Supporting Information

Copper-Catalyzed One-Pot Synthesis of Unsymmetrical Arylurea Derivatives via Tandem Reaction of Diaryliodonium Salts with *N*-Arylcyanamide

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List of ^{1}H NMR and ^{13}C NMR spectra for compounds 4a-r, 4ba-4bj

1) CIF file of 1-(3,5-Dimethylphenyl)-1,3-diphenylurea (4m)

Datablock:

Bond precision:	C–C = 0.0032 Å		Wavelength=1.54184
Cell:	a=10.1979	b=15.8821(4)	c=21.6227
	alpha=90	beta=90	gamma=90
Temperature:	291K		
	Calculated		Reported
Volume	3502.10(19)		3502.10(18)
Space group	p b c a		P b c a
Hall group	-P 2ac 2ab		-P 2ac 2ab
Moiety formula	C21 H20 N2 O		C21 H20 N2 O
Sum formula	C21 H20 N2 O		C21 H20 N2 O
Mr	316.39		316.39
Dx, g cm-3	1.200		1.200
Z	8		8
Mu (mm-1)	0.583		0.583
F000	1344.0		1344.0
F000'	1347.70		
h, k, lmax	12, 18, 25		12, 18, 25
Nref	3121		3109
Tmin, Tmax	0.890, 0.911		0.970, 1.000
Tmin'	0.890		
Correction method= MULTI-SCAN			
Data completeness= 0.996		Theta (max) = 67.030	
R (reflections) = 0.0450 (2324)		wR2 (reflections) = 0.1255 (3109)	
S = 1.026		Npar= Npar = 224	

2) Crystal structure and data of 1-(3,5-Dimethylphenyl)-1,3-diphenylurea (4m) (CCDC 1001202)

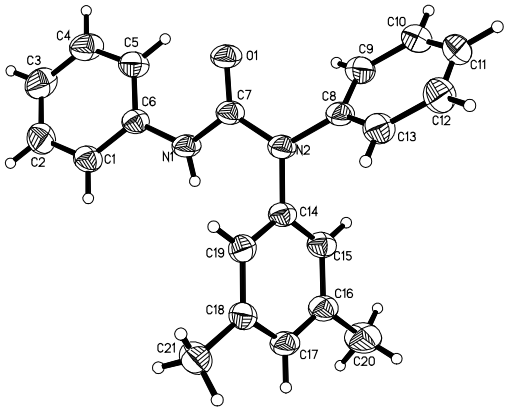


Table 1. Crystal data and structure refinement for 4m

Identification code	4m
Empirical formula	$C_{21}H_{20}N_2O$
Formula weight	316.39
Temperature	291(2) K
Wavelength	1.54184 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 10.1979 (3) Å $\alpha = 90^o$
	b = 15.8821 (4) Å $\beta = 90^o$
	a = 21.6227 (8) Å $\gamma = 90^o$
Volume	3502.10 (18) Å
Z, Calculated density	8, 1.2 Mg/m^3
Absorption coefficient	0.583 mm^{-1}
F(000)	1344.0
Crystal size	0.2 x 0.18 x 0.16 mm
Theta range for data collection	4.088 to 71.118^o
Limiting indices	-12<=h<=6, -16<=k<=18, -25<=l<=23
Reflections collected / unique	2614/31101 [R(int) = 0.0158]
Completeness to theta = 67.03	99.6 %
Max. and min. transmission	0.890 and 0.911
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3109/0/224
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.2324, wR2 = 0.3109
R indices (all data)	R1 = 0.045, wR2 = 0.1256
Largest diff. Peak and hole	0.12 and -0.14 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 4m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	74534(12)	49987(10)	21628(6)	6720(4)
N(1)	52858(15)	52406(12)	23410(7)	6190(4)
N(2)	65332(14)	44702(11)	30413(7)	6090(4)
C(1)	39279(19)	62178(14)	17916(10)	6740(5)
C(2)	35440(2)	66166(17)	12534(12)	8400(7)
C(3)	42000(2)	64678(19)	70900(12)	9380(8)
C(4)	52390(2)	59178(18)	70220(11)	8900(8)
C(5)	56390(2)	55202(16)	12360(9)	7280(6)
C(6)	49846(16)	56649(13)	17859(8)	5720(5)
C(7)	64866(17)	49130(13)	24867(8)	5650(4)
C(8)	76015(17)	39019(13)	31438(9)	5990(5)
C(9)	79700(2)	33343(15)	26959(10)	7650(6)
C(10)	89980(3)	27813(17)	28015(13)	9040(8)
C(11)	96480(2)	27972(18)	33579(13)	9220(8)
C(12)	92670(2)	33487(18)	38070(13)	9030(8)
C(13)	82478(19)	39055(16)	37045(10)	7150(6)
C(14)	55282(16)	45227(13)	35071(8)	5460(5)
C(15)	48431(17)	38082(14)	36661(9)	6100(5)
C(16)	38774(18)	38400(14)	41146(10)	6540(5)
C(17)	36218(18)	46015(14)	43977(9)	6490(5)
C(18)	42971(18)	53283(13)	42467(8)	6090(5)
C(19)	52710(18)	52796(13)	37966(9)	5910(5)
C(20)	31060(2)	30582(18)	42792(15)	10020(9)
C(21)	39900(2)	61545(16)	45559(11)	8470(7)

Table 3. Bond lengths [Å] and angles [^{o}] for 4m

O(1)-C(7)	1.217(2)
N(1)-C(6)	1.410(2)
N(1)-C(7)	1.367(2)
N(2)-C(7)	1.391(2)
N(2)-C(8)	1.432(2)
N(2)-C(14)	1.439(2)
C(1)-C(2)	1.382(3)
C(1)-C(6)	1.390(3)
C(2)-C(3)	1.375(3)
C(3)-C(4)	1.373(3)
C(4)-C(5)	1.378(3)
C(5)-C(6)	1.383(3)

C(8)-C(9)	1.375(3)
C(8)-C(13)	1.380(3)
C(9)-C(10)	1.387(3)
C(10)-C(11)	1.374(4)
C(11)-C(12)	1.364(4)
C(12)-C(13)	1.382(3)
C(14)-C(15)	1.376(3)
C(14)-C(19)	1.380(3)
C(15)-C(16)	1.383(3)
C(16)-C(17)	1.380(3)
C(16)-C(20)	1.512(3)
C(17)-C(18)	1.383(3)
C(18)-C(19)	1.393(3)
C(18)-C(21)	1.506(3)
C(7)-N(1)-C(6)	124.96(16)
C(7)-N(2)-C(8)	118.56(15)
C(7)-N(2)-C(14)	123.35(15)
C(8)-N(2)-C(14)	118.02(15)
C(2)-C(1)-C(6)	120.1(2)
C(3)-C(2)-C(1)	120.3(2)
C(4)-C(3)-C(2)	119.6(2)
C(3)-C(4)-C(5)	120.8(2)
C(4)-C(5)-C(6)	120.1(2)
C(1)-C(6)-N(1)	117.60(17)
C(5)-C(6)-N(1)	123.17(18)
C(5)-C(6)-C(1)	119.13(19)
O(1)-C(7)-N(1)	123.39(18)
O(1)-C(7)-N(2)	121.67(16)
N(1)-C(7)-N(2)	114.94(16)
C(9)-C(8)-N(2)	120.77(18)
C(9)-C(8)-C(1)	3119.41(19)
C(13)-C(8)-N(2)	119.79(19)
C(8)-C(9)-C(10)	120.4(2)
C(11)-C(10)-C(9)	119.8(3)
C(12)-C(11)-C(10)	119.8(2)
C(11)-C(12)-C(13)	120.7(2)
C(8)-C(13)-C(12)	119.8(2)
C(15)-C(14)-N(2)	119.25(18)
C(15)-C(14)-C(19)	120.55(17)
C(19)-C(14)-N(2)	120.19(18)
C(14)-C(15)-C(16)	120.4(2)
C(15)-C(16)-C(20)	120.4(2)
C(17)-C(16)-C(15)	118.5(2)
C(17)-C(16)-C(20)	121.11(19)

C(16)-C(17)-C(18)	122.17(18)
C(17)-C(18)-C(19)	118.28(19)
C(17)-C(18)-C(21)	121.24(19)
C(19)-C(18)-C(21)	120.5(2)
C(14)-C(19)-C(18)	120.04(19)

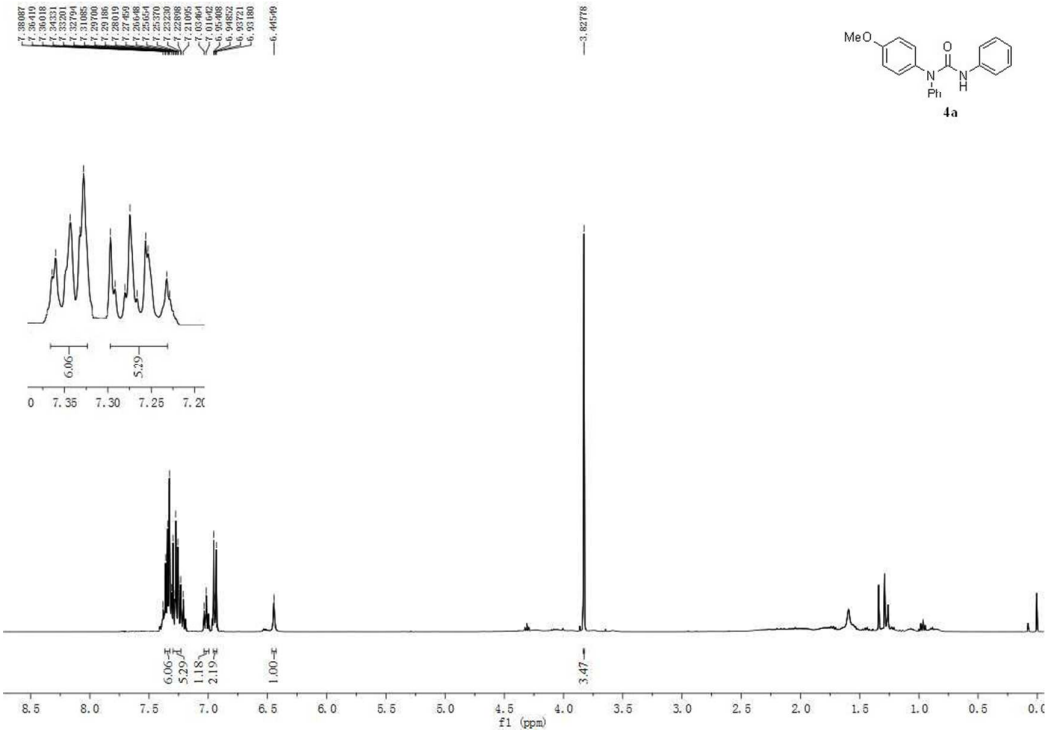
Table 4. Anisotropic displacement parameters ($Å^2$ x 10^4) for 4m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	417(6)	1020(11)	581(7)	143(7)	55(6)	42(7)
N1	411(8)	913(12)	533(9)	103(8)	45(7)	55(8)
N2	452(8)	856(11)	519(8)	85(8)	47(6)	100(7)
C1	495(10)	818(14)	709(12)	29(11)	-21(9)	42(10)
C2	576(12)	929(17)	1014(18)	181(15)	-134(12)	101(12)
C3	726(15)	131(2)	782(15)	340(16)	-149(13)	9(15)
C4	713(14)	137(2)	591(12)	161(14)	-16(11)	57(15)
C5	587(12)	1029(17)	569(11)	46(11)	-15(9)	108(11)
C6	419(9)	729(12)	568(10)	42(9)	-32(7)	-27(8)
C7	428(9)	763(12)	503(9)	27(9)	10(7)	19(8)
C8	403(9)	796(13)	598(10)	114(10)	63(8)	14(8)
C9	689(13)	949(16)	658(12)	80(12)	86(10)	143(12)
C10	846(16)	938(17)	927(17)	140(14)	271(14)	272(14)
C11	573(12)	111(2)	1087(19)	360(17)	104(13)	218(13)
C12	578(13)	120(2)	928(17)	231(16)	-161(12)	71(14)
C13	557(11)	913(16)	674(12)	51(11)	-58(9)	6(11)
C14	399(8)	767(13)	472(9)	27(9)	-18(7)	30(8)
C15	457(9)	775(13)	597(10)	-34(10)	-19(8)	-10(9)
C16	442(9)	842(14)	676(11)	48(11)	42(9)	-13(9)
C17	444(9)	944(15)	558(10)	104(11)	66(8)	97(10)
C18	550(10)	788(13)	488(9)	25(9)	-52(8)	158(9)
C19	506(10)	707(12)	560(10)	82(9)	-31(8)	30(9)
C20	680(14)	1033(19)	129(2)	51(18)	253(15)	-207(14)
C21	854(15)	921(17)	765(14)	-6(13)	13(12)	273(13)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 4m.

	x	y	z	U(eq)
H(1A)	3479	6319	2158	81
H(2)	2838	6987	1259	101
H(3)	3942	6738	347	113
H(4)	5677	5812	333	107

H(5)	6351	5154	1227	87
H(9)	7526	3321	2320	92
H(10)	9246	2401	2497	108
H(11)	10346	2433	3428	111
H(12)	9697	3350	4186	108
H(13)	7999	4281	4013	86
H(15)	5031	3301	3471	73
H(17)	2974	4627	4700	78
H(19)	5748	5757	3691	71
H(20A)	3288	2623	3983	150
H(20B)	2186	3185	4275	150
H(20C)	3354	2870	4684	150
H(21A)	4740	6518	4532	127
H(21B)	3773	6057	4982	127
H(21C)	3260	6416	4351	127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O
N
H
Ph
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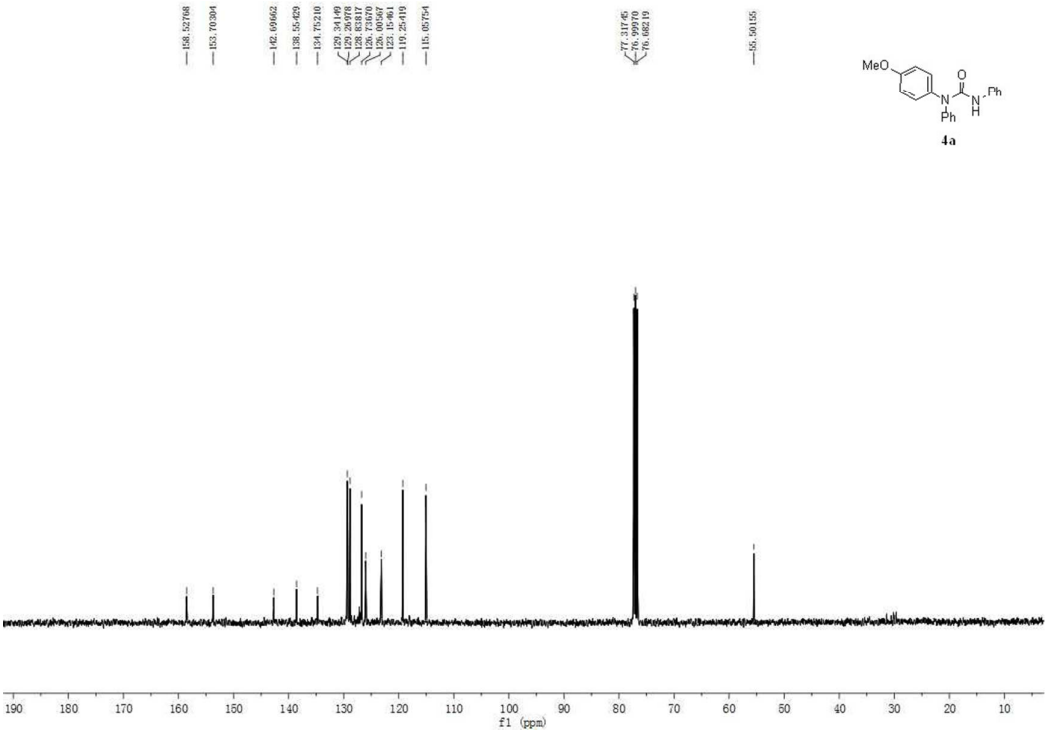
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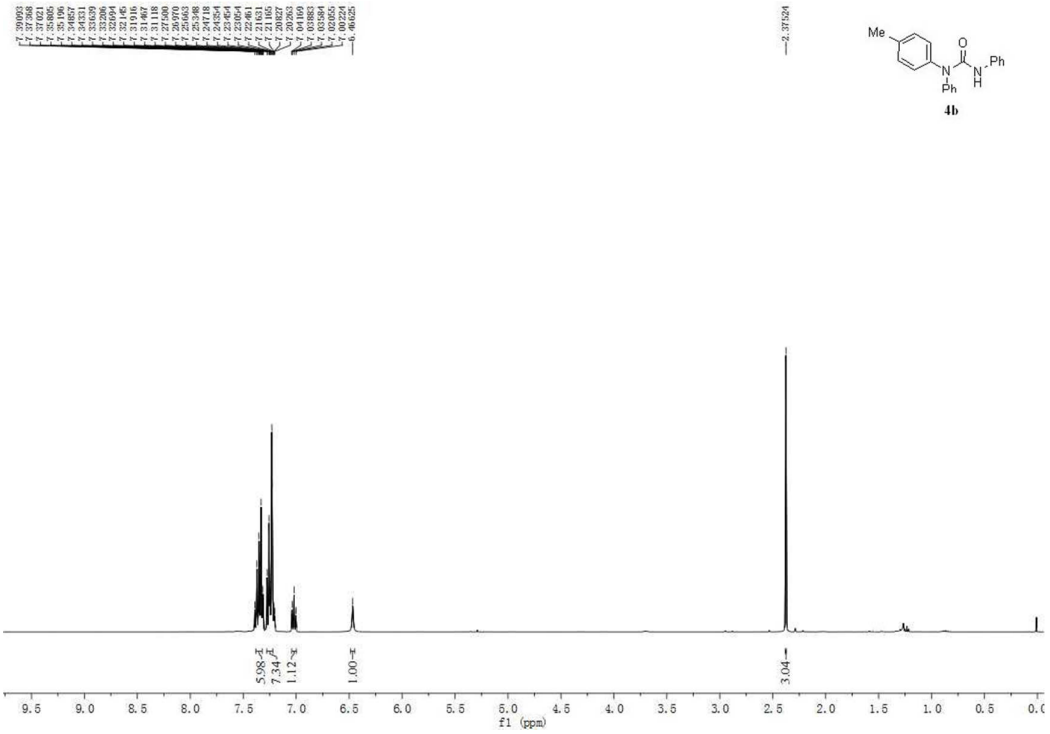
O
N
H
Ph
Ph
4a
f1 (ppm)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Ph
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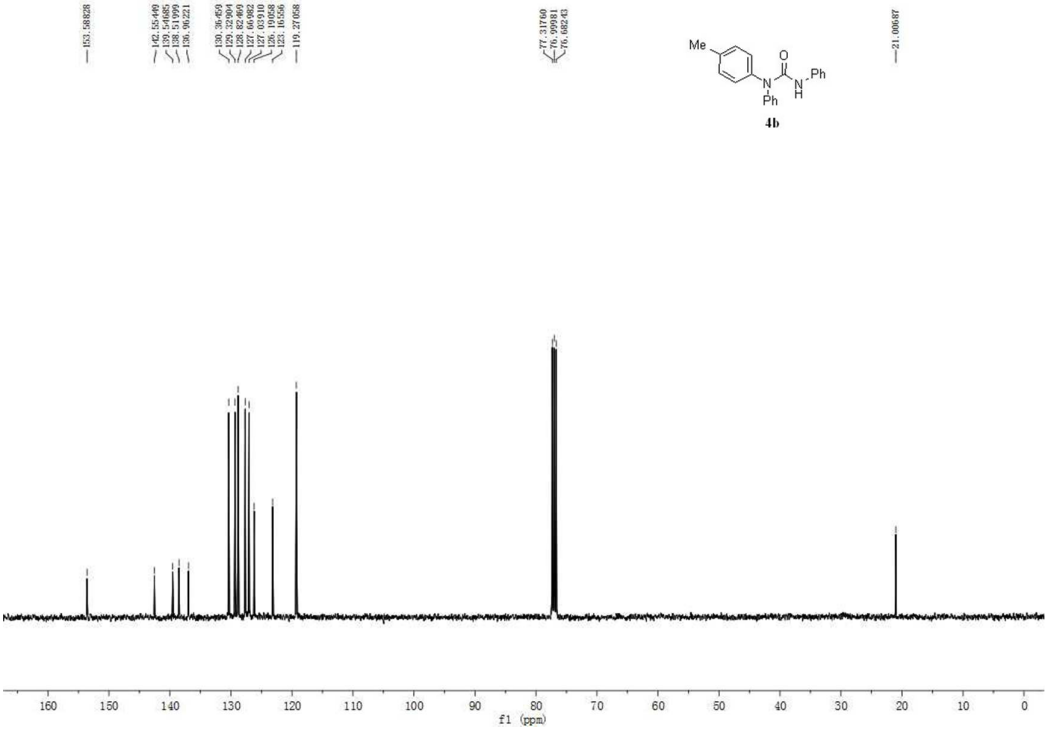
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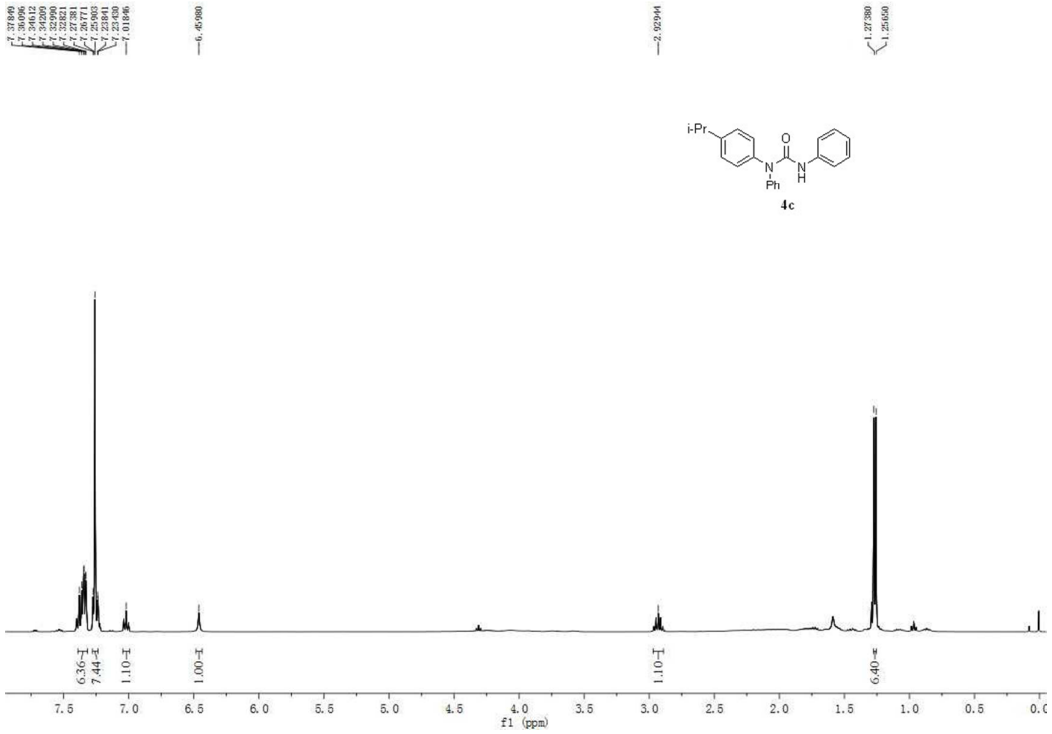
Ph
N
H
Ph
4b
f1 (ppm)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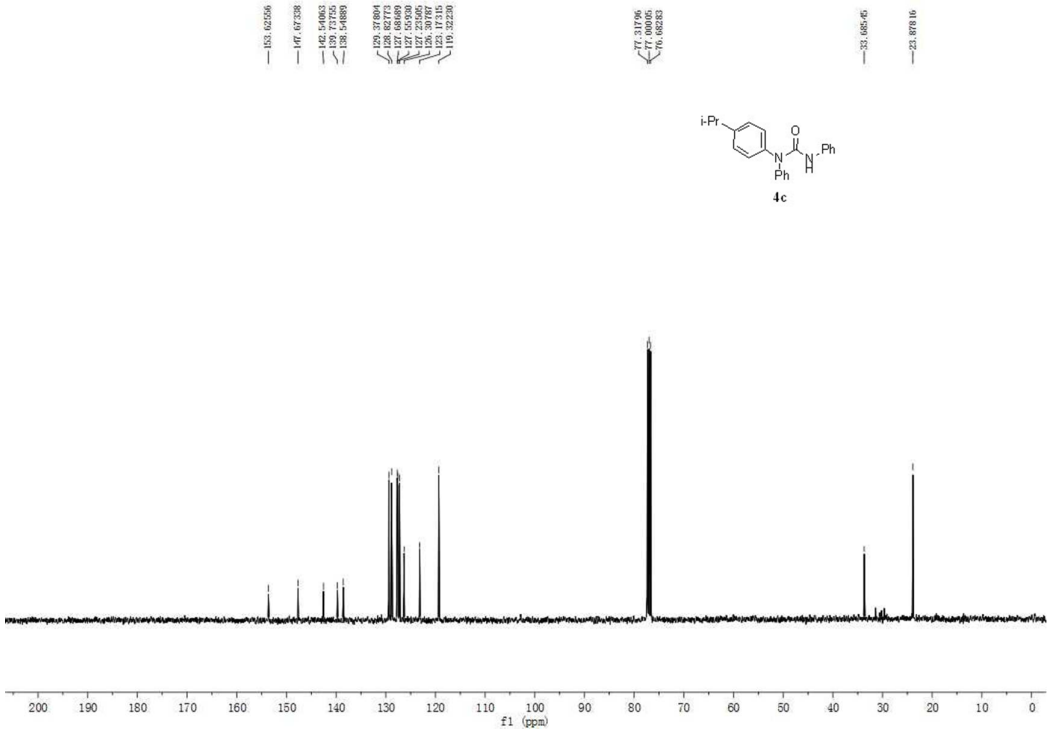
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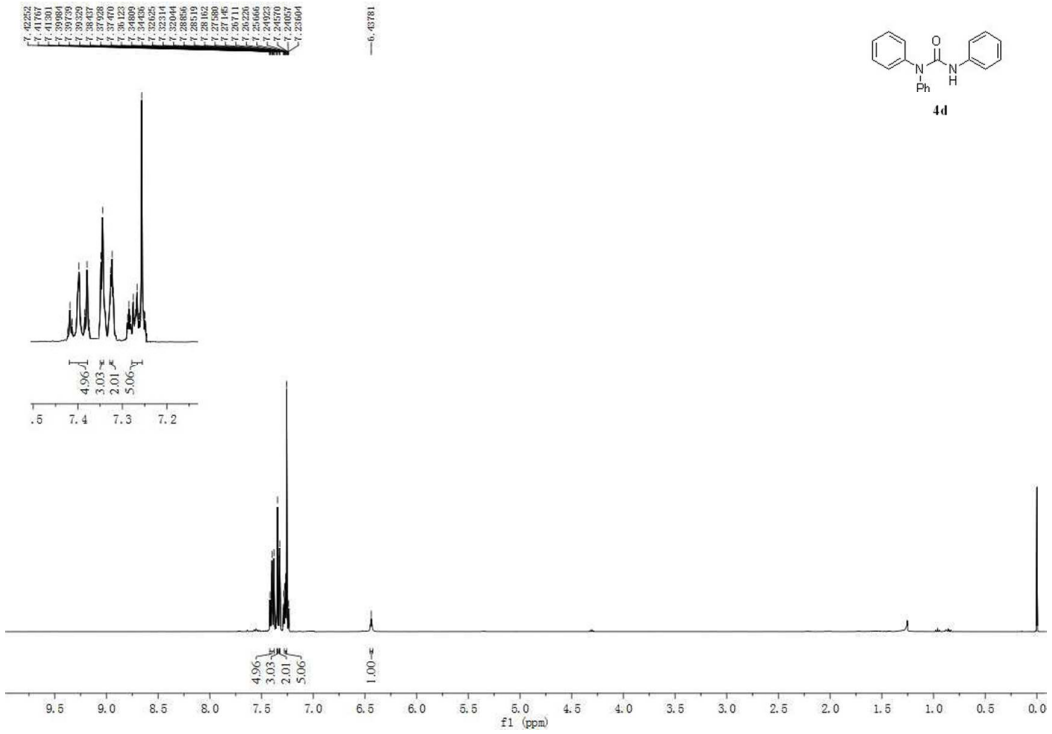
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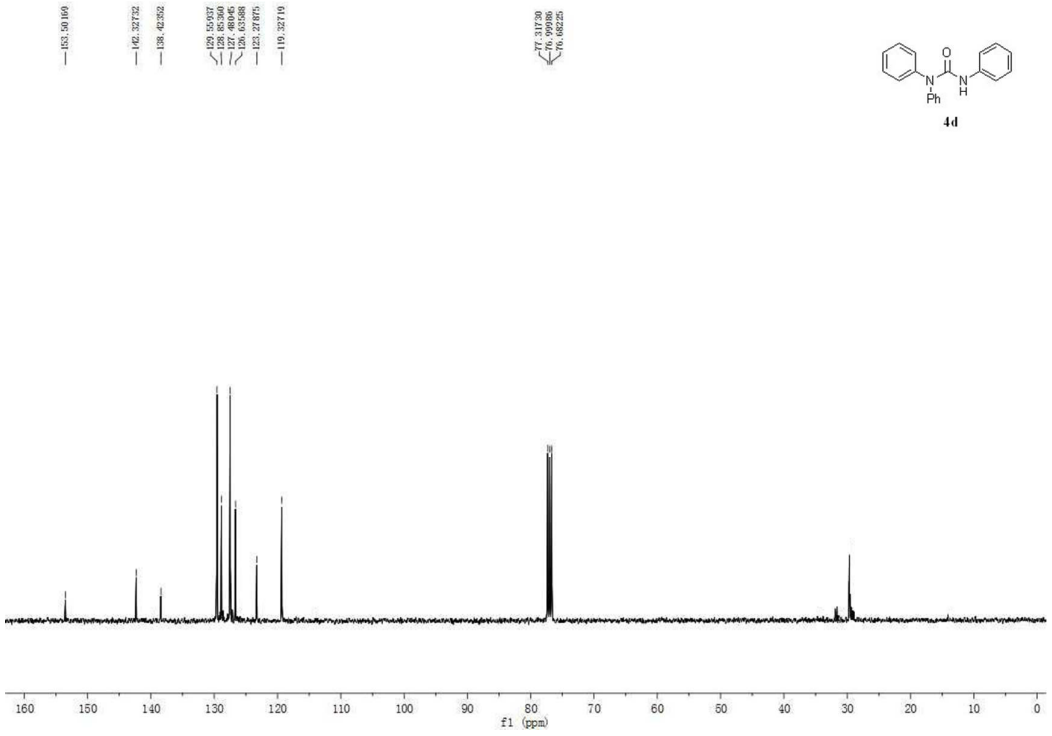
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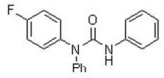

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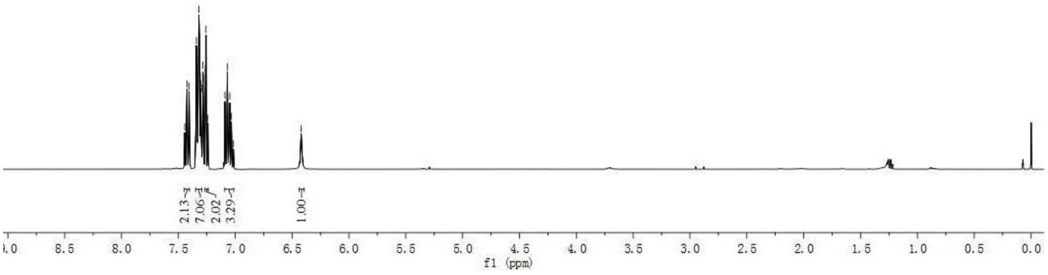

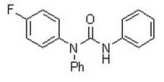

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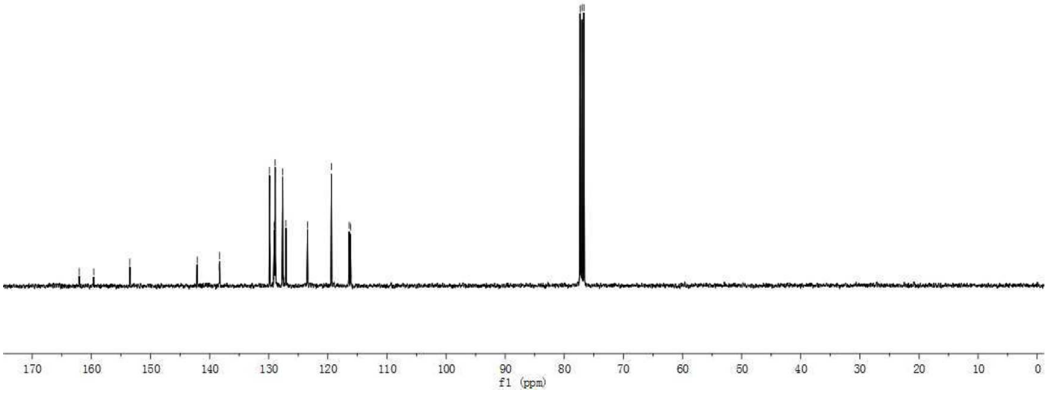

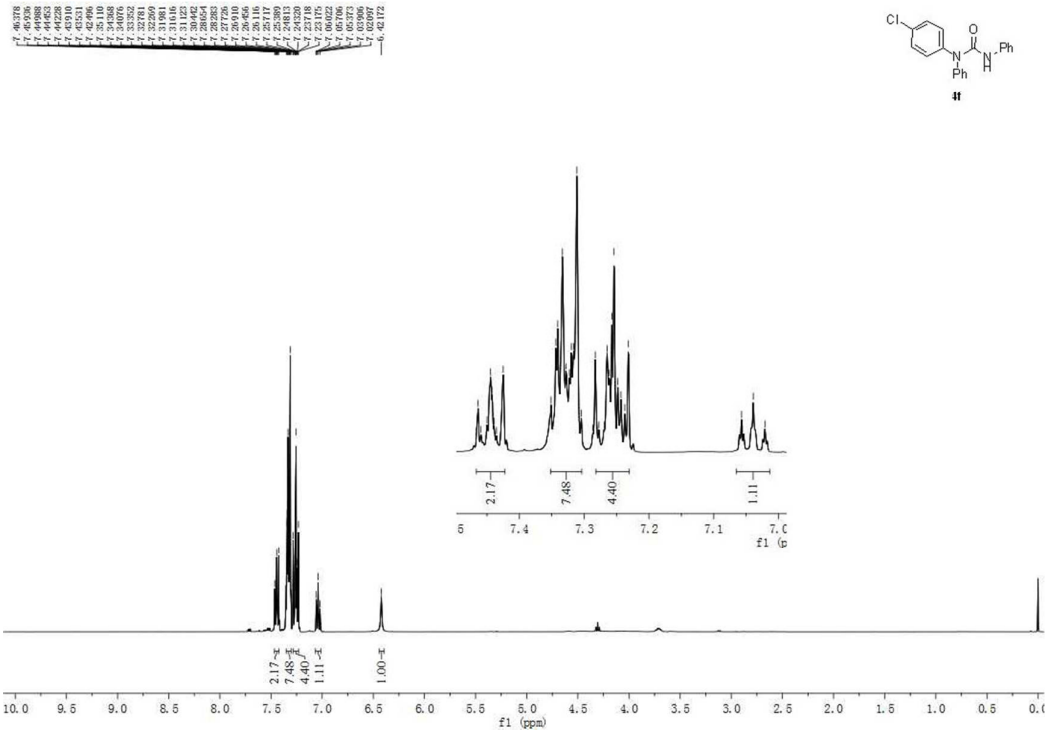
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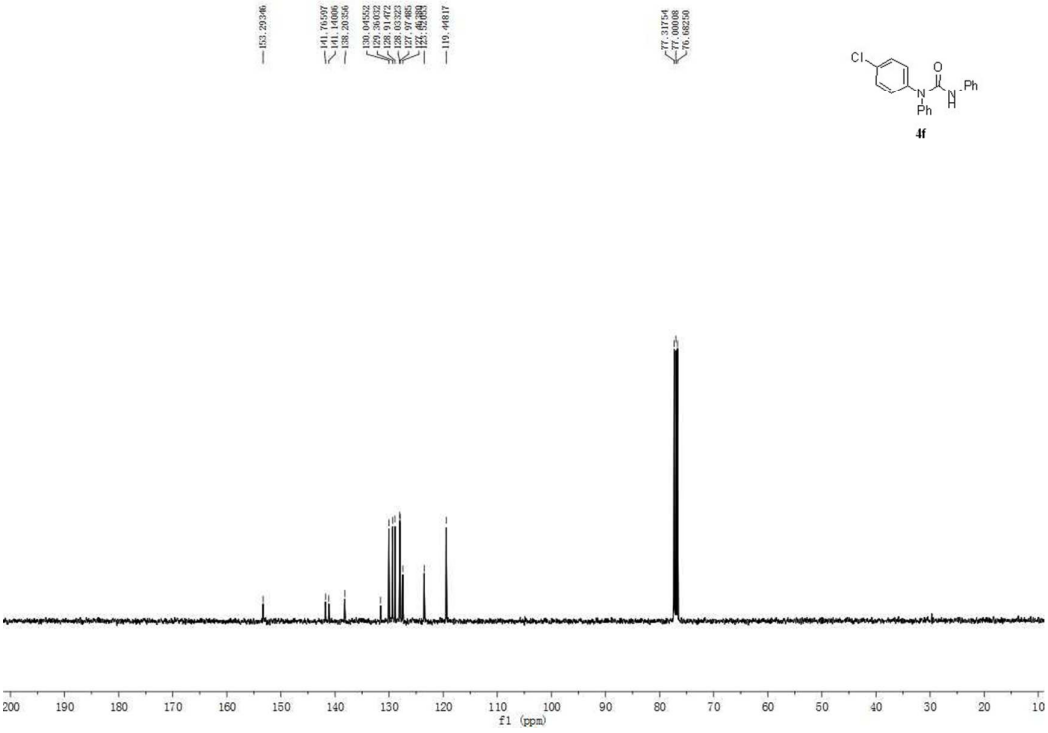
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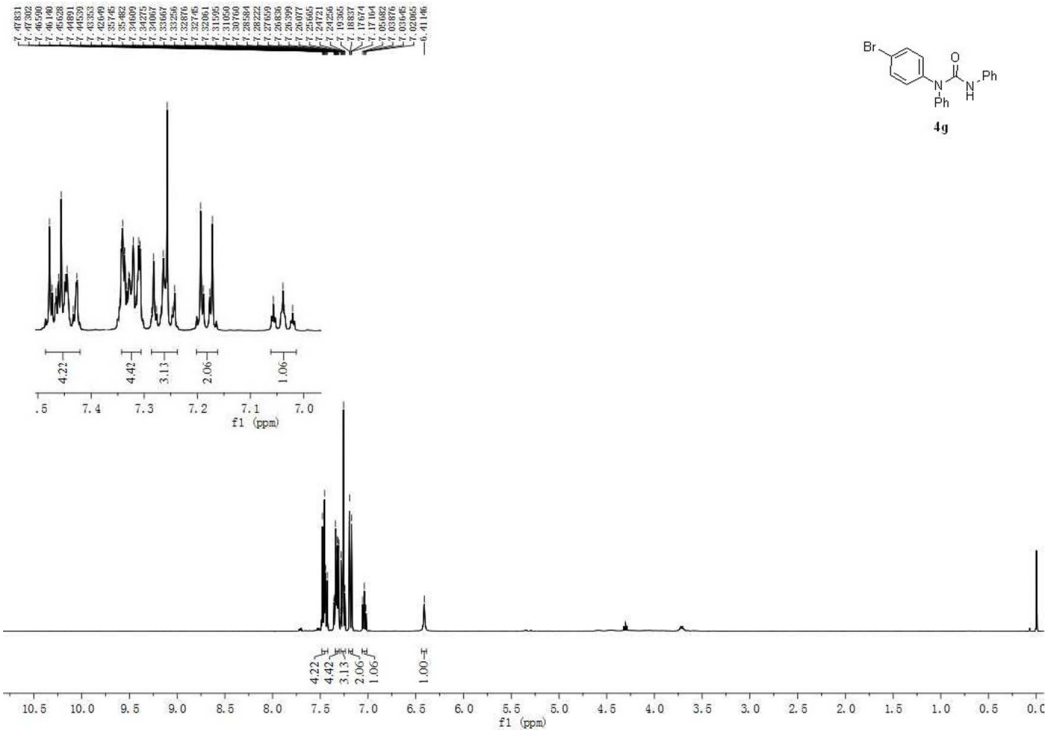

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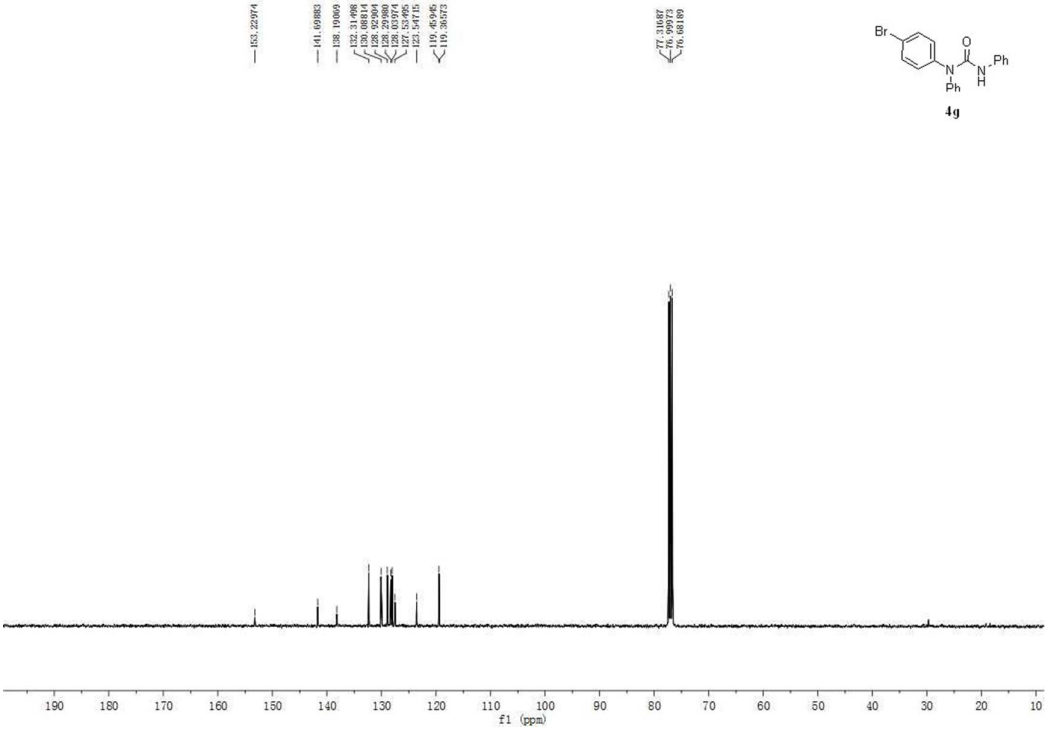

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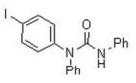

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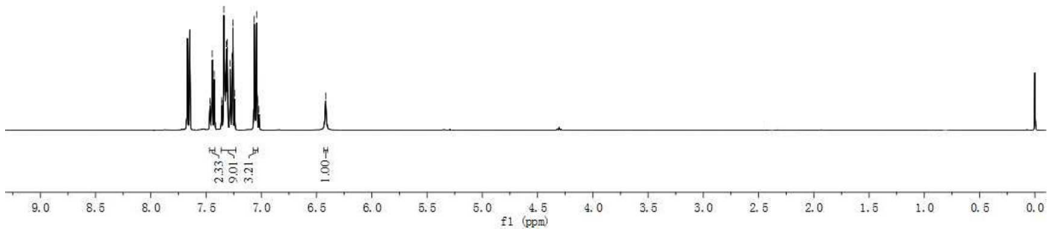
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6.5
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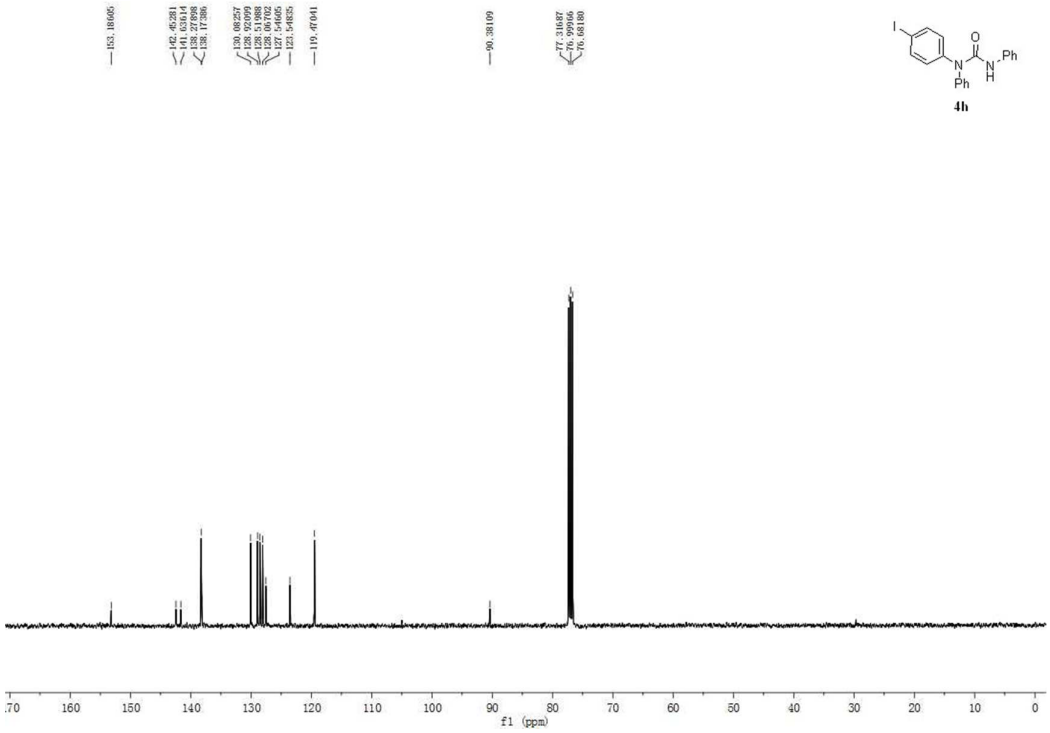
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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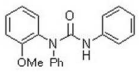
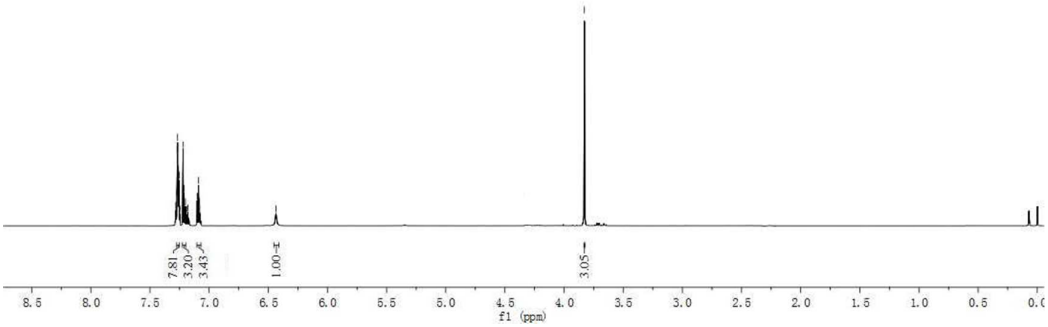
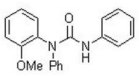
90.38109
77.31687
76.99966
76.68180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4h

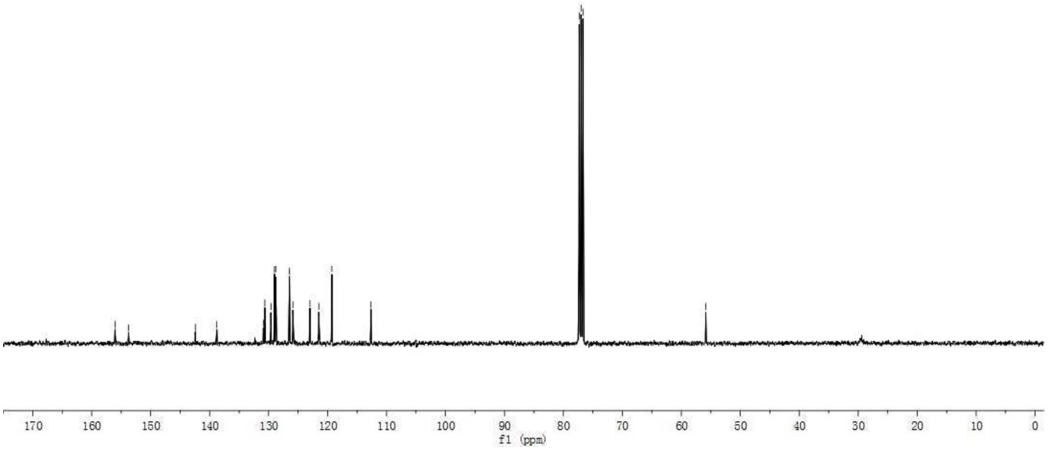

O
N
N
H
OMe Ph

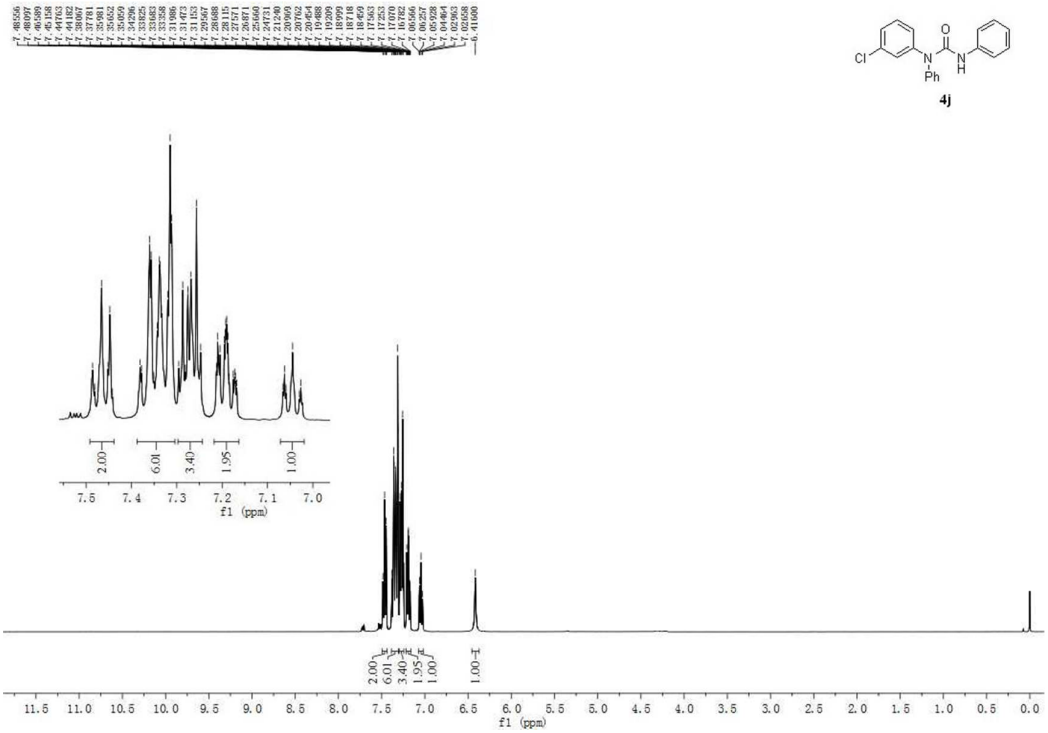
4i

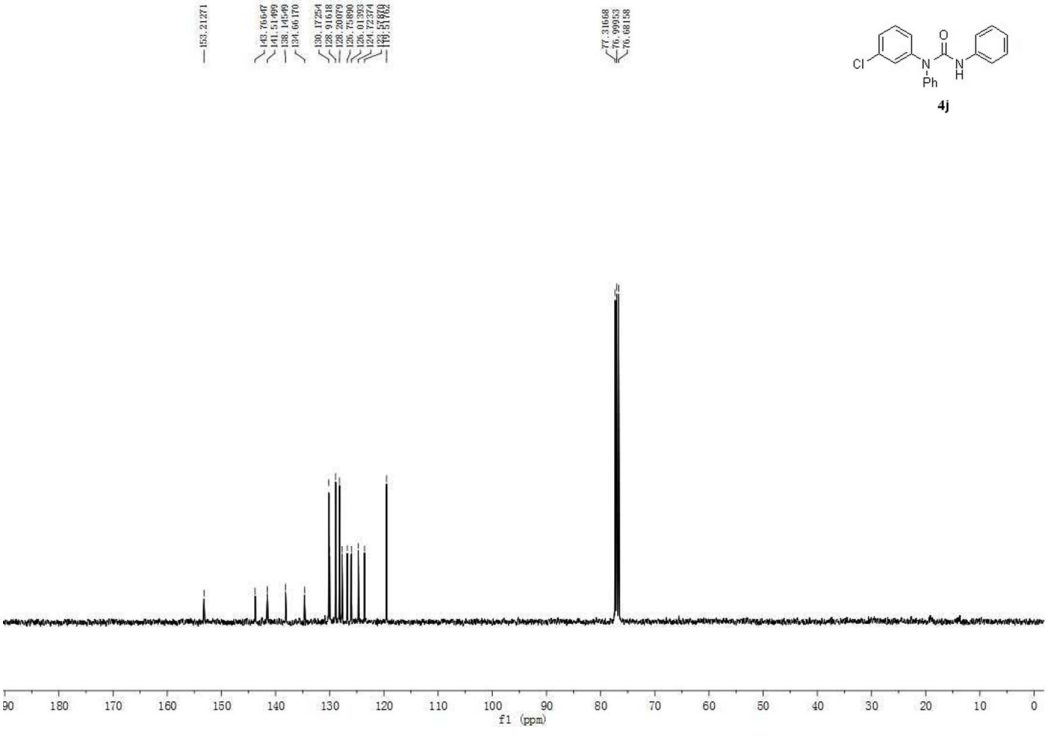

7.81
3.20
3.43
1.00
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

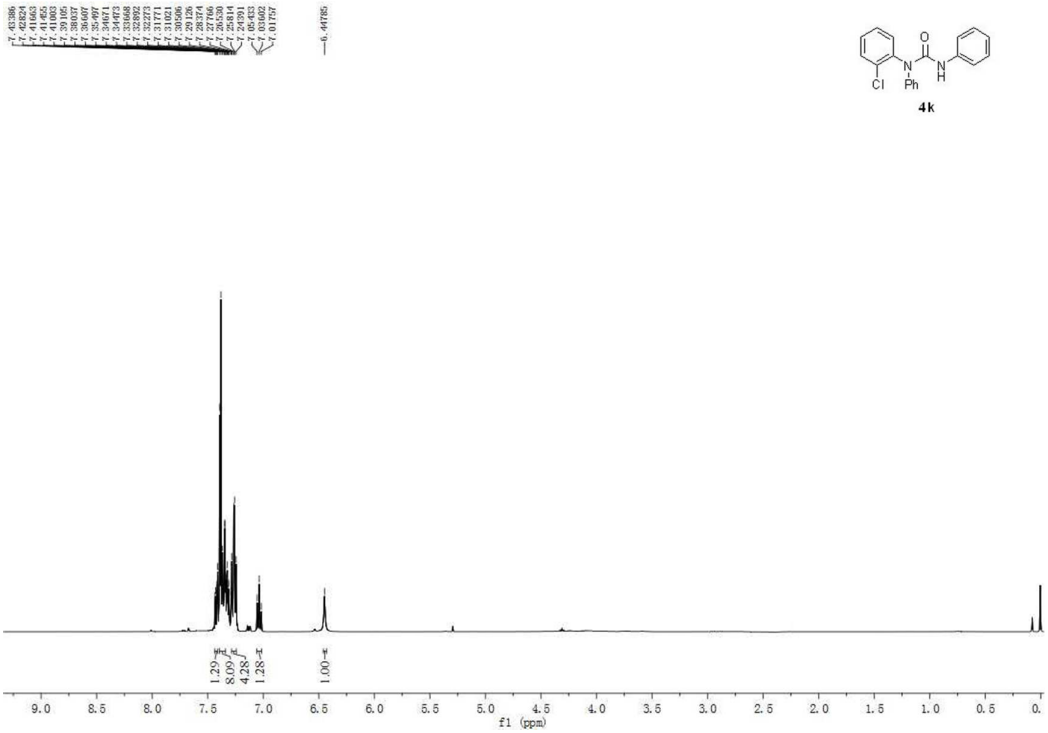

O
N
N
H
OMe Ph

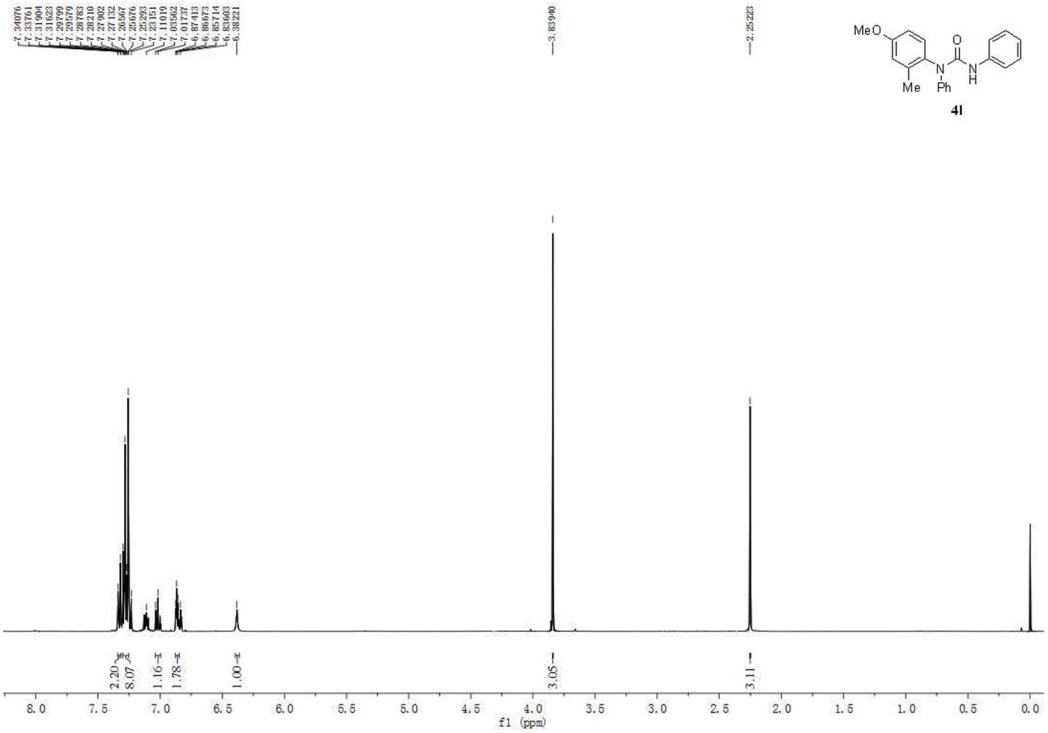
4i

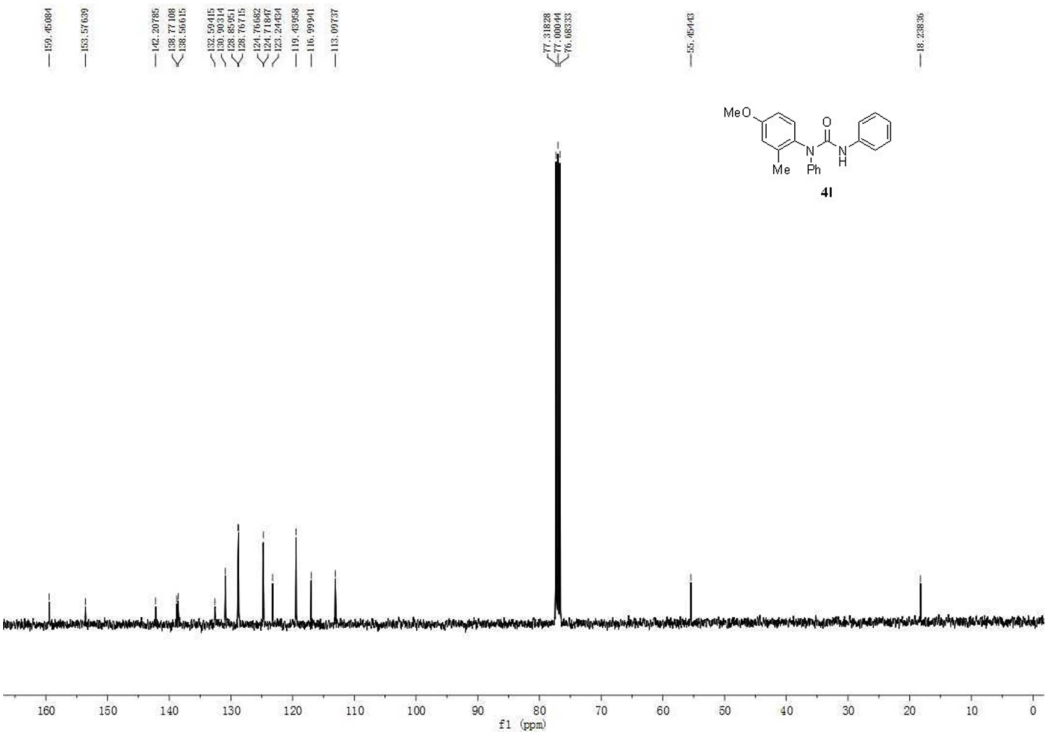

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

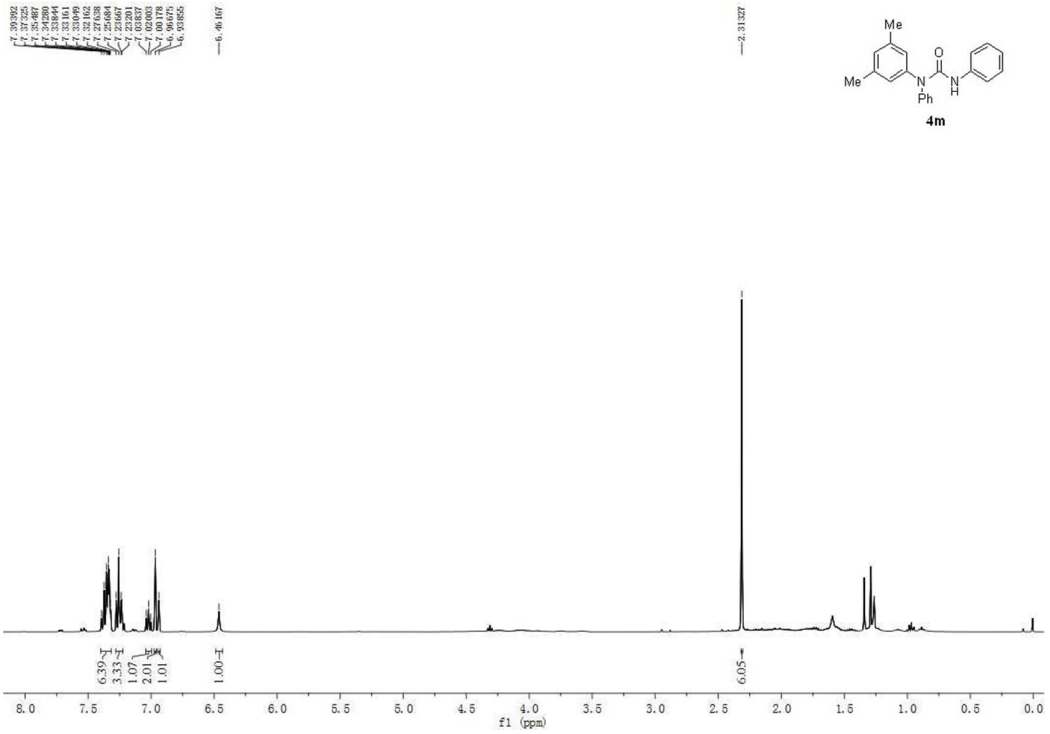

4j
2.00
6.01
3.40
1.95
1.00
1.00
f1 (ppm)


4j
f1 (ppm)


4k
1.29
8.09
4.28
1.28
1.00
f1 (ppm)
4k
f1 (ppm)


MeO
Me
Ph
4l
f1 (ppm)


MeO
Me
Ph
4l
f1 (ppm)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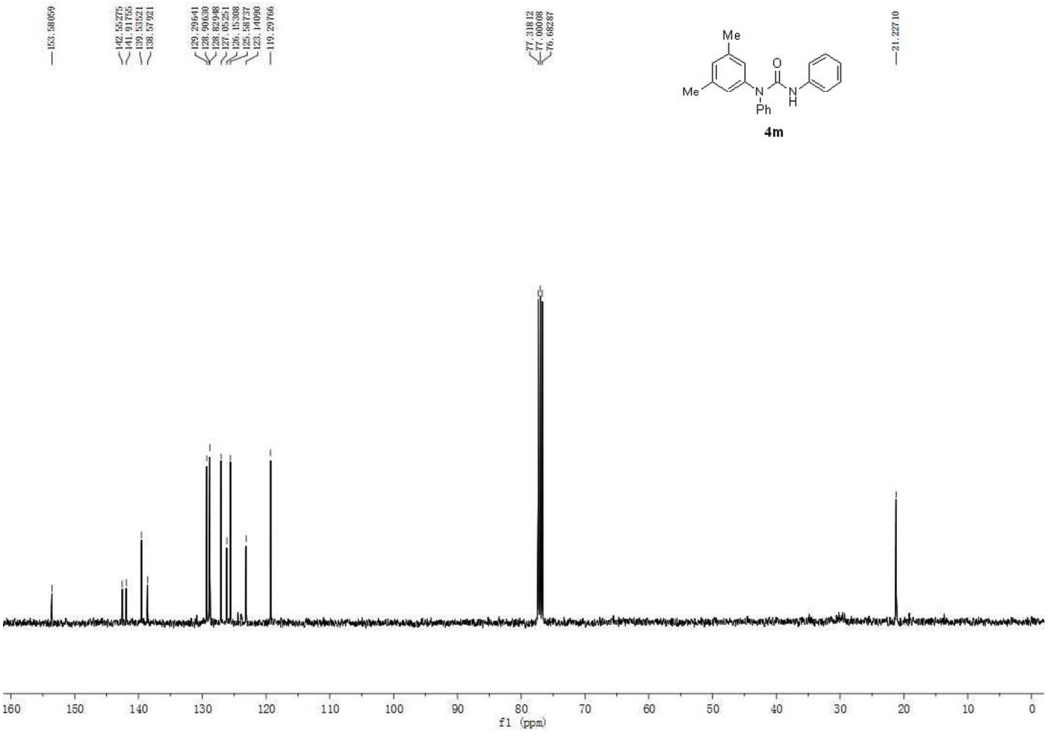
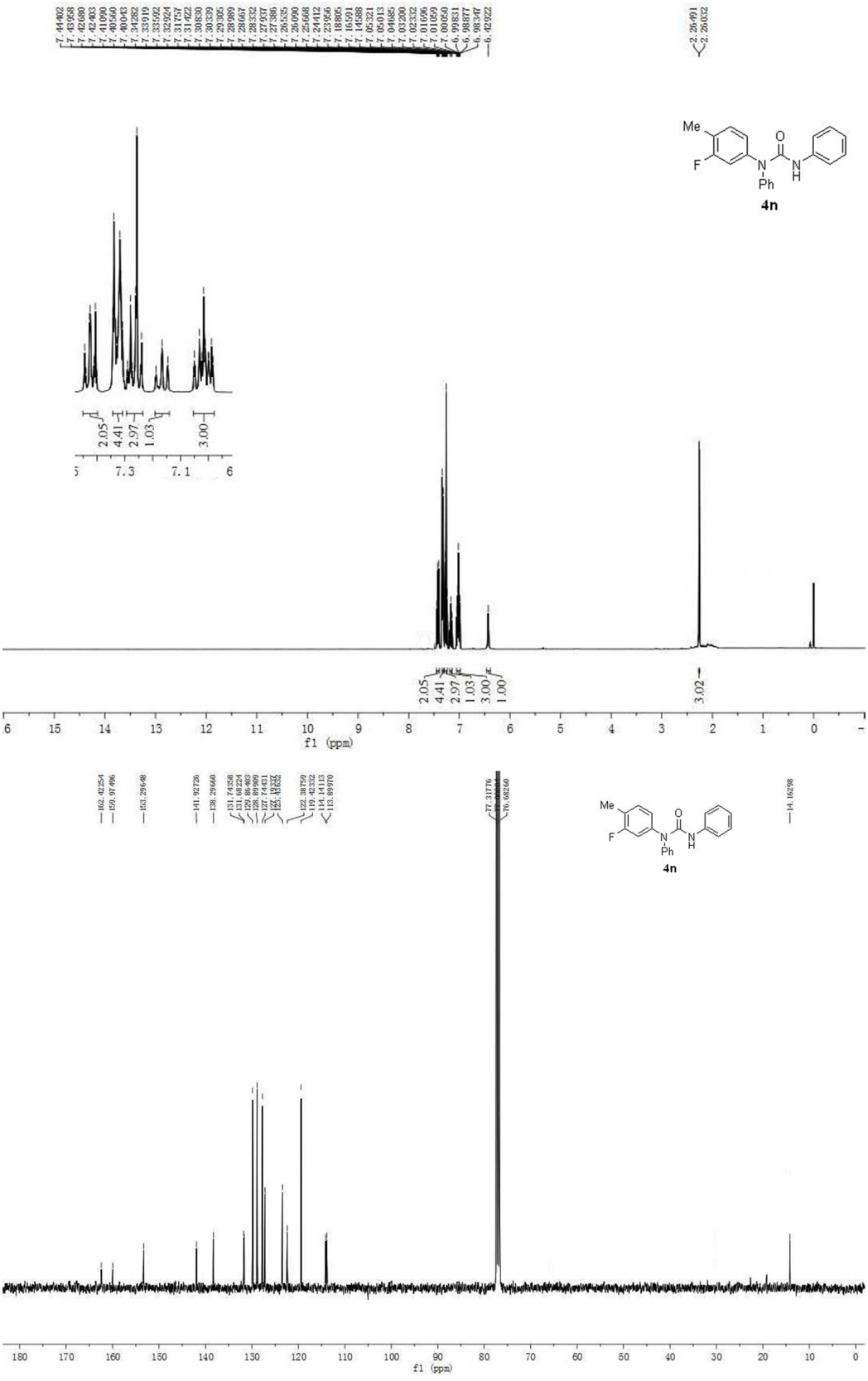
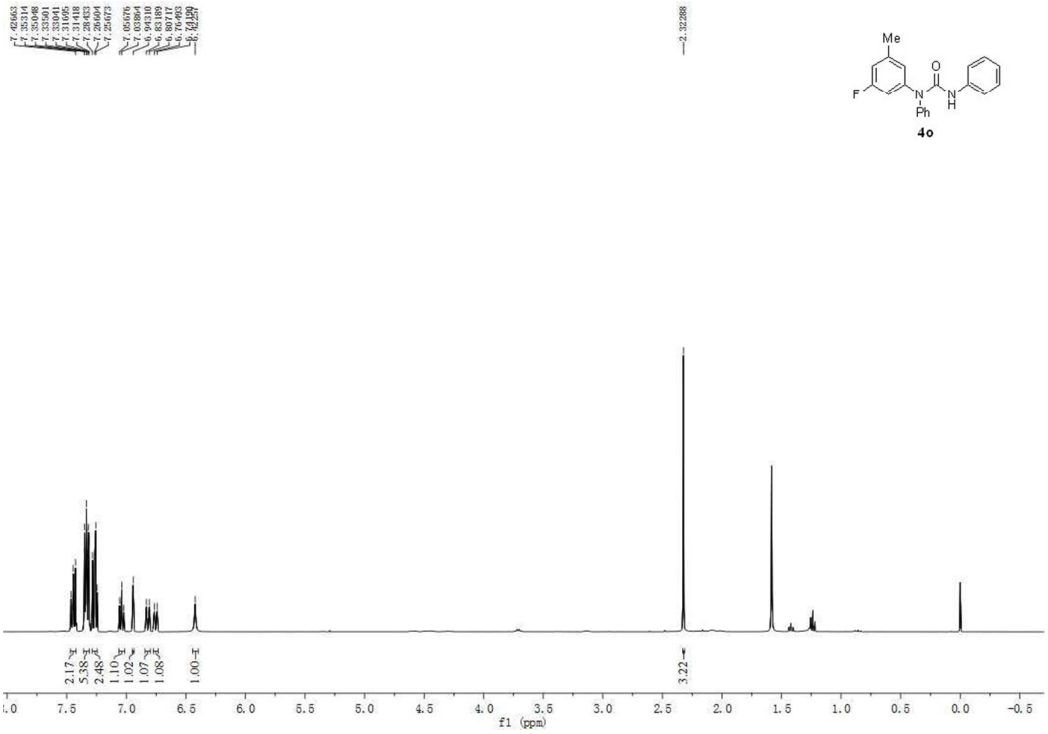
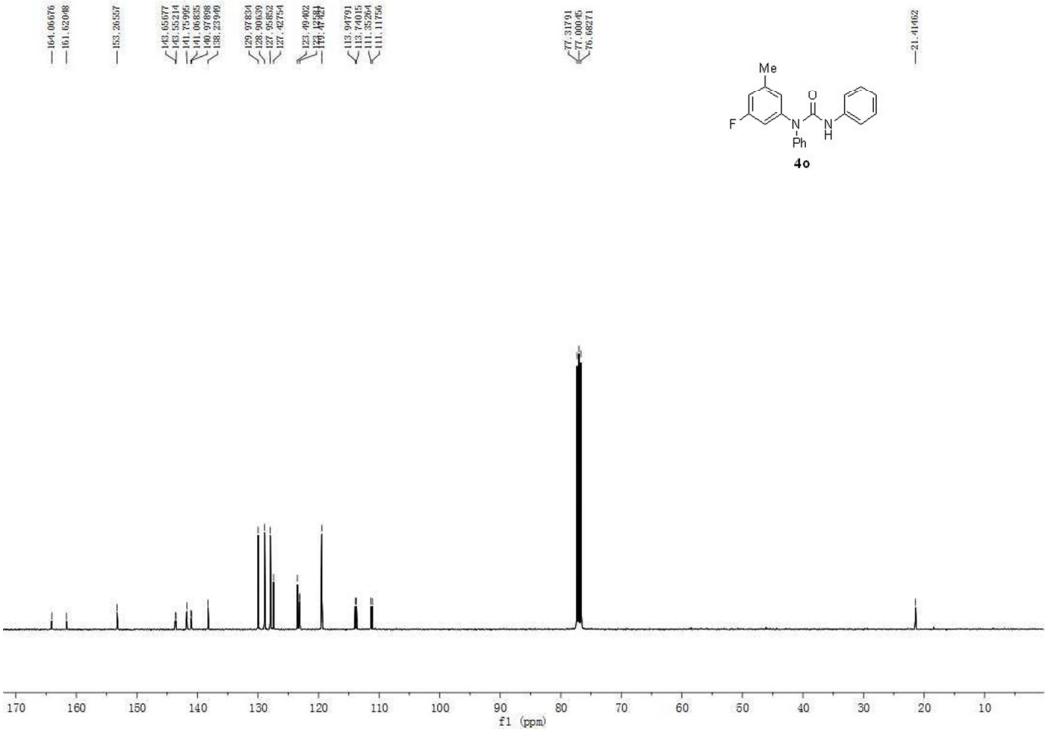
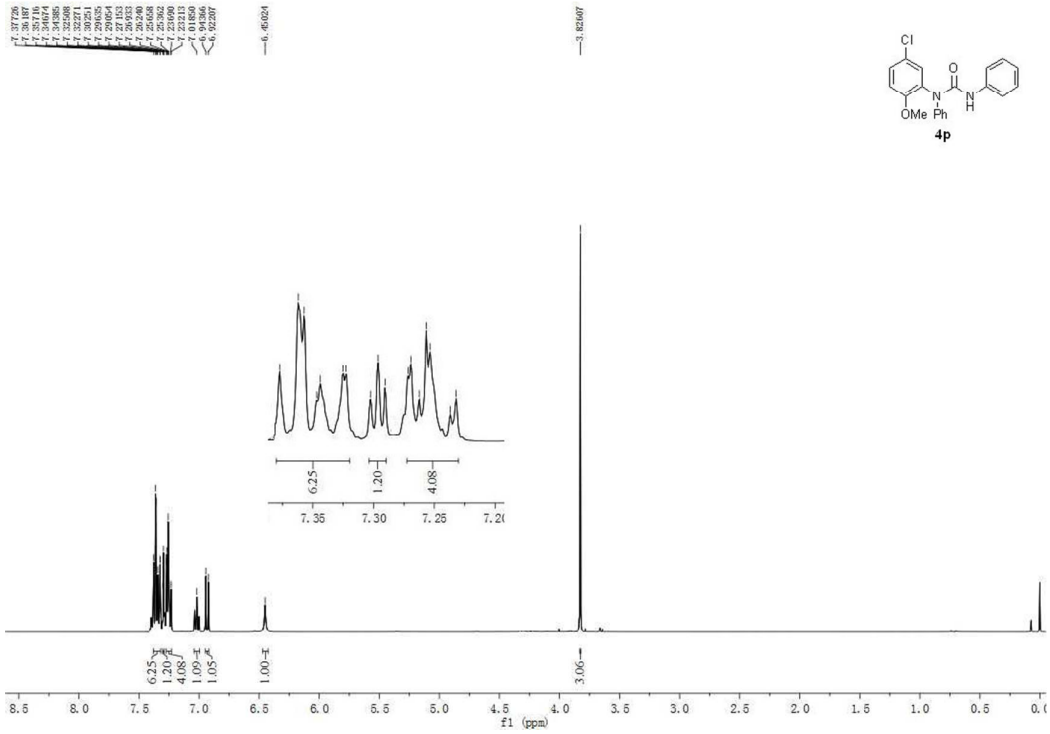
7.37225
7.35487
7.34280
7.33644
7.33161
7.33049
7.32162
7.27058
7.25684
7.23567
7.23201
7.10557
7.02003
7.00178
6.96675
6.93825
6.40167
2.31327
Me
Me
N
Ph
O
N
H
4m
6.39
3.33
1.07
2.01
1.01
1.00
6.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

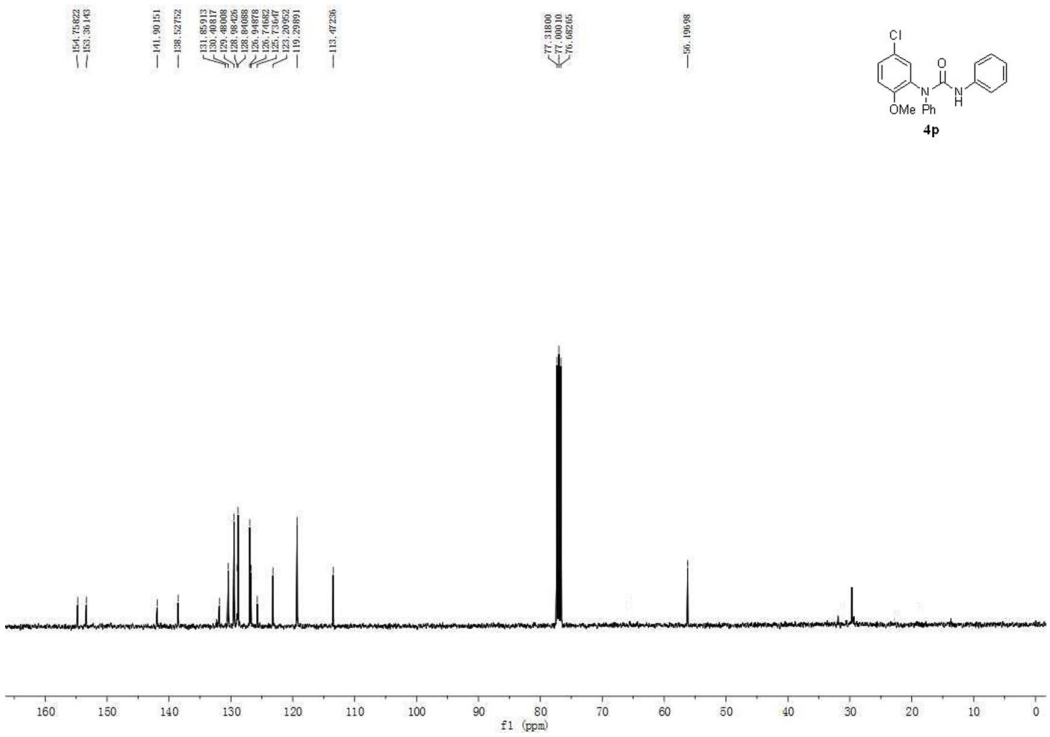

153.58959
142.55275
141.91755
139.15721
138.57921
129.29641
128.90630
128.82948
127.05251
125.58737
123.14090
119.29766
77.31812
77.00008
76.68287
21.22710
Me
Me
N
Ph
O
N
H
4m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

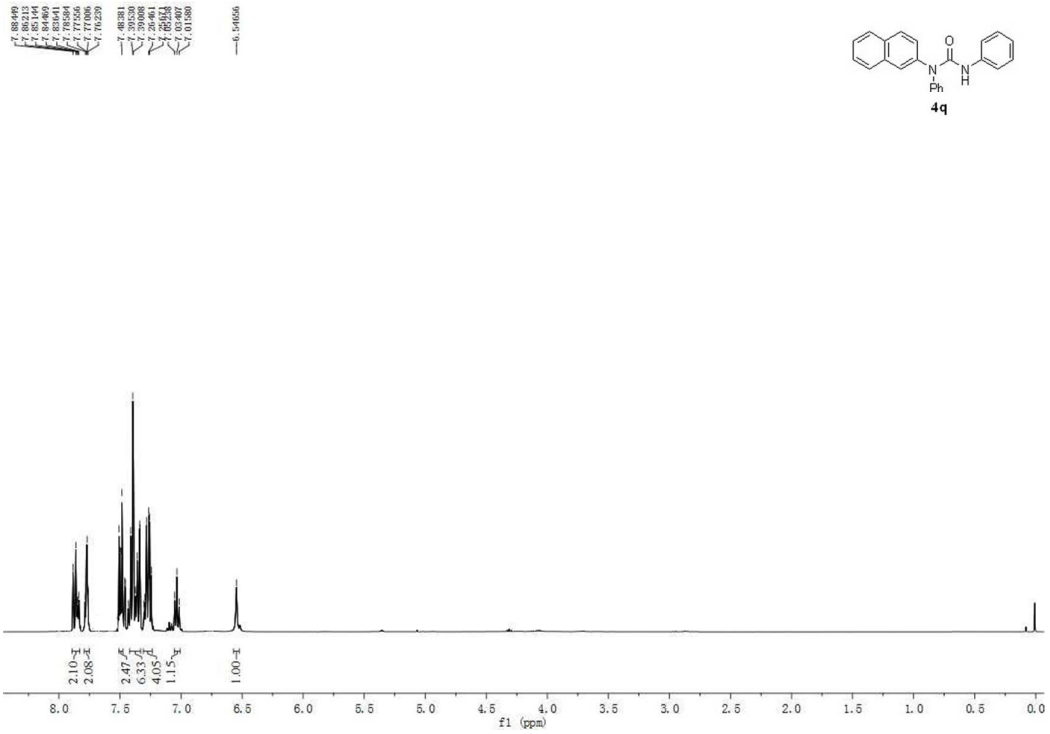

Me
F
N
Ph
O
N
H
4n
f1 (ppm)
f1 (ppm)

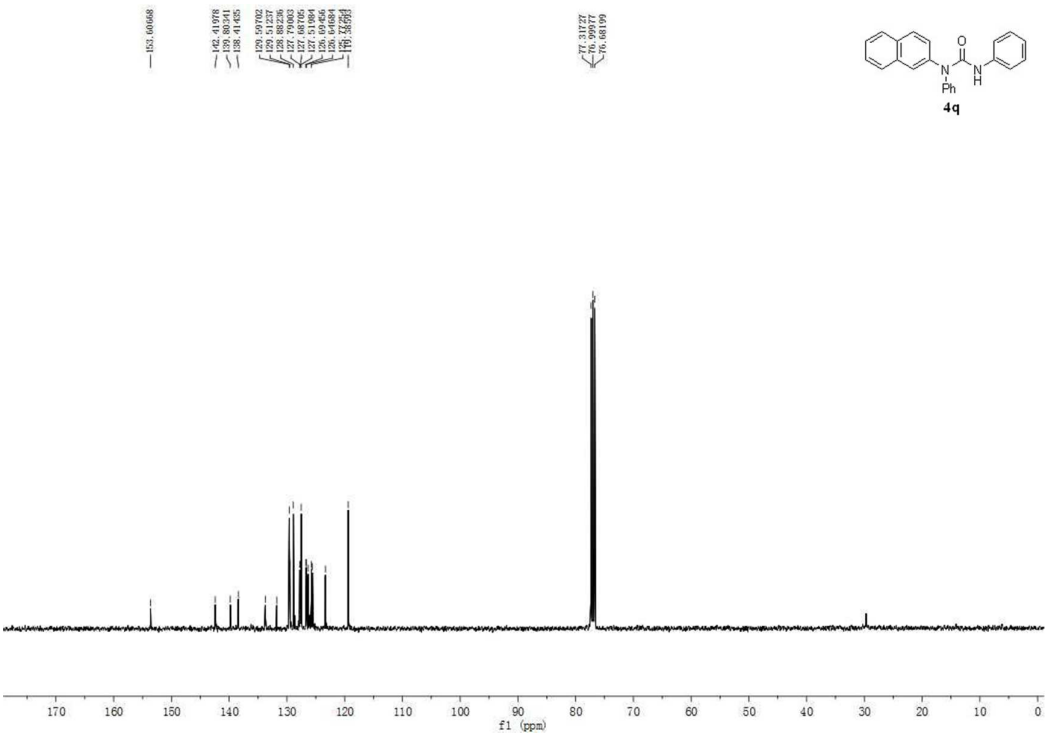

Me
F
N
Ph
O
N
H
4o
2.17
5.38
2.48
1.10
1.02
1.07
1.08
1.00
3.22
f1 (ppm)

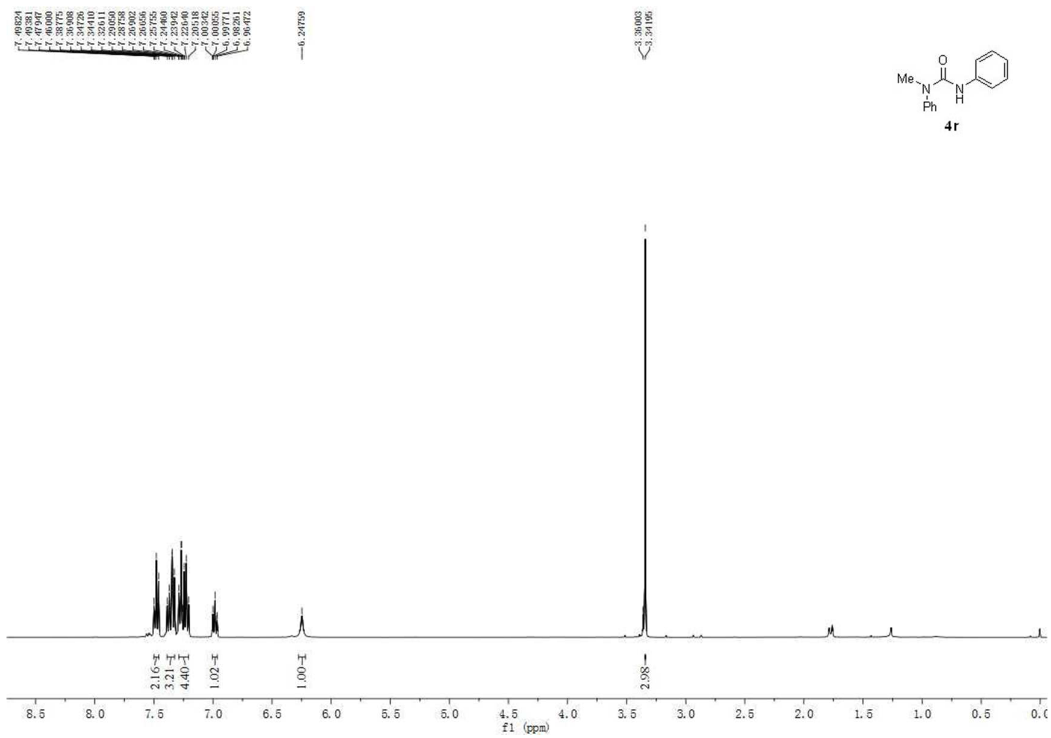

Me
F
N
Ph
O
N
H
4o
f1 (ppm)


Cl
OMe
N
Ph
O
N
H
4p
6.25
1.20
4.08
7.35
7.30
7.25
f1 (ppm)


Cl
OMe
N
Ph
O
N
H
4p
f1 (ppm)


4q
f1 (ppm)


4q
f1 (ppm)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7.47947
7.46000
7.38775
7.36908
7.34726
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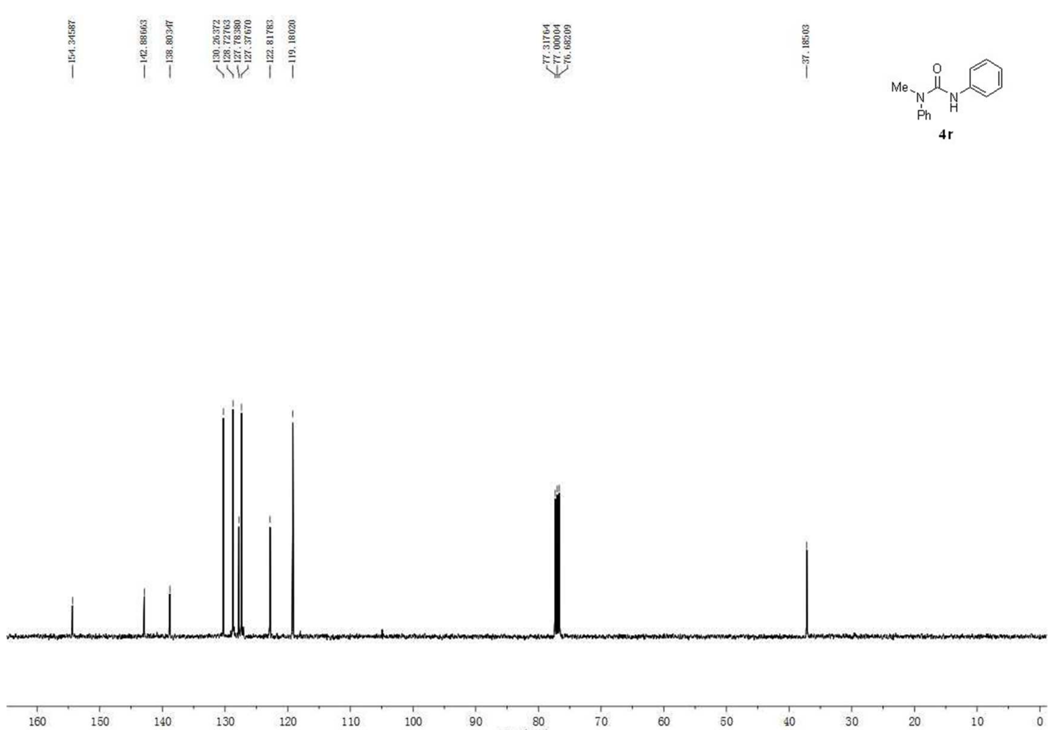
7.32611
7.29950
7.28758
7.26902
7.26656
7.25756
7.24460
7.23942
7.22640
7.20318
7.00342
7.00055
6.99771
6.98261
6.96472
6.24759
3.36003
3.34199
Me
N
Ph
O
N
H
4r
2.16
3.21
4.40
1.02
1.00
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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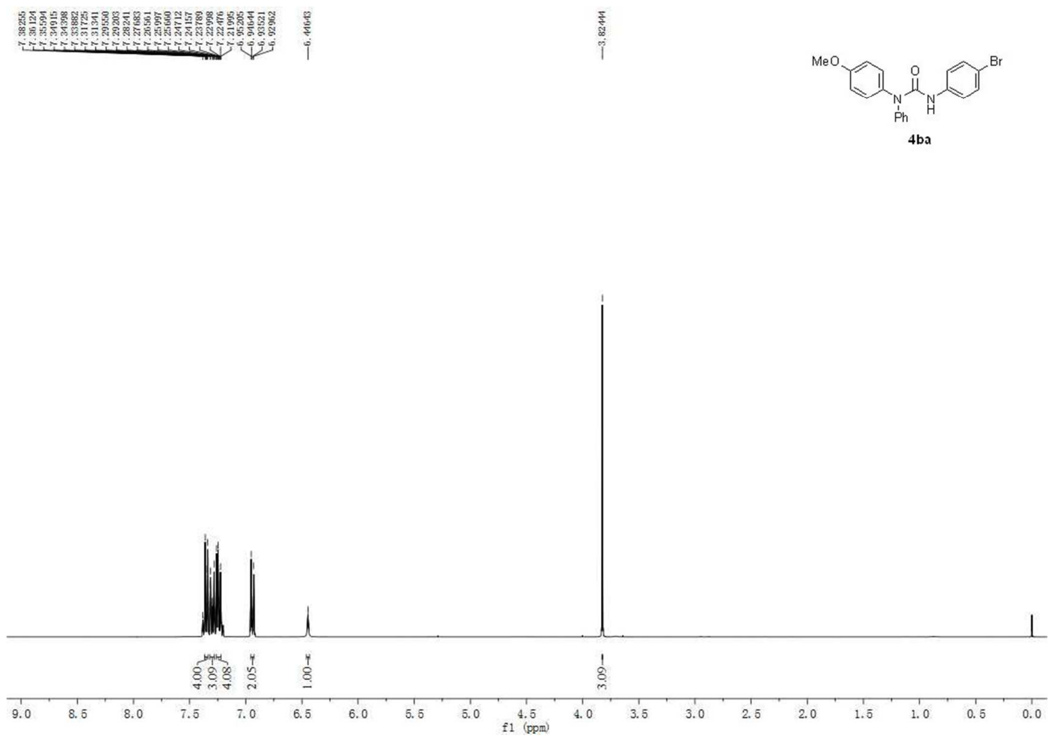
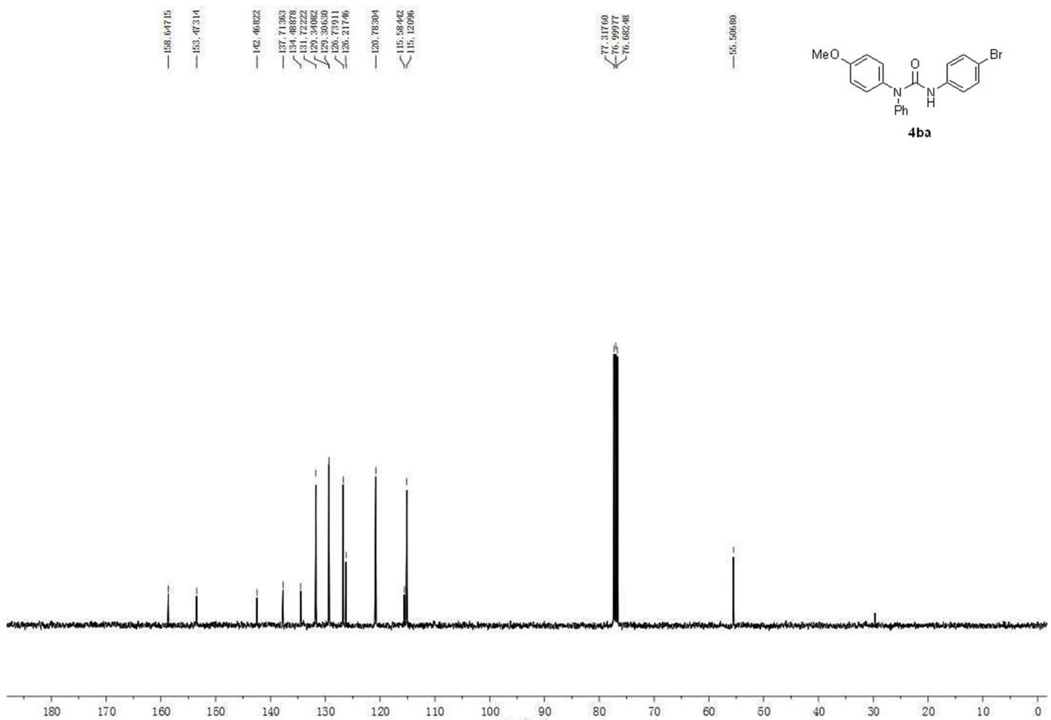
138.80347
130.26372
128.72763
127.78380
127.37670
122.81783
119.18020
77.31764
77.00004
76.68209
37.18503
Me
N
Ph
O
N
H
4r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.44643
3.82444
MeO
O
N
Ph
N
H
Br
4ba
4.00
3.09
4.08
2.05
1.00
3.09
f1 (ppm)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142.46822
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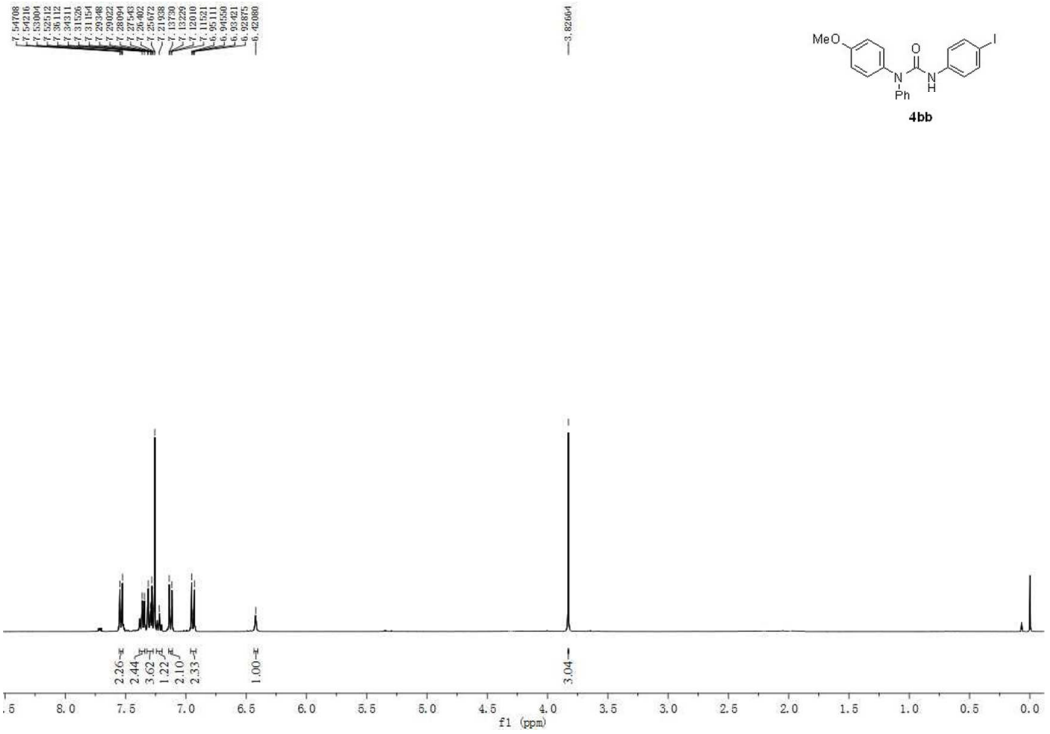
131.72222
129.34082
129.30630
126.73911
126.21746
120.78304
115.58442
115.12096
77.31760
76.99977
76.68248
55.50680
MeO
O
N
Ph
N
H
Br
4ba
f1 (ppm)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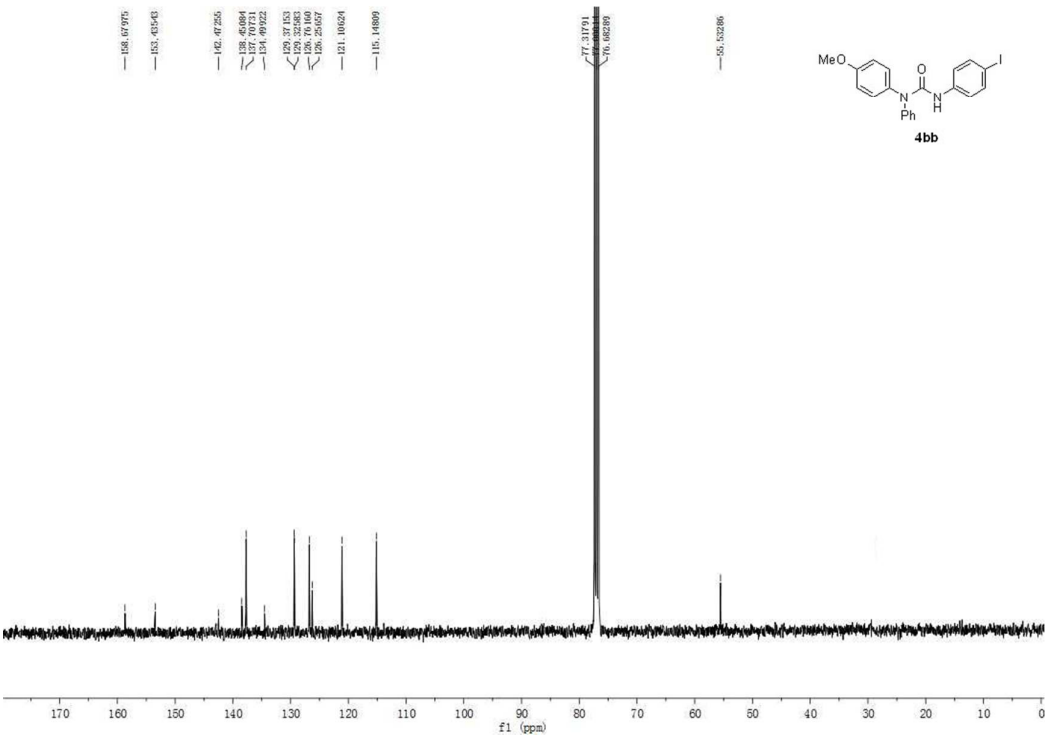
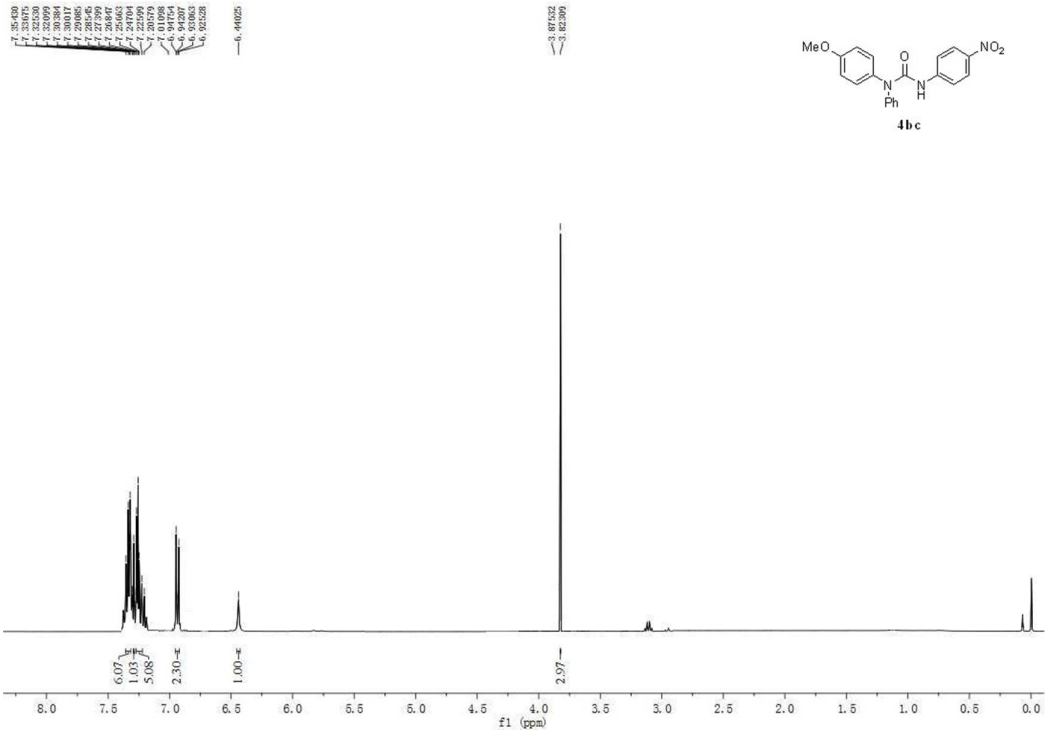
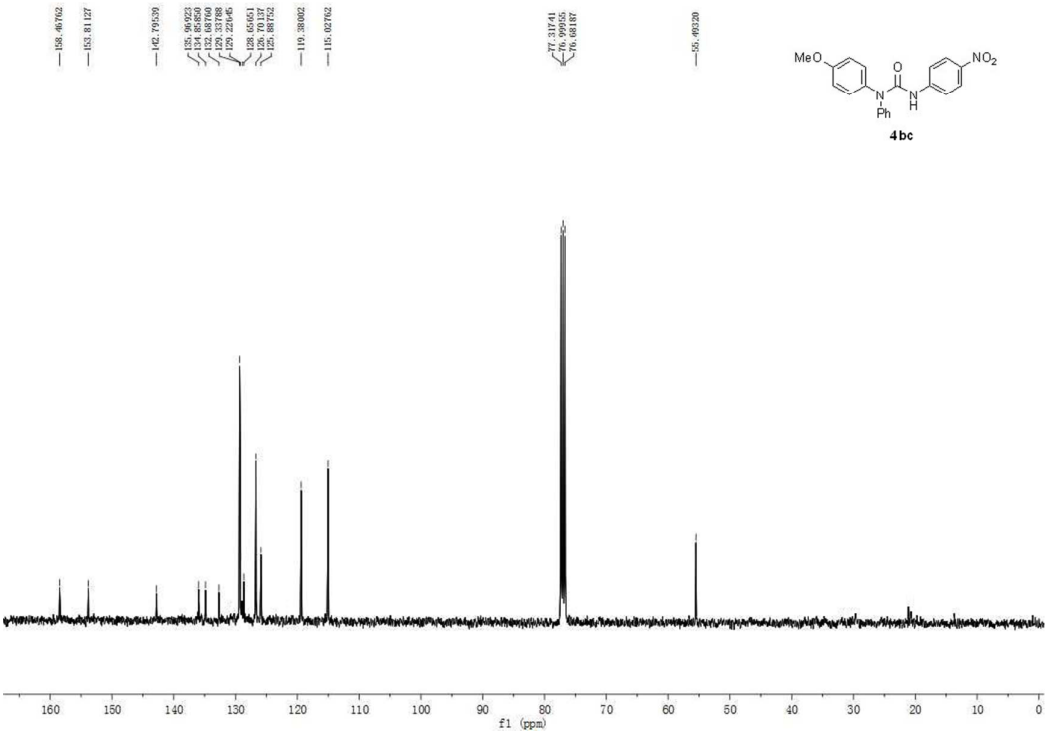
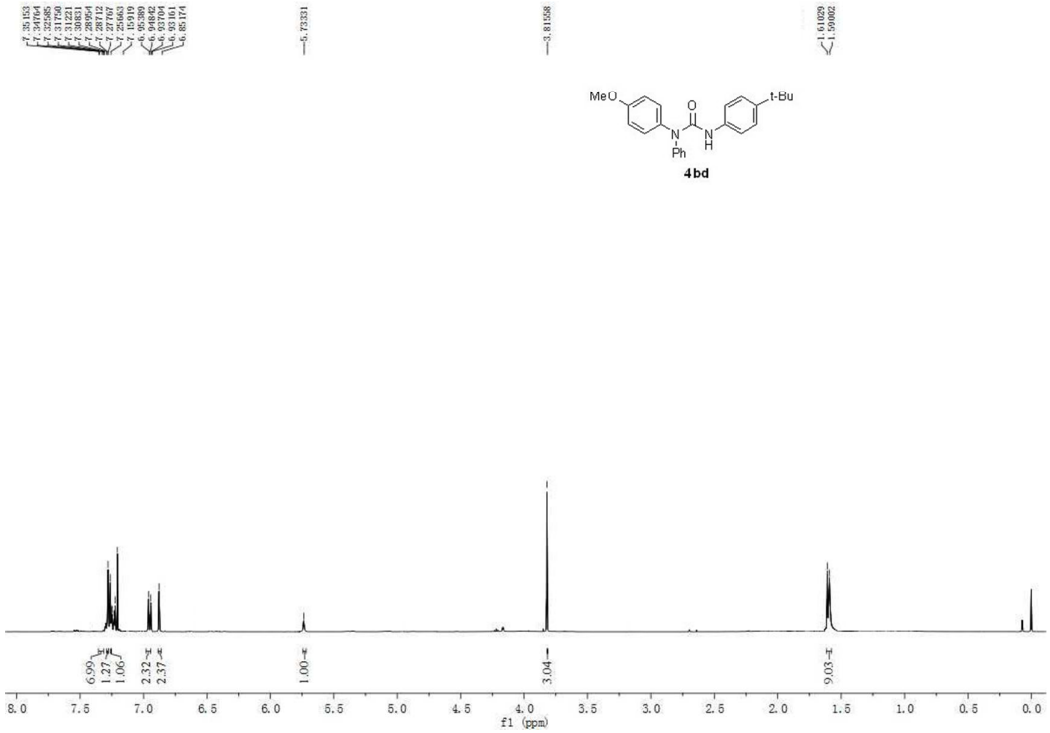
I
N
Ph
O
N
H
4bb
f1 (ppm)


MeO
I
N
Ph
O
N
H
4bb
f1 (ppm)


MeO
NO2
N
Ph
O
N
H
4bc
6.07
1.03
5.08
2.30
1.00
2.97
f1 (ppm)


MeO
NO2
N
Ph
O
N
H
4bc
f1 (ppm)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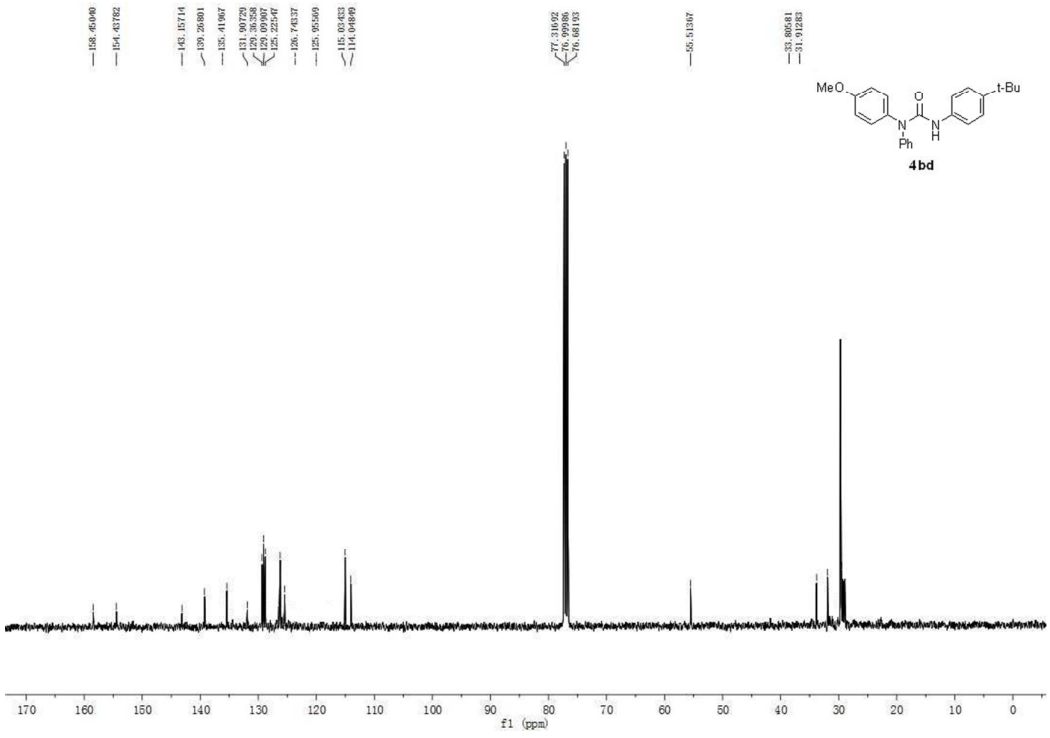
7.32585
7.31729
7.31321
7.30831
7.28954
7.28712
7.27767
7.25663
7.15919
6.95398
6.94842
6.93704
6.93161
6.82174
5.73331
3.81558
1.61029
1.59002
MeO
t-Bu
Ph
4bd
6.99
1.27
1.06
2.32
2.37
1.00
3.04
9.03
f1 (ppm)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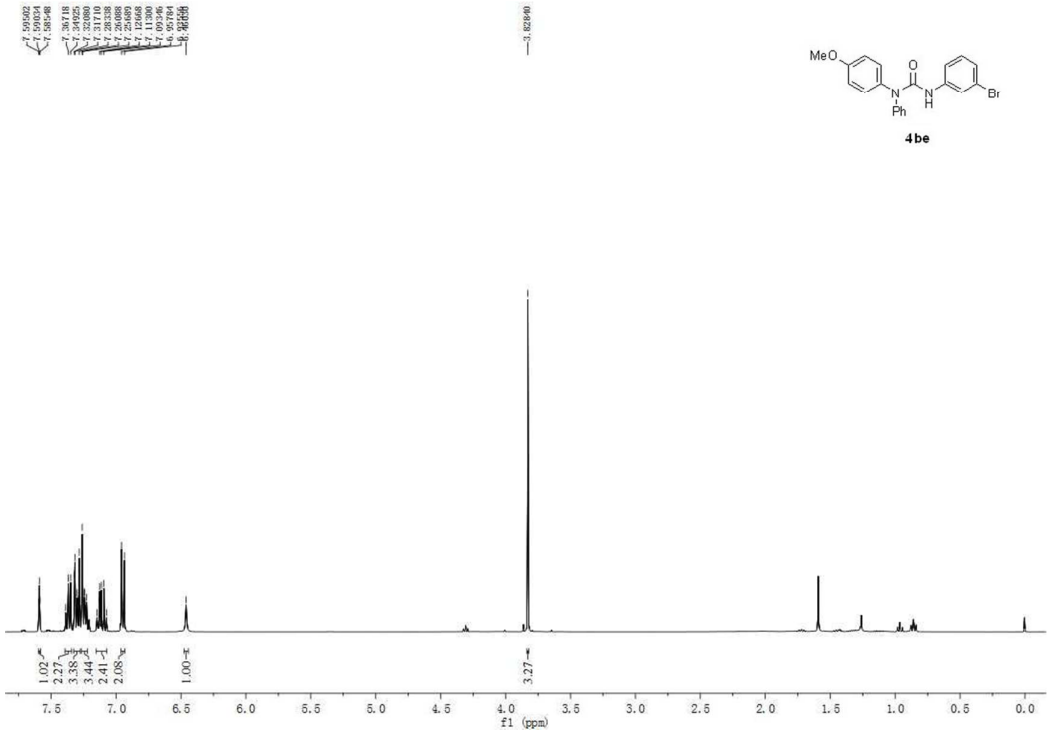
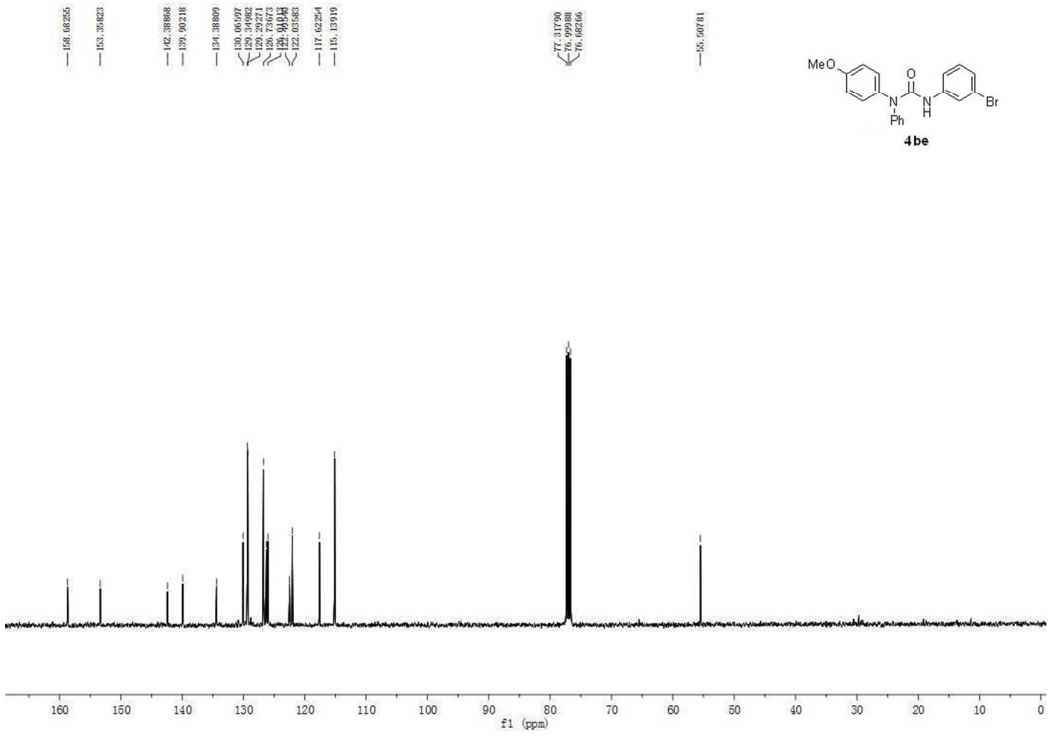
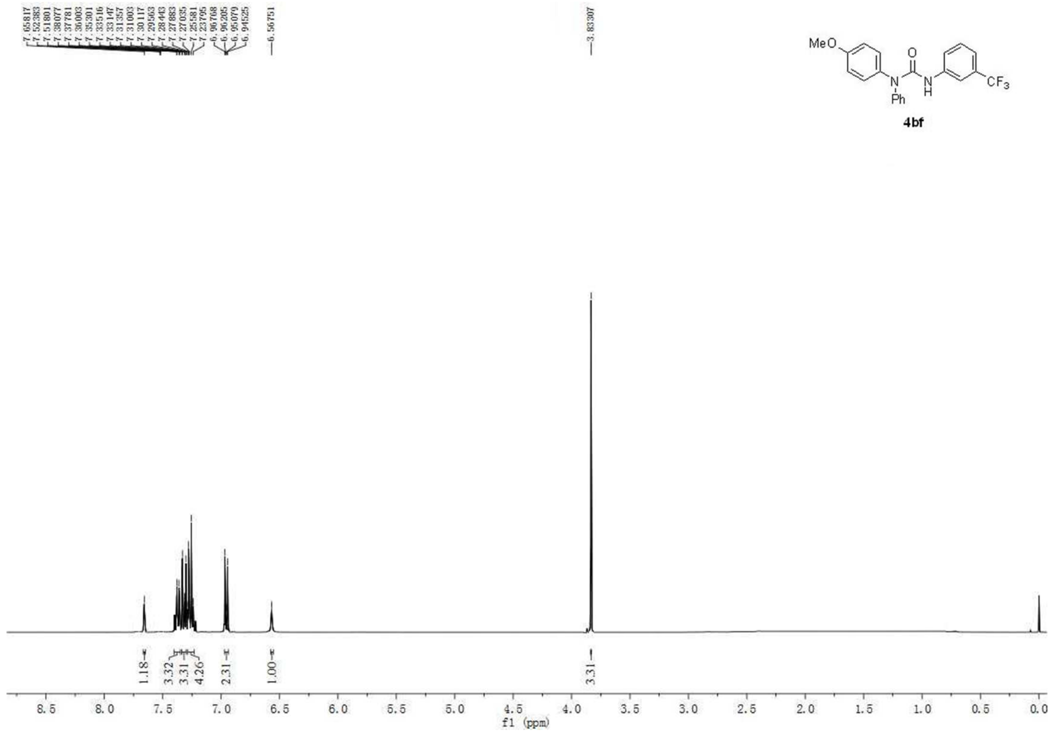
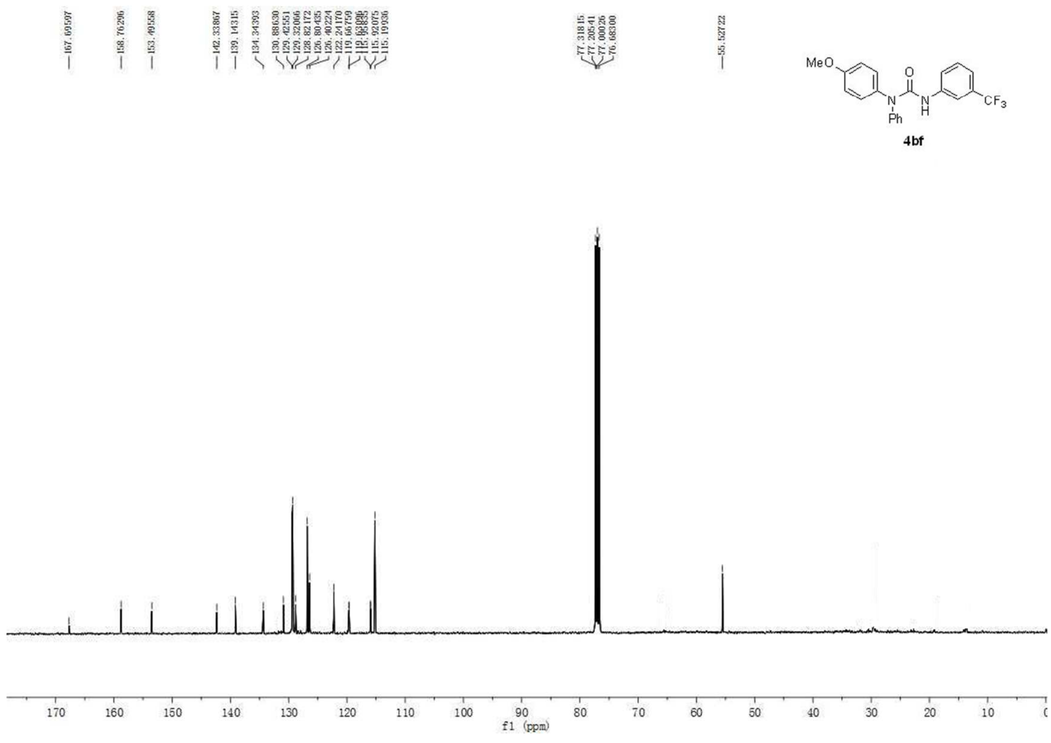
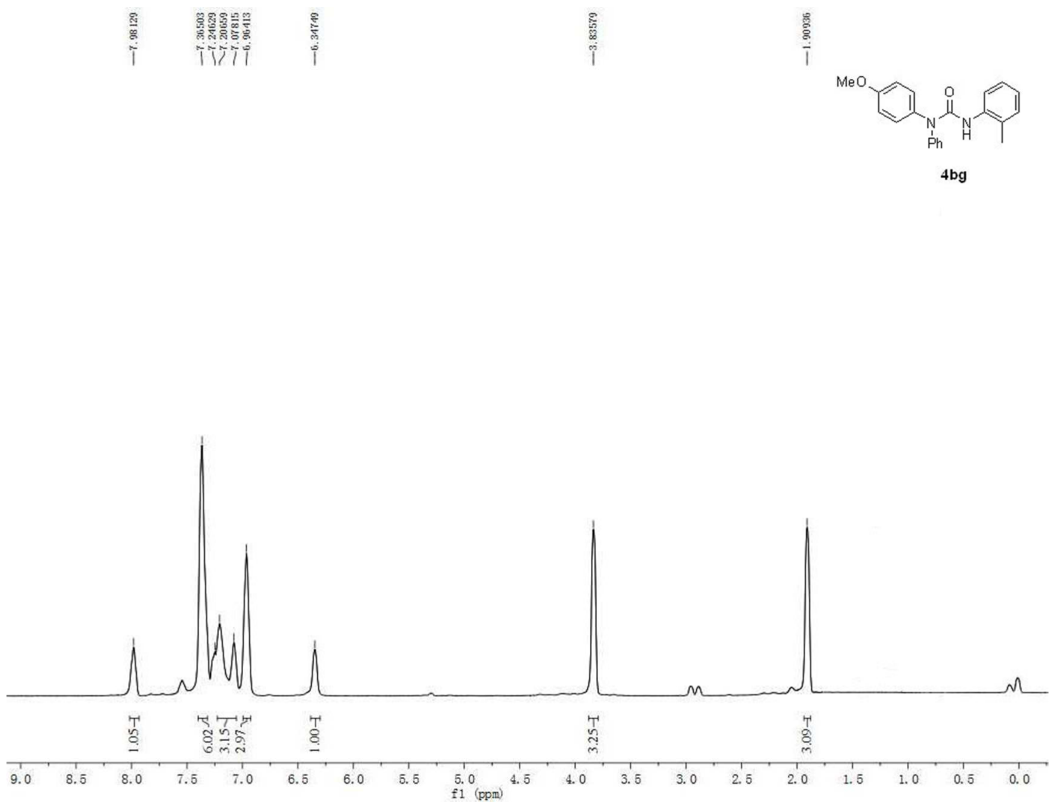
143.15714
139.26801
135.41967
131.90729
129.39238
129.09907
125.22547
126.74137
125.95569
115.03433
114.94899
77.31692
76.99986
76.68193
55.51367
33.89581
31.91265
MeO
t-Bu
Ph
4bd
f1 (ppm)


MeO
N
Ph
O
N
H
Br
4be
1.02
2.27
3.38
3.44
2.41
2.08
1.00
3.27
f1 (ppm)


MeO
N
Ph
O
N
H
Br
4be
f1 (ppm)



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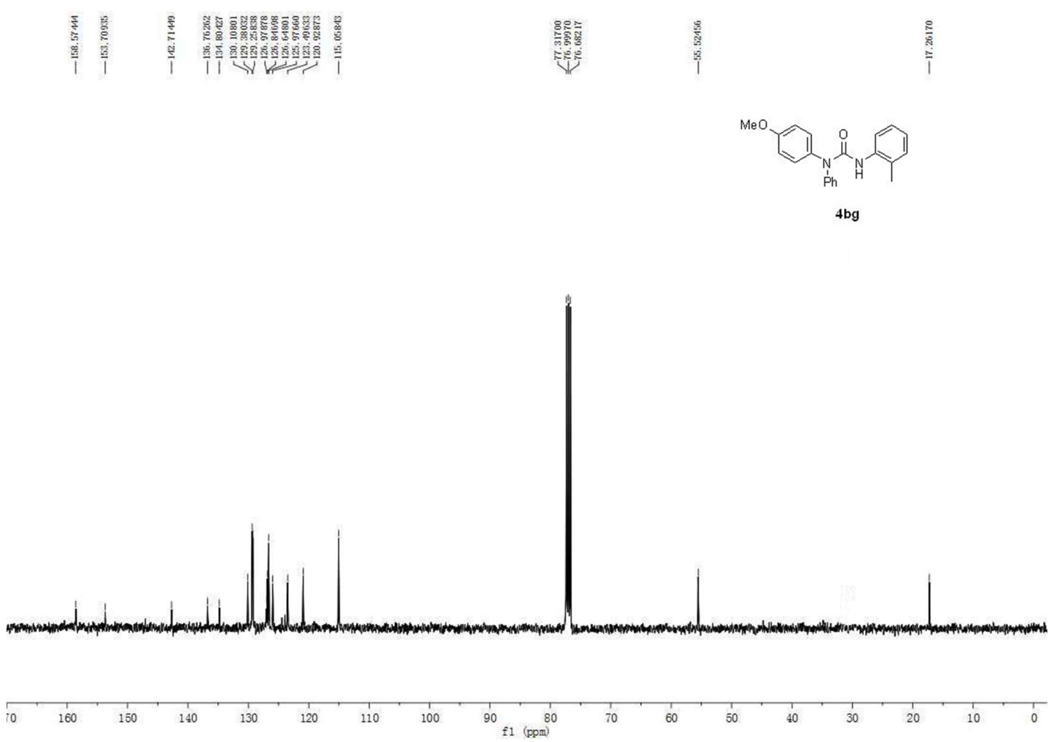
7.24629
7.20659
7.07815
6.96413
6.34749
3.83579
1.90936
MeO
O
N
H
Ph
4bg
1.05
6.02
3.15
2.97
1.00
3.25
3.09
f1 (ppm)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129.38032
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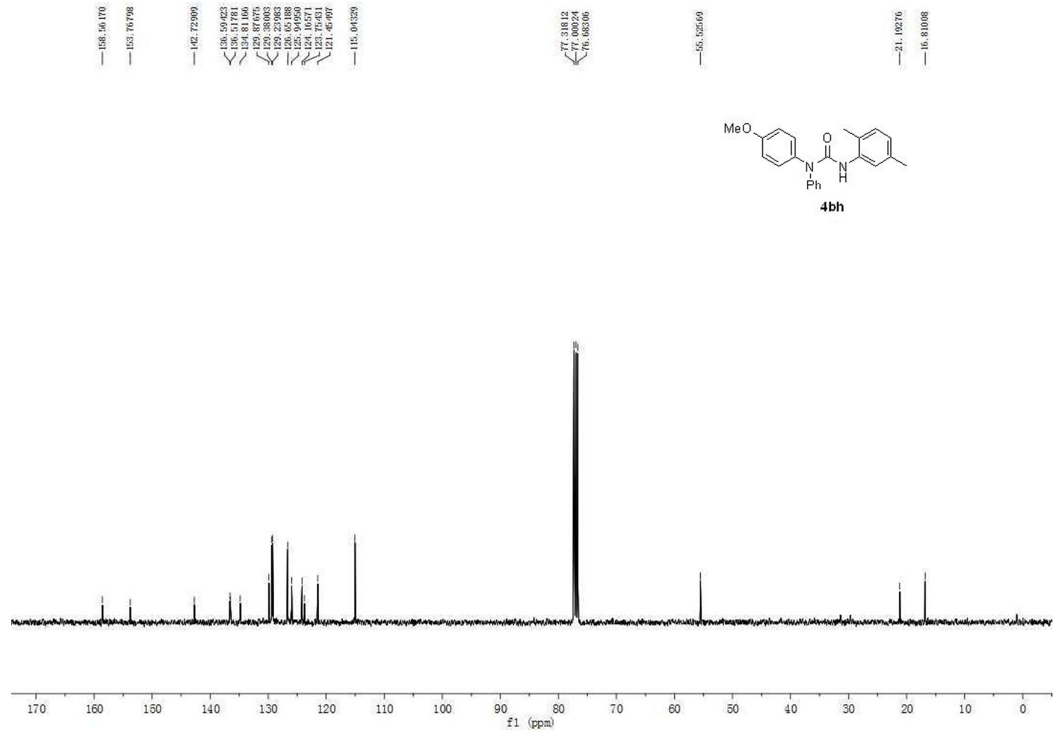
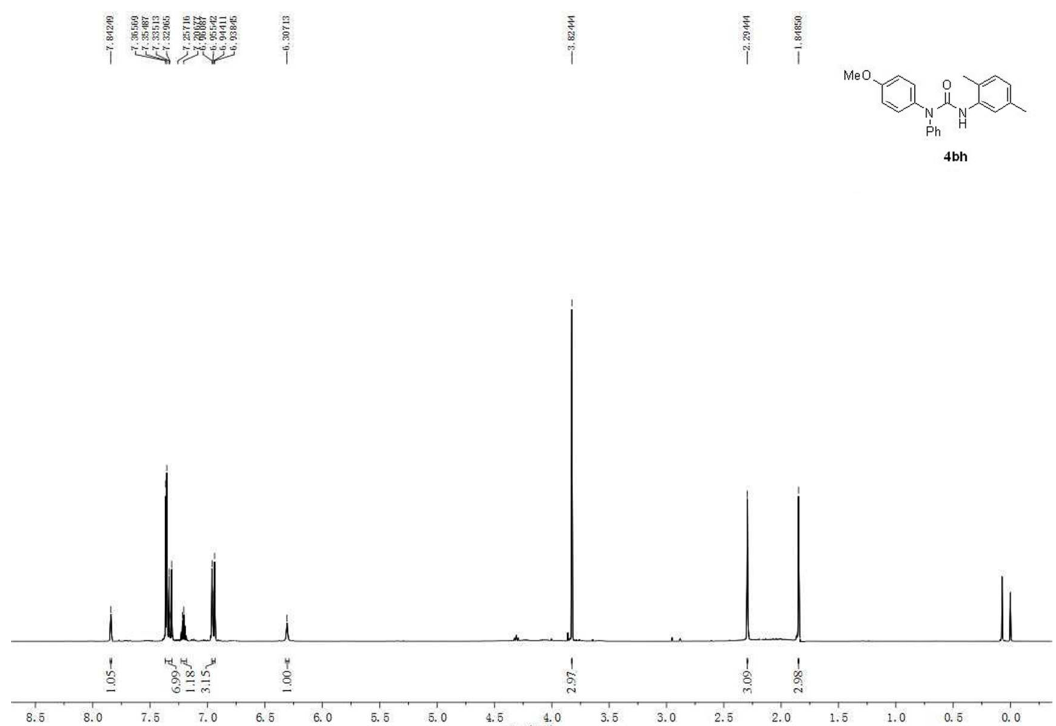
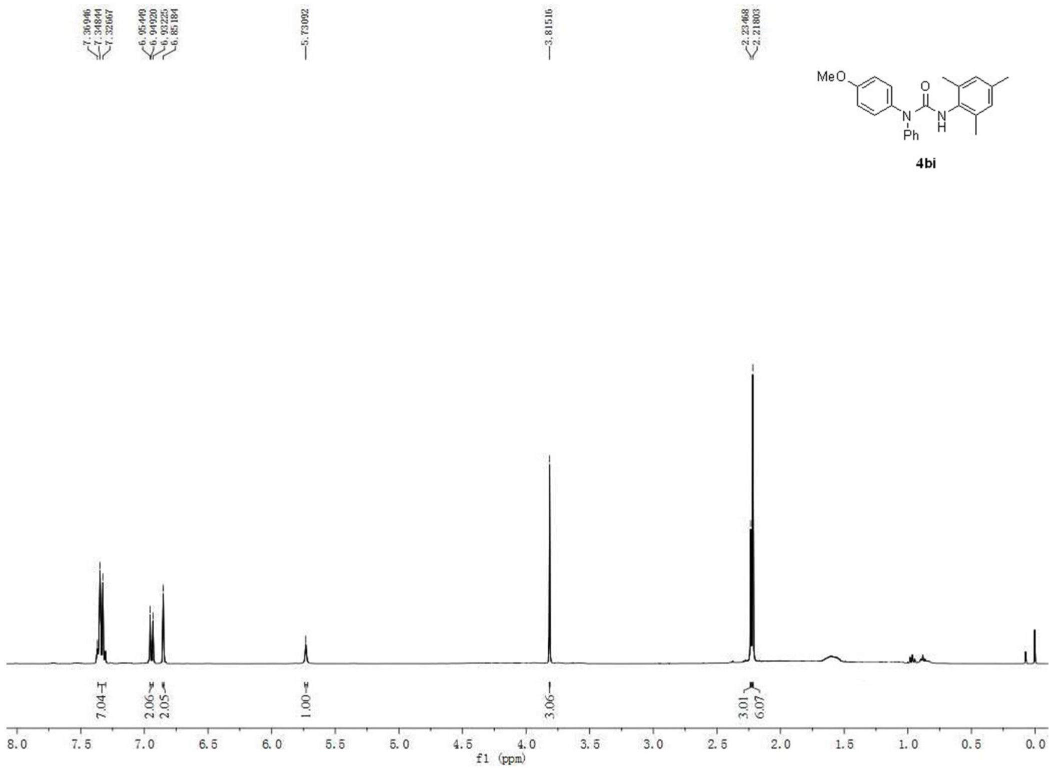
126.64801
125.97660
123.49633
120.92873
115.05843
77.31700
76.99970
76.68217
55.52456
17.26170
MeO
O
N
H
Ph
4bg
f1 (ppm)


MeO
Ph
4bh
f1 (ppm)


MeO
Ph
4bh
f1 (ppm)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7.32667
6.95440
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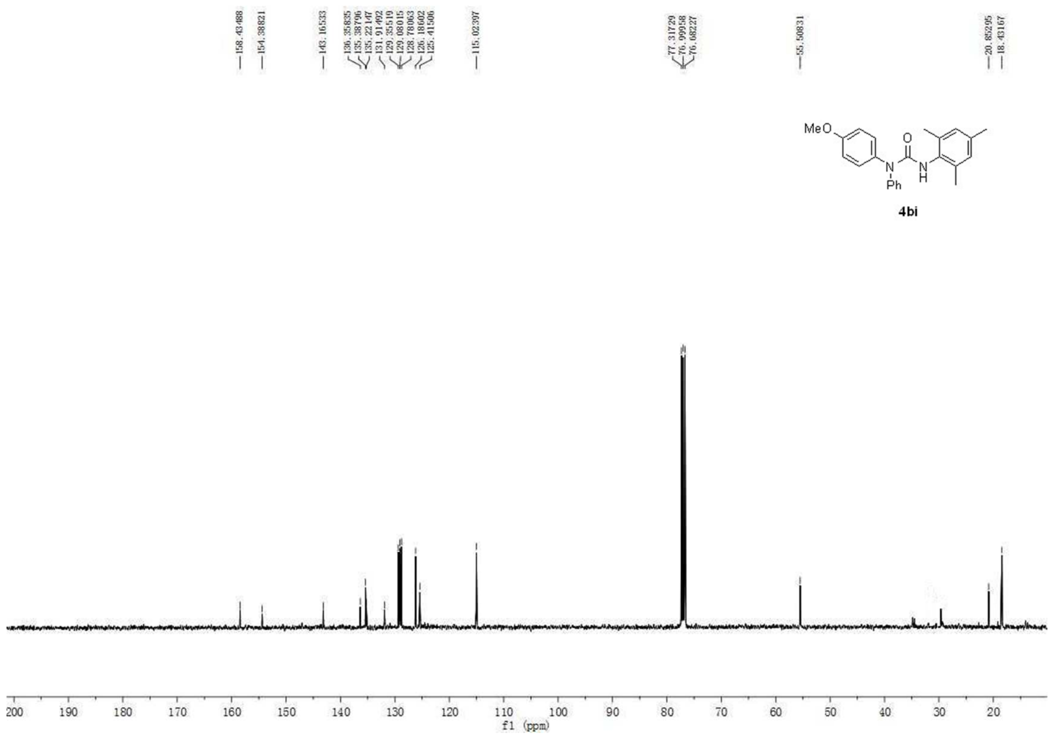
6.93225
6.85184
5.73092
3.81516
2.23468
2.21803
MeO
N
Ph
O
H
N
7.04
2.06
2.05
1.00
3.06
3.01
6.07
f1 (ppm)

4bi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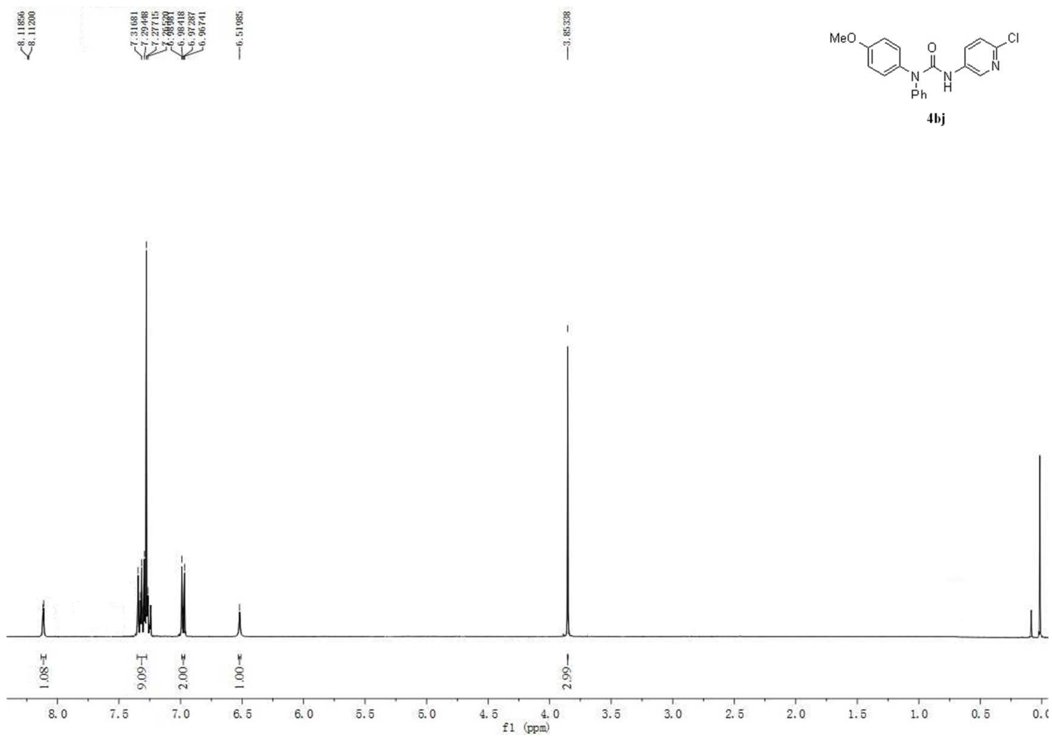
143.16533
136.35835
135.38796
135.22147
131.91492
129.35519
129.08015
128.78063
126.18602
125.41506
115.02397
77.31729
76.99958
76.68227
55.50831
20.85295
18.43167
MeO
N
Ph
O
H
N
f1 (ppm)

4bi



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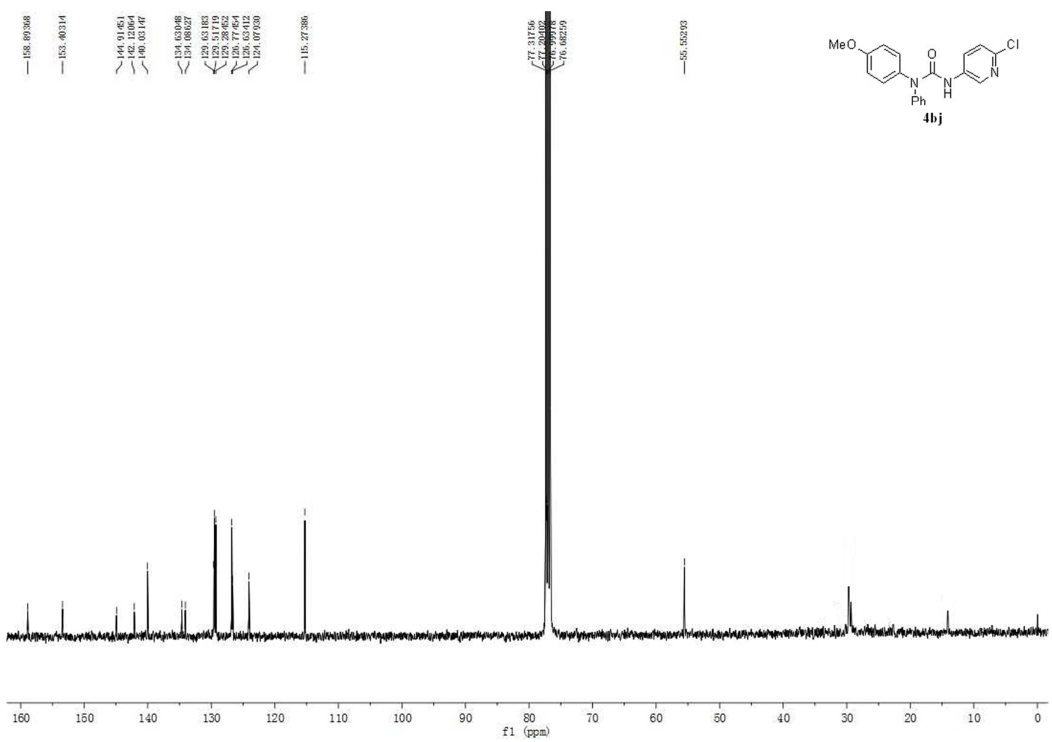
7.31681
7.29448
7.27715
6.98418
6.97287
6.96741
6.51985
3.85338
1.08
9.09
2.00
1.00
2.99
f1 (ppm)
MeO
O
N
Ph
N
H
N
Cl
4bj



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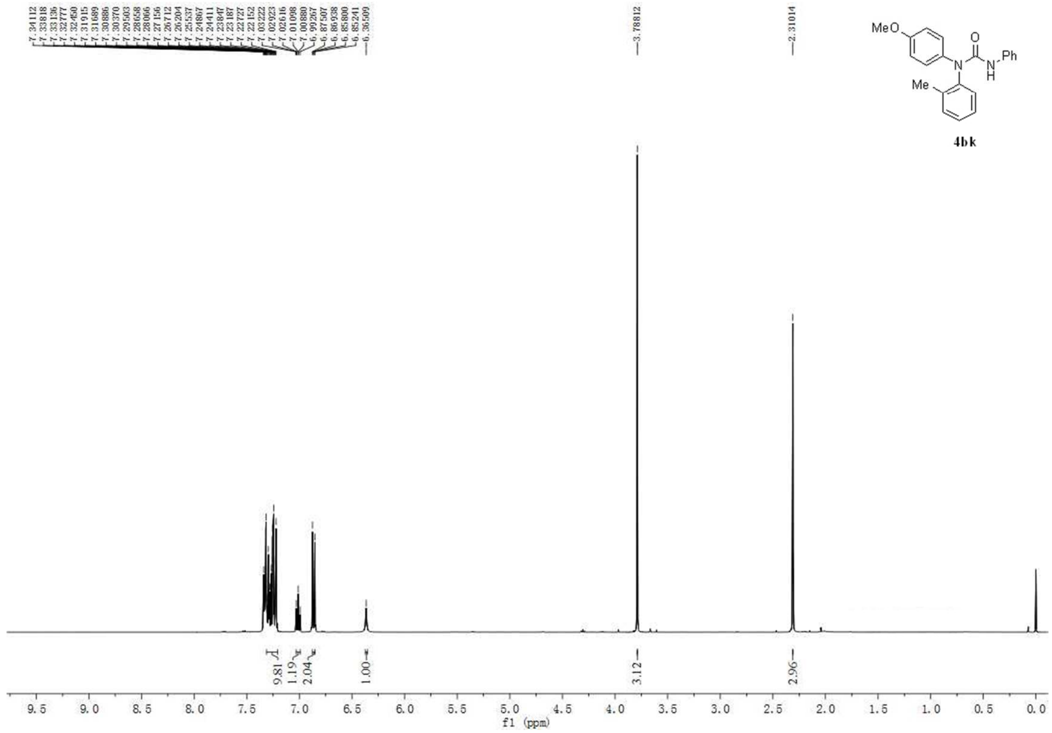
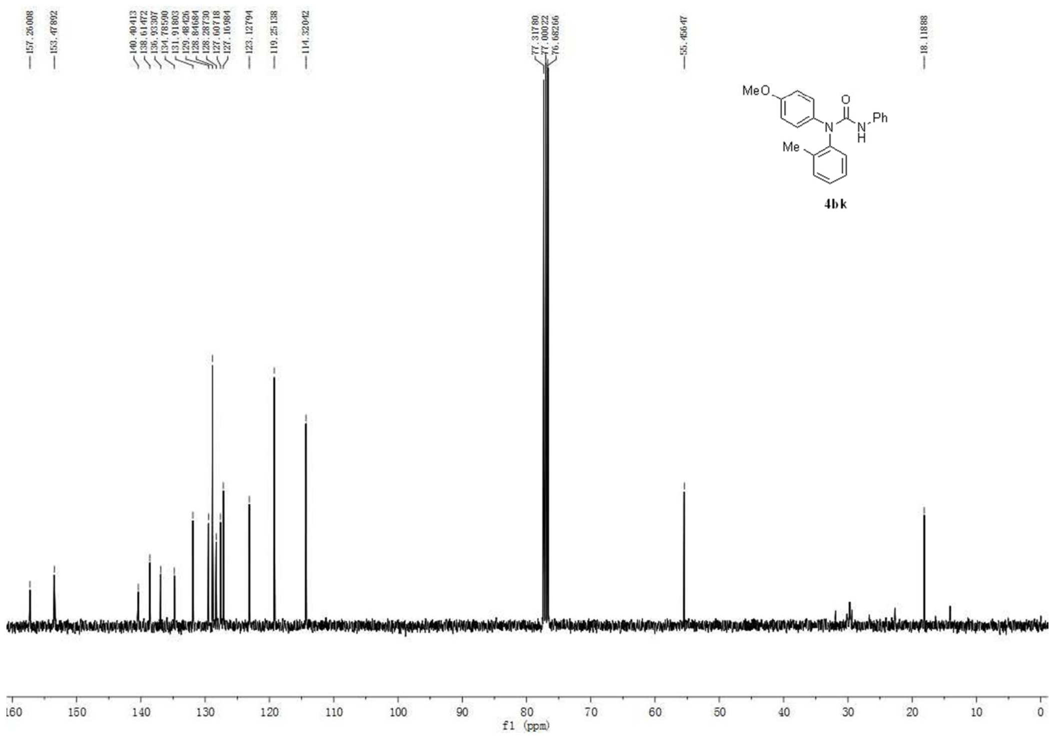
134.08627
129.63183
129.51719
129.28452
126.77454
126.63412
124.07930
115.27386
77.31756
76.68259
55.55293
f1 (ppm)
MeO
O
N
Ph
N
H
N
Cl
4bj


MeO
N
O
N
H
Ph
Me
4bk
3.78812
2.31014
9.81
1.19
2.04
1.00
3.12
2.96
f1 (ppm)


157.26008
153.47892
123.12794
119.25138
114.32042
55.45647
18.11888
MeO
N
O
N
H
Ph
Me
4bk
f1 (ppm)