Effective and chemoselective glycosylations using 2,3-unsaturated sugars

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Contents

• Synthesis of the glycosyl donors 18 and 30.
• Synthesis of the glycosyl acceptor 20.
• Synthesis of the glycosyl acceptor 23.
• ¹H- and ¹³C-NMR spectrum charts

Synthesis of the glycosyl donors 18 and 30.

6-O-Benzoyl-4-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl acetate (30): To a solution of methyl 2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (4) (1.86 g, 11.6 mmol) and pyridine (1.40 mL, 17.4 mmol) in dry CH₂Cl₂ (37.2 mL) was slowly added benzoyl chloride (1.61 mL, 13.9 mmol) at -78 ºC. After the mixture was stirred at -78 ºC for 1 h, the reaction was quenched by addition of water (100 mL). The resulting mixture was extracted with EtOAc (100 mL × 3). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification of the residue by silica-gel column chromatography (hexane/EtOAc = 1/1), gave methyl 6-O-benzoyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (SI-1) (2.67 g, 87%). White needles; m.p. 77.2-78.2 ºC; Rf 0.23 (2/1 hexane/EtOAc); [α]₂³⁺ +22.5º (c 1.80, CHCl₃); ¹H NMR (CDCl₃, TMS) δ 8.08 (2H, dd, Jₒ,m = 7.5 Hz, Jₒ,p = 1.5 Hz, Hₒ of Bz), 7.58 (1H, tt, Jₘ,p = 7.5 Hz, Jₐ,p = 1.5 Hz, Hₚ of Bz), 7.45 (2H, dd, Jₒ,m = Jₘ,p = 7.5 Hz, Hₘ of Bz),
5.99 (1H, br-dd, $J_{2,3} = 10.2$ Hz, H-3), 5.77 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{1,2} = J_{2,4} = 2.4$ Hz, H-2), 4.91 (1H, br-d, H-1), 4.79 (1H, dd, $J_{6,6} = 12.3$ Hz, $J_{5,6} = 4.8$ Hz, H-6), 4.52 (1H, dd, $J_{6,6} = 12.3$ Hz, $J_{5,6} = 2.4$ Hz, H-6), 4.14 (1H, br-ddd, $J_{4,5} = 9.6$ Hz, H-4), 3.93 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 4.8$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 3.46 (3H, s, OMe), 2.44 (1H, br-d, OH); Anal. Calcd for C$_{14}$H$_{16}$O$_{5}$: C, 63.63; H, 6.10.

To a solution of SI-1 (4.16 g, 15.7 mmol) in dry DMF (83.2 mL) were added 60% NaH (dispersion in paraffin liquid, 945 mg, 23.6 mmol) and benzyl bromide (3.69 mL, 31.5 mmol) at -40 ºC. After the mixture was stirred at -20 ºC for 3 h, the reaction was quenched by addition of sat. NH$_4$Cl aq. (500 mL). The mixture was extracted with EtOAc (80 mL × 4). The combined organic layer was washed with brine (500 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. Purification of the residue by silica-gel column chromatography (hexane/EtOAc = 4/1) gave methyl 6-O-benzoyl-4-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (SI-2) (5.22 g, 94%). Colorless syrup; $R_f$ 0.33 (4/1 hexane/EtOAc); [$\alpha$]$^2_{D}$ $^{+}$134.8º (c 1.40, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS) $\delta$ 8.01 (2H, dd, $J_{o,m} = 7.5$ Hz, $J_{o,p} = 1.5$ Hz, H$_o$ of Bz), 7.42 (2H, dd, $J_{o,m} = J_{m,p} = 7.5$ Hz, H$_m$ of Bz), 7.35-7.18 (5H, m, ArH of Bn), 6.14 (1H, br-dd, $J_{2,3} = 10.2$ Hz, H-3), 5.82 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{1,2} = 2.7$ Hz, H-2), 4.90 (1H, br-dd, $J_{1,2} = 2.7$ Hz, H-1), 4.69 & 4.54 (2H, ABq, $J = 11.4$ Hz, ArCH$_2$), 4.59 (1H, dd, $J_{6,6} = 11.7$ Hz, $J_{5,6} = 2.1$ Hz, H-6), 4.51 (1H, dd, $J_{6,6} = 11.7$ Hz, $J_{5,6} = 5.1$ Hz, H-5), 4.16 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 5.1$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 4.10 (1H, dd, $J_{4,5} = 9.6$ Hz, $J_{4,5} = 1.8$ Hz, H-4), 3.44 (3H, s, OMe); Anal. Calcd for C$_{21}$H$_{22}$O$_{5}$: C, 71.17; H, 6.26.

To a solution of SI-2 (2.00 g, 5.64 mmol) in Ac$_2$O (20.0 mL) was dropwisely added BF$_3$・OEt$_2$ (1.01 mL, 5.64 mmol) at -70 ºC. After the mixture was stirred in warming up to -60 ºC for 1 h, the reaction was quenched by triethylamine (2.36 mL, 16.9 mmol). The resulting mixture was poured into water (100 mL), and then extracted with EtOAc (100 mL × 3). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. Purification of the residue by silica-gel column chromatography (hexane/EtOAc/TEA = 15/5/1) gave the recovered SI-2 (900 mg, 45%) and 30 (971 mg, 45%). Colorless syrup; $R_f$ 0.38 (4/1 hexane/acetone); [$\alpha$]$^{25}_{D}$ $^{+}$50.2º (c 1.55, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS) $\delta$ 7.97 (2H, dd, $J_{o,m} = 7.8$ Hz, $J_{o,p} = 1.5$ Hz, H$_o$ of Bz), 7.56 (1H, tt, $J_{m,p} = 7.8$ Hz, H$_m$ of Bz), 7.35-7.16 (5H, m, ArH of Bn), 6.29 (1H, d, $J_{1,2} = 3.0$ Hz, H-1), 6.26 (1H, d, $J_{2,3} = 10.2$ Hz, H-3), 5.83 (1H, ddd, $J_{2,3} = 10.2$ Hz, $J_{1,2} = 3.0$ Hz, $J_{2,4} = 1.8$ Hz, H-2), 4.70 & 4.55 (2H, ABq, $J = 11.7$ Hz, ArCH$_2$), 4.59 (1H, dd, $J_{6,6} = 12.3$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 4.51 (1H, dd, $J_{6,6} = 12.3$ Hz, $J_{5,6} = 4.2$ Hz, H-6), 4.17 (1H, dd, $J_{4,5} = 9.6$ Hz, $J_{2,4} = 1.8$ Hz, H-4), 4.12 (1H, ddd, $J_{4,5} = 9.6$ Hz, $J_{5,6} = 4.2$ Hz, $J_{5,6} = 2.1$ Hz, H-5), 2.08 (3H, s, OAc); Anal. Calcd for C$_{22}$H$_{22}$O$_{6}$: C, 69.10; H, 5.80. Found: C, 69.14; H, 5.90.

6-O-Benzoyl-4-O-benzyl-2,3-dideoxy-α-D-erythro-hexopyranosyl Acetate (18): A suspension of 30 (516 mg, 1.35 mmol) and 5% Rh/Al$_2$O$_3$ (129 mg) in THF (25.8 mL) was stirred under H$_2$
atmosphere (balloon). After the suspension was stirred at 0 ºC for 2 h, it was filtered through celite pad. The filtrate was concentrated in vacuo. Purification of the residue by silica-gel column chromatography (hexane/EtOAc = 3/1) gave 18 (482 mg, 93%). White needles; m.p. 56.0-58.5 ºC; Rf 0.38 (4/1 hexane/acetone); [α]26D +105.5º (c 1.21, CHCl3); 1H NMR (CDCl3, TMS) δ 7.99 ( 2H, dd, Jm,p = 7.5 Hz, Jp,m = 1.5 Hz, H of Bz), 7.56 (1H, tt, Jm,p = 7.5 Hz, Jp,m = 1.5 Hz, H of Bz), 7.42 (2H, dd, Jm,p = 7.5 Hz, H of Bz), 7.34-7.16 (5H, m, ArH of Bn), 6.13 (1H, br-dd, H-1), 4.66 & 4.48 (2H, ABq, J = 11.7 Hz, ArCH2), 4.56-4.54 (2H, m, H-6), 4.04 (1H, ddd, J4,5 = 9.6 Hz, J5,6 = 3.3 Hz, H-5), 3.58 (1H, ddd, J3,4 = J4,5 = 9.6 Hz, J3,4 = 5.4 Hz, H-4), 2.24-2.14 (1H, m, H-3), 2.10 (3H, s, OAc), 1.98-1.80 (3H, m, H-2 × 2 & H-3); Anal. Calcd for C22H24O6: C, 68.74; H, 6.29. Found: C, 68.54; H, 6.29.

**Synthesis of the glycosyl acceptor 20.**

![Synthesis of the glycosyl acceptor 20.](image)

6-O-Benzoyl-2,3-dideoxy-α-D-erythro-hexopyranosyl Acetate (20): A suspension of 18 (220 mg, 0.57 mmol) and 10% Pd/C (110 mg) in EtOAc (10 mL) was stirred under H2 atmosphere (balloon). After the suspension was stirred at 25 ºC for 3 days, it was filtered through celite pad. The filtrate was concentrated in vacuo. Purification of the residue by silica-gel column chromatography (hexane/EtOAc = 1/1) gave 20 (166.9 mg, 99%). Colorless syrup; Rf 0.25 (4/1 hexane/EtOAc); [α]26D +27.4º (c 1.16, CHCl3); 1H NMR (CDCl3, TMS) δ 8.09 ( 2H, dd, Jm,p = 7.5 Hz, Jp,m = 1.5 Hz, H of Bz), 7.60 (1H, tt, Jm,p = 7.5 Hz, Jp,m = 1.5 Hz, H of Bz), 7.47 (2H, dd, Jm,p = 7.5 Hz, H of Bz), 6.14 (1H, br-dd, H-1), 4.98 (1H, dd, J6,6 = 12.6 Hz, J5,6 = 3.0 Hz, H-6), 4.30 (1H, dd, J6,6 = 12.6 Hz, J5,6 = 2.4 Hz, H-6), 3.84 (1H, ddd, J4,5 = 9.6 Hz, J5,6 = 3.0 Hz, H-5), 3.55-3.43 (1H, m, H-4), 3.26 (1H, d, J4,OH = 4.5 Hz, OH), 2.32 (3H, s, OAc), 2.05-1.78 (4H, m, H-2 × 2 & H-3 × 2); Anal. Calcd for C15H18O6: C, 61.22; H, 6.16. Found: C, 60.91; H, 6.17.

**Synthesis of the glycosyl acceptor 23.**

![Synthesis of the glycosyl acceptor 23.](image)
2,3-Dideoxy-α-D-glycelo-hex-2-enopyranos-4-ulosyl Acetate (23): To a solution of p-methoxyphenyl 2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (5) (3.08 g, 13.1 mmol) in dry CH₂Cl₂ (60 mL) was added imidazole (1.87 g, 27.5 mmol) and tert-butyldiphenylsilyl chloride (3.40 mL, 13.1 mmol) at -40 ºC under Ar atmosphere. After the mixture was stirred at -40 ºC for 2.5 h, the mixture was poured into water (30mL), and extracted with EtOAc (30 mL × 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification of the residue by silica-gel column chromatography (0→33% EtOAc in hexane), gave p-methoxyphenyl 6-O-tert-butyldiphenylsilyl-α-D-erythro-hex-2-enopyranoside (SI-3) (6.00 g, 97%). Colorless syrup; Rf 0.24 (3/1 hexane/EtOAc); [α]D +67.8º (c 1.71, CHCl₃); 1H NMR (CDCl₃, TMS) δ 7.69-7.66 (4H, m, ArH of TBDPS), 7.44-7.36 (6H, m, ArH of TBDPS), 6.96 & 6.76 (4H, m, ArH), 6.08 (1H, br-d, J2,3 = 10.2 Hz, H-3), 5.90 (1H, ddd, J2,3 = 10.2 Hz, J1,2 = 2.1 Hz, H-2), 5.48 (1H, m, H-1), 4.34 (1H, m, H-5), 3.98-3.82 (3H, m, H-4 & H-6 × 2), 3.75 (3H, s, OMe), 2.40 (1H, d, J = 4.5 Hz, OH), 1.05 (9H, s, t-Bu); Anal. Calcd for C₂₉H₃₄O₅Si: C, 70.99; H, 6.98. Found: C, 70.89; H, 7.15. To a solution of SI-3 (2.40 g, 4.89 mmol) in dry CH₂Cl₂ (48.0 mL) was added pyridinium dichromate (9.20 g, 24.5 mmol) under Ar atmosphere. After the mixture was stirred at 25 ºC for 17 h, the mixture was filtered through celite pad. The filtrate was concentrated in vacuo, and purification of the residue by silica-gel column chromatography (0→25% EtOAc in hexane) gave p-methoxyphenyl 6-O-tert-butyldiphenylsilyl-2,3-dideoxy-β-D-glycelo-hex-2-enopyrano-s-4-uloside (SI-4) (1.85 g, 77%). Pale yellow syrup; Rf 0.36 (4/1 hexane/EtOAc); [α]D +47.5º (c 1.84, CHCl₃); 1H NMR (CDCl₃, TMS) δ 7.69-7.65 (4H, m, ArH of TBDPS), 7.42-7.35 (6H, m, ArH of TBDPS), 7.10 & 6.81 (4H, m, ArH), 7.03 (1H, dd, J2,3 = 10.5 Hz, J1,2 = 3.6 Hz, H-2), 6.25 (1H, d, J2,3 = 10.5 Hz, H-3), 5.86 (1H, d, J1,2 = 3.6 Hz, H-1), 4.65 (1H, dd, J5,6 = 5.1 Hz, J5,6 = 3.0 Hz, H-5), 4.14 (1H, dd, J6,6 = 11.4 Hz, J5,6 = 5.1 Hz, J6,6 = 3.0 Hz, H-6), 4.08 (1H, dd, J6,6 = 11.4 Hz, J5,6 = 3.0 Hz, H-6), 3.77 (3H, s, OMe), 1.01 (9H, s, t-Bu); Anal. Calcd for C₂₉H₃₂O₅Si: C, 71.28; H, 6.60. Found: C, 71.55; H, 6.81.
        To a solution of SI-4 (4.05 g, 8.60 mmol) in aq. acetonitrile (acetonitrile/water = 4/1, 20 mL) was added cerium (IV) ammonium nitrate (7.06 g, 12.9 mmol) at 0 ºC. After the mixture was stirred at 0 ºC for 30 min, the mixture was poured into water (200 mL), and extracted with EtOAc (200 mL × 3). After the combined organic layer was washed with brine (200 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. Purification of the residue by silica-gel column chromatography (20→50% EtOAc in hexane) gave 6-O-tert-butyldiphenylsilyl-2,3-dideoxy-α-D-glycelo-hex-2-enopyranos-4-uloside (SI-5) as a mixture of anomers (2.63 g, 80%, α:β = 72:28). Pale yellow syrup; Rf 0.17 (4/1 hexane/EtOAc); 1H NMR (CDCl₃, TMS), β isomer (SI-5β): δ 7.71-7.55 (4H, m, ArH of TBDPS), 7.47-7.35 (6H, m, ArH of TBDPS), 6.93 (1H, dd, J2,3 = 10.2 Hz, J1,2 = 3.0 Hz, H-2), 6.18 (1H, d, J2,3 = 10.2 Hz, H-3), 5.78 (1H, dd, J1,OH = 5.4 Hz, J1,2 = 3.0 Hz, H-1), 4.59 (1H, dd, J5,6 = 4.5 Hz, J5,6 = 2.4 Hz, H-5),
4.17-3.93 (2H, m, H-6 × 2), 3.00 (1H, d, \( J_{1,OH} = 5.4 \) Hz, OH), 1.01 (9H, s, t-Bu), \( \beta \) isomer (SI-5\( \beta \)): \( \delta \) 7.71-7.55 (4H, m, ArH of TBDPS), 7.47-7.35 (6H, m, ArH of TBDPS), 7.04 (1H, dd, \( J_{2,3} = 10.2 \) Hz, \( J_{1,2} = 3.3 \) Hz, H-2), 6.27 (1H, d, \( J_{2,3} = 10.2 \) Hz, H-3), 5.53 (1H, dd, \( J_{1,OH} = 11.7 \) Hz, \( J_{1,2} = 3.3 \) Hz, H-1), 5.24 (1H, \( J_{1,OH} = 11.7 \) Hz, OH), 4.34 (1H, dd, \( J_{5,6} = J_{5,6} = 2.1 \) Hz, H-5), 4.17-3.93 (2H, m, H-6 × 2), 1.01 (9H, s, t-Bu); Anal. Calcd for C\(_{22}\)H\(_{26}\)O\(_4\)Si: C, 69.08; H, 6.85. Found: C, 68.95; H, 6.99.

To a solution of SI-5 (2.81 g, 7.34 mmol) in dry CH\(_2\)Cl\(_2\) (56.1 mL) was added pyridine (1.31 mL, 16.1 mmol) and acetyl chloride (783 \( \mu \)L, 11.0 mmol) under Ar atmosphere and ice-bath cooling. After the mixture was stirred for 2.5 h at 25 °C, the mixture was poured into water (80 mL), and extracted with EtOAc (50 mL × 3). After the combined organic layer was washed with brine (80 mL), dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo. Purification of the residue by flash silica-gel column chromatography (hexane/EtOAc = 2/1) gave 6-O-\( \text{tert} \)-butyldiphenylsilyl-2,3-dideoxy-\( \alpha \)-D-glycelo-hex-2-enopyranos-4-ulosyl acetate (SI-6\( \alpha \)) (2.11 g, 68%) and 6-O-\( \text{tert} \)-butyldiphenylsilyl-2,3-dideoxy-\( \beta \)-D-glycelo-hex-2-enopyranos-4-ulosyl acetate (SI-6\( \beta \)) (0.82 g, 26%). \( \alpha \) isomer (SI-6\( \alpha \)): Pale yellow syrup; \( R_f \) 0.24 (4/1 hexane/EtOAc); [\( \alpha \]\(_D\)]\( ^{32} \) -59.6º (c 1.64, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS) \( \delta \) 7.71-7.65 (4H, m, ArH of TBDPS), 7.43-7.30 (6H, m, ArH of TBDPS), 6.94 (1H, dd, \( J_{2,3} = 10.2 \) Hz, \( J_{1,2} = 3.7 \) Hz, H-2), 6.65 (1H, d, \( J_{1,2} = 3.7 \) Hz, H-1), 6.29 (1H, d, \( J_{2,3} = 10.2 \) Hz, H-3), 4.53 (1H, dd, \( J_{5,6} = 4.1 \) Hz, \( J_{5,6} = 2.4 \) Hz, H-5), 4.16 (1H, dd, \( J_{6,6} = 11.0 \) Hz, \( J_{5,6} = 4.1 \) Hz, H-6), 4.03 (1H, dd, \( J_{6,6} = 11.0 \) Hz, \( J_{5,6} = 2.4 \) Hz, H-6), 2.12 (3H, s, OAc), 1.00 (9H, s, t-Bu); Anal. Calcd for C\(_{24}\)H\(_{28}\)O\(_5\)Si: C, 67.90; H, 6.65. Found: C, 67.87; H, 6.89.

\( \beta \) isomer (SI-6\( \beta \)): Pale yellow syrup; \( R_f \) 0.18 (4/1 hexane/EtOAc); [\( \alpha \]\(_D\)]\( ^{32} \) +59.9º (c 3.51, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS) \( \delta \) 7.69-7.63 (4H, m, ArH of TBDPS), 7.43-7.30 (6H, m, ArH of TBDPS), 6.81 (1H, dd, \( J_{2,3} = 10.5 \) Hz, \( J_{1,2} = 2.9 \) Hz, H-2), 6.60 (1H, d, \( J_{1,2} = 3.7 \) Hz, H-1), 6.09 (1H, dd, \( J_{2,3} = 10.5 \) Hz, \( J_{1,3} = 1.2 \) Hz, H-3), 4.38 (1H, dd, \( J_{5,6} = 5.9 \) Hz, \( J_{5,6} = 3.7 \) Hz, H-5), 4.09 (1H, dd, \( J_{6,6} = 11.0 \) Hz, \( J_{5,6} = 5.9 \) Hz, H-6), 4.00 (1H, dd, \( J_{6,6} = 11.0 \) Hz, \( J_{5,6} = 3.7 \) Hz, H-6), 1.99 (3H, s, OAc), 1.03 (9H, s, t-Bu); Anal. Calcd for C\(_{24}\)H\(_{28}\)O\(_5\)Si: C, 67.90; H, 6.65. Found: C, 67.93; H, 6.74. To a solution of SI-6\( \alpha \) (344 mg, 0.81 mmol) in dry THF (7.0 mL) were added acetic acid (280 \( \mu \)L, 4.86 mmol) and 1.0 M TBAF in THF (3.56 mL, 3.56 mmol) at -30 °C under Ar atmosphere. After the mixture was stirred in warming up to 0 °C for 18 h, it was poured into water (20 mL), and then extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo. Purification of the residue by flash silica-gel column chromatography (hexane/EtOAc = 1/1) gave 23 (99.9 mg, 66%). White needles; m. p. 93.7-94.3 °C; \( R_f \) 0.20 (1/1 hexane/EtOAc); [\( \alpha \]\(_D\)]\( ^{32} \) -139.7º (c 1.58, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS) \( \delta \) 6.94 (1H, dd, \( J_{2,3} = 10.3 \) Hz, \( J_{1,2} = 3.7 \) Hz, H-2), 6.57 (1H, d, \( J_{1,2} = 3.7 \) Hz, H-1), 6.27 (1H, d, \( J_{2,3} = 10.3 \) Hz, H-3), 4.55 (1H, dd, \( J_{5,6} = J_{5,6} = 4.4 \) Hz, H-5), 4.03-3.97 (2H, m, H-6 × 2), 2.15 (3H, s, OAc), 2.18-2.13 (1H, m, OH); Anal. Calcd for C\(_8\)H\(_{10}\)O\(_5\): C, 51.61; H, 5.41. Found: C, 51.70; H, 5.45.
$^1$H- and $^{13}$C-NMR spectrum charts
$^1$H NMR spectrum of 1

$^1$H NMR spectrum of 2
$^1$H NMR spectrum of $3\alpha$

$^1$H NMR spectrum of $3\beta$
$^1$H NMR spectrum of 6

$^1$H NMR spectrum of 7
$^1$H NMR spectrum of 8

$^1$H NMR spectrum of 9
$^1$H NMR spectrum of 11α

$^1$H NMR spectrum of 11β
$^1$H NMR spectrum of 12α

$^1$H NMR spectrum of 12β
$^{1}H$ NMR spectrum of 15$\alpha$

$^{1}H$ NMR spectrum of 15$\beta$
$^1$H NMR spectrum of $16\alpha$

$^1$H NMR spectrum of $16\beta$
$^1$H NMR spectrum of 17$\alpha$

$^1$H NMR spectrum of 17$\beta$
$^1$H NMR spectrum of 18

$^1$H NMR spectrum of 19α
$^1$H NMR spectrum of 19β

$^1$H NMR spectrum of 20
$^1$H NMR spectrum of 21α

$^1$H NMR spectrum of 21β
$^1$H NMR spectrum of 22$\alpha$

$^{13}$C NMR spectrum of 22$\alpha$
$^{1}H$ NMR spectrum of $22\beta$

$^{13}C$ NMR spectrum of $22\beta$
$^1$H NMR spectrum of 23

$^1$H NMR spectrum of 24α
\textsuperscript{1}H NMR spectrum of 24\textbeta

\textsuperscript{1}H NMR spectrum of 25\textalpha
$^{13}$C NMR spectrum of $25\alpha$

$^1$H NMR spectrum of $25\beta$
$^{13}$C NMR spectrum of $25\beta$

$^1$H NMR spectrum of $26\alpha$
$^1$H NMR spectrum of 26 ($\alpha:\beta = 19:81$)

$^1$H NMR spectrum of 27$\alpha$
$^{13}$C NMR spectrum of $27\alpha$

$^1$H NMR spectrum of $27\beta$
$^{13}$C NMR spectrum of $27\beta$

$^1$H NMR spectrum of $30$
$^1$H NMR spectrum of 31α

$^1$H NMR spectrum of 31β
$^1$H NMR spectrum of $32\alpha$

$^1$H NMR spectrum of $32\beta$
$^1$H NMR spectrum of 34

$^1$H NMR spectrum of 35
$^1$H NMR spectrum of 38

$^1$H NMR spectrum of SI-1
$^1$H NMR spectrum of SI-2

$^1$H NMR spectrum of SI-3
$^1$H NMR spectrum of SI-4

$^1$H NMR spectrum of SI-5
$^1$H NMR spectrum of SI-6\(\alpha\)

$^1$H NMR spectrum of SI-6\(\beta\)