CuI nanoparticles Catalyzed Synthesis of Tetracyclic Heterocycles benzo[*e*]benzo[4,5]imidazo[1,2-*c*][1,3]thiazin-6-imine by S_NAr-Type C-S, C-N Bond Formation with isothiocyanatobenzenes and Benzimidazoles

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1. Crystal data of 3b

Table S1 Data collection and structure refinement of 3b (CCDC No. 1818722).

Compound	3b
Empirical formula	C21 H15 N3 S
Formula weight	341.42
Crystal system	monoclinic
Space group	C12/c1
T(K)	299
Λ (Å)	1.54184
A (Å)	23.3793(3)
B (Å)	7.23290(10)
C (Å)	19.5343(3)
α (°)	90
B (°)	92.6530(10)
Γ (°)	90
V(Å^3)	3299.71(8)
Z	8
D_{calc} (mg/m^3)	1.375
F(000)	1424
Crystal size (mm^3)	0.4 x 0.2 x 0.2
θ range for data collection (deg.)	3.785 to 66.565
Data/restraints/parameters	2882 / 0 / 226
Goodness-of-fit on F^2	1.094
Final R_1/wR_2 indices [I>2σ(I)]	0.0471 / 0.1295
R indices (all data)	0.0500
Largest diff. peak and hole(A^{-3})	0.199 and -0.491

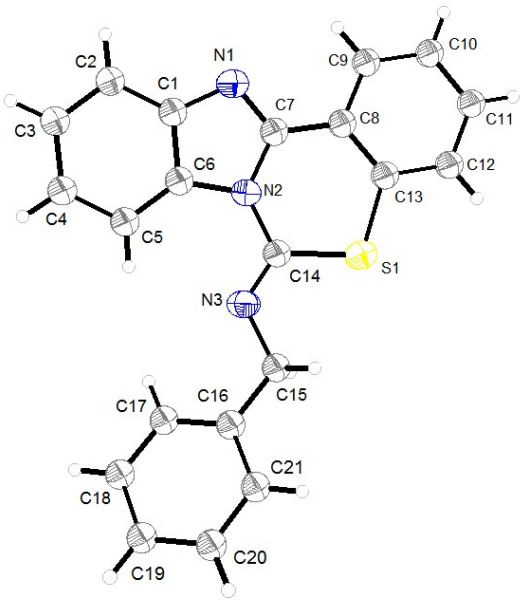


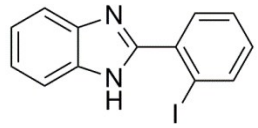
Figure S1. ORTEP plot of 3b showing thermal ellipsoids at the 50% probability level

2. General Procedures

General Procedure for the Preparation of Substituted 2-(2-Halophenyl)-1H-benzo[d]imidazoles (1)[1]

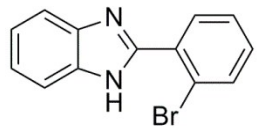
To a flask were added substituted 1,2-diaminobenzene (1.08 g, 10 mmol), 2-halobenzoic acid (10 mmol) and PPA (20 g), and the reaction mixture was heated at 170 °C in an oil bath for 7 h. After the reaction was complete, the reaction mixture was slowly poured into ice water, and the resulting mixture was basified with solid NaOH and $NaHCO_3$. Once the solution had reached pH 8-10, the precipitate was isolated by filtration, washed with cold water and recrystallized from hot aqueous ethanol. The solid was then dried to afford the corresponding 2-(2-halophenyl)-1*H*-benzo[*d*]imidazole.

2-(2-iodophenyl)-1H-benzo[d]imidazole



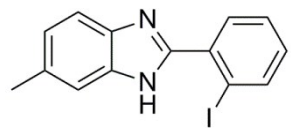
^{1}H NMR (600 MHz, dmso) δ 12.70 (s, 1H), 8.06 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.55 (ddd, *J* = 10.8, 8.5, 4.5 Hz, 2H), 7.30 – 7.19 (m, 3H).
^{13}C NMR (151 MHz, dmso) δ 152.54, 143.15, 139.61, 136.55, 134.32, 131.31, 131.16, 128.09, 122.51, 121.48, 119.10, 111.44, 97.34.

2-(2-iodophenyl)-1H-benzo[d]imidazole



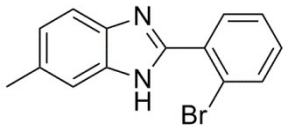
^{1}H NMR (600 MHz, dmso) δ 12.73 (s, 1H), 7.82 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.77 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.44 (m, 1H), 7.24 (dt, *J* = 15.1, 6.7 Hz, 2H).
^{13}C NMR (151 MHz, dmso) δ 150.38, 143.20, 134.45, 133.36, 132.38, 132.22, 131.32, 127.75, 122.62, 121.56, 121.51, 119.08, 111.54.

2-(2-iodophenyl)-6-methyl-1H-benzo[d]imidazole



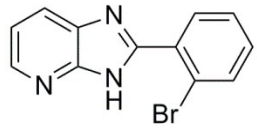
^{1}H NMR (600 MHz, dmso) δ 12.55 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 (s, 1H), 7.38 (s, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 2.44 (s, 3H).
^{13}C NMR (151 MHz, dmso) δ 166.18, 161.19, 160.49, 139.67, 136.66, 134.78, 131.31, 131.14, 130.01, 128.74, 128.14, 97.36, 21.33.

2-(2-bromophenyl)-6-methyl-1H-benzo[d]imidazole



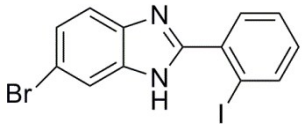
^{1}H NMR (600 MHz, dmso) δ 12.58 (s, 1H), 7.81 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.54 (td, *J* = 7.5, 0.9 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.45 (td, *J* = 7.8, 1.7 Hz, 1H), 7.39 (s, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 2.44 (s, 3H).
^{13}C NMR (151 MHz, dmso) δ 150.00, 133.35, 132.46, 132.17, 131.19, 127.72, 123.52, 121.47, 21.29.

2-(2-bromophenyl)-3H-imidazo[4,5-b]pyridine



^{1}H NMR (600 MHz, dmso) δ 13.27 (s, 1H), 8.40 (d, *J* = 4.1 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.58 (dd, *J* = 10.9, 4.1 Hz, 1H), 7.50 (td, *J* = 7.8, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.0, 4.7 Hz, 1H).
^{13}C NMR (151 MHz, dmso) δ 152.17, 143.99, 133.38, 132.20, 131.99, 131.73, 127.79, 121.63, 118.13.

6-bromo-2-(2-iodophenyl)-1H-benzo[d]imidazole



^{1}H NMR (600 MHz, dmso) δ 12.94 (s, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.89 (s, 0.5H), 7.71 (s, 0.5H), 7.68 – 7.63 (m, 0.5H), 7.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56 (td, *J* = 7.5, 0.8 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 0.5H), 7.37 (dd, *J* = 24.4, 16.2 Hz, 1H), 7.29 (td, *J* = 7.7, 1.6 Hz, 1H).
^{13}C NMR (151 MHz, dmso) δ 139.65, 136.02, 131.42, 131.32, 128.15, 125.27, 124.55, 121.50, 120.86, 114.11, 113.32, 97.24.

Preparation of CuI NPs

The nanocatalyst was produced by ultrasonic irradiation using copper sulfate ($CuSO_4$) as the Cu source. First, $CuSO_4$ (1 mmol) was cleaned for 20 s in acetone under ultrasonic irradiation followed. The dried substrate was then slowly dipped into a solution of potassium iodide (1 mmol) in 40 mL of distilled water, and the mixture was sonicated for 30 min. When the reaction was complete, the obtained gray precipitate was isolated by filtration, washed with distilled water and dried to afford pure CuI NPs.

According to the diffraction data card (JCPDS, 75-0832); all the peaks can be perfectly indexed to the peak positions characteristic of CuI (**Fig. S2**).

Scanning electron microscopy (SEM) was used to confirm the size of the CuI nanoparticles, and the SEM micrograph is shown in **Fig. S3**. This figure illustrates that, the CuI NPs obtained under ultrasonic irradiation had diameters on the order of nanometers.

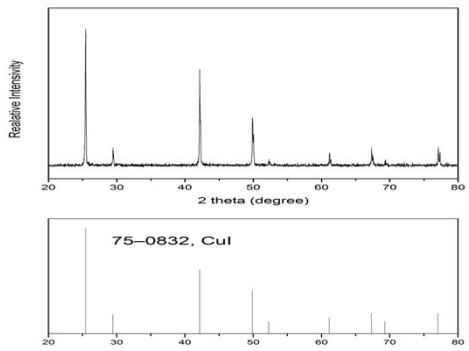


Fig S2. XRD spectra of CuI NPs

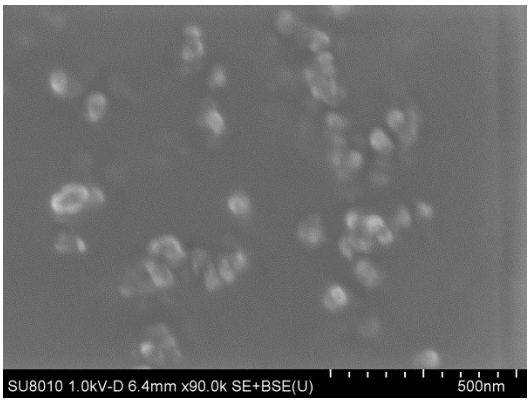


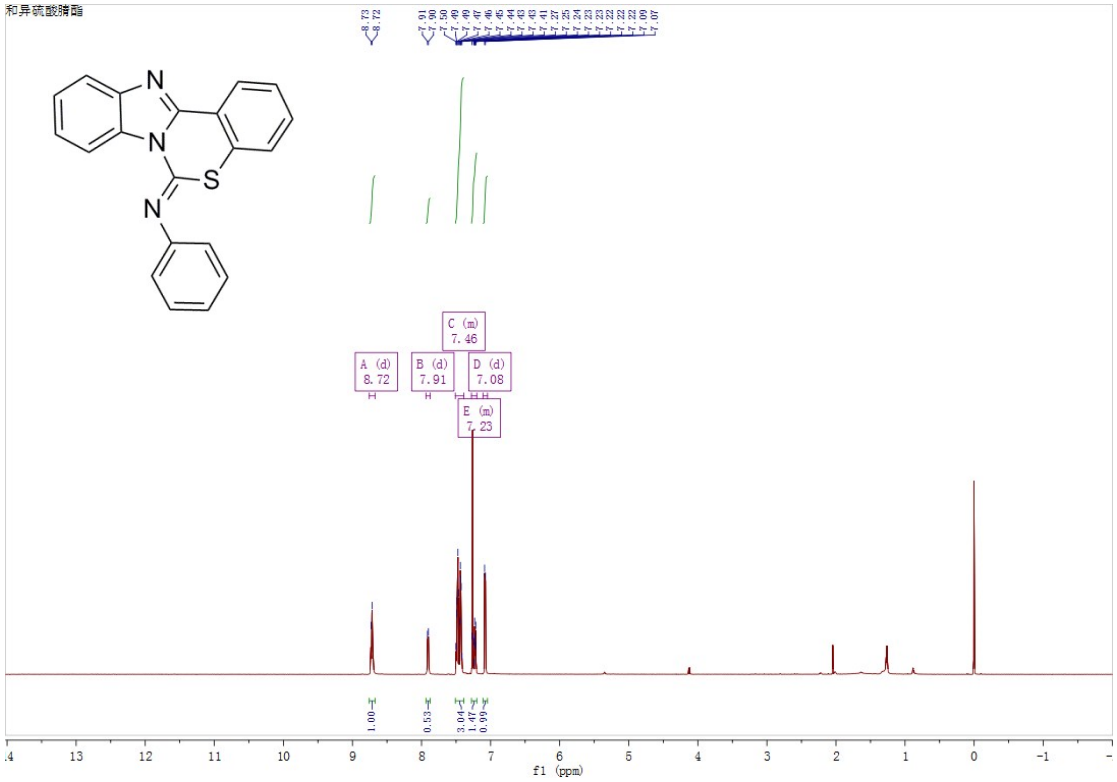
Fig S3. SEM image of CuI NPs

3. References

(1) Xu, S.; Lu, J.; Fu, H. Chem. Commum. 2011, 47, 5596.

(2) Javad, S-G.; Zeinab A.; Abolfazl Z. RSC Adv. 2014, 4, 16385.

4. Copies of ^{1}H and ^{13}C NMR Spectra


和异硫酸腈酯
A (d)
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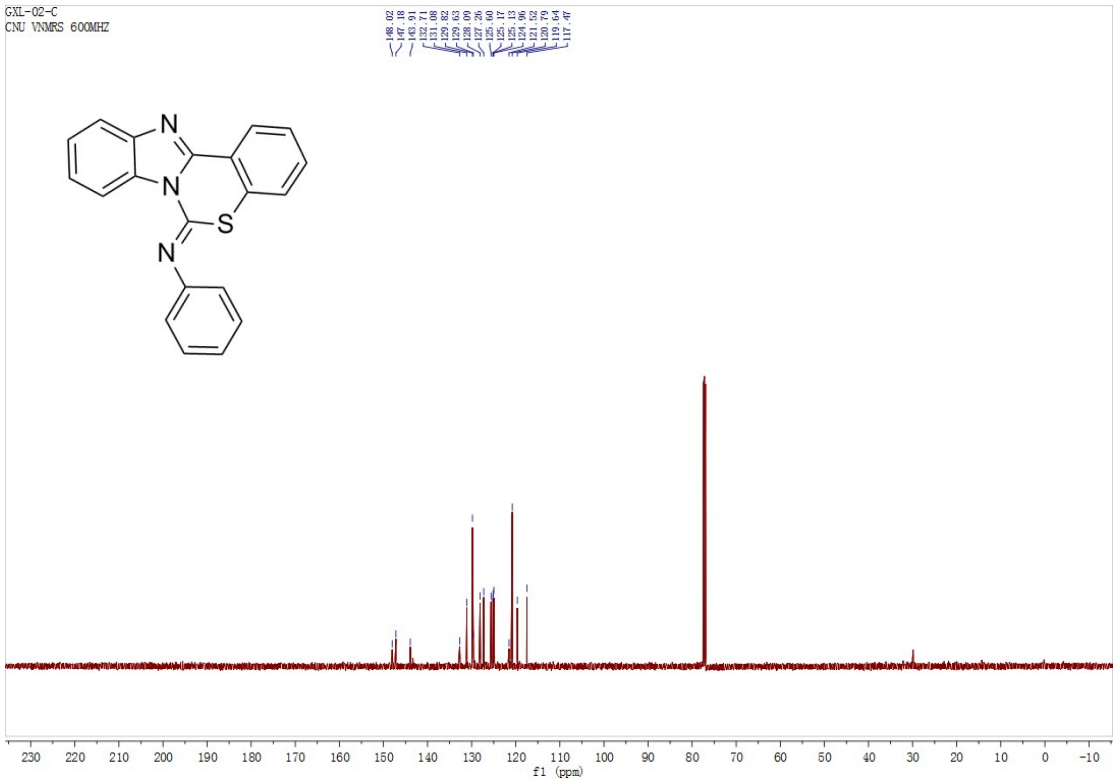
B (d)
7.91
C (m)
7.46
D (d)
7.08
E (m)
7.23
f1 (ppm)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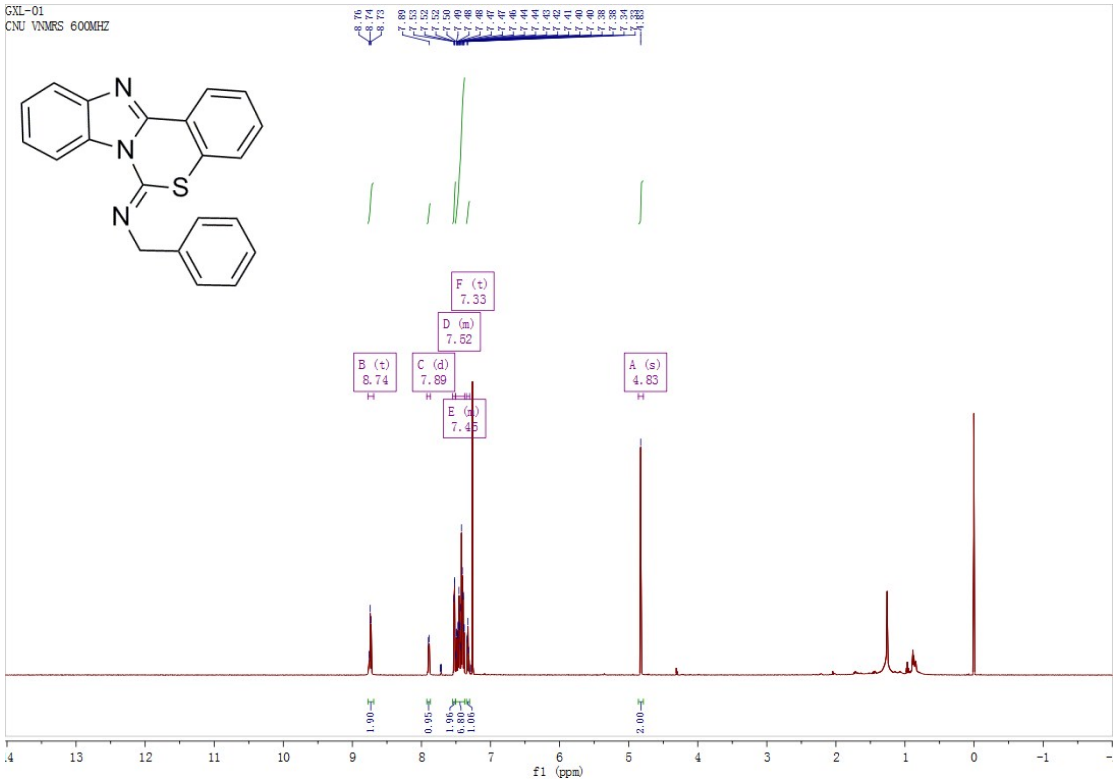
f1 (ppm)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E (m)
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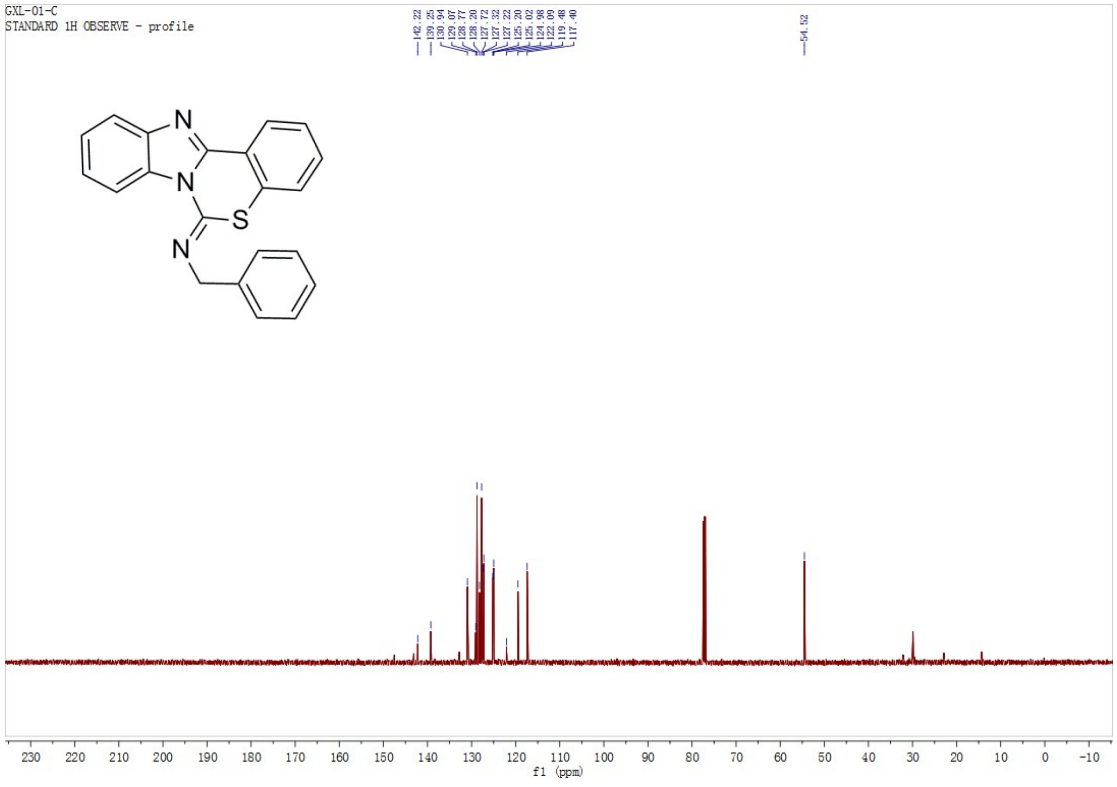
f1 (ppm)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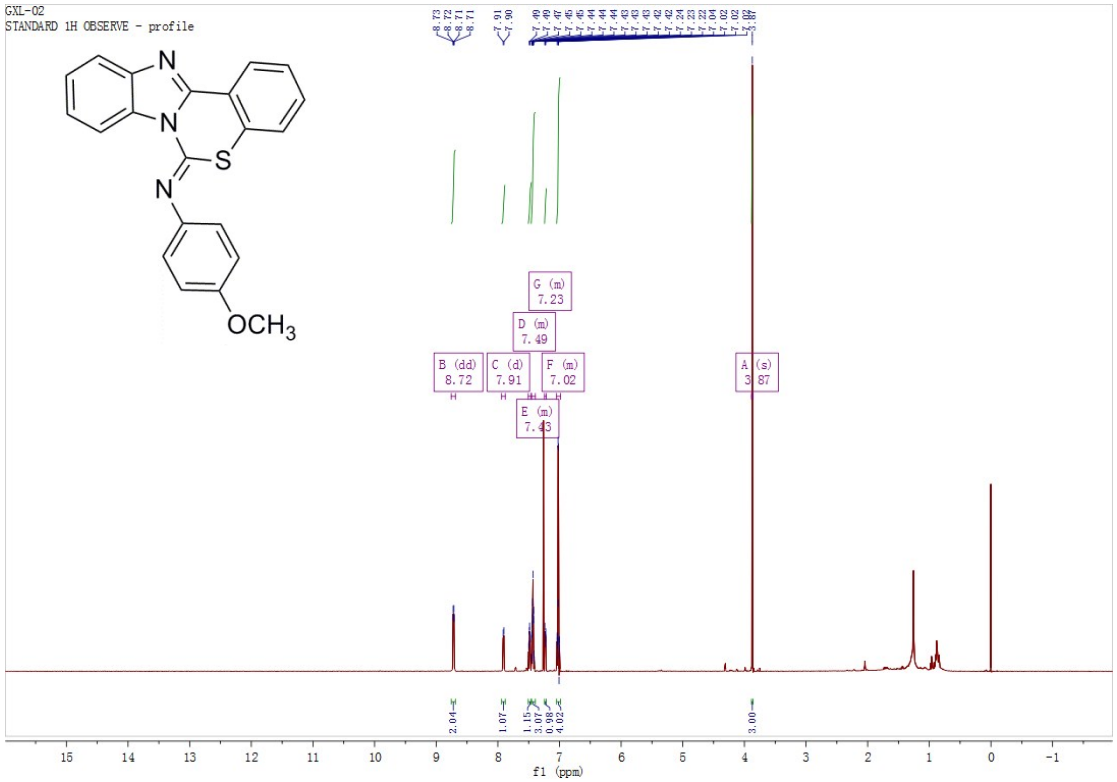
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7.23
D (m)
7.49
B (dd)
8.72
C (d)
7.91
F (m)
7.02
A (s)
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E (m)
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1.15
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0.98
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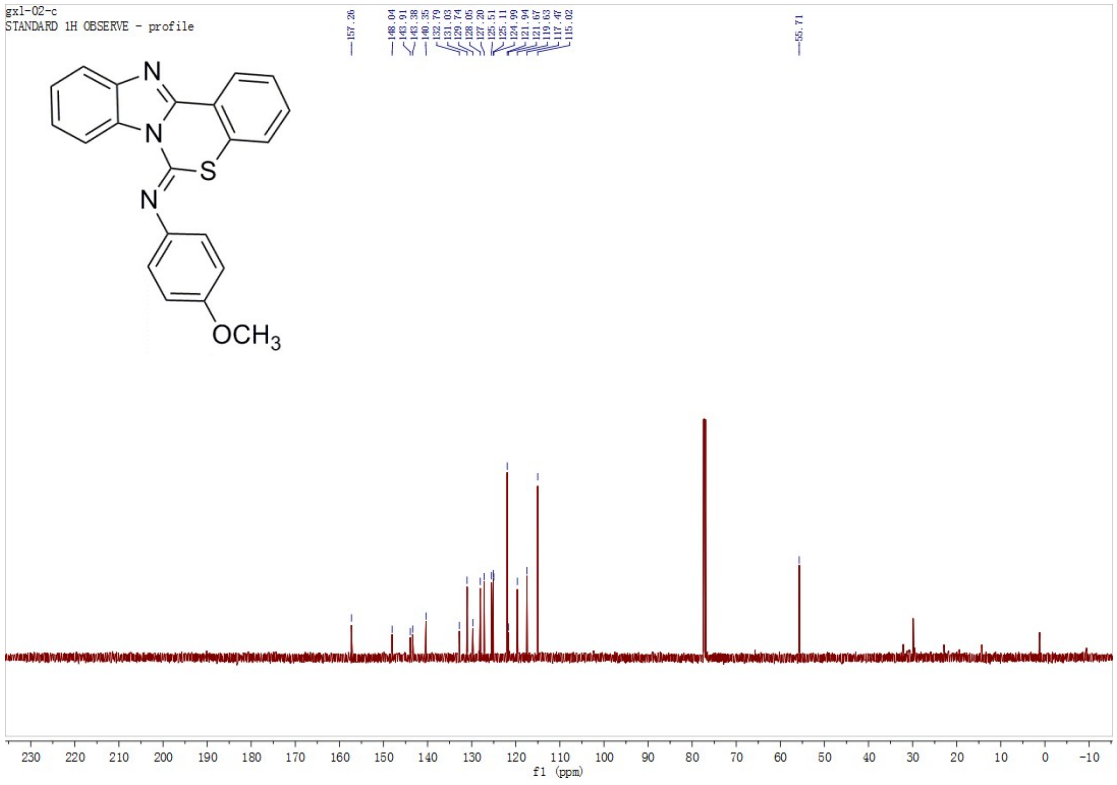
3.00
f1 (ppm)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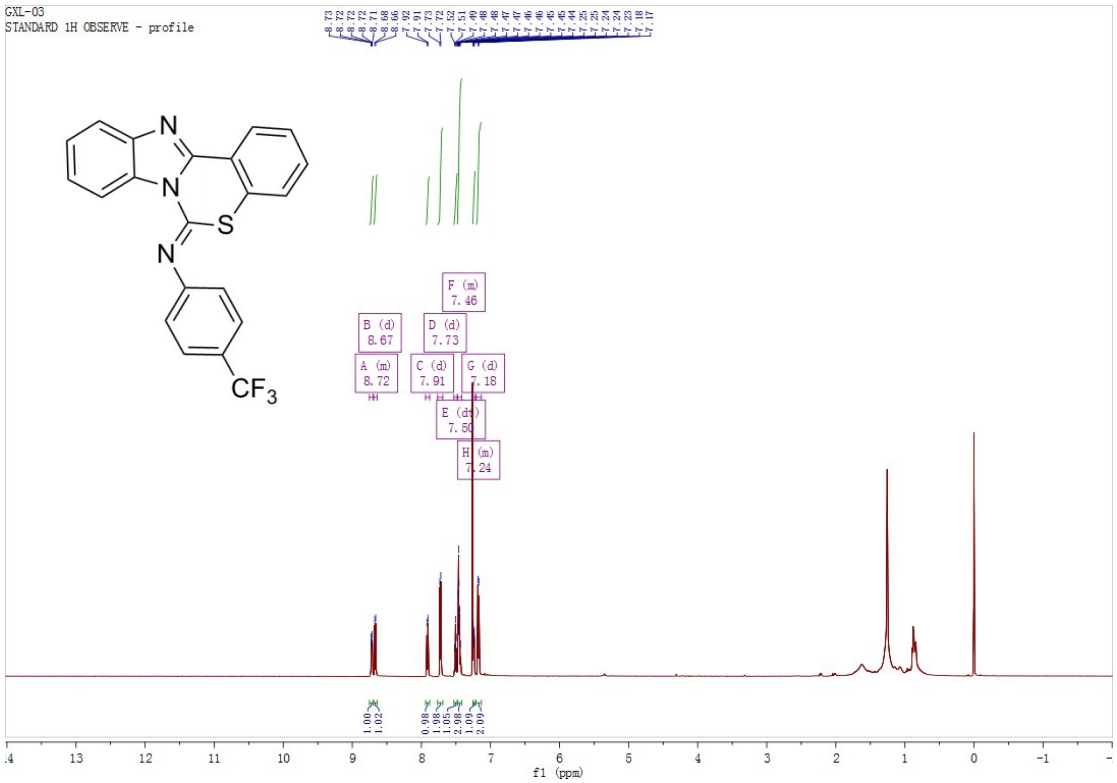
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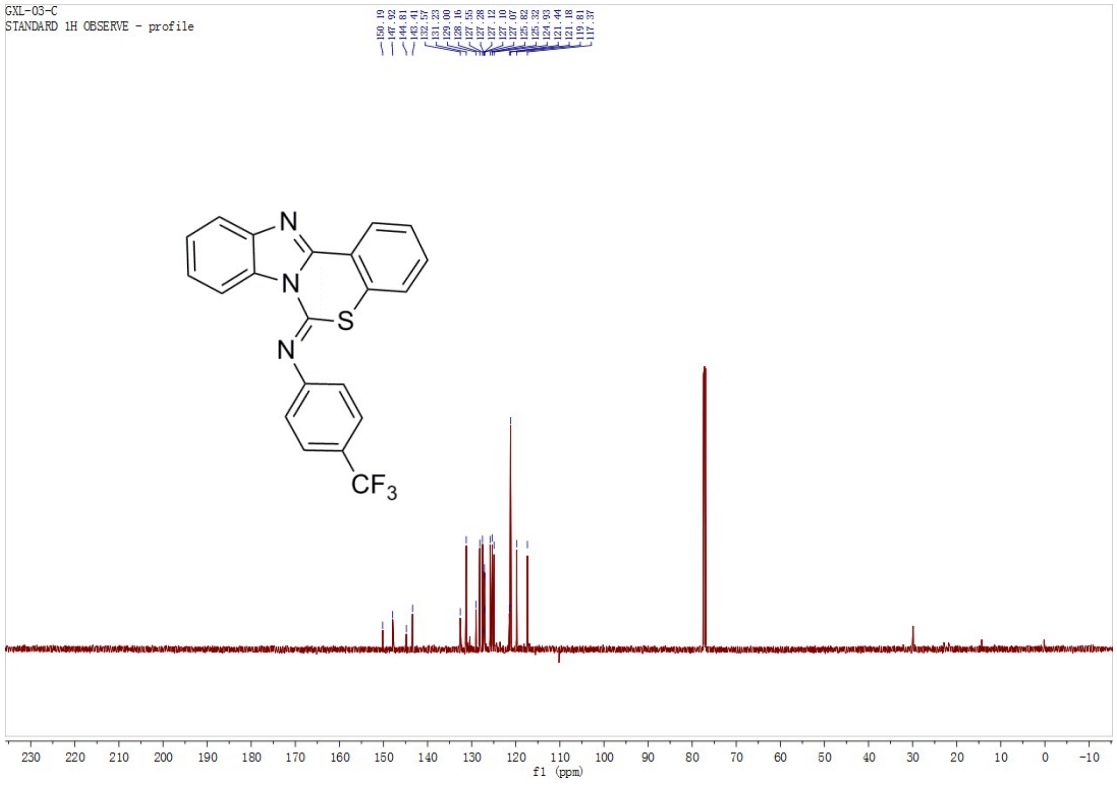
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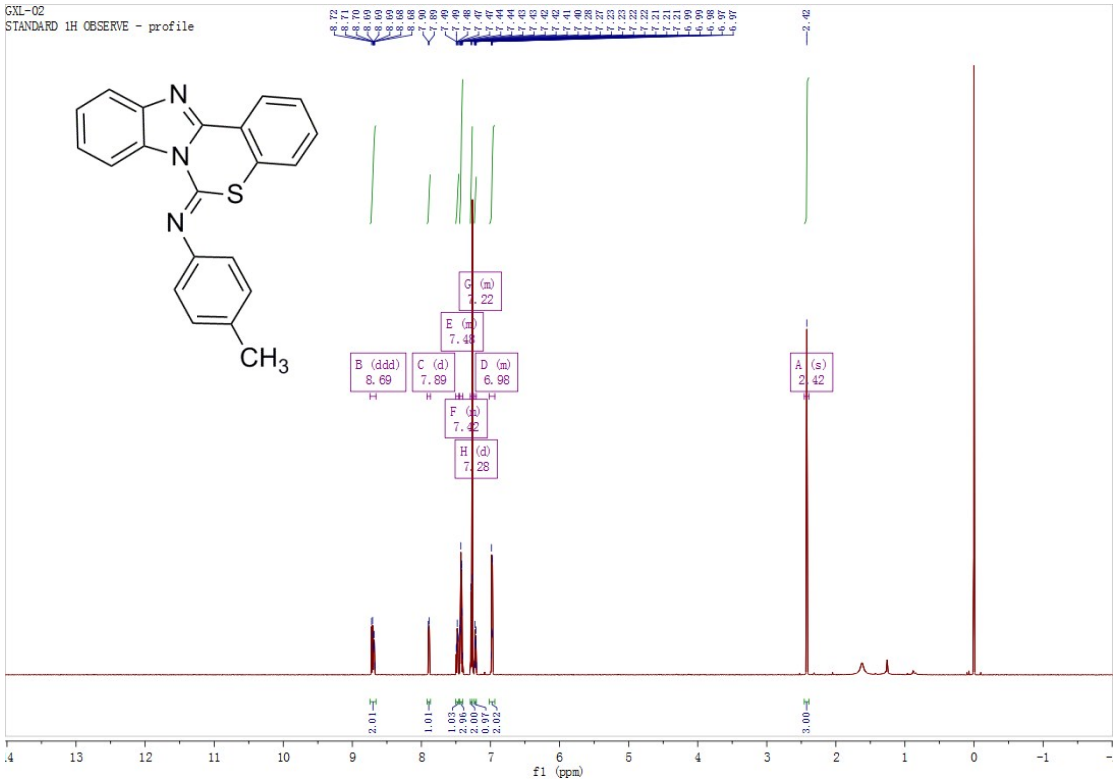
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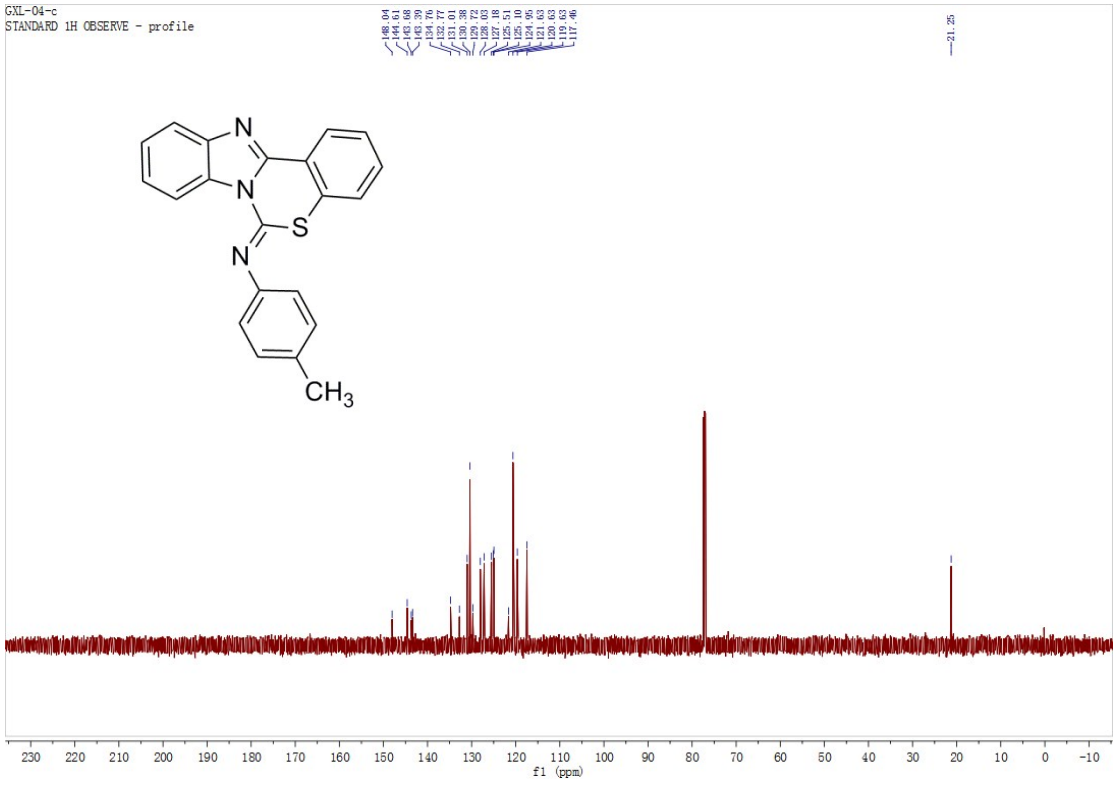
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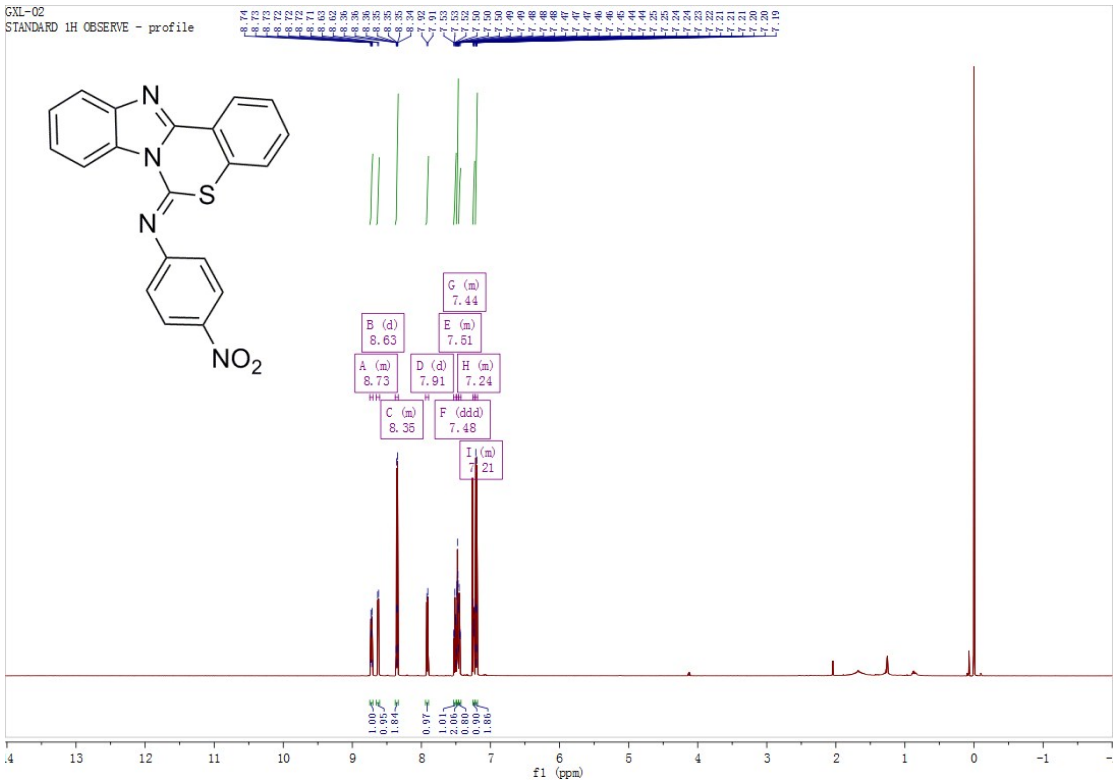
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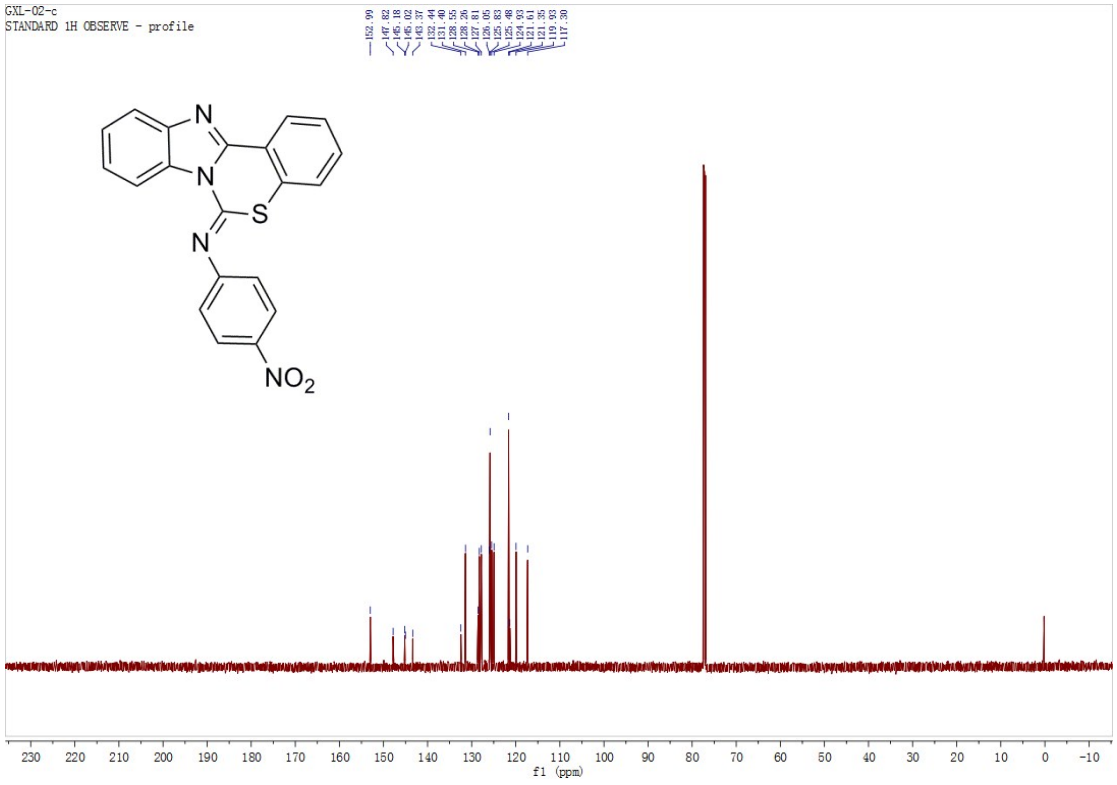
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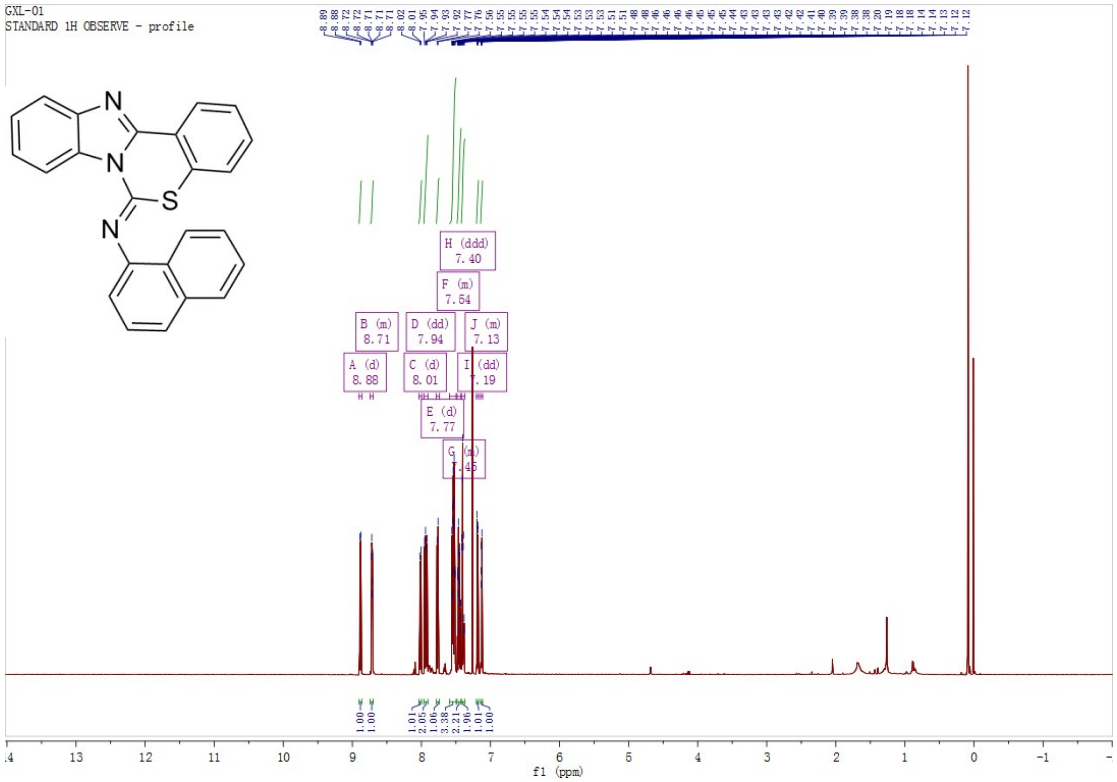
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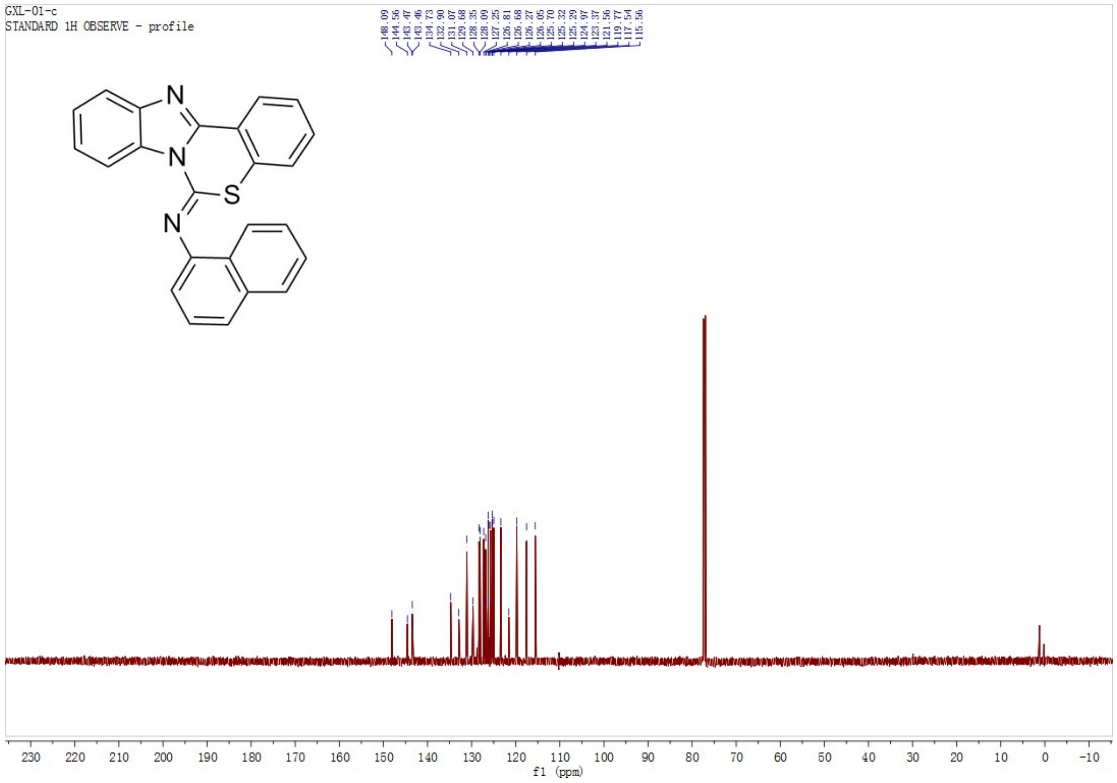
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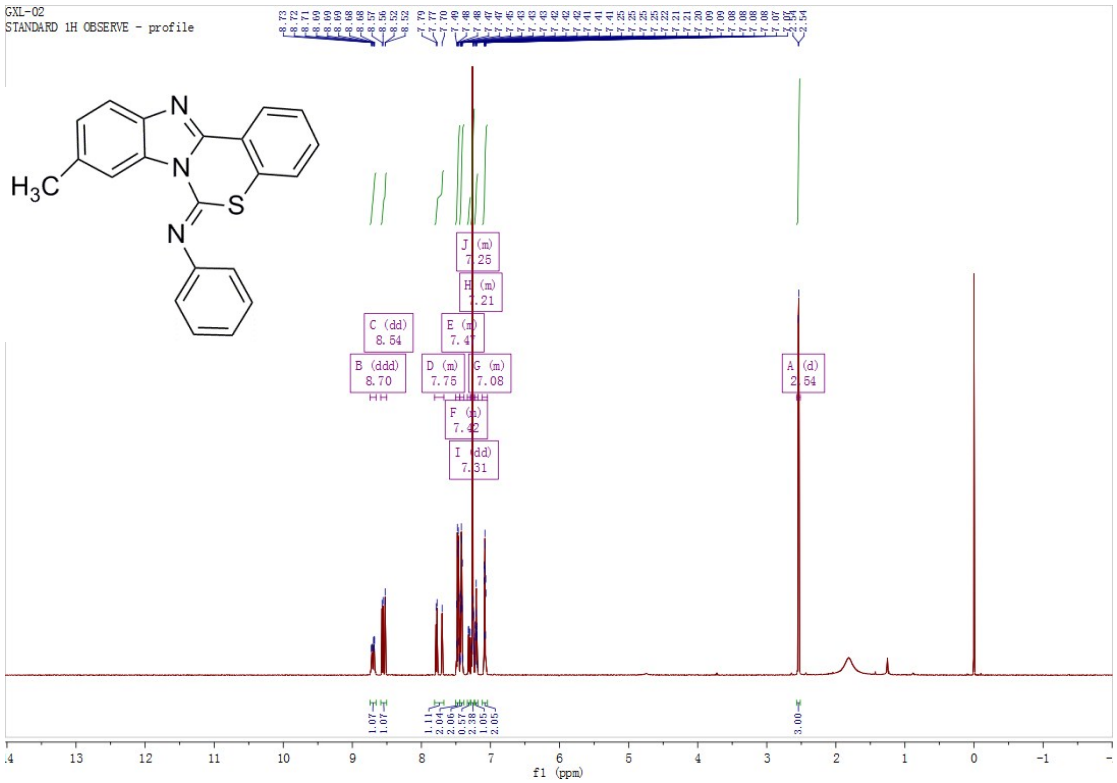
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2.05
3.00
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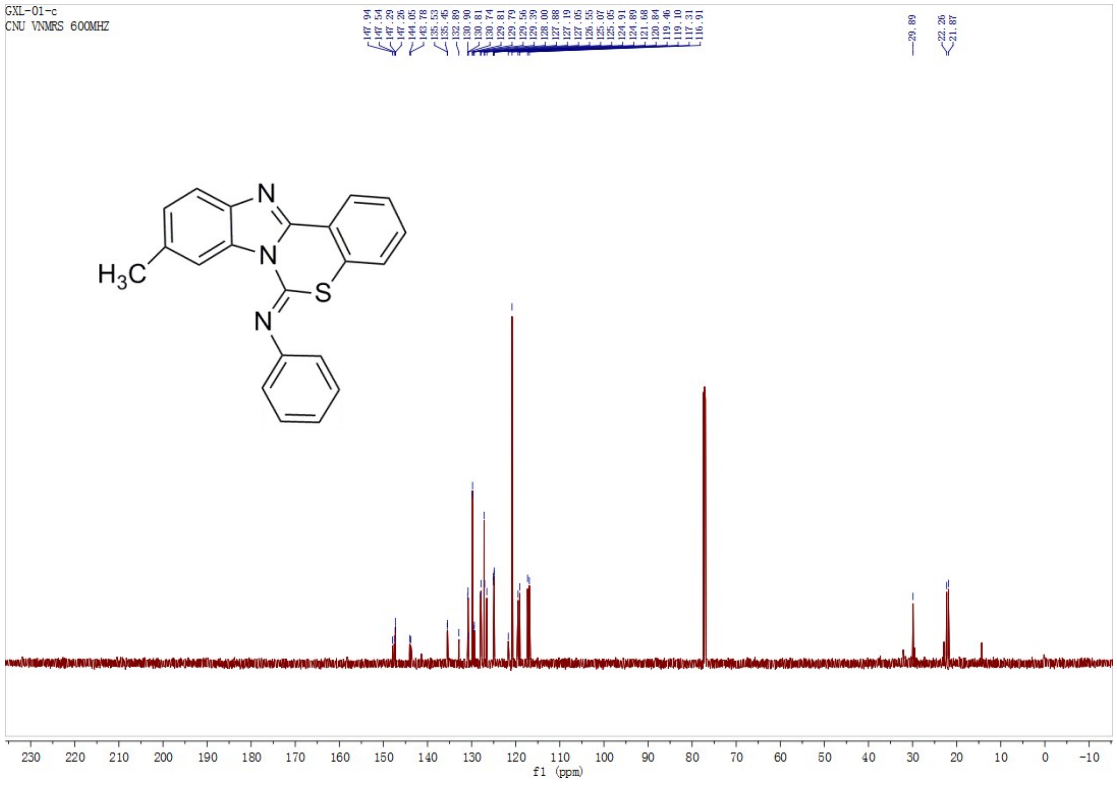
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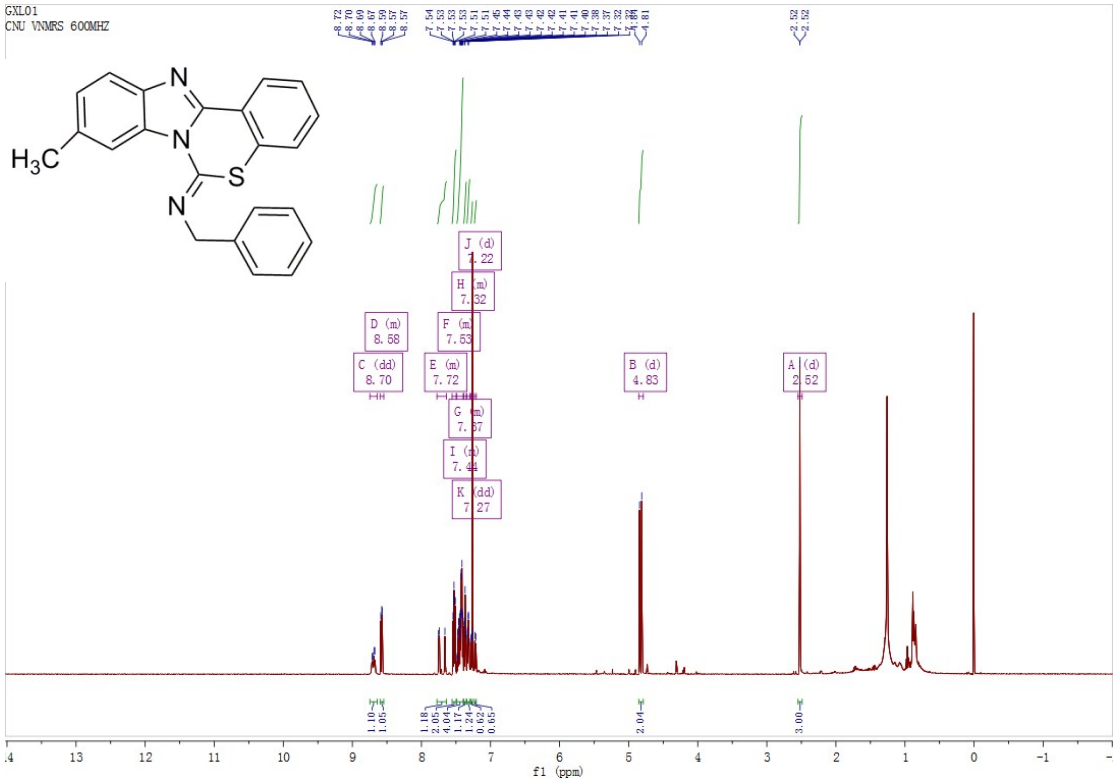
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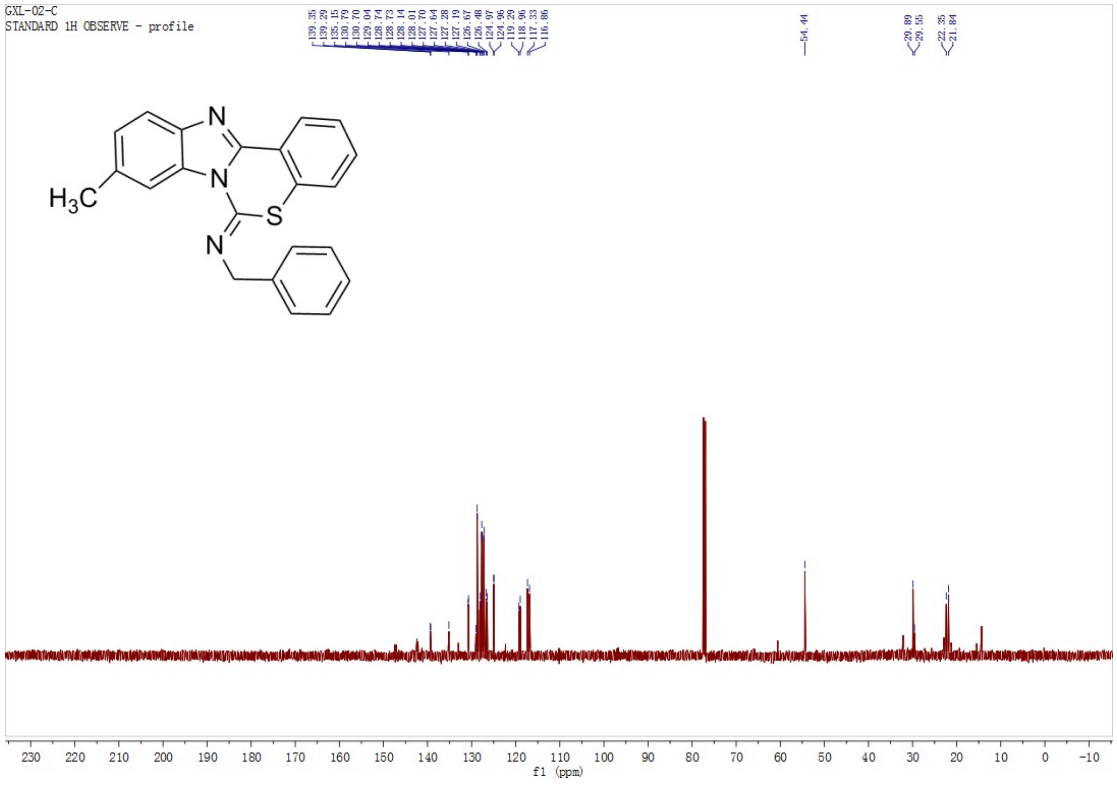
f1 (ppm)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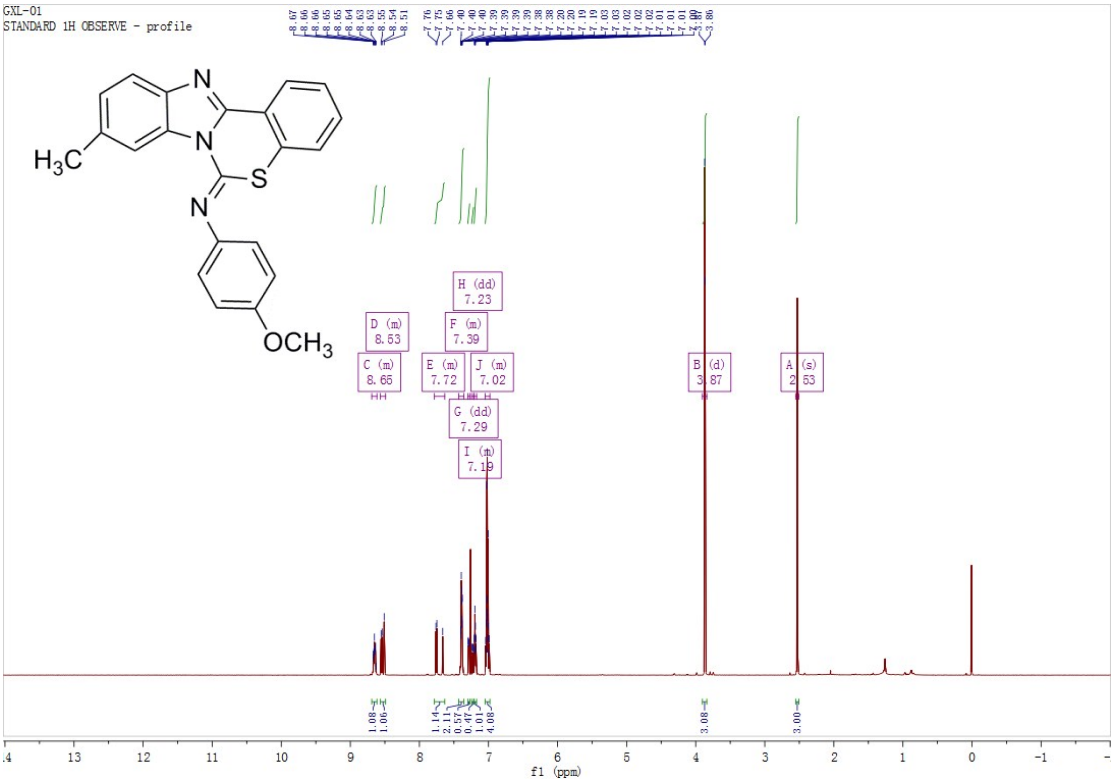
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N
S
N
OCH3
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E (m) 7.72
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B (d) 3.87
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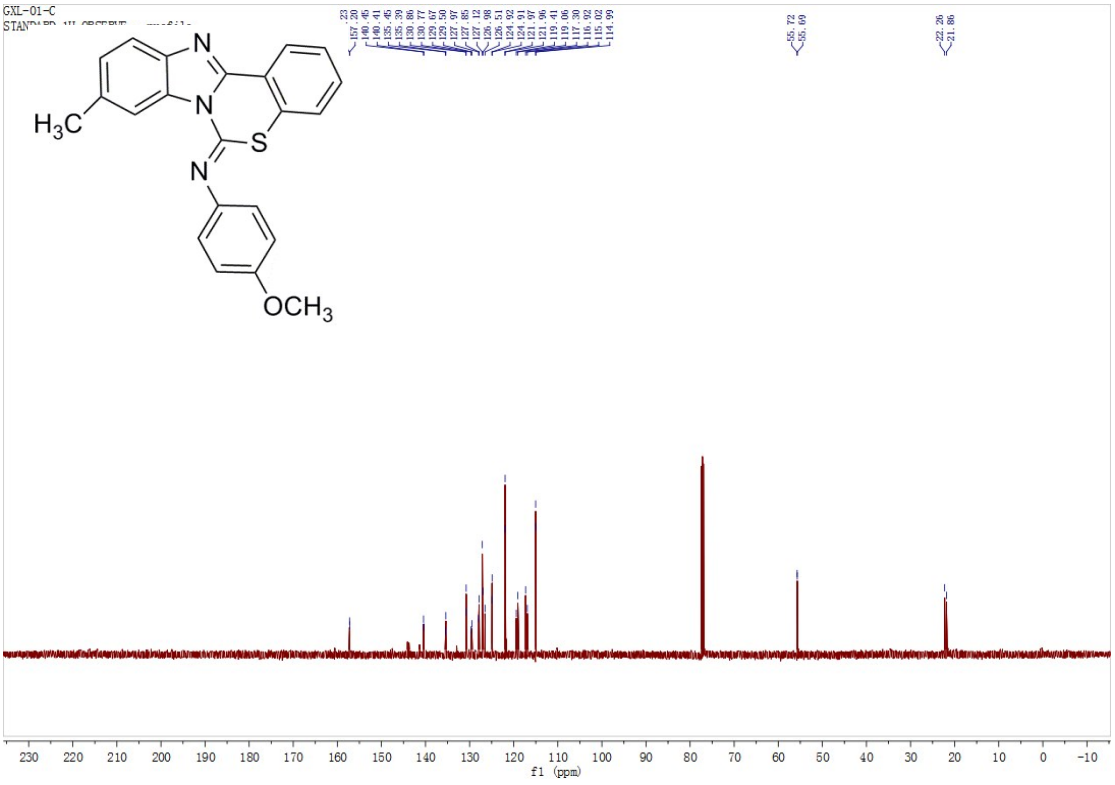
f1 (ppm)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N
S
N
OCH3
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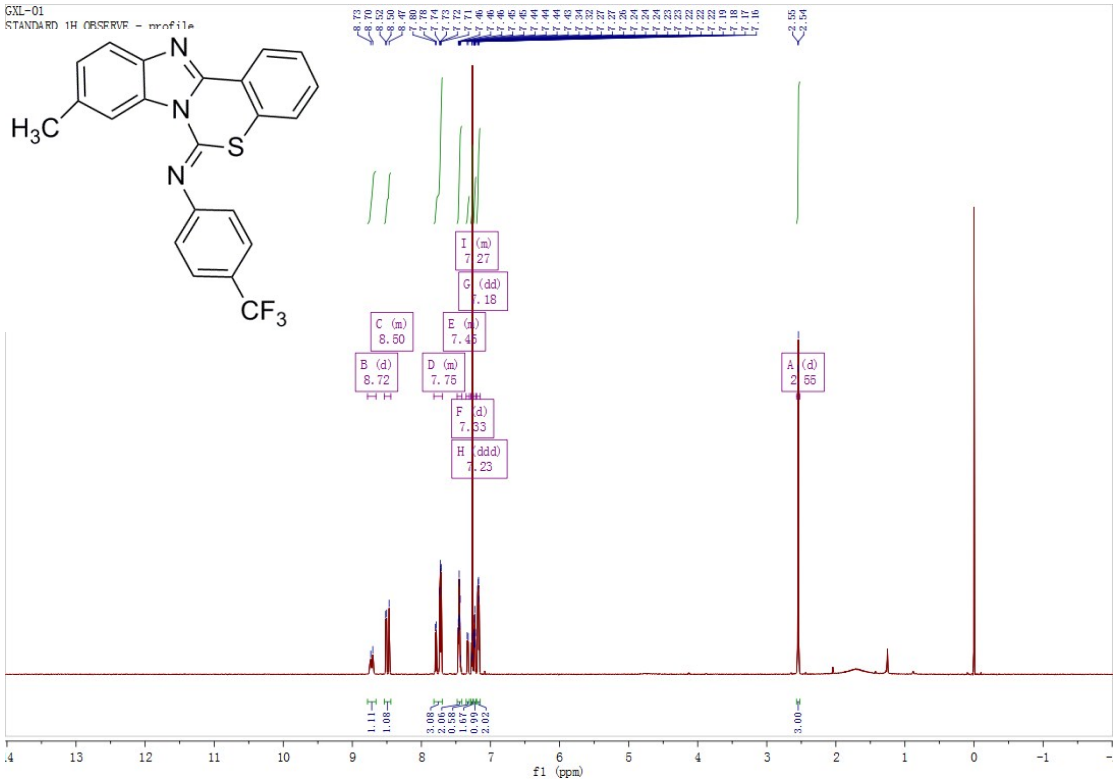
GXL-01
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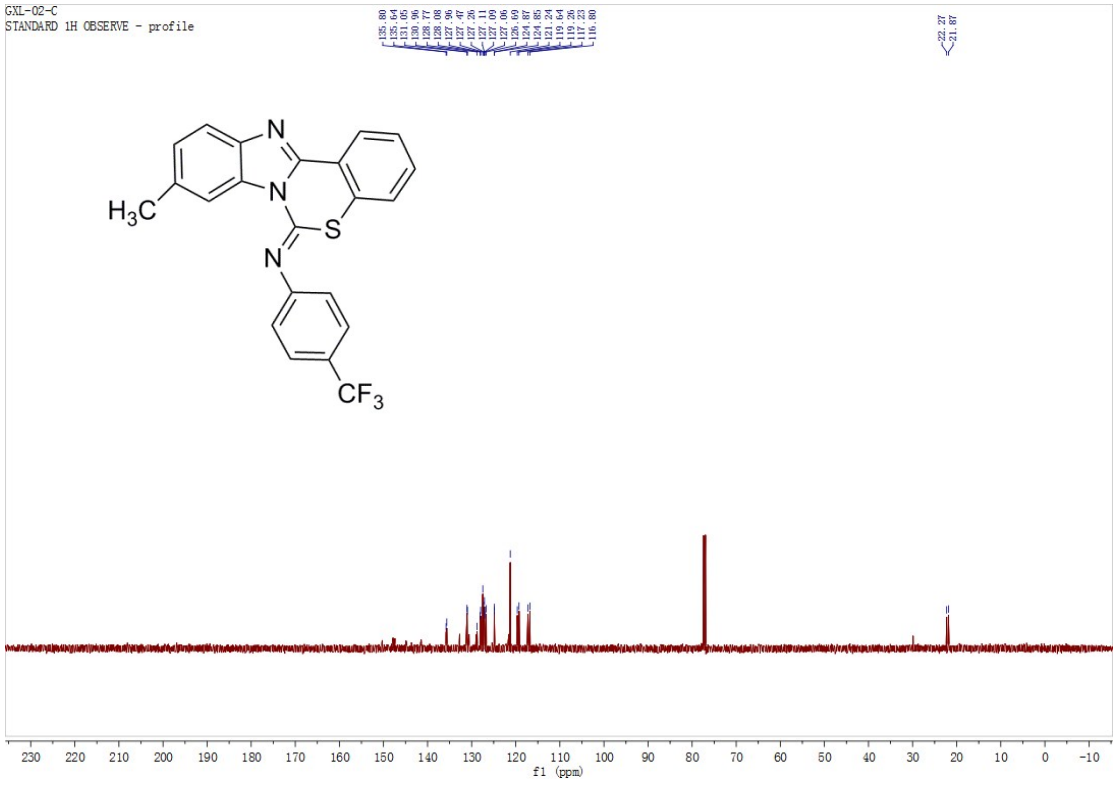
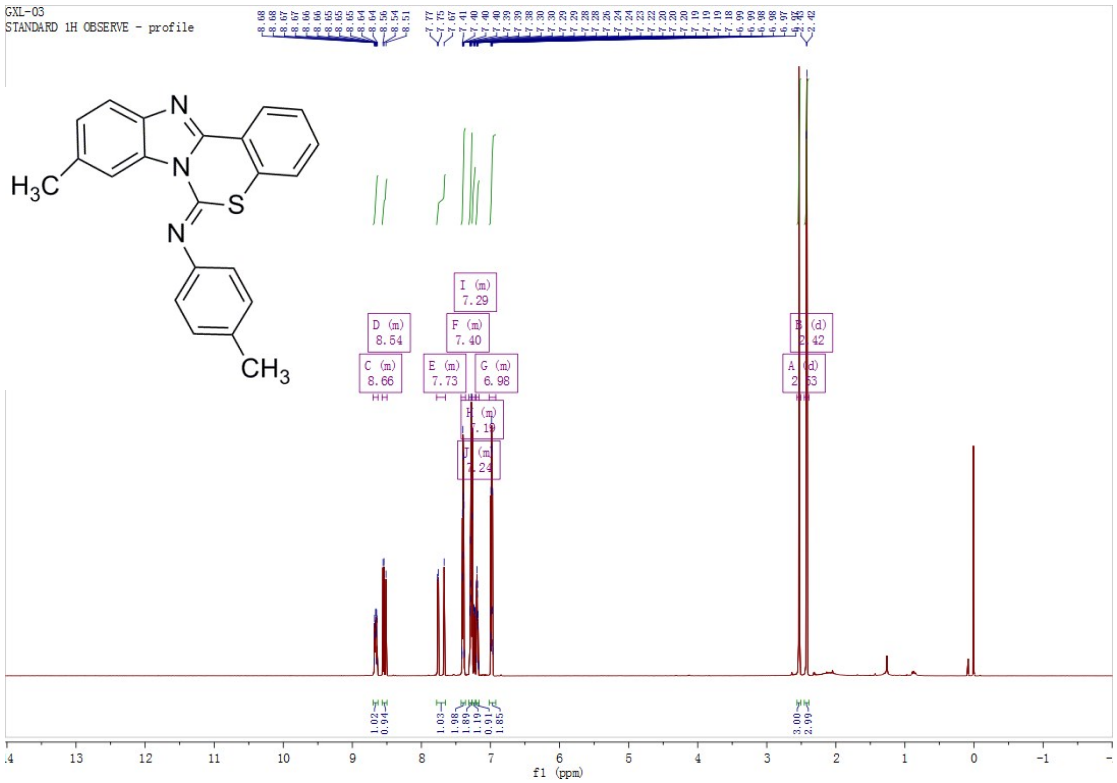
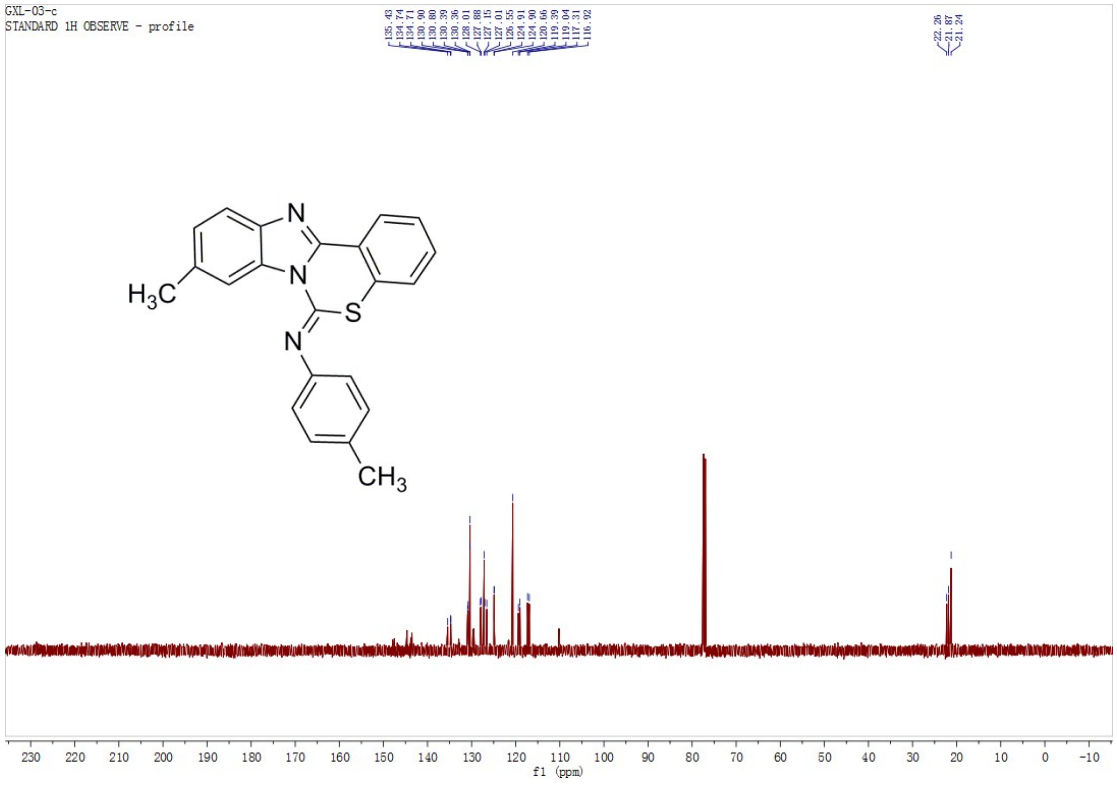
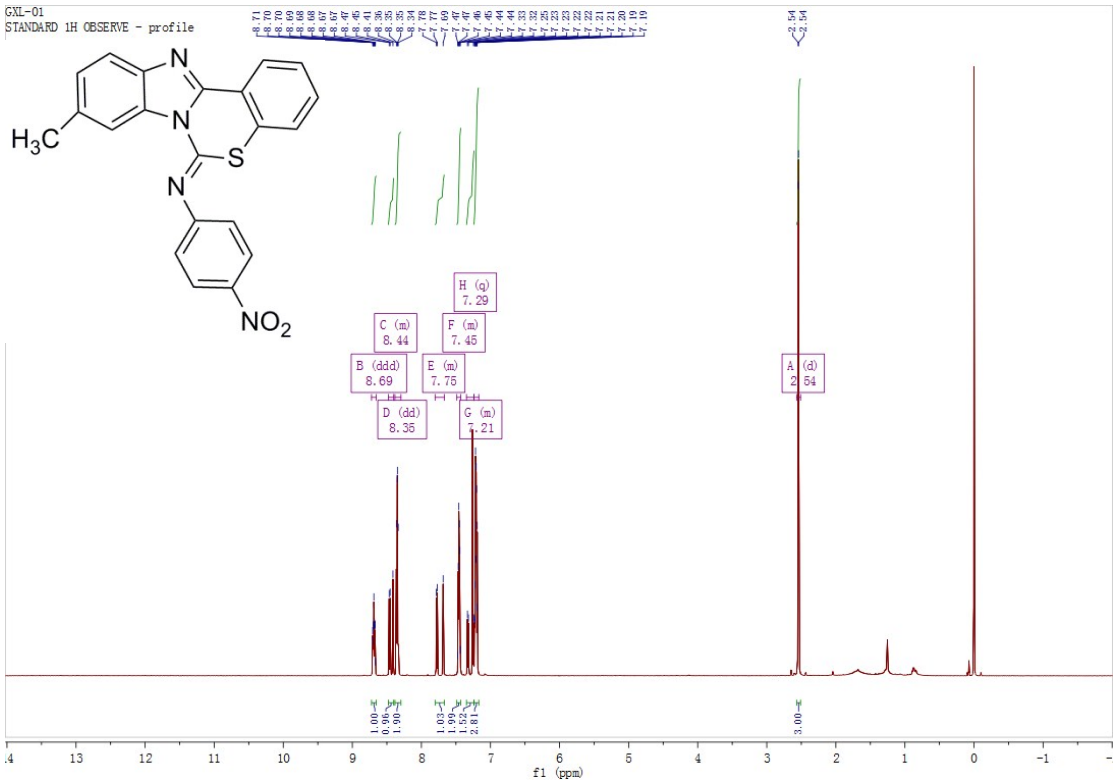
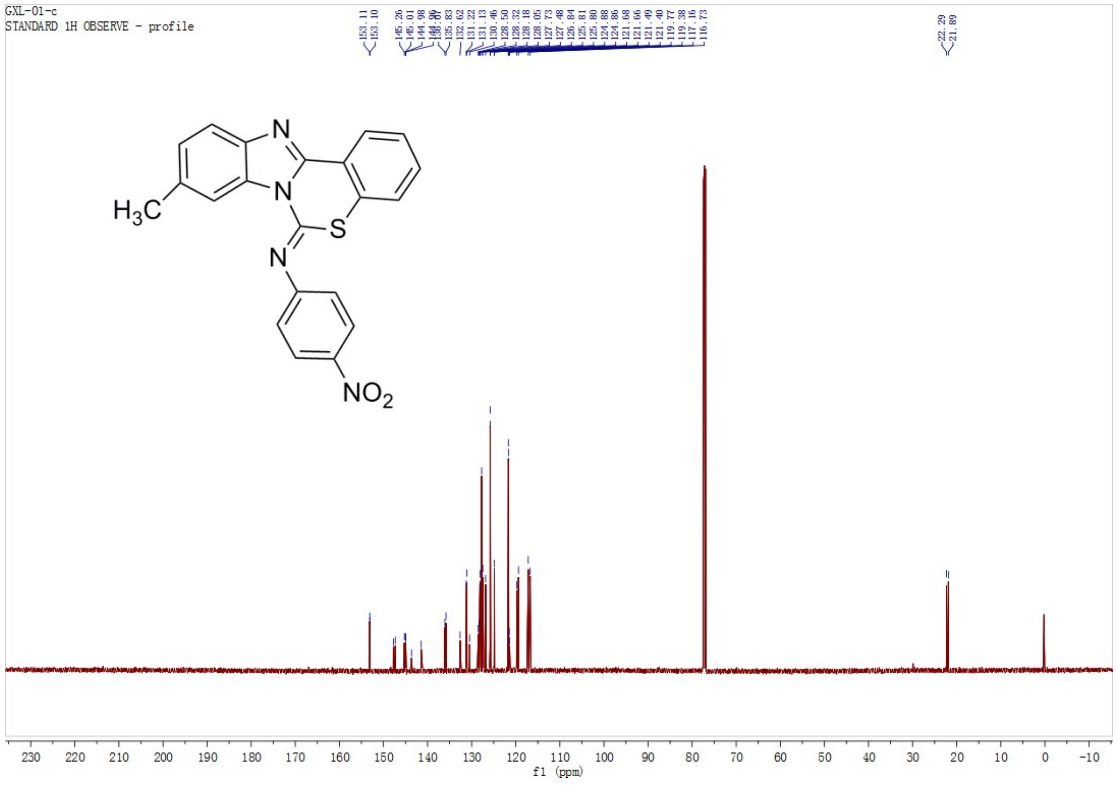
G (dd) 7.18
C (m) 8.50
E (m) 7.45
B (d) 8.72
D (m) 7.75
A (d) 2.55
F (d) 7.33
H (ddd) 7.23
1.11
1.08
3.08
2.06
0.58
1.67
0.99
2.02
3.00
f1 (ppm)

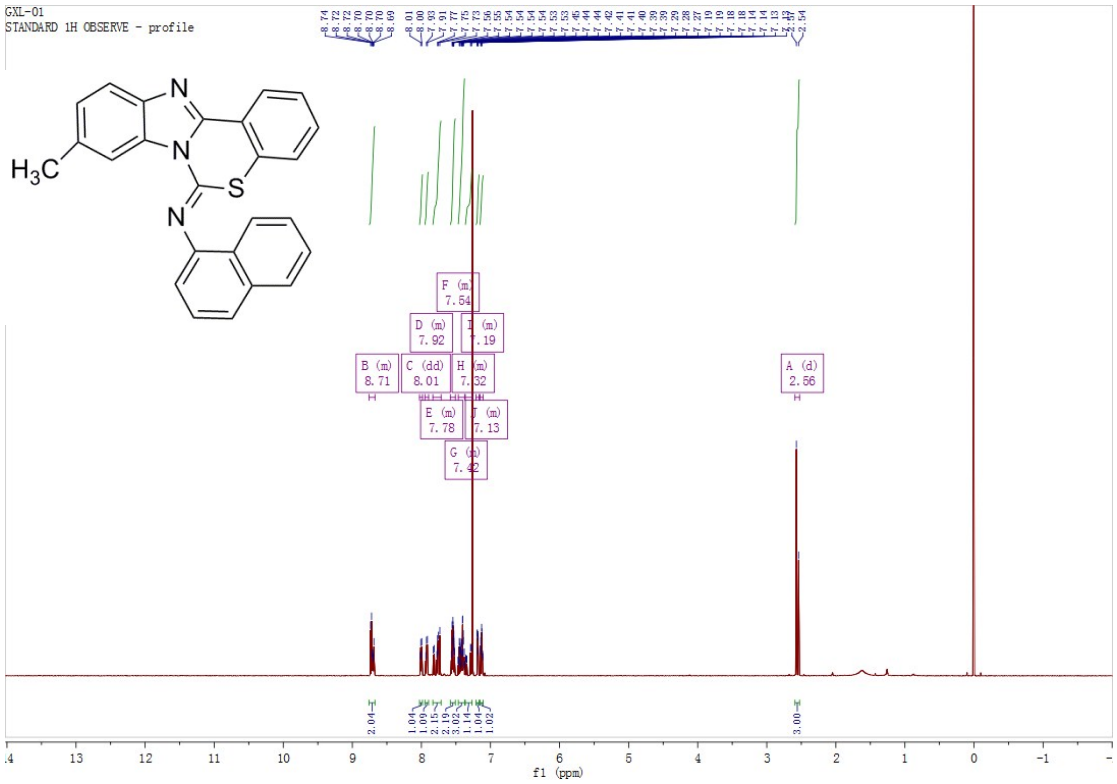

GXL-02-C
STANDARD 1H OBSERVE - profile
f1 (ppm)

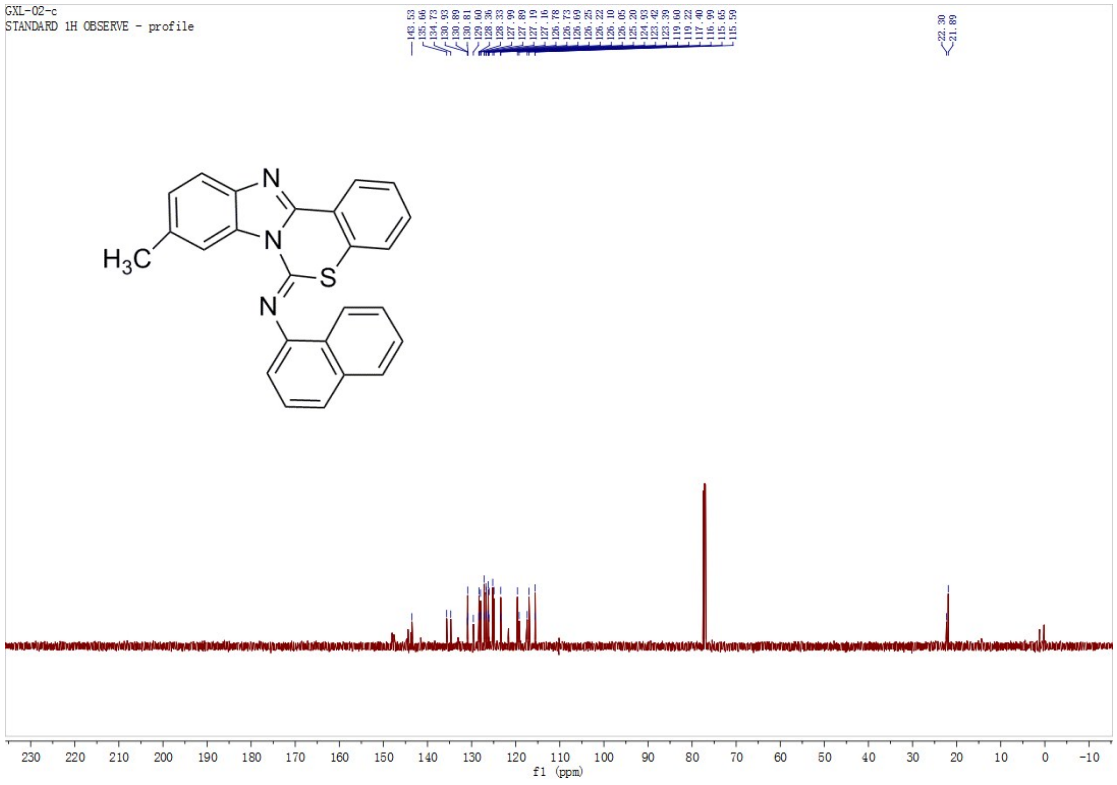

GXL-03
STANDARD 1H OBSERVE - profile
I (m) 7.29
D (m) 8.54
F (m) 7.40
B (d) 2.42
C (m) 8.66
E (m) 7.73
G (m) 6.98
A (d) 2.53
H (m) 7.19
J (m) 7.24
f1 (ppm)

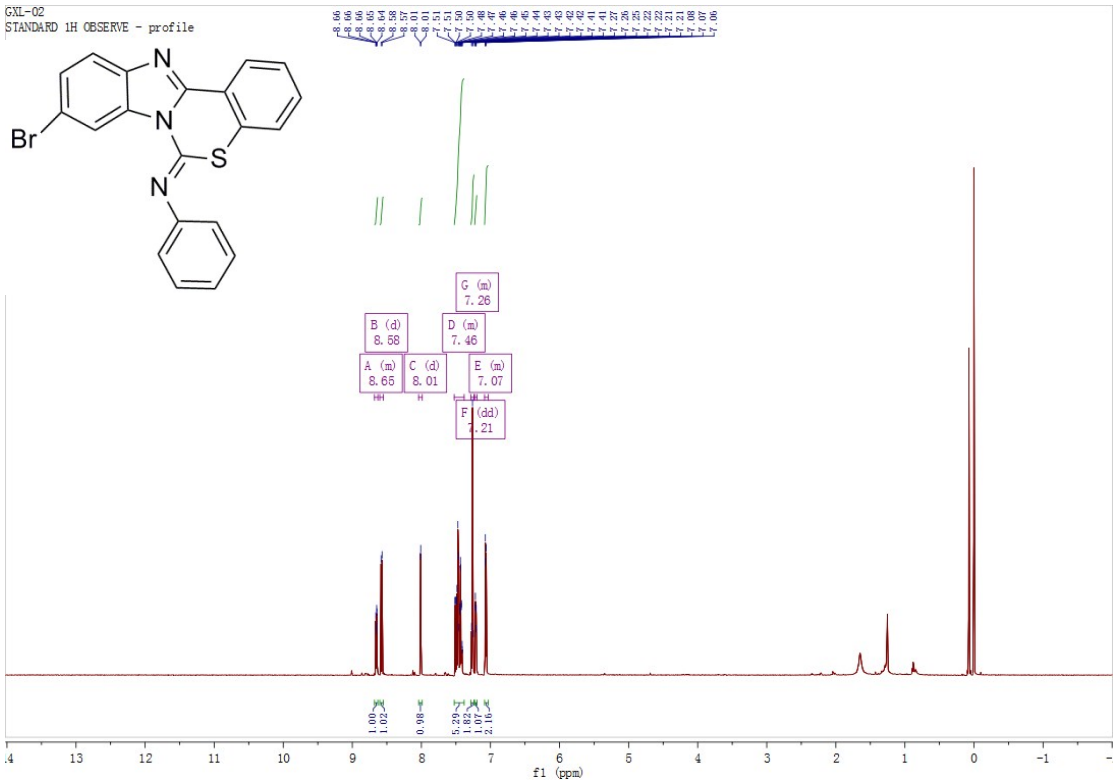

GXL-03-c
STANDARD 1H OBSERVE - profile
f1 (ppm)

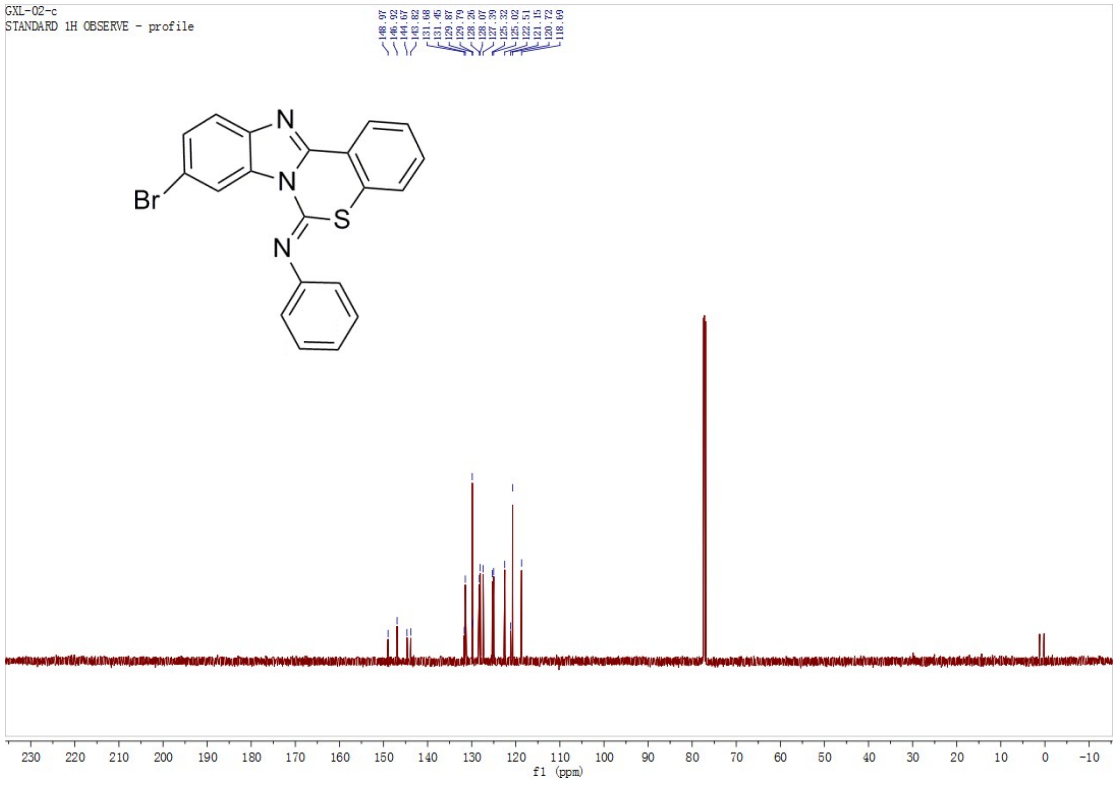

GXL-01
STANDARD 1H OBSERVE - profile
H (q)
7.29
C (m)
8.44
F (m)
7.45
B (ddd)
8.69
E (m)
7.75
A (d)
2.54
D (dd)
8.35
G (m)
7.21
f1 (ppm)

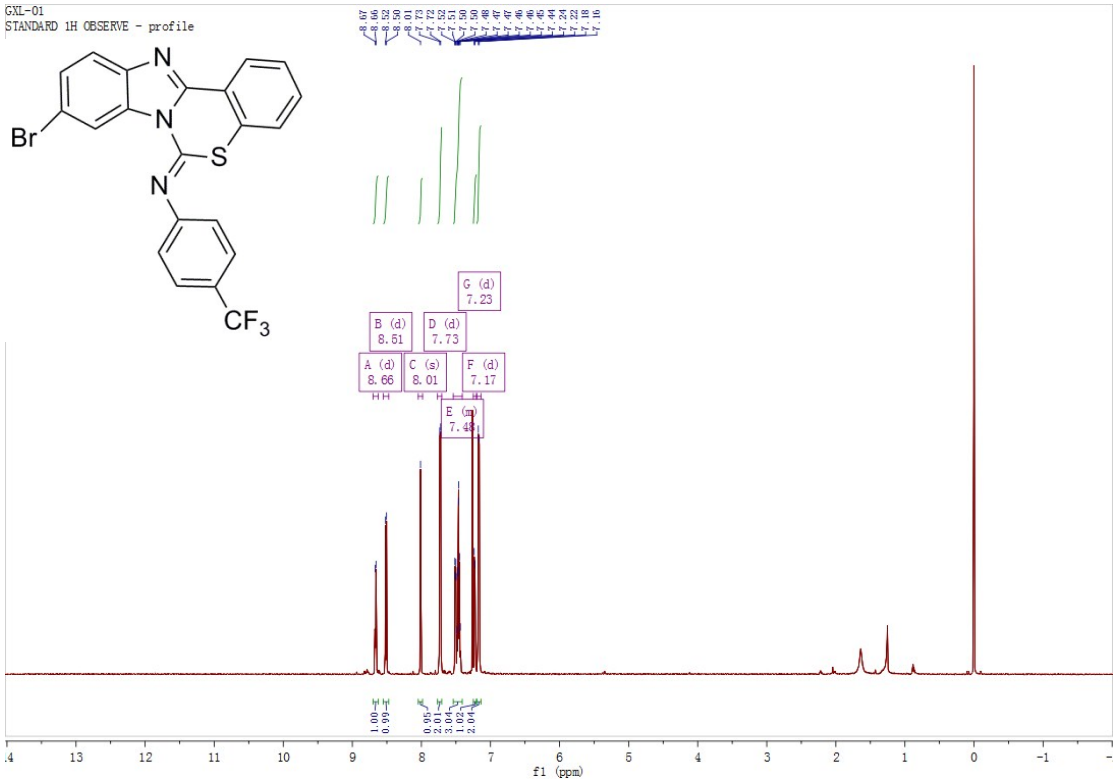

GXL-01-c
STANDARD 1H OBSERVE - profile
f1 (ppm)

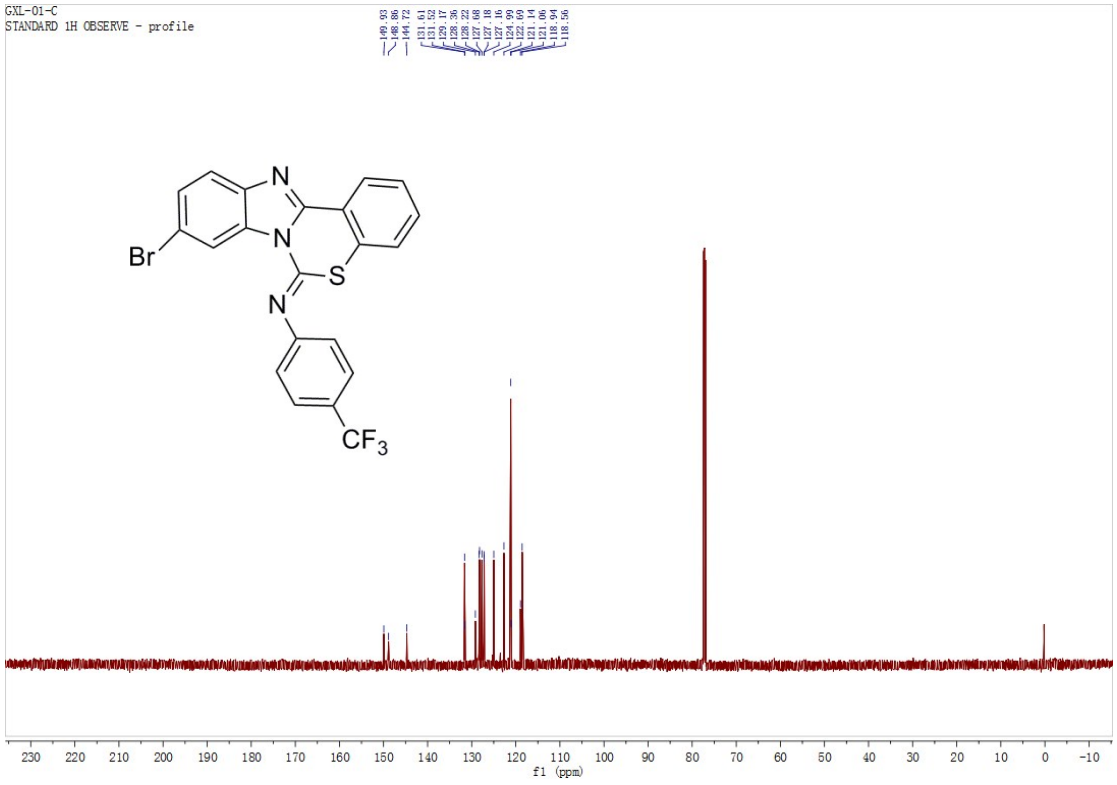

GXL-01
STANDARD 1H OBSERVE - profile
F (m) 7.64
D (m) 7.92
I (m) 7.19
B (m) 8.71
C (dd) 8.01
H (m) 7.52
A (d) 2.56
E (m) 7.78
J (m) 7.13
G (m) 7.42
f1 (ppm)

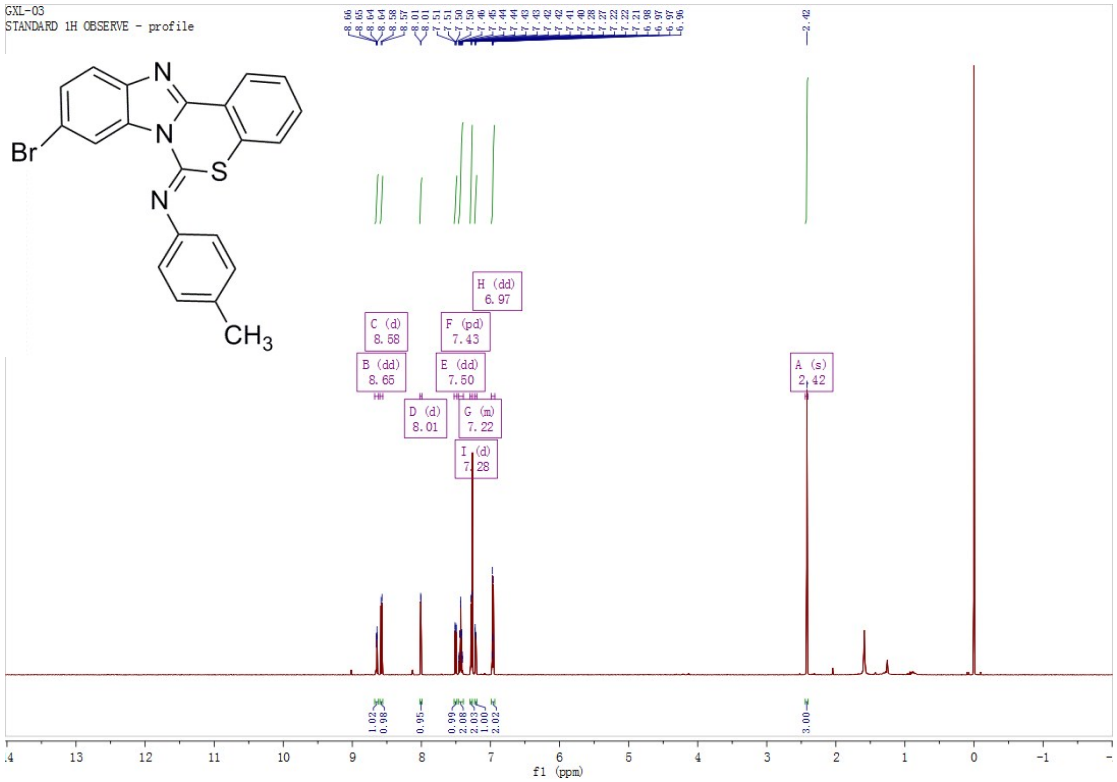

GXL-02-c
STANDARD 1H OBSERVE - profile
f1 (ppm)

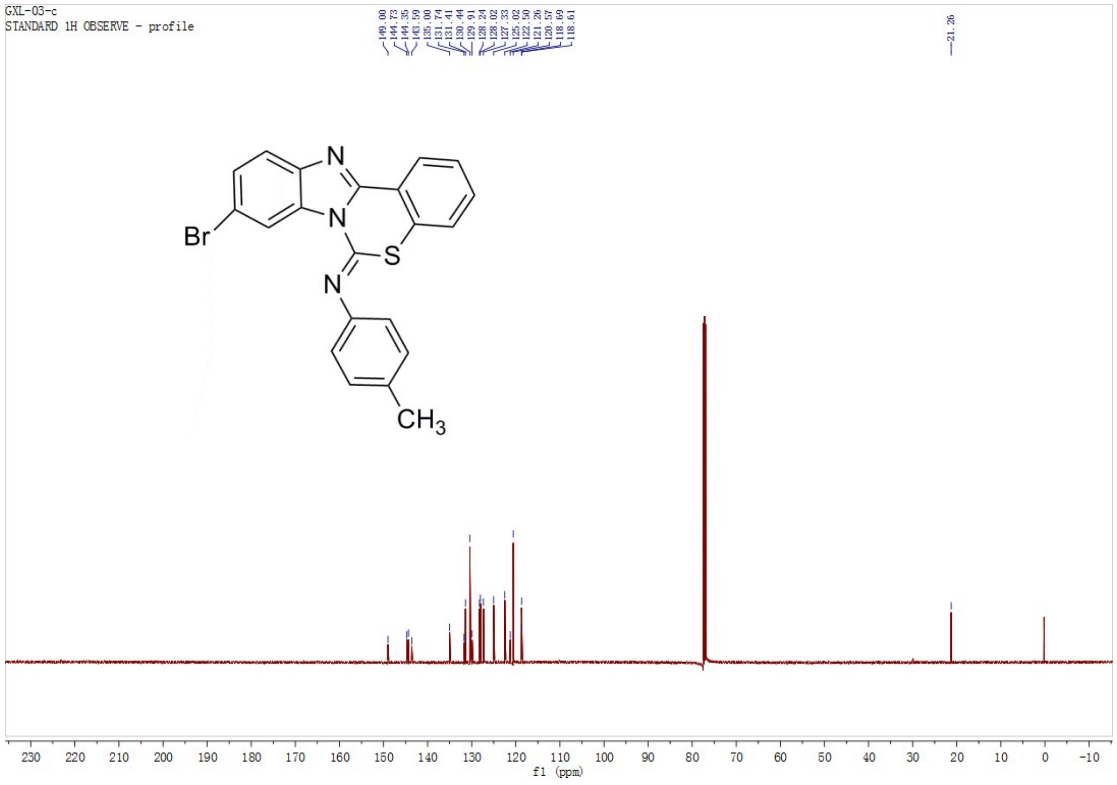

GXL-02
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
G (m)
7.26
B (d)
8.58
D (m)
7.46
A (m)
8.65
C (d)
8.01
E (m)
7.07
F (dd)
7.21
1.00
1.02
0.98
5.29
1.82
1.07
2.10
f1 (ppm)

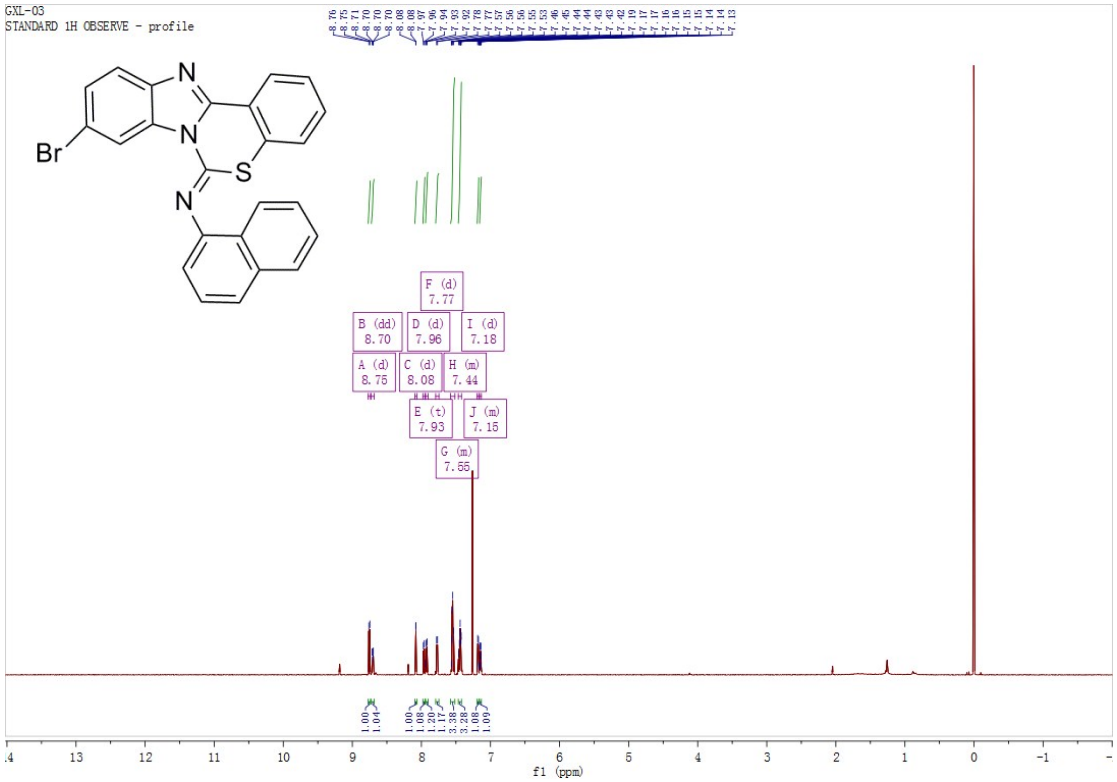

GXL-02-c
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
f1 (ppm)

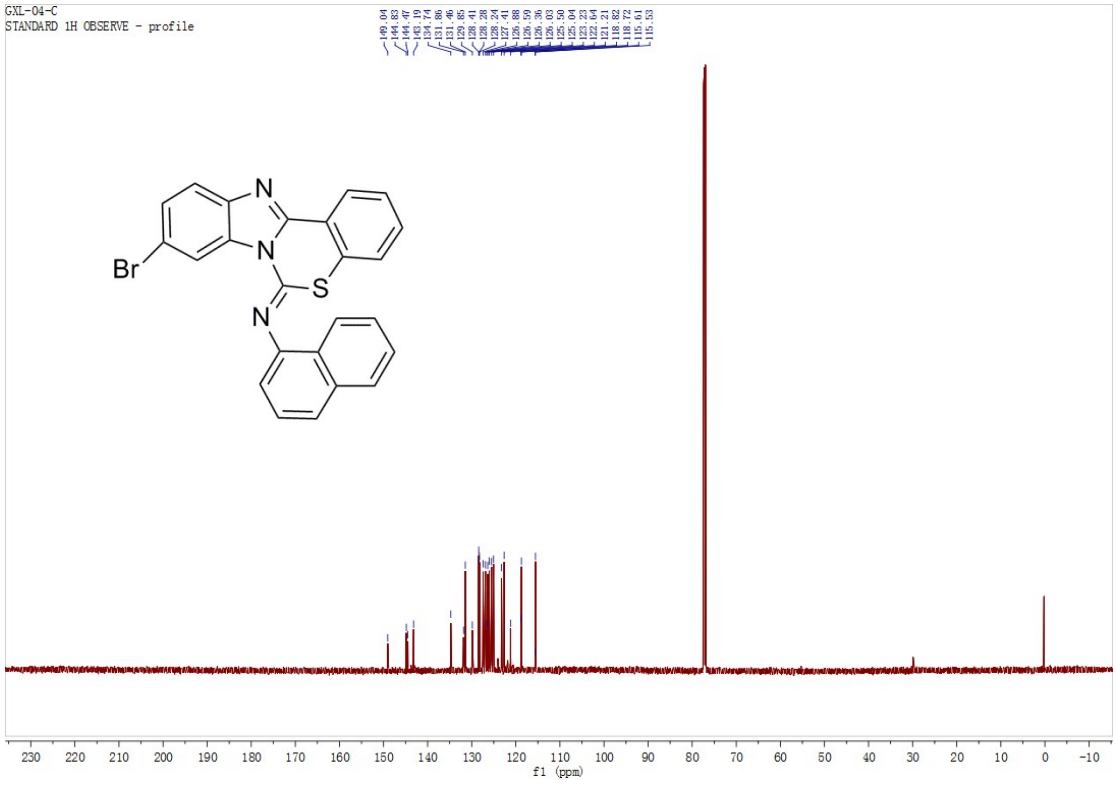

GXL-01
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
CF3
G (d)
7.23
B (d)
8.51
D (d)
7.73
A (d)
8.66
C (s)
8.01
F (d)
7.17
E (m)
7.48
f1 (ppm)

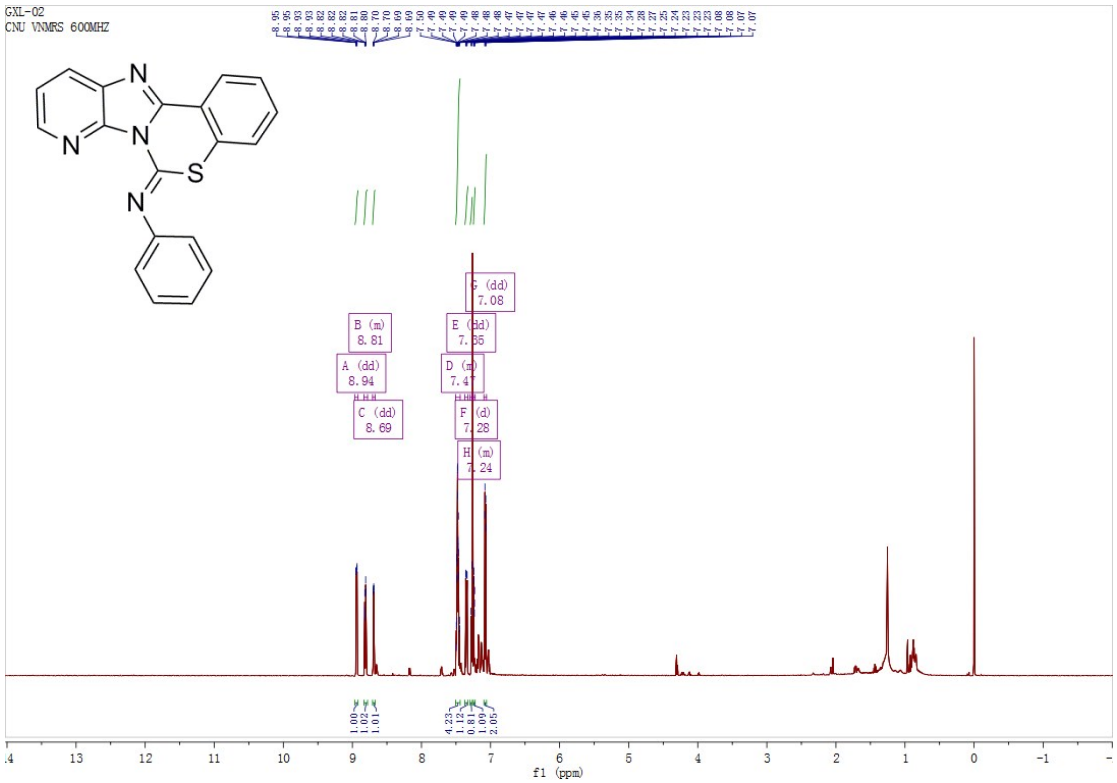

GXL-01-C
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
CF3
f1 (ppm)

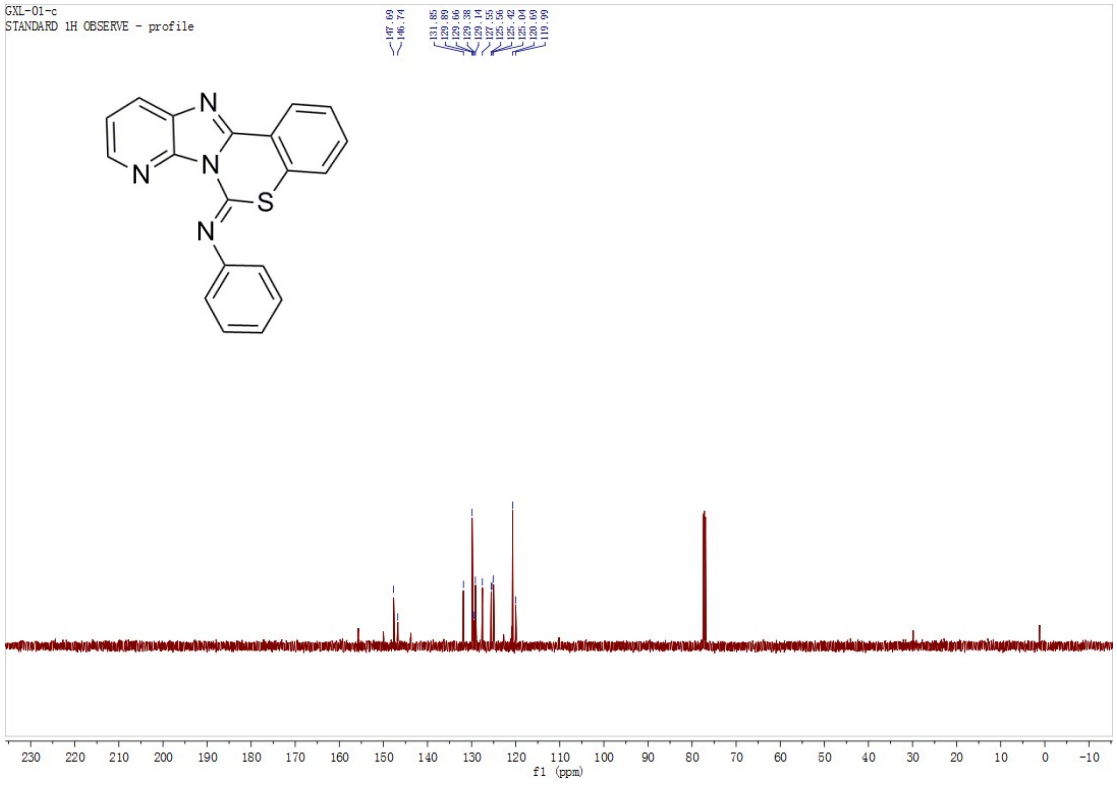

GXL-03
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
CH3
H (dd) 6.97
C (d) 8.58
F (pd) 7.43
B (dd) 8.65
E (dd) 7.50
A (s) 2.42
D (d) 8.01
G (m) 7.22
I (d) 7.28
f1 (ppm)

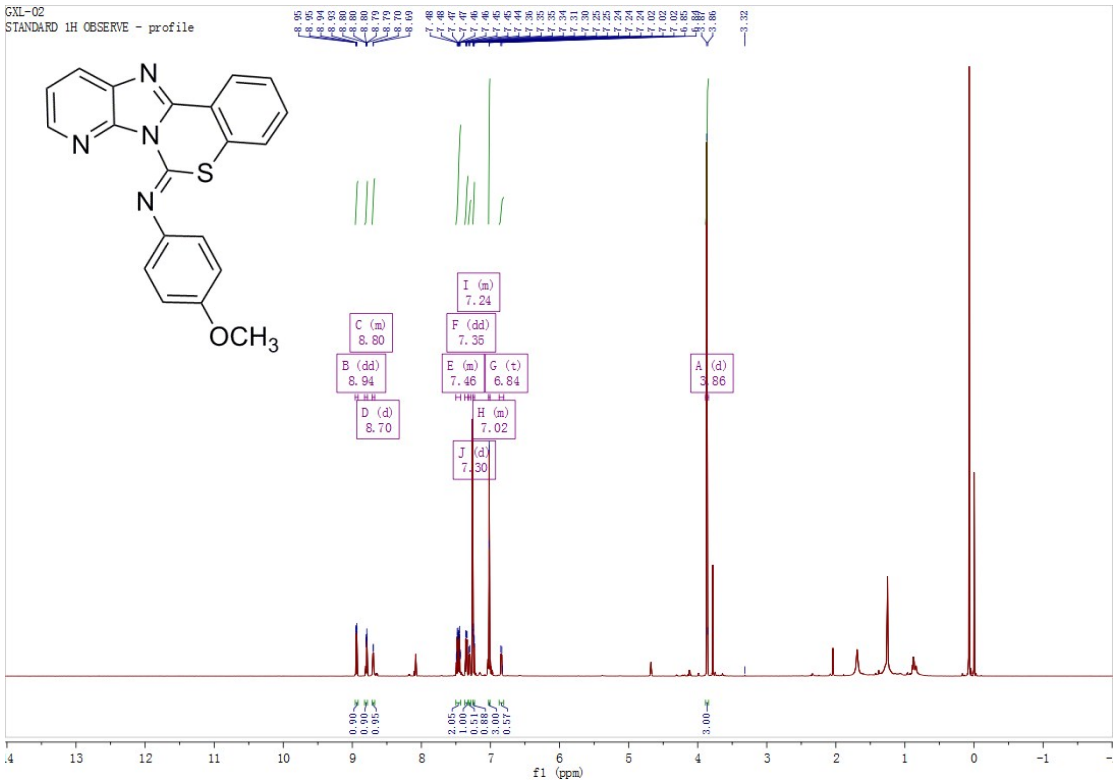

GXL-03-c
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
CH3
f1 (ppm)

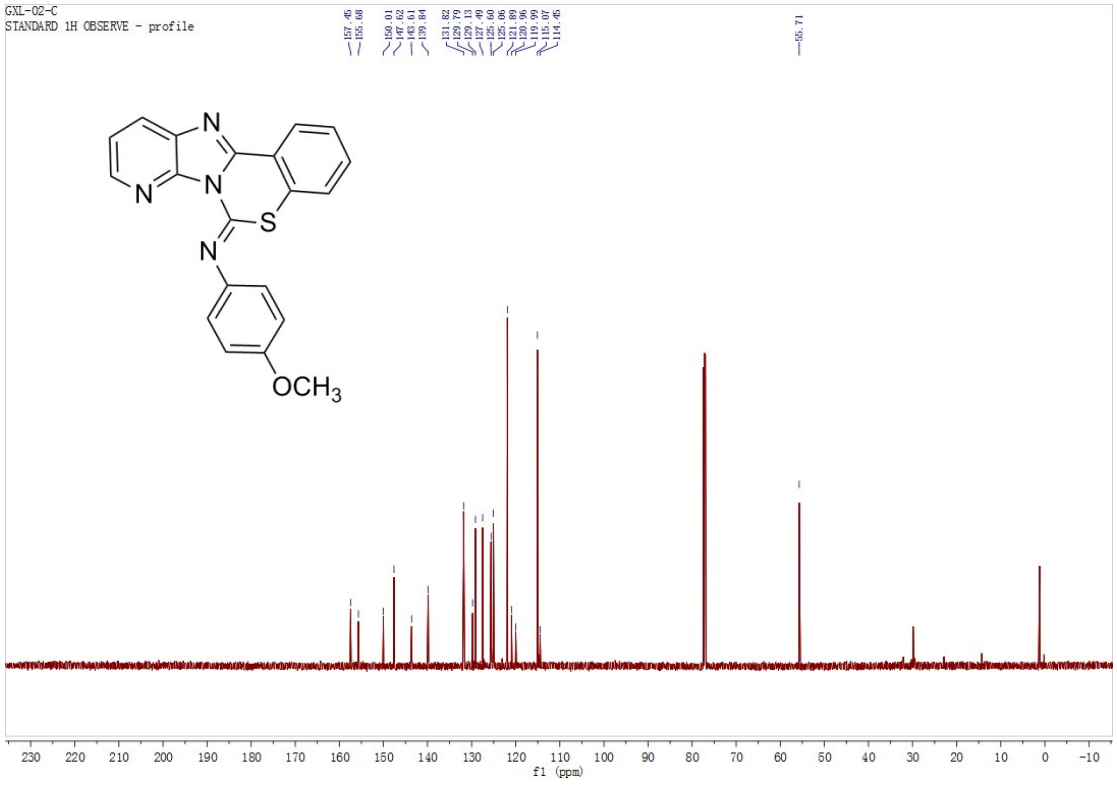

GXL-03
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
F (d) 7.77
B (dd) 8.70
D (d) 7.96
I (d) 7.18
A (d) 8.75
C (d) 8.08
H (m) 7.44
E (t) 7.93
J (m) 7.15
G (m) 7.55
f1 (ppm)

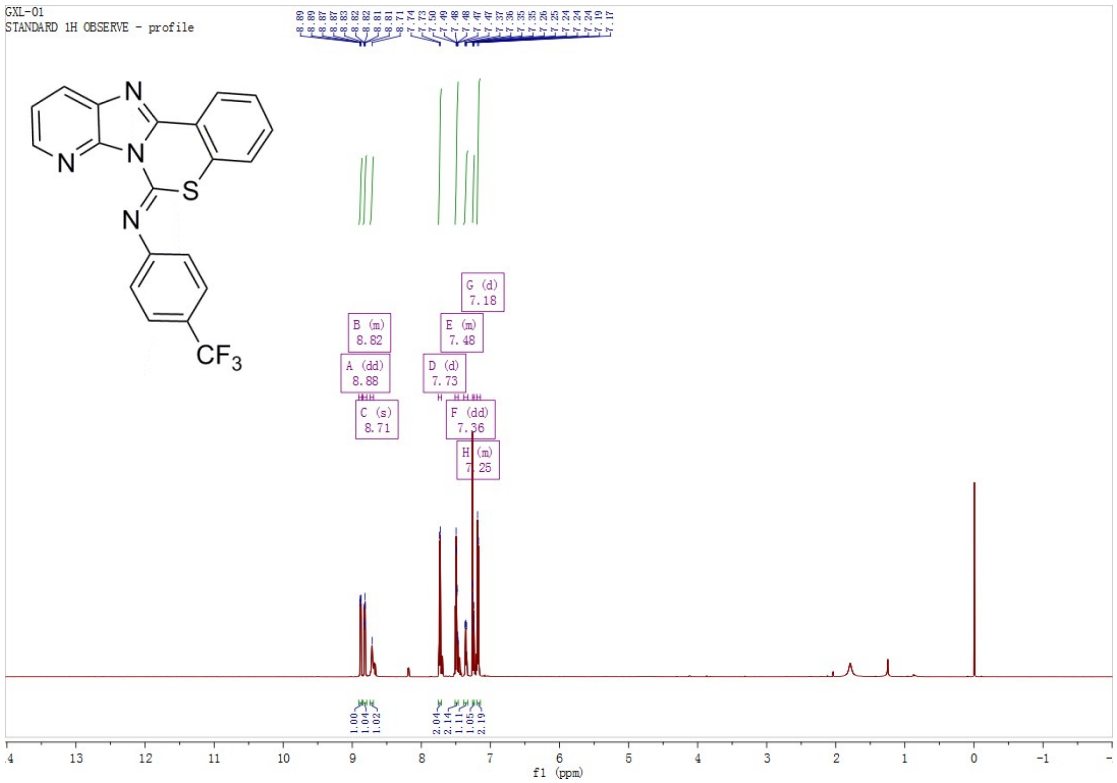

GXL-04-C
STANDARD 1H OBSERVE - profile
Br
N
N
S
N
f1 (ppm)

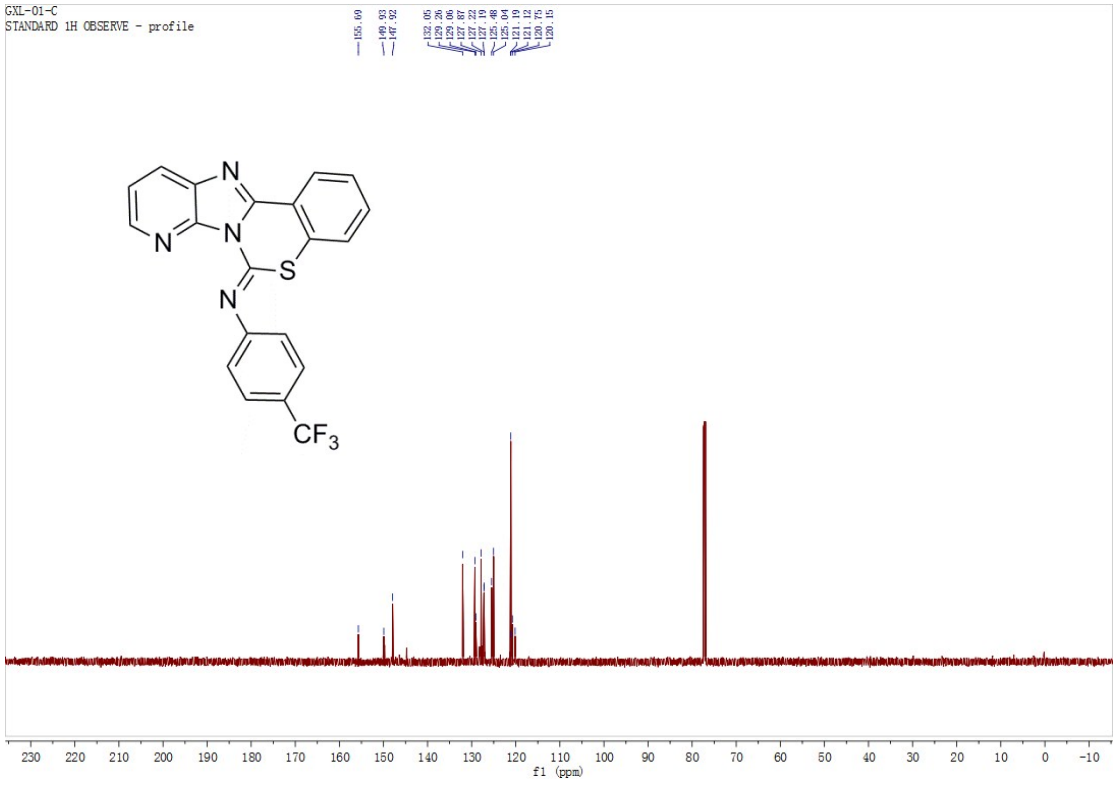

GXL-02
CNU VNMRS 600MHZ
G (dd)
7.08
B (m)
8.81
E (dd)
7.35
A (dd)
8.94
D (m)
7.47
C (dd)
8.69
F (d)
7.28
H (m)
7.24
f1 (ppm)

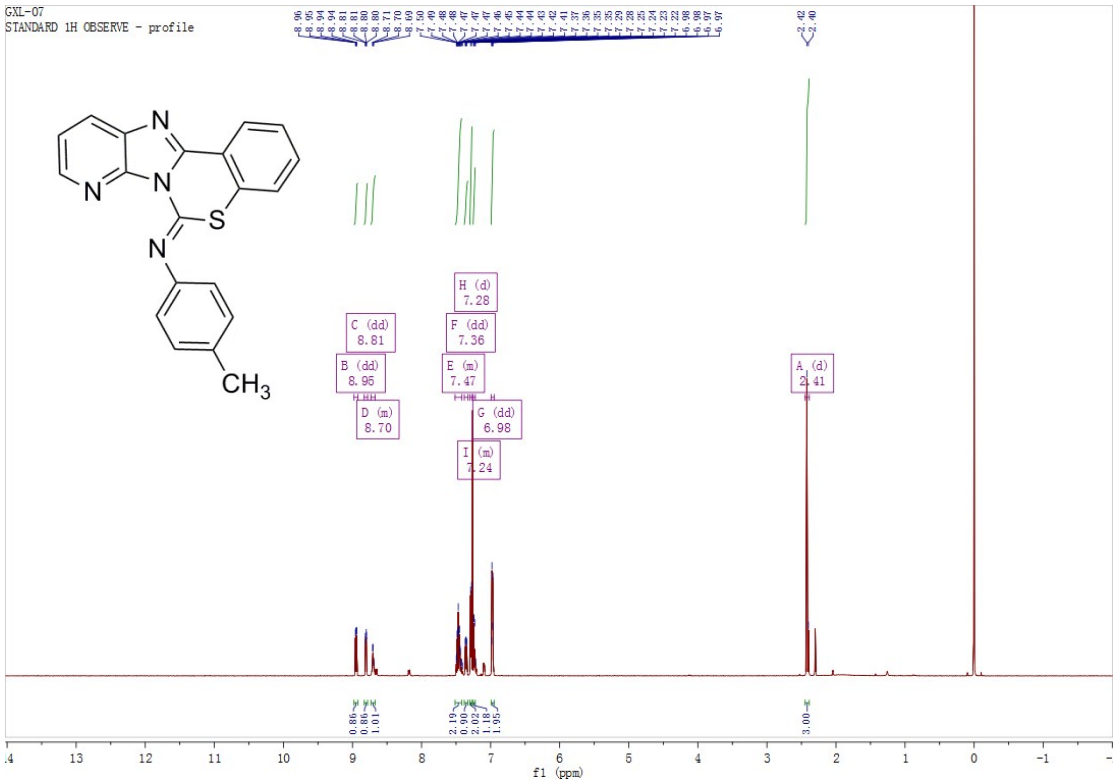

GXL-01-c
STANDARD 1H OBSERVE - profile
f1 (ppm)

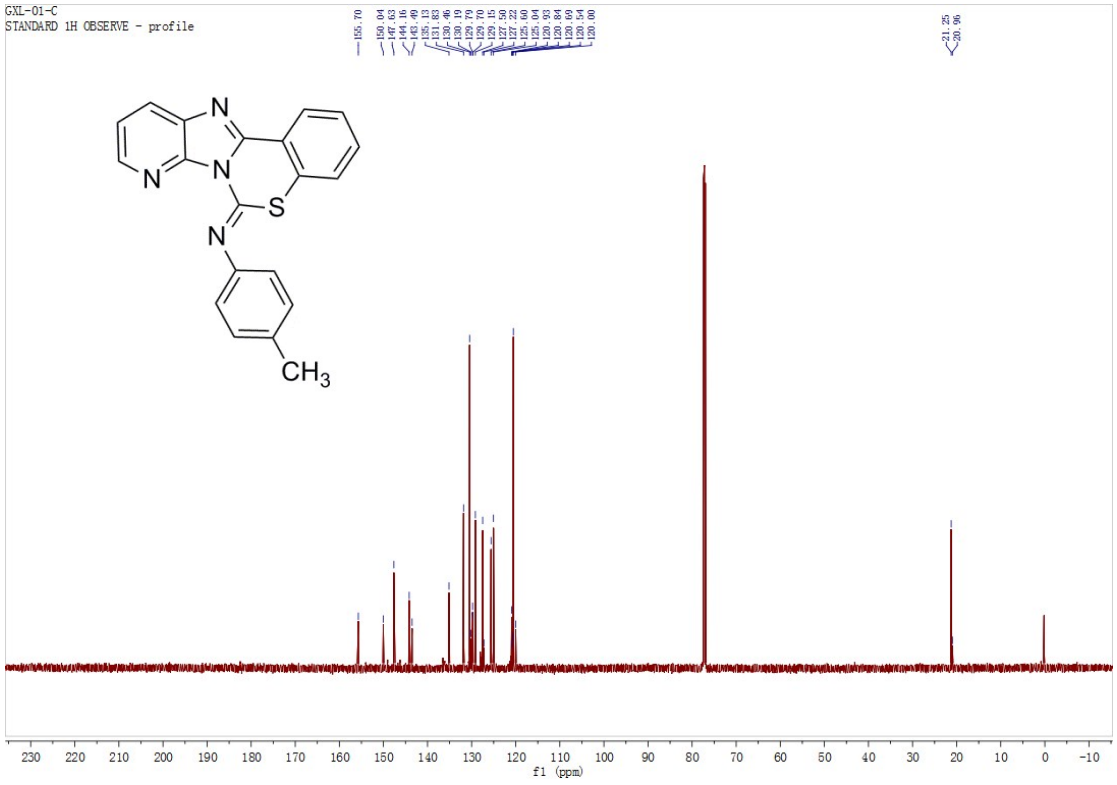

GXL-02
STANDARD 1H OBSERVE - profile
C (m) 8.80
B (dd) 8.94
D (d) 8.70
I (m) 7.24
F (dd) 7.35
E (m) 7.46
G (t) 6.84
H (m) 7.02
J (d) 7.30
A (d) 3.86
f1 (ppm)

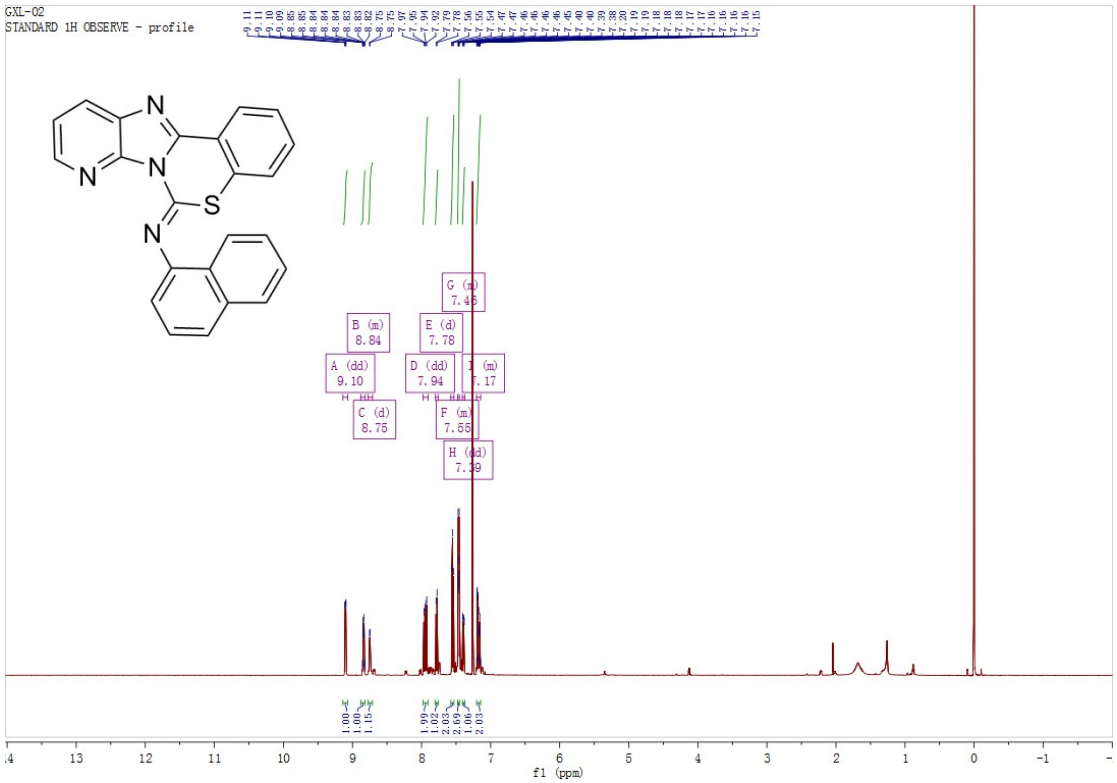

GXL-02-C
STANDARD 1H OBSERVE - profile
f1 (ppm)

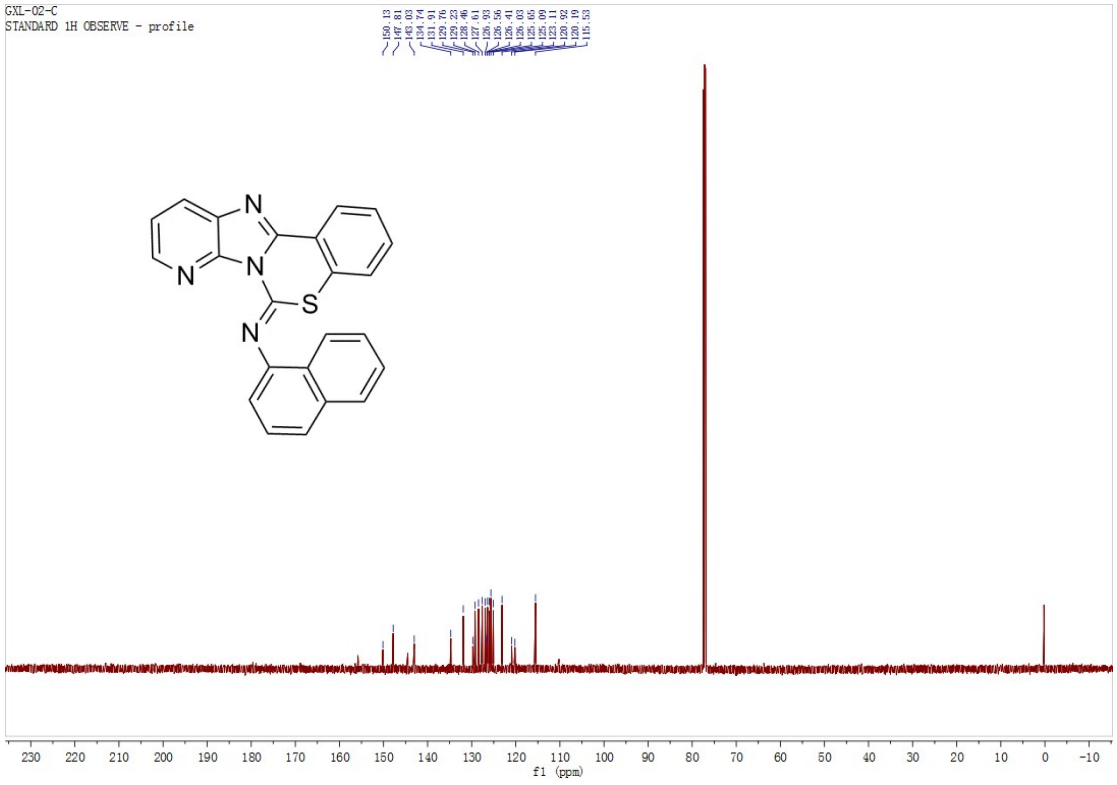

GXL-01
STANDARD 1H OBSERVE - profile
B (m)
8.82
A (dd)
8.88
C (s)
8.71
G (d)
7.18
E (m)
7.48
D (d)
7.73
F (dd)
7.36
H (m)
7.25
f1 (ppm)


GXL-01-C
STANDARD 1H OBSERVE - profile
f1 (ppm)


GXL-07
STANDARD 1H OBSERVE - profile
C (dd) 8.81
B (dd) 8.96
D (m) 8.70
H (d) 7.28
F (dd) 7.36
E (m) 7.47
G (dd) 6.98
I (m) 7.24
A (d) 2.41
f1 (ppm)


GXL-01-C
STANDARD 1H OBSERVE - profile
f1 (ppm)


GXL-02
STANDARD 1H OBSERVE - profile
B (m)
8.84
E (d)
7.78
G (m)
7.46
A (dd)
9.10
D (dd)
7.94
I (m)
7.17
C (d)
8.75
F (m)
7.65
H (dd)
7.39
f1 (ppm)


GXL-02-C
STANDARD 1H OBSERVE - profile
f1 (ppm)