Supplementary Information For

Visible light-induced C–H alkylation of 1,2,4-triazine-3,5*(2H,4H)*-diones using hypervalent iodine reagents as alkylating source

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Supplementary Information

1. General methods and materials

^{1}H, ^{13}C {^{1}H} and ^{19}F NMR spectra were recorded on a Bruker AC-P 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C {^{1}H}) in $CDCl_3$ (with TMS as internal standard). Chemical shifts (δ were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C {^{1}H} as internal standard. Coupling constants, J, are reported in hertz. High-resolution mass spectra (HRMS) were recorded on a quadrupole time-of-flight mass spectrometer (Q-TOF-MS) using electrospray ionization (ESI) as an ionization method. Melting points were obtained on the Shanghai Inesa WRS-3 melting point apparatus. Unless otherwise noted, the starting materials were purchased from J&K Chemical or Energy Chemicals and used without further purification. Some reactions were tried on a microreactor (Chemtrix BV, Kilo Flow, Labtrix Start or Protrix) in order to obtain the product in a better yield during the preparation of the substrates. Solvents were dried and purified according to the procedure from the "Purification of Laboratory Chemicals book". The crude products were purified by flash column chromatography on silica gel and the reported yields are the actual isolated yields of pure products. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates, visualized with short-wavelength UV light (254 nm).

Reactions were irradiated using a photo-reactor (Manufacturer： Xuzhou Fancai, Model: KL-647, λmax = 438 nm) shown in Figure S1. In order to keep the reaction temperature at room temperature, a simple cooling fan was installed above the reaction vessel. A borosilicate glass vessel was used for the reaction without a filter. The reaction vessel is secured by a three-claw clamp to keep a constant distance of 4 cm between the reaction vessel and the light source. The reaction was conducted in a microflow reactor using a flat-plane light source of the same model shown in Figure S1. The emission spectrum of the light source is shown in Figure S2.

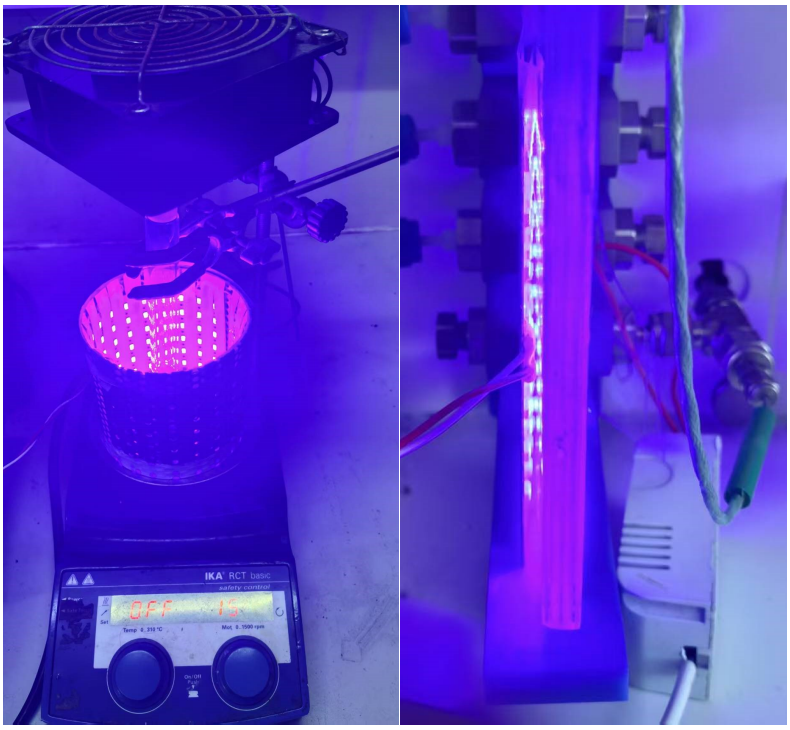


Figure S1. Photo-reactor (photographed by author Qun-qun Tian)

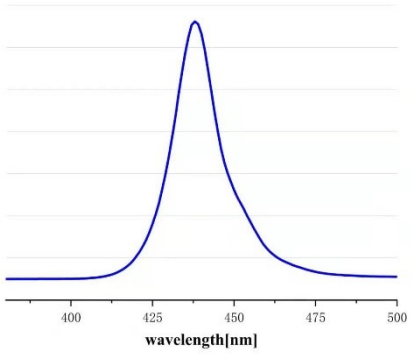
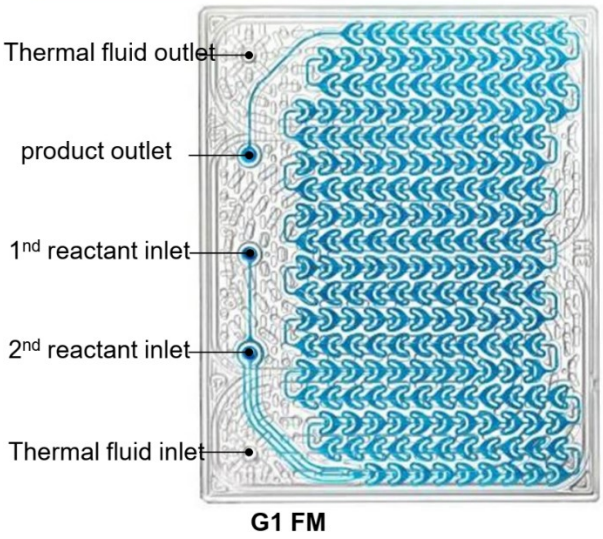


Figure S2. Emission spectrum of the light source

We performed the reactions using a Corning Advanced Flow Reactor (AFR), shown in Figure S3. The core apparatus comprised a G1 LF glass reactor module (2.7 mL hold-up volume), syringe pumps operating at 6 Bar, and a heat exchanger with an operational range of -5 to 200 °C, all under integrated wireless control for monitoring and regulating feed flow rates, temperature, and pressureshown in Figure S4.

Figure S3. Corning Advanced Flow Reactor (AFR)



Product characteristics	data	Unit
Temperature range (limited by chiller)	-5 / 120	°C
Maximum pressure (reactive pathway)	6	bar
Minimum Flow rate (get efficient mixing)	2	ml/min
Maximum Flow rate	limited by pressure drop	
Pressure drop @ 5 ml/min (water)	1,5	bar
Pressure drop @ 10 ml/min (water)	4	bar
Fluidic module internal volume	2,7	ml
Wetted materials	disposable plastic or glass for syringe, ETFE, PFA, PTFE, O-rings, glass	
Piping size (external diameter)	1/8	inch
Pump type	Syringe pump	
Syringe provided internal volume		
disposable plastic	30 / 20 / 10	ml
glass	25	ml
fluidic module inlets / outlets	2/1	
TcK (inlet / outlet HE)	2	
Power supply included (Reactor)	12V	
Size (L x W x H)	630 x 415 x 546	mm
Weight	15	Kg

Figure S4. G1 LF glass reactor module

1.1 General Procedure for the Preparation of 1,2,4-triazine-3,5*(2H,4H)*-diones.

The substrates of various 1,2,4-triazine-3,5*(2H,4H)*-diones were synthesized according to procedures described in the previous literature, and the spectral characteristics data were consistent with those reported previously in the literature.[1]

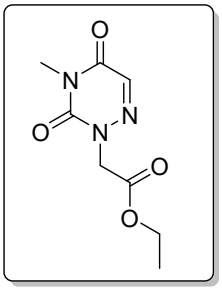


Table S1. Crystallographic data and refinement details for ethyl 2-(4-methyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3H)-yl)acetate (1n)

Identification code	CCDC 2518122
Empirical formula	$C_8H_{11}N_3O_4$
Formula weight	213.20
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.3836(5)
b/Å	4.82420(10)
c/Å	13.9318(6)
α/°	90
β/°	111.195(4)
γ/°	90
Volume/Å^3	963.99(6)
Z	4
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	0.119

F(000)	448.0
Crystal size/mm^3	0.23 × 0.2 × 0.14
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.68 to 52.74
Index ranges	-19 ≤ h ≤ 19, -6 ≤ k ≤ 6, -17 ≤ l ≤ 14
Reflections collected	7256
Independent reflections	1959 [R_{int} = 0.0192, R_{sigma} = 0.0174]
Data/restraints/parameters	1959/0/138
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0813
Final R indexes [all data]	R_1 = 0.0324, wR_2 = 0.0835
Largest diff. peak/hole / e Å^{-3}	0.22/-0.20

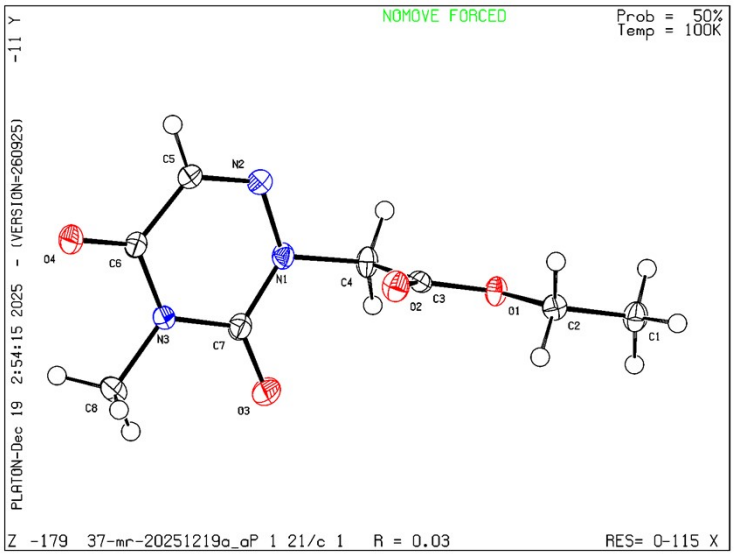


Figure S5. Molecular structure of compound 1n.

1.2 General Procedure for the Preparation of Hypervalent Iodine Reagents.

The substrates of various hypervalent iodine reagents were synthesized according to procedures described in the previous literature, and the spectral characteristics data were consistent with those reported previously in the literature.[2, 3]

2. Experimental Section

2.1 General experimental procedures for the desired product

An oven-dried Schlenk tube was charged with 1,2,4-triazine-3,5*(2H,4H)*-diones (0.3 mmol), hypervalent iodine reagent (0.69 mmol, 2.3 equiv.), DBU (0.54 mmol, 1.8 equiv.) and DMSO (0.8 mL) and a magnetic stirring bar. Then the reaction vessel was irradiated with a 25 W blue LED at room temperature for 2 h. After the reaction, the solvent was evaporated under vacuum. The crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as eluting solvent to give the desired products.

2.2 Gram-scale synthesis

A 50 mL reaction vessel was charged with 1,2,4-triazine-3,5*(2H,4H)*-diones (3.6 mmol), hypervalent iodine reagent (8.28 mmol, 2.3 equiv.), DBU (6.48 mmol, 1.8 equiv.) and DMSO (8.28 mL) and a magnetic stirring bar. Then the reaction vessel was irradiated with a 25 W blue LED at room temperature for 2 h. After the reaction, the solvent was evaporated under vacuum. The crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as the eluting solvent to give the desired products (92%, 1.06 g).

2.3 Sensitivity assessment of reaction

Table S2 Selected reaction conditions optimization[a]

Parameter	Variation	Description	Yield (%)[b]
Concentration (c)	High c c+ 10% c	0.88 mL DMSO	89
	Low c c- 10% c	0.72 mL DMSO	84
H_2O content	High H_2O + H_2O	50 μL H_2O in 0.8 mL DMSO	75
N_2	High N_2 N_2 balloon	N_2 instead of air	90
Temperature (T)	High T *T* + 10 °C	35 °C	88
	Low T *T* - 10 °C	15 °C	86

[a] Standard conditions: 2,4-dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (0.3 mmol), **2a** (0.69 mmol), DBU (0.54 mmol) and DMSO, blue LED, room temperature for 2h. [b] The average yield of three parallel reactions

2.4 Continuous synthesis experiment

In a typical experiment, 7.5 mmol of 1,2,4-triazine-3,5*(2H,4H)*-dione, 13.5 mmol of DBU and 10 mL of DMSO were added to an Erlenmeyer flask to give solution A. The other Erlenmeyer flask was charged with 17.25 mmol of hypervalent iodine reagents, followed by 10 mL of DMSO to afford solution B. The mixture entered the microchannel reactor to complete the reaction at a given pressure under the irradiation of a blue LED. The reactor pressure is monitored by a pressure gauge at the inlet and controlled by a back pressure valve. The reaction condition was monitored by TLC. If the residue of hypervalent iodine reagents was observed, ethyl acetate and water were used to extract the reaction mixture three times. The combined organic phase is washed with a large amount of water, and then the solvent is evaporated under vacuum. If not, the solvent was evaporated under vacuum directly. The crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as eluting solvent to give the desired products.

2.5 UV-Vis experiment for the conformation of EDA-complex

Ultraviolet-visible spectroscopy experiments were conducted using a quartz cuvette with a path length of 1.0 cm. First, the ultraviolet spectra of the starting materials N^2,N^4-dibenzyl-1,2,4-triazine-3,5(2H,4H)-dione (**1a**), DBU, and mesityl-λ^3-iodanediyl dipropionate (**2a**) were measured individually in DMSO (dimethyl sulfoxide) at a concentration of 2×10^{-3} M. Subsequently, these three starting materials were mixed in a 1:1 molar ratio, and after letting the mixture stand for 2 hours under identical concentration conditions, its ultraviolet-visible spectrum was recorded.

At this point, it was found that the peak of the mixture of **2a** and DBU developed a shoulder peak, accompanied by a decrease in the absorption intensity of the **2a** peak. For clarity, we prepared a solution at the same concentration as the reaction mixture and measured its ultraviolet absorption, discovering a broad absorption doublet between 300 nm and 500 nm.

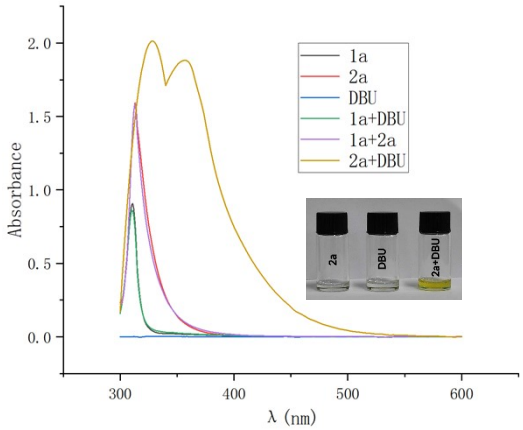


Figure S6. UV-Vis absorption of the EDA complex (2a + DBU, 1:1) compared to 2a, 1a, 1a+2a，1a+DBU and DBU.

2.6 NMR spectroscopy confirmed the existence of the EDA complex.

We performed NMR spectroscopy of DBU and mesityl-λ³-iodanediyl dipropionate (2a) in DMSO-d⁶ solvent at 600 MHz. We then mixed DBU and mesityl-λ³-iodanediyl dipropionate in a 1:1 ratio in DMSO-d⁶ solvent, allowed the mixture to stand for 24 hours, and subsequently performed NMR measurement. The results showed a clear formation of new substances.

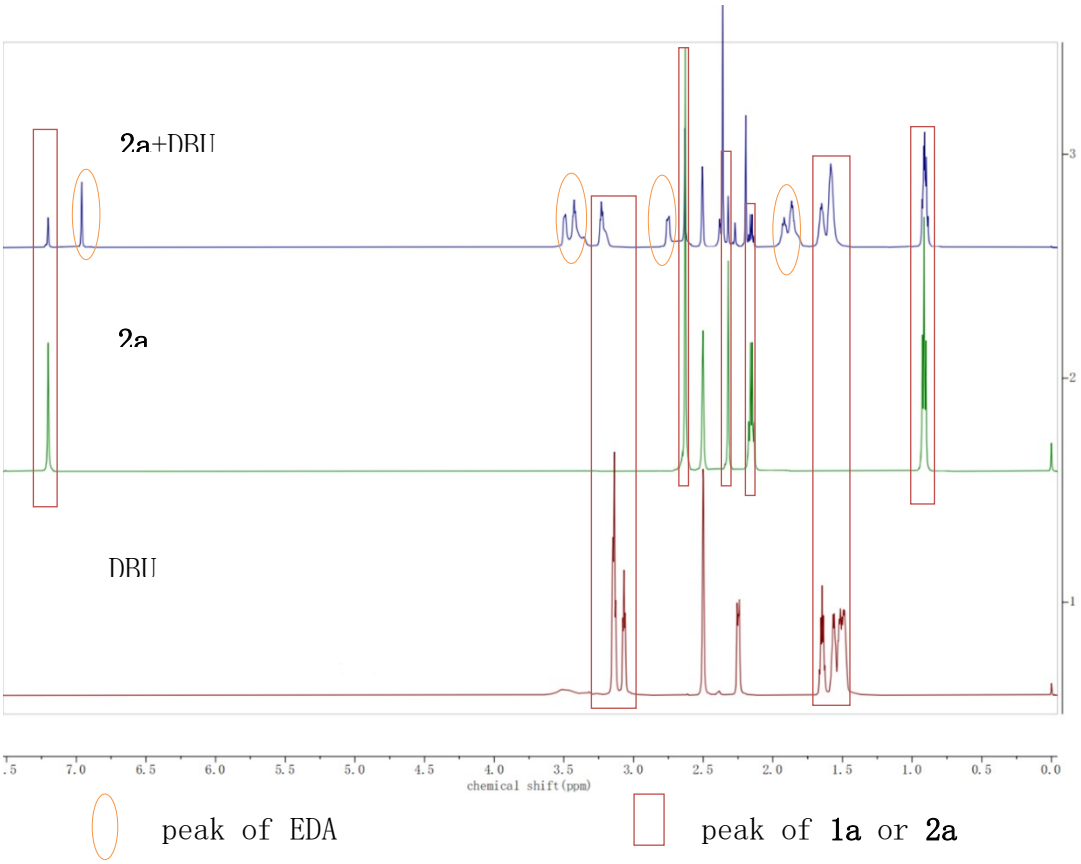


Figure S7. [1]H NMR spectra of EDA complex (**2a** + DBU, 1:1) compared to **2a** and DBU

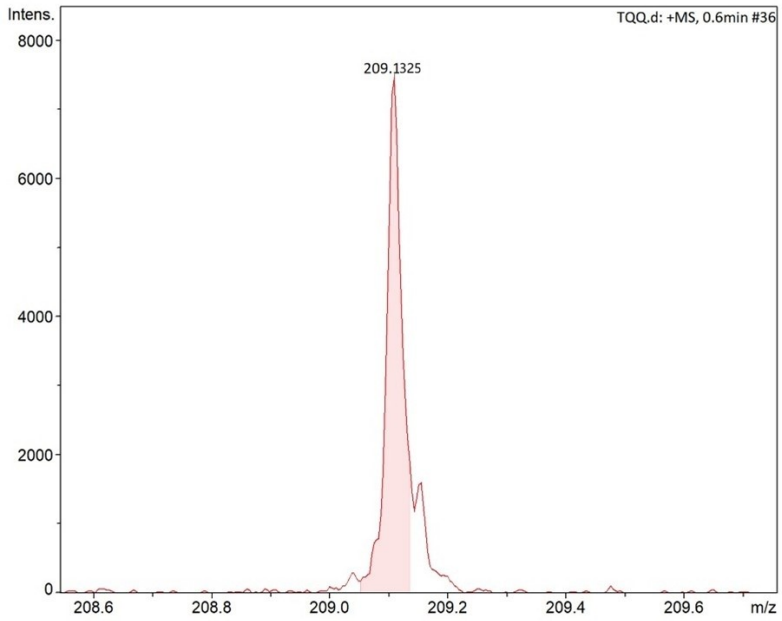


Figure S8 High-resolution mass spectrum of the radical adduct 2,2-diphenylethyl ethyl ether**.**

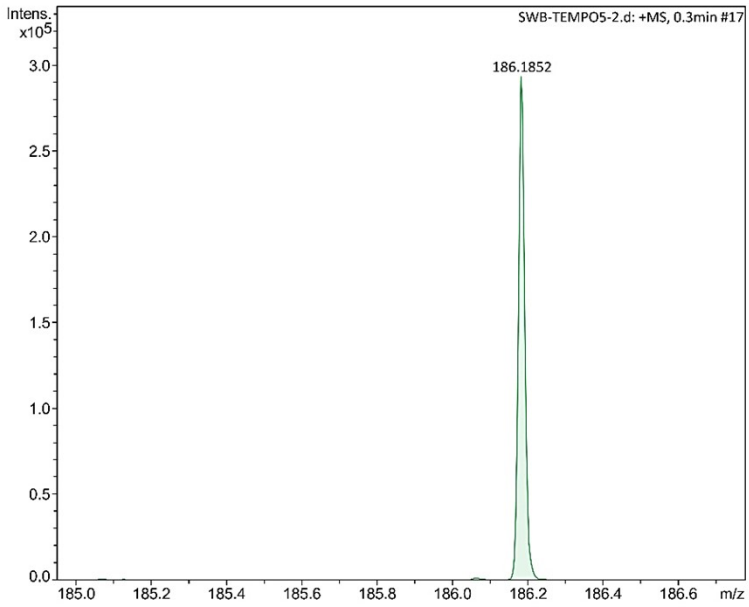


Figure S9 High-resolution mass spectrum of the TEMPO-ethyl radical adduct (TEMPO-Et).

3. Report of NMR Spectra

2,4-dibenzyl-6-ethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3a)[4]: Obtained as colorless oil (86.7 mg, 91% yield), Eluet (PET/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (d, J = 7.3 Hz, 2H), 7.43-7.41 (d, J = 7.4 Hz, 2H), 7.37-7.28 (m, 6H), 5.10 (s, 2H), 5.09 (s, 2H), 2.68-2.62 (q, J = 7.4 Hz, 2H), 1.22-1.18 (*t*, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 149.0, 146.5, 135.8, 135.7, 129.4, 128.7, 128.6, 128.5, 128.1, 128.0, 55.1, 44.1, 23.7, 10.3. HRMS (ESI): m/z calcd for $C_{19}H_{19}N_3NaO_2^+$ $[M+Na]^+$ 344.1369. Found 344.1369.

2,4,6-triethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3b) : Obtained as Colorless oil (45.0 mg, 76% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04-3.97 (m, 4H), 2.67-2.62 (q, J = 7.4 Hz, 2H), 1.35-1.31 (t, J = 7.1 Hz, 3H), 1.26-1.23 (t, J = 7.1 Hz, 3H), 1.22-1.18 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 148.6, 146.1, 46.6, 36.0, 23.7, 13.4, 12.5, 10.5. HRMS (ESI): m/z calcd for $C_9H_{15}N_3NaO_2^+$ $[M+Na]^+$220.1056. Found 220.1054.

6-ethyl-2,4-dipropyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3c): Obtained as Colorless oil (57.3 mg, 85% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91-3.86 (q, J = 7.4 Hz, 4H), 2.65-2.59 (q, J = 7.4 Hz, 2H), 1.80-1.71 (m, 2H), 1.68-1.60 (m, 2H), 1.19-1.15 (t, J = 7.4 Hz, 3H), 0.95-0.91 (t, J = 7.4 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.1, 149.0, 145.9, 52.9, 42.3, 23.7, 21.5, 20.6, 11.3, 10.9, 10.5. HRMS (ESI): m/z calcd for $C_{11}H_{19}N_3NaO_2^+$ $[M+Na]^+$248.1369. Found 248.1367.

6-ethyl-2,4-di(prop-2-yn-1-yl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3d)[4]: Obtained as Colorless oil (59.1 mg, 91% yield), Eluet (PET/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (s, 2H), 4.68 (s, 2H), 2.70-2.65 (q, J = 7.4 Hz, 2H), 2.35 (s, 1H), 2.21 (s, 1H), 1.22-1.18 (t, J = 7.4 Hz, 3H);

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.0, 147.6, 147.1, 76.9, 76.6, 73.3, 71.6, 41.2, 29.9, 23.8, 10.3. HRMS (ESI): m/z calcd for $C_{11}H_{11}N_3NaO_2^+$ $[M+Na]^+$240.0743. Found 270.0740.

6-ethyl-2,4-bis(4-fluorobenzyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3e): Obtained as Colorless oil (81.5 mg, 76% yield), Eluet (PET/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.49-7.46 (m, 2H), 7.41-7.38 (m, 2H), 7.04-6.96 (m, 4H), 5.05 (s, 2H), 5.03 (s, 2H), 2.67-2.61 (q, *J* = 7.4 Hz, 2H), 1.20-1.16 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.8, 163.7, 161.4, 161.2, 155.8, 148.9, 146.6, 131.6, 131.6, 131.5, 131.4, 130.7, 130.6, 115.7, 115.5, 115.4, 115.3, 54.4, 43.4, 23.7, 10.3; ^{19}F {^{1}H} NMR (565 MHz, $CDCl_3$) δ -102.90, -103.14. HRMS (ESI): m/z calcd for $C_{19}H_{17}F_2N_3NaO_2^+$ $[M+Na]^+$380.1180. Found 380.1180.

6-ethyl-2,4-bis(4-nitrobenzyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3f): Obtained as Pale yellow oil (84.9 mg, 69% yield), Eluet (PET/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.22-8.19 (d, *J* = 8.3 Hz, 2H), 8.17-8.15 (d, *J* = 8.2 Hz, 2H), 7.63-7.61 (d, *J* = 8.4 Hz, 2H), 7.57-7.55 (d, *J* = 8.3 Hz, 2H), 5.18 (s, 2H), 5.15 (s, 2H), 2.70-2.64 (q, *J* = 7.5 Hz, 2H), 1.21-1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 148.9, 147.8, 147.7, 147.3, 142.5, 142.3, 130.2, 129.5, 124.0, 123.8, 54.5, 43.5, 23.8, 10.2. HRMS (ESI): m/z calcd for $C_{19}H_{17}N_5NaO_6^+$ $[M+Na]^+$434.1071. Found 434.1070.

6-ethyl-2,4-bis(4-methoxybenzyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3g): Obtained as White solid (68.4 mg, 60% yield), Eluet (PET/EtOAc = 3:1): m. p. = 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98-7.95 (m, 4H), 6.98-6.95 (m, 4H), 5.37 (s, 2H), 5.35 (s, 2H), 3.88 (s, 6H), 2.71-2.65 (q, *J* = 7.4 Hz, 2H), 1.21-1.17 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.1, 188.8, 164.2, 164.1, 155.8, 149.2, 146.8, 130.4, 130.3, 127.6, 127.4, 114.0, 114.0, 57.1, 55.5, 46.1, 23.8, 10.3. HRMS (ESI): m/z calcd for $C_{21}H_{25}N_3O_4^+$ $[M+H]^+$382.1761. Found 382.1760.

6-ethyl-2,4-bis(2-oxo-2-phenylethyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3h)[4]: Obtained as Colorless oil (53.2 mg, 47% yield), Eluet (PET/EtOAc = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (t, J = 6.2 Hz, 4H), 7.65-7.61 (m, 2H), 7.53-7.49 (m, 4H), 5.42 (s, 2H), 5.40 (s, 2H), 2.72-2.67 (q, J = 7.2 Hz, 2H), 1.22-1.18 (t, J = 7.3 Hz, 3H); ^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) δ 191.7, 190.5, 155.8, 149.2, 147.0, 134.5, 134.4, 134.1, 134.0, 128.9, 128.8, 128.1, 128.1, 57.4, 46.5, 23.8, 10.3. HRMS (ESI): m/z calcd for $C_{21}H_{19}N_3NaO_4^+$ $[M+Na]^+$400.1267. Found 400.1261.

6-ethyl-2,4-bis(2-(4-fluorophenyl)-2-oxoethyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3i): Obtained as Pale yellow oil (49.8 mg, 40% yield), Eluet (PET/EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 4H), 7.21-7.16 (m, 4H), 5.39 (s, 2H), 5.36 (s, 2H), 2.71-2.66 (q, J = 7.4 Hz, 2H), 1.21-1.18 (t, J = 7.4 Hz, 3H);^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.1, 188.9, 167.5, 165.0, 155.7, 149.1, 147.0, 130.9, 130.8, 130.7, 116.3, 116.2, 116.1, 116.0, 57.3, 46.3, 23.8, 10.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.73, -113.82. HRMS (ESI): m/z calcd for $C_{21}H_{17}F_2N_3NaO_4^+$ $[M+Na]^+$436.1079. Found 436.1073.

2,4-bis(2-(4-chlorophenyl)-2-oxoethyl)-6-ethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3j): Obtained as Colorless oil (57.4 mg, 43% yield), Eluet (PET/EtOAc = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.91 (m, 4H), 7.50-7.47 (m, 4H), 5.37 (s, 2H), 5.35 (s, 2H), 2.71-2.66 (q, J = 7.4 Hz, 2H), 1.21-1.17 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.5, 189.4, 155.7, 149.1, 147.1, 140.7, 140.6, 132.8, 132.7, 129.5, 129.4, 129.3, 129.2, 57.3, 46.3, 23.8, 10.2. HRMS (ESI): m/z calcd for $C_{21}H_{17}Cl_2N_3NaO_4^+$ $[M+Na]^+$468.0488. Found 468.0480.

2-benzyl-4,6-diethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3k): Obtained as Colorless oil (57.5 mg, 74% yield), Eluet (PET/EtOAc = 25:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (d, J = 7.3 Hz, 2H), 7.33-7.28 (q, J = 8.1 Hz, 3H), 5.10 (s, 2H), 4.03-3.98 (q, J = 7.1 Hz, 2H), 2.67-2.62 (q, J

= 6.9 Hz, 2H), 1.34-1.30 (t, *J* = 7.1 Hz, 3H), 1.21-1.17 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 148.7, 146.2, 135.8, 129.4, 128.5, 127.9, 46.7, 43.9, 23.7, 13.3, 10.4. HRMS (ESI): m/z calcd for $C_{14}H_{17}N_3NaO_2^+$ $[M+Na]^+$282.1213. Found 282.1209.

tert-butyl 2-(2-benzyl-6-ethyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4*(3H)*-yl)acetate (3l)[4]: Obtained as Colorless oil (57.5 mg, 75% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47-7.45 (d, *J* = 6.7 Hz, 2H), 7.32-7.28 (m, 3H), 5.10 (s, 2H), 4.56 (s, 2H), 2.67-2.61 (q, *J* = 7.2 Hz, 2H), 1.45 (m, 9H), 1.19-1.15 (t, *J* = 7.4 Hz, 3H);^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 156.0, 149.2, 146.8, 135.5, 129.2, 128.5, 127.9, 82.8, 53.3, 44.0, 28.0, 23.7, 10.3. HRMS (ESI): m/z calcd for $C_{18}H_{23}N_3NaO_4^+$ $[M+Na]^+$368.1580. Found 368.1577.

2-benzyl-4-(4-chlorobenzyl)-6-ethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3m): Obtained as Colorless oil (86.3 mg, 81% yield), Eluet (PET/EtOAc = 35:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48-7.47 (d, *J* = 7.3 Hz, 2H), 7.36-7.28 (m, 7H), 5.08 (s, 2H), 5.05 (s, 2H), 2.67-2.62 (q, *J* = 7.4 Hz, 2H), 1.20-1.17 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.8, 149.0, 146.7, 135.6, 134.3, 134.1, 130.1, 129.4, 128.8, 128.5, 128.0, 54.4, 44.1, 23.7, 10.3. HRMS (ESI): m/z calcd for $C_{19}H_{18}ClN_3NaO_2^+$ $[M+Na]^+$378.0979. Found 378.0979.

ethyl 2-(4-methyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2*(3H)*-yl)acetate (3n): Obtained as Colorless oil (44.3 mg, 61% yield), Eluet (PET/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.66 (s, 2H), 4.25-4.20 (q, *J* = 6.2 Hz, 2H), 3.33 (s, 3H), 2.66-2.60 (q, *J* = 7.3 Hz, 2H), 1.30-1.26 (t, *J* = 8.1 Hz, 3H), 1.18-1.14 (t, J = 8.3 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.6, 156.2, 149.3, 146.6, 61.8, 52.5, 27.1, 23.8, 14.1, 10.3. HRMS (ESI): m/z calcd for $C_{10}H_{15}N_3NaO_4^+$ $[M+Na]^+$264.0954. Found 264.0954.

6-ethyl-4-methyl-2-(p-tolyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3o): Obtained as Colorless oil (50.1 mg, 68% yield), Eluet (PET/EtOAc = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.29 (d, J = 7.2 Hz, 2H), 7.10-7.08 (d, J = 7.5 Hz, 2H), 3.65 (s, 3H), 2.71-2.66 (q, J = 6.0 Hz, 2H), 2.40 (s, 3H), 1.25-1.21 (t, J = 6.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.2, 149.1, 146.8, 139.2, 130.5, 130.2, 127.5, 39.4, 23.9, 21.2, 10.5. HRMS (ESI): m/z calcd for $C_{13}H_{15}N_3NaO_2^+$ $[M+Na]^+$268.1056. Found 268.1056.

6-ethyl-4-methyl-2-(prop-2-yn-1-yl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3p)[4]: Obtained as Colorless oil (50.2 mg, 87% yield), Eluet (PET/EtOAc = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 2H), 3.63 (s, 3H), 2.69-2.62 (q, J = 11.7 Hz, 2H), 2.22 (s, 1H), 1.22-1.8 (t, J = 7.1 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.2, 148.3, 146.1, 76.8, 71.4, 39.2, 29.7, 23.7, 10.4. HRMS (ESI): m/z calcd for $C_9H_{11}N_3NaO_2^+$ $[M+Na]^+$216.0743. Found 216.0743.

6-ethyl-2-methyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3q) : Obtained as Colorless oil (17.2 mg, 37% yield), Eluet (PET/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 3.35 (s, 3H), 2.68-2.62 (q, J = 7.2 Hz, 2H), 1.21-1.17 (t, J = 7.3 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.4, 150.2, 147.0, 26.5, 23.7, 10.2. HRMS (ESI): m/z calcd for $C_6H_9N_3NaO_2^+$ $[M+Na]^+$178.0587. Found 178.0587.

2-allyl-6-ethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3r): Obtained as Colorless oil (28.2 mg, 52% yield), Eluet (PET/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 5.98-5.89 (m, 1H), 5.30-5.28 (d, J = 7.9 Hz, 2H), 4.55-4.53 (d, J = 5.9 Hz, 2H), 2.67-2.62 (q, J = 7.3 Hz, 2H), 1.21-1.18 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.1, 148.1, 147.6, 131.3, 119.0, 52.9, 23.3, 10.5. HRMS (ESI): m/z calcd for $C_8H_{11}N_3NaO_2^+$ $[M+Na]^+$204.0743. Found 204.0743.

2-benzyl-6-ethyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3s)[4]: Obtained as Colorless oil (38.2 mg, 55% yield), Eluet (PET/EtOAc = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.50-7.48 (d, J = 7.1 Hz, 2H), 7.34-7.28 (q, J = 6.4 Hz, 3H), 5.09 (s, 2H), 2.67-2.61 (q, J = 6.7 Hz, 2H), 1.20-1.16 (t, J = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 150.0, 149.6, 147.4, 135.4, 129.4, 128.6, 128.1, 43.5, 23.7, 10.2. HRMS (ESI): m/z calcd for $C_{12}H_{13}N_3NaO_2^+$ $[M+Na]^+$254.0900. Found 254.0900.

6-ethyl-2-(4-fluorobenzyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3t): Obtained as a White solid (46.4 mg, 62% yield), Eluet (PET/EtOAc = 6:1): m. p. = 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.51-7.48 (m, 2H), 7.01-6.97 (t, J = 8.3 Hz, 2H), 5.05 (s, 2H), 2.67-2.62 (q, J = 7.3 Hz, 2H), 1.20-1.16 (q, J = 7.3 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.8, 161.3, 156.0, 150.0, 147.5, 131.5, 131.4, 115.5, 115.3, 42.8, 23.7, 10.1;^{19}F NMR (565 MHz, $CDCl_3$) δ -113.66. HRMS (ESI): m/z calcd for $C_{12}H_{12}FN_3NaO_2^+$ $[M+Na]^+$272.0805. Found 272.0805.

2-(4-bromobenzyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3u): Obtained as a White solid (59.6 mg, 64% yield), Eluent (PET/EtOAc = 25:1): m. p. = 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.45-7.43 (d, J = 7.6 Hz, 2H), 7.39-7.37 (d, J = 7.8 Hz, 2H), 5.03 (s, 2H), 2.67-2.61 (q, J = 7.2 Hz, 2H), 1.20-1.16 (t, J = 7.2 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 149.9, 147.4, 134.3, 131.7, 131.3, 122.3, 42.9, 23.7, 10.1. HRMS (ESI): m/z calcd for $C_{12}H_{12}BrN_3NaO_2^+$ $[M+Na]^+$332.0005. Found 332.0005.

6-ethyl-2-(4-ethylphenyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3v): Obtained as Colorless oil (33.8 mg, 46% yield), Eluet (PET/EtOAc = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s,1H), 7.35-7.32 (d, J = 7.8 Hz, 2H), 7.17-7.15 (d, J = 7.9 Hz, 2H), 2.74-2.65 (m, 4H), 1.29-1.25 (t, J = 7.6 Hz, 3H), 1.23-1.19 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.1, 150.1,

147.9, 145.6, 129.7, 129.0, 127.5, 28.5, 23.8, 15.1, 10.2. HRMS (ESI): m/z calcd for $C_{13}H_{15}N_3NaO_2^+$ $[M+Na]^+$268.1056. Found 268.1056.

6-ethyl-2-phenyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3w): Obtained as Colorless oil (27.3 mg, 42% yield), Eluet (PET/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.54-7.45 (m, 3H), 7.25-7.24 (d, J = 4.9 Hz, 2H), 2.71-2.65 (q, J = 7.4 Hz, 2H), 1.23-1.19 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 150.0, 147.9, 132.3, 129.5, 129.4, 127.8, 23.8, 10.2. HRMS (ESI): m/z calcd for $C_{11}H_{11}N_3NaO_2^+$ $[M+Na]^+$240.0743. Found 240.0744.

4-benzyl-6-ethyl-2-(2-((4-methyl-2-oxo-2H-chromen-6-yl)oxy)ethyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3x): Obtained as colorless oil (87.0 mg, 67% yield), Eluet (PET/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 3H), 7.37-7.32 (q, J = 6.4 Hz, 3H), 7.26 (s, 1H), 6.80-6.78 (m, 2H), 6.13 (s, 1H), 5.11 (s, 2H), 4.40-4.37 (t, J = 5,6 Hz, 2H), 4.28-4.25 (t, J = 5.8 Hz, 2H), 2.68-2.62 (q, J = 7.4 Hz, 2H), 2.38 (s, 3H), 1.22-1.18 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.2, 156.0, 155.1, 152.4, 148.8, 146.3, 135.7, 128.8, 128.7, 128.2, 125.5, 113.9, 112.3, 112.2, 101.7, 64.2, 55.2, 39.3, 23.8, 18.6, 10.3. HRMS (ESI): m/z calcd for $C_{24}H_{23}N_3NaO_5^+$ $[M+Na]^+$456.1530. Found 456.1529.

4-(3-(6-ethyl-4-methyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2*(3H)*-yl)propyl)-3-methoxybenzaldehyde (3y) Obtained as colorless oil (86.2 mg, 87% yield), Eluet (PET/EtOAc = 8:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.41-7.39 (d, J = 7.9 Hz, 1H), 7.34 (s, 1H), 6.91-6.89 (d, J = 8.2 Hz, 1H), 4.18 (s, 2H), 4.17 (s, 2H), 3.82 (s, 3H), 3.53 (s, 3H), 2.59-2.54 (q, J = 6.6 Hz, 2H), 2.29-2.24 (m, 2H), 1.16-1.12 (t, J = 7.0 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.9, 156.4, 153.6, 149.6, 149.2, 145.8, 130.0, 126.9, 111.2, 108.8, 67.4, 55.7, 39.2, 38.7, 26.9, 23.7, 10.4. HRMS (ESI): m/z calcd for $C_{17}H_{21}N_3NaO_4^+$ $[M+Na]^+$354.1424. Found 354.1424.

2-(4-benzyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2*(3H)*-yl)ethyl 11-oxo-6,11-dihydrodibenzo[b,e]oxepine-2-carboxylate (3z) : Obtained as Pale yellow oil (121.3 mg, 84% yield), Eluet (PET/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.89-7.87 (m, 1H), 7.57-7.53 (t, J = 7.4 Hz, 1H), 7.48-7.44 (t, J = 7.6 Hz, 1H), 7.42-7.39 (t, J = 6.4 Hz, 2H), 7.37-7.29 (m, 5H), 7.01-6.99 (d, J = 8.4 Hz, 1H), 5.18 (s, 2H), 5.09 (s, 2H), 4.35-4.33 (t, J = 4.4 Hz, 2H), 4.24-4.21 (t, J = 4.7 Hz, 2H), 3.50 (s, 2H), 2.67-2.61 (q, J = 7.3 Hz, 2H), 1.21-1.17 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.8, 171.3, 160.4, 156.0, 148.9, 146.2, 140.4, 136.5, 135.8, 135.5, 132.7, 132.5, 129.4, 129.2, 128.7, 128.6, 128.1, 127.8, 127.5, 125.0, 120.9, 73.6, 61.2, 55.3, 39.7, 23.7, 10.3. HRMS (ESI): m/z calcd for $C_{29}H_{25}N_3NaO_6^+$ $[M+Na]^+$534.1636. Found 534.1635.

2-(4-benzyl-6-ethyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2*(3H)*-yl)ethyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3aa): Obtained as Colorless oil (79.0 mg, 52% yield), Eluet (PET/EtOAc = 6:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (d, J = 6.7 Hz, 2H), 7.35-7.29 (q, J = 7.7 Hz, 3H), 7.00-6.98 (d, J= 7.3 Hz, 1H), 5.07 (s, 2H), 4.32-4.30 (t, J = 5.1 Hz, 2H), 4.24-4.21 (t, J = 4.7 Hz, 2H), 3.87-3.85 (t, J = 5.2 Hz, 2H), 2.65-2.60 (q, J = 7,4 Hz, 2H), 2.30 (s, 3H), 2.16 (s, 3H), 1.68-1.61 (m, 4H), 1.20-1.16 (t, J = 7.3 Hz, 3H), 1.12 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.5, 156.9, 156.0, 148.8, 146.2, 136.4, 135.8, 130.2, 128.7, 128.6, 128.1, 123.5, 120.6, 111.9, 67.9, 60.7, 55.1, 42.0, 39.8, 36.9, 25.0, 24.9, 23.8, 21.4, 15.7, 10.4. HRMS (ESI): m/z calcd for $C_{29}H_{37}N_3NaO_5^+$ $[M+Na]^+$530.2625. Found 530.2616.

(2R,3S,5R)-5-(6-ethyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2*(3H)*-yl)-2-(((4-methylbenzoyl)oxy)methyl)tetrahydrofuran-3-yl 4-methylbenzoate (3ab)[5]: Obtained as Colorless oil (66.7 mg, 45% yield), Eluet (PET/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.95-7.91 (t, J = 8.3 Hz, 4H), 7.26-7.25 (d, J = 4.8 Hz, 2H), 7.21-7.19 (d, J = 7.6 Hz, 2H),

6.72-6.68 (t, *J* = 6.3 Hz, 1H), 5.72 (s, 1H), 4.58-4.49 (m, 3H), 3.03-2.97 (m, 1H), 2.66-2.61 (q, *J* = 7.3 Hz, 2H), 2.51-2.45 (m, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 1.23-1.19 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 155.6, 148.6, 148.5, 144.3, 143.9, 129.8, 129.7, 129.2, 129.1, 126.9, 126.5, 85.7, 82.0, 74.9, 64.4, 34.9, 23.4, 21.7, 10.3. HRMS (ESI): m/z calcd for $C_{26}H_{27}N_3NaO_7^+$ $[M+Na]^+$516.1741. Found 516.1736.

2,4-dibenzyl-6-methyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3ac)[6]: Obtained as Colorless oil (62.8 mg, 68% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48-7.47 (d, *J* = 6.1 Hz, 2H), 7.40-7.38 (d, *J* = 5.7 Hz, 2H), 7.35-7.29 (m, 6H), 5.07 (s, 4H), 2.22 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 156.2, 149.1, 142.9, 135.8, 135.6, 129.4, 128.7, 128.6, 128.5, 128.1, 128.0, 55.1, 44.1, 16.9. HRMS (ESI): m/z calcd for $C_{18}H_{17}N_3NaO_2^+$ $[M+Na]^+$330.1214. Found 330.1214.

2,4-dibenzyl-6-propyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3ad)[4]: Obtained as Colorless oil (76.4 mg, 76% yield), Eluet (PET/EtOAc = 30:1):; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48-7.46 (d, *J* = 7.1 Hz, 2H), 7.40-7.39 (d, *J* = 7.3 Hz, 2H), 7.37-7.27 (m, 6H), 5.07 (s, 4H), 2.59-2.56 (q, *J* = 7.5 Hz, 2H), 1.70-1.60 (m, 2H), 0.97-0.94 (q, *J* = 7.4 Hz, 3H);

2,4-dibenzyl-6-butyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3ae)[4]: Obtained as Colorless oil (74.5 mg, 71% yield), Eluet (PET/EtOAc = 30:1):; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48-7.46 (d, *J* = 7.2 Hz, 2H), 7.40-7.39 (d, *J* = 7.2 Hz, 2H), 7.36-7.27 (m, 6H), 5.07 (s, 4H), 2.62-2.58 (t, *J* = 7.6 Hz, 2H), 1.63-1.56 (m, 2H), 1.41-1.32 (m, 2H), 0.94-0.90 (t, *J* = 7.3 Hz, 3H);

2,4-dibenzyl-6-isopropyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3af)[7]: Obtained as Pale yellow oil (91.5 mg, 91% yield), Eluet (PET/EtOAc = 30:1):; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.49-7.47 (d, *J*

= 7.3 Hz, 2H), 7.41-7.39 (d, *J* = 7.4 Hz, 2H), 7.35-7.27 (m, 6H), 5.07 (s, 4H), 3.21-3.14 (m, 1H), 1.20 (s,3H), 1.18 (s, 3H);

2,4-dibenzyl-6-(tert-butyl)-1,2,4-triazine-3,5*(2H,4H)*-dione (3ag)[1] : Obtained as Colorless oil (96.3 mg, 92% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (d, *J* = 6.7 Hz, 2H), 7.42-7.40 (d, *J* = 6.4Hz, 2H), 7.34-7.29 (m, 6H), 5.06 (s, 4H), 1.32 (s, 9H);

2,4-dibenzyl-6-cyclopropyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3ah)[6] : Obtained as Colorless oil (64.0 mg, 64% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.48 (d, *J* = 7.3 Hz, 2H), 7.34-7.27 (m, 8H), 5.09 (s, 2H), 5.02 (s,2H), 2.27-2.22 (m, 1H), 0.96-0.92 (m, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.1, 148.7, 146.6, 135.8, 135.7, 129.4, 128.6, 128.5, 128.1, 128.0, 55.1, 44.2, 9.8, 9.2. HRMS (ESI): m/z calcd for $C_{20}H_{19}N_3NaO_2^+$ $[M+Na]^+$356.1369. Found 356.1365.

2,4-dibenzyl-6-cyclohexyl-1,2,4-triazine-3,5*(2H,4H)*-dione (3ai)[8]: Obtained as (105.6 mg`, 94% yield), Eluet (PET/EtOAc = 30:1); ^{1}H NMR (400 MHz, .$CDCl_3$) δ 7.50-7.48 (d, *J*=7.0 Hz, 2H), 7.42-7.40 (d, *J*=7.3 Hz, 2H), 7.37-7.28 (m, 6H), 5.08 (s, 2H), 5.07 (s, 2H), 2.90-2.85 (m, 1H), 1.88-1.86 (d, *J*=7.4 Hz, 2H), 1.82-1.80 (d, *J*=6.8 Hz, 2H), 1.74-1.71 (d, *J*=11.7 Hz, 1H), 1.42-1.31 (m, 3H), 1.27-1.22 (t, *J*=7.1 Hz, 1H).

(2R,3S,5R)-5-(6-isopropyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2*(3H)*-yl)-2-(((4-methylbenzoyl)oxy)methyl)tetrahydrofuran-3-yl 4-methylbenzoate (3aj) Obtained as Colorless oil (mg, 68% yield), Eluet (PET/EtOAc = 3:1) Obtained as Colorless oil (66.7 mg, 45% yield), Eluet (PET/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.95-7.90 (t, *J* = 8.3 Hz, 4H), 7.26-7.24 (d, *J* = 4.8 Hz, 2H), 7.20-7.18 (d, *J* = 7.6 Hz, 2H), 6.73-6.70 (t, *J* = 6.3 Hz, 1H), 5.75-5.71 (m, 1H), 4.56-4.47 (m, 3H), 3.24-3.17 (m, 1H), 3.01-2.95 (m, 1H), 2.52-2.46 (m, 1H),

2.43 (s, 3H), 2.39 (s, 3H), 1.27-1.24 (m, 6H);^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 166.0, 155.3, 151.8, 148.4, 144.3, 143.9, 129.8, 129.8, 129.2, 129.1, 126.9, 126.6, 85.8, 81.9, 75.0, 64.6, 34.9, 29.2, 21.7, 21.7, 20.0, 20.0. HRMS (ESI): m/z calcd for $C_{27}H_{29}N_3NaO_7^+$ $[M+Na]^+$530.1897. Found 530.1889.

4. Computational details

All density functional theory (DFT) calculations were performed using the Gaussian 09 [9] program package with the wB97XD[10] functional. All molecular structures were built using GaussView 6.0 [11] and optimized to their energy-minimum geometries. The absence of imaginary frequencies for the corresponding minima confirmed that the molecules reside at stable states on the potential energy surface (PES). The wB97XD functional, combined with the def2svp[12] basis set was used for all atoms. Solvent effect was also introduced by using the SMD[13] solvation model with the dielectric constant of DMSO.

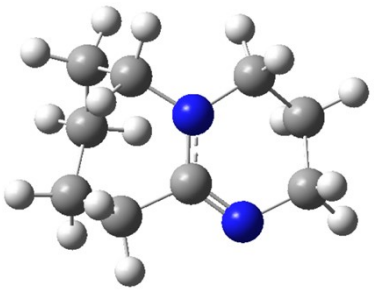


Figure S10. DFT-optimized geometry of **DBU**

Table S3. DFT-optimized cartesian coordinates of **DBU**

Zero-point correction=0.248152 (Hartree/Particle)

Thermal correction to Energy=0.257829

Thermal correction to Enthalpy=0.258773

Thermal correction to Gibbs Free Energy=0.212973

Sum of electronic and zero-point Energies=461.389017

Sum of electronic and thermal Energies=-461.379340

Sum of electronic and thermal Enthalpies=-461.378396

Sum of electronic and thermal Free Energies=-461.424196

C	-1.96160800	1.34546600	-0.21354200
C	-0.96125900	1.23467500	0.94831700
C	-1.96847700	0.10341400	-1.10529400
C	0.32524500	-0.79718600	0.41359900
C	-2.09147700	-1.23440500	-0.36943400
C	-0.97056400	-1.54063000	0.65658900
H	-2.96411800	1.52475400	0.20836300
H	-0.70618100	2.23366900	1.33102600
H	-1.04179200	0.09163000	-1.70356200
H	-2.09751600	-2.03115300	-1.12894900
H	-1.72115200	2.22433900	-0.83367900
H	-1.42453500	0.70736600	1.79380300
H	-2.79064000	0.18605000	-1.83339700
H	-3.06778500	-1.28922700	0.13866500
H	-0.71861300	-2.60762800	0.63149100
H	-1.31926300	-1.32648900	1.67814400
N	0.27771300	0.56795400	0.58503200
N	1.36578800	-1.47104200	0.06517000
C	2.58702100	-0.72700100	-0.17042800
H	3.14518400	-0.60847500	0.77908600
H	3.24085100	-1.31419900	-0.83524200
C	2.31952100	0.65007500	-0.76893700

H	3.25102700	1.21639700	-0.91217300
H	1.85178700	0.52559100	-1.75964500
C	1.38140000	1.41538200	0.14921900
H	0.96753400	2.29249800	-0.37397000
H	1.93190400	1.79775500	1.02808300

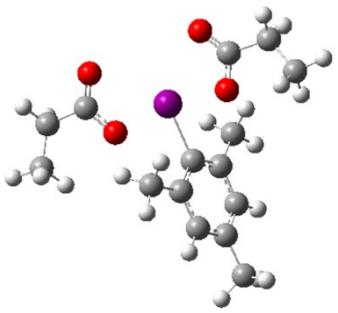


Figure S11. DFT-optimized geometry of **2a**

Table S4. DFT-optimized cartesian coordinates of **2a**

Zero-point correction=0.334978 (Hartree/Particle)

Thermal correction to Energy=0.359368

Thermal correction to Enthalpy=0.360312

Thermal correction to Gibbs Free Energy=0.277034

Sum of electronic and zero-point Energies=-1181.653790

Sum of electronic and thermal Energies=-1181.629401

Sum of electronic and thermal Enthalpies=-1181.628456

Sum of electronic and thermal Free Energies= -1181.711734

C	3.97833600	0.39422600	-2.30748100
C	2.69171100	-0.07770600	-1.58016500

C	2.79342000	-0.02702000	-0.07130300
C	5.28796200	0.19199100	-1.53498000
C	5.57128800	-1.24189400	-1.07518900
C	4.39752500	-1.87805700	-0.30544700
H	4.03599600	-0.11982700	-3.28104300
H	1.84796300	0.55907200	-1.87187300
H	5.28069300	0.85043000	-0.65000800
H	6.47318000	-1.23198500	-0.44108400
H	3.88267600	1.46914700	-2.52955800
H	2.43247500	-1.10071300	-1.88354400
H	6.12686900	0.54181000	-2.15835400
H	5.80382900	-1.88553500	-1.94024500
H	3.69940800	-2.37533300	-0.99055200
C	3.95425300	-0.84822600	1.93668400
C	3.63857600	0.53837600	2.47985700
C	2.24364900	0.95245700	2.02093200
H	3.71292200	0.53972900	3.57756700
H	3.37827000	-1.61893200	2.48063600
H	5.02031300	-1.08424500	2.07557000
H	1.48670400	0.32476800	2.53170000
H	2.02433700	1.98913900	2.32463900
H	4.37779600	1.26098900	2.09580600
N	3.64930400	-0.92047600	0.50689500

N	2.08480200	0.85479300	0.57588100
C	-4.83184300	-0.82647500	0.76368500
C	-5.34438700	-1.10707800	-0.51090500
C	-4.50675800	-0.94011800	-1.61929200
C	-3.17759600	-0.50818800	-1.49321400
C	-2.71460300	-0.25610300	-0.19091100
C	-3.51364600	-0.39716300	0.96033000
H	-5.47732000	-0.94352200	1.63822500
H	-4.89368600	-1.14854400	-2.61990400
C	-3.02242400	-0.08997600	2.35167000
H	-2.17301500	-0.73283100	2.63112600
H	-2.68021600	0.95281900	2.42050200
H	-3.82188400	-0.24939700	3.08727000
C	-6.76672900	-1.57583200	-0.67082500
H	-6.92695600	-2.52955600	-0.14184800
H	-7.47211200	-0.84801500	-0.23832900
H	-7.02863900	-1.72265700	-1.72793500
C	-2.32201600	-0.33809200	-2.72223400
H	-1.41937600	-0.96361500	-2.66314700
H	-2.88289000	-0.61400300	-3.62510700
H	-1.99210000	0.70781500	-2.83382900
I	-0.67400300	0.35580800	0.05471700
O	-1.43418800	2.24298500	0.81840400

O	-0.04291700	-1.56652000	-0.79507200
C	-1.01015200	3.44260000	0.43178800
C	0.66177500	-2.50934100	-0.18788300
O	-1.49273500	4.43769700	0.94117900
O	1.33887600	-3.28326200	-0.84615500
C	0.53399200	-2.63294700	1.32062700
H	0.66718500	-1.64703600	1.79084600
H	1.35053200	-3.27898600	1.67098600
C	0.07092600	3.50724600	-0.63497900
H	0.90915300	2.86135700	-0.31785800
H	-0.33308800	3.03448100	-1.54807800
C	0.54549700	4.92479500	-0.92615900
H	1.31698100	4.92160100	-1.71101100
H	-0.28652100	5.56186200	-1.26145500
H	0.97458000	5.38904000	-0.02512800
C	-0.82797700	-3.21934700	1.71475900
H	-1.65535300	-2.60451200	1.33130300
H	-0.94931700	-4.23305700	1.30278400
H	-0.92488100	-3.28068200	2.80878500
H	4.76195100	-2.66509600	0.36966100

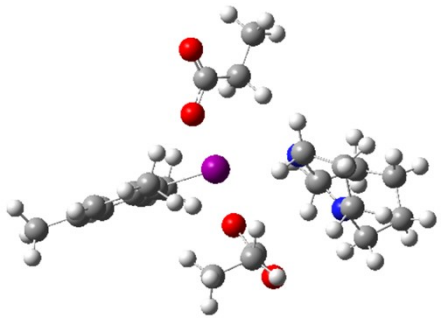


Figure S12. DFT-optimized geometry of **2a**

Table S5. DFT-optimized cartesian coordinates of **2a**

Zero-point correction=0.585202 (Hartree/Particle)

Thermal correction to Energy=0.620649

Thermal correction to Enthalpy=0.621593

Thermal correction to Gibbs Free Energy=0.513840

Sum of electronic and zero-point Energies=-1643.047864

Sum of electronic and thermal Energies=-1643.012417

Sum of electronic and thermal Enthalpies=-1643.011473

Sum of electronic and thermal Free Energies=-1643.119226

C	4.04281500	0.38530200	-2.26753900
C	2.72840400	-0.04931000	-1.57492700
C	2.80286200	-0.02591400	-0.06519000
C	5.32460700	0.15036700	-1.46347200
C	5.56776700	-1.29041700	-1.01228400
C	4.35712400	-1.91197100	-0.29744900
H	4.11327200	-0.12886400	-3.23914300
H	1.91618700	0.62655100	-1.86974000

H	5.30681200	0.80084200	-0.57270000
H	6.44372100	-1.30293200	-0.34392400
H	3.98181000	1.46141800	-2.49148000
H	2.43245900	-1.05593300	-1.90172900
H	6.18525100	0.48997900	-2.06045800
H	5.82381600	-1.92693200	-1.87477500
H	3.66811700	-2.37540000	-1.01552300
C	3.90826400	-0.90441000	1.94102900
C	3.62869500	0.48299100	2.49267000
C	2.25573100	0.94136600	2.02162000
H	3.68976900	0.47133800	3.58993800
H	3.30823600	-1.66214000	2.47603900
H	4.96652200	-1.16795300	2.08804400
H	1.47561000	0.33077700	2.51805100
H	2.06472400	1.97988400	2.33471200
H	4.39305200	1.18728400	2.12571900
N	3.61440400	-0.95640300	0.51368200
N	2.11309900	0.86561400	0.57835800
C	-4.77246400	-0.88620200	0.81069800
C	-5.31181600	-1.15236700	-0.45205000
C	-4.51230600	-0.94050800	-1.57641700
C	-3.19430700	-0.48086800	-1.47751400
C	-2.69996300	-0.24552600	-0.18591900

C	-3.46431200	-0.42809800	0.98061100
H	-5.39120100	-1.03939600	1.69892100
H	-4.92367800	-1.13574200	-2.57004400
C	-2.95066900	-0.13269300	2.36556100
H	-2.06169300	-0.73473100	2.60825800
H	-2.66808100	0.92611300	2.45492500
H	-3.71963700	-0.35373600	3.11620500
C	-6.72502600	-1.65204300	-0.58314700
H	-6.85788500	-2.59533100	-0.03223700
H	-7.43655300	-0.92609800	-0.16110600
H	-6.99499200	-1.82671300	-1.63301800
C	-2.38274300	-0.26105700	-2.72727300
H	-1.45374200	-0.84847400	-2.70282700
H	-2.95598200	-0.55391400	-3.61595100
H	-2.10881400	0.80006700	-2.83791600
I	-0.69148700	0.38706100	0.02022300
O	-1.46337200	2.23826100	0.76203800
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O	-1.52024800	4.42397100	0.93857900
O	1.26013700	-3.24245700	-0.94793300
C	0.54891600	-2.61250500	1.24857600

H	0.68632800	-1.63238900	1.73087500
H	1.38498400	-3.25162100	1.56208900
C	0.08020800	3.52887900	-0.61011400
H	0.90799900	2.87090000	-0.28935800
H	-0.30480900	3.08603300	-1.54563100
C	0.57375300	4.94560900	-0.85176100
H	1.35984800	4.95168700	-1.61999600
H	-0.24264800	5.60013900	-1.18843500
H	0.99134200	5.37986800	0.06812800
C	-0.78610700	-3.22843800	1.67484600
H	-1.63846300	-2.62831800	1.32266600
H	-0.89883300	-4.23877100	1.25493800
H	-0.84947700	-3.30396800	2.76925200
H	4.67871400	-2.72612600	0.36688700

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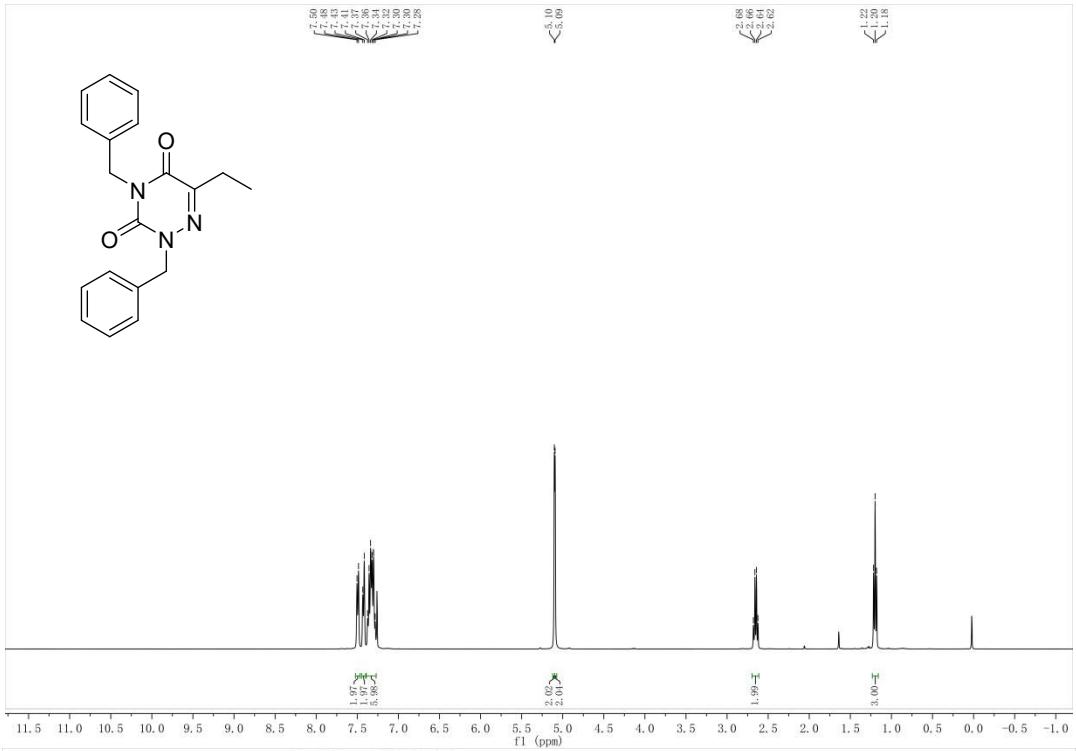
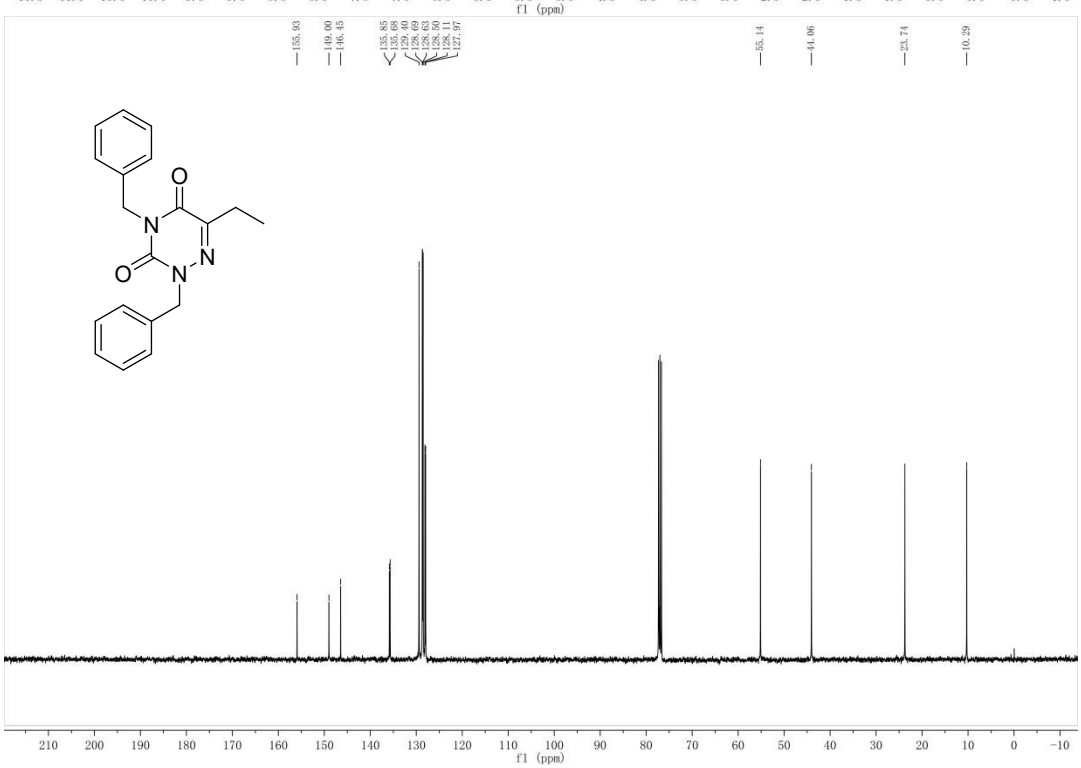
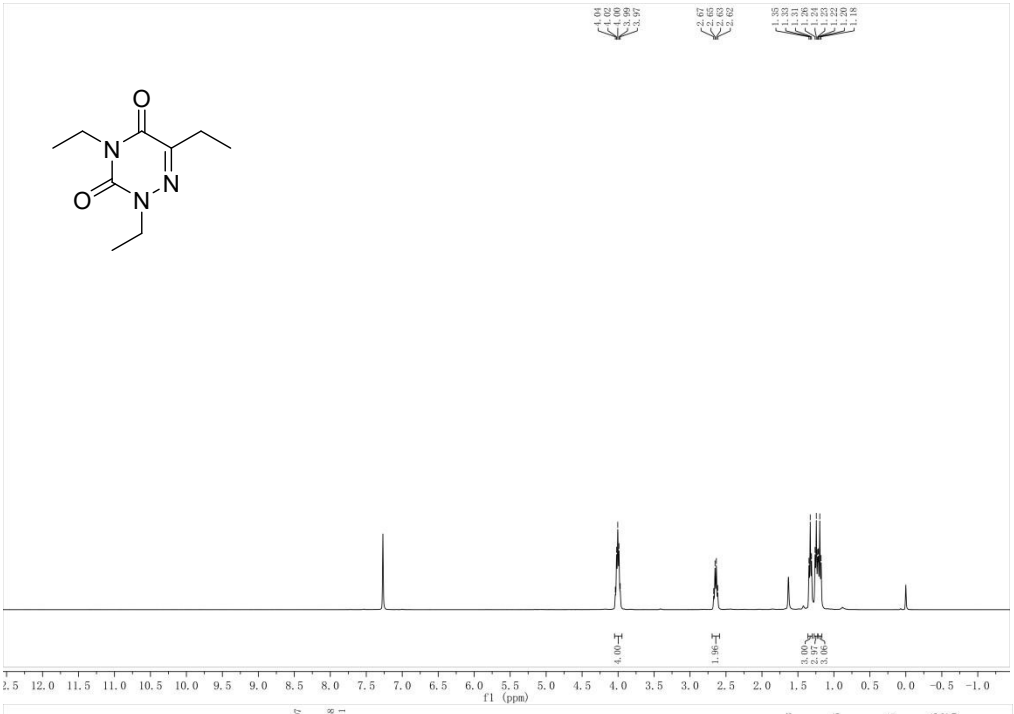
5. NMR Spectra of Compounds

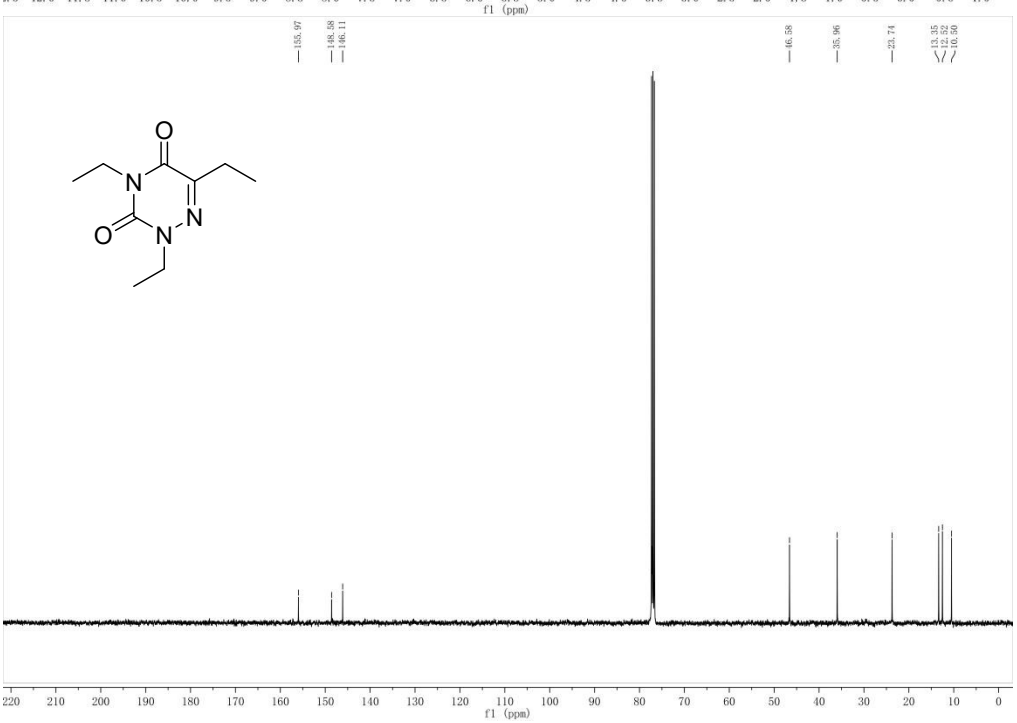
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3a** in $CDCl_3$



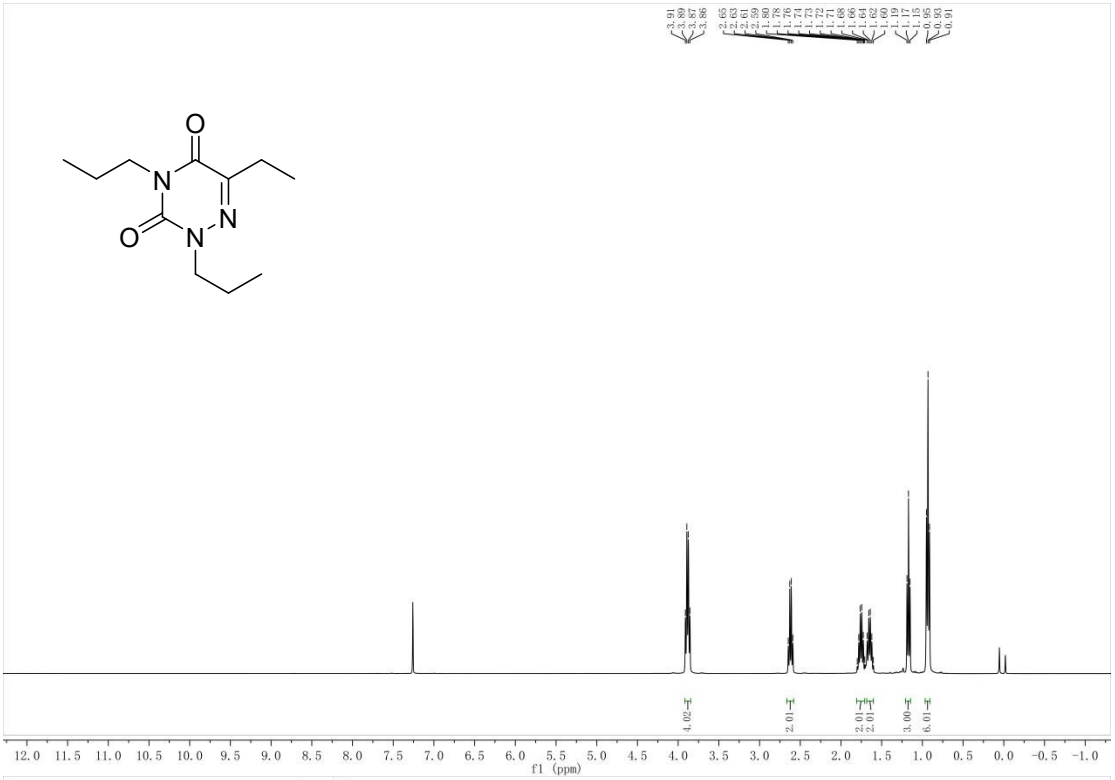


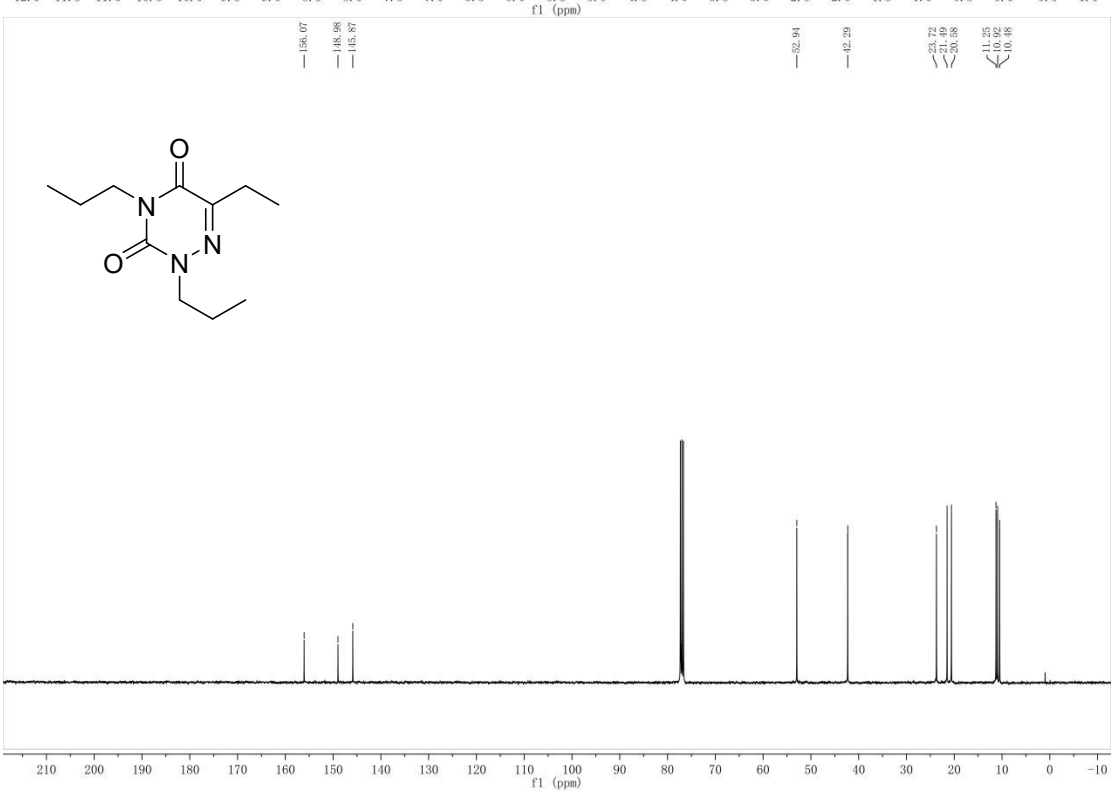
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3b** in $CDCl_3$



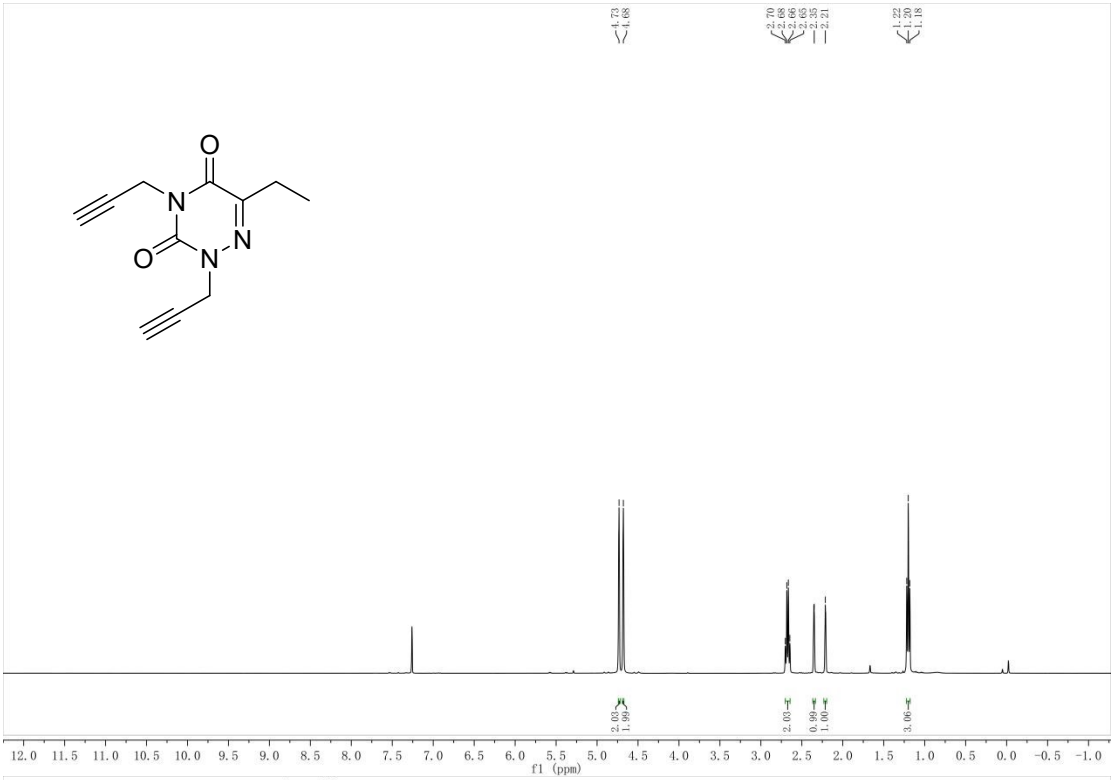


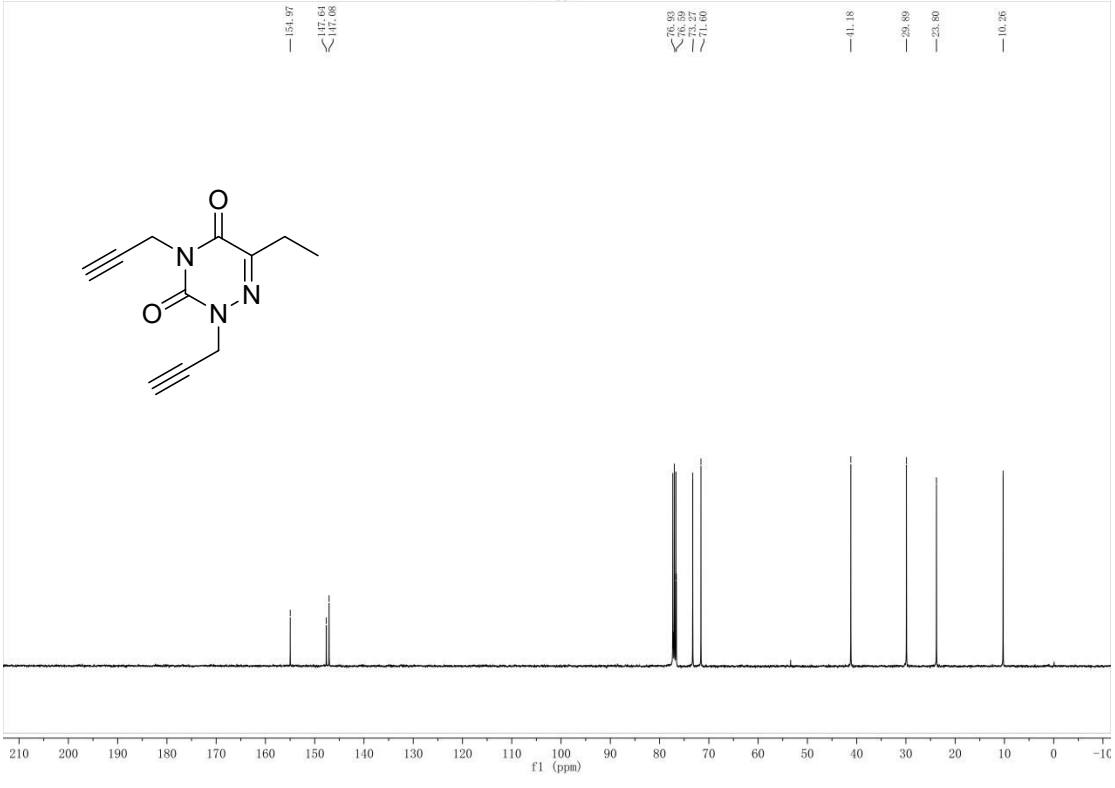
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3c** in $CDCl_3$



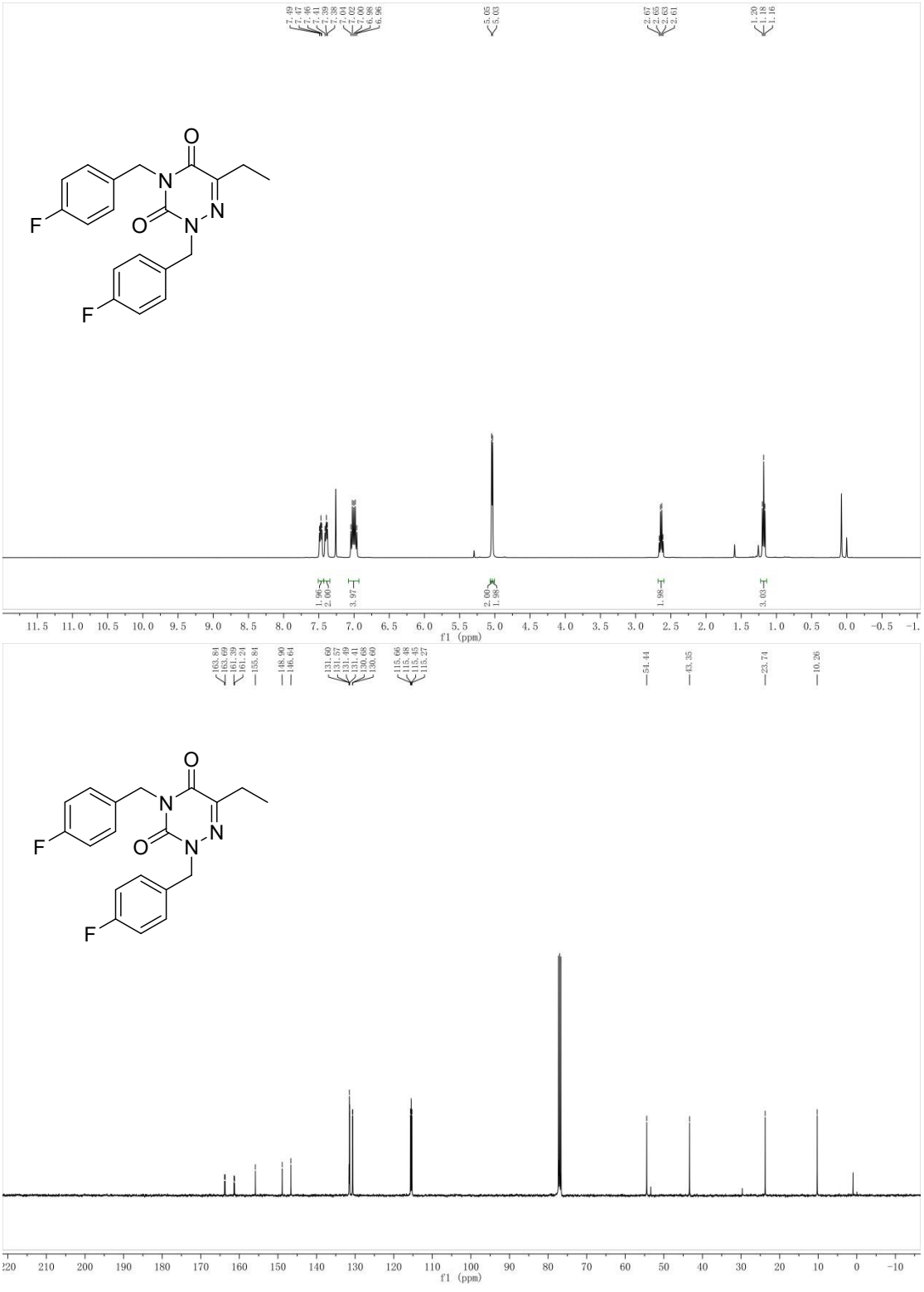


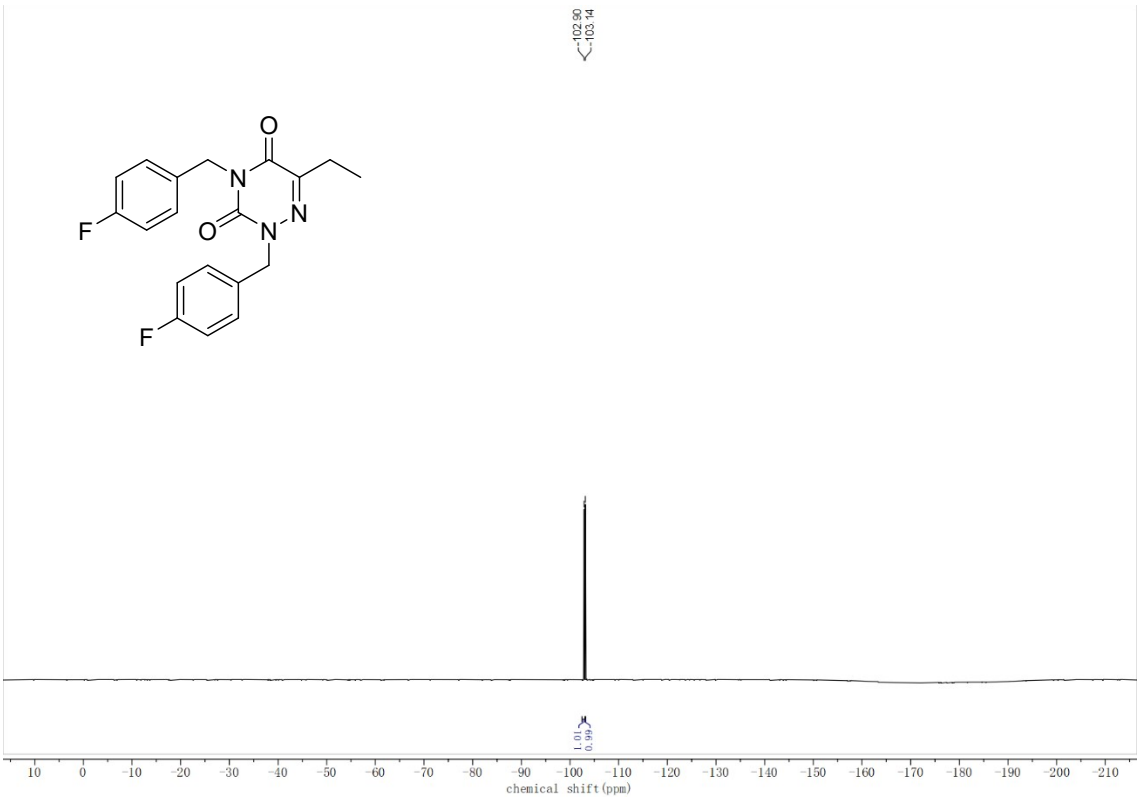
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3d** in $CDCl_3$





^{1}H NMR, ^{13}C $\{^{1}H\}$ NMR and ^{19}F NMRSpectrum of **3e** in $CDCl_3$

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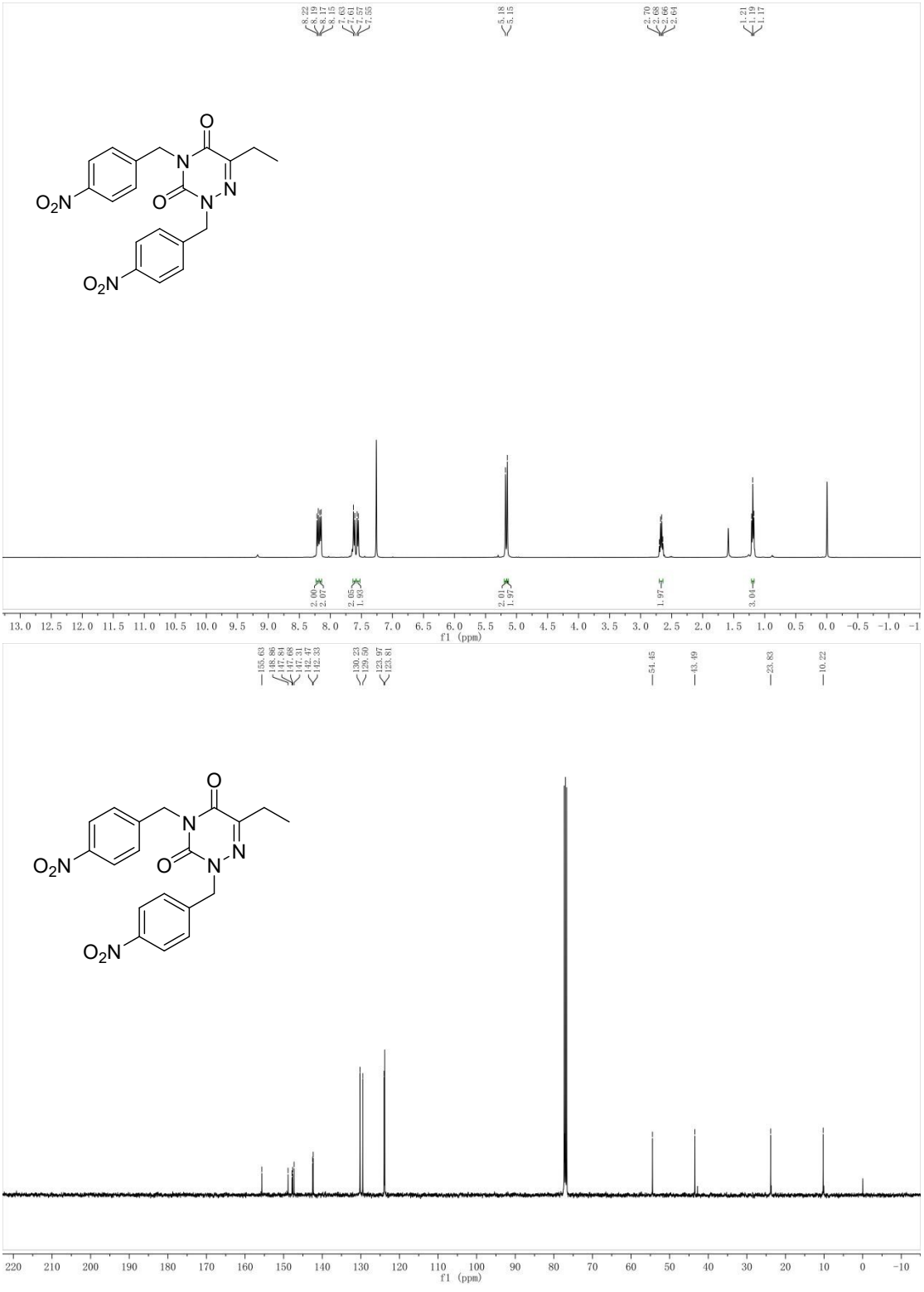
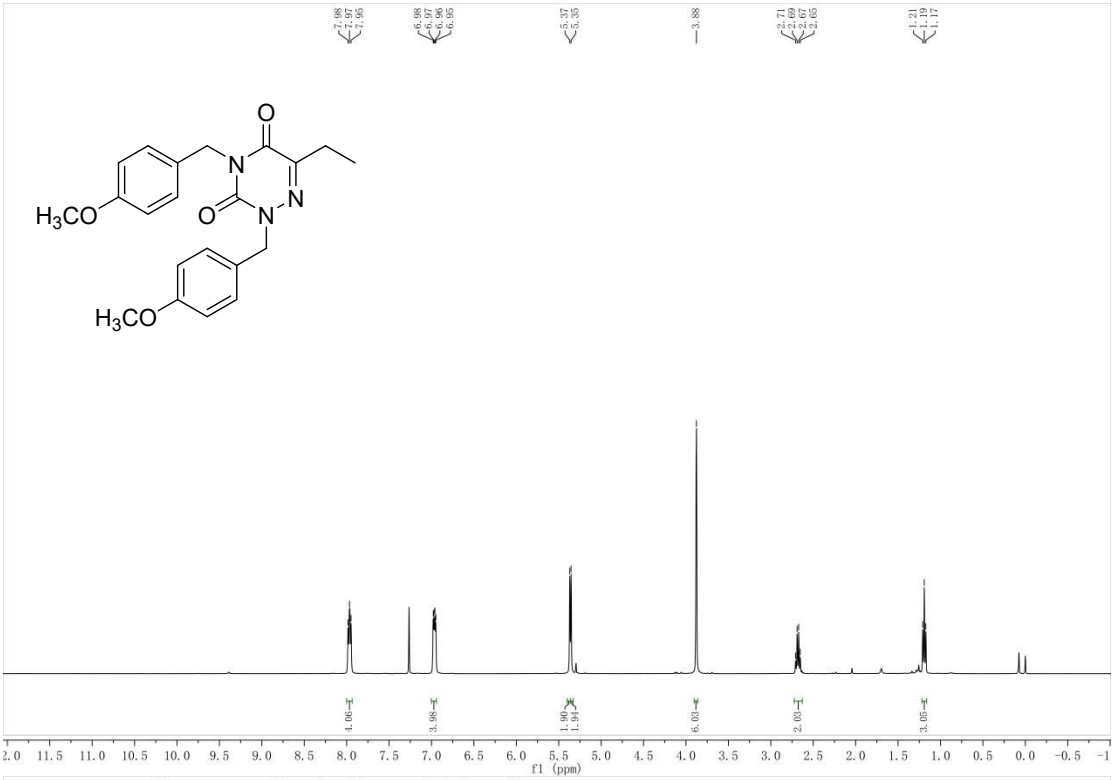
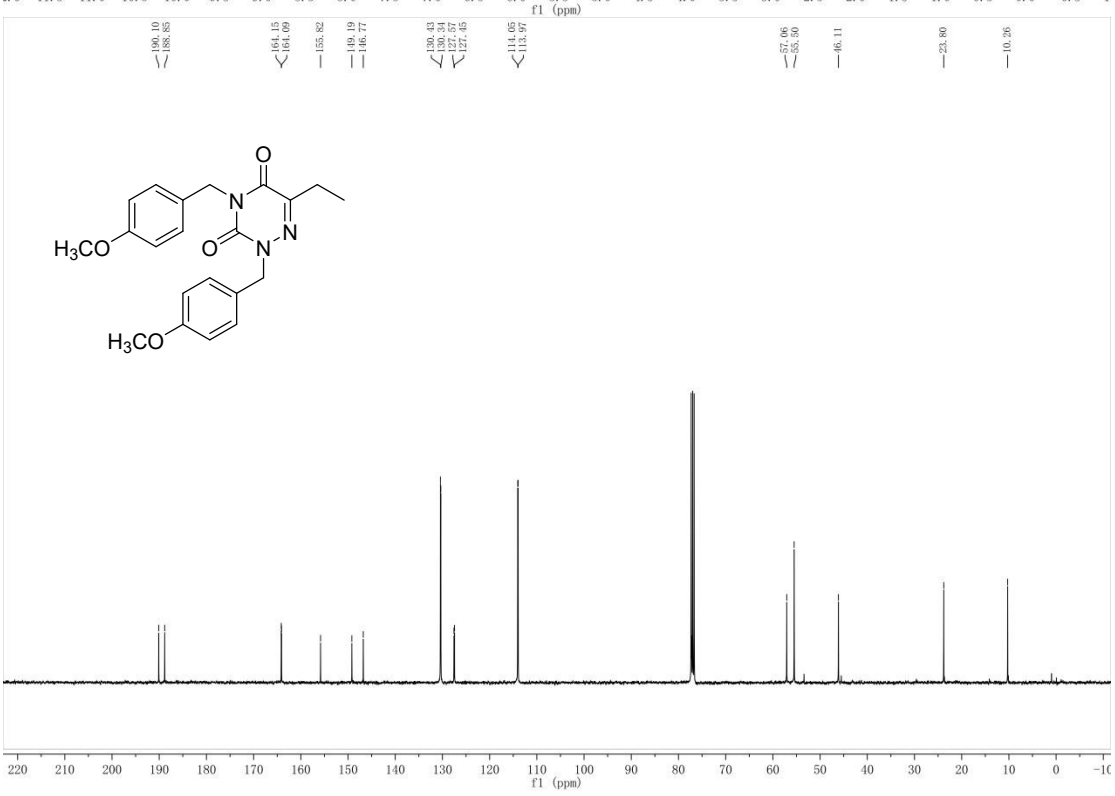
F
1.01
0.99
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
chemical shift(ppm)

^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3f** in $CDCl_3$

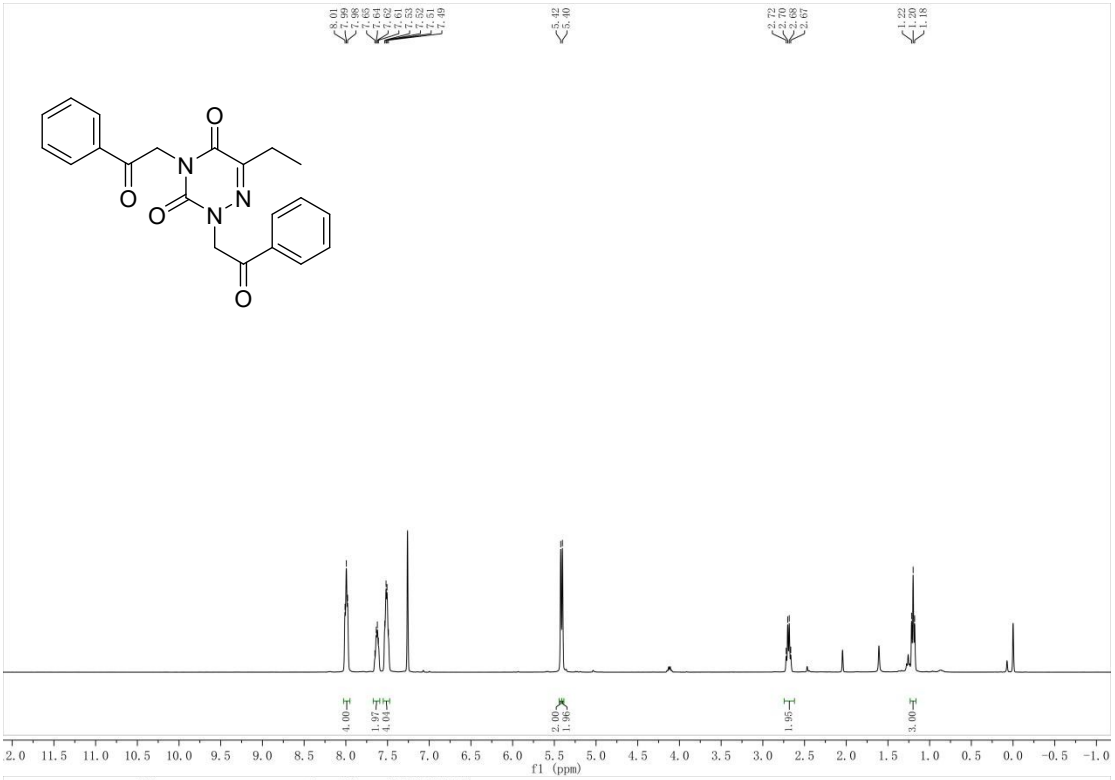


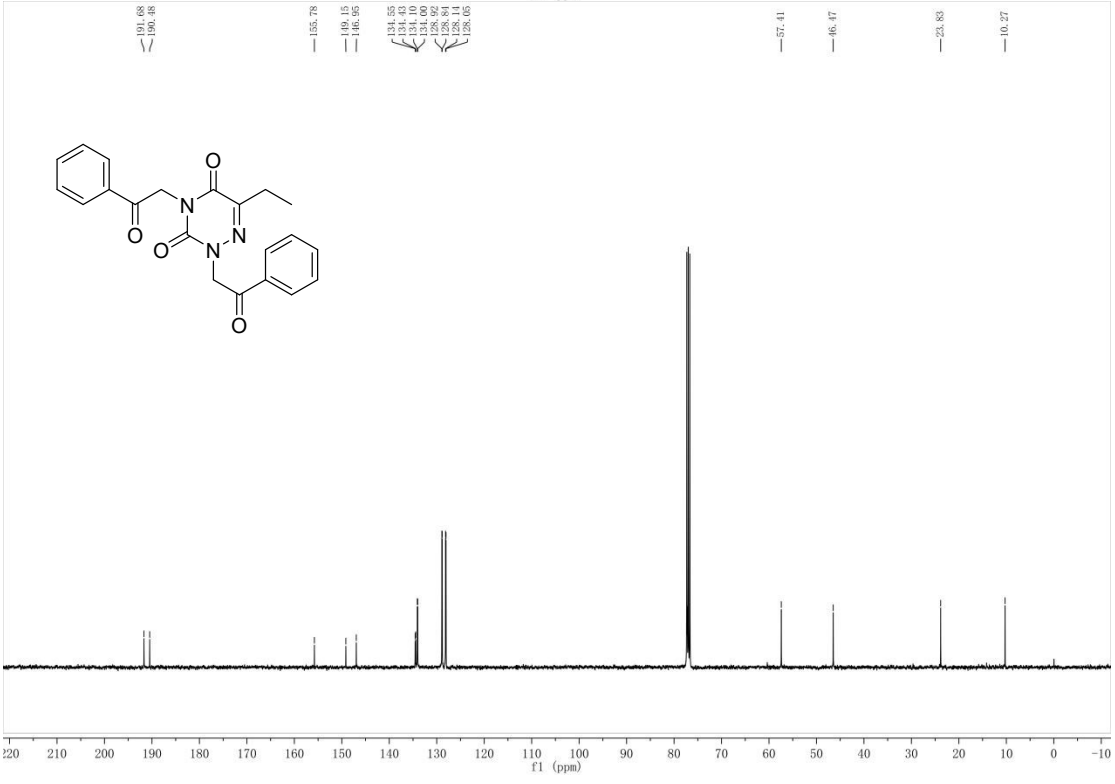
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3g** in $CDCl_3$



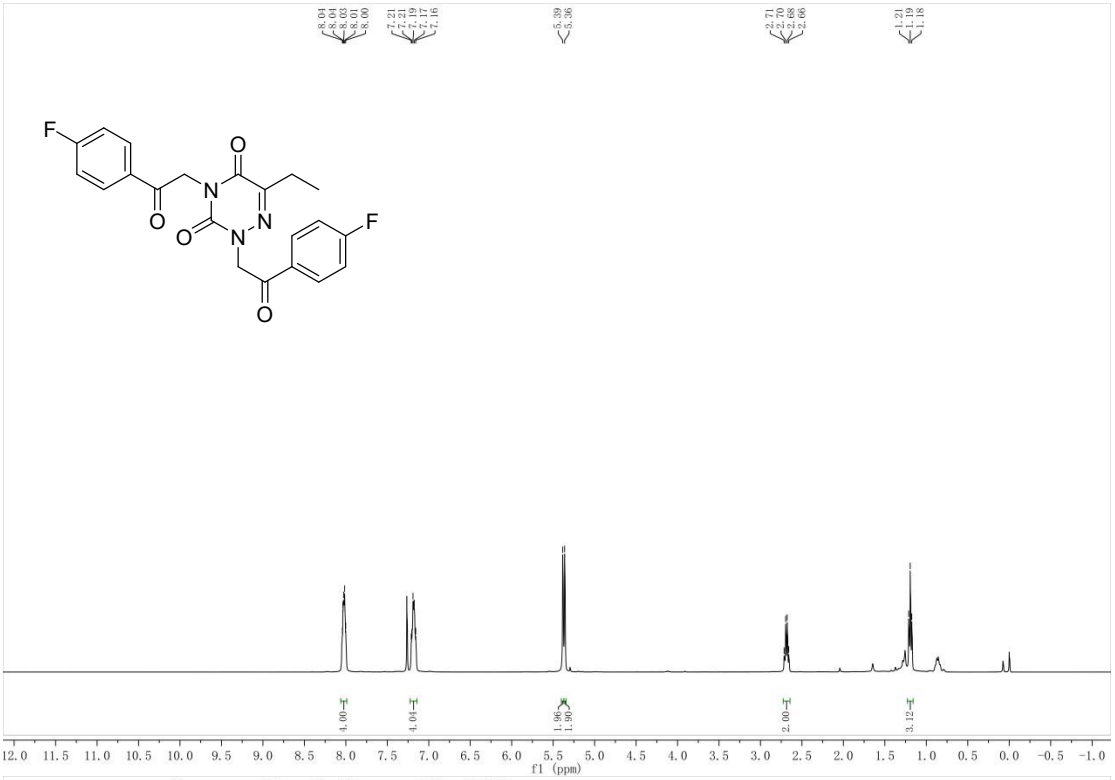


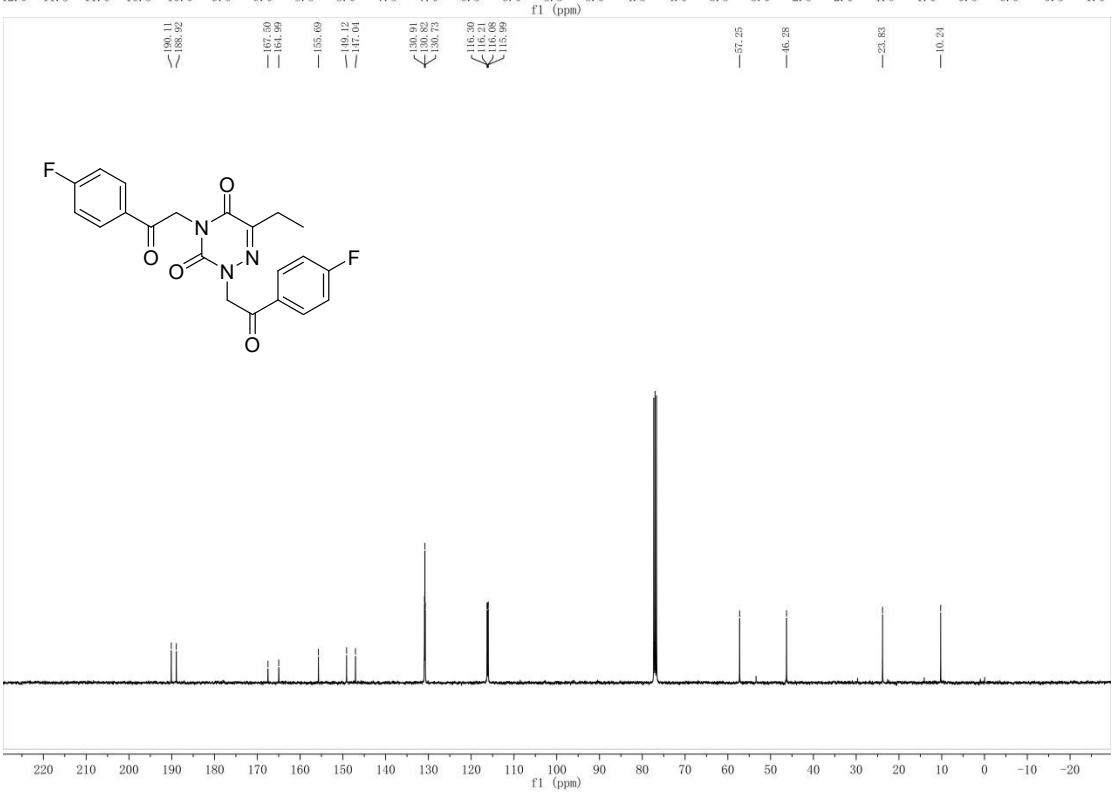
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3h** in $CDCl_3$

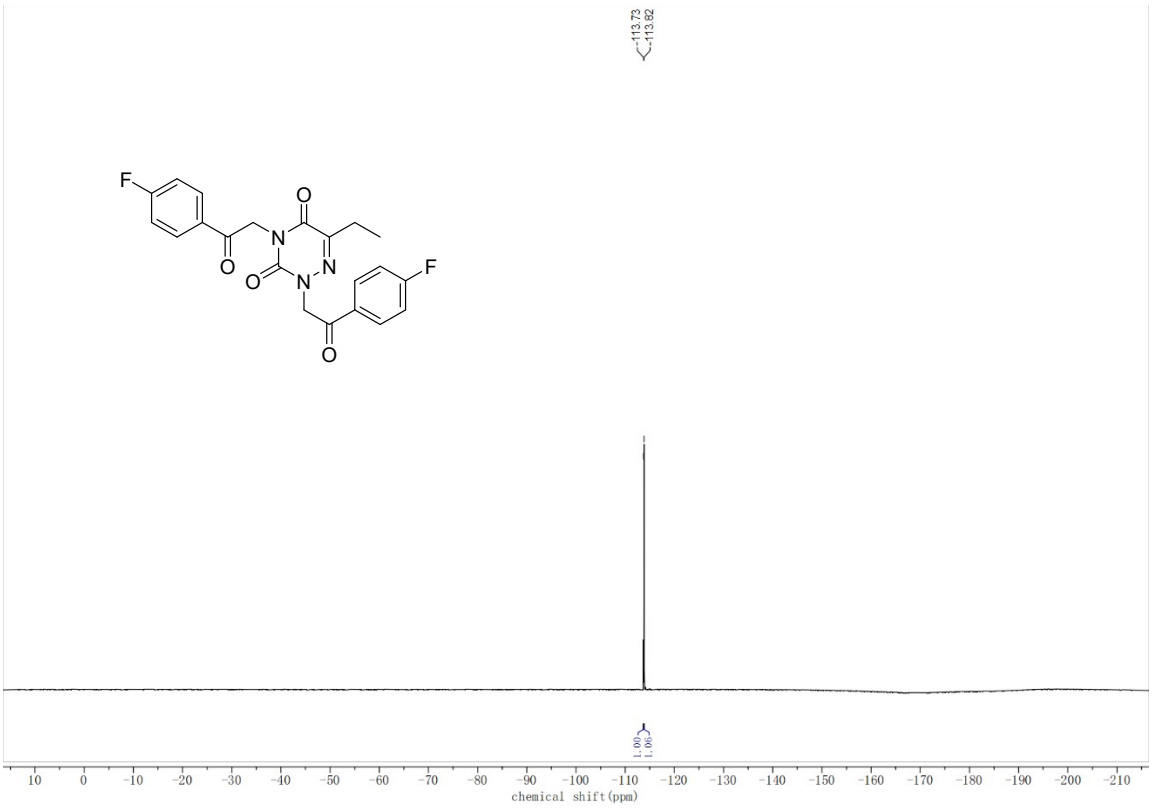




^{1}H NMR,^{13}C {^{1}H} NMR and ^{19}F {^{1}H} NMR Spectrum of **3i** in $CDCl_3$



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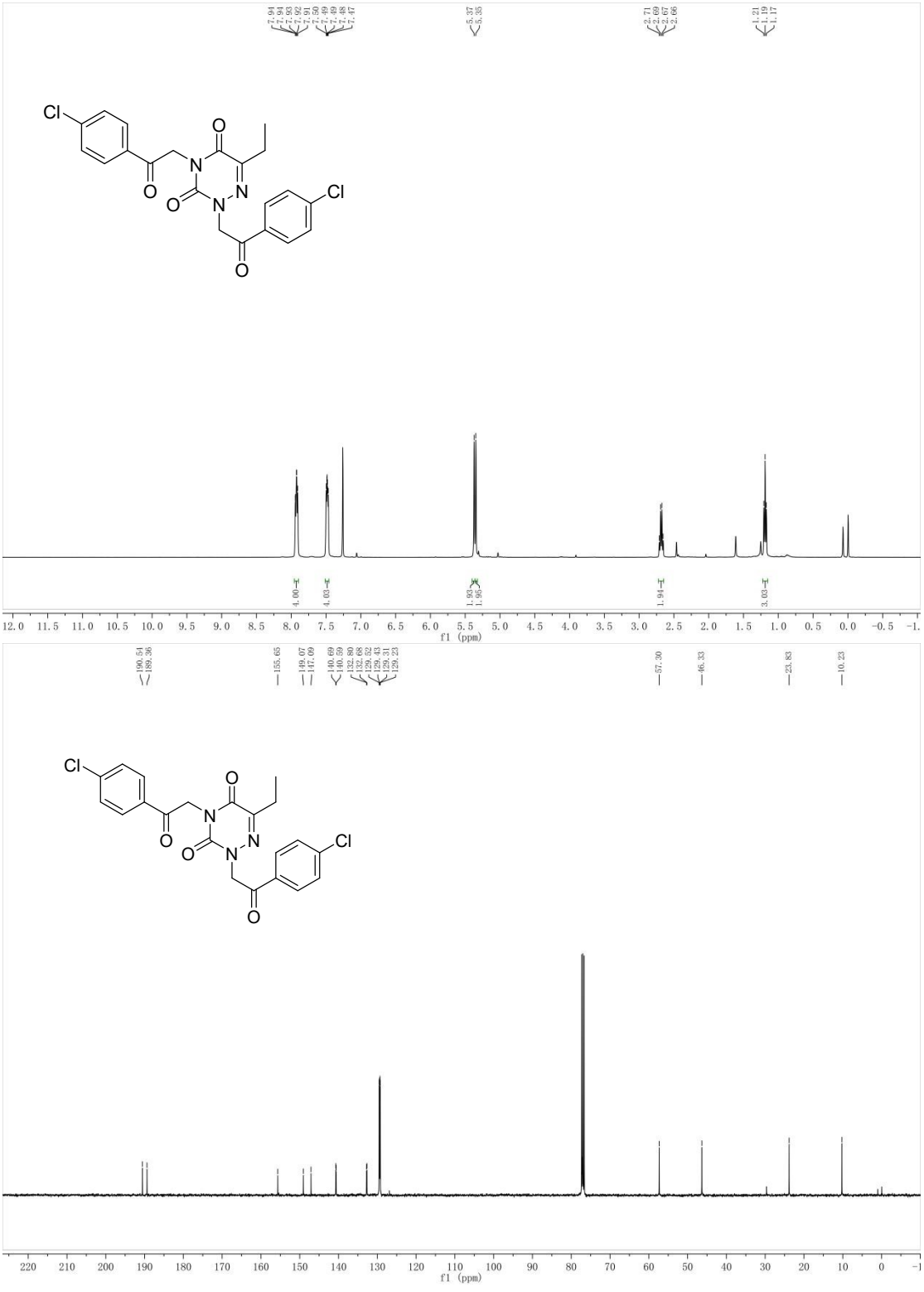
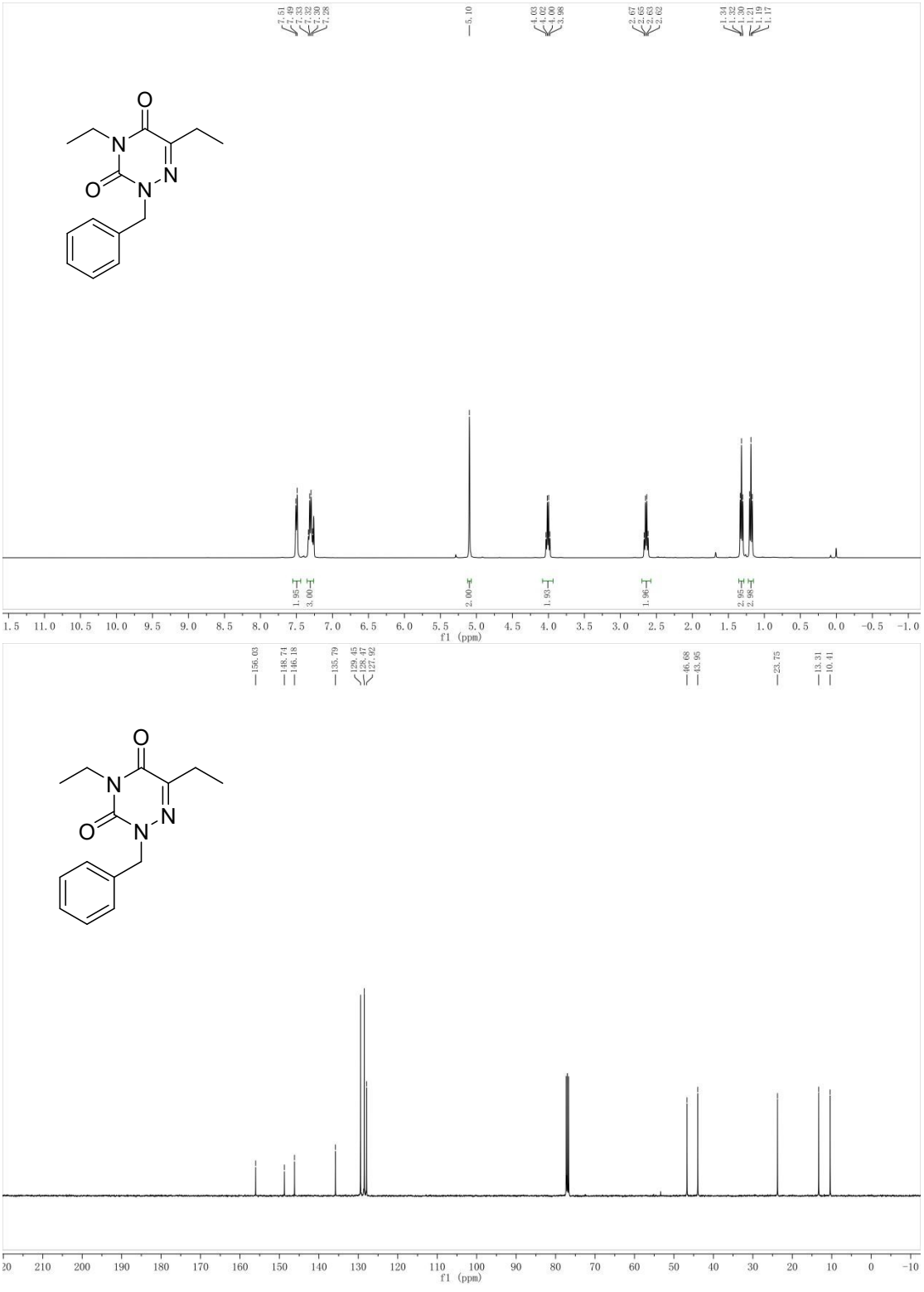
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
chemical shift(ppm)

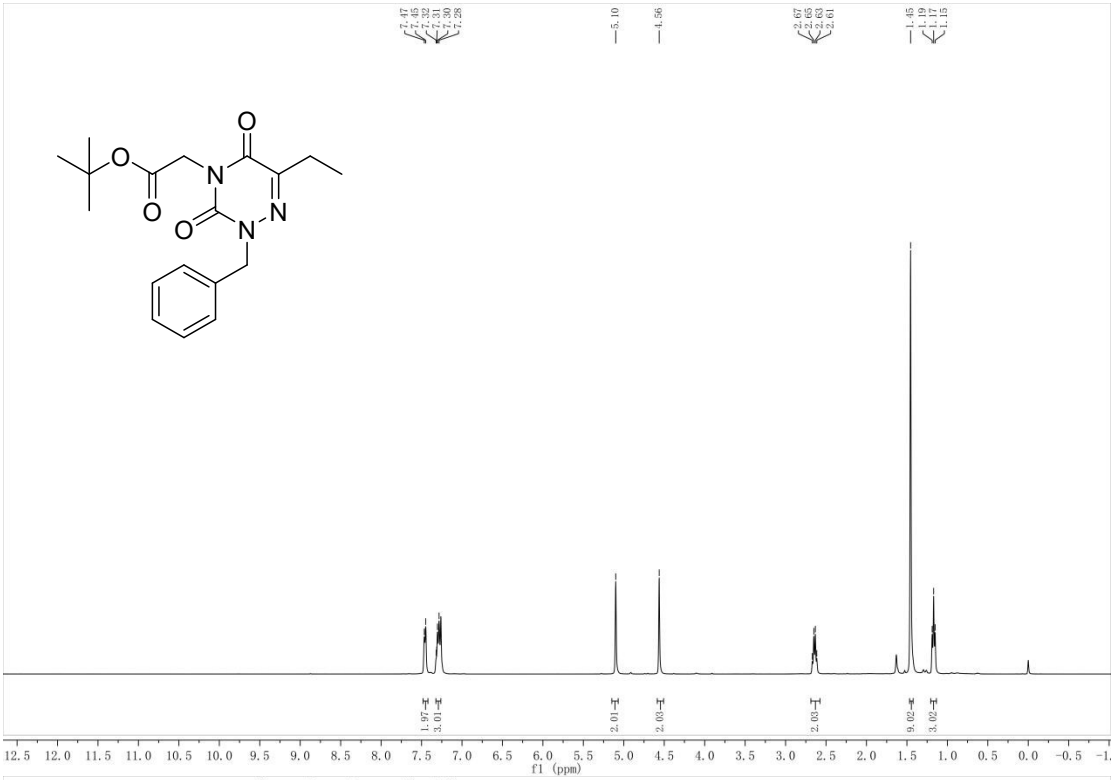
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3j** in $CDCl_3$

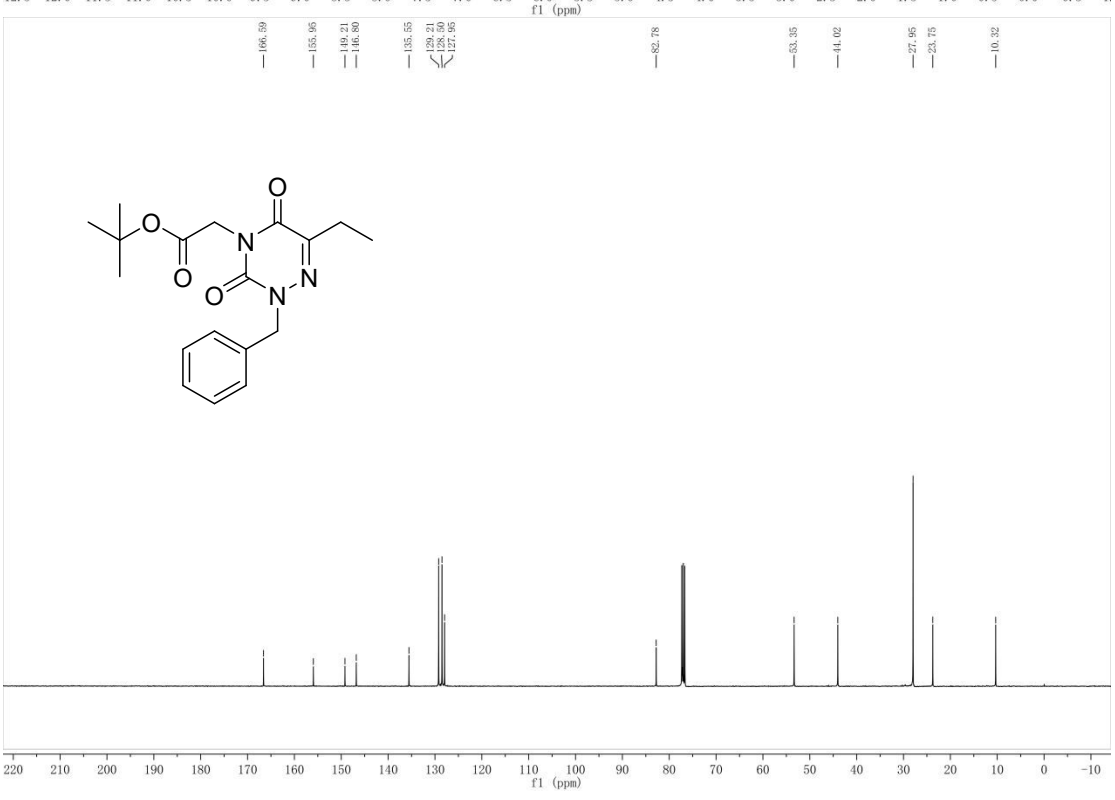


^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3k** in $CDCl_3$

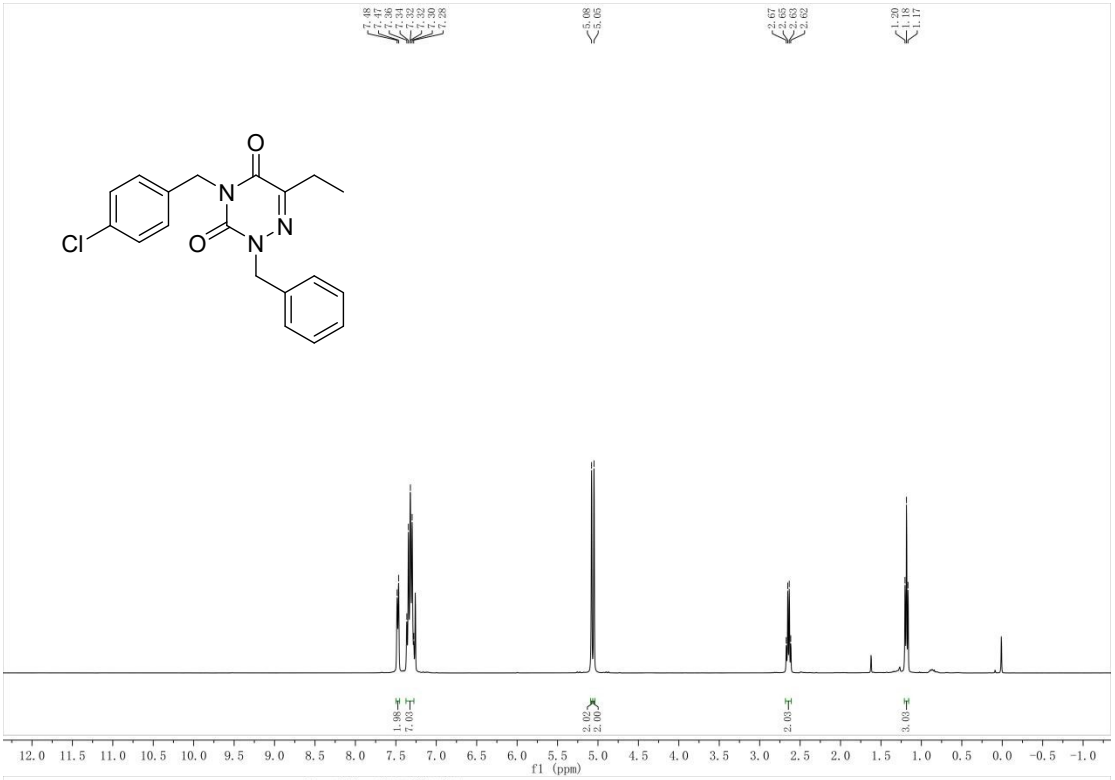


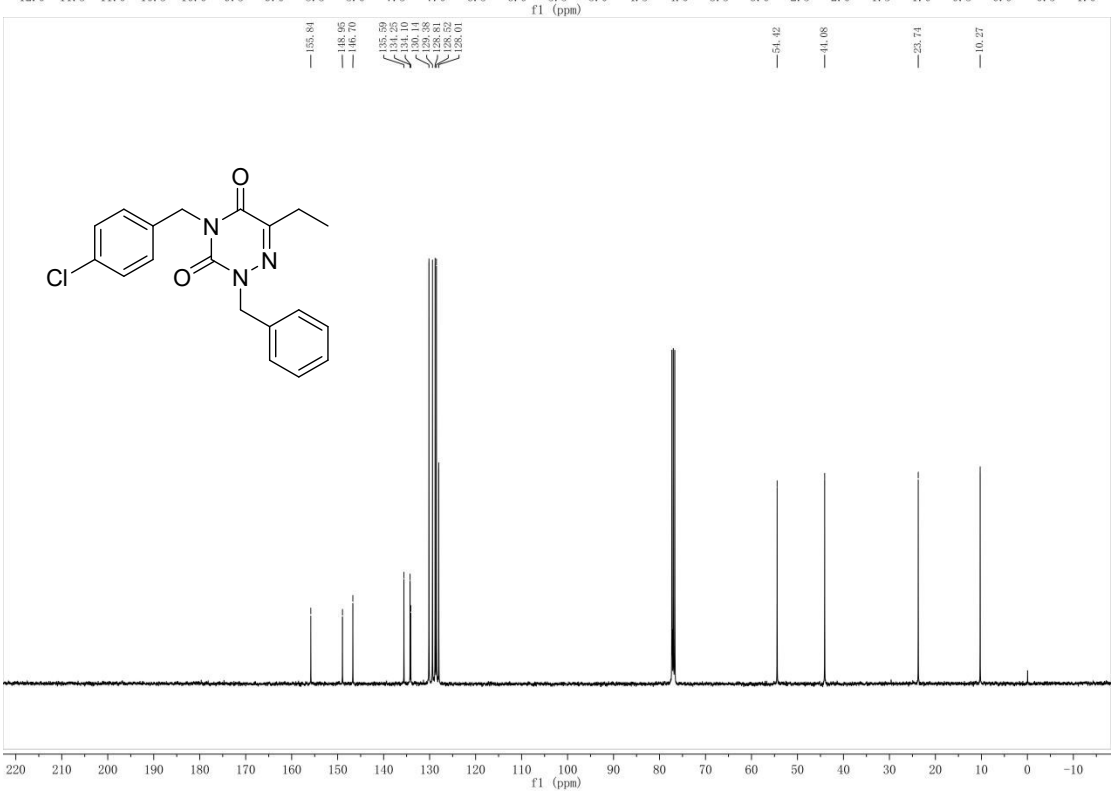
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3l** in $CDCl_3$





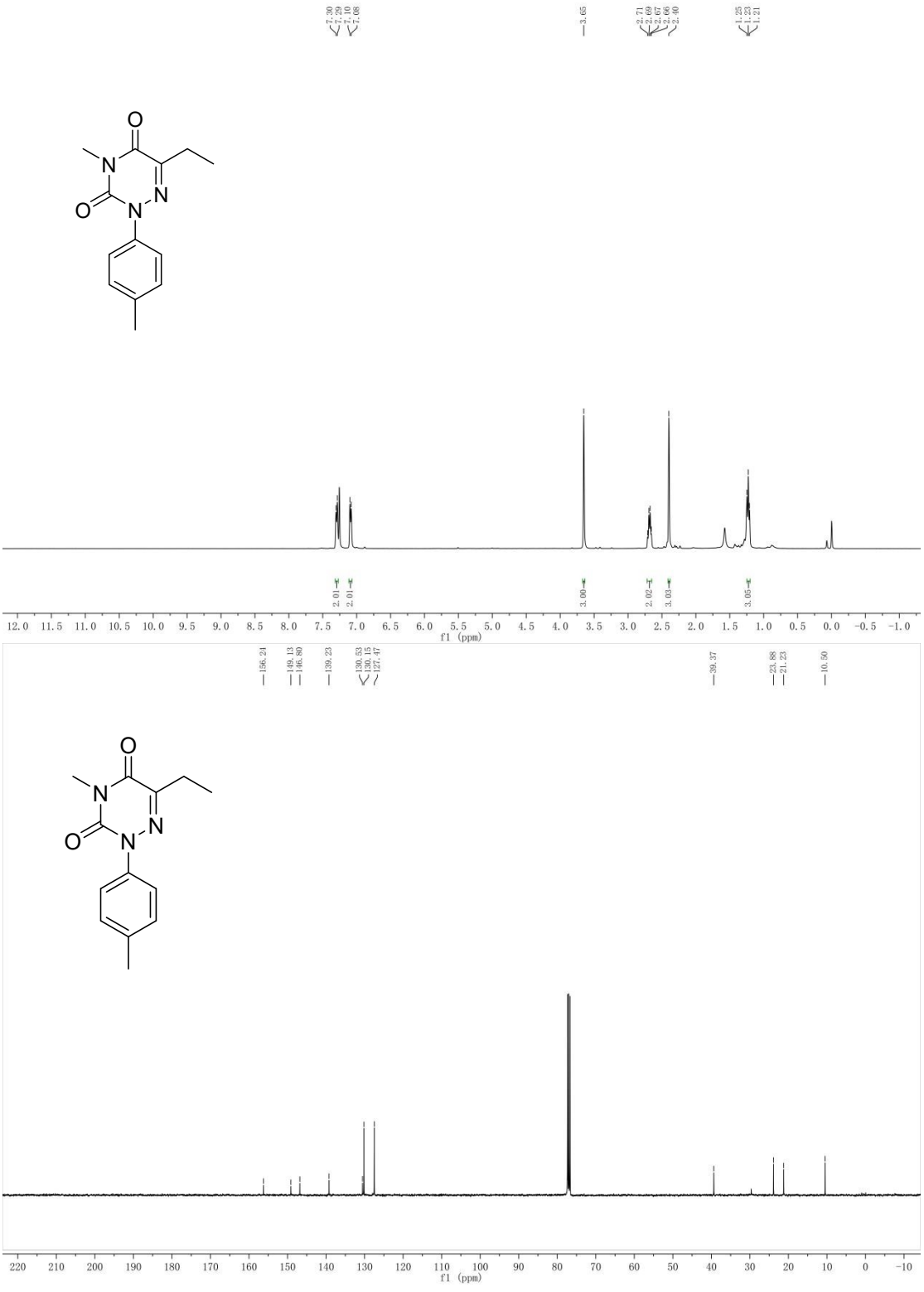
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3m** in $CDCl_3$



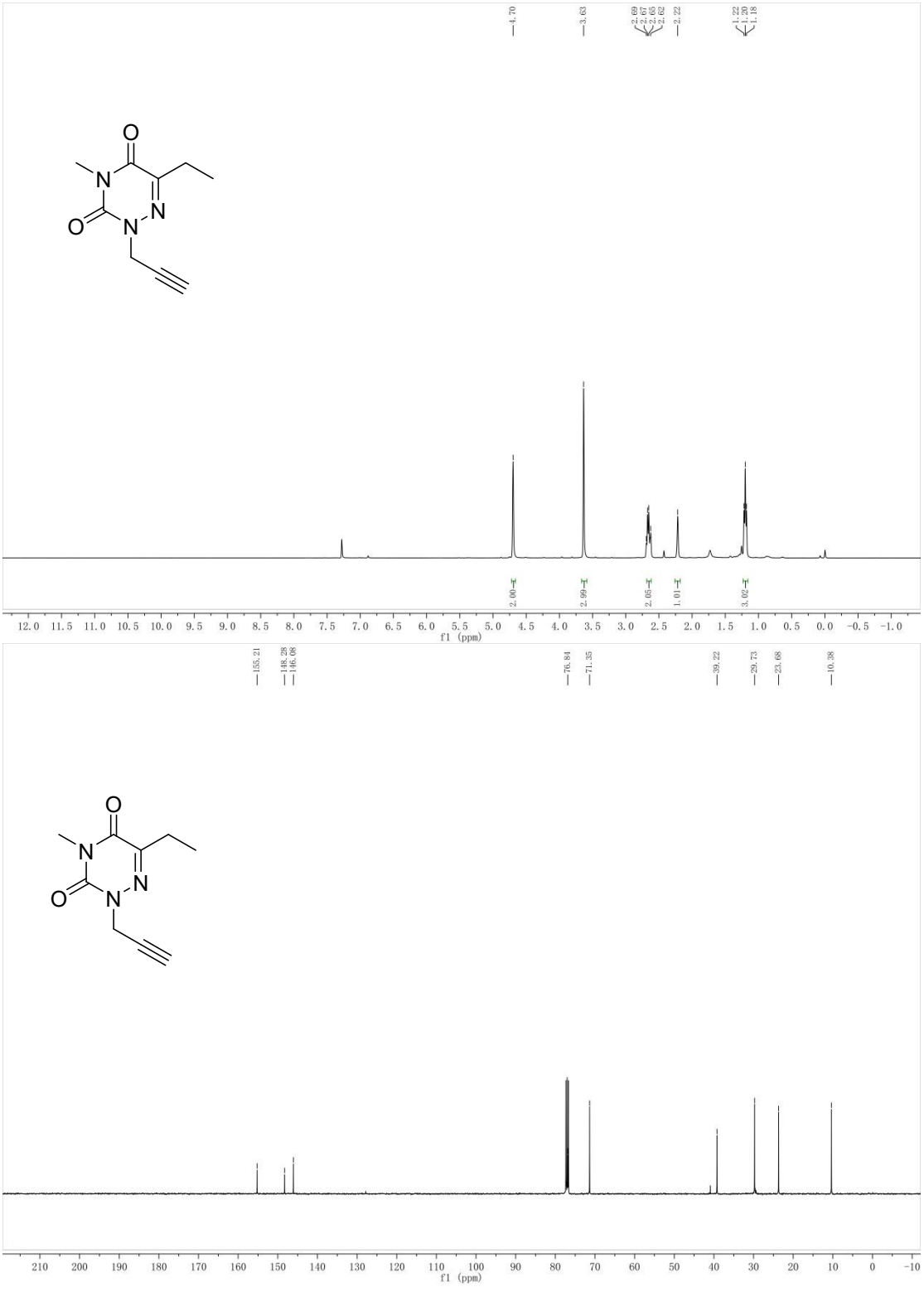


^{1}H NMR and ^{13}C $\{^{1}H\}$NMR Spectrum of **3n** in $CDCl_3$

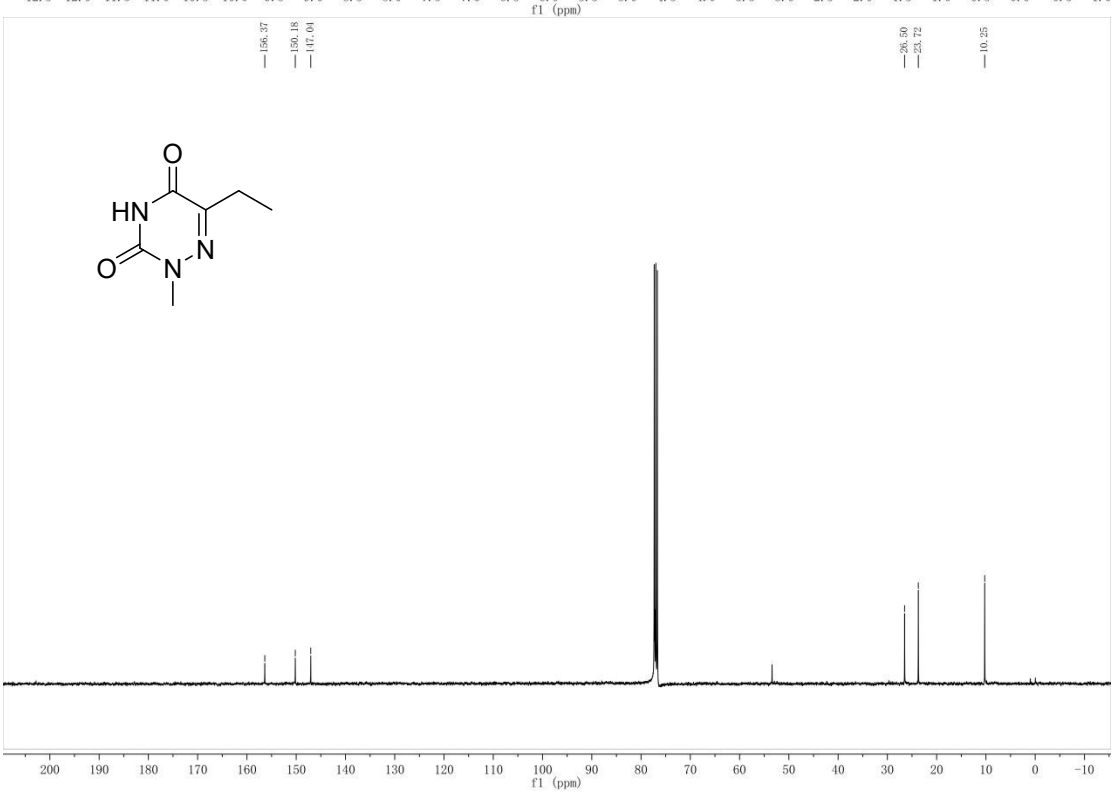
^{1}H NMR and^{13}C $\{^{1}H\}$ NMR Spectrum of **3o** in $CDCl_3$



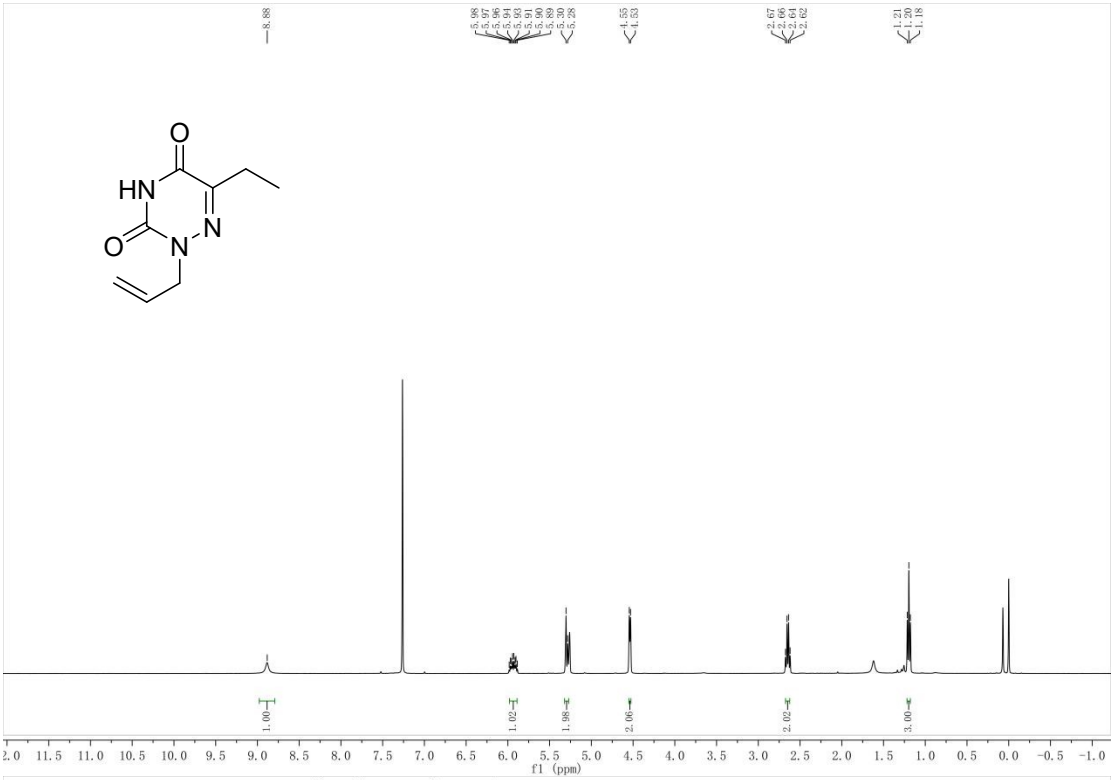
^{1}H NMR and ^{13}C $\{^{1}H\}$NMR Spectrum of **3p** in $CDCl_3$

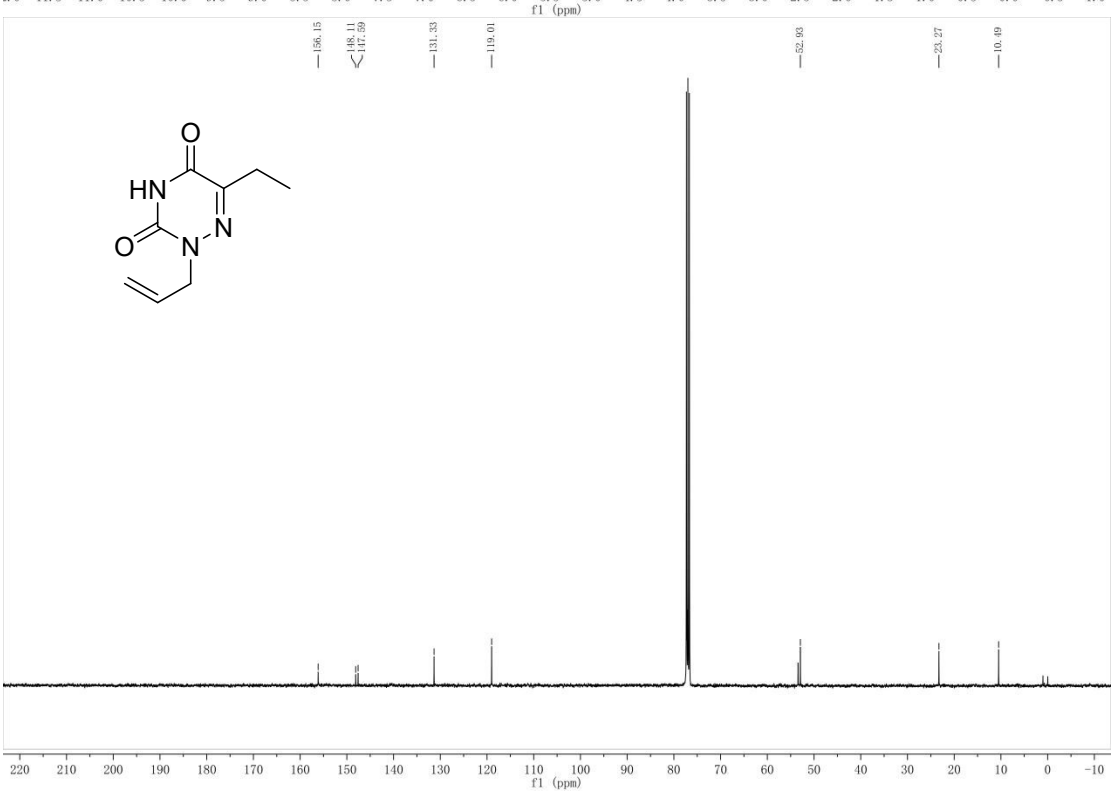


^{1}H NMR and ^{13}C $\{^{1}H\}$NMR Spectrum of **3q** in $CDCl_3$

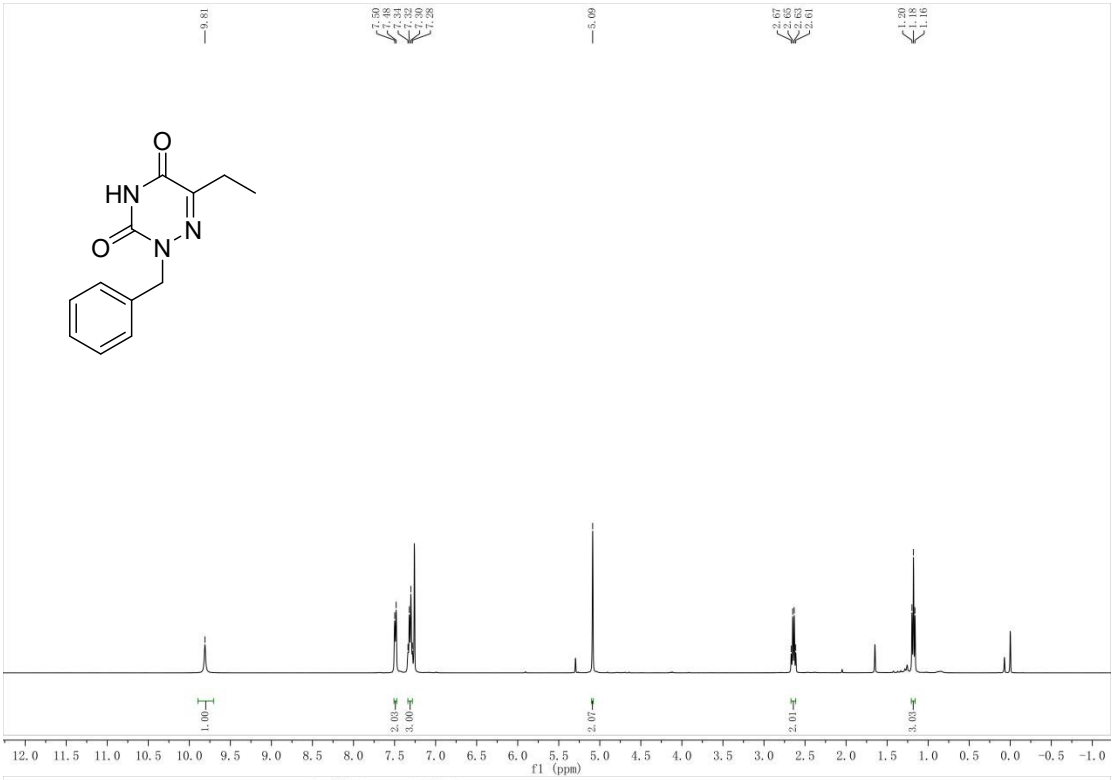


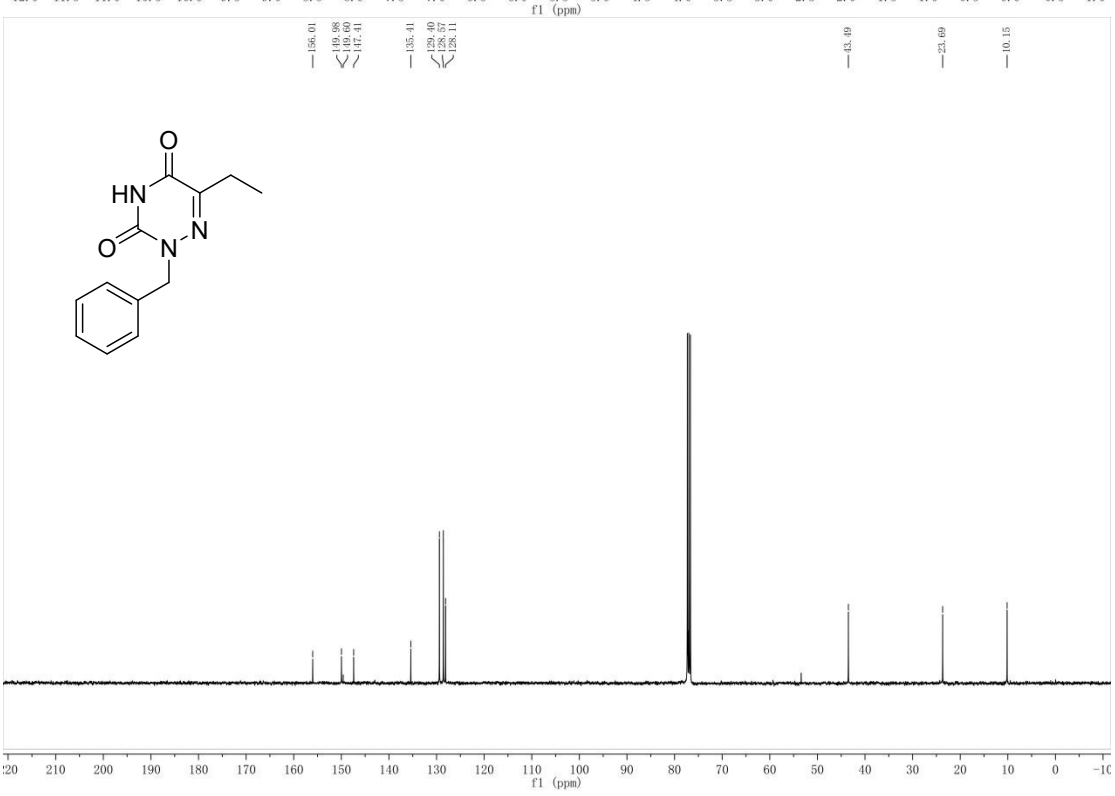
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3r** in $CDCl_3$



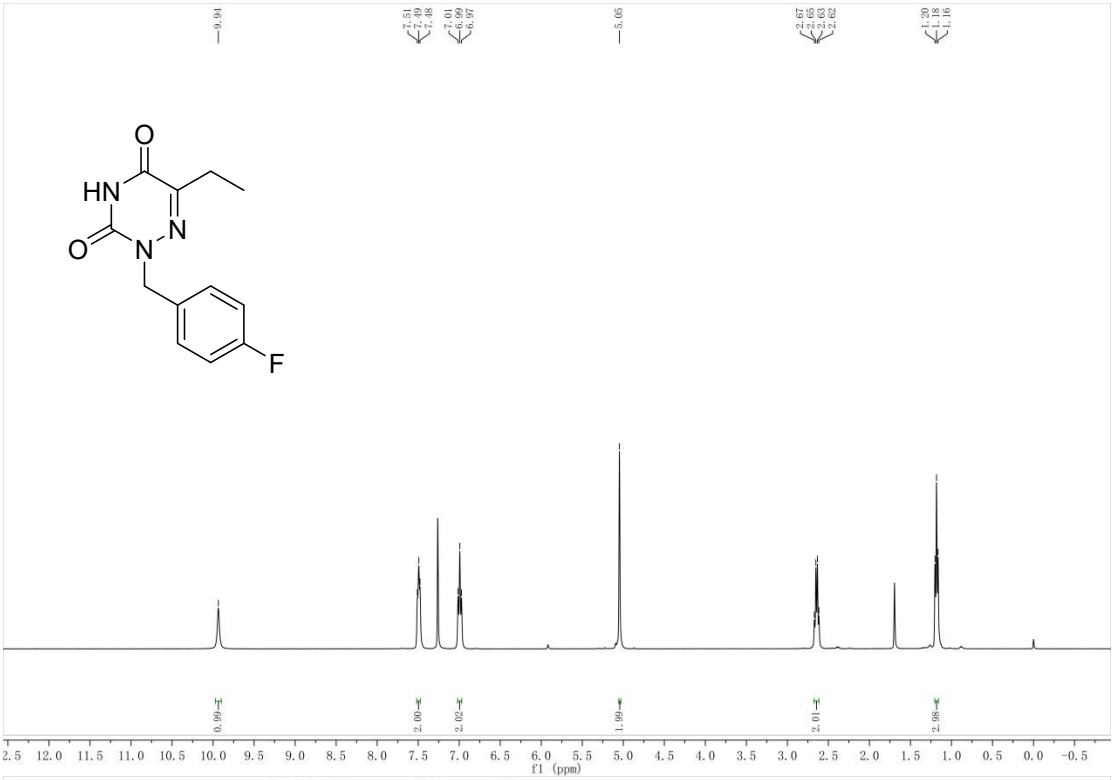


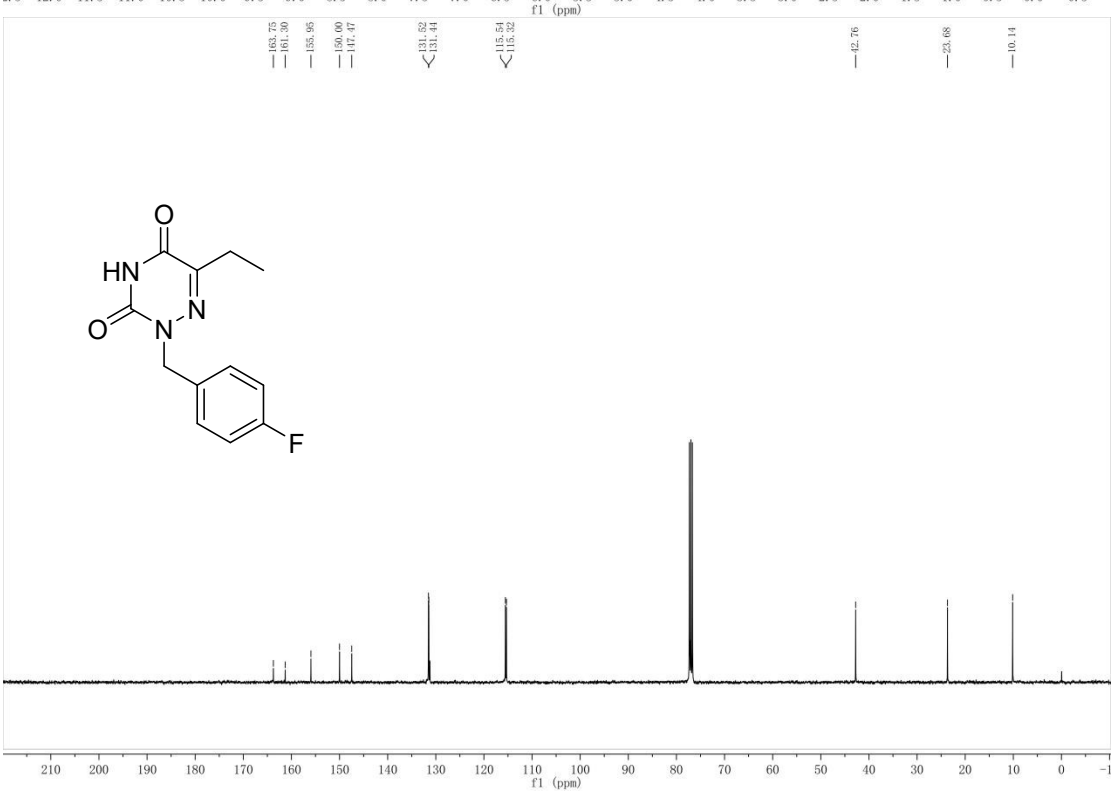
^{1}H NMR and ^{13}C $\{^{1}H\}$NMR Spectrum of **3s** in $CDCl_3$

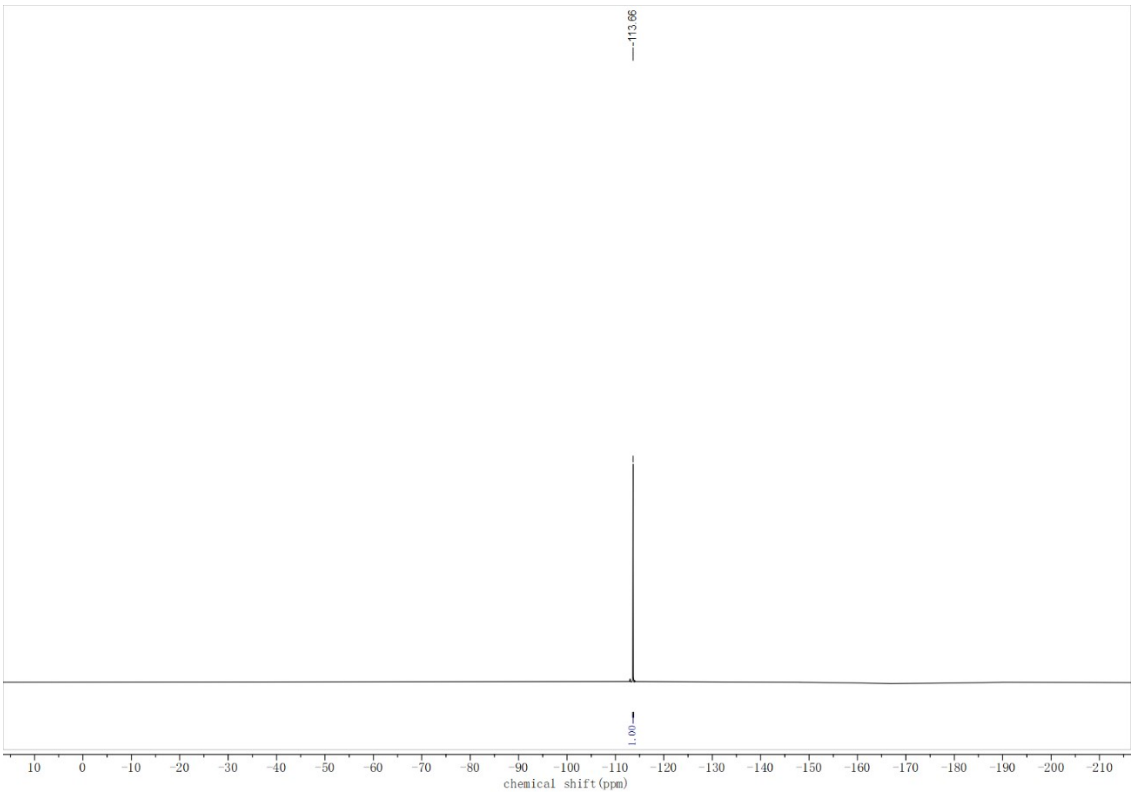




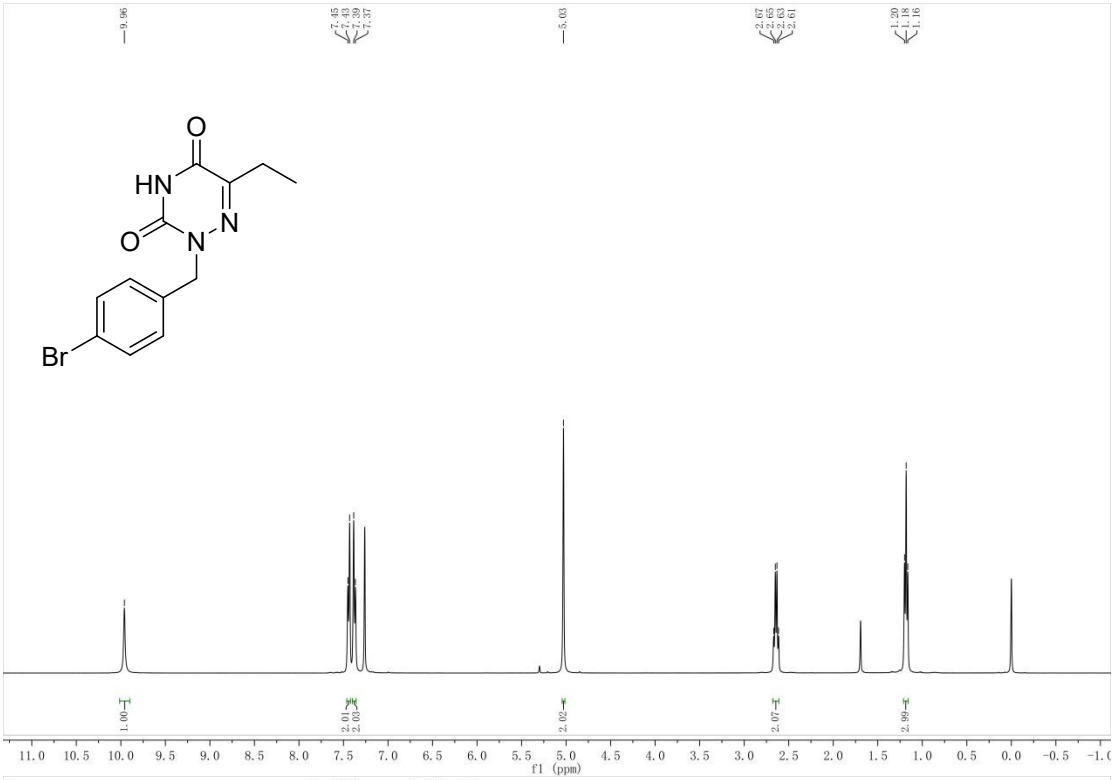
^{1}H NMR,^{13}C {^{1}H} NMR and ^{19}F {^{1}H} NMR Spectrum of **3t** in $CDCl_3$

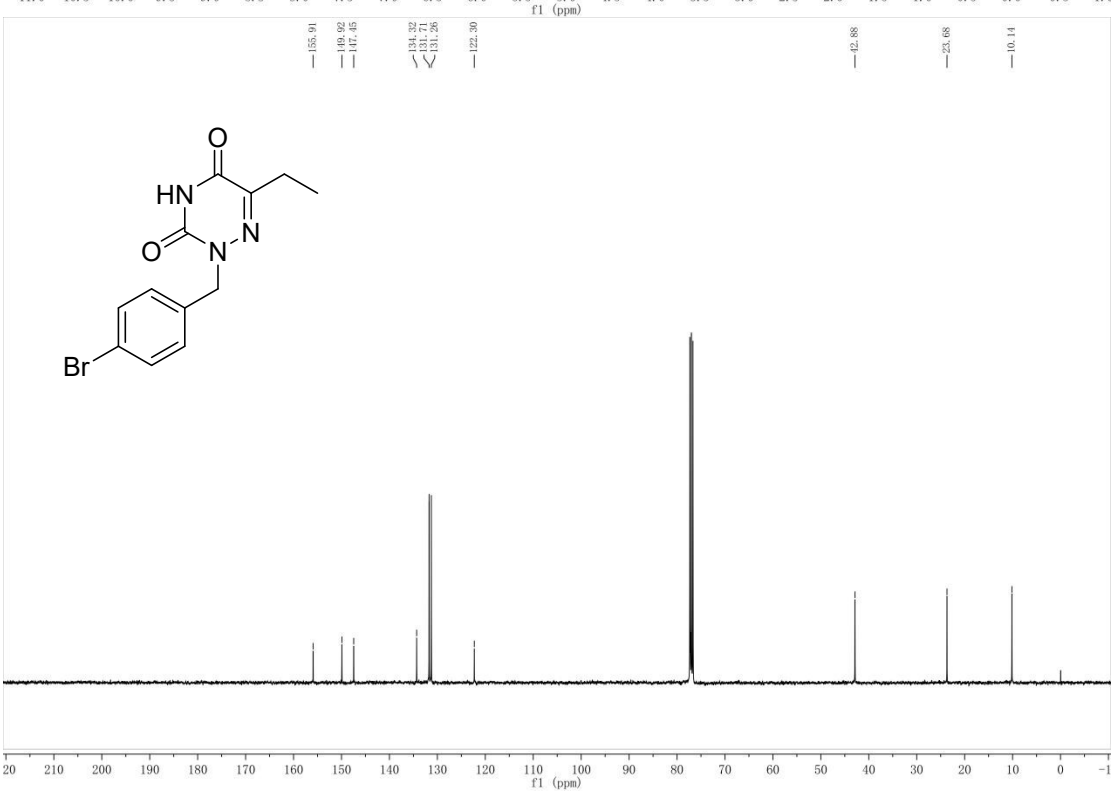




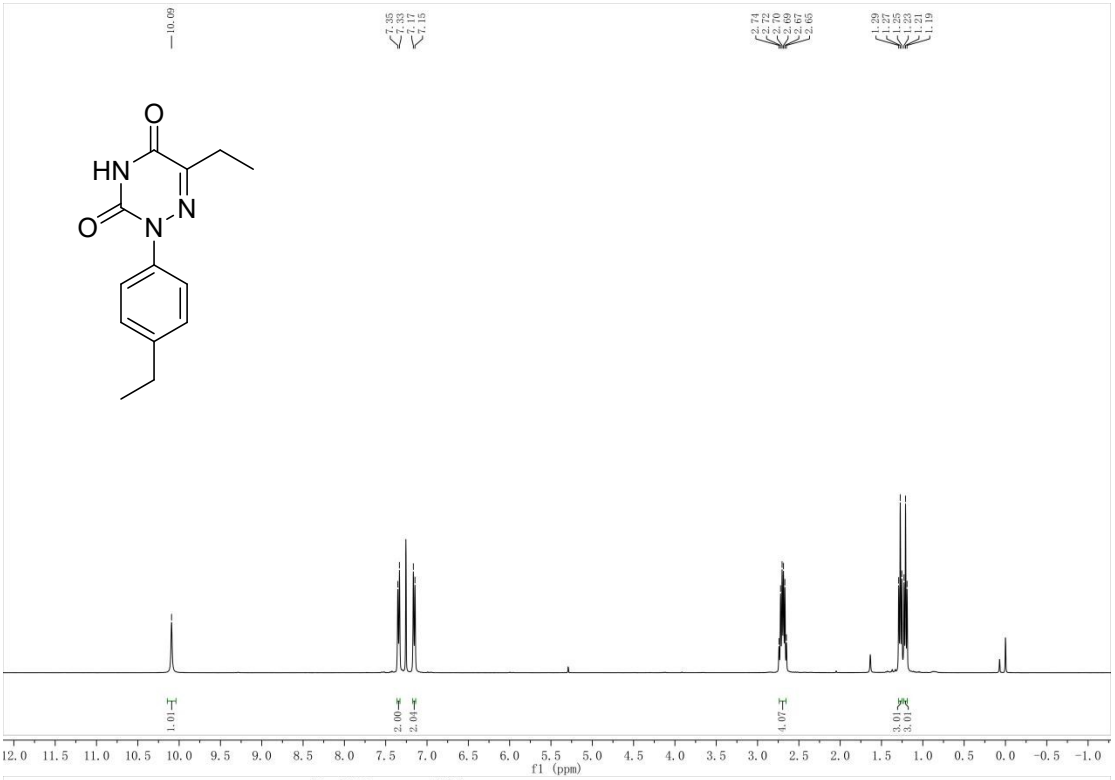

-113.66
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
chemical shift(ppm)

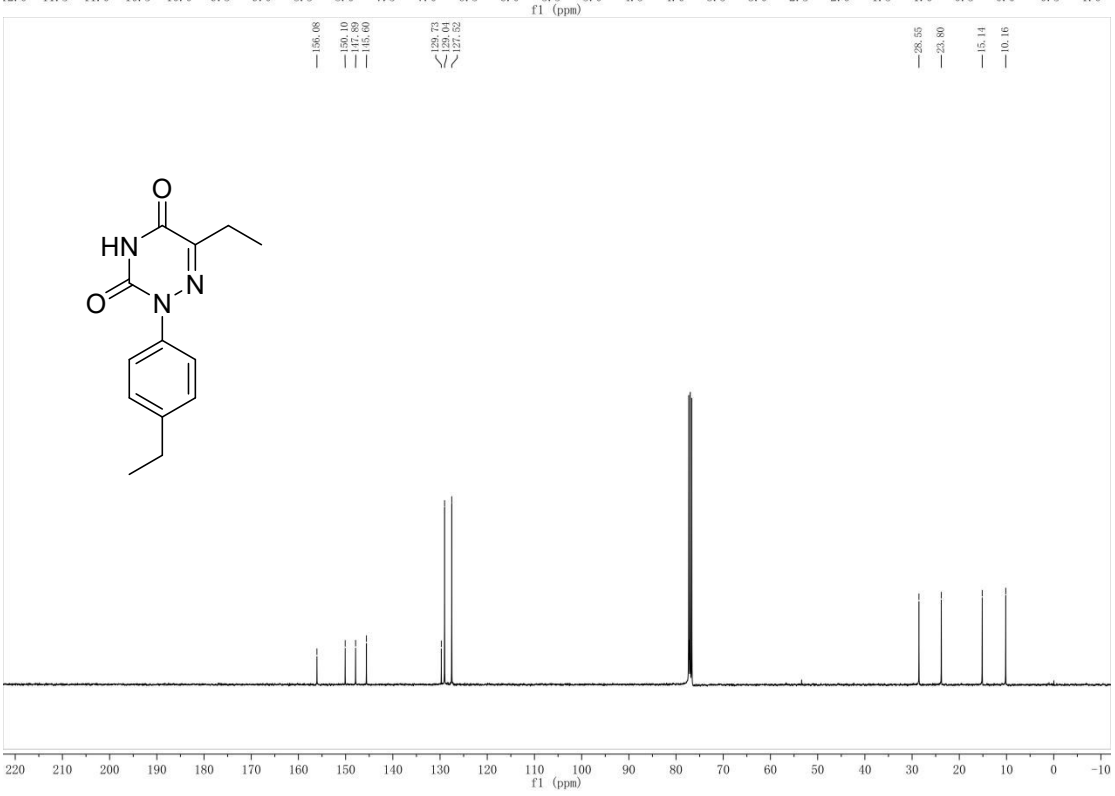
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3u** in $CDCl_3$



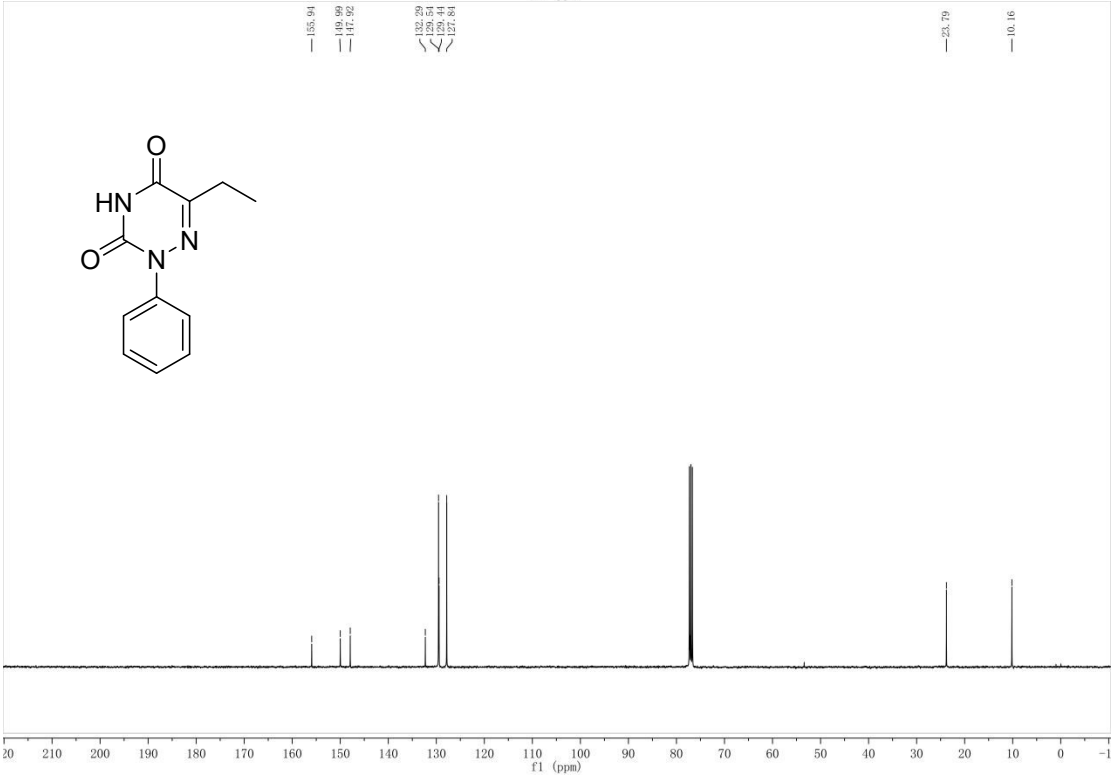


^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3v** in $CDCl_3$

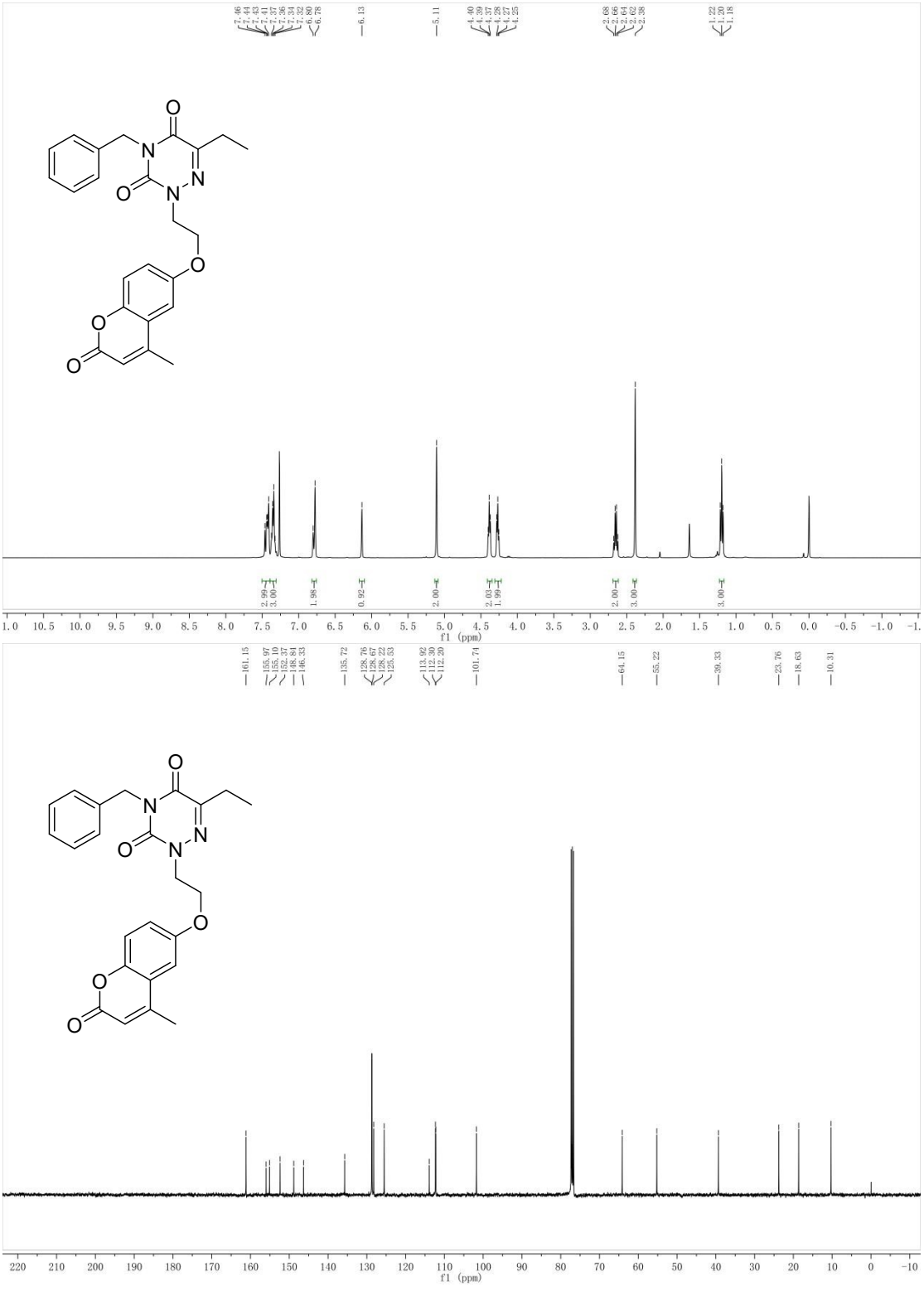




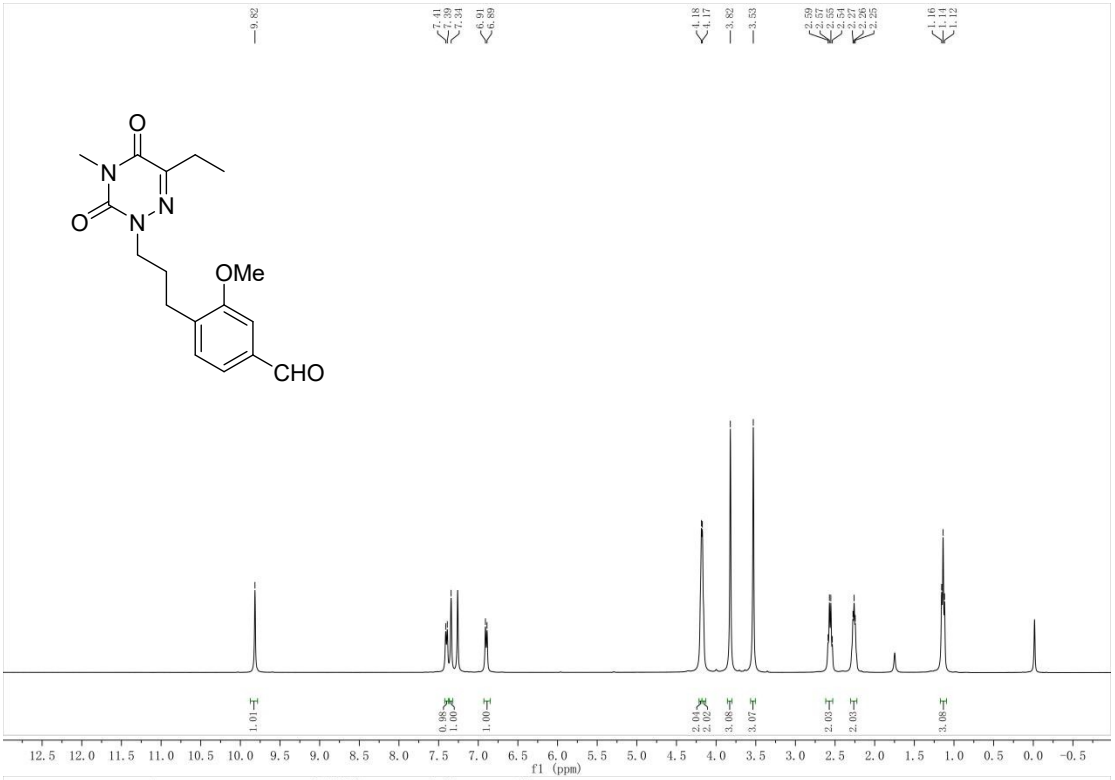
^{1}H NMR and ^{13}C $\{^{1}H\}$NMR Spectrum of **3w** in $CDCl_3$

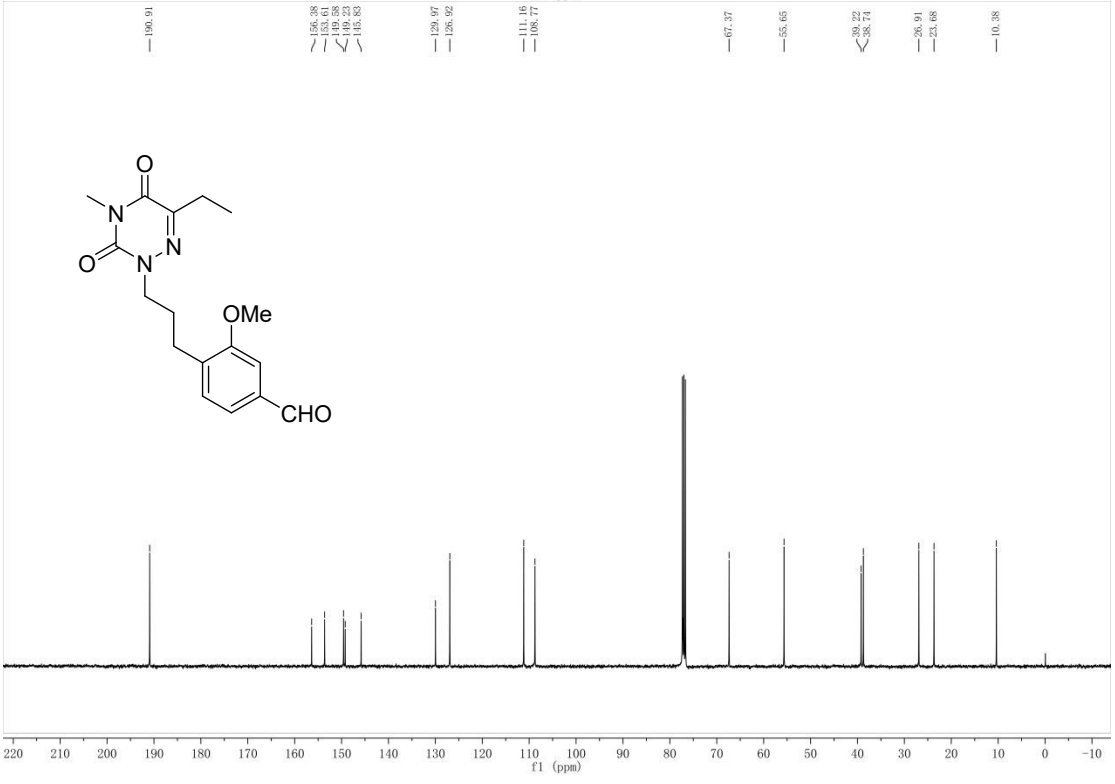


^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3x** in $CDCl_3$

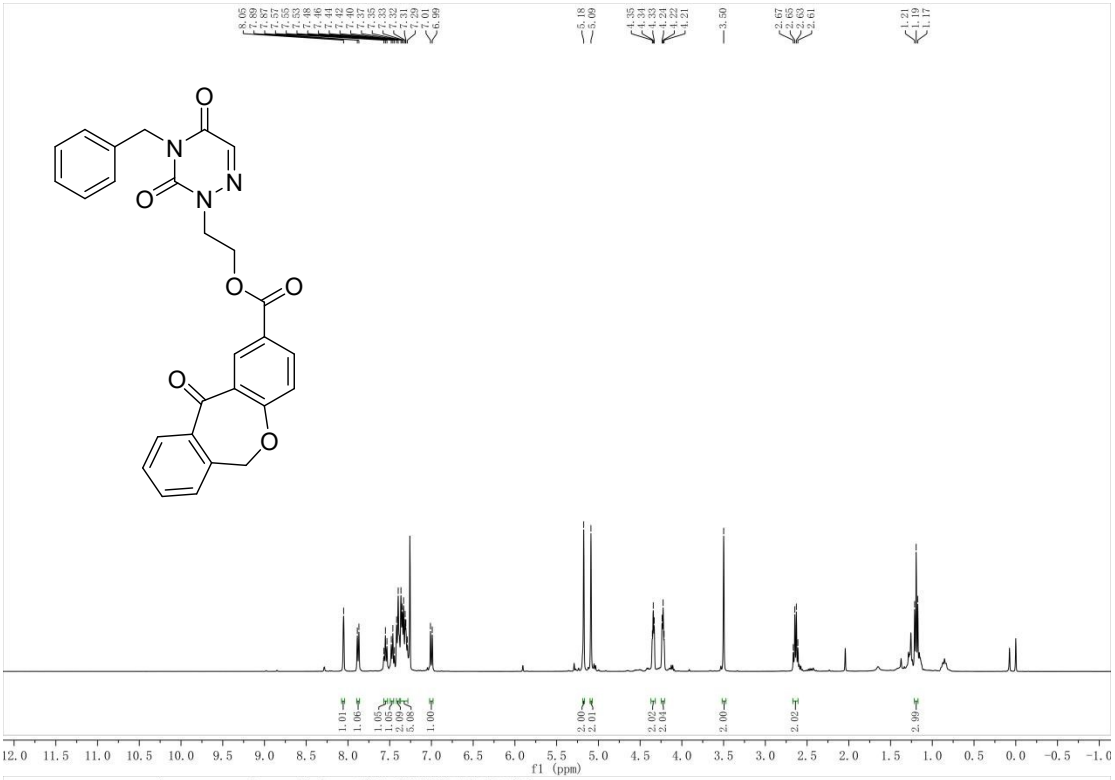


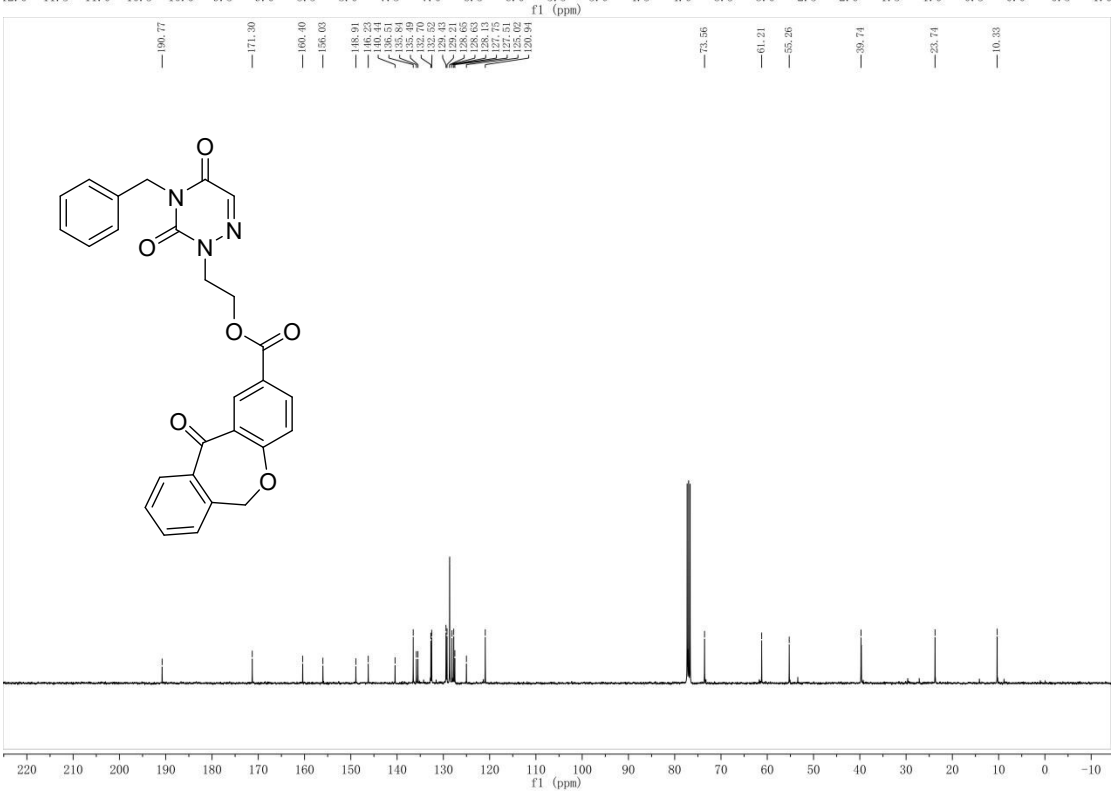
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3y** in $CDCl_3$



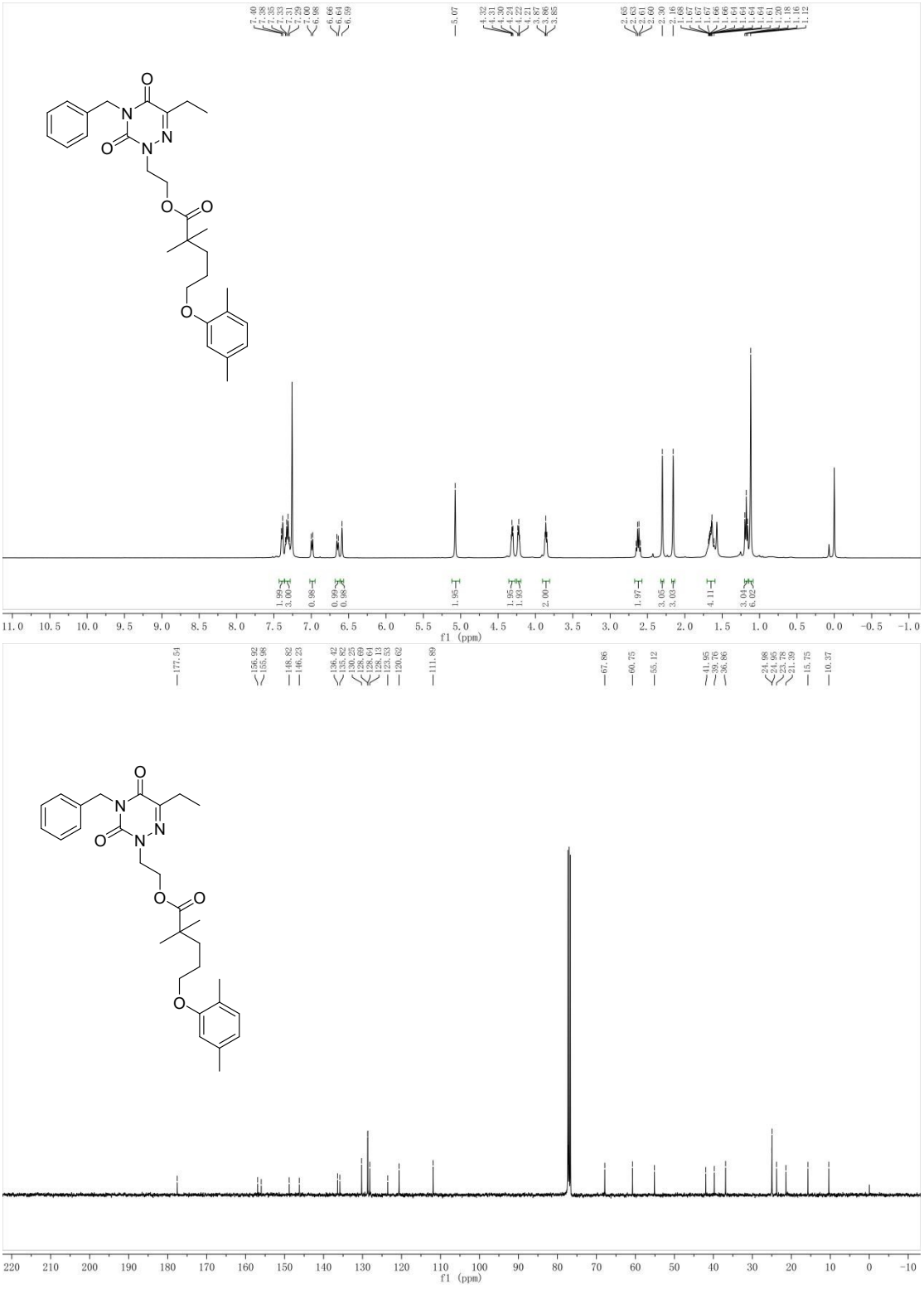


^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3z** in $CDCl_3$

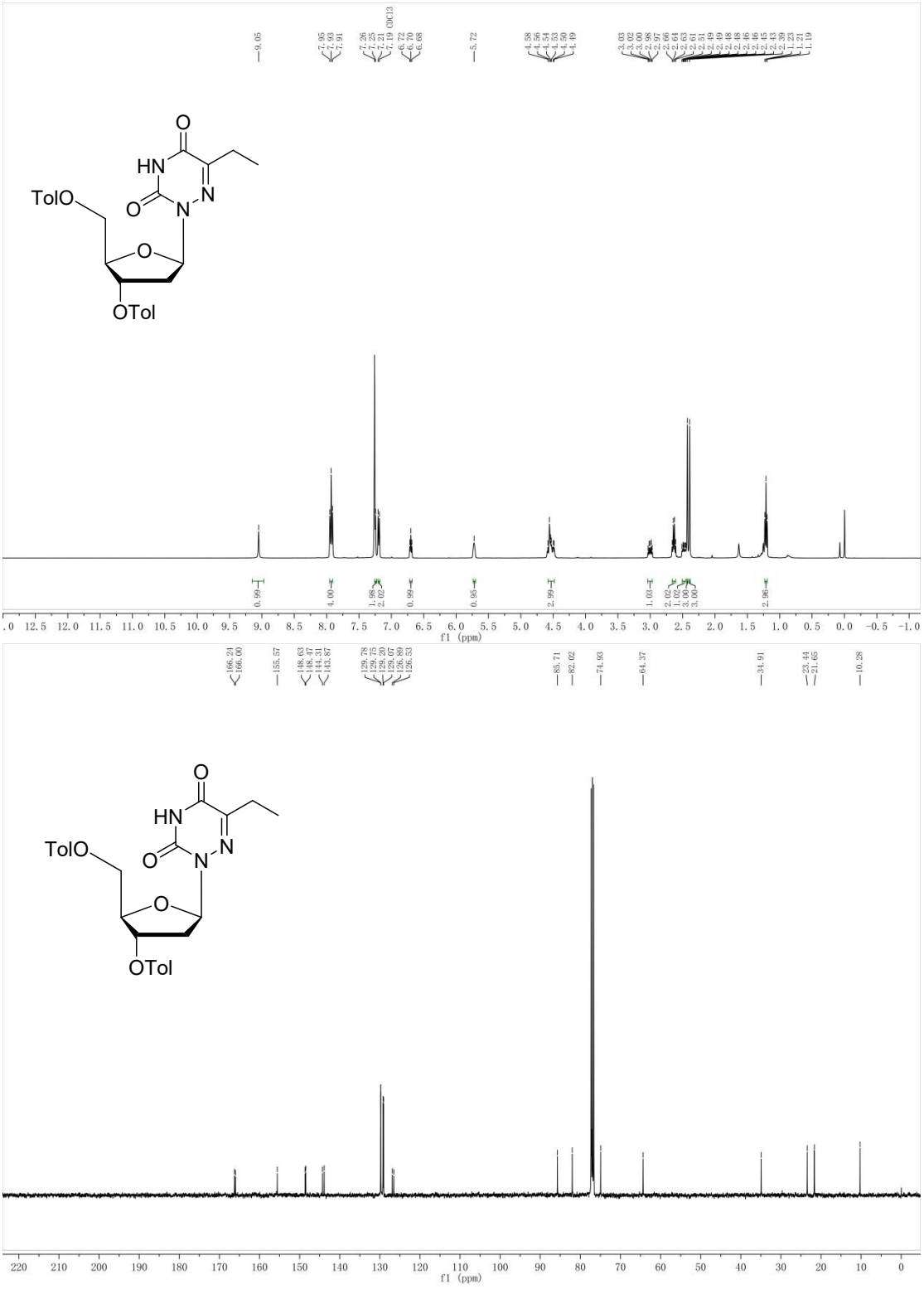




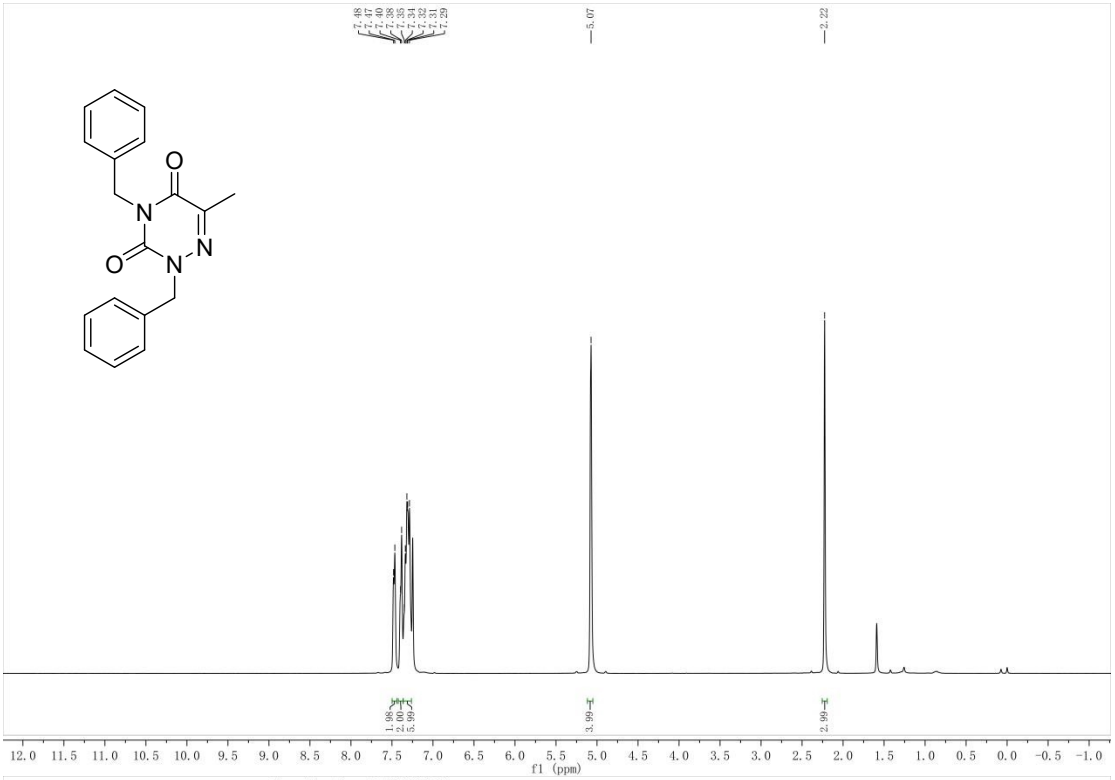
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3aa** in $CDCl_3$

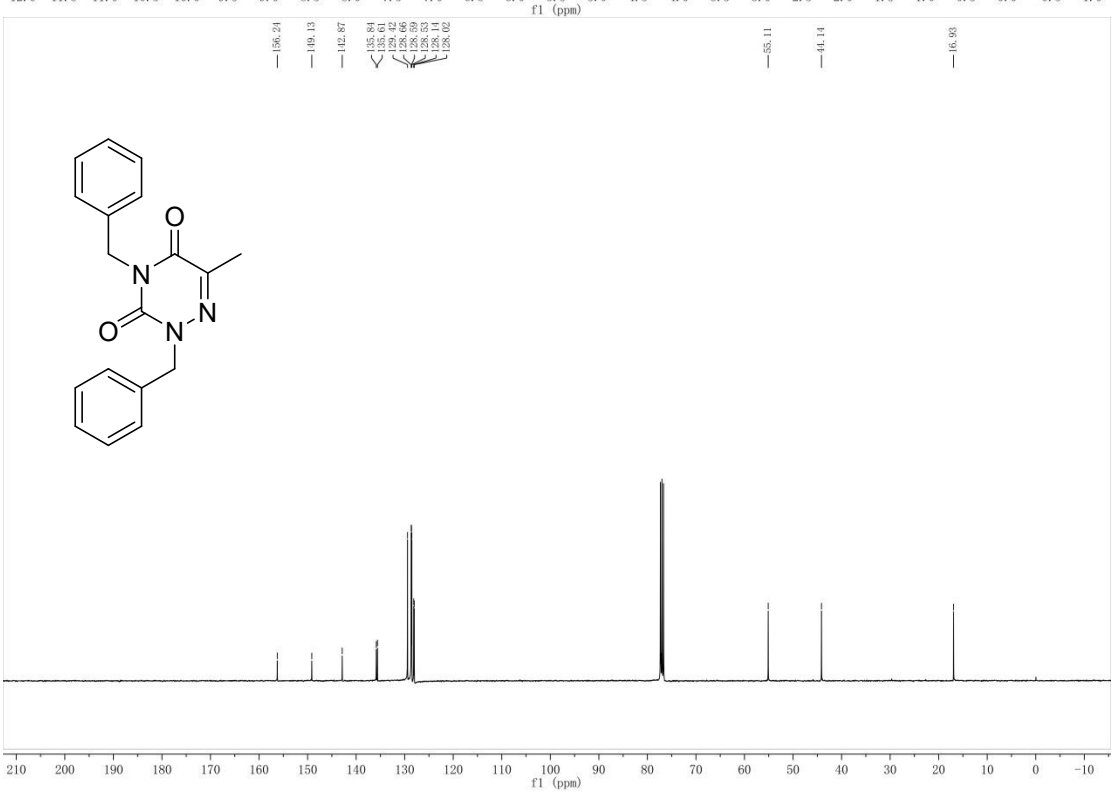


^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3ab** in $CDCl_3$



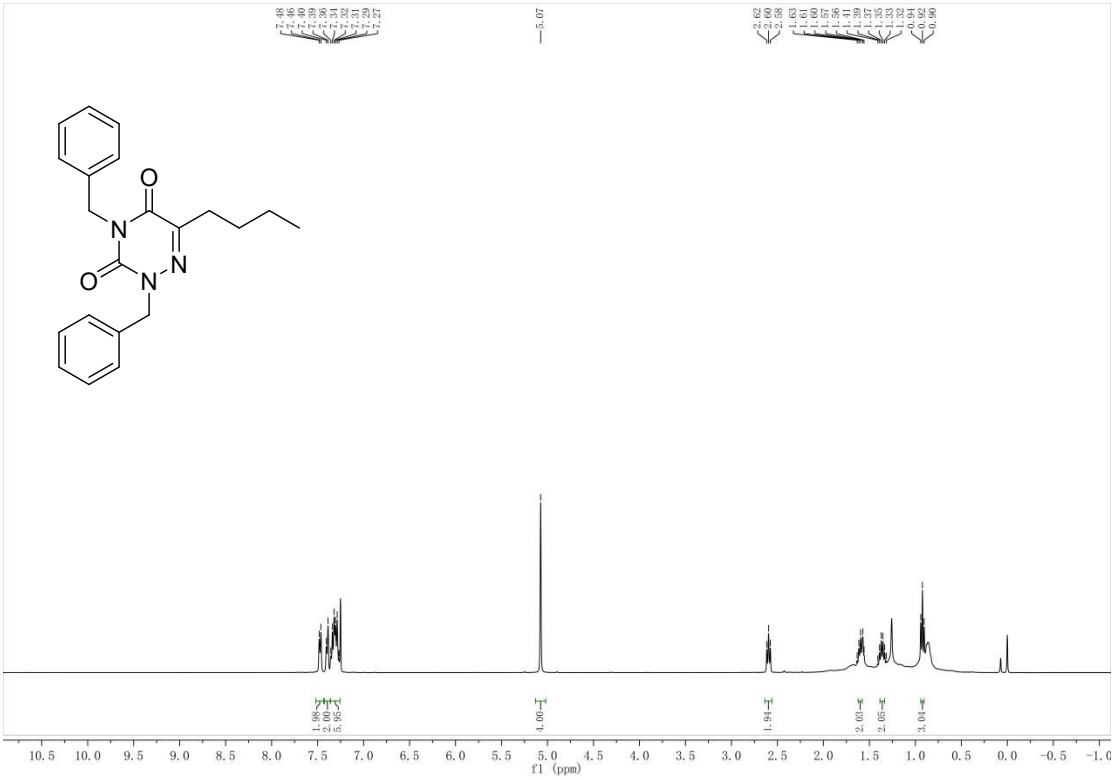
^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3ac** in $CDCl_3$



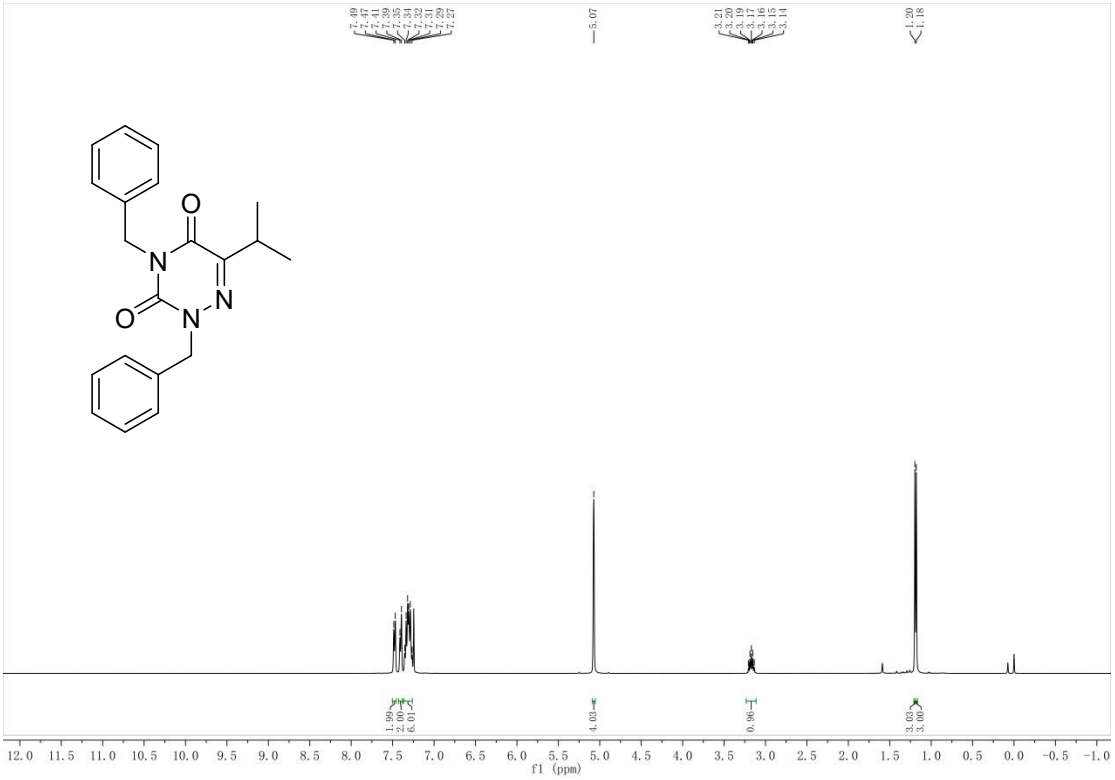


^{1}H NMR Spectrum of **3ad** in $CDCl_3$

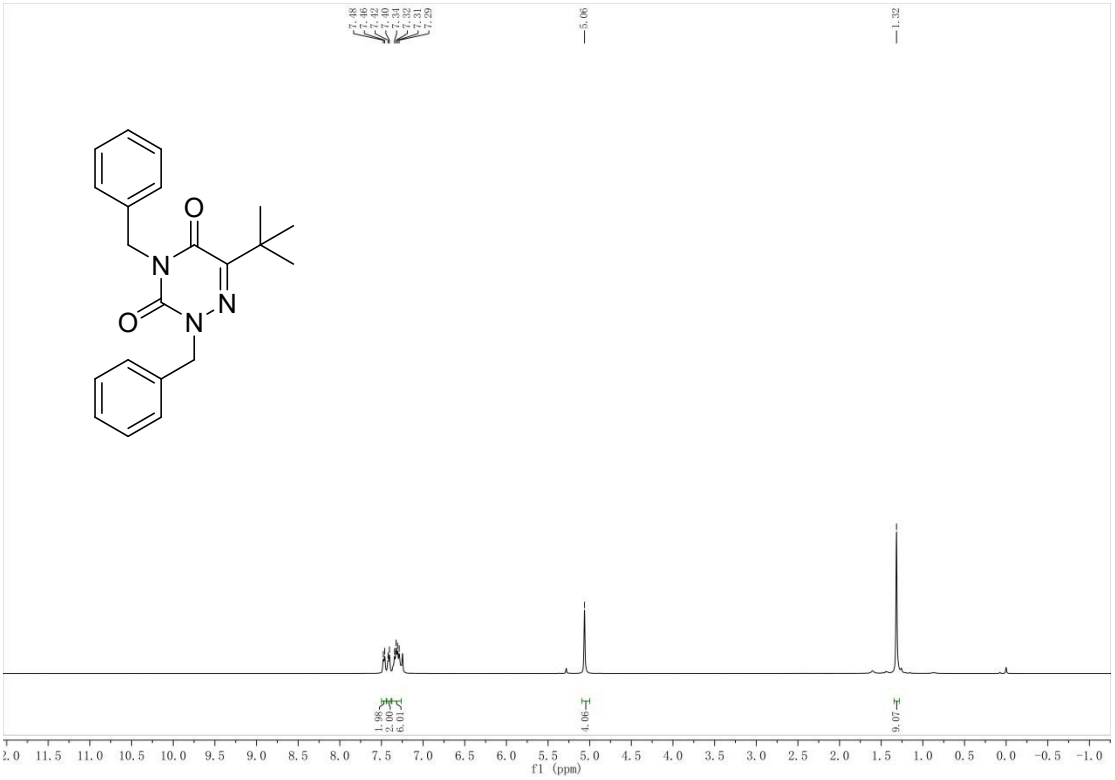
^{1}H NMR Spectrum of **3ae** in $CDCl_3$



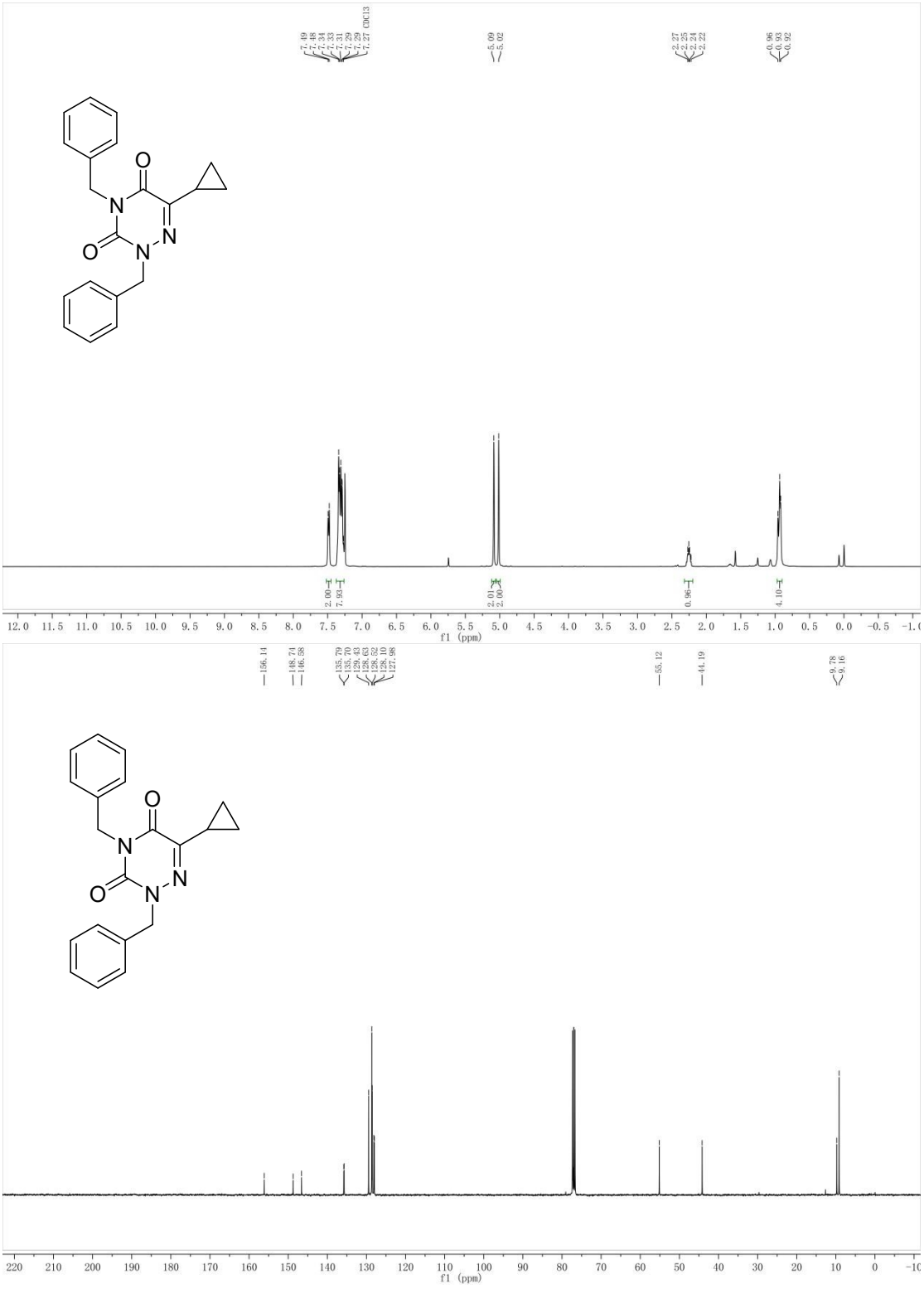
^{1}H NMR Spectrum of **3af** in $CDCl_3$



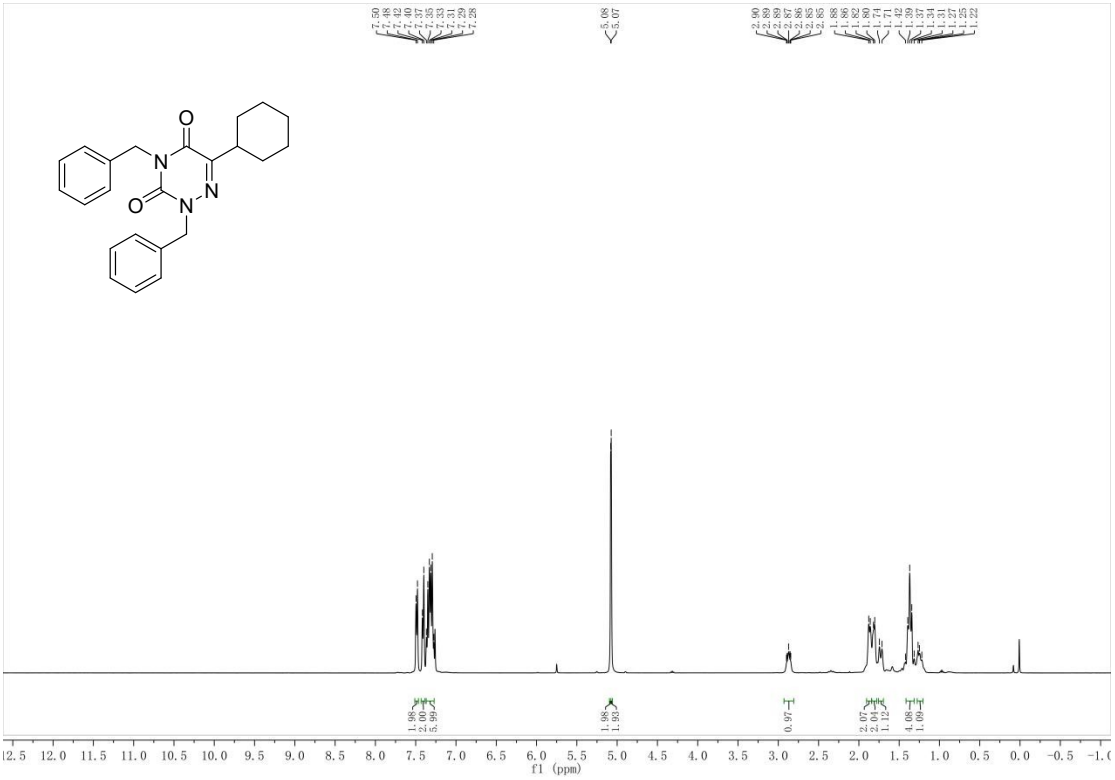
^{1}H NMR Spectrum of **3ag** in $CDCl_3$



^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3ah** in $CDCl_3$



^{1}H NMR Spectrum of **3ai** in $CDCl_3$



^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR Spectrum of **3aj** in $CDCl_3$