

*Supporting Information for*

**Synthesis of organoselenyl isoquinolinium imides via Iron (III) chloride-mediated tandem cyclization/selenation of N<sup>2</sup>-(2-alkynylbenzylidene)hydrazides and diselenides**

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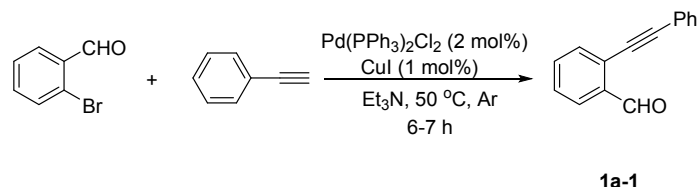
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## 1. General procedures for the synthesis of N'-(2-alkynylbenzylidene)hydrazides

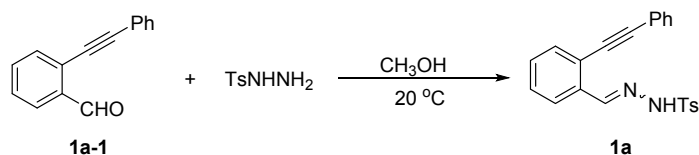
All of the substrates N'-(2-alkynylbenzylidene)hydrazides were prepared with the similar procedure as compound **1a**.

### 2-(phenylethynyl)benzaldehyde (**1a-1**)



To a solution of 2-bromobenzaldehyde (1.86 g, 10.0 mmol) and phenylacetylene (1.22 g, 12.0 mmol) in Et<sub>3</sub>N (40 mL) were added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (140 mg, 2 mol%) and CuI (20 mg, 1 mol%). The resulting mixture was then heated under an Ar atmosphere at 50 °C. The reaction was monitored by TLC to establish completion. When the reaction was complete, the mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography using 20:1 PE/EtOAc to afford 1.94 g (94%) of 2-(2-phenylethynyl)benzaldehyde **1a-1** as a yellow oil with spectral properties identical to those previously reported.<sup>[1]</sup>

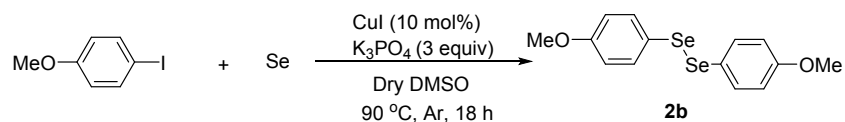
### 4-methyl-N'-(2-phenylethynyl)benzylidene)hydrazides (**1a**)



To an oven-dried 25 mL round-bottom flask containing 2.05 g of p-toluenesulfonyl hydrazide (11 mmol, 1.1 equiv) and 20 mL of CH<sub>3</sub>OH was added 2-(2-phenylethynyl)benzaldehyde (2.06 g, 10 mmol) obtained from the above step. The mixture was stirred at 20 °C for 2 h and the volatiles were evaporated in vacuo. The residue was recrystallized from minimum amount of CH<sub>3</sub>OH to afford 3.26 g of N'-(2-phenylethynyl)benzylidene)tosylhydrazides **1a** (87% yield) as white crystals.<sup>[2]</sup>

## 2. General procedures for the synthesis of di(hetero)aryl diselenides

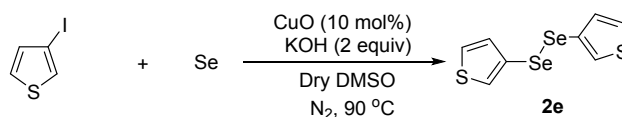
The synthesis of **2b**, **2c**, **2d**, **2f**, **2g**



To a solution of 1-iodo-4-methoxybenzene (1.17 g, 5.0 mmol) and selenium powder (1.19 g, 15.0 mmol) in dry DMSO (15 mL) were added CuI (95 mg, 10 mol %) and K<sub>3</sub>PO<sub>4</sub> (3.18 g, 15.0 mmol). The resulting mixture was then heated under an Ar atmosphere at 90 °C for 18 h. When the reaction was complete, the mixture was allowed to cool to room temperature, and excess K<sub>3</sub>PO<sub>4</sub> and selenium powder was

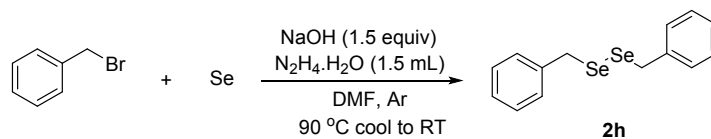
removed by filtration. After removing DMSO with water (20 mL), The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography use PE (**2b**, **2c**, **2d**), PE/EtOAc = 3:1 (**2f**, **2g**) to afford 0.79 g of 1,2-bis(4-methoxyphenyl)diselane **2b** (85% yield) as orange-red solid. [3]

The synthesis of **2e**



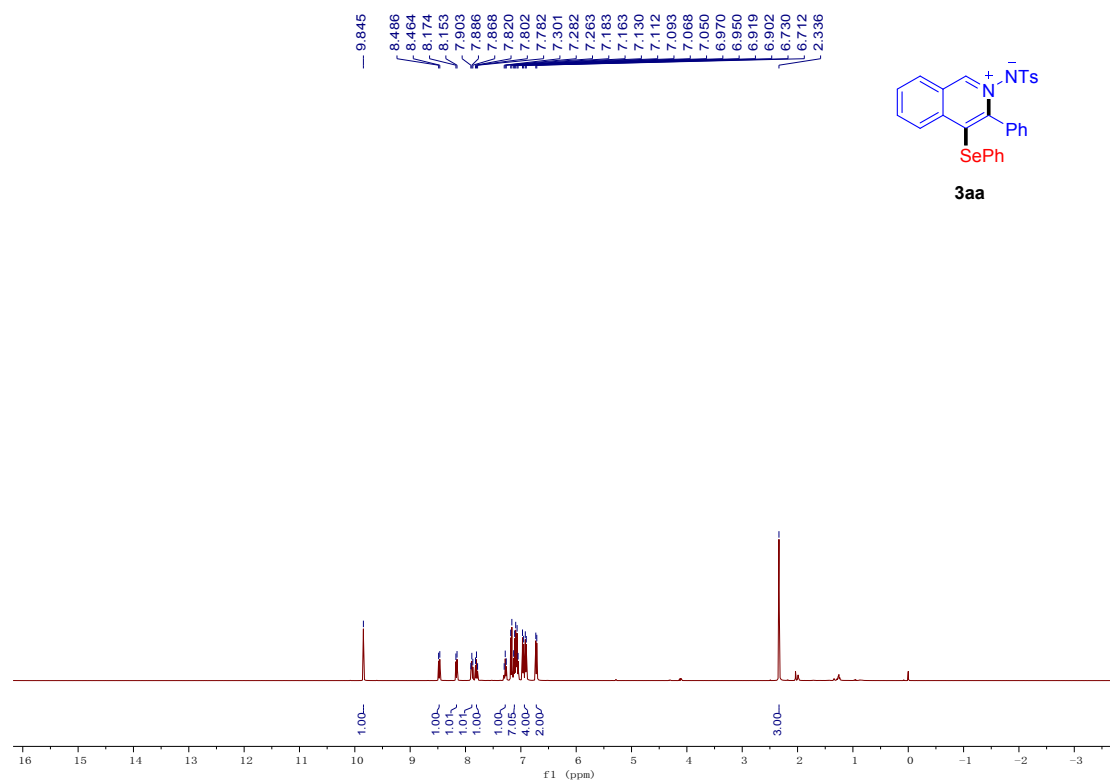
To a solution of 3-iodothiophene (1.68 g, 8.0 mmol) and selenium powder (1.26 g, 16.0 mmol) in dry DMSO (15 mL) were added CuO nanoparticles (64 mg, 10 mol %) and KOH (0.90 g, 16.0 mmol). The resulting mixture was then heated under a N<sub>2</sub> atmosphere at 90 °C for 18 h. When the reaction was complete, the mixture was allowed to cool to room temperature, and excess KOH and selenium powder was removed by filtration. After removing DMSO with water (20 mL), The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography use PE to afford 1.08 g of 1,2-di(thiophen-3-yl)diselane **2e** (83% yield) as orange-red solid. [4]

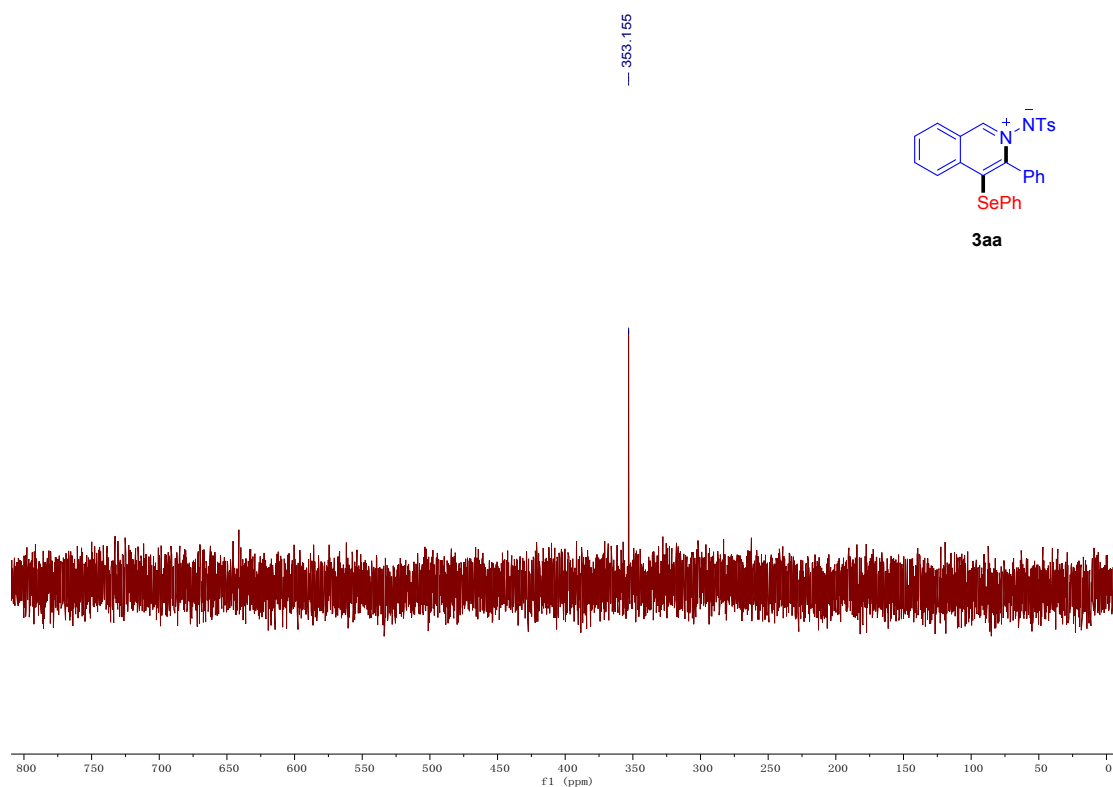
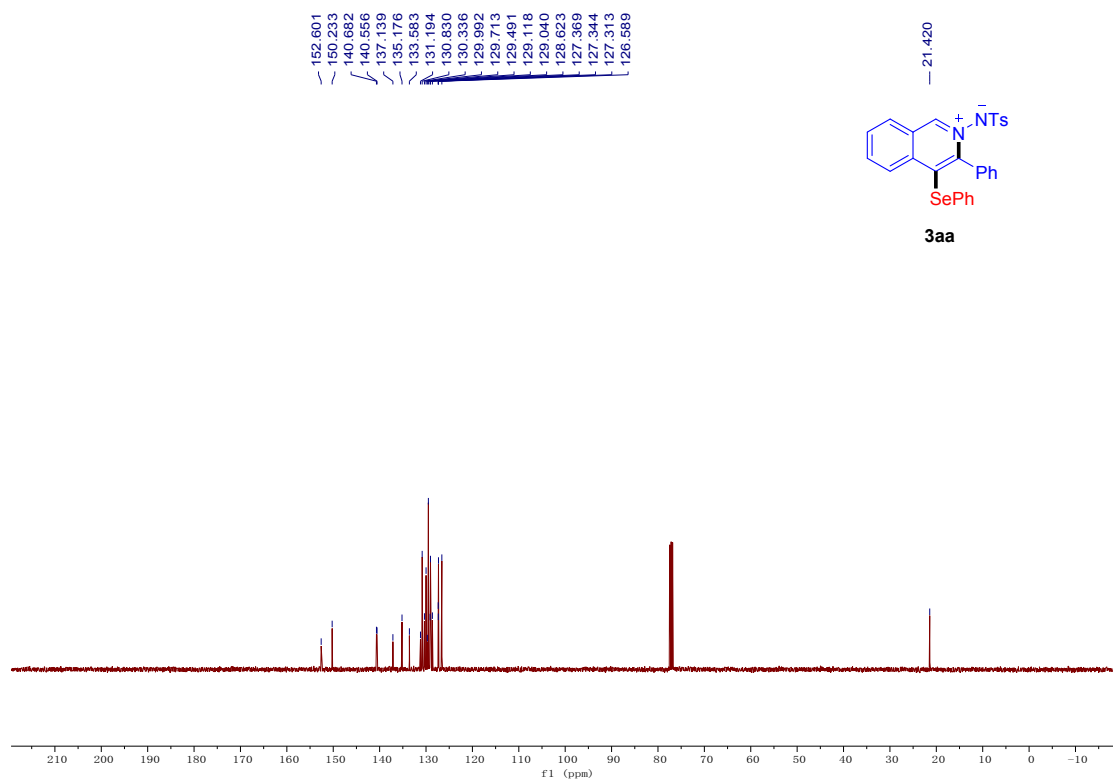
### 3. General procedures for the synthesis of dialkyl diselenides

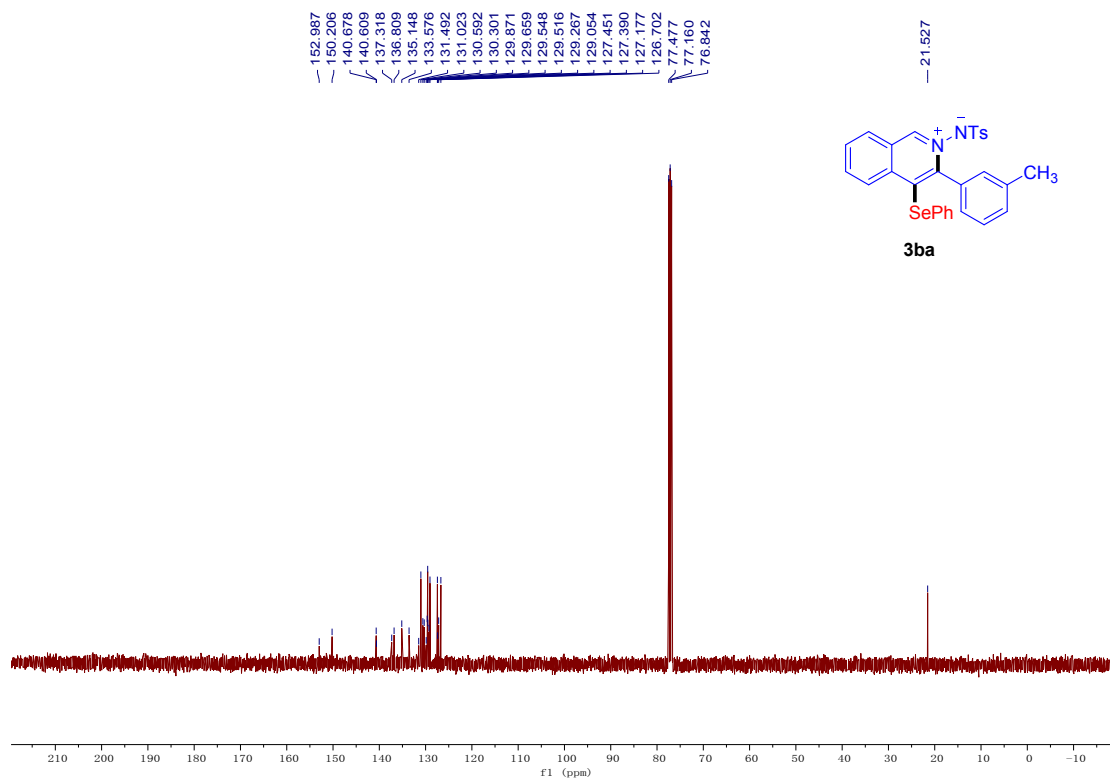
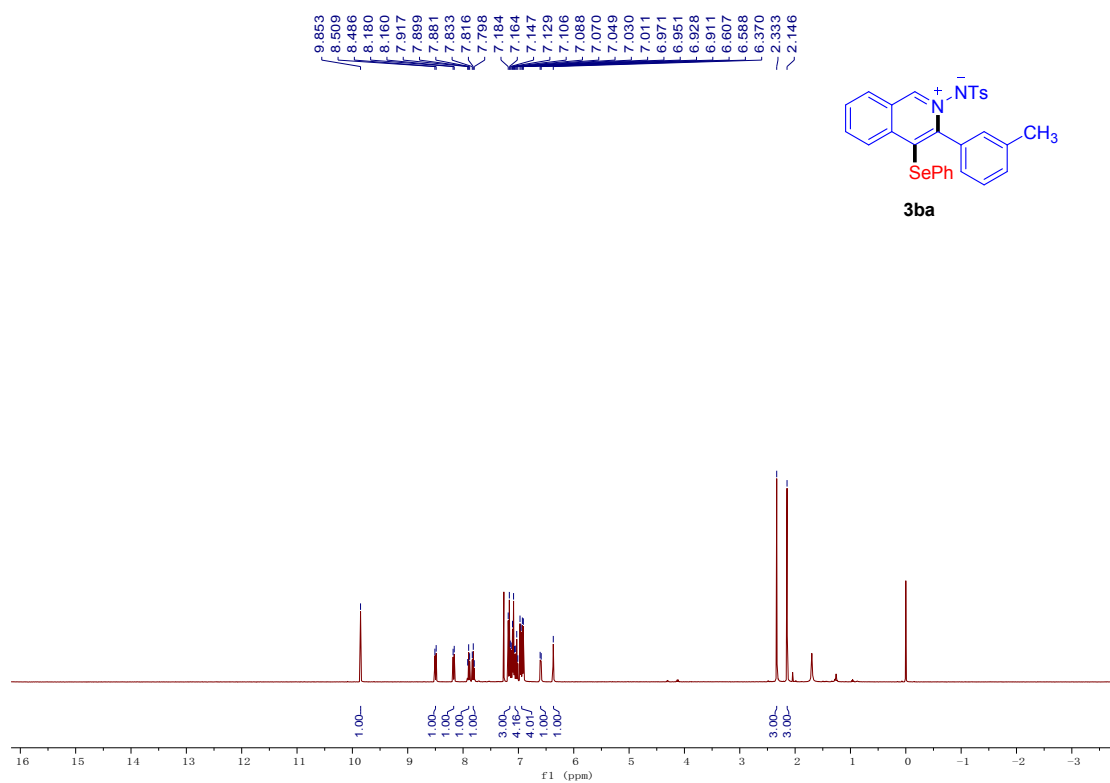


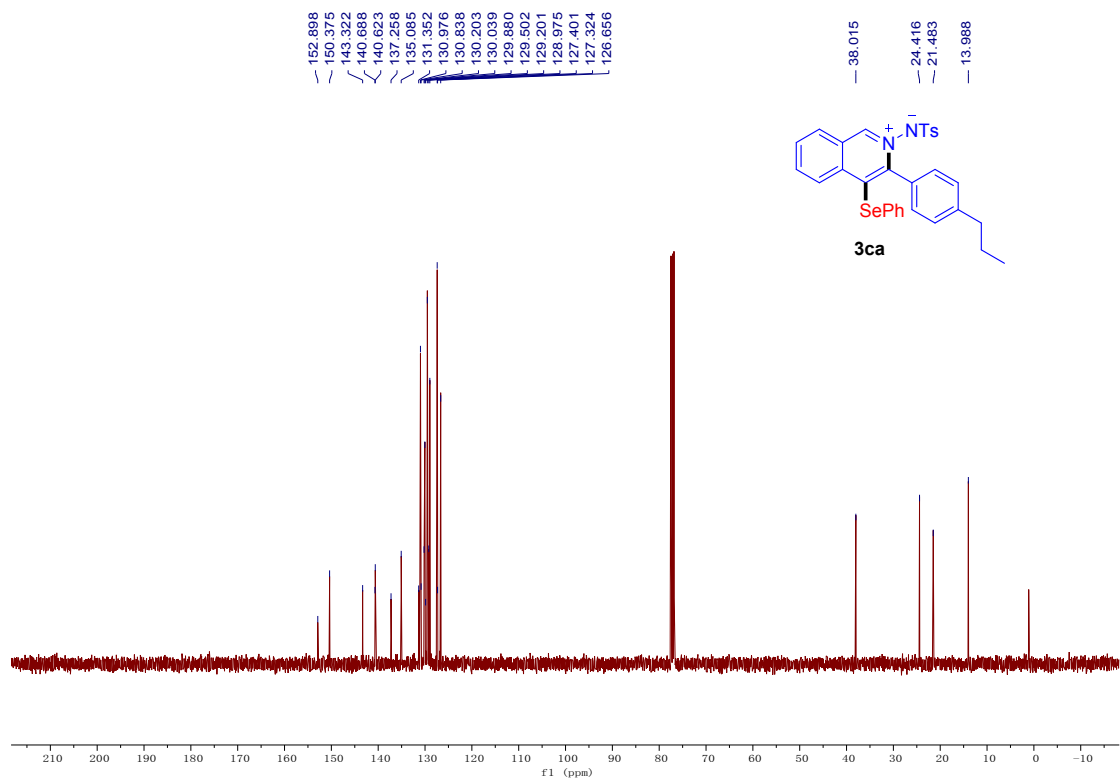
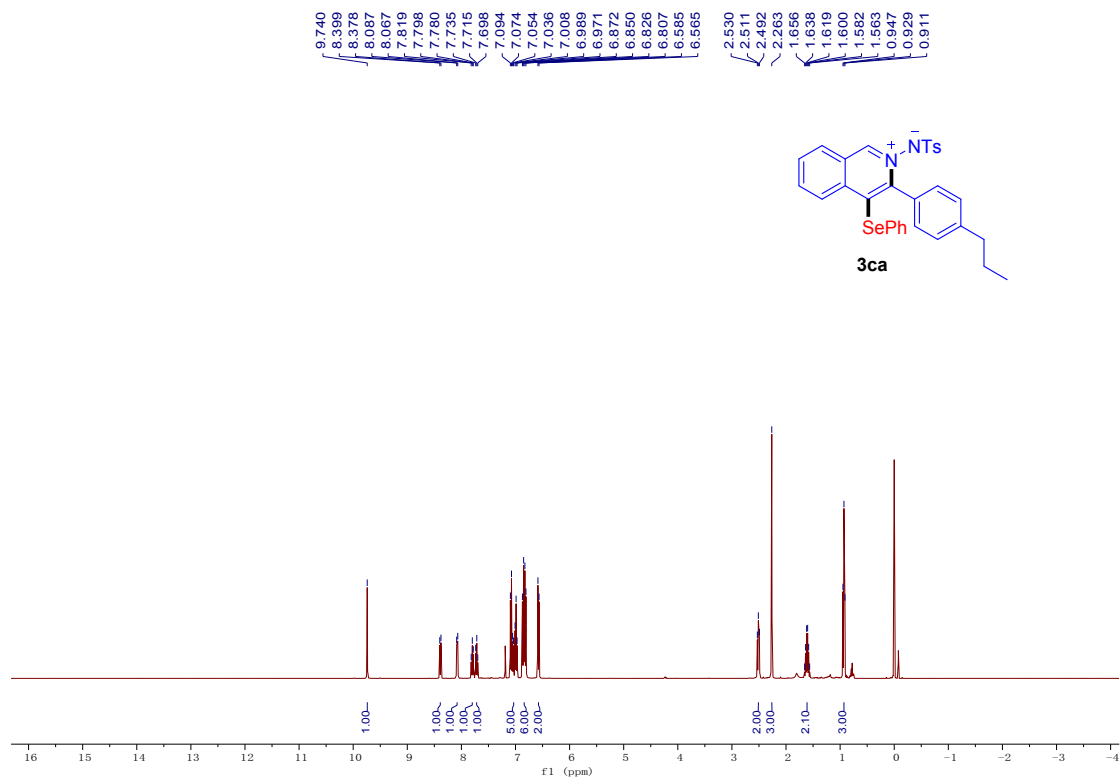
To a solution of sodium hydroxide (0.66 g, 16.5 mmol) and selenium powder (0.88 g, 11.0 mmol) in DMF (15 mL) were added hydrazine hydrate (1.5 mL). The resulting mixture was then heated under an Ar atmosphere at 90 °C until the reaction system turns red (Na<sub>2</sub>Se<sub>2</sub>). When the system cooled to room temperature, slowly injected (bromomethyl)benzene (2.02 mL, 16.5 mmol, dissolved in DMF) into the reaction flask under Ar atmosphere. Kept the reaction proceeding at room temperature for about 1 h until the system turned yellow. After removing DMF with water (20 mL), The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography use PE to afford 1.46 g of 1,2-dibenzyl diselane **2h** (78% yield) as orange-red solid. [5]

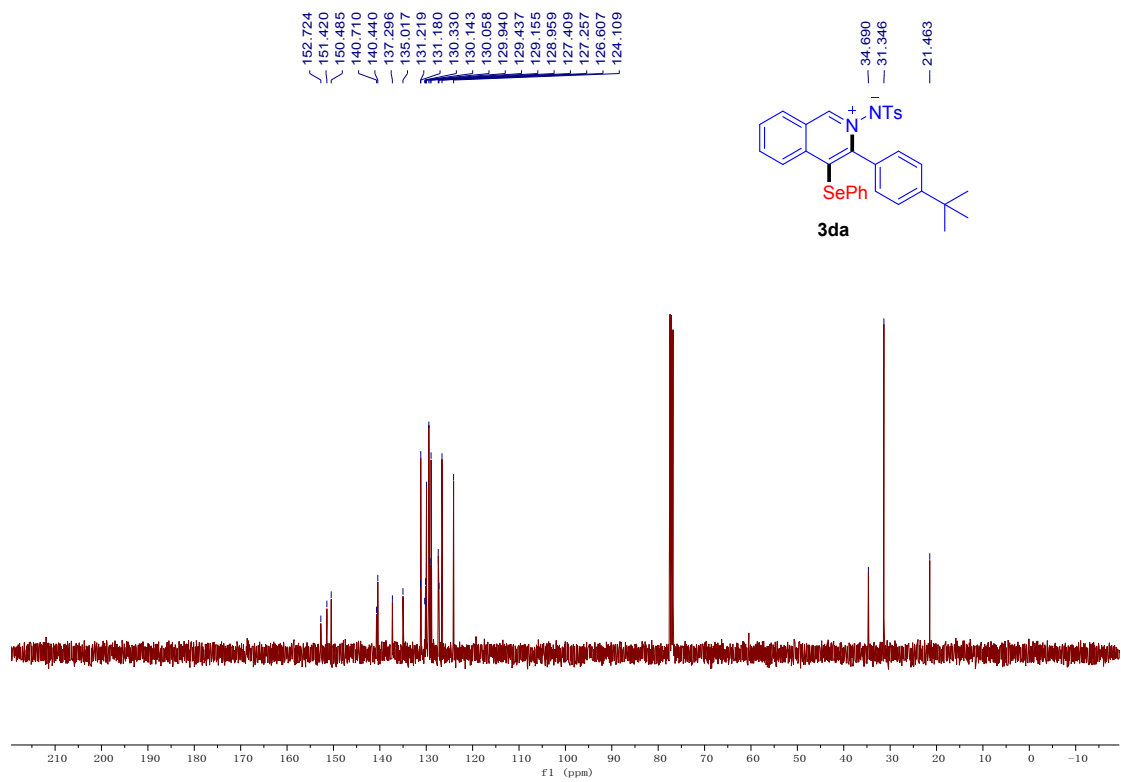
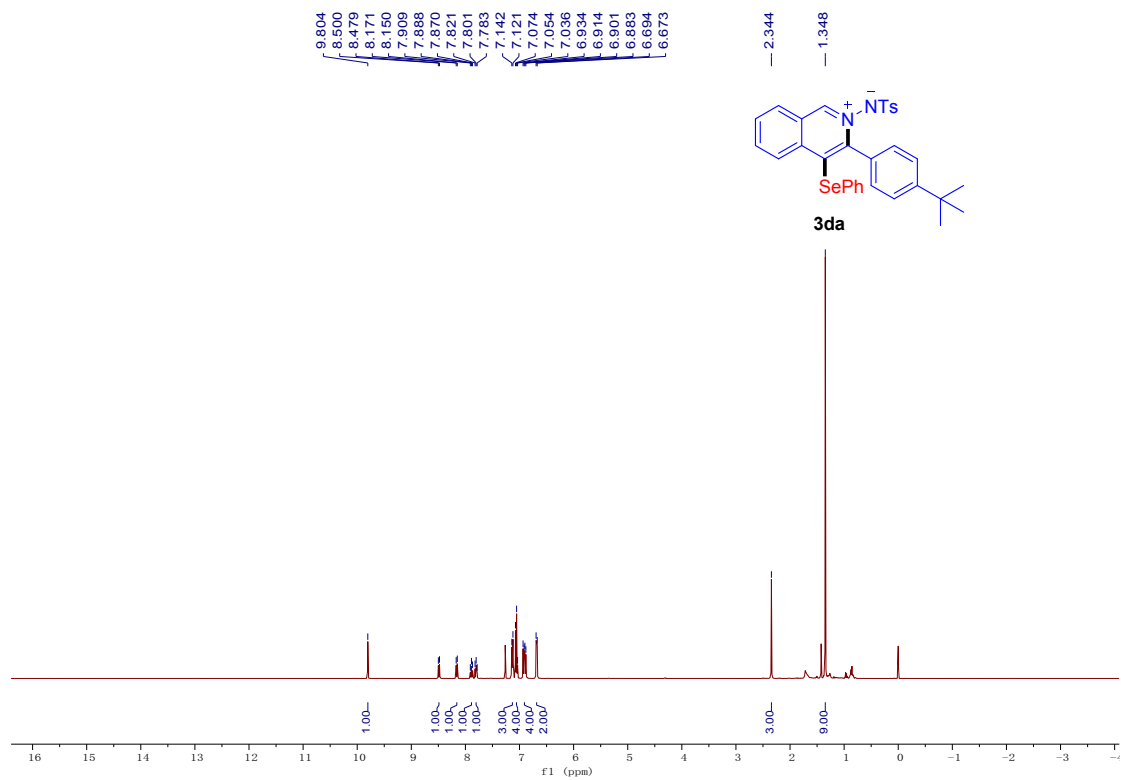
#### 4. NMR Spectra of 3 and 3-1



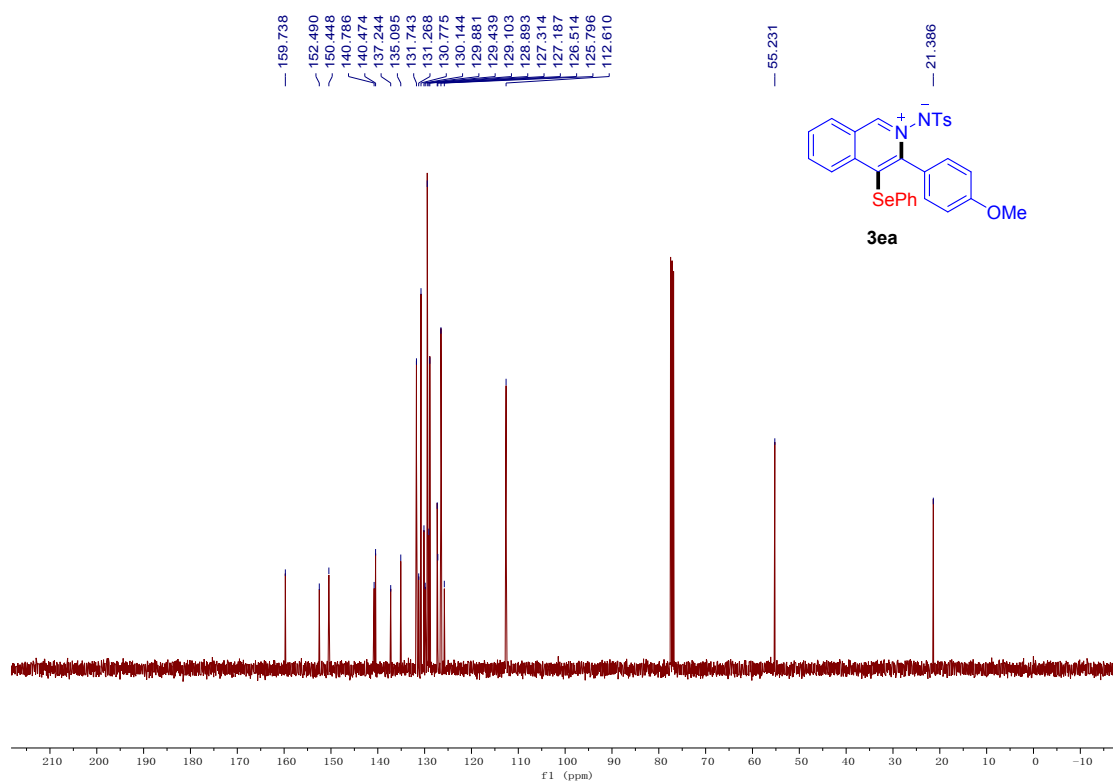
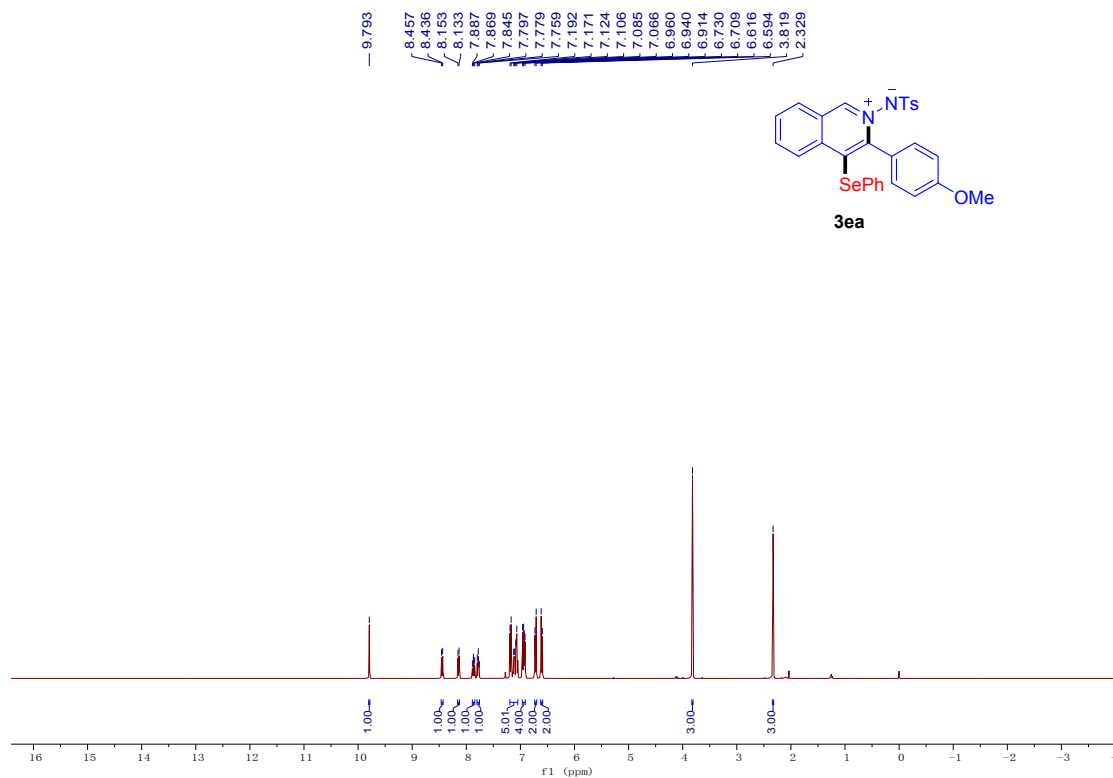


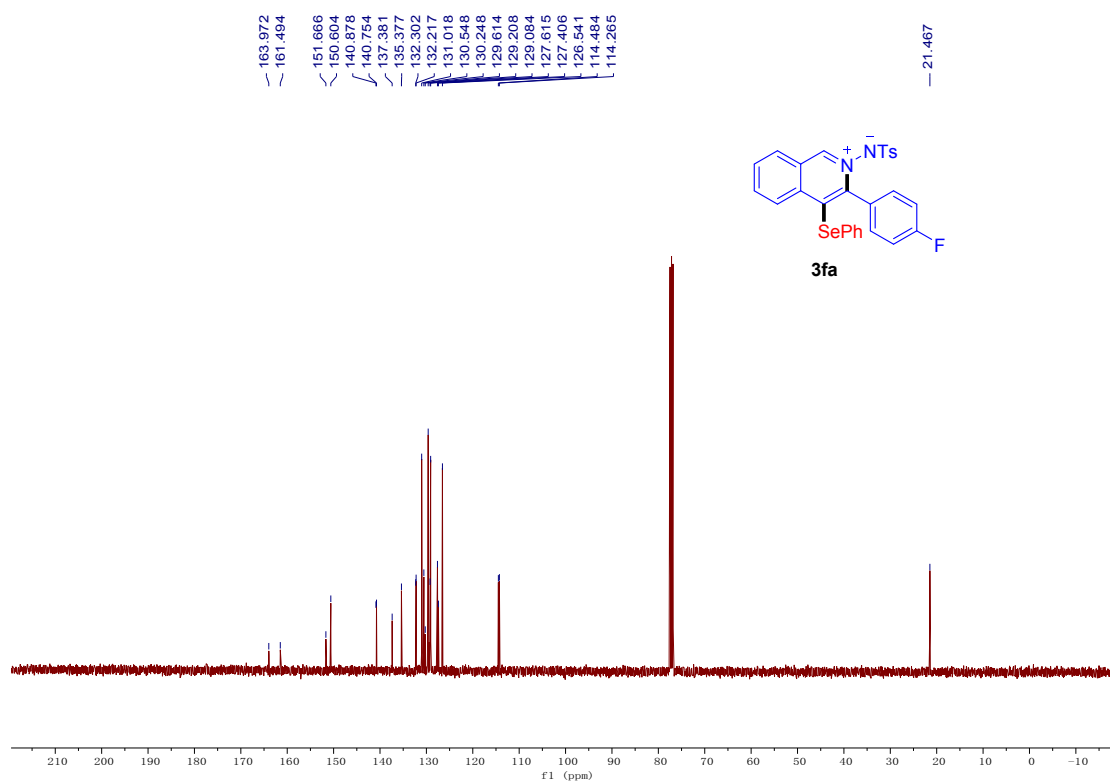
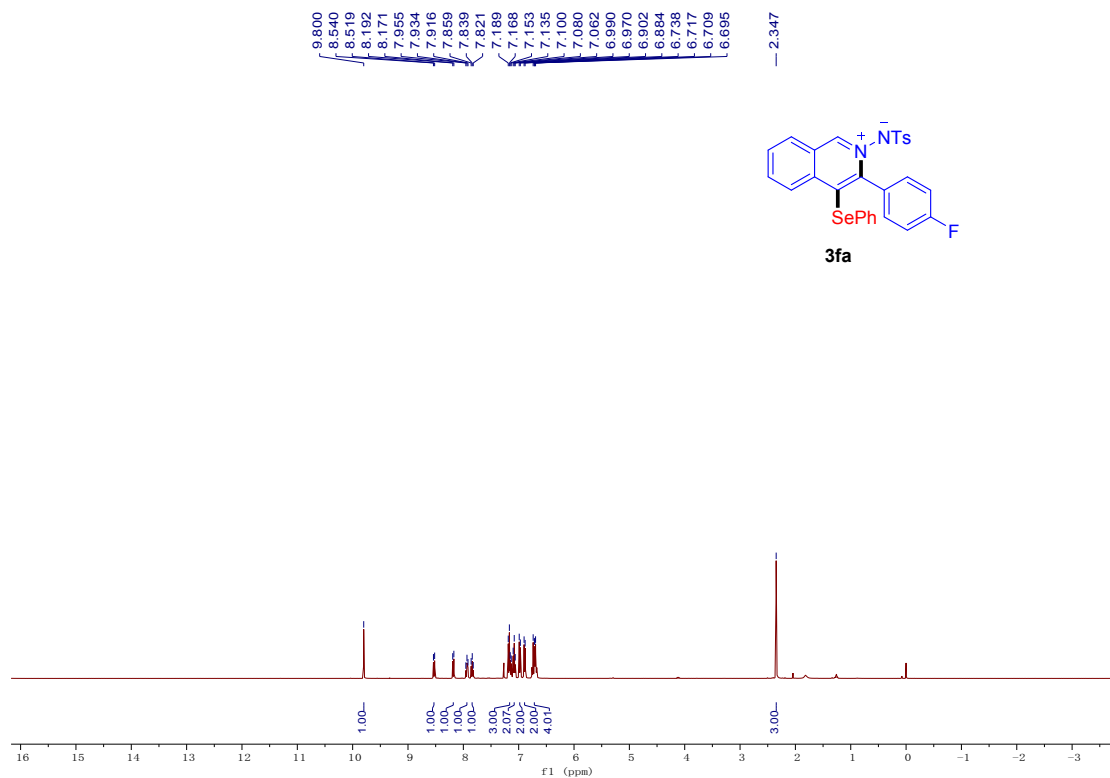


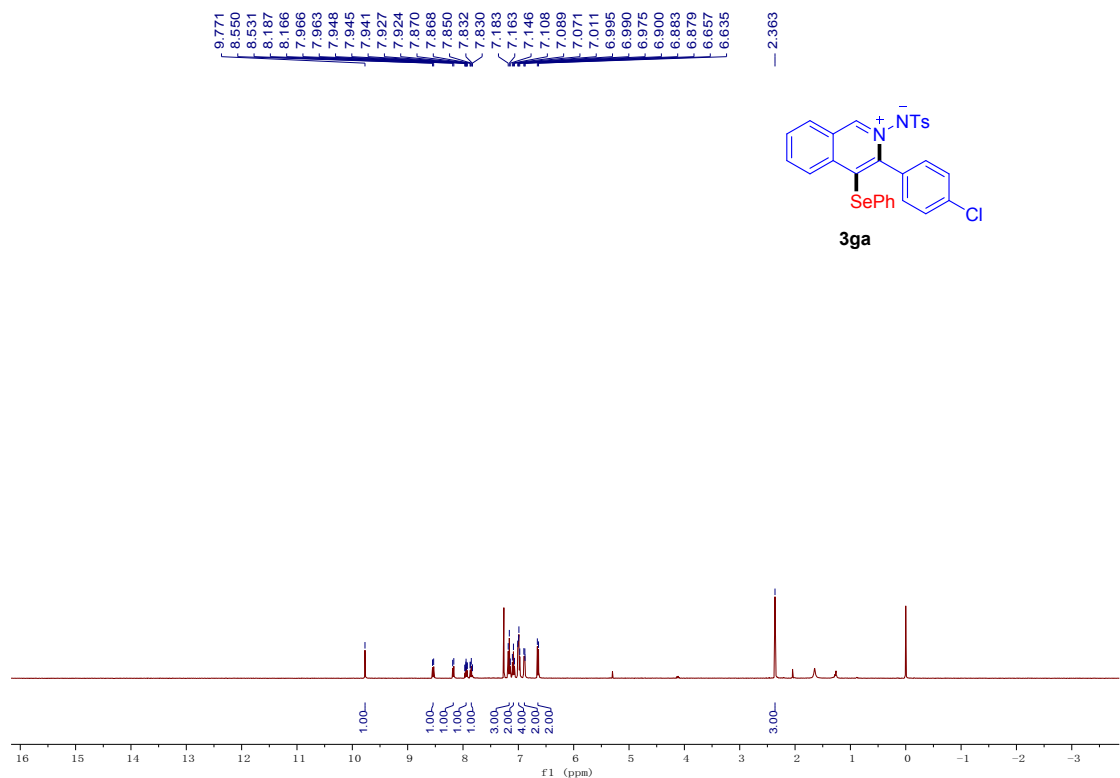
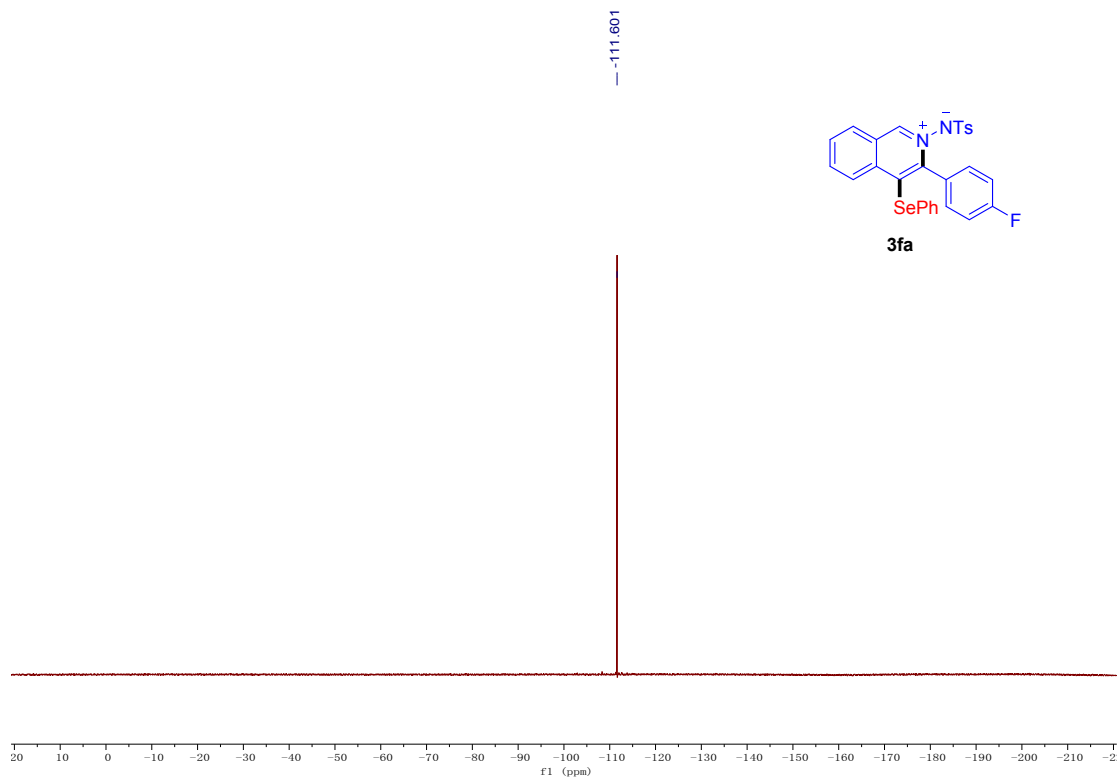


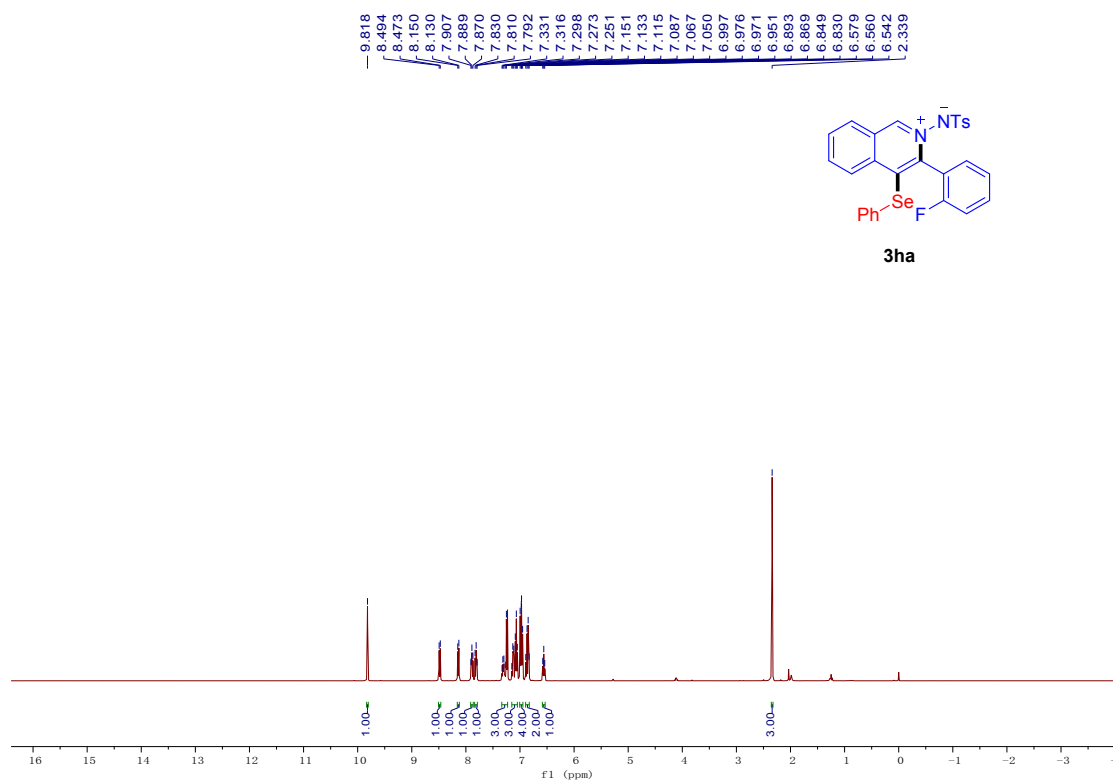
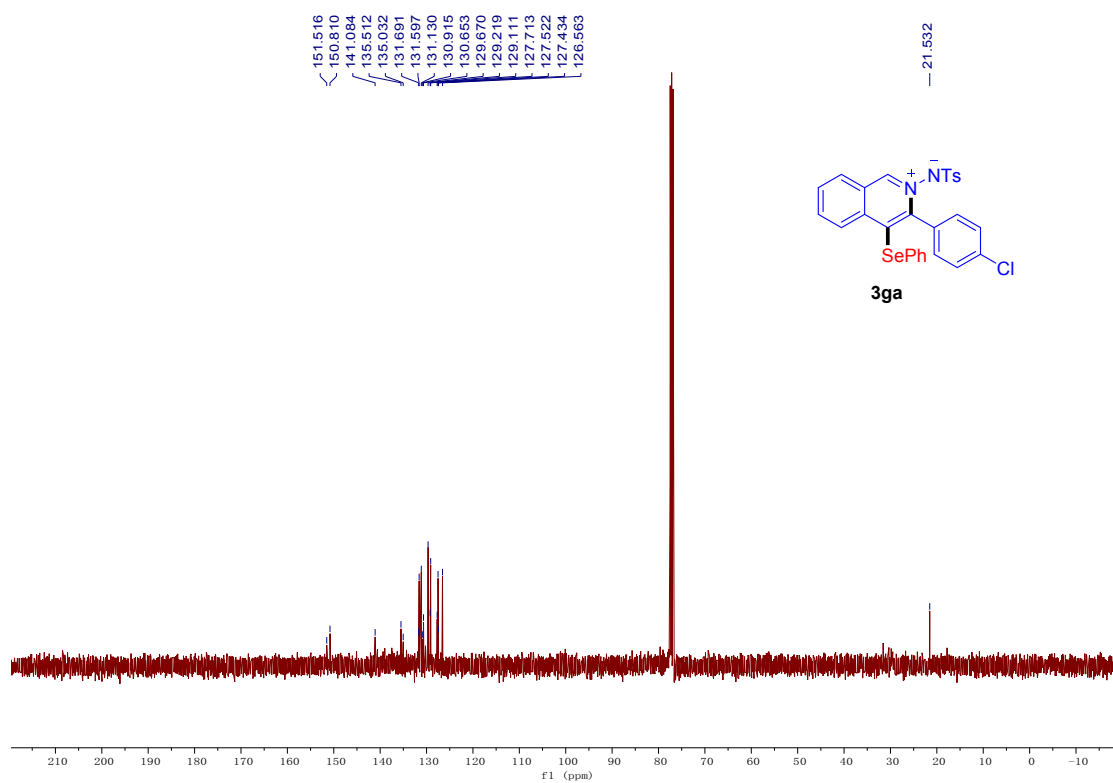


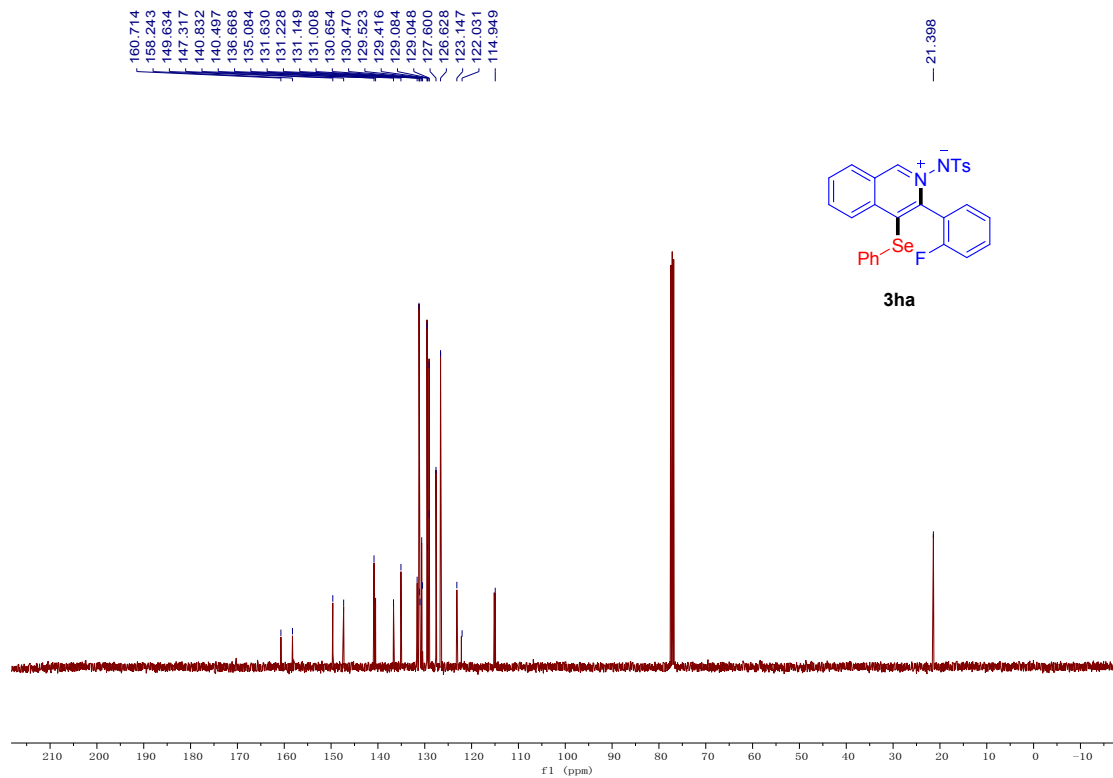


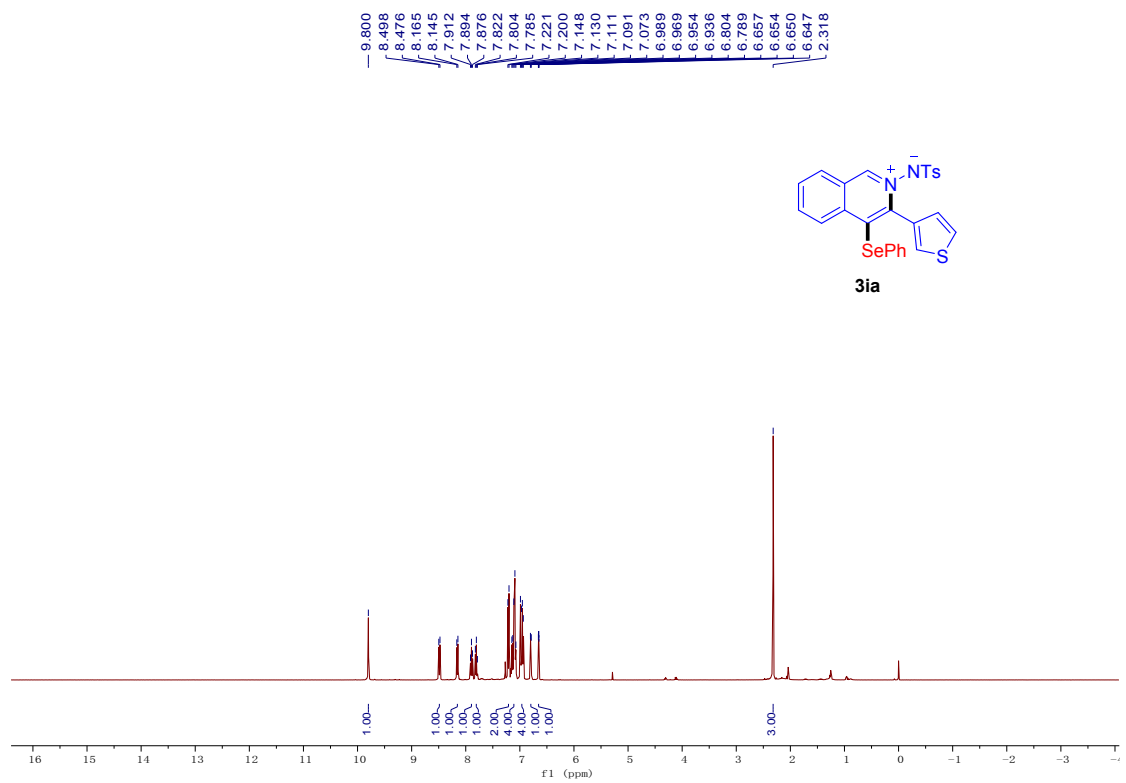
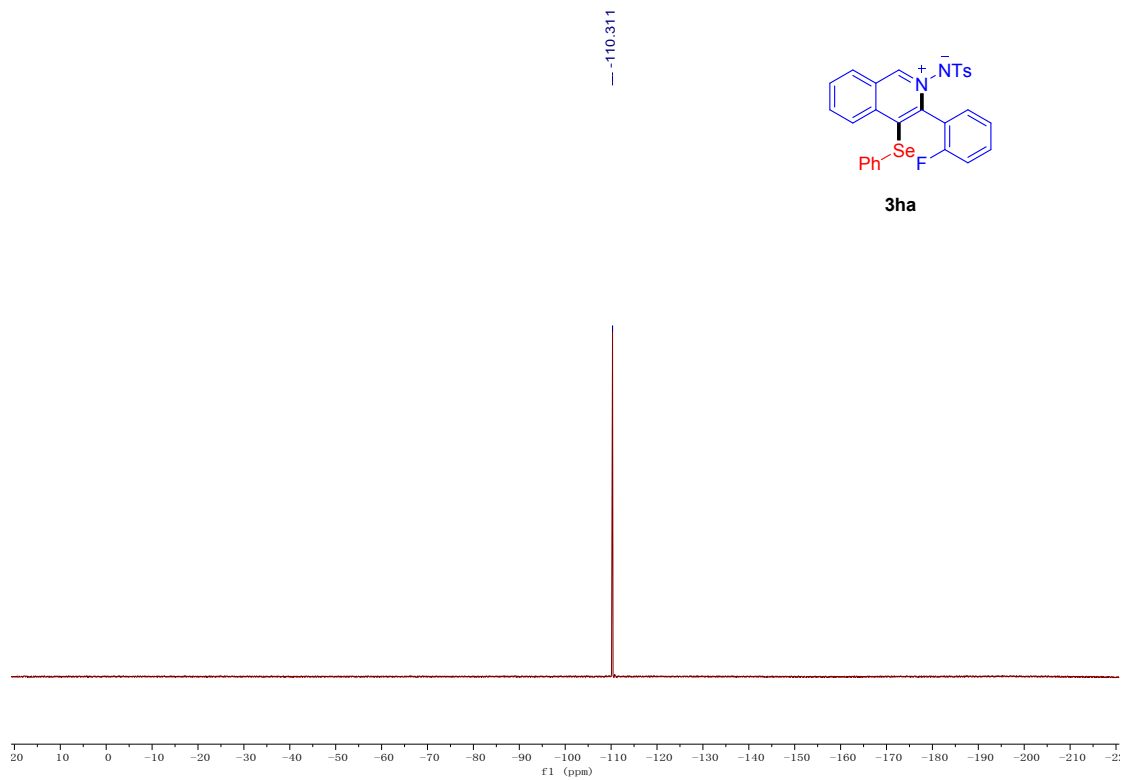


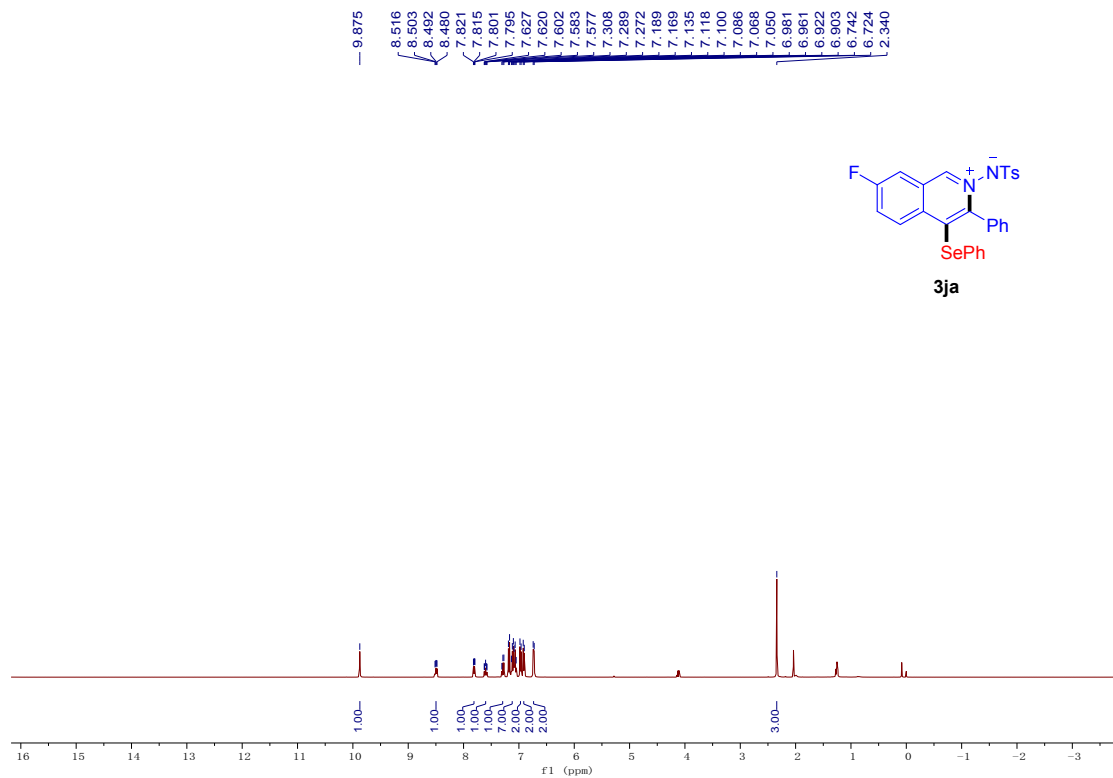
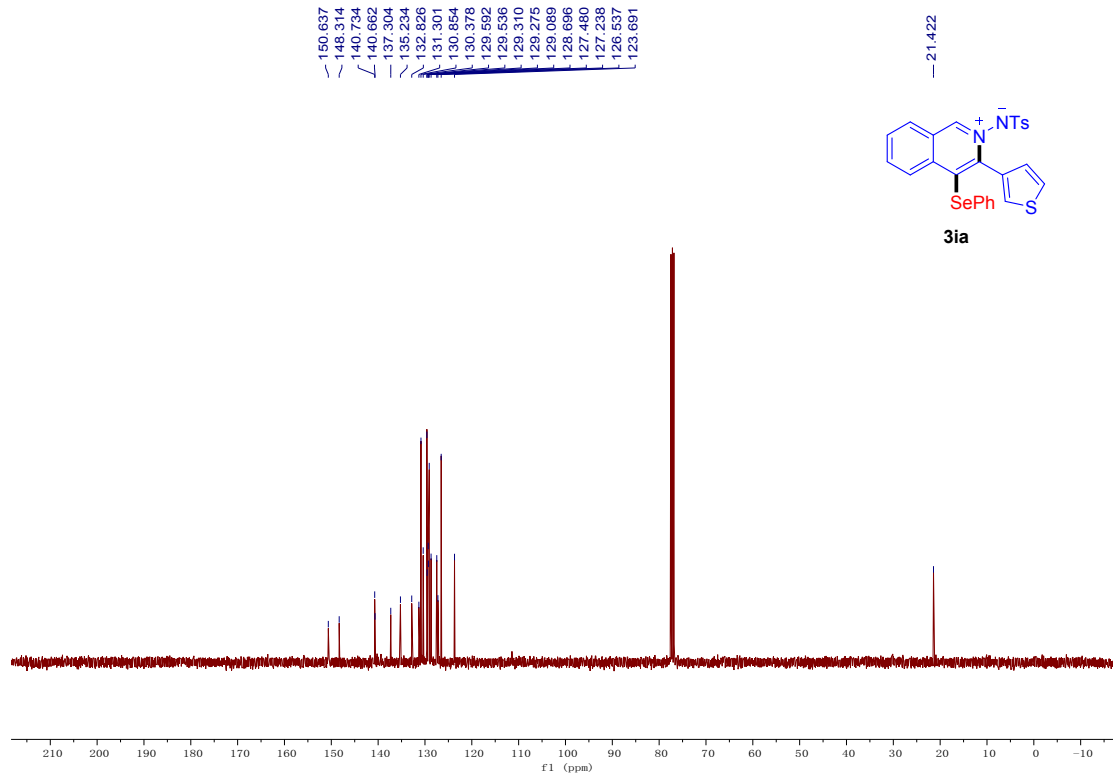


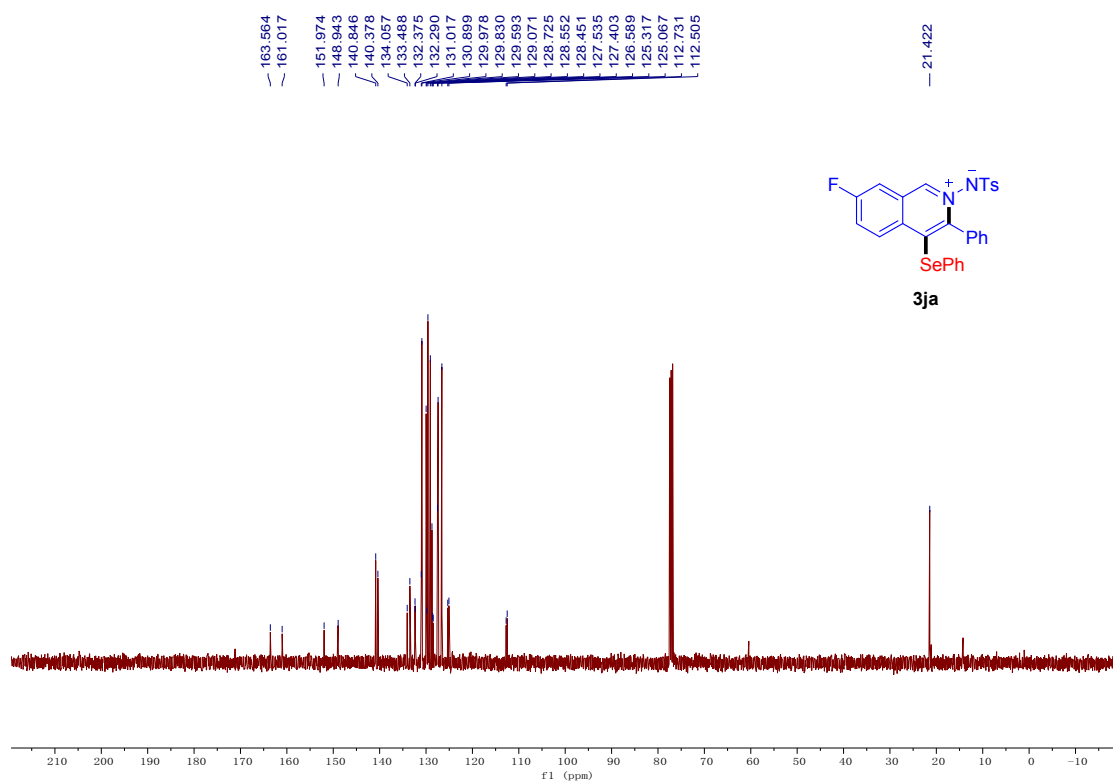




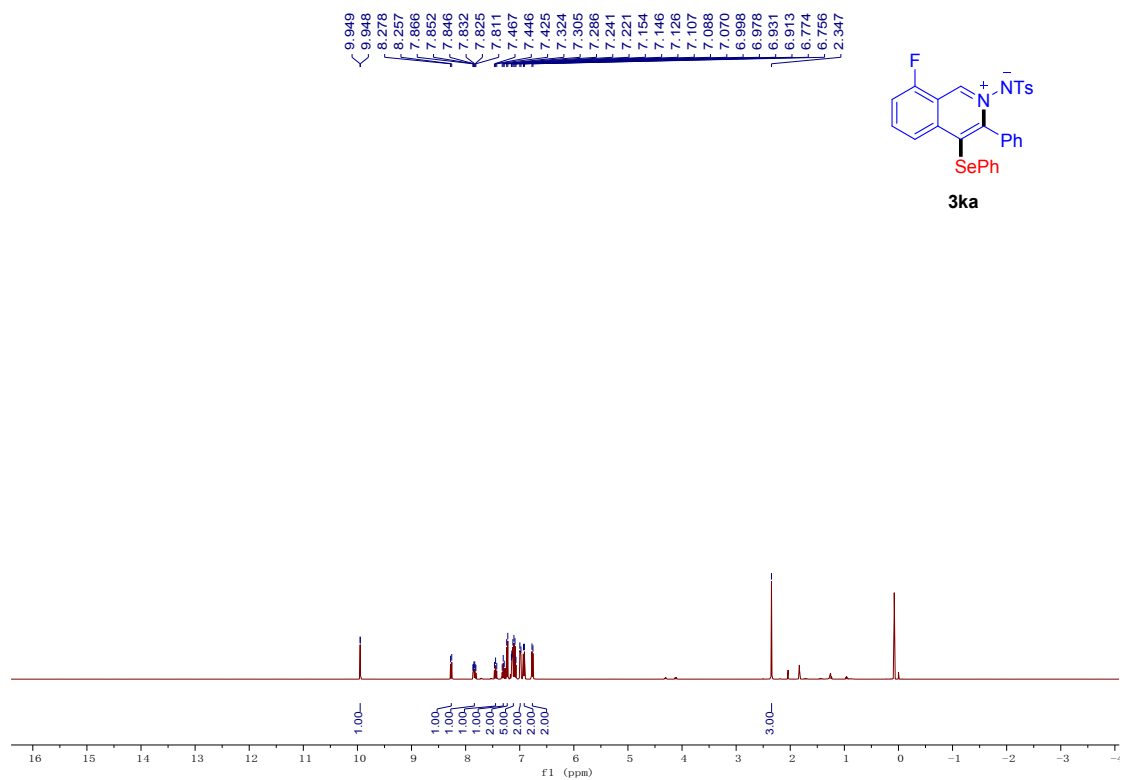
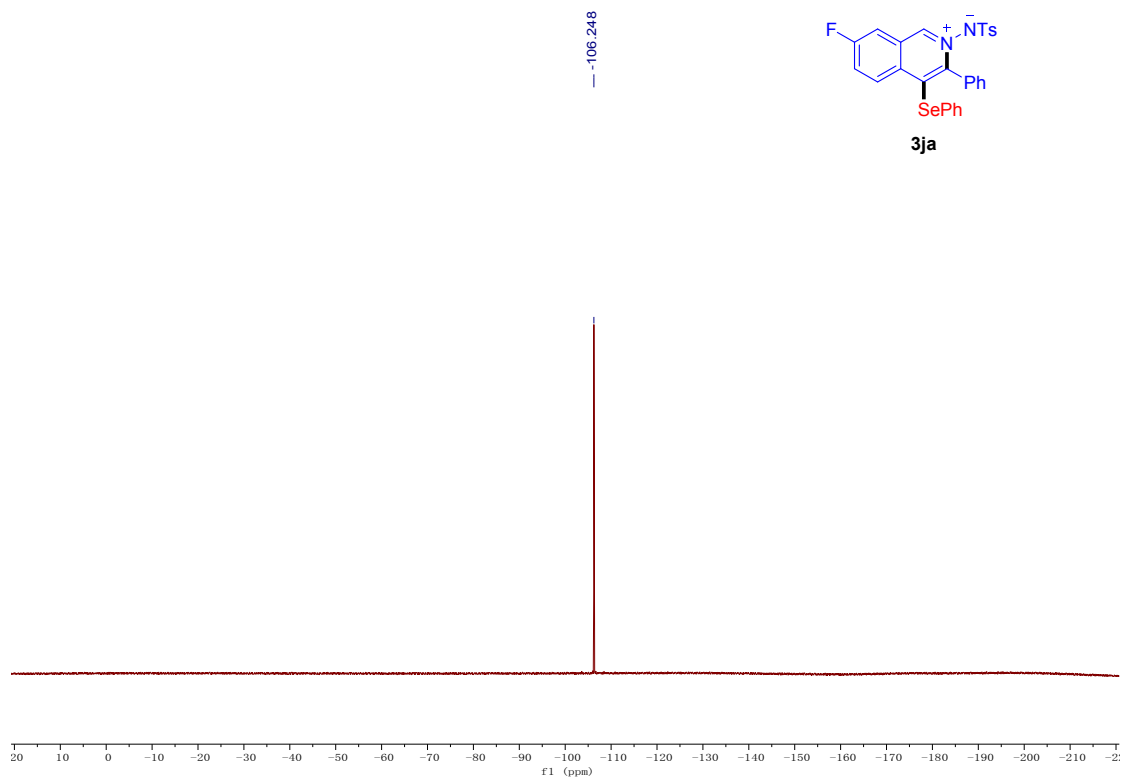


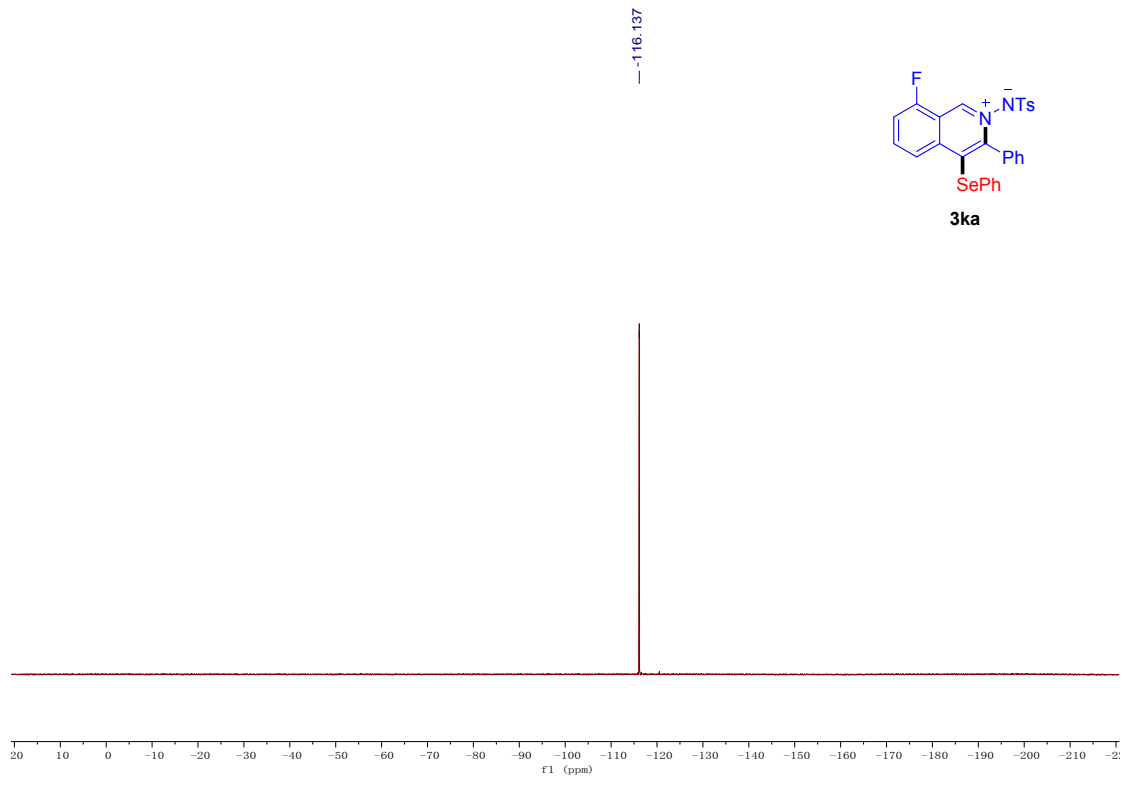
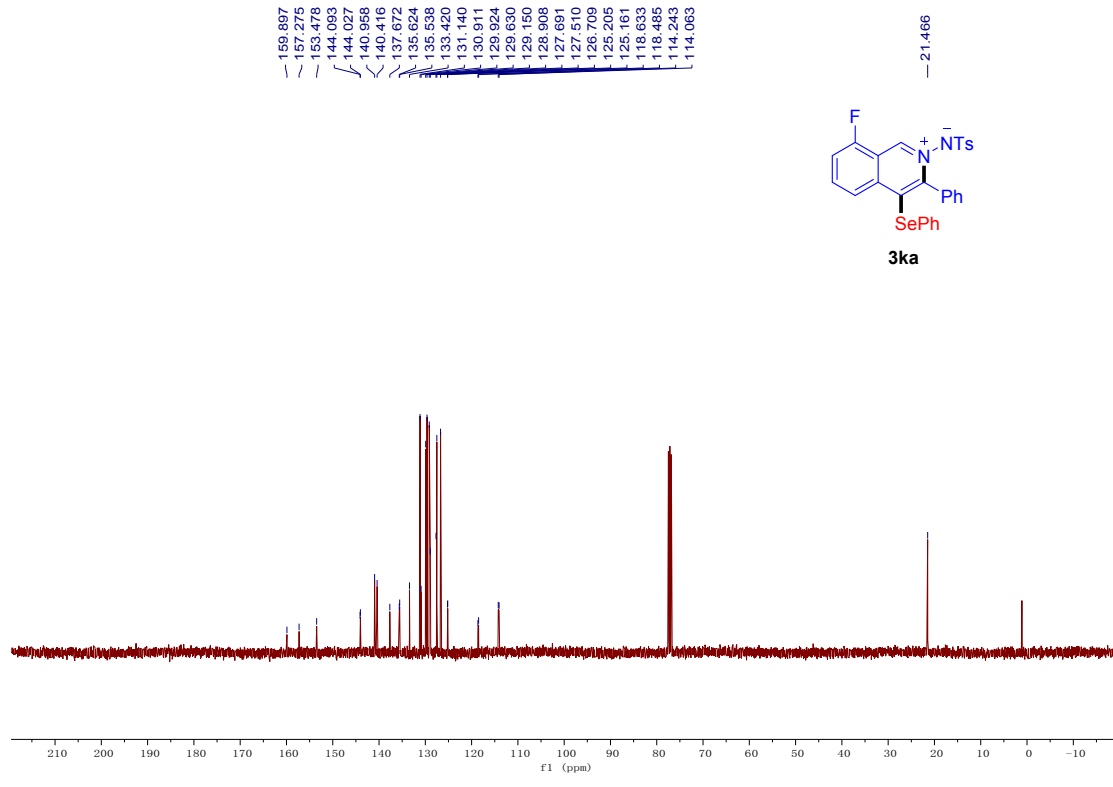


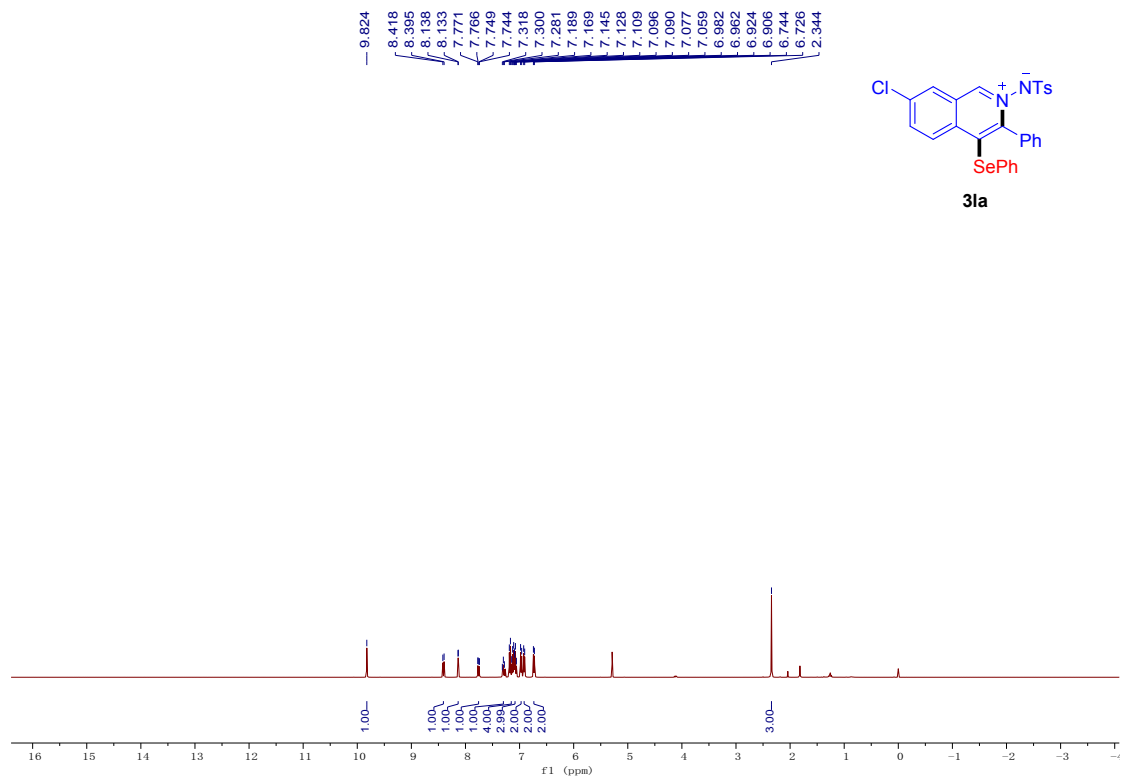


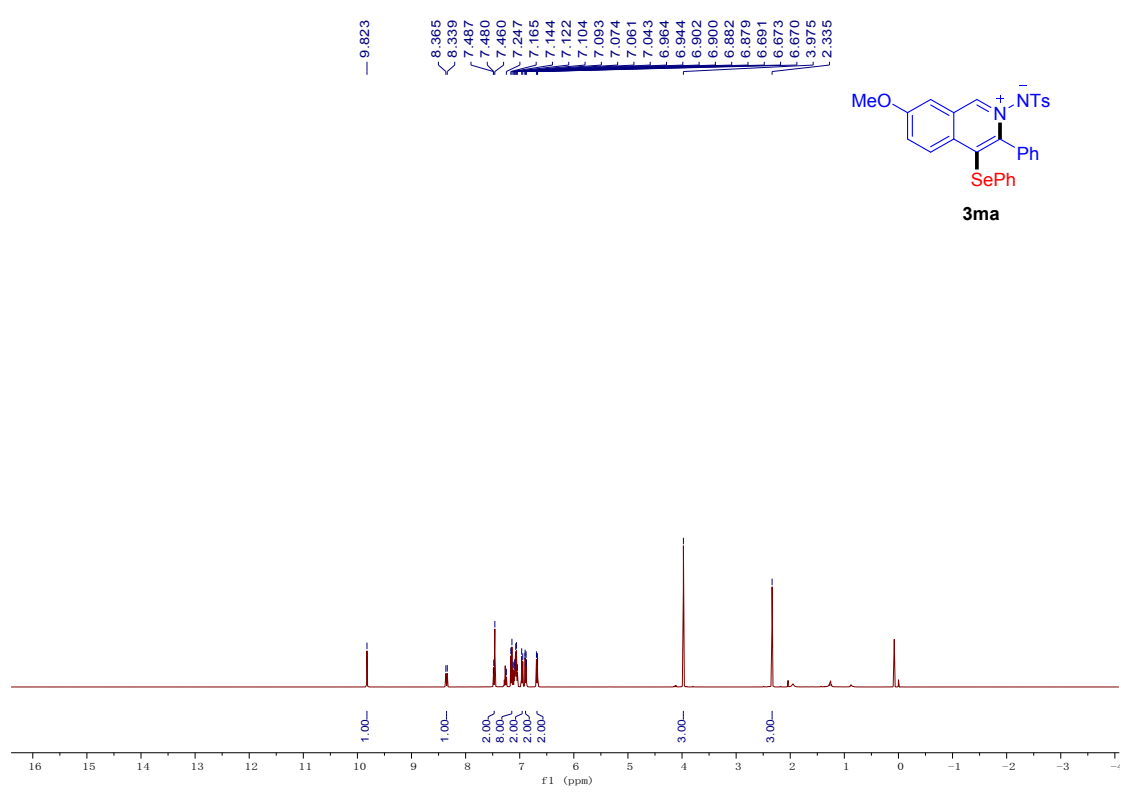
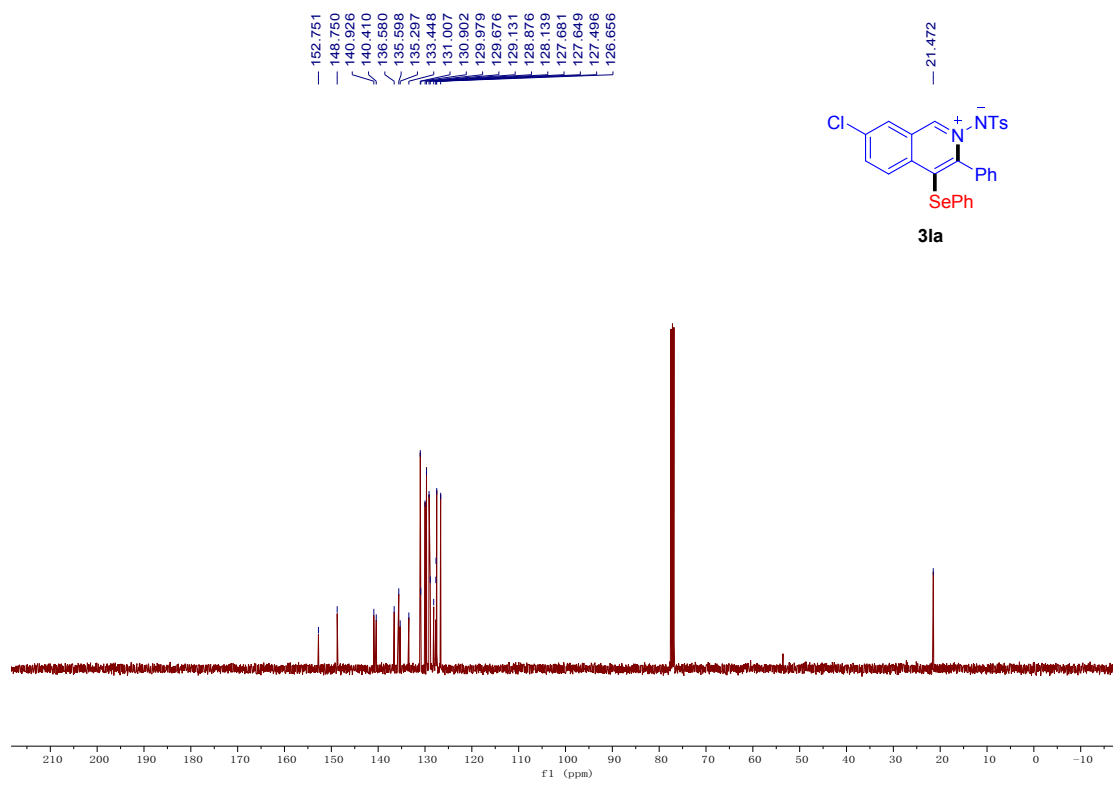


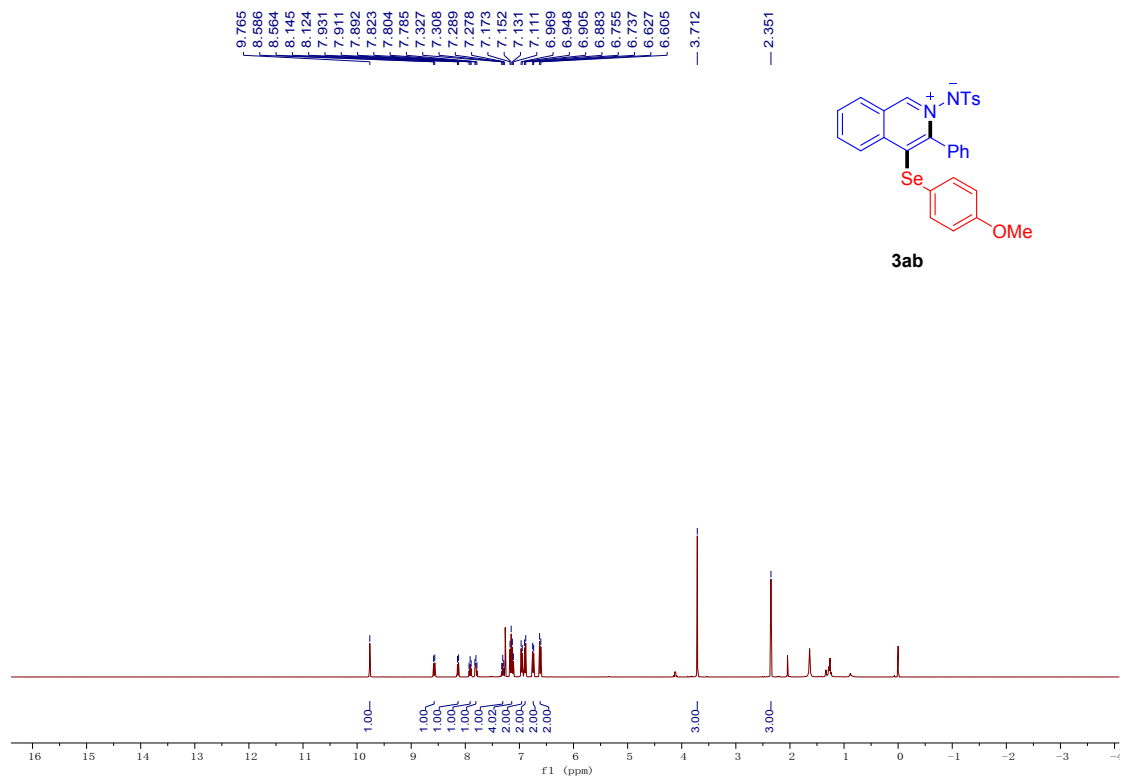
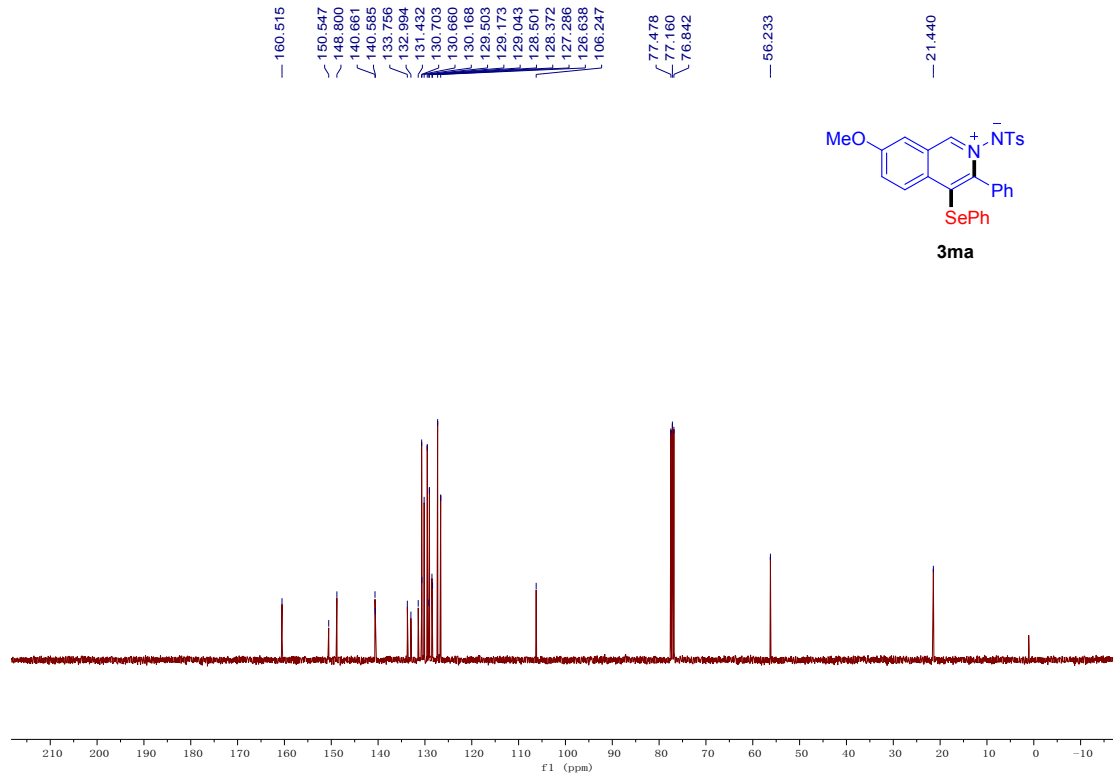


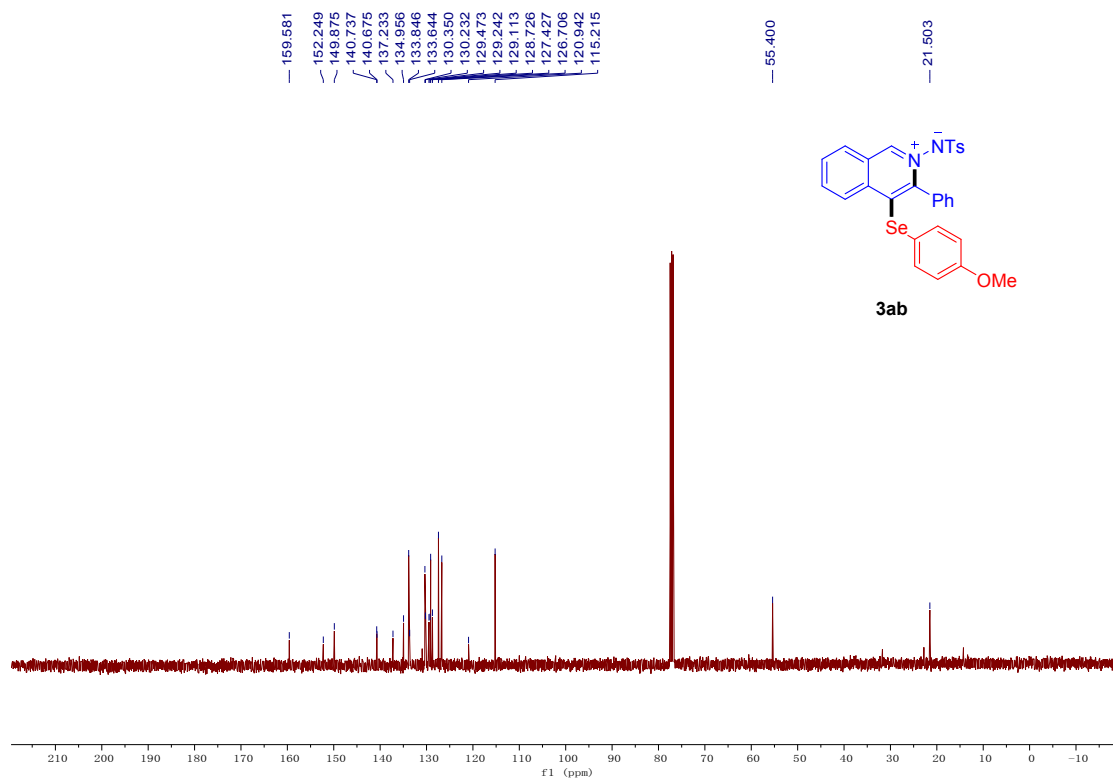


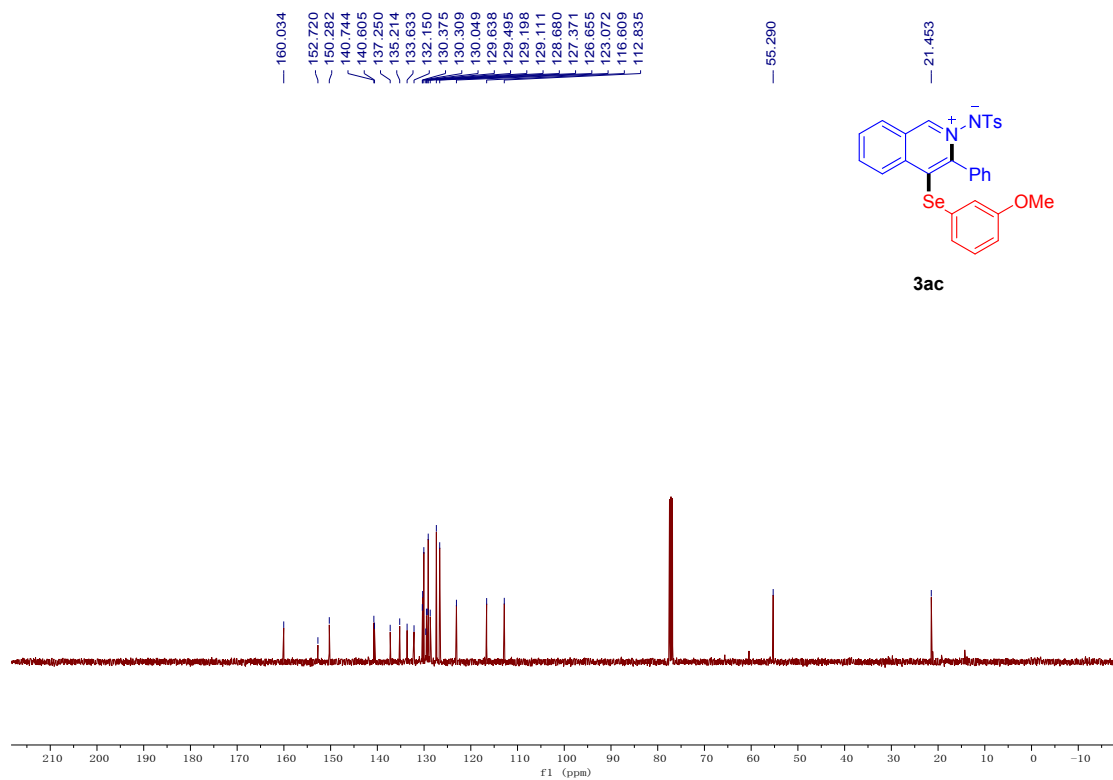
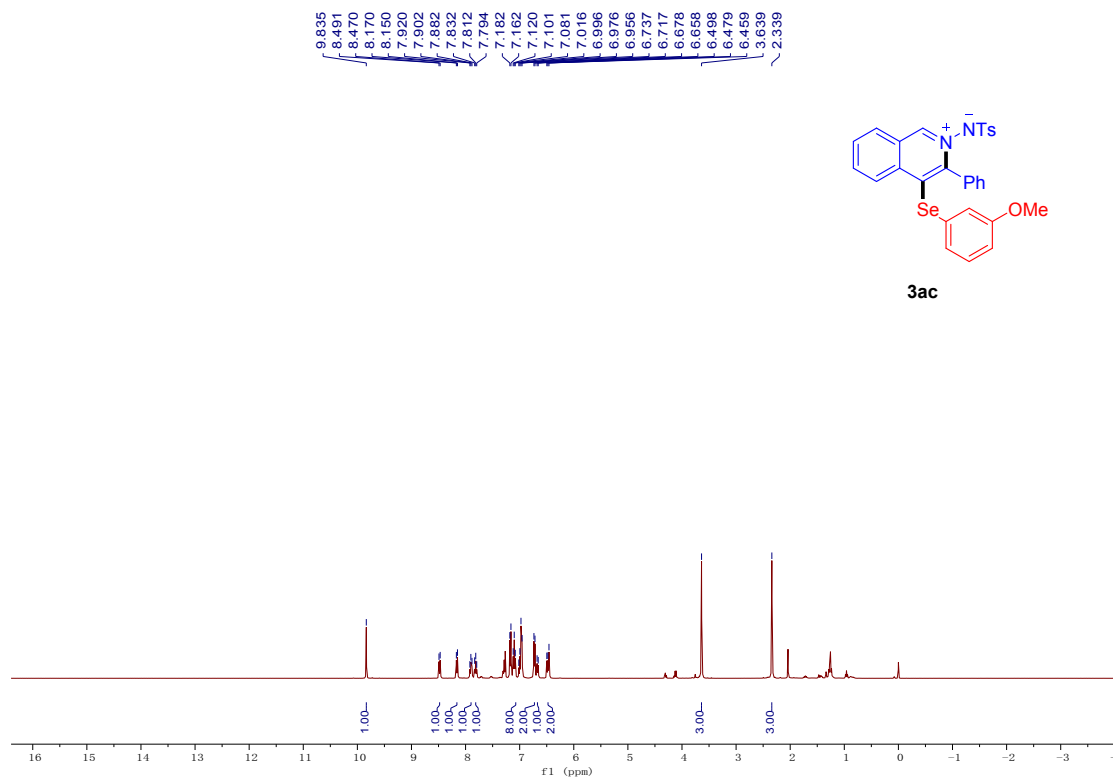


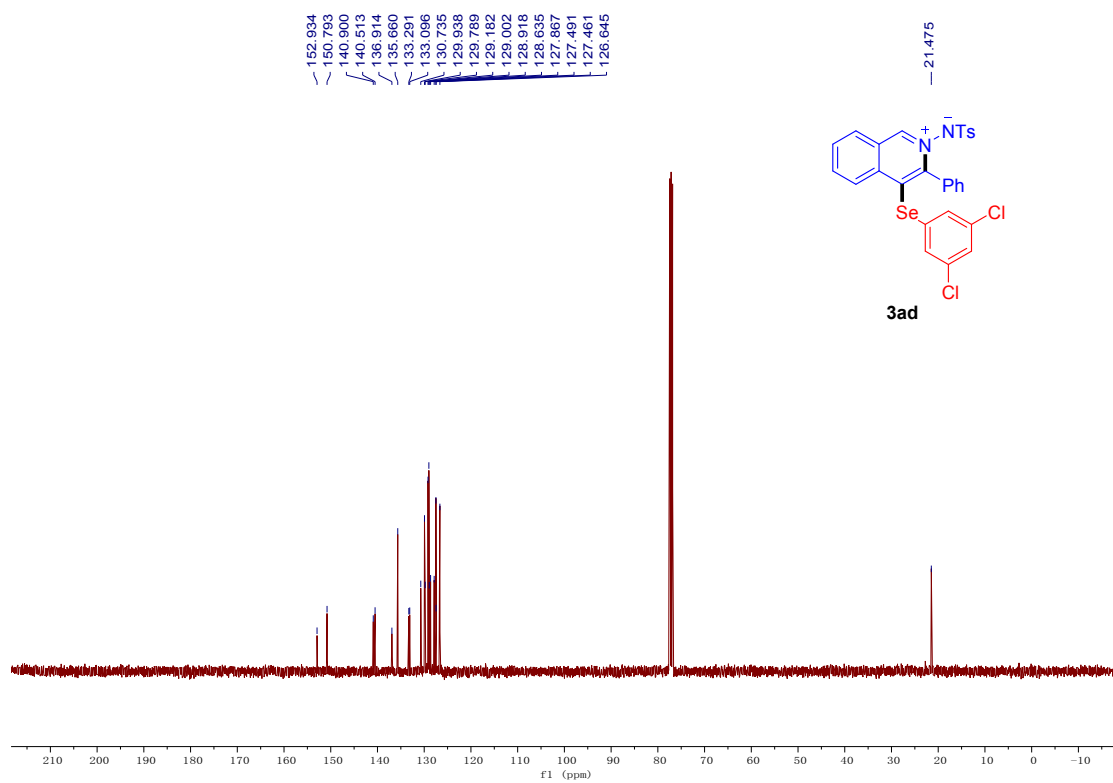
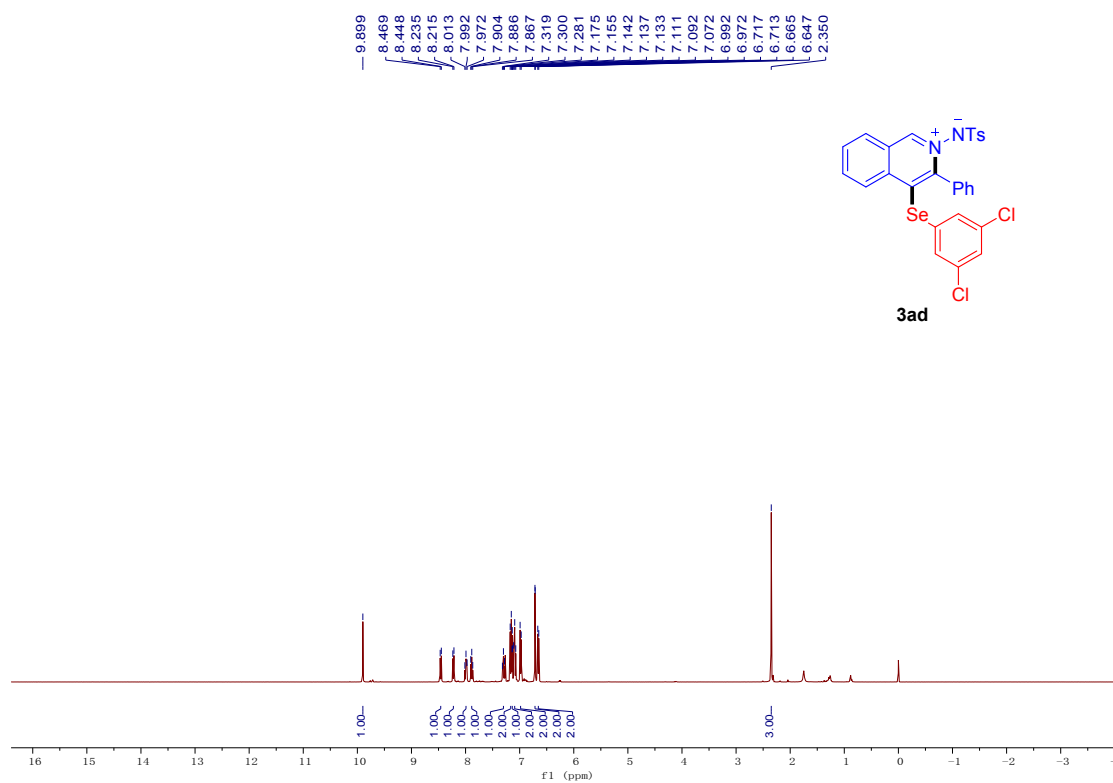




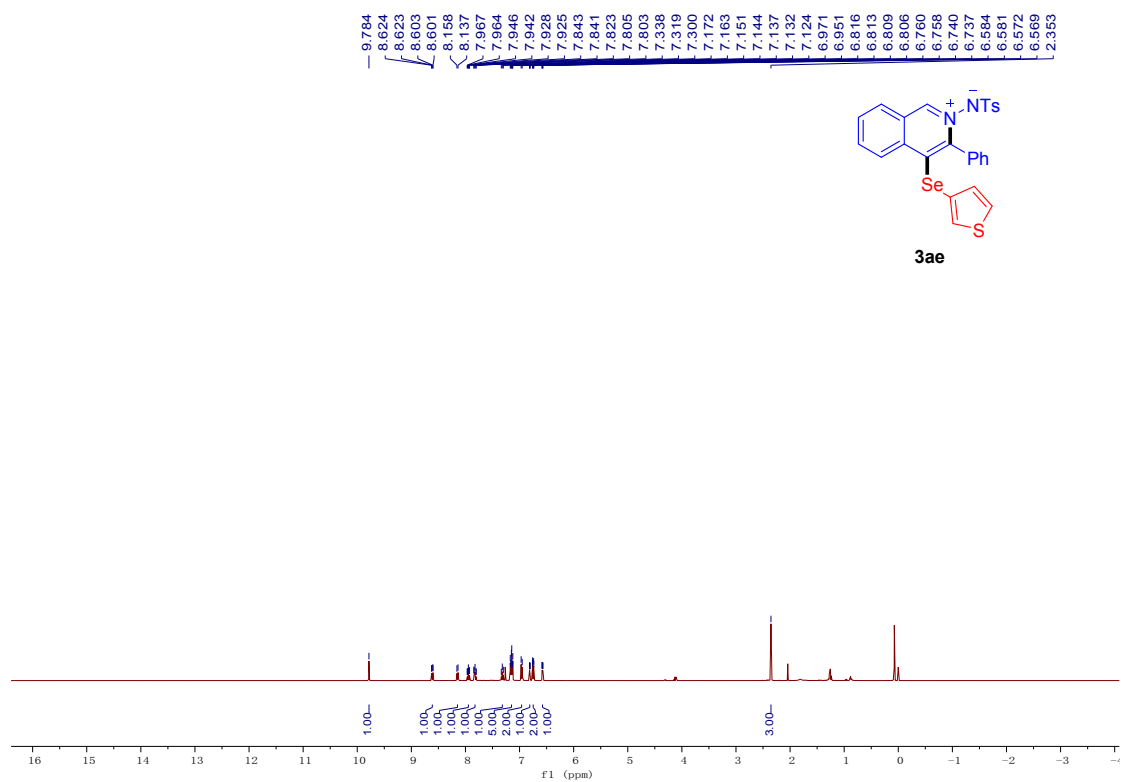


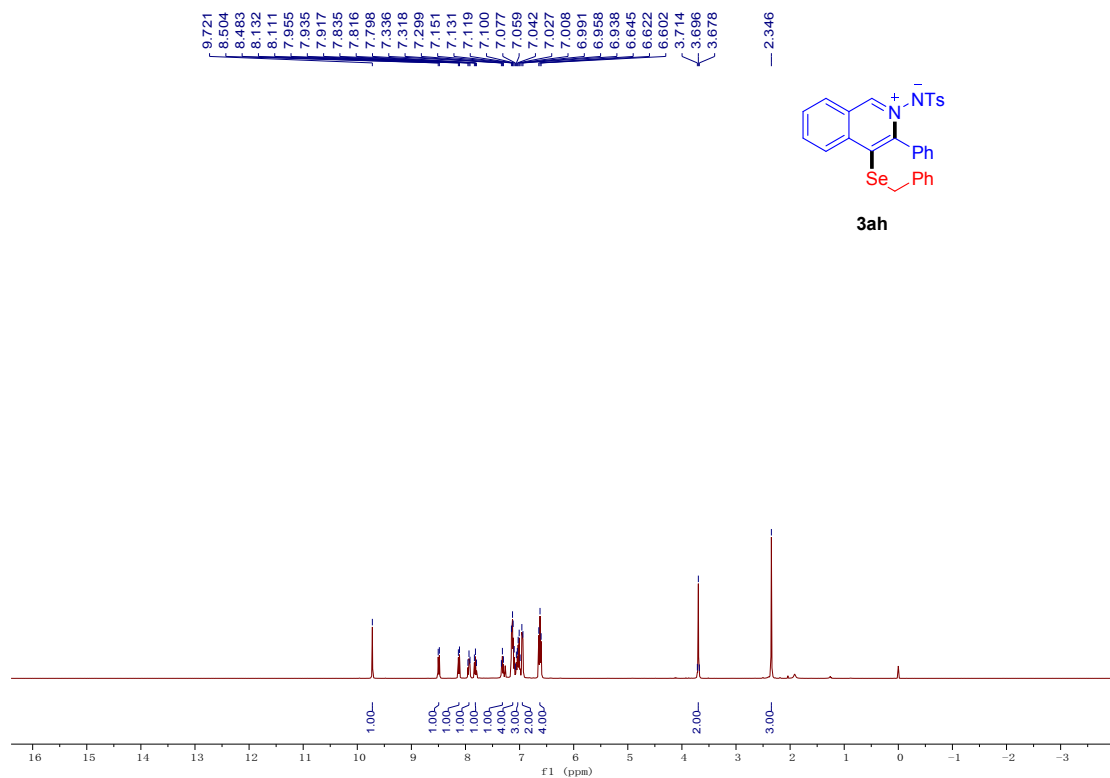
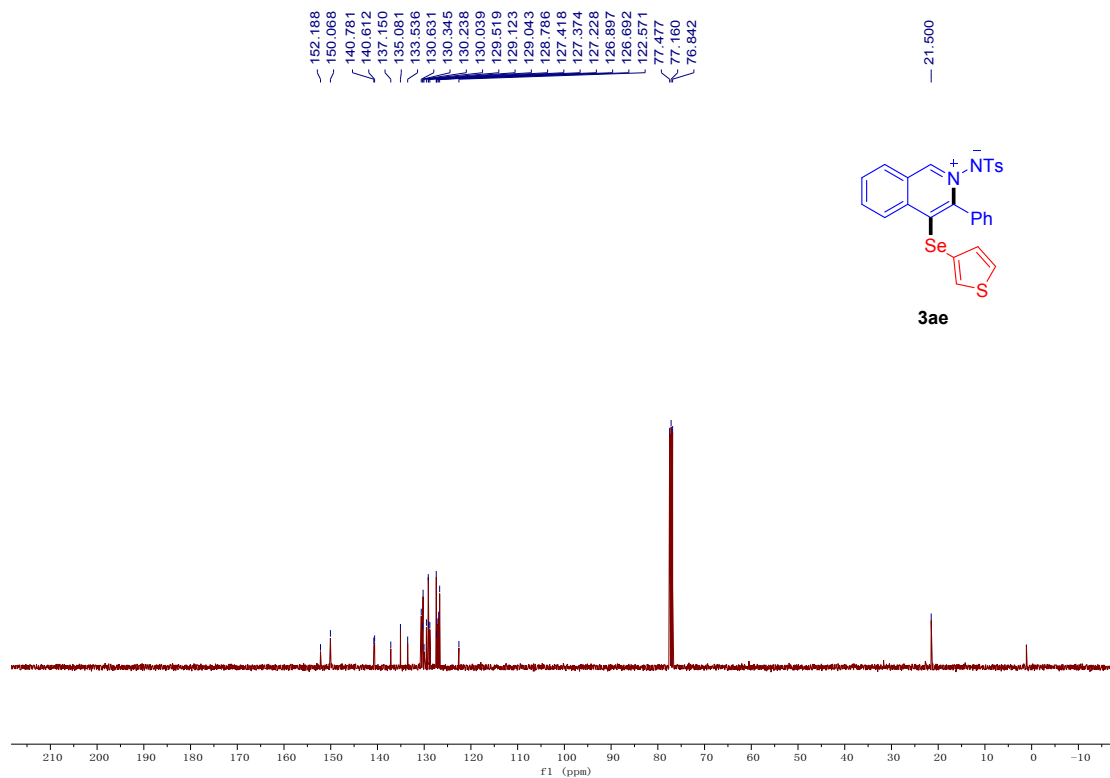


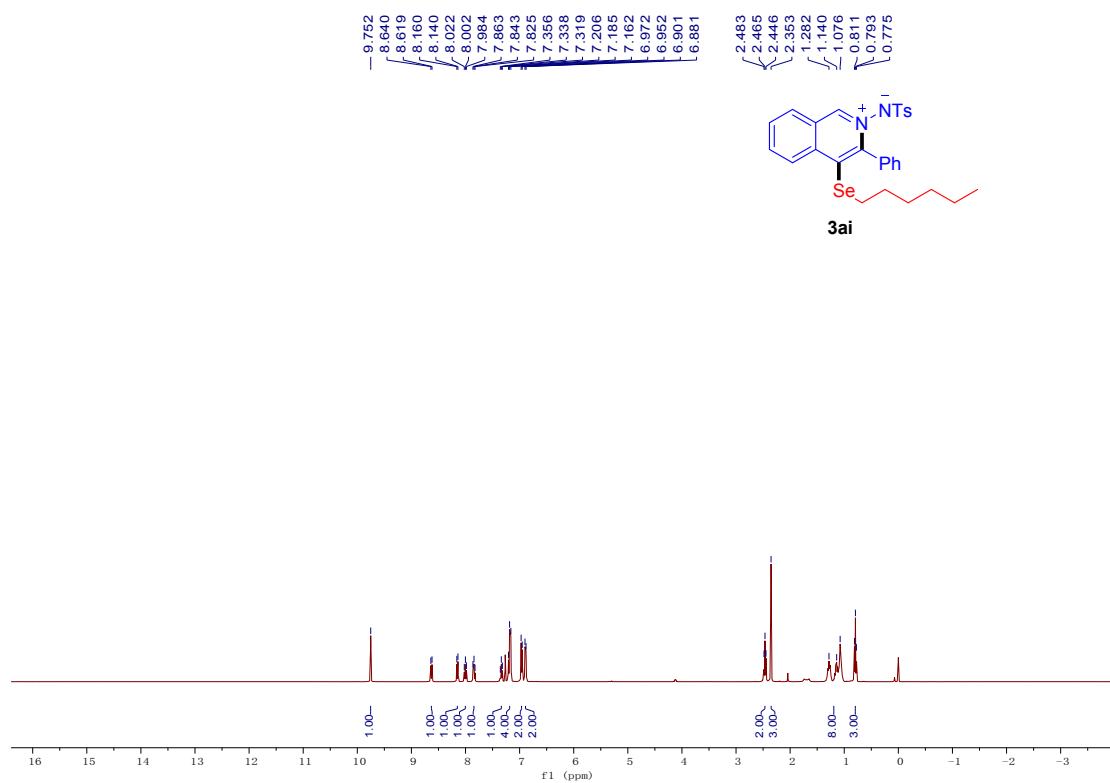
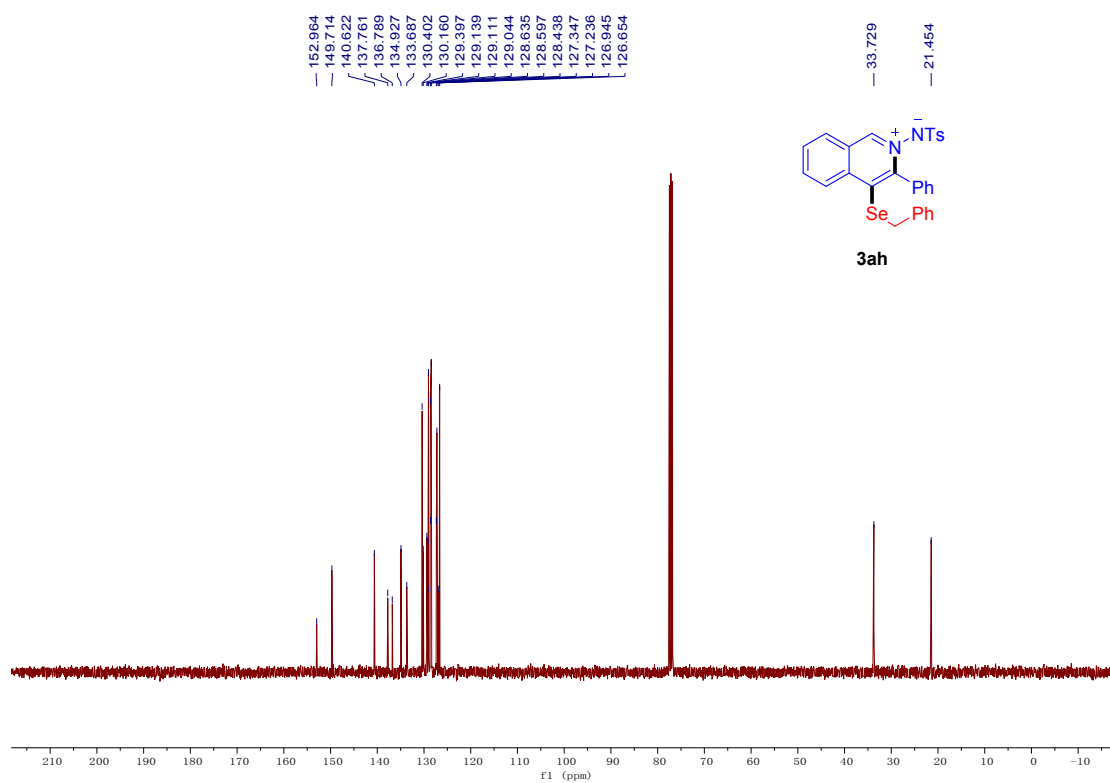


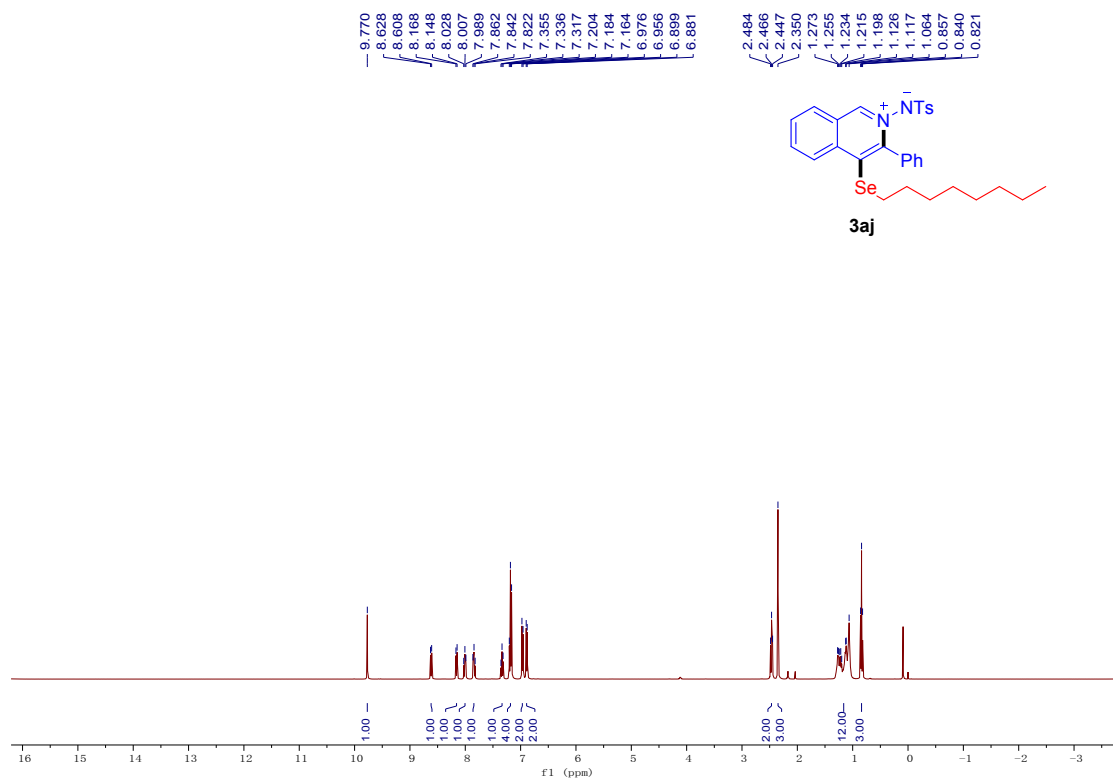
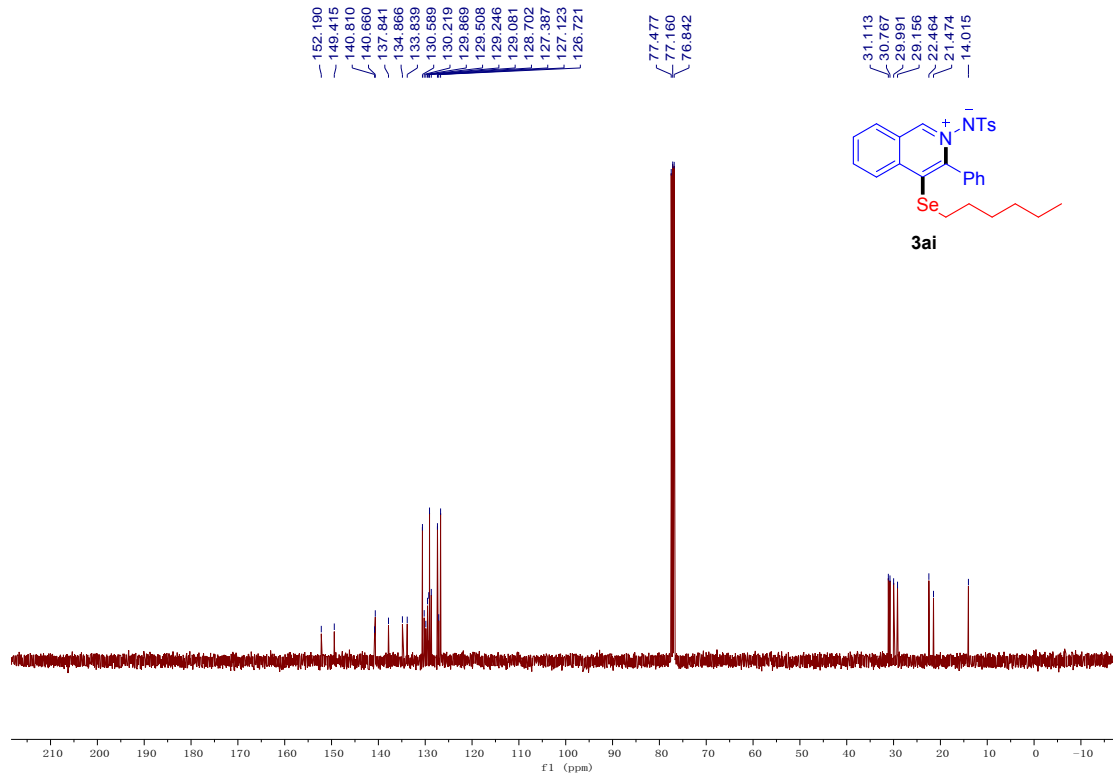


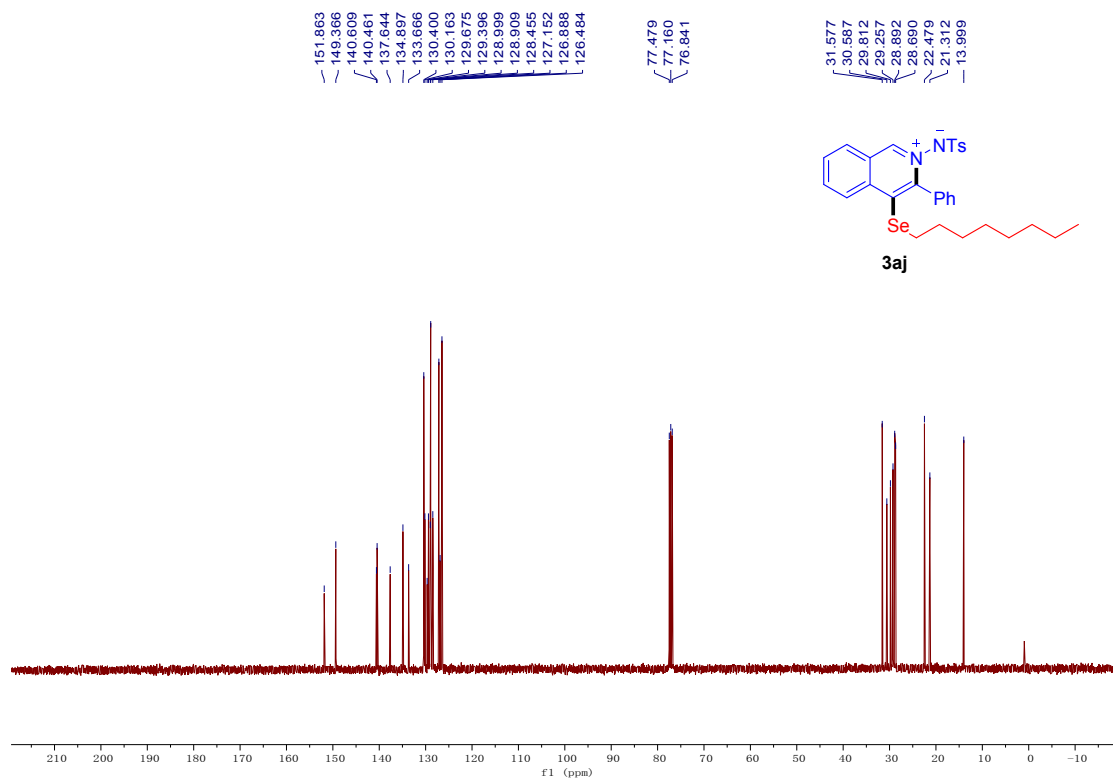


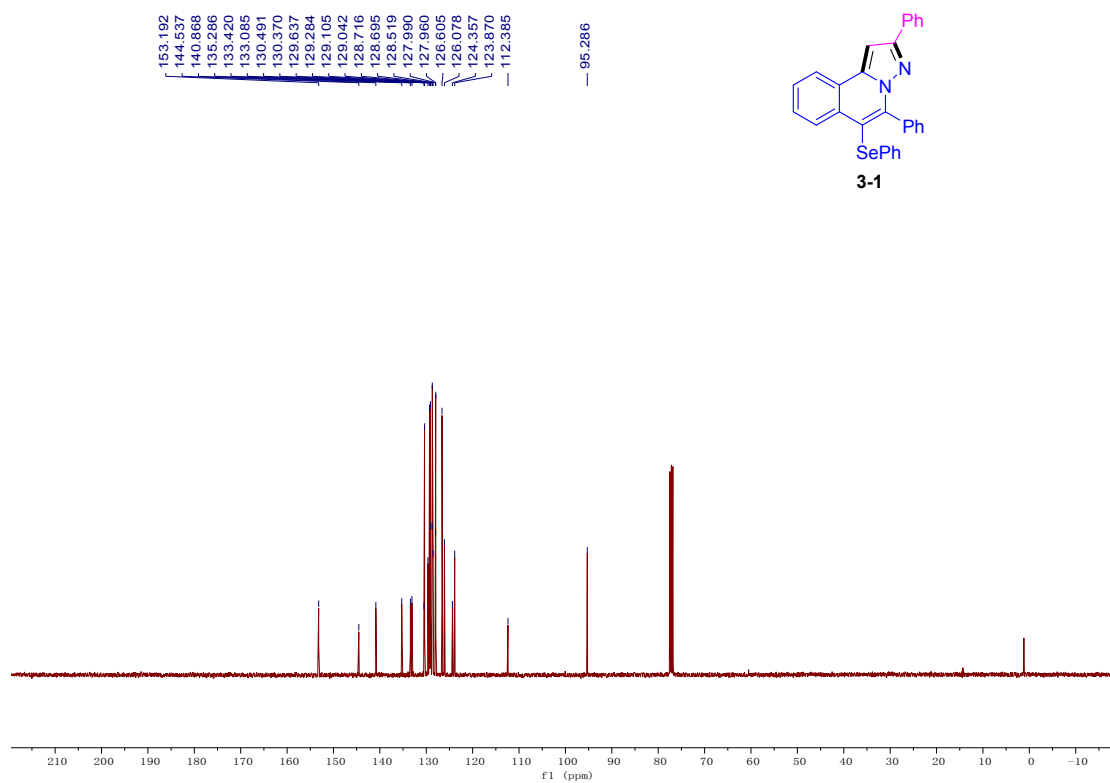
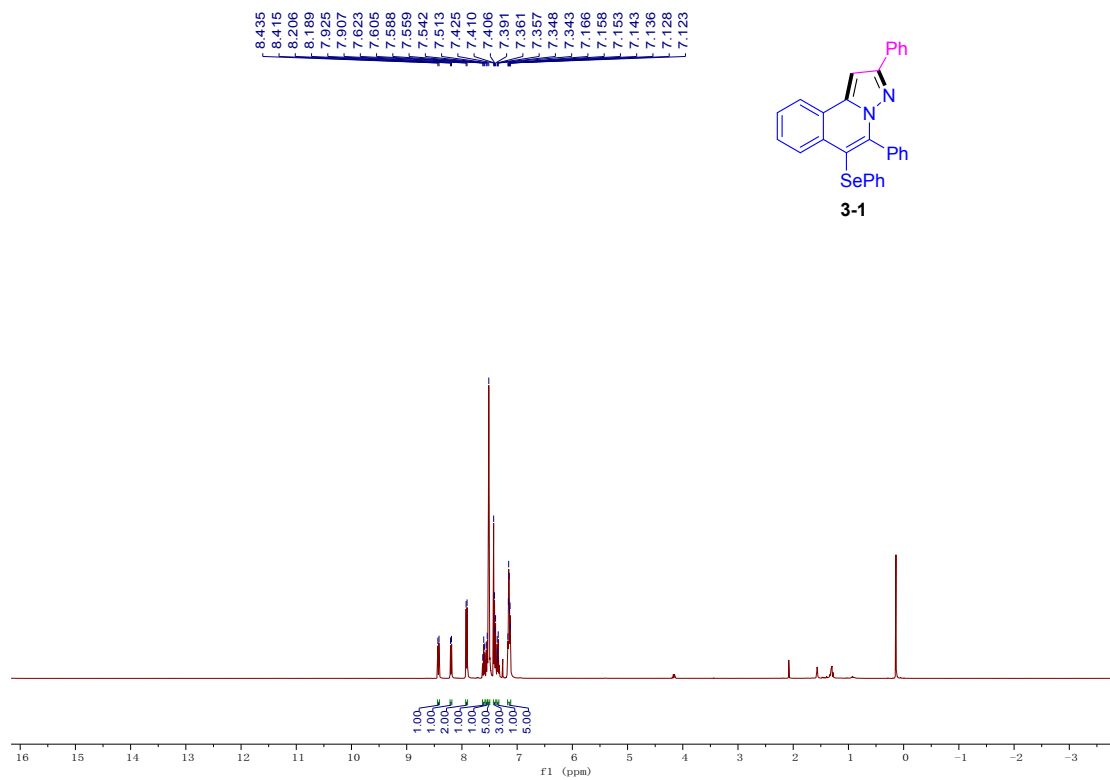








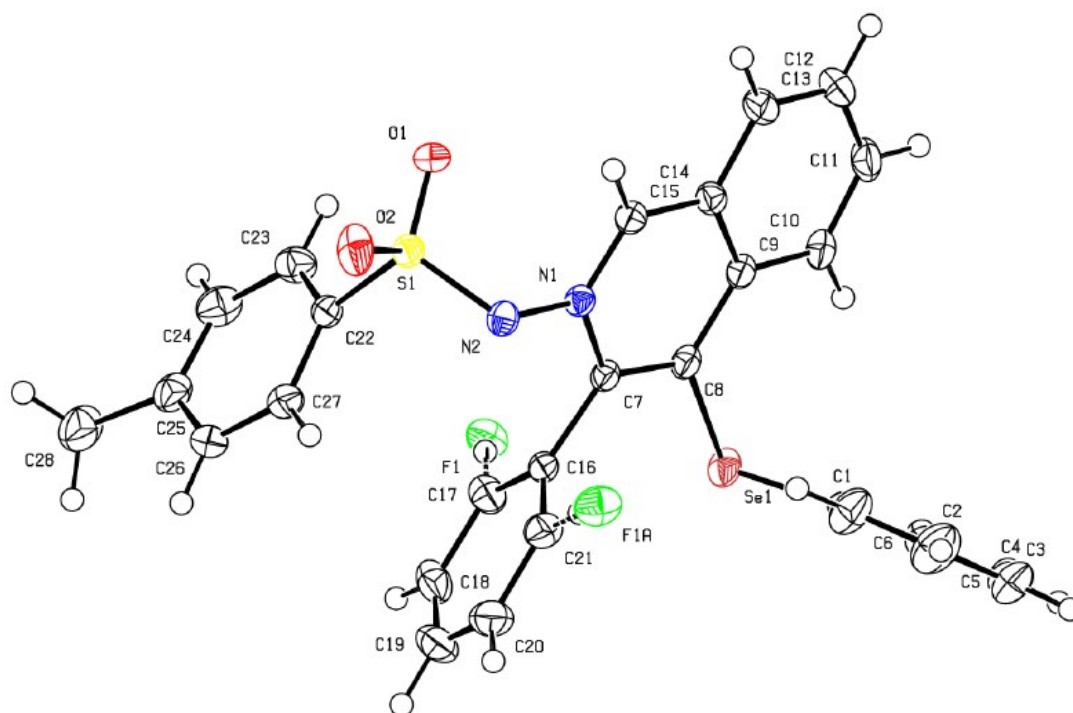




## 5. References

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- (2) X. Creary, W. W. Tam, K. F. Albizati and R. V. J. Stevens, *Org. Synth.*, 1990, **64**, 207.
- (3) Y.-M. Li, C.-P. Nie, H.-F. Wang, X.-Y. Li, F. Verpoort and C.-Y. Duan, *Eur. J. Org. Chem.* 2011, 7331-7338.
- (4) D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues and A. L. Braga, *Org. Lett.*, 2010, **12**, 3288-3291.
- (5) T. Nakamura, S. Yasuda, T. Miyamae, H. Nozoye, N. Kobayashi, H. Kondoh, I. Nakai, T. Ohta, D. Yoshimura and M. Matsumoto, *J. Am. Chem. Soc.*, 2002, **124**, 43, 12642-12643.

## 6. X-ray Structure of 3ha



**Crystal Number:** CCDC 1976346

**Empirical formula:** C<sub>28</sub>H<sub>21</sub>FN<sub>2</sub>O<sub>2</sub>SSe

**Formula weight:** 547.49

**Crystal system:** Monoclinic

**Space group:** P2<sub>1</sub>/n

**Unit cell parameters:** a: 13.215(3) Å, b: 11.927(2) Å, c: 15.344(3) Å

**Volume:** 2372.9(9) Å<sup>3</sup>

**Z:** 4

**Calculated density (g/cm<sup>3</sup>):** 1.532

**F (000):** 1112.0