Supporting Information File 1

for

Olefin cross metathesis based de novo synthesis of a partially protected L-amicetose and a fully protected L-cinerulose derivative

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Experimental procedures and analytical data
Experimental

General experimental methods. All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified using a commercial solvent purification system. $^1$H NMR spectra were obtained at 300 MHz or at 500 MHz in CDCl$_3$ with CHCl$_3$ ($\delta = 7.26$ ppm) as an internal standard. Coupling constants ($J$) are given in Hz. $^{13}$C NMR spectra were recorded at 125 MHz or at 75 MHz in CDCl$_3$ with CDCl$_3$ ($\delta = 77.0$ ppm) as an internal standard. The number of coupled protons was analyzed by APT-experiments and is denoted by a number in parantheses following the chemical shift value. IR spectra were recorded with a FTIR-spectrometer with an ATR-crystal unit. Wavenumbers ($\nu$) are given in cm$^{-1}$. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained either by EI or ESI/TOF measurements. Alcohol 2 was synthesized following a previously published procedure [1].

(4R,5S,E)-5-(tert-Butyldimethylsilyloxy)-4-hydroxyhex-2-enal (8). To a solution of 2 (500 mg, 2.3 mmol) and acroleine (1.7 mL, 23.1 mmol) in dry dichloromethane (2.3 mL, 1.0 M) was added Ru-catalyst B (97.6 mg, 0.12 mmol, 5 mol %). The mixture was heated to 40 °C and stirred for 16 h at this temperature. After removing all volatiles in vacuo the residue was purified by column chromatography on silica to give 8 (560 mg, 2.3 mmol, 99%). $\lbrack \alpha \rbrack_{D}^{23} = +33.0$ (c 0.48, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.59 (d, $J = 7.9$, 1H), 6.78 (dd, $J = 15.8$, 4.7, 1H), 6.36 (ddd, $J = 15.7$, 7.9, 1.6, 1H), 4.33 (m, 1H), 3.97 (qd, $J = 6.3$, 4.2, 1H), 2.51 (bs, 1H), 1.11 (d, $J = 6.3$), 0.90 (s, 9H), 0.10 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.3 (0), 154.4 (1), 132.3 (1), 75.0 (1), 70.7 (1), 25.7 (3), 20.1 (0), 18.1 (3), $-$4.4 (3), $-$4.9 (3); IR (ATR) $\nu$ 2930 (w), 1691 (m), 1253 (m), 1089 (m), 831 (s), 775 (s); MS (EI) m/z 227 (6), 187 (14),
169 (15), 159 (100), 145 (16), 115 (19), 73 (58), 43 (50); HRMS (ESI) calcd for \(C_{12}H_{24}O_3NaSi\) [M+Na]\(^+\) 267.1392, found 267.1388. Anal. calcd for \(C_{12}H_{24}O_3Si\): C, 59.0; H, 9.9. Found: C, 59.1; H, 9.9.

(2S,3R,E)-2-(tert-Butyldimethylsilyloxy)-6-oxohex-4-en-3-yl benzoate (9). A solution of 8 (738 mg, 3.0 mmol), benzoic acid (443 mg, 3.6 mmol), dicyclohexyl-carbodiimide (746 mg, 3.6 mmol) and DMAP (37 mg, 0.3 mmol) in dry dichloromethane (8.2 mL) was stirred at 20 °C for 12 h. The mixture was filtered and the solid was washed several times with MTBE. The combined organic layers were washed with HCl (aq, 1 M), followed by a saturated aqueous solution of NaHCO\(_3\). The organic extracts were dried with MgSO\(_4\), filtered and evaporated. The residue was purified by column chromatography to give 9 (860 mg, 1.6 mmol, 82%) as a colourless liquid. \([\alpha]_{D}^{25} = +64.9\) (c 0.59, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.60 (d, \(J = 7.8, 1H\)), 8.07 (dm, \(J = 7.1, 1H\)), 7.59 (m, 1H), 7.53-7.42 (m, 2H), 6.97 (dd, \(J = 15.9, 5.1, 1H\)), 6.32 (ddd, \(J = 15.9, 7.8, 1.5, 1H\)), 5.60 (ddd, \(J = 5.1, 4.7, 1.5, 1H\)), 4.16 (qd, \(J = 6.3, 4.7, 1H\)), 1.27 (d, \(J = 6.3, 1H\)), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 192.9, 165.4, 151.1, 133.4, 133.1, 129.7, 129.5, 128.5, 76.9, 69.8, 25.6, 20.4, 17.9, -4.5, -4.9; IR (ATR) \(\nu\) 2930 (m), 1697 (s), 1108 (s), 1040 (s), 834 (s); MS (El) \(m/z\) 304 (7), 247 (10), 179 (94), 159 (38), 105 (100), 73 (22); HRMS (ESI) calcd for \(C_{19}H_{29}O_4Si\) [M+H]\(^+\) 349.1835, found 349.1806. Anal. calcd for \(C_{19}H_{29}O_4Si\): C, 65.5; H, 8.1. Found: C, 65.1; H, 7.6.

(S)-tert-Butyl(1-(furan-2-yl)ethoxy)dimethylsilane (10). A solution of 8 (250 mg, 1.0 mmol) and benzoyl chloride (0.176 mL, 1.5 mmol) in pyridine (25 mL) was stirred at 65 °C for 12 h. After cooling to ambient temperature, the reaction mixture was poured onto ice water, and the aqueous layer was extracted three times with MTBE.
The combined organic layers were washed with a saturated aqueous solution of NaHCO$_3$ and dried with MgSO$_4$. After filtration, the solvent was removed under reduced pressure and the residue purified by chromatography on silica to furnish 10 (107 mg, 0.5 mmol, 47%) as a colourless liquid. $[\alpha]^{25}_D$ $-23.6$ (c 0.57, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33 (dd, $J = 1.8, 0.8, 1H$), 6.30 (dd, $J = 3.2, 1.8, 1H$), 6.16 (ddd, $J = 3.2, 0.8, 1H$), 4.88 (q, $J = 6.4, 1H$), 1.48 (d, $J = 6.5, 3H$), 0.90 (s, 9H), 0.09 (s, 3H), 0.03 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.3, 141.2, 109.9, 104.7, 64.5, 25.8, 22.9, 18.2, $-4.9$, $-5.0$; IR (ATR) $\nu$ 2930 (m), 1256 (m), 1152 (m), 1094 (m), 830 (s), 775 (s), 731 (s); MS (EI) $m/z$ 211 (2), 169 (50), 95 (21), 75 (100), 57 (19); HRMS (ESI) calcd for C$_{12}$H$_{23}$O$_2$Si [M+H]$^+$ 227.1467, found 251.1471. Anal. calcd for C$_{12}$H$_{22}$O$_2$Si: C, 63.7; H, 9.8. Found: C, 63.4; H, 9.7.

**Hydrogenation of enal 9 with Pd/C.** To a solution of 9 (250 mg, 0.72 mmol) in dry and degassed methanol (2 mL) was added Pd/C (10 wt %, 12.5 mg, 1.6 mol %). The suspension was stirred for 12 h under an atmosphere of hydrogen (1 bar). The mixture was filtered through a pad of celite, which was subsequently washed three times with MTBE. After evaporation of all volatiles the residue was chromatographed on silica to furnish 11 (89 mg, 0.22 mmol, 31%) as a colourless liquid, 13 (42 mg, 0.11 mmol, 16%) as a colourless liquid, and a fraction containing the inseparable alcohols 14 and 15 (ca. 45 mg, ca. 0.17 mmol, ca. 24% combined yield) in a 2:1 ratio ($^1$H NMR). Analytical data for (2S,3R)-2-(tert-butyldimethylsilyloxy)-6,6-dimethoxyhexan-3-yl benzoate (11): $[\alpha]^{24}_D$ +19.8 (c 0.33, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.08-8.00 (m, 2H), 7.55 (m, 1H), 7.50-7.38 (m, 2H), 5.00 (td, $J = 8.0, 4.2, 1H$), 4.38 (t, $J = 5.6, 1H$), 4.02 (qd, $J = 6.3, 4.2, 1H$), 3.30 (s, 6H), 1.86-1.53 (m, 4H), 1.19 (d, $J = 6.3, 3H$) 0.87 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); $^{13}$C NMR (75 MHz,
Hydrogenation of enal 9 with Pd(OH)$_2$/C. To a solution of 8 (250 mg, 0.72 mmol) in dry and degassed methanol (2 mL) was added Pd(OH)$_2$/C (10 wt %, 12.5 mg, 1.2 mol %). The suspension was stirred for 12 h under an atmosphere of hydrogen (1 bar). The mixture was filtered through a pad of celite, and the pad was washed three times with MTBE. Evaporation of the solvents furnished an inseparable mixture of 11 and 12 (226 mg, ca. 0.61 mmol, ca. 83% combined yield). Selected analytical data for (2S,3R)-2-(tert-butyldimethylsilyloxy)-6-oxohexan-3-yl benzoate (13) obtained from the mixture: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.08-8.15 (m, 2H), 7.55 (m, 1H), 7.48-7.38 (m, 2H), 5.02 (td, $J$ = 6.0, 4.1, 1H), 4.03 (qd, $J$ = 6.3, 4.1, 1H), 3.39 (td, $J$ = 6.5, 1.4, 2H), 3.31 (s, 3H), 1.86-1.52 (m, 4H), 1.19 (d, $J$ = 6.3, 3H) 0.87 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.3 (0), 132.8 (1), 130.6 (0), 129.6 (1), 128.3 (1), 78.3 (1), 72.4 (2), 69.5 (1), 58.5 (3), 25.8 (2), 25.7 (3), 25.6 (2), 19.8 (3), 18.0 (0), −4.5 (3), −4.9 (3); IR (ATR) $\nu$ 2929 (m), 1717 (s), 1271 (s), 1115 (s), 835 (s), 775 (s), 709 (s).
L-Amicetose-4-benzoate (16). The crude mixture of 11 and 12 (149 mg, ca. 0.38 mmol), obtained from the Pd(OH)$_2$/C-catalyzed hydrogenation as described above, was dissolved in dry dichloromethane (1.5 mL) and CF$_3$CO$_2$H (0.4 mL) was added at ambient temperature. The solution was stirred at ambient temperature for 20 h, followed by evaporation of all volatiles. The residue was redissolved in MTBE, and the solution was washed with a saturated aqueous solution of NaHCO$_3$. The organic layer was separated and dried with MgSO$_4$, filtered and evaporated. The residue was purified by chromatography on silica to furnish 16 (58 mg, 0.24 mmol, 65%) as a 58:42 mixture of anomers. [$\alpha$]$^25_D$ -53.4 (c 0.65, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.03 (ddm, $J = 7.1$, 6.5, 2H), 7.57 (dd, $J = 7.2$, 7.0, 1H), 7.44 (dd, $J = 7.7$, 7.4, 2H), 5.30 (m, 0.5H, major), 4.89 (dm, $J = 6.5$, 0.5H, minor), 4.81-4.65 (m, 1H), 4.23 (m, 0.5H, major), 3.75 (m, 0.5H, minor), 3.27 (bs, 0.5H, minor) 2.84 (bs, 0.5H, major), 2.36-1.96 (m, 2H), 1.96-1.56 (m, 2H), 1.30 (d, $J = 6.2$, 1.5H), 1.22 (d, $J = 6.3$, 1.5H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.8, 133.1, 133.0, 130.2, 130.1, 129.6, 129.6, 95.8, 90.9, 74.0, 73.6, 73.2, 66.8, 31.8, 29.2, 27.5, 23.5, 18.2, 18.0; IR (ATR) $\nu$ 3424 (m), 2937 (w), 1718 (s), 1316 (m), 1269 (s), 1114 (m), 1069 (m), 998 (m), 711 (s); HRMS (ESI) calcd for C$_{13}$H$_{15}$O$_3$ [M–OH]$^+$ 219.1021, found 219.1010.

Stepwise deprotection of 11. A solution of 11 (265 mg, 0.70 mmol) and TBAF·3H$_2$O (253 mg, 0.80 mmol) in THF (6.7 mL) was stirred for 4 h at ambient temperature. Aqueous HCl (1 M) was then added and stirring was continued for 12 h at ambient temperature. A saturated aqueous solution of NaHCO$_3$ and MTBE were then added, and the organic layer was separated. The aqueous layer was extracted twice with MTBE, the combined organic extracts were dried with MgSO$_4$, filtered and evaporated. The residue was chromatographed on silica to give a 1:1.7 mixture of lactols 16 and 17 (112 mg, 0.50 mmol, 71% combined yield). By repeated careful
chromatography a sample of the furanose product (S)-1-((R)-5-hydroxytetrahydrofuran-2-yl)ethyl benzoate (17) could be isolated as a 54 : 46 mixture of anomers for analytical purposes: $\left[\alpha\right]_{D}^{25} +12.0$ (c 0.80, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.10-7.96 (m, 2H), 7.61-7.49 (m, 1H), 7.49-7.36 (m, 2H), 5.57 (d, $J = 3.9$, 0.5H, minor), 5.51 (d, $J = 4.0$, 0.5H, major), 5.35-5.05 (m, 1H), 4.36 (m, 0.5H, minor), 4.18 (m, 0.5H, major), 4.05 (bs, 1H) 2.33-1.46 (m, 4H), 1.38 (d, $J = 6.3$, 1.5H), 1.33 (d, $J = 6.4$, 1.5H); $^{13}$C NMR (75MHz, CDCl$_3$) $\delta$ 165.9 (0), 132.9 (1), 129.6 (1), 129.6 (1), 128.3 (1), 99.0 (1), 98.6 (1), 82.6 (1), 80.2 (1), 72.3 (1), 72.0 (1), 33.6 (2), 32.6 (2), 24.8 (2), 24.7 (2), 16.4 (3), 16.2 (3); IR (ATR) $\nu$ 3423 (m), 2953 (w), 1713 (s), 1451 (m), 1268 (s), 1112 (m), 1069 (m), 988 (m), 709 (s); HRMS (ESI) calcd for C$_{13}$H$_{15}$O$_3$ [M–OH]$^+$ 219.1021, found 219.1016.

(S,E)-5-(tert-Butyldimethylsilyloxy)-4-oxohex-2-enal (21). To a solution of 8 (800 mg, 3.3 mmol) in dry dichloromethane (20 mL) was added Dess–Martin periodinane (1.67 g, 3.9 mmol) at 0 °C, and the mixture was stirred for 2 h at ambient temperature. The reaction mixture was diluted with MTBE, and subsequently washed with saturated aqueous solutions of NaHCO$_3$ and Na$_2$S$_2$O$_3$. The aqueous layer was extracted with MTBE, and the combined organic extracts were dried with MgSO$_4$, filtered and evaporated. The residue was chromatographed on silica to furnish 21 (712 mg, 2.9 mmol, 90%) as a yellowish liquid. $[\alpha]_{D}^{24} -10.1$ (c 0.51, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.76 (d, $J = 7.6$, 1H), 7.42 (d, $J = 16.0$, 1H), 6.92 (dd, $J = 16.0$, 7.6, 1H), 4.36 (q, $J = 6.8$, 1H), 1.35 (d, $J = 6.8$, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 201.2 (0), 192.9 (1), 140.1 (1), 138.6 (1), 74.5 (1), 25.7 (3), 20.7 (3), 18.1 (0), $-4.7$ (3), $-5.0$ (3); IR (ATR) $\nu$ 2932 (w), 1696 (m), 1254 (m), 1112 (m), 832 (s), 777 (s); MS (EI) m/z 185 (77), 159 (68), 157 (69), 143
(13), 115 (26), 75 (62), 73 (50), 57 (21), 43 (25); HRMS (ESI) calcd for C\textsubscript{12}H\textsubscript{23}O\textsubscript{3}Si [M+H]\textsuperscript{+} 243.1400, found 243.1386. Anal. calcd for C\textsubscript{12}H\textsubscript{22}O\textsubscript{3}Si: C, 59.5; H, 9.2. Found: C, 59.3; H, 9.0.

(S)-5-(tert-Butyldimethylsilyloxy)-4-oxohexanal (22). To a solution of 21 (380 mg, 1.57 mmol) in dry and degassed methanol (50 mL) was added Pd/C (“batch 1”, 10 wt %, 38 mg, 2.2 mol %). The suspension was stirred for 12 h under an atmosphere of hydrogen (1 bar). The mixture was filtered through a pad of Celite\textsuperscript{®}, and the pad was washed three times with MTBE. Evaporation of the solvents furnished 22 (326 mg, 1.33 mmol, 85%) as a colourless liquid. [\alpha]\textsuperscript{23}\textsubscript{D} −3.6 (c 0.56, CH\textsubscript{2}Cl\textsubscript{2}; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 9.79 (s, 1H), 4.19 (q, J = 6.8, 1H), 2.97 (ddd, J = 19.0, 6.4, 6.4, 1H), 2.83 (ddd, J = 19.0, 6.7, 5.3, 1H), 2.76-2.68 (m, 2H), 1.30 (d, J = 6.8, 3H), 0.91 (s, 9H), 0.08 (s, 6H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ 213.1 (0), 200.3 (1), 74.8 (1), 37.1 (2), 29.6 (2), 25.7 (3), 20.9 (3), 18.0 (0), −4.7 (3), −5.1 (3); IR (ATR) ν 2932 (w), 1716 (m), 1117 (m), 832 (s), 776 (s); MS (EI) m/z 187 (31), 159 (69), 143 (100), 73 (67); HRMS (ESI) calcd for C\textsubscript{12}H\textsubscript{24}O\textsubscript{3}Si [M]\textsuperscript{+} 244.1495, found 244.1486. Anal. calcd for C\textsubscript{12}H\textsubscript{24}O\textsubscript{3}Si: C, 59.0; H, 9.9. Found: C, 58.7; H, 10.0.

(S,E)-2-(tert-Butyldimethylsilyloxy)-6,6-dimethoxyhex-4-en-3-on (23). Details for conditions listed in Table 4, entry 1: to a solution of 21 (357 mg, 1.50 mmol) in dry and degassed methanol (50 mL) was added Pd/C (“batch 2”, 10 wt %, 36 mg, 2.2 mol %). The suspension was stirred for 12 h under an atmosphere of hydrogen (1 bar). The mixture was filtered through a pad of Celite\textsuperscript{®}, and the pad was washed three times with MTBE. Evaporation of the solvents furnished 23 (218 mg, 0.80 mmol, 52%) as a colourless liquid.
Details for conditions listed in Table 4, entry 4: Enal 21 (1.10 g, 4.5 mmol) was dissolved in dry methanol (20 mL) and Pd(OAc)₂ (10.2 mg, 0.045 mmol, 1 mol %) and activated charcoal (92 mg) were added. The reaction vessel was flushed with hydrogen, and the mixture was stirred under an atmosphere of hydrogen (1 bar) for 12 h. The mixture was filtered through a pad of Celite®, and the pad was washed three times with MTBE. All volatiles were evaporated to furnish 23 (1.10 g, 3.70 mmol, 82%) as a colourless liquid. [α]²³D −8.4 (c 0.62, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 6.87 (dd, J = 16.0, 1.0, 1H), 6.74 (dd, J = 16.0, 3.7, 1H), 4.95 (dd, J = 3.7, 1.0, 1H), 4.27 (q, J = 6.8, 1H), 3.32 (s, 3H), 3.32 (s, 3H), 1.31 (d, J = 6.8, 3H), 0.09 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 201.5 (0), 141.4 (1), 126.7 (1), 101.1 (1), 74.5 (1), 52.8 (3), 52.8 (3), 25.7 (3), 20.8 (3), 18.2 (0), −4.8 (3), −5.0 (3); IR (ATR) ν 2933 (w), 1702 (m), 1256 (m), 1123 (s), 1056 (s), 832 (s), 777 (s); MS (El) m/z 231 (32), 159 (32), 75 (100), 73 (98), 43 (22); HRMS (ESI) calcd for C₁₄H₂₈O₄NaSi [M+Na]⁺ 311.1655, found 311.1659. Anal. calcd for C₁₄H₂₈O₄Si: C, 58.3; H, 9.8. Found: C, 58.1; H, 9.7.

(S)-2-(tert-Butyldimethylsilyloxy)-6,6-dimethoxyhexan-3-one (24). To a solution of 23 (225 mg, 0.80 mmol) in dry and degassed methanol (20 mL) was added Pd(OH)₂/C (10 wt %, 11 mg, 1.0 mol %). The suspension was stirred for 12 h under an atmosphere of hydrogen (1 bar). The mixture was filtered through a pad of Celite®, and the pad was washed three times with MTBE. All volatiles were evaporated and the residue was purified by chromatography on silica to furnish 24 (190 mg, 0.70 mmol, 84%). [α]²⁴D −4.1 (c 0.23, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 4.36 (t, J = 5.7, 1H), 4.14 (q, J = 6.8, 1H), 3.30 (s, 6H), 2.65 (t, J = 7.1, 2H), 1.86 (td, J = 7.1, 5.8, 2H), 1.27 (d, J = 6.8, 3H), 0.91 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 213.4 (0), 103.8 (1), 74.9 (1), 53.0 (3), 53.0 (3), 31.8 (2), 26.0 (2), 25.7 (3),

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20.8 (3), 18.1 (0), −4.7 (3), −5.1 (3); IR (ATR) ν 2931 (w), 2856 (w), 1718 (m), 1118 (m), 834 (s), 777 (s); HRMS (ESI) calcd for C_{13}H_{27}O_{3}Si [M–OMe]$^+$ 259.1729, found 259.1703.

**Deprotection of 24.** To a solution of 24 (51 mg, 0.18 mmol) in THF (1.8 mL) was added TBAF·3H$_2$O (67 mg, 0.21 mmol). The mixture was stirred for 4 h at ambient temperature, followed by addition of aqueous HCl (1 M, 5.0 mL). Stirring at ambient temperature was continued for 12 h. The reaction mixture was then neutralized by the addition of a saturated aqueous solution of NaHCO$_3$, and the aqueous layer was extracted three times with MTBE. The solvents were carefully removed in vacuo, and the residue was purified by chromatography on silica to furnish L-cinerulose (5 mg, 0.04 mmol, ca. 20%) as a 2:1 mixture of its open chain aldose form 27 and its aldopyranose form 28. Analytical data were obtained from the mixture: [α]$^2_D$ −15.5 (c 0.25, CDCl$_3$); IR (ATR) ν 3425 (bm), 2938 (w), 1717 (s), 1369 (w), 1095 (s), 1012 (s); selected data for 27: $^1$H NMR (300 MHz, CDCl$_3$) δ 9.81 (s, 1H), 4.46 (q, J = 7.1, 1H), 1.43 (d, J = 7.1, 3H); selected data for 28: $^1$H NMR (300 MHz, CDCl$_3$) δ 5.45 (t, J = 4.9, 1H), 4.46 (q, J = 6.7, 1H), 1.29 (d, J = 6.7, 3H).

**Reference**