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Direct amidation of azoles with formamides via metal-free C–H activation in the presence of *tert*-butyl perbenzoate

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Table of Contents for Supporting Information

1. Physical measurements and materials

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. Products were purified by flash chromatography on 100–200 mesh silica gels, SiO_2. Unless otherwise noted, the chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company, China and were used without purification prior to use.

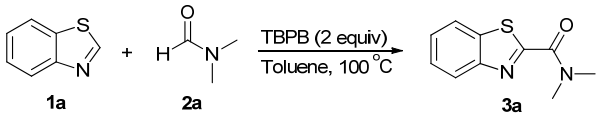
2. Typical procedure for amidation of benzthiazole with formamides

A suspension of *tert*-butyl perbenzoate (TBPB, 194 mg, 1.0 mmol), benzothiazole (68 mg, 0.5 mmol), dimethylformamide (DMF, 146 mg, 2.0 mmol), in toluene (3.0 mL) was stirred at 100 °C for 12 h. The reaction mixture was diluted with ethyl acetate (10.0 mL), washed with water (5.0

mL×2) and brine, dried over Mg_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to afford the direct cross-coupling product, *N,N*-dimethylbenzothiazole-2-carboxamide (**3a**, 77 mg, 75% yield).

3. Optimization of partial reaction conditions

Table Optimization of partial reaction conditions in the direct amidation of **1a** with **2a**[a]



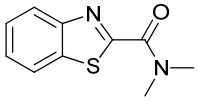
1a **2a** **3a**

Entry	Transition metal catalyst (mol%)	Yield (%)[b]
1	$FeBr_2$ (10)	20
2[c]	$Pd(OAc)_2$ (10)	N.R.
3	–	75
4[d]	–	51
5[e]	–	75

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (2.0 mmol), TBPB (1.0 mmol), toluene (3.0 mL), 100 °C for 12 h. [b]Isolated yield. [c]CF_3CO_2H (0.1 mmol) was added. [d]TBPB (0.75 mmol) was used. [e]TBPB (1.5 mmol) was used.

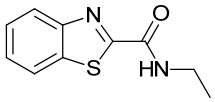
4. Characterization data for the amidation of azoles with formamides

***N, N'*-Dimethylbenzothiazole-2-carboxamide**[1]



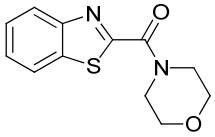
3a: *n*-hexane/EtOAc (5:1); pale yellow solid (77 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.09 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.56–7.44 (m, 2H), 3.64 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 164.82, 161.23, 153.15, 136.13, 126.53, 126.40, 124.52, 121.78, 38.76, 37.23.

***N*-Ethylbenzothiazole-2-carboxamide**



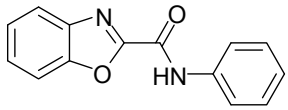
3b: *n*-hexane/EtOAc (5:1); pale yellow solid (72 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.04 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.58–7.43 (m, 3H), 3.61–3.49 (m, 2H), 1.33–1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 164.09, 159.62, 152.73, 136.91, 126.65, 126.51, 124.04, 122.30, 34.67, 14.66. HRMS (EI) ($[M]^+$) Calcd. for $C_{10}H_{10}N_2OS$: 206.0514, Found: 206.0509.

***N*-(Tetrahydro-2*H*-pyran-4-yl)benzothiazole-2-carboxamide**



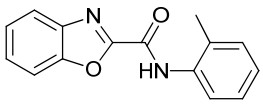
3c: *n*-hexane/EtOAc (5:1), pale yellow solid (71 mg, 58%); ^{1}H NMR (400MH_Z, $CDCl_3$) ; δ = 8.08 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.60–7.45 (m, 2H), 4.52 (t, *J* = 4.8 Hz, 2H), 3.91–3.79 (m, 6H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 164.44, 159.66, 153.01, 136.13, 126.75, 126.57, 124.59, 121.82, 67.19, 66.85, 47.13, 43.85. HRMS (EI) ($[M]^+$) Calcd. for $C_{12}H_{12}N_2O_2S$: 248.0619, Found: 248.0616.

***N*-Phenylbenzoxazole-2-carboxamide**[1]



3d: *n*-hexane/EtOAc (5:1); pale yellow solid (79 mg, 67%); ^{1}H NMR (400 MH_Z, $CDCl_3$): δ = 9.11 (br, 1H), 7.86 (d, *J* = 7.6 Hz , 1H), 7.80–7.65 (m, 3H), 7.60–7.40 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 155.45, 153.13, 151.36, 139.95, 136.69, 129.23, 127.60, 125.72, 125.27, 121.20, 119.85, 111.94.

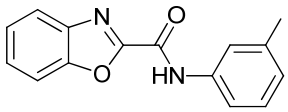
***N*-(*o*-Tolyl)benzoxazole-2-carboxamide**



3e: *n*-hexane/EtOAc (5:1); yellow solid (81 mg, 65%); ^{1}H NMR (400 MH_Z, $CDCl_3$)**:** δ = 9.06 (br, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.56–7.45 (m, 2H), 7.35–7.28 (m, 1H), 7.20–7.13 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ =

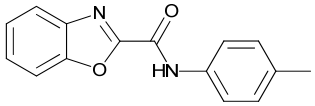
155.66, 153.23, 151.48, 140.08, 134.71, 130.64, 128.45, 127.56, 127.05, 125.72, 125.70, 122.02, 121.31, 111.96, 17.66. HRMS (EI) ($[M]^+$) Calcd. for $C_{15}H_{12}N_2O_2$: 252.0899, Found: 252.0897.

***N*-(*m*-Tolyl)benzoxazole-2-carboxamide**



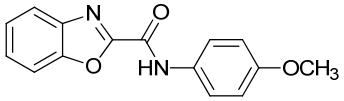
3f: *n*-hexane/EtOAc (5:1); yellow solid (86 mg, 69%); ^{1}H NMR (400 MH_Z, $CDCl_3$)：δ = 9.05 (br, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.45–7.61 (m, 4H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 155.60, 153.08, 151.45, 140.04, 139.26, 136.65, 129.08, 127.59, 126.14, 125.72, 121.23, 120.49, 117.02, 111.98, 21.50. HRMS (EI) ($[M]^+$) Calcd. for $C_{15}H_{12}N_2O_2$: 252.0899, Found: 252.0900.

***N*-(*p*-Tolyl)benzoxazole-2-carboxamide**



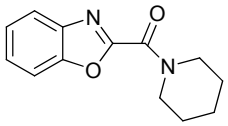
3g: *n*-hexane/EtOAc (5:1); yellow solid (92 mg, 73%); ^{1}H NMR (400 MH_Z, $CDCl_3$)：δ = 9.06 (br, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.55–7.43 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 153.01, 151.40, 140.03, 135.07, 134.19, 129.74, 127.54, 125.69, 121.18, 119.88, 111.95, 20.95. HRMS (EI) ($[M]^+$) Calcd. for $C_{15}H_{12}N_2O_2$: 252.0899, Found: 252.0901.

***N*-(4-Methoxyphenyl)benzoxazole-2-carboxamide**



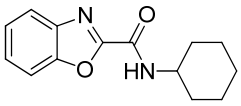
3h: *n*-hexane/EtOAc (5:1); yellow solid (95 mg, 71%); ^{1}H NMR (400 MH_Z, $CDCl_3$): δ = 9.02 (br, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.63–7.54 (m, 3H), 7.55–7.44 (m, 2H), 6.96 (s, 1H), 6.94 (s, 1H), 3.83 (S, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 157.06, 155.68, 152.94, 151.39, 140.06, 129.87, 127.50, 125.68, 121.55, 121.16, 114.38, 111.94, 55.48. HRMS (EI) ($[M]^+$) Calcd. for $C_{15}H_{12}N_2O_3$: 268.0848, Found: 268.0847.

Benzoxazol-2-yl (piperidin-1-yl)methadone



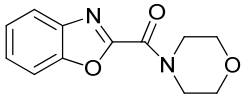
3i: *n*-hexane/EtOAc (5:1); yellow solid (71 mg, 62%); ^{1}H NMR (400 MH$_Z$, CDCl$_3$): δ = 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.47–7.37 (m, 2H), 4.04–3.90 (m, 2H), 3.85–3.73 (m, 2H), 1.78–1.63 (m, 6H); ^{13}C NMR (100 MH$_Z$, CDCl$_3$): δ = 156.24, 155.25, 149.82, 140.10, 126.76, 125.04, 121.09, 111.36, 47.98, 43.88, 26.57, 25.52, 24.36. HRMS (EI) ([M]$^+$) Calcd. for $C_{13}H_{14}N_2O_2$: 230.1055, Found: 230.1056.

_N_-Cyclohexylbenzoxazole-2-carboxamide



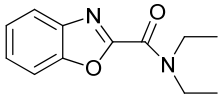
3j: *n*-hexane/EtOAc (5:1); yellow solid (80 mg, 66%); ^{1}H NMR (400 MH$_Z$, CDCl$_3$): δ = 7.79 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.53–7.40 (m, 2H), 7.19 (br, 1H), 4.10–3.95 (m, 1H), 2.10–2.00 (m, 2H), 1.86–1.74 (m, 2H), 1.72–1.62 (m, 1H), 1.20–1.50 (m, 5H); ^{13}C NMR (100 MH$_Z$, CDCl$_3$): δ = 155.74, 154.69, 151.09, 140.11, 127.24, 125.49, 121.05, 111.85, 48.82, 32.84, 25.36, 24.72. HRMS (EI) ([M]$^+$) Calcd. for $C_{14}H_{16}N_2O_2$: 244.1212, Found: 244.1210.

Benzoxazol-2-yl (morpholino)methanone



3k: *n*-hexane/EtOAc (5:1); pale yellow solid (69 mg, 60%); ^{1}H NMR (400 MH$_Z$, CDCl$_3$): δ = 7.80 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.51–7.39 (m, 2H), 4.27 (t, *J* = 4.8 Hz, 2H), 3.91–3.75 (m, 6H); ^{13}C NMR (100 MH$_Z$, CDCl$_3$): δ = 155.96, 154.51, 149.84, 140.02, 127.24, 125.29, 121.24, 111.52, 67.01, 66.67, 47.47, 43.23. HRMS (EI) ([M]$^+$) Calcd. for $C_{12}H_{12}N_2O_3$: 232.0848, Found: 232.0853.

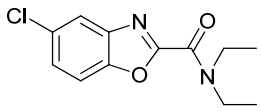
***N, N'*-Diethylbenzoxazole-2-carboxamide**[2]



3l: *n*-hexane/EtOAc (5:1); yellow oil (74 mg, 68%); ^{1}H NMR (400 MH$_Z$, CDCl$_3$)：δ = 7.81 (d, *J*

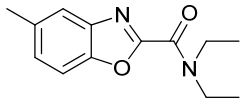
= 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.49–7.38 (m, 2H), 3.90–3.79 (m, 2H), 3.69–3.56 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 157.12, 155.39, 149.91, 140.33, 126.80, 125.03, 121.23, 111.40, 43.38, 41.26, 14.52, 12.55.

5-Chloro-*N, N'*-Diethylbenzooxazole-2-carboxamide



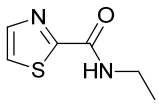
3m: *n*-hexane/EtOAc (5:1); pale yellow solid (90 mg, 72%); ^{1}H NMR (400 MH_Z, $CDCl_3$)**:** δ = 7.80 (s, 1H),7.56 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 3.86–3.78 (m, 2H), 3.67–3.56 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 156.58, 156.47, 148.43, 141.33, 130.56, 127.28, 121.10, 112.20, 43.41, 41.36, 14.48, 12.50. HRMS (EI) ($[M]^+$) Calcd. for $C_{12}H_{13}ClN_2O_2$: 252.0666, Found: 252.0665.

***N, N'*-Diethyl-5-methylbenzoxazole-2-carboxamide**



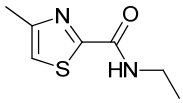
3n: *n*-hexane/EtOAc (5:1); pale yellow solid (62 mg, 53%); ^{1}H NMR (400 MH_Z, $CDCl_3$)**:** δ = 7.58 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 3.88–3.78 (m, 2H), 3.64–3.56 (m, 2H), 2.48 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 157.21, 155.48, 148.15, 140.53, 134.94, 128.03, 120.91, 110.70, 43.33, 41.21, 21.37, 14.48, 12.53. HRMS (EI) ($[M]^+$) Calcd. for $C_{13}H_{16}N_2O_2$: 232.1212, Found: 232.1211.

***N*-Ethylthiazole-2-carboxamide**



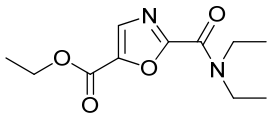
3o: *n*-hexane/EtOAc (5:1); yellow oil (53 mg, 68%); ^{1}H NMR (400 MH_Z, $CDCl_3$)**:** δ = 7.82 (d, *J* = 4.0 Hz, 1H), 7.54 (d, *J* = 3.2 Hz, 1H), 7.30 (br, 1H), 3.55–3.45 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 164.07, 159.25, 143.28, 124.31, 34.46, 14.67. HRMS (EI) ($[M]^+$) Calcd. for $C_6H_8N_2OS$: 156.0357, Found: 156.0355.

***N*-Ethyl-4-methylthiazole-2-carboxamide**



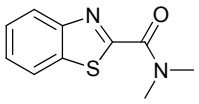
3p: *n*-hexane/EtOAc (5:1); yellow oil (54 mg, 63%); ^{1}H NMR (400 MH_Z, $CDCl_3$)**:** δ = 7.27 (br, 1H), 7.07 (s, 1H), 3.50–3.42 (m, 2H), 2.43 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 162.89, 159.34, 153.65, 119.11, 34.38, 16.87, 14.66. HRMS (EI) ($[M]^+$) Calcd. for $C_7H_{10}N_2OS$: 170.0514, Found: 170.0510.

Ethyl 2-(diethylcarbamoyl)oxazole-5-carboxylate

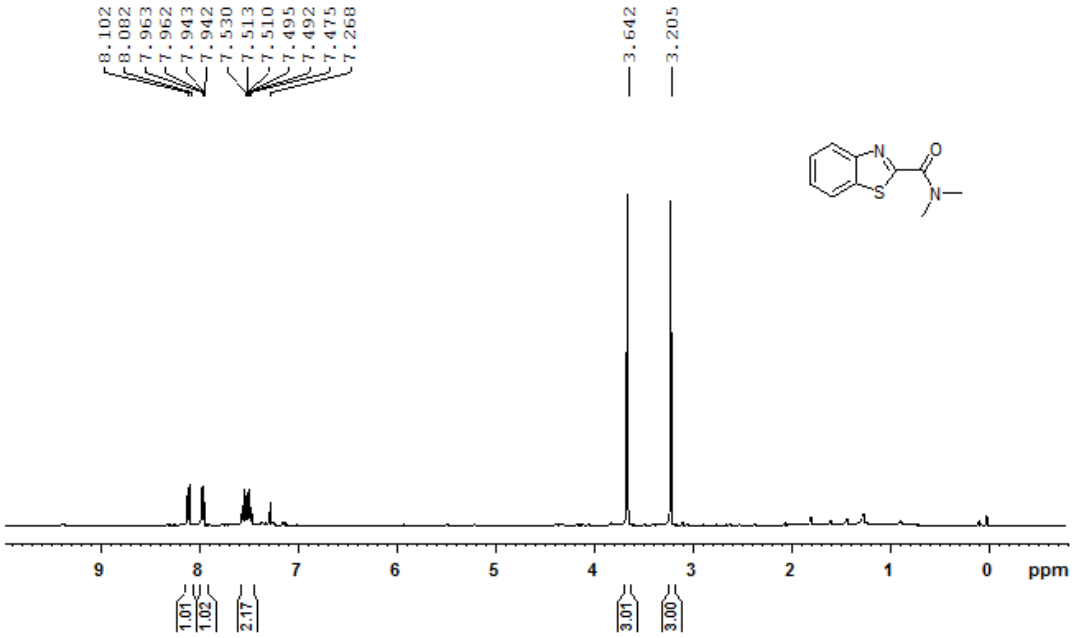


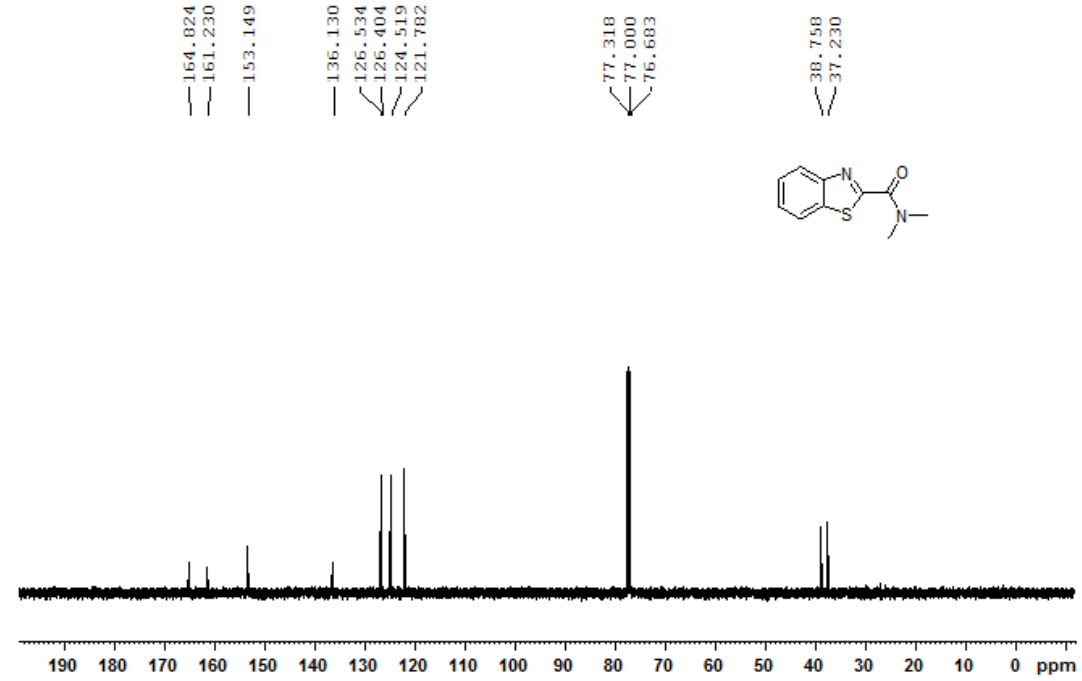
3q: *n*-hexane/EtOAc (5:1); pale yellow solid (71 mg, 59%); ^{1}H NMR (400 MH_Z, $CDCl_3$)**:** δ = 7.77 (s, 1H), 4.40–4.33 (m, 2H), 3.70–3.61 (m, 2H), 3.57–3.47 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ = 157.10, 156.52, 155.75, 142.87, 133.38, 61.72, 43.21, 41.16, 14.32, 14.05, 12.37. HRMS (EI) ($[M]^+$) Calcd. for $C_{11}H_{16}N_2O_4$: 240.1110, Found: 240.1114.

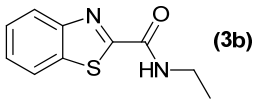
5. ^{1}H NMR, ^{13}C NMR spectra and HRMS data



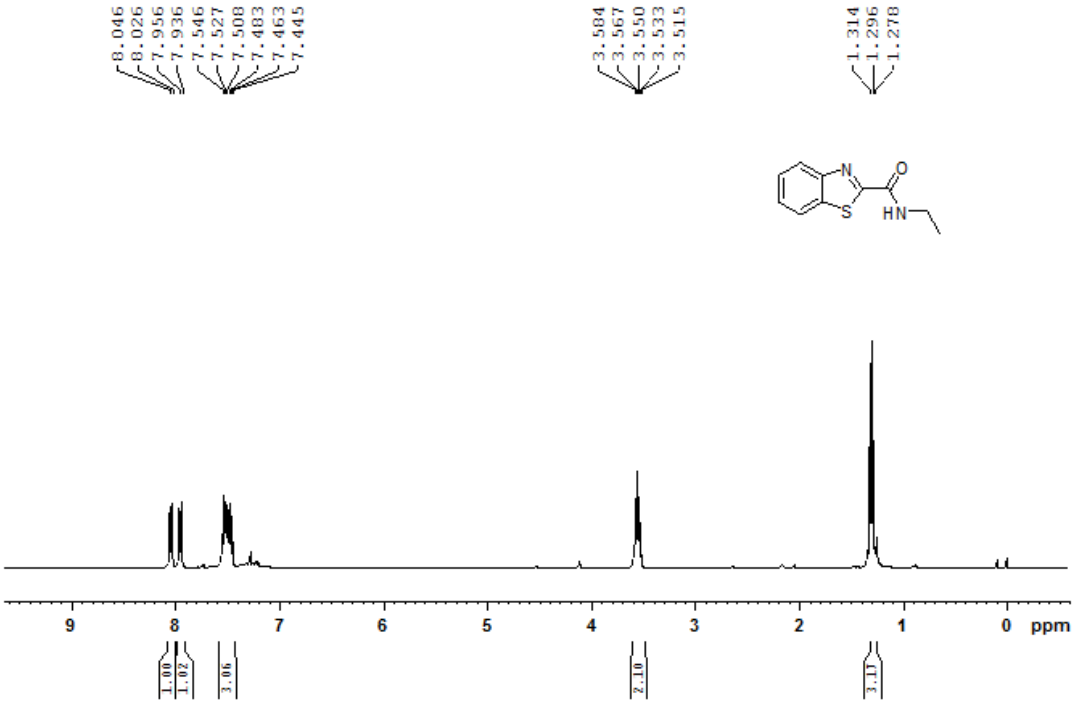
(3a)

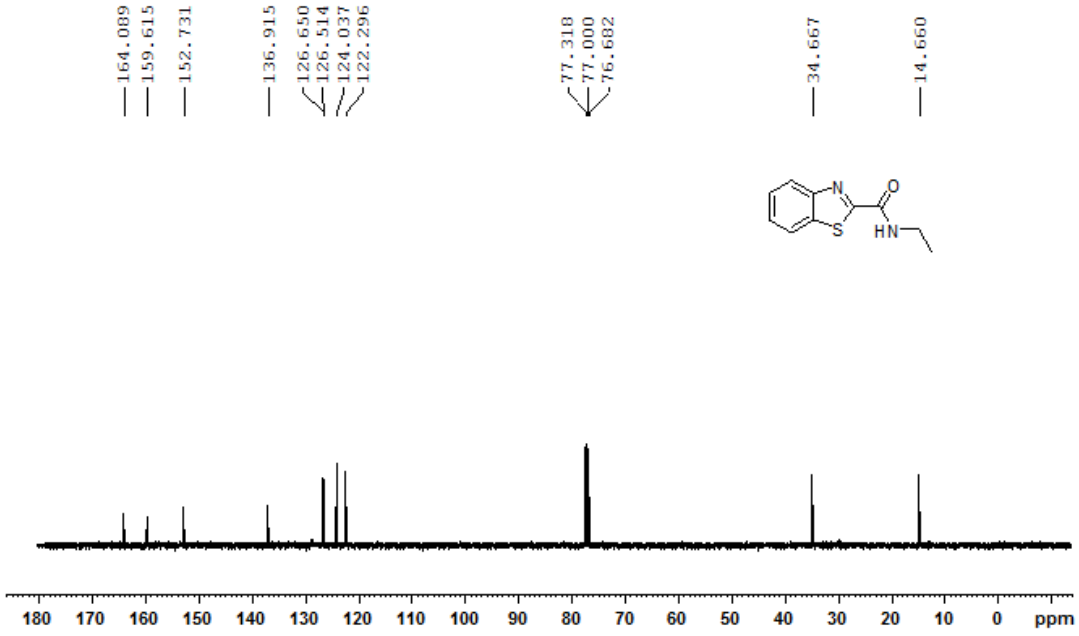


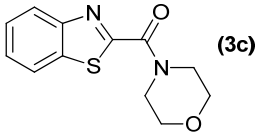

164.824
161.230
153.149
136.130
126.534
126.404
124.519
121.782
77.318
77.000
76.683
38.758
37.230
N
O
S
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
O
S
HN

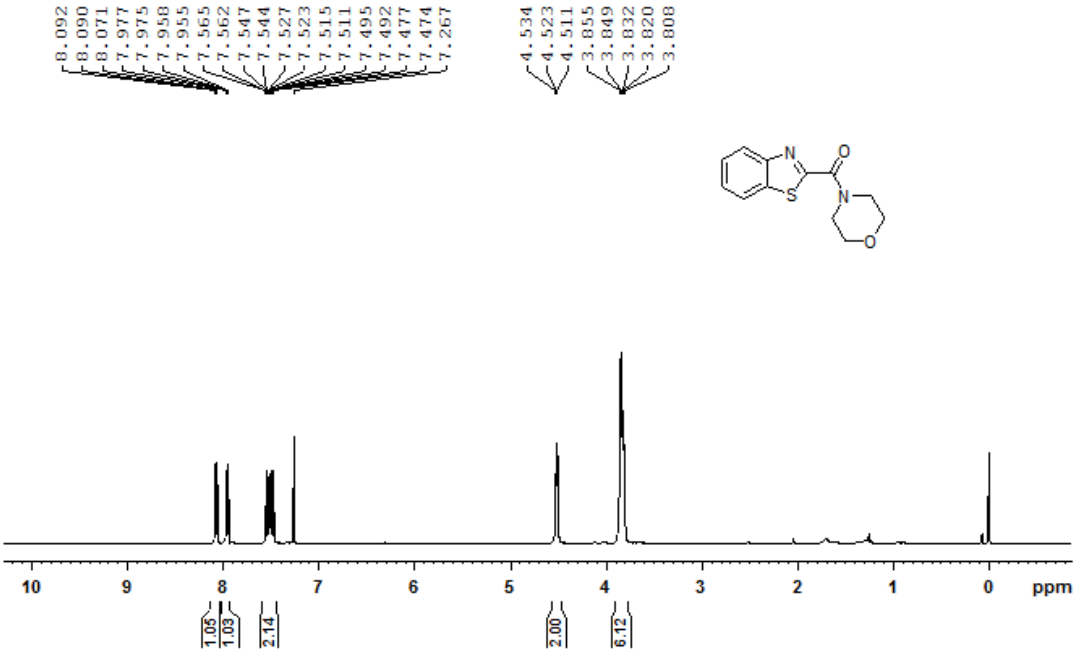
(3b)

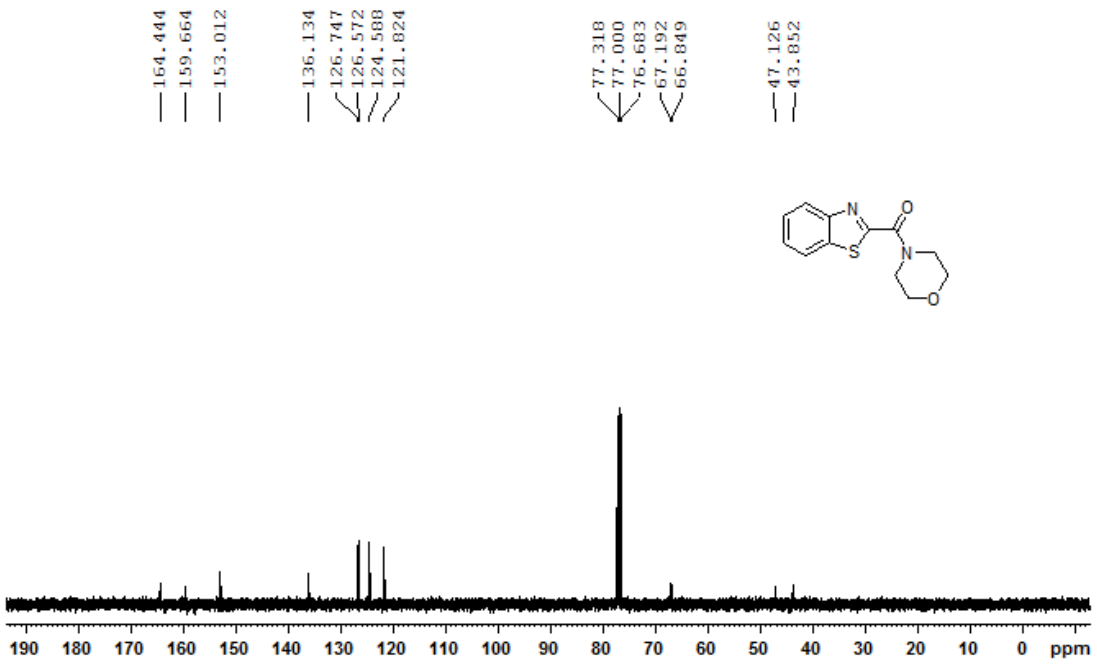

8.046
8.026
7.956
7.936
7.546
7.527
7.508
7.483
7.463
7.445
3.584
3.567
3.550
3.533
3.515
1.314
1.296
1.278
N
O
S
HN
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
3.06
2.10
3.17

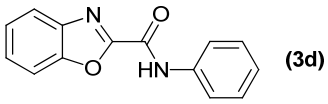

164.089
159.615
152.731
136.915
126.650
126.514
124.037
122.296
77.318
77.000
76.682
34.667
14.660
N
O
S
HN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
O
S
N
O

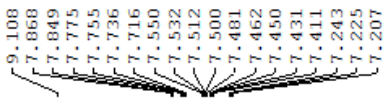
(3c)

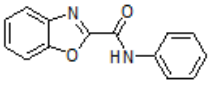

8.092
8.090
8.071
7.977
7.975
7.958
7.955
7.565
7.562
7.547
7.544
7.527
7.523
7.515
7.511
7.495
7.492
7.477
7.474
7.267
4.534
4.523
4.511
3.855
3.849
3.832
3.820
3.808
N
O
S
N
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.05
1.03
2.14
2.00
6.12

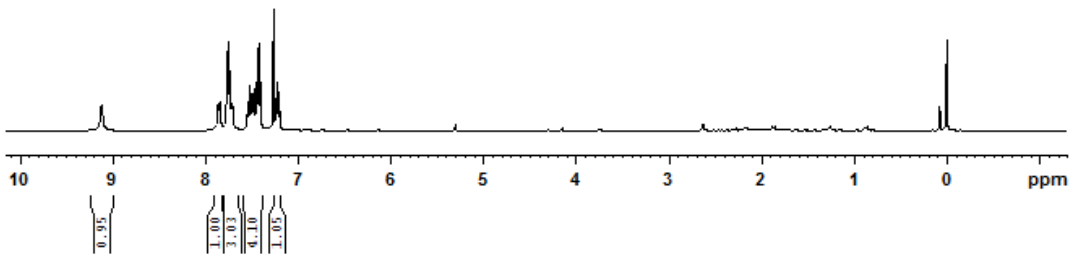

164.444
159.664
153.012
136.134
126.747
126.572
124.588
121.824
77.318
77.000
76.683
67.192
66.849
47.126
43.852
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

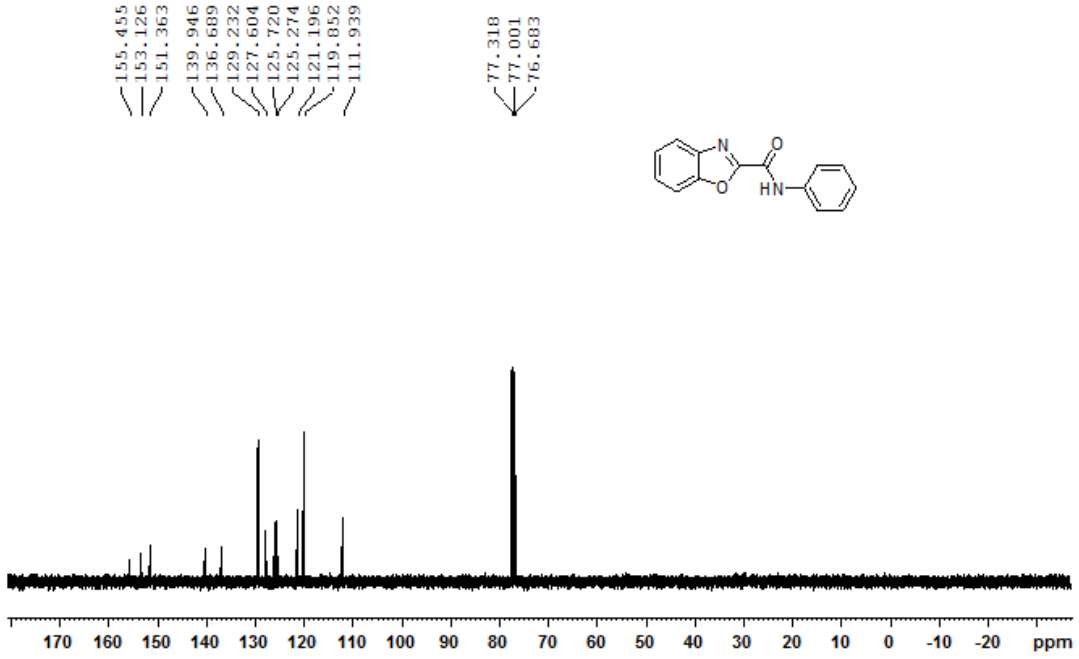

N
O
HN

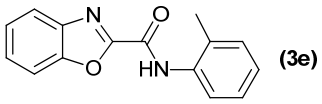
(3d)


9.108
7.868
7.849
7.775
7.755
7.736
7.716
7.550
7.532
7.512
7.500
7.481
7.462
7.450
7.431
7.411
7.243
7.225
7.207

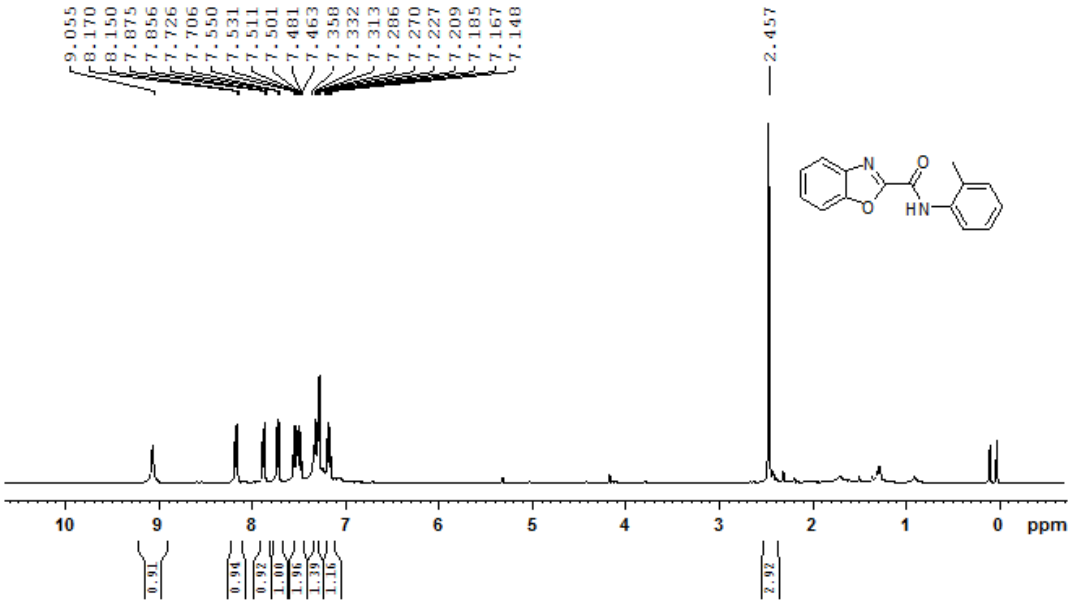

N
O
HN

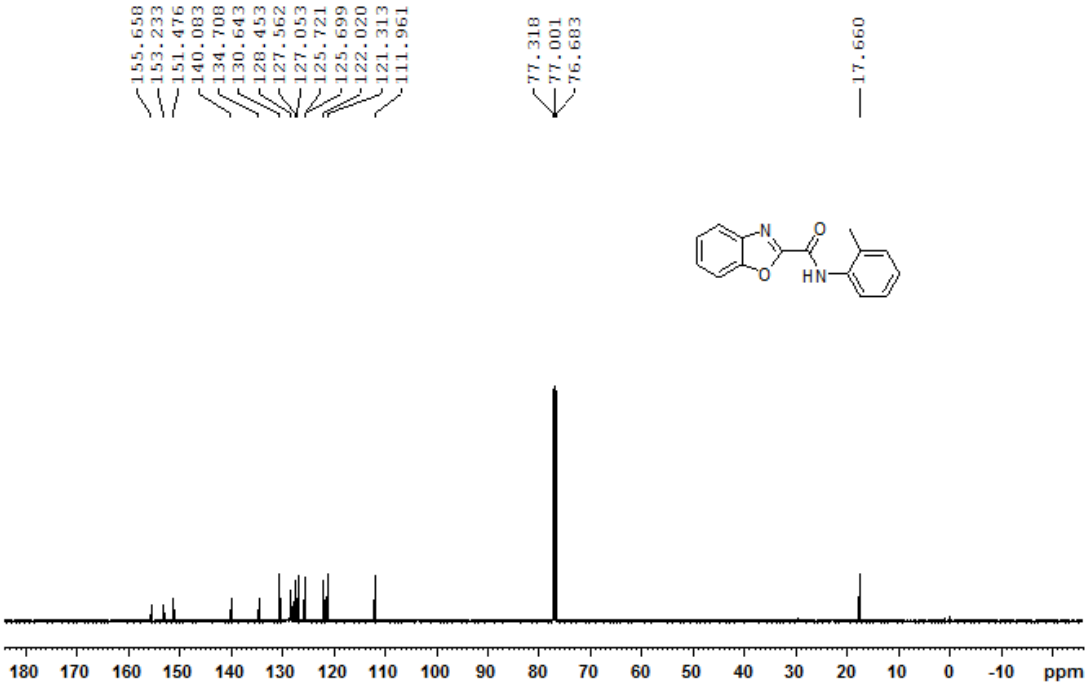

10 9 8 7 6 5 4 3 2 1 0 ppm
0.95
1.00
3.03
4.10
1.05

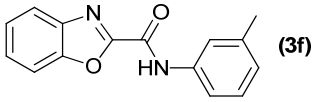

155.455
153.126
151.363
139.946
136.689
129.232
127.604
125.720
125.274
121.196
119.852
111.939
77.318
77.001
76.683
N
O
O
HN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 ppm


N
O
O
HN

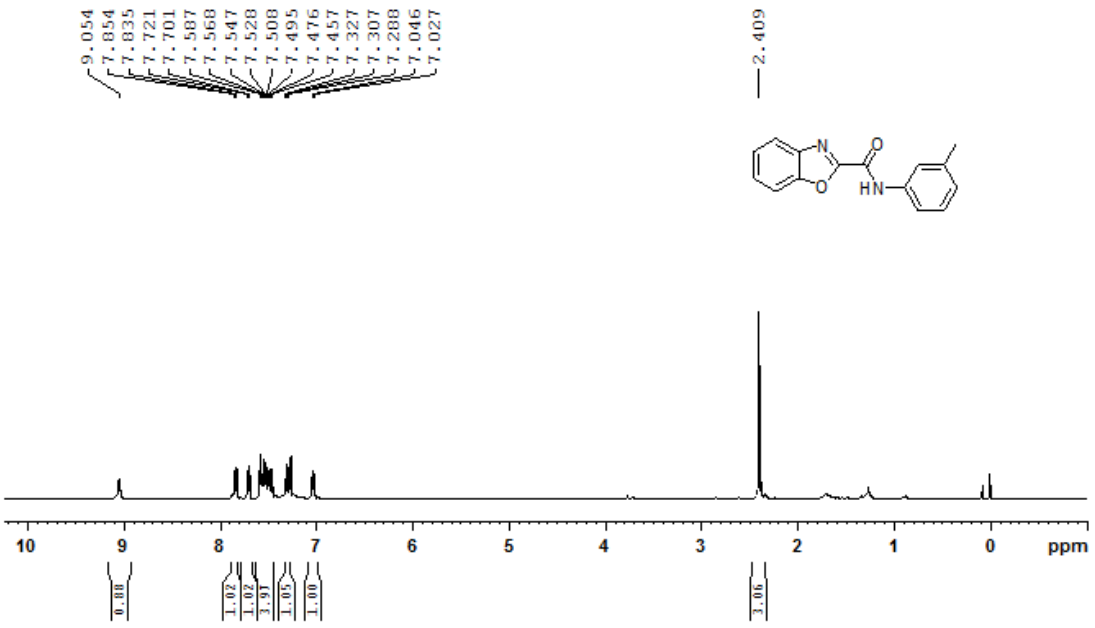
(3e)

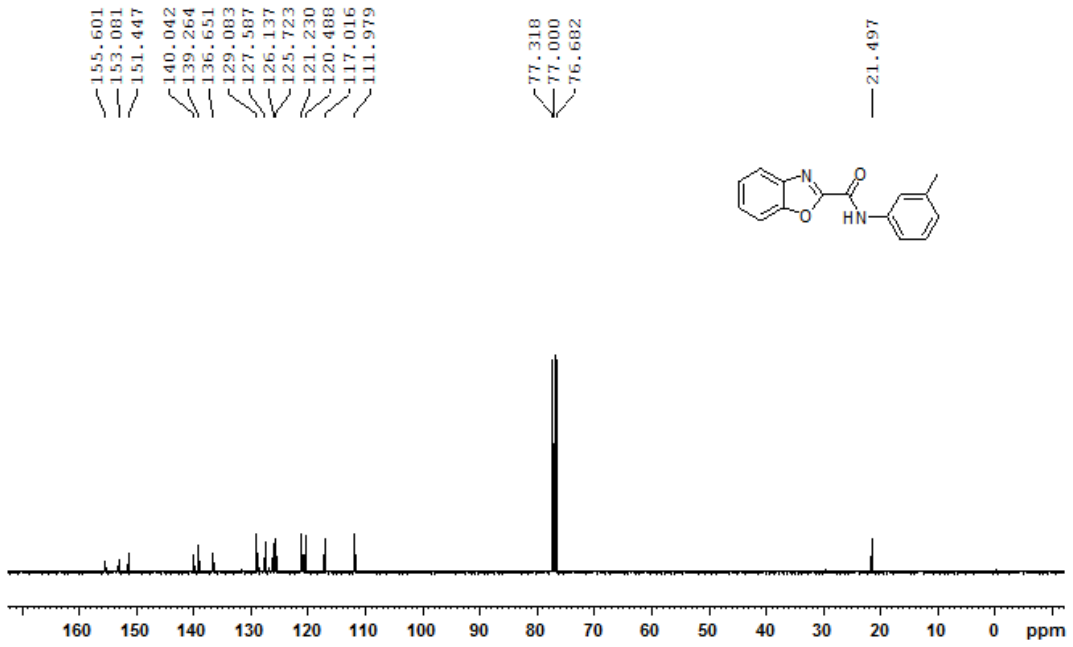

9.055
8.170
8.150
7.875
7.856
7.726
7.706
7.550
7.531
7.511
7.501
7.481
7.463
7.358
7.332
7.313
7.286
7.270
7.227
7.209
7.185
7.167
7.148
2.457
N
O
O
HN
10 9 8 7 6 5 4 3 2 1 0 ppm
0.91
0.94
0.92
1.00
1.96
1.39
1.16
2.92

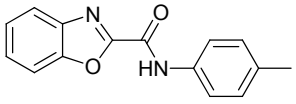

155.658
153.233
151.476
140.083
134.708
130.643
128.453
127.562
127.053
125.721
125.699
122.020
121.313
111.961
77.318
77.001
76.683
17.660
N
O
HN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


N
O
HN

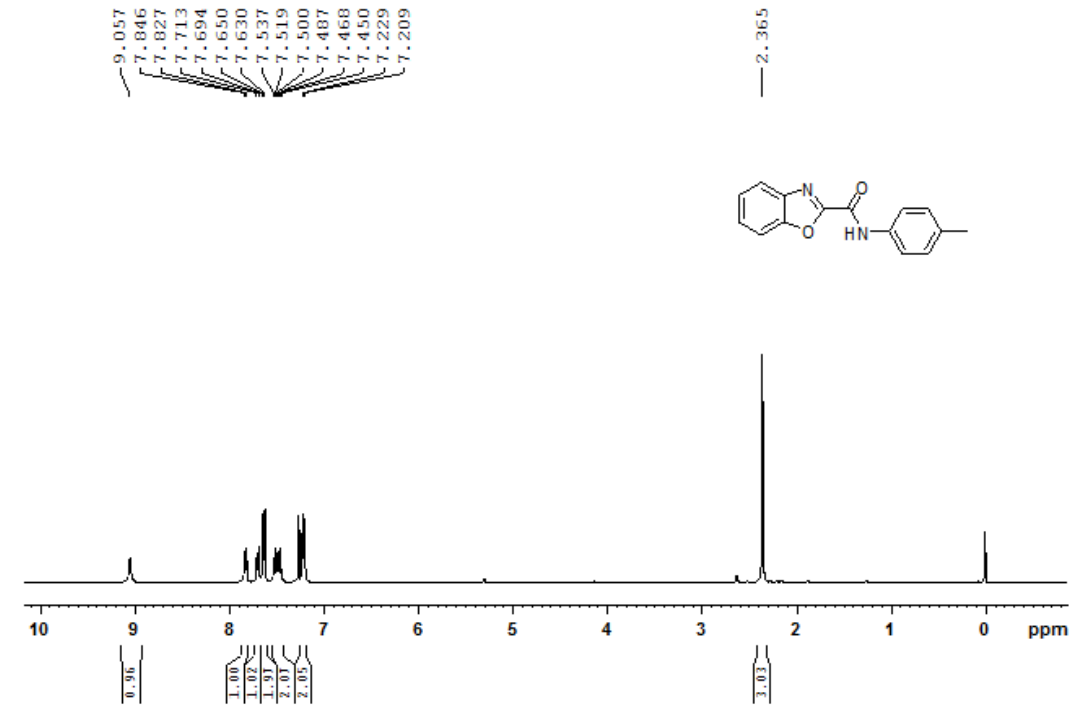
(3f)

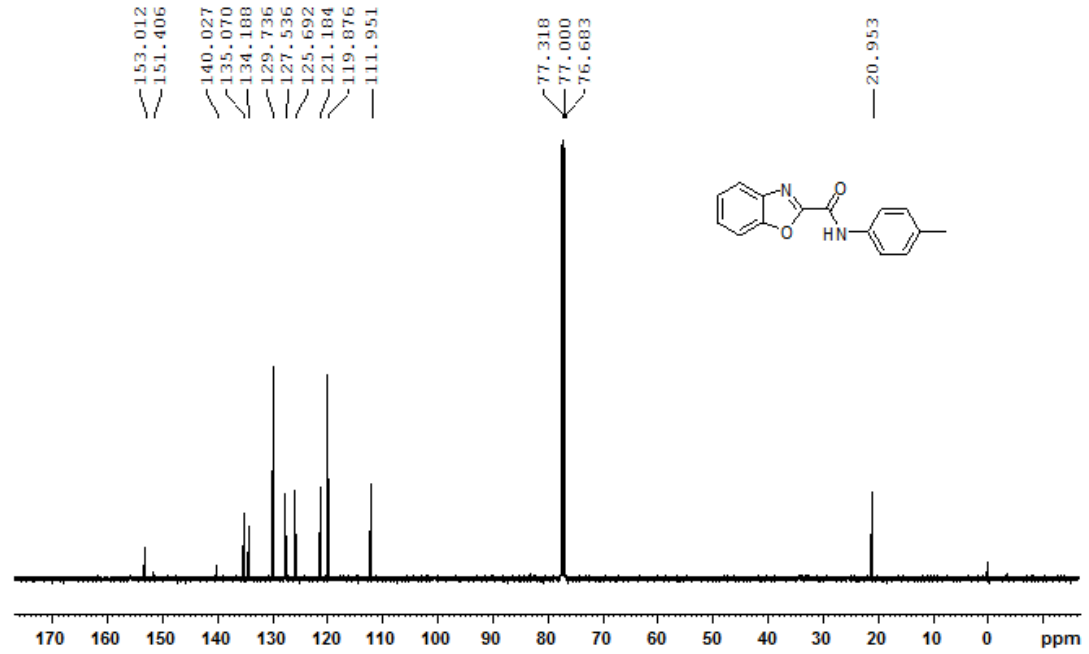

9.054
7.854
7.835
7.721
7.701
7.587
7.568
7.547
7.528
7.508
7.495
7.476
7.457
7.327
7.307
7.288
7.046
7.027
2.409
N
O
HN
10 9 8 7 6 5 4 3 2 1 0 ppm
0.88
1.02
1.02
3.93
1.05
1.00
3.06

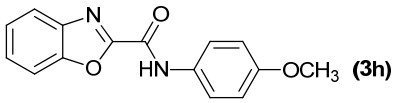

155.601
153.081
151.447
140.042
139.264
136.651
129.083
127.587
126.137
125.723
121.230
120.488
117.016
111.979
77.318
77.000
76.682
21.497
N
O
HN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

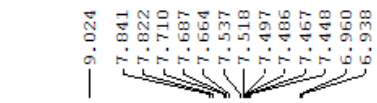

N
O
O
HN

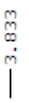
(3g)

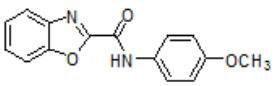

9.057
7.846
7.827
7.713
7.694
7.650
7.630
7.537
7.519
7.500
7.487
7.468
7.450
7.229
7.209
2.365
N
O
HN
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
1.00
1.02
1.91
2.07
2.05
3.03

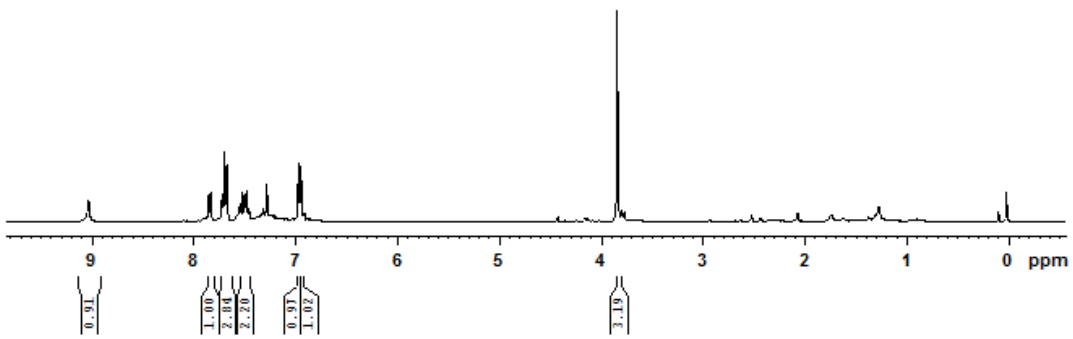

153.012
151.406
140.027
135.070
134.188
129.736
127.536
125.692
121.184
119.876
111.951
77.318
77.000
76.683
20.953
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

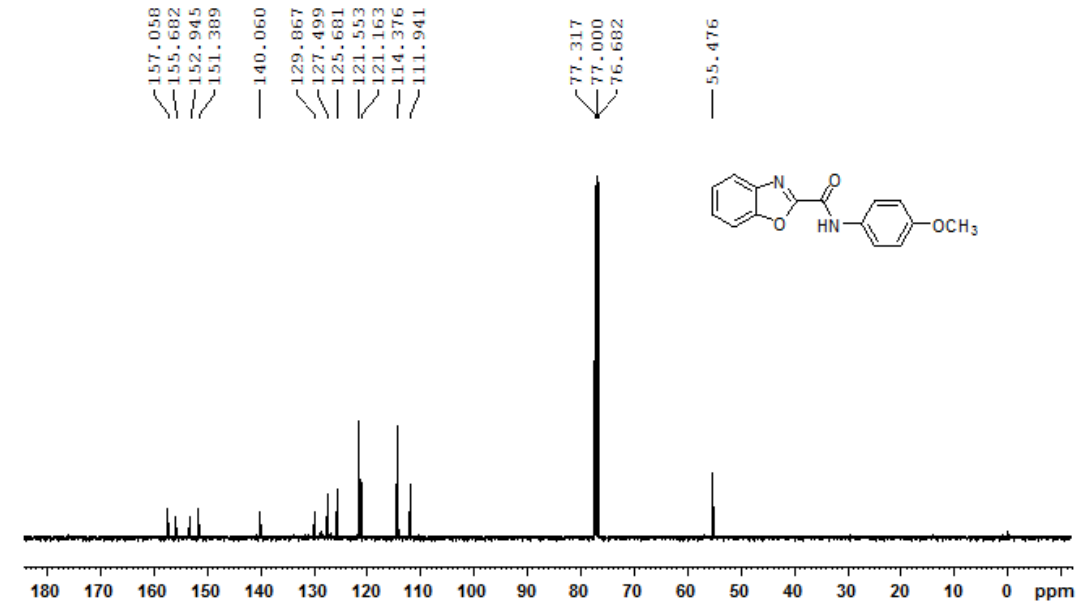

N
O
HN
OCH3
(3h)

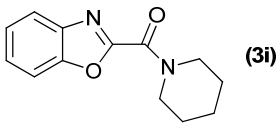

9.024
7.841
7.822
7.710
7.687
7.664
7.537
7.518
7.497
7.486
7.467
7.448
6.960
6.938


3.833

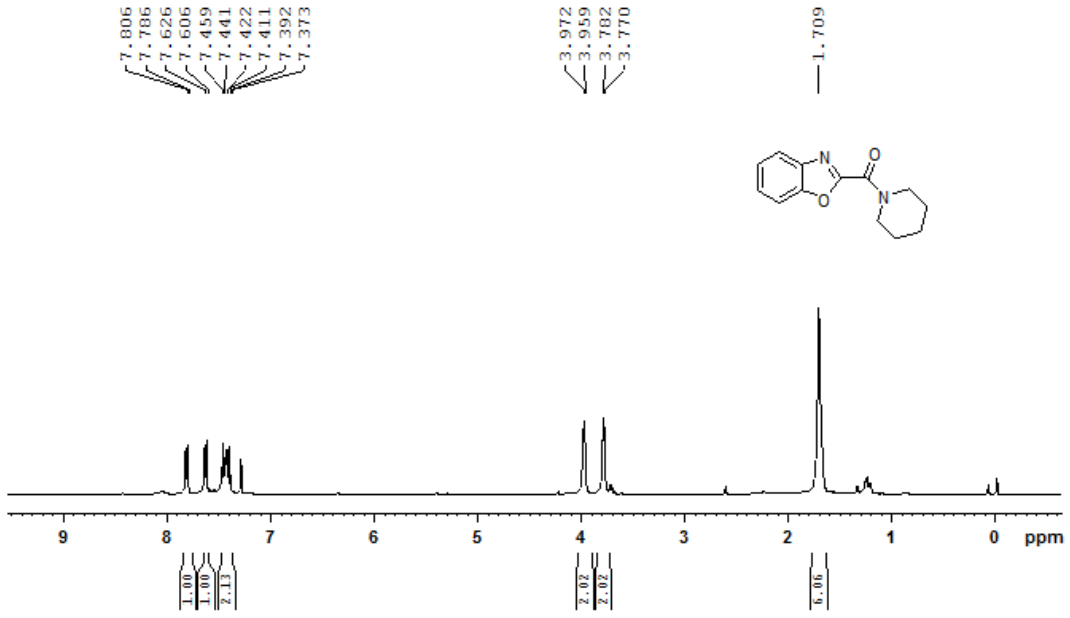

N
O
HN
OCH3

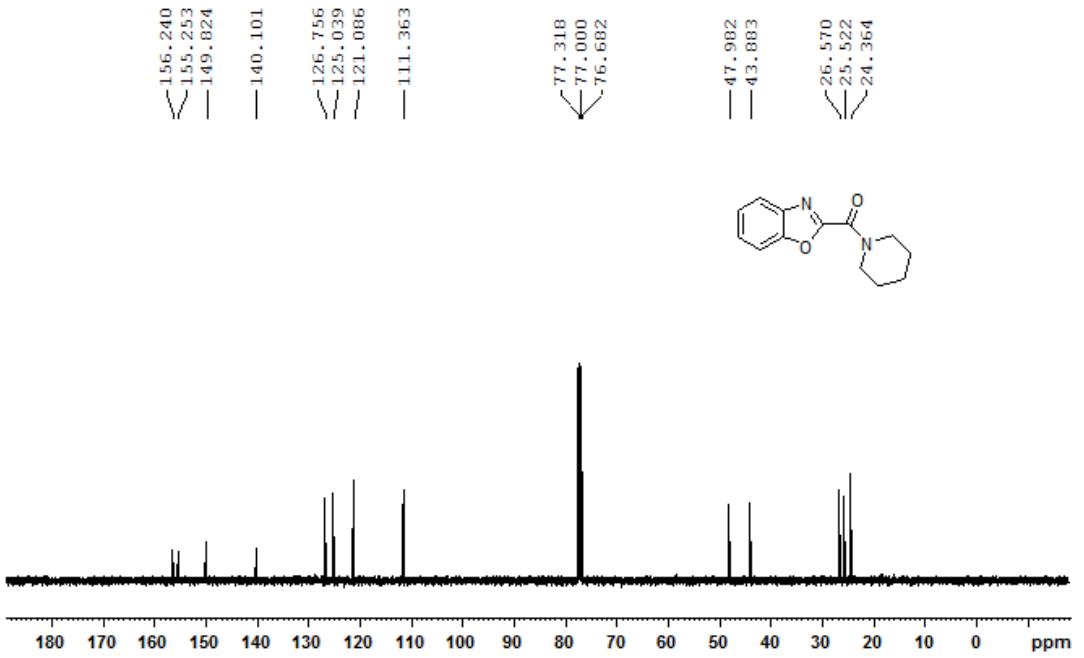

9 8 7 6 5 4 3 2 1 0 ppm
0.91
1.00
2.04
2.20
0.97
1.02
3.19


157.058
155.682
152.945
151.389
140.060
129.867
127.499
125.681
121.553
121.163
114.376
111.941
77.317
77.000
76.682
55.476
N
O
O
HN
OCH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

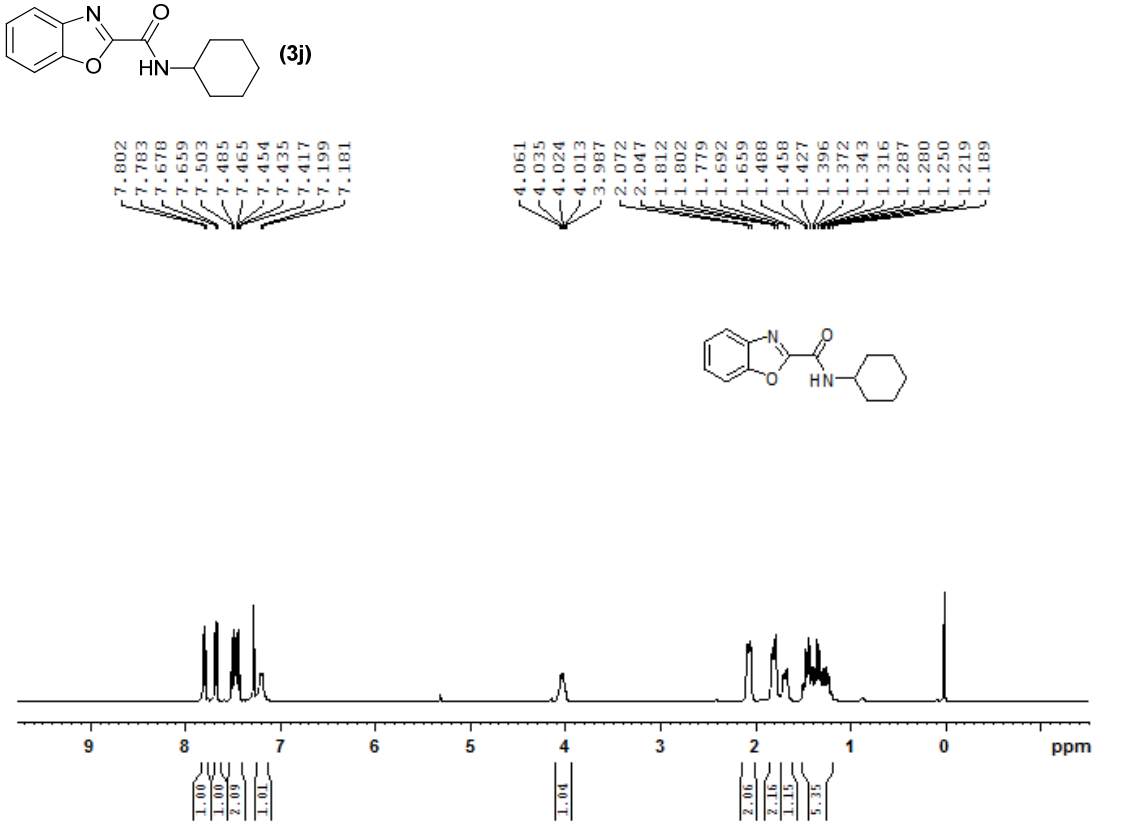

N
O
O
N

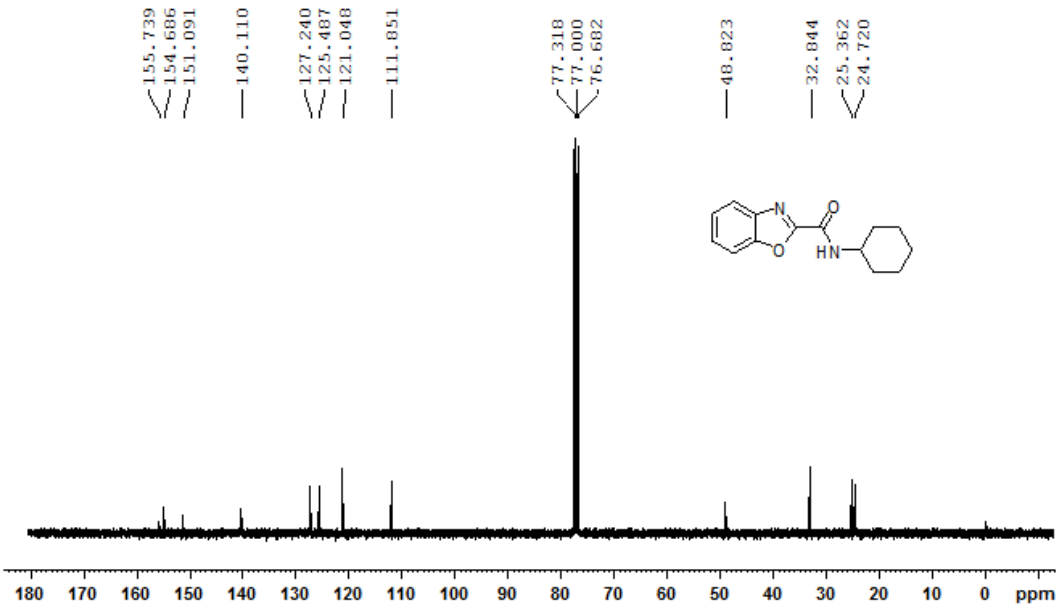
(3i)

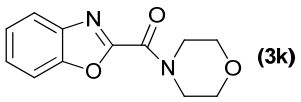

7.806
7.786
7.626
7.606
7.459
7.441
7.422
7.411
7.392
7.373
3.972
3.959
3.782
3.770
1.709
N
O
O
N
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.00
2.13
2.02
2.02
6.06


156.240
155.253
149.824
140.101
126.756
125.039
121.086
111.363
77.318
77.000
76.682
47.982
43.883
26.570
25.522
24.364
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(3j)

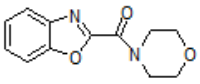

7.802
7.783
7.678
7.659
7.503
7.485
7.465
7.454
7.435
7.417
7.199
7.181
4.061
4.035
4.024
4.013
3.987
2.072
2.047
1.812
1.802
1.779
1.692
1.659
1.488
1.458
1.427
1.396
1.372
1.343
1.316
1.287
1.280
1.250
1.219
1.189
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.00
2.09
1.01
1.04
2.06
2.16
1.15
5.35

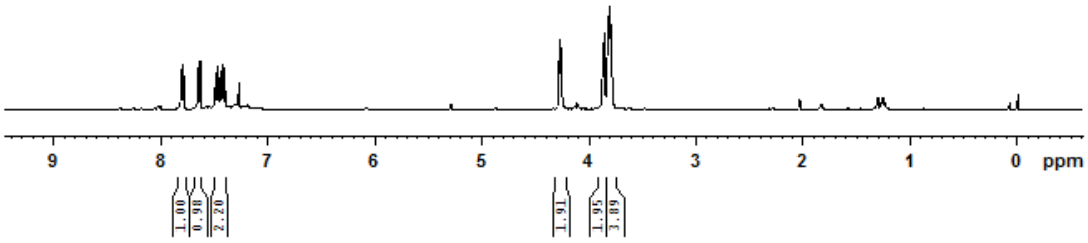

155.739
154.686
151.091
140.110
127.240
125.487
121.048
111.851
77.318
77.000
76.682
48.823
32.844
25.362
24.720
N
O
O
HN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

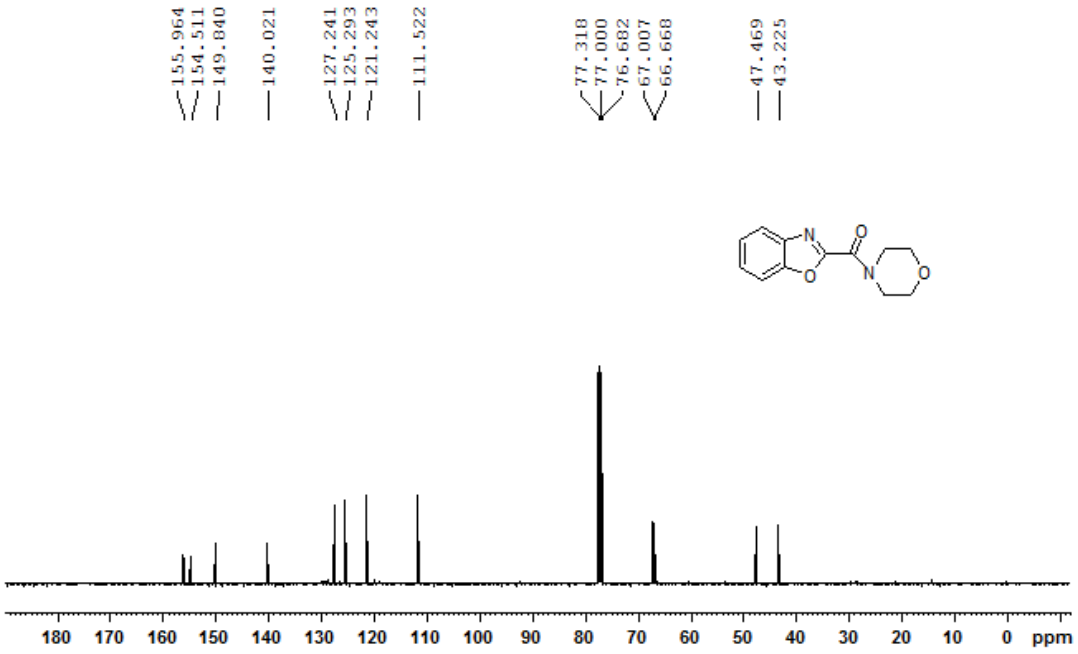

N
O
O
N
O

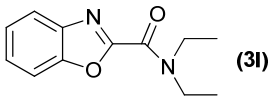
(3k)


7.815
7.795
7.656
7.636
7.497
7.479
7.459
7.439
7.420
7.401
4.282
4.271
4.259
3.878
3.868
3.856
3.830
3.814
3.802
3.789

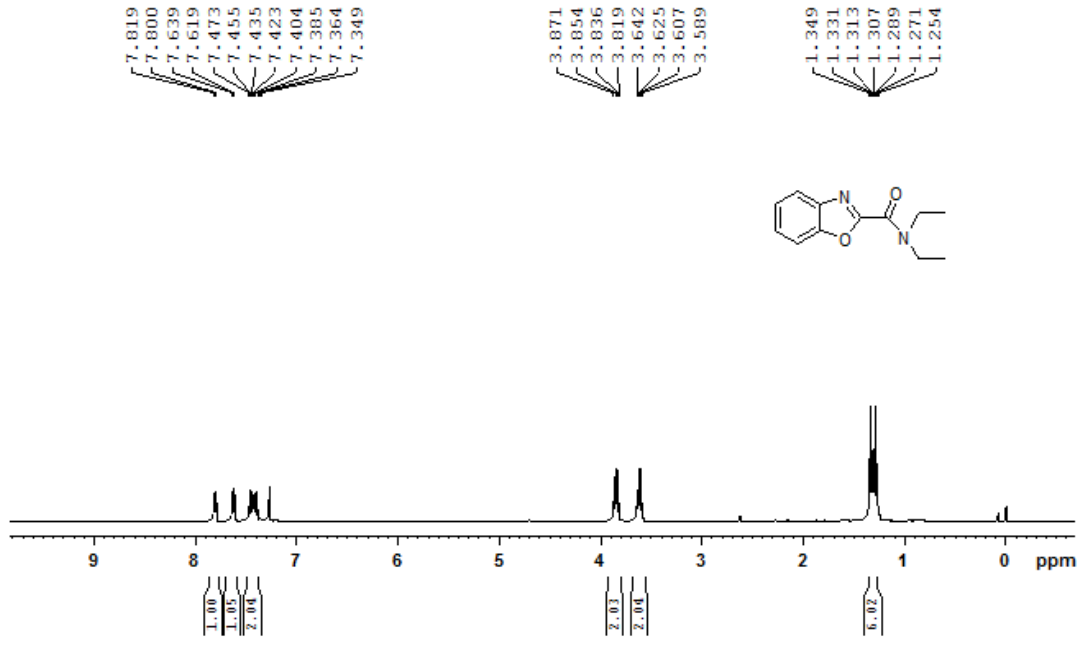

N
O
O
N
O

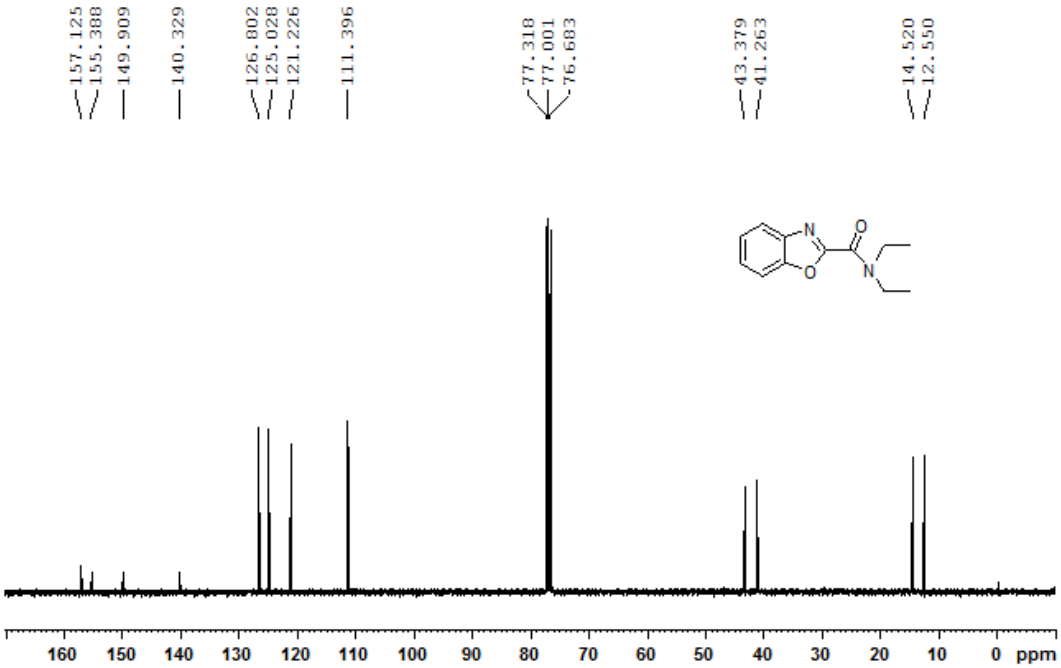

9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.98
2.20
1.91
1.95
3.09

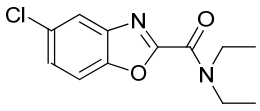

155.964
154.511
149.840
140.021
127.241
125.293
121.243
111.522
77.318
77.000
76.682
67.007
66.668
47.469
43.225
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



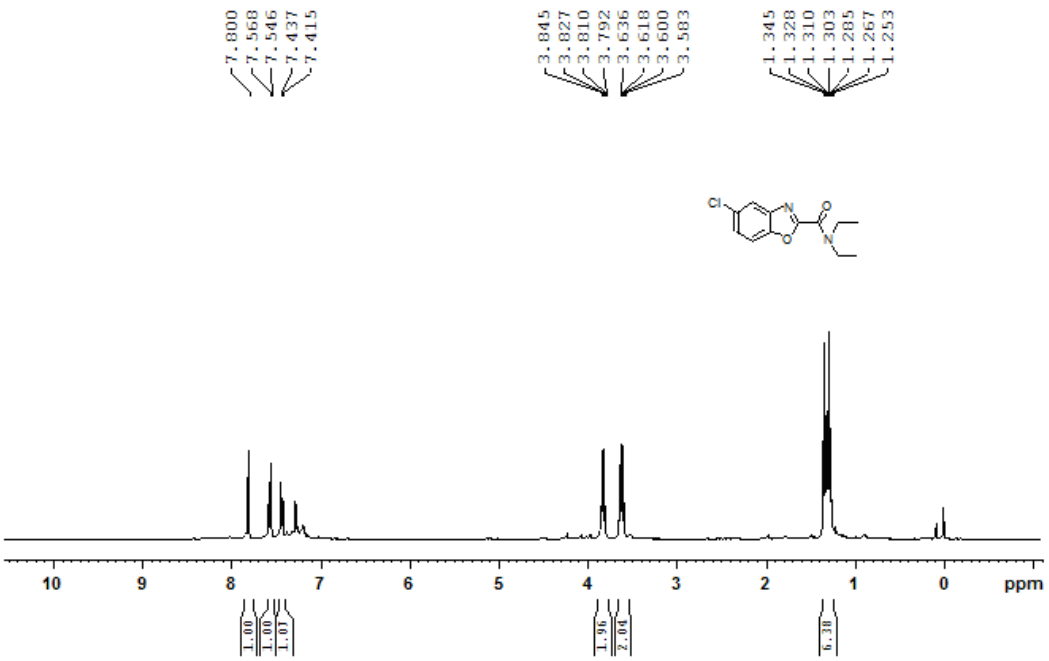
(3l)

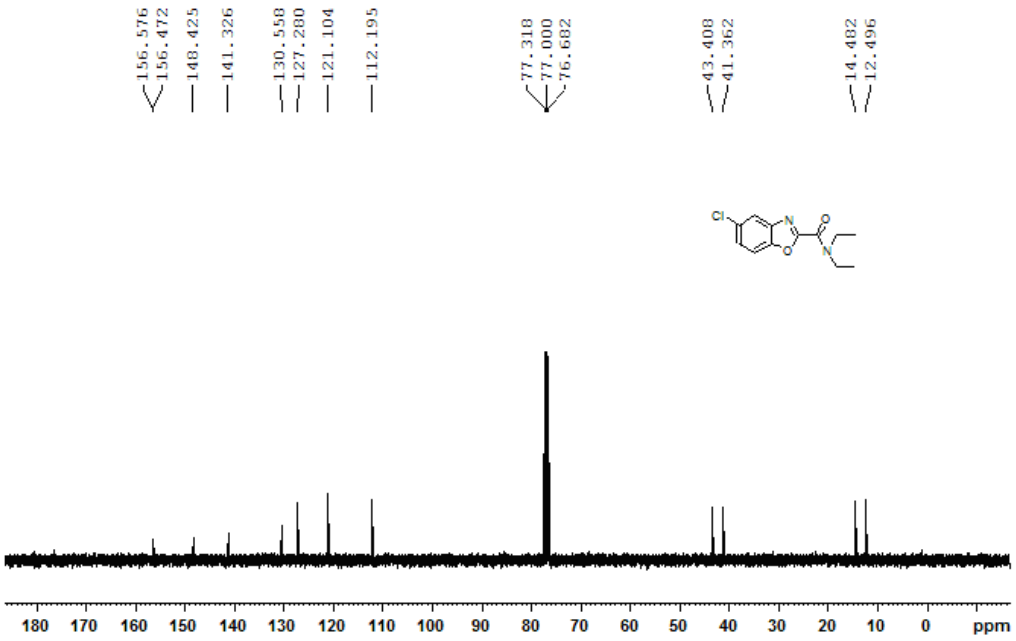

7.819
7.800
7.639
7.619
7.473
7.455
7.435
7.423
7.404
7.385
7.364
7.349
3.871
3.854
3.836
3.819
3.642
3.625
3.607
3.589
1.349
1.331
1.313
1.307
1.289
1.271
1.254
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.05
2.04
2.03
2.04
6.02

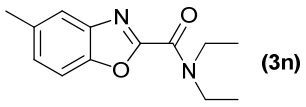

157.125
155.388
149.909
140.329
126.802
125.028
121.226
111.396
77.318
77.001
76.683
43.379
41.263
14.520
12.550
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Cl
N
O
O
N

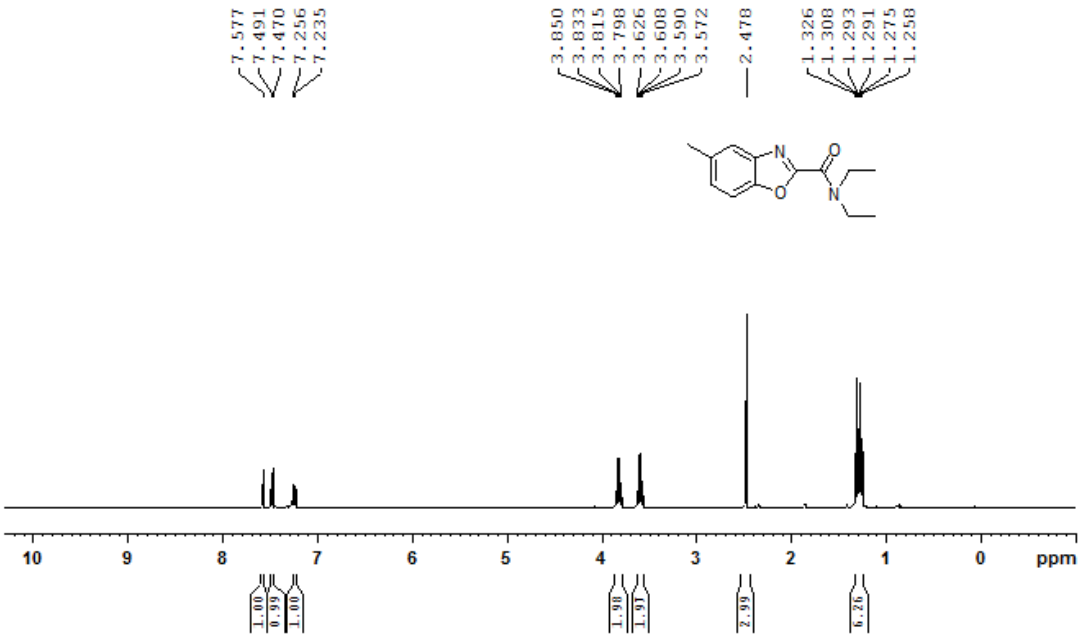
(3m)

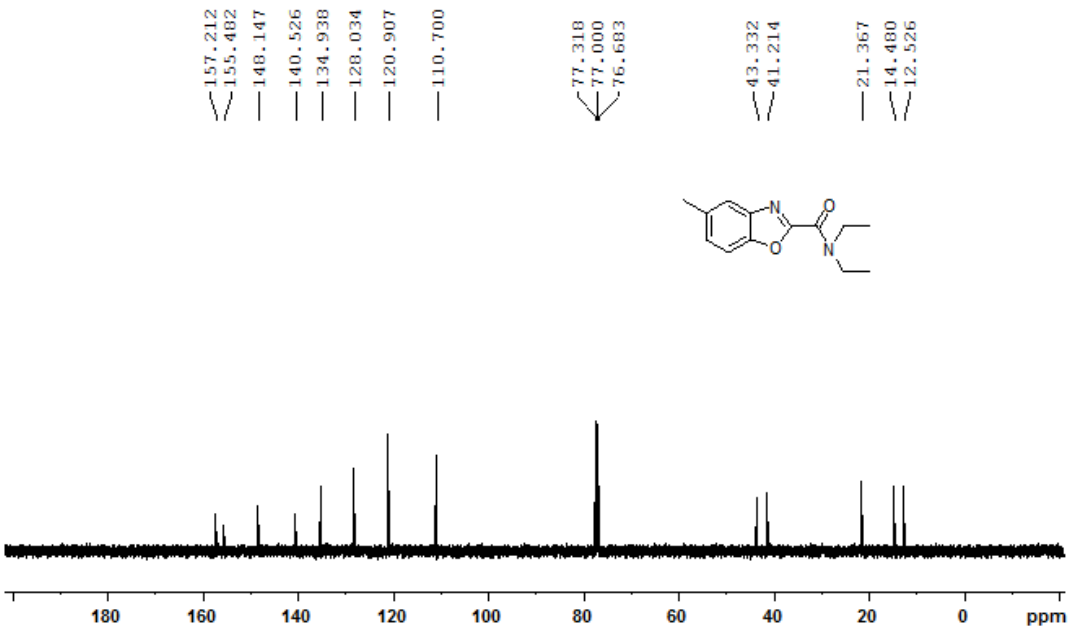

7.800
7.568
7.546
7.437
7.415
3.845
3.827
3.810
3.792
3.636
3.618
3.600
3.583
1.345
1.328
1.310
1.303
1.285
1.267
1.253
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.00
1.07
1.96
2.04
6.38

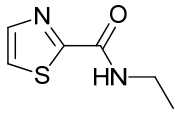

156.576
156.472
148.425
141.326
130.558
127.280
121.104
112.195
77.318
77.000
76.682
43.408
41.362
14.482
12.496
Cl
N
O
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
O
O
N

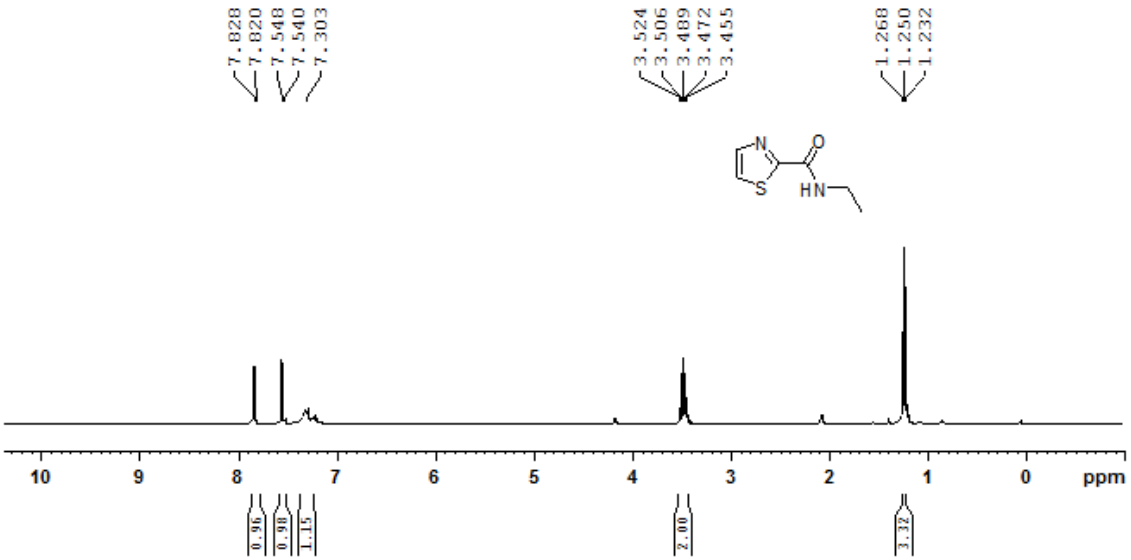
(3n)

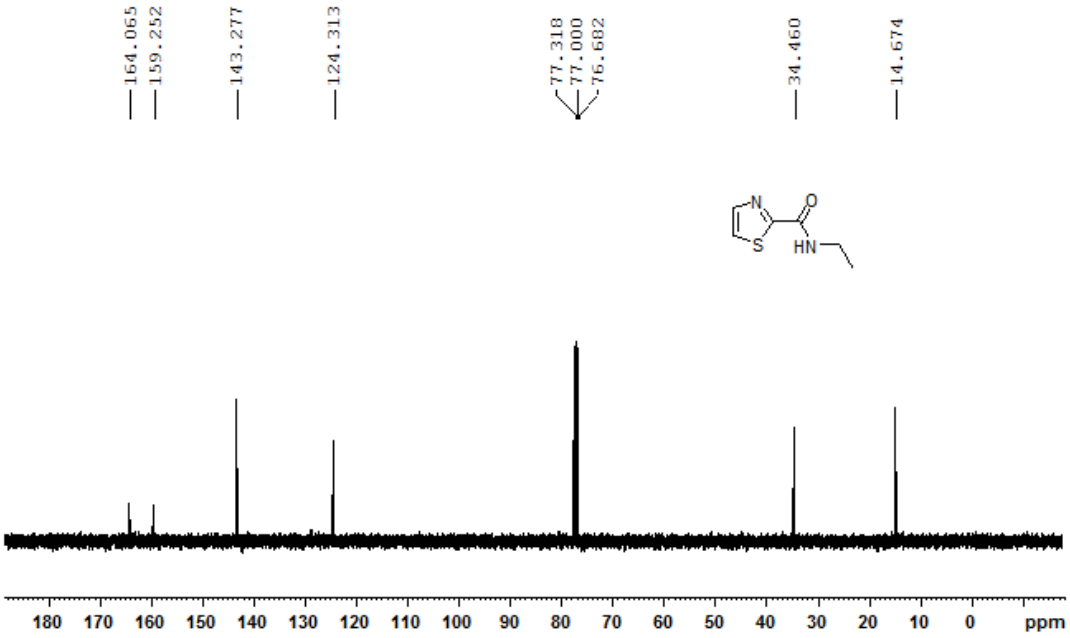

7.577
7.491
7.470
7.256
7.235
3.850
3.833
3.815
3.798
3.626
3.608
3.590
3.572
2.478
1.326
1.308
1.293
1.291
1.275
1.258
N
O
O
N
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.99
1.00
1.98
1.91
2.99
6.26

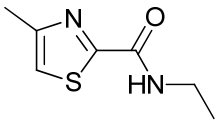

157.212
155.482
148.147
140.526
134.938
128.034
120.907
110.700
77.318
77.000
76.683
43.332
41.214
21.367
14.480
12.526
180
160
140
120
100
80
60
40
20
0
ppm



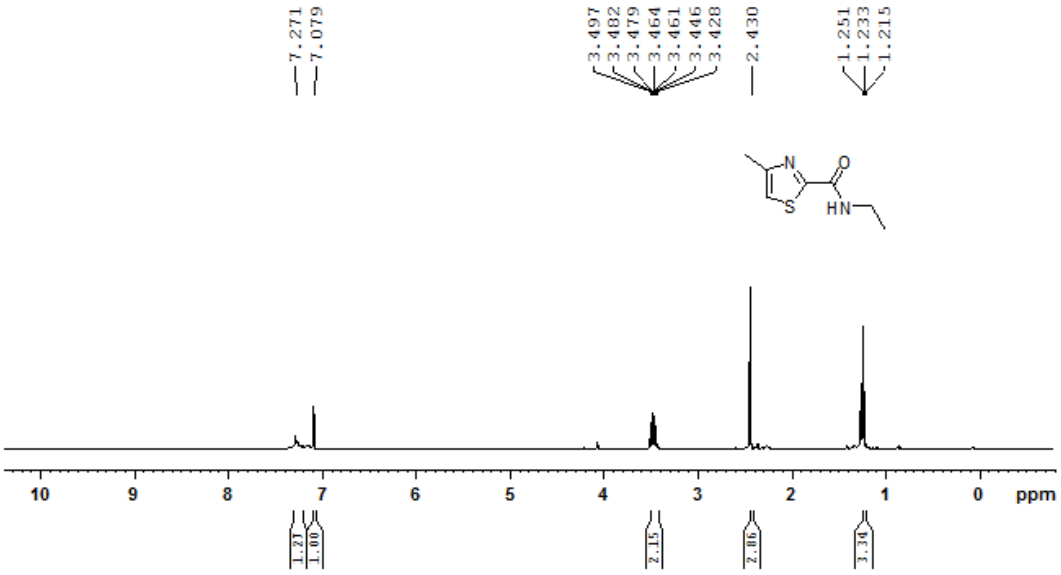
(3o)

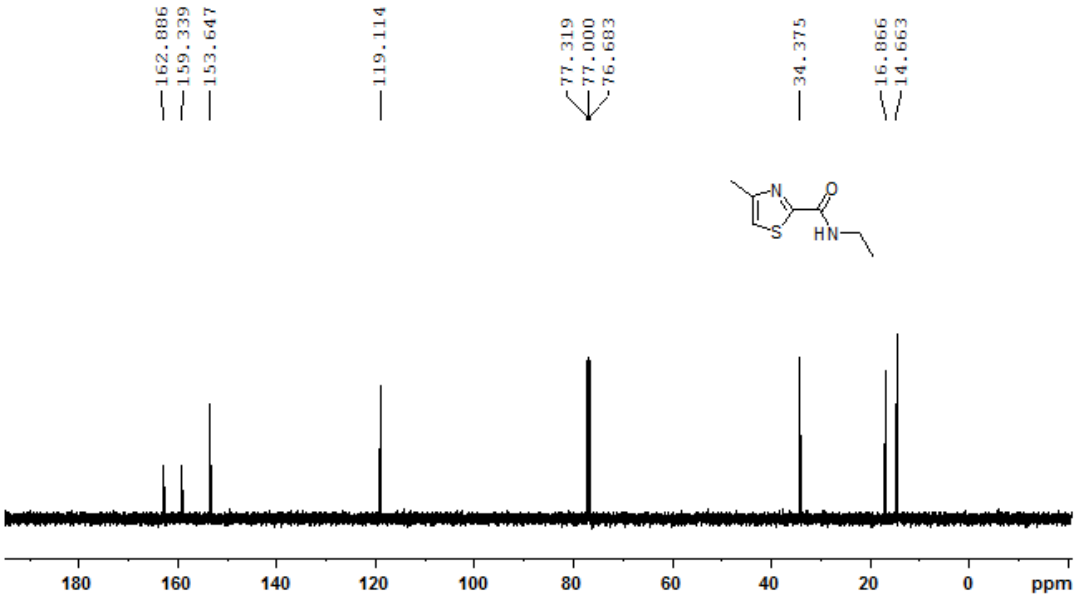

7.828
7.820
7.548
7.540
7.303
3.524
3.506
3.489
3.472
3.455
1.268
1.250
1.232
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
0.98
1.15
2.00
3.32

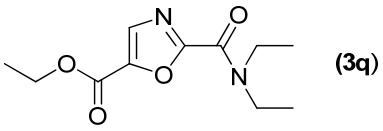

164.065
159.252
143.277
124.313
77.318
77.000
76.682
34.460
14.674
N
O
S
HN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


N
O
S
HN

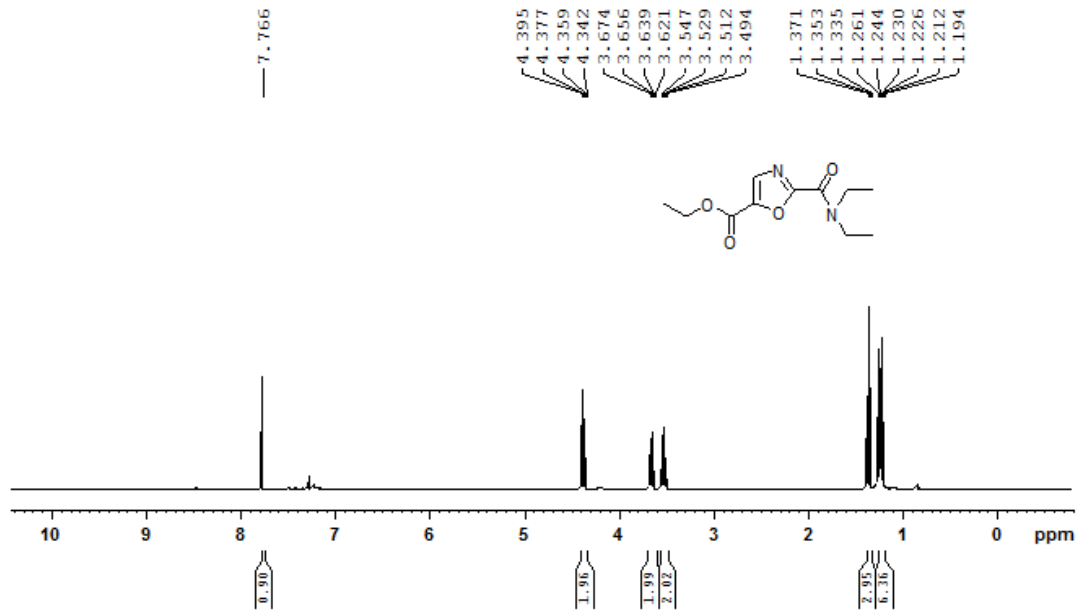
(3p)

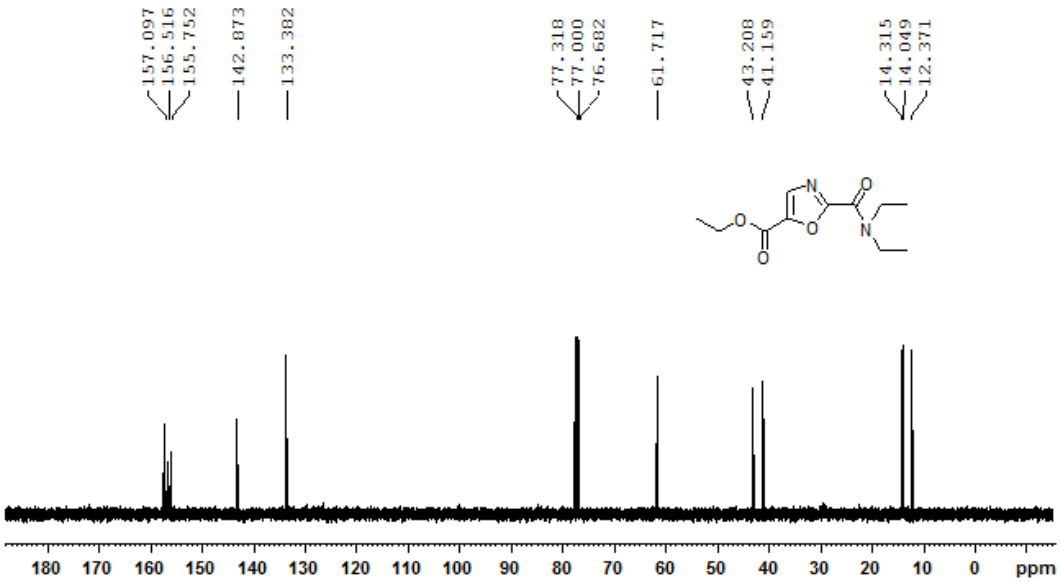

7.271
7.079
3.497
3.482
3.479
3.464
3.461
3.446
3.428
2.430
1.251
1.233
1.215
N
O
S
HN
10 9 8 7 6 5 4 3 2 1 0 ppm
1.27
1.00
2.15
2.86
3.34


162.886
159.339
153.647
119.114
77.319
77.000
76.683
34.375
16.866
14.663
N
O
S
HN
180
160
140
120
100
80
60
40
20
0
ppm


N
O
O
O
N

(3q)


7.766
4.395
4.377
4.359
4.342
3.674
3.656
3.639
3.621
3.547
3.529
3.512
3.494
1.371
1.353
1.335
1.261
1.244
1.230
1.226
1.212
1.194
N
O
O
O
N
10
9
8
7
6
5
4
3
2
1
0
ppm
0.90
1.96
1.99
2.02
2.96
6.36



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Shanghai Institute of Organic Chemistry

Chinese Academic of Sciences

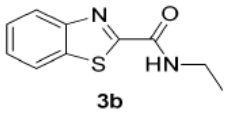
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0311

Sample Serial Number: HBSF-HT-9

Operator: Li



3b

Date: 2011/04/28
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
247 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 S: 0-1 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
206.0509	206.0514	-0.5	-2.4	7.0	61.5	C10 H10 N2 O S
	206.0519	-1.0	-4.9	2.5	6656.9	C7 H13 N3 S Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

Chinese Academic of Sciences
High Resolution MS Data Report

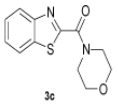
Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV

Card Serial Number: GCT-P-T11-04-OS0312

Sample Serial Number: HBSF-HT-10

Operator: Li

Date: 2011/04/28



3c

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
297 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: 0-4 O: 0-4 S: 0-1 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
248.0616	248.0619	-0.3	-1.2	8.0	105.9	C12 H12 N2 O2 S
	248.0624	-0.8	-3.2	3.5	241.4	C9 H15 N3 O S Cl
	248.0626	-1.0	-4.0	17.0	125.0	C20 H8
	248.0604	1.2	4.8	8.0	164.9	C14 H13 O2 Cl

Shanghai Mass Spectrometry Center

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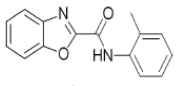
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0305

Sample Serial Number: HBSF-HT-3

Operator: Li



3e

Date: 2011/04/28
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
160 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
252.0897	252.0899	-0.2	-0.8	11.0	254.9	C15 H12 N2 O2
	252.0904	-0.7	-2.8	6.5	10236.4	C12 H15 N3 O Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

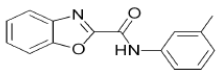
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0303

Sample Serial Number: HBSF-HT-1

Operator: Li



3f

Date: 2011/04/28
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
160 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
252.0900	252.0899	0.1	0.4	11.0	924.3	C15 H12 N2 O2
	252.0904	-0.4	-1.6	6.5	6571.1	C12 H15 N3 O Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

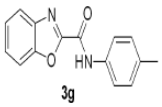
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0304

Sample Serial Number: HBSF-HT-2

Operator: Li



3g

Date: 2011/04/28
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
160 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
252.0901	252.0899	0.2	0.8	11.0	473.7	C15 H12 N2 O2
	252.0904	-0.3	-1.2	6.5	13966.1	C12 H15 N3 O Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

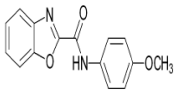
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0306

Sample Serial Number: HBSF-HT-4

Operator: Li



3h

Date: 2011/04/28
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
170 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
268.0847	268.0848	-0.1	-0.4	11.0	275.1	C15 H12 N2 O3
	268.0853	-0.6	-2.2	6.5	2188.1	C12 H15 N3 O2 Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

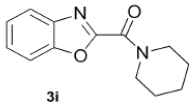
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0308

Sample Serial Number: HBSF-HT-6

Operator: Li



3i

Date: 2011/04/28
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
148 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
230.1056	230.1055	0.1	0.4	8.0	2773059.0	C13 H14 N2 O2
	230.1060	-0.4	-1.7	3.5	101.9	C10 H17 N3 O Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

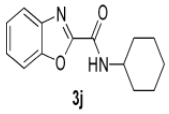
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-TII-04-OS0307

Sample Serial Number: HBSF-HT-5

Operator: Li



3j

Date: 2011/04/28
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
157 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
244.1210	244.1212	-0.2	-0.8	8.0	111.6	C14 H16 N2 O2
	244.1217	-0.7	-2.9	3.5	5911.4	C11 H19 N3 O Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

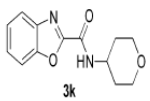
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-TII-04-OS0309

Sample Serial Number: HBSF-HT-7

Operator: Li



3k

Date: 2011/04/28
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
148 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
232.0853	232.0853	0.0	0.0	3.5	2777596.3	C9 H15 N3 O2 Cl
	232.0848	0.5	2.2	8.0	2775863.5	C12 H12 N2 O3

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

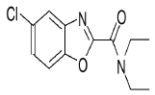
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-04-OS0310

Sample Serial Number: HBSF-HT-8

Operator: Li



3m

Date: 2011/04/28
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
160 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
252.0665	252.0666	-0.1	-0.4	7.0	5546559.0	C12 H13 N2 O2 Cl
	252.0661	0.4	1.6	11.5	2773647.5	C15 H10 N O3

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

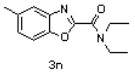
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-05-OS0468

Sample Serial Number: HBSF-HT-Sample-3

Operator: Li



3n

Date: 2011/06/20
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
524 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 F: 0-1 S: 0-1 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
232.1211	232.1212	-0.1	-0.4	7.0	5546214.5	C13 H16 N2 O2
	232.1217	-0.6	-2.6	2.5	5546232.0	C10 H19 N3 O Cl

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-T11-05-OS0466

Sample Serial Number: HBSF-HT-Sample-1

Operator: Li

3o

Date: 2011/06/20
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
177 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 S: 0-1 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
156.0355	156.0357	-0.2	-1.3	4.0	23.7	C6 H8 N2 O S
	156.0362	-0.7	-4.5	-0.5	902.8	C3 H11 N3 S Cl

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

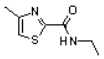
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-05-OS0467

Sample Serial Number: HBSF-HT-Sample-2

Operator: Li



3p

Date: 2011/06/20
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
355 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 F: 0-1 S: 0-1 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
170.0510	170.0510	0.0	0.0	0.0	424.7	C6 H12 O2 F Cl
	170.0514	-0.4	-2.4	4.0	7.6	C7 H10 N2 O S

Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry

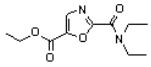
Chinese Academic of Sciences
High Resolution MS Data Report

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

Card Serial Number: GCT-P-T11-05-OS0469

Sample Serial Number: HBSF-HT-Sample-4

Operator: Li



3q

Date: 2011/06/20
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
534 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-80 N: 0-4 O: 0-4 F: 0-1 S: 0-1 Cl: 0-1

Minimum:				-1.5		
Maximum:		1.5	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
240.1114	240.1115	-0.1	-0.4	0.0	5546106.0	C11 H22 F S Cl
	240.1115	-0.1	-0.4	0.5	5546105.0	C8 H19 N3 O3 Cl
	240.1110	0.4	1.7	5.0	5546085.5	C11 H16 N2 O4

3. References

[1] Z.-X. Zhang, Z.-W. Yin, J. F. Kadow, N. A. Meanwell and T. Wang, *Synlett*, 2004, **13**, 2323–2326.

[2] Z.-X. Zhang, Z.-W. Yin, J. F. Kadow, N. A. Meanwell and T. Wang, *J. Org. Chem.*, 2004, **69**, 1360–1363.