Supporting Information

Diastereoselective Synthesis and Functionalization of Highly Substituted Cyclopentanones

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Table of contents

1. Materials and methods SI 2
2. Copies of NMR spectra of compounds 9 and 11 SI 3
3. Copies of NMR spectra of compound 4c SI 18
1. Materials and Methods

Unless otherwise stated, all solvents were purchased from Fisher Scientific and used without further purification. Substrates and reagents were purchased from Alfa Aesar or Sigma Aldrich and used as received.

$^1$H-NMR spectra were recorded on a Bruker Avance-400 or Varian VNMRS-600 instrument and are reported relative to residual solvent: CHCl$_3$ (δ 7.26 ppm) or DMSO (δ 2.50 ppm). $^{13}$C-NMR spectra were recorded on the same instruments and are reported relative to CHCl$_3$ (δ 77.16 ppm) or DMSO (δ 39.52 ppm). Data for $^1$H-NMR are reported as follows: chemical shift (δ/ ppm) (integration, multiplicity, coupling constant (Hz)). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br. s = broad singlet, app = apparent. Data for $^{13}$C-NMR are reported in terms of chemical shift (δ/ ppm) and multiplicity (C, CH, CH$_2$ or CH$_3$). Data for $^{19}$F-NMR were recorded on the above instrument at a frequency of 376 MHz using CFCl$_3$ as external standard. DEPT-135, COSY, HSQC, HMBC and NOESY experiments were used to aid the structural assignment.

IR spectra were obtained by use of a Perkin Elmer RX1 spectrometer (neat, ATR sampling) with the intensities of the characteristic signals being reported as weak (w, <20% of tallest signal), medium (m, 21-70% of tallest signal) or strong (s, >71% of tallest signal).

Low and high-resolution mass spectrometry was performed using the indicated techniques on either Waters LCT Premier XE or Waters TQD instruments equipped with Acquity UPLC and a lock-mass electrospray ion source.
2. Copies of NMR Spectra
3. Copies of NMR spectra of compound 4c (contaminated with ~10% compound 4)