# Supporting Information

# One-Pot Synthesis of Benzoxazole/Benzothiazole-Substituted Esters by Michael Addition: A Selective Construction of C-N/C-S Bonds

**Zhi-Ying Gong [1,†], Cheng-Li Yang [1,†], Dan Wang [1], Lang Huang [1] and Zhi-Bing Dong [1,2,3,*]**

[1] School of Chemistry and Environmental Engineering,Wuhan Institute of Technology,Wuhan 430205, China; m18235462356@163.com (Z.-Y.G.); ycl_carol@163.com (C.-L.Y.); zisedehua13@163.com (D.W.); 17362493690@163.com (L.H.)

[2] Key Laboratory of Green Chemical Process, Ministry of Education, Wuhan Institute of Technology, Wuhan 430205, China

[3] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China

***** Correspondence: dzb04982@wit.edu.cn

† These authors contributed equally to this work.

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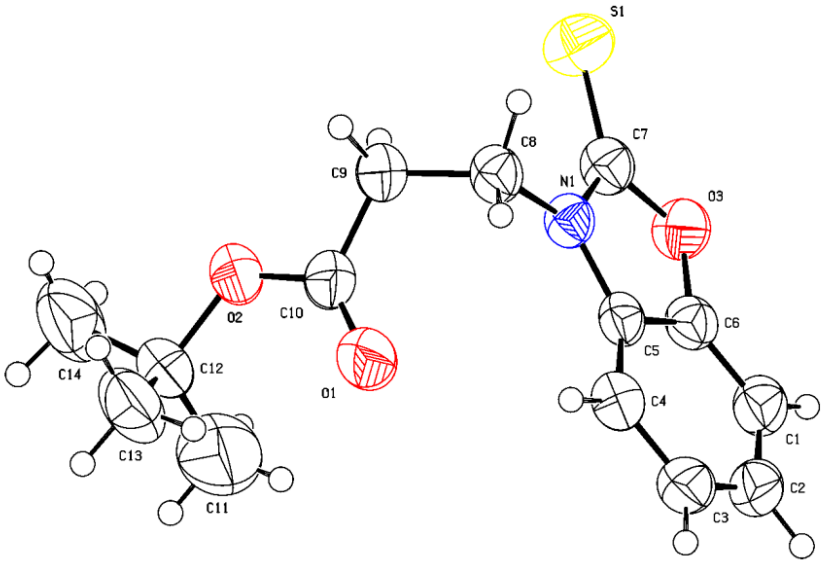
## I. X-ray diffraction analysis of compound 3ai

The method for crystal growth is slow volatilization using EA (Ethyl acetate) as a solvent.

The crystallographic data for the single crystal of the complex 3d was collected on a CrysAlis PRO 1.171.39.7a (Rigaku OD, 2015) employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the CrysAlisPro program at 300 K and 293 K respectively. The structure was solved by direct method and refined by least-squares. Program used to solve structure is SHELXS (Sheldrick, 2008); program used to refine structure is SHELXH (Sheldrick, 2015). Hydrogen atoms of -CH, -$CH_2$ , -$CH_3$ , groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters. Crystallography data and structure refinement for **3ai** (CCDC 2152821). Thermal ellipsoids are shown at 30% probability level.

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Bond precision: C-C = 0.0043 A Wavelength=0.71076

Cell: a=9.2629(8) b=6.4277(5) c=25.022(2)
alpha=90 beta=93.049(2) gamma=90
Temperature: 296 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1487.7(2) | 1487.7(2) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C14 H17 N O3 S | C14 H17 N O3 S |
| Sum formula | C14 H17 N O3 S | C14 H17 N O3 S |
| Mr | 279.35 | 279.34 |
| Dx,g cm-3 | 1.247 | 1.247 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.221 | 0.221 |
| F000 | 592.0 | 592.0 |
| F000' | 592.76 | |
| h,k,lmax | 11,7,29 | 11,7,29 |
| Nref | 2653 | 2636 |
| Tmin,Tmax | | |
| Tmin' | | |

Correction method= Not given

Data completeness= 0.994 Theta(max)= 25.113

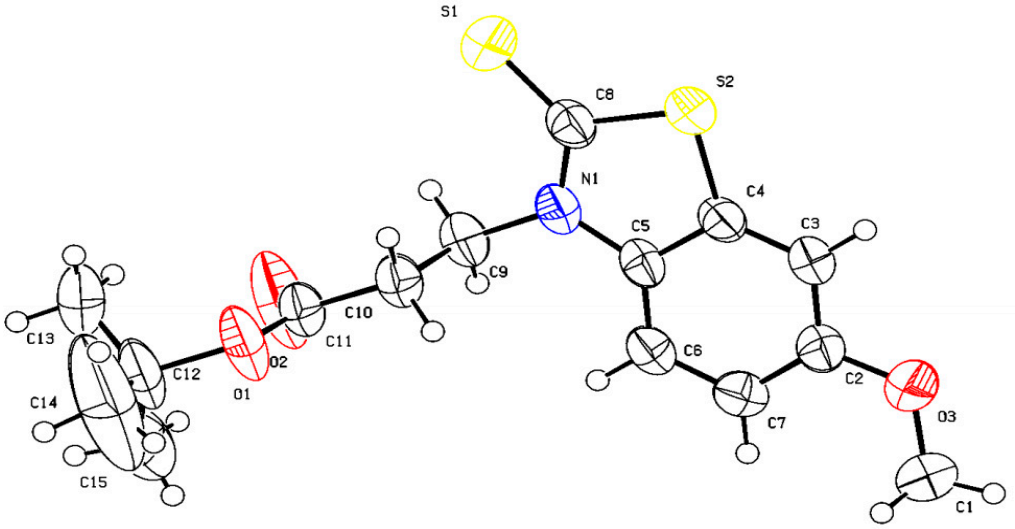
R(reflections)= 0.0516( 1573) wR2(reflections)= 0.1124( 2636)

S = 1.066 Npar= 176

**X-ray diffraction analysis of compound 5ag'**

The method for crystal growth is slow volatilization using EA (Ethyl acetate) as a solvent.

The crystallographic data for the single crystal of the complex **5ag'** was collected on a CrysAlis PRO 1.171.39.7a (Rigaku OD, 2015) employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the CrysAlisPro program at 300 K and 293 K respectively. The structure was solved by direct method and refined by least-squares. Program used to solve structure is SHELXS (Sheldrick, 2008); program used to refine structure is SHELXH (Sheldrick, 2015). Hydrogen atoms of -CH, $-CH_2$ , $-CH_3$ , groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters. Crystallography data and structure refinement for **5ag'** (CCDC 2152790). Thermal ellipsoids are shown at 30% probability level.

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Bond precision: C-C = 0.0088 A Wavelength=0.71076

Cell: a=5.613(2) b=9.721(4) c=15.530(6)
alpha=99.074(9) beta=93.439(9) gamma=99.797(9)
Temperature: 296 K

| | Calculated | Reported |
|---|---|---|
| Volume | 821.3(5) | 821.3(5) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | C15 H19 N O3 S2 | C15 H19 N O3 S2 |
| Sum formula | C15 H19 N O3 S2 | C15 H19 N O3 S2 |
| Mr | 325.43 | 325.43 |
| Dx,g cm-3 | 1.316 | 1.316 |
| Z | 2 | 2 |
| Mu (mm-1) | 0.333 | 0.332 |
| F000 | 344.0 | 344.0 |
| F000' | 344.63 | |
| h,k,lmax | 6,11,18 | 6,11,18 |
| Nref | 2979 | 2951 |
| Tmin,Tmax | | 0.662,0.745 |
| Tmin' | | |

Correction method= # Reported T Limits: Tmin=0.662 Tmax=0.745
AbsCorr = MULTI-SCAN

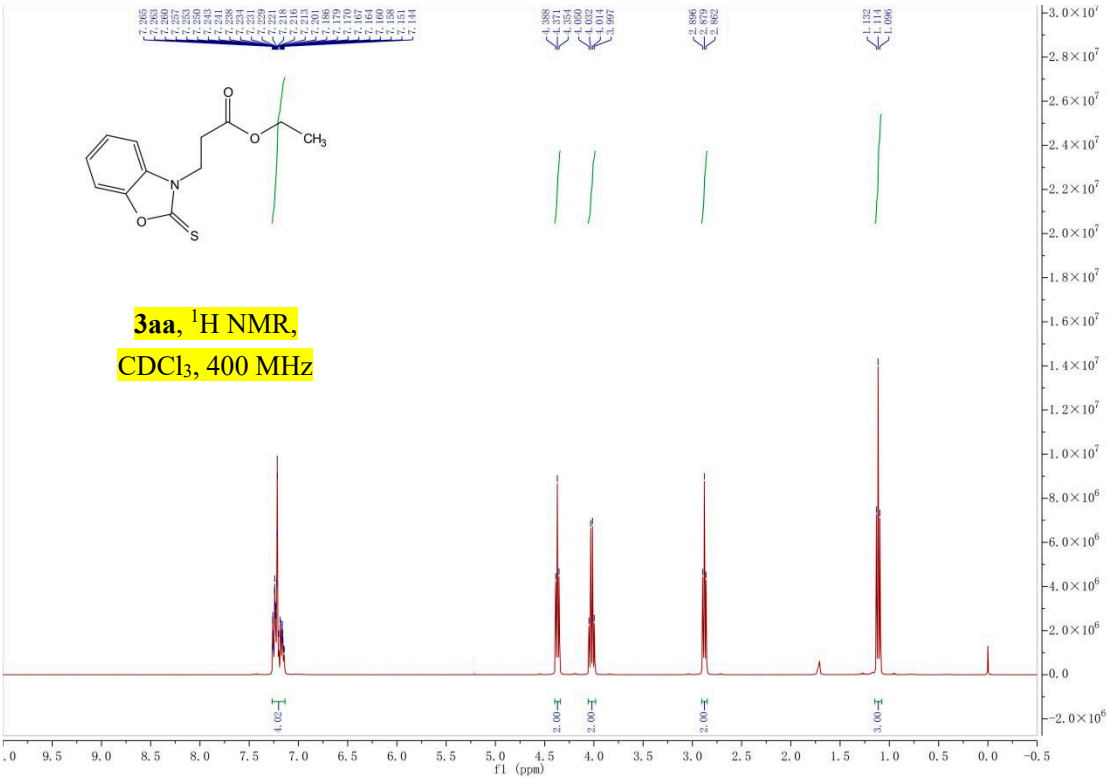
Data completeness= 0.991 Theta(max)= 25.220

R(reflections)= 0.0815( 1707) wR2(reflections)= 0.2623( 2951)

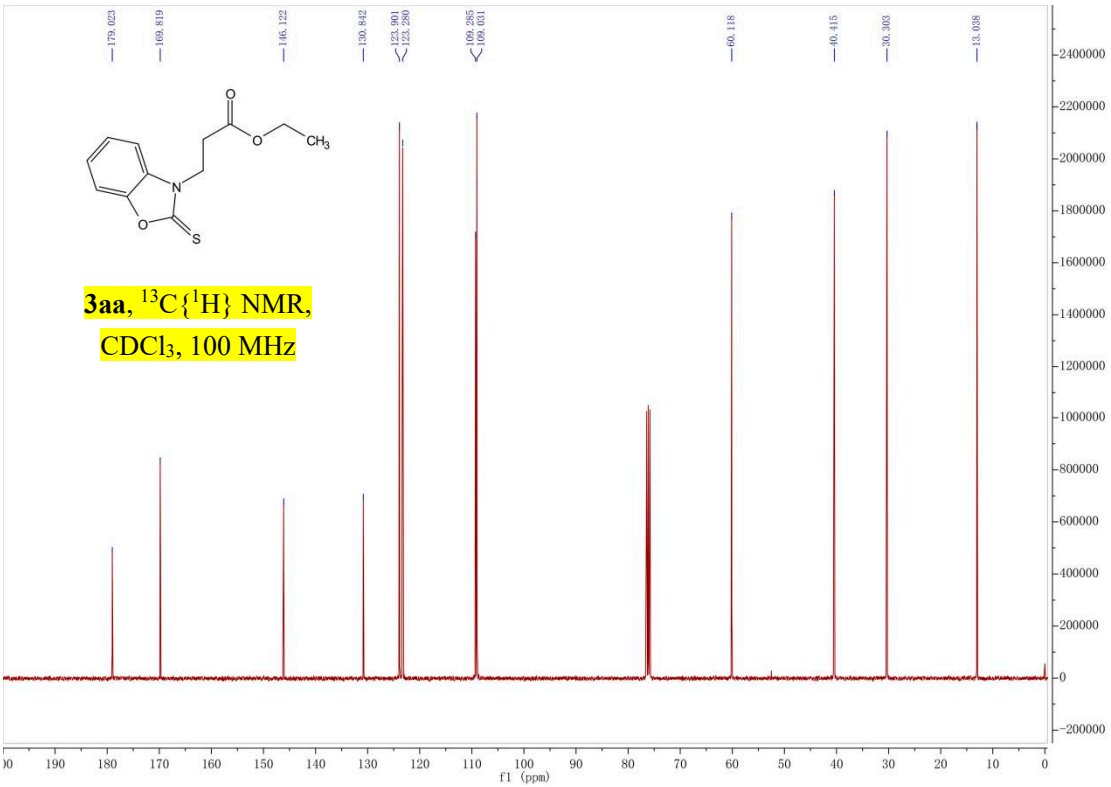
S = 1.053 Npar= 194

# II. $^{1}$H-NMR and $^{13}$C{$^{1}$H}-NMR spectra of all products

## ethyl 3-(2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3aa)

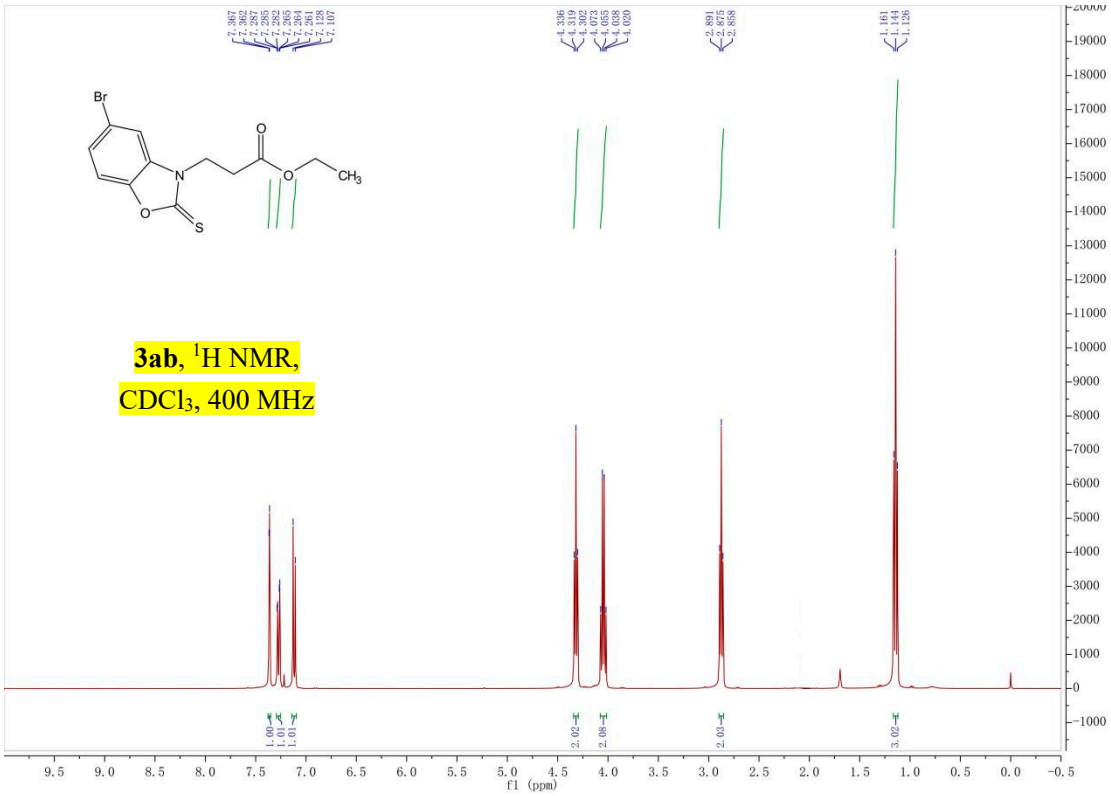



$^{1}$H NMR

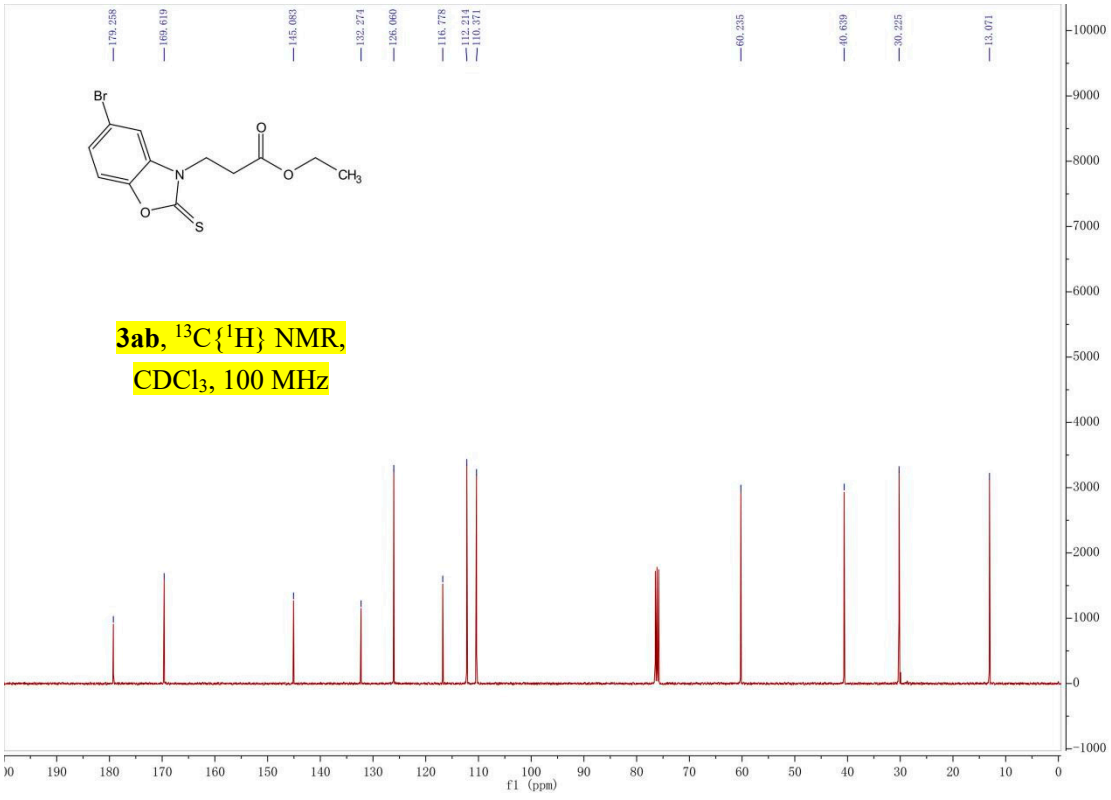



$^{13}$C{$^{1}$H} NMR

**ethyl 3-(5-bromo-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ab)**

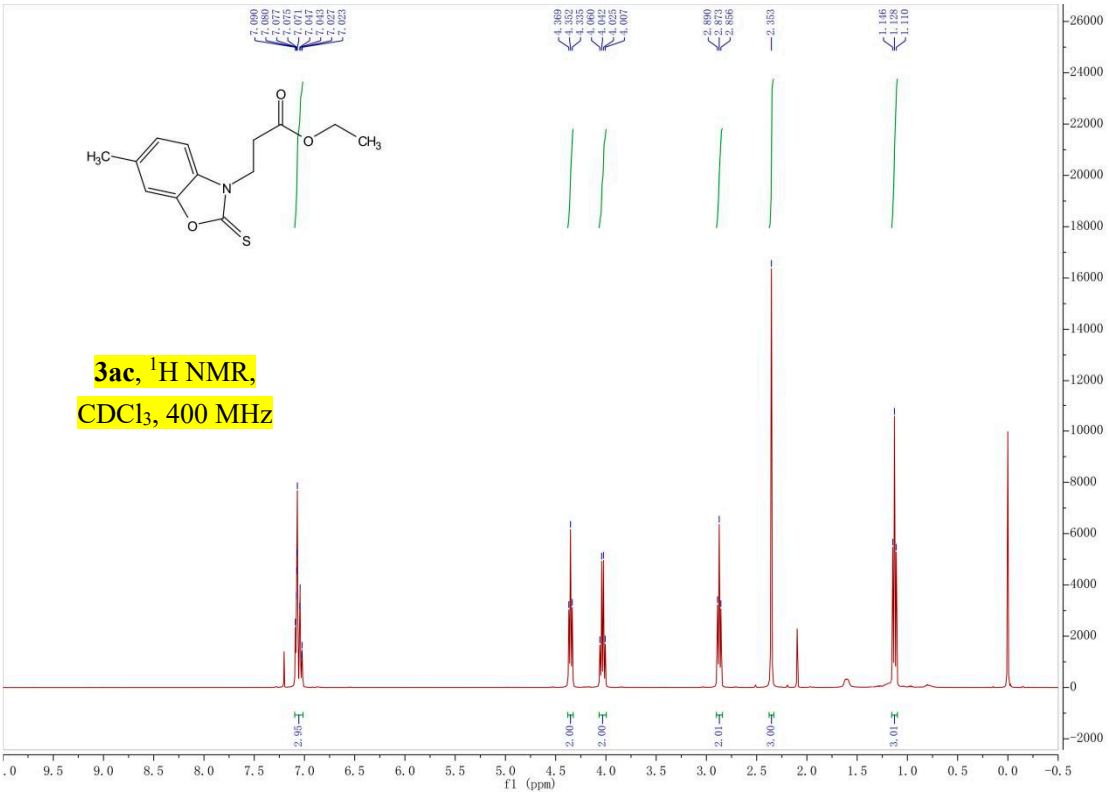



$^{1}$H NMR

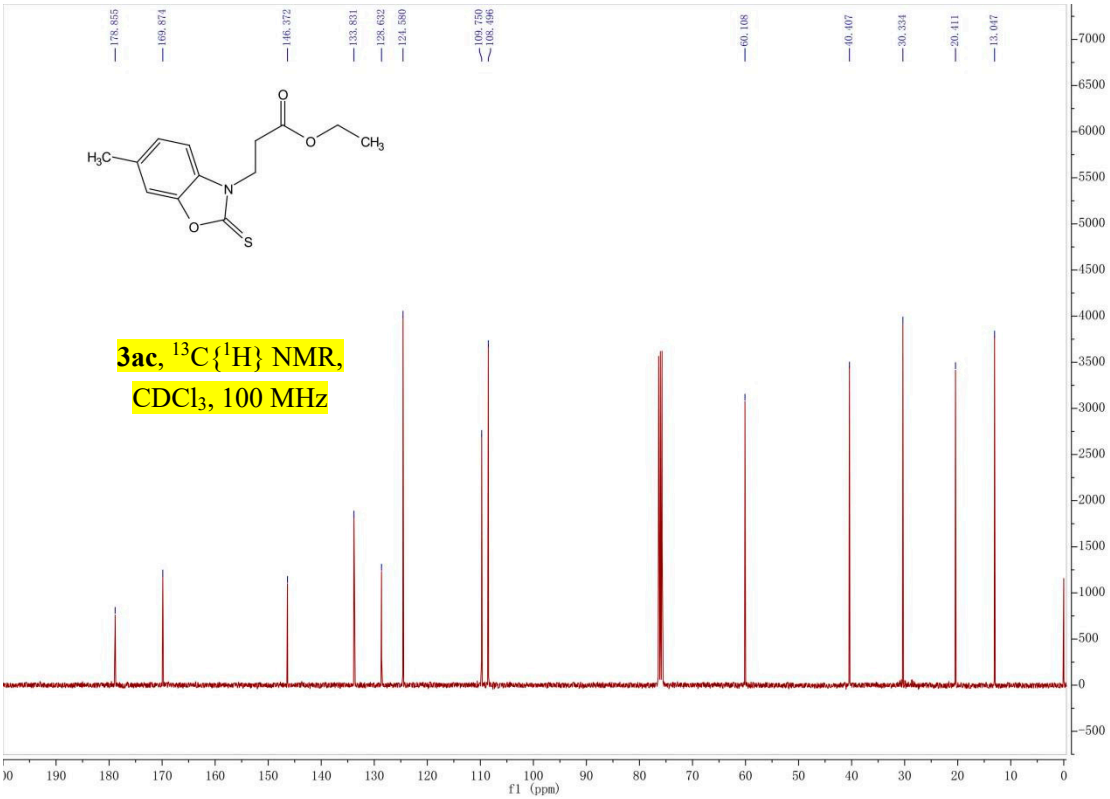



$^{13}$C{$^{1}$H} NMR

**ethyl 3-(6-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ac)**

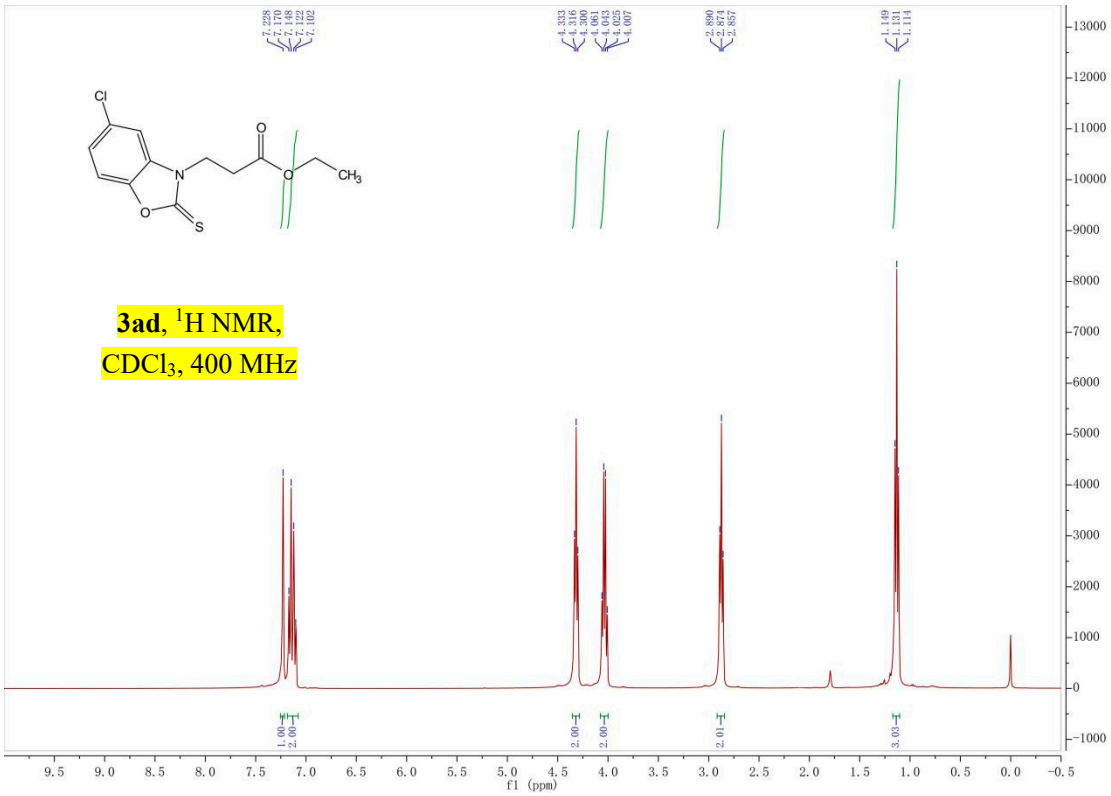



$^{1}$H NMR

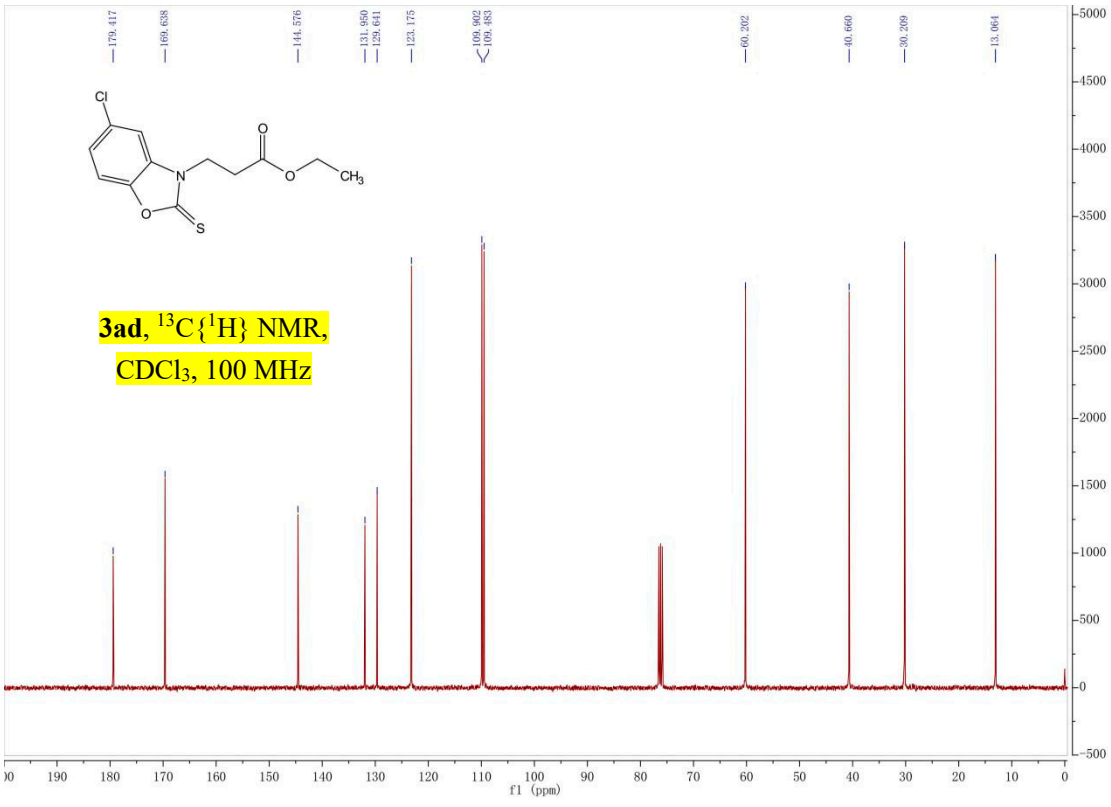



$^{13}$C{$^{1}$H} NMR

**ethyl 3-(5-chloro-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ad)**

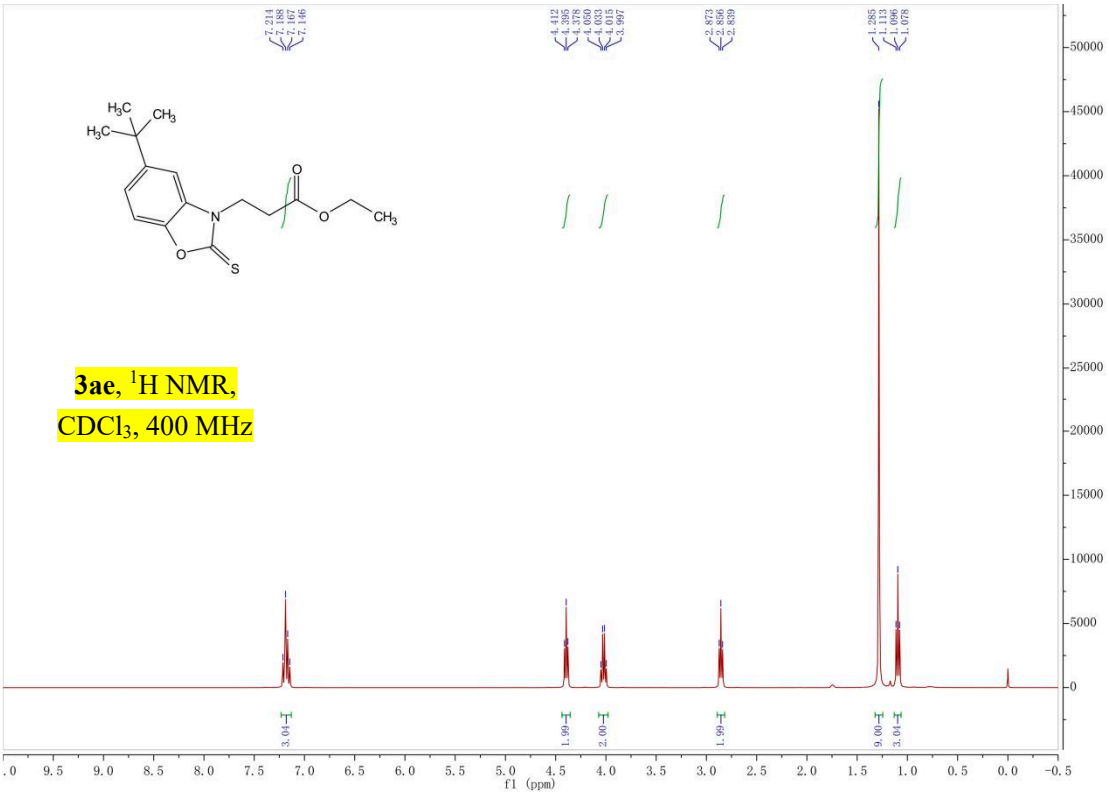



$^{1}$H NMR



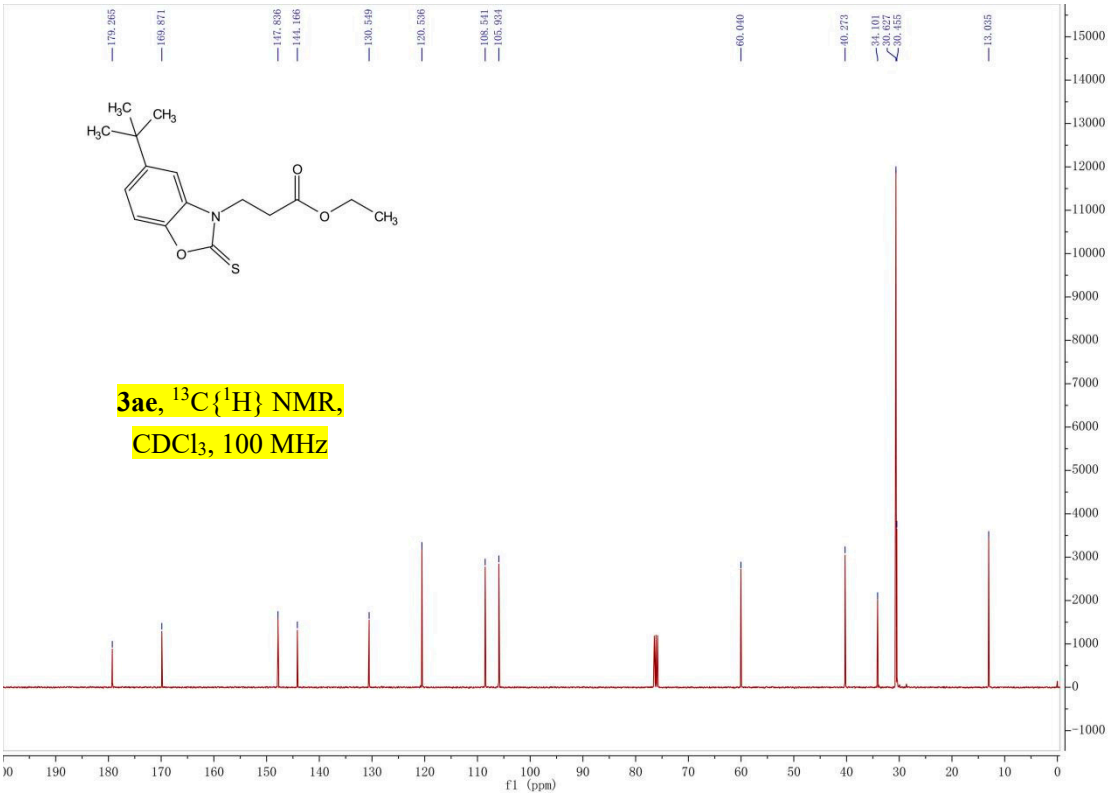

$^{13}$C{$^{1}$H} NMR

**ethyl 3-(5-(*tert*-butyl)-2-mercaptobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ae)**




**3ae**, $^{1}$H NMR,
$CDCl_3$, 400 MHz

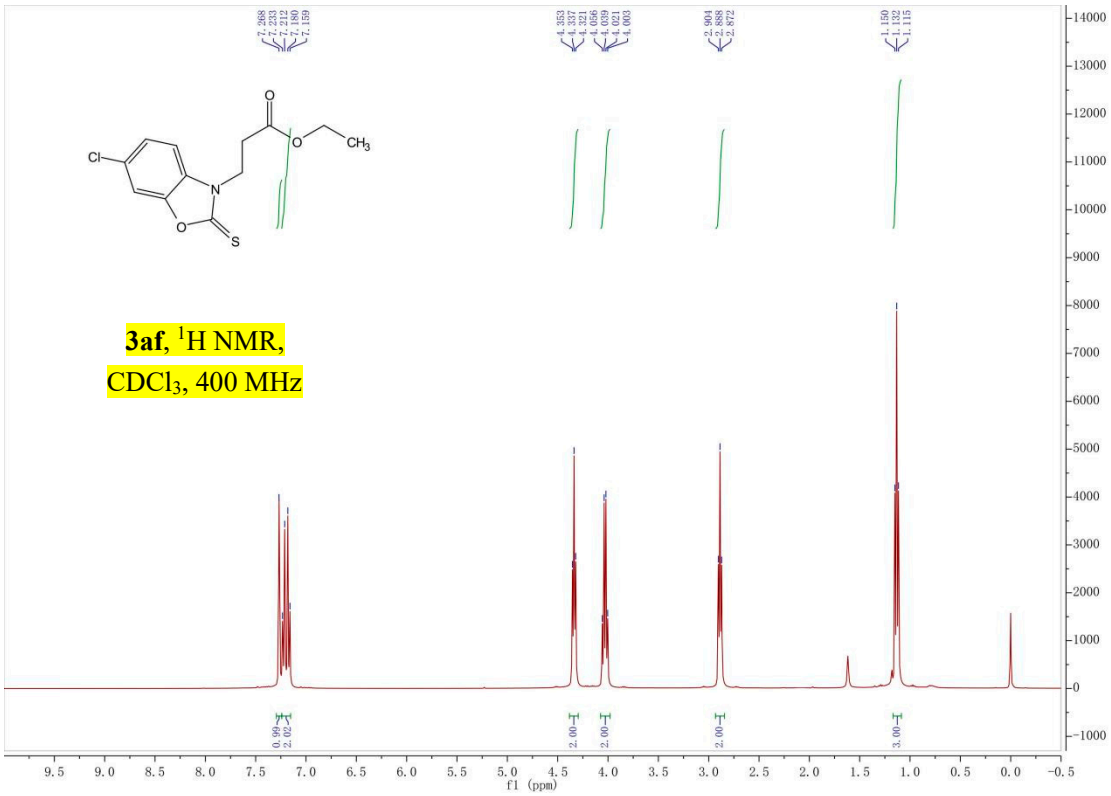
$^{1}$H NMR



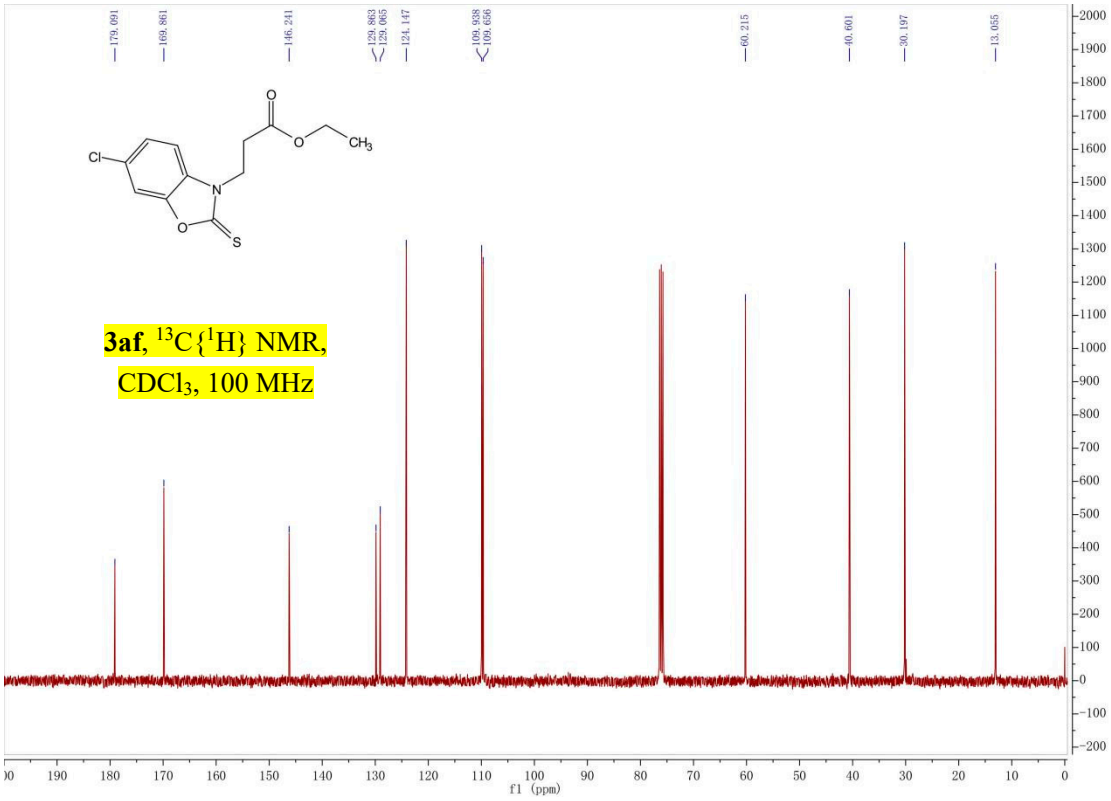

**3ae**, $^{13}$C{$^{1}$H} NMR,
$CDCl_3$, 100 MHz

$^{13}$C{$^{1}$H} NMR

**ethyl 3-(6-chloro-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3af)**

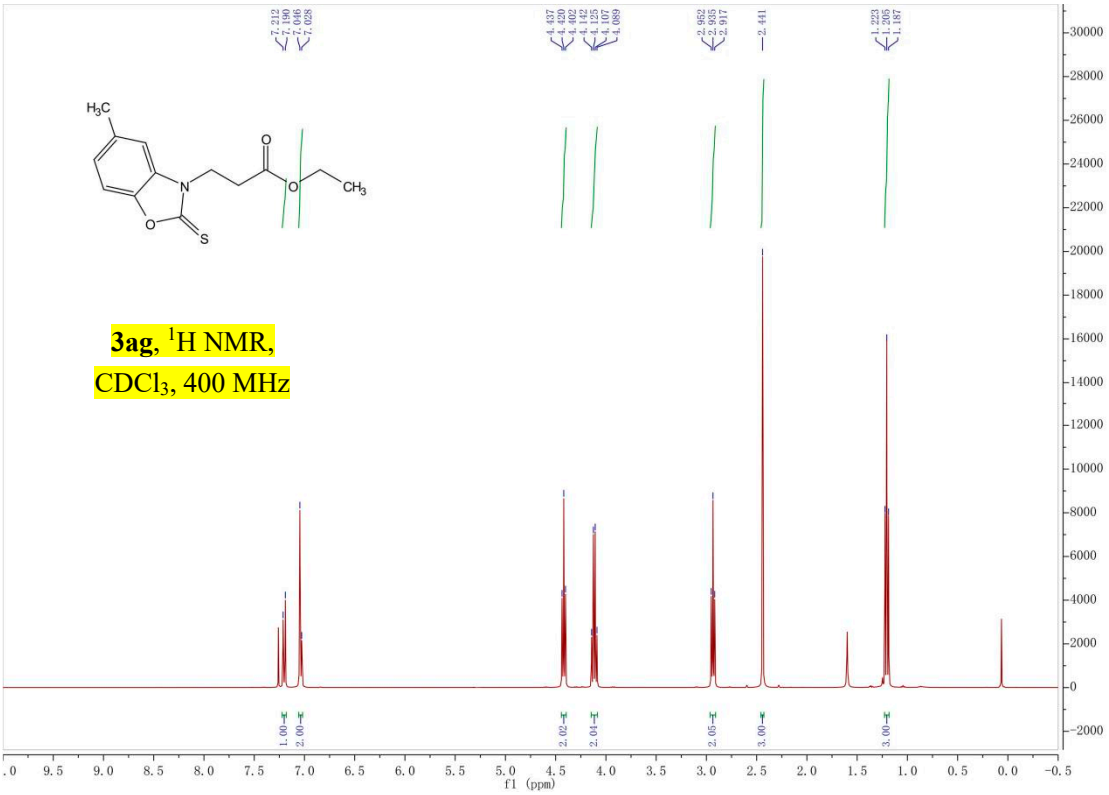



$^{1}$H NMR

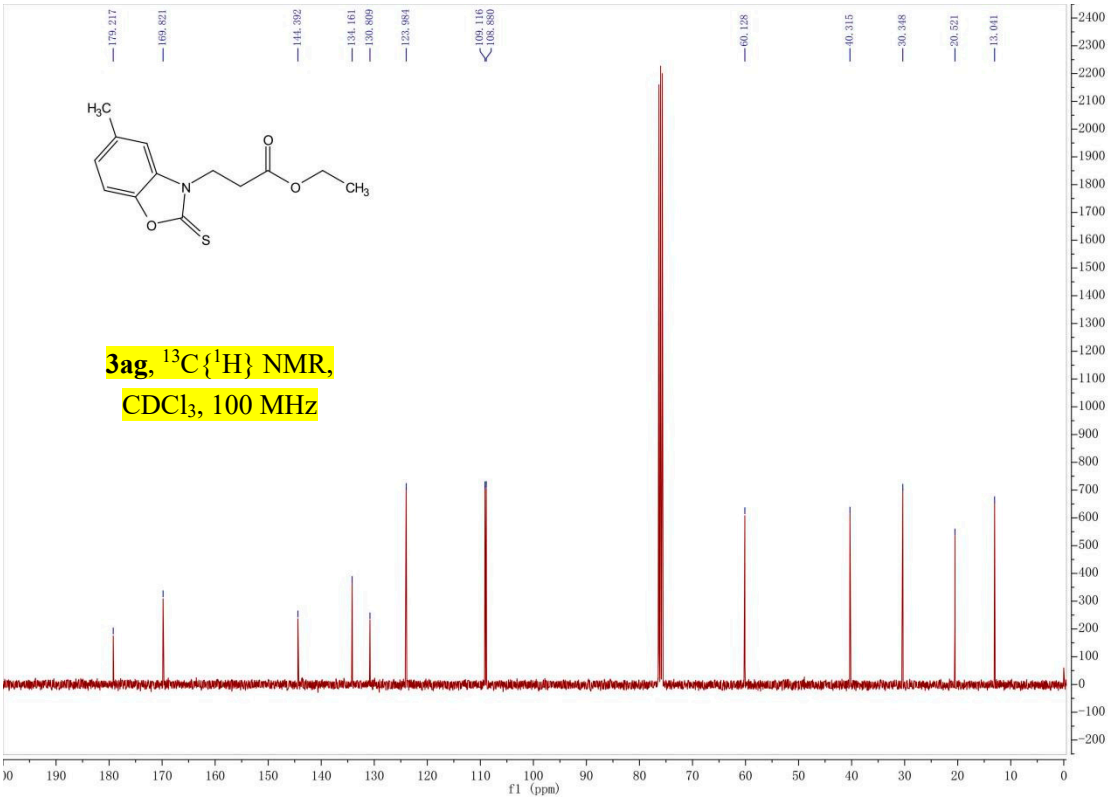



$^{13}$C{$^{1}$H} NMR

**ethyl 3-(5-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ag)**

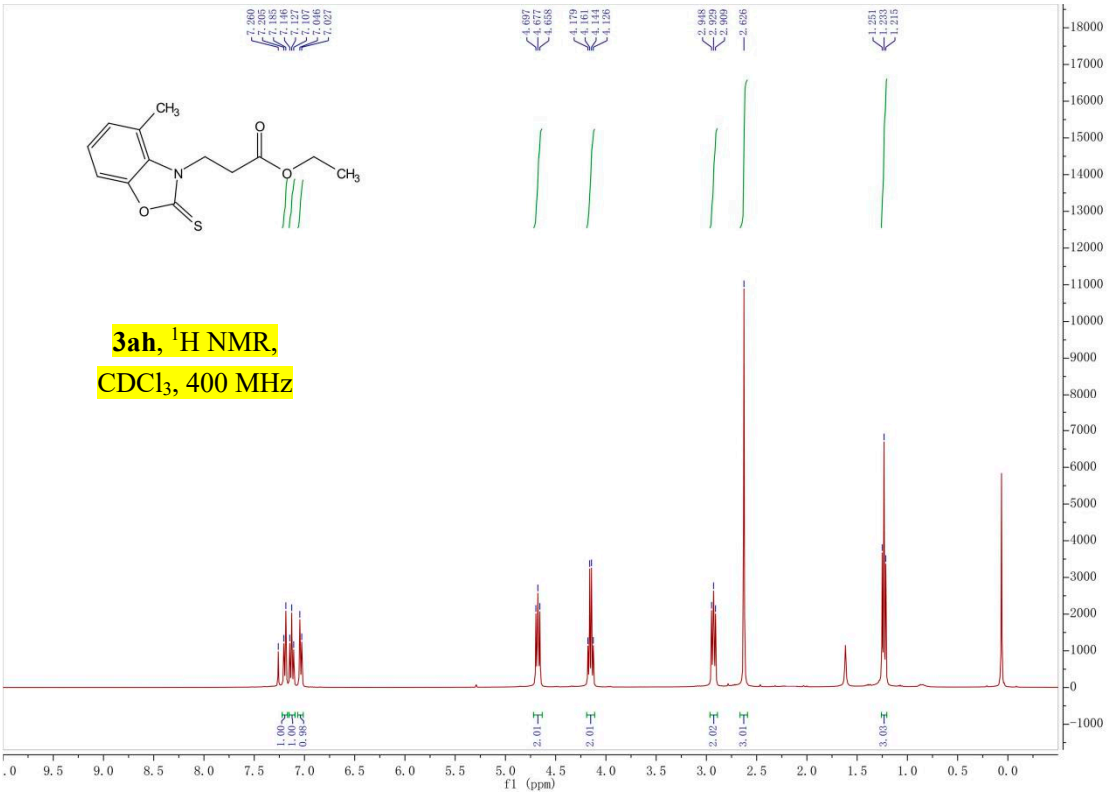



$^{1}$H NMR

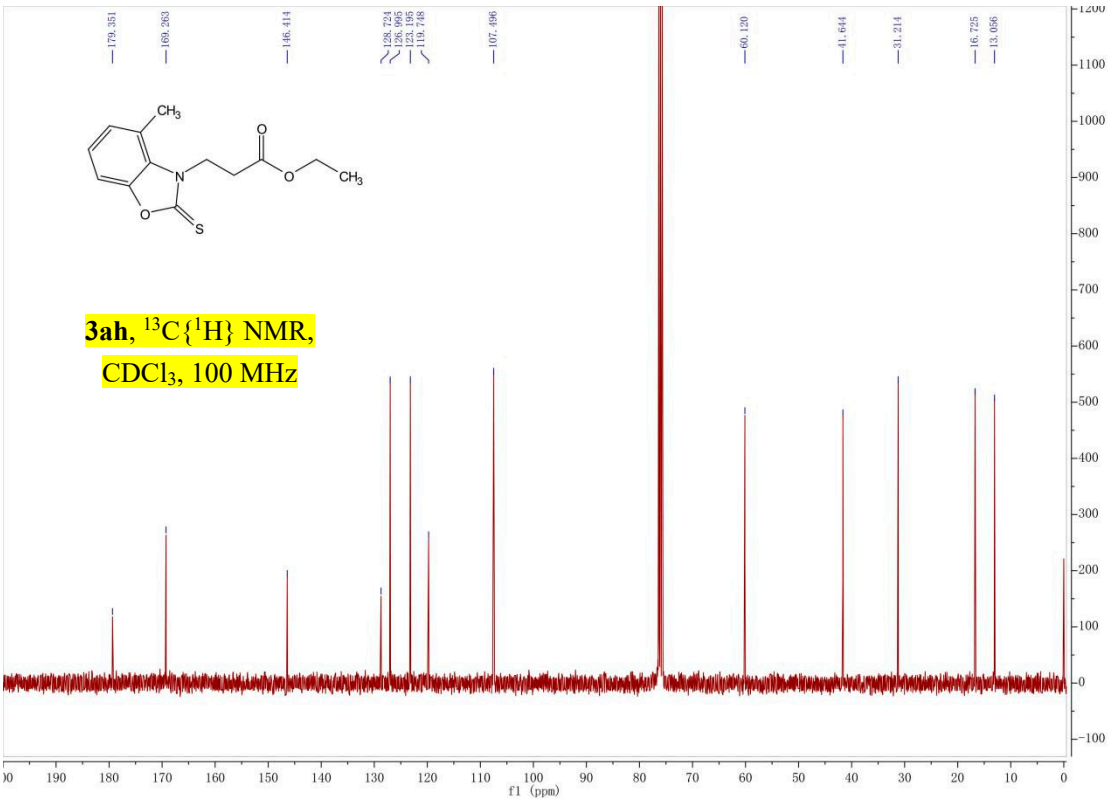



$^{13}$C{$^{1}$H} NMR

**ethyl 3-(4-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ah)**

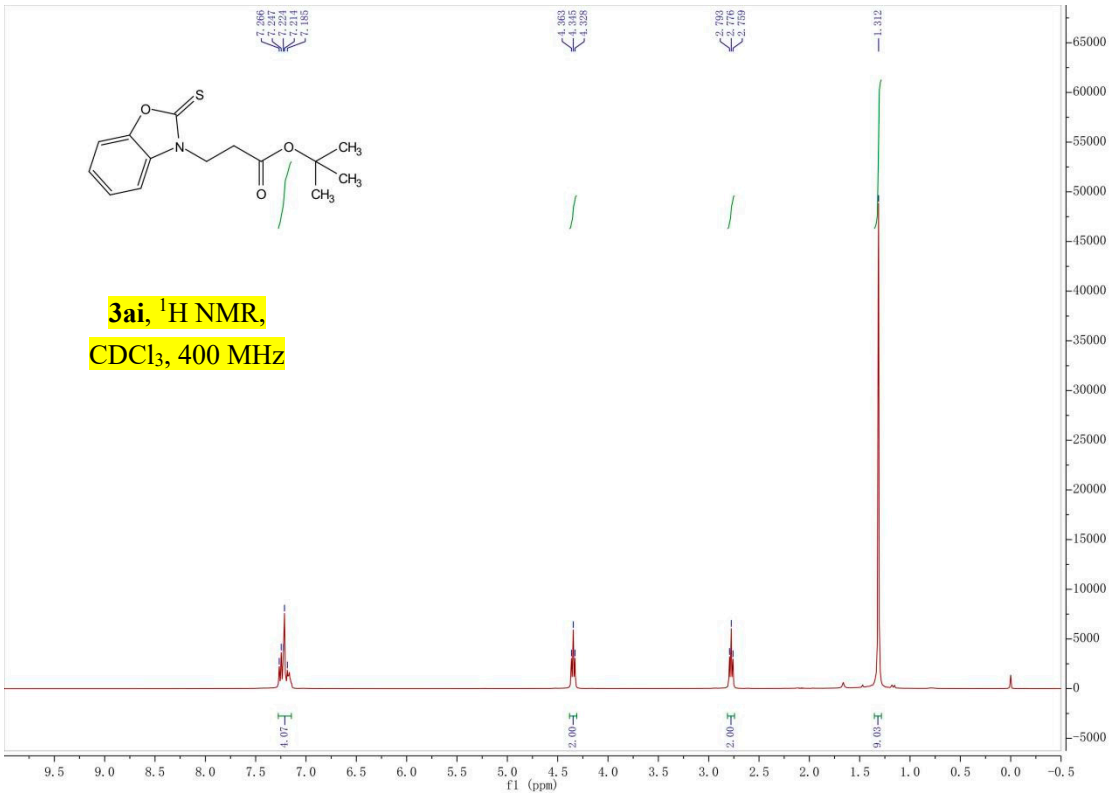



$^{1}$H NMR



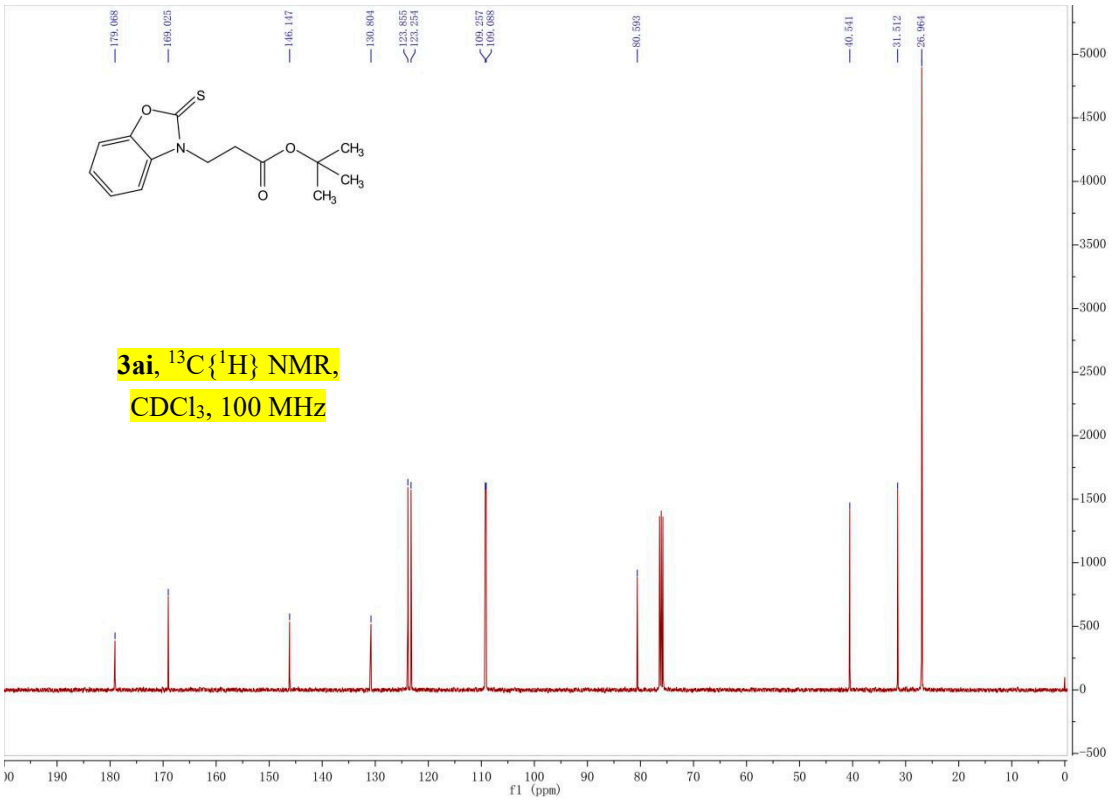

$^{13}$C{$^{1}$H} NMR

## *tert*-butyl 3-(2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ai)




**3ai**, $^{1}$H NMR,
$CDCl_3$, 400 MHz

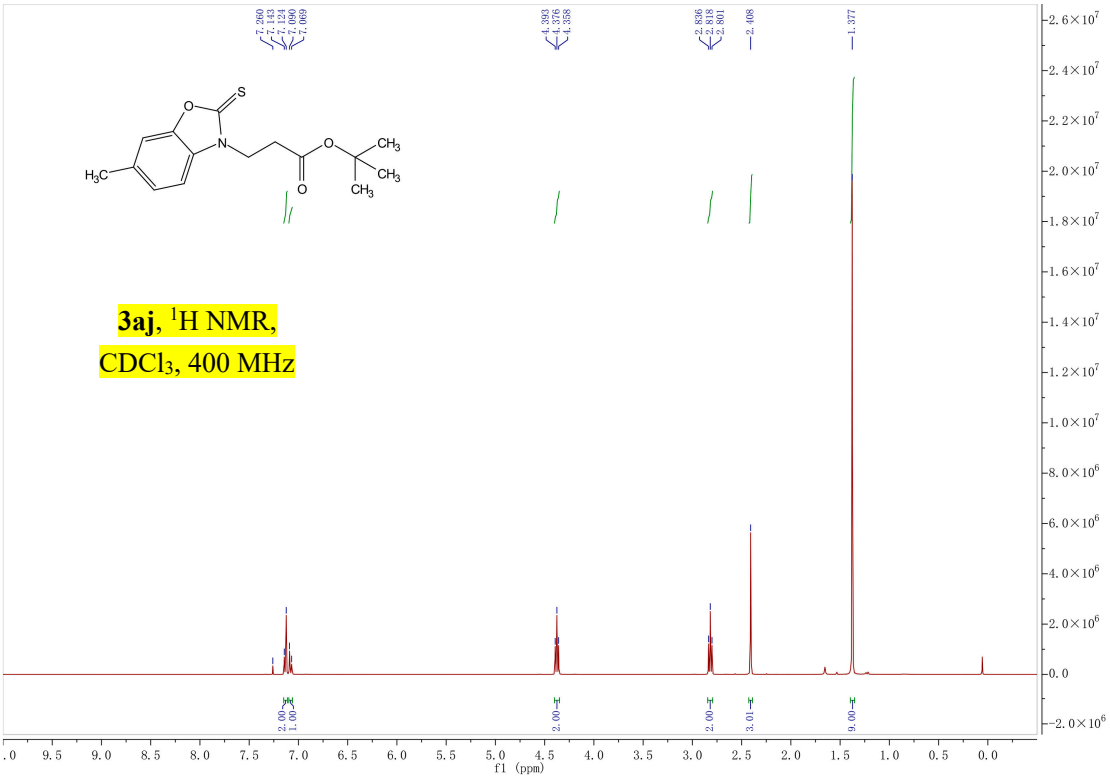
$^{1}$H NMR




**3ai**, $^{13}$C{$^{1}$H} NMR,
$CDCl_3$, 100 MHz

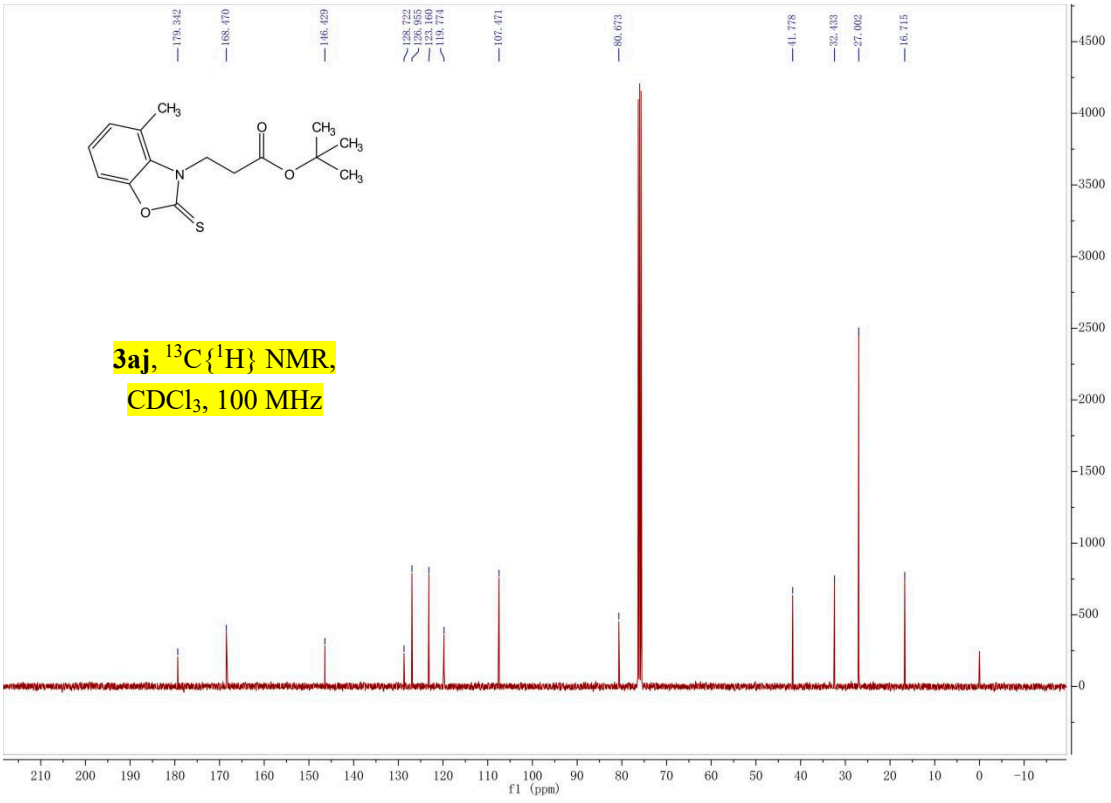
$^{13}$C{$^{1}$H} NMR

## *tert*-butyl 3-(4-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3aj)




**3aj**, $^{1}$H NMR,
$CDCl_3$, 400 MHz

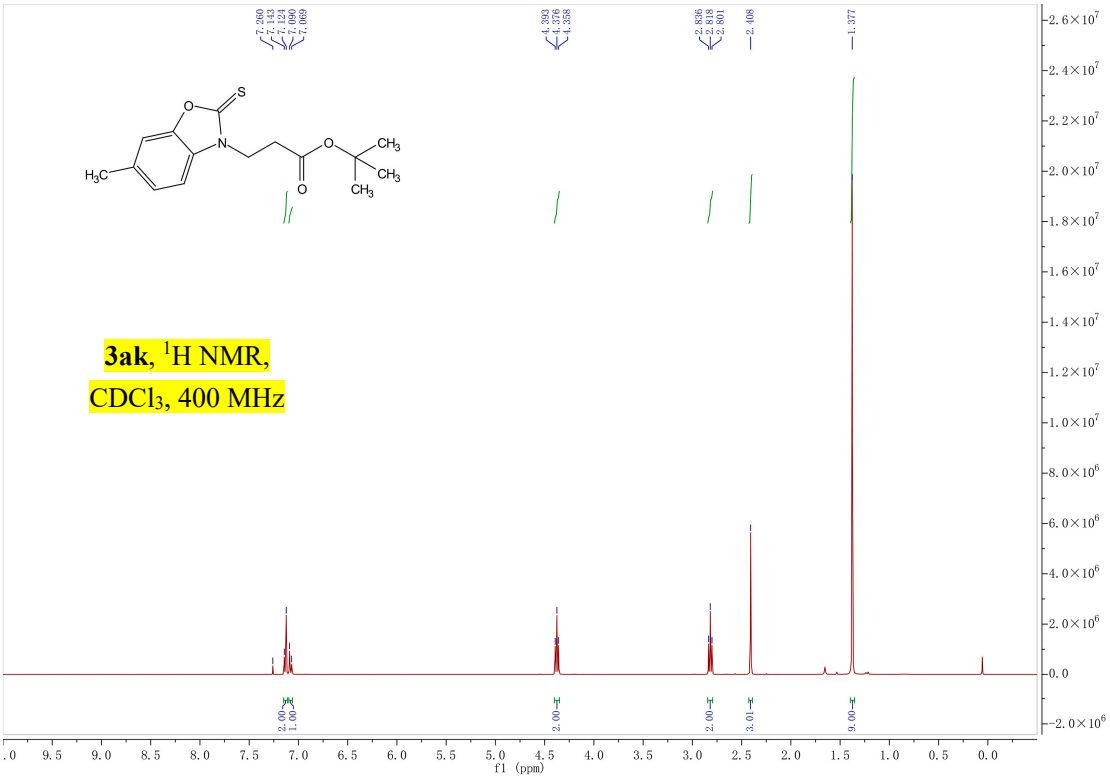
$^{1}$H NMR




**3aj**, $^{13}$C{$^{1}$H} NMR,
$CDCl_3$, 100 MHz

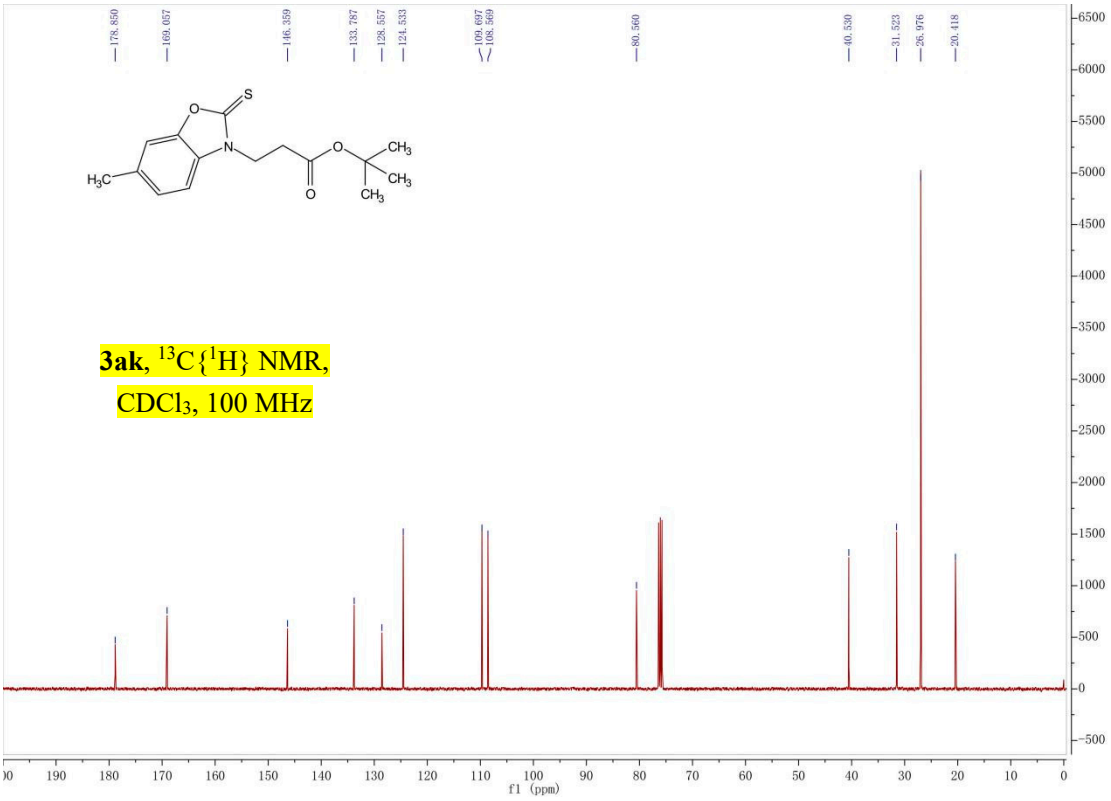
$^{13}$C{$^{1}$H} NMR

## *tert*-butyl 3-(6-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ak)




**3ak**, $^{1}$H NMR,
$CDCl_3$, 400 MHz

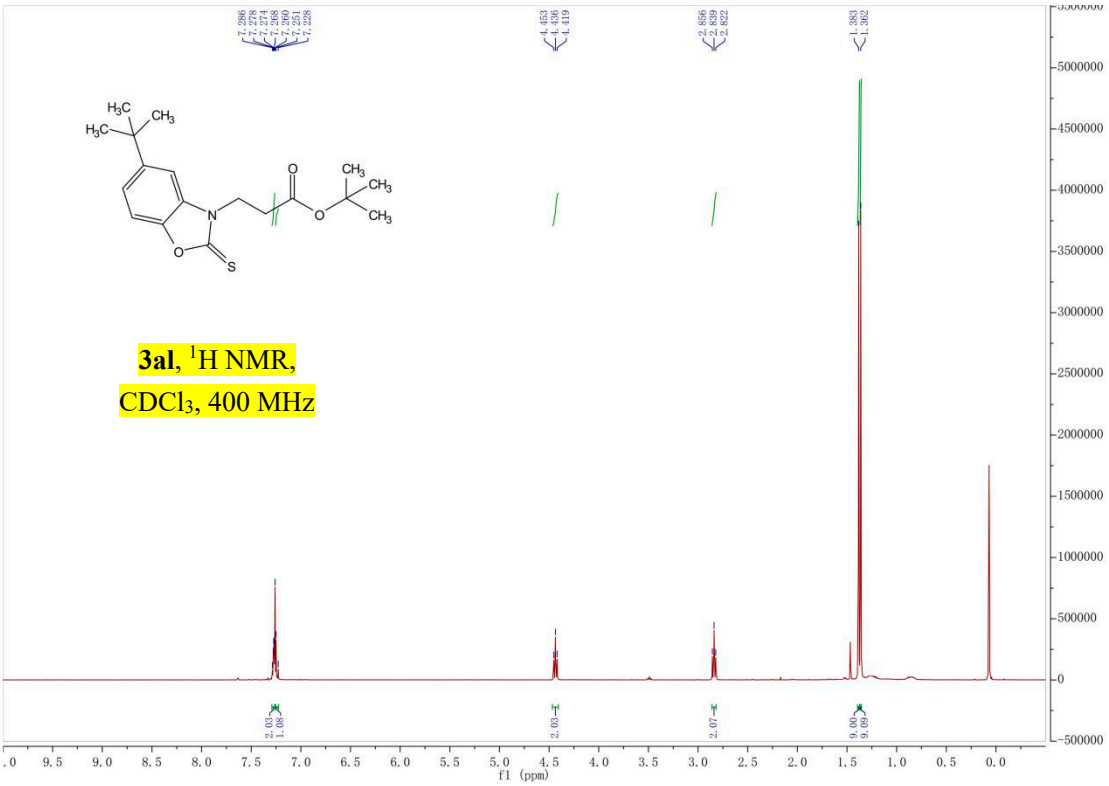
$^{1}$H NMR



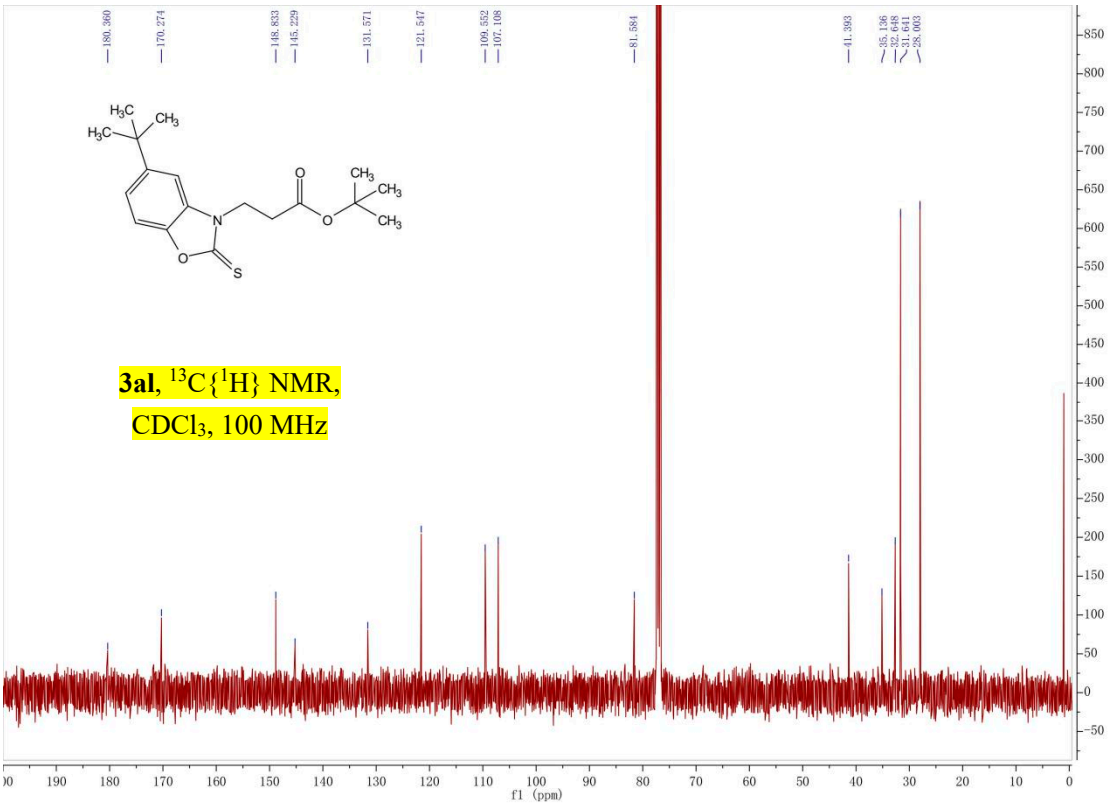

**3ak**, $^{13}$C{$^{1}$H} NMR,
$CDCl_3$, 100 MHz

$^{13}$C{$^{1}$H} NMR

## *tert*-butyl 3-(5-(tert-butyl)-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3al)

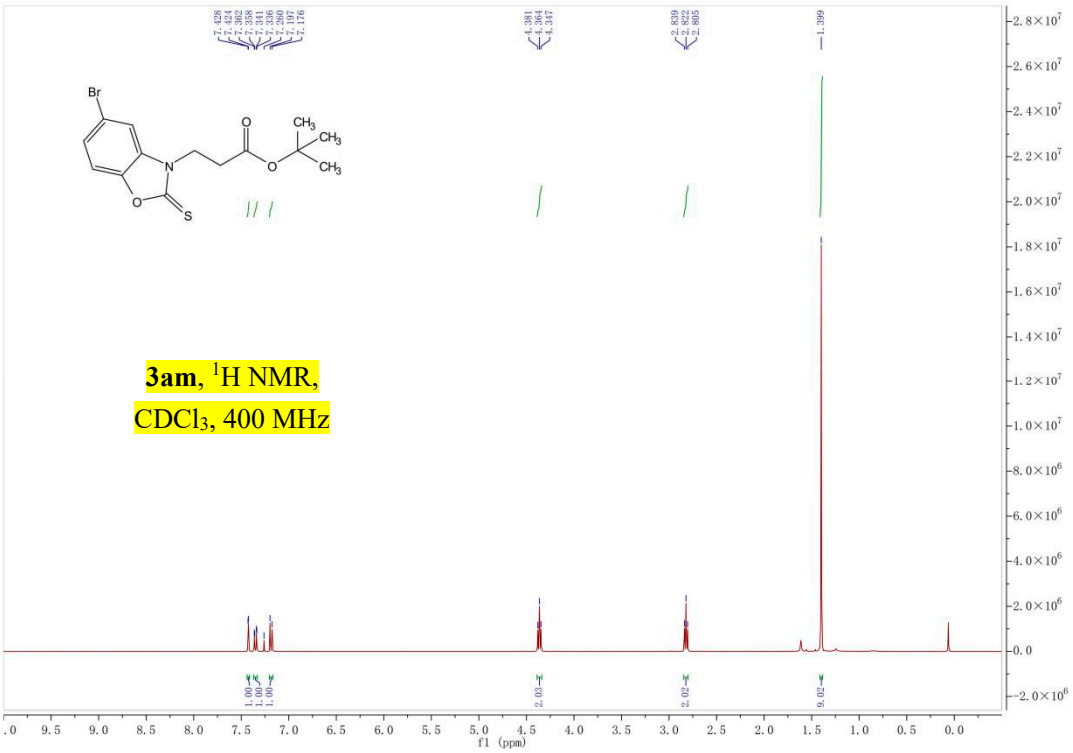



$^1$H NMR

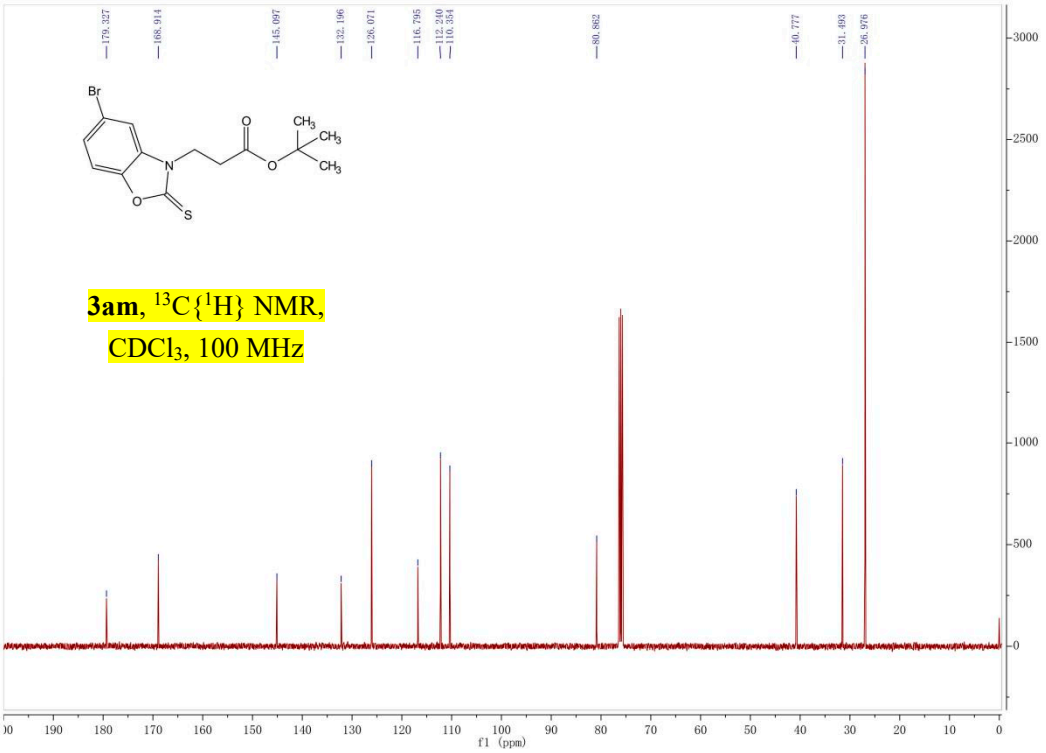



$^{13}$C{$^1$H} NMR

## *tert*-butyl 3-(5-bromo-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3am)

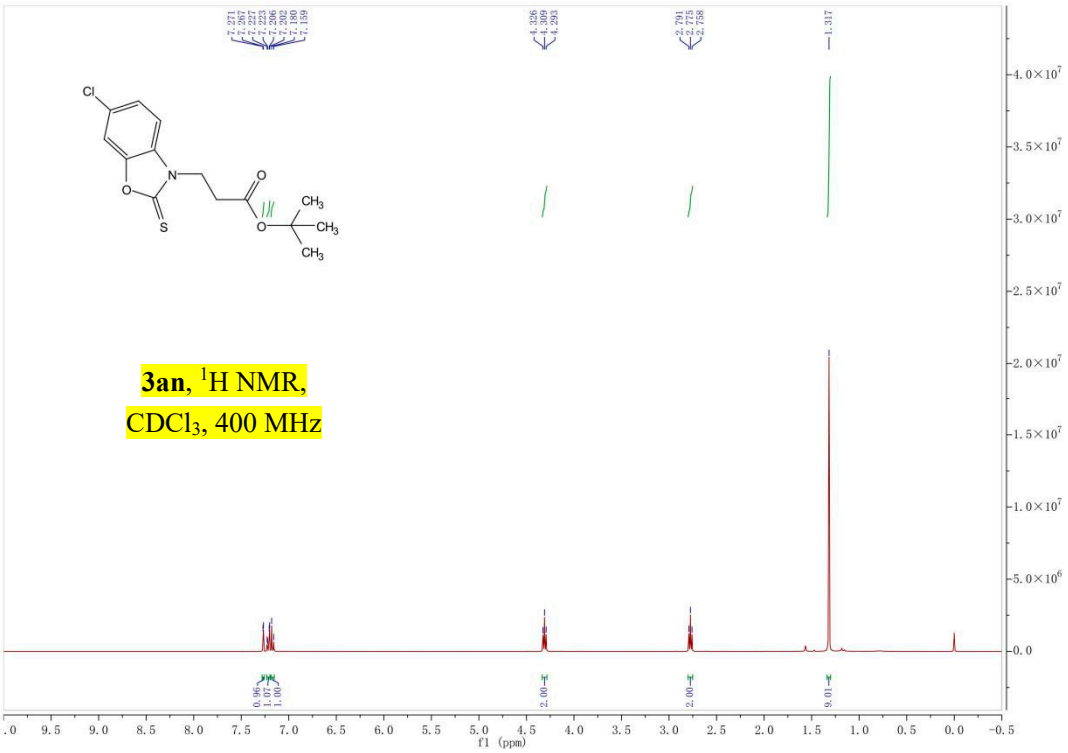



$^{1}$H NMR

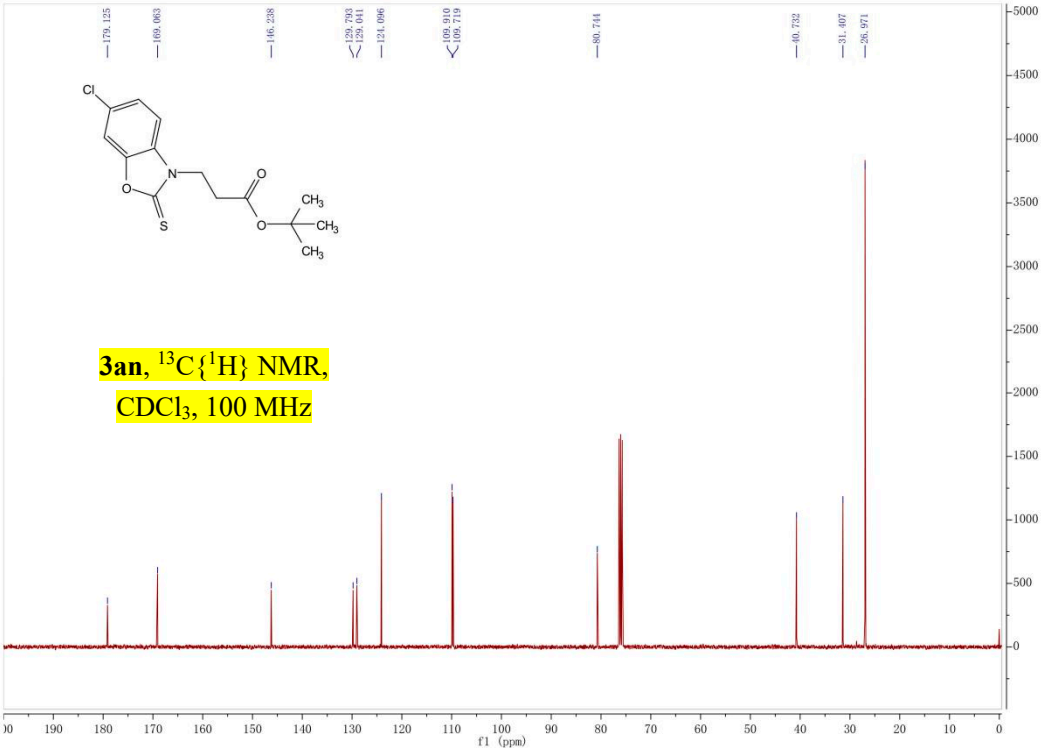



$^{13}$C{$^{1}$H} NMR

## *tert*-butyl 3-(6-chloro-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3an)

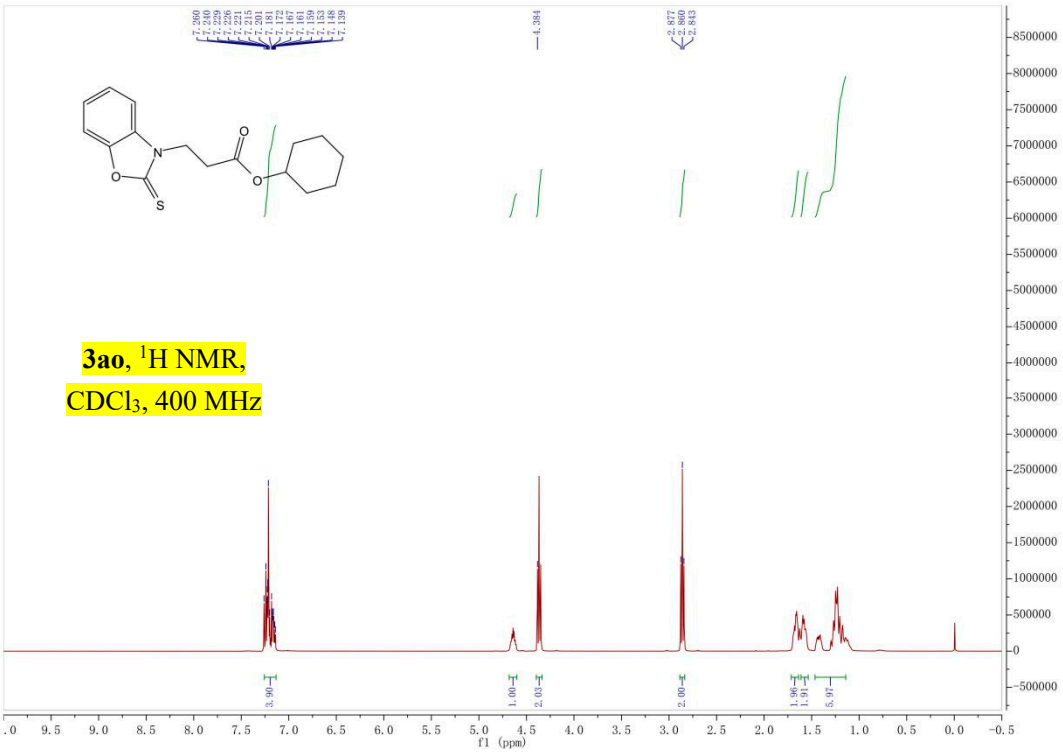



$^{1}$H NMR

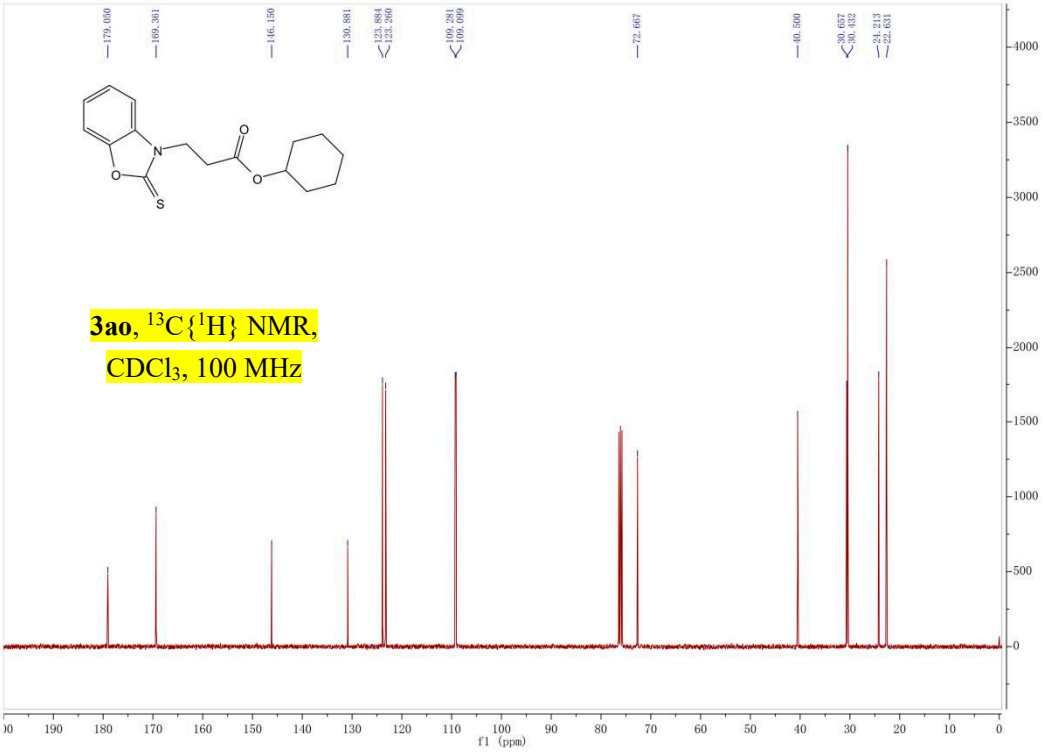



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ao)**

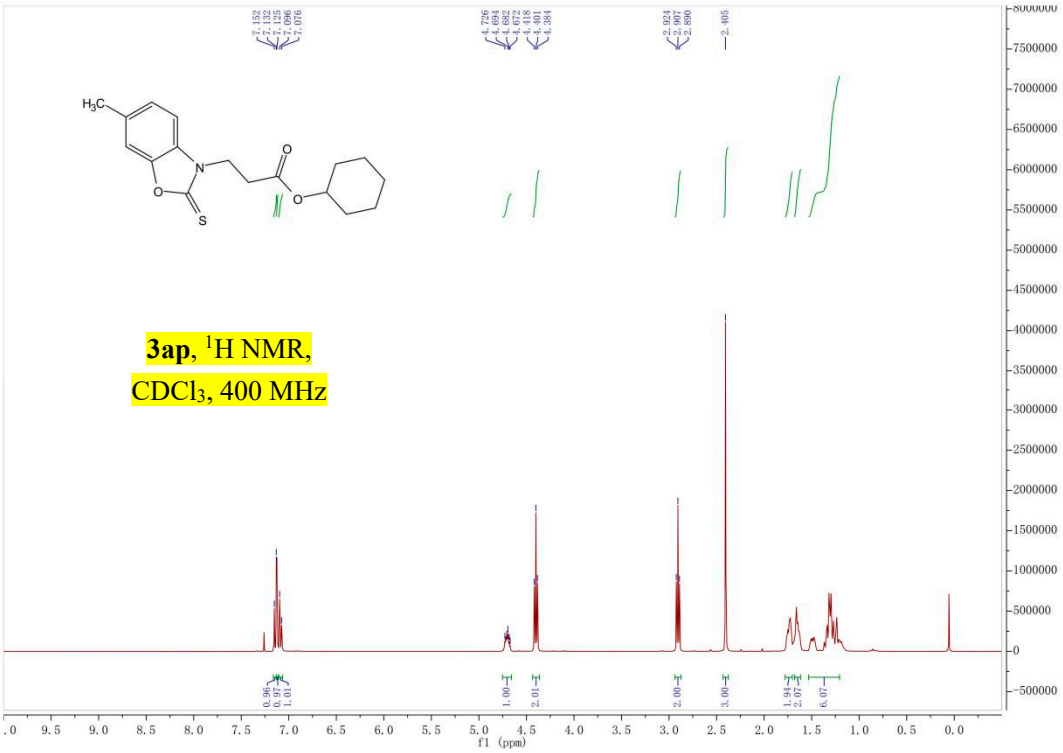



$^{1}$H NMR

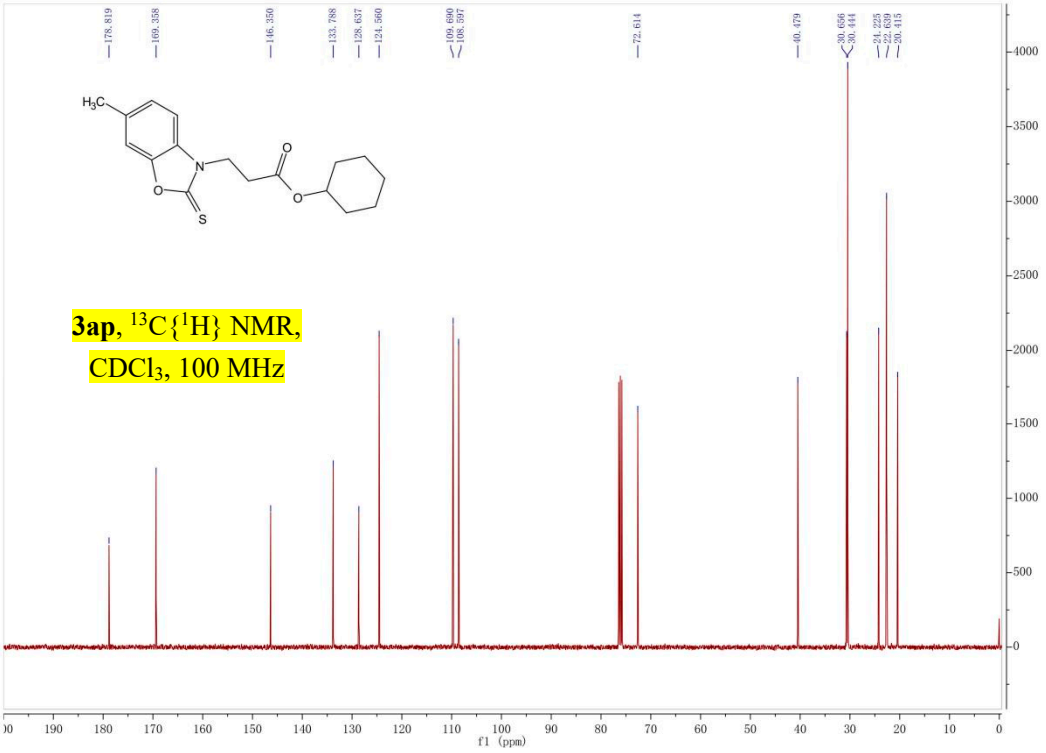



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-((6-methylbenzo[*d*]oxazol-2-yl)thio)propanoate (3ap)**

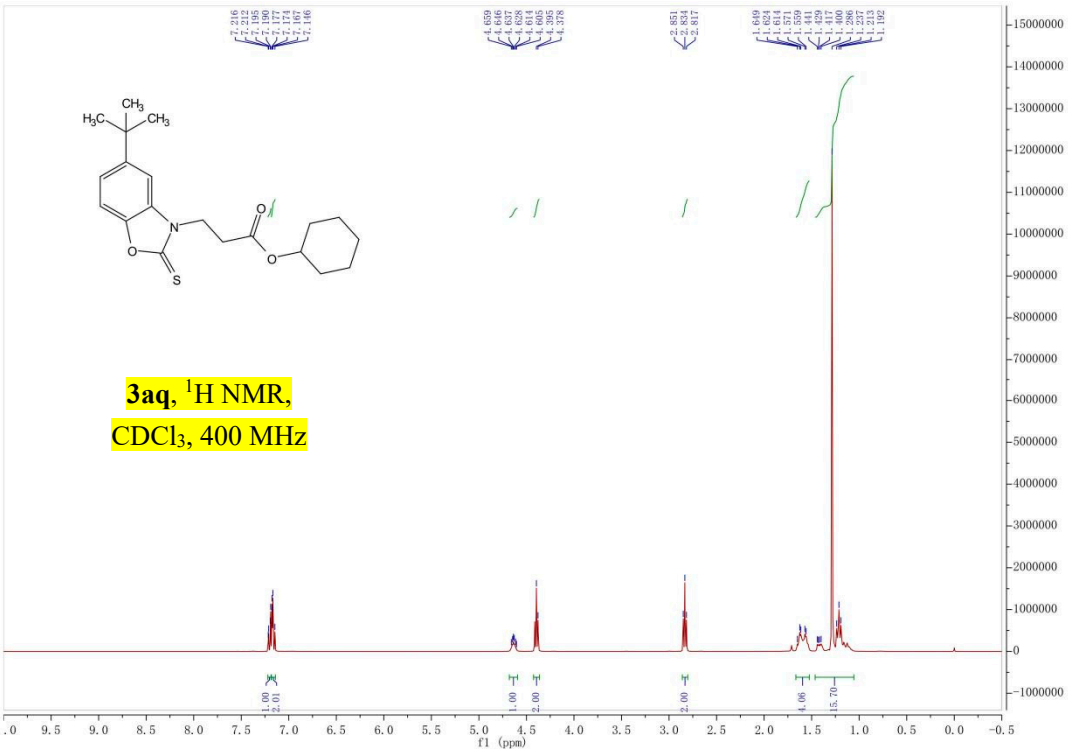



$^{1}$H NMR

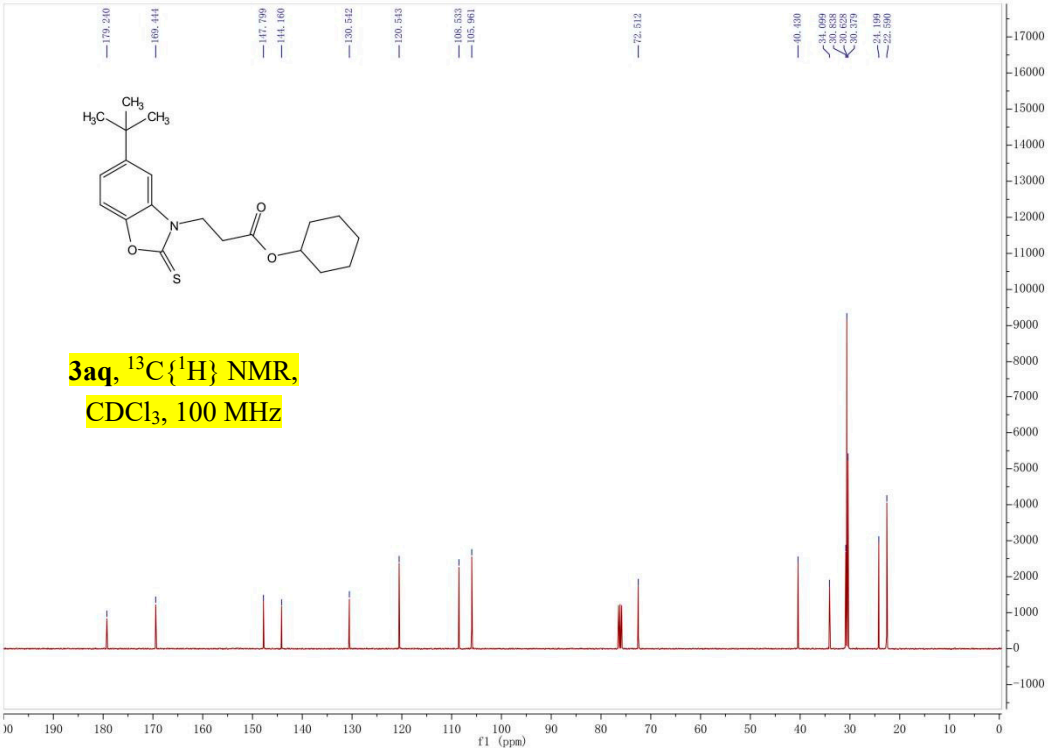



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(5-(*tert*-butyl)-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3aq)**

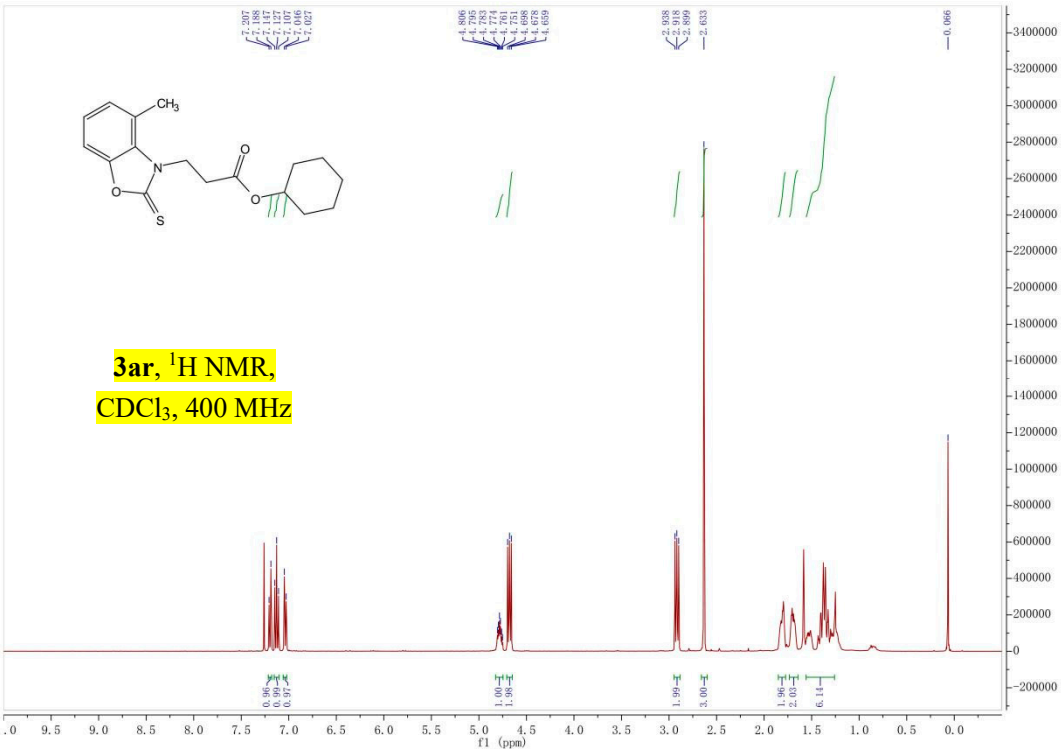



$^{1}$H NMR

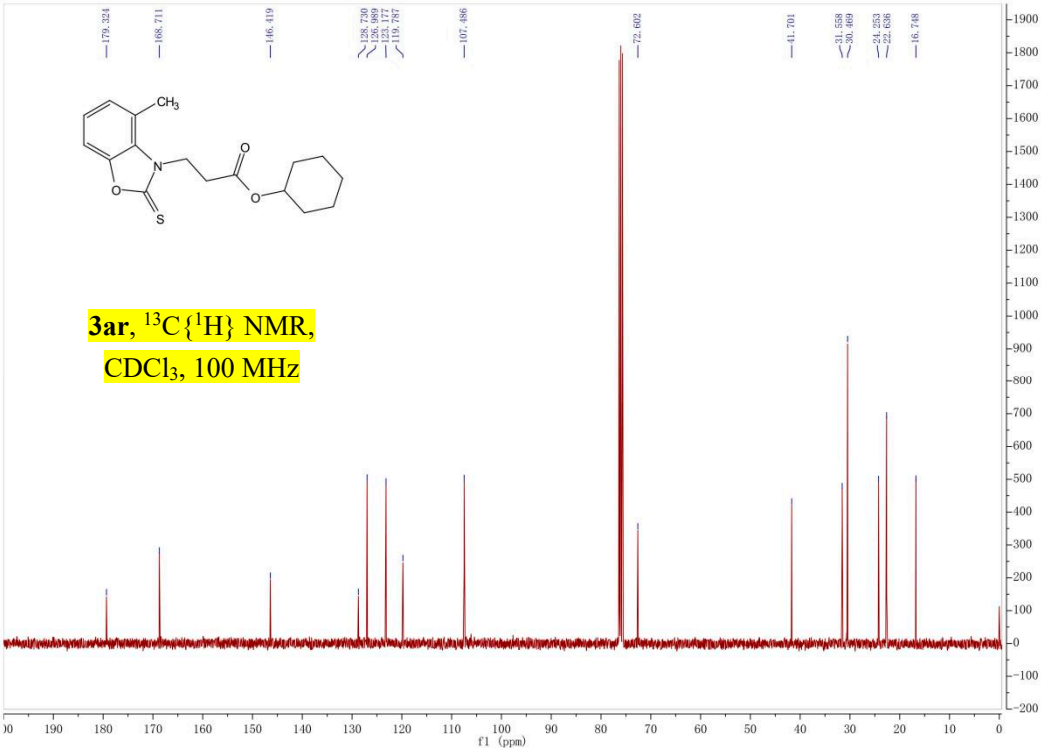



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(4-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3ar)**

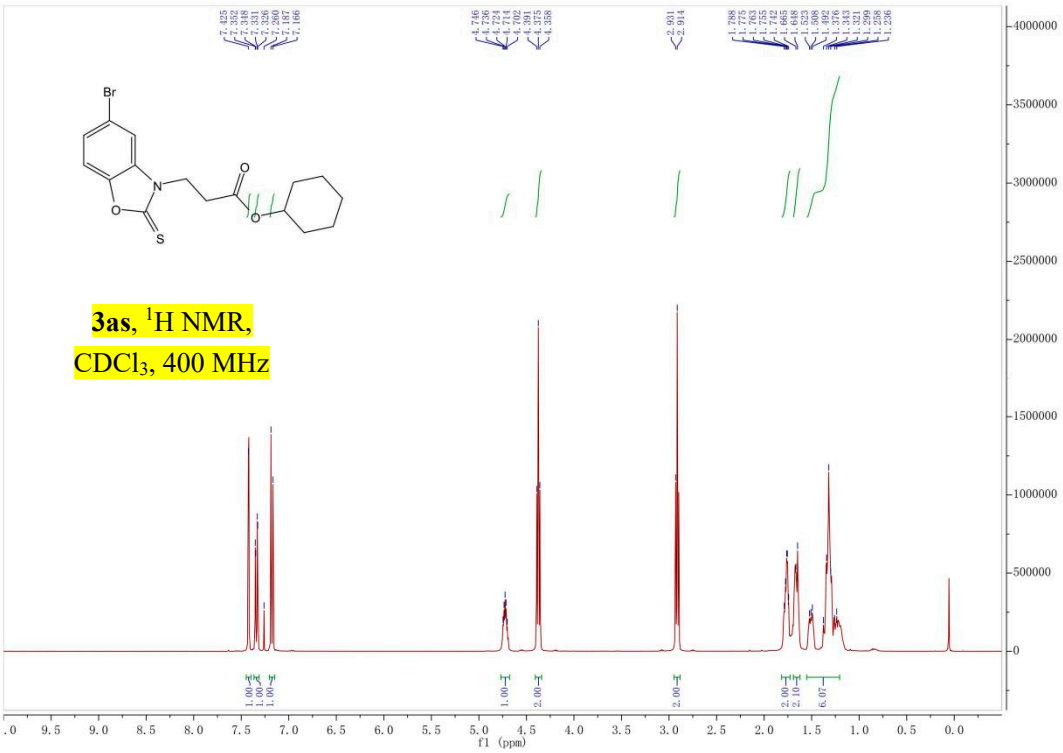



$^{1}$H NMR

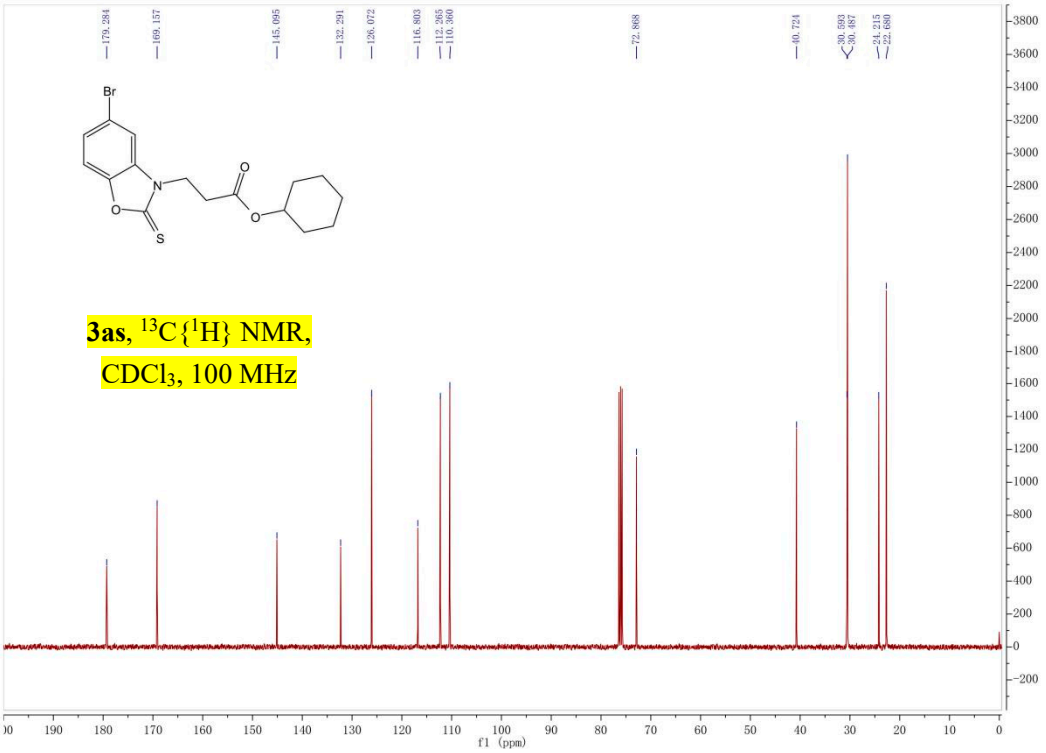



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(5-bromo-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3as)**

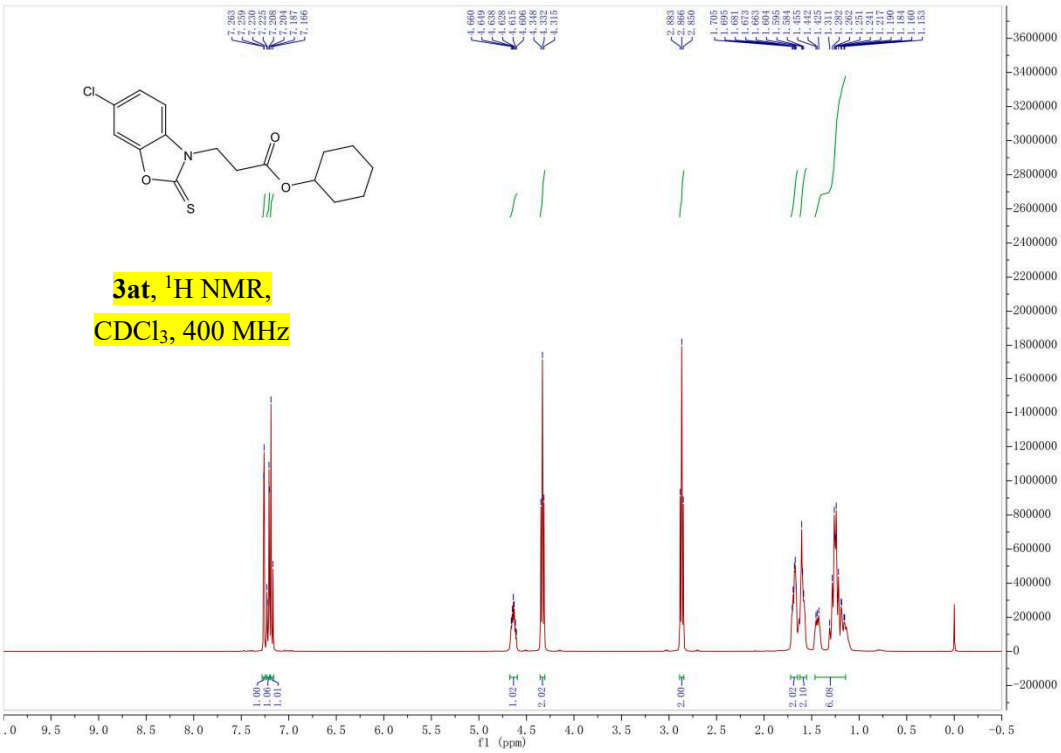



$^{1}$H NMR

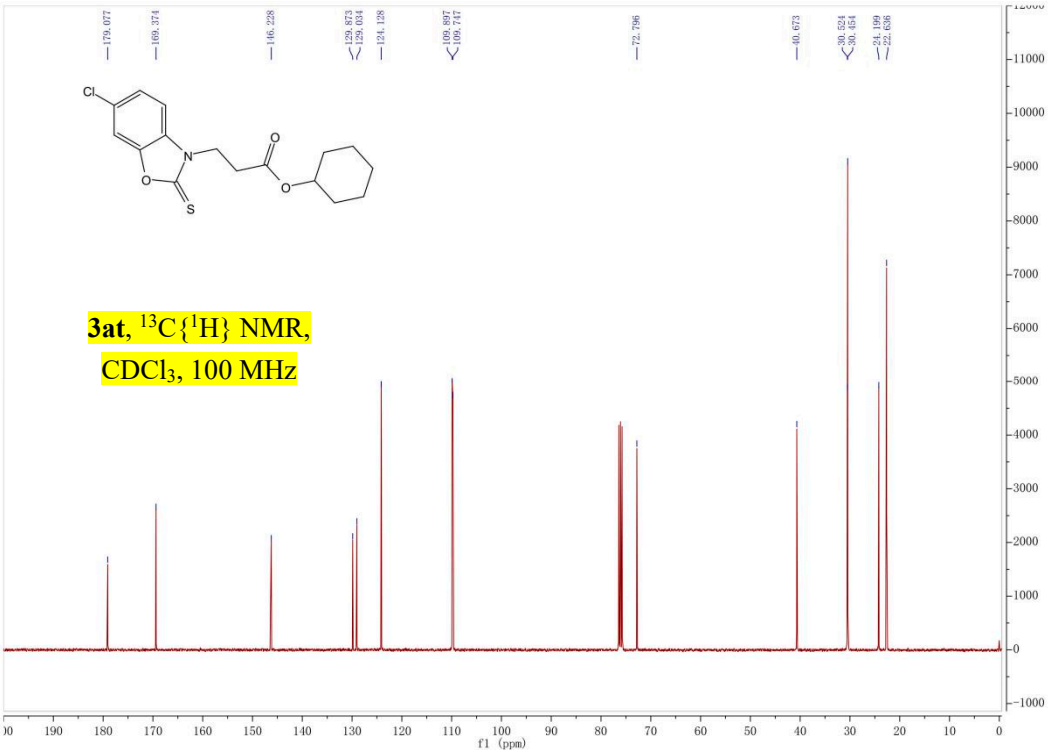



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(6-chloro-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3at)**

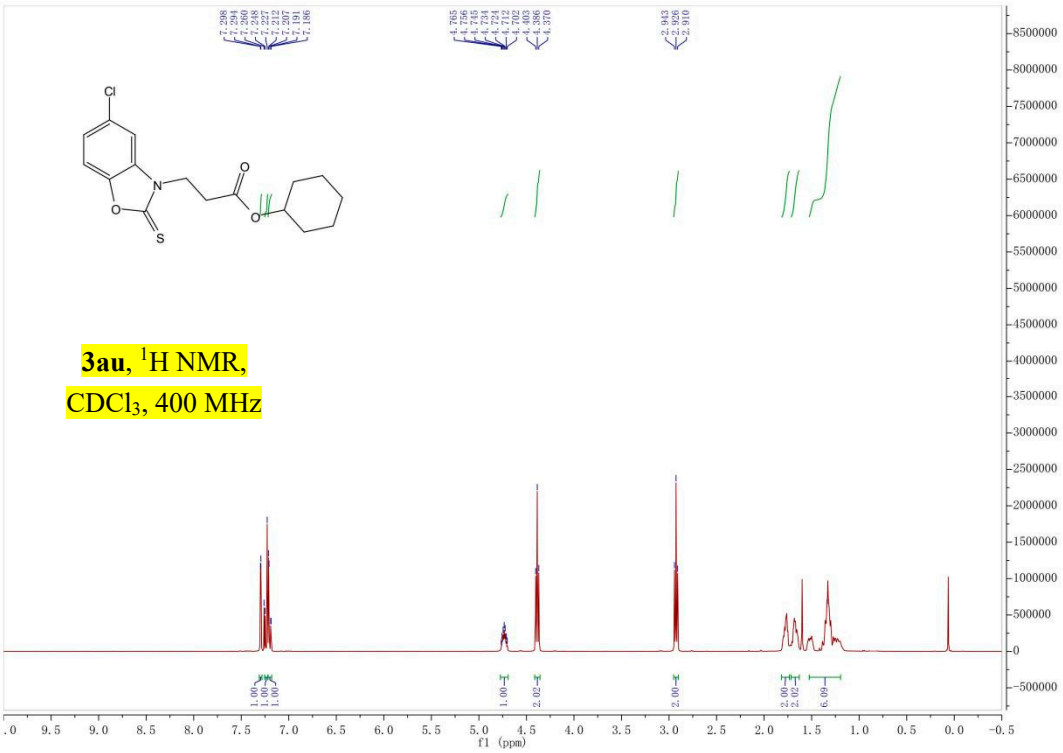



$^{1}$H NMR

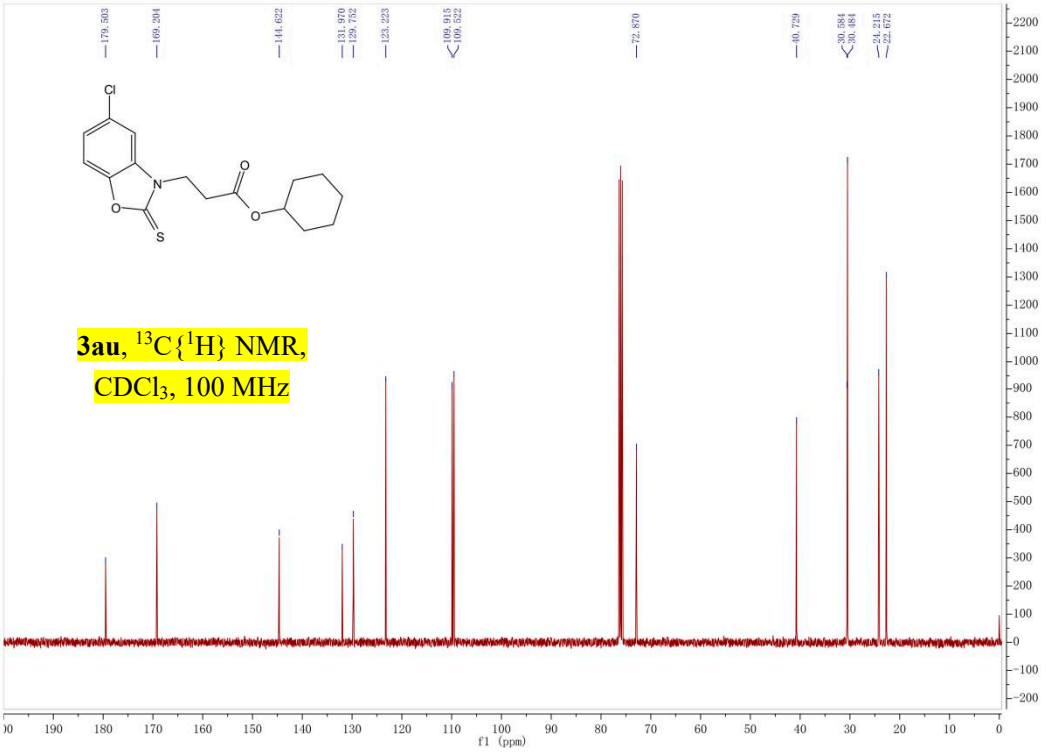



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(5-chloro-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3au)**

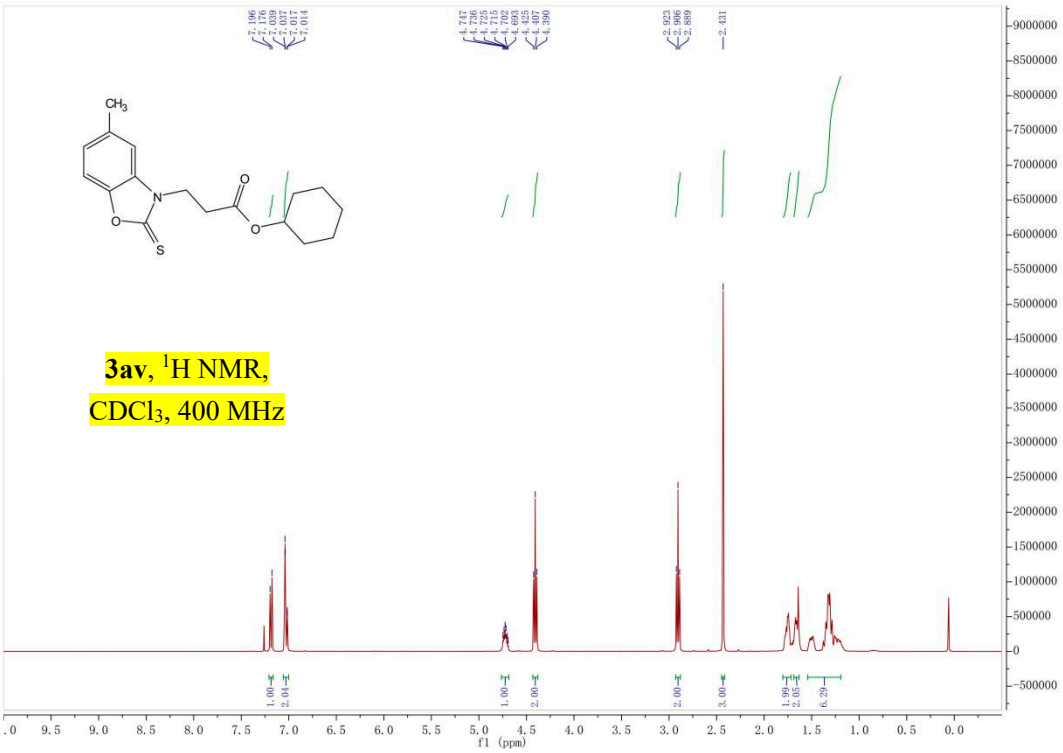



$^{1}$H NMR

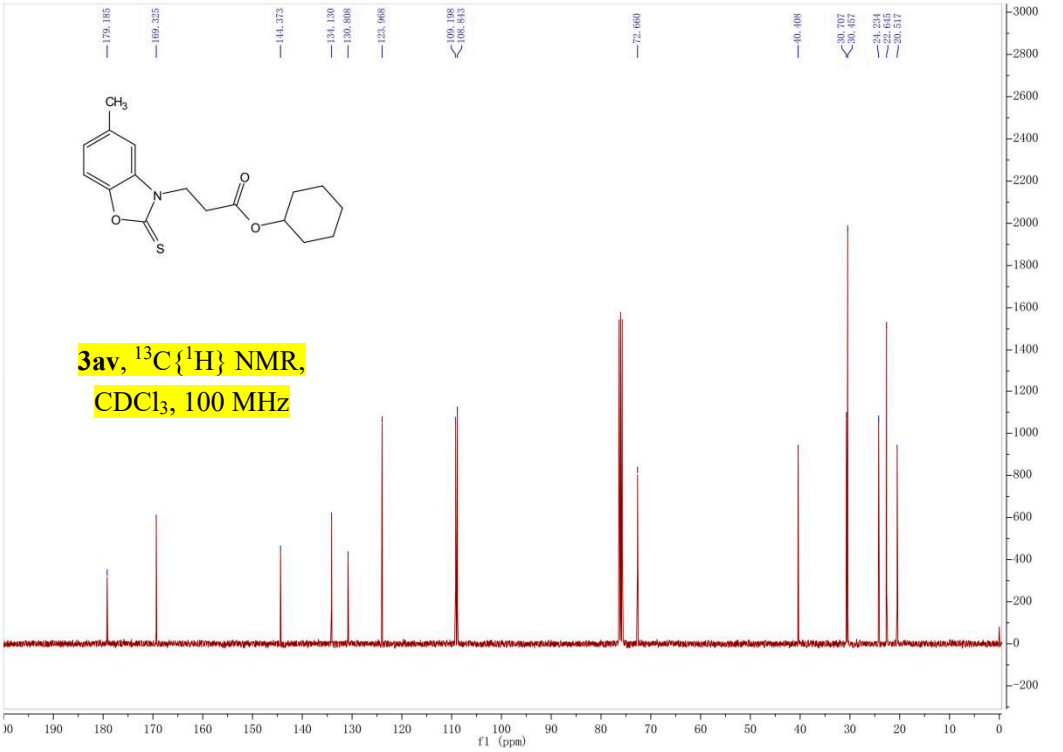



$^{13}C\{^{1}H\}$ NMR

**cyclohexyl 3-(5-methyl-2-thioxobenzo[*d*]oxazol-3(2*H*)-yl)propanoate (3av)**

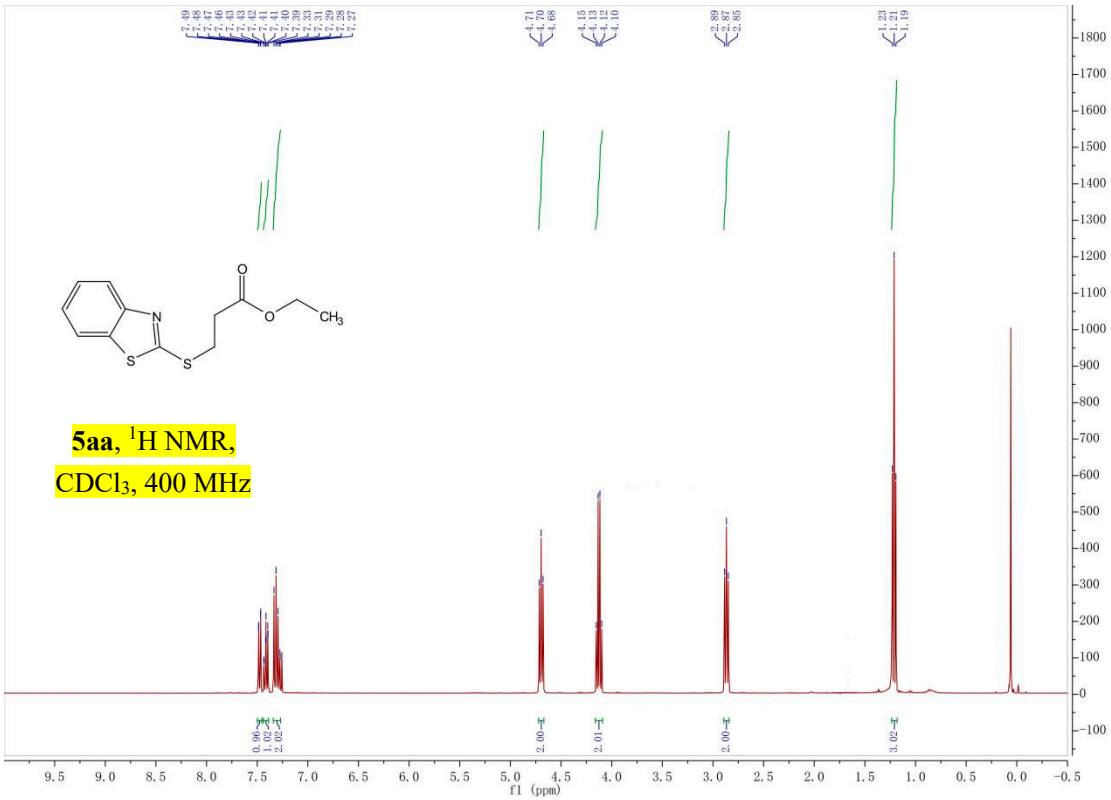



$^{1}$H NMR

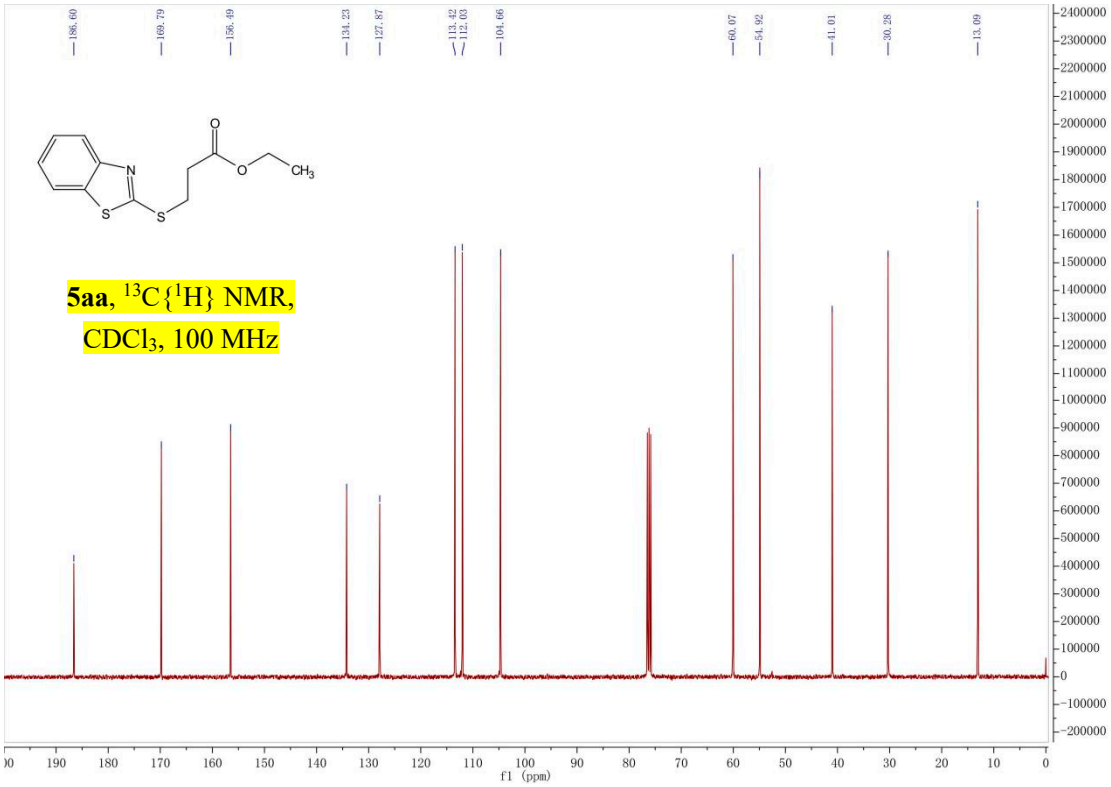



$^{13}$C{$^{1}$H} NMR

**ethyl 3-(benzo[*d*]thiazol-2-ylthio)propanoate (5aa)**



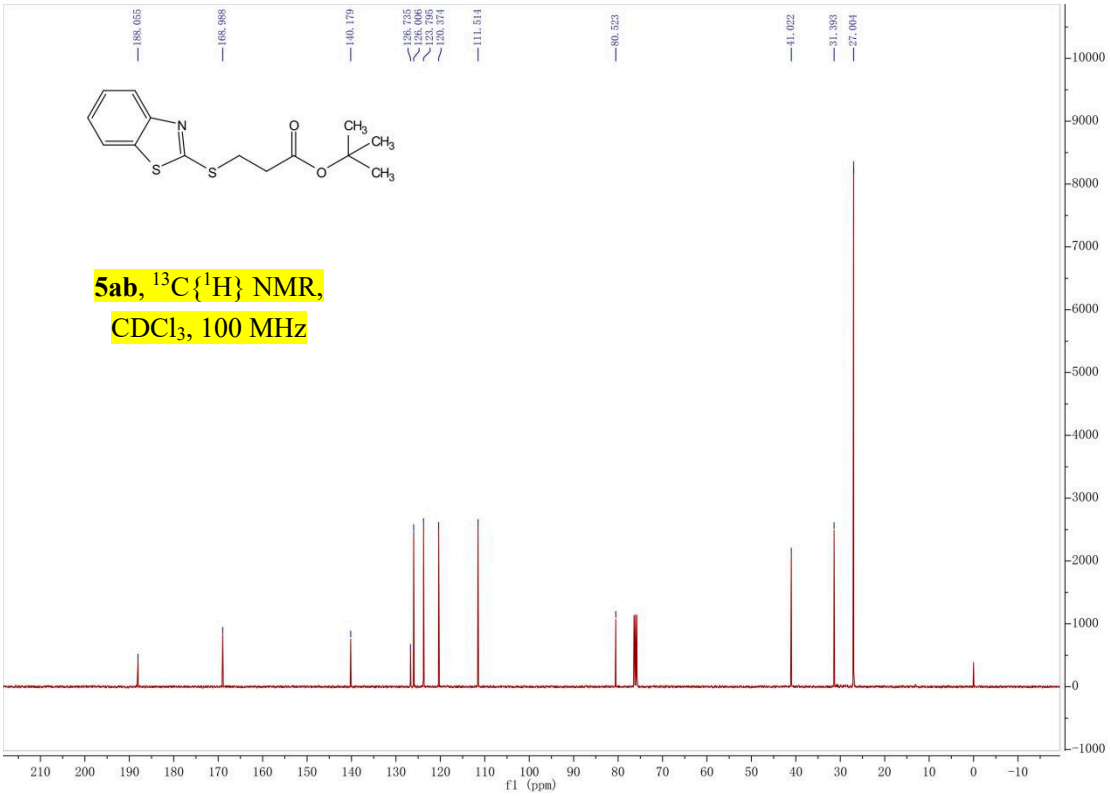

$^{1}$H NMR




$^{13}$C{$^{1}$H} NMR

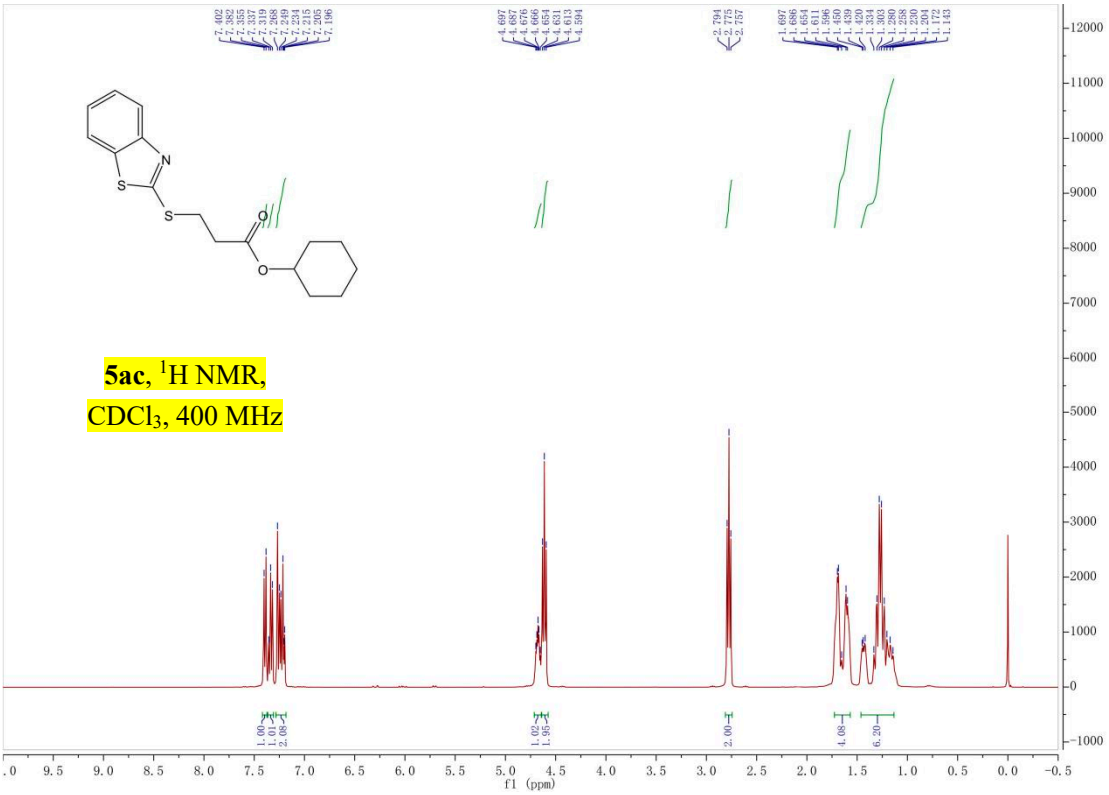
## *tert*-butyl 3-(benzo[*d*]thiazol-2-ylthio)propanoate (5ab)


$^{1}$H NMR

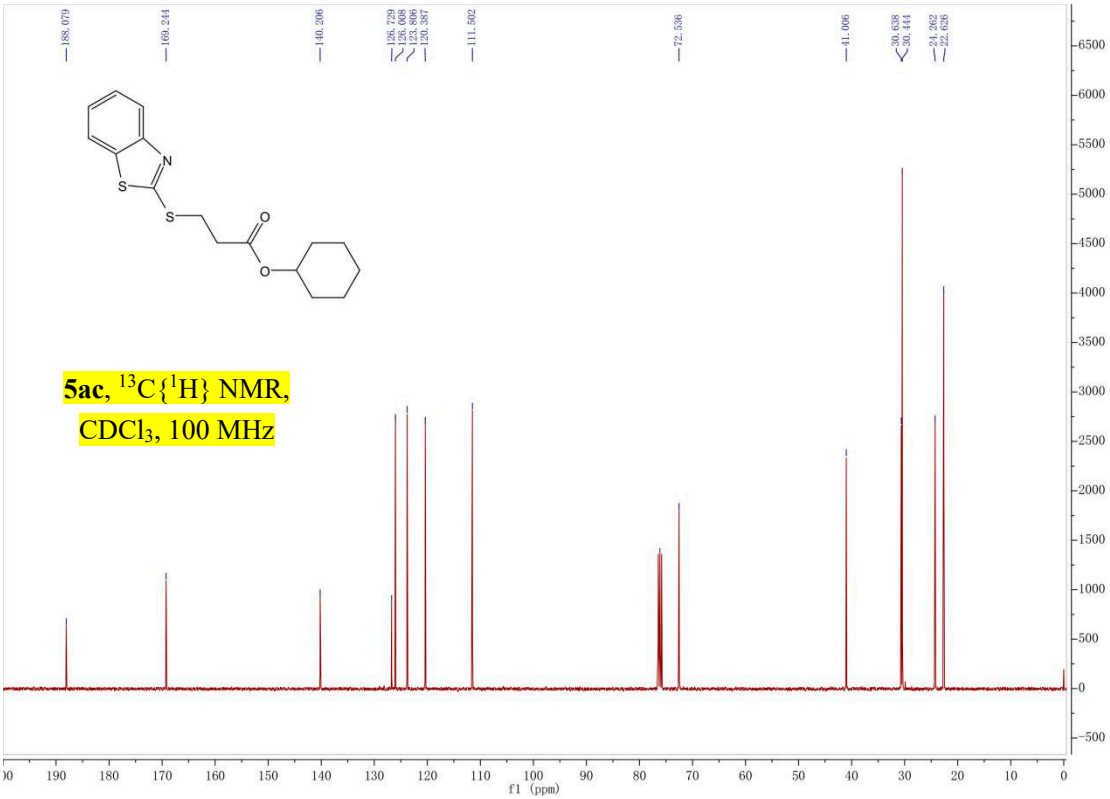



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-(benzo[*d*]thiazol-2-ylthio)propanoate (5ac)**

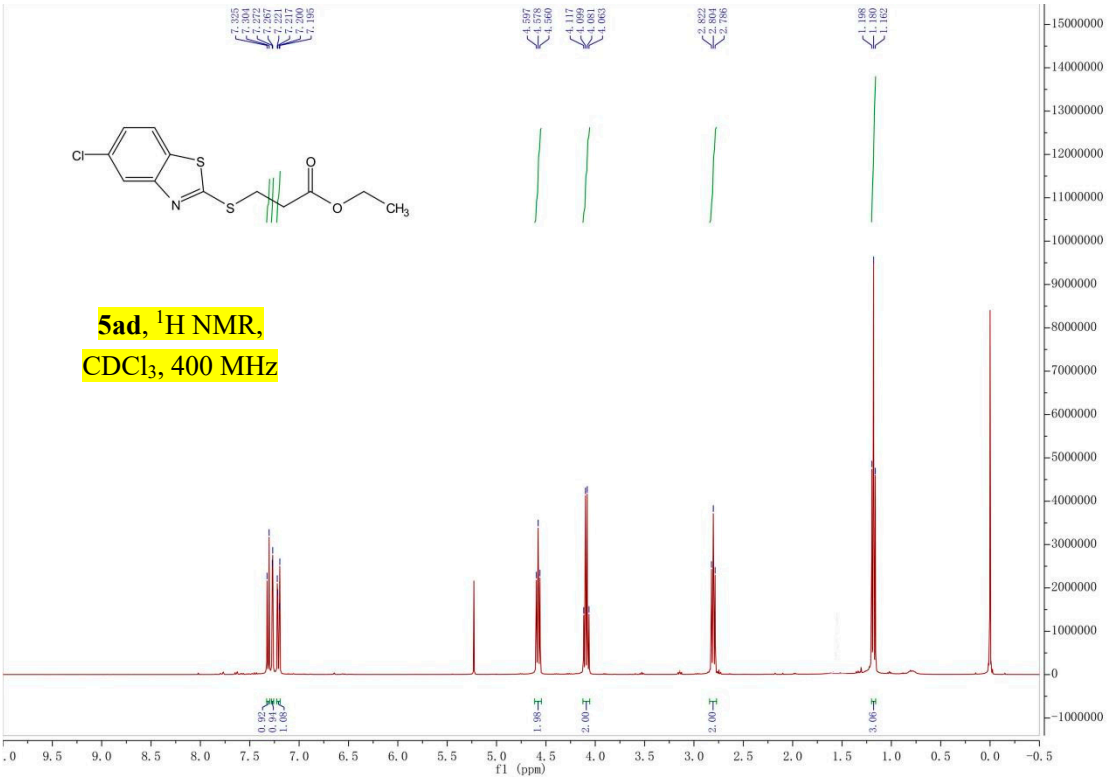



$^{1}$H NMR

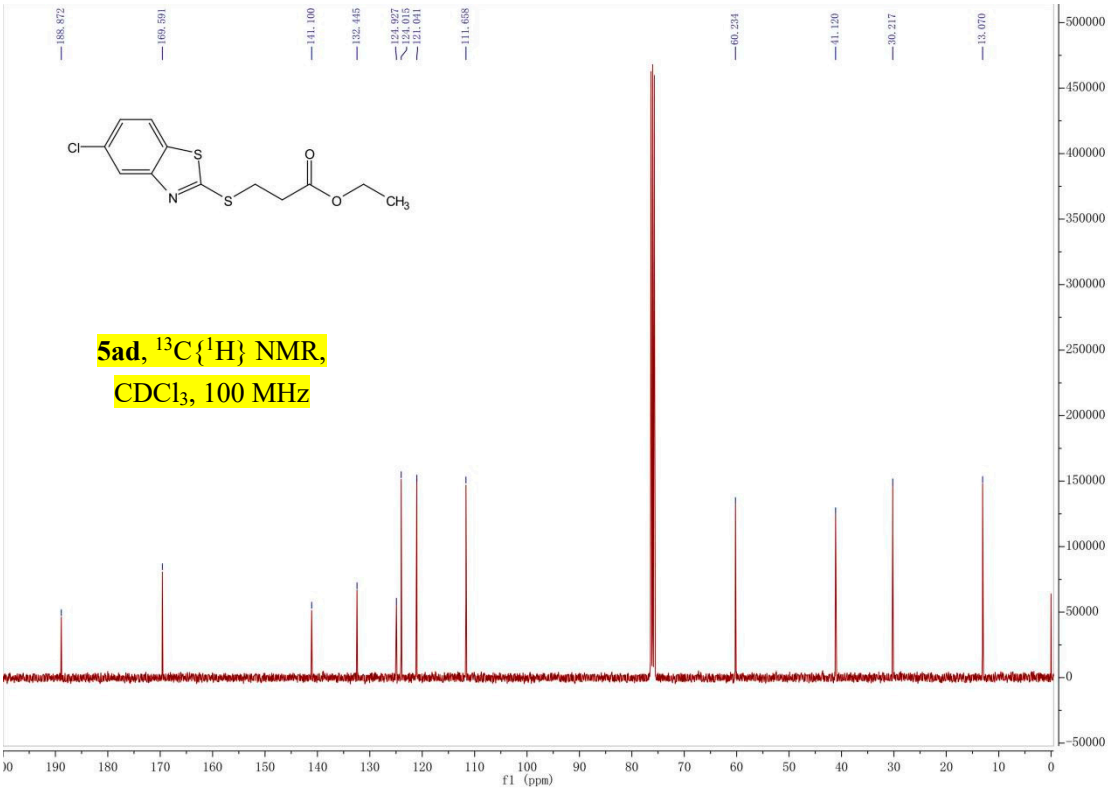



$^{13}$C{$^{1}$H} NMR

**ethyl 3-((5-chlorobenzo[*d*]thiazol-2-yl)thio)propanoate (5ad)**

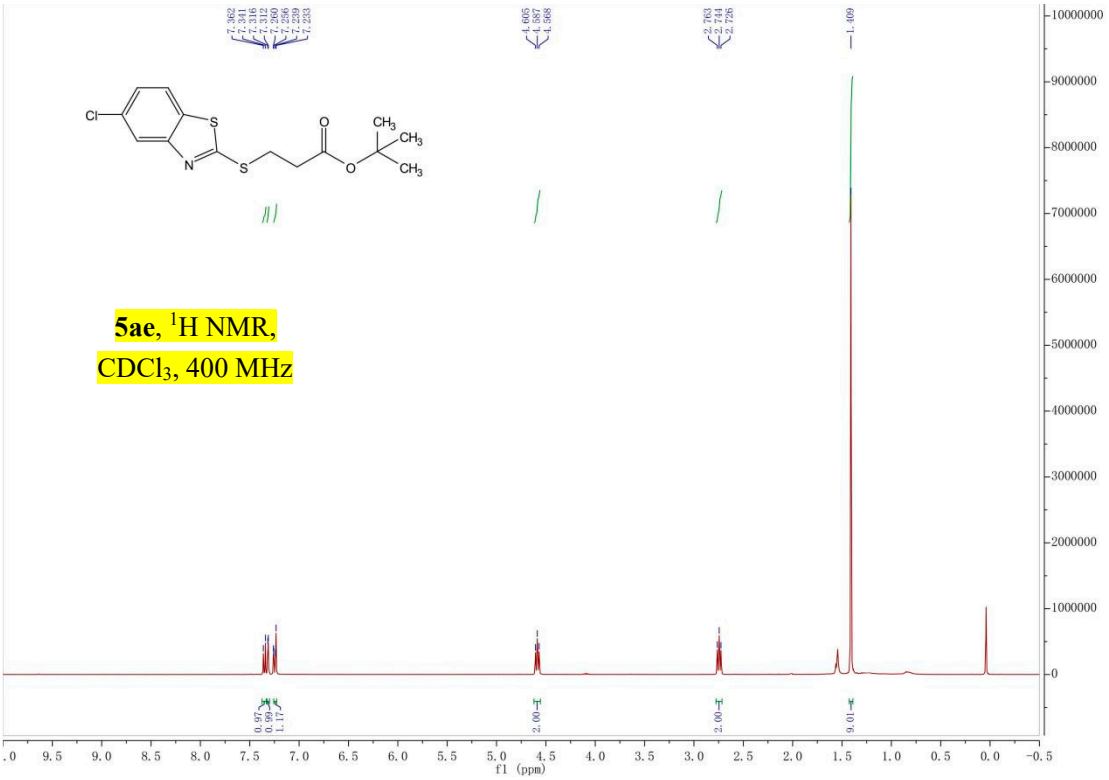



$^{1}$H NMR

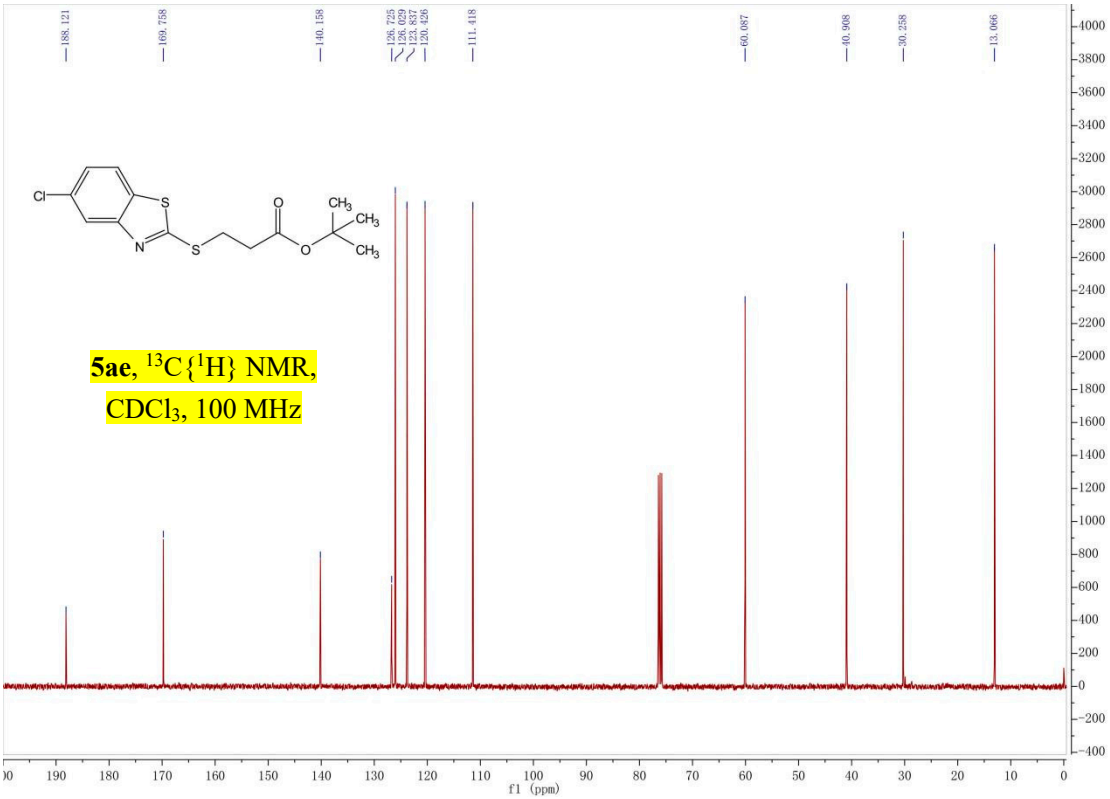



$^{13}$C{$^{1}$H} NMR

## *tert*-butyl 3-((5-chlorobenzo[*d*]thiazol-2-yl)thio)propanoate (5ae)

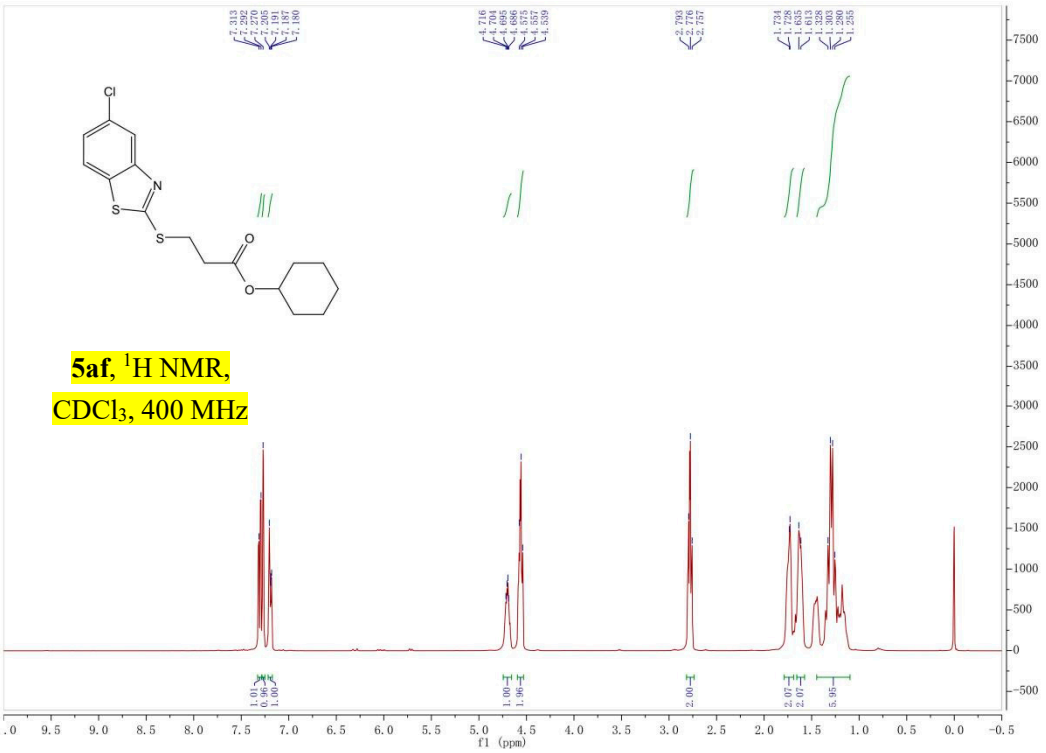



$^{1}$H NMR

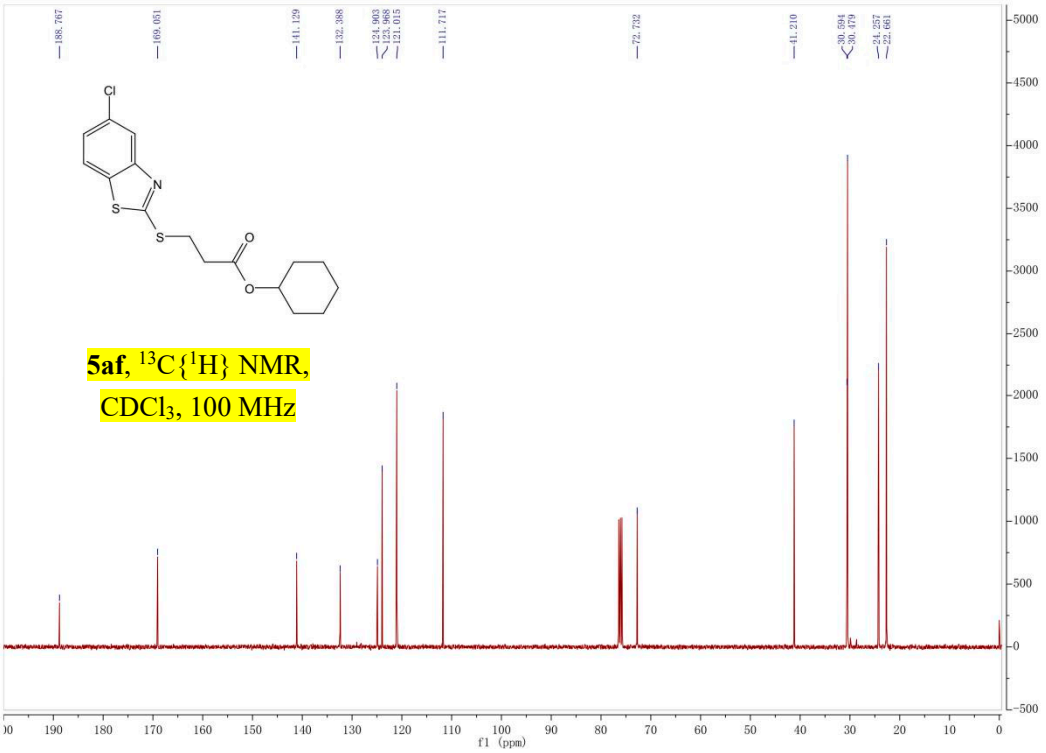



$^{13}$C{$^{1}$H} NMR

**cyclohexyl 3-((5-chlorobenzo[*d*]thiazol-2-yl)thio)propanoate (5af)**

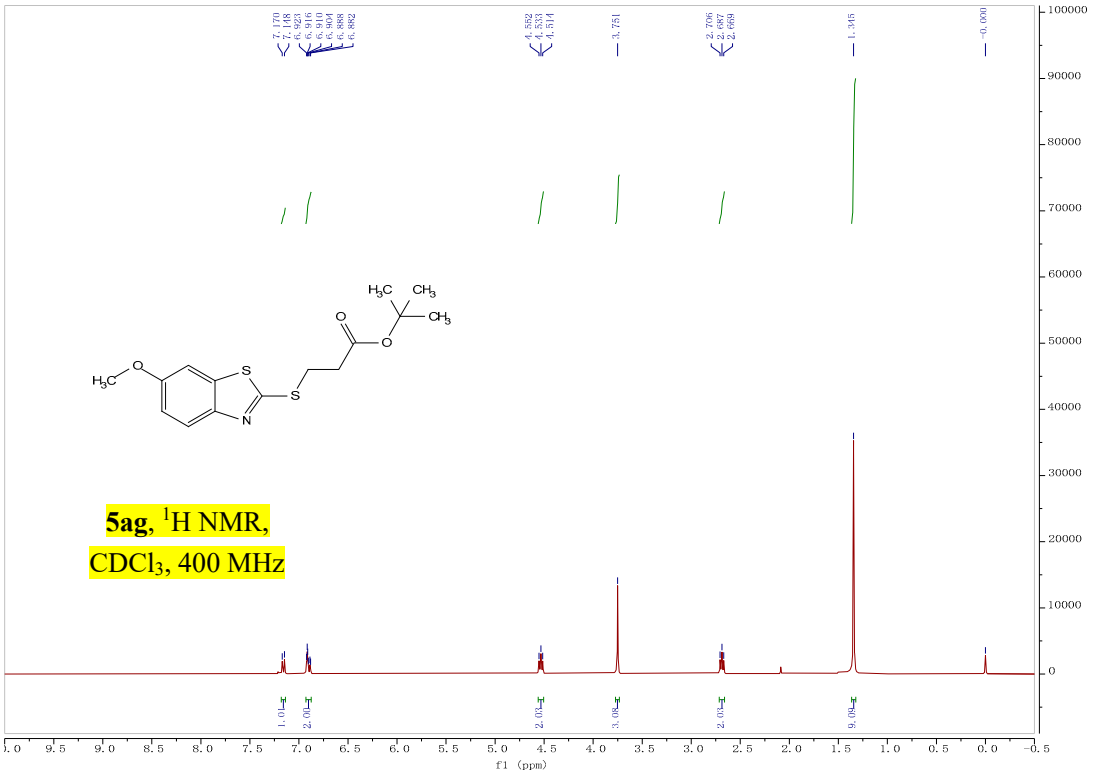



$^{1}$H NMR

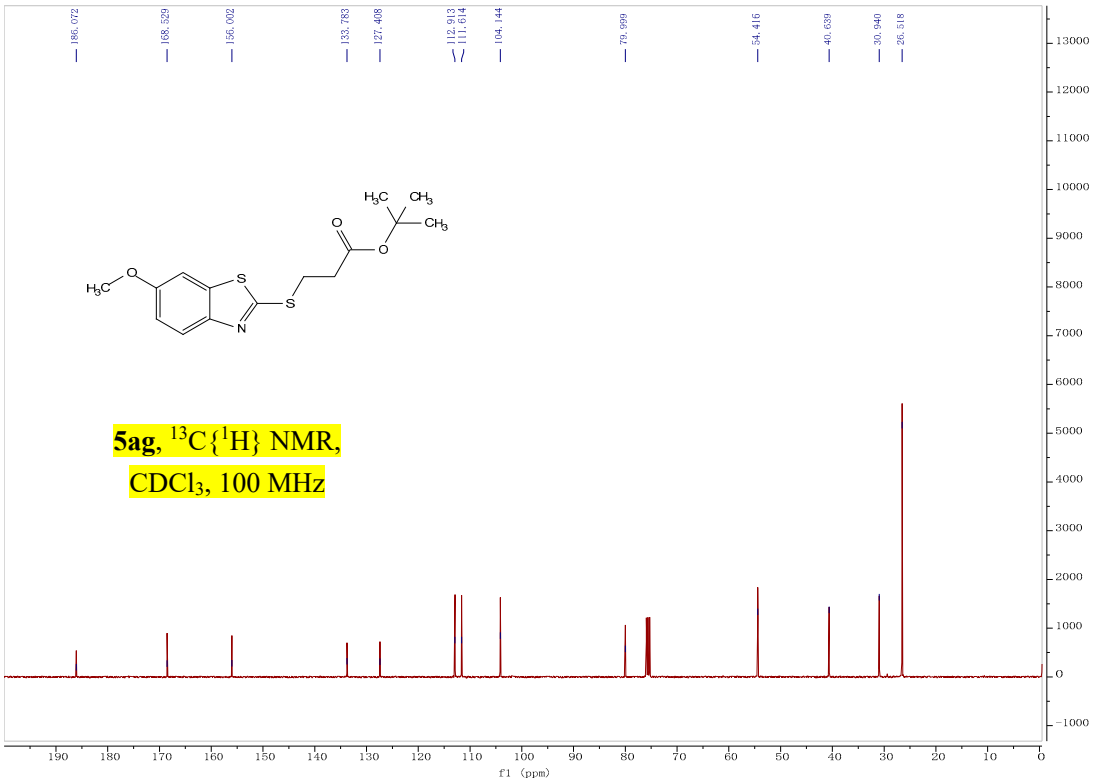



$^{13}$C{$^{1}$H} NMR

***tert*-butyl 3-((6-methoxybenzo[*d*]thiazol-2-yl)thio)propanoate (5ag)**




$^{1}$H NMR




$^{13}$C{$^{1}$H} NMR