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Palladium-Catalyzed Deamidative Arylation of Azoles with Arylamides through a Tandem Decarbonylation/C−H Functionalization

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1. General considerations

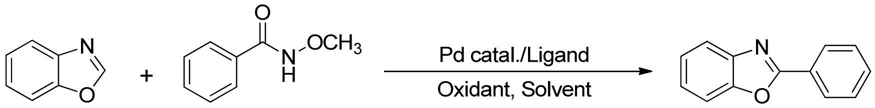
All palladium-catalyzed deamidative arylation of azoles with arylamides were carried out under an air atmosphere. All reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR, ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

2. Typical procedures for the palladium-catalyzed deamidative arylation

Under air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with azole (1.0 mmol), *N*-methoxybenzamide (1.0 mmol), $Pd(OAc)_2$ (0.05 mmol), 1,10-phenanthroline (0.10 mmol), $K_2S_2O_8$ (2.0 mmol), and toluene/DMSO (4:1, 2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 120 °C for 24 h. After the reaction was completed, it was cooled to room temperature and quenched with water and extracted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate) to give the desired deamidative arylation product.

3. Optimization of the reaction conditions for deamidative arylation of azoles with arylamides (Table S1)

Table S1. Optimization of the reaction conditions for deamidative arylation of **1a** with **2a**[a]



1a **2a** **3a**

Entry	Pd catalyst/Ligand[b]	Solvent	Oxidant[c]	Yield (%)[d]
1	$Pd(OAc)_2$	DMSO	$K_2S_2O_8$	31
2	$Pd(OAc)_2$	Toluene	$K_2S_2O_8$	20
3	$Pd(OAc)_2$	THF	$K_2S_2O_8$	0
4	$Pd(OAc)_2$	DCE	$K_2S_2O_8$	0
5	$Pd(OAc)_2$	NMP	$K_2S_2O_8$	0
6	$Pd(OAc)_2$	Toluene/DMSO (4:1)	$K_2S_2O_8$	55
7	$Pd(OAc)_2$	Toluene/DMSO (3:1)	$K_2S_2O_8$	42
8	$Pd(OAc)_2$	Toluene/DMSO (2:1)	$K_2S_2O_8$	29
9	$Pd(OAc)_2$	Toluene/DMSO (1:1)	$K_2S_2O_8$	30
10	$Pd(OAc)_2$	Toluene/DMSO (1:2)	$K_2S_2O_8$	25
11	$Pd(OAc)_2$	Toluene/DMSO (1:3)	$K_2S_2O_8$	26
12	$Pd(OAc)_2$	Toluene/DMSO (1:4)	$K_2S_2O_8$	23
13	$Pd(OAc)_2$	DCE/DMSO (4:1)	$K_2S_2O_8$	43
14	$Pd(OAc)_2$	THF/DMSO (4:1)	$K_2S_2O_8$	0
15	$Pd(OAc)_2$	DMF/DMSO (4:1)	$K_2S_2O_8$	0
16	$Pd(OAc)_2$	NMP/DMSO (4:1)	$K_2S_2O_8$	0
17	$Pd(OAc)_2$	MeCN/DMSO (4:1)	$K_2S_2O_8$	0
18	$Pd(OAc)_2$	Dioxane/DMSO (4:1)	$K_2S_2O_8$	0
19	$Pd(OAc)_2$	$MeNO_2$/DMSO (4:1)	$K_2S_2O_8$	0

20	$Pd(OAc)_2$	EtOH/DMSO (4:1)	$K_2S_2O_8$	0
21	$Pd(OAc)_2$	*t*-BuOH/DMSO (4:1)	$K_2S_2O_8$	0
22	$Pd(OAc)_2$	Toluene/DMSO (4:1)	DDQ	40
23	$Pd(OAc)_2$	Toluene/DMSO (4:1)	$(NH_4)_2S_2O_8$	32
24	$Pd(OAc)_2$	Toluene/DMSO (4:1)	Ag_2CO_3	27
25	$Pd(OAc)_2$	Toluene/DMSO (4:1)	TBHP	0
26	$Pd(OAc)_2$	Toluene/DMSO (4:1)	DTBP	0
27	$Pd(OAc)_2$	Toluene/DMSO (4:1)	DCP	0
28	$Pd(OAc)_2$	Toluene/DMSO (4:1)	CHP	0
29	$Pd(OAc)_2$	Toluene/DMSO (4:1)	$C_6H_5I(OAc)_2$	0
30	$Pd(OAc)_2$	Toluene/DMSO (4:1)	$Cu(OAc)_2$	0
31	$Pd(OAc)_2$/Phen	Toluene/DMSO (4:1)	$K_2S_2O_8$	75
32	$PdCl_2$/Phen	Toluene/DMSO (4:1)	$K_2S_2O_8$	59
33	$Pd(OAc)_2/PPh_3$	Toluene/DMSO (4:1)	$K_2S_2O_8$	48
34	$Pd(OAc)_2$/TMEDA	Toluene/DMSO (4:1)	$K_2S_2O_8$	57
35	$Pd(OAc)_2$/2,2'-bipyridine	Toluene/DMSO (4:1)	$K_2S_2O_8$	63
36	$Pd(OAc)_2$/8-hydroquinoline	Toluene/DMSO (4:1)	$K_2S_2O_8$	52
37	$Pd(CH_3CN)_2Cl_2$	Toluene/DMSO (4:1)	$K_2S_2O_8$	61
38	$Pd(PPh_3)_2Cl_2$	Toluene/DMSO (4:1)	$K_2S_2O_8$	55
39	$Pd(PPh_3)_4$	Toluene/DMSO (4:1)	$K_2S_2O_8$	46
40	$Pd(dba)_2$	Toluene/DMSO (4:1)	$K_2S_2O_8$	38

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), Pd catalyst (0.05 mmol), ligand (0.10 mmol) if necessary, oxidant (2.0 mmol) if necessary, in solvent (2.0 mL) at 120 °C for 24 h. [b] Phen = 1,10-phenanthroline, TMEDA = *N,N,N′,N′*-tetramethylethylenediamine. [c] DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone, TBHP = *tert*-butyl hydroperoxide, DTBP = di-*tert*-butyl peroxide, DCP = dicumyl peroxide, CHP = cumene hydroperoxide, . [d] Isolated yields.

4. FT-IR analysis of the products

After the reaction was completed, it was cooled to room temperature and quenched with water. The resulting gas was directly analyzed by a Bruker Tensor 27 FT-IR instrument using a gas cell, and the results were listed in Figure S1 and Table S2.

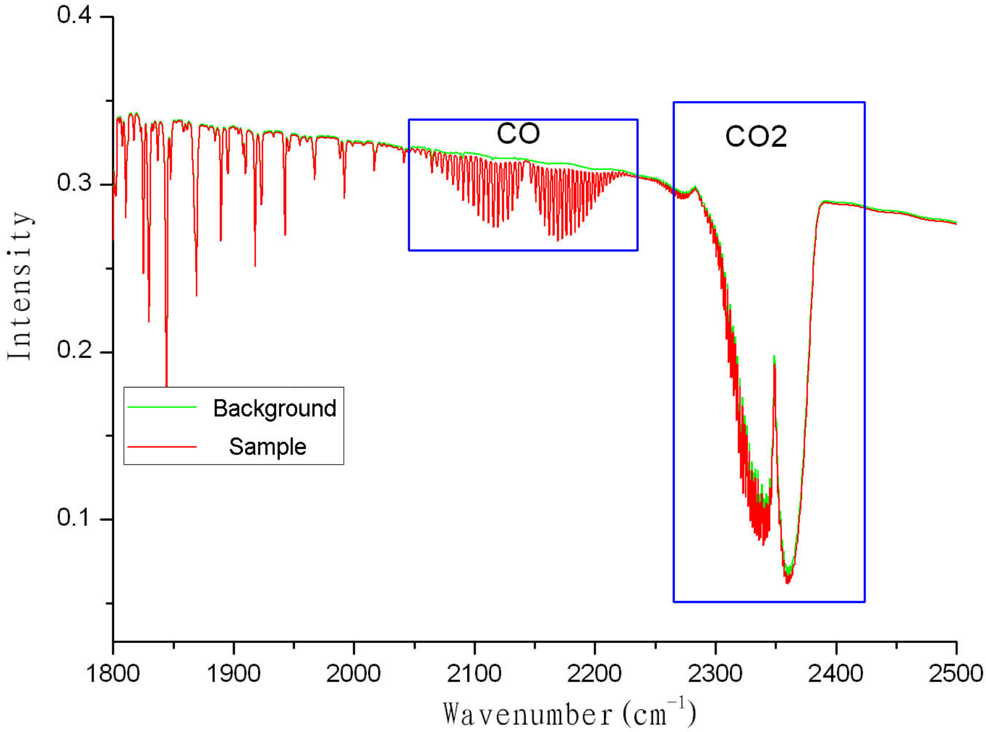
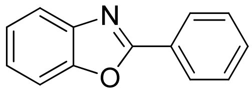


Figure S1. FT-IR analysis of the products

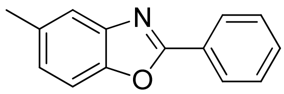
Table S2. FT-IR analysis of the products

Samples	**CO (ppm)**	**CO_2 (ppm)**
R1	1376.34	45.84
R2	1379.67	45.51
R3	1361.98	49.20
Average	1372.66	46.85
CO/CO_2 = 29.3/1		

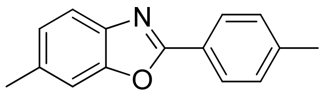
5. Characterization data for the products



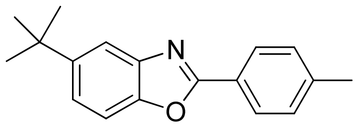
3a:[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29–8.27 (m, 2H), 7.81–7.79 (m, 1H), 7.61–7.54 (m, 4H), 7.38–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 142.0, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6.



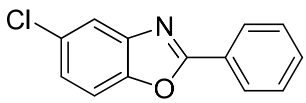
3b:[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27–8.24 (m, 2H), 7.57–7.52 (m, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.17–7.15 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 149.0, 142.3, 134.3, 131.3, 128.8, 127.5, 127.3, 126.2, 119.9, 109.9, 21.5.



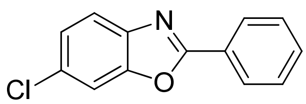
3c:[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.11 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.31–7.29 (m, 2H), 7.16–7.14 (m,1H), 2.49 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 150.9, 141.6, 140.0, 135.2, 129.5, 127.3, 125.6, 124.5, 119.1, 110.6, 21.7, 21.5.



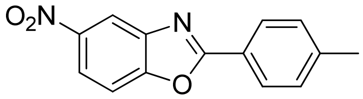
3d:[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.14 (m, 2H), 7.82 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41–7.39 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3, 148.6, 147.9, 142.1, 141.7, 129.5, 127.4, 124.5, 122.4, 116.3, 109.5, 34.8, 31.7, 21.5.



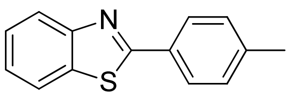
3e:[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.19 (m, 2H), 7.72 (s, 1H), 7.53–7.43 (m, 4H), 7.30–7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2, 149.2, 143.2, 131.8, 130.0, 128.9, 127.7, 126.6, 125.2, 119.9, 111.2.



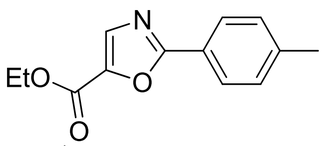
3f:[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.21 (m, 2H), 7.68–7.66 (m, 1H), 7.58–7.50 (m, 4H), 7.34–7.32 (m, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 150.8, 140.9, 131.7, 130.6, 128.9, 127.6, 126.7, 125.2, 120.4, 111.2.



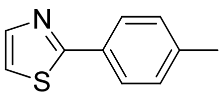
3g: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58–8.58 (m, 1H), 8.29–8.26 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 154.2, 145.3, 143.4, 142.6, 129.8, 128.0, 123.1, 120.8, 116.0, 110.5, 21.7. HRMS (ESI) ($[M]^+$) Calcd. for $C_{14}H_{10}N_2O_3$: 254.0691, Found: 254.0693.



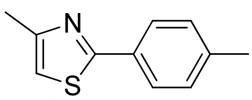
3h:[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 154.2, 141.4, 134.9, 131.0, 129.7, 127.5, 126.2, 125.0, 123.0, 121.5, 21.5.



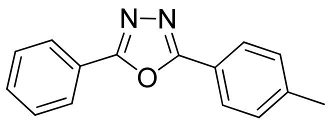
3i:[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 157.8, 142.0, 142.0, 135.2, 129.5, 127.1, 123.7, 61.3, 21.5, 14.2.



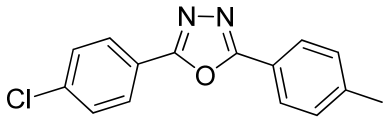
3j:[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 2H), 7.84–7.83 (m, 1H), 7.25– 7.22 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 168.4, 143.3, 140.0, 130.8, 129.7, 129.4, 126.3, 118.1, 21.1.



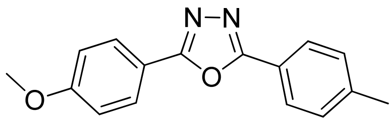
3k: ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.84 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 153.4, 139.7, 131.0, 129.4, 126.2, 112.7, 21.2, 17.1. HRMS (ESI) ($[M]^+$) Calcd. for $C_{11}H_{11}NS$: 189.0612, Found: 189.0614.



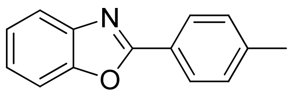
3l:[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.12 (m, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.54–7.52 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 164.3, 142.2, 131.5, 129.7, 129.0, 126.8, 124.0, 121.1, 21.6.



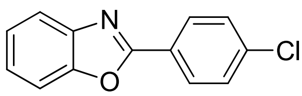
3m:[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 163.4, 142.4, 137.8, 129.7, 129.4, 128.0, 126.8, 122.5, 120.9, 21.6.



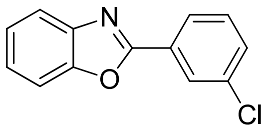
3n:[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.02 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 164.1, 162.1, 141.9, 129.6, 128.5, 126.6, 121.2, 116.4, 114.4, 55.3, 21.5.



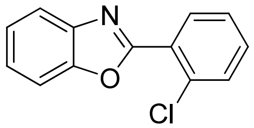
3o:[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.0 Hz, 2H), 7.79–7.76 (m, 1H), 7.59–7.57 (m, 1H), 7.36–7.33 (m, 4H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3, 150.7, 142.1, 142.0, 129.6, 127.6, 124.8, 124.4, 124.4, 119.8, 110.5, 21.6.



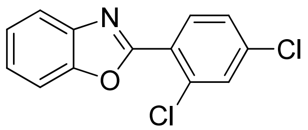
3p:[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.8 Hz, 2H), 7.79–7.76 (m, 1H), 7.60–7.76 (m, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.39–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 150.8, 142.0, 137.8, 129.3, 128.8, 125.7, 125.3, 124.7, 120.1, 110.6.



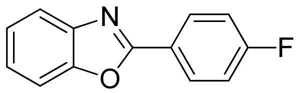
3q:[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.78–7.76 (m, 1H), 7.58–7.56 (m, 1H), 7.50–7.47 (m, 1H), 7.45–7.40 (m, 1H), 7.38–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 150.7, 141.9, 135.0 131.4, 130.1, 128.8, 127.5, 125.5, 125.4, 124.7, 120.2, 110.6.



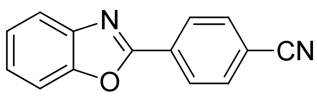
3r:[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.11 (m, 1H), 7.86–7.83 (m, 1H), 7.59–7.56 (m, 1H), 7.53–7.51 (m, 1H), 7.38–7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 150.4, 141.5, 133.3, 131.7, 131.6, 131.2, 126.7, 126.0, 125.4, 124.5, 120.3, 110.5.



3s:[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.4 Hz, 1H), 7.84–7.82 (m, 1H), 7.60–7.59 (m, 1H), 7.58–7.55 (m, 1H), 7.39–7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 150.4, 141.5, 137.4, 134.1, 132.4, 131.2, 127.3, 125.7, 124.7, 124.6, 120.5, 110.6.

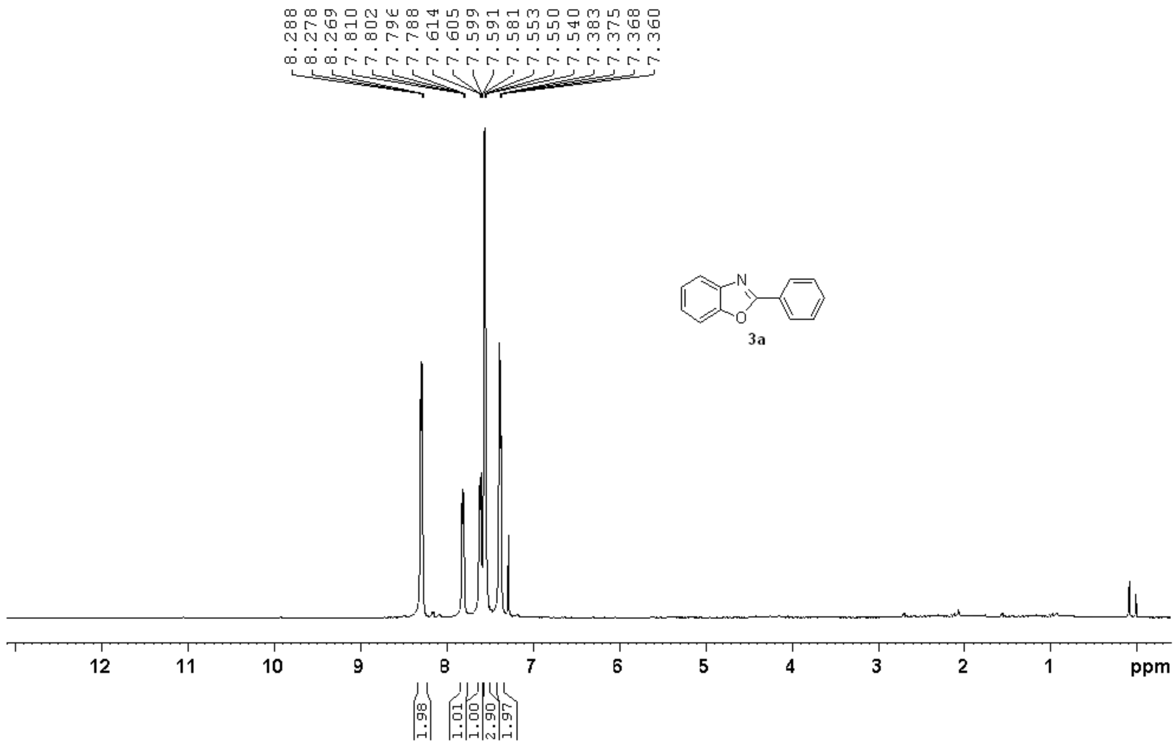


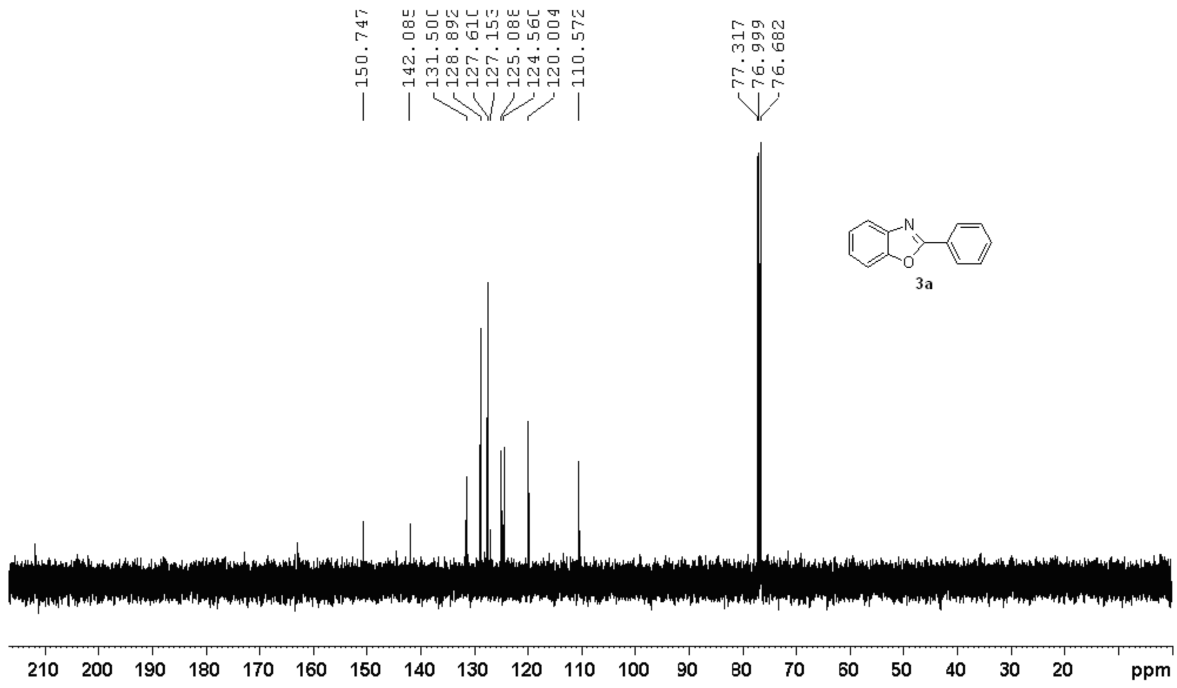
3t:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27–8.24 (m, 2H), 7.78–7.76 (m, 1H), 7.58– 7.56 (m, 1H), 7.37–7.34 (m, 2H), 7.23–7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8 (d, *J* = 251.2 Hz), 162.1, 150.7, 142.0, 129.7 (d, *J* = 8.8 Hz), 125.1, 124.6, 123.5 (d, *J* = 3.2 Hz), 120.0, 116.1 (d, *J* = 22.1 Hz), 110.5.

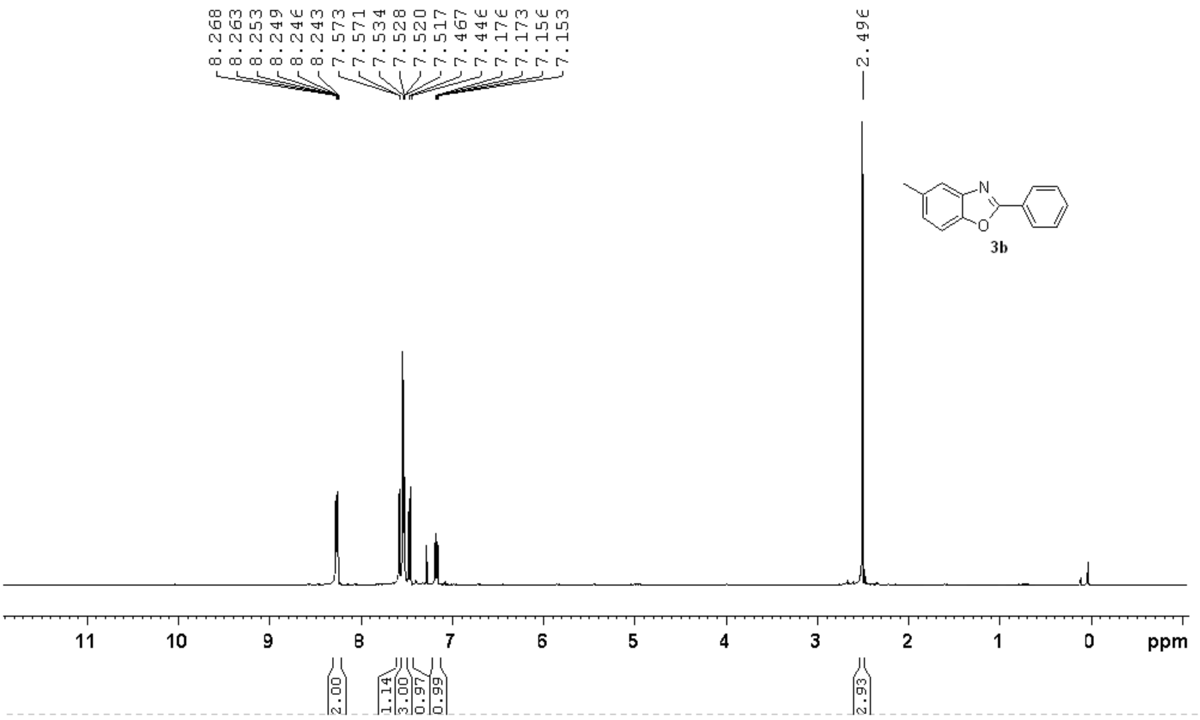


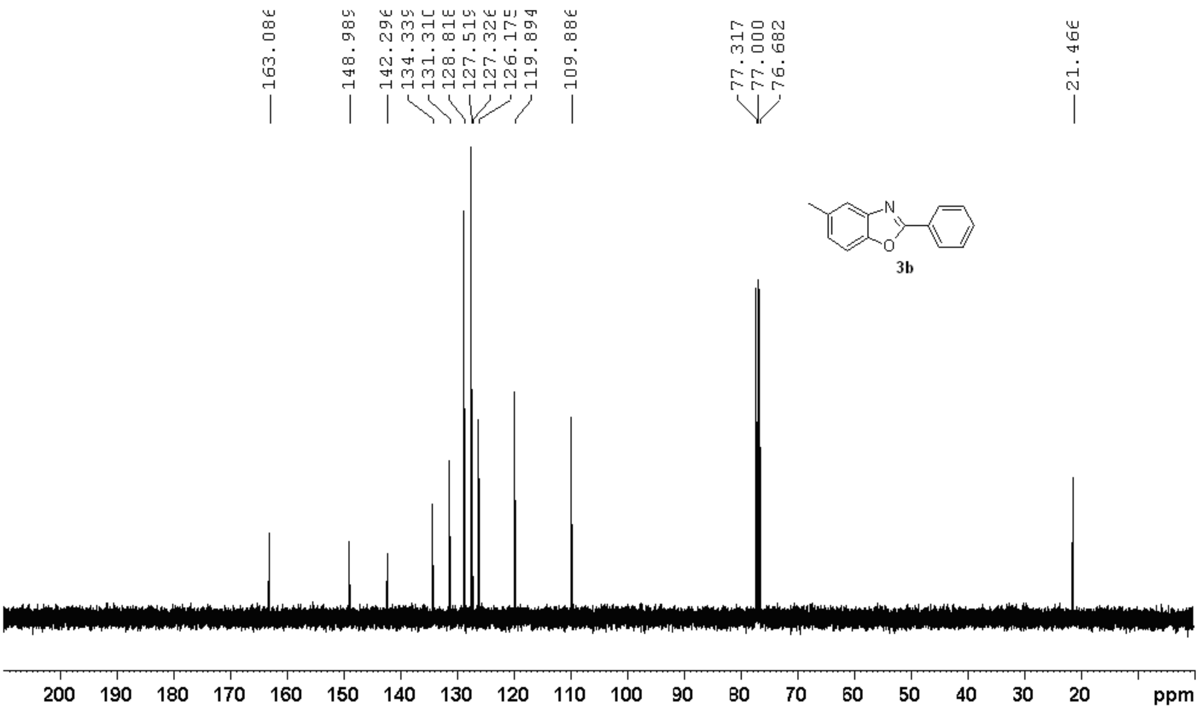
3u:[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35–8.32 (m, 2H), 7.81–7.78 (m, 3H), 7.61–7.59 (m, 1H), 7.42–7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 150.8, 141.8, 132.6, 131.0, 127.9, 126.1, 125.1, 120.5, 118.1, 114.7, 110.8.

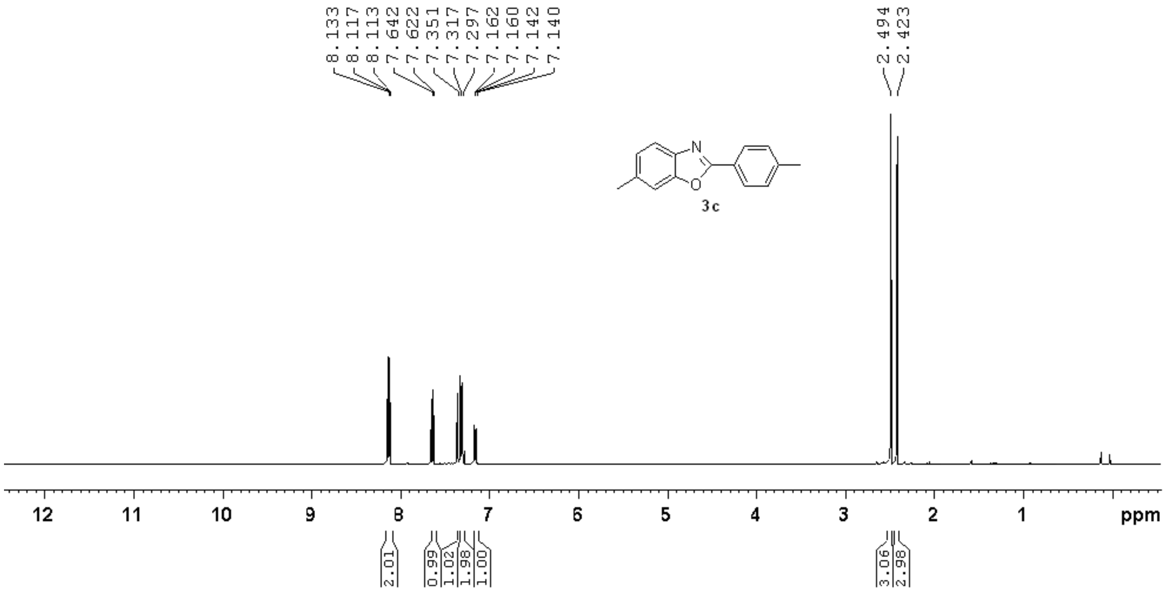
6. ^{1}H, ^{13}C NMR and HRMS spectra

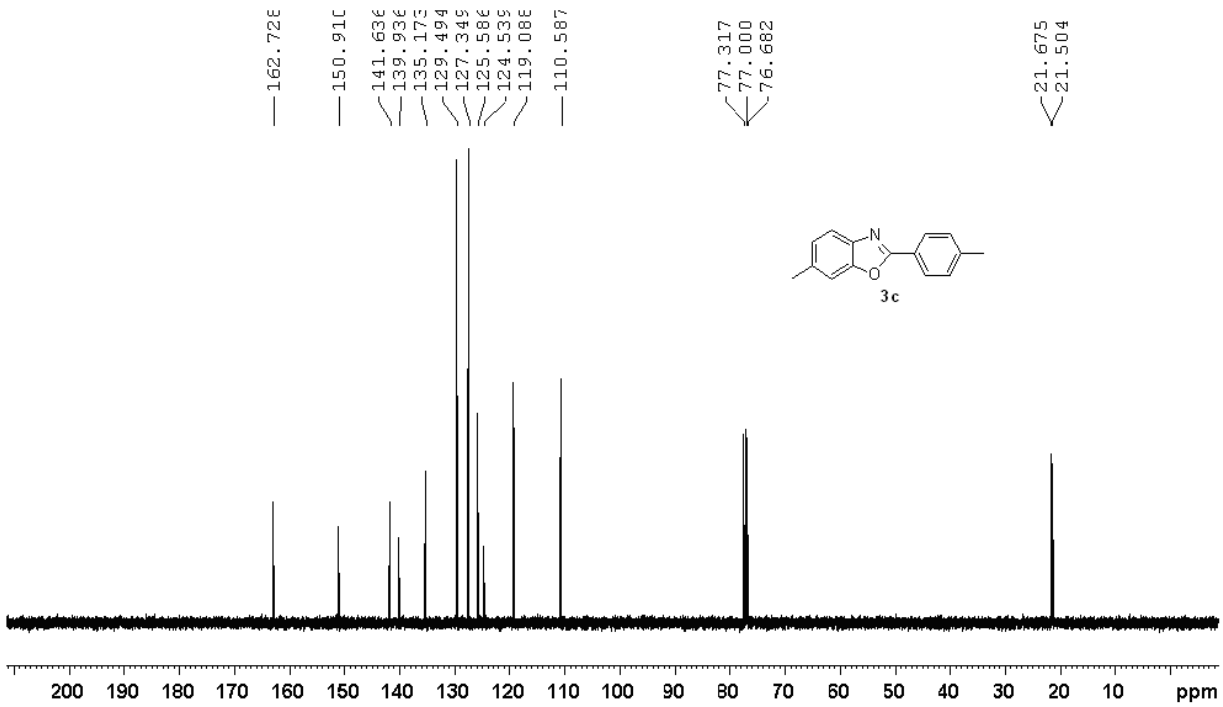


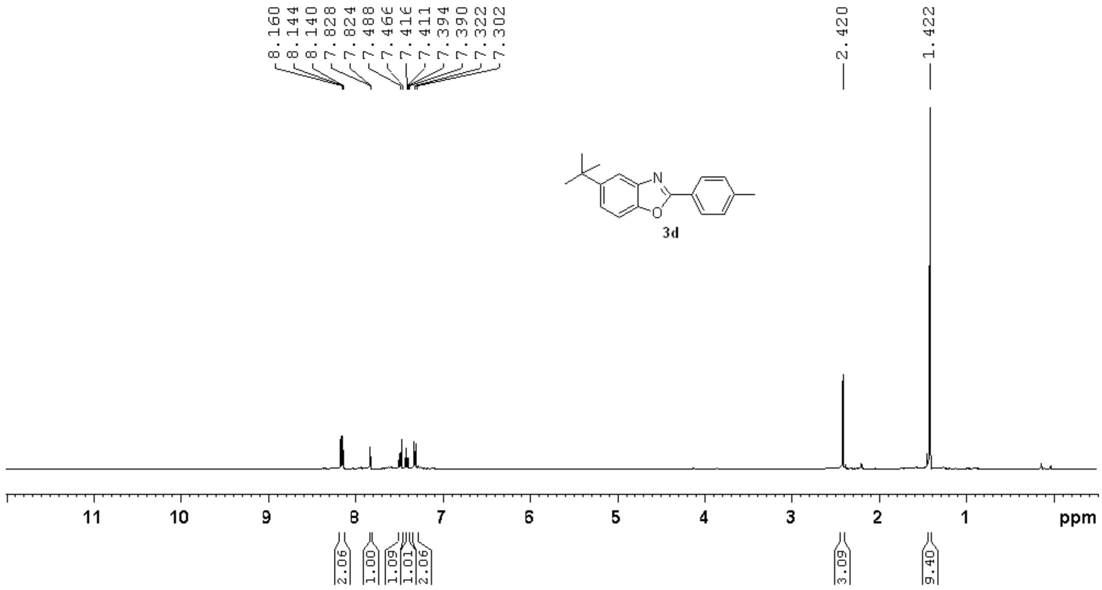


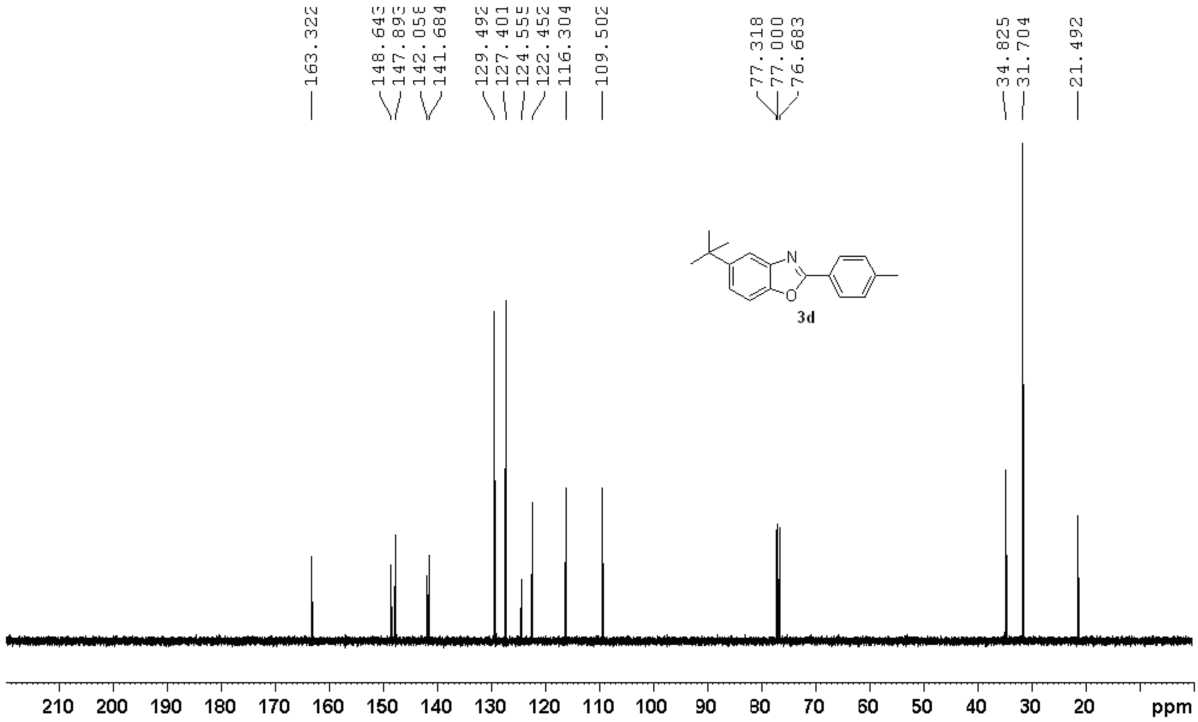

8.268
8.263
8.253
8.249
8.246
8.243
7.573
7.571
7.534
7.528
7.520
7.517
7.467
7.446
7.176
7.173
7.156
7.153
2.496
N
O
3b
ppm
2.00
1.14
3.00
0.97
0.99
2.93

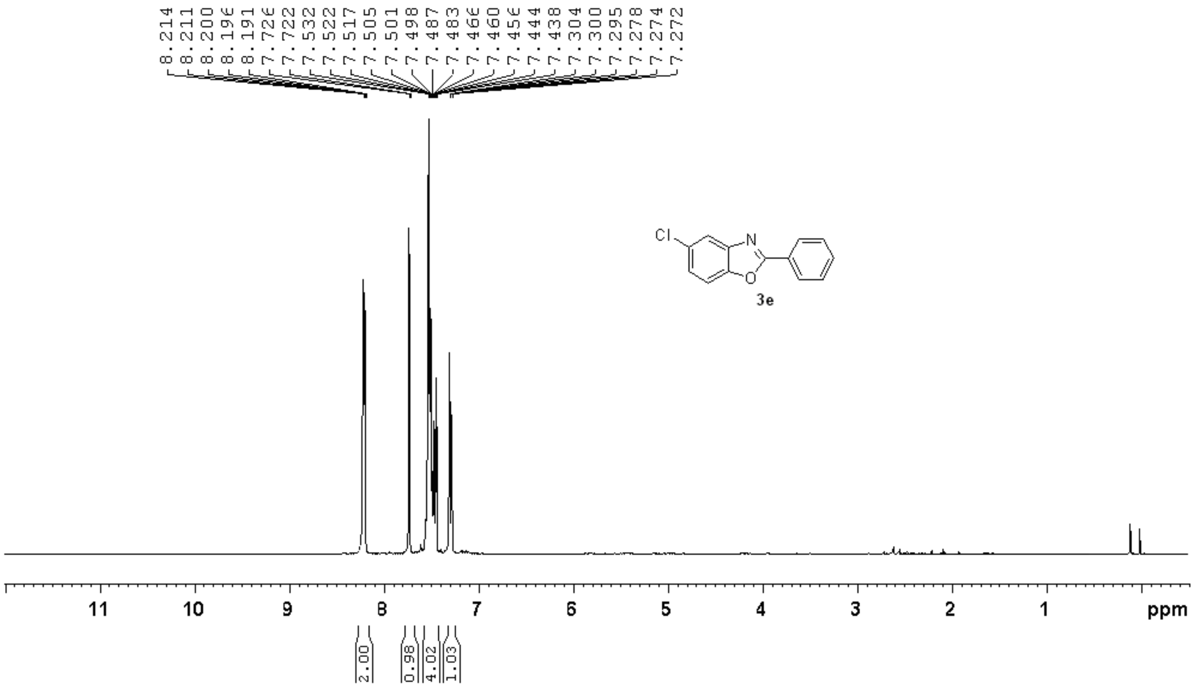

163.086
148.989
142.296
134.339
131.310
128.818
127.519
127.326
126.175
119.894
109.886
77.317
77.000
76.682
21.466
N
O
3b
ppm

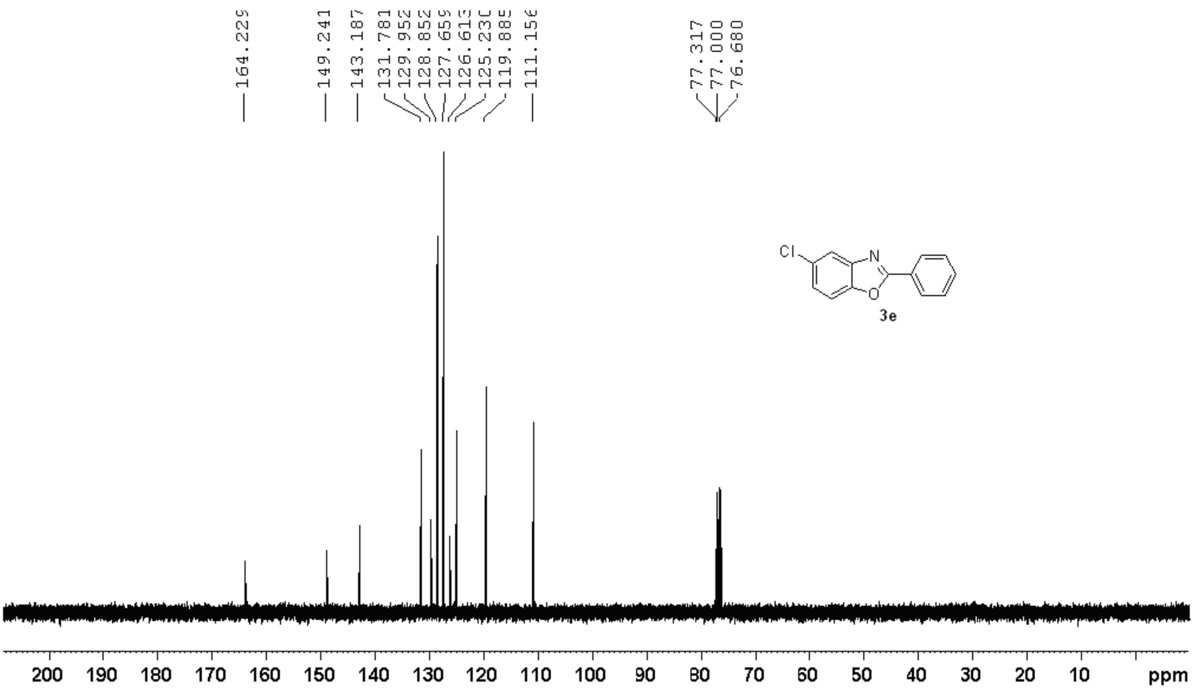

8.133
8.117
8.113
7.642
7.622
7.351
7.317
7.297
7.162
7.160
7.142
7.140
2.494
2.423
N
O
3c
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.01
0.99
1.02
1.98
1.00
3.06
2.98

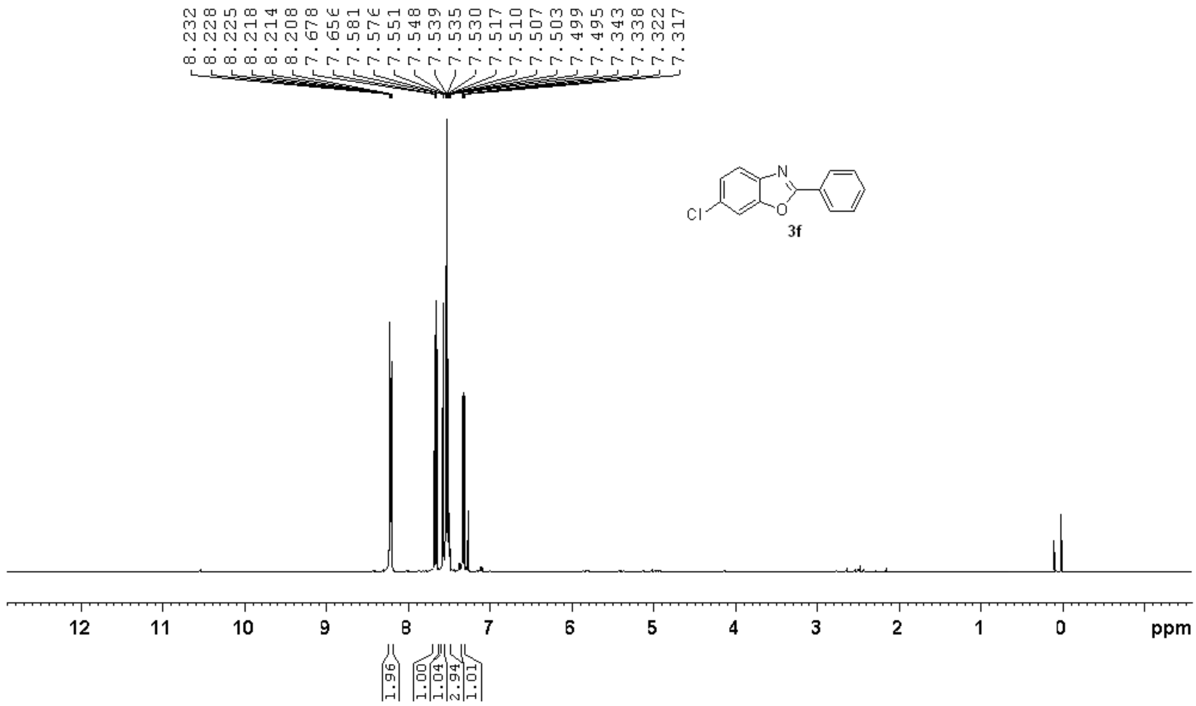

162.728
150.910
141.636
139.936
135.173
129.494
127.349
125.586
124.539
119.088
110.587
77.317
77.000
76.682
21.675
21.504
N
O
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

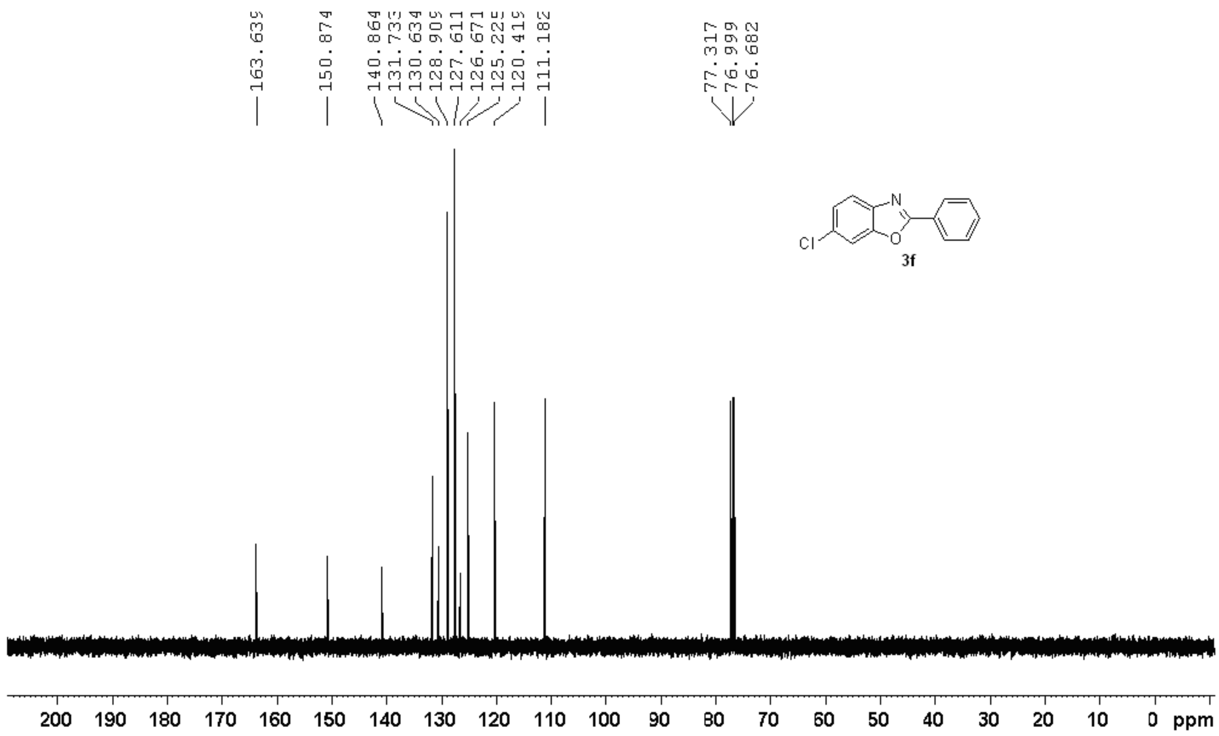

8.160
8.144
8.140
7.828
7.824
7.488
7.466
7.416
7.411
7.394
7.390
7.322
7.302
2.420
1.422
N
O
3d
11 10 9 8 7 6 5 4 3 2 1 ppm
2.06
1.00
1.09
1.01
2.06
3.09
9.40

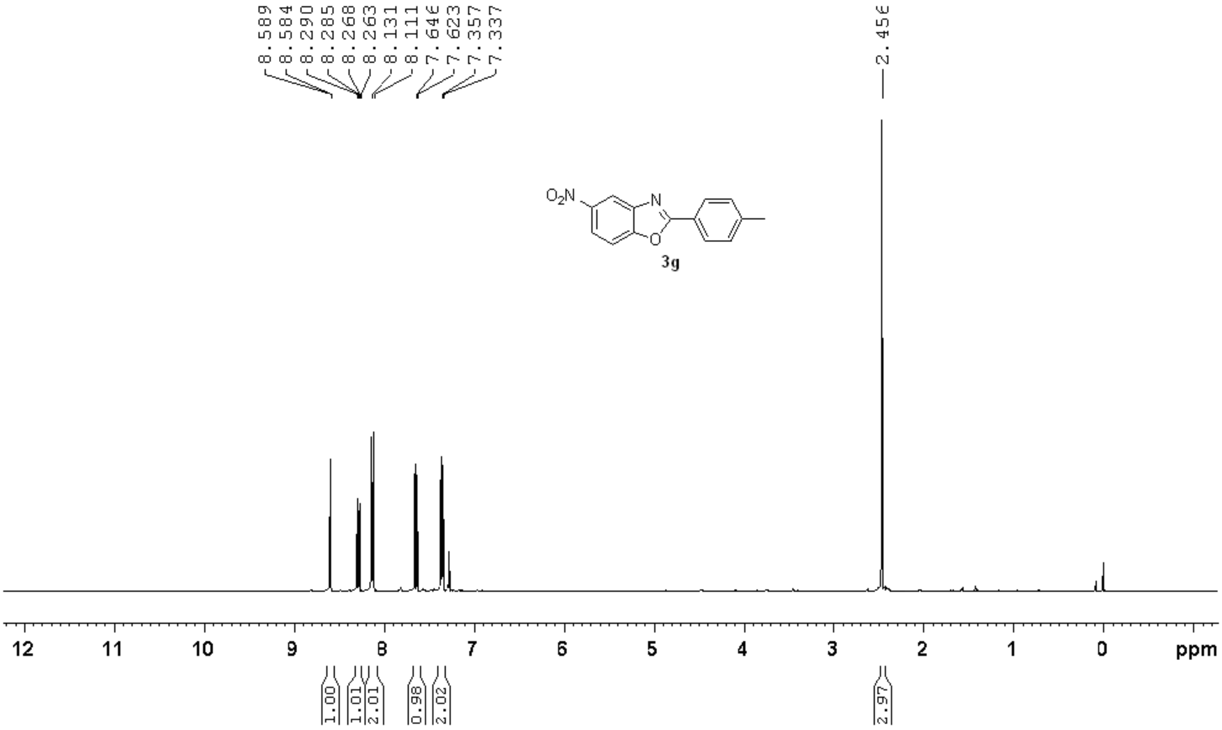

163.322
148.643
147.893
142.058
141.684
129.492
127.401
124.555
122.452
116.304
109.502
77.318
77.000
76.683
34.825
31.704
21.492
N
O
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

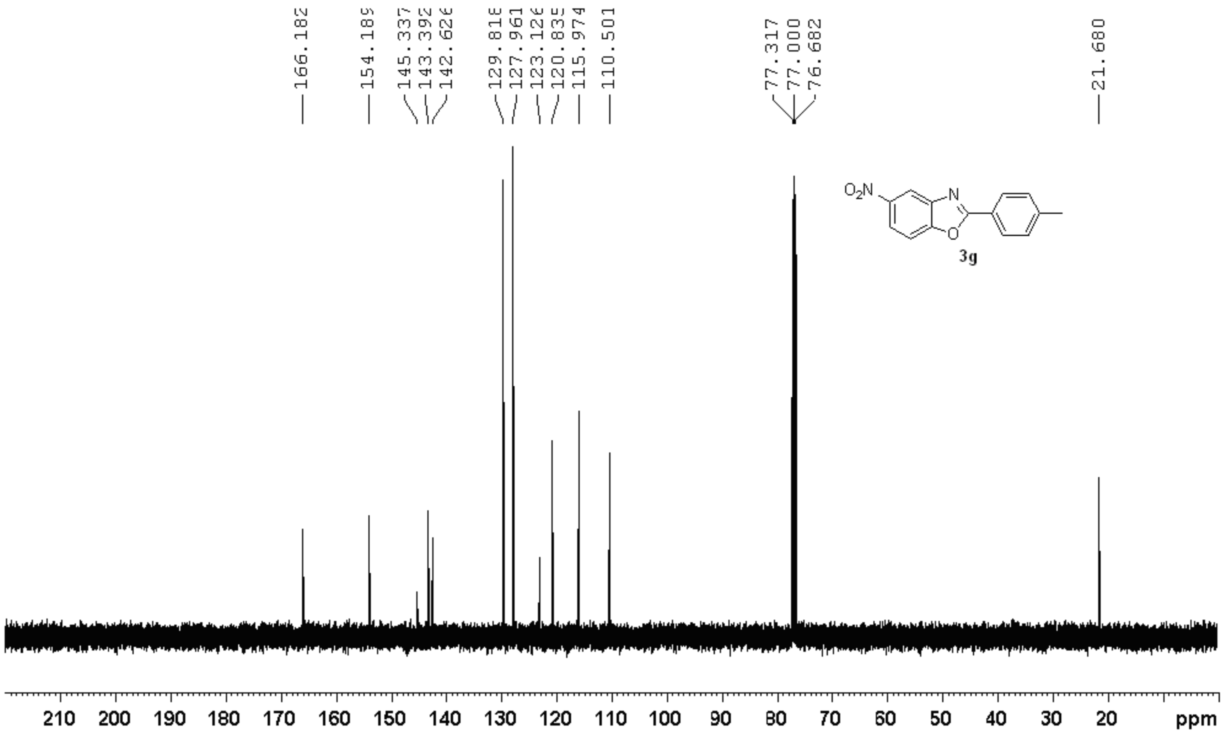

8.214
8.211
8.200
8.196
8.191
7.726
7.722
7.532
7.522
7.517
7.505
7.501
7.498
7.487
7.483
7.466
7.460
7.456
7.444
7.438
7.304
7.300
7.295
7.278
7.274
7.272
Cl
N
O
3e
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
0.98
4.02
1.03

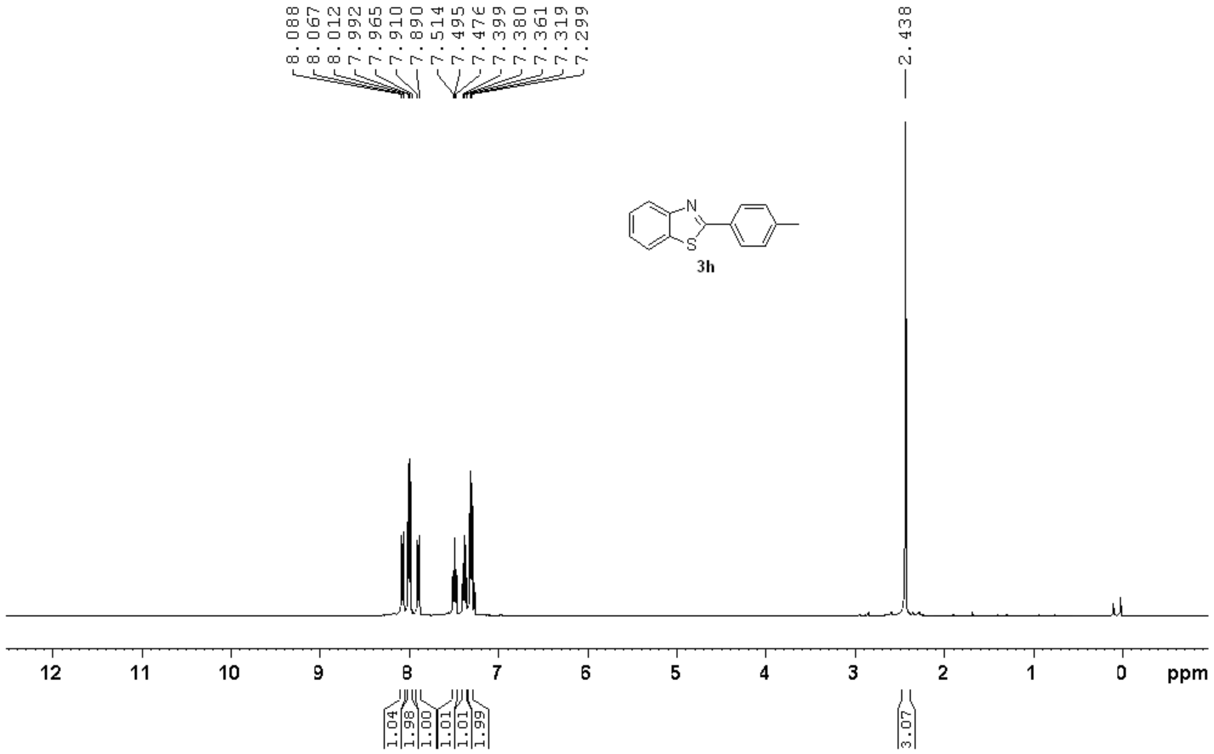

164.229
149.241
143.187
131.781
129.952
128.852
127.659
126.613
125.230
119.885
111.156
77.317
77.000
76.680
Cl
N
O
3e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

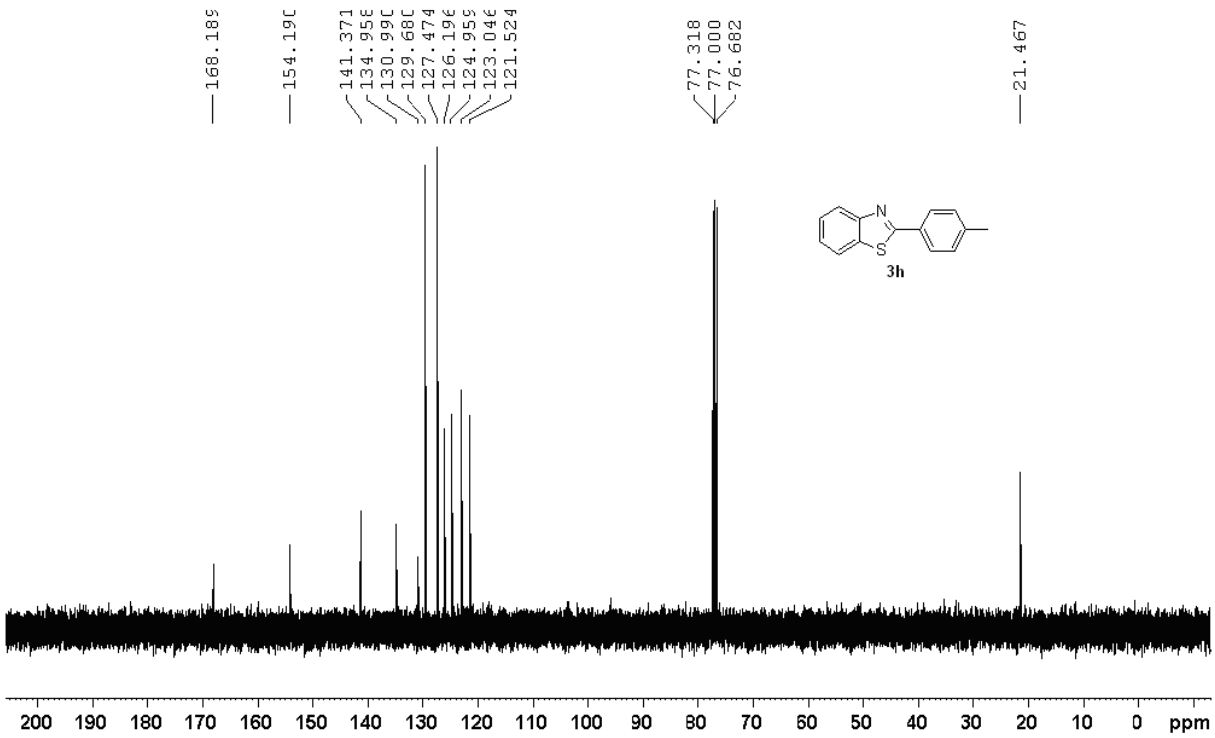

8.232 8.228 8.225 8.218 8.214 8.208 7.678 7.656 7.581 7.576 7.551 7.548 7.539 7.535 7.530 7.517 7.510 7.507 7.503 7.499 7.495 7.343 7.338 7.322 7.317
N
O
Cl
3f
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.96 1.00 1.04 2.94 1.01

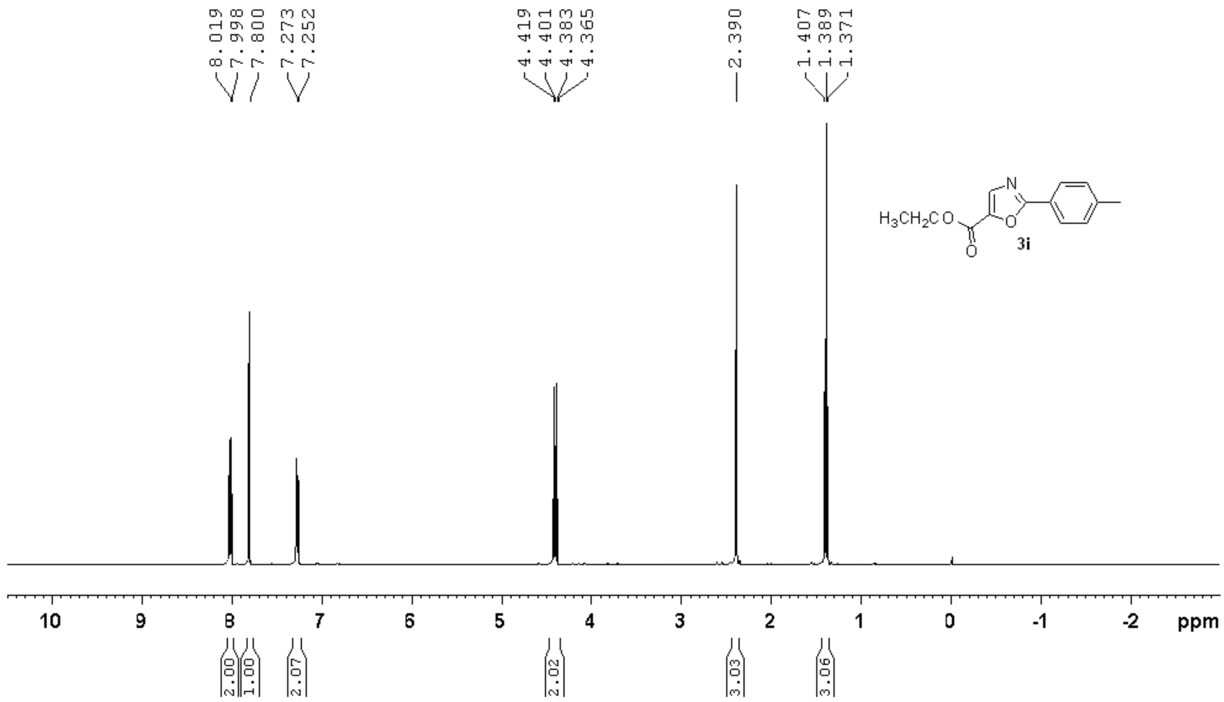

163.639 150.874 140.864 131.733 130.634 128.909 127.611 126.671 125.225 120.419 111.182 77.317 76.999 76.682
N
O
Cl
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

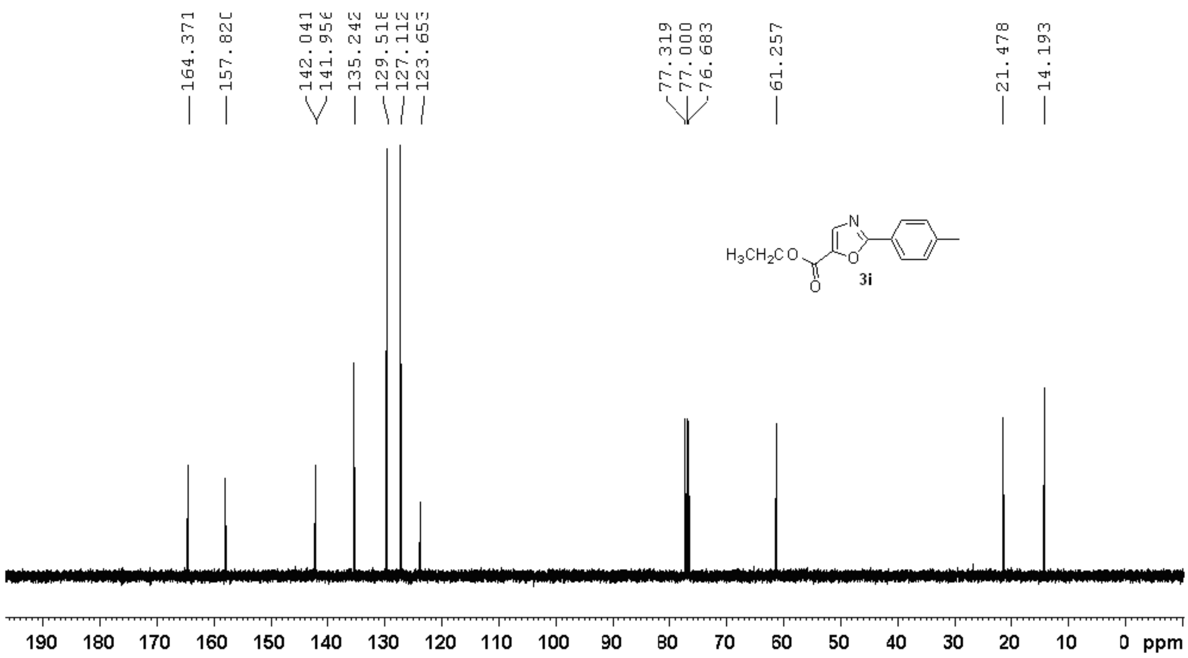

8.589
8.584
8.290
8.285
8.268
8.263
8.131
8.111
7.646
7.623
7.357
7.337
2.456
O_2N
N
O
3g
1.00
1.01
2.01
0.98
2.02
2.97
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm

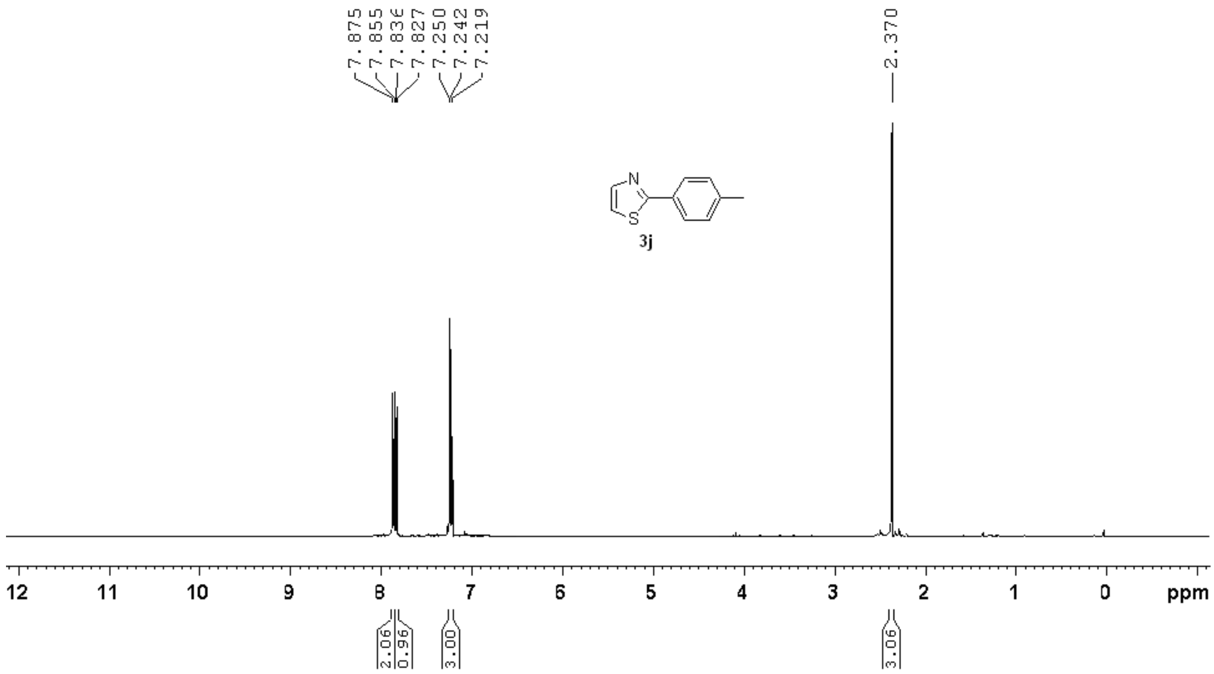

166.182
154.189
145.337
143.392
142.626
129.818
127.961
123.126
120.835
115.974
110.501
77.317
77.000
76.682
21.680
O_2N
N
O
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

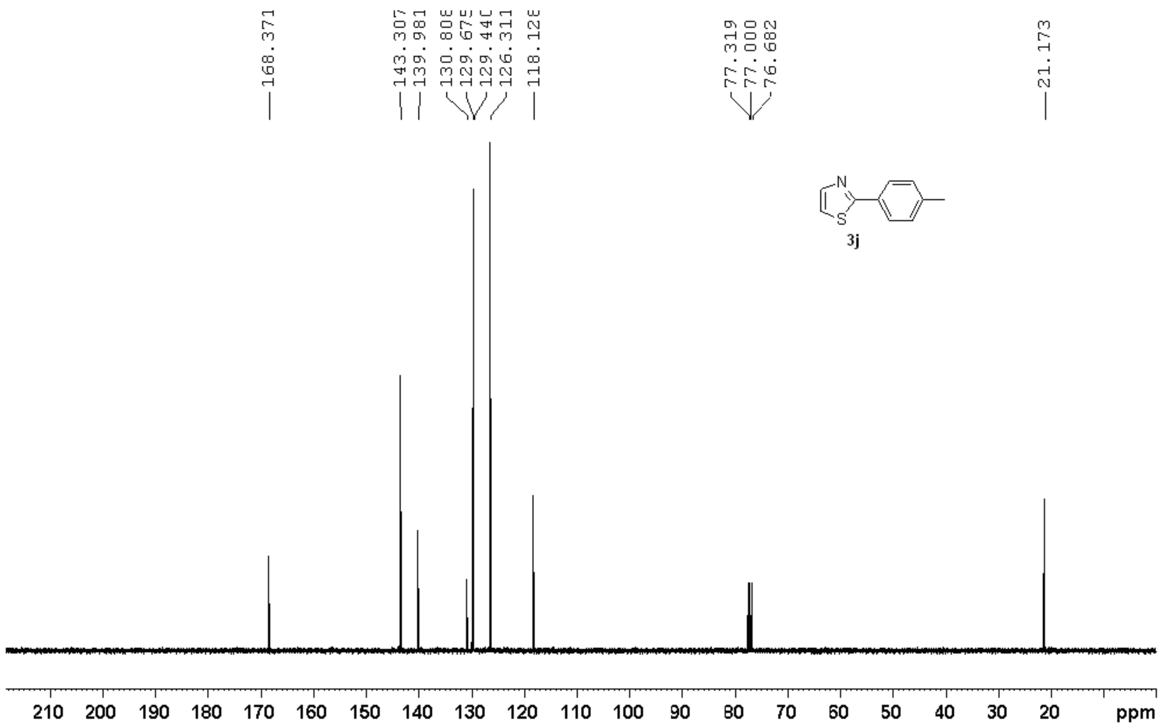

8.088
8.067
8.012
7.992
7.965
7.910
7.890
7.514
7.495
7.476
7.399
7.380
7.361
7.319
7.299
2.438
N
S
3h
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.04
1.98
1.00
1.01
1.01
1.99
3.07

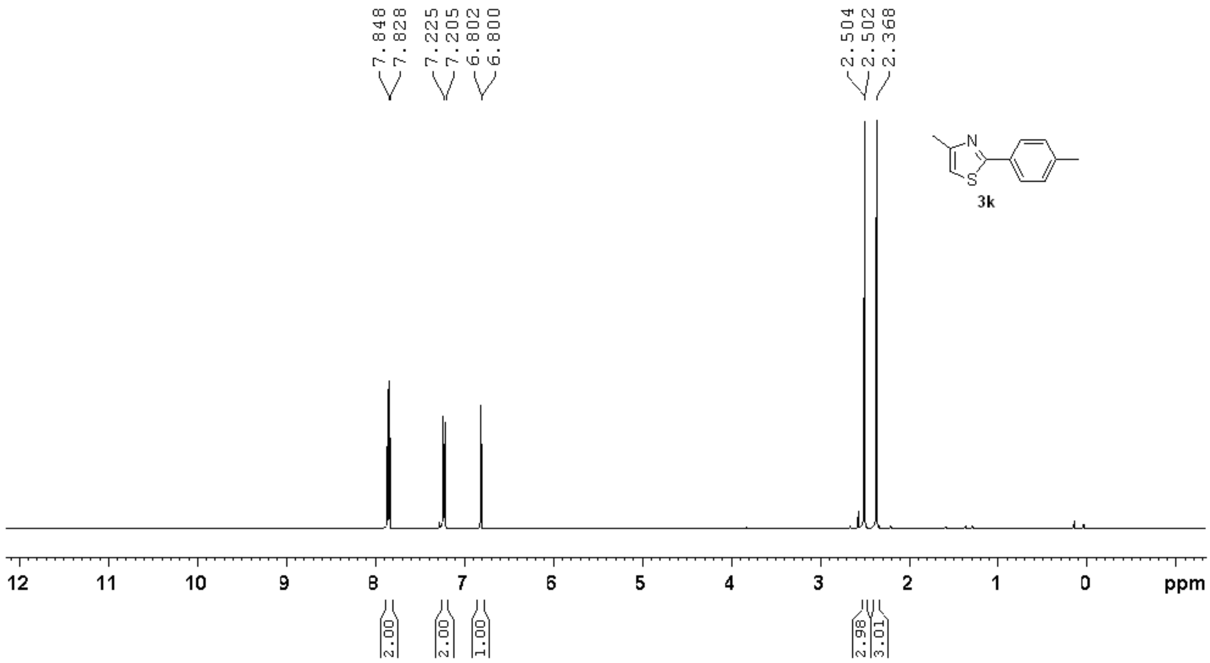

168.189
154.190
141.371
134.958
130.990
129.680
127.474
126.196
124.959
123.046
121.524
77.318
77.000
76.682
21.467
N
S
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

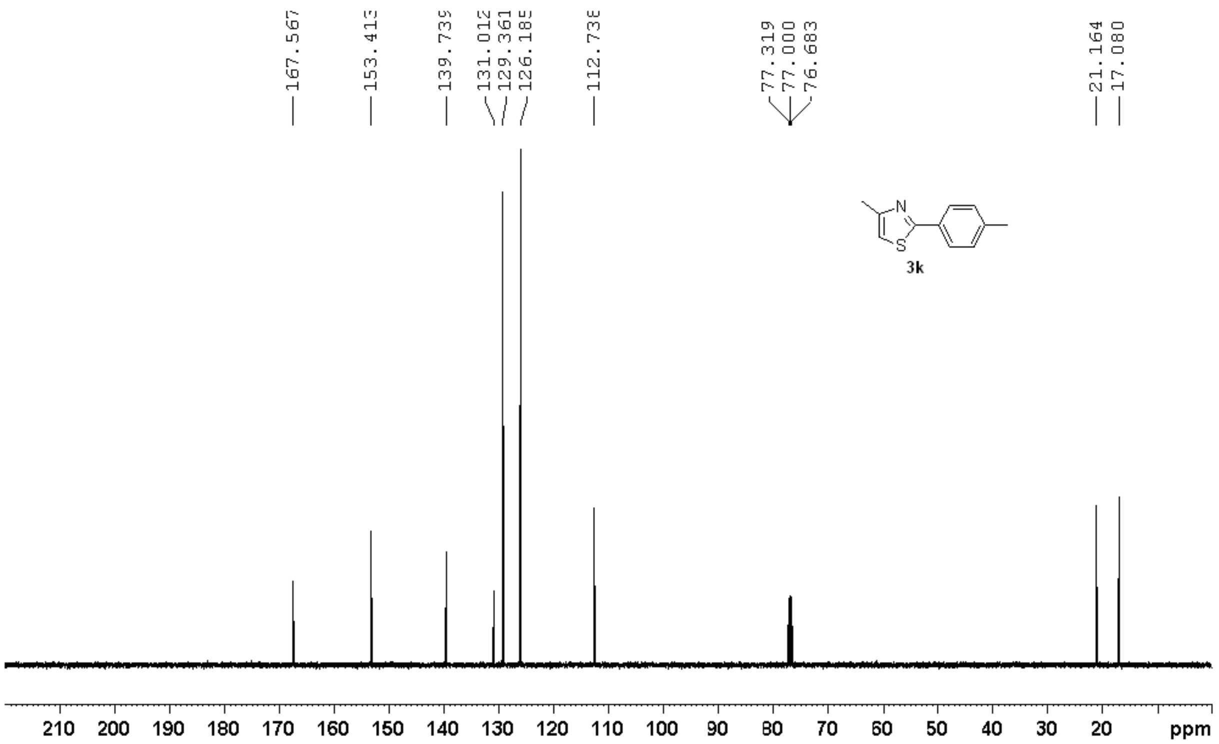

8.019
7.998
7.800
7.273
7.252
4.419
4.401
4.383
4.365
2.390
1.407
1.389
1.371
H3CH2CO
N
O
O
3i
10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm
2.00
1.00
2.07
2.02
3.03
3.06


164.371
157.820
142.041
141.956
135.242
129.518
127.112
123.653
77.319
77.000
76.683
61.257
21.478
14.193
H3CH2CO
N
O
O
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.875
7.855
7.836
7.827
7.250
7.242
7.219
2.370
N
S
3j
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
0.96
3.00
3.06


168.371
143.307
139.981
130.808
129.675
129.440
126.311
118.128
77.319
77.000
76.682
21.173
N
S
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.848
7.828
7.225
7.205
6.802
6.800
2.504
2.502
2.368
N
S
3k
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
1.00
2.98
3.01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139.739
131.012
129.361
126.185
112.738
77.319
77.000
76.683
21.164
17.080
N
S
3k
210
200
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180
170
160
150
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130
120
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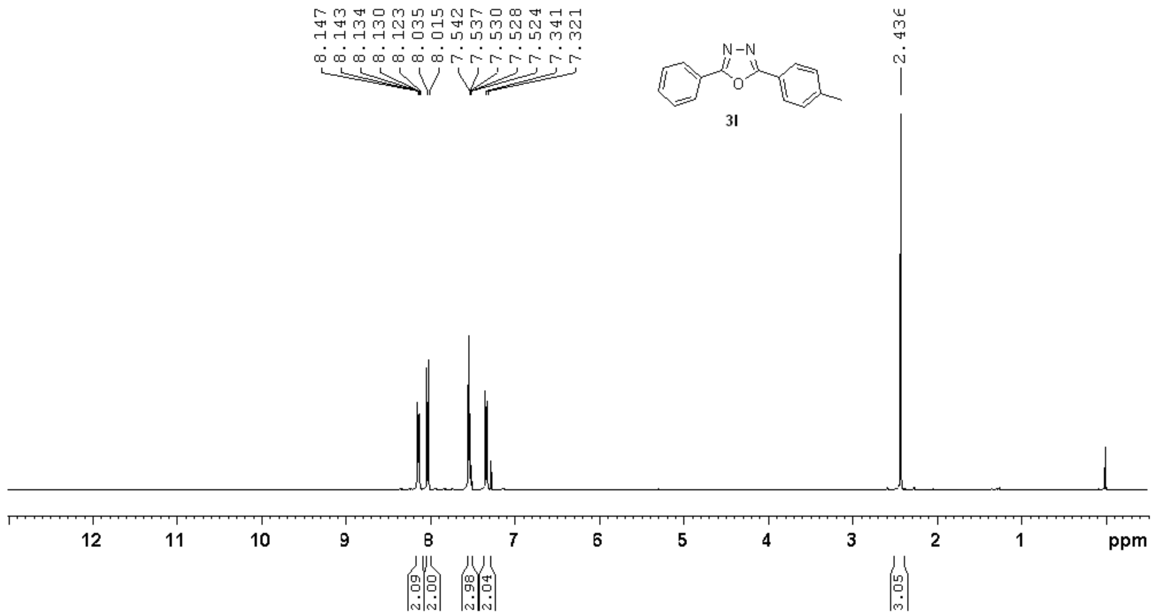
100
90
80
70
60
50
40
30
20
ppm


8.147
8.143
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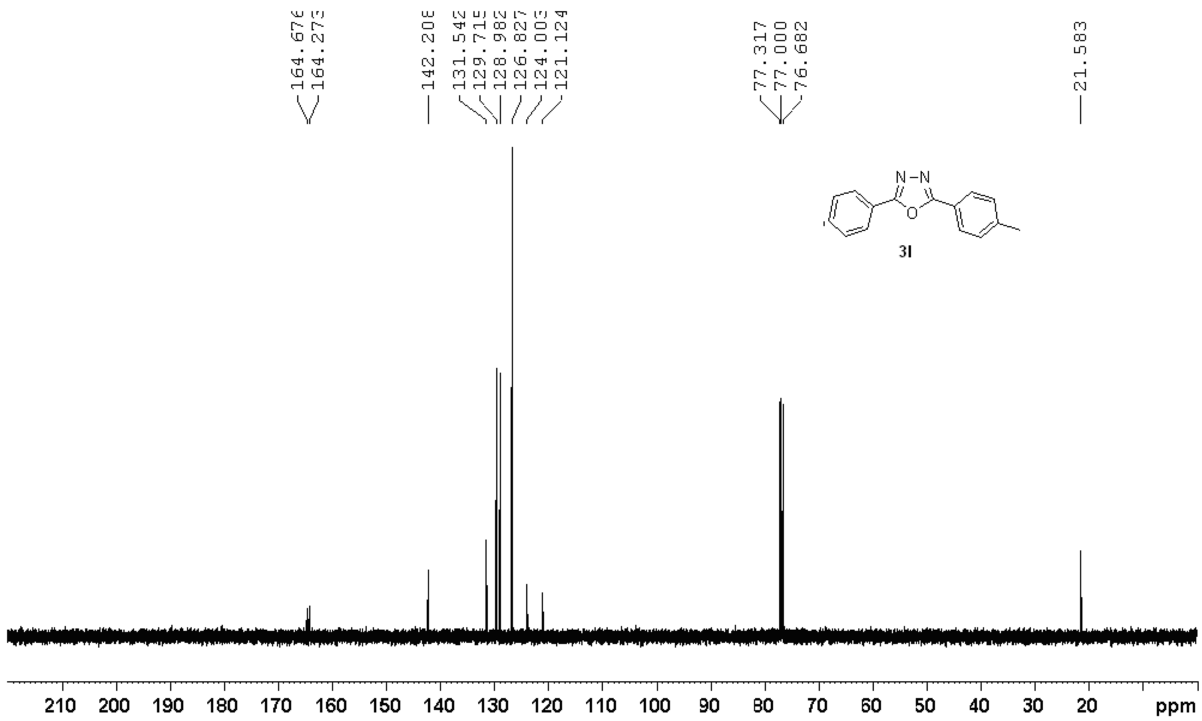
8.130
8.123
8.035
8.015
7.542
7.537
7.530
7.528
7.524
7.341
7.321
2.436
N–N
O
3l
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.09
2.00
2.98
2.04
3.05


164.676
164.273
142.208
131.542
129.715
128.982
126.827
124.003
121.124
77.317
77.000
76.682
21.583
N–N
O
3l
210
200
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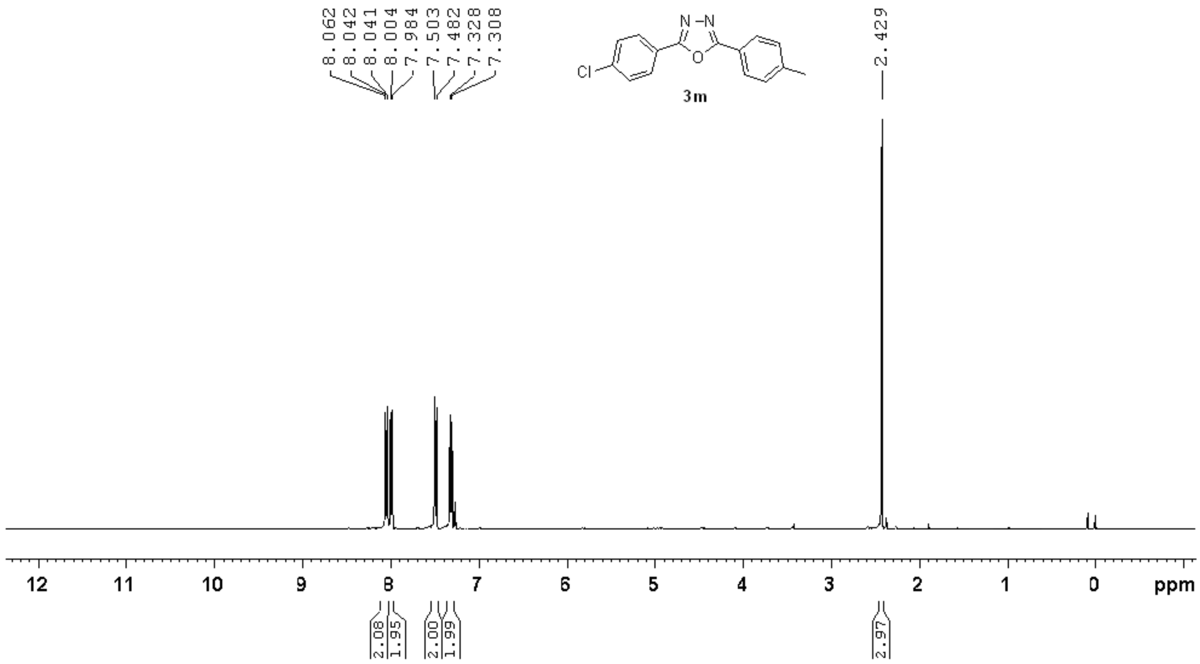
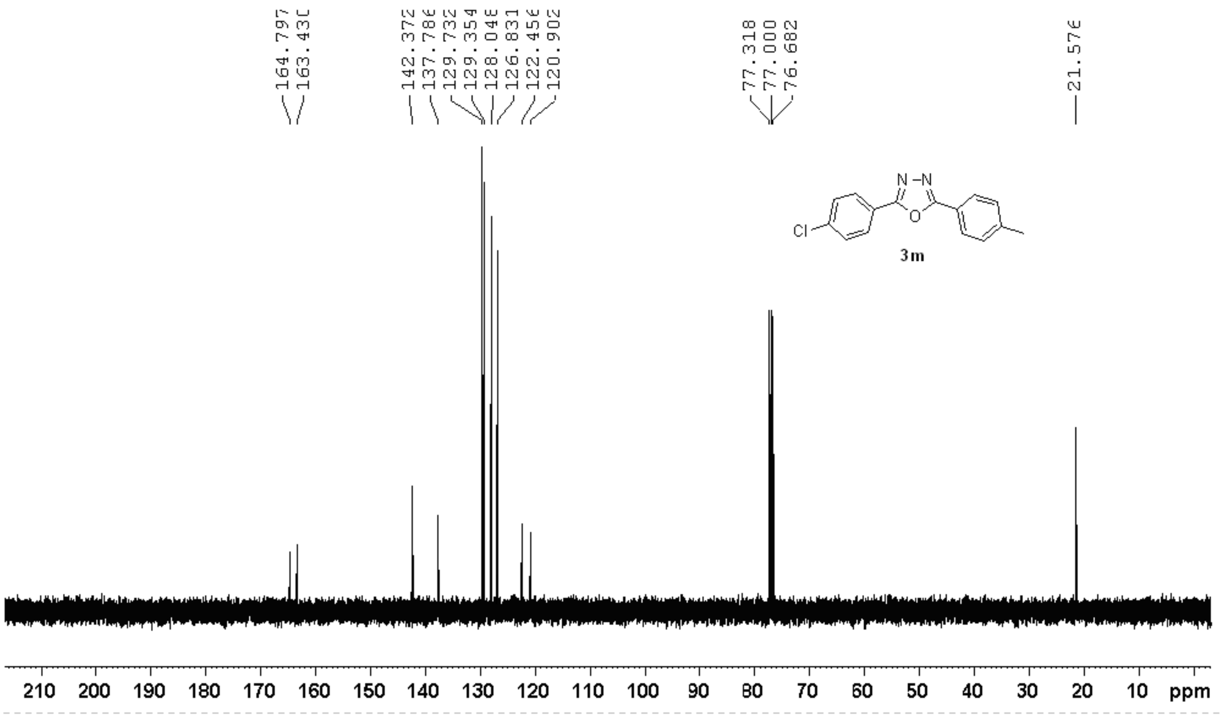
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.062
8.042
8.041
8.004
7.984
7.503
7.482
7.328
7.308
2.429
N–N
Cl
O
3m
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.95
2.00
1.99
2.97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137.786
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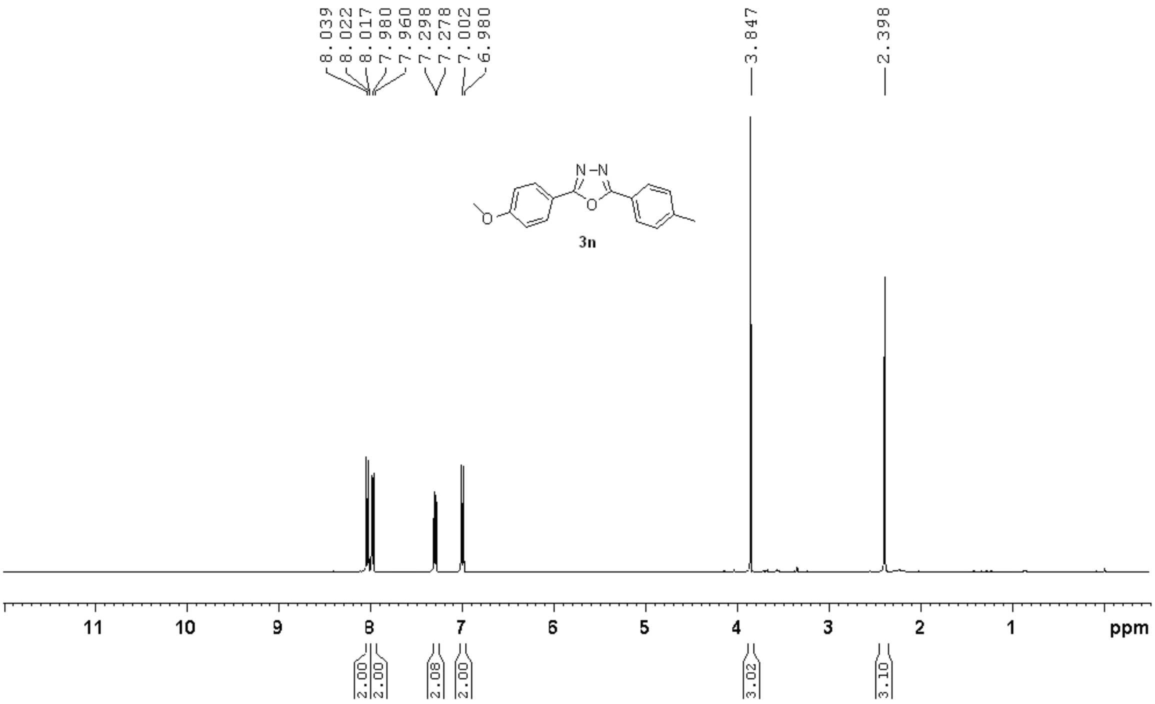
129.354
128.048
126.831
122.456
120.902
77.318
77.000
76.682
21.576
N–N
Cl
O
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.039
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8.017
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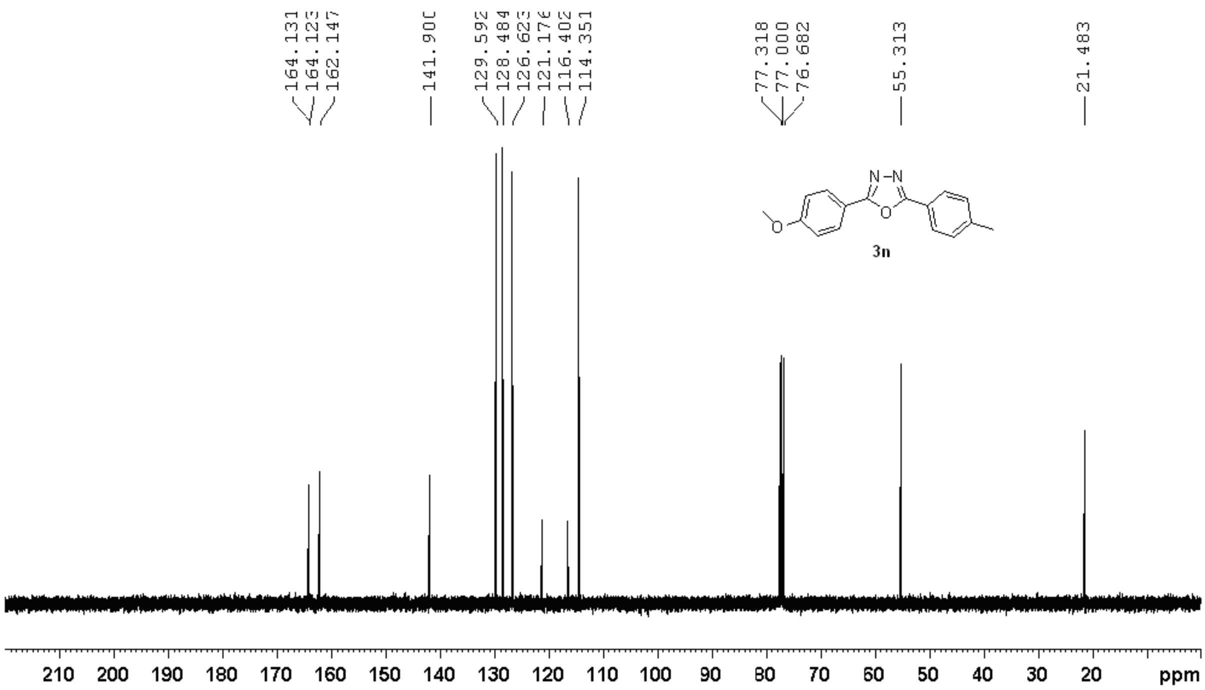
7.960
7.298
7.278
7.002
6.980
3.847
2.398
N–N
O
3n
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
2.08
2.00
3.02
3.10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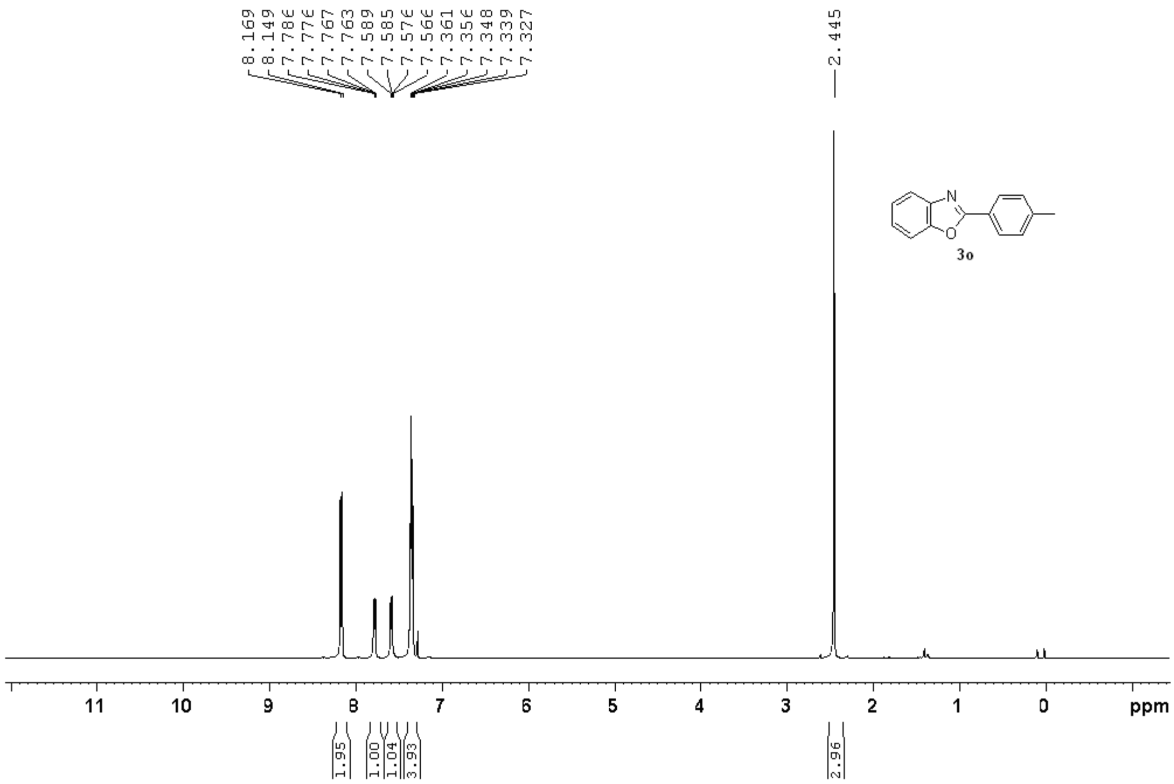
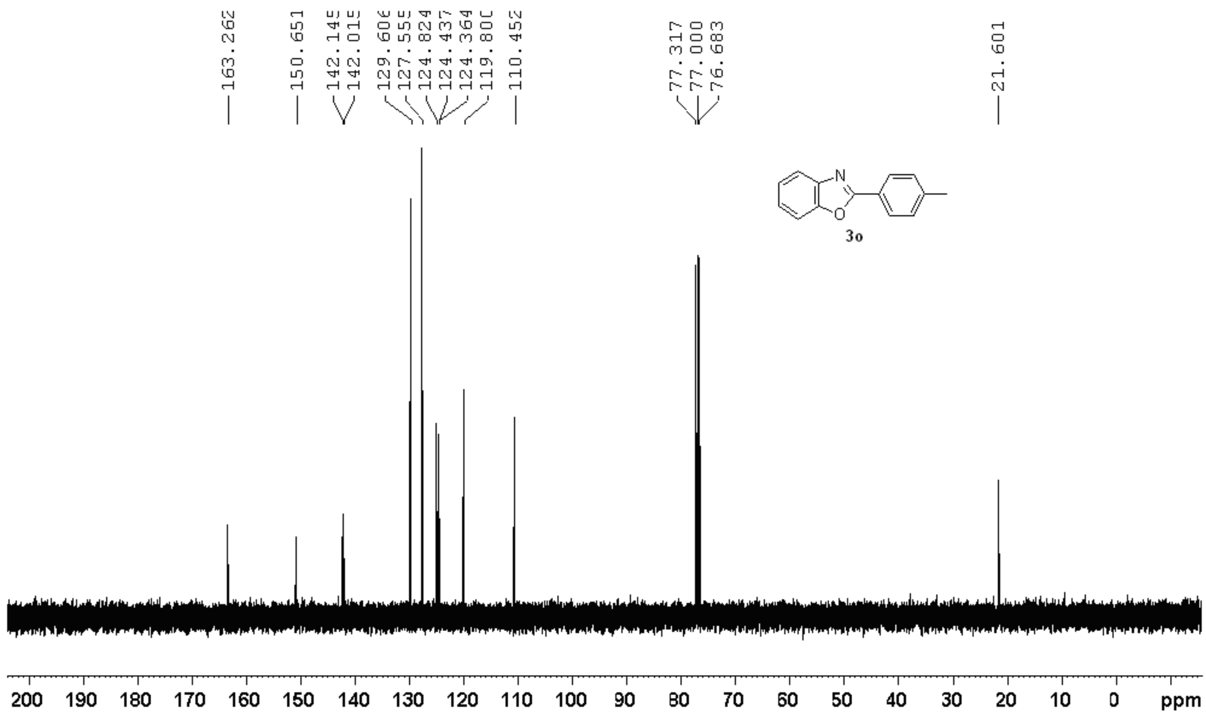
164.123
162.147
141.900
129.592
128.484
126.623
121.176
116.402
114.351
77.318
77.000
76.682
55.313
21.483
N–N
O
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.169
8.149
7.767
7.763
7.589
7.585
7.361
7.348
7.339
7.327
2.445
3o
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.00
1.04
3.93
2.96


142.145
142.015
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124.437
124.364
110.452
77.317
77.000
76.683
21.601
3o
200
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180
170
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150
140
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110
100
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80
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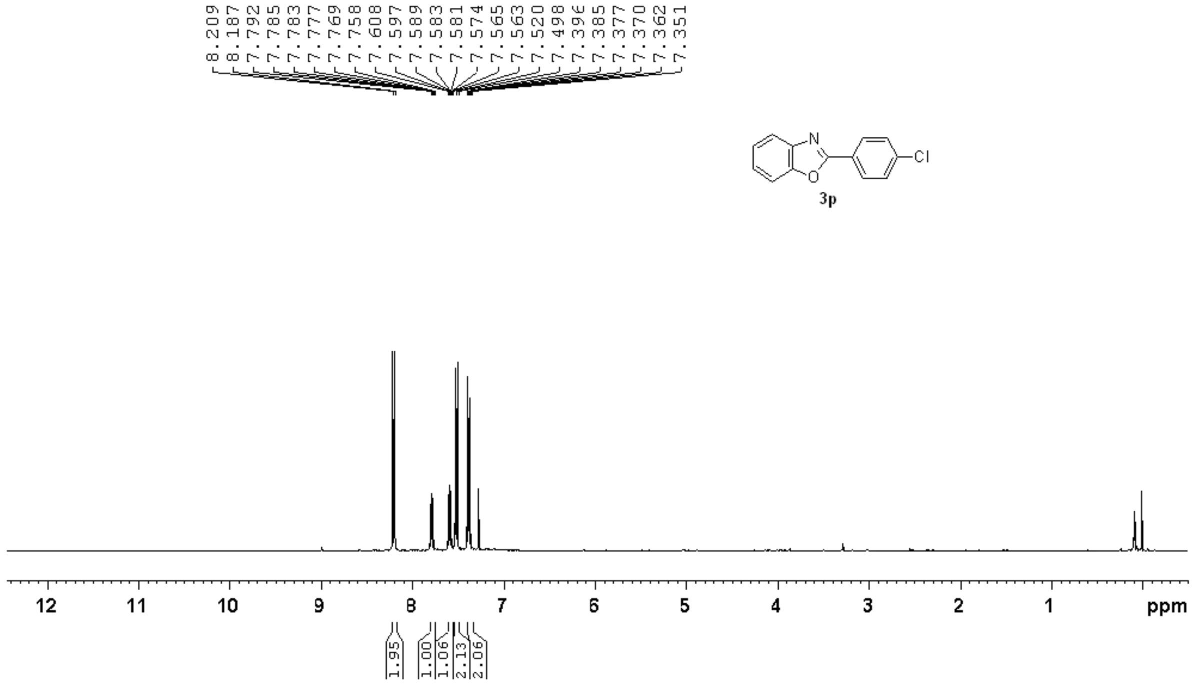
60
50
40
30
20
10
0
ppm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7.777
7.769
7.758
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7.597
7.589
7.583
7.581
7.574
7.565
7.563
7.520
7.498
7.396
7.385
7.377
7.370
7.362
7.351
N
O
Cl
3p
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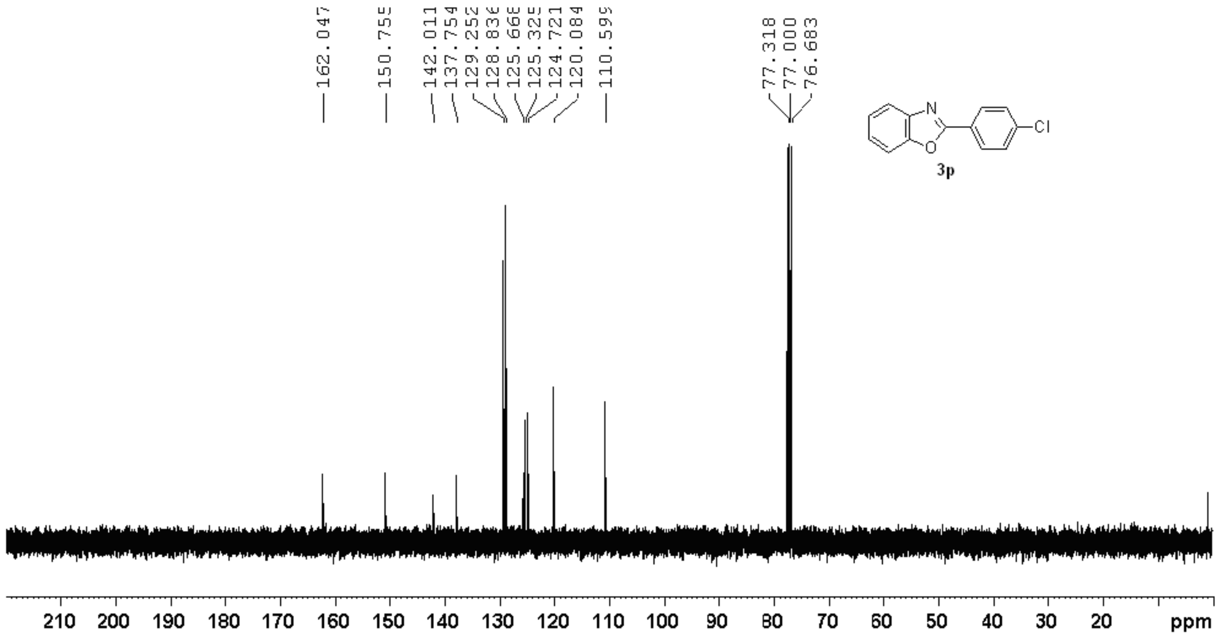
1.95
1.00
1.06
2.13
2.06


162.047
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142.011
137.754
129.252
128.836
125.666
125.325
124.721
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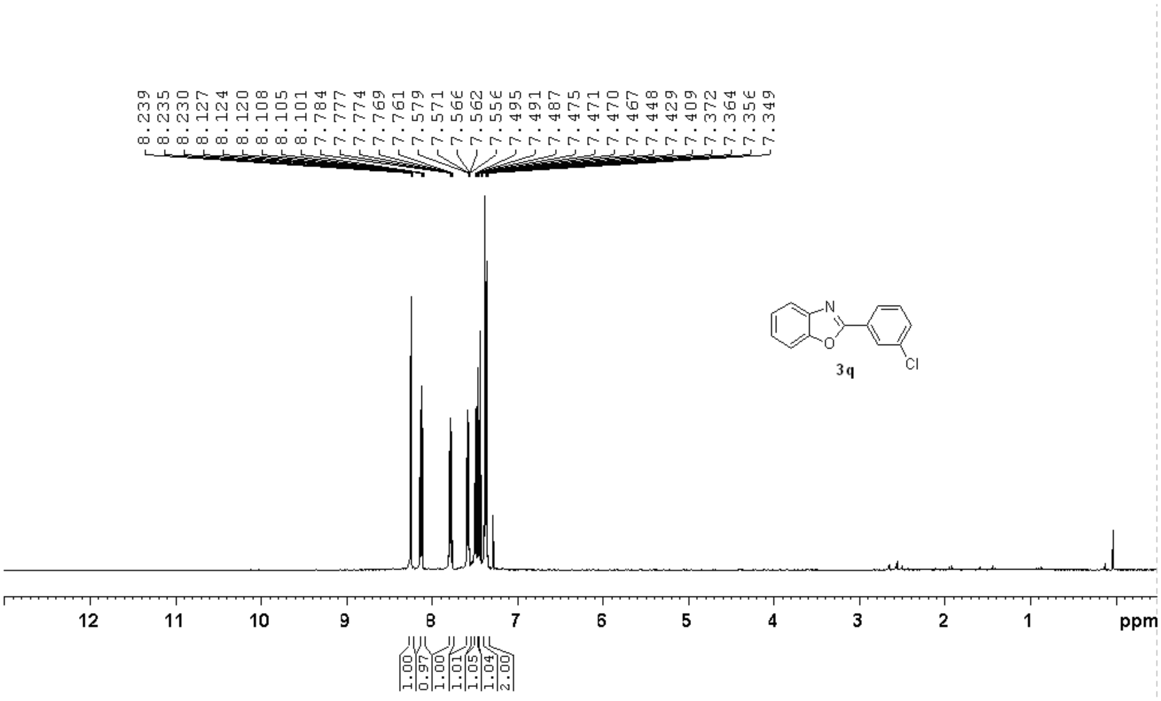
110.599
77.318
77.000
76.683
N
O
Cl
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.235
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8.127
8.124
8.120
8.108
8.105
8.101
7.784
7.777
7.774
7.769
7.761
7.579
7.571
7.566
7.562
7.556
7.495
7.491
7.487
7.475
7.471
7.470
7.467
7.448
7.429
7.409
7.372
7.364
7.356
7.349
N
O
Cl
3q
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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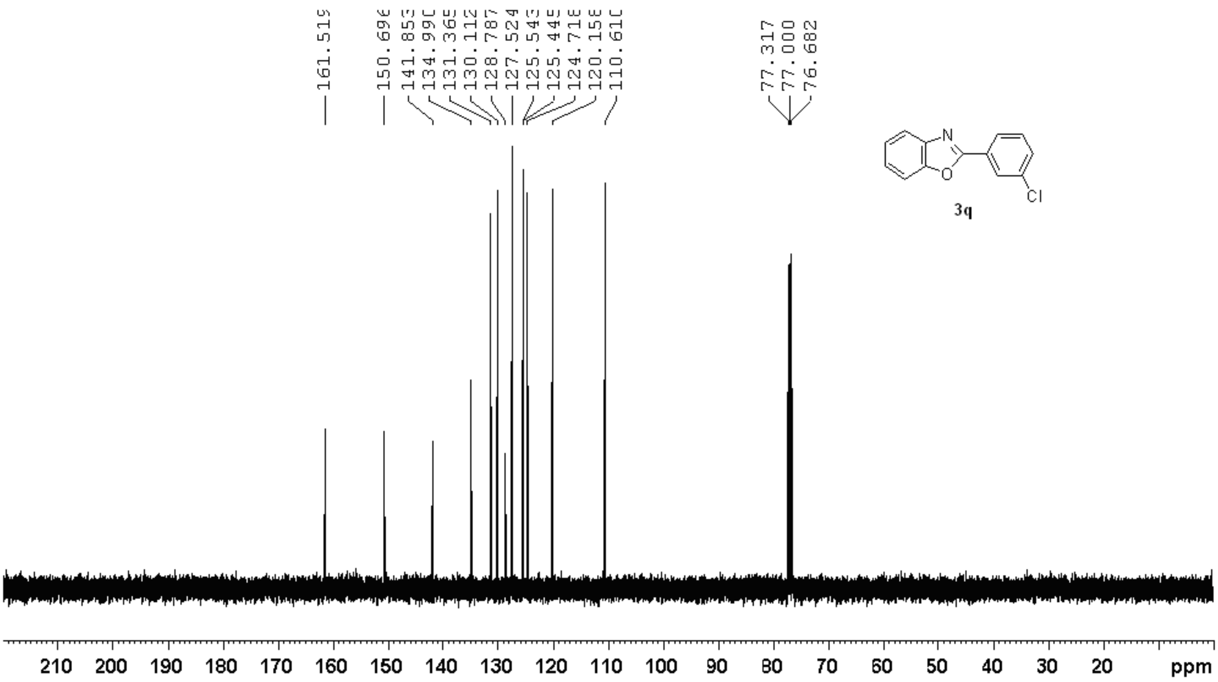
0.97
1.00
1.01
1.05
1.04
2.00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141.853
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131.365
130.112
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127.524
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125.445
124.718
120.158
110.610
77.317
77.000
76.682
N
O
Cl
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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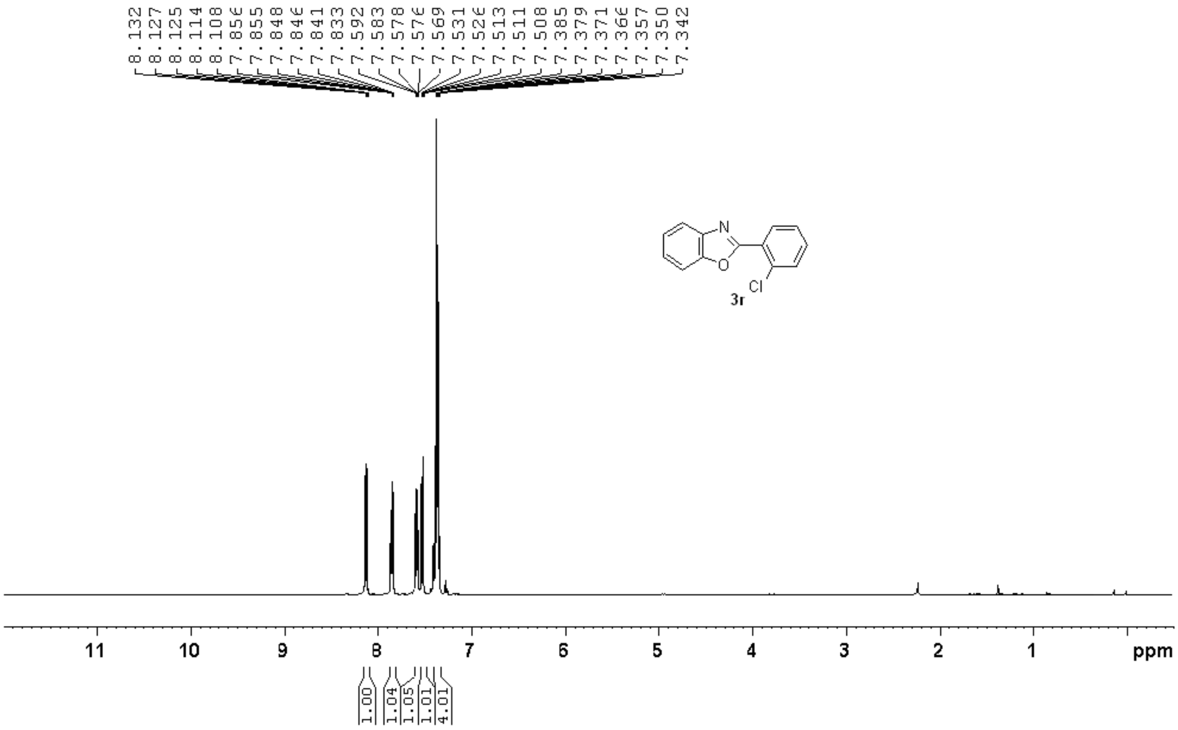
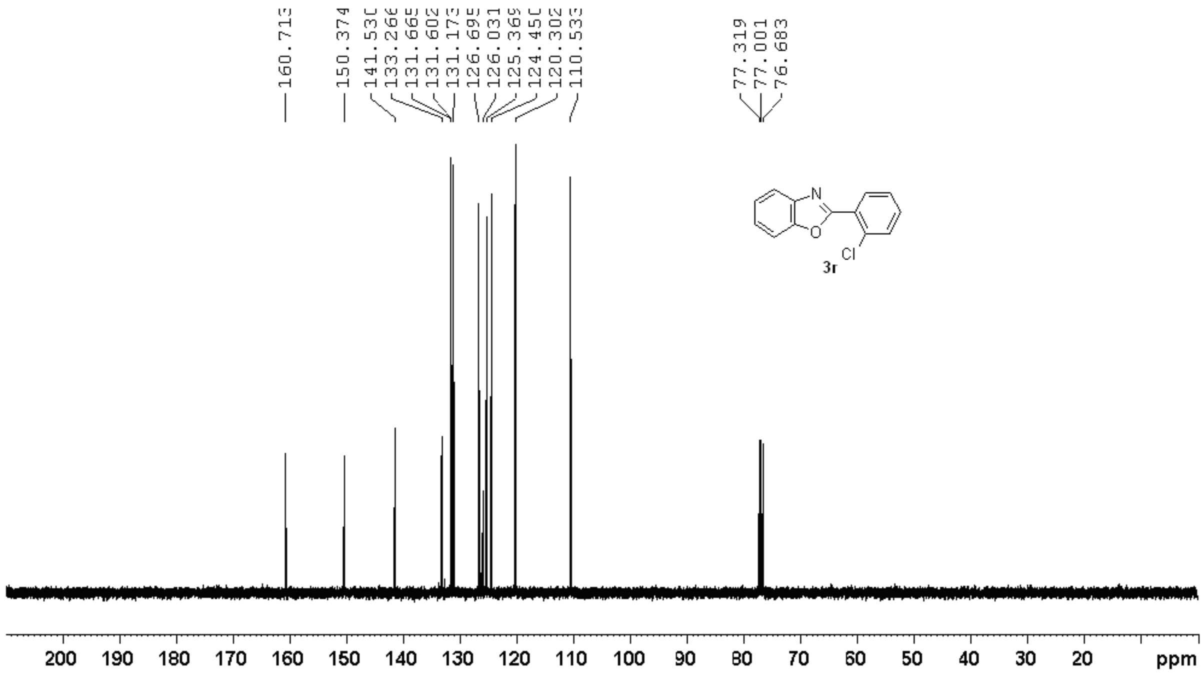
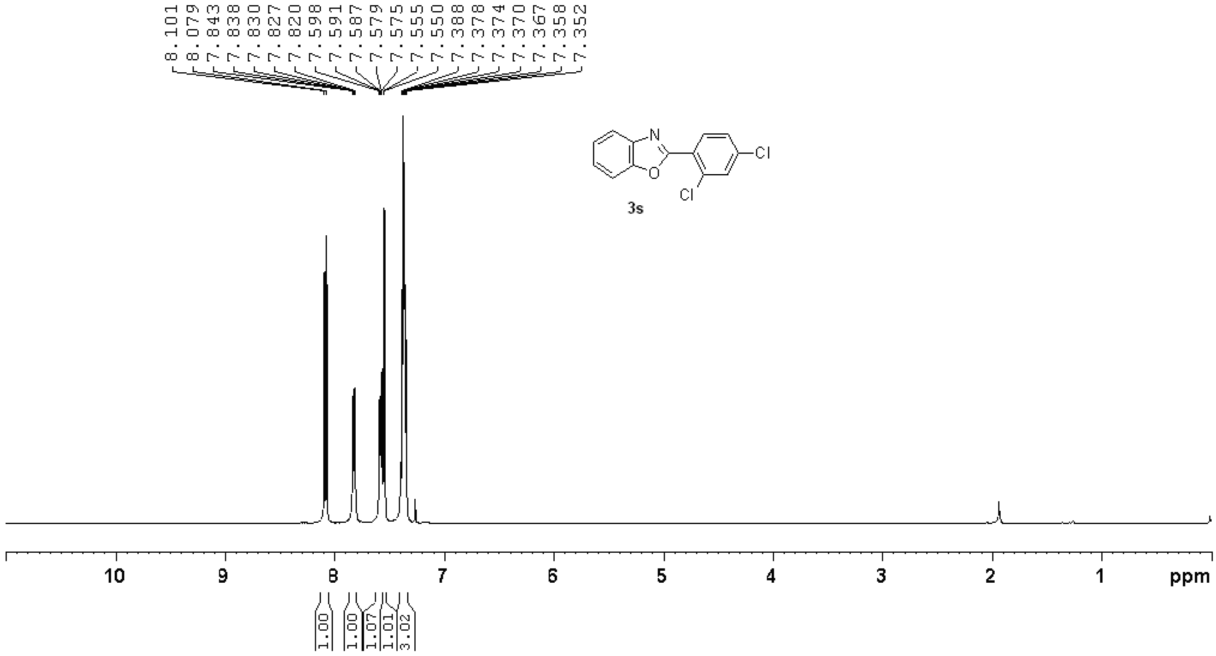
60
50
40
30
20
ppm


8.132
8.127
8.125
8.114
8.108
7.856
7.855
7.848
7.846
7.841
7.833
7.592
7.583
7.578
7.576
7.569
7.531
7.526
7.513
7.511
7.508
7.385
7.379
7.371
7.366
7.357
7.350
7.342
N
O
Cl
3r
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
1.05
1.01
4.01


160.713
150.374
141.530
133.266
131.665
131.602
131.173
126.695
126.031
125.369
124.450
120.302
110.533
77.319
77.001
76.683
N
O
Cl
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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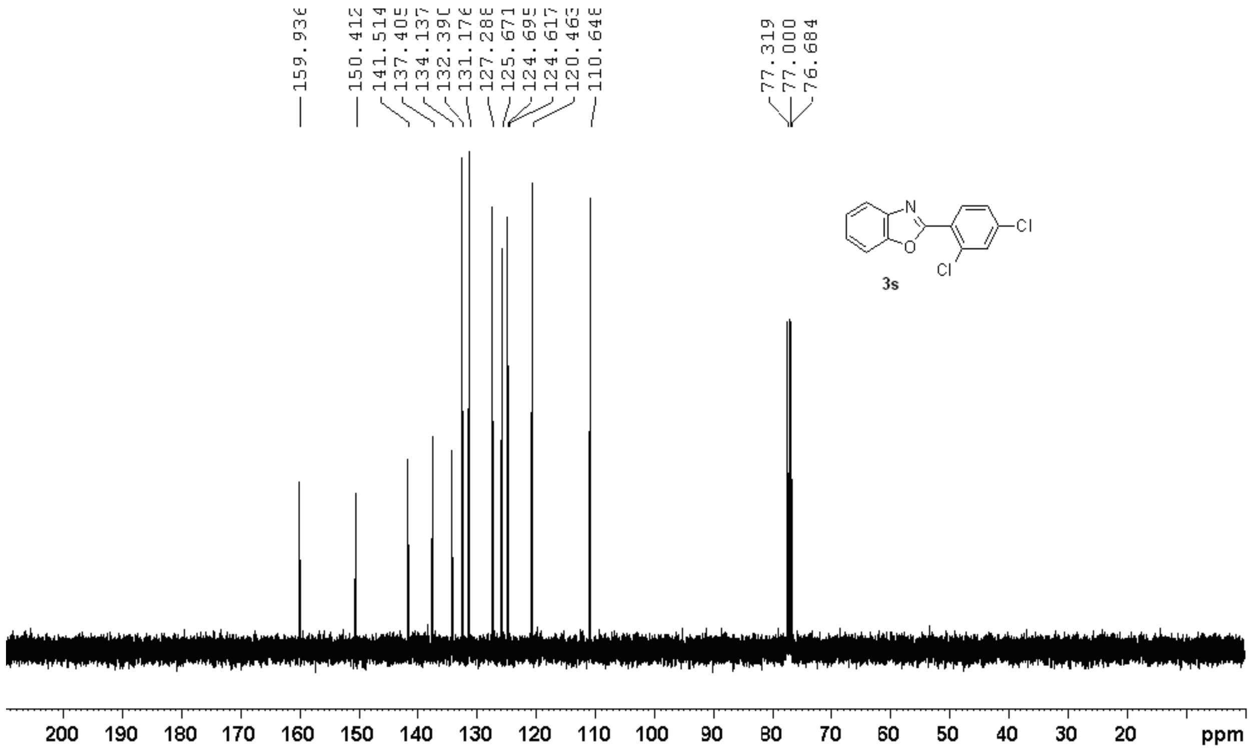
8.079
7.843
7.838
7.830
7.827
7.820
7.598
7.591
7.587
7.579
7.575
7.555
7.550
7.388
7.378
7.374
7.370
7.367
7.358
7.352
N
O
Cl
Cl
3s
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.07
1.01
3.02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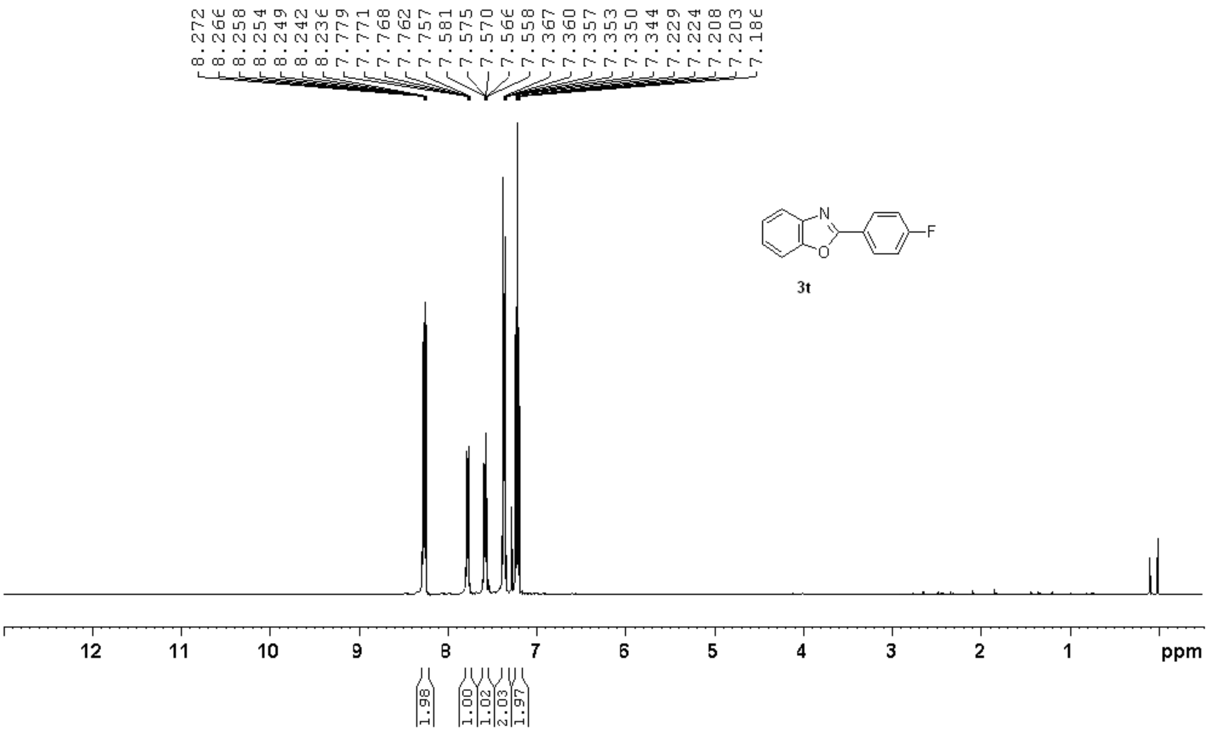
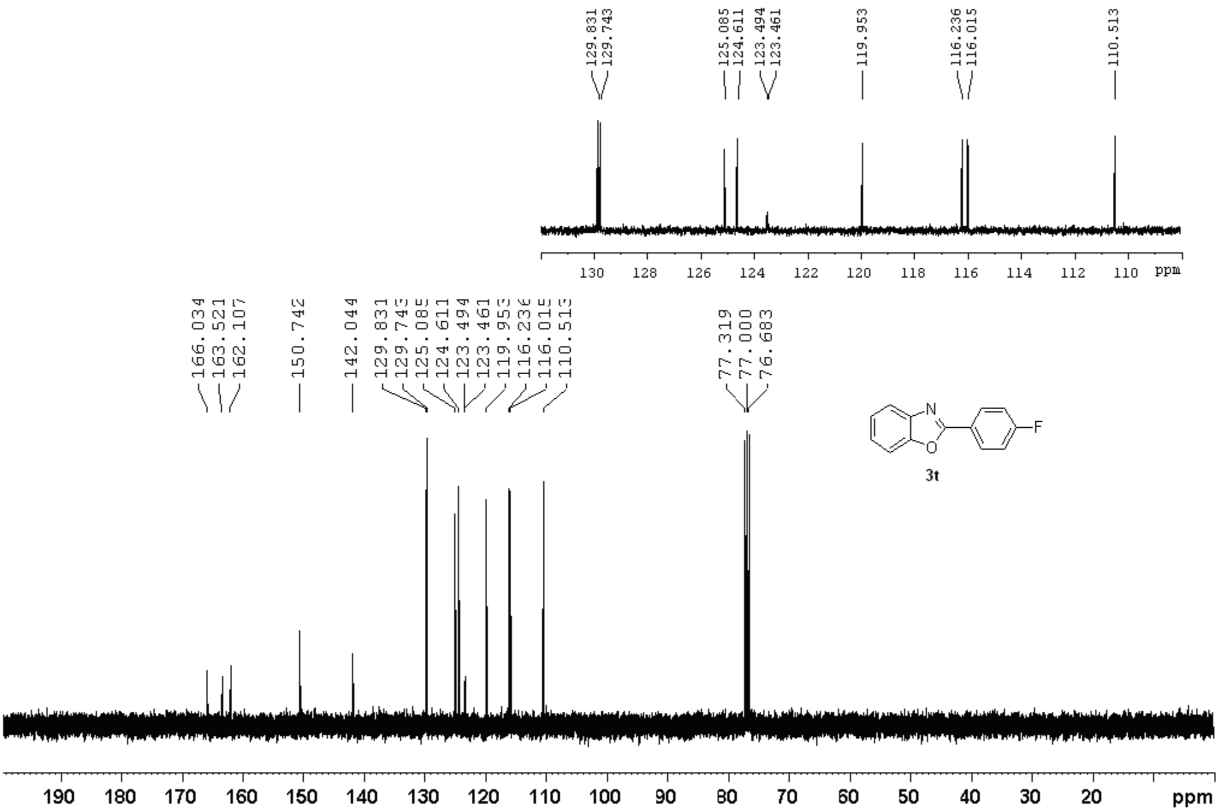
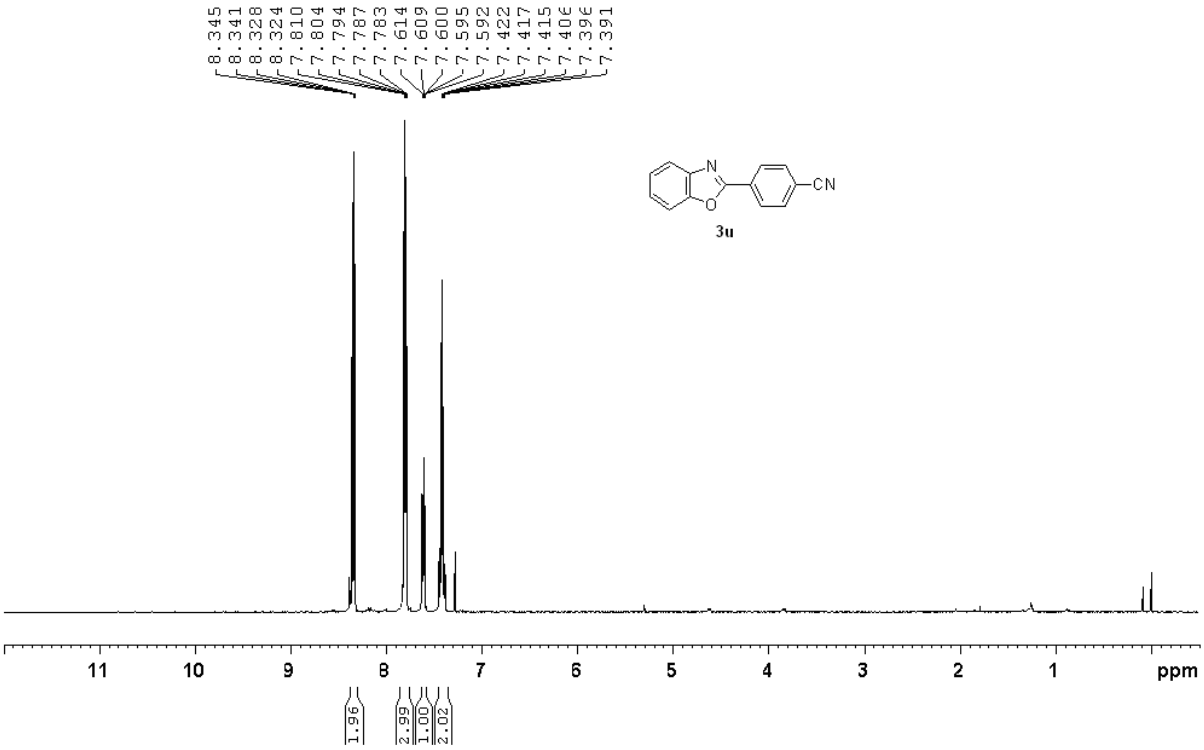
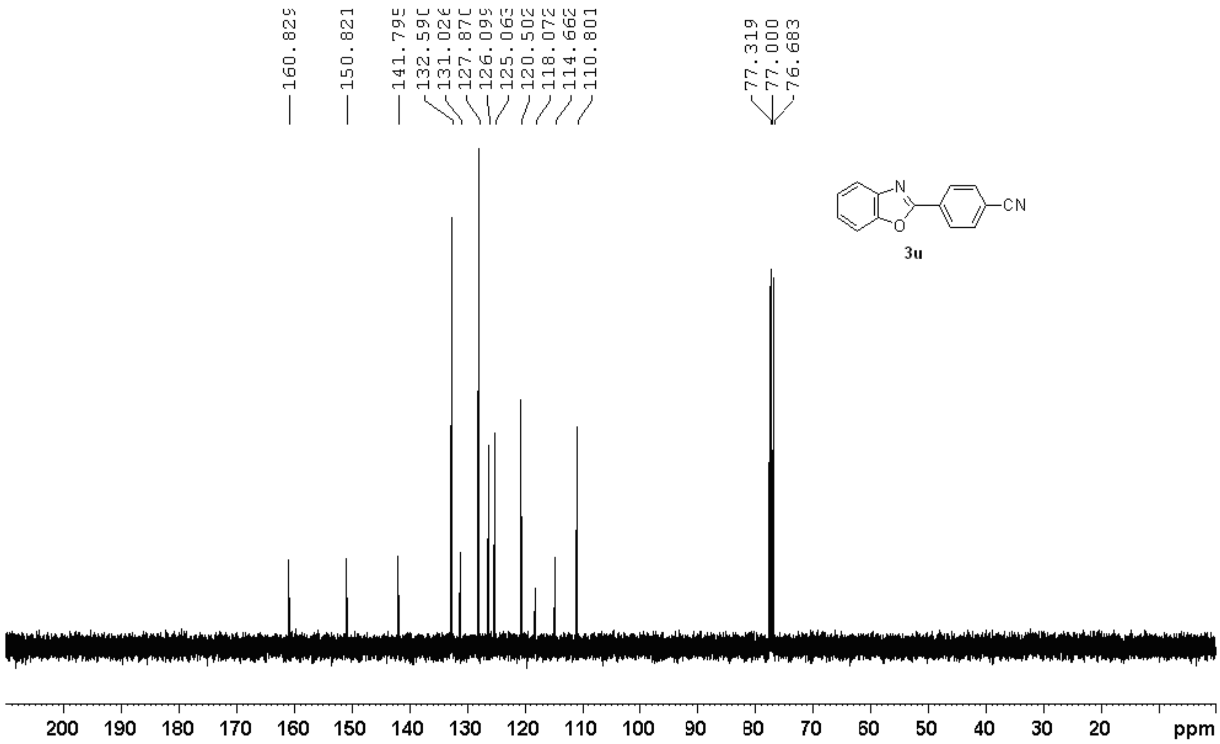
141.514
137.405
134.137
132.390
131.176
127.288
125.671
124.695
124.617
120.463
110.648
77.319
77.000
76.684
N
O
Cl
Cl
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.272
8.266
8.258
8.254
8.249
8.242
8.236
7.779
7.771
7.768
7.762
7.757
7.581
7.575
7.570
7.566
7.558
7.367
7.360
7.357
7.353
7.350
7.344
7.229
7.224
7.208
7.203
7.186
N
O
F
3t
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.98
1.00
1.02
2.03
1.97


129.831
129.743
125.085
124.611
123.494
123.461
119.953
116.236
116.015
110.513
130
128
126
124
122
120
118
116
114
112
110
ppm
166.034
163.521
162.107
150.742
142.044
129.831
129.743
125.085
124.611
123.494
123.461
119.953
116.236
116.015
110.513
77.319
77.000
76.683
N
O
F
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.345
8.341
8.328
8.324
7.810
7.804
7.794
7.787
7.783
7.614
7.609
7.600
7.595
7.592
7.422
7.417
7.415
7.406
7.396
7.391
N
O
CN
3u
11 10 9 8 7 6 5 4 3 2 1 ppm
1.96
2.99
1.00
2.02

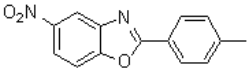

160.829
150.821
141.795
132.590
131.026
127.870
126.099
125.063
120.502
118.072
114.662
110.801
77.319
77.000
76.683
N
O
CN
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier   Ionisation Mode: EI+   Electron Energy: 70eV

Card Serial Number: GCT-P-T11-08-OS0642
Sample Serial Number: HBSF-A8-S6
Operator: Li Date: 2011/08/22
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
667 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used: C: 0-60 H: 0-80 N: 0-6 O: 0-4 S: 0-1 Cl: 0-1 Br: 0-1



3g

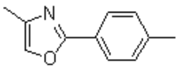
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
254.0693	254.0691	0.2	0.8	11.0	0.8	C14 H10 N2 O3
	254.0696	-0.3	-1.2	6.5	2219.2	C11 H13 N3 O2 Cl
	254.0683	1.0	3.9	7.0	2220.5	C9 H11 N6 O Cl
	254.0704	-1.1	-4.3	-1.0	2749.3	C10 H23 S Br

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier   Ionisation Mode: EI+   Electron Energy: 70eV

Card Serial Number: GCT-P-T11-08-OS0643
Sample Serial Number: HBSF-A8-S7
Operator: Li Date: 2011/08/22
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
402 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used: C: 0-60 H: 0-80 N: 0-6 O: 0-4 S: 0-1 Cl: 0-1 Br: 0-1



3k

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
189.0614	189.0612	0.2	1.1	7.0	1.1	C11 H11 N S

7. References

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