Automated Synthesis of a Protected *N*-linked Glycoprotein Core Pentasaccharide

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Supplementary Material

General Methods. All chemicals used were reagent grade and used as supplied except where noted. Trimethylsilyl trifluoromethanesulfonate (TMSOTf) was purchased from Acros Chemicals. Dichloromethane (CH₂Cl₂), diethyl ether (Et₂O), and tetrahydrofuran (THF) were purchased from J.T. Baker (CycletainerTM) and passed through neutral alumina columns prior to use. Toluene was purchased from J.T. Baker (CycletainerTM) and passed through a neutral alumina column and a copper (II) oxide column prior to use. Pyridine and acetonitrile were refluxed over calcium hydride and distilled prior to use. Analytical thin-layer chromatography was performed on E. Merck silica column 60 F₂₅₄ plates (0.25 mm). Compounds were visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution followed by heating. Liquid column chromatography was performed using forced flow of the indicated solvent on Silicycle 230-400 mesh (60 Å pore diameter) silica gel. Optical rotation was recorded on a Perkin-Elmer 241 polarimeter using a sodium lamp (589 nm) at 24°C. IR spectra were obtained on a Perkin-Elmer System 2000 series FTIR spectrometer. ¹H NMR spectra were obtained on a Bruker (400 MHz) or a Varian VXR-500 (500 MHz) and are reported in parts per million (ppm) relative to CHCl₃ (7.27 ppm). Coupling constants (*J*) are reported in Hertz. ¹³C NMR

spectra were obtained on a Bruker (100 MHz) or a Varian VXR-500 (125 MHz) and are reported in δ relative to CDCl_3 (77.23 ppm) as an internal reference. High-resolution mass spectrometry was performed on a Bruker DALTONICS APEX II, 3 Tesla, FT-ICR-MS.

***tert*-Butyldimethylsilyl 3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- β -D-glucopyranoside 6.** Differentially protected glucosamine **5**¹¹ (5.5 g, 8.9 mmol) was dissolved in CH_2Cl_2 (60 mL) and cooled to 0°C. Triethylsilane (8.5 mL, 53.5 mmol) was added and the resulting mixture was stirred for 10 min. Trifluoromethanesulfonic acid (3.4 mL, 44.5 mmol) and trifluoromethanesulfonic acid anhydride (1.3 mL, 8.9 mmol) were added simultaneously to the cooled solution and the mixture was stirred at 0°C for 30 min. The solution was warmed slowly to room temperature over a period of 1 h. The reaction mixture was poured into a saturated aqueous solution of Na_2CO_3 . The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the organic layer was dried over NaSO_4 , filtered, and solvents removed *in vacuo*. Purification by flash silica column chromatography (10%–25% EtOAc/hexanes) afforded **6** as an oil (3.47 g, 63% yield). $[\alpha]_D^{24}$: -13.4° (*c* 1.8, CH_2Cl_2); IR (thin film) 2929, 2858, 1692, 1529, 1070, 838 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.27 (m, 10H), 6.99 (d, J = 8.1 Hz, 1H), 5.05 (d, J = 7.8 Hz, 1H), 4.83–4.76 (m, 2H), 4.64–4.57 (m, 2H), 3.95 (dd, J = 8.6, 10.5 Hz, 1H), 3.76–3.71 (m, 3H), 3.62–3.55 (m, 2H), 2.92 (s, 1H), 0.92 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 161.9, 138.2, 137.8, 128.7, 128.6, 128.2, 128.0, 128.0, 127.8, 94.9, 92.7, 79.8, 74.4, 74.0, 73.8, 73.3, 70.7, 60.1, 25.8, 18.0, -4.0, -5.0; ESI MS m/z (M^+ + Na^+) calcd 640.1426, found 640.1400.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- β -D-glucopyranosyl

trichloroacetimidate 2. A solution of **6** (1.06 g, 1.71 mmol) in CH₂Cl₂ (20 mL) was cooled to 0°C. Acetic anhydride (0.24 mL, 2.57 mmol) was added and the resulting solution was stirred for 5 min. Dimethylaminopyridine (314 mg, 2.57 mmol) was added and the reaction was allowed to warm slowly to room temperature while stirring overnight. The mixture was diluted with CH₂Cl₂ (30 mL) and the organic layer was washed with 5% HCl (2 x 30 mL). The organic layer was dried over Na₂SO₄, filtered, and solvents removed in vacuo to afford *tert*-butyldimethylsilyl 3,6-di-*O*-benzyl-2-deoxy-4-*O*-acetyl-2-trichloroacetimido- β -D-glucopyranoside (1.13 g, 99%). $[\alpha]_D^{24}$: +9.0° (*c* 1.7, CH₂Cl₂); IR (thin film) 3354, 1715, 1527, 1249, 1067 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.25 (m, 10H), 7.12 (d, *J* = 7.7 Hz, 1H), 5.20 (d, *J* = 7.8 Hz, 1H), 5.09 (q t, *J* = 9.4 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.54 (s, 2H), 4.29 (q t, *J* = 10.3 Hz, 3H), 3.71-3.69 (m, 1H), 3.58-3.52 (m, 1H), 1.89 (s, 3H), 0.92 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 169.9, 161.9, 138.0, 137.8, 128.6, 128.4, 128.0, 127.8, 127.8, 94.3, 92.7, 77.4, 74.1, 73.6, 73.4, 71.8, 69.8, 60.8, 25.8, 21.0, 18.0, -4.0, -5.1; ESI MS *m/z* (M⁺ + Na⁺) calcd 682.1532, found 682.1543.

A solution *tert*-butyldimethylsilyl 3,6-di-*O*-benzyl-2-deoxy-4-*O*-acetyl-2-trichloroacetimido- β -D-glucopyranoside (1.13 g, 1.71 mmol) in THF (18 mL) was cooled to 0°C. Acetic acid (0.15 mL, 2.68 mmol) and then tetrabutylammonium fluoride (1.0 M in THF, 2.68 mL, 2.68 mmol) were added to the cooled solution. The reaction mixture was allowed to warm slowly to room temperature while stirring overnight. The reaction mixture was diluted with EtOAc and washed with NaHCO₃ (2 x 30 mL) and H₂O (1 x 30

mL). The organic layer was dried over Na₂SO₄, filtered, and solvents removed *in vacuo*. The crude material (887 mg, 1.62 mmol) was dissolved in CH₂Cl₂ (16 mL) and trichloroacetonitrile (4 mL). After stirring for 5 min, DBU (49 μ L, 0.32 mmol) was added and the reaction mixture was allowed to stir for 1.5 h. The reaction mixture was passed through a silica plug, washed with EtOAc and solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded **2** (942 mg, 76% two steps, 95:5 $\square$: $\square$). IR (thin film) 1747, 1722, 1678, 1514, 1226, 1036 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) $\square$ 8.79 (s, 1H), 7.37-7.27 (m, 10H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 3.5 Hz, 1H), 5.41 ($\square$ t, *J* = 9.7 Hz, 1H), 4.70-4.64 (m, 2H), 4.57-4.45 (m, 3H), 4.10-4.02 (m, 2H), 3.63-3.55 (m, 2H), 1.97 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) $\square$ 169.3, 161.8, 159.9, 137.6, 137.0, 128.8, 128.4, 128.4, 128.3, 128.1, 127.8, 94.3, 92.1, 90.7, 76.0, 73.6, 73.0, 72.1, 69.9, 68.4, 53.5, 20.9; ESI MS *m/z* (M⁺ + Na⁺) calcd 710.9763, found 710.9762.

***tert*-Butyldimethylsilyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene- $\square$ -D-mannopyranosyl-(1 $\square$ 4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- $\square$ -D-**

glucopyranoside 8. Phenyl sulfoxide **7** (1.50 g, 2.56 mmol) and **6** (2.53 g, 4.09 mmol) were coevaporated separately (important!) with toluene (3 x 10 mL) and dried under vacuum overnight. Sulfoxide **7** was dissolved in CH₂Cl₂ (26 mL) and cooled to -78°C. Di-*t*-butyl pyridine (1.15 mL, 5.12 mmol) was added to the cooled solution and stirred for 10 min. Triflic anhydride (474 μ L, 2.82 mmol) was added and the mixture was stirred for 5 min, during which time the colorless mixture turned orange. A solution of **6** in CH₂Cl₂ (10 mL) was slowly added to the reaction mixture via cannula and the reaction was stirred at -78°C for 1 h. The reaction was quenched with saturated NaHCO₃ (20 mL)

and diluted with CH₂Cl₂ (30 mL). The organic layer was washed with NaHCO₃ (2 x 30 mL), dried over Na₂SO₄, filtered, and solvents removed *in vacuo*. Purification by flash silica column chromatography (100% toluene → 25% EtOAc/toluene) afforded *tert*-butyldimethylsilyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-β-D-glucopyranoside (1.77 g, 68%). $[\alpha]_D^{24}$: -25.7° (*c* 3.1, CH₂Cl₂); IR (thin film) 3322, 2861, 1691, 1531, 1089 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.18 (m, 22H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.87-6.85 (m, 2H), 5.54 (s, 1H), 5.19 (d, *J* = 7.7 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.85 (d, *J* = 2.6 Hz, 2H), 4.68-4.45 (m, 6H), 4.14-4.06 (m, 3H), 3.99 (t, *J* = 8.7 Hz, 1H), 3.80 (s, 3H), 3.79-3.77 (m, 1H), 3.68-3.39 (m, 6H), 3.16-3.15 (m, 1H), 2.37 (s, 1H), 0.90 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 161.8, 159.3, 138.7, 138.6, 138.0, 137.8, 130.7, 129.3, 129.2, 129.1, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 126.3, 125.5, 113.9, 101.9, 101.5, 94.4, 92.7, 78.8, 78.3, 78.0, 77.4, 77.3, 75.2, 75.1, 74.8, 73.8, 72.5, 68.9, 68.7, 67.6, 60.7, 55.5, 25.9, 18.1, -4.0, -4.9; ESI MS *m/z* (*M*⁺ + Na⁺) calcd 1100.3312, found 1100.3278.

To a stirring solution of *tert*-butyldimethylsilyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-β-D-glucopyranoside (1.0 g, 0.93 mmol) in CH₂Cl₂ (4.5 mL) and H₂O (0.5 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (252 mg, 1.11 mmol). After stirring for 45 min, the reaction mixture was diluted with CH₂Cl₂ (45 mL). The organic layer was washed with NaHCO₃ (2 x 25 mL), H₂O (1 x 25 mL), dried over Na₂SO₃, filtered and solvents removed *in vacuo*. Purification by flash silica column chromatography (20% EtOAc/hexanes) gave a white solid. The solid (743 mg, 0.77

mmol) was dissolved in CH₂Cl₂ (8 mL) and cooled to 0°C. Acetic anhydride (147 μ L, 1.55 mmol) was added and stirred for 5 min. Dimethylaminopyridine (114 mg, 0.93 mmol) was added and the stirring mixture was warmed slowly to room temperature over 2 h. The reaction was diluted with CH₂Cl₂ (15 mL) and washed with 5% HCl (2 x 15 mL), H₂O (1 x 15 mL), NaHCO₃ (2 x 15 mL). The organic layer was dried over Na₂SO₄, filtered, and solvents removed in vacuo. Purification by flash silica column chromatography (33% EtOAc/hexanes) afforded **8** (771 mg, 79% for two steps). [α]_D²⁴: -45.0° (*c* = 0.7, CH₂Cl₂); IR (thin film) 3339, 2858, 1738, 1691, 1092, 1068 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.28 (m, 20H), 6.99 (d, *J* = 7.5 Hz, 1H), 5.48 (s, 1H), 5.22 (d, *J* = 7.7 Hz, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 4.87-4.82 (m, 2H), 4.74-4.50 (m, 5H), 4.18-4.02 (m, 5H), 3.71 (dq, *J* = 2.3, 5.6 Hz, 2H), 3.57-3.52 (m, 2H), 3.41-3.38 (m, 1H), 3.23-3.22 (m, 1H), 1.99 (s, 3H), 0.92 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 170.6, 161.8, 138.7, 138.2, 137.9, 137.4, 129.3, 128.8, 128.5, 128.4, 128.4, 128.4, 128.2, 128.2, 128.0, 128.0, 127.8, 126.4, 101.9, 101.3, 94.4, 92.7, 78.1, 77.3, 76.5, 75.9, 75.7, 75.1, 74.8, 73.8, 72.6, 68.8, 68.6, 67.5, 60.8, 25.8, 21.22, 18.1, -4.0, -4.9; ESI MS *m/z* (*M*⁺ + Na⁺) calcd 1022.2843, found 1022.2807.

***tert*-Butyldimethylsilyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- β -D-glucopyranoside **9**.** To a solution of **8** (213 mg, 0.213 mmol) in CH₂Cl₂ (2 mL) were added freshly dried 4Å molecular sieves (750 mg). After stirring for 1h, the mixture was cooled to -78°C. Triethylsilane (102 μ L, 0.64 mmol) was added and the resulting solution was stirred for 5 min. Dichlorophenylborane (83 μ L, 0.64 mmol) was added and the mixture was stirred for 30 min at -78°C. The reaction was quenched with the addition of triethylamine (0.4 mL)

and methanol (0.4 mL) and diluted with CH₂Cl₂ (20 mL). The organic layer was washed with NaHCO₃ (2 x 20 mL), H₂O (1 x 20 mL), dried over Na₂SO₄, filtered, and solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded a white solid. The solid (170 mg, 0.17 mmol) was dissolved in CH₂Cl₂ (2 mL) and cooled to 0°C. Acetic anhydride (32 μ l, 0.34 mmol) was added and stirred for 5 min. Dimethylaminopyridine (25 mg, 0.20 mmol) was added and the stirring mixture was warmed slowly to room temperature over 2.5 h. The reaction mixture was then diluted with CH₂Cl₂ (15 mL) and washed with 5% HCl (2 x 15 mL), H₂O (1 x 15 mL), and NaHCO₃ (2 x 15 mL). The organic layer was dried over Na₂SO₄, filtered, and the solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded **9** (163 mg, 82% two steps). $[\alpha]_D^{24}$: -23.5° (*c* 1.0, CH₂Cl₂); IR (thin film) 3342, 2858, 1742, 1691, 1234, 1073 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.22 (m, 20H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.15-5.11 (m, 2H), 4.86-4.49 (m, 9H), 4.25-4.08 (m, 4H), 3.94 (d, *J* = 3.0 Hz, 1H), 3.85 (t, *J* = 9.7 Hz, 1H), 3.74 (dd, *J* = 2.7, 11.1 Hz, 1H), 3.66 (dd, *J* = 3.4, 11.1 Hz, 1H), 3.54-3.37 (m, 3H), 1.93 (s, 3H), 1.89 (s, 3H), 0.89 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 171.0, 170.4, 161.8, 139.0, 138.5, 138.0, 128.7, 128.7, 128.5, 128.4, 128.1, 128.1, 127.9, 127.9, 127.6, 100.8, 94.5, 92.7, 77.9, 77.7, 77.4, 76.2, 75.9, 75.1, 74.9, 74.3, 73.8, 73.6, 73.3, 68.9, 63.6, 60.4, 25.8, 21.2, 20.9, 18.1, -4.0 -4.9; ESI MS *m/z* (*M*⁺ + Na⁺) calcd 1066.3105, found 1066.3124.

3,6-Di-*O*-acetyl-2,4-di-*O*-benzyl- α -D-mannopyranosyl-(1 $\rightarrow$ 4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- α -D-glucopyranosyl trichloroacetimidate **4.** A solution of **9** (330 g, 0.31 mmol) in THF (3 mL) was cooled to 0°C. Acetic acid (27 μ L, 0.47

mmol) and then tetrabutylammonium fluoride (1.0 M in THF, 470 μ L, 0.47 mmol) were added to the cooled solution. The reaction mixture was allowed to warm slowly to room temperature while stirring for 3 h. The reaction mixture was diluted with EtOAc and washed with NaHCO₃ (2 x 10 mL) and H₂O (1 x 10 mL). The organic layer was then dried over Na₂SO₄, filtered, and solvents removed in vacuo. The crude material (294 mg, 0.31 mmol) was dissolved in CH₂Cl₂ (3 mL) and trichloroacetonitrile (0.3 mL) and cooled to 0°C. After stirring for 5 min, DBU (9.3 μ L, 0.062 mmol) was added and the reaction mixture was allowed to stir for 1.5 h. The reaction mixture was passed through a silica plug, washed with EtOAc and the solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded **4** (298 mg, 89%, 95:5 ν : ν). IR (thin film) 1739, 1513, 1234, 1076, 1028 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.71 (s, 1H), 7.43-7.26 (m, 20H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 11.9 Hz, 1H), 4.87 (d, *J* = 12.1 Hz, 1H), 4.77-4.66 (m, 6H), 4.59-4.50 (m, 2H), 4.30-4.22 (m, 4H), 3.95-3.86 (m, 4H), 3.70 (s, 2H), 3.38-3.35 (m, 1H), 1.97 (s, 3H), 1.91 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 170.9, 170.3, 162.0, 160.1, 138.4, 138.4, 137.9, 137.5, 128.8, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 100.6, 94.5, 92.1, 91.0, 76.7, 76.2, 75.8, 75.7, 75.0, 74.8, 73.9, 73.8, 73.7, 73.4, 73.1, 67.9, 63.1, 54.1, 21.1, 20.8; ESI MS *m/z* (*M*⁺ + Na⁺) calcd 1095.1336, found 1095.1343.

***n*-Pentenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl- β -D-mannopyranosyl-(1 $\rightarrow$ 3)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl- β -D-mannopyranosyl-(1 $\rightarrow$ 6)]-2,4-di-*O*-benzyl- β -D-mannopyranosyl-(1 $\rightarrow$ 4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido- β -D-**

glucopyranoside 1. Glycosylated resin from automated synthesis was dried *in vacuo* for 18 h over phosphorous pentoxide and transferred into a solid-phase round bottom flask with glass frit. The resin was swelled with 5 ml CH₂Cl₂, purged with an atmosphere of ethylene followed by the addition of 10 mol % Grubbs' catalyst (bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride. The reaction mixture was stirred for 24 h under an atmosphere of ethylene, an additional 10 mol% Grubbs' catalyst was added, and the reaction was allowed to stir an additional 24 h under an atmosphere of ethylene. Triethylamine (100 equiv.) and tris hydroxymethylphosphine (50 equiv.) were added, and the mixture stirred 2 h at room temperature. The reaction was diluted in CH₂Cl₂ and washed 3 times with water. The aqueous fractions were washed with additional CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered, and dried to yield a dark oil.

The crude product was analyzed by HPLC (Waters Nova-pak[®] silica column (3.9 x 150 mm) with EtOAc/hexanes as the mobile phase), monitoring at 260 nm. A portion of the crude product was purified by semi-preparative HPLC using a Waters prep Nova-pak[®] silica column (7.8 x 300 mm) with a gradient of EtOAc/hexanes. Semi-preparative HPLC yielded 3 mg of **1** that corresponded to **1** made by solution phase synthesis. IR (thin film) 2867, 1746, 1711, 1693, 1235, 1077 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.08 (m, 60H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 5.80-5.72 (m, 1H), 5.48-5.46 (m, 1H), 5.37-5.35 (m, 1H), 5.14-4.27 (m, 31H), 4.42-3.14 (m, 30H), 2.14-2.06 (m, 5H), 1.98 (s, 3H), 1.68-1.63 (m, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 170.3, 170.3, 161.9, 161.8, 138.9, 138.8, 138.7, 138.7, 138.6, 138.5, 138.5, 138.2, 138.2, 138.2, 138.0, 137.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3,

128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.3,
115.1, 101.5, 99.8, 99.7, 99.0, 97.8, 92.7, 81.2, 78.5, 78.2, 78.1, 77.5, 77.2, 77.0, 75.5,
75.3, 75.2, 75.0, 75.0, 74.9, 74.5, 74.5, 74.4, 74.3, 74.2, 73.6, 73.5, 73.5, 72.5, 72.0, 71.7,
71.6, 71.5, 69.4, 69.2, 68.8, 68.6, 68.5, 66.7, 58.2, 57.4, 30.2, 29.9, 28.9, 28.9, 21.3, 21.2,
21.2; ESI MS m/z ($M^+ + Na^+$) calcd 2369.7303, found 2369.7401.

6

Current Data Parameters

NAME ERS-III-238z
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

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Time 20.14
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PROBHD 5mm BB0 BB-1
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TD 40062
SOLVENT CDCl3
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RG 32
DW 124.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

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PL1 0.00 dB
SFO1 400.1318006 MHz

F2 - Processing parameters

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SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 9.493 ppm
F1 3798.43 Hz
F2P -0.520 ppm
F2 -207.98 Hz
PPMCM 0.50064 ppm/cm
HZCM 200.32053 Hz/cm

6

Current Data Parameters

NAME ERS-III-239C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

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DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 14596.5
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.0300000 sec
d12 0.0000200 sec

===== CHANNEL f1 =====

VUC1 13C
P1 15.25 usec
PL1 3.00 dB
SF01 100.6237959 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
VUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz

F2 - Processing parameters

SF 32768
SF 100.6127614 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
F1P 234.536 ppm
F1 23597.30 Hz
F2P -15.190 ppm
F2 -1528.33 Hz
PPMCM 12.48630 ppm/cm
HZCM 1256.28137 Hz/cm

Current Data Parameters

NAME ERS-IV-02723
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030120
Time 20.56
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PULPROG zg30
TD 40062
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.100005 Hz
AQ 4.9997878 sec
RG 50.8
DW 124.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1318006 MHz

F2 - Processing parameters

SI 32768
SF 400.1300056 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 9.492 ppm
F1 3798.19 Hz
F2P -0.520 ppm
F2 -206.23 Hz
PPMCM 0.50064 ppm/cm
HZCM 200.32053 Hz/cm

Current Data Parameters
NAME ERS-IV-027C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030119
Time 19.24
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 1024
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 2048
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SF01 100.6237959 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 234.459 ppm
F1 23589.62 Hz
F2P -15.267 ppm
F2 -1536.01 Hz
FPMCM 12.48630 ppm/cm
FZCM 1256.28137 Hz/cm

Current Data Parameters
 NAME ERS-III-242dry
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20021028
 Time 16.02
 INSTRUM spect
 PROBHD 5mm BB0 BB-1
 PULPROG zg30
 TD 40062
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 4006.410 Hz
 FIDRES 0.100005 Hz
 AQ 4.9997878 sec
 RG 80.6
 DW 124.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.90 usec
 PL1 0.00 dB
 SFG1 400.1318006 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300060 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 9.491 ppm
 F1 3797.82 Hz
 F2P -0.521 ppm
 F2 -208.59 Hz
 PPMCM 0.50064 ppm/cm
 HZCM 200.32053 Hz/cm

Current Data Parameters
NAME ERS-111-242c13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021028
Time 16.48
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
VS 655
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SF01 100.6237959 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127530 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 234.620 ppm
F1 23605.72 Hz
F2P -15.106 ppm
F2 -1519.90 Hz
PPMCM 12.48630 ppm/cm
HZCM 1256.28137 Hz/cm

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Current Data Parameters

NAME ERS-III-166
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20020903
Time 21.38
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zg30
TD 40062
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.100005 Hz
AQ 4.9997878 sec
RG 143.7
DW 124.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

VOC1 1H
P1 7.90 usec
PL1 0.00 dB
SFO1 400.1318006 MHz

F2 - Processing parameters

SI 32768
SF 400.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 9.492 ppm
F1 3798.06 Hz
F2P -0.521 ppm
F2 -208.35 Hz
FPMCM 0.50064 ppm/cm
HZCM 200.32053 Hz/cm

Current Data Parameters
NAME ERS-III-168c13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020904
Time 2.15
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 6502
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SF01 100.6237959 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127492 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 234.658 ppm
F1 23609.56 Hz
F2P -15.068 ppm
F2 -1516.07 Hz
PPMCM 12.48630 ppm/cm
HZCM 1256.28137 Hz/cm

1D NMR plot parameters	
CX	20.00 cm
F1P	9.493 ppm
F1	3798.31 Hz
F2P	-0.520 ppm
F2	-208.10 Hz
PPMCM	0.50064 ppm/cm
HZCM	200.32053 Hz/cm

Current Data Parameters
NAME ERS-III-176C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030122
Time 14.43
INSTRUM spect
PROBHD 5mm BBO BB-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
VS 11498
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4096
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 15.25 usec
PL1 3.00 dB
SFO1 100.6237959 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 107.50 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127607 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 234.543 ppm
F1 23598.06 Hz
F2P -15.183 ppm
F2 -1527.57 Hz
PRMCM 12.48630 ppm/cm
F2CM 1256.28137 Hz/cm