## **Supplementary Material**

## Silver-catalyzed benzannulation, part 1: total synthesis of (7*S*,10*R*)-2,15-dihydroxycalamene, (7*S*,10*R*)-2-hydroxy-15-calamenenal and (7*S*,10*R*)-2hydroxy-15-calamenenoic acid

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Figure S1. <sup>1</sup>H NMR spectrum of 8 (600 MHz, CDCl<sub>3</sub>).



Figure S2. <sup>13</sup>C NMR spectrum of 8 (150 MHz, CDCl<sub>3</sub>).



Figure S3. <sup>1</sup>H NMR spectrum of 9 (600 MHz, CDCl<sub>3</sub>).



Figure S4. <sup>13</sup>C NMR spectrum of 9 (150 MHz, CDCl<sub>3</sub>).



Figure S5. <sup>1</sup>H NMR spectrum of **10** (600 MHz, CDCl<sub>3</sub>).



Figure S6. <sup>13</sup>C NMR spectrum of **10** (150 MHz, CDCl<sub>3</sub>).



Figure S7. <sup>1</sup>H NMR spectrum of **12** (600 MHz, CDCl<sub>3</sub>).



Figure S8. <sup>13</sup>C NMR spectrum of **12** (150 MHz, CDCl<sub>3</sub>).



Figure S9. <sup>1</sup>H NMR spectrum of **13** (600 MHz, CDCl<sub>3</sub>).



Figure S10. <sup>13</sup>C NMR spectrum of **13** (150 MHz, CDCl<sub>3</sub>).



**Figure S11.** <sup>1</sup>H NMR spectrum of **14** (600 MHz, CDCl<sub>3</sub>).



Figure S12. <sup>13</sup>C NMR spectrum of 14 (150 MHz, CDCl<sub>3</sub>).



Figure S13. <sup>1</sup>H NMR spectrum of 15 (600 MHz,  $CDCI_3$ ).



Figure S14. <sup>13</sup>C NMR spectrum of **15** (150 MHz, CDCl<sub>3</sub>).



Figure S15. <sup>1</sup>H NMR spectrum of 16 (600 MHz, CDCl<sub>3</sub>).



Figure S16. <sup>13</sup>C NMR spectrum of 16 (150 MHz, CDCl<sub>3</sub>).



Figure S17. <sup>1</sup>H NMR spectrum of **17** (600 MHz, CDCl<sub>3</sub>).



Figure S18. <sup>13</sup>C NMR spectrum of **17** (150 MHz, CDCl<sub>3</sub>).



Figure S19. <sup>1</sup>H NMR spectrum of **18** (600 MHz, CDCl<sub>3</sub>).



Figure S20. <sup>13</sup>C NMR spectrum of **18** (150 MHz, CDCl<sub>3</sub>).



Figure S21. <sup>1</sup>H NMR spectrum of **19** (600 MHz, CDCl<sub>3</sub>).



Figure S22. <sup>13</sup>C NMR spectrum of **19** (150 MHz, CDCl<sub>3</sub>).



Figure S23. <sup>1</sup>H NMR spectrum of 20 (600 MHz, CDCl<sub>3</sub>).



Figure S24. <sup>1</sup>H NMR spectrum of 22 (600 MHz, CDCl<sub>3</sub>).



Figure S25. <sup>13</sup>C NMR spectrum of 22 (150 MHz, CDCl<sub>3</sub>).



Figure S26. <sup>1</sup>H NMR spectrum of 23 (600 MHz, CDCl<sub>3</sub>).



Figure S27. <sup>13</sup>C NMR spectrum of 23 (150 MHz, CDCl<sub>3</sub>).



Figure S28. <sup>1</sup>H NMR spectrum of 24 (600 MHz, CDCl<sub>3</sub>).



Figure S29. <sup>13</sup>C NMR spectrum of 24 (150 MHz, CDCl<sub>3</sub>).



Figure S30. <sup>1</sup>H NMR spectrum of 25 (600 MHz, CDCl<sub>3</sub>).



Figure S31. <sup>13</sup>C NMR spectrum of 25 (150 MHz, CDCl<sub>3</sub>).



**Figure S32.** <sup>1</sup>H NMR spectrum of **(7S, 10R)-1** (600 MHz, CDCl<sub>3</sub>).



**Figure S33.** <sup>13</sup>C NMR spectrum of **(7S, 10R)-1** (150 MHz, CDCl<sub>3</sub>).



**Figure S34.** <sup>1</sup>H NMR spectrum of **(7S, 10R)-2** (600 MHz, CDCl<sub>3</sub>).



**Figure S35.** <sup>13</sup>C NMR spectrum of **(7S, 10R)-2** (150 MHz, CDCl<sub>3</sub>).



Figure S36. <sup>1</sup>H NMR spectrum of 26 (600 MHz, CDCl<sub>3</sub>).



Figure S37. <sup>13</sup>C NMR spectrum of **26** (150 MHz, CDCl<sub>3</sub>).



Figure S38. <sup>1</sup>H NMR spectrum of 27 (600 MHz, CDCl<sub>3</sub>).



Figure S39. <sup>13</sup>C NMR spectrum of 27 (150 MHz, CDCl<sub>3</sub>).



Figure S40. <sup>1</sup>H NMR spectrum of 28 (600 MHz, CDCl<sub>3</sub>).



Figure S41. <sup>13</sup>C NMR spectrum of 28 (150 MHz, CDCl<sub>3</sub>).



**Figure S42.** <sup>1</sup>H NMR spectrum of **(7S, 10R)-3** (600 MHz, 1% DMSO-d<sub>6</sub>/CDCl<sub>3</sub>).



**Figure S43.** <sup>13</sup>C NMR spectrum of **(7S, 10R)-3** (150 MHz, 1% DMSO-d<sub>6</sub>/CDCl<sub>3</sub>).