## **Supplementary Material**

## Stereoselective synthesis of linear oxa-triquinanes and oxadiquinanes via Lewis acid mediated nucleophilic addition to oxonium ions: study of nucleophile-dependent selectivity

Santosh J. Gharpure,<sup>\*,a</sup> P. Niranjana,<sup>b</sup> and Suheel K. Porwal<sup>c</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai – 400076, India <sup>b</sup>Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India <sup>c</sup>Analytical Chemistry Lab, Department of Chemistry, DIT University, Dehradun, Dehradun – 248009, India Email: sigharpure@iitb.ac.in

## **Table of Contents**

<sup>1</sup>H and <sup>13</sup>C NMR spectra......S3

General: Melting points are recorded using Tempo melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer and JASCO FT-IR-4100 spectrophotometer. <sup>1</sup>H (400 MHz, 500 MHz) and <sup>13</sup>C (100 MHz, 125 MHz) NMR spectrums were recorded on Bruker Avance 400 spectrophotometer and Bruker Avance 500 spectrophotometer, respectively. The chemical shifts (ppm) and coupling constants (Hz) are reported in the standard fashion with reference to chloroform. In the <sup>13</sup>C NMR spectra, the nature of the carbons (C, CH, CH<sub>2</sub> or CH<sub>3</sub>) was determined by recording the DEPT-135 experiment, and is given in parentheses. CHN analysis was carried out using Elemental analyzer VSM-VT. High resolution mass measurements were carried out using Micromass Q-ToF instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on glass plates (7.5 × 2.5 and 7.5 × 5.0 cm) coated with Merck silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F245 silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by exposure to iodine vapour and UV light. All compounds were purified using silica gel [Acme's silica gel (100-200 mesh)] column chromatography. All small-scale dry reactions were carried out using standard syringe septum technique. Syringe pump was used for slow rate of addition of the reagents. All the commercial reagents were used as such without further purification.



Figure 1. <sup>1</sup>H NMR spectrum of 9.



Figure 2. <sup>13</sup>C NMR spectrum of 9.



Figure 3. <sup>1</sup>H NMR spectrum of 7a.



Figure 4. <sup>13</sup>C NMR spectrum of 7a.



Figure 5. <sup>1</sup>H NMR spectrum of 7b.



Figure 6. <sup>13</sup>C NMR spectrum of 7b.



Figure 7. <sup>1</sup>H NMR spectrum of 7c.



Figure 8. <sup>13</sup>C NMR spectrum of 7c.



Figure 9. <sup>1</sup>H NMR spectrum of 7d.



Figure 10. <sup>13</sup>C NMR spectrum of 7d.



Figure 11. <sup>1</sup>H NMR spectrum of 1e.



Figure 12. <sup>13</sup>C NMR spectrum of 7e.



Figure 13. <sup>1</sup>H NMR spectrum of 7e'.







Figure 15. <sup>1</sup>H NMR spectrum of 7f.



Figure 16. <sup>13</sup>C NMR spectrum of 7f.



Figure 17. <sup>1</sup>H NMR spectrum of 7g.



Figure 18. <sup>13</sup>C NMR spectrum of 7g.



Figure 19. <sup>1</sup>H NMR spectrum of 12.







Figure 21. <sup>1</sup>H NMR spectrum of 15.



Figure 22. <sup>13</sup>C NMR spectrum of 15.



Figure 23. <sup>1</sup>H NMR spectrum of 18.



Figure 24. <sup>13</sup>C NMR spectrum of 18.



Figure 25. <sup>1</sup>H NMR spectrum of **19**.



Figure 26. <sup>13</sup>C NMR spectrum of 19.



Figure 27. <sup>1</sup>H NMR spectrum of 20.



Figure 28. <sup>13</sup>C NMR spectrum of 20.



Figure 29. <sup>1</sup>H NMR spectrum of 22.



Figure 30. <sup>13</sup>C NMR spectrum of 22.