Supporting Information

Formation and Reactivity of Novel Pyranosidic Nicholas Oxocarbenium Ions: Access to C-Ketosides and Branched-Chain C-Ketosides

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Materials and Methods. ^1H NMR spectra were recorded at 400 and 300 MHz, ^{13}C NMR spectra were recorded at 75 MHz, and chemical shifts are reported relative to internal Me_4Si . Optical rotations were determined for solutions in chloroform. Column chromatography was performed on silica gel (230-400 mesh). TLC was conducted in precoated Kiesel gel 60 F254 (Merck). Detection was first by UV light (254 nm) then charring with a 1/20/4 solution of sulfuric acid/acetic acid/ H_2O . All solvents were purified by standard techniques. Reactions requiring anhydrous conditions were performed under argon. Anhydrous magnesium sulfate was used for drying solutions. Starting alkynyl ketopyranosides were prepared from the corresponding aldono-lactone according to described procedures.¹¹

General Procedure for the Preparation of Cobalt-Complexed Propargyl Hemiketals 4-6. A solution of the corresponding alkynyl ketopyranoside (1 eq) in anhydrous CH_2Cl_2 was added to a solution of $\text{Co}_2(\text{CO})_8$ (1.2 eq) in CH_2Cl_2 (10 ml/mmol). The dark solution was stirred at room temperature until TLC showed complete formation of the complex (ca. 20 min). The solvent of the resulting reaction mixture was then removed under vacuum, and the residue was purified by flash chromatography.

General procedure for the coupling reaction of cobalt-complexed propargyl hemiketals. To a solution of the cobalt complex in dry CH_2Cl_2 and cooled to the appropriate temperature, freshly distilled (CaH_2) $\text{BF}_3 \cdot \text{OEt}_2$ was added dropwise. After 5 min of stirring, a dry CH_2Cl_2 solution of the nucleophile was added via cannula. The mixture was kept until no further progress was revealed by TLC analysis, and then quenched with saturated aqueous NaHCO_3 . The cooling bath was removed and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography.

General method for the demetalation reaction of the alkyne moiety.

Procedure A. A solution of an excess of I_2 in THF was added to a solution of the dicobalt hexacarbonyl complex in THF at 0 °C. The mixture was stirred at this temperature until no starting material was left (TLC analysis), quenched with saturated aqueous $Na_2S_2O_3$ solution, and extracted with Et_2O . The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography.

Procedure B. To a solution of the dicobalt hexacarbonyl complex in dry THF, NMO (3 eq) was added in one portion under argon atmosphere. After 3h the reaction mixture was filtered through a plug of silica gel eluting with ethyl acetate. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography.

Dicobalt hexacarbonyl complex 4.

Following the general procedure, complex **4** was prepared from 2,3,4,6-tetra-O-methyl-1-C-(2-phenylethynyl)-D-glucopyranose (504 mg, 1.5 mmol) and $Co_2(CO)_8$ (620mg, 1.8 mmol) in dry CH_2Cl_2 (15 mL). The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 9:1) to give a brownish oil (840mg, 90%); 1H -NMR (300MHz) δ 7.66 (m, 2H), 7.29 (m, 3H), 3.96 (ddd, 1H, J = 10.2, 4.2, 2.1 Hz), 3.66 (s, 3H), 3.58 (s, 3H), 3.59 (m, 2H), 3.32 (s, 3H), 3.31 (s, 3H), 3.49-3.24 (m, 2H); ^{13}C -NMR (75MHz) δ 199.6, 137.7, 130.3, 128.7, 127.9, 99.1, 98.5, 90.2, 86.7, 84.6, 80.2, 72.2, 71.3, 60.8, 60.6, 60.3, 59.1.

Dicobalt hexacarbonyl complex 5.

Complex **5** was prepared according to the general procedure from 2,3,4,6-tetra-O-benzyl-1-C-(2-phenylethynyl)-D-glucopyranose (967 mg, 1.5 mmol) and $\text{Co}_2(\text{CO})_8$ (620 mg, 1.8 mmol) in dry CH_2Cl_2 (15 mL). Silica gel chromatography (hexane/Ethyl acetate 9:1) provided pure **5** (1.35 g, 97%) as a brown syrup; ^1H -NMR (300 MHz) δ 7.59 (m, 2H), 7.12 (m, 23H), 5.01 (d, 1H, $J = 11.1$ Hz), 4.95 (d, 1H, $J = 11.1$ Hz), 4.85 (d, 1H, $J = 10.8$ Hz), 4.75 (m, 2H), 4.55 (d, 1H, $J = 11.1$ Hz), 4.45 (d, 1H, $J = 11.7$ Hz), 4.40 (d, 1H, $J = 11.4$ Hz), 4.20 (m, 1H), 4.12 (t, 1H, $J = 9.0$ Hz), 3.98 (d, 1H, $J = 9.6$ Hz), 3.90 (dd, 1H, $J = 10.5$, 3.3 Hz), 3.77 (m, 2H), 3.64 (bs, 1H); ^{13}C -NMR (75 MHz) δ 199.6, 138.2, 138.1, 138.0, 137.7, 137.2, 129.7, 128.6, 128.4, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.9, 99.1, 98.6, 89.9, 84.6, 83.3, 78.3, 75.5, 74.9, 74.1, 73.4, 71.9, 68.8.

Dicobalt hexacarbonyl complex 6.

Following the general procedure, complex **6** was prepared from 2,3,4,6-tetra-O-benzyl-1-C-(2-phenylethynyl)-D-glucopyranose (967 mg, 1.5 mmol) and $\text{Co}_2(\text{CO})_8$ (620 mg, 1.8 mmol) in dry CH_2Cl_2 (15 mL). The crude product was purified by silica gel chromatography (hexane/Ethyl acetate 95:5) to give a dark brownish oil (1.31g, 94%); ^1H -NMR (300 MHz) δ 7.57 (m, 2H), 7.14 (m, 23H), 4.99 (d, 1H, $J = 11.1$ Hz), 4.98 (d, 1H, $J = 11.4$ Hz), 4.79 (d, 1H, $J = 11.4$ Hz), 4.61 (d, 1H, $J = 11.4$ Hz), 4.57 (d, 1H, $J = 11.7$ Hz), 4.52 (d, 1H, $J = 11.7$ Hz), 4.45 (d, 1H, $J = 11.4$ Hz), 4.34 (d, 1H, $J = 11.1$ Hz), 4.32 (m, 1H), 4.22 (m, 2H),

4.05 (dd, 1H, $J = 9.3, 2.4$ Hz), 3.84- 3.76 (m, 2H), 3.66 (dd, 1H, $J = 8.7, 5.1$ Hz); ^{13}C -NMR (75MHz) δ 199.6, 139.0, 138.1, 137.9, 137.7, 137.4, 129.9, 128.5, 128.4, 128.1, 127.9, 127.9, 127.7, 127.7, 127.7, 127.5, 127.5, 127.3, 127.2, 127.1, 99.5, 99.0, 89.3, 82.3, 79.9, 74.6, 74.2, 73.5, 73.4, 71.8, 70.8, 68.0.

1-*C*-Cyano- β -2,3,4,6-tetra-*O*-methyl-1-*C*-(2-phenylethynyl)-D-glucopyranose (10):

Following the standard procedure, the cobalt complex **4** (100 mg, 0.16 mmol) was treated with trimethylsilyl cyanide **7** (40 μL , 0.32 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (20 μL , 0.16 mmol) in 5 mL of dry CH_2Cl_2) at 0 $^\circ\text{C}$. Silica gel chromatography (hexane: AcOEt 9:1) of the crude material afforded a new (single) compound (100 mg, 100%), which was demetalated using procedure A. Flash chromatography (hexane/EtOAc, 8:2) gave **10** (66 mg, 50 %) identical to the previously described^{11b} $[\alpha]_{\text{D}}^{21} = +45.9$ (c 0.65, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 3.48 (m, 6 H), 3.39 (s, 3 H), 3.54 (s, 3 H), 3.66 (s, 3 H), 3.74 (s, 3 H), 7.40 (m, 5 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ 59.7, 61.0, 61.7, 62.3, 70.7, 71.0, 76.8, 78.3, 82.6, 85.5, 85.7, 82.6, 87.3, 114.6, 121.0, 128.8 (x 2), 130.1, 132.4 (x 2) ppm. API-ES (positive): m/z 346.5 $[\text{M} + \text{H}]^+$. $\text{C}_{19}\text{H}_{23}\text{NO}_5$ (345.4): calcd. C 66.07, H 6.71, N 4.06; found C 65.94, H 6.92, N 3.95.

1-Azido- β -2,3,4,6-tetra-*O*-methyl-1-*C*-(2-phenylethynyl)-D-glucopyranose (11).

This compound was prepared according to the general procedure by treatment of cobalt complex **4** (100 mg, 0.16 mmol) with trimethylsilyl azide **8** (44 μ L, 0.32 mmol) and BF_3OEt_2 (20 μ L, 0.16 mmol) at -30°C . Work up and purification (hexane: AcOEt 8:2) gave the coupled product (105 mg, 100%), which was submitted to demetalation following procedure A. Purification by flash chromatography (hexane:AcOEt 9:1) gave **11** (35mg, 60%) identical to the previously described.^{11b} $[\alpha]_{\text{D}}^{21} = +61.9$ (c 1.08, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ 3.24 (m, 1 H), 3.37 (m, 1 H), 3.39 (s, 3 H), 3.52 (s, 3 H), 3.59 (m, 3 H), 3.63 (s, 3 H), 3.70 (s, 3H), 3.77 (m, 1 H), 7.35 (m, 5 H); ^{13}C NMR (50 MHz, CDCl_3): δ 59.5, 60.8, 61.3, 62.0 (4 x OMe), 70.9, 73.4, 78.9, 84.2, 86.2, 82.9, 88.0, 89.4, 121.2, 128.6 (x 2), 129.6, 132.4 (x 2). API-ES (positive): $m/z = 384.5$ $[\text{M} + \text{Na}]^+$; $\text{C}_{18}\text{H}_{23}\text{N}_3\text{O}_5$ (361.4): calcd. C 59.82, H 6.41, N 11.63; found C59.57, H 6.28, N 11.51

(2*R*, 3*S*, 4*S*) - 3, 5 – dimethoxy – 2 - (methoxymethyl) – 6 - (phenylethynyl) – 4 - (2 ,4, 6- trimethoxyphenyl) – 3, 4 –dihydro - 2H - pyran (12)

Following the standard procedure, the cobalt complex **4** (200 mg, 0.32 mmol) was treated with 1,3,5-trimethoxybenzene **9** (430 mg, 2.56 mmol) and $\text{BF}_3\cdot\text{OEt}_2$ (20 μ L, 0.16 mmol) in 5 mL of dry CH_2Cl_2) at -30°C and stirred for two hours.. Work up and purification (hexane: AcOEt 95:5) gave the coupled product which was (174 mg, 75%), demetalated with I_2 according to method A. Purification by flash chromatography (hexane:AcOEt 8:2) gave **12** (79mg, 74%); $[\alpha]_{\text{D}}^{21} = -77.1$ (c 1.1, CHCl_3). ^1H NMR (200 MHz, CDCl_3): δ 3.16 (s, 3H), 3.46 (s, 3H), 3.53 (s, 3H), 3.787 (m, 4H), 3.84 (s, 9H), 4.43 (d, 1H, $J = 8.0$ Hz), 6.18 (m, 2H), 7.38 (m, 3H), 7.47 (m, 2H). ^{13}C NMR (50 MHz, CDCl_3): δ 39.1, 55.2 (x 2), 56.1, 59.0, 59.3 (x 2), 71.5, 76.2, 79.1, 82.2, 91.5 (x 2), 92.4, 123.2, 126.9, 127.9, 128.1 (x

2), 128.3, 131.3 (x 2), 147.6, 159.8, 160.4 (x 2). API-ES (positive): $m/z = 477.5 [M + Na]^+$, 931.7 $[2M + Na]^+$. $C_{26}H_{30}O_7$ (454.2): calcd. C 68.71, H 6.65; found C 68.64, H 6.48.

(2*S*,3*R*,6*S*)-3,6-diallyl-5-methoxy-2-(methoxymethyl)-6-(phenylethynyl)-3,6-dihydro-2H-pyran (16)

This compound was prepared according to the general procedure by treatment of cobalt complex **4** (100 mg, 0.16 mmol) with allyltrimethylsilane **13** (32 μ L, 0.20 mmol) and BF_3OEt_2 (10 μ L, 0.08 mmol) at $-30\text{ }^\circ\text{C}$. Work up and purification (hexane: AcOEt 8:2) gave the coupled product (64 mg, 64%), which was submitted to demetalation following procedure A. Purification by flash chromatography (hexane:AcOEt 9:1) gave **16** (30 mg, 100%). $[\alpha]_D^{21} = +29.6$ (c 0.8, $CHCl_3$). 1H NMR (300 MHz, $CDCl_3$): δ 2.22 (m, 2H), 2.35 (m, 1H), 2.76 (m, 2H), 3.37 (s, 3H), 3.45 (dd, 1H, $J = 6.0, 9.8$ Hz), 3.60 (s, 3H), 3.63 (dd, 1H, $J = 7.0, 9.9$ Hz), 4.07 (dt, 1H, $J = 3.4, 6.8$ Hz), 4.85 (d, 1H, $J = 5.7$ Hz), 5.02-5.21 (m, 4H), 5.89 (m, 1H), 6.05 (m, 1H), 7.28 (m, 3H), 7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.7, 35.4, 42.2, 55.1, 59.4 (2 x), 71.7, 72.3, 73.5, 84.0, 89.7, 96.4, 116.3, 118.5, 123.2, 128.2, 128.4, 132.3, 133.3, 137.1, 154.7. API-ES (positive): $m/z = 339.3 [M+H]^+$, 361.3 $[M + Na]^+$. $C_{22}H_{26}O_3$ (338.4): calcd. C 78.07, H 7.74, found C 77.94, H 7.57.

(2*S*,3*R*,6*S*)-3,6-diallyl-5-benzyloxy-2-(benzyloxymethyl)-6-(phenylethynyl)-3,6-dihydro-2H-pyran (17)

Following the standard procedure, the cobalt complex **5** (250 mg, 0.29 mmol) was treated with allyltrimethylsilane **13** (63 μ L, 0.40 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (19 μ L, 0.15 mmol) in 10 mL of dry CH_2Cl_2 at -30°C and stirred for two hours. Work up and purification (hexane: AcOEt 9:1) gave the coupled product (150 mg, 66%), which was demetalated with NMO according to method B. Purification by flash chromatography (hexane:AcOEt 95:5) gave **17** (79 mg, 85 %); $[\alpha]_{435}^{21} = - +3.6$ (c 0.8, CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ 2.18 (m, 1H), 2.33 (m, 1H), 2.82 (bd, 1H, $J = 7.3$ Hz,), 3.55 (dd, 1H, $J = 6.7, 9.7$ Hz), 3.68 (dd, 1H, $J = 6.2, 9.6$ Hz), 4.12 (m, 1H), 4.48 (d, 1H, $J = 11.9$ Hz), 4.62 (d, 1H, $J = 11.7$ Hz), 4.92 (m, 4H), 5.19 (bd, 2 H, $J = 6.1$ Hz), 5.78 (m, 1H), 6.09 (m, 1H), 7.36 (m, 15H) ; ^{13}C NMR (75 MHz, CDCl_3): $\delta = 34.2, 35.2, 41.9, 69.0, 69.7, 71.4, 73.3, 73.5, 83.8, 89.4, 98.0, 116.0, 118.3, 122.1, 126.9, 127.6, 127.7, 128.0, 128.1, 128.3, 128.3, 131.9, 133.1, 136.7, 137.1, 138.2, 153.1$; API-ES (positive): $m/z = 513.5$ $[\text{M} + \text{Na}]^+$; $\text{C}_{34}\text{H}_{34}\text{O}_3$ (490.6): calcd. C 83.23, H 6.98; found C 82.96, H 7.04.

Dicobalt hexacarbonyl complex **18**.

This compound was prepared following the general procedure by treatment of cobalt complex **5** (120 mg, 0.13 mmol) with N-methyl pyrrole **14** (301 μ L, 2.3 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (19 μ L, 0.15 mmol) at -20°C . After stirring overnight (12-14 h) at -20°C , the mixture was worked up. Purification by flash chromatography (hexane: AcOEt 9:1) afforded recovered starting material **5** (45 mg) followed by the coupled product **18** (13 mg, 18 %, 42% corr). For **18**: ^1H -NMR (300MHz) δ 3.29 (dd, 1H, $J = 9.5, 6.1$ Hz), 3.46 (dd, 1H, $J = 9.5, 6.1$ Hz), 3.50 (s, 3H), 3.53 (s, 3H), 3.59 (m, 1H), 4.31 (d, 1H, $J = 11.5$ Hz), 4.44 (d, 1H, $J = 11.7$ Hz), 4.56 (m, 1H), 4.62 (d, 1H, $J = 11.0$ Hz), 4.69 (d, 1H, $J = 11.0$ Hz), 4.95 (d, 1H, $J = 5.4$ Hz), 6.15 (dd, 1H, $J = 3.2, 2.9$ Hz), 6.27 (t, 1H, $J = 1.7$ Hz), 6.29 (dd, 1H, $J = 2.2, 1.7$ Hz), 6.46 (dd, 1H, $J = 2.4, 2.2$ Hz), 6.55 (t, 1H, $J = 2.2$ Hz), 6.70 (t, 1H, $J = 1.9$ Hz), 6.89-7.43 (m, 15H); ^{13}C -NMR (75MHz) δ 33.8 , 34.2 , 36.1, 69.3, 70.9,

71.6, 73.1, 79.1, 93.6, 96.9, 105.0, 106.6, 107.8, 110.5, 120.4, 120.9, 121.5, 126.7, 126.9, 127.3 (x 2), 127.6 (x 2), 128.1, 128.2 (x 2), 128.4, 128.5, 129.8, 131.6, 135.9, 138.5, 138.6, 156.2, 199.8, 200.4.

Dicobalt hexacarbonyl complex **19**.

This compound was prepared following the general procedure by treatment of cobalt complex **5** (120 mg, 0.13 mmol) with N-methyl indole **15** (301 μ L, 2.3mmol) and BF_3OEt_2 (19 μ L, 0.15 mmol) at -20°C . After stirring for overnight (12-14 h) at -20°C the mixture was worked up. Purification by flash chromatography (hexane: AcOEt 9:1) afforded recovered starting material **5** (32 mg) followed by the coupled complex **19** (55mg, 45%, 61% corr.). For **19**: $^1\text{H-NMR}$ (300MHz) δ 3.53 (s, 3H), 3.60 (s, 3H), 3.62 (m, 2H), 3.96-4.15 (m, 2H), 4.23 (d, 1H, $J = 11.3$ Hz), 4.31 (d, 1H, $J = 11.3\text{Hz}$), 4.65 (m, 2H), 4.91 (d, 1H, $J = 2.0$ Hz), 6.60-7.40 (m, 25H). $^{13}\text{C-NMR}$ (75MHz) δ 32.8, 32.9, 34.5, 69.2, 72.0, 73.8, 74.5, 80.1, 92.8, 99.9, 105.4, 108.9, 109.4, 115.4, 117.4, 118.9, 119.2, 119.9, 121.6, 123.9, 126.1, 127.0, 127.2, 127.3, 127.4, 127.7, 128.0, 128.1 (x 2), 128.3, 128.6, 129.1, 129.9, 136.2, 137.0, 137.2, 138.9, 139.0, 156.4, 199.9, 200.6.

1-C-Allyl- β -2,3,4,6-tetra-O-benzyl-1-C-(2-phenylethynyl)-D-galactopyranose (**20**):

Following the standard procedure, the cobalt complex **6** (76 mg, 0.08 mmol) was treated at -30°C with allyltrimethylsilane **13** (30 μ L, 0.096 mmol) and BF_3OEt_2 (5 μ L, 0.04 mmol)

and stirred for 30 minutes. Silica gel chromatography (hexane: AcOEt 9:1) of the crude material afforded a new single compound (69 mg, 90%), which was demetalated with I₂ using procedure A. Flash chromatography (hexane/EtOAc, 9:1) gave **20** (32mg, 67%). $[\alpha]_D^{21} = +21.8$ (*c* 1.4, CHCl₃). ¹H NMR (200 MHz, CDCl₃): δ = 2.85 (m, 2H), 3.56 (dd, 1H, *J* = 4.15, 7.81 Hz), 3.66-3.75 (m, 3H), 4.03 (m, 1H), 4.38 (d, 1H, *J* = 10.2 Hz), 4.42 (d, 1H, *J* = 11.7 Hz), 4.48 (d, 1H, *J* = 11.7 Hz), 4.67 (d, 1H, *J* = 11.5 Hz), 4.74 (m, 2H), 4.93 (d, 1H, *J* = 10.7 Hz), 4.98 (d, 1H, *J* = 11.7 Hz), 5.05 (d, 1H, *J* = 10.7 Hz), 5.19 (m, 2H), 6.11 (m, 1H,), 7.32 (m, 25H); ¹³C NMR (50 MHz, CDCl₃): δ = 34.8, 68.7, 70.9, 72.8, 73.5, 74.3, 74.7, 76.2, 79.9, 81.2, 76.1, 84.8, 90.6, 118.0, 122.70, 127.4, 127.5, 127.5, 127.7, 127.9, 128.0, 128.1, 128.2, 128.2, 128.3, 128.4. API-ES (positive): *m/z* = 665.8 [M+H]⁺, 687.9 [M+Na]⁺. C₄₅H₄₄O₅ (664,8): calcd. C, 81.30; H, 6.67; found C 81.57, H 6.54.

1-*C*-(1-methyl-1*H*-pyrrol-2-yl)- β -2,3,4,6-tetra-*O*-benzyl-1-*C*-(2-phenylethynyl)-D-galactopyranose (21**):**

This compound was prepared according to the general procedure by treatment of cobalt complex **6** (100 mg, 0.108mmol) with N-methylpyrrole **14** (58 μ L, 0.64 mmol) and BF₃OEt₂ (13 μ L, 0.108mmol) at -30 °C. Work up and purification (hexane: AcOEt 9:1) gave recovered starting material **6** (9 mg, 8%) and the coupled product (87 mg, 82%); ¹H-NMR (300MHz) δ 3.62 (s, 3H), 3.73 (dd, 1H, *J* = 8.8, 5.4 Hz), 3.84 (t, 1H, *J* = 8.8 Hz), 3.93 (dd, 1H, *J* = 9.8, 2.4 Hz), 4.01 (m, 1H), 4.13 (m, 1H), 4.29 (d, 1H, *J* = 11.2 Hz), 4.34 (d, 1H, *J* = 9.8 Hz), 4.44 (d, 1H, *J* = 11.5 Hz), 4.54 (d, 1H, *J* = 11.7 Hz), 4.58 (d, 1H, *J* = 11.5 Hz), 4.67 (d, 1H, *J* = 11.5 Hz), 4.90 (d, 1H, *J* = 11.2 Hz), 5.00 (d, 1H, *J* = 11.5 Hz), 6.55 (m, 2H), 6.92-7.54 (m, 26H); ¹³C-NMR (75MHz) δ 36.3, 68.7, 71.5, 72.1, 73.4, 74.3, 74.8, 75.0, 80.9, 82.9, 83.0, 89.9, 108.4, 109.5, 120.9, 121.9, 124.5, 126.5, 126.7, 126.9,

127.0, 127.3, 127.5 (x 2), 127.6 (x 2), 128.0, 128.1, 128.2, 128.3, 129.7, 138.2, 138.3, 139.4, 139.5.

The coupled material was demetalated by treatment with I_2 following procedure A. Purification (hexane:AcOEt 9:1) gave **21** (40 mg, 65%); $[\alpha]_D^{21} = +6.9$ (c 2.4, $CHCl_3$); 1H -NMR (300MHz) δ 3.57 (s, 3H), 3.62 (dd, 1H, $J = 8.7, 4.8$ Hz), 3.77 (t, 1H, $J = 8.7$ Hz), 4.04 (dd, 1H, $J = 9.6, 2.7$ Hz), 4.14 (m, 2H), 4.30 (m, 2H, CH_2Ph), 4.43 (d, 1H, $J = 11.7$ Hz), 4.48 (d, 1H, $J = 11.7$ Hz), 4.60 (d, 1H, $J = 11.1$ Hz), 4.65 (d, 1H, $J = 12.0$ Hz), 4.77 (m, 2H), 5.04 (d, 1H, $J = 11.7$ Hz), 6.34 (m, 1H), 6.51 (m, 1H), 6.85 (m, 1H), 7.31 (m, 25H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 36.2, 68.5, 72.6, 72.8, 73.4, 74.5, 74.7, 74.9, 76.3, 81.6, 82.1, 87.3, 107.2, 120.9, 121.8, 122.9, 125.1, 126.9, 127.1, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1 (x 2), 128.2 (x 2), 128.3, 132.0, 138.0, 138.9, 139.2, 139.5. ppm. API-ES (positive): $m/z = 721.1$ $[M+NH_4]^+$. $C_{47}H_{45}NO_5$ (703,8): calcd. C, 80.20; H, 6.44; N, 1.99; found C 80.36, H 6.56; N 1.75.

1-C-(1-methyl-1*H*-indol-3-yl)- β -2,3,4,6-tetra-*O*-benzyl-1-C-(2-phenylethynyl)-D-galactopyranose (22**):**

Following the standard procedure, the cobalt complex **6** (93 mg, 0.1 mmol) was treated at -30 °C with 1-methylindole **14** (17 mg, 0.125 mmol) and BF_3OEt_2 (6.3 μ L, 0.05 mmol) and stirred for 30 minutes. Silica gel chromatography (hexane: AcOEt 9:1) of the crude material afforded a new single compound (101 mg, 97%), which was demetalated with I_2 using procedure A. Flash chromatography (hexane/EtOAc, 9:1) gave **22** (35mg, 46%). $[\alpha]_{435}^{21} = -13.9$ (c 1.0, $CHCl_3$). 1H NMR (300 MHz, $CDCl_3$): $\delta = 8.08$ (d, 1H, $J = 8.1$ Hz), 7.28 (m, 26H), 6.98 (m, 3H), 5.18 (d, 1H, $J = 11.1$ Hz), 4.83 (s, 2H), 4.71 (d, 1H, $J = 11.4$ Hz), 4.64 (d, 1H, $J = 9.9$ Hz), 4.53 (d, 1H, $J = 11.7$ Hz), 4.48 (d, 1H, $J = 11.7$ Hz), 4.41 (d, 1H, $J = 11.1$ Hz), 4.39 (m, 1H), 4.24 (d, 1H, $J = 2.4$ Hz), 4.11 (dd, 1H, $J = 9.9, 2.4$ Hz), 3.94 (d, 1H, J

= 11.7 Hz), 3.87 (m, 1H), 3.71 (s, 3H), 3.67 (dd, 1H, $J = 9.0, 5.1$ Hz); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 32.9, 68.7, 72.8, 72.9, 73.7, 74.9, 75.1, 77.4, 80.2, 81.7, 87.2, 87.5, 109.4, 115.2, 119.6, 121.9, 122.1, 123.0, 125.7, 127.0, 127.4, 127.5, 127.6, 127.7$ (x 2), 127.9, 128.2, 128.4 (x 2), 128.6, 128.7, 128.9, 132.3, 137.9, 138.2, 139.1, 139.2, 139.7. ppm. API-ES (positive): $m/z = 754.3$ $[\text{M}+\text{H}]^+$, 776.3 $[\text{M}+\text{Na}]^+$. $\text{C}_{51}\text{H}_{47}\text{NO}_5$ (753.92): calcd. C, 81.25; H, 6.28; N, 1.86; found C 81.39, H 6.34; N, 1.72.

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RG-9 noesy1d irr=3.94ppm

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: NOESY1D

12

Clara RG-9 noesy1d irr-4.82ppp

Archive directory: /export/home/vnmr1/vnmrSYS/data

Sample directory:

File: PROTON

Pulse Sequence: NOESY1D

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