A Tuneable Method for *N*-Debenzylation of Benzylaminoalcohols

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Supporting Information

Experimental

General Experimental

Dichloromethane and THF were distilled under N₂ from CaH₂ and Na/benzophenone respectively immediately prior to use. Methyl 2,2-*N,N*-dibenzylamino-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **1** was prepared as described in the literature.¹ All other chemicals were used as received from Sigma-Aldrich, Lancaster or Fluka. Thin layer chromatography was carried out on aluminium sheets coated with silica gel 60F254. Plates were developed using 10% phosphomolybdic acid in ethanol. Flash chromatography was performed using silica gel (Whatman, 60A, 230-400 mesh). Melting points were determined using an Electrothermal IA9000 series Gallenkamp melting point apparatus and are uncorrected. Optical rotations were measured on a Jasco P-1020 polarimeter with a path length of 1 dm. Concentrations are given in g/100 ml (10⁻¹ g⁻¹ cm²). IR spectra were recorded on a Perkin Elmer Series 1600 Fourier Transform spectrometer. ¹H- and ¹³C-NMR spectra were recorded on Varian Mercury 200, Varian Mercury 400 or Varian Inova-500 NMR spectrometers at the frequencies indicated. Where necessary, NMR assignments were made using COSY or HSQC experiments. All chemical shifts were referenced to residual solvent as an internal standard. Low and high resolution ESMS were acquired using a Micromass LCT mass spectrometer. High resolution ESMS was also performed by the EPSRC Mass

Spectrometry Service at Swansea, UK. Microanalyses were performed by the microanalysis service at Durham University Chemistry Department. Solvents were removed *in vacuo*.

EPR Experiments

EPR spectra were recorded using a Bruker EMX digital X-band (9.4 GHz) spectrometer equipped with Bruker ER 4121VT temperature controller within the temperature range $190 (\pm 0.1) \text{ K} \leq T \leq 320 (\pm 0.1) \text{ K}$. Solutions were placed into 5mm Wilmad quartz tubes which are EPR silent within the region of interest. All spectra were recorded at non-saturating microwave power of 2 mW and 100 kHz magnetic field modulation of 0.5 mT. *G*-factors were precisely determined by reference to DPPH ($g = 2.0036 \pm 0.0003$). Spectra processing (digital filtering, differentiation, numerical integration, etc.) was performed using Bruker WIN-EPR Software. Spectra simulation was conducted using Bruker SimFonia. The reaction mixture of **7** was analyzed with four scans of 512 points with a time constant and conversion time of 163.84 milliseconds. The sample temperature was 20° C.

Reactions of methyl 2,2-*N,N*-dibenzylamino-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **1** with NIS (10 eq)

a) The glucosamine derivative **1** (0.05 g, 0.108 mmol), NIS (0.24 g, 1.08 mmol) and activated powdered 4Å molecular sieves (0.15 g) were stirred in dichloromethane (3 ml) under argon at room temperature for 24 h. The mixture was then diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (2x15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.056 g crude product,

which was chromatographed on silica gel. Elution with hexane/ethyl acetate 7:3, methyl (2-*N*-benzoyl-2-*N*-benzyl)amino-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **6** (0.030 g, 58%) as a pale brown crystalline solid, m.p. 102-105 °C. $[\alpha]_D^{25.6} +35.8$ ($c = 1$, CHCl_3); IR (KBr disc) 3419 (OH), 3061, 3030 (Ar C-H), 2929, 2863, 2838 (C-H), 1955 (w, Ar C=C), 1636 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, d_6 -DMSO, COSY): $\delta = 7.54\text{--}7.10$ (m, 15H_{arom}), 5.83 (d, 1H, $J_{\text{OH},\text{H-3}} = 4.9$ Hz, OH), 5.55 (s, 1H, *CHPh*), 4.96 (d, 1H, $J_{\text{H-1},\text{H-2}} = 3.2$ Hz, H-1), 4.87 (d, 1H, *CHHPh*, $J = 15.5$ Hz), 4.47 (d, 1H, *CHHPh*, $J = 15.5$ Hz), 4.08 (m, 1H, H-6'), 4.03 (dt, 1H, $J_{\text{H-3},\text{OH}} = 4.9$ Hz, $J_{\text{H-3},\text{H-4}} = 9.2$ Hz, H-3), 3.77 (dd, 1H, $J_{\text{H-2},\text{H-1}} = 3.3$ Hz, $J_{\text{H-2},\text{H-3}} = 10.2$ Hz, H-2), 3.67- 3.58 (m, 2H, H-5, H-6), 3.26 (t, 1H, $J_{\text{H-4},\text{H-5}}$, $J_{\text{H-4},\text{H-3}} = 8.8$ Hz, H-4), 2.98 (s, 3H, OCH_3); $^{13}\text{C-NMR}$ (125 MHz, d_6 -DMSO, HSQC): $\delta = 173.69$ (C=O), 140.46, 138.36, 137.75, 130.08, 129.60, 129.26, 128.74, 128.60, 127.56, 127.07, 126.74 and 126.47 (C_{arom}), 101.41 (*CHPh*), 100.60 (C-1), 82.75 (C-4), 68.38 (C-6), 66.06 (C-3), 63.94 (C-2), 63.19 (C-5), 55.32 (OCH_3), 46.49 (CH_2Ph); ES-MS: m/z (%) = 973 (100) $[\text{2M}+\text{Na}]^+$, 541 (20), 498 (55) $[\text{M}+\text{Na}]^+$; HRMS: m/z calcd. for $\text{C}_{28}\text{H}_{30}\text{NO}_6^+ [\text{M} + \text{H}]^+$: 476.2073; found: 476.2074.

Elution with hexane/EtOAc, 3:1 and then 2:3 gave methyl 2-amino-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **5** (0.014 g, 33%) as a white solid, dec. 190 °C without melting. $[\alpha]_D^{24.5} +28.8$ ($c = 1$, CHCl_3); IR (KBr disc) 3393, 3274 (NH_2), 3035 (ArC-H), 2979, 2916, 2867, 2835 (C-H), 1719 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , COSY): $\delta = 8.01$ (m, 2H, *o*- $\text{C}_6\text{H}_5\text{CO}$), 7.5 (m, 1H, *p*- $\text{C}_6\text{H}_5\text{CO}$), 7.41-7.30 and 7.25-7.19 (m, 7H_{arom}), 5.45 (t, 1H, $J_{\text{H2-H3}}$, $J_{\text{H3-H4}} = 9.9$ Hz, H-3), 5.45 (s, 1H, *CHPh*), 4.75 (d, 1H, $J_{\text{H1-H2}} = 3.5$ Hz, H-1), 4.26 (dd, 1H, $J_{\text{H5-H6}} = 4.7$ Hz, $J_{\text{H6-H6'}} = 10.5$ Hz, H-6), 3.91 (dt, 1H, $J_{\text{H5-H6}}$, $J_{\text{H5-H6'}} = 4.7$ Hz, $J_{\text{H5-H4}} = 10.2$ Hz, H-5), 3.74 (t, 1H, $J_{\text{H6-H6'}}$, $J_{\text{H6-H5}} = 10.7$ Hz, H-6'), 3.66 (t, 1H, $J_{\text{H4-H5}}$, $J_{\text{H3-H4}} = 9.9$ Hz, H-4), 3.39 (s, 3H, OCH_3), 3.02 (dd, 1H, $J_{\text{H1-H2}} = 3.5$ Hz, $J_{\text{H2-H3}} = 9.9$ Hz, H-2), 1.37 (bs, 2H, NH_2 , disappears with D_2O); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , HSQC): $\delta = 166.29$ (C=O), 137.08, 133.15, 129.89, 129.80, 128.88, 128.38, 128.13 and 126.08 (C_{arom}),

101.38 (C-1 and CHPh), 79.73 (C-4), 74.25 (C-3), 69.09 (C-6), 62.90 (C-5), 55.73 (C-2), 55.43 (OCH₃); ES-MS: m/z (%) = 408 (85) [M+Na]⁺, 386 (100) [M+H]⁺; HRMS: m/z calcd. for C₂₁H₂₃NO₆H⁺ [M + H]⁺: 386.1603; found 386.1601.

b) The glucosamine derivative **1** (0.050 g, 0.108 mmol) and NIS (0.24 g, 1.08 mmol) were stirred with dichloromethane (3 ml) under argon at room temperature for 1 week. After 5 min TLC (hexane/ethyl acetate 7:3) indicated the presence of unreacted **1** and formation of **2**. After 20 min TLC (hexane/ethyl acetate 7:3) showed complete reaction of starting material, a trace of **3**, a trace of **2** and formation of **6**. After 3 h and after 3 days TLC (hexane/ethyl acetate 7:3) showed only **6** and baseline material. TLC (ethyl acetate/hexane 8:2) also showed **6**, but formation of **5** was difficult to detect because it was obscured by another spot with the same R_f due to succinimide. After 1 week the reaction mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.048 g crude product. TLC of the crude product (ethyl acetate/hexane 8:2) showed only **6**. The crude product was chromatographed on silica gel using hexane/ethyl acetate 7:3, then dichloromethane/methanol 9:1 to give **6** (0.026 g, 50%). The methanol/dichloromethane wash gave 0.013 g unidentifiable material.

c) The glucosamine derivative **1** (0.05 g, 0.108 mmol) and NIS (0.24 g, 1.08 mmol) were stirred with dichloromethane (3 ml) under argon at room temperature for 2 h. The mixture became dark maroon. Water (2 µl, 0.112 mmol) was then added. The reaction mixture was then stirred for a further 16 h. It was then diluted with dichloromethane (15 ml) and shaken with conc. aq. sodium thiosulfate (15 ml). 880 Ammonia was added and the mixture shaken again. The organic phase was separated and the aqueous phase re-extracted with dichloromethane (2x15 ml). The organic extracts were combined and dried (MgSO₄). Evaporation gave 0.056 g crude product, which was chromatographed on silica gel. Elution

with hexane/ethyl acetate 7:3 gave **6** (0.030 g, 39%). Elution with hexane/ethyl acetate 2:8 then ethyl acetate gave a mixture of **5** and NIS (0.032g). This mixture was dissolved in dichloromethane (15 ml) and the solution washed with satd. sodium bicarbonate (15 ml), and dried (MgSO₄). Evaporation gave pure **5** (0.021 g, 52%).

d) The glucosamine derivative **1** (0.037 g, 0.08 mmol) and NIS (0.18 g, 0.8 mmol) were placed under argon together with 4 Å molecular sieves (0.15 g). Dichloromethane (3 ml) was added, followed by 2,6-lutidine (9.5 µl, 0.08 mmol) (distilled from CaH₂). The mixture was stirred for 1 h at room temperature and became dark maroon. It was cooled to 0 °C and TESOTf (8.7 µl, 0.04 mmol) added. The mixture was allowed to warm to room temperature and was stirred for 4 h. The reaction mixture was diluted with dichloromethane (10 ml) and washed with aq. sodium thiosulfate (2x15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave a brown oil, which was purified by flash chromatography on silica gel using hexane/ethyl acetate 8:2, hexane/ethyl acetate 7:3, hexane/ethyl acetate 6:4, hexane/ethyl acetate 1:1, and finally ethyl acetate to give **5** (0.022 g, 68%)

Reaction of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside 1 with NIS (2 equiv)

a) The glucosamine derivative **1** (0.05 g, 0.108 mmol), NIS (0.048 g, 0.216 mmol) and activated powdered 4 Å molecular sieves (0.15 g) were stirred with dry dichloromethane (3 ml) under argon at room temperature for 20 h. The mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (2x15 ml), satd. aq. sodium

bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.056 g crude product, which was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2, then hexane/ethyl acetate 5.5:4.5 gave 0.002 g (4%) unreacted glucosamine derivative **1** and then methyl 2-*N*-benzylamino-3-benzoyl-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **3** (0.019 g, 37%) as an oil which slowly solidified to an off-white solid, m.p. 96-98 °C. $[\alpha]_D^{24.7}$ -16.6 (c = 1, CHCl₃); IR (film) 3350 (N-H), 3062, 3027 (Ar C-H), 2911, 2860, 2838 (C-H), 1957 (w, Ar C=C), 1721 (C=O) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃): δ = 8.00 (m, 2H, *o*-C₆H₅CO), 7.49 (m, 1H, *p*-C₆H₅CO), 7.38 (m, 2H, *m*-C₆H₅CO), 7.35 -7.30, 7.23-7.18 and 7.14-7.08 (m, 10H_{arom}), 5.52 (t, J_{H-3,H-2}, J_{H-3,H-4} = 9.9 Hz, 1H, H-3), 5.40 (s, 1H, CHPh), 4.71 (d, 1H, J_{H-1,H-2} = 3.5 Hz, 1H, H-1), 4.22 (dd, 1H, J_{H-6,H-5} = 4.7 Hz, J_{H-6,H-6'} = 10.3 Hz, 1H, H-6), 3.84 (dt, J_{H-5,H-6} = 5.3 Hz, J_{H-5,H-6'} = 9.9 Hz, 1H, H-5), 3.77 (d, 1H, J = 14.0 Hz, N(CHHPh)), 3.71 (d, 1H, J = 13.9 Hz, N(CHHPh)), 3.67 (t, J_{H-6',H-5}, J_{H-6,H-6'} = 10.1 Hz, 1H, H-6), 3.62 (t, J_{H-3,H-4}, J_{H-4,H-5} = 9.5 Hz, 1H, H-4), 3.34 (s, 3H, OCH₃), 2.87 (dd, 1H, J_{H-1,H-2} = 3.5 Hz, J_{H-2,H-3} = 10.1 Hz, 1H, H-2), 1.81 (bs, 1H, NH); ¹³C-NMR (125 MHz, CDCl₃) δ : 166.29 (C=O), 140.26, 137.10, 132.85, 130.33, 129.84, 128.85, 128.23, 128.20, 128.09, 127.95, 126.87 and 126.11 (C_{arom}), 101.36 (CHPh), 99.29 (C-1), 79.90 (C-4), 71.91 (C-3), 69.04 (C-6), 62.58 (C-5), 60.00 (C-2), 55.33 (OCH₃), 51.02 (CH₂Ph); ES-MS: m/z (%) = 973 (70) [2M+Na]⁺, 498 (100) [M+Na]⁺; HRMS: m/z calcd. for C₂₈H₃₀NO₆ [M + H]⁺: 476.2073; found: 476.2072.

Elution with hexane:EtOAc, 5.5:4.5 gave methyl 2-*N*-benzyl-amino-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **2** (0.024 g, 59%) ¹H-NMR (200 MHz, CDCl₃) δ : 2.32 (br s, 1H, OH), 2.62 (dd, 1H, H-2, J_{H-2,H-1} = 3.4 Hz, J = 10.0 Hz), 3.26 (s, 3H, OCH₃), 3.41-3.51 (m, 1H), 3.58-3.83 (m, 5H), 4.17 (dd, 1H, J = 2.7 Hz, J = 8.0 Hz), 4.55 (d, 1H, H-1, J_{H-1,H-2} = 3.5 Hz), 5.46 (s, 1H, PhCHO₂), 7.13-7.49 (m, 10H, Ph). It was identified by comparison with a

sample prepared previously.¹ m/z (ES) 765(2M+Na⁺, 100), 541 (15), 426 (50), 394 (M+Na⁺, 100).

b) The reaction procedure described in a) was repeated with a reaction time of 1 week instead of 20 h. The crude product (0.043 g) was chromatographed on silica gel. Elution on hexane/ethyl acetate 8:2 gave **3** (0.001 g, 2%) then hexane/ethyl acetate 5.5:4.5 gave **2** (0.028 g, 54%).

c) The glucosamine derivative **1** (0.05 g, 0.108 mmol), NIS (0.048 g, 0.216 mmol), TEMPO (0.017 g, 0.108 mmol) and activated powdered 4 Å molecular sieves (0.15 g) were placed under argon. Dry dichloromethane (2.5 ml) was added. The reaction mixture instantly turned dark maroon. After 8 min TLC showed complete disappearance of starting material. After 15 min the reaction mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (15 ml) and satd. aq. sodium bicarbonate (15 ml) and dried (MgSO₄). Evaporation gave 0.054 g crude product which was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2 gave **3** (0.004 g, 7%), then hexane/ethyl acetate 1:1 gave **2** (0.019 g, 47%).

*Reaction of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **1** with NIS (1 equivalent)*

The glucosamine derivative **1** (0.05 g, 0.108 mmol), NIS (0.024 g, 0.108 mmol) and activated powdered 4Å molecular sieves (0.15 g) were stirred with dry dichloromethane (1.5 ml) under argon at room temperature for 4 days. The mixture was diluted with dichloromethane (15 ml)

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and washed with aq. sodium thiosulfate (2 x15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.056 g crude product, which was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2 gave 0.025 g (50%) unreacted glucosamine derivative **1**, then hexane/ethyl acetate 1:1 gave **2** (0.020 g, 50%).

*Reactions of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **1** with NIS (3 equiv)*

a) The glucosamine derivative **1** (0.05 g, 0.108 mmol), NIS (0.072 g, 0.324 mmol) and activated powdered 4 Å molecular sieves (0.15 g) were stirred with dry dichloromethane (3 ml) under argon at room temperature for 4 h. TLC then showed complete disappearance of the glucosamine derivative **1**. The reaction mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (2x15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.057 g crude product, which was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2 gave **3** (0.026 g, 50%) then hexane/ethyl acetate 1:1 gave **2** (0.020 g, 50%).

b) The glucosamine derivative **1** (0.05 g, 0.108 mmol), NIS (0.072 g, 0.324 mmol) and activated powdered molecular sieves (0.15 g) were placed under argon. Dry dichloromethane (3 ml) was added. The reaction was monitored by TLC (hexane/ethyl acetate 7:3). After 5 min TLC showed the presence of unreacted **1** and **2**. After 20 min and 45 min TLC showed **1**, **3**, **2**, and **6**. After 1.5 h, 2.5 h and 20 h TLC showed **3**, **2**, and **6**. After 20 h the reaction

mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO_4). Evaporation gave 0.040 g crude product, which was chromatographed on silica gel. Elution hexane/ethyl acetate 8:2, gave **3** (0.022 g, 42%) then hexane/ethyl acetate 7:3 gave **6** (0.004 g, 7%) and **2** (0.009 g, 22%).

*Reaction of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **1** with iodine*

The glucosamine derivative **1** (0.05 g, 0.108 mmol) and iodine (0.027 g, 1.08 mmol) were stirred with dichloromethane (3 ml) under argon at room temperature. After 4 h TLC (hexane/ethyl acetate 8:2) showed largely unreacted starting material **1** with a hint of product on the baseline so a further portion of iodine (0.027 g, 1.08 mmol) was added. After 15 h the TLC was little changed so TTBP (0.025 g, 0.108 mmol) was added. After a further 15 h TLC was still little changed so a further portion of iodine (0.027 g, 1.08 mmol) was added. After a further 24 h TLC was still little changed so the mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (2x15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO_4). Evaporation gave 0.055 g crude product. This was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2 gave unreacted **1** (0.010 g, 20%). Elution with hexane/ethyl acetate 1:1 gave **2** (0.022 g, 54%).

*Preparation of methyl 2,2-N,N-dibenzylamino-3-tert-butyldimethylsilyloxy-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **7***

The glucosamine **1** (0.2 g, 0.432 mmol) was placed under argon. Dry dichloromethane (4 ml) was added, followed by dry pyridine (272 μ l, 3.46 mmol). *tert*-Butyldimethylsilyl triflate (0.58 ml, 2.58 mmol) was added. The reaction mixture was stirred at room temperature for 20 h. A white crystalline precipitate gradually formed. At the end of this time TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material. The reaction mixture was diluted with dichloromethane (20 ml) and washed with water (2x20 ml), brine (20 ml) and dried (MgSO_4). Evaporation gave an oil which was chromatographed on silica gel using hexane/ethyl acetate 95:5 gave methyl 2,2-*N,N*-dibenzylamino-3-*tert*-butyldimethylsilyloxy-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **7** (0.245, 98%) as an oil which gradually solidified to form colourless crystals, m.p. 63-66 $^{\circ}\text{C}$. $[\alpha]_{\text{D}}^{26.1} +13.5$ ($c = 1$, CHCl_3); IR (nujol) 3084, 3062, 3025 (Ar C-H), 2924 (C-H) cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.51$ -7.20 (m, 15H_{arom}), 5.41 (s, 1H, CHPh), 4.52 (dd, 1H, $J_{\text{H-3,H-4}} = 8.8$ Hz, $J_{\text{H-3,H-2}} = 10.2$ Hz, H-3), 4.51 (d, 1H, $J_{\text{H-1,H-2}} = 3.5$ Hz, H-1), 4.19 (dd, 1H, $J_{\text{H-6,H-5}} = 4.8$ Hz, $J_{\text{H-6,H-6'}} = 10.2$ Hz, H-6), 4.17 (m, 2H, CH_2Ph), 3.97 (d, 2H, $J = 13.3$ Hz, CHHPh), 3.81 (m, 1H, H-5), 3.65 (t, 1H, $J_{\text{H-6',H-6}} \text{ and } \text{H-6',H-5}} = 10.3$ Hz, H-6'), 3.44 (s, 3H, OCH_3), 3.38 (t, 1H, $J_{\text{H-4,H-3}} \text{ and } \text{H-4,H-5}} = 9.1$ Hz, H-4), 2.89 (dd, 1H, $J_{\text{H-2,H-1}} = 3.5$ Hz, $J = 10.1$ Hz, H-2), 0.97 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.21 and 0.00 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): $\delta = 141.23$, 137.28, 129.17, 128.71, 128.18, 128.13, 126.69 and 126.60 (C_{arom}), 104.27 (C-1), 102.43 (CHPh), 83.80 (C-4), 71.19 (C-3), 69.26 (C-6), 62.20 (C-5), 61.81 (C-2), 55.44 (OCH_3), 55.30 (NCH_2Ph), 26.32 ($(\text{CH}_3)_3\text{C}$), 18.63 ($(\text{CH}_3)_3\text{C}$), -3.43 and -4.04 ($(\text{CH}_3)_2\text{Si}$); ES-MS: m/z (%) = 576.4 (100) $[\text{M} + \text{H}]^+$; HRMS: m/z calcd. for $\text{C}_{34}\text{H}_{46}\text{NO}_5\text{Si}$ $[\text{M} + \text{H}]^+$: 576.3145; found 576.3189

Reaction of methyl 2,2-N,N-dibenzylamino-3-tert-butyldimethylsilyloxy-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside 7 with NIS (3 equivalents)

a) NIS (0.035 g, 0.156 mmol) and activated powdered 4Å molecular sieves (0.15 g) were placed under argon. A solution of the silylated glucosamine derivative **7** (0.030 g, 0.052 mmol) in dichloromethane (3 ml) was added. The reaction mixture was stirred at room temperature and gradually became dark maroon. After 3.5 h TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material. The reaction mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.038 g crude product. This was chromatographed on silica gel using hexane/ethyl acetate 8.5:1.5 giving methyl 2-*N*-benzylamino-3-*tert*-butyldimethylsilyloxy-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **8** (0.022 g, 87%) as an off-white solid m.p. 92.5-93 °C. $[\alpha]_{\text{D}}^{25.5} = +32.5$ ($c = 1$, CHCl₃); IR (nujol) 3341(N-H), 3067 (Ar C-H), 2922 (C-H) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃): $\delta = 7.52\text{--}7.48$ and $7.40\text{--}7.26$ (m, 10H_{arom}), 5.50 (s, 1H, CHPh), 4.66 (d, 1H, $J_{\text{H-1,H-2}} = 3.5$ Hz, 1H, H-1), 4.25 (dd, 1H, $J_{\text{H-6,H-5}} = 4.6$ Hz, $J_{\text{H-6,H-6'}} = 9.9$ Hz, 1H, H-6), 3.95 (t, 1H, $J_{\text{H-3,H-2}}$ and $J_{\text{H-3,H-4}} = 9.2$ Hz, 1H, H-3), 3.91 (d, 1H, $J = 13.5$ Hz, 1H, CHHPh), 3.86 (d, 1H, $J = 13.5$ Hz, 1H, CHHPh), 3.81 (m, 1H, H-5), 3.72 (t, 1H, $J_{\text{H-6',H-6}}$ and $J_{\text{H-6',H-5}} = 10.2$ Hz, 1H, H-6'), 3.46 (t, $J_{\text{H-4,H-3}}$ and $J_{\text{H-4,H-5}} = 9.1$ Hz, 1H, H-4), 3.39 (s, 3H, OCH₃), 2.78 (dd, 1H, $J_{\text{H-2,H-1}} = 3.5$ Hz, $J_{\text{H-2,H-3}} = 9.5$ Hz, H-2), 2.00 (bs, 1H, NH), 0.87 (s, 9H, (CH₃)₃CSi), 0.00 and 0.11 (2xs, 6H, (CH₃)₂Si); ¹³C-NMR (125 MHz, CDCl₃): $\delta = 140.24$, 137.34, 128.96, 128.41, 128.10, 128.09, 127.00 and 126.31 (C_{arom}), 102.00 (CHPh), 99.28 (C-1), 82.81 (C-4), 71.48 (C-3), 69.14 (C-6), 62.79 (C-2), 62.49 (C-5), 55.22 (OCH₃), 52.17

(CH₂NPh), 25.92 ((CH₃)₃C), 18.32 ((CH₃)₃C), -4.09 and -4.72 ((CH₃)₂Si); ES-MS: *m/z* (%) = 508.1 (10) [M + Na]⁺, 486.1 (100) [M + H]⁺; HRMS: *m/z* calcd. for C₂₇H₄₀NO₅Si [M + H]⁺: 486.2676; found 486.2703

b) The silylated glucosamine derivative **7** (0.030 g, 0.052 mmol), activated powdered molecular sieves (0.15 g), TEMPO (0.008 g, 0.052 mmol) and NIS (0.035 g, 0.156 mmol) were placed under argon. Dichloromethane (2.5 ml) was added. The reaction mixture was stirred at room temperature. The mixture became dark maroon within 5 min. After 10 min TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material and spots due to **8** and another compound with a slightly higher R_f. The reaction mixture was worked up as in a) and the crude product (0.040 g) chromatographed on silica gel. Elution with hexane/ethyl acetate 9:1 gave **8** (0.019 g, 75%) then ethyl acetate wash gave **9** (0.002 g, 10%).

Reaction of methyl 2,2-N,N-dibenzylamino-3-tert-butyldimethylsilyloxy-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside 7 with NIS (2 equivalents) and TEMPO

The silylated glucosamine derivative **7** (0.030 g, 0.052 mmol), 4 Å powdered molecular sieves (0.15 g), TEMPO (0.008 g, 0.052 mmol) and NIS (0.023 g, 0.104 mmol) were placed under argon. Dichloromethane (2.5 ml) was added. The reaction mixture was stirred at room temperature. The mixture became pink within 5 min and then dark maroon. After 45 min TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material and spots due to **8** and another compound with a slightly higher R_f. The reaction mixture was worked up as in 4.8 a) and the crude product (0.032 g) chromatographed on silica gel. Elution with

hexane/ethyl acetate 9:1 gave **8** (0.019 g, 75%) then ethyl acetate wash gave 0.004 g material containing **9** and other unidentified compounds.

*Reaction of methyl 2,2-N,N-dibenzylamino-3-tert-butyldimethylsilyloxy-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **7** with NIS (10 equivalents)*

a) The silylated glucosamine derivative **7** (0.024 g, 0.042 mmol) and NIS (0.094 g, 0.42 mmol) were placed under argon. Dichloromethane (2 ml) was added. The reaction mixture was stirred at room temperature. The mixture gradually became dark maroon. After 3 h TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material and spots due to **8** and **9**. The reaction mixture was stirred for a further 20 h. At the end of this time the TLC was little changed so the reaction mixture was worked up as in a). The crude product (0.018 g) was chromatographed on silica gel using hexane/ethyl acetate 8:2, and then hexane/ethyl acetate 4:6 giving methyl 2-amino-3-*tert*-butyldimethylsilyloxy-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside **9** (0.012, 72%). as a colourless oil. $[\alpha]_D^{26.9} = +54.7$ ($c = 1.8$, CHCl_3); IR (film) 3350, 3300 (N-H), 3066, 3036 (Ar C-H), 2951, 2928, 2855 (C-H) cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.52\text{--}7.47$ and $7.41\text{--}7.34$ (m, 5H_{arom}), 5.51 (s, 1H, CHPh), 4.78 (d, 1H, $J_{\text{H-1,H-2}} = 3.6$ Hz, 1H, H-1), 4.27 (dd, 1H, $J_{\text{H-6,H-5}} = 4.6$ Hz, $J_{\text{H-6,H-6'}} = 9.9$ Hz, 1H, H-6), 3.83 (m, 1H, H-5), 3.75 (t, $J_{\text{H-6',H-5}}$ and $\text{H-6',H-6}} = 10.0$ Hz, 1H, H-6'), 3.74 (t, $J_{\text{H-3,H-2}}$ and $\text{H-3,H-4}} = 9.0$ Hz, 1H, H-3), 3.43 (s, 3H, OCH_3), 3.42 (t, $J_{\text{H-4,H-3}}$ and $\text{H-4,H-5}} = 9.0$ Hz, 1H, H-4), 2.78 (dd, 1H, $J_{\text{H-2,H-1}} = 3.6$ Hz, $J_{\text{H-2,H-3}} = 9.2$ Hz, 1H, H-2), 1.47 (bs, 2H, NH_2), 0.88 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.09 and 0.00 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): $\delta = 137.36$, 128.96, 128.10 and 126.30 (C_{arom}), 101.93 (CHPh), 101.27 (C-1), 82.42 (C-4), 74.22

(C-3), 69.16 (C-6), 62.96 (C-5), 57.76 (C-2), 55.26 (OCH₃), 25.90 ((CH₃)₃C), 18.26 ((CH₃)₃C), -3.96 and -4.71 ((CH₃)₂Si); ES-MS: m/z (%) = 396.1 (100) [M + H]⁺, 364.2 (10); HRMS: m/z calcd. for C₂₀H₃₄NO₅Si [M + H]⁺: 396.2206; found 396.2185

Reaction of methyl 2,2-N,N-dibenzylamino-3-tert-butyldimethylsilyloxy-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside 7 with NIS (5 equivalents) and water

The silylated glucosamine derivative **7** (0.030 g, 0.052 mmol) and NIS (0.058 g, 0.26 mmol) were placed under nitrogen. Dichloromethane (2 ml) was added. The reaction mixture was stirred at room temperature for 2 h and gradually became dark maroon. Water (0.9 μ l, 0.052 mmol) was added. The reaction mixture was stirred for a further 20 h. At the end of this time the TLC (hexane/ethyl acetate 8:2) showed spots due to **8** and **9**, the latter being stronger. The reaction mixture was worked up as in 4.10 a). The crude product (0.034 g) was chromatographed on silica gel using hexane/ethyl acetate 9:1, then hexane/ethyl acetate 4:6 and then ethyl acetate giving **9** (0.018, 87%).

Preparation of methyl 2-N,N-dibenzylamino-3-O-benzoyl-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside

Benzoyl chloride (0.25 ml, 2.2 mmol) was added slowly to a solution of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **1** (0.50 g, 1.1 mmol) in

toluene/pyridine (4/1 (v/v), 25 mL). The reaction mixture was stirred for 24 h at room temperature, filtered through a silica plug and washed with saturated aq. copper sulfate (10 mL) and then 10 % aq. potassium carbonate (10 mL). The organic layer was dried (MgSO₄), filtered and evaporated. Column chromatography of the residue (eluent: hexane/EtOAc, 1/4) gave methyl 2-*N,N*-dibenzylamino-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside (0.6 g, 100 %) as a white solid (R_f (EtOAc/Hexane, 1/4) = 0.5); mp (hexane) = 127.5 °C; $[\alpha]_D^{24} = +21$ ($c = 2.50$, CHCl₃); ¹H NMR (500 MHz, CDCl₃); δ ppm: 3.25 (dd, $J_{2,3} = 11.4$ Hz, $J_{2,1} = 3.8$ Hz, 1H, H-2); 3.48 (s, 3H, CH₃O); 3.69 (m, 4H); 3.97 (m, 4H); 4.26 (dd, $J = 10.1$ Hz, $J = 4.8$ Hz, 1H); 4.79 (d, $J_{1,2} = 3.0$ Hz, 1H, H α -1); 5.43 (s, 1H, C₆H₅CH); 6.10 (dd, $J = 10.9$ Hz, $J = 9.2$ Hz, 1H, H-3); 7.28 (m, 14H, C₆H₅); 7.55 (m, 4H, C₆H₅); 8.17 (m, 2H, C₆H₅); ¹³C NMR (122.7 MHz, CDCl₃); δ ppm: 55.2 (q, CH₃O); 55.5 (t, C₆C₅CH₂); 59.8, 62.4, 69.7, 81.1 (dx4, C-2, C-3, C-4, C-5); 69.1 (t, C-6); 101.2, 101.9 (dx2, C β -1, C₆H₅CH); 126.1, 126.9, 128.1, 128.2, 128.5, 128.6, 128.8, 130.0, 133.1 (tx9, C₆H₅); 137.2, 140.3, 165.2 (sx3, C₆H₅CO); MS (ES⁺): 588 (100 %, MNa⁺); 566 (50 %, M⁺).

*Preparation of methyl 2,2-*N,N*-dibenzylamino-3-*O*-benzoyl-2-deoxy- α -D-glucopyranoside*

Methyl 2-*N,N*-dibenzylamino-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside (0.5 g, 0.9 mmol) was stirred at reflux in an acetic acid/water mixture (7/3 (v/v), 20 mL) for 2 h. The reaction mixture was then concentrated under reduced pressure. Flash chromatography of the residue (eluent EtOAc) furnished methyl 2-*N,N*-dibenzylamino-3-*O*-benzoyl-2-deoxy- α -D-glucopyranoside as a white solid (0.3 g, 68 %), (R_f (EtOAc/Hexane, 2/8) = 0.1); mp (Hexane) = 62.0 °C; $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3500 br (OH); 3087, 3068 (aromatic CH); 2972, 2931 (aliphatic CH); 1728 (C=O); $[\alpha]_D^{24} = +15$ ($c = 1.48$, CHCl₃); ¹H

NMR (500 MHz, CDCl₃); δ ppm: 3.15 (dd, $J_{2,3}$ = 11.2 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2); 3.46 (s, 3H, CH₃O); 3.67 (d, J = 8.6 Hz, 1H); 3.73 (m, 3H); 3.83 (dd, J = 8.6 Hz, J = 3.6 Hz, 2H); 3.96 (d, J = 13.2 Hz, 2H, C₆H₅CH₂); 4.80 (d, $J_{1,2}$ = 3.6 Hz, 1H, H_a-1); 5.82 (dd, $J_{3,2}$ = 11.2 Hz, $J_{3,4}$ = 8.5 Hz, 1H, H-3); 7.27 (m 10H, C₆H₅); 7.58 (t, J = 7.6 Hz, 2H, C₆H₅); 7.68 (t, J = 7.6 Hz, 1H, C₆H₅); 8.19 (d, J = 7.6 Hz, 2H, C₆H₅); ¹³C NMR (125.7 MHz, CDCl₃); δ ppm: 55.1 (q, CH₃O); 55.3 (t, C₆C₅CH₂); 59.2, 71.1, 71.6, 74.1 (dx4, C-2, C-3, C-4, C-5); 62.4 (t, C-6); 100.8 (d, C_a-1); 126.9, 128.2, 128.5, 130.0 (tx4, C₆H₅); 140.1, 167.5 (sx2, C₆H₅CO); MS (ES⁺): 952 (100 %, MH⁺); 477 (25 %, M⁺); 372 (100 %); HRMS (ES⁺): C₂₈H₃₂NO₆⁺ calculated 478.2224, found 478.2230.

*Preparation of methyl 2,2-*N,N*-dibenzylamino-3-*O*-benzoyl-4-*tert*-butyldimethylsilyloxy-2-deoxy- α -D-glucopyranoside 3*

A solution of *tert*-butyldimethylsilyl chloride (0.6 g, 4.0 mmol) in dry DMF (5 mL) was slowly added to a solution of methyl 2,2-*N,N*-dibenzylamino-3-*O*-benzoyl-2-deoxy- α -D-glucopyranoside (0.5 g, 1.0 mmol) and imidazole (0.5 g, 7.0 mmol) in dry DMF (20 mL). The reaction mixture was stirred overnight at room temperature. It was then concentrated under reduced pressure, dissolved in chloroform (30 mL), and washed successively with 1N aq. HCl (15 mL) and brine (10 mL). The organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. Flash chromatography of the residue (eluent EtOAc/hexane; 1.5/8.5) gave methyl 2,2-*N,N*-dibenzylamino-3-*O*-benzoyl-4-*tert*-

butylsilyloxy-2-deoxy- α -D-glucopyranoside **3** (0.37 g, 73 %) as a brown solid (R_f (EtOAc/Hexane, 1/9) = 0.2); mp (Hexane) = 47.2 °C; $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3479 br (OH); 3085, 3061, 3027 (CH Ar.); 2953, 2927, 2854 (CH aliph.); 1724 (COBz); 1273 (SiO); $[\alpha]_D^{24} = +7$ ($c = 0.64$, CHCl_3); ^1H NMR (500 MHz, CDCl_3); δ ppm: 0.06 (s, 3H, CH_3Si); 0.08 (s, 3H, CH_3Si); 0.88 (s, 9H, $(\text{CH}_3)_3\text{CSi}$); 3.07 (d, $J = 3.6$ Hz, 1H, OH); 3.13 (dd, $J_{2,3} = 10.4$ Hz, $J_{2,1} = 3.2$ Hz, 1H, H-2); 3.46 (s, 3H, CH_3O); 3.65 (dd, $J_{4,3} = 8.7$ Hz, $J_{4,5} = 9.2$ Hz, 1H, H-4); 3.74 (m, 3H, $\text{C}_6\text{H}_5\text{CH}_2$, H-5); 3.83 (t, $J_{5,6} = 5.5$ Hz, 2H, H-6); 3.95 (d, $J = 13.7$ Hz, 2H, $\text{C}_6\text{H}_5\text{CH}_2$); 4.78 (d, $J_{1,2} = 3.2$ Hz, 1H, H-1); 5.86 (dd, $J_{3,2} = 11.5$ Hz, $J_{3,4} = 8.7$ Hz, 1H, H-3); 7.25 (m, 10H, C_6H_5); 7.56 (t, $J = 7.5$ Hz, 2H, C_6H_5); 7.67 (t, $J = 7.5$ Hz, 1H, C_6H_5); 8.22 (d, $J = 7.6$ Hz, 2H, C_6H_5); ^{13}C NMR (122.7 MHz, CDCl_3); δ ppm: -5.1, -5.2 (qx2, $(\text{CH}_3)_2\text{Si}$); 18.7 (s, $(\text{CH}_3)_3\text{CSi}$); 26.1 (qx3, $(\text{CH}_3)_3\text{CSi}$); 55.2 (q, CH_3O); 55.6 (tx2, $\text{C}_6\text{H}_5\text{CH}_2$); 59.2, 70.9, 73.6, 73.9 (dx4, C-2, C-3, C-4, C-5); 64.8 (t, C-6); 101.0 (d, C-1); 127.1, 128.8, 128.4, 130.3 (tx4, C_6H_5); 133.6, 136.7, 172.1 (sx3, $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$); MS (ES⁺): 614 (100 %, MNa^+); 592 (23 %, MH^+).

*Reaction of methyl 2,2-N,N-dibenzylamino-3-O-benzoyl-4-tert-butyltrimethylsilyloxy-2-deoxy- α -D-glucopyranoside **3** with NIS (3 equiv)*

The glucosamine **3** (0.020 g, 0.034 mmol) and NIS (0.023 g, 0.101 mmol) were placed under argon. Dichloromethane (3 ml) was added. The reaction mixture was stirred at room temperature. The mixture gradually became dark maroon. After 4.5 h TLC (hexane/ethyl acetate 7:3) showed formation of products but the presence of unreacted starting material. The reaction mixture was stirred for a further 16 h. At the end of this time the TLC was little

changed so the reaction mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO₄). Evaporation gave 0.020 g crude product, which was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2, then hexane/ethyl acetate 2:8, then ethyl acetate and finally dichloromethane/methanol 9:1 gave unreacted **3** (0.004 g, 20%) and methyl 2-*N*-benzylamino-3-*O*-benzoyl-4-*tert*-butyldimethylsilyloxy-2-deoxy- α -D-glucopyranoside **11** (0.004 g, 23%) as an oil. $[\alpha]_D^{29.4} = +9.1$ ($c = 0.075$, CHCl₃); IR (film) 3488 (N-H), 3062, 3028 (Ar C-H), 2952, 2927, 2855 (C-H), 1723 (C=O); ¹H-NMR (400 MHz, CDCl₃): $\delta = 8.10$ (m, 2H, *o*-C₆H₅CO), 7.64 (m, 1H, *p*-C₆H₅CO), 7.48 (m, 2H, *m*-C₆H₅CO), 7.21-7.20 (m, 5H_{arom}), 5.34 (m, 1H, H-3), 4.76 (d, 1H, $J = 3.2$ Hz, H-1), 3.87 (m, 2H, H-4, 5, 6 or 6'), 3.86 (d, 1H, $J = 14.0$ Hz, N(CHHPh)), 3.80 (d, 1H, 1H, $J = 14.0$ Hz, N(CHHPh)), 3.69 (m, 2H, H-4, 5, 6 or 6'), 3.40 (s, 3H, OCH₃), 3.03 (bs, 1H, OH), 2.88 (dd, 1H, $J = 3.2$ Hz, $J = 10.4$ Hz, H-2), 1.62 (bs, 1H, NH), 0.90 (s, 9H, (CH₃)₃CSi), 0.09 (s, 6H, (CH₃)₂Si); ¹³C-NMR (100 MHz, CDCl₃): $\delta = 167.6$ (C=O), 140.4, 133.0, 130.1, 130.0, 128.3, 128.2, 127.9 and 126.8 (C_{arom}), 98.4 (C-1), 76.5, 71.6, 70.9, 64.2, 59.1, 55.1, 51.2, 25.9 ((CH₃)₃C), 18.3 (CH₃)₃C, -5.4 (CH₃)₂Si); ES-MS: m/z (%) = 502.3 (100) [M + H]⁺, 524.3 (30) [M + Na]⁺, 1025.5 (8) [2M + Na]⁺; HRMS: m/z calcd. for C₂₇H₄₀NO₆Si [M + H]⁺: 502.2625; found 502.2628. Elution with hexane:ethyl acetate, 2:3 gave methyl 2-amino-3-*O*-benzoyl-4-*tert*-butyldimethylsilyloxy-2-deoxy- α -D-glucopyranoside **12** (0.004 g, 28%) as an oil. $[\alpha]_D^{29.5} = +37.8$ ($c = 0.4$, CHCl₃); IR (film) 3379, 3306 (N-H), 3063 (Ar C-H), 2952, 2928, 2855 (C-H), 1713 (C=O); ¹H-NMR (400 MHz, CDCl₃): $\delta = 8.11$ (m, 2H, *o*-C₆H₅CO), 7.59 (m, 1H, *p*-C₆H₅CO), 7.47 (m, 2H, *m*-C₆H₅CO), 5.25 (m, 1H, H-3), 4.78 (d, 1H, $J = 3.6$ Hz, H-1), 3.91 (m, 2H, H-5, H-6), 3.73 (m, 2H, H-4, H-6'), 3.44 (s, 3H, OCH₃), 3.01 (d, 1H, $J = 3.6$ Hz, $J = 10.0$ Hz, H-2), 1.98 (bs, 3H, OH, NH₂), 0.91 (s, 9H, (CH₃)₃CSi), 0.11 (s, 6H, (CH₃)₂Si); ¹³C-NMR (100 MHz, CDCl₃): $\delta = 167.67$ (C=O), 133.35, 129.88, 129.63 and

128.44 (C_{arom}), 100.41 (C-1), 78.74, 71.50, 71.22, 64.21, 55.16, 54.46, 25.88 ((CH₃)₃C), 18.33 (CH₃)₃C), -5.43 (CH₃)₂Si); ES-MS: m/z (%) = 258.2 (15), 412.2 (100) [M + H]⁺, 434.2 (25) [M + Na]⁺; HRMS: m/z calcd. for C₂₀H₃₄NO₆Si [M + H]⁺: 412.2155; found 412.2197.

*Reaction of methyl 2,2-N,N-dibenzylamino-3-O-benzoyl-4-tert-butyltrimethylsilyloxy-2-deoxy- α -D-glucopyranoside **3** with NIS (10 equivalents)*

The glucosamine **3** (0.030 g, 0.051 mmol) and NIS (0.114 g, 0.51 mmol) were placed under argon. Dichloromethane (3 ml) was added. The reaction mixture was stirred at room temperature. The mixture gradually became dark maroon. After 4.5 h TLC (hexane/ethyl acetate 7:3) showed complete disappearance of starting material. The reaction mixture was then worked up as in the previous example. The crude product (0.025 g) was chromatographed on silica gel using hexane/ethyl acetate 8:2, then hexane/ethyl acetate 7:3, then ethyl acetate giving **12** (0.011 g, 50%).

*Preparation of (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(tert-butyltrimethylsilyloxy)propane **20***

The *N,N*-dibenzylphenylalaninol **16** (0.80 g, 2.4 mmol), imidazole (1.15 g, 16.91 mmol), and DMAP (0.016 g, 0.13 mmol) were placed under argon. Dry DMF (6 ml) was added. A solution of *tert*-butyldimethylsilyl chloride (1.44 g, 9.6 mmol) in dry DMF (6 ml) was added slowly from a syringe. The mixture became pale blue. The mixture was stirred for 16 h. At

the end of this time TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material. The reaction mixture was poured into water (200 ml) and extracted with ether (3x200 ml). The ether extracts were dried (MgSO_4), evaporated, taken up in DCM (100 ml), re-dried (MgSO_4) and evaporated. The residue was chromatographed on silica gel using hexane/ethyl acetate 95:5 giving (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(*tert*-butyldimethylsilyloxy)propane **20** (0.091 g, 92%) as a colourless oil. $[\alpha]_{\text{D}}^{26.8} -25.8$ ($c = 1$, CHCl_3); IR (film) 3084, 3062, 3026 (Ar C-H), 2953, 2928, 2893, 2856 (C-H) cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.25\text{--}7.14$ and $7.07\text{--}7.04$ (m, 15H_{arom}), 3.77 (bs, 4H, $\text{N}(\text{CH}_2\text{Ph})_2$), 3.73 (dd, 1H, $J = 4.4$ Hz, $J = 10.4$ Hz, H-1), 3.66 (dd, 1H, $J = 5.2$ Hz, $J = 10.4$ Hz, H-1'), 2.96 (m, 1H, H-2), 2.85 (m, 2H, H-3), 0.90 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.00 and 0.01 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): $\delta = 140.63$, 140.60, 129.47, 128.50, 128.04, 128.01, 126.52 and 125.68 (C_{arom}), 62.62 (C-1), 60.41 (C-2), 54.44 (NCH_2Ph)₂, 34.14 (C-3), 25.93 ($((\text{CH}_3)_3\text{C})$), 18.18 ($((\text{CH}_3)_3\text{C})$), -5.51 and -5.58 ($((\text{CH}_3)_2\text{Si})$); ES-MS: m/z (%) = 447.3 (20), 446.3 (100) $[\text{M} + \text{H}]^+$; HRMS: m/z calcd. for $\text{C}_{29}\text{H}_{40}\text{NOSi}$ $[\text{M} + \text{H}]^+$: 446.2879; found 446.2894.

Reaction of (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(tert-butyldimethylsilyloxy)propane 20 with NIS (3 equivalents)

NIS (0.034 g, 0.154 mmol) and activated powdered molecular sieves (0.12 g) were placed under nitrogen. A solution of **20** (0.023 g, 0.051 mmol) in dichloromethane (2 ml) was added. The reaction mixture was stirred at room temperature and quickly became dark maroon. After 1.5 h TLC (hexane/ethyl acetate 9:1) showed complete disappearance of starting material. The reaction mixture was diluted with dichloromethane (15 ml) and washed with

aq. sodium thiosulfate (15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO_4). Evaporation gave 0.022 g crude product. This was chromatographed on silica gel using hexane/ethyl acetate 95:5, then hexane/ethyl acetate 9:1 giving (S)-(-)-2-(benzylamino)-3-phenyl-1-(*tert*-butyldimethylsilyloxy)propane **21** (0.016 g, 88%) as a colourless oil. $[\alpha]_{\text{D}}^{26.7} -4.8$ ($c = 0.8$, CHCl_3); IR (film) 3331(N-H), 3084, 3061, 3026 (Ar C-H), 2952, 2927, 2884, 2855 (C-H) cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.29$ -7.11 (m, 10H_{arom}), 3.79 (bs, 2H, $\text{N}(\text{CH}_2\text{Ph})$), 3.53 (dd, 1H, $J = 4.7$ Hz, $J = 10.0$ Hz, H-1), 3.48 (d, 1H, $J = 5.6$ Hz, $J = 10.0$ Hz, H-1'), 2.88 (m, 1H, H-2), 2.76 (dd, 1H, $J = 6.2$ Hz, $J = 13.6$ Hz, H-3), 2.73 (dd, 1H, $J = 7.3$ Hz, $J = 13.5$ Hz, H-3'), 2.04 (bs, 1H, NH), 0.88 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.01 and 0.00 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): $\delta = 140.44$, 139.29, 129.30, 128.34, 128.30, 127.99, 126.80 and 126.07 (C_{arom}), 64.00 (C-1), 59.93 (C-2), 51.43 (NCH_2Ph), 37.89 (C-3), 25.89 ($(\text{CH}_3)_3\text{C}$), 18.22 ($(\text{CH}_3)_3\text{C}$), -5.41 and -5.43 ($(\text{CH}_3)_2\text{Si}$); ES-MS: m/z (%) = 357(20), 356.2 (100) $[\text{M} + \text{H}]^+$; HRMS: m/z calcd. for $\text{C}_{22}\text{H}_{34}\text{NOSi}$ $[\text{M} + \text{H}]^+$: 356.2410; found 356.2445.

Reaction of (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(tert-butyldimethylsilyloxy)propane 20 with NIS (10 equivalents)

The silylated phenylalaninol **20** (0.040g, 0.090 mmol) and NIS (0.21 g, 0.90 mmol) were placed under argon. Dichloromethane (3 ml) was added. The reaction mixture quickly became dark maroon. It was stirred at room temperature for 20 h and then worked up as in the previous example. The crude product (0.038 g) was chromatographed on silica gel using hexane/ethyl acetate 8:2 and, then ethyl acetate giving (S)-(-)-2-amino-3-phenyl-1-(*tert*-

butyldimethylsilyloxy)propane **22** (0.010 g, 42%). as a colourless oil. $[\alpha]_{\text{D}}^{27.1} -11.0$ ($c = 1$, CHCl_3) (lit.² $[\alpha]_{\text{D}}^{23} -3.6$ ($c = 1$, CHCl_3)); IR (film) 3372 (N-H), 3084, 3062, 3027, 2953, 2928, 2855 (C-H); $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.26\text{--}7.12$ (m, 5H_{arom}), 3.52 (dd, 1H, $J = 4.4$ Hz, $J = 9.7$ Hz, H-1), 3.38 (dd, 1H, $J = 6.5$ Hz, $J = 9.7$ Hz, H-1'), 3.03 (m, 1H, H-2), 2.73 (dd, 1H, $J = 5.3$ Hz, $J = 13.3$ Hz, H-3), 2.45 (dd, 1H, $J = 8.4$ Hz, $J = 13.3$ Hz, H-3'), 1.49 (bs, 2H, NH_2), 0.85 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.00 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 139.12$, 129.29, 129.18, 128.34 and 126.12 (C_{arom}), 67.41 (C-1), 54.27 (C-2), 40.38 (C-3), 25.84 ($(\text{CH}_3)_3\text{C}$), 18.21 ($(\text{CH}_3)_3\text{C}$), -5.42 and -5.44 ($(\text{CH}_3)_2\text{Si}$); ES-MS: m/z (%) = 266.0 (100) $[\text{M} + \text{H}]^+$. The NMR data were in accordance with those cited in the literature.²

*Reaction of N,N-dibenzyl-(tert-butyldimethylsilyloxy)serine methyl ester **25** with NIS (3 equivalents)*

A solution of the serine methyl ester **25** (0.20 g, 0.48 mmol) in dichloromethane (1 ml) was added to NIS (0.324 g, 1.45 mmol) and activated powdered 4 Å molecular sieves (0.2 g) in dichloromethane (5 ml) under argon. The reaction mixture turned maroon very gradually. After 4 h TLC (hexane/ethyl acetate 8:2) showed almost complete disappearance of starting material. After 5 h the reaction mixture was diluted with dichloromethane (50 ml) and washed with aq. sodium thiosulfate (10 ml), satd. aq. sodium bicarbonate (10 ml), water (15 ml) and brine (15 ml) and was dried (MgSO_4). Evaporation gave 0.3 g crude product. This

² Isobe, T.; Fukuda, K.; Yamaguchi, K.; Seki, H.; Tokunaga, T.; Ishikawa, T. *J. Org. Chem.* **2000**, *65*, 7779-7785.

was chromatographed on silica gel using hexane/ethyl acetate 9:1, to give *N*-benzyl-(*tert*-butyldimethylsilyloxy)serine methyl ester **26**³ (0.131 g, 83%) as a colourless oil. $[\alpha]_D^{26.3}$ -18.5 (c = 1.45, CHCl_3) (lit.³ $[\alpha]_D^{22}$ -11.25 (c = 3.2, CHCl_3)); IR (film) 3343 (N-H), 3086, 3063, 3028 (Ar C-H), 2952, 2929, 2884, 2856 (C-H), 1745 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 7.34-7.20 (m, 5H_{arom}), 3.89 (d, 1H, J = 13.1 Hz, $\text{N}(\text{CHHPh})$), 3.85 (dd, 1H, J = 4.8 Hz, J = 9.7 Hz, CHHOSi), 3.79 (dd, 1H, J = 4.8 Hz, J = 9.7 Hz, CHHOSi), 3.70 (s, 3H, OCH_3), 3.69 (d, 1H, J = 13.5 Hz, $\text{N}(\text{CHHPh})$), 3.37 (t, 1H, J = 4.8 Hz, NCH), 2.16 (bs, 1H, NH), 0.84 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.00 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 173.76 (C=O), 139.75, 128.36, 128.21 and 127.01 (C_{arom}), 64.54 (CH_2OSi), 62.17 (NCH), 51.87 ($\text{N}(\text{CH}_2\text{Ph})$), 51.69 (OCH_3), 25.71 ($(\text{CH}_3)_3\text{C}$), 18.16 ($(\text{CH}_3)_3\text{C}$), -5.52 and -5.61 ($(\text{CH}_3)_2\text{Si}$); ES-MS: m/z (%) = 346.2 (40) $[\text{M} + \text{Na}]^+$, 325 (10), 324.2 (100) $[\text{M} + \text{H}]^+$; HRMS: m/z calcd. for $\text{C}_{17}\text{H}_{30}\text{NO}_3\text{Si}$ $[\text{M} + \text{H}]^+$: 324.1995; found 324.2010. The $^1\text{H-NMR}$ data were in accordance with those cited in the literature.³

Reaction of N,N-dibenzyl-(tert-butyldimethylsilyloxy)serine benzyl ester 27 with NIS (3 equivalents)

A solution of the serine benzyl ester **27** (0.20 g, 0.408 mmol) in dichloromethane (5 ml) was added to NIS (0.272 g, 1.44 mmol) and activated powdered 4 Å molecular sieves (0.2 g) under argon. The reaction mixture turned maroon very gradually. After 5 h TLC (hexane/ethyl acetate 8:2) showed almost complete disappearance of starting material. The

reaction mixture was diluted with dichloromethane (50 ml) and washed with aq. sodium thiosulfate (10 ml), satd. aq. sodium bicarbonate (50 ml), water (50 ml) and brine (50 ml) and was dried (MgSO₄). Evaporation gave 0.060 g crude product. This was chromatographed on silica gel using hexane/ethyl acetate 9:1 to give *N*-benzyl-(*tert*-butyldimethylsilyloxy)serine benzyl ester **28** (0.029 g, 85%) as a colourless oil. $[\alpha]_D^{26.2}$ -22.5 (c = 1.45, CHCl₃); IR (film) 3346 (N-H), 3086, 3063, 3030 (Ar C-H), 2952, 2926, 2882, 2855 (C-H), 1740 (C=O) cm⁻¹; ¹H-NMR (500 MHz, CDCl₃): δ = 7.40-7.21 (m, 10H_{arom}), 5.17 (s, 2H, OCH₂Ph), 3.90 (d, 1H, J = 13.2, NCHHPh), 3.90 (d, 1H, J = 4.5, J = 9.6, CHHOSi), 3.83 (dd, 1H, J = 4.9 Hz, J = 9.8 Hz, CHHOSi), 3.70 (d, 1H, J = 13.1 Hz, NCHHPh), 3.43 (t, 1H, J = 4.7 Hz, NCH), 2.14 (bs, 1H, NH), 0.85 (s, 9H, (CH₃)₃CSi), 0.00 and 0.01 (2xs, 6H, (CH₃)₂Si); ¹³C-NMR (125 MHz, CDCl₃): δ = 173.14, 139.72, 135.78, 128.56, 128.53, 128.41, 128.35, 128.26, 128.24, 128.22 and 127.01 (C_{arom}), 66.46 (OCH₂Ph), 64.59 (CH₂OSi), 62.21 (NCH), 51.81 (NCH₂Ph), 25.75 ((CH₃)₃C), 18.18 ((CH₃)₃C), -5.52 and -5.59 ((CH₃)₂Si); ES-MS: m/z (%) = 422.1 (30) [M + Na]⁺, 400.1 (100) [M + H]⁺; HRMS: m/z calcd. for C₂₃H₃₄NO₃Si [M + H]⁺: at 400.2308; found 400.2296.

Reaction of N-benzyl-(tert-butyldimethylsilyloxy)serine benzyl ester 28 with NIS (3 equivalents)

A solution of the serine benzyl ester **28** (0.063 g, 0.157 mmol) in dichloromethane (3 ml) was added to NIS (0.102 g, 0.473 mmol) and activated powdered 4 Å molecular sieves (0.15 g)

³ Barco, A.; Benetti, S.; De Risi, C.; Pollini, G. P.; Romagnoli, R.; Zanirato, V. *Tetrahedron Lett.* **1996**, *37*, 7599-7602.

under argon. The reaction mixture turned yellow, then salmon coloured, then maroon very gradually. After 20 h the reaction mixture was diluted with dichloromethane (40 ml) and shaken with conc. aq. sodium thiosulfate (3 ml). 880 ammonia (2 ml) was added and the mixture shaken again. The aqueous phase was re-extracted with dichloromethane (10 ml). The organic extracts were dried (MgSO_4) and evaporated. The residue was treated with hexane (5 ml) to precipitate NIS and the mixture filtered and evaporated. This was repeated twice. The crude product (0.070 g) was chromatographed on silica gel using hexane/ethyl acetate 8:2, then hexane/ethyl acetate 1:1 to give (*tert*-butyldimethylsilyloxy)serine benzyl ester **29** (0.025 g, 51%). $[\alpha]_D^{27.2} -10.4$ ($c = 1.25$, CHCl_3); IR (film) 3384 (N-H), 3090, 3065, 3034 (Ar C-H), 2954, 2929, 2885, 2857 (C-H), 1744 (C=O); $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.37\text{--}7.30$ (m, 5H_{arom}), 5.17 (d, 1H, $J = 12.2$ Hz, OCHHPh), 5.15 (d, 1H, $J = 12.3$ Hz, OCHHPh), 3.97 (dd, 1H, $J = 4.0$ Hz, $J = 9.7$ Hz, CHHOSi), 3.85 (dd, 1H, $J = 3.5$ Hz, $J = 9.7$ Hz, CHHOSi), 3.60 (m, 1H, NCH), 2.46 (bs, 2H, NH_2), 0.85 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.03 and 0.00 (2xs, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): $\delta = 173.52$ (C=O), 135.55, 128.55, 128.43, 128.39, 128.36, 128.32, 128.28 and 128.23 (C_{arom}), 66.84 (OCH_2Ph), 64.93 (CH_2OSi), 56.41 (NCH), 25.72 ($(\text{CH}_3)_3\text{C}$), 18.17 ($(\text{CH}_3)_3\text{C}$), -5.54 and -5.63 ($(\text{CH}_3)_2\text{Si}$); ES-MS: m/z (%) = 310.2 (100) $[\text{M} + \text{H}]^+$; HRMS: m/z calcd. for $\text{C}_{16}\text{H}_{28}\text{NO}_3\text{Si}$ $[\text{M} + \text{H}]^+$: 310.1838; found: 310.1853.

Reaction of (S)-(-)-2-(dibenzylamino)-3-phenyl-1-propanol 16 with NIS (3 equivalents)

The phenylalaninol **16** (0.050 g, 0.15 mmol), NIS (0.10 g, 0.45 mmol) and activated powdered 4 Å molecular sieves (0.15 g) were placed under argon. Dichloromethane (3 ml)

was added. The mixture was stirred at room temperature. After 7 h TLC (hexane/ethyl acetate 6:4) showed formation of products but some unreacted starting material **16**. After a further 14 h the TLC was unchanged. The reaction mixture was diluted with dichloromethane (15 ml) and washed with aq. sodium thiosulfate (15 ml), satd. aq. sodium bicarbonate (15 ml), water (15 ml) and brine (15 ml) and was dried (MgSO_4). Evaporation gave 0.064 g crude product. This was chromatographed on silica gel using hexane/ethyl acetate 8:2, then hexane/ethyl acetate 6:4, then hexane/ethyl acetate 1:1 to give (S)-(-)-2-(benzylamino)-3-phenylpropyl benzoate **18** as a colourless oil (0.036 g, 69%). $[\alpha]_{\text{D}}^{28.8} -7.9$ ($c = 1$, CHCl_3); IR (film) 3336 (N-H), 3083, 3061, 3026 (Ar C-H), 2924, 2852 (C-H), 1720 (C=O) cm^{-1} ; ^1H -NMR (500 MHz, CDCl_3): $\delta = 7.95$ (m, 2H, $o\text{-C}_6\text{H}_5\text{CO}$), 7.48 (m, 1H, $p\text{-C}_6\text{H}_5\text{CO}$), 7.36 (m, 2H, $m\text{-C}_6\text{H}_5\text{CO}$), 7.08-7.22 (m, 10 H_{arom}), 4.25 (dd, 1H, $J = 5.0$ Hz, $J = 11.2$ Hz, H-1), 4.20 (dd, 1H, $J = 5.2$ Hz, $J = 11.2$ Hz, H-1'), 3.82 (d, 1H, $J = 13.4$ Hz, NCHHPh), 3.76 (d, 1H, $J = 13.4$ Hz, NCHHPh), 3.13 (m, 1H, H-2), 2.84 (dd, 1H, $J = 6.5$ Hz, $J = 13.9$ Hz, H-3), 2.79 (dd, 1H, $J = 7.1$ Hz, $J = 13.6$ Hz, H-3'), 1.56 (bs, 1H, NH); ^{13}C -NMR (125 MHz, CDCl_3): $\delta = 166.38$ (C=O), 140.12, 138.16, 132.97, 130.07, 129.54, 129.24, 128.52, 128.35, 128.34, 127.95, 126.90 and 126.43 (C_{arom}), 66.06 (C-1), 56.97 (C-2), 51.36 (PhCH_2N), 38.48 (C-3); ES-MS: m/z (%) = 368.0 (50) $[\text{M} + \text{Na}]^+$, 345.9 (100) $[\text{M} + \text{H}]^+$, 241.9 (60); HRMS: m/z calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 346.1807; found: 346.1838

*Reaction of 3-(dibenzylamino)-1-propanol **30** with NIS (3 equivalents)*

NIS (0.132 g, 0.59 mmol) and activated powdered 4 Å molecular sieves (0.15 g) were placed under argon. A solution of **30** (0.050 g, 0.19 mmol) in dichloromethane (3 ml) was added.

The reaction mixture was stirred at room temperature and quickly became dark maroon. After 30 min TLC (hexane/ethyl acetate 1:1) showed complete disappearance of starting material. The mixture was carefully reduced to a small volume on the rotary evaporator and the residue applied directly to a chromatography column. Elution with hexane/ethyl acetate 1:1, gave a single product, heavily contaminated by iodine. This was taken up in dichloromethane (10 ml). The solution was shaken with aq. sodium thiosulfate (5 ml). Satd. sodium bicarbonate (5 ml) was added and the mixture shaken again. The organic layer was separated, dried (MgSO₄) and evaporated to give 3-*N*-benzylaminopropyl benzoate **31** (0.028 g, 53%) as an oil, which gradually solidified to give a white solid m.p. 133-136 °C dec.. IR (nujol) 3400 (N-H), 2923, 2853 (C-H), 1723 (C=O); ¹H-NMR (500 MHz, CDCl₃): δ = 7.90-7.87, 7.53-7.47 and 7.38-7.18 (m, 10H_{arom}), 6.43 (bs, 1H, NH), 4.33 (t, 2H, J = 5.9 Hz, H-1), 4.05 (s, 2H, NCH₂Ph), 2.97 (t, 2H, J = 7.4 Hz, H-3), 2.28 (m, 2H, H-2); ¹³C-NMR (125 MHz, CDCl₃): δ = 166.79 (C=O), 133.26, 131.36, 130.14, 129.65, 129.55, 129.42, 129.22, 129.06, 128.50 and 128.40 (C_{arom}), 61.78 (C-1), 51.51 (NCH₂Ph), 43.95 (C-3), 26.24 (C-2); ES-MS: *m/z* (%) = 256.2 (15), 270.1 (100) [M + H]⁺; HRMS: *m/z* calcd. for C₁₇H₂₀NO₂ [M + H]⁺: 270.1494; found: 270.1485.

Preparation of (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(benzyloxy)propane 23

Phenylalaninol **16** (0.30 g, 0.90 mmol) and sodium hydride (0.072 g, 60% dispersion in mineral oil, 1.8 mmol) were placed under argon. Dry DMF (3 ml) was added, followed by benzyl bromide (117 µl, 0.99 mmol). The mixture was stirred for 18 h. At the end of this time TLC (hexane/ethyl acetate 8:2) showed complete disappearance of starting material and

formation of a single product. Water (20 ml) was added dropwise until effervescence ceased. The mixture was extracted with ether (3x20 ml). The ether extracts were dried (MgSO₄), evaporated, taken up in dichloromethane (20 ml), re-dried (MgSO₄) and evaporated. The residue was chromatographed on silica gel using hexane/ethyl acetate 95:5 to give (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(benzyloxy)propane **23** (0.338 g, 89%) as a colourless oil. $[\alpha]_D^{27.9}$ -38.6 ($c = 1$, CHCl₃); IR (film) 3083, 3060, 3025 (Ar C-H), 2922, 2853, 2798 (C-H); ¹H-NMR (500 MHz, CDCl₃): $\delta = 7.46$ -7.23 and 7.17-7.11 (m, 20H_{arom}), 4.56 (dd, 1H, $J = 4.6$ Hz, $J = 11.9$ Hz, OCHHPh), 4.51 (dd, 1H, $J = 4.5$ Hz, $J = 11.7$ Hz, OCHHPh), 3.86 (m, 4H, N(CH₂Ph)₂), 3.64 and 3.70 (2xm, 2H, H-1), 3.23 (m, 1H, H-2), 2.94 and 3.00 (2xm, 2H, H-3); ¹³C-NMR (125 MHz, CDCl₃): $\delta = 140.40$, 140.29, 138.59, 129.43, 128.56, 128.35, 128.29, 128.08, 128.04, 127.45, 127.41, 126.59 and 125.74 (C_{arom}), 73.02 (PhCH₂O), 70.23 (C-1), 58.83 (C-2), 54.31(PhCH₂N), 34.58 (C-3); ES-MS: m/z (%) = 422.3 (100) [M + H]⁺; HRMS: m/z calcd. for C₃₀H₃₂NO [M + H]⁺: 422.2484; found: 422.2441.

*Reaction of (S)-(-)-2-(dibenzylamino)-3-phenyl-1-(benzyloxy)propane **23** with NIS (2 equivalents)*

NIS (0.074 g, 0.33 mmol) and activated powdered 4 Å molecular sieves (0.15 g) were placed under argon. A solution of **23** (0.070 g, 0.17 mmol) in dichloromethane (3 ml) was added. The reaction mixture was stirred at room temperature and very quickly became dark maroon. After 45 min TLC (hexane/ethyl acetate 7:3) showed complete disappearance of starting material. After 1 h the reaction mixture was diluted with dichloromethane (15 ml) and shaken with aq. sodium thiosulfate (15 ml). 880 ammonia (2 ml) was added and the mixture shaken

again. The aqueous phase was re-extracted with dichloromethane (2x15 ml). The organic extracts were dried (MgSO₄) and evaporated to give 0.063 g crude product. This was chromatographed on silica gel. Elution with hexane/ethyl acetate 8:2, first gave an 8:1 mixture of (S)-(-)-2-(benzylamino)-3-phenyl-1-(benzyloxy)propane **24** and **18** (0.010 g). Further elution gave **24** (0.033 g). Estimated yield of **18**: 0.3%; estimated yield of **24**: 78%. Data for **24**: [α]_D^{29.3} -4.0 (*c* = 1.65, CHCl₃); IR (film) 3331 (N-H), 3083, 3060, 3025 (Ar C-H), 2919, 2853 (C-H); ¹H-NMR (500 MHz, CDCl₃): δ = 7.41 -7.17 (m, 15H_{arom}), 4.53 (d, 1H, *J* = 11.9 Hz, OCHHPh), 4.51 (d, 1H, *J* = 11.9 Hz, OCHHPh), 3.86 (bs, 2H, NCH₂Ph), 3.49 (dd 1H, *J* = 4.8 Hz, *J* = 9.3 Hz, H-1), 3.44 (dd, 1H, *J* = 5.7 Hz, *J* = 9.4 Hz, H-1'), 3.09 (m, 1H, H-2), 2.89 (dd, 1H, *J* = 6.4 Hz, *J* = 13.6 Hz, H-3), 2.83 (dd, 1H, *J* = 7.1 Hz, *J* = 13.4 Hz, H-3'), 1.90 (bs, 1H, NH); ¹³C-NMR (125 MHz, CDCl₃): δ = 140.43, 139.02, 138.30, 129.30, 128.33, 128.32, 128.02, 127.66, 127.57, 126.79 and 126.12 (C_{arom}), 73.12 (PhCH₂O), 71.56 (C-1), 58.00 (C-2), 51.40 (PhCH₂N), 38.15 (C-3); ES-MS: *m/z* (%) = 332.38 (100) [M + H]⁺; HRMS: *m/z* calcd. for C₂₃H₂₆NO [M + H]⁺: 332.2014; found: 332.2039.

Preparation of (S)-(-)-2-(dibenzylamino)-3-phenylpropyl benzoate 17

The phenylalaninol **16** (0.50 g, 1.5 mmol) and DMAP (0.012 g, 0.15 mmol) were placed under argon. Dry THF (6 ml) was added, followed by triethylamine (0.84 ml, 6 mmol). Benzoyl chloride (380 μ l, 3.3 mmol) was added dropwise. A white precipitate formed immediately. The mixture was stirred for 18 h. TLC then showed complete disappearance of starting material **16**. About two thirds of the THF was removed *in vacuo* and the residue taken up in ether (100 ml). The ether solution was washed with water (20 ml) and dried

MgSO₄), evaporated, taken up in dichloromethane (20 ml), re-dried (MgSO₄) and evaporated. The residue was chromatographed on silica gel using hexane/ethyl acetate 95:5 to give (S)-(-)-2-(dibenzylamino)-3-phenylpropyl benzoate **17** (0.493 g) as a colourless oil. $[\alpha]_D^{29.2}$ -43.3 ($c = 1$, CHCl₃); IR (film) 3083, 3061, 3026 (Ar C-H), 2929, 2833, 2801 (C-H), 1714 (C=O); ¹H-NMR (500 MHz, CDCl₃): $\delta = 8.08$ (m, 2H, *o*-C₆H₅CO), 7.63 (m, 1H, *p*-C₆H₅CO), 7.51 (m, 2H, *m*-C₆H₅CO), 7.23-7.36 and 7.14-7.17 (m, 15H_{arom}), 4.62 (dd, 1H, $J = 7.3$ Hz, $J = 11.6$, H-1), 4.36 (dd, 1H, $J = 4.4$ Hz, $J = 11.6$ Hz, H-1'), 3.89 (d, 2H, $J = 13.8$ Hz, N(CHHPh)₂), 3.83 (d, 2H, $J = 13.8$ Hz, N(CHHPh)₂), 3.43 (m, 1H, H-2), 3.18 (dd, 1H, $J = 6.1$ Hz, $J = 13.8$ Hz, H-3), 2.83 (dd, 1H, $J = 8.5$ Hz, $J = 13.8$ Hz, H-3'); ¹³C-NMR (125 MHz, CDCl₃): $\delta = 166.47$ (C=O), 134.73, 139.33, 132.93, 130.19, 129.62, 129.24, 128.61, 128.38, 128.34, 128.27, 128.15, 126.85 and 126.12 (C_{arom}), 63.76 (C-1), 58.29 (C-2), 53.91 (N(CH₂Ph)₂), 34.09 (C-3); ES-MS: m/z (%) = 458.2 (100) [M + Na]⁺, 436.2 (50) [M + H]⁺, 314.2 (25); HRMS: m/z calcd. for C₃₀H₃₀NO₂ [M + H]⁺: 436.2277; found 436.2297. Further elution gave a mixture of **17** and benzoyl chloride. Estimated yield of **17**: 79%.

Reaction of (S)-(-)-2-(dibenzylamino)-3-phenylpropyl benzoate 17 with NIS (3 equivalents)

NIS (0.076 g, 0.34 mmol) and activated powdered 4Å molecular sieves (0.15 g) were placed under argon. A solution of **17** (0.049 g, 0.11 mmol) in dichloromethane (3 ml) was added. The reaction mixture was stirred at room temperature and gradually became dark maroon. After 3.5 h TLC (hexane/ethyl acetate 7:3) showed the presence of both product and unreacted starting material. After the reaction mixture had been stirred for a further 18 h, the TLC was little changed. The reaction mixture was diluted with dichloromethane (15 ml) and

shaken with satd. sodium thiosulfate (10 ml). 880 ammonia (10 ml) was added and the mixture shaken again. The aqueous phase was re-extracted with dichloromethane (15 ml). The organic extracts were dried (MgSO_4) and evaporated to give 0.055 g crude product. This was chromatographed on silica gel. Elution with hexane/ethyl acetate 9:1 gave unreacted **17** (0.007 g, 14%) then hexane/ethyl acetate 7.5:2.5 gave **18** (0.30 g, 77%) then ethyl acetate. gave impure 2-amino-3-phenylpropyl benzoate **19** as an oil (0.004 g, 9%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.05-7.06 (m, 10H_{arom}), 4.32 (dd, 1H, J = 4.3 Hz, J = 11.0, H-1), 4.17 (dd, 1H, J = 6.8 Hz, J = 11.0 Hz, H-1'), 3.45 (m, 1H, H-2), 2.89 (dd, 1H, J = 5.6 Hz, J = 13.4 Hz, H-3), 2.70 (dd, 1H, J = 8.2 Hz, J = 13.6 Hz, H-3'), 1.72 (bs, 1H, NH_2); ES-MS: m/z (%) = 278.1 (20) $[\text{M} + \text{Na}]^+$, 256.1 (100) $[\text{M} + \text{H}]^+$.

*Reaction of methyl 2-N-benzylamino-3-benzoyl-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **3** with NaOMe/MeOH*

The glucosamine **3** (0.05g, 0.106 mmol) was dissolved in dry methanol (5 ml) under argon and NaOMe (0.1 M in MeOH, 300 μl , 0.3 mmol) was added. After 24 h (hexane/ethyl acetate 8:2) TLC showed that all the starting material had reacted. Silica gel (1 g) was added and the mixture stirred in air for 15 min. It was evaporated and the residue taken up in dichloromethane (5 ml) and re-evaporated. This procedure was repeated. The residue was purified by flash chromatography (hexane/ethyl acetate 3:2) to give **2** (0.39 g, 99%).

*Reaction of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **1** with 1) NIS (3 equivalents) 2) NaOMe/MeOH*

Glucosamine derivative **1** (0.10 g, 0.21 mmol), NIS (0.146 g, 0.65 mmol) and activated powdered 4Å molecular sieves (0.25 g) were stirred under nitrogen in dry dichloromethane (5 ml). After 4 h TLC (hexane:ethyl acetate, 8:2) showed loss of starting material and formation of mainly **3**, with small amounts of **2** and **6**. The reaction mixture was diluted with dichloromethane (50 ml), washed (aq. sodium thiosulfate 10 ml; satd. aq. sodium bicarbonate 10 ml), dried (anhydrous MgSO_4), filtered and the solvent removed. The resulting residue was either passed through a short silica plug (5 x 5 cm, hexane:ethyl acetate, 8:2) or used crude. After co-evaporation with toluene (3 x 20 ml) it was dissolved in dry methanol (5 ml) under nitrogen. A solution of NaOMe (0.1 M in MeOH, 1.2 ml, 1.2 mmol) was added dropwise. After 20 h, TLC showed loss of **3**. The reaction mixture was stirred with Dowex-H⁺ (0.1 g) and then purified by flash chromatography (hexane:ethyl acetate, 6:4. to give **2** (0.078 g, 98%).

*Reaction of methyl 2-amino-3-benzoyl-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **5** with NaOMe/MeOH*

The glucosamine **5** (0.018 g, 0.046 mmol) was placed under argon. Dry methanol (2 ml) was added, followed by NaOMe (0.1 M in MeOH, 132 μl , 0.132 mmol). The reaction mixture was stirred for 18 h. At the end of this time TLC (ethyl acetate) showed complete disappearance of starting material. The reaction was stirred with Dowex-H⁺ (0.05g), filtered

and the solvent removed. The final crude product was purified by chromatography using ethyl acetate and then dichloromethane/methanol 9:1 to give **4** (0.013 g, 100%) identified by comparison of the ^1H -NMR spectrum with that of an authentic sample.¹ ^1H -NMR (400 MHz, CDCl_3): δ = 7.47-7.41 and 7.34-7.29 (m, 5H_{arom}), 5.47 (s, 1H, CHPh), 4.61 (d, J = 3.4 Hz, 1H, H-1), 4.20 (dd, J = 4.1 Hz, J = 9.5 Hz, 1H), 3.78-3.61 (m, 3H), 3.40 (t, J = 9.2 Hz, 1H), 3.34 (s, 3H, OCH_3), 2.72 (dd, J = 3.7 Hz, J = 9.5 Hz, 1H), 1.90 (bs, 1H, OH).

Reaction of methyl 2,2-N,N-dibenzylamino-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside 1 with 1) NIS (10 equivalents) 2) NaOMe/MeOH

1 (0.075 g, 0.16 mmol), NIS (0.37 g, 1.6 mmol), 2,6-lutidine (20 μl) and 4 Å molecular sieves (0.5 g) were placed under argon in DCM (1 ml) and cooled to 0 °C. TESOTf (18 μl , 0.09 mmol) was added and the mixture warmed to room temperature. After 4.5 h the reaction mixture was diluted with dichloromethane (50 ml), washed (aq. sodium thiosulfate 50 ml, satd. aq. sodium bicarbonate 50 ml, water 50 ml and brine 50 ml), dried (anhydr. MgSO_4), filtered and the solvent removed. The resulting oil was partially purified using a silica plug (EtOAc eluant) and dissolved in dry methanol (10 ml) under nitrogen. A solution of NaOMe (0.1 M in MeOH, 1.5 ml, 1.5 mmol) was added dropwise. After 20 h, TLC showed loss of **3**. The reaction mixture was stirred with Dowex-H+ (0.15g) and then purified by flash chromatography (dichloromethane:methanol, 9:1) to give **4** (0.029 g, 64%).

Reaction of methyl 2-N-benzylamino-3-tert-butylidimethylsilyloxy-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside 8 with TBAF

The glucosamine **8** (0.025 g, 0.051 mmol) was placed under argon. Dry THF (1 ml) was added, followed by TBAF (0.31 ml, 1 M solution in THF, 0.31 mmol). After 16 h TLC (hexane/ethyl acetate 7:3) showed the presence of starting material and product. A further portion of TBAF (0.1 ml, 0.1 mmol) was added. After a further 5 h the TLC had only changed slightly so a further portion of TBAF (0.31 ml, 0.31 mmol) was added. The mixture was stirred for a further 16 h. Undried THF (1 ml) and silica gel (0.1 g) were added. The mixture was stirred in air for 30 min, evaporated and the residue chromatographed with hexane/ethyl acetate 6:4 to give **2** (0.018 g, 95%).

*Reaction of methyl 2-amino-3-tert-butyldimethylsilyloxy-4,6-O-benzylidene-2-deoxy- α -D-glucopyranoside **9** with TBAF*

The glucosamine **9** (0.025 g, 0.063 mmol) was placed under argon. Dry THF (1 ml) was added, followed by TBAF (0.31 ml, 1 M solution in THF, 0.31 mmol). After 16 h TLC (hexane/ethyl acetate 7:3) showed the disappearance of starting material. Undried THF (1 ml) and silica gel (0.1 g) were added. The mixture was stirred in air for 30 min, evaporated and the residue chromatographed with ethyl acetate (fractions 1-9) and then dichloromethane/methanol 9:1 to give **4** (0.013 g, 73%).

Factor: 1.00000 Constant: 0.00000 Offset: 0.00000 [G]

Supplementary Table 1. Comparison of the debenzylations – Full version.

Entry	Dibenzylamine R-NBn ₂	I ⁺ source	Equiv	Condi ons ^a	Additive lequiv	Time (h)	R-NHBn 2,8,11,2 1,23,26, 28,31	Yield (%) ^d R-NH ₂ 4,9,1 2,22	R-NBnBz 6	Other
1		NIS	1	A	-	96	50 (100)			50 1
2	1	NIS	2	A	-	20	59	-	-	37 3
3	1	NIS	2	A	-	168	54	-	-	23 3
4	1	NIS/TESOTf	2	A	TTBP	20	50	-		29 3
5	1	NIS/TESOTf	2	A	-	20	42	-	-	21 3
6	1	NIS	2	A	TEMPO ^c	15min	47	-	-	7 3
7	1	NIS	3	A	-	4	50			50 3
8	1	NIS	3	C	-	4	98	-	-	-
9	1	NIS	3	A	-	20	42	-	7	22 3
10	1	I ₂	3	A	-	48	54 (68)			20 1
11	1	NIS	6	B	-	20	-	-	46	21 5
12	1	NIS	10	A	-	24	-	-	58	33 5
13	1	NIS	10	B	-	20	-	-	39	52 5
14	1	NIS	10	B	-	168	-	-	50	-
15	1	NIS/ TESOTf ^b	10	A	lutidine	4	-	-	30	68 5
16	1	NIS/ TESOTf ^b	10	C	lutidine	4	-	64	-	-
17	1	NIS/TESOTf ^b	10	B	lutidine	2	-	-	68	5 5
18		NIS	3	A	-	4	87	-	-	-
19	7	NIS	10	A	-	4	-	63	-	-
20	7	NIS	10	B	-	4	-	72	-	-
21	7	NIS	5	B	-	2	-	87	-	-
22	7	NIS	3	A	TEMPO ^c	15min	75	10		-

23		NIS	6	A	-	24	-	79		
	8									
24		NIS	3	B	-	24	23 (29)	28 (35)	-	20 10
	10									
25	10	NIS	10	B	-	4	-	50	-	-
26		NIS	3	A	-	4	88	-	-	-
	20									
27	20	NIS	10	B	-	20		42	-	-
28	20	NIS	6	B	-	18		65		
29		NIS	3	A	-	5	83	-	-	-
	25									
30		NIS	3	A	-	5	85	-	-	-
	27									
31		NIS	3	A		20		51		
	28									
32		NIS	3	A	-	5	-	-	-	69 18
	16									
33		NIS	3	A	-	5	-	-	-	53 31
	30									
34		NIS	3	A	-	1	60	-	-	20 18
	23									
35	23	NIS	2	A	-	1	78	-	-	1 18
36		NIS	3	A	-	18	77 (90)	9	-	14 17
	17									

a. Reaction Conditions: **A**: "dry" - 4Å sieve, dry DCM, room temperature, under dry N₂; **B**: "wet" - DCM, room temperature, open to atmosphere or addition of up to 1 eq H₂O; **C**: conditions **A** then NaOMe, MeOH.
b. 0.5 eq of TESOTf
c. 1 eq TEMPO
d. Isolated yield Yield in parentheses indicates yield based on recovered starting material.

Automation directory: /export/home/vnmr1/automation/Thur0401_auto
 File: /data/m40307/04100520-01

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Sample #5
 File: /data/m40307/04100520-01
 Mercury-400BB "mudd"

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 4.000 sec
 Width 6393.9 Hz
 8 repetitions
 OBSERVE H1, 399.9694235 MHz
 DATA PROCESSING
 FT size 131072
 Total time 0 min, 43 sec

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
File: /data/c50205/21171650-02
Processed on "Korn"

Pulse 45.0 degrees
Acq. time 3.982 sec
Width 6286.3 Hz
16 repetitions
OBSERVE H1 499.9049563 MHz
DATA PROCESSING
F1 size 65536
Total time 1 min, 4 sec

EJG Expt 94 Fr 7-28

Pulse Sequence: s2pu1

Solvent: cdcl3

Ambient temperature

User: 1-14-87

File: /data/tempdat/21171650-03

Processed on "huple"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.399 sec

Width 31446.5 Hz

10000 repetitions

OBSERVE C13, 125.7011969 MHz

DECOUPLE H1, 499.9074048 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 12 hr, 14 min, 38 sec

EJG Expt 258 Fr 15-23

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

Sample #31

File: /data/m20308/14164905.fid

Mercury-200 "natel"

Relax. delay 1.000 sec

Pulse 30.1 degrees

Acq. time 8.000 sec

Width 3194.000 Hz

16 repetitions

OBSERVE H1 199.9906252 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 32768

Total time 21 min, 5 sec

EJG Expt 72 EtOAc wash

Pulse Sequence: szpu1
Solvent: cdcl3
Ambient temperature
File: /data/tempdat/18162740-02
Processed on "huple"

Pulse 45.0 degrees
Acq. time 4.000 sec
Width 4498.4 Hz
16 repetitions
OBSERVE H1 399.9694217 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 4 sec

Handwritten:
M to 0 to 2 H₂O
B₂O
5

EJG Expt 72 EtOAc wash

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

File: /data/tempdat/18162740-03

Processed on "hupie"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

10000 repetitions

OBSERVE C13, 100.5723855 MHz

DECOUPLE H1, 399.9714119 MHz

Power 39 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 11 hr, 41 min, 22 sec

129.798
128.883
128.380
128.132
126.085

133.148
129.828

137.083

166.295

101.382

79.726

77.320
77.206
77.000
76.684

74.248

69.094

62.899

55.732

55.435

ppm

Pulse Sequence: s2pul1

Solvent: dmsO

Ambient temperature

File: /data/c50207/08152635-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 3.992 sec

Width 6286.3 Hz

16 repetitions

OBSERVE H1, 499.9072797 MHz

DATA PROCESSING

FT size 65536

Total time 1 min, 4 sec

EJG Expt 72B fr 10-20

Pulse Sequence: s2pul1

Solvent: dmsc

Ambient temperature

User: 1-14-87

File: /data/c50207/08152635-03

Processed on "korn"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.399 sec

Width 31446.5 Hz

2000 repetitions

OBSERVE C13, 125.7017555 MHz

DECOUPLE H1, 499.9097793 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 2 hr, 26 min, 55 sec

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

File: /data/150302/06165035-02

Processed on "nicholas"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 4.100 sec

Width 4918.8 Hz

16 repetitions

OBSERVE HI, 499.7786793 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 0 min, 0 sec

3.442

5.409

7.384
7.379
7.375
7.367
7.327
7.312
7.297
7.229

32.26

7

6

5

4

3

2

1

ppm

13.08

0.04

20.55

0.28

0.01

0.04

2.29

29.15

2.26

0.02

EJG Expt 175 Fr 8-11

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: /data/tempdat/06165035-03

Processed on "huple"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.314 sec

Width 31421.8 Hz

1024 repetitions

OBSERVE C13 125.7694542 MHz

DECOUPLE H1 400.7811684 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total time 1 hr, 13 min, 43 sec

17

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: /data/c50212/19162851-02

Processed on "nicholas"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 4850.8 Hz

32 repetitions

OBSERVED F1: 499.8853627 MHz

DATA PROCESSING

FT size: 65536

Total time 2 min, 8 sec

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

File: /data/c50301/03163126-02

Processed on "nicholas"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5344.0 Hz

32 repetitions

OBSERVE H1, 499.8853644 MHz

DATA PROCESSING

FT size 65536

Total time 2 min, 8 sec

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 User: 1-14-87
 File: /data/tempdat/03163126-03
 Processed on "hupie"

Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.400 sec
 Width 31421.8 Hz
 10000 repetitions
 OBSERVE C13, 125.6962797 MHz
 DECOUPLE H1, 499.8878616 MHz
 Power 42 dB,
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 131072
 Total time 12 min, 49 sec

Fig. 21-2003-27

173/5-7

7.270
7.212

3.405

0.905

0.095

5.4

3.3

3.2

3.5

2.1

1.5

1.1

1.1

1.0

0.7

0.4

0.1 0.2

0.5

0.5

0.4

0.5

0.4

Instrument MXX500
Sarah Ward 1609 27/05/03

Current Data Parameters
NAME 16092705
EXNO 1
PROCNO 1

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F2 - Acquisition Parameters
Date_ 20030528
Time 8.07
INSTRUM axes500
PROBHD 5 mm Multina
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2502
DS 2
SWH 31333.132 Hz
FIDRES 0.508626 Hz
AQ 0.481090 sec
RG 32768
CW 15.000 usec
DE 21.43 usec
TE 100.0 K
HLL 1 dB
D1 2.0000000 sec
CPDPRG waltz16
P1 100.00 usec
S4 25 dB
D11 0.030000 sec
S2 19 dB
P1 7.10 usec
SFO1 125.7138502 MHz
NUC1 13C
F2 - Processing parameters
SI 32768
SF 125.7200912 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ID NMR plot parameters
CX 35.00 cm
FIP 215.000 ppm
F1 27029.82 Hz
F2P -5.000 ppm
F2 -628.60 Hz
PRGCM 6.23571 ppm/cm
HSCM 790.34060 Hz/cm

Instrument DOX400
Chemist SJW
Group BGD
174B/3-9
c13acq.au CDC13 e\ DPchemist 28

Page 55

75.00 Hz
B20
12

133.35
129.63
128.49

167.67

100.41

78.74
77.31
76.48
71.50
71.32

64.31

55.16
56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

64.31

55.16

56.46

25.88

18.33

-5.43

100.41

133.35

129.63

128.49

78.74

77.31

76.48

71.50

71.32

Ph-OBz
Bz
17

EJG Expt 212 Fr 8-11
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: /data/c50306/02124217-02
Processed on "nicholas"
Pulse 45.0 degrees
Acq. time 3.394 sec
Width 6211.2 Hz
32 repetitions
OBSERVE H1: 300.136 MHz
DATA PROCESSING
FT size 65536
Total time 2 min 8 sec

Automation directory: /export/home/vnmr1/automation/Mon0201_auto
File: /data/c50306/02124217-03

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Sample #2, user 1-14-87

File: /data/c50306/02124217-03
INOVA-500 "Off"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.397 sec

Width 31483.7 Hz

448 repetitions

OBSERVE C13, 125.6962443 MHz

DECOUPLE H1, 499.8876616 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 32 min, 53 sec

EJG Expt2278 Fr 6-11

Pulse Sequence: s2p1

Solvent: CDCl3

Ambient temperature

File: /data/c50306/174813-02

Processed on "micromas"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5130.8 Hz

Repetition time 1.200 sec

Number of scans 128

Observed width 17.85 Hz

Decoupling program WALTZ16

FT size 65536

Total time 0 min. 32.0 sec

3.809
3.777

8

7

6

5

4

3

2

1

ppm

62.11

0.25 0.05 0.02

17.85

13.24

0.01 0.24 4.86

1.04 0.26

0.07

Automation directory: /export/home/vnmr1/automation/Tue1702_auto
 File : /data/c50306/17174813-03

Pulse Sequence: s2pul

Solvent: CDCl3
 Ambient temperature
 Sample #5, user 1-14-87
 File: /data/c50306/17174813-03
 INOVA-500 "off"

Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.400 sec
 Width 31421.8 Hz
 256 repetitions
 OBSERVE C13, 125.6962443 MHz
 DECOUPLE H1, 499.8878616 MHz
 Power 42 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 131072
 Total time 18 min, 48 sec

Automation directory: /export/home/vnmr1/automation/Tuel003_auto
File : /data/m40306/10155257-01

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Sample #3

File: /data/m40306/10155257-01
Mercury-4008B "mudd"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 6393.9 Hz

8 repetitions

OBSERVE H1, 399.9694097 MHz

DATA PROCESSING

DATA PROCESSING
FT size 131072

Total time 0 min, 43 sec

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: /data/c50303/26163250-02
 Processed on "korn"

Pulse 45.0 degrees
 Acq time 4.000 sec
 Width 4783.3 Hz
 32 repetitions
 OBSERVE H1 499.8853901 MHz
 DATA PROCESSING
 File size 65536
 Total time 2 min, 8 sec

ppm

EJG Expt 182 Fr 6-8

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: /data/c50303/26163250-03

Processed on "cathcart"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.440 sec

Width 31421 Hz

10000 repetitions

OBSERVE C13 82.5 6962806 MHz

DECOUPLE H1 488.8878616 MHz

Power 42 dB

continuously on

VALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 12 hr, 14 min, 49 sec

77.252
77.000
76.744

129.472

126.516

125.680

140.603

140.626

62.623
60.411

54.445

34.140

25.932

18.177

-5.511
-5.576

140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

c1ccc(cc1)CC[C@H](N)CCOSi(F)(F)F

Solvent: CDC13

Ambient temperature

File: /data/c50304/07

Processed on "korn"

False 43.0 degrees
Acq. time 4.000 sec

width 337.0 Hz
32 repetitions

DATA PROCESSING
ET size 65536

FT size 65536
Total time 2 min 8 s

LOCAL TIME 2 MILL, 0 3

000-0

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

File: /data/c50304/07163251-03

Processed on "huple"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.400 sec

Width 31421.8 Hz

10000 repetitions

OBSERVE C13, 125.6962816 MHz

DECOUPLE H1, 499.8878616 MHz

Power 42 dB

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 125.30 min, 14 min, 49 sec

129.300

128.992

128.000

127.748

126.798

126.066

140.443

139.291

64.000

59.926

51.432

37.890

18.219

-5.412

-5.427

25.890

18.219

37.890

51.432

59.926

64.000

77.256
77.000
76.748-5.412
-5.427

ppm

Pulse Sequence: s2pul1

Solvent: CDC13

Ambient temperature

File: /data/m40308/12152807-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.003 sec

Width 3858.0 Hz

32 repetitions

OBSERVE H1, 399.9694181 MHz

DATA PROCESSING

FT size 131072

Total time 2 min, 8 sec

pk γ -OSi= 2H_v 22

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Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: /data/m40308/12152807-03

Processed on "korn"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.189 sec

Width 25125.6 Hz

10000 repetitions

OBSERVE C13, 100.5723921 MHz

DECOUPLE H1, 399.9714119 MHz

Power 39 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 11.000 hr, 41 min, 22 sec

Ph c1ccc(cc1)C2=CC=CC=C2
 2Bn
 23

EJG Expt 222 Fr 7-9

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: /data/c50306/17093219-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5752 Hz

32 repd 4 scans

OBSERVE on 499.8853621 MHz

DATA PROCESSING

FT size 165536

Total time 2 min, 8 sec

EJG Expt2278 Fr 6-11

Pulse Sequence: s2p1

Solvent: CDCl3

Ambient temperature

File: /data/c50306/174813-02

Processed on "micromas"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5130.8 Hz

Repetition time 1.200 sec

Repetition delay 0.200 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

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0.000 sec

0.000 sec

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0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

0.000 sec

3.809
3.777

62.11

0.25 0.05 0.02

17.85

13.24

0.01 0.24 4.86

1 1.04 0.26

0.07

ppm

Automation directory: /export/home/vnmr1/automation/Tue1702_auto
 File : /data/c50306/17174813-03

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Sample #5, user 1-14-87
 File: /data/c50306/17174813-03
 INOVA-500 "off"

Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.400 sec
 Width 31421.8 Hz
 256 repetitions
 OBSERVE C13, 125.6962443 MHz
 DECOUPLE H1, 499.8878616 MHz
 Power 42 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 131072
 Total time 18 min, 48 sec

EJG Expt 227 EtOAc wash

Automation directory: /export/home/vnmr1/automation/Tue1003_auto
File: /data/m40306/10155257-01

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Sample #3

File: /data/m40306/10155257-01
Mercury-400BB "mudd"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 6393.9 Hz

8 repetitions

OBSERVE H1 399.9694097 MHz

DATA PROCESSING

FT size 131072

Total time 0 min, 43 sec

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: /data/c50303/26163250-02
 Processed on "korn"

Pulse 45.0 degrees
 Acq time 4.000 sec
 Width 4783.3 Hz
 32 repetitions
 OBSERVE H1 499.8853901 MHz
 DATA PROCESSING
 File size 65536
 Total time 2 min, 8 sec

EJG Expt 182 Fr 6-8

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: /data/c50303/26163250-03

Processed on "cathcart"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.440 sec

Width 31421 Hz

10000 repetitions

OBSERVE C13 82.5 6962806 MHz

DECOUPLE H1 488.8878616 MHz

Power 42 dB

continuously on

VALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 12 hr, 14 min, 49 sec

77.252
77.000
76.744

129.472

126.516

125.680

140.603

140.626

62.623
60.411

54.445

34.140

25.932

18.177

-5.511
-5.576

140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

File: /data/c50304/07163251-03

Processed on "huple"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.400 sec

Width 31421.8 Hz

10000 repetitions

OBSERVE C13, 125.6962816 MHz

DECOUPLE H1, 499.8878616 MHz

Power 42 dB

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 125.30 min, 14 min, 49 sec

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Pulse Sequence: s2pul1

Solvent: CDCl3

Ambient temperature

File: /data/m40308/12152807-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.003 sec

Width 3858.0 Hz

32 repetitions

OBSERVE H1, 399.9694181 MHz

DATA PROCESSING

FT size 131072

Total time 2 min, 8 sec

pk γ -OSi= 2H_v 22

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Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: /data/m40308/12152807-03

Processed on "korn"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.189 sec

Width 25125.6 Hz

10000 repetitions

OBSERVE C13, 100.5723921 MHz

DECOUPLE H1, 399.9714119 MHz

Power 39 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 11.00 hr, 41 min, 22 sec

Ph c1ccc(cc1)C2=CC=CC=C2
 2Bn
 23

EJG Expt 222 Fr 7-9

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: /data/c50306/17093219-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5752.5 Hz

32 repd 4.000 s

OBSERVE on 499.8853621 MHz

DATA PROCESSING

FT size 165536

Total time 2 min, 8 sec

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Sample #1, user 1-14-87

File: /data/c50306/16170600-03

INOVA-500 "Orr"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.400 sec

Width 31421.8 Hz

9792 repetitions

OBSERVE C13, 125.6962869 MHz

DECOUPLE H1, 499.8878616 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 11 hr, 59 min, 32 sec

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

File: /data/c50306/25152315-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.000 sec

ACQ: Time 4:00
Width 50391.1 HZ

Subscriptions

499.8853621 MHz

DATA PROCESSING

DATA PROCESSING
T. 5196. 65536

Total time 85536 min

Size of job	total time	2 min, 8 sec
1	2 min, 8 sec	
2	4 min, 16 sec	
3	6 min, 24 sec	
4	8 min, 32 sec	
5	10 min, 40 sec	
6	12 min, 48 sec	
7	14 min, 56 sec	
8	16 min, 64 sec	
9	18 min, 72 sec	
10	20 min, 80 sec	
11	22 min, 88 sec	
12	24 min, 96 sec	
13	26 min, 104 sec	
14	28 min, 112 sec	
15	30 min, 120 sec	
16	32 min, 128 sec	
17	34 min, 136 sec	
18	36 min, 144 sec	
19	38 min, 152 sec	
20	40 min, 160 sec	
21	42 min, 168 sec	
22	44 min, 176 sec	
23	46 min, 184 sec	
24	48 min, 192 sec	
25	50 min, 200 sec	
26	52 min, 208 sec	
27	54 min, 216 sec	
28	56 min, 224 sec	
29	58 min, 232 sec	
30	60 min, 240 sec	
31	62 min, 248 sec	
32	64 min, 256 sec	
33	66 min, 264 sec	
34	68 min, 272 sec	
35	70 min, 280 sec	
36	72 min, 288 sec	
37	74 min, 296 sec	
38	76 min, 304 sec	
39	78 min, 312 sec	
40	80 min, 320 sec	
41	82 min, 328 sec	
42	84 min, 336 sec	
43	86 min, 344 sec	
44	88 min, 352 sec	
45	90 min, 360 sec	
46	92 min, 368 sec	
47	94 min, 376 sec	
48	96 min, 384 sec	
49	98 min, 392 sec	
50	100 min, 400 sec	
51	102 min, 408 sec	
52	104 min, 416 sec	
53	106 min, 424 sec	
54	108 min, 432 sec	
55	110 min, 440 sec	
56	112 min, 448 sec	
57	114 min, 456 sec	
58	116 min, 464 sec	
59	118 min, 472 sec	
60	120 min, 480 sec	
61	122 min, 488 sec	
62	124 min, 496 sec	
63	126 min, 504 sec	
64	128 min, 512 sec	
65	130 min, 520 sec	
66	132 min, 528 sec	
67	134 min, 536 sec	
68	136 min, 544 sec	
69	138 min, 552 sec	
70	140 min, 560 sec	
71	142 min, 568 sec	
72	144 min, 576 sec	
73	146 min, 584 sec	
74	148 min, 592 sec	
75	150 min, 600 sec	
76	152 min, 608 sec	
77	154 min, 616 sec	
78	156 min, 624 sec	
79	158 min, 632 sec	
80	160 min, 640 sec	
81	162 min, 648 sec	
82	164 min, 656 sec	
83	166 min, 664 sec	
84	168 min, 672 sec	
85	170 min, 680 sec	
86	172 min, 688 sec	
87	174 min, 696 sec	
88	176 min, 704 sec	
89	178 min, 712 sec	
90	180 min, 720 sec	
91	182 min, 728 sec	
92	184 min, 736 sec	
93	186 min, 744 sec	
94	188 min, 752 sec	
95	190 min, 760 sec	
96	192 min, 768 sec	
97	194 min, 776 sec	
98	196 min, 784 sec	
99	198 min, 792 sec	
100	200 min, 800 sec	

Oldal címe / min, 0 sec

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Automation directory: /export/home/vnmr1/automation/Wed2501_auto
 File : /data/c50306/25152315-03

Pulse Sequence: s2pul

Solvent: CDCl₃
 Ambient temperature
 Sample #1, user 1-14-87
 File: /data/c50306/25152315-03
 INOVA-500 "orr"

Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.400 sec
 Width 31421.8 Hz
 5000 repetitions
 OBSERVE C13, 125.6962443 MHz
 DECOUPLE H1, 499.8878616 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 131072
 Total time 6 hr, 7 min, 24 sec

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: /data/c50303/25153812-02

Processed on "nicholas"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 6350.7 Hz

32 repetitions

OBSERVE H1, 499.8853861 MHz

DATA PROCESSING

FT size 65536

Total time 2 min, 8 sec

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EUG Expt 191 Fr 6-15

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: /data/c50303/25153812-03

Processed on "huple"

Relax. delay 3.000 sec

Pulse 45.0 degrees

Acq. time 1.400 sec

Width 31421.8 Hz

768 repetitions

OBSERVE C13, 125.6962797 MHz

DECOUPLE H1, 499.8878616 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 56 min, 26 sec

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: /data/c50303/24170609-02
 Processed on "nicholas"

Pulse 45.0 degrees
 Acq. time 4.000 sec
 Width 2395.2 Hz
 16 repetitions
 OBSERVE H1 499.8853758 MHZ
 DATA PROCESSING
 FI size 65536
 Total time 1 min, 4 sec

25.752

77.256
77.000
76.744

66.457
64.588
62.211
51.809

18.184

-5.519
-5.595

128.534
128.354
128.263
128.244
128.225

127.008

139.718
135.785

173.136

160 140 120 100 80 60 40 20 0 ppm

EJG Expt 193 Fr4-9
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: i-14-87
File: /data/c50303/24170609-03
Processed on "hupl"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.400 sec
Width 31421.8 Hz
10000 repetitions
OBSERVE C13, 125.6962801 MHz
DECOUPLE H1, 499.8878616 MHz
Power 42 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.7 Hz
FT size 131072
Total time 12 hr, 14 min, 49 sec

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: /data/c50309/16160556-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5310.7 Hz

32 repetitions

OBSERVE: H1, 499.8723462 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 0 sec

Pulse Sequence: s2pul1

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

File: /data/c50309/16160556-03

Processed on "Korn"

Relax. delay 3.000 sec

pulse 45.0 degrees

Acq. time 1.400 sec

Width 31421.8 Hz

10000 repetitions

OBSERVE C13, 125.6930040 MHz

DECOUPLE H1, 499.8748328 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.7 Hz

FT size 131072

Total time 12 hr, 14 min, 49 sec

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: /data/c50308/15111435-02

Processed on "korn"

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5785.8 Hz

32 repetitions

OBSERVE H1 499.8723765 MHz

DATA PROCESSING

FI size 65536

Total time 0 min, 0 sec

EJG Expt 195B Fr 20-33

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

User: 1-14-87

File: /data/c50308/15111435-03

Processed on "Korn"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.400 sec
Width 31421.8 Hz
10000 repetitions
OBSERVE C13, 125.6930069 MHz
DECOUPLE H1, 499.8748328 MHz
power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.7 Hz
FT size 131072
Total time 12 hr, 14 min, 49 sec

128.402
128.497
129.058
129.225
129.420
129.546
129.653
130.141

133.265
131.365

166.788

127.448

77.252
77.000
76.744

61.780

58.419

51.515

43.954

26.236

160 140 120 100 80 60 40 20 ppm