

Supplementary Information

**Silyl-assisted 1,2-*cis*- α -glucosylation for the synthesis of a
triglucoside moiety in high-mannose-type oligosaccharides**

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1) General Methods & Materials.....	2
2) Experimental Procedures.....	3
3) ¹H NMR & ¹³C NMR Spectra for the Key Compounds.....	15
4) References.....	25

1) General Methods & Materials

Unless otherwise indicated, all reactions were performed under a dinitrogen atmosphere in oven-dried glassware. All reagents and dry solvents were used as purchased without further purification. Column chromatography on silica gel was carried out with silica gel 60N (40-50 μm) or silica gel 60N (40-100 μm) from Kanto Chemical Co. TLC was performed on pre-coated glass plates using silica gel (Merck, 60, F254) and detected by UV light (254 nm) and/or by staining reagents such as Orcinol/ H_2SO_4 . Molecular sieves (4A) used in the reactions, were activated for 12 h *in vacuo* at 180 $^\circ\text{C}$. ^1H NMR spectra were recorded on a JEOL JNM-ECA500 (500 MHz) spectrometer using CDCl_3 (δ_{H} 7.26) or CD_3OD [δ_{H} 3.31 (central line of a quintet)] as the NMR solvents, whereby the spectra were referenced to the corresponding residual protonated solvent signals. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA500 (125 MHz) spectrometer with CDCl_3 [δ_{C} 77.2 (central line of a triplet)] or CD_3OD [δ_{C} 49.2 (central line of a septet)], whereby the spectra were referenced to the solvent signals. High-resolution mass spectra (HRMS) were obtained from a Thermo SCIENTIFIC Q-Exactive (ESI-TOF) mass spectrometer. MALDI-TOF mass spectra were obtained on a Shimadzu-KRATOS AXIMA-CFR plus mass spectrometer.

2) Experimental Procedures

3-*O*-Allyl-1,2:5,6-di-*O*-isopropiridene- α -D-glucopyranose (**7**).

A solution of **6** (1.00 kg, 3.84 mol) in DMF (1.5 L) and allyl bromide (487 mL, 5.76 mol) was added to a cold (0 °C) solution of NaH (60% in oil; 184 g, 4.60 mol) in DMF (2.34 L). After stirring the reaction mixture for 1 h at 40 °C, another portion of NaH (60% in oil; 46.0 g, 0.958 mol) was added at 0 °C. After stirring the mixture for 3 h at 40 °C, the reaction was quenched at 0 °C by adding MeOH (60 mL). The mixture was diluted with water (4 L) and extracted with EtOAc (4 x 2 L). The combined organic layers were washed with brine (2 L), dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was co-evaporated with toluene to give **7** in quantitative yield (1.15 kg). Physical data were consistent with those reported previously (Ref. 1): ¹H NMR (500 MHz, CDCl₃) δ 5.95-5.78 (m, 2H), 5.26 (dd, *J* = 1.5, 18.5 Hz, 1H), 5.16 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.51 (d, *J* = 3.0 Hz, 1H), 4.33-4.26 (m, 1H), 4.12-4.05 (m, 4H), 4.05 (dd, *J* = 3.0, 5.5 Hz, 1H), 3.92 (d, *J* = 3.0 Hz, 1H), 1.52 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H).

3-*O*-Allyl-D-glucopyranose (**8**).

Compound **7** (1.15 kg, 3.84 mol) was dissolved in H₂SO₄ (0.1 M, 2.3 L). After stirring the reaction mixture for 15 h at 60 °C, the mixture was extracted with EtOAc (1.5 L). The organic layer was neutralized with Ba(OH)₂·8H₂O, and the mixture was filtered through a pad of celite. The filtrate and the washings were concentrated *in vacuo*, and the remaining residue was co-evaporated with toluene and EtOH to give crude crystals, which were recrystallized from CH₂Cl₂/*i*Pr₂O to give **8** (757 g, 90%). Physical data were consistent with those reported previously (Ref. 2): ¹H NMR for the β -isomer (500 MHz, CD₃OD) δ 6.03-5.95 (m, 1H), 5.26 (dd, *J* = 1.5, 18.0 Hz, 1H), 5.11 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.46 (d, *J* = 6.0 Hz, 1H), 4.36-4.33 (m, 2H), 3.83 (dd, *J* = 2.5, 11.5 Hz, 1H), 3.63 (dd, *J* = 6.0, 12.0 Hz, 1H), 3.37-3.16 (m, 4H).

3-*O*-Allyl-1,2,4,6-tetra-*O*-acetyl-D-glucopyranose (**9**).

DMAP (84.1 g, 0.6888 mol) and Ac₂O (1.95 L, 20.6 mol) were added to a cold (0 °C) solution of **8** (757 g, 3.44 mol) in THF (3.78 L). After the reaction mixture was stirred for 20 min at room temperature, the reaction was quenched at 0 °C by adding MeOH

(64 mL). The mixture was concentrated *in vacuo*, before the obtained residue was dissolved in EtOAc (500 mL) and washed with saturated aq. NaHCO₃ (250 mL) and brine (250 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residual crude crystals were recrystallized from CH₂Cl₂/*i*Pr₂O to give **9** (999 g, 75%). Physical data were consistent with those reported previously (Ref. 3): ¹H NMR for the β-isomer (500 MHz, CDCl₃) δ 5.82-5.73 (m, 1H), 5.65 (d, *J* = 9.0 Hz, 1H), 5.24-5.08 (m, 4H), 4.25-4.14 (m, 2H), 4.12-4.08 (m, 2H), 3.75-3.71 (m, 1H), 3.65 (t, *J* = 9.5 Hz, 1H), 2.10 (s, 3H × 4).

4-Methoxyphenyl 3-*O*-allyl-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (10).

Et₃N (179 mL, 1.28 mol) and BF₃·Et₂O (651 mL, 5.14 mol) were added to a cold (0 °C) solution of **9** (999 g, 2.57 mol) and 4-methoxyphenol (479 g, 3.86 mol) in CH₂Cl₂ (4.99 L). After stirring the reaction mixture for 18 h at room temperature, the mixture was washed with saturated aq. NaHCO₃ (2.5 L) and brine (2.5 L). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the residual crude crystals were washed with *i*Pr₂O to give **10** (693 g, 60%). Physical data were consistent with those reported previously (Ref. 4): ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.20 (m, 4H), 5.82-5.74 (m, 1H), 5.26-5.11 (m, 4H), 4.86 (d, *J* = 8.2 Hz, 1H), 4.25-4.14 (m, 2H), 4.13-4.05 (m, 2H), 3.77 (s, 3H), 3.73-3.64 (m, 2H), 2.10 (s, 3H × 3).

4-Methoxyphenyl 3-*O*-allyl-β-D-glucopyranoside (11).

NaOMe (28% in MeOH; 29.5 mL, 0.153 mol) was added to a cold (0 °C) solution of **10** (693 g, 1.53 mol) in THF (1.17 L) and MeOH (2.30 L). After stirring the reaction mixture for 3.5 h at room temperature, a second portion of NaOMe (28% in MeOH; 15.0 mL, 0.0777 mol) was added at 0 °C. After stirring the reaction mixture for 2.5 h at room temperature, a third portion of NaOMe (28% in MeOH; 15.0 mL, 0.0777 mol) was added at 0 °C. After stirring the reaction mixture for 0.2 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0 °C. The mixture was filtered and concentrated *in vacuo*, before the obtained residual crude crystals were recrystallized from MeOH/*i*Pr₂O to give **11** (463 g, 93%): ¹H NMR (500 MHz, CD₃OD) δ 7.35-7.18 (m, 4H), 6.04-5.95 (m, 1H), 5.30-5.09 (m, 2H), 4.73 (d, *J* = 8.0 Hz, 1H), 4.41-4.31 (m, 2H), 3.87-3.64 (m, 5H), 3.49-3.27 (m, 4H); ¹³C NMR (125 MHz, CD₃OD) δ 155.30, 151.89, 135.67, 117.89, 115.45, 114.13, 102.12, 84.45, 76.62, 73.84, 73.69,

69.75, 61.15, 54.72; HRMS calcd for C₁₆H₂₂O₇Na [M+Na]⁺ *m/z* 349.1263, found 349.1242

4-Methoxyphenyl 3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranoside (12).

TsOH (28.9 g, 0.284 mol) was added to a solution of **11** (463 g, 1.42 mol) and PhCH(OMe)₂ (257 mL, 1.71 mol) in CH₃CN/THF (1:1, v/v, 2.3 L). The reaction mixture was stirred for 24 h at 50 °C, whereby the solvents were evaporated and replaced with CH₃CN/THF (1:1, v/v, 2.3 L) every 6 h to remove the resulting MeOH. The reaction mixture was neutralized with Et₃N at room temperature and concentrated *in vacuo*. The residual crude crystals were recrystallized from CH₂Cl₂/*i*Pr₂O to give **12** (399 g, 68%). Physical data were consistent with those reported previously (Ref. 4): ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.23 (m, 5H), 6.88-6.77 (m, 4H), 6.02-5.93 (m, 1H), 5.58 (s, 1H), 5.35-5.20 (m, 2H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.49-4.28 (m, 3H), 3.64-3.58 (m, 7H), 3.55-3.49 (m, 1H).

4-Methoxyphenyl 2-*O*-acetyl-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranoside (5).

DMAP (11.7 g, 95.8 mmol) and Ac₂O (136 mL, 1.44 mol) were added to a cold (0 °C) solution of **12** (399 g, 0.963 mol) in THF (4 L). After stirring the reaction mixture for 30 min at room temperature, the reaction was quenched with MeOH (100 mL). The mixture was concentrated *in vacuo*, before the residual crude crystals were washed with water to give **5** (379 g, 87%). Physical data were consistent with those reported previously (Ref. 5). This compound is also commercially available from Tokyo Chemical Industry Co., Ltd. (M2065): ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.25 (m, 5H), 6.89-6.78 (m, 4H), 5.90-5.80 (m, 1H), 5.58 (s, 1H), 5.34-5.14 (m, 3H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.40-4.12 (m, 3H), 3.56-3.50 (m, 7H), 2.12 (s, 3H).

3-*O*-Allyl-4,6-*O*-benzylidene-D-glucopyranose (13).

Ceric ammonium nitrate (CAN) (39.4 mg, 0.0720 mmol) was added to a cold (0 °C) solution of **12** (20 mg, 0.048 mmol) in toluene/CH₃CN/H₂O (2:2:1, v/v, 18.0 mL). After stirring the reaction mixture for 2 h at 0 °C, another portion of CAN (26 mg, 0.048 mmol) was added at 0 °C. After stirring the reaction mixture for 1.5 h at 0 °C, the mixture was diluted with EtOAc (25 mL) and washed with saturated aq. NaHCO₃ (25 mL) and brine (25 mL). The organic layer was dried over Na₂SO₄, filtered, and

concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:3, v/v) to give **13** (13.3 mg, 90%): ¹H NMR (500 MHz, CDCl₃) δ 7.46-7.34 (m, 5H), 5.96-5.90 (m, 1H), 5.53 (s, 1H), 5.31-5.26 (m, 2H), 5.18 (dd, *J* = 1.0, 1.5 Hz, 1H), 4.45 (dd, *J* = 5.5, 11.0 Hz, 1H), 4.28-4.20 (m, 2H), 4.06 (ddd, *J* = 5.0, 5.0, 10.0 Hz, 1H), 3.77 (t, *J* = 10.0 Hz, 1H), 3.73-3.62 (m, 2H), 3.57 (t, *J* = 9.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.21, 155.67, 150.98, 136.73, 128.37, 126.25, 118.54, 114.56, 100.81, 80.62, 73.92, 72.26, 68.51, 66.26, 55.63, 20.90; HRMS calcd for C₁₆H₂₀O₆Na [*M*+Na]⁺ *m/z* 331.1158, found 331.1150.

Phenyl 3-*O*-allyl-4,6-*O*-benzylidene-1-deoxy-1-thio-β-D-glucopyranoside (14).

Et₃N (223 μL, 1.60 mmol), PhSH (81.0 μL, 0.800 mmol), and 2-chloro-1,3-dimethyl-2-imidazolium chloride (DMC; 81.1 mg, 0.480 mmol) were added to a cold (0 °C) solution of **13** (50.0 mg, 0.160 mmol) in CH₃CN/H₂O (1:1, v/v, 1.0 mL). After stirring the reaction mixture for 20 min at room temperature, the mixture was diluted with EtOAc (10 mL) and washed with saturated aq. NaHCO₃ (10 mL) and brine (10 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:8, v/v) to give **14** (61.3 mg, 96%): ¹H NMR (500 MHz, CDCl₃) δ 7.44-7.23 (m, 10H), 5.97-5.88 (m, 1H), 5.56 (s, 1H), 5.29 (dd, *J* = 1.5, 17.0 Hz, 1H), 5.17 (dd, *J* = 1.5, 10.0 Hz, 1H), 4.64 (d, *J* = 9.5 Hz, 1H), 4.47-4.35 (m, 2H), 4.28-4.21 (m, 1H), 3.78 (t, *J* = 10.0 Hz, 1H), 3.66-3.53 (m, 2H), 3.51-3.45 (m, 2H), 2.55 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 137.26, 134.81, 133.31, 131.37, 129.16, 129.11, 128.50, 128.36, 126.07, 117.72, 101.31, 88.55, 81.44, 81.20, 73.87, 72.19, 70.81, 68.69; HRMS calcd for C₂₂H₂₄O₅SNa [*M*+Na]⁺ *m/z* 423.1242, found 423.1242.

Phenyl

3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-benzyl-1-deoxy-1-thio-β-D-glucopyranoside (3a).

NaH (60% in oil; 53.9 mg, 1.23 mmol) was added to a cold (0 °C) solution of **14** (247 mg, 0.617 mmol) in DMF (5.0 mL). After stirring the reaction mixture for 10 min at room temperature, BnBr (112 μL, 0.926 mmol) was added at 0 °C. After stirring the mixture for 18 h at room temperature, the reaction was quenched with MeOH (10 mL) at 0 °C. The mixture was concentrated *in vacuo*, before the residue was diluted with EtOAc (200 mL) and washed with saturated aq. NaHCO₃ (200 mL) and brine (200 mL).

The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:15, v/v) to give **3a** (286 mg, 95%): ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.25 (m, 15H), 5.86-5.80 (m, 1H), 5.44 (s, 1H), 5.18 (dd, *J* = 2.0, 17.5 Hz, 1H), 5.06 (dd, *J* = 2.0, 10.0 Hz, 1H), 4.76, 4.71 (ABq, *J* = 12.6 Hz, 2H), 4.63 (d, *J* = 9.5 Hz, 1H), 4.29 (dd, *J* = 5.5, 17.5 Hz, 1H), 4.26 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.14 (dd, *J* = 5.5, 11.5 Hz, 1H), 3.68 (t, *J* = 9.5 Hz, 1H), 3.60 (t, *J* = 9.5 Hz, 1H), 3.52 (t, *J* = 9.5 Hz, 1H), 3.37-3.34 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 138.12, 137.36, 135.04, 133.24, 132.44, 129.13, 129.07, 128.52, 128.43, 128.35, 128.03, 127.96, 126.09, 117.23, 101.22, 88.38, 82.81, 81.40, 80.52, 76.08, 74.26, 70.34, 68.78; HRMS calcd for C₂₉H₃₀O₅SNa [*M*+Na]⁺ *m/z* 513.1712, found 513.1718.

Phenyl

3-*O*-allyl-4,6-*O*-benzylidene-1-deoxy-1-thio-2-*O*-triethylsilyl-β-D-glucopyranoside (3b).

Imidazole (34.3 mg, 0.504 mmol) and TES-Cl (71.2 μL, 0.420 mmol) were added to a cold (0 °C) solution of **14** (34.0 mg, 0.084 mmol) in DMF (2.0 mL). After stirring the reaction mixture for 1 h at room temperature, the mixture was diluted with EtOAc (50 mL) and washed with saturated aq. NaHCO₃ (50 mL) and brine (50 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:12, v/v) to give **3b** (41.6 mg, 96%): ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.25 (m, 10H), 5.99-5.92 (m, 1H), 5.55 (s, 1H), 5.26 (dd, *J* = 2.0, 17.0 Hz, 1H), 5.15 (dd, *J* = 2.0, 10.0 Hz, 1H), 4.69 (d, *J* = 9.5 Hz, 1H), 4.48 (dd, *J* = 6.0, 12.0 Hz, 1H), 4.34 (dd, *J* = 5.5, 11.0 Hz, 1H), 4.18 (dd, *J* = 6.5, 13.0 Hz, 1H), 3.78 (t, *J* = 10.0 Hz, 1H), 3.69-3.63 (m, 2H), 3.52-3.43 (m, 2H), 1.00 (s, 3H × 3), 0.75 (dd, *J* = 8.0, 16.0 Hz, 2H × 3); ¹³C NMR (125 MHz, CDCl₃) δ 137.42, 135.04, 134.35, 131.43, 129.02, 128.32, 127.48, 126.03, 116.87, 101.15, 90.51, 82.96, 81.92, 74.04, 73.87, 70.04, 68.82, 7.10, 5.41; HRMS calcd for C₂₈H₃₈O₅SSiNa [*M*+Na]⁺ *m/z* 537.2107, found 537.2104.

Phenyl

3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1-thio-β-D-glucopyranoside (3c).

Imidazole (98.0 mg, 1.44 mmol) and TBS-Cl (163 mg, 1.08 mmol) were added to a cold (0 °C) solution of **14** (146 mg, 0.364 mmol) in DMF (2.0 mL). After stirring the reaction mixture for 15 h at 50 °C, imidazole (38.0 mg, 0.558 mmol) and TBS-Cl (112 mg, 0.743 mmol) were added at 0 °C. After stirring the mixture for 9 h at 50 °C, the mixture was diluted with EtOAc (50 mL) and washed with saturated aq. NaHCO₃ (50 mL) and 0.1 M HCl (50 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the resulting residue was purified by column chromatography on silica gel (toluene/hexane, 1:1, v/v) to give **3c** (185 mg, 99%): ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.13 (m, 10H), 6.01-5.93 (m, 1H), 5.56 (s, 1H), 5.25-5.15 (m, 2H), 4.70 (d, *J* = 9.5 Hz, 1H), 4.52-4.46 (dd, *J* = 6.0, 12.0 Hz, 1H), 4.35 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.20 (dd, *J* = 6.0, 12.0 Hz, 1H), 3.68 (t, *J* = 10.0 Hz, 1H), 3.64 (dd, *J* = 2.0, 10.0 Hz, 1H), 3.54 (t, *J* = 10.0 Hz, 1H), 3.52 (dd, *J* = 1.5, 10.0 Hz, 1H), 3.48-3.43 (m, 1H), 0.97 (s, 3H × 3), 0.16 (s, 3H), 0.13 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.30, 134.82, 134.23, 131.34, 128.89, 128.20, 127.36, 125.89, 117.10, 101.04, 90.30, 82.59, 81.90, 73.74, 73.06, 68.69, 26.12, 18.32, -3.61, -4.29; HRMS calcd for C₂₈H₃₈O₅SSiNa [*M*+Na]⁺ *m/z* 537.2107, found 537.2113.

Phenyl

3-*O*-allyl-4,6-*O*-benzylidene-1-deoxy-1-thio-2-*O*-triisopropylsilyl-β-D-glucopyranoside (3d).

TIPS-OTf (134 μL, 0.500 mmol) was added to a solution of **14** (20.0 mg, 0.0500 mmol) in 2,6-lutidine (2.0 mL). After stirring the reaction mixture for 2 h at 90 °C, TIPS-OTf (67.0 μL, 0.250 mmol) was added at room temperature. After stirring the mixture for 30 min at 90 °C, the reaction was diluted with EtOAc (50 mL) and washed with saturated aq. NaHCO₃ (50 mL) and brine (50 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the resulting residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:12, v/v) to give **3d** (27.7 mg, 100%): ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.25 (m, 10H), 5.97-5.89 (m, 1H), 5.53 (s, 1H), 5.20 (dd, *J* = 2.0, 17.0 Hz, 1H), 5.12 (dd, *J* = 2.0, 10.0 Hz, 1H), 4.72 (d, *J* = 9.0 Hz, 1H), 4.53 (dd, *J* = 6.0, 12.0 Hz, 1H), 4.48 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.10 (dd, *J* = 6.0, 12.0 Hz, 1H), 3.83-3.71 (m, 3H), 3.53-3.47 (m, 2H), 1.14-1.10 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 137.42, 135.09, 134.62, 131.29, 129.02, 128.35, 127.46, 126.05, 116.49, 101.18, 90.75, 83.36, 82.21, 74.13, 73.76, 69.64, 68.89, 18.52, 13.67; HRMS calcd for

$C_{31}H_{44}O_5SSiNa$ [$M+Na$]⁺ m/z 579.2576, found 579.2576.

4-Methoxyphenyl 2-O-acetyl-4,6-O-benzylidene- β -D-glucopyranoside (4).

[Ir(COD)(PMePh₂)₂][PF₆] (3.8 mg, 0.0044 mmol) was dissolved in degassed THF (1 mL) and stirred under a dihydrogen atmosphere for 15 min, before being stirred under a dinitrogen atmosphere for 1 min. A solution of **5** (200 mg, 0.438 mmol) in THF (3 mL) was added at 0 °C, and stirring under dinitrogen was continued for 2 h at room temperature. Then, water (2 mL), NaHCO₃ (1.40 g, 17.6 mmol), and iodine (223 mg, 0.880 mmol) were added at 0 °C. After stirring for 20 min at room temperature, the mixture was diluted with EtOAc (50 mL) and washed with saturated aqueous Na₂S₂O₃·5H₂O (50 mL) and brine (25 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the residue was purified by chromatography on silica gel (EtOAc/hexane, 1:4, v/v) to give **4** (183 mg, 100%): ¹H NMR (500 MHz, CDCl₃) δ 7.51-7.36 (m, 5H), 6.95-6.80 (m, 4H), 5.57 (s, 1H) 5.18 (dd, $J = 8.5, 9.5$ Hz, 1H), 4.98 (d, $J = 8.0$ Hz, 1H), 4.38 (dd, $J = 3.0, 10.0$ Hz, 1H), 3.95 (dd, $J = 3.5, 10.0$ Hz, 1H), 3.84 (t, $J = 9.5$ Hz, 1H), 3.78 (s, 3H), 3.68 (t, $J = 9.5$ Hz, 1H), 3.58-3.54 (m, 1H), 2.80 (d, $J = 3.5$ Hz, 1H), 2.16 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.22, 155.67, 150.99, 136.74, 129.38, 128.37, 126.26, 118.55, 114.56, 101.94, 100.82, 80.63, 73.92, 72.26, 68.51, 66.26, 55.63, 20.91; HRMS calcd for C₂₂H₂₄O₈Na [$M+Na$]⁺ m/z 439.1369, found 439.1369.

General procedure for the glycosylation of glycosyl donor **3 with glycosyl acceptor **4**.**

This reaction was carried out under an argon atmosphere. Glycosyl donor **3** (0.15 mmol), glycosyl acceptor **4** (0.10 mmol), and MS4A (1.0 g) were dissolved in 2.0 mL of the corresponding solvent (CH₂Cl₂, toluene, Et₂O, or CH₃CN). The mixture was stirred for 15 min at room temperature before MeOTf (0.40 mmol) was added at -40 °C. The reaction mixture was stirred at 0 °C (**3b-d**) or 10 °C (**3a**) for 32 h, before the reaction was quenched with Et₃N (0.40 mmol) at -10 °C. The mixture was filtered through a pad of celite, and the filtrate and washings were concentrated *in vacuo*. The residue was diluted with EtOAc (50 mL) and washed with saturated aq. NaHCO₃ (50 mL) and brine (50 mL), before the organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (for **5a**:

EtOAc/toluene, 1:20→1:10, v/v; for **5c**: EtOAc/hexane, 1:5, v/v; for **5d**: EtOAc/hexane, 1:12, v/v) to give disaccharide **15**.

4-Methoxyphenyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-benzyl- α -D-glucopyranosyl)-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene- β -D-glucopyranoside (15a**).**

¹H NMR for the α -isomer (500 MHz, CDCl₃) δ 7.45-7.36 (m, 15H), 6.96-6.81 (m, 4H), 6.00-5.88 (m, 1H), 5.49 (s, 1H), 5.47 (s, 1H), 5.47 (d, $J = 2.3$ Hz, 1H), 5.40 (dd, $J = 8.0, 9.7$ Hz, 1H), 5.28 (dd, $J = 1.8, 17.2$ Hz, 1H), 5.13 (dd, $J = 1.8, 10.4$ Hz, 1H), 4.98 (d, $J = 8.0$ Hz, 1H), 4.59, 4.47 (ABq, $J = 12.6$ Hz, 2H), 4.40-4.18 (m, 5H), 3.96 (t, $J = 9.5$ Hz, 1H), 3.89-3.81 (m, 3H), 3.78 (s, 3H), 3.70 (t, $J = 10.3$ Hz, 1H), 3.64-3.56 (m, 1H), 3.48 (t, $J = 9.5$ Hz, 1H), 3.41 (dd, $J = 3.8, 9.5$ Hz, 1H), 2.19 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.37, 155.83, 151.20, 137.95, 137.45, 136.88, 135.19, 129.57, 129.03, 128.29, 127.17, 126.16, 118.74, 116.84, 114.67, 102.15, 101.66, 101.61, 97.27, 81.77, 77.89, 74.04, 74.02, 71.84, 68.94, 68.81, 66.33, 62.83, 55.74, 31.68, 29.79, 22.74, 21.02, 14.22; MALDI-TOF MS calcd for C₄₅H₄₈O₁₃Na [$M+Na$]⁺ m/z 819.30, found 819.21.

4-Methoxyphenyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranosyl)-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene- β -D-glucopyranoside (15c**).**

¹H NMR for the α -isomer (500 MHz, CDCl₃) δ 7.54-7.31 (m, 10H), 6.90-6.78 (m, 4H), 5.90-5.84 (m, 1H), 5.47 (s, 1H), 5.46 (s, 1H), 5.33 (dd, $J = 8.0, 9.0$ Hz, 1H), 5.29 (d, $J = 3.5$ Hz, 1H), 5.19 (dd, $J = 1.5, 18.0$ Hz, 1H), 5.08 (dd, $J = 1.5, 9.0$ Hz, 1H), 4.98 (d, $J = 8.0$ Hz, 1H), 4.33 (dd, $J = 4.5, 9.0$ Hz, 1H), 4.28-4.24 (m, 2H), 4.20 (t, $J = 9.0$ Hz, 1H), 4.15 (dd, $J = 5.5, 12.0$ Hz, 1H), 3.90-3.80 (m, 3H), 3.74 (s, 3H), 3.70 (t, $J = 10.5$ Hz, 1H), 3.61-3.53 (m, 3H), 3.47 (t, $J = 9.5$ Hz, 1H), 2.14 (s, 3H), 0.79 (s, 3H × 3), -0.06 (s, 3H), -0.22 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.34, 155.81, 151.19, 137.60, 136.78, 135.20, 129.50, 128.94, 128.34, 128.28, 128.22, 126.49, 126.04, 118.78, 117.04, 114.66, 102.04, 101.51, 98.80, 82.19, 81.96, 77.60, 74.42, 73.56, 72.00, 69.11, 68.89, 66.29, 62.77, 60.49, 55.74, 25.74, 21.15, 18.13, -4.60, -5.27; HRMS calcd for C₄₄H₅₆O₁₃SiNa [$M+Na$]⁺ m/z 843.3380, found 843.3385.

4-Methoxyphenyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-triisopropylsilyl- α -D-glucopyranosyl)-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene- β -D-glucopyranoside (15d**).**

¹H NMR for the α -isomer (500 MHz, CDCl₃) δ 7.45-7.25 (m, 10H), 6.90-6.80 (m, 4H),

5.90-5.87 (m, 1H), 5.51 (s, 1H), 5.46 (s, 1H), 5.42 (d, $J = 3.5$ Hz, 1H), 5.34 (dd, $J = 8.0, 9.0$ Hz, 1H), 5.21 (dd, $J = 1.5, 18.0$ Hz, 1H), 5.09 (dd, $J = 1.5, 9.0$ Hz, 1H), 4.98 (d, $J = 8.0$ Hz, 1H), 4.36-4.27 (m, 3H), 4.24 (t, $J = 9.0$ Hz, 1H), 4.17 (dd, $J = 6.0, 12.0$ Hz, 1H), 3.95-3.82 (m, 3H), 3.78-3.70 (m, 5H), 3.61-3.53 (m, 2H), 3.50 (t, $J = 9.5$ Hz, 1H), 2.14 (s, 3H), 1.11-0.79 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.34, 155.80, 151.73, 137.60, 136.77, 135.29, 129.38, 128.93, 128.75, 126.30, 118.80, 116.79, 114.67, 101.91, 101.49, 98.60, 82.57, 81.86, 77.72, 74.25, 73.41, 71.95, 69.18, 69.16, 68.72, 66.23, 62.62, 55.74, 25.82, 21.15, 18.13, 12.84; HRMS calcd for $\text{C}_{47}\text{H}_{62}\text{O}_{13}\text{SiNa}$ [$M+\text{Na}$] $^+$ m/z 885.3857, found 885.3852.

4-Methoxyphenyl(3-*O*-allyl-4,6-*O*-benzylidene- α -D-glucopyranosyl)-(1 \rightarrow 3)-2-*O*-acetyl-4,6-*O*-benzylidene- β -D-glucopyranoside (2).

TBAF (3.00 mL, 3.09 mmol) was added to a cold (0 °C) solution of **15c** (423 mg, 0.515 mmol) in THF/AcOH (5:1, v/v, 6 mL). After stirring the reaction mixture for 3 days at room temperature, the mixture was diluted with EtOAc (200 mL) and washed with saturated aq. NaHCO_3 (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4 , filtered, and concentrated *in vacuo*, before the resulting residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:2, v/v) to give **2** (318 mg, 87%): ^1H NMR (500 MHz, CDCl_3) δ 7.50-7.34 (m, 10H), 6.97-6.82 (m, 4H), 5.93-5.80 (m, 1H), 5.60 (s, 1H), 5.51 (s, 1H), 5.34 (dd, $J = 8.0, 9.5$ Hz, 1H), 5.28-5.10 (m, 3H), 4.96 (d, $J = 8.0$ Hz, 1H), 4.41 (dd, $J = 5.5, 10.5$ Hz, 1H), 4.36-4.33 (m, 1H), 4.27 (dd, $J = 5.0, 10.5$ Hz, 1H), 4.29-4.21 (m, 1H), 4.07 (t, $J = 10.0$ Hz, 1H), 3.90 (t, $J = 7.0$ Hz, 1H), 3.87 (t, $J = 6.5$ Hz, 1H), 3.84 (dd, $J = 5.5, 10.5$ Hz, 1H), 3.77 (s, 3H), 3.68 (t, $J = 10.5$ Hz, 1H), 3.63-3.50 (m, 4H), 2.58 (d, $J = 8.5$ Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.29, 155.78, 150.95, 137.34, 136.42, 134.97, 129.28, 128.91, 128.38, 128.17, 126.04, 125.90, 118.63, 117.17, 114.58, 101.60, 101.38, 101.18, 100.54, 81.47, 80.39, 78.17, 77.65, 72.73, 72.16, 68.67, 66.26, 63.44, 55.62, 20.92; HRMS calcd for $\text{C}_{38}\text{H}_{42}\text{O}_{13}\text{Na}$ [$M+\text{Na}$] $^+$ m/z 729.2523, found 729.2515.

4-Methoxyphenyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranosyl)-(1 \rightarrow 2)-*O*-(3-*O*-allyl-4,6-*O*-benzylidene- α -D-glucopyranosyl)-(1 \rightarrow 3)-2-*O*-acetyl-4,6-*O*-benzylidene- β -D-glucopyranoside (1).

This reaction was carried out under an argon atmosphere. MS4A (1.0 g), **2** (294 mg,

0.416 mmol), and **3c** (340 mg, 0.661 mmol) were dissolved in CH₂Cl₂ (12 mL). After stirring the mixture for 15 min at room temperature, MeOTf (367 μL, 3.33 mmol) was added at -30 °C. The reaction mixture was stirred for 24 h at 10 °C, before the reaction was quenched with Et₃N (0.466 mL, 3.33 mmol) at -10 °C. The mixture was filtered through a pad of celite, and the filtrate and washings were concentrated *in vacuo*. The resulting residue was diluted with EtOAc (200 mL) and washed with saturated aq. NaHCO₃ (200 mL) and brine (200 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated *in vacuo*, before the resulting residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5, v/v) to give **1** (368.2 mg, 80%): ¹H NMR for α-isomer (500 MHz, CDCl₃) δ 7.50-7.33 (m, 15H), 6.97-6.81 (m, 4H), 6.00-5.83 (m, 2H), 5.66 (d, *J* = 3.5 Hz, 1H), 5.56 (s, 1H), 5.53 (s, 1H), 5.49 (s, 1H), 5.35-5.29 (m, 2H), 5.18 (d, *J* = 3.5 Hz, 1H), 5.19-5.07 (m, 4H), 4.96 (d, *J* = 8.0 Hz, 1H), 4.38 (dd, *J* = 4.5, 10.0 Hz, 1H), 4.43-4.19 (m, 6H), 4.07-4.02 (m, 2H), 3.98 (t, *J* = 10.0 Hz, 1H), 3.92 (ddd, *J* = 5.0, 5.0, 10.0 Hz, 1H), 3.87 (t, *J* = 9.0 Hz, 1H), 3.77-3.69 (m, 7H), 3.63 (dd, *J* = 4.0, 9.0 Hz, 1H), 3.59-3.51 (m, 3H), 3.45 (t, *J* = 9.5 Hz, 1H), 2.18 (s, 3H), 1.00 (s, 3H × 3), 0.19 (s, 3H), 0.15 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.81, 155.72, 151.11, 137.62, 137.35, 136.53, 135.16, 135.09, 129.09, 128.91, 128.78, 128.24, 128.17, 128.10, 126.18, 126.02, 125.93, 118.65, 116.85, 116.73, 114.55, 101.58, 101.48, 101.26, 101.19, 96.10, 95.44, 82.06, 81.47, 81.39, 77.93, 76.26, 74.14, 74.02, 73.38, 72.66, 71.60, 68.81, 68.50, 66.15, 63.00, 62.67, 60.38, 55.62, 25.88, 20.98, 18.16, 14.18, -4.36; HRMS calcd for C₆₀H₇₄O₁₈SiNa [*M*+Na]⁺ *m/z* 1133.4542, found 1133.4548.

Glycosylation of donor **3c** with acceptor **20**, **21**, **22** or **23**.

Experiments were carried out in accordance with “General procedure for the glycosylation of glycosyl donor **3** with glycosyl acceptor **4**”.

Methyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside (**20**).

¹H NMR for the α-isomer (500 MHz, CDCl₃) δ 8.08-9.05 (m, 2H), 8.02-8.00 (m, 2H), 7.96-7.93 (m, 2H), 7.59-7.30 (m, 14H), 6.01-5.93 (m, 1H), 5.75 (dd, *J* = 2.8, 10.9 Hz, 1H), 5.68 (dd, *J* = 3.4, 10.9 Hz, 1H), 5.47 (s, 1H), 5.29-5.25 (m, 1H), 5.21 (d, *J* = 3.4 Hz, 1H), 5.16-5.13 (m, 1H), 4.89 (d, *J* = 3.4 Hz, 1H), 4.76 (dd, *J* = 4.3, 11.8 Hz, 1H), 4.70 (dd, *J* = 7.7, 11.7 Hz, 1H), 4.51 (d, *J* = 2.1 Hz, 1H), 4.44-4.38 (m, 2H), 4.29-4.20 (m,

2H), 4.06 (dd, $J = 5.1, 10.3$ Hz, 1H), 3.88 (t, $J = 9.4$ Hz, 1H), 3.66 (dd, $J = 3.5, 9.4$ Hz, 1H), 3.53 (t, $J = 10.3$ Hz, 1H), 3.50 (t, $J = 9.4$ Hz, 1H), 3.41 (s, 3H), 0.91 (s, 9H), 0.14 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.30, 166.20, 165.94, 137.66, 135.24, 133.43, 133.22, 130.00, 129.89, 129.75, 129.53, 129.23, 128.82, 128.61, 128.55, 128.40, 128.16, 126.21, 126.08, 117.21, 101.35, 101.27, 97.52, 82.75, 76.69, 74.38, 74.17, 70.75, 69.11, 68.94, 68.90, 64.36, 63.99, 55.40, 26.16, 18.42, -4.29, -4.38; HRMS calcd for $\text{C}_{50}\text{H}_{58}\text{O}_{14}\text{SiNa}$ [$M+\text{Na}$] $^+$ m/z 933.3494, found 933.3480.

(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranosyl)-(1 \rightarrow 2)-1,3,4,6-tetra-*O*-acetyl- β -D-mannopyranose (21).

^1H NMR for the α -isomer (500 MHz, CDCl_3) δ 7.41-7.34 (m, 5H), 5.98-5.90 (m, 1H), 5.82 (s, 1H), 5.50 (s, 1H), 5.37 (t, $J = 9.8$ Hz, 1H), 5.24-5.21 (m, 1H), 5.21 (dd, $J = 2.3, 9.7$ Hz, 1H), 5.13 (d, $J = 3.4$ Hz, 1H), 5.12-5.10 (m, 1H), 4.37 (dd, $J = 5.8, 12.1$ Hz, 1H), 4.34-4.26 (m, 1H), 4.32 (d, $J = 2.0$ Hz, 1H), 4.25-4.18 (m, 1H), 4.23 (dd, $J = 2.3, 12.1$ Hz, 1H), 4.18 (dd, $J = 5.2, 12.1$ Hz, 1H), 4.13 (dd, $J = 5.2, 10.4$ Hz, 1H), 3.88 (t, $J = 9.2$ Hz, 1H), 3.81-3.78 (m, 1H), 3.71 (dd, $J = 4.0, 9.2$ Hz, 1H), 3.67 (t, $J = 10.4$ Hz, 1H), 3.55 (t, $J = 9.5$ Hz, 1H), 2.18 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 0.95 (s, 3H \times 3), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.89, 169.83, 169.20, 168.85, 137.58, 135.46, 128.98, 128.29, 126.03, 117.09, 116.81, 101.50, 99.28, 91.64, 89.86, 82.49, 77.80, 74.38, 73.76, 73.56, 73.22, 70.00, 68.94, 66.47, 62.68, 62.48, 25.82, 20.99, 20.92, 18.26, -4.19, -4.60; HRMS calcd for $\text{C}_{36}\text{H}_{52}\text{O}_{15}\text{SiNa}$ [$M+\text{Na}$] $^+$ m/z 775.2973, found 775.2964.

Methyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranosyl)-(1 \rightarrow 6)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (22).

^1H NMR for the α -isomer (500 MHz, CDCl_3) δ 7.99-7.97 (m, 2H), 7.95-7.93 (m, 2H), 7.88-7.86 (m, 2H), 7.52-7.26 (m, 14H), 6.15 (t, $J = 9.7$ Hz, 1H), 6.00-5.90 (m, 1H), 5.53 (t, $J = 10.3$, 1H), 5.51 (s, 1H), 5.28-5.20 (m, 3H), 5.12 (dd, $J = 2.0, 10.6$ Hz, 1H), 4.70 (d, $J = 3.7$ Hz, 1H), 4.36-4.29 (m, 2H), 4.23-4.17 (m, 2H), 3.93 (dt, $J = 4.6, 10.0$ Hz, 1H), 3.90 (dd, $J = 6.9, 11.1$ Hz, 1H), 3.75 (t, $J = 9.2$ Hz, 1H), 3.68-3.64 (m, 2H), 3.61 (dd, $J = 1.7, 11.2$ Hz, 2H), 3.51 (t, $J = 9.5$ Hz, 1H), 3.49 (s, 3H), 0.91 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.97, 165.44, 137.80, 135.47, 133.51, 133.47, 133.19, 130.08, 129.98, 129.83, 129.41, 129.25, 129.09, 128.92, 128.55,

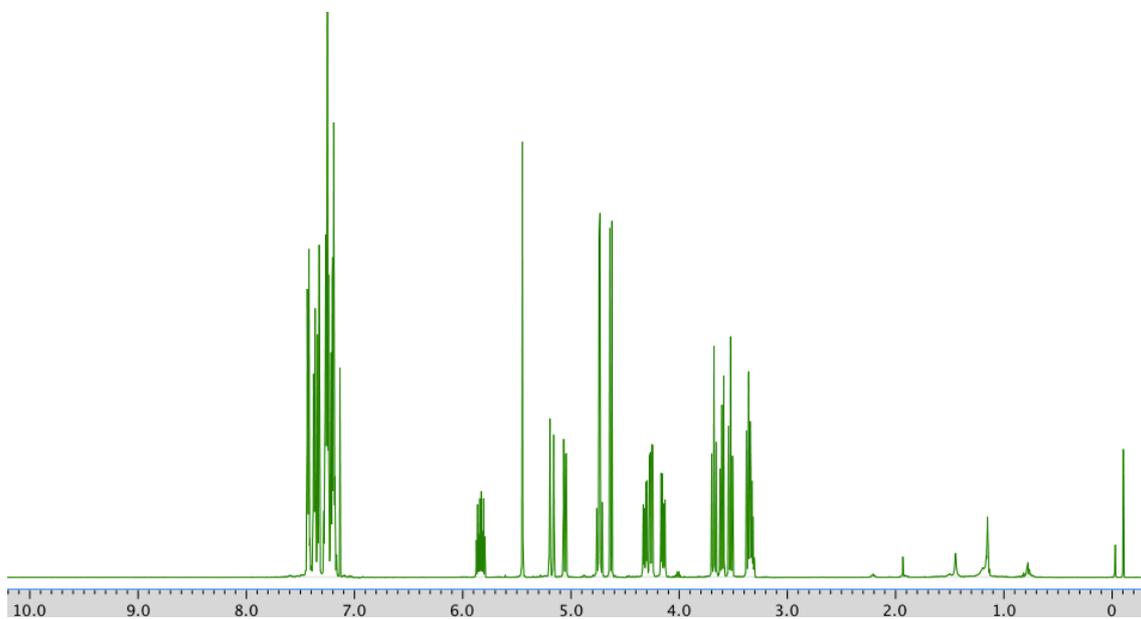
128.41, 128.29, 126.19, 116.84, 101.30, 100.78, 96.94, 82.30, 78.15, 74.33, 73.43, 72.30, 70.77, 69.61, 69.16, 69.09, 67.72, 62.84, 55.69, 25.86, 18.24, -4.33, -4.77; HRMS calcd for C₅₀H₅₈O₁₄SiNa [M+Na]⁺ *m/z* 933.3494, found 933.3488.

Methyl(3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranosyl)-(1 \rightarrow 6)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (23).

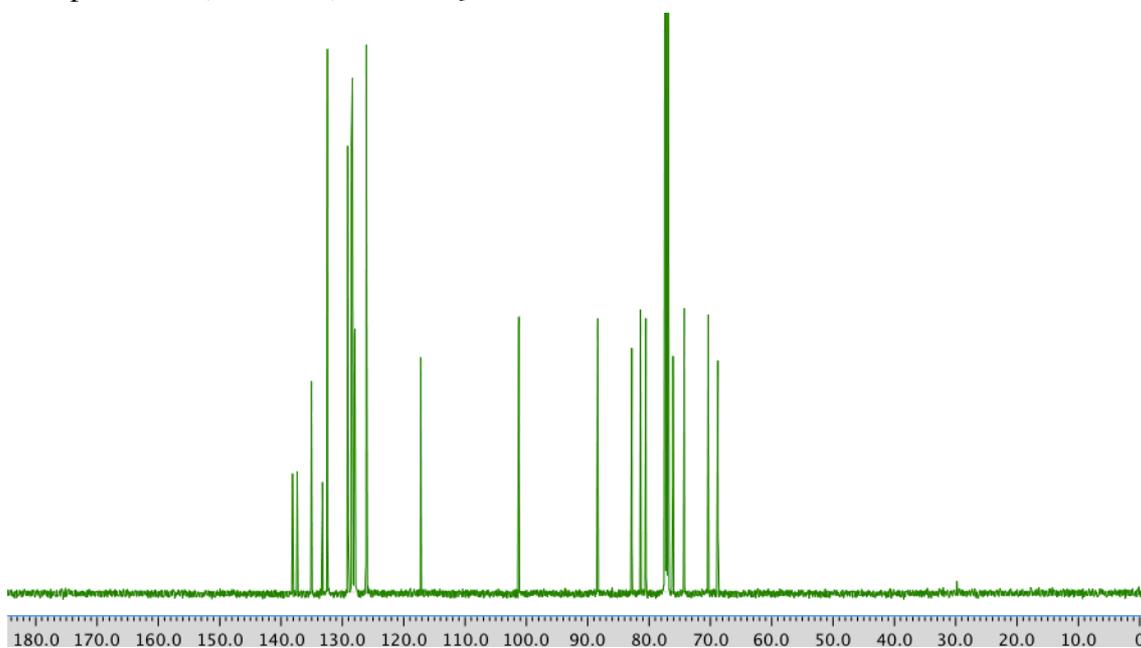
¹H NMR for the α -isomer (500 MHz, CDCl₃) δ 7.46-7.24 (m, 20H), 5.96-5.88 (m, 1H), 5.51 (s, 1H), 5.22 (dd, *J* = 1.4, 17.5 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.99, 4.63 (ABq, *J* = 10.9 Hz, 2H), 4.92, 4.83 (ABq, *J* = 11.2 Hz, 2H), 4.77, 4.67 (ABq, *J* = 12.3 Hz, 2H), 4.75 (d, *J* = 3.7 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 3.4 Hz, 1H), 4.32 (dd, *J* = 5.7, 12.0 Hz, 1H), 4.21-4.17 (m, 2H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.88 (dt, *J* = 4.9, 9.7 Hz, 1H), 3.81-3.63 (m, 6H), 3.57-3.50 (m, 3H), 3.39 (s, 3H), 0.88 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.96, 138.41, 138.27, 137.72, 135.40, 128.95, 128.60, 128.56, 128.51, 128.30, 128.01, 127.94, 127.85, 127.68, 126.15, 116.87, 101.38, 100.67, 97.99, 82.46, 82.34, 79.90, 78.09, 78.06, 75.83, 75.20, 74.28, 73.45, 73.36, 70.31, 69.24, 67.06, 62.83, 55.27, 25.95, 18.22, -4.41, -4.64; HRMS calcd for C₅₀H₆₄O₁₁SiNa [M+Na]⁺ *m/z* 891.4116, found 891.4110.

3) ^1H -NMR & ^{13}C -NMR Spectra for the Key Compounds

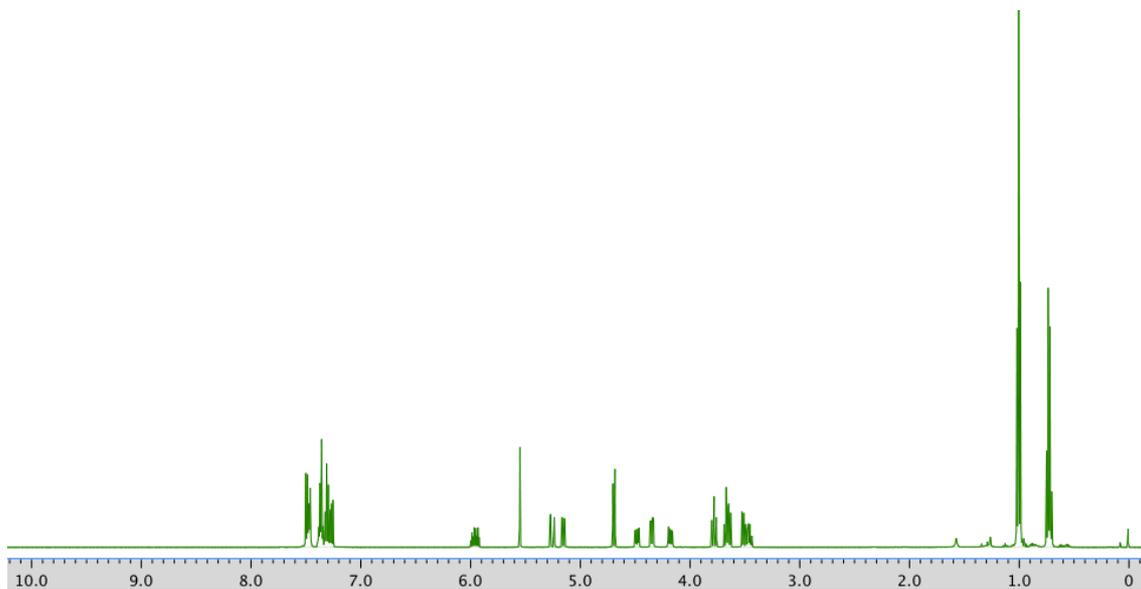
Compound **3a** (^1H NMR) in CDCl_3



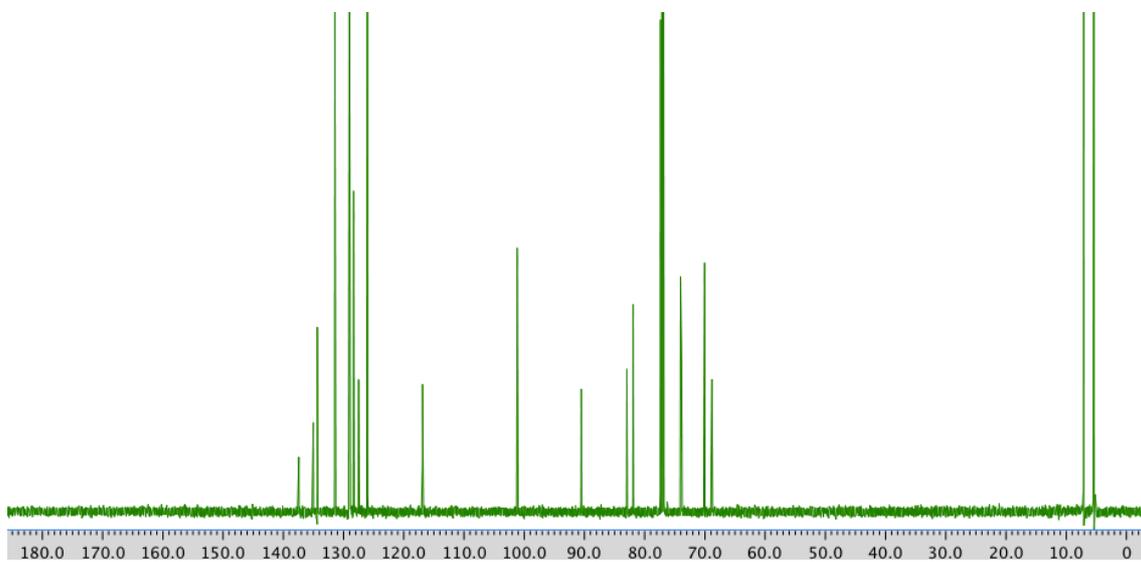
Compound **3a** (^{13}C NMR) in CDCl_3



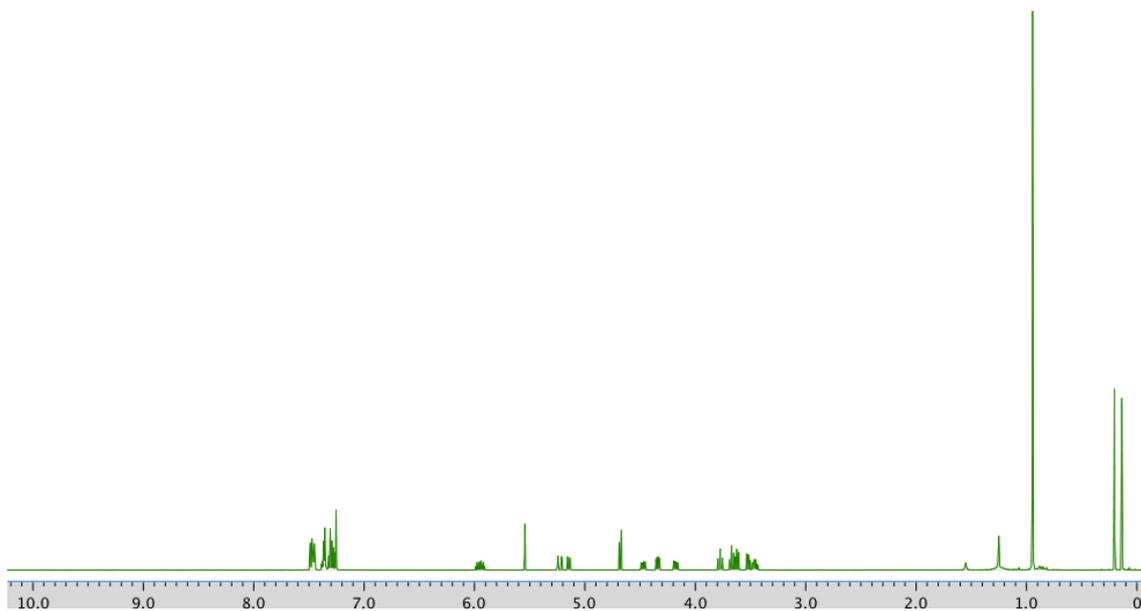
Compound **3b** (^1H NMR) in CDCl_3



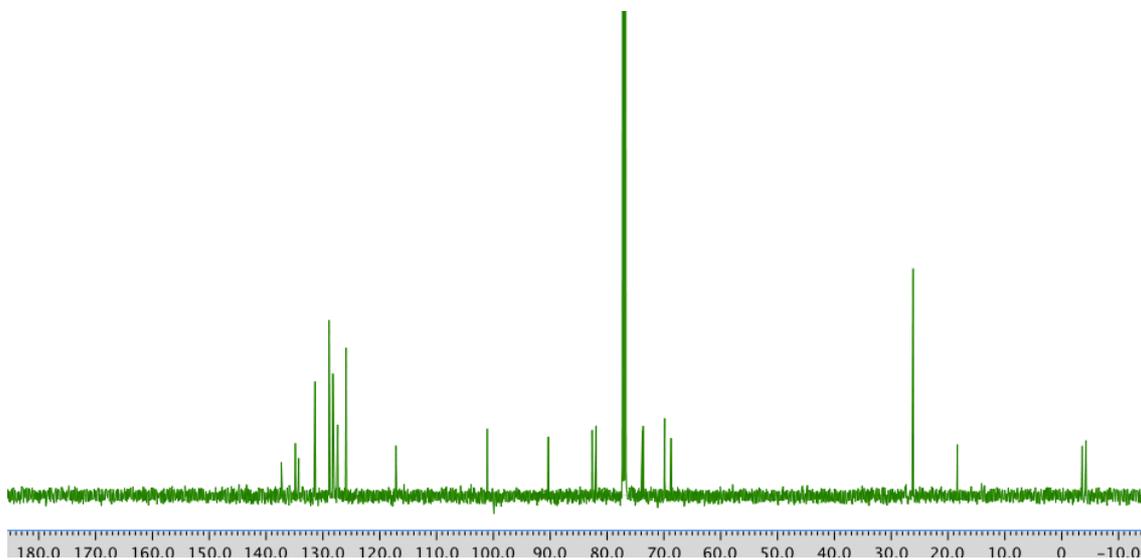
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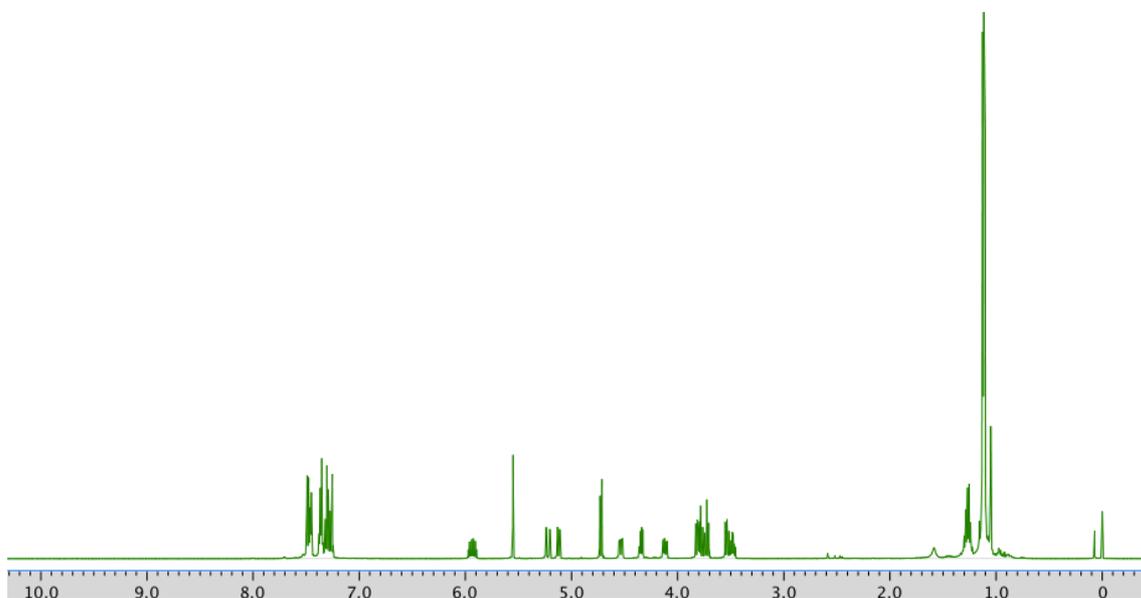
Compound **3c** (^1H NMR) in CDCl_3



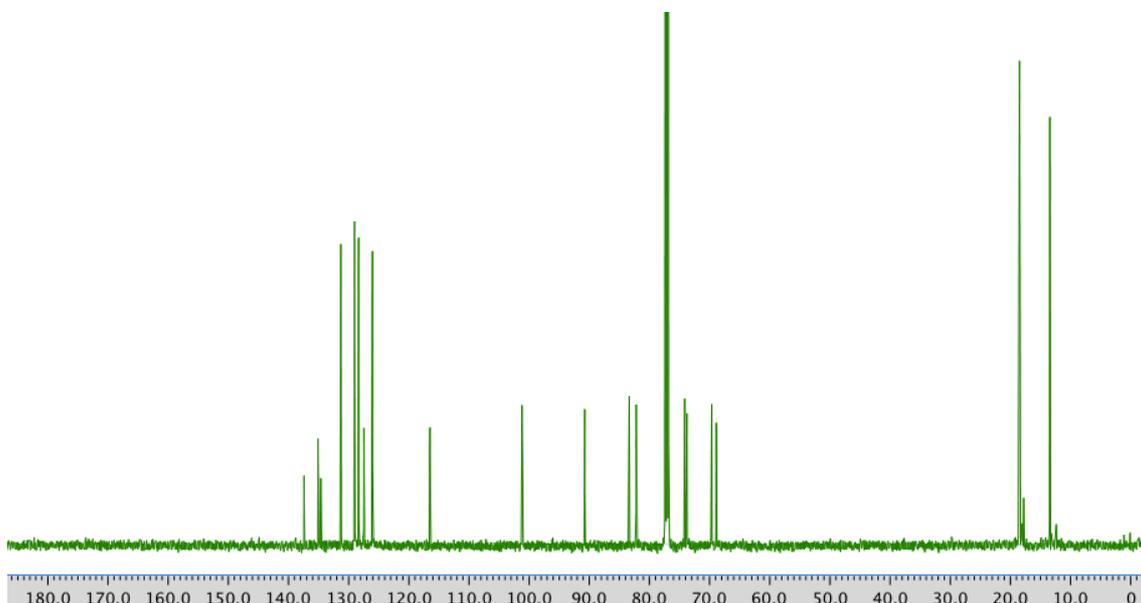
Compound **3c** (^{13}C NMR) in CDCl_3



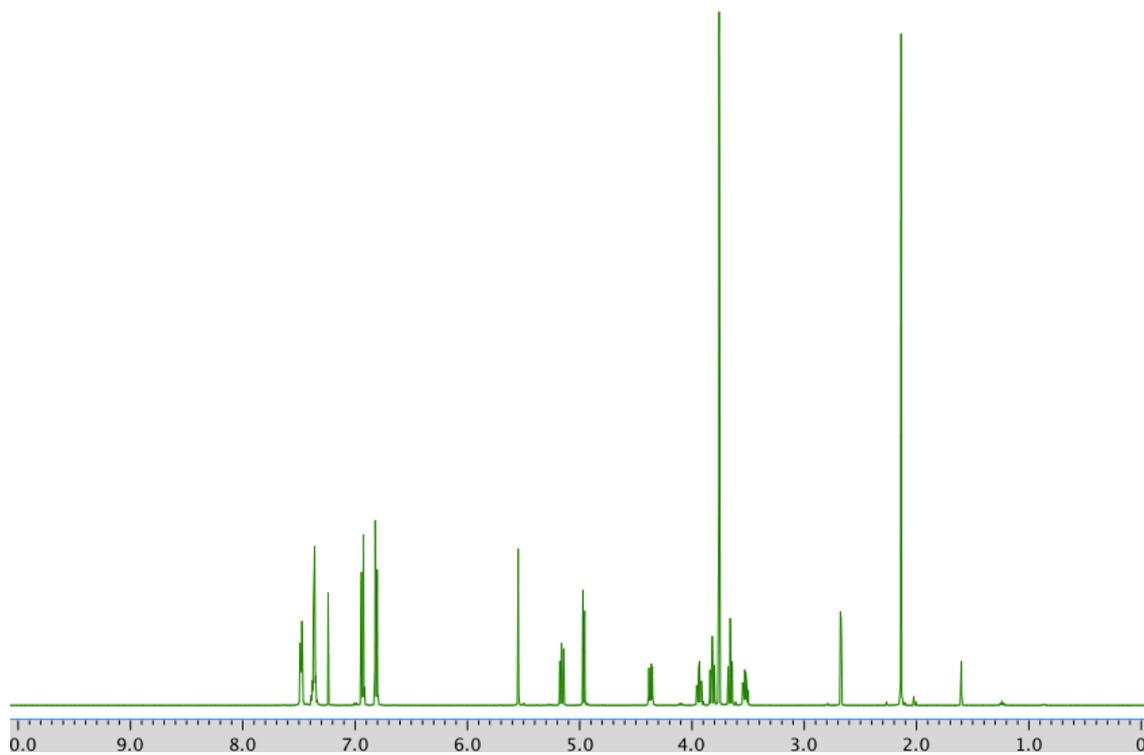
Compound **3d** (^1H NMR) in CDCl_3



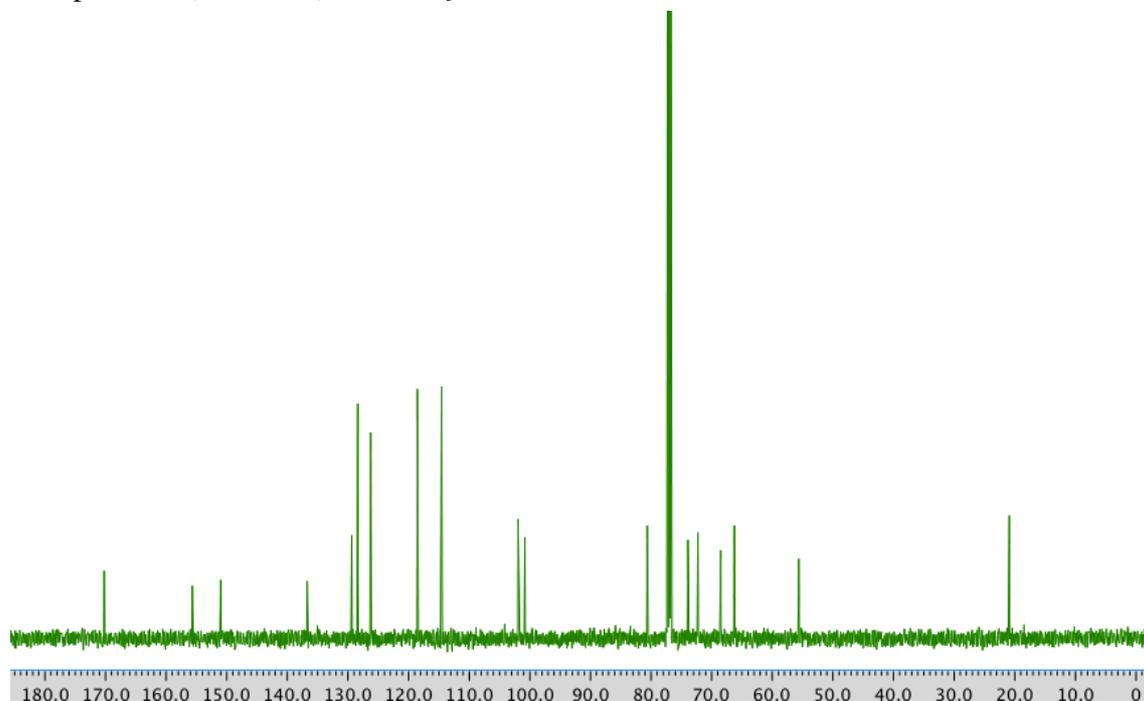
Compound **3d** (^{13}C NMR) in CDCl_3



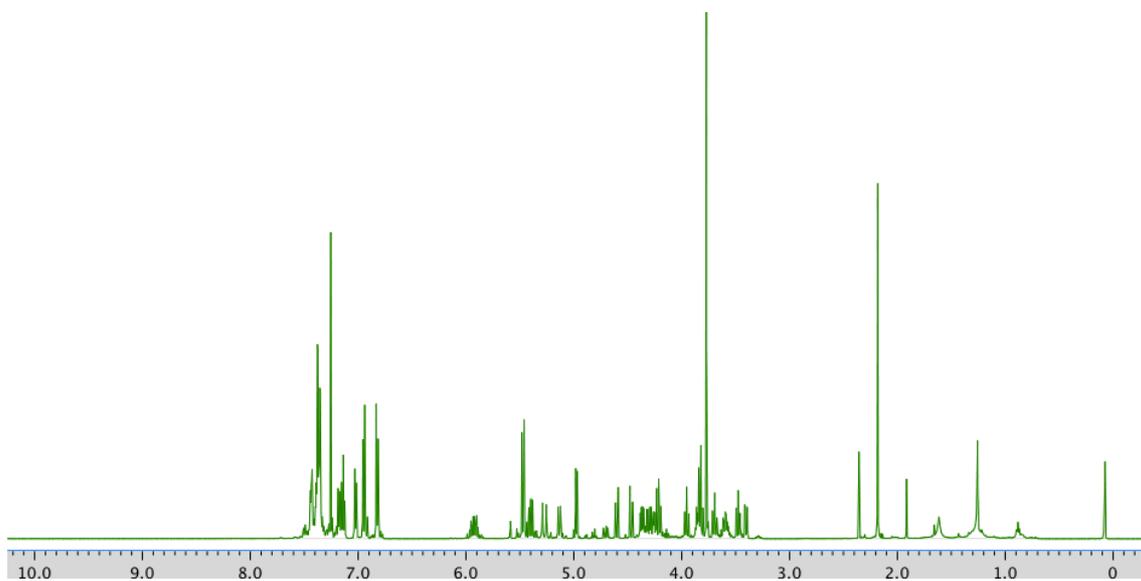
Compound **4** (^1H NMR) in CDCl_3



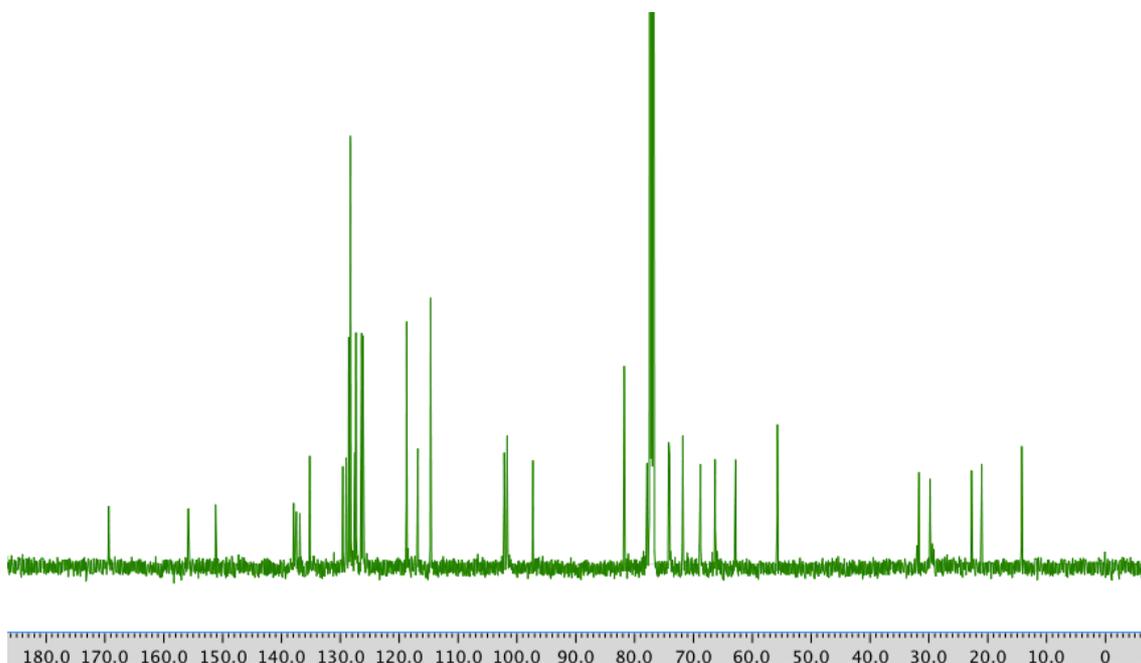
Compound **4** (^{13}C NMR) in CDCl_3



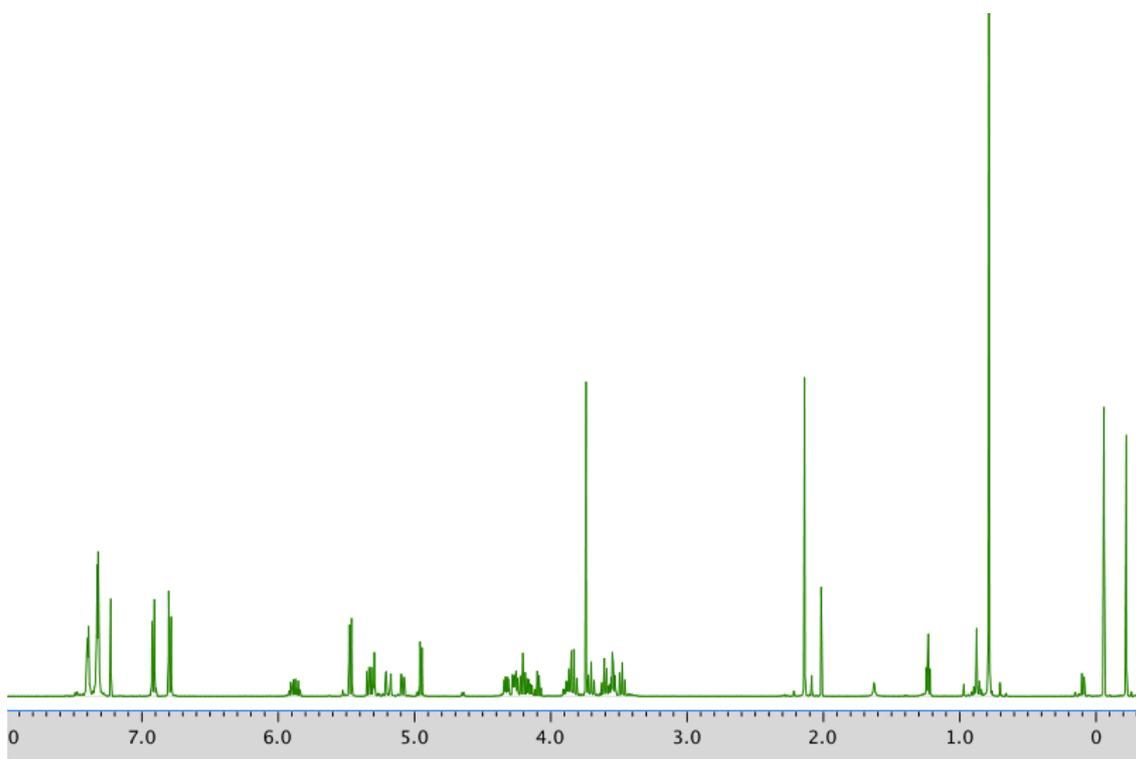
Compound **15a** (^1H NMR) in CDCl_3



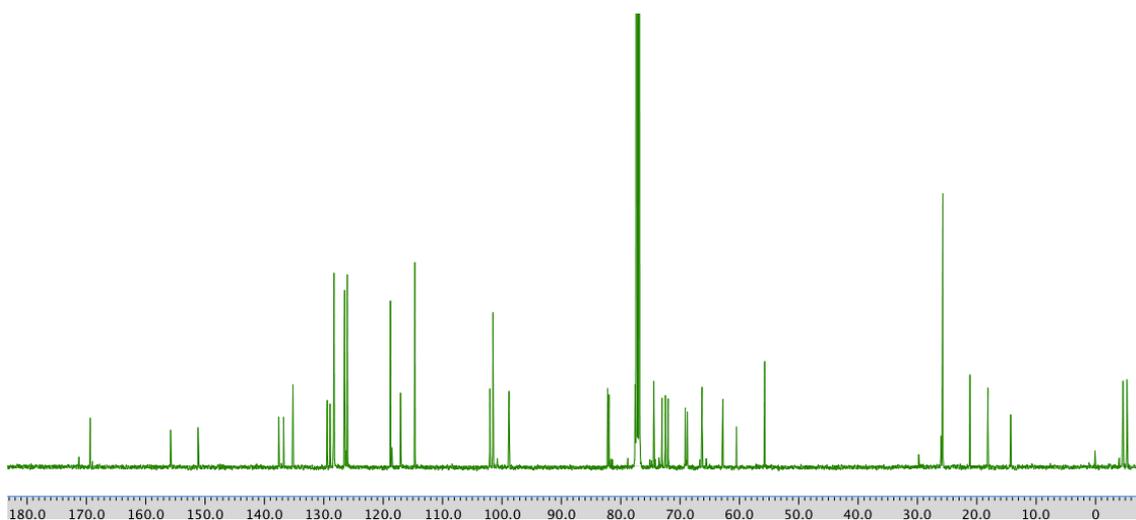
Compound **15a** (^{13}C NMR) in CDCl_3



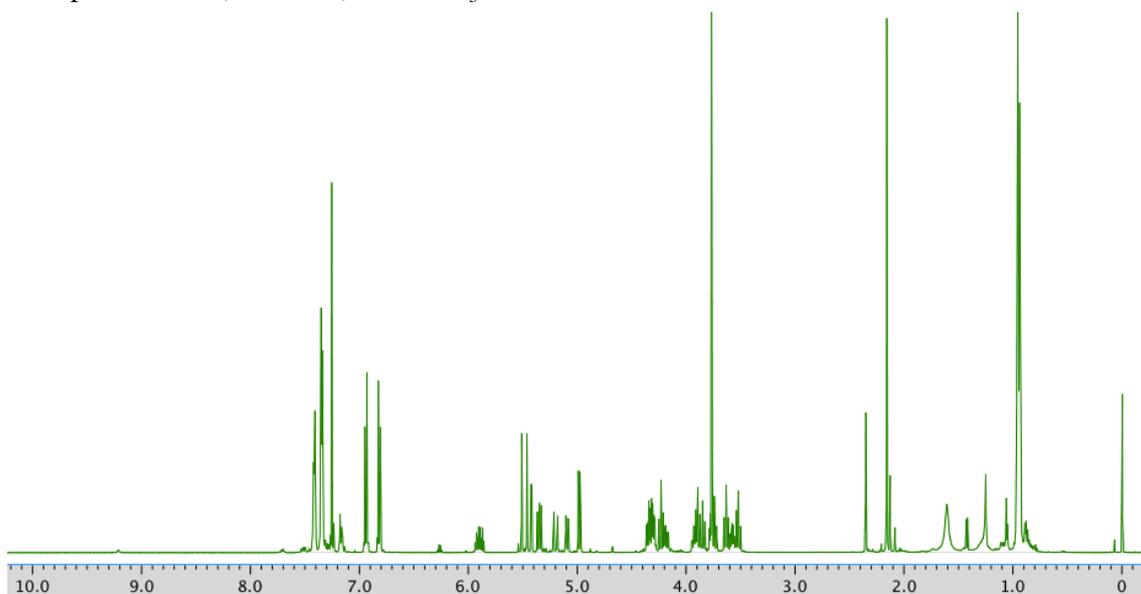
Compound **15c** (^1H NMR) in CDCl_3



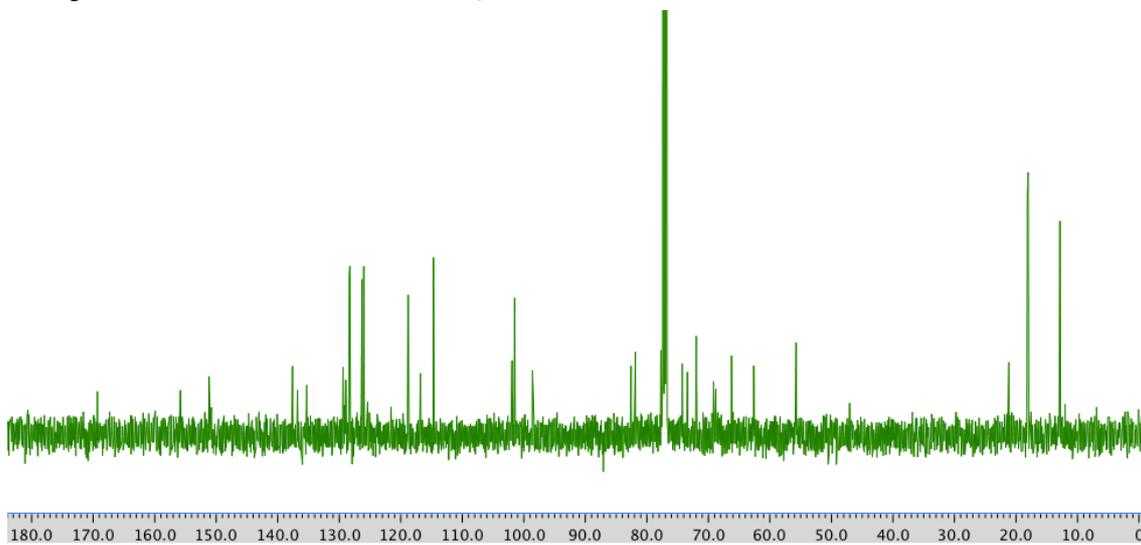
Compound **15c** (^{13}C NMR) in CDCl_3



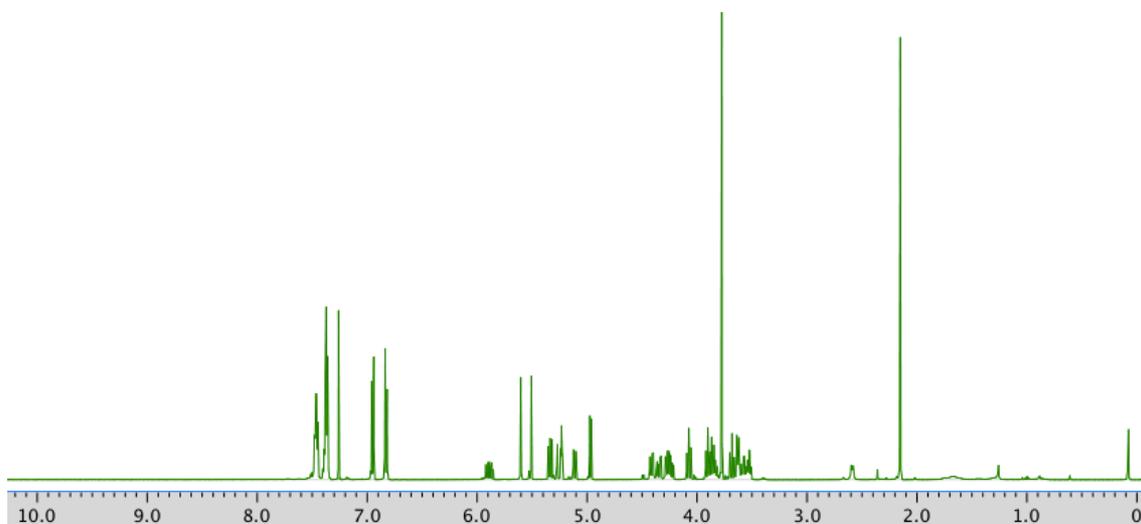
Compound **15d** (^1H NMR) in CDCl_3



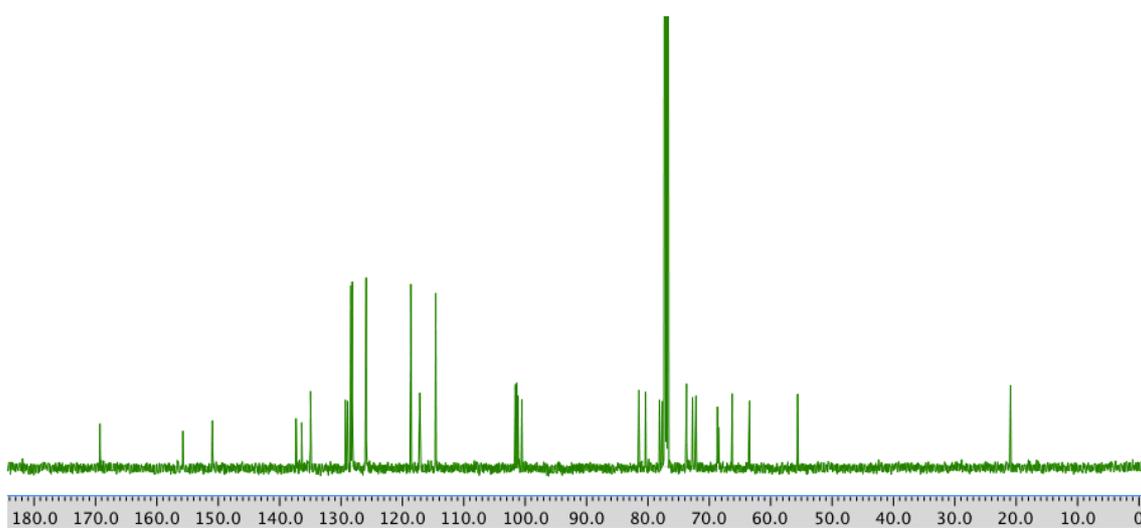
Compound **15d** (^{13}C NMR) in CDCl_3



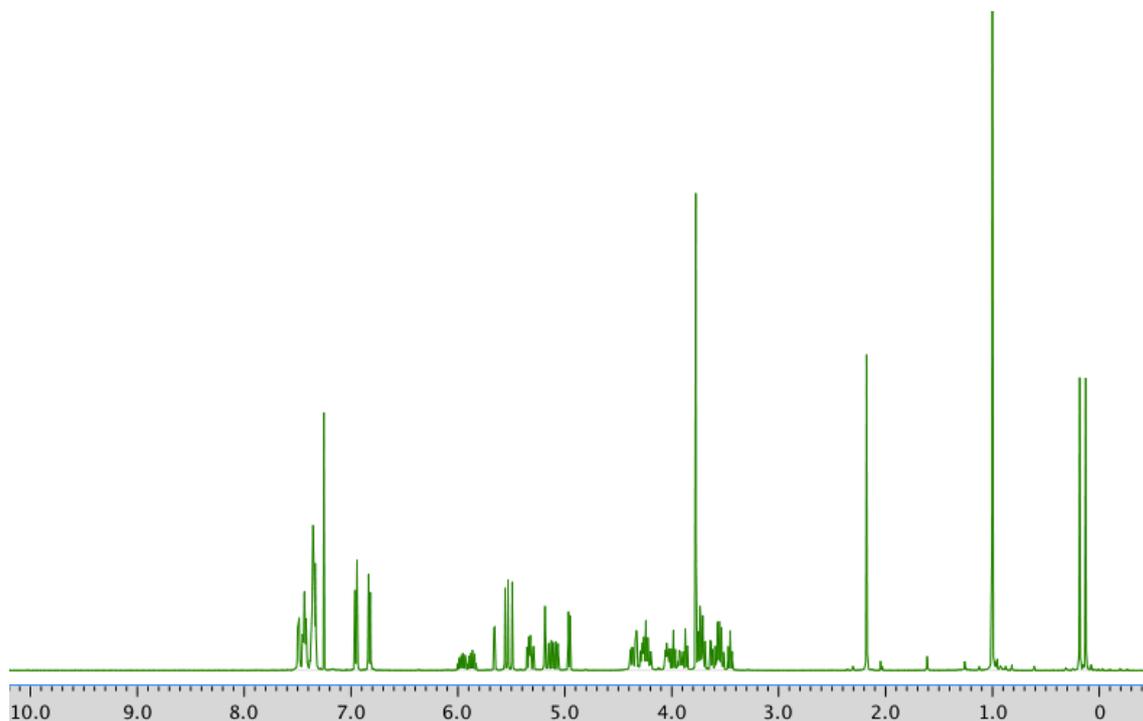
Compound **2** (^1H NMR) in CDCl_3



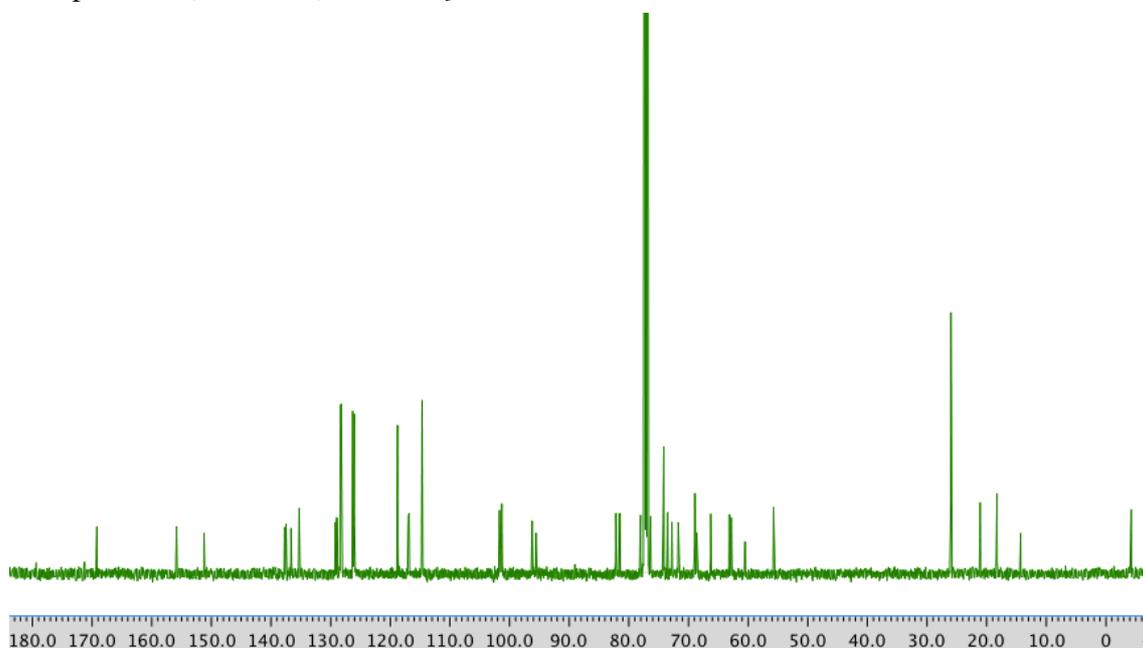
Compound **2** (^{13}C NMR) in CDCl_3



Compound **1** (^1H NMR) in CDCl_3



Compound **1** (^{13}C NMR) in CDCl_3



4) References

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