Supporting Information

Ultrasonic exfoliation of a Cd-based metal–organic framework into ultrathin nanosheet for visible-light-initiated trifluoromethylation and sequential oxidation–cyclisation reaction

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Experimental Section

Materials and Measurements.

All reagents and solvents are commercially available (Beijing innoChem Science & Technology Co. Ltd.), and they were further dried by the vacuum rotary evaporator to remove all traces of water and then stored in the air-filled glovebox. The 15 mL Schlenk tube charged with a magnetic stirrer, which was used as the reactor in the thioether oxidation and benzyl alcohol dehydrogenation reactions. The light was provided by a 30 W red LED light.

The chemical structures of the products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC 7890B, MS 5977A) data. GC equipped with a FID detector (Agilent Technologies, GC 7890 B) and a HP-5 5% phenyl methyl siloxane column (30m × 0.32mm × 0.5 μm), which was used for the quantifiable measure of benzotrifluoride and 2-phenylbenzimidazole. The size and morphology of catalysts were measured by a Hitachi New Generation SU8010 field emission scanning electron microscope (FE-SEM, JSM-670 F). The transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images (with an acceleration voltage of 200 kV), and selected area fast Fourier transform (FFT) pattern were measured on a JEOL JEM-3000F microscope, which with a CCD camera as the detector. A Varian Cary 500 UV-Vis spectrophotometer was used to record the UV-Vis diffuse reflectance spectra (DRS) of various solid samples. The photoelectrochemical characterization was performed on a Metrohm-Autolab AUT302N Electrochemical workstation. Photocurrent measurements were carried out in a typical three-electrode configuration with an Ag/AgCl electrode, a coiled Pt wire as the reference and counter electrode, respectively. X-ray diffraction (XRD) studies of catalyst were carried out with a Bruker D8 Advance instrument. The electron paramagnetic resonance (EPR) experiments were carried out on Bruker A300 instrument operating in the X-band at room temperature.

Single-crystal X-ray crystallography.

Diffraction data for all complexes were measured on a Bruker SMART CCD diffractometer (Mo Kα radiation and λ = 0.71073 Å) in Φ and ω scan modes. All structures were solved by direct methods, followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques on F^2 using SHELXL.[1] All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated position and refined in the isotropic direction using a riding model. Table S1 summarizes X-ray crystallographic data and refinement details for the complexes. The CCDC reference number is 2494196 for **XAIU-5**.

[1] Sheldrick, G. M. *Acta Crystallogr., Sect. C: Struct. Chem*. **2015**, *71*, 3-8.

Table S1. Crystallographic data of **XAIU-5**.

Complex	**XAIU-5**
Formula	$C_{20}H_{18}CdNO_6$
Formula weight	480.75
T (K)	100.00 (10)
Crystal system	Triclinic
Space group	P-1
a (Å)	9.0623 (2)
b (Å)	10.2537 (2)
c (Å)	13.1574 (2)
α (°)	103.975 (2)
β (°)	94.456 (2)
γ (°)	90.700 (2)
V (Å^3)	1182.23 (4)
Z	2
D_c(g cm^{-3})	1.351
μ (mm^{-1})	7.665
Reflns coll.	13486
Unique reflns	4670
R_{int}	0.0322
$^aR_1[I \geq 2\sigma(I)]$	0.0440
$^bwR_2$(all data)	0.1513
GOF	1.175

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) of **XAIU-5**.

Bond lengths (Å)					
Cd1—O2^{i}	2.307 (4)	Cd1—O4^{ii}	2.345 (4)	Cd1—O5	2.257 (4)
Cd1—O3^{ii}	2.399 (4)	Cd1—O1	2.232 (4)	Cd1—O6	2.345 (5)
Bond angles (°)					
O2^{i}—Cd1—O3^{ii}	93.80 (13)	O5—Cd1—O4^{ii}	145.94 (14)	O1—Cd1—O3^{ii}	141.99 (13)
O2^{i}—Cd1—O4^{ii}	100.87 (14)	O5—Cd1—O6	85.21 (18)	O1—Cd1—O5	126.61 (14)
O2^{i}—Cd1—O6	165.81 (18)	O4^{ii}—Cd1—O3^{ii}	55.42 (12)	O1—Cd1—O4^{ii}	86.91 (13)
O5—Cd1—O2^{i}	81.62 (14)	O4^{ii}—Cd1—O6	92.99 (19)	O1—Cd1—O6	84.92 (17)
O5—Cd1—O3^{ii}	90.58 (13)	O1—Cd1—O2^{i}	98.72 (14)	O6—Cd1—O3^{ii}	91.58 (17)
Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) x, y-1, z; (iii) -x+2, -y+2, -z+2; (iv) x, y+1, z.					

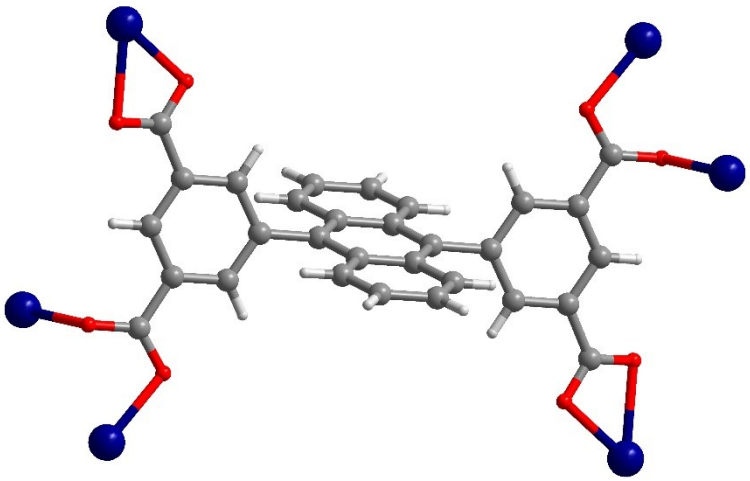


Figure S1. The coordinated mode for **ADPA**$^{4-}$ ligand for **XAIU-5**.

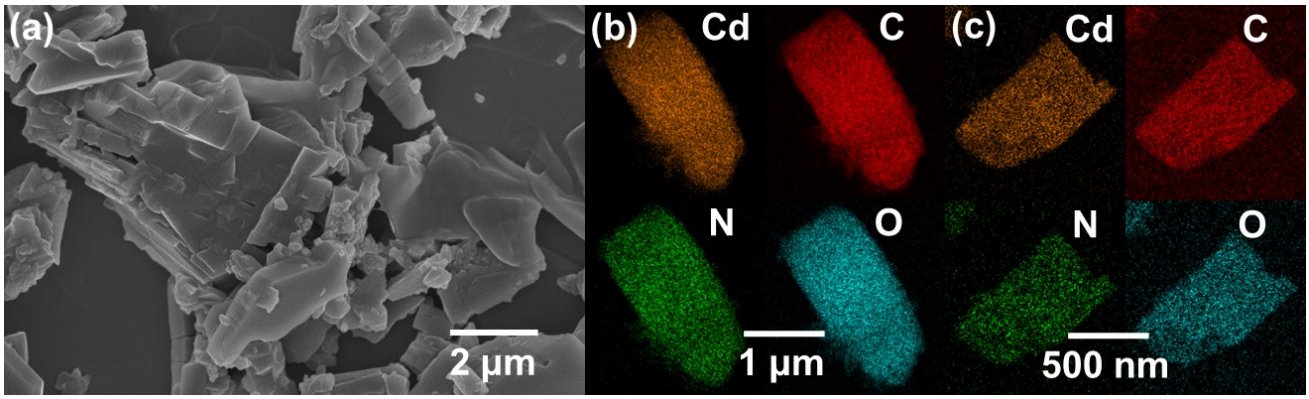


Figure S2. (a) The FE-SEM images of XAIU-5; TEM mapping images of **XAIU-5** (b) and **XAIU-5-NS** (c).

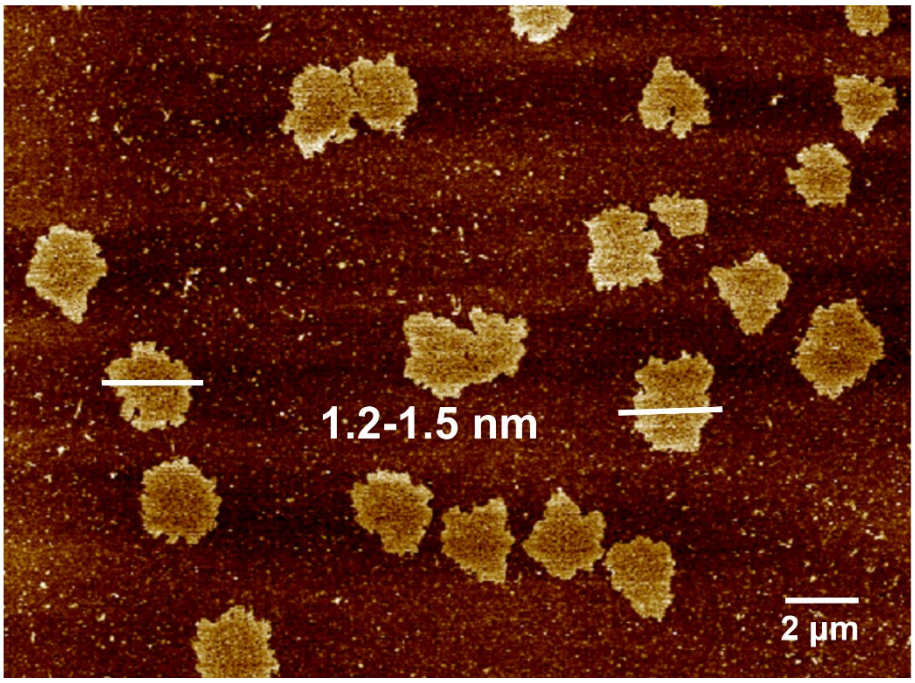


Figure S3. AFM image of **XAIU-5-NS**.

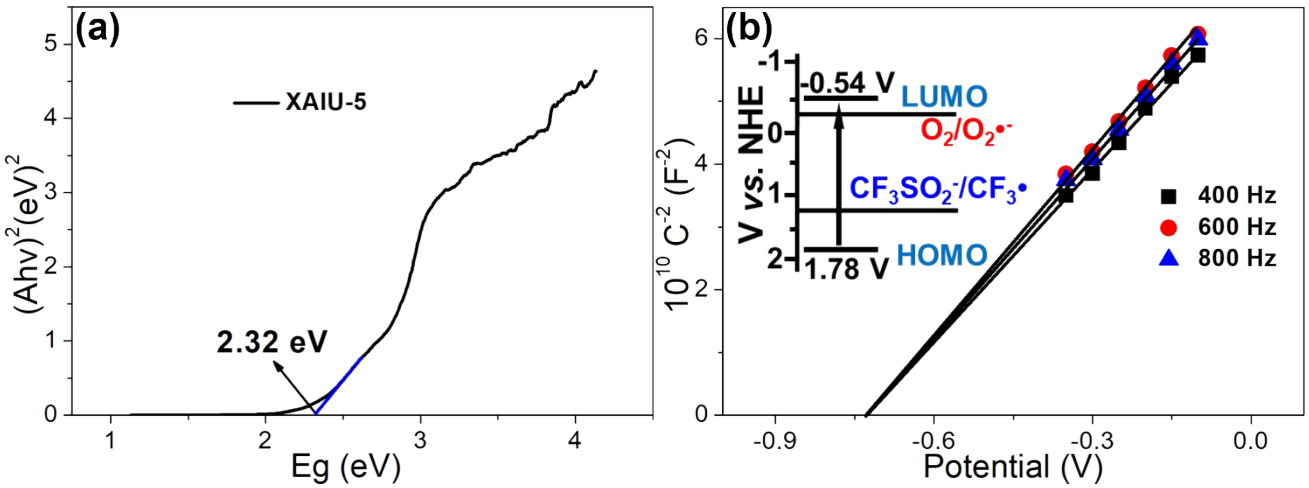


Figure S4. (a) The Tauc plot of **XAIU-5**; (b) the Mott–Schottky plots for **XAIU-5** in 0.2 mol/L Na_2SO_4 aqueous solution.

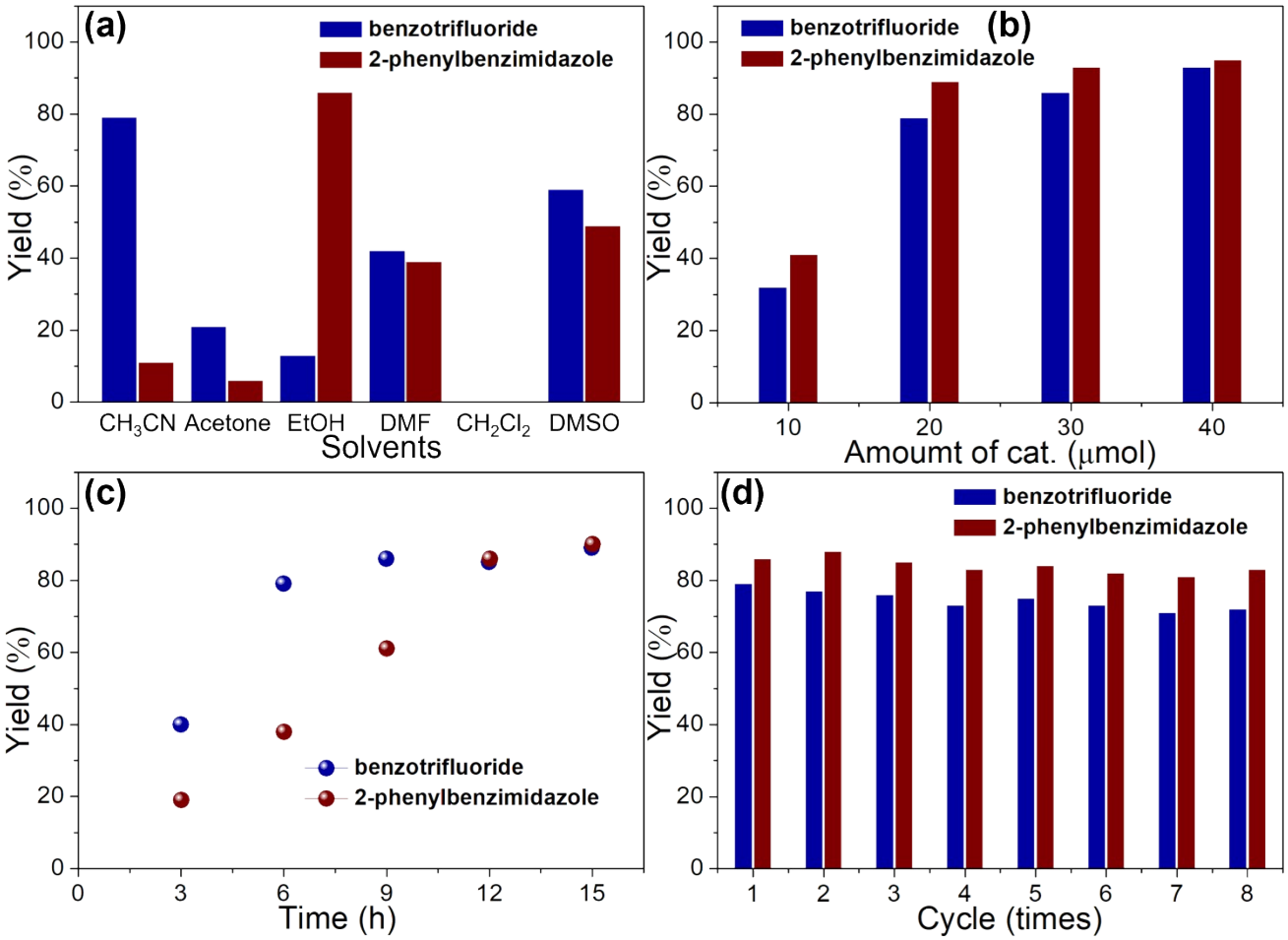


Figure S5. (a) Yields of benzotrifluoride and 2-phenylbenzimidazole in different solvents; (b) the influence of photocatalyst amounts in photocatalytic reactions; (c) the influence of irradiation time on the yield of benzotrifluoride and 2-phenylbenzimidazole of **XAIU-5-NS**; (d) cycling runs for the photocatalytic trifluoromethylation reaction and the sequential oxidation–cyclisation reaction in the presence of **XAIU-5-NS**.

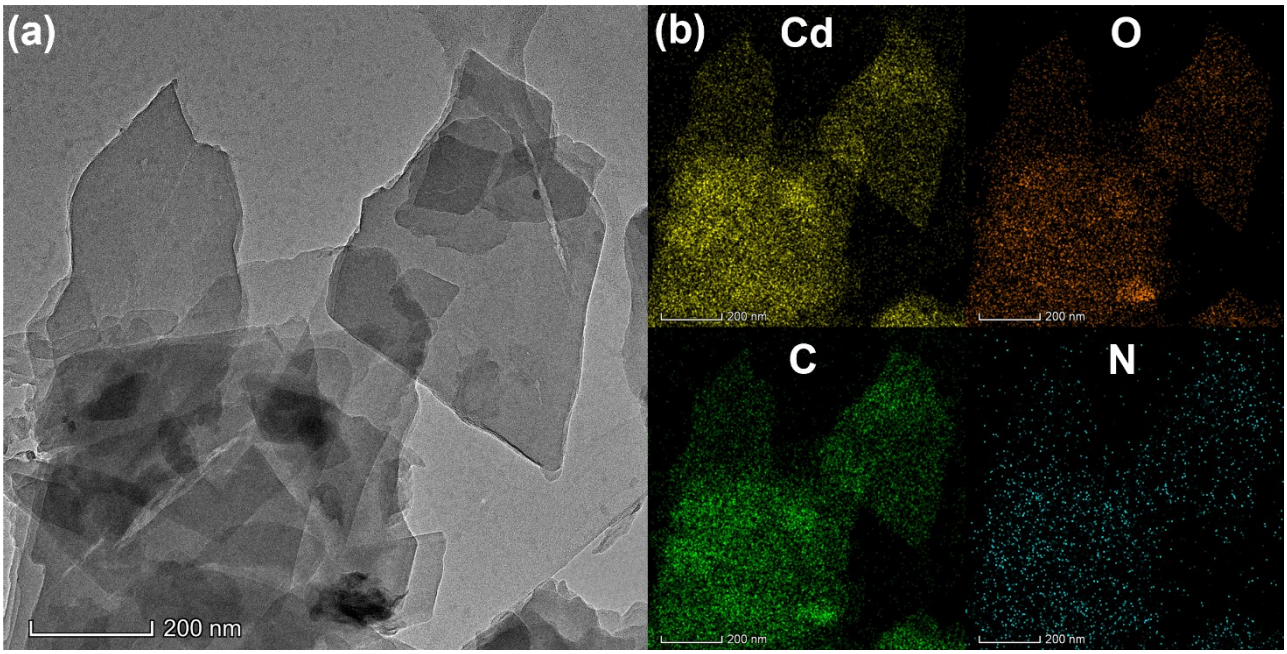
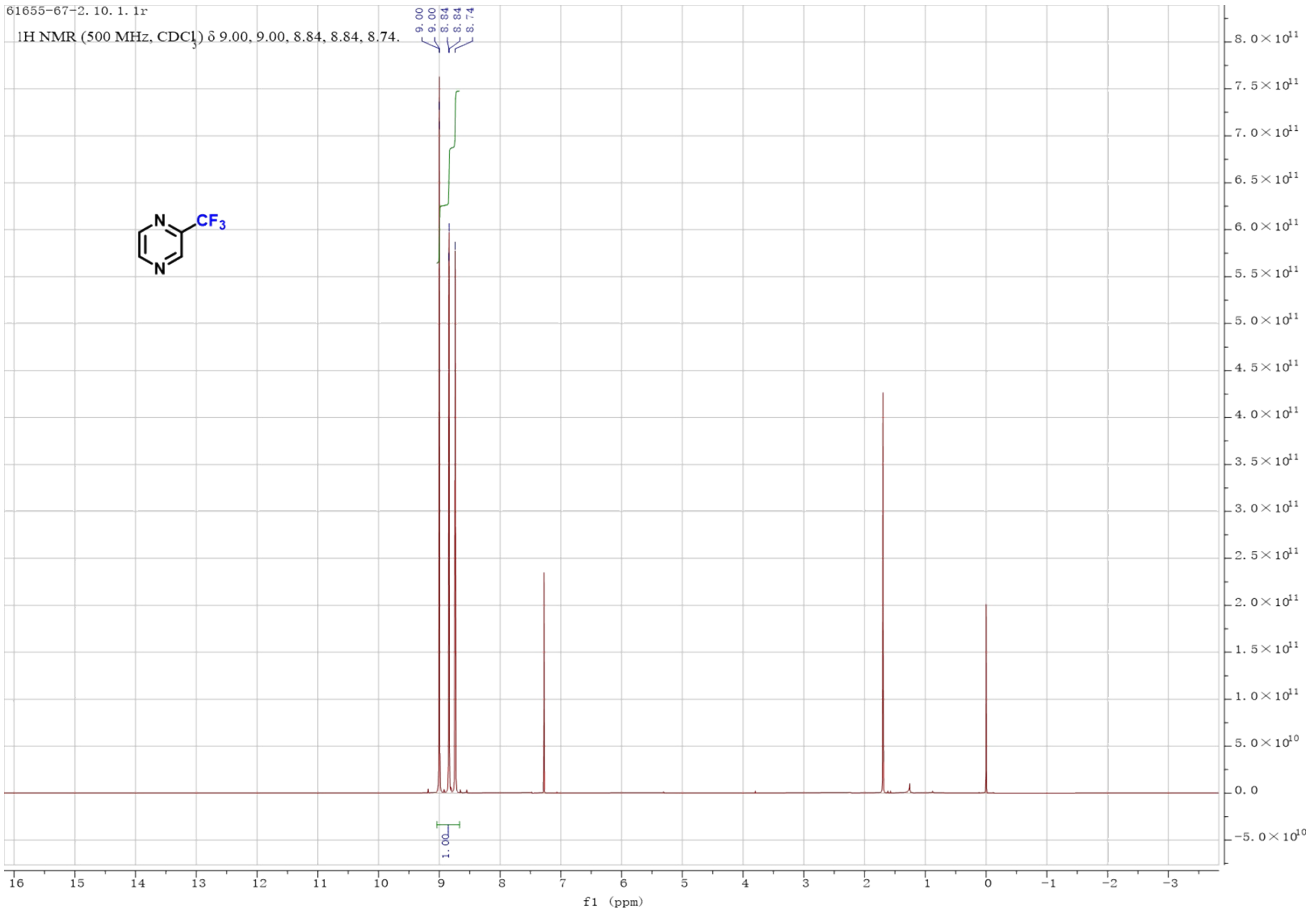


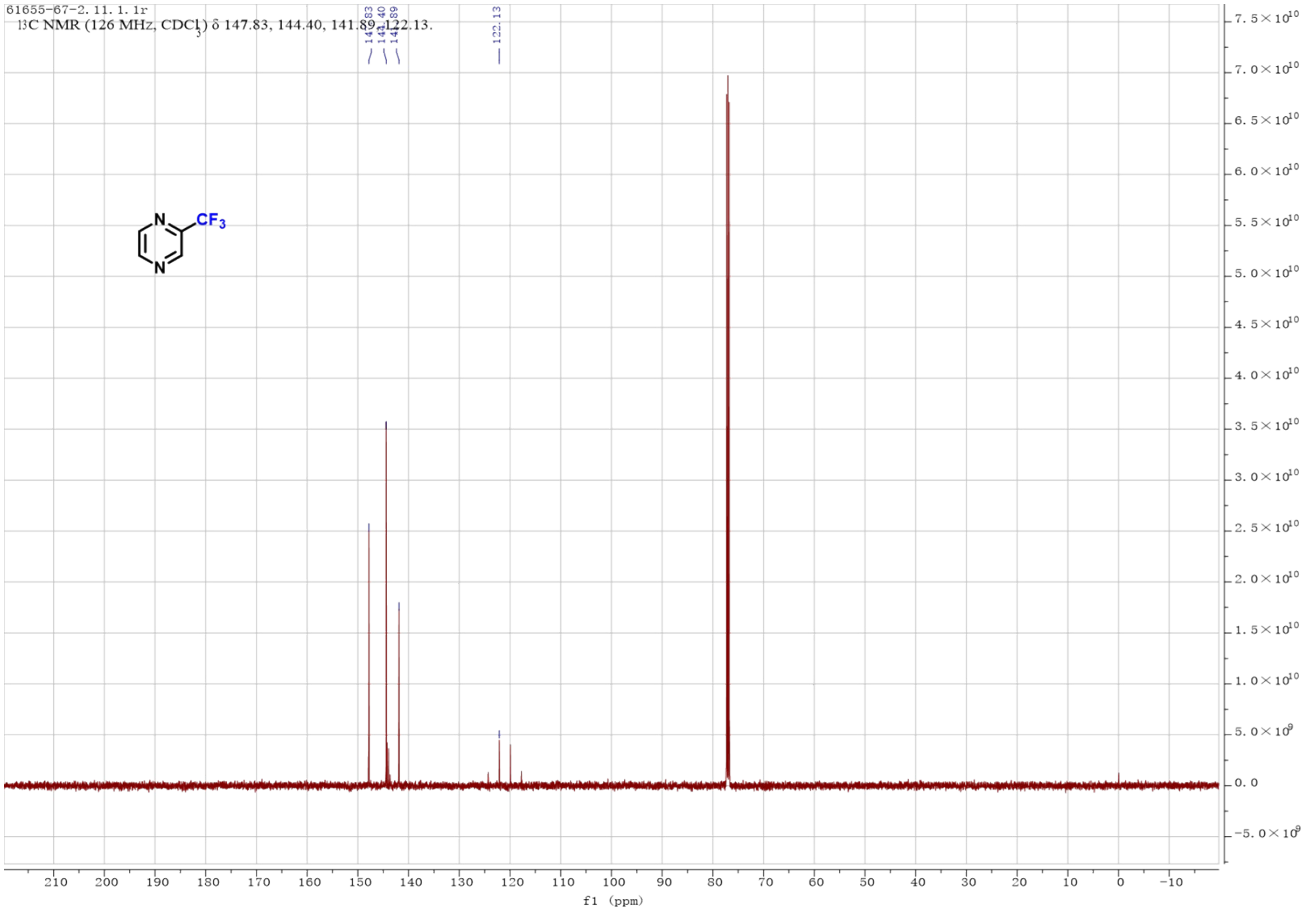
Figure S6. (a) The TEM image of **XAIU-5-NS** after eight cycles of reaction; (b) TEM mapping images of **XAIU-5-NS** after eight cycles of reaction.

NMR Data of Products

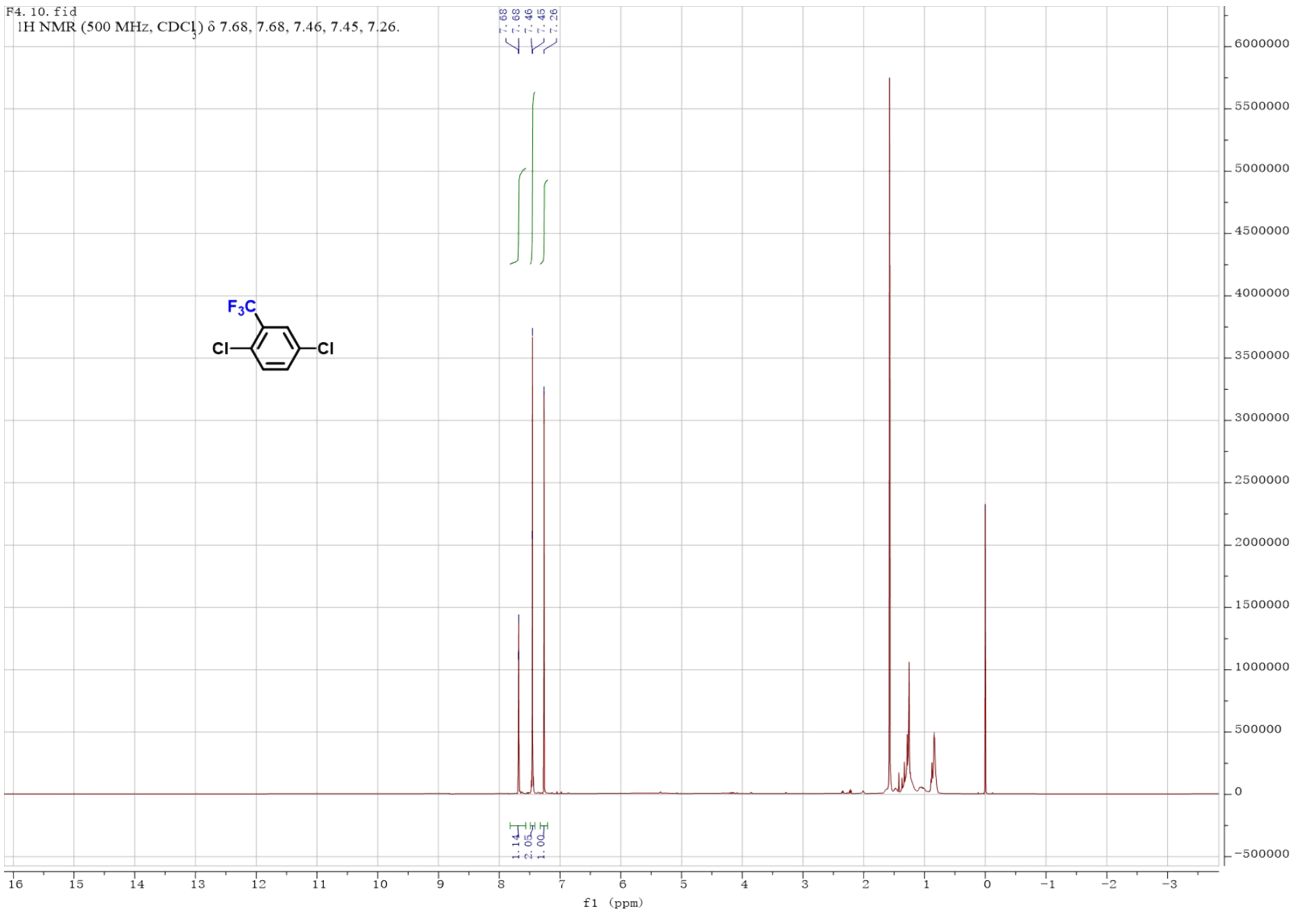
Separation process for target products

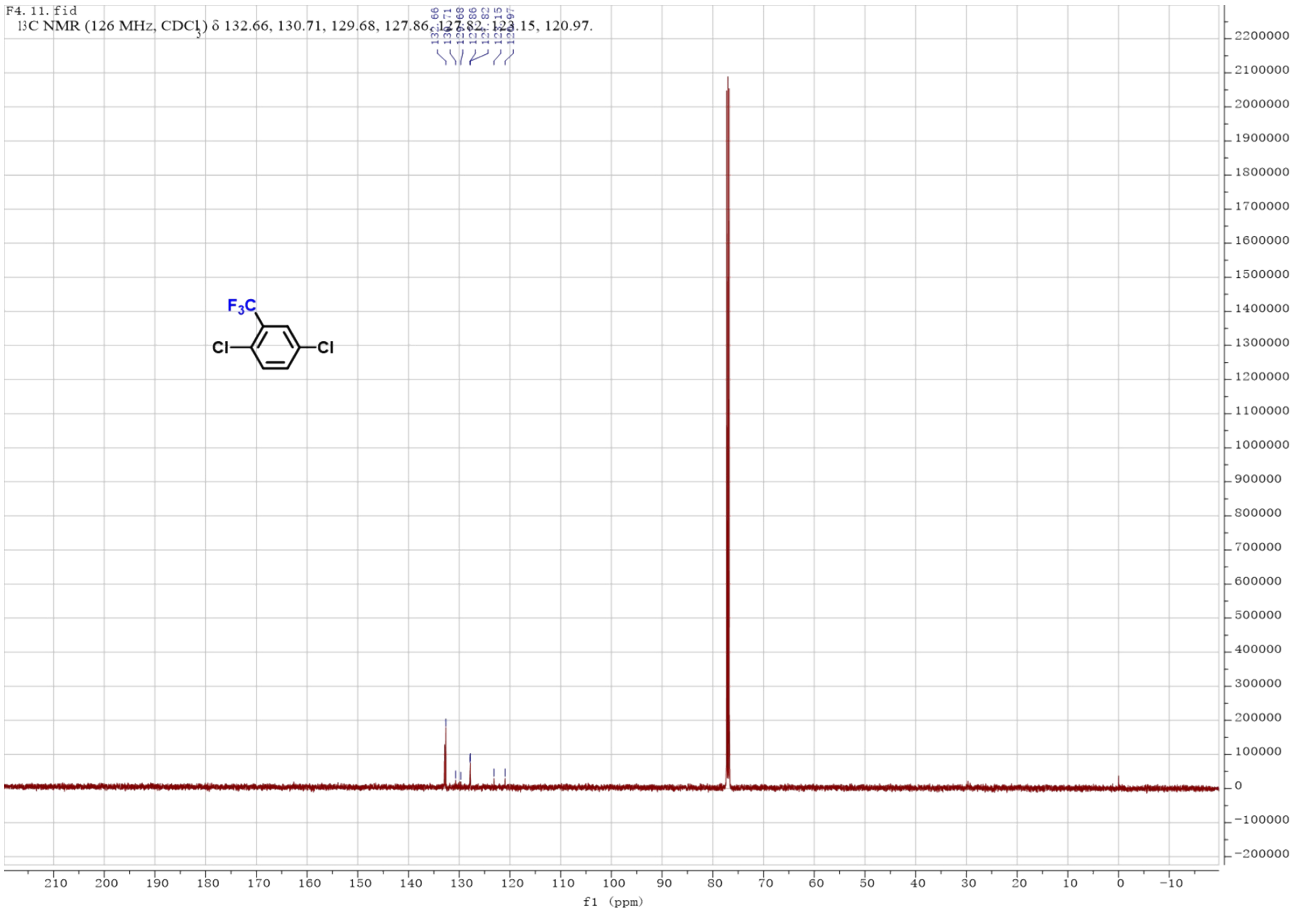
After reaction, solvent not participating in the reaction was removed under reduced pressure. The crude products were purified by SiO_2/Al_2O_3 column chromatography using acetic ether and petroleum ether (V:V=1:1) as an eluent so that the white solids acylamide derivatives can be obtained. 0.25 mm silica gelcoated glass plates were used in the thin layer chromatography (TLC).

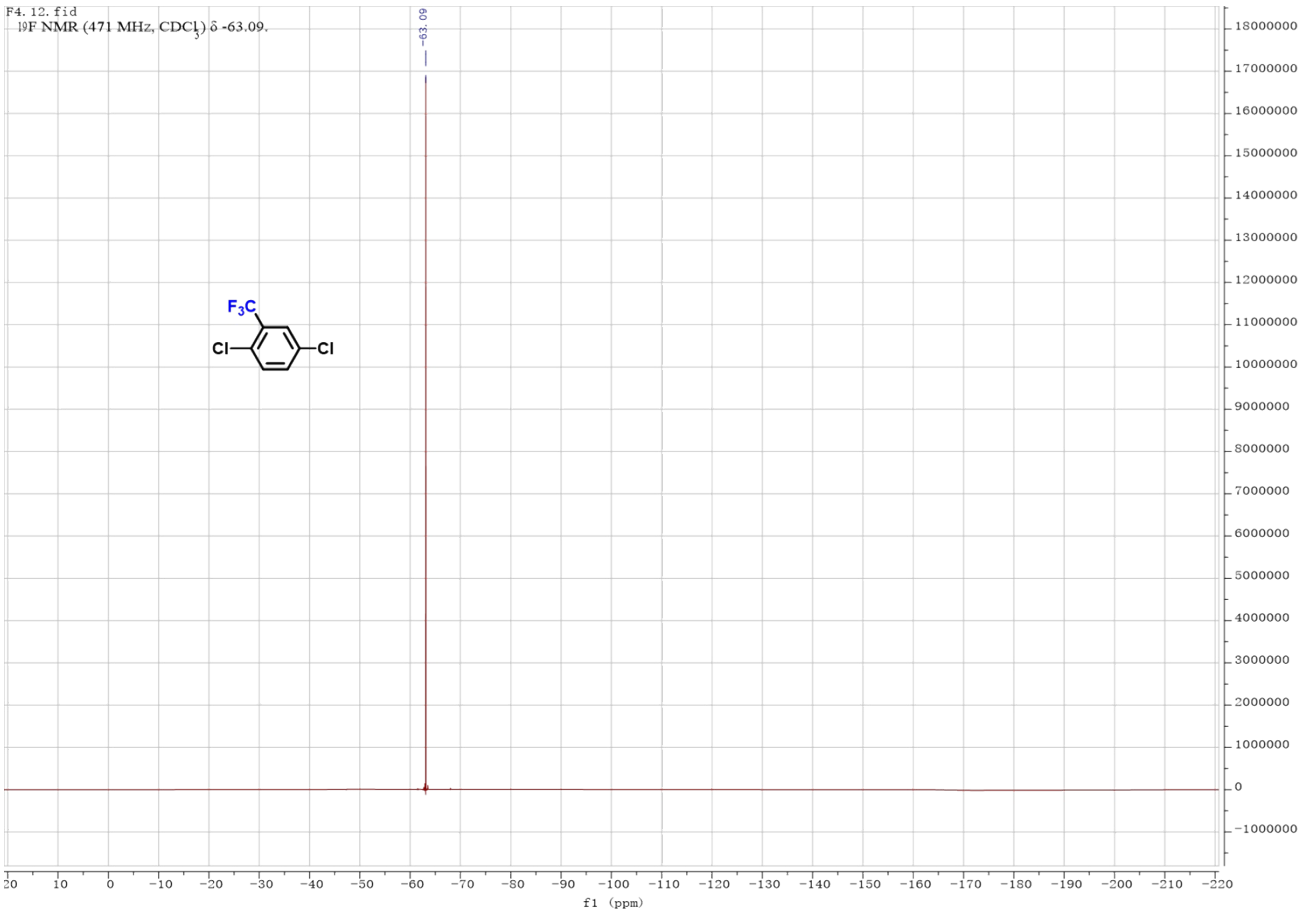

61655-67-2. 10. 1. 1r
1H NMR (500 MHz, CDCl3) δ 9.00, 9.00, 8.84, 8.84, 8.74.
9.00
9.00
8.84
8.84
8.74
CF3
1.00
f1 (ppm)


61655-67-2. 11. 1. 1r
13C NMR (126 MHz, CDCl3) δ 147.83, 144.40, 141.89, 122.13.
147.83
144.40
141.89
122.13
CF3
f1 (ppm)


61655-67-2. 12. 1. 1r
19F NMR (471 MHz, CDCl3) δ -67.86.
-67.86
CF3
f1 (ppm)

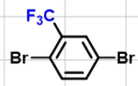

F4. 10. fid
1H NMR (500 MHz, CDCl3) δ 7.68, 7.68, 7.46, 7.45, 7.26.
7.68
7.68
7.46
7.45
7.26
F3C
Cl
Cl
1.14
2.05
1.00
f1 (ppm)


F4. 11. fid
13C NMR (126 MHz, CDCl3) δ 132.66, 130.71, 129.68, 127.86, 127.82, 123.15, 120.97.
F3C
Cl
Cl
f1 (ppm)


F4. 12. fid
19F NMR (471 MHz, CDCl3) δ -63.09.
-63.09
F3C
Cl
Cl
f1 (ppm)

F5. 10. fid

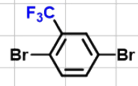
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82, 7.81, 7.58, 7.56, 7.52, 7.52, 7.26.



f1 (ppm)

F5. 11. fid

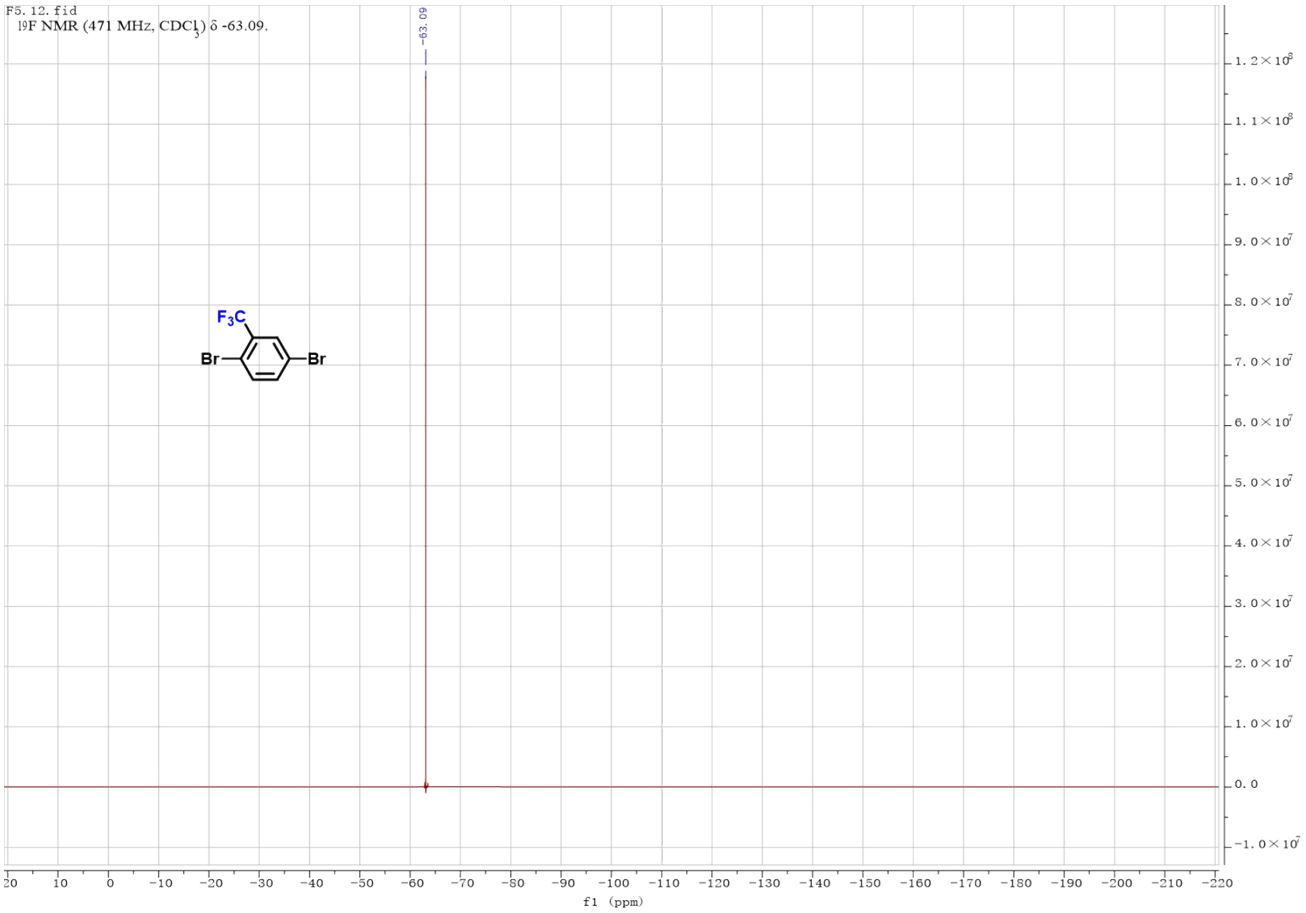
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.33, 135.99, 131.84, 131.03, 130.98, 130.94, 130.89, 125.28, 123.10, 121.17, 120.93, 118.79, 118.77.



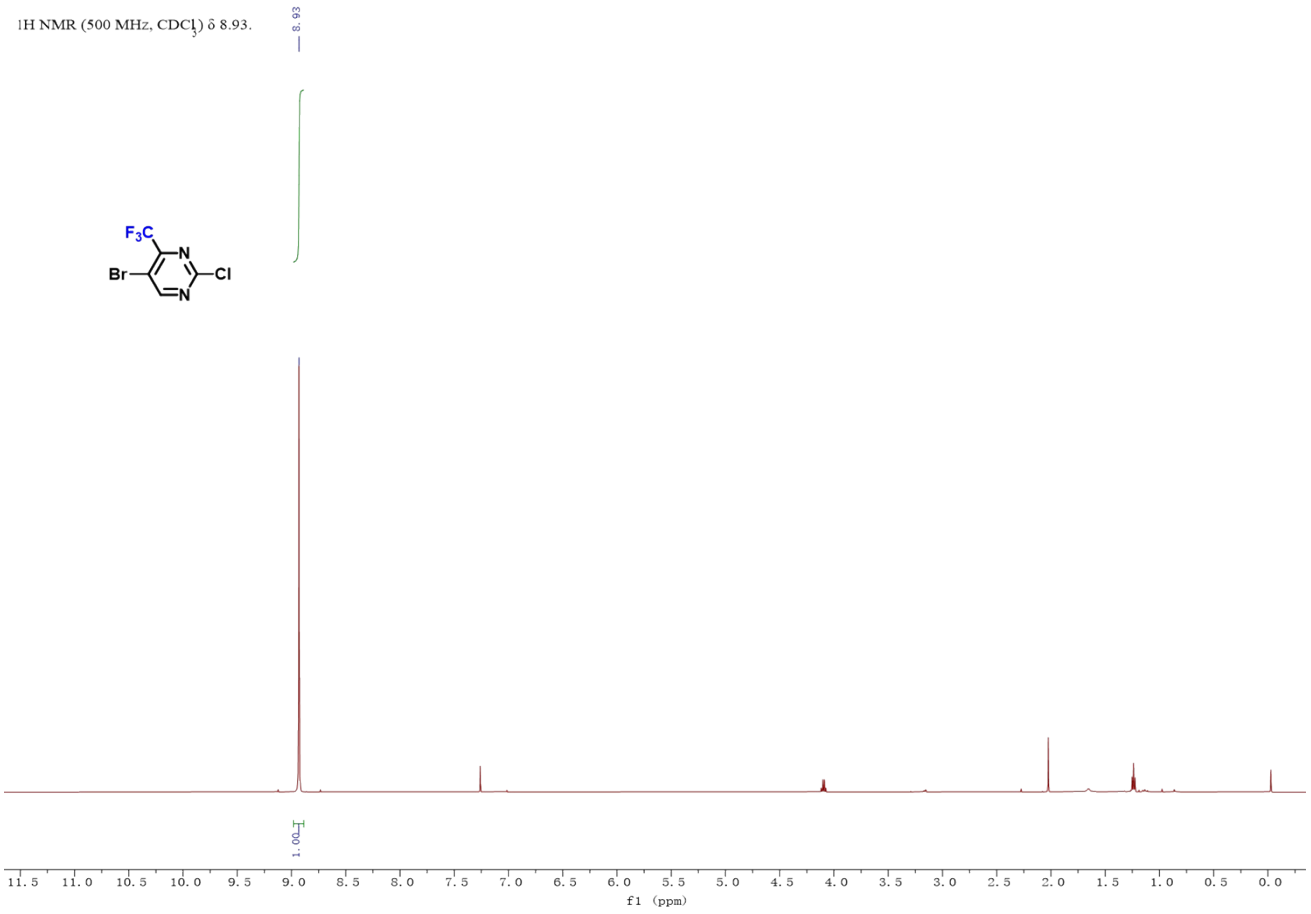
f1 (ppm)

F5. 12. fid

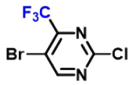
^{19}F NMR (471 MHz, $CDCl_3$) δ -63.09.

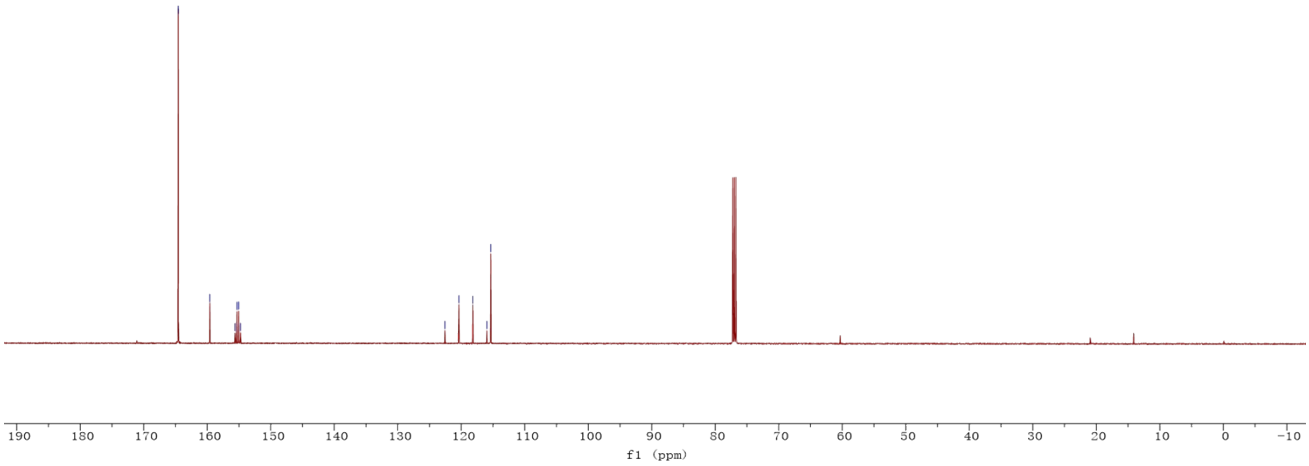


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93.

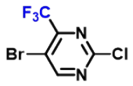


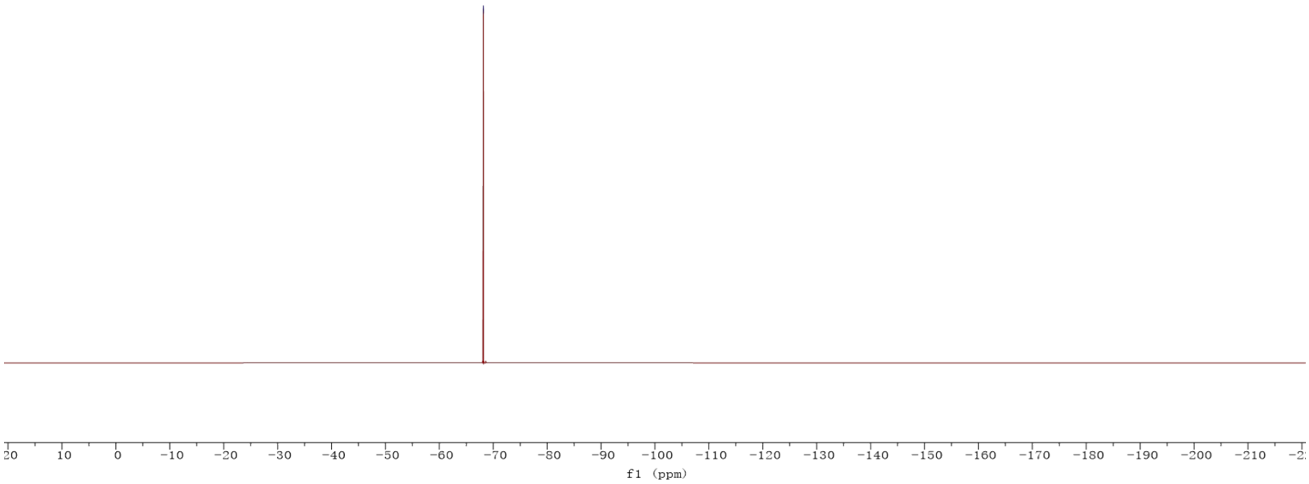
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.56, 159.60, 155.63, 155.33, 155.04, 154.75, 122.58, 120.38, 118.17, 115.97, 115.34.

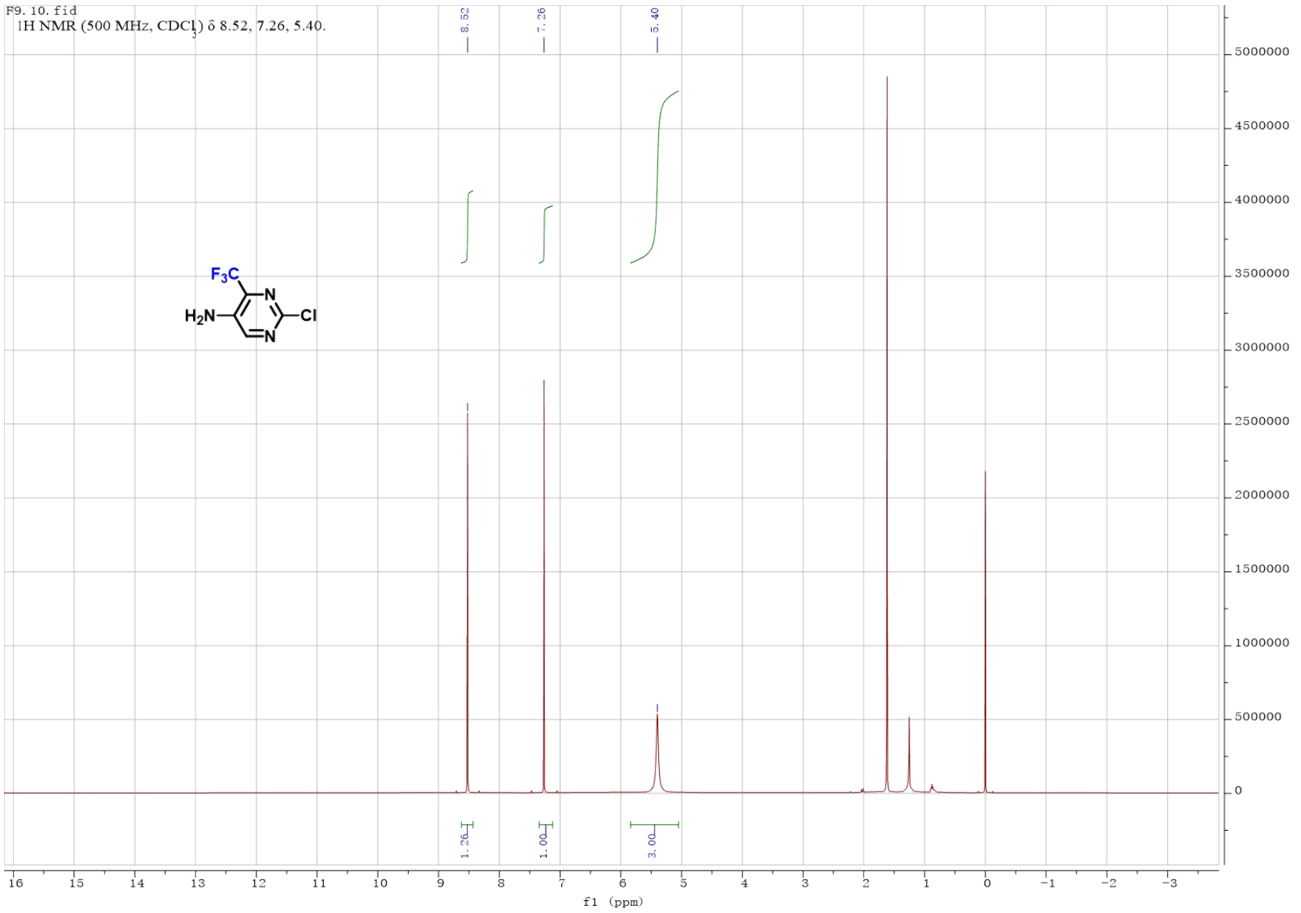


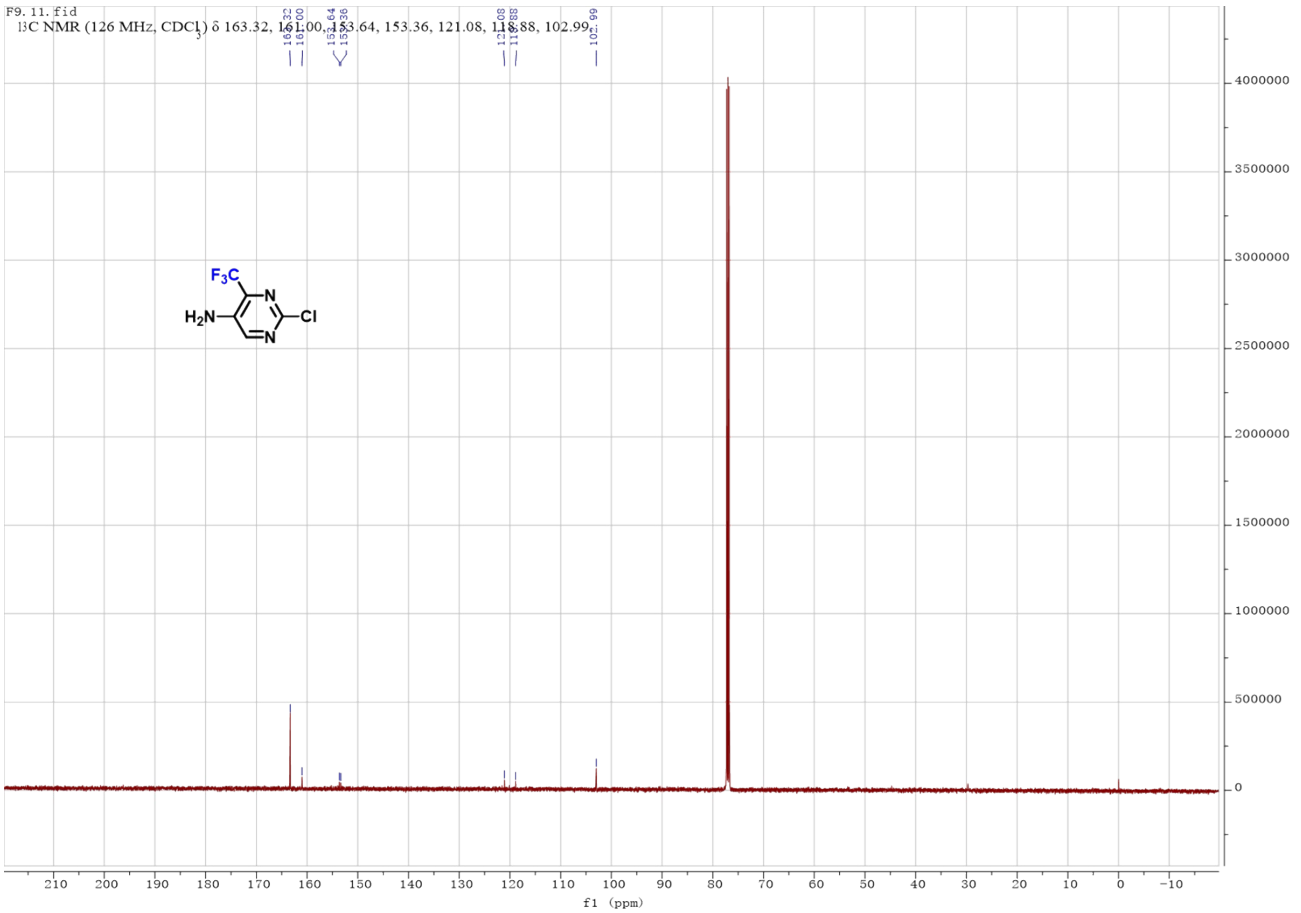


^{19}F NMR (471 MHz, $CDCl_3$) δ -68.20.



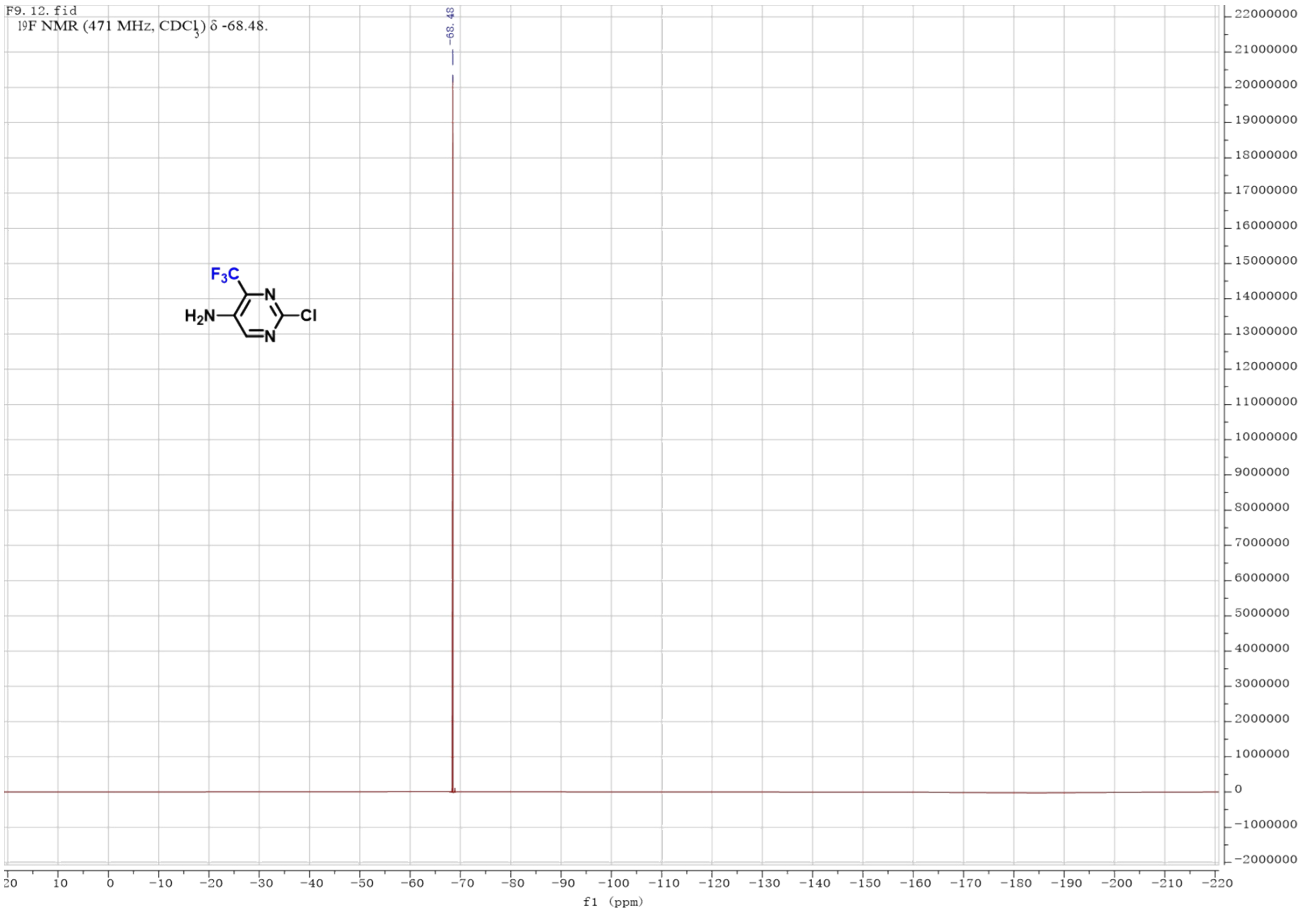



F9. 10. fid
1H NMR (500 MHz, CDCl3) δ 8.52, 7.26, 5.40.
8.52
7.26
5.40
F3C
H2N
N
Cl
1.26
1.00
3.00
f1 (ppm)

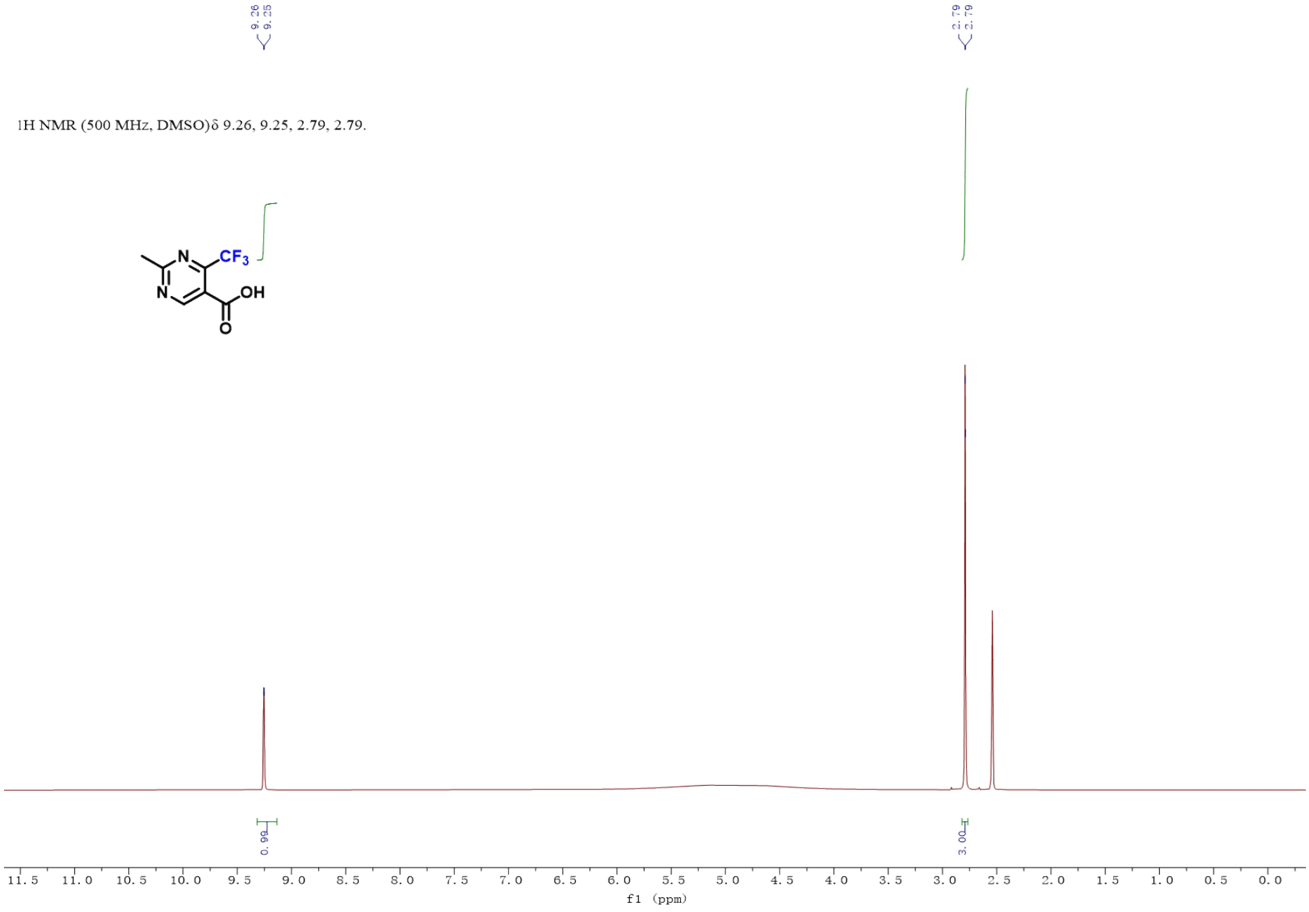

F9. 11. fid
13C NMR (126 MHz, CDCl3) δ 163.32, 161.00, 153.64, 153.36, 121.08, 118.88, 102.99.
163.32
161.00
153.64
153.36
121.08
118.88
102.99
F3C
H2N
N
Cl
f1 (ppm)

F9. 12. fid

^{19}F NMR (471 MHz, $CDCl_3$) δ -68.48.

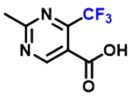


^{1}H NMR (500 MHz, DMSO)δ 9.26, 9.25, 2.79, 2.79.



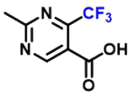
170.05
165.01
160.44
151.89
151.61
151.32
151.04
123.98
122.82
121.78
119.59
117.39
26.02
26.00

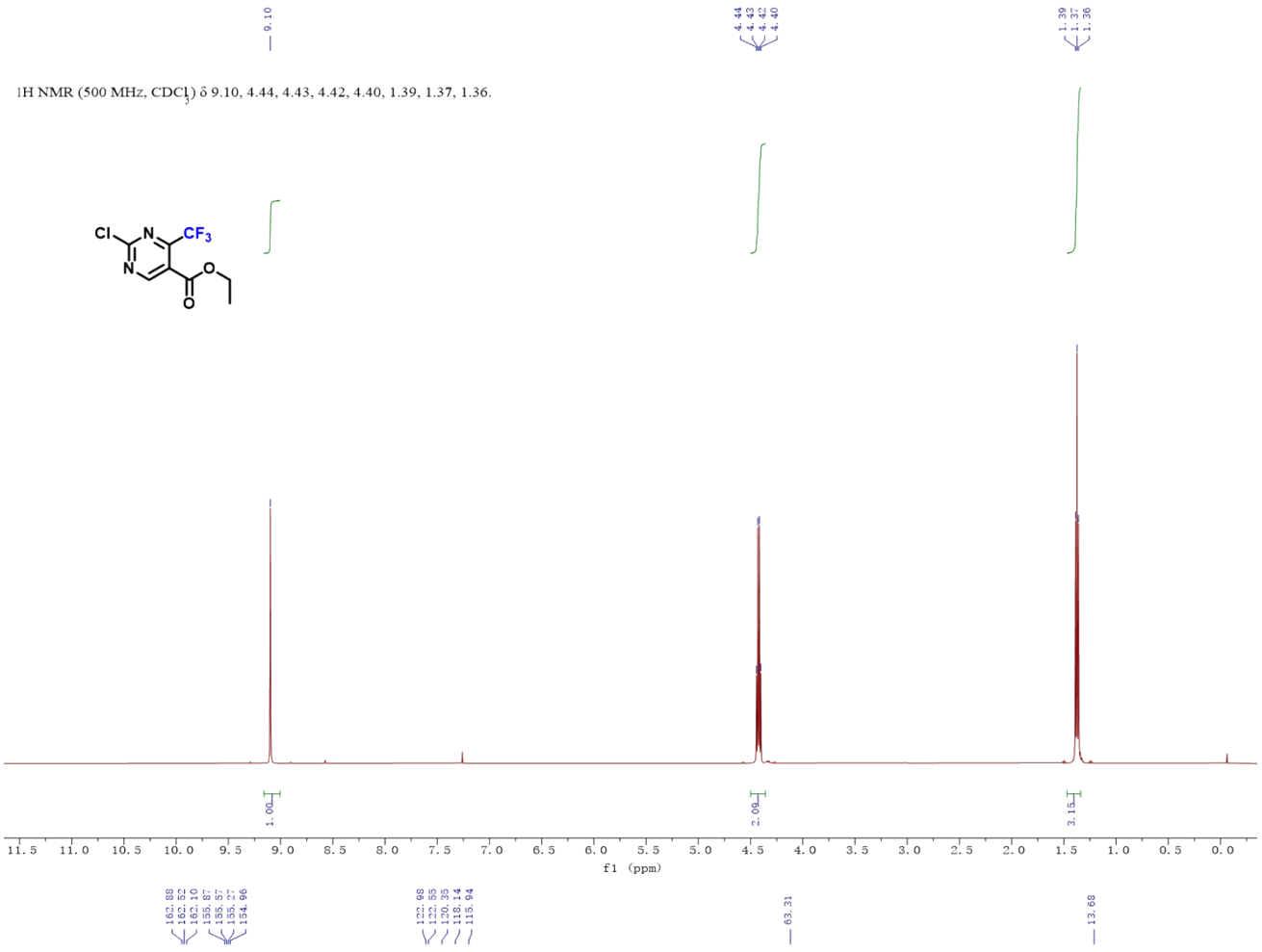
^{13}C NMR (126 MHz, DMSO)δ 170.05, 165.01, 160.44, 151.89, 151.61, 151.32, 151.04, 123.98, 122.82, 121.78, 119.59, 117.39, 26.02, 26.00.



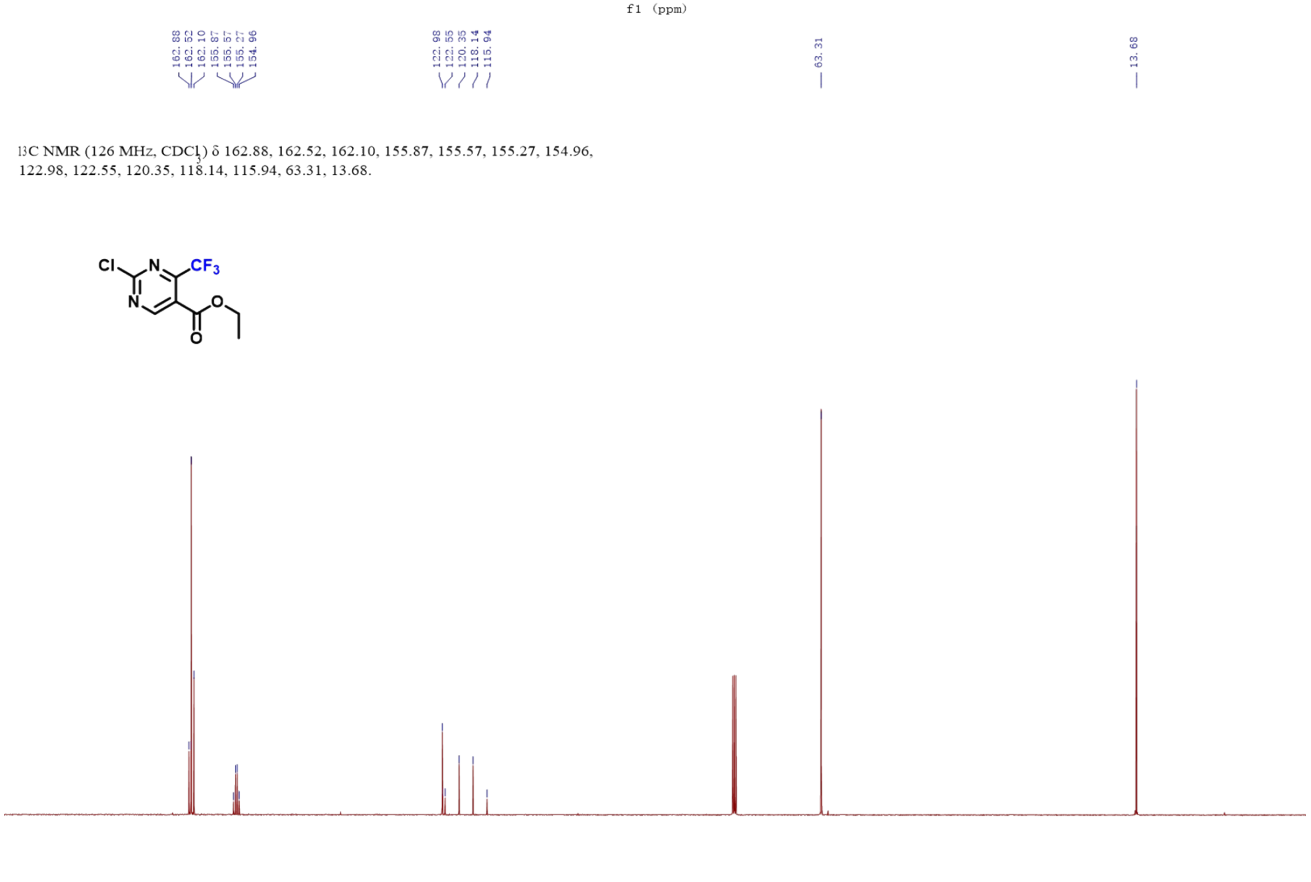
^{19}F NMR (471 MHz, DMSO)δ -65.37, -65.38, -65.39, -65.41.

-65.37
-65.38
-65.39
-65.41



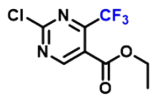


^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10, 4.44, 4.43, 4.42, 4.40, 1.39, 1.37, 1.36.



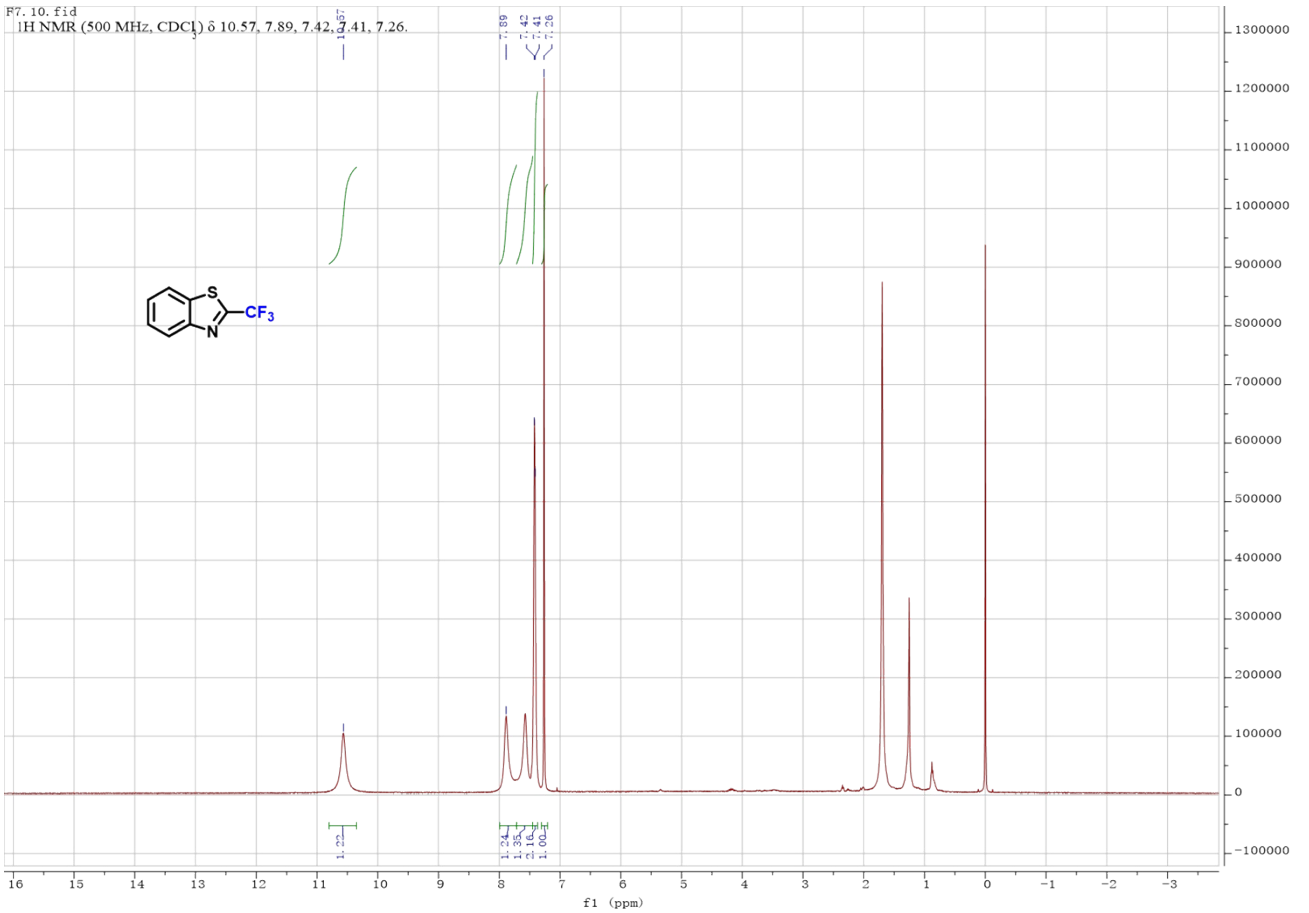
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.88, 162.52, 162.10, 155.87, 155.57, 155.27, 154.96, 122.98, 122.55, 120.35, 118.14, 115.94, 63.31, 13.68.

^{19}F NMR (471 MHz, $CDCl_3$) δ -66.37.



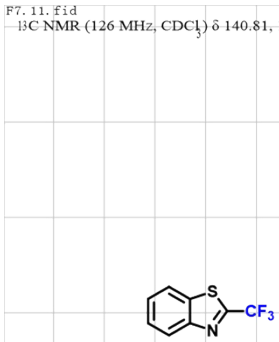
F7. 10. fid

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57, 7.89, 7.42, 7.41, 7.26.



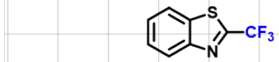
F7. 11. fid

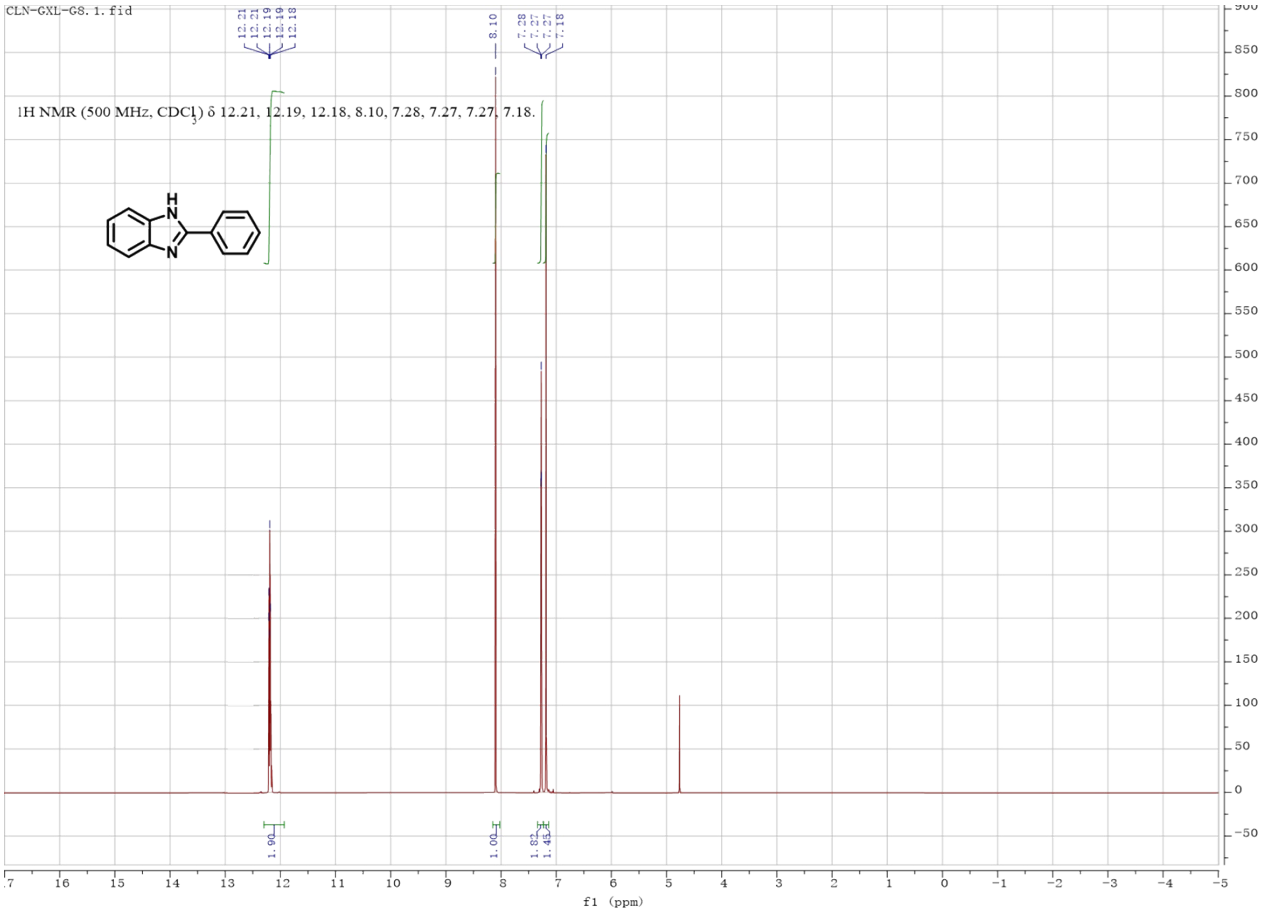
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.81, 140.49, 125.75, 124.02, 119.82, 117.67.

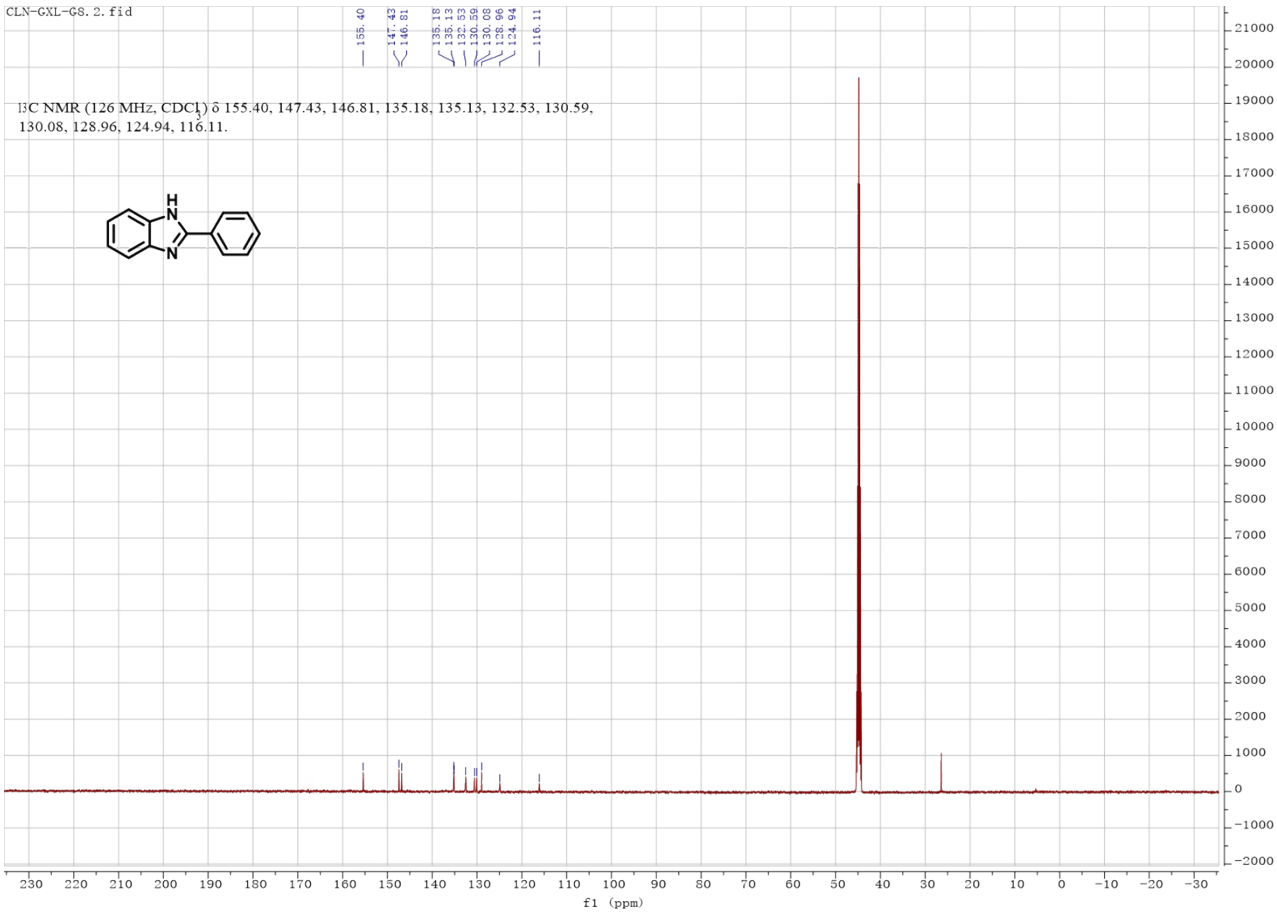


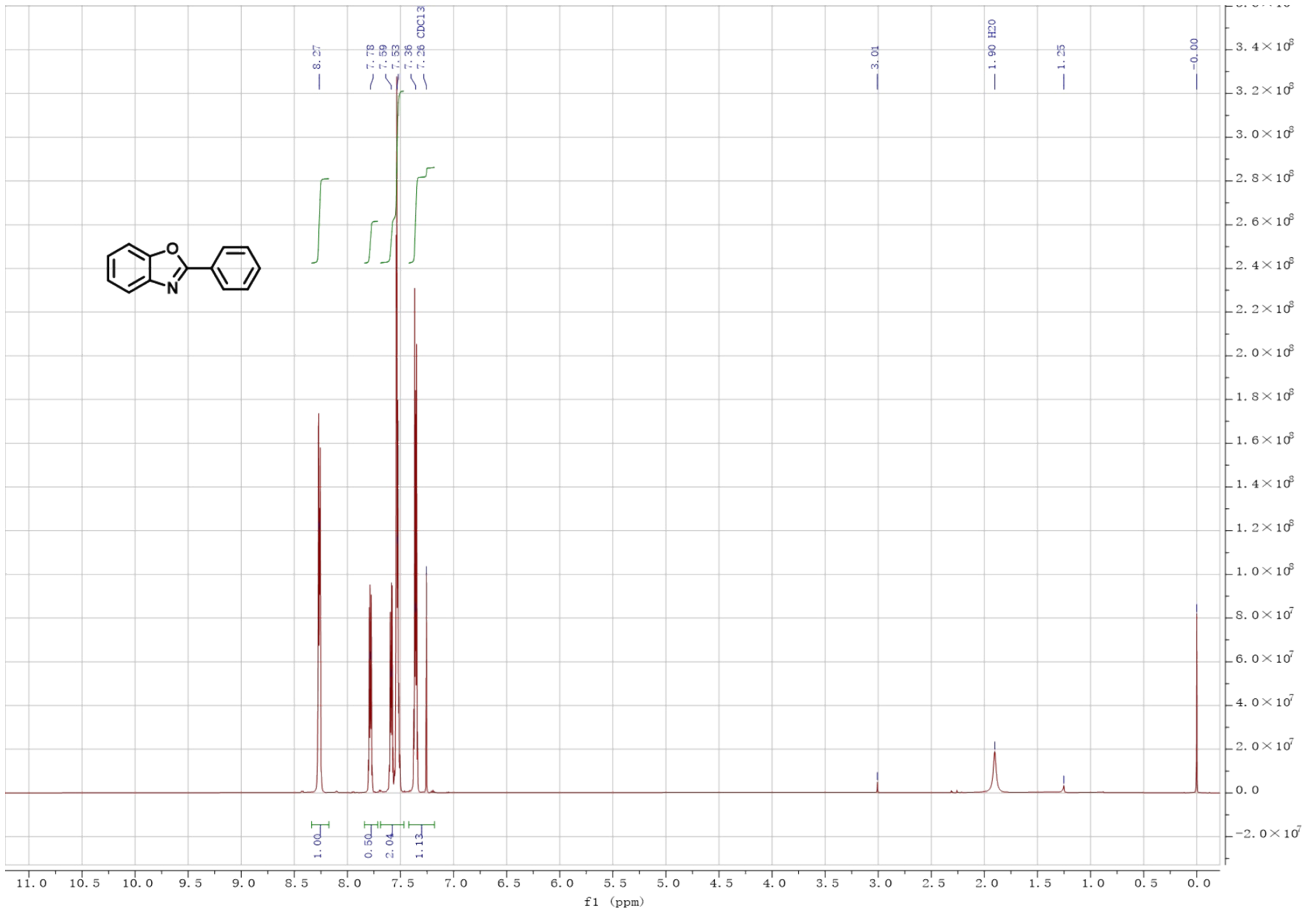
F7. 12. fid

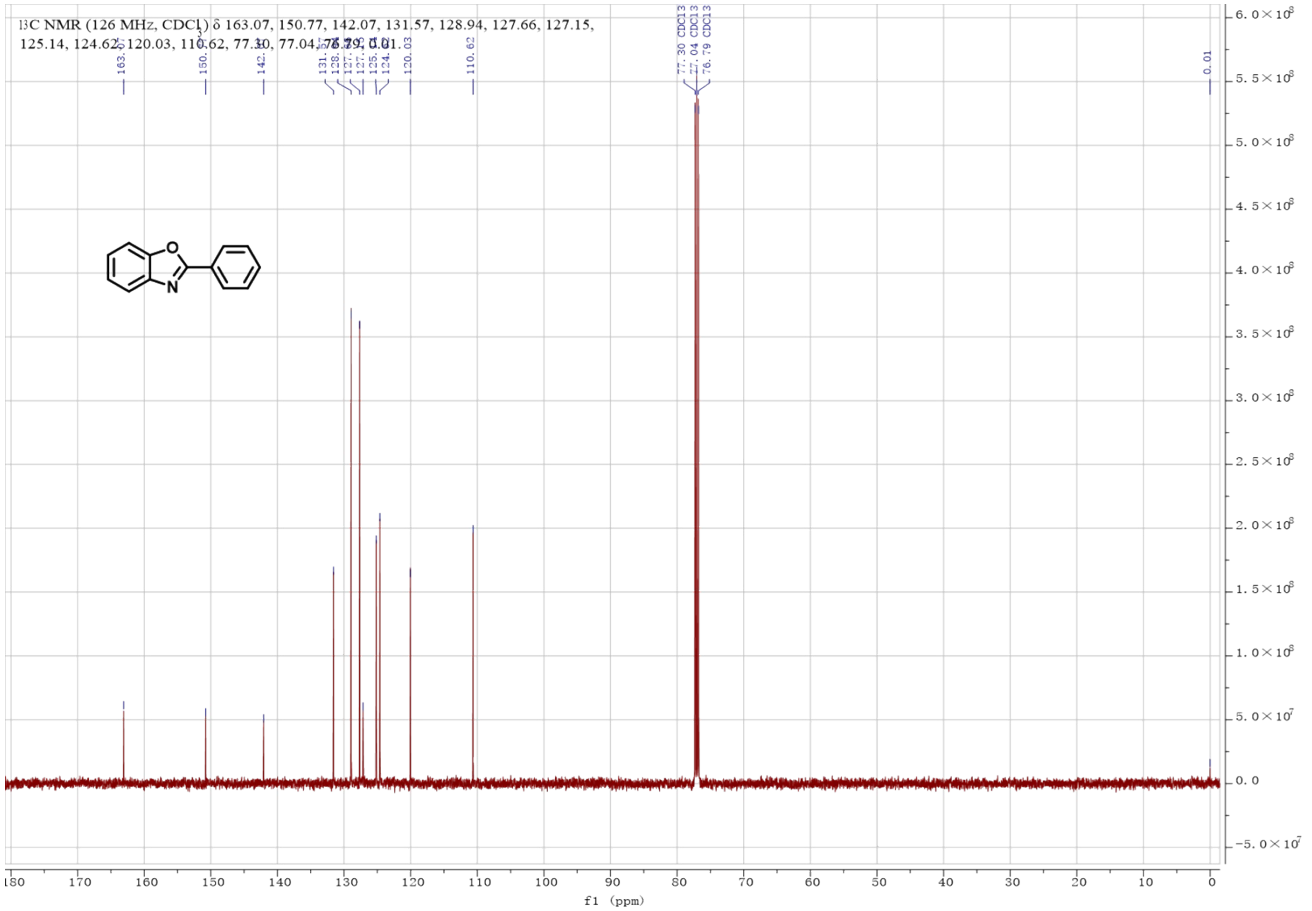
^{19}F NMR (471 MHz, $CDCl_3$) δ -64.14.

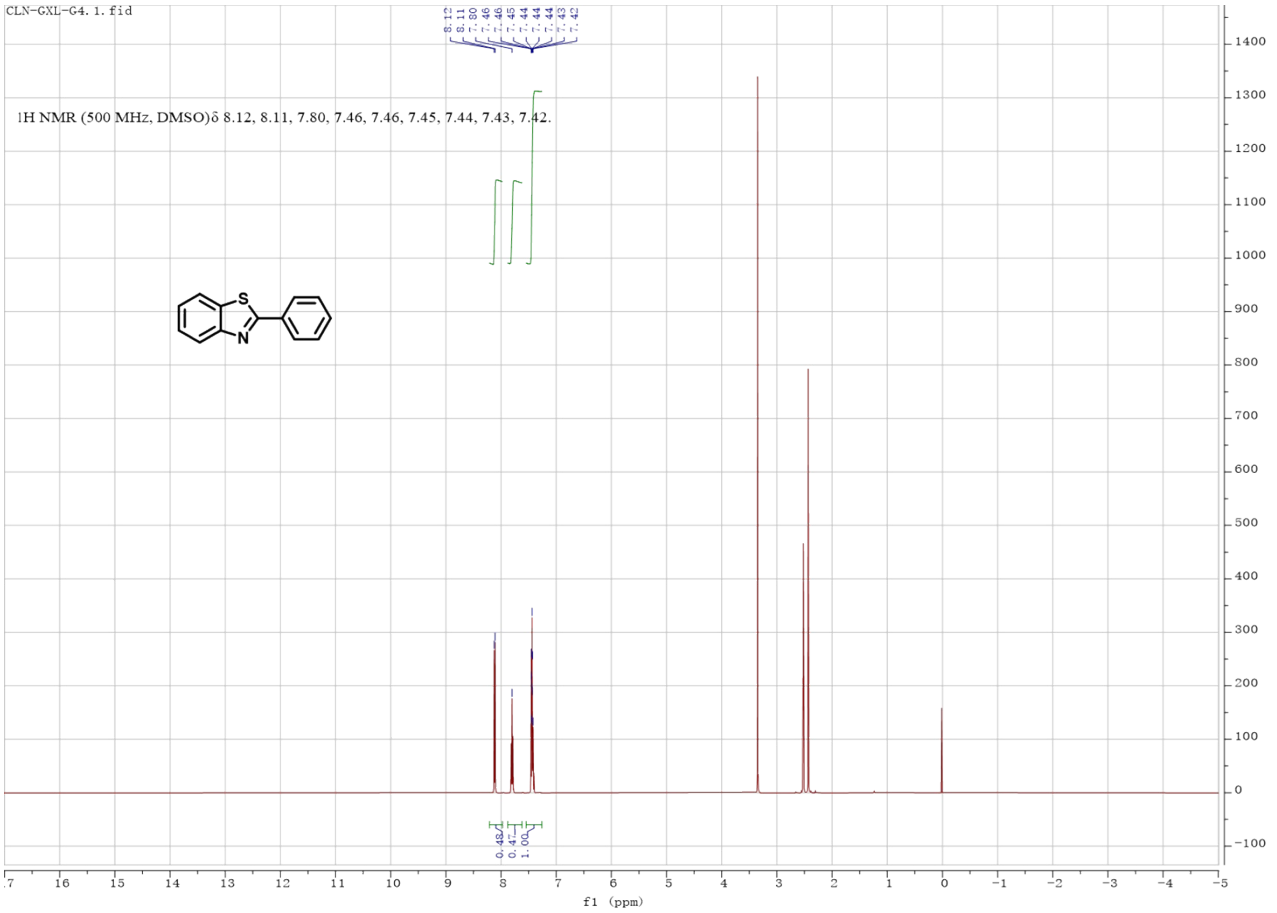


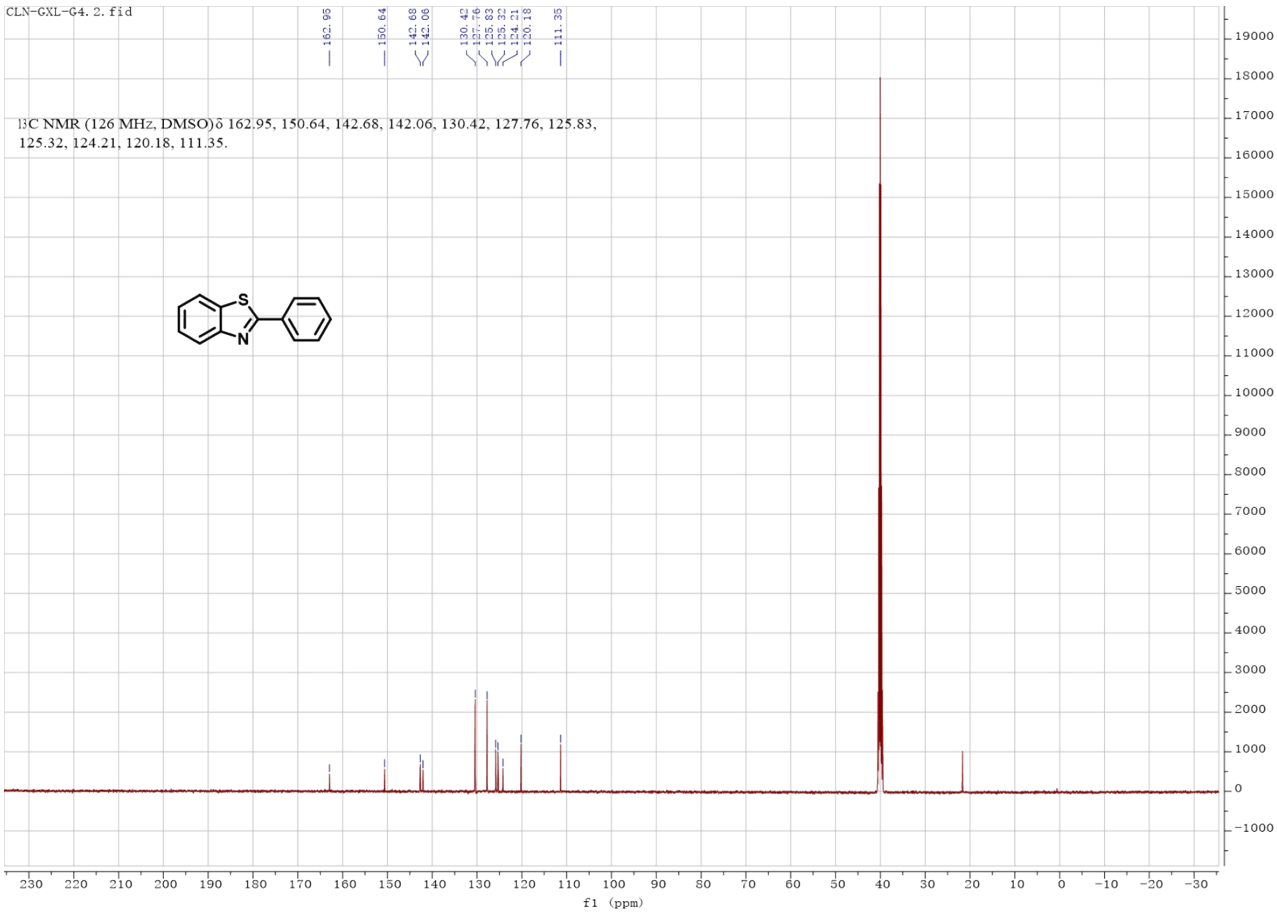

CLN-GXL-GS. 1. fid
12.21
12.21
12.19
12.19
12.18
8.10
7.28
7.27
7.27
7.18
1H NMR (500 MHz, CDCl3) δ 12.21, 12.19, 12.18, 8.10, 7.28, 7.27, 7.27, 7.18.
1.90
1.00
1.62
1.45
f1 (ppm)

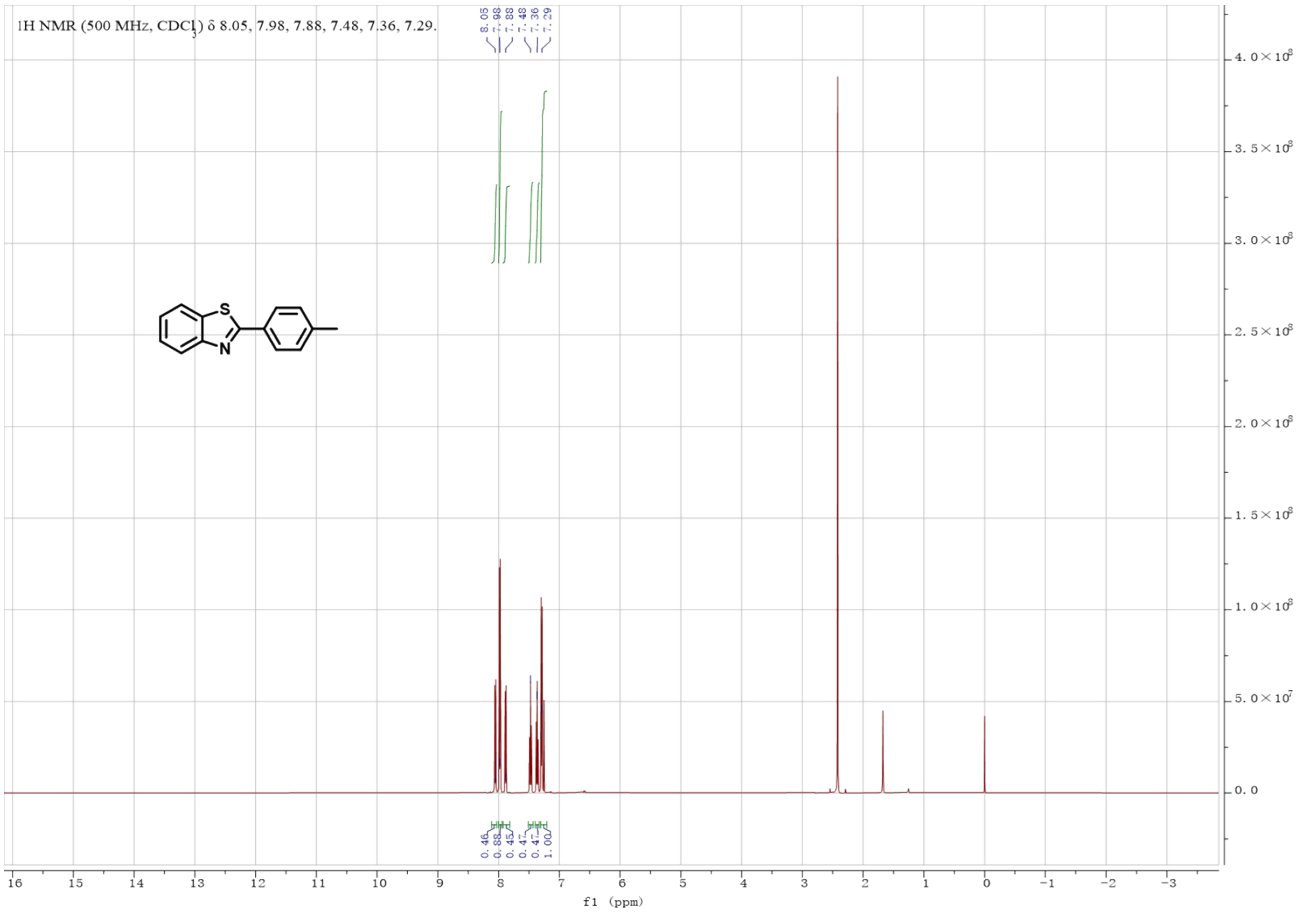

CLN-GXL-GS. 2. fid
155.40
147.43
146.81
135.18
135.13
132.53
130.59
130.08
128.96
124.94
116.11
13C NMR (126 MHz, CDCl3) δ 155.40, 147.43, 146.81, 135.18, 135.13, 132.53, 130.59, 130.08, 128.96, 124.94, 116.11.
f1 (ppm)

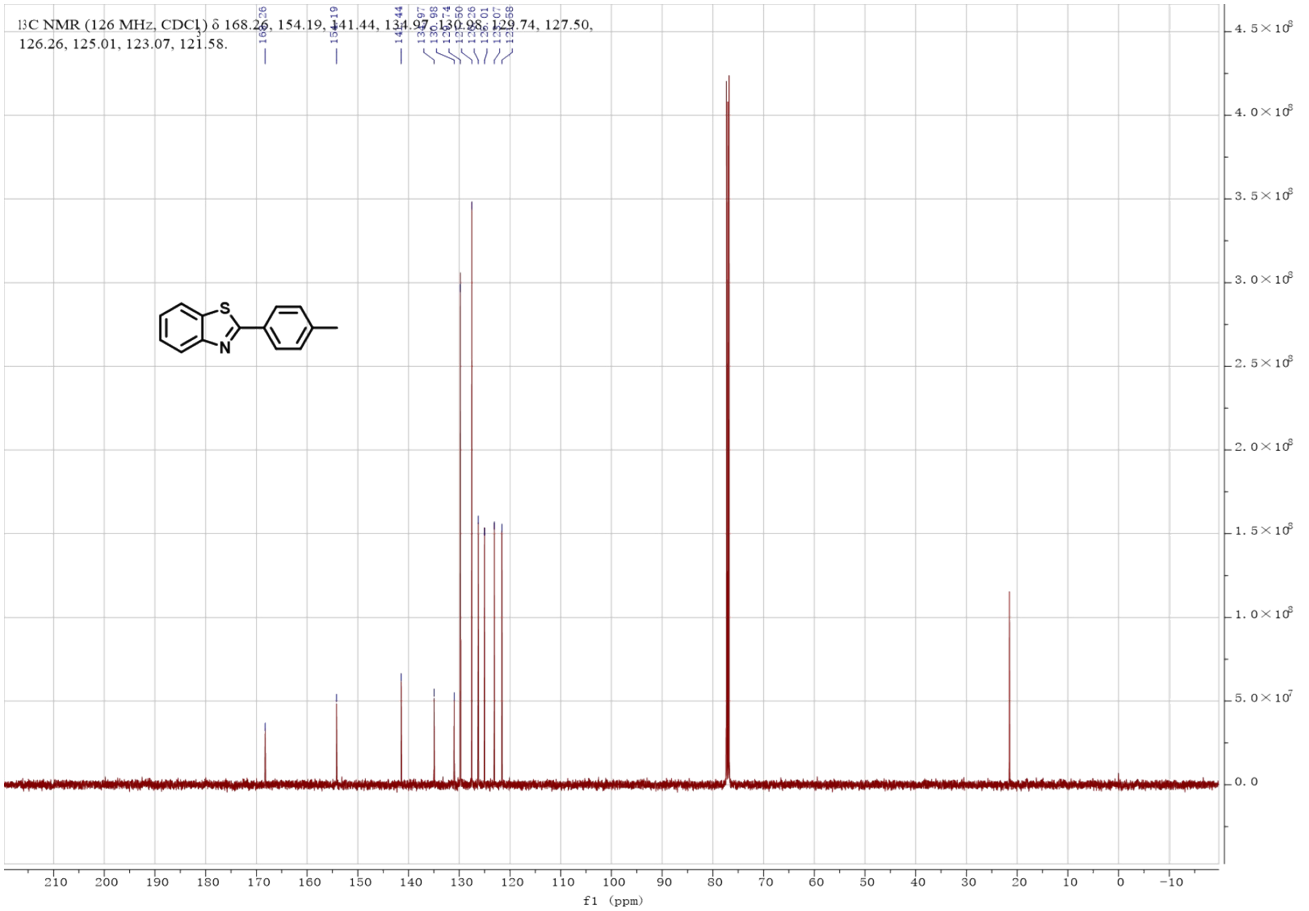

8.27
7.78
7.59
7.53
7.36
7.26 CDCl3
3.01
1.90 H2O
1.25
0.00
1.00
0.50
2.04
1.13
f1 (ppm)

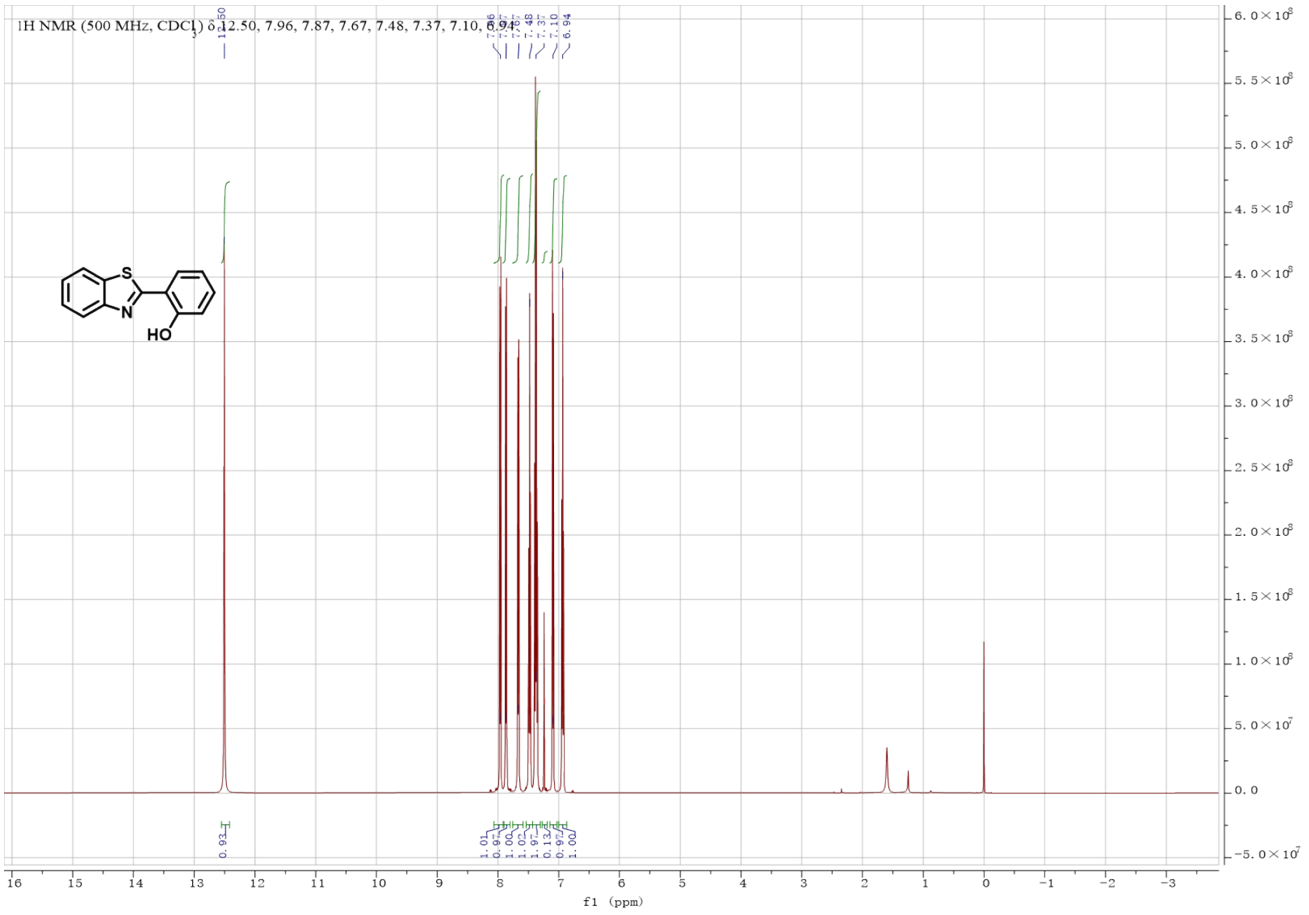

13C NMR (126 MHz, CDCl3) δ 163.07, 150.77, 142.07, 131.57, 128.94, 127.66, 127.15, 125.14, 124.62, 120.03, 110.62, 77.30, 77.04, 76.79, 0.01.
163.
150.
142.
131.
128.
127.
127.
125.
124.
120.03
110.62
77.30 CDCl3
77.04 CDCl3
76.79 CDCl3
0.01
f1 (ppm)

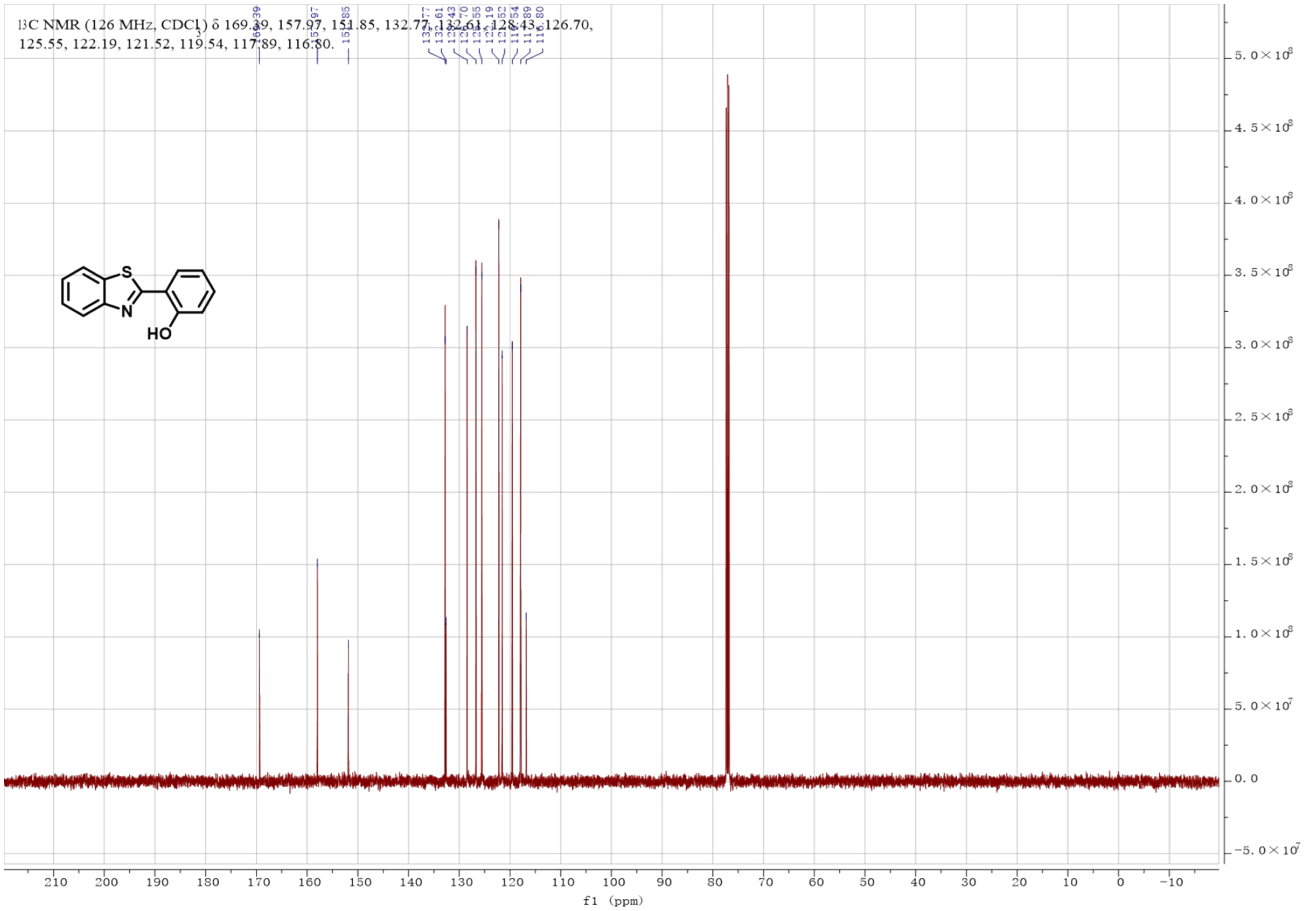

CLN-GXL-G4. 1. fid
8.12
8.11
7.80
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.42
1H NMR (500 MHz, DMSO)δ 8.12, 8.11, 7.80, 7.46, 7.46, 7.45, 7.44, 7.43, 7.42.
0.48
0.47
1.00
f1 (ppm)

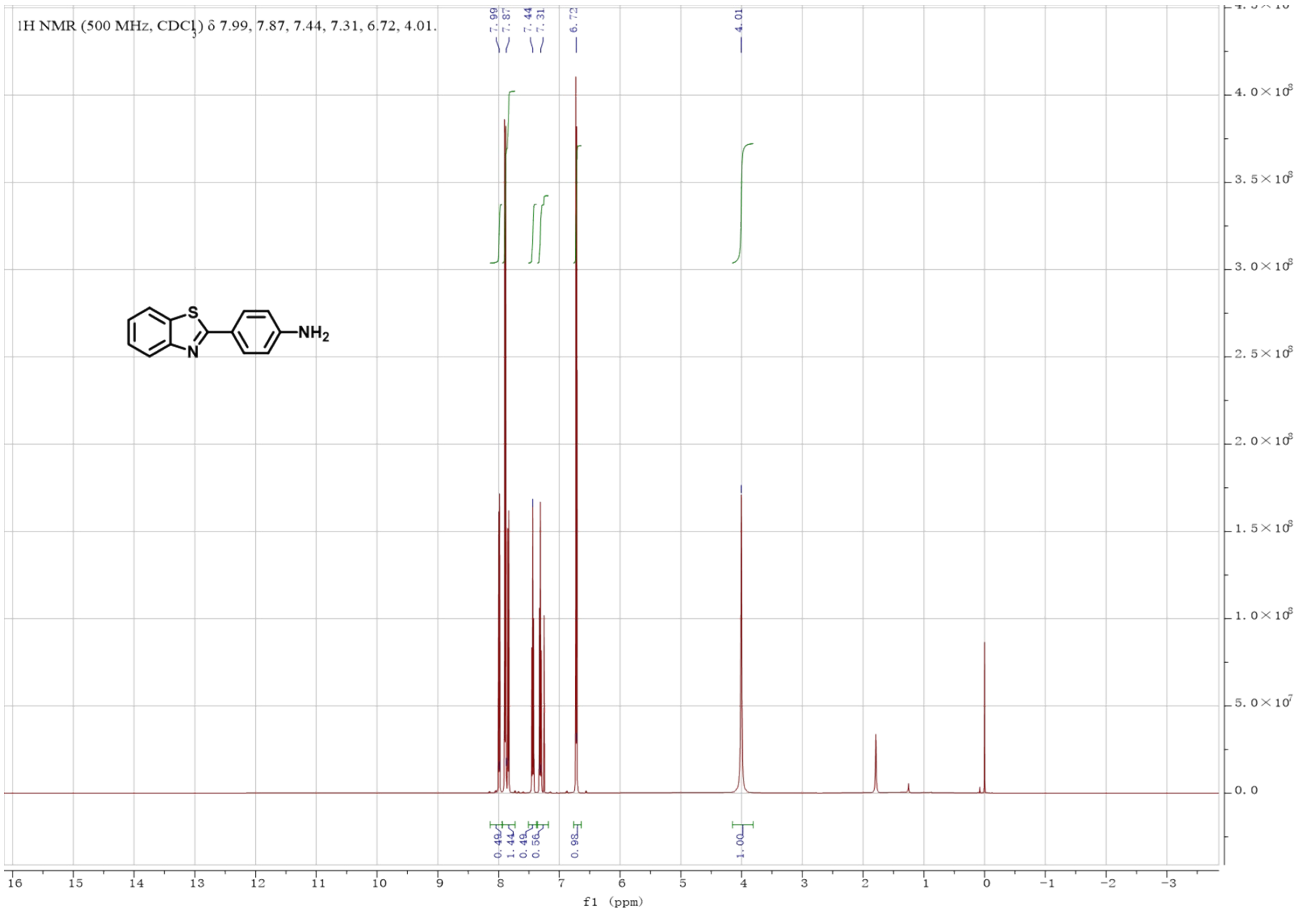

CLN-GXL-G4. 2. fid
162.95
150.64
142.68
142.06
130.42
127.76
125.83
125.32
124.21
120.18
111.35
13C NMR (126 MHz, DMSO)δ 162.95, 150.64, 142.68, 142.06, 130.42, 127.76, 125.83, 125.32, 124.21, 120.18, 111.35.
f1 (ppm)

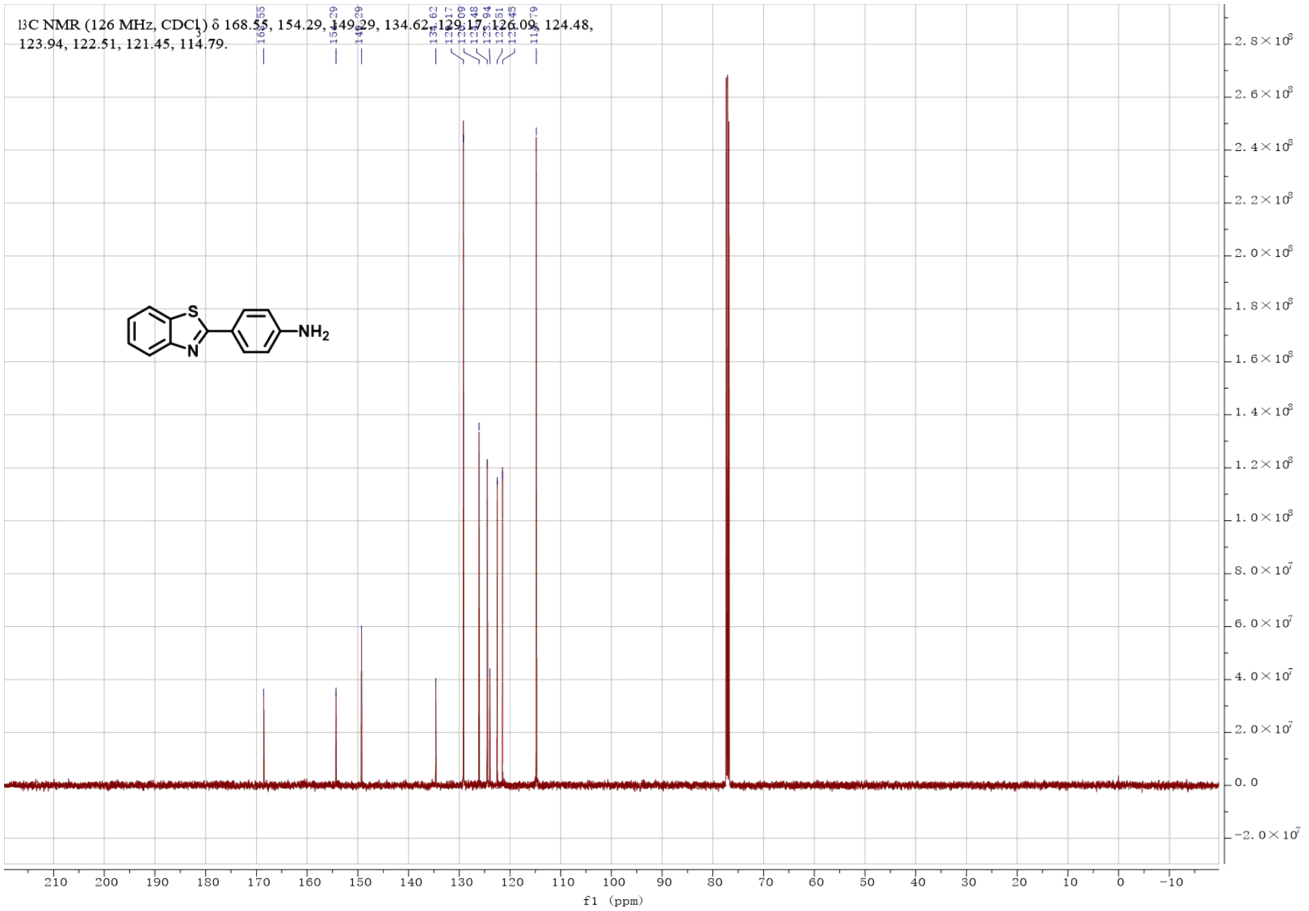

1H NMR (500 MHz, CDCl3) δ 8.05, 7.98, 7.88, 7.48, 7.36, 7.29.
8.05
7.98
7.88
7.48
7.36
7.29
S
N
f1 (ppm)

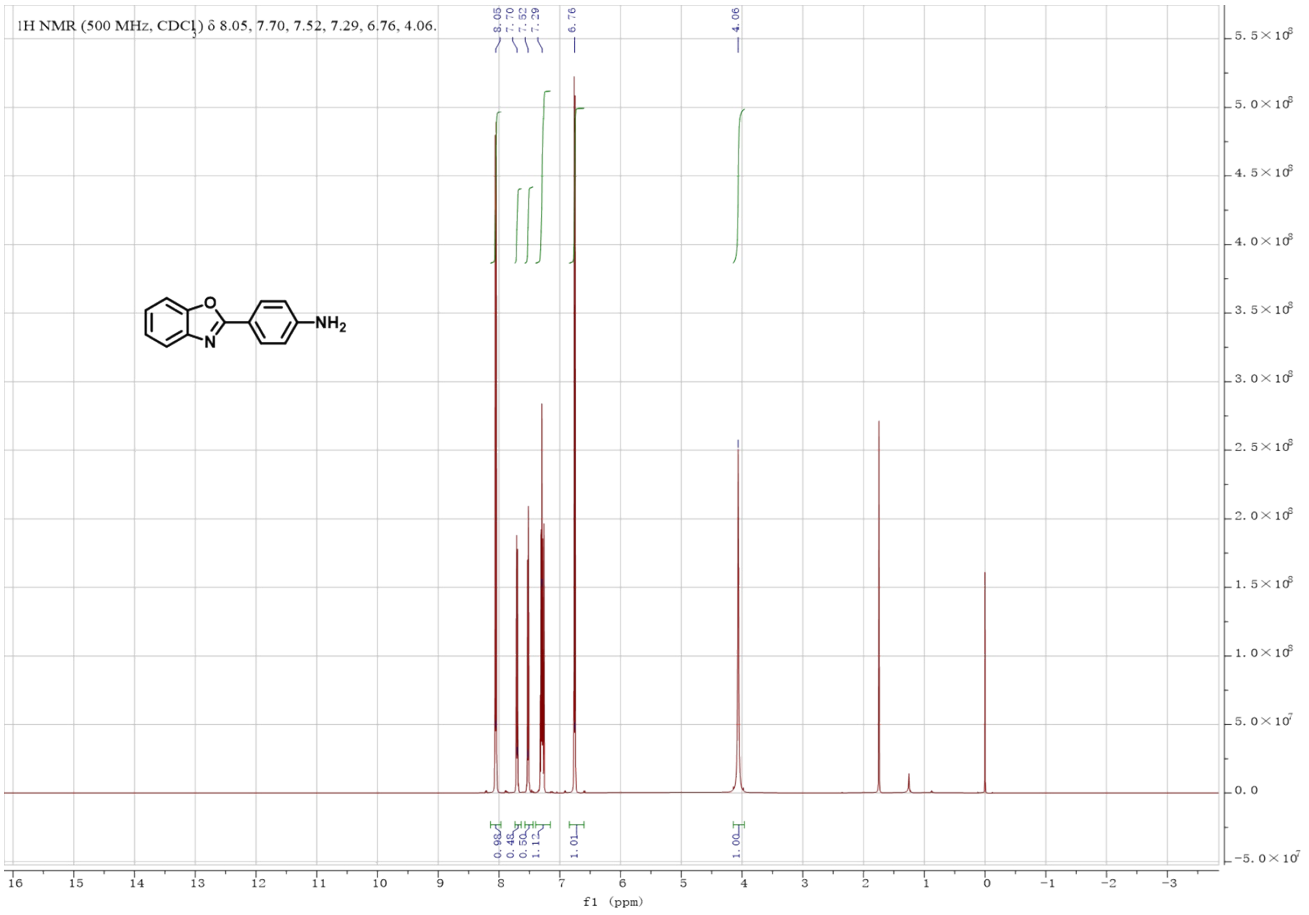

13C NMR (126 MHz, CDCl3) δ 168.26, 154.19, 141.44, 134.97, 130.98, 129.74, 127.50, 126.26, 125.01, 123.07, 121.58.
S
N
f1 (ppm)

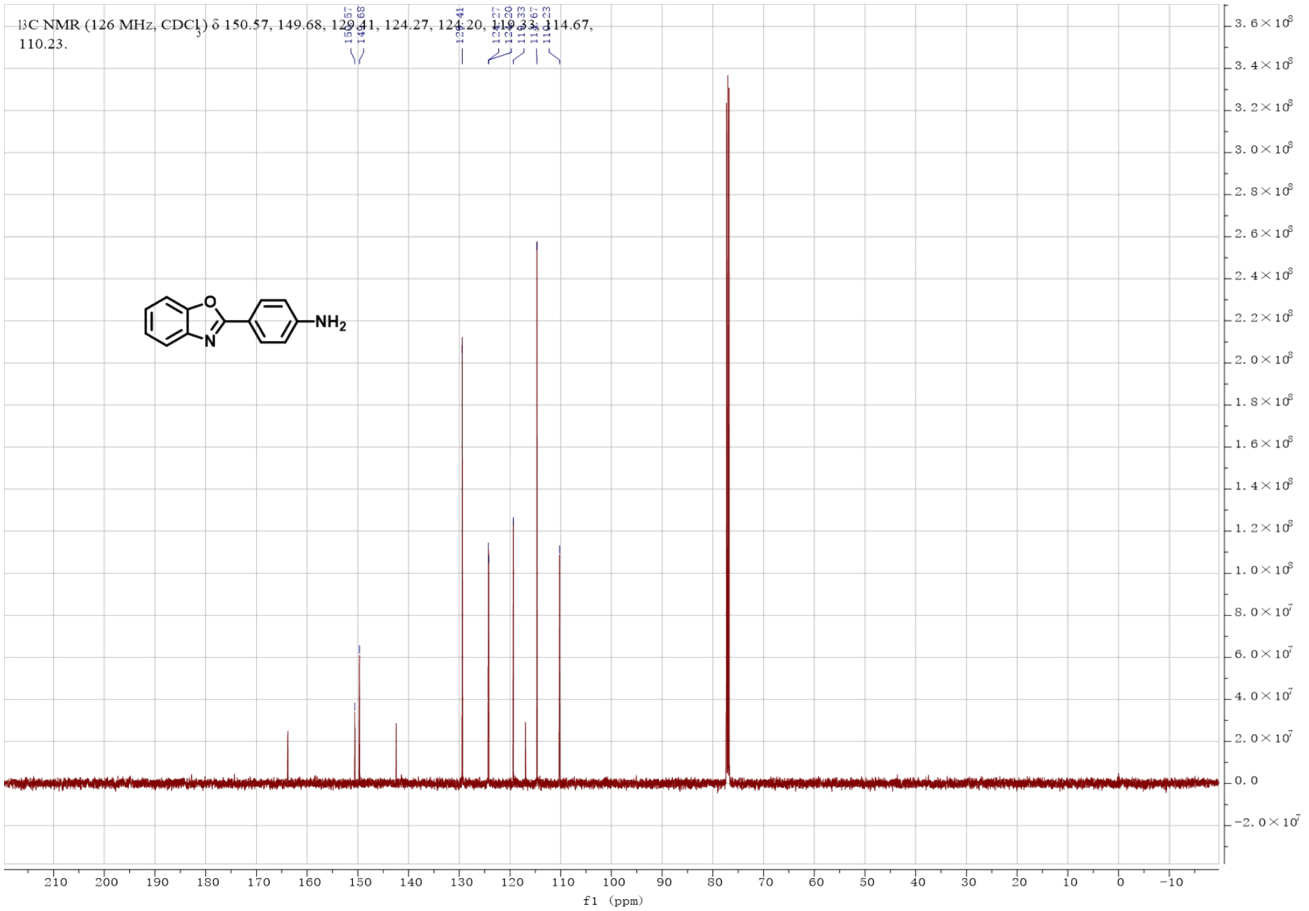

1H NMR (500 MHz, CDCl3) δ 12.50, 7.96, 7.87, 7.67, 7.48, 7.37, 7.10, 6.94.
HO
f1 (ppm)

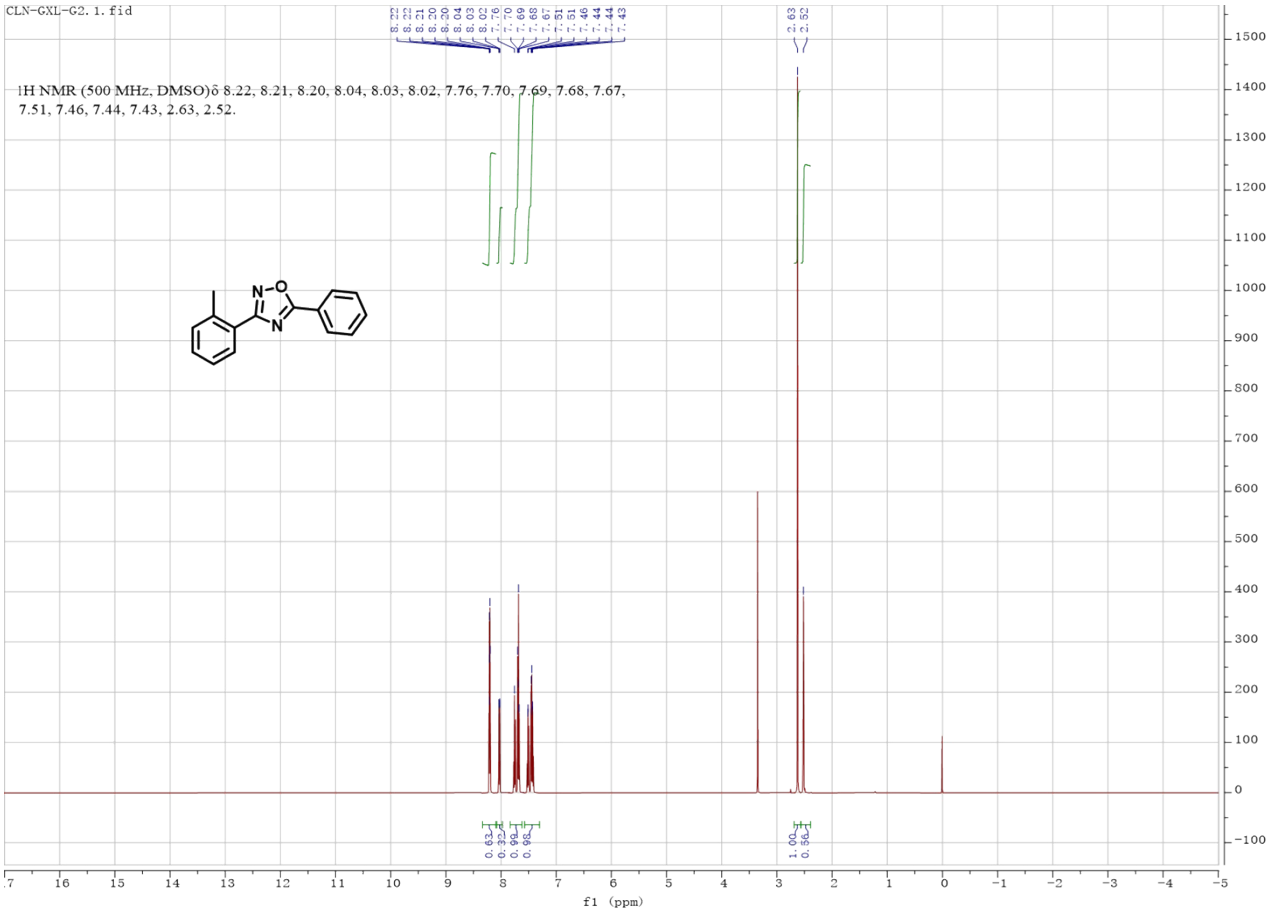

13C NMR (126 MHz, CDCl3) δ 169.39, 157.97, 151.85, 132.77, 132.61, 128.43, 126.70, 125.55, 122.19, 121.52, 119.54, 117.89, 116.80.
HO
f1 (ppm)

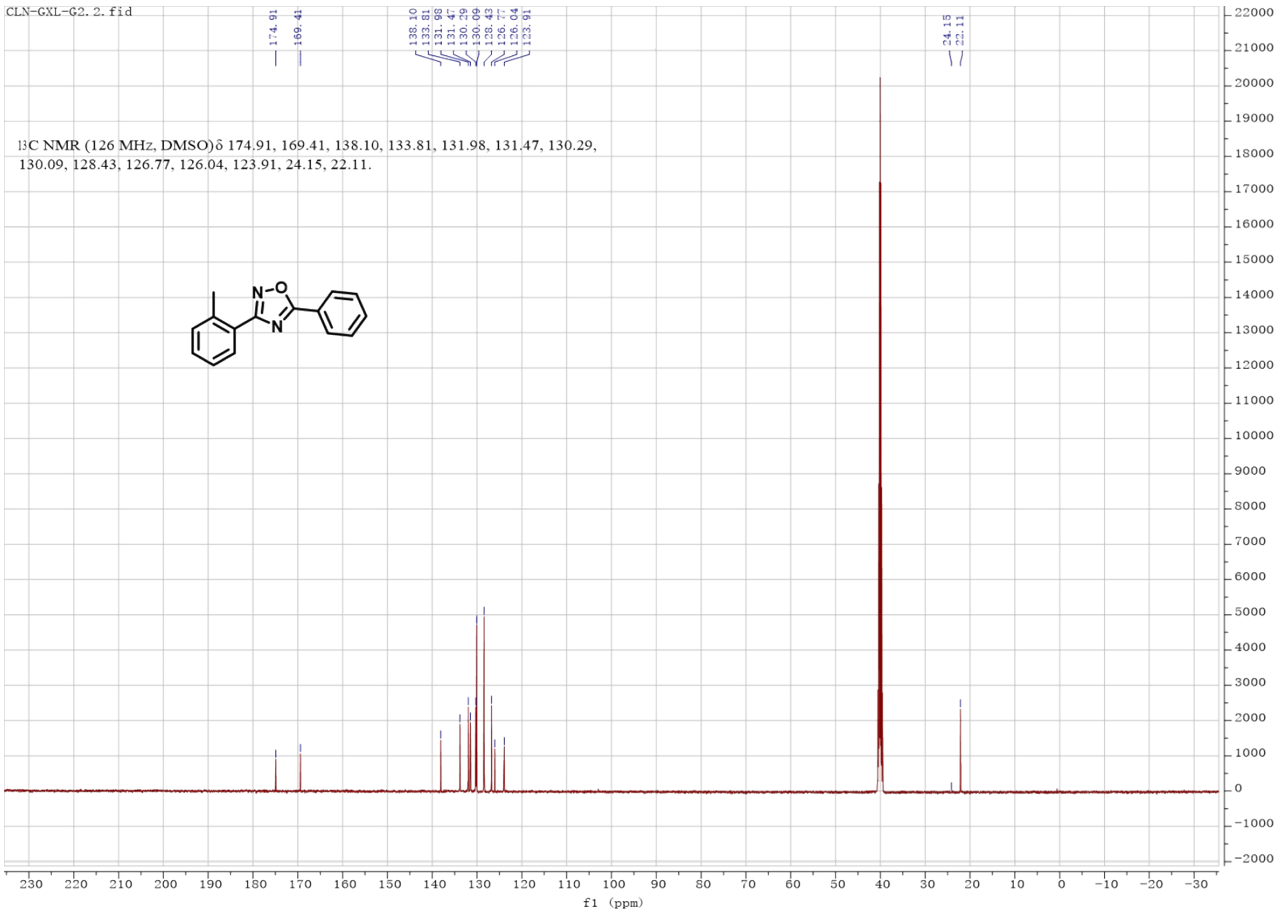

1H NMR (500 MHz, CDCl3) δ 7.99, 7.87, 7.44, 7.31, 6.72, 4.01.
7.99
7.87
7.44
7.31
6.72
4.01
NH2
f1 (ppm)


13C NMR (126 MHz, CDCl3) δ 168.55, 154.29, 149.29, 134.62, 129.17, 126.09, 124.48, 123.94, 122.51, 121.45, 114.79.
NH2
f1 (ppm)


1H NMR (500 MHz, CDCl3) δ 8.05, 7.70, 7.52, 7.29, 6.76, 4.06.
8.05
7.70
7.52
7.29
6.76
4.06
NH2
f1 (ppm)


13C NMR (126 MHz, CDCl3) δ 150.57, 149.68, 129.41, 124.27, 124.20, 119.33, 114.67, 110.23.
NH2
f1 (ppm)


CLN-GXL-G2. 1. fid
1H NMR (500 MHz, DMSO)δ 8.22, 8.21, 8.20, 8.04, 8.03, 8.02, 7.76, 7.70, 7.69, 7.68, 7.67, 7.51, 7.46, 7.44, 7.43, 2.63, 2.52.
f1 (ppm)


CLN-GXL-G2. 2. fid
13C NMR (126 MHz, DMSO)δ 174.91, 169.41, 138.10, 133.81, 131.98, 131.47, 130.29, 130.09, 128.43, 126.77, 126.04, 123.91, 24.15, 22.11.
f1 (ppm)