Supporting Information

for

SILVER-MEDIATED 2-ARYLATION/ALKYLATION/ACYLATION OF BENZOTHIAZOLES WITH ALDEHYDES IN WATER

Min Hua, Chunqin Wang, Qixing Liu,* Danyi Chen, Hao Fu, and Haifeng Zhou*

Address

Research Center of Green Pharmaceutical Technology and Process, Hubei Key Laboratory of Natural Products Research and Development, College of Biological and Pharmaceutical Sciences, China Three Gorges University, Yichang 443002, China

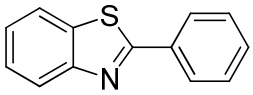
E-mail:

qixingliu86@163.com (Qixing Liu); zhouhf@ctgu.edu.cn (Haifeng Zhou)

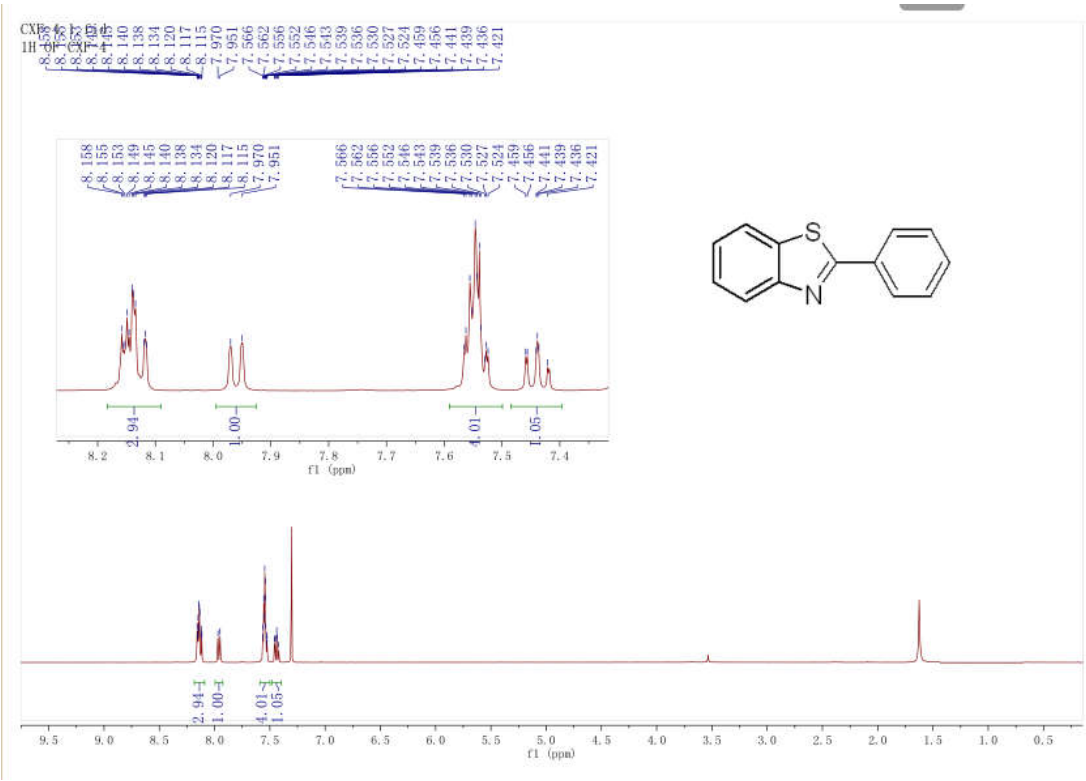
*Corresponding author

Table of contents

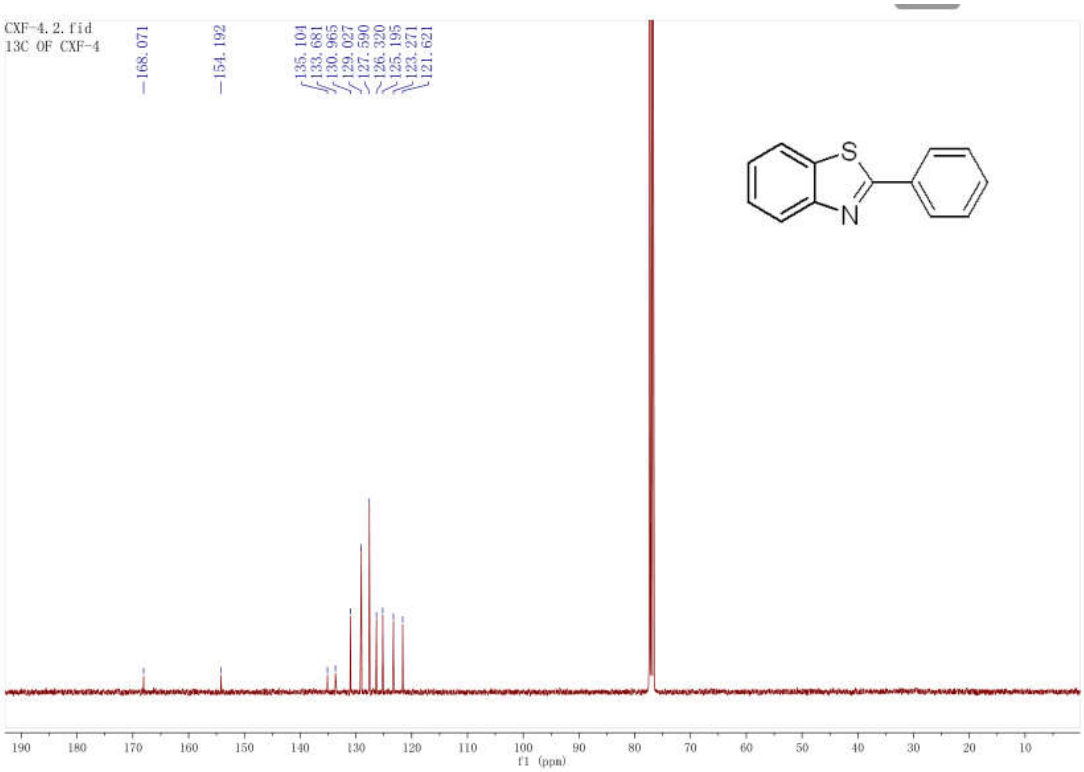
1. NMR Spectra of the Products

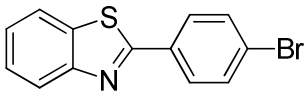


^{1}H NMR of 3a

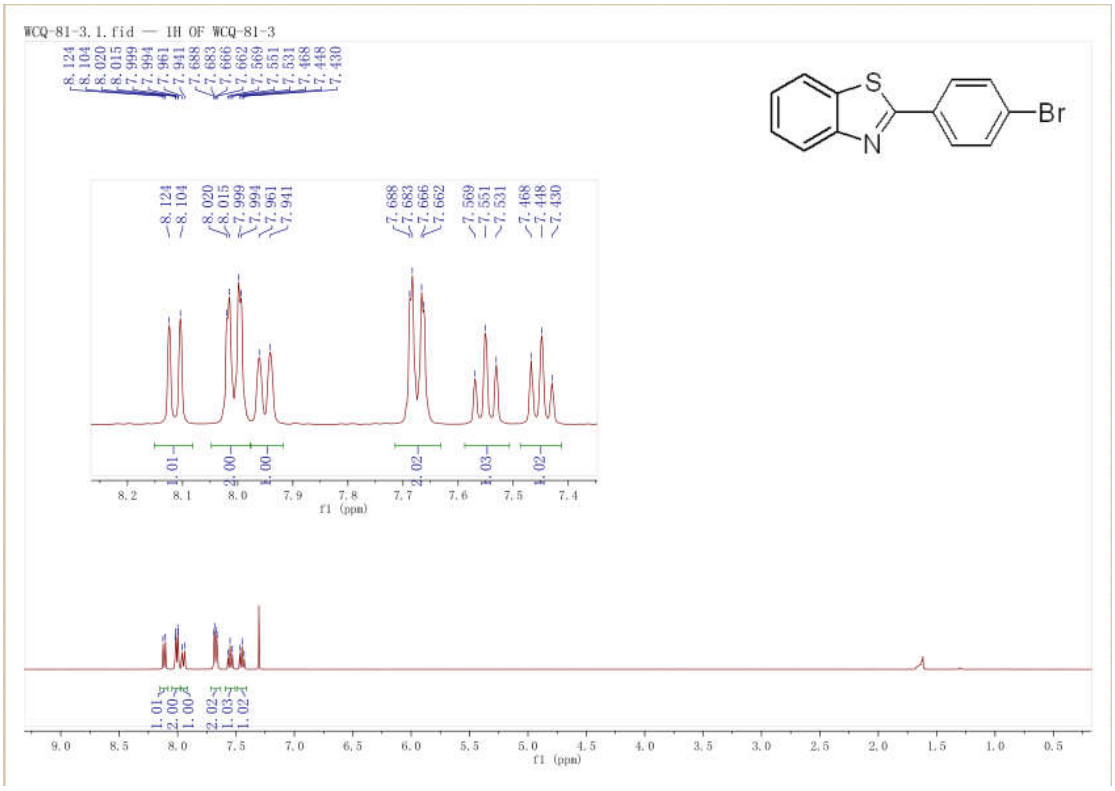


^{13}C NMR of 3a

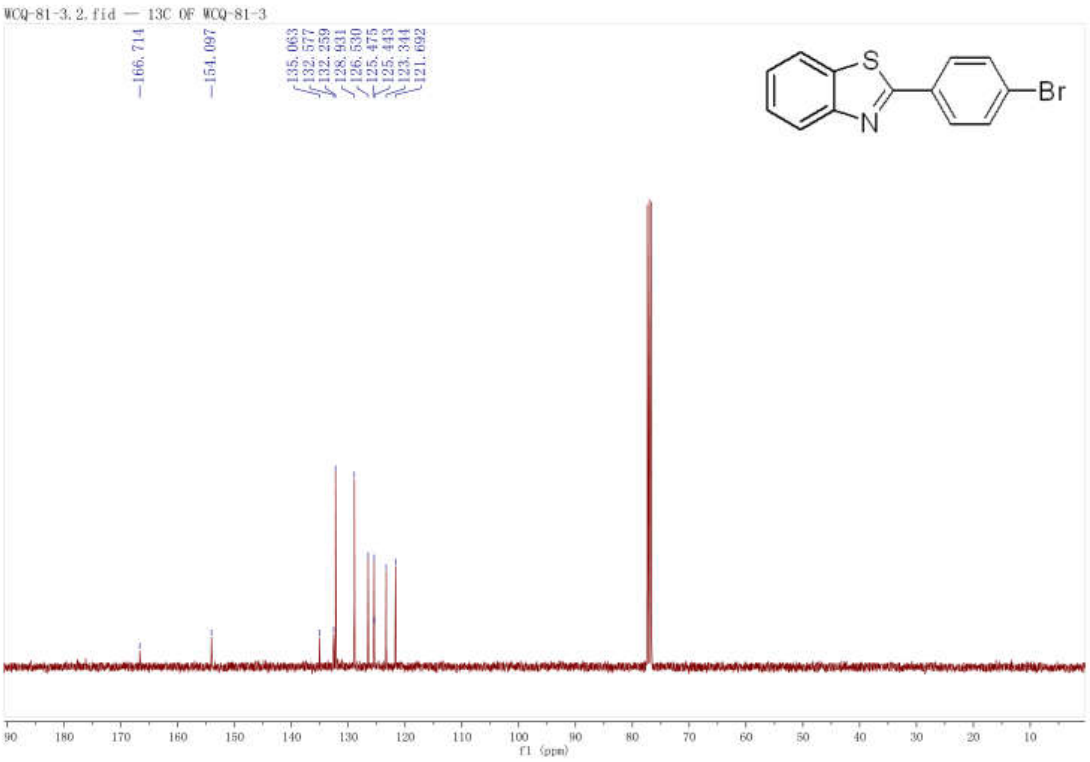


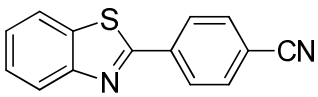


^{1}H NMR of 3b

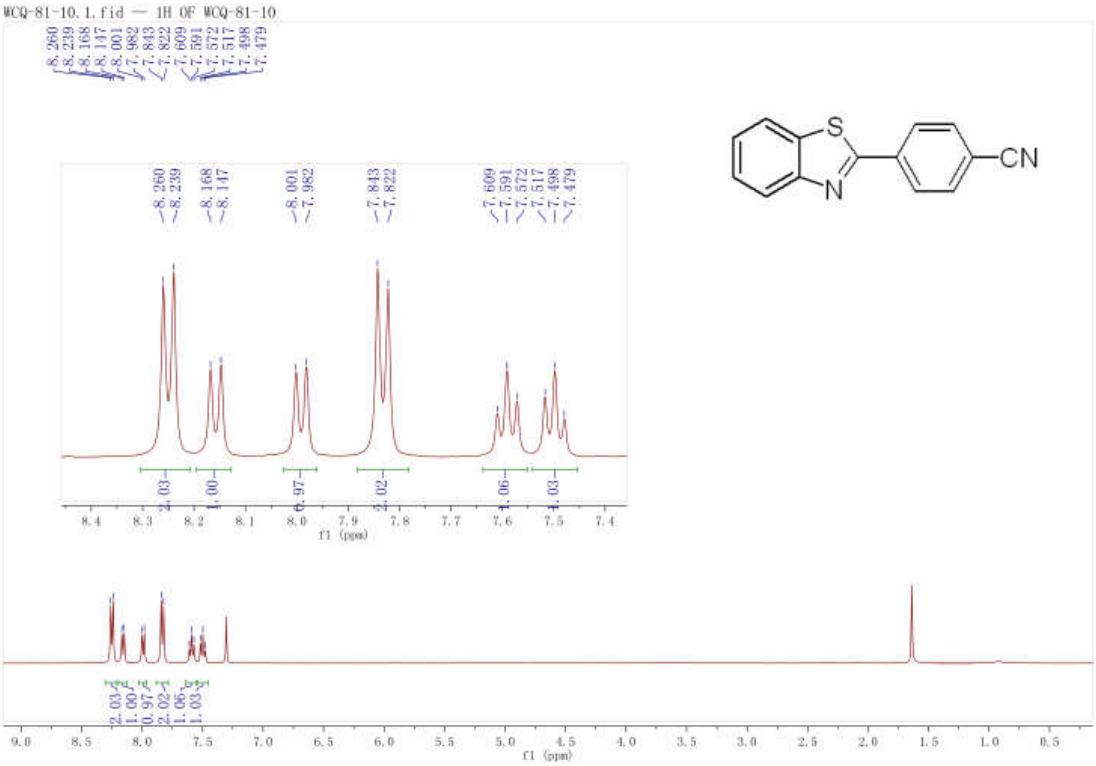


^{13}C NMR of 3b

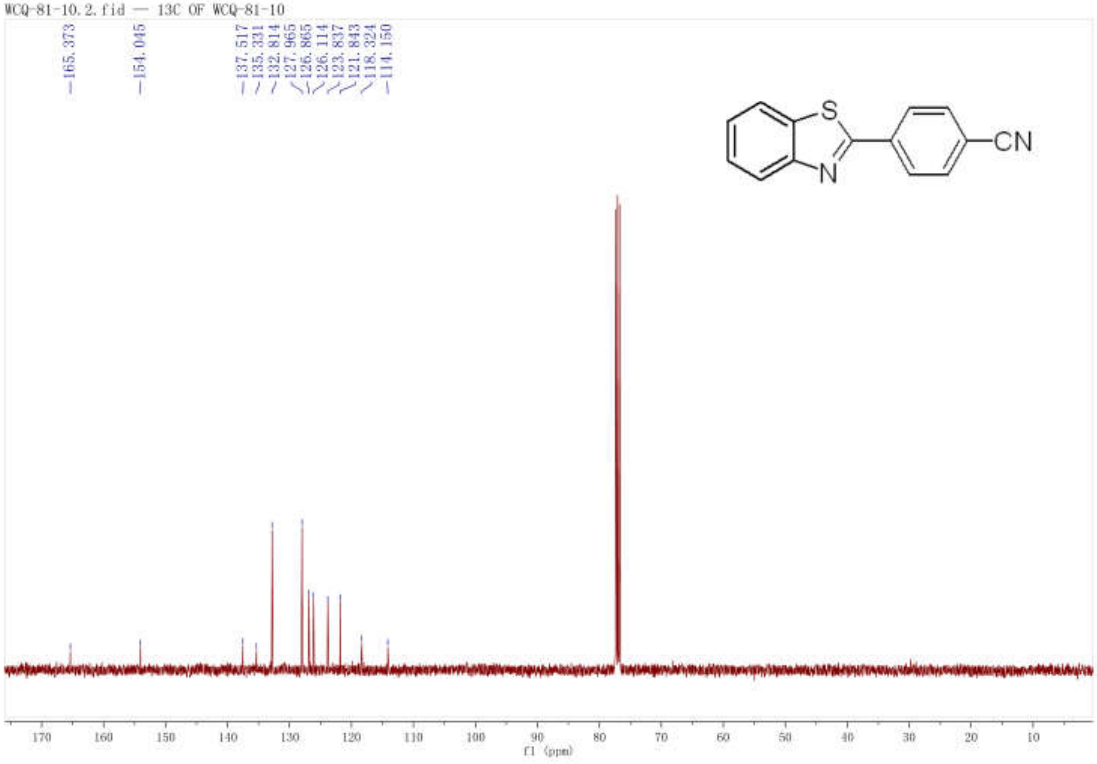


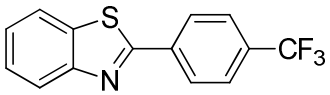


^{1}H NMR of 3c

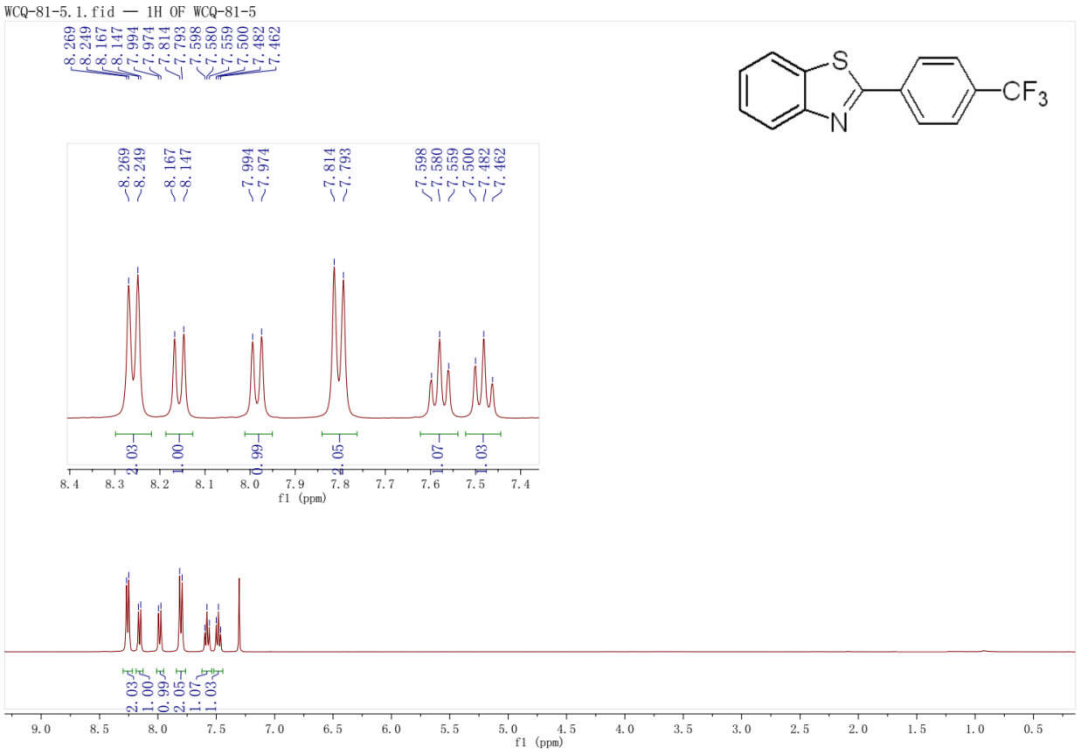


^{13}C NMR of 3c

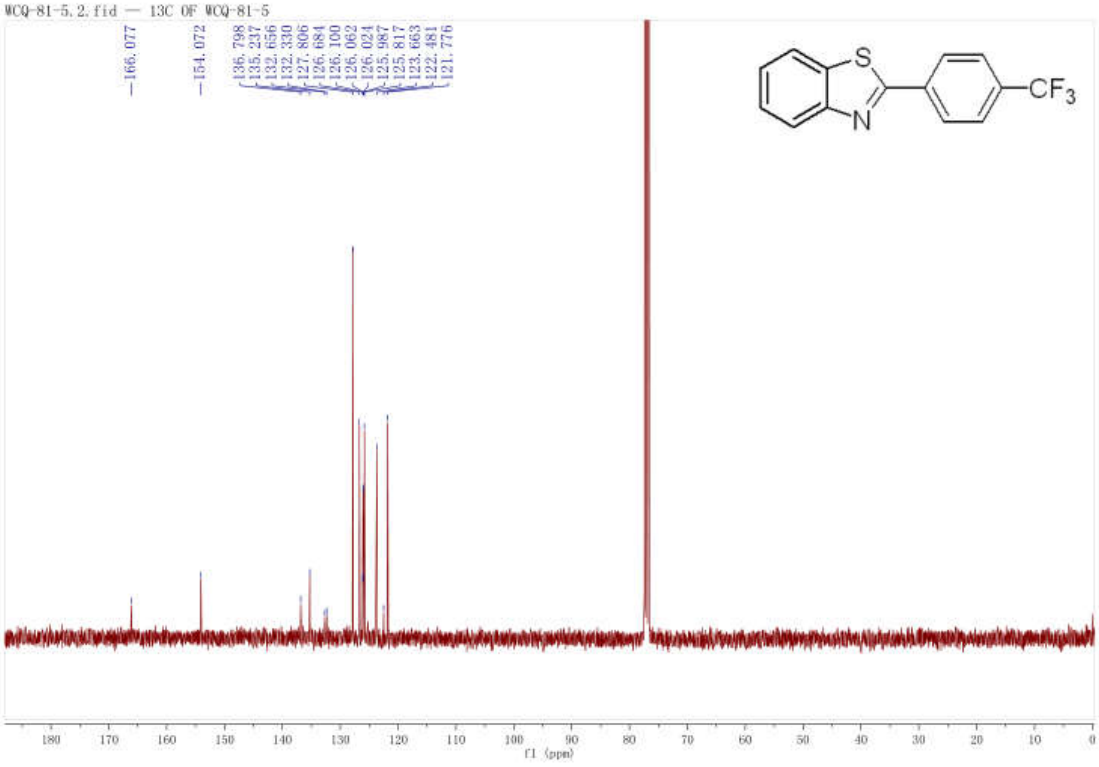


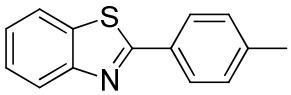


^{1}H NMR of 3d

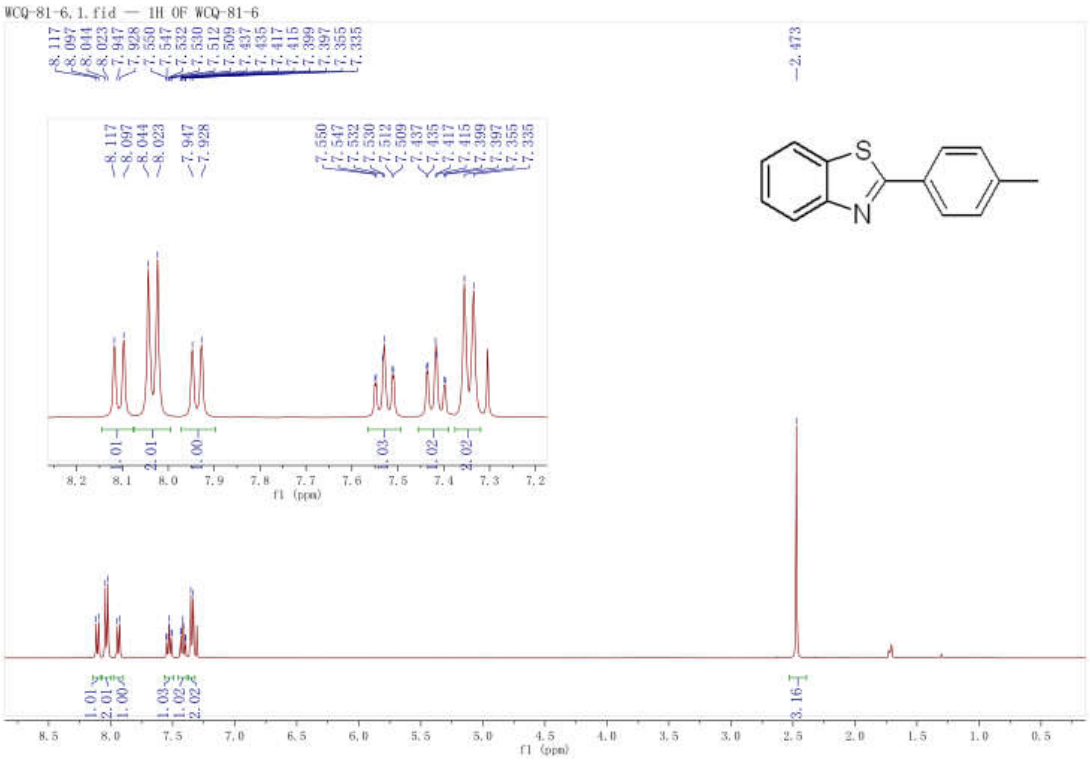


^{13}C NMR of 3d

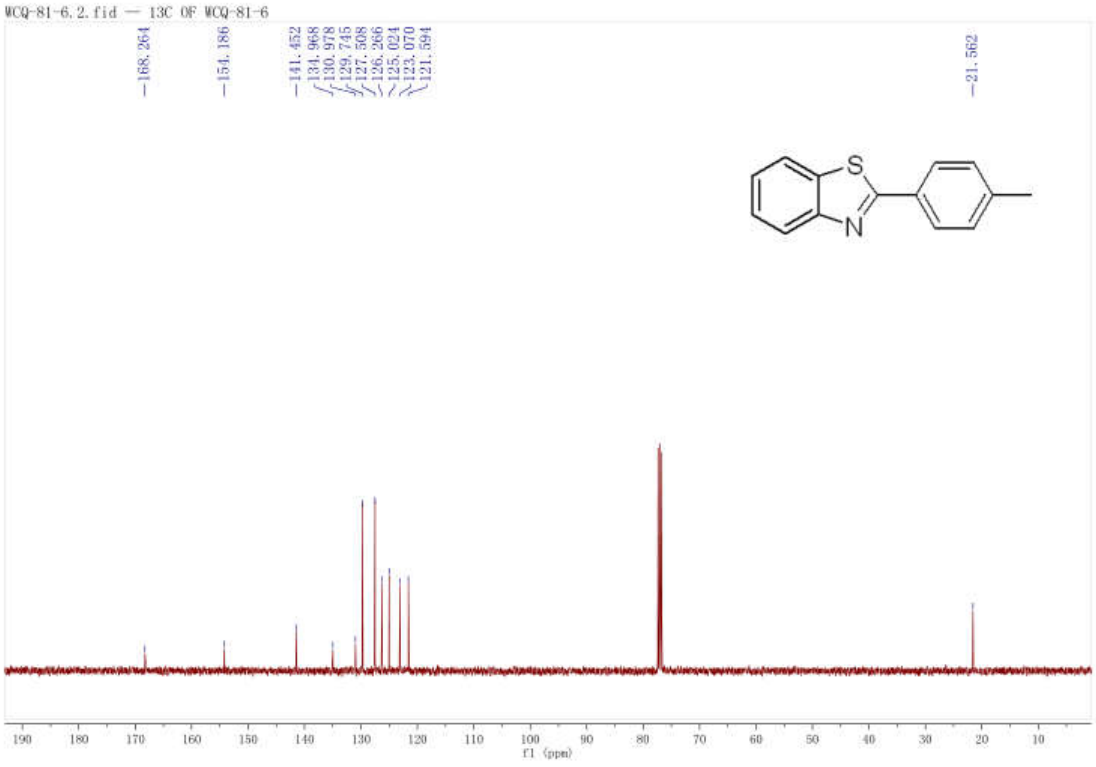


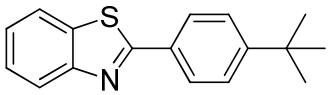


^{1}H NMR of 3e

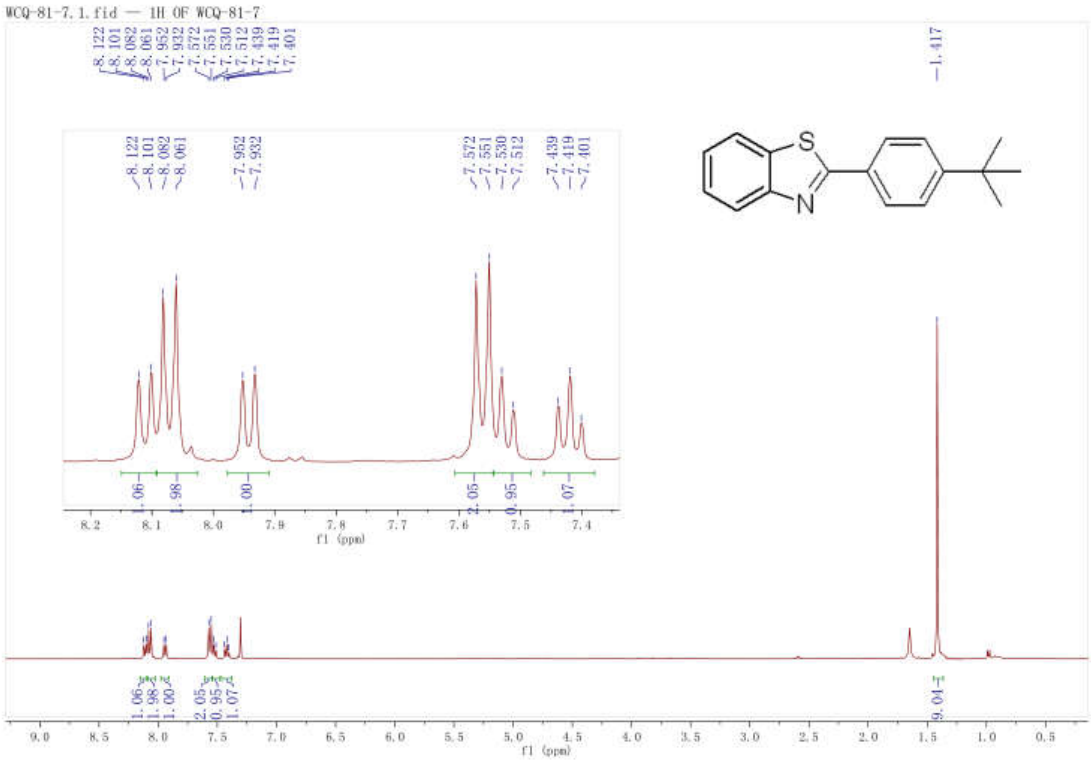


^{13}C NMR of 3e

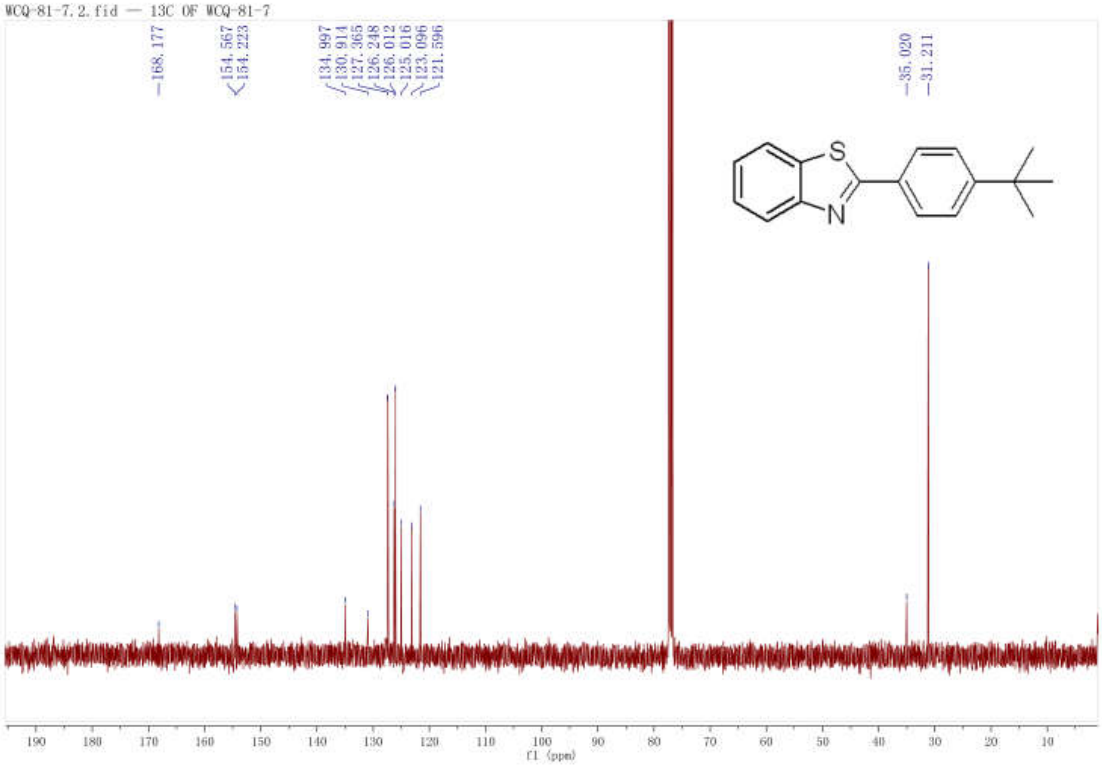


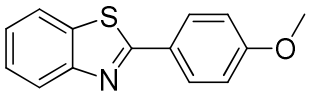


^{1}H NMR of 3f

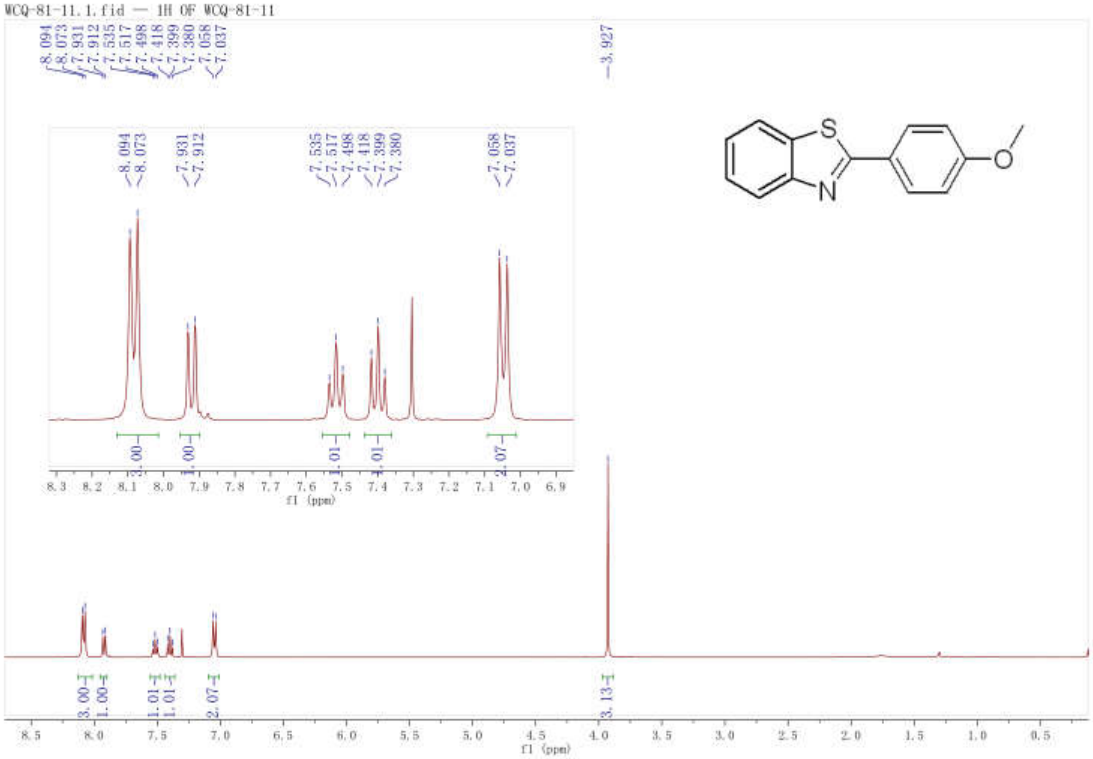


^{13}C NMR of 3f

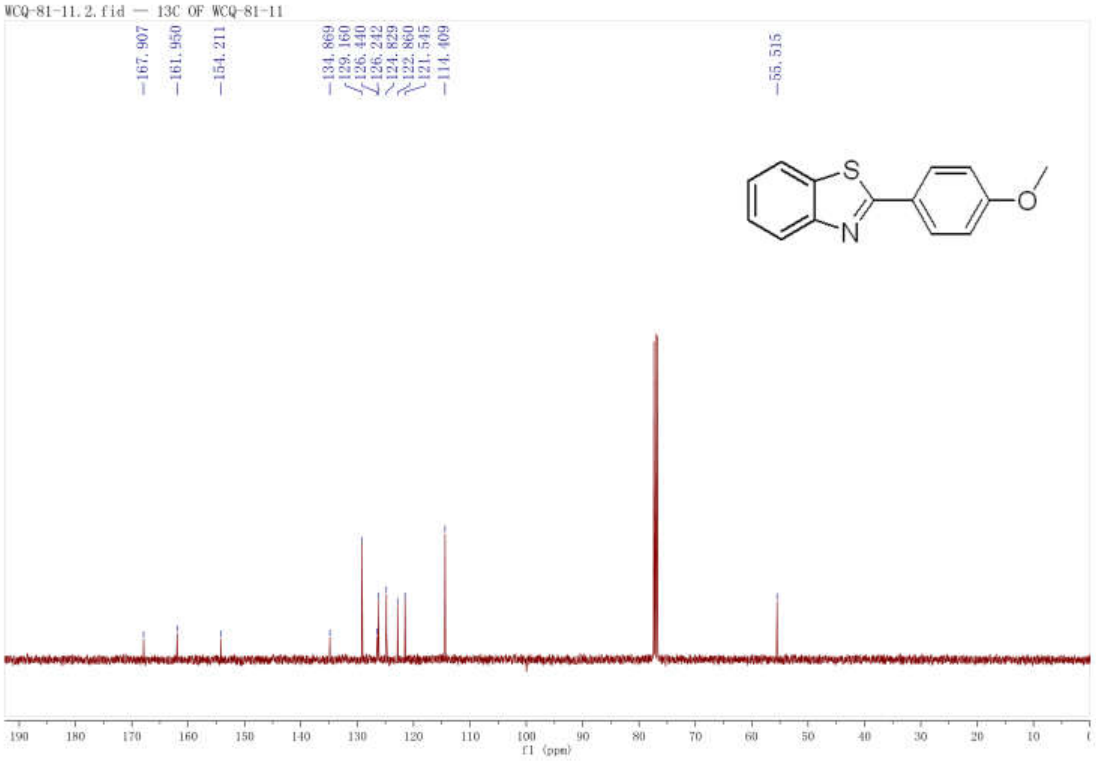


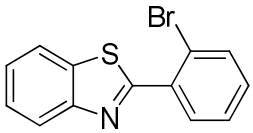


^{1}H NMR of 3g

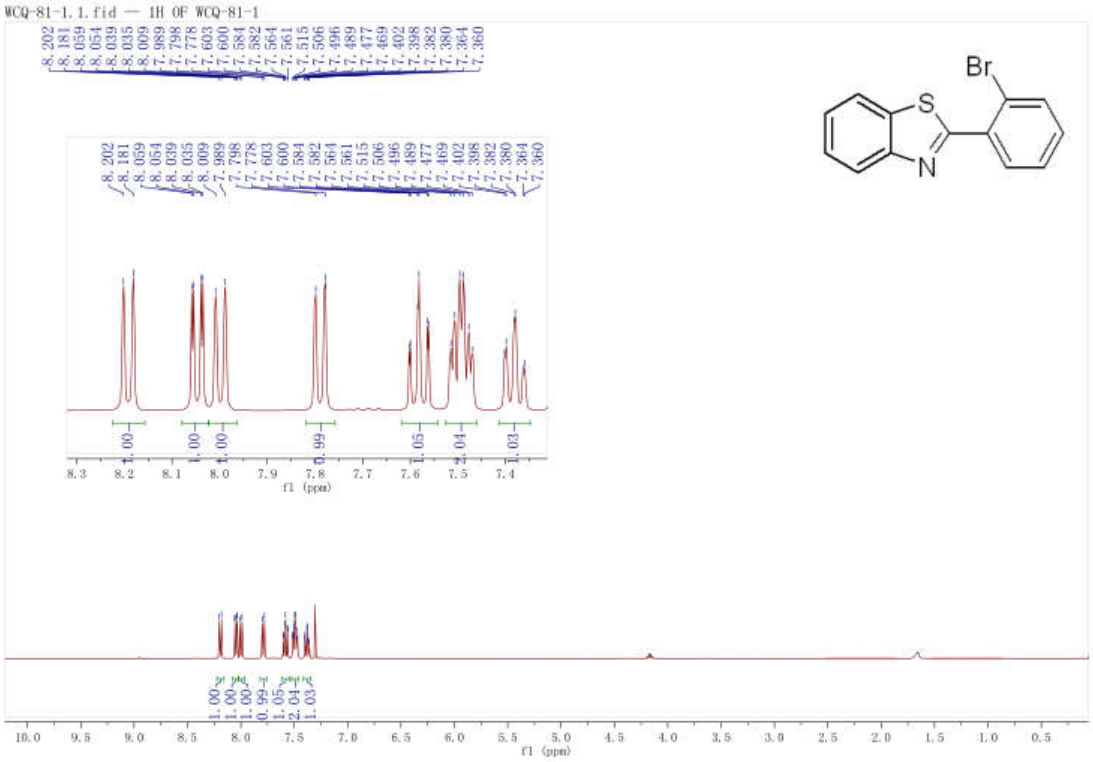


^{13}C NMR of 3g

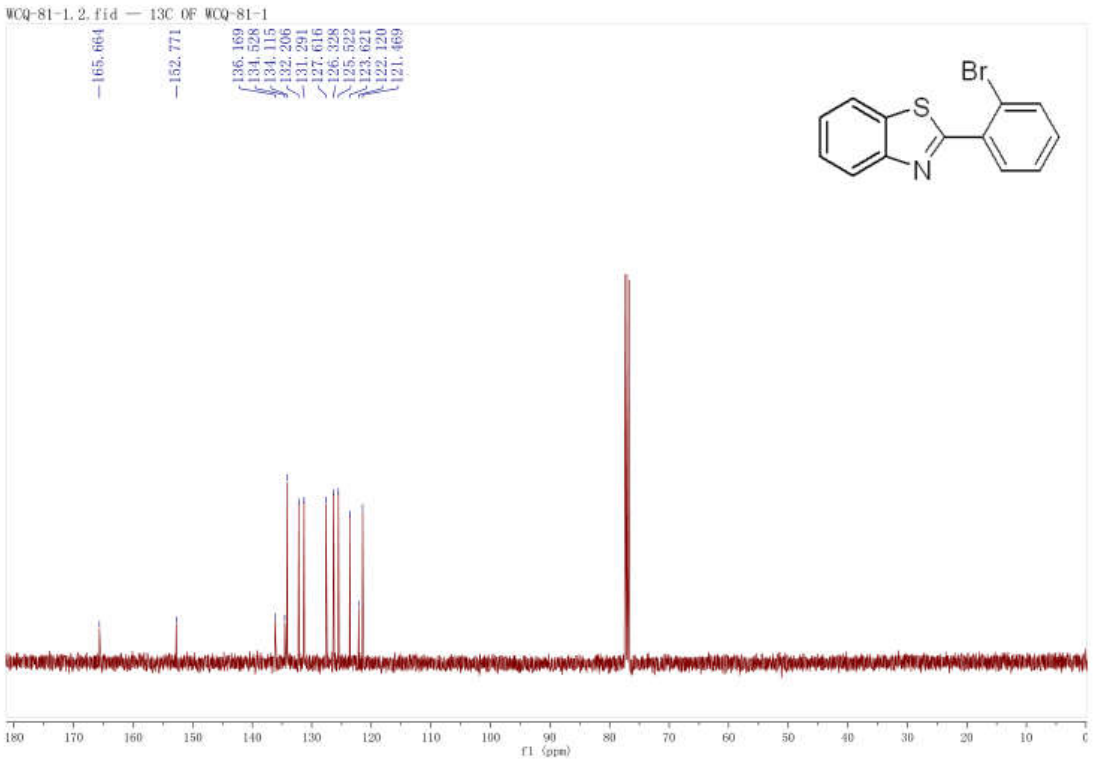


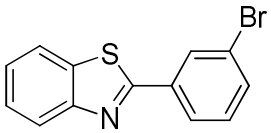


^{1}H NMR of 3h

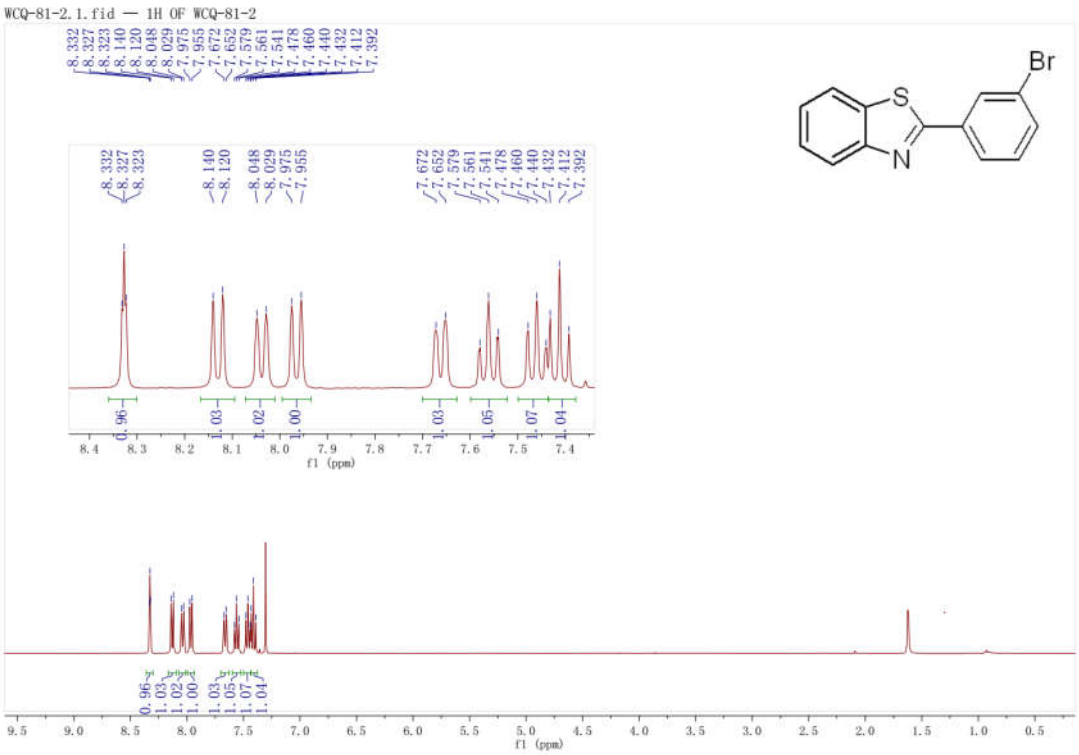


^{13}C NMR of 3h

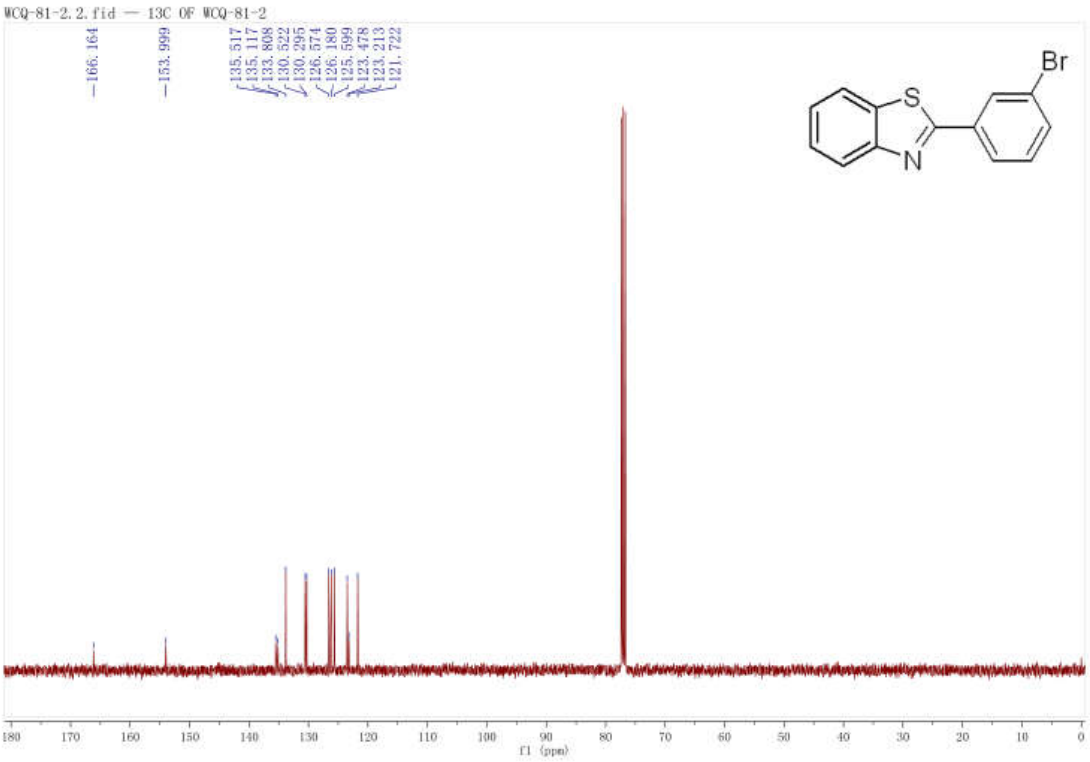


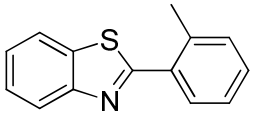


^{1}H NMR of 3i

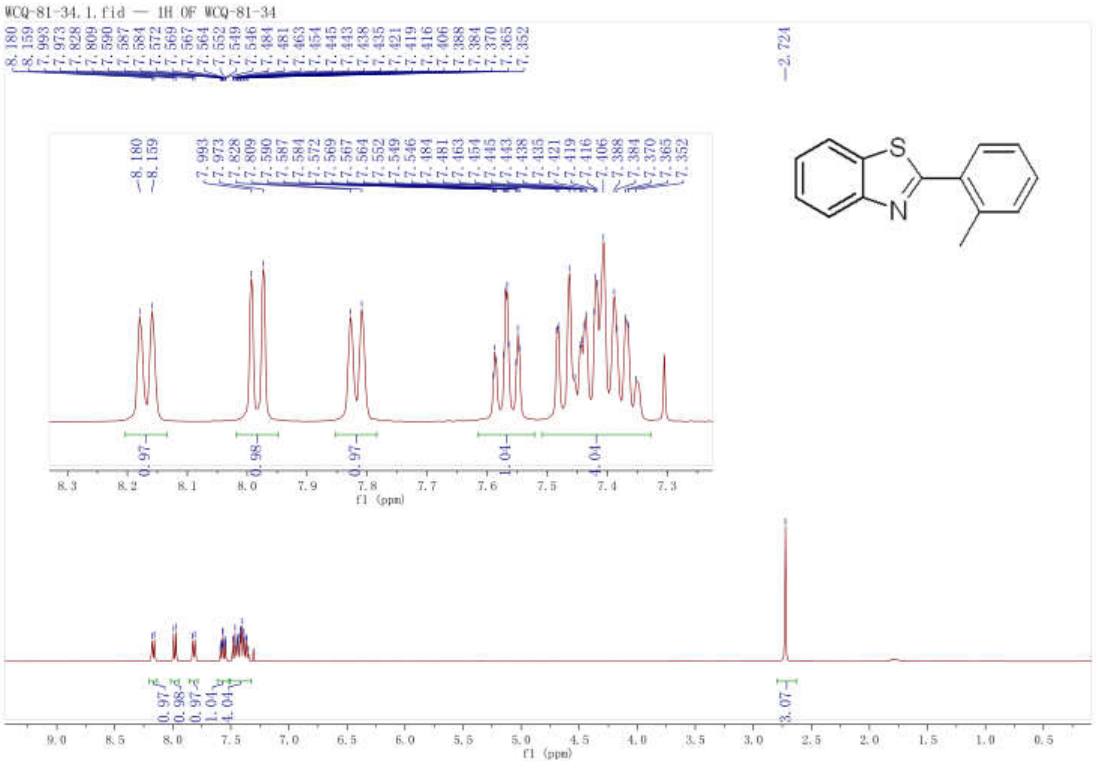


^{13}C NMR of 3i

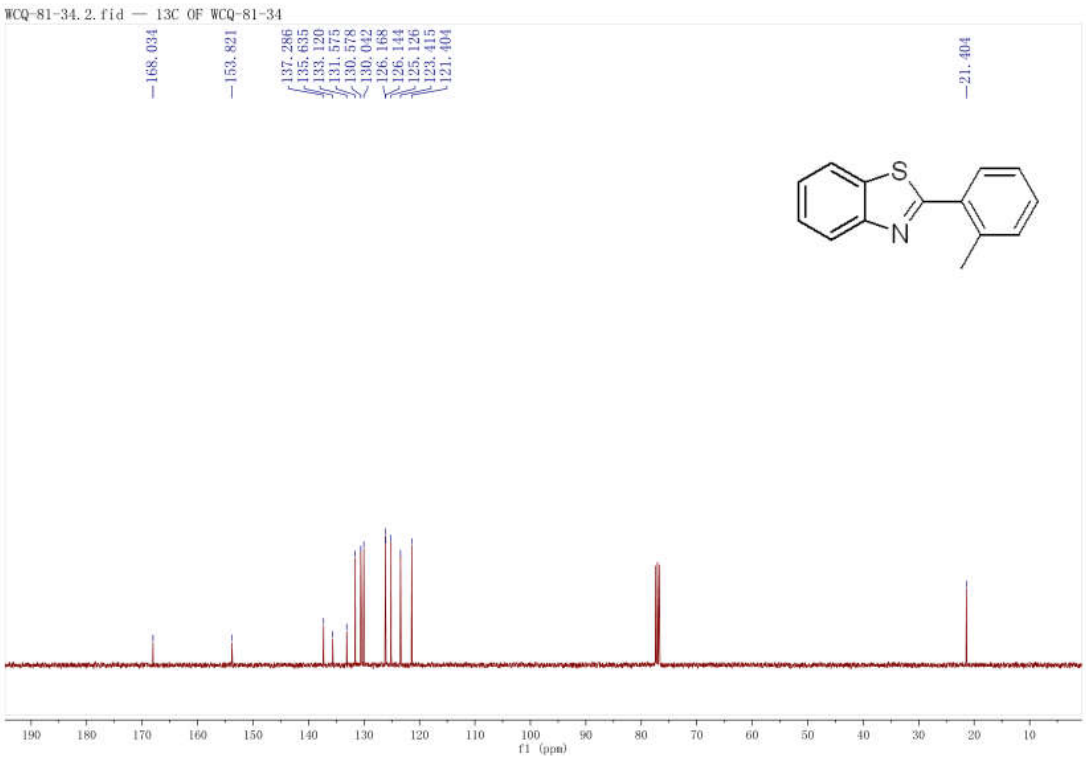


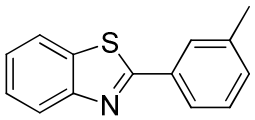


^{1}H NMR of 3j

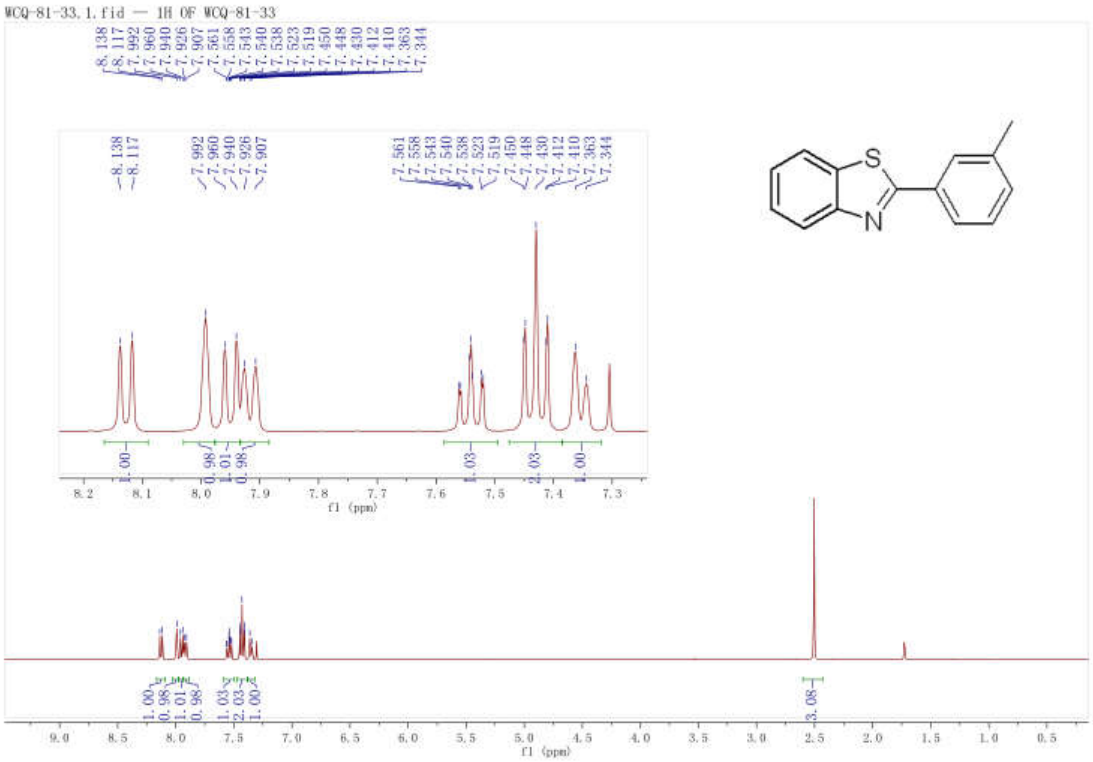


^{13}C NMR of 3j

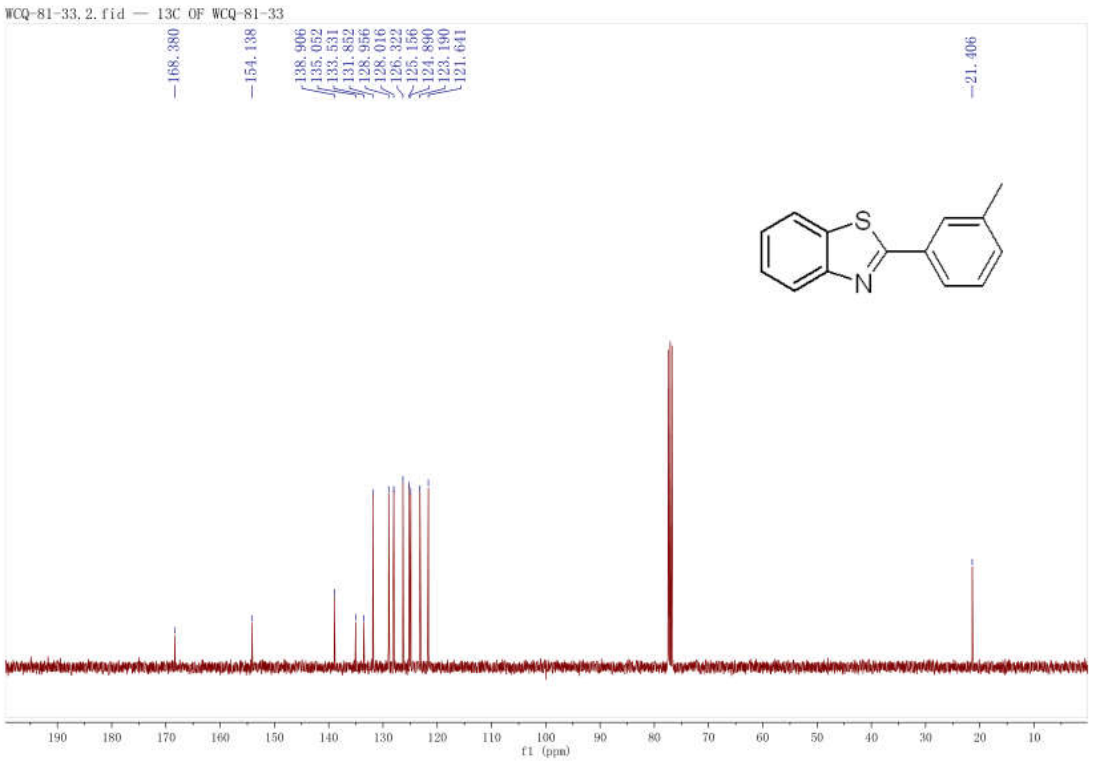


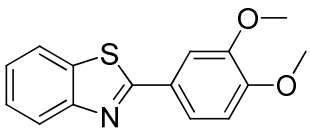


^{1}H NMR of 3k

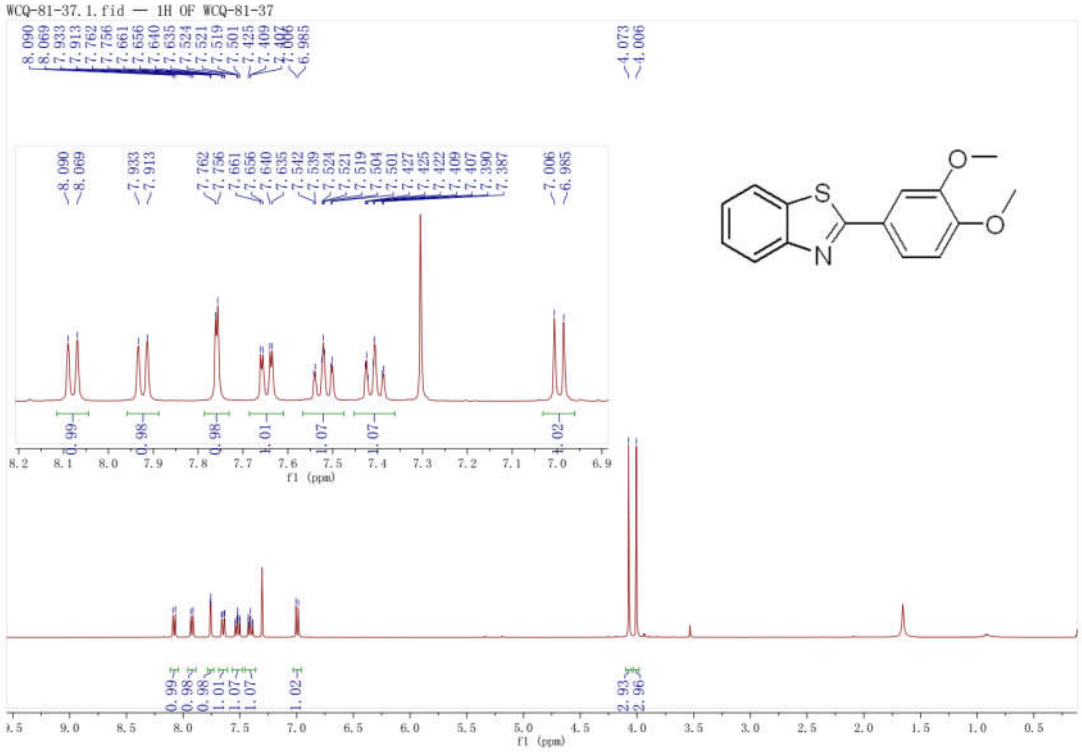


^{13}C NMR of 3k

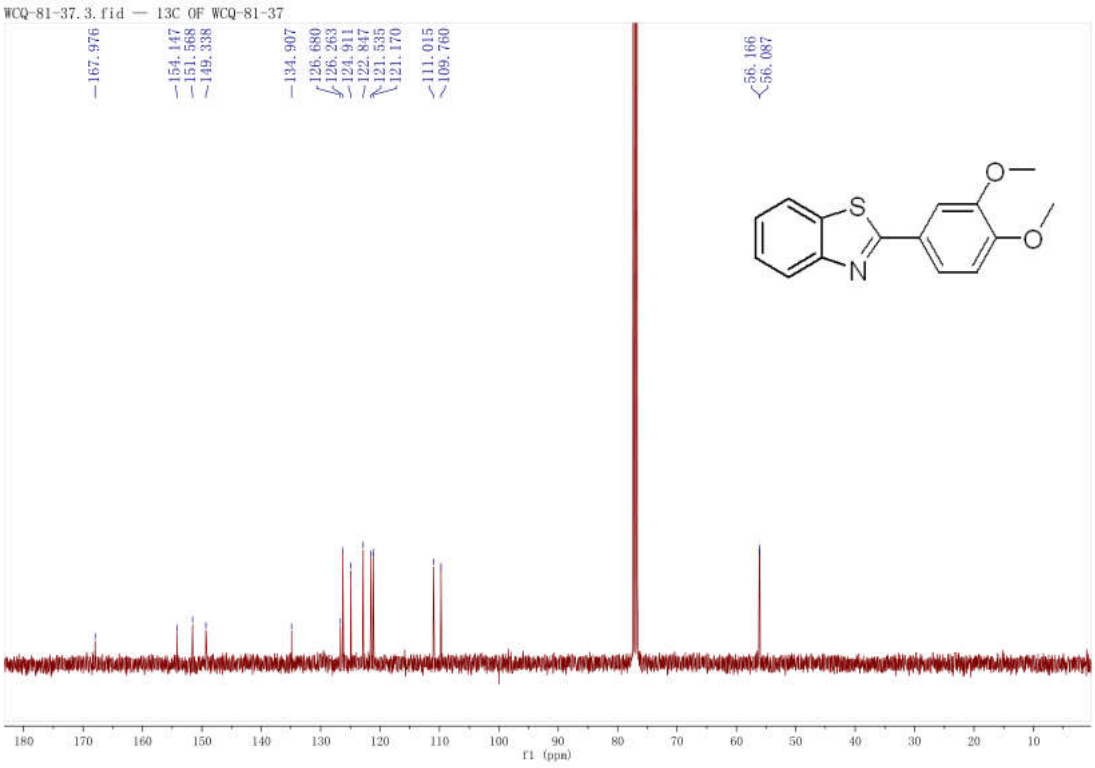


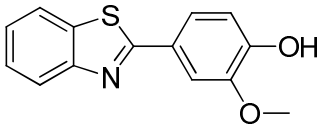


^{1}H NMR of 3l

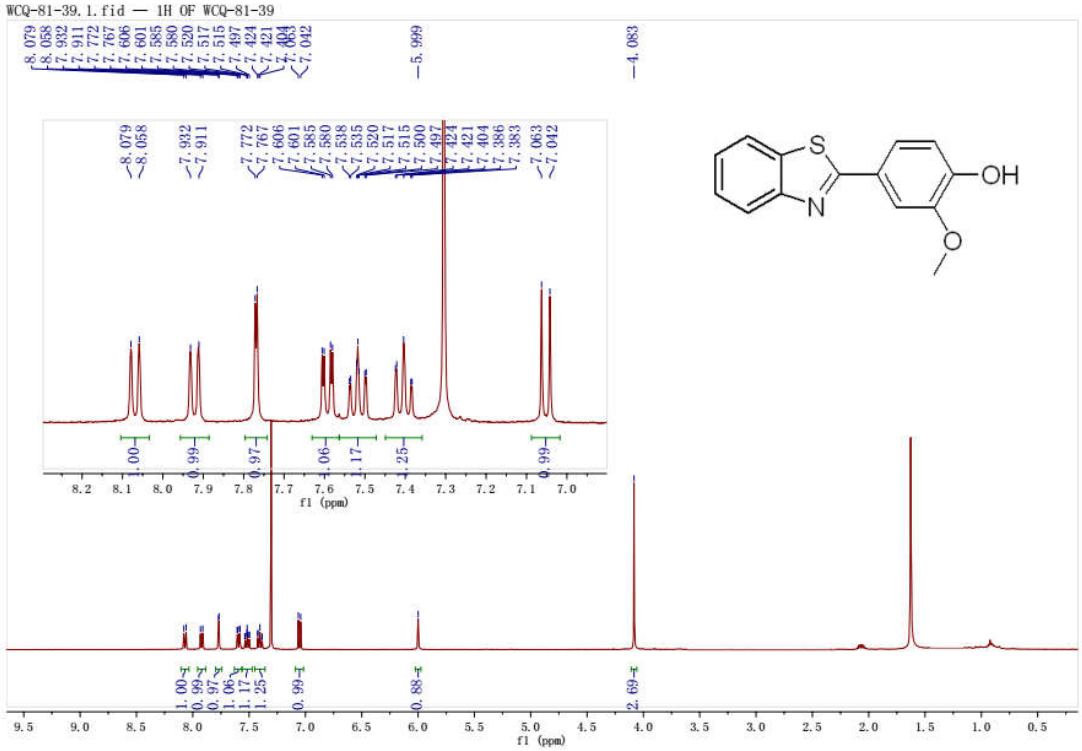


^{13}C NMR of 3l

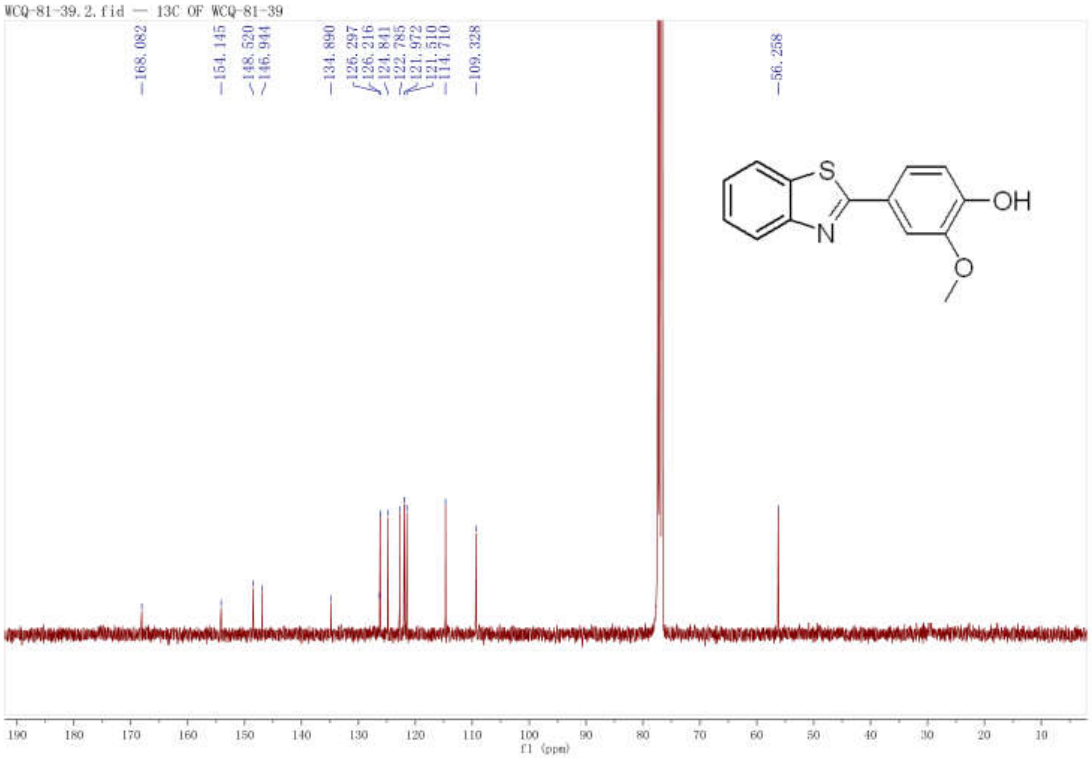


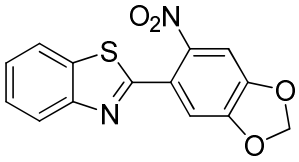


^{1}H NMR of 3m

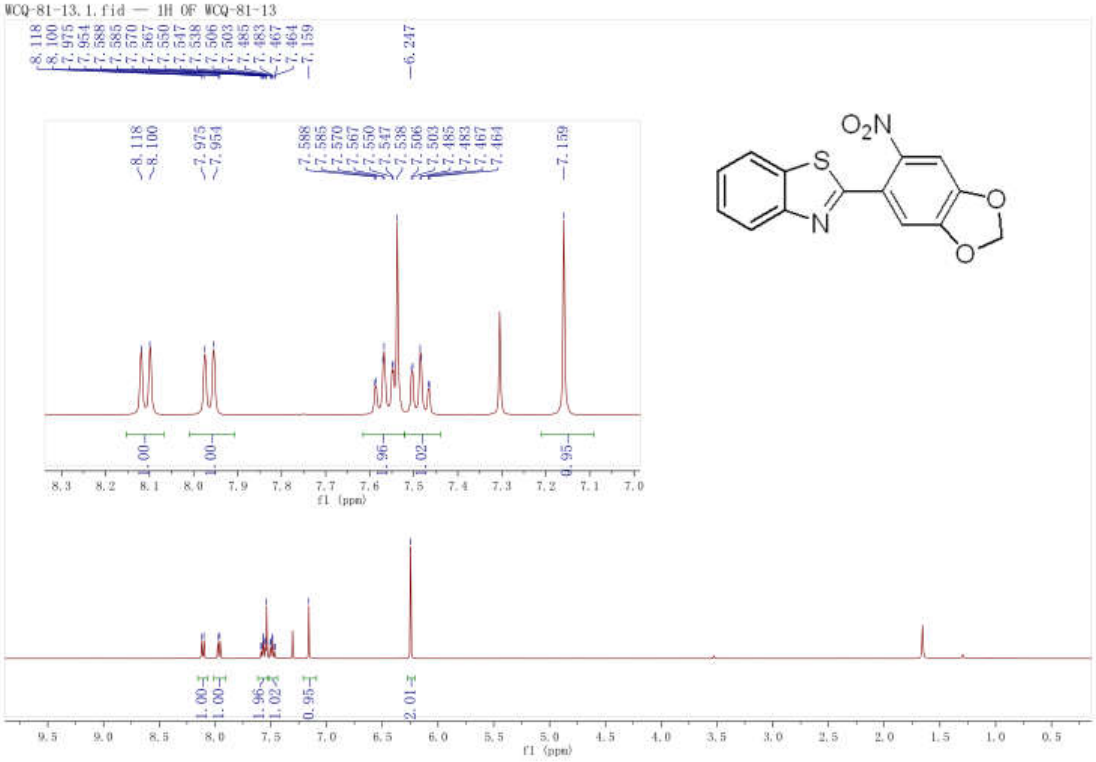


^{13}C NMR of 3m

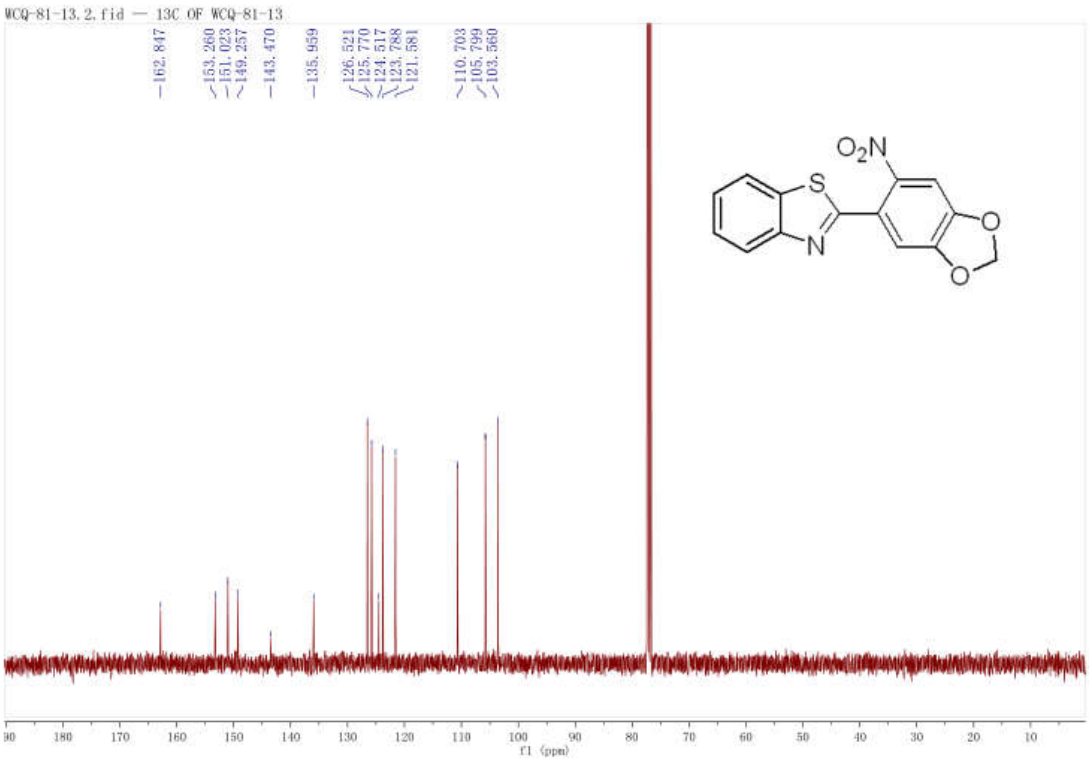


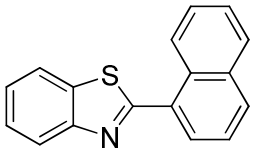


^{1}H NMR of 3n

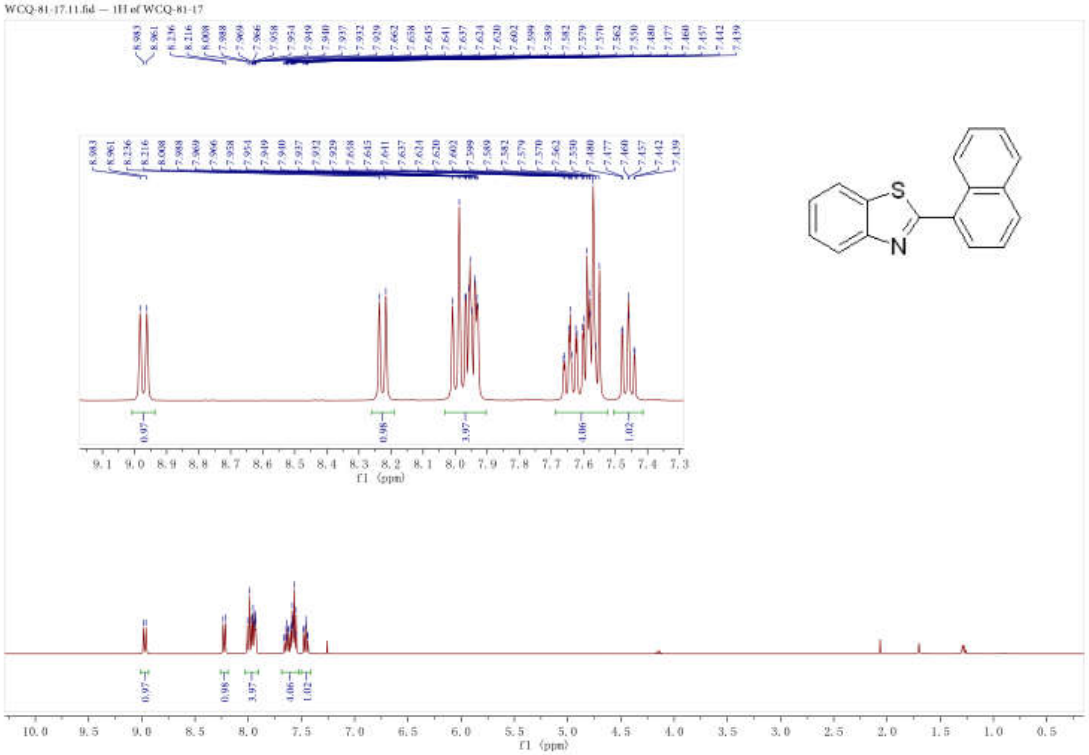


^{13}C NMR of 3n

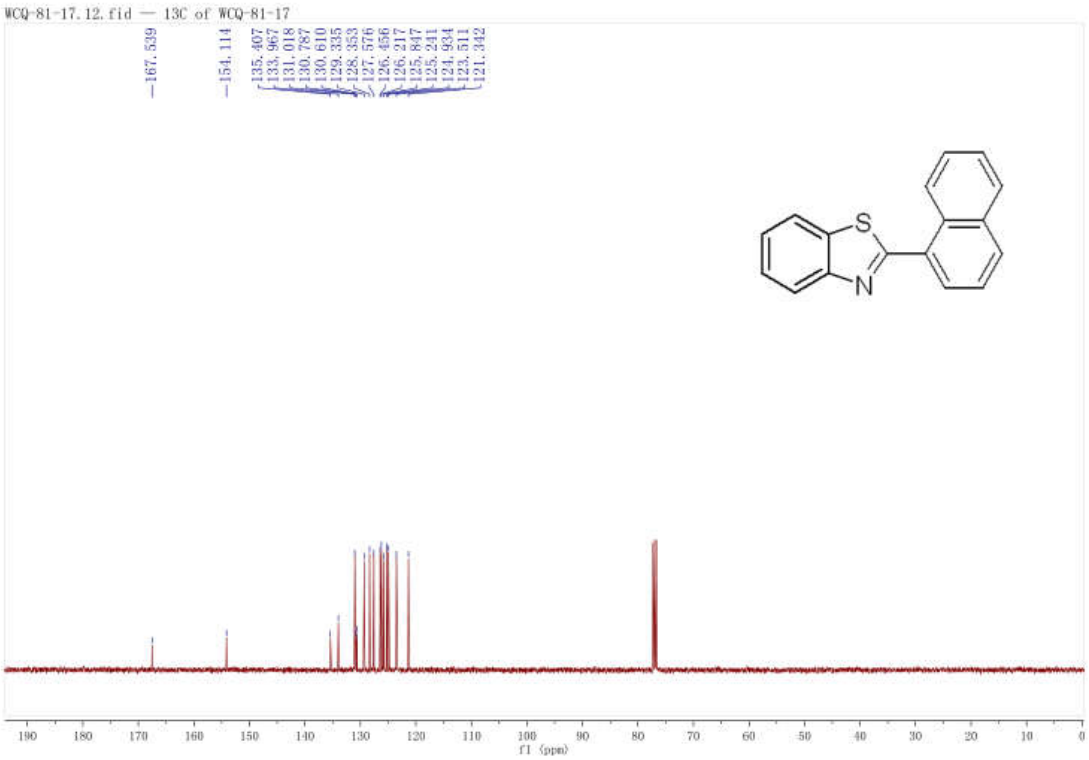


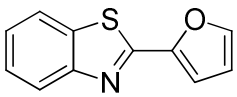


^{1}H NMR of 3o

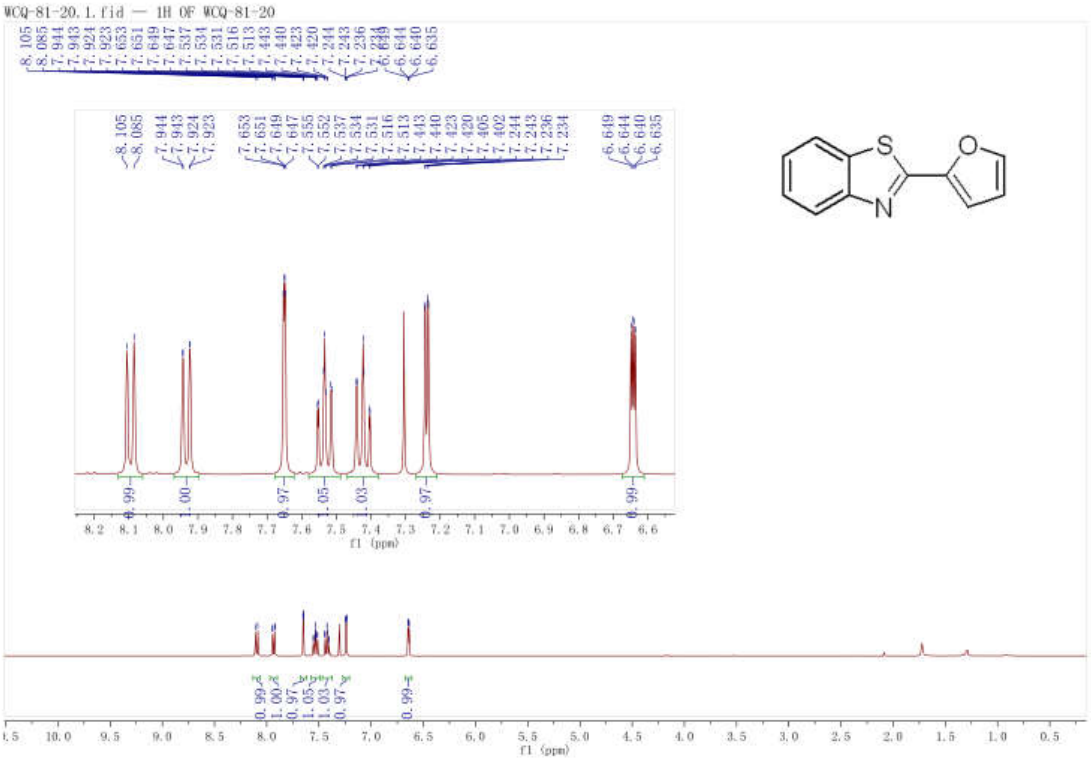


^{13}C NMR of 3o

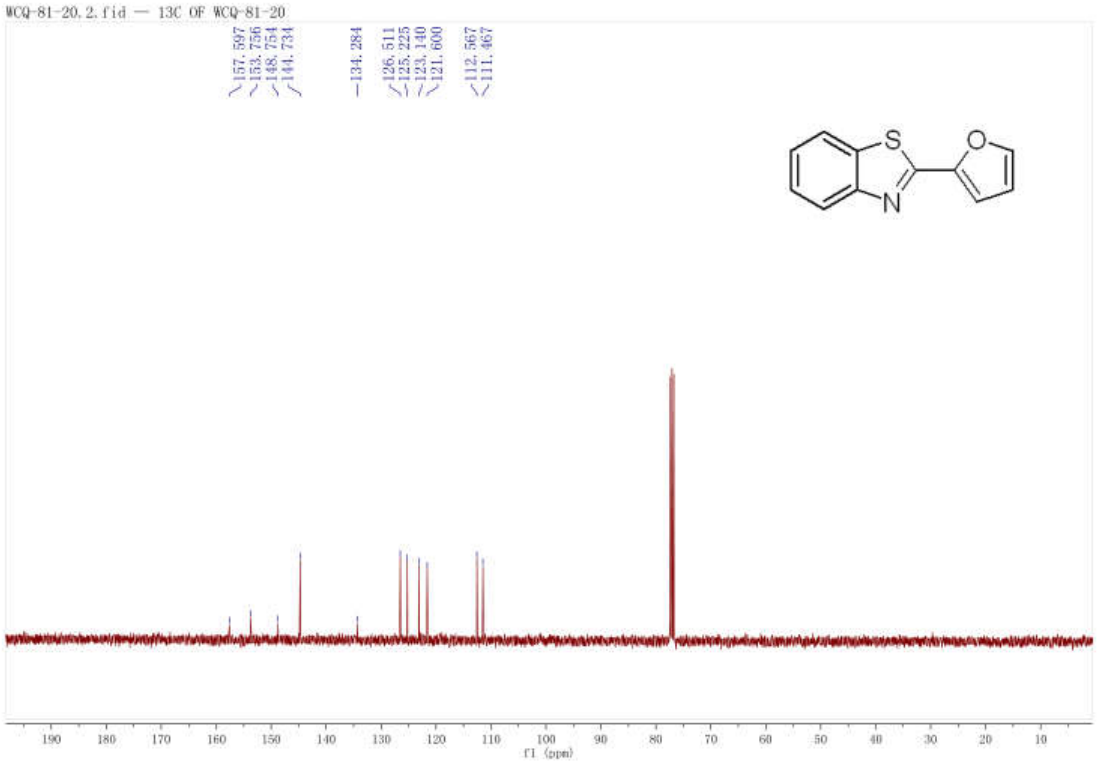


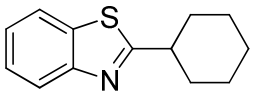


^{1}H NMR of 3p

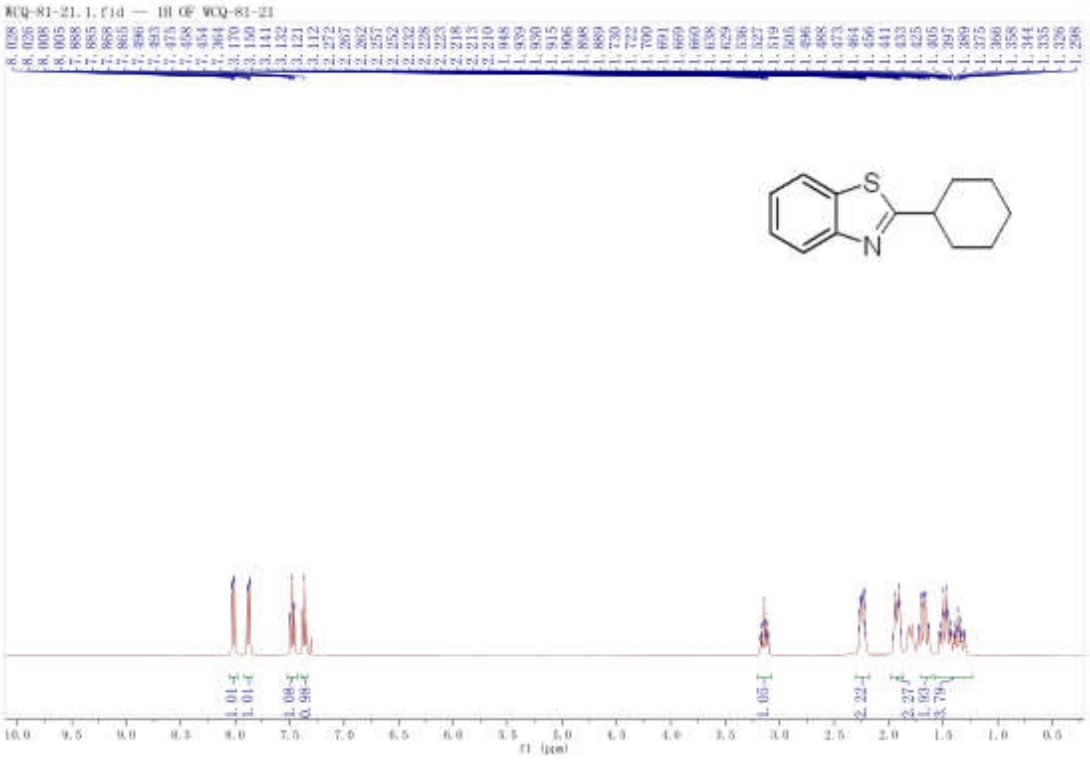


^{13}C NMR of 3p

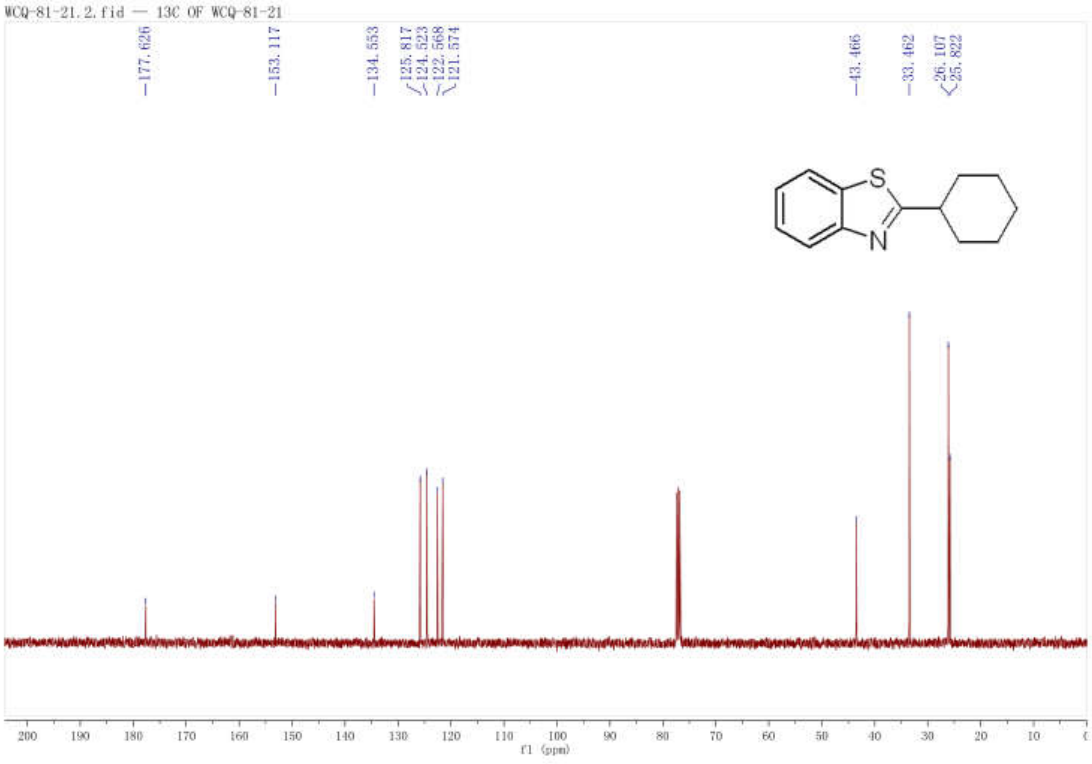


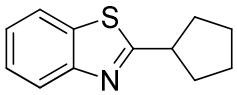


^{1}H NMR of 3q

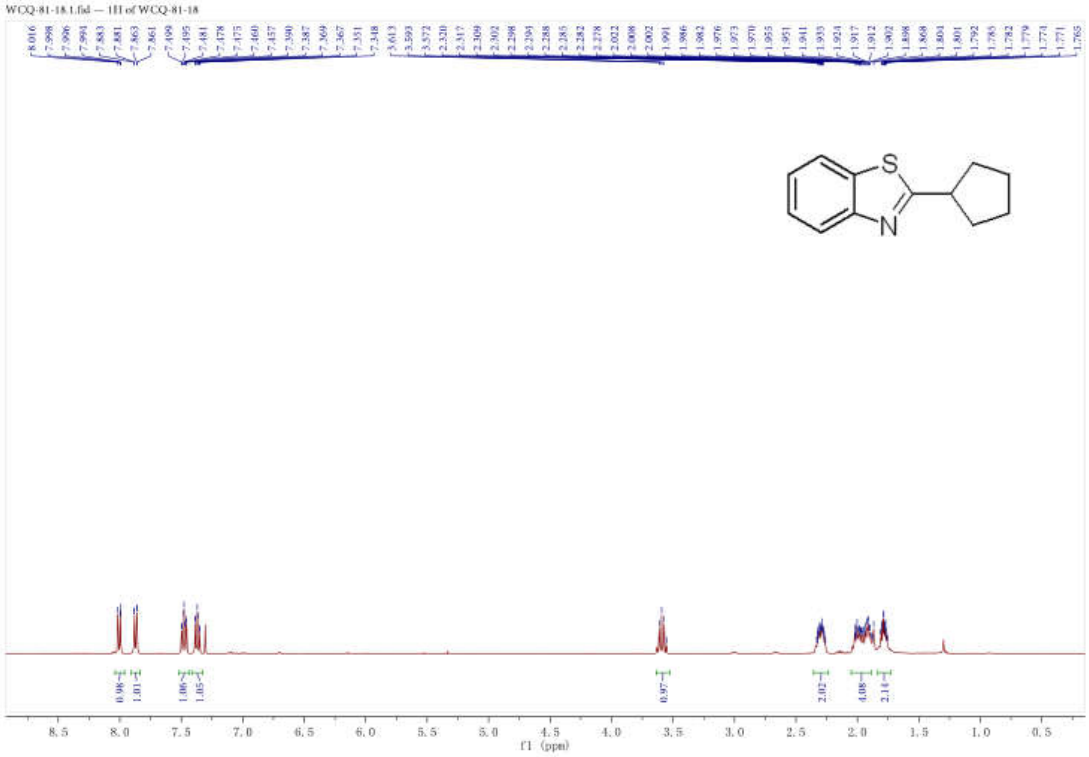


^{13}C NMR of 3q

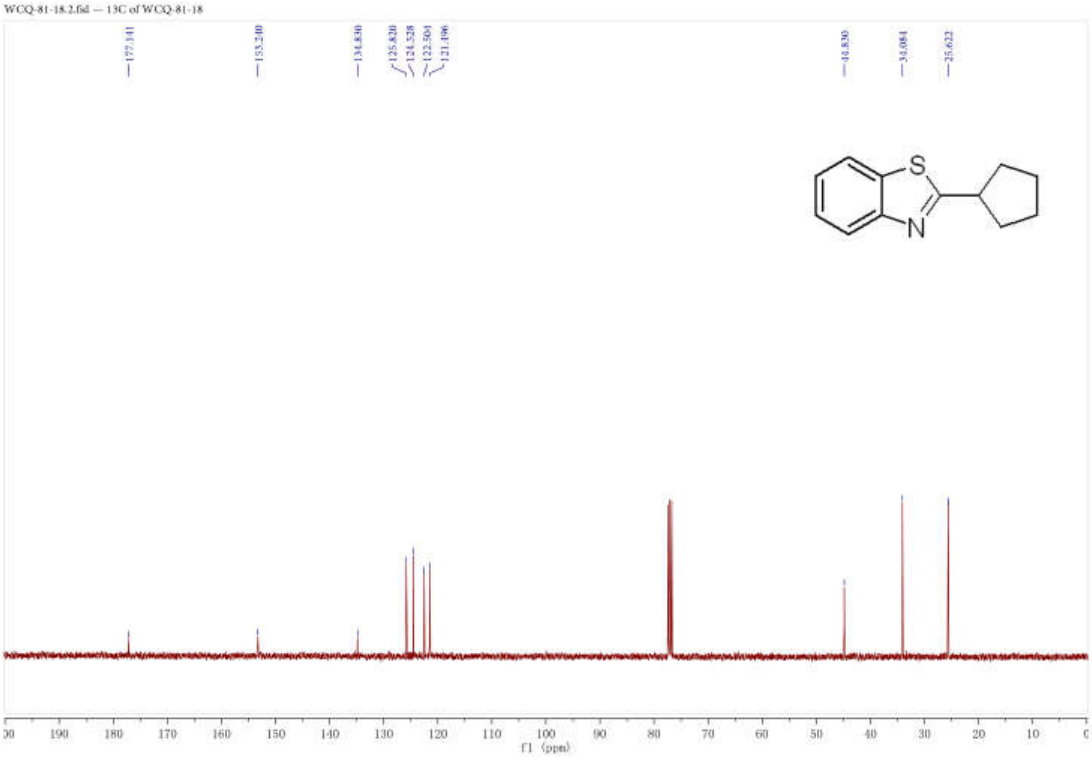


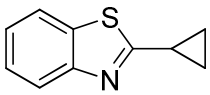


^{1}H NMR of 3r

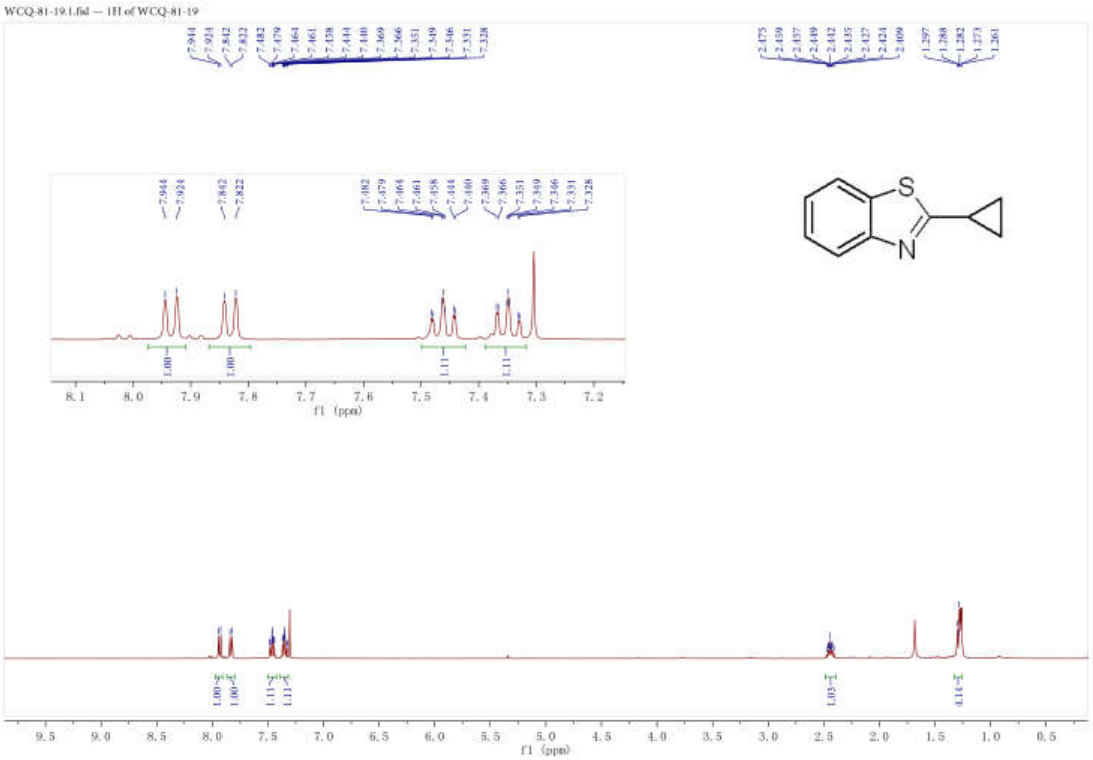


^{13}C NMR of 3r

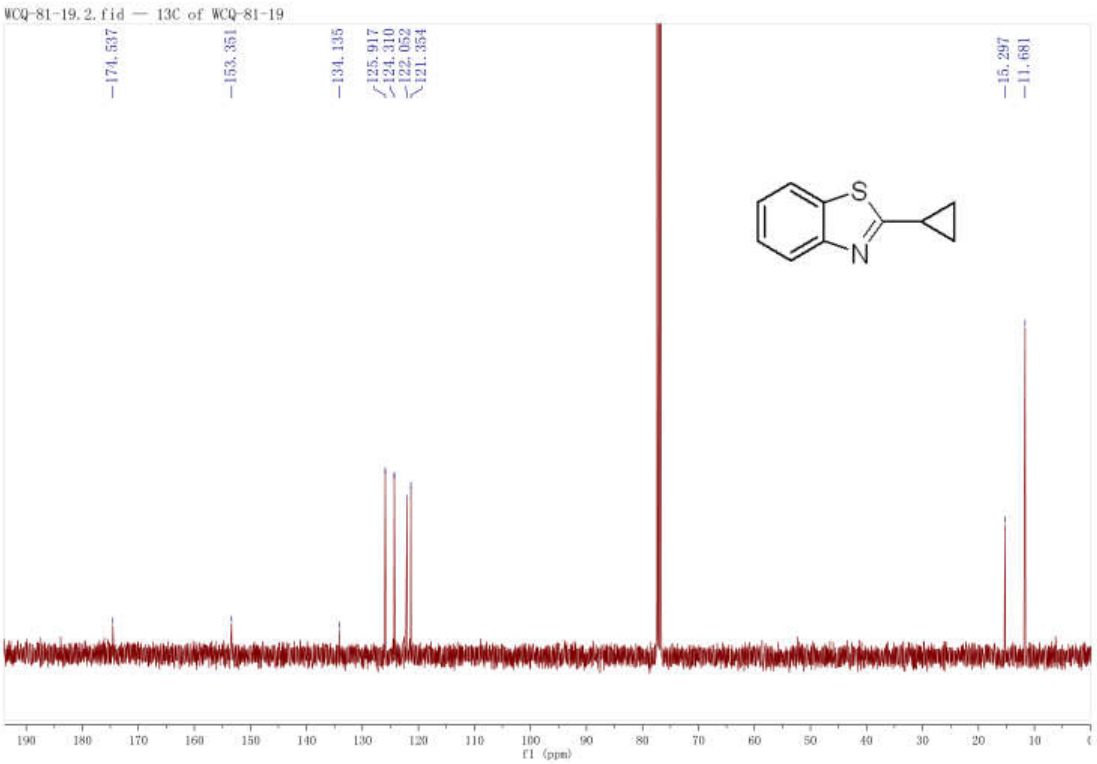


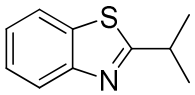


^{1}H NMR of 3s

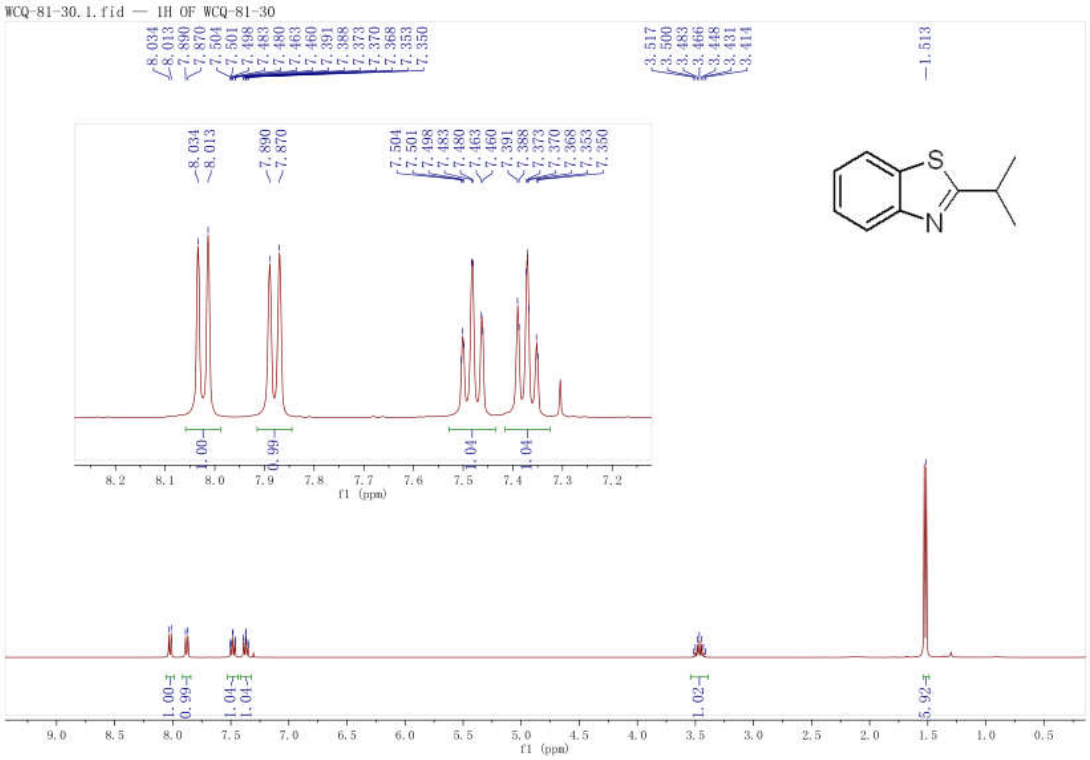


^{13}C NMR of 3s

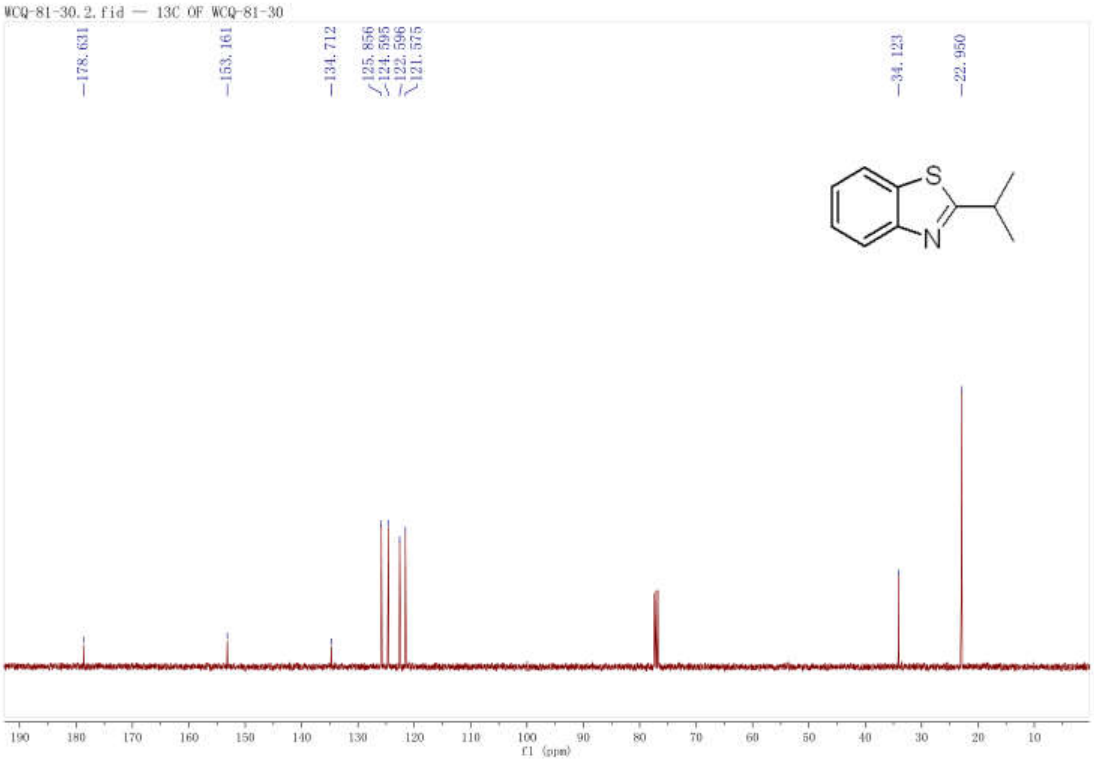


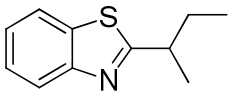


^{1}H NMR of 3t

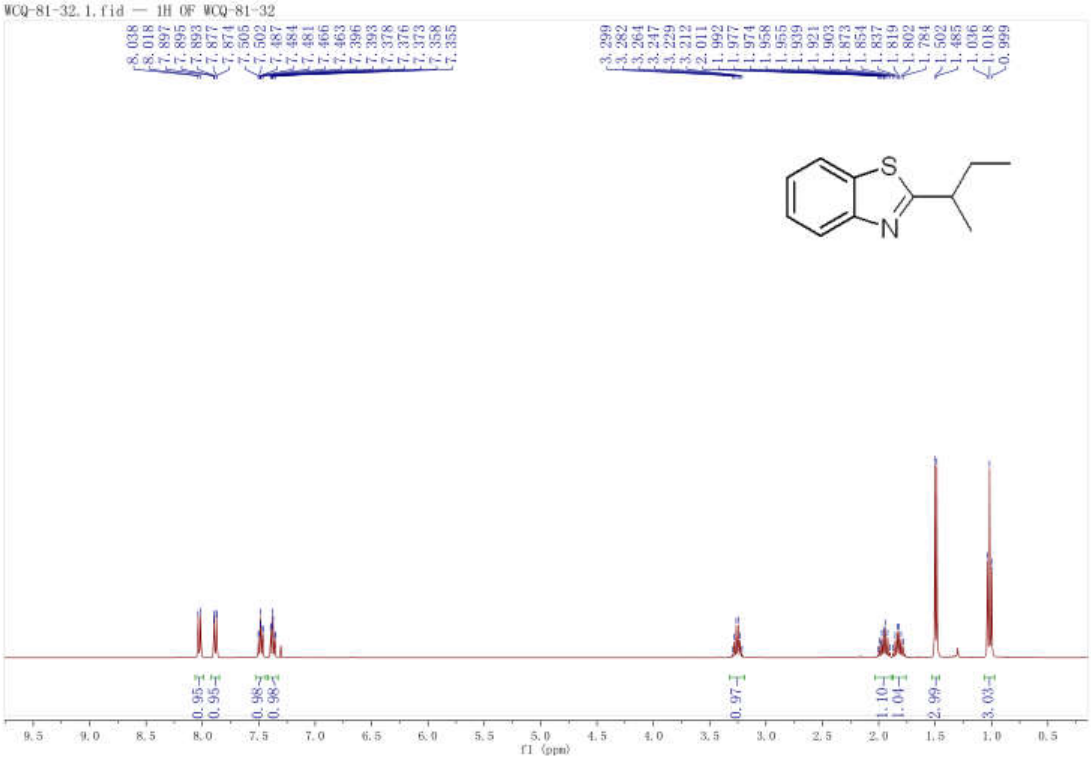


^{13}C NMR of 3t

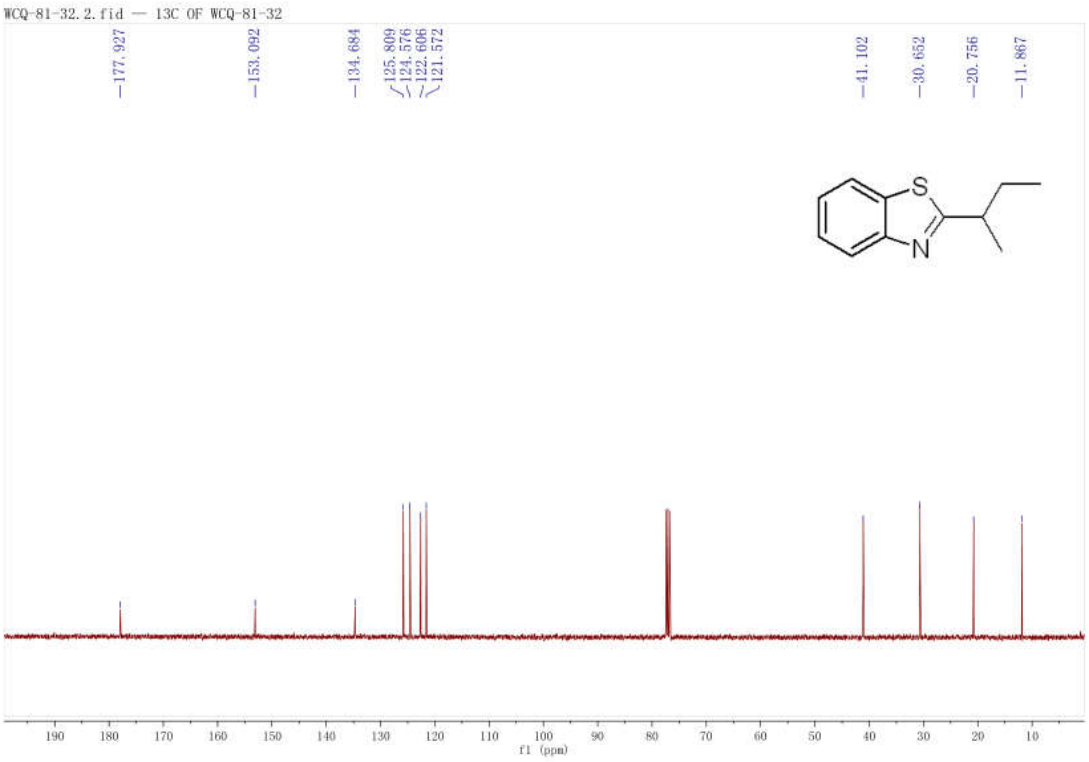


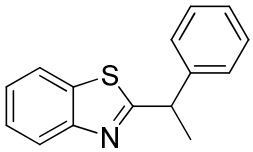


^{1}H NMR of 3u

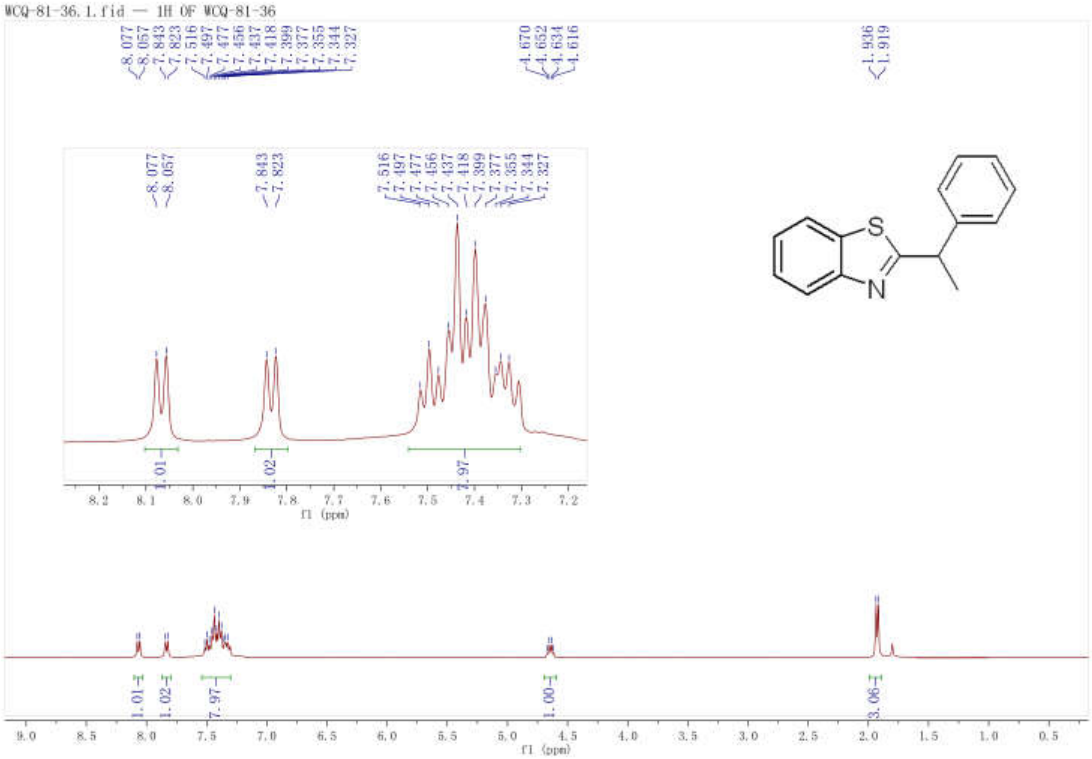


^{13}C NMR of 3u

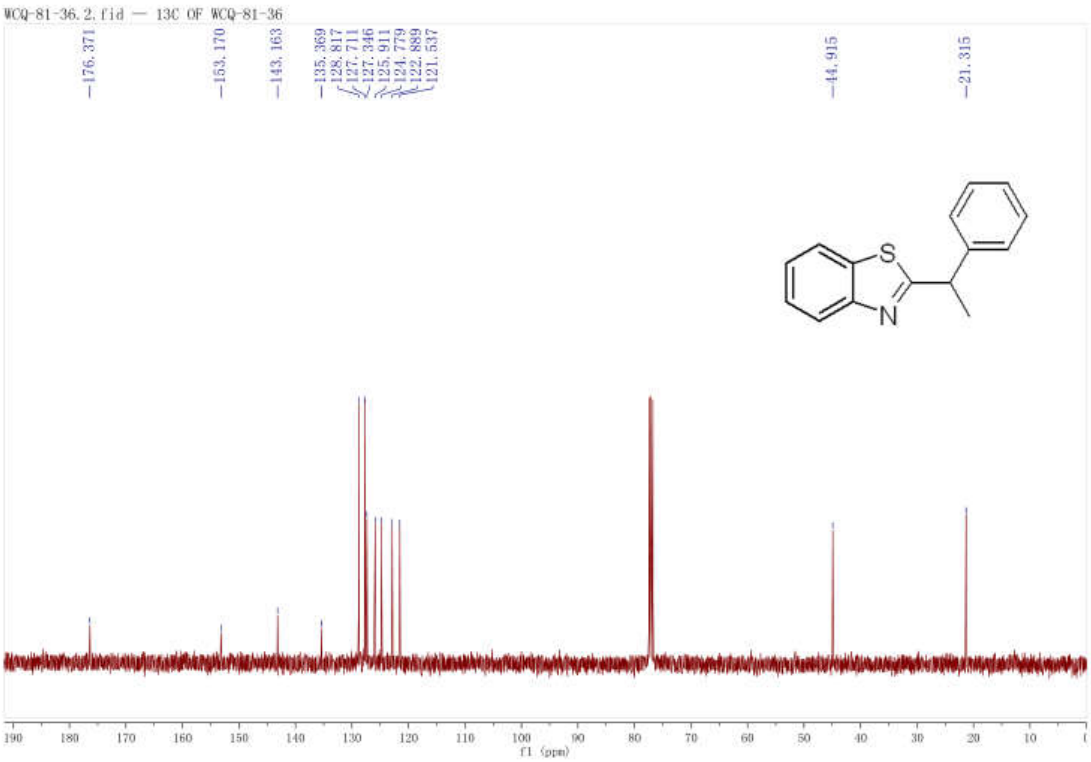


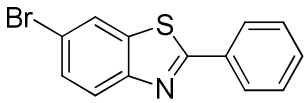


^{1}H NMR of 3v

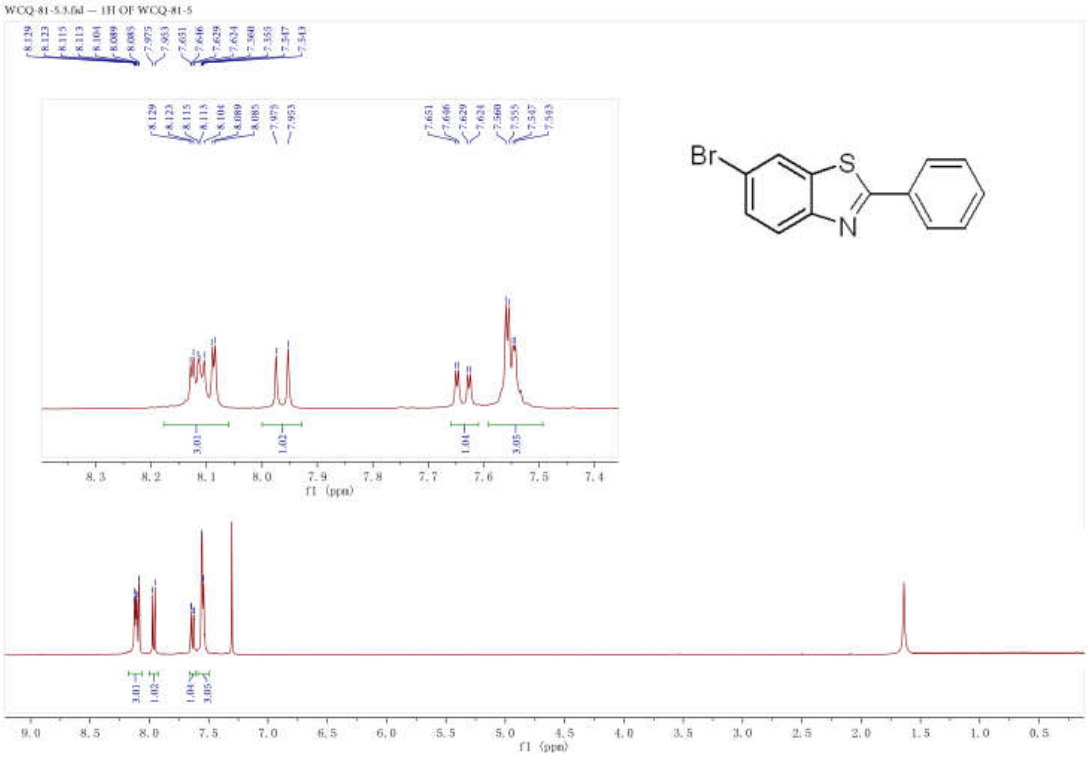


^{13}C NMR of 3a

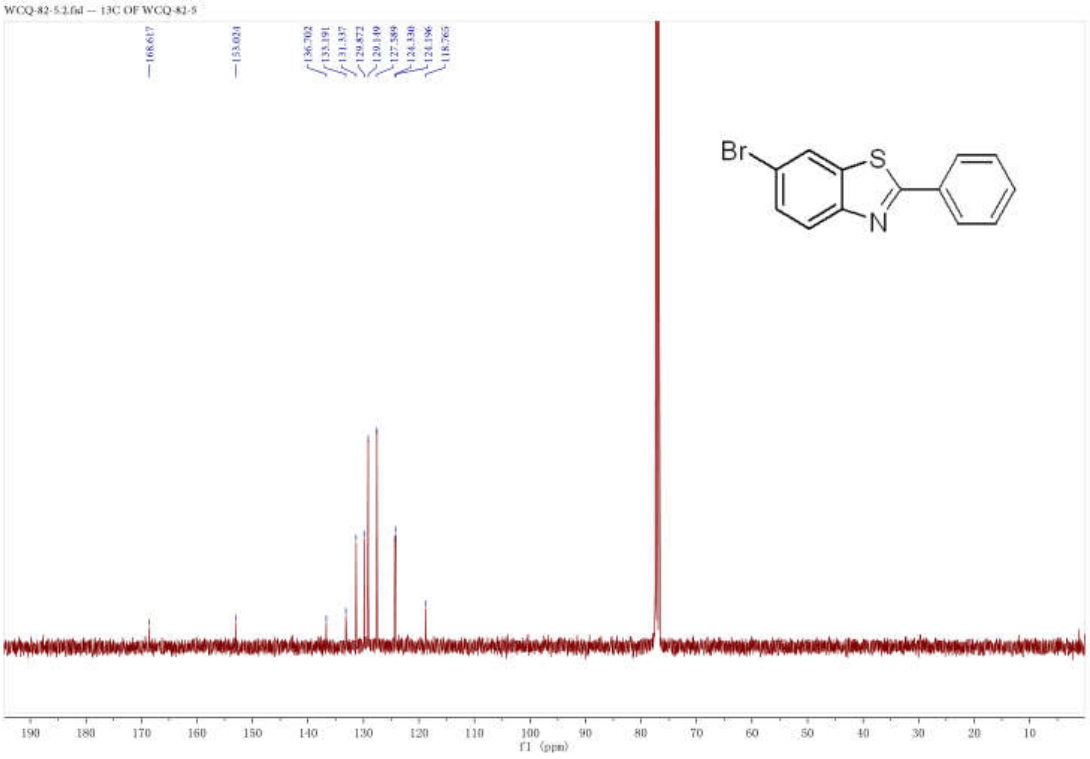


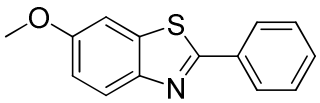


^{1}H NMR of 3w

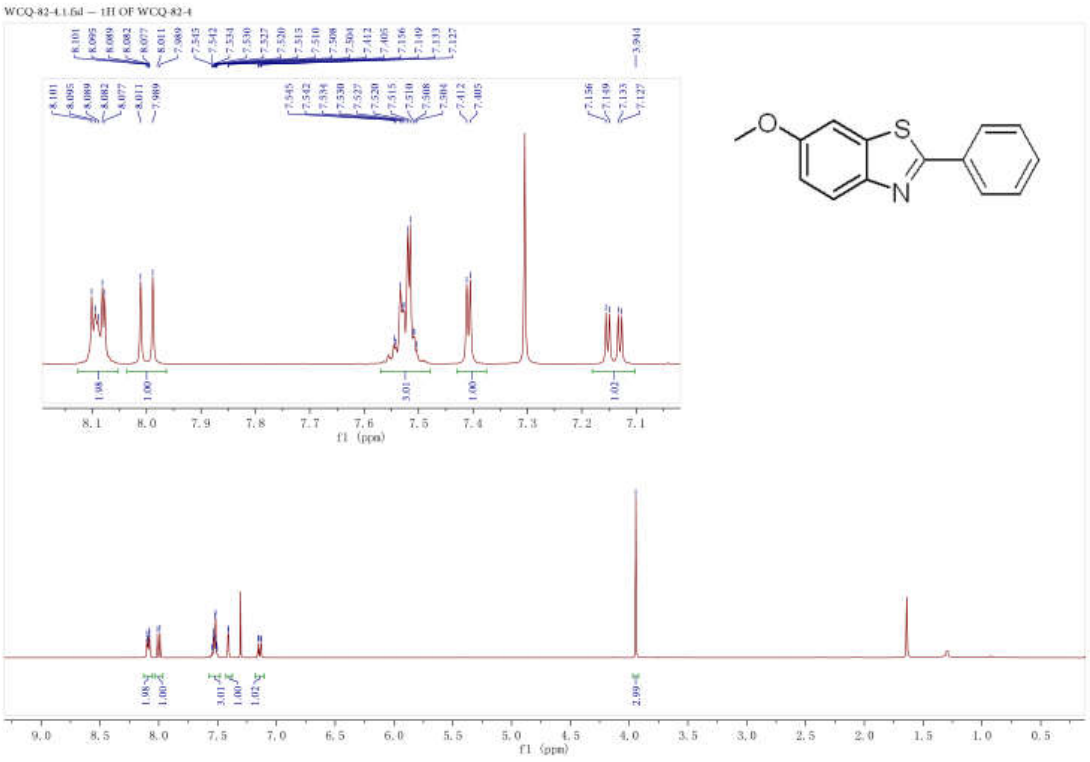


^{13}C NMR of 3w

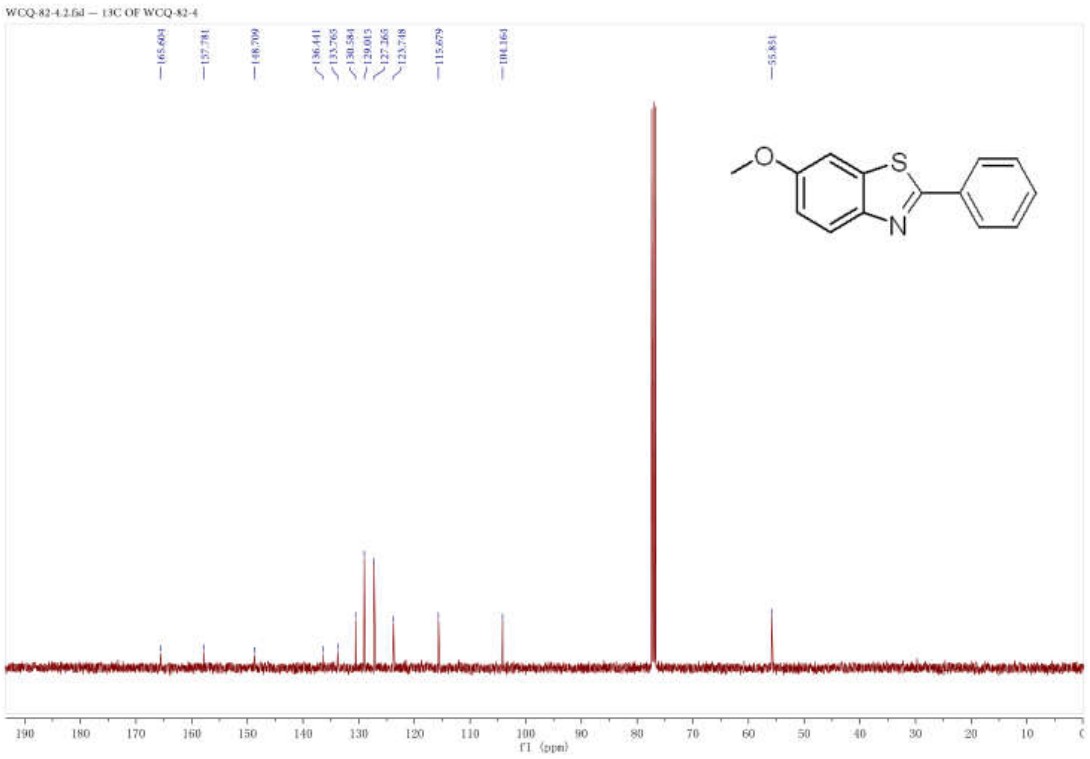


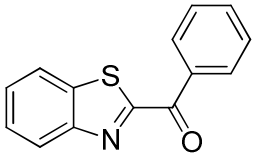


^{1}H NMR of 3x

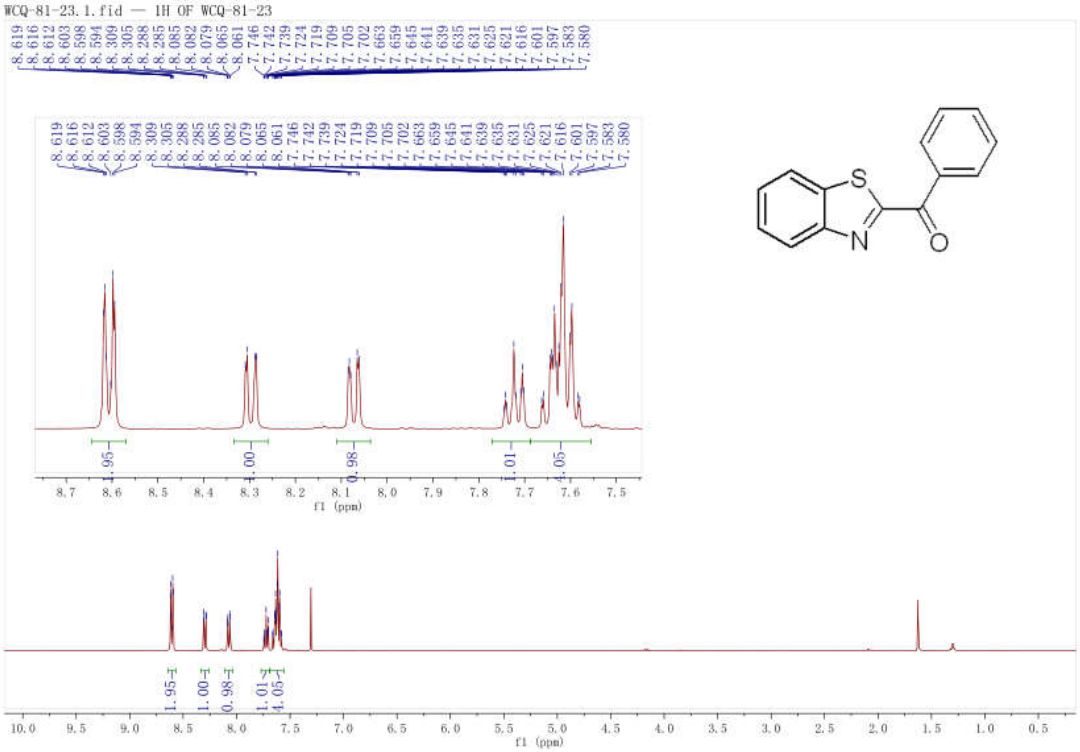


^{13}C NMR of 3x

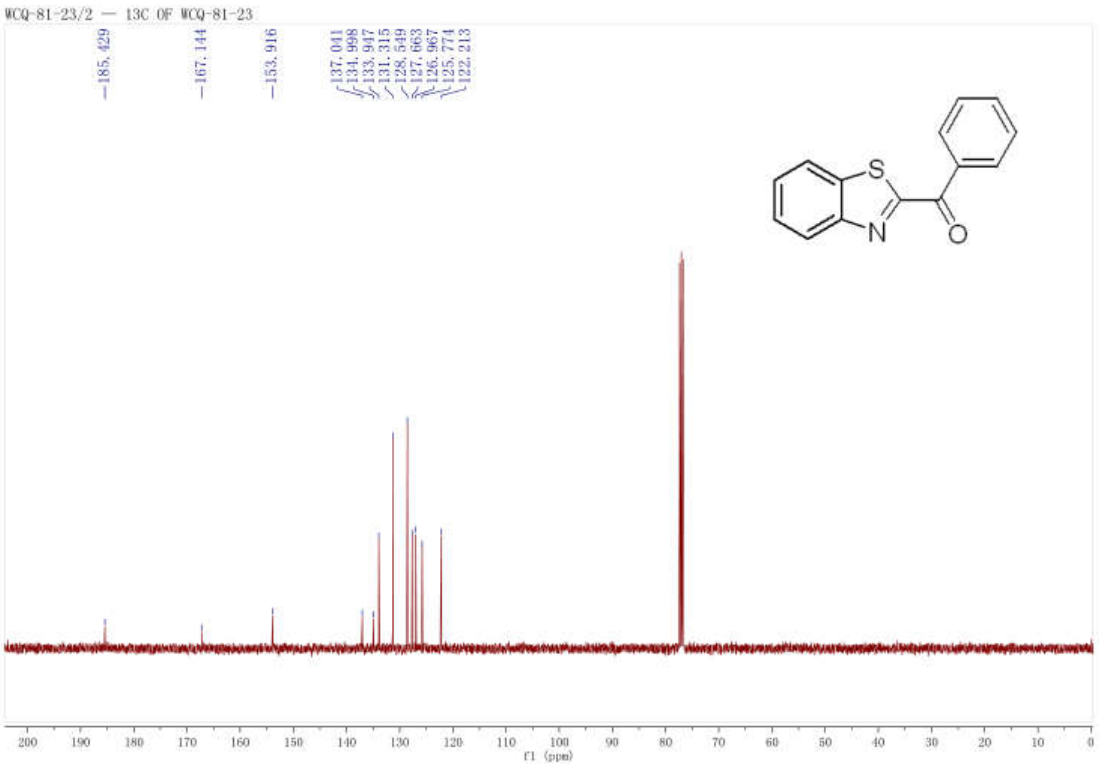


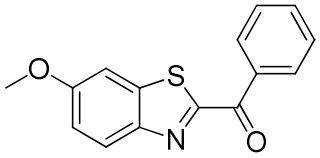


^{1}H NMR of 5a

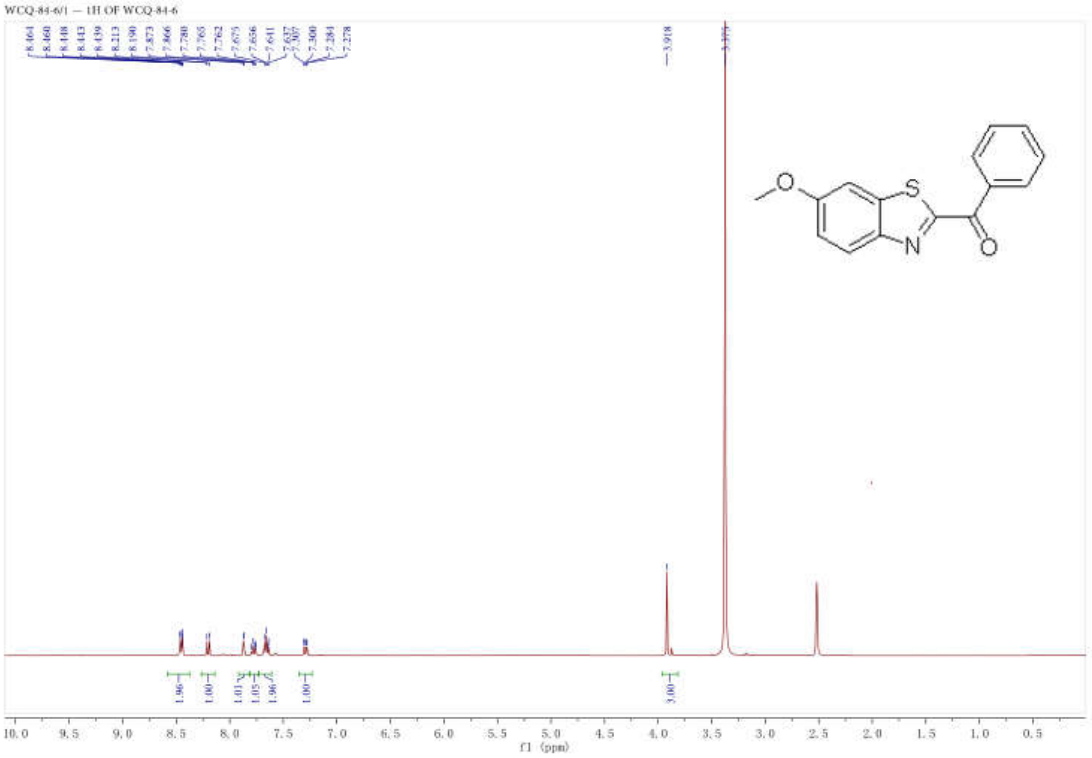


^{13}C NMR of 5a

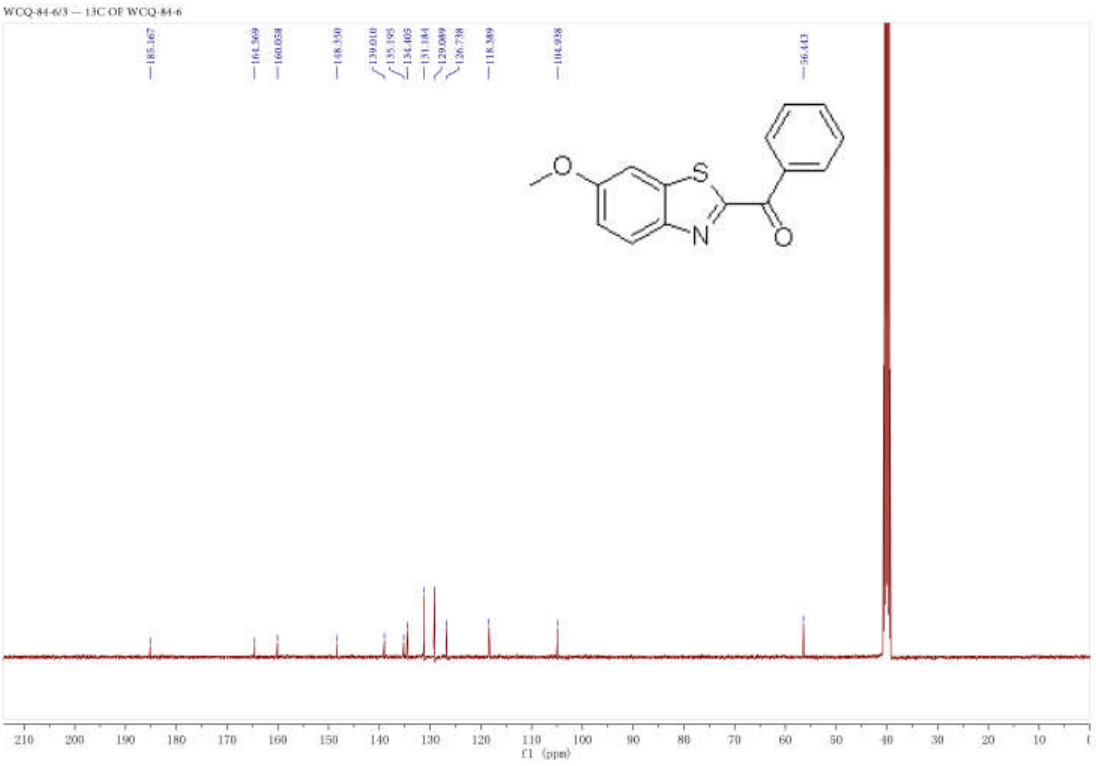


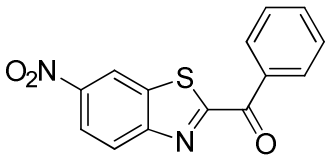


^{1}H NMR of 5b

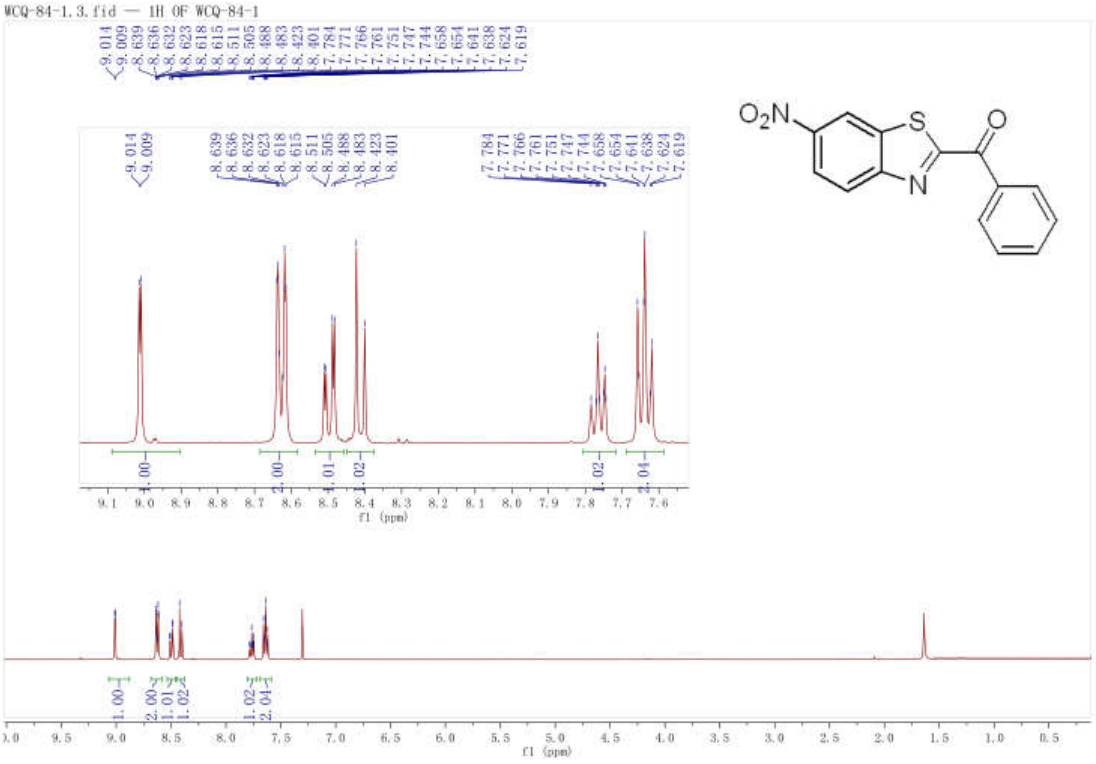


^{13}C NMR of 5b

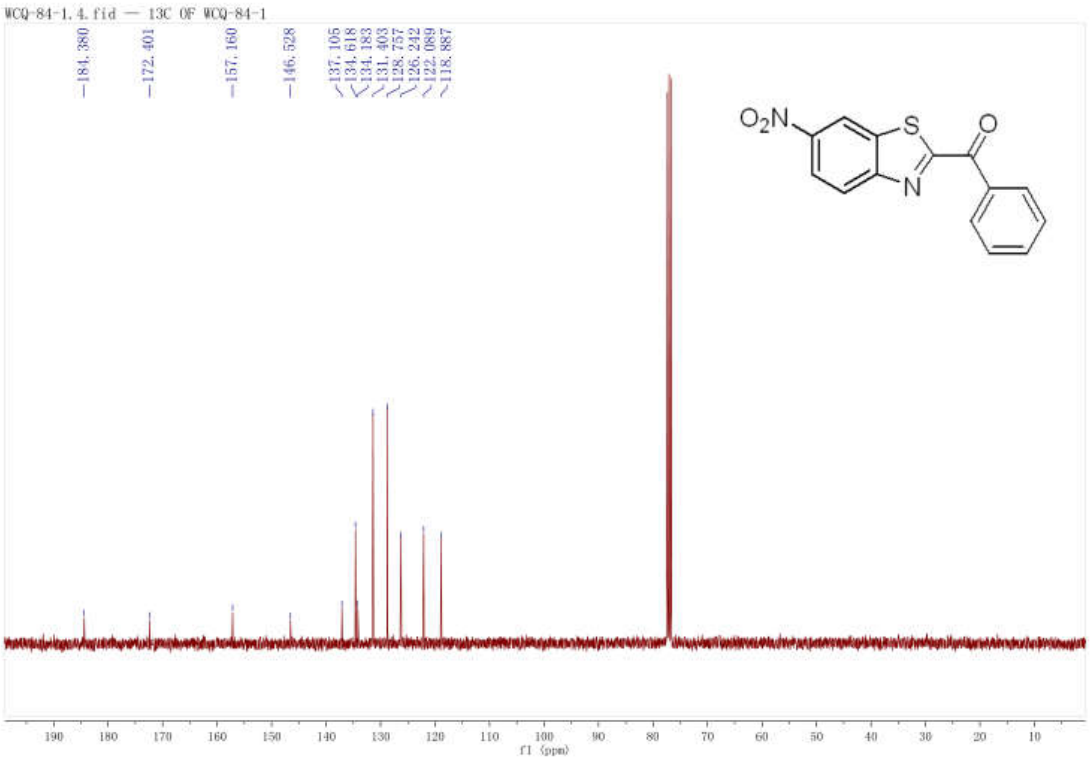


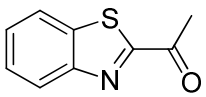


^{1}H NMR of 5c

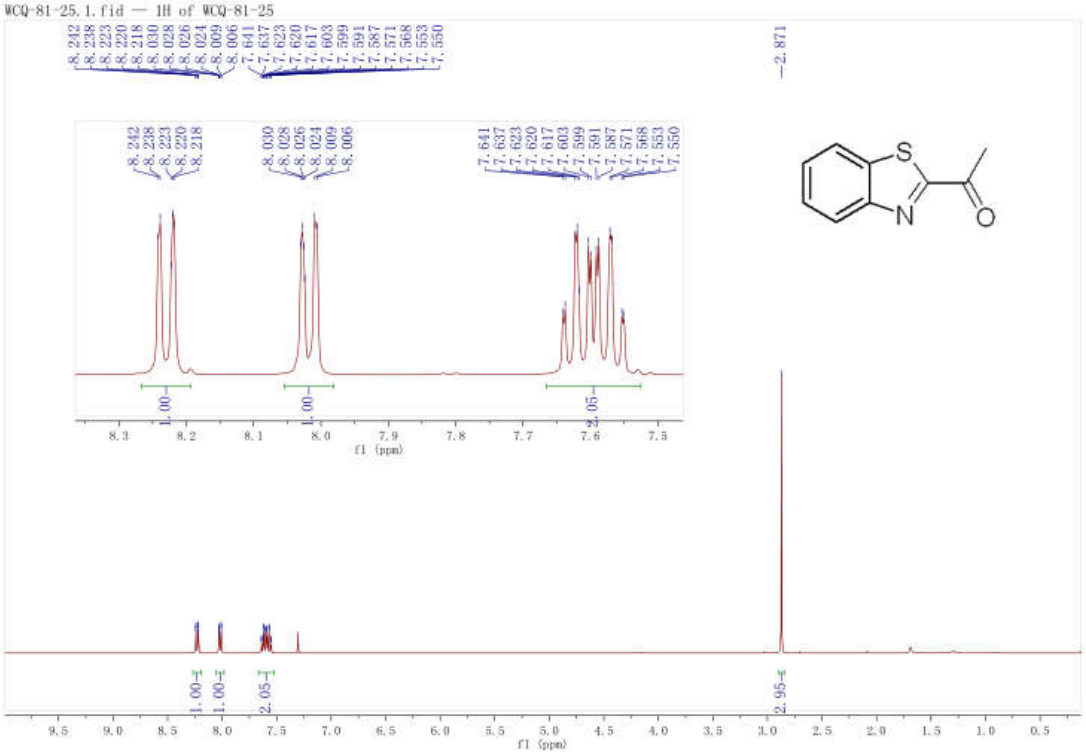


^{13}C NMR of 5c

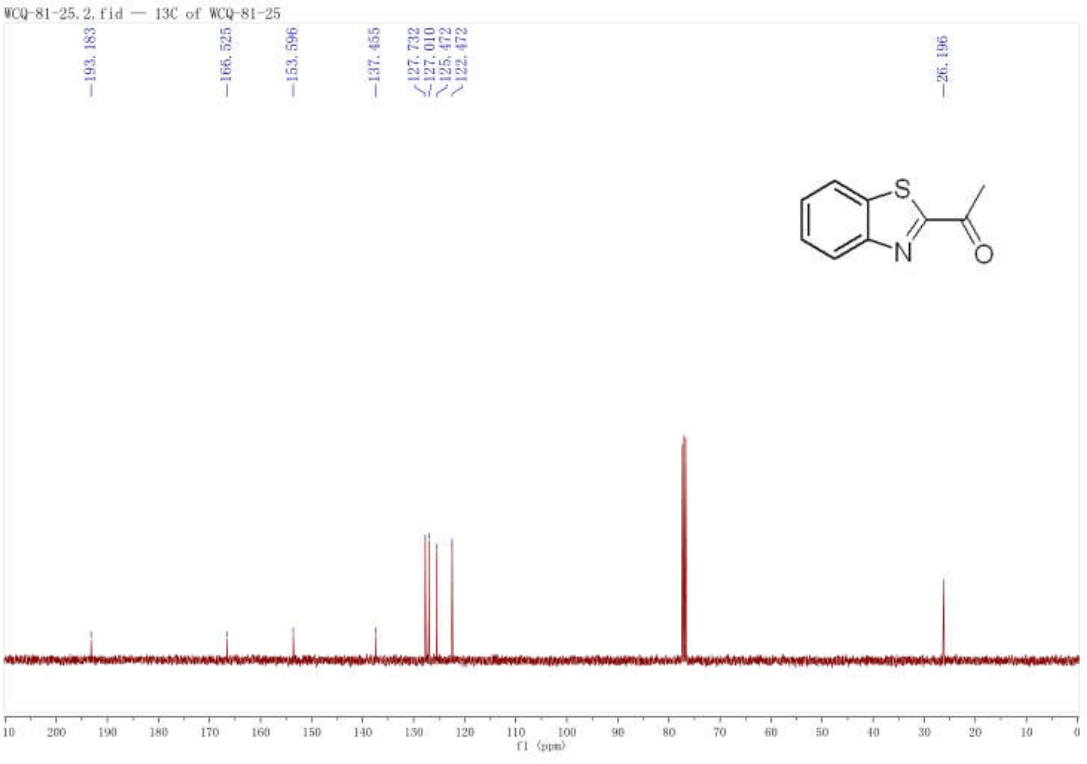




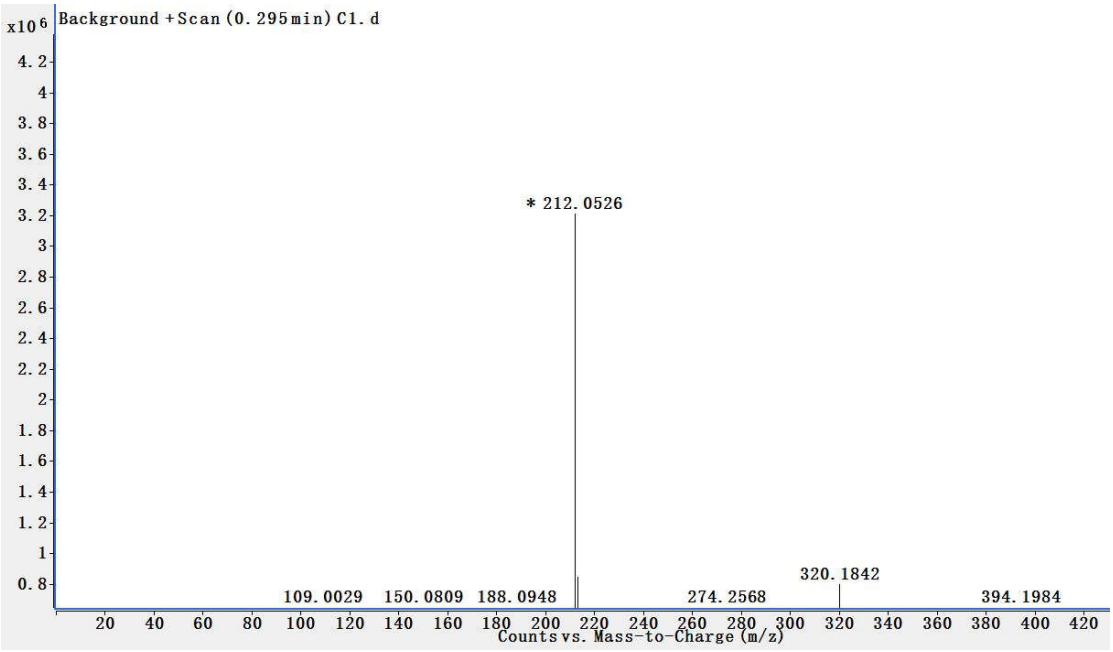
^{1}H NMR of 5d



^{13}C NMR of 5d



2. HRMS Spectra of 3a



m/z $[M + H]^+$ Calc. MS: 212.0528, Found: 212.0526

3. X-ray Crystallography of 3a

Compounds **3a** were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCDusing Cu Kα radiation. Data reduction was carried out with the diffractometer's software [1].The structures were solved by direct methods using Olex2 software[2], and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2014 [3] using a full-matrix least squares procedure based on F^2.The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2.The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.

[1] Agilent Technologies, CrysAlisPRO, Version 1.171.36.28, 2013.
[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J. J. Appl. Cryst. 2009, 42, 339.
[3] Kratzert, D.; Holstein, J. J.; Krossing, I. J. Appl. Crystallogr. 2015, 48, 933.

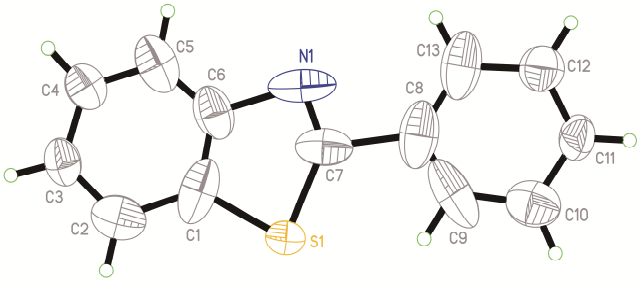


Table 1 Crystal data and structure refinement for Co-2.

Identification code	Co-2
Empirical formula	$C_{13}H_9NS$
Formula weight	211.27
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	16.3558(13)
b/Å	11.1760(9)
c/Å	5.8410(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1067.69(15)
Z	4
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	2.367
F(000)	440.0

Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.584 to 148.586
Index ranges	-20 ≤ h ≤ 20, -13 ≤ k ≤ 13, -6 ≤ l ≤ 6
Reflections collected	5010
Independent reflections	1875 [R_{int} = 0.0654, R_{sigma} = 0.0451]
Data/restraints/parameters	1875/10/147
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0953, wR_2 = 0.2831
Final R indexes [all data]	R_1 = 0.1093, wR_2 = 0.3007
Largest diff. peak/hole / e Å^{-3}	0.46/-0.31

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Co-2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S(1A)	-4001.8(13)	-4916.9(18)	-2765(7)	76.2(6)
C(8)	-4738(3)	-2836.8(19)	-563(2)	137.1(13)
C(7)	-4063(4)	-3945(7)	-542(15)	102(2)
C(10)	-5784(5)	-2031(7)	-2760(20)	123(3)
N(1)	-3740(4)	-3807(7)	1142(12)	127(2)
C(4)	-2135(4)	-6183(6)	1921(18)	101(2)
C(11)	-5958(4)	-1163(6)	-1167(17)	99(2)
C(3)	-2146(4)	-6882(6)	5(15)	92(2)
C(6)	-3157(5)	-4949(7)	776(15)	109(3)
C(2)	-2699(5)	-6603(7)	-1653(16)	113(3)
C(12)	-5492(4)	-1106(8)	721(18)	115(3)
C(1)	-3240(4)	-5584(6)	-1227(14)	122(3)
C(13)	-4893(3)	-1970.9(19)	1114(2)	139.0(13)
C(5)	-2611(5)	-5269(6)	2250(20)	123(3)
C(9)	-5153(5)	-2825(6)	-2210(20)	151(4)
S(1)	-4603(2)	-4140(4)	-2789(11)	84.5(11)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Co-2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1A)	83.6(11)	77.7(10)	67.4(11)	-11.7(11)	-5.1(13)	-2.2(9)

C(8)	78(2)	136(2)	198(3)	67(2)	26(2)	18(2)
C(7)	101(4)	123(4)	80(5)	-16(4)	15(3)	-61(3)
C(10)	109(5)	137(6)	124(7)	-23(7)	9(6)	-26(4)
N(1)	147(4)	170(5)	65(4)	-22(4)	4(4)	-86(3)
C(4)	101(4)	97(4)	106(6)	-4(5)	18(4)	8(3)
C(11)	77(3)	97(4)	123(6)	-1(4)	-20(4)	21(3)
C(3)	93(3)	82(3)	102(5)	17(4)	21(4)	18(3)
C(6)	98(4)	106(5)	123(6)	9(5)	47(4)	17(4)
C(2)	136(6)	109(5)	94(6)	-2(4)	23(5)	-33(4)
C(12)	94(4)	135(6)	117(7)	-18(5)	-7(5)	15(4)
C(1)	70(3)	122(4)	174(7)	87(4)	0(4)	-9(3)
C(13)	80(2)	140(2)	197(3)	66(2)	23(2)	17(2)
C(5)	129(5)	94(4)	144(7)	9(6)	48(6)	16(4)
C(9)	145(5)	68(3)	239(10)	-14(5)	109(5)	-6(4)
S(1)	87(2)	92(2)	75(2)	-12(2)	-12(2)	-9.8(18)

Table 4 Bond Lengths for Co-2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1A)	C(7)	1.696(8)	N(1)	C(6)	1.608(10)
S(1A)	C(1)	1.708(7)	C(4)	C(3)	1.365(12)
C(8)	C(7)	1.659(9)	C(4)	C(5)	1.299(9)
C(8)	C(13)	1.4000(13)	C(11)	C(12)	1.342(12)
C(8)	C(9)	1.179(13)	C(3)	C(2)	1.361(11)
C(8)	S(1)	1.965(5)	C(6)	C(1)	1.376(9)
C(7)	N(1)	1.127(10)	C(6)	C(5)	1.290(13)
C(7)	C(6)	2.012(12)	C(2)	C(1)	1.463(11)
C(7)	S(1)	1.597(9)	C(12)	C(13)	1.396(9)
C(10)	C(11)	1.374(13)	C(9)	S(1)	1.756(8)
C(10)	C(9)	1.399(12)			

Table 5 Bond Angles for Co-2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(7)	S(1A)	C(1)	85.4(4)	C(2)	C(3)	C(4)	117.5(7)
C(7)	C(8)	S(1)	51.4(3)	N(1)	C(6)	C(7)	34.0(3)
C(13)	C(8)	C(7)	129.1(4)	C(1)	C(6)	C(7)	83.7(6)
C(13)	C(8)	S(1)	174.7(4)	C(1)	C(6)	N(1)	117.7(7)
C(9)	C(8)	C(7)	113.4(5)	C(5)	C(6)	C(7)	156.9(7)

C(9)	C(8)	C(13)	117.4(5)	C(5)	C(6)	N(1)	122.8(7)
C(9)	C(8)	S(1)	62.1(4)	C(5)	C(6)	C(1)	119.4(7)
S(1A)	C(7)	C(6)	83.8(4)	C(3)	C(2)	C(1)	117.3(8)
C(8)	C(7)	S(1A)	120.8(5)	C(11)	C(12)	C(13)	120.1(8)
C(8)	C(7)	C(6)	155.4(5)	C(6)	C(1)	S(1A)	107.1(6)
N(1)	C(7)	S(1A)	136.8(8)	C(6)	C(1)	C(2)	119.2(7)
N(1)	C(7)	C(8)	102.4(7)	C(2)	C(1)	S(1A)	133.7(7)
N(1)	C(7)	C(6)	53.0(6)	C(12)	C(13)	C(8)	119.4(5)
N(1)	C(7)	S(1)	174.3(7)	C(6)	C(5)	C(4)	122.4(11)
S(1)	C(7)	C(8)	74.2(4)	C(8)	C(9)	C(10)	128.2(9)
S(1)	C(7)	C(6)	130.2(5)	C(8)	C(9)	S(1)	81.5(5)
C(11)	C(10)	C(9)	116.5(10)	C(10)	C(9)	S(1)	150.0(10)
C(7)	N(1)	C(6)	93.0(7)	C(7)	S(1)	C(8)	54.3(3)
C(5)	C(4)	C(3)	124.2(9)	C(7)	S(1)	C(9)	90.6(5)
C(12)	C(11)	C(10)	118.2(7)	C(9)	S(1)	C(8)	36.4(4)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Co-2.

Atom	***x***	***y***	***z***	**U(eq)**
H(10)	-6071.59	-2087.9	-4130.41	148
H(4)	-1761.38	-6373.21	3065.77	122
H(11)	-6387.12	-629.87	-1390.5	119
H(3)	-1790.28	-7524.91	-160.68	111
H(2)	-2732.07	-7042.43	-3002.19	136
H(12)	-5569.39	-490.21	1768.94	138
H(1)	-3634.43	-5369.32	-2296.77	146
H(13)	-4598.51	-1971.56	2476.32	167
H(5)	-2556.65	-4828.87	3590	147
H(9)	-5046.37	-3419.18	-3288.62	181

Table 7 Atomic Occupancy for Co-2.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
S(1A)	0.632(3)	H(1)	0.368(3)	H(9)	0.632(3)
S(1)	0.368(3)				