

Supporting Information for

**Iron(III) chloride-promoted cyclization of α,β -
alkynic tosylhydrazones with diselenides: Synthesis
of 4- (arylselanyl)-1*H*-pyrazoles**

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Technology, Soochow University, Suzhou, 215123, P. R. China*

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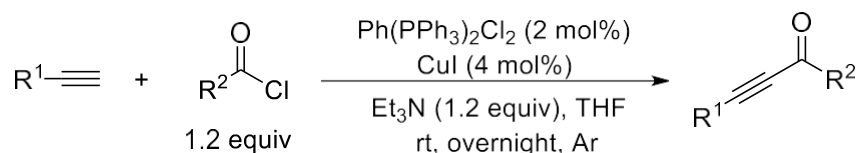
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Experimental Section

1. General procedures for the synthesis of N-Tosylhydrazones

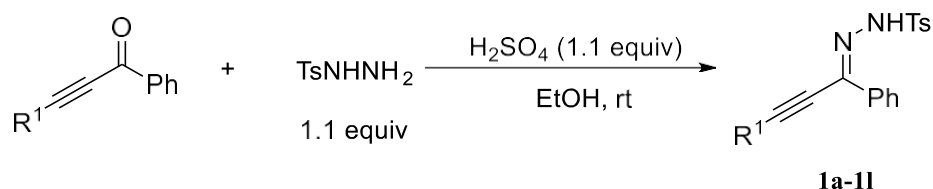
1a -1p were prepared by the following methods



Preparation of 1,3-Diphenylprop-2-yn-1-one

Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol) and CuI (76.2 mg, 0.4 mmol) were charged into a Schlenk tube and the tube was refilled with argon. Then THF (30 mL) was added to the tube. Benzoyl chloride (1.40 mL, 1.2 equiv), phenyl acetylene (1.10 mL, 10 mmol), and triethylamine (1.66 mL, 1.2 equiv) were added to the mixture at room temperature. The reaction mixture was stirred at room temperature overnight. Saturated NaCl solution was added to the mixture and the resulting aqueous phase was extracted with EtOAc (15 mL × 3). The combined organic phase was washed with brine, dried over Na₂SO₄. After removal of the solvent, the resulting crude mixture was purified by silica gel column chromatography (PE/EtOAc = 20/1) to give 1,3-diphenylprop-2-yn-1-one as a pale yellow solid.

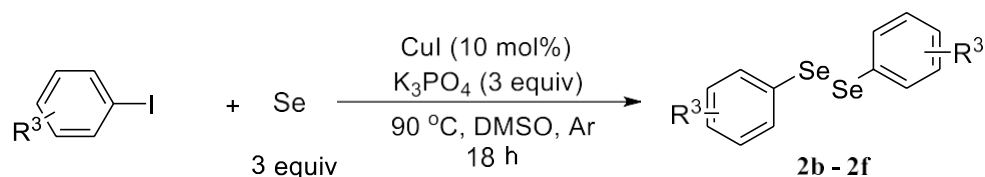
Preparation of (E)-N¹-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazone (**1a**)



Concentrated sulfuric acid (0.6 mL, 1.1 equiv) was added dropwise to α,β-alkynic ketone (10 mmol, 1 equiv) and hydrazine (1.1 equiv) in EtOH at room temperature. The reaction mixture was stirred at room temperature for 15 hours. After the reaction was completed, the mixture was concentrated and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the α,β-alkynic hydrazone.

2. Procedure for the preparation of diaryl diselenides

2b -2f were prepared by the following methods

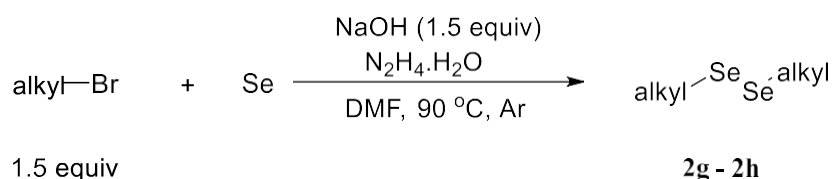


Preparation of 1,2-diphenyldiselenane (**2b**)

To a stirred solution of Se powder (3.0 equiv, 1.185g) and indobenzene (5 mmol, 0.56 mL) in dry DMSO (10.0 mL) was added CuCl (10 mol %, 0.01g) followed by K₃PO₄ (3.0 equiv, 3.184g) under argon atmosphere at 90 °C. And the reaction lasted for 18 h. After the reaction was complete, EtOAc (15 mL) was added and the mixture was washed successively with water (20 mL×2). The organic layer was separated and dried by adding anhydrous Na₂SO₄. Removal of the solvent under reduced pressure could afford the products. Further purification was achieved by column chromatography on silica gel (PE/EtOAc = 50/1) to give pure product in good to excellent yield.

3. Procedure for the preparation of dialkyl diselenides

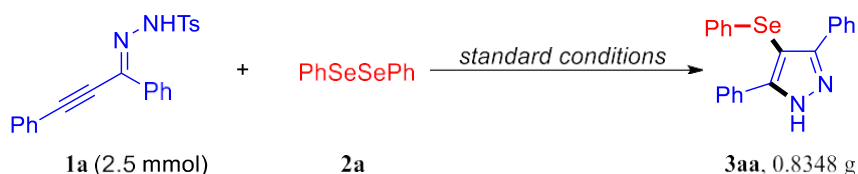
2g -2h were prepared by the following methods



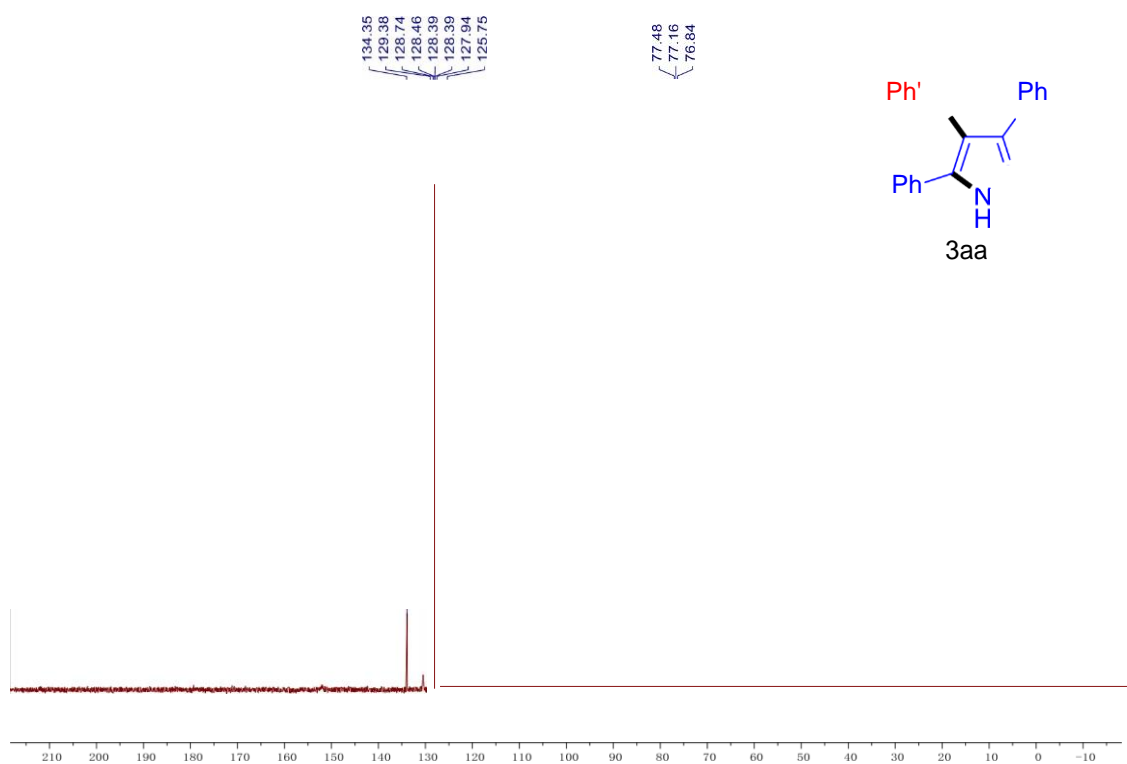
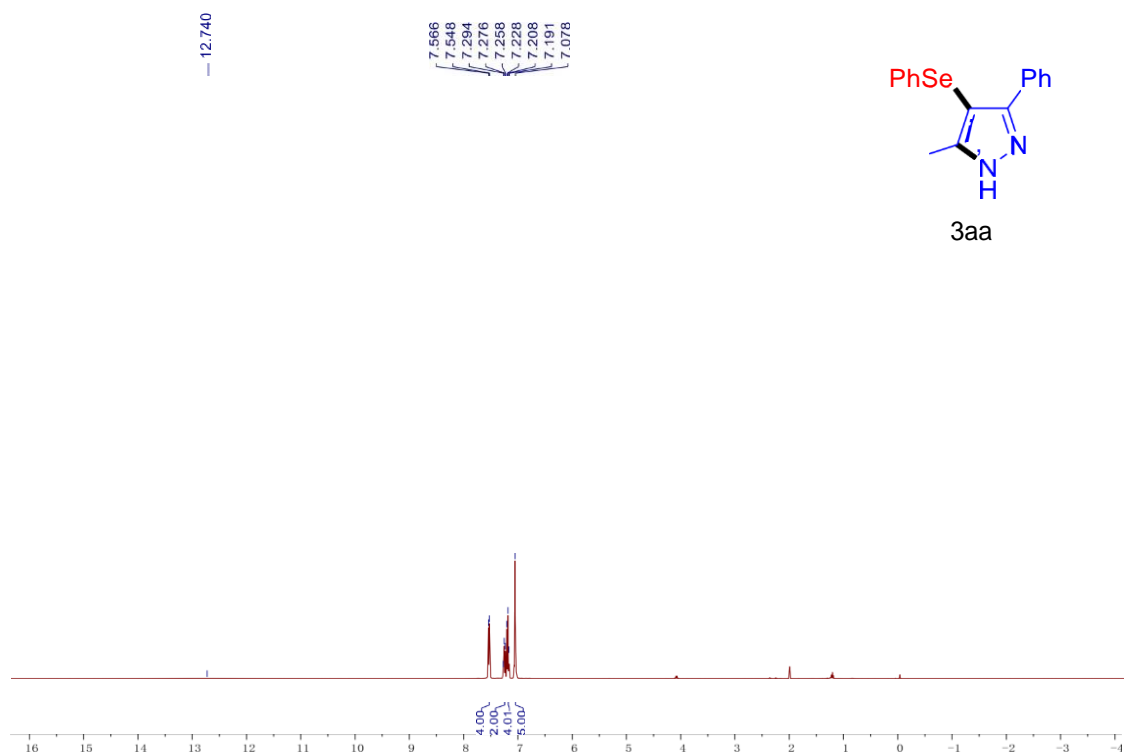
To a mixture of selenium powder (0.869 g, 11 mmol) and sodium hydroxide (1.5 equiv, 0.66 g) was added 70% hydrazine hydrate (0.15 mL) under argon. The mixture was heated to 90 °C with stirring in DMF. Then butyl bromide (1.5 equiv, 1.77 mL) was added into the tube and led to the forming of a heavy oil. When the mixture cooled down, the organic layer was extracted with petroleum ether (15 mL×2). The combined organic layer was washed with water (10 mL×2), and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure could afford the products.

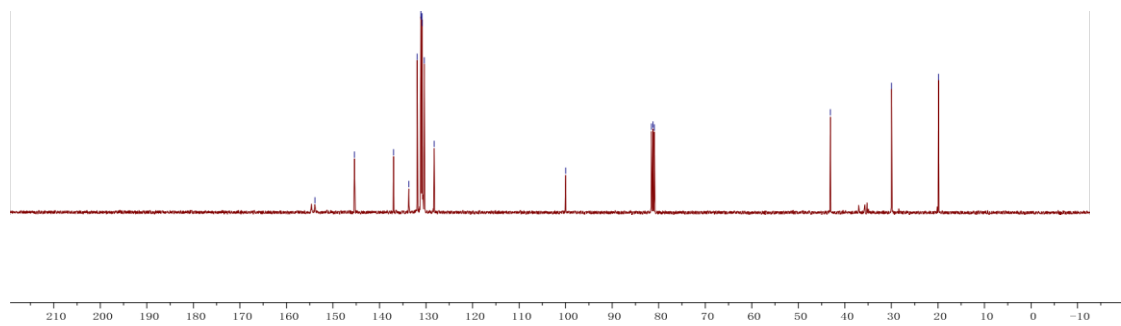
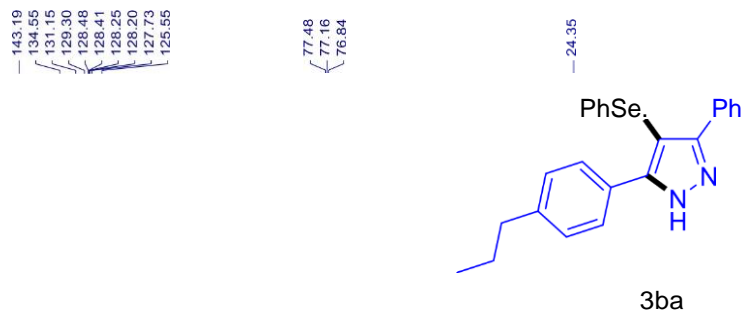
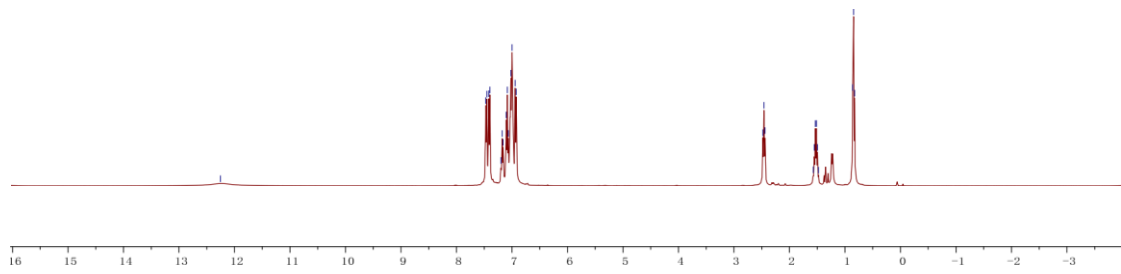
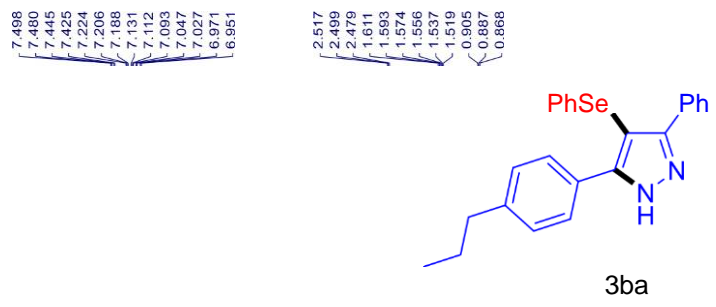
4. Procedure for scale up synthesis of **3aa**.

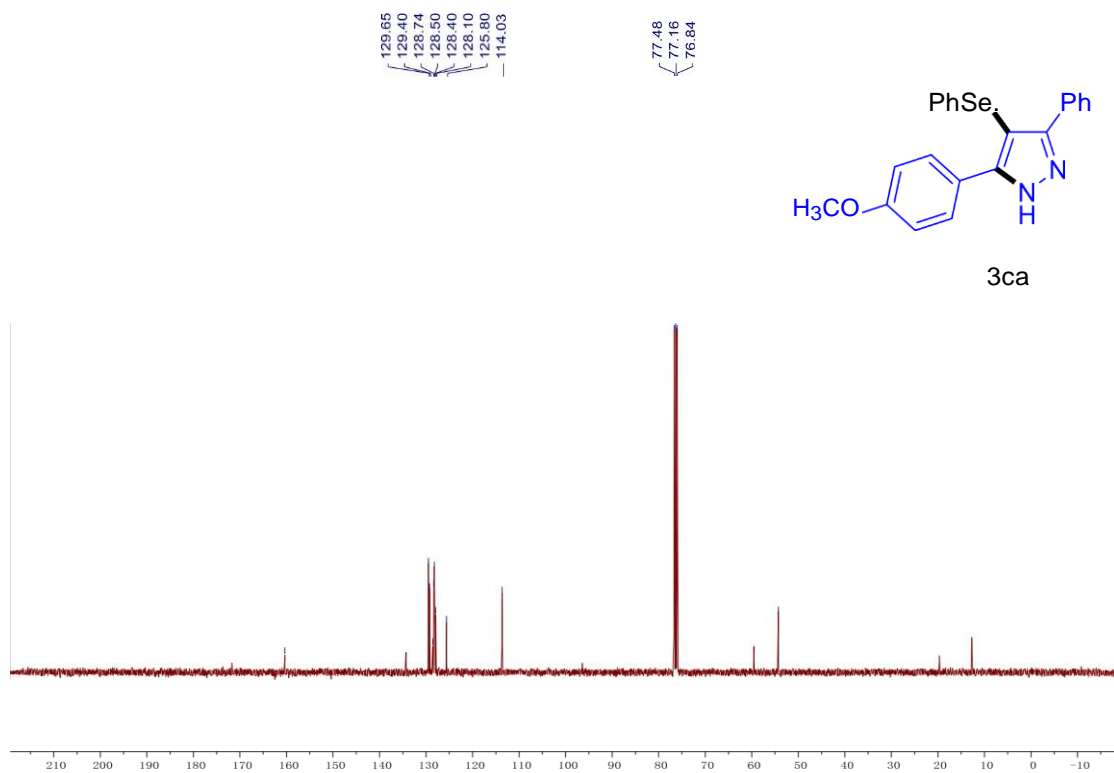
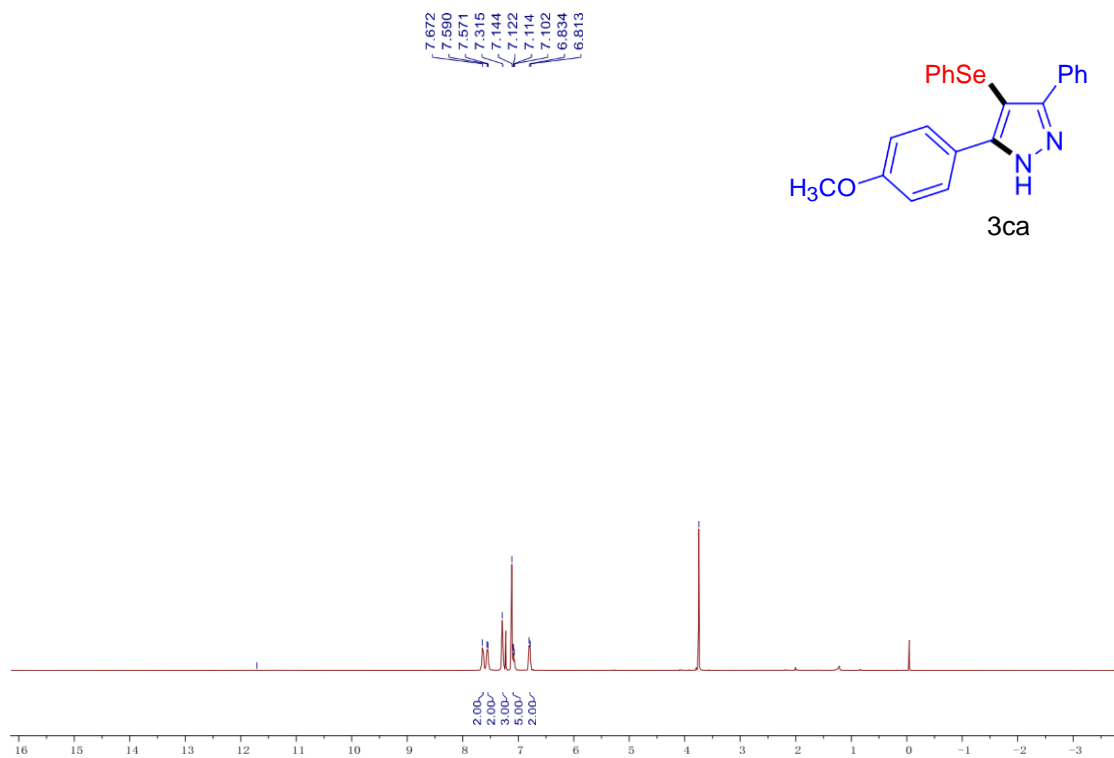
To a solution of N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonylhydrazide **1a** (2.5 mmol, 0.9361 g), diselenides **2** (5.0 mmol, 1.5612 g) in DCE (20 mL) was added FeCl₃ (1 mmol, 0.8110g). The reaction system was stirred at room temperature under air for 12 hours. After the reaction completed, the mixture was diluted with ethyl acetate (150 mL) and washed with water (50 mL ×2), and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 3 : 1) as an eluent to give the desired product **3aa** 0.8348 g (yield 89%).



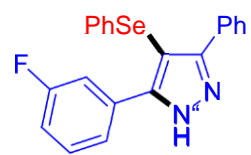
5. ^1H NMR and ^{13}C NMR of 3



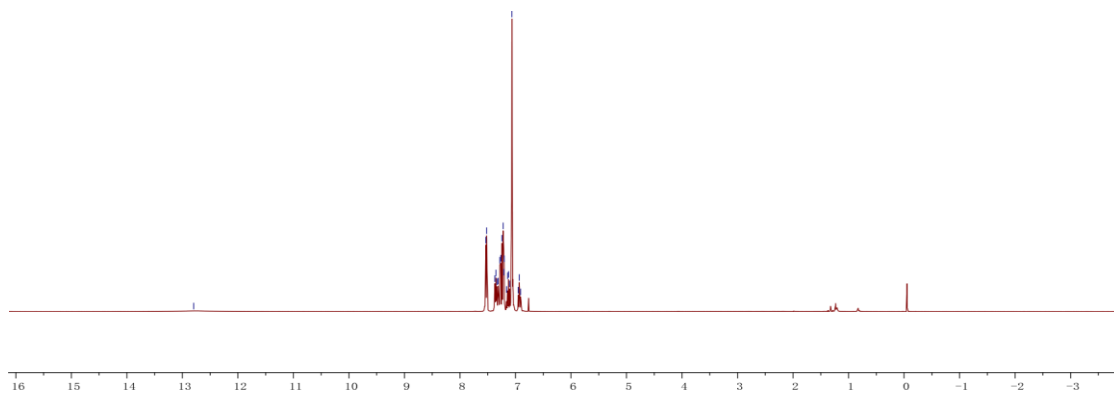




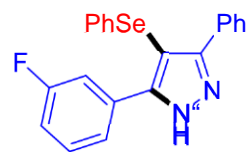
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6.963
6.942



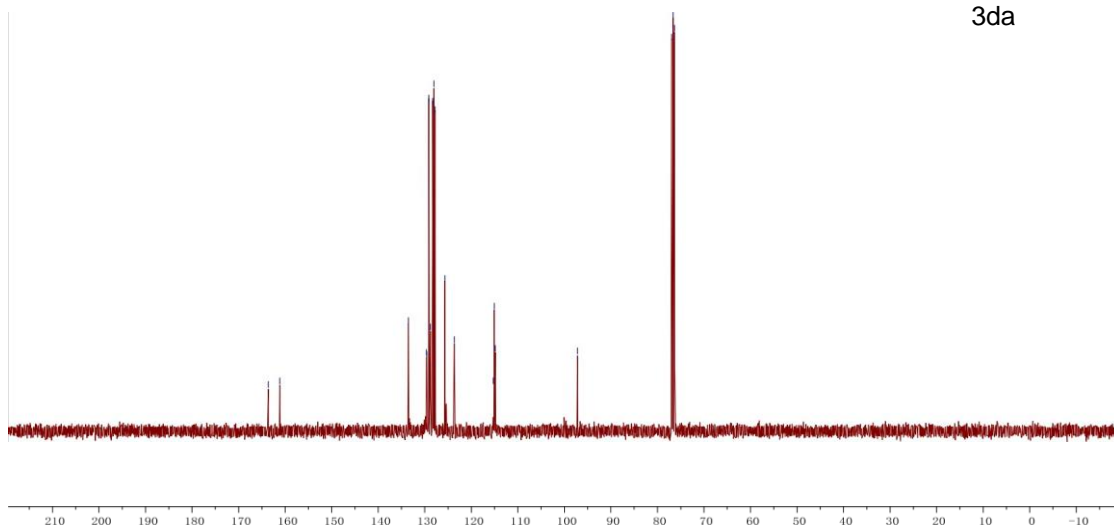
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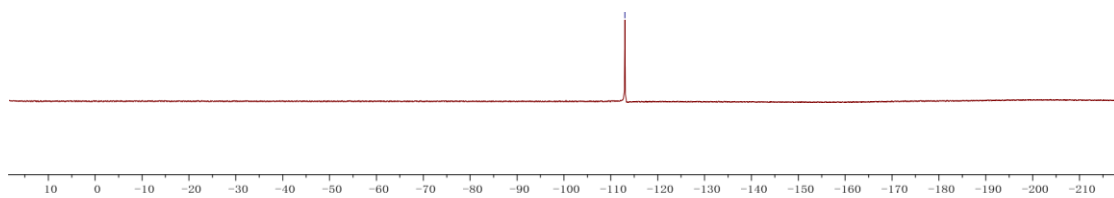
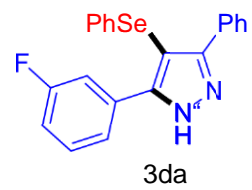


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129.96
129.88
129.46
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77.16
76.84

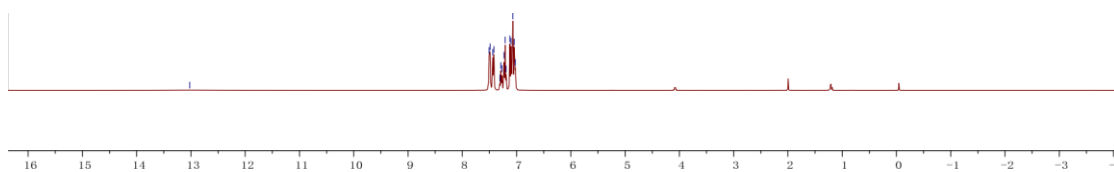
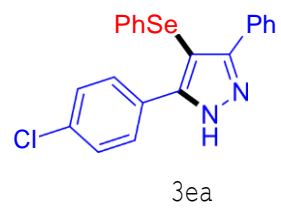


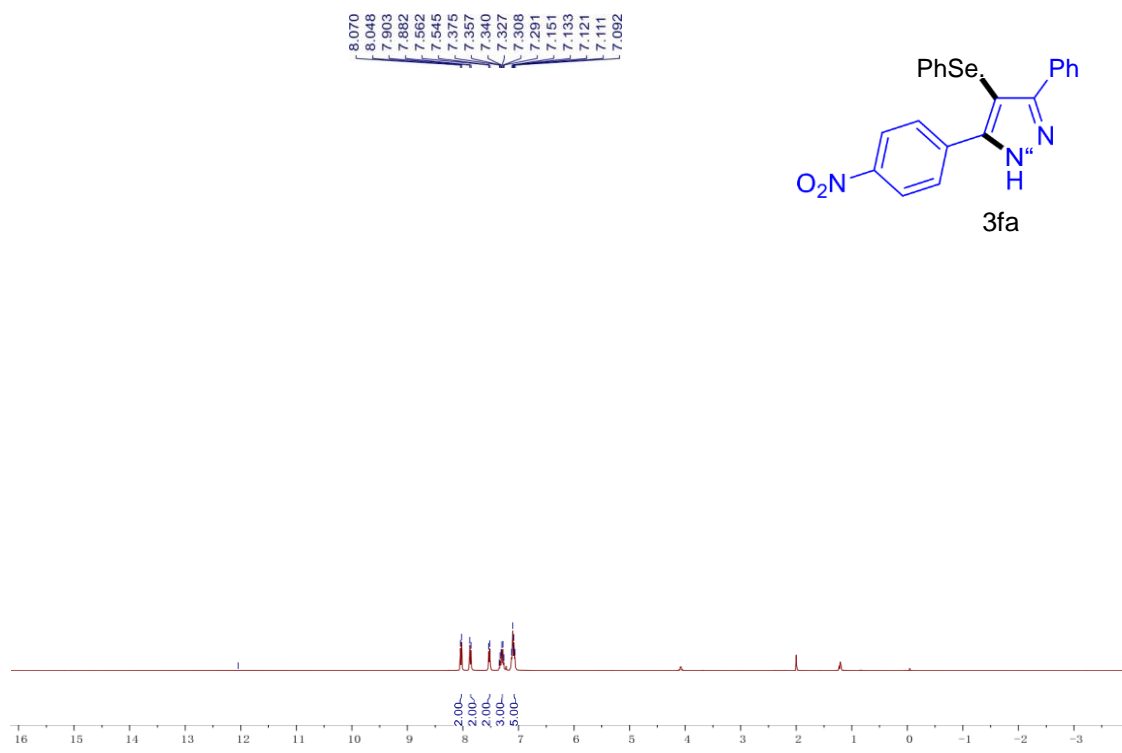
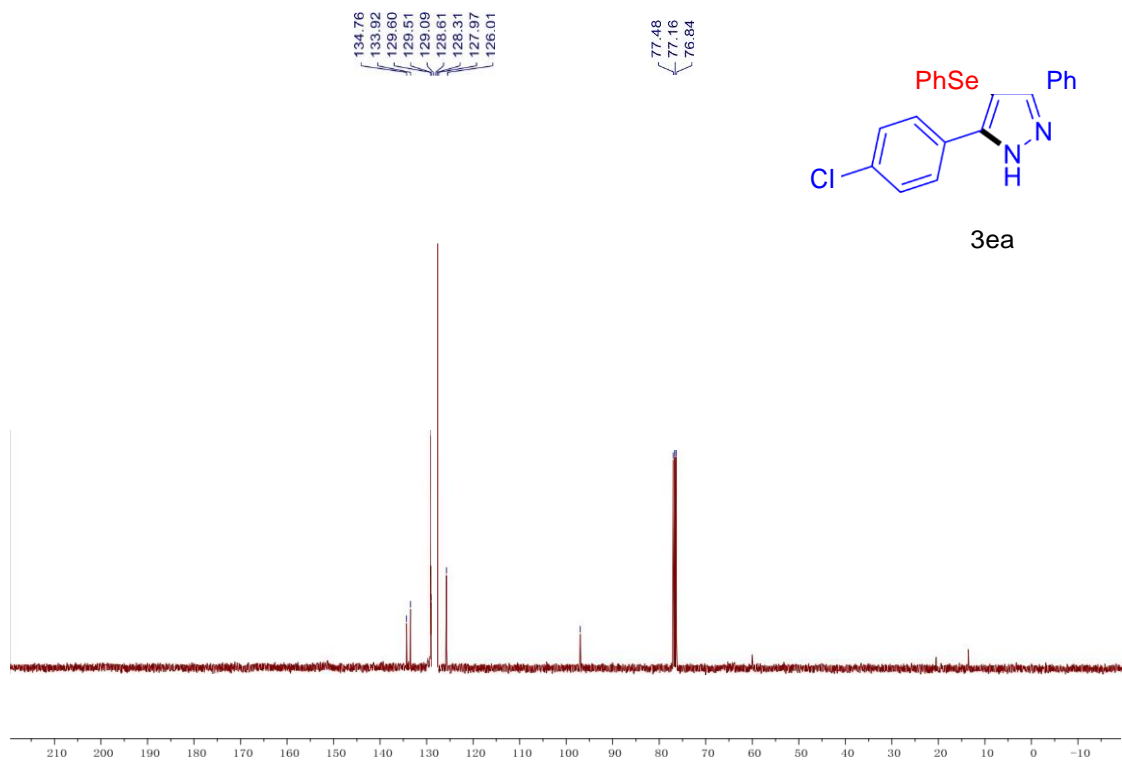
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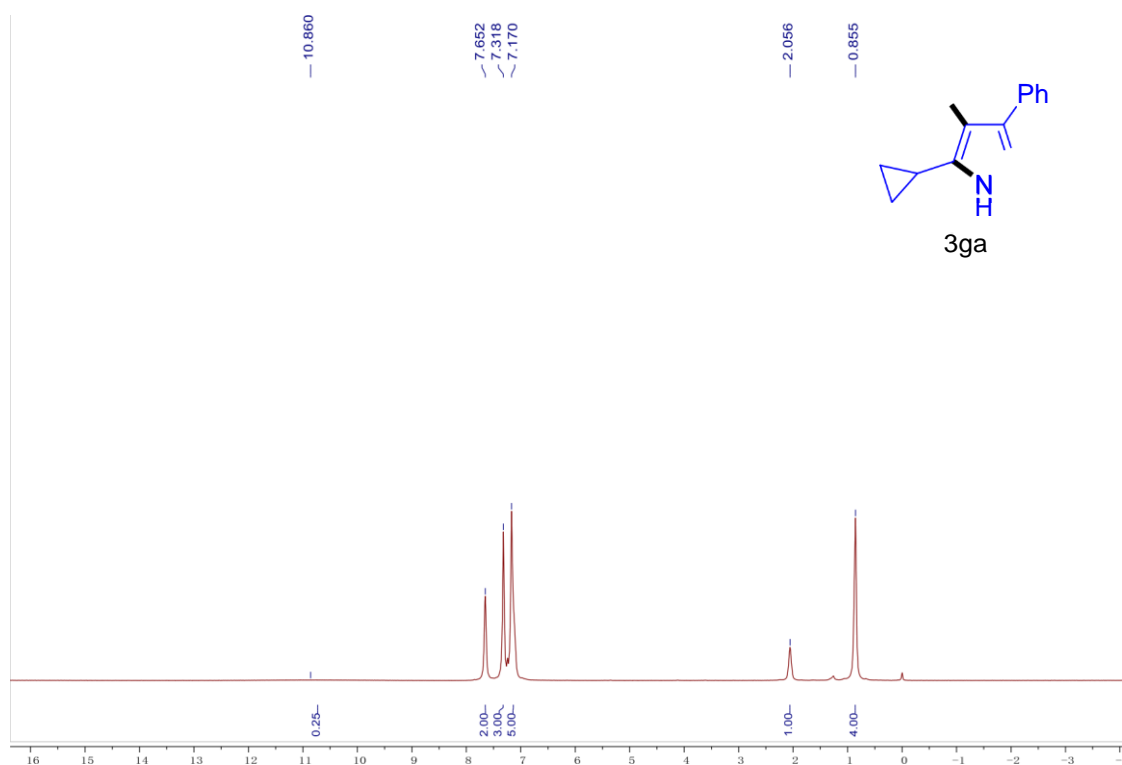
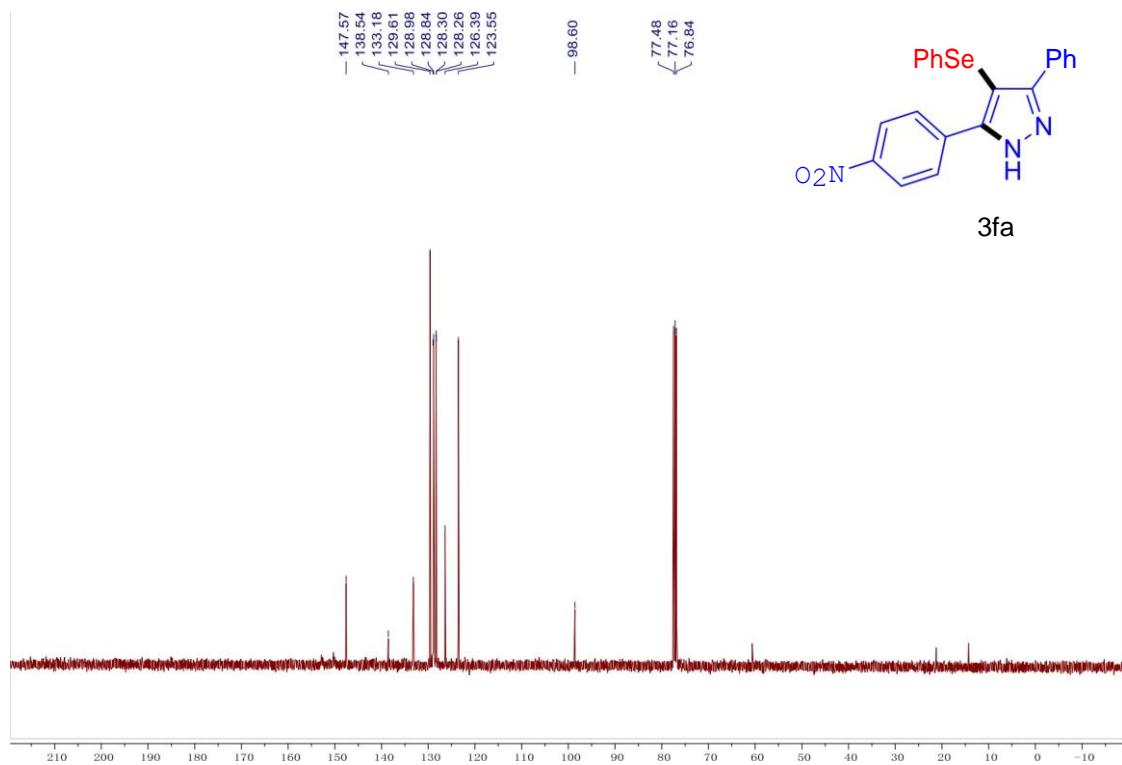


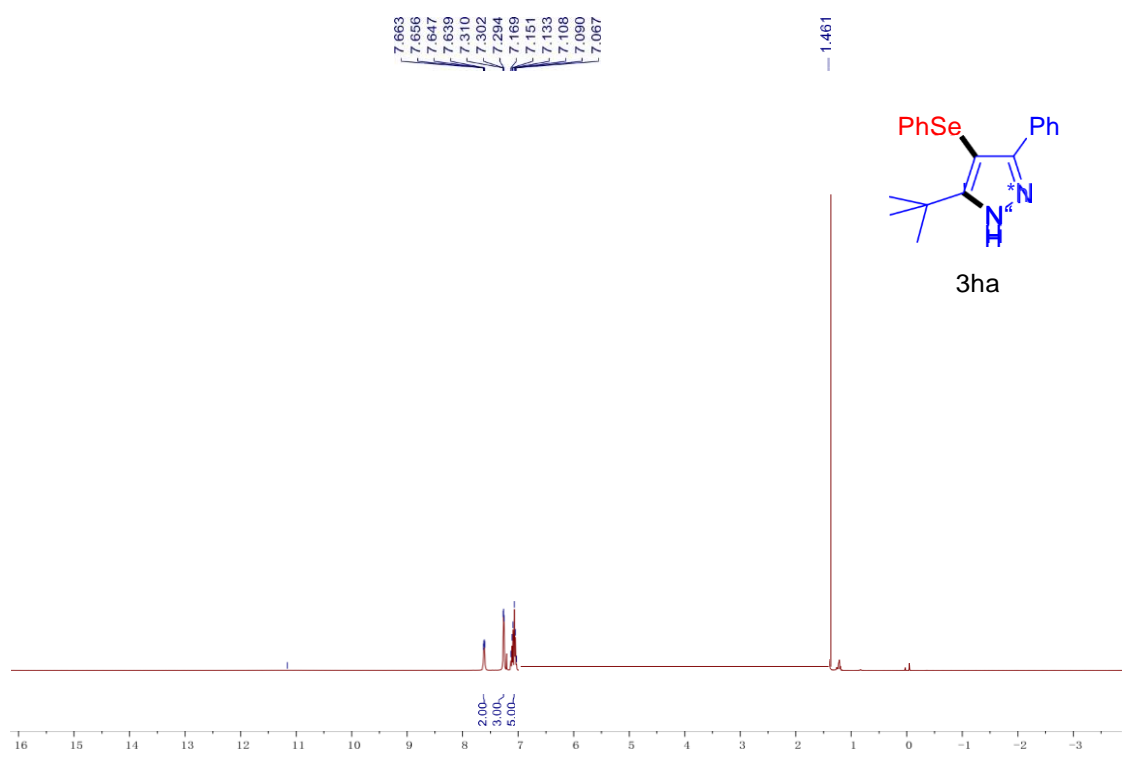
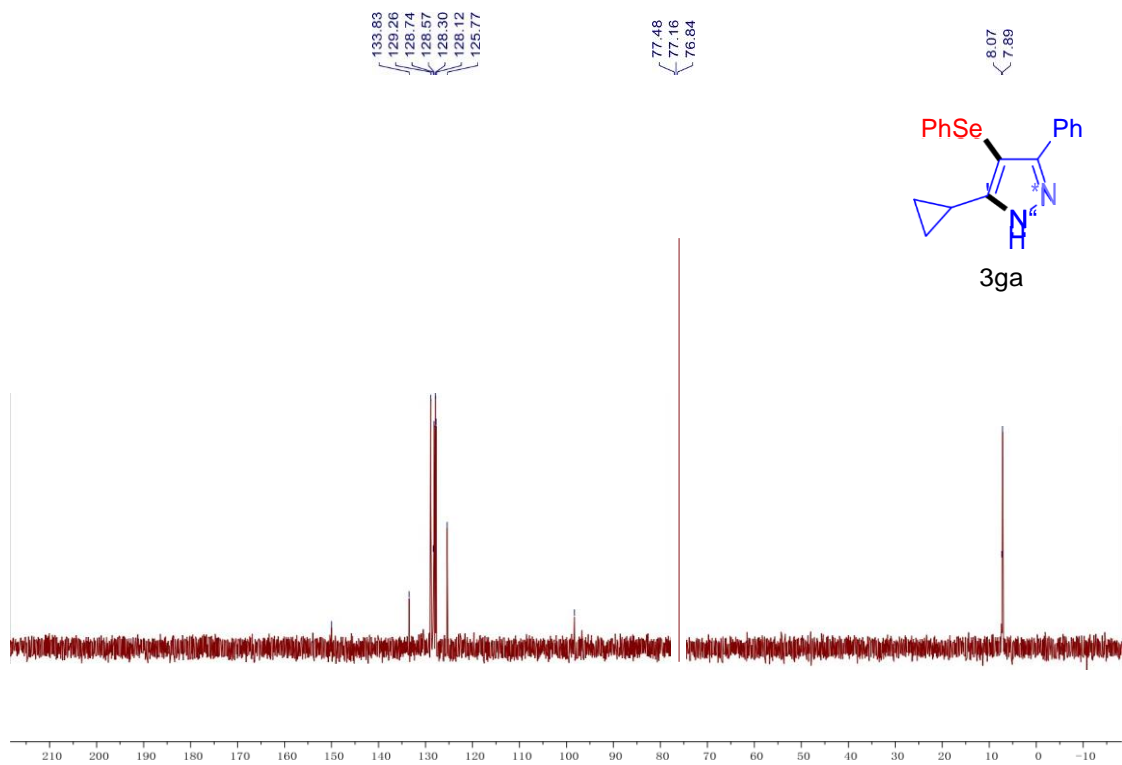


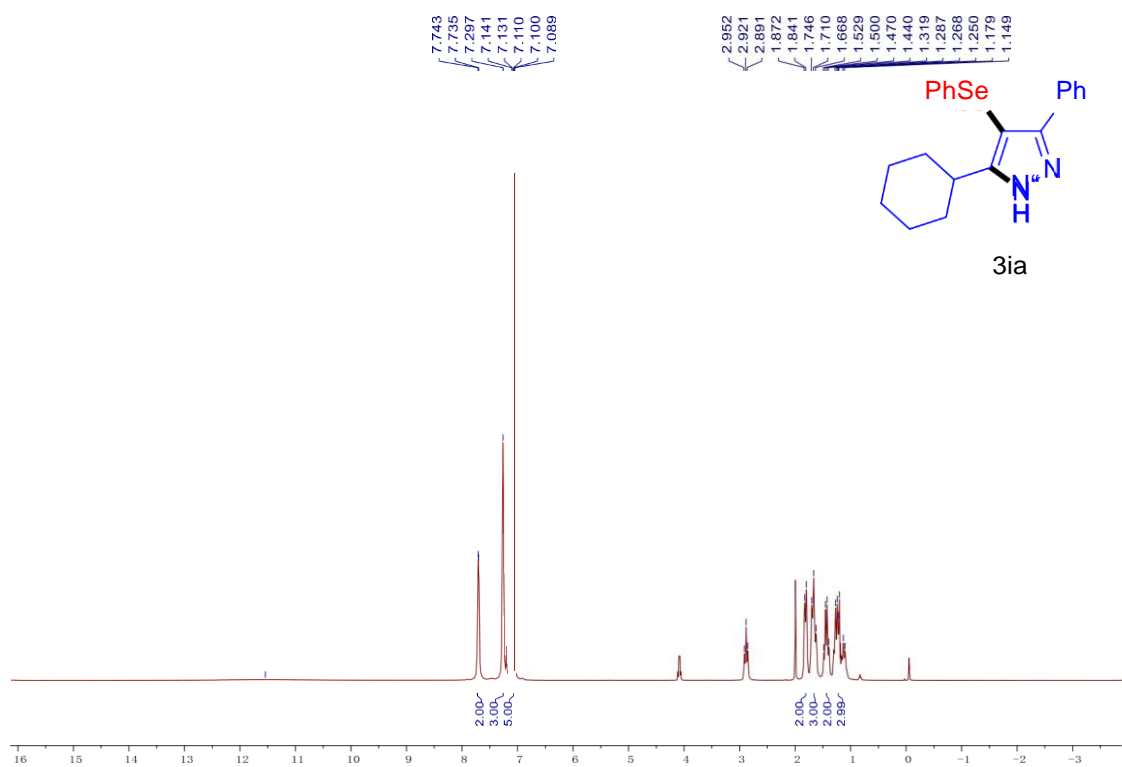
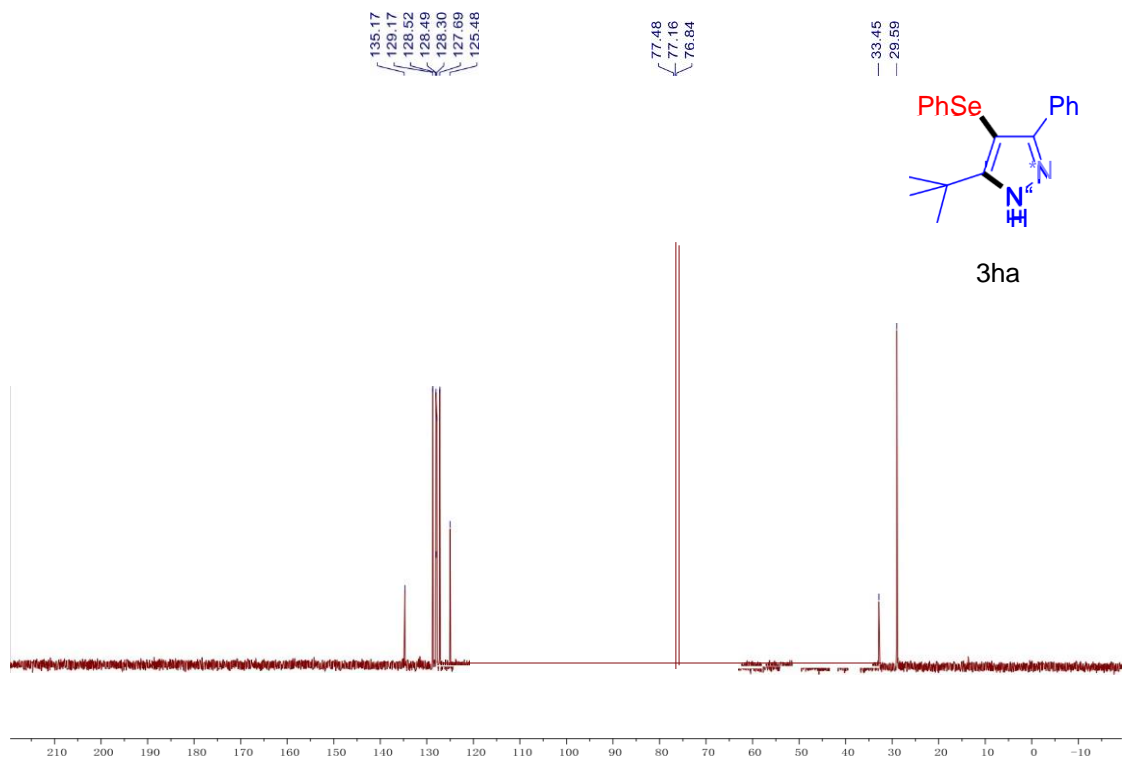
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7.094
7.068
7.049







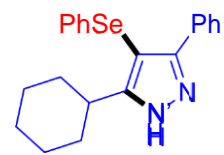




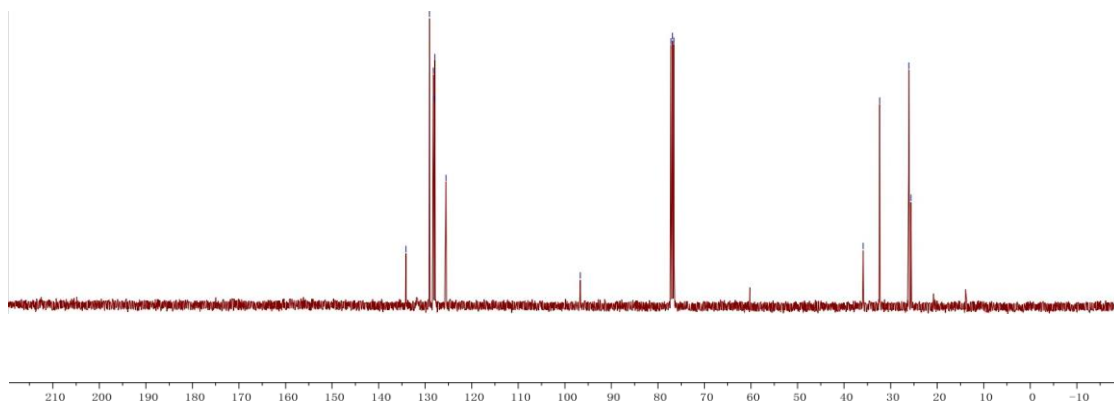
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26.02

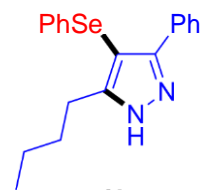


3ia

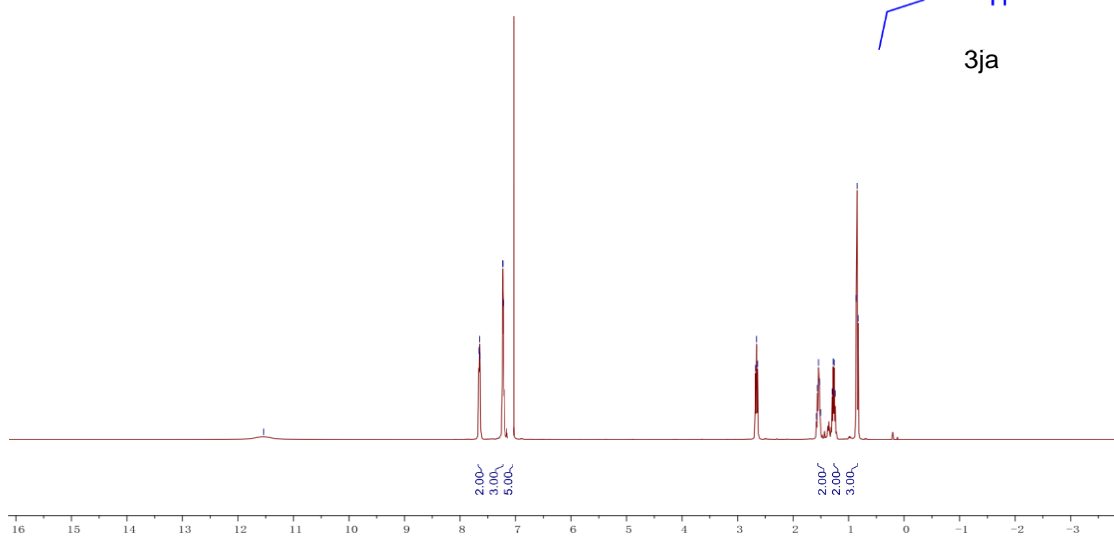


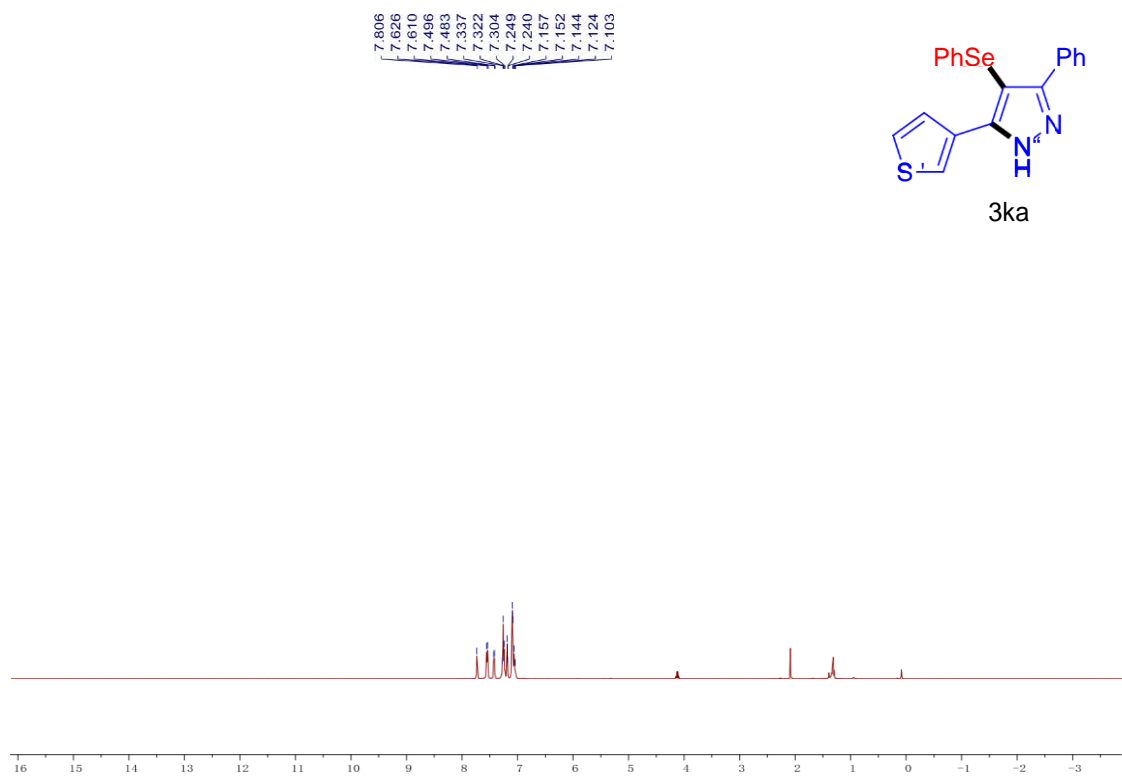
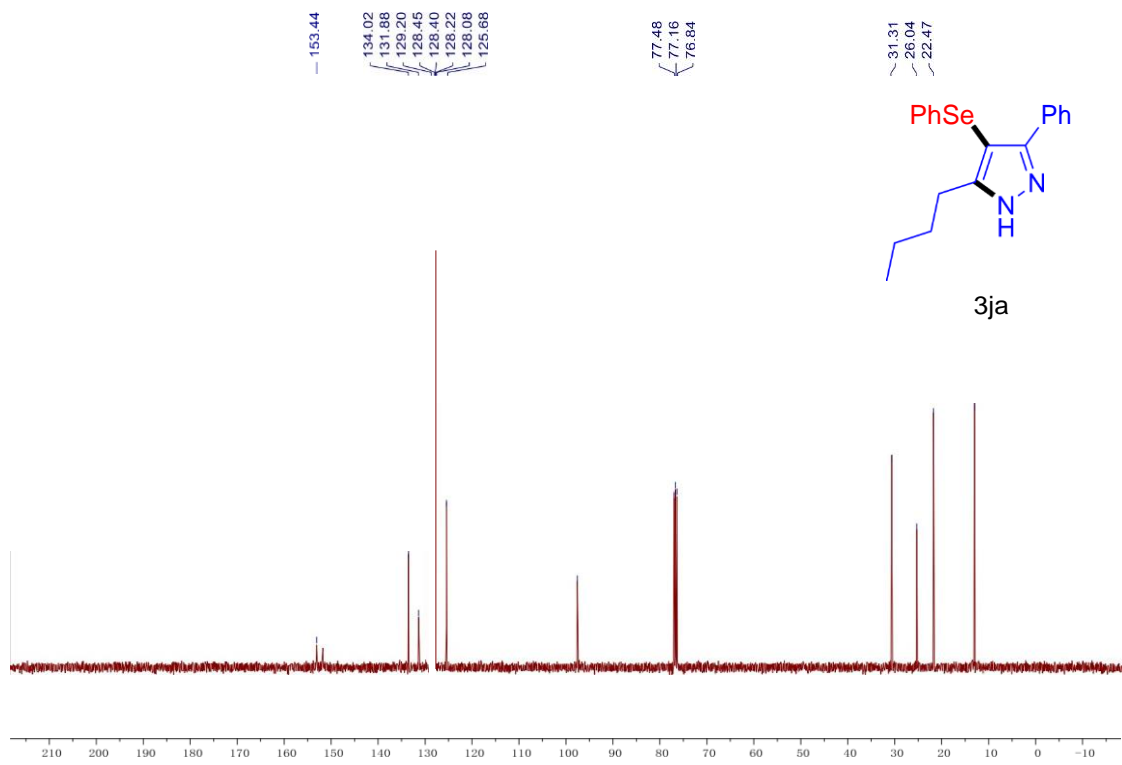
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7.102

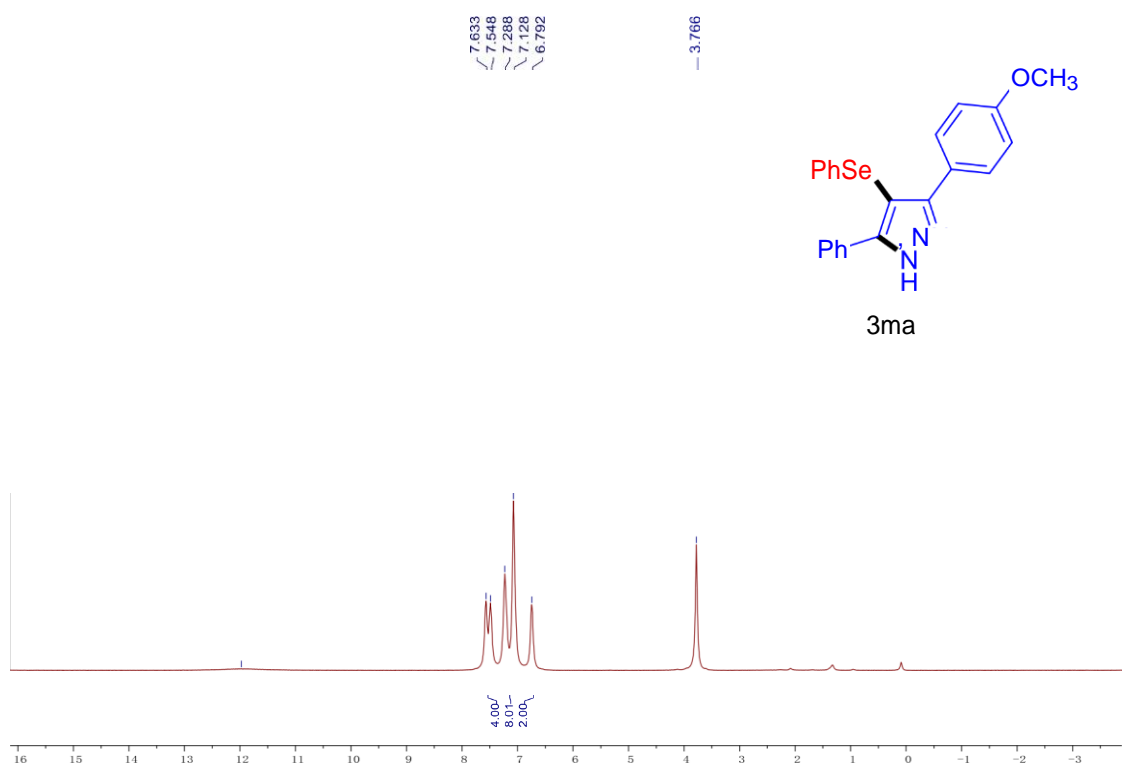
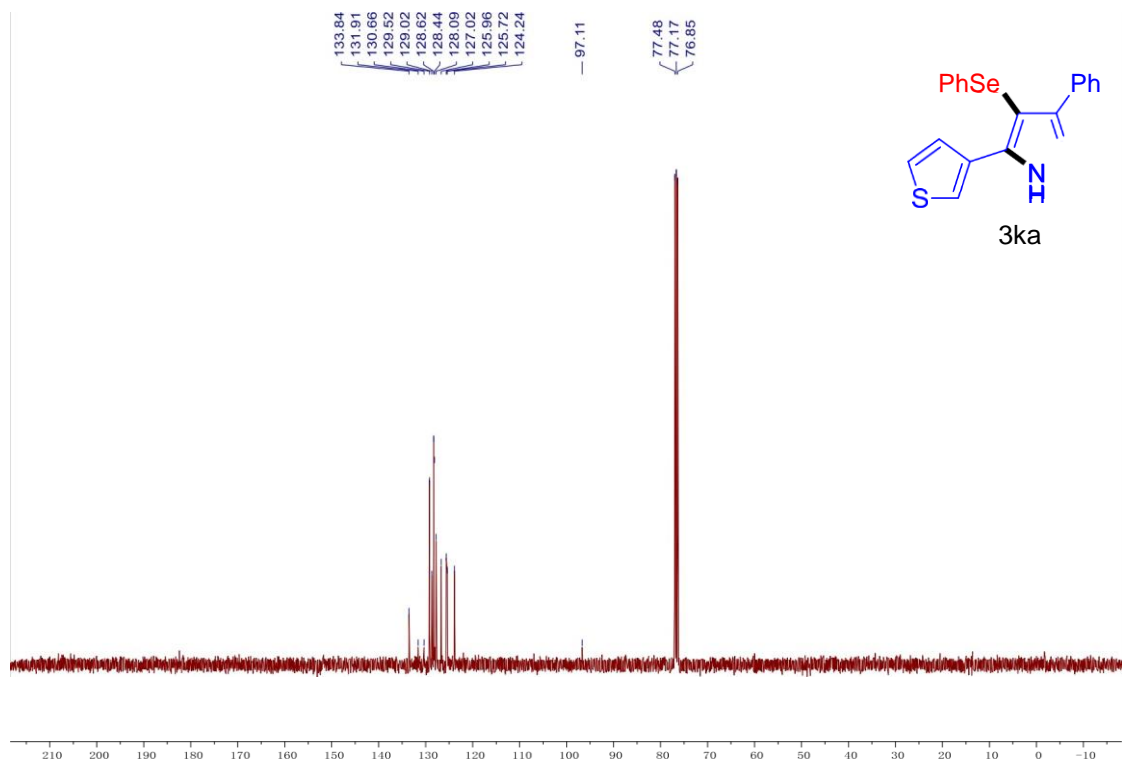
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0.723

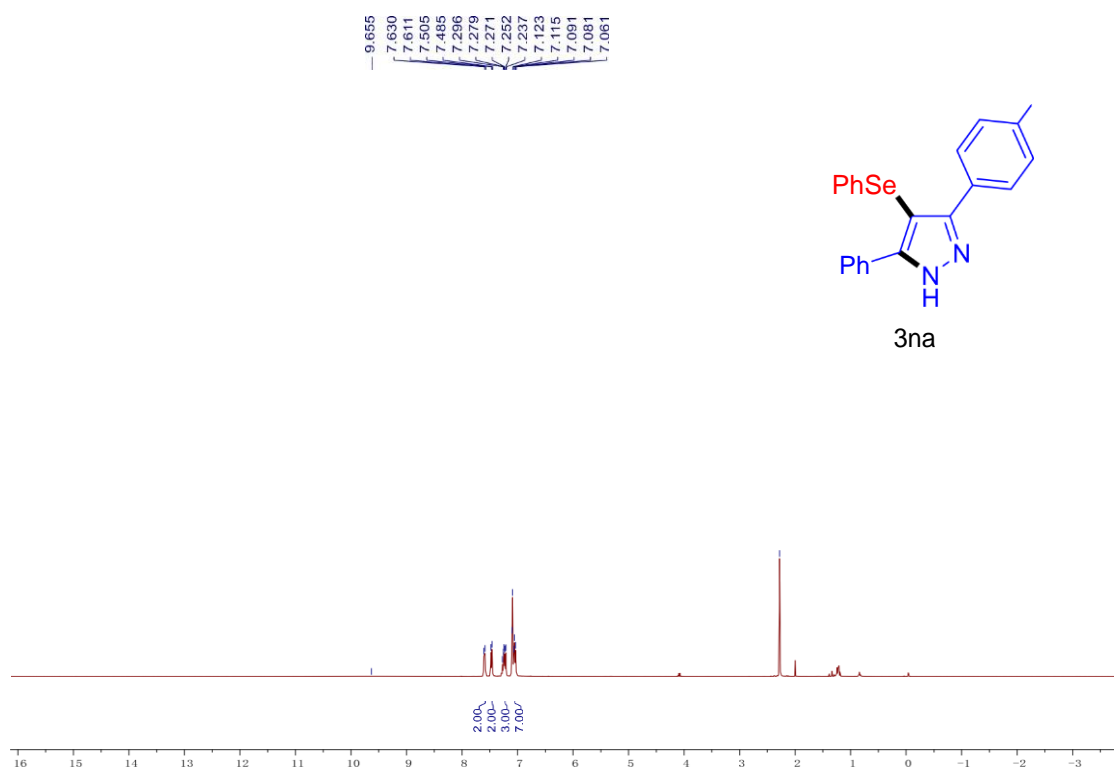
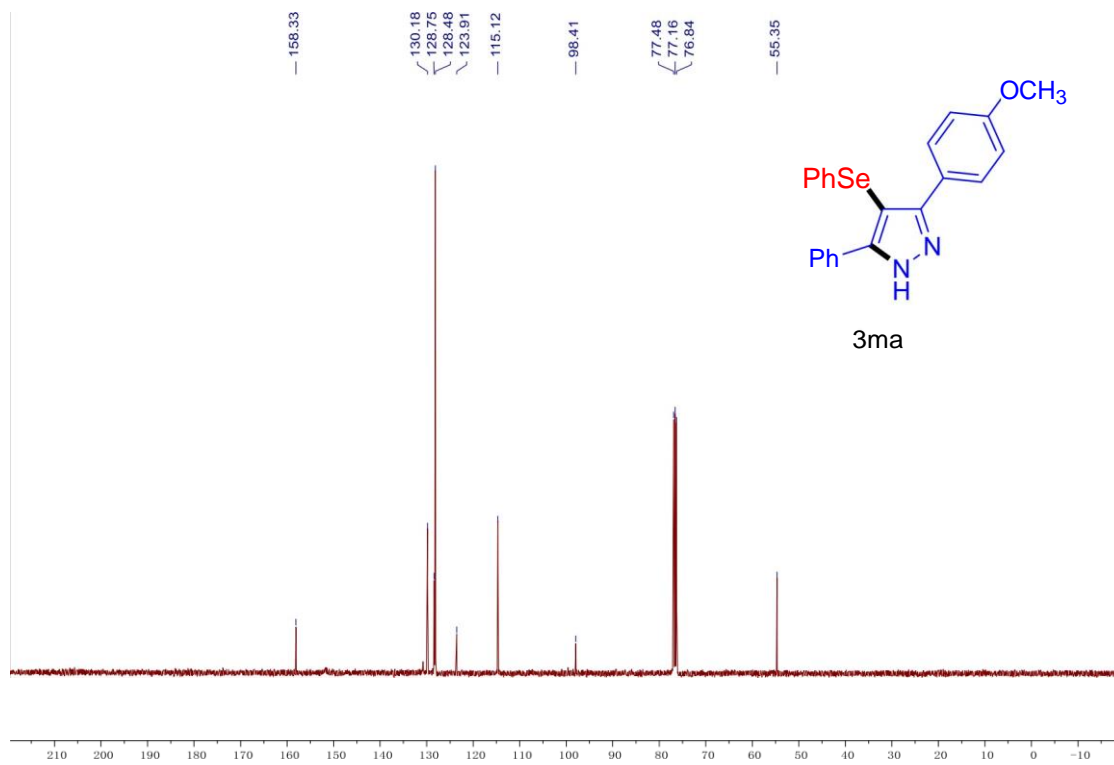


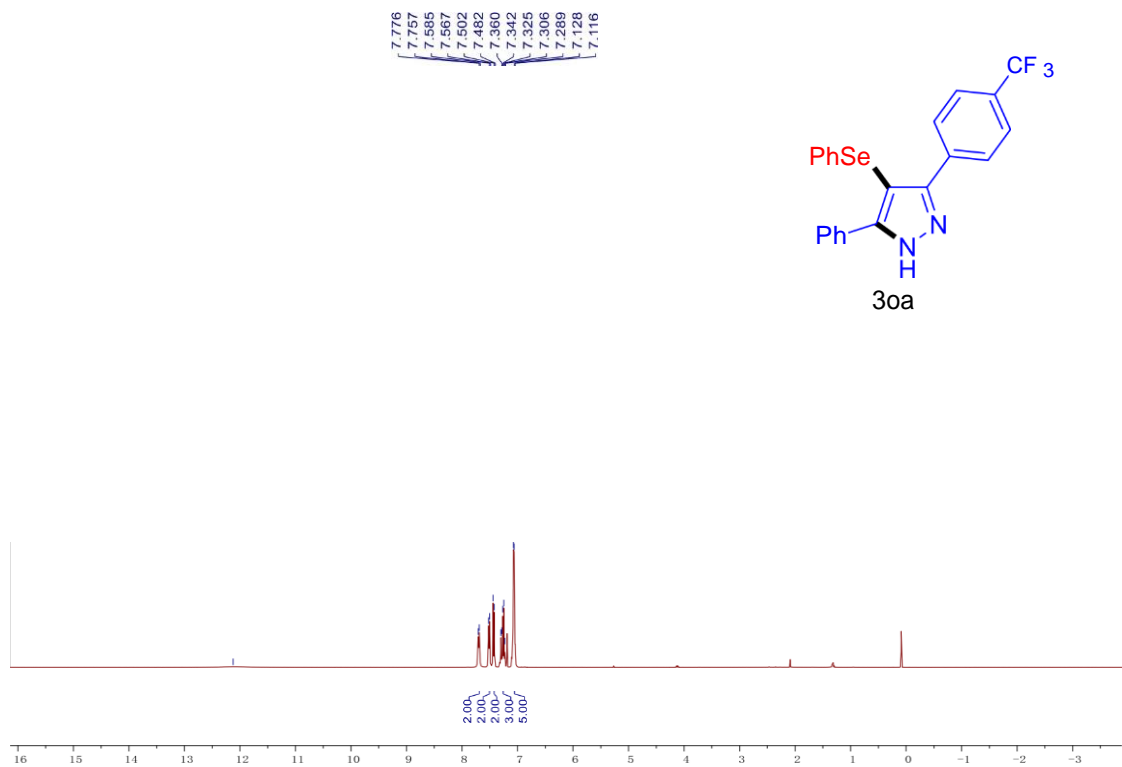
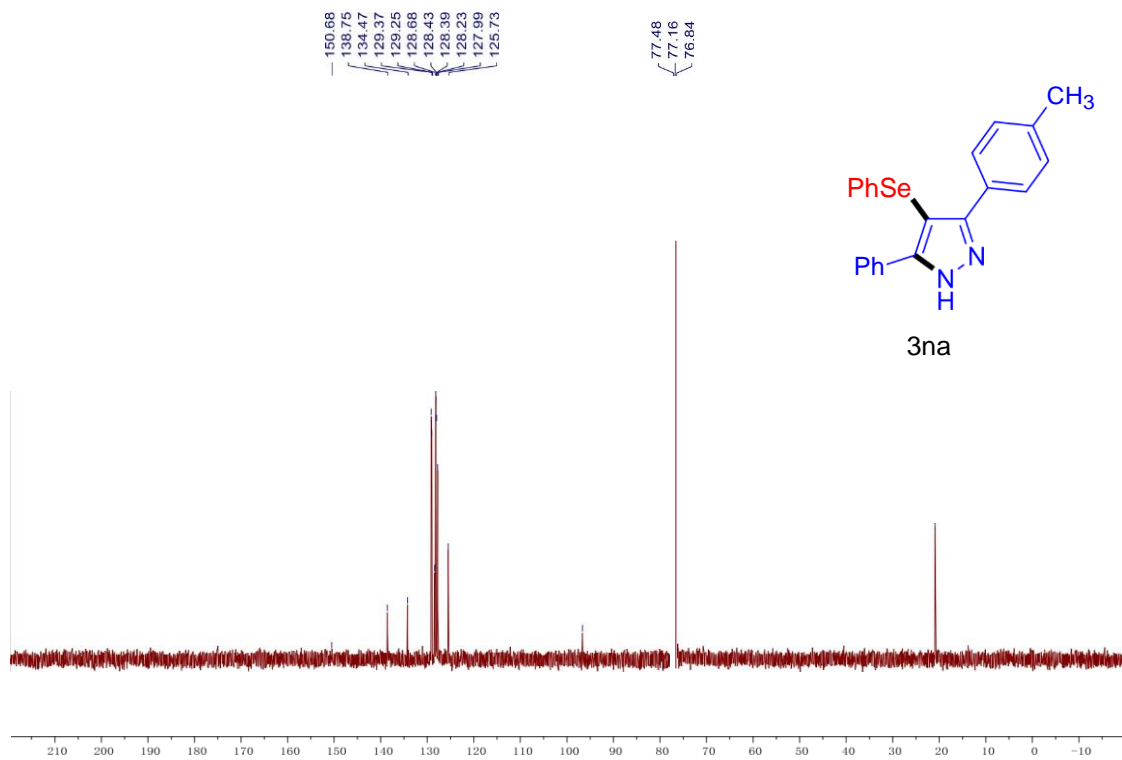
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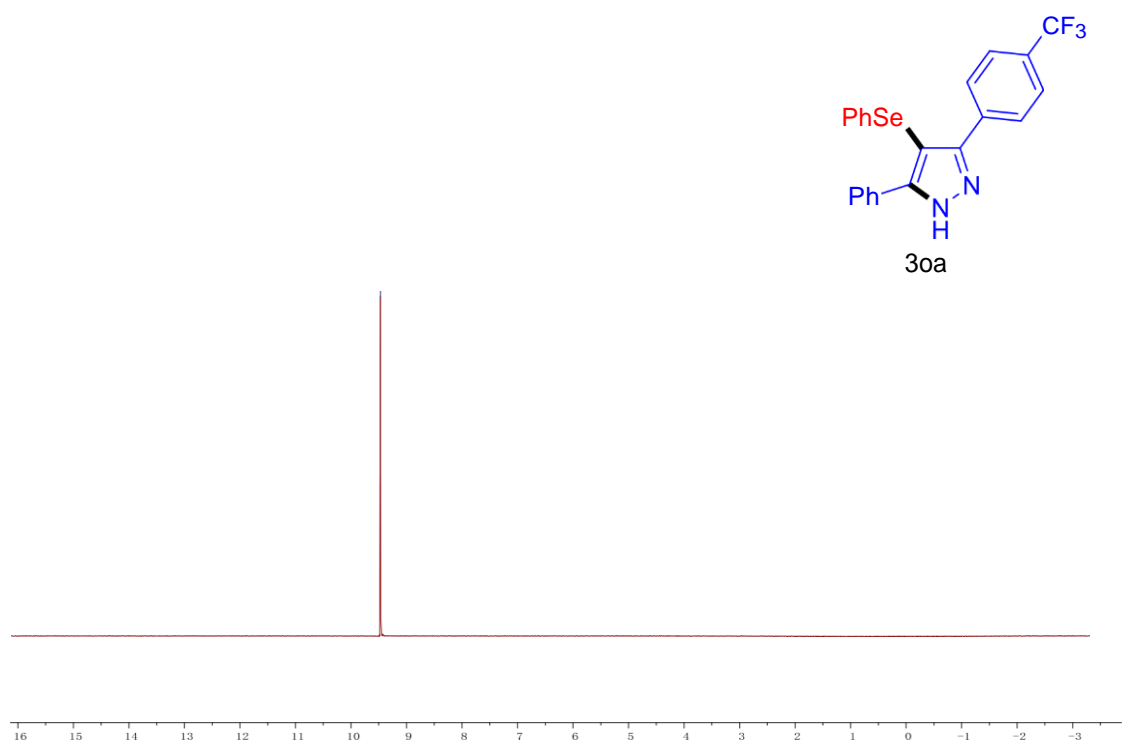
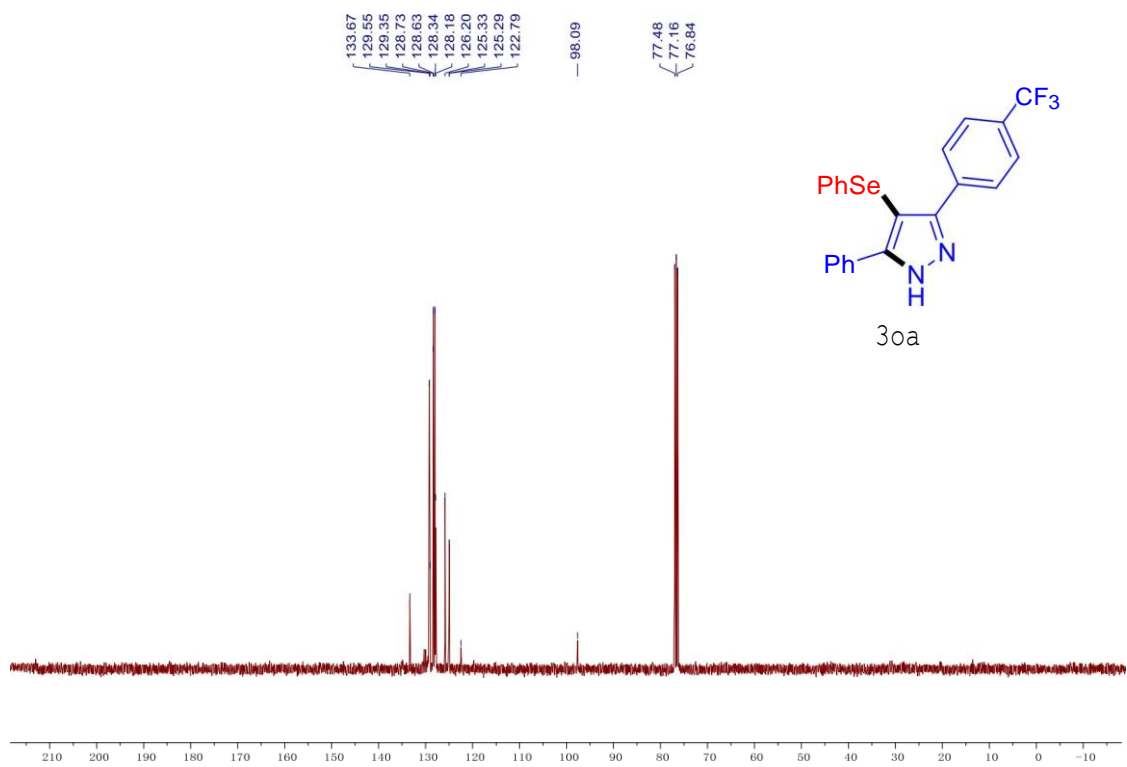


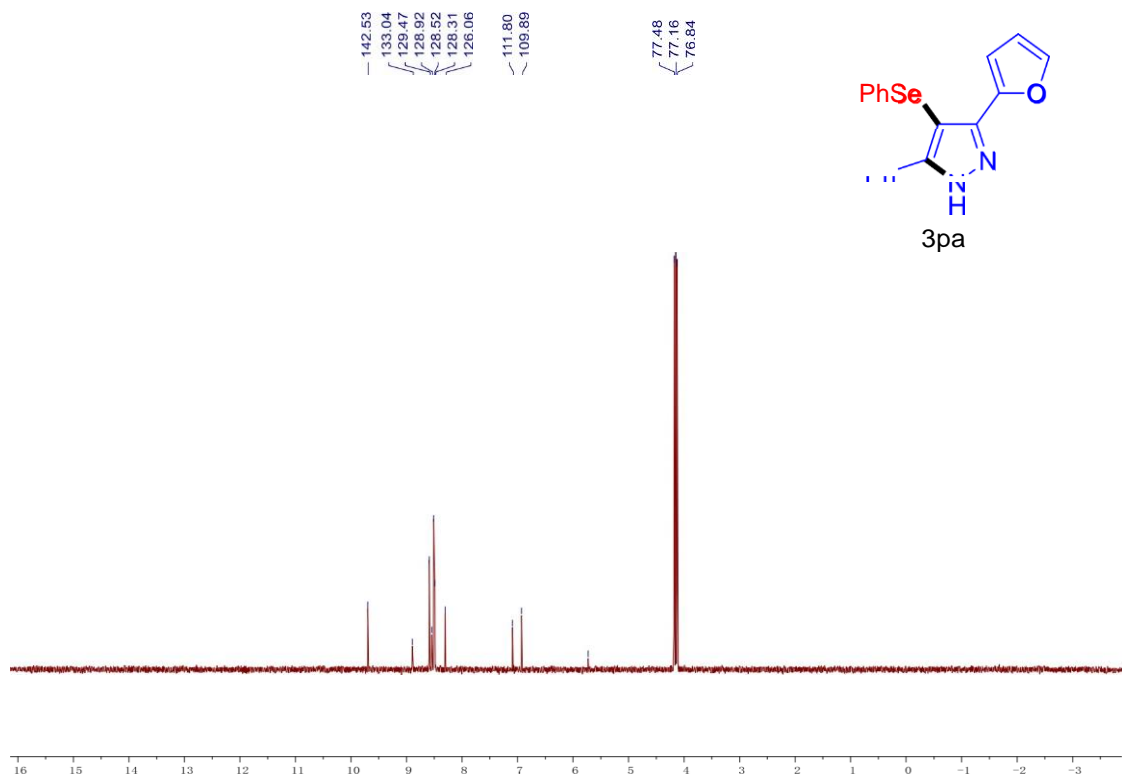
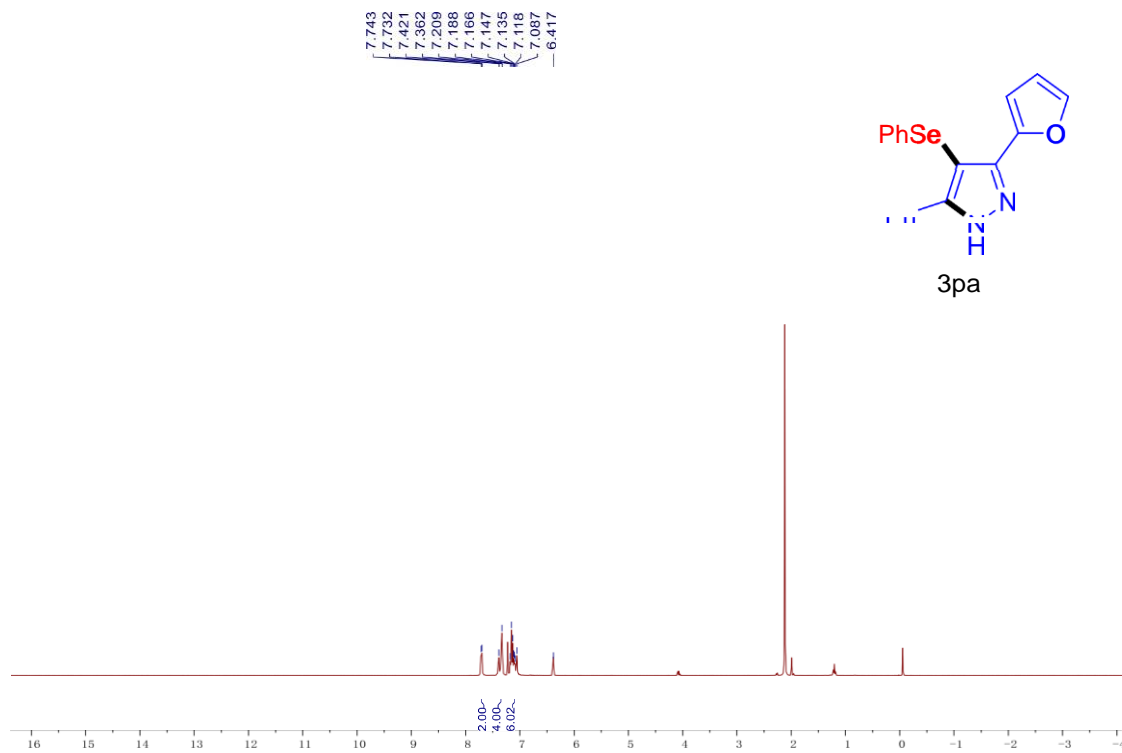




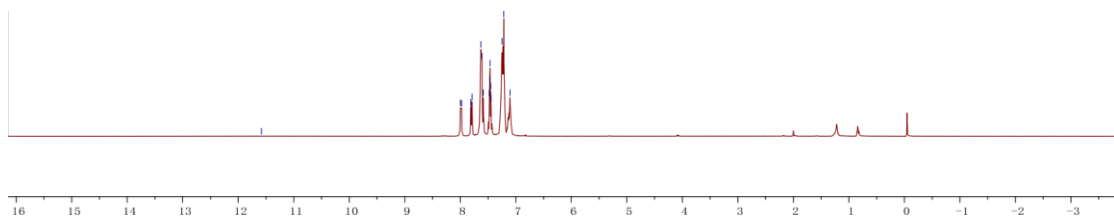
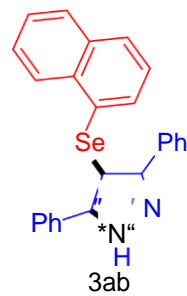








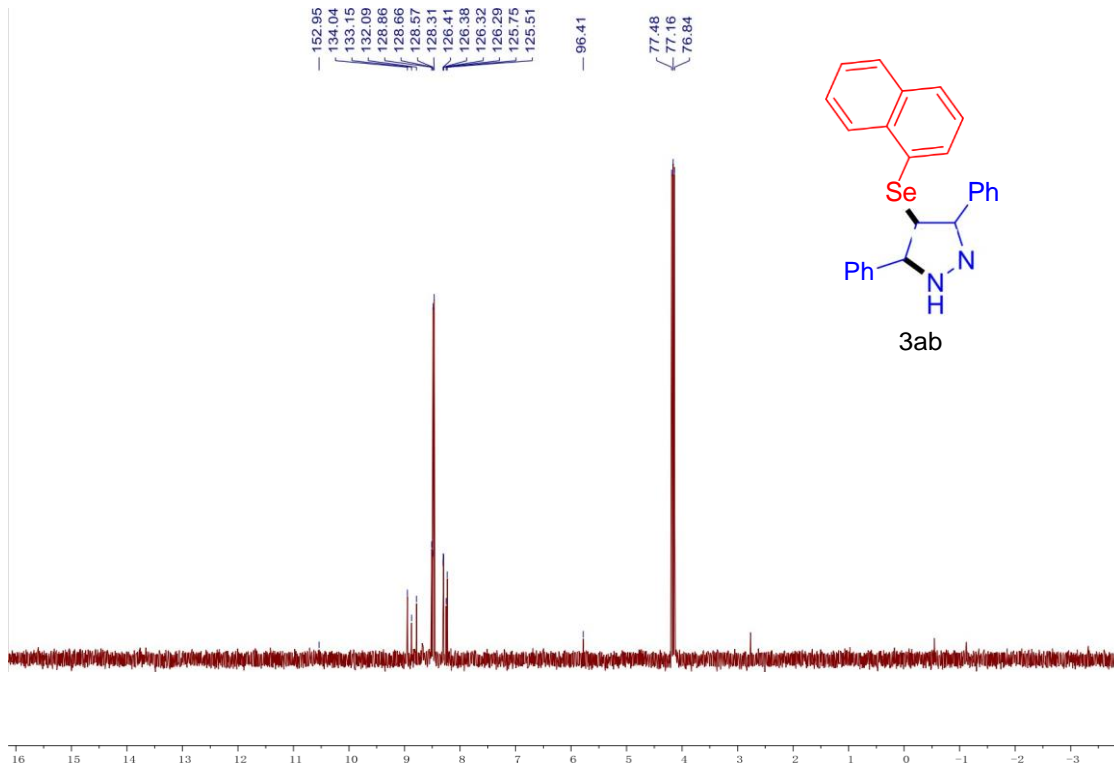
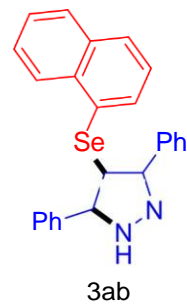
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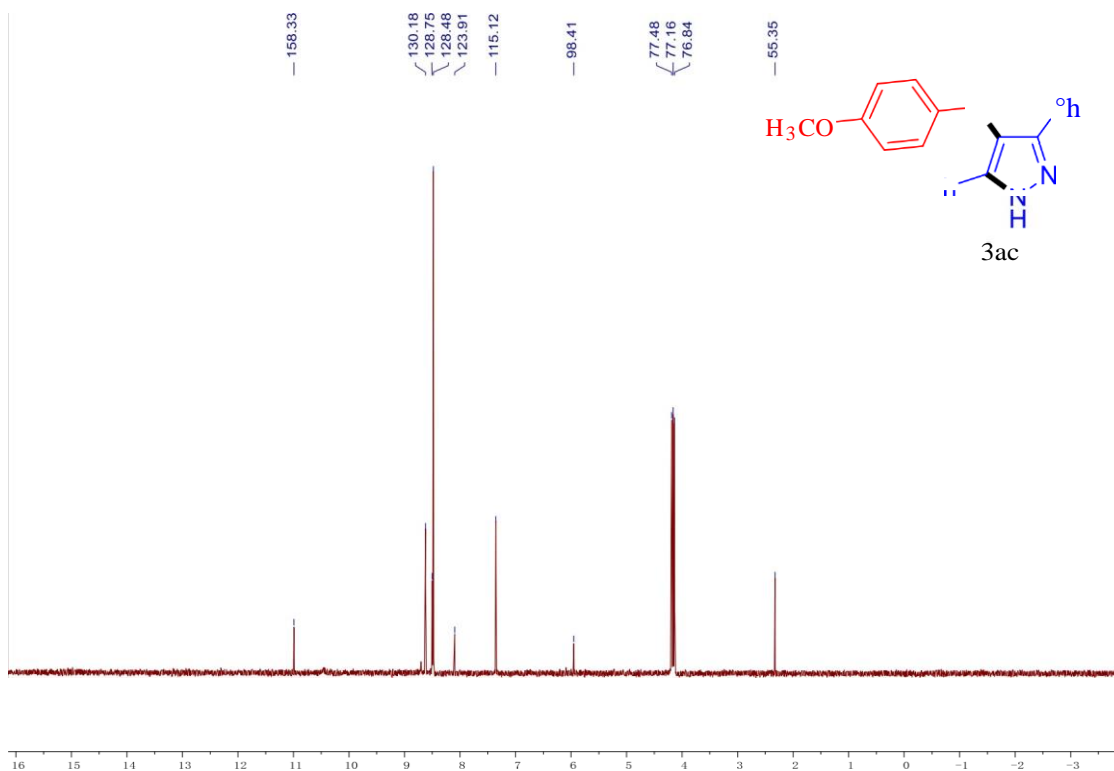
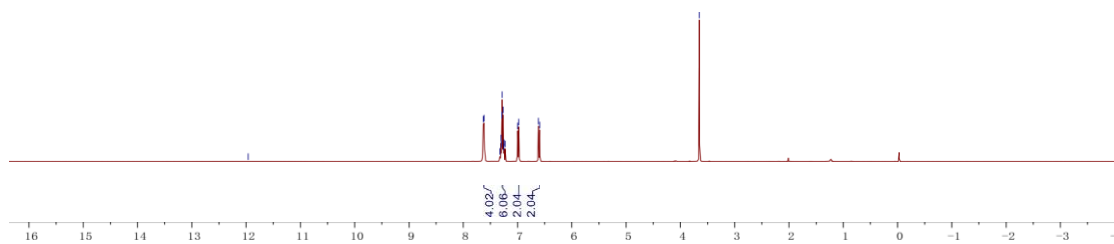
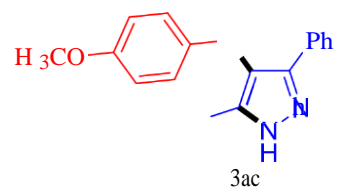
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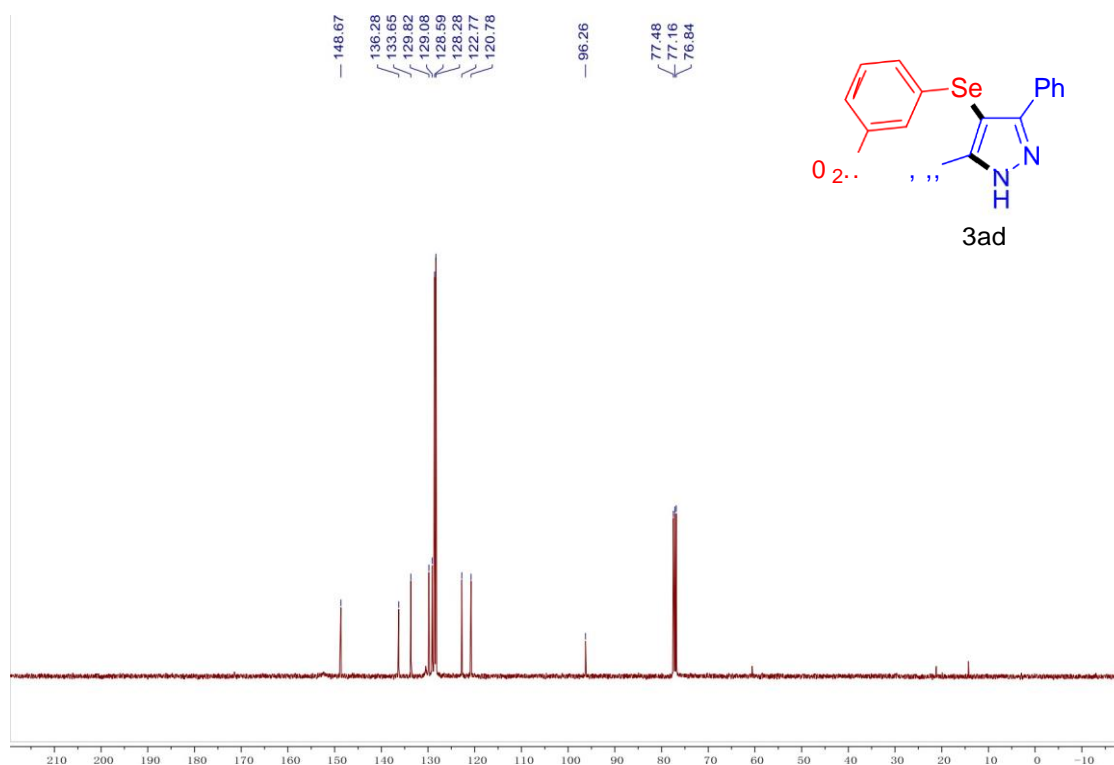
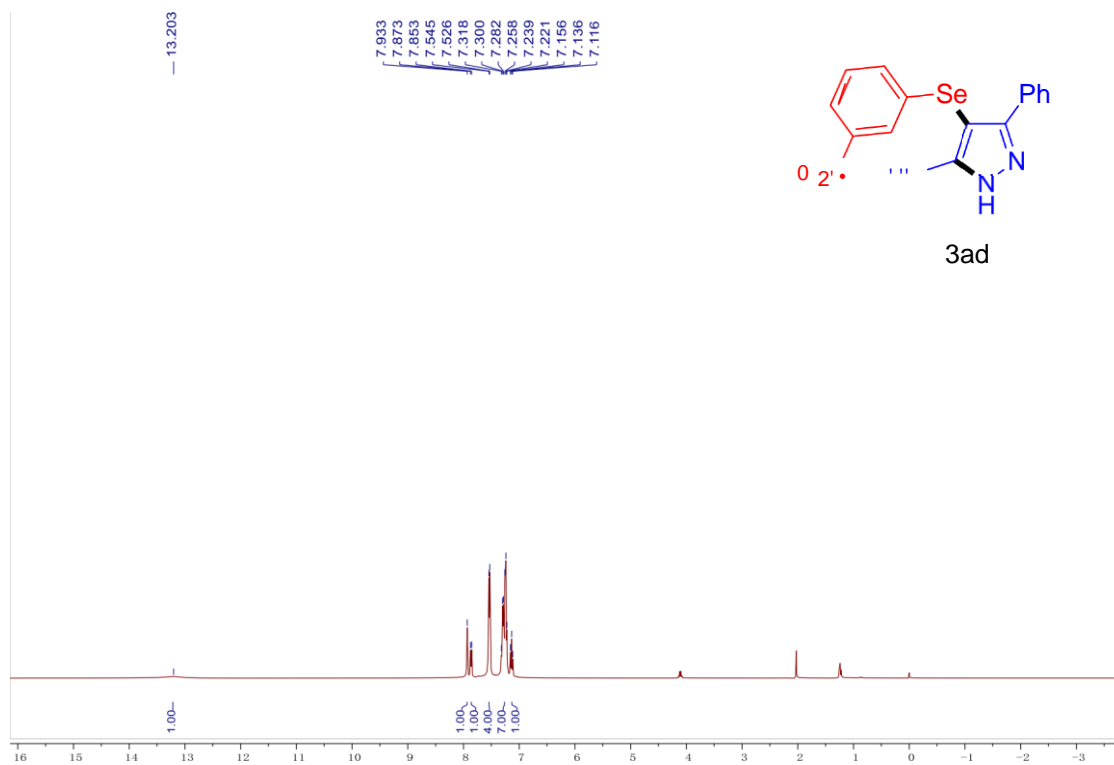
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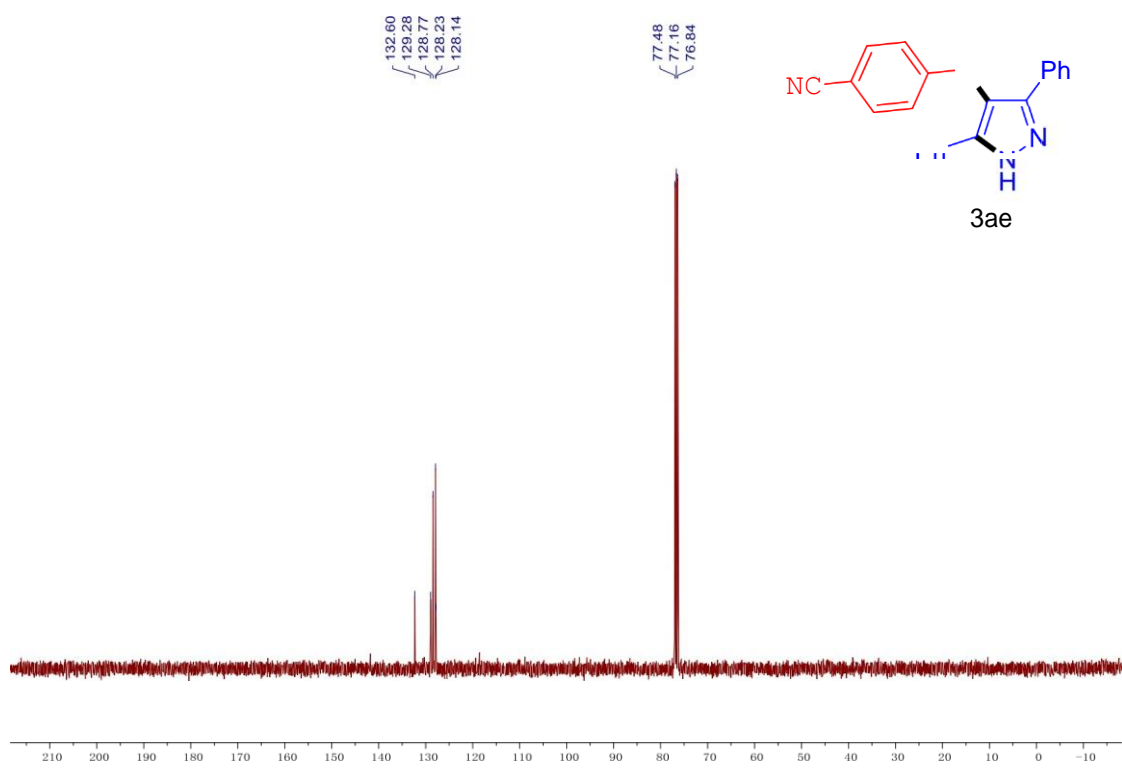
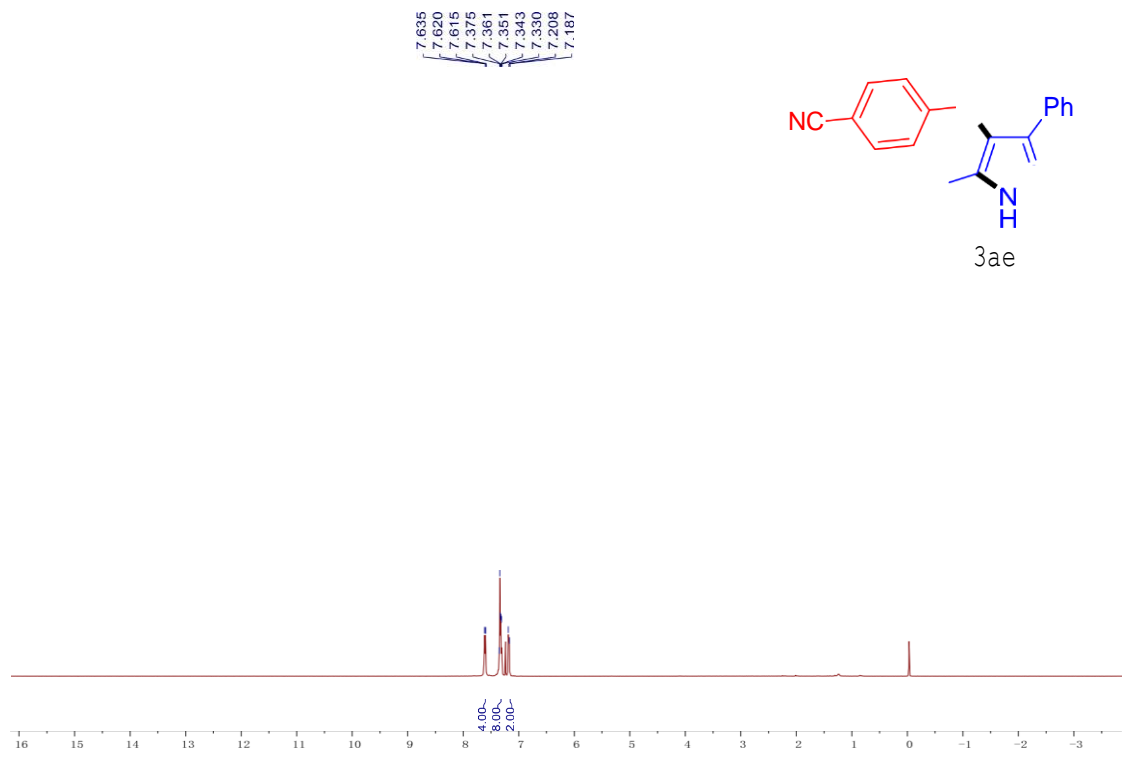
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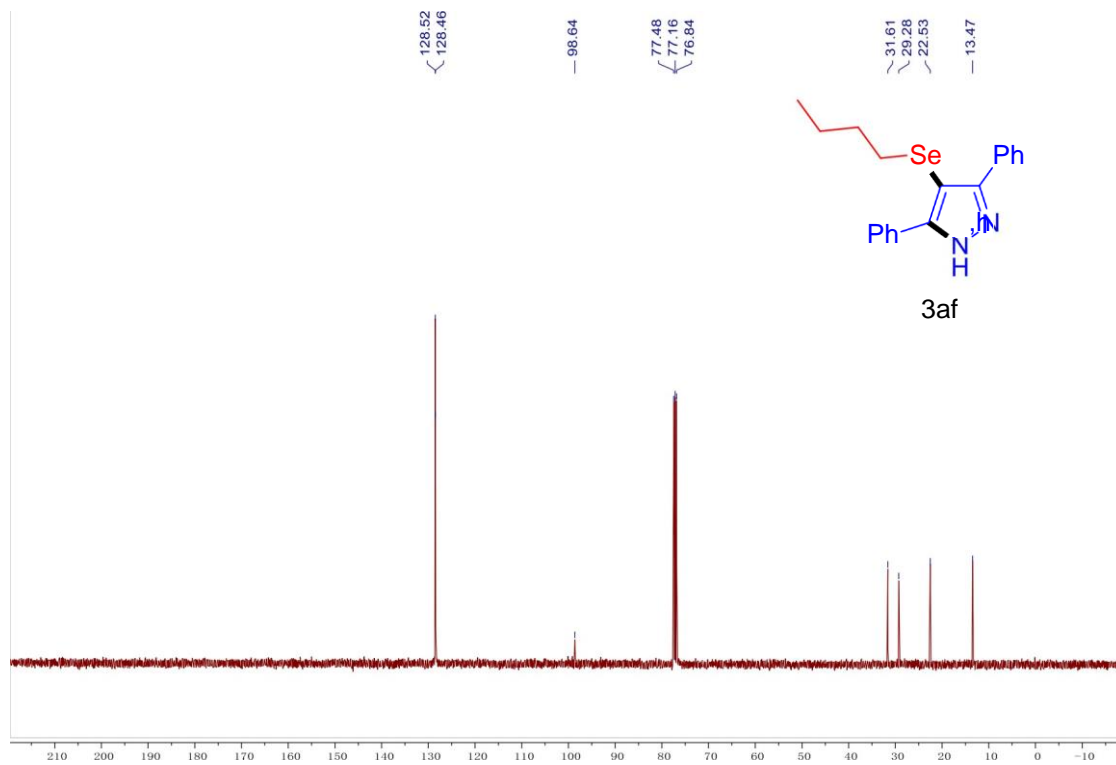
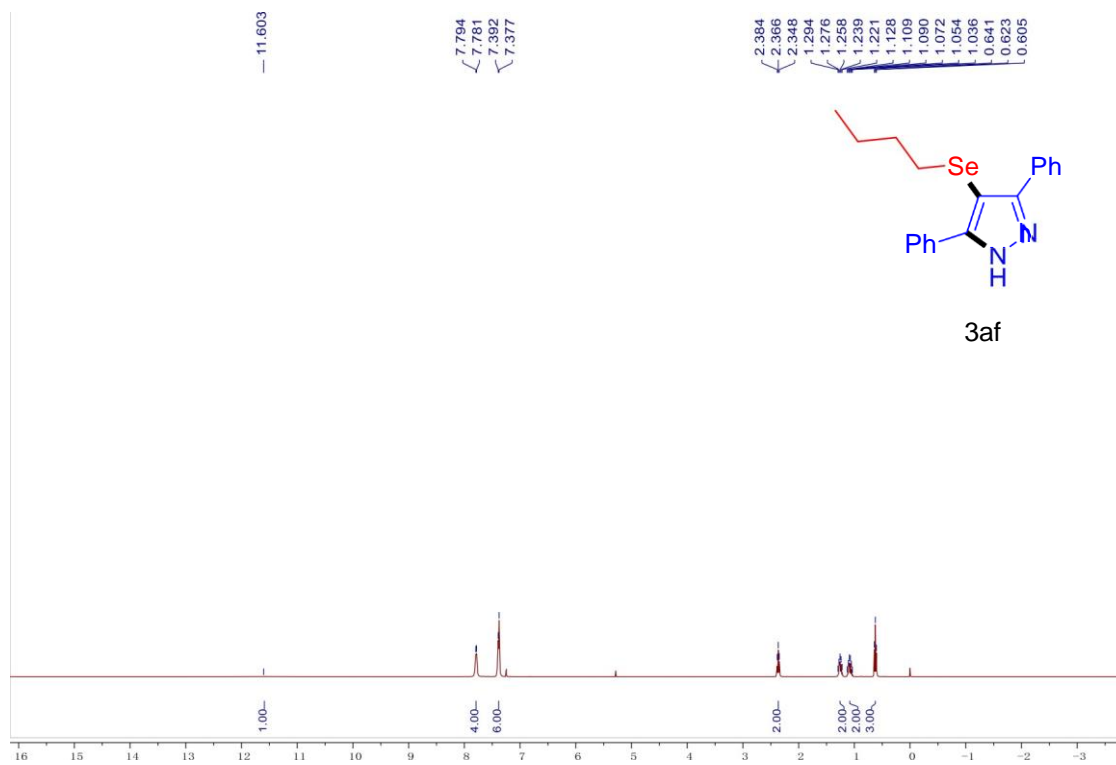


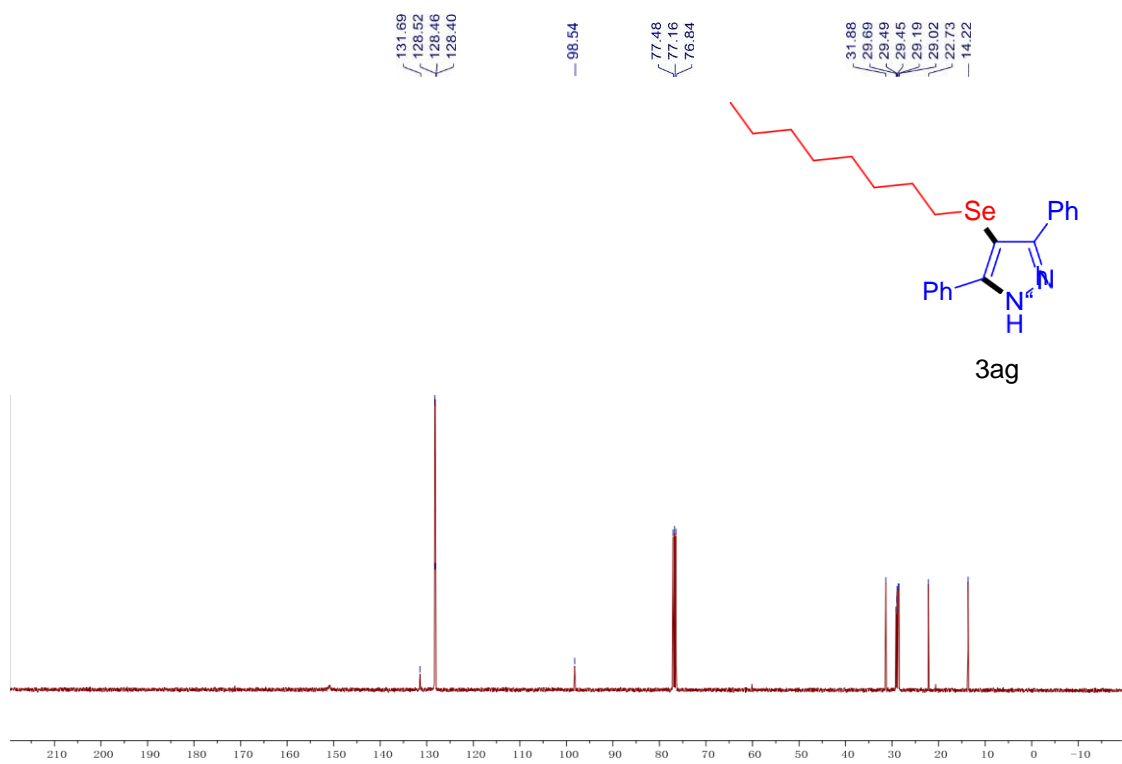
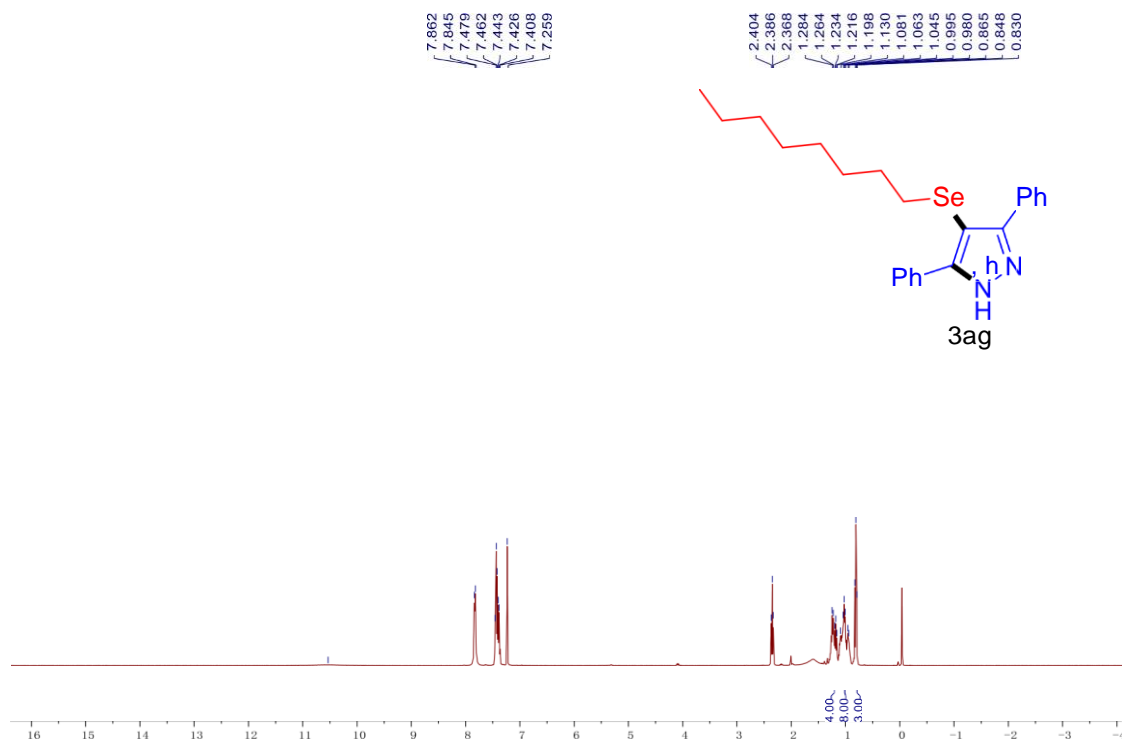
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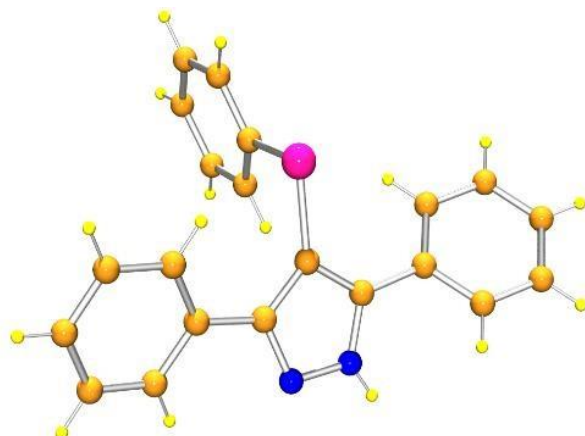








6. X-ray Structure of 3aa



Crystal Number: CCDC 1976347

Empirical formula: C₂₁H₁₆N₂Se

Formula weight: 375.32

Crystal system: Monoclinic

Space group: P21/n

Unit cell parameters: *a* (Å): 10.244(2), *b* (Å): 9.6663(19), *c* (Å): 16.765(3)

Volume: 1658.1(6)

Z: 4

Calculated density (mg/m³): 1.504

F(000): 760.0