Supporting information

Ball-milling synthesized hydrotalcite supported Cu-Mn mixed oxide under solvent-free conditions: an active catalyst for aerobic oxidative synthesis of 2-acylbenzothiazoles and quinoxalines

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1. General Information

All reagents were purchased from commercial suppliers and used without further purification. Hydrophobic hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$, CAS No: 11097-59-9) was purchased from Sigma-Aldrich and used directly in the catalyst preparation. Hydrophilic HT was synthesized according to the literature procedure.[1] All experiments were carried out under air or using O_2 balloon. Flash chromatography was carried out with Merck silica gel 60 (200-300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (400 and 100 MHz respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz.

The planetary ball mill (QM-3SP, Scheme S1) with 4 agate balling pots (100 mL) was purchased from Laibu Technology limited Company, China (website: http://www.nju-qm.com). The grinding is carried out in the agate balling pots containing agate balls with different sizes (5~15 mm diameter). When the pots rotate vigorously, the balls and the raw materials in pots go up along the pot wall under the centrifugal force and friction, and then free fall or roll down. The grinding of the raw is mainly due to the impact of the agate balls and the stripping effect.

Scheme S1. The planetary ball mill used in preparation of Cu-Mn/HT.

2. Catalysts preparation

Cu-Mn/HT-WI prepared via wet-impregnation. 1.5 g of $Cu(NO_3)_2{\cdot}3H_2O$ (theoretical loading: 8wt% to HT) and 0.225 g of $Mn(NO_3)_2{\cdot}4H_2O$ (theoretical loading: 2wt% to HT) were dissolved into 40 mL of EtOH. 5 g of HT was added into the as-prepared mixed metal solution with stirring at room temperature. The mixture was stirred for 24 h. After that, the solution was removed by distillation under reduced pressure and the resulting solid was dried in oven at 80 ^{o}C for 5 h and calcined in muffle furnace at 350 ^{o}C for 2 h.

Cu-Mn/HT-G prepared via physical grinding. 1.5 g of $Cu(NO_3)_2{\cdot}3H_2O$ (theoretical loading: 8wt% to HT) and 0.225 g of $Mn(NO_3)_2{\cdot}4H_2O$ (theoretical loading: 2wt% to HT) and 5 g of HT were added to an agate mortar, and the mixture was grinded using a pestle by hand for 30 minutes. Then, the resulting powders were directly calcined in muffle furnace at 350 ^{o}C for 2 h.

3. Characterizations of materials

3.1. Analysis methods

Nitrogen adsorption-desorption measurements were performed at 76 K using an ASAP 2020M analyzer utilizing the BET model for the calculation of specific surface areas. The element contents of samples were determined by ICP-AES (ContrAA 700). The crystal phase and composition were determined by power X-ray diffraction using a X-Pert PRO X-ray diffractometer with Cu Ka radiation in the 2θ range of 10–90^{o}. The morphologies of the samples were characterized by a TF20 transmission electron microscope and SM-5600LV or Quanta 250 FEG scanning electron microscope. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS Ultra DLD high performance electron spectrometer using nonmonochromatized Al Kα excitation source (hv = 1486.6 eV). Binding energies were calibrated by using the contaminant carbon (C 1s = 284.6 eV).

3.2. Characterizations of HT materials

From the XRD patterns, we can see that ball-milling did not change the crystal structure of original HT. Calcination at 350 °C would make HT release CO_2 and H_2O, which transfer it into MgO-Al_2O_3 oxides partially (Figure S1).[2] Moreover, from the SEM images of HT materials, ball-milling or calcination did not change its morphology and all HT materials exhibited uniform layered morphology (Figure S2).

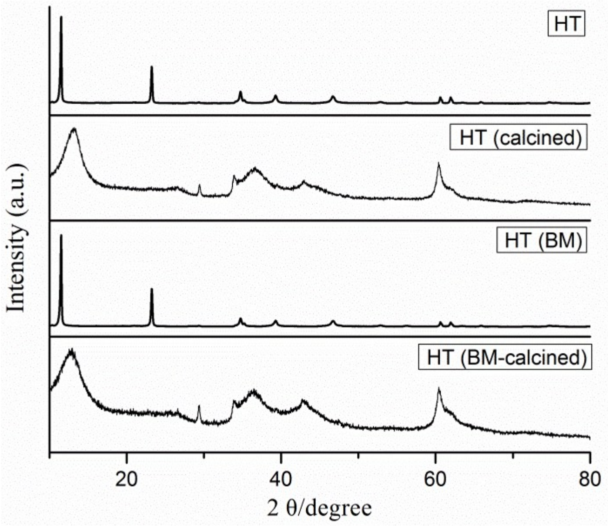


Figure S1. XRD patterns HT materials.

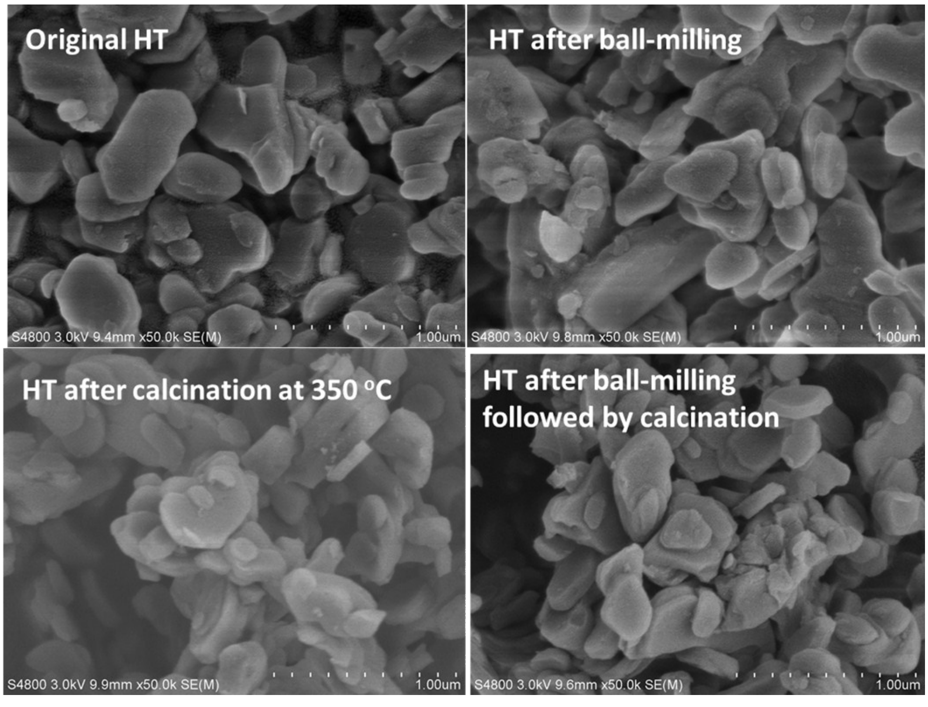


Figure S2. SEM images of HT materials.

3.3. Characterizations of Cu-Mn/HT

The morphology of Cu-Mn/HT catalysts prepared by different methods was investigated by transmission electron microscope (TEM). From Figure S3, metal aggregation was obvious on Cu-Mn/HT-G, which might result from crude grinding by hand. In the case of Cu-Mn/HT-WI, well-dispersed metal particles were observed on the catalyst. Towards Cu-Mn/HT made by ball-milling, there is no obvious metal aggregation phenomenon and metal particles dispersed very well.

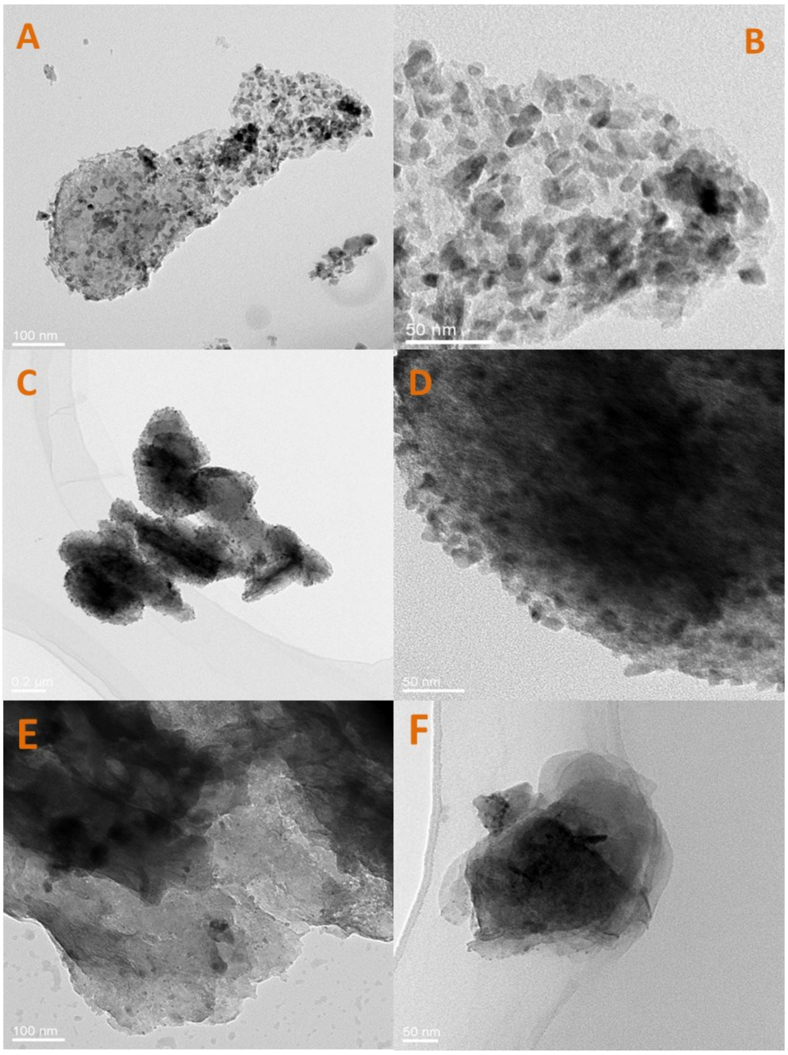


Figure S3. TEM images of Cu-Mn/HT-G (A and B), Cu-Mn/HT-WI (C and D) and Cu-Mn/HT (E and F).

X-ray photoelectric spectroscopy was employed to examine the surface properties of Cu and Mn of the catalysts. Form Figure S4, there is no difference of metal oxidative state caused by preparation methods.

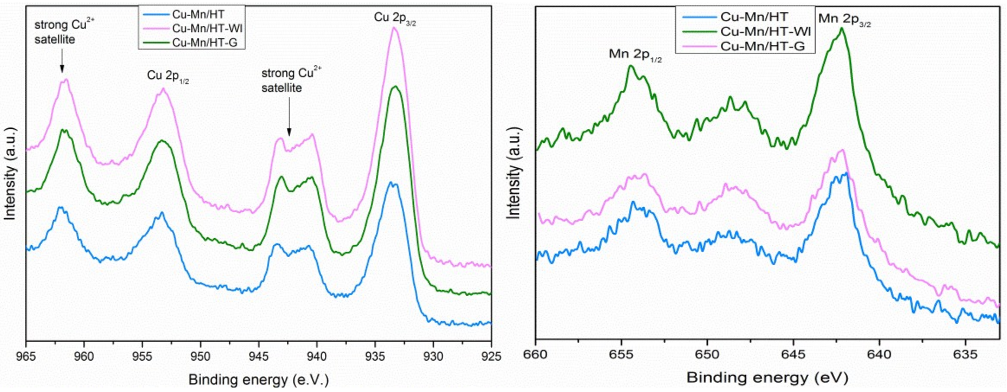
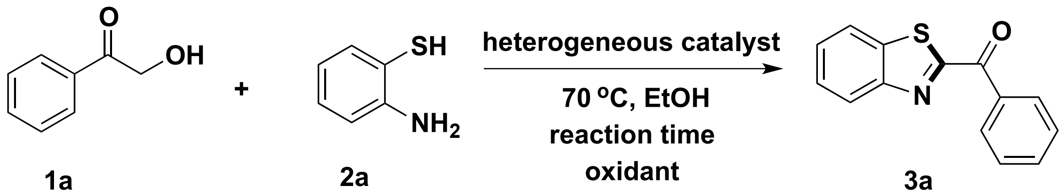


Figure S4. XPS patterns of Cu 2p and Mn 2p of catalysts.

4. Optimization of reaction conditions

Table S1. Optimization of oxidative synthesis of 2-acylbenzothiazole over different catalysts[a]



Entry	Catalyst	Metal wt% on HT		Oxidant	Reaction time (h)	Yield[b] (%)
		Cu	Mn			
1	Cu/HT	2	-	O_2	12	35
2	Mn/HT	-	8	O_2	12	trace
3[c]	Cu-Mn oxide			H_2O_2	12	36
4	Cu-Mn/HT	8	1	O_2	12	58
5	Cu-Mn/HT	4	2	O_2	12	66
6[c]	Cu-Mn/HT	8	2	H_2O_2	12	46
7[d]	Cu-Mn/HT	8	2	air	12	12
8	Cu-Mn/HT	8	2	N_2	24	8
9	Cu-Mn/HT	8	2	O_2	24	88

10	Cu-Mn/HT	8	2	O_2	6	70
11[e]	Cu-Mn oxide + HT	8	2	O_2	12	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (20 mg), EtOH (1 mL), 70 ^{o}C.

[b] NMR yields using anisole as internal standard.

[c] 50 uL of H_2O_2 was used.

[d] Under air (1 atm).

[e] Physical mixture of Cu-Mn oxide (5 mg) and HT (20 mg) was used.

5. Hot filtration experiment

Hot-filtration experiment between a-hydroxyacetophenone **1a** and 2-aminothiophenol **2a** was carried out. After the reaction performed for 2 h, the catalyst was removed by filtration from the reaction medium, and the NMR yield of **3a** was roughly 45% of NMR yield. Meanwhile, the filtrate was kept running, and no more product was detected (Figure S5). The filtrate was further analyzed by ICP-AES, which shows that metal species, including Cu and Mn, were hardly observed.

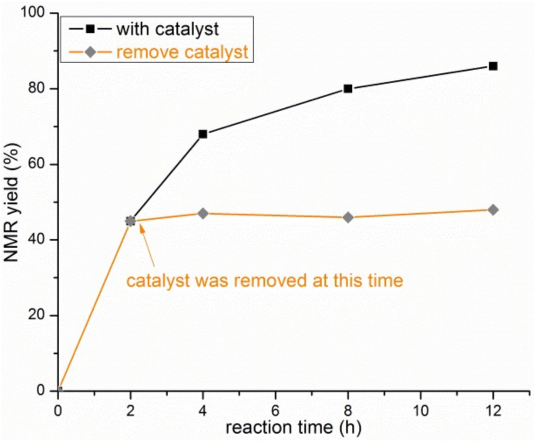


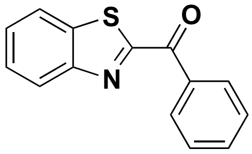
Figure S5. Reaction profiles.

6. Recycling experiment

After each run, the catalyst was isolated by filtration and stirred in 0.5 M Na_2CO_3 solution under reflux conditions for 24 h. Next, the catalyst was filtrated from the solution and dried followed by calcination at 350 ^{o}C for 2 h for the next run. The reconstruction of HT occurs via a simple dissolution-reprecipitation mechanism.[2]

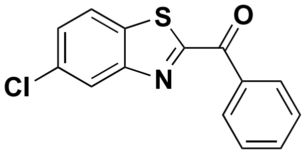
7. Spectrum data of products

benzothiazol-2-yl(phenyl)methanone[3] (**3a**)



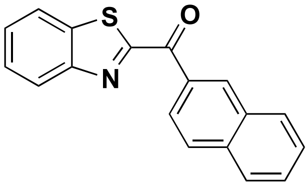
Yellow solid, isolated yield 86%, m.p. 99-102 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.56 (d, J = 8.4 Hz, 2H), 8.25 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.63-7.53 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.2, 167.0, 153.7, 136.9, 134.8, 133.8, 131.2, 128.4, 127.5, 126.8, 125.6, 122.1.

(5-chlorobenzothiazol-2-yl)(phenyl)methanone[3] (**3b**)



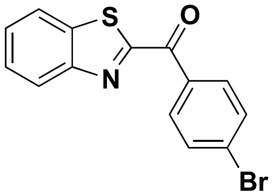
Yellow solid, isolated yield 90%, m.p. 125-127 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.55 (d, J = 7.9 Hz, 2H), 8.24 (s, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.61-7.50 (m, 3H);); ^{13}C NMR (100MHz, $CDCl_3$): δ = 185.0, 168.9, 154.6, 135.2, 134.6, 134.2, 133.0, 131.3, 128.6, 128.3, 125.2, 123.1.

benzothiazol-2-yl(naphthalen-2-yl)methanone[3] (**3c**)



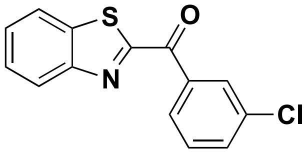
Yellow solid, isolated yield 82%, m.p. 166-168 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 9.39 (s, 1H), 8.48 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.67-7.56 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 185.0, 167.4, 153.9, 135.9, 134.4, 132.5, 132.1, 130.2, 129.0, 128.8, 128.3, 127.8, 127.6, 126.9, 126.7, 125.8, 125.7, 122.2.

benzothiazol-2-yl(4-bromophenyl)methanone[3] (**3d**)



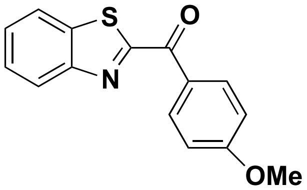
Yellow solid, isolated yield 88%, m.p. 121-123 ^{o}C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.48 (d, J = 8.5 Hz, 2H), 8.24 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.62-7.56 (m, 2H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 184.1, 166.7, 153.7, 137.0, 133.5, 133.1, 132.5, 131.6, 131.2, 129.5, 124.8, 122.3.

benzo[*d*]thiazol-2-yl(3-chlorophenyl)methanone[3] (**3e**)



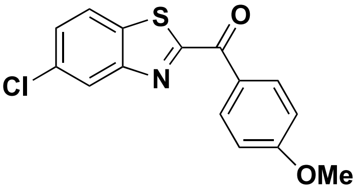
Yellow solid, isolated yield 85%, m.p. 98-100 ^{o}C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.50 (d, J = 8.5 Hz, 2H), 8.26 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.66-7.57 (m, 2H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 184.1, 166.7, 153.8, 137.1, 133.6, 132.7, 132.2, 131.8, 129.5, 128.8, 127.8, 127.0, 125.8, 122.2.

benzothiazol-2-yl(4-methoxyphenyl)methanone[3] (**3f**)



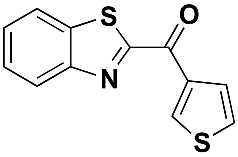
Yellow solid, isolated yield 75%, m.p. 99-102 ^{o}C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.64 (d, J = 8.6 Hz, 2H), 8.23 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.59-7.51 (m, 2H), 7.04 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 183.4, 167.9, 164.4, 153.8, 136.8, 133.8, 127.7, 127.4, 126.8, 125.5, 122.1, 113.9, 55.6.

(5-chlorobenzothiazol-2-yl)(4-methoxyphenyl)methanone[3] (**3g**)



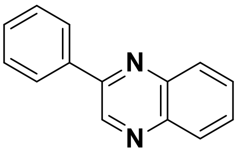
Yellow solid, isolated yield 80%, m.p. 105-107 ^{o}C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.62 (d, J = 7.6 Hz, 2H), 8.21 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 7.6 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 182.8, 169.7, 154.5, 135.0, 134.4, 132.8, 127.3, 123.0, 114.6, 114.1, 113.6, 113.2, 55.4.

benzothiazol-2-yl(thiophen-3-yl)methanone[3] (**3h**)



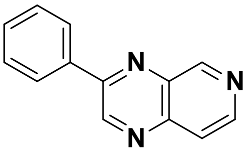
Yellow solid, isolated yield 65%, m.p. 99-102 ^{o}C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.81 (d, J = 3.8 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 4.8 Hz, 1H), 7.63-7.57 (m, 2H), 7.31 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 176.9, 166.5, 153.6, 139.7, 137.4, 137.0, 136.7, 128.2, 127.6, 126.9, 126.3, 122.3.

2-phenylquinoxaline[4] (**5a**)



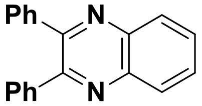
Yellow solid, isolated yield 96%, m.p. 123-125 ^{o}C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 9.34 (s, 1H), 8.22-8.08 (m, 4H), 7.83-7.70 (m, 2H), 7.63-7.47 (m, 3H);); ^{13}C NMR (100MHz, CDCl$_3$): δ = 151.8, 143.3, 142.2, 141.5, 136.7, 130.2, 130.1, 129.6, 129.5, 129.1, 129.1, 127.5.

3-phenylpyrido[3,4-b]pyrazine (**5b**)



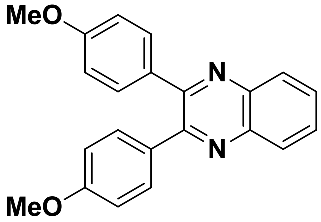
White solid, isolated yield 95%, m.p. 134-136 °C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 9.57 (s, 1H), 9.45 (s, 1H), 8.87 (d, J = 5.7 Hz, 1H), 8.25 (d, J = 4.1 Hz, 2H), 7.99 (d, J = 5.6 Hz, 1H), 7.62 (s, 3H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 155.8, 154.2, 147.8, 145.0, 144.8, 136.6, 135.7, 131.3, 129.3, 128.0, 121.8.

2,3-diphenylquinoxaline[4] (**5c**)



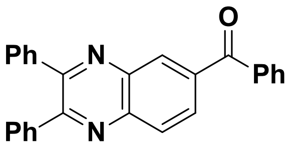
Yellow solid, isolated yield 95%, m.p. 92-95 °C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.19 (dd, J = 6.4, 3.4 Hz, 2H), 7.77 (dd, J = 6.4, 3.4 Hz, 2H), 7.60-7.45 (m, 4H), 7.41-7.30 (m, 6H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 153.4, 141.2, 139.0, 129.9, 129.8, 129.2, 128.8, 128.3.

2,3-bis(4-methoxyphenyl)quinoxaline[4] (**5d**)



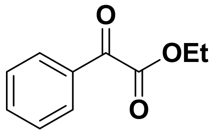
White solid, isolated yield 95%, m.p. 105-107 °C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.16 (dd, J = 6.2, 3.4 Hz, 2H), 7.75 (dd, J = 6.2, 3.4 Hz, 2H), 7.54 (d, J = 8.0 Hz, 4H), 6.92 (d, J = 8.1 Hz, 4H), 3.86 (s, 6H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 160.1, 153.0, 141.0, 132.4, 131.6, 131.2, 129.0, 113.7, 55.3.

(2,3-diphenylquinoxalin-6-yl)(phenyl)methanone (**5e**)



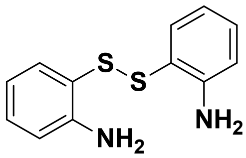
White solid, isolated yield 92%, m.p. 99-102 °C. ^{1}H NMR (400MHz, CDCl$_3$): δ = 8.59 (s, 1H), 8.33 (s, 2H), 7.96 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 7.64-7.52 (m, 7H), 7.49-7.35 (m, 7H); ^{13}C NMR (100MHz, CDCl$_3$): δ = 195.8, 155.1, 154.6, 143.0, 140.1, 138.6, 138.5, 138.2, 137.1, 132.8, 132.5, 130.1, 129.9, 129.9, 129.8, 129.7, 129.4, 129.1, 128.6, 128.5, 128.4.

ethyl 2-oxo-2-phenylacetate[5] (**6**)



Colorless liquid, isolated yield 95%. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.02 (d, J = 7.3 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 186.4, 163.7, 134.8, 132.4, 130.0, 128.8, 62.3, 14.1.

2,2'-disulfanediyldianiline[6] (**7**)



Yellow solid, isolated yield 95%, m.p. 90-92 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.17-7.14 (m, 4H), 6.71 (d, J = 8.4 Hz, 2H), 6.59 (t, J = 7.1 Hz, 2H), 4.34 (s, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 148.5, 136.7, 131.5, 118.6, 118.1, 115.1.

Reference:

[1] M. J. Climent, A. Corma, S. Iborra and L. Martí, *ACS Catal.*, 2015, **5**, 157-166.

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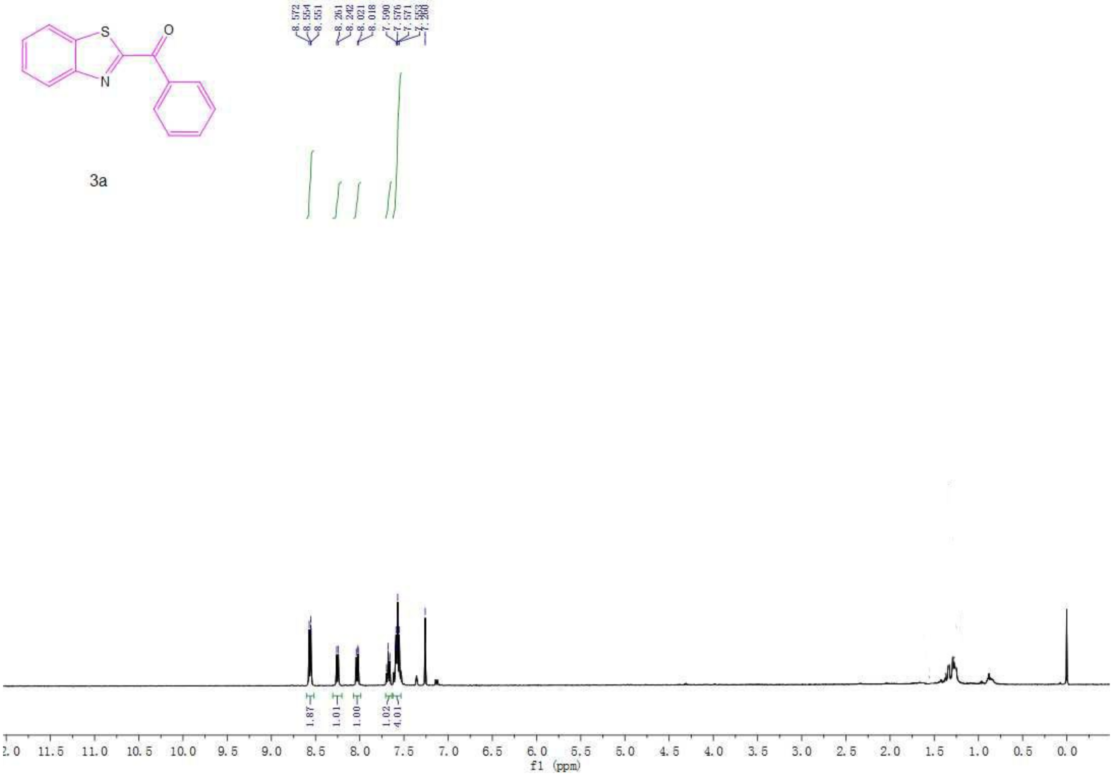
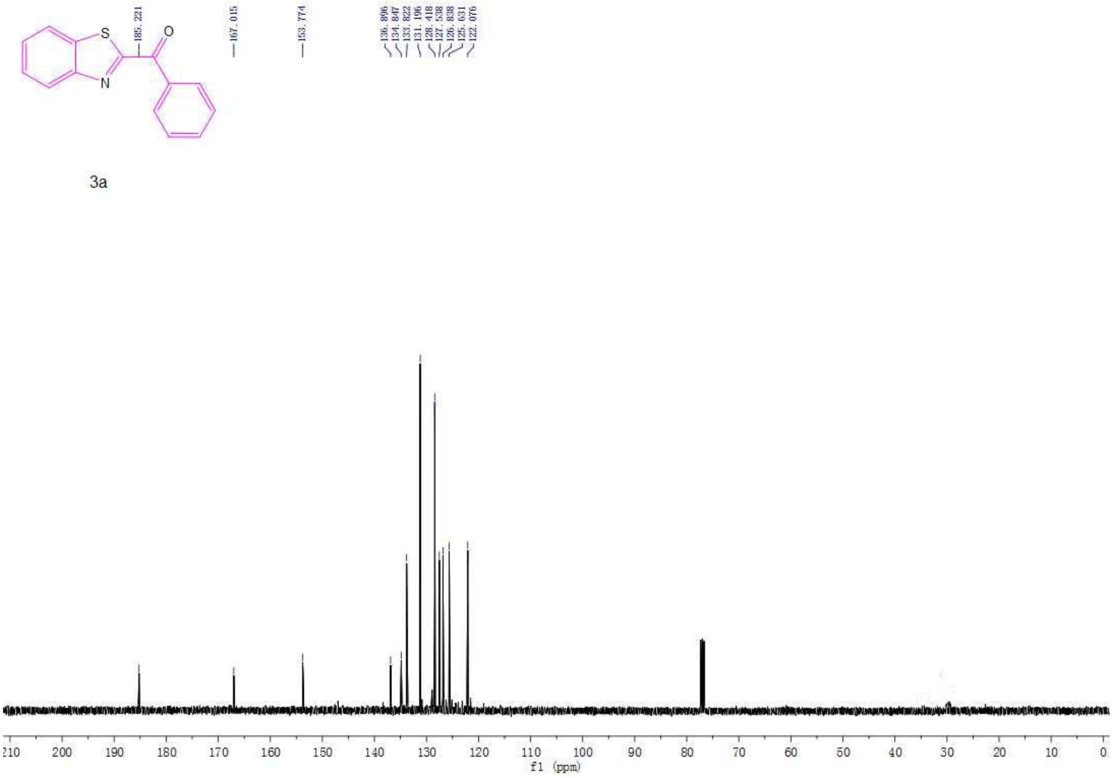
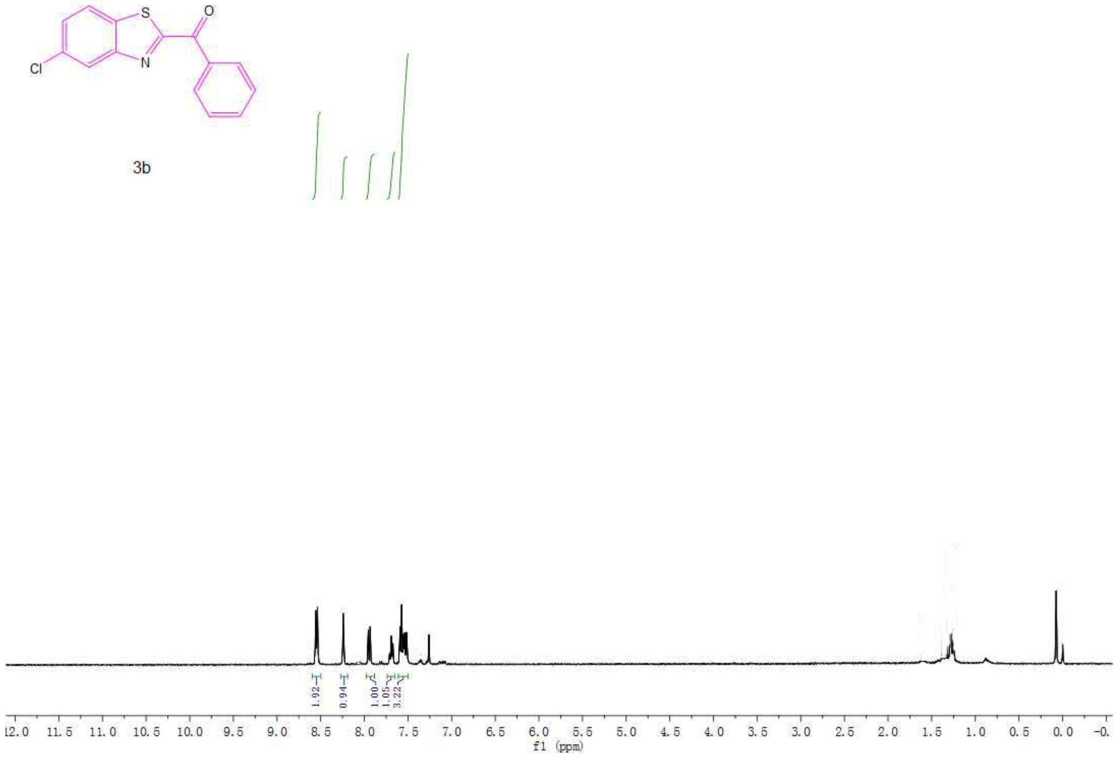
[4] S. Sithambaram, Y. Ding, W. Li, X. Shen, F. Gaenzlera and S. L. Suib, *Green Chem.*, 2008, **10**, 1029-1032.

[5] T. Chatterjee and B. C. Ranu, *RSC Adv.*, 2013, **3**, 10680-10686.

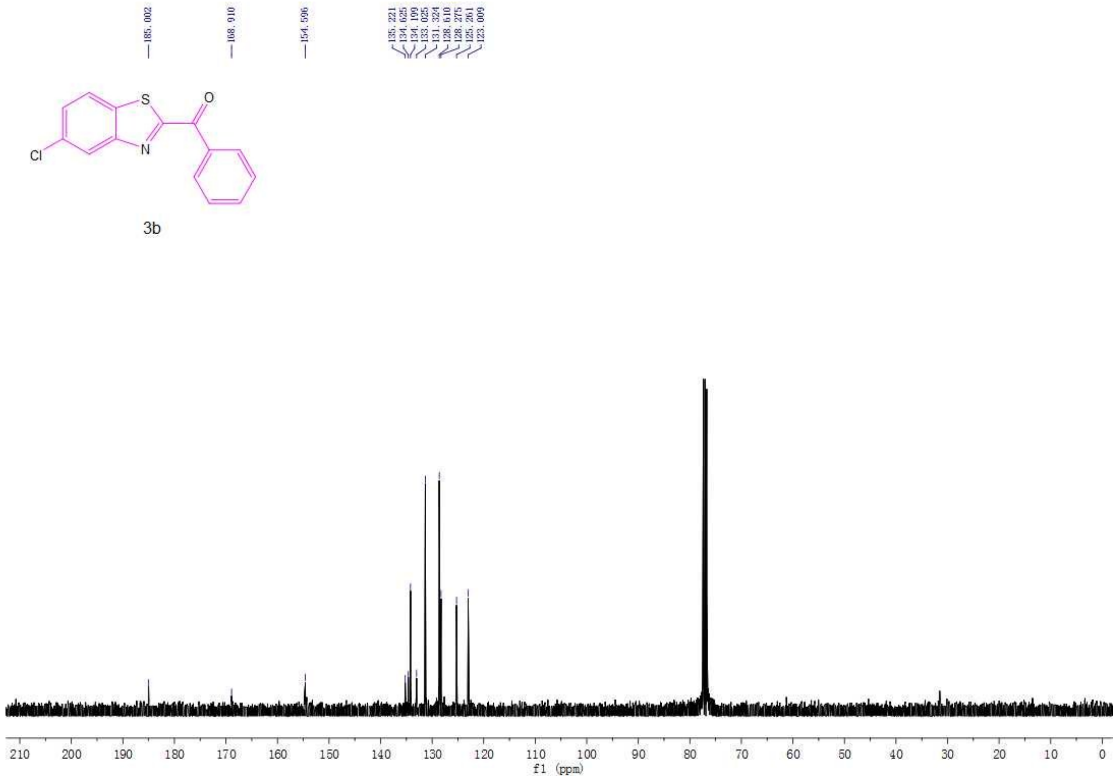
8. Copy of ^{1}H NMR and ^{13}C NMR Spectra for Products



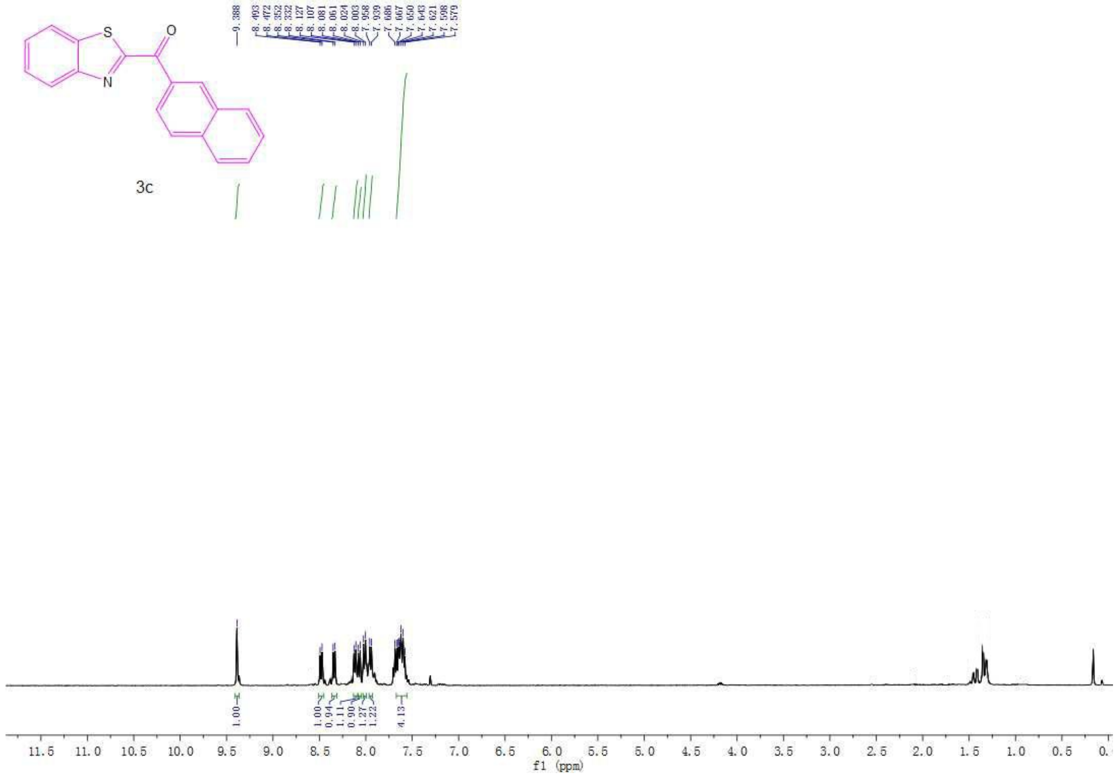


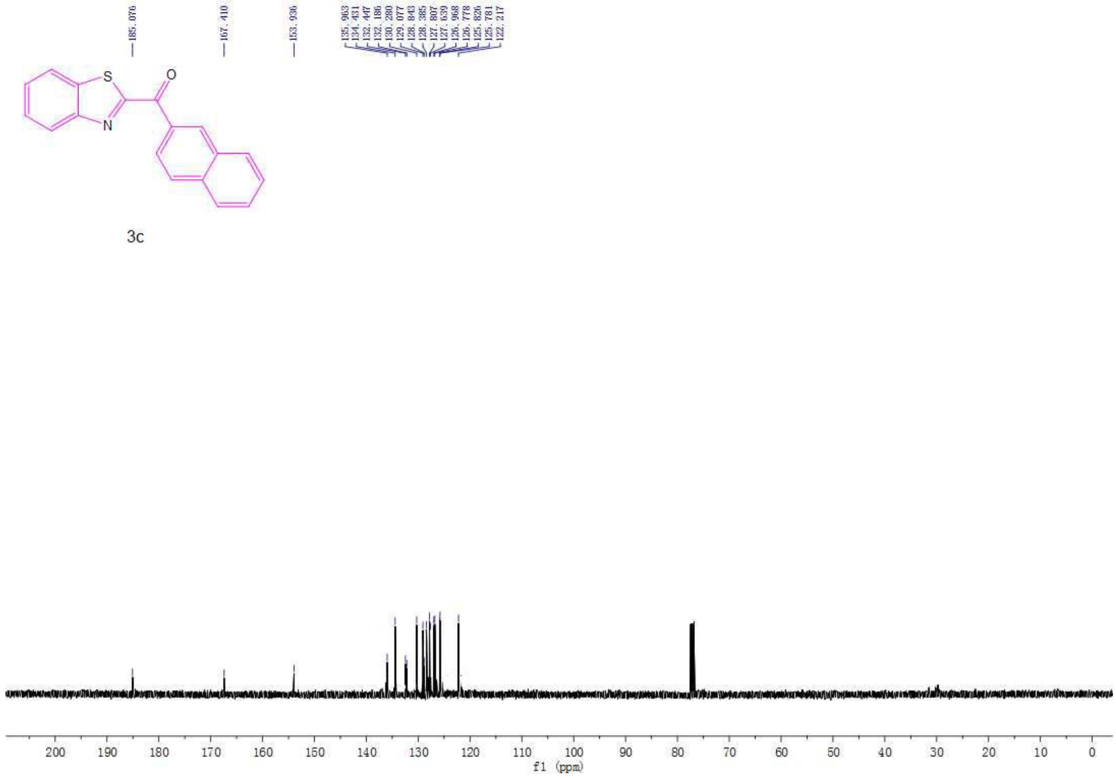

3b

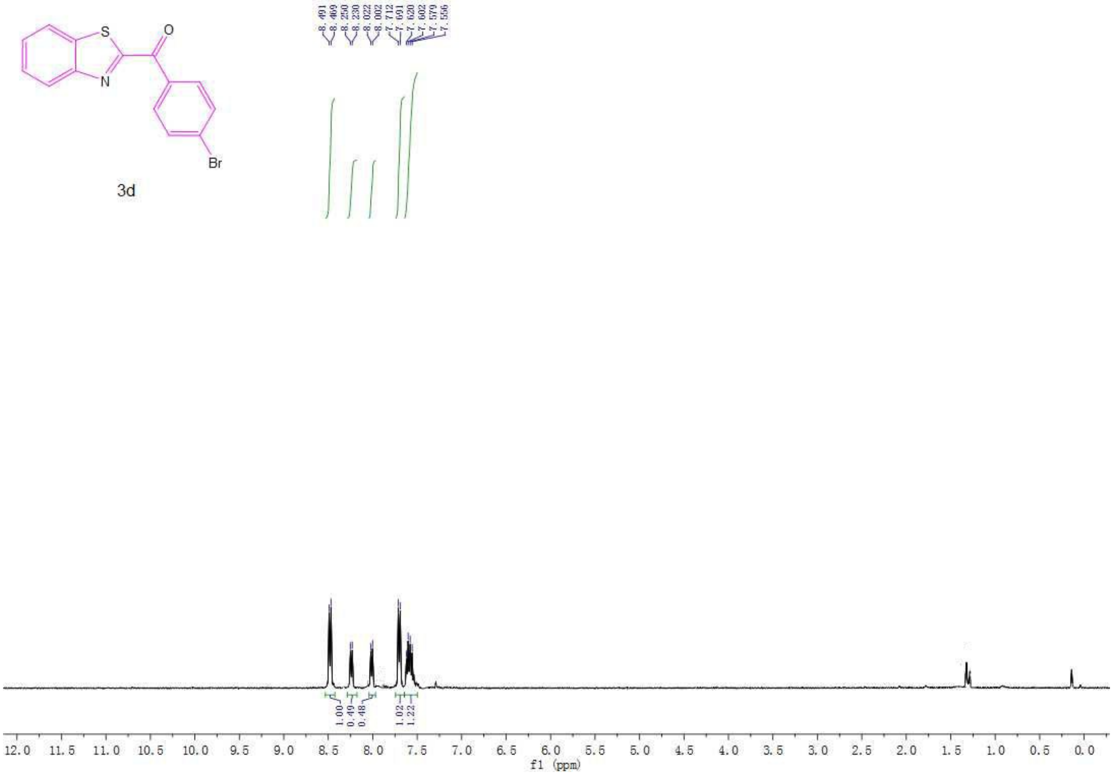
S
O
N
Cl
1.92
0.94
1.00
1.05
3.22
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

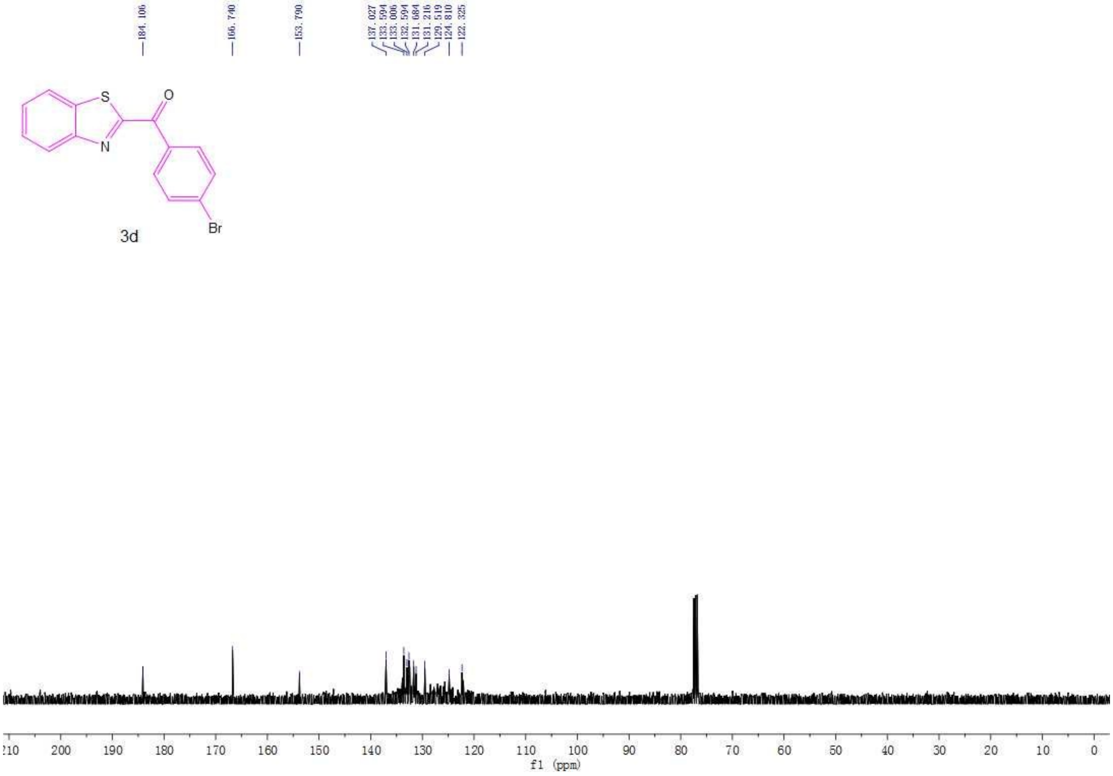

3b

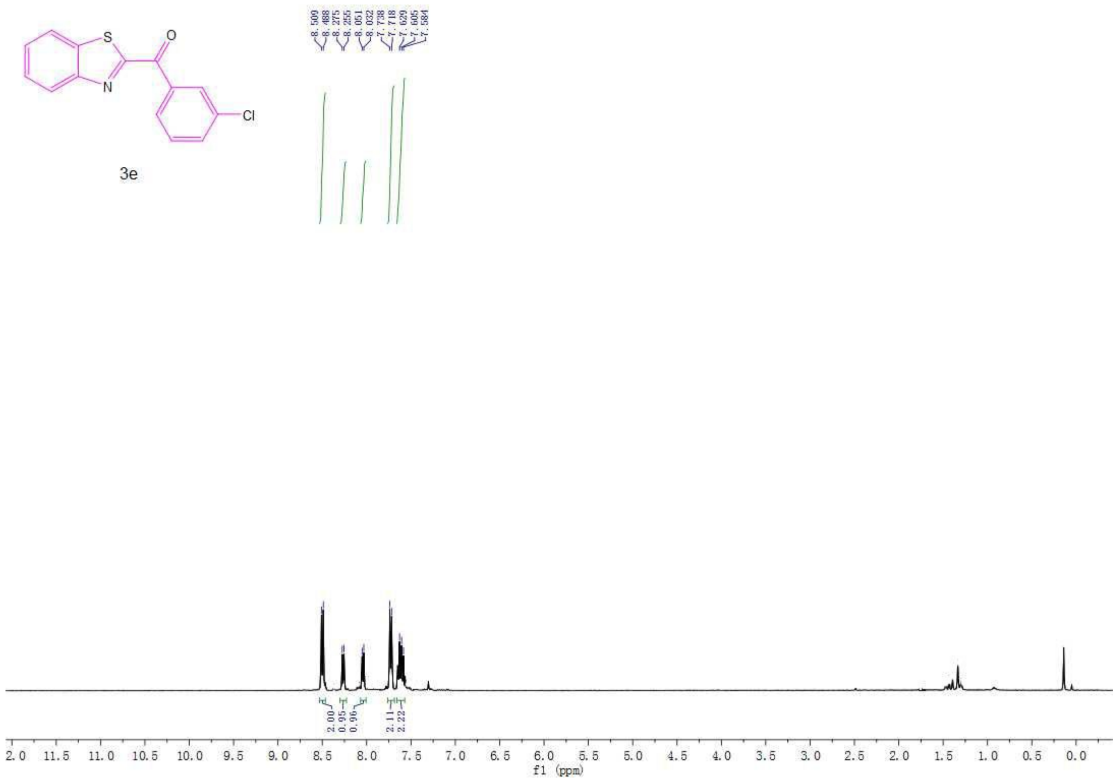
185.002
168.910
154.596
135.221
134.625
134.199
133.025
131.324
128.610
128.275
125.261
123.009
S
O
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

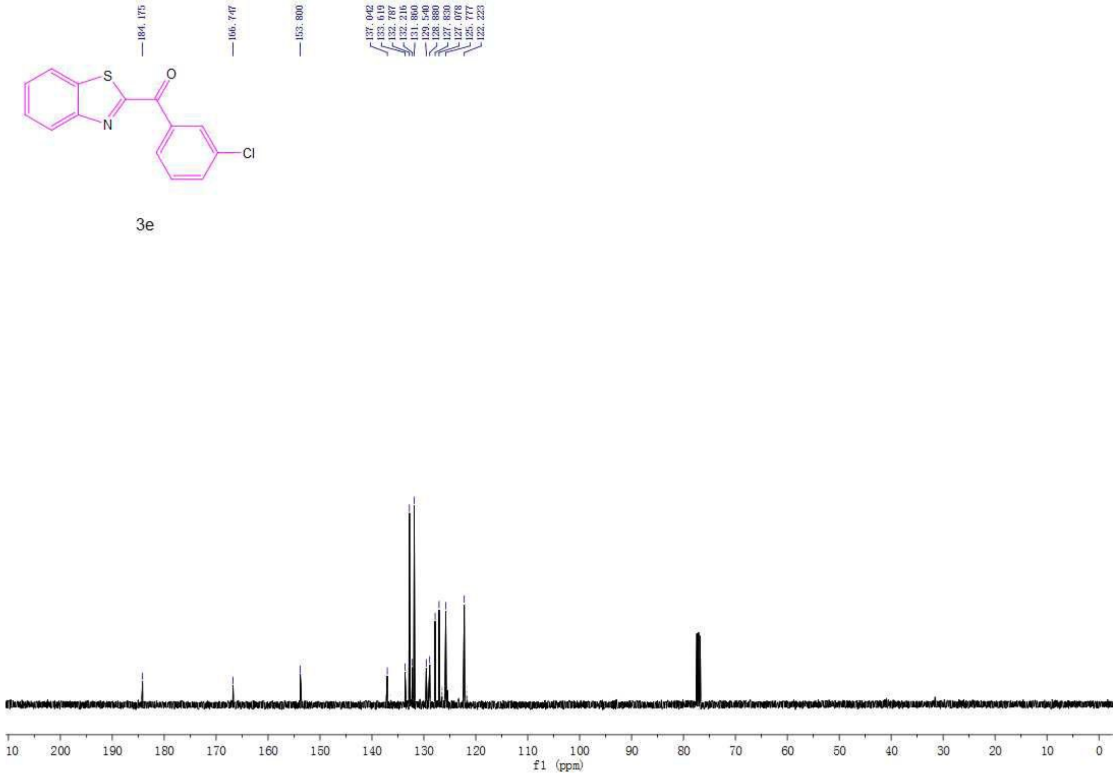

S
O
N
3c
9.388
8.493
8.472
8.352
8.332
8.127
8.107
8.081
8.061
8.024
8.003
7.968
7.939
7.686
7.667
7.650
7.643
7.621
7.598
7.579
1.00
1.00
0.94
1.11
0.90
1.27
1.22
4.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

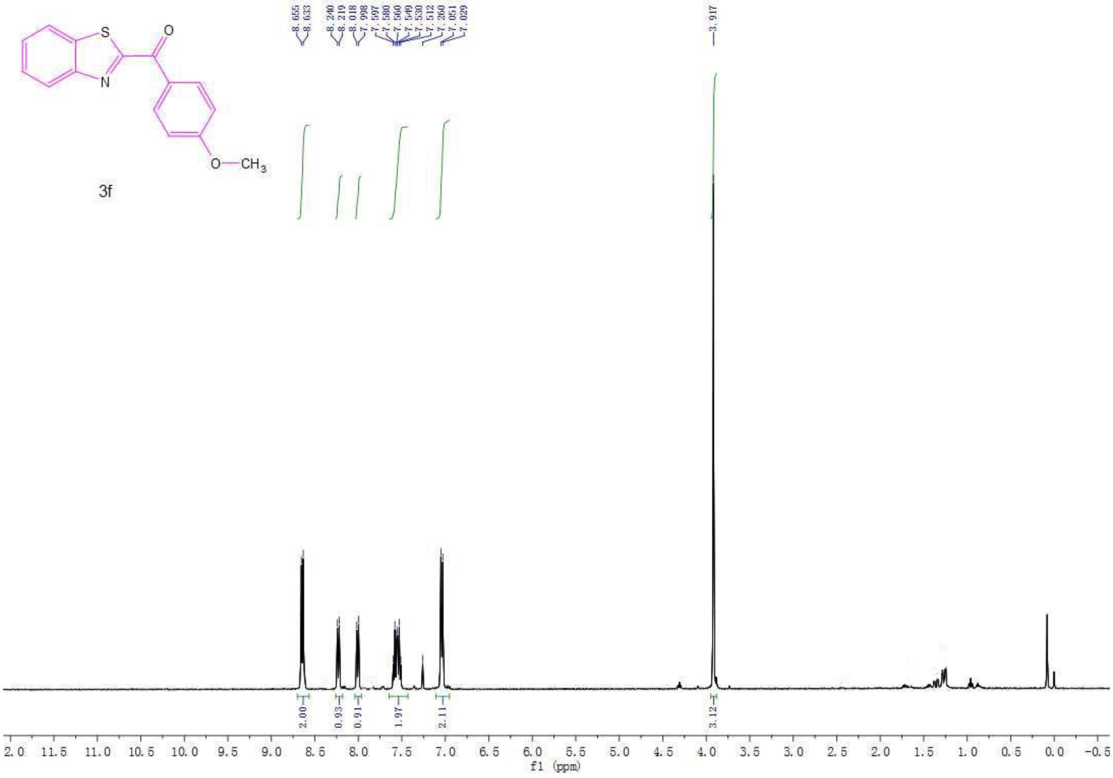

S
O
N
3c
185.076
167.410
153.936
135.963
134.431
132.447
132.186
130.280
129.077
128.843
128.385
127.807
127.639
126.968
126.778
125.826
125.781
122.217
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
O
N
Br
3d
8.491
8.469
8.250
8.230
8.022
8.002
7.712
7.691
7.620
7.602
7.579
7.556
1.00
0.49
0.48
1.02
1.22
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

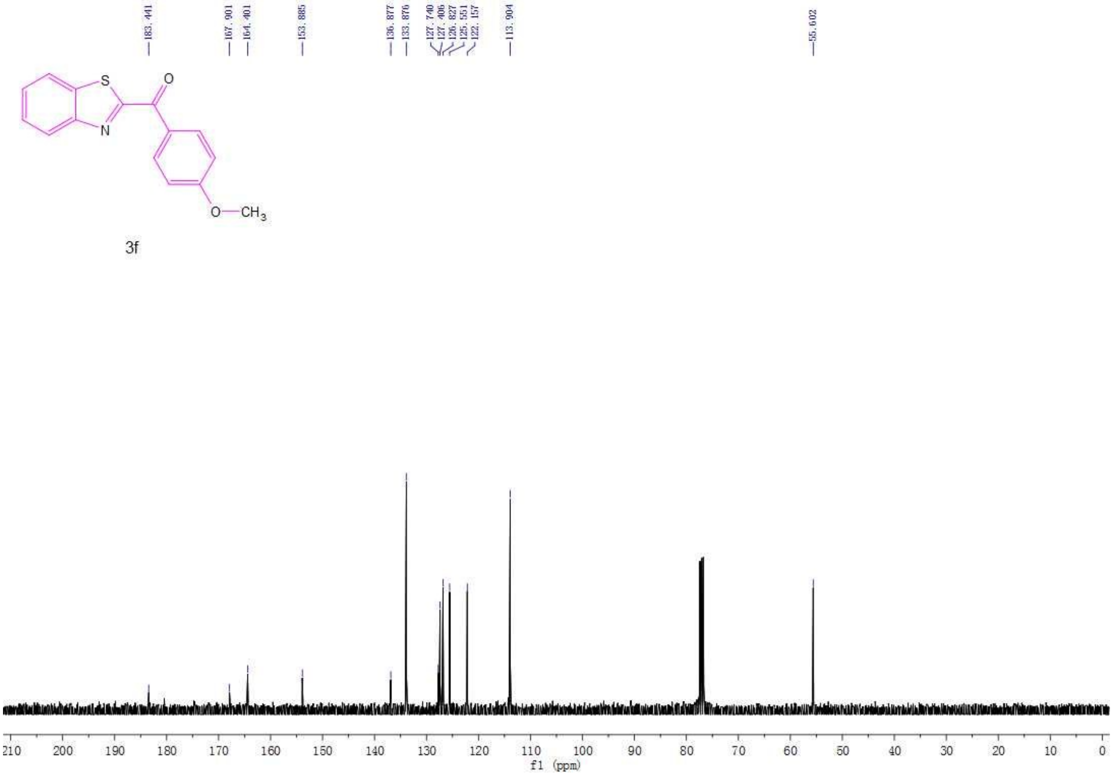

184.106
166.740
153.790
137.027
133.594
133.066
132.594
131.684
131.216
129.519
124.810
122.325
S
O
N
Br
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3e
S
O
N
Cl
8.509
8.488
8.275
8.255
8.051
8.032
7.738
7.718
7.629
7.605
7.584
2.00
0.95
0.96
2.11
2.22
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

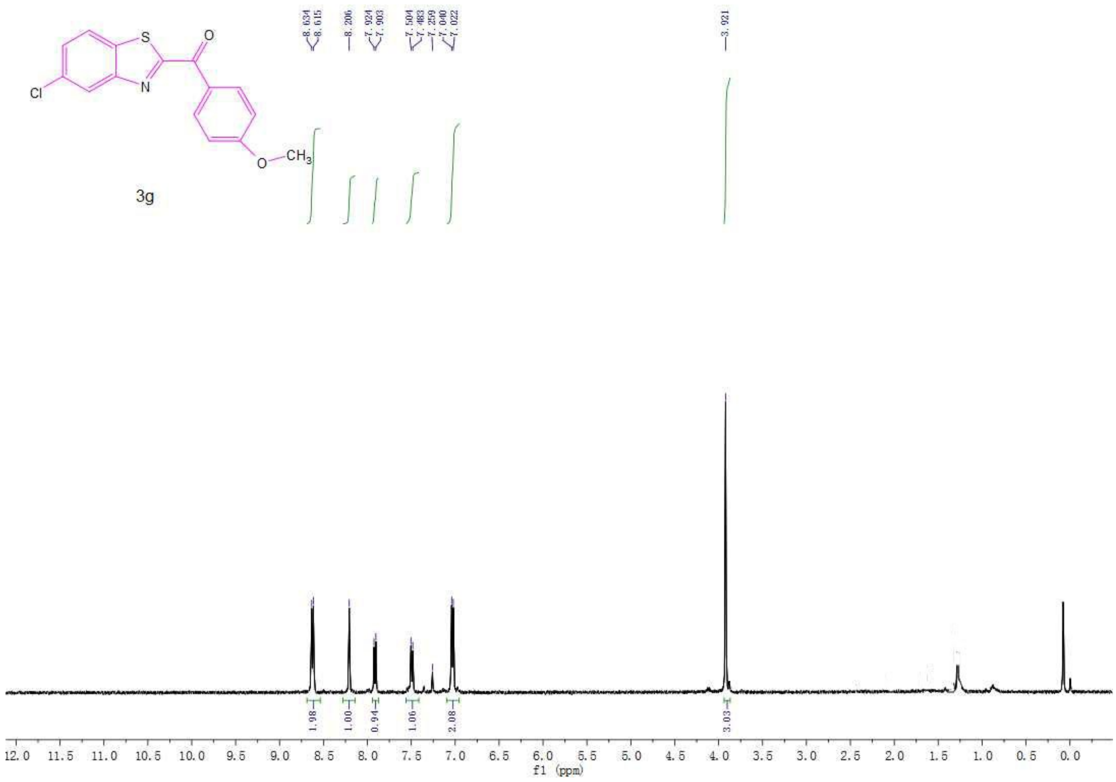

3e
184.175
166.747
153.800
137.042
133.619
132.787
132.216
131.860
129.540
128.880
127.830
127.078
125.777
122.223
S
O
N
Cl
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



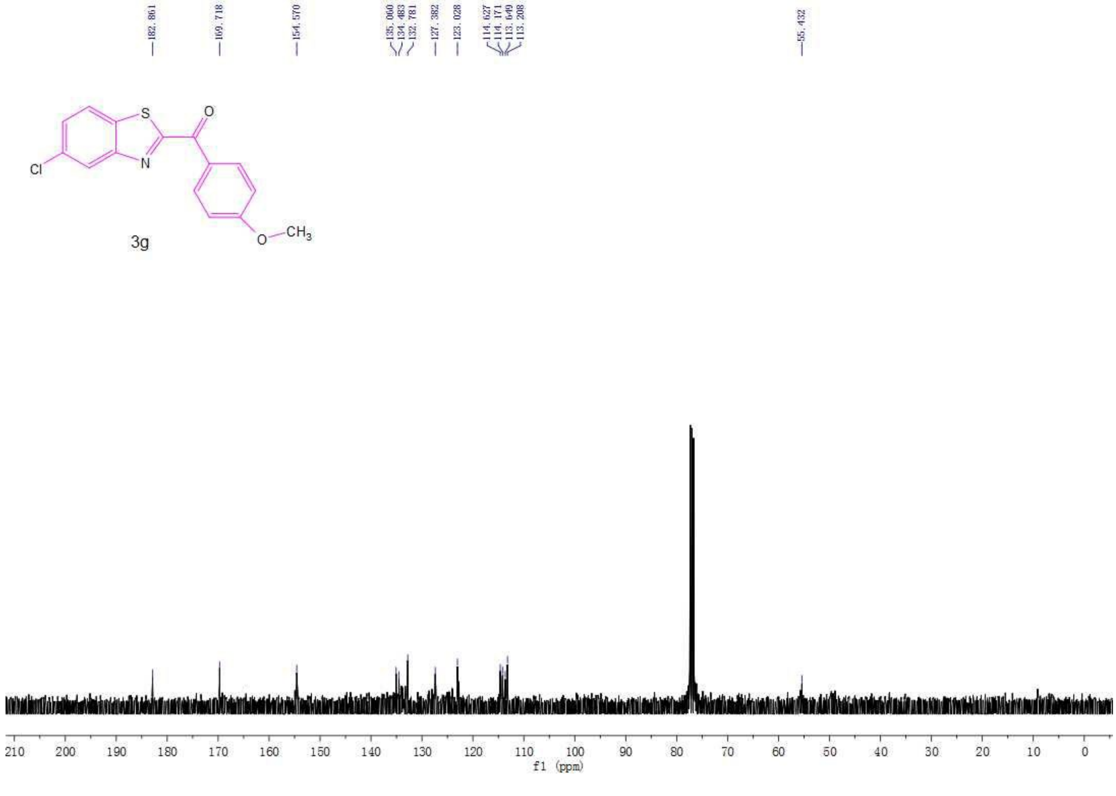
S
O
N
O
CH3
3f
8.655
8.633
8.240
8.219
8.018
7.998
7.597
7.580
7.560
7.549
7.530
7.512
7.260
7.051
7.029
3.917
2.00
0.93
0.91
1.97
2.11
3.12
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



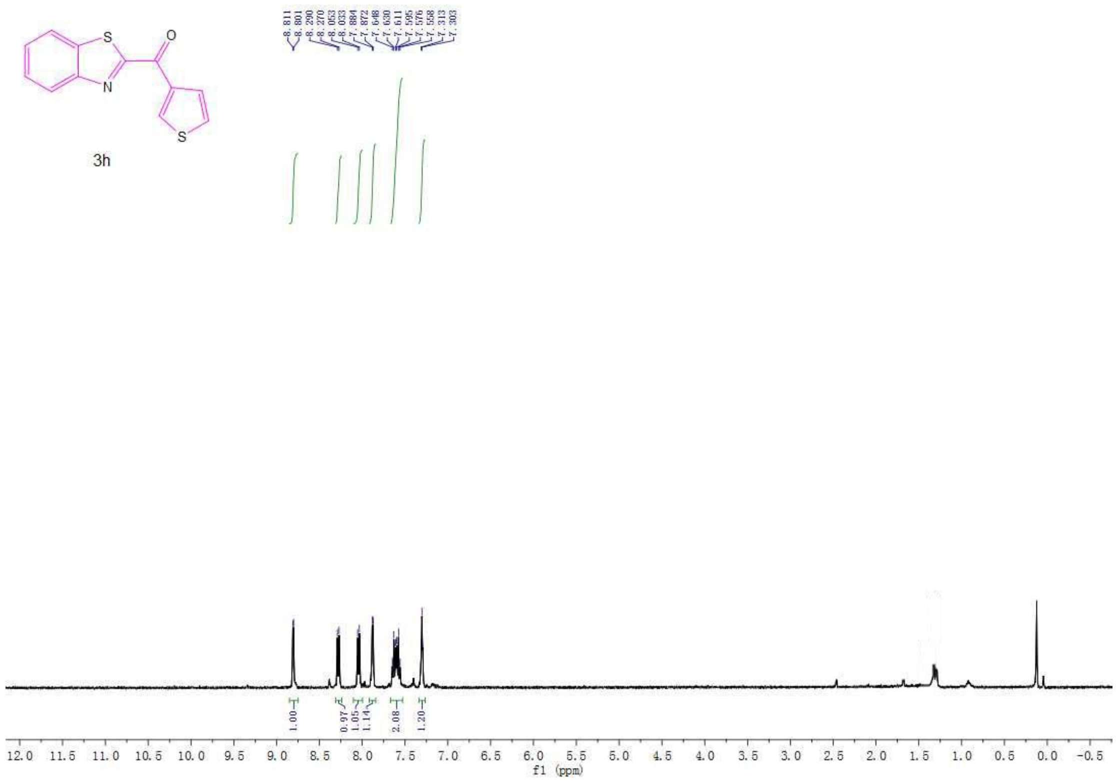
183.441
167.901
164.401
153.885
136.877
133.876
127.740
127.406
126.827
125.551
122.157
113.904
55.602
S
O
N
O
CH3
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

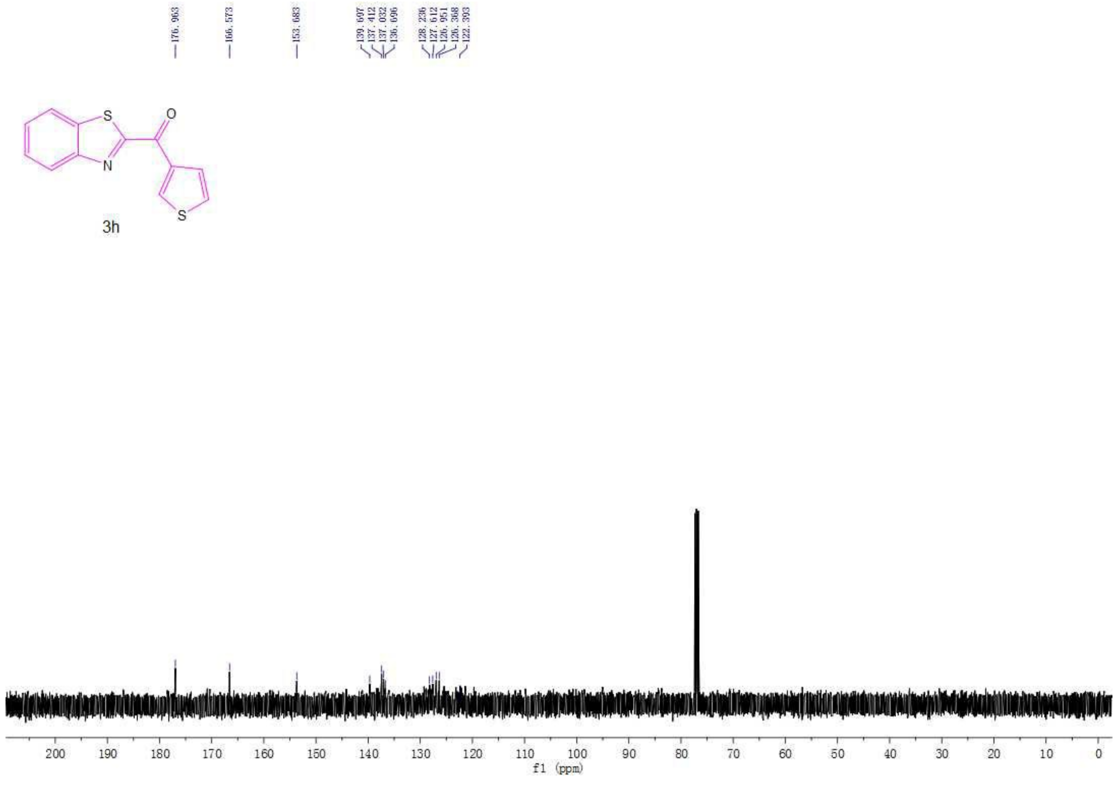


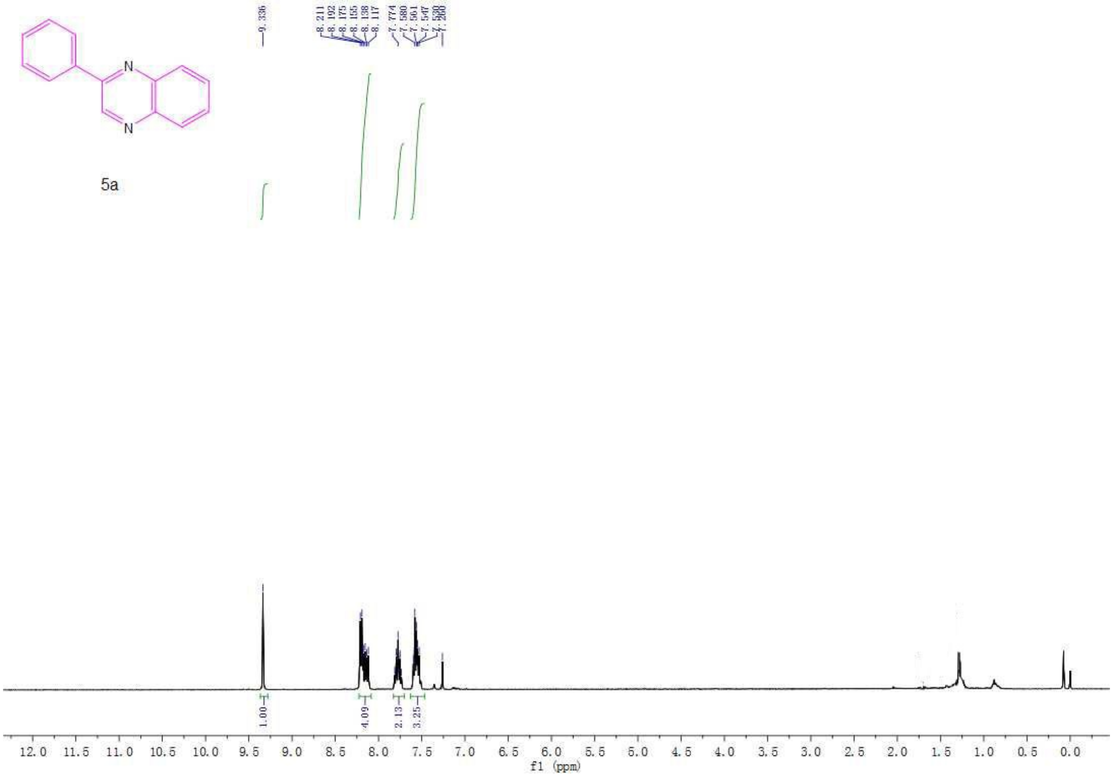
S
O
Cl
N
O
CH3
3g
8.634
8.615
8.206
7.924
7.903
7.504
7.483
7.259
7.040
7.022
3.921
1.98
1.00
0.94
1.06
2.08
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

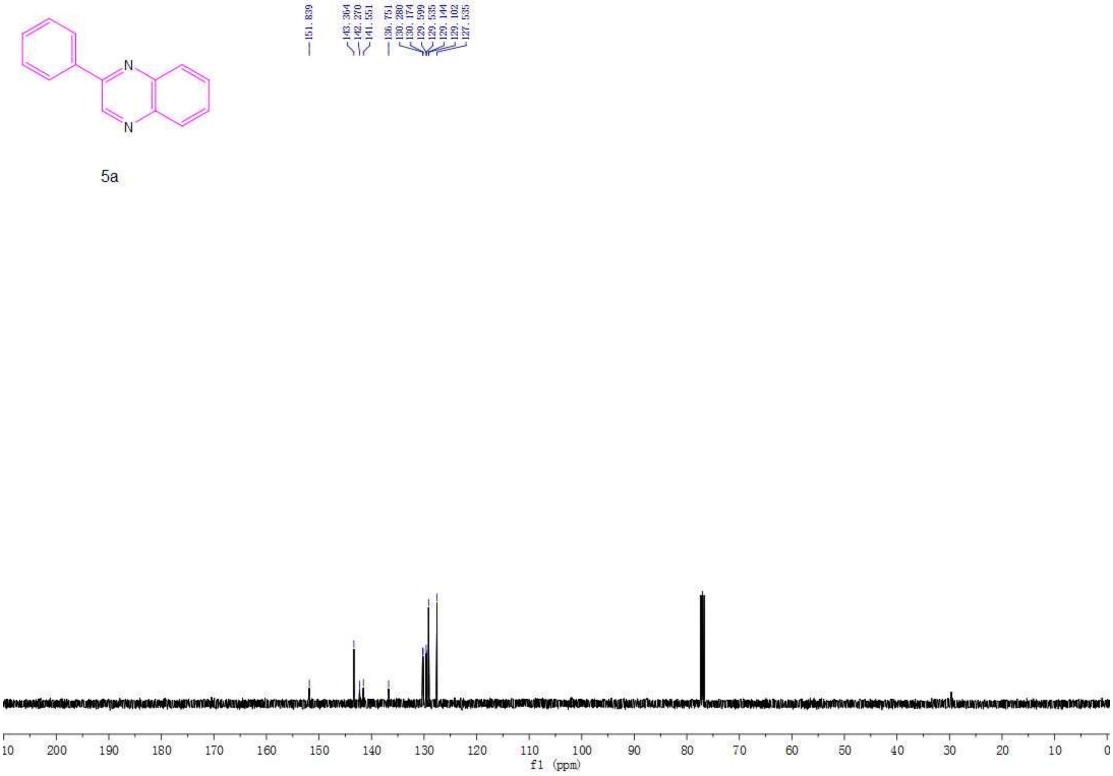


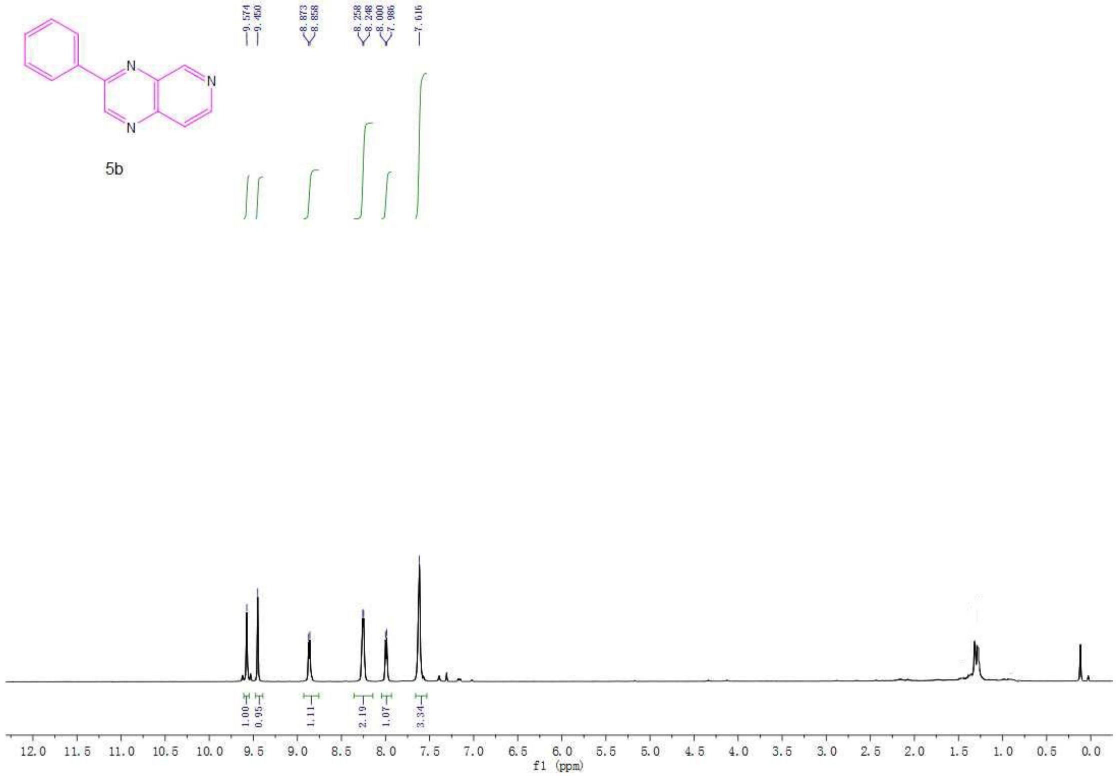
182.861
169.718
154.570
135.060
134.483
132.781
127.382
123.028
114.627
114.171
113.649
113.208
55.432
S
O
Cl
N
O
CH3
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

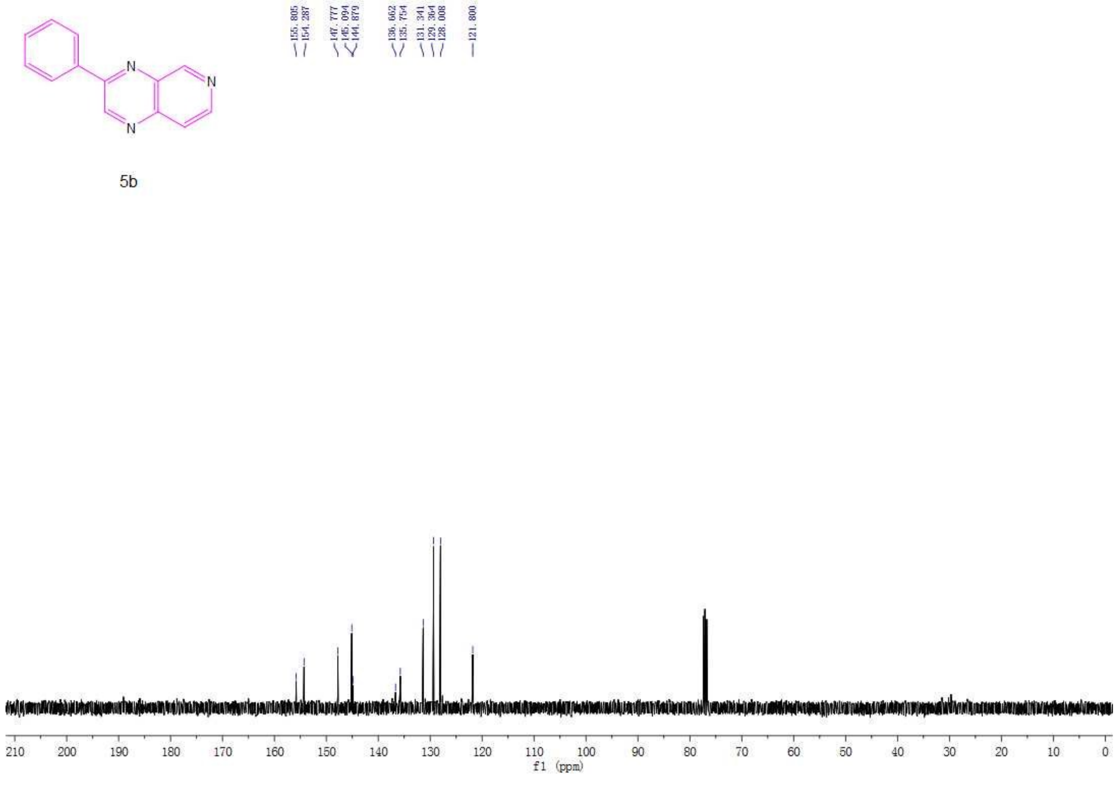

3h
8.811
8.801
8.290
8.270
8.053
8.033
7.884
7.872
7.648
7.630
7.611
7.595
7.576
7.558
7.313
7.303
S
N
O
S
1.00
0.97
1.05
1.14
2.08
1.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

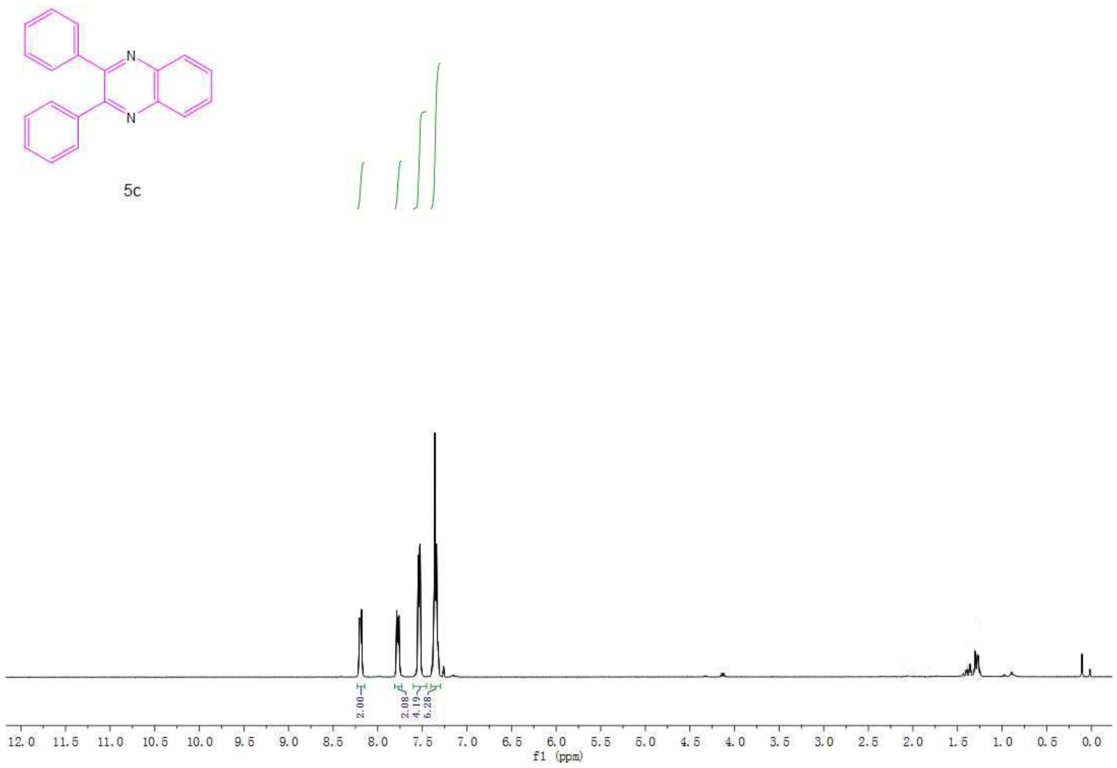

3h
176.963
166.573
153.683
139.697
137.412
137.032
136.696
128.236
127.612
126.951
126.368
122.393
S
N
O
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

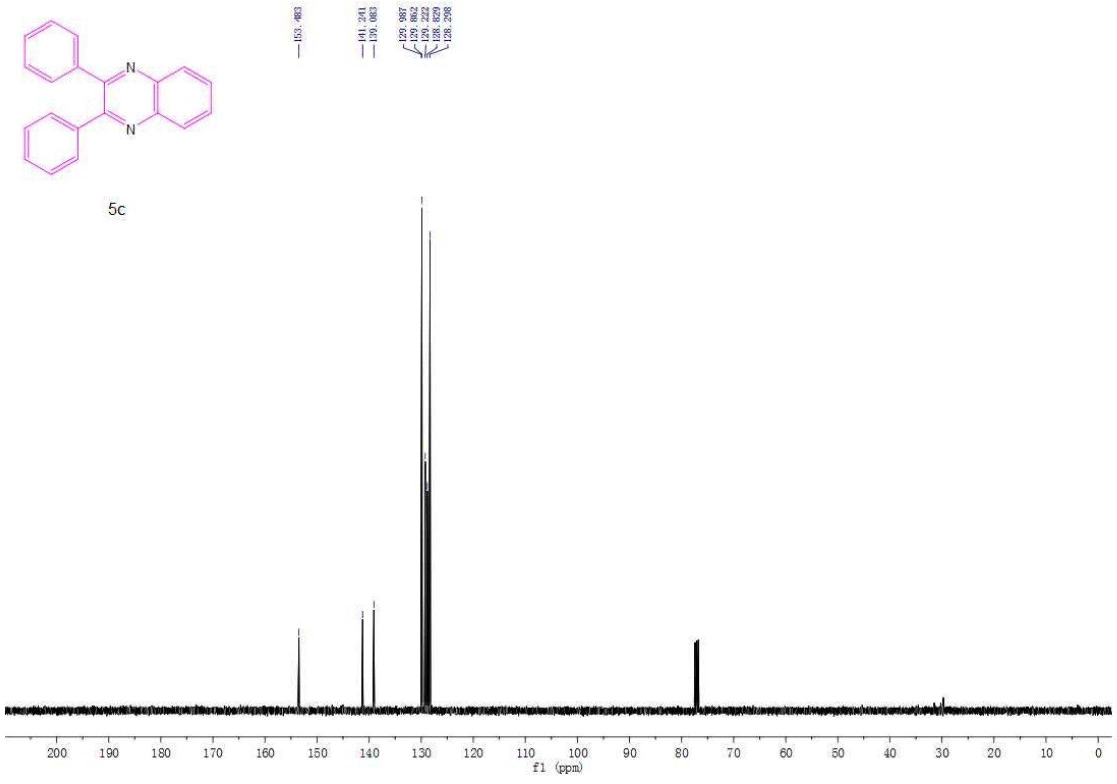

N
N
5a
9.336
8.211
8.192
8.175
8.155
8.138
8.117
7.774
7.580
7.561
7.547
7.530
7.260
1.00
4.09
2.13
3.25
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

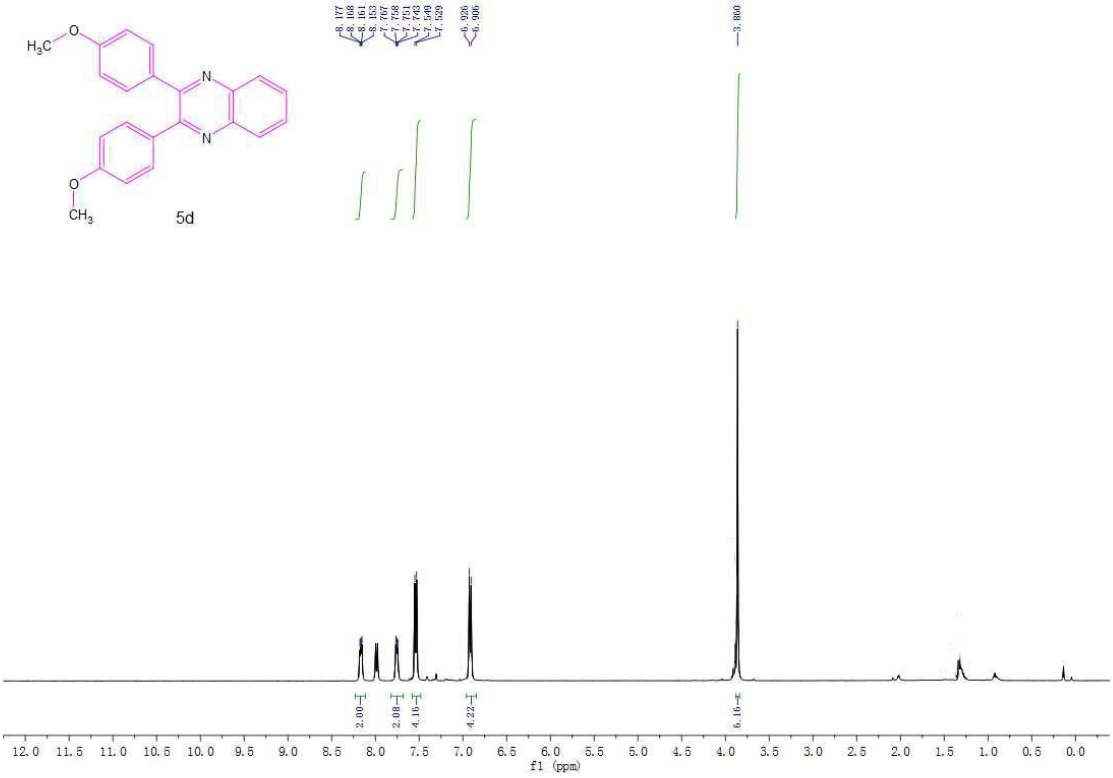

N
N
5a
151.839
143.364
142.270
141.551
136.751
130.280
130.174
129.599
129.535
129.144
129.102
127.535
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

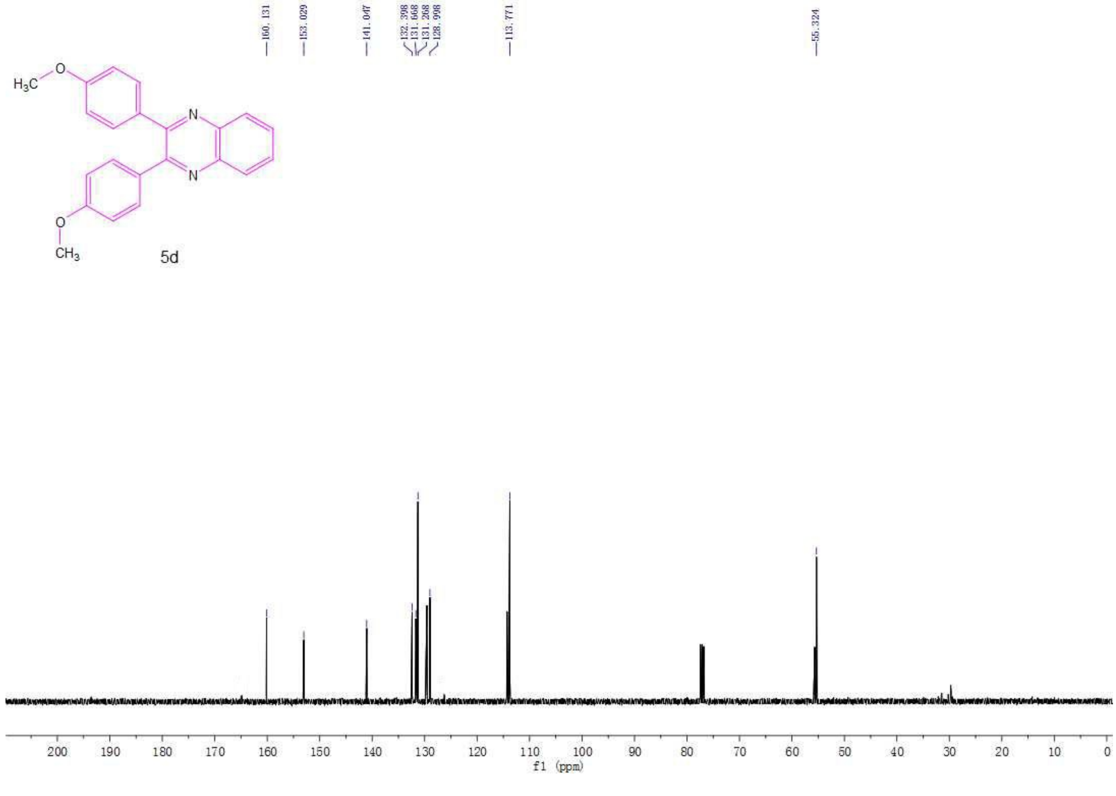

5b
N
N
N
9.574
9.490
8.873
8.858
8.258
8.248
8.000
7.986
7.616
1.00
0.95
1.11
2.19
1.07
3.34
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

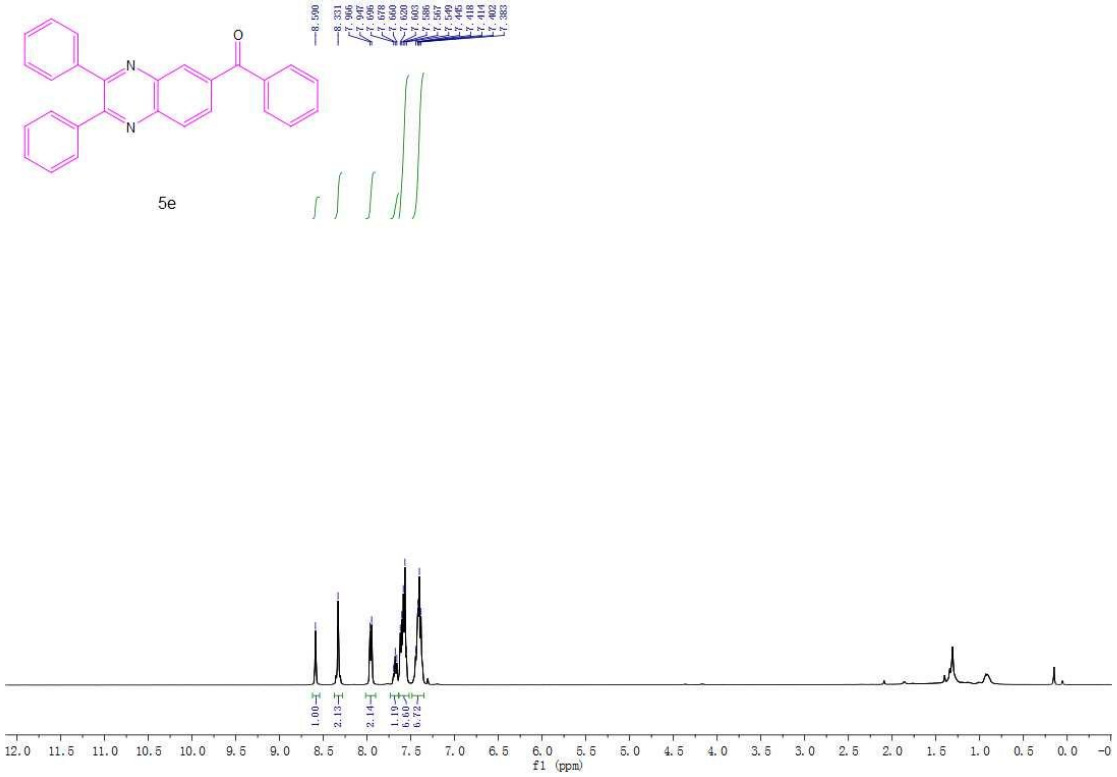

5b
N
N
N
155.895
154.287
147.777
145.094
144.879
136.662
135.754
131.341
129.364
128.008
121.800
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

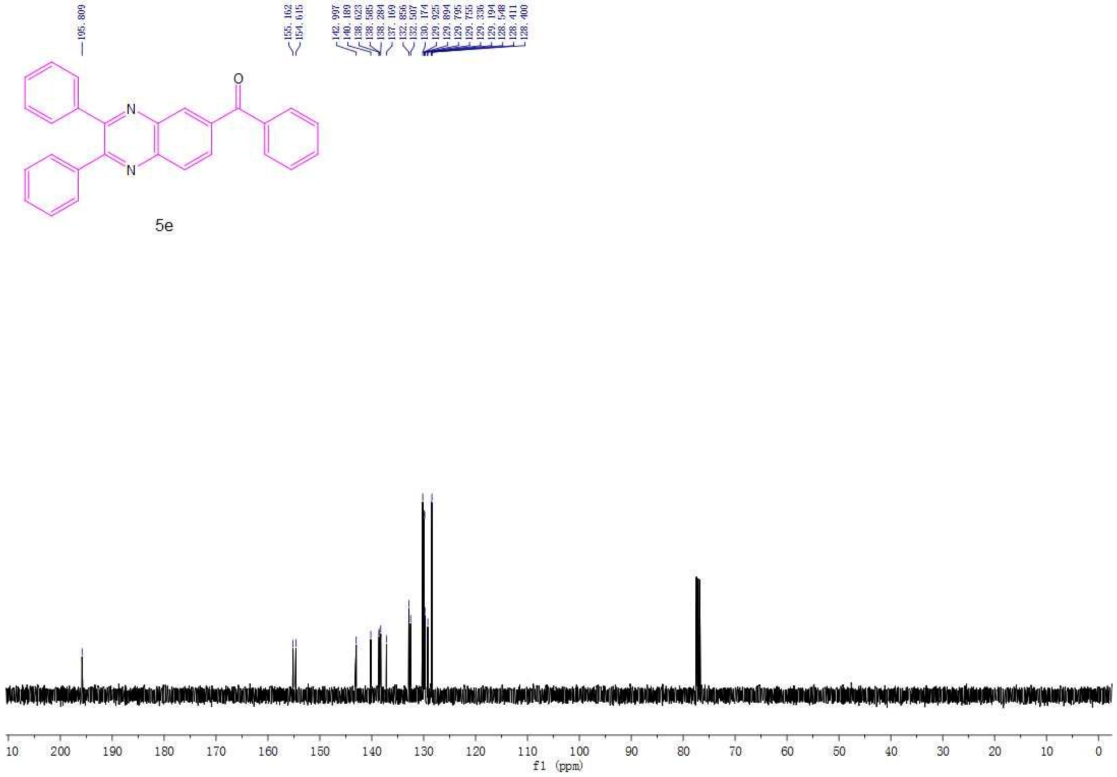

N
N
5c
2.00
2.08
4.19
6.28
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

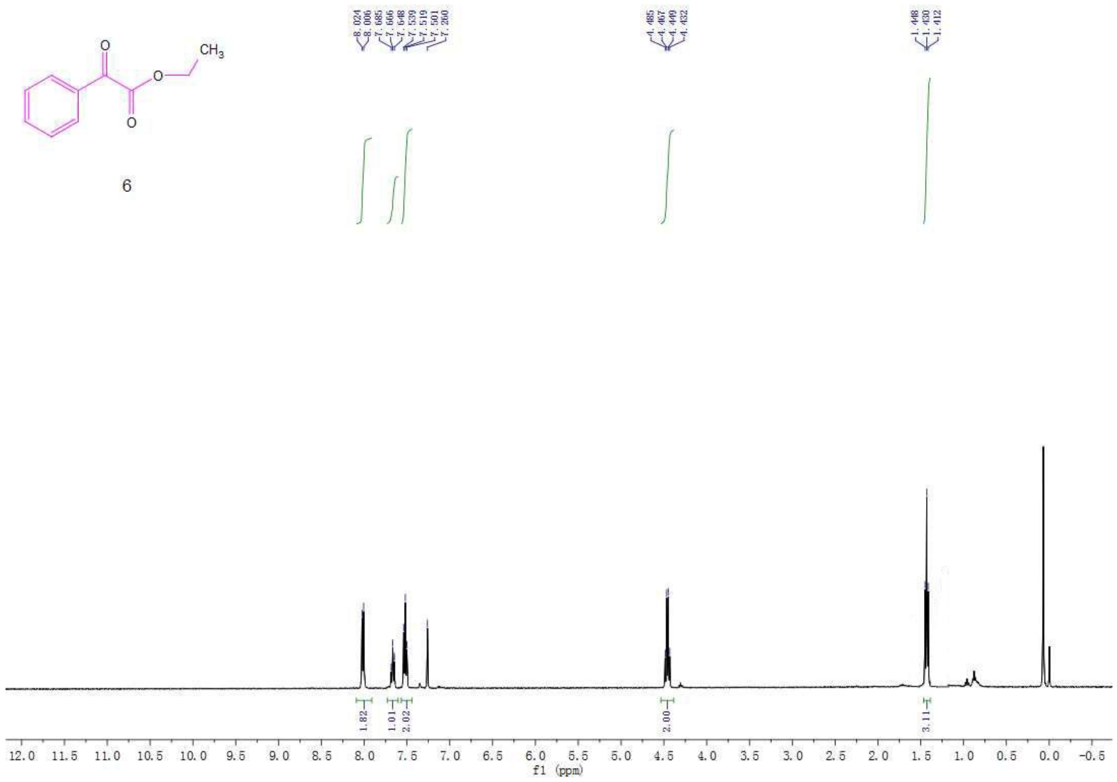

153.483
141.241
139.083
129.987
129.862
129.222
128.829
128.298
N
N
5c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H_3C
O
N
N
O
CH_3
5d
8.177
8.168
8.161
8.153
7.767
7.758
7.751
7.743
7.549
7.529
6.926
6.906
3.860
2.00
2.08
4.16
4.22
6.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

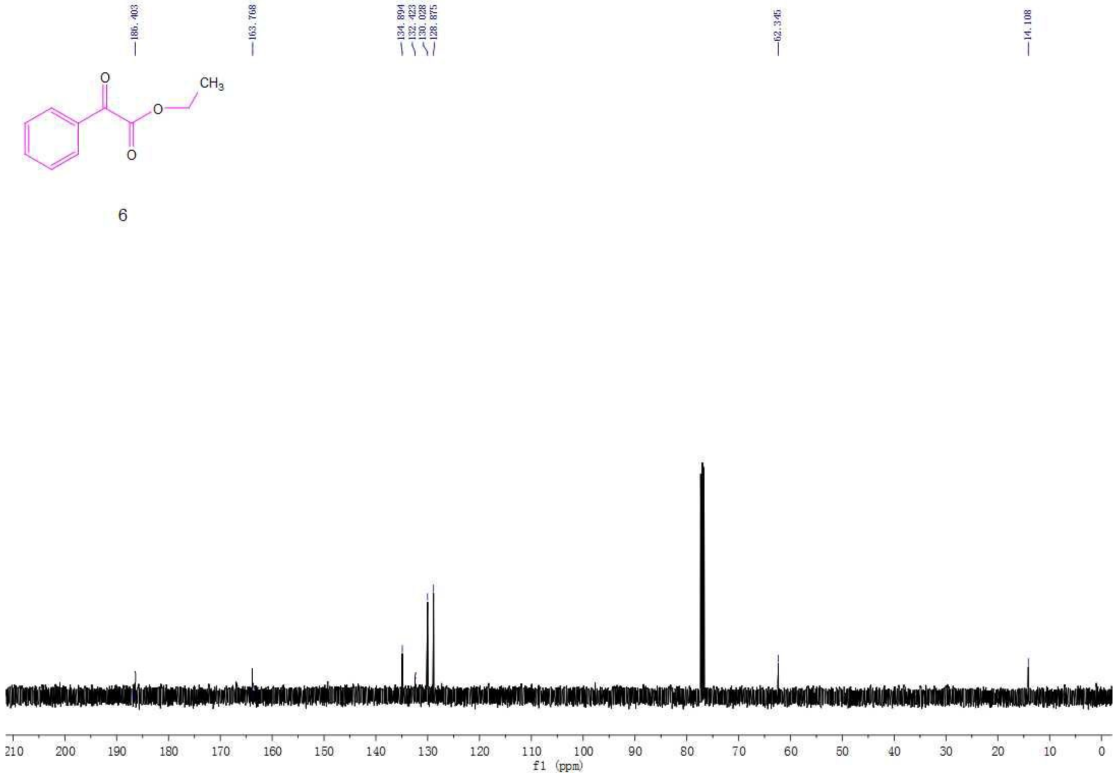

160.131
153.029
141.047
132.398
131.668
131.268
128.998
113.771
55.324
H_3C
O
N
N
O
CH_3
5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5e
N
N
O
8.590
8.331
7.966
7.947
7.696
7.678
7.660
7.620
7.603
7.586
7.567
7.549
7.445
7.418
7.414
7.402
7.383
1.00
2.13
2.14
1.19
6.60
6.72
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

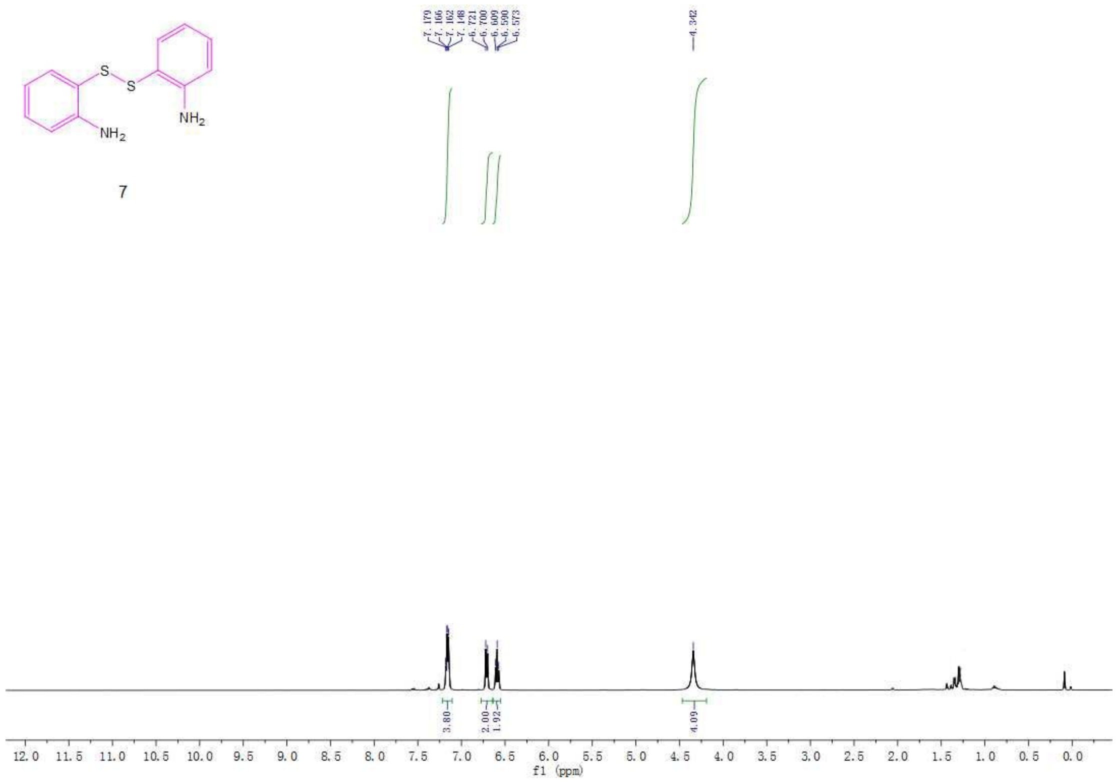

5e
N
N
O
195.809
155.162
154.615
142.997
140.189
138.623
138.585
138.284
137.169
132.856
132.507
130.174
129.925
129.894
129.795
129.755
129.336
129.194
128.548
128.411
128.400
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
CH3
O
O
8.024
8.006
7.685
7.666
7.648
7.539
7.519
7.501
7.260
4.485
4.467
4.449
4.432
1.448
1.430
1.412
1.82
1.01
2.02
2.00
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

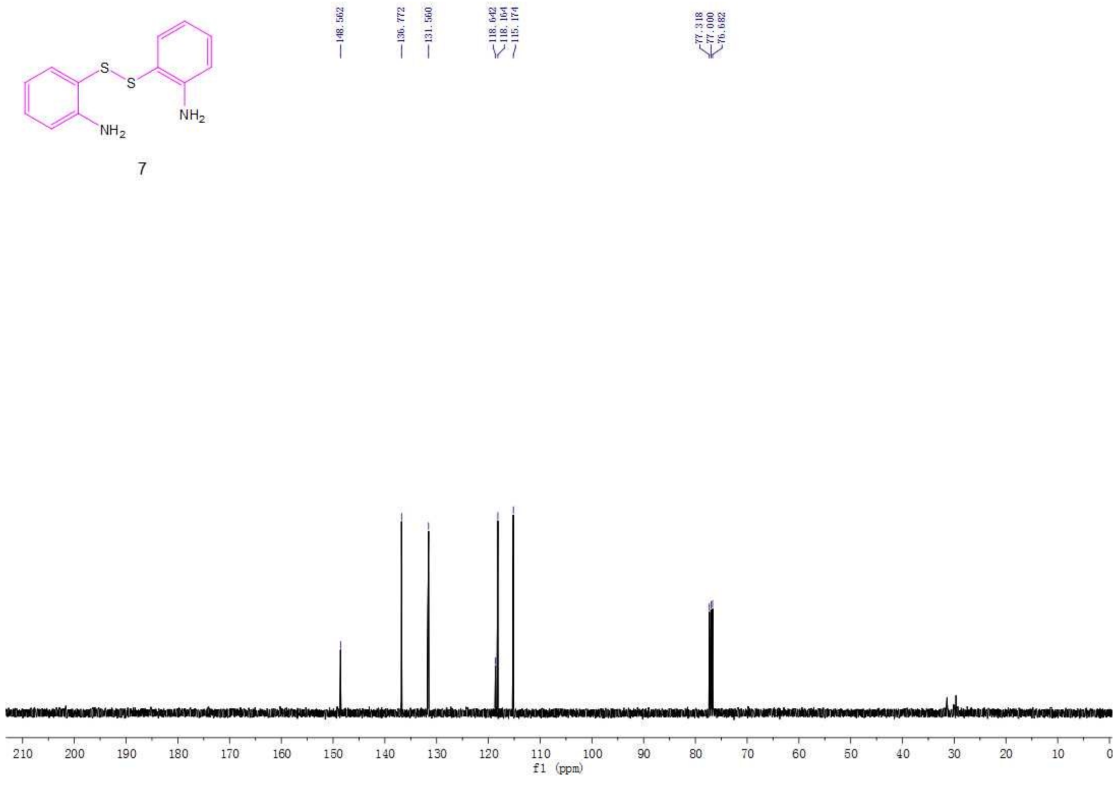
6


O
CH3
O
O
186.403
163.768
134.894
132.423
130.028
128.875
62.345
14.108
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6


S
S
NH2
NH2
7.179
7.166
7.162
7.148
6.721
6.700
6.609
6.590
6.573
4.342
3.80
2.00
1.92
4.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

7


S
S
NH2
NH2
148.562
136.772
131.560
118.642
118.164
115.174
77.318
77.000
76.682
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7