

## Supporting Information for

### **Synthesis of Functionalized Tetrahydropyridazines via Catalyst-free Self [4 + 2] Cycloaddition of in Situ Generated 1,2-Diaza-1,3-Dienes**

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## General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions were performed in anhydrous solvents. Reactions were monitored by thin layer chromatography (TLC), and column chromatography purifications were performed using 200-300 mesh silica gel. Melting points were obtained on a melting point apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in DMSO- $d_6$  or  $\text{CDCl}_3$  using a 300 MHz spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). High-resolution mass spectra were recorded in ESI mode on a QTOF MS spectrometer. The  $\alpha$ -chloro-N-acylhydrazones were prepared according to literature procedures.<sup>1</sup>

General procedure for synthesis of structurally diverse functionalized tetrahydropyridazines.

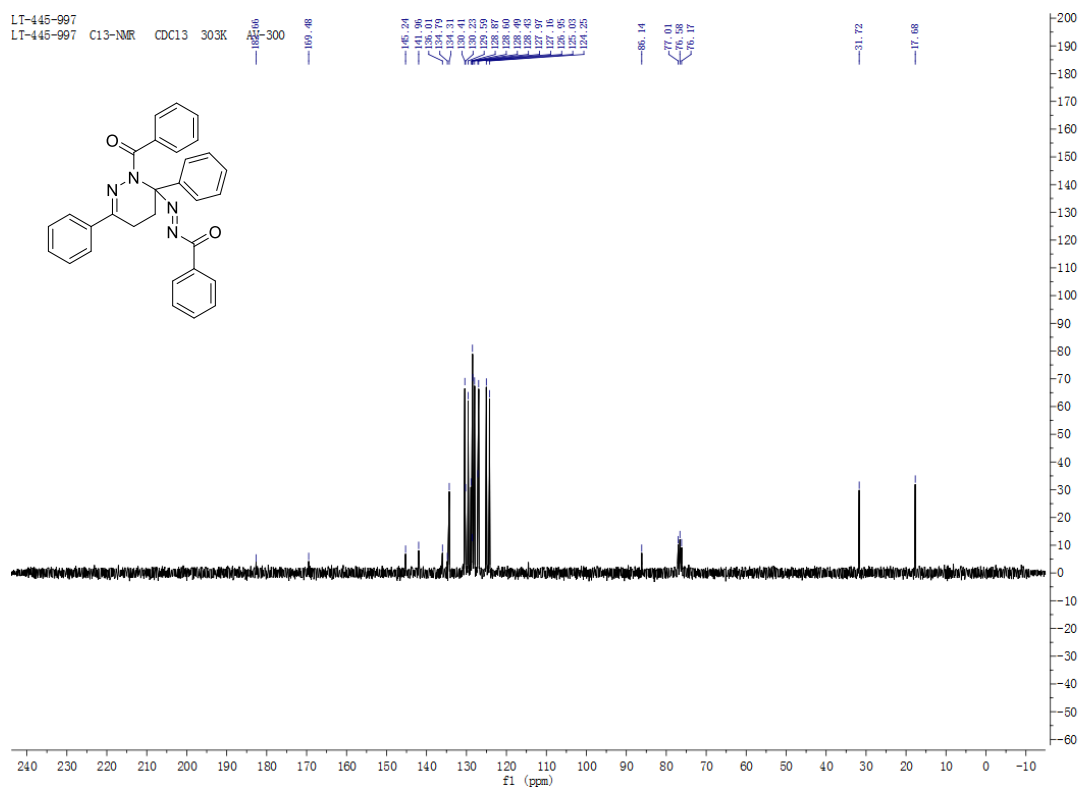
To the solution of  $\alpha$ -chloro-N-acylhydrazones (0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL) was added  $\text{K}_2\text{CO}_3$  (69.1 mg, 0.5 mmol). The resulting mixture was stirred at room temperature for the required period of time. After completion of the reaction as monitored by TLC, the reaction mixture was diluted with 15 mL  $\text{CH}_2\text{Cl}_2$ , which was washed with water and brine successively, dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. Purification by flash chromatography (ethyl acetate / PE, 1 : 20–1 : 5) yielded the desired products.

1. J.-R. Chen, W.-R. Dong, M. Candy, F.-F. Pan, M. Jörres and C. Bolm, *J. Am. Chem. Soc.*, 2012, **134**, 6924.

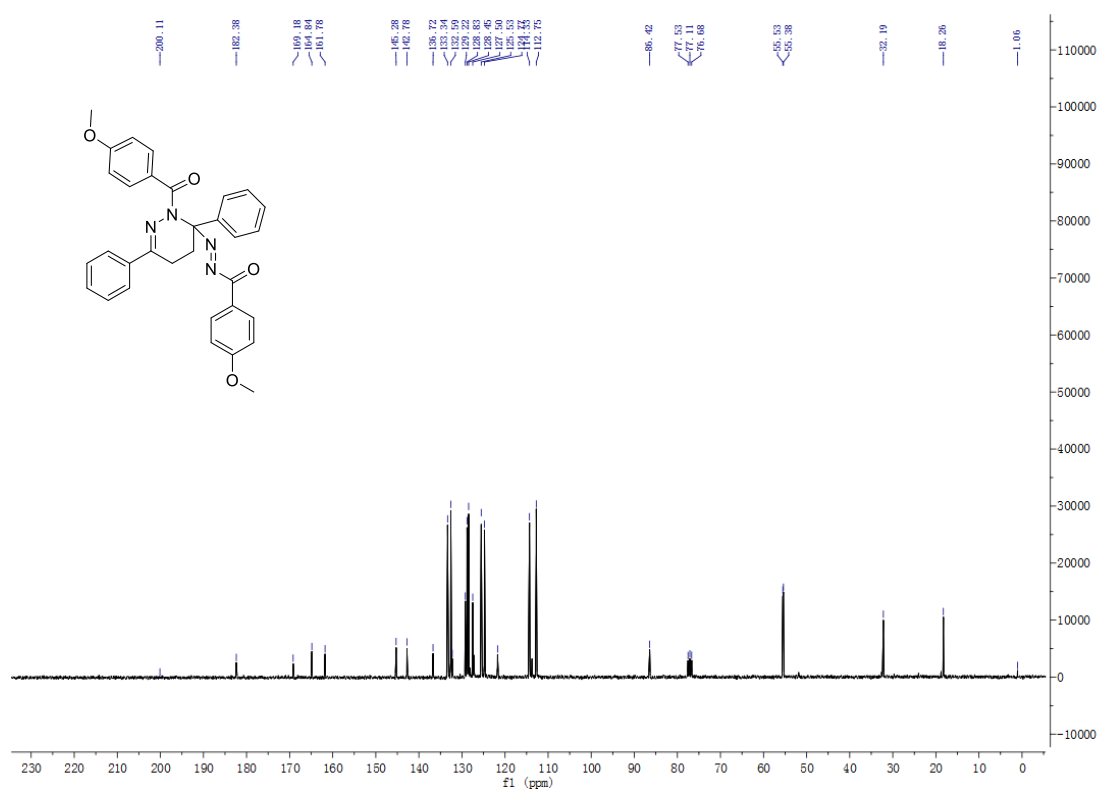
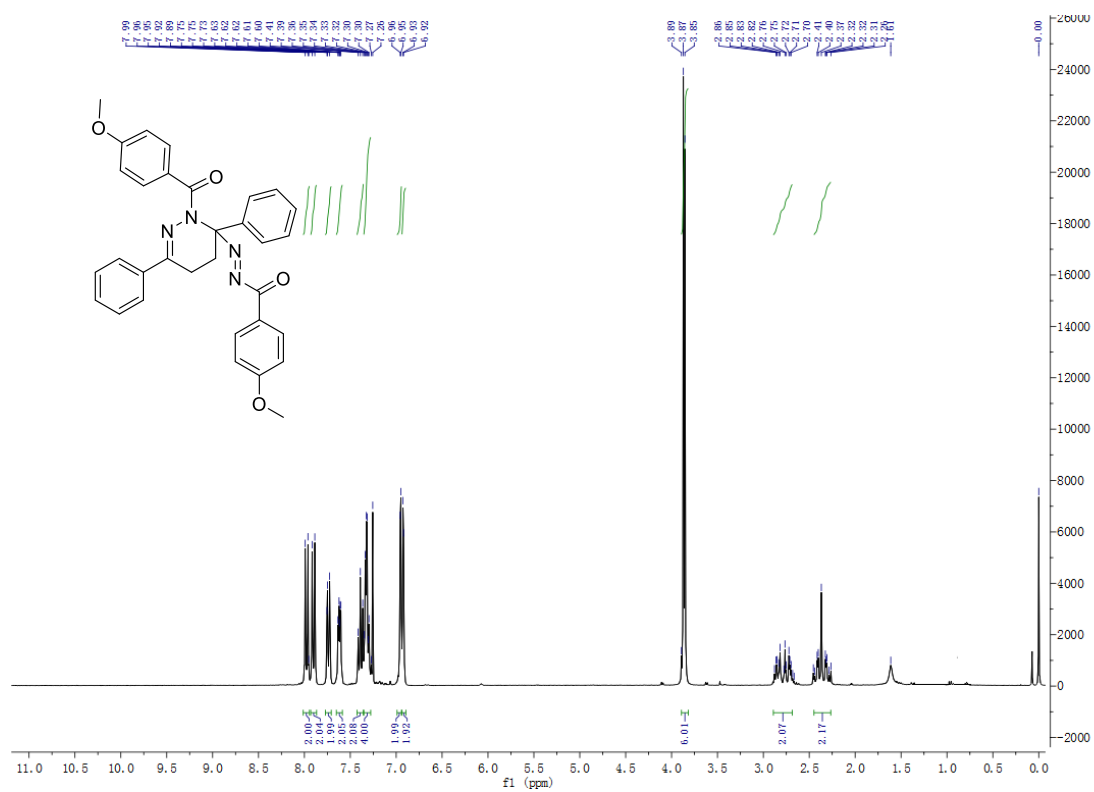
Chemical structure of compound 10 is shown above the spectrum. The structure is a complex molecule featuring a central benzene ring substituted with a phenyl group, a benzoyl group, and a 1-phenyl-2-phenyl-1H-imidazole-4-ylmethyl group.

The  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) shows the following peaks and integrations:

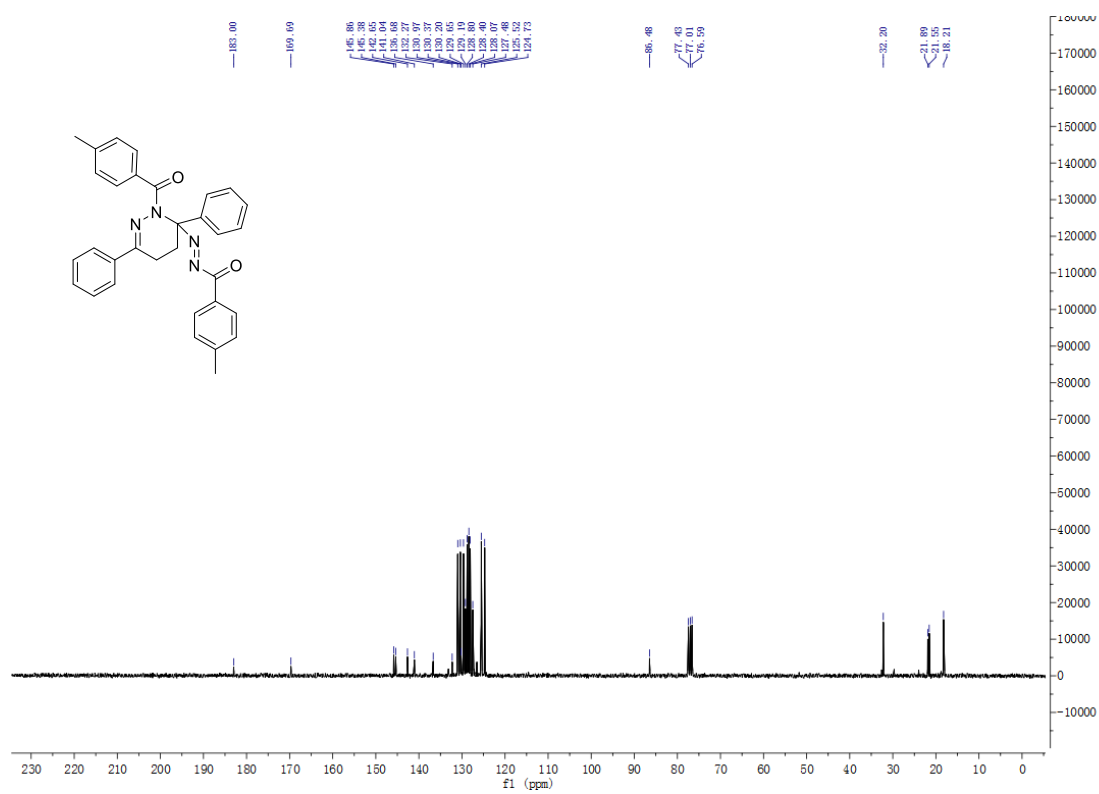
- Aromatic region (7.2-7.9 ppm): Multiple peaks with integrations of 1.00, 1.00, 1.99, 2.10, and 2.03.
- Aliphatic region (2.3-3.1 ppm): Two multiplets with integrations of 1.03 and 1.18.
- Solvent peak (7.26 ppm): A small peak corresponding to the  $\text{CDCl}_3$  solvent.



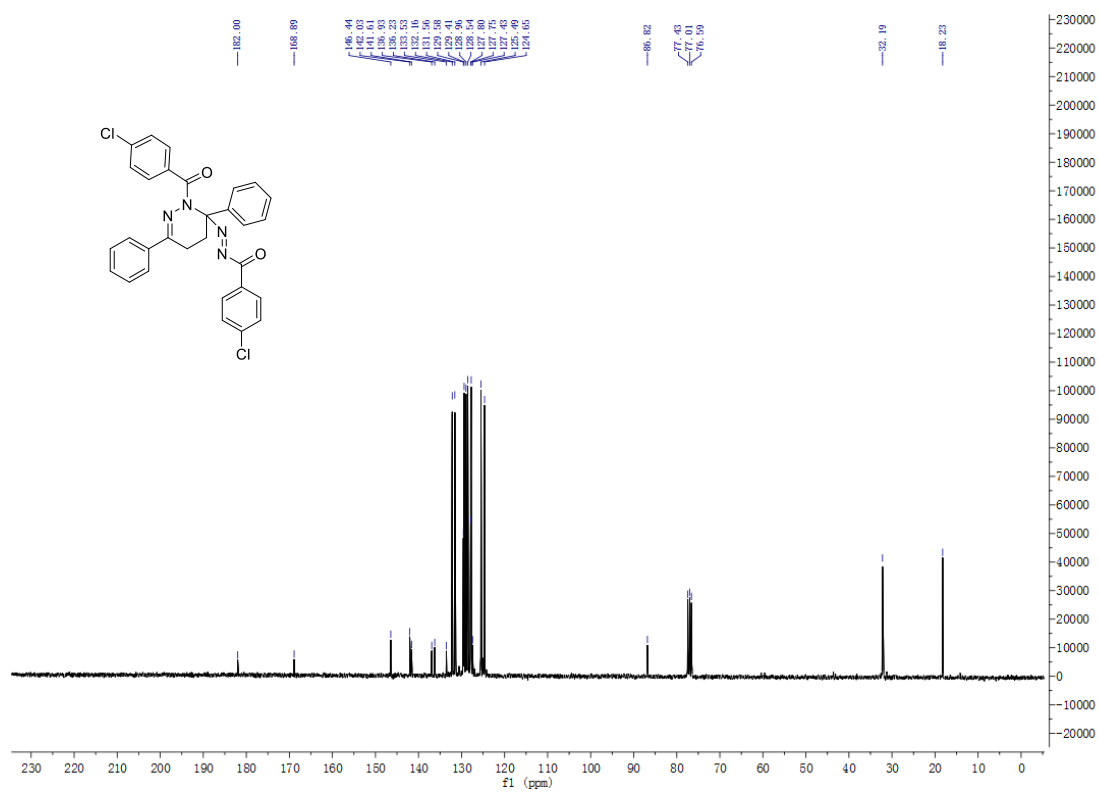
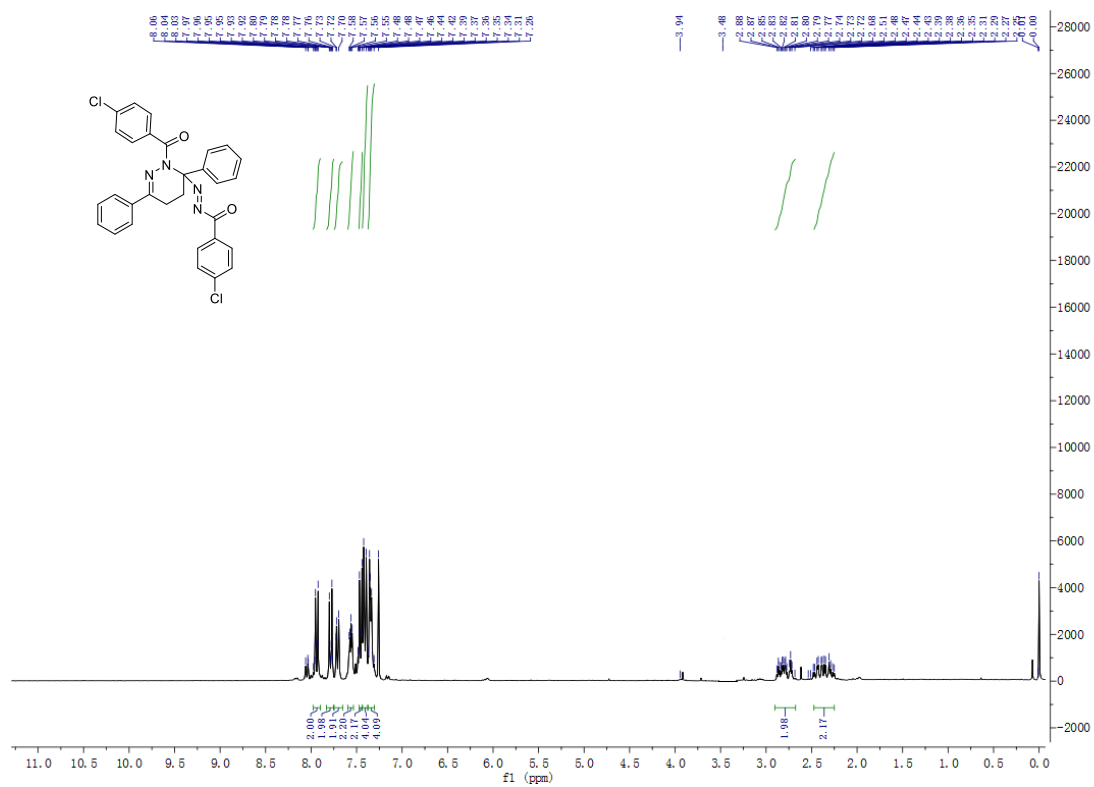
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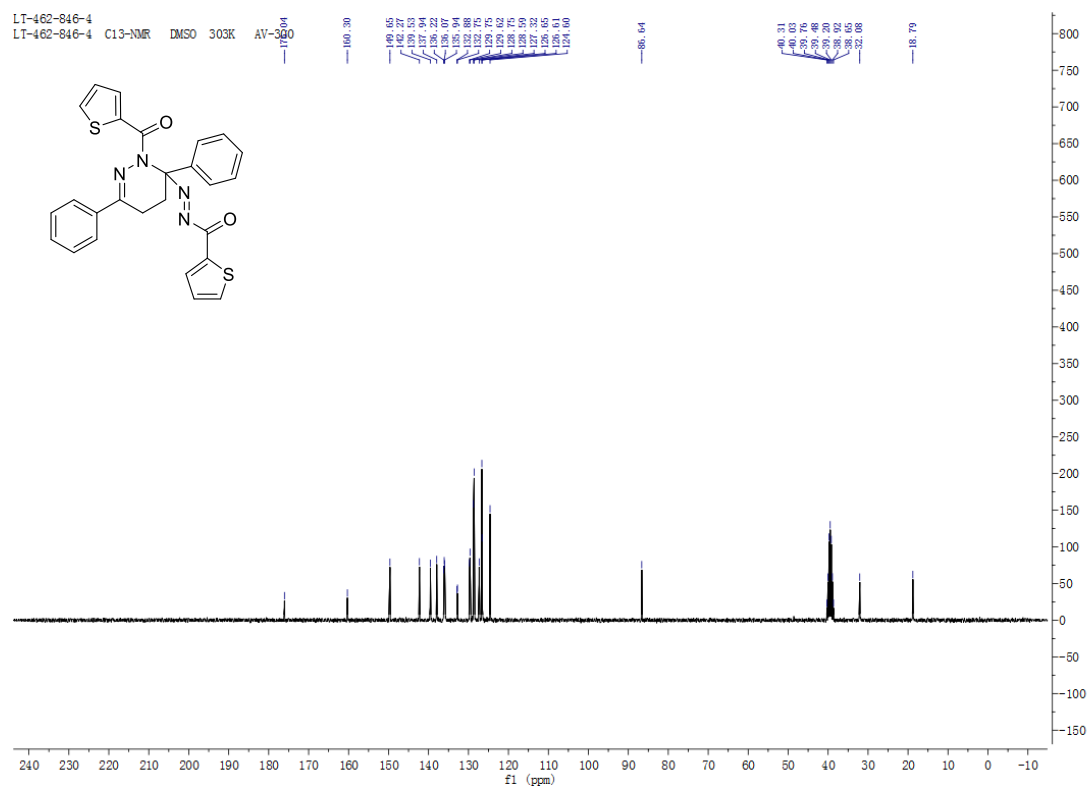
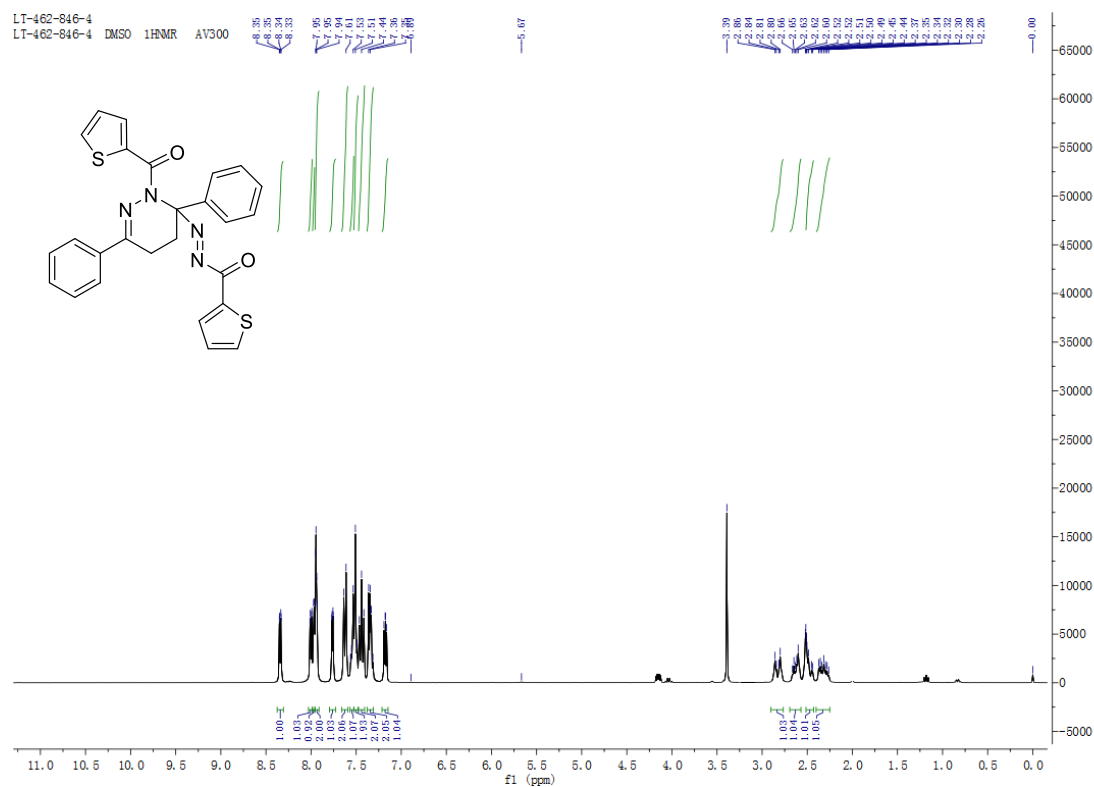
Chemical structure of 1-(4-methylphenyl)-4-((4-methylphenyl)imino)-2-phenyl-1,2,3,4-tetrahydropyridine is shown. The  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) displays peaks in the aromatic region (7.0-7.5 ppm), an imine proton region (3.0-3.5 ppm), and aliphatic regions (2.0-2.5 ppm). Integration values are provided below the peaks.



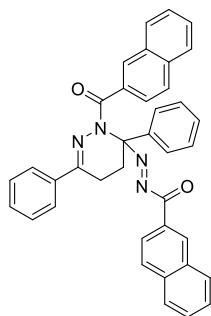
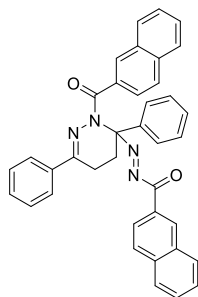
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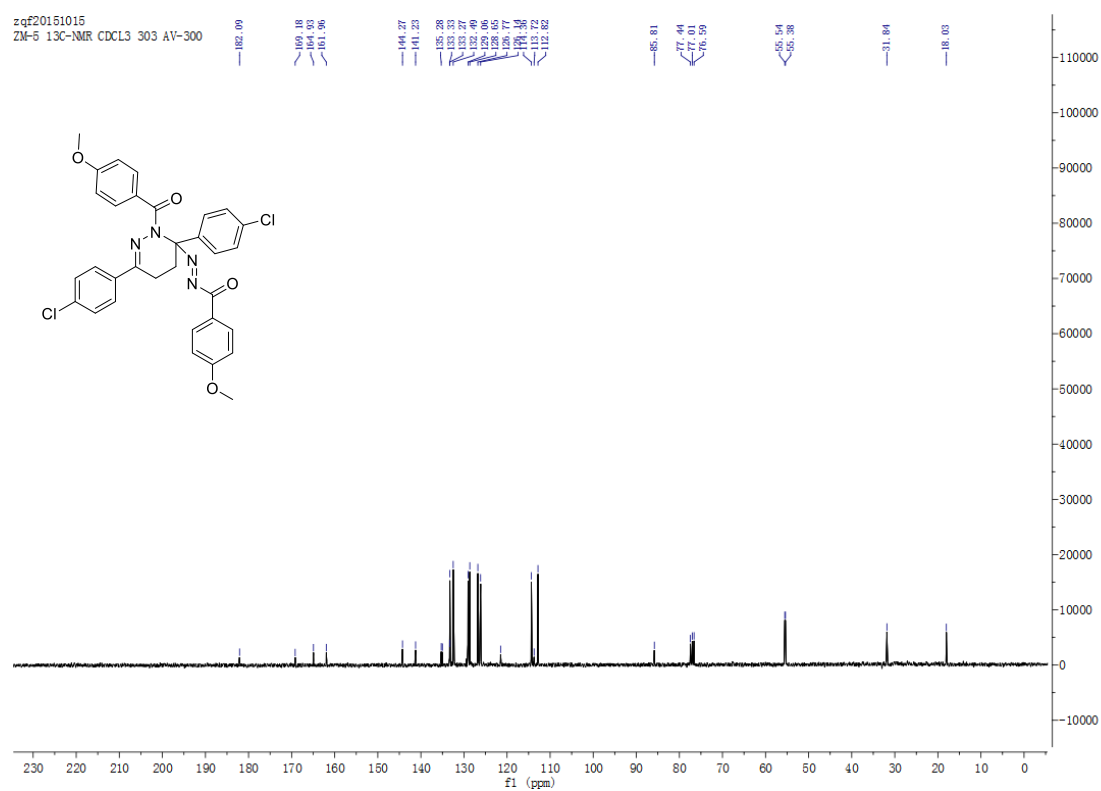
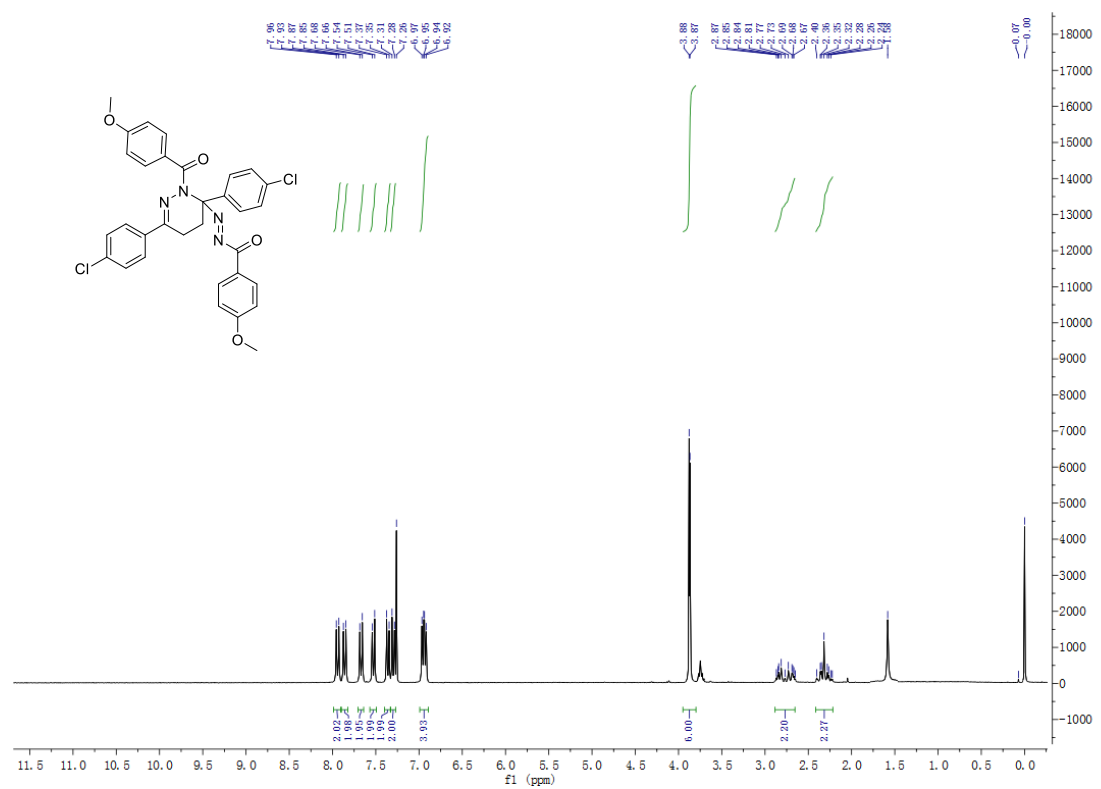
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LT-484-945-2  
LT-484-945-2 1HNMR DCDC13 AV300

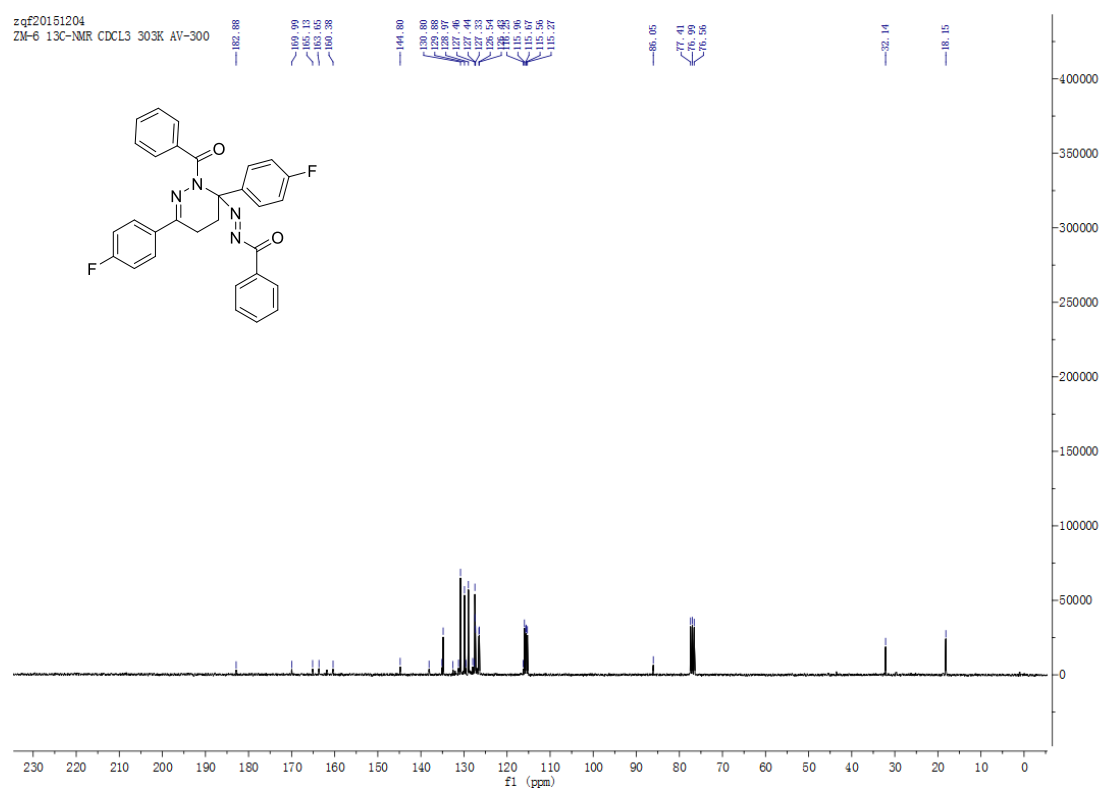
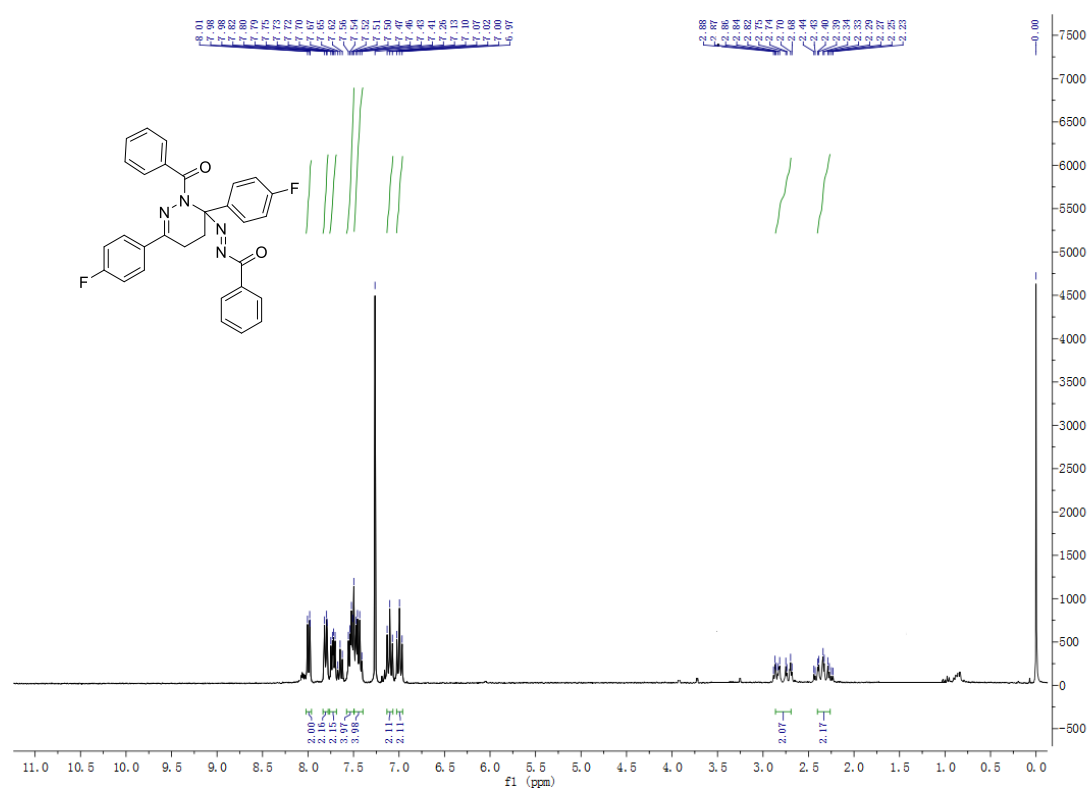


2j

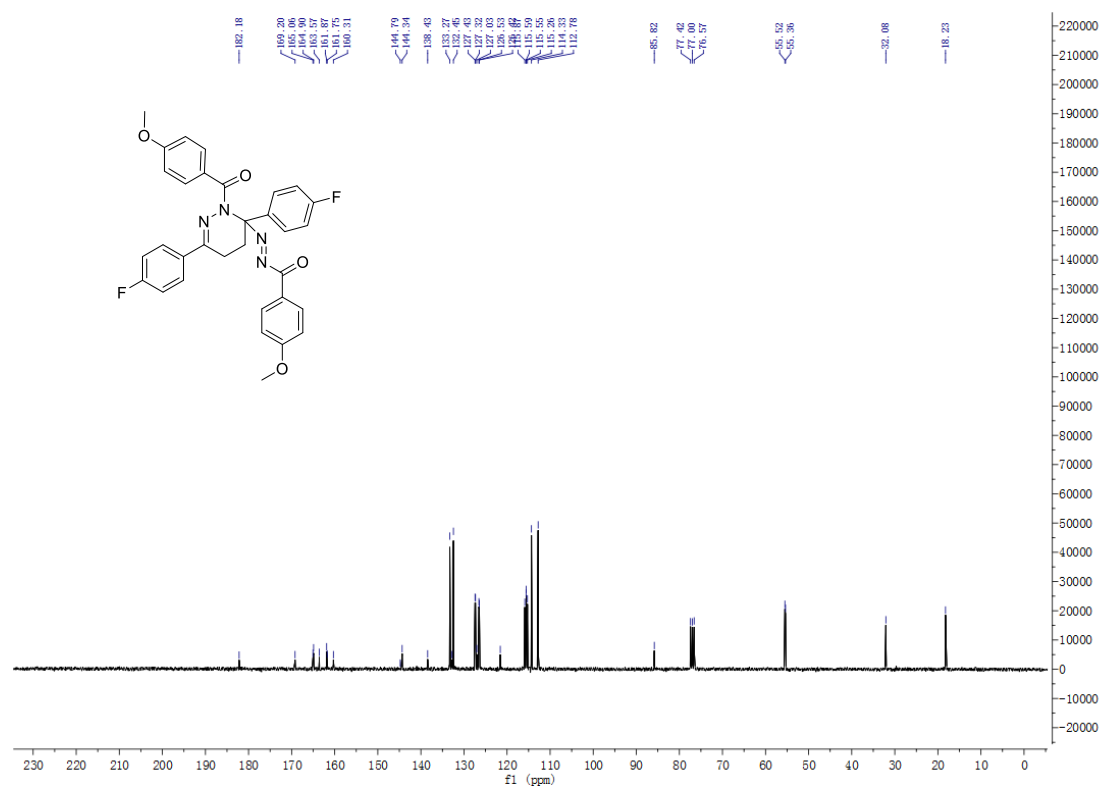
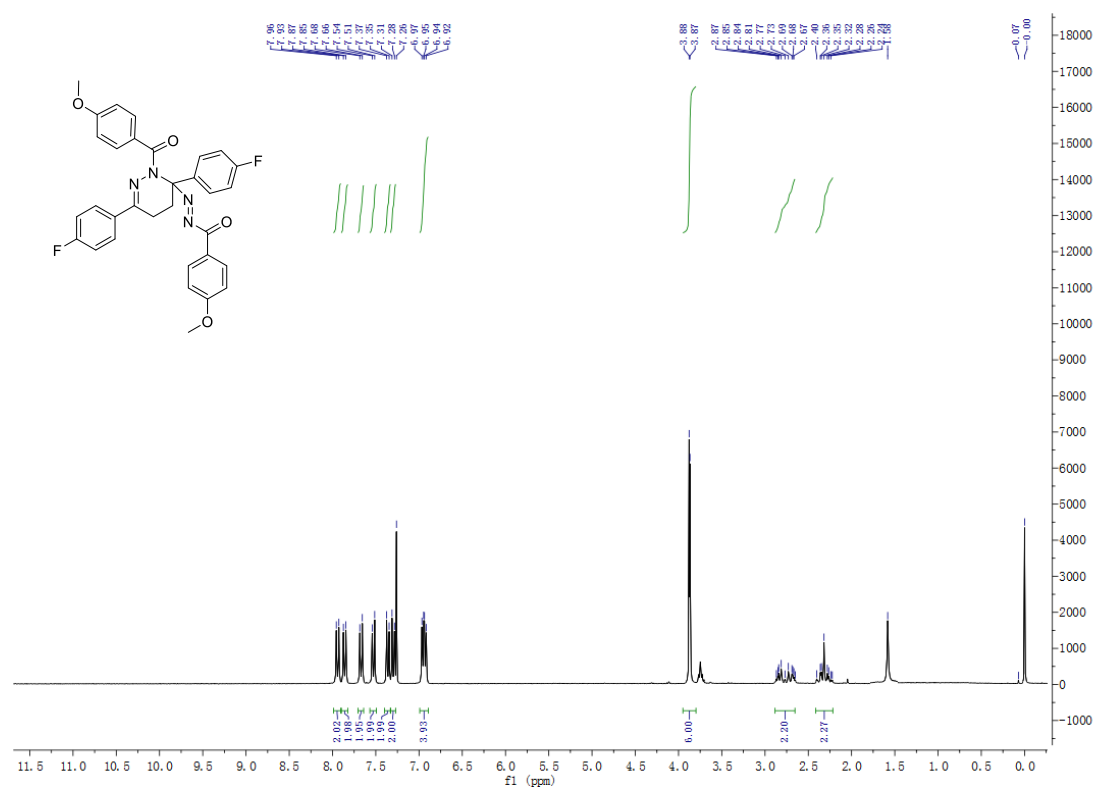




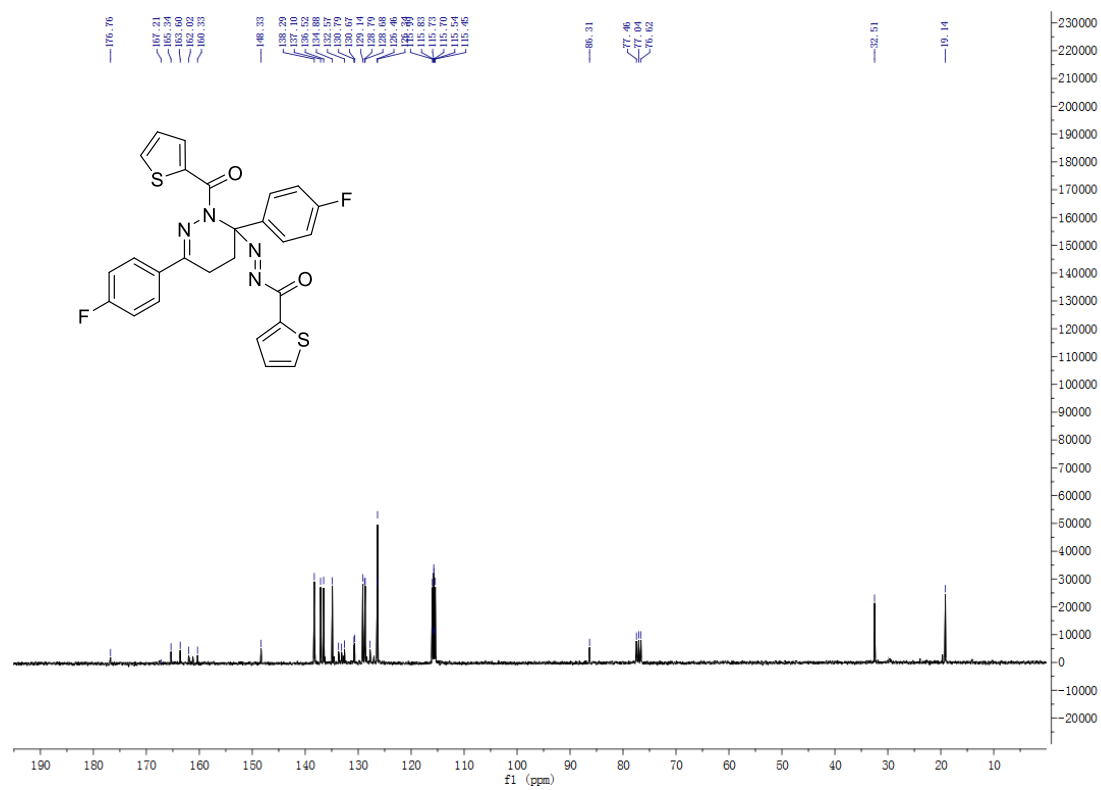
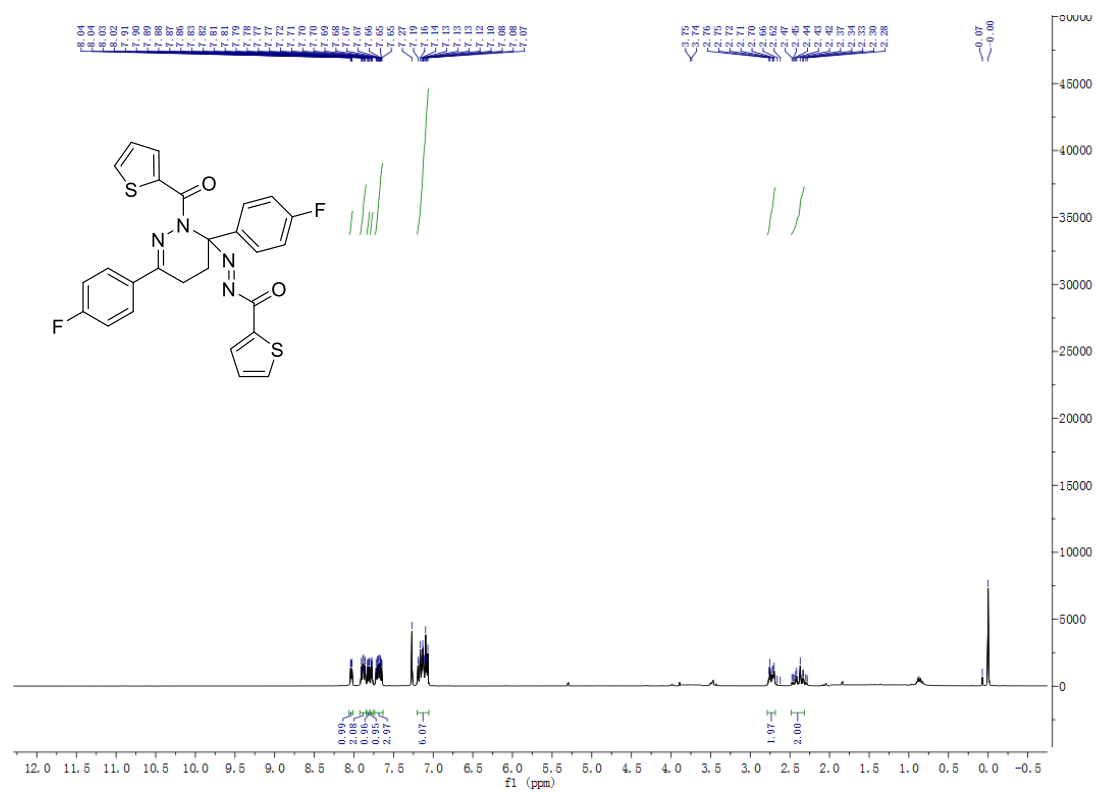
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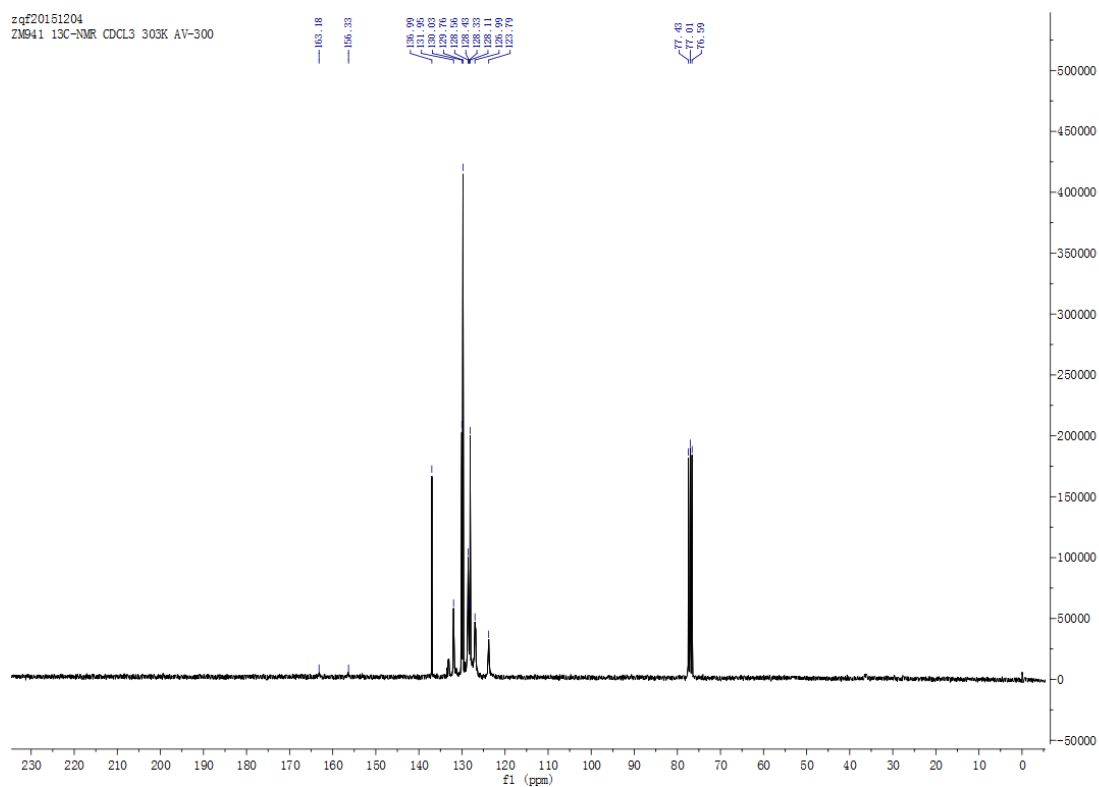
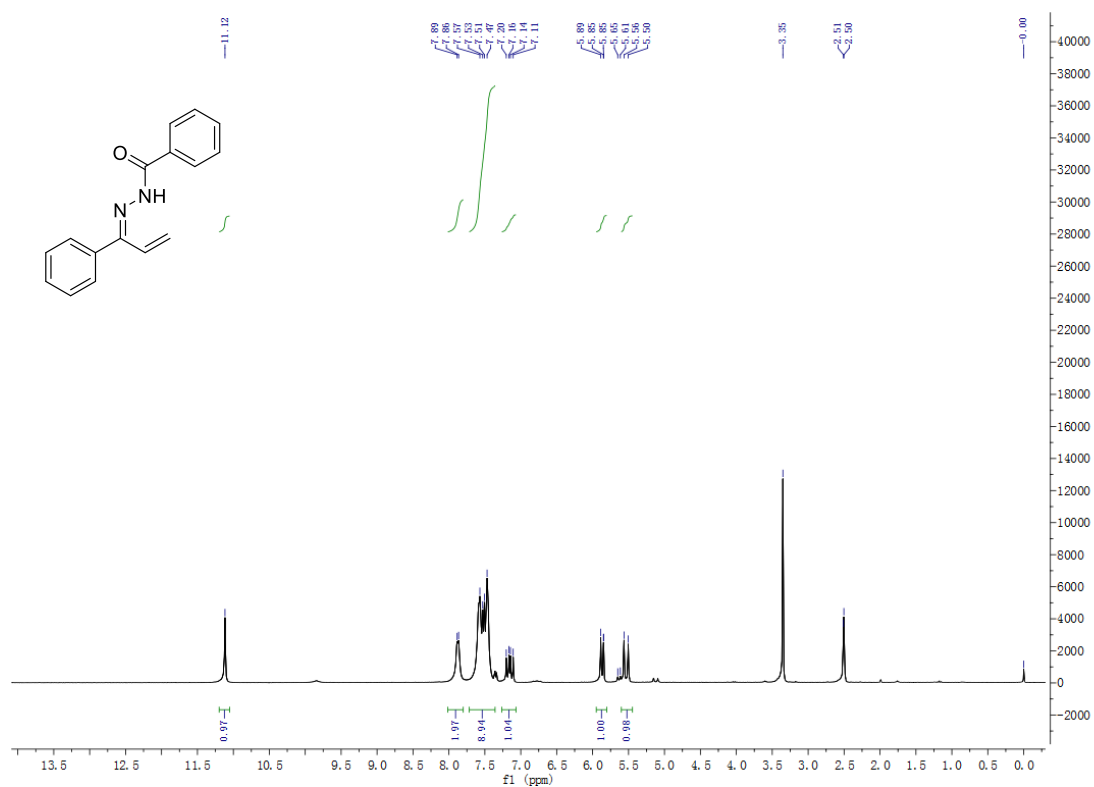
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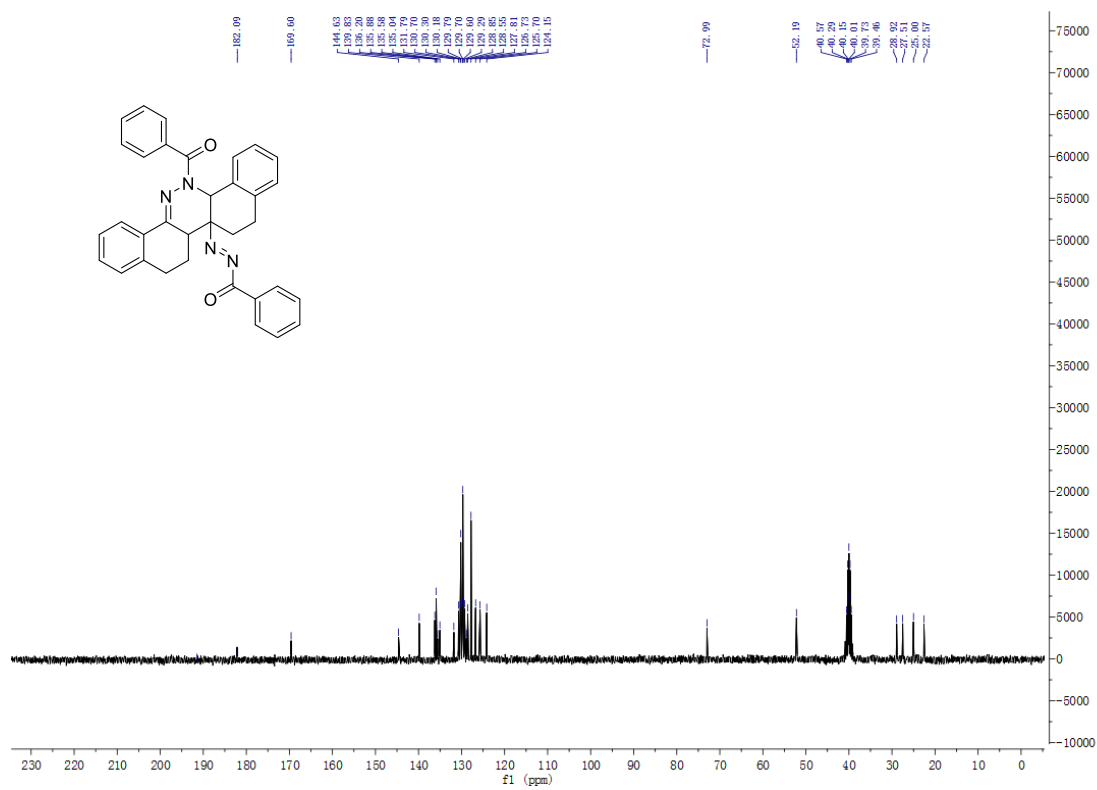
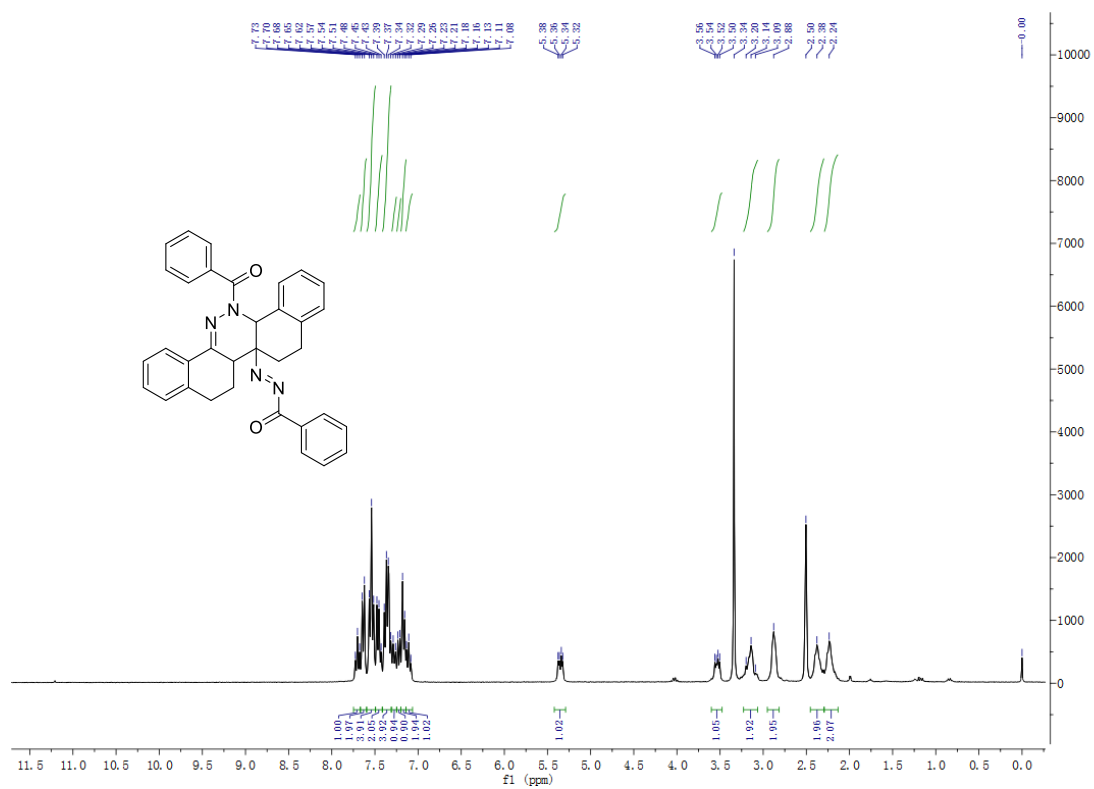
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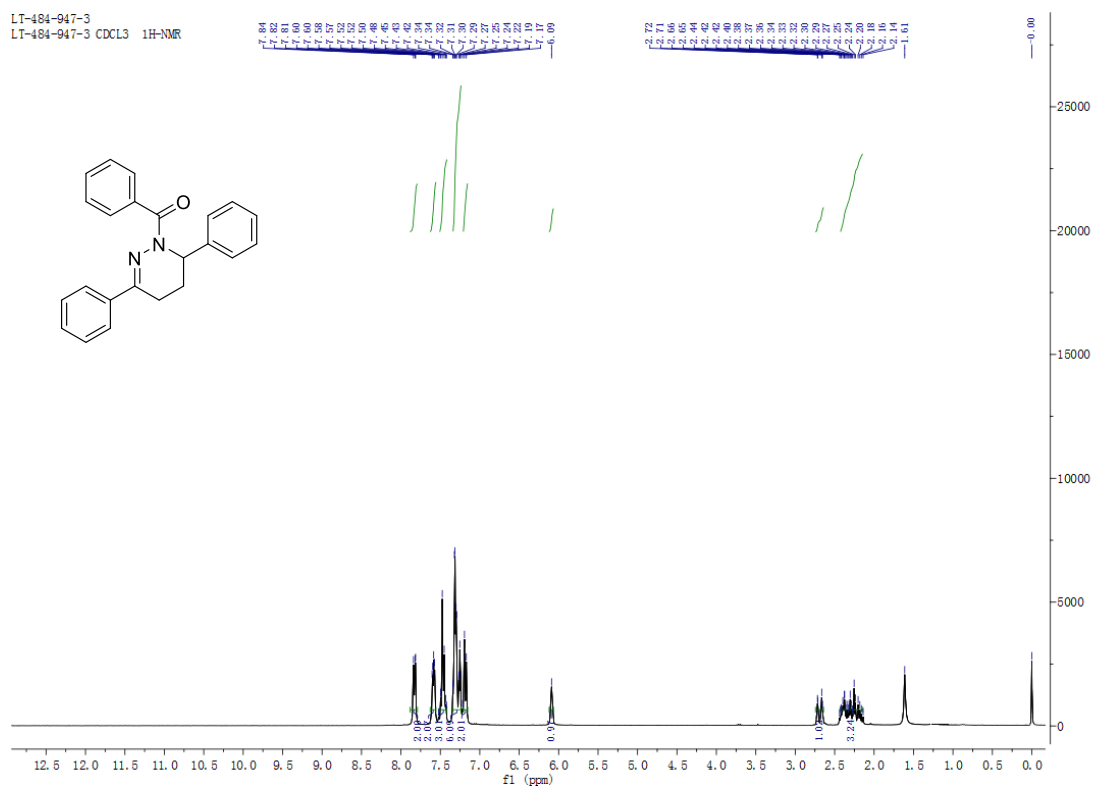


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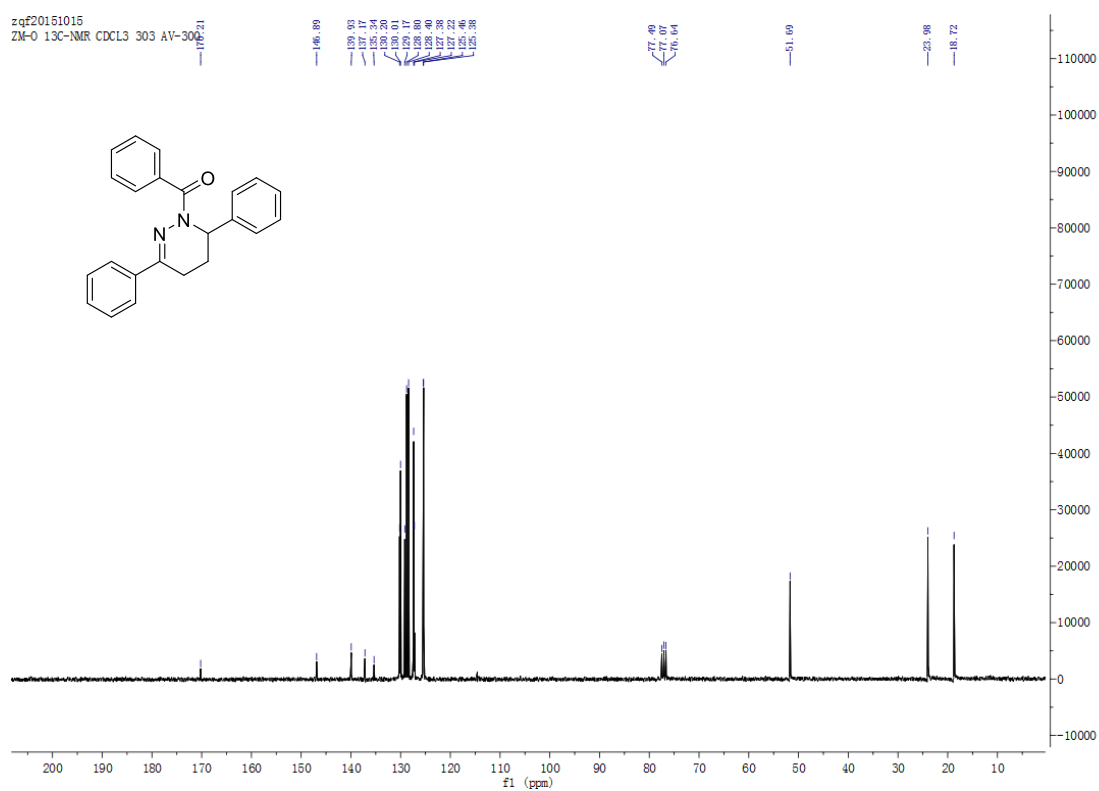


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LT-484-947-3  
LT-484-947-3 CDCL<sub>3</sub> 1H-NMR



zqf20151015  
ZM-O 13C-NMR CDCL<sub>3</sub> 303 AV-300



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