Supporting Information

Synthesis of 1,2,4- trioxepanes and 1,2,4-trioxanes via H$_2$O$_2$ mediated reaction of tertiary carbinols

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General Experimental Details:

All glass apparatus were oven dried prior to use. Melting points were determined on COMPLAB melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker DRX-300 and Bruker Avance-400 using CDCl$_3$ as solvent and tetramethylsilane as internal reference. Splitting patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). Atmospheric pressure chemical ionization Mass Spectra (APCI-MS) were obtained on Thermo LCQ Advantage Max Spectrometer. Elemental analyses were done on Vario EL-III C H N S analyzer (Germany). Reactions were monitored on silica gel TLC plates (coated with TLC grade silica gel, obtained from Merck). Detecting agents used (for TLC) were: iodine vapours and/or spraying with an aq. solution of vanillin in 10% sulfuric acid followed by heating at 100 °C. Column chromatography was performed over silica gel (60-120 Mesh) procured from Qualigens™ (India), flash silica gel (230-400 Mesh) procured from Spectrochem (India). All chemicals and reagents were obtained from Aldrich (USA), Lancaster (England) or Spectrochem (India) and were used without further purification.

Representative procedure for the synthesis of 1,2,4-trioxepane (5): To an ice-cooled (0-5°C) solution of 1,3-diol 4 (1g, 5.2 mmol) in DCM (50 ml) was added 30% H$_2$O$_2$ (0.64 mL, 20.8 mmol) followed by drop wise addition of conc. H$_2$SO$_4$ (0.14 mL, 2.6 mmol) with constant stirring and then at 0-5°C for 3h. The reaction mixture was diluted with cold water (25 mL) and the aqueous layer extracted with dichloromethane (3×25 mL). The combined organic layers were washed with saturated aq. NaHSO$_3$ solution (25 mL) and water (2×25 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$ and the solvent were reduced for 50 mL under vacuum and the crude hydroxyhydroperoxide was reacted with cyclohexanone (0.74 mL, 7.2 mmol) in the presence of PTSA (0.2g, 1 mmol) stirred for 1.5h at 0-5°C. The reaction mixture was concentrated on a rotatory evaporator at rt and the crude product was purified by column chromatography over silica gel using 1.0% ethyl acetate-hexane as eluent to furnish 0.973g (65%) of 6 as white solid.

Compound Characterization Data:

**Compound (5):** Yield 65% as white solid, mp 94-95°C; FT-IR (KBr, Cm$^{-1}$) 2933.9, 1659.3, 755.6; $^1$HNMR (300 MHz,CDCl$_3$) δ 0.14-0.37 (m, 4H), 1.03 (brs, 1H), 1.33-1.57 (m, 8H), 1.96 (brd, 2H), 2.28 (brd, 1H), 2.57 (brd, 1H), 3.73-3.85 (m, 2H), 7.25-7.37 (m, 5H); $^{13}$C NMR (75MHz, CDCl$_3$) 1.02(CH$_2$), 1.36 (CH$_2$), 20.43(CH$_2$), 22.81 (CH$_2$), 23.07 (CH$_2$), 25.5 (2×CH$_2$), 32.73 (CH$_2$), 41.12 (CH$_2$), 59.17 (CH$_2$), 87.86 (C), 106.19 (C), 126.85 (CH), 127.05 (CH), 127.64 (CH), 141.31 (C), APCI-MS(m/z) 289 (M+H)$^+$; Anal.Calcd for C$_{18}$ H$_{24}$O$_3$; C , 74.97; H, 8.39. Found: C, 74.91; H, 8.43.

**Compound (6):** Yield 62% as white solid, mp 103-105°C; FT-IR (KBr, cm$^{-1}$) 2914.2, 1656.8, 767.5; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.10-0.38 (m, 4H), 1.04 (brs, 1H), 1.51-2.01 (m, 12H), 2.18-2.33 (m,
2H), 2.60 (brs, 2H), 3.73-3.89 (m, 2H), 7.27-7.44 (m, 5H); $^{13}$C NMR (300 MHz, CDCl$_3$) δ 0.85 (CH$_2$), 1.41 (CH$_3$), 20.41 (CH), 27.23 (2×CH), 27.29 (2×CH), 33.53 (CH$_2$), 33.99 (CH$_2$), 34.16 (CH$_2$), 37.5 (2×CH$_2$), 58.81 (CH$_2$), 87.00 (C), 108.00 (C), 126.77 (CH), 127.05 (CH), 127.58 (CH), 141.00 (C), APCI-MS (m/z) 341 (M+H)$^+$; Anal. Calcd for C$_{22}$H$_{28}$O$_3$: C, 77.61; H, 8.29. Found: C, 77.70; H, 8.33.

**Compound (7):** Yield 55%, as white solid, mp 79-80°C; FT-IR (KBr, cm$^{-1}$) 2967.8, 1676.6, 765.6; $^1$H NMR (400 MHz, CD$_3$OD) δ 0.05-0.35 (m, 4H), 1.05 (brs, 1H), 1.60-1.70 (m, 6H), 1.79-1.86 (m, 1H), 2.37 (brt, 2H), 2.62 (brs, 1H), 3.73-3.78 (m, 1H), 3.94-4.00 (m, 1H), 7.20-7.24 (m, 1H), 7.29-7.32 (m, 2H), 7.36-7.38 (m, 2H); $^{13}$C NMR (100 MHz, CD$_3$OD) δ 0.06 (CH$_2$), 0.37 (CH$_2$), 19.61 (CH), 23.25 (CH$_2$), 23.73 (CH$_2$), 34.08 (CH$_2$), 35.47 (CH$_2$), 41.45 (CH$_2$), 60.72 (CH$_2$), 87.91 (C), 117.44 (C), 126.55 (CH), 126.67 (CH), 127.24 (3×CH), 141.59 (C), APCI-MS (m/z): 275 (M+H)$^+$; Anal. Calcd for C$_{17}$H$_{22}$O$_3$: C, 74.42; H, 8.08. Found: C, 74.39; H, 8.16.

**Compound (8):** Yield 50%, oily; FT-IR (neat, cm$^{-1}$) 3021.3, 1658.5, 765.2; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.13-0.40 (m, 4H), 1.13 (s, 3H), 1.30-1.38 (m, 1H), 1.62 (s, 3H), 2.28-2.36 (m, 1H), 2.59-2.66 (dd, $J$= 14.7 Hz and 5.1 Hz, 1H), 3.76-3.92 (m, 2H), 7.25-7.42 (m, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 0.91 (CH$_2$), 1.32 (CH$_2$), 20.46 (CH), 23.63 (2×CH$_2$), 40.96 (CH$_2$), 59.57 (CH$_2$), 87.99 (C), 106.12 (C), 127.00 (2×CH), 127.71 (3×CH), 141.09 (C), ESI-MS (m/z): 271 (M+Na)$^+$; Anal. Calcd for C$_{13}$H$_{20}$O$_3$: C, 72.55; H, 8.12. Found: C, 72.60; H, 8.07.

**Compound (12):** Yield 63%, as white solid, mp 108-110°C; FT-IR (KBr, cm$^{-1}$) 2967.8, 1667.6, 768.7; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.66-2.02 (m, 12H), 2.29 (brd, 2H), 4.55 (s, 2H), 7.26-7.36 (m, 6H), 7.46-7.49 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 26.85 (CH), 27.18 (CH), 34.91 (2×CH$_2$), 34.98 (2×CH$_2$), 37.22 (2×CH), 37.27 (CH$_2$), 74.76 (CH$_2$), 85.83 (C), 113.71 (C), 126.11 (2×CH), 127.05 (2×CH), 128.10 (2×CH), 145.12 (2×C); ESI-MS (m/z): 385 (M+Na)$^+$; Anal. Calcd for C$_{24}$H$_{26}$O$_3$: C, 79.53; H, 7.23. Found: C, 79.59; H, 7.18.

**Compound (13):** Yield 62%, as white solid, mp 100-101°C; FT-IR (KBr, cm$^{-1}$) 2937, 1661.2, 764.9; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.46-1.76 (m, 10H), 4.54 (s, 2H), 7.26-7.37 (m, 6H), 7.43-7.46 (m, 4H); $^{13}$C NMR (75MHz, CDCl$_3$) δ 24.01 (2×CH$_2$), 25.23 (CH$_2$), 36.12 (2×CH$_2$), 74.80 (CH$_2$), 85.72 (C), 111.33 (C), 126.22 (4×CH), 127.16 (2×CH), 128.16 (4×CH), 144.88 (2×C); APCI-MS (m/z): 311 (M+H)$^+$; Anal. Calcd for C$_{20}$H$_{22}$O$_3$: C, 77.39; H, 7.14. Found: C, 77.43; H, 7.20.
$^1$H NMR Spectra of 5 (300 MHz, CDCl$_3$)
13CNMR Spectra of 5 (75 MHz, CDCl₃)
$^1$H NMR Spectra of 6 (300 MHz, CDCl$_3$)
$^{13}$CNMR Spectra of 6 (75 MHz, CDCl$_3$)
$^1$H NMR Spectra of 7 (400 MHz, CD$_3$OD)
$^{13}$CNMR Spectra of $7$ (100 MHz, CD$_3$OD)
DEPT-135° of Compound 7 (100 MHz, CD₃OD)
COSY Spectra of Compound 7 (400 MHz, CD$_3$OD)
HSQC Spectra of Compound 7 (400 MHz, CD$_3$OD)
HMBC Spectra of Compound 7 (400 MHz, CD$_3$OD)
$^1$H NMR Spectra of 8 (300 MHz, CDCl$_3$)
$^{13}$CNMR Spectra of 8 (75 MHz, CDCl$_3$)
$^1$H NMR Spectra of 12 (300 MHz, CDCl$_3$)
13C NMR Spectra of 12 (75 MHz, CDCl₃)
RV-13D
PROTON CDC13 [0:cdcl3] user 105

1H NMR Spectra of 13 (300 MHz, CDCl₃)
13CNMR Spectra of 13 (75 MHz, CDCl₃)