

Supporting Information

Catalyst-free tandem reaction for the synthesis of tetrahydro-1,2,3-triazine derivatives

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1. General remarks

NaN₃ was purchased from Energy Chemical Company. Potassium carbonate, nitromethane, toluene, ethanol, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd. 1,2-Dibromoethane, 3-oxo-*N*-phenylbutanamide, 3-oxo-*N*-(*o*-tolyl)butanamide, and *N*-(4-methoxyphenyl)-3-oxobutanamide were purchased from BePharm Co. Ltd. *N*-(4-chlorophenyl)-3-oxobutanamide, *N*-(4-chloro-2-methoxyphenyl)-3-oxobutanamide, and *N*-(2,4-dimethylphenyl)-3-oxobutanamide were purchased from Aladdin Industrial Corporation. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-500 or AV-400. Melting points were determined by microscopic melting pointmeter and were uncorrected. High-resolution mass spectra (HRMS) were obtained on Bruker Compass Data Analysis 4.0. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

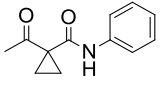
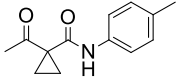
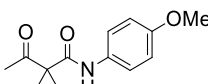
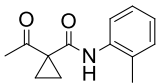
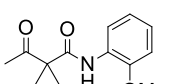
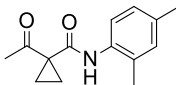
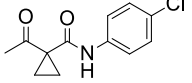
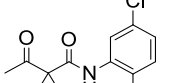
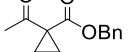
2. Experimental section

General procedure for preparing substrates **1a-i**

The procedure for preparing substrates **1a-i** were according to the reported method.^[1] In a typical procedure, 1,2-dibromoethane (0.95 mL, 11 mmol), *N*-(2-methoxyphenyl)-3-oxobutanamide (2070 mg, 10 mmol), and K₂CO₃ (2950 mg, 23 mmol) were added in DMF (25 mL). The reaction system was stirred for 10 h (monitored by TLC). Then the mixture was slowly poured into ice-water (200 mL). White solid was precipitated, filtrated and dried in vacuum to obtain compound **1a** (1971 mg, 97%). The synthetic

procedure of **1b–i** are similar to the above-mentioned method. The yields of **1a–h**^[1] and **1i** are listed in **Table S1**.

Table S1. The yields of **1a–i**

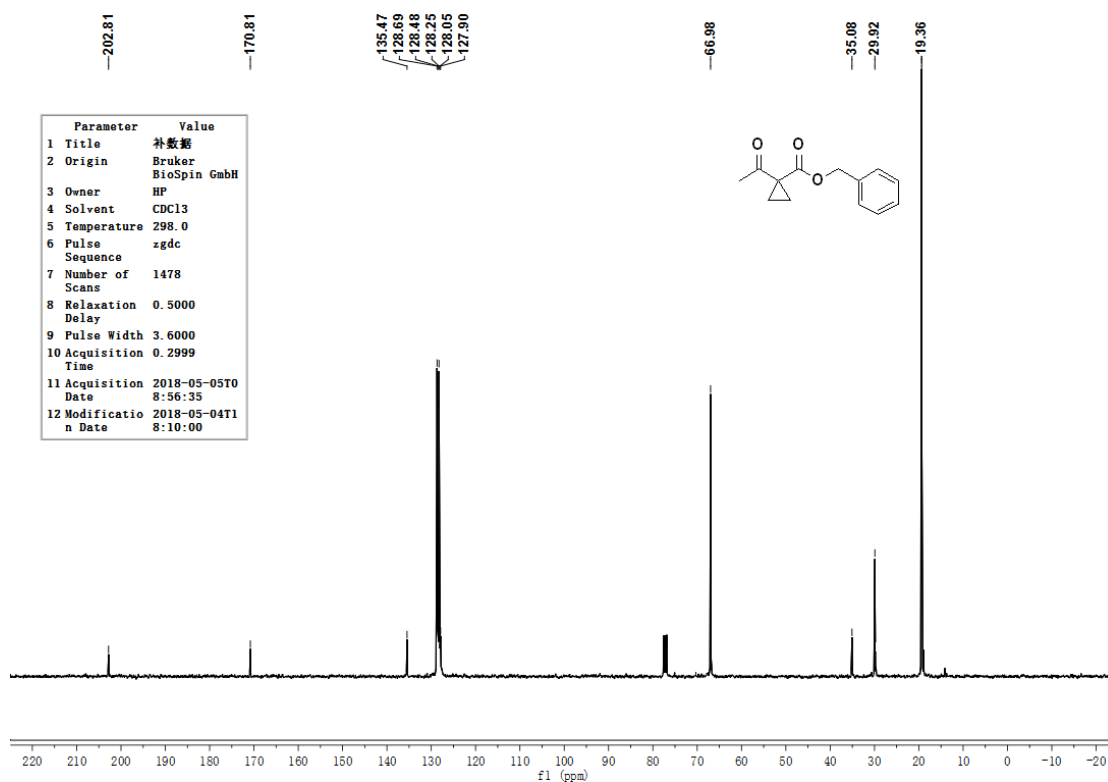
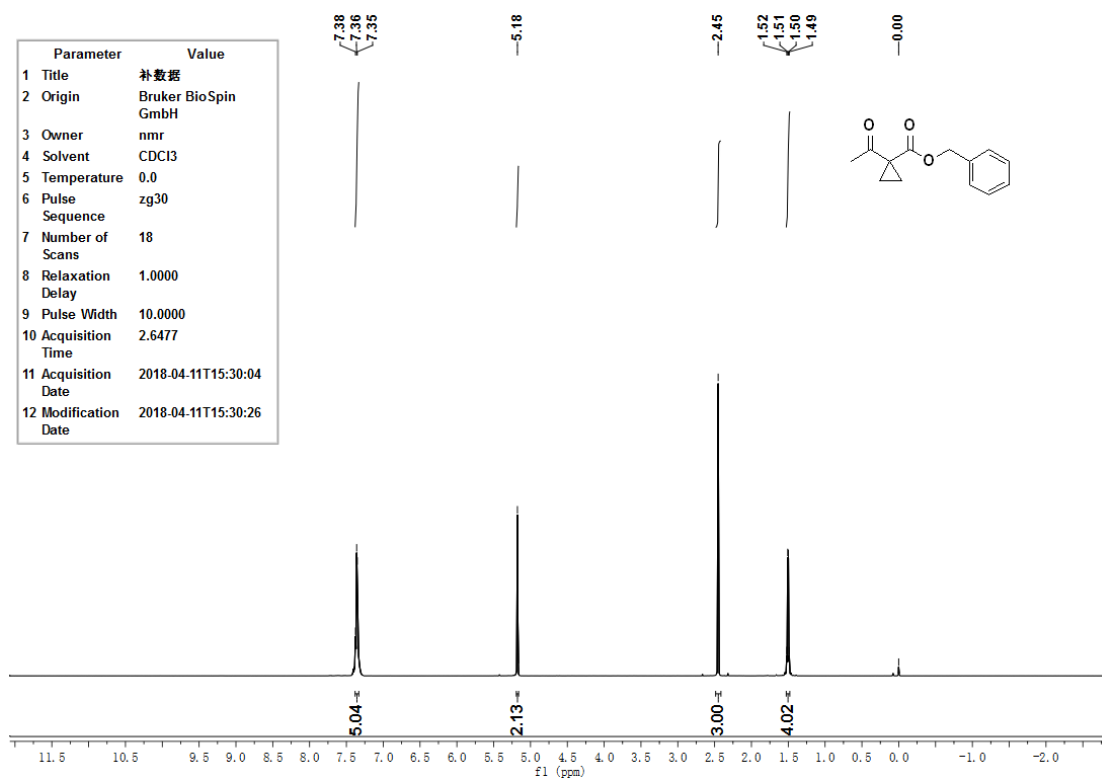
Entry	Substrate		Yield (%)
1		1a	97
2		1b	90
3		1c	93
4		1d	86
5		1e	93
6		1f	92
7		1g	88
8		1h	87
9		1i	91

3. Spectroscopic data of compounds

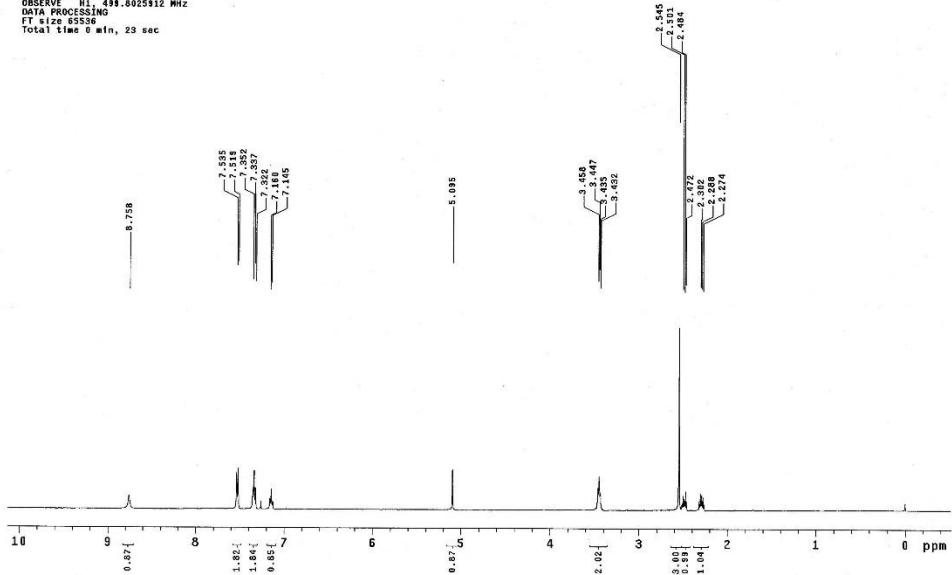
Benzyl 1-acetylcyclopropane-1-carboxylate (1i): White solid. mp: 118–120 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.38–7.35 (m, 5H), 5.18 (s, 2H), 2.45 (s, 3H), 1.52–1.49 ppm (m, 4H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 202.8, 170.8, 135.5, 128.7, 128.5, 128.3, 128.1, 127.9, 67.0, 35.1, 29.9, 19.4 ppm; HRMS (ESI): *m/z*: calcd for C₁₃H₁₄NaO₃:241.0841 [M +Na]⁺; found: 241.0844.

2-Acetyl-4-azido-*N*-(2,4-dimethylphenyl)butanamide (I): Colorless liquid. ^1H NMR (500 MHz, CDCl_3 , 20 °C, TMS): δ = 7.97 (s, 1H), 7.61–7.57 (m, 1H), 7.04 (d, J = 8.00 Hz, 2H), 3.65–3.47 (m, 1H), 3.46–3.89 (m, 2H), 2.37 (s, 3H), 2.28 (s, 3H), 2.22–2.18 ppm (m, 5H); ^{13}C NMR (125 MHz, CDCl_3 , 20 °C): δ = 206.0, 165.7, 135.2, 132.1, 130.9, 129.4, 126.9, 122.9, 58.3, 49.0, 29.2, 22.2, 20.5, 17.3 ppm; HRMS (ESI): m/z : calcd for $\text{C}_{14}\text{H}_{18}\text{N}_4\text{NaO}_2$: 297.1327 $[\text{M} + \text{Na}]^+$; found: 297.1332.

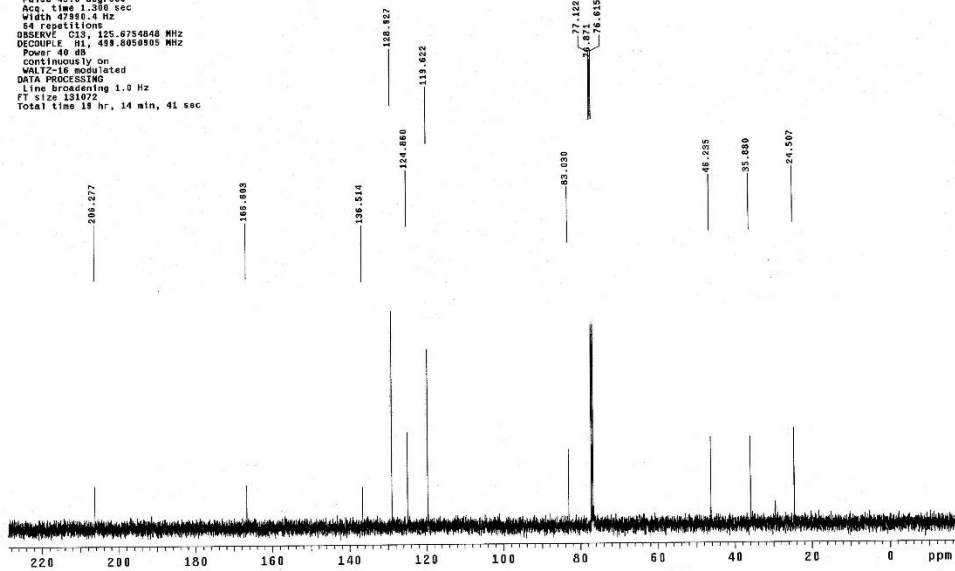
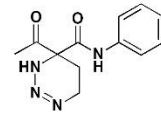
4. ¹H NMR and ¹³C NMR spectra



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 DATA PROCESSING
 FT size 65536
 Total time 0 min, 23 sec

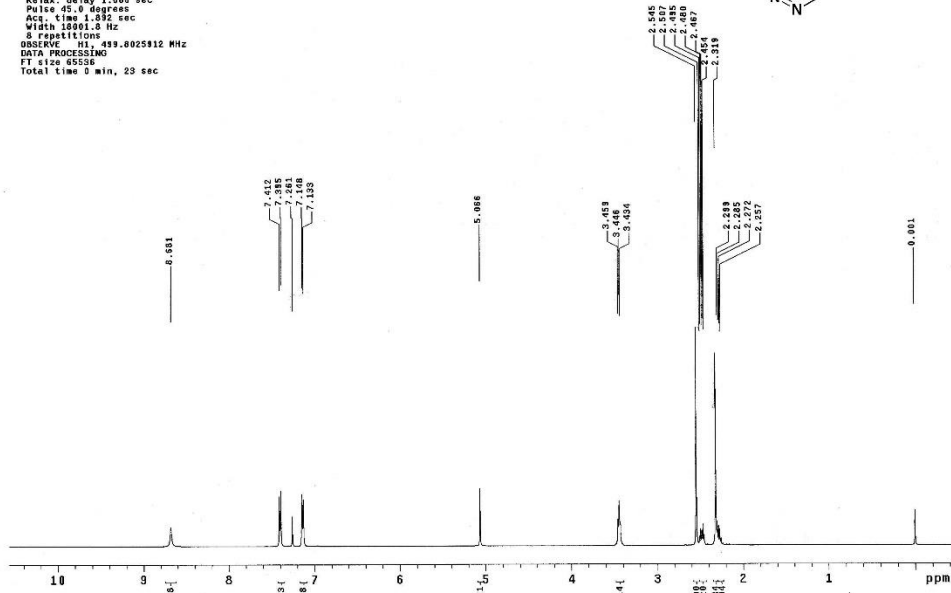
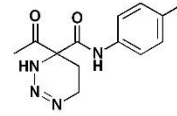


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 FT size 131072
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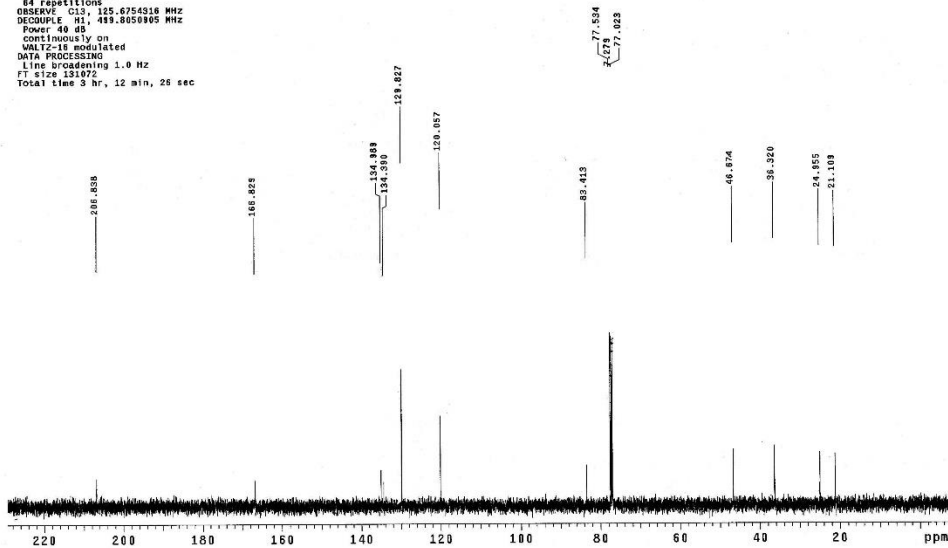
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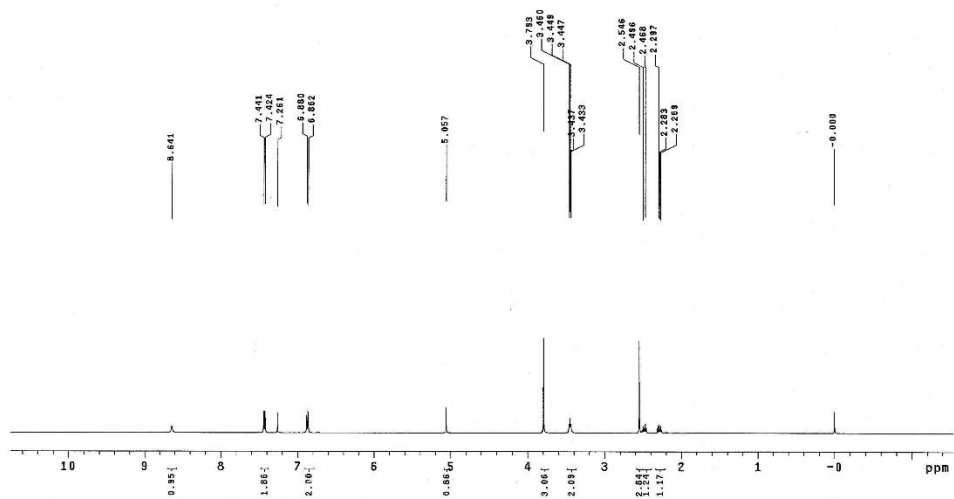
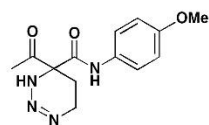
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 64 repetitions
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 DECOUPLE H1, 499.8050105 MHz
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 cont. inously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131872
 Total time 3 hr, 12 min, 26 sec



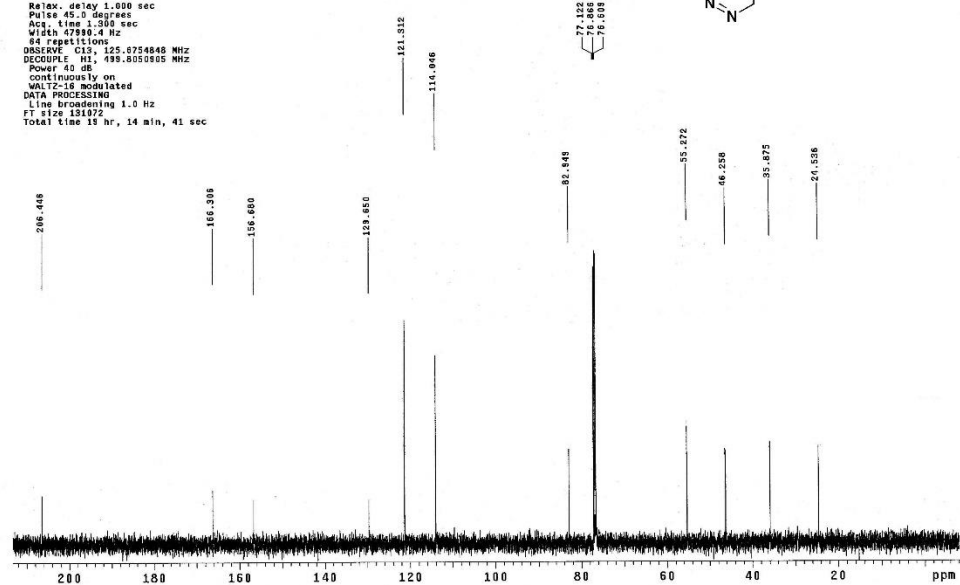
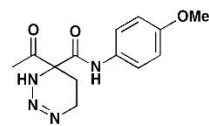
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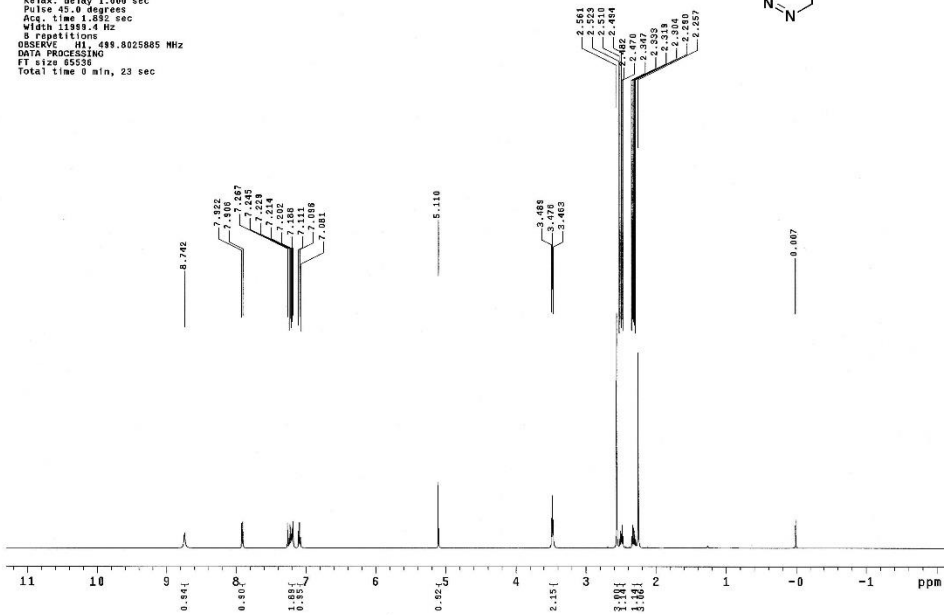
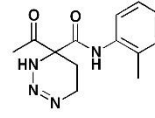
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 DECOUPLE: H1, 499.8050905 MHz
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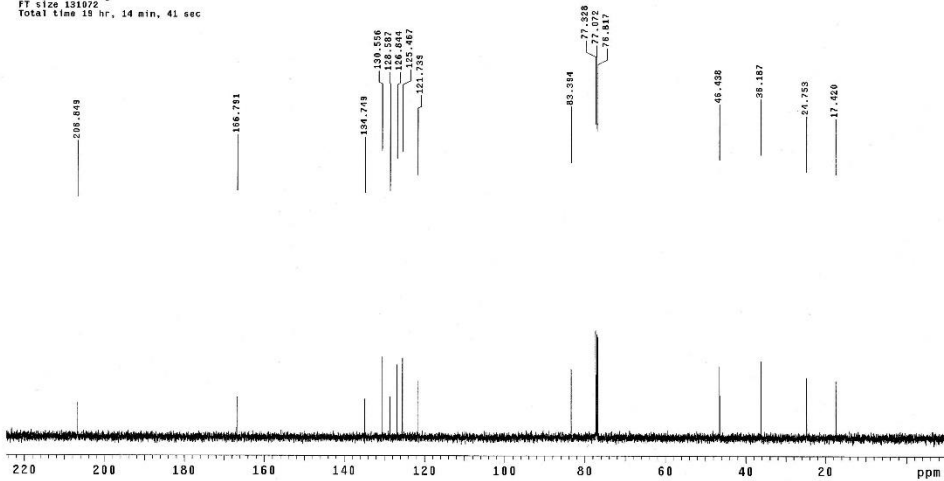
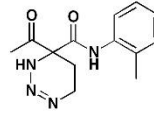
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 Acq. time 1.832 sec
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 DATA PROCESSING
 FT size 45536
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

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 Solvent: CDCl3
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 User: ll-14-87
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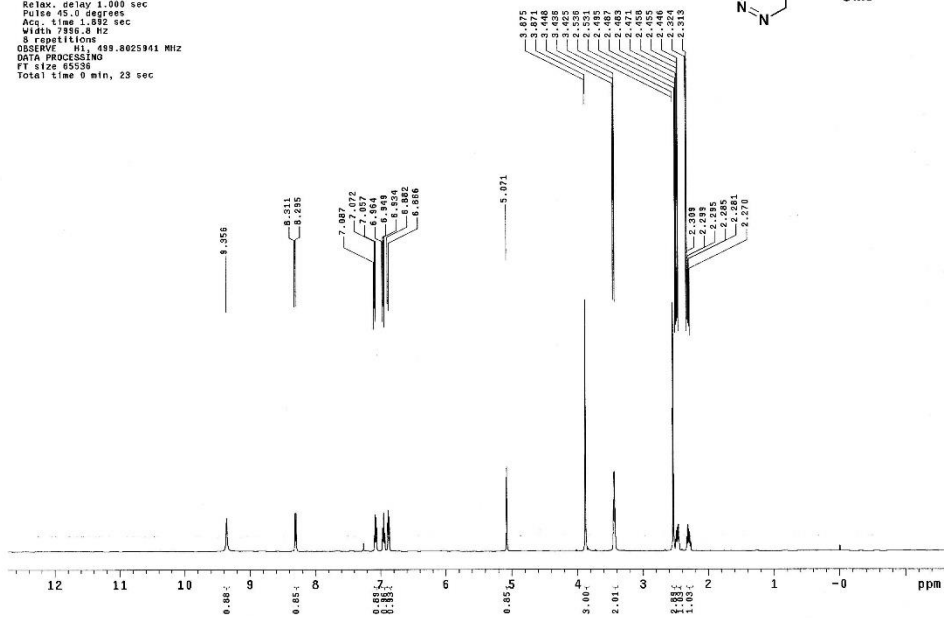
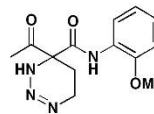


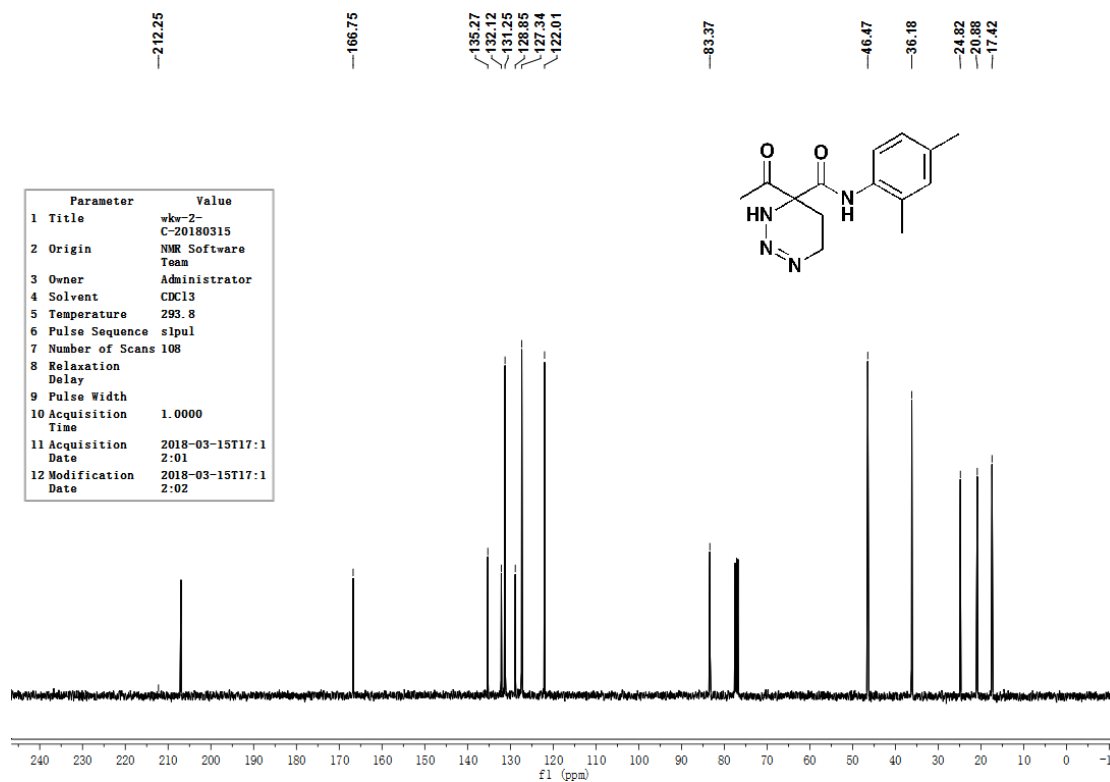
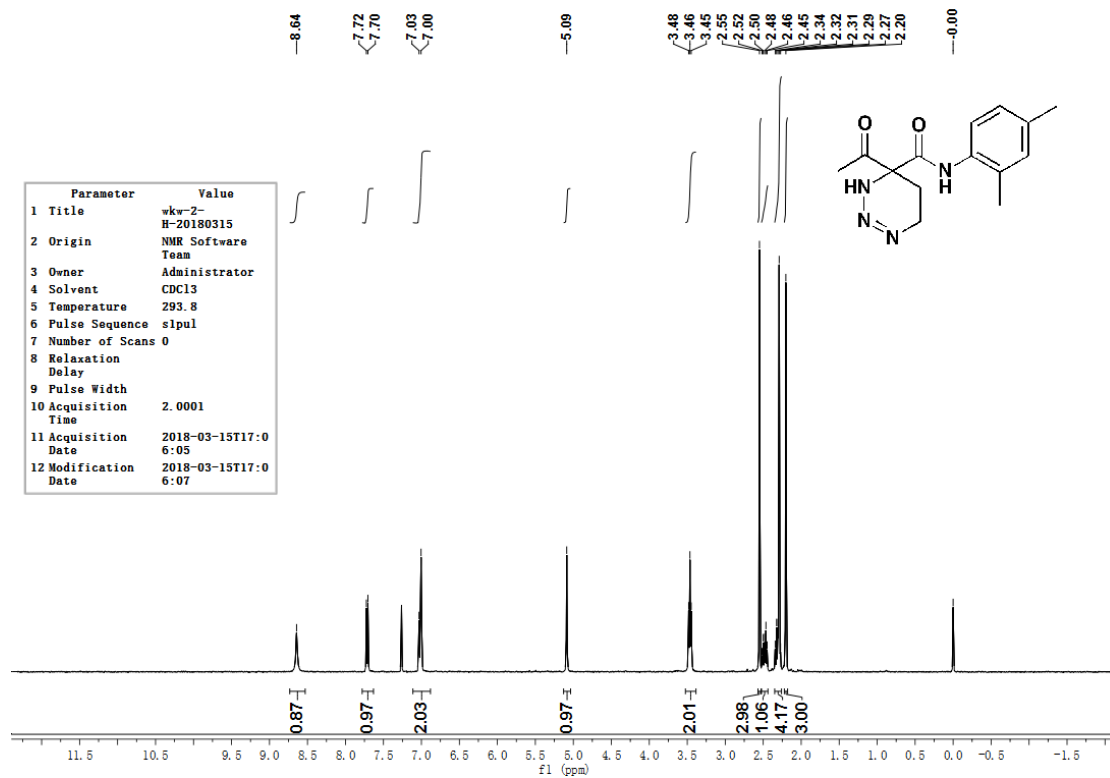
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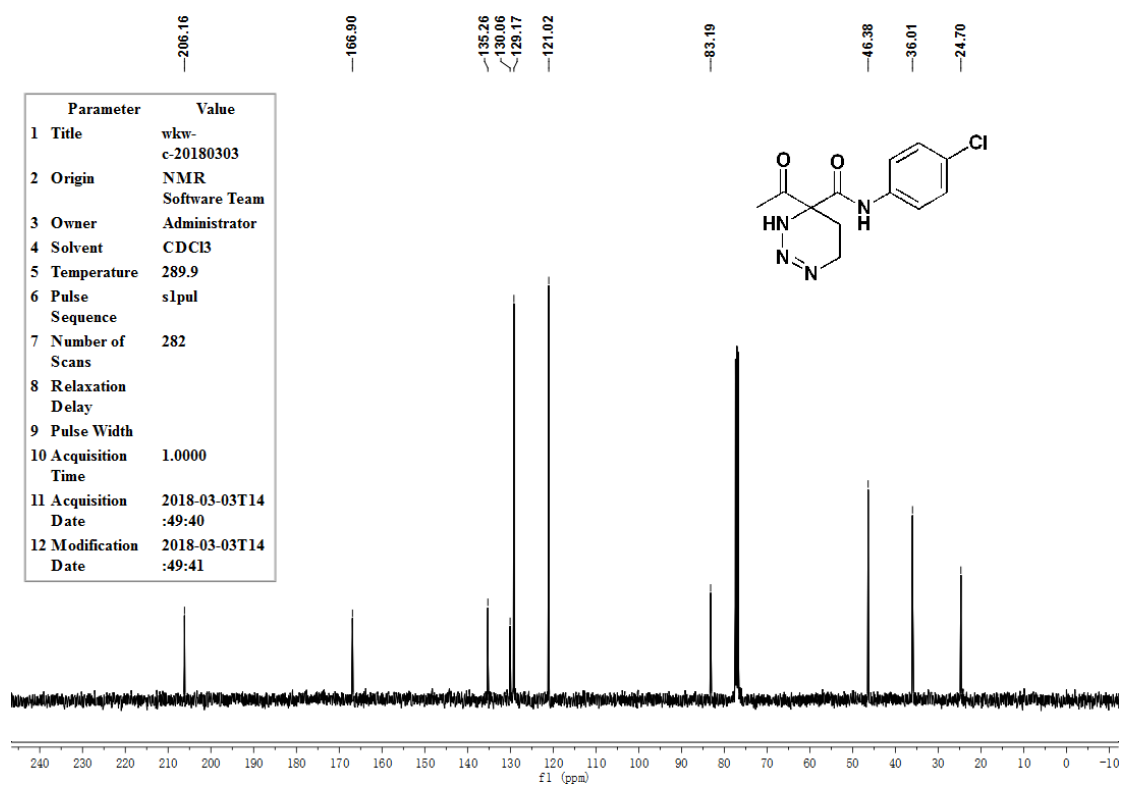
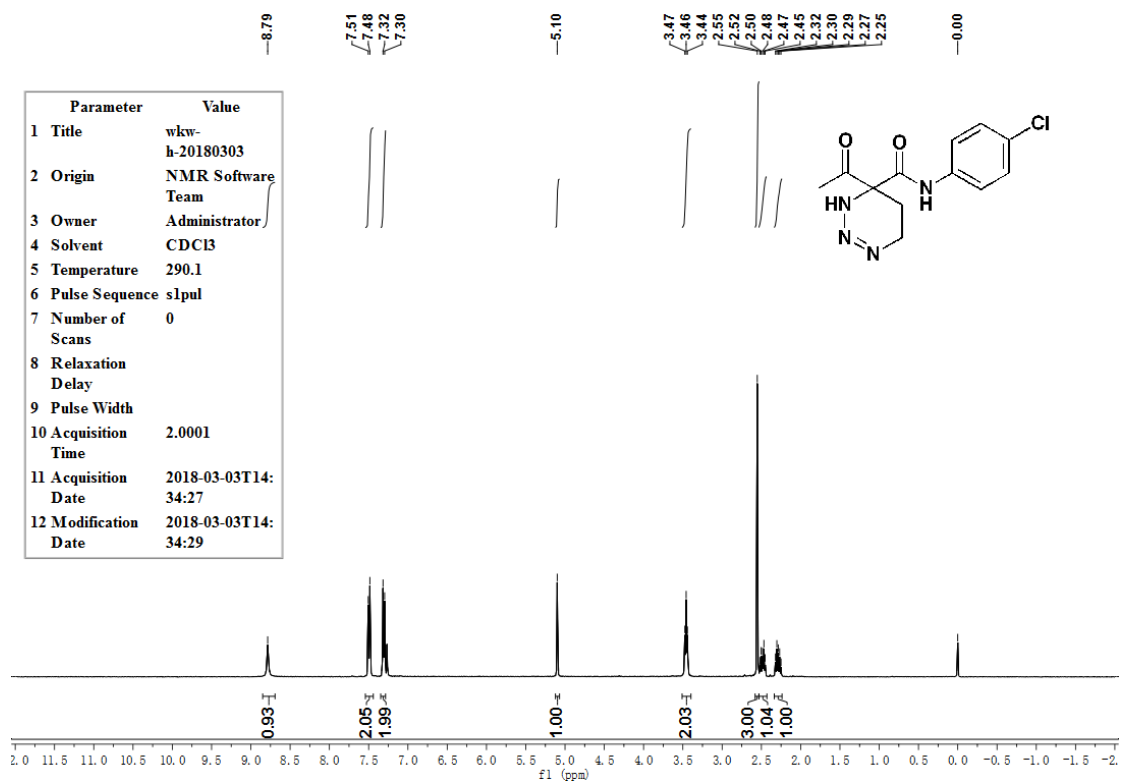
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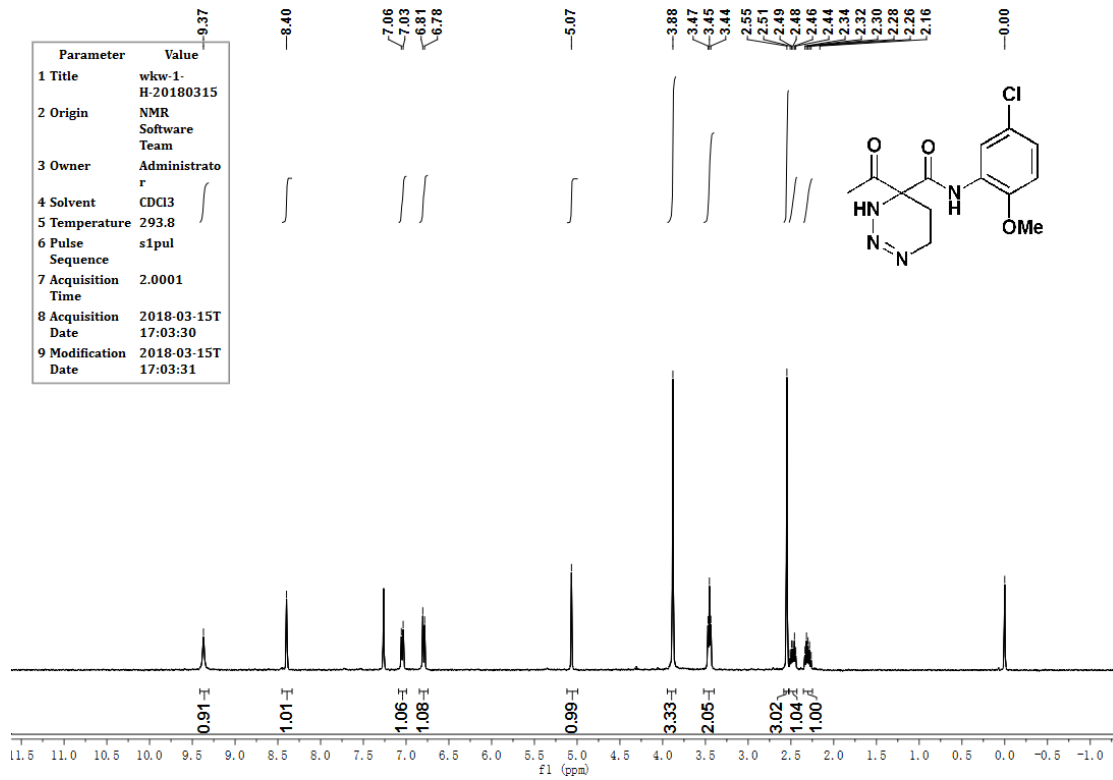
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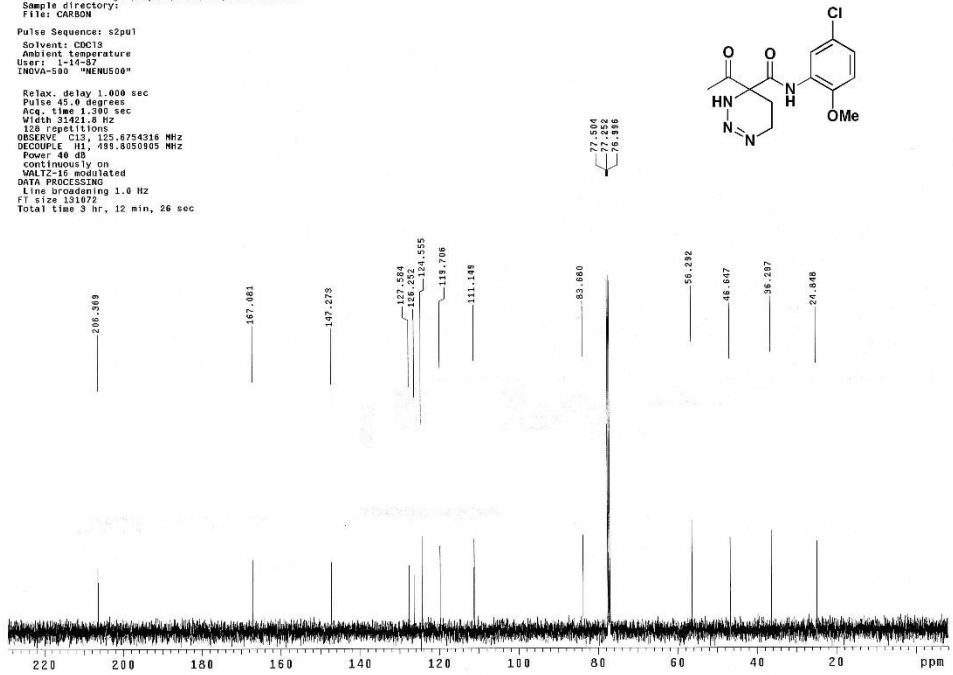


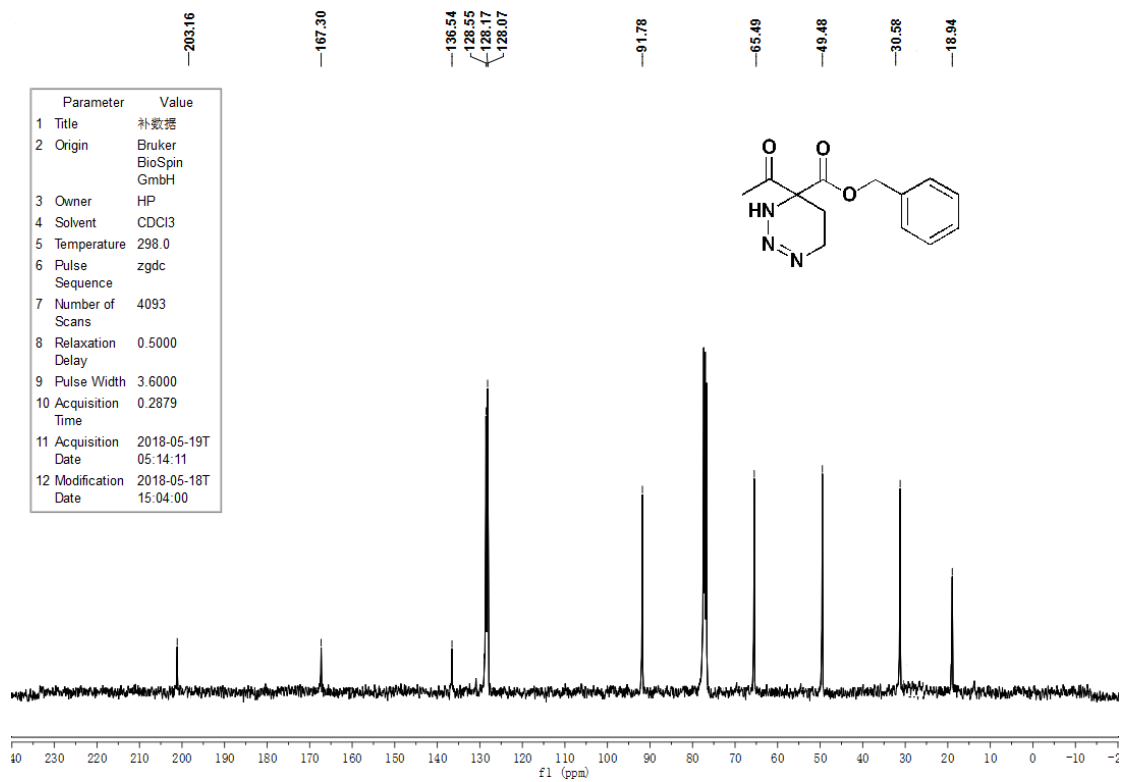
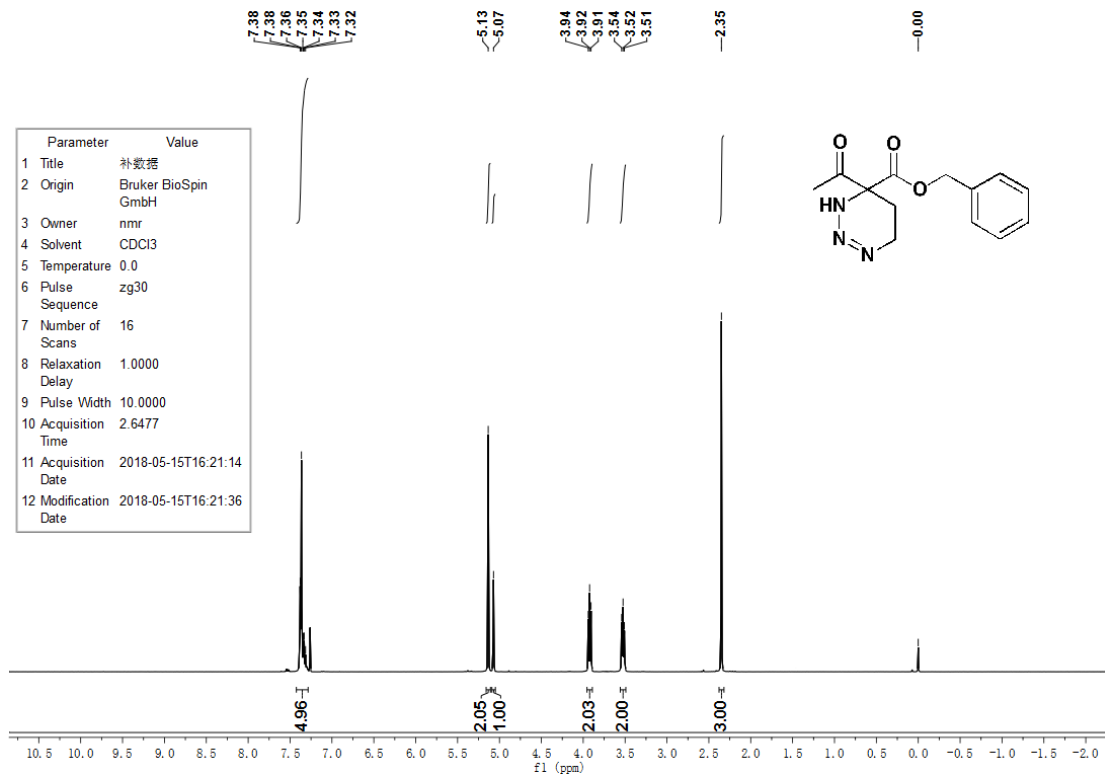




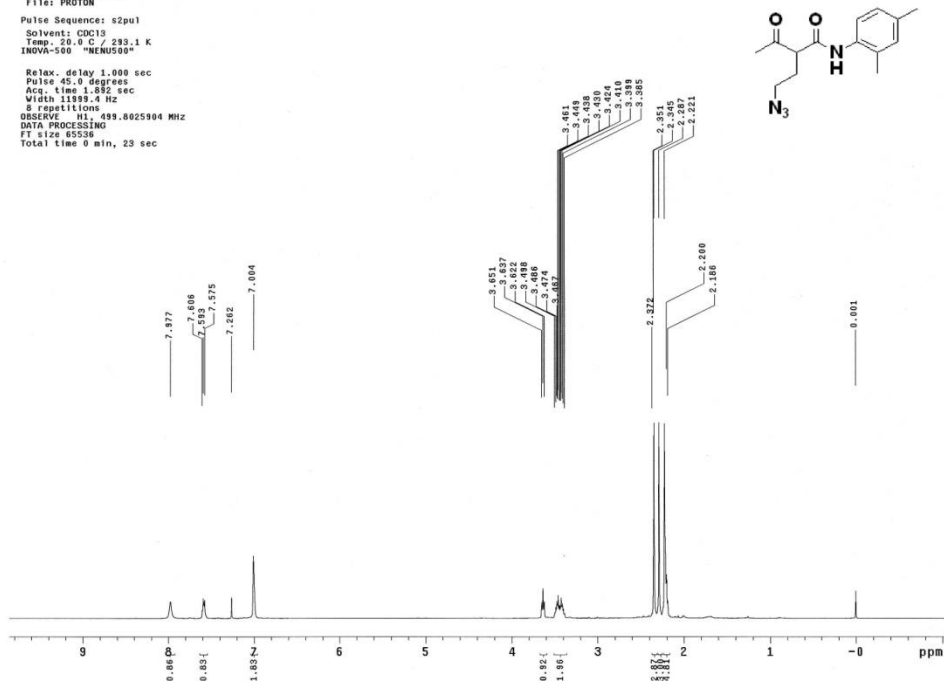


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 Width 31421.8 Hz
 150 Scans
 OBSERVE C13, 125.6754316 MHz
 DECOUPLE H1, 499.9050905 MHz
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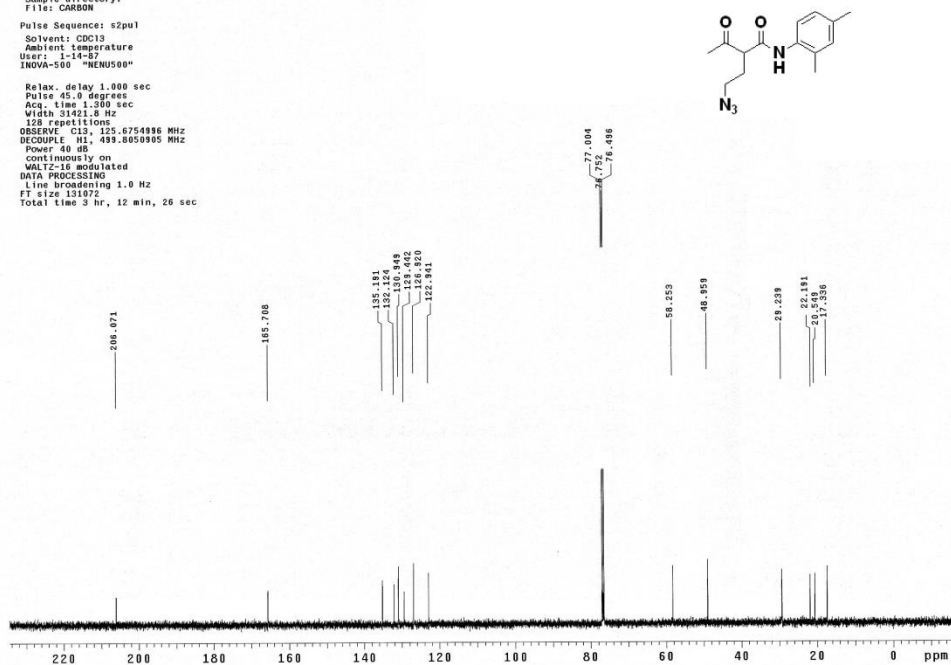




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 Total time 0 min, 23 sec



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 Power 40 dB
 continuously on
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 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total time 3 hr, 12 min, 26 sec



5. References

[1] Zhang, R.; Liang, Y.; Zhou, G.; Wang, K.; Dong, D. *J. Org. Chem.* **2008**, *73*, 8089–8092.