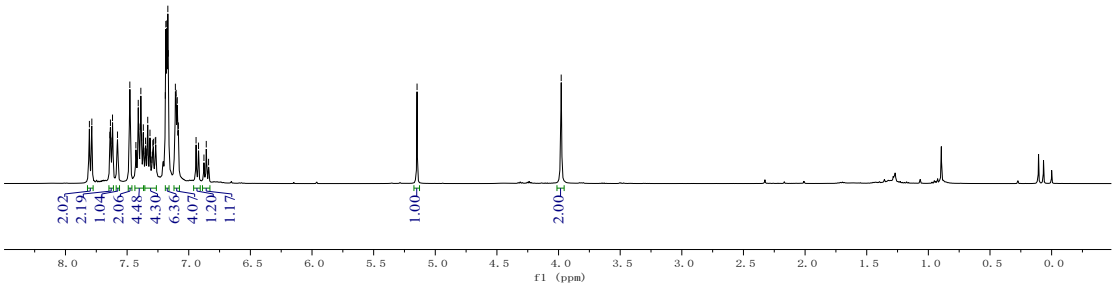


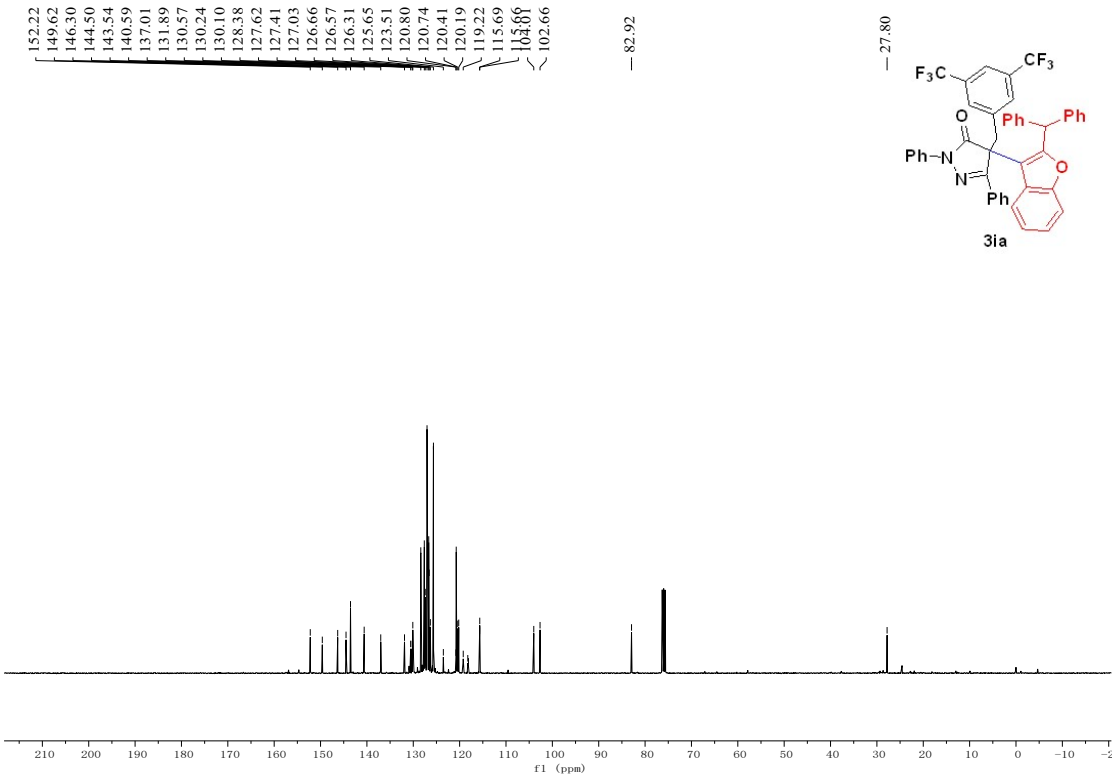

O_2N
O
Ph
Ph
Ph–N
N
O
Ph

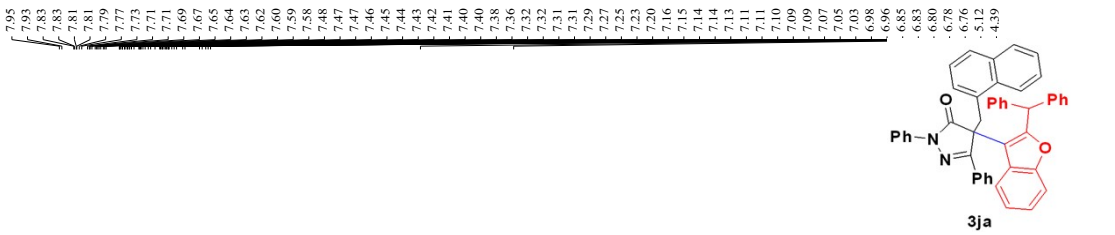
3ha

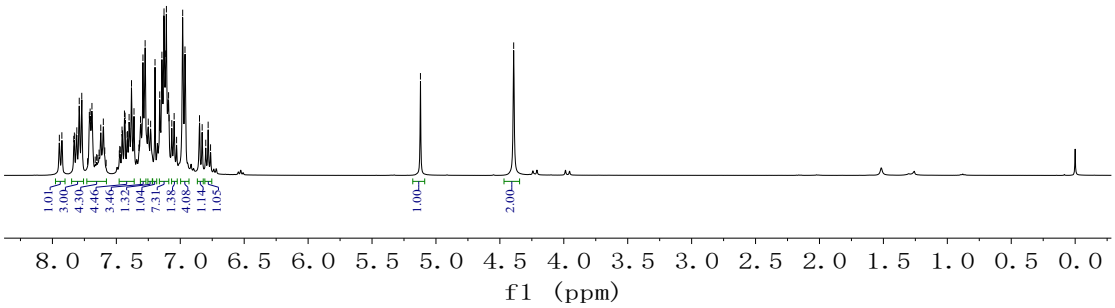

f1 (ppm)

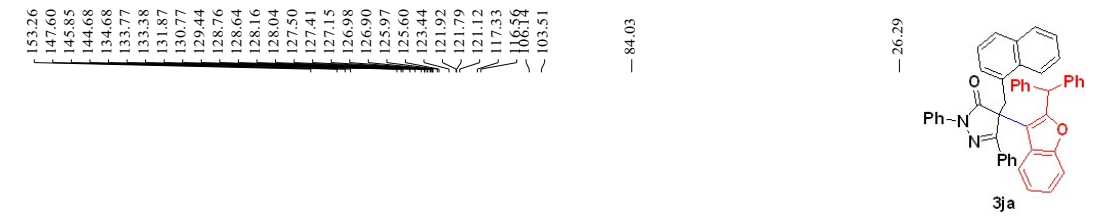

7.81 7.79 7.64 7.64 7.62 7.62 7.58 7.48 7.43 7.42 7.41 7.41 7.40 7.39 7.38 7.37 7.35 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.27 7.27 7.19 7.19 7.18 7.17 7.17 7.11 7.10 7.10 7.09 7.08 6.94 6.92 6.88 6.86 6.84 5.15 3.98
F3C
CF3
O
Ph
Ph
Ph–N
N
Ph
O
3ia

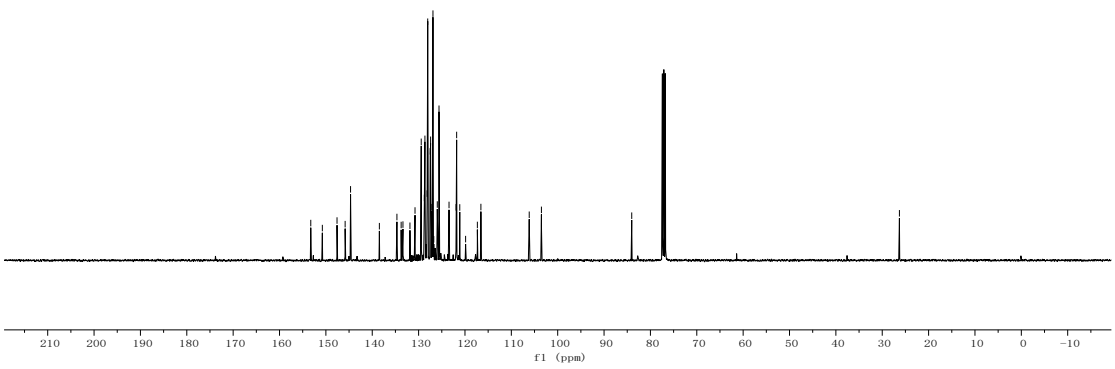

2.02 2.19 1.04 2.06 4.48 4.30 6.36 4.07 1.20 1.17 1.00 2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

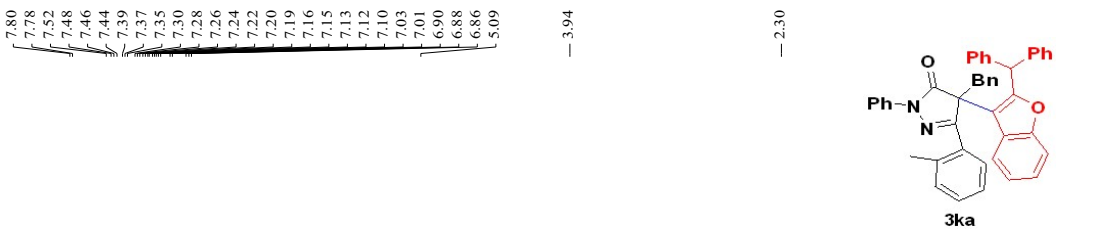

152.22 149.62 146.30 144.50 143.54 140.59 137.01 131.89 130.57 130.24 130.10 128.38 127.62 127.41 127.03 126.66 126.57 126.31 125.65 123.51 120.80 120.74 120.41 120.19 119.22 115.69 115.66 104.01 102.66
82.92
27.80
F3C
CF3
O
Ph
Ph
Ph–N
N
Ph
O
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

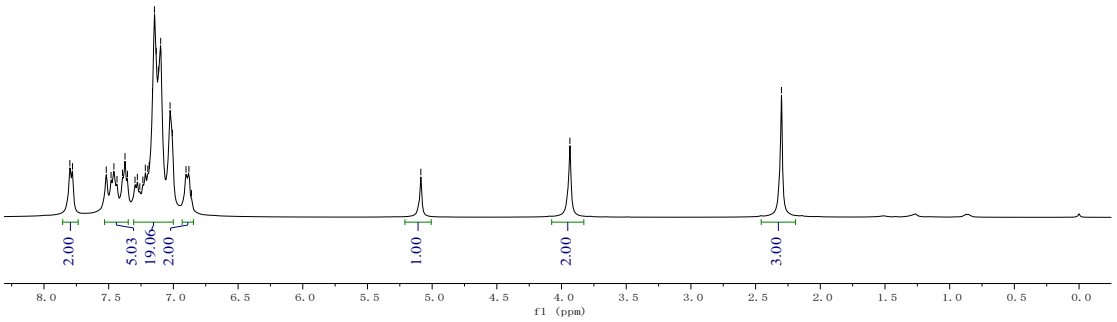

7.95 7.93 7.83 7.83 7.81 7.81 7.79 7.77 7.73 7.71 7.71 7.69 7.67 7.65 7.64 7.63 7.62 7.60 7.59 7.58 7.48 7.47 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.40 7.38 7.36 7.32 7.32 7.31 7.31 7.29 7.27 7.25 7.23 7.20 7.16 7.15 7.14 7.14 7.13 7.11 7.11 7.10 7.09 7.09 7.07 7.05 7.03 6.98 6.96 6.85 6.83 6.80 6.78 6.76 5.12 4.39
O
Ph
Ph
Ph–N
N
Ph
O
3ja

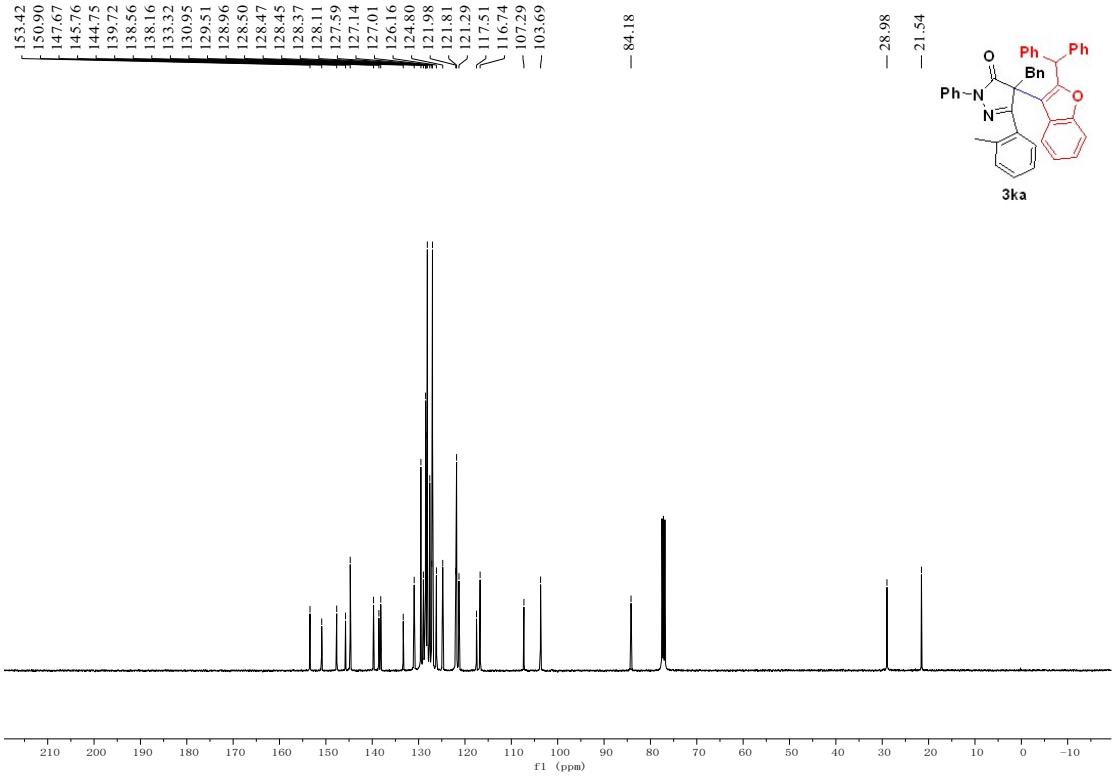

1.01
3.00
4.30
4.46
3.46
1.32
1.04
7.31
1.38
4.08
1.14
1.05
1.00
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

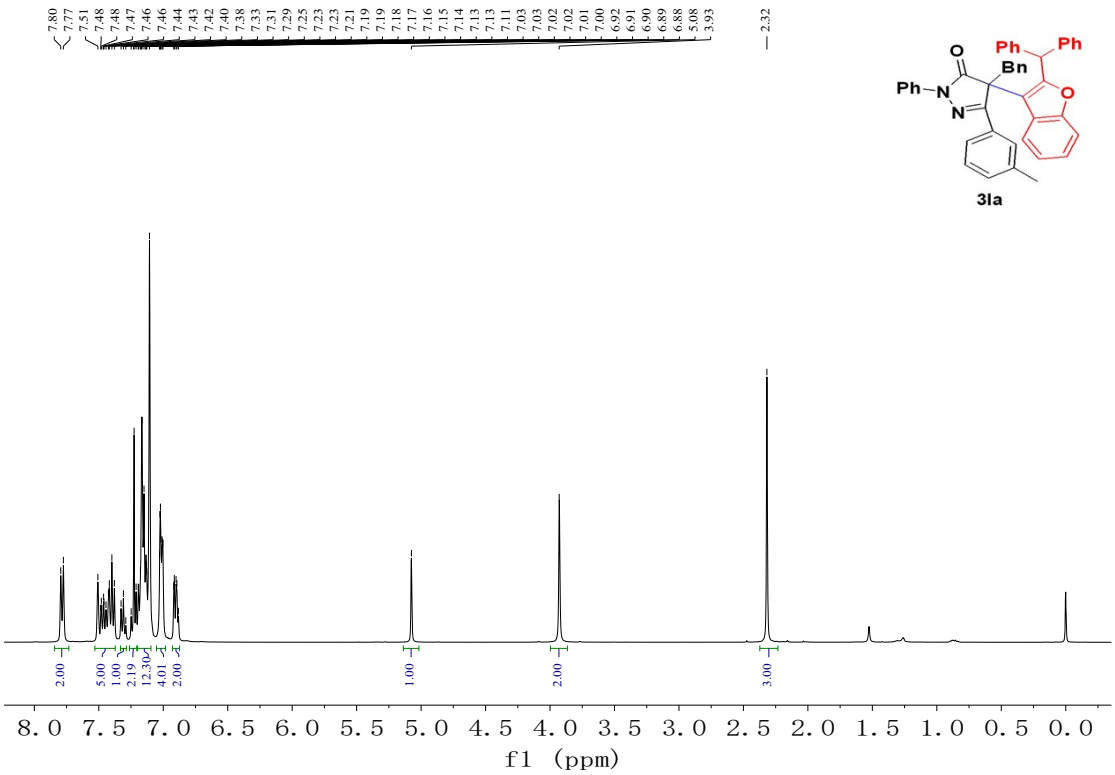

153.26
147.60
145.85
144.68
134.68
133.77
133.38
131.87
130.77
129.44
128.76
128.64
128.16
128.04
127.50
127.41
127.15
126.98
126.90
125.97
125.60
123.44
121.92
121.79
121.12
117.33
116.56
116.14
103.51
84.03
26.29
O
Ph
Ph
Ph–N
N
Ph
O
3ja

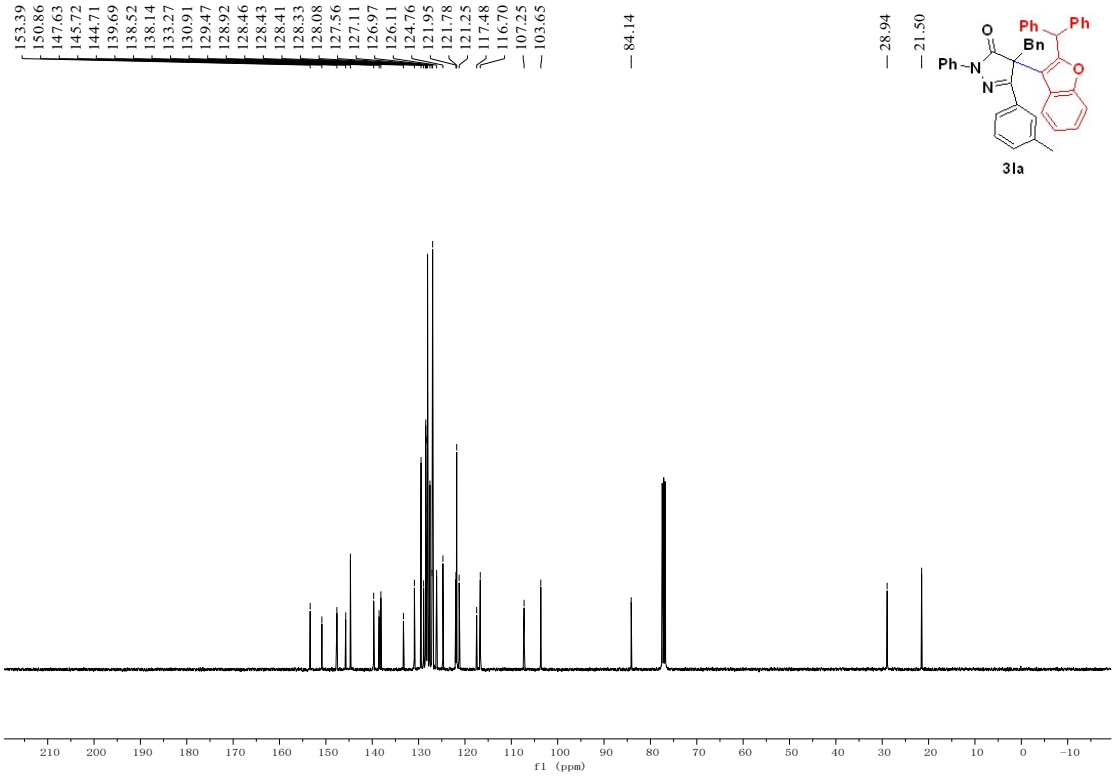

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

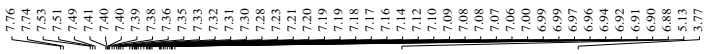

7.80
7.78
7.52
7.48
7.46
7.44
7.39
7.37
7.35
7.30
7.28
7.26
7.24
7.22
7.20
7.19
7.16
7.15
7.13
7.12
7.10
7.03
7.01
6.90
6.88
6.86
5.09
3.94
2.30
O
Ph
Ph
Bn
Ph
N
N
O
3ka

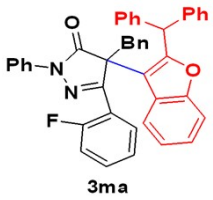

2.00
5.03
19.06
2.00
1.00
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.42
150.90
147.67
145.76
144.75
139.72
138.56
138.16
133.32
130.95
129.51
128.96
128.50
128.47
128.45
128.37
128.11
127.59
127.14
127.01
126.16
124.80
121.98
121.81
121.29
117.51
116.74
107.29
103.69
84.18
28.98
21.54
O
Ph
Ph
Bn
Ph
N
N
O
3ka
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)

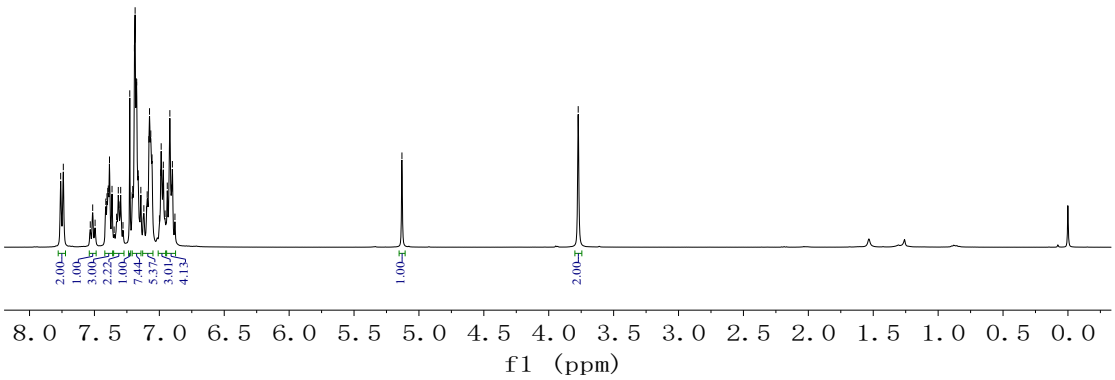

7.80
7.77
7.51
7.48
7.48
7.47
7.46
7.46
7.44
7.43
7.42
7.40
7.38
7.33
7.31
7.29
7.25
7.23
7.23
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.13
7.11
7.03
7.03
7.02
7.02
7.01
7.00
6.92
6.91
6.90
6.89
6.88
5.08
3.93
2.32
Ph
Ph
Bn
O
Ph
N
N
O
3la
2.00
5.00
1.00
2.19
12.30
4.01
2.00
1.00
2.00
3.00
8.0 7.5 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)


153.39
150.86
147.63
145.72
144.71
139.69
138.52
138.14
133.27
130.91
129.47
128.92
128.46
128.43
128.41
128.33
128.08
127.56
127.11
126.97
126.11
124.76
121.95
121.78
121.25
117.48
116.70
107.25
103.65
84.14
28.94
21.50
Ph
Ph
Bn
O
Ph
N
N
O
3la
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)

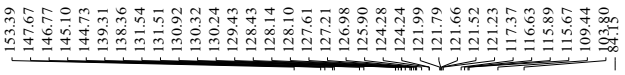


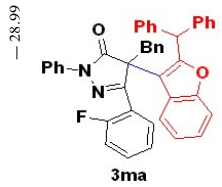

O
Ph
Ph
Bn
Ph
N
N
O
F

3ma

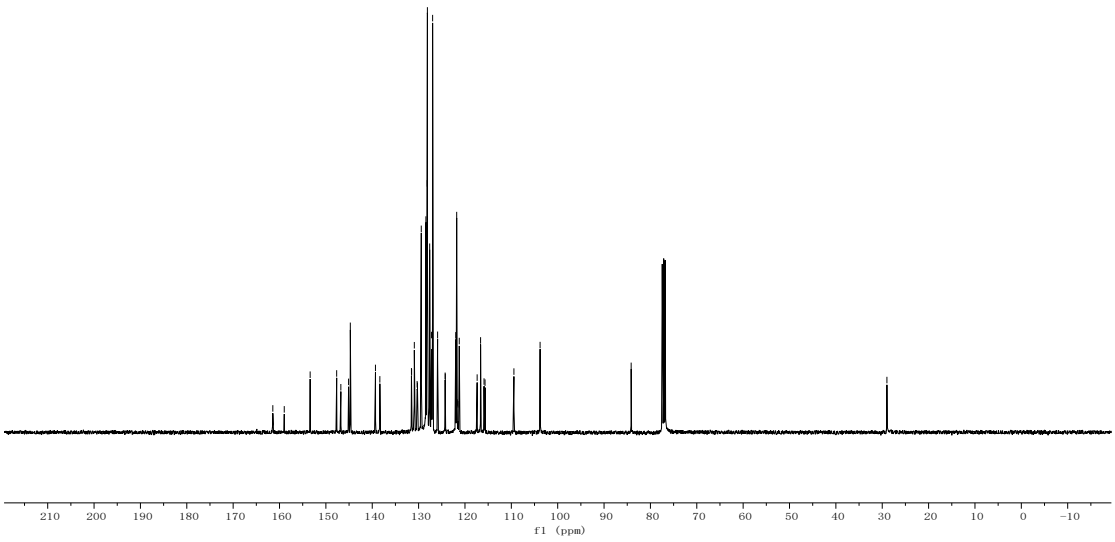

2.00
1.00
3.00
2.22
1.00
7.44
5.37
3.01
4.13
1.00
2.00

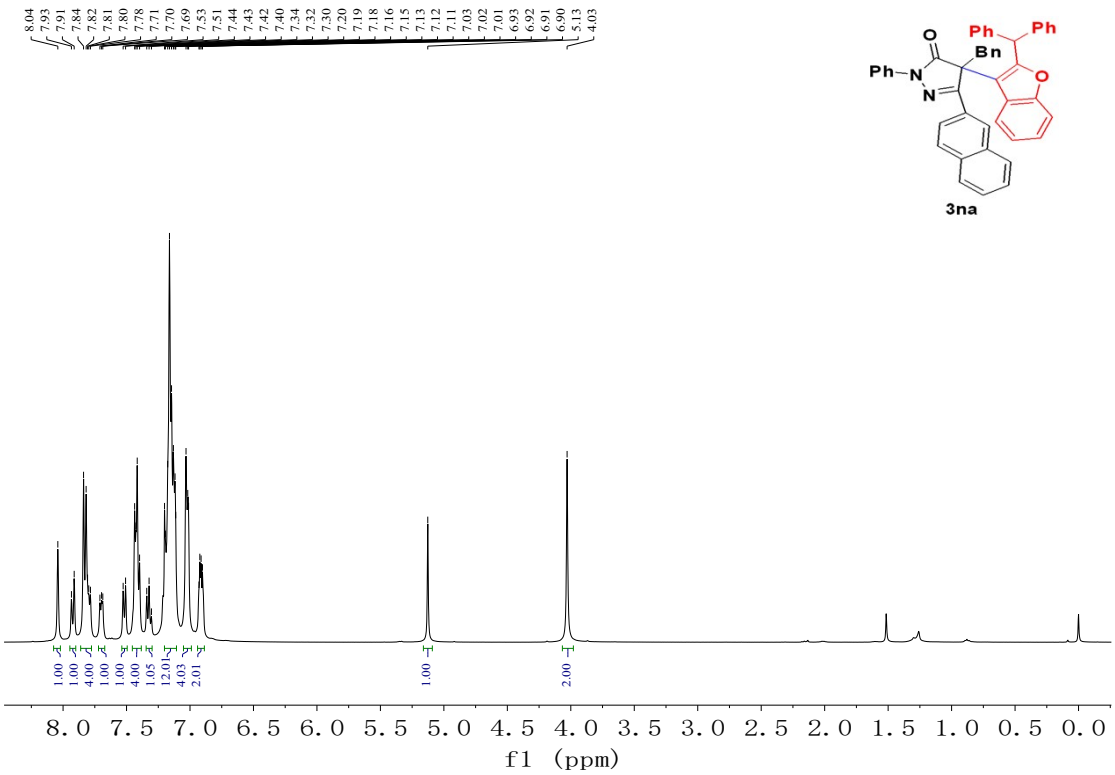
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

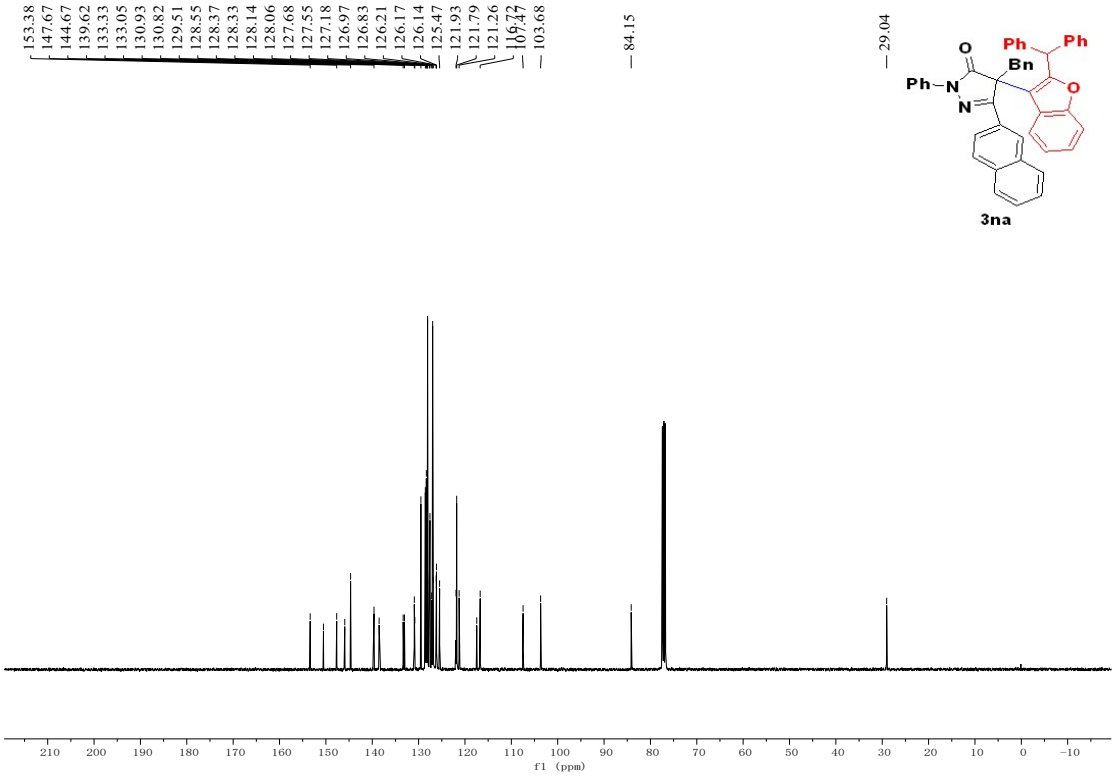


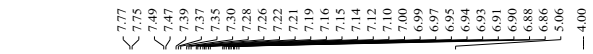

28.99
O
Ph
Ph
Bn
Ph
N
N
O
F

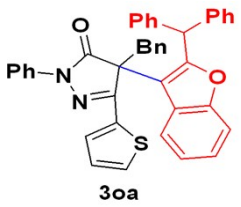
3ma


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)

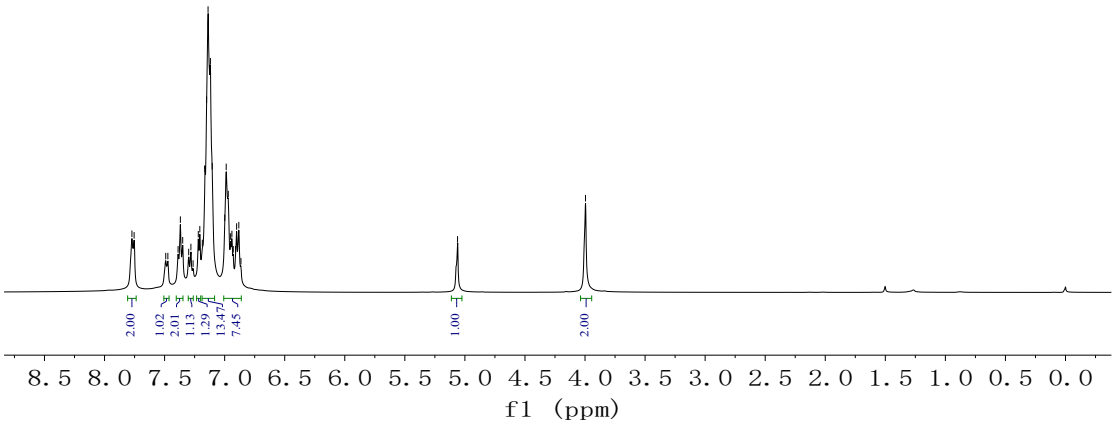

8.04
7.93
7.91
7.84
7.82
7.81
7.80
7.78
7.71
7.70
7.69
7.53
7.51
7.44
7.43
7.42
7.40
7.34
7.32
7.30
7.20
7.19
7.18
7.16
7.15
7.13
7.12
7.11
7.03
7.02
7.01
6.93
6.92
6.91
6.90
5.13
4.03
O
Ph
Ph
Bn
Ph–N
N
O
3na
1.00
1.00
4.00
1.00
1.00
4.00
1.05
12.01
4.03
2.01
1.00
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

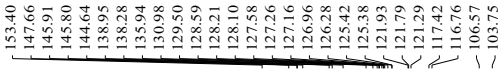

153.38
147.67
144.67
139.62
133.33
133.05
130.93
130.82
129.51
128.55
128.37
128.33
128.14
128.06
127.68
127.55
127.18
126.97
126.83
126.21
126.17
126.14
125.47
121.93
121.79
121.26
116.72
107.47
103.68
84.15
29.04
O
Ph
Ph
Bn
Ph–N
N
O
3na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

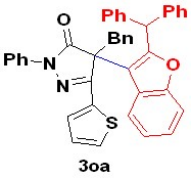

7.77
7.75
7.49
7.47
7.39
7.37
7.35
7.30
7.28
7.26
7.22
7.21
7.19
7.16
7.15
7.14
7.12
7.10
7.00
6.99
6.97
6.95
6.94
6.93
6.91
6.90
6.88
6.86
5.06
4.00


O
Ph
Ph
Bn
Ph–N
N
O
S

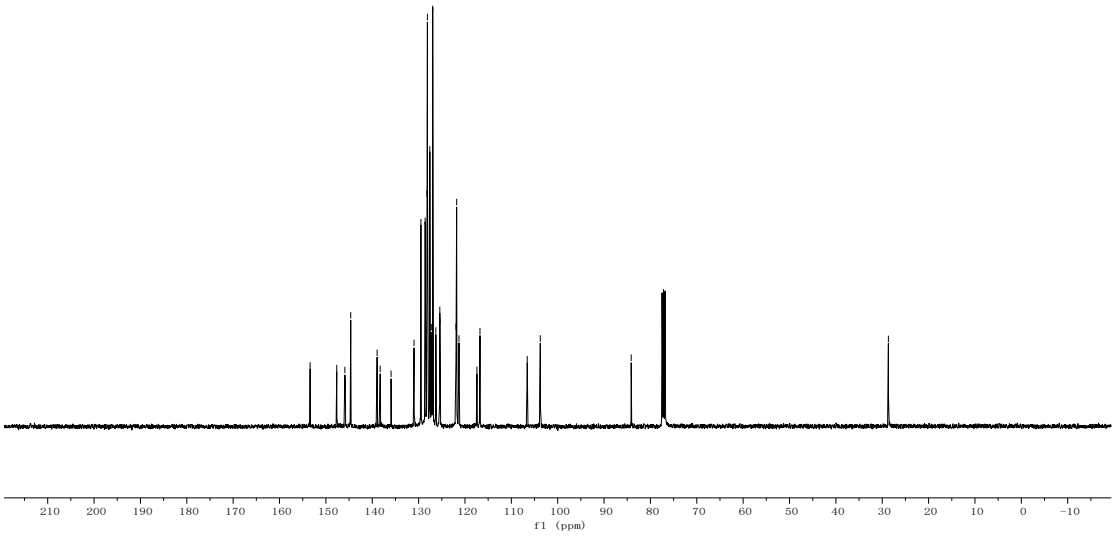
3oa

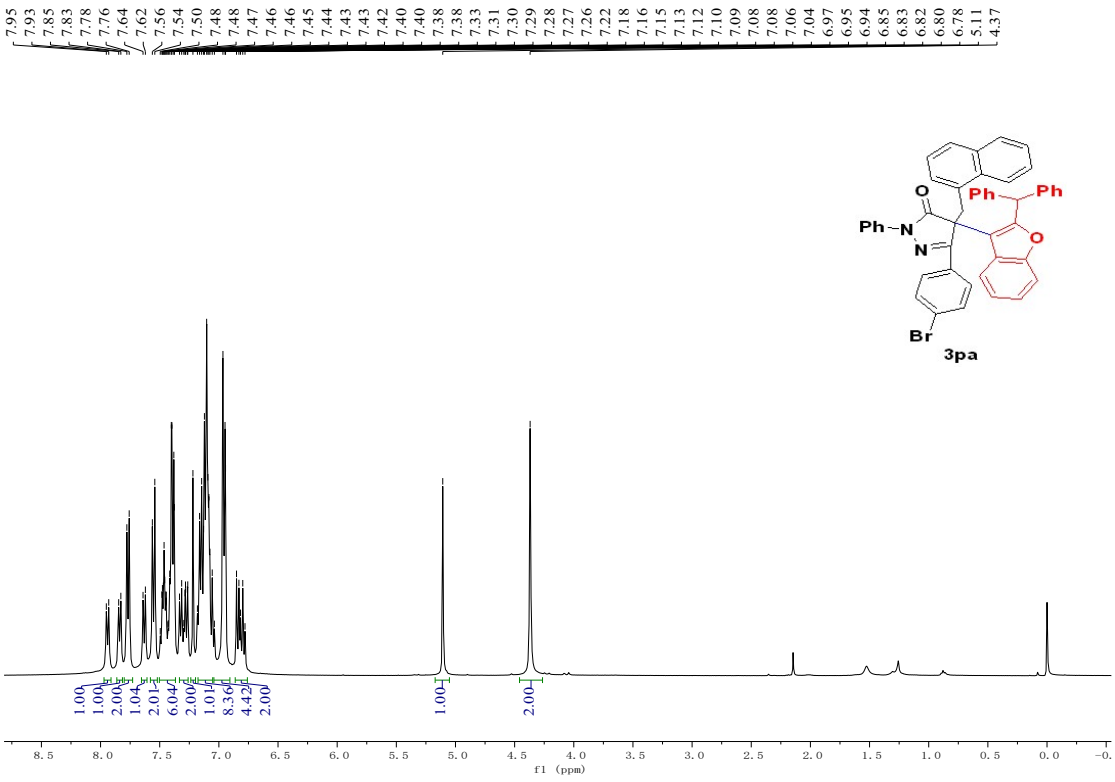

2.00
1.02
2.01
1.13
1.29
13.47
7.45
1.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

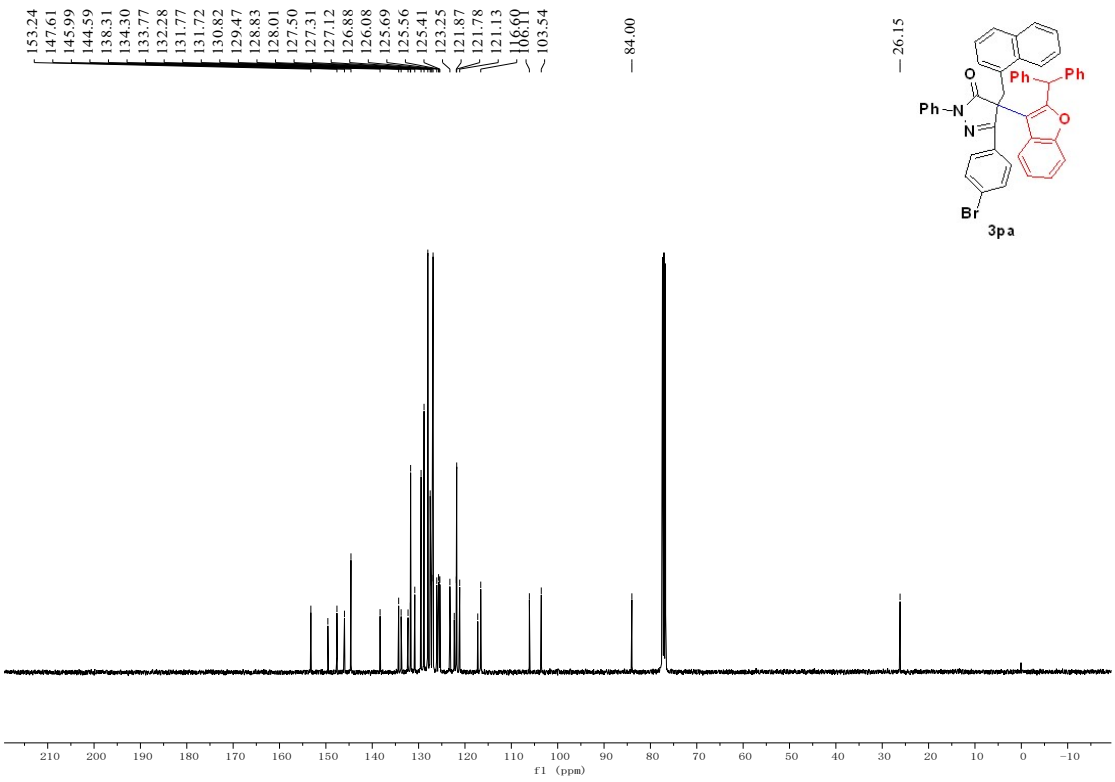

153.40
147.66
145.91
145.80
144.64
138.95
138.28
135.94
130.98
129.50
128.59
128.21
128.10
127.58
127.26
127.16
126.96
126.28
125.42
125.38
121.93
121.79
121.29
117.42
116.76
106.57
103.75
84.14
28.67


O
Ph
Ph
Bn
Ph–N
N
O
S

3oa


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)


7.95 7.93 7.85 7.83 7.78 7.76 7.64 7.62 7.56 7.54 7.50 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.43 7.43 7.42 7.40 7.40 7.38 7.38 7.33 7.31 7.30 7.29 7.28 7.27 7.26 7.22 7.18 7.16 7.15 7.13 7.12 7.10 7.09 7.08 7.08 7.06 7.04 6.97 6.95 6.94 6.85 6.83 6.82 6.80 6.78 5.11 4.37
O
Ph
Ph
Ph–N
N
O
Br
3pa
1.00 1.00 2.00 1.04 2.01 6.04 2.00 1.01 8.36 4.42 2.00 1.00 2.00
f1 (ppm)


153.24 147.61 145.99 144.59 138.31 134.30 133.77 132.28 131.77 131.72 130.82 129.47 128.83 128.01 127.50 127.31 127.12 126.88 126.08 125.69 125.56 125.41 123.25 121.87 121.78 121.13 116.60 116.11 103.54
84.00
26.15
O
Ph
Ph
Ph–N
N
O
Br
3pa
f1 (ppm)