

# Supporting Information

## **Copper and manganese co-mediated cascade aza-Michael addition/cyclization and azidation of 1,3-enynes: Regioselective synthesis of fully-substituted azido pyrroles**

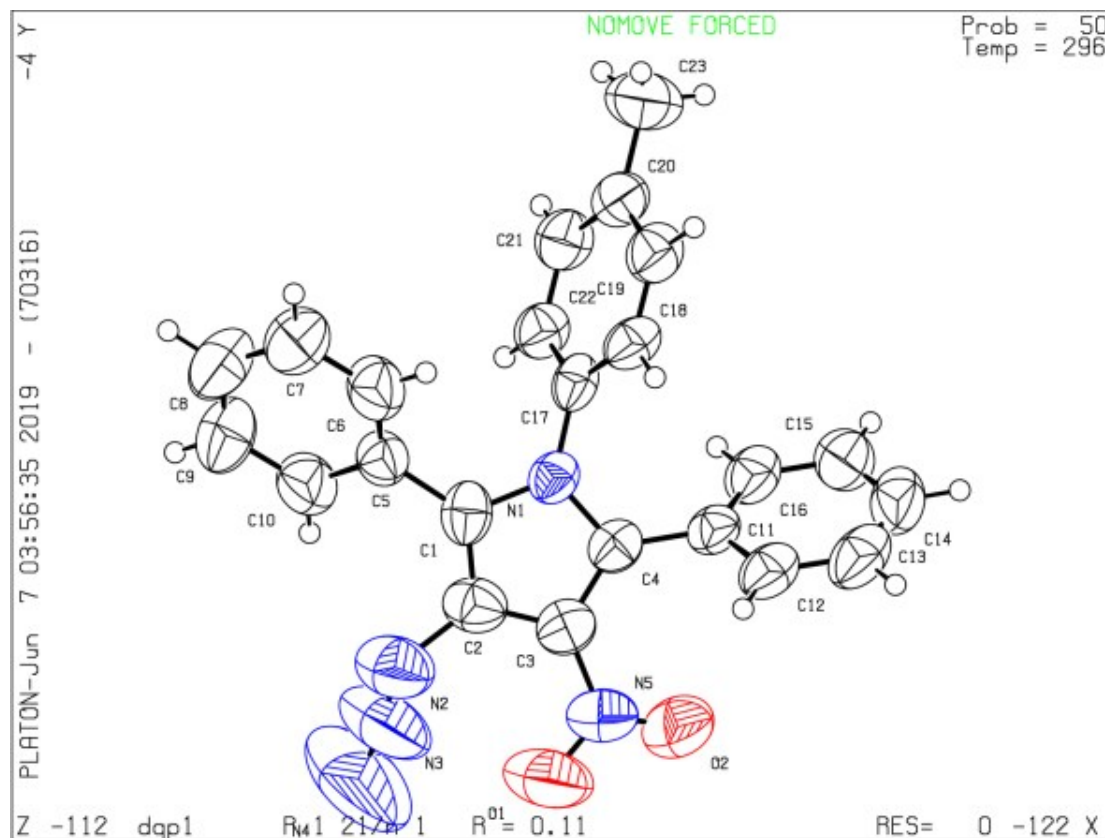
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Key Laboratory of Green Chemistry, and College of Chemistry & Chemical  
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## 1. X-ray Crystallography Data of 4a

The crystal of **4a** was slowly grown by evaporation of the solvents (a mixture of Ethyl acetate/ petroleum ether = 1:10 in volume) at room temperature in the air.



Crystal data and structure refinement of product **4a**

CCDC Number 1962959

Compound Name 3-azido-4-nitro-2,5-diphenyl-1-(p-tolyl)-1H-pyrrole

Empirical formula  $C_{23}H_{17}N_5O_2$

Formula weight 395.42

Temperature 296(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic,  $P2(1)/n$

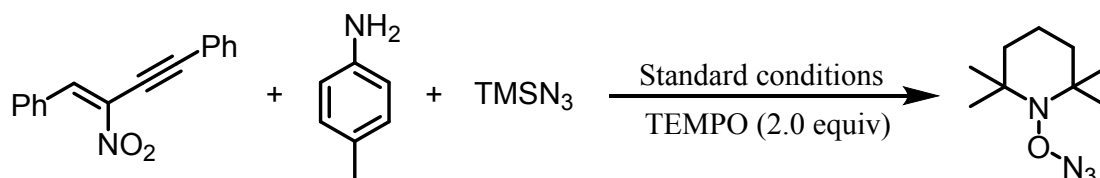
Unit cell dimensions  
a = 11.158(2) Å    alpha = 90 deg.  
b = 11.434(2) Å    beta = 96.925(4) deg.  
c = 15.708(3) Å    gamma = 90 deg.

Volume	1989.4(6) Å <sup>3</sup>
Z, Calculated density	4, 1.320 Mg/m <sup>3</sup>
Absorption coefficient	0.088 mm <sup>-1</sup>
F(000)	824
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	2.21 to 25.10 deg.
Limiting indices	-13 ≤ h ≤ 8, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18
Reflections collected / unique	9906 / 3518 [R(int) = 0.0265]
Completeness to theta = 25.10	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9826 and 0.9826
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3518 / 0 / 272
Goodness-of-fit on F <sup>2</sup>	1.160
Final R indices [I > 2σ(I)]	R1 = 0.1017, wR2 = 0.2944
R indices (all data)	R1 = 0.1534, wR2 = 0.3298
Largest diff. peak and hole	0.627 and -0.412 e.Å <sup>-3</sup>

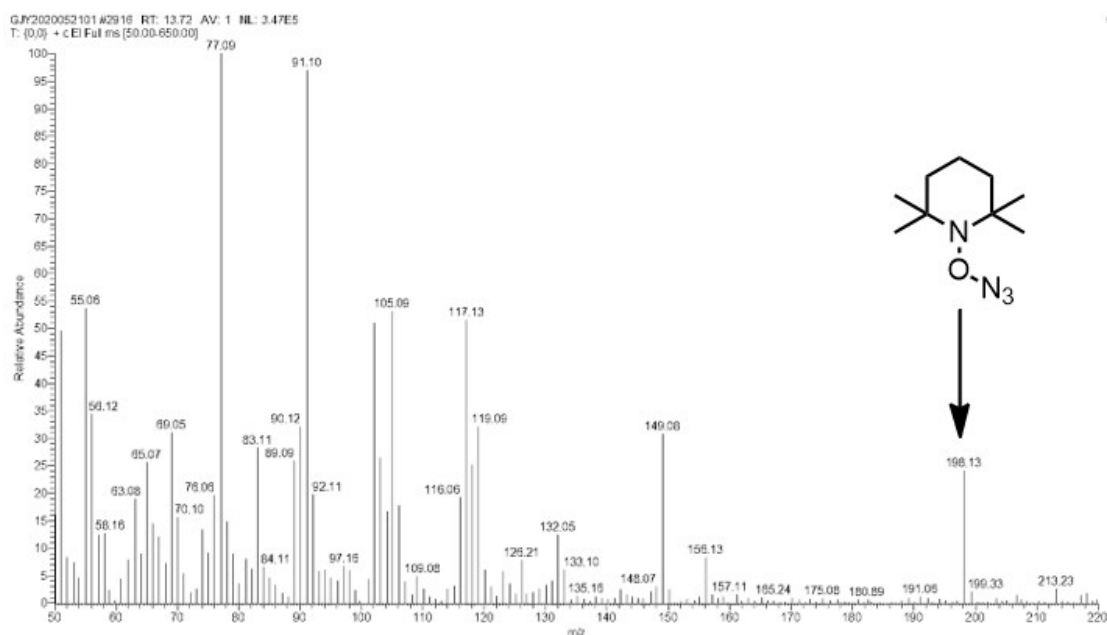
## 2. Experimental Procedures

2.1 General procedure for Preparing Conjugated 1,3-Enyne **1** According to the Reference<sup>1-4</sup>

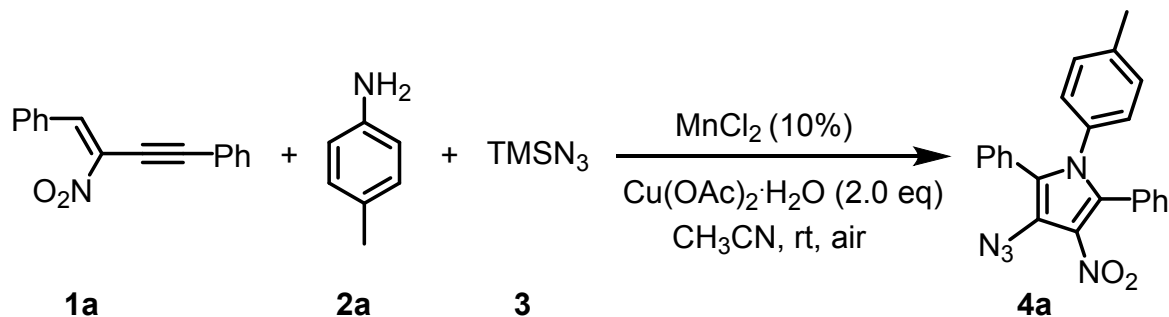
2.2 Experiments of Radical Inhibition



To an oven-dried Schlenk tube were added 1,3-enyne **1a** (0.1 mmol, 25 mg), 4-methylaniline **2a** (0.11 mmol, 11.8 mg), MnCl<sub>2</sub> (10 mol%, 1.3 mg), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol, 40.0 mg), CH<sub>3</sub>CN (1.0 mL), TMSN<sub>3</sub> (0.3 mmol, 40 μL) and TEMPO (0.2 mmol, 31.3 mg) under air atmosphere. The mixture was stirred at room temperature for 20 min. The reaction mixture was detected by GC-MS measurement.



2.3 Gram scale experiment for the synthesis of **4a**



To an oven-dried 100 mL round-bottomed flask was charged with 1,3-enyne **1a** (0.3 g, 1.2 mmol), 4-methylaniline **2a** (0.142 g, 1.32 mmol), manganese chloride (15.1

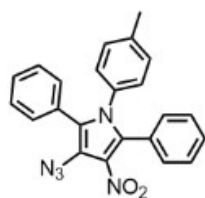
mg, 10 mol%), copper acetate monohydrate (0.48 g, 2.4 mmol), acetonitrile (12 mL), trimethylsilylazide TMSN<sub>3</sub> **3** (480 μL, 3.6 mmol) under air atmosphere. The mixture was stirred at room temperature. After the reaction was accomplished (detected by TLC), the mixture was leached through diatomite. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on basic silica gel (PE / EA = 40/1) to afford product **4a** 0.28 g (59% yield).

#### References:

- (1) Ganesh, M.; Namboothiri, I. N. N. Stereospecific approach to  $\alpha,\beta$ -disubstituted nitroalkenes via coupling of  $\alpha$ -bromonitroalkenes with boronic acids and terminal acetylenes. *Tetrahedron* 2007, **63**, 11973-11983.
- (2) Bharathiraja, G; Sakthivel, S; Sengoden, M and Punniyamurthy, T. A Novel Tandem Sequence to Pyrrole Syntheses by 5-endo-digCyclization of 1,3-Enynes with Amines. *Org. Lett.*, 2013, **15**, 4996-4999.
- (3) Bharathiraja, G.; Sengoden, M.; Kannan, M.; Punniyamurthy, T. Expedient synthesis of tetrasubstituted pyrroles via a copper-catalyzed cascade inter-/intramolecular cyclization of 1,3-enynes carry a nitro group with amines. *Org. Biomol. Chem.*, 2015, **13**, 2786-2792.
- (4) Ge, J.; Ding, Q.; Wang, X.; Peng, Y. Three-Component Cascade Synthesis of Fully-substituted Trifluoromethyl Pyrroles via a Cu(II)/Rh(III)-promoted aza-Michael Addition/Trifluoromethylation Cyclization/Oxidation Reaction. *J. Org. Chem.* 2020, **85**, 7658-7665.

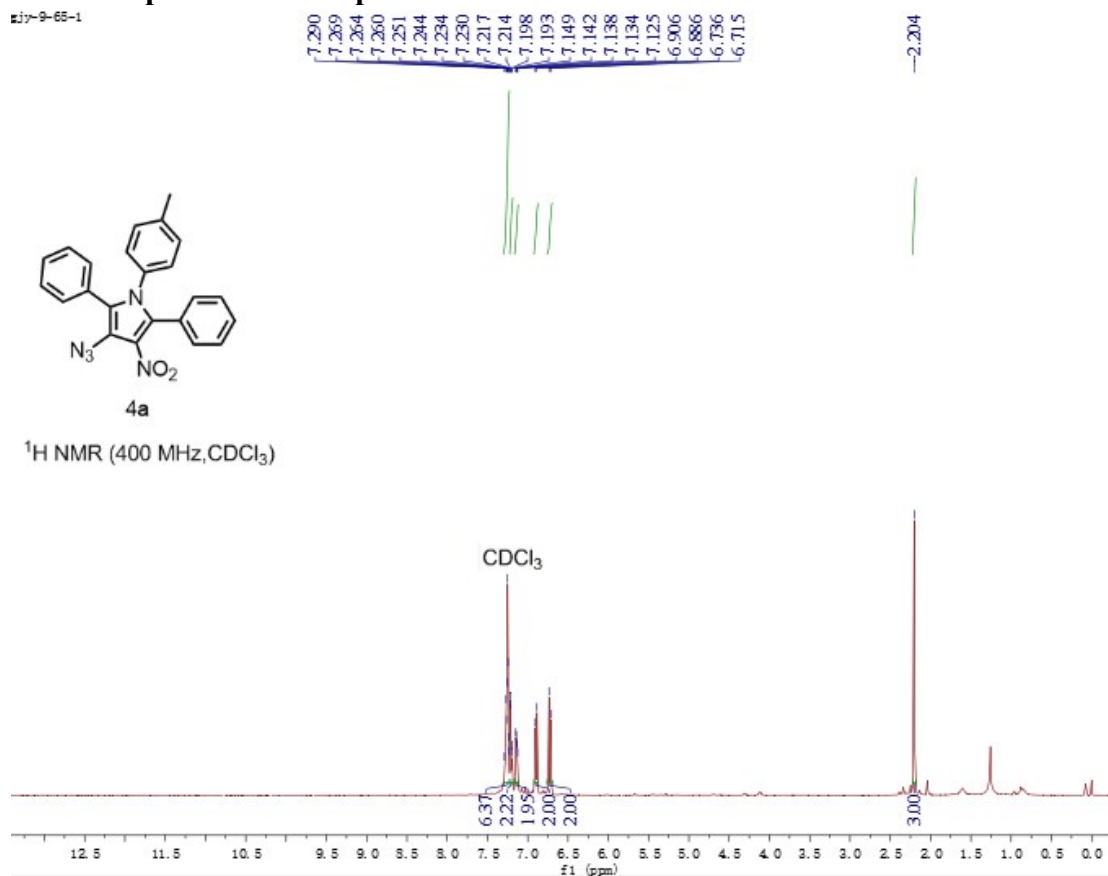
## 4. NMR Spectra for Compounds 4 and 5

217-9-66-1

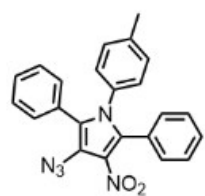


4a

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

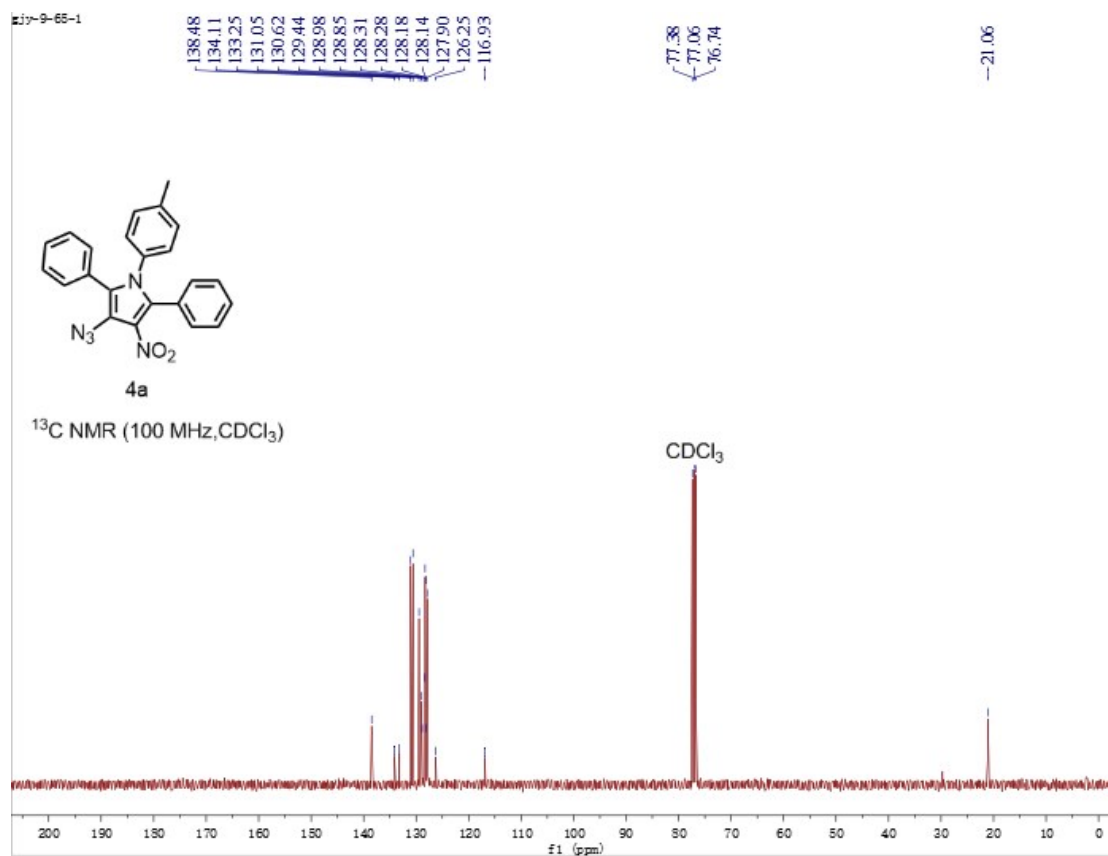


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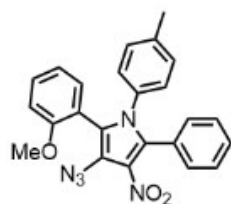


4a

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

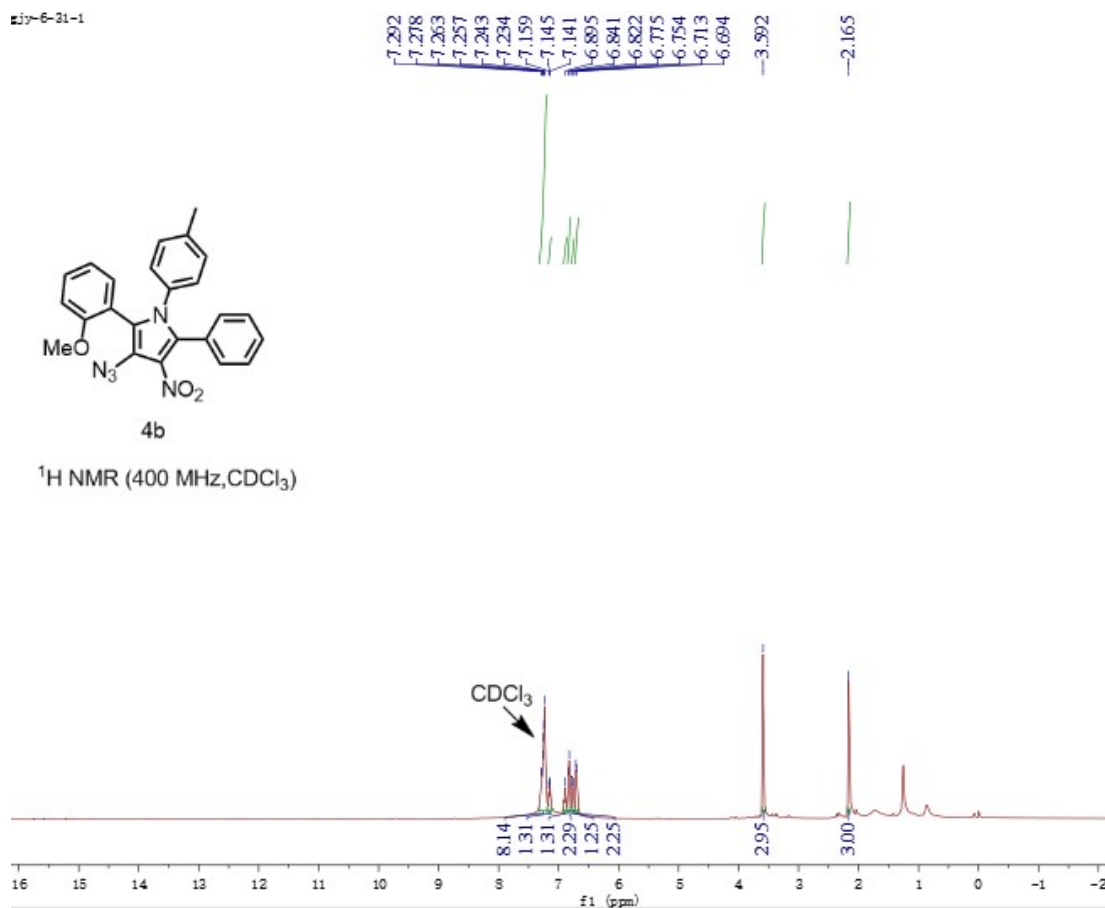


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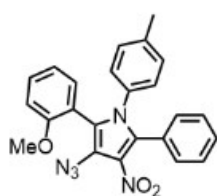


4b

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

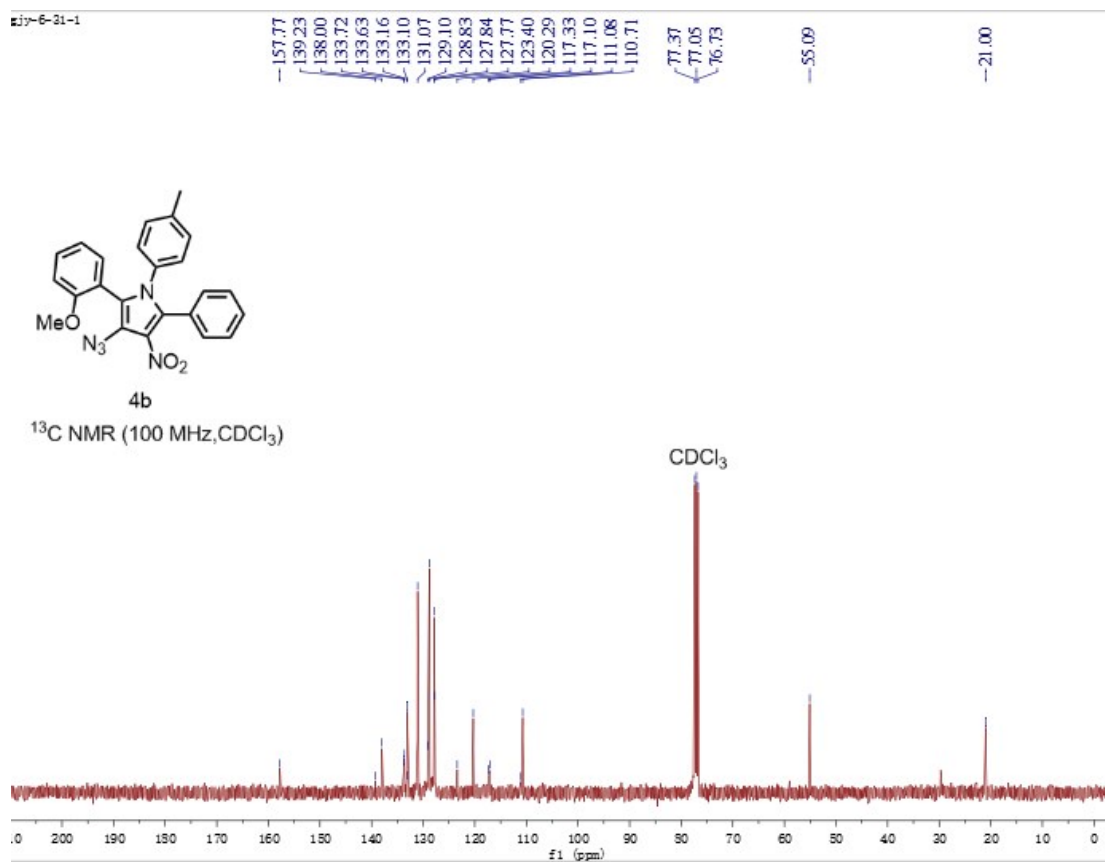


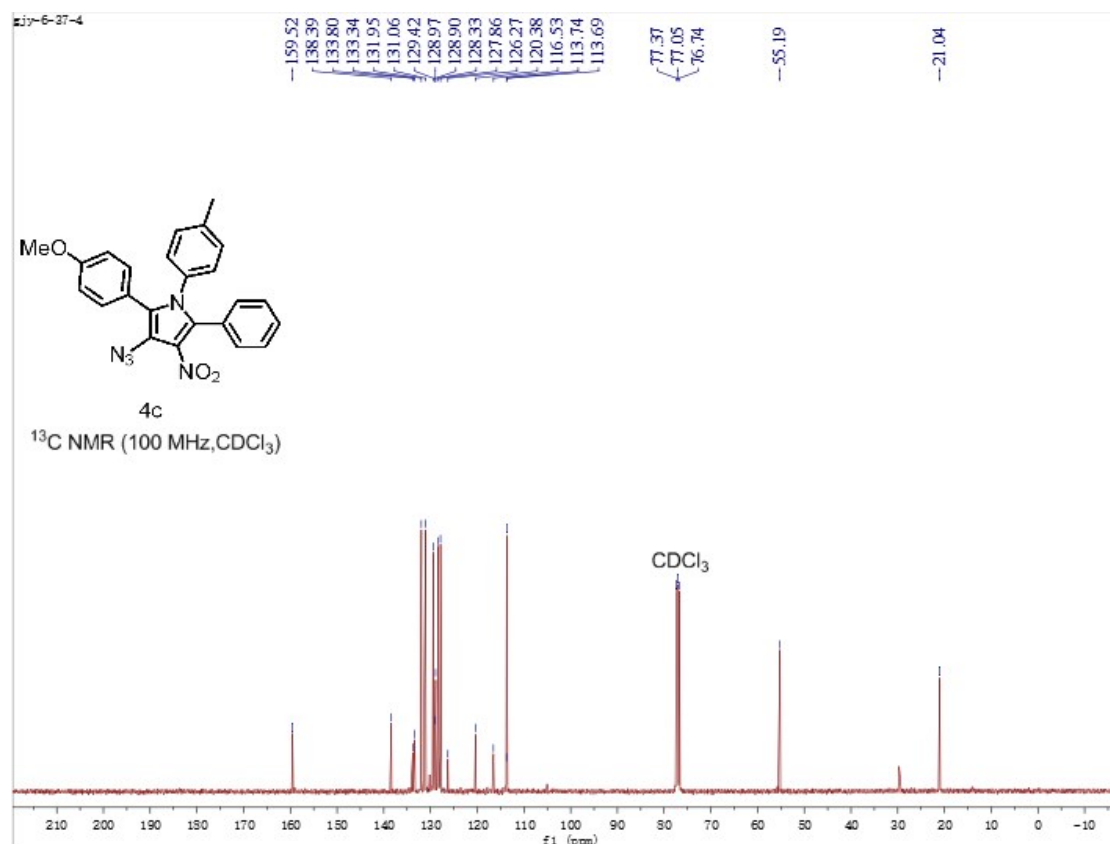
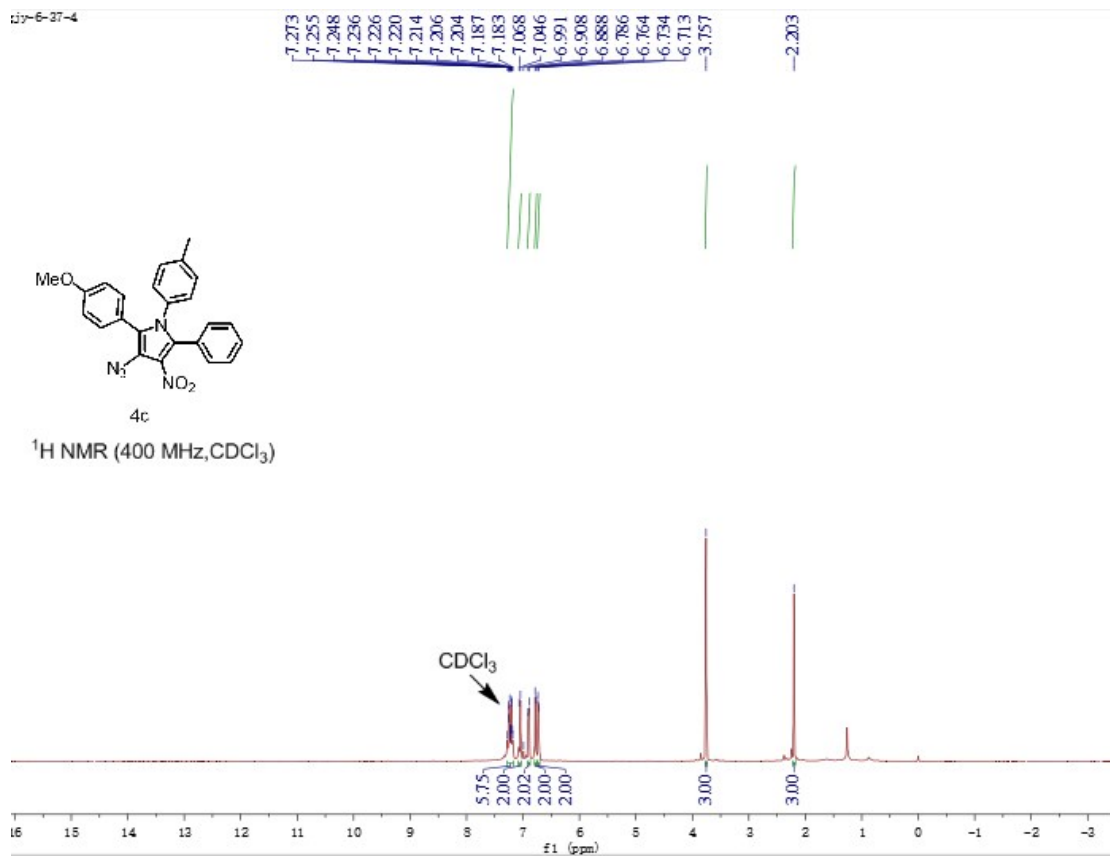
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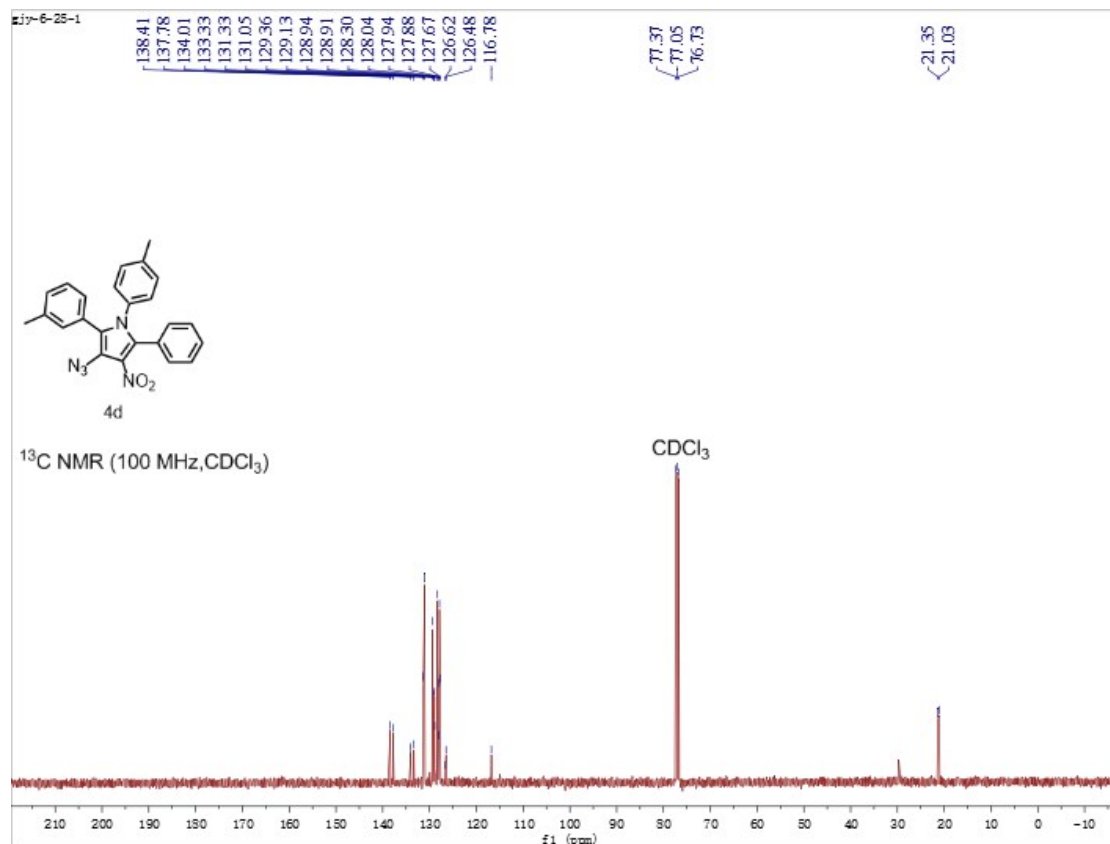
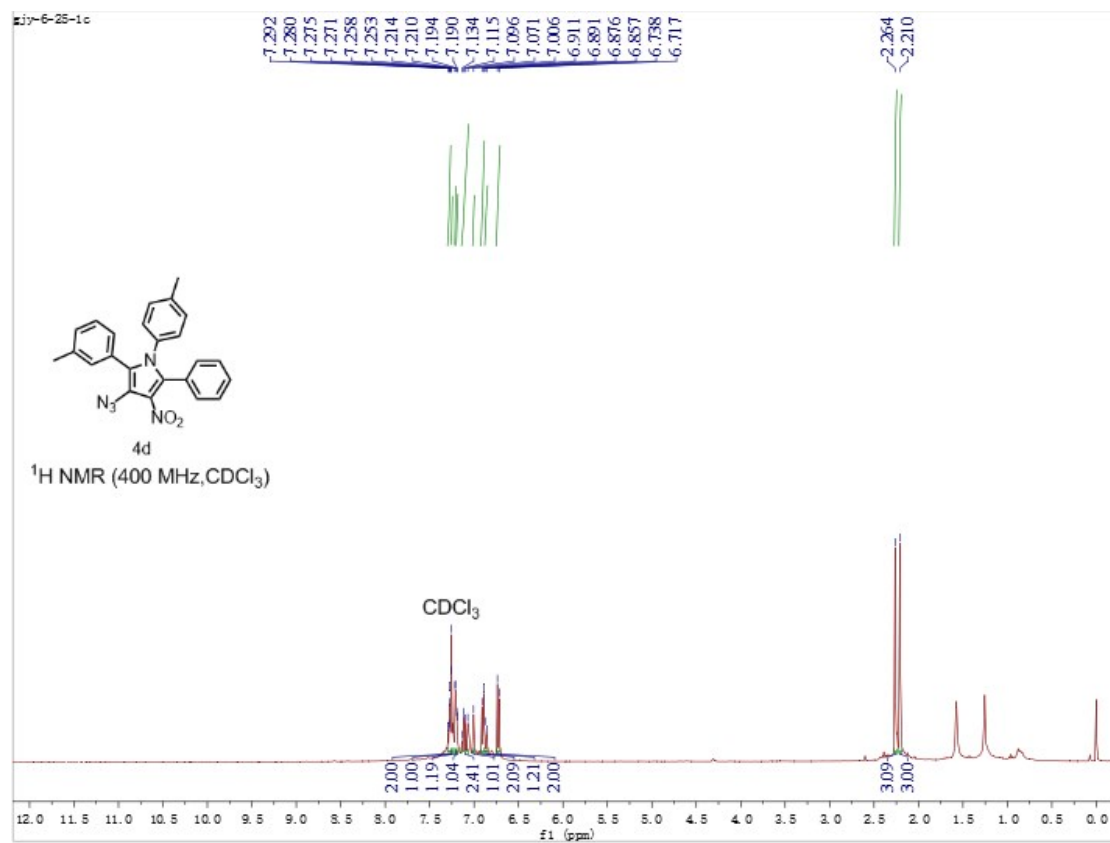
4b

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

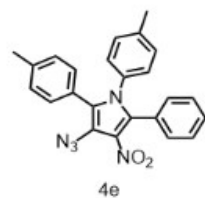




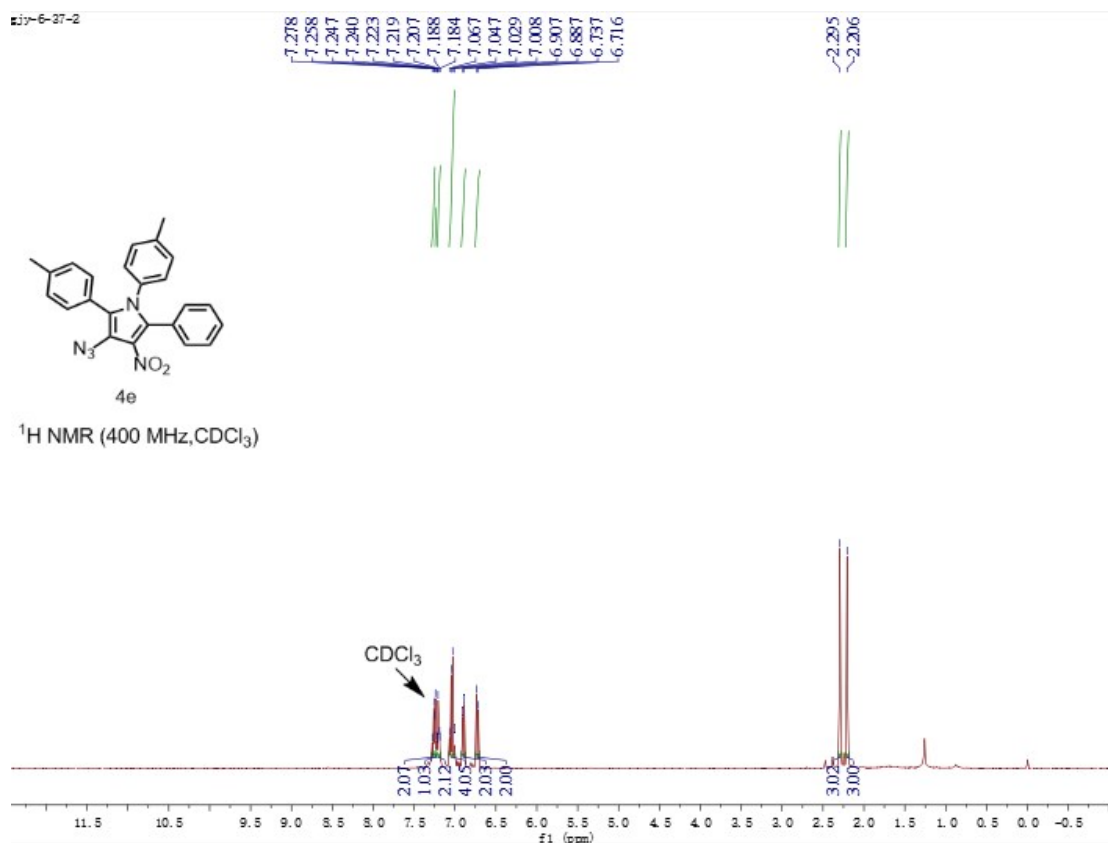




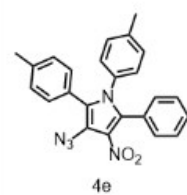
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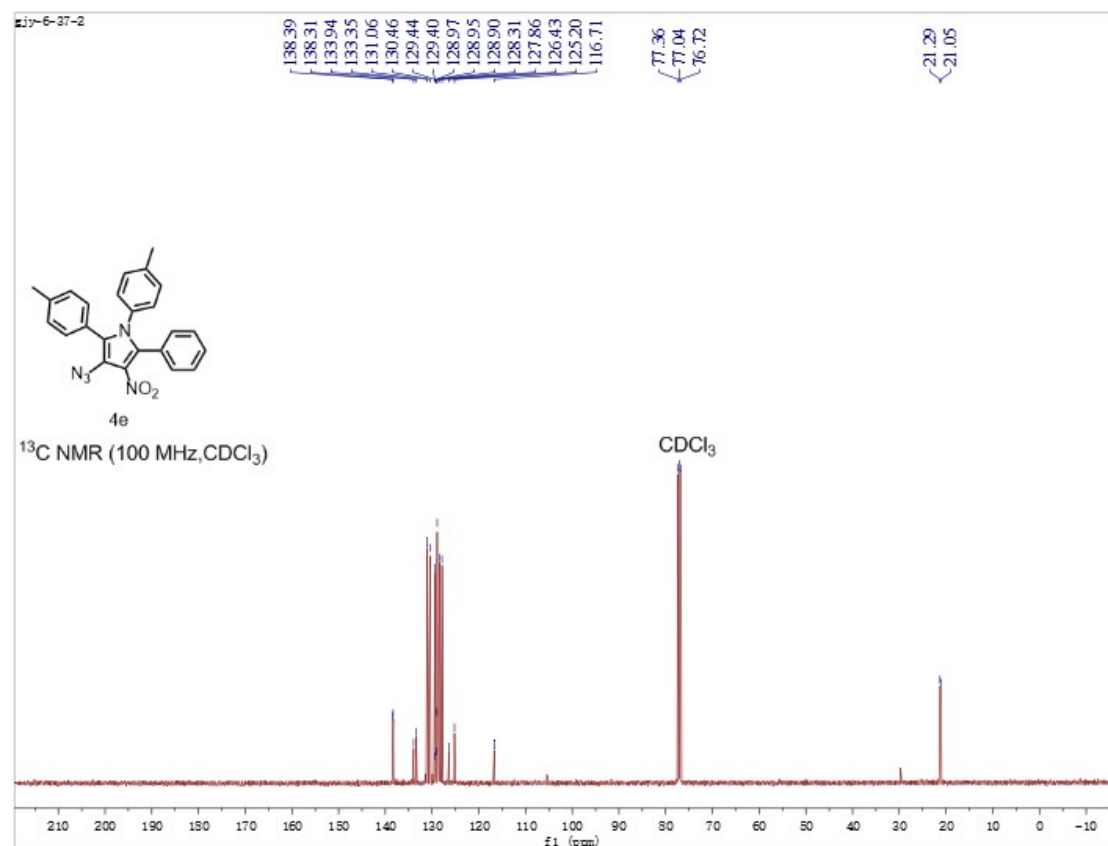
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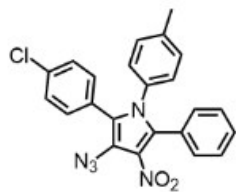
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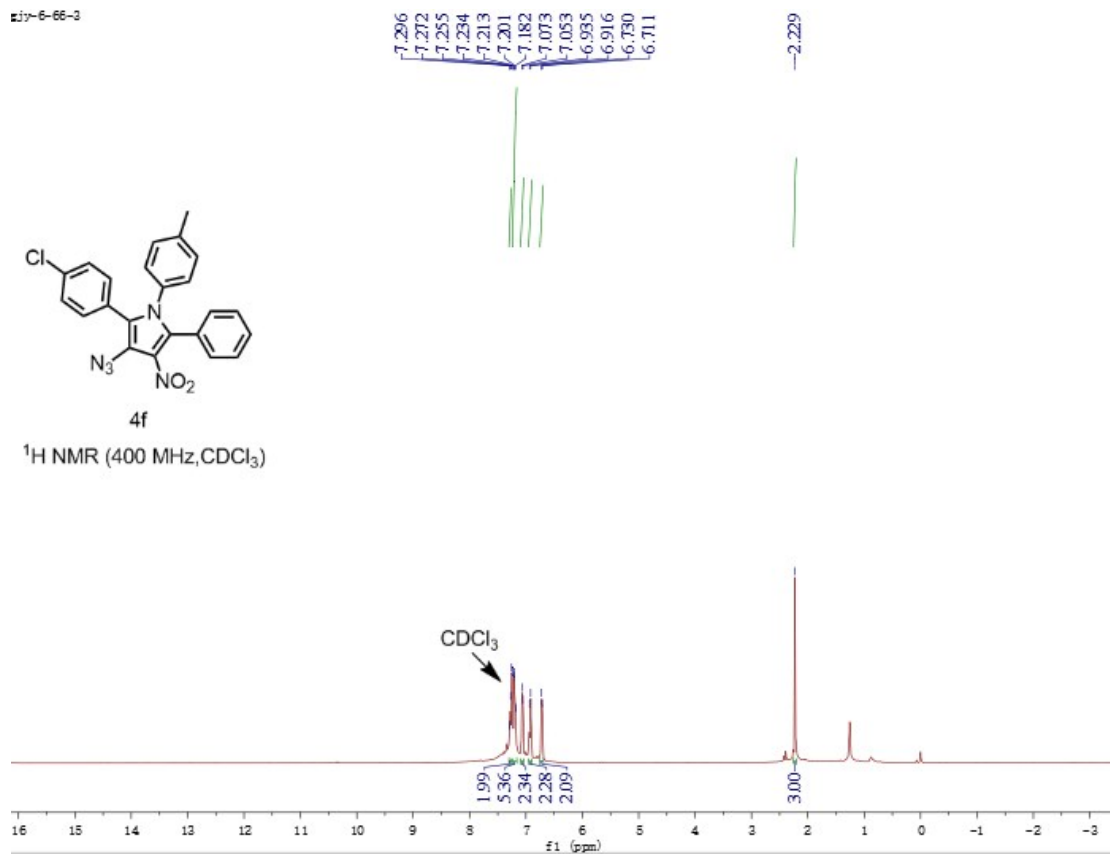


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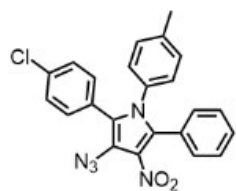


4f

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

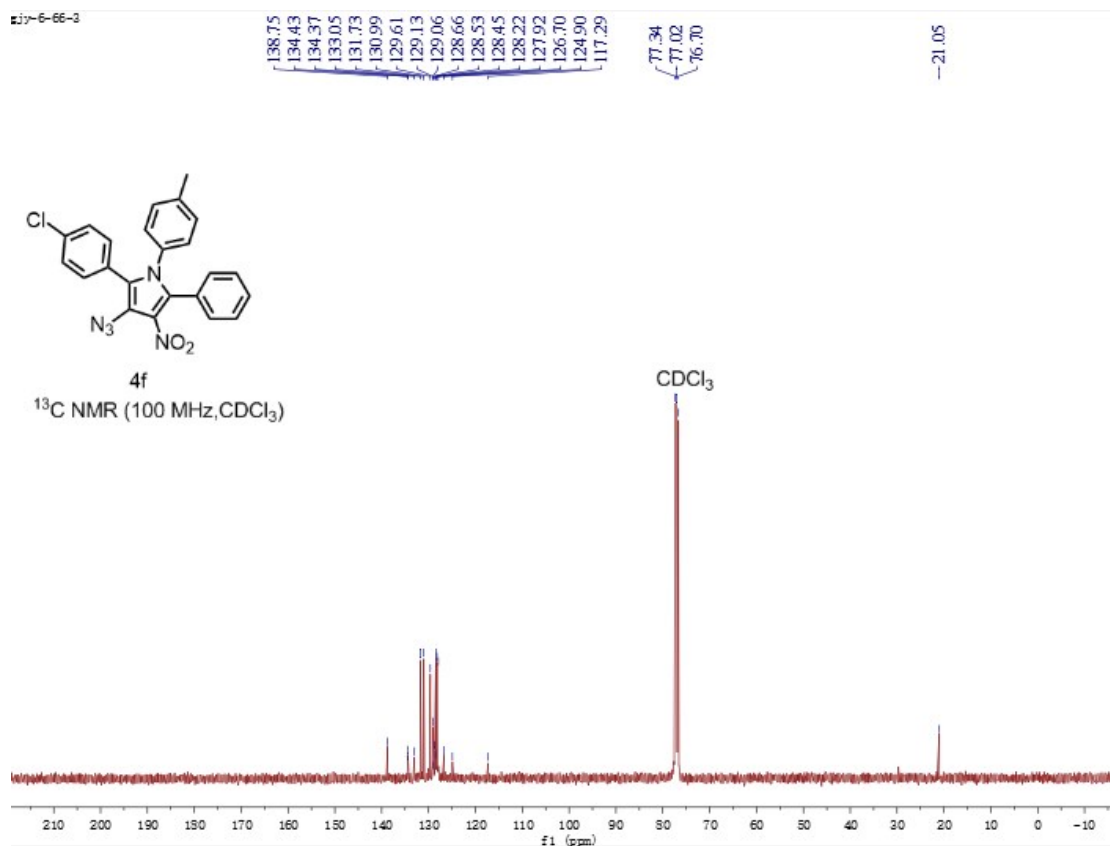


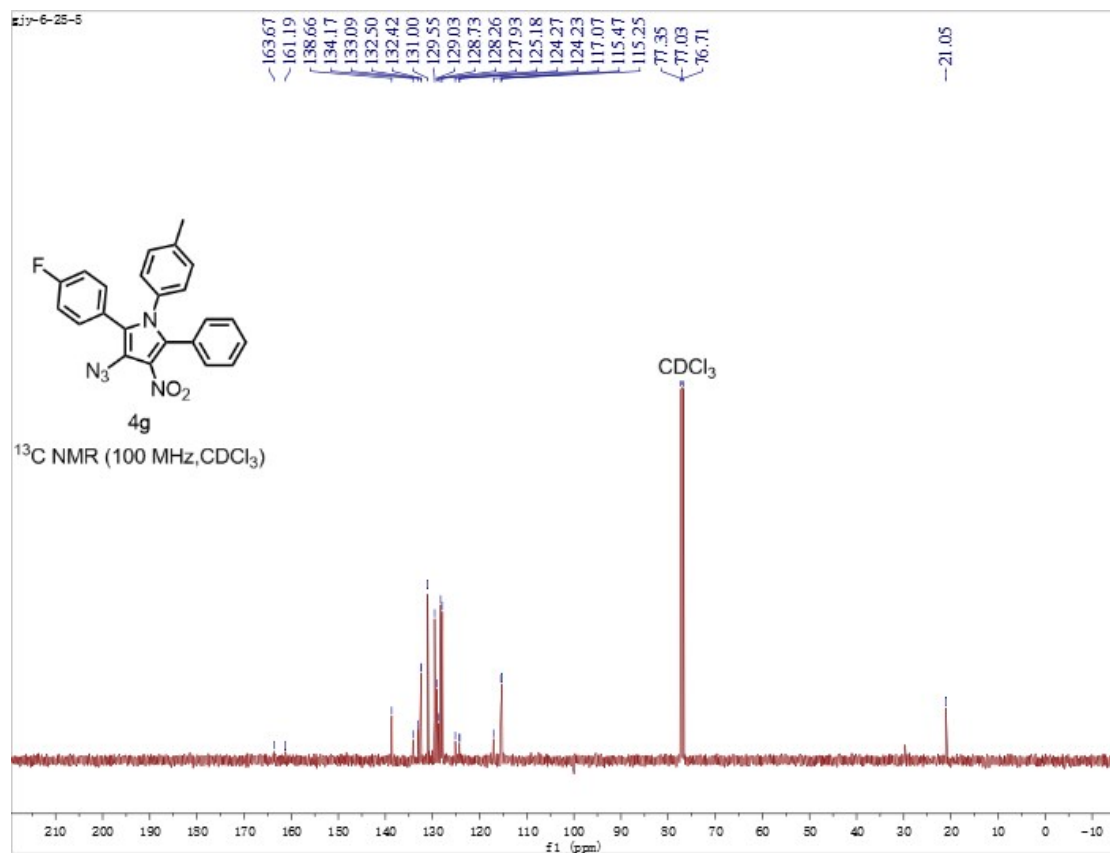
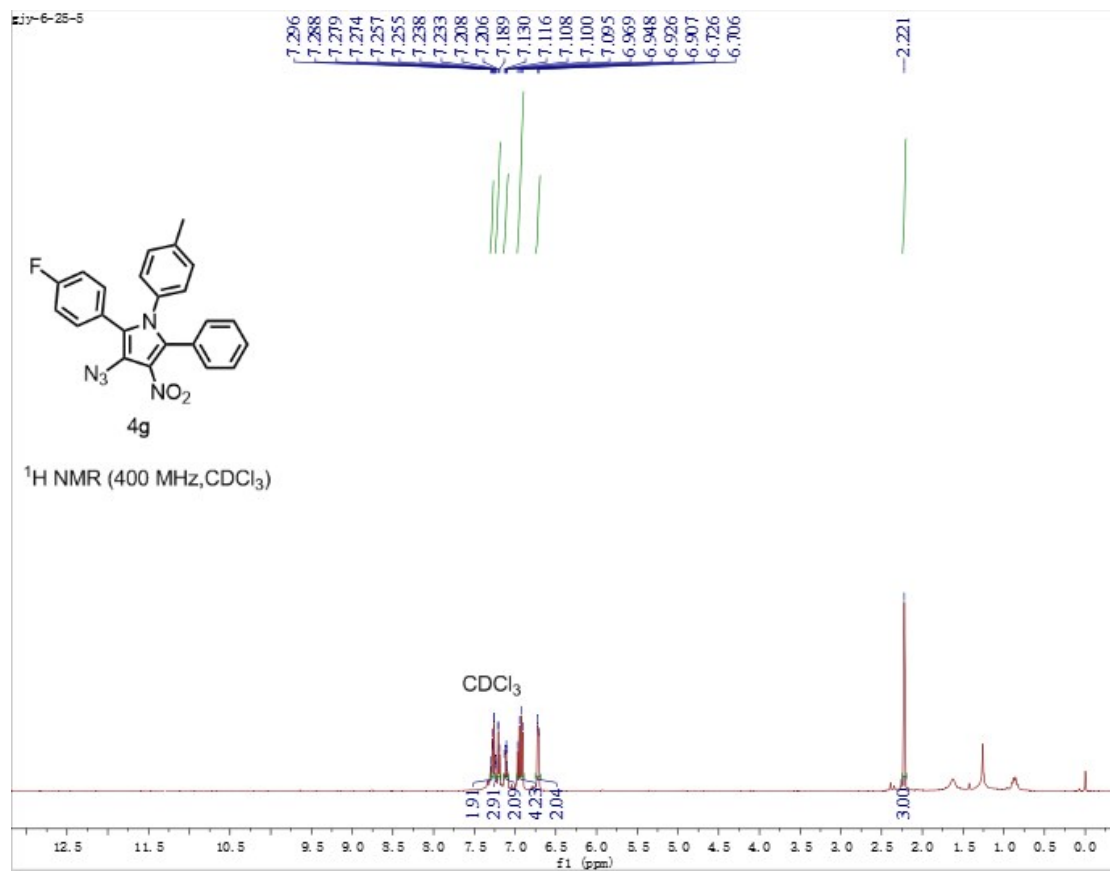
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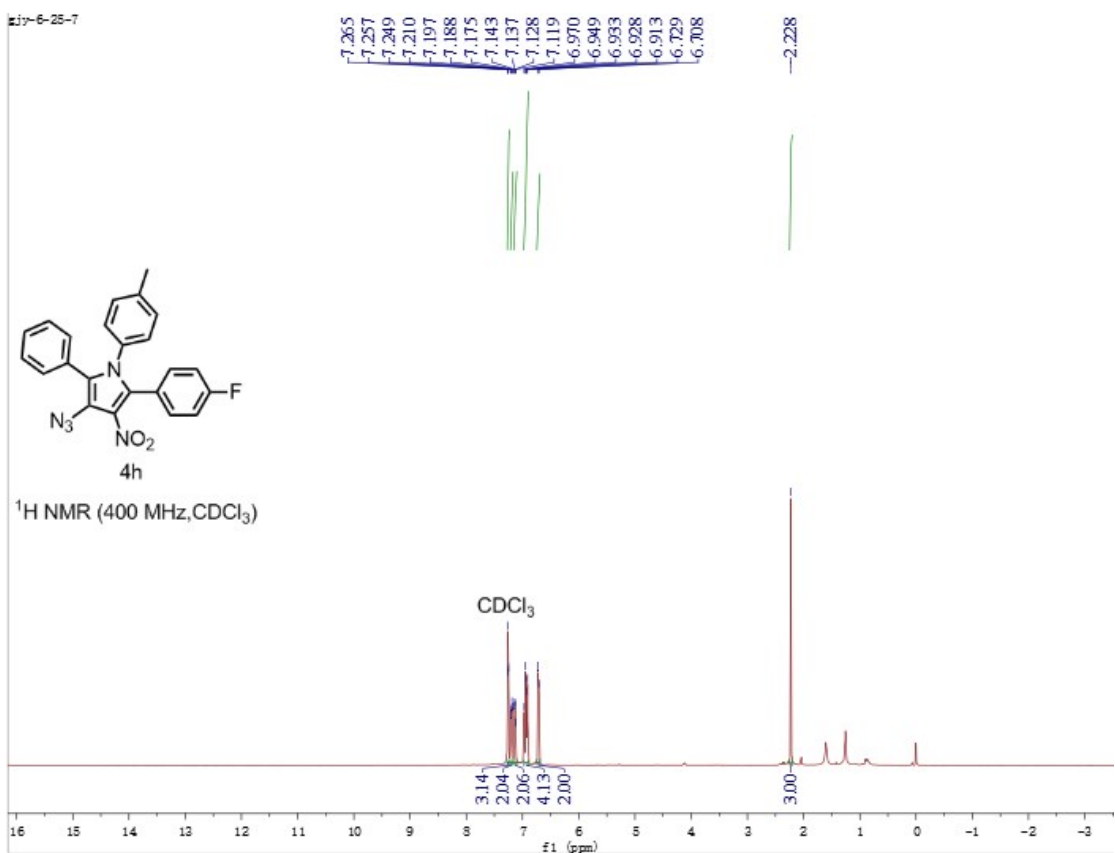
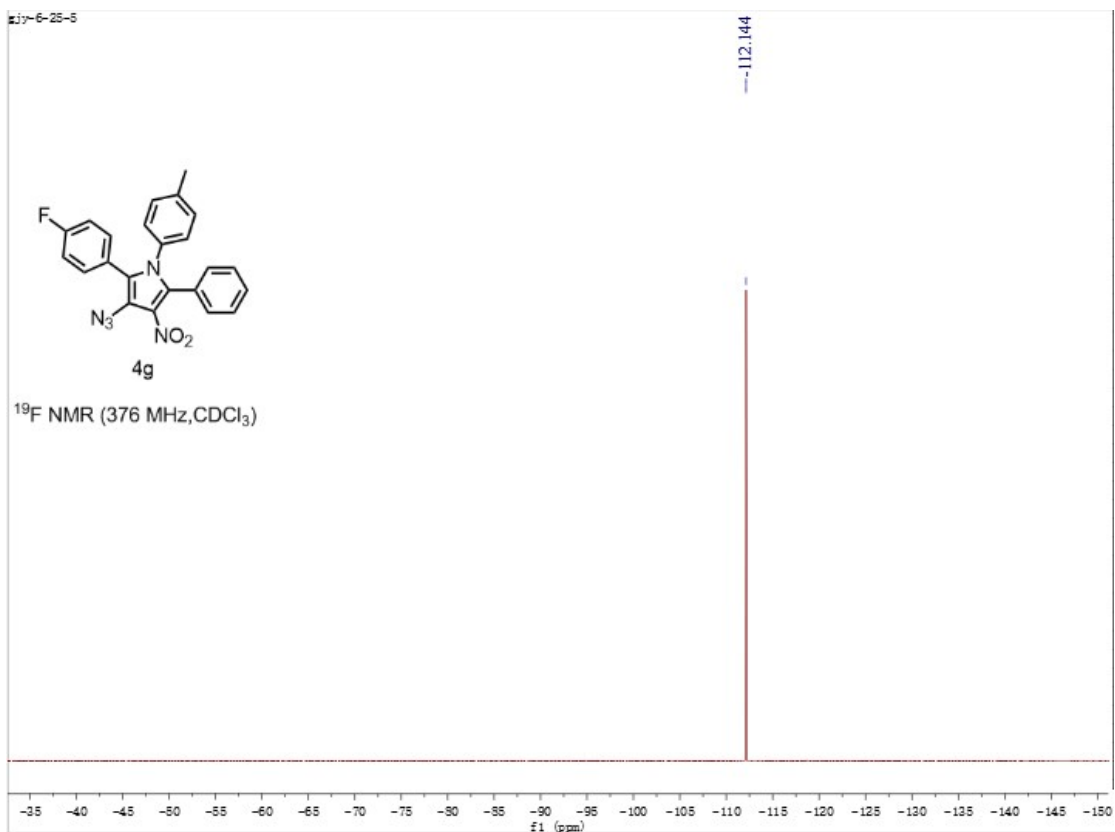


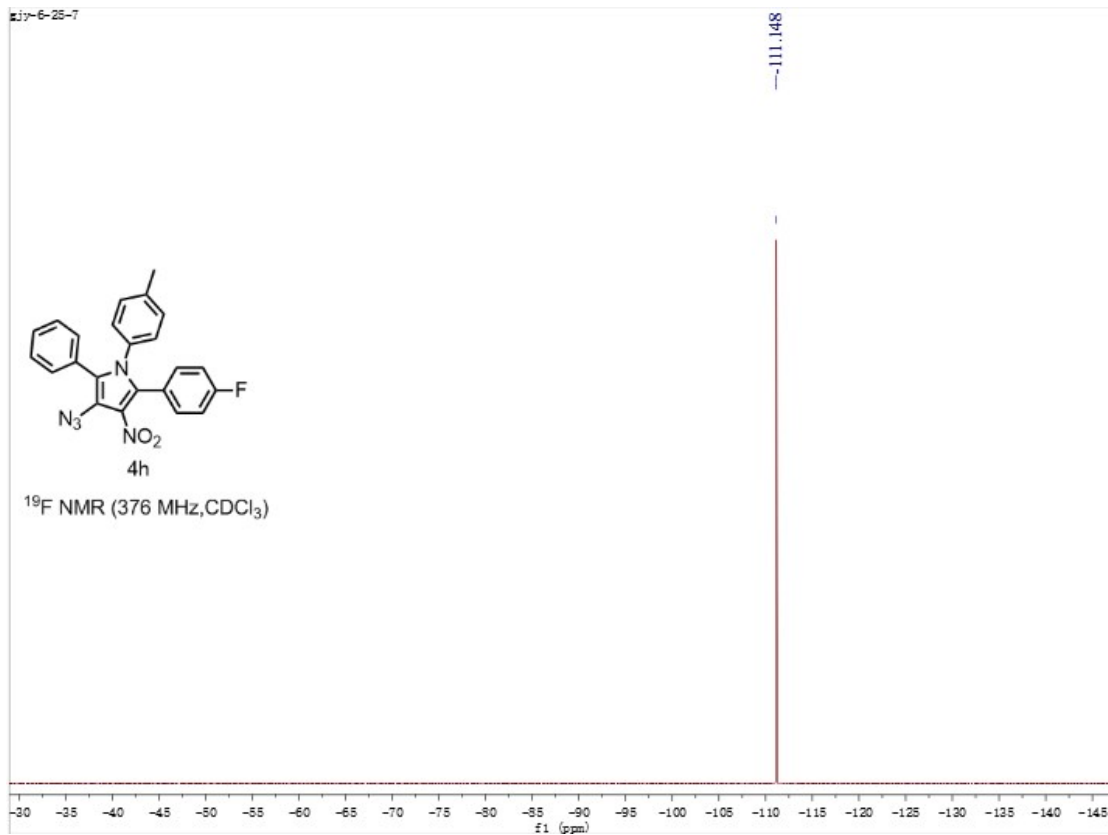
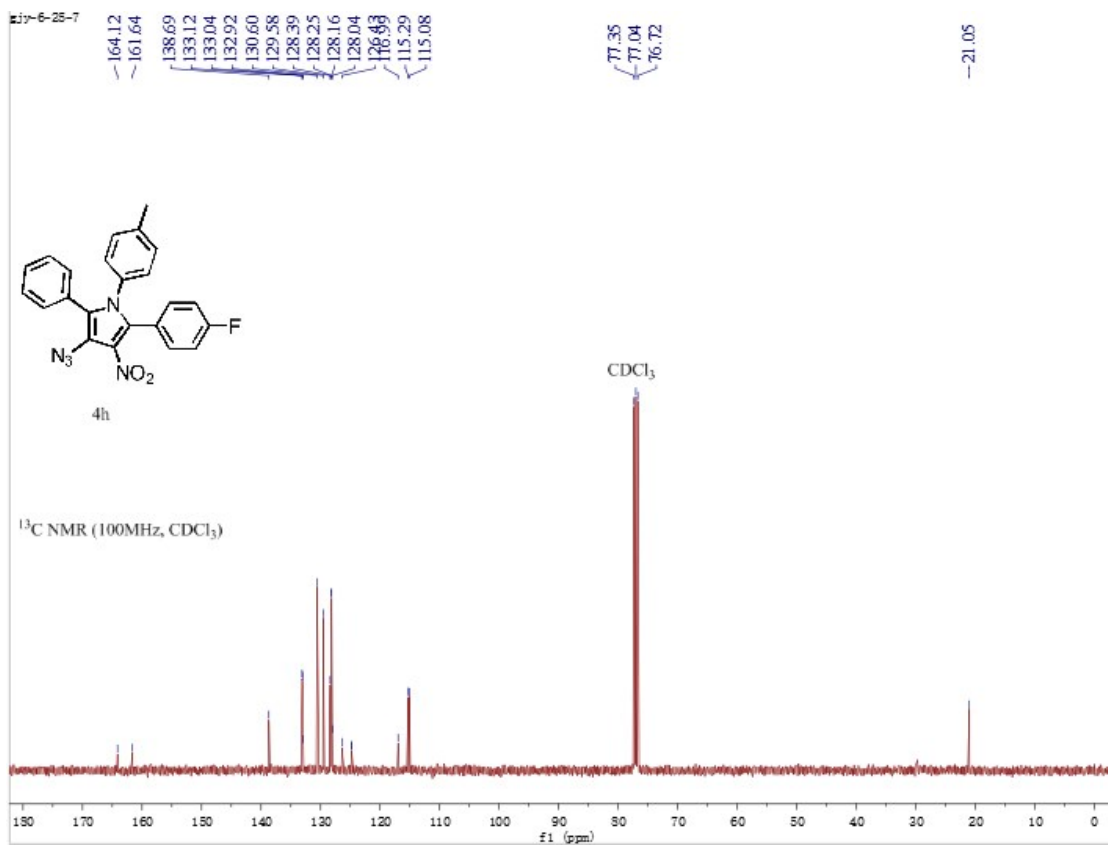
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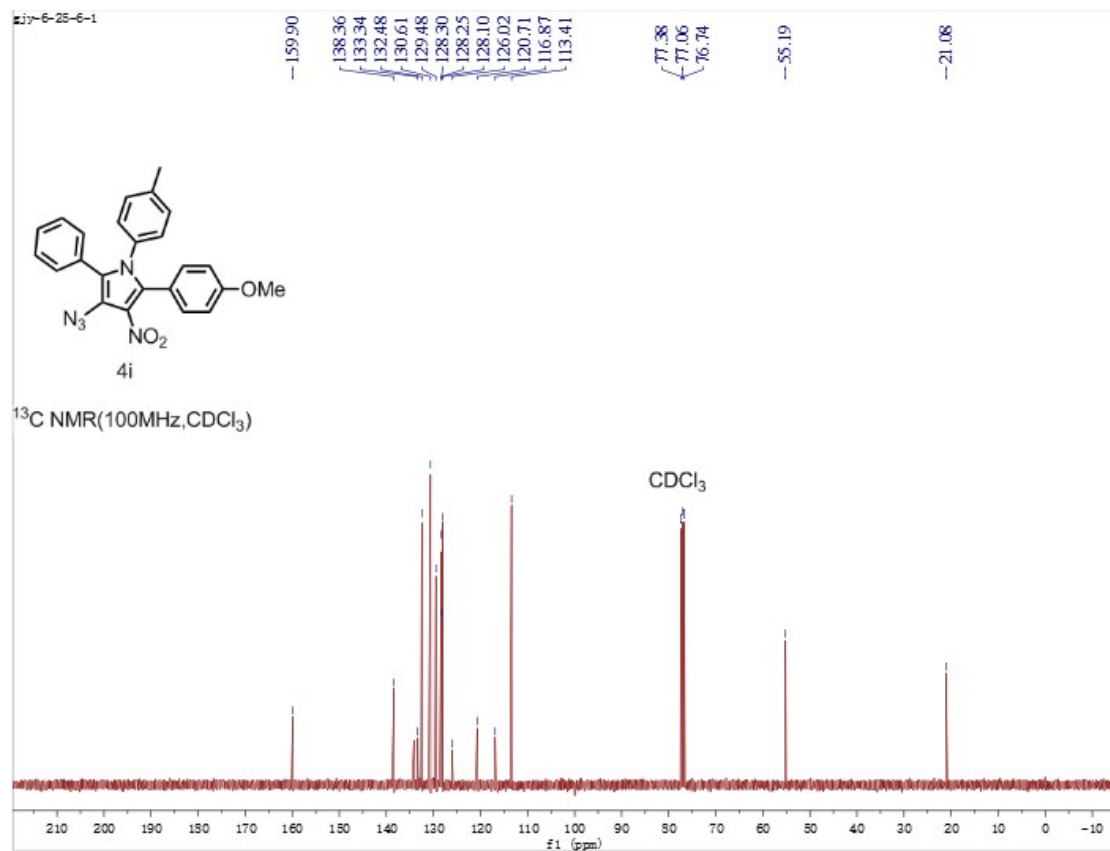
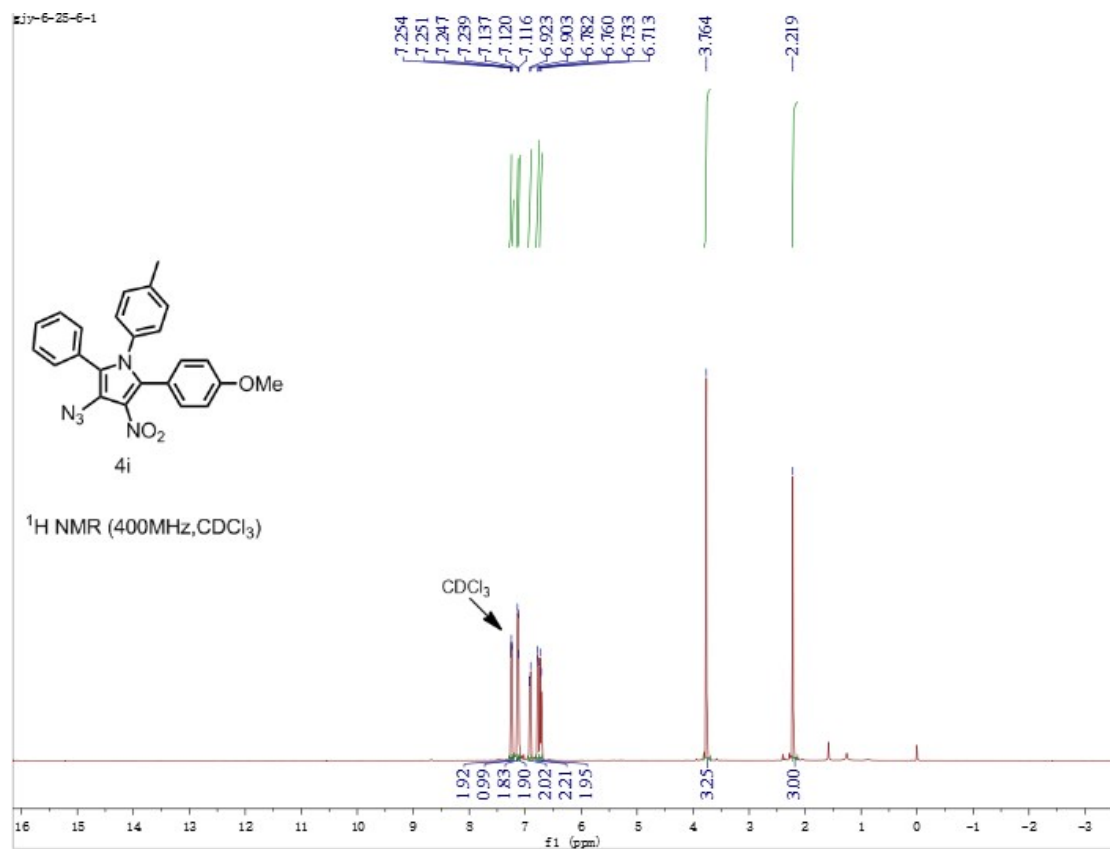
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

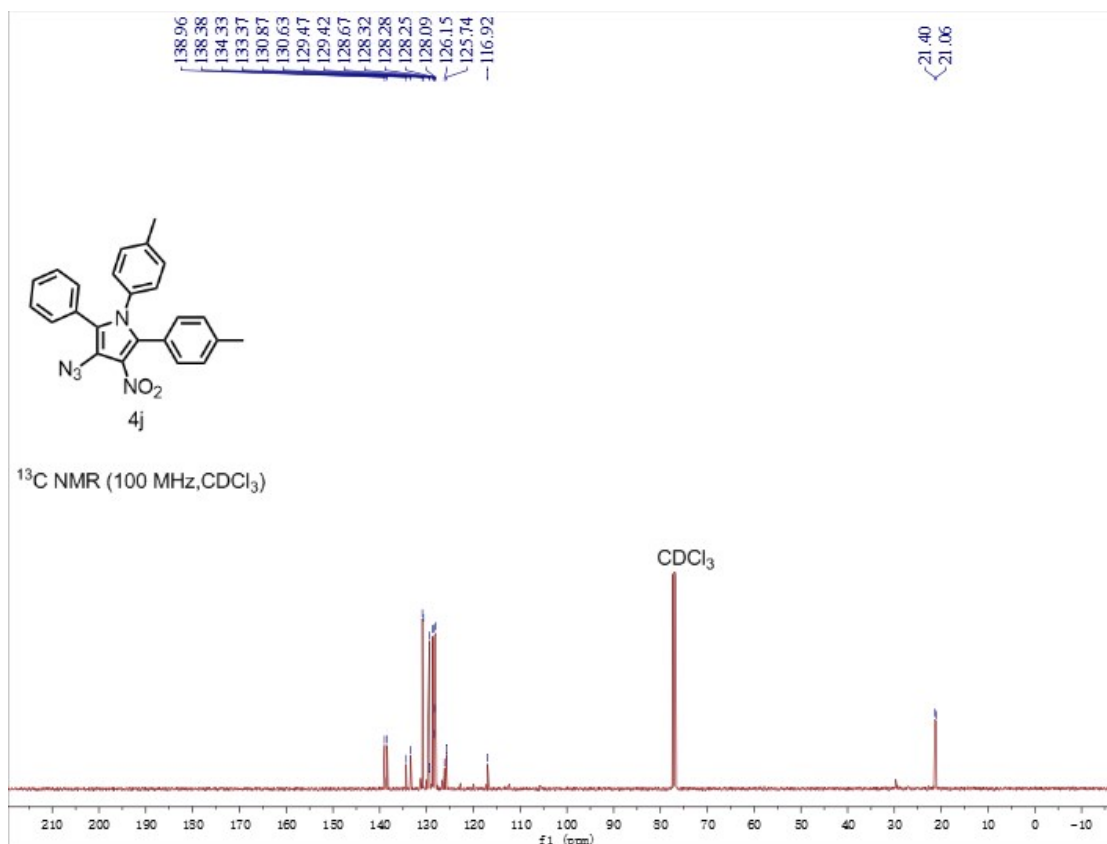
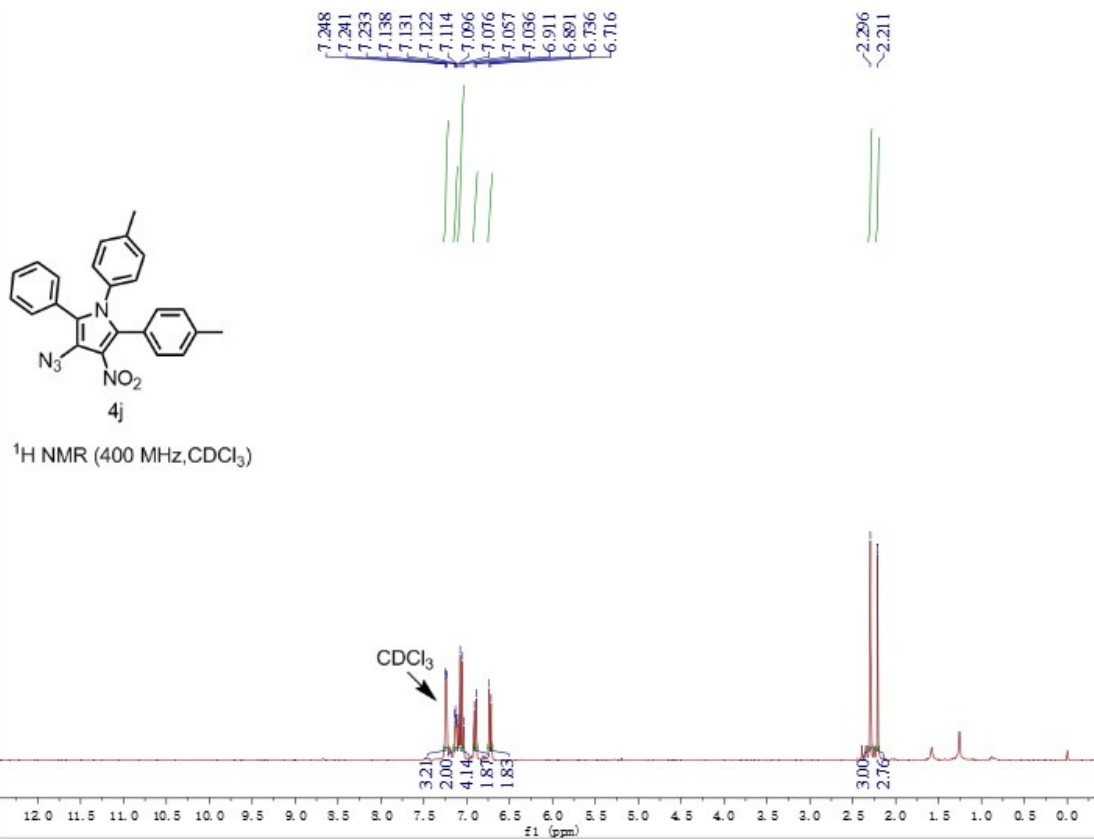




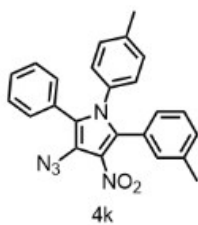




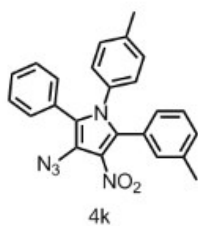
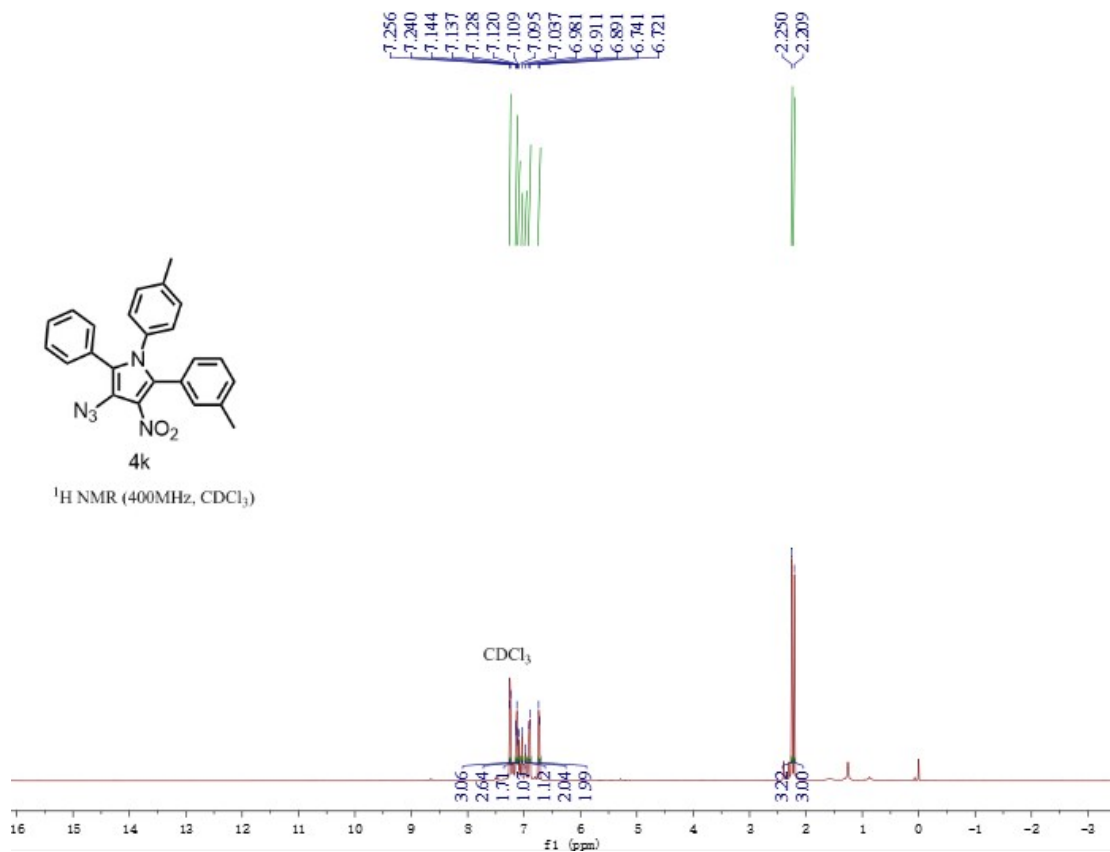




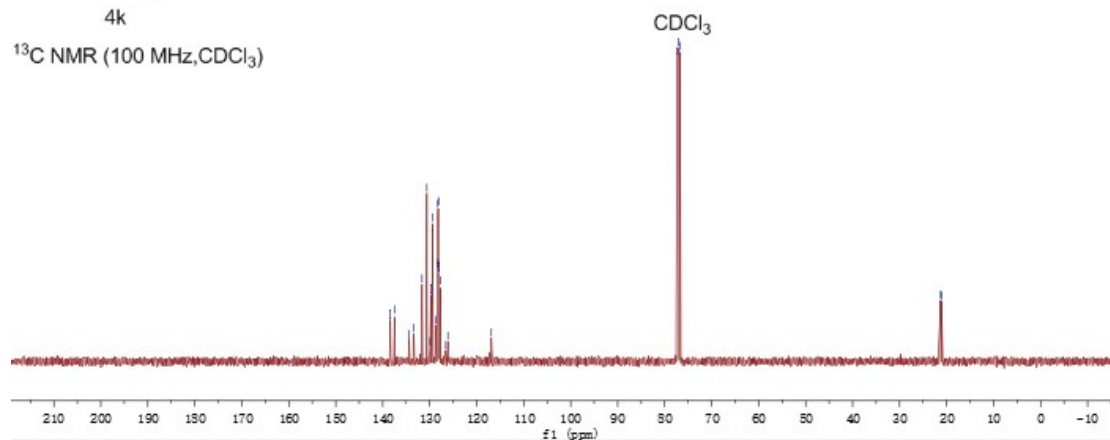


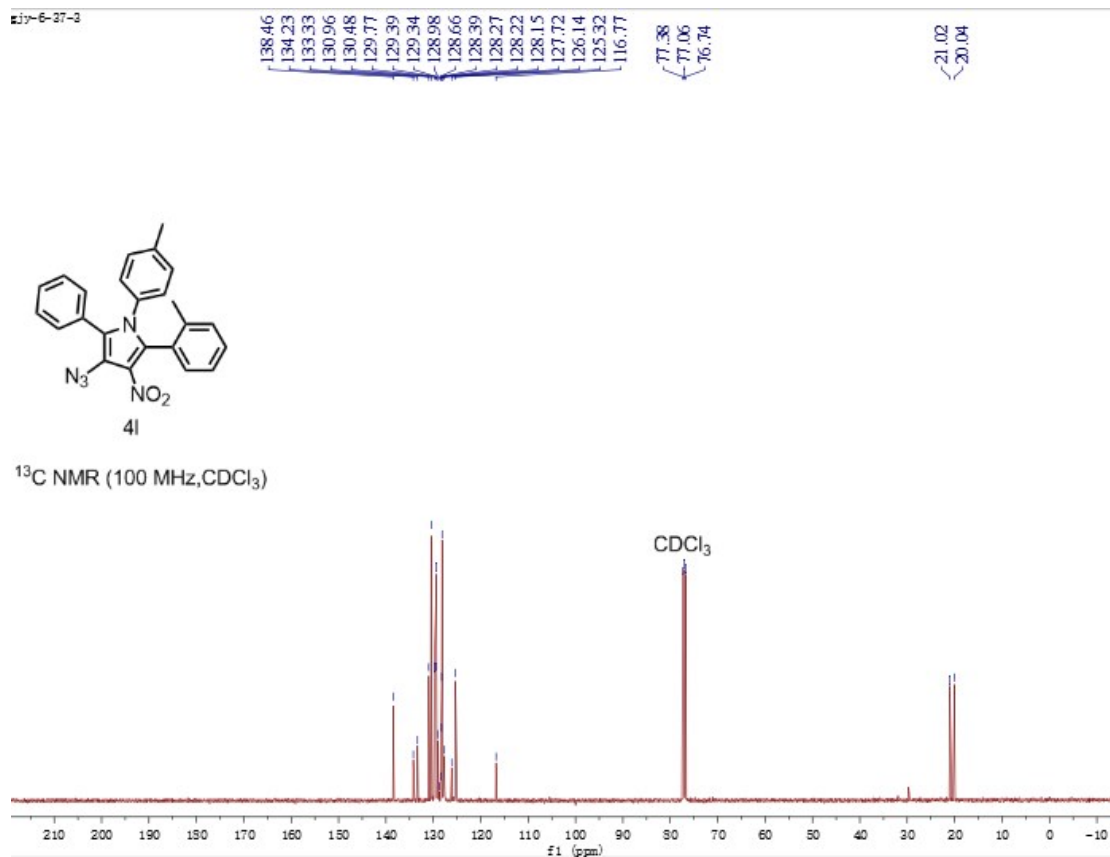
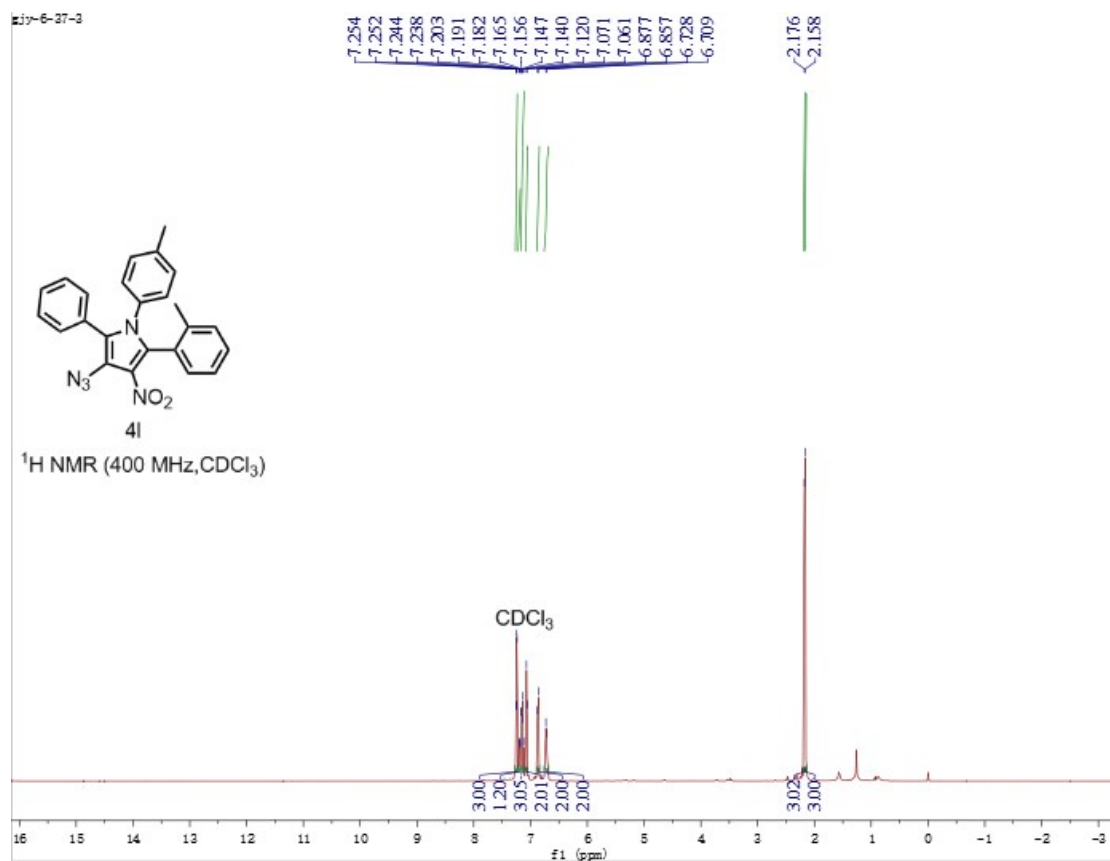


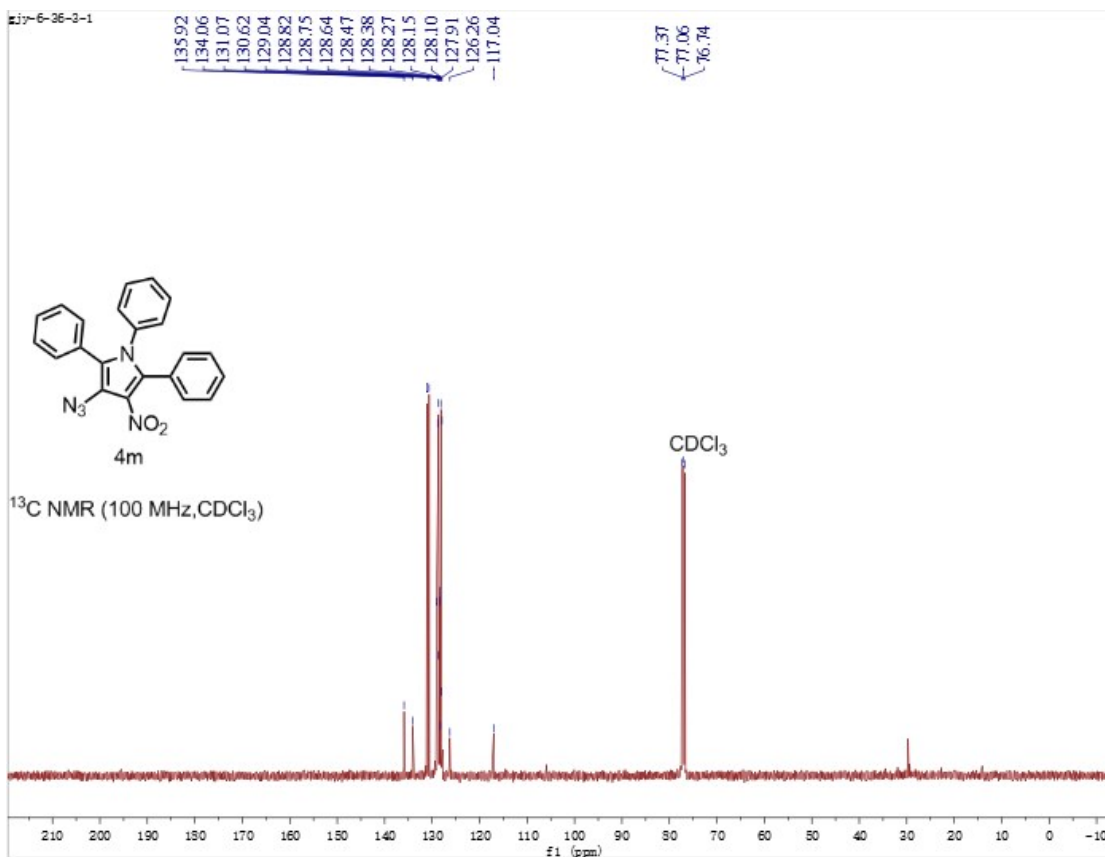
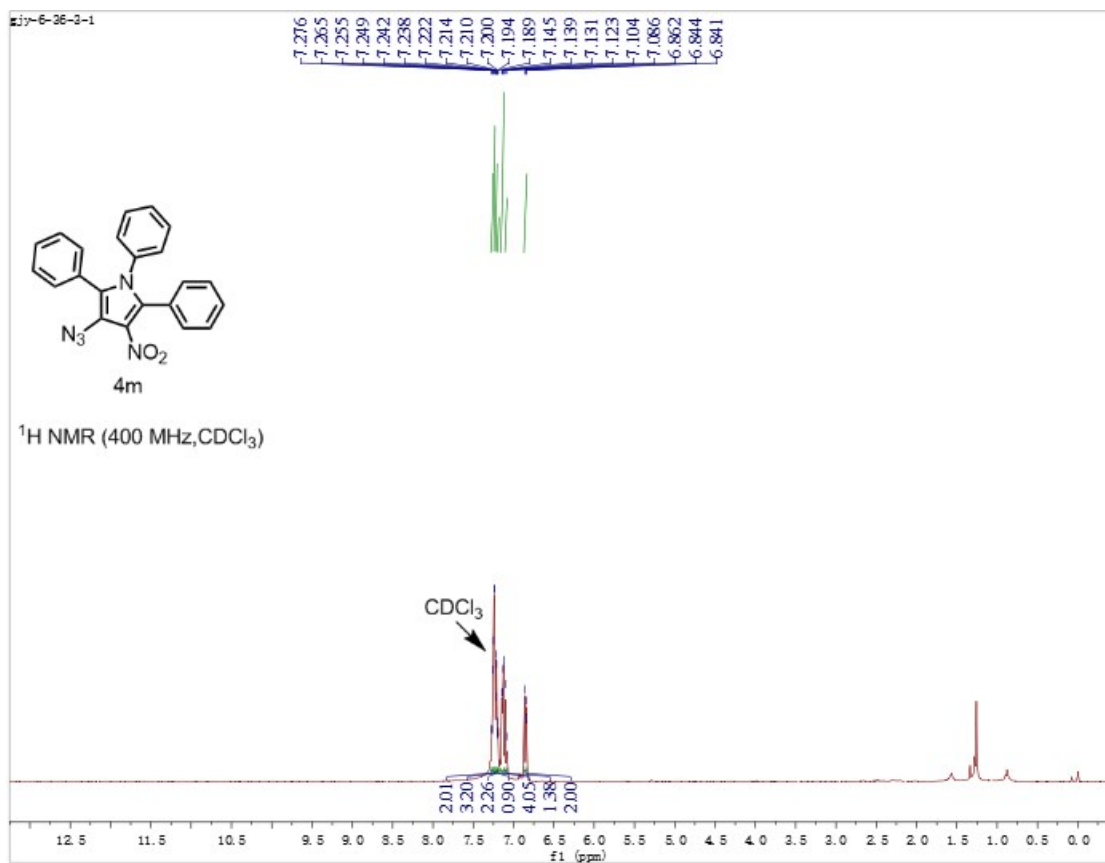
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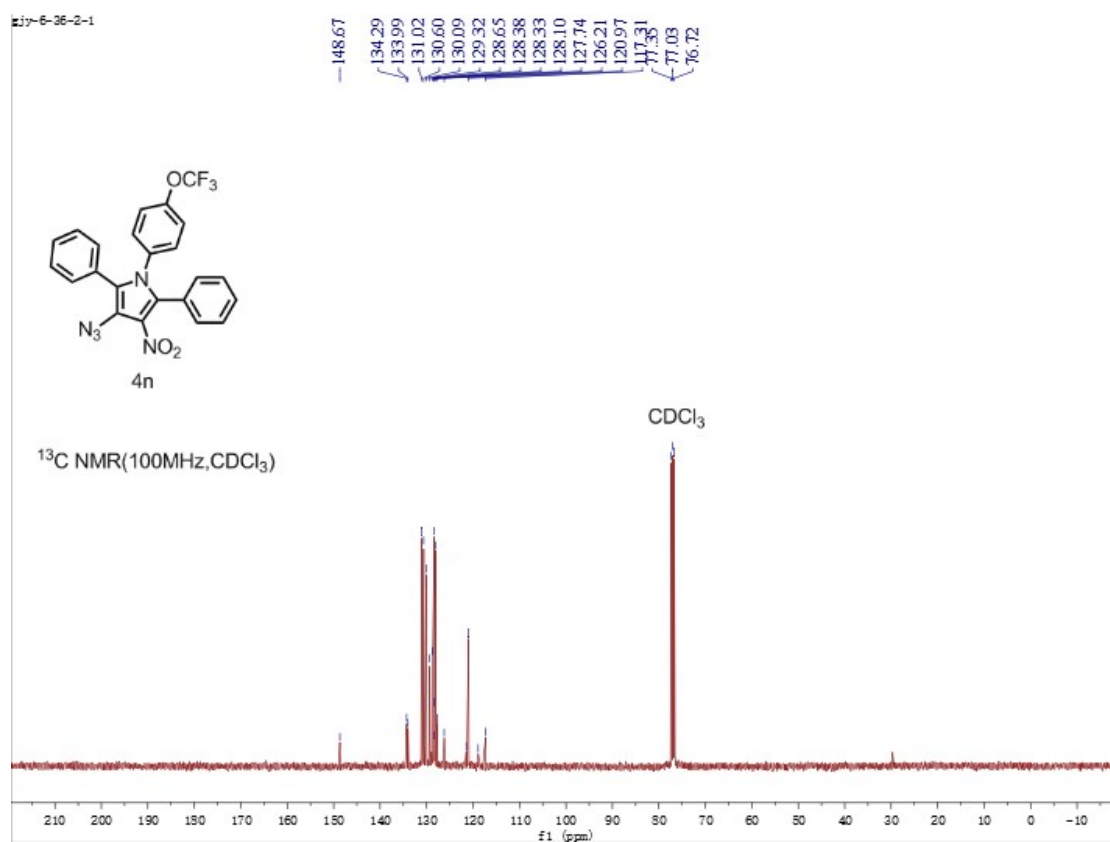
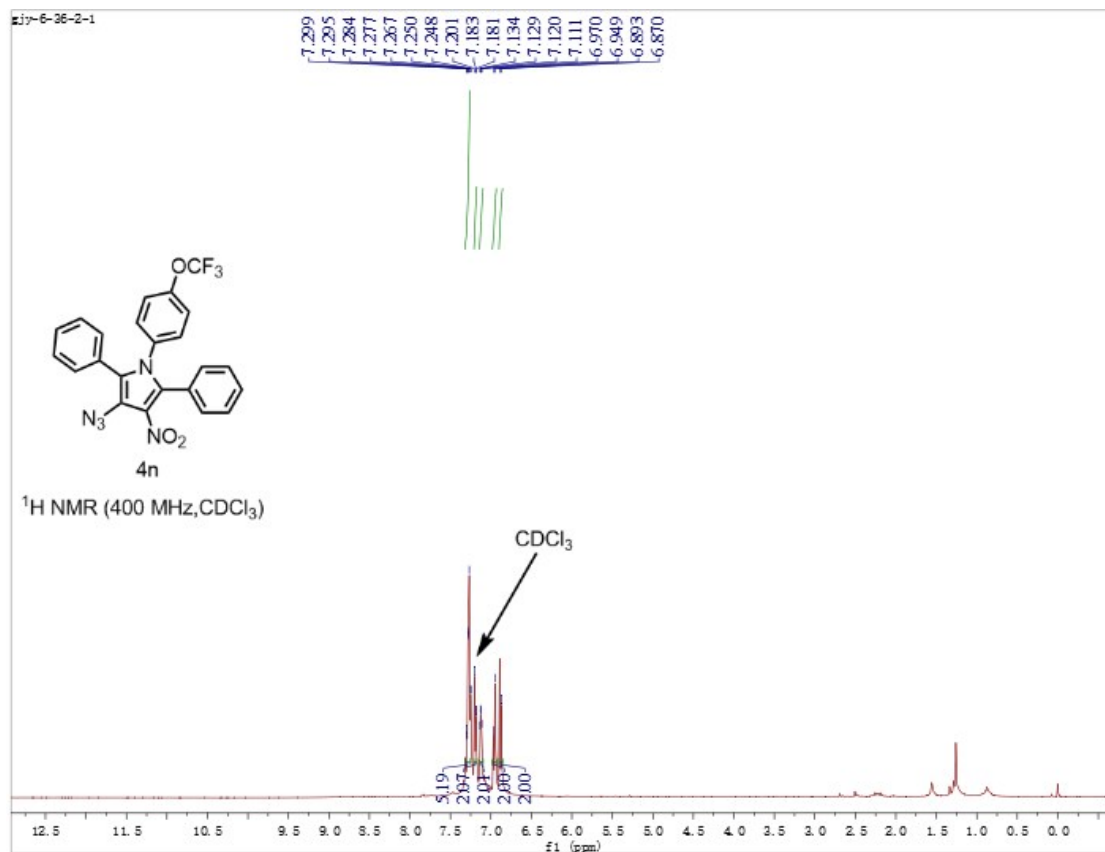


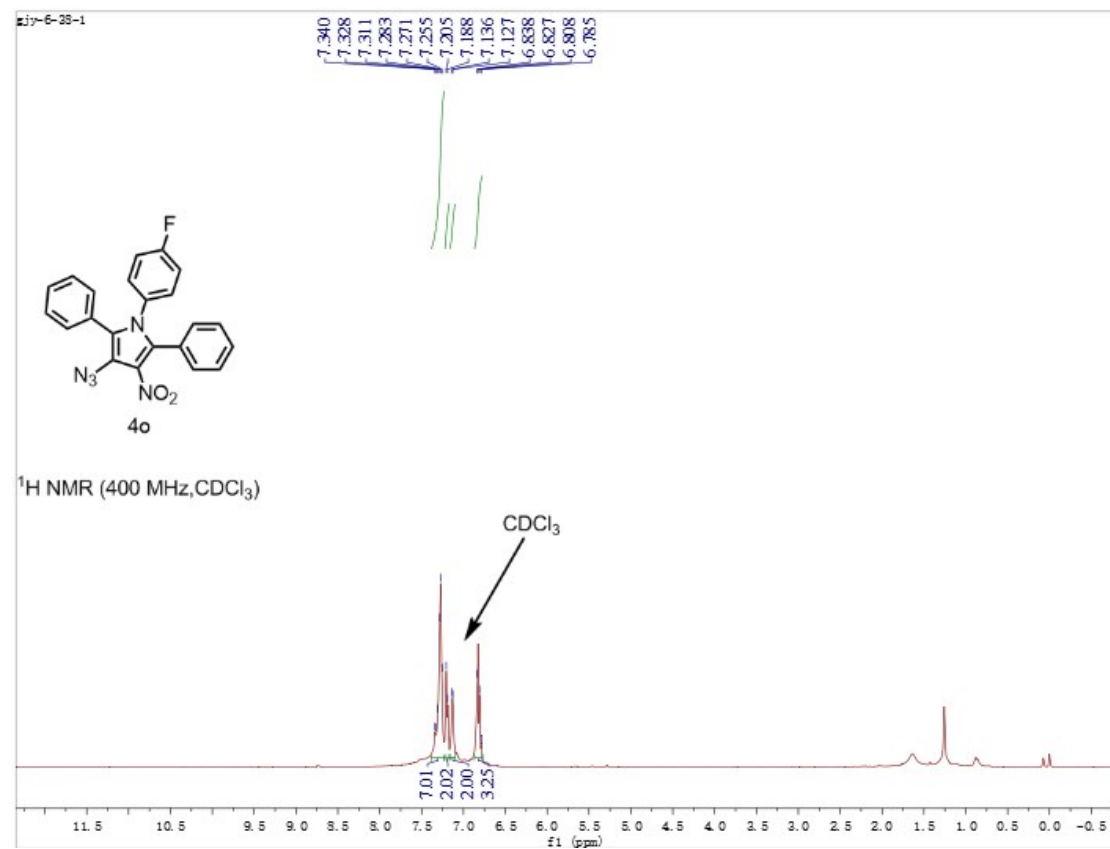
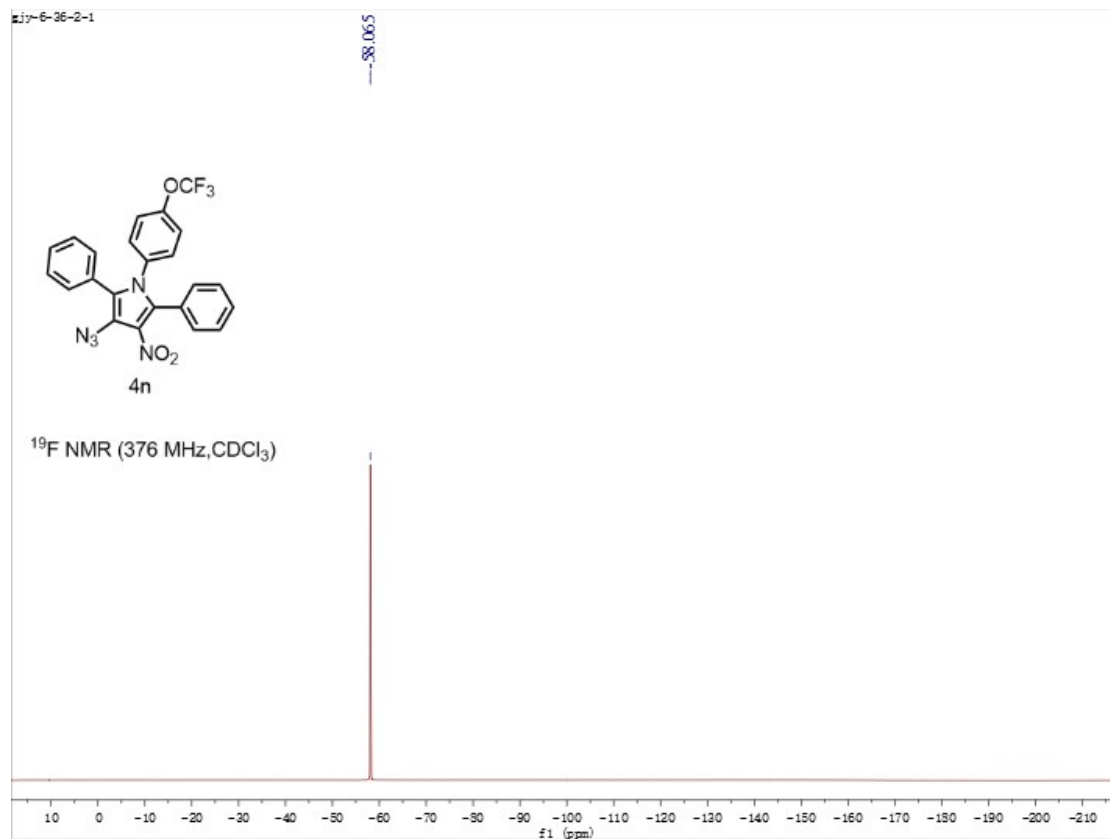
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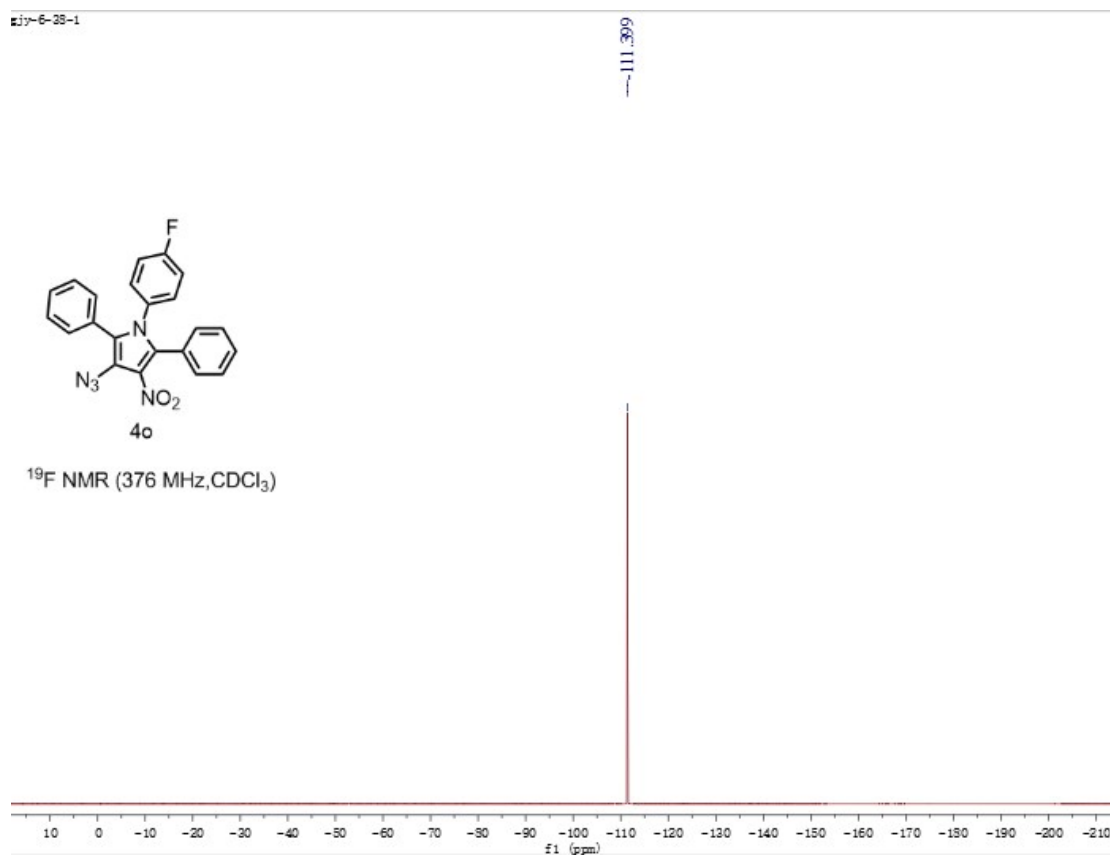
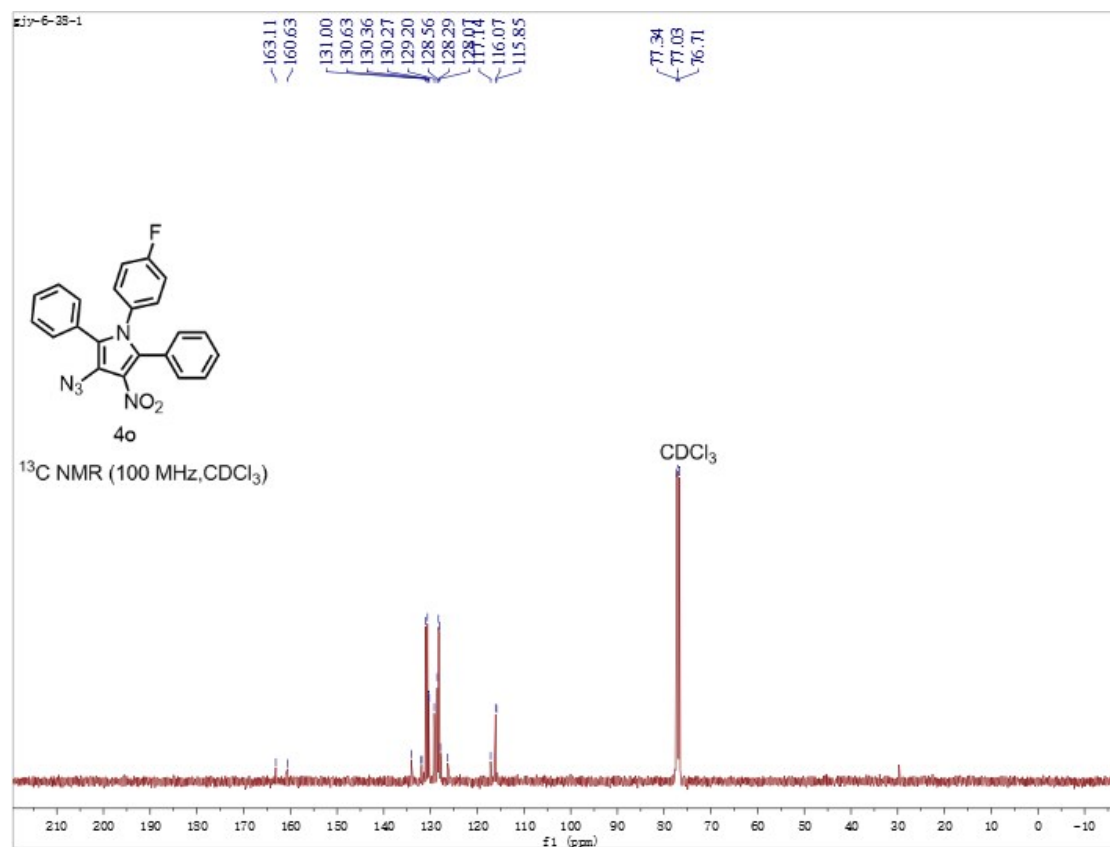


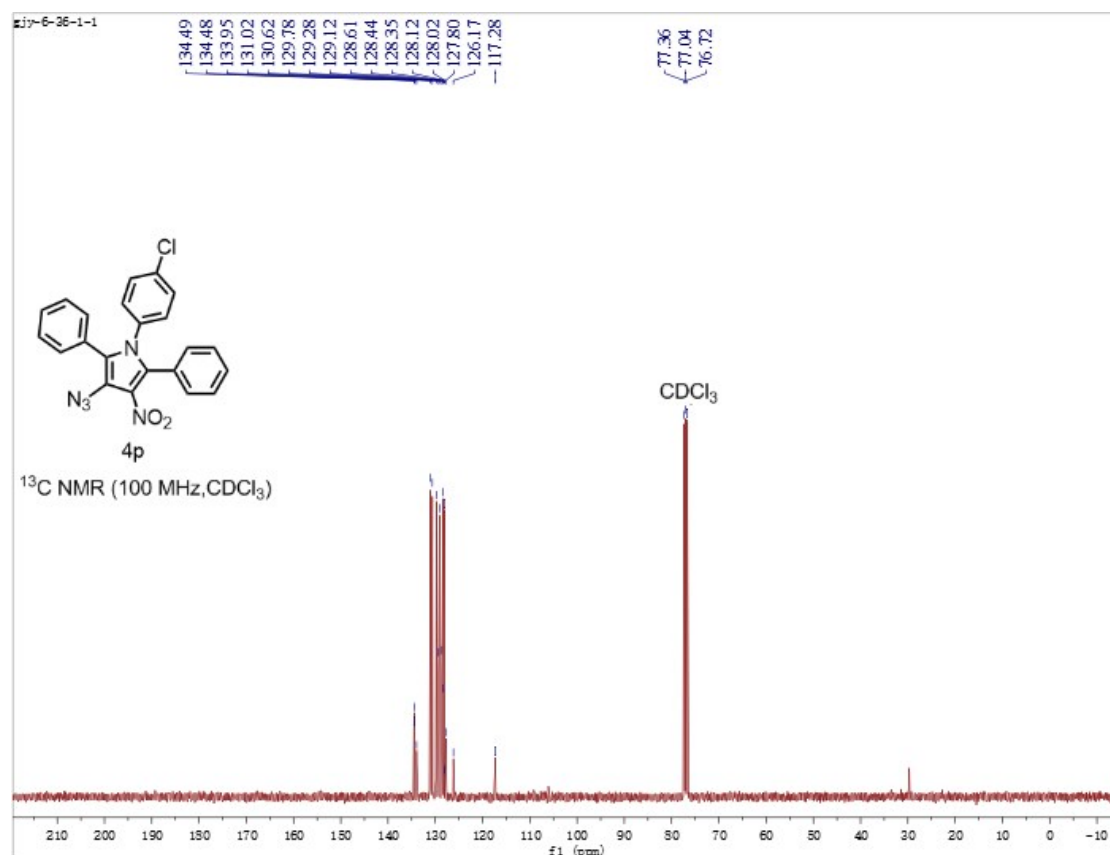
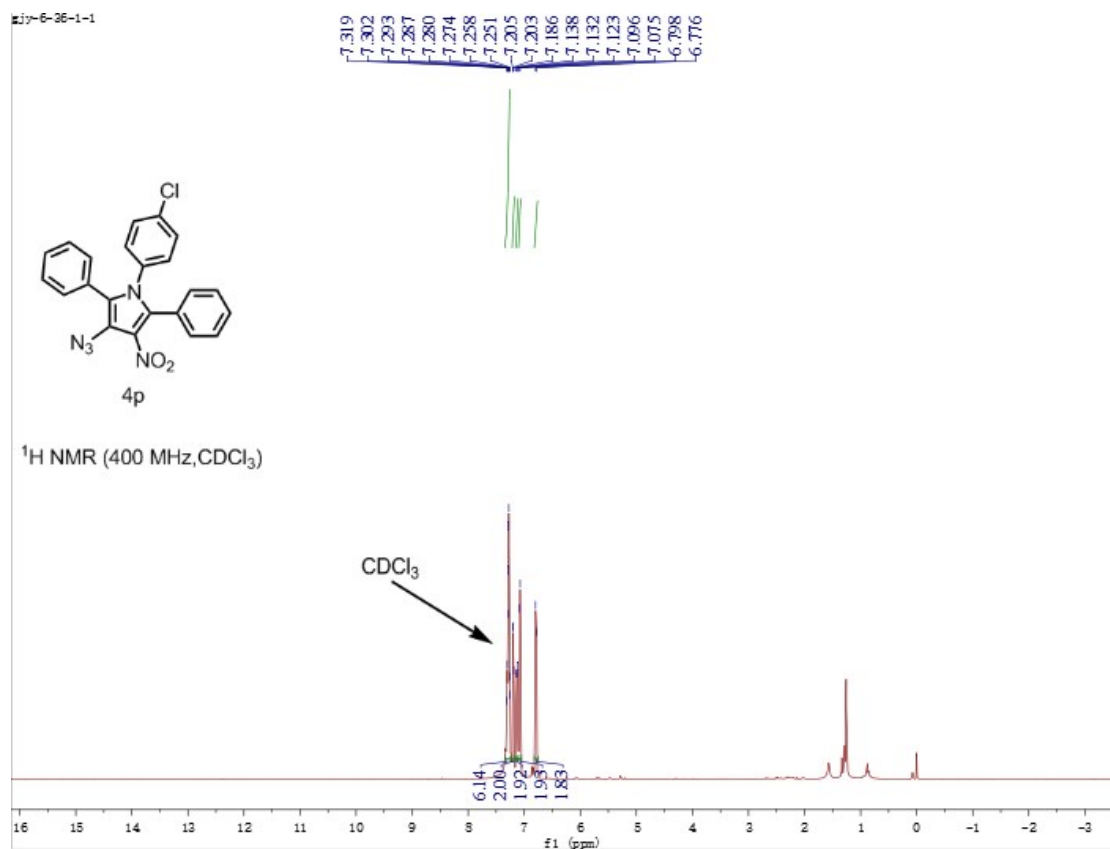




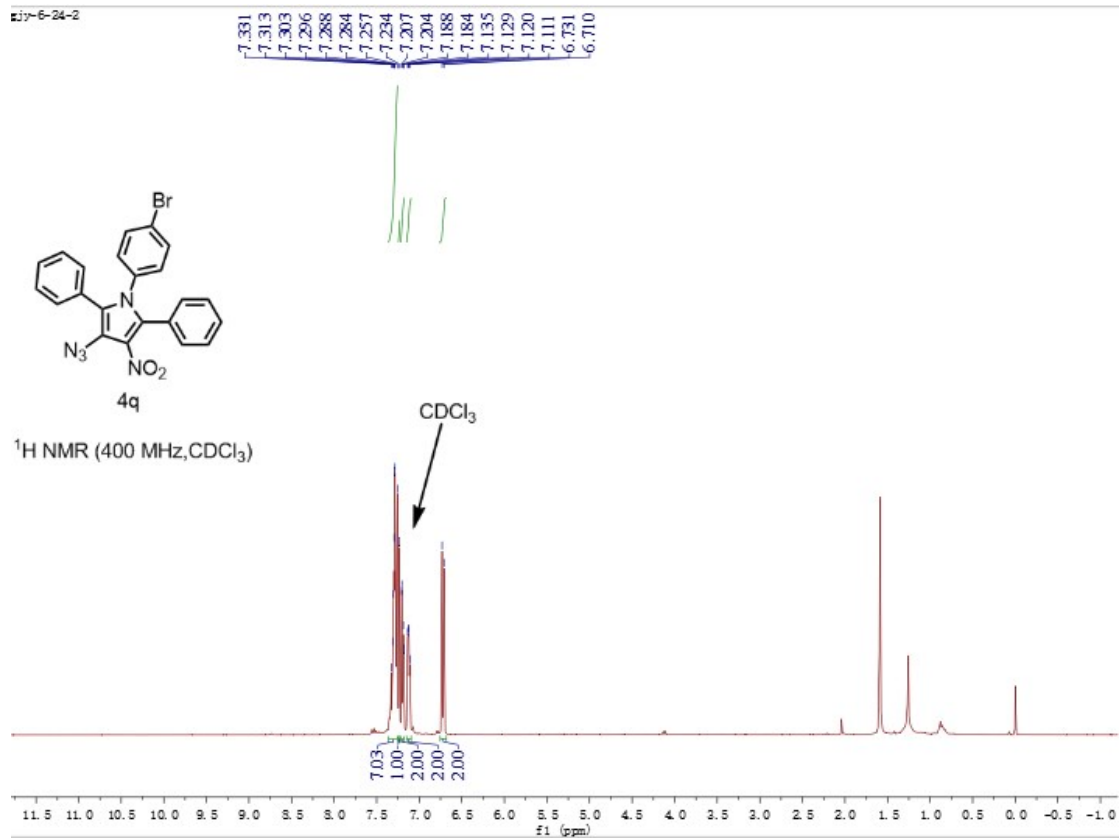




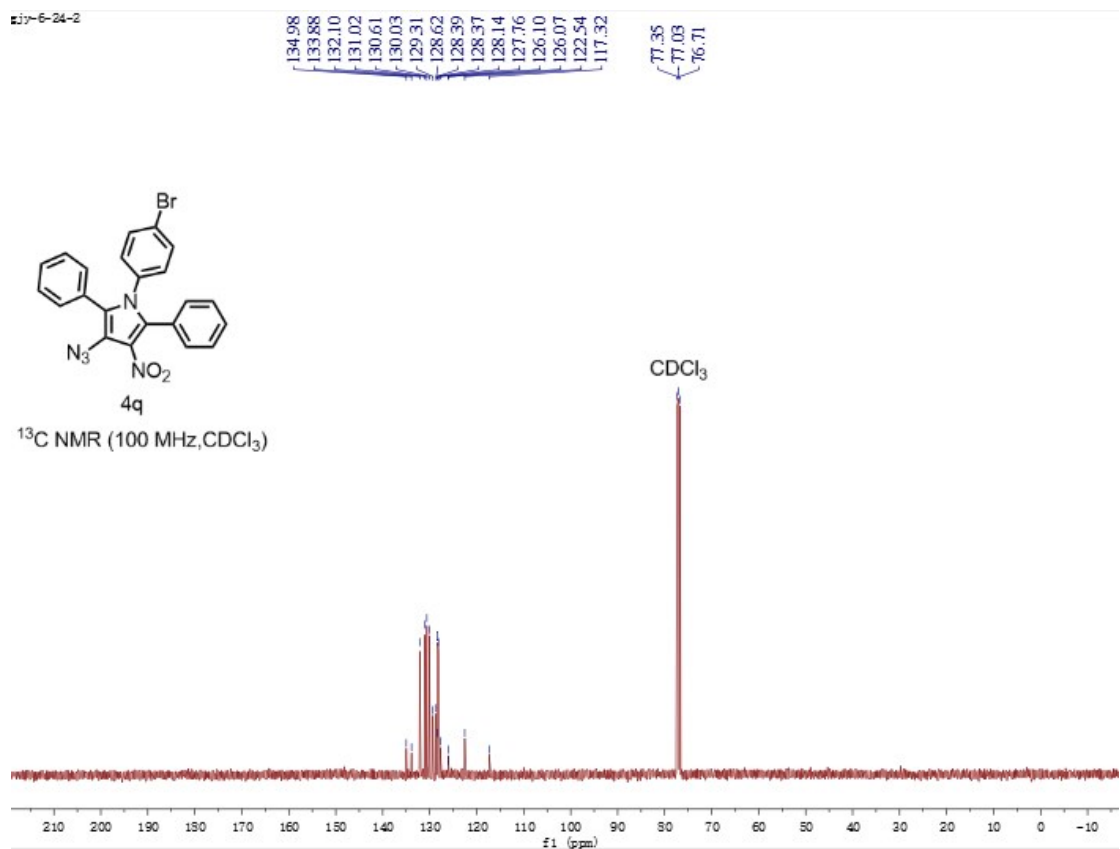




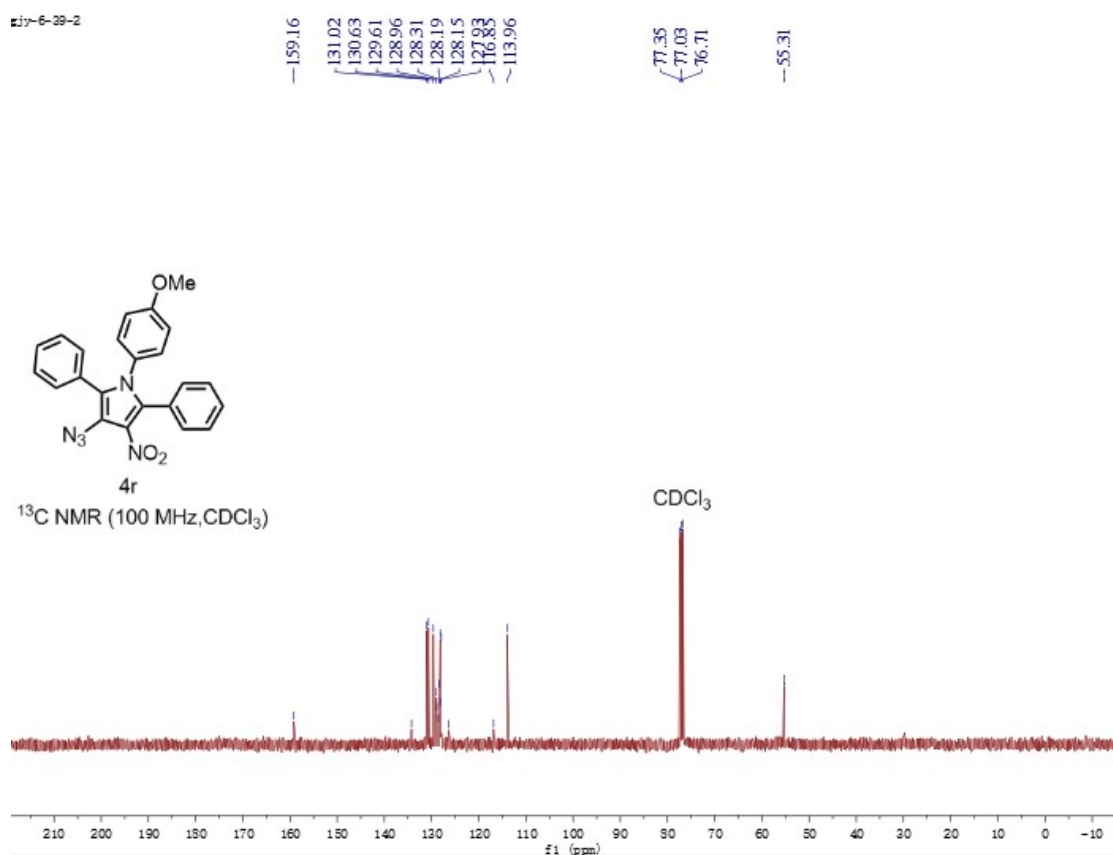
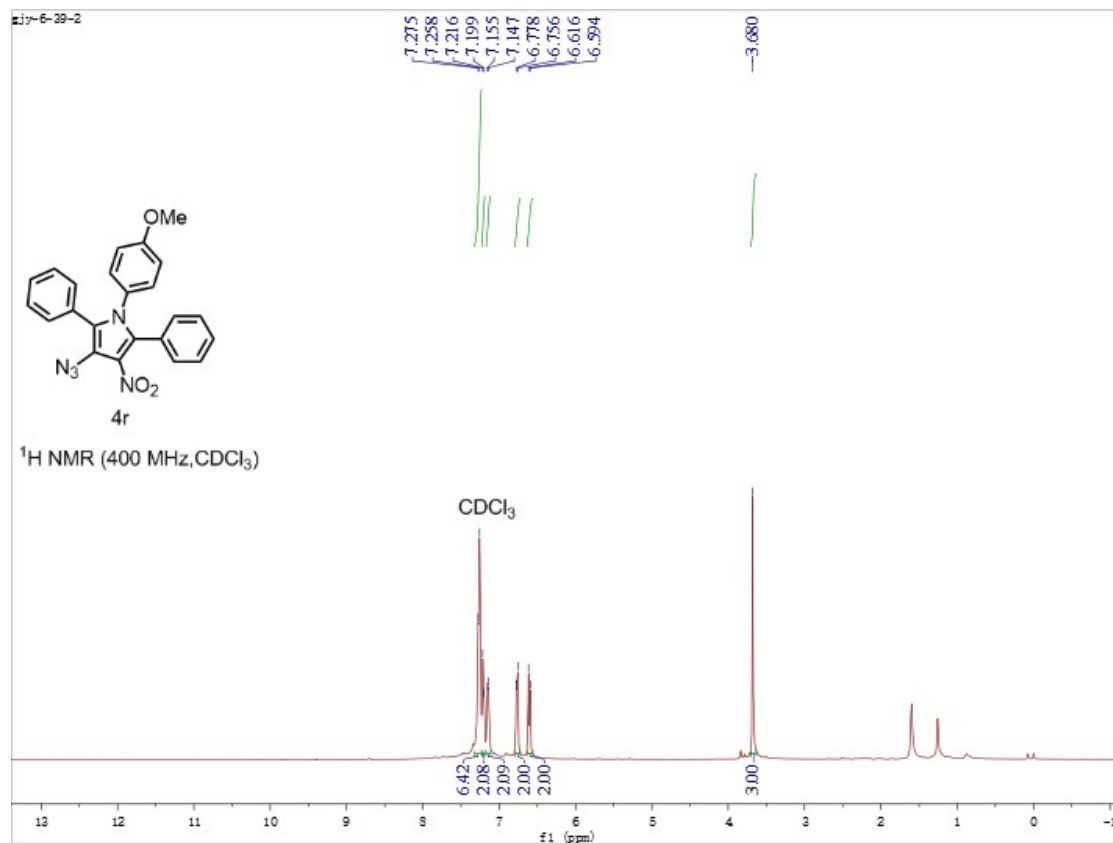
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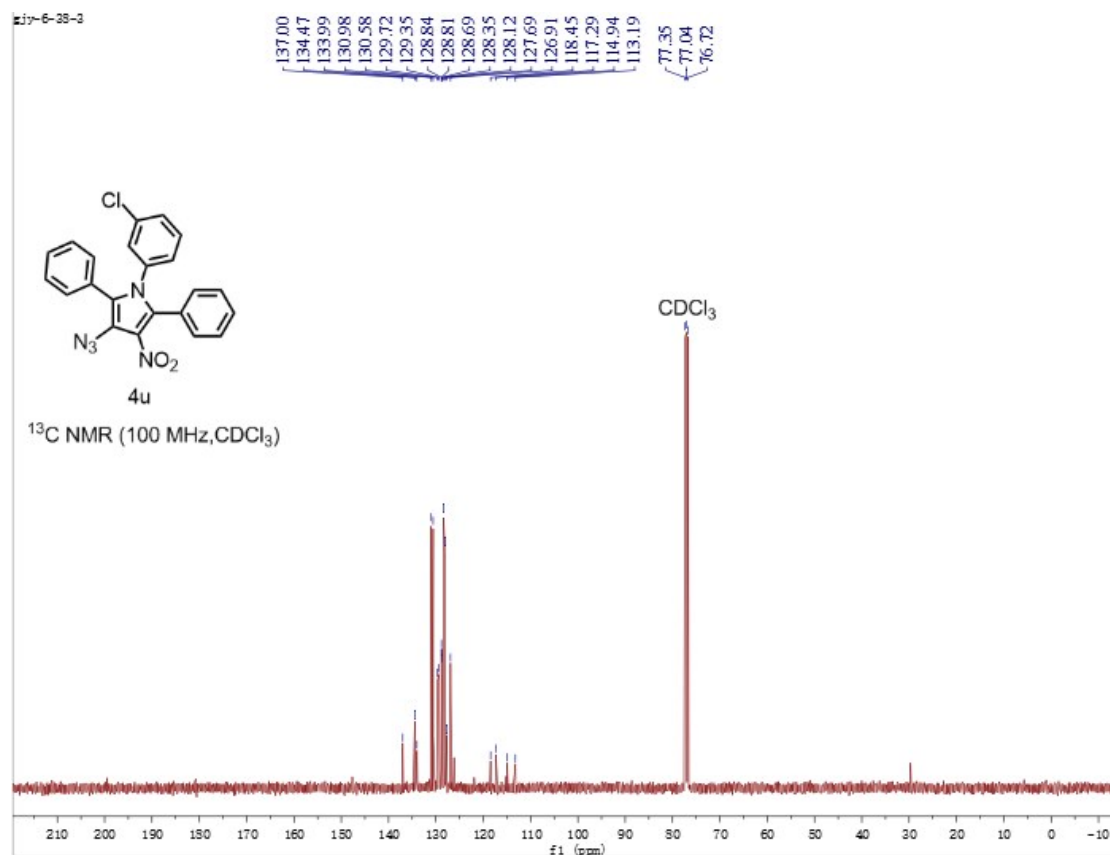
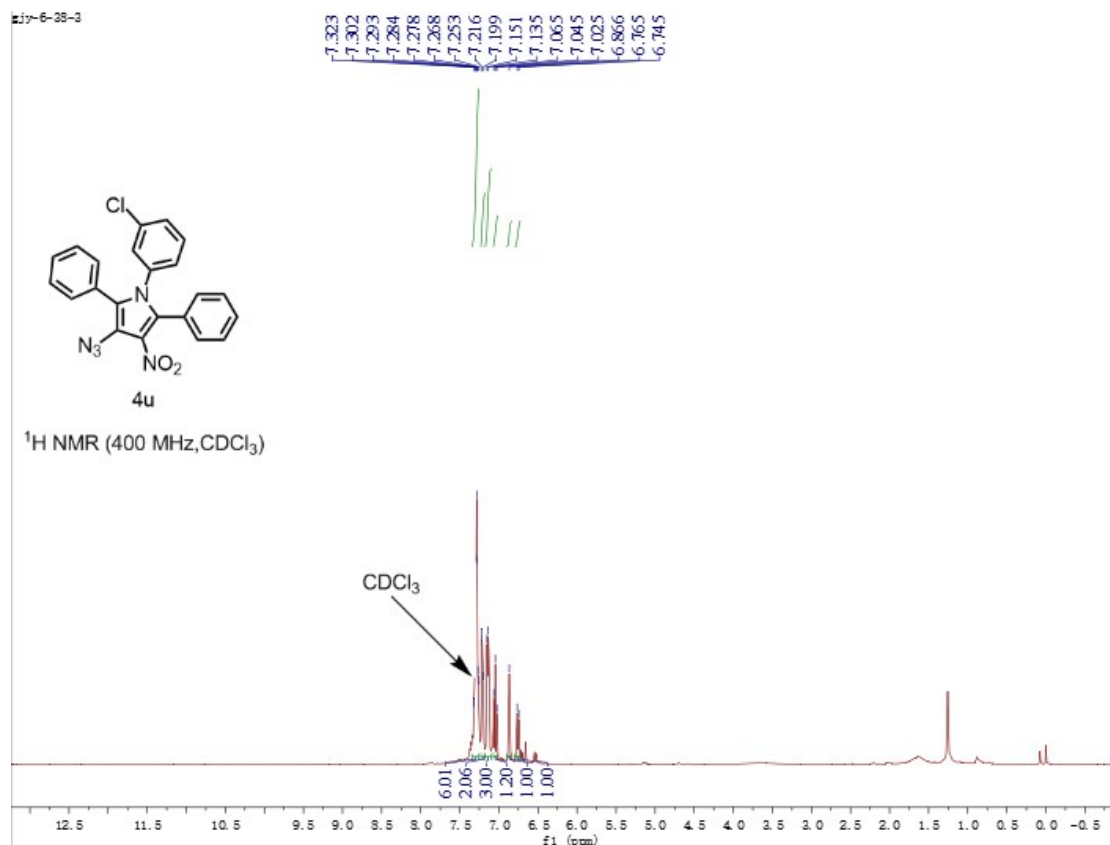


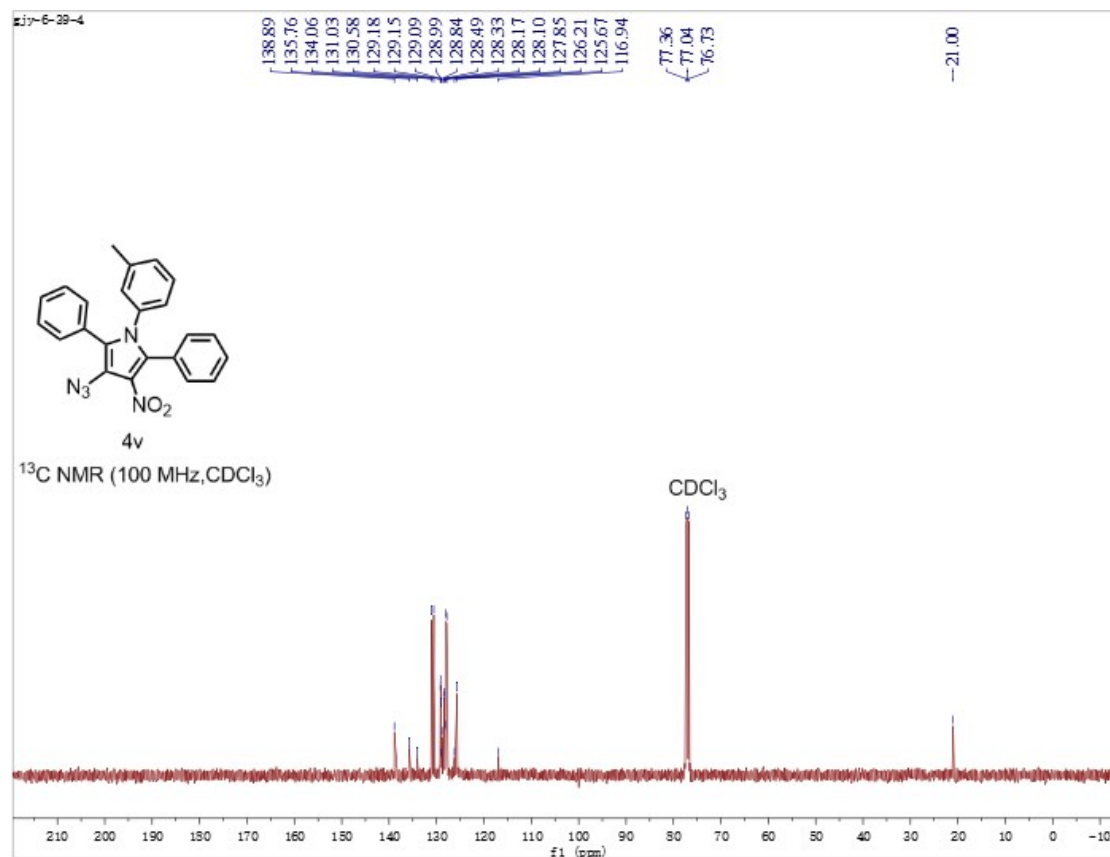
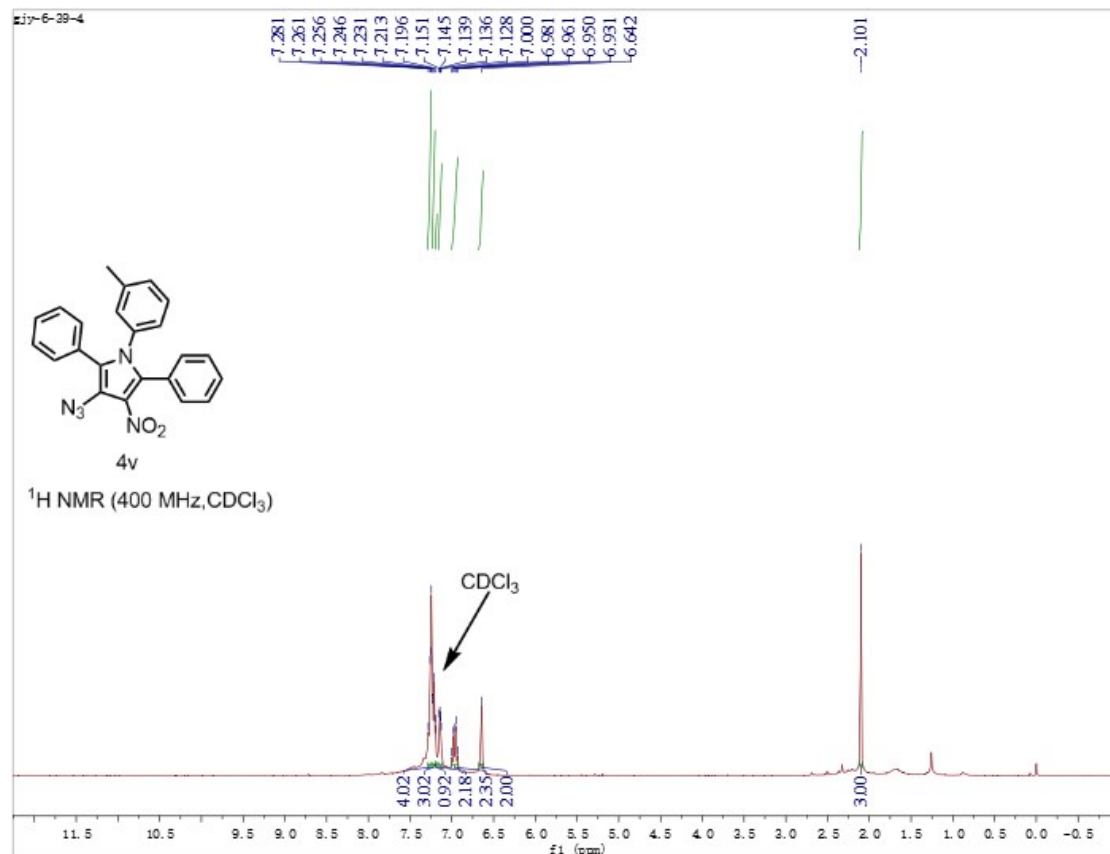
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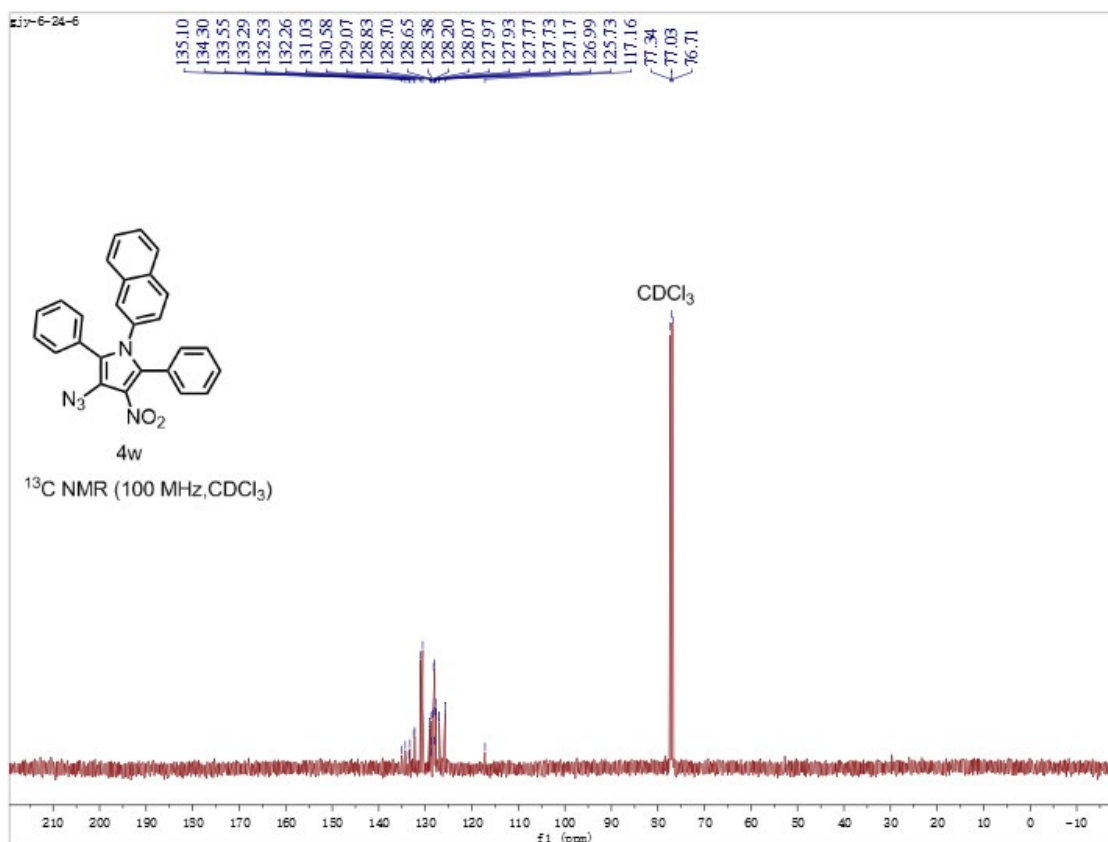
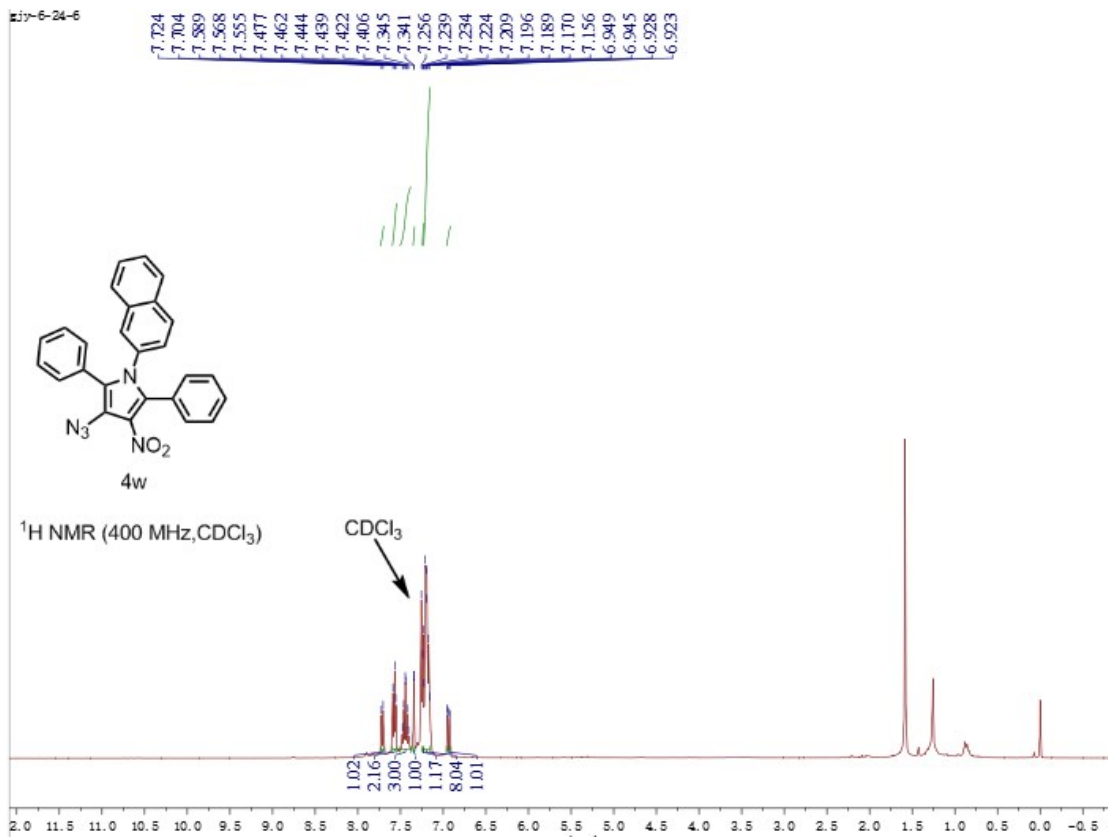




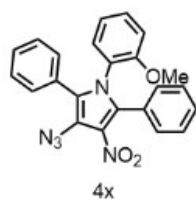




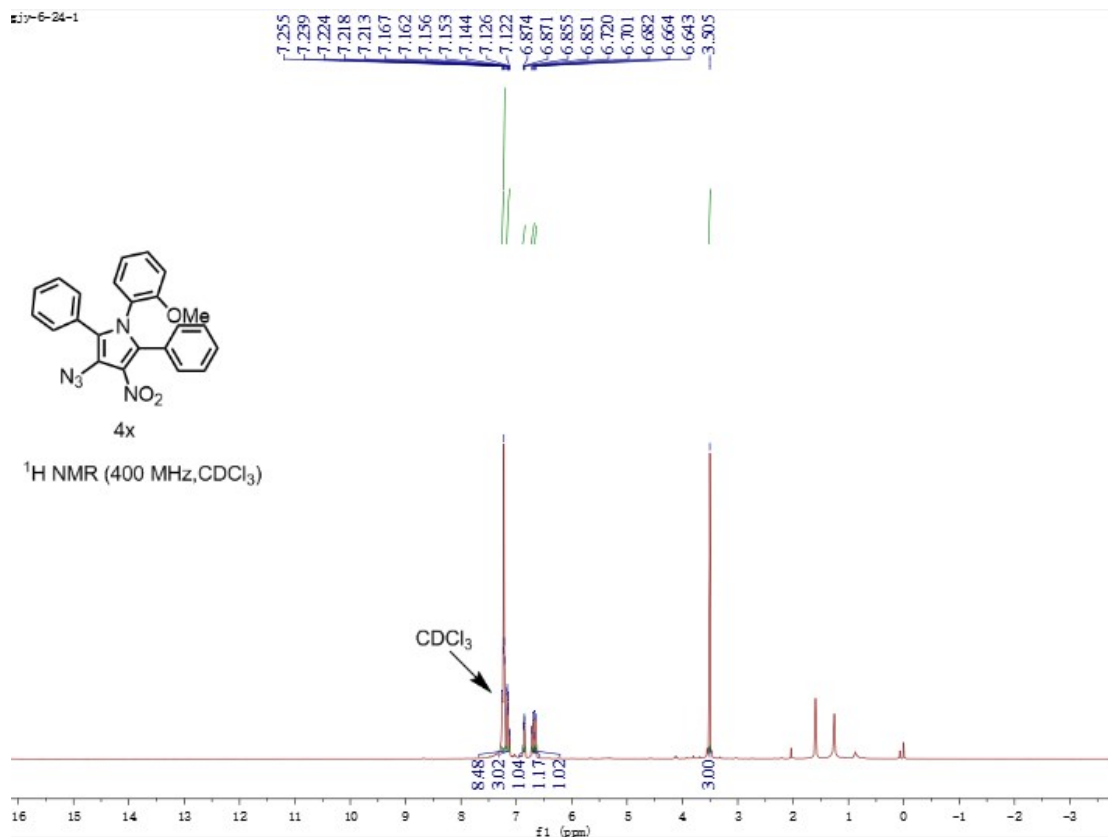




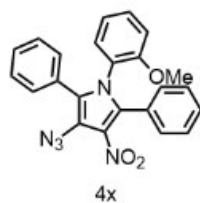
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<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



zjy-6-24-1



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

