Supporting Information

A Powerful tool for acid catalyzed organic addition and substitution reactions

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General

$^1$H and $^{13}$C NMR spectra were recorded on a 500 MHz spectrometer operating at 500.1 and 125.8 MHz, respectively. The solvent residual peak was used as a standard for $^1$H and $^{13}$C measurements in CDCl$_3$ and CD$_2$OD (7.26 ppm or 77.16 ppm for CDCl$_3$ and 3.31 ppm or 49.00 ppm for CD$_2$OD, respectively),$^1$ in D$_2$O 4.79 ppm in $^1$H measurements and trimethylsilyl propionic acid sodium salt (TSP) in $^{13}$C measurements (0.00 ppm). The proton-coupled $^{13}$C NMR spectrum was measured for compound 5a to confirm the number of protons on each carbon and marked after each carbon by the letters s (singlet), d (doublet), t (triplet), q (quartet) or qv (quintet). The $^nJ_{PP}$ couplings were calculated from the proton spectra and all $J$ values are given in Hz. Mass spectra were recorded on a quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI) with positive ionization mode for compound 27 and negative ionization mode for compound 25. The purity of the products was determined from $^1$H spectrum and was $\geq 95\%$ unless stated otherwise. Ion exchange resins (Dowex®, Diphonix® and Amberlyst®) were oven dried for approx. 20 hours at 120°C before use. The used conditions and yields have not been optimized, except in the preparation of 13a and 17 some conditions optimizations were made. We were unable to measure the correct MS peaks for the compounds 5a and 5b probably due to high reactivity or instability of the compounds in used conditions.

Preparation of Dowex® D$^+$ ion exchange resin: Na$^+$ form Dowex® (approx. 5 g) were stirred for 1 hour in 3.8 M DCl solution (10 ml in D$_2$O) at room temperature before it was filtered, washed with D$_2$O and dried in vacuo. Dowex® D$^+$ resin was stored in a desiccator.

Preparation of 3-Iodo-3-methylbutan-1-ol (5a): MgSO$_4$ dried 3-methyl-3-buten-1-ol (59 µl, 50.2 mg, 0.58 mmol) was dissolved to dry MeOH (4 ml), oven dried NaI (87 mg, 0.58 mmol, 1 eq) and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 400 mg) were added and the reaction mixture was stirred for 10-15 min at room temperature. Dowex was filtered off and MeOH was removed by evaporation in vacuo. The residue was dissolved in DCM and any solids were removed and DCM evaporated to dryness in vacuo. 3-Iodo-3-methyl-butan-1-ol (81 mg, 65%) was obtained as a brownish yellow oil. $^1$H NMR (CDCl$_3$): $\delta$ 3.93 (t, 2H, $^3J_{HH} = 7.0$), 3.57 (br, 1H + some H$_2$O), 1.99 (t, 2H, $^3J_{HH} = 7.0$), 1.98 (s, 6H); $^{13}$C NMR (CDCl$_3$): $\delta$ 63.2 (t), 51.2 (t), 47.1 (s), 38.7 (q, 2C).

Preparation of deuterated 3-Iodo-3-methylbutan-1-ol (5b): Prepared similarly to 5a, except Dowex D$^+$ was used instead of Dowex H$^+$ and CD$_2$OD instead of MeOH. 5b (67 mg, 54%) was obtained as a brownish yellow oil. The purity of the compound was approx.
90%. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 3.97 (t, 2H, \(^3J_{HH} = 7.0\)), 2.01 (t, 2H, \(^3J_{HH} = 7.0\)), 1.97 (s, 3H), 1.96-1.94 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 63.2, 51.5, 47.3, 38.9, 38.6 (1:1:1 triplet, \(^{1}J_{CD} = 19.7\)).

**Preparation of 3-methoxy-3-methyl-butan-1-ol (8a):** Commercially available in many sources. 3-methyl-3-buten-1-ol (59 \(\mu\)l, 50.2 mg, 0.58 mmol) was dissolved in dry MeOH (2.5 ml) followed by adding dry NaI (10 mg, 0.067 mmol, 0.1 eq). The reaction mixture was stirred overnight at 40°C, solids were filtered off and the reaction mixture evaporated to dryness in vacuo. 3-Methoxy-3-methyl-butan-1-ol (35 mg, 51%) was obtained as a colourless liquid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 3.80 (t, 2H, \(^3J_{HH} = 6.0\)), 3.52 (br, 1H), 3.22 (s, 3H), 1.75 (t, 2H, \(^3J_{HH} = 6.0\)), 1.23 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 76.7, 60.1, 49.3, 42.3, 24.5 (2C).

**Preparation of 3-butoxy-3-methyl-butan-1-ol (8b):** 3-Methyl-3-buten-1-ol (89 \(\mu\)l, 75.7 mg, 0.88 mmol) was dissolved in BuOH (2.5 ml) followed by adding dry NaI (7 mg, 0.047 mmol, 0.05 eq). The reaction mixture was stirred for overnight at 50°C, solids were filtered off and the reaction mixture evaporated to dryness in vacuo. 3-butoxy-3-methyl-butan-1-ol (72 mg, 45%) was obtained as colorless liquid. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 3.80 (t, 2H, \(^3J_{HH} = 6.0\)), 3.37 (t, 2H, \(^3J_{HH} = 6.5\)), 3.26 (br, 1H), 1.74 (t, 2H, \(^3J_{HH} = 5.5\)), 1.52-1.46 (m, 2H), 1.39-1.32 (m, 2H), 1.23 (s, 3H), 0.91 (t, 3H, \(^3J_{HH} = 7.5\)); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 76.6, 61.2, 60.1, 42.9, 32.7, 25.0 (2C), 19.6, 14.0.

**Preparation of 5-Isopropyl-2-methylphenol, carvacrol (9):** Oven dried NaI (96 mg, 0.64 mmol, 1.0 eq) was dissolved in dry acetone (3 ml), \(\text{R}(-)-\text{carvone}\) (100 \(\mu\)l, 96 mg, 0.64 mmol) and oven dried Dowex 50W-X8 ion exchange resin (H\(^+\)-form, 400 mg) was added and the reaction mixture was stirred in the dark overnight at room temperature. Dowex was filtered off and acetone was removed by evaporation in vacuo. The crude product was dissolved in DCM (5 ml) and washed with 10% Na\(_2\)S\(_2\)O\(_3\) (sodium thiosulfate, 4 ml), DCM layer was separated, dried with MgSO\(_4\) and removed by evaporation in vacuo. Carvacrol (85 mg, 89%) was obtained as brownish oil. All \(^1\)H and \(^{13}\)C NMR data were comparable with those reported elsewhere. \(^2\) \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.04 (d, 1H, \(^3J_{HH} = 8.0\)), 6.73-6.71 (m, 1H) 6.66-6.65 (m, 1H), 4.64 (s, 1H), 2.82 (qv, 1H), 2.21 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 153.8, 148.7, 131.0, 121.0, 119.0, 113.2, 33.9, 24.2 (2C), 15.5.
Preparation of 5-(1-iodo-1-methyl-ethyl)-2-methyl-cyclohex-2-enone (7): When the synthesis of carvacrol (9) was stopped after 2 h, solvent was removed and the crude product purified by TLC using ethyl acetate/hexane (1:9) as eluent, 5-(1-iodo-1-methyl-ethyl)-2-methyl-cyclohex-2-enone (80 mg, 45%, Rf. 0.44) was obtained as a colorless oil. All $^1$H NMR data were comparable with those reported elsewhere.$^3$ $^1$H NMR (CDCl$_3$): $\delta$ 6.75-6.73 (m, 1H), 2.76-2.71 (m, 1H), 2.63-2.55 (m, 1H), 2.39-2.30 (m, 2H), 1.98 (s, 3H), 1.96 (s, 3H), 1.80-1.78 (m, 3H), 1.28-1.20 (m, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ 198.8, 143.9, 135.3, 56.2, 49.9, 43.1, 36.0, 35.8, 31.2, 15.5.

Preparation of (E)-2,3-diiodo-prop-2-en-1-ol (11): Propargyl alcohol (50 µl, 48.2 mg, 0.86 mmol) and oven dried NaI (130 mg, 0.87 mmol, 1 eq) were dissolved to isopropanol (3 ml), oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 500 mg) was added and the reaction mixture was stirred overnight (ca. 16 h) at 65°C. Dowex was filtered off and isopropanol was removed by evaporation in vacuo. (E)-2,3-Diiodo-prop-2-en-1-ol (80 mg, 60%) was obtained as a slightly yellow solid. All $^1$H and $^{13}$C NMR data were comparable with those reported elsewhere.$^4$ $^1$H NMR (CDCl$_3$): $\delta$ 7.05 (s, 1H), 4.29 (s, 2H), 1.90 (br, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ 104.1, 79.9, 71.0.

Preparation of 5-iodo-pentanol (13a): Oven dried NaI (500 mg, 3.34 mmol), tetrahydropyran (8 ml), and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 2 g) were refluxed for overnight at dark. Dowex was filtered off, the reaction mixture evaporated in vacuo. The crude product was dissolved in DCM (10 ml) and washed with 10% Na$_2$S$_2$O$_3$ (sodium thiosulfate, 3 ml), DCM layer was separated, dried with MgSO$_4$ and removed by evaporation in vacuo. The residue was purified by silica column chromatography using ethyl acetate/hexane (1:1) as eluent. 5-Iodo-pentanol (235 mg, 33%) was obtained as a very slightly yellow oil. 1,5-Diiodopentane 13c was isolated from the same reaction mixture (see below). The total yield was approx. 63% if calculated as both products 13b (33%) and 13c (30%) together. It is possible to influence the ratio of the products by the relative amount of tetrahydropyran used in the reaction, as an example, when the following amounts of starting materials were used the calculated yields (not isolated) for 13b and 13c were 45% and 23%, respectively, according to the $^1$H NMR spectrum: NaI (200 mg), tetrahydropyran (8 ml), and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 800 mg). All $^1$H NMR data were comparable with those reported elsewhere.$^5$ $^1$H NMR (CDCl$_3$): $\delta$ 3.66 (t, 2H, $^3$J$_{HH}$ = 7.0), 3.20
(t, 2H, $^3\text{J}_{\text{HH}} = 7.0$), 1.86 (qv, 2H), 1.63-1.56 (m, 2H), 1.52-1.45 (m, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$ 62.9, 33.5, 31.8, 27.0, 7.0.

**Preparation of 2-(2-Iodo-ethoxy)-ethanol (13b):** Oven dried NaI (1 g, 6.67 mmol), distilled 1,4-dioxane (20 ml), and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 4 g) were refluxed for overnight. Dowex was filtered off, washed with DCM and the reaction mixture with DCM was evaporated *in vacuo*. The crude product was dissolved in DCM (20 ml) and washed with 10% Na$_2$S$_2$O$_3$ (sodium thiosulfate, 6 ml), DCM layer was separated, dried with MgSO$_4$ and removed by evaporation *in vacuo*. The residue was purified by silica column chromatography using ethyl acetate as eluent. 2-(2-Iodo-ethoxy)-ethanol (980 mg, 68%) was obtained as a very slightly yellow oil. All $^1$H NMR data were comparable with those reported elsewhere.$^6$ $^1$H NMR (CDCl$_3$): $\delta$ 3.79-3.73 (m, 4H), 3.62 (virtual t, 2H), 3.29 (t, 2H, $^3\text{J}_{\text{HH}} = 6.5$) 2.00 (t, -OH, $^3\text{J}_{\text{HH}} = 6.5$); $^{13}$C NMR (CDCl$_3$): $\delta$ 71.7, 71.5, 61.9, 3.1.

**Preparation of 1,5-diiodopentane (13c):** See the above procedure, 1,5-diiodopentane was isolated as a co-product from the synthesis of 13b. 1,5-Diiodopentane (160 mg, 30%) was isolated as a very slightly yellow liquid. All $^1$H and $^{13}$C NMR data were comparable with those reported elsewhere.$^7$ $^1$H NMR (CDCl$_3$): $\delta$ 3.19 (t, 4H, $^3\text{J}_{\text{HH}} = 7.0$), 1.82 (qv, 2H), 1.43-1.36 (m, 2H), 1.34-1.24 (m, 8H), 0.89 (t, 2H, $^3\text{J}_{\text{HH}} = 7.0$); $^{13}$C NMR (CDCl$_3$): $\delta$ 32.5 (2C), 31.6, 6.3 (2C).

**Preparation of octyl iodide (15a):** 1-Octanol (183 µl, 151.3 mg, 1.16 mmol) and oven dried NaI (346 mg, 2.31 mmol, 2 eq) were dissolved in di-isopropyl ketone (12 ml), oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 1.5 g) was added to it and the reaction mixture was stirred for overnight (ca. 16 h) at 100°C. Dowex was filtered off and di-isopropyl ketone was removed by evaporation *in vacuo*. The crude product was purified in a silica column chromatography using hexane/ethyl acetate (9:1) as eluent. Octyl iodide (120 mg, 43%) was obtained as colorless oil. All $^1$H NMR data were comparable with those reported elsewhere.$^8$ $^1$H NMR (CDCl$_3$): $\delta$ 3.19 (t, 2H, $^3\text{J}_{\text{HH}} = 7.0$), 1.82 (qv, 2H), 1.43-1.36 (m, 2H), 1.34-1.24 (m, 8H), 0.89 (t, 2H, $^3\text{J}_{\text{HH}} = 7.0$); $^{13}$C NMR (CDCl$_3$): $\delta$ 33.7, 31.9, 30.7, 29.2, 28.7, 22.8, 14.2, 7.4.

**Preparation of 12-Iodo-dodecanoic acid (15b):** 12-Hydroxydodecanoic acid (200 mg, 0.92 mmol) was dissolved in dry acetonitrile (8 ml), oven dried NaI (300 mg, 2.0 mmol, 2.15 eq) and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 1.2 g) were added and the
reaction mixture was refluxed for 5 h. Dowex was filtered off and the reaction mixture evaporated to dryness in vacuo. The crude product was purified by silica column chromatography using ethyl acetate/hexane (1:3) as eluent. 12-Iodo-dodecanoic acid (215 mg, 71%) was obtained as a yellow solid. All 1H and 13C NMR data were comparable with those reported elsewhere.9,10 1H NMR (CDCl3): δ 3.19 (t, 2H, 3JHH=7.0), 2.35 (t, 2H, 3JHH=7.5), 1.82 (qv, 2H, 3JHH=7.5), 1.67-1.60 (m, 2H), 1.40-1.35 (m, 2H), 1.34-1.24 (m, 12H); 13C NMR (CDCl3): δ 180.2, 34.2, 33.7, 30.6, 29.6, 29.50, 29.48, 29.3, 29.2, 28.7, 24.8, 7.4.

Preparation of (Z)-Octadec-9-enoic acid methyl ester (17): (Z)-Octadec-9-enoic acid (250 µl, 223.8 mg, 0.79 mmol) was dissolved in MeOH (6 ml), oven dried NaI (12 mg, 0.08 mmol, 0.1 eq) and oven dried Dowex 50W-X8 ion exchange resin (H+-form, 1.0 g) were added and the reaction mixture was stirred for 1 h at room temperature. Dowex was filtered off, washed with MeOH and the liquids evaporated to dryness in vacuo. (Z)-Octadec-9-enoic acid methyl ester (232 mg, 99%) was obtained as a colorless oil. All 1H NMR data were comparable with those reported elsewhere.11 1H NMR (CDCl3): δ 5.38-5.32 (m, 2H), 3.67 (s, 3H), 2.31 (t, 2H, 3JHH=7.5), 2.03-1.98 (m, 4H), 1.65-1.58 (m, 2H), 1.37-1.20 (m, 20H), 0.88 (t, 3H, 3JHH=7.0); 13C NMR (CDCl3): δ 174.7, 130.2, 129.9, 51.7, 34.3, 32.1, 29.9, 29.8, 29.7, 29.48, 29.47, 29.30, 29.28, 29.24, 27.37, 27.32, 25.1, 22.8, 14.3.

Preparation of 12-hydroxy-dodecanoic acid isopropyl ester (18): 12-hydroxydodecanoic acid (200 mg, 0.92 mmol) was dissolved in 2-propanol (8 ml), oven dried NaI (28 mg, 0.19 mmol, 0.2 eq) and oven dried Dowex 50W-X8 ion exchange resin (H+-form, 1.5 g) were added and the reaction mixture was refluxed for 4 h. Dowex was filtered off and any excess of 2-propanol was removed by evaporation in vacuo. The crude product was purified by silica column chromatography using ethyl acetate/hexane (3:2) as eluent. 12-Hydroxy-dodecanoic acid isopropyl ester (168 mg, 70%) was obtained as a white solid. 1H NMR (CDCl3): δ 4.99 (qv, 1H, 3JHH=6.5), 3.62 (t, 2H, 3JHH=6.5), 2.24 (t, 2H, 3JHH=7.5), 1.62-1.51 (m, 4H), 1.46 (br, 1H), 1.35-1.23 (m, 14H), 1.21 (d, 6H, 3JHH=6.5); 13C NMR (CDCl3): δ 173.6, 67.4, 63.2, 34.9, 32.9, 29.7, 29.6, 29.5 (2C), 29.4, 29.2, 25.9, 25.2, 22.0 (2C).

Preparation of octyl acetate (19a): 1-Octanol (400 µl, 330.8 mg, 2.54 mmol) was dissolved in dry acetonitrile (8 ml), oven dried Dowex 50W-X8 ion exchange resin (H+-form, 1.5 g) and H2O (91 µl, 2 eq) were added and the reaction mixture was refluxed for 48 h. Dowex was
filtered off and acetonitrile was removed by evaporation in vacuo. The crude product was purified by silica column chromatography using hexane/ethyl acetate (9:1) as the eluent. Acetic acid octyl ester (175 mg, 40%) was obtained as a colorless oil. All $^1$H and $^{13}$C NMR data were comparable with those reported elsewhere.$^{12}$ $^1$H NMR (CDCl$_3$): $\delta$ 4.05 (t, 2H, $^3$J$_{HH}$ = 7.0), 2.04 (s, 3H), 1.61 (qv, 2H), 1.38-1.22 (m, 10H), 0.88 (t, 3H, $^3$J$_{HH}$ = 7.0). $^{13}$C NMR (CDCl$_3$): $\delta$ 171.4, 64.8, 31.9, 29.36, 29.32, 28.8, 26.1, 22.8, 21.2, 14.2.

**Preparation of propionic acid octyl ester (19b):** 1-Octanol (400 µl, 330.8 mg, 2.54 mmol) was dissolved in propionitrile (8 ml) and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 1.0 g) was added and the reaction mixture was refluxed overnight. Dowex was filtered off and propionitrile was removed by evaporation in vacuo. The crude product was purified by silica column chromatography using hexane/ethyl acetate (9:1) as the eluent. Propionic acid octyl ester (195 mg, 41%) was obtained as a colorless oil. All $^1$H and $^{13}$C NMR data were comparable with those reported elsewhere.$^{13,14}$ $^1$H NMR (CDCl$_3$): $\delta$ 4.06 (t, 2H, $^3$J$_{HH}$ = 7.0), 2.32 (q, 2H, $^3$J$_{HH}$ = 7.5), 1.62 (qv, 2H), 1.38-1.22 (m, 10H), 1.14 (t, 3H, $^3$J$_{HH}$ = 7.5), 0.88 (t, 3H, $^3$J$_{HH}$ = 7.0). $^{13}$C NMR (CDCl$_3$): $\delta$ 171.8, 64.6, 31.9, 29.37, 29.32, 28.8, 27.8, 26.1, 22.8, 14.2, 9.3.

**Preparation of isoamyl acetate (21):** Isoamyl alcohol (2.0 ml, 1.62 g, 18.4 mmol) was dissolved in acetic acid (2 ml, 2.1 g, 34.9 mmol, 1.9 eq), oven dried NaI (275 mg, 1.83 mmol, 0.1 eq) and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 1.0 g) were added and the reaction mixture stirred for 2 h at 50°C. 100%, complete, conversion of isoamyl alcohol to isoamyl acetate was achieved according to the $^1$H NMR spectrum. **Isolation of 21:** Dowex was filtered off and the reaction mixture moved to a separation funnel and washed with a saturated NaHCO$_3$ solution (20 ml) and with 10% Na$_2$S$_2$O$_3$ (sodium thiosulfate, 5 ml). The organic layer was separated and dried over MgSO$_4$. Isoamyl acetate (1.53 g, 64%) was obtained as a colorless liquid. All $^1$H NMR data were comparable with those reported elsewhere.$^{15}$ $^1$H NMR (CDCl$_3$): $\delta$ 4.09 (t, 2H, $^3$J$_{HH}$ = 7.0), 2.03 (s, 3H), 1.72-1.64 (m, 1H), 1.51 (q, 2H, $\Sigma^3$J$_{HH}$ = 7.0), 0.92 (d, 6H, $^3$J$_{HH}$ = 6.5).

**Preparation of biodiesel (23):** Used cooking oil (5 g) was dissolved to MeOH (100 ml), oven dried NaI (850 mg, 5.67 mmol,) and oven dried Dowex 50W-X8 ion exchange resin (H$^+$-form, 5 g) were added and the reaction mixture was refluxed overnight. Dowex was
filtered off and MeOH was removed by evaporation in vacuo. The residue was dissolved in hexane (20 ml), washed with water (10 ml) and the hexane layer was dried over MgSO₄ before evaporated in vacuo. Biodiesel 23 (4.3 g) was obtained as a colorless oil. ¹H NMR (CDCl₃): δ 5.38-5.32 (m), 3.67 (s, 3H), 2.31 (t), 2.03-1.98 (m), 1.65-1.58 (m), 1.37-1.20 (m), 0.88 (t).

Preparation of 3-(Formyloxy)-2-phenylpropanoic acid (25): Tropic acid (200 mg, 1.20 mmol), dry NaI (180 mg, 1.20 mmol, 1 eq), dried Dowex 50W-X8 ion exchange resin (H⁺-form, 800 mg) and dry DMF (5 ml) were stirred overnight at 115°C followed by evaporation to dryness. The residue was dissolved in DCM (10 ml) and washed with 10% Na₂S₂O₃ (sodium thiosulfate, 5 ml). The aqueous phase was extracted with DCM (5 ml), combined DCM fractions were washed with 0.2 M HCl (7 ml) and water (7 ml) before being dried over MgSO₄ and evaporated to dryness. The residue was dissolved into a mixture of diethyl ether (2 ml) and n-hexane (2 ml) followed by cooling overnight at approx. -18°C. The precipitate formed was filtered and dried in vacuo. 3-(formyloxy)-2-phenylpropanoic acid (131 mg, 56%) was obtained as a white solid. M.p. 69-72°C (decomposed). ¹H NMR (CDCl₃): δ 8.03 (s, 1 H), 7.39-7.32 (m, 5H), 4.68 (t, 3H, ³J₃H₃ = 10.0), 4.48-4.43 (m, 1H), 4.03-3.98 (m, 1 H). ¹³C NMR (CDCl₃): δ 176.8, 160.6, 134.0, 129.3 (2C), 128.6, 128.3 (2C), 64.2, 50.5. MS (ESI⁻) calcd. for C₁₀H₉O₄ [M-H]⁻ 193.0501, found: 193.0496.

Preparation of (2S,3R,4S,5S)-6-(isopropoxymethyl)tetrahydro-2H-pyran-2,3,4,5-tetraol (27): D(+)-glucose (100 mg, 0.56 mmol) was dissolved in distilled 2-propanol (4 ml), dry NaI (125 mg, 0.83 mmol, 1.5 eq) and dried Dowex 50W-X8 ion exchange resin (H⁺-form, 500 mg) were added and the reaction mixture was refluxed overnight. Solids were filtered off and 2-propanol was removed by evaporation in vacuo. The crude product was purified by silica column chromatography using ethyl acetate/methanol (8:2) as eluent yielding 12 (102 mg, 83%, 1:2 mixture of isomers) as a brownish solid. ¹H NMR (CD₃OD): Major isomer: δ 4.89 (d, 1H, ³J₃H₃ = 3.9 Hz), 3.94 (sep, 1H, ³J₃H₃ = 6.2 Hz), 3.79 (dd, 1H, ²J₃H₃ = 11.3 Hz, ³J₃H₃ = 1.9 Hz), 3.68-3.59 (m, 3H), 3.38-3.23 (m, 2H), 1.24 (d, 3H, ³J₃H₃ = 6.2 Hz), 1.18 (d, 3H, ³J₃H₃ = 6.2 Hz); Minor isomer: 4.33 (d, 1H, ³J₃H₃ = 7.8 Hz), 4.04 (sep, 1H, ³J₃H₃ = 6.2 Hz), 3.85 (dd, 1H, ²J₃H₃ = 11.8 Hz, ³J₃H₃ = 2.2 Hz), 3.68 (d, 1H, ²J₃H₃ = 11.8 Hz), 3.38-3.23 (m, 3H) 3.16-3.11 (m, 1H), 1.23 (d, 3H, ³J₃H₃ = 6.2 Hz), 1.19 (d, 3H, ³J₃H₃ = 6.2 Hz). ¹³C NMR (CDCl₃): Major isomer: δ 98.2, 75.1, 73.6, 73.5, 72.0, 70.9, 62.7, 23.7, 21.6; Minor isomer: 102.6,
78.1, 77.9, 75.2, 72.6, 71.7, 62.8, 23.8, 22.0. MS (ESI+) calcd. for C$_9$H$_{18}$O$_6$Na [M+Na]$^+$
245.1001, found: 245.0995.
References


