Supporting Information

Synthesis of α -Glucuronic Acid and Amide Derivatives in the Presence of a Participating 2-Acyl Protecting Group

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Experimental Section

General

NMR spectra were recorded with Varian Inova 300 and 500 spectrometers. Chemical shifts are reported relative to internal Me₄Si in CDCl₃ (δ 0.0) or HOD for D₂O (δ 4.63) for ¹H and (δ 77.0) for ¹³C. ¹³C Signals were assigned with the aid of DEPT and multiplicities are indicated in parentheses. Coupling constants are reported in hertz. IR spectra were recorded with a Mattson Galaxy Series FTIR 3000 using either thin film between NaCl plates or KBr discs, as specified. Melting points were measured on a Gallenkamp melting point apparatus. Elemental analysis was performed on an Exeter Analytical CE440 elemental analyser. Low and high resolution mass spectra were measured at the University of York, UK. TLC was performed on aluminium sheets precoated with Silica Gel 60 (HF₂₅₄, E. Merck) and spots visualized by UV and charring with H₂SO₄-EtOH (1:20). Flash Column Chromatography was carried out with Silica Gel 60 (0.040-0.630 mm, E. Merck) and using a stepwise solvent polarity gradient correlated with TLC mobility. Chromatography solvents used were EtOAc and MeOH (Riedel-deHaen) and petroleum ether (b.p. 40-60°C, BDH laboratory supplies) and CH₂Cl₂ reaction solvents were freshly distilled from calcium hydride.

Preparation of 4. D-Glucuronic acid (5.0 g, 25.24 mmol) was suspended in acetic anhydride (75 mL) and stirred at 0 °C. Iodine (350 mg, 1.65 mmol) was added slowly and the red solution was stirred for 2 h on ice and for further 3 h at room temperature. Acetic anhydride was mostly removed *in vacuo* and the remaining mixture taken up in dichloromethane (70 mL). The organic layer was then washed twice with Na₂S₂O₃ (1.0 M, 80 mL), dried, (MgSO₄) filtered and concentrated to afford **4** as a white solid (10.12 g, 99%). The β -anomer **1** can be separated from its α -anomer (present as minor impurity)

by recrystallization from dichloromethane/petroleum ether (70-80% yield); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 5.82 (d, 1H, $J_{1,2}$ 6.9, H-1), 5.38 (apt t, 1H, J = 9.0, H-4), 5.29 (apt t, 1H, J 8.5, H-3), 5.12 (dd, 1H, H-2), 4.34 (d, 1H, H-5), 2.28 (s, 3H, COOCOCH_3), 2.13, 2.06, 2.05, 2.04 (each s, each 3H, each COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 170.0, 169.5, 169.4, 168.8 165.0 (each s, each C=O), 91.6 (d, C-1), 73.3, 71.6, 70.4, 68.3 (each d, C-2—5), 22.2 (q, COOCOCH_3), 20.9, 20.4 (each q, each COCH_3), 20.7 (2 q, overlapping, each COCH_3); CI-HRMS: Found 422.1300, required 422.1299 $[\text{M}+\text{NH}_4]^+$.

Preparation of 1,2,3,4-Tetra-O-acetyl- β -D-glucopyranuronic acid 3: The anhydride **4** (9.61 g, 23.77 mmol) was dissolved in water and THF (180 mL, 1:2) and stirred overnight. The solution was concentrated and the product extracted into dichloromethane, dried on MgSO_4 and filtered. After evaporation *in vacuo* a white fluffy material was obtained and identified as **3** (7.81 g, 91%). Compound **3** can also be obtained more quickly stirring **4** in water/THF for 3 hours and evaporating the solvents directly from the reaction mixture without any workup (97-99% yield); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 5.80 (d, 1H, $J_{1,2}$ 7.5, H-1), 5.31 (m, 2H, H-3 and H-4 overlapping), 5.14 (m, 1H, $J_{2,3}$ 9.0, H-2), 4.24 (m, 1H, $J_{4,5}$ 9.5, H-5), 3.46 (br s, 1H, COOH), 2.12, 2.05, 2.04, 2.03 (each s, each 3H, each COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 170.2 (s, COOH), 169.9, 169.5, 169.1 (each s, each COCH_3), 91.5 (d, C-1), 72.7, 72.1, 70.4, 68.9 (each d, C-2—C-5), 20.9 (q, COCH_3), 20.7 (3 q, overlapping, each COCH_3); CI-LRMS: 380 $[\text{M}+\text{NH}_4]^+$, 320 $[\text{M}+\text{H}-\text{CH}_3\text{CO}]^+$, 303 $[\text{M}-\text{OAc}]^+$, 243 $[\text{M}+\text{H}-2\text{HOAc}]^+$.

Preparation of amides 6 and 7 from anhydride 4: To a solution of **4** in dry dichloromethane (0.1 g/mL) and under N_2 atmosphere an equivalent of primary amine is added, and the reaction mixture is stirred overnight. The product is extracted into dichloromethane and washed with HCl (dil.), NaHCO_3 (satd.) and deionised water and dried (MgSO_4). The organic layer was concentrated after filtration to afford the amide as a white solid which can be further purified by recrystallization from Et_2O (or dichloromethane/petroleum ether) or by column chromatography (EtOAc /pet.ether gradient).

Analytical data for 6: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.94 (s, 1H, NH), 7.47 (dd, 2H, J 8.2, J 1.1, Ar H), 7.32 (apt t, J 7.5, 2H, Ar H), 7.13 (apt t, 1H, Ar H), 5.85 (d, 1H, $J_{1,2}$ 7.3, H-1), 5.36 (m, 2H, H-3 and H-4), 5.16 (m, 1H, $J_{2,3}$ 8.9, H-2), 4.24 (m, 1H, $J_{4,5}$ 9.3, H-5), 2.14, 2.10, 2.07, 2.03 (each s, each 3H, each COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 170.0, 169.8, 169.5, 169.1 (each s, each COCH_3), 164.3 (s, CONH), 136.7 (s, Ar C ipso), 129.3 (d, Ar C-b and C-b'), 125.3 (d, Ar C-c), 120.7 (d, Ar C-a and C-a'), 91.9 (d, C-1), 73.7, 72.1, 70.8, 69.9 (each d, C-2—C-5), 21.0, 20.9 (each q, each COCH_3), 20.8 (2 q, overlapping, each COCH_3); CI-HRMS: Found 455.1663, required 455.1666 $[\text{M}+\text{NH}_4]^+$.

Analytical data for 7: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 6.10 (br d, 1H, $J_{\text{CH-NH}}$ 7.8, NH), 5.75 (d, 1H, $J_{1,2}$ 8.0, H-1), 5.30 (apt t, 1H, $J_{2,3}$ 9.0, $J_{3,4}$ 9.3, H-3), 5.18 (apt t, 1H, $J_{4,5}$ 9.7, H-4), 5.11 (dd, 1H, H-2), 4.02 (d, 1H, H-5), 3.96 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.14, 2.07, 2.02 (each s, each 3H, each COCH_3), 1.15 (d, 6H, J 6.6, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C-NMR}$ (CDCl_3): δ 170.0, 169.8, 169.5, 169.0 (each s, each COCH_3), 165.3 (s, CONH), 91.6 (d, C-1), 73.4, 72.3, 70.6, 69.3 (each d, C-2—C-5), 41.6 (d, $\text{CH}(\text{CH}_3)_2$), 22.7, 22.6 (each q, each $\text{CH}(\text{CH}_3)_2$), 21.0, 20.9 (each q, each COCH_3), 20.8 (2 q, overlapping, each COCH_3); CI-HRMS: Found 404.1556, required 404.1557 $[\text{M}+\text{H}]^+$.

Alternative procedure for preparation of amides from 3. Dicyclohexylcarbodiimide (1 eq) was added to a solution of **3** in dry dichloromethane (0.1 g / mL) at 0 °C and under N_2 . Formation of a white precipitate was observed and after 10 minutes the amine was added and after a further 60 minutes the reaction was judged complete as there was no starting material **3** (R_F = 0.0, EtOAc / petroleum ether 1:1) detected by TLC. The solution was diluted with dichloromethane, filtered and washed with NaHCO_3 (satd. aq.) and HCl (1 M). The organic layer was dried (MgSO_4) and solvent removed. This gave the amide product as a white solid. This was recrystallized from dichloromethane/petroleum ether or purified by column chromatography (EtOAc/pet.ether gradient).

Analytical data for 1,2,3,4-Tetra-*O*-acetyl- β -D-glucopyranuron-N-methyl-N-phenylamide

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.49 (apt t, 2H, J 8.0, Ar H), 7.41 (apt t, 1H, Ar H), 7.24 (d, 2H, Ar H), 5.57 (apt t, 1H, J 9.4, H-4), 5.31 (d, 1H, $J_{1,2}$ 8.0, H-1), 5.18 (apt t, 1H, J 9.4, H-2), 5.03 (apt t, 1H, J 9.4, H-3), 4.04 (d, 1H, $J_{4,5}$ 9.8, H-5), 3.30 (s, 3H, OCH_3), 2.11 (s, 3H, COCH_3), 1.98 (s, 6H, 2 COCH_3 , overlapping), 1.97 (s, 3H, COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 170.6, 169.1, 169.0, 168.8 (each s, each COCH_3), 164.8 (s, CONMePh), 142.4 (s, aromatic C), 130.3, 128.6, 127.1 (each d, aromatic CH), 91.8 (d, C-1), 73.0, 70.5, 70.1, 69.6 (each d, C-2—5), 37.9 (q, N CH_3Ph), 21.0 (q, COCH_3), 20.8 (two q, overlapping, each COCH_3), 20.7 (q, each COCH_3); CI-HRMS: Found 474.1381, required 474.1376 $[\text{M}+\text{Na}]^+$.

Preparation of α -azides (Table 1)

TMSN₃ (2.5 eq.) and SnCl₄ (0.5 eq.) were added to a solution of the tetraacetate in anhydrous dichloromethane (0.1 g / mL) under N₂ and the reaction mixture was stirred overnight (15 h). The mixture was diluted with dichloromethane and the solution vigorously stirred for further 30-40 minutes in presence of an equal volume of satd. NaHCO₃. A white emulsion is formed and the organic and aqueous layers can be more easily separated after filtering through filter paper. **10** can be recovered from the aq. layer as the salt or as acid after acidification using Amberlite IR-120 and be purified further by column chromatography (EtOAc/MeOH gradient). For amides the products **12-14** are recovered from the organic extracts after drying (MgSO₄), removal of solvent and column chromatography (EtOAc / petroleum ether gradient).

Analytical data for 10: ¹H-NMR (300 MHz, D₂O): δ 5.85 (d, 1H, $J_{1,2}$ 4.0, H-1), 5.37 (apt t, 1H, J 9.2 H-3), 5.24 (apt t, 1H, J 9.2, H-4), 5.15 (dd, 1H, H-2), 4.67 (d, 1H, H-5), 2.13, 2.11, 2.08 (each s, each 3H, each COCH₃); ¹³C-NMR (D₂O): δ 173.7 (s, COOH), 173.3, 172.7, 172.6 (each s, each COCH₃), 85.6 (d, C-1), 71.7, 70.1, 69.8, 69.7 (each d, C-2—5), 20.4, 20.3, 20.2 (each q, each COCH₃); CI-HRMS: Found 368.0702, required 368.0706 [M+Na]⁺.

Analytical data for 12: ¹H-NMR (300 MHz, CDCl₃): δ 6.12 (br d, 1H, J_{CH-NH} 7.9, NH), 5.54 (apt t, 1H, J 9.8, H-3), 5.44 (d, 1H, $J_{1,2}$ 3.3, H-1), 5.06 (dd, 1H, $J_{4,5}$ 10.2, H-4), 4.76 (dd, 1H, H-2), 4.29 (d, 1H, H-5), 4.03 (m, 1H, CH(CH₃)₂), 2.11, 2.07, 2.02 (each s, each 3H, each COCH₃), 1.18 and 1.16 (2 d, each 3H); ¹³C-NMR (CDCl₃): δ 170.3, 169.9, 169.8 (each s, each COCH₃), 165.7 (s, CONH), 86.3 (d, C-1), 70.4, 70.3, 69.5, 69.0 (each d, C-2—5), 41.5 (d, CH(CH₃)₂), 22.7, 22.6 (each q, each CH(CH₃)₂), 20.9, 20.8, 20.7 (each q, each COCH₃); CI-HRMS: Found 387.1511, required 387.1516 [M+H]⁺.

Analytical data for 13: ¹H-NMR (300 MHz, CDCl₃): δ 8.00 (s, 1H, NH), 7.48 (dd, 2H, J 8.5, J 1.1, aromatic H), 7.33 (apt t, 2H, J 7.5, aromatic H), 7.14 (apt t, 1H, J 7.5, aromatic H), 5.77 (d, 1H, J 4.2, H-1), 5.49 (apt t, 1H, J 9.8, H-3), 5.22 (apt t, 1H, $J_{4,5}$ 10.0, H-4), 4.96 (dd, 1H, H-2), 4.50 (d, 1H, H-5), 2.12, 2.09, 2.03 (each s, each 3H, each COCH₃); ¹³C-NMR (CDCl₃): δ 170.3, 169.9, 169.8 (each s, each COCH₃), 164.5 (s, CONH), 136.7 (s aromatic C), 129.3, 125.3, 120.7 (each d), 86.3 (d, C-1), 70.5, 70.3, 69.4, 69.0 (each d, C-2—5), 20.9, 20.8, 20.7 (each q, each COCH₃); CI-HRMS: Found 421.1353, required 421.1359 [M+H]⁺.

Analytical data for 14: ¹H-NMR (300 MHz, CDCl₃): δ 7.49-7.43 (m, 3H, aromatic H), 7.34-7.23 (m, 2H, aromatic H), 5.54 (d, 1H, $J_{1,2}$ 4.5, H-1), 5.52 (apt t, 1H, H-4), 5.16 (apt t, 1H, J 10.0, H-3), 4.92 (dd, 1H, H-2), 4.48 (d, 1H, J 9.8, H-5), 3.30 (s, 3H, OCH₃), 2.03, 2.01, 1.99 (each s, each 3H, each COCH₃); ¹³C-NMR (CDCl₃): δ 170.5, 170.0, 168.9 (each s, each COCH₃), 165.7 (s, CONMePh), 142.5 (s, aromatic C), 130.2, 128.8, 127.5 (each d), 87.3 (d, C-1), 69.9, 69.8, 69.7, 67.3 (each d, C-2—5), 38.2 (q, NCH₃Ph), 20.9 (two q, overlapping, each COCH₃), 20.7 (q, COCH₃); CI-HRMS: Found 435.1512, required 435.1516 [M+H]⁺.

2,3,4-Tri-*O*-acetyl-1-azido-1-deoxy- β -D-glucopyranuronic acid 2. 2,3,4-Tri-*O*-acetyl-1-azido-1-deoxy- β -D-glucopyranuronic acid, methyl ester¹ (0.623 g, 1.73 mmol) was suspended in LiOH (0.1 M) which in MeOH/water/THF (2.5/1.0/0.5, 80 mL) at 0 °C and stirring was continued for 2 h. The mixture was diluted with water and the pH was adjusted to 2 using Amberlite IR-120. Filtration and evaporation of the solvents gave pure 1-azido-1-deoxy- β -D-glucopyranuronic acid (0.381 g, 100%). This material was then suspended in acetic anhydride (10 mL), in presence of sodium acetate (0.16 g, 1.87 mmol, 1.1 eq), and stirred for 6 days, after which the reaction did not seem to proceed further (monitoring by TLC). Water was added to the clear solution and after stirring for an hour the product was extracted with EtOAc. The organic layer was washed twice with water, dried (MgSO₄) and concentrated to afford a yellow oil. Chromatography (EtOAc/pet.ether gradient) gave 2,4-di-*O*-acetyl-1-azido-1-deoxy- β -D-glucopyranuronolactone (0.123 g, 25%). Lyophilisation of the aq. layer and chromatography of the residue (EtOAc/MeOH gradient) gave **2** as a white solid; ¹H-NMR (300 MHz, D₂O): δ 5.36 (apt t, 1H, *J* 9.5, H-3), 5.15 (apt d, 1H, *J* 9.8, H-4), 5.08 (d, 1H, *J*_{1,2} 9.0, H-1), 4.94 (apt t, 1H, H-2), 4.14 (d, 1H, *J* 10.1, H-5), 2.10, 2.05, 2.03 (each s, each 3H, each COCH₃); ¹³C-NMR (D₂O): δ 173.2 (s, COOH), 172.8, 172.7, 172.5 (each s, each COCH₃), 87.5 (d, C-1), 74.7, 72.9, 71.2, 69.9 (each d, C-2—5), 20.4, 20.3, 20.2 (each q, each COCH₃); CI-LRMS: 344 [M-H]⁺, 302 [M-H-N₃]⁺, 284 [M-H-HOAc]⁺.

Preparation of amides 15 and 16

Acid **2** is suspended in dry dichloromethane (0.02 g / mL) under N₂ atmosphere and cooled to 0 °C. Oxalyl chloride (1 eq.) and DMF (0.3-0.5 mL / mmol) are added and the reaction mixture is stirred for 30 minutes at 0 °C and for a further 2 h at room temperature. Evolution of gas is observed and when this had stopped the acyl chloride formation had completed. In a separate vessel amine (1 eq.) and pyridine (2 eq.) are dissolved in a small volume of dry dichloromethane and this solution is carefully transferred into vessel containing the acyl chloride. Stirring was continued for 45-60 minutes until TLC showed no more starting material. Satd. NaHCO₃ was added and the product was extracted into dichloromethane, washed with aq. 1.0 M HCl and brine, dried (MgSO₄) and the solvent removed. The amide was then recrystallized from an EtOAc:petroleum ether mixture.

Analytical data for amide 15: ¹H-NMR (300 MHz, CDCl₃): δ 8.03 (s, 1H, NH), 7.48 (dd, 2H, *J* 8.0, *J* 1.1, aromatic H), 7.34 (apt t, 2H, *J* 7.5, aromatic H), 7.15 (apt t, 1H, aromatic H), 5.34 (apt t, 1H, *J* 9.8, H-3), 5.26 (apt t, 1H, *J* 9.3, H-4), 4.99 (apt t, 1H, *J* 9.0, H-2), 4.85 (d, 1H, *J* 8.9, H-1), 4.15 (d, 1H, *J* 9.1, H-5), 2.10, 2.09, 2.02 (each s, each 3H, each COCH₃); ¹³C-NMR (CDCl₃): δ 168.8, 168.6, 168.2 (each s, each COCH₃), 162.8 (s, CONH), 135.4 (s, aromatic C), 128.1, 124.2, 119.8 (each d, aromatic CH), 87.0 (d, C-1), 73.7, 70.8, 69.6, 68.2 (each d, C-2—5), 19.6, 19.5, 19.4 (each q, each COCH₃); CI-HRMS: Found 421.1355, required 421.1359 [M+H]⁺.

¹ von Roedern, E. G.; Lohof, E.; Hessler, G.; Hoffmann, M.; Kessler, H. *J. Am. Chem. Soc.* **1996**, *118*, 10156- 10167.

Analytical data for amide 16: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.43-7.35 (m, 3H, aromatic H), 7.25-7.21 (m, 2H, aromatic H), 5.47 (apt t, 1H, J 9.5, H-4), 4.95 (apt t, 1H, J 9.5, H-3), 4.80 (apt t, 1H, J 8.8, H-2), 4.04 (d, 1H, J 8.8, H-1), 3.90 (d, 1H, H-5), 3.24 (s, 3H, OCH_3), 1.93, 1.92, 1.91 (each s, each 3H, each COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 169.4, 167.9, 167.6 (each s, each COCH_3), 163.1 (s, CONMePh), 141.2 (s, aromatic C), 128.9, 127.6, 126.5 (each d, aromatic C), 87.5 (d, C-1), 71.7, 71.0, 69.2, 68.1 (each d, C-2—5), 36.8 (q, NCH_3Ph), 19.6, 19.5, 19.4 (each q, each COCH_3); CI-HRMS: Found 435.1518, required 435.1516 $[\text{M}+\text{H}]^+$.

2,3,4-Tri-O-acetyl- β -D-glucopyranurono-6,1-lactone 17:

1,2,3,4-Tetra-O-acetyl- β -D-glucopyranuronic acid **3** (0.3 g, 0.83 mmol) was dissolved in dry dichloromethane (10 mL) under N_2 atmosphere, SnCl_4 (0.05 mL, 0.5 eq.) was added and the reaction mixture was left stirring overnight. The solution was then diluted with dichloromethane and an equal volume of satd. NaHCO_3 added, forming a thick white emulsion. This was stirred for 30-40 minutes and filtered using paper and the organic and aqueous layer were then more easily separated. The organic layer was washed with satd. NaHCO_3 , dried (MgSO_4) and concentrated: a white solid was recovered and identified as **17**² (0.12 g, 48%); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 5.88 (m, 1H, H-1), 4.89 (m, 1H, H-3), 4.76 (m, 1H, H-4), 4.72 (dd, 1H, $J_{1,2}$ 1.5, $J_{2,3}$ 1.5, H-2), 4.55 (apt t, 1H, $J_{3,4}$ 2.0, $J_{4,5}$ 2.0, H-5), 2.12 (s, 6H, 2 COCH_3 , overlapping), 2.04 (s, 3H, COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 169.6, 169.5, 168.7 (each s, each COCH_3), 168.0 (s, COO), 100.6 (d, C-1), 71.3, 69.2, 66.3, 66.1 (each d, C-2—5), 20.9 (q, COCH_3), 20.8 (2 q, overlapping, each COCH_3); CI-HRMS: Found 320.0984, required 320.0982 $[\text{M}+\text{NH}_4]^+$.

2,3,4-Tri-O-acetyl-1-chloro-1-deoxy- α -D-glucopyranuron-N-phenylamide 18

1,2,3,4-Tetra-O-acetyl- β -D-glucopyranuronic acid **3** (0.3 g, 0.83 mmol) was dissolved in dry dichloromethane (10 mL) under N_2 atmosphere, SnCl_4 (0.05 mL, 0.5 eq.) was added and the reaction mixture was left stirring overnight. The solution was then diluted with dichloromethane and an equal volume of satd. NaHCO_3 added, forming a thick white emulsion. This was stirred for 30-40 minutes and filtered using paper and the organic and aqueous layer were then more easily separated. The organic layer was washed with satd. NaHCO_3 , dried (MgSO_4) and concentrated. Chromatography gave **18** (30%); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.89 (s, 1H, NH), 7.46 (d, 2H, J 7.9, aromatic H), 7.33 (apt t, 2H, aromatic H), 7.14 (apt t, 1H, J 7.5, aromatic H), 6.42 (d, 1H, $J_{1,2}$ 4.0, H-1), 5.66 (apt t, 1H, J 10.0, H-3), 5.31 (apt t, 1H, H-4), 5.03 (dd, 1H, H-2), 4.64 (d, 1H, $J_{4,5}$ 10.4, H-5), 2.12, 2.11, 2.06 (each s, each 3H, each COCH_3); $^{13}\text{C-NMR}$ (CDCl_3): δ 170.1, 169.8, 169.7 (each s, each COCH_3), 163.8 (s, CONH), 136.5 (s, aromatic C), 126.2, 125.6, 120.1 (each d, aromatic CH), 88.9 (d, C-1), 70.8, 70.7, 68.8, 68.7 (each d, C-2—5), 20.8, 20.7, 20.6 (each q, each COCH_3).

² Takeda, Y., Akimoto, T., *Carbohydr. Res.*, **1982**, 106, 175.

2,3,4-Tri-*O*-acetyl-1-*O*-isopropyl- α -D-glucopyranuronic acid **23.** Lactone **17** (0.200 g, 0.662 mmol) was dissolved in dry dichloromethane (10 mL) under N₂ atmosphere; freshly distilled isopropanol (0.13 mL, 2.5 eq), TMSOTf (0.30 mL, 2.5 eq.) and SnCl₄ (0.04 mL, 0.5 eq) were added respectively, and the reaction was left stirring overnight (18 hs). The crude solution was diluted with dichloromethane, filtered through Celite and then usual work up followed: satd. NaHCO₃ (50 mL) was added and the two layers were easily separated. The aqueous layer was washed with dichloromethane and acidified with Amberlite IR-120, after adjusting the pH to 2 it was possible to extract **23** into EtOAc. Drying (MgSO₄) and removal of solvent gave **23** (102 mg, 43%); ¹H-NMR (300 MHz, CDCl₃): δ 5.53 (apt t, 1H, *J* 10.0, H-3), 5.29 (d, 1H, *J*_{1,2} 3.8, H-1), 5.20 (apt t, 1H, *J* 10.1, H-4), 5.40-5.00 (br s, 1H, COOH), 4.83 (dd, 1H, H-2), 4.43 (d, 1H, H-5), 3.91 (m, 1H, CH(CH₃)₂), 2.06, 2.05, 2.03 (each s, each 3H, each COCH₃), 1.27, 1.14 (each d, each 3H, *J* 6.0, CH(CH₃)₂); ¹³C-NMR (CDCl₃): δ 171.3 (s, COOH), 170.4 (s, COCH₃), 170.2 (2 s, overlapping, each COCH₃), 94.5 (d, C-1), 72.0, 70.8, 69.7, 67.9 (each d, C-2—5), 29.8 (d, CH(CH₃)₂), 23.3, 21.6 (each q, each CH(CH₃)₂), 20.8 (q, COCH₃), 20.7 (two q, overlapping, each COCH₃); CI-HRMS: Found 380.1559, required 380.1557 [M+NH₄]⁺.

2,3,4-Tri-*O*-acetyl-1-*O*-phenyl- α -D-glucopyranuronic acid **24.** Lactone **17** (0.80 g, 2.65 mmol) was dissolved in dry dichloromethane (10 mL) under N₂; SnCl₄ (0.15 mL, 0.5 eq) and phenol (0.78 g, 2.5 eq) were added. The reaction was stirred overnight, diluted with dichloromethane, stirred again in presence of saturated aqueous NaHCO₃ (20 mL) for 1 h and filtered through paper. When the organic and aqueous layers were separated, the majority of carbohydrate product was found to be in the aqueous layer, therefore the latter was freeze-dried to give a white solid which included salts (1.336 g). NMR analysis showed this to be mainly the sodium salt of **24**, contaminated by some phenol and other inorganic salts. This solid was redissolved in water and the pH adjusted to 2 with Amberlite IR-120. The product was then extracted into EtOAc, dried (MgSO₄) concentrated and recrystallized from dichloromethane / petroleum ether to give **24** (0.672 g, 64%); ¹H-NMR (300 MHz, CDCl₃): δ 8.15 (br s, 1H, COOH), 7.30 (dd, 2H, *J* 8.9, *J* 7.1, aromatic H), 7.09 (m, 3H, aromatic H), 5.81 (d, 1H, *J*_{1,2} 3.5, H-1), 5.76 (apt t, 1H, *J*_{2,3} 10.0, *J*_{3,4} 9.5, H-3), 5.31 (dd, 1H, *J*_{4,5} 10.1, H-4), 5.07 (dd, 1H, H-2), 4.49 (d, 1H, H-5), 2.06, 2.05, 2.04 (each s, each 3H, each COCH₃); ¹³C-NMR (, CDCl₃): δ 171.1 (s, COOH), 170.6, 170.5, 170.3 (each s, each COCH₃), 156.3 (s, aromatic C), 130.0, 123.7, 116.9 (each d, aromatic CH), 94.7 (d, C-1), 70.4, 69.7, 69.6, 68.5 (each d, C-2—5), 20.9, 20.8, 20.7 (each q, each COCH₃); CI-HRMS: Found 414.1397, required 414.1400 [M+NH₄]⁺.

2,3-Di-O-acetyl-1-O-phenyl- Δ^4 - α -D-glucopyranuronic acid

The sodium salt of **24** (1.34 mmol), obtained as described above, was suspended in acetic anhydride/pyridine 1:1 (10 mL) and stirred for 3 days in presence of DMAP (cat.). Most of the solvents were evaporated *in vacuo*, the crude material was extracted into EtOAc, washed with water, dried (MgSO₄) and the solvent was removed to give a brown-red oil which was the anhydride (0.332 g, 66%); ¹H-NMR (300 MHz, CDCl₃): δ 7.15 (apt, 2H, *J* 8.5, aromatic H), 7.09 (m, 3H, aromatic H), 6.24 (d, 1H, *J*_{3,4} 3.1, H-4), 5.84 (m, 2H, H-1 and H-3), 5.31 (dd, 1H, *J* 2.6, *J* 8.1, H-2), 2.25 (s, 3H, COOCOCH₃), 2.13, 2.12 (each s, each 3H, each COCH₃); ¹³C-NMR (CDCl₃): δ 170.3, 170.2 (each s, each COCH₃), 166.6 (s, COOCOCH₃), 165.4 (s, COOCOCH₃), 156.5 (s, aromatic C), 141.2 (s, C-5), 130.0, 123.9, 117.3 (each d, aromatic CH), 112.0 (d, C-4), 96.0 (d, C-1), 68.7, 66.4 (each d, C-2 and C-3), 21.1, 20.9 (each q, each COCH₃). This intermediate (0.150 g, 0.396 mmol) was stirred in water/THF (1:2, 7.5 mL) for 3h. The solvents were removed *in vacuo* to give a white solid (0.142 g) which was further purified on a short column of silica gel (EtOAc/MeOH gradient as eluant) to give **25** (0.106 mg, 80%); ¹H-NMR (300 MHz, CD₃OD): δ 7.31 (dd, 2H, *J* 8.7, *J* 7.2, aromatic H), 7.14 (m, 3H, aromatic H), 7.06 (apt t, 1H, aromatic H), 6.01 (d, 1H, *J*_{3,4} 2.9, H-4), 5.88 (d, 1H, *J*_{1,2} 2.7, H-1), 5.81 (dd, 1H, *J*_{2,3} 8.1, H-3), 5.29 (dd, 1H, H-2), 2.10, 2.09 (each s, each 3H, each COCH₃); ¹³C-NMR (CD₃OD): δ 170.9 (s, COOH), 170.6 (2 s, overlapping, each COCH₃), 156.9 (s, aromatic C), 129.5, 123.1, 117.2 (each d, aromatic CH), 105.1 (d, C-4), 95.9 (d, C-1), 69.4, 67.2 (each d, C-2 and C-3), 19.8, 19.5 (each q, each COCH₃);); CI-LRMS: 335 [M-H]⁻.

Preparation of 1-O-Phenyl- Δ^4 - α -D-glucopyranuronic acid 25. 2,3-Di-O-acetyl-1-O-phenyl- Δ^4 - α -D-glucopyranuronic acid (0.064 g, 0.190 mmol) was suspended in LiOH 0.1N (10 mL) in MeOH/water/THF (2.5/1.0/0.5) at 0 °C (ice-bath) and stirred for 2 h. The solution was diluted with water and acidified to pH 2 using Amberlite IR-120. Removing the solvents gave pure 1-O-phenyl- Δ^4 - α -D-glucopyranuronic acid **20** (48 mg, 99%); ¹H-NMR (300 MHz, D₂O): δ 7.33 (dd, 2H, *J* 8.0, *J* 7.5, aromatic H), 7.10 (m, 3H, aromatic H), 6.02 (d, 1H, *J*_{3,4} 2.9, H-4), 5.72 (d, 1H, *J*_{1,2} 2.6, H-1), 4.50 (dd, 1H, *J*_{2,3} 7.8, H-3), 3.93 (dd, 1H, H-2); ¹³C-NMR (D₂O): δ 166.8 (s, COOH), 156.4 (s, aromatic C), 142.2 (s, C-5), 130.2, 123.9, 117.8 (each d aromatic CH), 111.4 (d, C-4), 98.2 (d, C-1), 70.0, 66.1 (each d, C-2 and C-3); CI-HRMS: Found 270.0976, required 270.0978 [M+NH₄]⁺.

NI sopr. amide, mt, column.
STANDARD 1H OBSERVE

exp4 .szput

7

SAMPLE
date Apr 22 2002 temp 30.0
solvent cdc13 gain not used
file /export/home/~ hsf 0.008
publ1c/auto_22.04~ hsf 9.000
1.02/P.-Murphy-25~ pw90 9.150
01-f1d atfa
ACQUISITION
sw 4798.2 11
at 3.744 1n
np 35928 dp
fb 3000 hs
bs 16
dl 1.000 fn
nt 16
ct 16
TRANSMITTER
tn H1
sfreq 299.890 rfp
iof 599.7
lpwr 57 1p
pw 4.500
DECOUPLER
dn C13
dof 0
dm vs
dmm th
dpmr c
dmf 33
100d3
SPECIAL
not used
0.008
9.000
9.150
FLAGS
n
y
nn
not used
not used
DISPLAY
1071.9
800.3
307.7
53.1
2.2
PLOT
250
0
739
18
ph

AS 8.2
STANDARD 1H OBSERVE

300 MHz, CDCl₃

expd s2pu1

Ac₂O
OAc
OAc
4

4

SAMPLE SPECIAL
date Feb 11 2002 temp 30.0
solvent cdcl3 gain not used
file /export/home/~ hst 20
public/auto_11.02.~ spin 0.008
02/P_Murphy_07_01~ pw90 9.000
fid alfa 9.150

ACQUISITION FLAGS
sw 4798.2 11
at 3.744 1n
np 35928 dp
fb 3000 hs
bs 16
dl 1.000 fn
nt 8 not used
ct 8
tn 8
sfreq 299.890 f1
tof 589.6 f2
tpwr 57 1p
pw 4.500 PLOT
DECOUPLER WC 250
dn C13 SC
dot 0 VS
dm 0 vs
dmm nmh th
dpwr 33 cdc ph
dmt 10043

PROCESSING
not used
nm
nm
nm

DISPLAY
568.3
1297.7
304.7
-24.3
-26.9

4

Pulse Sequence: szpul
 Solvent: cdcl3
 Temp. 30.0 C / 303.1 K
 Sample #20
 File: P_Murphy_20_02
 Date: Oct 8 2001
 INOVA-300 "sunucd300"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.139 sec
 Width 25000.0 Hz
 1024 repetitions
 OBSERVE C13, 75.4069355 MHz
 DECOUPLE H1, 299.8897221 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 37 min, 41 sec

ml-b acid from 3rd anh.
STANDARD 1H OBSERVE

exp4 szpul

SAMPLE

SPECIAL

30.0

not used

20

0.008

9.000

9.150

1.02/P.-Murphy.09

01-fid

atfa

ACQUISITION

4788.2

11

1

1

1

1

1

1

1

1

1

1

1

1

3

Acid
OAK

date May 1 2002 temp gain not used
solvent cdcl3 gain 20
file /export/home/~ hst
public/auto.01.05~ hst
1.02/P.-Murphy.09~ pw90
01-fid atfa
ACQUISITION
sw 4788.2 11
at 3.744 1n
nd 35928 dp
fd 3000 hs
bs 16
dl 1.000 fn
nt 16 not used
ct TRANSMITTER H1 485.6
tn 299.890 f1 1365.2
tof 599.7 f1 308.1
tpwr 57 tp -31.2
pw 4.500 0.3
DECOUPLER C13 WC 250
dn C13 SC 0
dof 0 VS 65
dm nmh th 4
dmm C
dpwr 33
dmf 10043

Pulse Sequence: szpu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 Sample #24
 File: P_Murphy_24_02
 Date: Oct 10 2001
 INOVA-300 "snucl300"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1024 repetitions
 OBSERVE C13, 75.4069395 MHz
 DECOUPLE H1, 299.8897221 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 37 min, 41 sec

3

300 MHz, CDCl₃

mt-Anamide, recr.
STANDARD 1H OBSERVE

exp2 s2pul

6

SAMPLE
date May 22 2002
solvent cdcl3
file /net/sunucd30-
0/export/home/vnmr-
3/vnmr-sys/data/pub-
11c/aut_22.05.02/~
P_murphy_10_01.f1~
SPECIAL 30.0
not used
0.008
9.000
9.150
P_murphy_10_01.f1~
ACQUISITION
sw 4798.2
at 3.744
np 35928
fb 4000
bs 16
nt 16
ct 16
TRANSMITTER
tn H1
sfreq 299.890
tof 599.7
tqwr 57
pw 4.500
DECOUPLER C13
dn 0
dof 0
dm nmh
dmm c
dpr 33
dnt 10043
PROCESSING
not used
545.6
1924.1
308.1
-35.0
1.0
PLOT
wc 250
sc 0
vs 66
th 3
al cdc
ph

Pulse Sequence: s2pu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_03_02
 INOVA-500 "sunucddds1"
 PULSE SEQUENCE
 Relax: delay 1.000 sec
 Pulse: 45.0 degrees
 Acq: time 1.199 sec
 Width 18850.1 Hz
 2000 Repetitions
 OBSERVE C13, 75.4069355 MHz
 DECOUPLE H1, 259.8897221 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 1 hr, 13 min, 36 sec

6

Pulse Sequence: szpu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_35_02
 INOVA-500 "sunucddsi"
 PULSE SEQUENCE
 Relax delay 1.000 sec
 Pulse 45.0 degrees
 Acq time 1.39 sec
 Width 25000 Hz
 1024 repetitions
 OBSERVE G13, 75.4069355 MHz
 DECOUPLE H1, 293.887221 MHz
 Power 58 db
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 37 min, 41 sec

D₂O, 300 MHz

10

Pulse Sequence: s2pu1
 Solvent: D2O
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_34_02
 INOVA-500 "sunucds1"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.199 sec
 Width 18850.1 Hz
 5000 repetitions
 OBSERVE C13 75.4071293 MHz
 DECOUPLE H1 299.8904528 MHz
 Power 58 dB
 continuously ON
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 3 hr, 4 min, 0 sec

mt-13d-fastest spot
STANDARD 1H OBSERVE

exp2 szpul

SAMPLE

date Nov 11 2001

solvent cdc13

file /export/home/~

public/autol0.11.~

01/p_murphy_03_02~

fid

alpha

ACQUISITION

sw 3132.6

at 3.744

np 23456

fb 2000

bs 16

d1 1.800

nt 512

ct 512

TRANSMITTER

tn 289.889

sfreq -312.9

tof -312.9

tpwr 4.500

pw 4.500

DECOUPLER

dn C13

uof 0

dm 0

dmm mn

dpvr 33

dmt 10043

12

(CH₂)₂

15.69

6.0

5.8

5.6

5.4

5.2

5.0

4.8

4.6

4.4

ppm

33.00

17.38

18.08

15.85

Pulse Sequence: szpul
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_25_03
 INOVA-500 "sunucdcl3"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.19 sec
 Width 18850.1 Hz
 2000 repetitions
 OBSERVE C13, 75.4069355 MHz
 DECOUPLE H1, 299.8897221 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 85536
 Total time 1 hr, 13 min, 36 sec

12

100.00

Pulse Sequence: szpu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_24_02
 INOVA-500 "sunucds1"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.199 sec
 Width 18850.1 Hz
 2000 repetitions
 OBSERVE C13, 75.4069355 MHz
 DECOUPLE H1, 299.8897221 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 F1 size 65536
 Total time 1 hr, 13 min, 36 sec

13

mt-144
STANDARD 1H OBSERVE

exp4 s2put1

SPECIAL

date Jan 21 2002 temp 30.0
solvent cdc13 gain not used
file /export/home/~ hst 20
pub1c/aut0_21.01~ hst 0.008
02/P_Murphy_19.01~ pw90 9.000
.fid alfa 9.150

ACQUISITION

sw 4198.2 11
at 3.744 in
np 35928 dp
fb 3000 hs
bs 16
dl 1.900 fn
nt 8.8

PROCESSING

ct TRANSMITTER 8 sp 1136.5
tn 11 rfi 583.4
sfreq 299.890 rfp 300.2
tofr 399.6 tp -31.2
cpwr 4.500 tp 5.2
pw DECOUPLER C13 WC PLOT 250
dn C13 SC 0
dm 0 VS 0
dmm mn tn 376
dpwr al cdc ph 29
dmf

99.90

Pulse Sequence: s2pu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_13_02
 INOVA-500 "sunucds1"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1024 Repetitions
 OBSERVE C13 75.4070277 MHz
 DECOUPLE H1 299.8897221 MHz
 Power 38 dB
 Continuously on
 WAIT 2.18 sec
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 37 min, 41 sec

16

COOH, D₂O

mt-138-C(28-32)
STANDARD 1H OBSERVE

exp4 s2pu1

SAMPLE

SPECIAL

date Nov 24 2001 temp 30.0
solvent D2O gain not used
file /export/home/~ hst 0.008
public/auto.24.11.~ pw90 9.000
01/P_Murphy_04.01~ a1fa 9.150

ACQUISITION

FLAGS

sw 4798.2 11

not used

at 3.744 1n

nm

np 35928 dp

hs

td 3000

fn

bs 16

not used

d1 1.000

sp

nt 8

display

ct TRANSMITTER

548.2

tn

1146.9

sfreq 299.891

rfp

tof 599.6

rp

tpwr 57

157.3

pw 4.500

1P

DECOUPLER

250

dn C13

SC

dof 0

VS

dm 0

th

dmm nmh

at

dpwr C

cdc

dmf 10043

ph

COOH
A₃ X N₃
OK

2

Pulse Sequence: szpu1
Solvent: D2O
Temp: 30.0 C / 303.1 K
File: P_Murphy_04_02
INOVA-500 "sunucds1"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.19 sec
Width 18850.1 Hz
5000 repetitions
OBSERVE C13, 75.4071293 MHz
DECOUPLE H1, 299.8904928 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
Ft size 65536
Total time 3 hr, 4 min, 0 sec

2

CD0 31 300 MHz

mt-145-recr.?
STANDARD 1H OBSERVE

exp4 s2pul1

SAMPLE SPECIAL

date Jan 25 2002 temp 30.0

solvent cdc13 gain not used

file /export/home/~stn spin 20

public/auto 25.01~ hst 0.008

02/P..Murphy_20.01~ pw90 9.000

ACQUISITION .fid a1fa 9.150

SW 4798.2 11

AT 3.744 11

NP 35928 11

FB 3000 11

BS 16

DI 1.000 11

NE 32

CT 32

TRANSMITTER H1

STFQ 299.890

TOF 599.7

TPW 57

PW 4.500

DECOUPLER C13

DN 0

DOF 0

DM 0

DMM 33

DPWR 33

DMF 10043

PROCESSING

not used

nm

nm

nm

nm

nm

nm

nm

nm

nm

nm

nm

nm

nm

nm

nm

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nm

nm

15

Pulse Sequence: s2pu1
Solvent: cdcl3
Temp: 30.0 C / 303.1 K
File: P_Murphy_27_03
INOVA-500 "sunucddsl"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
1024 repetitions
OBSERVE C13 75.4070285 MHz
DECOUPLE H1 299.8897221 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FI size 65536
Total time 37 min, 43 sec

300 MHz, CDCl₃

mt-lact, ftoh, fccf
STANDARD IN OBSERVE

exp2 szpul

SAMPLE
date May 30 2002 temp 30.0
solvent cdcl3 gain not used
file /net/sunucd30- sp1n 20
0/export/home/vnmr- hst 0.008
3/vnmr/sys/data/pub- pvs0 9.000
1/c/auto_30.05.02/ a1fa 9.150
P_Murphy_12.01.f1~

SPECIAL
30.0
not used
20
0.008
9.000
9.150

FLAGS

17

ACQUISITION
sw 4798.2 dp 11
at 3.744 hs
np 35828 fn
fb 3000
bs 16
di 1.000 sb
nt 8 wp
ct 8 rff
TRANSMITTER
tn H1
sfra 299.890 1p
tofr 589.6 wc
tpwr 4.500 vs
pw DECOUPLER C13 th
dn 0 at
dof 0 cdc ph
dm nm
dmnm c
dmnm 33
dpwr 10043
dmf

PROCESSING
not used
not used
-50.5
2297.8
292.6
-10.0
250
24
4

DISPLAY

PLOT

250
24
4

6.80

7.05 14.14 6.84

43.92 21.24

ppm

Pulse Sequence: szpu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P_Murphy_23_02
 INOVA-500 "suncoads1"
 PULSE SEQUENCE
 Relax: delay 1.000 sec
 Pulse: 45.0 degrees
 Acq. time: 1.199 sec
 Width: 25000.0 Hz
 1024 repetitions
 OBSERVE C13, 75.4069355 MHz
 DECOUPLE H1, 299.8897221 MHz
 Power: 38 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening: 1.0 Hz
 FI size: 65536
 Total time: 37 min, 41 sec

17

mt-rxn120-27-cust.carbon
STANDARD 1H OBSERVE

exp4 s2pul

SAMPLE

SPECIAL

30.0

date Jun 29 2002

temp not used

solvent cdcl3

gain 20

file /export/home/~

spin 0.008

public/auto.29.06.~

hst 9.000

02/p..Murphy_02_01~

pw90 9.150

.fid alfa

9.150

ACQUISITION

FLAGS

sw 4798.2

11

at 3.744

in

np 35928

dp

fb 3000

hs

bs 16

not used

di 1.900

fn

nt 8

DISPLAY

ct TRANSMITTER

8 569.3

tn 298.890

rfi 1871.9

sfq 589.0

rfp 289.4

tof 57

tp 52.8

tpwr 4.500

ip 5.2

pw DECOUPLER

WC 250

dn C13

sc 0

dof 0

vs 145

dm nnn

th

dmm c

at cdc ph

dpwr 33

4

dmf 10043

10043

18

Pulse Sequence: s2pu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P.-Murphy_02_02
 INOVA-500 "sunucddsi"
 PULSE SEQUENCE
 Relax: delay 1.000 sec
 Pulse: 45.0 degrees
 Acq. time 1.189 sec
 Width 18850.1 Hz
 5000 repetitions
 OBSERVE C13: 75.4069355 MHz
 DECOUPLE H1: 253.6897221 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 3 hr, 4 min; 0 sec

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mt-rxn128-recf
STANDARD 1H OBSERVE

exp2 s2pu1

SAMPLE		SPECIAL	
date	Aug 21 2002	temp	30.0
solvent	cdcl3	gain	not used
file	/net/sunucd30~	spin	20
0/export/home/vnmr~	hst	0.008	
3/vmrsys/data/pub~	pw90	9.000	
1/c/auto_21.08.02/~	alfa	9.150	
P_Murphy_05_01.f1~			

ACQUISITION		PROCESSING	
sw	4798.2	dp	nm
at	3.744	hs	nm
np	35928	fn	not used
fb	3000	fn	not used
bs	16	sp	285.4
dt	1.000	wd	1719.3
nt	32	rfl	308.2
ct	32	rfl	-126.6

TRANSMITTER		PLOT	
tn	299.890	lp	2.6
strq	599.7	wc	250
tof	57	sc	0
lpwr	4.500	vs	102
pw		th	5

DECOUPLER		PLOT	
dn	0	cdc	ph
dof	nmn		
dm	nmn		
dmm	33		
dpwr	10043		
dmf			

W₂H
AcT
AcT
AcT
AcT

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Pulse Sequence: s2pul
Solvent: cdcl3
Temp: 30.0 C / 303.1 K
File: P_Murphy_01.02
INOVA-500 "nuucds1"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 18850.1 Hz
2000 repetitions
OBSERVE C13, 75.4069355 MHz
DECOUPLE H1, 299.8897221 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening, 1.0 Hz
FI size 65536
Total time 1 hr, 13 min, 36 sec

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mt-olfa 0Ph..frecr.?
STANDARD 1H OBSERVE

exp2 szpul

SAMPLE date May 13 2002 temp 30.0 SPECIAL

solvent cdc13 gain not used
file /export/home/~ spin 20
public/auto_13.05~ hst 0.008
02/P..Murphy_19.01~ pw90 9.000
ACQUISITION fid atfa 9.150

SW 4798.2 11 FLAGS n

at 3774 11 n

fb 35828 40 y

bs 3000 16 ns

di 1.000 8 fn not used

nt 8 8 DISPLAY 545.2

ct TRANSMITTER H1 WP 2035.9

in sfreq 299.890 rft 304.0

tof 539.6 rfp -36.0

tpwr 57 tp -0.2

pw 4.500 WC PLOT 250

dn C13 SC 0

dof 0 VS 0

dm nm th 51

dmm C 8

dpwr 33 al cdc ph

dmf 10043

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Pulse Sequence: szpu1
 Solvent: cdcl3
 Temp: 30.0 C / 303.1 K
 File: P. Murphy.19.02
 INOVA-500 "suncdcl3"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1024 repetitions
 OBSERVE C13, 75.4069355 MHz
 DECOUPLE H1, 299.8897221 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 37 min, 41 sec

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