Supplementary Material (ESI) for Chemical Communications

Proline Organocatalysis as a New Tool for the Asymmetric Synthesis of Ulosonic Acid Precursors

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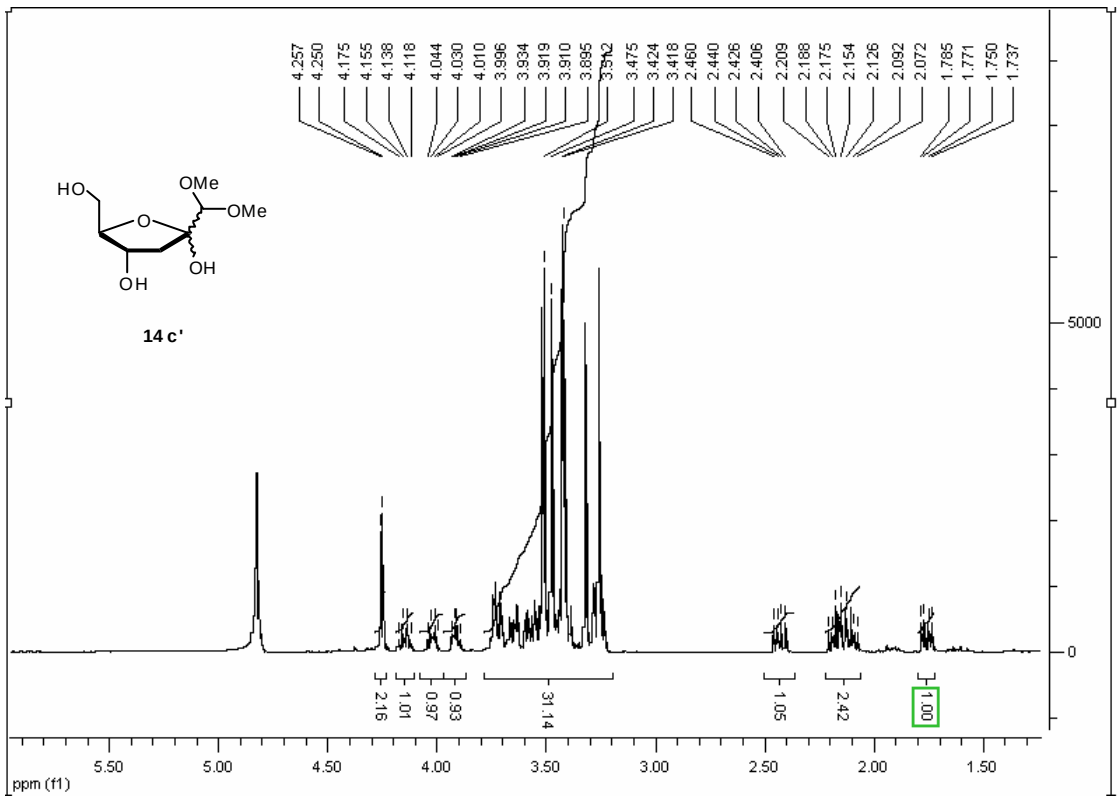
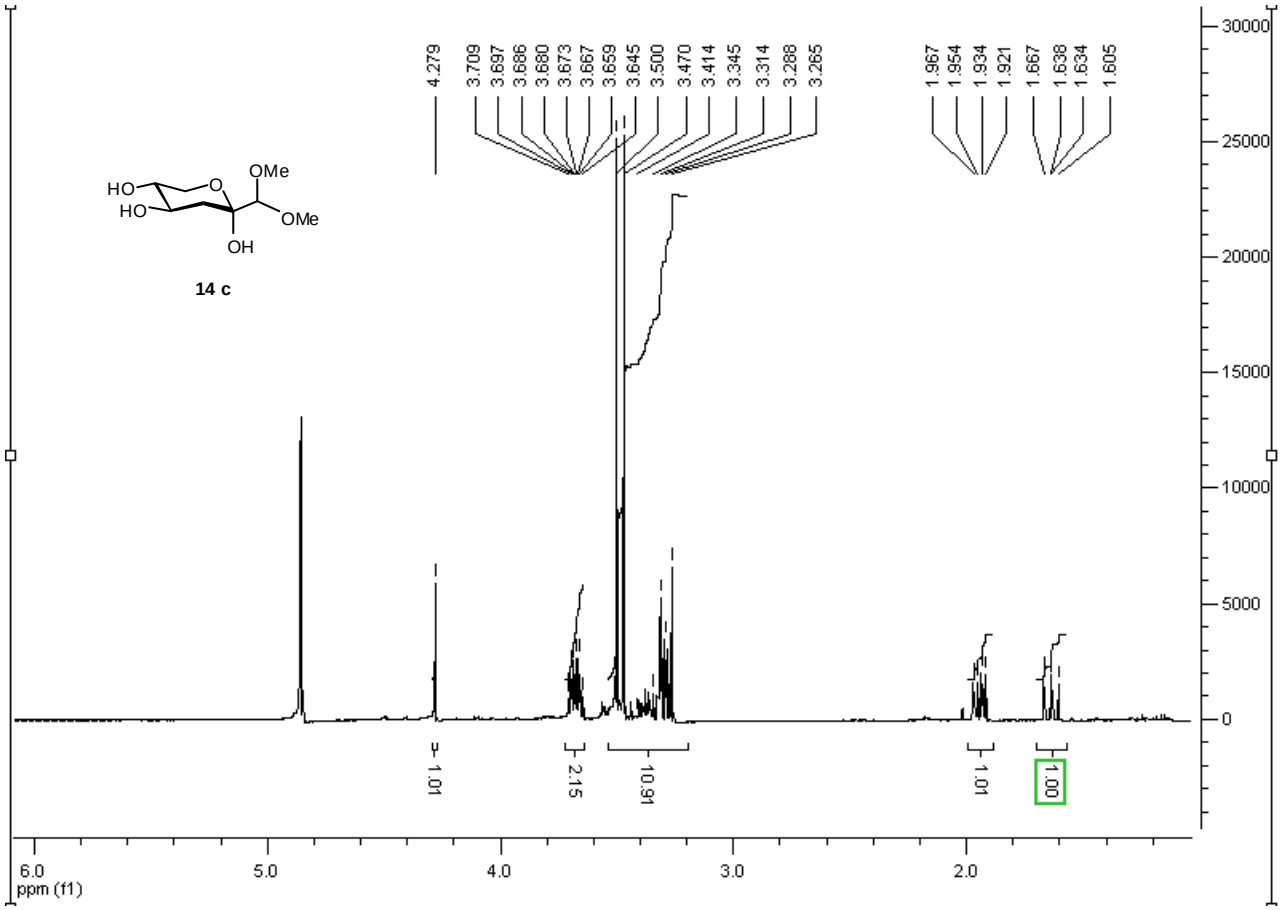


14c': To a stirred solution of aldol product (*S*,*R*)-**8c** (248 mg, 1 mmol) in dry MeOH (10 mL) Amberlyst®-15 (496 mg) was added. After complete conversion (monitored by TLC, ~ 4 h) the acid ion-exchange resin was removed by filtration and the solvent was evaporated under vacuum. The hemiketal **14c'** was purified by flash chromatography (ethyl acetate/ methanol, 65:5) affording a colourless sticky oil as mixture of α and β furanose rings (185 mg, 89%). $[\alpha]_D^{24}$ +23.4 (*c* 0.97 in MeOH); Found C, 46.3, H 7.4. Calc, for $C_8H_{16}O_6$: C, 46.1, H, 7.7; IR ($CHCl_3$) ν_{max}/cm^{-1} 3422, 2938, 2837, 1646, 1454, 1195, 1086, 755; ^{1}H NMR δ_H (400 MHz, CD_3OD) 1.76 (dd, 1H, CC*H*H, *J* 5.4 Hz, *J* 13.7 Hz), 2.10 (dd, 1H, CC*H*H, *J* 7.8 Hz, *J* 13.6 Hz), 2.18 (dd, 1H, CCH*H*, *J* 8.4 Hz, *J* 13.6 Hz), 2.43 (dd, 1H, CCH*H*, *J* 8.0 Hz, *J* 13.7 Hz), 3.4-3.7 (m, 11H, CH_2CHOH, CH_2, OH), 3.41 (s, 3H, OCH_3), 3,42 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.51(s, 3H, OCH_3), 3.91 (dt, 1H, CH_2CHOH, *J* 3.6 Hz, *J* 5.4 Hz), 4.02 (dt, 1H, CHOH, *J* 5.4 Hz, *J* 8.0 Hz), 4.16 (*pseudo* q, 1H, C*H*OH, *J* 8.1 Hz), 4.25 (s, 1H, $CH(OCH_3)_2$), 4.26 (s, 1H, $CH(OCH_3)_2$); ^{13}C NMR δ_C (125 MHz; CD_3OD) 39.1 (CH_2C), 40.3 (CH_2C), 56.6 (2 x CH_3), 58.3 (CH_3), 58.5 (CH_3), 63.6 (CH_2OH), 63.7 (CH_2OH), 71.4 (CH_2CHOH), 72.7 (CH_2CHOH), 87.7 (CH_2CHO), 88.0 (CH_2CHO), 106.0 ($CH(OCH_3)_2$), 106.9 ($CH(OCH_3)_2$), 109.6 (C), 110.2 (C). *m/z* (ESI): 209 (M^++1, 4), 191 (M^+-17, 24), 176 (M^+-32, 100), 158 (M^+-50, 40) 148 (M^+-60,55).



14c: To a stirred solution of aldol product (*R*,*R*)-**8c** (124 mg, 0.5 mmol) in dry MeOH (5 mL) Amberlyst®-15 (248 mg) was added. After complete conversion (monitored by TLC, ~3.5 h) the acid ion-exchange resin was removed by filtration and the solvent was evaporated under vacuum. The hemiketal **14c** was purified by flash chromatography (ethyl acetate/ methanol, 95:5) affording a colourless sticky oil as a single pyranose form (90 mg, 87%). $[\alpha]_D^{24}$ -10.8 (*c* 1.01 in MeOH); Found C, 46.5, H 8.1. Calc, for $C_8H_{16}O_6$: C, 46.1, H, 7.7; ^{1}H NMR δ_H (400 MHz, CD_3OD+D_2O) 1.61 (dd, 1H, CC*H*H, *J* 11.6 Hz, *J* 13.1 Hz), 1.92 (dd, 1H, CCH*H*, *J* 5.3 Hz, *J* 13.1 Hz), 3.23-3.52 (m, 5H ,OCH_2, OCH_2CHOH, CCH_2CHOH, COH), 3.45 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.62-3.70 (m, 2H, OCH_2CHOH, CCH_2CHOH), 4.25 (s, 1H, $CH(OCH_3)_2$), ^{13}C NMR δ_C (125 MHz; CD_3OD+D_2O) 35.8 (CH_2C), 56.8 (OCH_3), 58.4 (OCH_3), 64.6 (CH_2O), 70.4 (CHOH), 72.5 (CHOH), 102.4 (COH), 105.8 ($CH(OCH_3)_2$); *m/z* (EI): 208 (M^+, 0.1), 191 (M^+-17, 2), 158 (M^+-50, 18), 147 (M^+-61, 100), 96 (M^+-112, 43).