Supporting Information:

Total Synthesis of 4-Ketoclonostachydiol

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4-ketoclonostachydiol

Contents: Page No

General 2

1H and 13C spectrum of all new compounds 3 – 15
General techniques: All reactions requiring anhydrous conditions were conducted in flame dried glass apparatus under an atmosphere of nitrogen. THF and Et₂O were freshly distilled from sodium benzophenone ketyl prior to use. CH₂Cl₂ was freshly distilled on CaH₂, toluene and benzene were distilled on molten sodium metal. Anhydrous MeOH was obtained by distillation from magnesium alkoxide and stored under nitrogen over activated 4 Å molecular sieves. Reactions were followed by TLC analysis using silica plates with fluorescent indicator (254 nm) and visualized with a UV lamp, phosphomolybdic acid or anisaldehyde or β-naphthol solution or alkaline KMnO₄ solution. All commercially available reagents were purchased and were typically used as supplied. Optical rotations were measured at ambient temperature (25 °C) on CHCl₃ solutions with polarimeter using 1 ml capacity cell with 100 mm path length. Infrared spectra were recorded using a thin film supported between NaCl plates or as a solid embedded in a KBr disc. ¹H and ¹³C NMR spectra were recorded in Fourier transform mode at the field strength specified either on a 200 MHz or 300 MHz or 500 MHz spectrometer. Spectra were obtained on CDCl₃ solutions in 5 mm diameter tubes; Chemical shifts in ppm are quoted relative to the residual signals of chloroform (δH 7.26 ppm or δC 77.0 ppm). Multiplicities in the ¹H NMR spectra are described as: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of double, q = quartet, p = pentet, m = multiplet, br = broad; coupling constants are reported in Hz. For low (MS) and high (HRMS) resolution mass spectra ion mass/charge (m/z) ratios are reported as values in atomic mass units.
(2S,5S)-5-({tert-butyldimethylsilyloxy}hexane-1,2-diol (9):

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
Tert-butyldimethyl((S)-4-((S)-oxiran-2-yl)butan-2-yloxy)silane (11):

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$):
(3S,6S)-6-(tert-butyldimethylsilyloxy)hept-1-en-3-ol (12):

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
(5S,8S)-8,10,10,11,11-pentamethyl-5-vinyl-2,4,9-trioxa-10-siladodecane (13):

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$):
(2S,5S)-5-(methoxymethoxy)hept-6-en-2-ol (4):

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
(E)-ethyl 3-[(4R,5R)-5-ethyl-2,2-dimethyl-1,3-dioxolan-4-yl]acrylate (15):

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(E)-3-((4R,5R)-5-ethyl-2,2-dimethyl-1,3-dioxolan-4-yl)acrylic acid (7):

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(E)-((2S,5S)-5-(methoxymethoxy)hept-6-en-2-yl)-3-((4R,5R)-2,2,5-trimethyl-1,3-dioxolan-4-yl)acrylate (16):

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
(4S,5S,E)-[(2S,5S)-5-(methoxymethoxy)hept-6-en-2-yl]-4,5-dihydroxyhex-2-enoate (17):

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
(S,E)-((2S,5S)-5-(methoxymethoxy)hept-6-en-2-yl) 5-hydroxy-4-oxohex-2-enoate (18):

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(S,E)-((2S,5S)-5-(methoxymethoxy)hept-6-en-2-yl) 5-(acryloyloxy)-4-oxohex-2-enolate (3):

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
(3E,6S,9E,11S,14S)-11-(methoxymethoxy)-6,14-dimethyl-1,7-dioxacyclotetradeca-3,9-diene-2,5,8-trione (19):

$^1$H NMR (500 MHz, CDCl$_3$):

$^{13}$C NMR (125 MHz, CDCl$_3$):
(3E,6S,9E,11S,14S)-11-hydroxy-6,14-dimethyl-1,7-dioxacyclotetradeca-3,9-diene-2,5,8-trione (1):

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)