## Generation of Unusual Angucyclinones by Incorporation of Phenylamine Analogues into a Biosynthetic Intermediate

Hua Xiao<sup>1,†</sup>, Guiyang Wang<sup>1,†</sup>, Zhengdong Wang<sup>1</sup>, Yi Kuang<sup>1</sup>, Juan Song<sup>1</sup>, Jing Jin<sup>1</sup>, Min

Ye<sup>1</sup>, Donghui Yang<sup>1,\*</sup>, and Ming Ma<sup>1,\*</sup>

<sup>1</sup> State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences,

Peking University, 38 Xueyuan Road, Haidian District, Beijing 100191

<sup>†</sup>These authors contributed equally

\* Correspondence: ydhui@bjmu.edu.cn (D.Y.); mma@bjmu.edu.cn (M.M.)

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Figure S1. HPLC analysis of reactions of the phenylamine analogues (3a-6a) with 2 to generate compounds 3-6. Lane I, the standard 2; lane II, the reaction of (3-ethynyl)phenylamine (3a) with 2; lane III, the reaction of (3,4-dimethyl)phenylamine (4a) with 2; lane IV, the reaction of (3,4-methylenedioxy)phenylamine (5a) with 2; lane V, the reaction of (4-bromo-3-methyl)phenylamine (6a) with 2. Compound 2 was fully converted into 3-6 in each reaction. The compound labelled with asterisk was an unknown impurity in (3,4-methylenedioxy)phenylamine (5a) sample.



Figure S2. The <sup>1</sup>H NMR (600 MHz) spectrum of 3 in DMSO- $d_6$ .



Figure S3. The  ${}^{13}$ C NMR (150 MHz) spectrum of 3 in DMSO- $d_6$ .







Figure S5. The IR spectrum of 3.



Figure S6. The <sup>1</sup>H NMR (600 MHz) spectrum of 4 in DMSO-*d*<sub>6</sub>.



Figure S7. The  ${}^{13}$ C NMR (150 MHz) spectrum of 4 in acetone- $d_6$ .







Figure S9. The IR spectrum of 4.



Figure S10. The <sup>1</sup>H NMR (600 MHz) spectrum of 5 in DMSO- $d_6$ .



Figure S11. The  ${}^{13}$ C NMR (150 MHz) spectrum of 5 in DMSO- $d_6$ .



![](_page_13_Figure_0.jpeg)

Figure S12. The HRESIMS spectrum of 5.

Figure S13. The IR spectrum of 5.

![](_page_14_Figure_1.jpeg)

Figure S14. The <sup>1</sup>H NMR (600 MHz) spectrum of 6 in DMSO- $d_6$ .

![](_page_15_Figure_1.jpeg)

Figure S15. The <sup>13</sup>C NMR (150 MHz) spectrum of 6 in DMSO-d<sub>6</sub>.

![](_page_16_Figure_1.jpeg)

![](_page_17_Figure_0.jpeg)

Figure S16. The HRESIMS spectrum of 6.

![](_page_18_Figure_0.jpeg)

Figure S17. The IR spectrum of 6.