

## Electronic Supplementary Information

### **Iron-mediated deuterium addition cascade cyano insertion/cyclization of *N*-arylacrylamides to access deuterium-labelled phenanthridines**

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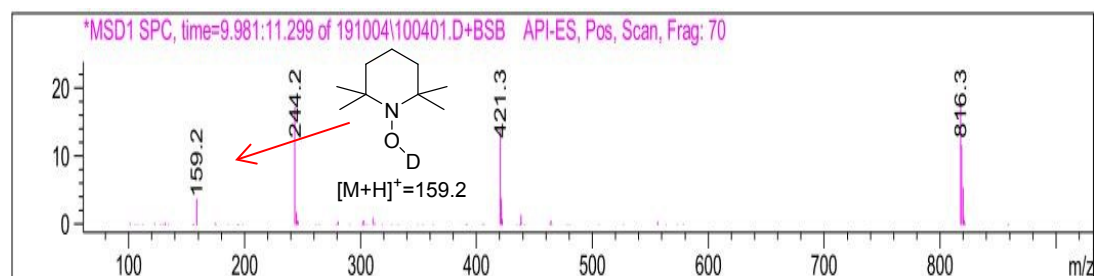
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## 1 Mechanistic studies

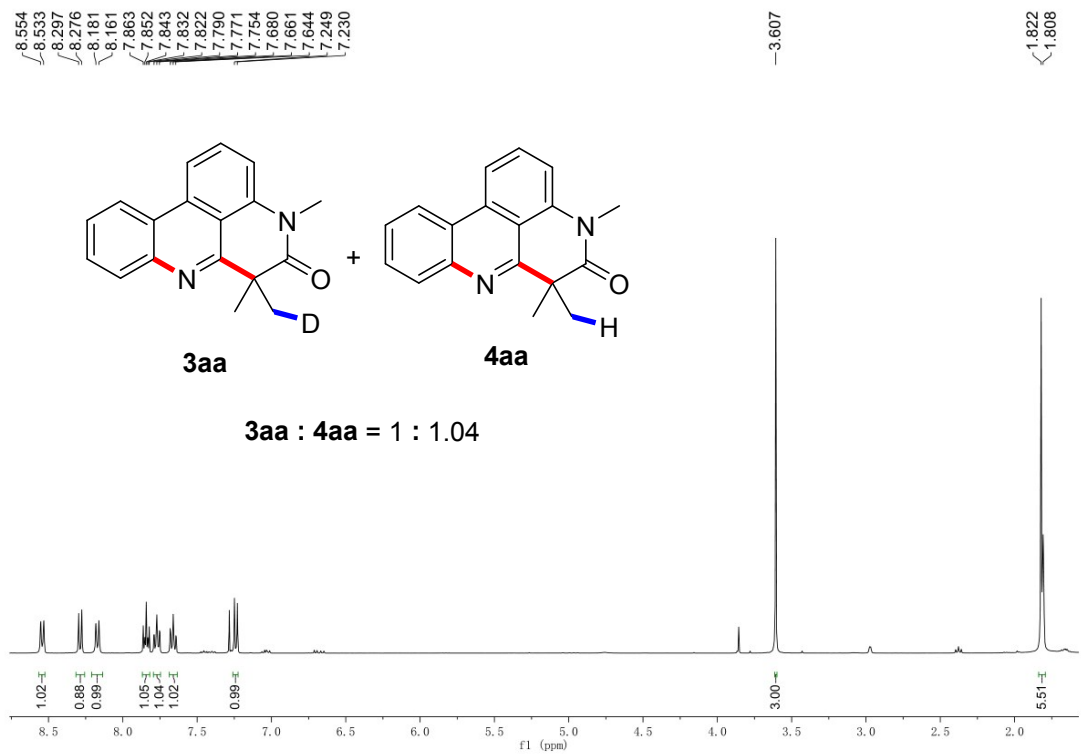
### Free radical-trapping experiment

To a sealed tube were added *N*-(2-cyano-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide (**1a**, 0.2 mmol, 55.3 mg, 1.0 equiv.),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.8 mmol, 323.2 mg, 4.0 equiv.), TEMPO (0.8 mmol, 125.0 mg, 4.0 equiv.),  $\text{CH}_3\text{CN}$  (2 mL), MeOH (2 mL) and  $\text{NaBD}_4$  (0.4 mmol, 16.7 mg, 2.0 equiv.). The resulting mixture was stirred at room temperature for 15 min. After the reaction was stopped, no desired product **3aa** was detected by TLC and LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a deuterium radical trapping product **5** was detected by LC-MS analysis of the reaction solution.



### The reaction of **1a** with $\text{NaBD}_4$ and $\text{NaBH}_4$

The reaction of **1a** (0.2 mmol, 55.3 mg, 1 equiv.) with  $\text{NaBD}_4$  (0.2 mmol, 8.4 mg, 1.0 equiv.) and  $\text{NaBH}_4$  (0.2 mmol, 7.6 mg, 1.0 equiv.) was conducted under standard conditions, and the ratio of the products **3aa** and **4aa** was 1 : 1.04, indicating that generation and introduction of deuterium atom may not be the rate-determining step.



## 2 <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products 3

