Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Sweet (hetero)aromatics: Glycosylated templates for the construction of saccharide mimetics

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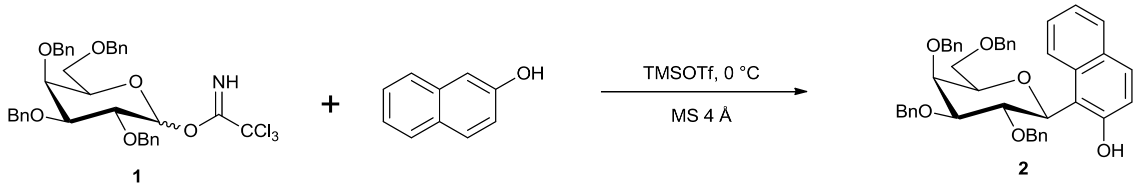
Contents

1. General Methods

Moisture sensitive reactions were carried out under argon atmosphere in dried glasware sealed by rubber septa. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator with a Vacuubrand vacuum pump. Unless otherwise specified, chemicals were obtained from commercial suppliers and were used without further purification. CH_2Cl_2 and Et_3N were dried over CaH_2 and distilled under argon atmosphere prior to use. THF was dried over sodium and distilled under argon atmosphere prior to use. Flash chromatography was performed on silica gel 60 (0.035–0.070 mm, Acros). Chromatography solvents (cyclohexane, EtOAc) were distilled prior to use. For analytical TLC, Merck silica gel aluminium sheets (60 F_{254}) were used. Visualisation was accomplished by UV (254 nm) and sugar reagent (1 M ethanolic H_2SO_4/0.2 % ethanolic 3-methoxyphenol solution 1:1). Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot in analytical TLC.

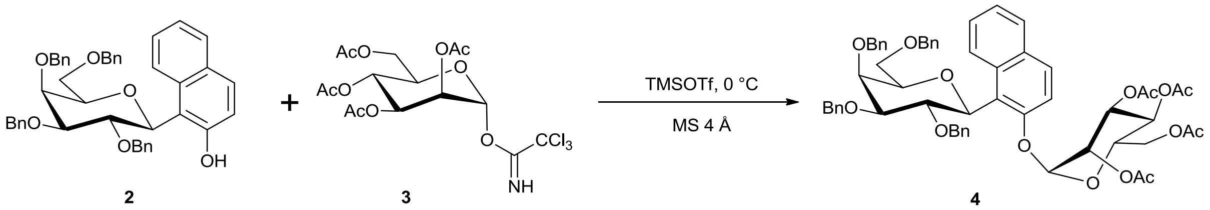
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC300, AV 400 or DRX 500 in $CDCl_3$, Methanol-d_4 or DMSO- d_6 using the residual solvent peak as internal reference ($CDCl_3$, δ_H = 7.26, δ_C = 77.16, methanol-d_4, δ_H = 3.31, δ_C = 49.0, DMSO- d_6, δ_H = 2.50, δ_C = 39.52). Optical rotations were measured at room temperature on a Krüss P8000 polarimeter at 589 nm, or on a Perkin Elmer 241 polarimeter at 546 and 578 nm; the optical rotation at 589 nm was extrapolated using the Drude equation. IR spectra were recorded on a ThermoNicolet Avatar 370 FT-IR spectrometer. FAB mass spectrometry was carried out on with a VG70S (Xe-FAB ionisation) with *m*-nitrobenzylalcohol as matrix. For exact mass determination (FAB-HRMS), PEG 300 or PEG 600 was used as internal standard. ESI mass spectrometry was carried out on an Agilent 1200 LC/MSD Trap XCT. The samples were dissolved in acetonitrile (c ≈ 0.1 g/l) and injected via an Agilent 1200 HPLC with an Ascentis Express C8 (30 x 2 mm, 2.7 µm particle size) columm (acetonitrile/water 80:20, Flow: 0.5 ml/min). Exact mass determination (ESI-HRMS) was carried out on a Q-ToF-Ultima 3-Instrument with Lock Spray™-interface. NaI/CsI clusters or leucin-enkephalin (1 ng/µl in H_2O/acetonitrile 1:1) were used as external standard.

2. Experimental Procedures and characterization data



A mixture of 2,3,4,6-tetra-*O*-benzyl-D-galactosyl trichloroacetimidate[1] (**1**) (1.31 g, 1.91 mmol), 2-naphthol (350 mg, 2.43 mmol) and activated 4 Å molecular sieves (1 g) in anhydrous CH_2Cl_2 (10 mL) was stirred at 0 °C for 20 min under argon atmosphere to remove traces of water from the reactants. Then, TMSOTf (440µl, 2.43 mmol) in anhydrous CH_2Cl_2 (2 mL) was added and the mixture was stirred until TLC-monitoring showed no further progress. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by flash chromatography (cyclohexane/EtOAc, 7:1) to give 1-*C*-(2',3',4',6'-tetra-*O*-benzyl-β-D-galactosyl)-2-naphthol (**2**) (663 mg, 0.994 mmol, 52 %).

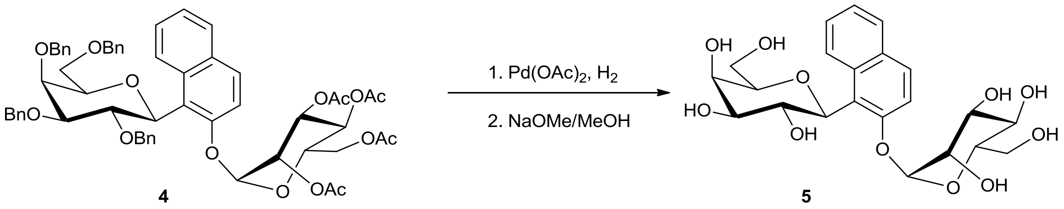
2: colorless oil: R_f = 0.12 (cyclohexane/EtOAc, 20:1). ^{1}H NMR, COSY (400 MHz, $CDCl_3$) : δ = 8.18 (s, 1 H, OH), 7.93 (d, $^3J_{8,7}$ = 8.5 Hz, 1 H, H-8^{naph}), 7.69 (m, 2 H, H-4^{naph}, H-5^{naph}), 7.37–7.13 (m, 17 H, H-6^{naph}, H-7^{naph}, 15 H-Ph), 7.09 (d, $^3J_{3,4}$ = 8.8 Hz, 1 H, H-3^{naph}), 7.00 (t, ^3J = 7.4 Hz, 1 H, H-Ph), 6.90 (t, ^3J = 7.5 Hz, 2 H, H-Ph), 6.36–6.27 (m, 2 H, H-Ph), 5.27 (d, $^3J_{1,2}$ = 9.6, 1 H, H-1^{gal}), 5.04 (d, ^2J = 11.8 Hz, 1 H, CH_2Ph), 4.71 (s, 2 H, CH_2Ph), 4.64 (d, ^2J = 11.8 Hz, 1 H, CH_2Ph), 4.39–4.29 (m, 3 H, H-2^{gal}, 2 CH_2Ph), 4.20 (d, ^2J = 9.8, 1 H, CH_2Ph), 4.06 (pseudo-d, $^3J_{app}$ = 2.2 Hz, 1 H, H-4^{gal}), 3.75–3.69 (m, 2 H, H-3^{gal}, H-5^{gal}), 3.52 (d, ^3J = 6.5 Hz, 2 H, H-6^{gal}), 3.45 (d, ^2J = 9.7 Hz, 1 H, CH_2Ph) ppm. ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ = 155.1 (C-2^{naph}), 138.9, 138.8, 138.0, 137.5 (4x, C-1^{Ph}), 133.1 (C-8a^{naph}), 130.7 (C-4^{naph}), 129.0 (C-5^{naph}, C-4a^{naph}), 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7 (CH^{arom}), 126.8 (C-7^{naph}), 123.3 (C-6^{naph}), 123.1 (C-8^{naph}), 119.8 (C-3^{naph}), 115.8 (C-1^{naph}), 84.3 (C-5^{gal}), 79.4 (C-2^{gal}), 77.8 (C-3^{gal}), 76.8 (C-1^{gal}), 76.0, 74.8 (CH_2Ph), 74.1 (C-4^{gal}), 74.0, 73.2 (CH_2Ph), 68.8 (C-6^{gal}) ppm. FAB-MS *m/z* (%) = 666.3 $[M]^+$ (100). FAB-HRMS: calc. for $[C_{44}H_{42}O_6]^+$: *m/z* = 666.2981, found: 666.2993. $[\alpha]^{26}_D$ = + 56.7 (c = 1.0, $CHCl_3$). IR $\tilde{\nu}$ (cm^{-1}): 3386, 2924, 2360, 1453, 1266, 1224, 1096, 1028, 735, 697.



2 3 4

A mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-mannosyl-trichloracetimidate[2] (**3**) (493 g, 1.00 mmol), 1-*C*-(2',3',4',6'-tetra-*O*-benzyl-galactosyl)-2-naphthol (**2**) (663 mg, 994 µmol) and activated 4 Å molecular sieves (1 g) in anhydrous CH_2Cl_2 (10 mL) was stirred at 0 °C for 20 min under argon atmosphere to remove traces of water from the reactants. Then, TMSOTf (190 µl, 1.05 mmol) in anhydrous CH_2Cl_2 (2 mL) was added and the mixture was stirred until TLC-monitoring showed no further progress. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by flash chromatography (cyclohexane/EtOAc, 3:1) to give 1-(2',3',4',6'-tetra-*O*-benzyl-β-D-galactosyl)-2-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl-α-D-mannosyl)-2-naphthol (**4**) (320 mg, 321 µmol, 32 %).

4: colorless oil: R_f = 0.16 (cyclohexane/EtOAc, 3:1). ^{1}H NMR, COSY (500 MHz, $CDCl_3$): δ = 8.75 (d, $^3J_{7,8}$ = 8.7 Hz, 1 H, H-8^{naph}), 7.78 (d, $^3J_{3,4}$ = 9.1 Hz, 1 H, H-4^{naph}), 7.75 (d, $^3J_{5,6}$ = 8.0 Hz, 1 H, H-5^{naph}), 7.47–7.23 (m, 17 H, H-3^{naph}, H-6^{naph}, 15 H-Ph), 7.22–7.19 (m, 1 H, H-7^{naph}), 7.01 (d, ^3J = 7.49 Hz, 1 H, H-Ph), 6.94 (t, ^3J = 7.5 Hz, 2 H, H-Ph), 6.60 (d, ^3J = 7.3 Hz, 2 H, H-Ph), 5.61 (dd, $^3J_{3,4}$ = 10.2 Hz, $^3J_{2,3}$ = 3.2 Hz, 1 H, H-3^{man}), 5.58 (d, $^3J_{1,2}$ = 1.5 Hz, 1 H, H-1^{man}), 5.52 (m, 1 H, H-2^{man}), 5.41 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, H-1^{gal}), 5.36 (pseudo-t, $^3J_{app,4,3/5}$ = 10.2 Hz, 1 H, H-4^{man}), 5.15 (d, ^2J = 11.2 Hz, 1 H, CH_2Ph), 4.89 (d, ^2J = 11.8 Hz, 1 H, CH_2Ph), 4.83 (d, ^2J = 11.8 Hz, 1 H, CH_2Ph), 4.69 (d, ^2J = 11.2 Hz, 1 H CH_2Ph), 4.63 (pseudo-t, $^3J_{app,2,1/3}$ = 9.5 Hz, 1 H, H-2^{gal}), 4.52 (d, ^2J = 11.9 Hz, 1 H, CH_2Ph), 4.46 (d, ^2J = 11.9 Hz, 1 H, CH_2Ph), 4.35 (d, ^2J = 11.4 Hz, 1 H, CH_2Ph), 4.27 (pseudo-d, $^3J_{app}$ = 2.1 Hz, 1 H, H-4^{gal}), 3.98–3.93 (m, 3 H, H-3^{gal}, H-5^{gal}. H-6a^{man}), 3.82–3.75 (m, 3 H, CH_2Ph, H-5^{man}, H-6a^{gal}), 3.69 (dd, ^2J = 12.5 Hz, $^3J_{5,6b}$ = 1.9 Hz, 1 H, H-6b^{man}), 3.65 (dd, ^2J = 8.9 Hz, $^3J_{5,6b}$ = 5.2 Hz, 1 H, H-6b^{gal}), 2.18 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.03(s, 3 H, CH_3) ppm. ^{13}C NMR, HSQC, HMBC (126 MHz, $CDCl_3$): δ = 170.9, 170.3, 170.2, 170.0 (4 C=O), 151.8 (C-2), 139.8, 139.2, 138.7, 138.4 (4 C-1^{Ph}), 132.9 (C-8a^{naph}), 131.0 (C-4a^{naph}), 130.8 (C-4^{naph}), 128.8 (C-5^{naph}), 128.7, 128.6, 128.3, 128.0, 127.6, 127.3 (CH^{arom}), 126.9 (C-8^{naph}), 126.8 (C-7^{naph}), 124.6 (C-6^{naph}), 121.9 (C-1^{naph}), 114.8 (C-3^{naph}), 96.4 (C-1^{man}), 85.6 (C-3^{gal}), 78.4 (C-2^{gal}), 77.3 (C-5^{gal}), 75.2 (C-1^{gal}), 74.8 (CH_2Ph), 74.7 (CH_2Ph, C-4^{gal}), 73.8 (CH_2Ph), 72.6 (CH_2Ph), 69.9, 69.7 (C-2^{man}, C-5^{man}), 69.4 (C-3^{man}), 68.7 (C-6^{gal}), 65.6 (C-4^{man}), 62.1 (C-6^{man}), 21.3, 21.2, 21.1 (4 CH_3) ppm. ESI-HRMS: calc. for $[C_{58}H_{60}O_{15}+Na]^+$: m/z = 1019.3824, found: 1019.3821. $[\alpha]^{23}_D$ = + 33.3 (c = 0.40, $CDCl_3$). IR $\tilde{\nu}$ (cm^{-1}): 2922, 1749, 1632, 1454, 1367, 1224, 1085, 748, 698.

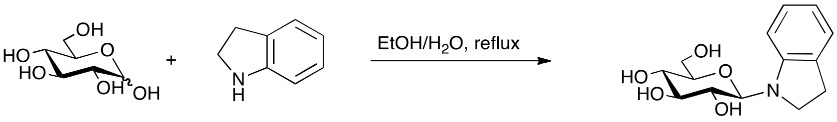


1-(2’,3’,4’,6’-tetra-*O*-benzyl-β-D-galactosyl)-2-*O*-(2’’,3’’,4’’,6’’-tetra-*O*-acetyl-α-D-mannosyl)-2-naphthol (**4**) (100 mg, 0.10 mmol) was dissolved in MeOH (20 mL). $Pd(OAc)_2$ (5 mg, 22.3 µmol) was added, the mixture was degassed under Ar and flushed with H_2. The mixture was stirred for 22 h at room temperature. The mixtures was filtered through Celite® and washed with MeOH (60 ml). The solvent was removed in vacuo the residue filtered through silica gel (10 cm, EtOAc/EtOH, 20:1) to give 1-β-D-galactosyl-2-*O*-(2’’,3’’,4’’,6’’-tetra-*O*-acetyl-mannosyl)-2-naphthol (32 mg, 50 µmol, 51 %).

colorless oil: R_f = 0.42 (EtOAc/MeOH, 20:1) ^{1}H NMR (300 MHz, CD_3OD): δ = 8.88 (d, $^3J_{3\text{-}4}$ = 9.0 Hz, 1 H, H-4^{naph}), 7.88–7.81 (m, 2 H, H^{naph}), 7.50–7.44 (m, 1 H, H^{naph}), 7.48 (d, $^3J_{3,4}$ = 9.0, 1 H, H-3^{naph}), 7.39 (ddd, ^3J = 8.0 Hz, ^3J = 6.8 Hz, ^4J = 1.2 Hz, 1 H, H^{naph}), 5.81 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, H-1^{man}), 5.77 (dd, $^3J_{3,4}$ = 10.3 Hz, $^3J_{2,3}$ = 3.3 Hz, 1 H, H-3^{man}), 5.61 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{1,2}$ = 1.8 Hz, H-2^{man}), 5.44 (pseudo-t, $^3J_{app,4,3/5}$ = 10.2 Hz, 1 H, H-4^{man}), 5.38 (d, $^3J_{1,2}$ = 9.9 Hz, 1 H, H-1^{gal}), 4.51 (pseudo-t, $^3J_{app,2,1/3}$ = 9.4 Hz, 1H, H-2^{gal}), 4.44 (ddd, $^3J_{4,5}$ = 10.1 Hz, $^3J_{5,6a}$ = 4.8 Hz, $^3J_{5,6b}$ = 2.2 Hz, 1 H, H-5^{man}), 4.30 (dd, ^2J = 12.4 Hz, $^3J_{5,6a}$ = 4.8 Hz, H-6a^{man}), 4.15 (d, $^3J_{app}$ = 2.8 Hz, H-4^{gal}), 4.04 (dd, ^2J = 12.4 Hz, $^3J_{5,6b}$ = 2.2 Hz, 1 H, H-6b^{man}), 3.90–3.75 (m, 4 H, H^{gal}), 2.09 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3) ppm. ESI-HRMS: calc. for $[C_{30}H_{36}O_{15}+Na]^+$: m/z = 659.1952, found: 659.1964. IR $\tilde{\nu}$ (cm^{-1}): 3456, 2942, 1748, 1513, 1370, 1226, 1135, 1049, 813, 753 cm^{-1}

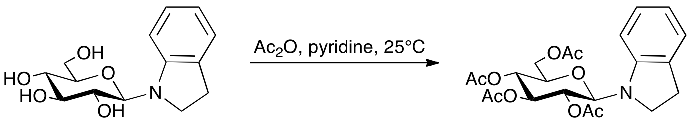
1-*C*-galactosyl-2-*O*-(2’’,3’’,4’’,6’’-tetra-*O*-acetyl-mannosyl)-2-naphthol (32 mg, was dissolved in MeOH (20 ml). NaOMe in MeOH was added until pH ≈ 10. The mixture was stirred 4 h, neutralized by stirring with Amberlyst 15® for 10 min, filtered and washed with MeOH (50 ml). The solvent was removed in vacuo to give 1-β-D-galactosyl-2-*O*-α-D-mannosyl-2-naphthol (**5**) (23 mg, 50 µmol, quant.).

colorless oil: R_f = 0.10 (EtOAc/MeOH 4:1) . ^{1}H NMR (300 MHz, CD_3OD): δ = 8.85 (d, $^3J_{3,4}$ = 9.2 Hz, 1 H, H-4^{naph}), 7.88–7.77 (m, 2 H, H^{naph}), 7.57 (d, $^3J_{3,4}$ = 9.2 Hz, 1 H, H-3^{naph}), 7.45 (ddd, ^3J = 8.6 Hz, ^3J = 6.8 Hz, ^4J = 1.4 Hz, H^{naph}), 7.36 (ddd, ^3J = 7.9 Hz, ^3J = 6.8 Hz, ^3J = 1.1 Hz, 1 H, H^{naph}), 5.64 (d, $^3J_{1,2}$ = 1.7 Hz, 1 H, H-1^{man}), 5.26 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, H-1^{gal}), 4.52 (t, ^3J = 9.5 Hz, 1 H), 4.17 – 4.06 (m, 3 H), 3.93–3.66 (m, 8 H) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 153.87 (C-2^{naph}), 134.0, 131.9 (C4a^{naph}, C8a^{naph}), 131.2, 129.3, 127.7, 126.9, 124.8 (5 CH^{naph}), 121.7 (C-1^{naph}), 116.7 (CH^{naph}), 100.3 (C-1^{man}), 81.0, 77.6, 77.0, 75.4, 72.4, 72.2, 71.2, 71.0, 68.5, 63.2 (CH_2OH), 62.7 (CH_2OH) ppm. ESI-MS: *m/z* (%) = 491 $[M+Na]^+$ (100). ESI-HRMS calc. for $[C_{22}H_{28}O_{11}+Na]^+$: *m/z* = 491.1529, found: 491.1526.



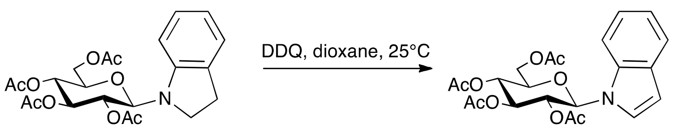
To a solution of indoline (5.32 ml, 47.4 mmol) in a mixture of ethanol (345 ml) and water (dist., 8.5 ml) D-glucose (3.98 g, 22.1 mmol) was added. The reaction mixture was refluxed for 26 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent EtOAc/MeOH, 15:1) to give 1-(β-D-glucopyranosyl)-indoline (6.41 g, quant.). (For a similar procedure, see:[3]).

rose solid; R_f = 0.41 ($CHCl_3$/MeOH/AcOH, 5:1:0.1). 1H NMR (300 MHz, DMSO-d_6): δ = 6.94–7.02 (m, 2H, H-4^{indoline}, H-6^{indoline}), 6.54–6.60 (m, 2H, H-5^{indoline}, H-7^{indoline}), 5.02 (s, 2H, broad, OH), 4.93 (s, 2H, broad, OH), 4.64 (d, $^3J_{1,2}$ = 8.4 Hz, 1H, H-1^{gluc}), 3.07–3.67 (m, 7H H-2^{gluc}, H-3^{gluc}, H-4^{gluc}, H-5^{gluc}, H-6^{gluc}, H-2^{indoline}), 2.87–2.94 (m, 2H, H-3^{indoline}). IR $\tilde{\nu}$ (cm^{-1}): 3391, 2931, 2907, 2882, 1605, 1491, 1464, 1417, 1372, 1333, 1265, 1082, 1021, 756. ESI-MS: *m/z* (%) = 282.2 $[M+H]^+$ (100), 304.2 $[M+Na]^+$ (20). ESI-HRMS: calcd for $[C_{14}H_{19}NO_5+Na]^+$: *m/z* = 304.1161, found: 304.1158. $[\alpha]^{22}_D$: −11.8 (c = 1.00, MeOH).



A solution of 1-β-D-glucopyranosyl-indoline (1.665 g, 5.961 mmol), pyridine (25 ml) and acetic anhydride (9.01 ml, 9.42 mmol) was stirred at room temperature for 16 h and then concentrated in vacuo. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 8:1) to give 1-(3,4,5,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-indoline (6.12 g, 95%). (For a similar procedure, see:[4]).

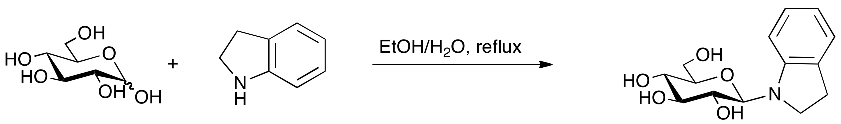
colorless solid; R_f = 0.58 (cyclohexane/EtOAc, 1:1). ^{1}H NMR, COSY, HSQC (400 MHz, $CDCl_3$): δ = 7.06–7.10 (m, 2H, H-4^{indoline}, H-6^{indoline}), 6.74 (d-pseudo-t, $^3J_{5,6}$ = 7.4 Hz, $^4J_{5,3/6}$ = 0.9 Hz, 1H, H-5^{indoline}), 6.55 (d, $^3J_{7,6}$ = 7.8 Hz, 1H, H-7^{indoline}), 5.28–5.37 (m, 2H, this multiplet contains: 5.34 (pseudo-t, $^3J_{app,3,2/3}$ = 9.3 Hz, H-3^{gluc}), 5.30 (pseudo-t, $^3J_{app,2,1/3}$ = 9.3 Hz, H-2^{gluc})), 5.09 (pseudo-t, $^3J_{app,4,3/5}$ = 9.6 Hz, 1H, H-4^{gluc}), 5.01 (d, $^3J_{1,2}$ = 8.7 Hz, 1H, H-1^{gluc}), 4.25 (dd, $^3J_{6a/6b}$ = 12.3 Hz, $^3J_{6a/5}$ = 4.7 Hz, 1H, H-6a^{gluc}), 4.03 (dd, $^3J_{6b/6a}$ = 12.3 Hz, $^3J_{6b/5}$ = 2.4 Hz, 1H, H-6b^{gluc}), 3.76 (ddd, $^3J_{5/4}$ = 10.0 Hz, $^3J_{5/6a}$ = 4.7 Hz, $^3J_{5/6b}$ = 2.4 Hz, 1H, H-5^{gluc}), 3.54–3.65 (m, 2H, H-2^{indoline}), 2.90–3.03 (m, 2H, H-3^{indoline}), 2.04, 2.03, 2.00, 1.99 (4x s, each 3H, $COCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8, 170.4, 169.8, 169.7 (4x C=O), 149.5 (C-7a^{indoline}), 130.7 (C-3a^{indoline}), 127.2 (C-6^{indoline}), 125.1 (C-4^{indoline}), 119.6 (C-5^{indoline}), 107.8 (C-7^{indoline}), 84.4 (C-1^{gluc}), 74.1 (C-3^{gluc}), 73.4 (C-5^{gluc}), 68.9 (C-2^{gluc}), 68.6 (C-4^{gluc}), 62.1 (C-6^{gluc}), 45.9 (C-2^{indoline}), 28.3 (C-3^{indoline}), 20.9, 20.81, 20.77 (2C), (4x $COCH_3$). IR $\tilde{\nu}$ (cm^{-1}): 3483, 2957, 1752, 1607, 1490, 1427, 1368, 1229, 1097, 1035, 910, 752. ESI-MS: *m/z* (%) = 450.1 $[M+H]^+$ (100), 472.0 $[M+Na]^+$ (22). ESI-HRMS: calcd for $[M+Na]^+$: *m/z* = 472.1584, found: 472.1600. MS (ESI): 450.1 $[C_{22}H_{28}NO_9]^+$ (100), 472.0 $[C_{22}H_{27}NNaO_9]^+$ (22). HRMS (ESI): calcd for $[C_{22}H_{27}NO_9+Na]^+$: 472.1584; found: 472.1600. $[\alpha]^{22}_D$: + 7.4 (c = 1.00, $CHCl_3$).



6a

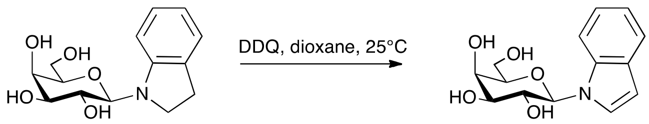
A solution of 1-(3,4,5,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-indoline (2.36 g, 5.24 mmol) and DDQ (1.43 g, 6.29 mmol) in 1,4-dioxane (160 ml) was stirred at room temperature for 16 h. After addition of saturated aqueous $NaHCO_3$ and extraction with EtOAc, the organic phases were dried over Na_2SO_4 and concentrated in vacuo to give a residue that was purified by flash chromatography (eluent cyclohexane/EtOAc, 8:1) to afford compound **6a** (2.213 g, 94%). (For a similar procedure, see: et al.[3]).

6a: colorless solid; R_f = 0.60 (cyclohexane/EtOAc, 1:1). ^{1}H NMR, COSY, HSQC (400 MHz, $CDCl_3$): δ = 7.60 (d-pseudo-t, $^3J_{4,5}$ = 7.9 Hz, $^4J_{app,4,3/6}$ = 0.9 Hz, 1H, H-4^{indole}), 7.41 (dd, $^3J_{7,6}$ = 8.4 Hz, $^4J_{7,5}$ = 0.9 Hz, 1H, H-7^{indole}), 7.23–7.27 (m, 2H, this multiplet contains: 7.25 (ddd, $^3J_{6,5}$ = 7.1 Hz, $^3J_{6,7}$ = 8.4 Hz, 1H, H-6^{indole}), 7.23 (d, $^3J_{2,3}$ = 3.4 Hz, 1H, H-2^{indole})), 7.15 (ddd, $^4J_{5,7}$ = 0.9 Hz, $^3J_{5,4}$ = 7.9 Hz, $^3J_{5,6}$ = 7.1 Hz, $^4J_{6,4}$ = 1.3 Hz, 1H, H-5^{indole}), 6.57 (d, $^3J_{3,2}$ = 3.4 Hz, 1H, H-3^{indole}), 5.64 (d, $^3J_{1,2}$ = 9.2 Hz, 1H, H-1^{gluc}), 5.55 (pseudo-t, $^3J_{app,2,1/3}$ = 9.2 Hz, 1H, H-2^{gluc}), 5.45 (pseudo-t, $^3J_{app,3,2/4}$ = 9.3 Hz, 1H, H-3^{gluc}), 5.29 (dd, $^3J_{4,5}$ = 10.0 Hz, $^3J_{4,3}$ = 9.4 Hz, 1H, H-4^{gluc}), 4.30 (dd, $^3J_{6a,6b}$ = 12.4 Hz, $^3J_{6a,5}$ = 4.9 Hz, 1H, H-6a^{gluc}), 4.15 (dd, $^3J_{6b,6a}$ = 12.4 Hz, $^3J_{6b,5}$ = 2.3 Hz, 1H, H-6b^{gluc}), 4.00 (ddd, $^3J_{5,4}$ = 10.0 Hz, $^3J_{5,6a}$ = 4.9 Hz, $^3J_{5,6b}$ = 2.3 Hz, 1H, H-5^{gluc}), 2.08, 2.07, 2.03, 1.67 (4x s, each 3H, $COCH_3$). ^{13}C NMR, HSQC (101 MHz, $CDCl_3$): δ = 170.8, 170.3, 169.6, 168.9 (4x C=O), 136.3 (C-7a^{indole}), 129.2 (C-3a^{indole}), 124.5 (C-2^{indole}), 122.5 (C-6^{indole}), 121.5 (C-4^{indole}), 120.9 (C-5^{indole}), 109.7 (C-7^{indole}), 104.5 (C-3^{indole}), 83.3 (C-1^{gluc}), 74.7 (C-5^{gluc}), 73.5 (C-3^{gluc}), 70.5 (C-2^{gluc}), 68.3 (C-4^{gluc}), 62.0 (C-6^{gluc}), 20.9, 20.8 (2C), 20.3 (4x $COCH_3$). IR $\tilde{\nu}$ (cm^{-1}): 2939, 1743, 1523, 1457, 1379, 1315, 1230, 1220, 1089, 1035, 919, 902, 820, 753, 728. ESI-MS: *m/z* (%) = 331.0 [M − indole]$^+$ (100), 448.2 [M+H]$^+$ (63), 470.1 [M+Na]$^+$ (44). ESI-HRMS: calcd for $[C_{22}H_{25}NO_9+Na]^+$: *m/z* = 470.1427, found: 470.1422. $[\alpha]^{20}_D$: +0.5 (c = 1.00, CH_2Cl_2).



To a solution of indoline (2,00 g, 16.8 mmol) in a mixture of ethanol (120 ml) and water (dest., 4 ml) D-galactose (1.41 g, 7.82 mmol) was added. The reaction mixture was refluxed for 17.5 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent EtOAc/MeOH, 40:1) to give 1-(β-D-galactopyranosyl)-indoline (1.80 g, 82%). (For a similar procedure, see:[3]).

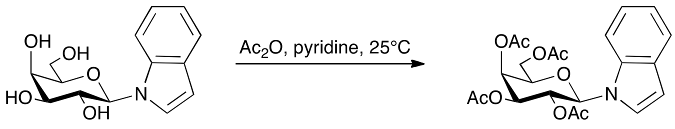
colorless solid, mp.: 112-114 °C; R_f = 0.30 ($CHCl_3$/MeOH/AcOH, 5:1:0.1). ^{1}H NMR, COSY (500 MHz, MeOH): δ = 6.97–7.04 (m, 2H, H-4^{indoline}, H-6^{indoline}), 6.61–6.55 (m, 2H, H-5^{indoline}, H-7^{indoline}), 4.74 (d, $^3J_{1,2}$ = 9.0 Hz, 1H, H-1^{gal}), 3.87–3.92 (m, 2H, this multiplet contains: 3.91 (dd, ^3J = 1.0, 3.3 Hz, H-4^{gal}), 3.90 (dd, $^3J_{2,1}$ = 9.0, Hz, $^3J_{2,3}$ = 9.4 Hz, H-2^{gal})), 3.64–3.72 (m, 4H, H-2^{indoline}, H-6^{gal}), 3.56–3.62 (m, 2H, H-3^{gal}, H-5^{gal}), 2.96–3.01 (m, 1H, H-3^{indoline}). ^{13}C NMR, HSQC (101 MHz, CD_3OD): δ = 151.8 (C-7a^{indoline}), 131.7 (C-3a^{indoline}), 128.1 (C-6^{indoline}), 125.5 (C-4^{indoline}), 119.7 (C-5^{indoline}), 109.1 (C-7^{indoline}), 87.8 (H-1^{gal}), 78.0, 76.3 (C-3^{gal}, C-5^{gal}), 70.7 (C-4^{gal}), 69.6 (C-2^{gal}), 62.6 (C-6^{gal}), 46.9 (C-2^{indoline}), 29.1 (C-3^{indoline}). IR $\tilde{\nu}$ (cm^{-1}): 3425, 2910, 1608, 1486, 1409, 1257, 1080, 1034. FAB-MS: *m/z* (%) = 281.1 $[M]^+$ (100), 282.1 $[M+H]^+$ (90). FAB-HRMS: calcd for $[C_{14}H_{19}NO_5]^+$: *m/z* = 281.1263, found: 281.1259; calcd for $[C_{14}H_{19}NO_5+H]^+$: *m/z* = 282.1341, found: 282.1136. Anal. calcd for $C_{14}H_{19}NO_5$: C 59.78, H 6.81, N 4.98; found: C 59.77, H 6.88, N 5.03. $[\alpha]^{22}_{D}$: +3.3 (*c* 1.00, MeOH). (these data match those reported in the literature)[3].



A solution of 1-(β-D-galactopyranosyl)-indoline (1.524 g, 5.418 mmol) and DDQ (1.48 g, 6.51 mmol) in 1,4-dioxane (250 ml) was stirred at room temperature for 16 h. After addition of saturated aqueous $NaHCO_3$ and extraction with EtOAc the organic phases were dried over Na_2SO_4 and concentrated in vacuo to give a residue that was purified by flash chromatography (eluent cyclohexane/EtOAc, 40:1) to afford 1-(β-D-galactopyranosyl)-indole (1.46 g, 97%). (For a similar procedure, see:[3]).

colorless solid; R_f = 0.31 ($CHCl_3$/MeOH/AcOH, 5:1:0.1). ^{1}H NMR, COSY (500 MHz, DMSO-d$_6$): δ = 7.64 (dd, $^3J_{7,6}$ = 8.2 Hz, $^4J_{7,5}$ = 1.0 Hz, 1H, H-7^{indole}), 7.55 (ddd, $^3J_{4,5}$ = 7.8 Hz, $^4J_{4,6}$ = 1.1 Hz, 1H, H-4^{indole}), 7.44 (d, $^3J_{2,3}$ = 3.3 Hz, 1H, H-2^{indole}), 7.13 (ddd, $^4J_{6,7}$ = 8.2 Hz, $^3J_{6,5}$ = 7.1 Hz, $^4J_{6,4}$ = 1.1 Hz, 1H, H-6^{indole}), 7.04 (ddd, $^3J_{5,4}$ = 7.8 Hz, $^3J_{5,6}$ = 7.1 Hz, $^4J_{5,7}$ = 1.0 Hz, 1H, H-5^{indole}), 6.45 (dd, $^2J_{3,2}$ = 3.3 Hz, $^4J_{3,4}$ = 0.6 Hz, 1H, H-3^{indole}), 5.34 (d, $^3J_{1,2}$ = 9.0 Hz, 1H, H-1^{gal}), 4.39 (s, broad, 4H, OH), 4.11 (pseudo-t, $J_{app,2,1/3}$ = 9.1 Hz, 1H, H-2^{gal}), 3.82 (dd, $^3J_{4,3}$ = 2.6 Hz, $^3J_{4,5}$ = 1.0 Hz, 1H, H-4^{gal}), 3.70 (ddd, $^3J_{5,6b}$ = 6.6 Hz, $^3J_{5,6a}$ = 5.7 Hz, $^3J_{5,4}$ = 1.0 Hz, 1H, H-5^{gal}), 3.60–3.52 (m, 2H, H-3^{gal}, H-6a^{gal}), 3.49 (dd, $^3J_{6b,6a}$ = 11.0 Hz, $^3J_{6b,5}$ = 6.6 Hz, 1H, H-6b^{gal}). ^{13}C NMR, HSQC (101 MHz, DMSO-d$_6$): δ = 135.8 (C-7a^{indole}), 128.6 (C-3a^{indole}), 126.9 (C-2^{indole}), 121.0 (C-6^{indole}), 120.3 (C-4^{indole}), 119.5 (C-5^{indole}), 111.4 (C-7^{indole}), 101.2 (C-3^{indole}), 86.1 (C-1^{gal}), 77.7 (C-5^{gal}), 74.3 (C-3^{indole}), 68.9 (C-2^{indole}), 68.6 (C-4^{indole}), 60.6 (C-6^{indole}). IR $\tilde{\nu}$ (cm^{-1}): 3420, 2912, 1610, 1483, 1407, 1251, 1078, 1025. FAB-MS: *m/z* (%) = 279.1 $[M]^+$ (100), 280.1$[M+H]^+$ (75). FAB-HRMS: calcd for $[C_{14}H_{17}O_5]^+$: *m/z* =

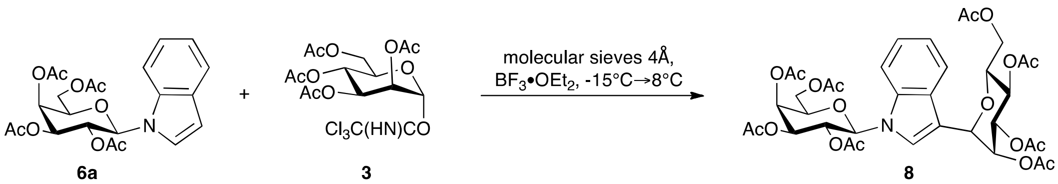
279.1107, found: 279.1115; calcd for $[C_{14}H_{17}O_5+H]^+$: *m/z* = 280.1185, found: 280.1188. $[\alpha]^{22}_D$: +1.8 (*c* 1.00, MeOH). (these data match those reported in the literature)[3].



6b

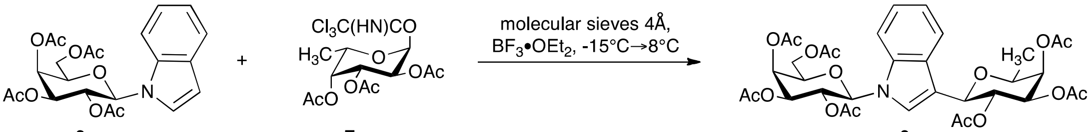
A solution of 1-(β-D-galactopyranosyl)-indole (411 g, 1.47 mmol), pyridine (6 ml) and acetic anhydride (2.2 ml, 2.3 mmol) was stirred at room temperature for 16 h. After addition of EtOAc the mixture was washed with HCl (1M) and saturated aqueous $NaHCO_3$. The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure to afford compound **6b** (603 mg, 92%). (For a similar procedure, see:[4])

6b: colorless solid; R_f = 0.49 (cyclohexane/EtOAc, 2:1). ^{1}H NMR, COSY (500 MHz, $CDCl_3$): δ = 7.58 (d, $^3J_{4,5}$ = 7.8 Hz, 1H, H-4^{indole}), 7.45 (d, $^3J_{7,6}$ = 8.2 Hz, 1H, H-7^{indole}), 7.25 (d, $^3J_{2,3}$ = 3.4 Hz, 1H, H-2^{indole}), 7.22 (ddd, $^3J_{6,7}$ = 8.2 Hz, $^3J_{6,5}$ = 7.1 Hz, $^4J_{6,4}$ = 1.0 Hz, 1H, H-6^{indole}), 7.12 (ddd, $^3J_{5,4}$ = 7.8 Hz, $^3J_{5,6}$ = 7.1 Hz, $J_{5,7}$ = 1.0 Hz, 1H, H-5^{indole}), 6.55 (d, $^3J_{3,2}$ = 3.4 Hz, 1H, H-3^{indole}), 5.72 (dd, $^3J_{2,3}$ = 10.2 Hz, $^3J_{2,1}$ = 9.1 Hz, 1H, H-2^{gal}), 5.54–5.56 (m, 2H, this multiplet contains: 5.55 (d, $^3J_{1,2}$ = 9.1 Hz, 1H, H-1^{gal}), 5.54 (dd, $^3J_{4,3}$ = 3.4 Hz, $^3J_{4,5}$ = 0.7, 1H, H-4^{gal})), 5.26 (dd, $^3J_{3,2}$ = 10.2 Hz, $^3J_{3,4}$ = 3.4 Hz, 1H, H-3^{gal}), 4.09–4.21 (m, 3H, H-5^{gal}, H-6^{gal}), 2.23, 2.01, 1.99, 1.65 (s, 3H, $COCH_3$). ^{13}C NMR, HSQC (126 MHz, $CDCl_3$): δ = 170.6, 170.3, 170.2, 168.9 (4x C=O), 136.2 (C-7a^{indole}), 129.3 (C-3a^{indole}), 125.0 (C-2^{indole}), 122.5 (C-6^{indole}), 121.5 (C-4^{indole}), 120.8 (C-5^{indole}), 110.0 (C-7^{indole}), 104.2 (C-3^{indole}), 84.1 (C-1^{gal}), 73.5 (C-5^{gal}), 71.7 (C-3^{gal}), 68.2 (C-2^{gal}), 67.4 (C-4^{gal}), 61.6 (C-6^{gal}), 20.9, 20.8, 20.7, 20.3 (4x $COCH_3$). IR $\tilde{\nu}$ (cm^{-1}): 2917, 1750, 1461, 1370, 1223, 1087, 1057, 921, 745. FAB-MS: *m/z* (%) = 331.2 $[M\text{-indole}]^+$ (100), 447.2 $[M]^+$ (75). FAB-HRMS: calcd for $[C_{22}H_{25}NO_9+H]$: *m/z* = 448.1608, found: 448.1590. Anal. calcd for $C_{22}H_{25}NO_9$: C, 59.06, H, 5.63, N, 3.13; found: C 59.10, H 5.77, N 3.13. $[\alpha]^{20}_D$: +10.2 (*c* 1.00, $CHCl_3$).



To a cooled (-60°C), stirred mixture of compound **6** (50 mg, 0.112 mmol), compound **3** (83 mg, 0.168 mmol), activated 4-Å molecular sieves (2.0 g), and anhydrous CH_2Cl_2 was added BF_3•OEt_2 (0.01 ml, 0.08 mmol). Stirring was continued for 4.5 h and the mixture was allowed to warm to 0°C. The mixture was filtered diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent cyclohexane/EtOAc, 5:1→1:1) to afford compound to afford compound **8** (48 mg, 55%). (For a similar procedure, see:[5])

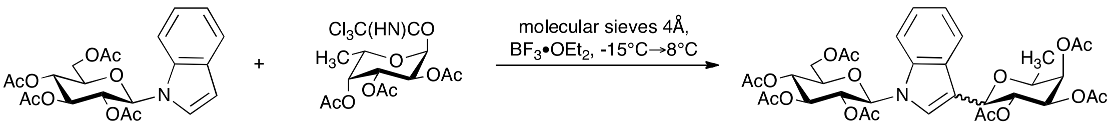
8: colorless oil; R_f = 0.30 (cyclohexane/EtOAc, 1:1). ^{1}H NMR, COSY, HSQC, HMBC, NOESY (400 MHz, $CDCl_3$): δ = 7.80 (dd, $^3J_{4,5}$ = 8.0 Hz, $^4J_{4,6}$ = 1.0 Hz, 1H, H-4^{indole}), 7.53 (dd, $^3J_{7,6}$ = 8.2 Hz, $^4J_{7,5}$ = 1.0 Hz, 1H, H-7^{indole}), 7.44 (d, J = 1.0 Hz, 1H, H-2^{indole}), 7.26 (ddd, $^3J_{6,7}$ = 8.2 Hz, $^3J_{6,5}$ = 7.0 Hz, $^4J_{6,4}$ = 1.0 Hz, 1H, H-6^{indole}), 7.14 (ddd, $^3J_{5,4}$ = 8.0 Hz, $^3J_{5,6}$ = 7.0 Hz, $^4J_{5,7}$ = 1.0 Hz, 1H, H-5^{indole}), 5.94 (dd, $^3J_{2,3}$ = 2.8 Hz, $^3J_{2,1}$ = 1.9 Hz, 1H, H-2^{man}), 5.70 (dd, $^3J_{2,3}$ = 10.2 Hz, $^3J_{2,1}$ = 8.9 Hz, 1H, H-2^{gal}), 5.56 (dd, $J_{4,3}$ = 3.3 Hz, $^3J_{4,5}$ = 0.9 Hz, 1H, H-4^{gal}), 5.51 (d, $J_{1,2}$ = 8.9 Hz, 1H, H-1^{gal}), 5.34–5.40 (m, 3H, H-1^{man}, H-4^{man}, H-3^{man}), 5.25 (dd, $J_{3,2}$ = 10.2 Hz, $^3J_{3,4}$ = 3.3 Hz, 1H, H-3^{gal}), 3.99–4.21 (m, 5H, H-5^{gal}, H-6^{gal}, H-6^{man}), 3.55–3.60 (m, 1H, H-5^{man}), 2.31, 2.20, 2.04, 2.03, 2.02, 1.99, 1.95, 1.70 (8x $COCH_3$). ^{13}C NMR, DEPT, HSQC, HMBC (126 MHz, $CDCl_3$): δ = 171.0, 170.75, 170.73, 170.71, 170.5, 170.3, 169.8, 168.7 (C=O), 136.3 (C-3a^{indole}), 127.6 (C-7a^{indole}), 124.5 (C-2^{indole}), 123.5 (C-6^{indole}), 121.3 (C-5^{indole}), 121.2 (C-4^{indole}), 111.6 (C-3^{indole}), 111.3 (C-7^{indole}), 85.4 (C-1^{gal}), 73.5 (2C, C-1^{man}, C-5^{gal}), 71.5 (C-3^{gal}), 70.9, 70.8 (C-3^{man}, C-5^{man}), 69.6 (C-2^{man}), 68.4 (C-2^{gal}), 67.2 (C-4^{gal}), 66.4 (C-4^{man}), 62.8, 61.7 (C-6^{man}, C-6^{gal}), 21.3, 21.03, 21.00, 20.97, 20.95, 20.91, 20.8, 20.3 ($COCH_3$). IR $\tilde{\nu}$ (cm^{-1}): 3062, 2982, 2939, 2853, 1746, 1467, 1370, 1211, 1039, 911, 741. ESI-MS: m/z (%) = 778.2551 $[M+H]^+$ (100), 800.2377 $[M+Na]^+$ (90), 816.2131 $[M+K]^+$ (45). ESI-HRMS: calcd for $[C_{36}H_{43}NO_{18}+H]^+$: m/z = 778.2553, found: 778.2551; calcd for $[C_{36}H_{41}NO_{18}+Na]^+$: m/z = 800.2372, found: 800.2377; calcd for $[C_{36}H_{43}NO_{18}+K]^+$: m/z = 816.2117, found: 816.2131. $[\alpha]^{20}_{D}$: +36.8 (c 1.00, $CHCl_3$).



6a 7 9

To a cooled (−60°C), stirred mixture of compound **6** (50 mg, 0.112 mmol), compound **7** (72 mg, 0.168 mmol), activated 4-Å molecular sieves (2.0 g), and anhydrous CH_2Cl_2 was added BF_3•OEt_2 (0.01 ml, 0.08 mmol). Stirring was continued for 4.5 h and the mixture was allowed to warm to 0°C. The mixture was filtered diluted with EtOAc and washed with and washed with saturated aqueous $NaHCO_3$. The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was that was purified by flash chromatography (eluent cyclohexane/EtOAc, 3:1→1:1) to afford compound **9** (40 mg, 33%). (For a similar procedure, see:[5]).

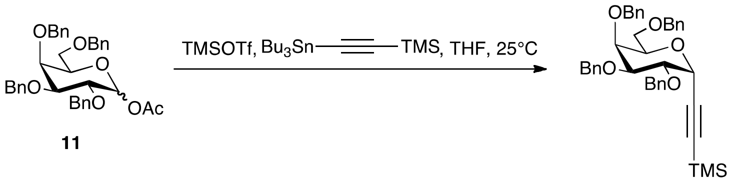
9: colorless oil; R_f = 0.38 (cyclohexane/EtOAc, 2:1). ^{1}H NMR, COSY, HSQC, HMBC (400 MHz, $CDCl_3$): δ = 7.68 (d, $^3J_{4,5}$ = 7.9 Hz, 1H, H-4^{indole}), 7.38 (d, $^3J_{7,6}$ = 8.2 Hz, 1H, H-7^{indole}), 7.31 (s, 1H, H-2^{indole}), 7.22 (ddd, $^3J_{6,7}$ = 8.2 Hz, $^3J_{6,5}$ = 7.1 Hz, $^4J_{6,4}$ = 1.1 Hz, 1H, H-6^{indole}), 7.14 (ddd, $^3J_{5,4}$ = 7.9 Hz, $^3J_{5,6}$ = 7.1 Hz, $^4J_{5,7}$ = 1.1 Hz, 1H, H-5^{indole}), 5.50–5.61 (4H, H-2^{fuc}, H-3^{fuc}, H-1^{gal}, H-2^{gal}), 5.37 (dd, $^3J_{4,3}$ = 3.4 Hz, $^3J_{4,5}$ = 0.8 Hz, 1H, H-4^{gal}), 5.18–5.24 (m, 2H, H-4^{fuc}, H-3^{gal}), 4.73 (d, $^3J_{1,2}$ = 9.8 Hz, 1H, H-1^{fuc}), 4.09–4.21 (m, 3H, H-5^{gal}, H-6a,b^{gal}), 3.99 (dq, $^3J_{5,6}$ = 6.4 Hz, $^3J_{5,4}$ = 1.0 Hz, 1H, H-5^{fuc}), 2.26, 2.24, 2.02 (3x s, each 3H, $COCH_3$), 1.98 (s, 6H, 2x $COCH_3$), 1.77, 1.65 (s, 3H, $COCH_3$), 1.23 (d, $^3J_{6,5}$ = 6.4 Hz, 3H, H-6^{fuc}). ^{13}C NMR, DEPT, HSQC, HMBC (101 MHz, $CDCl_3$): δ = 171.0, 170.62, 170.57, 170.4, 170.3, 169.6, 168.8 (7x C=O), 136.8 (C-3a^{indole}), 127.9 (C-7a^{indole}), 123.3 (C-3^{indole}), 123.0 (C-6^{indole}), 121.0 (C-5^{indole}), 120.1 (C-4^{indole}), 114.3 (C-3^{indole}), 110.1 (C-7^{indole}), 83.9 (C-1^{gal}), 74.5 (C-1^{fuc}), 73.7 (C-5^{gal}), 73.4 (C-5^{fuc}), 73.3 (C-3^{gal}), 71.8 (C-4^{fuc}), 71.4 (C-4^{gal}), 69.6 (C-2^{fuc}), 68.5 (C-3^{fuc}), 67.5 (C-2^{gal}), 61.7 (C-6^{gal}), 21.0, 20.94, 20.92, 20.87, 20.80, 20.77, 20.33 (7x $COCH_3$), 16.9 (C-6^{fuc}). IR $\tilde{\nu}$ (cm^{-1}): 3057, 2981, 2940, 2857, 1743, 1468, 1369, 1212, 1041, 916, 744. ESI-MS: *m/z* (%) = 742.2312 $[M+Na]^+$ (100). ESI-HRMS: calcd for $[C_{34}H_{41}NO_{16}+Na]^+$: *m/z* = 742.2318, found: 742.2312. $[\alpha]^{20}_D$: − 3.5 (*c* 1.00, $CHCl_3$).



6a 7 10

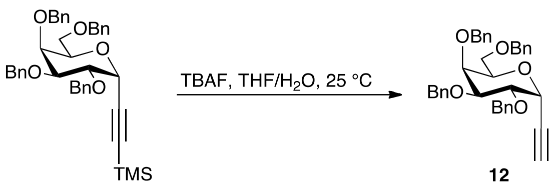
To a cooled (−15°C), stirred mixture of compound **6a** (310 mg, 0.698 mmol), compound **7** 450 mg, 1.04 mmol), activated 4-Å molecular sieves (2.8 g), and anhydrous CH_2Cl_2 (10 ml) was added BF_3•OEt_2 (0.06 ml, 0.48 mmol). Stirring was continued for 4.5 h and the mixture was allowed to warm to 8°C. The mixture was filtered diluted with EtOAc and washed with saturated aqueous $NaHCO_3$. The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was that was purified by flash chromatography (eluent cyclohexane/EtOAc, 3:1) to afford compound **10** (141 mg, 45%, α:β = 1:1.8, determined by NMR-spectroscopy). (For a similar procedure, see:[5]).

10 colorless oil, R_f = 0.43 (cyclohexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.9 Hz, 1H, H-4$^{indole\alpha}$), 7.71 (d, J = 7.8 Hz, 1.8H, H-4$^{indol\beta}$), 7.49 (s, 1H, H-2$^{indol\alpha}$), 7.40 (d, J = 8.3 Hz, 1H, H-7$^{indol\alpha}$), 7.35 (d, J = 8.2 Hz, 1.8H, H-7$^{indol\beta}$), 7.23–7.34 (m, 4.6H, H-2$^{indol\beta}$, H-6$^{indol\alpha/\beta}$), 7.16 (t, J = 7.5 Hz, 2.8H, H-5$^{Indol\alpha/\beta}$), 5.20–5. 76 (m, 12.6 H, H-1$^{gluc\alpha/\beta}$, H-2$^{gluc\alpha/\beta}$, H-3$^{gluc\alpha/\beta}$, H-4$^{gluc\alpha/\beta}$, H-1$^{fuc\alpha}$, H-2$^{fuc\alpha/\beta}$, H-3$^{fuc\alpha/\beta}$, H-4$^{fuc\alpha/\beta}$), 4.71 (d, J = 9.8 Hz, 1.8H, H-1$^{fuc\beta}$), 4.26–4.32 (m, 2.7H, this multiplet contains: 4.29 (dd, $^2J_{6a,6b}$ = 12.4 Hz, $^3J_{6a,5}$ = 4.9 Hz, 1H, H-6a$^{man\alpha}$), 4.28 (dd, $^2J_{6a,6b}$ = 12.5 Hz, $^3J_{6a,5}$ = 5.0 Hz, 1.8H, H-6a$^{gluc\beta}$)), 4.19 (dd, $^2J_{6b,6a}$ = 12.4 Hz, $^3J_{6b,5}$ = 2.1 Hz, 1H,. H-6b$^{gluc\alpha}$), 4.12 (dd, $^2J_{6b,6a}$ = 12.5 Hz, $^3J_{6b,5}$ = 2.0 Hz, 1.8H, H-6b$^{gluc\beta}$), 5.20–5.77 (m, 4.6H, H-5$^{fuc\beta}$, H-5$^{gluc\alpha/\beta}$), 3.60 (dq, $^3J_{5,6}$ = 6.4 Hz, $^3J_{5,4}$ = 1.2 Hz, 1H, H-5$^{fuc\alpha}$), 2.26 (s, 5.4H), 2.21 (s, 3H), 2.09 (s, 3H), 2.08 (s, 6H), 2.07 (s, 8.4H), 2.06 (s, 5.4H), 2.03 (s, 8.4H), 1.99 (s, 5.4H), 1.76 (s, 5.4H), 1.69 (s, 5.4H), 1.62 (s, 3H), 1.25 (s, 3H), ($COCH_3$), 1.24 (d, $^3J_{6,5}$ = 6.3 Hz, 1.8H, H-6$^{fuc\beta}$), 1.04 (d, $^3J_{6,5}$ = 6.4 Hz, 4H, H-6$^{fuc\alpha}$). **1-(3,4,5,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-indole:** ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 170.7, 170.5, 170.3 (2C), 169.6, 168.8 (7x C=O), 136.8 (C-7a^{indole}), 127.6 (C-3a^{indole}), 123.0 (C-2^{indole}), 122.8 (C-6^{indole}), 121.0 (C-4^{indole}), 120.1 (C-5^{indole}), 114.4 (C-7^{indole}), 109.7 (C-3^{indole}), 82.9 (C-1^{gluc}), 74.8 (C-5^{gluc}), 74.5 (C-1^{fuc}), 73.5 (C-3^{gluc}), 73.2 (C-5^{fuc}), 73.0 (C-3^{fuc}), 71.3 (C-4^{fuc}), 70.5 (C-2^{gluc}), 69.4 (C-2^{fuc}), 68.2 (C-4^{gluc}), 62.1 (C-6^{gluc}), 21.0, 20.9, 20.8, 20.7 (2C), 20.6, 20.2 (7x $COCH_3$), 16.8 (C-6^{fuc}). **1-(3,4,5,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-3-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-indole:** ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 170.6, 170.3 (2C), 170.0, 169.6, 168.6 (C=O), 136.2 (C-7a^{indole}), 128.5 (C-3a^{indole}), 124.1 (C-2^{indole}), 123.3 (C-6^{indole}), 121.2 (C-4^{indole}), 121.1 (C-5^{indole}), 111.7 (C-7^{indole}), 109.8 (C-3^{indole}), 83.5 (C-1^{gluc}), 74.9, 73.1, 71.7, 70.4, 70.2, 69.1, 68.7, 68.4 (C-2^{gluc}, C-3^{gluc}, C-4^{gluc}, C-5^{gluc}, C-1^{fuc}, C-2^{fuc}, C-3^{fuc}, C-4^{fuc}), 66.2 (C-5^{fuc}), 62.0 (C-6^{gluc}), 21.99, 20.94, 20.87, 20.81, 20.72 (2C), 20.06 (7x $COCH_3$), 16.4 (C-6^{fuc}). IR $\tilde{\nu}$ (cm^{-1}): 3060, 2981, 2942, 2857, 1746, 1468, 1372, 1212, 1039, 915, 742.



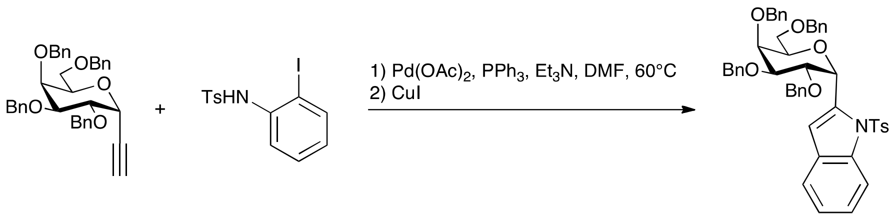
A mixture of 1-acetyl-2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranose (850 mg, 1.46 mmol), tributylstannyl(trimethylsilyl)ethyne (905 mg, 2.34 mmol), activated 4-Å molecular sieves (0.8 g), and anhydrous CH_2Cl_2 (21 ml) was stirred at room temperature for 1 h. Then the mixture was cooled to 0°C and TMSOTf (0.52 ml, 0.0020 mmol) was added dropwise. The dark brown mixture was allowed to warm to room temperature, and stirred for additional 20 h. After dilluting with CH_2Cl_2, the mixture was filtered and washed with saturated aqueous $NaHCO_3$, and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 20:1) to give trimethyl-(2,3,4,6-tetra-*O*-benzyl-α-D-fucosyl-2-ylethynyl)-silane (393 mg, 43%). (For a similar procedure, see:[6]).

colorless oil; R_f = 0.65 (cyclohexane/EtOAc, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.39 (m, 20H, H-Ph), 4.93 (d, ^2J = 11.4 Hz, 1H, CH_2Ph), 4.84 (d, $^3J_{1,2}$ = 5.7 Hz, 1H, H-1), 4.80 (d, ^2J = 12.0 Hz, 1H, CH_2Ph), 4.69–4.76 (m, 3H, CH_2Ph), 4.58 (d, ^2J = 11.4 Hz, 1H, CH_2Ph), 4.49 (d, ^2J = 11.7 Hz, 1H, CH_2Ph), 4.41 (d, ^2J = 11.7 Hz, 1H, CH_2Ph), 4.10–4.13 (m, 1H, H-5), 4.07 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{2,1}$ = 5.7 Hz, 1H, H-2), 3.94 (dd, $^3J_{4,3}$ = 2.7 Hz, $^3J_{4,5}$ = 1.2 Hz, 1H, H-4), 3.85 (dd, $^3J_{3,2}$ = 9.8 Hz, $^3J_{3,4}$ = 2.7 Hz, 1H, H-3), 3.56 (dd, $^2J_{6a,6b}$ = 8.4 Hz, $^3J_{6a,\ 5}$ = 4.9 Hz, 1H, H-6a), 3.53 (dd, $^2J_{6b,6a}$ = 8.4 Hz, $^3J_{6b,5}$ = 6.0 Hz, 1H, H-6b), 0.18 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.93, 138.87 (2C), 138.2 (4x, C-1^{Ph}), 128.6 (2C), 128.53 (2C), 128.49 (2C), 128.43 (2C), 128.42 (2C), 128.1 (2C), 128.0, 127.9 (2C), 127.8 (3C), 127.69, 127.67 (H-Ph), 100.7 (gal-<u>C</u>≡CTMS), 93.8 (gal-C≡<u>C</u>TMS), 79.5 (C-3), 75.7 (C-2), 75.1 (C-4), 75.0 (CH_2Ph), 73.6 (CH_2Ph), 73.1 (CH_2Ph), 72.7 (2C, C-5, CH_2Ph), 68.9 (C-6), 67.8 (C-1), 0.14 (3C, $Si(CH_3)_3$)). $[\alpha]^{20}_D$: 82.9 (*c* 1.00, CH_2Cl_2). (these data match those reported in the literature)[7]



To a solution of trimethyl-(2,3,4,6-tetra-*O*-benzyl-α-D-galactosyl-2-ylethynyl)-silane (382 mg, 0.615 mmol), in THF/H_2O (8.5 ml, 10:1) was added TBAF (0.3 ml, 1M in THF, 0.3 mmol). The reaction was stirred at room temperature for 23 h, diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 15:1) to give compound **12** (251 mg, 74%). (For a similar procedure, see:[6])

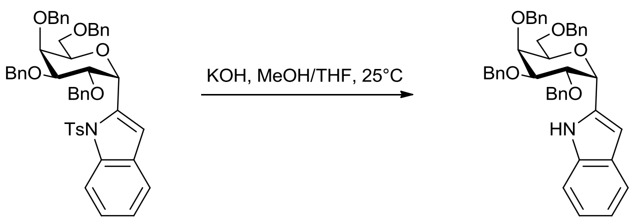
colorless oil; R_f = 0.54 (cyclohexane/EtOAc, 2:1); ^{1}H NMR, COSY, HSQC, HMBC (500 MHz, $CDCl_3$) δ = 7.22–7.37 (m, 20H, H-Ph), 4.91 (d, ^2J = 11.4 Hz, 1H, CH_2Ph), 4.83 (d, ^2J = 11.7 Hz, 1H, CH_2Ph), 4.76–4.78 (m, 2H, CH_2Ph, H-1), 4.73 (d, ^2J = 13.0 Hz, 1H, CH_2Ph), 4.70 (d, ^2J = 12.2 Hz, 1H, CH_2Ph), 4.55 (d, ^2J = 11.4 Hz, 1H, CH_2Ph), 4.47 (d, ^2J = 11.8 Hz, 1H, CH_2Ph), 4.39 (d, ^2J = 11.8 Hz, 1H, CH_2Ph), 4.06–4.13 (m, 2H, this multiplet contains: 4.10 (ddd, $^3J_{5,6b}$ = 6.0 Hz, $^3J_{5,6a}$ = 4.9 Hz, $^3J_{5,4}$ = 1.0 Hz, 1H, H-5), 4.08 (dd, $^3J_{2,3}$ = 9.9 Hz, $^3J_{2,1}$ = 5.9 Hz, 1H, H-2)), 3.96 (dd, $^3J_{4,3}$ = 2.9 Hz, $^3J_{4,5}$ = 1.0 Hz, 1H, H-4), 3.88 (dd, $^3J_{3,2}$ = 9.9 Hz, $^3J_{3,4}$ = 2.9 Hz, 1H, H-3), 3.54 (dd, $^2J_{6a,6b}$ = 8.4 Hz, $^3J_{6a,5}$ = 5.9 Hz, 1H, H-6a), 3.51 (d, $^2J_{6b,6a}$ = 8.4 Hz, $^3J_{6b,5}$ = 6.0 Hz, 1H, H-6b), 2.51 (d, $^4J_{C\equiv C\underline{H},1}$ = 2.2 Hz, 1H, C≡C<u>H</u>). ^{13}C NMR, DEPT, HSQC, HMBC (126 MHz, $CDCl_3$) δ = 138.9, 138.8, 138.5, 138.2 (4x C-1^{Ph}), 128.62 (2C), 128.61 (2C), 128.59 (2C), 128.51(2C), 128.46 (2C), 128.16 (4C), 127.98 (2C), 127.83, 127.74, 127.69 (2C) (20x CH-Ph), 80.4 (C-3), 79.2 (<u>C</u>≡CH), 76.7 (C≡<u>C</u>H), 75.4 (C-2), 75.1 (CH_2Ph), 75.0 (C-4), 73.7, 73.5, 73.5 (CH_2Ph), 72.9 (C-5), 68.9 (C-6), 67.5 (C-1). IR $\tilde{\nu}$ (cm^{-1}): 3281, 3087, 3062, 3029, 2902, 2870, 1723, 1496, 1454, 1368, 1269, 1208, 1098, 736, 698. FAB-MS: *m/z* (%) = 49.4 [M+H]$^+$ (70), 571.4 [M+Na]$^+$ (100). FAB-HRMS: calcd for [$C_{36}H_{36}O_5$+H]$^+$: *m/z* = 549.2641, found: 549.2664. Anal. for $C_{36}H_{36}O_5$ calcd: C 78.81, H 6.61; found: C 79.28, H 6.77. $[\alpha]^{20}_D$: 32.2 (*c* 1.00, CH_2Cl_2). (these data match those reported in the literature)[7]



12 **13**

A solution of *o*-iodoaniline **(**789 mg, 2.12 mmol), acetylene **12** (1.06 mg, 1.92 mmol), PPh_3 (54 mg, 0.21 mol), and $Pd(OAc)_2$ (30 mg, 13 mmol), in Et_3N (30 ml) and DMF (5 ml) was stirred at 70°C for 16.5 h. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$, and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 10:1) to give compound **13** (1.19 mg, 78%). (this compound was prepared to according to Nishikawa et al. and the data match those reported in the literature[7])

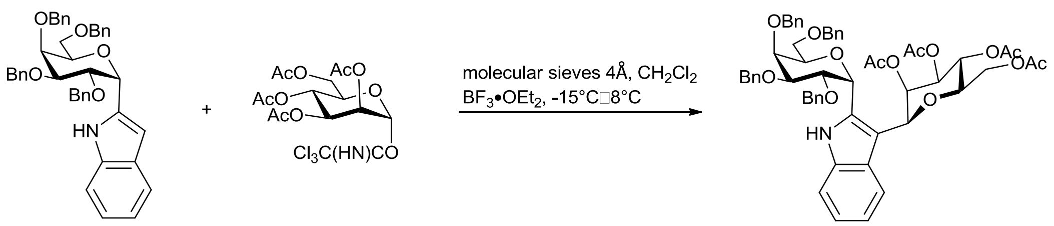
13: yellow oil; R_f = 0.43 (cyclohexane/EtOAc, 3:1); ^{1}H NMR, COSY, HMBC, HSQC (500 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.4 Hz, 1H, H-4^{indole}), 7.50 (part of a AA′BB′X-spinsystem, 2H, H-3,5^{Ts}), 7.42 (d, J = 7.6 Hz, 1H, H^{indole}), 7.35–7.37 (m, 2H, H-Ph), 7.18–7.37 (m, 15H, H-Ph), 7.15–7.17 (m, 1H, H-Ph), 7.09–7.12 (m, 2H, H-Ph), 6.91–6.95 (m, 5H; this multiplet contains: H-4,6^{Ts}, H-3^{indole}), 5.82 (s, 1H, H-1^{gal}), 4.74 (d, ^2J = 12.1 Hz, 1H, CH_2Ph), 4.55 (d, ^2J = 11.0 Hz, 2H, CH_2Ph), 4.51 (d, ^2J = 11.8 Hz, 1H, CH_2Ph), 4.46 (d, ^2J = 11.9 Hz, 1H, CH_2Ph), 4.38–4.33 (m, 1H, H-4^{gal}), 4.31 (d, ^2J = 11.9 Hz, 1H, CH_2Ph), 4.24 (dd, $^3J_{2,3}$ = 4.6 Hz, $^3J_{2,1}$ = 2.0 Hz, 1H, H-2^{gal}), 4.13 (d, ^2J = 11.9 Hz, 1H, CH_2Ph), 4.09 (d, ^2J = 11.9 Hz, 1H CH_2Ph), 4.05 (dd, ^3J = 5.8 Hz, ^3J = 2.9 Hz, 1H, H-5^{gal}), 3.94–4.00 (m, 1H, H-6a^{gal}), 3.73–3.79 (m, 2H, H-3^{gal}, H-6b^{gal}), 2.12 (s, 3H, CH_3^{Ts}). ^{13}C NMR, DEPT, HMBC, HSQC (126 MHz, $CDCl_3$): δ = 144.9 (C-4^{Ts}), 138.73, 138.68, 138.6, 137.9 (4x C-1^{Ph}), 137.73 (C-2^{indole}), 137.66 (C-1^{Ts}), 135.59 (C-7a^{indole}), 130.3 (C-3a^{indole}), 129.9 (C-3,5^{Ts}), 128.53, 128.47, 128.43, 128.40, 128.30, 127.94, 127.93, 127.83, 127.82, 127.69, 127.60 (CH-Ph), 126.49 (C-4,6^{Ts}), 124.6, 124.0 (C-5^{indole}, C-6^{indole}), 121.1 (C-7^{indole}), 115.5 (C-4^{indole}), 113.5 (C-3^{indole}), 76.1 (C-2^{gal}), 75.3 (C-4^{gal}), 74.9 (C-3^{gal}), 73.6 (CH_2Ph), 73.4 (CH_2Ph), 73.1 (C-5^{gal}), 72.4 (CH_2Ph), 72.0 (CH_2Ph), 66.8 (C-6^{gal}), 65.8 (C-1^{gal}), 21.6 (Ts$\underline{C}H_3$). IR $\tilde{\nu}$ (cm^{-1}): 2924, 2854, 1597, 1452, 1368, 1172, 1148, 1091, 1027, 746, 697, 581, 542. ESI-MS: m/z (%) = 794.7 $[M+H]^+$ (55). ESI-HRMS: calcd for $[C_{49}H_{47}NO_7S+Na]^+$: m/z = 816.2971, found: 816.2994. $[\alpha]^{20}_D$: + 95.0 (c = 1.00, $CHCl_3$).



13 **14**

A solution of the *N*-tosylindole **13** (320 mg, 0.403 mmol) in a mixture of THF (3 ml) and MeOH (15 % KOH, 2 ml) was stirred at room temperature for 11 d. The mixture was diluted with H_2O and extracted with EtOAc, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 20:1) to give compound **14** (208 mg, 82%). (these data match those reported in the literature)[7]

14: colorless oil; R_f = 0.49 (cyclohexane/EtOAc, 5:1); ^{1}H NMR, COSY, HMBC, HSQC (400 MHz, $CDCl_3$): δ = 8.86 (s, 1H, NH), 7.56 (d, $^3J_{4,5}$ = 7.7 Hz, 1H, H-4^{indole}), 7.26–7.38 (m, 20H, H-Ph), 7.13 (dd, $^3J_{7,6}$ = 8.1 Hz, $^4J_{7,5}$ = 0.8 Hz, 1H, H-7^{indole}), 7.04 (mc, 1H, H-6^{indole}), 6.98 (mc, 1H, H-5^{indole}), 6.59 (s, 1H, H-3^{indole}), 5.38 (s, $^3J_{1,2}$ = 5.0 Hz, 1H, H-1^{gal}), 4.87 (d, ^2J = 11.6 Hz, 1H, CH_2Ph), 4.65–4.78 (m, 4H, CH_2Ph), 4.59 (d, 1H, ^2J = 11.7 Hz, CH_2Ph), 4.51 (d, 1H, ^2J = 11.9 Hz, CH_2Ph), 4.44 (d, 1H, ^2J = 11.9 Hz, CH_2Ph), 4.31 (mc, 1H, H-2^{gal}), 3.96 (mc, 1H, H-5^{gal}), 3.90 (pseudo-t, $^3J_{app,4,3/5}$ = 2.5 Hz, 1H, H-4^{gal}), 3.84 (dd, 1H, $^3J_{3,2}$ = 9.0 Hz, $^3J_{3,4}$ = 2.8 Hz, Hz, H-3^{gal}), 3.78 (dd, $^3J_{6a,6b}$ = 10.0 Hz, $^3J_{6a,5}$ = 7.5 Hz, 1H, H-6a^{gal}), 3.54 (dd, 1H, $^3J_{6b,6a}$ = 10.0 Hz, $^3J_{6b,5}$ = 5.0 Hz, H-6b^{gal}). ^{13}C NMR, DEPT, HMBC, HSQC (101 MHz, $CDCl_3$): δ = 138.7 (2C), 138.4, 138.2 (4x, C-1^{Ph}), 135.9 (C-7a^{indole}), 135.3 (C-2^{indole}), 128.7 (2C), 128.6 (4C), 128.5 (2C), 128.4 (2C), (10x CH-Ph), 128.3 (C-3a^{indole}), 128.2 (2C), 128.1, 127.89 (3C), 127.86 (2C) 127.8 (2C, 10x CH-Ph), 127.1 (C-3a^{indol}), 121.8 (C-6^{indole}), 120.6 (C-4^{indole}), 119.8 (C-5^{indole}), 111.1 (C-7^{indole}), 102.0 (C-3^{indole}), 78.9 (C-3^{gal}), 78.0 (C-2^{gal}), 74.4 (C-4^{gal}), 72.2, 73.6 (2C, 3x CH_2Ph), 73.3 (C-5^{gal}), 73.2 (CH_2Ph), 71.0 (C-1^{gal}), 68.9 (C-6^{gal}). IR $\tilde{\nu}$ (cm^{-1}): 3423, 3029, 2867, 1496, 1454, 1326, 1206, 1092, 735, 697, 516. EI-MS: *m/z* (%) = 91 $[C_7H_7]^+$ (100), 639 $[M]^+$ (10). FAB-HRMS: calcd for [M]: *m/z* = 639.2985, found: 639.3002; calcd for $[C_{42}H_{41}NO_5+H]^+$: *m/z* = 640.3063, found: 640.3037. $[\alpha]^{20}_D$: + 52.32 (*c* 1.00, $CHCl_3$).

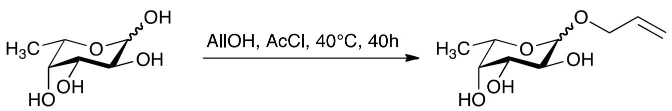


14 3 15

To a cooled (−60°C), stirred mixture of compound **14** (31 mg, 0.032 mmol), compound **3** (36 mg, 0.073 mmol), activated 4-Å molecular sieves (1.4 g), and anhydrous CH_2Cl_2 (4 ml) was added BF_3•OEt_2 (0.01 ml, 0.08 mmol). Stirring was continued for 2 h and the mixture was allowed to warm to 0°C. The mixture was filtered diluted with EtOAc and washed with and washed with saturated aqueous $NaHCO_3$. The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was that was purified by flash chromatography (eluent cyclohexane/EtOAc, 3:1), and subsequent HPLC-chromatography (*n*-

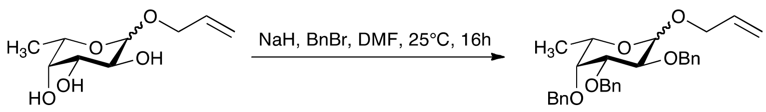
hexane/*i*-propanol, 97:3) to afford compound to afford compound **15** (7 mg, 23%). (For a similar procedure, see:[5]).

15: colorless oil; R_f = 0.34 (cyclohexane/EtOAc, 5:1); ^{1}H NMR, COSY, HSQC, NOESY (400 MHz, $CDCl_3$): δ = 9.04 (s, 1H, NH), 7.90 (d, $^3J_{4,5}$ = 8.0 Hz, 1H, H-4^{indole}), 7.22–7.38 (m, 19H, H-Ph), 7.08–7.16 (m, 3H, H-6^{indole}, H-7^{indole}, H-Ph), 7.04 (ddd, $^3J_{5,4}$ = 8.0 Hz, $^3J_{5,6}$ = 6.8 Hz, $^4J_{5,7}$ = 1.4 Hz, 1H, H-5^{indole}), 5.51 (d, $^3J_{1,2}$ = 3.8 Hz, 1H, H-1^{gal}), 5.44 (dd, $^3J_{2,3}$ = 3.5 Hz, $^3J_{2,1}$ = 1.2 Hz, 1H, H-2^{man}), 5.40 (t, $^3J_{4,3/5}$ = 10.1 Hz, 1H, H-4^{man}), 5.36 (s, broad, 1H, H-1^{man}), 5.17 (dd, $^3J_{3,4}$ = 10.1 Hz, $^3J_{3,2}$ = 3.5 Hz, 1H, H-3^{man}), 4.76 (d, ^2J = 11.6 Hz, 1H, CH_2Ph), 4.74 (d, ^2J = 12.0 Hz, 1H, CH_2Ph), 4.69 (d, ^2J = 12.0 Hz, 1H, CH_2Ph), 4.55 (d, ^2J = 11.6 Hz, 1H, CH_2Ph), 4.53 (d, ^2J = 12.2 Hz, 1H, CH_2Ph), 4.47–4.50 (m, 2H, CH_2Ph), 4.36 (d, broad, ^2J = 11.0 Hz, 1H, CH_2Ph), 4.11–4.22 (m, 4H, this multiplet contains: 4.20 (dd, $^3J_{6a,6b}$ = 12.1 Hz, $^3J_{6a,5}$ = 4.9 Hz, H-6a^{man}), 4.13 (dd, $^2J_{6b,6a}$ = 12.1 Hz, $^3J_{6b,5}$ = 2.5 Hz, H-6b^{man}), H-2^{gal}, H-5^{gal}), 3.97 (dd, $^3J_{4,5}$ = 3.9 Hz, $^3J_{4,3}$ = 2.8 Hz, 1H, H-4^{gal}), 3.92–3.95 (m, 1H, H-6^{gal}), 3.84 (dd, $^3J_{3,2}$ = 7.3 Hz, $^3J_{3,4}$ = 2.8 Hz, 1H, H-3^{gal}), 3.58–3.65 (m, 2H, H-5^{man}, H-6^{gal}), 2.00, 1.90, 1.58 (3x s, each 3H, $COCH_3$). ^{13}C NMR, HSQC (101 MHz, $CDCl_3$): δ = 170.9, 170.4, 170.2, 170.0 (C=O), 138.5, 138.4 (2C), 137.8 (4x C-1^{Ph}), 135.4 (C-7a^{indole}), 131.4 (C-2^{indole}), 128.7 (6C), 128.6 (2C), 128.3 (2C), 128.2, 128.09 (2C), 128.06 (2C), 127.98 (3C), 127.94, 127.85 (20x H-Ph), 127.0 (C-3a^{indole}), 122.2, 122.0 (C-4^{indole}, C-6^{indole}), 119.6 (C-5^{indole}), 111.0 (C-7^{indole}), 100.2 (C-3^{indole}), 78.7 (C-5^{gal}), 76.7 (C-3^{gal}), 76.2 (C-5^{man}), 74.5 (C-1^{man}), 74.2 (H-4^{gal}, H-2^{gal}), 74.1, 73.5, 73.4, 72.9 ($BnCH_2$), 72.5 (H-3^{man}), 71.7 (C-2^{man}), 68.4 (C-6^{man}), 67.6 (C-1^{gal}), 66.7 (C-4^{man}), 63.4 (C-6^{gal}), 21.0 (2C), 20.9, 20.7 ($COCH_3$). IR $\tilde{\nu}$ (cm^{-1}): 3423, 3029, 2867, 17.42, 1496, 1461, 1346, 1210, 1065, 741, 697, 516. FAB-HRMS: calcd for [$C_{56}H_{59}NO_{14}$+H]: *m/z* = 970.4008, found: 970.4007; calcd for [$C_{56}H_{59}NO_{14}$+Na]: *m/z* = 992.3828, gef.: 992.3835.



Allyl alcohol (70.0 ml, 1.03 mol) was slowly added to a mixture of acetyl chloride (5.5 ml, 77 mmol). To this solution was added fucose (5.00 g, 31.2 mmol) and the reaction mixture was stirred at 40°C for 40 h. The reaction was quentched with $NaHCO_3$ filtered over a pad of Celite and concentrated in vacuo. The residue was purified by flash chromatography (eluent cyclohexane/EtOAc, 15:1) to afford O-allyl-α/β-D-fucopyranose (5.18 g, 80%, α:β = 4.25:1, determined by NMR-spectroscopy). %). (For a similar procedure, see:[8])

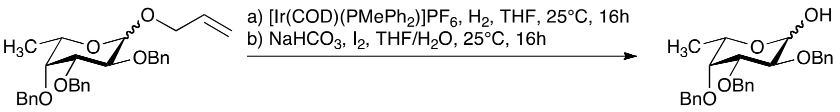
colorless oil; R_f = 0.49 ($CHCl_3$/MeOH/AcOH, 3:1:0.1). Characteristic NMR-signals to determine the anomeric ratio: ^{1}H NMR (400 MHz, CD_3OD): δ 4.80 (d, $^3J_{1,2}$ = 3.1 Hz, 1H, H-1$^{fuc\alpha}$), 4.23 (d, $^3J_{1,2}$ = 7.2 Hz, 1H, H-1$^{fuc\beta}$). Spectroscopic data of *O*-allyl-α-D-fucopyranose: ^{1}H NMR (400 MHz, CD_3OD): δ = 5.98 (dddd, $^3J_{CH,CH2}$ = 5.4, 5.9 Hz, $^3J_{CH,=CH2}$ = 10.5, 17.2 Hz, 1H, $CH_2C\underline{H}=CH_2$), 5.34 (d-pseudo-q, $^2J_{app,=CH2a,=CH2b/CH2}$ = 1.6 Hz, $^3J_{CH2,CH}$ = 17.3 Hz, 1H, $CH_2CH=C\underline{H}_{2a}$), 5.18 (d-pseudo-q, $^2J_{app,=CH2a,=CH2b/,CH2}$ = 1.5 Hz, $^3J_{=CH2b,CH}$ = 10.5 Hz, 1H, $CH_2CH=C\underline{H}_{2b}$), 4.82 (d, $^3J_{1,2}$ = 3.1 Hz, 1H, H-1), 4.18 (ddt, $^4J_{CH2,=CH2}$ = 1.5 Hz, $^3J_{CH2,CH}$ = 5.3 Hz, $^2J_{CH2,CH2}$ = 13.0 Hz,1H, $C\underline{H}_{2a}CH=CH_2$), 4.04 (ddt, $^4J_{CH2,=CH2}$ = 1.4 Hz, $^3J_{CH2,CH}$ = 6.0 Hz, $^2J_{CH2,CH2}$ = 13.0 Hz, 1H, $C\underline{H}_{2b}CH=CH_2$), 3.97 (qd, $^3J_{5,4}$ = 1.1 Hz, $^3J_{5,6}$ = 6.6 Hz, 1H, H-5), 3.76–3.77 (m, 2H, this multiplet contains: 3.78 (dd, $^3J_{3,4}$ = 2.6 Hz, $^3J_{3,2}$ = 12.0 Hz, 1H, H-3), 3.75 (dd, $^3J_{2,1}$ = 3.1 Hz, $^3J_{2,3}$ = 12.0 Hz, 1H, H-2)), 3.68 (dd, $^3J_{4,5}$ = 1.1 Hz, $^3J_{4,3}$ = 2.6 Hz, 1H, H-4), 1.23 (d, $^3J_{6,5}$ = 6.6 Hz, 3H, H-6). ^{13}C NMR (101 MHz, CD_3OD): δ 135.9 ($CH_2\underline{C}H=CH_2$), 117.5 ($CH_2CH=\underline{C}H_2$), 99.8 (C-1), 73.8 (C-4), 71.9 (C-2), 70.2 (C-3), 69.7 ($\underline{C}H_2CH=CH_2$), 67.8 (C-5), 16.7 (C-6).



To a solution of *O*-allyl-α/β-D-fucopyranose (5.1 g, 25.0 mmol) in anhydrous DMF (105 ml) was slowly added NaH (6.14 g, 60% dispersion in mineral oil, 165 mmol). After stirring for 45 min at room temperature, benzyl bromide (9.08 ml, 76.1 mmol) was added and stirring was continued for 16 h. The reaction was quenched with methanole and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent cyclohexane/EtOAc, 20:1) to give *O*-allyl-2,3,4,6-tetra-*O*-benzyl-α/β-D-fucopyranose (10.8 g, 91%; α:β = 9:2, determined by NMR-spectroscopy).

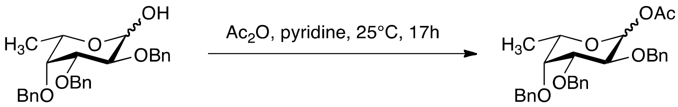
colorless oil; R_f = 0.76 (cyclohexane/EtOAc, 2:1). Characteristic NMR-signals to determin the anomeric ratio: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84 (d, $^3J_{1,2}$ = 3.7 Hz, 1H, H-1$^{fuc\alpha}$), 4.36 (d, $^3J_{1,2}$ = 7.7 Hz, 1H, H-1$^{fuc\beta}$). Spectroscopic data of allyl 2,3,4,6-tetra-*O*-benzyl-α-D-fucopyranoside: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.40 (m, 15H, H-Ph), 5.91 (dddd, $^3J_{CH,=CH2}$ = 17.0, 10.4 Hz, $^3J_{CH, CH2}$ = 6.5, 5.2 Hz, 1H, $CH_2C\underline{H}=CH_2$), 5.29 (d-pseudo-q,

$^{3}J_{CH2,CH}$ = 17.1 Hz, $^{2}J_{app,=CH2,=CH2/CH2}$ = 1.3 Hz, 1H, $CH_2CH=C\underline{H}_{2a}$), 5.17 (d-pseudo-q, $^{3}J_{=CH2,CH}$ = 10.3 Hz, $^{2}J_{app,=CH2,=CH2/CH2}$ = 1.3 Hz, 1H, $CH_2CH=C\underline{H}_{2b}$), 4.97 (d, ^{2}J = 11.4 Hz, 1H, CH_2Ph), 4.87 (d, ^{2}J = 11.8 Hz, 1H, CH_2Ph), 4.84 (d, $^{3}J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.79 (d, ^{2}J = 12.0 Hz, 1H, CH_2Ph), 4.72 (d, ^{2}J = 11.8 Hz, 1H, CH_2Ph), 4.66 (d, ^{2}J = 12.0 Hz, 1H, CH_2Ph), 4.64 (d, ^{2}J = 11.4 Hz, 1H, CH_2Ph), 4.11 (ddt, $^{2}J_{CH2,CH2}$ = 13.0 Hz, $^{3}J_{CH2,CH}$ = 5.2 Hz, $^{4}J_{CH2,=CH2}$ = 1.4 Hz, 1H, $C\underline{H}_{2a}CH=CH_2$), 3.97–4.05 (m, 2H, this multiplet contains: 4.03 (dd, $J_{2,3}$ = 10.1 Hz, $J_{2,1}$ = 3.7 Hz, 1H, H-2), 4.06 (ddt, $^{2}J_{CH2,CH2}$ = 13.0 Hz, $^{3}J_{CH2,CH}$ = 6.5 Hz, $^{4}J_{CH2,=CH2}$ = 1.2 Hz, 1H, $C\underline{H}_{2b}CH=CH_2$)), 3.95 (dd, $^{3}J_{3,2}$ = 10.1 Hz, $^{3}J_{3,4}$ = 2.8 Hz, 1H, H-3), 3.88 (qd, $^{3}J_{5,6}$ = 6.4 Hz, $^{3}J_{5,4}$ = 1.1 Hz, 1H, H-5), 3.64 (dd, $^{3}J_{4,3}$ = 2.8 Hz, $^{3}J_{4,5}$ = 1.1 Hz, 1H, H-4), 1.09 (d, $^{3}J_{6,5}$ = 6.5 Hz, 3H, H-6). MS (ESI): 497.2 $[M+Na]^+$ (100), 513.2 $[M+K]^+$ (75). HRMS (ESI): calcd for $[C_{30}H_{34}O_5+Na]^+$: 497.2304; found: 497.2299; calcd for $[C_{30}H_{34}O_5+K]^+$: 513.2038; found: 513.2041.



A solution of 1,5-cyclooctadien-bis(methyldiphenylphosphine)iridium(I)-hexafluorophosphate (359 mg , 0.424 mmol) in dry THF (500 ml) was stirred under hydrogen atmosphere for 10 min. This solution was added to allyl-α-D-mannopyranoside (2.90 g, 6.12 mmol) and stirring was continued for 16 h at room temperature. The mixture was concentrated under reduced pressure and the residue dissolved in CH_2Cl_2. The organic phases were subsequently washed with saturated aqueous $NaHCO_3$ and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in a mixture of THF (100 ml) and H_2O (63 ml) and $NaHCO_3$ (1.88 g, 22.3 mmol) and I_2 (3.75 g, 14.8 mol) were added. After stirring for 16h at room temperature, the reaction is quenched with $NaHSO_3$. The mixture was diluted with EtOAc and the organic phases were washed with saturated aqueous $NaHCO_3$ and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 4:1) to give 2,3,4,6-tetra-*O*-benzyl-α/β-D-fucopyranose (2.23 g, 84%, α:β = 8:3, determined by NMR-spectroscopy). (For a similar procedure, see:[8])

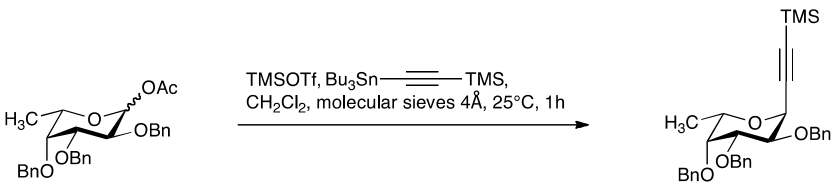
yellow solid; mp.: 84-85°C; R_f = 0.51 (cyclohexane/EtOAc, 5:1). Characteristic NMR-signals to determine the anomeric ratio: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.4 Hz, 3H, H-6$^{fuc\beta}$), 1.13 (d, $^{3}J_{6,5}$ = 6.5 Hz, 3H, H-6$^{fuc\alpha}$). Spectroscopic data of 2,3,4,6-tetra-benzyl-α-D-fucopyranoside: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.40 (m, 15H, H-Ph), 5.25 (d, $^{3}J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.96 (d, ^{2}J = 11.6 Hz, 1H, CH_2Ph), 4.82 (d, ^{2}J = 11.7 Hz, 1H, CH_2Ph), 4.81 (d, ^{2}J = 11.9 Hz, 1H, CH_2Ph), 4.74 (d, ^{2}J = 11.9 Hz, 1H, CH_2Ph), 4.70 (d, ^{2}J = 11.7 Hz, 1H, CH_2Ph), 4.65 (d, ^{2}J = 11.6 Hz, 1H, CH_2Ph), 4.09 (dq, $^{3}J_{5,6}$ = 6.5 Hz, $^{3}J_{5,4}$ = 0.8 Hz, 1H, H-5), 4.03 (dd, $^{3}J_{2,3}$ = 9.9 Hz, $^{3}J_{2,1}$ = 3.7 Hz, 1H, H-2), 3.88 (dd, $^{3}J_{3,2}$ = 9.9 Hz, $^{3}J_{3,4}$ = 2.8 Hz, 1H, H-3), 3.65 (dd, $^{3}J_{4,3}$ = 2.8 Hz, $^{3}J_{4,5}$ = 0.8 Hz, 1H, H-4), 1.13 (d, $^{3}J_{6,5}$ = 6.5 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 138.8, 138.4 (3x, C-1^{Ph}), 128.63 (4C), 128.60 (2C), 128.4 (2C), 128.2 (2C), 128.0, 127.83, 127.80, 127.7 (2C), (15x H-Ph), 92.1 (C-1), 79.3 (C-3),77.6 (C-4), 76.8 (C-2), 75.0 (CH_2Ph), 73.7 (CH_2Ph), 73.2 (CH_2Ph), 66.9 (C-5), 16.9 (C-6). IR $\tilde{\nu}$ (cm^{-1}): 697, 735, 1064, 1098, 1360, 1454, 1496, 2924, 3062, 3405. MS (ESI): 457.1990 $[M+Na]^+$ (100), 891.4080 $[2M+Na]^+$ (50). HRMS (ESI): calcd for $[C_{27}H_{30}O_5+Na]^+$: 457.1991; found: 457.1990.



A solution of 2,3,4,6-tetra-O-benzyl-α/β-D-fucopyranose (1.07 g, 2.45 mmol), pyridine (128 ml) and acetic anhydride (0.98 ml, 10.4 mmol,) was stirred at room temperature for 17 h and then concentrated in vacuo. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 7:1) to give 1-acetyl-2,3,4,6-tetra-*O*-benzyl-α/β-D-fucopyranoside (1.09 g, 93%, α:β = 5:6, determined by NMR-spectroscopy). (For a similar procedure, see:[4]).

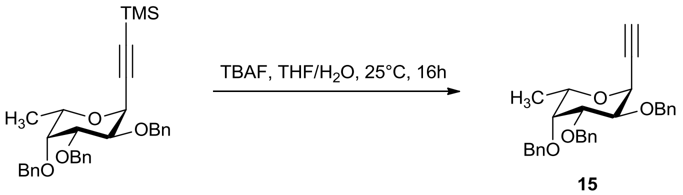
colorless solid; R_f = 0.47 (cyclohexane/EtOAc, 2:1). Characteristic NMR-signals to determine the anomeric ratio: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.36 (d, $^{3}J_{1,2}$ = 3.7 Hz, 1H, H-1$^{Fuc\alpha}$), 5.54 (d, $^{3}J_{1,2}$ = 8.1 Hz, 1H, H-1$^{Fuc\beta}$). Spectroscopic data of 1-acetyl-2,3,4,6-tetra-*O*-benzyl-α/β-D-fucopyranose: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.39 (m, 30H, H-Ph$^{\alpha,\beta}$), 6.36 (d, $^{3}J_{1,2}$ = 3.7 Hz, 1H, H-1$^{\alpha}$), 5.54 (d, $^{3}J_{1,2}$ = 8.1 Hz, 1H, H-1$^{\beta}$), 4.97 (d, ^{2}J = 11.5 Hz, 2H, $BnCH_2^{\alpha,\beta}$), 4.85 (d, ^{3}J = 11.8 Hz, 1H, $CH_2Ph^{\alpha,\beta}$), 4.83 (d, ^{3}J = 11.5 Hz, 1H, $CH_2Ph^{\alpha,\beta}$), 4.63–7.67 (m, 8H, $CH_2Ph^{\alpha,\beta}$), 4.15 (dd, $^{3}J_{2,1}$ = 3.7 Hz, $^{3}J_{2,3}$ = 10.1 Hz, 1H, H-2$^{\alpha}$), 3.96 (dq, $^{3}J_{5,4}$ = 0.9 Hz, $^{3}J_{5,6}$ = 6.5 Hz, 1H, H-5$^{\alpha}$), 3.94 (ddd, $^{2}J_{2,4}$ = 1.1 Hz, $^{3}J_{2,1}$ = 8.1 Hz, , $^{3}J_{2,3}$ = 10.5 Hz, 1H, H-2$^{\beta}$), 3.87 (dd, $^{3}J_{3,4}$ = 2.8 Hz, $^{3}J_{3,2}$ = 10.1 Hz, 1H, H-3$^{\alpha}$), 3.69 (dd, $^{3}J_{4,5}$ = 0.9 Hz, $^{3}J_{4,3}$ = 2.8 Hz, 1H, H-4$^{\alpha}$), 3.57–3.62 (m, 3H, H-3$^{\beta}$, H-4$^{\beta}$, H-5$^{\beta}$), 2.10 (s, 3H, $COCH_3^{\alpha}$), 2.02 (s, 3H, $OCCH_3^{\beta}$), 1.16 (d, $^{3}J_{6,5}$ = 6.4 Hz, 3H, H-6$^{\beta}$), 1.13 (d, $^{3}J_{6,5}$ = 6.5 Hz, 3H, H-6$^{\beta}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 169.7 (C=O$^{\alpha,\beta}$), 139.0, 138.7, 138.64, 138.60, 138.5, 138.3 (6x

C-1$^{Ph,\alpha,\beta}$), 128.7 (4C), 128.60 (2C), 128.57 (3C), 128.55 (2C), 128.46 (2C), 128.43 (2C), 128.2 (2C), 128.1 (2C), 127.94, 127.92, 127.89 (3C), 127.85, 127.82 (2C), 127.76, 127.6 (2C, H-Ph $^{\alpha,\beta}$), 94.5 (C-1$^{\beta}$), 91.1 (C-1$^{\alpha}$), 83.0 (C-3$^{\beta}$), 79.2 (C-3$^{\alpha}$), 78.3 (C-2$^{\beta}$), 77.7 (C-4$^{\alpha}$), 76.3 (C-4$^{\beta}$), 75.6 (C-2$^{\alpha}$), 75.5, 75.2, 74.9, 73.5, 73.44, 73.36 ($CH_2Ph^{\alpha,\beta}$), 71.7 (C-5$^{\beta}$), 69.3 (C-5$^{\alpha}$), 21.4, 21.3 (C-6$^{\alpha}$, C-6$^{\beta}$), 16.9 (2C, $COCH_3^{\alpha,\beta}$). MS (ESI): 457.1990 $[C_{29}H_{32}NaO_6]^+$ (100). IR $\tilde{\nu}$ (cm^{-1}): 3029, 2876, 1748, 1496, 1453, 1366, 1229, 1101, 1057, 734, 697. ESI-MS: *m/z* (%) = 499.2 $[M+Na]^+$ (100). ESI-HRMS: calcd for $[C_{29}H_{32}O_6+Na]^+$: *m/z* = 499.2091, found: 499.2092.



A mixture of 1-acetyl-2,3,4-tri-*O*-benzyl-α/β-D-fucopyranose (480 mg, 1.01 mmol), tributylstannyl(trimethylsilyl)ethyne (624 mg, 1.61 mmol), activated 4-Å molecular sieves (1.08 g), and anhydrous CH_2Cl_2 (5 ml) was mixture was stirred at room temperature for 30 min. Then, TMSOTf (0.36 ml, 0.0016 mmol) was added dropwise. The dark brown was stirred at room temperature for additional 1 h, diluted with CH_2Cl_2, filtered, washed with saturated aqueous $NaHCO_3$ and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 15:1) to give trimethyl-(2,3,4-tri-*O*-benzyl-α-D-fucosyl-2-ylethynyl)-silane (472 mg, 91%). (For a similar procedure, see:[6]).

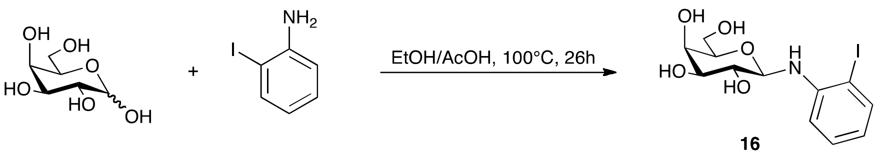
colorless Oil; R_f = 0.70 (cyclohexane/EtOAc, 5:1), ^{1}H NMR, HSQC (400 MHz, $CDCl_3$): δ = 7.23–7.39 (m, 5H, H-Ph), 4.95 (d, ^2J = 11.6 Hz, 1H, CH_2Ph), 4.82 (d, ^2J = 12.1 Hz, 1H, CH_2Ph), 4.80 (d, $^3J_{1,2}$ = 5.7 Hz, 1H, H-1), 4.73 (d, ^2J = 11.9 Hz, 1H, CH_2Ph), 4.72 (d, ^2J = 12.1 Hz, 1H, CH_2Ph), 4.69 (d, ^2J = 11.9 Hz, 1H, CH_2Ph), 4.64 (d, ^2J = 11.6 Hz, 1H, CH_2Ph), 4.05 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{2,1}$ = 5.7 Hz, 1H, H-2), 3.99 (qd, $^3J_{5,6}$ = 6.4 Hz, $^3J_{5,4}$ = 1.2 Hz, 1H, H-5), 3.83 (dd, $^3J_{3,2}$ = 9.7 Hz, $^3J_{3,4}$ = 2.8 Hz, 1H, H-3), 3.59 (dd, $^3J_{4,3}$ = 2.8 Hz, $^3J_{4,5}$ = 1.2 Hz, 1H, H-4), 1.12 (d, $^3J_{6,5}$ = 6.4 Hz, 3H, H-6), 0.16 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR, HSQC (101 MHz, $CDCl_3$): δ = 139.1, 138.9, 138.8 (3x, C-1^{Ph}), 128.7 (2C), 128.5 (2C), 128.42 (2C), 128.41 (2C), 127.9 (2C), 127.81, 127.78 (2C), 127.7, 27.6 (15x, H-Ph), 101.3 (fuc-<u>C</u>≡$CSi(CH_3)_3$), 93.3 (fuc-C≡<u>C</u>$Si(CH_3)_3$), 79.8 (C-3), 77.8 (C-4), 75.7 (C-2), 75.1, 73.3, 72.6 (CH_2Ph), 69.9 (C-5), 67.5 (C-1), 17.1 (C-6), 0.2 ($Si(CH_3)_3$). IR $\tilde{\nu}$ (cm^{-1}): 3030, 2898, 1496, 1454, 1332, 1250, 844, 737, 697. MS (ESI): 537.2431 $[M+Na]^+$ (100). ESI-MS: *m/z* (%) = 537.2431 $[M+Na]^+$ (100). ESI-HRMS: calcd for $[C_{32}H_{38}O_4Si+H]^+$: *m/z* = 515.2612, found: 515.2614. Anal. for $C_{32}H_{38}O_4Si$ calcd: C 74.67, H 7.44, found: C 74.61, H 7.43. $[\alpha]^{20}_D$: −95.5 (*c* 1.00, $CHCl_3$).



15

To a solution of trimethyl-(2,3,4-tri-*O*-benzyl-α-D-fucosyl-2-ylethynyl)-silane (412 mg, 0.800 mmol), in THF/H_2O (6 ml, 5:1) was added TBAF (0.66 ml, 1M in THF, 0.66 mmol). The reaction was stirred at room temperature for 16 h, diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent EtOAc/MeOH, 5:1) to give (2,3,4-Tri-*O*-benzyl-α-D-fucosyl)acetylene (320 mg, 90%). (For a similar procedure, see:[6]).

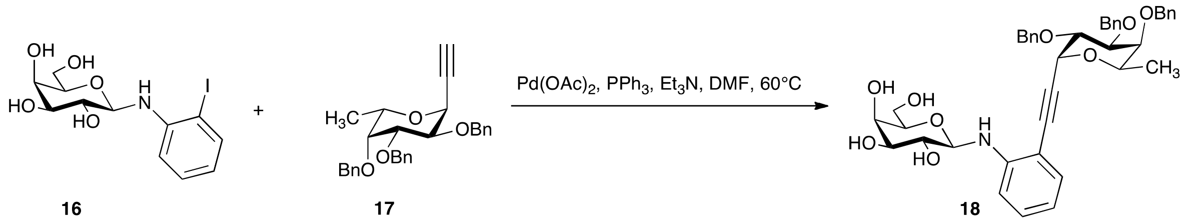
colorless oil; R_f = 0.47 (cyclohexane/EtOAc, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.39 (m, 15H, H-Ph), 4.96 (d, ^2J = 11.5 Hz, 1H, CH_2Ph), 4.87 (d, ^2J = 11.8 Hz, 1H, CH_2Ph), 4.69–4.79 (m, 4H, H-1, 3x CH_2Ph), 4.63 (d, ^2J = 11.5 Hz, 1H, CH_2Ph), 4.07 (dd, $^3J_{2,1}$ = 5.8 Hz, $^3J_{2,3}$ = 9.9 Hz, 1H, H-2), 4.02 (qd, $^3J_{5,4}$ = 1.2 Hz, $^3J_{5,6}$ = 6.4 Hz, 1H, H-5), 3.87 (dd, $^3J_{3,4}$ = 2.8 Hz, $^3J_{3,2}$ = 9.9 Hz, 1H, H-3), 3.64 (dd, $^3J_{4,5}$ = 1.2 Hz, $^3J_{4,3}$ = 2.8 Hz, 1H, H-4), 2.47 (d, $^4J_{C\equiv C\underline{H},1}$ = 2.3 Hz, 1H, C≡C<u>H</u>), 1.13 (d, $^3J_{6,5}$ = 6.4 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.1, 138.8, 138.5 (3x, C-1^{Ph}), 128.7 (2C), 128.6 (4C), 128.4 (2C), 128.2 (2), 127.9, 127.8, 127.73, 127.70 (2C), (15x, H-Ph), 80.8 (C-3), 79.6 (<u>C</u>≡CH), 77.8 (C-4), 76.0 (C≡<u>C</u>H), 75.3 (C-2), 75.2, 73.6, 73.4 (3x CH_2Ph), 70.0 (C-5), 67.3 (C-1), 17.1 (C-6). IR $\tilde{\nu}$ (cm^{-1}): 3287, 2924, 1652, 1454, 1073. ESI-MS: *m/z* (%) = 465.2036 $[M+Na]^+$ (100). ESI-HRMS: calcd for: $[C_{29}H_{30}O_4+ Na]^+$: *m/z* = 465.2036, found: 465.2036. Anal. for $C_{29}H_{30}O_4$ calcd for: C 78.71, H 6.83; found: C 78.43, H 6.90. $[\alpha]^{20}_D$: −129.32 (*c* 1.00, CH_2Cl_2).



16

A mixture of *o*-iodoaniline (1.25 g, 5.71 mmol), and D-galactose (0.82 g, 4.57 mmol) in ethanol (30 ml), water (dest., 1 ml), and AcOH (0.3 ml) was refluxed for 2 h and then concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent MeOH/EtOAc:, 5:1) to give compound **16** (670 mg, 31%). (For a similar procedure, see:[3]).

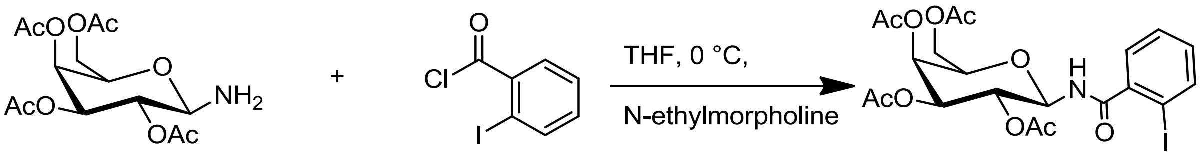
16: brownish solid; mp.: 135-136°C; R_f = 0.46 ($CHCl_3$/MeOH/AcOH, 5:1:0.1); ^{1}H NMR (400 MHz, CD_3OD): δ = 7.65 (dd, $^{3}J_{3,4}$ = 7.8 Hz, $^{4}J_{3,5}$ = 1.5 Hz, 1H, H-3^{aniline}), 7.21 (ddd, $^{3}J_{5,6}$ = 8.3 Hz, $^{3}J_{5,4}$ = 7.3 Hz, $^{4}J_{5,3}$ = 1.5 Hz, 1H, H-5^{aniline}), 6.93 (dd, $^{3}J_{6,5}$ = 8.3 Hz, $^{4}J_{6,4}$ = 1.5 Hz, 1H, H-6^{aniline}), 6.52 (ddd, $^{3}J_{4,3}$ = 7.8 Hz, $^{3}J_{4,5}$ = 7.3 Hz, $^{4}J_{4,6}$ = 1.5 Hz, 1H, H-4^{aniline}), 4.53 (d, $^{3}J_{1,2}$ = 8.5 Hz, 1H, H-1^{gal}), 3.92 (dd, $^{3}J_{4,3}$ = 3.4 Hz, $^{3}J_{4,5}$ = 0.8 Hz, 1H, H-4^{gal}), 3.64–3.76 (m, 4H, H-2^{gal}, H-3^{gal}, H-6^{gal}), 3.58 (dd, $J_{3,2}$ = 9.4 Hz, $^{3}J_{3,4}$ = 3.4 Hz, 1H, H-3^{gal}). ^{13}C NMR (101 MHz, CD_3OD): δ = 147.7 (C-1^{aniline}), 140.3 (C-3^{aniline}), 130.6 (C-5^{aniline}), 121.6 (C-4^{aniline}), 114.6 (C-6^{aniline}), 87.7 (C-1^{gal}), 86.2 (C-2^{aniline}), 77.6 (C-5^{gal}), 76.1 (C-3^{gal}), 72.3 (C-2^{gal}), 70.8 (C-4^{gal}), 62.7 (C-6^{gal}). IR $\tilde{\nu}$ (cm^{-1}): 3500, 2947, 2897, 2870, 1633, 1589, 1517, 1460, 1435, 1417, 1311, 1268 1142, 1083, 1069, 973, 929, 742, 499. ESI-MS: *m/z* (%) = 403.9965 $[M+Na]^+$ (50), 382.0147 $[M+H]^+$, 219.9615 $[o\text{-iodoaniline}+H]^+$ (100). ESI-HRMS: calcd for: $[C_{12}H_{16}INO_5+H]^+$: *m/z* = 382.0151, found: 382.0147; calcd for: $[C_{12}H_{16}INO_5+Na]^+$: *m/z* = 403.9971, found: 403.9965. $[\alpha]^{20}_{D}$: +13.8 (c = 1.00, MeOH).



A solution of the aniline **16** (168 mg, 0.441 mmol), acetylene **17** (112 mg, 0.294 mmol), PPh_3 (8 mg, 0.03 mmol), and $Pd(OAc)_2$ (4 mg, 0.018 mmol), in Et_3N (5 ml) and DMF (3 ml) was stirred at 70°C for 18.5 h. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$, and brine, then dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent cyclohexane/EtOAc, 1:2) to give to give compound **18** (134 mg, 66%). %). (For a similar procedure, see:[7])

colorless oil; R_f = 0.37 ($CHCl_3$/MeOH/HOAc, 10:1:0.1); ^{1}H-NMR, COSY, HSQC (400 MHz, $CDCl_3$): δ = 7.19–7.43 (m, 17H, H-Ph, H-4^{aniline}, H-6^{aniline}), 6.82 (dd, $^{3}J_{3,4}$ = 7.9 Hz, $^{4}J_{3,5}$ = 1.0 Hz, 1H, H-3^{aniline}), 6.76 (td, $^{3}J_{5,4/6}$ = 7.5 Hz, $^{4}J_{5,3}$ = 1.0 Hz, 1H, H-5^{aniline}), 5.74 (d, broad, $^{3}J_{NH,1gal}$ = 4.5 Hz, 1H, NH), 5.16 (d, $^{3}J_{1,2}$ = 5.9 Hz, 1H, H-1^{fuc}), 4.91 (d, ^{2}J = 11.5 Hz, 1H, CH_2Ph), 4.82 (d, ^{2}J = 11.5 Hz, 1H, CH_2Ph), 4.74 (d, ^{2}J = 10.9 Hz, 1H, $BnCH_2$), 4.73

(d, ^2J = 11.5 Hz, 1H, CH_2Ph), 4.63 (d, ^2J = 11.5 Hz, 1H, CH_2Ph), 4.57 (d, ^2J = 10.9 Hz, 1H, CH_2Ph), 4.25–4.31 (m, 2H, this multiplet contains: 4.29 (dd, $^3J_{2,3}$ = 10.1 Hz, $^3J_{2,1}$ = 5.9 Hz, 1H, H-2^{fuc}), 4.26 (dd, $^3J_{1,2}$ = 9.4 Hz, $^3J_{1,NH}$ = 4.5 Hz, 1H, H-1^{gal})), 4.09 (dq, $^3J_{5,6}$ = 6.4 Hz, $^3J_{5,4}$ = 1.0 Hz, 1H, H-5^{fuc}), 3.98 (dd, , $^3J_{3,2}$ = 10.1 Hz, $^3J_{3,4}$ = 2.6 Hz, 1H, H-3^{fuc}), 3.90 (dd, $^3J_{6a,6b}$ = 11.9 Hz, $^3J_{6a,5}$ = 6.8 Hz, 1H, H-6a^{gal}), 3.86 (dd, $^3J_{4,3}$ = 3.4 Hz, $^3J_{4,5}$ = 1.1 Hz, 1H, H-4^{gal}), 3.79 (dd, $^3J_{4,3}$ = 2.6, $^3J_{4,5}$ = 1.0 Hz, 1H, H-4^{fuc}), 3.75 (dd, $^2J_{6b,6a}$ = 11.9 Hz, $^3J_{6b,5}$ = 3.8 Hz, 1H, H-6b^{gal}), 3.56 (ddd, $^3J_{5,6a}$ = 6.8 Hz, $^3J_{5,6b}$ = 4.0 Hz, $^3J_{5,4}$ = 1.1 Hz, 1H, H-5^{gal}), 3.40 (dd, $^3J_{3,2}$ = 9.4 Hz, $^3J_{3,4}$ = 3.4 Hz, 1H, H-3^{gal}), 2.92 (t, $^3J_{3,1/2}$ = 9.4 Hz , 1H, H-2^{gal}), 1.23 (d, $^3J_{6,5}$ = 6.4 Hz, 3H, H-6^{fuc}). ^{13}C NMR, HSQC (101 MHz, $CDCl_3$): δ = 148.3 (C-2^{aniline}), 138.6, 138.5, 137.4 (3x, C-1^{Ph}), 131.1, 130.5 (C-4^{aniline}, C-6^{aniline}), 129.1 (2C), 128.8 (2C), 128.8, 128.6 (2C), 128.5 (2C), 128.4 (2C), 128.0, 127.9, 127.6 (2C), (15x, H-Ph), 118.9 (C-5^{aniline}), 112.4 (C-3^{aniline}), 108.4 (C-1^{aniline}), 90.8 (PhC≡Cfuc), 86.9 (C-1^{gal}), 85.2 (PhC≡Cfuc), 80.4 (C-3^{fuc}), 76.7 (2C, C-2^{fuc}, C-4^{fuc}), 75.4 (CH_2Ph), 75.1 (C-5^{gal}), 74.2 (CH_2Ph), 73.8 (C-3^{gal}), 71.5 (CH_2Ph), 70.2 (C-2^{gal}), 70.1 (C-5^{fuc}), 69.5 (C-4^{gal}), 67.6 (C-1^{fuc}), 63.0 (C-6^{gal}), 17.4 (C-6^{fuc}). IR $\tilde{\nu}$ (cm^{-1}): 3512, 3395, 3359, 3062, 3034, 2886, 2217, 1955, 1874, 1813, 1658, 1602, 1577, 1506, 1453, 1383, 1333, 1311, 1269, 1212, 1067, 834, 745, 699. ESI-MS: *m/z* (%) = 696.3168 $[M+H]^+$ (100), 534.2637 $[M\text{-gal}+2H]^+$ (40). ESI-HRMS: calcd for: [$C_{41}H_{45}NO_9$+ H]: *m/z* = 696.3167, found: 696.3168. $[\alpha]^{20}_D$: −65.1 (*c* 1.00, DMSO-d_6).

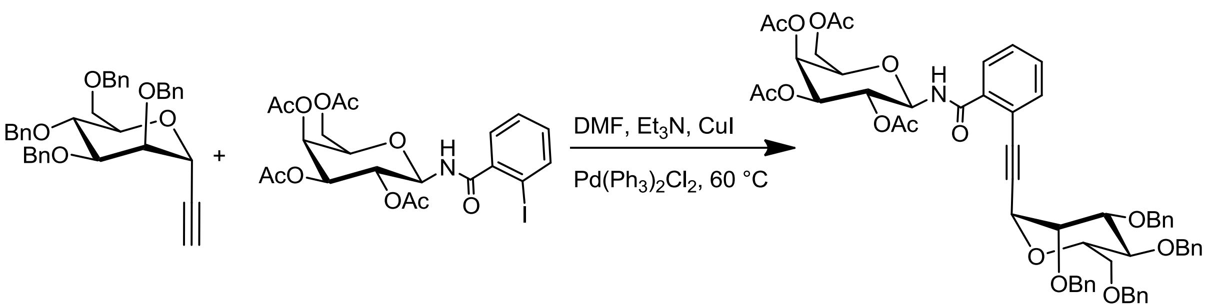


20 21

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosylamine (213 mg, 0.61 mmol) was dissolved in anhydrous THF 84 mL). To this solution *N*-ethylmorpholine (0.08 ml, 0.64 mmol, 1.05 eq.) was added and the resulting mixture was stirred for 10 minutes. *o*-Iodobenzoic acid chloride (168 mg, 0.63 mmol, 1.03 eq.) was dissolved in anhydrous THF (1 mL) and precooled to 0 °C before addition of the above mixture. After complete addition, the reaction was stirred for an additional 30 minutes. The amine hydrochloride was filtered off and washed with THF. The resulting solution was concentrated under reduced pressure and the crude product was purified by flash chromatography (eluent EtOAc/cylohexane, 3:1) to give 2-iodo-*N*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-benzamide (315 mg, 90.2%). (For a similar procedure, see:[9]).

colourless crystals; Smp.: 181.5–185 °C; R_f = 0.47 (EtOAc/cyclohexane, 2:1). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 9.38 (d, 1 H, $^3J_{N\text{-}H,H\text{-}1}$ = 9.4 Hz, N-H), 7.88 (dd, 1 H, $^4J_{4,6}$ = 1.3 Hz, $^3J_{5,6}$ = 7.9 Hz, H-6), 7.44 (dt, 1 H, $^4J_{3,5}$ = 1.6 Hz, $^3J_{4,5}$ = 7.5 Hz, H-5), 7.22 (dd, 1 H, $^3J_{3,4}$ = 7.6 Hz, $^4J_{3,5}$ = 1.6 Hz, H-3), 7.18 (dt, 1 H, $^3J_{3,4}$ = 7.6 Hz, $^3J_{4,5}$ = 7.5 Hz, H-4), 5.52 (pseudo-t, 1 H, $^3J_{N\text{-}H,H\text{-}1}$ = 9.4 Hz, H-1^{gal}), 5.33 (dd, 1 H, $^3J_{2,3}$ = 9.9 Hz, $^3J_{3,4}$ = 3.6 Hz, H-3^{gal}), 5.30 (dd, 1 H, $^3J_{3,4}$ = 3.6 Hz, $^3J_{4,5}$ = 0.9 Hz, H-4^{gal}), 5.13 (pseudo-t, 1 H, $^3J_{1,2}$ = 9.4 Hz, $^3J_{2,3}$ = 9.9 Hz, H-2^{gal}), 4.39 (dt, 1 H, $^3J_{4,5}$ = 0.9 Hz, $^3J_{5,6}$ = 6.5 Hz, H-5^{gal}), 4.05 (d, 2 H, $^3J_{5,6}$ = 6.5 Hz, H-6^{gal}), 2.10, 2.03, 2.01, 1.92 (4x s, 4x 3 H, COCH$_3$). ^{13}C-NMR (101 MHz, CDCl$_3$) δ = 171.4, 170.5, 170.1, 169.9 (4x COC=O), 169.1 (C=O^{amide}), 140.7 (C-2), 140.5 (C-3),131.9 (C-4), 128.2 (C-5), 127.7 (C-6), 92.2 (C-2), 78.9 (C-1^{gal}), 72.7, 71.1, 68.5, 67.3 (C-2^{gal}, C-3^{gal}, C-4^{gal}, C-5^{gal}), 61.2 (C-6^{gal}), 21.3, 20.8, 20.7, 20.5 (4x AcCH$_3$). ESI-MS: *m/z* (%) = 577.9 $[M+H]^+$ (100), 599.9 $[M+Na]^+$ (87).

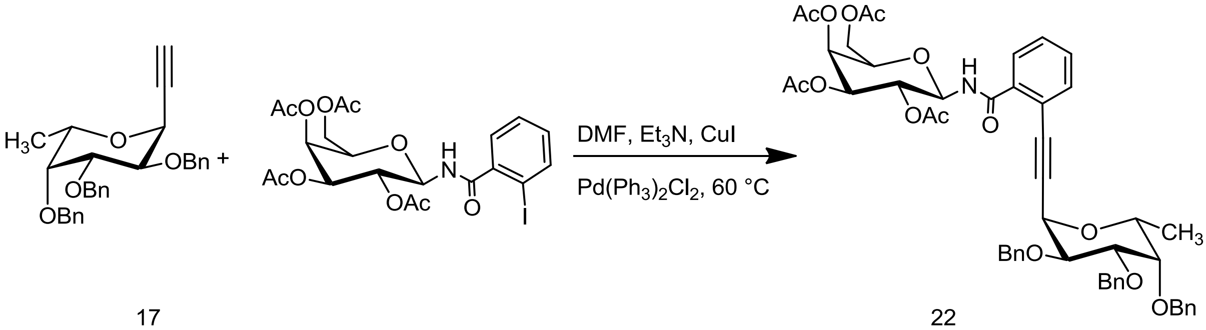
$[\alpha]_D^{28}$ = +24.5 (c = 1.00, CHCl$_3$).



23

2-Iodo-*N*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-benzamide (121 mg, 0.21 mmol) was dissolved in anhydrous DMF (2.9 mL) together with bis-triphenylphosphine-palladium(II)dichloride (5.9 mg, 0.008 mmol, 3.8 mol%) and copper(I)iodide (3.0 mg, 16 µmol, 7.2 mol%). To this solution anhydrous Et_3N (0.12 mL) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. Then, 2-*C*-(2',3',4',6'-tetra-*O*-benzyl-α-D-mannopyranosyl)-acetylene (136 mg, 0.25 mmol, 1.2 eq.) dissolved in anhydrous DMF (2.9 mL) was added and the solution was warmed to 60 °C and stirred at this temperature overnight. The resulting dark brown mixture was coevaporated twice with toluene (3 mL). The crude product was redissolved in $CHCl_3$ washed with water (3x 10 mL), dried over anhydous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (eluent cylohexane/EtOAc, 2:1) to give *N*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-ethynyl-*C*-(2'',3'',4'',6''-tetra-*O*-benzyl-α-D-mannopyranosyl)-benz-amide (199 mg, 76%). (For a similar procedure, see:[10]).

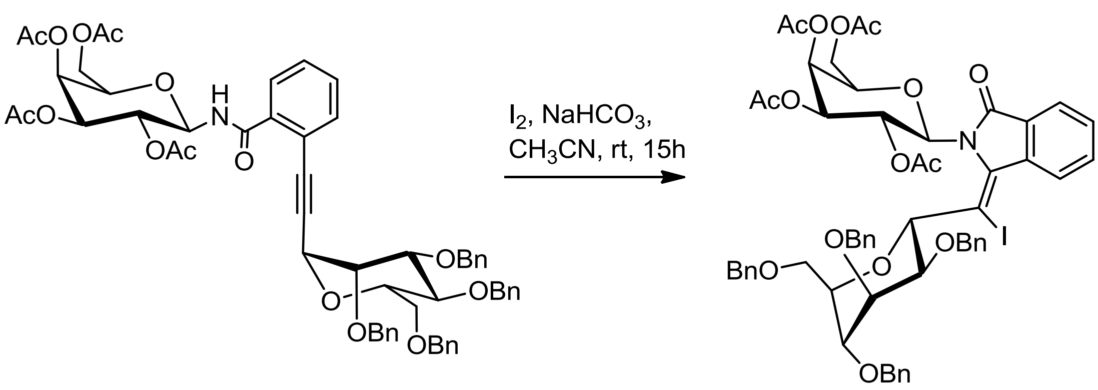
slightly yellow oil; R_f = 0.51 (EtOAc/cyclohexane, 3:2). ^{1}H NMR, COSY (400 MHz, $CDCl_3$) δ = 7.44–7.11 (m, 24 H, H-Ph, H-3, H-4, H-5, H-6), 7.17–7.19 (m, 1 H, N-H), 5.37 (pseudo-t, 1 H, $^3J_{1,2}$ = 9.2 Hz, H-1^{gal}), 5.31 (dd, 1 H, $^3J_{3,4}$ = 3.4 Hz, $^3J_{4,5}$ = 0.8 Hz, H-4^{gal}), 5.18 (pseudo-t, 1 H, $^3J_{1,2}$ = 9.2 Hz, $^3J_{2,3}$ = 10.3 Hz, H-2^{gal}), 5.15 (d, 1H, $^3J_{1,2}$ = 2.1 Hz, H-1^{man}), 5.09 (dd, 1 H, $^3J_{2,3}$ = 10.3 Hz, $^3J_{3,4}$ = 3.4 Hz, H-3^{gal}), 4.92 (d, 1 H, ^2J = 10.6 Hz, CH_2Ph), 4.81 (d, 1 H, ^2J = 12.6 Hz, CH_2Ph), 4.77–4.71 (m, 3 H, CH_2Ph); 4.68 (d, 1 H, ^2J = 12.0 Hz, CH_2Ph), 4.58 (d, 1 H, ^2J = 10.6 Hz, CH_2Ph), 4.56 (d, 1 H, ^2J = 12.0 Hz, CH_2Ph), 4.26 (dd, 1 H, $^3J_{3,4}$ = 9.3 Hz, $^3J_{2,3}$ = 2.9 Hz, H-3^{man}), 4.11 (pseudo-t, 1 H, $^3J_{3,4}$ = 9.3 Hz, $^3J_{4,5}$ = 9.6 Hz, H-4^{man}), 4.05–4.01 (m, 4 H, H-6a^{gal}, H-6b^{gal}, H-5^{man}, H-2^{man}), 3.88 (dd, 1 H, $^3J_{5,6}$ = 4.4 Hz, ^3J = 10.9 Hz, H-6a^{man}), 3.78 (dd, 1 H, $^3J_{5,6}$ = 1.3 Hz, ^2J = 10.9 Hz, H-6b^{man}), 3.69 (dt, 1 H, $^3J_{4,5}$ = 0.8 Hz, H-5^{gal}), 2.06, 2.01, 2.00, 1.98 (4x s, 4x 3 H, $COCH_3$). ^{13}C-NMR, HSQC (101 MHz, $CDCl_3$) δ = 171.3, 170.4, 170.1, 169.8 (4x AcC=O), 169.6 (C=O^{amide}), 138.7, 138.6, 138.5, 138.2 (4x C-1^{Ph}), 134.2 (C-1), 129.1 (C-2), 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4 (C-3, C-4, C-5, C-6, CH-Ph), 90.3 (C^{alkyne}-man), 83.2 (C^{alkyne}-arom), 80.6 (C-3^{man}), 79.2 (C-1^{gal}), 77.4 (C-5^{man}), 75.5 (CH_2Ph), 75.4 (C-2^{man}), 75.1 (C-4^{man}), 73.6 (CH_2Ph), 72.5 (C-5^{gal}), 72.2 (CH_2Ph), 71.9 (CH_2Ph), 71.1 (C-3^{gal}), 69.7 (C-6^{man}), 68.7 (C-2^{gal}), 67.4 (C-4^{gal}), 67.0 (C-1^{man}), 61.2 (C-6^{gal}), 20.7, 20.6, 20.5, 20.4 (4x $COCH_3$). FAB-MS: *m/z* (%) = 998.1 $[M]^+$ (100). ESI-HRMS: calcd for $[C_{57}H_{59}NO_{15}+H]$: *m/z* = 998.3957, found: 998.3965. $[\alpha]_D^{22}$ = +15.7 (c = 1.00, $CHCl_3$).



17 22

2-Iodo-*N*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-benzamide (96 mg, 0.17 mmol) was dissolved in anhydrous DMF (2.9 mL) together with bis-triphenylphosphine-palladium(II)dichloride (4.7 mg, 8.0 µmol, 3.8 mol%) and copper(I)iodide (2.3 mg, 16.0 µmol, 7.2 mol%). To this solution, anhydrous Et_3N (0.1 mL) were added dropwise and the reaction mixture was stirred for 1 h at room temperature. Then, 2-*C*-(2',3',4',6'-tetra-*O*-benzyl-α-L-fucopyranosyl)-acetylene (89 mg, 0.20 mmol, 1.2 eq.) dissolved in anhydrous DMF (2.9 mL) was added and the solution was warmed to 80 °C and stirred at this temperature overnight. The resulting dark brown mixture was coevaporated twice with toluene (3 mL). The crude product was redissolved in $CHCl_3$ washed with water (3x 10 mL), dried over anhydous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (eluent cylohexane/EtOAc, 2:1) to give *N*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-ethynyl-*C*-(2'',3'',4''-tri-*O*-benzyl-α-L-fucopyranosyl)-benzamide (90 mg, 60%). (For a similar procedure, see:[10]).

colourless oil; R_f = 0.56 (EtOAc/cyclohexane 3:2). ^{1}H NMR, COSY (400 MHz, $CDCl_3$) δ = 7.95–7.89 (m, 2 H, H-3, H6), 7.49–7.28 (m, 17 H, H-4, H-5, CH-Ph), 5.47 (d, 1 H, $^3J_{1,2}$ = 8.9 Hz, H-1^{gal}), 5.44 (d, 1 H, $^3J_{3,4}$ = 3.8 Hz, H-4^{gal}), 5.25 (pseudo-t, 1 H, $^3J_{1,2}$ = 8.9 Hz, $^3J_{2,3}$ = 9.9 Hz, H-2^{gal}), 5.21 (d, 1H, $^3J_{1,2}$ = 5.7 Hz, H-1^{fuc}), 5.09 (dd, 1 H, $^3J_{2,3}$ = 9.9 Hz, $^3J_{3,4}$ = 3.8 Hz, H-3^{Gal}), 4.99 (d, 1 H, ^2J = 11.3 Hz, CH_2Ph), 4.89 (d, 1 H, ^2J = 12.3 Hz, CH_2Ph), 4.83–4.81 (m, 3 H, CH_2Ph), 4.66 (d, 1 H, ^2J = 11.3 Hz, CH_2Ph), 4.22–4.14 (m, 2 H, H-2^{fuc}, H-5^{fuc}), 4.12–4.06 (m, 2 H, H-6^{gal}), 4.04–4.00 (m, 2 H, H-5^{gal}, H-3^{fuc}), 3.72 (d, 1 H, $^3J_{4,5}$ = 1.9 Hz, H-4^{fuc}), 1.21 (d, 3 H, $^3J_{5,CH3}$ = 6.6 Hz, CH_3^{fuc}), 2.06, 2.02, 1.98, 1.94 (4x s, 4x 3 H, $COCH_3$). ^{13}C-NMR, HSQC (101 MHz, $CDCl_3$) δ = 170.6, 170.3, 170.2, 169.7 (4x AcC=O), 166.2 (C=O^{amide}), 138.9, 138.7, 138.6 (3x C-1^{Ph}), 134.5 (C-1), 131.1 (C-2), 129.4, 128.8, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4 (C-3, C-4, C-5, C-6, CH-Ph), 92.9 (C^{alkyne}-fuc), 85.3 (C^{alkyne}-arom), 80.5 (C-3^{fuc}), 79.4 (C-1^{gal}), 77.6 (C-4^{fuc}), 75.7 (C-2^{fuc}), 75.2 (CH_2Ph), 73.3 (CH_2Ph), 73.0 (CH_2Ph),72.9 (C-5^{gal}), 71.4 (C-3^{gal}), 70.5 (C-5^{fuc}), 68.5 (C-2^{gal}), 67.9 (C-1^{fuc}), 67.3 (C-4^{gal}), 61.4 (C-6^{gal}), 20.6, 20.6, 20.5, 20.5 (4x $COCH_3$), 17.2 (CH_3^{fuc}). FAB-MS: *m/z* (%) =998.1 $[M]^+$ (100). ESI-HRMS: calcd for $[C_{50}H_{53}NO_{14}+H]$: *m/z* = 892.3539, found: 892.3532, calcd for $[C_{50}H_{53}NO_{14}+Na]$: *m/z* = 914.3358, found: 914.3351. $[\alpha]_D^{22}$ = −76.3 (c = 1.00, $CHCl_3$).

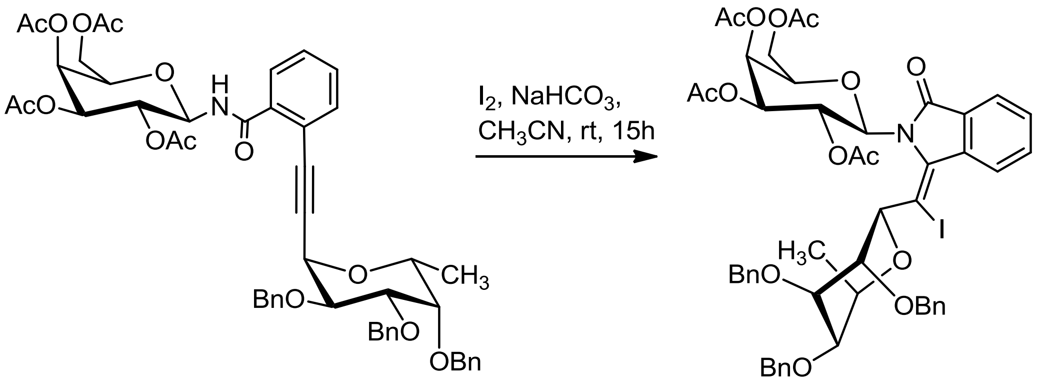


23 25

N-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-ethynyl-*C*-(2'',3'',4'',6''-tetra-*O*-benzyl-α-D-mannopyranosyl)-benzamide (199 mg, 0.19 mmol) and $NaHCO_3$ (49.4 mg, 0.57 mmol, 3 eq.) were suspended in acetonitrile (19.9 mL) under an argon atmosphere. At room temperature iodine (144 mg, 0.57 mmol, 3 eq.) was added and the resulting brown mixture was stirred overnight. The reaction was diluted with ether and washed with saturated $Na_2S_2O_3$-solution (2x 15 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. After flash chromatography (eluent cylohexane/EtOAc, 2:1) (E)-3-((2'',3'',4'',6''-tetra-*O*-benzyl-α-D-mannopyranosyl)iodomethylene)-*N*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-isoindolinone was obtained (202 mg, 94%). (For a similar procedure, see:[11]).

yellow oil; R_f = 0.58 (EtOAc/cyclohexane 3:2). ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$) δ = 8.79 (d, 1H, $^3J_{3,4}$ = 8.1 Hz, H-3), 7.99, (d, 1H, $^3J_{5,6}$ = 7.7 Hz, H-6), 7.67 (pseudo-t, 1H, $^3J_{4,3}$ = 8.05 Hz, $^3J_{4,5}$ = 7.4 Hz, H-4), 7.58 (pseudo-t, 1H, $^3J_{4,5}$ = 7.4 Hz, $^3J_{5,6}$ = 7.7 Hz, H-5), 7.36–7.09 (m, 20H, CH-Ph), 5.34–5.28 (m, 2H, H-2^{gal}, H-4^{gal}), 5.27 (d, 1H, $^3J_{1,2}$ = 8.5 Hz, H-1^{gal}), 5.09 (d, 1H, $^3J_{1,2}$ = 9.1 Hz, H-1^{man}), 5.05 (dd, 1H, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 3.3 Hz, H-3^{gal}), 4.66–4.58 (m, 4H, CH_2Ph), 4.54 (d, 1H, ^2J = 12.5 Hz, CH_2Ph), 4.45–4.32 (m, 4H, 3x CH_2Ph, H-5^{man}), 4.12–4.08 (m, 2H, H-6a^{gal}, H-6a^{man}), 4.05–3.99 (m, 3H, H-2^{man}, H-3^{man}, H-6b^{man}), 3.97 (dd, 1H, $^3J_{H6b,5}$ = 6.8 Hz, ^2J = 10.3 Hz, H-6b^{gal}), 3.83 (dd, 1H, $^3J_{3,4}$ = 2.9 Hz, $^3J_{4,5}$ = 1.8 Hz, H-4^{man}), 3.57 (t, 1H, $^3J_{5,6}$ = 6.5 Hz, H-5^{gal}), 2.14, 1.99, 1.91, 1.58 (4x s, 4x 3H, $COCH_3$). ^{13}C-NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 170.4, 170.3, 169.9, 169.8 (4x AcC=O), 155.9 (C-1), 150.2 (C-3), 138.4, 138.3, 138.2, 138.0 (4x C-1^{Ph}), 135.7 (C-3a), 132.5 (C-5), 131.5 (C-7a), 131.2 (C-6), 128.5, 128.4, 128.4, 128.2, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4 (CH-Ph), 124.9 (C-4), 124.7 (C-7), 85.7 (C-I), 81.7 (C-1^{gal}), 77.1 (C-2^{man}), 75.0 (C-5^{man}), 74.7 (C-4^{man}), 73.1 (C-3^{man}), 72.9 (CH_2Ph), 72.4 (C-5^{gal}), 71.9 (CH_2Ph), 71.7 (CH_2Ph), 71.6 (C-3^{gal}), 69.9 (C-2^{gal}), 68.8 (C-6^{man}), 68.4 (C-1^{man}), 67.6 (C-4^{gal}), 61.9 (C-6^{gal}), 20.9, 20.8, 20.7, 20.4 (4x $COCH_3$). FAB-MS: *m/z* (%) = 1124.3 $[M]^+$ (100). ESI-HRMS: calcd for $[C_{57}H_{58}INO_{15}+H]$: *m/z* = 892.3539, found: 892.3532, calcd for $[C_{57}H_{58}INO_{15}+Na]$: *m/z* = 914.3358, found: 914.3351.

$[\alpha]_D^{22}$ = +32.1 (c = 1.00, $CHCl_3$).

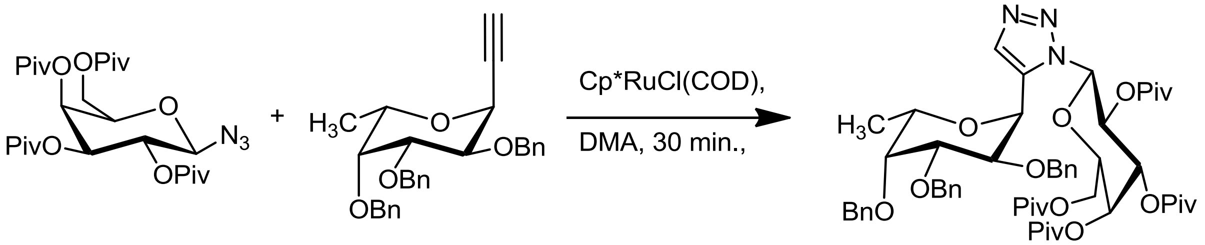


22 24

N-(2’,3’,4’,6’-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2-ethynyl-*C*-(2’’,3’’,4’’-tri-*O*-benzyl-α-L-fucopyranosyl)-benzamide (78 mg, 0.087 mmol) and $NaHCO_3$ (24 mg, 0.26 mmol, 3 eq.) were suspended in acetonitrile (10.8 mL) under an argon atmosphere. At room temperature, iodine (70 mg, 0.26 mmol, 3 eq.) was added and the brown suspension was stirred overnight. The next day the reaction was diluted with ether and washed with saturated $Na_2S_2O_3$-solution (2x 8 mL). The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The resulting brown oil was purified by flash chromatography (eluent: cylohexane/EtOAc, 3:1) to obtain (E)-3-((2’’,3’’,4’’-tri-*O*-benzyl-α-L-fucopyranosyl)iodomethylene)-*N*-(2’,3’,4’,6’-tetra-*O*-acetyl-β-D-galactopyranosyl)-isoindolinone (53 mg, 60%).(For a similar procedure, see:[11]).

yellow oil; R_f = 0.59 (EtOAc/cyclohexane 3:2). ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$) δ = 8.78 (d, 1H, $^3J_{3,4}$ = 7.9 Hz, H-3), 7.95 (d, 1H, $^3J_{5,6}$ = 7.7 Hz, H-6), 7.66 (pseudo-t, 1H, $^3J_{3,4}$ = 7.9 Hz, $^3J_{4,5}$ = 7.5 Hz, H-4), 7.56 (pseudo-t, 1H, $^3J_{4,5}$ = 7.5 Hz, $^3J_{5,6}$ = 7.7 Hz, H-5), 7.41–7.22 (m, 12H, CH-Ph), 7.13–7.06 (m, 3H, CH-Ph), 5.22 (s broad, 1H, H-1^{fuc}), 5.19 (pseudo-t, 1H, $^3J_{1,2}$ = 9.14 Hz, $^3J_{2,3}$ = 9.8 Hz, H-2^{gal}), 5.06 (d, 1H, $^3J_{1,2}$ = 9.14 Hz, H-1^{gal}), 5.04 (d, 1H, $^3J_{3,4}$ = 3.26 Hz, H-4^{gal}), 4.86 (d, 1H, ^2J = 12.7 Hz, CH_2Ph), 4.77 (dd, 1H, $^3J_{2,3}$ = 9.83 Hz, $^3J_{3,4}$ = 3.26 Hz, H-3^{gal}), 4.76 (d, 1H, ^2J = 12.4 Hz, CH_2Ph), 4.64 (d, 1H, ^2J = 11.8 Hz, CH_2Ph), 4.58 (d, 1H, ^2J = 12.4 Hz, CH_2Ph), 4.53–4.47 (m, 3H, 2x CH_2Bn, H-5^{fuc}), 4.10, (dd, 1H, $^3J_{3,4}$ = 2.7 Hz, $^3J_{4,5}$ = 5.7 Hz, H-4^{fuc}), 4.06–3.98 (m, 2H, H-6^{gal}), 3.95 (pseudo-t, 1H, $^3J_{2,3}$ = 3.4 Hz, $^3J_{3,4}$ = 2.7 Hz, H-3^{gal}), 3.87–3.83 (m, 1H, H-2^{fuc}), 2.94 (pseudo-t, 1H, $^3J_{5,6}$ = 6.55 Hz, $^3J_{5,6}$ = 6.25 Hz, H-5^{gal}), 2.12, 2.06, 1.96, 1.77 (4x $COCH_3$), 1.64 (d, 3H, $^3J_{5,CH3}$ = 6.6 Hz, CH_3^{fuc}). ^{13}C-NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 170.5, 170.3, 169.9, 169.5 (4x AcC=O), 155.5 (C-1), 146.4 (C-3), 139.2, 138.6, 137.4 (3x C-1^{Ph}), 135.6 (C-3a), 132.5 (C-5), 130.89 (C-7a), 130.89 (C-6), 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 127.0 (CH-Ph), 124.8 (C-4), 124.5 (C-7), 86.4 (C-1^{gal}), 81.3 (C-I), 78.5 (C-2^{fuc}), 75.9 (C-3^{fuc}), 74.7 (C-4^{fuc}), 73.6 (CH_2Ph), 73.3 (CH_2Ph), 71.9 (CH_2Ph), 71.8 (CH_2Ph), 71.7 (C-5^{gal}), 71.7 (C-5^{fuc}), 71.1 (C-3^{gal}), 70.4 (C-2^{gal}), 67.6 (C-4^{gal}), 63.9 (C-1^{fuc}), 61.9 (C-6^{gal}), 20.9, 20.8, 20.7, 20.6 (4x $COCH_3$). ESI-HRMS: calcd for [$C_{50}H_{52}INO_{14}$+H]: *m/z* = 1018.2505, found: 1018.2493, calcd for [$C_{50}H_{52}INO_{14}$+Na]: *m/z* = 1040.2332, found: 1040.2322.

$[\alpha]_D^{22}$ = +114.2 (c = 1.00, $CHCl_3$).



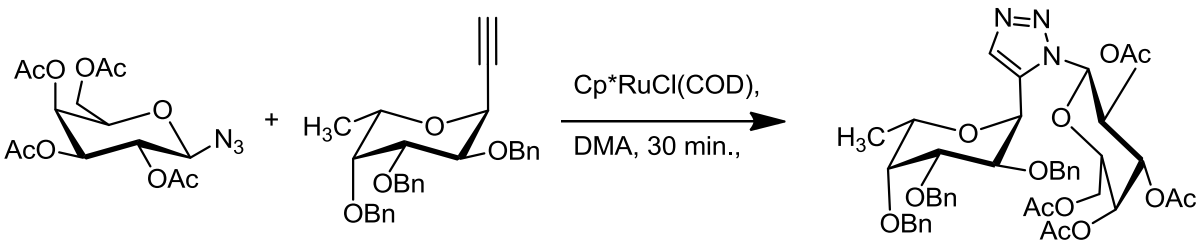
27 17 29

Acetylene **17** (44.5 mg, 0.1 mmol) was dissolved in *N,N*-dimethyl acetamide (1.5 mL). After successive addition of azide **27** (108 mg, 0.2 mmol, 2 eq.) and Cp*RuCl(COD) (2.3 mg, 0.006 mmol, 6 mol %) the reaction mixture was placed in the microwave for 30 min. at 100 °C and 120 W. The dark brown solution was diluted with EtOAc and washed with water (3 x 2 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. After flash chromatography, 1-(2',3',4',6'-tetra-*O*-pivaloyl-β-D-galactopyranosyl)-5-(2'',3'',4''-tri-*O*-benzyl-α-L-fucopyranosyl)-1*H*-1,2,3-triazole (58 mg, 60%) could be obtained (eluent: cyclohexane/EtOAc, 6:1). (For a similar procedure, see:[12]).

Greenish-yellow resin; Smp.: 83–85.5 °C; R_f = 0.54 (EtOAc/cyclohexane 1:1). ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$) δ = 7.86 (d, 1H, $^3J_{H\text{-triazole},C\text{-}1\text{-}Fuc}$ = 0.4 Hz, H^{triazole}), 7.37–7.27 (m, 13H, CH-Ph), 7.22–7.19 (m, 2H, CH-Ph), 6.38 (pseudo-t, 1H, $^3J_{1,2}$ = 9.6 Hz, $^3J_{2,3}$ = 10.1 Hz, H-2^{gal}), 6.10 (d, 1H, $^3J_{1,2}$ = 9.6 Hz, H-1^{gal}), 5.52 (dd, 1H, $^3J_{3,4}$ = 3.0 Hz, $^3J_{4,5}$ = 0.6 Hz, H-4^{gal}), 5.37 (d, 1H, $^3J_{1,2}$ = 5.9 Hz, H-1^{fuc}), 5.20 (dd, 1H, $^3J_{2,3}$ = 10.1 Hz, $^3J_{3,4}$ = 3.0

Hz, H-3^{gal}), 4.99 (d, 1H, ^{2}J = 11.6 Hz, CH_2Ph), 4.86 (d, 1H, ^{2}J = 11.9 Hz, CH_2Ph), 4.80 (d, 1H, ^{2}J = 11.9 Hz, CH_2Ph), 4.74 (d, 1H, ^{2}J = 11.6 Hz, CH_2Ph), 4.68 (d, 1H, ^{2}J = 11.4 Hz, CH_2Ph), 4.58 (d, 1H, ^{2}J = 11.6 Hz, CH_2Ph), 4.38 (dd, 1H, $^{3}J_{1,2}$ = 6.1 Hz, $^{3}J_{2,3}$ = 9.8 Hz, H-2^{fuc}), 4.16–4.11 (m, 1H, H-5^{gal}), 4.00 (d, 2H, $^{3}J_{5,6}$ = 7.6 Hz, H-6^{gal}), 3.91 (dd, 1H, $^{3}J_{2,3}$ = 9.8 Hz, $^{3}J_{3,4}$ = 2.9 Hz, H-3^{fuc}), 3.64 (d, 1H, $^{3}J_{3,4}$ = 2.2 Hz, H-4^{fuc}), 3.21 (q, 1H, $^{3}J_{5,CH3}$ = 6.0 Hz, H-5^{fuc}), 1.29, 1.16 (2x s, 2x $C(CH_3)_3$), 1.14 (m, 12H, 1x $C(CH_3)_3$, CH_3^{fuc}), 0.89 (s, 9H, $C(CH_3)_3$). ^{13}C-NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 177.8, 177.7, 177.0, 175.3 (4x PivC=O), 138.3, 138.2, 137.8 (3x C-1^{Ph}), 135.6 (C-4), 133.5 (C-5), 128.7, 128.6, 128.5, 128.4, 128.0, 127.8, 127.7, 127.7 (CH^{Ph}), 83.9 (C-1^{gal}), 78.8 (C-3^{fuc}), 76.5 (C-4^{fuc}), 75.5 (C-2^{fuc}), 74.9 (CH_2Ph), 73.9 (CH_2Ph), 73.8 (C-5^{gal}), 73.3 (CH_2Ph), 72.4 (C-3^{gal}), 69.9 (C-5^{fuc}), 67.4 (C-1^{fuc}), 66.8 (C-4^{gal}), 66.0 (C-2^{gal}), 61.1 (C-6^{gal}), 39.3, 38.9, 38.8, 38.6 (4x Cq^{Piv}), 27.3, 27.2, 27.2, 26.8 (12x CH_3^{Piv}), 16.9 (CH_3^{fuc}). ESI-MS: *m/z* (%) = 984.4 [M+H] (100), 1006.4 [M+Na] (7). ESI-HRMS: calcd for [$C_{55}H_{73}N_3O_{13}$+Na]: *m/z* = 1006.5041, found: 1006.5051.

$[\alpha]_D^{22}$ = −29.9 (c = 1.00, $CHCl_3$).



26 17 28

Acetylene **17** (44.5 mg, 0.1 mmol) was dissolved in *N,N*-dimethyl acetamide (1.5 mL). After successive addition of azide **26** (74.7 mg, 0.2 mmol, 2 eq.) and Cp*RuCl(COD) (2.3 mg, 0.006 mmol, 6mol%) the reaction mixture was placed in the microwave for 30 min. at 100 °C and 120 W. The dark brown solution was diluted with EtOAc and washed with water (3x 2 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. After flash chromatography, 1-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-5-(2'',3'',4''-tri-*O*-benzyl-α-L-fucopyranosyl)-1*H*-1,2,3-triazole (62 mg, 76%) could be obtained (eluent: cyclohexane/EtOAc, 6:1 - 3:1). (For a similar procedure, see:[12]).

colourless resin; R_f = 0.54 (EtOAc/cyclohexane 1:1). ^{1}H NMR, H-H COSY, NOESY (400 MHz, $CDCl_3$) δ = 7.85 (s broad, 1H, H-4), 7.36–7.28 (m, 13H, CH-Ph), 7.23–7.20 (m, 2H, CH-Ph), 6.30 (pseudo-t, 1H, $^{3}J_{1,2}$ = 9.6 Hz, $^{3}J_{2,3}$ = 9.8 Hz, H-2^{gal}), 6.04 (d, 1H, $^{3}J_{1,2}$ = 9.6 Hz, H-1^{gal}), 5.47 (d, 1H, $^{3}J_{3,4}$ = 3.2 Hz, H-4^{gal}), 5.35 (d, 1H, $^{3}J_{1,2}$ = 5.2 Hz, H-1^{fuc}), 5.15 (dd, 1H, $^3J_{2,3}$ = 9.8 Hz, $^3J_{3,4}$ = 3.2 Hz, H-3^{gal}), 4.93 (d, 1H, ^2J = 11.3 Hz, CH_2Ph), 4.80 (s broad, 2H, CH_2Ph), 4.72 (d, 1H, ^2J = 11.8 Hz, CH_2Ph), 4.64 (d, 1H, ^2J = 11.3 Hz, CH_2Ph), 4.60 (d, 1H, ^2J = 11.8 Hz, CH_2Ph), 4.32 (dd, 1H, $^3J_{1,2}$ = 5.2 Hz, $^3J_{2,3}$ = 8.2 Hz, H-2^{fuc}), 4.13 (dd, 1H,^{2}J = 10.2 Hz, $^3J_{5,6a}$ = 5.3 Hz, H-6a^{gal}), 4.07–4.04 (m, 1H, H-5^{gal}), 4.01 (dd, 1H, ^2J = 10.2 Hz, $^3J_{5,6b}$ = 6.3 Hz, H-6b^{gal}), 3.88 (d, 1H, $^3J_{2,3}$ = 8.2 Hz, H-3^{fuc}), 3.67 (s broad, 1H, H-4^{fuc}), 3.32 (s broad, 1H, H-5^{fuc}), 2.16, 2.01, 1.98, 1.83 (4x $COCH_3$), 1.18 (d, 3H, $^3J_{5,CH3}$ = 5.8 Hz, CH_3^{fuc}). ^{13}C-NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 170.4, 170.3, 170.3, 168.2 (4x AcC=O), 138.2, 138.2, 137.7 (3x C-1^{Ph}), 135.5 (C-4), 134.1 (C-5), 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8 (CH-Ph), 84.2 (C-1^{gal}), 77.9 (C-3^{fuc}), 76.1 (C-4^{fuc}), 75.5 (C-2^{fuc}), 74.6 (CH_2Ph), 73.8 (CH_2Ph), 73.7 (C-5^{gal}), 73.2 (CH_2Ph), 72.2 (C-3^{gal}), 70.2 (C-5^{fuc}), 67.1 (C-4^{gal}), 66.7 (C-1^{fuc}), 66.7 (C-2^{gal}), 61.3 (C-6^{gal}), 20.8, 20.7, 20.7, 20.6 ($COCH_3$), 16.3 (CH_3^{fuc}). ESI-MS: *m/z* (%) = 816.3 [M+H] (100), 838.3 [M+Na] (17). ESI-HRMS: calcd for $[C_{43}H_{49}N_3O_{13}+Na]$: *m/z* = 838.3163, found: 838.3156.

$[\alpha]_D^{22}$ = −30.1 (c = 1.00, $CHCl_3$).

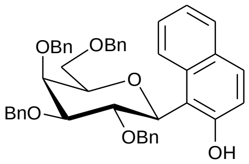
Acetylene **17** (58.0 mg, 0.13 mmol) was dissolved in *N,N*-dimethyl formamide (2 mL). After successive addition of azide **26** (51.4 mg, 0.13 mmol), copper(I)iodide (3.9 mg, 0.01 mmol) and *N,N*-diisopropyl-ethylamine (45.0 µL) the reaction mixture was placed in the microwave for 50 min. at 80 °C and 120 W. The brown solution was diluted with EtOAc and washed with water (3x 2 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. After flash chromatography, 1-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-4-(2'',3'',4''-tri-*O*-benzyl-α-L-fucopyranosyl)-1*H*-1,2,3-triazole (80.1 mg, 75%) could be obtained (eluent: cyclohexane/EtOAc, 6:1 - 3:1). (For a similar procedure, see Ref. [13]).

colourless resin; R_f = 0.54 (EtOAc/cyclohexane 1:1). ^{1}H NMR, H-H COSY, NOESY (400 MHz, $CDCl_3$) δ = 7.90 (s broad, 1H, H-4), 7.38–7.25 (m, 13H, CH-Ph), 7.16–7.14 (m, 2H, CH-Ph), 5.83 (d, 1H, $^3J_{1,2}$ = 9.2 Hz, H-1^{gal}), 5.56 (pseudo-t, 1H, $^3J_{1,2}$ = 9.6 Hz, $^3J_{2,3}$ = 10.1 Hz, H-2^{gal}), 5.53 (m, 1H, H-4^{gal}), 5.31 (d, 1H, $^3J_{1,2}$ = 4.3 Hz, H-1^{fuc}), 5.24 (dd, 1H, $^3J_{2,3}$ = 10.1 Hz, $^3J_{3,4}$ = 3.3 Hz, H-3^{gal}), 4.77 (d, 1H, ^2J = 11.9 Hz, CH_2Ph), 4.74 (s broad, 2H, CH_2Ph), 4.61 (d, 1H, ^2J = 12.1 Hz, CH_2Ph), 4.52 (d, 1H, ^2J = 11.8 Hz, CH_2Ph), 4.46 (d, 1H, ^2J = 11.8 Hz,

CH_2Ph), 4.24–4.21 (m, 2H, H-2^{fuc}, H-5^{gal}), 4.18 (dd, 1H,^2J = 11.4 Hz, $^3J_{5,6a}$ = 6.0 Hz, H-6a^{gal}), 4.11 (dd, 1H, ^2J = 11.4 Hz, $^3J_{5,6b}$ = 6.7 Hz, H-6b^{gal}), 4.08–4.05 (m, 2H, H-3^{fuc}, H-5^{fuc}), 3.84 (pseudo-t, 1H, $^3J_{4,5}$ = 2.9 Hz, H-4^{fuc}), 2.19, 2.04, 2.01, 1.82 (4x $COCH_3$), 1.30 (d, 3H, $^3J_{5,CH3}$ = 5.5 Hz, CH_3^{fuc}). ^{13}C-NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 170.5, 170.1, 169.9, 169.1 (4x AcC=O), 146.5 (C-5), 138.8, 138.6, 138.3 (3x C-1^{Ph}), 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6 (CH-Ph) 122.1 (C-4), 86.3 (C-1^{gal}), 77.6 (C-3^{fuc}), 76.6 (C-2^{fuc}), 75.8 (C-4^{fuc}), 73.5 (CH_2Ph), 73.5 (CH_2Ph), 73.3 (C-5^{gal}), 73.2 (CH_2Ph), 70.9 (C-3^{gal}), 70.2 (C-5^{fuc}), 67.9 (C-2^{gal}), 67.2 (C-1^{fuc}), 66.9 (C-4^{gal}),61.3 (C-6^{gal}), 20.8, 20.6, 20.3 ($COCH_3$), 15.5 (CH_3^{fuc}). ESI-MS: *m/z* (%) = 816.3 [M+H] (100), 838.3 [M+Na] (44).

$[\alpha]_D^{21} = -62.9$ (c = 1.00, $CHCl_3$).

3. ^{1}H- and ^{13}C-NMR spectra



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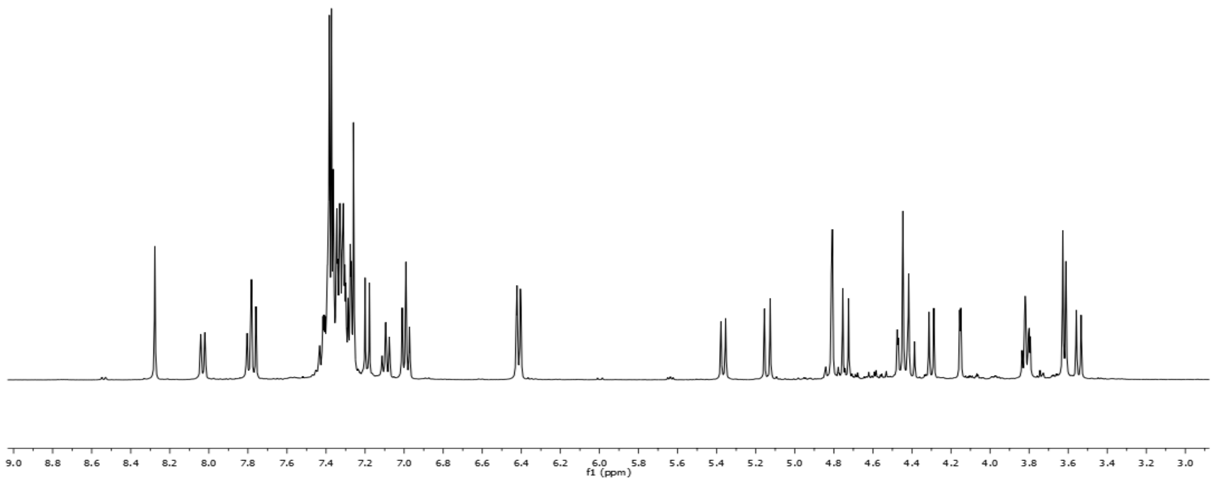
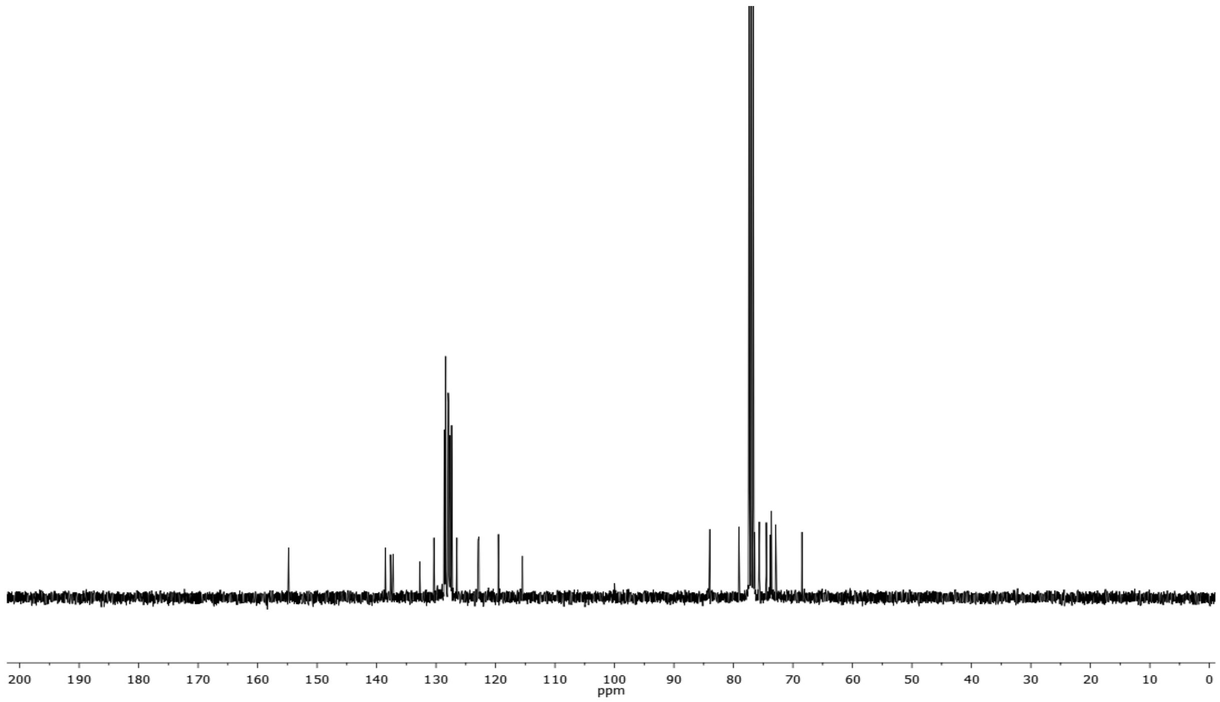
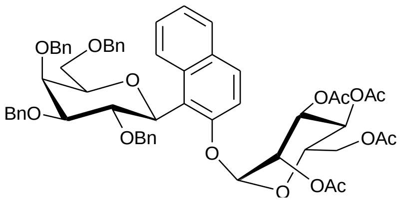


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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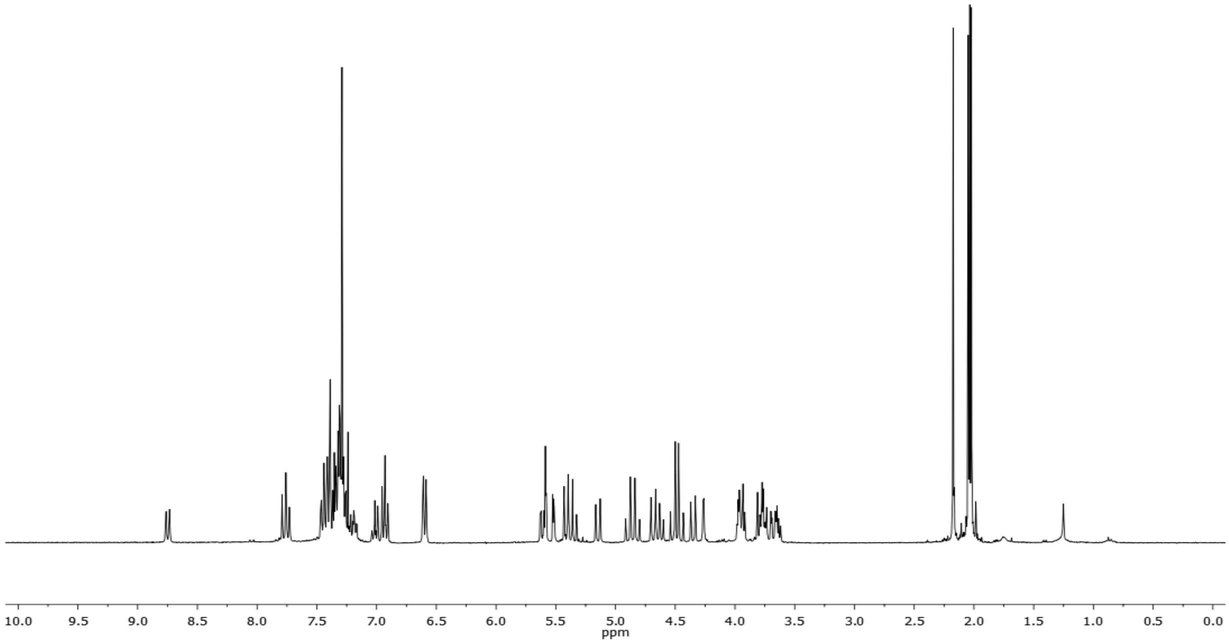
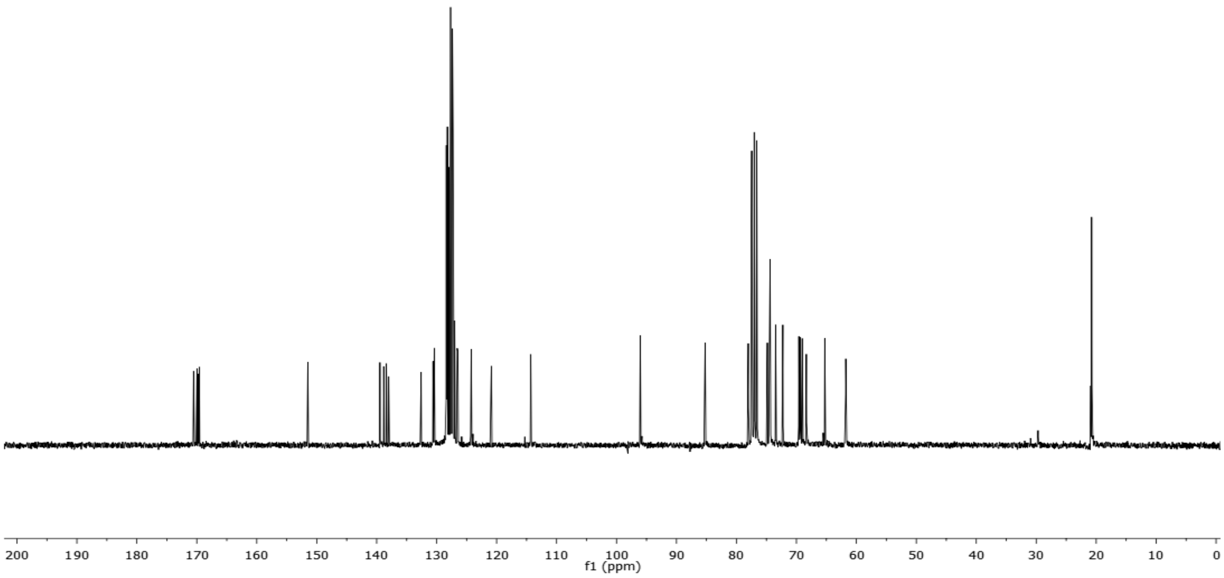
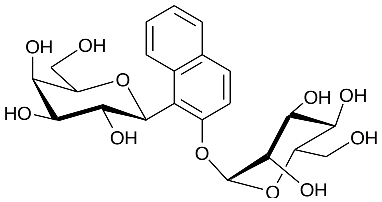


^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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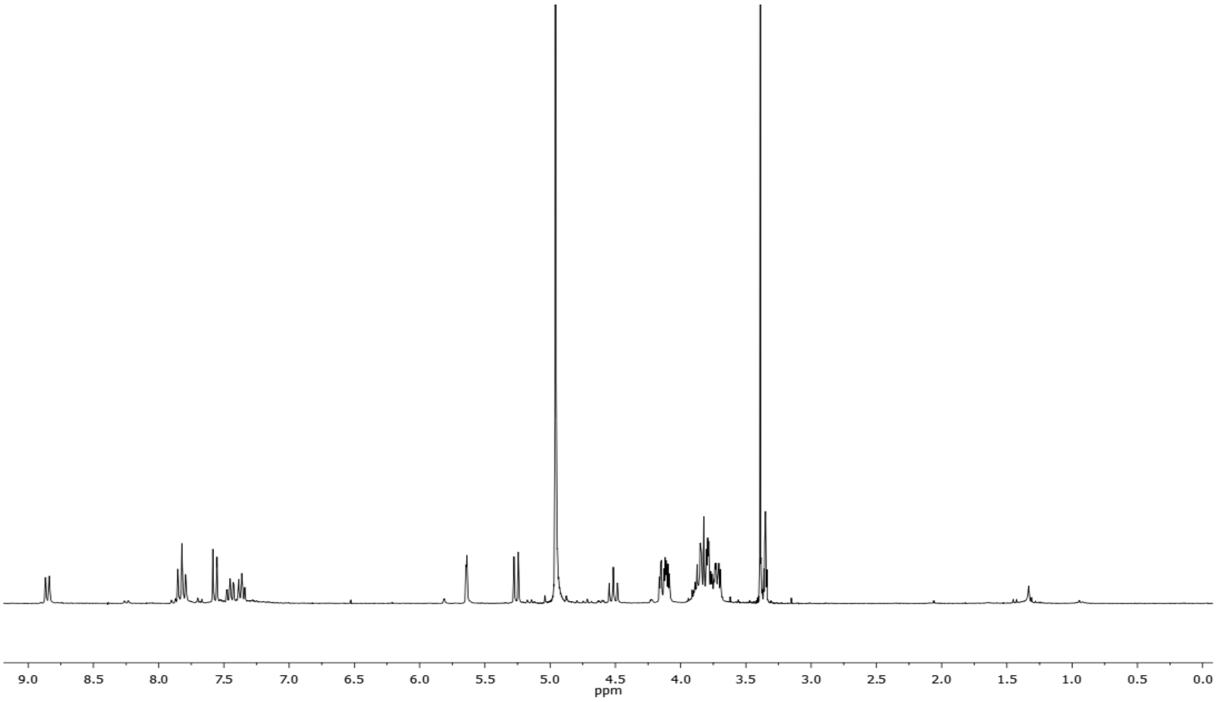
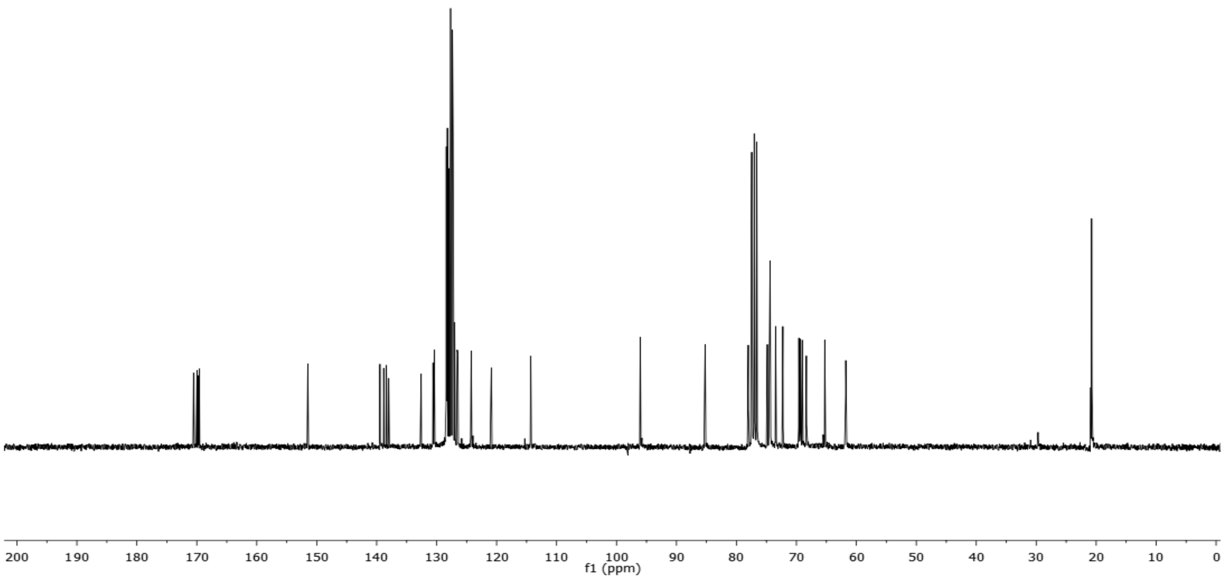
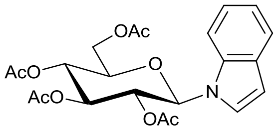


^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (101 MHz, CD_3OD)



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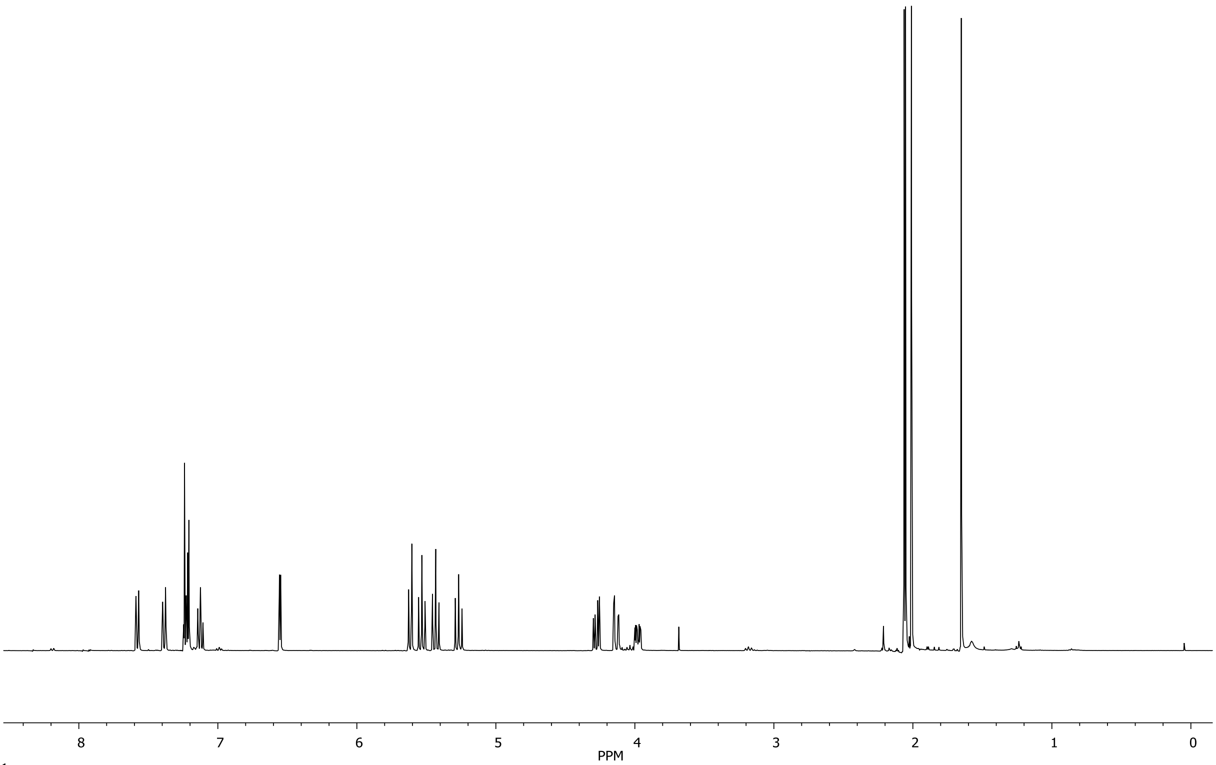
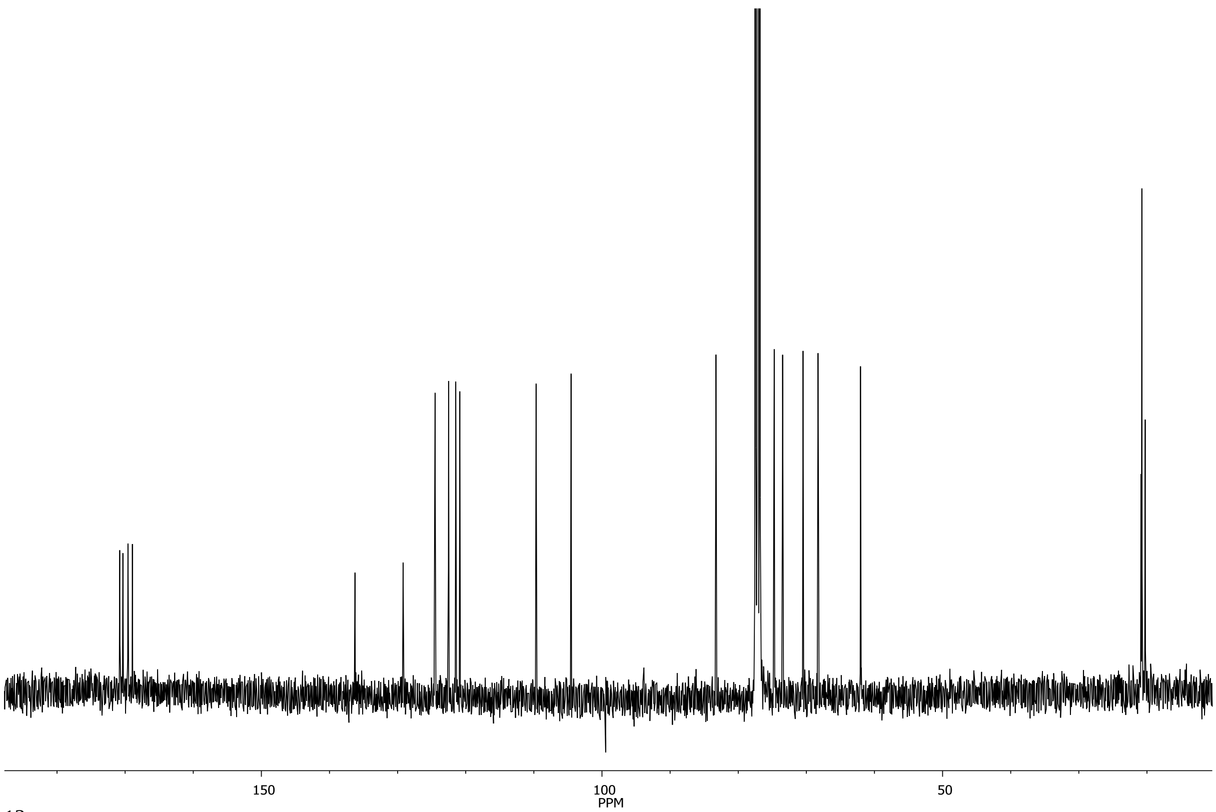
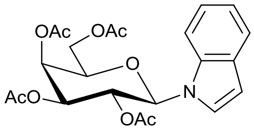


[1]H-NMR (400 MHz, $CDCl_3$)



[13]C-NMR (101 MHz, $CDCl_3$)



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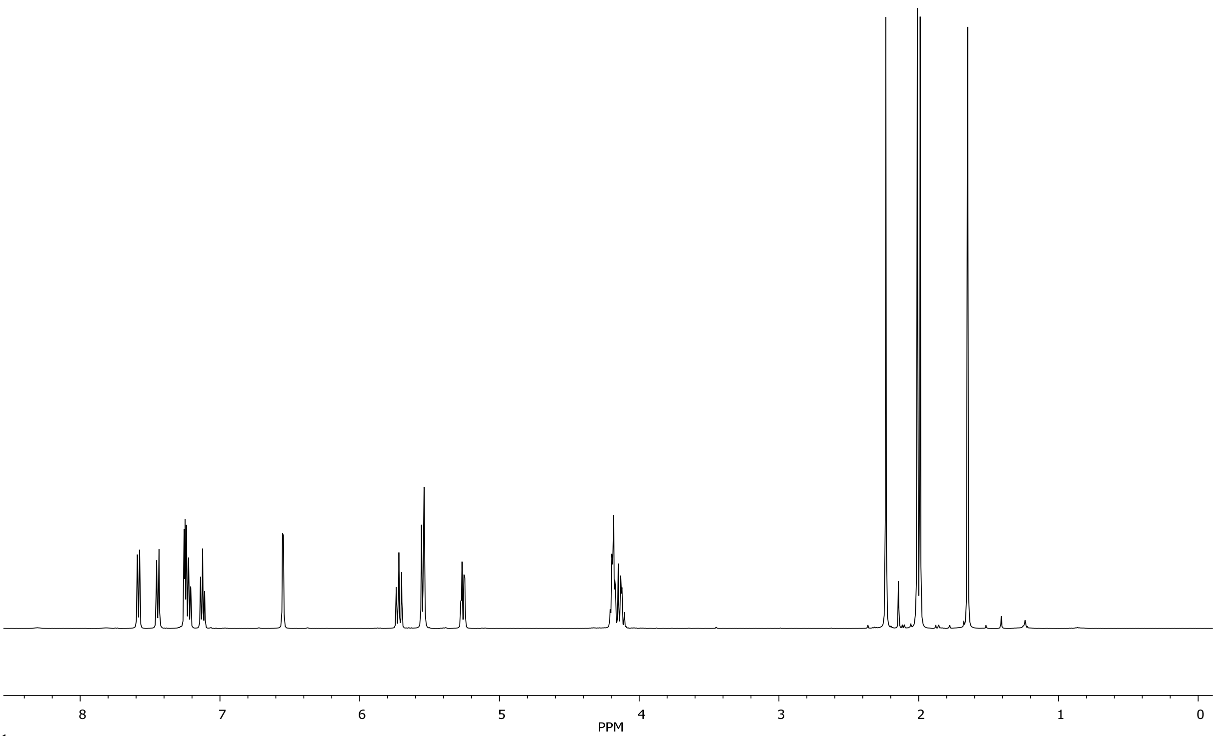
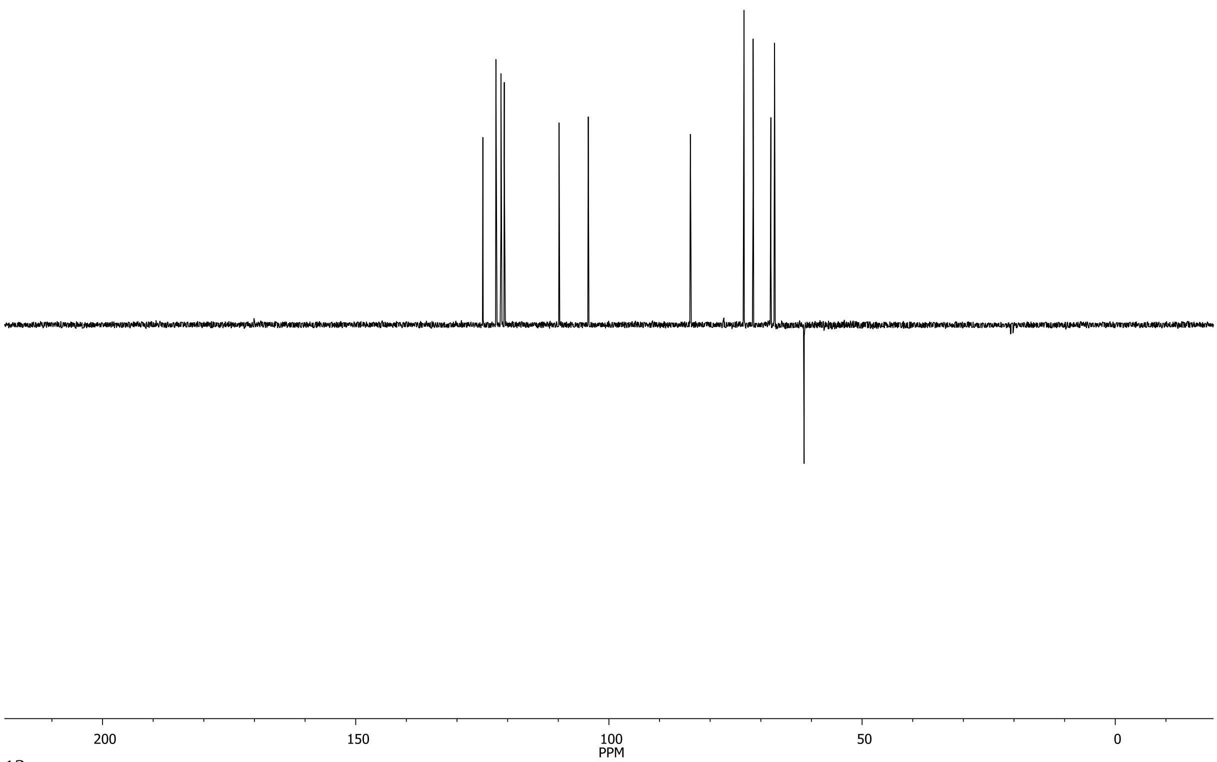
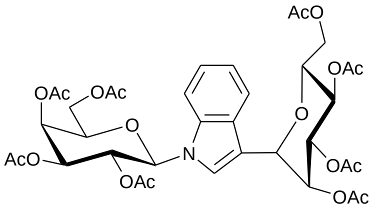


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



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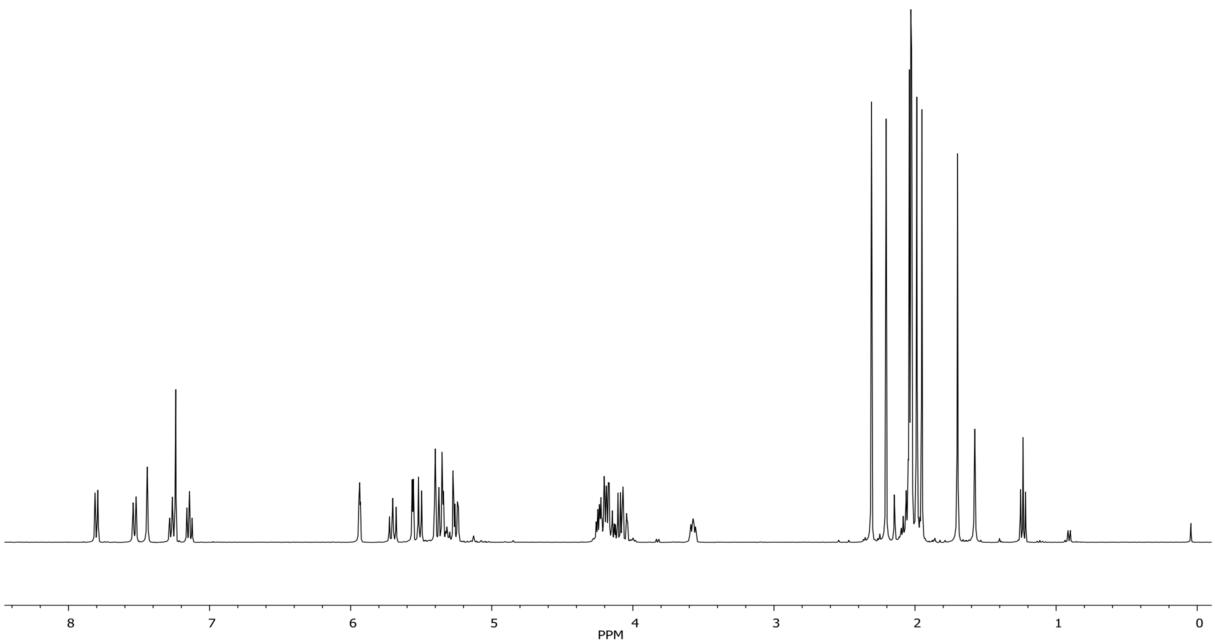
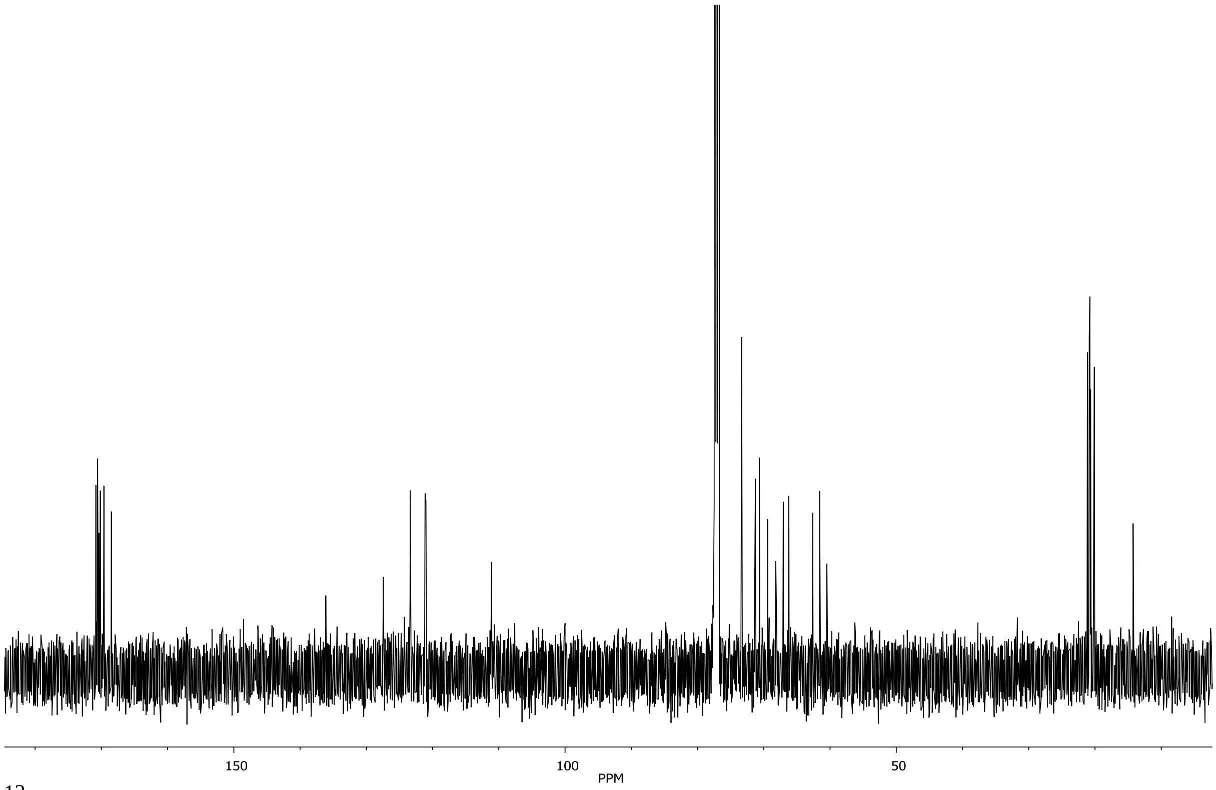
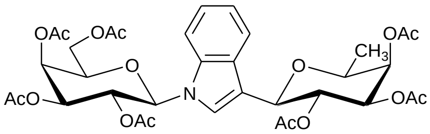


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



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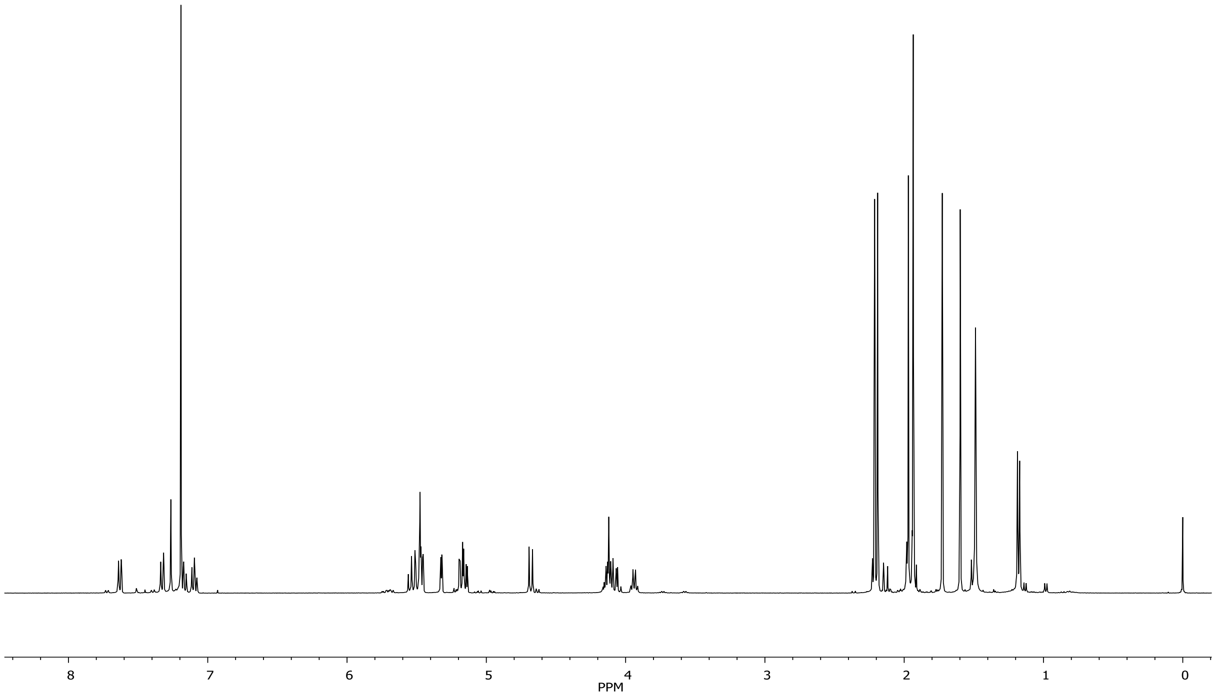
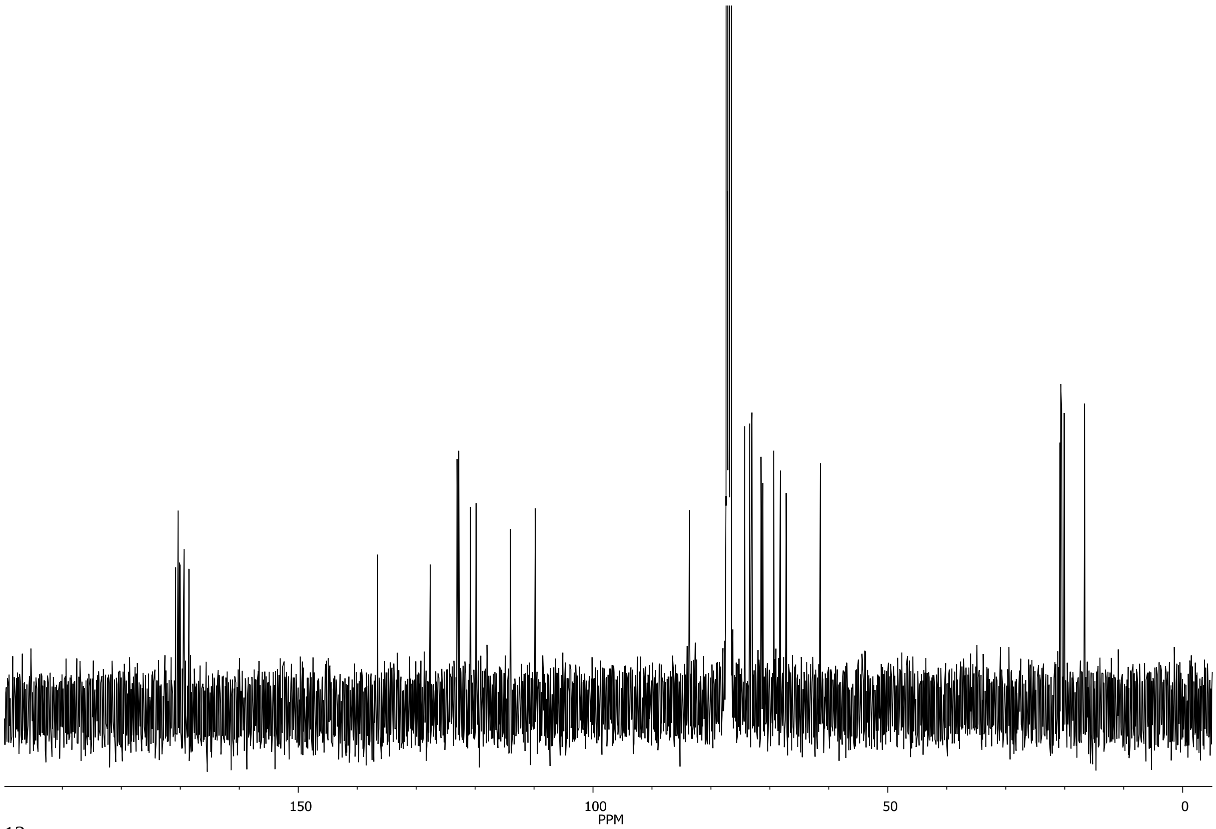
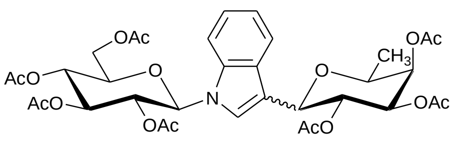


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



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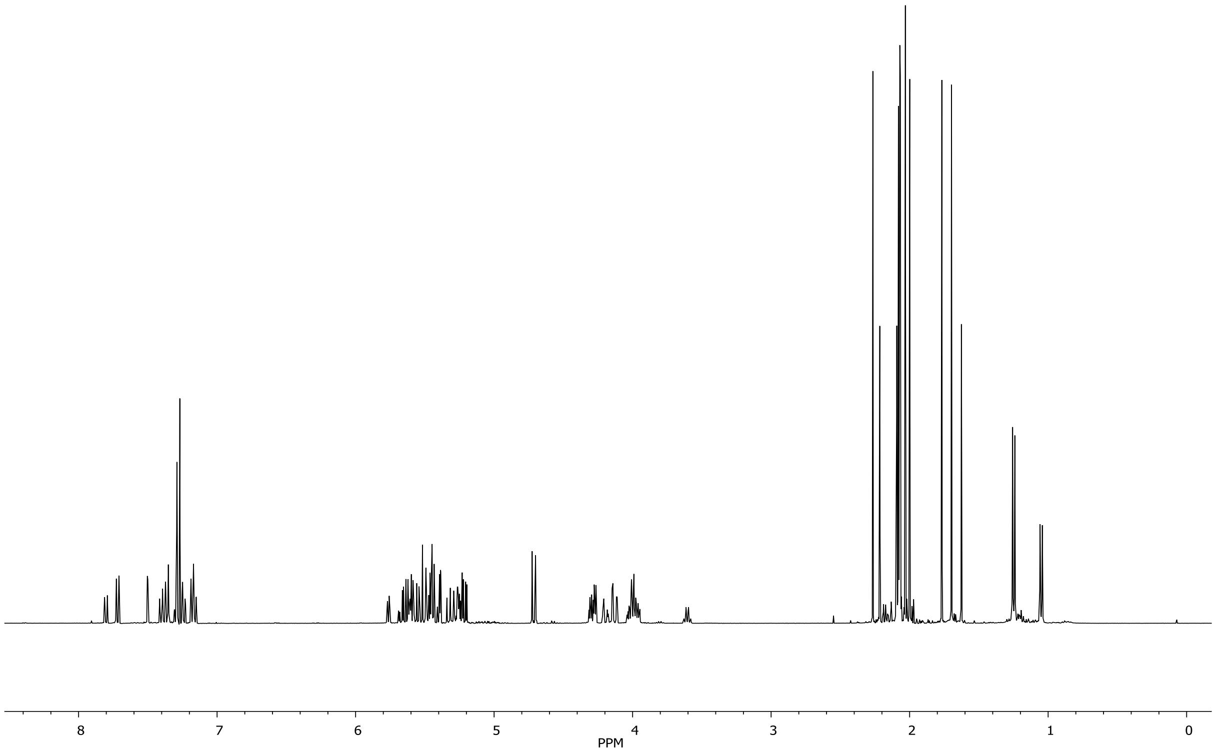
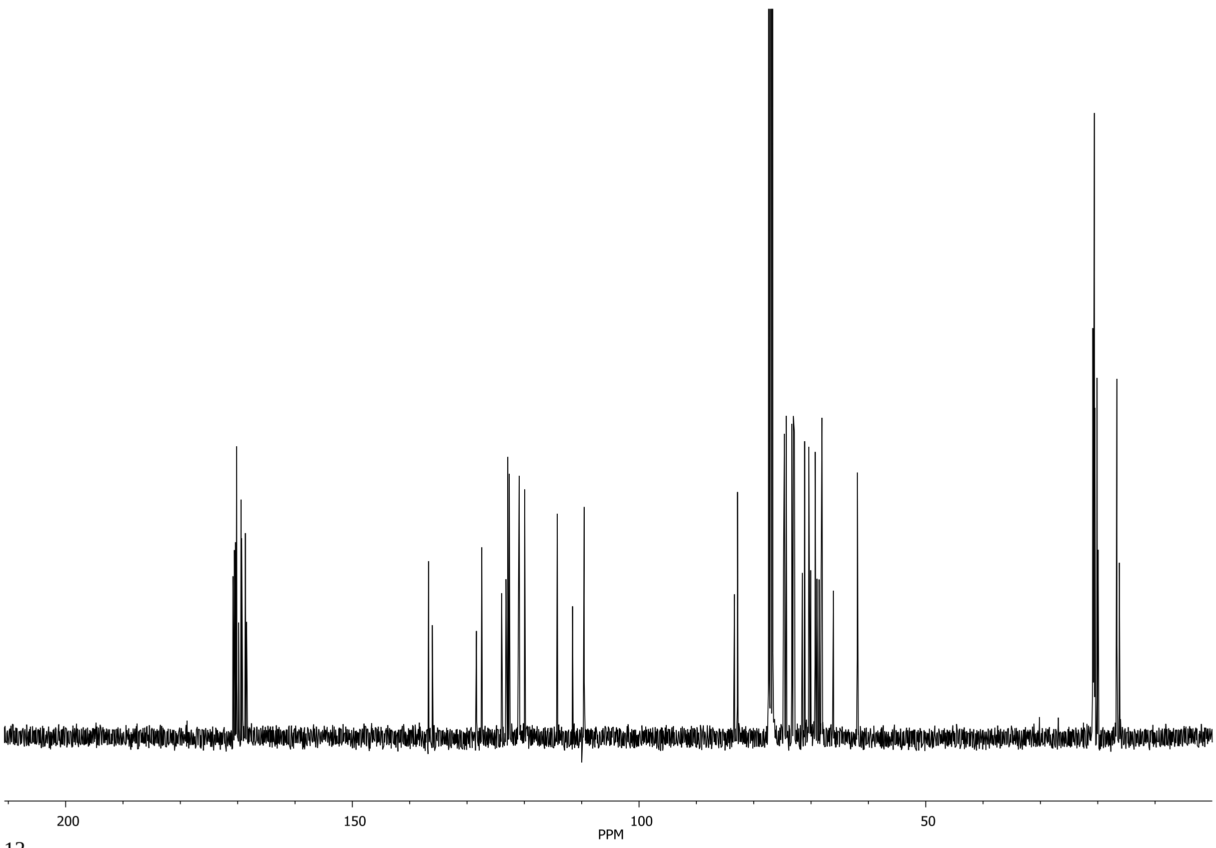


^{1}H-NMR (400 MHz, $CDCl_3$)



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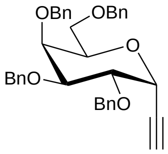

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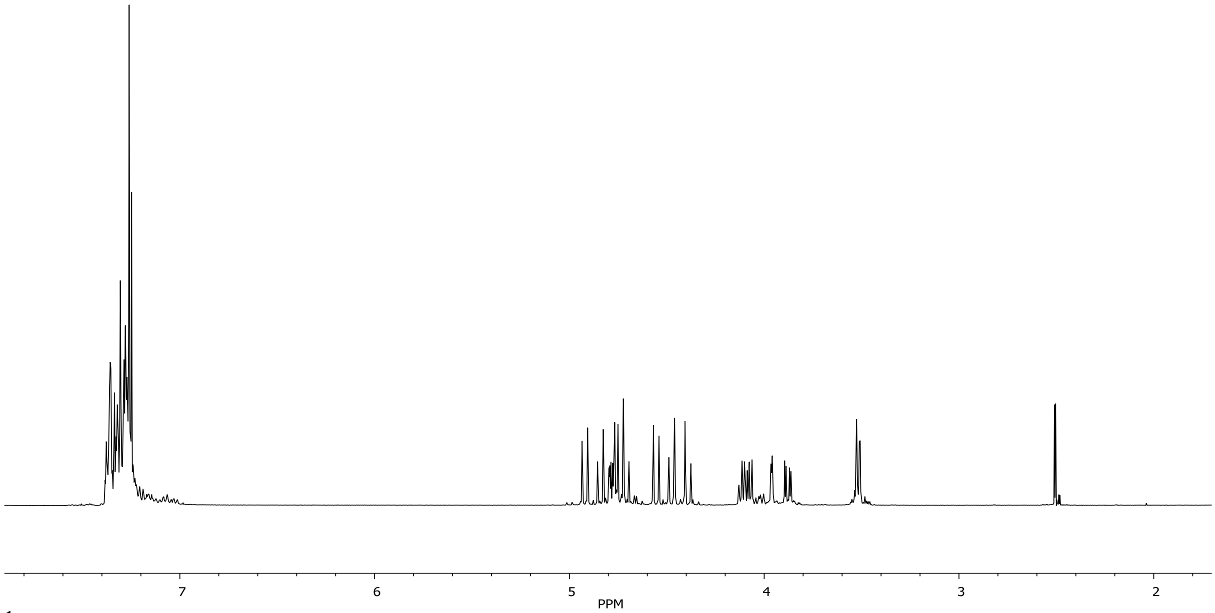
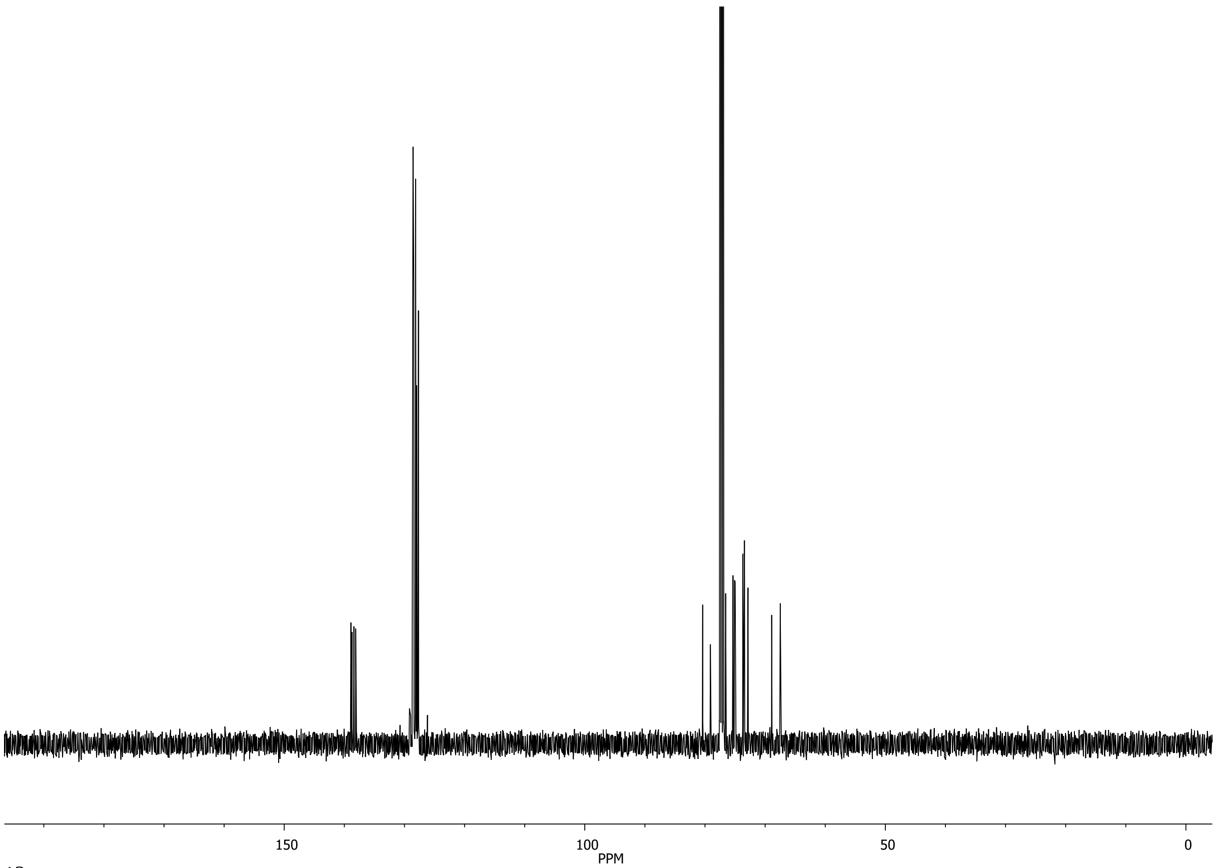
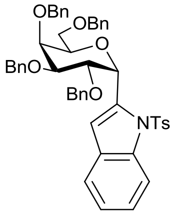


[1]H-NMR (400 MHz, $CDCl_3$)



[13]C-NMR (101 MHz, $CDCl_3$)

Electronic Supplementary Material (ESI) for Chemical Communications



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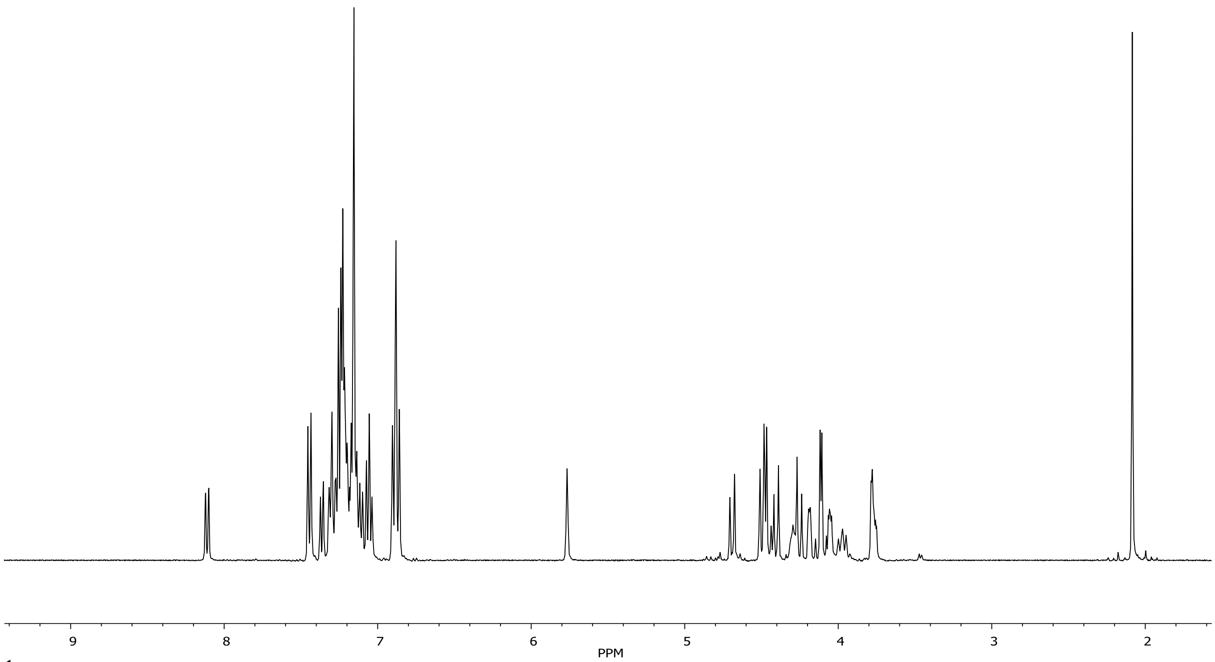

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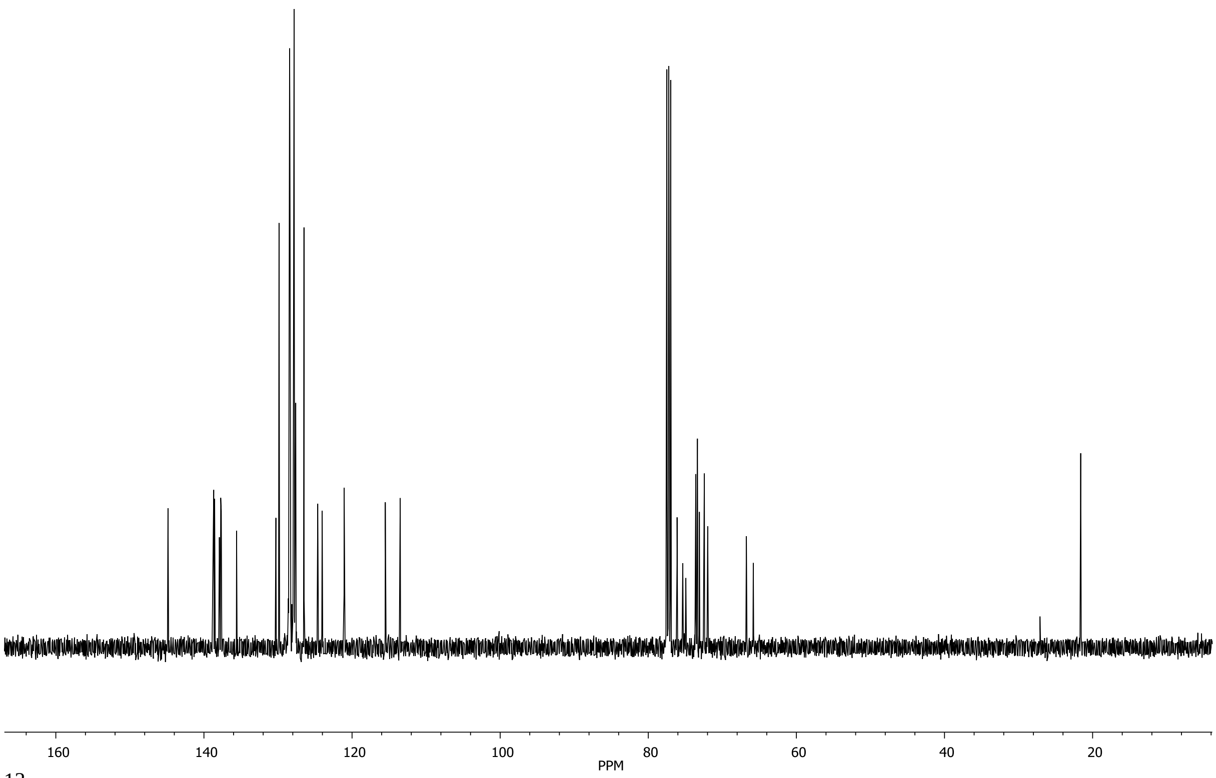

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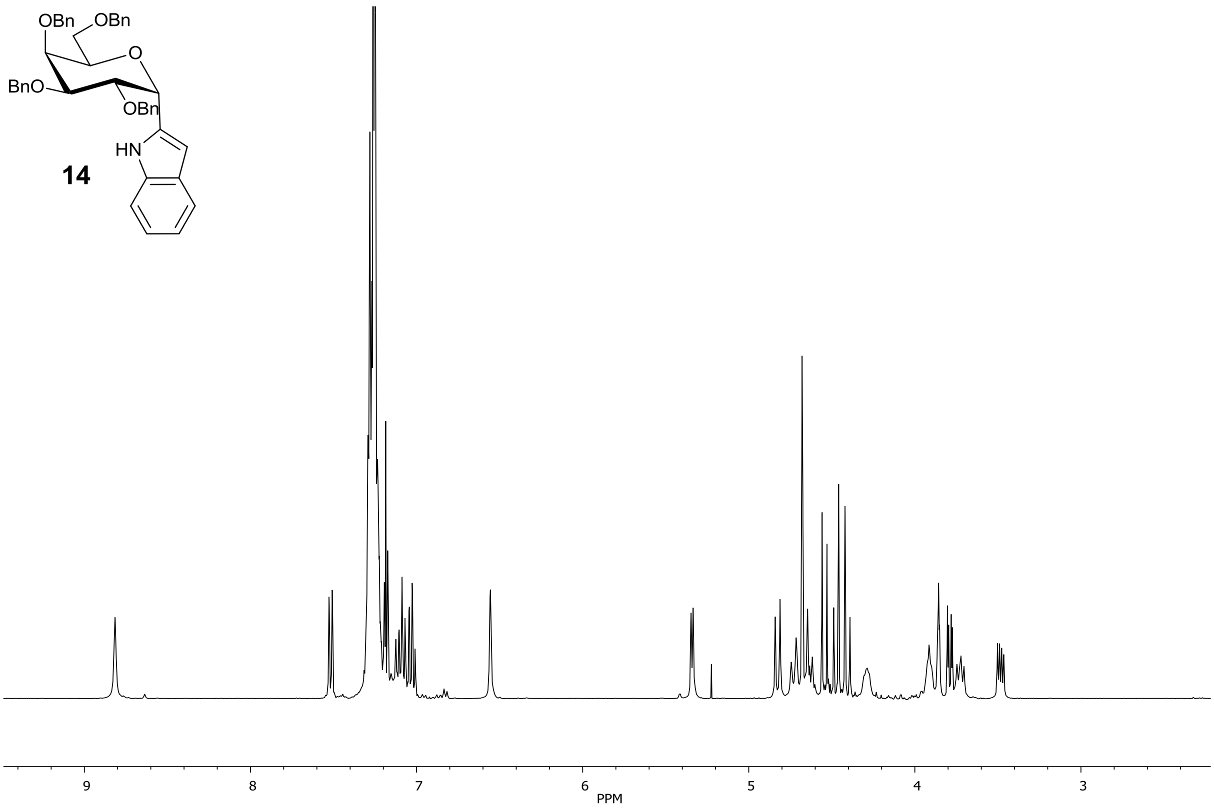
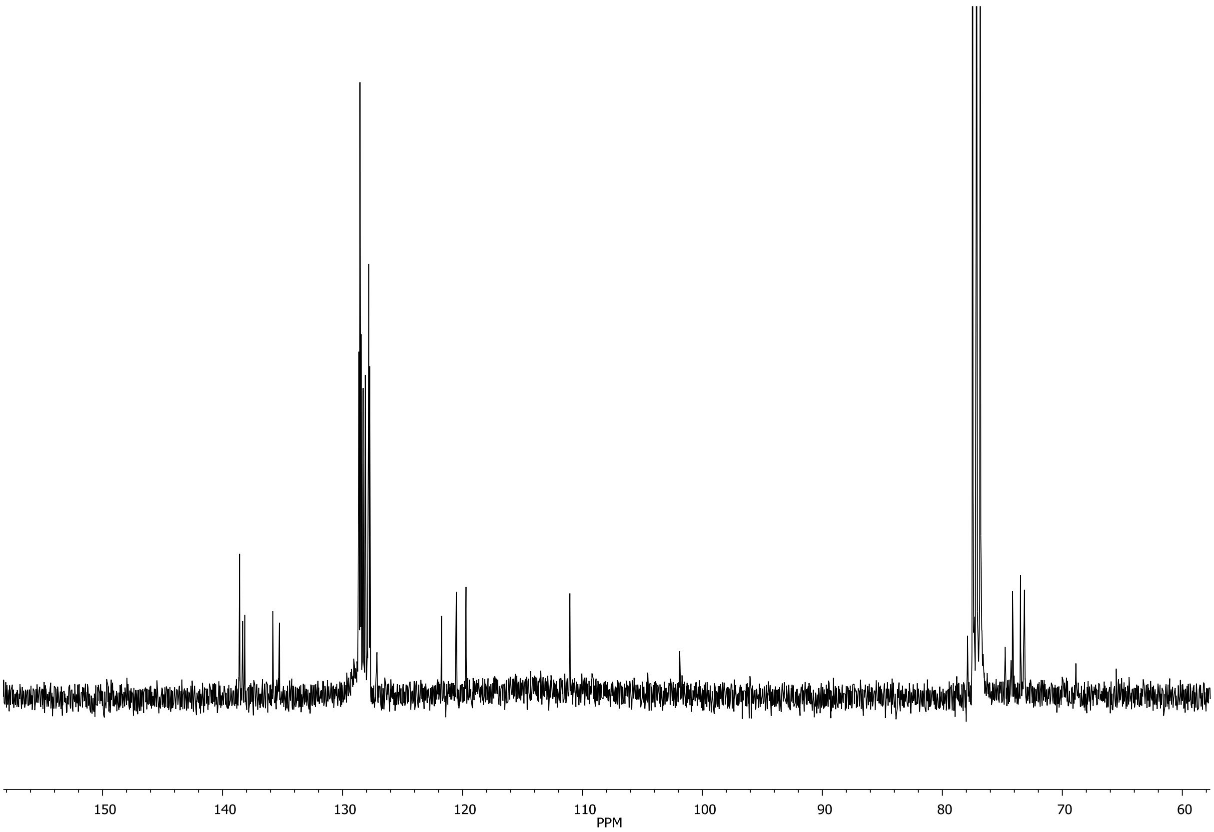


^{1}H-NMR (400 MHz, $CDCl_3$)



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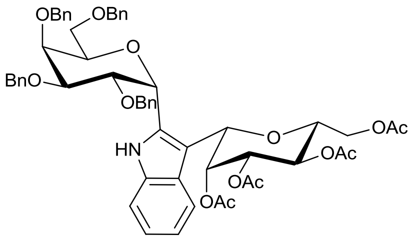

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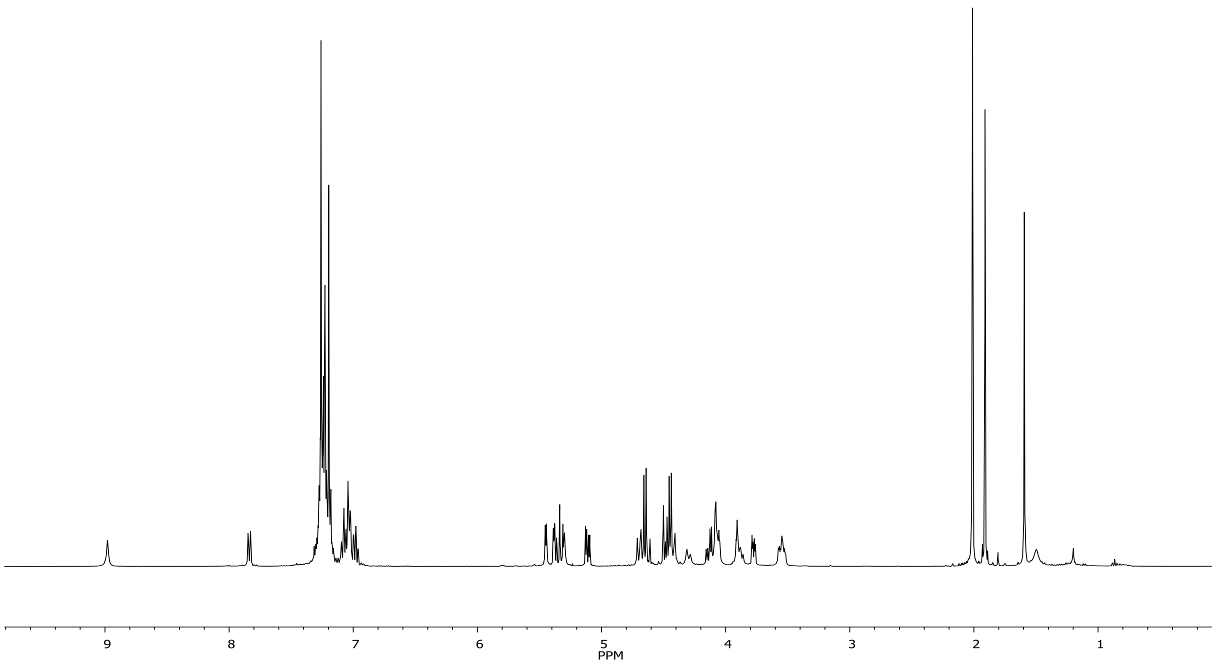

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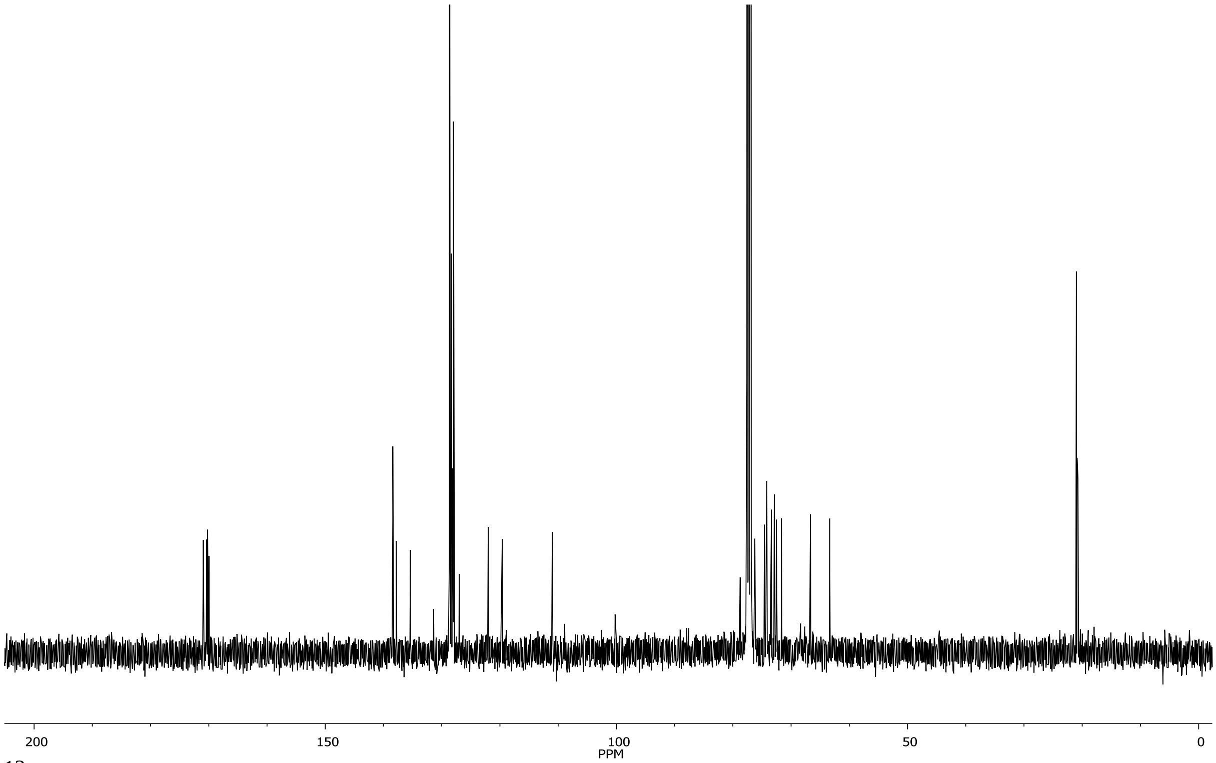

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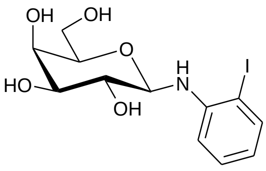

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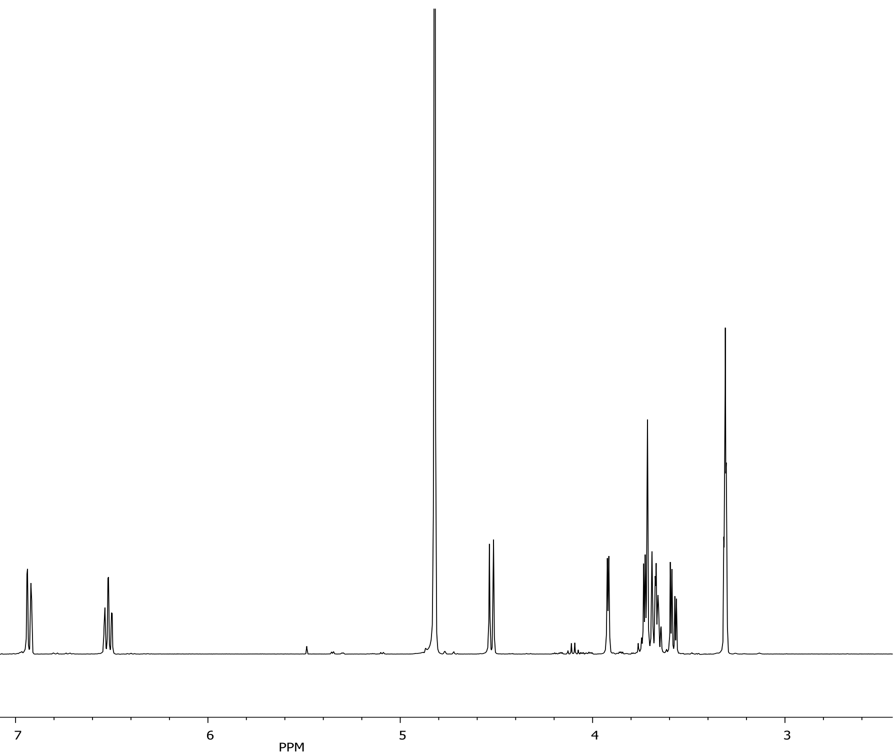

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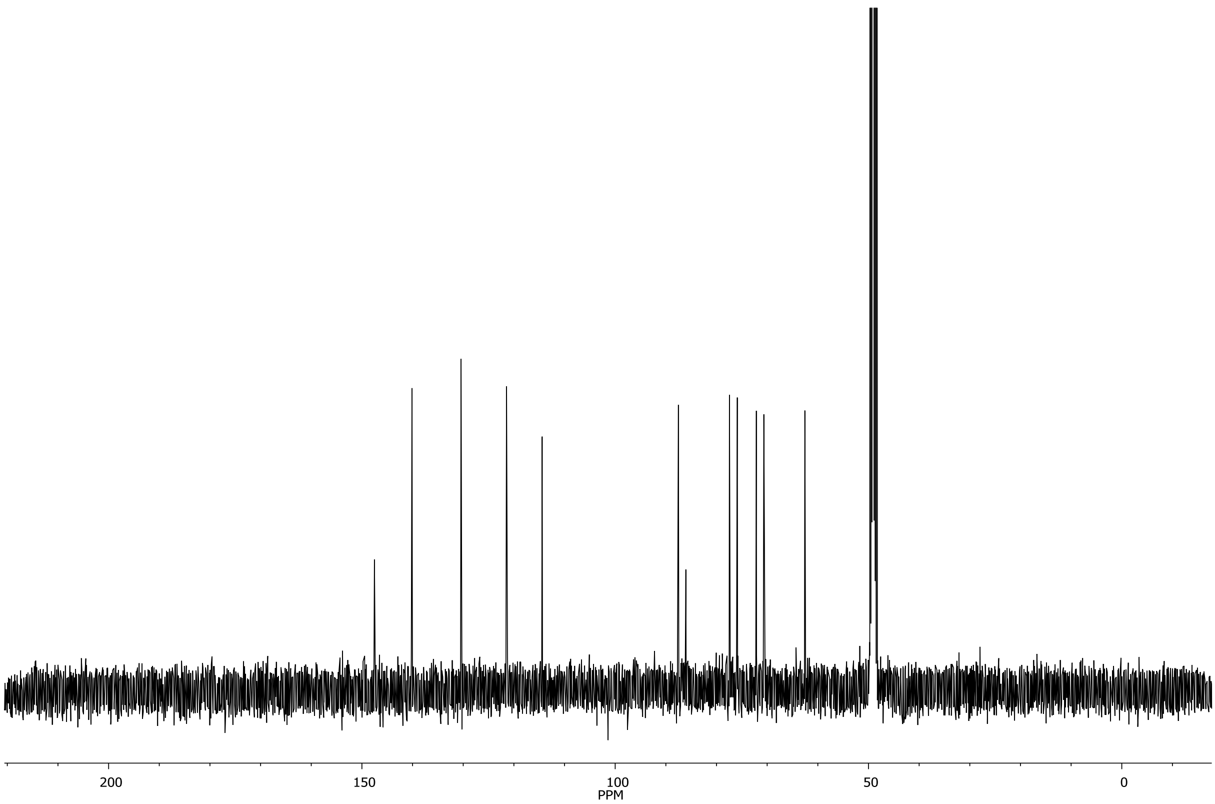

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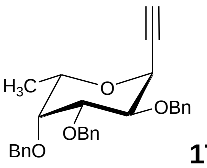

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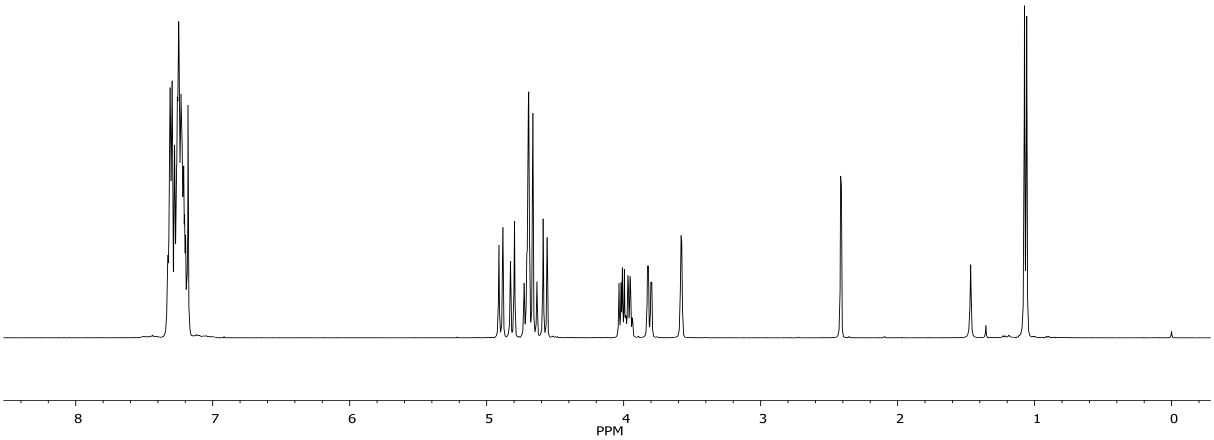
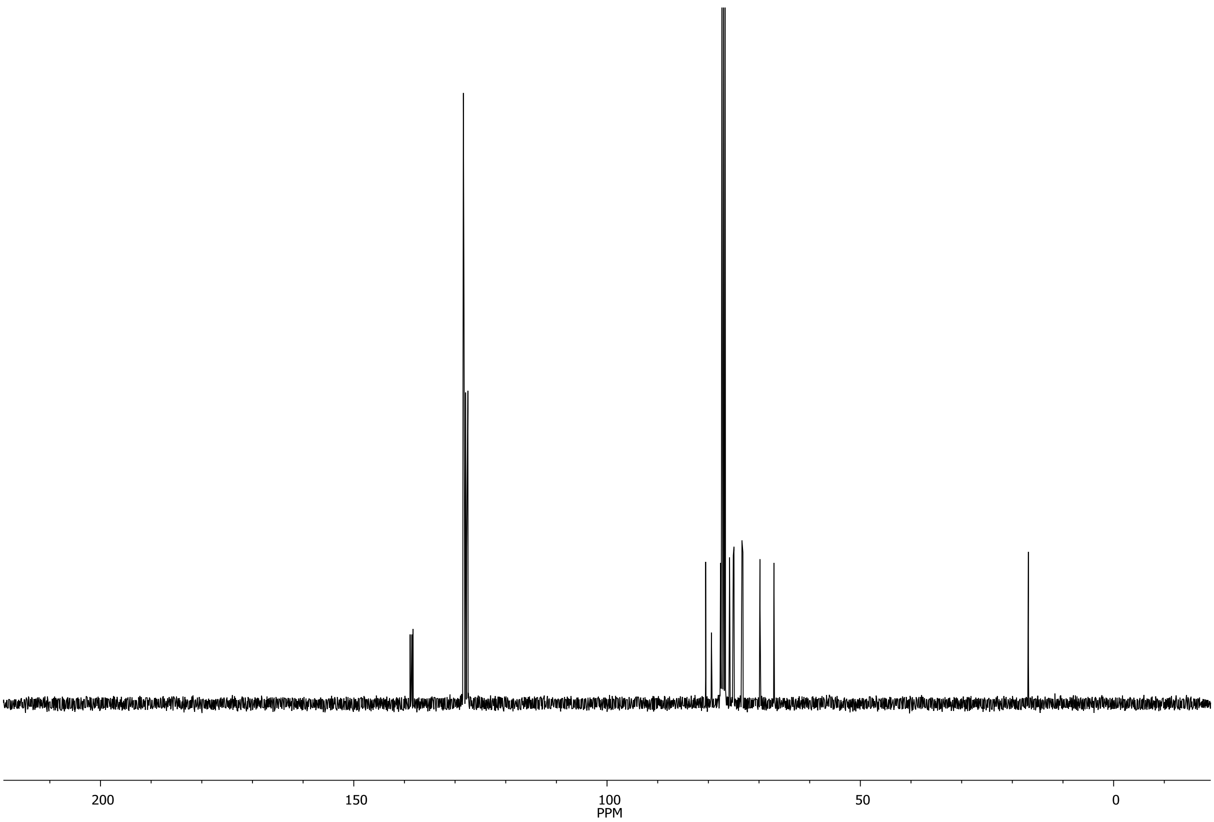


^{1}H-NMR (400 MHz, $CDCl_3$)



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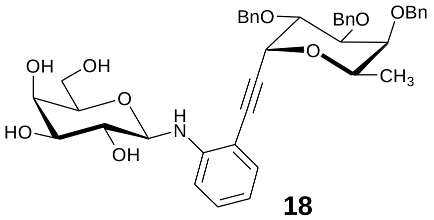

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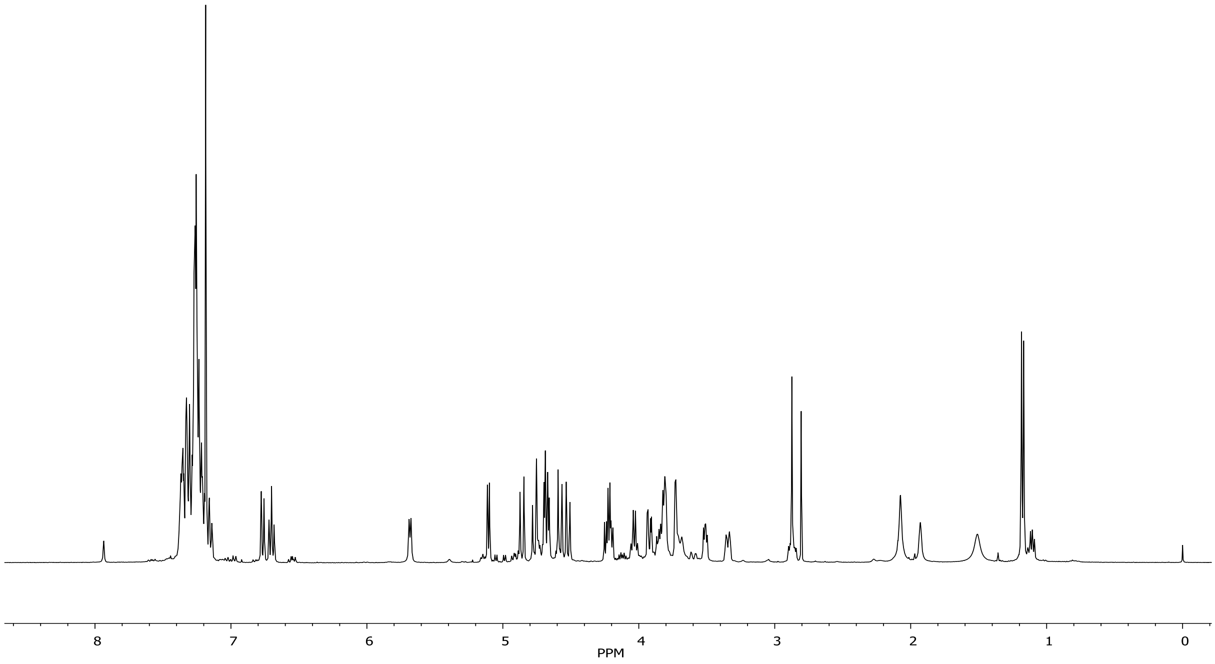
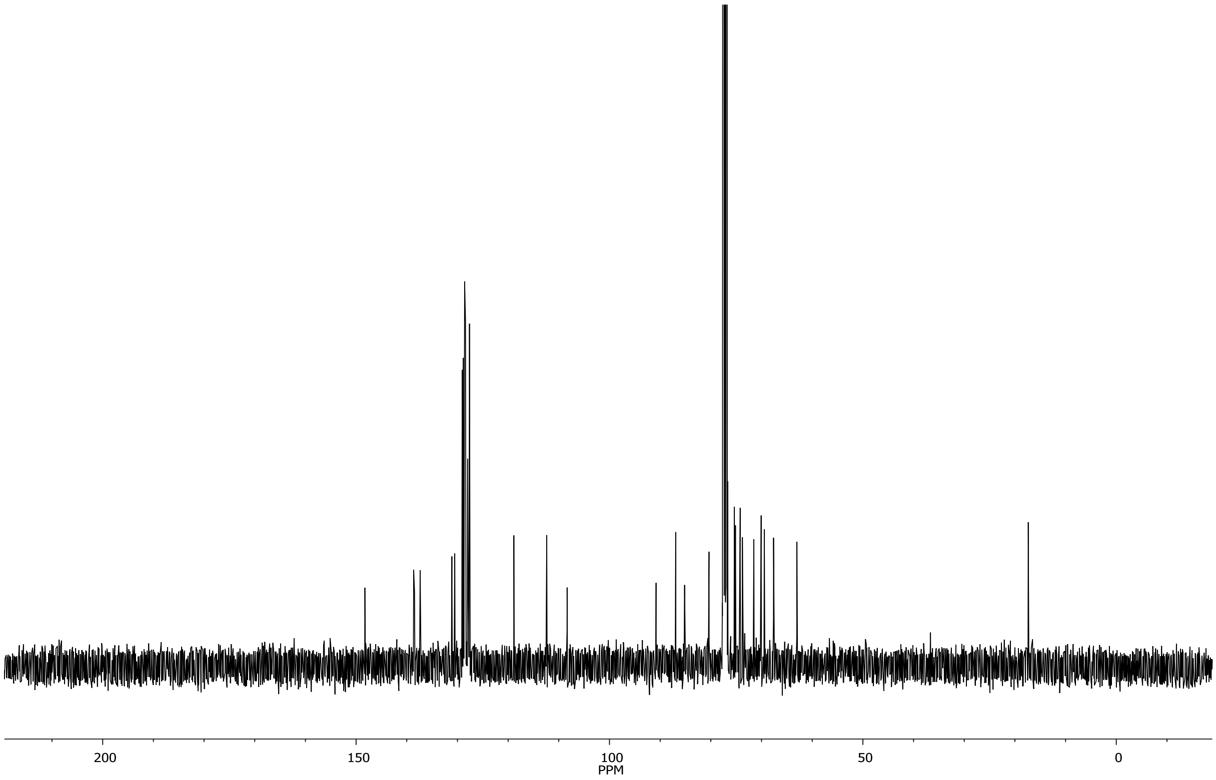
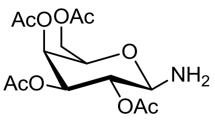


[1]H-NMR (400 MHz, $CDCl_3$)



[13]C-NMR (101 MHz, $CDCl_3$)



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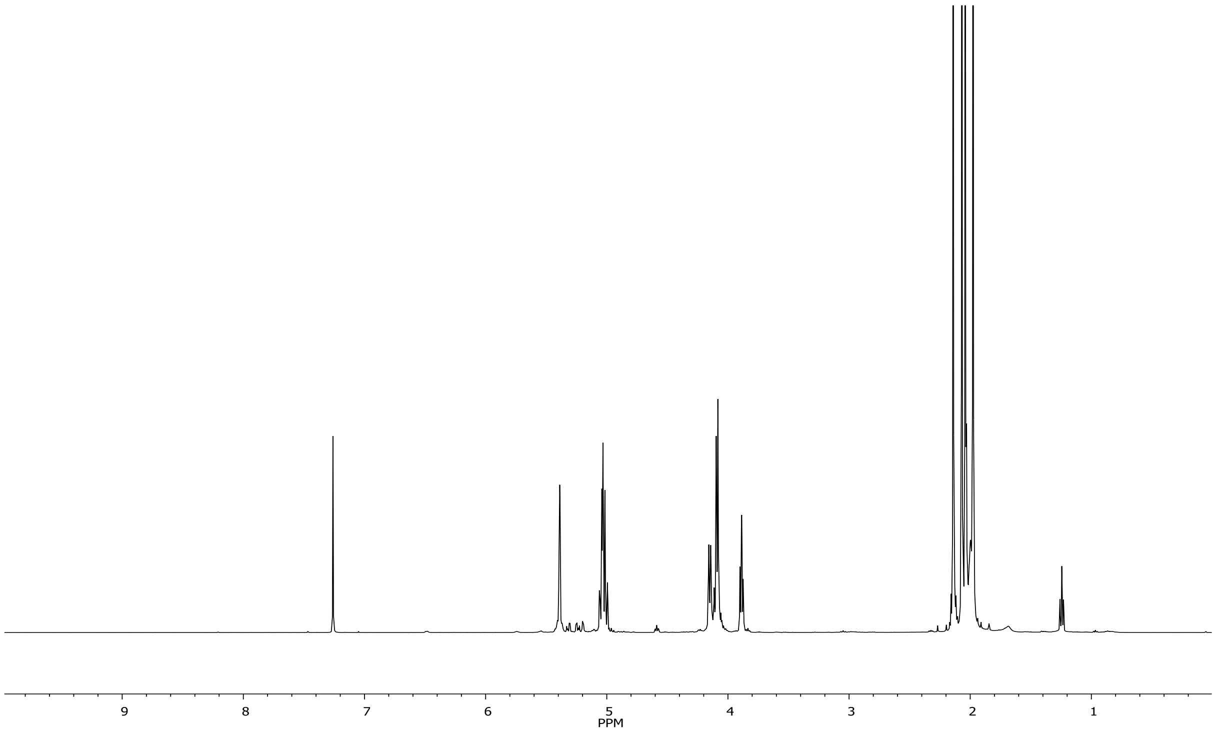

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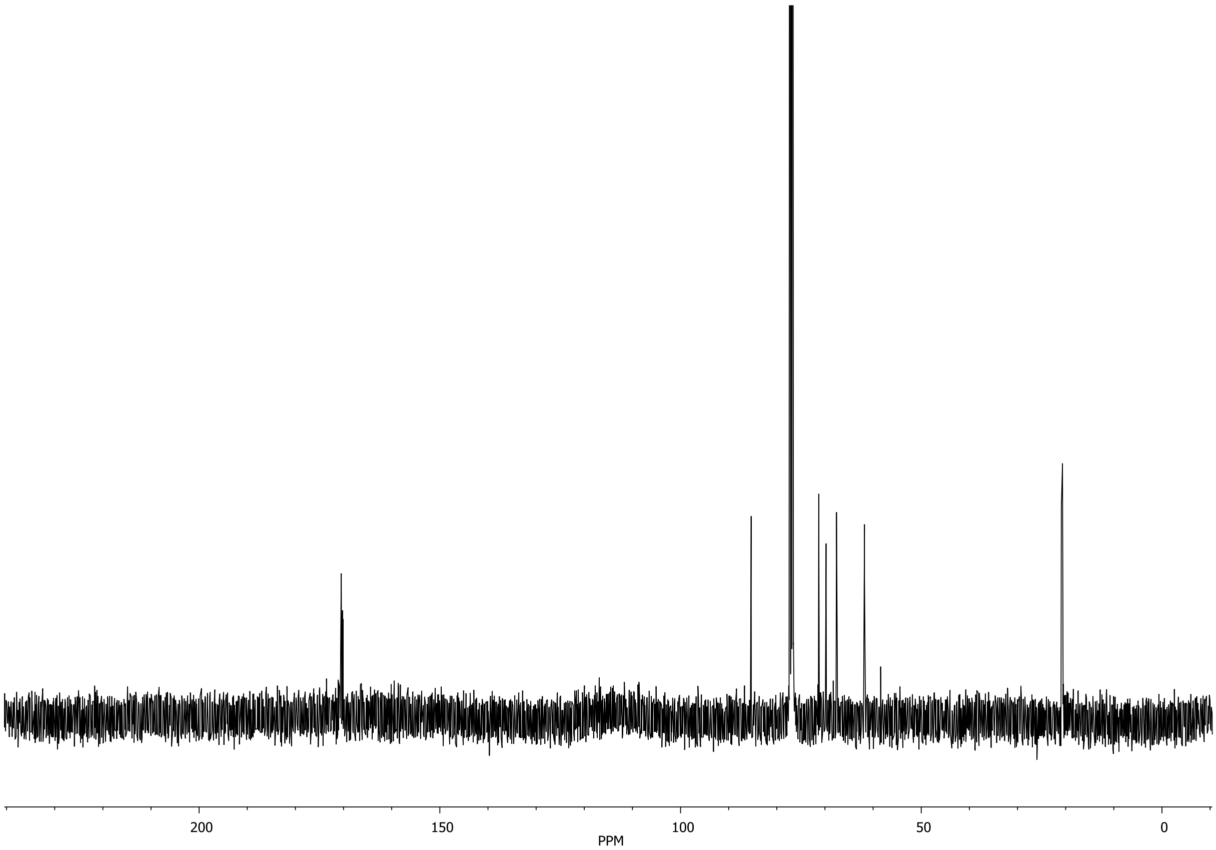
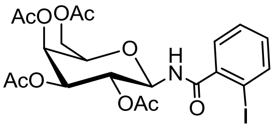


^{13}C-NMR (101 MHz, $CDCl_3$)

Electronic Supplementary Material (ESI) for Chemical Communications



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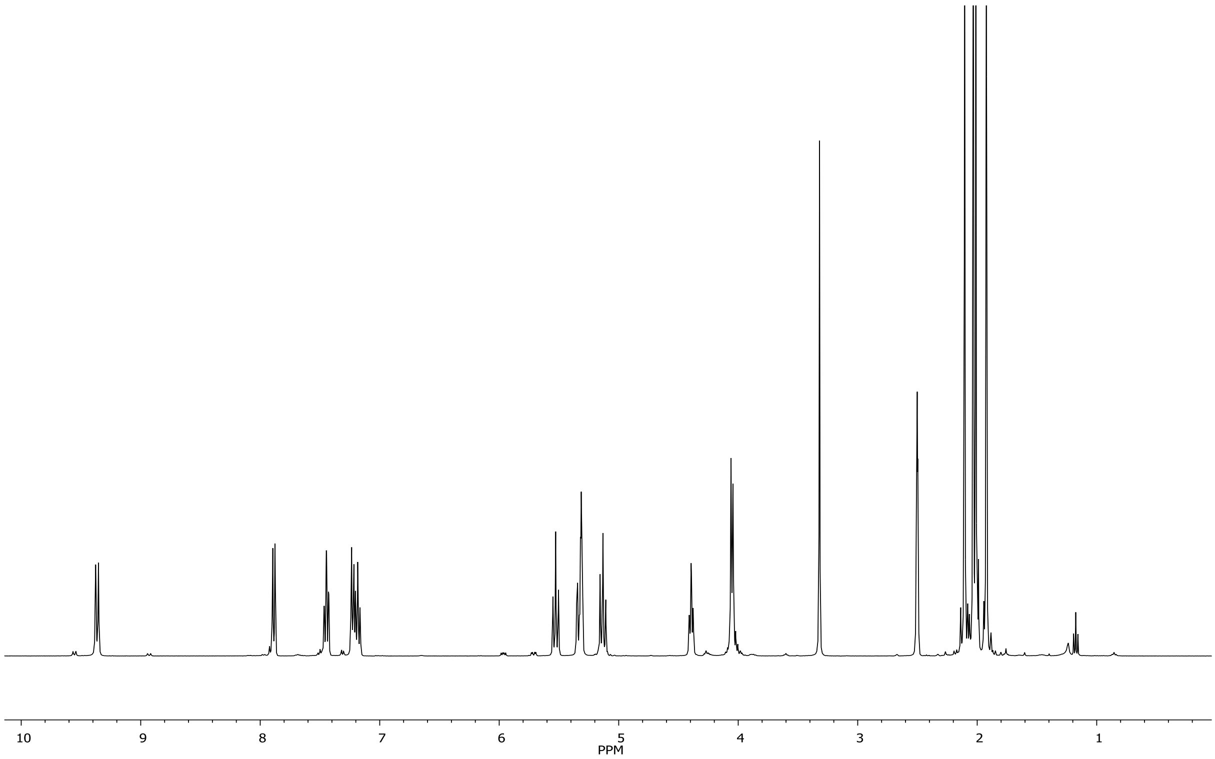

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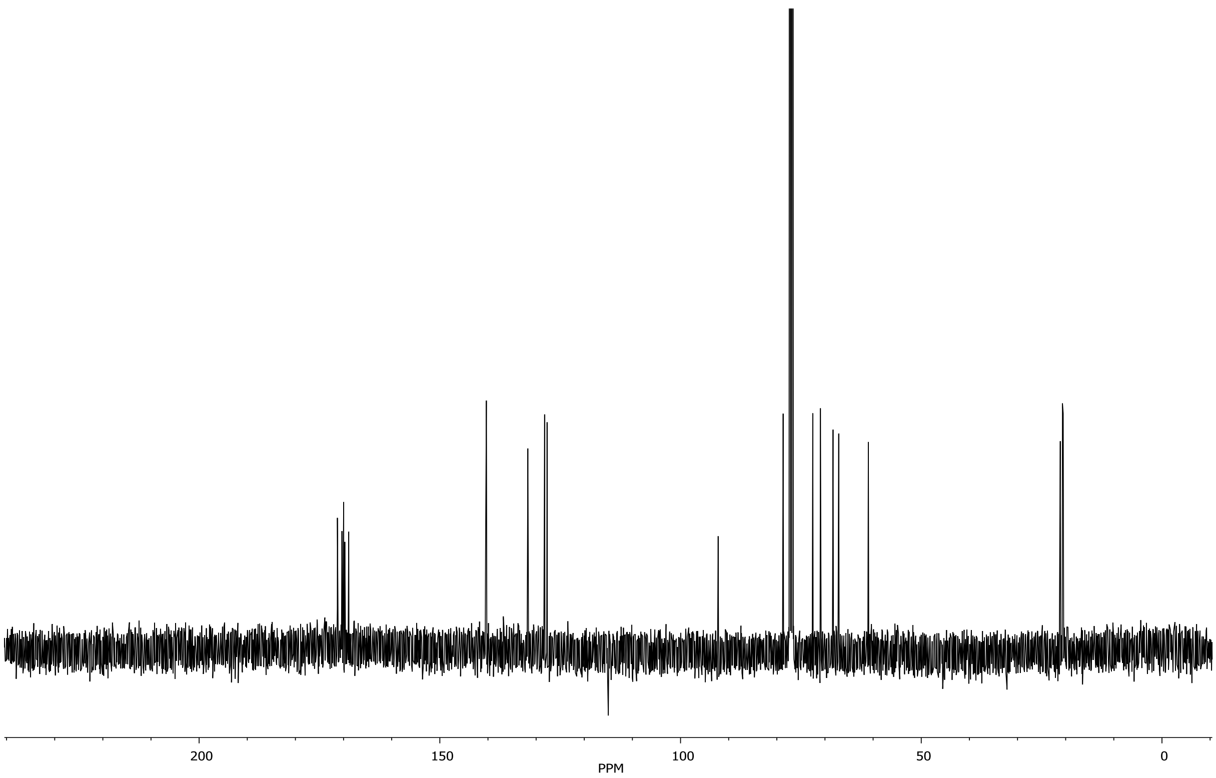

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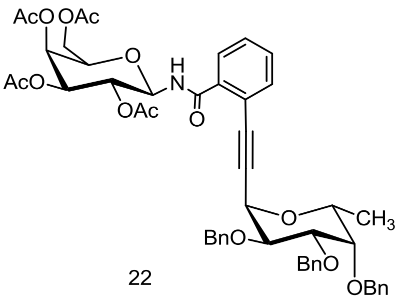

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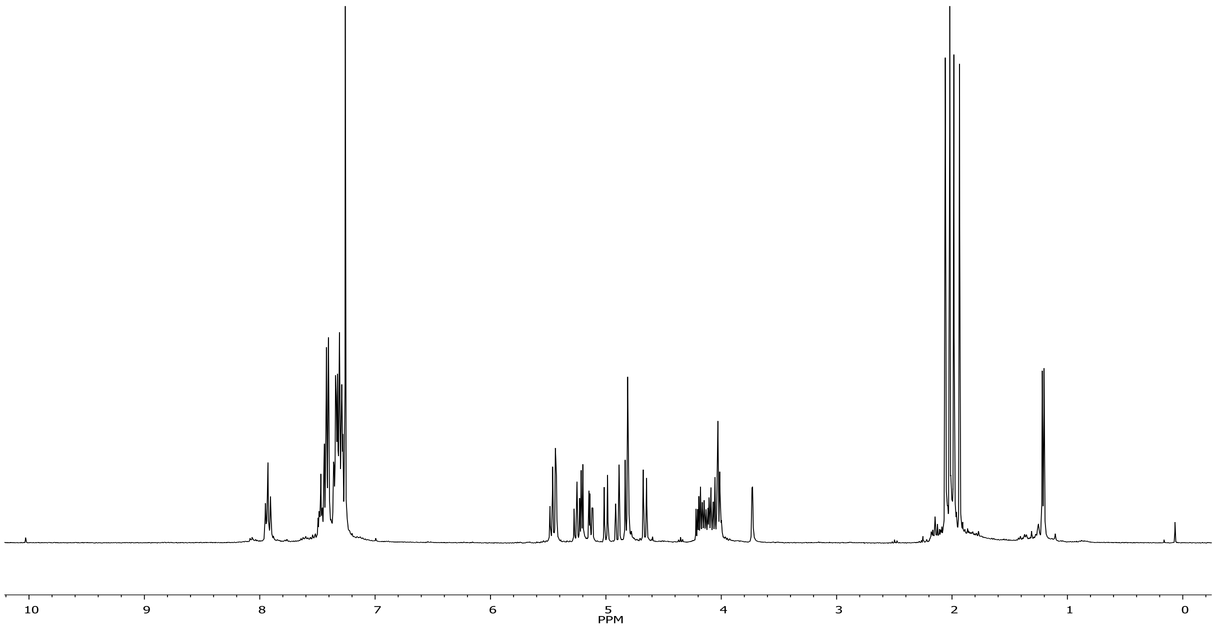
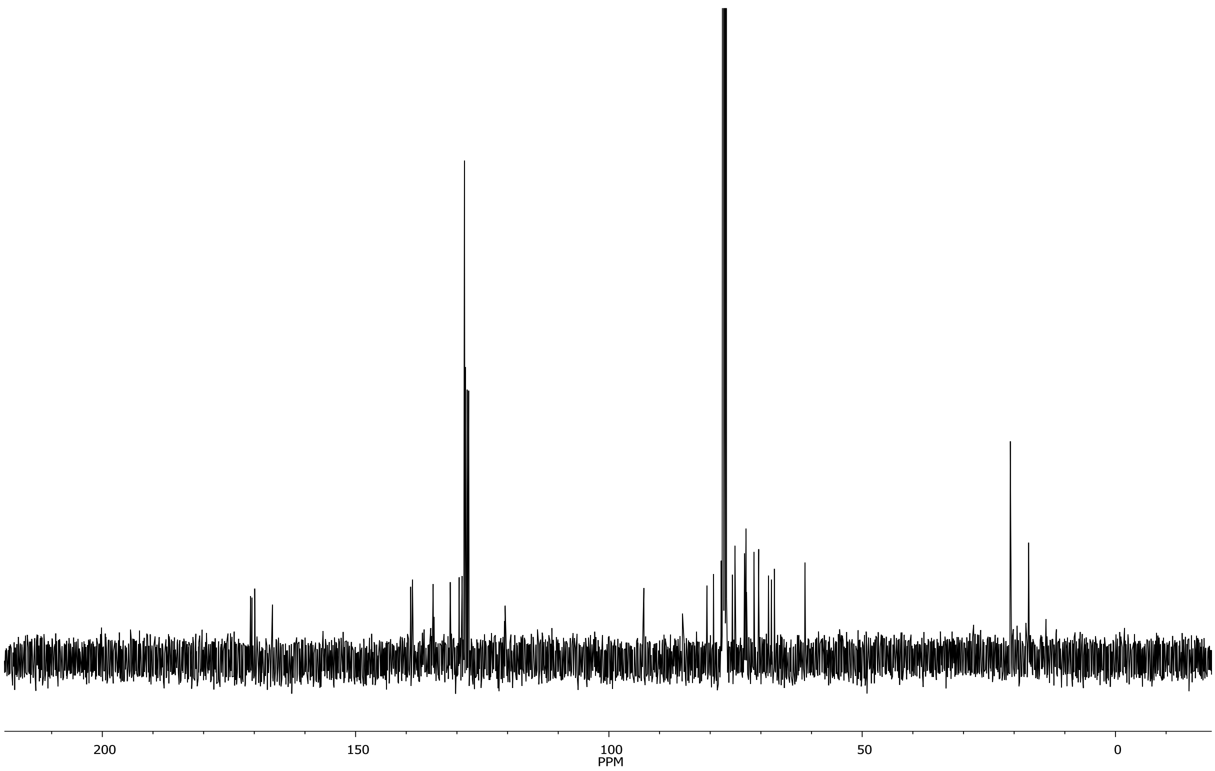


^{1}H-NMR (400 MHz, $CDCl_3$)



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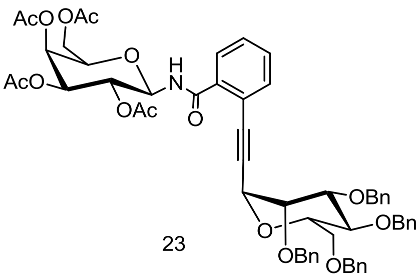

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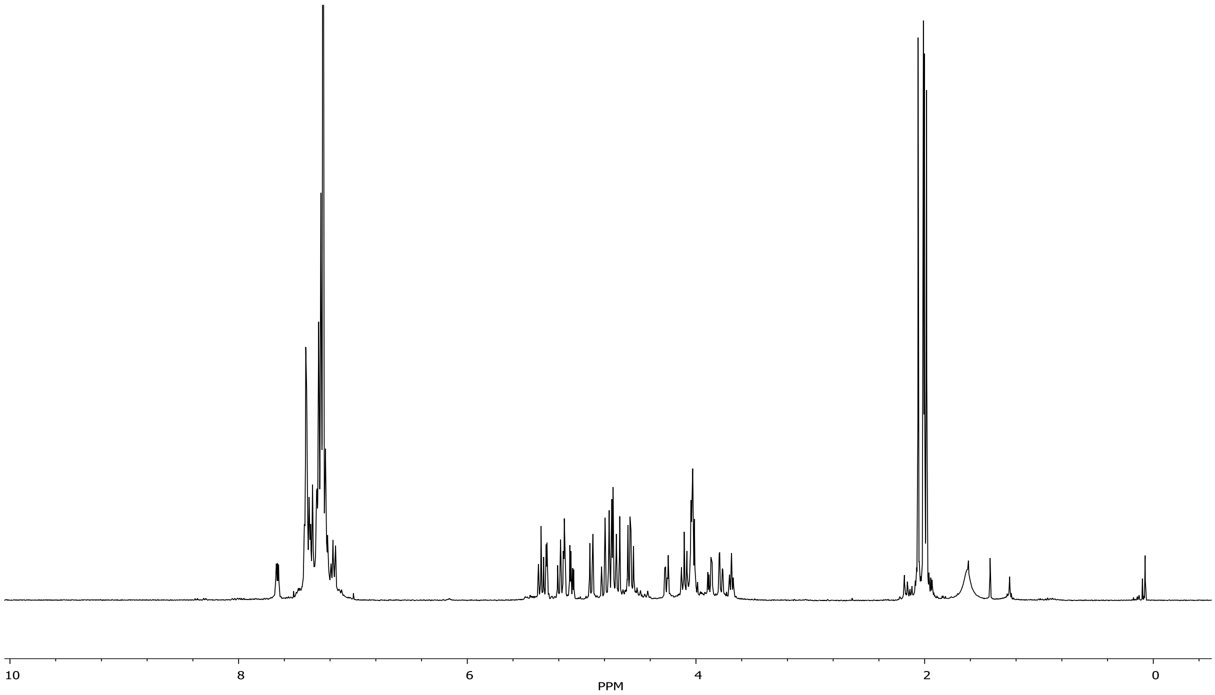
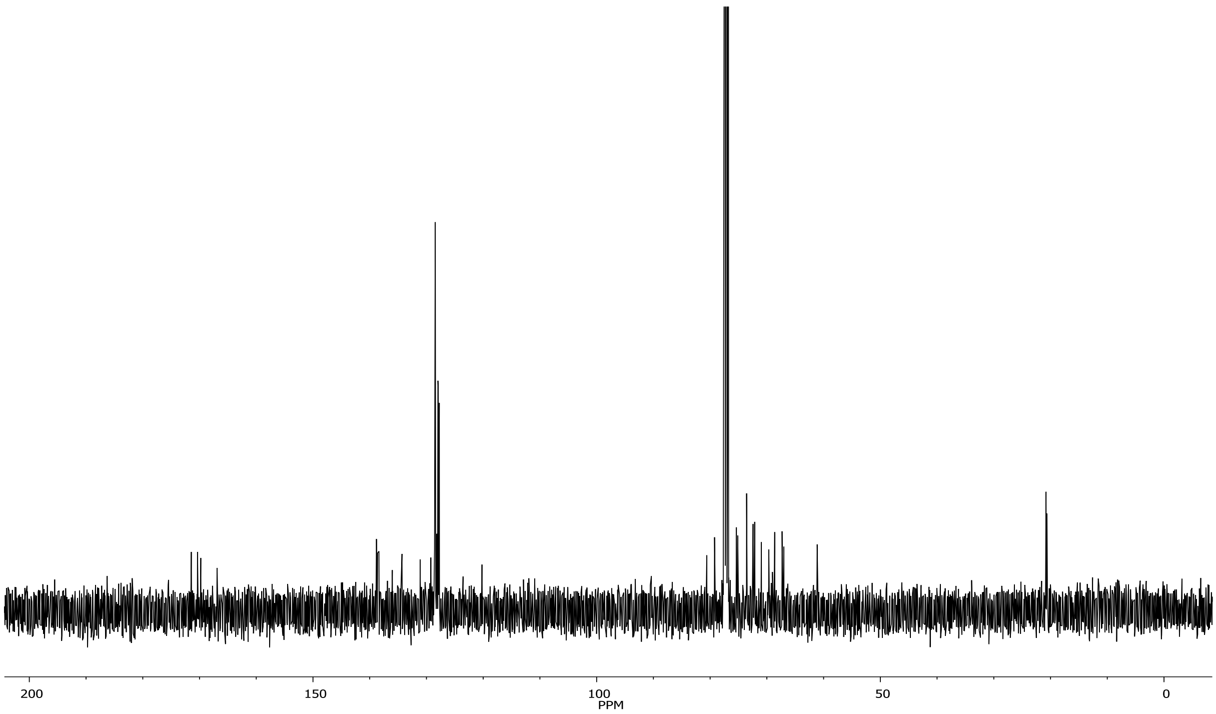


^{1}H-NMR (400 MHz, $CDCl_3$)



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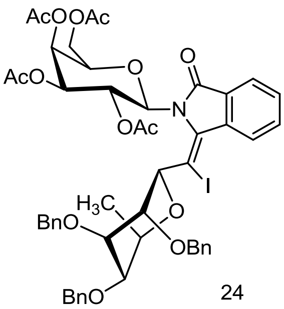

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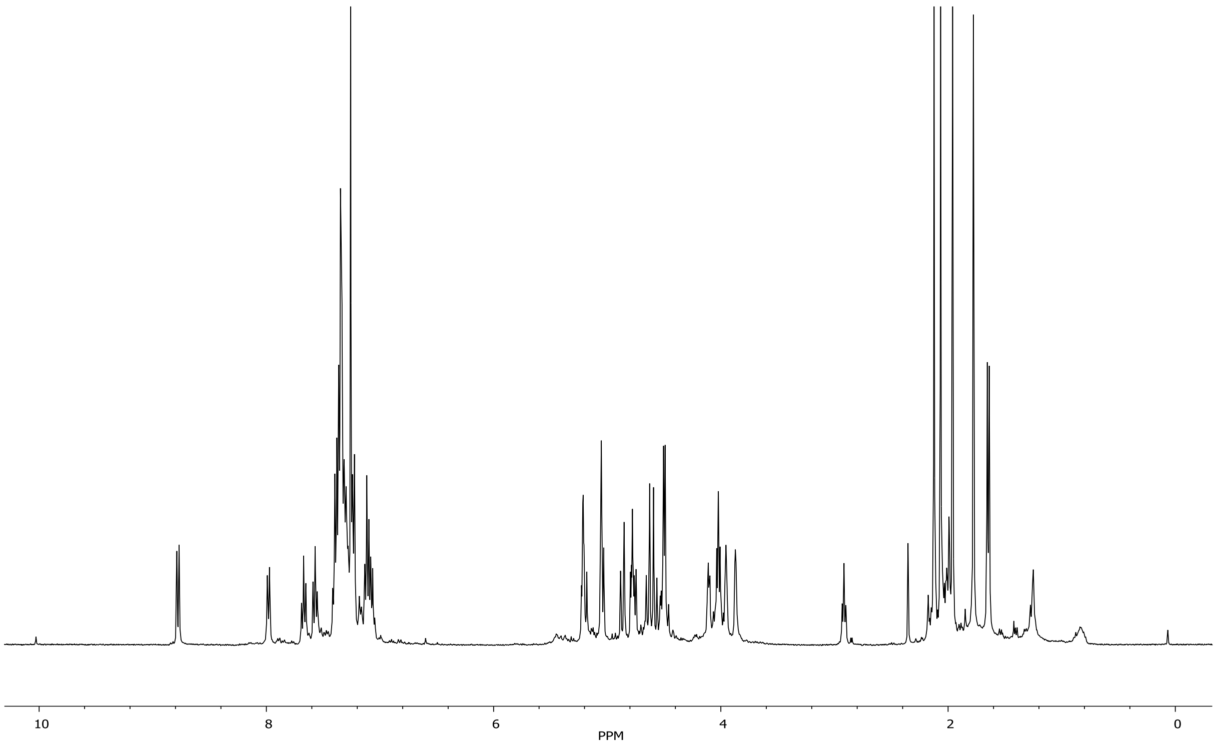

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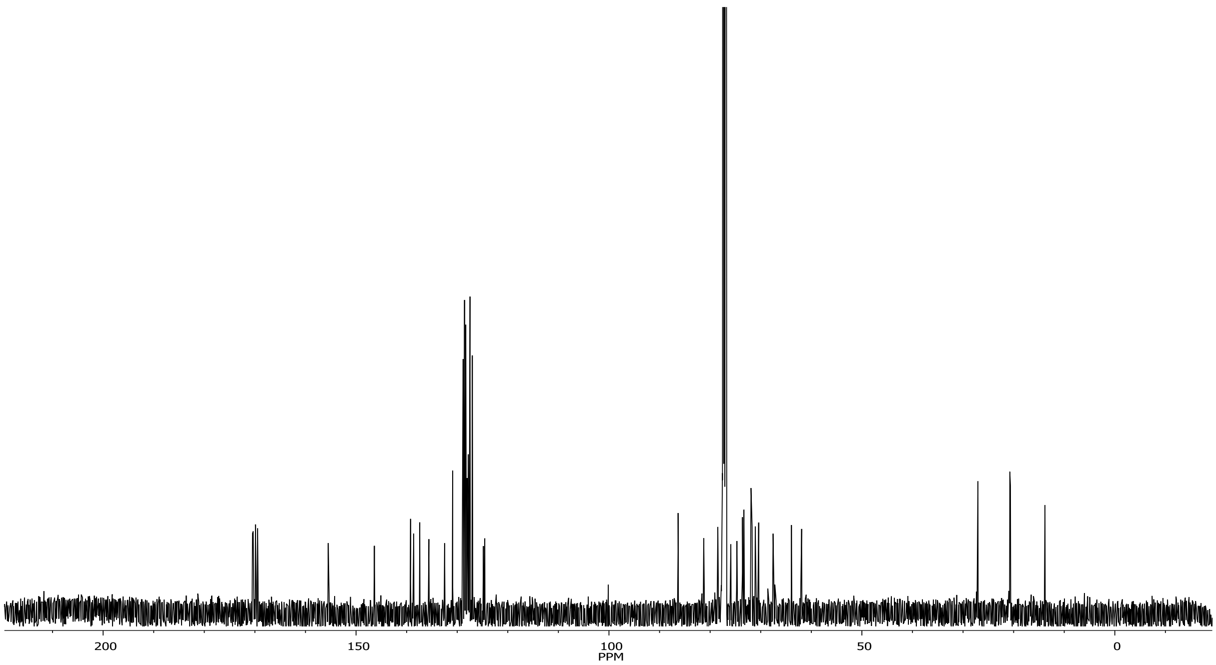
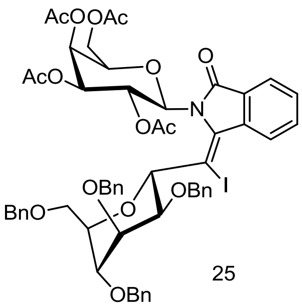


^{13}C-NMR (101 MHz, $CDCl_3$)



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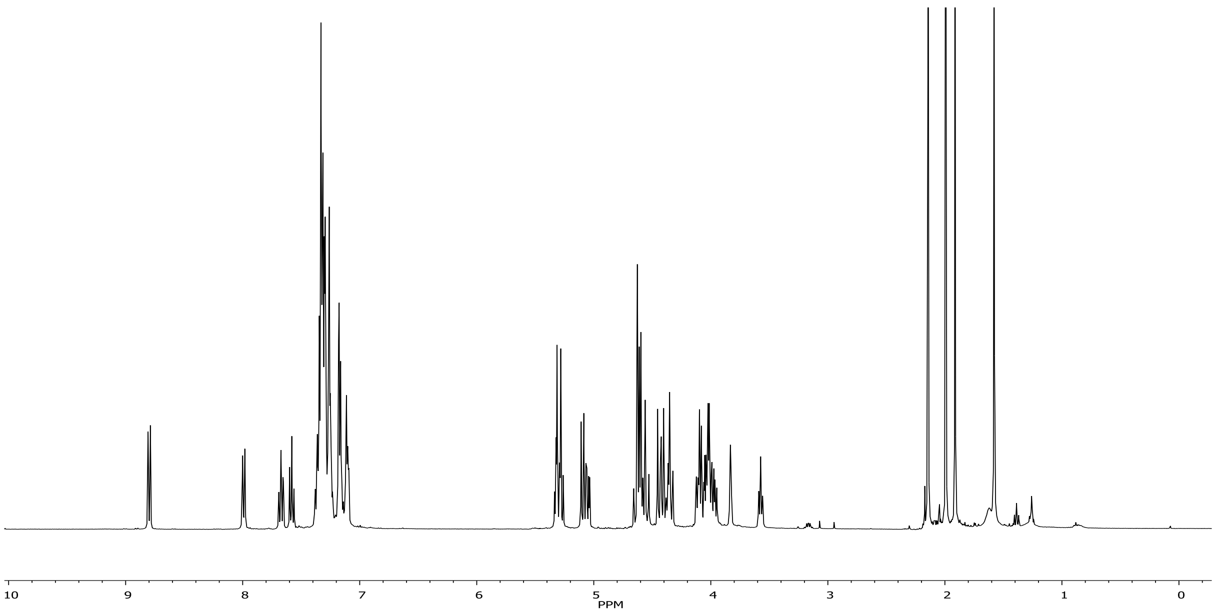
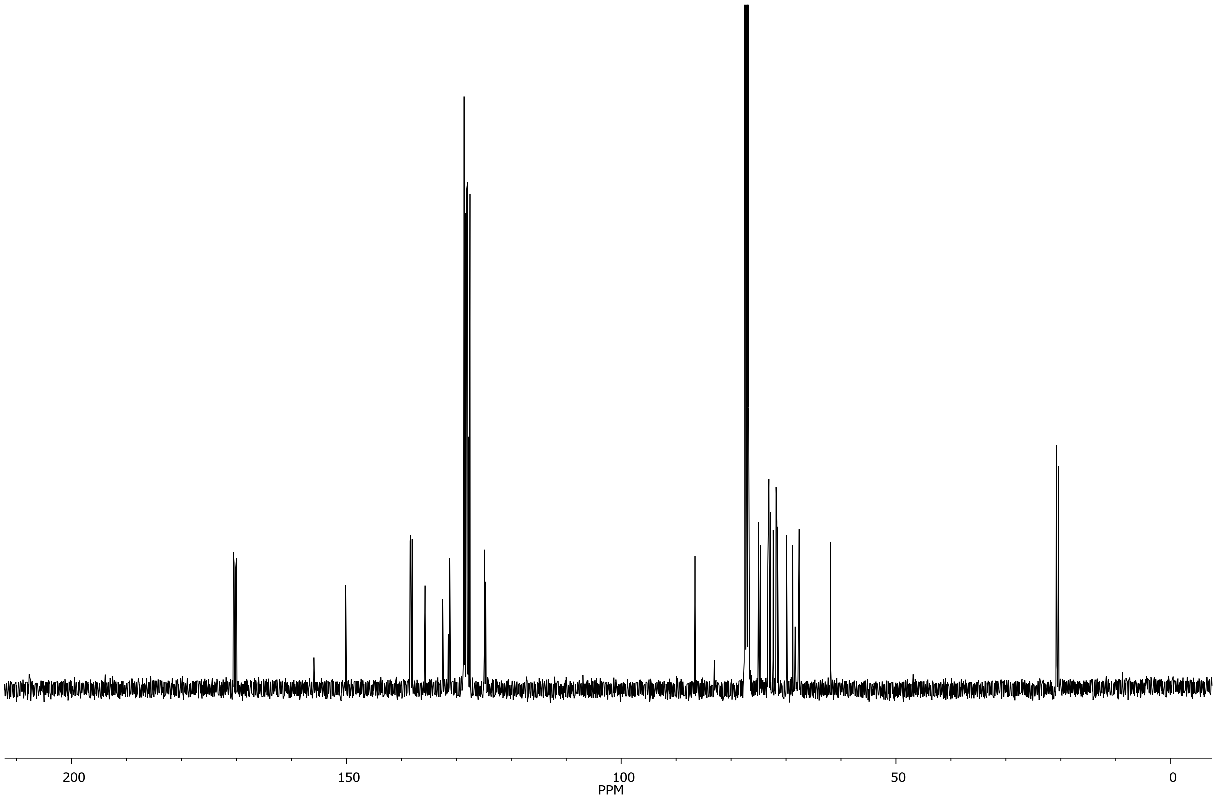
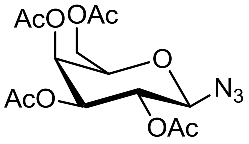


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



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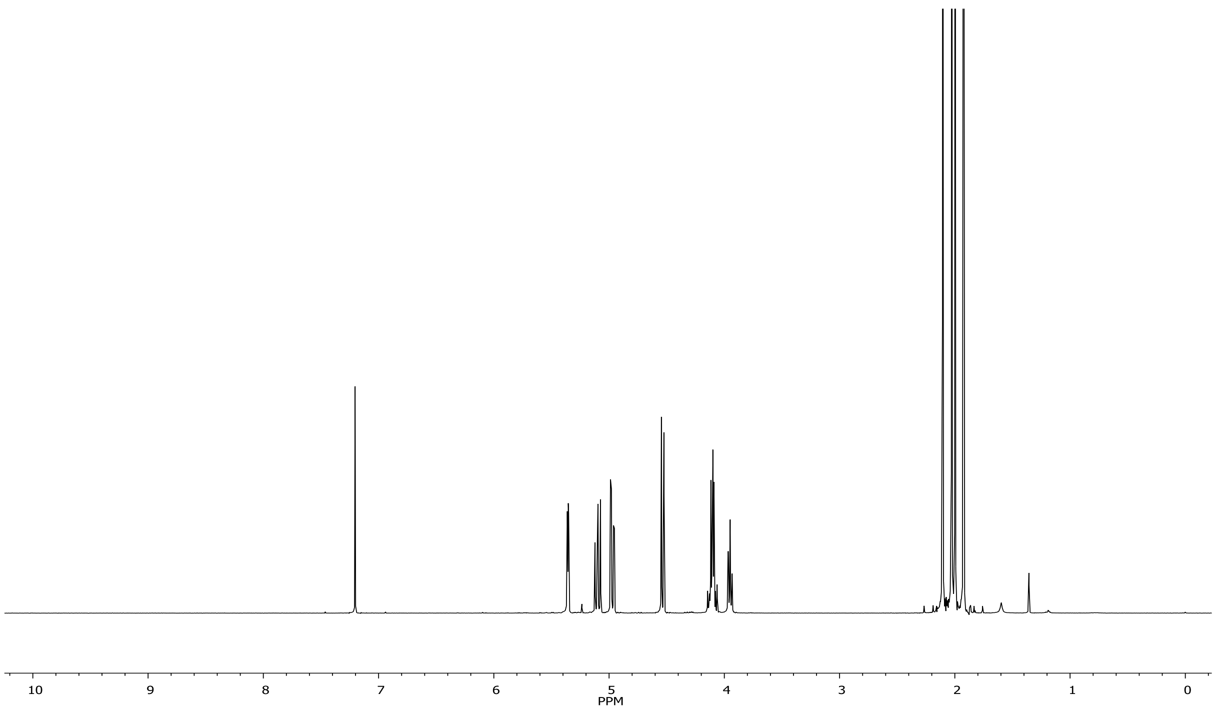

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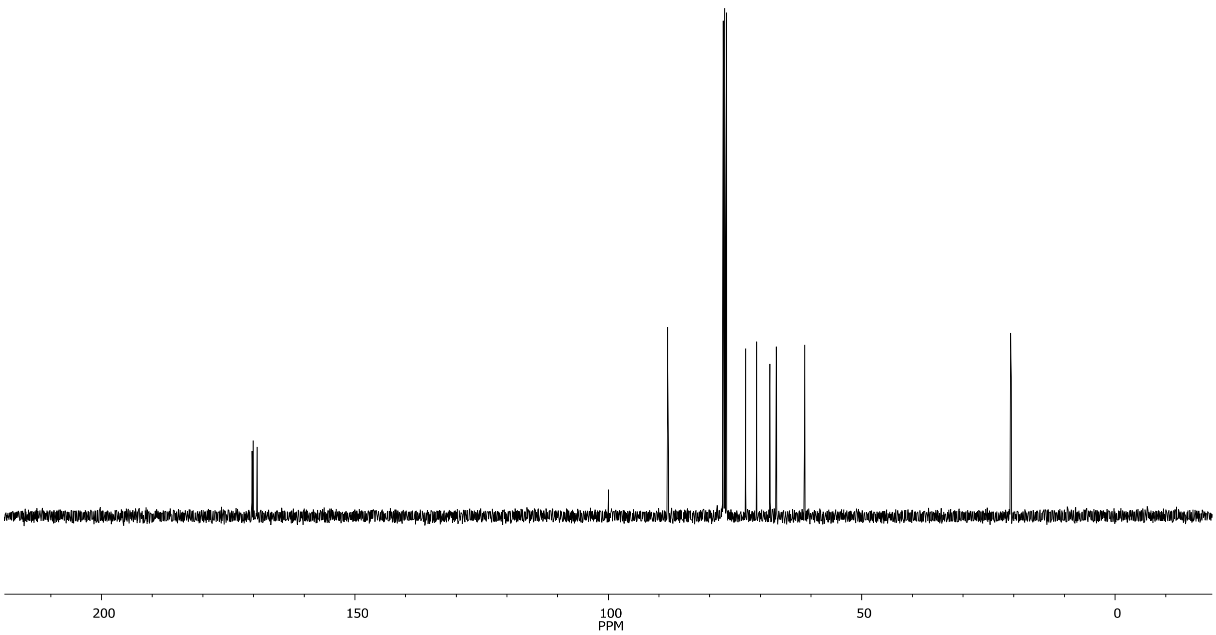

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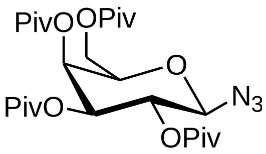

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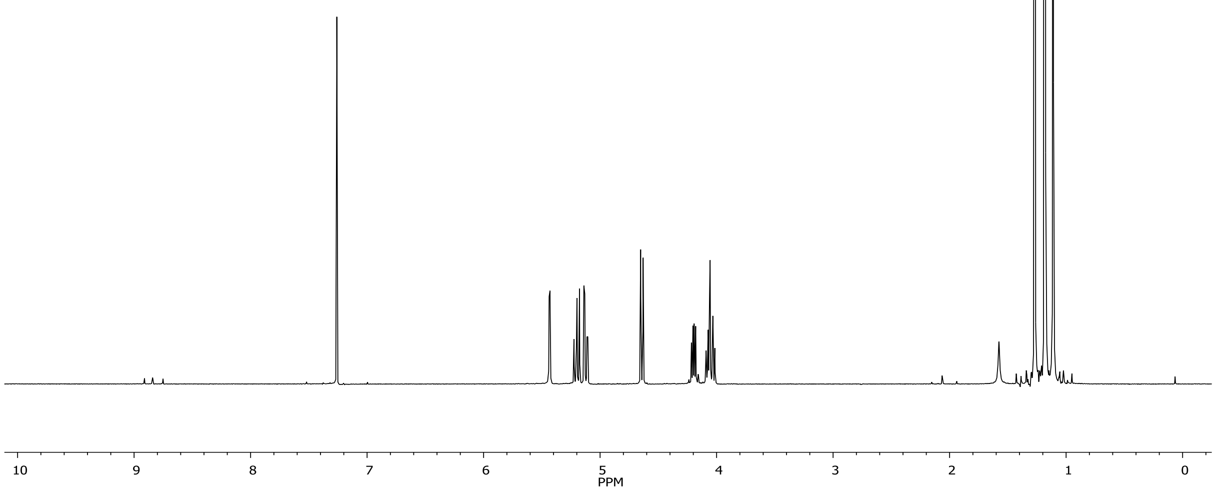

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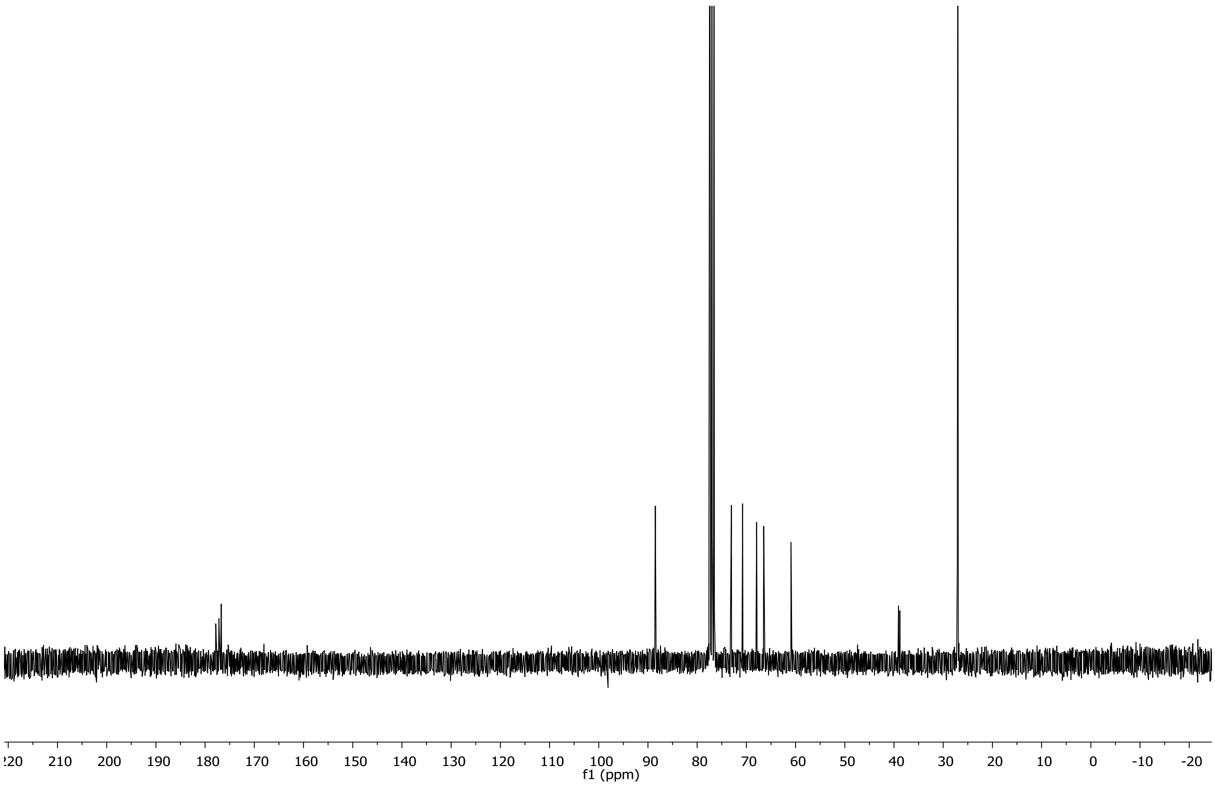

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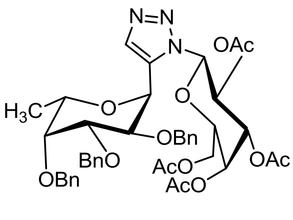

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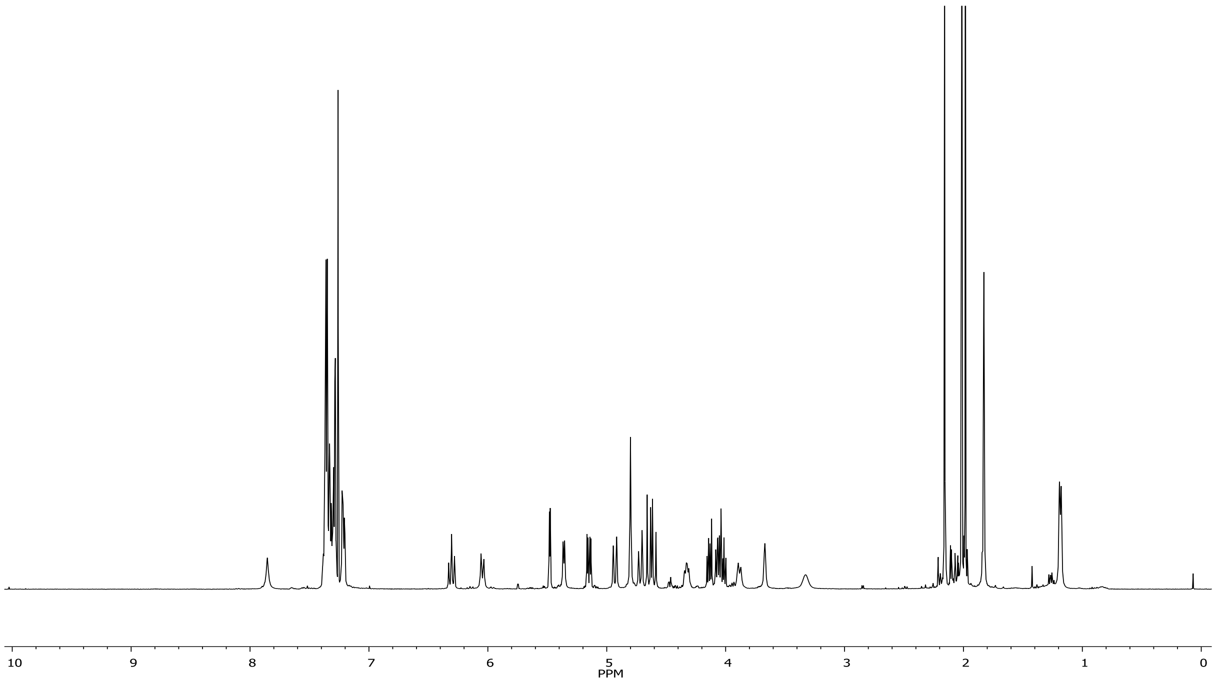

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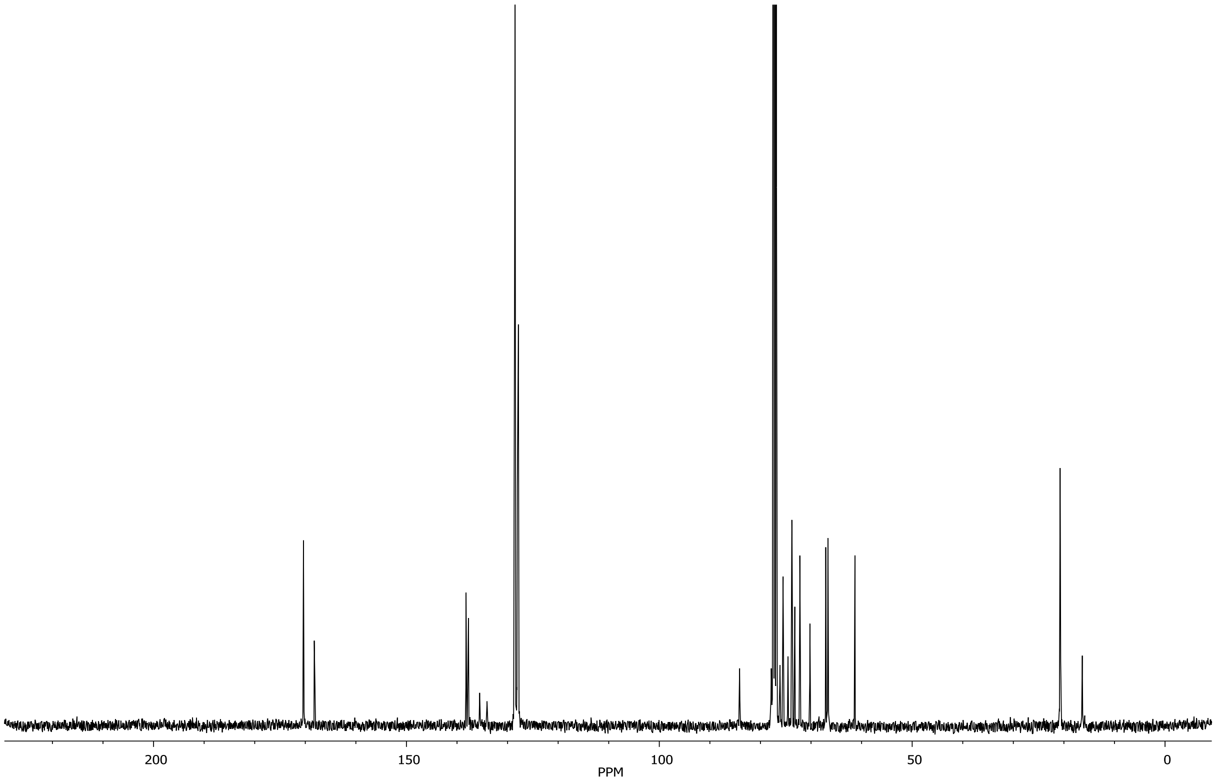
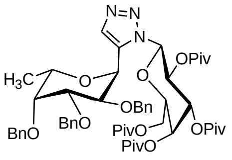


^{13}C-NMR (101 MHz, $CDCl_3$)



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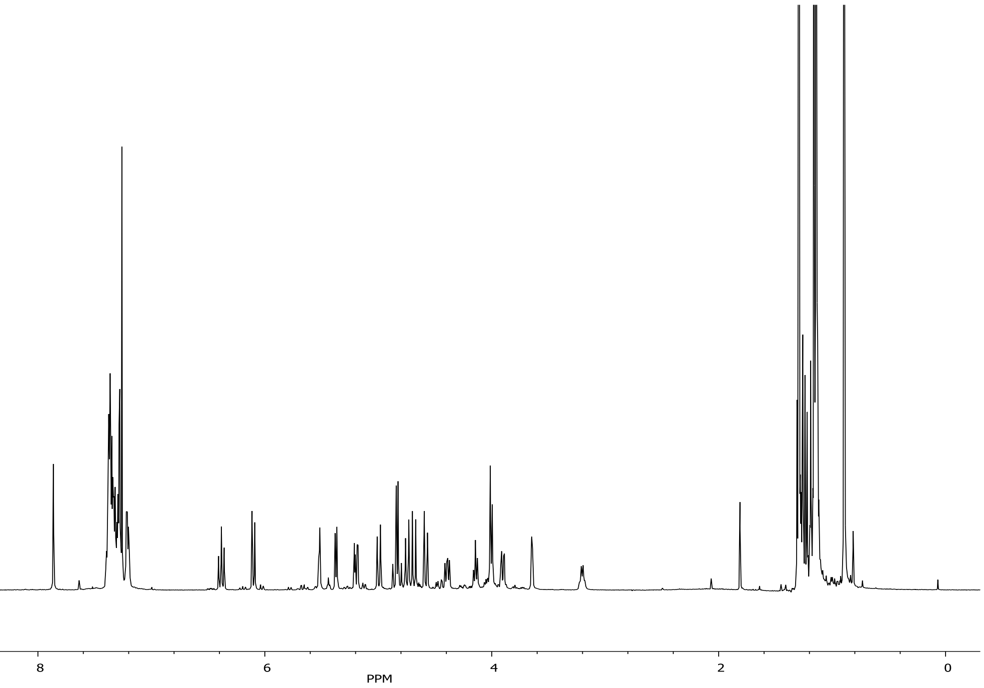
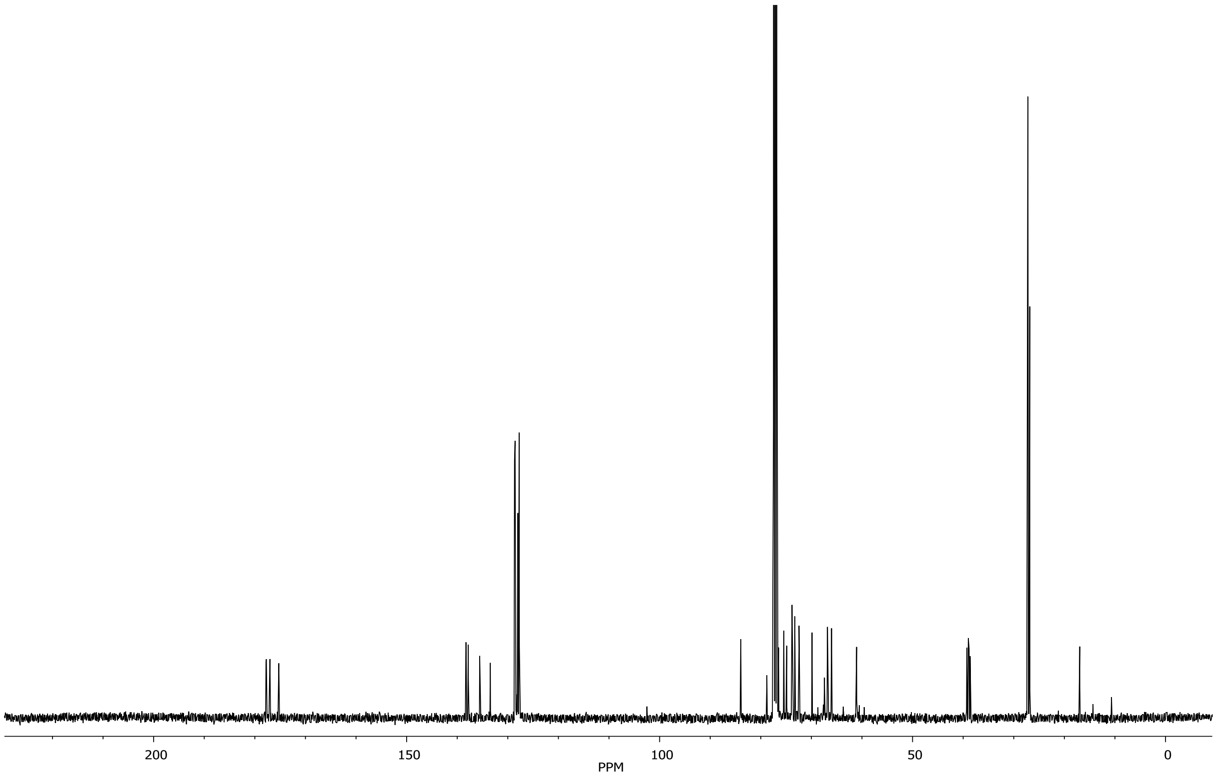
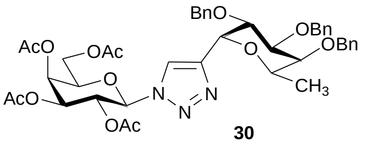


^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



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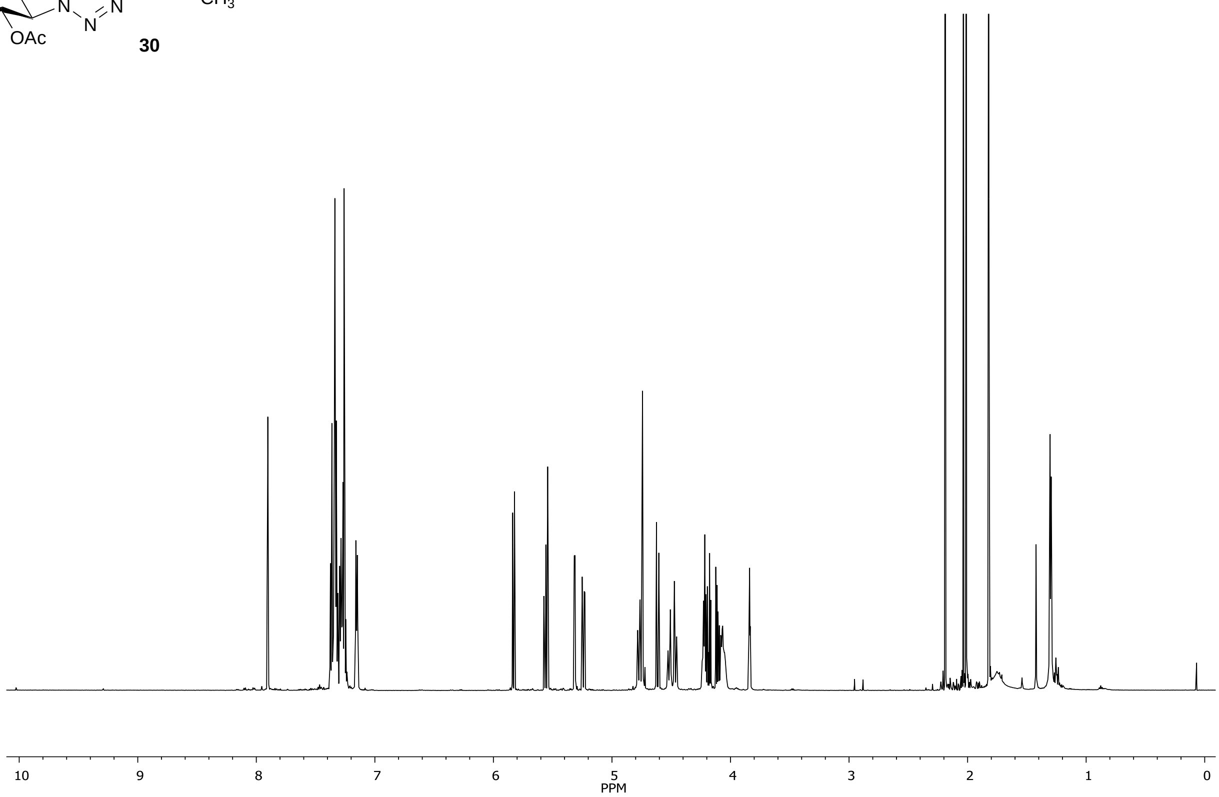
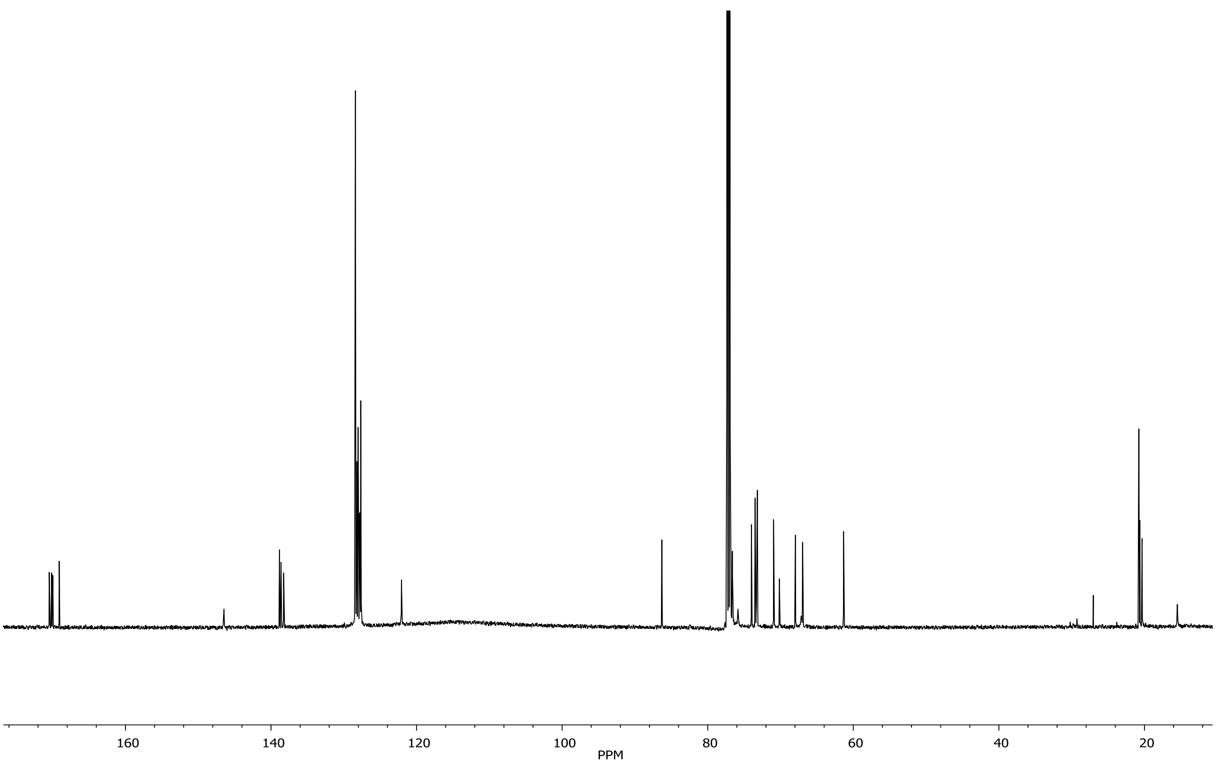


^{1}H-NMR (600 MHz, $CDCl_3$)



^{13}C-NMR (150 MHz, $CDCl_3$)

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