# Electronic Supplementary Information

## *for*

# $S_8$-Promoted Triple Cleavage of Bromodifluoro Compounds for the Assembly of *N*-containing Heterocycles

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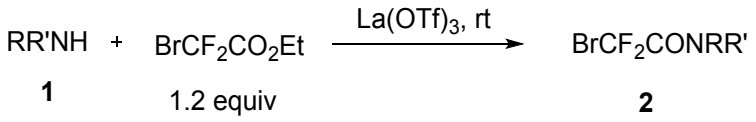
## 1. General information

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. Unless stated otherwise, reactions were performed in oven-dried or flame-dried glassware using a Schlenkline under a nitrogen atmosphere. All solvents were commercially obtained, and reactions were performed without specific drying of solvents. Flash column chromatography was performed over silica gel (200-300 mesh). $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz $^{1}$H, 125 MHz $^{13}$C) at room temperature. Chemical shifts were

reported in ppm on the scale relative to $CDCl_3$ ($\delta$ = 7.26 for $^{1}$H-NMR , $\delta$ = 77.00 for $^{13}$C-NMR) as an internal reference. Coupling constants (*J*) were reported in Hertz (Hz). The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument.

## 2. General procedure for starting materials

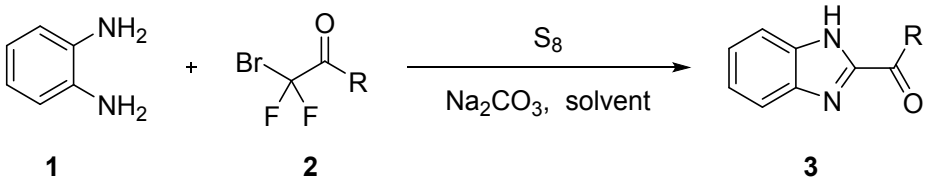
### General procedure for the synthesis of bromodifluoroacetamides




To a round-bottom flask equipped with stir bar was added amine (5 mmol) under argon, then ethyl bromodifluoroacetate (1.2 equiv) was added with lanthanum trifluoromethanesulfonate (5 mol %). The mixture was stirred at the room temperature and monitored by TLC. After the amine was exhausted, the mixture was extracted with AcOEt, and then the extract was washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel to give the corresponding amide **2**.

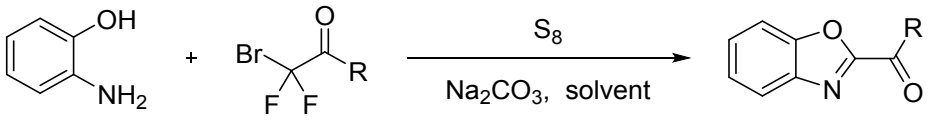
## 3. General process for the synthesis of 2-carbonylbenzoxazole

### General process for the synthesis of 2-carbonylbenzimidazole （1）




To a mixture of O-phenylenediamine **1** (0.3 mmol, 1.0 equiv), $S_8$ (15.39 mg, 20 mol %) and $Na_2CO_3$ (95.4 mg, 3 equiv) with $BrCF_2COR$ (1.2 equiv) was added MeCN (1 mL). The resulting mixture was heated to 130 °C. After 16 h, the mixture was cooled to room temperature. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography to give the desired product **3**.

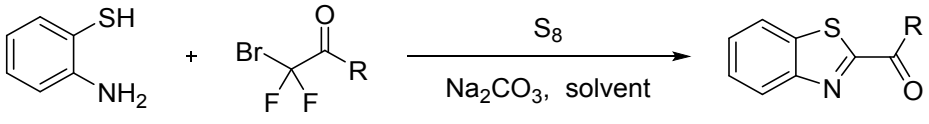
## General process for the synthesis of 2-carbonylbenzoxazole（2）




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

To a mixture of O-aminophenol **1** (0.3 mmol, 1.0 equiv), $S_8$ (15.39 mg, 20 mol %) and $Na_2CO_3$ (95.4 mg, 3 equiv) with $BrCF_2COR$ (1.2 equiv) was added MeCN (2 mL). The resulting mixture was heated to 120 °C. After 12 h, the mixture was cooled to room temperature. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography to give the desired product **3**.

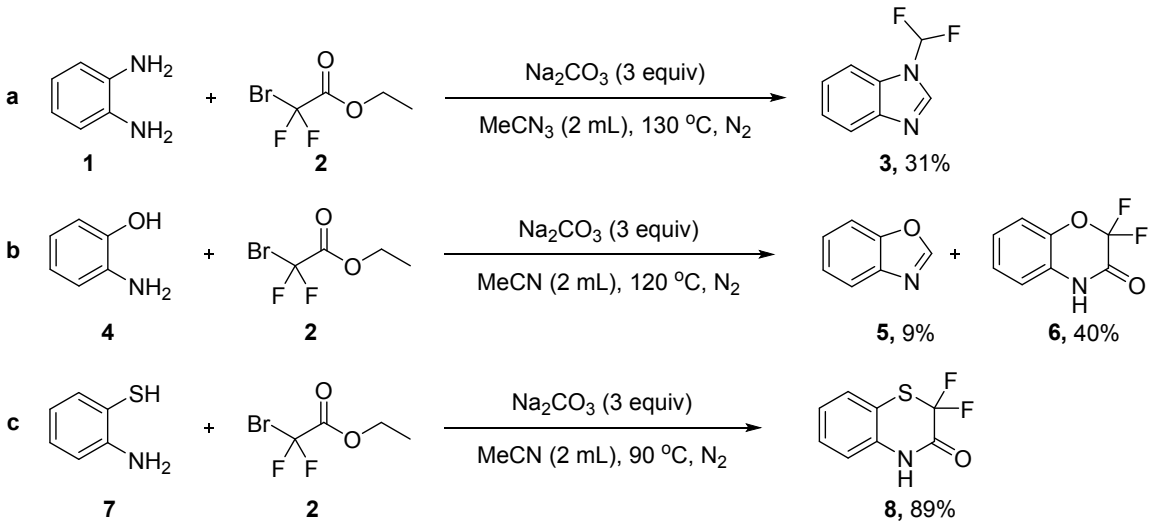
## General process for the synthesis of 2-carbonylbenzothiazole（3）




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

To a mixture of O-aminothiophenol **1** (0.2 mmol, 1.0 equiv), $S_8$ (5.12 mg, 10 mol %) and $Na_2CO_3$ (63.6 mg, 3 equiv) with $BrCF_2COR$ (1.2 equiv) was added MeCN (2 mL). The resulting mixture was heated to 90 °C. After 12 h, the mixture was cooled to room temperature. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography to give the desired product **3**.

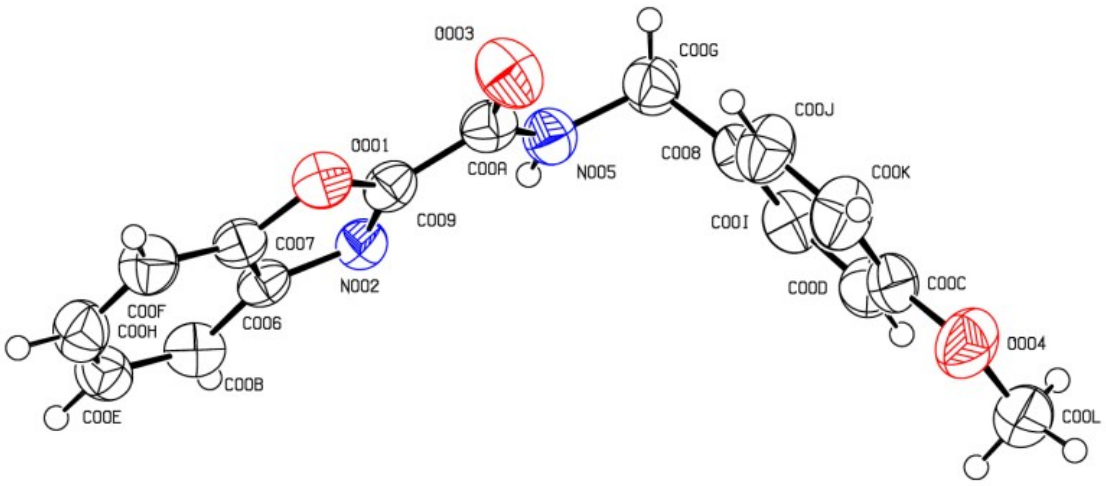
## 4. Control experiments




## 5. Crystal Structure

### Crystal Structure of 5h (1)

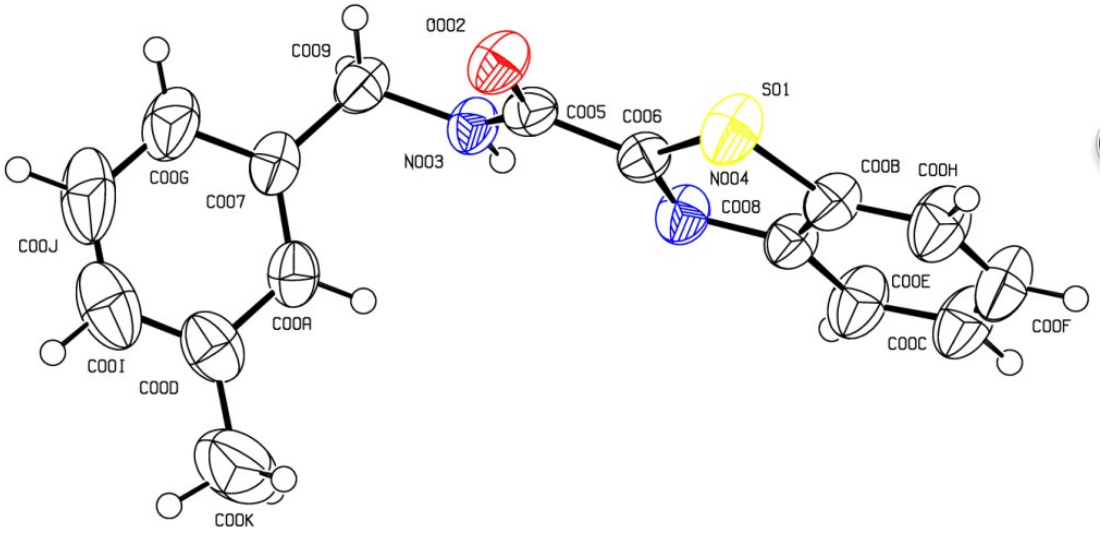
Crystallographic data for compound **5h** (CCDC-1883275) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



```
Bond precision:  C-C = 0.0031 A          Wavelength=0.71073

Cell:          a=6.3315(8)       b=6.8983(9)       c=16.780(2)
               alpha=97.492(10)  beta=98.979(10)   gamma=100.301(11)
Temperature:   298 K

                 Calculated                Reported
Volume           702.73(16)                702.72(16)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C16 H14 N2 O3             C16 H14 N2 O3
Sum formula      C16 H14 N2 O3             C16 H14 N2 O3
Mr               282.29                    282.30
Dx,g cm-3        1.334                     1.334
Z                2                         2
Mu (mm-1)        0.094                     0.094
F000             296.0                     296.2
F000'            296.14
h,k,lmax         7,8,19                    7,8,19
Nref             2478                      2474
Tmin,Tmax                                  0.524,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.524 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 24.990

R(reflections)= 0.0492( 1783)     wR2(reflections)= 0.1539( 2474)

S = 0.929                 Npar= 190
```

**Crystal Structure of 7h (2)**

Crystallographic data for compound **7h** (CCDC-1883277) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).




Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=8.4561(8) b=18.2584(11) c=9.6555(7)
alpha=90 beta=99.111(7) gamma=90
Temperature: 298 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1472.0(2) | 1472.0(2) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C16 H14 N2 O S | C16 H14 N2 O S |
| Sum formula | C16 H14 N2 O S | C16 H14 N2 O S |
| Mr | 282.35 | 282.37 |
| Dx,g cm-3 | 1.274 | 1.274 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.216 | 0.216 |
| F000 | 592.0 | 592.7 |
| F000' | 592.70 | |
| h,k,lmax | 10,21,11 | 10,21,11 |
| Nref | 2593 | 2586 |
| Tmin,Tmax | | 0.766,1.000 |
| Tmin' | | |

Correction method= # Reported T Limits: Tmin=0.766 Tmax=1.000
AbsCorr = MULTI-SCAN

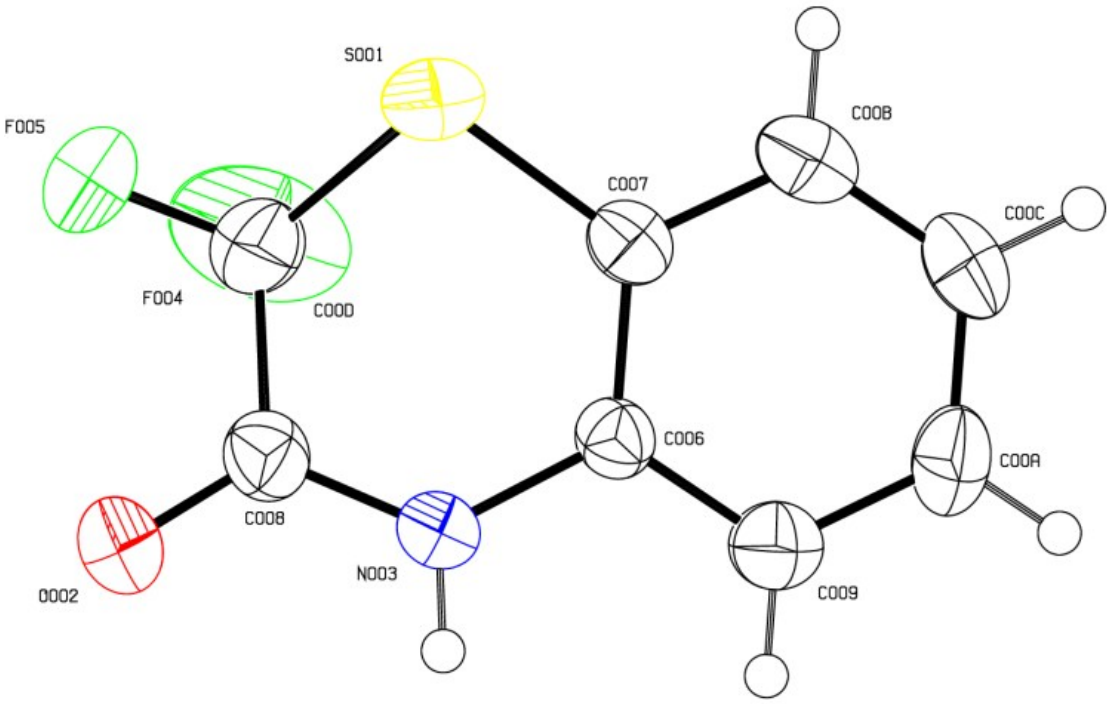
Data completeness= 0.997 Theta(max)= 25.000

R(reflections)= 0.0471( 1874) wR2(reflections)= 0.1584( 2586)

S = 0.998 Npar= 181

**Crystal Structure of S4-c7 (3)**

Crystallographic data for compound **S4-c7** (CCDC-1875544) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0057 A Wavelength=0.71073

Cell: a=6.9739(6) b=16.0078(17) c=7.5851(8)
alpha=90 beta=98.787(9) gamma=90
Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 836.84(15) | 836.84(15) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | : -P 2ybc | -P 2ybc |
| Moiety formula | C8 H5 F2 N O S | C8 H5 F2 N O S |
| Sum formula | C8 H5 F2 N O S | C8 H5 F2 N O S |
| Mr | 201.19 | 201.19 |
| Dx,g cm-3 | 1.597 | 1.597 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.374 | 0.374 |
| F000 | 408.0 | 408.0 |
| F000' | 408.75 | |
| h,k,lmax | 8,19,9 | 8,19,9 |
| Nref | 1465 | 1461 |
| Tmin,Tmax | | 0.862,1.000 |
| Tmin' | | |

Correction method= # Reported T Limits: Tmin=0.862 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 24.994

R(reflections)= 0.0894( 1154) wR2(reflections)= 0.2188( 1461)

S = 1.396 Npar= 118

## 6. Computation

### Complete Reference for Gaussian 09 （1）

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

### Computational Methods （2）

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3-LYP[2] with a standard 6–31G(d) basis set was used for geometry optimizations. Harmonic vibrational frequency calculations were performed for all of the stationary points to confirm them as a local minima or transition structures, and to derive the thermochemical corrections for the enthalpies and free energies. The M11[3] functional in combination with the 6–311+G(d,p) basis set was used to calculate the solvation single point energies to give more accurate energy information. The solvent effects were considered by single point calculations on the gas-phase stationary points with an SMD[4] solvation model in the acetonitrile solvent.

**Absolute Calculation Energies, Enthalpies, and Free Energies （3）**

| Geometry | $E_{(elec\text{-}B3LYP)}$[1] | $G_{(corr\text{-}B3LYP)}$[2] | $H_{(corr\text{-}B3LYP)}$[3] | $E_{(solv,\ M11)}$[4] | IF[5] |
|---|---|---|---|---|---|
| **I** | -3870.793318 | 0.065287 | 0.140946 | -3870.810277 | - |
| **TS** | -4316.483541 | 0.120500 | 0.213145 | -4316.502257 | -520.06 |
| **II** | -4316.589433 | 0.122465 | 0.216572 | -4316.604421 | - |
| **2** | -3017.779291 | 0.041354 | 0.087197 | -3020.213226 | - |
| **$CO_3^{2-}$** | -263.580371 | -0.011581 | 0.018134 | -264.035249 | - |
| **$HCO_3^-$** | -264.42022 | 0.00048 | 0.03072 | -264.555088 | - |
| **$Br^-$** | -2571.464366 | -0.016176 | 0.00236 | -2574.003173 | - |

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M11 in diethylether solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.

**B3LYP Geometries for All the Optimized Compounds and Transition State （4）**

**I**

| | | | |
|---|---|---|---|
| S | -2.31106300 | -0.03086500 | 1.62448600 |
| C | -3.70183700 | -0.18714100 | 0.53278800 |
| C | -4.48238000 | 0.94894800 | 0.17617100 |
| C | -4.08215700 | -1.44731300 | 0.04422600 |
| C | -5.62560300 | 0.76586900 | -0.62249900 |
| C | -5.21369100 | -1.61507500 | -0.75344900 |
| H | -3.47177400 | -2.30285500 | 0.31728600 |
| C | -5.98764000 | -0.49830500 | -1.08062400 |
| H | -6.22135300 | 1.63614400 | -0.89384200 |
| H | -5.48713800 | -2.60329400 | -1.11428800 |
| H | -6.87608000 | -0.60801400 | -1.69914400 |
| N | -4.09828700 | 2.22233400 | 0.57361400 |
| H | -4.84899700 | 2.88752900 | 0.70356800 |
| H | -3.41022300 | 2.22221100 | 1.32060400 |
| S | 2.96203300 | 2.37096700 | 0.22299300 |
| S | 4.46809600 | 0.99769300 | -0.36405500 |
| S | 1.31915500 | 2.25909700 | -0.99579400 |
| S | 4.29965800 | -0.82791700 | 0.70664600 |
| S | -0.46926400 | 0.64789300 | 0.21244500 |
| S | 3.19300200 | -2.22933500 | -0.40810900 |
| S | -0.07462100 | -1.11343000 | -0.82271400 |
| S | 1.21071800 | -2.36097400 | 0.29728200 |

**TS**

| | | | |
|---|---|---|---|
| S | -1.97333400 | -2.57277000 | 1.68947600 |
| C | -2.75877000 | -1.95149300 | 0.24051000 |
| C | -3.04712200 | -0.54812400 | 0.06123400 |
| C | -3.18110900 | -2.90749200 | -0.70754900 |
| C | -3.79713800 | -0.21637500 | -1.11315800 |
| C | -3.90780700 | -2.53817900 | -1.82755900 |
| H | -2.92932000 | -3.95053700 | -0.53425600 |
| C | -4.20447700 | -1.17303900 | -2.01949000 |
| H | -4.00992500 | 0.83393300 | -1.27939600 |

| | | | |
|---|---|---|---|
| H | -4.23446700 | -3.28551800 | -2.54564500 |
| H | -4.76463100 | -0.86370500 | -2.90025800 |
| N | -2.65640300 | 0.44880100 | 0.88333900 |
| H | -2.12234400 | 0.05541200 | 1.66098200 |
| S | 1.91615600 | -2.34719700 | -1.19567700 |
| S | 3.90241600 | -1.71721400 | -0.68621700 |
| S | 1.22435400 | -3.31620600 | 0.53307300 |
| S | 4.16489300 | 0.33557200 | -0.79413700 |
| S | 0.10140200 | -2.00373900 | 1.74186500 |
| S | 3.22409400 | 1.20654600 | 0.95082300 |
| S | 0.88603900 | 2.88563600 | -1.03625900 |
| S | 2.39745100 | 3.05980800 | 0.32134400 |
| C | -0.90836500 | 1.52766600 | 0.00867100 |
| F | -0.71320400 | 0.59124100 | -0.88060200 |
| C | -1.90397400 | 2.62276600 | -0.20027900 |
| O | -2.43284500 | 2.79405100 | -1.29010100 |
| N | -2.09552300 | 3.41344300 | 0.90145800 |
| H | -1.87097500 | 2.97848800 | 1.78612800 |
| C | -3.21101100 | 4.34167100 | 0.90057200 |
| H | -3.06338300 | 5.08432600 | 1.69084900 |
| H | -3.24039600 | 4.84689000 | -0.06625700 |
| H | -4.17499100 | 3.83516400 | 1.05471500 |
| F | -0.26904200 | 1.36943000 | 1.15993500 |

**II**

| | | | |
|---|---|---|---|
| S | 1.31957000 | -1.05554000 | 1.49490500 |
| C | 2.55794600 | -1.87695800 | 0.51914300 |
| C | 3.38840400 | -1.16043800 | -0.37921800 |
| C | 2.77846300 | -3.25885500 | 0.65910700 |
| C | 4.42028400 | -1.81083500 | -1.06304000 |
| C | 3.80583900 | -3.90394800 | -0.02667300 |
| H | 2.13743800 | -3.81526900 | 1.33629400 |
| C | 4.63808200 | -3.17555400 | -0.88089700 |
| H | 5.03901500 | -1.23100400 | -1.74054000 |
| H | 3.95846500 | -4.97218500 | 0.10872200 |
| H | 5.44426200 | -3.66954900 | -1.41790200 |
| N | 3.15495500 | 0.22364200 | -0.60087300 |
| H | 2.21138700 | 0.47897800 | -0.32599900 |
| S | -4.51181400 | -1.89122500 | 0.71905300 |
| S | -5.60697800 | -0.30037800 | -0.15316600 |
| S | -3.00254800 | -2.51640900 | -0.52578000 |
| S | -4.83437500 | 1.55986400 | 0.48185100 |
| S | -0.86492600 | -1.40684400 | 0.23135600 |
| S | -3.46767600 | 2.28832100 | -0.94446600 |
| S | -0.75187300 | 0.13665000 | -1.16801900 |
| S | -1.48570800 | 1.92847500 | -0.33170400 |
| C | 4.11634800 | 1.17253500 | -0.20311000 |
| F | 5.09539000 | 1.31664400 | -1.14474700 |
| C | 3.48515800 | 2.55827500 | 0.10008500 |
| O | 3.88581300 | 3.58079700 | -0.43395000 |
| N | 2.48868900 | 2.48787500 | 1.02263500 |
| H | 2.25949200 | 1.58860200 | 1.44020600 |
| C | 1.77866900 | 3.66720700 | 1.48389700 |
| H | 2.05941100 | 3.92584000 | 2.51321200 |
| H | 2.04574700 | 4.49564900 | 0.82601000 |
| H | 0.69774900 | 3.49976900 | 1.44181600 |
| F | 4.79806900 | 0.78524200 | 0.94665700 |

**$CO_3^{2-}$**

| | | | |
|---|---|---|---|
| C | -0.00000500 | -0.00004600 | 0.00001400 |
| O | 0.31103400 | -1.27573000 | 0.00003700 |
| O | -1.26040000 | 0.36853500 | 0.00000000 |
| O | 0.94936900 | 0.90723000 | -0.00004700 |

**$HCO_3^-$**

| | | | |
|---|---|---|---|
| C | 0.15861700 | 0.07240400 | 0.00029200 |
| O | -1.00658600 | -0.79737800 | -0.00005500 |
| O | -0.13913200 | 1.29196700 | -0.00008000 |
| O | 1.24135000 | -0.53203000 | -0.00008100 |
| H | -1.71675800 | -0.13489100 | -0.00002200 |

**2**

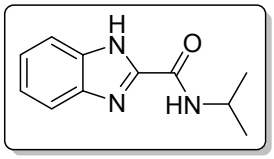
| | | | |
|---|---|---|---|
| C | -0.21555100 | 0.72923900 | 0.15174200 |
| F | -0.60973200 | 1.81511900 | -0.51438600 |
| C | 1.13816900 | 0.22061300 | -0.40454200 |
| O | 1.36314200 | 0.27417200 | -1.59933700 |
| N | 1.96133400 | -0.26984300 | 0.55286000 |
| H | 1.66910500 | -0.20281600 | 1.51704500 |
| C | 3.26878100 | -0.82333800 | 0.24036700 |
| H | 3.36204000 | -1.83797100 | 0.64185900 |
| H | 3.36436500 | -0.85391700 | -0.84561700 |
| H | 4.07029900 | -0.19992700 | 0.65283200 |
| F | -0.12978500 | 1.04688800 | 1.46982000 |
| Br | -1.58837200 | -0.67791400 | -0.04473600 |

**$Br^-$**

| | | | |
|---|---|---|---|
| Br | 0.00000000 | 0.00000000 | 0.00000000 |

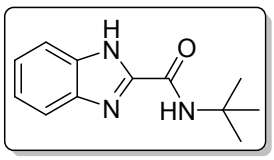
## 7. Characterization data for products

### N-isopropyl-1H-benzo[*d*]imidazole-2-carboxamide (3a) (CAS Number: 214962-82-0)



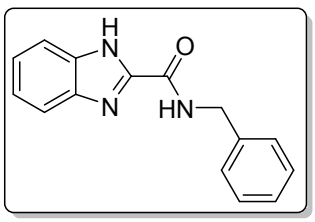
Compound **3a** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 89 % yield (54 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.24 (s, 1H), 8.71 (d, $J$ = 8.5 Hz, 1H), 7.71 (d, $J$ = 6.2 Hz, 1H), 7.54 (d, $J$ = 6.3 Hz, 1H), 7.34 – 7.20 (m, 2H), 4.28 – 4.03 (m, 1H), 1.20 (t, $J$ = 8.8 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO) δ 158.3, 146.4, 143.0, 134.9, 124.4, 122.8(d, $J$ = 21.2 Hz), 120.2, 113.0, 109.9, 41.3, 22.5.

### N-(tert-butyl)-1H-benzo[*d*]imidazole-2-carboxamide (3b) (CAS Number: 306992-74-5)



Compound **3b** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 93% yield (59 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.21 (s, 1H), 7.95 (s, 1H), 7.71 (d, $J$ = 6.1 Hz, 1H), 7.53 (d, $J$ = 6.1 Hz, 1H), 7.28 (d, $J$ = 6.8 Hz, 2H), 1.43 (s, 9H). $^{13}$C NMR (125 MHz, DMSO) δ 158.6, 146.7, 142.8, 135.0, 124.5, 123.0, 120.3, 113.0, 51.5, 28.9.

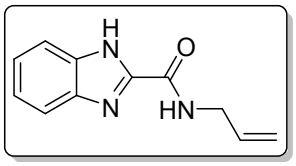
### N-benzyl-1H-benzo[*d*]imidazole-2-carboxamide (3c) (CAS Number: 82755-99-5 )



Compound **3c** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 55% yield (41 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 12.93 (s, 1H), 8.70 (t, $J$ = 5.5 Hz, 1H), 7.76 (d, $J$ = 5.2 Hz, 1H), 7.43 – 7.27 (m, 8H), 4.73 (d, $J$ = 6.1 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$)

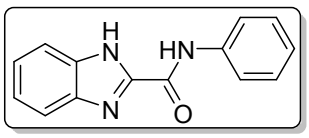
δ 159.8, 145.0, 142.7, 137.4, 134.5, 129.1, 128.8, 128.0 – 127.6, 125.0, 123.4, 120.3, 112.8, 43.8.

## N-allyl-1H-benzo[*d*]imidazole-2-carboxamide (3d) (CAS Number: 82755-98-4 )



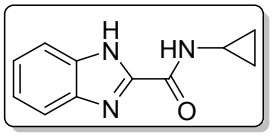
Compound **3d** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 75% yield (45 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.29 (s, 1H), 9.15 (t, *J* = 6.0 Hz, 1H), 7.78 – 7.49 (m, 2H), 7.28 (s, 2H), 5.96 – 5.85 (m, 1H), 5.19 – 5.14 (m, 1H), 5.10 – 5.06 (m, 1H), 3.94 (t, *J* = 5.6 Hz, 2H). $^{13}$C NMR (125 MHz, DMSO) δ 159.1, 146.1, 135.3, 123.8, 122.9 – 121.9, 120.3, 115.8, 113.1, 41.6.

## N-phenyl-1H-benzo[*d*]imidazole-2-carboxamide (3e) (CAS Number: 13745-42-1 )



Compound **3e** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 68% yield (48 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.49 (s, 1H), 10.92 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO) δ 157.8, 146.1, 143.0, 138.7, 135.2, 129.2, 124.9, 124.6, 123.2, 121.0, 120.5, 113.1.

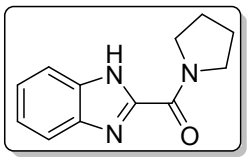
## N-cyclopropyl-1H-benzo[*d*]imidazole-2-carboxamide (3f) (CAS Number: 1531657-68-7 )



Compound **3f** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 32% yield (19 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.23 (s, 1H), 9.00 (d, *J* = 4.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.22 (m, 2H), 3.06 – 2.80 (m,

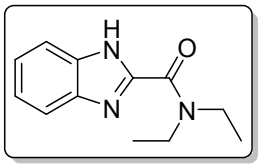
1H), 0.76 – 0.64 (m, 4H). $^{13}$C NMR (125 MHz, DMSO) δ 160.4, 146.1, 143.0, 134.9, 124.5, 122.9, 120.2, 113.0, 23.3, 6.1.

## (1H-benzo[*d*]imidazol-2-yl)(pyrrolidin-1-yl)methanone (3g) (CAS Number: 73902-99-5 )



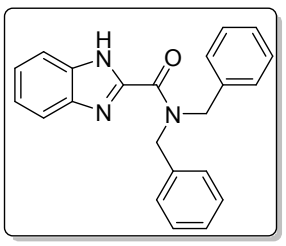
Compound **3g** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 74% yield (48 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.10 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.19 (m, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 3.57 (t, *J* = 6.9 Hz, 2H), 2.00 – 1.79 (m, 4H). $^{13}$C NMR (125 MHz, DMSO) δ 158.1, 146.7, 143.4 (s), 134., 124.6, 122.7, 120.8, 112.7, 49.3, 47.5, 26.6, 23.7.

## N,N-diethyl-1H-benzo[*d*]imidazole-2-carboxamide (3h) (CAS Number: 30183-06-3 )



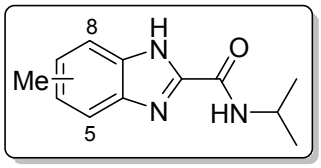
Compound **3h** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 45% yield (29 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.08 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.11 (m, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.50 (q, *J* = 7.1 Hz, 2H), 1.27 – 1.20 (m, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, DMSO) δ 159.5, 146.4, 143.1, 133.8, 124.5, 122.75, 120.7, 112.6, 43.0, 41.3, 15.1, 13.2.

## N,N-dibenzyl-1H-benzo[*d*]imidazole-2-carboxamide (3i) (CAS Number: 1222279-35-7 )



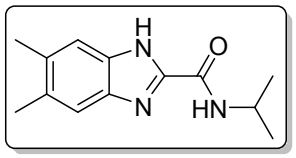
Compound **3i** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 91% yield (93 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.37 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.22 (m, 12H), 5.53 (s, 2H), 4.61 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ 160.4, 145.9, 142.9, 137.7, 137.2, 134.0, 129.1 (d, *J* = 8.6 Hz), 128.1 (d, *J* = 18.5 Hz), 127.8 , 124.9, 123.0, 120.8, 112.8, 51.1, 48.7.

## N-isopropyl-5-methyl-1H-benzo[*d*]imidazole-2-carboxamide (3j)



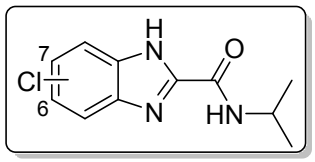

Compound **3j** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 64% yield (42 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.20 (d, *J* = 54.6 Hz, 1H), 8.74 – 8.37 (m, 1H), 7.57 – 7.28 (m, 1H), 7.20 – 7.01 (m, 2H), 4.26 – 4.11 (m, 1H), 2.56 (d, *J* = 25.2 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO) δ 158.4, 146.4, 145.6, 142.6, 134.5, 130.1, 124.8, 124.4, 123.2, 123., 117.5, 110.3, 41.3, 22.6, 17.5, 17.2. HRMS (ESI, m/z) calcd for $C_{12}H_{15}N_3O[M+H]^+$: 218.1288; found: 218.1289.

## N-isopropyl-5,6-dimethyl-1H-benzo[*d*]imidazole-2-carboxamide (3k)



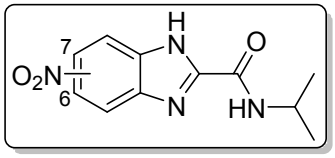

Compound **3k** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 77% yield (53 mg). $^{1}$H NMR (500 MHz, DMSO) δ 12.97 (s, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 82.8 Hz, 2H), 4.19 – 4.08 (m, 1H), 2.31 (s, 6H), 1.19 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO) δ 158.4, 145.5, 141.6, 133.5 , 131.6, 119.9, 112.7, 41.2, 22.5, 20.5. HRMS (ESI, m/z) calcd for $C_{13}H_{17}N_3O[M+H]^+$: 232.1444; found: 232.1445.

## 5-chloro-N-isopropyl-1H-benzo[*d*]imidazole-2-carboxamide (3l)



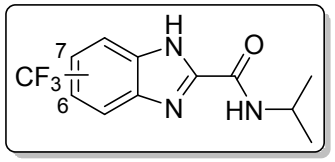

Compound **3l** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 68% yield (49 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.40 (d, *J* = 35.3 Hz, 1H), 8.84 – 8.68 (m, 1H), 7.79 – 7.60 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.22 (m, 1H), 4.20 – 4.09 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO) δ 157.9, 147.7, 147.4, 143.8, 141.7, 135.5, 133.7, 128.8, 127.3, 124.7, 123.5, 121.7, 119.5), 114.4, 112.6, 41.4, 22.5. HRMS (ESI, m/z) calcd for $C_{11}H_{12}ClN_3O[M+H]^+$: 238.0742; found: 238.0741.

## N-isopropyl-5-nitro-1H-benzo[*d*]imidazole-2-carboxamide (3m)



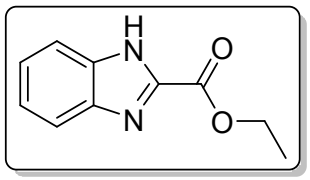
Compound **3m** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 57% yield (42 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.88 (s, 1H), 8.92 (d, *J* = 8.3 Hz, 1H), 8.44 (d, *J* = 88.8 Hz, 1H), 8.17 (s, 1H), 7.95 – 7.59 (m, 1H), 4.22 – 4.09 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO) δ 157.4, 119.8, 116.6, 113.6, 109.7, 41.6, 22.4.
HRMS (ESI, m/z) calcd for $C_{11}H_{12}FN_3O[M+H]^+$: 249.0982; found: 249.0980.

## N-isopropyl-5-(trifluoromethyl)-1H-benzo[*d*]imidazole-2-carboxamide (3n)



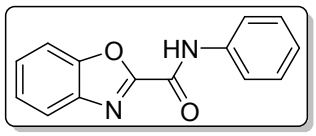
Compound **3n** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 30% yield (24 mg). $^{1}$H NMR (500 MHz, DMSO) δ 8.87 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 77.4 Hz, 2H), 7.63 – 7.57 (m, 1H), 4.21 – 4.13 (m, 1H), 1.21 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, DMSO) δ 157.7, 148.8, 128.5, 126.3, 124.2, 122.0, 120.4 (s), 41.5, 22.5. $^{19}$F NMR (471 MHz, DMSO) δ -59.19 (s). HRMS (ESI, m/z) calcd for $C_{12}H_{12}F_3N_3O[M+H]^+$: 272.1005; found: 272.1006.

## ethyl 1H-benzo[*d*]imidazole-2-carboxylate (3o) (CAS Number: 1865-09-4)



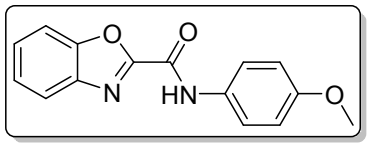
Compound **3o** was prepared according to the general procedure (petroleum ether/ethyl acetate = 5:1 v/v). The product was obtained as a yellow solid in 47% yield (27 mg). $^{1}$H NMR (500 MHz, DMSO) δ 13.48 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 4.45 – 4.37 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, DMSO) δ 159.8, 143.3, 142.2, 134.7, 125.5, 123.4, 121.2, 113.1, 62.1, 14.6.

## N-phenylbenzo[*d*]oxazole-2-carboxamide (5a) (CAS Number: 27411-63-8)



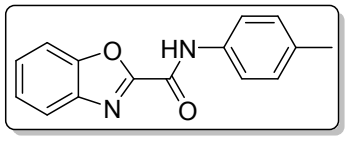
Compound **5a** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 73% yield (52 mg). $^{1}$H NMR (500 MHz, CDCl3) δ 9.13 (s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.69 – 7.57 (m, 1H), 7.52 – 7.46 (m, 1H), 7.46 – 7.34 (m, 3H), 7.23 – 7.06 (m, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.6, 153.26, 151.46, 140.06, 136.86, 129.3, 127.6, 125.6, 125.3, 121.3, 112.0, 112.0.

## N-(4-methoxyphenyl)benzo[*d*]oxazole-2-carboxamide (5b) (CAS Number: 56735-19-4)



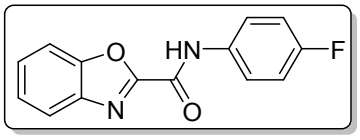
Compound **5b** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 68% yield (55 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.81 – 7.73 (m, 1H), 7.70 – 7.57 (m, 3H), 7.49 – 7.38 (m, 2H), 6.94 – 6.86 (m, 2H), 3.79 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 157.1, 155.7, 153.0, 151.3, 140.1, 130.0, 127.5, 125.7, 121.6, 121.2, 114.4, 111.9, 55.5.

## N-(p-tolyl)benzo[*d*]oxazole-2-carboxamide (5c) (CAS Number: 921782-65-2)



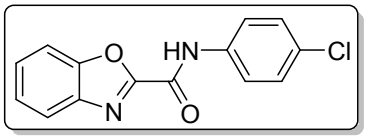
Compound **5c** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 61% yield (46 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.85 – 7.75 (m, 1H), 7.74 – 7.64 (m, 1H), 7.64 – 7.55 (m, 2H), 7.51 – 7.41 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7, 153.1, 151.4, 140.1, 135.1, 134.3, 129.8, 127.6, 125.7, 121.2, 119.9, 112.0, 21.0.

## N-(4-fluorophenyl)benzo[*d*]oxazole-2-carboxamide (5d) (CAS Number: 921505-14-8)



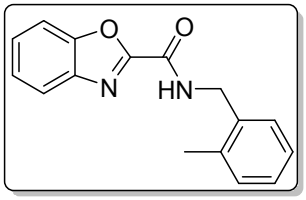

Compound **5d** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 70% yield (54 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.80 (t, *J* = 8.7 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.11 – 7.03 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 160.9, 158.9, 155.4, 153.2, 151.4, 140.0, 132.8, 127.7, 125.8, 121.7, 121.3, 116.1, 115.9, 112.0.$^{19}$F NMR (471 MHz, $CDCl_3$) δ -116.2 – -116.3.

## N-(4-chlorophenyl)benzo[*d*]oxazole-2-carboxamide (5e) (CAS Number: 27411-66-1)



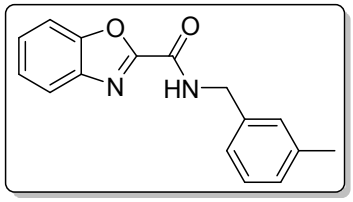

Compound **5e** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 72% yield (59 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.79 – 7.72 (m, 1H), 7.72 – 7.66 (m, 2H), 7.65 – 7.53 (m, 1H), 7.50 – 7.45 (m, 1H), 7.45 – 7.39 (m, 1H), 7.36 – 7.28 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.3, 153.2, 151.4 139.9, 135.4, 130.4, 129.3, 127.8, 125.8, 121.2, 111.9.

## *N*-(2-methylbenzyl)benzo[*d*]oxazole-2-carboxamide (5f)



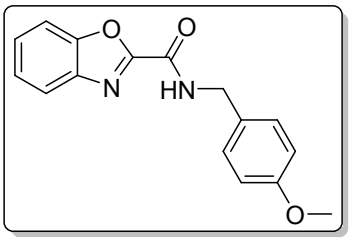

Compound **5f** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 60% yield (48 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.38 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.13 (m, 3H), 4.69 (d, *J* = 5.7 Hz, 2H), 2.39 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.4(d, *J* = 7.0 Hz), 151.2, 140.1, 136.6 , 134.6, 130.7 , 128.9 , 128.3, 127.4, 126.4, 125.6, 121.2, 111.9, 42.1, 19.1. HRMS (ESI, m/z) calcd for $C_{16}H_{15}N_2O_2[M+H]^+$: 267.1128; found: 267.1126.

## *N*-(3-methylbenzyl)benzo[*d*]oxazole-2-carboxamide (5g)



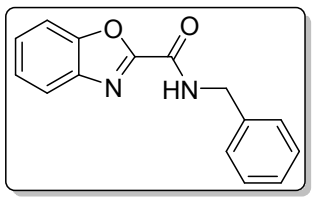
Compound **5g** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 64% yield (51 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, $J$ = 8.0 Hz, 1H), 7.66 (d, $J$ = 8.2 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.32 (d, $J$ = 7.2 Hz, 1H), 7.26 – 7.18 (m, 3H), 4.69 (d, $J$ = 5.7 Hz, 2H), 2.39 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.5(d, $J$ = 12.6 Hz), 151.2, 140.1, 138.7, 136.9, 128.7 (d, $J$ = 11.6 Hz), 127.4, 125.6, 125.1, 121.21, 111.8, 43.90, 21.4. HRMS (ESI, m/z) calcd for $C_{16}H_{15}N_2O_2[M+H]^+$: 267.1128; found: 267.1132.

## N-(4-methoxybenzyl)benzo[*d*]oxazole-2-carboxamide (5h)



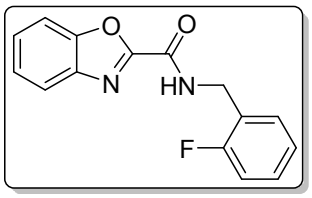
Compound **5h** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 70% yield (59 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 1H), 7.67 – 7.60 (m, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 1H), 7.27 (d, $J$ = 8.6 Hz, 2H), 6.86 (d, $J$ = 8.6 Hz, 2H), 4.61 (d, $J$ = 5.9 Hz, 2H), 3.78 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.3, 155.5, 151.1, 140.1, 129.4, 129.1, 127.4, 125., 121.2, 114.2, 111.8, 55.3, 43.4. HRMS (ESI, m/z) calcd for $C_{16}H_{14}N_2O_3[M+H]^+$: 283.1077; found: 283.1078.

## N-benzylbenzo[*d*]oxazole-2-carboxamide (5i) (CAS Number: 27383-78-4)



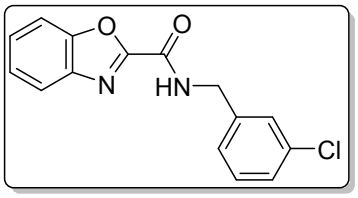
Compound **5i** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 61% yield (49 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 1H), 7.68 – 7.59 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 1H), 7.37 (s, 1H), 7.37 – 7.34 (m, 2H), 4.69 (d, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.6, 155.4, 151.2, 140.1, 137.0, 128.9, 128.0, 127.4, 125.6, 121.2, 111.9, 77.3, 77.1, 76.8, 43.9, 29.7.

## *N*-(2-fluorobenzyl)benzo[*d*]oxazole-2-carboxamide (5j)



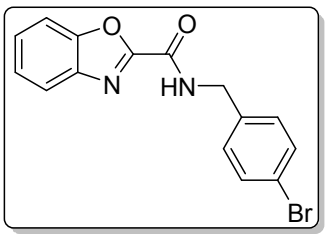

Compound **5j** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 62% yield (50 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.44 – 7.37 (m, 2H), 7.32 – 7.26 (m, 1H), 7.15 – 7.09 (m, 1H), 7.10 – 7.01 (m, 1H), 4.74 (d, *J* = 6.2 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 162.0, 160.1, 155.6, 155.3, 151.3, 140.5, 130.4 , 129.8, 127.4, 125.6, 124.5, 124.0, 121.2, 115.6, 115.5, 111.6, 37.8. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -60.4. HRMS (ESI, m/z) calcd for $C_{15}H_{11}FN_2O_2[M+H]^+$: 271.0877; found: 271.0878.

## *N*-(3-chlorobenzyl)benzo[*d*]oxazole-2-carboxamide (5k)



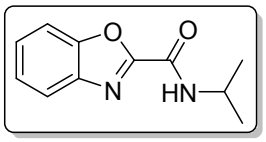

Compound **5k** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 57% yield (49 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.36 (s, 1H), 7.29 – 7.26 (m, 2H), 7.25 (d, *J* = 4.3 Hz, 1H), 4.67 (d, *J* = 6.2 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7, 155.2, 151.2, 140.1, 139.1, 134.7, 130.1, 128.1 , 127.5, 126.1, 125.7, 121.2, 111.9, 43.2. HRMS (ESI, m/z) calcd for $C_{15}H_{12}ClN_2O_2[M+H]^+$: 287.0582; found: 287.0584.

## N-(3-bromobenzyl)benzo[*d*]oxazole-2-carboxamide (5l)



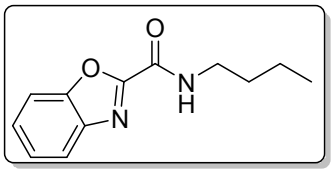

Compound **5l** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 67% yield (67 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75 – 7.69 (m, 1H), 7.66 – 7.56 (m, 1H), 7.49 (t, *J* = 1.6 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.43 – 7.33 (m, 2H), 7.29 – 7.26 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.65 (d, *J* = 6.2 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7, 155.2, 151.1, 140.0, 139.4, 131.0, 130.4, 127.5, 126.5, 125.6, 122.8, 121.2, 111.9, 43.2.HRMS (ESI, m/z) calcd for $C_{15}H_{11}BrN_2O_2[M+H]^+$: 331.0077; found: 331.0076.

## *N*-isopropylbenzo[*d*]oxazole-2-carboxamide (5m) (CAS Number: 27383-73-9)



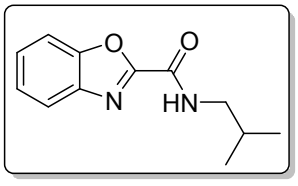
Compound **5m** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 54% yield (33 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.14 (s, 1H), 4.42 – 4.23 (m, 1H), 1.31 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7, 154.8, 151.1, 140.1, 127.3, 125.5, 121.1, 111.9, 42.2, 29.7, 22.6.

## *N*-butylbenzo[*d*]oxazole-2-carboxamide (5n) (CAS Number: 27383-75-1)



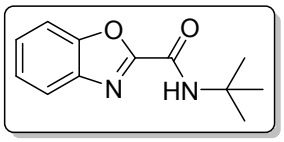
Compound **5n** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 59% yield (39 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.31 (s, 1H), 3.55 – 3.46 (m, 2H), 1.68 – 1.60 (m, 2H), 1.48 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7, 151.1, 140.2, 127.3, 125.5, 121.1, 111.9, 39.6, 31.4, 29.7, 20.0, 13.7.

## N-isobutylbenzo[*d*]oxazole-2-carboxamide (5o) (CAS Number: 27383-76-2)



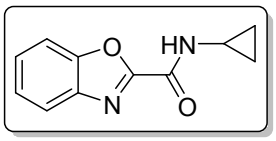
Compound **5o** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow oil in 49% yield (32 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.49 – 7.40 (m, 2H), 7.37 (s, 1H), 3.38 – 3.31 (m, 2H), 1.99 – 1.89 (m, 1H), 1.02 – 0.97 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7 (d, *J* = 14.4 Hz), 151.1, 140.1, 127.3, 125.5, 121.1 , 111.9, 47.1, 29.7, 28.6, 20.1.

## N-(tert-butyl)benzo[*d*]oxazole-2-carboxamide (5p) (CAS Number: 95114-65-1)



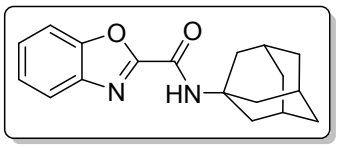
Compound **5p** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 39% yield (26 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 1H), 7.68 – 7.55 (m, 1H), 7.51 – 7.32 (m, 2H), 7.15 (s, 1H), 1.50 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 156.1, 154.8, 151.2, 140.1, 127.2, 125, 121.0, 111.8, 52.4, 28.6.

## N-cyclopropylbenzo[*d*]oxazole-2-carboxamide (5q) (CAS Number: 1511739-08-4)



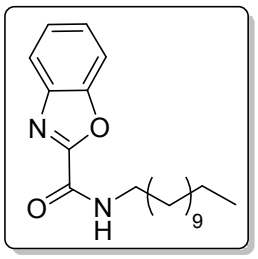
Compound **5q** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 67% yield (41 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, $J$ = 7.7 Hz, 1H), 7.62 (d, $J$ = 8.1 Hz, 1H), 7.48 – 7.34 (m, 3H), 3.02 – 2.88 (m, 1H), 0.93 – 0.88 (m, 2H), 0.73 – 0.69 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 156.9, 155.4, 151.1, 140.1, 127.4, 125.5, 121.1, 111.9, 22.9, 6.8.

## N-((3s,5s,7s)-adamantan-1-yl)benzo[*d*]oxazole-2-carboxamide (5r)



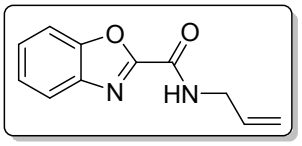
Compound **5r** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 44% yield (39 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 1H), 7.63 (d, $J$ = 7.9 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.02 (s, 1H), 2.15 (s, 9H), 1.76 – 1.68 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 156.2, 154.4, 151.2, 140.2, 127.1, 125.4, 121.0, 111.8, 53.1, 41.3, 36.2, 29.4. HRMS (ESI, m/z) calcd for $C_{18}H_{21}N_2O_2[M+H]^+$: 297.1598; found: 297.1601.

## *N*-dodecylbenzo[*d*]oxazole-2-carboxamide (5s) (CAS Number: 50486-32-3)



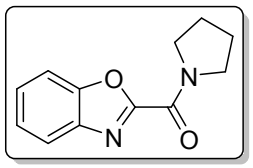
Compound **5s** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a white solid in 44% yield (44 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, $J$ = 7.4 Hz, 1H), 7.65 (d, $J$ = 8.2 Hz, 1H), 7.51 – 7.37 (m, 2H), 7.30 (s, 1H), 3.55 – 3.43 (m, 2H), 1.25 (s, 12H), 0.87 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.6 (d, $J$ = 2.7 Hz), 151.1, 140.2, 127.3, 125.5, 121.1, 111.9, 39.9, 31.9 , 29.7 – 29.2 , 26.9, 22.7, 14.1.

## *N*-allylbenzo[*d*]oxazole-2-carboxamide (5t) (CAS Number: 27383-71-7)



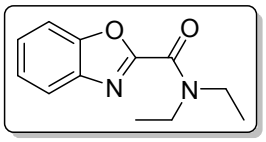
Compound **5t** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 45% yield (27 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.65 (d, $J$ = 8.1 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.45 – 7.35 (m, 2H), 6.02 – 5.85 (m, 1H), 5.36 – 5.27 (m, 1H), 5.27 – 5.17 (m, 1H), 4.16 – 4.11 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.5, 151.2, 140.1, 132.9, 127.4, 125.6, 121.2, 117.5, 111.9, 77.3, 77.0, 76.8, 42.1, 29.7.

## benzo[*d*]oxazol-2-yl(pyrrolidin-1-yl)methanone (5u) (CAS Number: 50486-33-4)



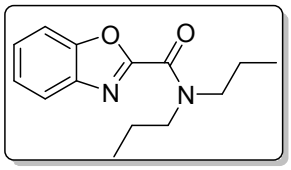
Compound **5u** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 63% yield (41 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 1H), 7.63 (d, $J$ = 8.1 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.41 – 7.35 (m, 1H), 4.11 (t, $J$ = 6.8 Hz, 2H), 3.73 (t, $J$ = 6.9 Hz, 2H), 2.06 – 1.99 (m, 2H), 1.99 – 1.91 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.7, 155.3, 150.0, 140.6, 127.1, 125.1, 121.4, 111.6, 49.3, 47.5, 26.5, 23.9.

## *N*,*N*-diethylbenzo[*d*]oxazole-2-carboxamide (5v) (CAS Number: 27383-70-6)



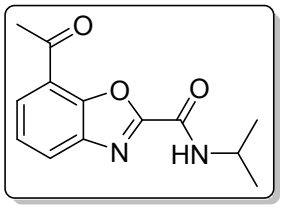
Compound **5v** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow oil in 38% yield (25 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.33 (m, 2H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.61 (q, *J* = 7.1 Hz, 2H), 1.34 – 1.26 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 157.2, 155.4, 149.9, 140.4, 126.9, 125.1, 121.3, 111.5, 43.4, 41.3, 14.6, 12.6.

## N,N-dipropylbenzo[*d*]oxazole-2-carboxamide (5w) (CAS Number: 27383-74-0)



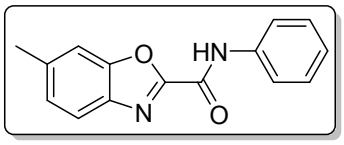
Compound **5w** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow oil in 39% yield (29 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.38 (m, 2H), 3.77 – 3.72 (m, 2H), 3.53 – 3.48 (m, 2H), 1.74 – 1.70 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 157.7, 155.5, 149.9, 140.3, 126.8, 125.1, 121.2, 111.4, 50.5, 48.5 , 22.4, 20.6, 11.4 11.0.

## 6-acetyl-N-isopropylbenzo[*d*]oxazole-2-carboxamide (5x)



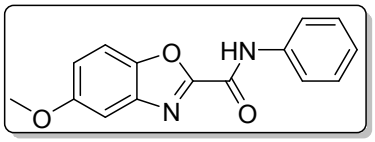
Compound **5x** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 43% yield (32 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 1H), 8.00 – 7.85 (m, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 4.47 – 4.18 (m, 1H), 2.89 (s, 3H), 1.32 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.4, 156.2, 154.2, 149.6, 141.3, 127.8, 126.1, 125.6, 122.7, 42.4, 30.7, 29.7, 22.5. HRMS (ESI, m/z) calcd for $C_{13}H_{15}N_2O_3[M+H]^+$: 247.1077; found: 247.1079.

## 6-methyl-N-phenylbenzo[*d*]oxazole-2-carboxamide (5y) (CAS Number: 1539536-18-9)



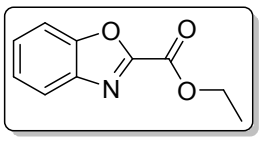

Compound **5z** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a white solid in 68% yield (51 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.75 – 7.72 (m, 2H), 7.68 – 7.64 (m, 1H), 7.45 (s, 1H), 7.42 – 7.37 (m, 2H), 7.25 (d, *J* = 9.8 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.51 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 155.1, 153.4, 151.8, 138.6, 137.9, 136.9, 129.3, 127.3, 125.2, 120.5, 119.9, 111.9, 22.0.

## 5-methoxy-N-phenylbenzo[*d*]oxazole-2-carboxamide (5z) (CAS Number: 1504693-37-1)



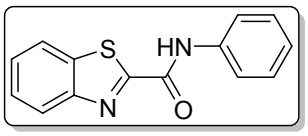

Compound **5za** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 34% yield (27 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.05 (m, 1H), 3.87 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 158.2, 156.1, 153.2, 146.2, 140.9, 136.8, 129.3, 125.3, 119.9, 117.2, 112.2, 103.0, 56.0.

## ethyl benzo[*d*]oxazole-2-carboxylate (5za) (CAS Number: 27383-87-5)



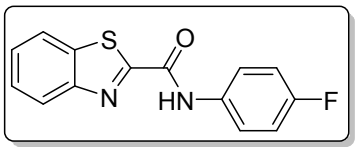

Compound **5zd** was prepared according to the general procedure (petroleum ether/ethyl acetate = 10:1 v/v). The product was obtained as a yellow solid in 42% yield (24 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.48 – 7.40 (m, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 156.5, 152.8, 150.9, 140.5, 128.2, 125.8, 122.2, 111.8, 63.3, 14.2.

## N-phenylbenzo[*d*]thiazole-2-carboxamide (7a) (CAS Number: 68070-62-2)



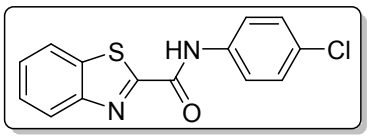
Compound **7a** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 85% yield (43 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.48 (m, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.1, 157.6, 152.7, 137.4, 137.0, 129.3, 127.0, 125.0, 124.4, 122.5, 119.8.

## N-(4-fluorophenyl)benzo[*d*]thiazole-2-carboxamide (7b) (CAS Number: 801242-43-3)



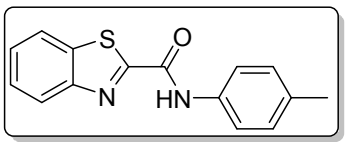
Compound **7b** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a white solid in 80% yield (44 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.67 (m, 2H), 7.59 – 7.56 (m, 1H), 7.54 – 7.48 (m, 1H), 7.11 – 7.07 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.8, 160.7, 158.8, 157.6, 152.6, 137.4, 133.1, 127.1, 124.4, 122.6 – 122.3, 121.6, 116.2, 116.0, 115.9. $^{19}$F NMR (471 MHz, $CDCl_3$) δ -116.89 (s).

## N-(4-chlorophenyl)benzo[*d*]thiazole-2-carboxamide (7c) (CAS Number: 847470-22-8)



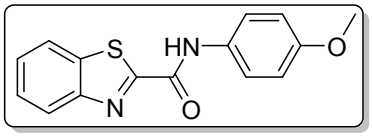
Compound **7c** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 65% yield (37 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.59 – 7.47 (m, 2H), 7.37 – 7.31 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.6, 157.6, 152.6, 137.4, 135.6, 130.0, 129.3, 127.1, 124.4, 122.5, 121.0.

## N-(p-tolyl)benzo[*d*]thiazole-2-carboxamide (7d) (CAS Number: 68070-63-3)



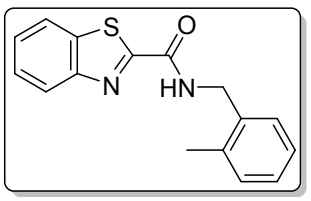
Compound **7d** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a white solid in 55% yield (30 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.13 – 8.09 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.59 – 7.55 (m, 1H), 7.53 – 7.49 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.3, 157.5, 152.7, 137.4, 134.7, 134.5, 129.8, 126.9, 124.3, 122.5, 120.5, 119.8, 21.0.

## N-(4-methoxyphenyl)benzo[*d*]thiazole-2-carboxamide(7e) (CAS Number: 722461-39-4)



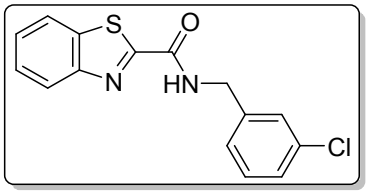
Compound **7e** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 83% yield (47 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.60 – 7.46 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.3, 157.3, 156.8, 152.7, 137.4, 130.2, 126.9, 124.3, 122.5, 121.4, 114.4, 55.5.

## N-(2-methylbenzyl)benzo[*d*]thiazole-2-carboxamide (7f)



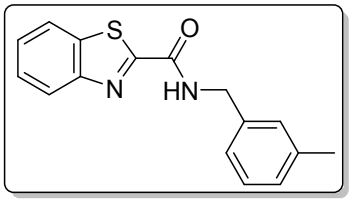
Compound **7f** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 90% yield (51 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 8.00 – 7.94 (m, 1H), 7.62 (s, 1H), 7.57 – 7.45 (m, 2H), 7.38 – 7.30 (m, 1H), 7.26 – 7.17 (m, 3H), 4.70 (d, *J* = 5.8 Hz, 2H), 2.40 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.7, 159.7, 152.9, 137.1, 136.6, 135.0, 130.7, 128.9, 128.1, 126.8, 126.4, 124.3, 122.4, 42.1, 19. HRMS (ESI, m/z) calcd for $C_{16}H_{15}N_2OS[M+H]^+$: 283.0900; found: 283.0897.

## N-(3-chlorobenzyl)benzo[*d*]thiazole-2-carboxamide (7g)



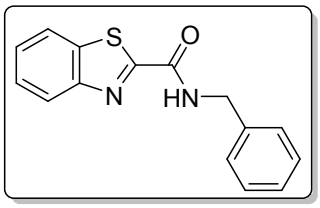
Compound **7g** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a colorless oil in 57% yield (34 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 1H), 8.00 – 7.94 (m, 1H), 7.87 (s, 1H), 7.56 – 7.47 (m, 2H), 7.36 (s, 1H), 7.28 – 7.25 (m, 3H), 4.66 (d, $J$ = 6.2 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.4, 160.0, 152.8, 139.5, 137.1, 134.7, 130.1, 128.0 (t, $J$ = 3.6 Hz), 126.9 (d, $J$ = 6.4 Hz), 126.1, 124.3, 122.4, 43.3. HRMS (ESI, m/z) calcd for $C_{15}H_{11}ClN_2OS[M+H]^+$: 303.0353; found: 303.0354.

## N-(3-methylbenzyl)benzo[*d*]thiazole-2-carboxamide (7h)



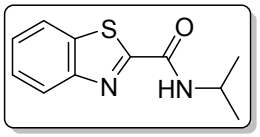
Compound **7h** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 84% yield (47 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 1H), 8.00 – 7.95 (m, 1H), 7.78 (s, 1H), 7.59 – 7.43 (m, 2H), 7.25 (2, $J$ = 7.4, 4.6 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.15 – 7.08 (m, 1H), 4.66 (d, $J$ = 6.0 Hz, 2H), 2.35 (d, $J$ = 5.7 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.8, 159.8, 152.9, 138.6, 137.2, 128.8, 128.6, 126.8, 125.1, 124.3, 122.4, 43.9, 21.4. HRMS (ESI, m/z) calcd for $C_{16}H_{15}N_2OS[M+H]^+$: 283.0900; found: 283.0904.

## N-benzylbenzo[*d*]thiazole-2-carboxamide (7i) (CAS Number: 148149-23-9)



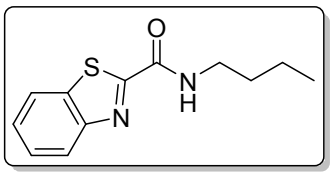
Compound **7i** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 55% yield (30 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, $J$ = 8.2 Hz, 1H), 7.97 (d, $J$ = 7.9 Hz, 1H), 7.79 (s, 1H), 7.57 – 7.46 (m, 2H), 7.42 – 7.34 (m, 4H), 7.32 (d, $J$ = 6.9 Hz, 1H), 4.70 (d, $J$ = 6.1 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.6, 159.8, 152.9, 137.4, 137.1, 128.9, 128.1 – 127.6, 126.8, 124.8, 122.4, 43.9).

## N-isopropylbenzo[*d*]thiazole-2-carboxamide (7j) (CAS Number: 41124-28-1)



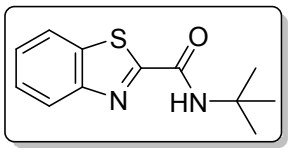
Compound **7j** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 54% yield (24 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 1H), 7.99 – 7.85 (m, 1H), 7.56 – 7.51 (m, 1H), 7.51 – 7.45 (m, 1H), 7.28 (d, *J* = 5.2 Hz, 1H), 4.36 – 4.23 (m, 1H), 1.32 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.5, 159.0, 152.9, 137.1, 126.7, 124.1 122.4, 42.2, 22.7.

## N-butylbenzo[*d*]thiazole-2-carboxamide (7k) (CAS Number: 41039-01-4)



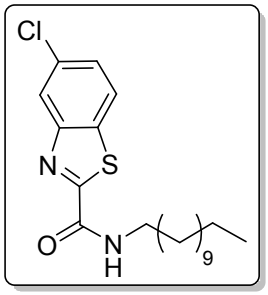
Compound **7k** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 78 % yield (37 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.39 (m, 2H), 3.55 – 3.47 (m, 2H), 1.69 – 1.62 (m, 2H), 1.49 – 1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.3, 159.9, 152.9, 137.1, 126.7, 124.2, 122.4, 39.6, 31.6, 20.1, 13.7.

## N-(tert-butyl)benzo[*d*]thiazole-2-carboxamide (7l) (CAS Number: 41039-02-5)



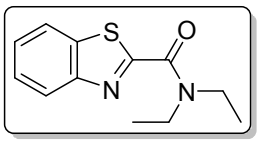
Compound **7l** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow oil in 77 % yield (36 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.84 (m, 1H), 7.61 – 7.50 (m, 1H), 7.49 – 7.41 (m, 1H), 7.33 (s, 1H), 1.52 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.6, 159.0, 152.9, 137.2, 126.7, 126.5, 124.1, 122.4, 52.1, 28.7.

## 5-chloro-N-dodecylbenzo[d]thiazole-2-carboxamide (7m)



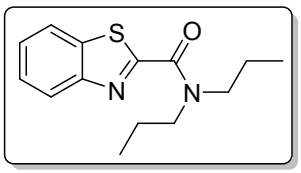
Compound **7m** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 76 % yield (25 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.51 – 7.44 (m, 2H), 3.52 – 3.46 (m, 2H), 1.24 (s, 18H), 0.89 – 0.84 (m, 5H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.2, 159.8, 152.9, 137.1, 126.7, 124.2, 122.4, 40.3, 39.9, 31.9, 29.7 – 29.1, 29.0, 26.9, 26.7, 22.7, 14.1. HRMS (ESI, m/z) calcd for $C_{20}H_{29}ClN_2OS[M+H]^+$: 381.1762; found: 381.1761.

## N,N-diethylbenzo[*d*]thiazole-2-carboxamide (7n) (CAS Number: 673485-50-2)



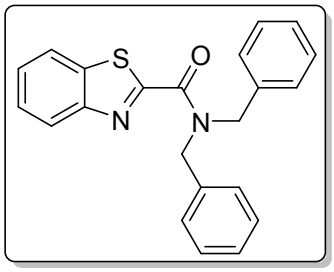
Compound **7n** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow oil in 41% yield (19 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 1H), 7.99 – 7.85 (m, 1H), 7.62 – 7.36 (m, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.60 (q, *J* = 7.1 Hz, 2H), 1.34 – 1.27 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.2, 160.6, 153.4, 136.2, 126.4, 124.6, 121.8, 43.2, 42.3, 14.6, 12.7.

## N,N-dipropylbenzo[*d*]thiazole-2-carboxamide (7o) (CAS Number: 1024441-13-1)



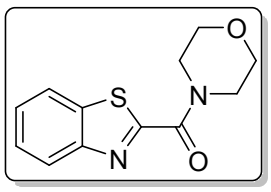
Compound **7o** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow oil in 38 % yield (20 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.41 (m, 2H), 4.08 – 3.91 (m, 2H), 3.58 – 3.42 (m, 2H), 1.82 – 1.68 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.4, 161.0, 153.4, 136.3, 126.4, 124.6, 121.8, 50.3, 49.8, 22.6, 20.8, 11.5, 11.0.

## N,N-dibenzylbenzo[*d*]thiazole-2-carboxamide (7p)



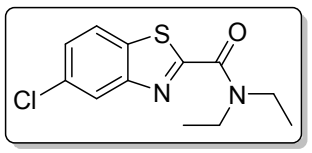
Compound **7p** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a white solid in 32 % yield (23 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 1H), 8.00 – 7.95 (m, 1H), 7.53 – 7.46 (m, 2H), 7.41 – 7.28 (m, 10H), 5.42 (s, 2H), 4.72 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.8, 161.5, 153.2, 136.8, 136.4 (d, $J$ = 15.4 Hz), 128.7 (d, $J$ = 18.0 Hz), 127.9, 127.7, 126.8, 126.5, 124.8, 121.8 50.5, 49.1. HRMS (ESI, m/z) calcd for $C_{22}H_{19}N_2OS[M+H]^+$: 359.1213; found: 359.1212.

## benzo[*d*]thiazol-2-yl(morpholino)methanone (7q) (CAS Number: 78224-61-0)



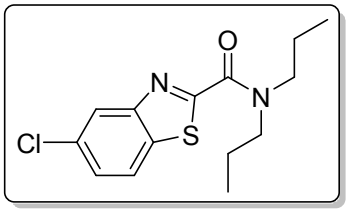
Compound **7m** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 72 % yield (36 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, $J$ = 8.1 Hz, 1H), 7.95 (d, $J$ = 7.8 Hz, 1H), 7.56 – 7.46 (m, 2H), 4.56 – 4.47 (m, 2H), 3.87 – 3.79 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 164.5, 159.7, 153.1, 136.2, 126.8, 126.6, 124.6, 121.87 (s), 67.2, 66.9, 47.2, 43.9.

## 5-chloro-N,N-diethylbenzo[*d*]thiazole-2-carboxamide (7r)



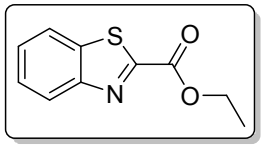
Compound **7r** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a white solid in 47% yield (25 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 1H), 7.90 – 7.82 (m, 1H), 7.49 – 7.41 (m, 1H), 4.05 (q, $J$ = 7.0 Hz, 2H), 3.59 (q, $J$ = 7.1 Hz, 2H), 1.34 – 1.27 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.2, 160.1, 154.2, 134.6, 132.4, 127.1, 124.3, 122.6, 43.2, 42.5, 14.6, 12.7. HRMS (ESI, m/z) calcd for $C_{16}H_{15}N_2OS[M+H]^+$: 269.0510; found: 269.0513.

## 5-chloro-N,N-dipropylbenzo[*d*]thiazole-2-carboxamide (7s)



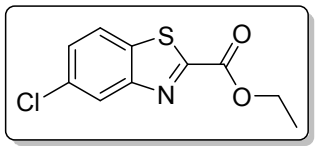
Compound **7s** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 65% yield (39 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 4.02 – 3.92 (m, 2H), 3.53 – 3.43 (m, 2H), 1.78 – 1.69 (m, 4H), 1.00 – 0.90 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.5, 160.4, 154.2, 134.6, 132.4, 127.1, 124.3, 122.6, 50.3, 49.9, 22.6, 20.8, 11.5, 11.0. HRMS (ESI, m/z) calcd for $C_{14}H_{17}ClN_2OS[M+H]^+$: 297.0823; found: 297.0821.

## ethyl benzo[*d*]thiazole-2-carboxylate (7t) (CAS Number: 32137-76-1)



Compound **7t** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 75% yield (31 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.15 (m, 1H), 8.09 – 7.81 (m, 1H), 7.61 – 7.47 (m, 2H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 160.7, 158.6, 153.2, 136.8, 127.5, 127.1, 125.5, 122.1, 63.1, 14.3.

## ethyl 5-chlorobenzo[*d*]thiazole-2-carboxylate (7u) (CAS Number: 857081-41-5)



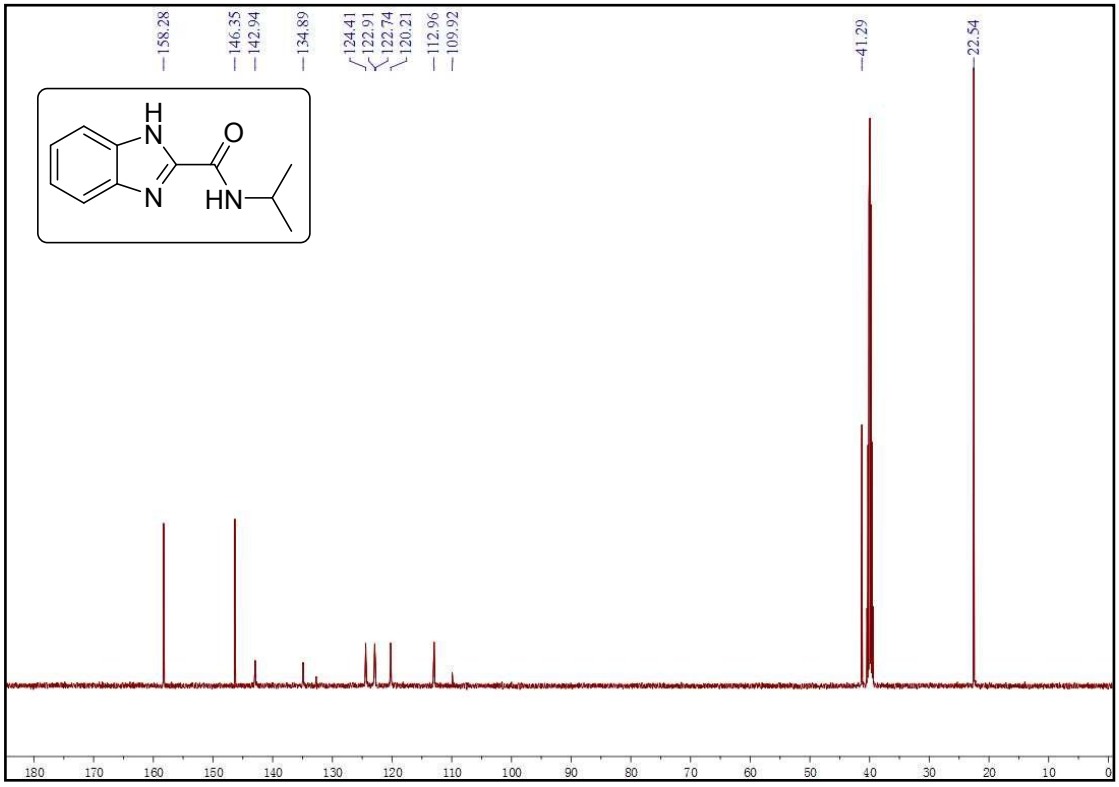
Compound **7u** was prepared according to the general procedure (petroleum ether/ethyl acetate = 20:1 v/v). The product was obtained as a yellow solid in 46% yield (22 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.8 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.56 – 7.42 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 160.3 (d, *J* = 8.5 Hz), 153.9, 135.0, 133.3, 128.2, 125.0, 122.9, 63.3, 14.3.

## 8. References

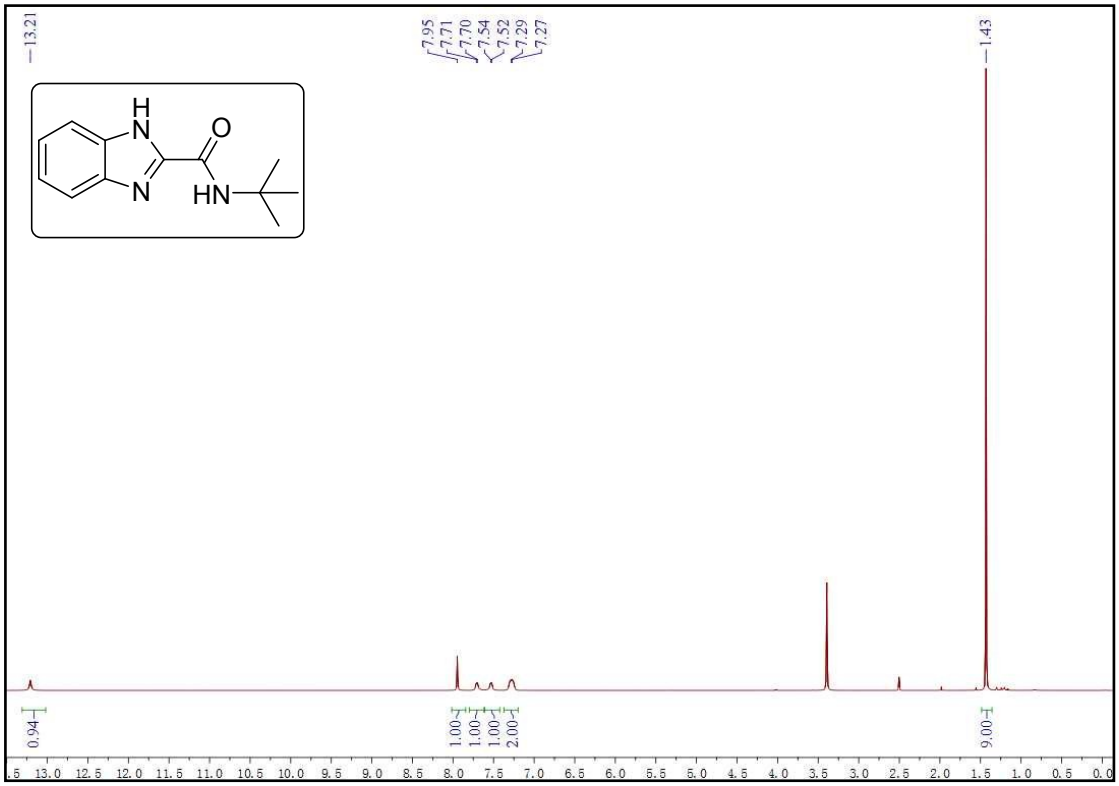
1. W. Fu, Q. Song, *Org. Lett*., 2018, **20**, 393.
2. a) A. D. Becke, *J. Chem. Phys*. 1993, **98**, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* 1988, **37**, 785.
3. R. Peverati, D. G. Truhlar, *J. Phys. Chem. Lett.* 2011, **2**, 2810.
4. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B.* 2009, **113**, 6378.

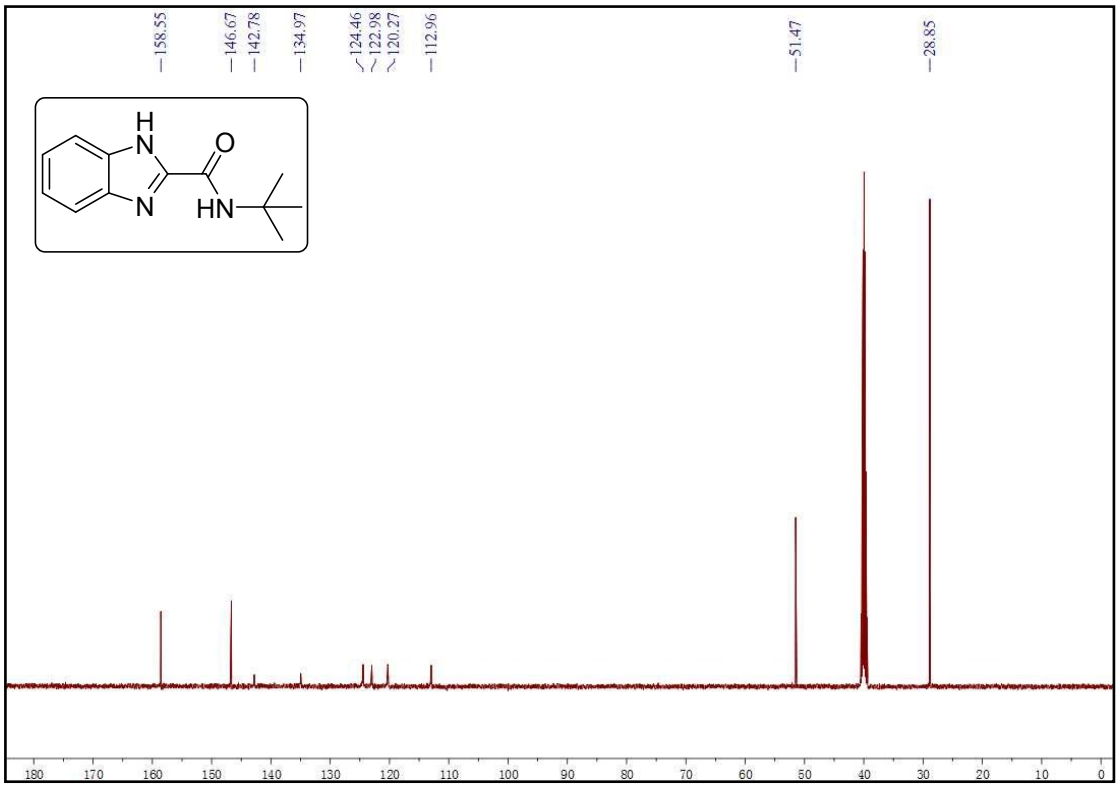
## 9. NMR spectroscopic data

## N-isopropyl-1H-benzo[*d*]imidazole-2-carboxamide (3a)

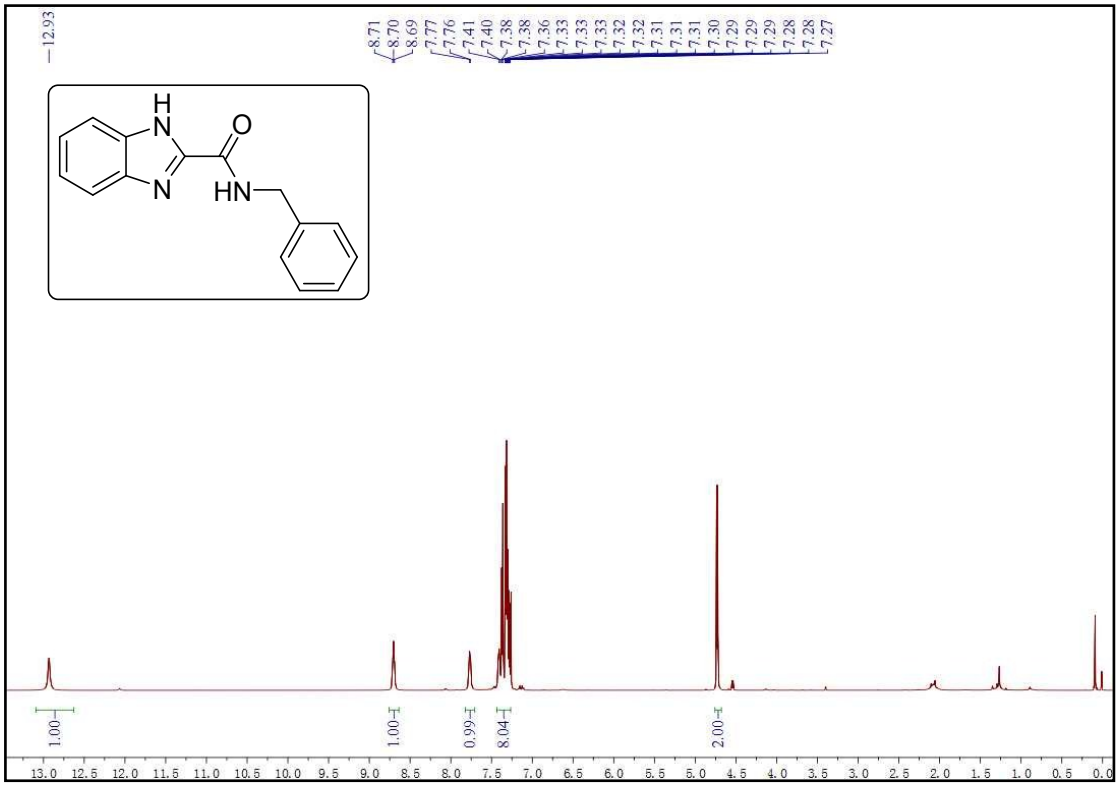



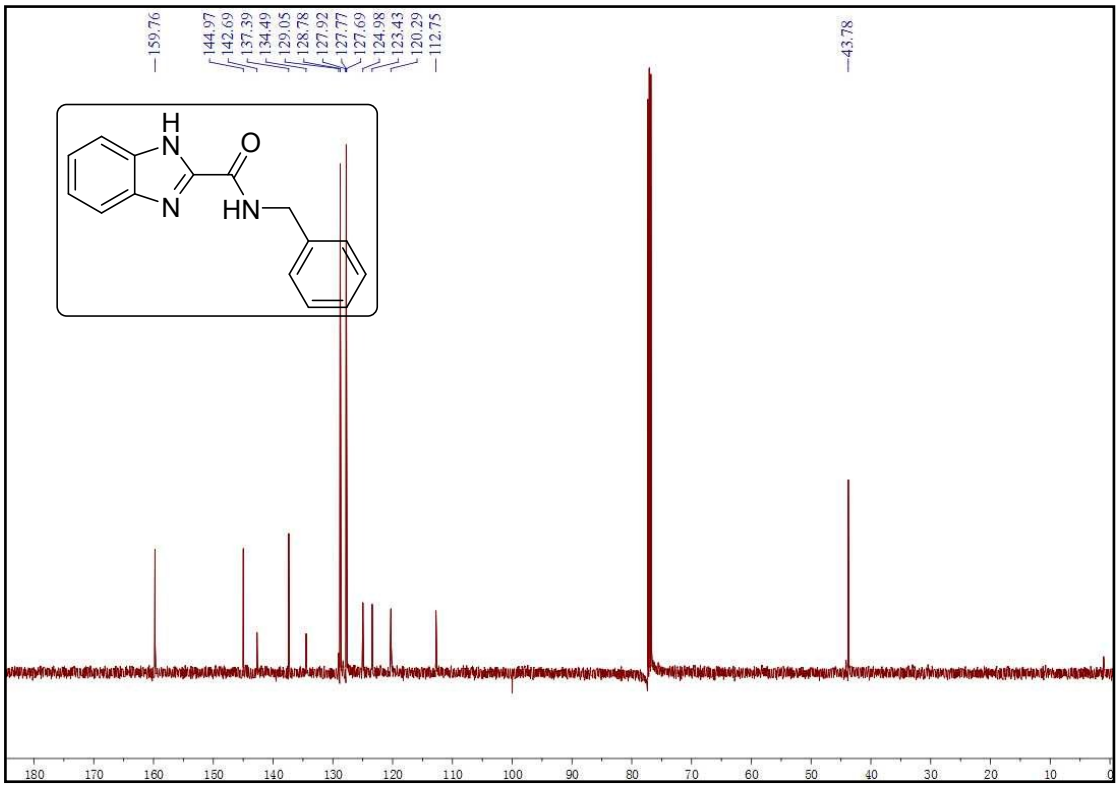

## N-(tert-butyl)-1H-benzo[d]imidazole-2-carboxamide (3b)



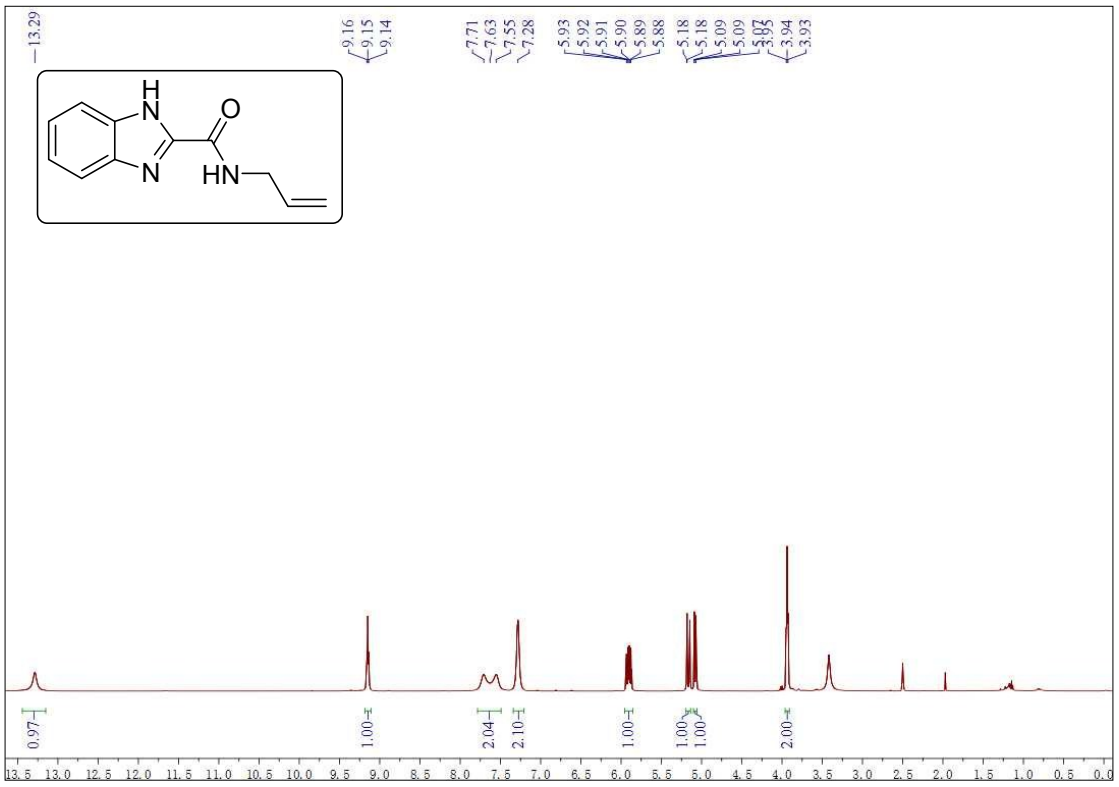



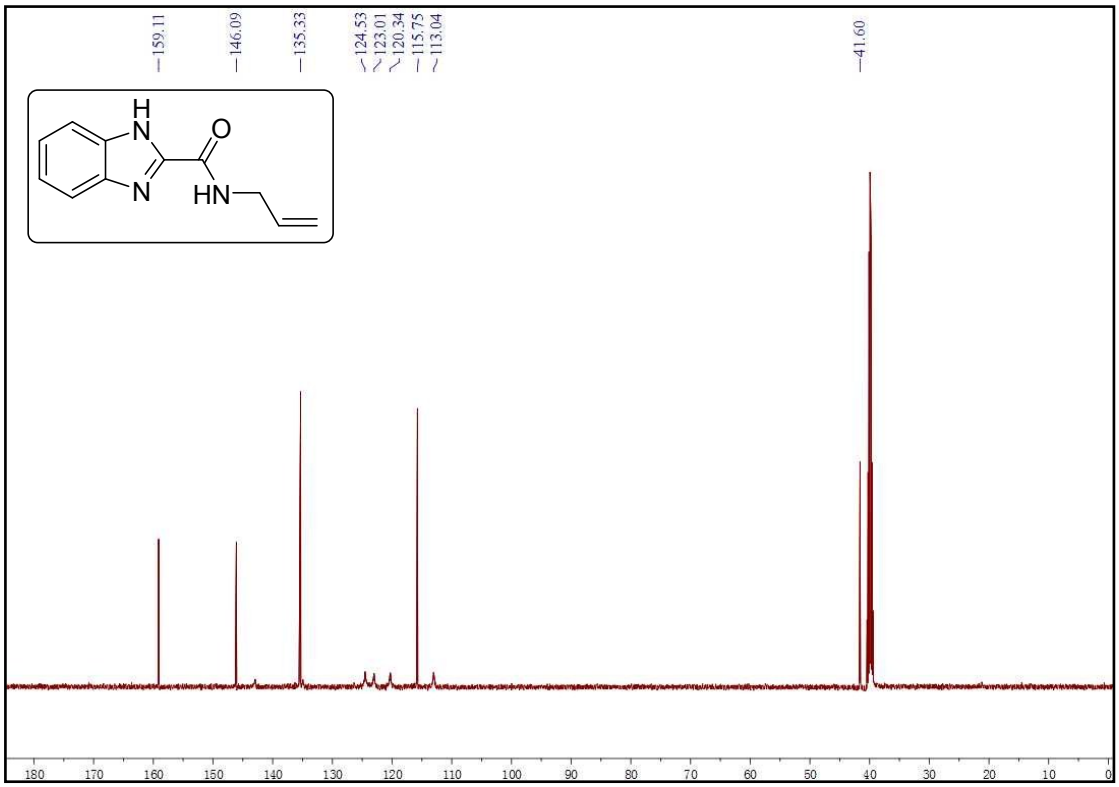

## N-benzyl-1H-benzo[d]imidazole-2-carboxamide (3c)



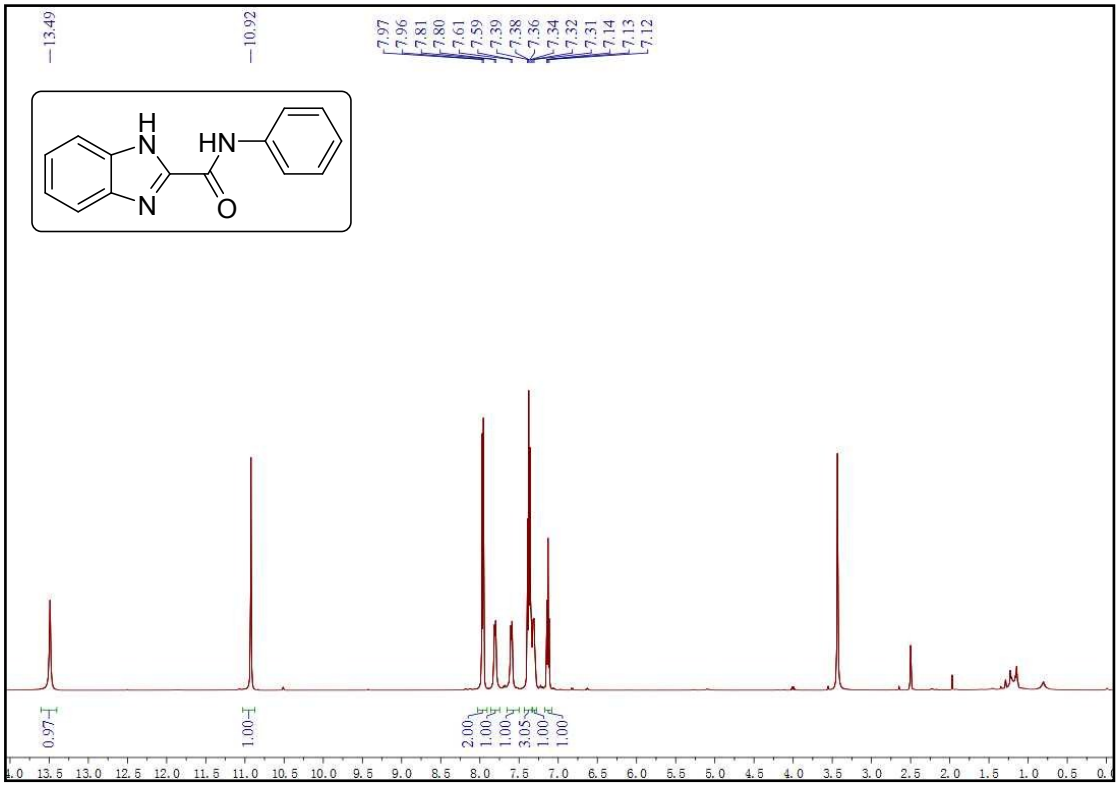



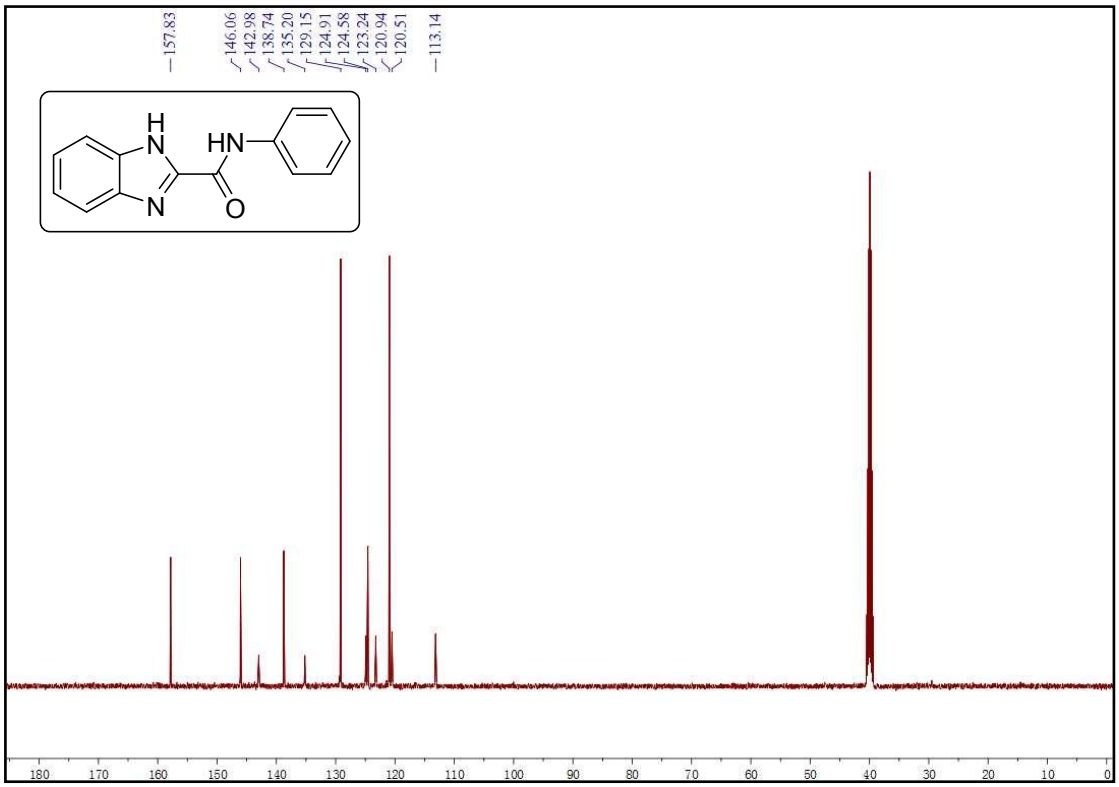

## O-allyl-1H-benzo[d]imidazole-2-carboxamide (3d)



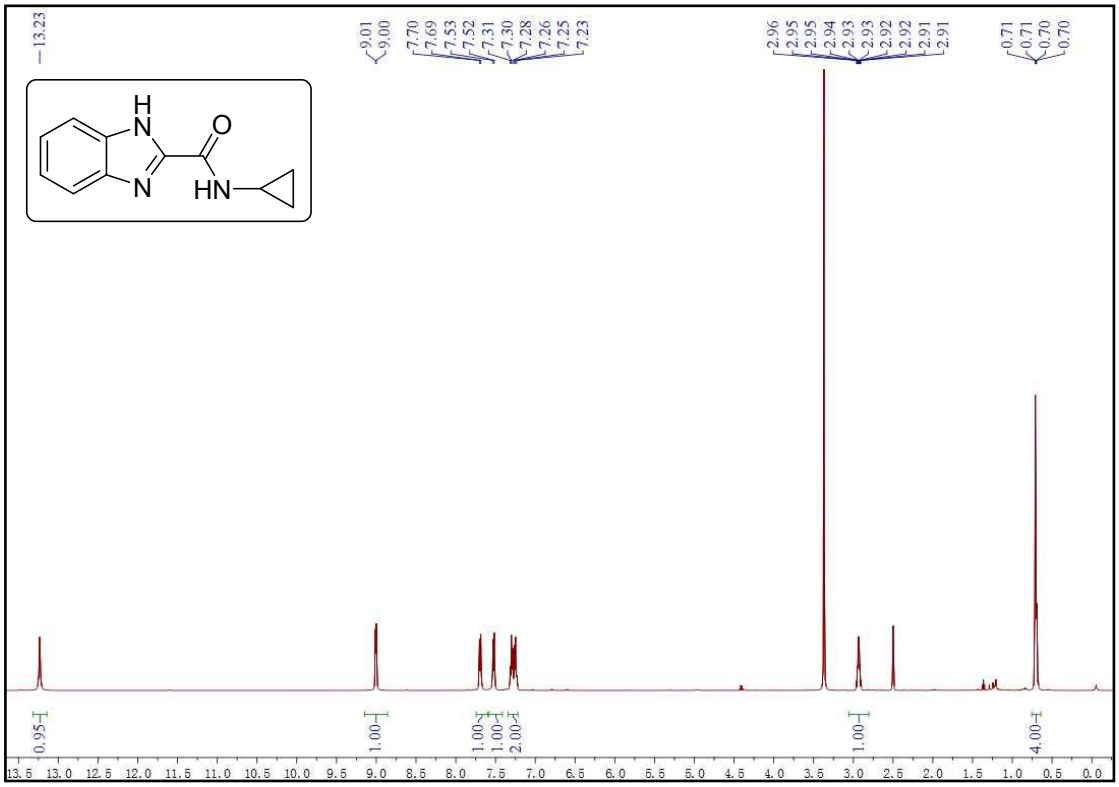



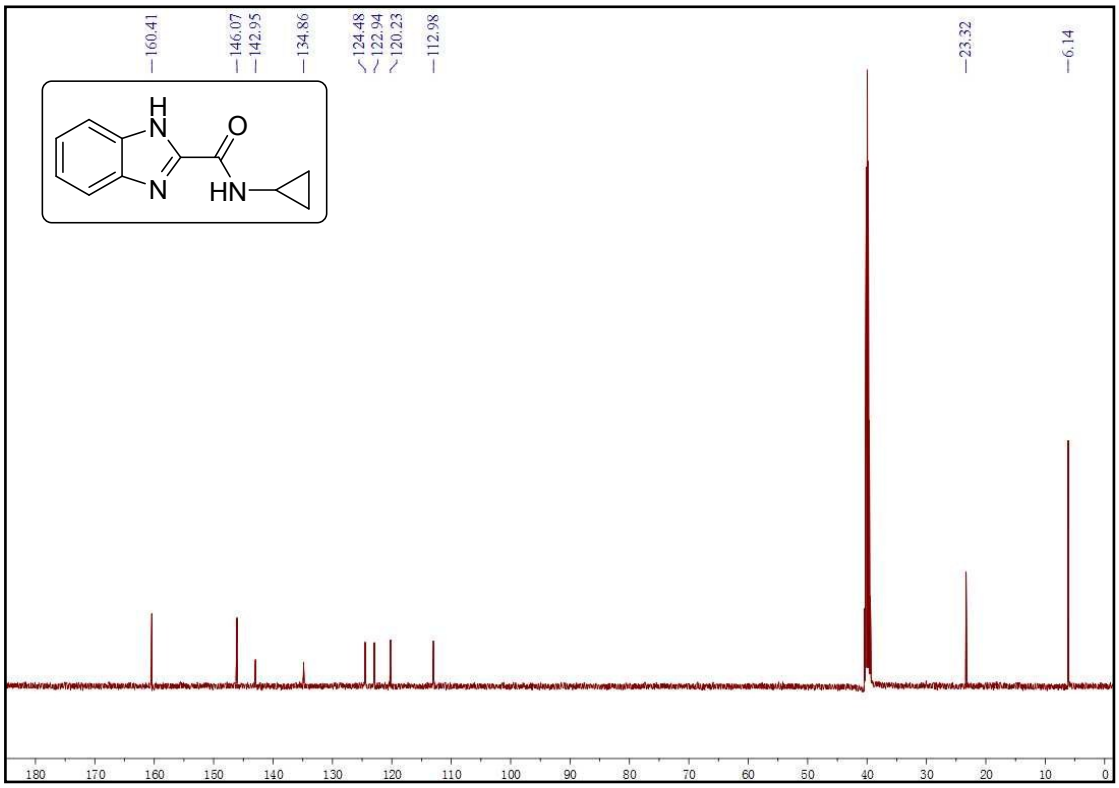

**N-phenyl-1H-benzo[d]imidazole-2-carboxamide (3e)**


13.49
10.92
7.97
7.96
7.81
7.80
7.61
7.59
7.39
7.38
7.36
7.34
7.32
7.31
7.14
7.13
7.12
H
N
HN
N
O
0.97
1.00
2.00
1.00
1.00
3.05
1.00
1.00

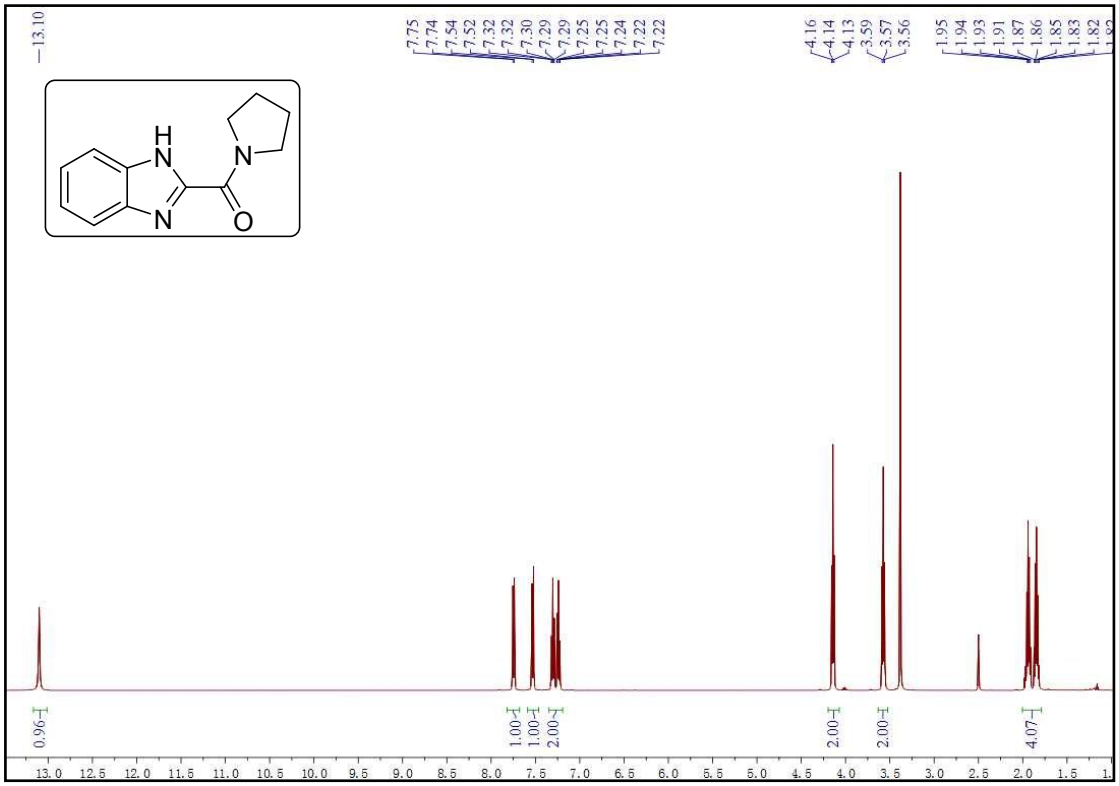

157.83
146.06
142.98
138.74
135.20
129.15
124.91
124.58
123.24
120.94
120.51
113.14
H
N
HN
N
O

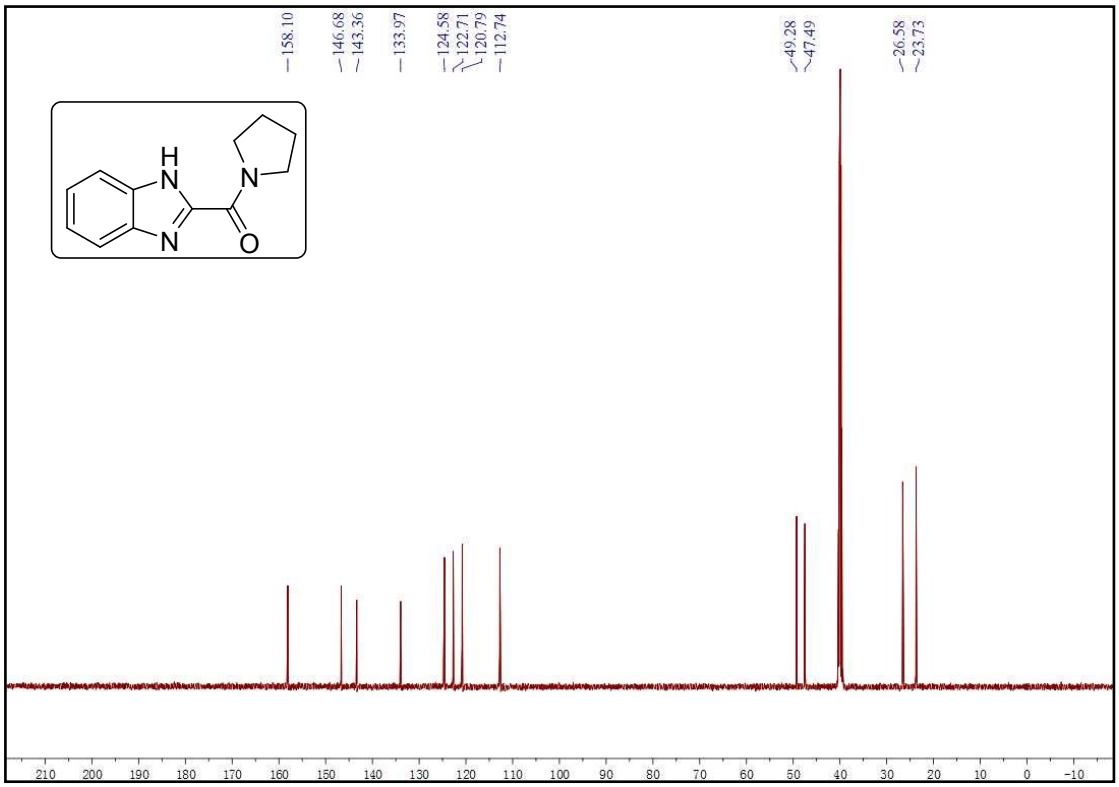
## N-cyclopropyl-1H-benzo[d]imidazole-2-carboxamide (3f)



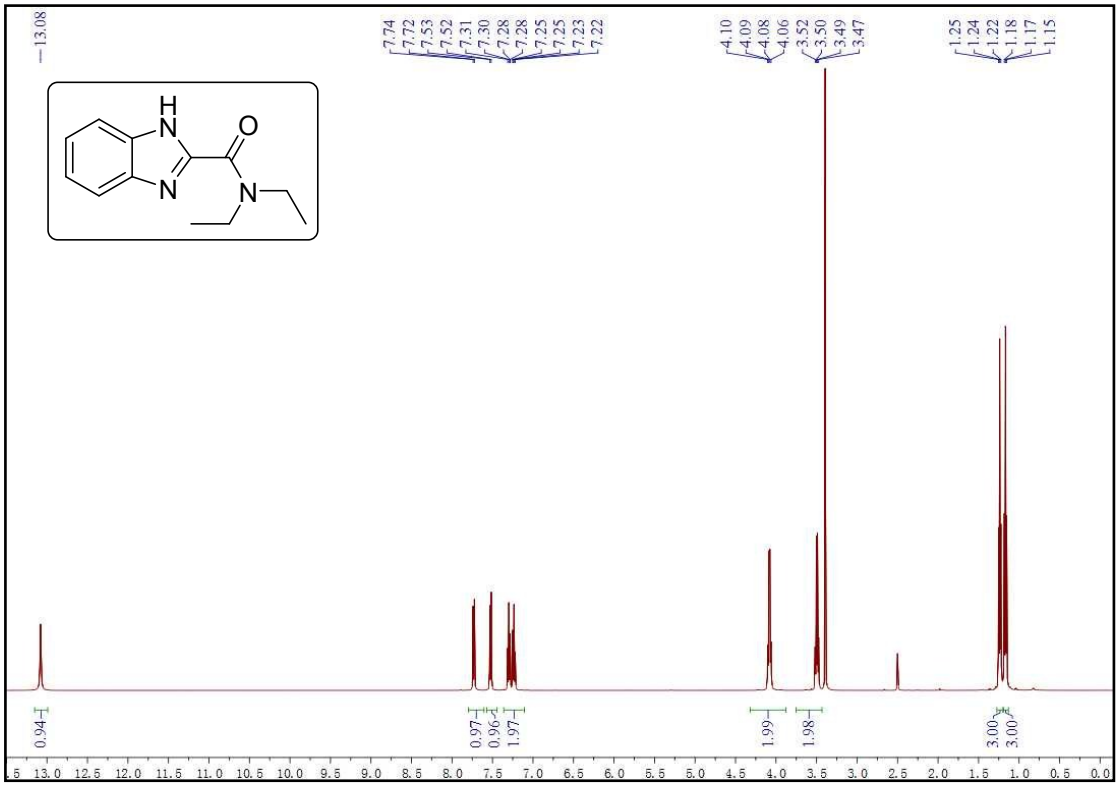



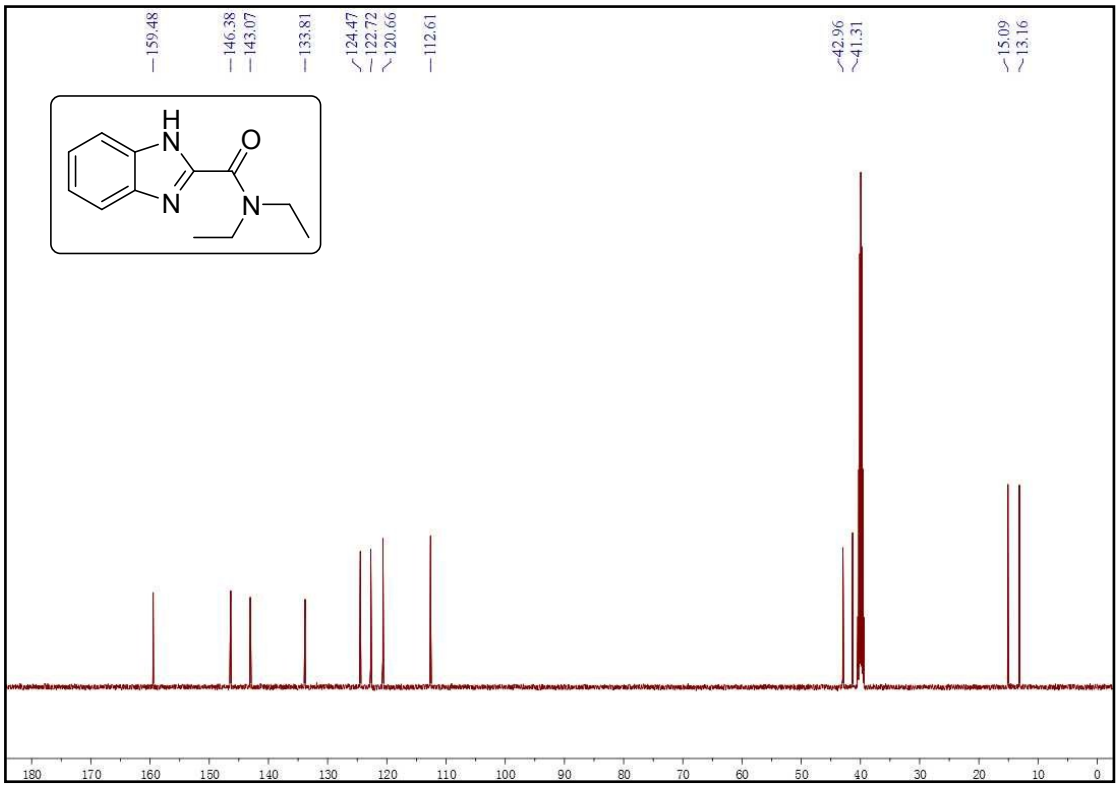

## (1H-benzo[d]imidazol-2-yl)(pyrrolidin-1-yl)methanone (3g)



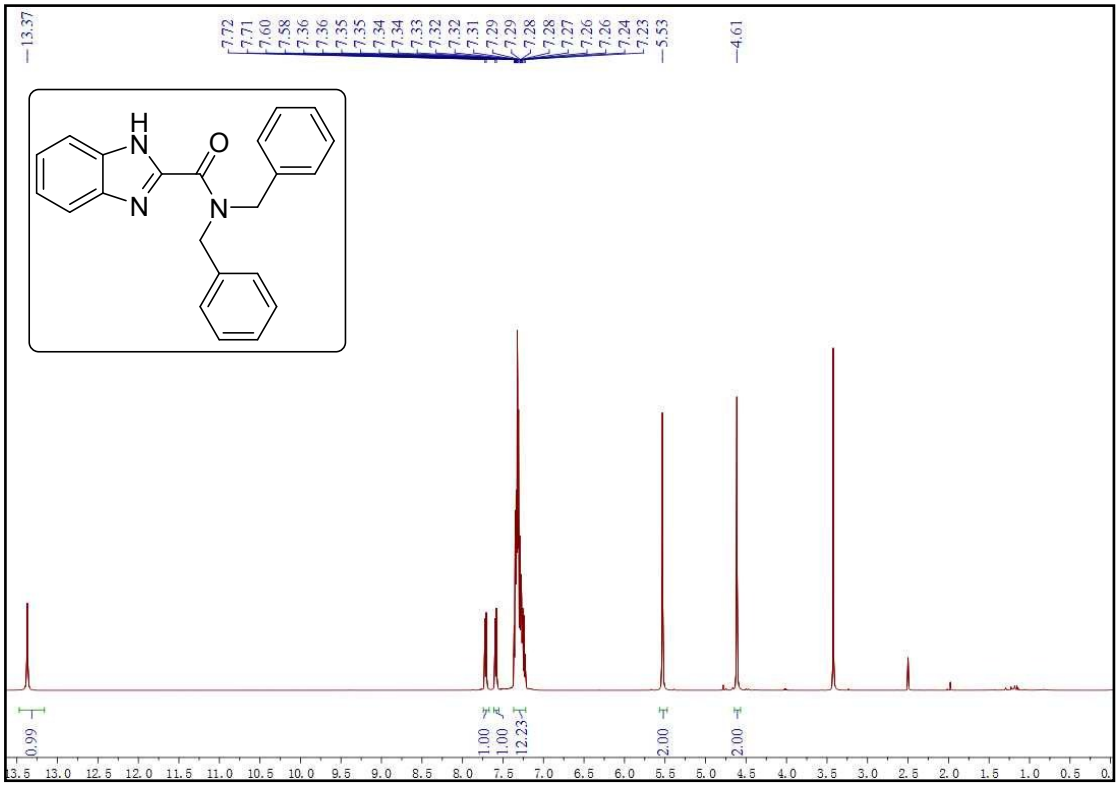



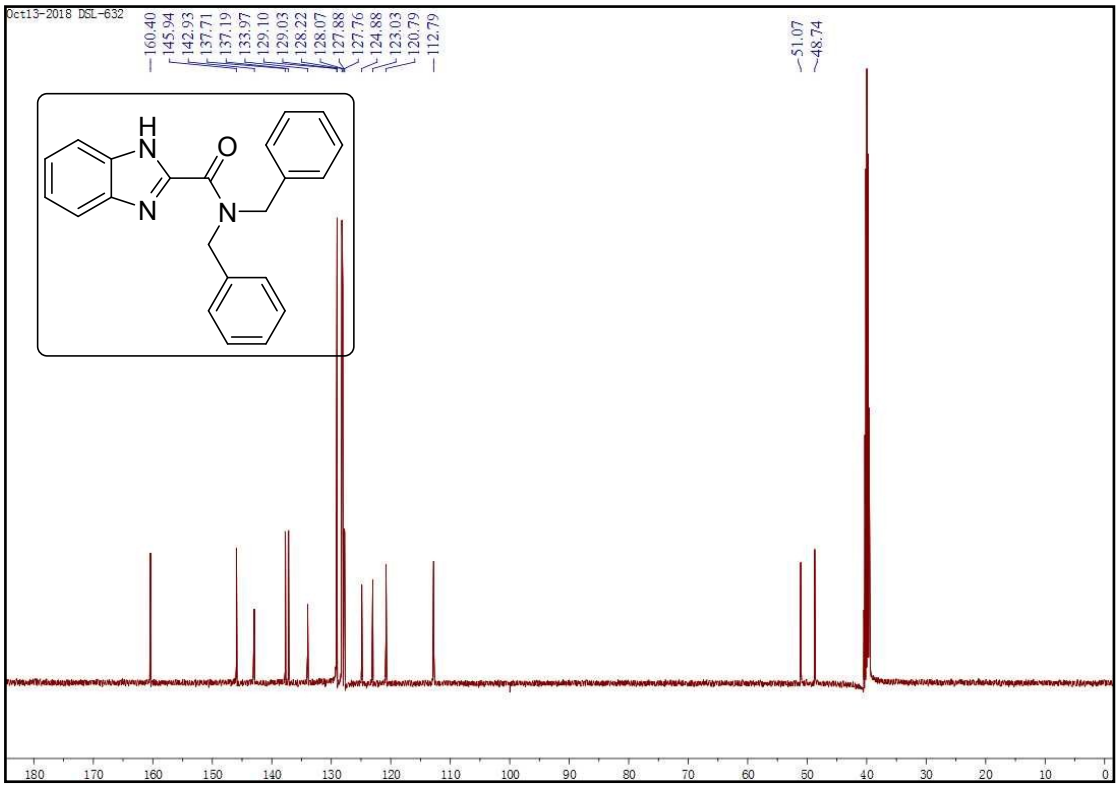

## N,N-diethyl-1H-benzo[d]imidazole-2-carboxamide (3h)



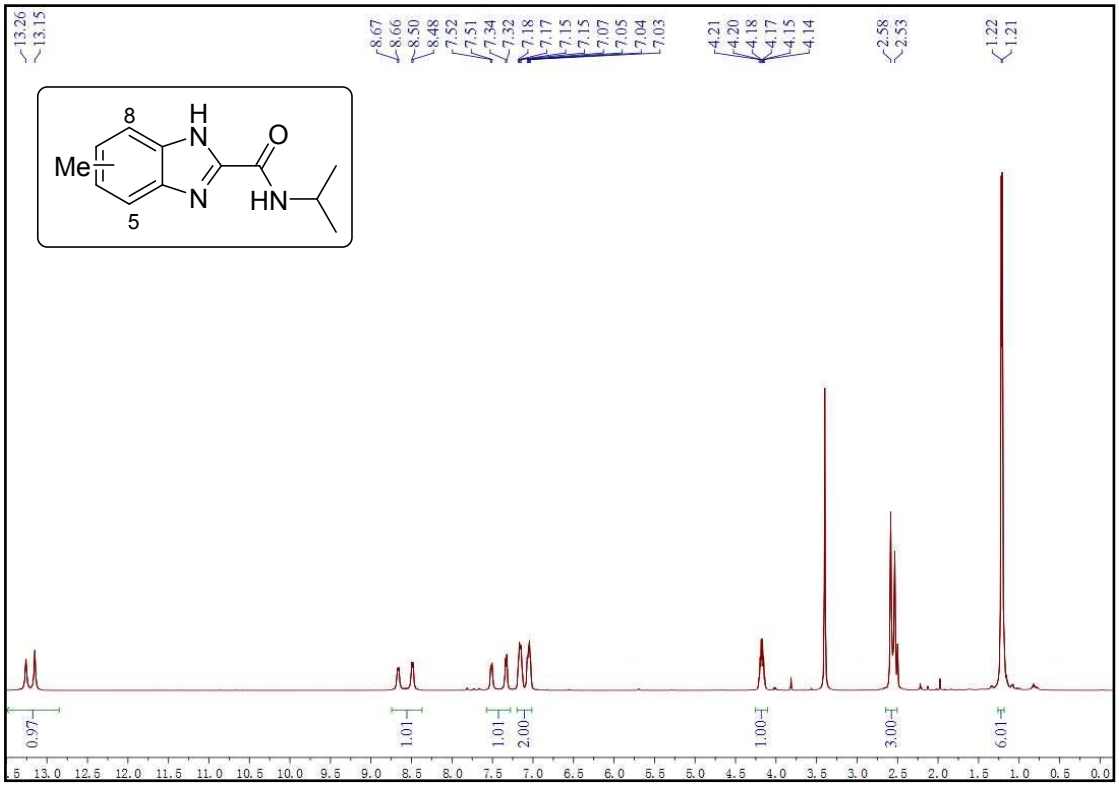



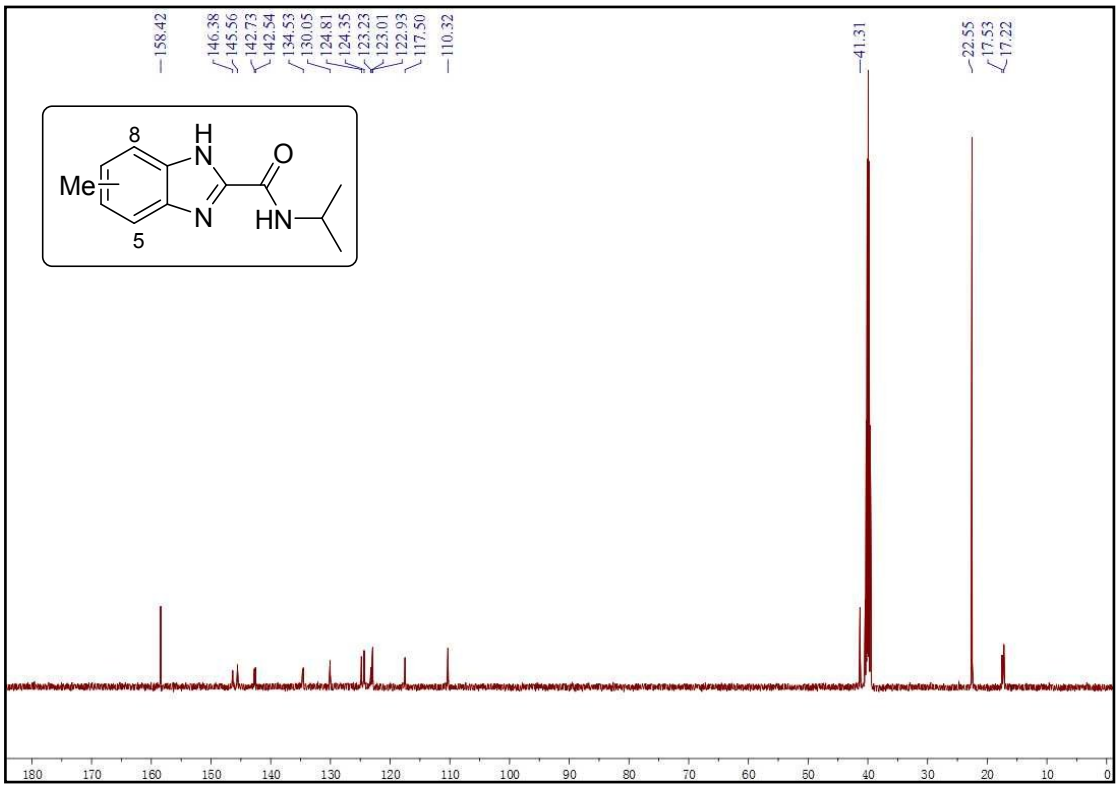

## N,N-dibenzyl-1H-benzo[d]imidazole-2-carboxamide (3i)



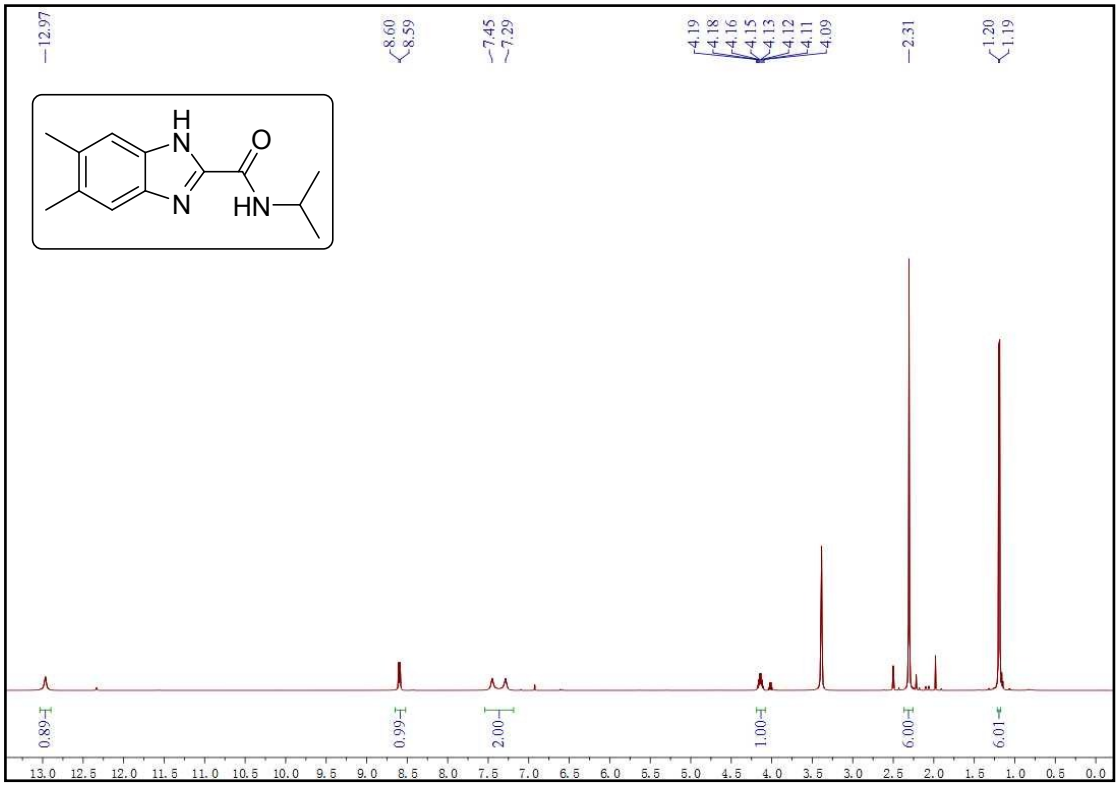


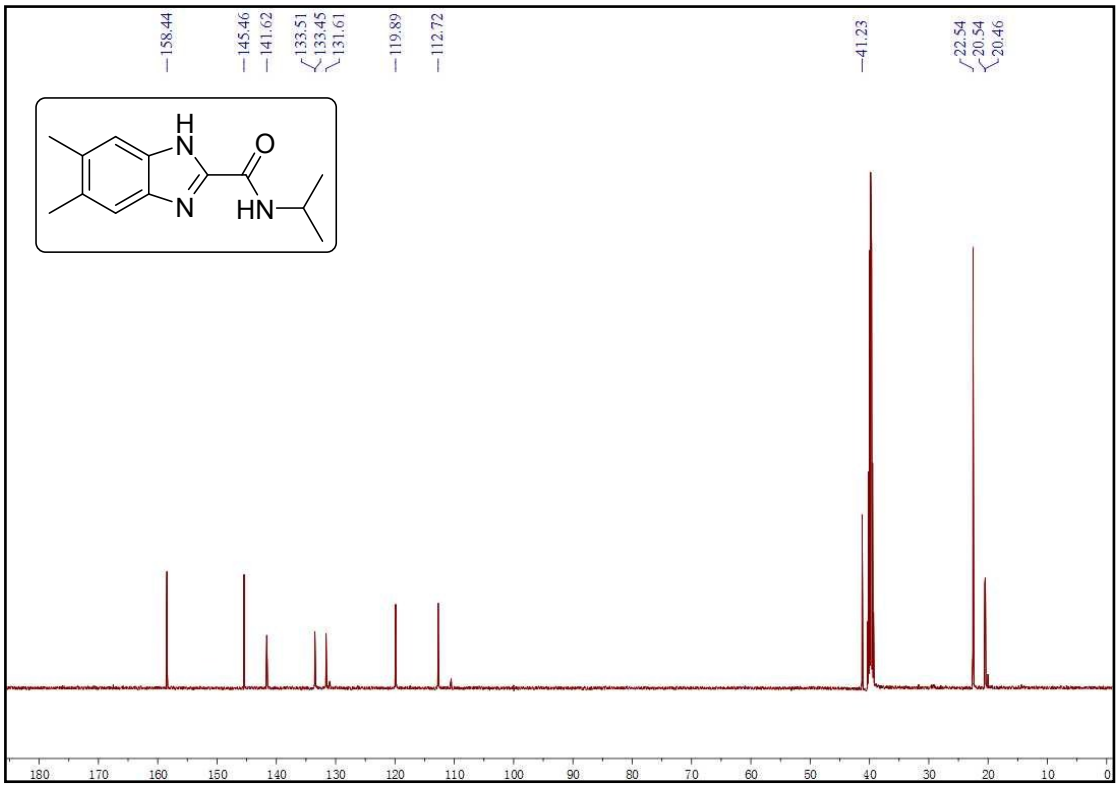
**N-isopropyl-5-methyl-1H-benzo[*d*]imidazole-2-carboxamide (3j)**



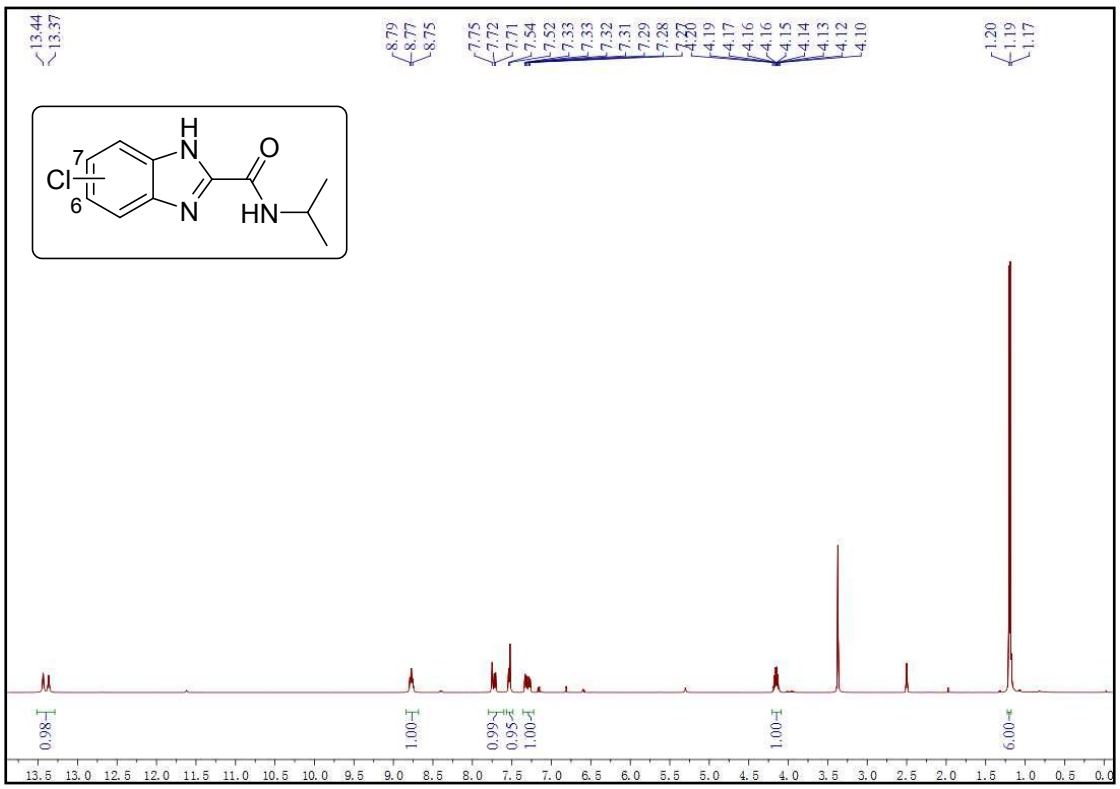



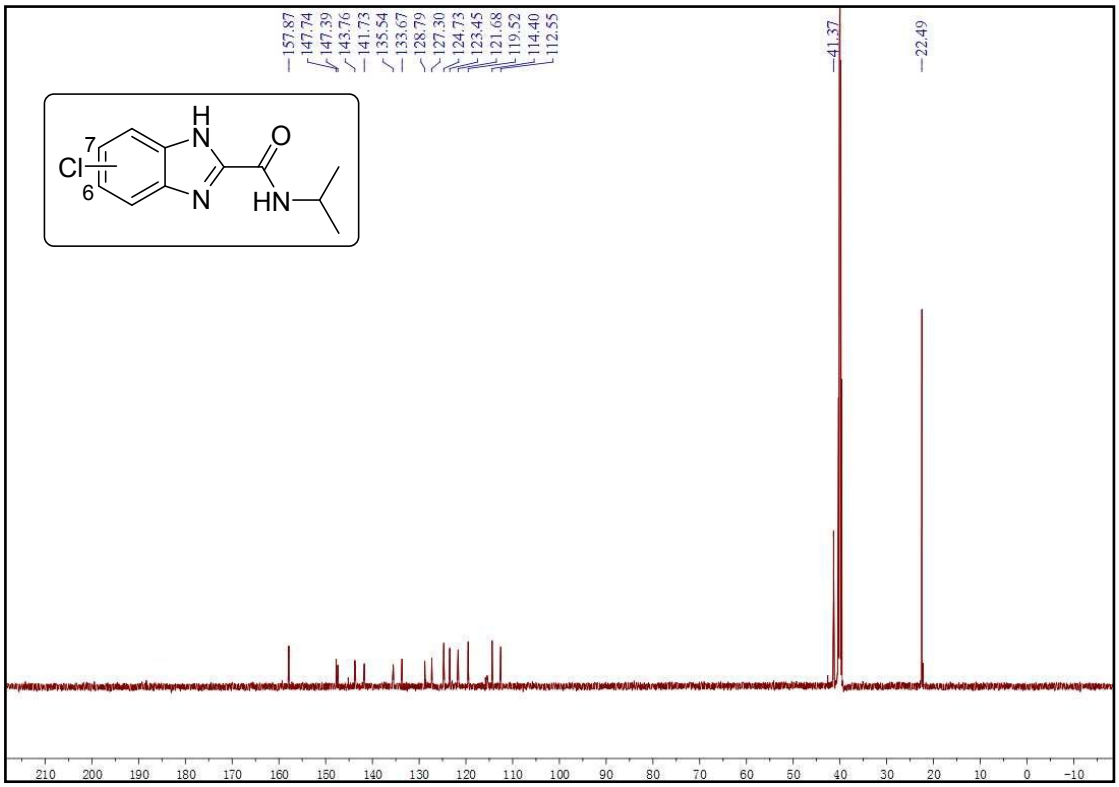

**O-isopropyl-5,6-dimethyl-1H-benzo[*d*]imidazole-2-carboxamide (3k)**




**5-chloro-N-isopropyl-1H-benzo[*d*]imidazole-2-carboxamide (3l)**





**N-isopropyl-5-nitro-1H-benzo[*d*]imidazole-2-carboxamide (3m)**


13.88
8.93
8.91
8.63
8.36
8.17
7.86
7.86
7.69
4.20
4.19
4.18
4.16
4.15
4.15
4.13
4.12
4.11
1.21
1.20
O2N
7
6
H
N
N
O
HN
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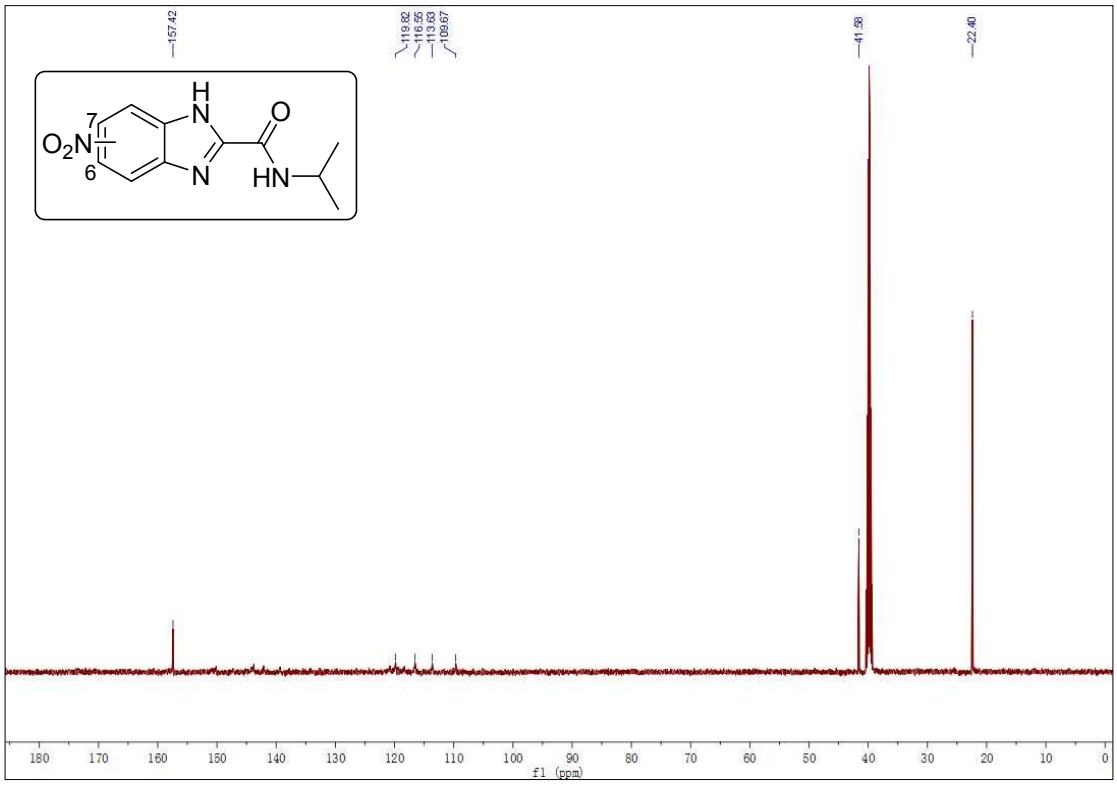
1.00
0.95
0.97
1.00
0.98
6.00
f1 (ppm)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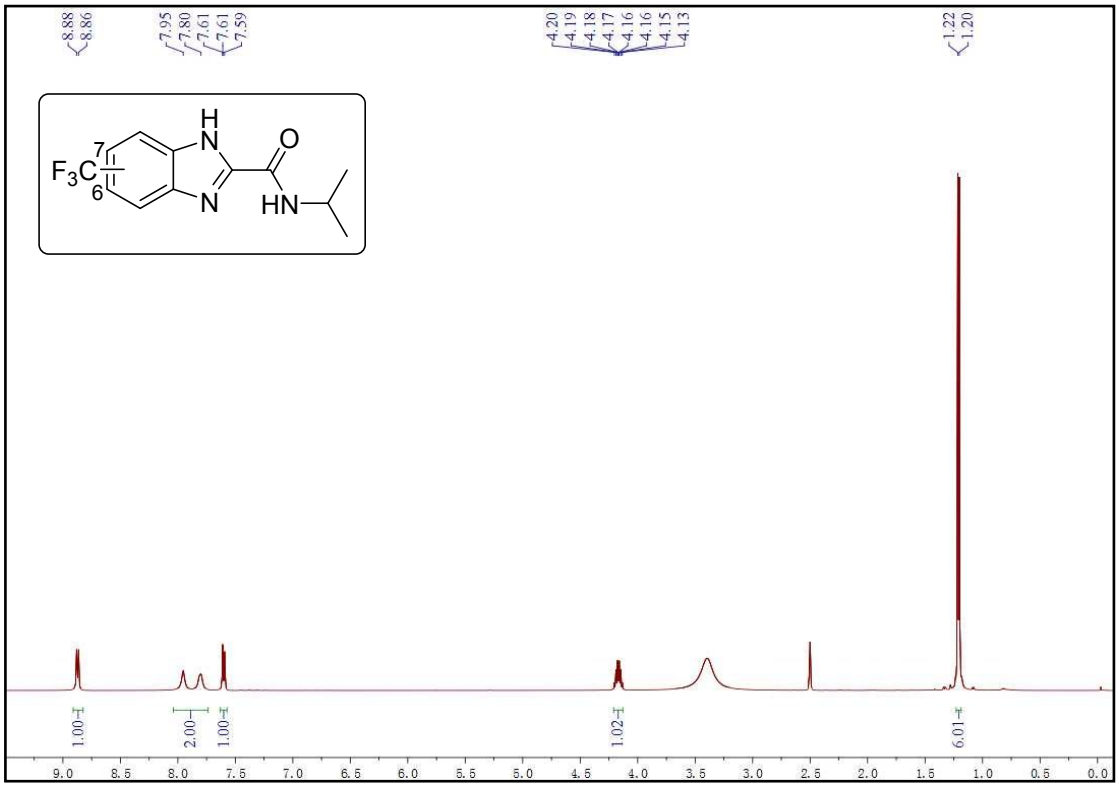
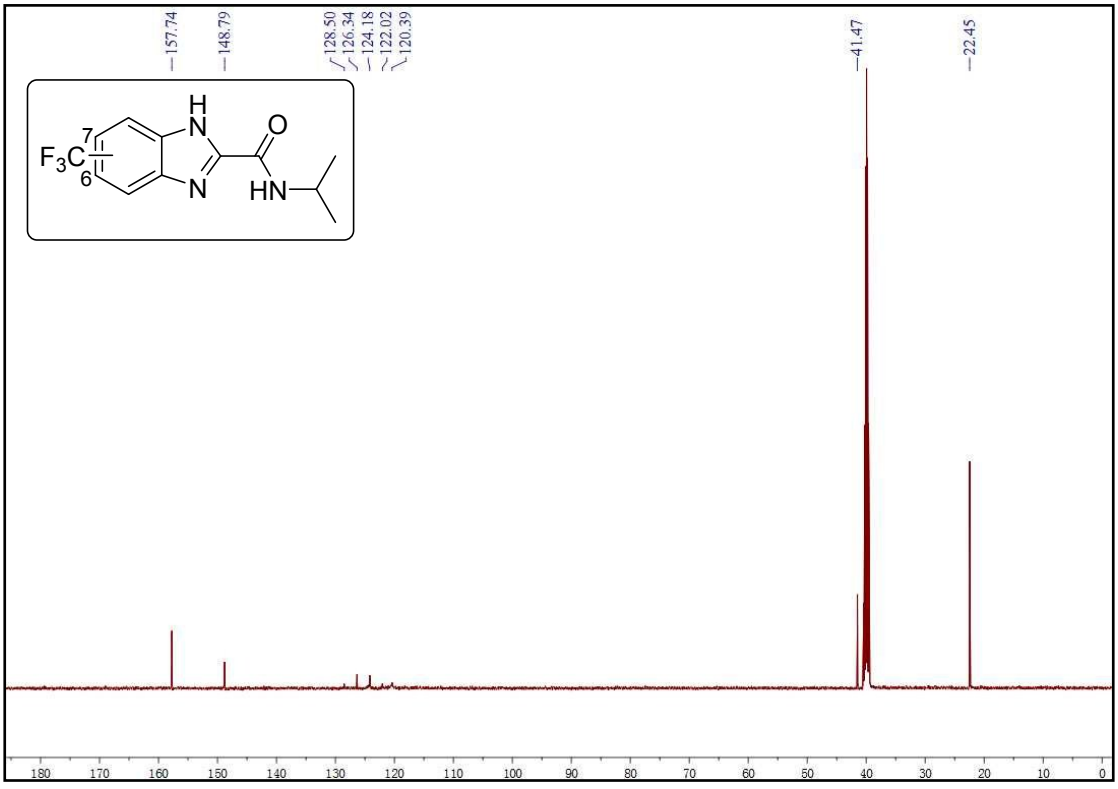
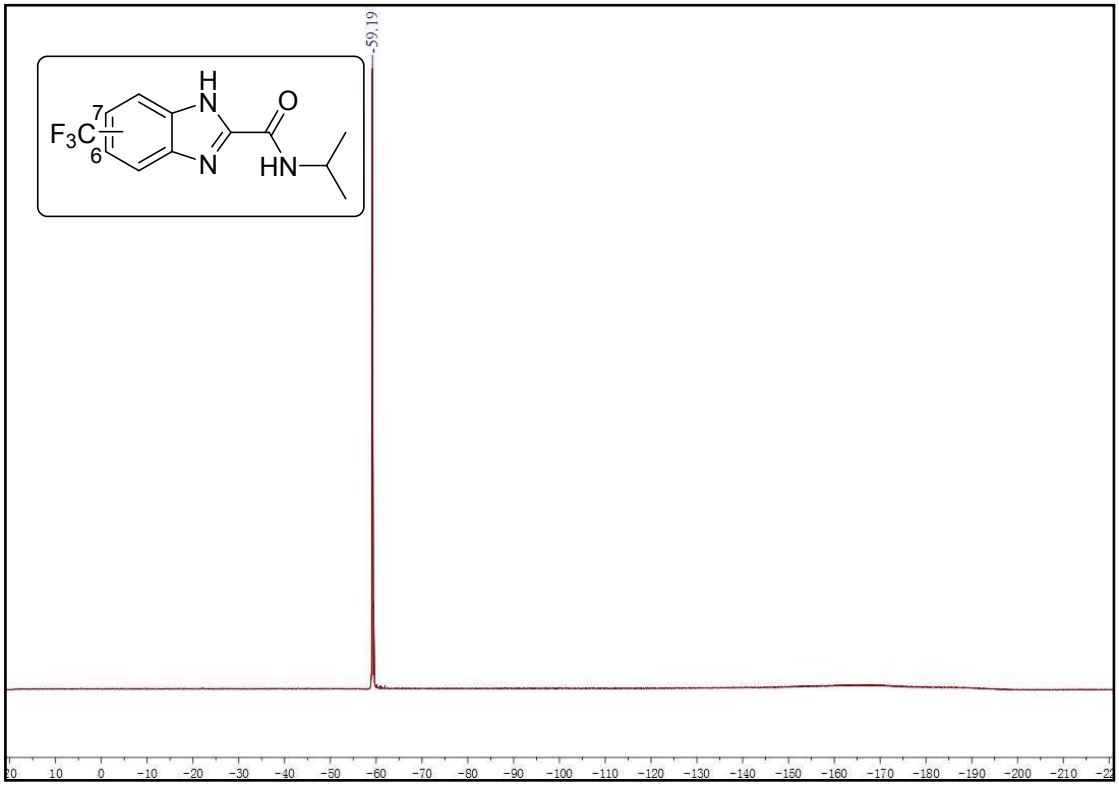
O2N
7
6
H
N
N
O
HN
f1 (ppm)

**N-isopropyl-5-(trifluoromethyl)-1H-benzo[*d*]imidazole-2-carboxamide (3n)**

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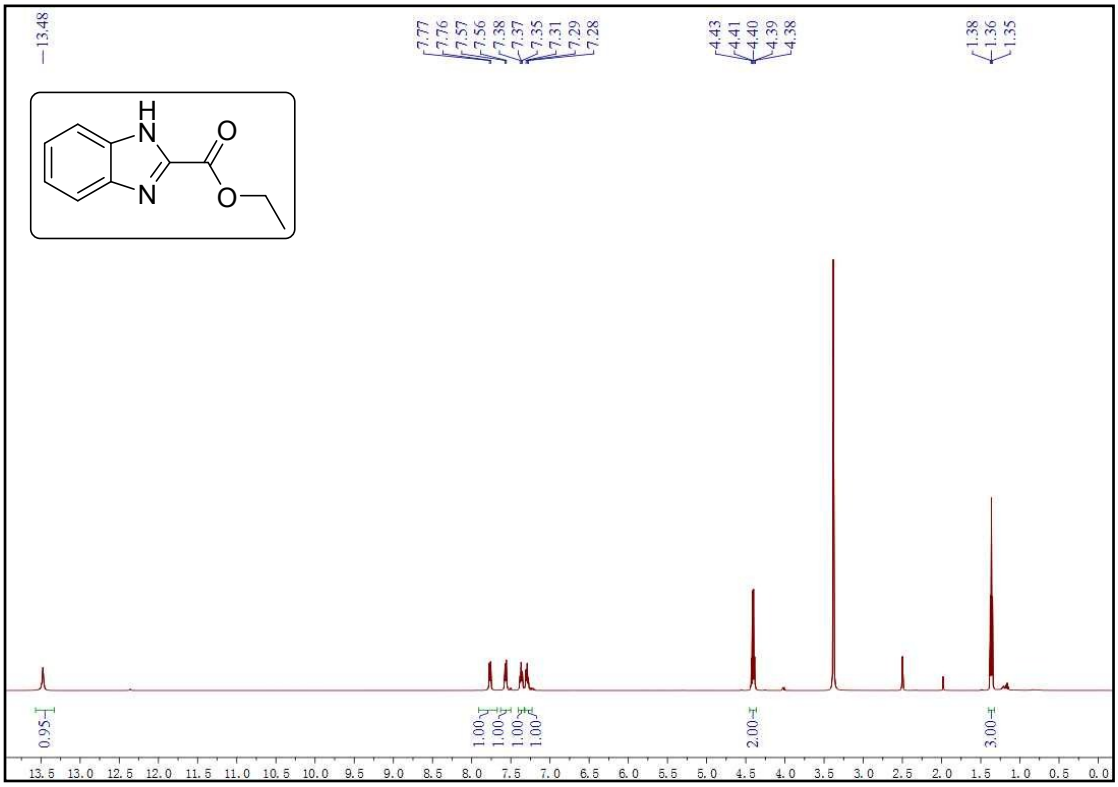
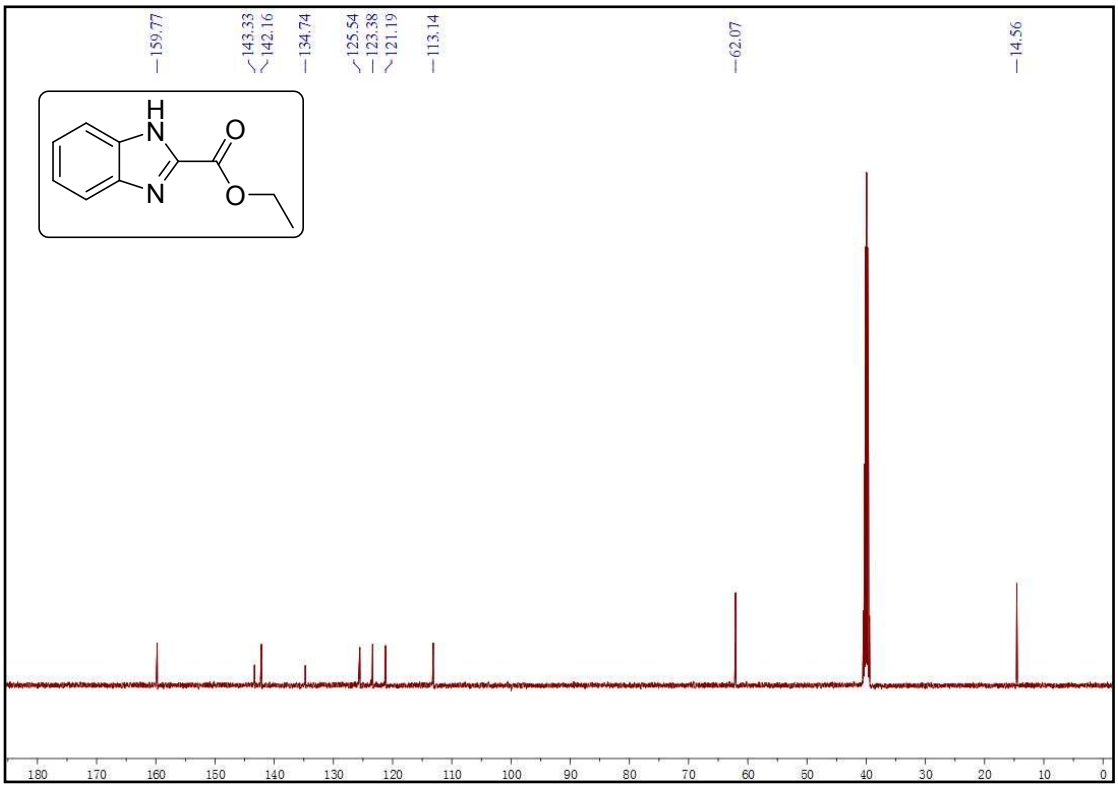
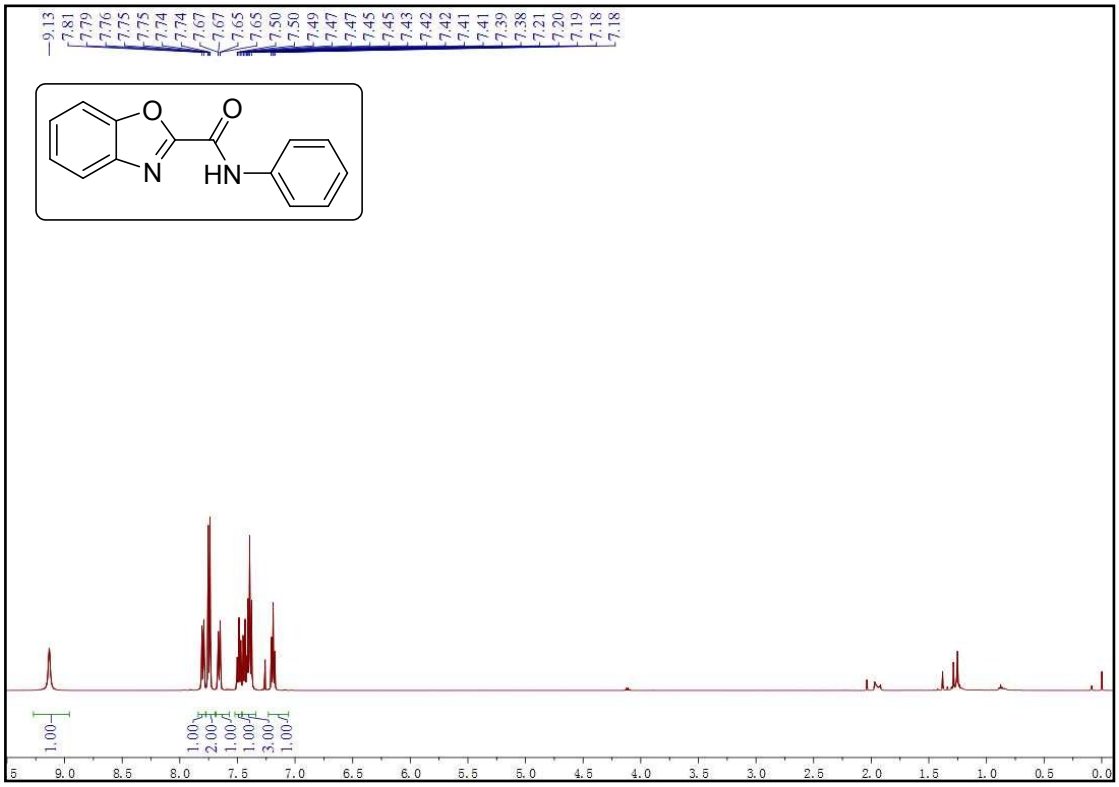
H
N
O
7
F3C
6
N
HN
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

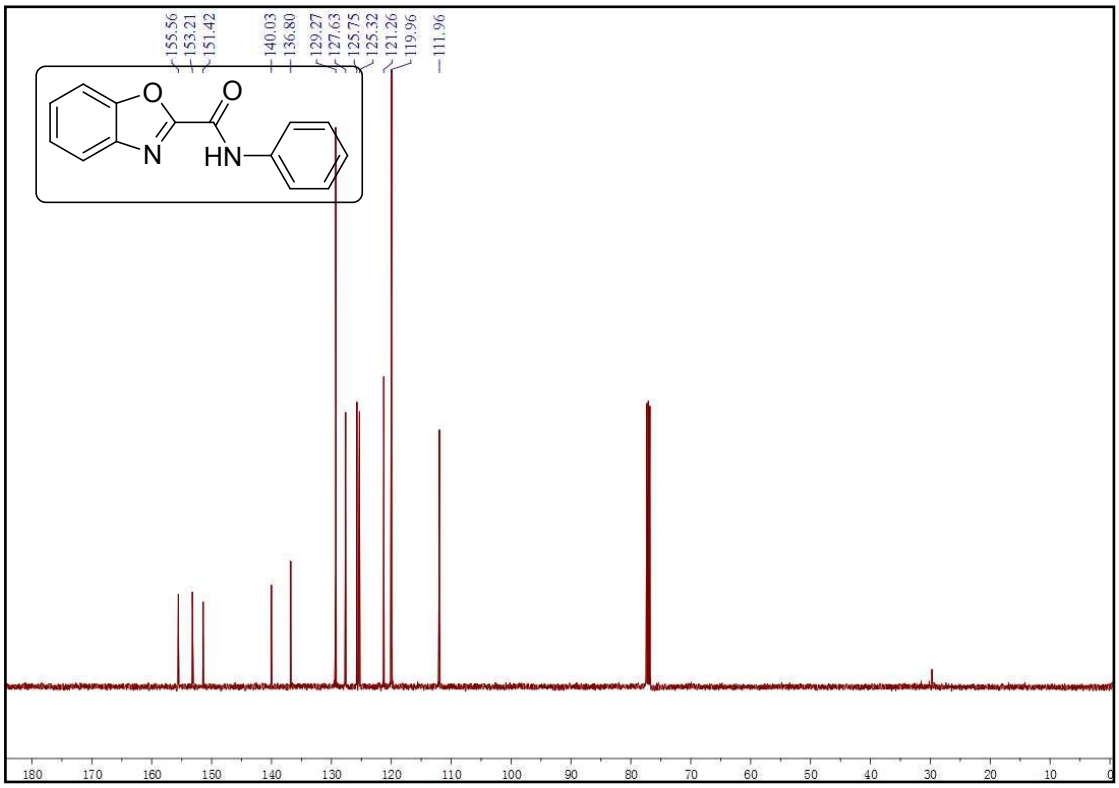
## ethyl 1H-benzo[*d*]imidazole-2-carboxylate (3o)



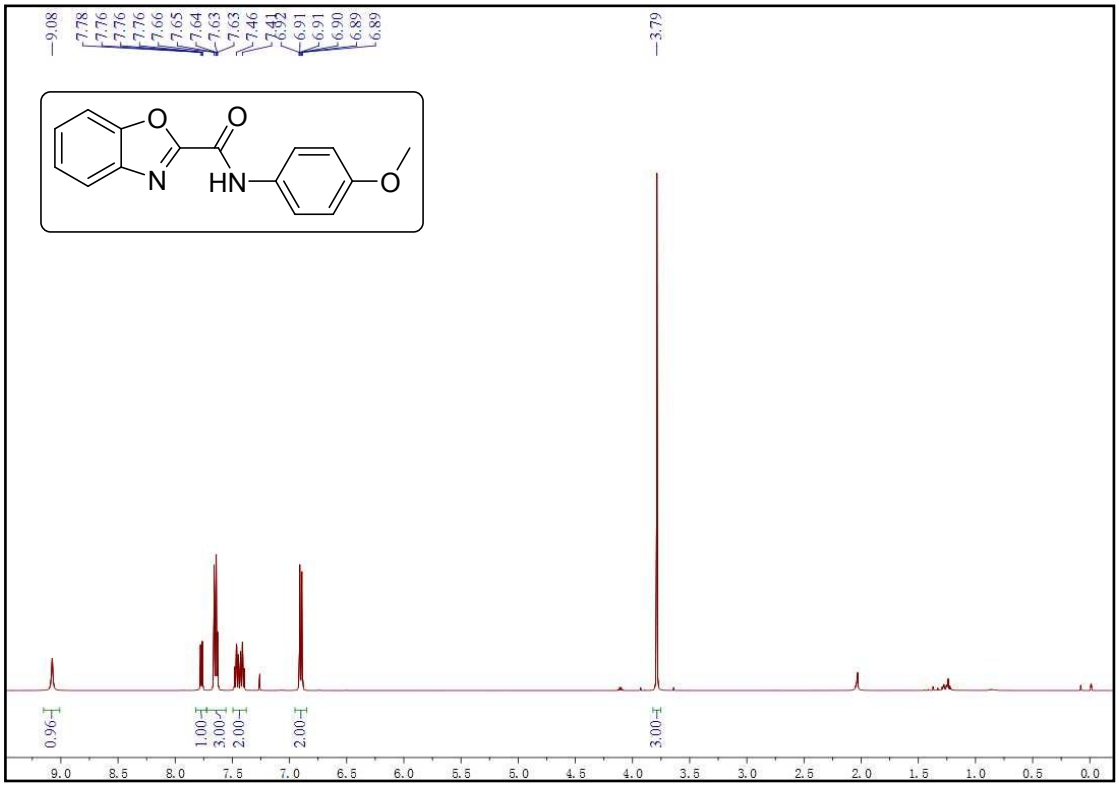



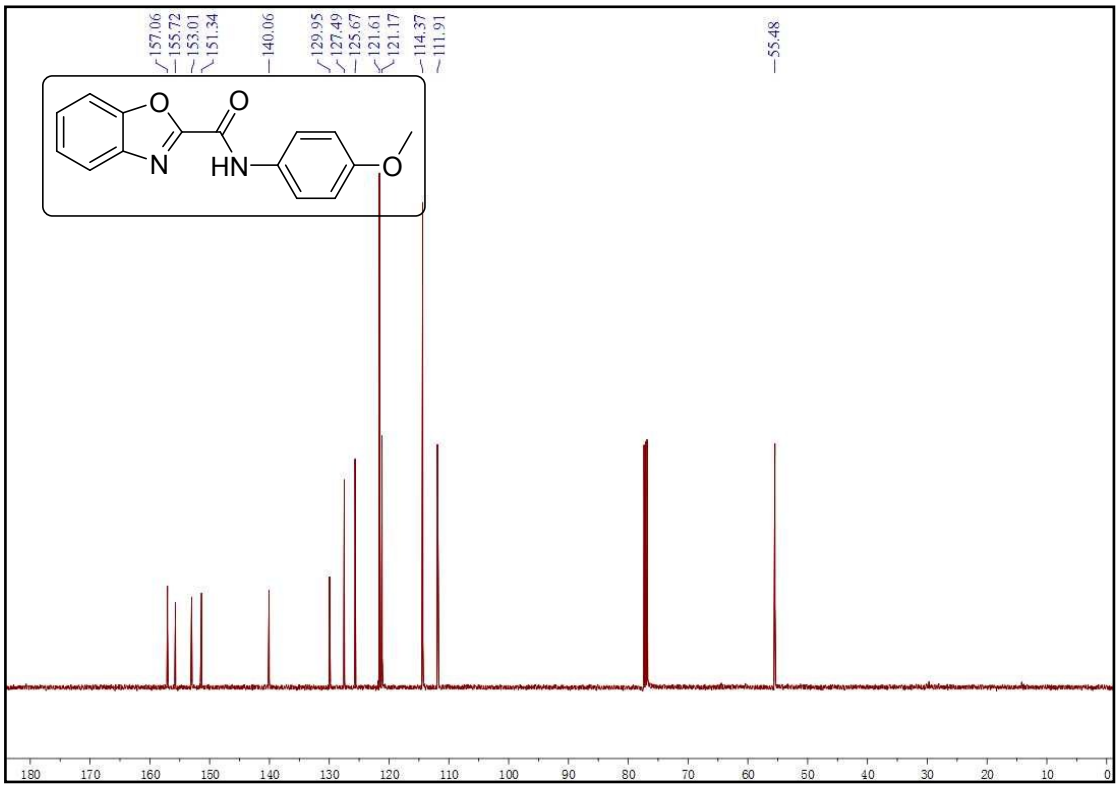
## N-phenylbenzo[*d*]oxazole-2-carboxamide (5a)



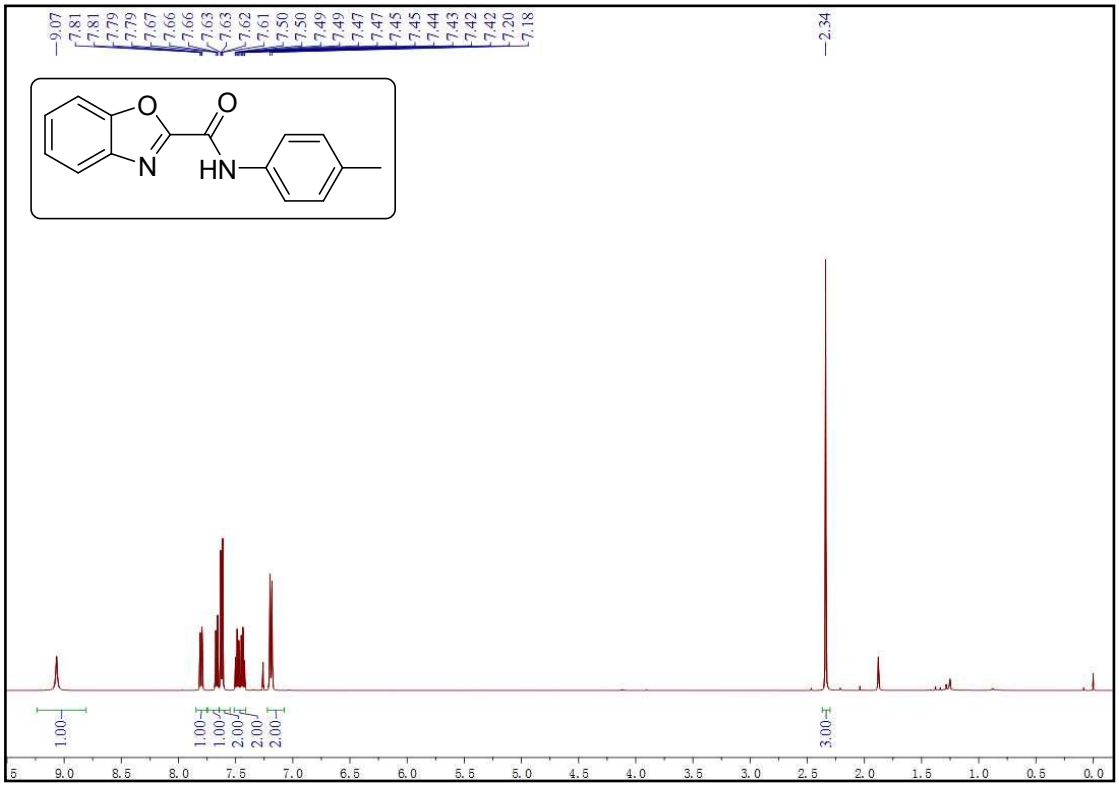



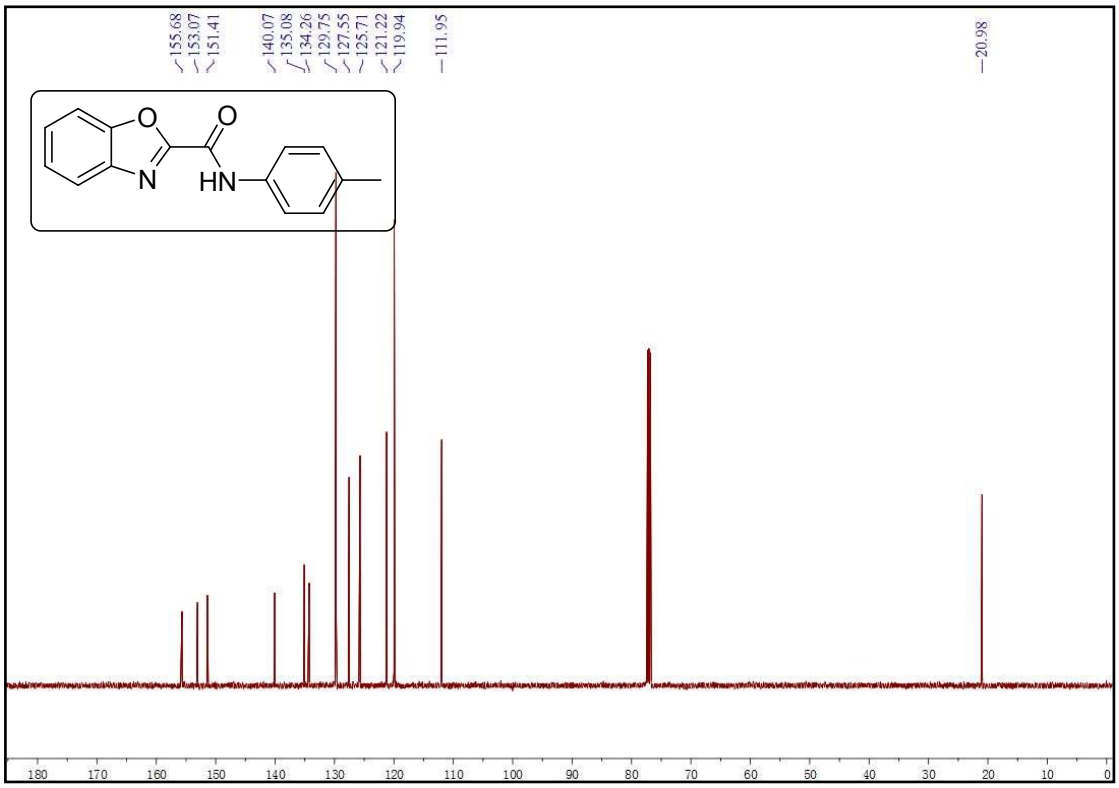
## N-(4-methoxyphenyl)benzo[*d*]oxazole-2-carboxamide (5b)



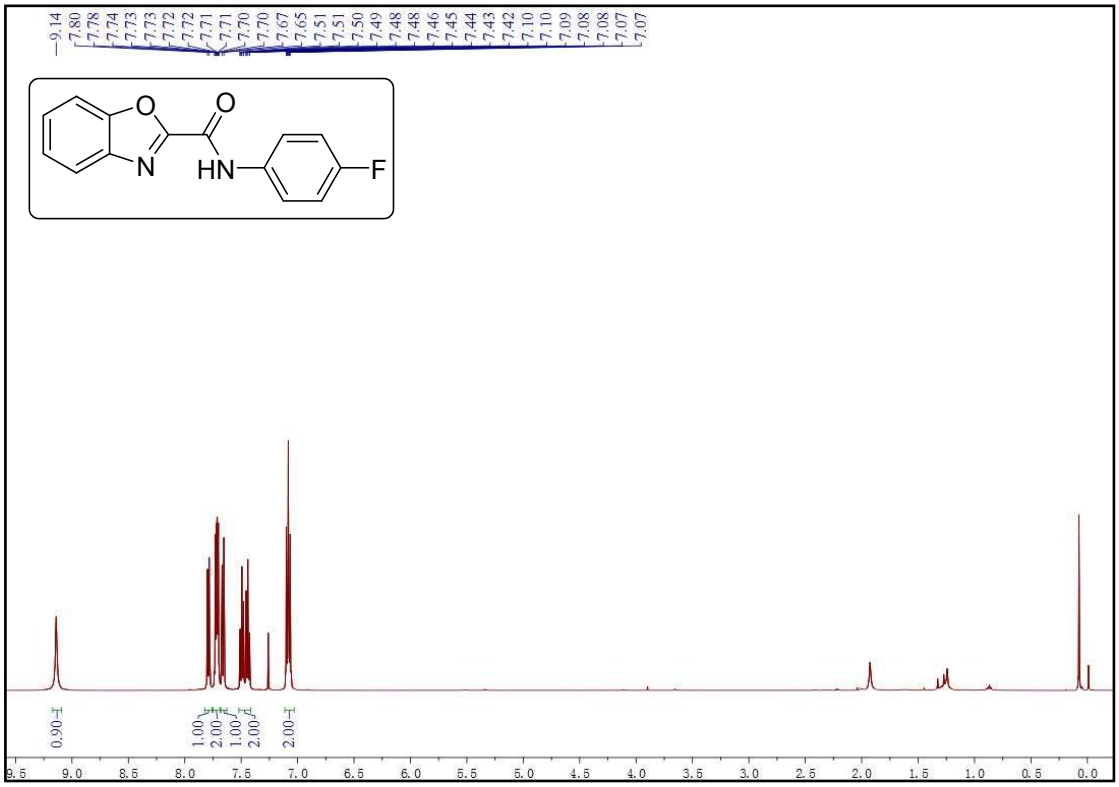



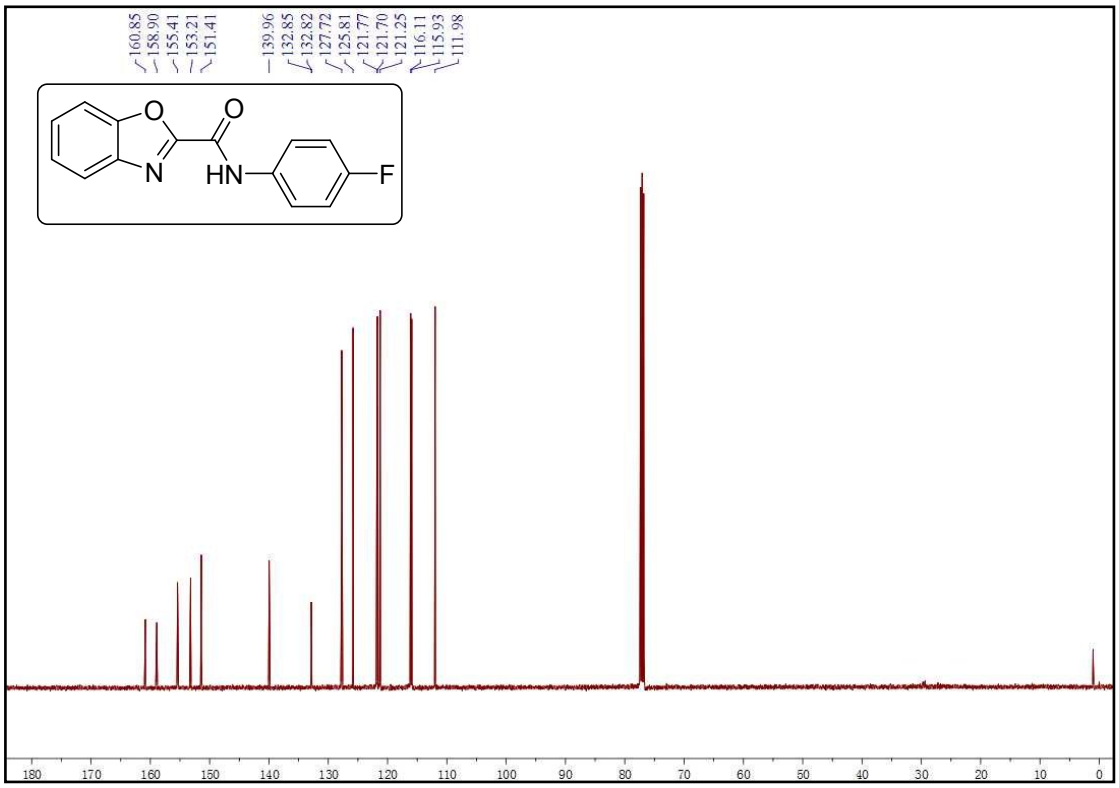
## N-(p-tolyl)benzo[*d*]oxazole-2-carboxamide (5c)

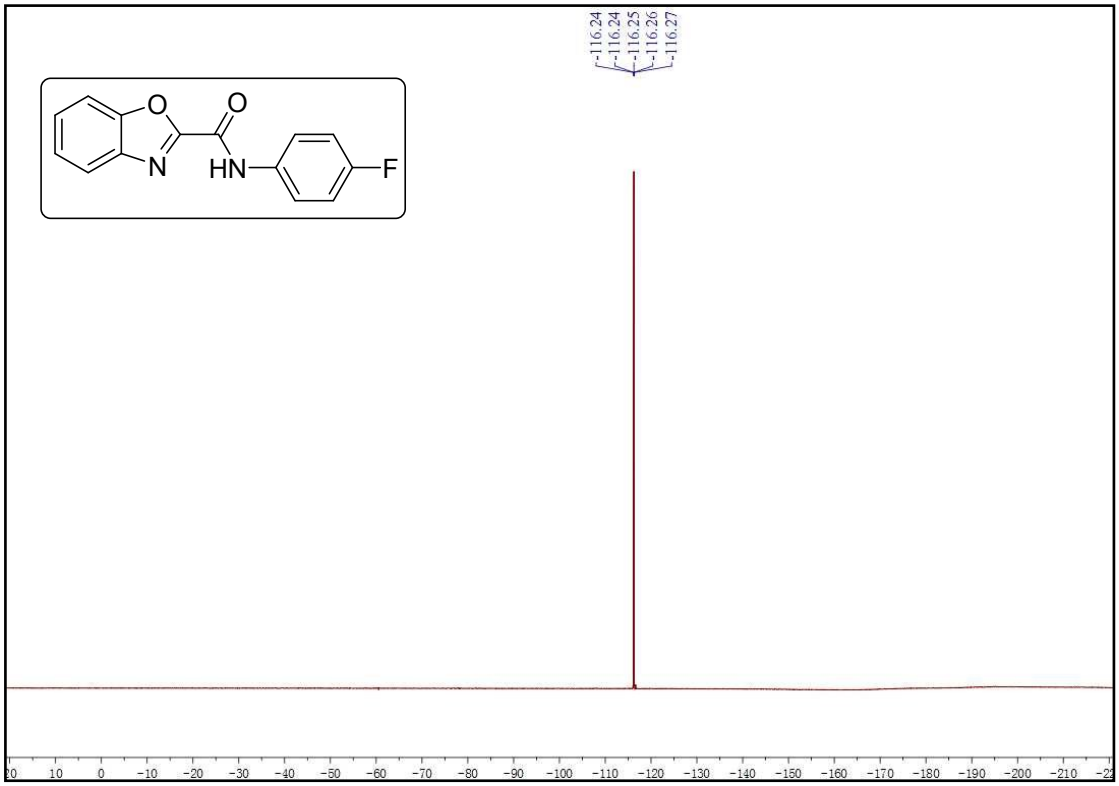


## N-(4-fluorophenyl)benzo[*d*]oxazole-2-carboxamide (5d)

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N
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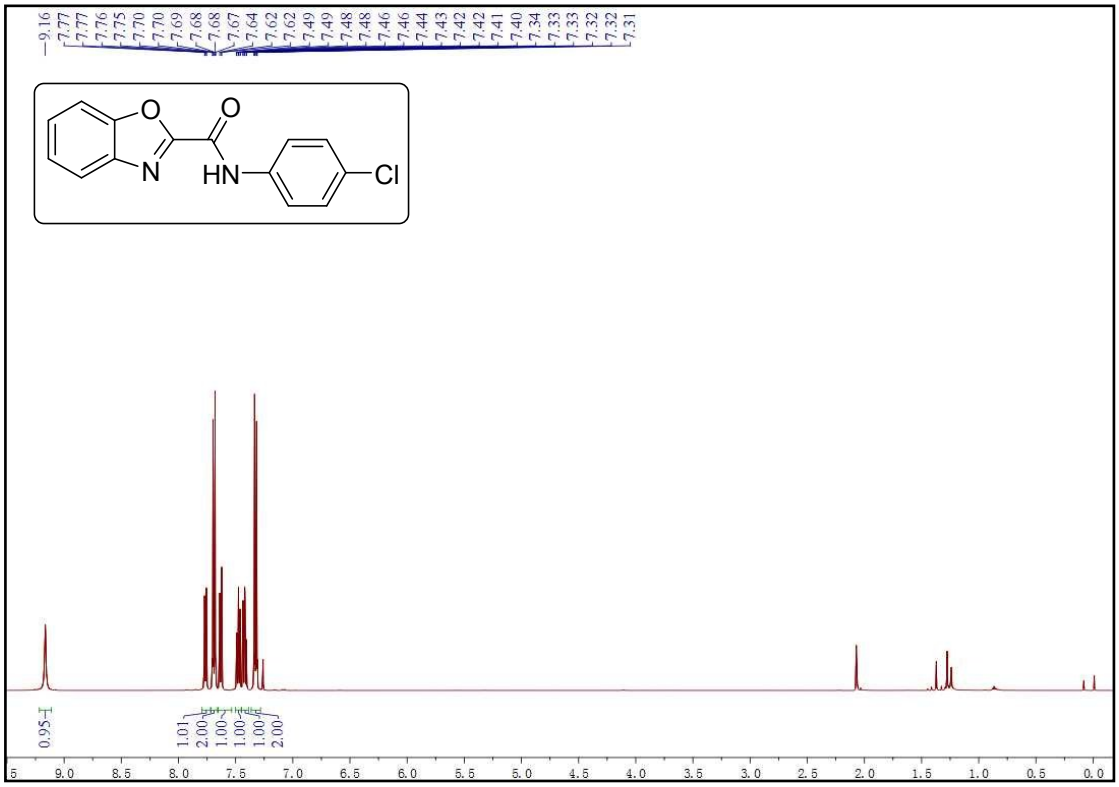
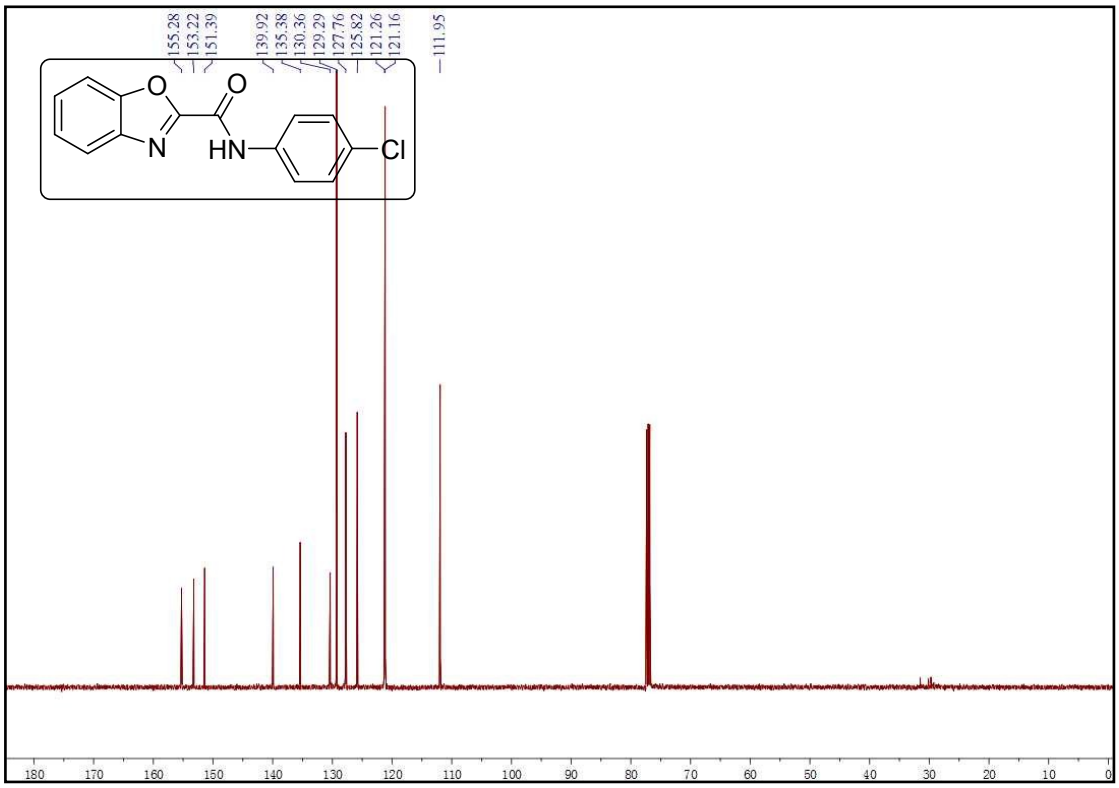
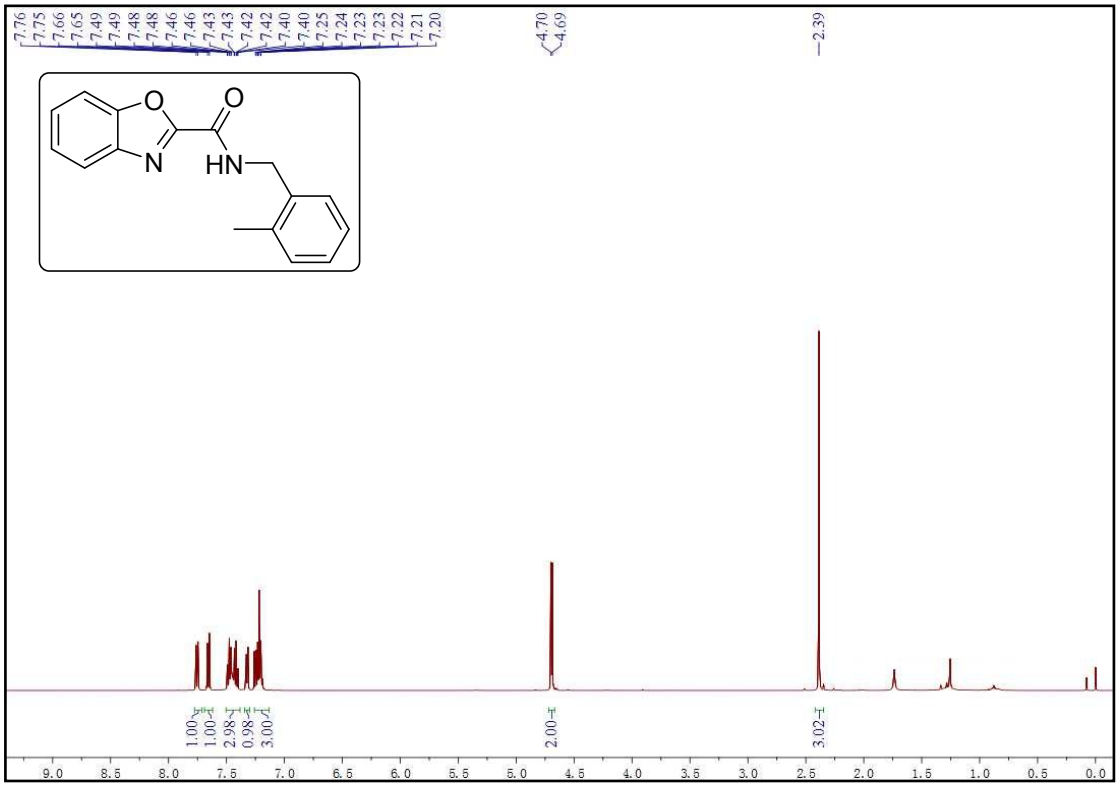
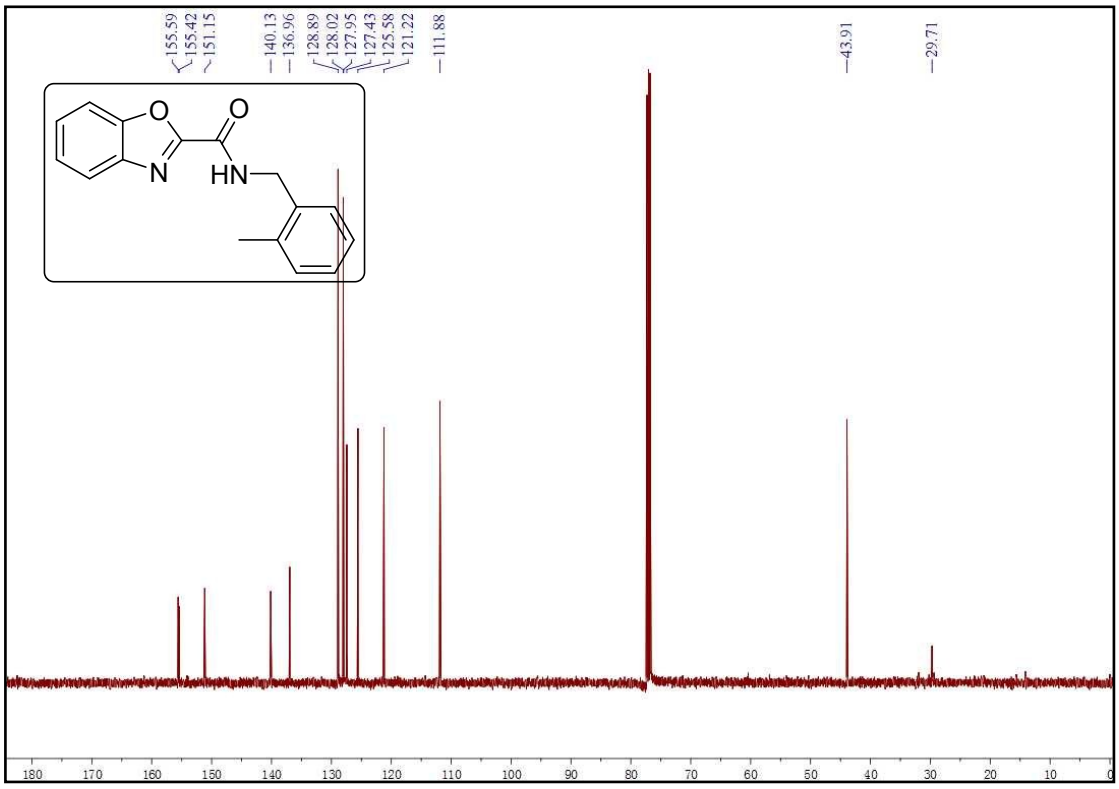
## N-(4-chlorophenyl)benzo[*d*]oxazole-2-carboxamide (5e)



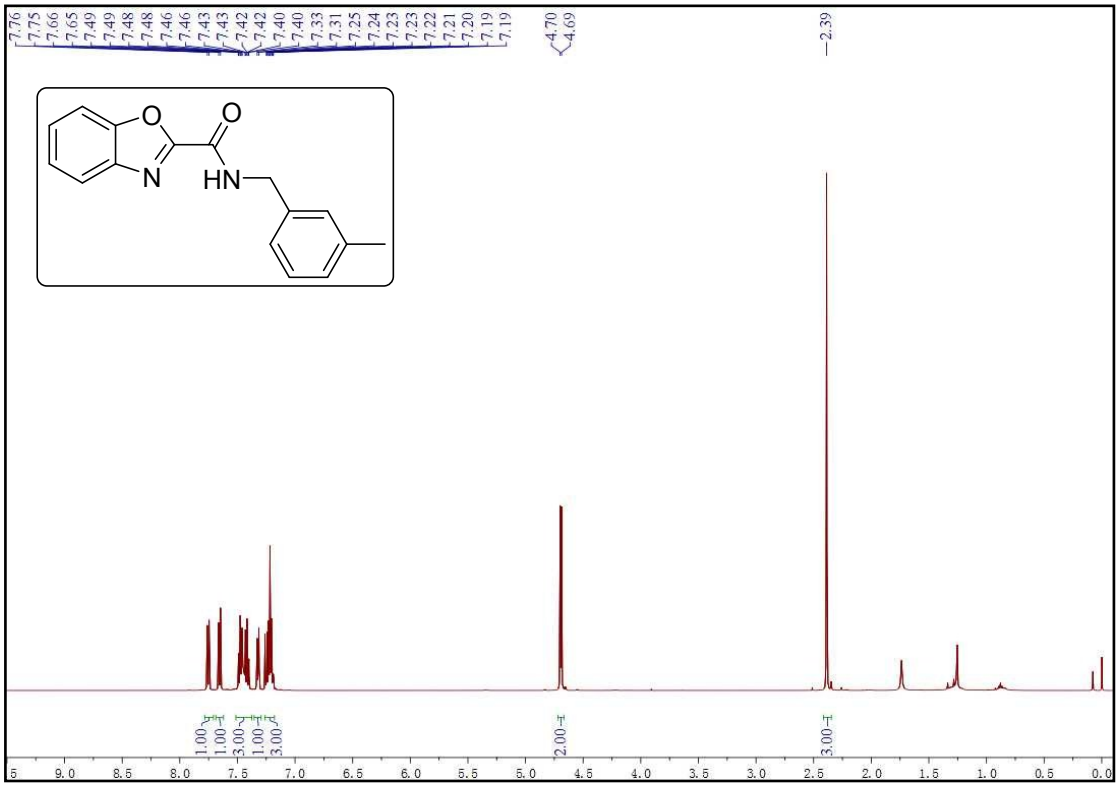



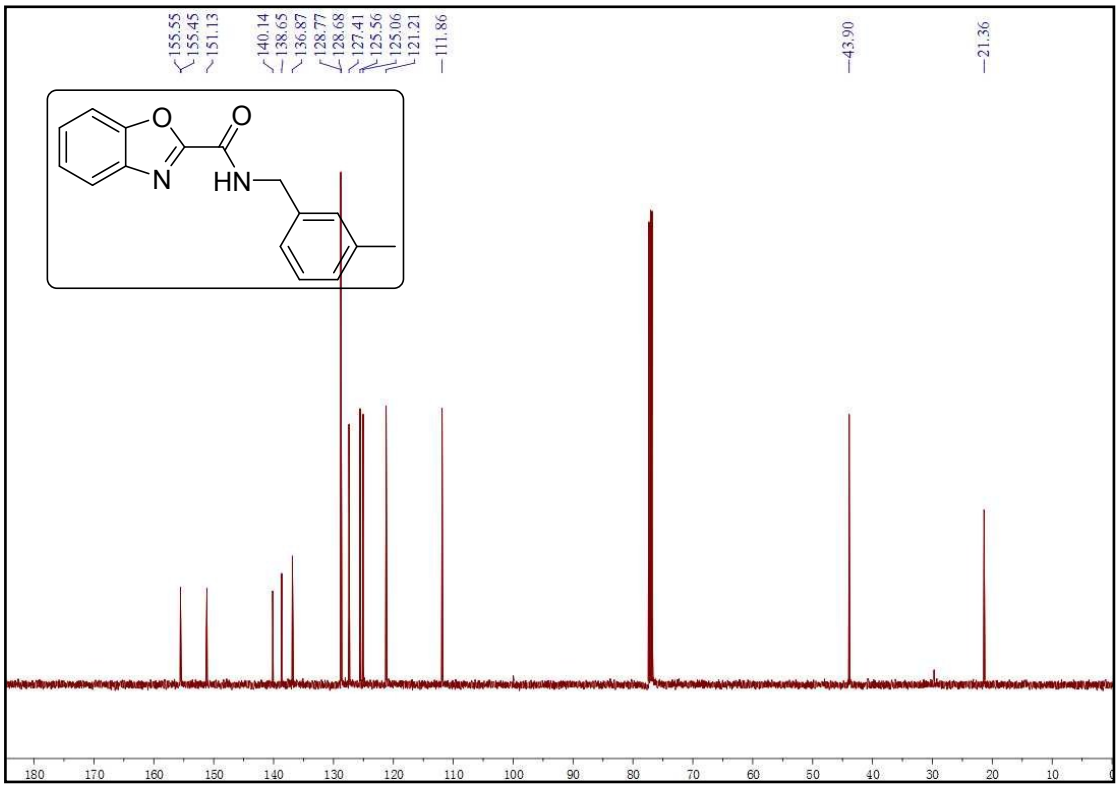
## *N*-(2-methylbenzyl)benzo[*d*]oxazole-2-carboxamide (5f)



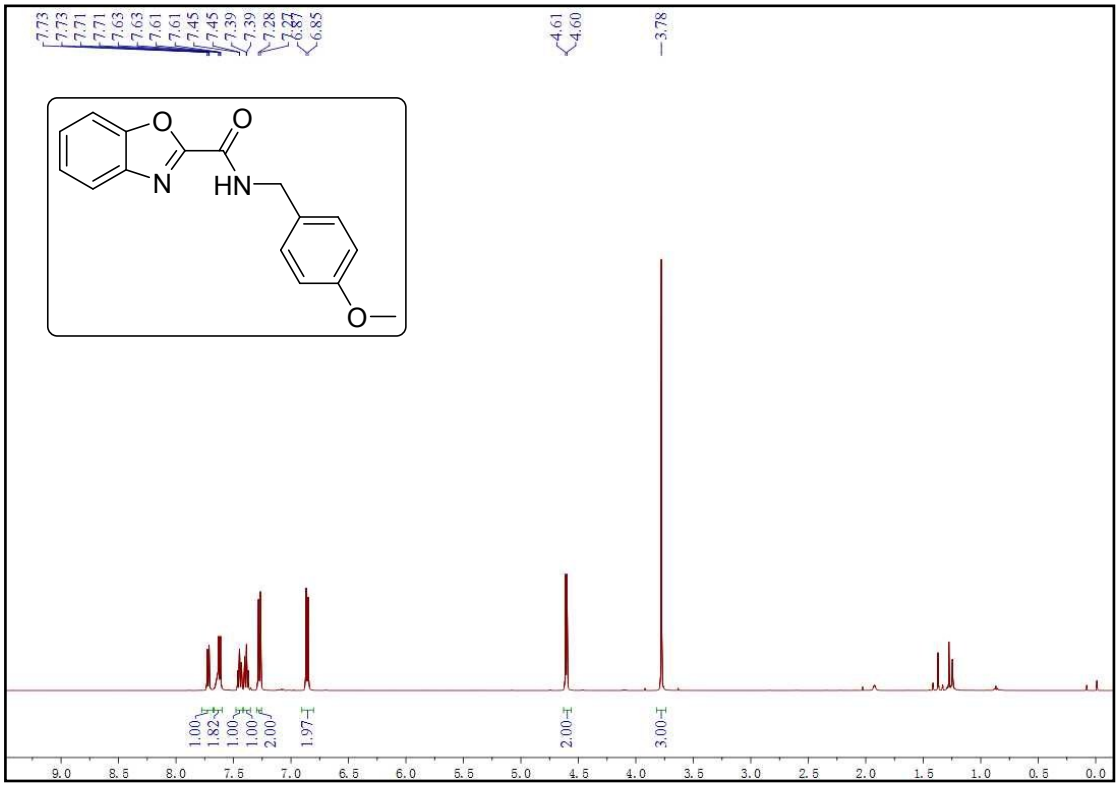



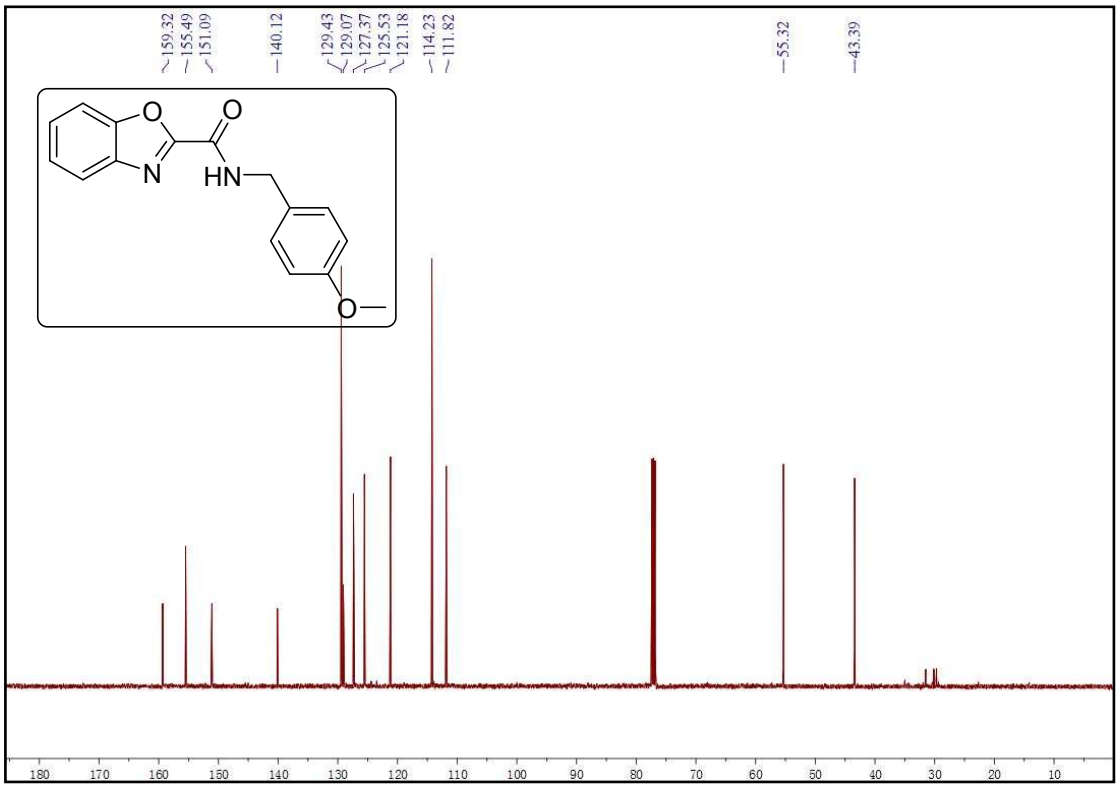
## *N*-(3-methylbenzyl)benzo[*d*]oxazole-2-carboxamide (5g)



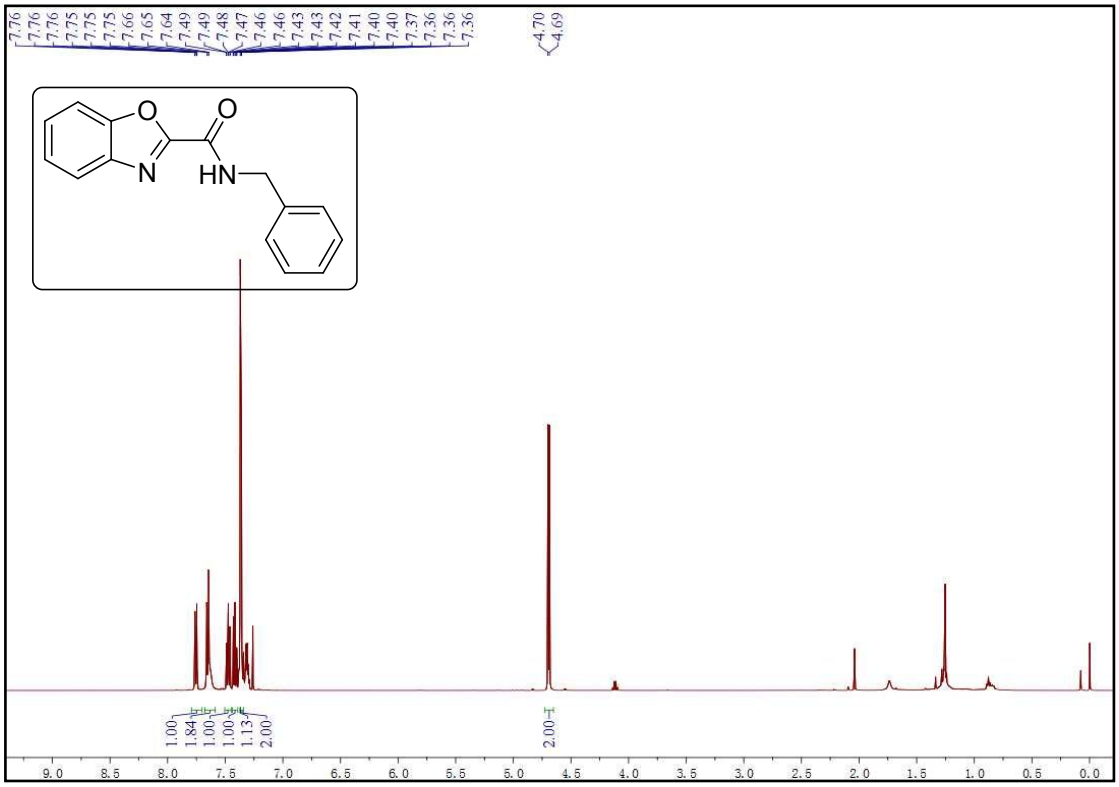



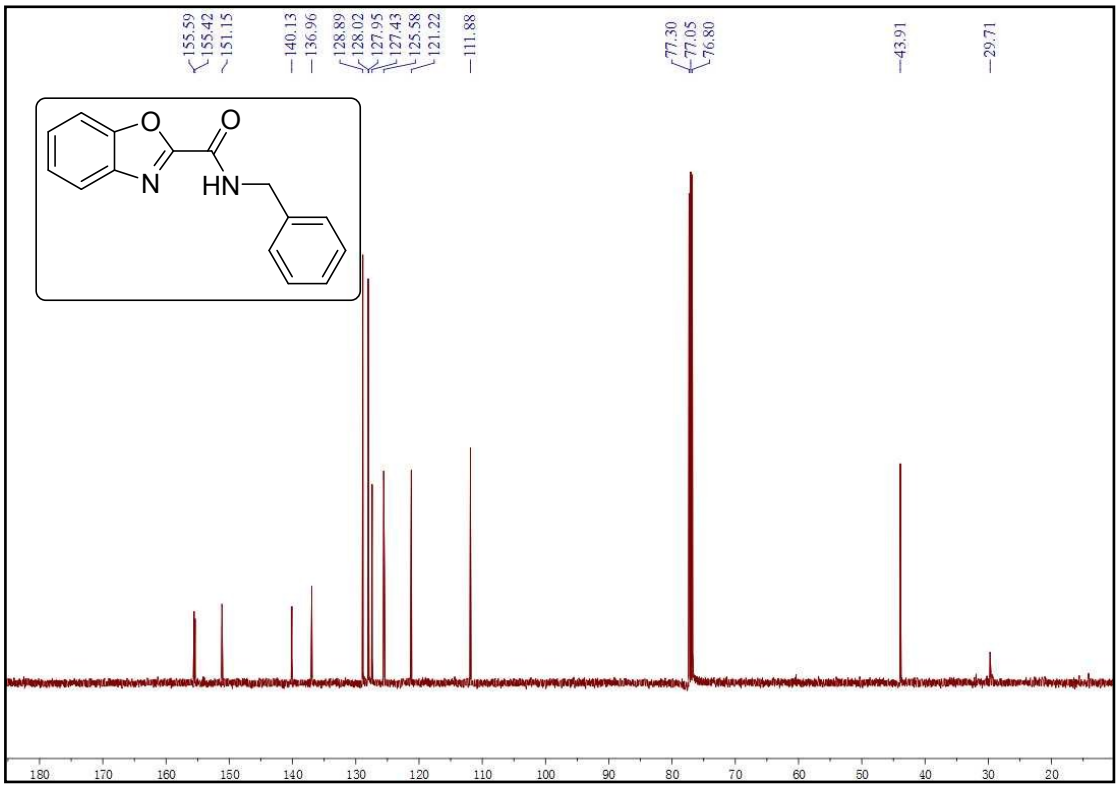
## N-(4-methoxybenzyl)benzo[*d*]oxazole-2-carboxamide (5h)



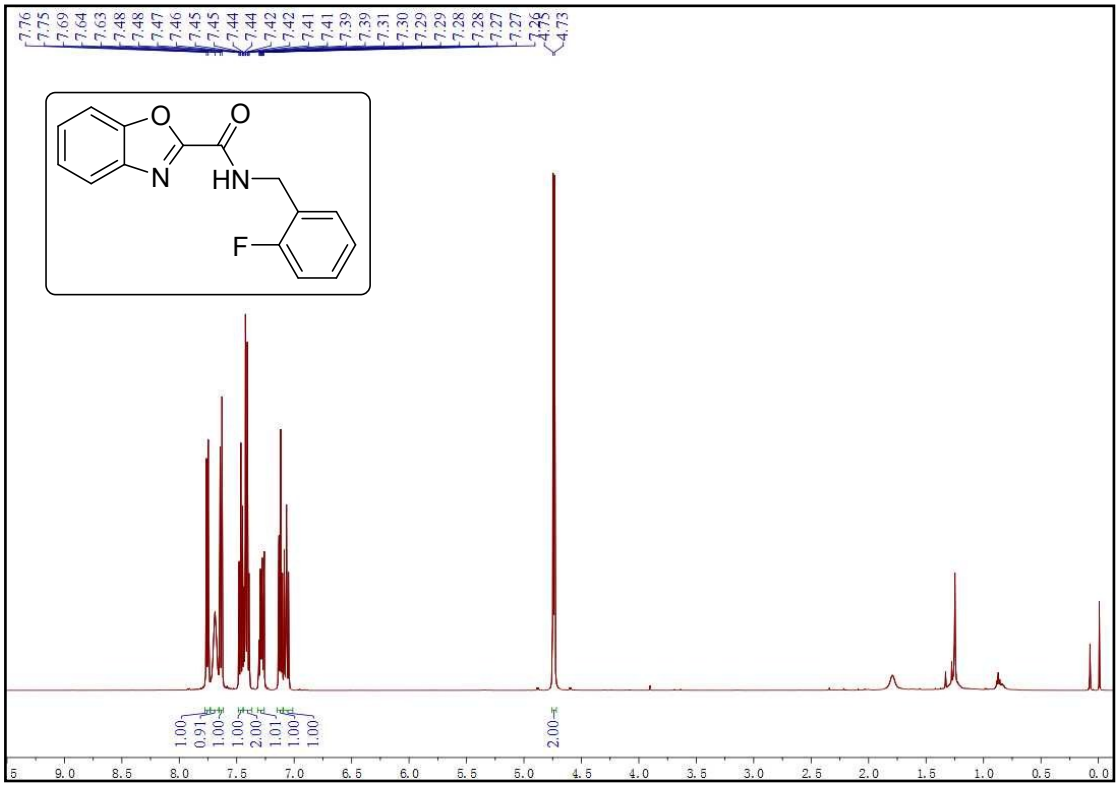



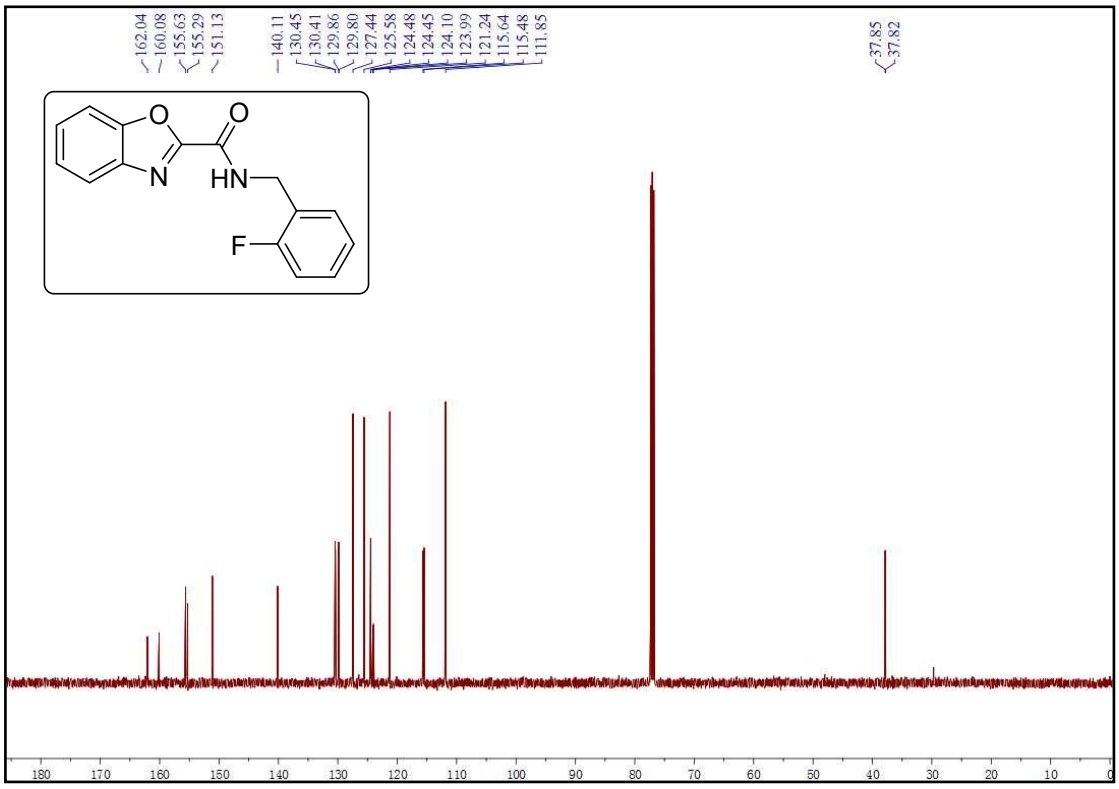
## N-benzylbenzo[*d*]oxazole-2-carboxamide (5i)

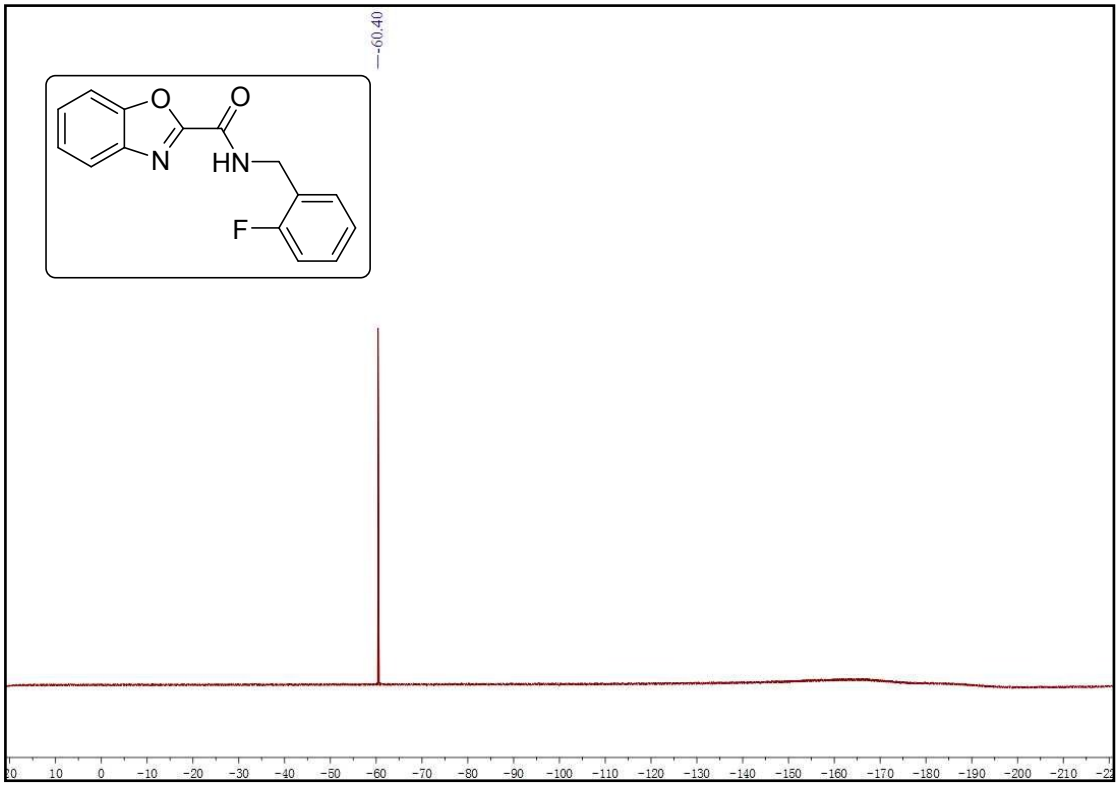


## *N*-(2-fluorobenzyl)benzo[*d*]oxazole-2-carboxamide (5j)

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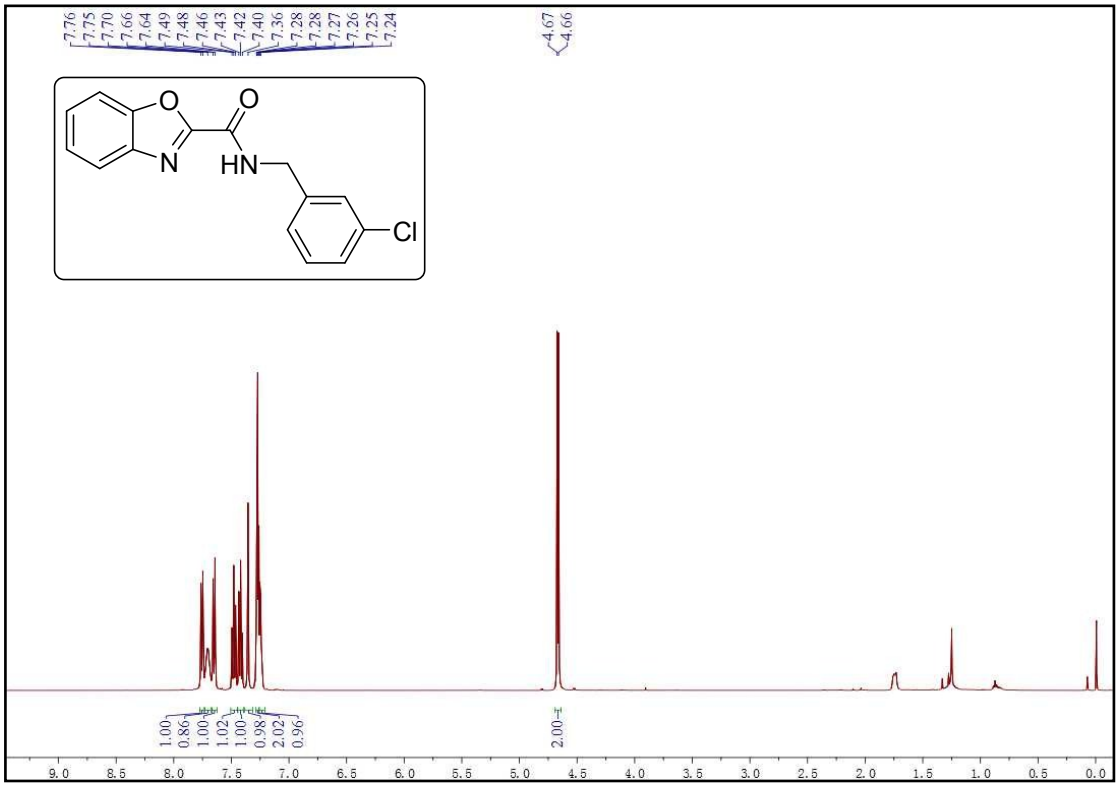
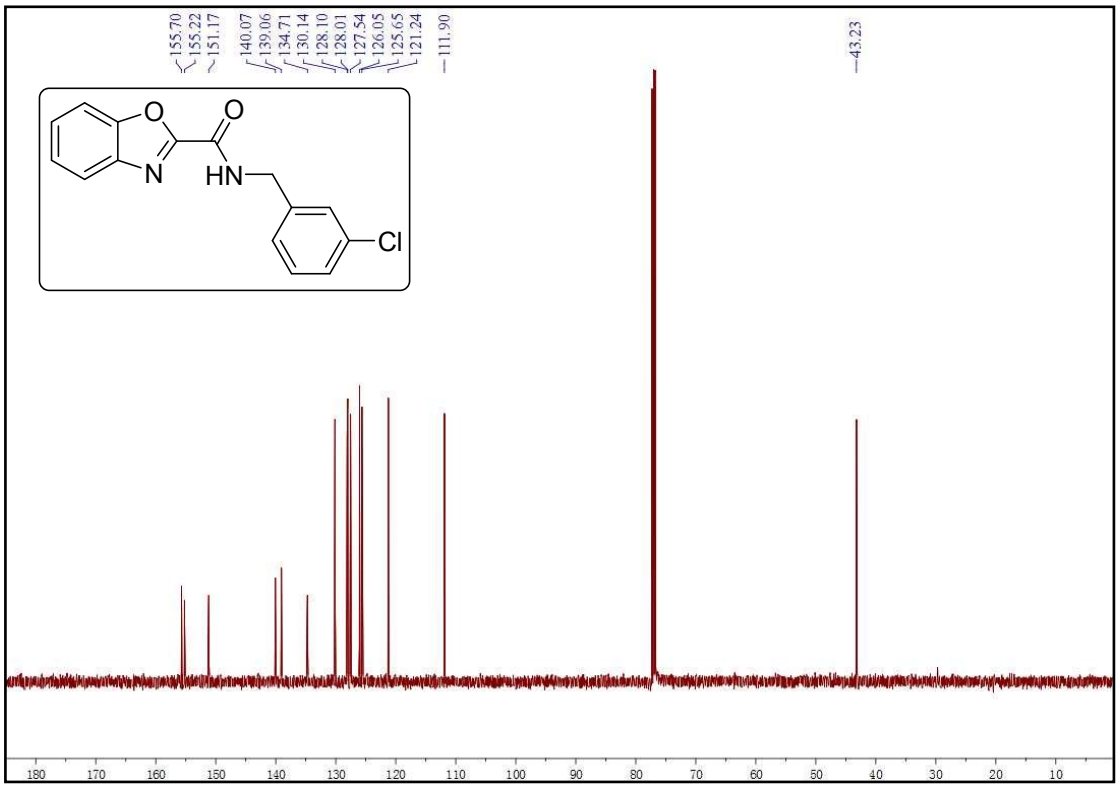
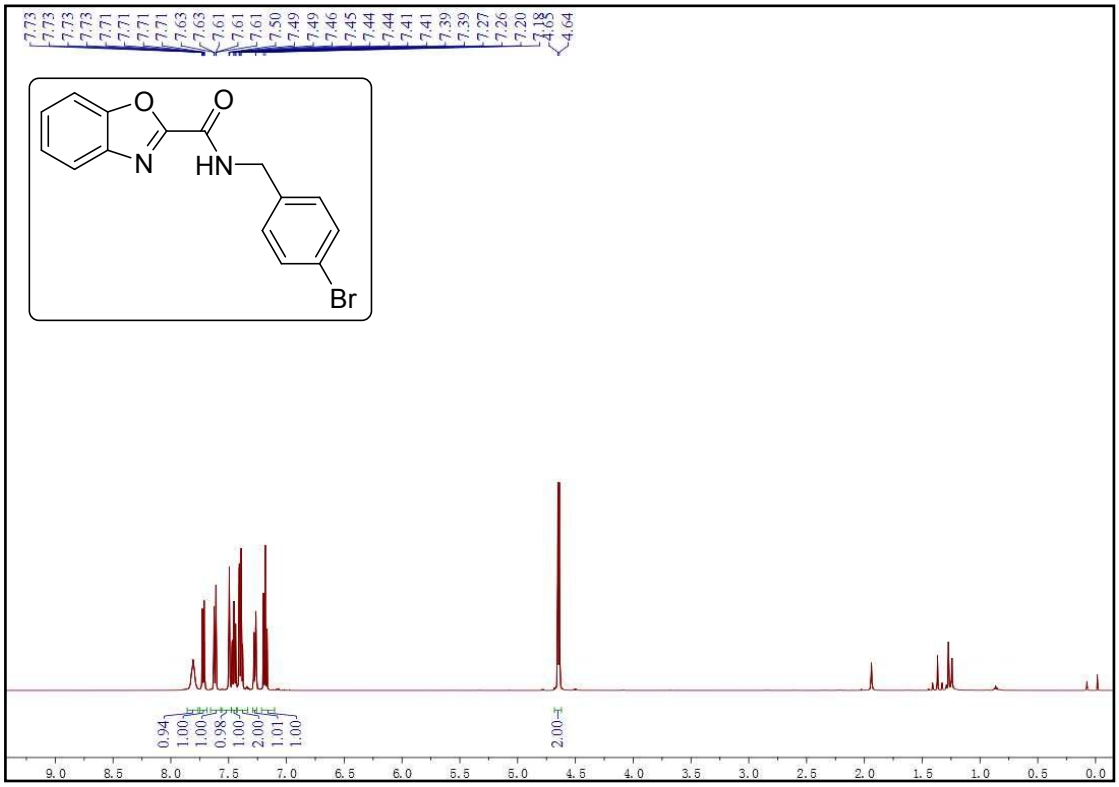
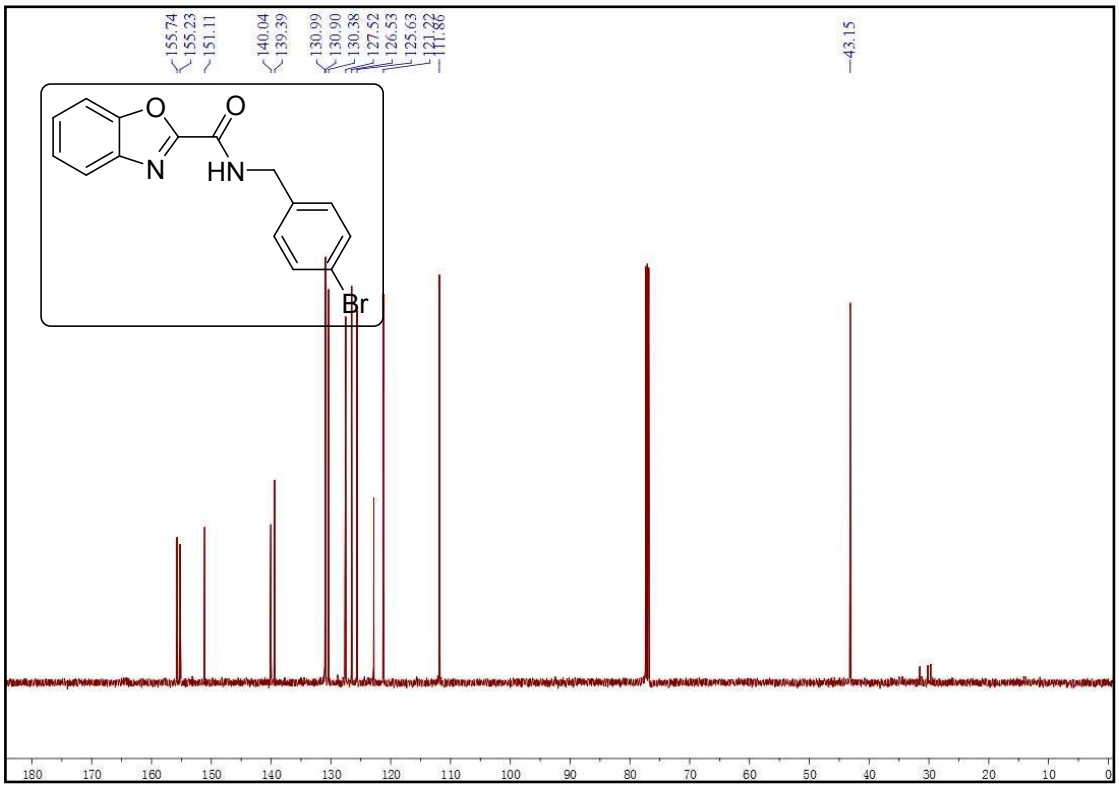
## *N*-(3-chlorobenzyl)benzo[*d*]oxazole-2-carboxamide (5k)



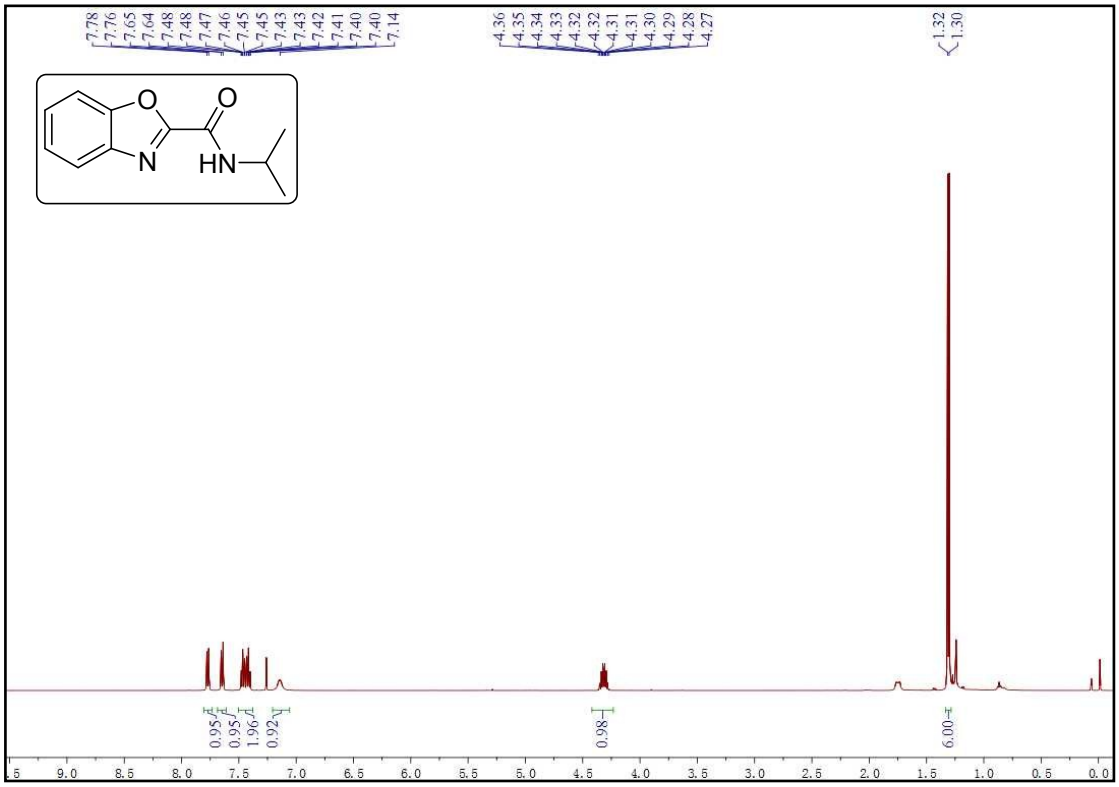



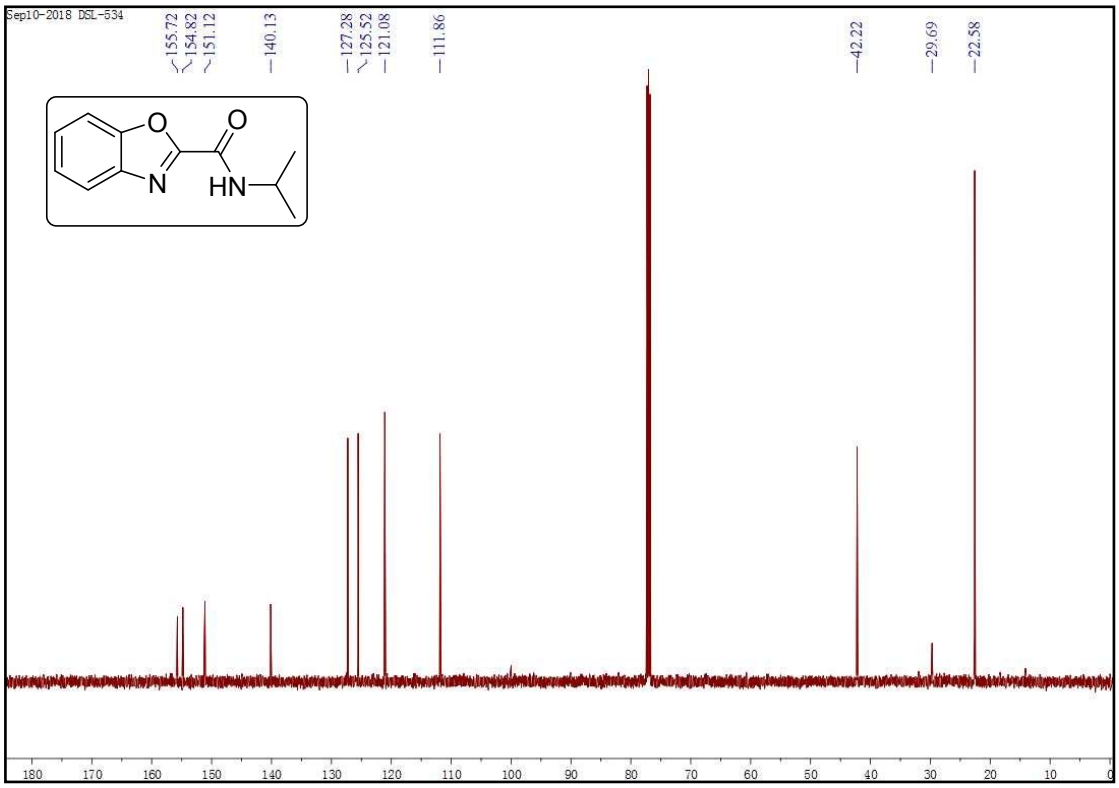
## N-(3-bromobenzyl)benzo[*d*]oxazole-2-carboxamide (5l)



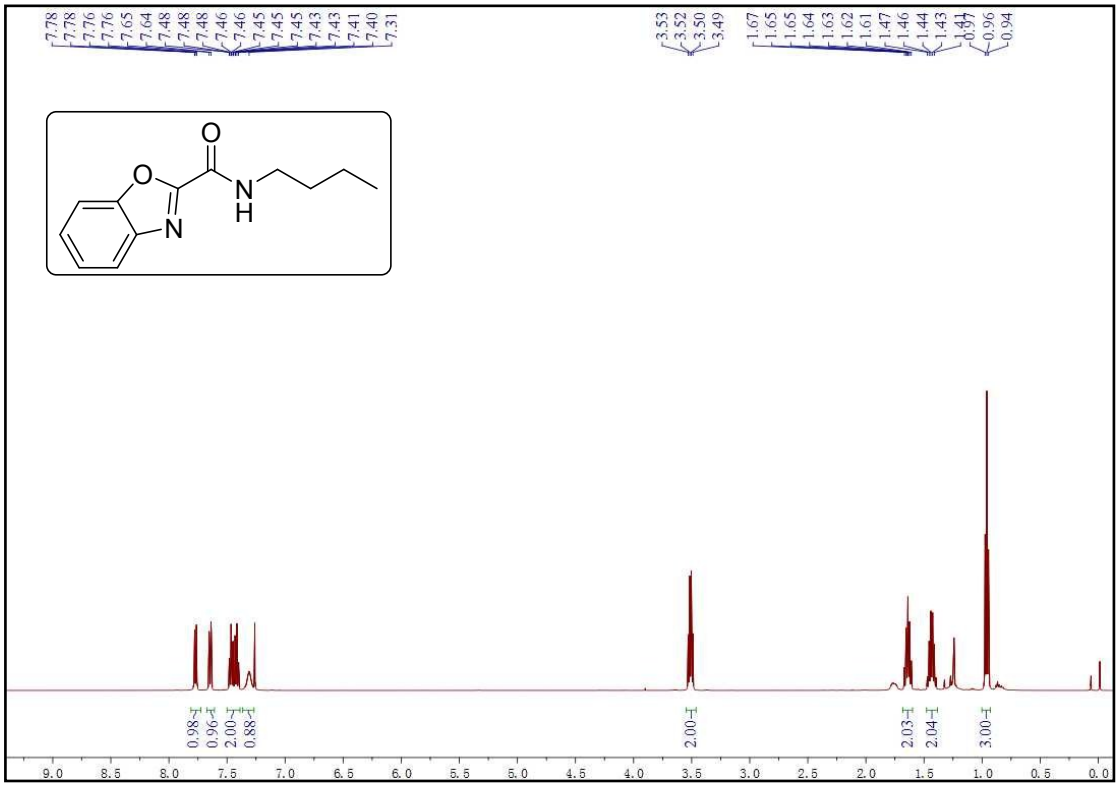



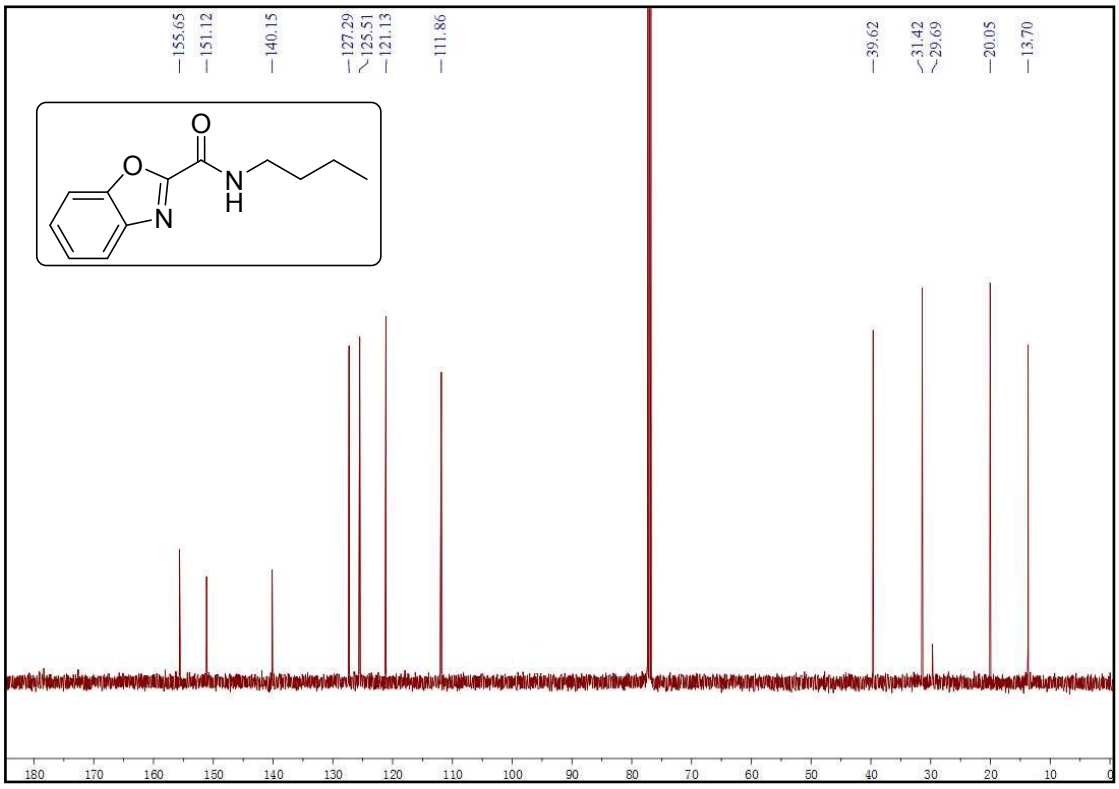
## *N*-isopropylbenzo[*d*]oxazole-2-carboxamide (5m)



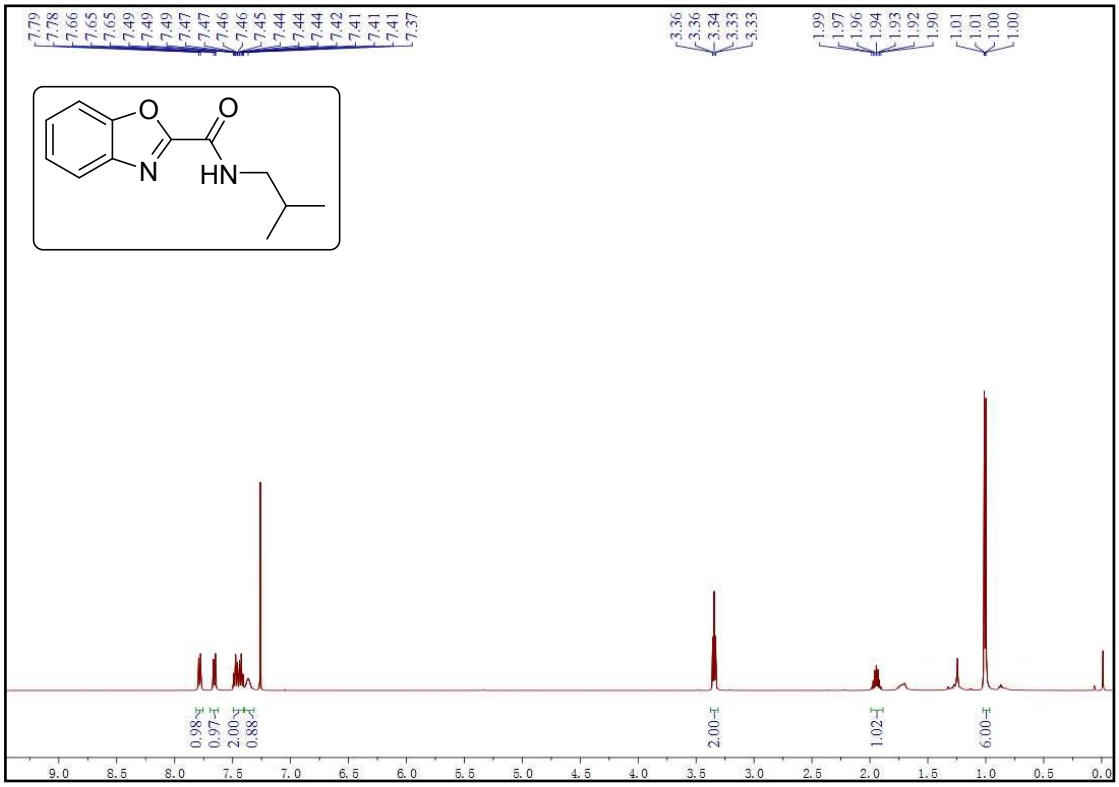



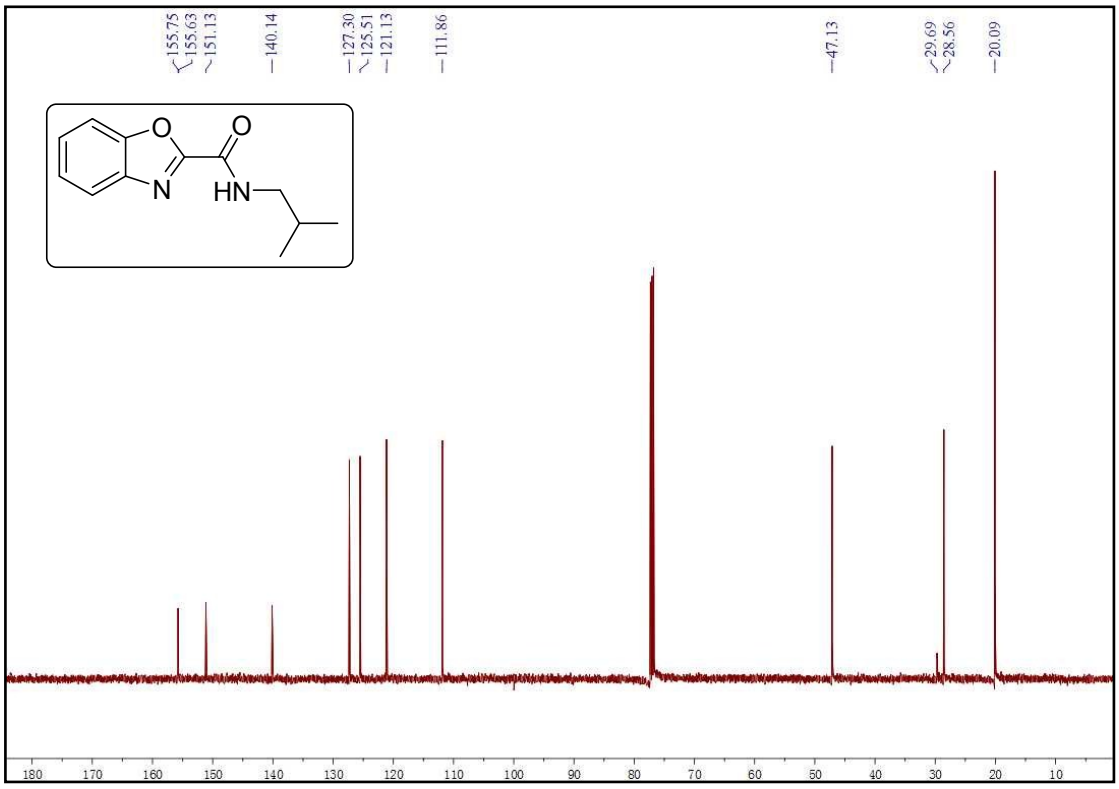
## *N*-butylbenzo[*d*]oxazole-2-carboxamide (5n)



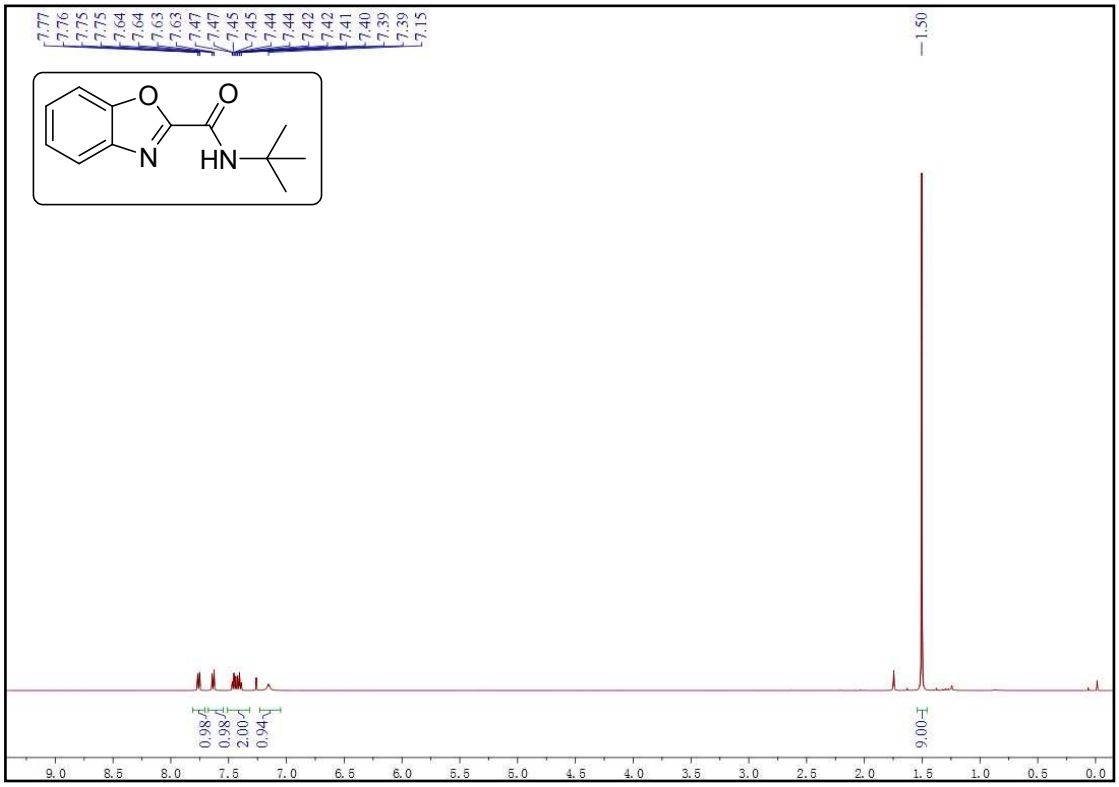



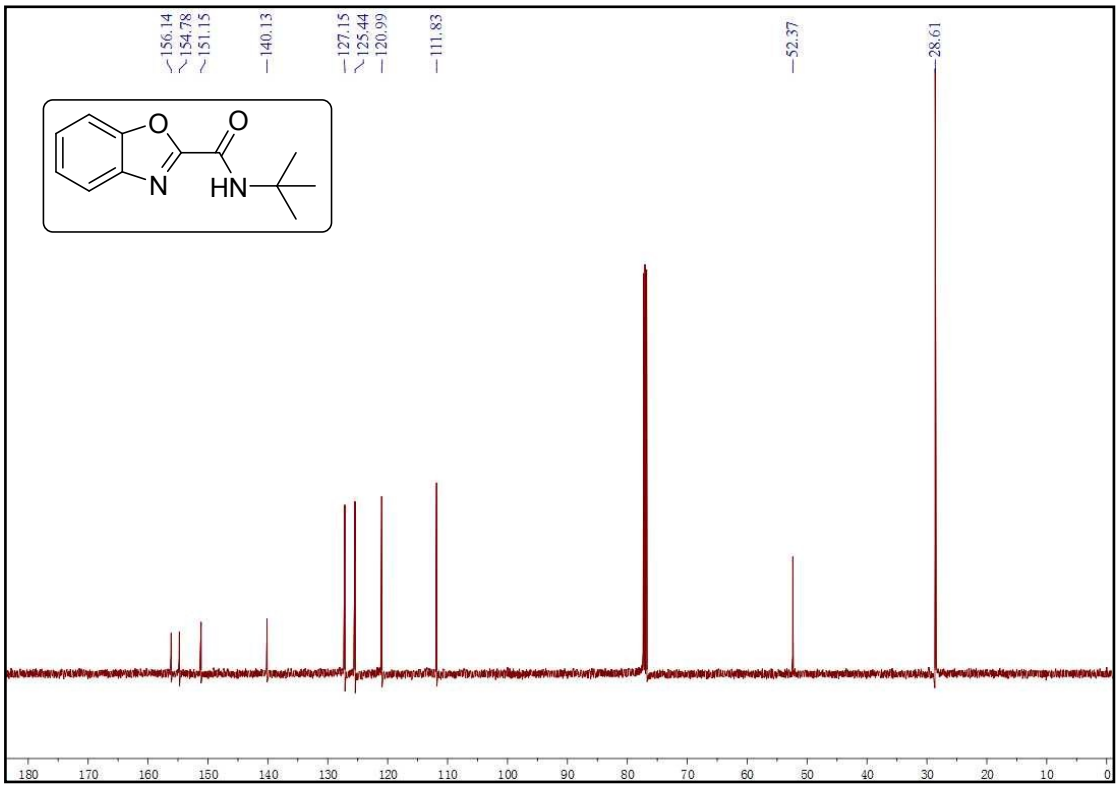
## N-isobutylbenzo[*d*]oxazole-2-carboxamide (5o)



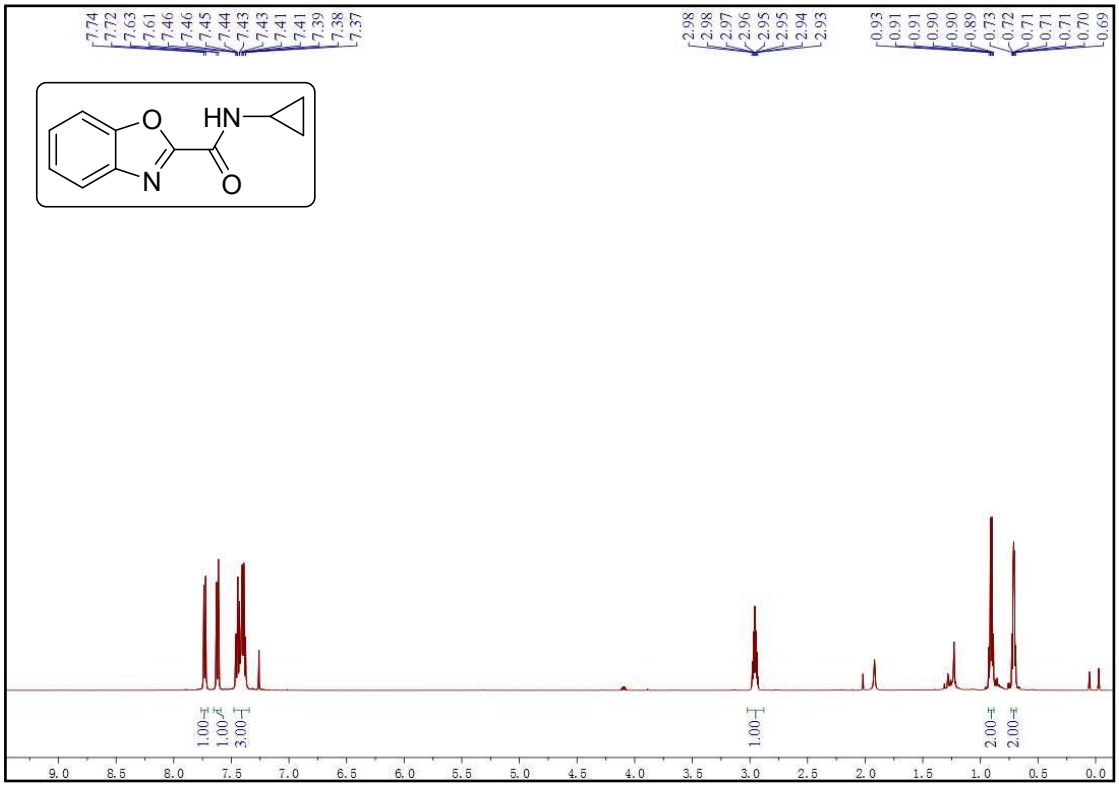



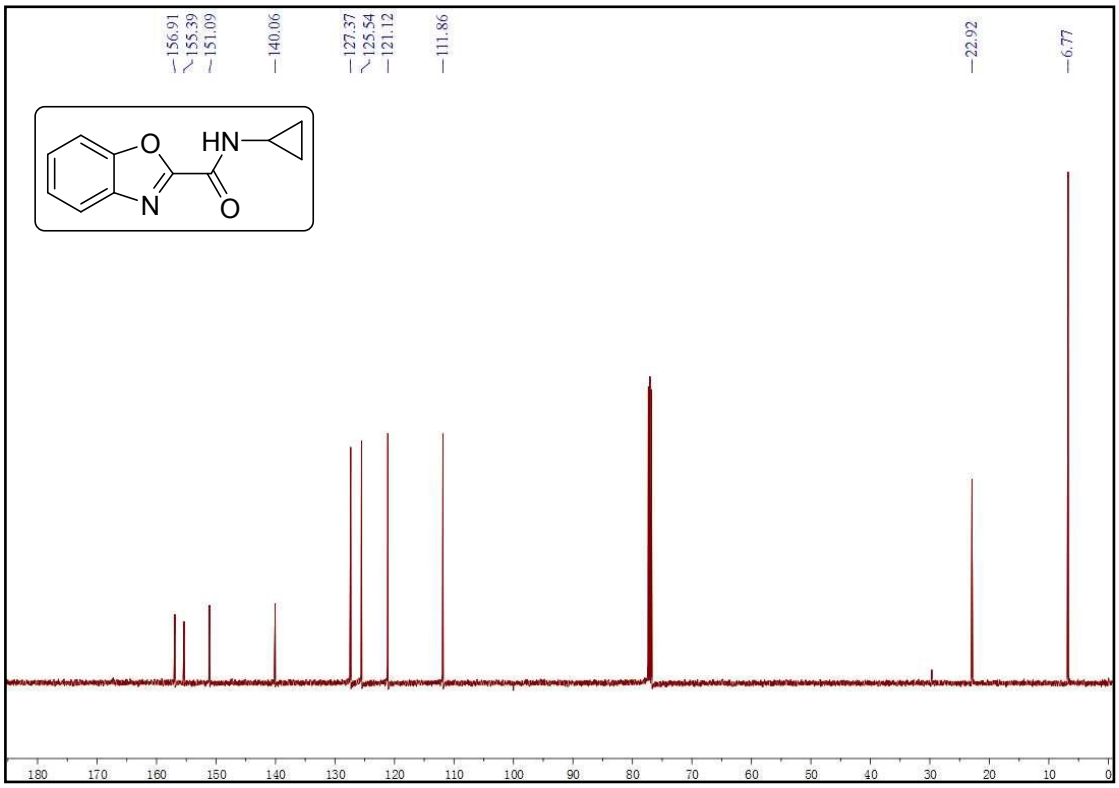
## N-(tert-butyl)benzo[*d*]oxazole-2-carboxamide (5p)



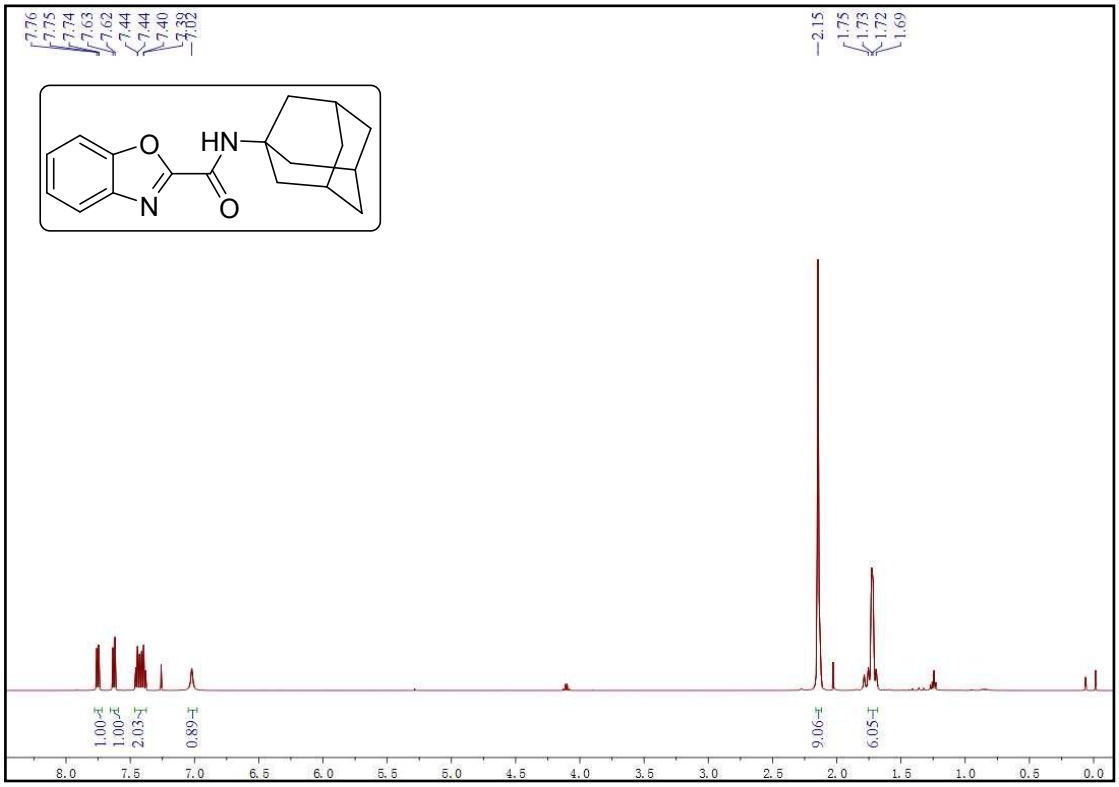



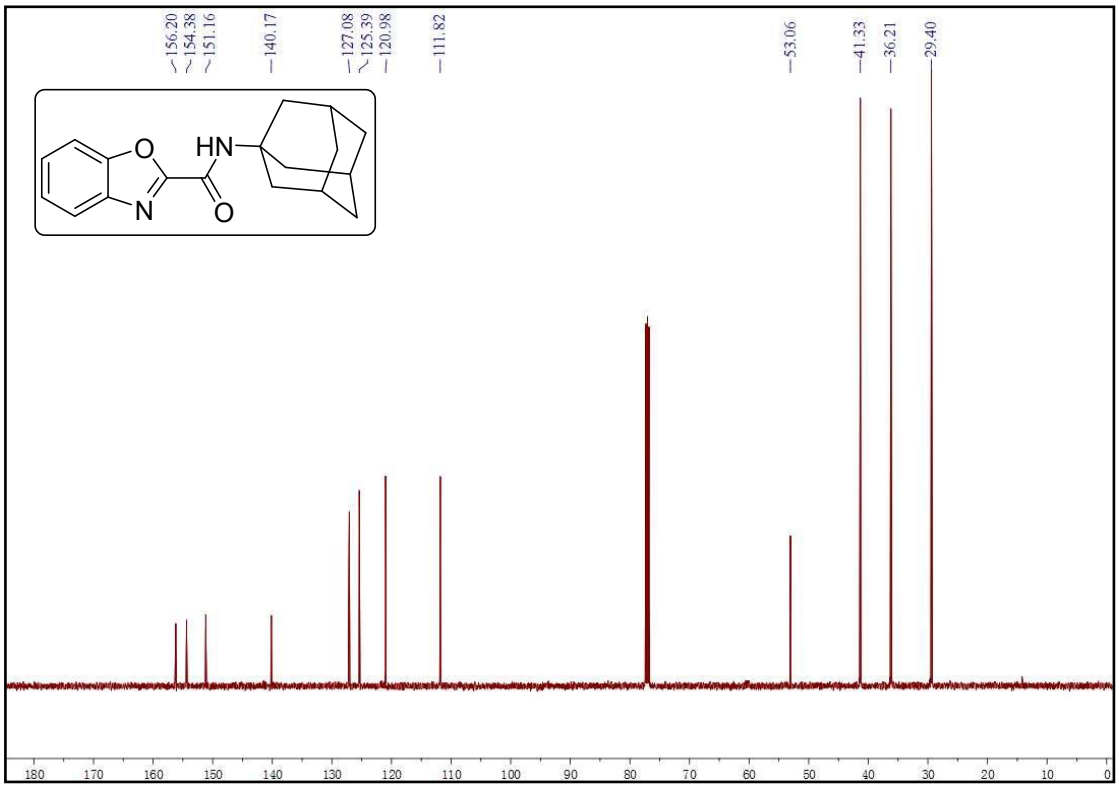
## N-cyclopropylbenzo[*d*]oxazole-2-carboxamide (5q)



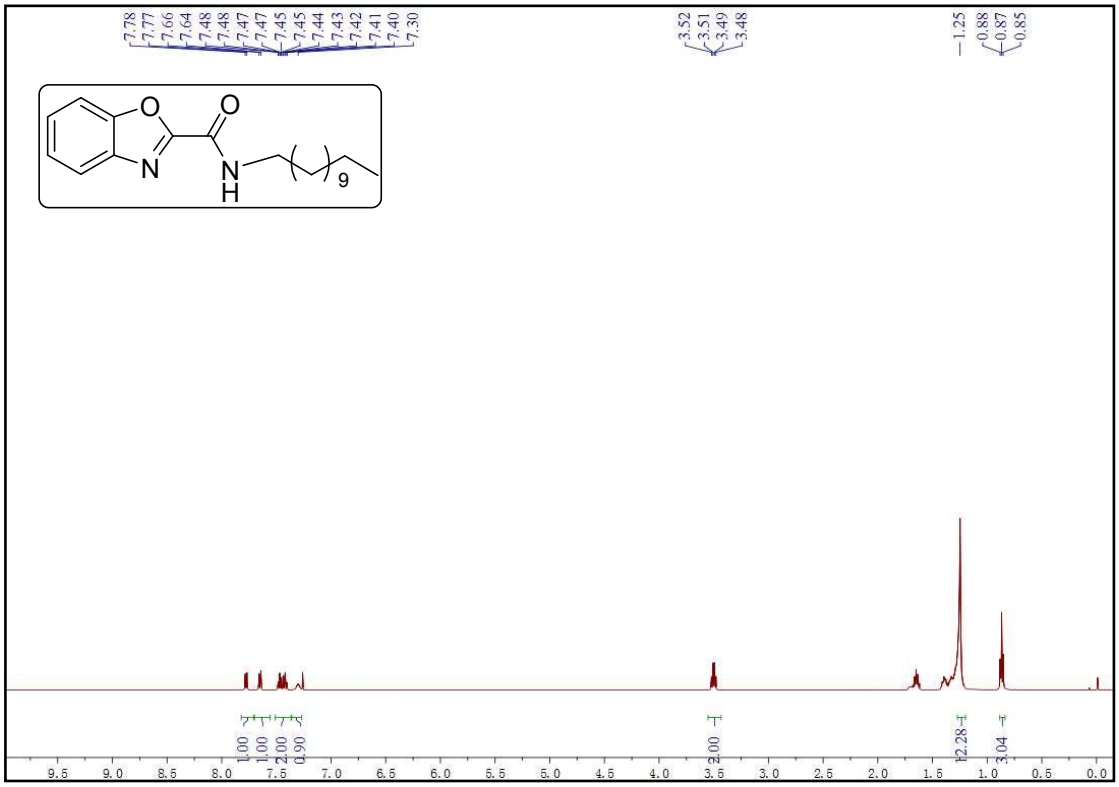



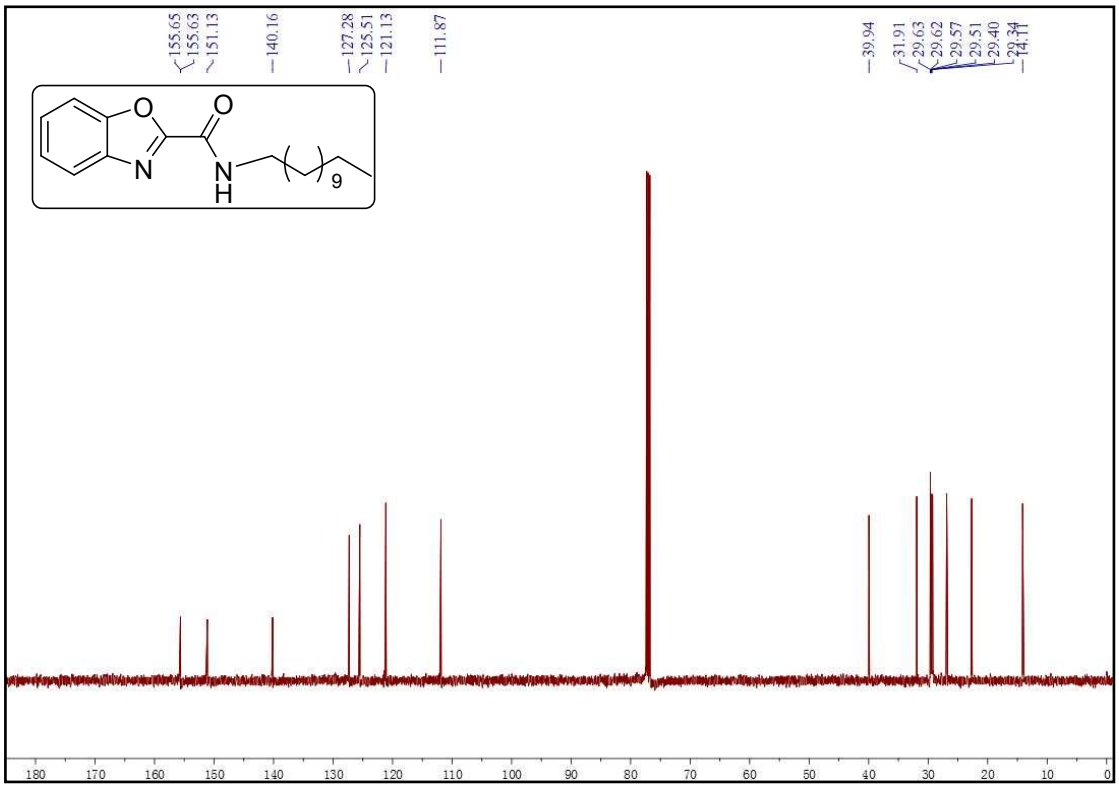
## N-((3s,5s,7s)-adamantan-1-yl)benzo[*d*]oxazole-2-carboxamide (5r)



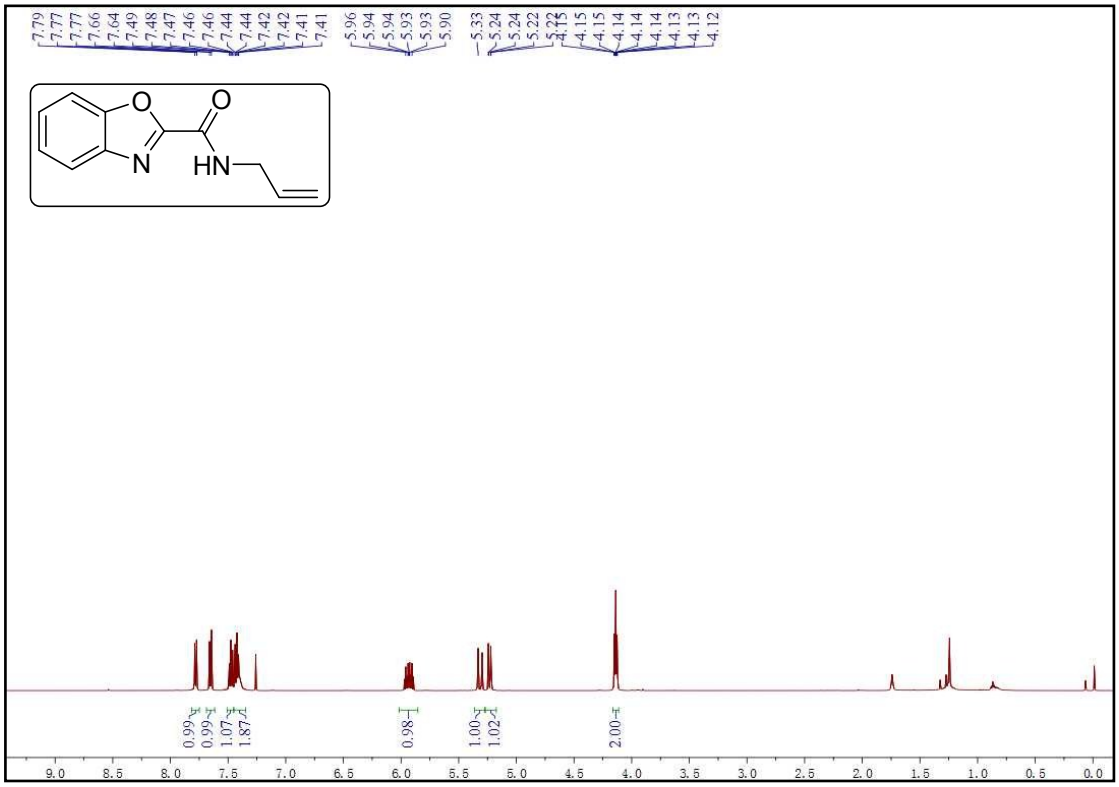



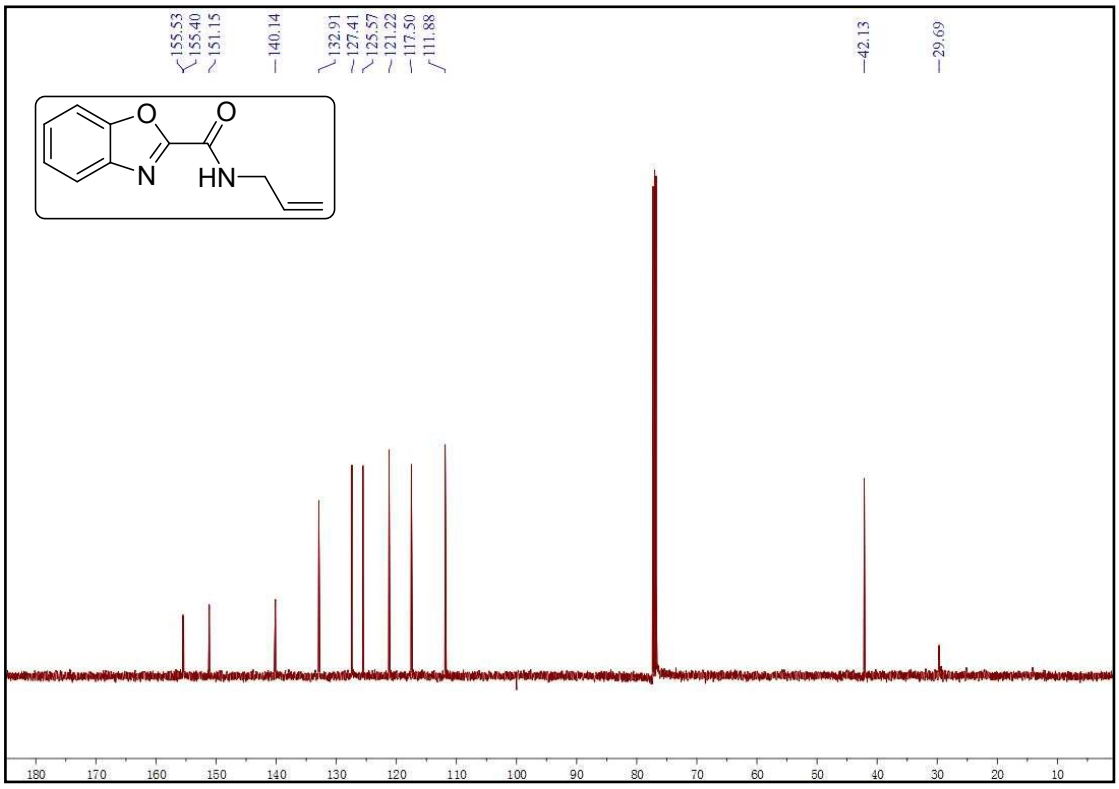
## *N*-dodecylbenzo[*d*]oxazole-2-carboxamide (5s)



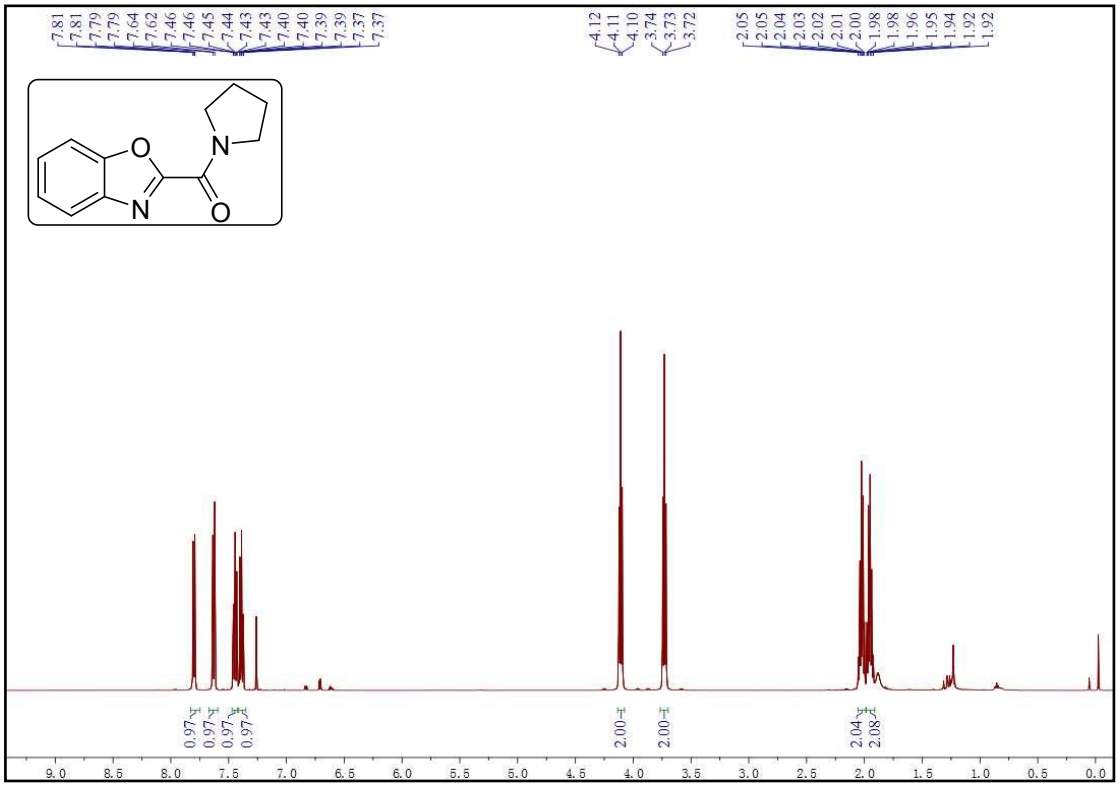



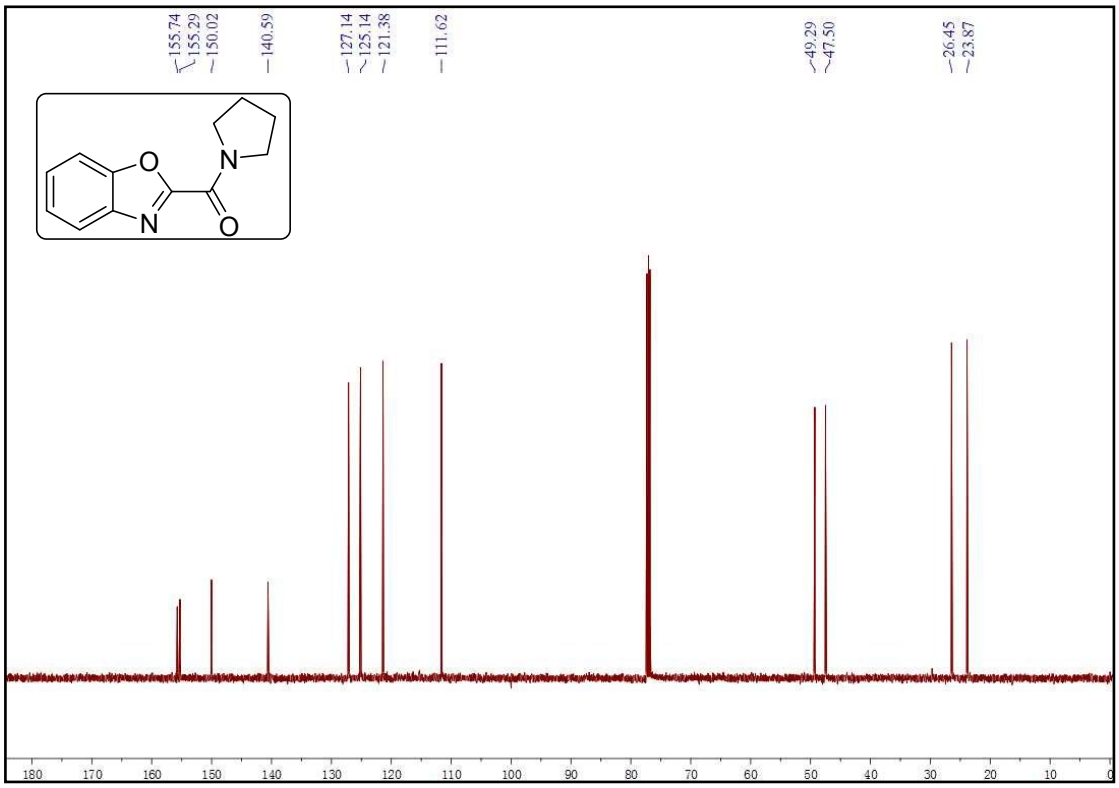
## *N*-allylbenzo[*d*]oxazole-2-carboxamide (5t)



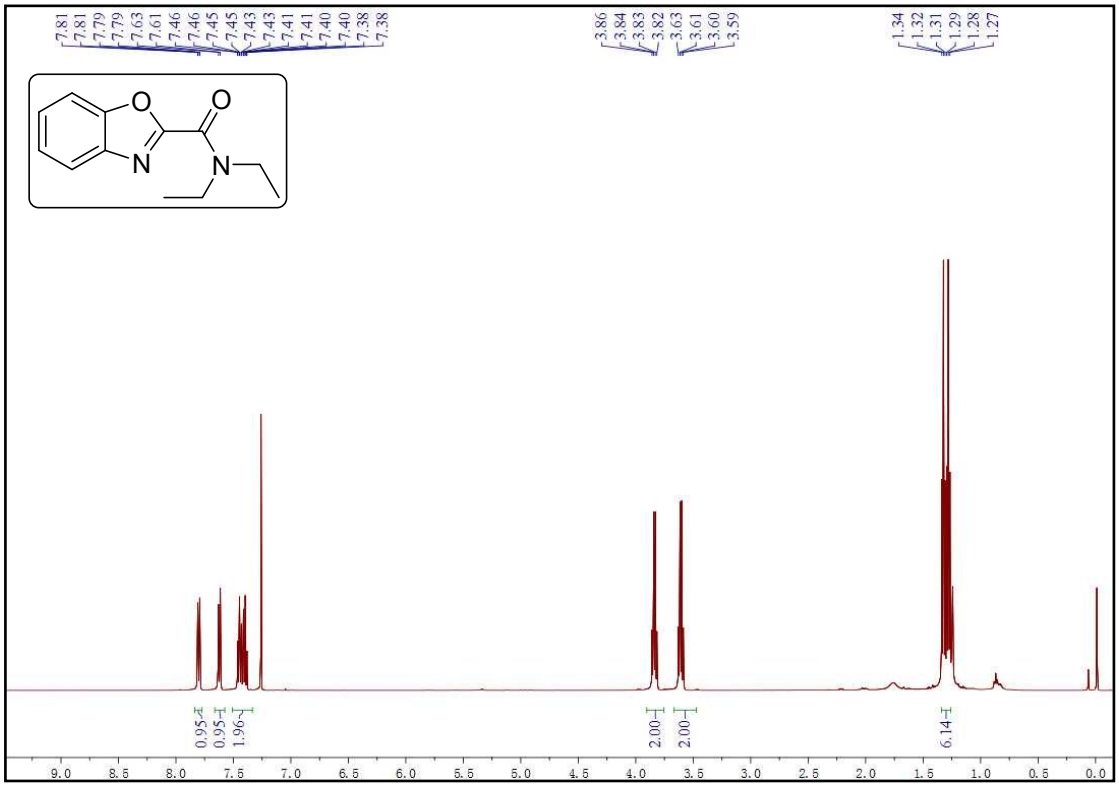



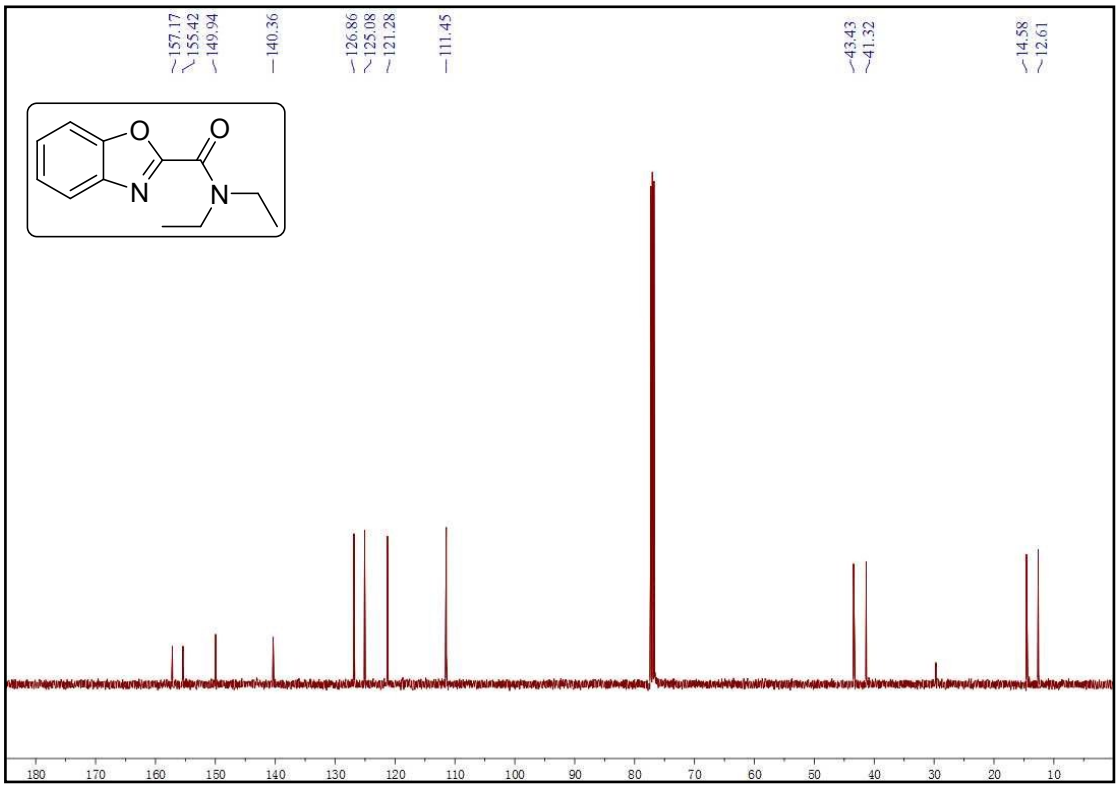
## benzo[*d*]oxazol-2-yl(pyrrolidin-1-yl)methanone (5u)



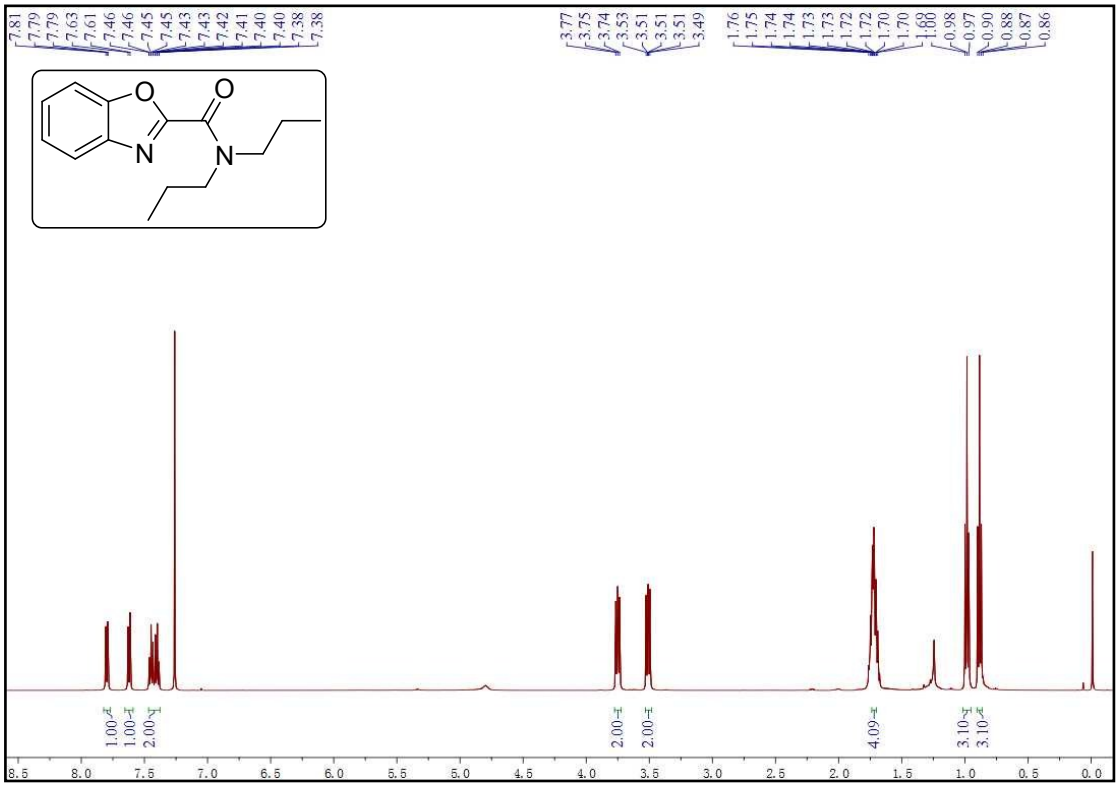



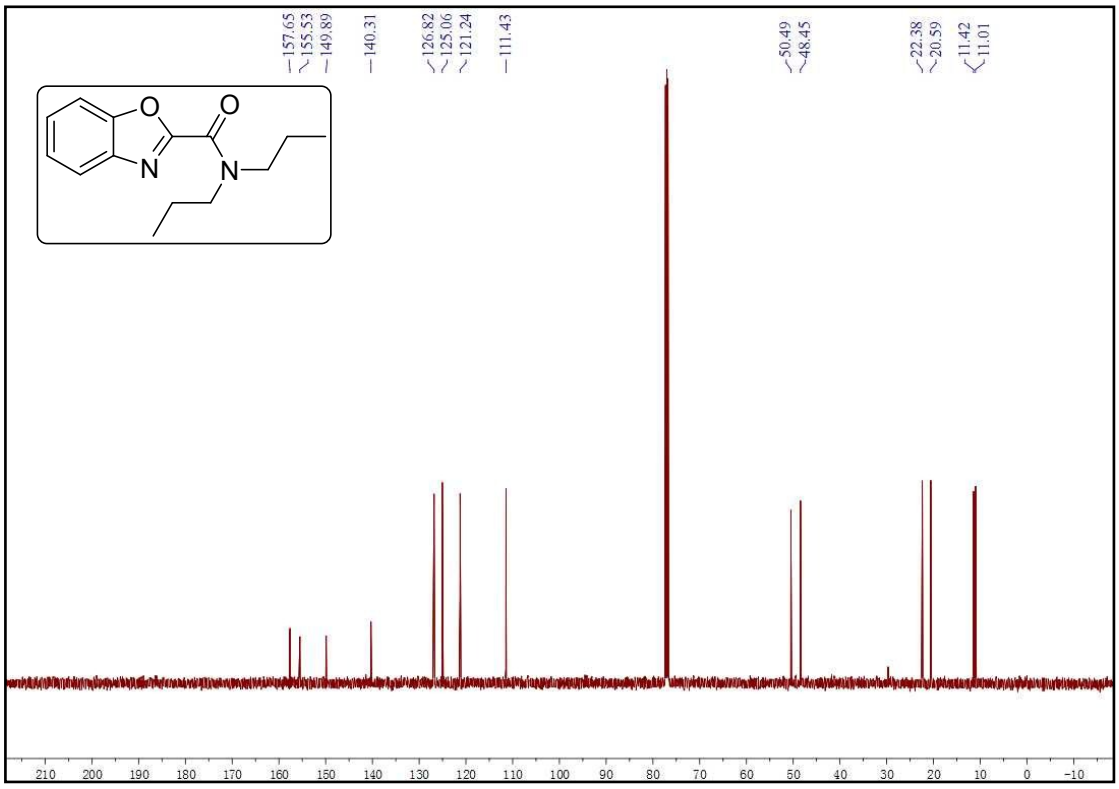
## *N*,*N*-diethylbenzo[*d*]oxazole-2-carboxamide (5v)



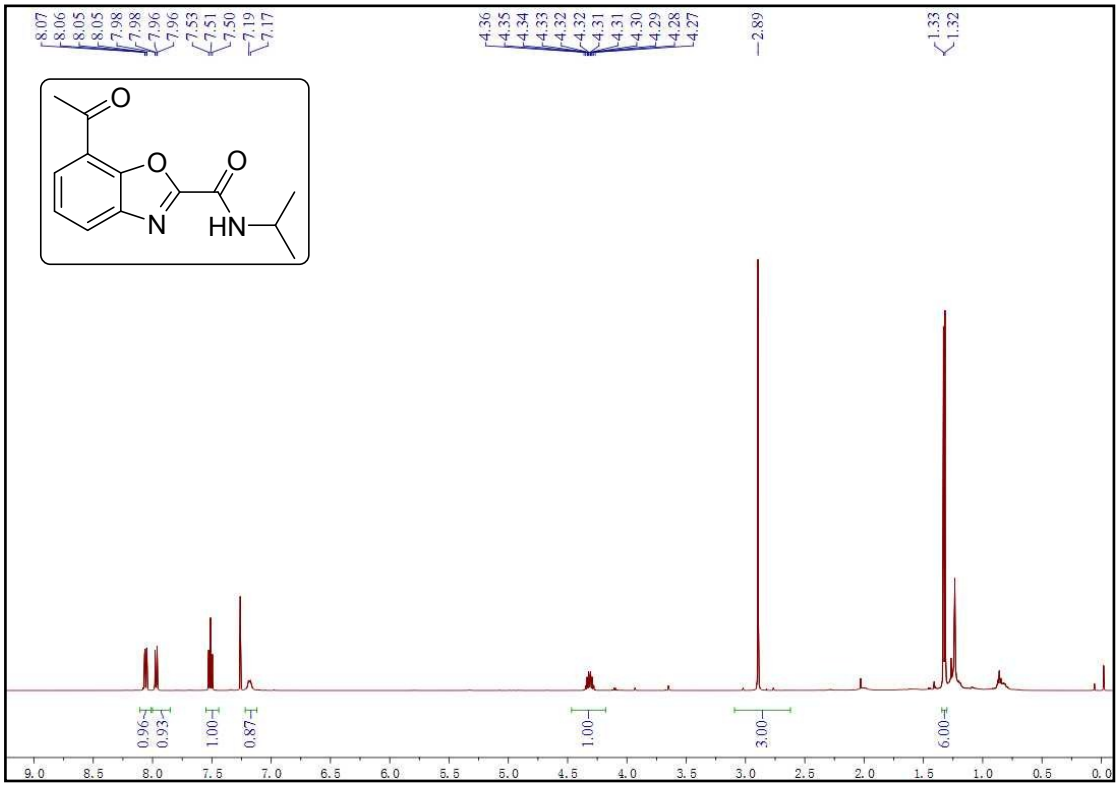



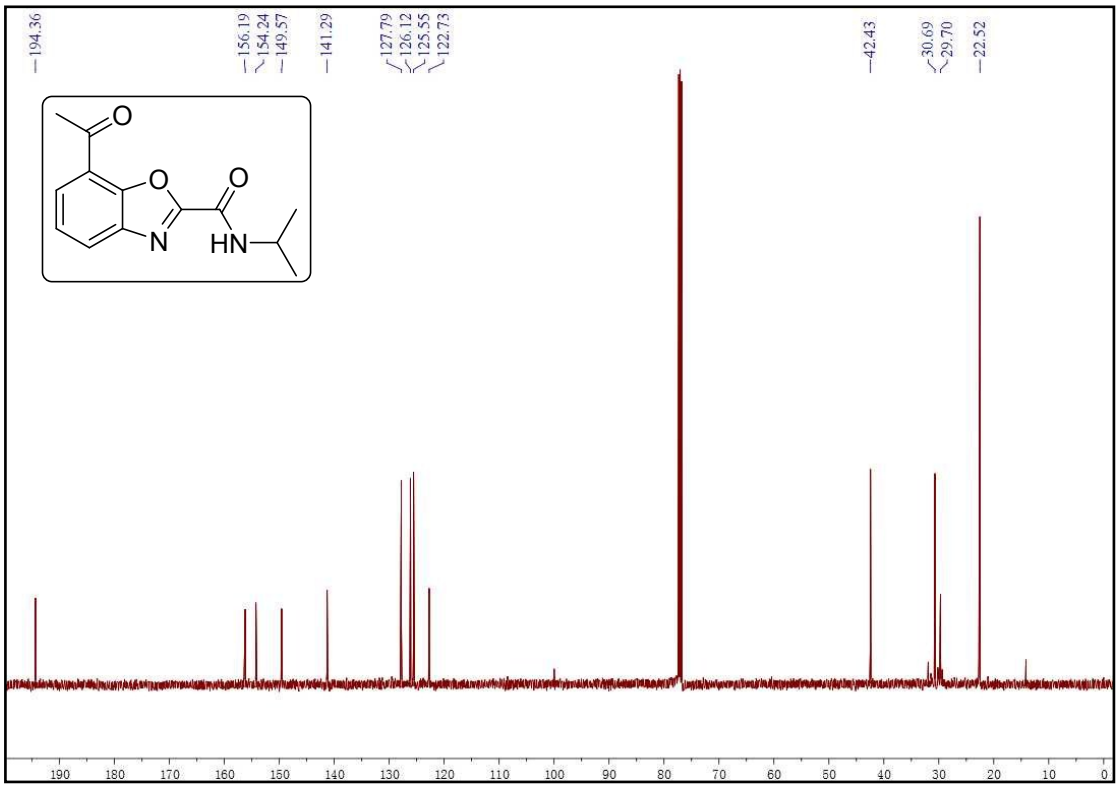
## N,N-dipropylbenzo[*d*]oxazole-2-carboxamide (5w)



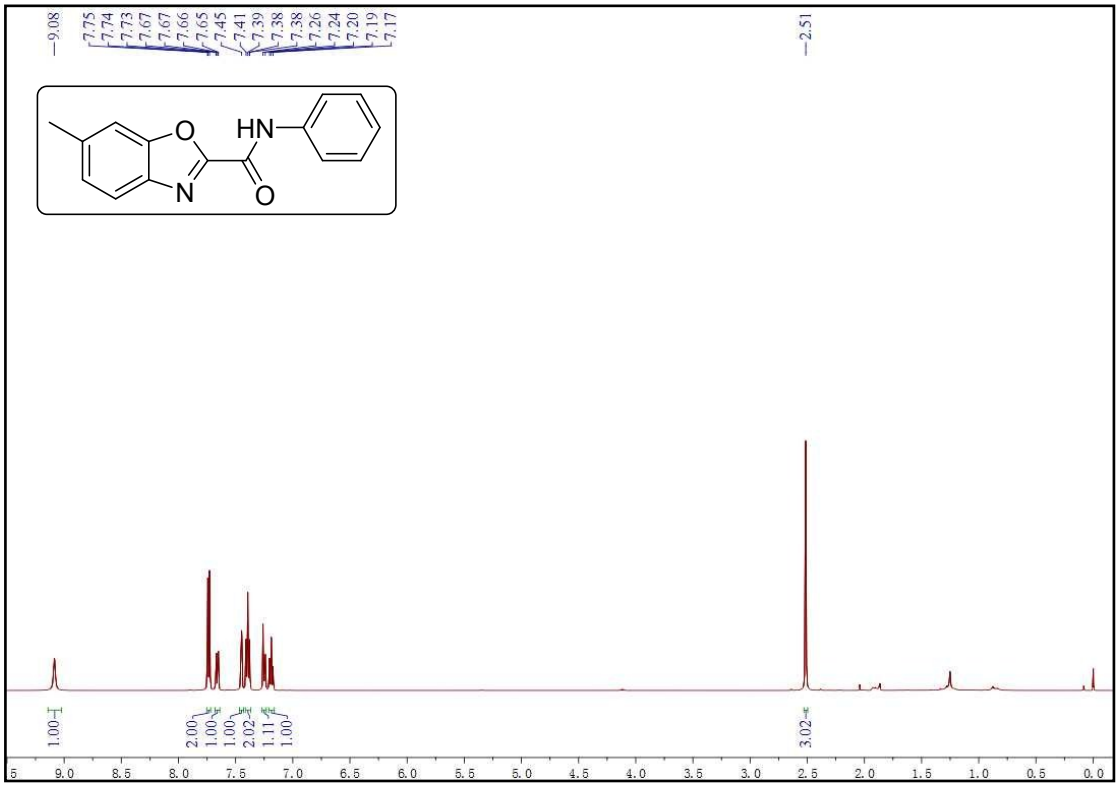



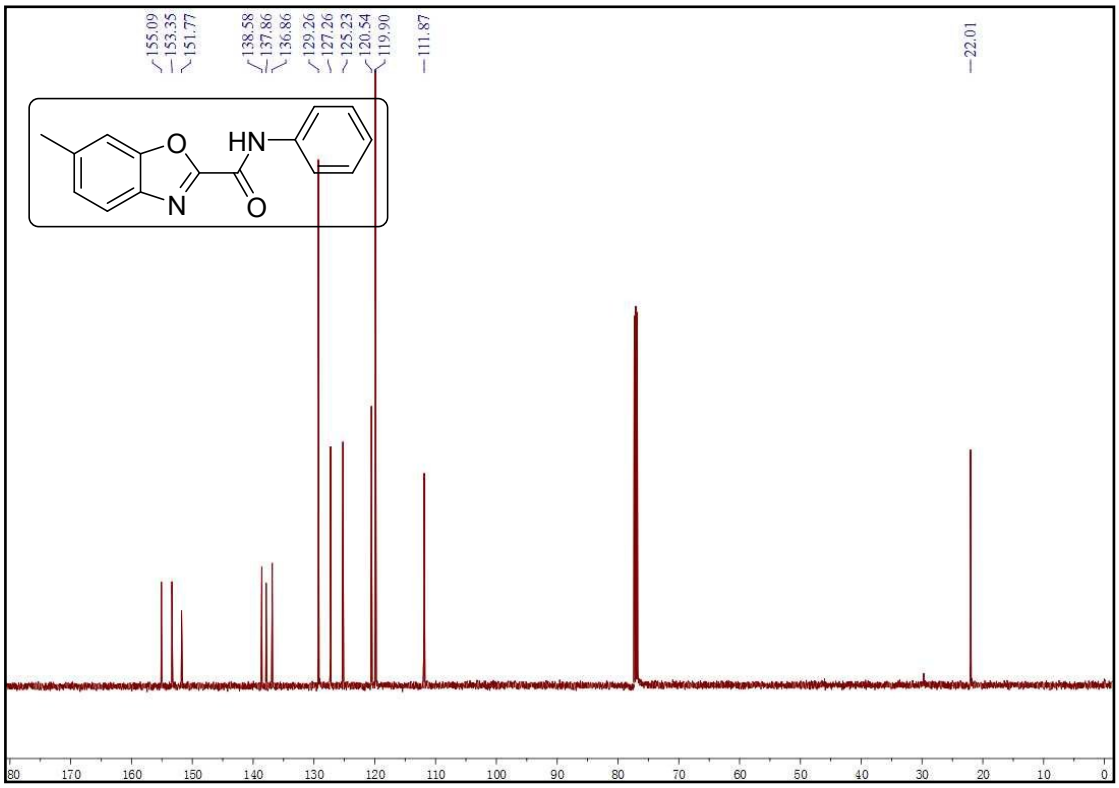
## 6-acetyl-N-isopropylbenzo[*d*]oxazole-2-carboxamide (5x)



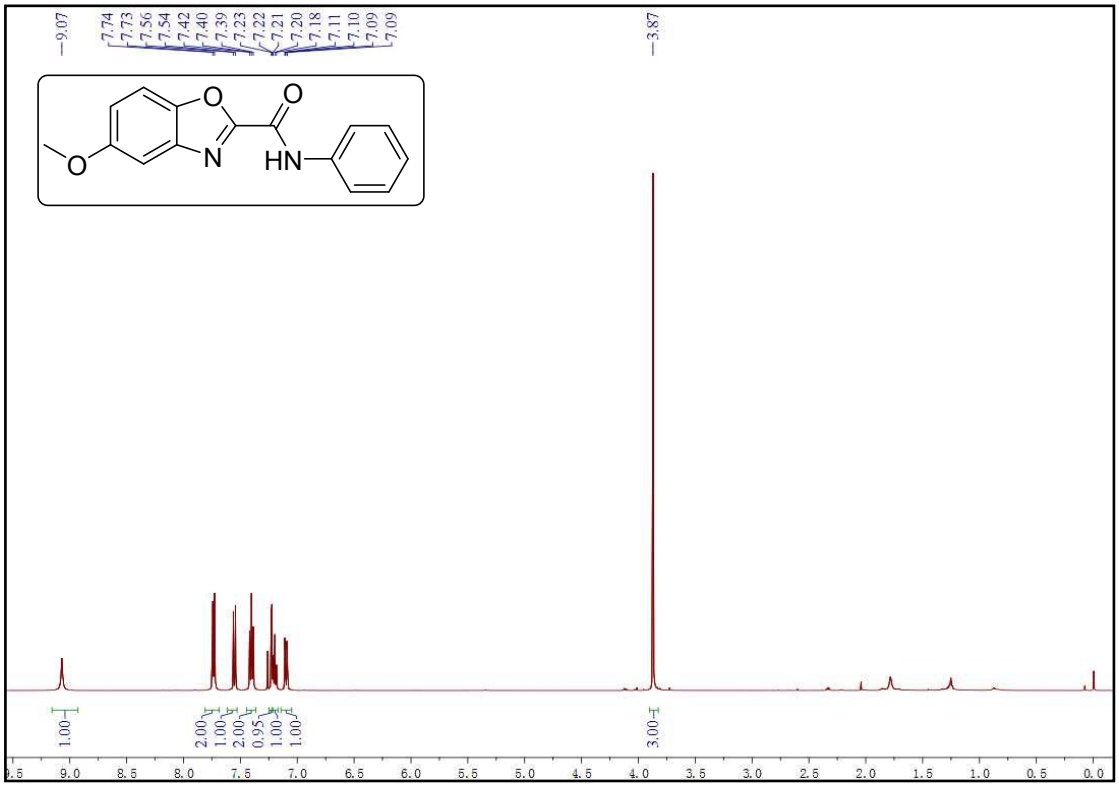



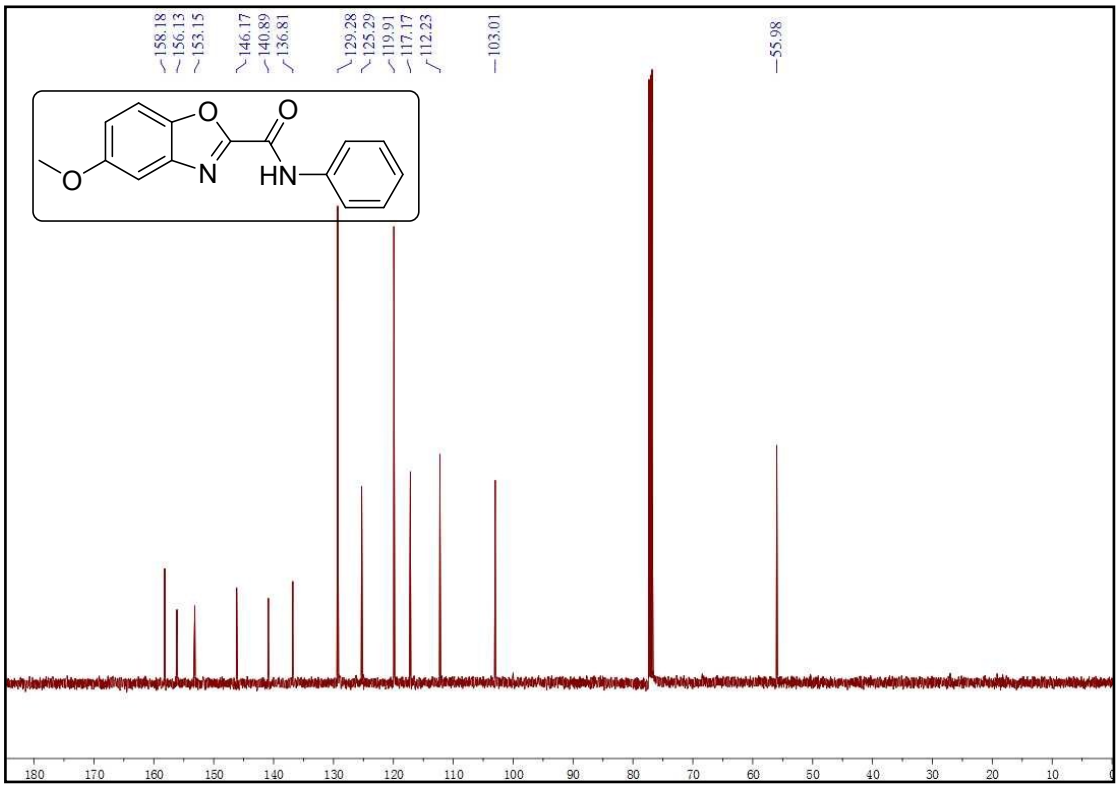
## 6-methyl-N-phenylbenzo[*d*]oxazole-2-carboxamide (5y)



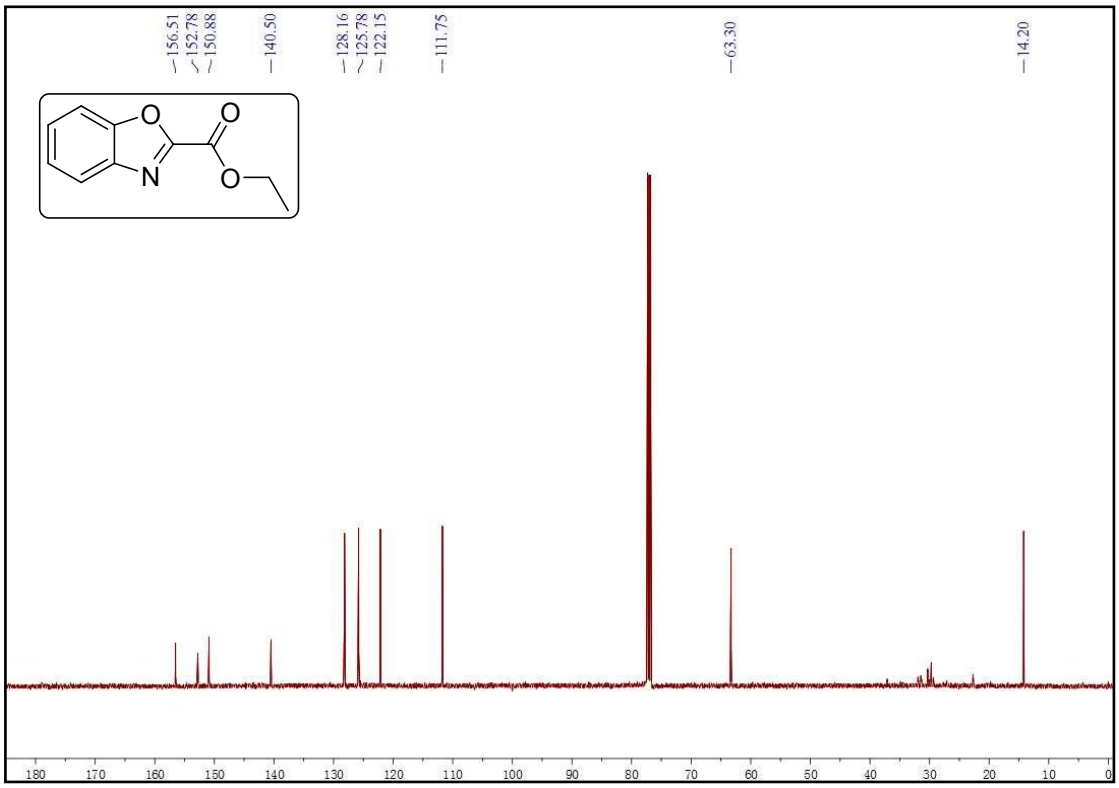



## 5-methoxy-N-phenylbenzo[*d*]oxazole-2-carboxamide (5z)

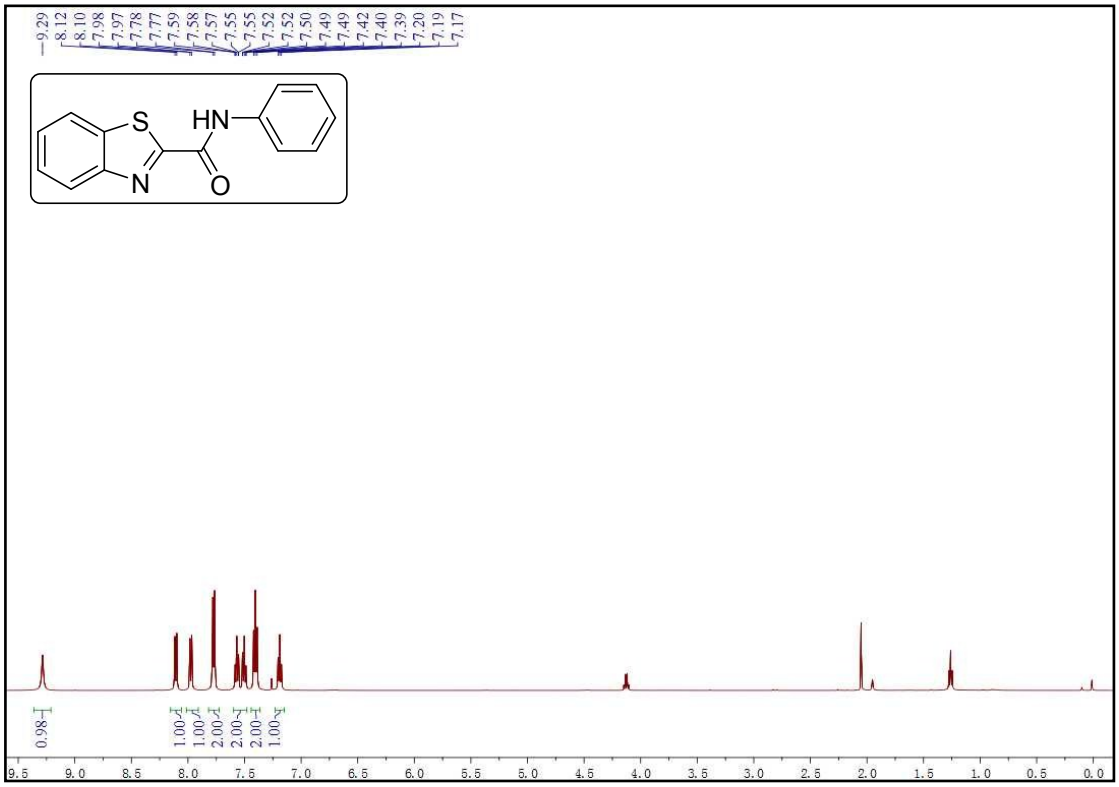


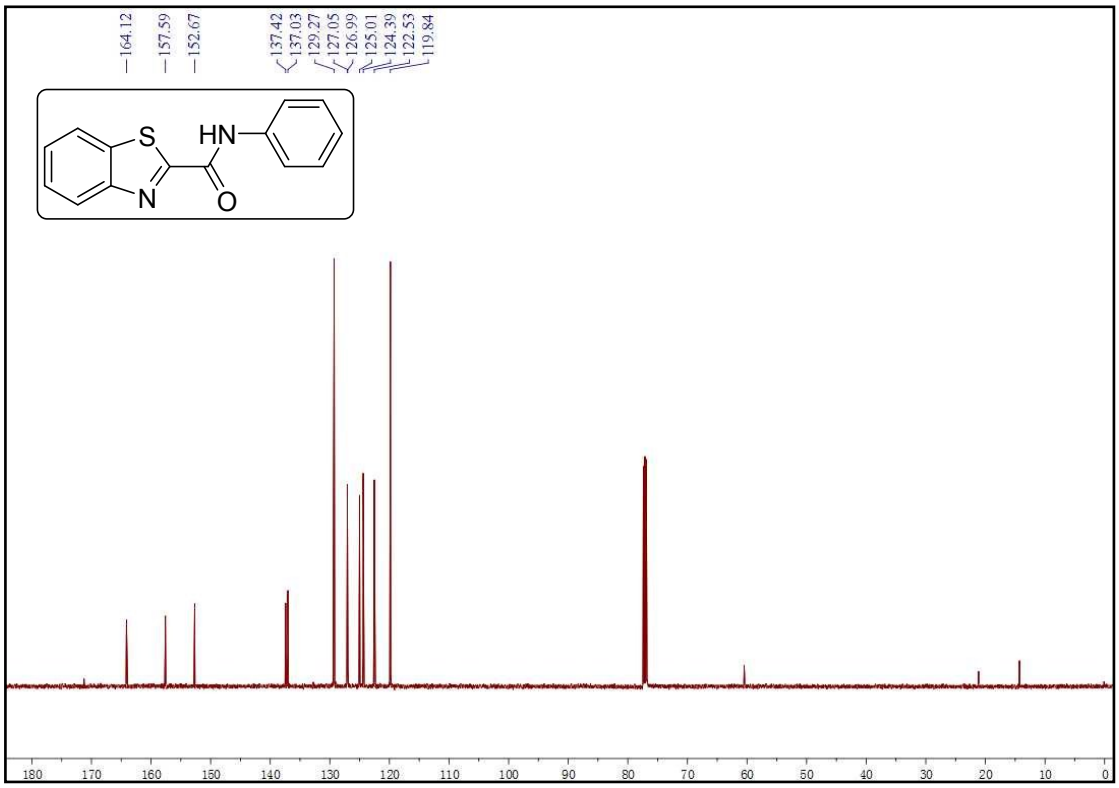



## ethyl benzo[*d*]oxazole-2-carboxylate (5za)

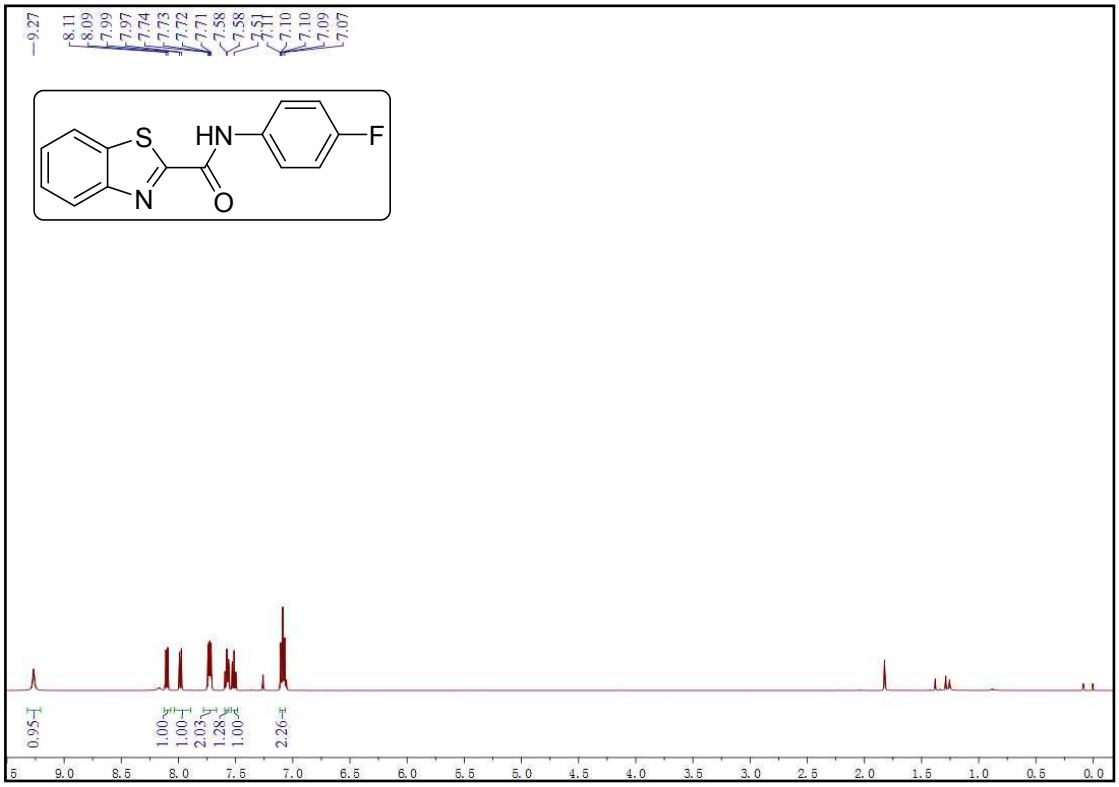



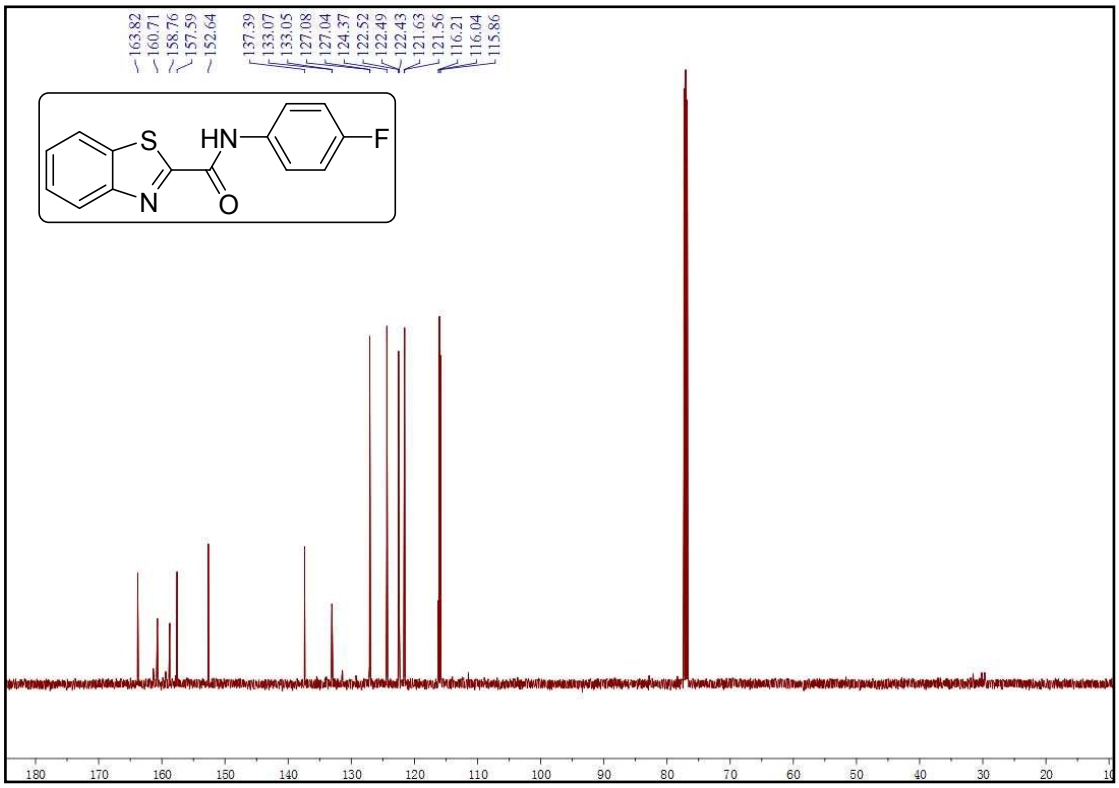
## N-phenylbenzo[*d*]thiazole-2-carboxamide (7a)

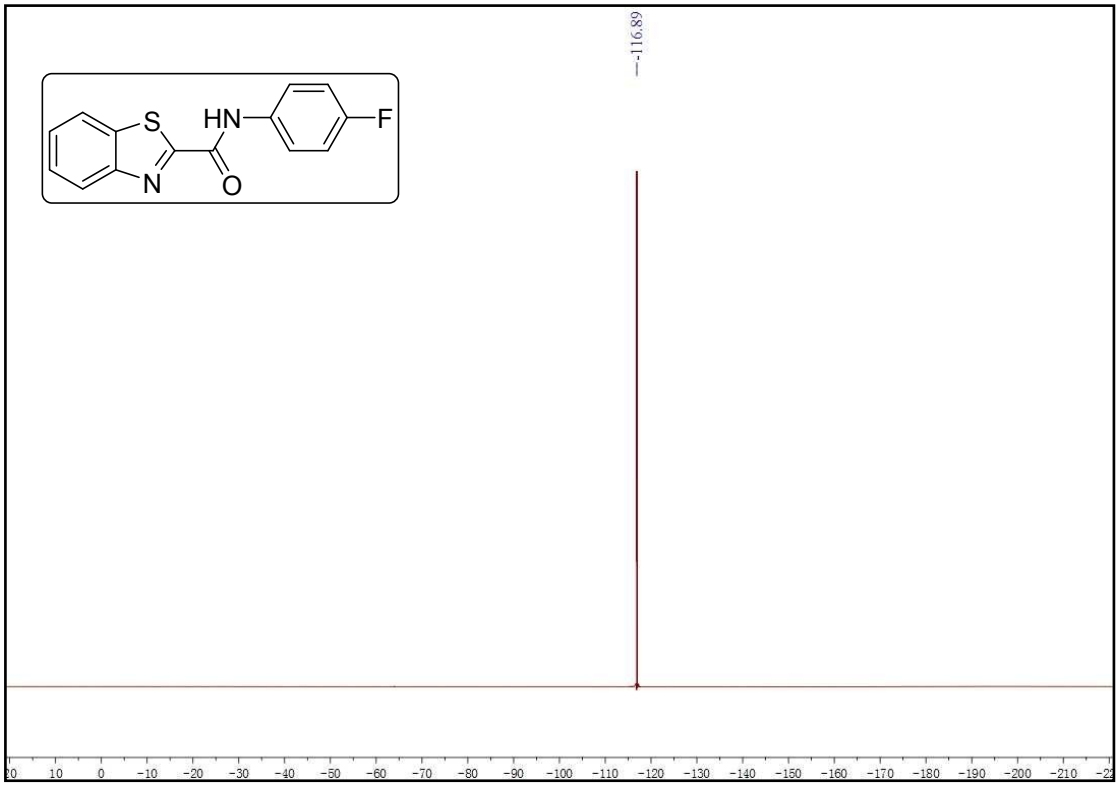


## N-(4-fluorophenyl)benzo[*d*]thiazole-2-carboxamide (7b)

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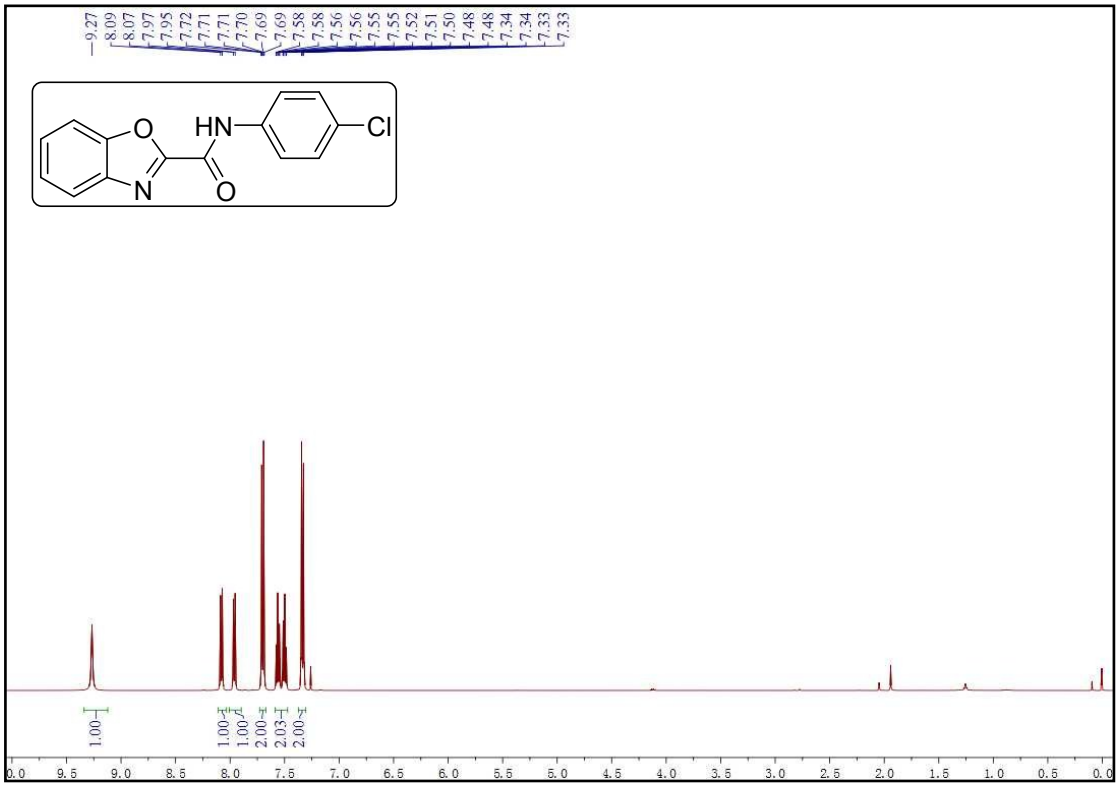
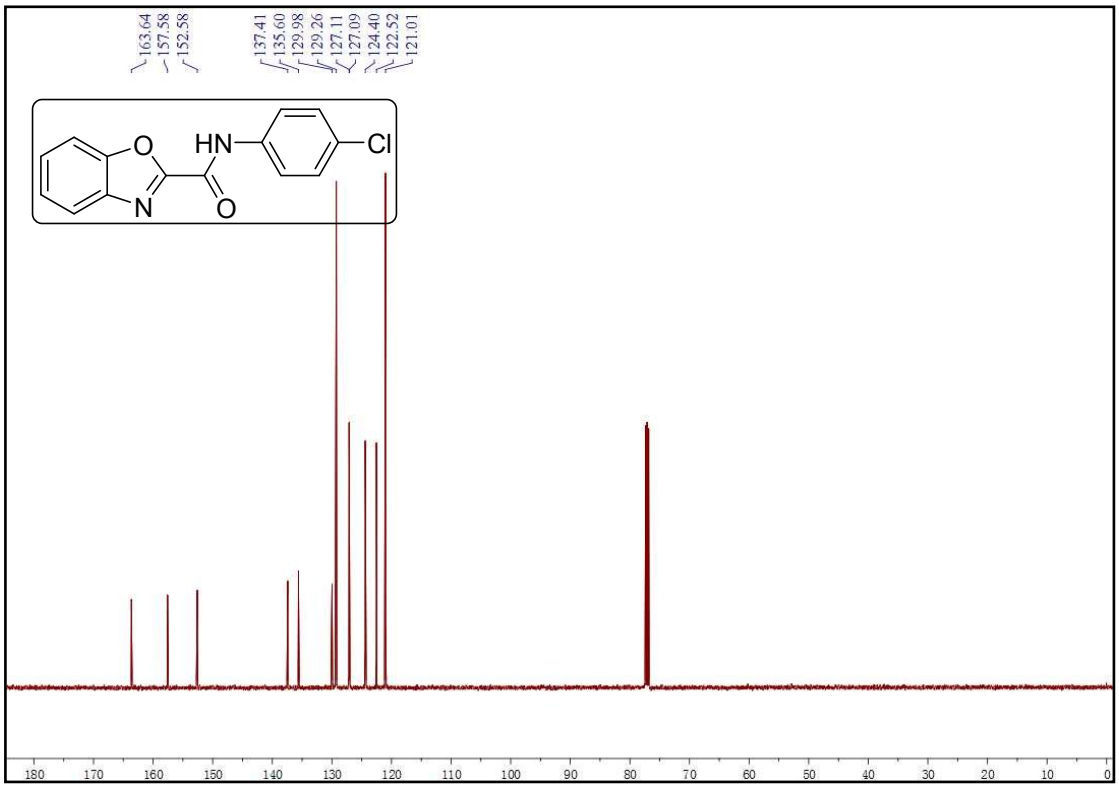
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

## N-(4-chlorophenyl)benzo[*d*]thiazole-2-carboxamide (7c)



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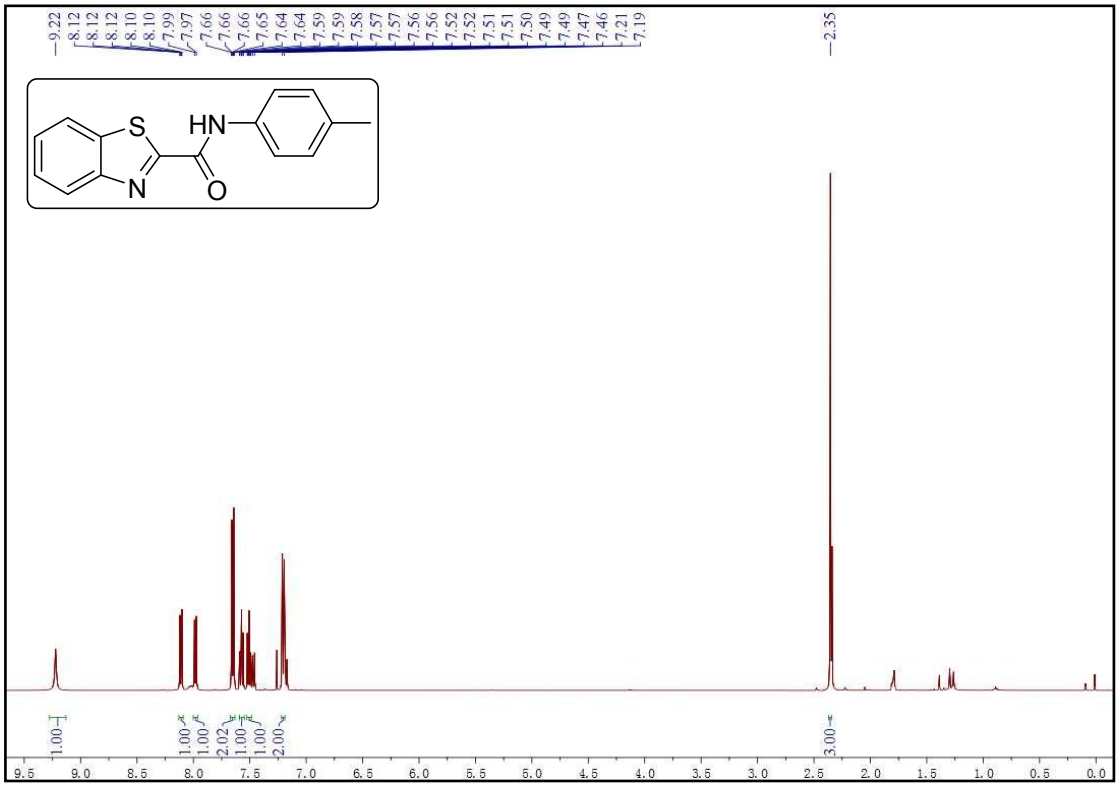
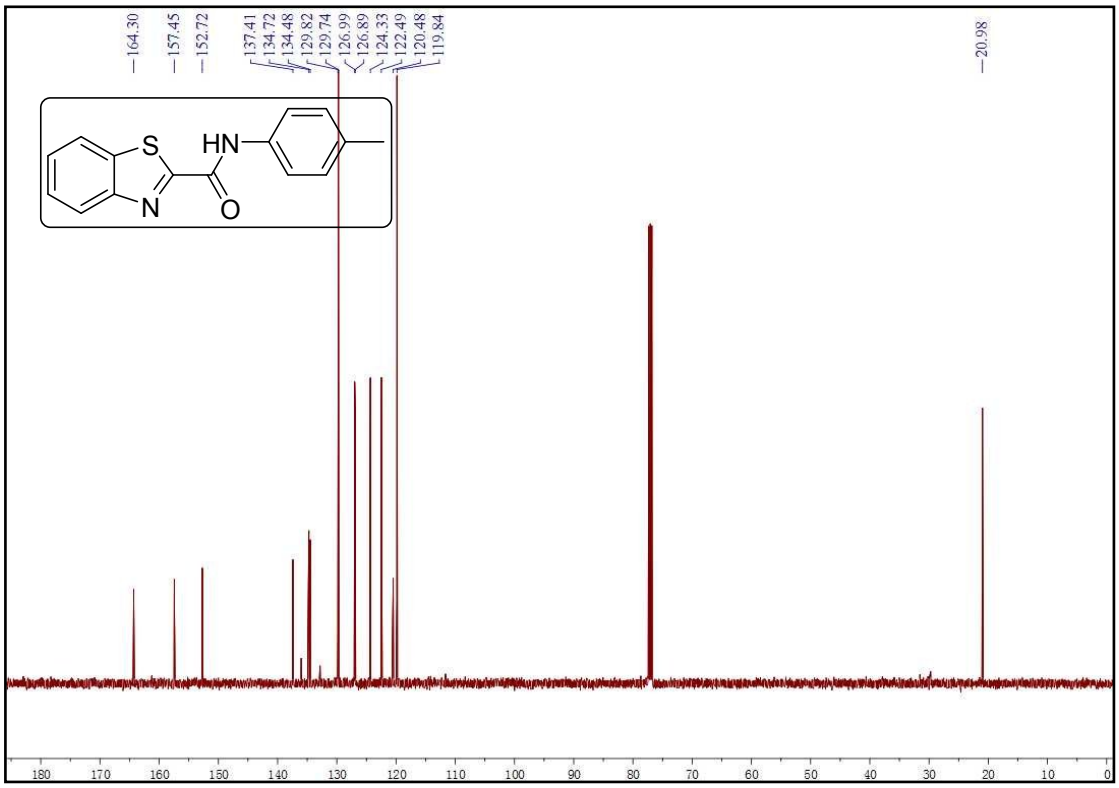
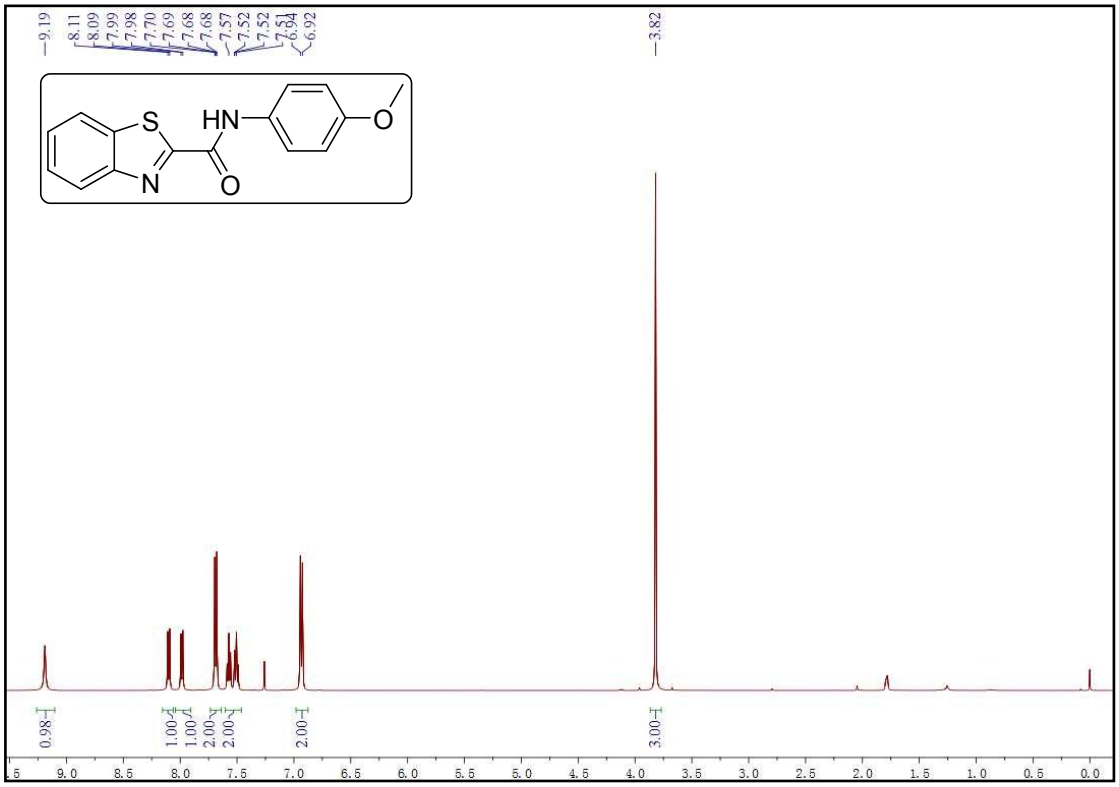
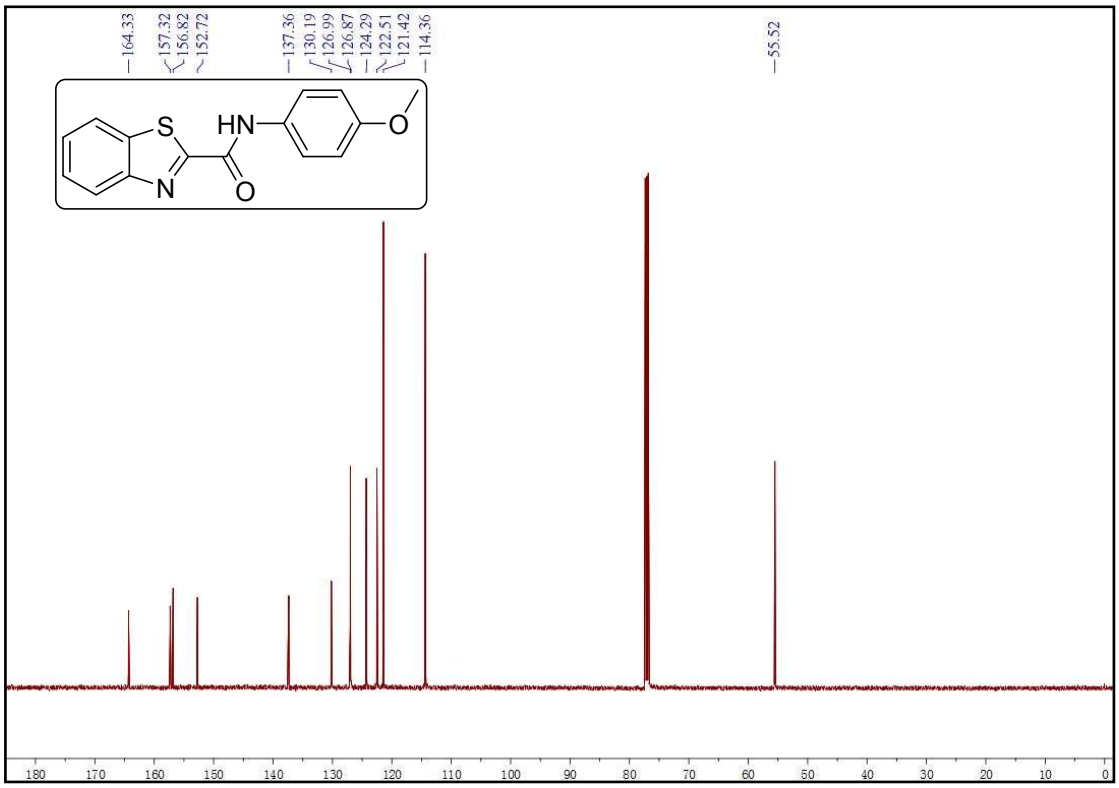


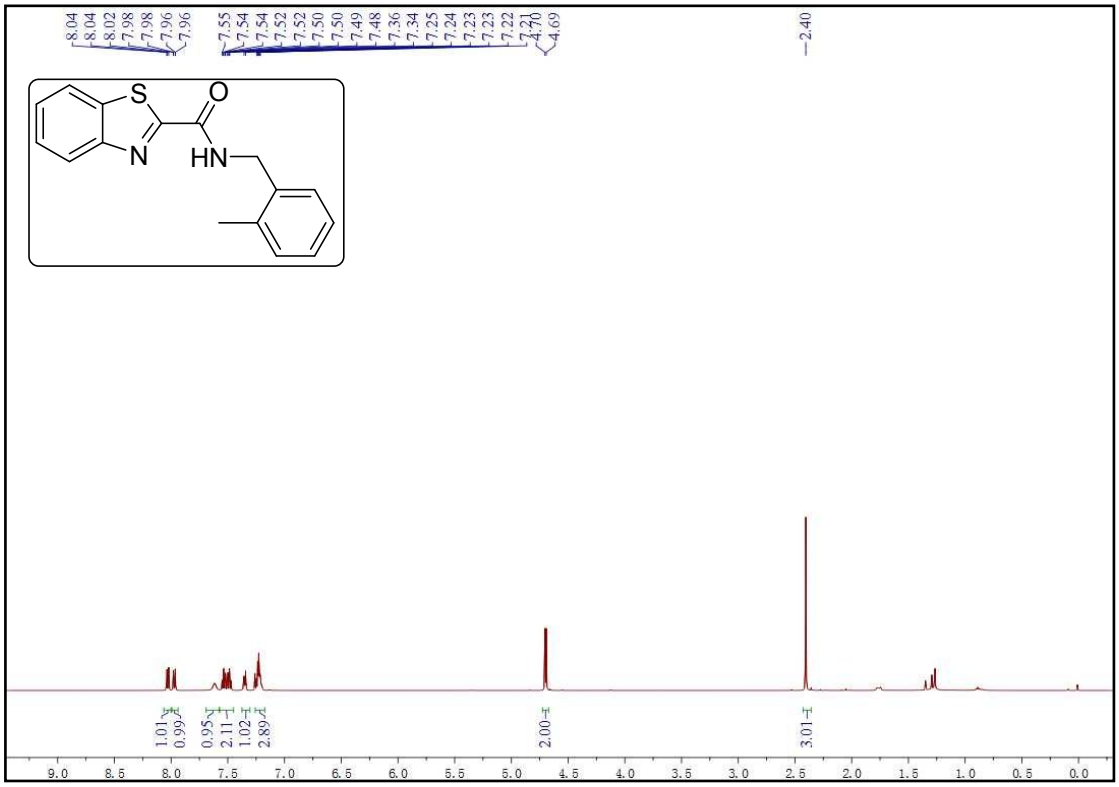



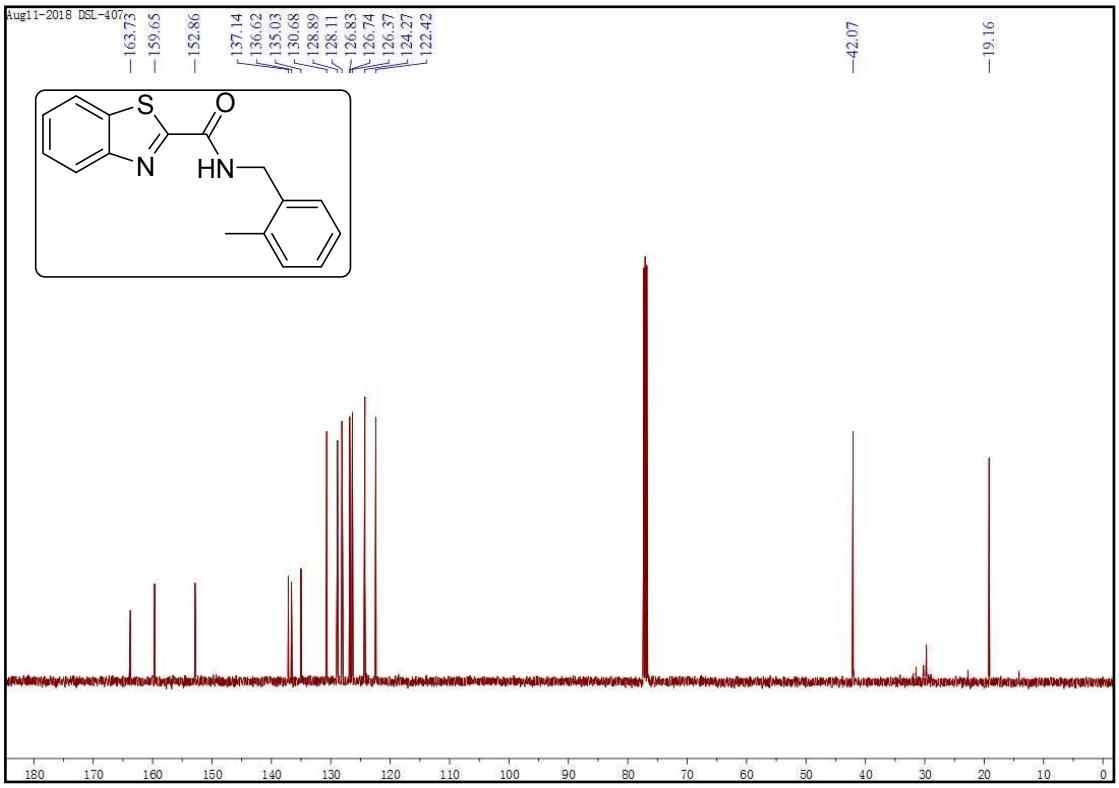
## N-(4-methoxyphenyl)benzo[*d*]thiazole-2-carboxamide(7e)



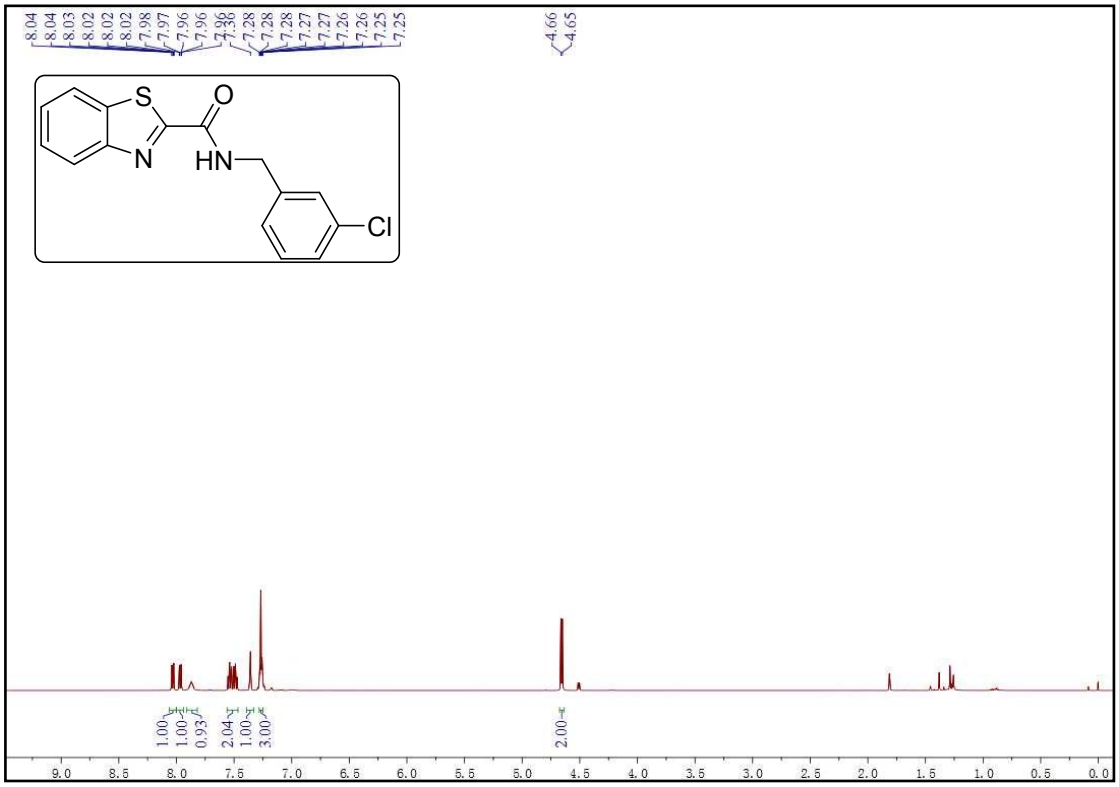



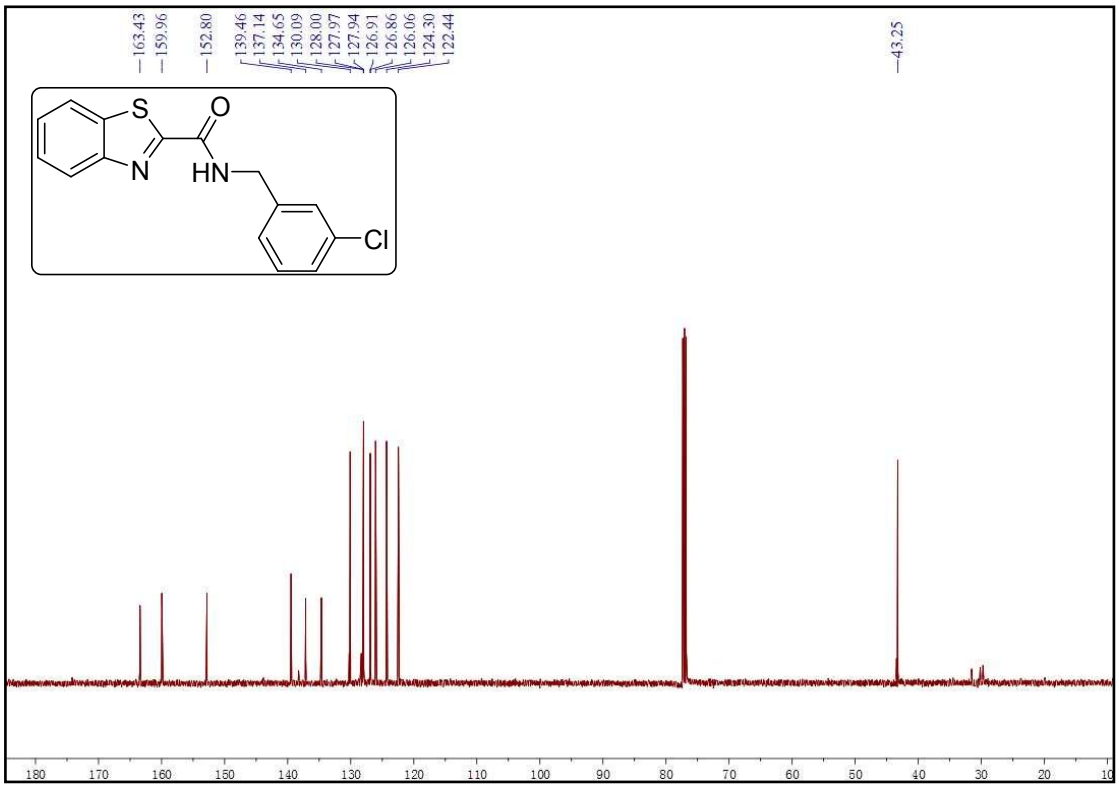
## N-(2-methylbenzyl)benzo[*d*]thiazole-2-carboxamide (7f)



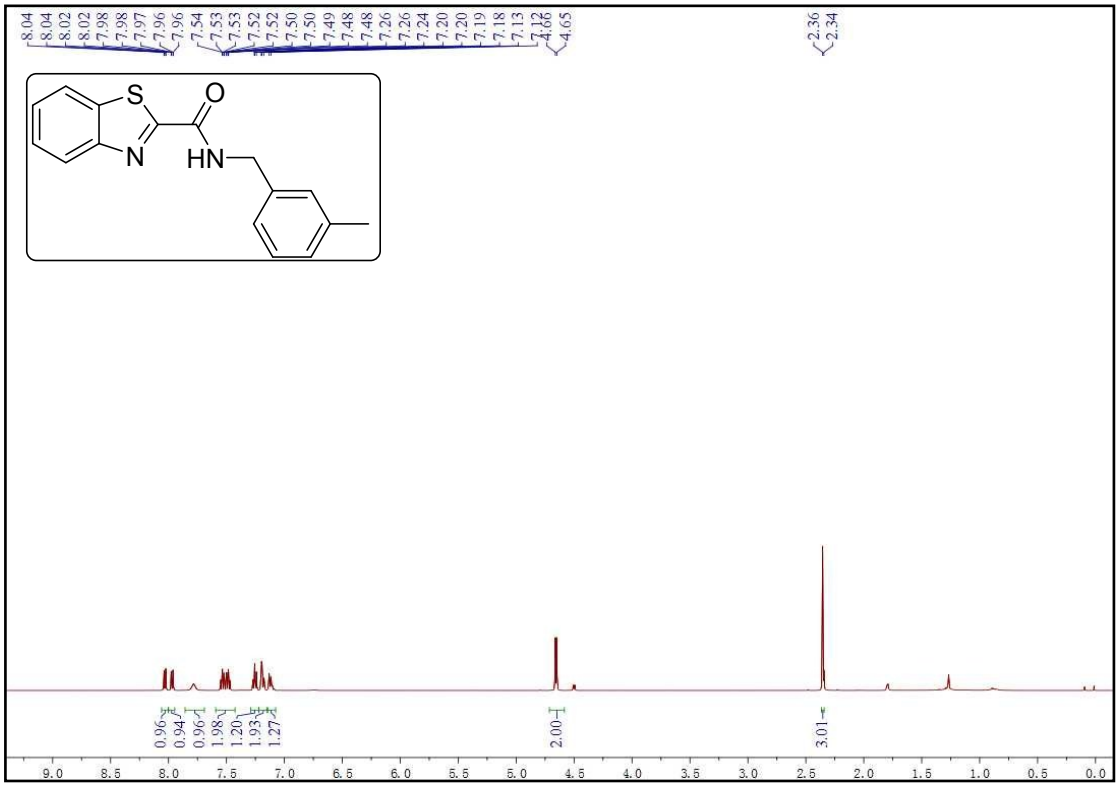



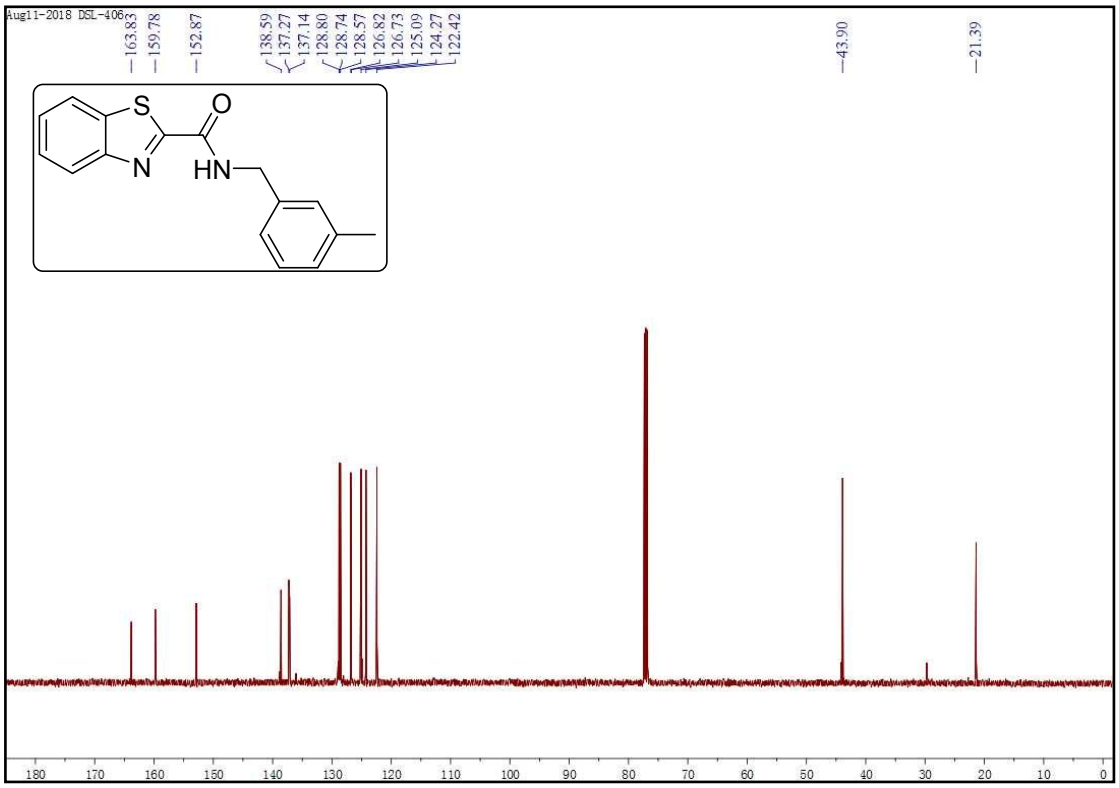
## N-(3-chlorobenzyl)benzo[*d*]thiazole-2-carboxamide (7g)



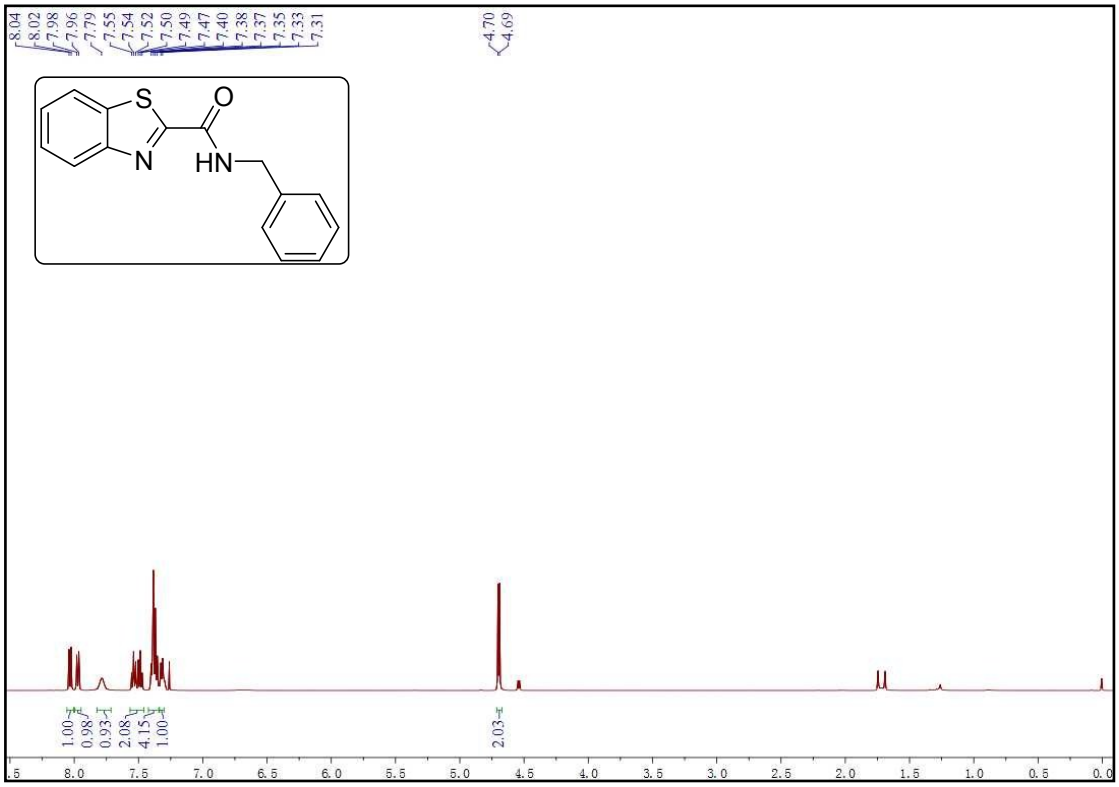



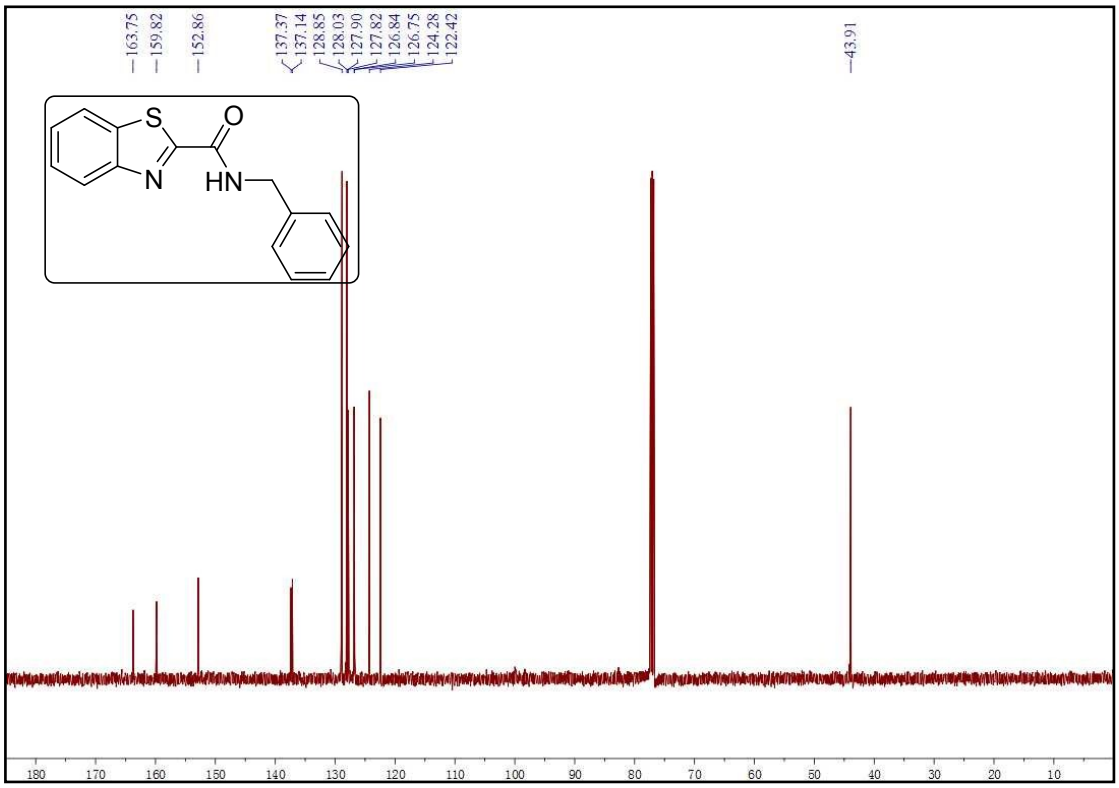
## N-(3-methylbenzyl)benzo[*d*]thiazole-2-carboxamide (7h)



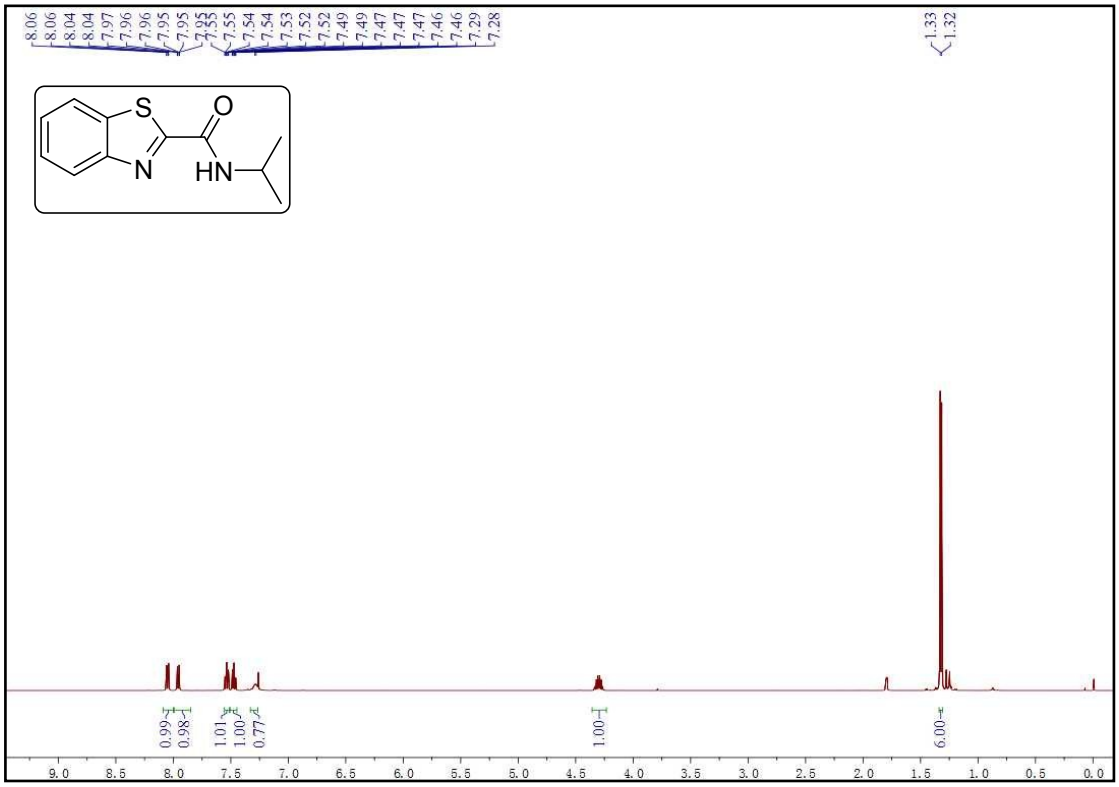



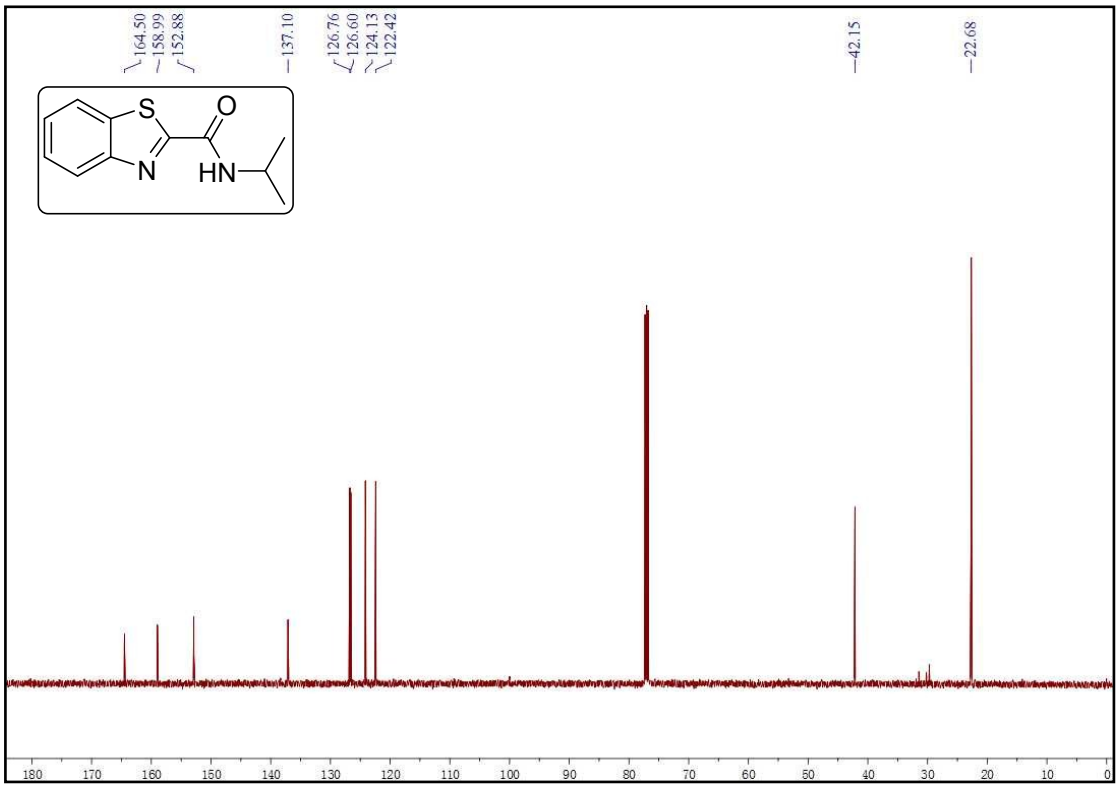
## N-benzylbenzo[*d*]thiazole-2-carboxamide (7i)



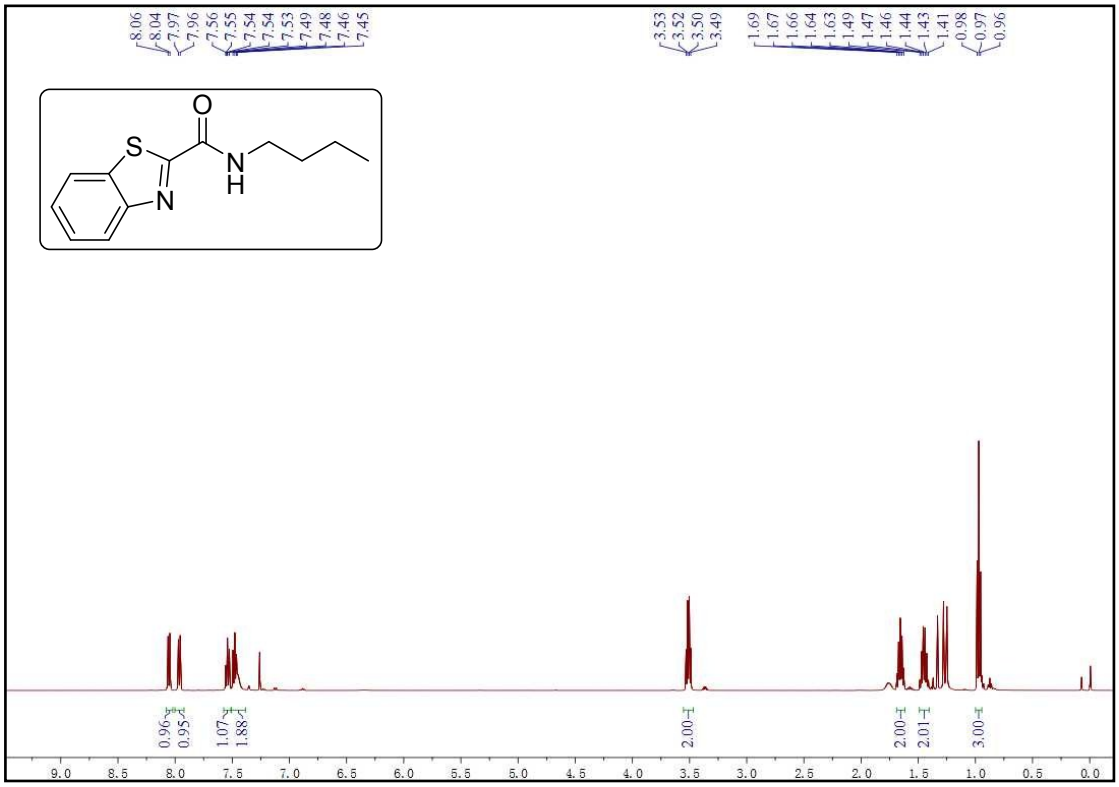



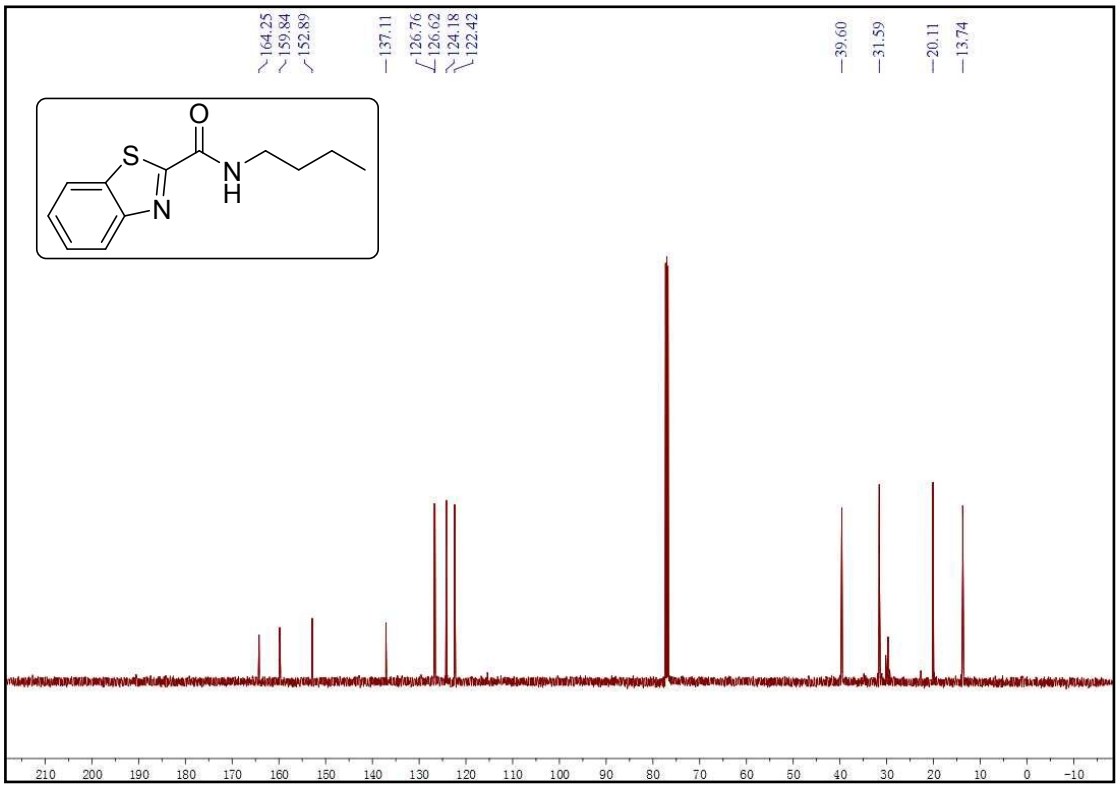
## N-isopropylbenzo[*d*]thiazole-2-carboxamide (7j)



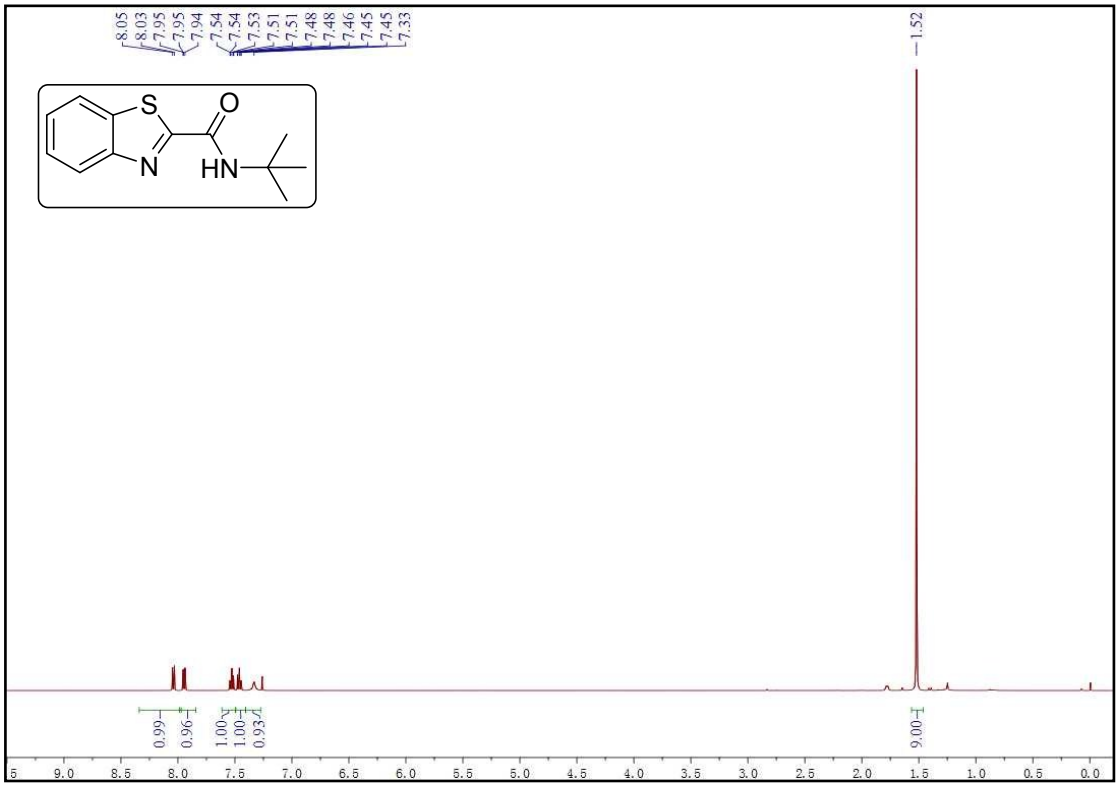



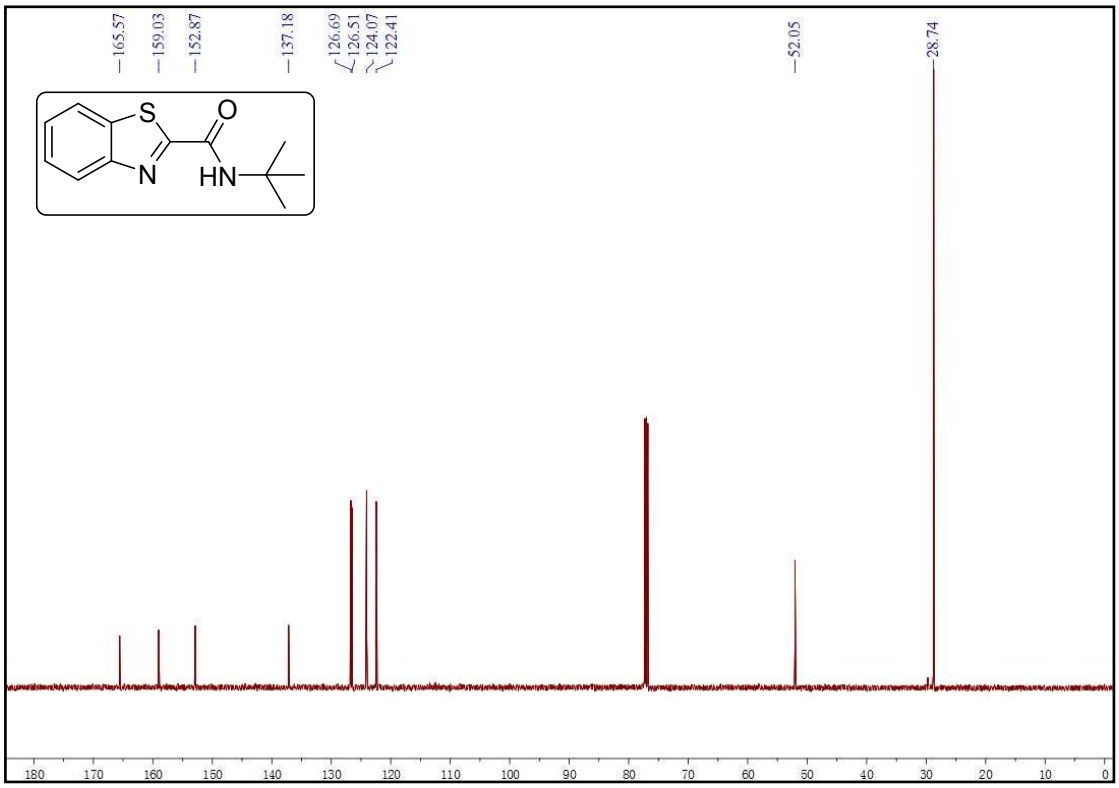
## N-butylbenzo[*d*]thiazole-2-carboxamide (7k)



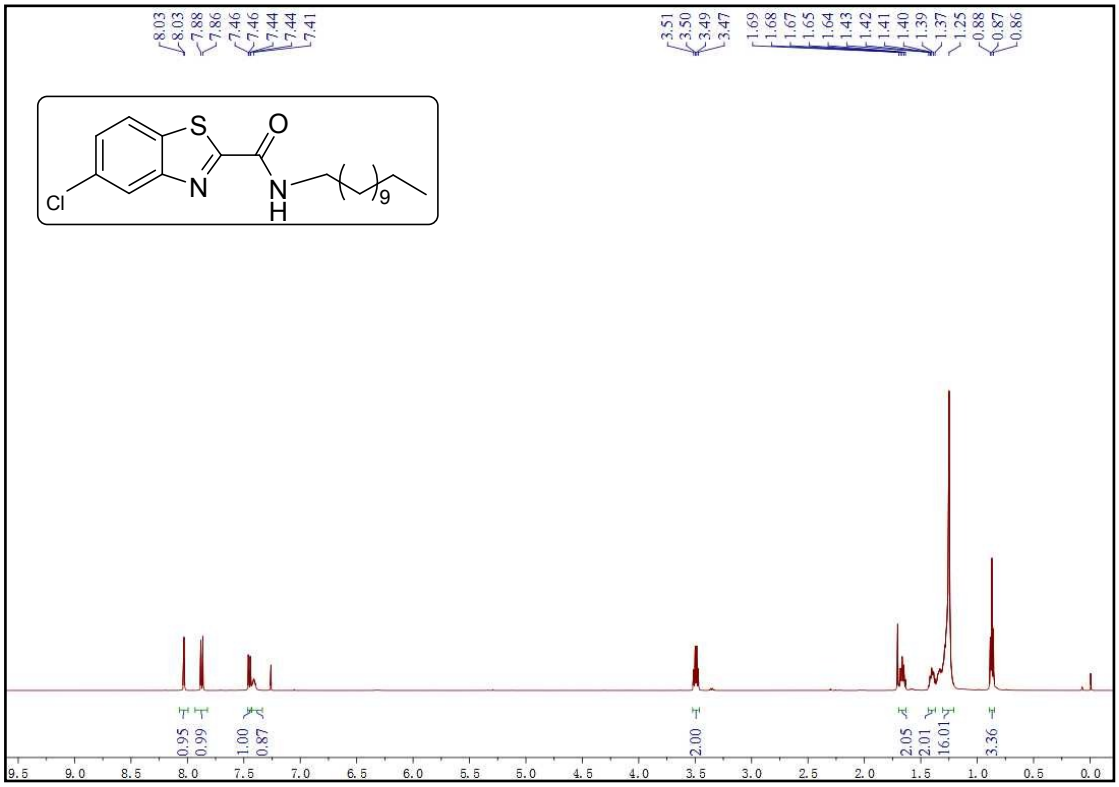



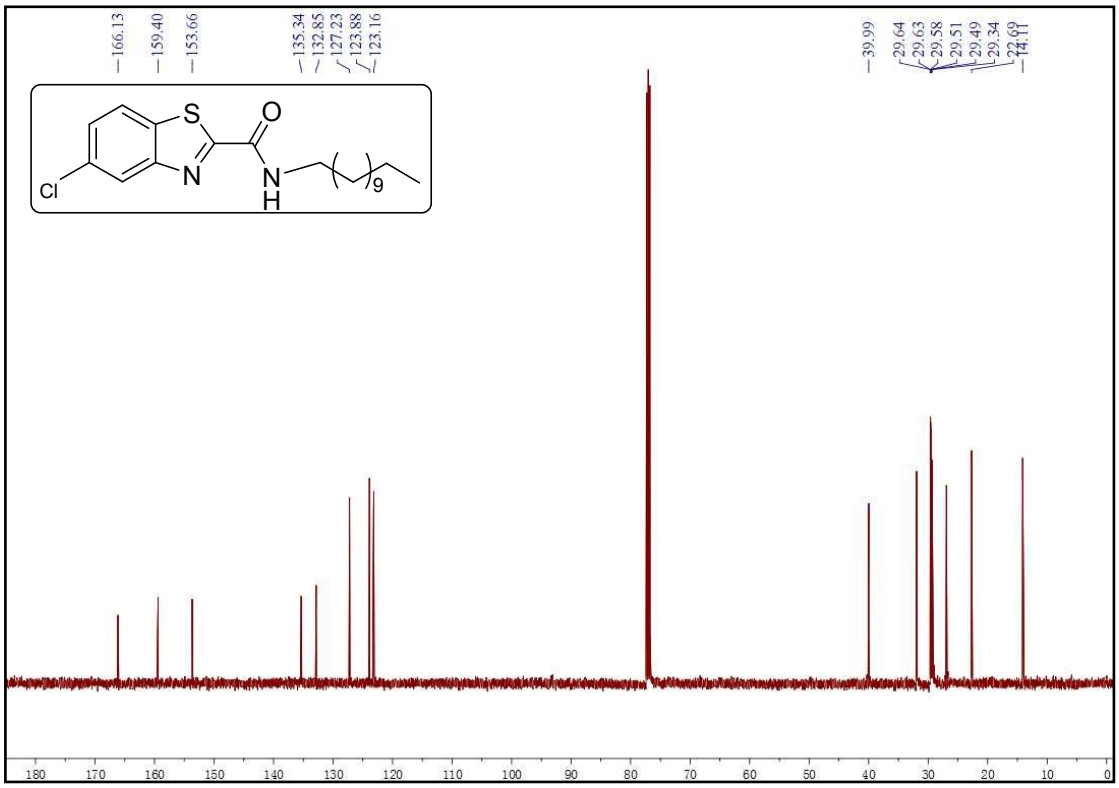
## N-(tert-butyl)benzo[*d*]thiazole-2-carboxamide (7l)



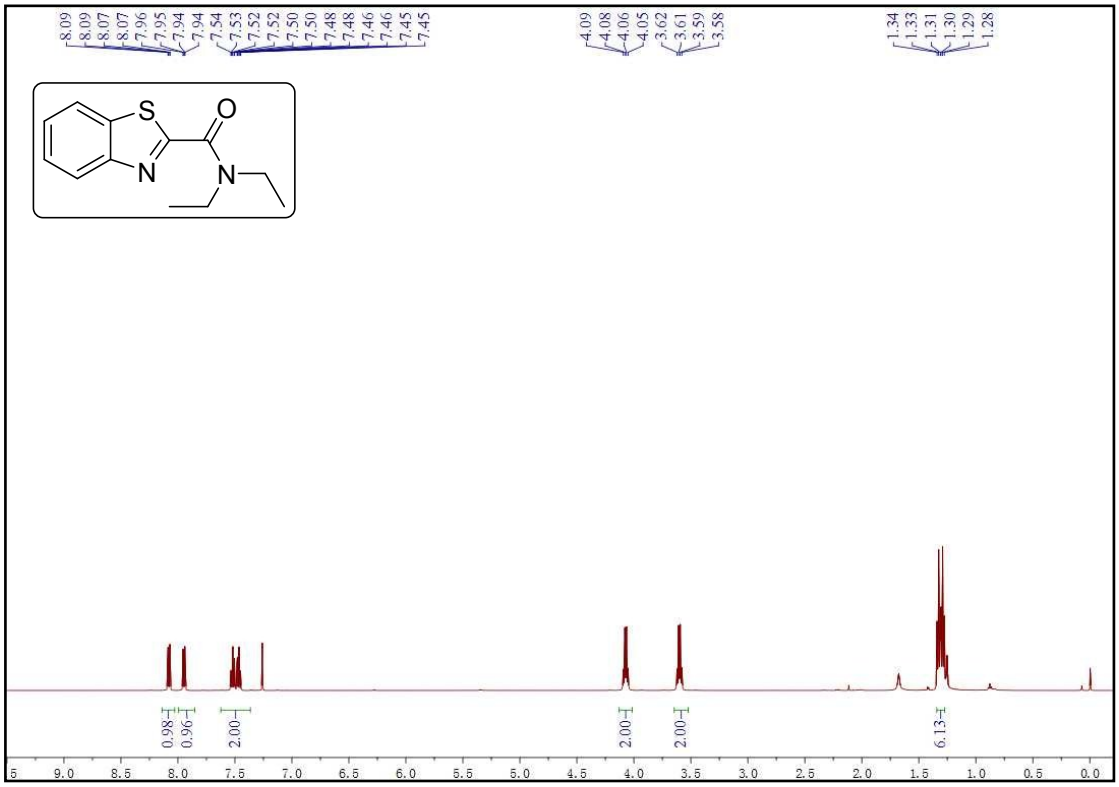



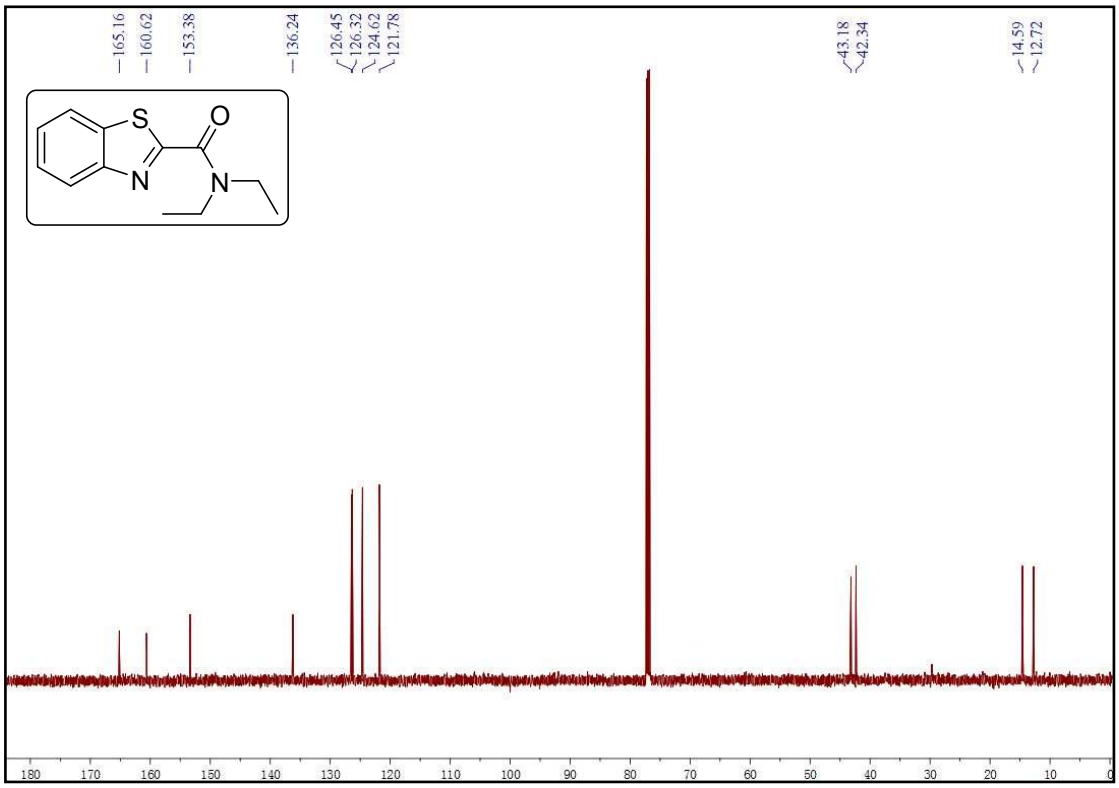
## 5-chloro-N-dodecylbenzo[d]thiazole-2-carboxamide (7m)



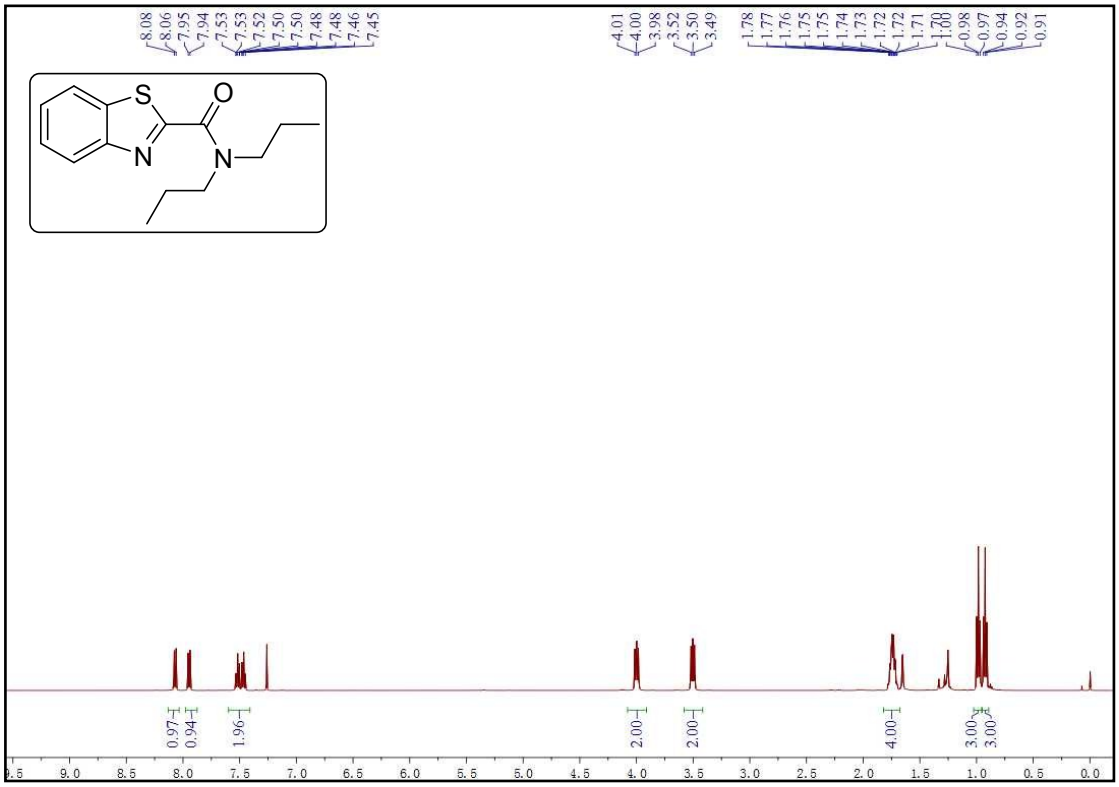



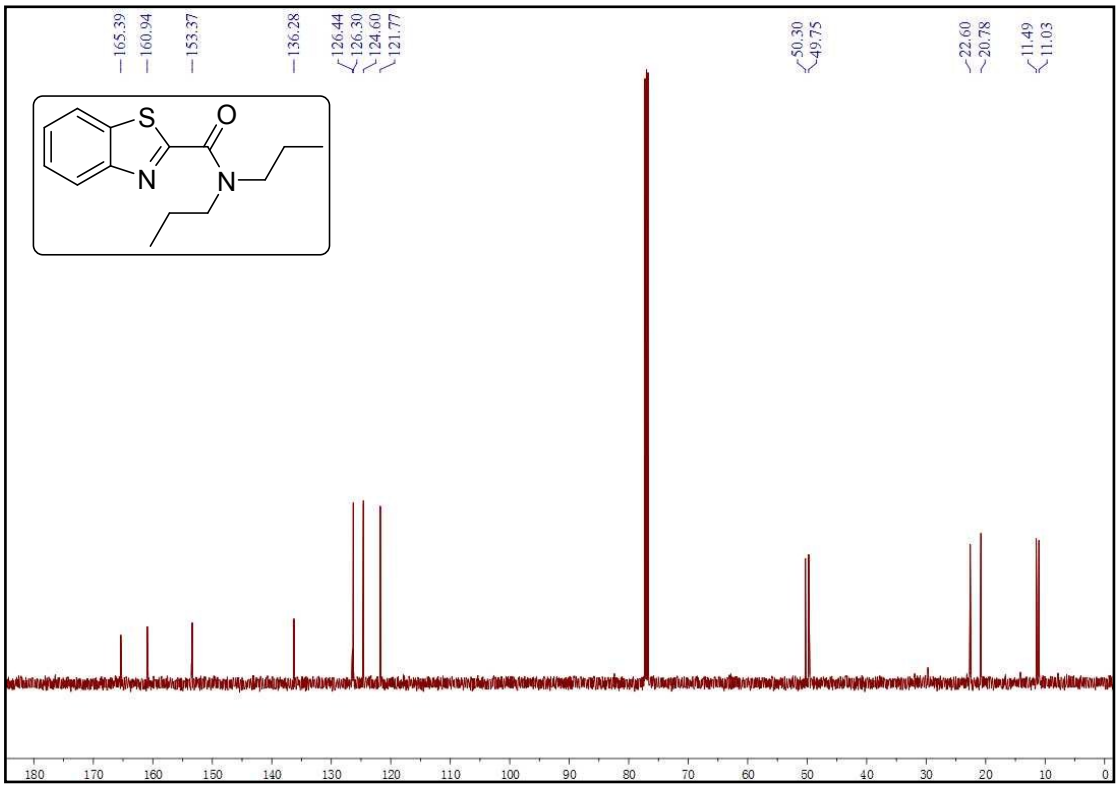
## N,N-diethylbenzo[*d*]thiazole-2-carboxamide (7n)



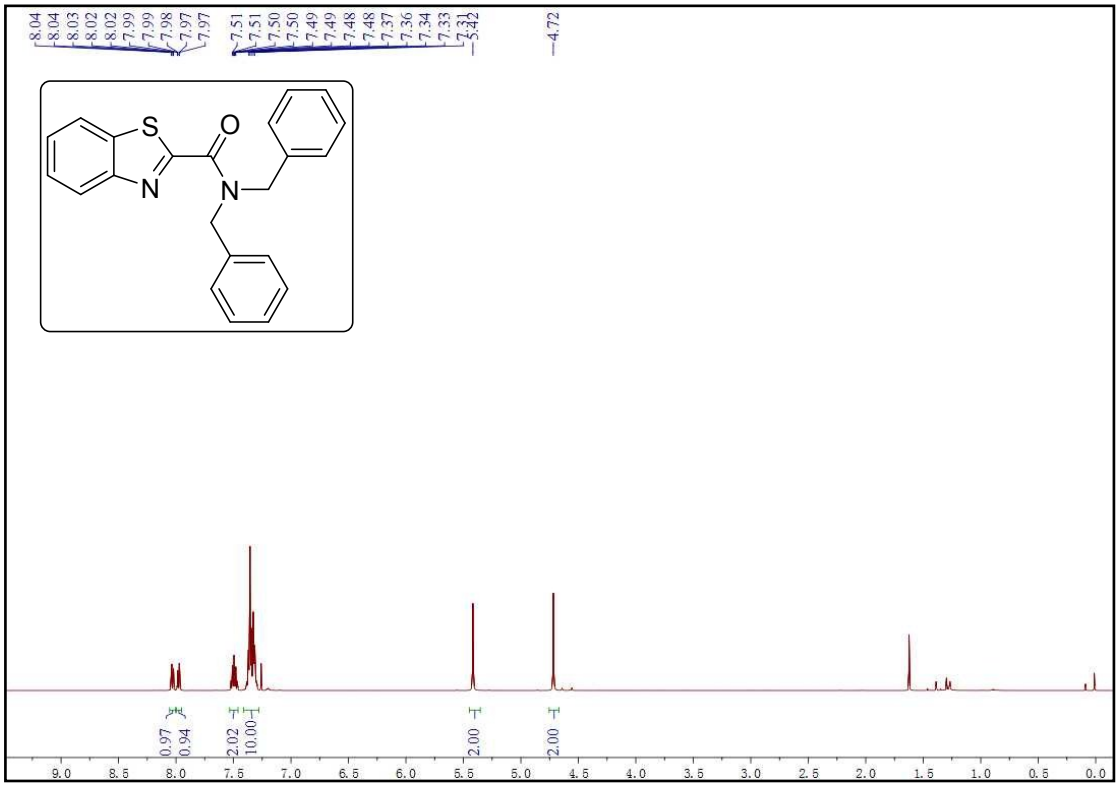



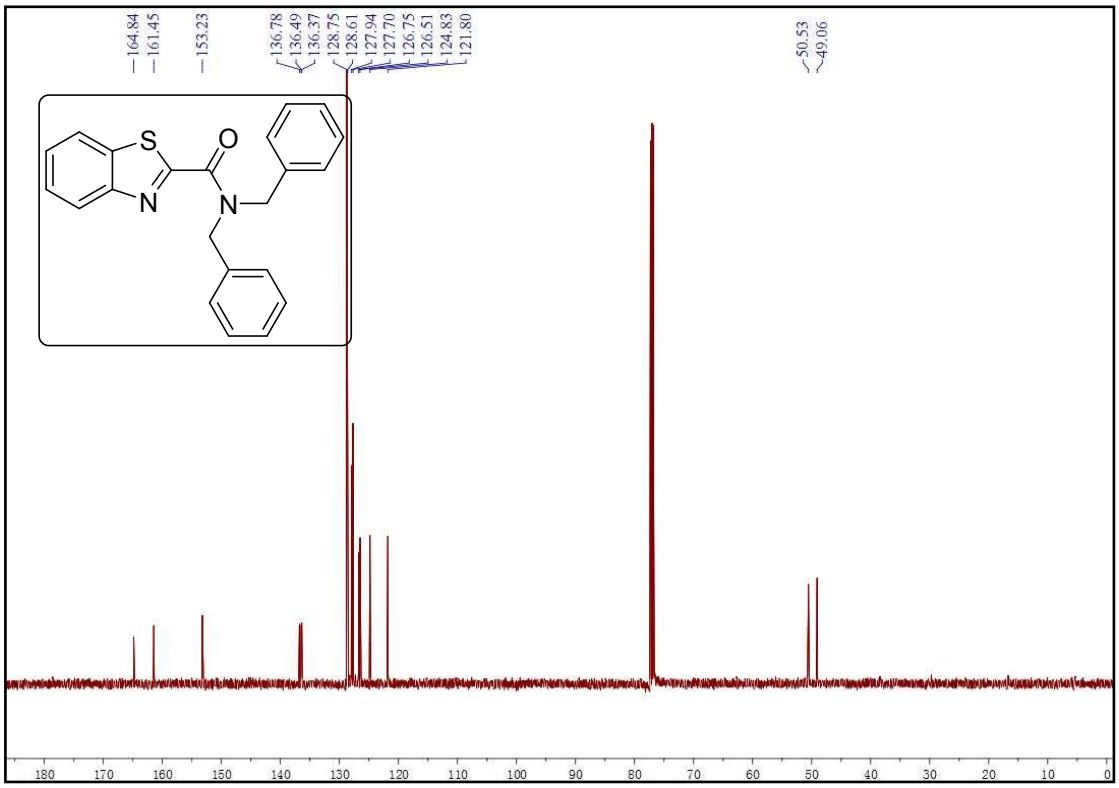
## N,N-dipropylbenzo[*d*]thiazole-2-carboxamide (7o)



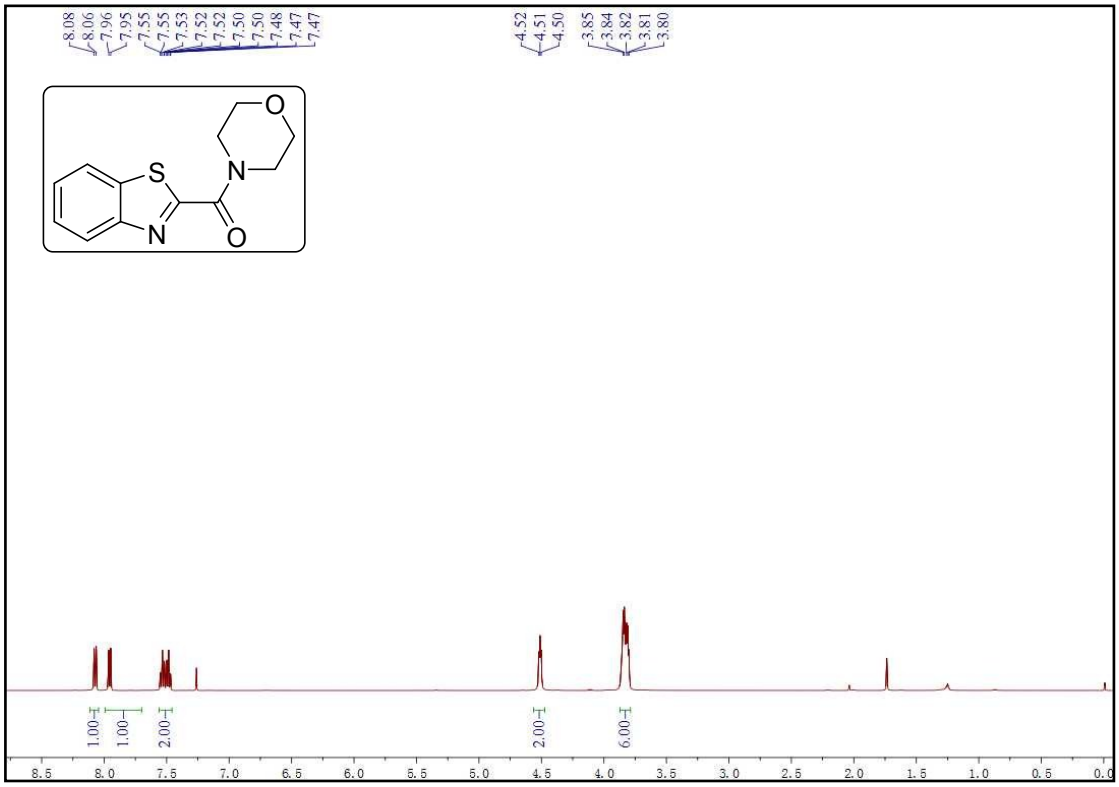



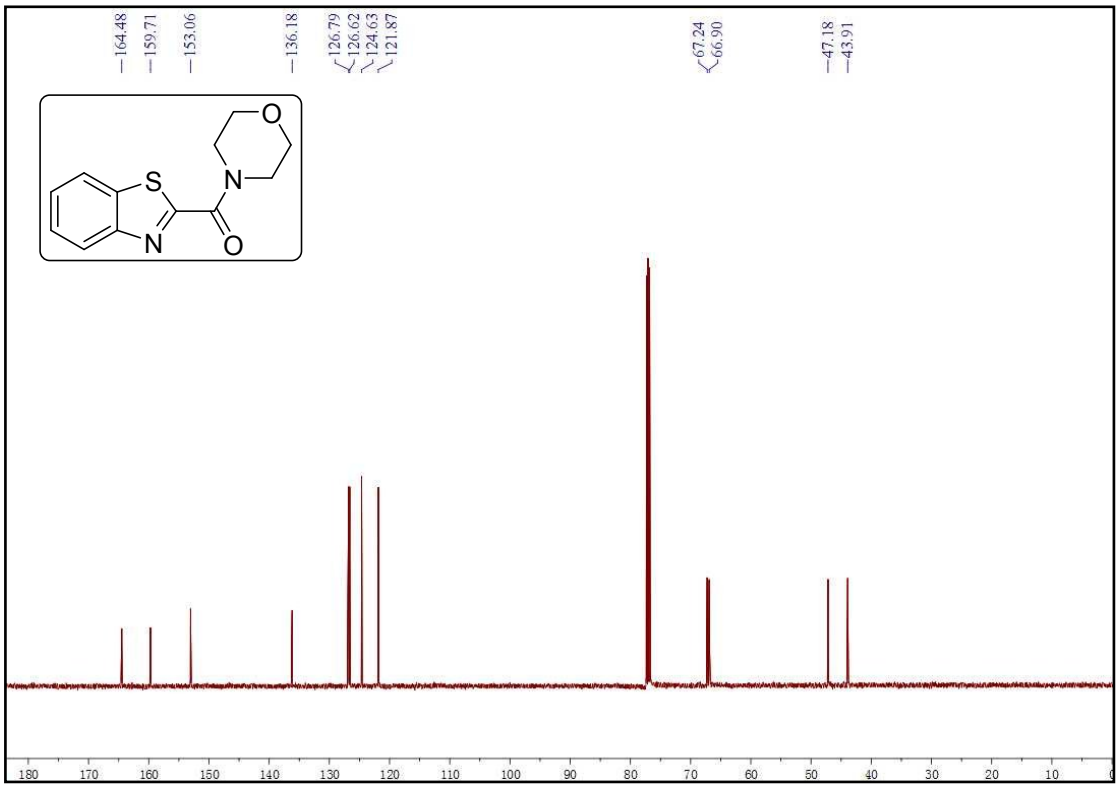
## N,N-dibenzylbenzo[*d*]thiazole-2-carboxamide (7p)



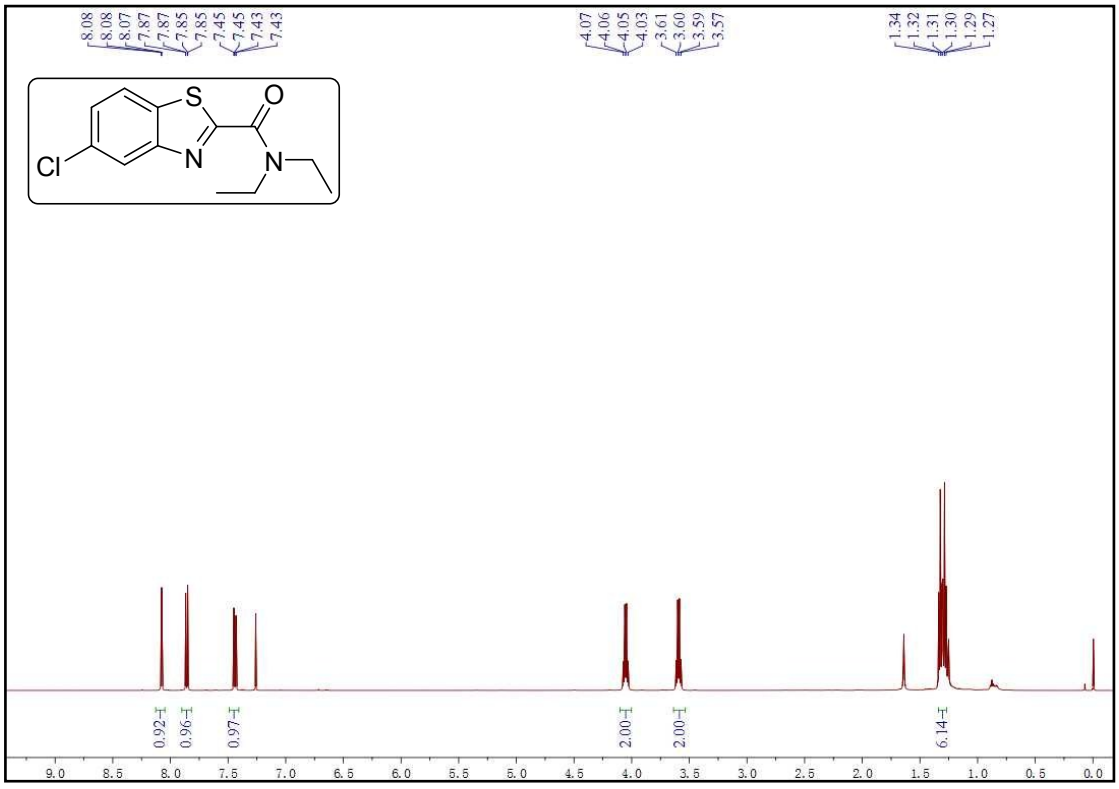



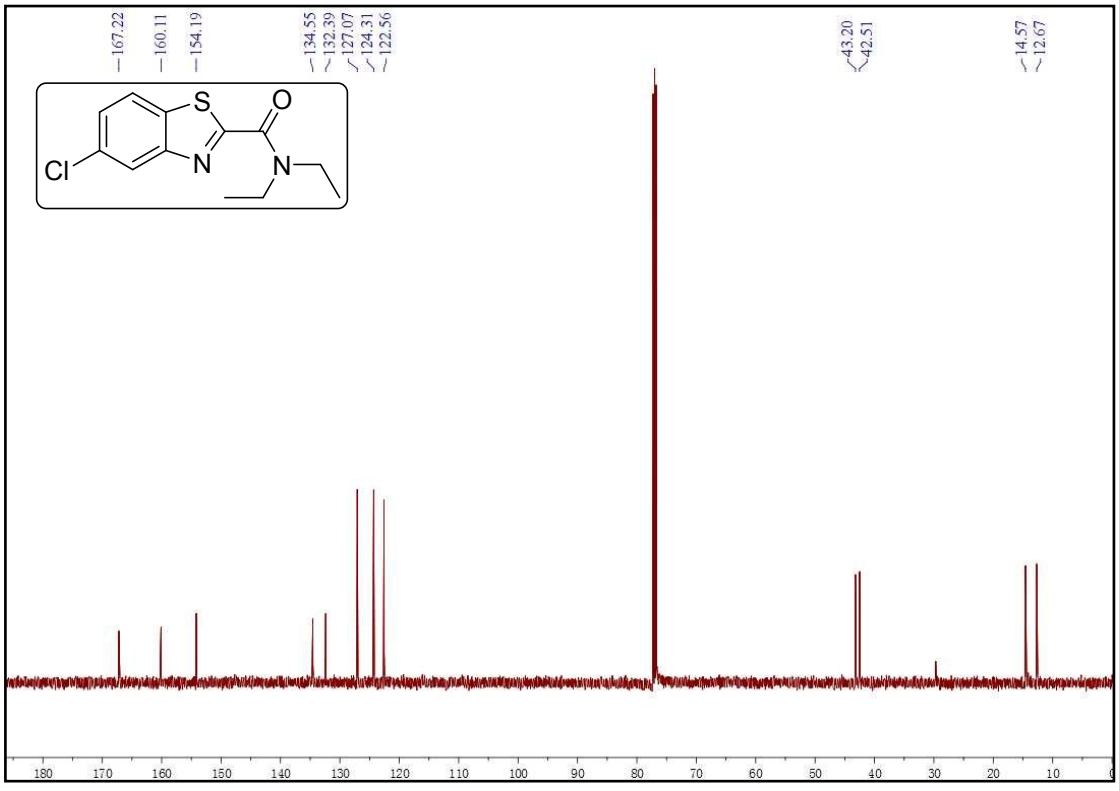
## benzo[d]thiazol-2-yl(morpholino)methanone (7q)



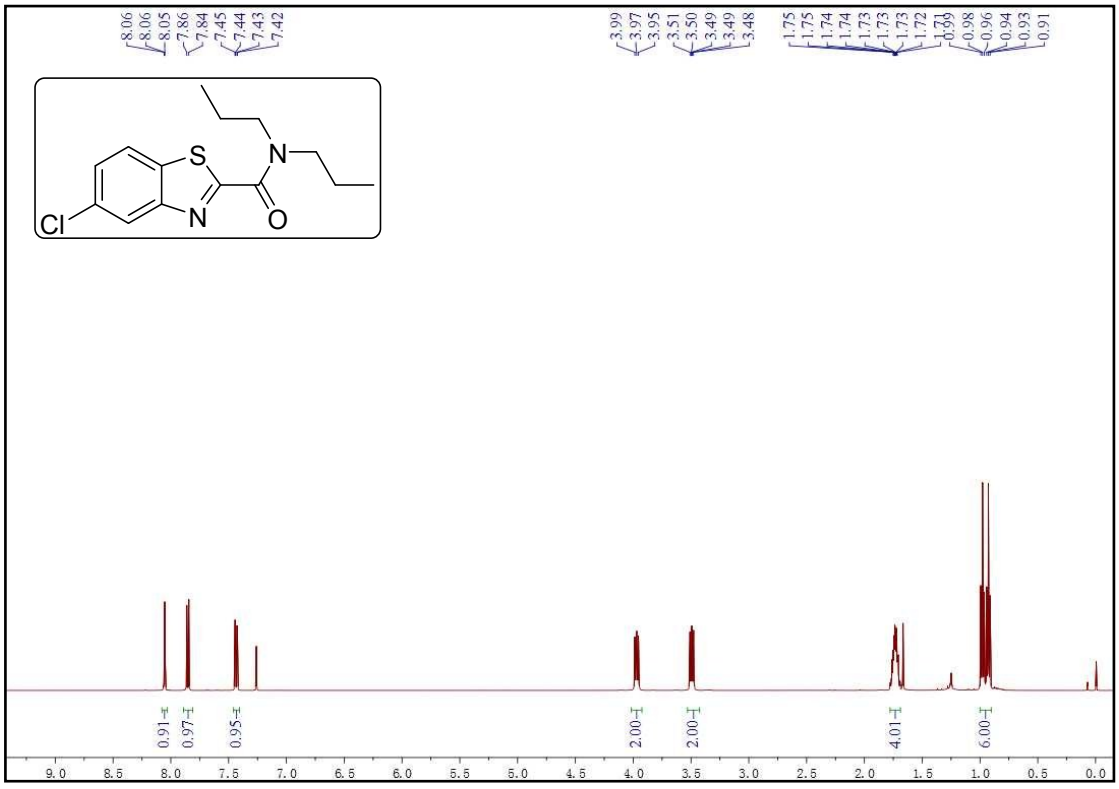



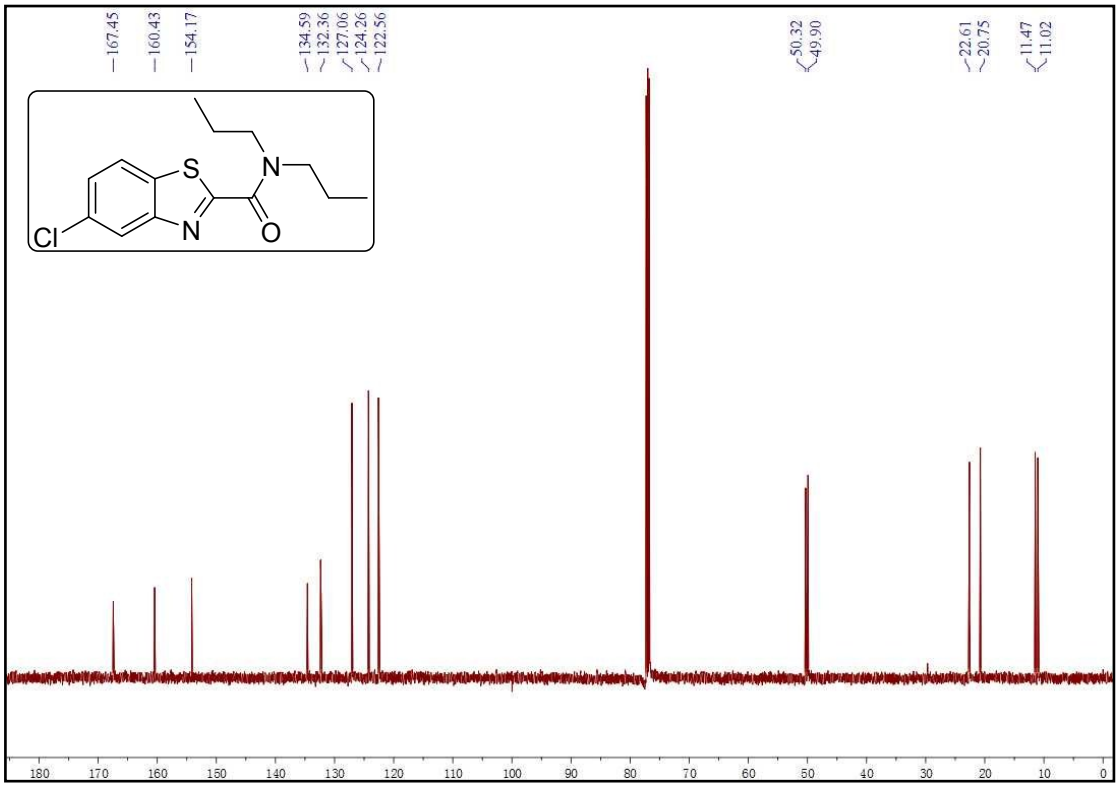
## 5-chloro-N,N-diethylbenzo[*d*]thiazole-2-carboxamide (7r)



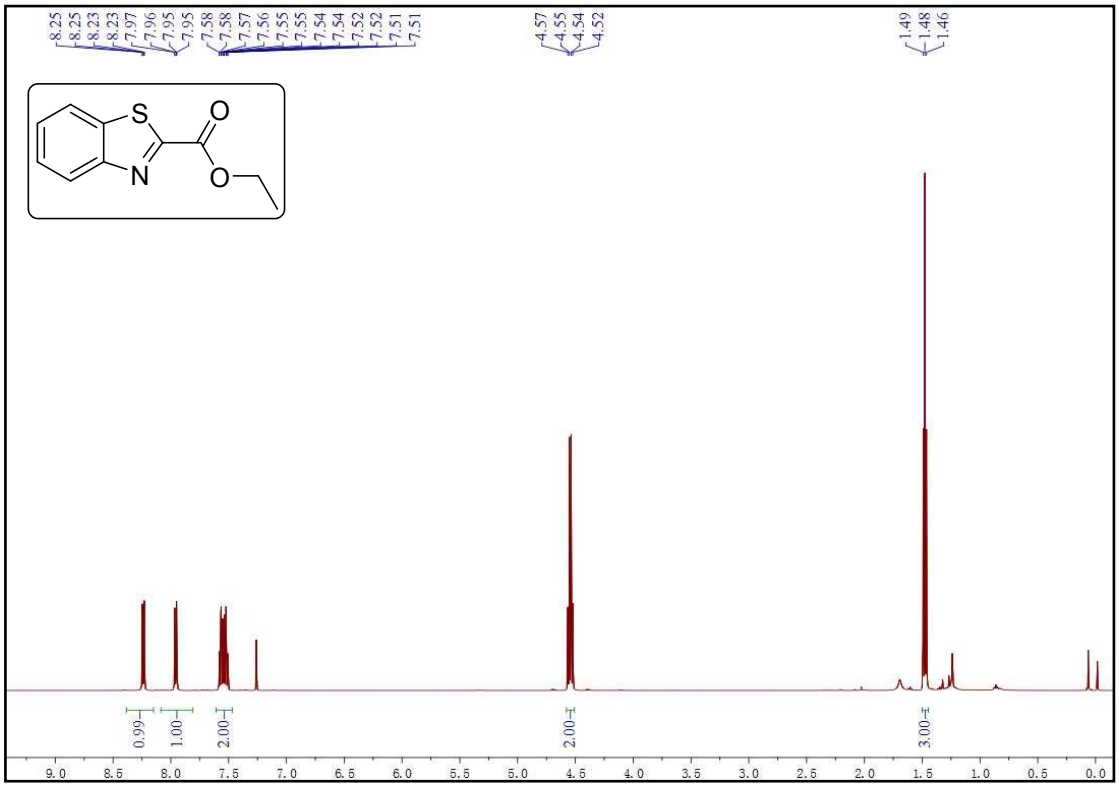



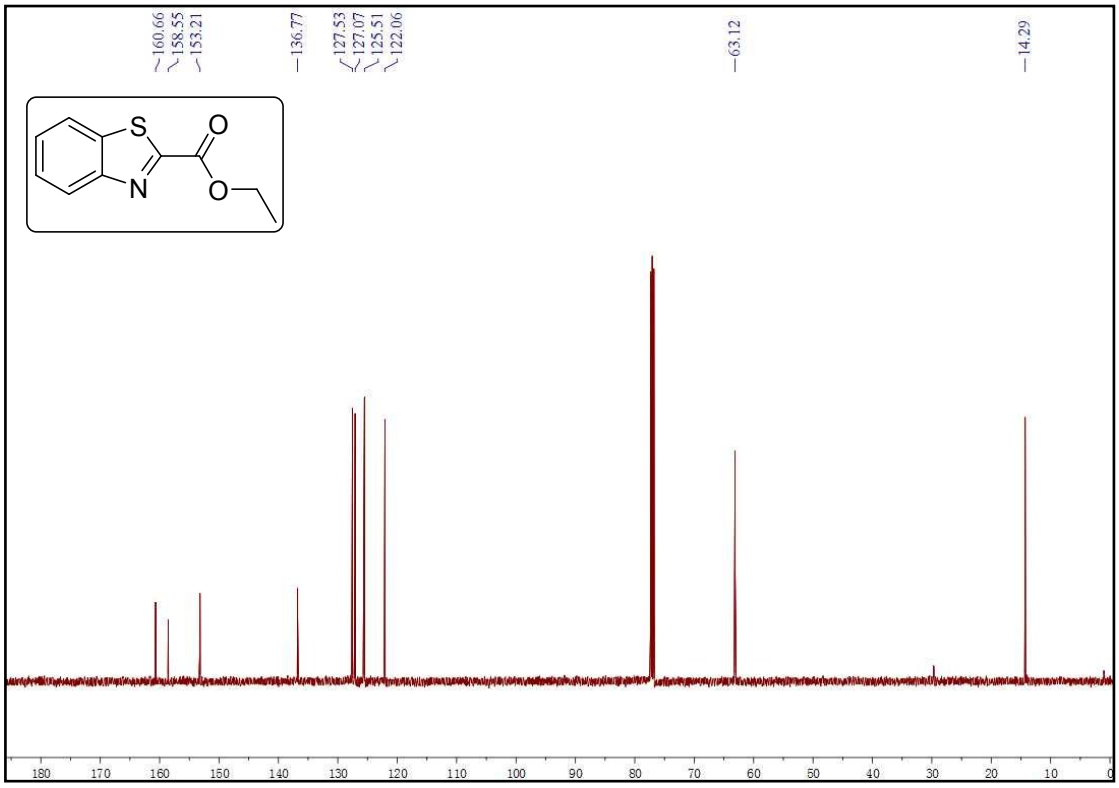
## 5-chloro-N,N-dipropylbenzo[*d*]thiazole-2-carboxamide (7s)



## ethyl benzo[*d*]thiazole-2-carboxylate (7t)



## ethyl 5-chlorobenzo[*d*]thiazole-2-carboxylate (7u)