

Supporting Information

Iridium-promoted Deoxyglycoside Synthesis: Stereoselectivity and Mechanistic Insight

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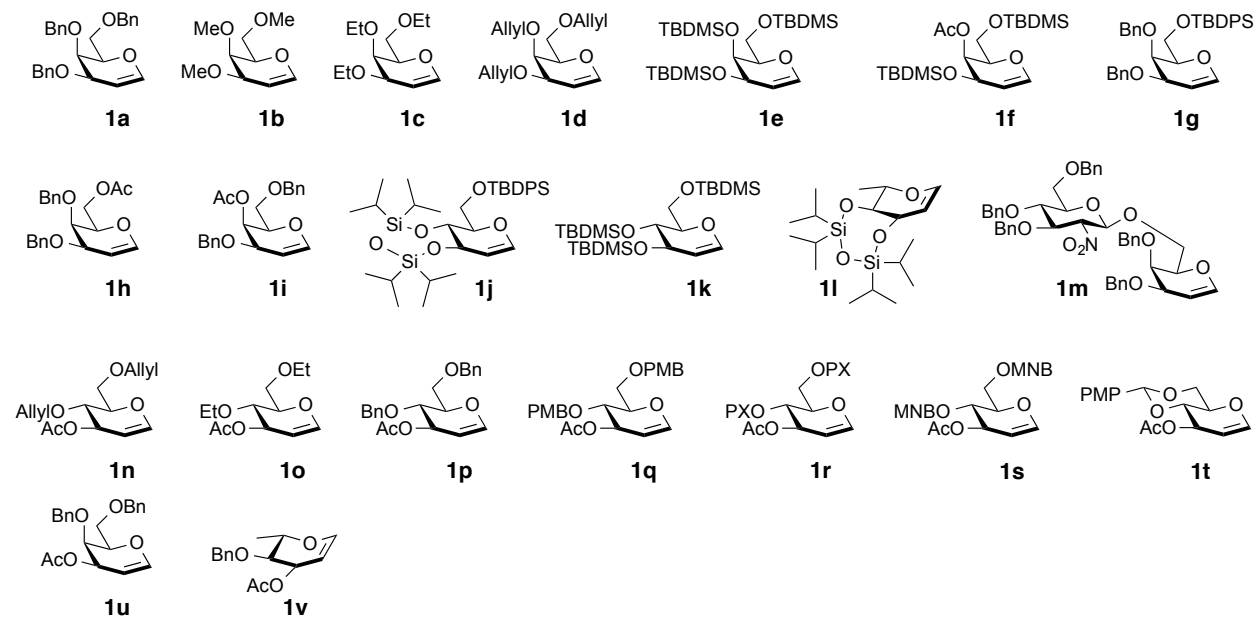
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I. Experimental Procedures

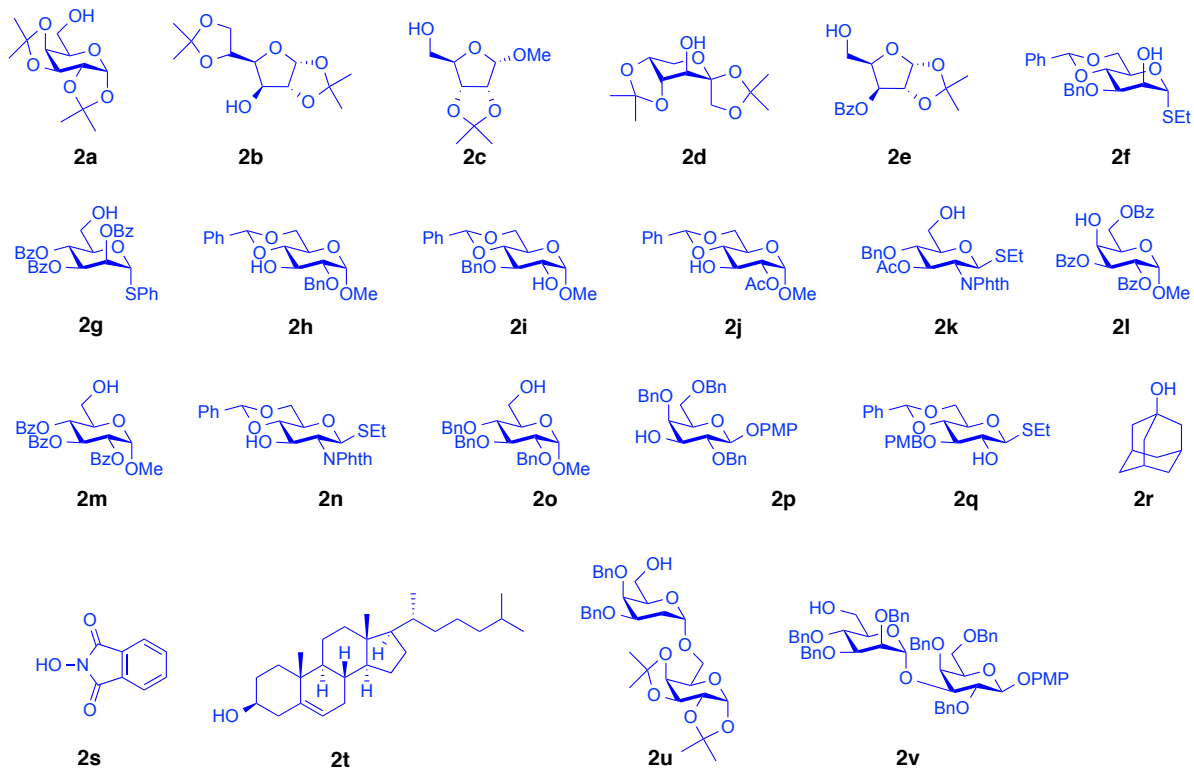
I.1 General experimental procedures

All reactions were carried out in oven-dried glassware and the reactions dealing with moisture-sensitive compounds were performed under nitrogen atmosphere. All solvents and reagents purchased from commercial sources were used without further purifications or synthesized *via* literature protocol. TLC analyses were performed on pre-coated Merck silica gel 60 F₂₅₄ plates using UV light and charring solution (10 mL conc. H₂SO₄/ 90 mL EtOH) for visualization. Flash column chromatography purifications were conducted on SiO₂ purchased from Aldrich (technical grade, 60 Å pore size, 230-400 mesh, 40-63 µm). All NMR spectra were recorded with Bruker AV-400/BBFO-400 (400 MHz) or Bruker AV-500 (500 MHz) NMR spectrometers at ambient temperature using CDCl₃ as solvent. Chemical shifts are given in ppm relative to the residual solvent peak (¹H NMR: CDCl₃ δ 7.26; ¹³C NMR: CDCl₃ δ 77.16) with multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. High resolution mass analyses were performed using Micromass Q-TOF Premier LC HR mass spectrometer. Analytical data is given if the compound is novel or not fully characterized in previous literature.

List of glycal donors used in the study:

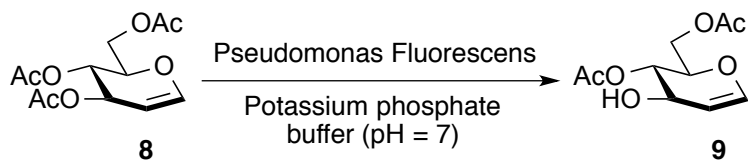


List of glycosyl acceptors used in the study:



Synthesis of glycal donors:

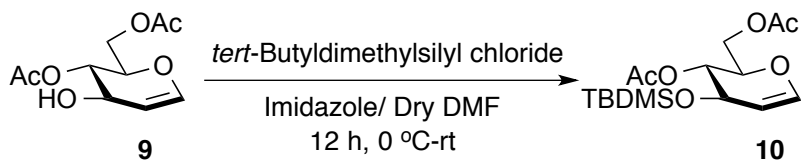
Procedure for the preparation of 4,6-di-*O*-acetyl-D-glucal (**9**):



Scheme S1. Synthesis of glucal **9**.

Following the reported synthesis¹, 3,4,6-tri-*O*-acetyl-D-glucal, **8** (25.0 g, 91.88 mmol) and *Pseudomonas Fluorescens* (25.0 g) were taken in a 1L round bottom flask. Into the reaction flask 0.1 (M) potassium phosphate buffer (250 mL, pH = 7) was added and the reaction mixture was stirred for 5 h. After 5 h (after TLC analysis indicated complete consumption of the starting material), EtOAc (300 mL) and brine solution (300 mL) were added and stirred for another 30 minutes. The organic layer was collected, further washed brine solution (300 mL) and dried over anhydrous Na₂SO₄. The solvent was then removed *in vacuo* and the crude material was purified by flash column chromatography (hexane:EtOAc = 1:1) to obtain 4,6-di-*O*-acetyl-D-glucal, **9** in 70% (14.8 g, 64.33 mmol) yield. HRMS calcd. for C₁₀H₁₄O₆+Na⁺ (M+Na)⁺: 253.0688, found: 253.0691. [α]_D²⁵ +50.9 (*c* 1.1, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.40 (dd, *J* 1.2 Hz, *J* 6.0 Hz, 1H), 4.98 (dd, *J* 6.0 Hz, 8.8 Hz, 1H), 4.86 (dd, *J* 2.8 Hz, *J* 6.0 Hz, 1H), 4.40 (dd, *J* 5.6 Hz, *J* 8.4 Hz, 1H), 4.31 (t, *J* 6.0 Hz, 1H), 4.25 (dd, *J* 2.8 Hz, *J* 12.4 Hz, 1H), 4.15-4.11 (m, 1H), 2.48 (d, *J* 5.6 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 171.1, 170.8, 144.2, 103.1, 74.2, 71.9, 67.3, 62.0, 21.1, 20.9 ppm.

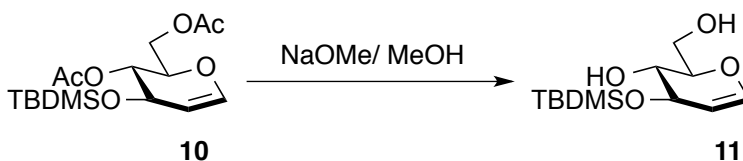
Procedure for the preparation of 4,6-Di-*O*-acetyl-3-*O*-*tert*-butyldimethylsilyl-D-glucal (**10**):



Scheme S2. Synthesis of glucal **10**.

4,6-Di-*O*-acetyl-D-glucal, **9** (14.0 g, 60.85 mmol) and imidazole (8.3 g, 121.70 mmol) were dissolved in dry DMF (100 mL) taken in a 250 mL round bottom flask and the solution was placed in an ice-bath. *tert*-Butyldimethylsilyl chloride (13.76 g, 91.28 mmol) was then added to the reaction mixture and the solution was stirred in the ice-bath for 15 minutes. Then the reaction mixture was warmed to room temperature and further stirred for 12 h. After that, the solvent was removed under vacuum and the crude material was dissolved in EtOAc (200 mL) and it was successively washed with water (500 mL) and sat. brine solution (500 mL). Then the organic layer was collected, dried over Na₂SO₄, concentrated *in vacuo* and purified by flash column chromatography (hexane:EtOAc = 20:1) to obtain 4,6-di-*O*-acetyl-3-*O*-*tert*-butyldimethylsilyl-D-glucal, **10** in 81% (16.96 g, 49.28 mmol) yield. HRMS calcd. for C₁₆H₂₈O₆Si+H⁺ (M+H)⁺: 345.1733, found: 345.1731. [α]_D²⁵ -27.7 (*c* 0.9, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.32 (dd, *J* 0.8 Hz, *J* 6.4 Hz, 1H), 5.03 (t, *J* 6.0 Hz, 1H), 4.74 (dd, *J* 3.6 Hz, *J* 6.4 Hz, 1H), 4.40 (dd, *J* 6.4 Hz, *J* 12.0 Hz, 1H), 4.21-4.13 (m, 3H), 2.063 (s, 3H), 2.059 (s, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 170.8, 169.7, 143.2, 103.0, 74.1, 70.5, 65.1, 62.1, 25.7, 21.1, 20.9, 18.0, -4.5, -4.8 ppm.

Procedure for the preparation of 3-*O*-*tert*-butyldimethylsilyl-D-glucal (11**):**

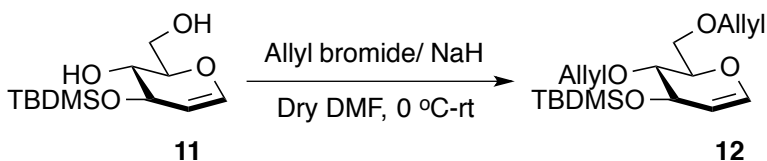


Scheme S3. Synthesis of glucal **11**.

Freshly prepared NaOMe/MeOH (100 mL) was added to the solution of 4,6-di-*O*-acetyl-3-*O*-*tert*-butyldimethylsilyl-D-glucal, **10** (16.0 g, 46.49 mmol) in MeOH (100 mL). The reaction mixture was stirred at room temperature for 3 h till TLC analysis showed complete consumption of the starting material. Then the solvent was evaporated *in vacuo* and the crude material was purified by flash column chromatography (hexane:EtOAc = 3:1) to obtain 3-*O*-*tert*-butyldimethylsilyl-D-glucal, **11** in 85% (10.28 g, 39.52 mmol) yield. HRMS calcd. for C₁₂H₂₄O₄Si+Na⁺ (M+Na)⁺: 283.1342, found: 283.1346. [α]_D²⁵ -53.5 (*c* 1.7, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.30 (dd,

J 1.2 Hz, 6.0 Hz, 1H), 4.66 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.25-4.22 (m, 1H), 3.93-3.90 (m, 3H), 3.81-3.76 (m, 1H), 2.42 (d, *J* 4.8 Hz, 1H), 4.25 (t, *J* 5.2 Hz, 1H), 0.91 (s, 9H), 0.12 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 143.7, 103.6, 77.9, 70.8, 69.9, 62.3, 25.9, 18.2, -4.2, -4.4 ppm.

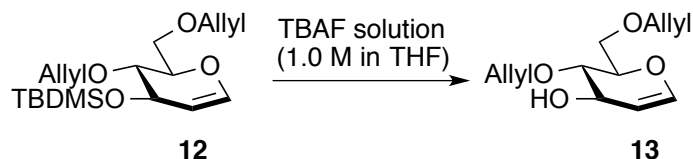
Procedure for the preparation of 4,6-di-*O*-allyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal (12**)**



Scheme S4. Synthesis of glucal **12**.

A solution of 3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **11** (4.0 g, 15.37 mmol) in dry DMF (25 mL) was cooled to 0 °C. Then, sodium hydride (60% dispersion in mineral oil) (1.47 g, 61.48 mmol) was added into the solution pinch by pinch. Allyl bromide (4 mL, 46.11 mmol) was added dropwise over 15 min and the solution was stirred at room temperature for 1 h. The reaction was poured over ice cooled water (50 mL) and extracted twice with EtOAc (100 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to obtain the crude mixture. The crude mixture was purified by silica gel flash column chromatography (hexane:EtOAc = 16:1) to give compound **12** (2.77 g, 8.14 mmol, 53%) as a colourless oil. HRMS calcd. for C₁₈H₃₂O₄Si+H⁺ (M+H)⁺: 341.2148, found: 341.2140. [α]_D²⁵ +10.2 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.31 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 5.97-5.87 (m, 2H), 5.23-5.31 (m, 2H), 5.20-5.15 (m, 2H), 4.62 (d, *J* 2.4, 6.0 Hz, 1H), 4.30-4.26 (m, 2H), 4.17-3.97 (m, 4H), 3.75 (dd, *J* 5.2, 11.2 Hz, 1H), 3.68 (d, *J* 6.4, 11.2 Hz, 1H), 3.53 (d, *J* 6.0, 8.4 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 143.5, 134.9, 134.8, 117.3, 117.2, 103.7, 77.0, 76.8, 73.1, 72.6, 69.2, 68.8, 25.9, 18.1, -4.3, -4.5 ppm.

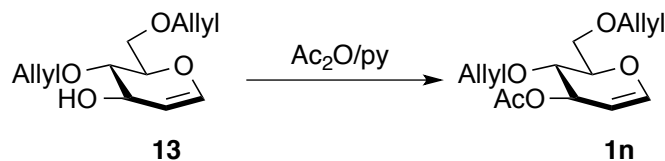
Procedure for the preparation of 4,6-di-*O*-allyl-D-glucal (**13**)



Scheme S5. Synthesis of glucal **13**.

A solution of 4,6-di-*O*-allyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **12** (2.6 g, 7.64 mmol) in THF (25 mL) was cooled to 0 °C. Tetrabutylammonium fluoride solution (1.0 M in THF, 8.4 mL, 8.4 mmol) was then added dropwise over 5 minutes into the solution and the reaction mixture was stirred at 0 °C for 5 minutes, then warmed to room temperature. The reaction mixture was stirred for 12 h and was concentrated under reduced pressure to obtain the crude mixture. The crude mixture was purified by silica gel flash column chromatography (hexane:EtOAc = 4:1) to obtain compound **13** (1.57 g, 6.94 mmol, 91%) as a colourless oil. HRMS calcd. for C₁₂H₁₈O₄+H⁺ (M+H)⁺: 227.1283, found: 227.1285. [α]_D²⁵ +41.1 (*c* 2.2, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.37 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 6.00-5.87 (m, 2H), 5.30 (dq, *J* 1.6, 17.2 Hz, 2H), 5.20 (d, *J* 1.2, 14.4 Hz, 2H), 4.74 (d, *J* 2.4, 6.0 Hz, 1H), 4.32-4.20 (m, 3H), 4.12-4.01 (m, 2H), 3.94 (dt, *J* 3.2, 9.2 Hz, 1H), 3.78-3.72 (m, 2H), 3.57 (d, *J* 6.4, 9.2 Hz, 1H), 2.09 (d, *J* 4.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 144.7, 135.0, 134.5, 117.6, 117.5, 102.9, 77.4, 76.9, 72.9, 72.7, 68.99, 68.97 ppm.

Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-allyl-D-glucal (**1n**)

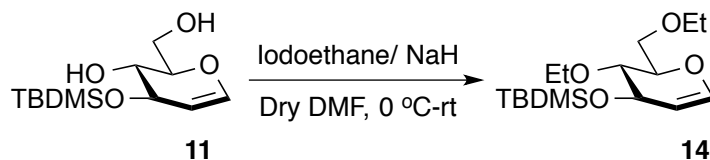


Scheme S6. Synthesis of glucal donor **1n**.

4,6-Di-*O*-allyl-D-glucal, **13** (1.45 g, 6.41 mmol) was dissolved pyridine (10 mL) taken in a 50 mL round bottom flask. The solution was cooled in an ice bath (0-5 °C) and stirred for 10 minutes.

Acetic anhydride (10 mL) and a pinch of DMAP were then added into the cooled solution and the reaction mixture was stirred for 5 minutes at 0 °C. Then the reaction mixture was slowly warmed to the room temperature and stirred for 12 h. The solvent was then removed under vacuum by co-evaporation with toluene (25 mL×3) and crude material was purified by flash column chromatography (hexane:EtOAc = 5:1) to afford 3-*O*-acetyl-4,6-di-*O*-allyl-*D*-glucal, **1n** in 85% (1.46 g, 5.45 mmol) yield. HRMS calcd. for C₁₄H₂₀O₅+Na⁺ (M+Na)⁺: 291.1208, found: 291.1197. [α]_D²⁵ -16.6 (c 1.4, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 6.41 (d, 1H, *J* 6.0 Hz), 5.96-5.83 (m, 2H), 5.34-5.15 (m, 3H), 4.73 (dd, 1H, *J* 2.8, 6.0 Hz), 4.21-4.11 (m, 2H), 4.09-3.99 (m, 3H), 3.79 (d, 1H, *J* 6.4, 8.4 Hz), 3.74 (dd, 1H, *J* 4.8, 10.8 Hz), 3.69 (d, 1H, *J* 3.2, 10.8 Hz), 2.06 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 170.6, 145.9, 134.6, 134.5, 117.4, 117.3, 99.1, 76.8, 73.2, 72.6, 70.8, 68.1, 21.3.

Procedure for the preparation of 4,6-di-*O*-ethyl-3-*O*-(*tert*-butyldimethylsilyl)-*D*-glucal (14**)**

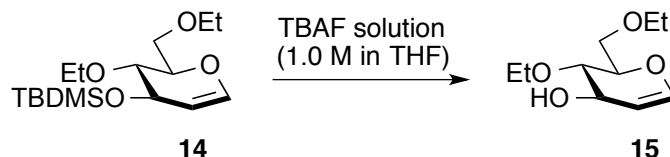


Scheme S7. Synthesis of glucal **14**.

A solution of 3-*O*-(*tert*-butyldimethylsilyl)-*D*-glucal, **11** (1.0 g, 3.84 mmol) in dry DMF (10 mL) was cooled to 0 °C. Sodium hydride (60% dispersion in mineral oil) (369 mg, 15.36 mmol) was added into the solution pinch by pinch. Iodoethane (926 μL, 11.52 mmol) was added dropwise over 10 min under N₂ atmosphere into the mixture and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured over ice cooled water (25 mL) and extracted twice with EtOAc (25 mL×2). The combined organic layers were washed with brine (25 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography (hexane:EtOAc=14:1) to obtain compound **14** (620 mg, 1.96 mmol, 51%) as a colourless oil. HRMS calcd. for C₁₆H₃₂O₄Si+H⁺ (M+H)⁺: 317.2148, found: 317.2144. [α]_D²⁵ -35.8 (c 1.1, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.29 (d, *J* 6.0 Hz, 1H), 4.60 (dd, *J* 2.8 Hz, 6.4 Hz, 1H), 4.27 (dt, *J* 1.6 Hz, 6.4 Hz, 1H), 3.91-3.95 (m, 1H), 3.84-3.76

(m, 1H), 3.74-3.67 (m, 3H), 3.63-3.49 (m, 2H), 3.45 (dt, J 6.4 Hz, 8.8 Hz, 1H), 1.24 (t, J 7.2 Hz, 3H), 1.20 (t, J 7.2 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 143.5, 103.9, 77.2, 77.1, 69.5, 69.3, 67.8, 67.0, 58.6, 25.9, 18.6, 18.1, 15.7, 15.3, -4.3, -4.6 ppm.

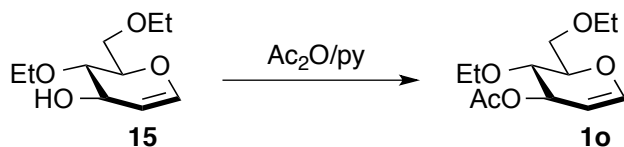
Procedure for the preparation of 4,6-di-*O*-ethyl-D-glucal (**15**)



Scheme S8. Synthesis of glucal **15**.

A solution of 4,6-di-*O*-ethyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **14** (550 mg, 1.74 mmol) in dry THF (10 mL) was cooled to 0 °C. Tetrabutylammonium fluoride solution (1.0 M in THF, 1.9 mL, 1.91 mmol) was added into the solution dropwise over 5 minutes. After stirring at 0 °C for 5 minutes, the reaction mixture was warmed to room temperature, stirred for another 12 h and concentrated under reduced pressure. The crude was purified by silica gel flash column chromatography (hexane:EtOAc = 3:1) to obtain compound **15** (323 mg, 1.6 mmol, 92%) as a colourless oil. HRMS calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_4+\text{H}^+$ ($\text{M}+\text{H}$) $^+$: 203.1283, found: 203.1284. $[\alpha]_{\text{D}}^{25}$ -3.4 (c 0.8, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ = 6.37 (dd, J 1.0, 6.0 Hz, 1H), 4.74 (dd, J 2.0 Hz, 6.0 Hz, 1H), 4.27-4.24 (m, 1H), 3.93-3.90 (m, 1H), 3.86-3.80 (m, 1H), 3.76-3.68 (m, 3H), 3.63-3.50 (m, 2H), 3.48 (dd, J 6.0 Hz, 8.5 Hz, 1H), 2.19 (d, J 6.5 Hz, 1H), 1.23 (t, J 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 144.7, 102.8, 77.8, 69.6, 68.7, 67.5, 67.2, 15.9, 15.2 ppm.

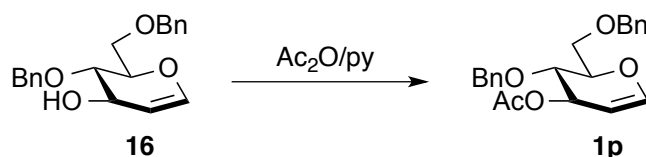
Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-ethyl-D-glucal (**1o**)



Scheme S9. Synthesis of glucal donor **1o**.

4,6-Di-*O*-ethyl-glucal, **15** (250 mg, 1.24 mmol) was dissolved in pyridine (5 mL) in a 25 mL round bottom flask. The solution was cooled in an ice bath (0-5 °C) and stirred for 10 minutes. Acetic anhydride (5mL) and a pinch of DMAP were then added into the cooled solution, and the reaction mixture was stirred for 5 minutes at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was then removed *in vacuo* by co-evaporation with toluene (10 mL×3), and crude material was purified by flash column chromatography (hexane:EtOAc = 4:1) to obtain 3-*O*-acetyl-4,6-di-*O*-ethyl-D-glucal, **1o** in 89% (269 mg, 1.1 mmol) yield. HRMS calcd. for C₁₂H₂₀O₅+Na⁺ (M+Na)⁺: 267.1208, found: 267.1205. [α]_D²⁵ -16.6 (*c* 1.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 6.42 (dd, *J* 0.8 Hz, 6.4 Hz, 1H), 5.33 (dq, *J* 1.2 Hz, 6.4 Hz, 1H), 4.73 (dd, *J* 1.6 Hz, 6.0 Hz, 1H), 4.03-3.99 (m, 1H), 3.76-3.63 (m, 5H), 3.61-3.49 (m, 2H), 2.07 (s, 1H), 1.23 (t, *J* 7.2 Hz, 3H), 1.19 (t, *J* 7.2 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 170.8, 145.9, 99.3, 77.0, 73.7, 71.2, 68.6, 67.3, 67.1, 21.4, 15.8, 15.3 ppm.

Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-benzyl-D-glucal (**1p**)

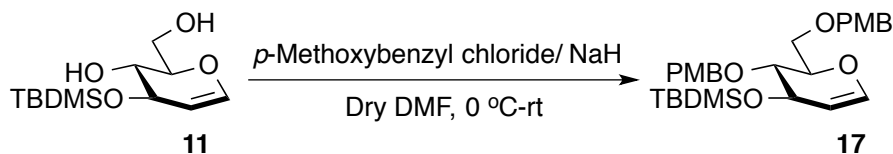


Scheme S10. Synthesis of glucal donor **1p**.

4,6-Di-*O*-benzyl-D-glucal, **16**² (650 mg, 2.0 mmol) was dissolved in pyridine (7.5 mL) in a 50 mL round bottom flask. The solution was cooled in an ice bath (0-5 °C) and stirred for 10 minutes. Acetic anhydride (7.5 mL) and a pinch of DMAP were then added into the cooled solution, and the reaction mixture was stirred for another 5 minutes at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was then removed *in vacuo* by co-evaporation with toluene (25 mL×3), and crude material was purified by flash column chromatography (hexane:EtOAc = 7:1) to afford 3-*O*-acetyl-4,6-di-*O*-benzyl-D-glucal, **1p** as a colourless oil in 73% (536 mg, 1.46 mmol) yield. HRMS calcd. for C₂₂H₂₄O₅+H⁺ (M+H)⁺: 369.1702, found: 369.1690. [α]_D²⁵ -8.2 (*c* 2.5, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.35-7.25

(m, 10H), 6.44 (dd, 1H, J 0.4, 6.0 Hz), 6.42 (ddd, 1H, J 1.2, 2.4, 6.0 Hz), 4.76 (d, 1H, J 2.8, 6.0 Hz), 4.69 (d, 1H, J 11.2 Hz), 4.63 (d, 1H, J 11.6 Hz), 4.62 (d, 1H, J 12.0 Hz), 4.56 (d, 1H, J 12.0 Hz), 4.12-4.08 (m, 1H), 3.93 (dd, 1H, J 6.4, 8.8 Hz), 3.83 (dd, 1H, J 4.8, 10.8 Hz), 3.75 (dd, 1H, J 3.2, 10.8 Hz), 1.98 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 170.7, 146.0, 138.1, 138.0, 128.6, 128.0, 127.94, 127.90, 99.3, 77.0, 73.7, 73.5, 71.1, 68.2, 21.3.

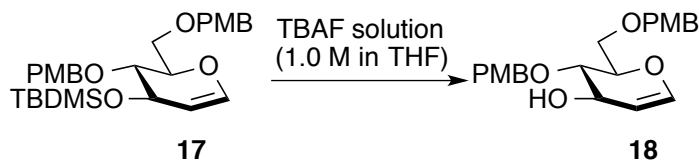
Procedure for the preparation of 4,6-di-*O*-*p*-methoxybenzyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal (17**):**



Scheme S11. Synthesis of glucal **17**.

A solution of 3-*O*-*tert*-butyldimethylsilyl-D-glucal, **11** (1.1 g, 4.23 mmol) in dry DMF (15 mL) was cooled to 0 °C. Then solution sodium hydride (60% dispersion in mineral oil) (406 mg, 16.92 mmol) was added into the solution pinch by pinch. *p*-Methoxybenzyl chloride (1.7 mL, 12.69 mmol) was added dropwise over 15 min and the solution was stirred at room temperature for 1 h. The reaction was poured over ice cooled water (30 mL) and extracted twice with EtOAc (30 mL \times 2). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4 , and then concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexane:EtOAc = 15:1) to give compound **17** (994 mg, 1.99 mmol, 47%) as a colorless oil. HRMS calcd. for $\text{C}_{28}\text{H}_{40}\text{O}_6\text{Si}+\text{H}^+$ ($\text{M}+\text{H}$) $^+$: 501.2672, found: 501.2670. $[\alpha]_{\text{D}}^{25}$ -2.5 (c 1.6, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ = 7.25 (d, J 8.8 Hz, 2H), 7.15 (d, J 8.8 Hz, 2H), 6.85 (t, J 8.4 Hz, 4H), 6.32 (dd, J 1.2 Hz, 6.0 Hz, 1H), 4.72 (d, J 10.8 Hz, 1H), 4.63 (dd, J 2.8 Hz, J 10.4 Hz, 1H), 4.53 (d, J 10.8 Hz, 1H), 4.51 (d, J 11.6 Hz, 1H), 4.48 (d, J 11.6 Hz, 1H), 4.32 (dq, J 1.2 Hz, 6.0 Hz, 1H), 4.04-4.00 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.73 (dd, J 5.6 Hz, 10.8 Hz, 1H), 3.65 (dd, J 2.4 Hz, 10.8 Hz, 1H), 3.61 (dd, J 2.4 Hz, 8.4 Hz, 1H), 0.90 (s, 9H), 0.09 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 159.5, 143.5, 130.6, 129.6, 114.0, 103.7, 76.9, 76.8, 73.7, 73.3, 69.3, 68.6, 55.44, 55.42, 26.0, 18.2, -4.2, -4.4 ppm.

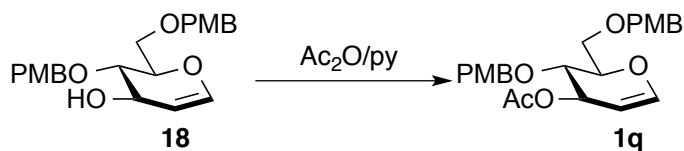
Procedure for the preparation of 4,6-di-*O*-*p*-methoxybenzyl-D-glucal (18):



Scheme S12. Synthesis of glucal **18**.

A solution of 4,6-di-*O*-*p*-methoxybenzyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **17** (900 mg, 1.8 mmol) in THF (10 mL) was cooled to 0 °C. Tetrabutylammonium fluoride solution (1.0 M in THF, 1.98 mL, 1.98 mmol) was added into the solution dropwise over 5 min. The mixture was stirred at 0 °C for 5 minutes, warmed to room temperature, stirred for another 12 h at rt., and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography (hexane:EtOAc = 3:1) to afford compound **18** (618 g, 1.6 mmol, yield 89%) as a colorless oil. HRMS calcd. for C₂₂H₂₆O₆+H⁺ (M+H)⁺: 387.1808, found: 387.1807. [α]_D²⁵ -14.8 (*c* 1.7, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.29-6.84 (m, 8H), 6.37 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.71 (dd, *J* 2.8 Hz, 6.0 Hz, 1H), 4.68 (d, *J* 11.2 Hz, 1H), 4.60 (d, *J* 11.2 Hz, 2H), 4.58 (d, *J* 11.6 Hz, 1H), 4.50 (d, *J* 11.6 Hz, 1H), 4.29 (d, *J* 5.2 Hz, 1H), 3.97-3.93 (m, 1H), 3.81-3.76 (m, 8H), 3.63 (dd, *J* 6.4 Hz, *J* 9.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 159.54, 159.47, 144.6, 130.5, 130.0, 129.8, 129.7, 114.1, 114.0, 102.8, 77.0, 76.9, 73.5, 73.4, 69.1, 68.6, 55.4 ppm.

Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-*p*-methoxybenzyl-D-glucal (1q)

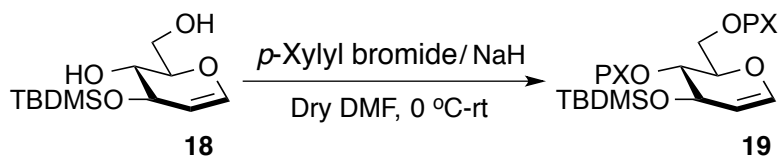


Scheme S13. Synthesis of glucal donor **1q**.

4,6-Di-*O*-*p*-methoxybenzyl-glucal, **18** (550 mg, 1.42 mmol) was dissolved in pyridine (10 mL) in a 50 mL round bottom flask. The solution was cooled in an ice bath (0-5 °C) and stirred for 10

minutes. Acetic anhydride (10 mL) and a pinch of DMAP were then added into the cooled solution, and the reaction mixture was stirred for 5 minutes at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was then removed *in vacuo* by co-evaporation with toluene (20 mL×3), and crude material was purified by flash column chromatography (hexane:EtOAc = 4:1) to afford 3-*O*-acetyl-4,6-di-*O*-*p*-methoxybenzyl-D-glucal, **1q** in 89% (538 mg, 1.26 mmol) yield as a colourless oil. HRMS calcd. for C₂₄H₂₈O₇+Na⁺ (M+Na)⁺: 451.1733, found: 451.1735. [α]_D²⁵ +10.2 (*c* 1.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.26 (d, *J* 8.8 Hz, 2H), 7.16 (d, *J* 8.8 Hz, 2H), 6.88 (dd, *J* 2.0 Hz, 6.8 Hz, 2H), 6.84 (dd, *J* 2.0 Hz, 6.8 Hz, 2H), 6.43 (dd, *J* 1.2 Hz, 6.4 Hz, 1H), 5.39 (dq, *J* 1.2 Hz, *J* 6.0 Hz, 1H), 4.74 (dd, *J* 2.8 Hz, *J* 6.0 Hz, 1H), 4.60 (d, *J* 11.2 Hz, 1H), 4.55 (d, *J* 10.8 Hz, 1H), 4.53 (d, *J* 10.4 Hz, 1H), 4.48 (d, *J* 12.0 Hz, 1H), 4.07-4.03 (m, 1H), 3.88 (dd, *J* 6.4 Hz, *J* 8.8 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.77 (dd, *J* 4.4 Hz, 10.8 Hz, 1H), 3.70 (dd, *J* 3.2 Hz, 10.8 Hz, 1H), 2.00 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 170.7, 159.51, 159.48, 146.0, 130.2, 130.1, 129.7, 129.6, 113.98, 113.97, 99.3, 77.3, 73.4, 73.3, 73.0, 71.1, 67.9, 55.4, 21.4 ppm.

Procedure for the preparation of 4,6-di-*O*-*p*-xylyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal (19**)**

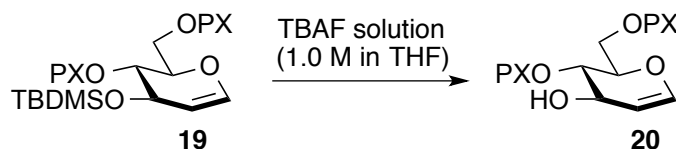


Scheme S14. Synthesis of glucal **19**.

A solution of 3-*O*-*tert*-butyldimethylsilyl-D-glucal, **11** (1.3 g, 5.0 mmol) in dry DMF (25 mL) was cooled to 0 °C. Then solution sodium hydride (60% dispersion in mineral oil) (480 mg, 20.0 mmol) was added into the solution pinch by pinch. After 15 minutes, *p*-xylyl bromide (2.8 g, 15.0 mmol) was added dropwise over 10 min and the solution was stirred at room temperature for 1 h. The reaction was poured over ice cooled water (50 mL) and extracted twice with EtOAc (50 mL×2). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure. The crude mixture was purified by flash column

chromatography (hexane:EtOAc = 17:1) to give compound **19** (1.45 g, 3.1 mmol, 62%) as a colorless oil. HRMS calcd. for $C_{28}H_{40}O_4Si+Na^+$ ($M+Na$)⁺: 491.2594, found: 491.2580. $[\alpha]_D^{25} +8.9$ (*c* 2.0, $CHCl_3$). 1H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* 7.6 Hz, 2H), 7.14-7.10 (m, 6H), 6.33 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.76 (d, *J* 11.2 Hz, 1H), 4.64 (d, *J* 2.8, 6.0 Hz, 1H), 4.57 (d, *J* 11.2 Hz, 1H), 4.54 (d, *J* 11.6 Hz, 1H), 4.51 (d, *J* 12.4 Hz, 1H), 4.33 (ddd, *J* 1.2, 2.4, 9.2 Hz, 1H), 4.06-4.02 (m, 1H), 3.76 (ddd, *J* 5.6, 10.8 Hz, 1H), 3.67 (dd, *J* 2.4, 10.8 Hz, 1H), 3.63 (dd, *J* 6.0, 8.4 Hz, 1H), 2.34 (s, 6H), 0.91 (s, 9H), 0.092 (s, 3H), 0.085 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5, 137.5, 137.4, 135.3, 135.1, 129.2, 128.1, 103.7, 76.9, 73.9, 73.5, 69.2, 68.8, 26.0, 21.3, 18.1, -4.2, -4.5 ppm.

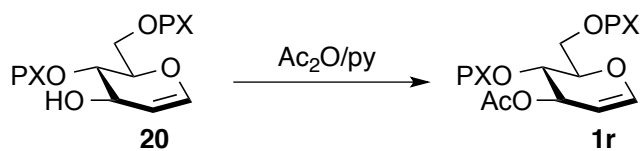
Procedure for the preparation of 4,6-di-*O*-*p*-xylyl-D-glucal (**20**)



Scheme S15. Synthesis of glucal **20**.

A solution of 4,6-di-*O*-*p*-xylyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **19** (1.36 g, 2.9 mmol) in THF (25 mL) was cooled to 0 °C. Tetrabutylammonium fluoride solution (1.0 M in THF, 3.2 mL, 3.19 mmol) was added into the solution dropwise over 5 min. The mixture was stirred at 0 °C for 5 minutes, warmed to room temperature, stirred for another 12 h at room temperature, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexane:EtOAc = 5:1) to obtain compound **20** (872 mg, 2.46 mmol, 85%) as a white solid. HRMS calcd. for $C_{22}H_{26}O_4+H^+$ ($M+H$)⁺: 355.1909, found: 355.1930. $[\alpha]_D^{25} +30.7$ (*c* 0.6, $CHCl_3$). 1H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* 8.0 Hz, 2H), 7.19-7.13 (m, 6H), 6.38 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 4.72 (dd, *J* 2.4, 6.0 Hz, 1H), 4.71 (d, *J* 11.2 Hz, 1H), 4.64 (d, *J* 11.2 Hz, 1H), 4.61 (d, *J* 11.6 Hz, 1H), 4.53 (d, *J* 11.6 Hz, 1H), 4.30 (bs, 1H), 3.96 (dt, *J* 3.2, 8.8 Hz, 1H), 3.82-3.76 (m, 2H), 3.65 (dd, *J* 6.4, 9.2 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 1.92 (d, *J* 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.7, 137.8, 137.6, 135.4, 134.9, 129.4, 129.2, 128.24, 128.17, 102.8, 77.2, 77.0, 73.73, 73.69, 69.1, 68.8 ppm. Melting point: 81 °C.

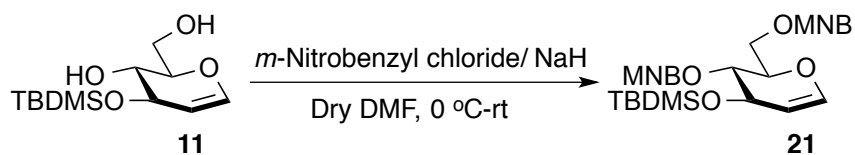
Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-*p*-xylyl-D-glucal (1r**)**



Scheme S16. Synthesis of glucal donor **1r**.

4,6-Di-*O*-*p*-xylyl-D-glucal, **20** (800 mg, 2.26 mmol) was dissolved in pyridine (10 mL) in a 50 mL round bottom flask. The solution was cooled in an ice bath (0-5 °C) and stirred for 10 minutes. Acetic anhydride (10 mL) and a pinch of DMAP were then added into the cooled solution, and the reaction mixture was stirred for 5 minutes at 0 °C. After that, the reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was then removed *in vacuo* by co-evaporation with toluene (25 mL×3), and crude material was purified by flash column chromatography (hexane:EtOAc = 6:1) to afford 3-*O*-acetyl-4,6-di-*O*-*p*-xylyl-D-glucal, **1r** in 83% (743 mg, 1.88 mmol) yield. HRMS calcd. for C₂₄H₂₈O₅+H⁺ (M+H)⁺: 397.2015, found: 397.2034. [α]_D²⁵ -3.2 (*c* 0.9, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.24 (d, *J* 7.6 Hz, 2H), 7.16 (d, *J* 8.0 Hz, 2H), 7.14 (s, 4H), 6.44 (dd, *J* 1.2 Hz, 6.0 Hz, 1H), 5.41 (dq, *J* 1.2 Hz, 6.0 Hz, 1H), 4.76 (dd, *J* 2.8 Hz, 6.0 Hz, 1H), 4.61 (d, *J* 11.2 Hz, 1H), 4.59 (dd, *J* 11.6 Hz, 1H), 4.57 (d, *J* 11.6 Hz, 1H), 4.52 (d, *J* 12.0 Hz, 1H), 4.10-4.06 (m, 1H), 3.92 (dd, *J* 6.4, 8.8 Hz, 1H), 3.80 (d, *J* 4.4, 10.8 Hz, 1H), 3.73 (dd, *J* 2.8, 10.8 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 2.00 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ = 170.7, 145.9, 137.61, 137.56, 135.1, 134.9, 129.20, 129.17, 128.11, 128.09, 99.2, 77.0, 73.6, 73.5, 73.2, 71.1, 68.0, 21.3 ppm. Melting point: 87 °C.

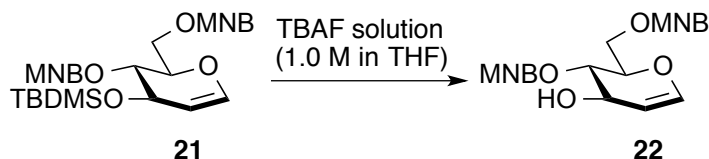
Procedure for the preparation of 4,6-di-*O*-*m*-nitrobenzyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal (21**)**



Scheme S17. Synthesis of glucal **21**.

A solution of 3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **11** (1.2 g, 4.61 mmol) in dry DMF (25 mL) was cooled to 0 °C. Then solution sodium hydride (60% dispersion in mineral oil) (322 mg, 18.44 mmol) was added into the solution pinch by pinch. *m*-Nitrobenzyl chloride (2.4 g, 13.83 mmol) was added in portions over 10 min in to the cooled solution. Then the reaction mixture was slowly warmed to room temperature and further stirred for 1 h. The reaction was poured over ice cooled water (50 mL) and extracted twice with EtOAc (50 mL×2). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure. The crude mixture was purified with silica gel flash column chromatography (hexane:EtOAc = 12:1) to give compound **21** (1.05 g, 1.98 mmol, 43%) as a colourless oil. HRMS calcd. for C₂₆H₃₄N₂O₈Si+Na⁺ (M+Na)⁺: 553.1982, found: 553.1977. [α]_D²⁵ +21.1 (*c* 2.2, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 8.19 (d, *J* 8.0 Hz, 2H), 8.14-8.10 (m, 2H), 7.63 (d, *J* 7.2 Hz, 2H), 7.49 (t, 2H, *J* 7.6 Hz), 6.42 (dd, 1H, *J* 0.8, 6.0 Hz), 4.94 (d, 1H, *J* 12.0 Hz), 4.88 (d, 1H, *J* 12.4 Hz), 4.85 (dd, 1H, *J* 2.4, 6.4 Hz), 4.75 (d, 1H, *J* 12.4 Hz), 4.62 (d, 1H, *J* 12.4 Hz), 4.29 (dt, 1H, *J* 1.6, 6.8 Hz), 3.99 (d, 1H, *J* 3.2, 11.6 Hz), 3.96-3.91 (m, 2H), 3.88 (dt, 1H, *J* 2.8, 9.2 Hz), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 148.5, 145.5, 140.8, 140.6, 133.4, 129.5, 129.4, 122.8, 122.7, 122.3, 99.2, 78.1, 77.1, 75.1, 72.9, 69.3, 61.7, 26.0, 18.5, -5.0, -5.3.

Procedure for the preparation of 4,6-di-*O*-*m*-nitrobenzyl-D-glucal (**22**)

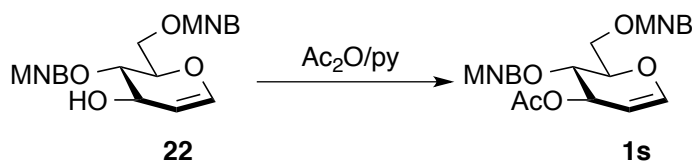


Scheme S18. Synthesis of glucal **22**.

A solution of 4,6-di-*O*-*m*-nitrobenzyl-3-*O*-(*tert*-butyldimethylsilyl)-D-glucal, **21** (960 mg, 1.81 mmol) in THF (20 mL) was cooled to 0 °C. Tetrabutylammonium fluoride solution (1.0 M in THF, 2.0 mL, 1.99 mmol) was added into the solution dropwise over 5 min. The mixture was stirred at 0 °C for 5 minutes, warmed to room temperature, stirred for another 12 h at room temperature, and concentrated under reduced pressure. The crude mixture was purified by flash

column chromatography (hexane:EtOAc = 3:1) to obtain compound **22** (640 mg, 2.46 mmol, 85%) as a white solid. HRMS calcd. for $C_{20}H_{20}N_2O_8+H^+$ (M+H)⁺: 417.1298, found: 417.1281. $[\alpha]_D^{25}$ -64.4 (*c* 0.6, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 8.18 (d, *J* 7.6 Hz, 2H), 8.12 (t, *J* 8.4 Hz, 2H), 7.64-7.61 (m, 2H), 7.49 (t, 1H, *J* 7.6 Hz), 7.48 (t, 1H, *J* 7.6 Hz), 6.44 (dd, 1H, *J* 1.2, 6.0 Hz), 4.95 (d, 1H, *J* 12.4 Hz), 4.92-4.87 (m, 2H), 4.76 (d, 1H, *J* 12.4 Hz), 4.62 (d, 1H, *J* 12.4 Hz), 4.33 (d, 1H, *J* 6.4 Hz), 3.97-3.89 (m, 4H), 1.92 (bs, 1H). ¹³C NMR (100 MHz; CDCl₃) δ : 148.5, 145.2, 140.5, 133.4, 133.2, 129.6, 129.5, 122.8, 122.3, 122.2, 99.8, 77.7, 77.0, 75.1, 72.9, 69.3, 61.5, 21.0. Melting point: 108 °C.

Procedure for the preparation of 3-*O*-acetyl-4,6-di-*O*-*m*-nitrobenzyl-D-glucal (**1s**)

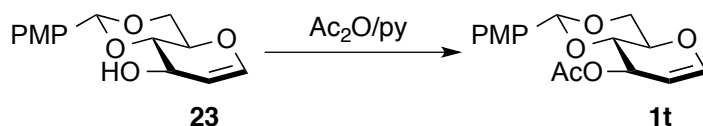


Scheme S19. Synthesis of glucal donor **1s**.

4,6-Di-*O*-*m*-nitrobenzyl-D-glucal, **22** (420 mg, 1.0 mmol) was dissolved in pyridine (7 mL) in a 25 mL round bottom flask. The solution was cooled in ice bath (0-5 °C) and stirred for 10 minutes. Acetic anhydride (7 mL) and a pinch of DMAP were added to the solution at 0 °C, and the reaction mixture was stirred for 5 minutes at 0 °C. Then the mixture was slowly warmed the room temperature and stirred for another 12 h at rt. The solvent was removed *in vacuo* by co-evaporation with toluene (25 mL×3) and the crude material was purified by flash column chromatography (hexane:EtOAc = 6:1) to afford 3-*O*-acetyl-4,6-di-*O*-*m*-nitrobenzyl-D-glucal (**1s**) as a white solid in 85% (389 mg, 0.85 mmol) yield. HRMS calcd. for $C_{22}H_{22}N_2O_9+H^+$ (M+H)⁺: 459.1404, found: 459.1413. $[\alpha]_D^{25}$ -41.7 (*c* 1.1, CHCl₃). $[\alpha]_D^{25}$ -15.5 (*c* 1.3, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 8.19-8.11 (m, 4H), 7.63-7.60 (m, 2H), 7.50 (dt, 2H, *J* 8.0 Hz), 6.44 (dd, 1H, *J* 0.8, 6.0 Hz), 4.94 (dd, 1H, *J* 2.4, 6.0 Hz), 4.93 (d, 1H, *J* 12.0 Hz), 4.80 (d, 1H, *J* 11.6 Hz), 4.77 (d, 1H, *J* 12.0 Hz), 4.60 (d, 1H, *J* 12.4 Hz), 4.47 (dd, 1H, *J* 2.4, 12.0 Hz), 4.37 (dd, 1H, *J* 5.2, 12.0 Hz), 4.30 (ddd, 1H, *J* 1.6, 2.4, 6.4 Hz), 4.16-4.12 (m, 1H), 3.83 (dd, 1H, *J* 6.0,

8.8 Hz), 2.10 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 170.8, 145.2, 140.2, 133.4, 133.2, 129.60, 129.58, 122.9, 122.4, 122.3, 99.3, 76.5, 75.2, 75.1, 72.7, 69.2, 62.6, 21.0. Melting point: 89 °C.

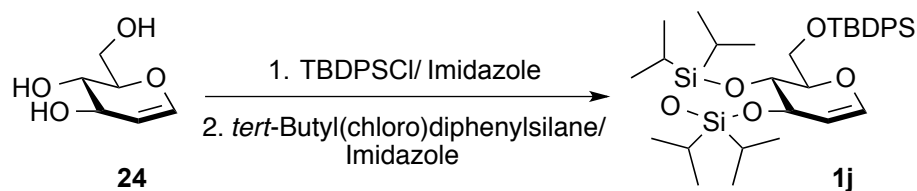
Procedure for the preparation of 3-*O*-acetyl-4,6-*O*-*p*-methoxybenzylidene-D-glucal (1t**)**



Scheme S20. Synthesis of glucal donor **1t**.

4,6-*O*-*p*-Methoxybenzylidene-D-glucal, **23**³ (530 mg, 2.0 mmol) was dissolved in pyridine (7 mL). The solution was cooled in ice bath (0-5 °C) and stirred for 10 minutes. Acetic anhydride (7 mL) and a pinch of DMAP were added to the solution and the reaction mixture was stirred for 5 minutes at 0 °C. Then the reaction mixture was slowly warmed to room temperature and stirred for another 12 h. The solvent was removed under vacuum by co-evaporation with toluene (25 mL \times 3) and crude material was purified by flash column chromatography (hexane:EtOAc = 6:1) to obtain 3-*O*-acetyl-4,6-*O*-*p*-methoxybenzylidene-D-glucal (**1t**) as a white solid in 87% (534 mg, 1.74 mmol) yield. HRMS calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_6+\text{H}^+$ ($\text{M}+\text{H}$)⁺: 307.1182, found: 307.1170. $[\alpha]_{\text{D}}^{25}$ -37.6 (*c* 1.9, CHCl_3). ^1H NMR (400 MHz; CDCl_3) δ : 7.41 (d, 2H, *J* 8.8 Hz), 6.89 (d, 2H, *J* 8.8 Hz), 6.39 (dd, 1H, *J* 1.2, 6.0 Hz), 5.55 (s, 1H), 5.51 (d, 1H, *J* 7.6 Hz), 4.80 (dd, 1H, *J* 2.0, 6.0 Hz), 4.37 (dd, 1H, *J* 4.0, 6.4 Hz), 4.04-3.95 (m, 2H), 3.83 (t, 1H, *J* 10.0 Hz), 3.80 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 170.9, 160.4, 145.6, 129.6, 127.7, 113.8, 101.8, 100.9, 77.0, 69.1, 69.0, 68.4, 55.4, 21.3. Melting point: 122 °C.

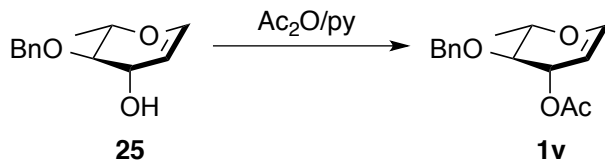
1,2-Dideoxy-3,4-*O*-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)-6-*O*-*tert*-butyldiphenylsilyl-D-arabino-1-hexenopyranose (1j**)**



Scheme S21. Synthesis of glucal donor **1j**.

Following the reported synthetic procedure⁴, D-glucal, **24** (500 mg, 3.42 mmol) and imidazole (466 mg, 6.84 mmol) were dissolved in anhydrous DMF (10 mL) under N₂ atmosphere in an oven-dried round-bottom flask and the solution was cooled to 0 °C. *tert*-Butyl(chloro)diphenylsilane (1.3 mL, 5.13 mmol) was added dropwise to the solution, the reaction was warmed to room temperature and stirred for 12 h. The reaction mixture was concentrated *in vacuo* and the residue was dissolved in EtOAc (20 mL), and washed with H₂O (20 mL). The aqueous phase was then washed with EtOAc (10 mL) and the combined organic phases were washed with saturated brine solution (10 mL×2), dried over Na₂SO₄, and concentrated *in vacuo*. Next the crude material and imidazole (466 mg, 6.84 mmol) were dissolved in dry pyridine (10 mL) under N₂ atmosphere and the solution was cooled to 0 °C. 1,3-Dichloro-1,1,3,3-tetraisopropylidisiloxane (1.6 mL, 5.13 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched with H₂O (25 mL), extracted with EtOAc (50 mL). The organic layer was washed with brine (20 mL), dried over Na₂SO₄, and concentrated *in vacuo*. Following purification by flash column chromatography (hexane:EtOAc = 99.6:0.4 to 99:1) afforded glucal **1j** as an oil (1.61 g, 2.57 mmol, 75%). HRMS calcd. for C₃₄H₅₄O₅Si₃+H⁺ (M+H)⁺: 627.3357, found: 627.3356. [α]_D²⁵ +16.4 (*c* 2.3, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.73 (d, 4H, *J* 7.2 Hz), 7.45-7.37 (m, 6H), 6.38 (d, 1H, *J* 6.0 Hz), 4.68 (d, 1H, *J* 6.0 Hz), 4.44 (dd, 1H, *J* 6.8 Hz), 4.07 (d, 1H, *J* 10.8 Hz), 4.00-3.95 (m, 2H), 3.83 (dd, 1H, *J* 3.6, 10.4 Hz), 1.13-0.94 (m, 37H). ¹³C NMR (100 MHz; CDCl₃) δ: 144.1, 136.0, 135.8, 134.0, 133.6, 129.7, 129.6, 127.7, 103.0, 79.2, 72.9, 72.4, 63.4, 27.0, 19.5, 17.8, 17.60, 17.56, 17.5, 17.4, 17.34, 17.27, 13.2, 13.0, 12.7, 12.5.

Procedure for the preparation of 3-*O*-acetyl-4-*O*-benzyl-L-rhamnal (1v**)**

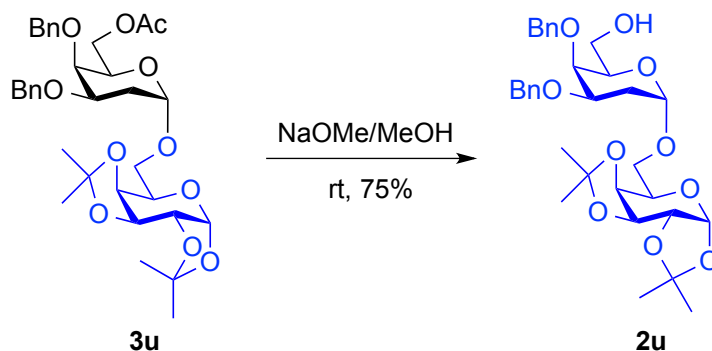


Scheme S22. Synthesis of rhamnal donor **1v**.

4-*O*-Benzyl-L-rhamnal, **25** (220 mg, 1.0 mmol) was dissolved in pyridine (4 mL) in a 25 mL round bottom flask. The solution was cooled in an ice bath (0-5 °C) and stirred for 10 minutes. Acetic anhydride (4 mL) and a pinch of DMAP were then added into the cooled solution, and the reaction mixture was stirred for another 5 minutes at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was then removed *in vacuo* by co-evaporation with toluene (15 mL×3), and crude material was purified by flash column chromatography (hexane:EtOAc = 12:1 to 8:1) to afford 3-*O*-acetyl-4-*O*-benzyl-L-rhamnal, **1v** as a colourless oil in 77% (202 mg, 0.077 mmol) yield. HRMS calcd. for C₁₅H₁₈O₄+H⁺ (M+H)⁺: 263.1283, found: 263.1291. [α]_D²⁵ +47.2 (*c* 1.4, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.38-7.27 (m, 5H), 6.39 (dd, 1H, *J* 1.2, 6.0 Hz), 5.41 (ddd, 1H, *J* 1.2, 2.8, 6.4 Hz), 4.76 (d, 1H, *J* 2.8, 6.0 Hz), 4.73 (d, 1H, *J* 11.2 Hz), 4.68 (d, 1H, *J* 11.6 Hz), 4.62 (d, 1H, *J* 12.0 Hz), 4.08-4.01 (m, 1H), 3.53 (dd, 1H, *J* 6.4, 8.8 Hz), 2.02 (s, 3H), 1.39 (d, 1H, *J* 6.8 Hz). ¹³C NMR (100 MHz; CDCl₃) δ: 170.6, 145.8, 138.0, 128.4, 127.9, 99.2, 78.2, 73.9, 73.6, 71.0, 53.5, 21.2, 17.2.

Synthesis of disaccharide acceptor **2u**:

6-*O*-(2-Deoxy-3,4-di-*O*-benzyl- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (**2u**)

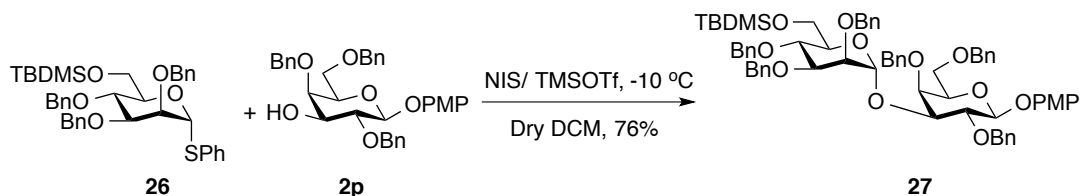


Scheme S23. Synthesis of disaccharide acceptor **2u**.

Freshly prepared NaOMe in MeOH (5 mL) solution was added to a solution of disaccharide, **3u** (108 mg, 0.1719 mmol) dissolved in MeOH (5 mL) followed by the addition of freshly prepared NaOMe in MeOH (5 mL). The reaction mixture was stirred at room temperature for 2 h till TLC showed complete conversion of the starting material. Then the solvent was evaporated under vacuum and the crude material was purified by flash column chromatography (hexane:EtOAc = 2:1) to obtain disaccharide acceptor **2u** in 75% (76.1 mg, 0.1298 mmol) yield. HRMS calcd. for $C_{32}H_{42}O_{10}+Na^+$ ($M+Na$) $^+$: 609.2676, found: 609.2685. $[\alpha]_D^{25} +15.1$ (c 1.2, $CHCl_3$). 1H NMR (400 MHz; $CDCl_3$) δ : 7.36-7.28 (m, 10H), 5.51 (d, 1H, J 4.8 Hz), 5.06 (d, 1H, J 3.2 Hz), 4.94 (d, 1H, J 11.6 Hz), 4.67 (d, 1H, J 12.0 Hz), 4.65-4.59 (m, 3H), 4.30 (d, 1H, J 2.4, 4.8 Hz), 4.22 (dd, 1H, J 1.2, 8.0 Hz), 3.98-3.92 (m, 2H), 3.87-3.68 (m, 5H), 3.57-3.51 (m, 1H), 2.23 (dt, 1H, J 3.6, 12.4 Hz), 2.05 (dd, 1H, J 4.4, 12.4 Hz), 2.05 (dd, 1H, J 3.2, 8.4 Hz), 1.51 (s, 3H), 1.43 (s, 3H), 1.33 (s, 6H). ^{13}C NMR (100 MHz; $CDCl_3$) δ : 138.66, 138.65, 128.60, 128.55, 128.0, 127.7, 127.4, 109.6, 108.7, 98.1, 96.5, 75.1, 74.2, 71.4, 70.84, 70.79, 70.7, 66.6, 66.5, 63.3, 31.2, 26.2, 26.1, 25.1, 24.7.

Synthesis of disaccharide acceptor **2v**:

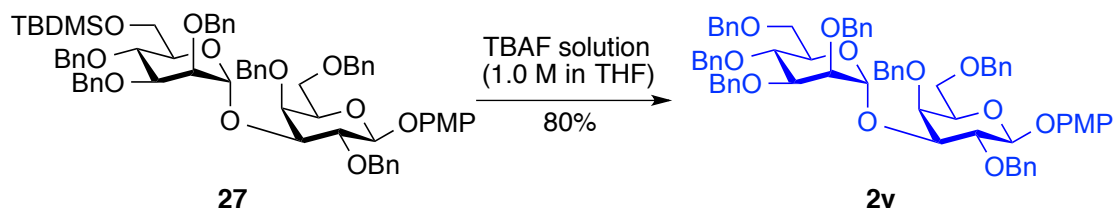
p-Methoxyphenyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)- α -D-mannopyranosyl)- β -D-galactopyranoside (**27**)



Scheme S24. Synthesis of disaccharide **27**.

A mixture of donor **26**⁵ (853 mg, 1.3 mmol), acceptor **2p** (556 mg, 1.0 mmol) and MS 4 Å (1.2 g) in anhydrous CH₂Cl₂ (25 mL) was stirred under nitrogen atmosphere for 30 min at -10 °C. NIS (380 mg, 1.69 mmol) was then added to the solution, followed by TMSOTf (71 μ L, 0.39 mmol) and the mixture was stirred for another 30 min at -10 °C, when TLC (hexane:EtOAc = 7:1) showed complete consumption of the acceptor. The mixture was filtered through a pad of Celite[®] and the filtrate was washed successively with aq. Na₂S₂O₃ (30 mL \times 2) saturated aq. NaHCO₃ (30 mL \times 2) and H₂O (30 mL). The organic layer was collected, dried (over anhydrous Na₂SO₄) and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography (hexane:EtOAc = 6:1) to afford pure disaccharide **27** (838 mg, 0.76 mmol, 76%) as a white solid. HRMS calcd. for C₆₇H₇₈O₁₂Si+Na⁺ (M+Na)⁺: 1125.5160, found: 1125.5162; C₆₇H₇₈O₁₂Si+H⁺ (M+H)⁺: 1103.5341, found: 1103.5341. [α]_D²⁵ -85.1 (*c* 0.7, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 7.42-7.24 (m, 26H), 7.23-7.15 (m, 2H), 7.09-7.01 (m, 4H), 6.84-6.80 (m, 2H), 5.05 (d, 1H, *J* 1.2), 5.01 (d, 1H, *J* 10.8 Hz), 4.86 (d, 1H, *J* 7.6 Hz), 4.85 (d, 1H, *J* 10.0 Hz), 4.80 (d, 1H, *J* 12.8 Hz), 4.73-4.67 (m, 4H), 4.59 (d, 1H, *J* 12.8 Hz), 4.54 (d, 1H, *J* 12.0 Hz), 4.47 (d, 1H, *J* 11.6 Hz), 4.43 (d, 1H, *J* 11.6 Hz), 4.31 (d, 1H, *J* 11.6 Hz), 4.11-3.86 (m, 6H), 3.79 (s, 3H), 3.75-3.65 (m, 6H), 0.90 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ : 155.4, 151.8, 139.4, 138.69, 138.65, 138.6, 138.1, 138.0, 129.14, 129.11, 128.60, 128.49, 128.47, 128.43, 128.40, 127.94, 127.87, 127.74, 127.67, 127.5, 118.6, 114.6, 103.3, 94.3, 79.9, 77.5, 75.70, 75.66, 75.14, 75.11, 75.0, 74.9, 73.8, 73.4, 73.2, 72.9, 72.6, 72.5, 68.7, 62.5, 55.8, 26.1, 18.4, -5.0, -5.3. Melting point: 160 °C.

***p*-Methoxyphenyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)- β -D-galactopyranoside (**2v**)**



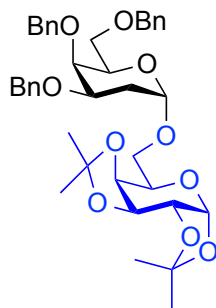
Scheme S25. Synthesis of disaccharide acceptor **2v**.

A solution of disaccharide **27** (800 mg, 0.73 mmol) in THF (25 mL) was cooled to 0 °C. Then tetrabutylammonium fluoride solution (1.0 M in THF, 0.8 mL, 0.8 mmol) was added dropwise over 5 min to the solution and stirred at 0 °C for 5 minutes. The reaction mixture was then warmed to room temperature and stirred for another 4 h at room temperature, then concentrated under reduced pressure. The concentrated crude was purified by flash column chromatography with hexane:EtOAc (3:1) to obtain disaccharide acceptor **2v** (574 mg, 0.58 mmol, 80%) as a white foam. HRMS calcd. for $C_{61}H_{64}O_{12}+Na^+$ ($M+Na$) $^+$: 1011.4295, found: 1011.4297. $[\alpha]_D^{25}$ -66.8 (c 1.8, $CHCl_3$). 1H NMR (400 MHz; $CDCl_3$) δ : 7.39-7.14 (m, 28H), 7.07 (t, 2H, J 7.2 Hz), 7.00 (d, 1H, J 9.2 Hz), 6.78 (d, 1H, J 9.2 Hz), 4.97 (d, 1H, J 11.2 Hz), 4.95 (d, 1H, J 1.2 Hz), 4.88 (d, 1H, J 10.0 Hz), 4.84 (d, 1H, J 7.6 Hz), 4.80 (d, 1H, J 12.8 Hz), 4.69-4.61 (m, 4H), 4.57 (d, 1H, J 12.8 Hz), 4.51 (d, 1H, J 11.6 Hz), 4.44 (d, 1H, J 11.6 Hz), 4.32 (d, 1H, J 11.6 Hz), 4.26 (d, 1H, J 11.6 Hz), 4.03-3.88 (m, 4H), 3.79-3.76 (m, 5H), 3.69-3.54 (m, 6H), 1.70 (bs, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ : 155.4, 151.6, 138.9, 138.53, 138.50, 138.3, 138.0, 137.7, 129.1, 128.60, 128.56, 128.5, 128.4, 128.3, 128.13, 128.07, 128.0, 127.9, 127.8, 127.71, 127.68, 127.6, 118.5, 114.6, 103.2, 95.2, 80.0, 77.3, 76.3, 75.6, 75.3, 74.9, 74.5, 73.8, 73.3, 72.8, 72.6, 72.4, 68.5, 62.1, 55.8.

General procedure for Iridium catalyzed stereoselective glycosylation to synthesize 2-deoxyglycosides:

In an oven-dried 10 mL round bottom flask glycal donor (0.15 mmol, 1.5 equiv.) and acceptor (0.1 mmol, 1.0 equiv.) were weighed and placed under vacuum for 2 h, then the round bottom flask was filled with N₂. In a seal tube, a suspension of active catalyst was prepared by mixing [Ir(COD)Cl]₂ (0.00525 mmol, 3.5 mol% w.r.t. glycal donor) and AgOTf (0.01575 mmol, 10.5 mol% w.r.t. glycal donor) in anhydrous DCM (1 mL) and stirred vigorously for 30 minutes under N₂ atmosphere. Then the mixture of donor and acceptor was dissolved in anhydrous DCM (2 mL), and the solution was transferred to the seal tube containing Ir(I) catalyst using a cannula under N₂ atmosphere. The reaction mixture was stirred at ambient temperature for 24 h under N₂ atmosphere, after which the solvent was removed, and the crude product was purified by flash column chromatography (Hexane/EtOAc).

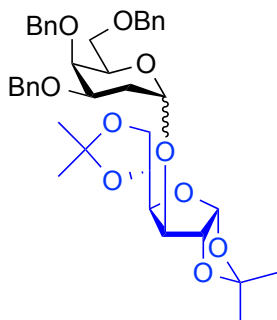
6-*O*-(2-Deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl)-1,2:3,4-Di-*O*-isopropylidene- α -D-galactopyranose (**3a**)



Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 4:1) product **3a** was obtained as a colourless oil (52 mg, 0.077 mmol, 77%). HRMS calcd. for C₃₉H₄₈O₁₀+Na⁺ (M+Na)⁺: 699.3145, found: 699.3160. [α]_D²⁵ +37.5 (c 1.6, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.36-7.25 (m, 15H), 5.53 (d, 1H, *J* 5.2 Hz), 5.04 (d, 1H, *J* 2.8 Hz), 4.93 (d, 1H, *J* 11.6 Hz), 4.63 (d, 1H, *J* 11.6 Hz), 4.62 (d, 1H, *J* 12.0 Hz), 4.60 (d, 1H, *J* 7.6 Hz), 4.58 (d, 1H, *J* 12.4 Hz), 4.50 (d, 1H, *J* 12.0 Hz), 4.43 (d, 1H, *J* 11.6 Hz), 4.32 (d, 1H, *J* 2.4, 4.8 Hz), 4.22 (d, 1H,

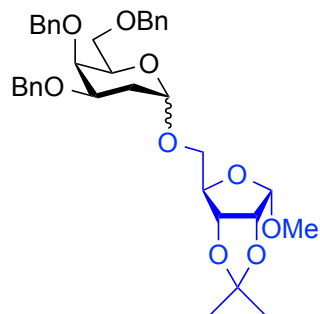
J 1.6, 8.0 Hz), 4.00-3.95 (m, 4H), 3.76 (dd, 1H, J 6.8, 10.8 Hz), 3.68 (dd, 1H, J 6.8, 11.2 Hz), 3.63 (dd, 1H, J 7.2, 8.8 Hz), 3.56 (dd, 1H, J 5.6, 8.8 Hz), 2.23 (dt, J 3.2, 11.6 Hz), 2.04 (dd, J 4.4, 12.4 Hz), 1.53 (s, 3H), 1.44 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (100 MHz; CDCl_3) δ : 139.1, 138.8, 138.3, 128.5, 128.33, 128.30, 127.9, 127.7, 127.6, 127.4, 109.4, 108.7, 97.7, 96.5, 74.9, 74.4, 73.5, 73.1, 71.3, 70.84, 70.79, 70.6, 70.0, 69.4, 66.1, 65.7, 31.3, 26.3, 26.1, 25.1, 24.7. Spectroscopic data was in agreement with the previously reported literature.⁶

3-*O*-(2-Deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl)1,2:5,6-Di-*O*-isopropylidene- α -D-glucopyranose (3b**)**



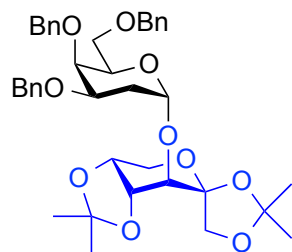
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2b**: 26 mg (0.1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$: 3.4 mg (0.00525 mmol), AgOTf : 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 9:1 to 4:1) product **3b** was obtained as a colourless oil (45 mg, 0.067 mmol, 67%). HRMS calcd. for $\text{C}_{39}\text{H}_{48}\text{O}_{10}+\text{H}^+$ ($\text{M}+\text{H}$) $^+$: 677.3326, found: 677.3332. ^1H NMR (400 MHz; CDCl_3) δ : 7.38-7.24 (m, 17.38H), 5.99 (d, 0.19H, J 3.6 Hz), 5.83 (d, 1H, J 3.6 Hz), 5.25 (d, 1H, J 3.2 Hz), 5.03 (d, 0.19H, J 3.2 Hz), 4.94 (d, 1H, J 11.6 Hz), 4.93 (d, 0.2H, J 11.6 Hz), 4.68 (d, 1.08H, J 3.6 Hz), 4.50 (d, 1H, J 12.0 Hz), 4.64-4.57 (m, 4H), 4.52 (d, 1.32H, J 11.6 Hz), 4.43 (d, 1.24H, J 11.6 Hz), 4.27 (dd, 0.25H, J 3.6, 6.4 Hz), 4.22 (d, 1H, J 2.8 Hz), 4.20-4.15 (m, 1.27H), 4.10-4.07 (m, 2.17H), 4.00-4.80 (m, 4.8H), 3.73-3.54 (m, 3.22H), 2.23 (dt, J 3.6, 12.4 Hz), 2.00 (dd, J 4.0, 12.4 Hz), 1.48 (s, 3.66H), 1.40 (s, 3H), 1.33 (s, 4.8H), 1.21 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 138.9, 138.5, 138.2, 128.6, 128.53, 128.51, 128.47, 128.4, 128.3, 112.3, 111.9, 109.2, 106.5, 105.4, 100.9, 99.7, 97.7, 84.2, 83.7, 81.5, 81.1, 79.6, 75.1, 74.7, 74.6, 74.4, 73.8, 73.5, 73.24, 73.19, 72.7, 71.3, 71.1, 70.6, 70.5, 70.2, 69.9, 69.4, 67.8, 67.4, 31.2, 27.3, 27.0, 26.9, 26.7, 26.3, 25.5, 24.2, 24.1.⁶

Methyl 2,3-*O*-isopropylidene-5-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl-*D*-galactopyranosyl)- α -*D*-ribofuranoside (3c)



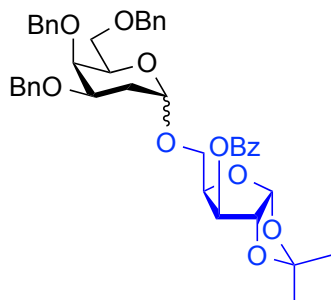
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2c**⁷: 20.4 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 6:1 to 2:1) product **3c** was obtained as a colourless oil (53 mg, 0.085 mmol, 85%). HRMS calcd. for C₃₆H₄₄O₉+H⁺ (M+H)⁺: 621.3064, found: 621.3059. ¹H NMR (400 MHz; CDCl₃) δ : 7.36-7.25 (m, 15H), 4.98 (d, 1H, *J* 2.8 Hz), 4.95 (s, 1H), 4.93 (d, 1H, *J* 11.6 Hz), 4.68-4.56 (m, 5H), 4.50 (d, 1H, *J* 12.0 Hz), 4.42 (d, 1H, *J* 11.6 Hz), 4.32 (d, 1H, *J* 5.6, 8.8 Hz), 3.96-3.90 (m, 3H), 3.68 (dd, 1H, *J* 5.6, 10.0 Hz), 3.62 (dd, 1H, *J* 7.2, 9.2 Hz), 3.56 (dd, 1H, *J* 6.0, 9.2 Hz), 3.36 (d, 1H, *J* 9.2, 10.0 Hz), 3.28 (s, 3H), 2.22 (dt, 1H, *J* 3.6, 12.4 Hz), 2.03 (dd, 1H, *J* 4.4, 12.8 Hz), 1.49 (s, 3H), 1.34 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ : 139.0, 138.7, 138.3, 128.53, 128.50, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 112.5, 109.5, 98.7, 85.4, 85.3, 82.5, 74.9, 74.5, 73.6, 73.1, 70.7, 70.2, 69.5, 68.7, 55.0, 31.2, 26.6, 25.2 ppm. Spectroscopic data was in agreement with the previously reported literature.⁸

3-*O*-(2-Deoxy-3,4,6-tri-*O*-benzyl-*D*-galactopyranosyl)-1,2:4,5-Di-*O*-isopropylidene- α -*D*-fructopyranose (3d)



Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2d**⁷: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 6:1 to 3:1) product **3d** was obtained as a colourless oil (52 mg, 0.077 mmol, 77%). HRMS calcd. for C₃₉H₄₈O₁₀+H⁺ (M+H)⁺: 677.3326, found: 677.3326. [α]_D²⁵ -50.9 (*c* 1.4, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 7.34-7.25 (m, 15H), 5.57 (d, 1H, *J* 3.2 Hz), 4.92 (d, 1H, *J* 11.6 Hz), 4.62 (d, 1H, *J* 11.6 Hz), 4.59 (d, 1H, *J* 12.4 Hz), 4.56 (d, 1H, *J* 12.4 Hz), 4.47 (d, 1H, *J* 12.0 Hz), 4.42 (d, 1H, *J* 12.0 Hz), 4.26 (dd, 1H, *J* 5.2, 7.2 Hz), 4.16-4.09 (m, 3H), 4.01 (d, 1H, *J* 13.2 Hz), 3.93-3.84 (m, 4H), 3.76 (d, 1H, *J* 7.6 Hz), 3.57-3.59 (m, 2H), 2.28 (dt, 1H, 4.0, 12.4 Hz), 2.08 (dd, *J* 4.4, 12.4 Hz), 1.50 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ : 138.9, 138.6, 138.3, 128.6, 128.5, 128.3, 127.84, 127.76, 127.7, 127.5, 112.1, 104.5, 97.6, 78.2, 74.4, 74.0, 73.9, 73.6, 73.0, 72.4, 70.9, 70.3, 69.8, 60.5, 31.5, 28.3, 26.6, 26.5, 26.3.

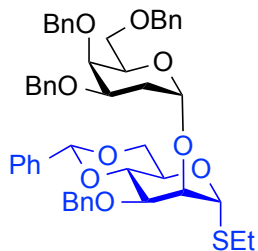
3-*O*-Benzoyl-5-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl)-1,2-*O*-isopropylidene- α -D-xylofuranose (3e**)**



Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2e**⁹: 29.4 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 6:1 to 3:2) product **3e** was obtained as a colourless oil (56 mg, 0.079 mmol, 79%). HRMS calcd. for C₄₂H₄₆O₁₀+H⁺ (M+H)⁺: 711.3169, found: 711.3168. ¹H NMR (400 MHz; CDCl₃) δ : 8.05 (dd, 2H, *J* 1.2, 8.4 Hz), 7.57 (t, 1H, *J* 7.6 Hz), 7.45 (t, 1H, *J* 7.6 Hz), 7.36-7.25 (m, 20H), 5.91 (d, 1H, *J* 3.6 Hz), 5.11 (d, 1H, *J* 3.2 Hz), 4.92 (d, 1H, *J* 11.6 Hz), 4.86 (d, 1H, *J* 3.6 Hz), 4.62-4.55 (m, 4H), 4.54-4.42 (d, 4H), 4.22 (d, 1H, *J* 2.8 Hz), 3.93 (t, 1H, *J* 6.0 Hz), 3.89-3.85 (m, 2H), 3.62 (dd, 1H, *J* 6.8, 10.0 Hz), 3.47 (dd, 1H, *J* 5.2, 10.0 Hz), 2.20 (dt, 1H, *J* 3.6, 11.6 Hz), 1.99 (dd, 1H, *J*

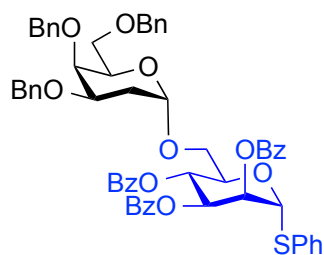
4.4, 12.8 Hz), 1.49 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 166.3, 138.8, 138.4, 138.1, 133.3, 129.8, 128.6, 128.5, 128.40, 128.38, 127.9, 127.83, 127.78, 127.75, 127.5, 111.9, 105.3, 100.4, 83.2, 82.5, 78.0, 74.40, 74.35, 73.8, 73.3, 71.4, 70.7, 70.5, 62.2, 31.3, 26.9, 26.2.

Ethyl 4,6-O-benzylidene-3-O-benzyl-2-O-(2-deoxy-3,4,6-tri-O-benzyl- α -D-galactopyranosyl)-1-thio- α -D-mannopyranoside (3f)



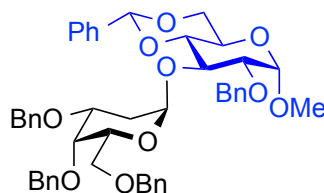
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2f**¹⁰: 40.2 mg (0.1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$: 3.4 mg (0.00525 mmol), AgOTf : 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 7:1 to 3:1) product **3f** was obtained as a colourless oil (53 mg, 0.065 mmol, 65%). HRMS calcd. for $\text{C}_{49}\text{H}_{54}\text{O}_9\text{S}+\text{H}^+$ ($\text{M}+\text{H}$)⁺: 819.3567, found: 819.3572. $[\alpha]_{\text{D}}^{25} +27.2$ (c 1.2, CHCl_3). ^1H NMR (400 MHz; CDCl_3) δ : 7.54-7.27 (m, 25H), 5.63 (s, 1H), 5.37 (s, 1H), 5.18 (d, 1H, J 2.4 Hz), 4.94 (d, 1H, J 11.6 Hz), 4.81 (d, 1H, J 12.0 Hz), 4.65-4.61 (m, 4H), 4.49 (d, 1H, J 12.0 Hz), 4.43 (d, 1H, J 12.0 Hz), 4.24-3.98 (m, 6H), 3.92-3.89 (m, 2H), 3.86-3.80 (m, 1H), 3.59 (dd, 1H, J 6.8, 9.6 Hz), 3.51-3.46 (m, 1H), 2.46 (q, 1H, J 7.2 Hz), 2.26-2.16 (m, 2H), 1.17 (t, 1H, J 7.6 Hz). ^{13}C NMR (100 MHz; CDCl_3) δ : 138.9, 138.6, 138.5, 138.2, 137.8, 129.0, 128.6, 128.52, 128.48, 128.40, 128.36, 128.3, 127.9, 127.80, 127.77, 127.70, 127.65, 127.6, 126.3, 101.7, 100.7, 85.5, 79.3, 78.2, 76.4, 74.6, 74.3, 73.6, 73.3, 73.0, 70.9, 70.53, 70.48, 68.9, 64.7, 31.1, 25.8, 15.1.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl- α -D-galactopyranosyl)-1-thio- α -D-mannopyranoside (3g)



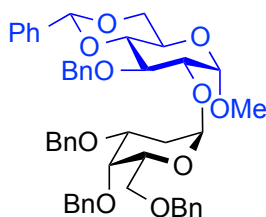
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2g**¹¹: 58.4 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 7:1 to 3:2) product **3g** was obtained as a colourless oil (75 mg, 0.075 mmol, 75%). HRMS calcd. for C₆₀H₅₆O₁₂S+Na⁺ (M+Na)⁺: 1023.3390, found: 1023.3407. [α]_D²⁵ +3.1 (*c* 1.6, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 8.08 (dd, 2H, *J* 1.2, 8.4 Hz), 7.98 (dd, 2H, *J* 1.2, 8.4 Hz), 7.86 (dd, 2H, *J* 1.2, 8.4 Hz), 7.58-7.14 (m, 29H), 6.10 (d, 1H, *J* 10.0 Hz), 5.94 (dd, 1H, *J* 2.0, 3.2 Hz), 5.82 (dd, 1H, *J* 3.2, 10.0 Hz), 5.76 (d, 1H, *J* 1.6 Hz), 5.02 (d, 1H, *J* 3.2 Hz), 4.87 (d, 1H, *J* 11.6 Hz), 4.81-4.77 (m, 1H), 4.55 (d, 1H, *J* 11.2 Hz), 4.53 (d, 1H, *J* 11.6 Hz), 4.47 (d, 1H, *J* 11.6 Hz), 4.29 (d, 1H, *J* 12.0 Hz), 4.21 (d, 1H, *J* 12.0 Hz), 3.98-3.92 (m, 2H), 3.88 (bs, 1H), 3.85 (t, 1H, *J* 6.4 Hz), 3.67 (dd, 1H, *J* 1.6, 11.6 Hz), 3.44 (dd, 1H, *J* 7.2, 9.2 Hz), 3.40 (dd, 1H, *J* 6.0, 9.2 Hz), 2.18 (dt, 1H, *J* 3.6, 12.4 Hz), 1.98 (dd, 1H, *J* 4.4, 12.8 Hz). ¹³C NMR (100 MHz; CDCl₃) δ : 165.64, 165.62, 165.5, 139.0, 138.7, 138.3, 133.7, 133.5, 133.4, 133.1, 132.1, 130.0, 129.9, 129.5, 129.34, 129.32, 129.1, 128.7, 128.6, 128.49, 128.46, 128.4, 128.27, 128.25, 128.2, 127.63, 127.59, 127.55, 127.4, 98.1, 86.0, 75.2, 74.4, 73.3, 73.1, 72.1, 70.8, 70.6, 70.0, 67.5, 66.1, 31.1.

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl- α -D-galactopyranosyl)- α -D-glucopyranoside (3h)



Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2h**^{6c}: 37.2 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 7:1 to 2:1) product **3h** was obtained as a white solid (53 mg, 0.067 mmol, 67%). HRMS calcd. for C₄₈H₅₂O₁₀+H⁺ (M+H)⁺: 789.3639, found: 789.3636. [α]_D²⁵ +41.4 (*c* 1.8, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.45-7.25 (m, 25H), 5.56 (d, 1H, *J* 2.8 Hz), 5.52 (s, 1H), 4.92 (d, 1H, *J* 11.6 Hz), 4.72 (d, 1H, *J* 11.6 Hz), 4.64 (d, 1H, *J* 11.2 Hz), 4.59 (d, 1H, *J* 11.6 Hz), 4.56 (d, 1H, *J* 11.2 Hz), 4.55 (d, 1H, *J* 4.0 Hz), 4.52 (d, 1H, *J* 12.4 Hz), 4.45 (d, 1H, *J* 11.6 Hz), 4.40 (d, 1H, *J* 11.6 Hz), 4.33-4.23 (m, 3H), 3.97-3.92 (m, 2H), 3.85-3.79 (m, 1H), 3.72-3.63 (m, 3H), 3.57 (t, 1H, *J* 9.2 Hz), 3.80 (dd, 1H, *J* 3.6, 9.6 Hz), 3.35 (s, 3H), 2.23 (dt, 1H, 3.6, 12.8 Hz), 2.06 (dd, 1H, *J* 4.4, 12.8 Hz). ¹³C NMR (100 MHz; CDCl₃) δ: 139.2, 138.8, 138.6, 138.2, 137.3, 129.1, 128.6, 128.5, 128.4, 128.34, 128.27, 128.1, 128.0, 127.59, 127.55, 127.5, 127.4, 126.1, 101.4, 99.1, 97.9, 83.1, 78.3, 74.54, 74.45, 73.6, 73.2, 72.6, 70.2, 69.7, 69.2, 69.1, 62.1, 55.3, 31.3. Melting point: 126 °C. Spectroscopic data was in agreement with the previously reported literature.^{6c,8}

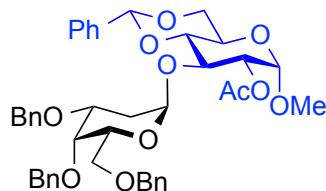
Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl-α-*D*-galactopyranosyl)-α-*D*-glucopyranoside (3i)



Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2i**^{6c}: 37.2 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 6:1 to 2:1) product **3i** was obtained as a white solid (42 mg, 0.053 mmol, 53%). HRMS calcd. for C₄₈H₅₂O₁₀+Na⁺ (M+Na)⁺: 811.3458, found: 811.3462. [α]_D²⁵ +48.6 (*c* 1.1, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.49-7.20 (m, 25H), 5.52 (s, 1H), 5.15 (d, 1H, *J* 2.4 Hz), 4.92-4.90 (m, 2H), 4.86 (d, 1H, *J* 11.2 Hz), 4.66 (d, 1H, *J* 11.6 Hz), 4.59 (d, 1H, *J* 11.6 Hz), 4.53 (s, 2H), 4.55 (d, 1H, *J* 4.0 Hz), 4.52 (d, 1H, *J* 12.4 Hz), 4.45 (d, 1H, *J* 11.6 Hz), 4.40 (d, 1H, *J* 11.6 Hz), 4.39 (d, 1H, *J*

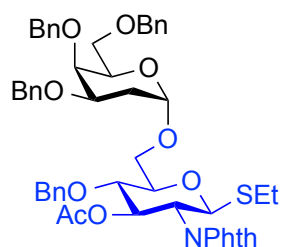
12.4 Hz), 4.36 (d, 1H, *J* 12.4 Hz), 4.28 (dd, 1H, *J* 4.8, 10.0 Hz), 4.17 (d, 1H, *J* 6.8 Hz), 3.96-3.88 (m, 3H), 3.85-3.79 (m, 1H), 3.76 (bs, 1H), 3.70 (t, 1H, *J* 10.0 Hz), 3.62-3.52 (m, 2H), 3.48-3.44 (m, 4H), 2.25 (dt, 1H, 3.6, 12.4 Hz), 2.08 (dd, 1H, *J* 4.0, 12.8 Hz). ¹³C NMR (100 MHz; CDCl₃) δ: 139.0, 138.9, 138.7, 138.6, 137.6, 129.0, 128.37, 128.35, 128.33, 128.31, 128.1, 127.72, 127.66, 127.6, 127.54, 127.47, 126.2, 101.3, 97.4, 94.2, 82.3, 75.5, 74.6, 74.5, 73.1, 73.0, 70.6, 69.7, 69.6, 69.2, 62.5, 55.4, 31.0. Melting point: 129 °C. Spectroscopic data was in agreement with the previously reported literature.^{6c}

Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl- α -D-galactopyranosyl)- α -D-glucopyranoside (3j)



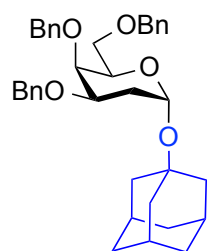
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2j**¹²: 32.4 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc, 6:1 to 3:2) product **3j** was obtained as a colourless oil (52 mg, 0.07 mmol, 70%). HRMS calcd. for C₄₃H₄₈O₁₁+NH₄⁺ (M+NH₄)⁺: 758.3540, found: 758.3540; C₄₃H₄₈O₁₁+H⁺ (M+H)⁺: 741.3275, found: 741.3277. [α]_D²⁵ +55.9 (*c* 1.7, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.46-7.26 (m, 29H), 5.58 (s, 1H), 5.47 (d, 1H, *J* 3.2 Hz), 4.96 (d, 1H, *J* 3.6 Hz), 4.93 (d, 1H, *J* 12.0 Hz), 4.82 (dd, 1H, *J* 4.0, 10.0 Hz), 4.63 (d, 1H, *J* 11.6 Hz), 4.61 (s, 2H), 4.51 (d, 1H, *J* 11.6 Hz), 4.42 (d, 1H, *J* 11.6 Hz), 4.34 (d, 1H, *J* 9.6 Hz), 4.30 (t, 1H, *J* 5.2 Hz), 4.05 (d, 1H, *J* 5.6, 9.2 Hz), 3.97 (bz, 1H), 3.92-3.84 (m, 2H), 3.78 (t, 1H, *J* 10.0 Hz), 3.71 (d, 1H, *J* 8.8 Hz), 3.66 (d, 1H, *J* 9.6 Hz), 3.62 (dd, 1H, *J* 5.2, 8.8 Hz), 3.40 (s, 3H), 2.23 (dt, 1H, 3.6, 12.4 Hz), 2.06 (dd, 1H, *J* 4.4, 13.2 Hz), 2.05 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 170.7, 139.0, 138.7, 138.3, 137.2, 129.2, 128.5, 128.44, 128.41, 128.3, 128.0, 127.8, 127.6, 127.5, 126.0, 101.4, 98.5, 97.7, 82.7, 74.8, 74.5, 73.6, 73.1, 72.3, 71.9, 70.6, 70.3, 69.2, 69.1, 62.1, 55.4, 31.2, 20.9.

Ethyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-6-*O*-(2-deoxy-3,4,6-tri-*O*-benzyl- α -D-galactopyranosyl)-1-thio- β -D-glucopyranoside (3k**)**



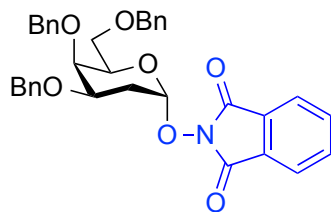
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2k**¹³: 48.5 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 6:1 to 3:2) product **3k** was obtained as a colourless oil (42 mg, 0.047 mmol, 47%). HRMS calcd. for C₅₂H₅₅NO₁₁S+H⁺ (M+H)⁺: 902.3574, found: 902.3577; C₅₂H₅₅NO₁₁S+NH₄⁺ (M+NH₄)⁺: 919.3840, found: 919.3845. [α]_D²⁵ +21.6 (*c* 1.9, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 7.88-7.22 (m, 24H), 5.83 (dd, 1H, *J* 8.4, 10.0 Hz), 5.49 (d, 1H, *J* 10.4 Hz), 5.14 (d, 1H, *J* 2.8 Hz), 5.97 (d, 1H, *J* 10.6 Hz), 4.67 (s, 2H), 4.66 (d, 1H, *J* 11.6 Hz), 4.60 (d, 1H, *J* 11.6 Hz), 4.57 (d, 1H, *J* 11.6 Hz), 4.51 (d, 1H, *J* 12.0 Hz), 4.43 (d, 1H, *J* 11.6 Hz), 4.30 (t, 1H, *J* 10.4 Hz), 3.99-3.94 (m, 3H), 3.89 (dd, 1H, *J* 3.6, 12.0 Hz), 3.80 (d, 1H, *J* 11.6 Hz), 3.75-3.68 (m, 2H), 3.64-3.57 (m, 2H), 2.72-2.56 (m, 2H), 2.27 (dt, 1H, 3.2, 12.4 Hz), 2.11 (dd, 1H, *J* 3.6, 12.4 Hz), 1.80 (s, 3H), 1.20 (t, 3H, *J* 7.6 Hz). ¹³C NMR (100 MHz; CDCl₃) δ : 170.1, 167.8, 167.7, 139.0, 138.6, 138.3, 137.9, 134.4, 134.1, 131.9, 131.3, 129.8, 129.1, 128.5, 128.4, 128.3, 127.9, 127.8, 127.67, 127.65, 127.60, 127.56, 127.5, 123.7, 123.6, 98.6, 80.8, 78.8, 77.0, 74.5, 74.4, 74.2, 73.4, 73.2, 70.4, 70.2, 69.5, 66.0, 54.4, 31.1, 24.3, 20.6, 15.2.

1-Adamantyl 2-deoxy-3,4,6-tri-*O*-benzyl- α -D-galactopyranoside (3l**)**



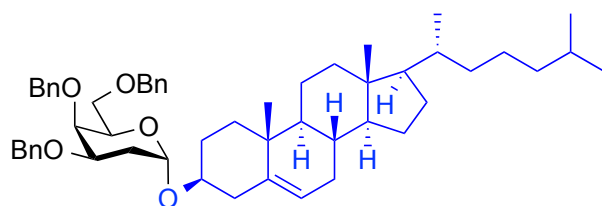
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2r**: 15.2 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc, 10:1 to 6:1) product **3l** was obtained as a colourless oil (36 mg, 0.063 mmol, 63%). HRMS calcd. for C₃₇H₄₄O₅+H⁺ (M+H)⁺: 569.3267, found: 569.3273. [α]_D²⁵ -26.3 (c 1.3, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.38-7.24 (m, 15H), 5.41 (d, 1H, *J* 2.8 Hz), 4.93 (d, 1H, *J* 11.6 Hz), 4.65-4.58 (m, 3H), 4.50 (d, 1H, *J* 11.6 Hz), 4.43 (d, 1H, *J* 11.6 Hz), 4.11 (t, 1H, *J* 6.8 Hz), 4.02-3.97 (m, 1H), 3.95 (bs, 1H), 3.63 (dd, 1H, *J* 7.6, 8.8 Hz), 3.53 (dd, 1H, *J* 5.6, 9.2 Hz), 2.23 (dd, 1H, *J* 3.6, 12.0 Hz), 2.10 (bs, 3H), 1.85-1.75 (m, 7H), 1.64-1.57 (m, 6H). ¹³C NMR (100 MHz; CDCl₃) δ: 139.3, 138.9, 138.5, 128.49, 128.45, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 91.1, 75.3, 74.4, 73.8, 73.6, 73.5, 70.5, 69.8, 69.5, 42.7, 36.5, 32.9, 30.8.

Phthalimidyl 2-deoxy-3,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**3m**)



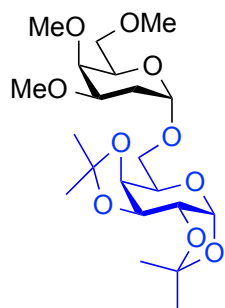
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2s**: 16.3 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 7:1 to 2:1) product **3m** was obtained as a colourless oil (45 mg, 0.078 mmol, 78%). HRMS calcd. for C₃₅H₃₃NO₇+H⁺ (M+H)⁺: 580.2335, found: 580.2335; C₃₅H₃₃NO₇+Na⁺ (M+Na)⁺: 602.2155, found: 602.2151. [α]_D²⁵ +104.7 (c 2.0, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.82-7.78 (m, 2H), 7.74-7.70 (m, 2H), 7.37-7.25 (m, 15H), 5.60 (bs, 1H), 4.95 (d, 1H, *J* 11.6 Hz), 4.80 (t, 1H, *J* 6.8 Hz), 4.65 (s, 2H), 4.64 (d, 1H, *J* 11.6 Hz), 4.55 (d, 1H, *J* 12.0 Hz), 4.48 (d, 1H, *J* 12.0 Hz), 4.13-4.08 (m, 2H), 3.66 (dd, 1H, *J* 8.0, 9.6 Hz), 3.55 (dd, 1H, *J* 5.6, 9.2 Hz), 2.43-2.39 (m, 2H). ¹³C NMR (100 MHz; CDCl₃) δ: 163.7, 138.9, 138.5, 138.4, 134.5, 129.2, 128.40, 128.37, 128.3, 127.8, 127.7, 127.6, 127.5, 123.6, 104.0, 74.6, 73.8, 73.3, 72.8, 71.9, 70.7, 68.8, 28.9.

Cholesteryl 2-deoxy-3,4,6-tri-*O*-benzyl- α -D-galactopyranoside (**3n**)



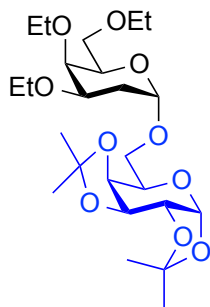
Following *General Glycosylation Procedure*. Galactal **1a**: 62 mg (0.15 mmol), acceptor **2t**: 39 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 12:1 to 7:1) product **3n** was obtained as a white solid (55.2 mg, 0.069 mmol, 69%). HRMS calcd. for C₅₄H₇₄O₅+H⁺ (M+H)⁺: 803.5615, found: 803.5626. [α]_D²⁵ +30.8 (*c* 2.0, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.35-7.24 (m, 15H), 5.26 (d, 1H, *J* 4.4 Hz), 5.15 (d, 1H, *J* 2.8 Hz), 4.94 (d, 1H, *J* 11.6 Hz), 4.63 (d, 1H, *J* 9.6 Hz), 4.62 (s, 2H), 4.51 (d, 1H, *J* 11.6 Hz), 4.43 (d, 1H, *J* 12.0 Hz), 4.03-3.95 (m, 3H), 3.64-3.56 (m, 2H), 3.50-3.42 (m, 1H), 2.30-2.27 (m, 2H), 2.22 (dd, 1H, *J* 3.6, 12.0 Hz), 2.03-2.79 (m, 6H), 1.60-0.87 (m, 37H), 0.68 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 141.1, 139.2, 138.8, 138.3, 128.52, 128.50, 128.3, 127.9, 127.7, 127.61, 127.58, 127.5, 121.8, 95.9, 76.3, 75.2, 74.4, 73.6, 73.3, 70.6, 70.0, 69.8, 56.9, 56.3, 50.3, 42.5, 40.2, 39.9, 39.7, 37.3, 36.9, 36.4, 35.9, 32.09, 32.05, 31.8, 28.4, 28.2, 28.0, 24.5, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. Melting point: 132 °C. Spectroscopic data was in agreement with the previously reported literature.^{6a, 8}

6-*O*-(2-Deoxy-3,4,6-tri-*O*-methyl- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (**3o**)



Following *General Glycosylation Procedure*. Galactal **1b**^{6c}: 28.2 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 6:1 to 3:2) product **3o** was obtained as a colourless oil (37 mg, 0.083 mmol, 83%). HRMS calcd. for C₂₁H₃₆O₁₀+Na⁺ (M+Na)⁺: 471.2206, found: 471.2219. [α]_D²⁵ +23.8 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 5.52 (d, 1H, *J* 4.8 Hz), 4.99 (d, 1H, *J* 3.2 Hz), 4.60 (dd, 1H, *J* 2.4, 8.0 Hz), 4.31 (dd, 1H, *J* 2.4, 5.2 Hz), 4.23 (dd, 1H, *J* 2.0, 8.0 Hz), 3.96 (dt, 1H, *J* 1.6, 6.4 Hz), 3.88 (t, 1H, *J* 6.8 Hz), 3.74 (dd, 1H, *J* 6.8, 10.8 Hz), 3.67-3.61 (m, 3H), 3.57 (dd, 1H, *J* 7.2, 9.2 Hz), 3.55 (s, 3H), 3.47 (dt, 1H, *J* 6.0, 9.2 Hz), 3.40 (m, 3H), 3.39 (s, 3H), 2.00 (dt, 1H, *J* 3.6, 12.8 Hz), 1.93 (dd, 1H, *J* 5.2, 12.4 Hz), 1.53 (s, 3H), 1.43 (s, 3H), 1.33 (s, 6H). ¹³C NMR (100 MHz; CDCl₃) δ: 109.5, 108.7, 97.8, 96.5, 76.0, 74.6, 71.6, 71.3, 70.9, 70.8, 69.6, 66.1, 65.8, 61.0, 59.3, 56.2, 30.9, 26.2, 26.1, 25.1, 24.7. The spectroscopic data was in agreement the with previously reported literature.^{6c, 8}

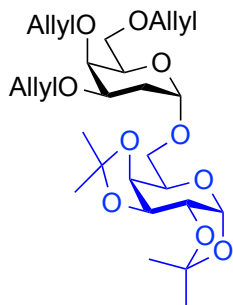
6-*O*-(2-Deoxy-3,4,6-tri-*O*-ethyl-α-D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (3p)



Following *General Glycosylation Procedure*. Galactal **1c**^{6c}: 35 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 7:1 to 3:1) product **3p** was obtained as a colourless oil (38 mg, 0.078 mmol, 78%). HRMS calcd. for C₂₄H₄₂O₁₀+Na⁺ (M+Na)⁺: 513.2676, found: 513.2669. ¹H NMR (400 MHz; CDCl₃) δ: 5.51 (d, 1H, *J* 4.8 Hz), 4.97 (d, 1H, *J* 3.2 Hz), 4.59 (dd, 1H, *J* 2.4, 8.0 Hz), 4.30 (dd, 1H, *J* 2.4, 4.8 Hz), 4.23 (dd, 1H, *J* 2.0, 8.0 Hz), 3.94 (dt, 1H, *J* 1.6, 6.8 Hz), 3.91-3.84 (m, 2H), 3.74-3.70 (m, 3H), 3.66-3.45 (m, 8H), 2.06 (dt, 1H, *J* 3.6, 12.4 Hz), 1.86 (dd, 1H, *J* 4.8, 12.4 Hz), 1.52 (s, 3H), 1.43

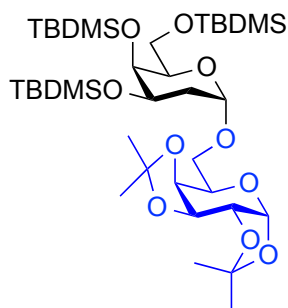
(s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.20 (t, 1H, J 7.2 Hz), 1.194 (t, 1H, J 7.2 Hz), 1.189 (t, 1H, J 7.2 Hz). ^{13}C NMR (100 MHz; CDCl_3) δ : 109.4, 108.6, 97.9, 96.5, 74.1, 73.0, 71.2, 70.8, 69.7, 69.2, 68.3, 66.8, 66.1, 65.7, 63.8, 31.5, 26.2, 26.1, 25.1, 24.7, 15.8, 15.6, 15.3. The spectroscopic data was in agreement with previously reported literature.^{6c}

6-*O*-(2-Deoxy-3,4,6-tri-*O*-allyl- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3q)



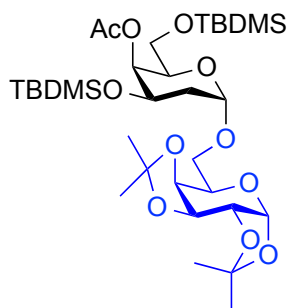
Following *General Glycosylation Procedure*. Galactal **1d**^{6c}: 40 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$: 3.4 mg (0.00525 mmol), AgOTf : 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc, 8:1 to 3:1) product **3q** was obtained as a colourless oil (43 mg, 0.082 mmol, 82%). HRMS calcd. for $\text{C}_{27}\text{H}_{42}\text{O}_{10}+\text{H}^+$ ($\text{M}+\text{H}$)⁺: 527.2856, found: 527.2858. $[\alpha]_{\text{D}}^{25} +29.2$ (c 1.6, CHCl_3). ^1H NMR (400 MHz; CDCl_3) δ : 5.97-5.84 (m, 3H), 5.49 (d, 1H, J 4.8 Hz), 5.28-5.09 (m, 6H), 4.97 (d, 1H, J 3.2 Hz), 4.58 (dd, 1H, J 2.0, 8.0 Hz), 4.32 (dd, 1H, J 5.6, 12.4 Hz), 4.28 (dd, 1H, J 2.4, 4.8 Hz), 4.21 (dd, 1H, J 1.6, 8.0 Hz), 4.11-3.87 (m, 7H), 3.79-3.75 (d, 2H), 3.71 (dd, 1H, J 6.8, 10.8 Hz), 3.64-3.58 (m, 2H), 3.48 (dd, 1H, J 6.0, 9.6 Hz), 2.07 (dt, 1H, J 3.6, 11.6 Hz), 1.89 (dd, 1H, J 5.2, 12.4 Hz), 1.50 (s, 3H), 1.41 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (100 MHz; CDCl_3) δ : 135.8, 135.0, 134.7, 117.1, 116.8, 116.5, 109.4, 108.6, 97.7, 96.4, 74.0, 73.6, 72.5, 72.3, 71.2, 70.8, 70.7, 69.7, 69.3, 69.0, 66.0, 65.7, 31.2, 26.2, 26.1, 25.0, 24.6. The spectroscopic data was in agreement with previously reported literature.^{6c,8}

6-*O*-(2-Deoxy-3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3r**)**



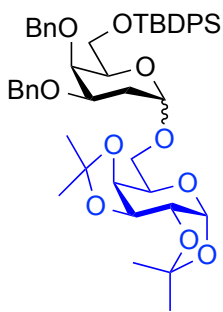
Following *General Glycosylation Procedure*. Galactal **1e**^{6c}: 73.2 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 50:1 to 20:1) product **3r** was obtained as a colourless oil (60 mg, 0.08 mmol, 80%). HRMS calcd. for C₃₆H₇₂O₁₀Si₃+Na⁺ (M+Na)⁺: 771.4331, found: 771.4334. [α]_D²⁵ +31.4 (*c* 2.1, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 5.49 (d, 1H, *J* 4.8 Hz), 4.90 (d, 1H, *J* 2.8 Hz), 4.59 (dd, 1H, *J* 2.4, 8.0 Hz), 4.29 (dd, 1H, *J* 2.4, 4.8 Hz), 4.20 (dd, 1H, *J* 1.6, 8.0 Hz), 4.05 (dq, 1H, *J* 2.0, 11.6 Hz), 3.94 (t, 1H, *J* 5.6 Hz), 3.84 (bs, 1H), 3.74 (dd, 1H, *J* 6.8, 10.0 Hz), 3.71-3.54 (m, 1H), 2.08 (dt, 1H, *J* 3.6, 12.0 Hz), 1.61 (dd, 1H, *J* 4.0, 12.4 Hz), 1.52 (s, 3H), 1.43 (s, 3H), 1.33 (s, 6H), 0.901 (s, 9H), 0.895 (s, 9H), 0.88 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H), 0.074 (s, 3H), 0.068 (s, 3H), 0.05 (s, 6H). ¹³C NMR (100 MHz; CDCl₃) δ : 109.4, 108.6, 97.6, 96.5, 74.1, 72.6, 71.4, 70.9, 70.1, 68.4, 66.7, 65.5, 62.2, 33.8, 26.4, 26.31, 26.26, 26.1, 26.0, 25.2, 24.6, 18.74, 18.66, 18.3, -3.8, -4.2, -4.6, -4.8, -5.1, -5.2. The spectroscopic data was in agreement with the previously reported literature.^{6c}

6-O-(4-O-Acetyl-2-deoxy-3,6-di-O-(tert-butyldimethylsilyl)- α -D-galactopyranosyl)-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (3s)



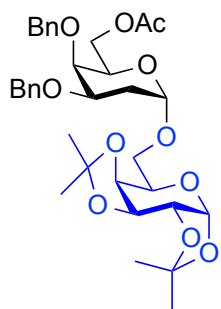
Following *General Glycosylation Procedure*. Galactal **1f**⁴: 73.2 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 50:1 to 15:1) product **3s** was obtained as a colourless oil (51.5 mg, 0.076 mmol, 76%). HRMS calcd. for C₃₂H₆₀O₁₁Si₂+H⁺ (M+H)⁺: 677.3752, found: 677.3754. [α]_D²⁵ +17.1 (*c* 1.7, CHCl₃). ¹H NMR (500 MHz; CDCl₃) δ : 5.52 (d, 1H, *J* 5.0 Hz), 4.94 (d, 1H, *J* 3.0 Hz), 4.75 (d, 1H, *J* 10.0 Hz), 4.61 (dd, 1H, *J* 2.0, 8.0 Hz), 4.31 (dd, 1H, *J* 2.0, 5.0 Hz), 4.20 (dd, 1H, *J* 2.0, 8.0 Hz), 4.10-4.05 (m, 1H), 3.99-3.96 (m, 1H), 3.77 (dd, 1H, *J* 7.0, 10.5 Hz), 3.72-3.68 (m, 1H), 3.63-3.59 (m, 3H), 2.08-2.05 (m, 4H), 1.75-1.70 (m, 1H), 1.54 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 0.88 (s, 9H), 0.84 (s, 9H), 0.044 (s, 3H), 0.037 (s, 3H), 0.034 (s, 3H), 0.030 (s, 3H). ¹³C NMR (125 MHz; CDCl₃) δ : 169.9, 109.5, 108.7, 96.53, 96.48, 73.5, 71.5, 71.3, 70.8, 68.0, 66.1, 65.4, 63.4, 39.0, 26.2, 26.12, 26.10, 26.1, 25.7, 25.1, 24.6, 21.4, 18.5, 18.0, -4.4, -4.7, -5.16, -5.22.

6-O-(3,4-Di-O-benzyl-2-deoxy-6-O-(tert-butyldiphenylsilyl)- α -D-galactopyranosyl)-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (3t)



Following *General Glycosylation Procedure*. Galactal **1g**¹⁴: 85 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 50:1 to 17:1) product **3t** was obtained as a colourless oil (65 mg, 0.079 mmol, 79%). HRMS calcd. for C₄₈H₆₀O₁₀Si+Na⁺ (M+Na)⁺: 847.3853, found: 847.3852. ¹H NMR (400 MHz; CDCl₃) δ: 7.71-7.63 (m, 4.58H), 7.43-7.19 (m, 19.14H), 5.52 (d, 1H, *J* 4.8 Hz), 5.45 (d, 0.1H, *J* 4.8 Hz), 5.09 (d, 0.11H, *J* 11.2 Hz), 5.00 (d, 1H, *J* 2.8 Hz), 4.94 (d, 1H, *J* 11.2 Hz), 4.78 (d, 0.12H, *J* 2.8 Hz), 4.65-4.61 (m, 3H), 4.57 (dd, 1H, *J* 2.4, 8.0 Hz), 4.54 (dd, 0.12H, *J* 2.4, 8.4 Hz), 4.44 (d, 1H, *J* 12.0 Hz), 4.36 (d, 1H, *J* 12.0 Hz), 4.30 (dd, 1H, *J* 2.4, 4.8 Hz), 4.27 (dd, 0.12H, *J* 2.0, 8.0 Hz), 4.15 (dd, 1H, *J* 1.6, 8.0 Hz), 4.01-4.91 (m, 3.2H), 3.87-3.80 (m, 2.21H), 3.72-3.76 (m, 1.23H), 3.68 (dd, 1H, *J* 6.8, 10.8 Hz), 3.60 (dd, 1H, *J* 6.0, 11.2 Hz), 3.56 (dd, 0.11H, *J* 7.2, 9.2 Hz), 3.48 (dd, 0.12H, *J* 6.0, 9.6 Hz), 3.41 (dd, 0.11H, *J* 7.6, 9.2 Hz), 2.20 (dt, 1H, *J* 3.6, 12.0 Hz), 2.02 (dd, 1H, *J* 4.4, 12.0 Hz), 1.69 (s, 0.33H), 1.51 (s, 3H), 1.48 (s, 0.33H), 1.41 (s, 3H), 1.37 (s, 0.33H), 1.32 (s, 3H), 1.31 (s, 3H), 1.29 (s, 0.31H), 1.11 (s, 0.9H), 1.07 (s, 9H). ¹³C NMR (100 MHz; CDCl₃) δ: 139.3, 139.1, 138.8, 138.3, 136.0, 135.9, 135.7, 133.60, 133.55, 129.79, 129.77, 129.7, 128.5, 128.4, 128.3, 128.22, 128.16, 128.1, 128.83, 128.81, 128.75, 127.64, 128.58, 127.5, 127.42, 127.40, 109.4, 109.1, 108.6, 108.5, 98.1, 97.2, 96.5, 96.4, 76.2, 75.0, 74.5, 73.3, 73.1, 71.6, 71.3, 70.8, 70.7, 70.6, 70.5, 69.9, 69.5, 69.4, 66.2, 65.8, 65.4, 62.9, 34.0, 31.2, 27.1, 27.0, 26.3, 26.1, 26.0, 25.1, 24.6, 19.32, 19.28.

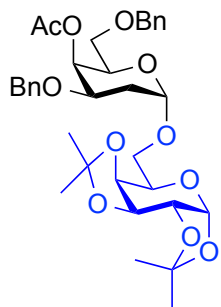
6-*O*-(6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3u**)**



Following *General Glycosylation Procedure*. Galactal **1h**^{6c}: 221 mg (0.6 mmol), acceptor **2a**: 104 mg (0.4 mmol), [Ir(COD)Cl]₂: 14.1 mg (0.021 mmol), AgOTf: 16.2 mg (0.063 mmol), DCM: 12

mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 7:2) product **3u** was obtained as a colourless oil (217 mg, 0.3438 mmol, 86%). HRMS calcd. for $C_{34}H_{44}O_{11}+Na^+$ ($M+Na$)⁺: 651.2781, found: 651.2785. ¹H NMR (400 MHz; CDCl₃) δ: 7.39-7.27 (m, 10H), 5.53 (d, 1H, *J* 5.2 Hz), 5.07 (d, 1H, *J* 2.8 Hz), 4.97 (d, 1H, *J* 11.6 Hz), 4.67 (d, 1H, *J* 12.0 Hz), 4.66 (d, 1H, *J* 12.0 Hz), 4.64 (d, 1H, *J* 12.4 Hz), 4.33 (d, 1H, *J* 2.4, 5.2 Hz), 4.24 (dd, 1H, *J* 1.6, 8.0 Hz), 4.18 (dd, 1H, *J* 7.2, 11.2 Hz), 4.14 (d, 1H, *J* 5.6, 11.2 Hz), 4.01-3.95 (m, 3H), 3.86 (bs, 1H), 3.76 (d, 1H, *J* 6.8, 10.4 Hz), 3.67 (dd, 1H, *J* 5.6, 10.8 Hz), 2.25 (dt, 1H, *J* 3.6, 12.4 Hz), 2.07 (dd, 1H, *J* 4.4, 12.4 Hz), 2.01 (s, 3H), 1.54 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 170.7, 138.61, 138.57, 128.50, 128.47, 128.4, 127.7, 127.6, 127.4, 109.4, 108.6, 97.5, 96.4, 74.9, 74.1, 72.6, 71.2, 70.8, 70.7, 70.6, 69.1, 66.2, 65.8, 64.1, 31.0, 26.2, 26.1, 25.0, 24.6, 21.0. The spectroscopic data agreed previously reported literature.^{6c}

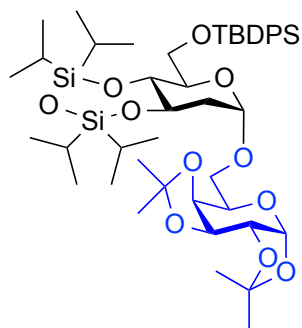
6-*O*-(4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3v**)**



Following *General Glycosylation Procedure*. Galactal **1i**¹⁵: 55 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 3:1) product **3v** was obtained as a colourless oil (51 mg, 0.081 mmol, 81%). HRMS calcd. for $C_{34}H_{44}O_{11}+Na^+$ ($M+Na$)⁺: 651.2781, found: 651.2786, $C_{34}H_{44}O_{11}+NH_4^+$ ($M+NH_4$)⁺: 646.3227, found: 646.3224. $[\alpha]_D^{25} +25.2$ (*c* 1.0, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.37-7.24 (m, 10H), 5.58 (d, 1H, *J* 1.6 Hz), 5.52 (d, 1H, *J* 5.2 Hz), 5.04 (d, 1H, *J* 2.4 Hz), 4.74 (d, 1H, *J* 10.8 Hz), 4.60 (d, 1H, *J* 2.0, 8.0 Hz), 4.57 (d, 1H, *J* 11.6 Hz), 4.47 (d, 1H, *J* 12.0 Hz), 4.40 (dd, 1H, *J* 11.6 Hz), 4.32 (dd, 1H, *J* 2.4, 5.2 Hz), 4.22 (d, 1H, *J* 1.6, 8.0 Hz), 4.11 (d, 1H, *J* 6.4 Hz), 3.97-3.92 (m, 2H),

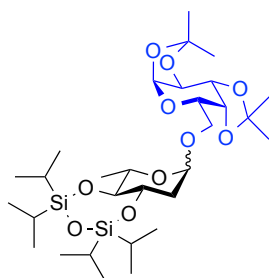
3.78 (dd, 1H, *J* 6.8, 10.8 Hz), 3.67 (dd, 1H, *J* 6.0, 10.4 Hz), 3.53 (dd, 1H, *J* 6.4, 10.0 Hz), 3.49 (dd, 1H, *J* 6.8, 9.2 Hz), 2.07 (s, 3H), 2.05-1.93 (m, 2H), 1.52 (s, 3H), 1.43 (s, 3H), 1.34 (s, 6H). ¹³C NMR (100 MHz; CDCl₃) δ: 170.5, 138.2, 138.0, 128.48, 128.45, 128.03, 128.0, 127.8, 127.7, 109.4, 108.6, 97.6, 96.4, 73.6, 71.5, 70.8, 70.7, 70.6, 68.8, 68.1, 66.3, 66.1, 65.9, 31.8, 26.2, 26.1, 25.0, 24.6, 21.0.

6-*O*-(2-Deoxy-3,4-*O*-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)-6-*O*-*tert*-butyldiphenylsilyl)- α -D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3w)



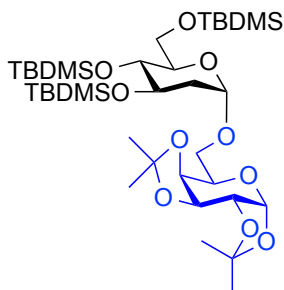
Following *General Glycosylation Procedure*. Galactal **1j**: 92 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 100:1 to 50:1) product **3w** was obtained as a colourless oil (68 mg, 0.078 mmol, 78%). HRMS calcd. for C₄₆H₇₄O₁₁Si₃+Na⁺ (M+Na)⁺: 909.4437, found: 909.4430. [α]_D²⁵ +43.8 (*c* 1.2, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.71 (d, 4H, *J* 6.4 Hz), 7.42-7.32 (m, 6H), 5.53 (d, 1H, *J* 4.8 Hz), 5.00 (d, 1H, *J* 3.2 Hz), 4.61 (dd, 1H, *J* 2.4, 8.0 Hz), 4.32 (dd, 1H, *J* 2.4, 4.8 Hz), 4.19 (dd, 1H, *J* 1.6, 8.0 Hz), 4.10-4.01 (m, 2H), 3.97 (dd, 1H, *J* 1.6, 10.8 Hz), 3.85 (dd, 1H, *J* 5.6, 10.8 Hz), 3.80 (dd, 1H, *J* 7.2, 10.8 Hz), 3.68 (dd, 1H, *J* 6.0, 10.8 Hz), 3.55 (dd, 1H, *J* 8.4, 9.2 Hz), 2.14 (dd, 1H, *J* 5.2, 13.2 Hz), 1.74-1.67 (m, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.09-0.86 (s, 37H). ¹³C NMR (100 MHz; CDCl₃) δ: 136.0, 135.8, 134.3, 133.8, 129.54, 129.52, 127.62, 127.59, 109.4, 108.6, 96.5, 95.9, 74.7, 73.3, 71.8, 71.3, 70.9, 70.8, 65.6, 64.7, 63.8, 38.2, 27.1, 27.0, 26.2, 26.1, 25.1, 24.6, 19.5, 17.8, 17.6, 17.53, 17.47, 17.43, 17.39, 13.1, 13.0, 12.54, 12.48.

6-*O*-(2-deoxy-3,4-*O*-(1,1,3,3-tetraisopropylidisiloxane-1,3-diyl)- α -L-rhamnopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3x)



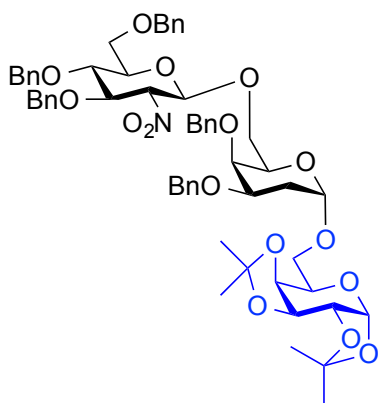
Following the *General Glycosylation Procedure*: Galactal **11**⁴: 56 mg (0.15 mmol), acceptor **2a** 26 mg (0.1 mmol), [Ir(cod)Cl]₂ (3.4 mg, 0.00525 mmol) and AgOTf (4.1 mg, 0.01575 mmol). Following purification by column chromatography (Hexane:EtOAc = 100:1 to 40:1) product **3x** was obtained as a colourless oil (47 mg, 0.074 mmol, 74%). HRMS calcd. for C₃₀H₅₆O₁₀Si₂+H⁺ (M+H)⁺: 633.3490, found: 633.3495. ¹H NMR (400 MHz; CDCl₃) δ : 5.50 (d, 1H, *J* 5.2 Hz), 5.48 (d, 0.24H, *J* 4.8 Hz), 4.85 (d, 1H, *J* 2.8 Hz), 4.58 (dd, 1H, *J* 2.4, 8.0 Hz), 4.50 (dd, 0.23H, *J* 1.6, 10.0 Hz), 4.22 (d, 1H, *J* 1.2, 8.0 Hz), 4.02-3.94 (m, 2.32H), 3.85 (dd, 0.24H, *J* 6.0, 10.0 Hz), 3.78-3.65 (m, 2.57H), 3.50 (dd, 1H, *J* 6.8, 10.4 Hz), 3.23-3.19 (m, 1.49H), 2.15 (ddd, 0.25H, *J* 2.0, 1.6, 12.8 Hz), 2.10 (dd, 1H, *J* 5.2, 13.2 Hz), 1.70-1.61 (m, 1.25H), 1.51 (s, 3.83H), 1.42 (s, 0.82H), 1.41 (s, 3H), 1.33-1.28 (m, 8.39H), 1.25 (s, 1.79H), 1.23 (s, 3H), 1.06-0.98 (m, 33.48H), 0.96-0.84 (m, 3.79H). ¹³C NMR (100 MHz; CDCl₃) δ : 109.3, 109.2, 108.6, 100.5, 97.2, 96.4, 96.3, 80.1, 79.6, 74.1, 72.3, 71.6, 71.2, 70.9, 70.8, 70.72, 70.67, 68.1, 67.6, 67.2, 66.2, 65.3, 39.8, 38.4, 26.23, 26.16, 26.1, 26.0, 25.1, 25.0, 24.6, 24.3, 18.2, 18.0, 17.8, 17.7, 17.51, 17.46, 17.42, 17.39, 17.35, 17.3, 13.1, 13.0, 12.43, 12.39, 12.36.

6-*O*-(2-Deoxy-3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)- α -D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (3y)



Following *General Glycosylation Procedure*. Galactal **1k**⁴: 73 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 4.1 mg (0.01575 mmol), DCM: 3 mL. Reaction time: 24 hours. Following purification by column chromatography (Hexane:EtOAc = 50:1 to 20:1) product **3y** was obtained as a colourless oil (6 mg, 0.008 mmol, 8%). HRMS calcd. for C₃₆H₇₂O₁₀Si₃+H⁺ (M+H)⁺: 749.4512, found: 749.4516. [α]_D²⁵ +12.1 (c 0.6, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 5.51 (d, *J* 5.2 Hz, 1H), 4.87 (t, *J* 2.4 Hz, 1H), 4.60 (dd, *J* 2.4, 8.0 Hz, 1H), 4.30 (dd, *J* 2.4, 5.2 Hz, 1H), 4.22 (dd, *J* 1.6, 7.6 Hz, 1H), 4.00-3.94 (m, 2H), 3.82 (dd, *J* 2.4, 11.2 Hz, 1H), 3.77 (dd, *J* 6.4, 10.0 Hz, 1H), 3.72 (d, *J* 5.2, 11.2 Hz, 1H), 3.56 (dd, *J* 7.2, 10.4 Hz, 1H), 3.48-3.52 (m, 1H), 3.41 (d, *J* 8.4 Hz, 1H), 2.04-2.09 (m, 1H), 1.62-1.55 (m, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.33 (s, 6H), 0.90 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.093 (s, 3H), 0.088 (s, 3H), 0.084 (s, 3H), 0.078 (s, 3H), 0.04 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 109.3, 108.6, 96.6, 96.5, 74.4, 72.9, 71.2, 71.1, 70.9, 70.8, 66.2, 65.2, 62.9, 38.9, 26.4, 26.2, 26.1, 25.1, 24.5, 18.6, 18.5, 18.3, -2.86, -2.90, -4.0, -4.5, -4.7, -5.2. The spectroscopic data was in agreement with the previously reported literature.⁸ **4r** obtained as a major product (71%).

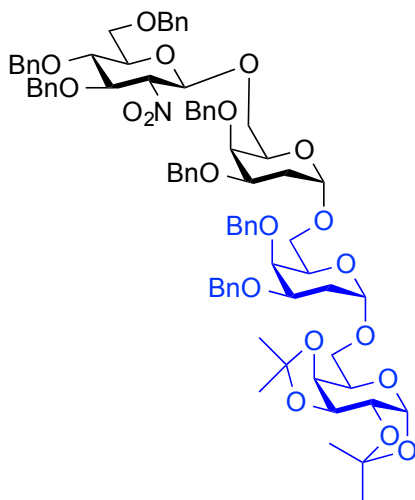
1,2:3,4-Di-*O*-isopropylidene (3,4,6-tri-*O*-benzyl-2-deoxy-2-nitro-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-(1→6)-α-D-galactopyranose (5)



Following the *General Glycosylation Procedure*: galactal **1m**¹⁶ (118 mg, 0.15 mmol), acceptor **2a** (26 mg, 0.1 mmol), [Ir(cod)Cl]₂ (3.4 mg, 0.00525 mmol) and AgOTf (4.1 mg, 0.01575 mmol). Following purification by column chromatography (Hexane:EtOAc = 8:1 to 5:2) product **5** was obtained as a colourless oil (72 mg, 0.069 mmol, 69%). HRMS calcd. for C₅₉H₆₉NO₁₆+H⁺ (M+H)⁺: 1048.4695, found: 1048.4699. ¹H NMR (400 MHz; CDCl₃) δ: 7.40-7.27 (m, 21H), 7.24-7.17 (m,

4H), 5.54 (d, 1H, J 4.8 Hz), 5.02 (d, 1H, J 2.8 Hz), 4.91 (d, 1H, J 11.2 Hz), 4.90 (d, 1H, J 8.0 Hz), 4.79 (d, 1H, J 11.2 Hz), 4.76 (d, 1H, J 11.2 Hz), 4.67 (d, 1H, J 11.6 Hz), 4.63 (dd, 1H, J 2.4, 7.6 Hz), 4.60-4.57 (m, 5H), 4.53 (dd, 1H, J 8.0, 10.4 Hz), 4.46 (d, 1H, J 12.0 Hz), 4.33 (dd, 1H, J 2.4, 5.2 Hz), 4.28-4.23 (m, 2H), 4.01-3.87 (m, 4H), 3.82 (bs, 1H), 3.80-3.66 (m, 6H), 3.58 (dq, J 1.6, 9.6 Hz), 2.20 (dt, J 3.6, 12.4 Hz), 2.01 (dd, J 4.4, 12.4 Hz), 1.54 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 139.0, 138.7, 137.8, 137.7, 138.1, 128.61, 128.58, 128.55, 128.5, 128.4, 128.3, 128.2, 128.13, 128.10, 128.0, 127.9, 127.58, 127.56, 127.5, 109.4, 108.7, 99.9, 97.5, 96.5, 89.9, 81.5, 77.6, 77.4, 75.5, 75.3, 75.2, 74.5, 73.7, 72.6, 71.2, 70.8, 70.5, 69.3, 68.4, 68.1, 65.9, 31.2, 26.3, 26.1, 25.1, 24.6.

1,2:3,4-Di-*O*-isopropylidene (3,4,6-tri-*O*-benzyl-2-deoxy-2-nitro- β -D-galactopyranosyl)-(1 \rightarrow 6)-(3,4-di-*O*-benzyl-2-deoxy- α -D-galactopyranosyl)-(1 \rightarrow 6)-(3,4-di-*O*-benzyl-2-deoxy- α -D-galactopyranosyl)-(1 \rightarrow 6)- α -D-galactopyranose (6)



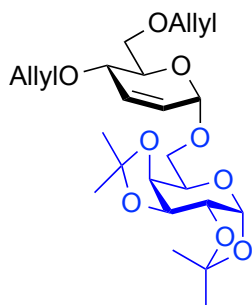
Following the *General Glycosylation Procedure*: galactal **1m**¹⁶ (118 mg, 0.15 mmol), acceptor **2u** (59 mg, 0.1 mmol), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (3.4 mg, 0.00525 mmol) and AgOTf (4.1 mg, 0.01575 mmol). Following purification by column chromatography (Hexane:EtOAc = 8:1 to 2:1) product **6** was obtained as a colourless oil (83 mg, 0.063 mmol, 63%). HRMS calcd. for $\text{C}_{79}\text{H}_{91}\text{NO}_{20}+\text{Na}^+$ ($\text{M}+\text{Na}$)⁺: 1396.6032, found: 1396.6046. $[\alpha]_{\text{D}}^{25} +17.9$ (c 1.0, CHCl_3). ^1H NMR (400 MHz; CDCl_3) δ : 7.37-7.15 (m, 35H), 5.49 (d, 1H, J 4.8 Hz), 5.05 (d, 1H, J 2.8 Hz), 4.93 (d, 1H, J 11.2 Hz), 4.88 (d, 1H, J 11.2 Hz), 4.86 (d, 1H, J 8.0 Hz), 4.75 (d, 1H, J 11.2 Hz), 4.73 (d, 1H, J 3.2 Hz), 4.72 (d, 1H, J 11.2 Hz), 4.65 (dd, 1H, J 1.2 Hz), 4.63-4.52 (m, 8H), 4.48 (dd, 1H, J 8.0, 10.4 Hz), 4.29 (dd,

1H, *J* 2.4, 5.2 Hz), 4.26-4.21 (m, 2H), 4.00-3.63 (m, 14H), 3.52 (dq, *J* 1.6, 9.6 Hz), 3.42 (dd, *J* 6.4, 9.6 Hz), 2.23 (dt, *J* 3.2, 12.0 Hz), 2.09 (dt, *J* 3.2, 12.4 Hz), 2.04 (dd, *J* 4.4, 13.2 Hz), 2.23 (dd, *J* 3.6, 12.0 Hz), 1.50 (s, 3H), 1.41 (s, 3H), 1.29 (s, 6H). ¹³C NMR (100 MHz; CDCl₃) δ: 139.20, 139.16, 138.9, 138.8, 138.0, 137.8, 137.3, 128.62, 128.59, 128.57, 128.53, 128.50, 128.4, 128.33, 128.30, 128.2, 128.13, 128.08, 128.0, 127.9, 127.6, 127.52, 127.48, 109.6, 108.6, 100.0, 97.6, 97.4, 96.5, 90.0, 81.7, 75.5, 75.4, 75.3, 75.2, 74.8, 74.5, 74.2, 73.8, 73.2, 72.9, 71.4, 71.0, 70.8, 70.7, 70.6, 69.5, 69.4, 68.6, 68.2, 66.4, 66.2, 65.7, 31.3, 31.2, 26.3, 26.2, 25.1, 24.7.

General procedure for Iridium catalyzed stereoselective glycosylation to synthesize 2,3-unsaturated glycosides:

In an oven-dried 10 mL round bottom flask glycal donor (0.15 mmol, 1.5 equiv.) and acceptor (0.1 mmol, 1.0 equiv.) were weighed and placed under vacuum for 2 h, then the round bottom flask was filled with N₂. In a seal tube, a suspension of active catalyst was prepared by mixing [Ir(COD)Cl]₂ (0.00525 mmol, 3.5 mol% w.r.t. glycal donor) and AgOTf (0.021 mmol, 14.0 mol% w.r.t. glycal donor) in anhydrous DCM (1 mL) and was stirred vigorously for 30 minutes under N₂ atmosphere. Ag₂CO₃ (0.1 mmol, 1.0 equiv.) was then added into the seal tube under N₂ atmosphere. The mixture of donor and acceptor was dissolved in anhydrous DCM (2 mL) and the solution was transferred to the seal tube containing Ir(I) catalyst using a cannula under N₂ atmosphere. The reaction mixture was stirred at ambient temperature for 48-72 h under N₂ atmosphere, after which the solvent was removed, and the crude product was purified by flash column chromatography (Hexane/EtOAc).

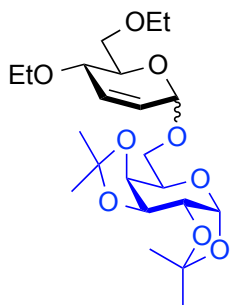
6-*O*-(2,3-Dideoxy-4,6-di-*O*-allyl- α -D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (**4a**)



Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 10:1 to 2:1) product **4a** was obtained as a colourless oil (34 mg, 0.073 mmol, 73%). HRMS calcd. for C₂₄H₃₆O₉+H⁺ (M+H)⁺: 469.2438, found: 469.2440. [α]_D²⁵ +21.8 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 6.02 (d, 1H, *J* 10.0 Hz), 5.96-5.84 (m, 2H), 5.74 (ddd, 1H, *J* 2.0, 2.4, 10.4 Hz), 5.49 (ddq, 1H, *J* 1.6, 4.8, 17.2 Hz), 5.18-5.14 (m, 1H), 5.05

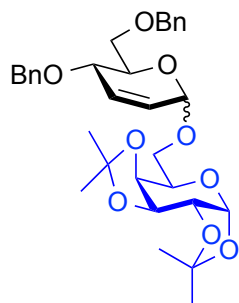
(bs, 1H), 4.58 (dd, 1H, J 2.4, 8.0 Hz), 4.28 (dd, 1H, J 2.0, 4.8 Hz), 4.26 (d, 1H, J 1.6, 8.0 Hz), 4.14-4.06 (m, 3H), 4.03-3.97 (m, 3H), 3.87-3.80 (m, 2H), 3.74 (dd, 1H, J 8.0, 10.4 Hz), 3.69 (dd, 1H, J 3.6, 10.4 Hz), 3.64 (dd, 1H, J 2.0, 10.8 Hz), 1.51 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz; CDCl_3) δ : 134.9, 134.8, 131.1, 126.5, 117.3, 117.2, 109.3, 108.6, 96.4, 95.1, 72.6, 70.9, 70.8, 70.7, 70.3, 70.0, 69.5, 68.8, 66.8, 66.1, 26.2, 26.1, 25.1, 24.6. The spectroscopic data was in agreement with previously reported literature.¹⁷

6-*O*-(2,3-Dideoxy-4,6-di-*O*-ethyl- α -D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (4b**)**



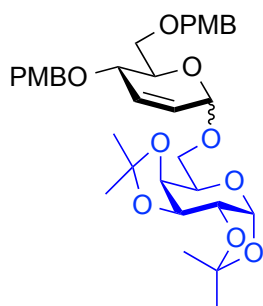
Following *General Glycosylation Procedure*. Glucal **1o**: 37 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$: 3.4 mg (0.00525 mmol), AgOTf : 4.1 mg (0.021 mmol), Ag_2CO_3 : 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 2:1) product **4b** was obtained as a colourless oil (27 mg, 0.061 mmol, 61%). HRMS calcd. for $\text{C}_{22}\text{H}_{36}\text{O}_9 + \text{H}^+$ ($\text{M} + \text{H}$) $^+$: 445.2438, found: 445.2436. ^1H NMR (400 MHz; CDCl_3) δ : 6.02 (d, 1.13H, J 10.0 Hz), 5.73 (dt, 1H, J 2.4, 10.4 Hz), 5.71 (dt, 0.13H, J 2.4, 10.8 Hz), 5.49 (d, 1H, J 5.2 Hz), 5.39 (bs, 0.12H), 5.06 (bs, 1H), 4.58 (dd, 1H, J 2.4, 8.0 Hz), 4.29 (dd, 1H, J 2.4, 5.2 Hz), 4.26 (dd, 1H, J 1.6, 8.0 Hz), 4.04-3.95 (m, 2.2H), 3.85-3.71 (m, 3.33H), 3.70-3.57 (m, 4.61H), 3.54-3.46 (m, 2.33H), 1.52 (s, 3.15H), 1.43 (s, 3.13H), 1.33 (s, 3.19H), 1.31 (s, 3.05H), 1.21 (t, 3.32H, J 7.2 Hz), 1.19 (t, 3.42H, J 6.8 Hz). ^{13}C NMR (100 MHz; CDCl_3) δ : 131.4, 131.2, 126.6, 126.3, 109.3, 108.6, 96.5, 95.2, 91.1, 70.9, 70.8, 70.7, 70.5, 70.2, 69.8, 69.6, 69.5, 69.2, 67.0, 66.8, 66.1, 64.7, 64.5, 26.2, 26.1, 25.1, 24.7, 15.6, 15.3, 15.2.

6-*O*-(4,6-Di-*O*-benzyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (4c**)**



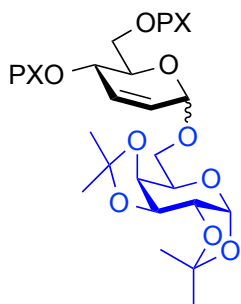
Following *General Glycosylation Procedure*. Glucal **1p**: 55 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 10:1 to 3:1) product **4c** was obtained as a colourless oil (45 mg, 0.079 mmol, 79%). HRMS calcd. for C₃₂H₄₀O₉+Na⁺ (M+Na)⁺: 591.2570, found: 591.2568. ¹H NMR (400 MHz; CDCl₃) δ: 7.39-7.26 (m, 11.40H), 6.09 (d, 1H, *J* 10.0 Hz), 6.06 (d, 0.11H, *J* 10.4 Hz), 5.93 (dt, 0.12H, *J* 1.2, 9.2 Hz), 5.81 (d, 1H, *J* 2.4, 10.4 Hz), 5.57 (d, 0.12H, *J* 5.2 Hz), 5.54 (d, 1H, *J* 4.8 Hz), 5.23 (q, 0.11H, *J* 1.2 Hz), 5.12 (bs, 1H), 4.68 (d, 1H, *J* 12.0 Hz), 4.64-4.56 (m, 2.64H), 4.52 (d, 1H, *J* 12.4 Hz), 4.46 (d, 1H, *J* 11.6 Hz), 4.33 (d, 1H, *J* 2.4, 4.8 Hz), 4.31 (d, 1H, *J* 2.0, 8.0 Hz), 4.25 (dq, 1H, *J* 1.2, 9.6 Hz), 4.24-4.21 (m, 0.11H), 4.08-4.04 (m, 1H), 4.02-4.00 (m, 0.37H), 4.97 (dt, 1H, *J* 2.4, 9.2 Hz), 3.89 (dd, 1H, *J* 6.0, 10.0 Hz), 3.82 (dd, 1H, *J* 8.0, 10.4 Hz), 3.78 (d, 1H, *J* 3.6, 7.2 Hz), 3.76-3.73 (m, 0.33H), 3.72 (dd, 1H, *J* 2.0, 10.8 Hz), 1.56 (s, 0.39H), 1.55 (s, 3H), 1.47 (s, 3.39H), 1.37 (s, 3H), 1.35 (s, 3.78H). ¹³C NMR (100 MHz; CDCl₃) δ: 138.4, 138.2, 138.11, 138.07, 130.7, 129.2, 128.40, 128.37, 128.36, 128.0, 127.90, 127.87, 127.74, 127.69, 127.60, 127.57, 126.5, 109.3, 109.2, 108.6, 108.5, 96.41, 96.36, 95.1, 75.3, 73.4, 73.3, 71.3, 71.2, 71.0, 70.9, 70.7, 70.6, 70.5, 70.3, 69.9, 69.5, 69.4, 68.7, 67.5, 67.2, 66.8, 66.0, 26.12, 26.10, 26.02, 24.99, 24.96, 24.6, 24.5.

6-O-(2,3-Dideoxy-4,6-di-O-p-methoxybenzyl- α -D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (4d)



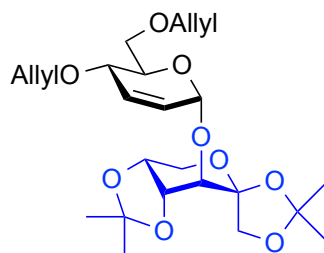
Following *General Glycosylation Procedure*. Glucal **1q**: 64 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 9:1 to 2:1) product **4d** was obtained as a colourless oil (47 mg, 0.075 mmol, 75%). HRMS calcd. for C₃₄H₄₄O₁₁+Na⁺ (M+Na)⁺: 651.2781, found: 651.2783. ¹H NMR (400 MHz; CDCl₃) δ : 7.28-7.24 (m, 2.69H), 7.15-7.12 (m, 2H), 6.88-6.82 (m, 4.61H), 6.07 (d, 0.15H, *J* 10.4 Hz), 6.03 (d, 1H, *J* 10.4 Hz), 5.80 (dt, 0.16H, *J* 2.0, 10.4 Hz), 5.75 (d, 1H, *J* 2.4, 10.4 Hz), 5.07 (bs, 1H), 5.04 (d, 0.15H, 2.4 Hz), 4.60-4.57 (m, 2.46H), 4.49 (d, 1.18H, *J* 11.2 Hz), 4.42 (d, 0.20H, *J* 11.2 Hz), 4.40 (d, 1H, *J* 11.2 Hz), 4.35-4.25 (m, 3.54H), 4.21 (dd, 0.20H, *J* 2.0, 12.0 Hz), 4.16 (dq, 1H, *J* 1.2, 9.6 Hz), 4.03-3.97 (m, 1.43H), 3.91-3.81 (m, 2.31H), 3.80-3.74 (m, 8.21H), 3.70 (dd, 1.14H, *J* 3.6, 10.8 Hz), 3.70 (dd, 1.15H, *J* 2.0, 10.8 Hz), 1.51 (s, 3.62H), 1.43 (s, 3.65H), 1.33 (s, 3.57H), 1.32 (s, 3.78H). ¹³C NMR (100 MHz; CDCl₃) δ : 159.4, 159.3, 131.0, 130.44, 130.35, 129.9, 129.7, 129.6, 129.5, 126.8, 126.5, 114.0, 113.89, 113.88, 109.4, 109.3, 108.69, 108.66, 96.5, 95.2, 94.9, 73.1, 71.01, 70.96, 70.9, 70.8, 70.7, 70.5, 70.0, 69.5, 68.3, 68.0, 66.8, 66.3, 66.1, 63.6, 55.39, 55.37, 26.24, 26.19, 26.1, 25.1, 24.7.

6-*O*-(2,3-Dideoxy-4,6-di-*O*-*p*-xylyl- α -D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (4e**)**



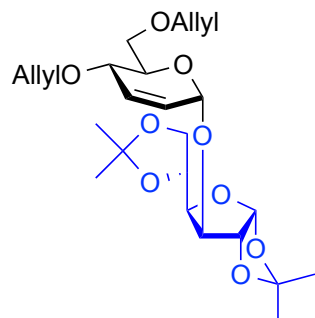
Following *General Glycosylation Procedure*. Glucal **1r**: 59.4 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 10:1 to 4:1) product **4e** was obtained as a colourless oil (42 mg, 0.070 mmol, 70%). HRMS calcd. for C₃₄H₄₄O₉+H⁺ (M+H)⁺: 597.3064, found: 597.3063. ¹H NMR (400 MHz; CDCl₃) δ : 7.24 (d, 2H, *J* 8.0 Hz), 7.15 (d, 2H, *J* 8.0 Hz), 7.12 (s, 4H), 6.06 (d, 1H, *J* 10.4 Hz), 5.78 (dt, 1H, *J* 2.0, 10.0 Hz), 5.52 (d, 1H, *J* 5.2 Hz), 5.10 (bs, 1H), 4.63 (d, 1H, *J* 12.0 Hz), 4.60 (dd, 1H, *J* 2.4, 8.0 Hz), 4.54 (d, 1H, *J* 11.6 Hz), 4.45 (d, 1H, *J* 12.0 Hz), 4.37 (d, 1H, *J* 11.2 Hz), 4.31 (dd, 1H, *J* 2.0, 4.8 Hz), 4.28 (dd, 1H, *J* 1.6, 8.0 Hz), 4.20 (dq, 1H, *J* 1.2, 9.6 Hz), 4.06-4.02 (m, 1H), 3.92 (dt, 1H, *J* 2.4, 9.2 Hz), 3.87 (dd, 1H, *J* 6.0, 10.4 Hz), 3.79 (dd, 1H, *J* 8.0, 10.0 Hz), 3.74 (dd, 1H, *J* 3.2, 10.4 Hz), 3.66 (dd, 1H, *J* 2.0, 10.8 Hz), 2.343 (s, 3H), 2.336 (s, 3H), 1.53 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ : 137.4, 137.3, 135.24, 135.16, 130.9, 129.1, 128.1, 128.0, 126.4, 109.2, 108.6, 96.4, 95.1, 73.3, 71.1, 70.9, 70.8, 70.7, 70.1, 69.5, 68.5, 66.8, 66.1, 26.2, 26.1, 25.0, 24.6, 21.2.

3-O-(2,3-Dideoxy-4,6-di-O-allyl- α -D-erythro-hex-2-enopyranosyl)-1,2:4,5-di-O-isopropylidene- α -D-fructopyranose (4f)



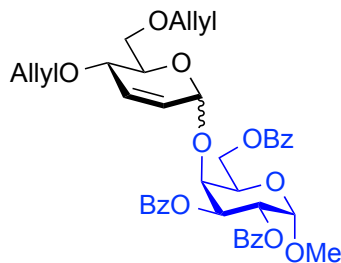
Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2d**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 9:1 to 2:1) product **4f** was obtained as a colourless oil (30.5 mg, 0.065 mmol, 65%). HRMS calcd. for C₂₄H₃₆O₉+H⁺ (M+H)⁺: 469.2438, found: 469.2435. [α]_D²⁵ -4.3 (*c* 1.4, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 6.01 (d, 1H, *J* 10.0 Hz), 5.93-5.83 (m, 2H), 5.79 (dt, 1H, *J* 2.0, 10.0 Hz), 5.47 (bs, 1H), 5.26 (d, 1H, *J* 17.2 Hz), 5.16 (d, 1H, *J* 10.4 Hz), 4.26 (d, 1H, *J* 5.6, 7.6 Hz), 4.22 (d, 1H, *J* 8.8 Hz), 4.16-3.96 (m, 8H), 3.91 (d, 1H, *J* 8.4 Hz), 3.83 (d, 1H, *J* 7.6 Hz), 3.79 (dq, 1H, *J* 2.0, 10.0 Hz), 3.66 (dd, 1H, *J* 4.0, 10.8 Hz), 3.62 (dd, 1H, *J* 2.0, 10.4 Hz), 1.51 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ : 134.7, 134.6, 130.8, 126.6, 117.5, 117.3, 112.2, 109.2, 104.5, 94.9, 78.1, 74.9, 74.0, 72.6, 72.0, 70.3, 70.1, 69.9, 68.9, 60.1, 28.3, 26.9, 26.5, 26.2.

3-O-(4,6-Di-O-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-1,2:5,6-di-O-isopropylidene- α -D-glucopyranose (4g)



Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2b**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 10:1 to 2:1) product **4g** was obtained as a colourless oil (29 mg, 0.062 mmol, 62%). HRMS calcd. for C₂₄H₃₇O₉+H⁺ (M+H)⁺: 469.2438, found: 469.2442. [α]_D²⁵ +29.1 (c 1.3, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 6.04 (d, 1H, *J* 10.0 Hz), 5.97-5.85 (m, 2H), 5.84 (d, 1H, *J* 3.6 Hz), 5.73 (ddd, 1H, *J* 2.0, 2.8, 10.4 Hz), 5.30 (dq, 1H, *J* 1.6, 8.4 Hz), 5.26 (dq, 1H, *J* 1.6, 8.4 Hz), 5.20 (q, 1H, *J* 1.2 Hz), 5.19-5.16 (m, 1H), 4.74 (d, 1H, *J* 3.2 Hz), 4.27 (d, 1H, *J* 3.2 Hz), 3.79 (dq, 1H, *J* 2.0, 10.0 Hz), 4.22-3.87 (m, 10H), 3.72 (dd, 1H, *J* 1.6, 10.4 Hz), 3.64 (dd, 1H, *J* 5.2, 10.4 Hz), 1.48 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 134.8, 134.6, 130.9, 128.2, 127.9, 127.7, 126.1, 117.5, 117.3, 111.1, 109.1, 105.5, 96.0, 84.1, 81.5, 81.4, 72.8, 72.7, 70.3, 70.2, 69.9, 69.4, 67.8, 27.1, 27.0, 26.4, 25.5.

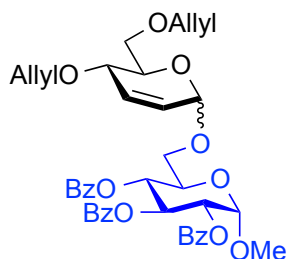
Methyl 4-O-(4,6-di-O-allyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-2,3,6-tri-O-benzoyl-α-D-galactopyranoside (4h)



Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2l**: 51 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 3:2) product **4h** was obtained as a colourless oil (38.8 mg, 0.054 mmol, 54%). HRMS calcd. for C₄₀H₄₂O₁₂+H⁺ (M+H)⁺: 715.2755, found: 715.2753. ¹H NMR (400 MHz; CDCl₃) δ: 8.06-8.03 (m, 2H), 7.99-7.94 (m, 4H), 7.61-7.56 (m, 1H), 7.52-7.44 (m, 4H), 7.38-7.31 (m, 4H), 6.07 (d, 1H, *J* 10.4 Hz), 5.89-5.80 (m, 2H), 5.75 (dd, 1H, *J* 3.2, 10.8 Hz), 5.71-5.61 (m, 2H), 5.26-5.12 (m, 4H), 5.07-5.00 (m, 3H), 4.60-4.56 (m, 2H), 4.43-4.37 (m, 2H), 4.11-4.02 (m, 2H), 3.96-3.92 (m, 1H), 3.82 (dt, 1H, *J* 2.4, 9.2 Hz), 3.71-3.66 (m, 1H), 3.51-

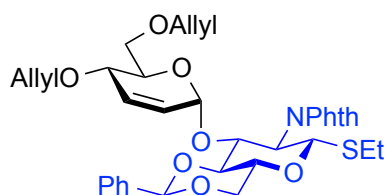
3.46 (m, 1H), 3.43 (s, 3H), 2.95 (dd, 1H, J 2.4, 10.8 Hz), 2.62 (dd, 1H, J 1.2, 10.8 Hz). ^{13}C NMR (100 MHz; CDCl_3) δ : 166.3, 166.2, 166.1, 134.9, 134.6, 133.5, 133.34, 133.28, 131.8, 130.0, 129.93, 129.87, 129.6, 128.7, 128.6, 128.5, 125.4, 117.2, 117.0, 97.7, 95.8, 74.3, 72.3, 70.3, 70.2, 69.5, 69.4, 69.2, 68.3, 67.9, 62.8, 55.7.

Methyl 6-*O*-(4,6-di-*O*-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzoyl- α -D-glucopyranoside (4i**)**



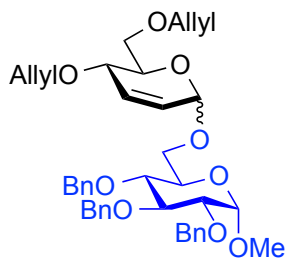
Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2m**¹⁸: 51 mg (0.1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$: 3.4 mg (0.00525 mmol), AgOTf : 5.4 mg (0.021 mmol), Ag_2CO_3 : 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 1:1) product **4i** was obtained as a colourless oil (51.5 mg, 0.072 mmol, 72%). HRMS calcd. for $\text{C}_{40}\text{H}_{42}\text{O}_{12}+\text{Na}^+$ ($\text{M}+\text{Na}$)⁺: 737.2574, found: 737.2575. ^1H NMR (400 MHz; CDCl_3) δ : 8.00-7.93 (m, 4H), 7.88-7.86 (m, 2H), 7.53-7.47 (m, 2H), 7.43-7.35 (m, 5H), 7.28 (t, 1H, J 7.2 Hz), 6.12 (d, 1H, J 9.6 Hz), 6.03 (d, 1H, J 10.4 Hz), 5.96-5.76 (m, 2H), 5.73-5.68 (m, 2H), 5.31-5.24 (m, 3H), 5.22-5.10 (m, 3H), 5.03 (bs, 1H), 4.24 (dt, 1H, J 3.6, 10.4 Hz), 4.14-4.09 (m, 2H), 4.04-3.90 (m, 3H), 3.86-3.80 (m, 2H), 3.70 (dd, 1H, J 2.8, 11.2 Hz), 3.55 (dd, 1H, J 3.6, 10.8 Hz), 3.47 (s, 3H), 3.30 (dd, 1H, J 1.6, 10.8 Hz). ^{13}C NMR (100 MHz; CDCl_3) δ : 165.94, 165.93, 165.1, 135.0, 133.4, 133.3, 133.1, 131.6, 130.02, 130.0, 129.8, 129.5, 129.4, 129.3, 128.5, 128.3, 126.0, 117.1, 97.2, 94.8, 72.4, 72.3, 70.9, 70.0, 69.9, 69.6, 69.3, 68.6, 68.5, 66.4, 55.7.

Ethyl 4,6-*O*-benzylidene-3-*O*-(4,6-di-*O*-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-2-deoxy-2-phthalimido-1-thio- β -D-glucopyranoside (4j)



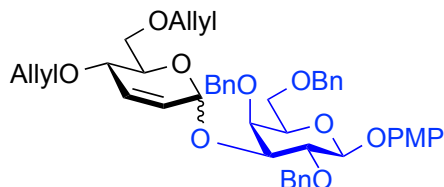
Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2n**¹⁹: 44 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 7:1 to 3:2) product **4j** was obtained as a colourless oil (40 mg, 0.061 mmol, 61%). HRMS calcd. for C₃₅H₃₉NO₉S+H⁺ (M+H)⁺: 650.2424, found: 650.2422; C₃₅H₃₉NO₉S+H⁺ (M+H)⁺: 672.2243, found: 672.2246. [α]_D²⁵ +23.0 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 7.89-7.86 (m, 2H), 7.77-7.72 (m, 2H), 7.44-7.40 (m, 2H), 7.37-7.32 (m, 3H), 5.88 (d, 1H, *J* 10.0 Hz), 5.80-5.69 (m, 2H), 5.65 (dt, 1H, *J* 2.4, 10.4 Hz), 5.57 (s, 1H), 5.47 (d, 1H, *J* 10.4 Hz), 5.39 (bs, 1H), 5.18-5.05 (m, 4H), 4.79 (dd, 1H, *J* 8.4, 10.0 Hz), 4.39 (dd, 1H, *J* 4.0, 10.4 Hz), 4.33 (t, 1H, *J* 10.4 Hz), 3.99 (dq, 1H, *J* 1.2, 9.2 Hz), 3.92-3.65 (m, 7H), 3.11 (dt, 1H, *J* 2.0, 9.2 Hz), 2.97 (dd, 1H, *J* 2.4, 10.8 Hz), 2.75-2.60 (m, 2H), 1.18 (t, 1H, *J* 7.6 Hz). ¹³C NMR (100 MHz; CDCl₃) δ : 167.8, 167.2, 137.2, 134.8, 134.3, 134.2, 131.9, 131.6, 131.0, 129.1, 128.3, 126.0, 125.9, 124.0, 123.4, 116.9, 116.8, 101.4, 95.5, 83.0, 81.9, 74.6, 72.4, 70.4, 69.8, 69.5, 69.1, 68.7, 67.6, 54.5, 24.1, 14.9.

Methyl (4,6-di-*O*-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzyl-6-*O*- α -D-glucopyranoside (4k)



Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2o**: 46 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 9:1 to 5:2) product **4k** was obtained as a colourless oil (51 mg, 0.076 mmol, 76%). HRMS calcd. for C₄₀H₄₈O₉+H⁺ (M+H)⁺: 673.3377, found: 673.3371. ¹H NMR (400 MHz; CDCl₃) δ: 7.37-7.27 (m, 15H), 6.02 (d, 1H, *J* 10.0 Hz), 5.93-5.81 (m, 2H), 5.77 (dt, 1H, *J* 2.4, 10.0 Hz), 5.29-5.12 (m, 4H), 5.08 (bs, 1H), 4.96 (d, 1H, *J* 10.8 Hz), 4.87 (d, 1H, *J* 10.8 Hz), 4.78 (d, 1H, *J* 12.0 Hz), 4.66 (d, 1H, *J* 12.0 Hz), 4.64 (d, 1H, *J* 10.8 Hz), 4.61 (d, 1H, *J* 3.6 Hz), 4.13-3.96 (m, 6H), 3.93-3.73 (m, 3H), 3.69 (dd, 1H, *J* 1.6, 9.2 Hz), 3.63-3.46 (m, 4H), 3.36 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ: 139.0, 138.8, 138.4, 134.8, 131.0, 128.6, 18.5, 128.2, 128.0, 127.73, 127.70, 127.6, 126.5, 117.3, 117.2, 98.3, 95.3, 82.2, 80.1, 78.0, 75.8, 75.0, 73.5, 72.6, 70.3, 70.2, 70.1, 69.6, 68.8, 67.0, 55.3.

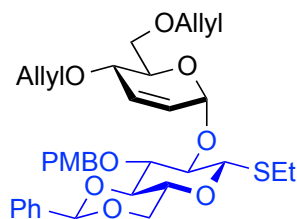
***p*-Methoxyphenyl 3-*O*-(4,6-di-*O*-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-2,4,6-tri-*O*-benzyl- β -D-galactopyranoside (**4l**)**



Following *General Glycosylation Procedure*. Galactal **1n**: 40 mg (0.15 mmol), acceptor **2p**: 55 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 9:1 to 2:1) product **4l** was obtained as a colourless oil (58.3 mg, 0.076 mmol, 76%). HRMS calcd. for C₄₆H₅₂O₁₀+H⁺ (M+H)⁺: 765.3639, found: 765.3641. ¹H NMR (400 MHz; CDCl₃) δ: 7.36-7.24 (m, 15H), 7.04-7.00 (m, 2H), 6.81-6.77 (m, 2H), 6.09 (d, 1H, *J* 10.0 Hz), 5.95-5.77 (m, 2H), 5.65 (dt, 1H, *J* 2.0, 10.0 Hz), 5.27 (dq, 1H, *J* 1.2, 17.2 Hz), 5.20-5.10 (m, 4H), 5.00 (d, 1H, *J* 10.4 Hz), 4.88 (d, 1H, *J* 6.8 Hz), 4.84 (d, 1H, *J* 11.6 Hz), 4.75 (d, 1H, *J* 10.8 Hz), 4.58 (d, 1H, *J* 11.6 Hz), 4.50 (d, 1H, *J* 12.0 Hz), 4.44 (d, 1H, *J* 11.6 Hz), 4.16-3.92 (m, 8H), 3.79-3.74 (m, 4H), 3.71-3.65 (m, 3H), 3.24 (d, 1H, *J* 2.0 Hz). ¹³C NMR (100 MHz;

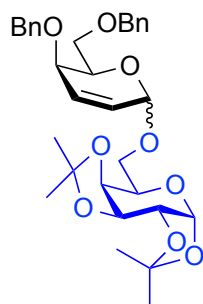
CDCl₃) δ : 155.3, 151.9, 138.7, 138.5, 138.1, 135.0, 134.8, 132.2, 128.6, 128.5, 128.4, 128.31, 128.26, 127.90, 127.87, 127.81, 127.6, 125.9, 118.5, 117.1, 116.9, 114.6, 103.4, 91.3, 77.8, 77.3, 75.4, 75.0, 73.7, 72.6, 72.4, 70.3, 69.9, 69.2, 68.9, 68.3, 55.8.

Ethyl 4,6-*O*-benzylidene-2-*O*-(4,6-di-*O*-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-3-*O*-*p*-methoxybenzyl-1-thio- β -D-glucopyranoside (4m**)**



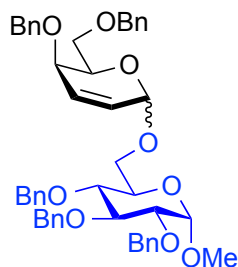
Following *General Glycosylation Procedure*. Glucal **1n**: 40 mg (0.15 mmol), acceptor **2q**²⁰: 43 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 3:2) product **4m** was obtained as a colourless oil (45 mg, 0.07 mmol, 70%). HRMS calcd. for C₃₅H₄₄O₉S+Na⁺ (M+Na)⁺: 663.2604, found: 663.2611. [α]_D²⁵ -27.5° (*c* 1.6, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 7.47-7.43 (m, 2H), 7.38-7.33 (m, 3H), 7.27 (d, 1H, *J* 8.4 Hz), 6.81 (d, 1H, *J* 8.4 Hz), 6.07 (d, 1H, *J* 10.0 Hz), 5.97-5.81 (m, 2H), 5.78 (dt, 1H, *J* 2.4, 10.0 Hz), 5.58 (s, 1H), 5.52 (s, 1H), 5.29 (dq, 1H, *J* 1.6, 17.2 Hz), 5.20-5.11 (m, 3H), 4.92 (d, 1H, *J* 10.4 Hz), 4.59 (d, 1H, *J* 10.8 Hz), 4.48 (d, 1H, *J* 9.6 Hz), 4.48 (dd, 1H, *J* 5.2, 10.4 Hz), 4.17-4.08 (m, 2H), 4.04-3.93 (m, 2H), 3.85 (dt, 1H, *J* 2.4, 9.2 Hz), 3.79-3.66 (m, 8H), 3.50-3.44 (m, 1H), 3.16 (dd, 1H, *J* 2.0, 10.8 Hz), 3.08 (dd, 1H, *J* 1.2, 10.8 Hz), 2.80-2.65 (m, 2H), 1.28 (t, 1H, *J* 7.6 Hz). ¹³C NMR (100 MHz; CDCl₃) δ : 159.4, 137.4, 135.1, 134.9, 131.8, 130.8, 130.2, 129.1, 128.4, 126.1, 125.9, 117.2, 116.9, 113.8, 101.3, 94.9, 86.4, 82.3, 81.3, 76.5, 75.2, 72.5, 70.6, 69.8, 69.5, 68.9, 68.1, 55.4, 25.0, 15.1.

6-*O*-(2,3-Dideoxy-4,6-di-*O*-benzyl- α -D-threo-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (4n**)**



Following *General Glycosylation Procedure*. Galactal **1u**²¹: 55 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 10:1 to 5:2) product **4n** was obtained as a colourless oil (39 mg, 0.069 mmol, 69%). HRMS calcd. for C₃₂H₄₀O₉+H⁺ (M+H)⁺: 569.2751, found: 569.2747. ¹H NMR (400 MHz; CDCl₃) δ : 7.34-7.27 (m, 15H), 6.10 (dd, 1H, *J* 4.8, 10.0 Hz), 5.98 (dd, 1H, *J* 2.8, 10.0 Hz), 5.51 (d, 1H, *J* 4.8 Hz), 5.13 (d, 1H, *J* 2.8 Hz), 4.64-4.54 (m, 5H), 4.31-4.26 (m, 3H), 4.07-4.03 (m, 1H), 3.88-3.77 (m, 3H), 3.74-3.69 (m, 2H), 1.52 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). ¹³C NMR (100 MHz; CDCl₃) δ : 138.6, 138.4, 129.6, 128.52, 128.48, 127.9, 127.83, 127.79, 127.7, 127.2, 109.4, 108.7, 96.5, 94.7, 77.4, 73.6, 71.3, 71.0, 70.81, 70.78, 69.6, 69.3, 67.3, 66.8, 66.1, 58.6, 26.2, 26.1, 25.1, 24.7.

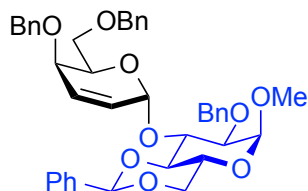
Methyl 6-*O*-(4,6-di-*O*-benzyl-2,3-dideoxy- α -D-threo-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (4o**)**



Following *General Glycosylation Procedure*. Galactal **1u**: 55 mg (0.15 mmol), acceptor **2o**: 46 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃:

27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 10:1 to 3:1) product **4o** was obtained as a colourless oil (60.5 mg, 0.079 mmol, 79%). HRMS calcd. for $C_{48}H_{52}O_9+H^+$ ($M+H$) $^+$: 773.3690, found: 773.3688. 1H NMR (500 MHz; $CDCl_3$) δ : 7.37-7.26 (m, 22H), 7.25-7.22 (m, 3H), 6.09 (dd, 1H, J 5.5, 10.5 Hz), 5.99 (dd, 1H, J 3.0, 10.5 Hz), 5.14 (d, 1H, J 2.5 Hz), 4.96 (d, 1H, J 11.0 Hz), 4.84 (d, 1H, J 10.5 Hz), 4.80 (d, 1H, J 11.0 Hz), 4.78 (d, 1H, J 11.0 Hz), 4.67-4.65 (m, 4H), 4.54 (d, 1H, J 12.0 Hz), 4.46 (d, 1H, J 12.0 Hz), 4.40 (d, 1H, J 12.0 Hz), 4.23 (dd, 1H, J 2.5, 6.5 Hz), 4.06 (d, 1H, J 3.0, 11.5 Hz), 3.98 (d, 1H, J 9.5 Hz), 3.80-3.71 (m, 4H), 3.62 (dd, 1H, J 6.0, 9.5 Hz), 3.58 (t, 1H, J 9.5 Hz), 3.52 (dd, 1H, J 3.5, 9.5 Hz), 3.37 (s, 3H). ^{13}C NMR (125 MHz; $CDCl_3$) δ : 138.9, 138.6, 138.5, 138.4, 138.3, 129.6, 128.6, 128.52, 128.50, 128.46, 128.4, 128.2, 128.1, 128.02, 127.97, 127.9, 127.80, 127.77, 127.70, 127.65, 98.2, 94.7, 82.2, 80.0, 78.0, 75.9, 75.1, 73.5, 71.3, 70.2, 69.8, 69.3, 67.2, 66.8, 55.3.

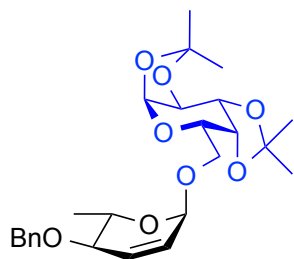
Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(4,6-di-*O*-benzyl-2,3-dideoxy- α -D-threo-hex-2-enopyranosyl)- α -D-glucopyranoside (4p**)**



Following *General Glycosylation Procedure*. Galactal **1u**: 55 mg (0.15 mmol), acceptor **2h**: 37 mg (0.1 mmol), $[Ir(COD)Cl]_2$: 3.4 mg (0.00525 mmol), $AgOTf$: 5.4 mg (0.021 mmol), Ag_2CO_3 : 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 3:2) product **4p** was obtained as a white solid (39 mg, 0.057 mmol, 57%). HRMS calcd. for $C_{41}H_{44}O_9+H^+$ ($M+H$) $^+$: 681.3064, found: 681.3062. $[\alpha]_D^{25} +31.8$ (c 1.5, $CHCl_3$). 1H NMR (400 MHz; $CDCl_3$) δ : 7.44-7.22 (m, 20H), 6.09 (dd, 1H, J 5.2, 10.0 Hz), 5.99 (dd, 1H, J 3.2, 10.0 Hz), 5.52 (d, 1H, J 3.2 Hz), 5.51 (s, 1H), 4.83 (d, 1H, J 12.4 Hz), 4.61 (d, 1H, J 12.0 Hz), 4.58 (d, 2H, J 13.2 Hz), 4.51-4.39 (m, 4H), 4.37 (t, 1H, J 9.2 Hz), 4.23 (dd, 1H, J 4.8, 10.4 Hz), 3.84 (t, 1H, J 9.2 Hz), 3.83-3.77 (m, 2H), 3.72 (t, 1H, J 5.2, 8.8 Hz), 3.70 (t, 1H, J 10.4 Hz), 3.54 (t, 1H, J 9.2 Hz), 3.46 (dd, 1H, J 3.6, 9.2 Hz), 3.35 (s, 3H). ^{13}C NMR (100 MHz; $CDCl_3$) δ : 138.8, 138.7, 138.6, 137.4, 129.6, 129.1, 128.6, 128.42, 128.39, 128.2,

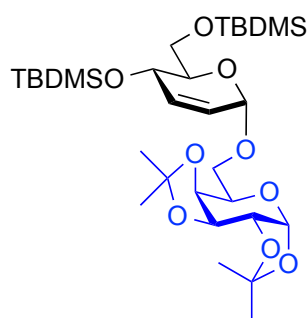
128.0, 127.94, 127.89, 127.7, 127.6, 127.3, 126.1, 101.5, 99.5, 94.8, 82.9, 78.2, 74.8, 73.9, 73.5, 71.7, 69.4, 69.2, 68.9, 67.2, 62.1, 55.4. Melting point: 133 °C.

6-*O*-(4-*O*-Benzyl-2,3,6-trideoxy- α -L-erythro-hex-2-enopyranoside)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (4q**)**



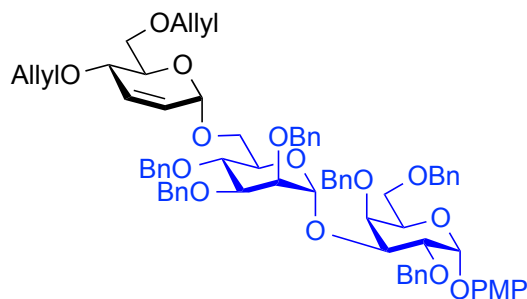
Following *General Glycosylation Procedure*. Rhamnol **1v**²²: 39 mg (0.15 mmol), acceptor **2a**: 26 mg (0.1 mmol), [Ir(COD)Cl]₂: 3.4 mg (0.00525 mmol), AgOTf: 5.4 mg (0.021 mmol), Ag₂CO₃: 27.6 mg (1 mmol), DCM: 3 mL. Reaction time: 48 hours. Following purification by column chromatography (Hexane:EtOAc = 9:1 to 4:1) product **4q** was obtained as a colourless oil (35 mg, 0.076 mmol, 76%). HRMS calcd. for C₂₅H₃₄O₈+H⁺ (M+H)⁺: 463.2332, found: 463.2328. [α]_D²⁵ -53.1 (*c* 1.1, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ: 7.36-7.26 (m, 5H), 6.04 (d, 1H, *J* 10.0 Hz), 5.79 (dt, 1H, *J* 2.4, 10.4 Hz), 5.52 (d, 1H, *J* 5.2 Hz), 4.99 (t, 1H, *J* 0.8 Hz), 4.65 (d, 1H, *J* 11.6 Hz), 4.58 (d, 1H, *J* 2.4, 7.6 Hz), 4.53 (d, 1H, *J* 11.6 Hz), 4.30 (d, 1H, *J* 2.4, 5.2 Hz), 4.27 (d, 1H, *J* 1.6, 8.0 Hz), 3.99- 3.89 (m, 3H), 3.70 (dq, 1H, *J* 1.6, 9.2 Hz), 3.64 (dd, 1H, *J* 8.8, 12.4 Hz), 1.53 (s, 3H), 1.44 (s, 3H), 1.32 (s, 6H), 1.29 (d, 1H, *J* 6.0 Hz). ¹³C NMR (100 MHz; CDCl₃) δ: 138.2, 130.6, 128.5, 127.9, 127.8, 126.9, 109.2, 108.6, 96.4, 94.4, 76.5, 71.2, 71.0, 70.7, 67.2, 66.3, 65.8, 26.2, 26.1, 25.0, 24.5, 18.2.

6-*O*-(4,6-Di-*O*-*tert*-butyldimethylsilyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)- α -D-galactopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (4r**)**



Procedure: See experimental part of **3y**. **4r** obtained as a white solid (44 mg, 0.071 mmol, 71%). HRMS calcd. for $C_{30}H_{56}O_9Si_2+H^+$ ($M+H$)⁺: 617.3541, found: 617.3540. ¹H NMR (400 MHz; CDCl₃) δ : 5.84 (d, 1.16H, *J* 10.4 Hz), 5.74 (dt, 0.13H, *J* 1.2, 10.0 Hz), 5.68 (dd, 1H, *J* 2.0, 10.0 Hz), 5.52 (m, 1.14H), 5.19 (q, 0.13H, *J* 1.6 Hz), 5.01 (bs, 1H), 4.59 (m, 1.16H), 4.31-4.22 (m, 3.51H), 4.00-3.94 (m, 1.32H), 3.89-3.75 (m, 3.39H), 3.71-3.61 (m, 2.25H), 3.55-3.52 (m, 0.15H), 1.525-1.517 (m, 3.50H), 1.44 (s, 3.51H), 1.34-1.32 (s, 7.02H), 0.89-0.88 (m, 21.80H), 0.08-0.06 (m, 14.26H). ¹³C NMR (100 MHz; CDCl₃) δ : 134.8, 133.0, 127.8, 125.5, 109.4, 109.3, 108.7, 108.6, 97.1, 96.5, 94.3, 79.4, 72.6, 71.4, 70.9, 71.0, 70.9, 70.8, 70.7, 67.6, 66.7, 66.14, 66.06, 63.9, 63.4, 62.8, 62.5, 26.3, 26.14, 26.09, 25.93, 25.87, 25.09, 25.06, 24.7, 24.6, 18.61, 18.55, 18.2, 18.1, -4.17, -4.24, -4.67, -4.72, -4.88, -4.94, -5.1, -5.2. Melting point: 85 °C.

***p*-Methoxyphenyl (4,6-di-*O*-allyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 3)-2,4,6-tri-*O*-benzyl- β -D-galactopyranoside (**7**)**



Following *General Glycosylation Procedure*. Glucal **1n**: 20 mg (0.075 mmol), acceptor **2v**: 49 mg (0.05 mmol), [Ir(COD)Cl]₂: 1.7 mg (0.002625 mmol), AgOTf: 2.7 mg (0.0105 mmol), Ag₂CO₃: 13.8 mg, DCM: 1.5 mL. Reaction time: 72 hours. Following purification by column chromatography (Hexane:EtOAc = 8:1 to 2:1) product **7** was obtained as a colourless oil (31 mg, 0.053 mmol, 53%). HRMS calcd. for C₇₃H₈₀O₁₅+H⁺ (M+H)⁺: 1197.5575, found: 1197.5581. [α]_D²⁵ -19.6 (*c* 0.7, CHCl₃). ¹H NMR (400 MHz; CDCl₃) δ : 7.39-7.00 (m, 32H), 6.80 (d, 1H, *J* 8.8 Hz), 5.96-5.84 (m, 3H), 5.75 (dt, 1H, *J* 2.0, 10.4 Hz), 5.30-5.22 (m, 2H), 5.18-5.14 (m, 2H), 5.02-4.97 (m, 3H), 4.86-4.83 (m, 2H), 4.78 (d, 1H, *J* 12.4 Hz), 4.68-4.61 (m, 4H), 4.56 (d, 1H, *J* 12.8 Hz), 4.53 (d, 1H, *J* 12.8 Hz), 4.45 (d, 1H, *J* 11.6 Hz), 4.36 (d, 1H, *J* 11.6 Hz), 4.27 (d, 1H, *J* 11.6 Hz), 4.13-3.77 (m, 17H), 3.69-3.63 (m, 5H), 3.58 (dd, 1H, *J* 3.2, 10.8 Hz), 3.49 (d, 1H, *J* 10.4 Hz). ¹³C NMR (100 MHz; CDCl₃) δ : 155.3, 151.4, 139.2, 138.6, 138.5, 138.1, 137.9, 135.0, 130.4, 129.0, 128.54, 128.50, 128.49, 128.4, 128.31, 128.28, 128.0, 127.89, 127.87, 127.82, 127.75, 127.7, 127.6, 127.4, 127.0, 118.6, 117.1, 114.6, 103.2, 95.1, 94.5, 79.9, 77.3, 75.9, 75.6, 75.13, 75.06, 74.8, 74.6, 73.6, 73.3, 73.0, 72.6, 72.5, 72.4, 72.0, 70.2, 69.4, 68.9, 68.6, 66.9, 55.8.

¹H NMR Experiments:

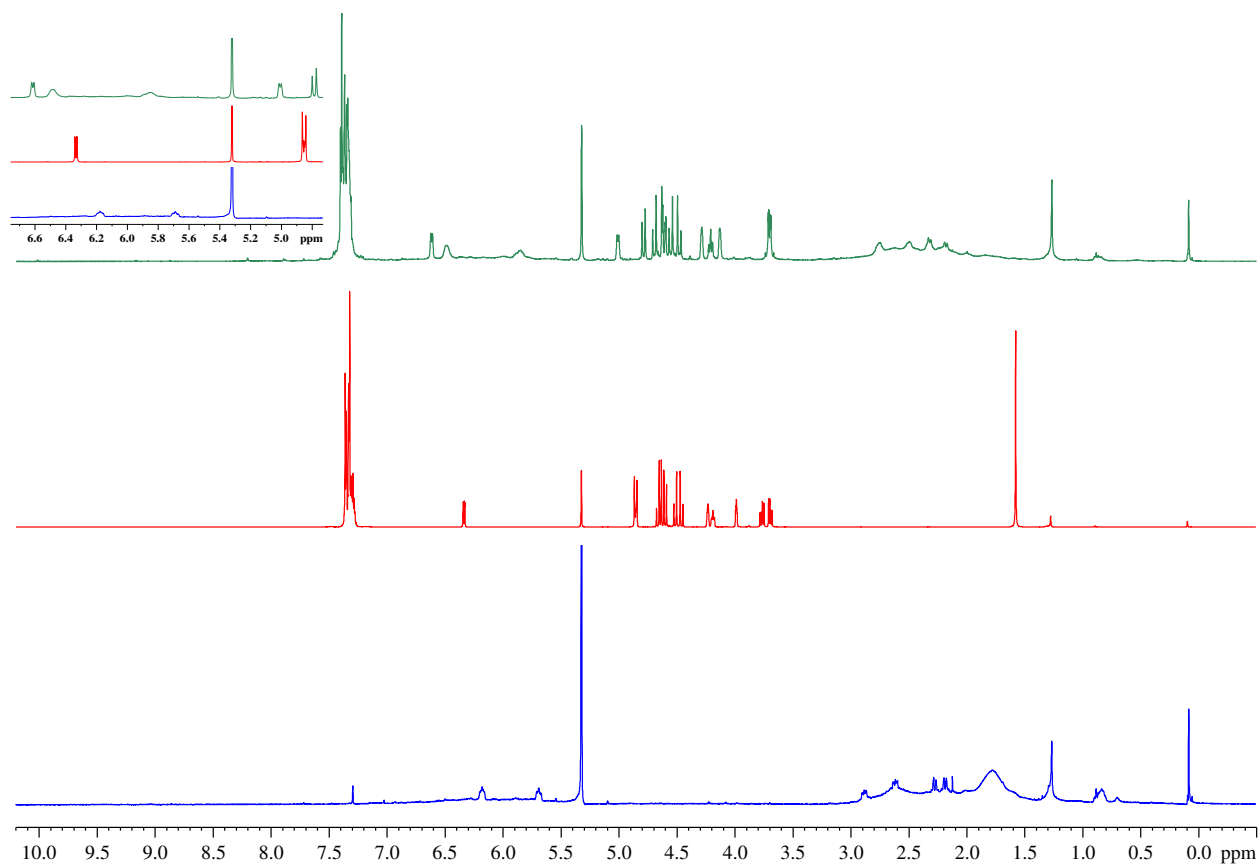


Figure S1. ¹H-NMR spectra in CD₂Cl₂ of (A) [Ir(COD)Cl]₂/AgOTf; (B) Glycal donor **1a**; (C) Glycal donor **1a**, [Ir(COD)Cl]₂/AgOTf.

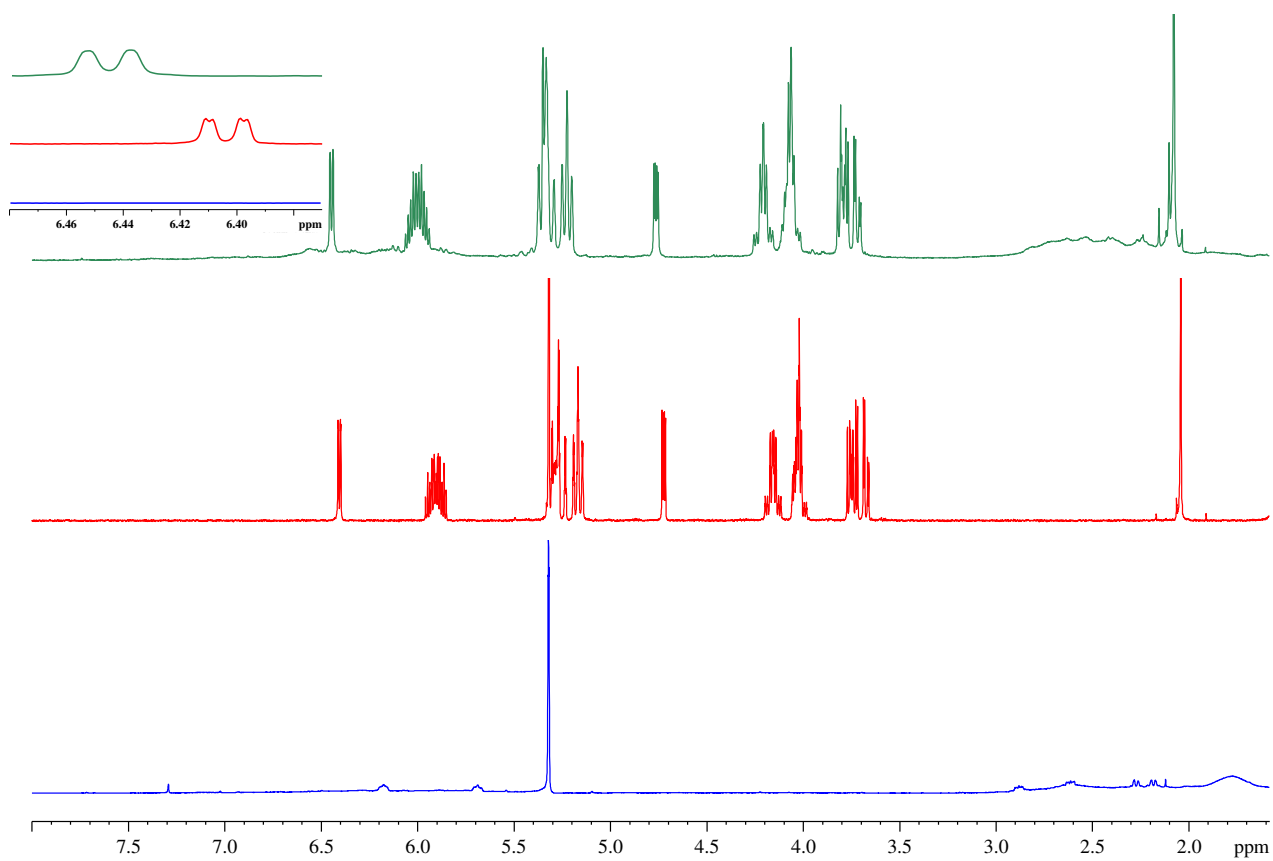


Figure S2. $^1\text{H-NMR}$ spectra in CD_2Cl_2 of (A) $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{AgOTf}$; (B) Glycal donor **1n**; (C) Glycal donor **1n**, $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{AgOTf}$.

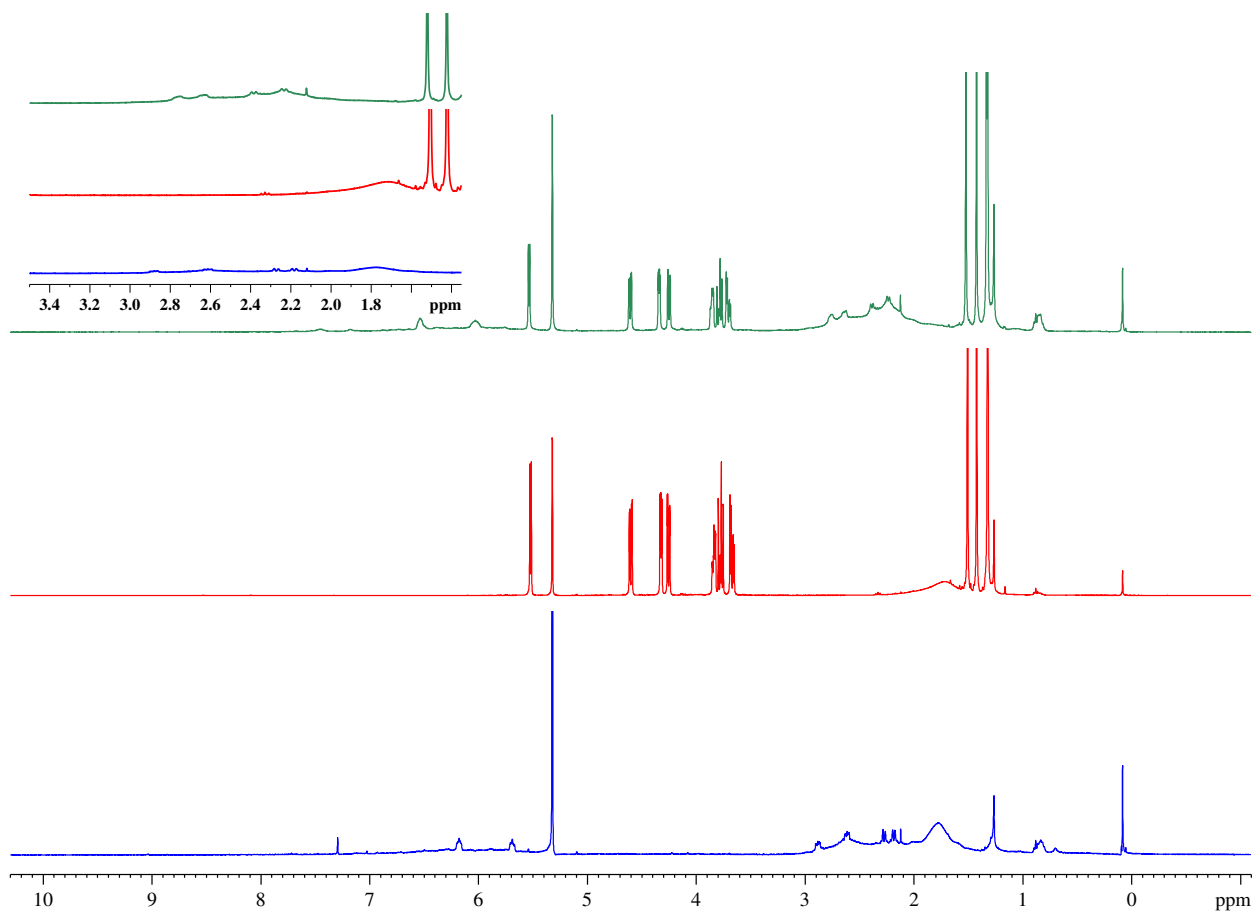


Figure S3. ^1H -NMR spectra in CD_2Cl_2 of (A) $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{AgOTf}$; (B) Glycosyl acceptor **2a**; (C) Glycosyl acceptor **2a**, $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{AgOTf}$.

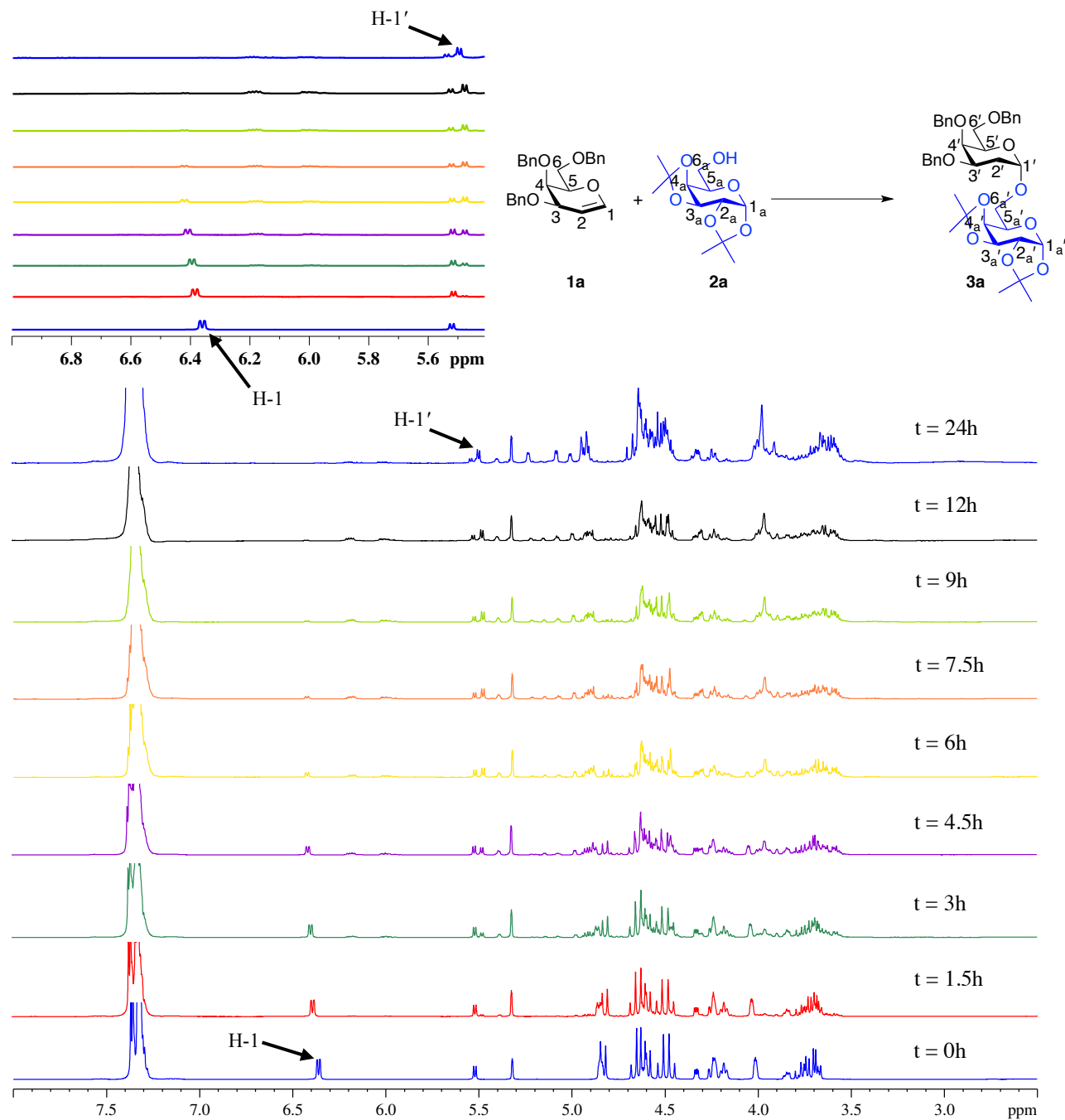


Figure S4. $^1\text{H-NMR}$ monitoring of reaction between galactal **1a** and glycosyl acceptor **2a** using General Glycosylation Procedure for the synthesis of 2-deoxy glycosides in CD_2Cl_2 .

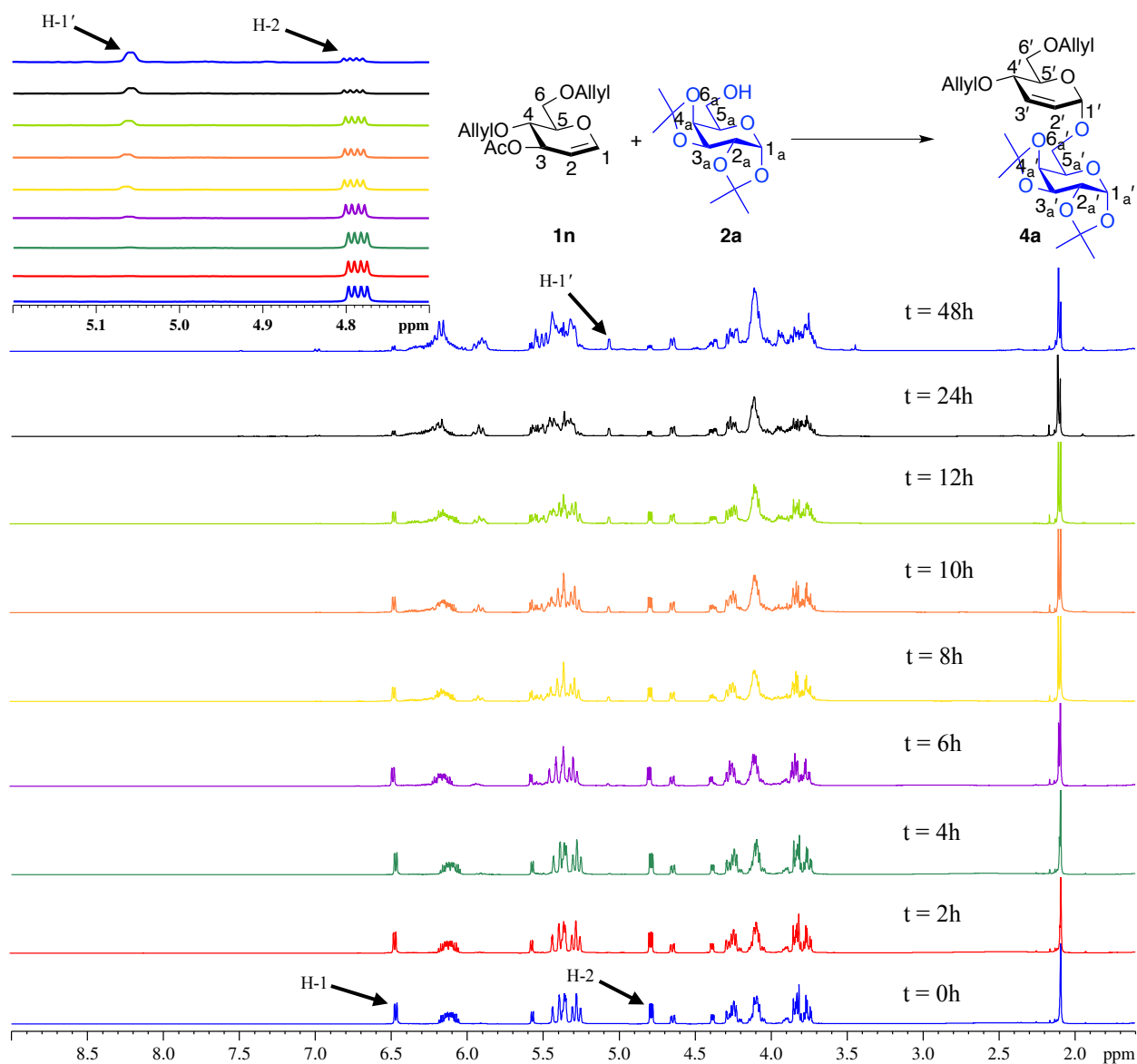


Figure S5. $^1\text{H-NMR}$ monitoring of reaction between galactal **1m** and glycosyl acceptor **2a** using General Glycosylation Procedure for the synthesis of 2,3-unsaturated glycosides in CD_2Cl_2 .

In Situ Anomerization experiment of **3x with **2a**:**

Disaccharide **3x** (4:1, α : β mixture 0.1 mmol), acceptor **2a** (0.1 mmol) were weighed into a 10 mL round bottom flask and dried under vacuum for 2 h. In a separate seal tube $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.5 mol% w.r.t. glycal donor) and AgOTf (10.5 mol% w.r.t. glycal donor) in anhydrous CD_2Cl_2 (1 mL) were taken and stirred vigorously for 30 minutes under N_2 atmosphere. Then the mixture of donor and acceptor was dissolved in anhydrous CD_2Cl_2 (2 mL), and the solution was

transferred to the seal tube containing Ir(I) catalyst using a cannula under N₂ atmosphere. The reaction mixture was stirred at ambient temperature for 24 h under N₂ atmosphere, after which the ¹H NMR was checked with the crude mixture that showed no change in the anomeric ratio (4:1, α:β mixture). (Figure S6)

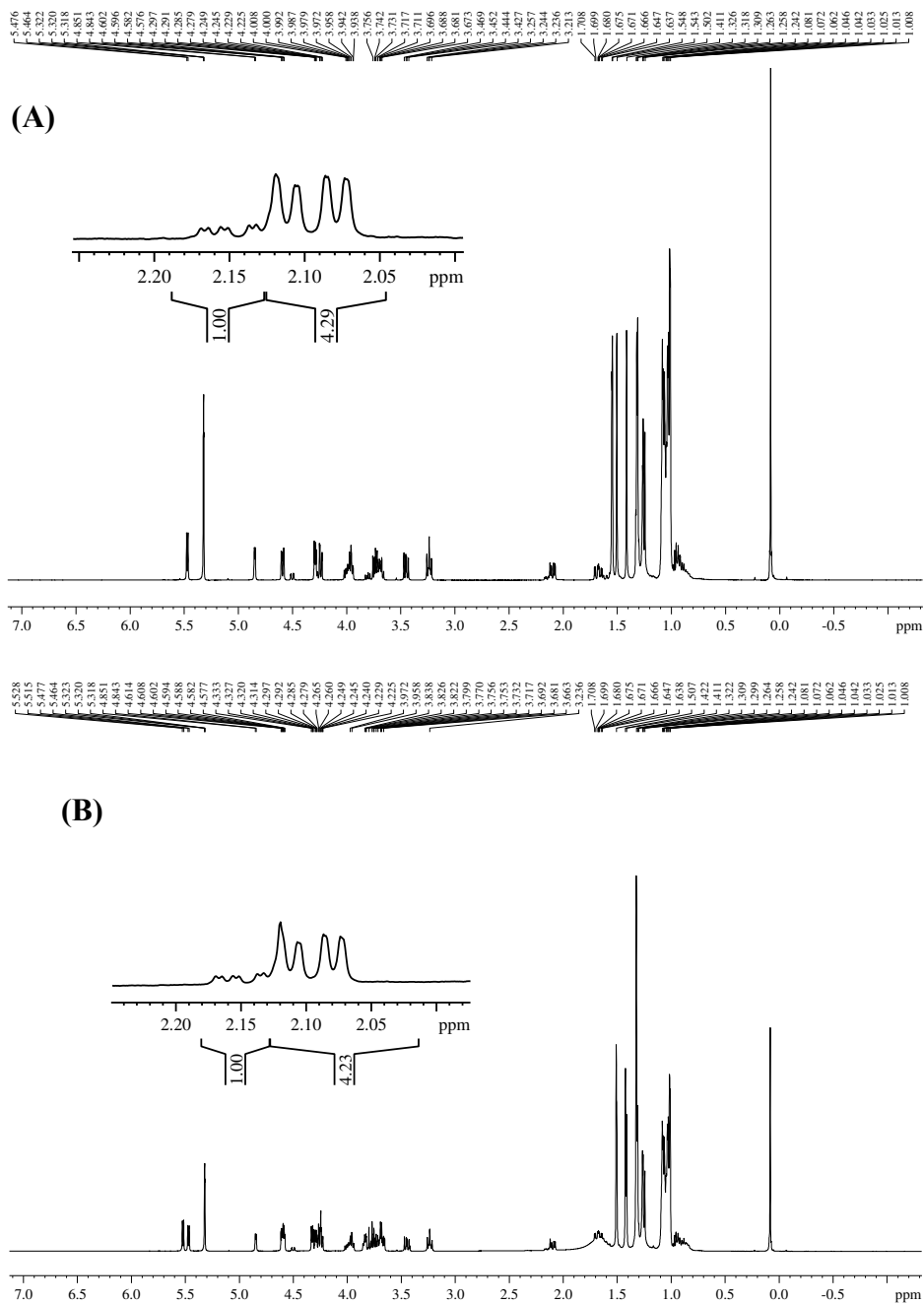


Figure S6. ¹H-NMR spectra in CD₂Cl₂ of : (A) a 4:1 α:β mixture of **3x** and (B) reaction mixture containing **3x** (4:1, α:β) after being subjected to the reaction conditions in the presence of Ir (I)-catalyst, AgOTf and glycoside acceptor **2a**. This result reveals that the obtained α-selectivity is not the result of *in situ* anomerization.

Mechanistic insight:

We initially hypothesized that the observed α -stereoselectivity of the iridium catalyzed glycosylation in experiments involving 3,4,6-tri-*O*-benzyl-D-galactal (**1a**), 3-*O*-acetyly-4,6-di-*O*-benzyl-D-galactal (**1u**) donors and 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose acceptor (**2a**) could arise from either of the two plausible mechanisms, blocking or directing. For both mechanisms, the catalytic cycles involve formation of intermediates with the glycal substrate coordinated to the iridium.

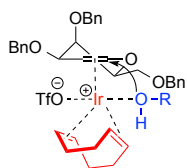
In the blocking mechanism, Ir(COD) shields the face from which it coordinates to the pyranose ring, and the acceptor approaches the anomeric center as a free nucleophile from the opposite face to exclusively afford the corresponding glycoside product (Figure S7 and Figure S8). On the contrary, in the directing mechanism, the acceptor alcohol coordinates to the iridium metal center as a ligand in the intermediate complexes. Upon formation of the complexed iridium-glycal intermediates, the acceptor is delivered to the vicinity of anomeric center from the same face of the metal center to which it is coordinated to, and the nucleophilic attack occur at the same face from which the metal coordinates.

DFT results suggest significant stabilizations associated with acceptor coordinating to the metal center in both free Ir(COD)OTf and glycal coordinated Ir(COD)OTf complexes, thus we hypothesized that the iridium catalyzed glycosylation reaction favourably proceed through directing mechanism, and the catalytic cycle of glycosylation by the galacatal **1a** proceed through the following stages: [Ir(COD)OTf]₂ dimer and free **1a** and **2a** → Ir(COD)OTf monomers (*2) and free reagents → Ir(COD)OTf-**1a** η^2 π -allyl complex (**IM1**) and free **2a** → Ir(COD)OTf-**1a-2a** complex (**IM2**) → transition state of the nucleophilic attack (**TS**) → glycosidic product (**3a**) and Ir(COD)OTf complexes; while the catalytic cycle of glycosylation by the 3-*O*-acetyl galacatal **1u** proceed through the following stages: [Ir(COD)OTf]₂ and free reagents → Ir(COD)OTf (*2) and free reagents → Ir(COD)OTf-**1u** η^2 π -allyl complex (**IM1'**) and free **2a** → Ir(COD)-OAc-**1u** η^3 π -allyl complex (**IM2'**), free triflate anion and free **2a** → Ir(COD)OAc-**1u-2a** complex (**IM3'**) and free OTf anion → transition state of nucleophilic attack (**TS'**) → glycosidic product (**4a**), Ir(COD)OAc complex and triflate anion → glycosidic product (**4a**), Ir(COD)OTf complex and acetate anion (Figure S11 and Figure S12).

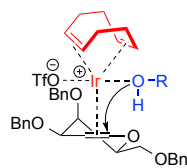
Computation Details:

All reagents, catalysts, possible glycosylation products, and key intermediate structures were built and subjected to geometry optimization at B3LYP-d3/BSI level of theory, where BSI denotes a combined basis set of LANL2DZ is for description of the iridium atom and def2-ma-TZVP for the rest atoms. Integral equation formalism variant (IEFPCM) method was applied at the same level of theory to account for the solvent effects exerted by CH_2Cl_2 . From the optimized intermediates which directly undergo nucleophilic attack by **2a**, transition states structures of the nucleophilic attack process were explored. Frequency analysis were performed at same level of theory on the optimized structures to ensure there is no imaginary frequency for the ground state species and exactly one imaginary frequency for each transition state structure. Gibbs free energy of each stage of the catalytic cycle were computed from optimized structure of the chemical species on the species Gibbs free energy were computed from the optimized structure at the same level of theory, and energy profile.

The hypothesis that the glycosylation reaction probably proceeds through directing mechanism is supported by the computation results that coordination of acceptor **2a** to the Ir(COD)OTf complex is energetically favourable, with associated Gibbs energy change ~ 38.5 kcal/mol. Geometry optimization of the proposed intermediates converged to optimized structures with no imaginary frequency, and the energy profile of the stages in the catalytic cycles of glycosylation of **1a** and **1u** are shown in Figure S9 and Figure S10. Unexpectedly, the $[\text{Ir}(\text{COD})\text{OTf}]_2$ dimer with a symmetrical starting structure converged to a non-symmetrical optimized structure. (Figure S16.) With one iridium metal center further away from both triflate anions with respect to another. The result prompted us to investigate the probability of heterolysis of the dimer, forming Ir(COD) and Ir(COD)OTf₂ complex. Further computations indicate that formation of two Ir(COD)OTf complex is energetically favourable over formation of an Ir(COD) and an Ir(COD)OTf₂, though by a small margin. Which justify our hypothesis that Ir(COD)OTf complexes are formed as the catalytic species that coordinates to the glycal. The Ir(COD)OTf species is less stable than the $[\text{Ir}(\text{COD})\text{OTf}]_2$ dimer by a moderate ~ 15 kcal under the reaction conditions, indicating that $[\text{Ir}(\text{COD})\text{OTf}]_2$ serve as a reservoir of active catalytic species, which can promptly convert to Ir(COD)OTf complexes to participate in the following steps in the catalytic cycle.

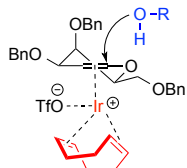
Directing pathway

Intermediate: α -Complex
Product: α -Glycoside
 $E_{rel} = 0.00$ Kcal/mol

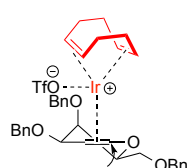


Intermediate: β -Complex
Product: β -Glycoside
 $E_{rel} = 6.27$ Kcal/mol

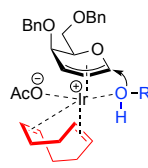
ROH = 2a

Blocking pathway

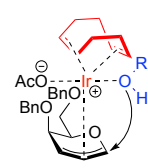
Intermediate: α -Complex
Product: β -Glycoside
 $E_{rel} = 4.08$ Kcal/mol



Intermediate: β -Complex
Product: α -Glycoside
 $E_{rel} = 7.15$ Kcal/mol

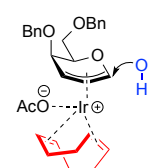
Directing pathway

Intermediate: α -Complex
Product: α -Glycoside
 $E_{rel} = 0.00$ Kcal/mol

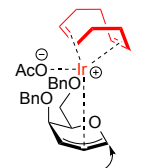


Intermediate: β -Complex
Product: β -Glycoside
 $E_{rel} = 6.62$ Kcal/mol

ROH = 2a

Blocking pathway

Intermediate: α -Complex
Product: β -Glycoside
 $E_{rel} = 4.69$ Kcal/mol



Intermediate: β -Complex
Product: α -Glycoside
 $E_{rel} = 8.13$ Kcal/mol

Figure S7. Schematic representation of the plausible intermediates arising from **1a**, **2a** and Ir(I)-catalyst.

Figure S8. Schematic representation of the plausible intermediates arising from **1u**, **2a** and Ir(I)-catalyst.

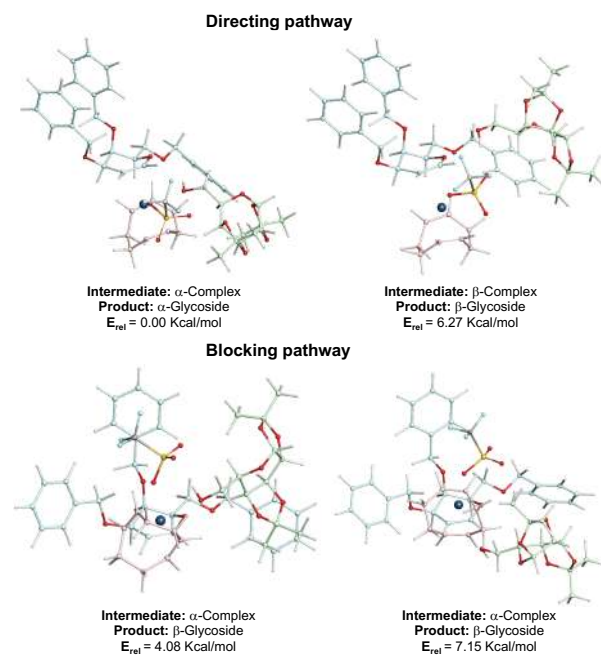


Figure S9. Calculated structures and relative energies of plausible intermediates arising from glycosylation of **1a** and **2a**.

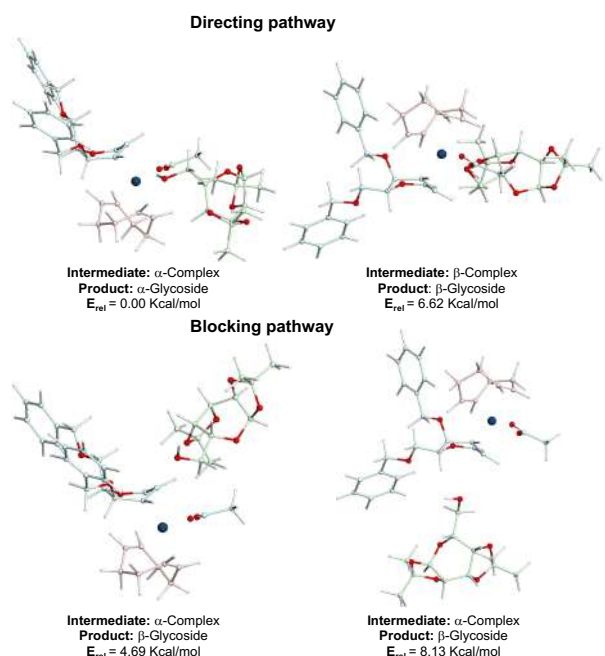


Figure S10. Calculated structures and relative energies of plausible intermediates arising from glycosylation of **1u** and **2a**.

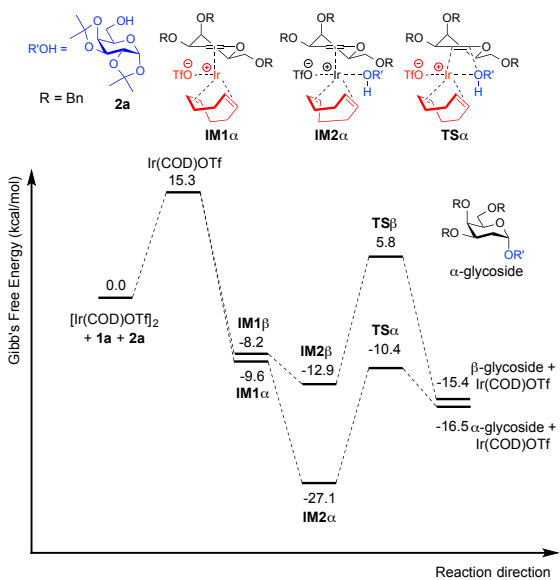


Figure S11. Free energy profile for the catalytic cycle of iridium catalyzed glycosylation of 3,4,6-tri-*O*-benzyl galactal (**1a**).

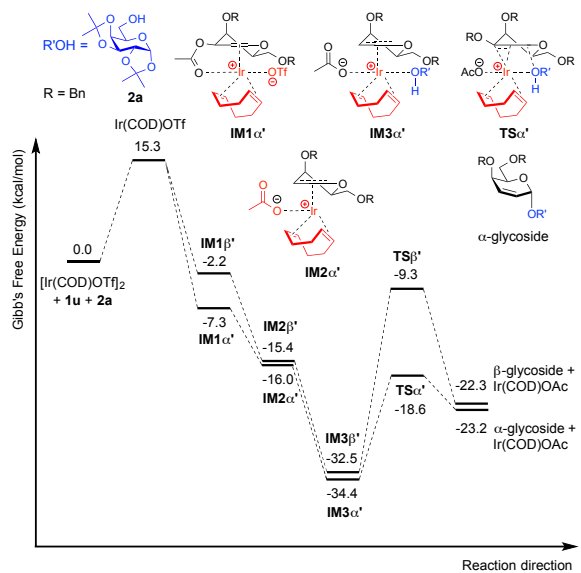


Figure S12. Free energy profile for the catalytic cycle of iridium catalyzed glycosylation of 3-*O*-acetyl-4,6-di-*O*-benzyl galactal (**1u**).

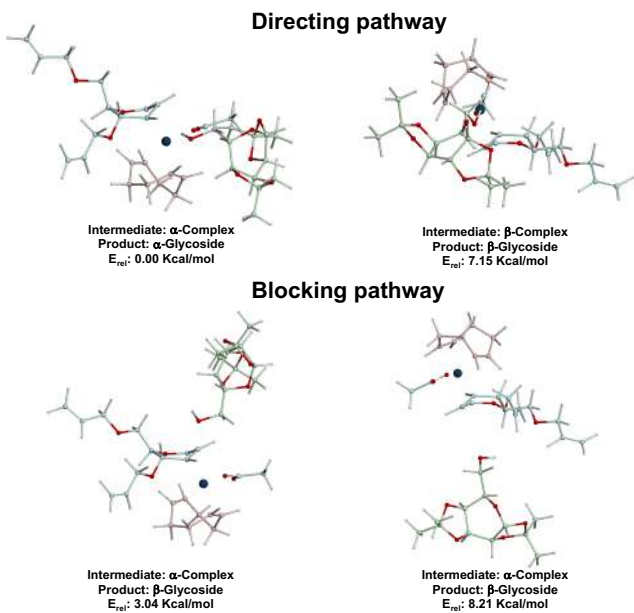


Figure S13. Schematic representation of the plausible intermediates arising from **1n**, **2a**, and Ir(I)-catalyst.

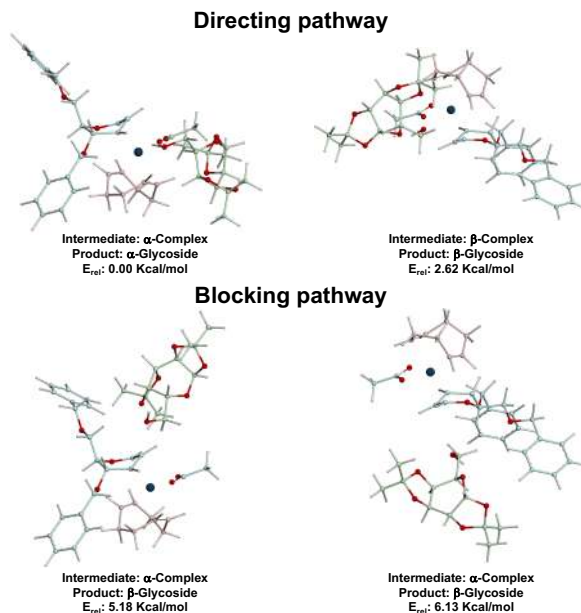


Figure S14. Schematic representation of the plausible intermediates arising from **1p**, **2a**, and Ir(I)-catalyst.

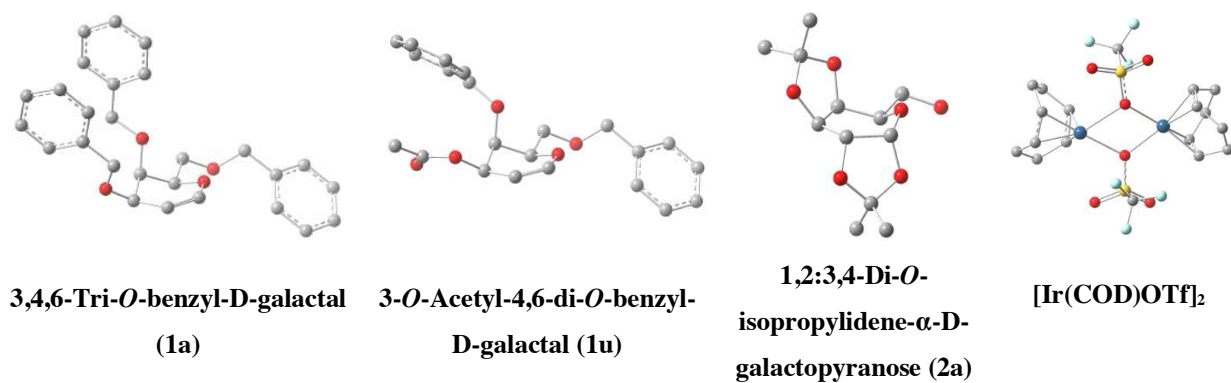


Figure S15. Optimized structures of free glycol donors (**1a** and **1u**), model acceptor (**2a**) and the active catalyst.

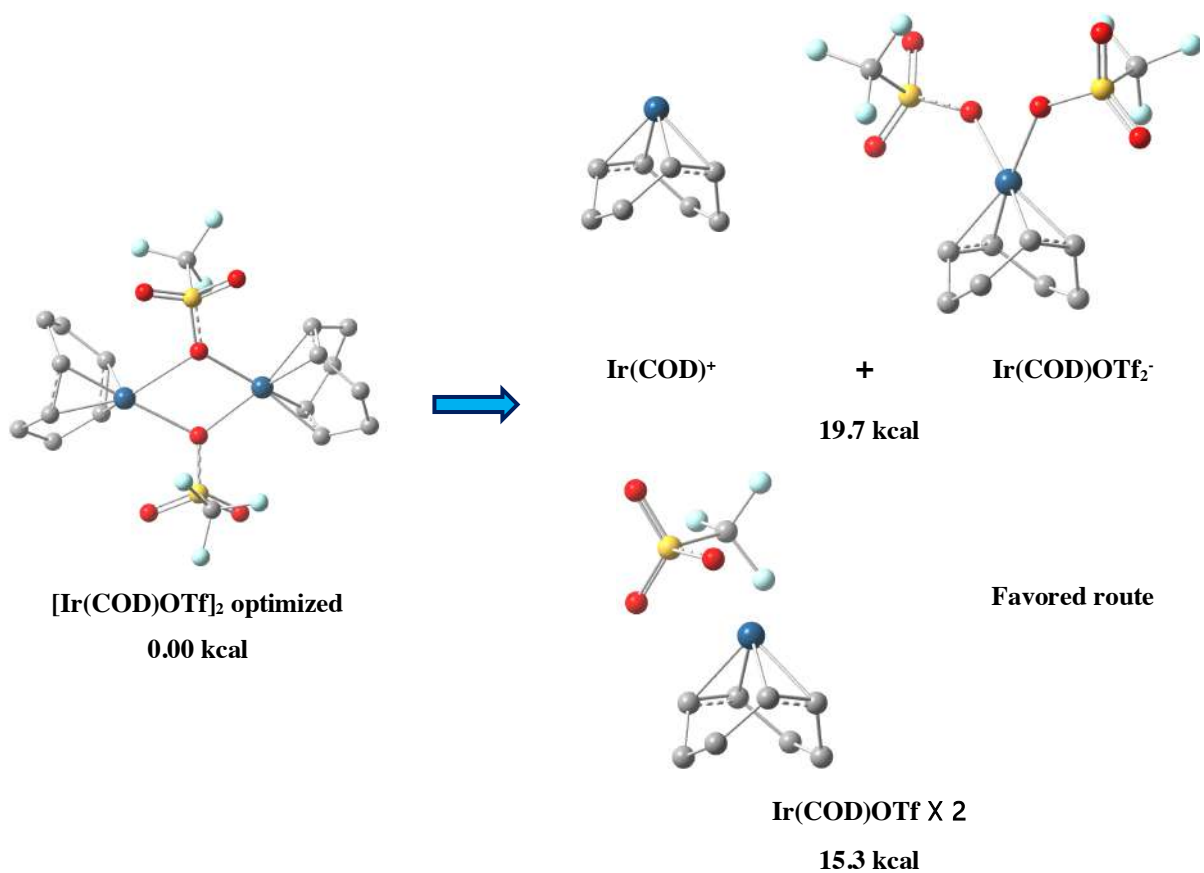
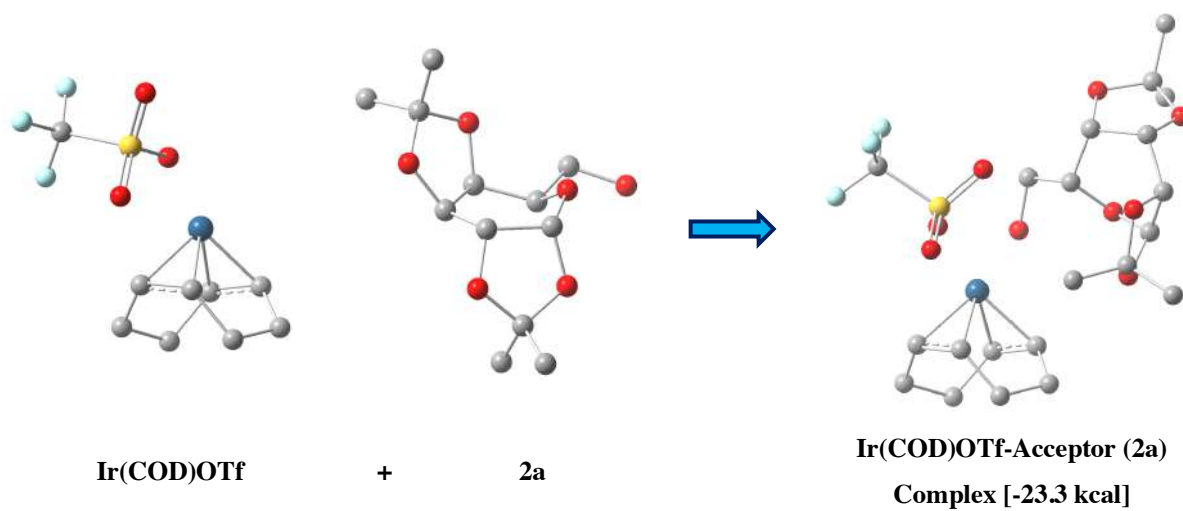


Figure S16. Dissociation of the catalyst dimer (Gibb's free energy w.r.t. [Ir(COD)OTf]₂).



Acceptor coordination highly energetically favorable (stabilization energy: ~38.5 kcal/mol), implying probable directing mechanism.

Figure S17. Coordination of the Ir(COD)OTf and the acceptor (**2a**)

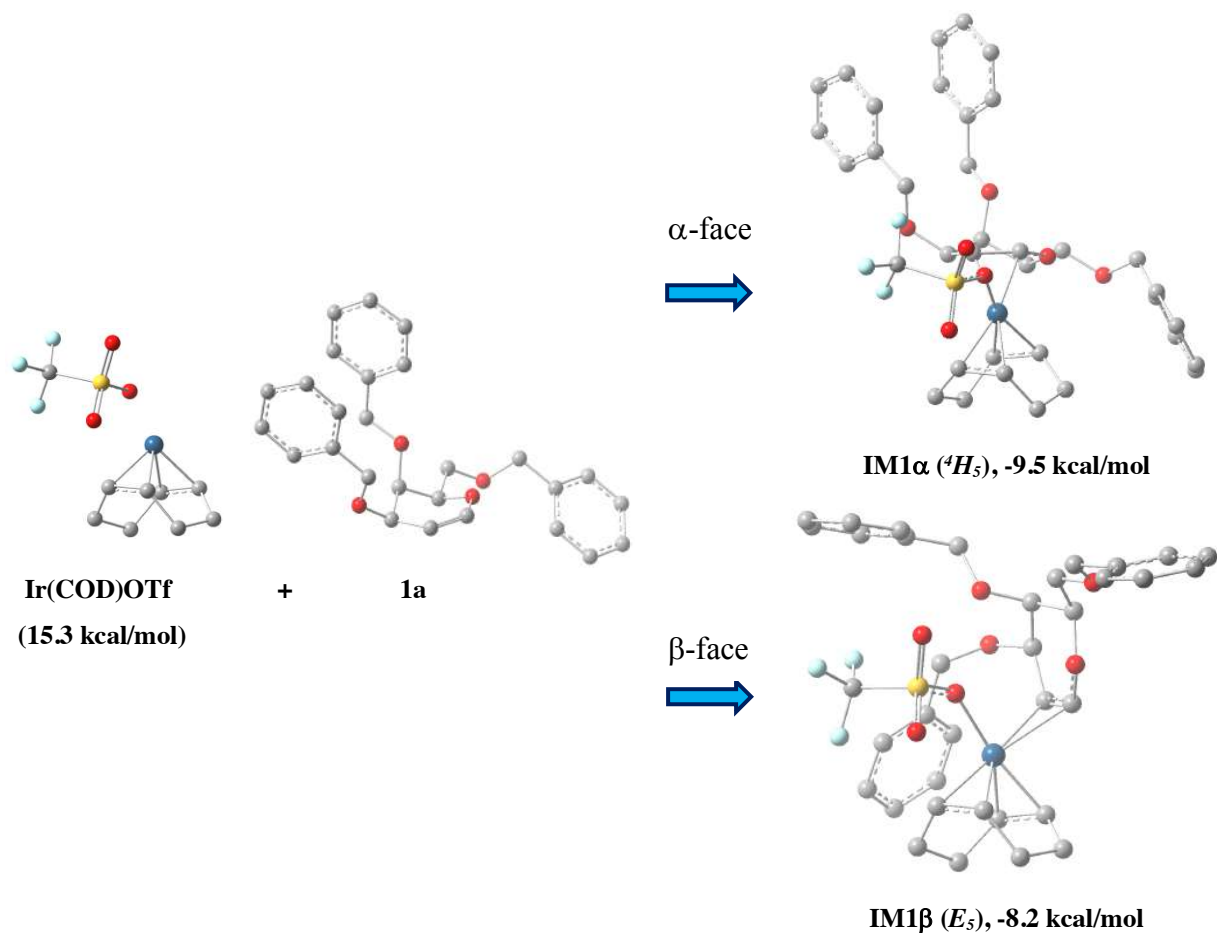


Figure S18. Coordination of Ir(COD)OTf to 3,4,6-tri-*O*-benzyl-D-galactal donor (**1a**)

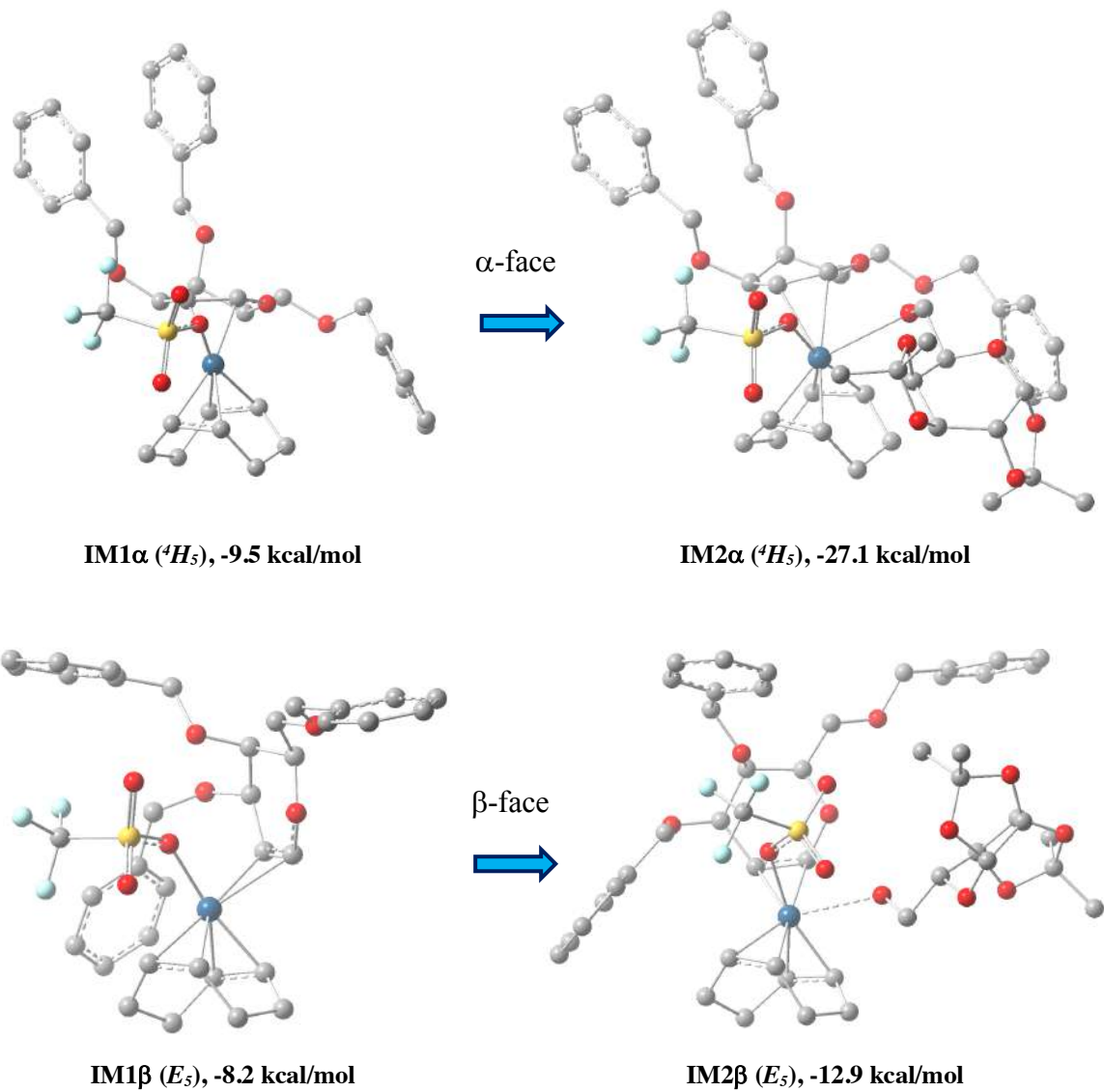


Figure S19. Coordination of acceptor **2a** to the Ir(COD)-galactal (**1a**) complex.

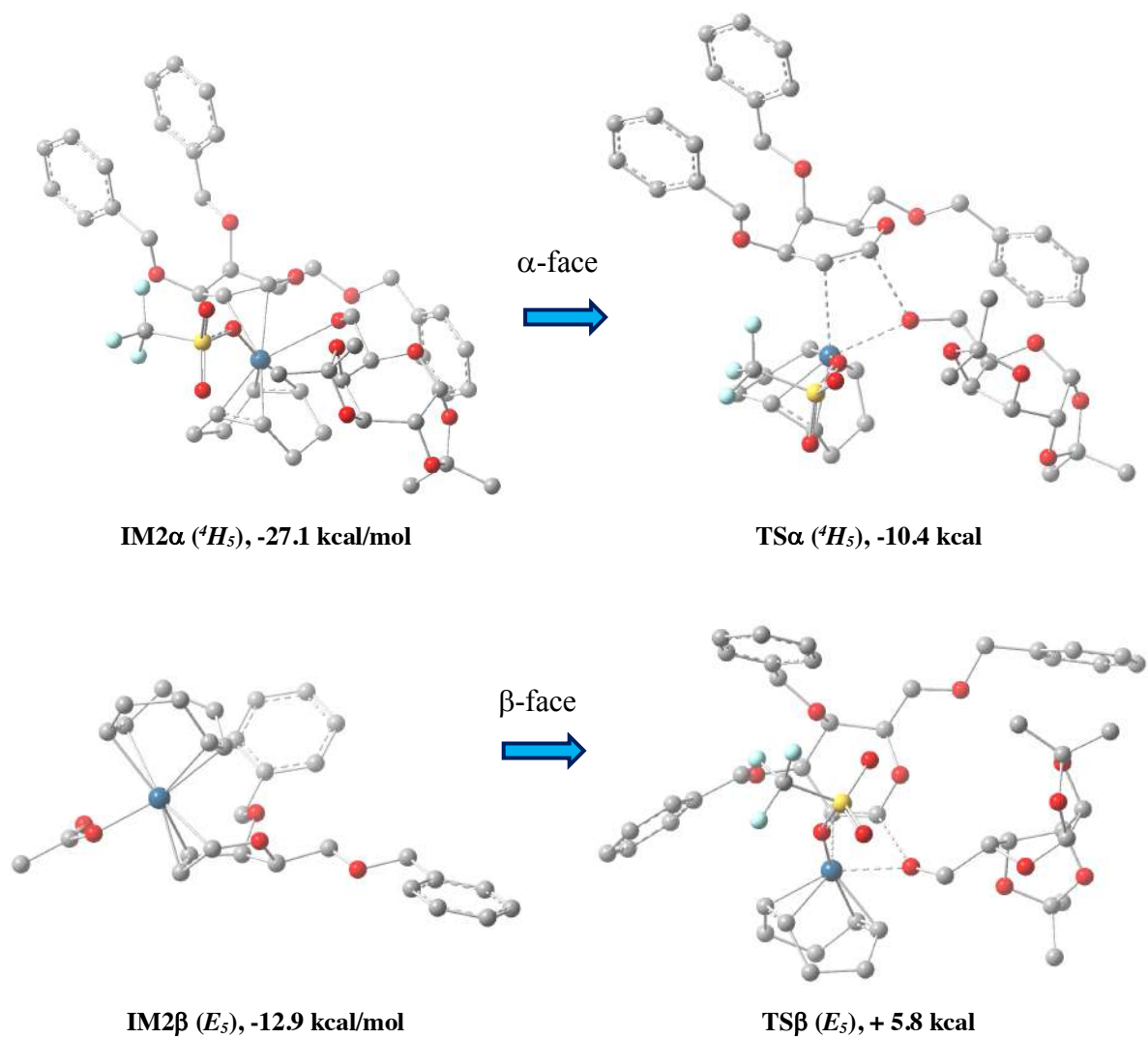


Figure S20. Nucleophilic attack of **2a** to Ir(COD)OTf-**1a** complex (transition state).

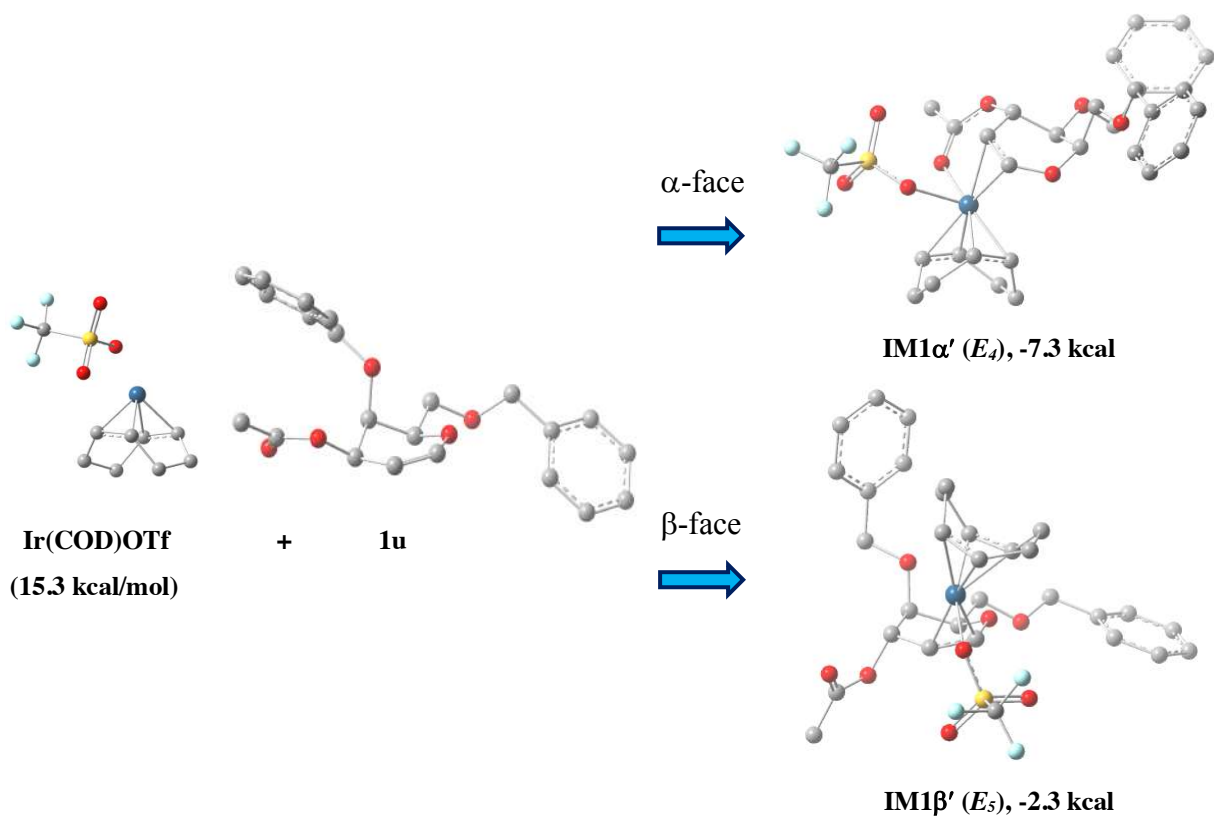


Figure S21. Coordination of Ir(COD)OTf to 3-*O*-acetyl-4,6-di-*O*-benzyl-D-galactal donor (**1u**).

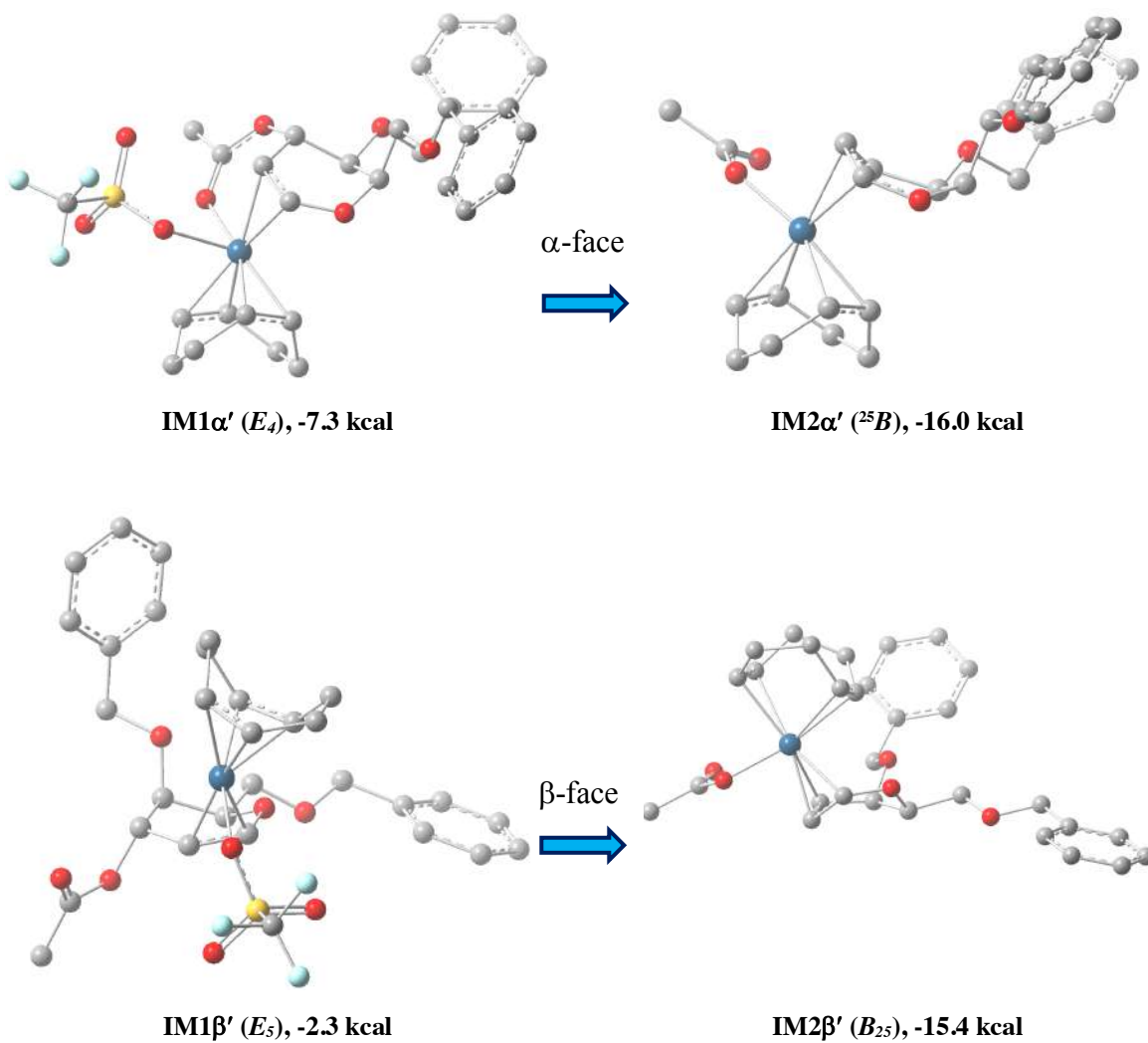


Figure S22. Dissociation of OAc group from C3 of 3-O-acetyl-4,6-di-O-benzyl-D-galactal (**1u**).

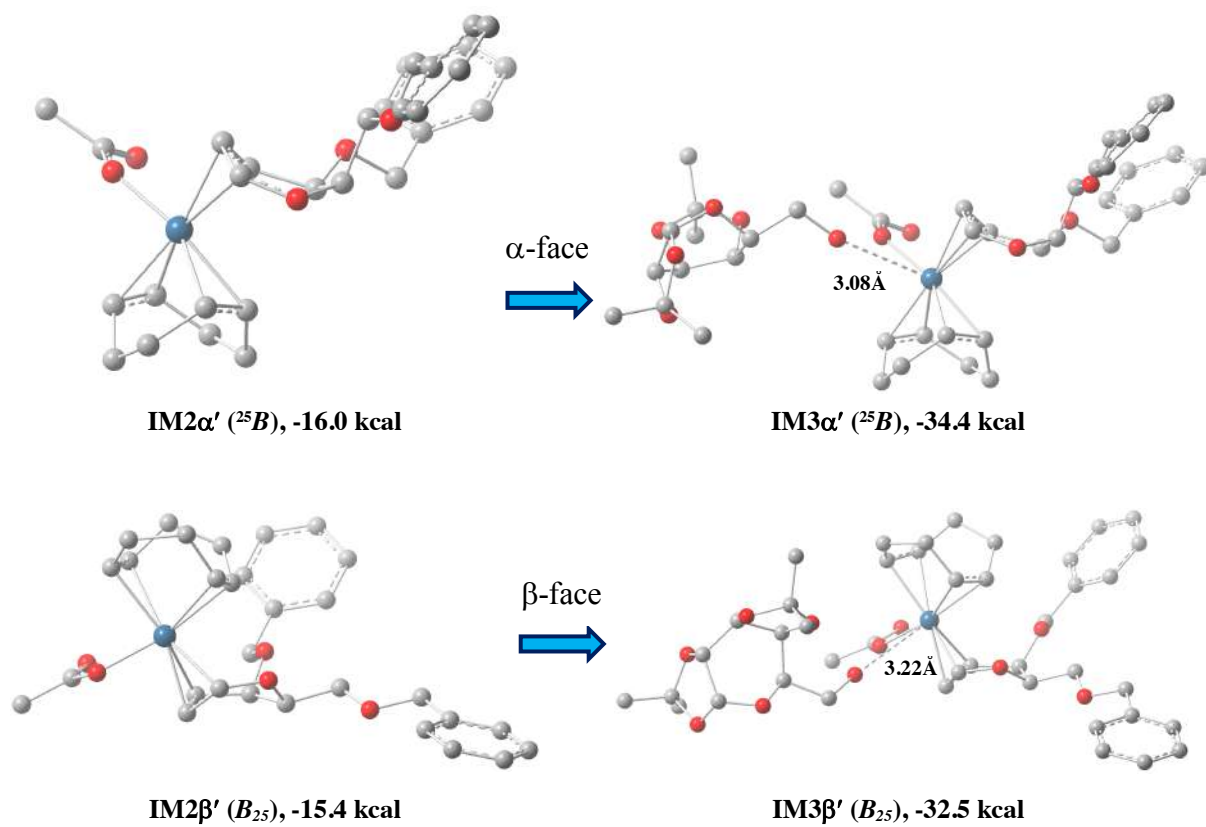


Figure S23. Coordination of acceptor **2a** to the Ir(COD)-D-galactal (**1u**) complex.

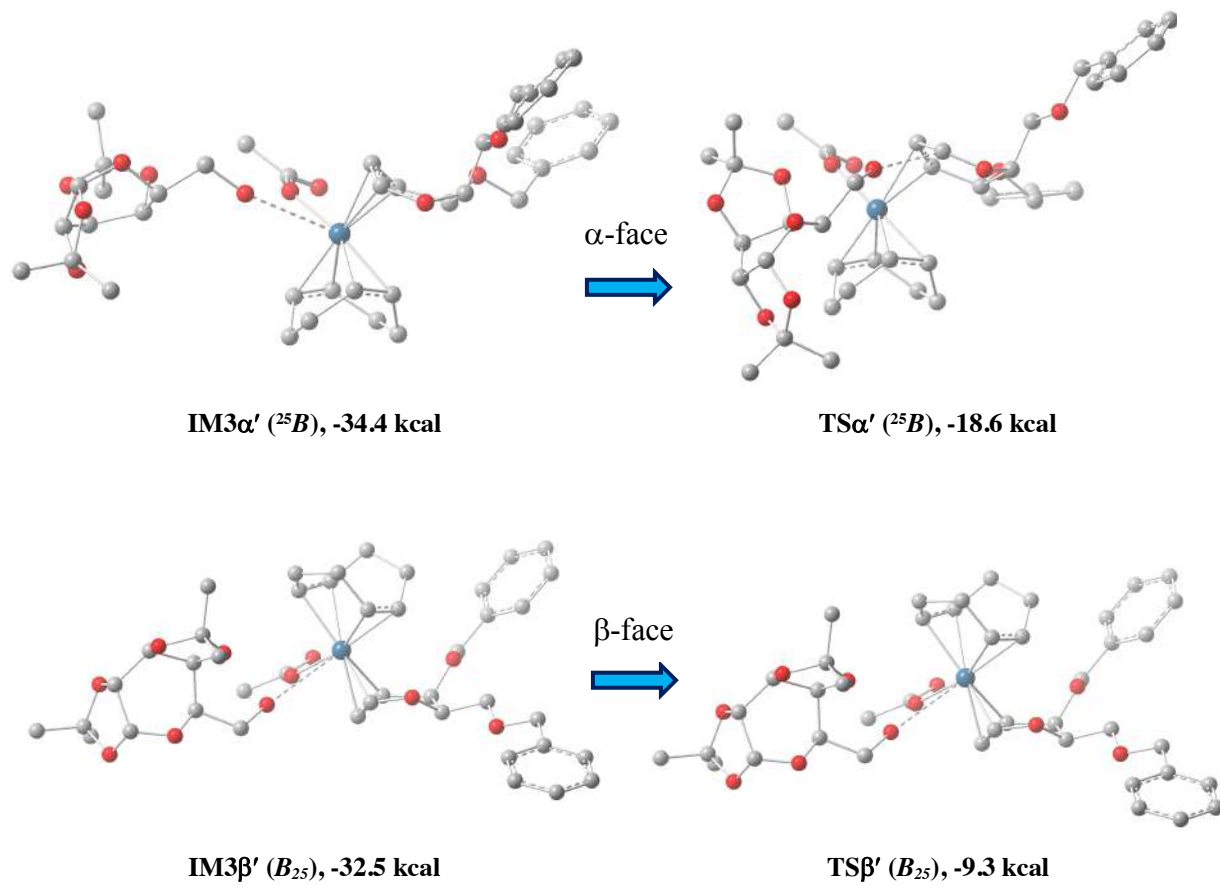


Figure S24. Nucleophilic attack of **2a** to Ir(COD)OTf-**1u** complex (transition state).

Computational details:

All calculations in this paper were performed with the Gaussian 09 software package.²² All energies discussed are Gibbs free energies at experimental temperature (298.15K) in dichloromethane ($\Delta G_{\text{dichloromethane, 298.15K}}$) unless otherwise specified. For each of the three donor species 3,4,6-tri-*O*-benzyl-galactal (**1a**), 3-*O*-acetyl-4,6-di-*O*-allyl-galactal (**1n**), 3-*O*-acetyl-4,6-di-*O*-benzyl-glucal (**1p**) and 3-*O*-acetyl-4,6-di-*O*-benzyl-galactal (**1u**), models of four plausible intermediates arising from the iridium-cyclooctadiene complex coordinated to the glycal from 2 different faces (α/β), with the model acceptor either coordinated to the metal center or attacking as a free species from opposite face arising from were built and subjected to geometry optimization and frequency analysis at DFT(B3LYP)/def2-TZVP level of theory²³ at 298.15 K, with polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) method²⁴ applied at the same level of theory to account for the solvent effects exerted by dichloromethane. The relative level of free energy of geometry optimized intermediates were computed and compared with each other. To compare the change in partial charge of pyranose C1 and C2 in both isolated and coordinated glycal **1a**, model of isolated **1a** were built and subjected to computation of same methods. Mulliken charges (with hydrogen summed into heavy atoms) on the optimized structures were taken as the measure of partial charges of atoms in the corresponding structures.

Plausible intermediates arising from the iridium-catalyzed glycosylation of 3,4,6-tri-*O*-benzyl-D-galactal (**1a**), 3-*O*-acetyl-4,6-di-*O*-allyl-galactal (**1n**), 3-*O*-acetyl-4,6-di-*O*-benzyl-galactal (**1u**) and 3-*O*-acetyl-4,6-di-*O*-benzyl-glucal (**1p**) substrates by 1,2:3,4-di-*O*-isopropyl- α -D-galactopyranose acceptor through both blocking and directing mechanisms. For each glycal substrate, models of four plausible intermediate structures, in which either α - or β -face of the glycal pyranose ring coordinates to the iridium catalyst, and the acceptor alcohol either coordinated to the metal center of the Ir(I)-glycal complex (directing mechanism), or placed at the opposite face of the iridium catalyst as a free molecule with the C6 hydroxy group at the vicinity of donor anomeric carbon (blocking mechanism), were built and subjected to geometry optimization and frequency analysis. Considering of the presence of triflate in the experimental reaction systems, a triflate anion is included as a ligand in each of the plausible intermediates arising from **1a**, while no triflate is included in the intermediates arising from **1n**, **1p** and **1u**, and the dissociated acetate

was treated as a ligand coordinated to the metal center for these scenarios. Such treatments ensure that the metal center in the built model of intermediates arising from directing mechanism satisfies the 18-electron rule of the transition metal valence orbitals. Gibbs free energy of optimized structure of intermediates are computed and compared with each other.

Coordinates of the Computed Structures:

Coordinates of Optimized Intermediate Structures:

3,4,6-Tri-*O*-benzyl galactal- α -[Ir(COD)OTf]-Acceptor (Acceptor Coordinated to the Iridium):

Ir	-0.64973632	2.70388337	-0.40929174
C	-0.71925893	4.34754455	-3.03895684
C	-0.61249536	5.36242739	-1.88209886
C	-3.34327099	3.78969058	-1.46890472
C	-3.09701685	2.44411092	-2.17829973
H	0.05565438	4.55983112	-3.79232114
H	-1.68224496	4.45641025	-3.56280429
H	0.43685287	5.66814111	-1.75051467
H	-1.17717501	6.28520365	-2.11244397
H	-4.34388629	3.78504933	-1.01019622
H	-3.34768610	4.62204456	-2.19106631
H	-3.64315943	1.64651767	-1.65177025
H	-3.49045192	2.45924709	-3.21274728
C	0.34026368	-0.46711663	-2.19029174
H	-0.15173632	0.43088337	-2.60229174
O	-0.03473632	-0.53811663	-0.80329174
C	-0.24173632	-1.69511663	-2.85729174
H	0.18626368	-1.77011663	-3.87729174
H	0.08226368	-2.57811663	-2.27829174
O	-1.65773632	-1.51511663	-2.88829174

O	2.43626368	-1.47911663	-1.76429174
C	3.50026368	-1.97311663	-2.51729174
H	4.14026368	-1.14811663	-2.90429174
H	3.10226368	-2.54811663	-3.38129174
C	4.37326368	-2.88311663	-1.68829174
C	5.56226368	-3.37611663	-2.25129174
C	4.04926368	-3.23311663	-0.36129174
C	6.41926368	-4.18711663	-1.50029174
H	5.83426368	-3.11711663	-3.26729174
C	4.90926368	-4.04611663	0.38370826
H	3.14126368	-2.87611663	0.10770826
C	6.09326368	-4.52011663	-0.18429174
H	7.33826368	-4.55211663	-1.93929174
H	4.65826368	-4.30411663	1.40470826
H	6.76026368	-5.14411663	0.39670826
C	-2.29973632	-2.68711663	-3.27229174
H	-1.83473632	-3.11611663	-4.19129174
H	-2.22473632	-3.43911663	-2.45729174
C	1.84426368	-0.31811663	-2.34829174
H	2.03826368	-0.20911663	-3.43229174
C	0.44226368	0.45388337	-0.02629174
H	0.04126368	0.44288337	0.98670826
C	-3.59046092	0.96090976	1.23280462
H	-3.90589968	-0.05963488	0.98097126
H	-3.18527731	0.97504364	2.25866206
C	-4.81648511	1.86739432	1.10677127
C	-4.75858874	3.15796294	1.90817170
H	-4.89011868	2.14100943	0.04123906
C	-7.15101526	1.71923603	1.10707480
C	-6.05747069	3.98346564	1.85217180
H	-3.91676249	3.77932824	1.53984615

C	-7.35264886	3.18915065	1.55949928
H	-7.96351658	1.07299741	1.48458541
H	-5.98746072	4.78245730	1.09317186
H	-7.97249997	3.23188213	2.46847211
O	-2.61534245	1.33168241	0.27244655
H	-2.59370625	0.70193268	-0.46314379
O	-5.96940970	1.12468158	1.48812108
O	-4.61470967	2.87506794	3.29120107
O	-6.10849248	4.58923995	3.13564960
O	-8.07269009	3.77313824	0.48763776
O	-7.20825715	1.81935043	-0.30676447
C	-5.23778355	3.90181438	4.02328076
C	-3.75373632	-2.39111663	-3.52229174
C	-4.35773632	-2.74711663	-4.74129174
C	-4.52673632	-1.75911663	-2.53329174
C	-5.71273632	-2.47811663	-4.96029174
H	-3.78373632	-3.23511663	-5.51929174
C	-5.88073632	-1.49311663	-2.75629174
H	-4.08273632	-1.46811663	-1.59129174
C	-6.47373632	-1.85311663	-3.96929174
H	-6.17273632	-2.75611663	-5.90029174
H	-6.46973632	-1.00711663	-1.98929174
H	-7.52173632	-1.64711663	-4.14129174
C	-7.92923913	2.96363486	-0.67225883
C	-9.31980441	2.57877974	-1.16984577
H	-9.89743836	3.48639555	-1.44349621
H	-9.24128675	1.91650312	-2.05917453
H	-9.87179134	2.03451819	-0.37263891
C	-7.13915865	3.70920317	-1.75012930
H	-7.01153645	3.07102800	-2.64974701
H	-7.66793358	4.64283961	-2.04017250

H	-6.13211484	3.98090079	-1.36673370
C	-4.20062043	4.88452014	4.56561738
H	-4.69366348	5.67462002	5.17169553
H	-3.45842305	4.35294126	5.19925130
H	-3.66693960	5.37420929	3.72708573
C	-6.03060992	3.27815996	5.16777302
H	-6.77645257	2.56055239	4.76358606
H	-5.35194742	2.73086543	5.85587105
H	-6.57164033	4.06398155	5.73822942
C	1.44426368	1.29888337	-0.42129174
H	1.84026368	1.99088337	0.32370826
C	0.79740567	5.23626965	2.81002142
F	0.59055353	6.34771470	3.51080321
F	1.48439817	5.54054150	1.70972376
F	1.52102679	4.39058628	3.54550025
S	-0.84832610	4.45946047	2.37004364
O	-1.46607559	4.09144933	3.64503162
O	-0.29542455	3.24500081	1.58981508
O	-1.54538355	5.40593280	1.49692048
C	-1.63030580	2.05225270	-2.18460917
H	-1.48225738	0.97539064	-2.33541624
C	-0.55563841	2.91118564	-2.54587531
H	0.35307351	2.42207197	-2.90675821
C	-1.08777966	4.77419691	-0.56990576
H	-0.68800409	5.26280000	0.32686262
C	-2.30480249	4.04288573	-0.37980216
H	-2.71047768	4.07287462	0.63888047
O	3.70726368	1.08388337	-1.47729174
C	2.29026368	1.01088337	-1.65229174
H	2.10926368	1.80888337	-2.39029174
C	4.16626368	0.57688337	-0.25629174

H	3.52426368	-0.24711663	0.12770826
H	4.17126368	1.39388337	0.49670826
C	5.57126368	0.03888337	-0.37229174
C	6.32826368	0.15288337	-1.55529174
C	6.13326368	-0.62311663	0.73370826
C	7.60926368	-0.40311663	-1.63029174
H	5.93326368	0.66188337	-2.42529174
C	7.41326368	-1.17811663	0.65270826
H	5.57026368	-0.72511663	1.65270826
C	8.15026368	-1.07111663	-0.52929174
H	8.18126368	-0.32011663	-2.54529174
H	7.83226368	-1.69711663	1.50470826
H	9.13926368	-1.50511663	-0.59129174

3,4,6-Tri-*O*-benzyl galactal- α -[Ir(COD)-OTf]- β -Acceptor (Free Acceptor attacking from the β face):

Ir	0.73780700	-2.82392000	-0.64473900
C	1.78180800	-5.56446100	0.30442200
C	1.62519400	-5.66111800	-1.22733800
C	-1.24859400	-5.15392000	-0.04345200
C	-1.00089400	-4.37564400	1.26188500
H	2.79195200	-5.89709100	0.58851400
H	1.08638400	-6.25038400	0.81284600
H	2.59310500	-5.46135300	-1.71282700
H	1.33598600	-6.68555400	-1.52734500
H	-2.33137500	-5.27711700	-0.19601200
H	-0.83541000	-6.17195900	0.02313700
H	-1.79521800	-3.61857700	1.38951700
H	-1.06757100	-5.03844900	2.14543000
C	2.05184300	-0.70336000	2.48524500

H	1.97601300	-1.79775700	2.60929100
O	0.99917700	-0.30394800	1.58656900
C	1.75038600	-0.05886600	3.83542800
H	2.52759900	-0.39802200	4.54397200
H	1.87990500	1.03363000	3.73188900
O	0.49762700	-0.52727100	4.32088200
O	3.50626800	1.04879800	1.75819100
C	4.68885400	1.58157300	2.26777800
H	5.56210200	0.94074900	2.01014400
H	4.61445400	1.64894300	3.37493400
C	4.95407100	2.95928900	1.71337600
C	6.17710800	3.58314600	2.01154600
C	4.03011800	3.62803300	0.88495200
C	6.47896300	4.84117900	1.48224100
H	6.90416100	3.08642900	2.64233700
C	4.33704200	4.88667400	0.35903100
H	3.07611900	3.18209500	0.63540600
C	5.56076500	5.49142300	0.65492300
H	7.42796100	5.30939200	1.70915900
H	3.62639400	5.39201800	-0.28204400
H	5.79764100	6.46366600	0.24276100
C	0.16442690	0.02638656	5.55474046
H	0.62485744	-0.59099451	6.35677846
H	0.54280714	1.06541955	5.67653496
C	3.42875800	-0.37219100	1.90816300
H	4.17268700	-0.80561600	2.60351400
C	1.15671800	-0.52167900	0.28687300
H	0.30936300	-0.16156600	-0.28999200
C	-1.74747500	2.29803300	0.61657900
H	-1.58380000	1.71032600	1.53803200
H	-1.65198900	3.36372200	0.87914900

C	-3.19154000	2.05040800	0.18095300
C	-3.60917100	2.84783000	-1.04825900
H	-3.32173400	0.97680900	-0.04427400
C	-5.32757200	2.00688800	1.19399900
C	-5.13080800	2.77094400	-1.33559600
H	-3.03333600	2.50621500	-1.92886300
C	-6.01487100	2.22001300	-0.19869400
H	-5.86381800	2.54607000	1.99361400
H	-5.33369100	2.12659000	-2.20602000
H	-6.86421600	2.91760700	-0.09154600
O	-0.80518800	2.00382400	-0.38042900
H	-1.09894600	1.20016800	-0.84132100
O	-4.01518100	2.42385200	1.28469900
O	-3.38648500	4.22960500	-0.80494600
O	-5.49690500	4.11046700	-1.63162300
O	-6.46951300	0.92860100	-0.57476300
O	-5.42266500	0.60525700	1.40334300
C	-4.37857000	4.96386200	-1.46823300
C	-1.33007646	0.06416797	5.70676396
C	-2.15839500	-0.68905263	4.85719728
C	-1.91187895	0.83039338	6.73029635
C	-3.54656991	-0.66989310	5.02885230
H	-1.73244336	-1.29332569	4.06598085
C	-3.29882421	0.85047548	6.89450927
H	-1.29385335	1.40294142	7.40780985
C	-4.11643930	0.09983891	6.04643355
H	-4.18041874	-1.25361878	4.37392014
H	-3.73808996	1.44381117	7.68415809
H	-5.19033296	0.11108405	6.18099473
C	-6.38395600	0.06386600	0.53268500
C	-7.74563700	-0.03740300	1.23068200

H	-8.50537900	-0.45454600	0.53570100
H	-7.67188900	-0.69406900	2.12391200
H	-8.08460800	0.96745500	1.56069000
C	-5.91548400	-1.30676100	0.05760900
H	-5.87030500	-2.01826000	0.90899800
H	-6.61465500	-1.70930700	-0.70623800
H	-4.90411900	-1.22707200	-0.39610000
C	-3.88207300	5.43356900	-2.84006000
H	-4.67651000	6.00814200	-3.36258000
H	-2.98473800	6.07830600	-2.72474000
H	-3.60990000	4.55929200	-3.46870800
C	-4.77888000	6.15061700	-0.59871400
H	-5.14214900	5.79060400	0.38783500
H	-3.90770800	6.81989500	-0.43226000
H	-5.59309700	6.72981400	-1.08458900
C	2.31115500	-1.02242300	-0.27237100
H	2.39028800	-0.98992700	-1.36130100
C	-0.72988500	-0.03219700	-4.19336200
F	-1.88729500	0.35433800	-4.72510800
F	-0.00544900	-0.64825800	-5.12181000
F	-0.07170300	1.03846400	-3.75996000
S	-1.07773500	-1.18994500	-2.76838700
O	-1.65670200	-0.32575400	-1.71641600
O	0.34008400	-1.63068600	-2.41035000
O	-1.92044600	-2.25598800	-3.30805900
C	0.31361400	-3.62066400	1.26023200
H	0.33351000	-2.81617400	2.00497300
C	1.56408600	-4.13462900	0.80718300
H	2.45240500	-3.68159800	1.25814800
C	0.62509300	-4.66086800	-1.77007000
H	0.78552000	-4.35442200	-2.81083900

C	-0.66189000	-4.42228800	-1.24281300
H	-1.38394700	-3.95027800	-1.91701300
O	4.80805300	-0.76830900	-0.12897600
C	3.59523800	-1.10957300	0.54330000
H	3.76558800	-2.16645700	0.80864600
C	4.73200700	0.34704000	-0.97245500
H	3.91639200	1.04653700	-0.68532300
H	4.53019600	-0.00200500	-2.00757500
C	6.02336100	1.12809100	-0.98294200
C	7.17026800	0.69908500	-0.28553600
C	6.07268100	2.33930900	-1.69392000
C	8.32970600	1.48081100	-0.28636100
H	7.17280600	-0.23007500	0.26903700
C	7.23416100	3.11682700	-1.69122300
H	5.20289900	2.69052000	-2.23560900
C	8.36079800	2.68951100	-0.98555300
H	9.20407500	1.15068000	0.25941500
H	7.25785000	4.05482600	-2.23060600
H	9.25770300	3.29512300	-0.98014400

3,4,6-Tri-*O*-benzyl galactal- β -[Ir(COD)-OTf]-Acceptor (Acceptor Coordinated to the Iridium):

C	1.48459300	-3.37231400	-2.06866700
C	1.87842100	-3.92554600	-0.80592000
C	3.27564400	-4.51488500	-0.57603900
C	4.30166200	-3.44319500	-0.13976700
C	3.87892500	-2.04104800	-0.54706200
C	3.55545800	-1.65030600	-1.90605300
C	3.67280300	-2.62441100	-3.08044600
C	2.32526000	-3.31820000	-3.33486500
C	-0.55021500	-0.32626900	2.87807700

C	-1.73153000	0.61419600	3.04755800
C	0.98179800	2.64768800	2.95881300
C	1.06865100	3.79025100	1.98910900
C	2.16206200	4.67318700	2.01659900
C	0.04067100	3.99726500	1.05461400
C	2.23118300	5.73571800	1.10978200
C	0.11468700	5.05987200	0.14911200
C	1.20989200	5.92715000	0.17517100
C	-4.04264300	0.59290600	3.26543700
C	0.83508600	0.31069000	3.12412300
C	0.29077800	-1.83780200	1.28503000
C	-5.26203400	-0.28569100	3.24036200
C	-6.36213400	0.03278700	2.42564700
C	-5.31912600	-1.42948700	4.05469800
C	-7.48823500	-0.79581800	2.40673700
C	-6.44885600	-2.25318000	4.03568300
C	-7.53112900	-1.93854900	3.20966400
C	1.55446700	-1.79957000	1.78587400
C	1.89231600	-0.81779800	2.90792200
C	3.74931700	0.50126100	2.24037300
C	5.23128300	0.36202900	1.99505700
C	5.97302400	-0.73897900	2.46912500
C	5.88434700	1.34685900	1.23495000
C	7.33847500	-0.84316700	2.18665200
C	7.24984000	1.23802600	0.95656600
C	7.97633900	0.14403400	1.43192900
C	-1.25058800	-0.90722100	-2.46938400
C	-2.50818800	-0.10947500	-2.13619100
C	-3.27604400	-0.68399600	-0.95525600
C	-4.35263300	0.86383500	-3.21289900
C	-4.64885000	-0.00930900	-0.74102300

C	-5.23281600	0.80254500	-1.92794100
C	-4.82425800	-2.32813500	-0.58729800
C	-4.49793100	2.98406600	-2.26503800
C	-5.27275500	4.07311700	-3.00686200
C	-3.50112900	3.60135900	-1.28215200
C	-4.56784900	-2.98819600	0.77161500
C	-5.65514400	-3.24129300	-1.48360400
C	2.76902700	2.60308400	-1.57825800
O	-0.63457200	-0.88285200	1.56126400
O	-2.91576300	-0.16768400	2.96338000
O	1.02050500	1.43840300	2.26520100
O	3.27190900	-0.51479500	3.06689500
O	-0.45980700	-0.99955200	-1.28282700
O	-3.34261100	-0.08200000	-3.28660000
O	-3.61175200	-2.04050000	-1.23061500
O	-5.50200600	-1.09660300	-0.40642900
O	-5.41464900	2.16107700	-1.56846600
O	-3.80461000	2.16940800	-3.18134100
O	1.46324100	0.83920400	-3.09696700
O	0.13719900	2.07756500	-1.36956500
O	1.75286900	0.37068200	-0.63717700
F	3.89769500	2.07037300	-2.05606400
F	2.96831900	2.93645100	-0.30787400
F	2.48034800	3.69726100	-2.27635200
Ir	1.81597800	-1.79331900	-0.72051000
S	1.37318000	1.36928700	-1.73311000
H	0.40351600	-3.40329800	-2.26276200
H	1.08195500	-4.39648200	-0.21492400
H	4.30345300	-1.26500900	0.09458600
H	3.70830400	-0.59762800	-2.16039300
H	3.21338800	-5.30027000	0.19295600

H	3.61621300	-5.02647000	-1.49213400
H	4.40714500	-3.45317700	0.95746300
H	5.30862500	-3.67063700	-0.53683900
H	3.99247800	-2.07423000	-3.97786900
H	4.46481800	-3.36421000	-2.88027400
H	1.75752000	-2.74862400	-4.08552700
H	2.44910400	-4.33751400	-3.74851900
H	-0.69179000	-1.15288300	3.60028800
H	-1.60504900	1.10309900	4.03643500
H	-1.67078800	1.38746600	2.25956700
H	1.82088500	2.69687400	3.68821400
H	0.03360400	2.75470000	3.52853400
H	2.96440400	4.53534100	2.73069400
H	-0.81434600	3.33411900	1.02402200
H	3.07847400	6.40880900	1.12956100
H	-0.67650700	5.21030500	-0.57352000
H	1.26669100	6.74795100	-0.52791400
H	-3.95889900	1.02633600	4.28788000
H	-4.14887000	1.42726500	2.53498200
H	0.90851900	0.55388400	4.20235700
H	-0.13514700	-2.69061700	0.75144400
H	-6.35163400	0.92009800	1.80561900
H	-4.48620300	-1.68538800	4.69799400
H	-8.32878600	-0.55049600	1.77062800
H	-6.48415300	-3.13679700	4.65960900
H	-8.40361000	-2.57870000	3.19357900
H	2.16705700	-2.70026100	1.76571700
H	1.71072700	-1.45598900	3.79480200
H	3.58588800	1.47657500	2.74126800
H	3.24143800	0.50895600	1.25794800
H	5.50284800	-1.52468000	3.04585000

H	5.33360300	2.19814500	0.85462500
H	7.90201400	-1.69257600	2.55052600
H	7.74424300	2.00127500	0.36960600
H	9.03313800	0.06020500	1.21384900
H	-0.69152100	-0.41039500	-3.27915900
H	-1.51649800	-1.93141700	-2.76227800
H	-2.18713500	0.91828300	-1.89090500
H	-2.67471700	-0.62079500	-0.03279700
H	-4.95679300	0.71986100	-4.12520400
H	-4.60539600	0.69454700	0.10705800
H	-6.21685200	0.36301000	-2.15136800
H	-0.34965700	-0.12138900	-0.87758000
H	-5.84415800	4.70004500	-2.28924400
H	-4.57505700	4.72129000	-3.57911900
H	-5.98826900	3.60926900	-3.71887300
H	-4.02613600	4.26906500	-0.56616300
H	-2.99047300	2.80619500	-0.69964200
H	-2.73371100	4.18915600	-1.82942500
H	-5.52949700	-3.20367100	1.28315100
H	-4.00774800	-3.93826800	0.63927100
H	-3.96662800	-2.31475400	1.41729600
H	-5.83396600	-2.74771900	-2.46289700
H	-5.12165400	-4.19946500	-1.66205100
H	-6.63798400	-3.45542600	-1.01169600

3,4,6-Tri-*O*-benzyl galactal- β -[Ir(COD)-OTf]- α -Acceptor (Free Acceptor attacking from the α face):

C	1.44898100	-3.54001800	-0.67147400
C	2.54920100	-3.46492900	0.23435100
C	3.97718700	-3.89898900	-0.10476700

C	4.82422600	-2.72741000	-0.63925200
C	3.97856900	-1.69105600	-1.34503500
C	3.02419100	-1.95609900	-2.36095600
C	2.70524800	-3.35187200	-2.88915000
C	1.52901200	-3.99371500	-2.12147500
C	-0.67976900	1.15319700	1.59836200
C	-1.28276100	2.39582300	0.98091900
C	1.92465200	3.32935800	2.02933600
C	2.68651600	4.14032700	1.02284000
C	4.07928000	4.29311200	1.12835200
C	2.00288100	4.76373300	-0.03380800
C	4.77576200	5.05784900	0.18705900
C	2.70256700	5.52950800	-0.97125600
C	4.08812500	5.67635100	-0.86112000
C	-3.25092000	3.08171200	-0.03072300
C	0.66406900	1.37976800	2.29146200
C	-4.74372800	3.09651700	0.11478200
C	-5.57396400	2.80309800	-0.98061700
C	-5.32434400	3.43941600	1.34729300
C	-6.96421900	2.84902500	-0.84074600
C	-6.71526700	3.47715400	1.48404400
C	-7.53439700	3.18452500	0.39048900
C	0.92661000	-1.14387300	1.77502300
C	1.26592400	0.00204800	2.71536500
C	3.57686000	0.19073600	2.19754300
C	4.82353600	-0.52886700	2.62574400
C	4.77011700	-1.89733300	2.93900500
C	6.05474800	0.14537600	2.69606900
C	5.93087300	-2.58175400	3.31052900
C	7.21326100	-0.54282200	3.07013200
C	7.15174500	-1.90523700	3.37563300

C	-3.69105400	-0.84872800	2.73576600
C	-4.18257200	-0.94863700	1.28910500
C	-5.54769500	-0.48860600	0.81612800
C	-3.87753300	-2.69868300	-0.32245000
C	-5.81449300	-1.00983100	-0.64010300
C	-4.67935400	-1.79624300	-1.29209000
C	-7.58253600	-1.54351800	0.69816500
C	-2.46657900	-1.58433900	-1.79890200
C	-2.25476100	-2.32796100	-3.12116300
C	-1.34335000	-0.59618200	-1.54170300
C	-8.66950600	-0.49612200	0.42932100
C	-8.17035100	-2.81375000	1.28753100
C	2.94071700	2.06628800	-2.84318100
O	-0.62529300	0.16097900	0.54408400
O	-2.69386700	2.16816900	0.85687900
O	1.50815900	2.14212900	1.43826700
O	2.60522900	0.05792200	3.19955000
O	-2.32638200	-1.21140300	2.57108600
O	-4.01356700	-2.34869100	1.01554900
O	-6.62526800	-1.00523000	1.58188200
O	-6.92356300	-1.87004500	-0.50039900
O	-3.69913400	-0.89951900	-1.78292400
O	-2.53372600	-2.52606200	-0.73830400
O	0.89233200	0.43208300	-3.26380400
O	0.55194800	2.46320800	-1.80923900
O	1.90428000	0.54457100	-0.96173300
F	3.72058000	1.12386900	-3.39216900
F	3.63100900	2.65545400	-1.87108000
F	2.64496700	2.96650300	-3.77579100
Ir	2.01638500	-1.51601100	-0.50458000
S	1.36233900	1.30370400	-2.18016500

H	0.45975300	-3.70841100	-0.22245500
H	2.29653800	-3.57133100	1.29393900
H	4.39951000	-0.67697900	-1.34206900
H	2.77874200	-1.13638100	-3.04051800
H	4.45152600	-4.31281700	0.79811300
H	3.95343900	-4.72398000	-0.83363100
H	5.34697600	-2.22907500	0.19180600
H	5.61758600	-3.08770400	-1.32196300
H	2.44452700	-3.27656300	-3.95601200
H	3.60049700	-3.99063500	-2.83994600
H	0.58604100	-3.69993500	-2.60763200
H	1.57482700	-5.09794000	-2.17679500
H	-1.40321400	0.75070400	2.31775000
H	-1.07937800	3.26043400	1.64300100
H	-0.77043100	2.56275700	0.02011200
H	2.56432800	3.10903800	2.91349000
H	1.05954700	3.93629300	2.37916000
H	4.62628600	3.81894200	1.93384600
H	0.92878400	4.66106000	-0.12641300
H	5.84897500	5.17070100	0.27006400
H	2.17101100	6.00686200	-1.78419300
H	4.62902000	6.26717100	-1.58889700
H	-2.88861600	4.11762500	0.16896100
H	-2.96320800	2.80705800	-1.07063100
H	0.40891900	1.87975600	3.24614300
H	-5.14826700	2.53809000	-1.94036400
H	-4.69929900	3.67432200	2.20011900
H	-7.60012100	2.61860400	-1.68565500
H	-7.15804000	3.73622100	2.43701000
H	-8.61095100	3.21385300	0.49779200
H	1.21551000	-2.15272400	2.14367200

H	0.68355300	-0.26420400	3.61763800
H	3.80177800	1.26352100	2.03867500
H	3.26377400	-0.23830000	1.22252600
H	3.83119500	-2.43328100	2.89083900
H	6.12110100	1.19936900	2.45578700
H	5.88391000	-3.63713200	3.54578900
H	8.15974200	-0.02018300	3.12043600
H	8.04996600	-2.43646800	3.66261700
H	-4.27915100	-1.46389800	3.43972200
H	-3.70720900	0.19252500	3.09058000
H	-3.47108900	-0.34338600	0.70554700
H	-5.57188000	0.61322700	0.85530400
H	-4.15749300	-3.76253000	-0.38124500
H	-6.06580500	-0.17941500	-1.32264200
H	-5.10653000	-2.39881500	-2.11709300
H	-2.32856400	-2.04173300	2.06741800
H	-2.42306700	-1.64020000	-3.97728800
H	-1.23220800	-2.72949300	-3.19624700
H	-2.97040900	-3.17226500	-3.21115000
H	-1.25387200	-0.11856000	-2.53448300
H	-1.77672700	0.36835600	-1.19403200
H	-0.31914100	-1.01811900	-1.58919400
H	-9.43302400	-0.90363300	-0.26715800
H	-9.16650500	-0.20455900	1.37914100
H	-8.23056000	0.41176400	-0.02994700
H	-7.36203400	-3.55256800	1.47597200
H	-8.67863600	-2.59315900	2.25054200
H	-8.90502000	-3.26349800	0.58565400
C	-0.04907300	-1.00471400	0.82256300
H	-0.49399900	-1.84392000	0.28029200

3-*O*-Acetyl-4,6-di-*O*-benzyl galactal- α -[Ir(COD)-OTf]-Acceptor (Acceptor Coordinated to the Iridium):

Ir	-0.27685600	-0.30390800	0.53588700
C	0.86146500	-1.09999700	3.45134300
C	0.65027600	-2.41476100	2.68157100
C	-2.17322800	-1.04266300	2.98745100
C	-1.84982700	0.46040300	3.10469500
H	1.88447800	-1.07833800	3.85414900
H	0.19466300	-1.04478300	4.32378200
H	1.59396000	-2.72995200	2.21236400
H	0.37239800	-3.23093600	3.37318500
H	-3.26447300	-1.17418700	2.99794700
H	-1.79321200	-1.59235200	3.86048900
H	-2.65329600	1.04786800	2.64116300
H	-1.82185100	0.77456700	4.16443400
O	1.77193000	2.00630100	0.64702800
O	4.05824900	-0.72312200	-0.27614200
C	5.20286400	-1.09948800	0.49725600
H	4.86619500	-1.70625600	1.36001600
H	5.71387700	-0.20264800	0.88078700
C	6.13711300	-1.90196200	-0.37272800
C	5.71713500	-3.12466600	-0.92300200
C	7.43208100	-1.44285200	-0.65090300
C	6.57564200	-3.87245100	-1.73139100
H	4.70753900	-3.49013800	-0.71648000
C	8.29722600	-2.19405500	-1.45529100
H	7.76639300	-0.48754400	-0.23767400
C	7.87032000	-3.40893900	-1.99820000
H	6.23710200	-4.82245100	-2.15307400
H	9.30472100	-1.82391700	-1.66179000

H	8.54352700	-3.99554600	-2.62867200
C	0.81429600	1.57763700	-0.19887500
H	0.08206300	2.35692700	-0.42973000
C	-3.54351062	1.34069909	-0.65142000
H	-3.29913332	2.21983290	-1.26839638
H	-3.79754024	0.50527979	-1.30960766
C	-4.72590295	1.67671630	0.25280324
C	-5.21514396	0.51145609	1.12280831
H	-4.44458987	2.50400729	0.93038023
C	-6.83585402	2.75223839	-0.00023531
C	-6.68085847	0.72973950	1.59582517
H	-4.53776028	0.38718102	1.98315412
C	-7.23431802	2.12993569	1.36197748
H	-7.64971494	2.72909648	-0.73916014
H	-6.78033518	0.49679967	2.67074072
H	-8.33422740	2.08297242	1.44951613
O	-5.76116861	2.10353332	-0.62378372
O	-5.27235782	-0.69352632	0.37162925
O	-7.42913876	-0.16850999	0.79952729
O	-6.67470440	3.01863457	2.31274274
O	-6.51103147	4.08577438	0.32663388
C	-6.59115435	-1.25307146	0.42885091
C	-6.68311319	4.31893537	1.73293304
C	-8.01828807	5.02313626	1.97877180
H	-8.16662305	5.19484470	3.05516560
H	-8.03256571	5.99297129	1.46048651
H	-8.85788704	4.42118721	1.60075271
C	-5.50051766	5.10759218	2.26863463
H	-5.45950068	6.09674865	1.79072682
H	-5.60062647	5.24790504	3.35464671
H	-4.56131040	4.57450450	2.06409441

C	-6.63933535	-2.36303704	1.48026900
H	-7.65858385	-2.76951107	1.55886164
H	-5.95583704	-3.17942981	1.20425813
H	-6.33932721	-1.98056526	2.46770876
C	-6.99629869	-1.72493053	-0.95706715
H	-6.92800586	-0.88487368	-1.66211691
H	-6.33545049	-2.53702762	-1.29265186
H	-8.02997033	-2.09992294	-0.94320159
C	0.99690700	0.45784000	-1.02131400
H	0.46570800	0.33634200	-1.96354800
C	-0.53315900	0.85488100	2.46941400
H	-0.43490400	1.91627000	2.21727700
C	0.66126100	0.14137500	2.59348500
H	1.55625100	0.72728600	2.40577800
C	-0.39346500	-2.31504500	1.59931000
H	-0.25610700	-3.01239900	0.76879500
C	-1.63600200	-1.67668200	1.71105100
H	-2.38765500	-1.91770800	0.95393100
O	0.24373200	-3.11163900	-1.40977100
C	1.72841400	-0.58035400	-0.34461300
H	1.79330800	-1.56519800	-0.81108100
C	-0.69524400	-2.39425500	-1.72595500
O	-1.03733700	-1.27529100	-1.12336100
C	-1.61601300	-2.72046600	-2.88879500
H	-2.64880000	-2.83336900	-2.52592200
H	-1.61362700	-1.89430800	-3.61571400
H	-1.28902200	-3.64762000	-3.37547100
C	2.97189800	-0.18404000	0.44363400
H	2.95145000	-0.63595300	1.44831600
C	3.07855600	1.37230300	0.56535100
H	3.56440700	1.64967800	1.51008800

C	3.88286500	2.04285200	-0.55672500
H	4.59199513	1.33952713	-1.02968448
H	3.16608920	2.38039297	-1.33015270
O	4.56084019	3.14110175	0.00440961
C	5.40905545	3.81361596	-0.90825086
H	6.24181204	3.15510050	-1.22142314
H	4.83692087	4.06311760	-1.82669552
C	5.95080966	5.07875063	-0.28599229
C	5.14442436	5.87400613	0.54365706
C	7.26057120	5.49910082	-0.56166764
C	5.63918066	7.06354151	1.08583309
H	4.12621247	5.54994276	0.76872872
C	7.75375884	6.69420052	-0.02727022
H	7.90330692	4.88416568	-1.19818639
C	6.94453731	7.47932733	0.80001109
H	5.00148274	7.67085461	1.73369913
H	8.77649355	7.00779523	-0.25191221
H	7.33036224	8.41018109	1.22341116
O	-2.40269014	0.92236256	0.10251844
H	-1.61579713	0.98910680	-0.44332458

3-*O*-Acetyl-4,6-di-*O*-benzyl galactal- α -[Ir(COD)-OTf]- β -Acceptor (Free Acceptor attacking from the β face):

Ir	2.44712500	-1.55624100	0.40566800
C	4.83562000	-0.12018200	2.04612500
C	5.49511500	-1.23151800	1.20936200
C	3.48630500	-2.61640100	3.20829000
C	2.35644500	-1.59381300	3.43728100
H	5.35944000	0.82354100	1.84301400
H	4.95346400	-0.31556700	3.12143500

H	5.88416400	-0.80957200	0.27349900
H	6.37123300	-1.64730600	1.74063200
H	3.24437000	-3.54045300	3.75275400
H	4.43549400	-2.25389900	3.62505700
H	1.38458300	-2.11338800	3.45344700
H	2.45159000	-1.11745600	4.43067800
O	1.15031600	1.21452900	0.16039000
O	3.15075147	1.43722966	-2.77284421
C	4.10284806	2.44425733	-3.11313264
H	5.08684434	2.16286652	-2.68754843
H	3.82399234	3.41694857	-2.66965151
C	4.20093477	2.56909224	-4.61397610
C	3.64694587	1.58666492	-5.45120738
C	4.87887181	3.65127347	-5.19375750
C	3.76953258	1.68717505	-6.83924511
H	3.11272452	0.74264550	-5.00908063
C	5.01025740	3.74792666	-6.58357598
H	5.30895231	4.42660855	-4.55326242
C	4.45409073	2.76715899	-7.40962506
H	3.33143495	0.91749920	-7.47994358
H	5.54269642	4.59644142	-7.02059509
H	4.55101916	2.84383785	-8.49553143
C	0.81393700	-0.04104200	-0.14891700
H	-0.13614500	-0.34897700	0.30447700
C	-3.34299400	-1.08279600	0.64530100
H	-3.03738700	-2.13164600	0.48000700
H	-3.33978600	-0.88821000	1.72647700
C	-4.76133900	-0.91644200	0.10492100
C	-5.41397500	0.43695700	0.42380200
H	-4.72575100	-1.01491900	-0.99614000
C	-6.76957500	-2.18888800	0.02218100

C	-6.96059500	0.35753500	0.33716300
H	-5.00912500	1.20145700	-0.25771400
C	-7.50142500	-0.87906600	-0.36870500
H	-7.34567000	-2.81113100	0.72211400
H	-7.37075800	1.25568200	-0.15871000
H	-8.57857100	-0.96446900	-0.13959700
O	-2.42883300	-0.16833200	0.06074600
H	-2.41256100	-0.31578400	-0.89629800
O	-5.53452800	-1.98103900	0.65016500
O	-5.17095800	0.83704800	1.76545600
O	-7.37076700	0.27976700	1.68944900
O	-7.27539400	-0.76866500	-1.76256200
O	-6.61399100	-2.85992600	-1.21074300
C	-6.39180300	0.89673500	2.51434800
C	-7.17936700	-2.09021900	-2.28244100
C	-8.56007600	-2.64241000	-2.64052200
H	-9.01105200	-2.04774900	-3.44873500
H	-8.47281800	-3.68622400	-2.97579600
H	-9.23295200	-2.61862300	-1.77048000
C	-6.22767100	-2.08721000	-3.46682700
H	-6.10340300	-3.10839800	-3.85470300
H	-6.62772100	-1.45364300	-4.27167200
H	-5.24479800	-1.69908100	-3.16457000
C	-6.75760100	2.35650800	2.78168200
H	-7.70620400	2.41553300	3.33595500
H	-5.97169100	2.84479100	3.37674200
H	-6.86913500	2.90633100	1.83494600
C	-6.24618400	0.07330300	3.78496200
H	-5.98026900	-0.95864600	3.51662400
H	-5.45926500	0.49697900	4.42575100
H	-7.19167600	0.06774500	4.34705500

C	1.36418700	-0.72606200	-1.24787300
H	0.84087100	-1.54565500	-1.73817900
C	2.28457900	-0.50361200	2.39021800
H	1.34461700	0.05606500	2.38656700
C	3.36261500	0.09441600	1.73348800
H	3.14819300	1.04181300	1.24859800
C	4.56432200	-2.35985500	0.86471500
H	4.77268800	-2.87275200	-0.07930800
C	3.65649000	-2.96069300	1.73701300
H	3.22973800	-3.91570100	1.41422300
O	3.81857000	-3.27258800	-2.18681600
C	2.74708900	-0.40022200	-1.45079400
H	3.34125200	-1.03574300	-2.11340200
C	2.81276400	-3.77552300	-1.70317100
O	2.11605100	-3.25385200	-0.71628500
C	2.23679900	-5.09101100	-2.19274200
H	2.21464800	-5.82107000	-1.36925200
H	1.19827800	-4.94600500	-2.52731000
H	2.84387500	-5.48105400	-3.01893500
C	3.11043500	1.07700500	-1.41330600
H	4.06525296	1.25035096	-0.87411960
C	2.00037200	1.93966800	-0.76316800
H	2.47607700	2.71143900	-0.14491400
C	1.11453700	2.62463800	-1.80285500
H	1.71692104	2.76473193	-2.72342591
H	0.25487275	1.97613983	-2.07342892
O	0.67939735	3.84182621	-1.26905070
C	0.58129499	4.90531187	-2.20154501
H	0.31353789	5.85090893	-1.69213170
H	1.56854868	5.06693495	-2.68196819
C	-0.44932632	4.55588883	-3.24854216

C	-0.95366186	3.24648083	-3.32486318
C	-0.90830181	5.51372755	-4.16253310
C	-1.89677854	2.90446020	-4.29710489
H	-0.61025294	2.48711703	-2.61804842
C	-1.84786257	5.17151925	-5.14279524
H	-0.53044300	6.53878766	-4.10727645
C	-2.34520231	3.86713105	-5.21096895
H	-2.27571431	1.87999646	-4.33942188
H	-2.19661878	5.92977492	-5.84870378
H	-3.08283774	3.59999896	-5.97232062

3-*O*-Acetyl-4,6-di-*O*-benzyl galactal- α -[Ir(COD)-OTf]- β -Acceptor (Acceptor Coordinated to the Iridium):

Ir	2.44712500	-1.55624100	0.40566800
C	4.83562000	-0.12018200	2.04612500
C	5.49511500	-1.23151800	1.20936200
C	3.48630500	-2.61640100	3.20829000
C	2.35644500	-1.59381300	3.43728100
H	5.35944000	0.82354100	1.84301400
H	4.95346400	-0.31556700	3.12143500
H	5.88416400	-0.80957200	0.27349900
H	6.37123300	-1.64730600	1.74063200
H	3.24437000	-3.54045300	3.75275400
H	4.43549400	-2.25389900	3.62505700
H	1.38458300	-2.11338800	3.45344700
H	2.45159000	-1.11745600	4.43067800
O	1.15031600	1.21452900	0.16039000
O	3.15075147	1.43722966	-2.77284421
C	4.10284806	2.44425733	-3.11313264
H	5.08684434	2.16286652	-2.68754843

H	3.82399234	3.41694857	-2.66965151
C	4.20093477	2.56909224	-4.61397610
C	3.64694587	1.58666492	-5.45120738
C	4.87887181	3.65127347	-5.19375750
C	3.76953258	1.68717505	-6.83924511
H	3.11272452	0.74264550	-5.00908063
C	5.01025740	3.74792666	-6.58357598
H	5.30895231	4.42660855	-4.55326242
C	4.45409073	2.76715899	-7.40962506
H	3.33143495	0.91749920	-7.47994358
H	5.54269642	4.59644142	-7.02059509
H	4.55101916	2.84383785	-8.49553143
C	0.81393700	-0.04104200	-0.14891700
H	-0.13614500	-0.34897700	0.30447700
C	-3.34299400	-1.08279600	0.64530100
H	-3.03738700	-2.13164600	0.48000700
H	-3.33978600	-0.88821000	1.72647700
C	-4.76133900	-0.91644200	0.10492100
C	-5.41397500	0.43695700	0.42380200
H	-4.72575100	-1.01491900	-0.99614000
C	-6.76957500	-2.18888800	0.02218100
C	-6.96059500	0.35753500	0.33716300
H	-5.00912500	1.20145700	-0.25771400
C	-7.50142500	-0.87906600	-0.36870500
H	-7.34567000	-2.81113100	0.72211400
H	-7.37075800	1.25568200	-0.15871000
H	-8.57857100	-0.96446900	-0.13959700
O	-2.42883300	-0.16833200	0.06074600
H	-2.41256100	-0.31578400	-0.89629800
O	-5.53452800	-1.98103900	0.65016500
O	-5.17095800	0.83704800	1.76545600

O	-7.37076700	0.27976700	1.68944900
O	-7.27539400	-0.76866500	-1.76256200
O	-6.61399100	-2.85992600	-1.21074300
C	-6.39180300	0.89673500	2.51434800
C	-7.17936700	-2.09021900	-2.28244100
C	-8.56007600	-2.64241000	-2.64052200
H	-9.01105200	-2.04774900	-3.44873500
H	-8.47281800	-3.68622400	-2.97579600
H	-9.23295200	-2.61862300	-1.77048000
C	-6.22767100	-2.08721000	-3.46682700
H	-6.10340300	-3.10839800	-3.85470300
H	-6.62772100	-1.45364300	-4.27167200
H	-5.24479800	-1.69908100	-3.16457000
C	-6.75760100	2.35650800	2.78168200
H	-7.70620400	2.41553300	3.33595500
H	-5.97169100	2.84479100	3.37674200
H	-6.86913500	2.90633100	1.83494600
C	-6.24618400	0.07330300	3.78496200
H	-5.98026900	-0.95864600	3.51662400
H	-5.45926500	0.49697900	4.42575100
H	-7.19167600	0.06774500	4.34705500
C	1.36418700	-0.72606200	-1.24787300
H	0.84087100	-1.54565500	-1.73817900
C	2.28457900	-0.50361200	2.39021800
H	1.34461700	0.05606500	2.38656700
C	3.36261500	0.09441600	1.73348800
H	3.14819300	1.04181300	1.24859800
C	4.56432200	-2.35985500	0.86471500
H	4.77268800	-2.87275200	-0.07930800
C	3.65649000	-2.96069300	1.73701300
H	3.22973800	-3.91570100	1.41422300

O	3.81857000	-3.27258800	-2.18681600
C	2.74708900	-0.40022200	-1.45079400
H	3.34125200	-1.03574300	-2.11340200
C	2.81276400	-3.77552300	-1.70317100
O	2.11605100	-3.25385200	-0.71628500
C	2.23679900	-5.09101100	-2.19274200
H	2.21464800	-5.82107000	-1.36925200
H	1.19827800	-4.94600500	-2.52731000
H	2.84387500	-5.48105400	-3.01893500
C	3.11043500	1.07700500	-1.41330600
H	4.06525296	1.25035096	-0.87411960
C	2.00037200	1.93966800	-0.76316800
H	2.47607700	2.71143900	-0.14491400
C	1.11453700	2.62463800	-1.80285500
H	1.71692104	2.76473193	-2.72342591
H	0.25487275	1.97613983	-2.07342892
O	0.67939735	3.84182621	-1.26905070
C	0.58129499	4.90531187	-2.20154501
H	0.31353789	5.85090893	-1.69213170
H	1.56854868	5.06693495	-2.68196819
C	-0.44932632	4.55588883	-3.24854216
C	-0.95366186	3.24648083	-3.32486318
C	-0.90830181	5.51372755	-4.16253310
C	-1.89677854	2.90446020	-4.29710489
H	-0.61025294	2.48711703	-2.61804842
C	-1.84786257	5.17151925	-5.14279524
H	-0.53044300	6.53878766	-4.10727645
C	-2.34520231	3.86713105	-5.21096895
H	-2.27571431	1.87999646	-4.33942188
H	-2.19661878	5.92977492	-5.84870378
H	-3.08283774	3.59999896	-5.97232062

3-*O*-Acetyl-4,6-di-*O*-benzyl galactal- β -[Ir(COD)-OTf]- α -Acceptor (Free acceptor attacking from the α face):

Ir	-0.46069700	-1.43520800	0.51109800
C	-0.96994900	-2.54793100	3.58175200
C	-1.84510200	-1.30797200	3.34555600
C	1.22221500	-0.39126700	2.99345800
C	1.86361200	-1.72597800	2.55752100
H	-1.58862700	-3.34919300	4.01111100
H	-0.18106500	-2.33071100	4.31579300
H	-2.84387700	-1.62690400	3.00974100
H	-2.00692000	-0.76158900	4.29282600
H	1.99481300	0.38743700	2.94023700
H	0.89642400	-0.43880400	4.04436100
H	2.68978700	-1.51234200	1.86587100
H	2.31973700	-2.23339500	3.42680500
O	-1.86079300	1.23741200	-0.04403200
O	-3.72570104	-0.77852126	1.49564258
C	-5.07439867	-1.01861779	1.91526268
H	-5.46975202	-1.90809236	1.39206047
H	-5.71231459	-0.15817055	1.64198379
C	-5.09191250	-1.22865631	3.40658280
C	-4.96238850	-0.13415138	4.27692154
C	-5.20939883	-2.51679902	3.94820791
C	-4.95145618	-0.32465074	5.66055788
H	-4.87206126	0.87495369	3.86524126
C	-5.20415142	-2.71020029	5.33366982
H	-5.31103082	-3.37662988	3.27997579
C	-5.07335205	-1.61428738	6.19185769
H	-4.85281913	0.53512331	6.32810249

H	-5.30174728	-3.71897657	5.74273753
H	-5.06948179	-1.76315237	7.27462272
C	-0.98483000	0.38640100	-0.61927300
H	-0.02910400	0.85120600	-0.88338500
C	-1.81152391	2.97219447	-3.89728947
H	-1.92629783	3.85339687	-3.24205163
H	-0.74162918	2.83409355	-4.10435030
C	-2.54300527	3.25051201	-5.20764431
C	-1.87662466	2.63709383	-6.44728606
H	-3.56308216	2.82973798	-5.13701719
C	-3.51668781	5.12425462	-6.30717842
C	-2.31841838	3.35829569	-7.74836809
H	-2.11077410	1.56136535	-6.48545558
C	-3.53167431	4.26740017	-7.59859683
H	-3.23350044	6.17104237	-6.48871743
H	-2.52541407	2.62639328	-8.54971004
H	-3.58367487	4.92241808	-8.48643745
O	-2.26497246	1.78438751	-3.26591842
H	-3.18362630	1.90519290	-2.98526293
O	-2.61768605	4.66626480	-5.33541758
O	-0.46594498	2.81363400	-6.42178778
O	-1.21247841	4.17976876	-8.07118344
O	-4.70091596	3.47918964	-7.46621540
O	-4.85063535	5.05423038	-5.84974112
C	-0.03027322	3.60045140	-7.53770250
C	-5.64745966	4.24563147	-6.72829452
C	-6.46774257	5.14538579	-7.65393074
H	-7.07207720	4.53550781	-8.34175120
H	-7.14097924	5.78116373	-7.06063222
H	-5.81422254	5.80109300	-8.24817707
C	-6.51577576	3.30509861	-5.91005102

H	-7.22355482	3.88194923	-5.29775196
H	-7.08814824	2.64302965	-6.57586919
H	-5.89162639	2.68982496	-5.24684889
C	0.64137996	2.69586149	-8.57125405
H	0.95701846	3.28431546	-9.44561943
H	1.52746587	2.21102542	-8.13546374
H	-0.05291558	1.91150070	-8.90865512
C	0.87216323	4.71975017	-7.04290594
H	0.32869579	5.31771113	-6.29824794
H	1.78042280	4.30406767	-6.58291921
H	1.16896673	5.36837504	-7.88012617
C	-1.43920000	-0.79304800	-1.25661800
H	-0.92696600	-1.24610700	-2.10353400
C	0.91907400	-2.68564700	1.86691500
H	1.37478300	-3.31600900	1.09871200
C	-0.34744300	-3.04766700	2.30216100
H	-0.84385200	-3.87629000	1.78771700
C	-1.29356800	-0.34253500	2.32578600
H	-2.02706200	0.37377300	1.96351300
C	0.03480700	0.06110700	2.14996300
H	0.17191900	1.02014400	1.64314500
O	-1.49520200	-4.48175200	-0.37621800
C	-2.44708500	-1.43778000	-0.46926200
H	-2.72819200	-2.46739200	-0.70242700
C	-0.51364600	-4.09310900	-0.99428500
O	0.05421400	-2.91469700	-0.83465000
C	0.18317900	-4.93628600	-2.04560300
H	-0.31148500	-5.91162200	-2.13049900
H	0.15749400	-4.41934100	-3.01713800
H	1.24163700	-5.07543200	-1.77808700
C	-3.55870000	-0.56479300	0.10922000

H	-4.51622385	-0.75803184	-0.40159334
C	-3.26009000	0.91084200	-0.22068100
H	-3.48819900	1.03715300	-1.29310600
C	-4.08967900	1.89608900	0.57423800
H	-5.13858600	1.54143800	0.55284800
H	-3.76366200	1.90892800	1.63469900
O	-3.96300300	3.16433800	-0.01021600
C	-4.70307600	4.17891200	0.63760100
H	-5.78909900	3.96614600	0.58134300
H	-4.44315200	4.20146500	1.71756100
C	-4.40248700	5.52116800	0.01205100
C	-3.14451200	5.78602600	-0.54991600
C	-5.37088900	6.53604200	0.01847800
C	-2.86082700	7.04349400	-1.09144700
H	-2.39399700	4.99358900	-0.56762800
C	-5.08518200	7.79641700	-0.51558300
H	-6.36012000	6.33810800	0.44169900
C	-3.82845300	8.05385000	-1.07342000
H	-1.87803100	7.23555100	-1.53029900
H	-5.85038400	8.57693600	-0.50403000
H	-3.60590300	9.03662400	-1.49685300

3-*O*-Acetyl-4,6-di-*O*-benzyl glucal- α -[Ir(COD)OTf]-Acceptor (Acceptor coordinated to the Iridium):

Ir	-0.31563100	-0.69340300	0.27430600
C	-1.78619200	-2.44073900	-2.01711100
C	-1.32808300	-3.43531500	-0.93838300
C	1.25414200	-2.09052900	-2.11745100
C	0.76117600	-0.72382100	-2.63703200
H	-2.85604900	-2.59703500	-2.20859100

H	-1.26669700	-2.62671400	-2.96860800
H	-2.15920200	-3.64215400	-0.25189300
H	-1.05821900	-4.40722300	-1.39133300
H	2.34077400	-2.15819600	-2.26748400
H	0.81207900	-2.91054800	-2.70127900
H	1.55939000	0.02126600	-2.52658500
H	0.54190900	-0.77379900	-3.71948600
O	-2.48613000	1.43938900	-0.22323600
O	-3.99489000	-1.56686200	0.14083300
C	-4.62283800	-2.65317800	0.81815300
H	-5.39381700	-2.24937000	1.50468200
H	-3.89555100	-3.20621400	1.43934800
C	-5.25878100	-3.58392700	-0.18575100
C	-6.00893100	-3.07442000	-1.25844400
C	-5.14060000	-4.97370200	-0.03994800
C	-6.62821500	-3.93937500	-2.16409500
H	-6.10137000	-1.99324700	-1.38381000
C	-5.76749700	-5.84097800	-0.94159600
H	-4.55274600	-5.38279400	0.78670800
C	-6.51147800	-5.32569100	-2.00682200
H	-7.20772100	-3.53040000	-2.99584300
H	-5.66751900	-6.92181500	-0.81388100
H	-6.99808800	-6.00132000	-2.71480300
C	-1.39624200	1.31338700	0.54956100
H	-0.68110200	2.12822300	0.40253900
C	2.83484800	0.79085200	0.84223000
H	2.66483500	1.66119800	1.49544000
H	2.83398500	-0.11309600	1.45759800
C	4.18053900	0.94750900	0.14049600
C	4.57154400	-0.23157100	-0.76041400
H	4.16082800	1.85490900	-0.49046400

C	6.39114500	1.56879700	0.77602500
C	6.10737100	-0.27933100	-1.00154800
H	4.02278700	-0.15988900	-1.71327800
C	6.86770400	0.96867000	-0.57039900
H	7.06509200	1.33855000	1.61364900
H	6.32758900	-0.46672700	-2.06753700
H	7.94080400	0.71396900	-0.51233400
O	1.76041200	0.64214900	-0.09511700
H	1.61573500	1.47938000	-0.55983100
O	5.13252900	1.10620900	1.18519800
O	4.28517400	-1.47231600	-0.12910300
O	6.54239200	-1.35080000	-0.18674300
O	6.62960900	2.00761400	-1.50346500
O	6.37461700	2.95801600	0.53264300
C	5.47219900	-2.27166300	-0.03744400
C	6.78507600	3.24332100	-0.81348500
C	8.24489700	3.69929700	-0.82089800
H	8.57327400	3.91110300	-1.84919200
H	8.35594100	4.61301200	-0.21904300
H	8.90304900	2.92757000	-0.39491100
C	5.84974900	4.27251000	-1.42513800
H	5.91892800	5.22062900	-0.87294600
H	6.12440800	4.45783600	-2.47366200
H	4.81130000	3.91427900	-1.38750900
C	5.48778500	-3.30997700	-1.16056000
H	6.41563300	-3.89974400	-1.12040300
H	4.63228500	-3.99415600	-1.06067900
H	5.42653200	-2.82269800	-2.14556000
C	5.55377500	-2.88778100	1.34885200
H	5.53117700	-2.08921500	2.10337700
H	4.70619700	-3.56818500	1.51522100

H	6.48716000	-3.45920700	1.45669400
C	-1.37075100	0.51260900	1.70171500
H	-0.69001100	0.71382200	2.52710200
C	-0.47734500	-0.20807700	-1.93464900
H	-0.64202700	0.87169200	-2.01105200
C	-1.59491400	-0.98479100	-1.62108000
H	-2.51765700	-0.44026100	-1.45349300
C	-0.16290400	-2.94080800	-0.12380200
H	-0.11228100	-3.33397800	0.89489000
C	0.97760200	-2.31237700	-0.63662100
H	1.85377200	-2.25908400	0.01455800
O	-0.32819200	-2.70798700	3.07380000
C	-2.13032200	-0.70096100	1.53114700
H	-2.01003400	-1.49005700	2.27684600
C	0.61530100	-1.93499700	2.96605000
O	0.77584000	-1.05977600	1.99906000
C	1.76157100	-1.90916300	3.96249400
H	2.68028000	-2.26708300	3.47134900
H	1.95320300	-0.88176400	4.30496400
H	1.52950100	-2.55713800	4.81690200
C	-3.53500600	-0.52264200	0.96656800
H	-4.17597800	-0.48991700	1.87099600
C	-3.71953900	0.84159800	0.25404600
H	-4.31364800	0.68308900	-0.65494700
C	-4.44798300	1.84600700	1.14291600
H	-5.41059500	1.38930400	1.44892700
H	-3.87051100	2.03508700	2.07181200
O	-4.64963700	3.02883300	0.42263700
C	-5.31296000	4.04141200	1.15101300
H	-6.34937000	3.73282900	1.39332900
H	-4.79967600	4.20145900	2.12311600

C	-5.32520800	5.33304100	0.36665600
C	-4.33694300	5.60714900	-0.58989300
C	-6.31195800	6.29788800	0.62075500
C	-4.33369900	6.82626300	-1.27560000
H	-3.57649000	4.85226900	-0.79728300
C	-6.30460800	7.51940700	-0.05889600
H	-7.09537200	6.09144300	1.35620700
C	-5.31449700	7.78752300	-1.01064700
H	-3.55999000	7.02630900	-2.02177700
H	-7.07962300	8.26136100	0.15027700
H	-5.31086200	8.74016100	-1.54645400

3-*O*-Acetyl-4,6-di-*O*-benzyl glucal- α -[Ir(COD)OTf]- β -Acceptor (Free acceptor attacking from the β face):

Ir	2.44712500	-1.55624100	0.40566800
C	4.83562000	-0.12018200	2.04612500
C	5.49511500	-1.23151800	1.20936200
C	3.48630500	-2.61640100	3.20829000
C	2.35644500	-1.59381300	3.43728100
H	5.35944000	0.82354100	1.84301400
H	4.95346400	-0.31556700	3.12143500
H	5.88416400	-0.80957200	0.27349900
H	6.37123300	-1.64730600	1.74063200
H	3.24437000	-3.54045300	3.75275400
H	4.43549400	-2.25389900	3.62505700
H	1.38458300	-2.11338800	3.45344700
H	2.45159000	-1.11745600	4.43067800
O	1.15031600	1.21452900	0.16039000
O	4.35934900	1.37254100	-0.83658800
C	5.47815800	1.28797700	-1.71835000

H	5.25273000	1.86620100	-2.63671300
H	5.65766200	0.24306800	-2.02900700
C	6.70653900	1.84451800	-1.04079700
C	6.64452000	3.05315100	-0.32778700
C	7.93712000	1.17977400	-1.14398200
C	7.79094300	3.58350000	0.26905700
H	5.68947000	3.57564300	-0.23768200
C	9.08785200	1.71498500	-0.55443600
H	7.99757100	0.23433200	-1.69063800
C	9.01699500	2.91705100	0.15521200
H	7.72881700	4.52339700	0.82363700
H	10.03999200	1.18609300	-0.64475200
H	9.91360700	3.33378100	0.62092700
C	0.81393700	-0.04104200	-0.14891700
H	-0.13614500	-0.34897700	0.30447700
C	-3.34299400	-1.08279600	0.64530100
H	-3.03738700	-2.13164600	0.48000700
H	-3.33978600	-0.88821000	1.72647700
C	-4.76133900	-0.91644200	0.10492100
C	-5.41397500	0.43695700	0.42380200
H	-4.72575100	-1.01491900	-0.99614000
C	-6.76957500	-2.18888800	0.02218100
C	-6.96059500	0.35753500	0.33716300
H	-5.00912500	1.20145700	-0.25771400
C	-7.50142500	-0.87906600	-0.36870500
H	-7.34567000	-2.81113100	0.72211400
H	-7.37075800	1.25568200	-0.15871000
H	-8.57857100	-0.96446900	-0.13959700
O	-2.42883300	-0.16833200	0.06074600
H	-2.41256100	-0.31578400	-0.89629800
O	-5.53452800	-1.98103900	0.65016500

O	-5.17095800	0.83704800	1.76545600
O	-7.37076700	0.27976700	1.68944900
O	-7.27539400	-0.76866500	-1.76256200
O	-6.61399100	-2.85992600	-1.21074300
C	-6.39180300	0.89673500	2.51434800
C	-7.17936700	-2.09021900	-2.28244100
C	-8.56007600	-2.64241000	-2.64052200
H	-9.01105200	-2.04774900	-3.44873500
H	-8.47281800	-3.68622400	-2.97579600
H	-9.23295200	-2.61862300	-1.77048000
C	-6.22767100	-2.08721000	-3.46682700
H	-6.10340300	-3.10839800	-3.85470300
H	-6.62772100	-1.45364300	-4.27167200
H	-5.24479800	-1.69908100	-3.16457000
C	-6.75760100	2.35650800	2.78168200
H	-7.70620400	2.41553300	3.33595500
H	-5.97169100	2.84479100	3.37674200
H	-6.86913500	2.90633100	1.83494600
C	-6.24618400	0.07330300	3.78496200
H	-5.98026900	-0.95864600	3.51662400
H	-5.45926500	0.49697900	4.42575100
H	-7.19167600	0.06774500	4.34705500
C	1.36418700	-0.72606200	-1.24787300
H	0.84087100	-1.54565500	-1.73817900
C	2.28457900	-0.50361200	2.39021800
H	1.34461700	0.05606500	2.38656700
C	3.36261500	0.09441600	1.73348800
H	3.14819300	1.04181300	1.24859800
C	4.56432200	-2.35985500	0.86471500
H	4.77268800	-2.87275200	-0.07930800
C	3.65649000	-2.96069300	1.73701300

H	3.22973800	-3.91570100	1.41422300
O	3.81857000	-3.27258800	-2.18681600
C	2.74708900	-0.40022200	-1.45079400
H	3.34125200	-1.03574300	-2.11340200
C	2.81276400	-3.77552300	-1.70317100
O	2.11605100	-3.25385200	-0.71628500
C	2.23679900	-5.09101100	-2.19274200
H	2.21464800	-5.82107000	-1.36925200
H	1.19827800	-4.94600500	-2.52731000
H	2.84387500	-5.48105400	-3.01893500
C	3.11043500	1.07700500	-1.41330600
H	3.14224500	1.36122500	-2.48599200
C	2.00037200	1.93966800	-0.76316800
H	2.47607700	2.71143900	-0.14491400
C	1.11453700	2.62463800	-1.80285500
H	1.76472400	3.26065100	-2.43743200
H	0.64311200	1.87400600	-2.47150500
O	0.14751900	3.37335500	-1.12451900
C	-0.81198000	4.00681800	-1.95413200
H	-0.36077500	4.86054700	-2.49534400
H	-1.16601600	3.28918700	-2.72306800
C	-1.97416700	4.46901000	-1.10785800
C	-2.60921200	3.56653500	-0.23780900
C	-2.44622800	5.78630000	-1.18133200
C	-3.69467300	3.97547400	0.54080800
H	-2.25248300	2.53624400	-0.16435800
C	-3.53884500	6.19659100	-0.40761100
H	-1.95426500	6.50078600	-1.84771100
C	-4.16397500	5.29287300	0.45606100
H	-4.17467300	3.25730100	1.21068600
H	-3.89554200	7.22762800	-0.47557700

H -5.01364400 5.61336500 1.06472300

3-*O*-Acetyl-4,6-di-*O*-benzyl glucal- β -[Ir(COD)-OTf]-Acceptor (Acceptor coordinated to the Iridium):

Ir -0.46069700 -1.43520800 0.51109800
C -0.96994900 -2.54793100 3.58175200
C -1.84510200 -1.30797200 3.34555600
C 1.22221500 -0.39126700 2.99345800
C 1.86361200 -1.72597800 2.55752100
H -1.58862700 -3.34919300 4.01111100
H -0.18106500 -2.33071100 4.31579300
H -2.84387700 -1.62690400 3.00974100
H -2.00692000 -0.76158900 4.29282600
H 1.99481300 0.38743700 2.94023700
H 0.89642400 -0.43880400 4.04436100
H 2.68978700 -1.51234200 1.86587100
H 2.31973700 -2.23339500 3.42680500
O -1.86079300 1.23741200 -0.04403200
O -4.76388400 -0.86532200 -0.56379600
C -5.53532500 -1.92465700 0.01534200
H -5.79307100 -1.66462600 1.05801200
H -4.93848500 -2.85480200 0.03983300
C -6.78218700 -2.12588600 -0.80520700
C -6.71544300 -2.78363500 -2.04420600
C -8.01962900 -1.63803900 -0.36111800
C -7.86331900 -2.95043400 -2.82229200
H -5.75584900 -3.16974100 -2.39921900
C -9.17198300 -1.80829800 -1.13573300
H -8.08358200 -1.12433600 0.60230900
C -9.09501100 -2.46331700 -2.36847200

H	-7.79957400	-3.46642000	-3.78367200
H	-10.13108600	-1.42779400	-0.77541500
H	-9.99422100	-2.59779400	-2.97501400
C	-0.98483000	0.38640100	-0.61927300
H	-0.02910400	0.85120600	-0.88338500
C	3.16986200	1.19834900	-1.06020100
H	3.02114700	1.71286500	-2.02569800
H	2.97925100	1.91876700	-0.25317800
C	4.62153500	0.73327600	-0.98333700
C	5.01268800	0.09849700	0.35871800
H	4.78991100	-0.02484800	-1.77041600
C	6.77108700	1.60298600	-1.52275800
C	6.54799600	0.13530400	0.58143500
H	4.62666800	-0.93262100	0.39419800
C	7.36930500	0.46362000	-0.65894900
H	7.29315500	2.56171500	-1.39161000
H	6.90586200	-0.82467600	0.99501400
H	8.39101000	0.73093900	-0.33541700
O	2.24971100	0.13166000	-0.88519500
H	2.32632100	-0.47913500	-1.63242100
O	5.42649300	1.87832100	-1.24251600
O	4.49116600	0.83696700	1.45622000
O	6.73036300	1.19488700	1.50130300
O	7.37662200	-0.65206500	-1.53137100
O	6.93737700	1.13620100	-2.84488800
C	5.54984300	1.34733900	2.27651300
C	7.56348400	-0.15552000	-2.85289700
C	9.05025600	-0.00518900	-3.17867900
H	9.54338500	-0.98858400	-3.17352500
H	9.17334800	0.44685900	-4.17364900
H	9.55179400	0.64278800	-2.44468000

C	6.84183800	-1.06712100	-3.83080700
H	6.93646400	-0.67397400	-4.85310800
H	7.27976400	-2.07541000	-3.80193600
H	5.77546900	-1.13465600	-3.57340200
C	5.64032900	0.52831400	3.56439500
H	6.46716000	0.89357600	4.19157500
H	4.70353000	0.61020000	4.13521000
H	5.81616200	-0.53381300	3.33619200
C	5.32529900	2.83085500	2.52310000
H	5.25920000	3.35034500	1.55708200
H	4.39351300	2.98864800	3.08540900
H	6.15986200	3.25146900	3.10304200
C	-1.43920000	-0.79304800	-1.25661800
H	-0.92696600	-1.24610700	-2.10353400
C	0.91907400	-2.68564700	1.86691500
H	1.37478300	-3.31600900	1.09871200
C	-0.34744300	-3.04766700	2.30216100
H	-0.84385200	-3.87629000	1.78771700
C	-1.29356800	-0.34253500	2.32578600
H	-2.02706200	0.37377300	1.96351300
C	0.03480700	0.06110700	2.14996300
H	0.17191900	1.02014400	1.64314500
O	-1.49520200	-4.48175200	-0.37621800
C	-2.44708500	-1.43778000	-0.46926200
H	-2.72819200	-2.46739200	-0.70242700
C	-0.51364600	-4.09310900	-0.99428500
O	0.05421400	-2.91469700	-0.83465000
C	0.18317900	-4.93628600	-2.04560300
H	-0.31148500	-5.91162200	-2.13049900
H	0.15749400	-4.41934100	-3.01713800
H	1.24163700	-5.07543200	-1.77808700

C	-3.55870000	-0.56479300	0.10922000
H	-3.68901000	-0.73156400	1.19103800
C	-3.26009000	0.91084200	-0.22068100
H	-3.48819900	1.03715300	-1.29310600
C	-4.08967900	1.89608900	0.57423800
H	-5.13858600	1.54143800	0.55284800
H	-3.76366200	1.90892800	1.63469900
O	-3.96300300	3.16433800	-0.01021600
C	-4.70307600	4.17891200	0.63760100
H	-5.78909900	3.96614600	0.58134300
H	-4.44315200	4.20146500	1.71756100
C	-4.40248700	5.52116800	0.01205100
C	-3.14451200	5.78602600	-0.54991600
C	-5.37088900	6.53604200	0.01847800
C	-2.86082700	7.04349400	-1.09144700
H	-2.39399700	4.99358900	-0.56762800
C	-5.08518200	7.79641700	-0.51558300
H	-6.36012000	6.33810800	0.44169900
C	-3.82845300	8.05385000	-1.07342000
H	-1.87803100	7.23555100	-1.53029900
H	-5.85038400	8.57693600	-0.50403000
H	-3.60590300	9.03662400	-1.49685300

3-*O*-Acetyl-4,6-di-*O*-benzyl glucal- β -Ir(COD)-OTf- α -Acceptor (Free acceptor attacking from the α face):

Ir	-3.26126800	-1.33904300	0.52361200
C	-5.87527700	-0.39109300	2.32017300
C	-4.70668800	0.57957000	2.55771400
C	-3.76211500	-2.34257700	3.50248200
C	-4.56603100	-3.26335200	2.56602800

H	-6.78084900	0.18898300	2.09099200
H	-6.09304200	-0.96876800	3.22917800
H	-4.79163100	1.42706700	1.85983600
H	-4.76784200	1.01634900	3.57134600
H	-3.09815400	-2.96188200	4.12137200
H	-4.42952200	-1.81837700	4.20260300
H	-3.94059100	-4.11902000	2.26982000
H	-5.43305300	-3.69650200	3.09702800
O	-0.68402600	0.16151600	1.21191000
O	-2.00412200	2.65578500	-1.04802900
C	-3.16125100	3.43664100	-1.37335600
H	-3.52213200	3.94949800	-0.46322400
H	-3.97342200	2.78093600	-1.73462800
C	-2.78298000	4.43602300	-2.43465900
C	-2.85775900	4.09470500	-3.79390000
C	-2.30559900	5.70655600	-2.07831200
C	-2.46598500	5.00615900	-4.77844900
H	-3.22894100	3.10734900	-4.08279500
C	-1.91362900	6.62072800	-3.06064100
H	-2.24507300	5.98361300	-1.02201000
C	-1.99258500	6.27115000	-4.41289300
H	-2.53244300	4.73010800	-5.83383300
H	-1.54775900	7.60889200	-2.77051500
H	-1.68901800	6.98581900	-5.18211100
C	-1.10124800	-0.88862400	0.47714000
H	-0.57380400	-1.81546700	0.72534700
C	2.30731600	-0.49401500	-0.29237600
H	2.35870800	0.29550300	0.47589500
H	1.83209100	-1.37706400	0.15626300
C	3.72244100	-0.88187000	-0.71301200
C	3.76575800	-1.99870100	-1.75935600

H	4.22636400	0.00197800	-1.14485500
C	5.78415000	-1.44333200	0.35984600
C	5.17510600	-2.65422300	-1.84474300
H	3.45108500	-1.59175900	-2.73427300
C	6.25509100	-1.96375800	-1.01934600
H	6.07281200	-2.10289400	1.19067100
H	5.52431400	-2.69699200	-2.89161600
H	7.09069100	-2.67389700	-0.88629500
O	1.49887900	-0.10042900	-1.38786400
H	1.84822100	0.72625300	-1.75046300
O	4.39599400	-1.29619500	0.47193500
O	2.91136400	-3.06592000	-1.37161600
O	4.98674300	-3.95058900	-1.30847900
O	6.67700700	-0.78789100	-1.68926900
O	6.45185500	-0.20411000	0.48528300
C	3.61517000	-4.30314100	-1.44405900
C	7.19670700	0.10024200	-0.70714100
C	8.68250400	-0.16253100	-0.45850300
H	9.26457000	0.05072800	-1.36732800
H	9.04875300	0.48144500	0.35430500
H	8.85444200	-1.20982200	-0.16887400
C	6.91901100	1.53062800	-1.13767300
H	7.27868400	2.23327600	-0.37261200
H	7.43670500	1.74734800	-2.08345500
H	5.83990100	1.68365600	-1.27876600
C	3.36149200	-4.97885100	-2.79394100
H	3.92951800	-5.91836800	-2.86500100
H	2.29086000	-5.20299100	-2.91099900
H	3.66752600	-4.32331400	-3.62351300
C	3.21908200	-5.16789800	-0.25922700
H	3.42175500	-4.61982900	0.67158100

H	2.14852200	-5.41440600	-0.30830500
H	3.79511100	-6.10463800	-0.26039800
C	-1.71786800	-0.69681800	-0.78180800
H	-1.64088500	-1.41386500	-1.59697600
C	-5.04517300	-2.59378400	1.29697900
H	-5.15759900	-3.26192600	0.43860500
C	-5.60303300	-1.33141100	1.17303400
H	-6.02565200	-1.06496400	0.19917300
C	-3.33902100	-0.03385400	2.38296000
H	-2.54007300	0.69852300	2.29845400
C	-2.90970900	-1.30658000	2.77745600
H	-1.83108600	-1.41497600	2.91913000
O	-5.28645900	-0.81226400	-2.05908800
C	-2.64989100	0.38609600	-0.72417100
H	-3.37814900	0.50731200	-1.52959100
C	-4.65967900	-1.86016700	-2.13255000
O	-3.77869900	-2.26770100	-1.24090100
C	-4.81821000	-2.83730200	-3.28173000
H	-5.57240300	-2.46622200	-3.98645300
H	-3.85493500	-2.96523200	-3.79897000
H	-5.11627800	-3.82536200	-2.89945000
C	-2.19456500	1.67717900	-0.04646900
H	-2.93274500	2.03851800	0.68884800
C	-0.79920700	1.45750400	0.57224000
H	-0.08910800	1.44996300	-0.27058700
C	-0.39973500	2.52384900	1.56844600
H	-0.68740300	3.50415800	1.14075500
H	-0.96611800	2.39459900	2.51307400
O	0.98496800	2.46267500	1.79878200
C	1.42204500	3.36883600	2.79295800
H	1.07151500	4.39362600	2.55881900

H	0.96478700	3.09938800	3.76918700
C	2.92850500	3.36918800	2.91432900
C	3.70306400	2.26110000	2.54290800
C	3.57500200	4.49919100	3.44098900
C	5.09554600	2.28495400	2.68317100
H	3.21969000	1.37448700	2.13079600
C	4.96337000	4.51873900	3.59952700
H	2.98575600	5.37571900	3.72720200
C	5.72919300	3.41172500	3.21672700
H	5.68103400	1.42210000	2.35648600
H	5.44959100	5.40660700	4.01225100
H	6.81641200	3.43071800	3.32870100

3-*O*-Acetyl-4,6-di-*O*-allyl Glucal- α -Ir(COD)- α -Acceptor (Acceptor coordinated to the Iridium):

Ir	-0.87777700	-0.49757700	0.09564400
C	-2.30117500	-2.10030400	-2.32241400
C	-2.01493200	-3.13083300	-1.22476100
C	0.73267400	-2.03259500	-2.18935700
C	0.39169700	-0.64350000	-2.75842300
H	-3.34940300	-2.16273900	-2.59548300
H	-1.73354600	-2.32009500	-3.22237700
H	-2.90525600	-3.26064500	-0.61585600
H	-1.79389900	-4.10774400	-1.66273300
H	1.80454400	-2.19327300	-2.26809500
H	0.26312900	-2.81283300	-2.78179700
H	1.23924300	0.01716200	-2.61741000
H	0.22984200	-0.69902900	-3.83789400
O	-2.80661800	1.83326000	-0.54221000
O	-4.54056300	-1.08455100	-0.32577500
C	-5.85637100	-1.56779100	-0.03872700

H	-6.56752300	-0.73316800	0.02114900
H	-5.85433600	-2.06099600	0.93359000
C	-1.80273600	1.59228700	0.31383500
H	-1.02283900	2.33476100	0.24200500
C	2.30419900	0.87086400	0.81764000
H	2.12032100	1.73890500	1.44684700
H	2.21807100	-0.02216100	1.42322300
C	3.69484600	0.98370100	0.21292800
C	4.11944600	-0.20930900	-0.64322900
H	3.73987300	1.87705200	-0.41407100
C	5.87083000	1.55692200	0.99579900
C	5.66007600	-0.29656600	-0.77972400
H	3.64714900	-0.13171800	-1.62176400
C	6.42185300	0.92989400	-0.30143200
H	6.46715000	1.32584600	1.87218300
H	5.94216900	-0.49650100	-1.81410200
H	7.46921700	0.65710400	-0.16753500
O	1.29407800	0.76777600	-0.20374900
H	1.21680200	1.61100900	-0.66492300
O	4.57057100	1.13496600	1.32878000
O	3.75143700	-1.44327900	-0.03216900
O	6.01765900	-1.38494800	0.06017300
O	6.28433500	1.96725100	-1.26599400
O	5.91010500	2.95036700	0.74397700
C	4.90880300	-2.27803000	0.12839200
C	6.42949900	3.20870200	-0.57478000
C	7.89439300	3.61745300	-0.47928000
H	8.29530600	3.80552400	-1.47224200
H	7.98635900	4.52463100	0.11264300
H	8.48633200	2.83863600	-0.00498500
C	5.57897600	4.25563400	-1.26187800

H	5.64044300	5.19590900	-0.72060900
H	5.93600100	4.41652200	-2.27584700
H	4.54107700	3.93685300	-1.29931200
C	4.96820800	-3.30473100	-0.99697000
H	5.86245800	-3.91544400	-0.89806500
H	4.09688000	-3.95351700	-0.95641200
H	4.98725600	-2.81434600	-1.96759700
C	4.88116700	-2.91095800	1.50382700
H	4.83232900	-2.13800200	2.26510900
H	4.01500300	-3.56075800	1.59758700
H	5.77752300	-3.50652100	1.65761900
C	-1.94651500	0.78369600	1.44178900
H	-1.33575100	0.91352800	2.31636700
C	-0.82833700	-0.00998300	-2.13535700
H	-0.89054000	1.06639300	-2.22468200
C	-2.02053200	-0.67327700	-1.89718000
H	-2.89365300	-0.05971000	-1.78986700
C	-0.88450900	-2.73956900	-0.31900900
H	-0.95046900	-3.13827100	0.68217600
C	0.33476500	-2.21193600	-0.73463800
H	1.14890600	-2.24251300	-0.02518100
O	-1.24397600	-2.50323300	2.86854500
C	-2.78910900	-0.35030500	1.19014400
H	-2.81704100	-1.14433700	1.91901800
C	-0.24516800	-1.79890300	2.83429500
O	0.04642200	-0.94299100	1.88671200
C	0.81398300	-1.84058800	3.91678000
H	1.73194600	-2.25749500	3.50688700
H	1.04031400	-0.83741100	4.26831200
H	0.47704600	-2.45676600	4.74241200
C	-4.11004700	-0.04130900	0.52875000

H	-4.80702000	0.03025300	1.36645600
C	-4.13112100	1.35627800	-0.15543300
H	-4.66639000	1.25474700	-1.09368200
C	-4.84125100	2.45915000	0.65488500
H	-5.05860800	2.14649700	1.68119600
H	-4.19370700	3.33655300	0.70962500
O	-6.04654100	2.75669800	-0.02233400
C	-6.78567900	3.80185600	0.60090300
H	-7.11853800	3.50011000	1.60440000
H	-6.14190800	4.67826000	0.73087300
C	-7.92704800	4.23340900	-0.24142700
H	-7.81602000	4.05658200	-1.31303300
C	-9.02998000	4.77104400	0.27616000
H	-9.21955000	4.75456000	1.34849900
H	-9.78098100	5.25716300	-0.34151500
C	-6.24891100	-2.57437800	-1.07408900
H	-5.50188000	-2.74771100	-1.84890500
C	-7.44110200	-3.16469700	-1.12049500
H	-7.64121200	-3.99755300	-1.78953200
H	-8.26438200	-2.84835900	-0.48006300

3-*O*-Acetyl-4,6-di-*O*-allyl Glucal- β -Ir(COD)- α -Acceptor (Free acceptor attacking from the α face):

Ir	-2.21179400	-1.59902400	-0.02827600
C	-4.96039000	-1.42987000	-1.62861800
C	-5.14021400	-2.11351200	-0.27465900
C	-3.27440400	-3.99523500	-1.94710500
C	-2.51580300	-3.02284900	-2.84647500
H	-5.64302400	-0.58462400	-1.70808200
H	-5.20166700	-2.09720700	-2.45635400

H	-5.42912300	-1.36832000	0.46587500
H	-5.95872000	-2.84515300	-0.30737800
H	-2.92143100	-5.01604700	-2.09899300
H	-4.33722800	-4.00136700	-2.18577400
H	-1.49874300	-3.38172000	-3.00856300
H	-2.97301400	-2.95524000	-3.84186100
O	-1.18686100	0.97646200	-1.45582900
O	-4.07152800	1.57093800	0.34043700
C	-4.78844100	2.63588400	0.97381800
H	-4.34352200	3.60149500	0.68791600
H	-4.70711200	2.54765200	2.06086300
C	-0.69071000	-0.02937300	-0.73055400
H	0.13682800	-0.53548100	-1.22783500
C	3.03726500	-0.84371700	-0.98621000
H	2.58168800	-1.56221500	-0.29904900
H	3.41870500	-1.38095300	-1.85218100
C	4.18234400	-0.13947600	-0.26458900
C	5.23463600	0.47359500	-1.19855300
H	3.76689300	0.67247800	0.34587000
C	5.66901900	-0.59189000	1.54768700
C	6.58491100	0.71351400	-0.47330300
H	4.84317400	1.40605700	-1.61396700
C	6.53589500	0.58152800	1.04082100
H	6.25605500	-1.44668600	1.88042800
H	6.98400300	1.70275900	-0.71959700
H	7.56056500	0.47862800	1.41164600
O	2.04889600	0.06981100	-1.48371000
H	2.01745200	0.84562900	-0.91055400
O	4.78926200	-1.11288100	0.58431700
O	5.56516900	-0.41963100	-2.25572300
O	7.42752800	-0.31417300	-0.96971800

O	5.90431800	1.73093500	1.58883600
O	4.96065700	-0.03957200	2.64191300
C	6.97717500	-0.67004000	-2.27282800
C	5.31952600	1.34108900	2.83004600
C	6.32162200	1.46116500	3.97383300
H	6.60598600	2.50444500	4.11707000
H	5.87697200	1.08879500	4.89743000
H	7.22069300	0.87870000	3.76899200
C	4.07015600	2.16533600	3.06546100
H	3.58233300	1.84742600	3.98708800
H	4.33025100	3.22030000	3.15681000
H	3.37398700	2.04330100	2.23585900
C	7.64432900	0.19878200	-3.33501700
H	8.72370500	0.04028800	-3.32755900
H	7.26017700	-0.05617900	-4.32346800
H	7.44619500	1.25605600	-3.15151100
C	7.21945100	-2.15171800	-2.48128400
H	6.71461600	-2.71962100	-1.70033700
H	6.83673600	-2.46097700	-3.45430100
H	8.28823700	-2.36586900	-2.44479500
C	-0.85905700	-0.11202600	0.66045200
H	-0.14433400	-0.63537500	1.27845900
C	-2.48263700	-1.62354000	-2.29304200
H	-1.66986400	-1.01878500	-2.67619600
C	-3.53988800	-0.92370600	-1.72606600
H	-3.42176500	0.14786600	-1.72678700
C	-3.87078700	-2.79565200	0.22112400
H	-3.78640400	-2.83288100	1.30489800
C	-3.02991000	-3.62662200	-0.50830900
H	-2.37906000	-4.28543100	0.05387700
O	-2.88574500	-1.64067000	3.35389100

C	-2.13446000	0.30377500	1.08805400
H	-2.43249000	0.06523400	2.10255800
C	-2.11652200	-2.50738500	2.95738600
O	-1.73837100	-2.65709300	1.71215800
C	-1.52044700	-3.54842200	3.88231600
H	-1.92940400	-4.53010900	3.63352200
H	-0.43948400	-3.60236600	3.74955100
H	-1.75966300	-3.31056600	4.91621000
C	-2.67585900	1.59044700	0.52295600
H	-2.42360600	2.32470200	1.30233400
C	-1.94528800	2.02047300	-0.79086100
H	-2.84020400	2.10528300	-1.42072300
C	-1.24531600	3.35976100	-0.90003300
H	-0.48694800	3.47960400	-0.11083200
H	-0.72284500	3.39916100	-1.86358500
O	-2.23469900	4.35179300	-0.79617900
C	-1.72294100	5.67074900	-0.93129600
H	-1.03925000	5.90105700	-0.09607400
H	-1.13225300	5.74953700	-1.85141800
C	-6.23505400	2.55038200	0.58760100
H	-6.50523800	1.74557400	-0.09061900
C	-7.15760700	3.43794600	1.00559400
H	-8.17903500	3.13570000	1.20434000
H	-6.90570900	4.48236900	1.16243000
C	-2.86022400	6.64637500	-1.00930400
H	-3.85989000	6.22205200	-0.97262400
C	-2.67667100	7.97873900	-1.08461100
H	-1.85181800	8.46549700	-0.57313800
H	-3.34550300	8.60594100	-1.66235400

3-*O*-Acetyl-4,6-di-*O*-allyl Glucal- β -Ir(COD)- β -Acceptor (Acceptor coordinated to the Iridium):

Ir	3.55318200	-0.89898600	-0.30557200
C	5.36513050	-1.53905651	-2.84450282
C	4.50272135	-2.77931142	-2.61096003
C	6.36016064	-2.32612495	-0.01178225
C	6.52236830	-0.79726358	-0.03757100
H	5.30020649	-1.23780646	-3.88989833
H	6.41666857	-1.72563463	-2.63175311
H	3.59915598	-2.68894154	-3.21547077
H	4.99532219	-3.70331565	-2.93160574
H	6.80180612	-2.70548358	0.90826386
H	6.87966401	-2.81943351	-0.83402298
H	6.55952104	-0.43664562	0.99033215
H	7.46429211	-0.48730333	-0.50132418
O	1.18797800	0.78712900	-1.27438300
O	1.32629900	2.15041700	2.07546200
C	2.21417500	2.70307300	3.05377500
H	2.79549100	3.51161000	2.59463600
H	2.92200800	1.94135200	3.39864200
C	1.46737900	-0.47945100	-0.89220600
H	1.19487900	-1.20436400	-1.65086000
C	2.60761071	-2.43794325	-4.73843347
H	3.07646541	-1.67335358	-5.36304600
H	3.34734677	-3.20292391	-4.51454833
C	1.43199748	-3.03627536	-5.51600800
C	1.11641619	-4.49421129	-5.16443712
H	0.54030106	-2.44621497	-5.27974343
C	0.64060101	-3.13827232	-7.76537632
C	0.28981984	-5.19787250	-6.26584237
H	0.59278523	-4.51293047	-4.20582311

C	-0.30536662	-4.27042044	-7.31223567
H	1.08370642	-3.31689930	-8.74360719
H	-0.51568763	-5.79341243	-5.82575093
H	-0.61280485	-4.86865172	-8.17486636
O	1.73040021	-2.91444211	-6.90986149
O	2.29869131	-5.28540690	-5.06337141
O	1.23200922	-6.03400688	-6.92398061
O	-1.41652356	-3.58272144	-6.74949852
O	-0.20314223	-1.99937828	-7.82621166
C	2.26082324	-6.37191303	-5.99779000
C	-1.54817384	-2.34831279	-7.45424408
C	-2.40136511	-2.51873458	-8.70732881
H	-3.41993672	-2.79486382	-8.43339966
H	-2.43039622	-1.58269779	-9.26535146
H	-1.99149539	-3.29189431	-9.35736963
C	-2.10460950	-1.30119074	-6.51117857
H	-2.17075104	-0.34005733	-7.02043414
H	-3.10352556	-1.58862846	-6.18293236
H	-1.46128856	-1.19653661	-5.63860924
C	1.92355741	-7.66613330	-5.26371108
H	1.87151226	-8.49687239	-5.96820331
H	2.69064264	-7.88521971	-4.52049848
H	0.96372329	-7.57890573	-4.75319765
C	3.57867688	-6.44140233	-6.74494449
H	3.77289656	-5.48956640	-7.23717898
H	4.39077660	-6.65892939	-6.05112174
H	3.54345626	-7.23204096	-7.49484678
C	1.57198100	-0.82427500	0.46724700
H	1.32279200	-1.79797900	0.85744200
C	5.34899742	-0.12246131	-0.71233555
H	5.00587608	0.81722355	-0.30851997

C	4.82740374	-0.44347209	-1.96335939
H	4.13844028	0.25544880	-2.42608724
C	4.09536643	-2.89297405	-1.17058702
H	3.23138210	-3.51263376	-0.99113405
C	4.88996804	-2.70268102	-0.03986472
H	4.52316962	-3.18388992	0.85891669
O	5.75227655	0.46284335	1.98973584
C	2.30144400	0.16905400	1.17742500
H	2.65664000	-0.05761900	2.17433400
C	4.85365170	-0.03965662	2.64865586
O	3.85347036	-0.73066146	2.15041940
C	4.78180791	0.07756291	4.15684903
H	5.63619560	0.63785994	4.52800301
H	3.85789591	0.58120658	4.44397287
H	4.76647254	-0.91517710	4.60835514
C	1.96028600	1.63184300	0.92023700
H	2.85262000	2.22096400	0.69648700
C	0.90777800	1.71464700	-0.19692100
H	-0.04400900	1.40964400	0.24893700
C	0.75652900	3.09678300	-0.78800800
H	0.70675500	3.81606500	0.03884300
H	1.62940400	3.35110100	-1.40432900
O	-0.42356400	3.13134500	-1.55835400
C	-0.65768900	4.39762400	-2.16418100
H	-0.77927300	5.16472800	-1.38749700
H	0.21334900	4.68365900	-2.76882100
C	-1.88151500	4.29961100	-3.02897200
H	-2.30504900	3.30378700	-3.11334100
C	-2.44893200	5.32552200	-3.64981800
H	-2.08252900	6.34005000	-3.53395300
H	-3.29919500	5.18604600	-4.30436600

C	1.38607000	3.21845600	4.19593500
H	0.31345300	3.11371800	4.06853100
C	1.88266300	3.76261300	5.29821000
H	1.23429400	4.13192000	6.08167200
H	2.95039100	3.86325400	5.46079600
O	2.20351673	-1.90708883	-3.47360082
H	2.92243446	-1.39450682	-3.09674941

3-*O*-Acetyl-4,6-di-*O*-allyl Glucal- β -Ir(COD)- β -Acceptor (Free acceptor attacking from the α face):

Ir	3.55318200	-0.89898600	-0.30557200
C	6.39723500	0.52990300	-0.39861000
C	5.37271100	1.58977200	-0.80302600
C	5.26661700	-0.80563200	-2.96218500
C	5.67789500	-2.00053400	-2.08614100
H	7.04775000	0.92612200	0.38091500
H	7.03731500	0.24069700	-1.23075400
H	5.07119500	2.13602500	0.09180700
H	5.78421200	2.33411300	-1.49286400
H	4.96812500	-1.17999900	-3.94004000
H	6.08543100	-0.10572800	-3.13246400
H	5.13434400	-2.88170200	-2.42688400
H	6.74069600	-2.24285700	-2.18662200
O	1.18797800	0.78712900	-1.27438300
O	1.32629900	2.15041700	2.07546200
C	2.21417500	2.70307300	3.05377500
H	2.79549100	3.51161000	2.59463600
H	2.92200800	1.94135200	3.39864200
C	1.46737900	-0.47945100	-0.89220600
H	1.19487900	-1.20436400	-1.65086000

C	-2.93524200	-0.72267200	-0.92128200
H	-2.91434200	-0.11028500	-1.82632800
H	-2.76781200	-1.75991200	-1.20169200
C	-4.30789100	-0.55718600	-0.26314900
C	-4.77673800	-1.77585300	0.53922500
H	-4.24462300	0.28457300	0.43438500
C	-6.48812900	0.22217800	-0.84239300
C	-6.30640500	-1.77590400	0.76641000
H	-4.23702900	-1.79275300	1.48891400
C	-7.00342300	-0.46569400	0.43950200
H	-7.16112400	0.10614100	-1.69021300
H	-6.54560900	-2.05301100	1.79751800
H	-8.07804700	-0.65272700	0.35745000
O	-1.86867600	-0.38414400	-0.03490100
H	-1.91314100	0.56087000	0.15328400
O	-5.24783200	-0.25140300	-1.29742300
O	-4.53222400	-2.99701500	-0.15572500
O	-6.79081700	-2.75478300	-0.14305600
O	-6.72963400	0.47867200	1.46784300
O	-6.41032300	1.59182600	-0.48087700
C	-5.75753700	-3.70869600	-0.37294800
C	-6.82723100	1.77734600	0.88330600
C	-8.26382900	2.28940000	0.91776100
H	-8.59080000	2.42134800	1.94948400
H	-8.32691300	3.24933600	0.40498400
H	-8.93958900	1.59199600	0.42248500
C	-5.86232800	2.70770700	1.58959800
H	-5.89133800	3.69399500	1.12711800
H	-6.14225500	2.80859100	2.63824600
H	-4.84715300	2.31780000	1.52973300
C	-5.85953500	-4.86518000	0.61688400

H	-6.79815900	-5.40176000	0.47471400
H	-5.03299900	-5.56013700	0.46636300
H	-5.81815100	-4.49715900	1.64273100
C	-5.83011300	-4.15928200	-1.81915400
H	-5.73960400	-3.29684300	-2.47795200
H	-5.02352500	-4.86059000	-2.03315600
H	-6.78105800	-4.65743800	-2.00954200
C	1.57198100	-0.82427500	0.46724700
H	1.32279200	-1.79797900	0.85744200
C	5.31700900	-1.77893800	-0.63420400
H	4.97123800	-2.62717200	-0.06433700
C	5.63485800	-0.65674000	0.12725000
H	5.51780900	-0.71818700	1.20419100
C	4.14964100	0.96005700	-1.40393400
H	3.26745200	1.57991600	-1.39097900
C	4.09198300	-0.07287100	-2.33981400
H	3.16983600	-0.12091800	-2.90660100
O	4.11866100	-0.96608900	2.60372200
C	2.30144400	0.16905400	1.17742500
H	2.65664000	-0.05761900	2.17433400
C	3.72569600	-2.02640500	2.13948400
O	3.48159100	-2.24435800	0.86708500
C	3.46472700	-3.24748200	2.99646400
H	3.69779100	-3.02988000	4.03569300
H	2.41874500	-3.54367200	2.90756200
H	4.07176500	-4.08436900	2.64897200
C	1.96028600	1.63184300	0.92023700
H	2.85262000	2.22096400	0.69648700
C	0.90777800	1.71464700	-0.19692100
H	-0.04400900	1.40964400	0.24893700
C	0.75652900	3.09678300	-0.78800800

H	0.70675500	3.81606500	0.03884300
H	1.62940400	3.35110100	-1.40432900
O	-0.42356400	3.13134500	-1.55835400
C	-0.65768900	4.39762400	-2.16418100
H	-0.77927300	5.16472800	-1.38749700
H	0.21334900	4.68365900	-2.76882100
C	-1.88151500	4.29961100	-3.02897200
H	-2.30504900	3.30378700	-3.11334100
C	-2.44893200	5.32552200	-3.64981800
H	-2.08252900	6.34005000	-3.53395300
H	-3.29919500	5.18604600	-4.30436600
C	1.38607000	3.21845600	4.19593500
H	0.31345300	3.11371800	4.06853100
C	1.88266300	3.76261300	5.29821000
H	1.23429400	4.13192000	6.08167200
H	2.95039100	3.86325400	5.46079600

Table S1. Mulliken Charge of C1 and C2 atoms on the galactal **1a** and coordinated galactal **1a** pyranose ring.

	Atom	Free Galactal 1a	Coordinated Galactal 1a
Mulliken Charge	C1	0.187466	0.229897
	C2	-0.167808	-0.147098

Acetonitrile Solvent Effect:

The stabilization energy (computed at B3LYP/def2tzvp level of theory) associated with acetonitrile coordinating to the anomeric center of the activated glucal oxocarbenium (with 3-acetate dissociated) is significantly smaller than that associated with the coordination of the catalyst to the metal center. In the reaction system, the predominant reactive intermediate is the

glycal coordinated to the iridium catalyst at the α -face of the pyranose ring, which is simultaneously coordinated to the acceptor.

	MeCN α -coordination	Ir-Acceptor complex α -coordination
ΔG (kcal/mol)	-4.3	-27.6

N.B. The stabilization energy is calculated from subtracting the sum of energy of dissociated.

Species from the complexed species:

$$\Delta G_{\text{nitrile}} = G_4 - (G_2 + G_3)$$

$$\Delta G_{\text{Ir-complex}} = G_7 - (G_1 + G_3 + G_6 - G_5)$$

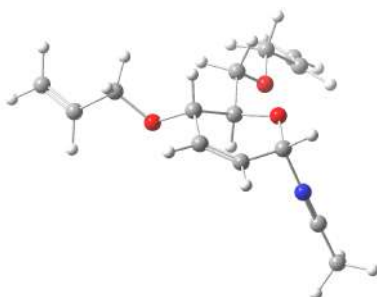
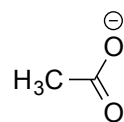


Figure S25. Structure of the acetonitrile coordinated allyl-protected glucal

Coordinates of the species involved:

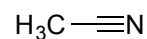
Acetate (G_1)



O	1.09726500	0.81210200	0.00000000
C	0.00000000	0.20474100	0.00000000
O	-1.15221400	0.70335300	0.00000000
C	0.05273400	-1.35326800	0.00000000
H	-0.48035000	-1.74579900	0.88347000

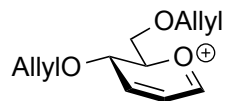
H	-0.48035000	-1.74579900	-0.88347000
H	1.08389100	-1.74087800	0.00000000

Acetonitrile (G₂)



N	1.43221100	0.00199500	-0.00125900
C	0.27117300	-0.00416900	0.00246400
C	-1.16658300	0.00120000	-0.00087300
H	-1.55044800	-0.37131000	0.96139500
H	-1.55040900	1.02093000	-0.15854900
H	-1.55215600	-0.64577200	-0.80357800

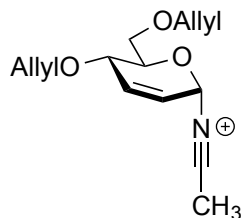
Free glycal oxocarbenium (G₃)



O	-0.68427200	-2.24901100	-1.15156200
O	-1.93124600	0.34485900	0.13724600
C	-1.95348200	1.74927300	0.45132600
H	-1.14487000	2.26638800	-0.09506700
H	-1.77161200	1.87932000	1.53499400
C	-1.41415700	-2.65429300	1.08568100
H	-1.83401100	-3.40254400	1.75845200
C	-1.17375100	-1.36815700	1.46237200
C	-0.73854400	-0.34111300	0.45856500
H	0.01873600	0.33464300	0.88921700
C	-0.09784500	-0.95684400	-0.78579900
H	-0.30544400	-0.31451500	-1.65127300
C	1.41475900	-1.18377200	-0.66126400
H	1.63411600	-1.90073100	0.15579200
H	1.78505400	-1.62860900	-1.60405800
O	1.97604900	0.07243500	-0.41371900

C	3.39750300	0.06538600	-0.28973000
H	3.70646500	-0.56582200	0.56511000
H	3.83665200	-0.37778200	-1.20658400
C	3.87706800	1.47394900	-0.11825100
H	3.55735600	2.17706800	-0.89685000
C	4.66303400	1.88605000	0.87962400
H	4.99411900	1.20314100	1.66936100
H	5.01457000	2.91981300	0.93918800
C	-3.29578800	2.29707500	0.08101200
H	-4.15388700	1.81124900	0.56051300
C	-3.48095100	3.32389200	-0.75256200
H	-4.48102400	3.71110300	-0.96604400
H	-2.63965900	3.82321400	-1.24488400
C	-1.22090200	-3.00627800	-0.27435300
H	-1.55708400	-3.96925400	-0.67724800
H	-1.40540400	-1.02396600	2.47393200

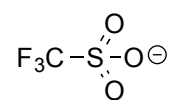
Acetonitrile-coordinated oxocarbenium (G₄)



O	-2.71180000	1.91870000	-0.37080000
O	-4.14753684	-0.81274392	-0.01406690
C	-5.33653684	-1.37594392	-0.56916690
H	-5.79613684	-0.64994392	-1.26856690
H	-6.06763684	-1.58444392	0.23753310
C	-2.20870000	0.87420000	1.82480000
H	-1.49680000	0.88880000	2.65990000
C	-3.44580000	0.38780000	1.94520000
C	-4.37253684	0.37965608	0.73573310

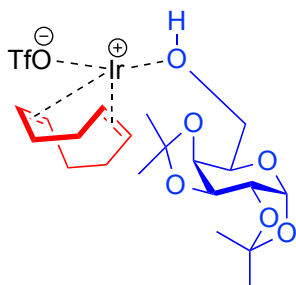
H	-5.42753684	0.44775608	1.10473310
C	-4.10010000	1.68680000	-0.09570000
H	-4.48310000	1.55000000	-1.13670000
C	-4.69420000	2.96690000	0.53870000
H	-4.49500000	3.01070000	1.62780000
H	-4.25360000	3.87570000	0.08130000
O	-6.08810000	2.90820000	0.29870000
C	-6.77020000	4.10270000	0.67430000
H	-6.76337532	4.20679983	1.77716994
H	-6.24958902	4.98333236	0.24757883
C	-8.15569522	4.00382247	0.12548271
H	-8.35072473	3.19684256	-0.59193814
C	-9.10609987	4.86574199	0.46755879
H	-8.95192380	5.67679755	1.17485415
H	-10.10965013	4.82122767	0.05418871
C	-4.94483684	-2.64024392	-1.26066690
H	-3.93153684	-3.02054392	-1.08426690
C	-5.79873684	-3.29794392	-2.03666690
H	-5.54223684	-4.23154392	-2.52906690
H	-6.81343684	-2.95764392	-2.22956690
C	-1.75540000	1.47440000	0.53480000
H	-1.02700000	2.31460000	0.65690000
N	-1.07143474	0.40022039	-0.26251076
C	-0.56356595	-0.41850308	-0.91044776
C	0.07895453	-1.42625041	-1.70969308
H	-0.53281844	-1.65611905	-2.59567834
H	1.06780825	-1.08065587	-2.04846495
H	0.21189874	-2.35161605	-1.12866019
H	-3.80930000	-0.05850000	2.87910000

Triflate anion (G₅)



O	-1.24307300	1.40873700	-0.15471500
S	-0.91782200	0.00004200	-0.00001000
O	-1.24260900	-0.57049500	1.29729700
O	-1.24289100	-0.83846600	-1.14255300
C	0.94697600	0.00005600	-0.00002700
F	1.43838700	0.50213300	-1.14787100
F	1.43818100	-1.24513600	0.13908800
F	1.43808600	0.74308900	1.00879300

Iridium-acceptor-triflate complex (G₆)

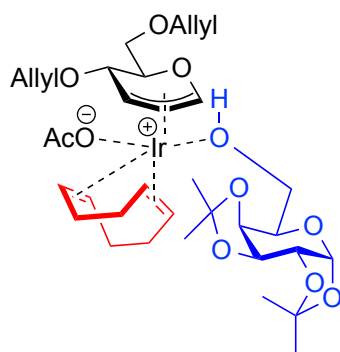


C	3.19149000	3.27966800	-1.26106600
C	3.20159300	3.25825800	0.27166300
C	0.18034700	3.23003800	-0.63463700
C	0.22352300	2.61500200	-2.03509200
H	4.18945400	3.50291400	-1.63815300
H	2.53696700	4.06701300	-1.63532500
H	4.17242900	2.90779300	0.62457400
H	3.06286300	4.26378700	0.68574300
H	-0.85195300	3.42340800	-0.34417800
H	0.69577100	4.19104300	-0.60222900
H	-0.68758100	2.04040800	-2.19763600
H	0.25598200	3.37944500	-2.82022000

C	-1.34315600	-1.20337200	-0.05472500
H	-1.18534400	-2.26778900	-0.23759900
H	-0.98796600	-0.96141700	0.94374500
C	-2.82040100	-0.86266900	-0.14534700
C	-3.09943300	0.60463400	0.17431300
H	-3.17717900	-1.07035200	-1.15941500
C	-4.89130100	-1.70827200	0.64920700
C	-4.56784100	0.84116900	0.59369000
H	-2.83055200	1.21699600	-0.68723700
C	-5.49738800	-0.32722700	0.33188200
H	-5.26511900	-2.13328400	1.57849400
H	-4.97417700	1.72494100	0.09420500
H	-6.41756900	-0.18463500	0.90488100
O	-0.58442400	-0.39959800	-0.95881700
H	-0.71201300	-0.72932200	-1.85695000
O	-3.49623500	-1.70837200	0.78225500
O	-2.34490800	1.01585500	1.30908200
O	-4.50052400	1.03852100	1.99801100
O	-5.76659500	-0.38393300	-1.06260700
O	-5.29676600	-2.51355500	-0.44319800
C	-3.21303000	1.56833700	2.29951100
C	-6.07126400	-1.74098500	-1.37465700
C	-7.55249900	-2.02670800	-1.16874100
H	-8.14769700	-1.43605500	-1.86508300
H	-7.75334800	-3.08364000	-1.34220700
H	-7.85551500	-1.78171900	-0.15086200
C	-5.60704700	-2.03300100	-2.78415300
H	-5.78876800	-3.07949200	-3.02586100
H	-6.15514300	-1.41205700	-3.49229500
H	-4.54217100	-1.82572200	-2.87845100
C	-3.21553400	3.08836000	2.19500400

H	-3.89932500	3.51629100	2.92819200
H	-2.21315600	3.47358500	2.38090000
H	-3.52624700	3.40386700	1.19869700
C	-2.78922000	1.06578600	3.66173600
H	-2.80061800	-0.02303200	3.66868900
H	-1.78260900	1.41571400	3.88903200
H	-3.46833000	1.43862300	4.42809200
C	1.37982800	1.65499400	-2.16065200
H	1.24642700	0.89563800	-2.92937200
C	2.73450900	1.93635500	-1.80738600
H	3.49985300	1.36776000	-2.32301700
C	2.15534900	2.31060500	0.80400700
H	2.36197900	1.94245900	1.80588100
C	0.79590800	2.26326800	0.36032700
H	0.08128300	1.82548900	1.05090400
Ir	1.87329000	0.64695600	-0.40802400
O	2.81937700	-1.19979300	0.23537400
S	4.29038400	-1.37571600	0.19027200
O	4.99908100	-0.59385900	1.18203500
O	4.82091300	-1.42163100	-1.15702700
C	4.38944600	-3.13385500	0.80658700
F	3.84215600	-3.24526700	2.02524200
F	3.74401600	-3.96883200	-0.01989000
F	5.67240900	-3.51525300	0.87996600

Glycal-Iridium complex (G₇)



Ir	-0.87777700	-0.49757700	0.09564400
C	-2.30117500	-2.10030400	-2.32241400
C	-2.01493200	-3.13083300	-1.22476100
C	0.73267400	-2.03259500	-2.18935700
C	0.39169700	-0.64350000	-2.75842300
H	-3.34940300	-2.16273900	-2.59548300
H	-1.73354600	-2.32009500	-3.22237700
H	-2.90525600	-3.26064500	-0.61585600
H	-1.79389900	-4.10774400	-1.66273300
H	1.80454400	-2.19327300	-2.26809500
H	0.26312900	-2.81283300	-2.78179700
H	1.23924300	0.01716200	-2.61741000
H	0.22984200	-0.69902900	-3.83789400
O	-2.80661800	1.83326000	-0.54221000
O	-4.54056300	-1.08455100	-0.32577500
C	-5.85637100	-1.56779100	-0.03872700
H	-6.56752300	-0.73316800	0.02114900
H	-5.85433600	-2.06099600	0.93359000
C	-1.80273600	1.59228700	0.31383500
H	-1.02283900	2.33476100	0.24200500
C	2.30419900	0.87086400	0.81764000
H	2.12032100	1.73890500	1.44684700
H	2.21807100	-0.02216100	1.42322300

C	3.69484600	0.98370100	0.21292800
C	4.11944600	-0.20930900	-0.64322900
H	3.73987300	1.87705200	-0.41407100
C	5.87083000	1.55692200	0.99579900
C	5.66007600	-0.29656600	-0.77972400
H	3.64714900	-0.13171800	-1.62176400
C	6.42185300	0.92989400	-0.30143200
H	6.46715000	1.32584600	1.87218300
H	5.94216900	-0.49650100	-1.81410200
H	7.46921700	0.65710400	-0.16753500
O	1.29407800	0.76777600	-0.20374900
H	1.21680200	1.61100900	-0.66492300
O	4.57057100	1.13496600	1.32878000
O	3.75143700	-1.44327900	-0.03216900
O	6.01765900	-1.38494800	0.06017300
O	6.28433500	1.96725100	-1.26599400
O	5.91010500	2.95036700	0.74397700
C	4.90880300	-2.27803000	0.12839200
C	6.42949900	3.20870200	-0.57478000
C	7.89439300	3.61745300	-0.47928000
H	8.29530600	3.80552400	-1.47224200
H	7.98635900	4.52463100	0.11264300
H	8.48633200	2.83863600	-0.00498500
C	5.57897600	4.25563400	-1.26187800
H	5.64044300	5.19590900	-0.72060900
H	5.93600100	4.41652200	-2.27584700
H	4.54107700	3.93685300	-1.29931200
C	4.96820800	-3.30473100	-0.99697000
H	5.86245800	-3.91544400	-0.89806500
H	4.09688000	-3.95351700	-0.95641200
H	4.98725600	-2.81434600	-1.96759700

C	4.88116700	-2.91095800	1.50382700
H	4.83232900	-2.13800200	2.26510900
H	4.01500300	-3.56075800	1.59758700
H	5.77752300	-3.50652100	1.65761900
C	-1.94651500	0.78369600	1.44178900
H	-1.33575100	0.91352800	2.31636700
C	-0.82833700	-0.00998300	-2.13535700
H	-0.89054000	1.06639300	-2.22468200
C	-2.02053200	-0.67327700	-1.89718000
H	-2.89365300	-0.05971000	-1.78986700
C	-0.88450900	-2.73956900	-0.31900900
H	-0.95046900	-3.13827100	0.68217600
C	0.33476500	-2.21193600	-0.73463800
H	1.14890600	-2.24251300	-0.02518100
O	-1.24397600	-2.50323300	2.86854500
C	-2.78910900	-0.35030500	1.19014400
H	-2.81704100	-1.14433700	1.91901800
C	-0.24516800	-1.79890300	2.83429500
O	0.04642200	-0.94299100	1.88671200
C	0.81398300	-1.84058800	3.91678000
H	1.73194600	-2.25749500	3.50688700
H	1.04031400	-0.83741100	4.26831200
H	0.47704600	-2.45676600	4.74241200
C	-4.11004700	-0.04130900	0.52875000
H	-4.80702000	0.03025300	1.36645600
C	-4.13112100	1.35627800	-0.15543300
H	-4.66639000	1.25474700	-1.09368200
C	-4.84125100	2.45915000	0.65488500
H	-5.05860800	2.14649700	1.68119600
H	-4.19370700	3.33655300	0.70962500
O	-6.04654100	2.75669800	-0.02233400

C	-6.78567900	3.80185600	0.60090300
H	-7.11853800	3.50011000	1.60440000
H	-6.14190800	4.67826000	0.73087300
C	-7.92704800	4.23340900	-0.24142700
H	-7.81602000	4.05658200	-1.31303300
C	-9.02998000	4.77104400	0.27616000
H	-9.21955000	4.75456000	1.34849900
H	-9.78098100	5.25716300	-0.34151500
C	-6.24891100	-2.57437800	-1.07408900
H	-5.50188000	-2.74771100	-1.84890500
C	-7.44110200	-3.16469700	-1.12049500
H	-7.64121200	-3.99755300	-1.78953200
H	-8.26438200	-2.84835900	-0.48006300

m-Nitrobenzyl vs benzyl ether reactivity:

Compared with 3-*O*-acetyl-4,6-di-benzyl-D-glucal (**1p**), coordination of the 3-*O*-acetyl-4,6-di-*O*-*m*-nitrobenzyl-D-glucal (**1s**) to the iridium catalyst is less favourable. The difference is pronounced in the NBO charge of the iridium metal center in the glycal coordinated complex **1p_i** (coordination with **1p**) and complex **1s_i** (coordination with **1s**): The metal centre is more positively charged in **1s_i**, indicating less electron transfer from the π -allyl system of **1s** to the metal center, which translate into less favourable formation of the activated reacting intermediates.

	<i>O</i> -Benzyl complex 1p_i	<i>O</i> - <i>m</i> -Nitrobenzyl complex 1s_i
NBO charge of Ir (a.u.)	0.431	0.469

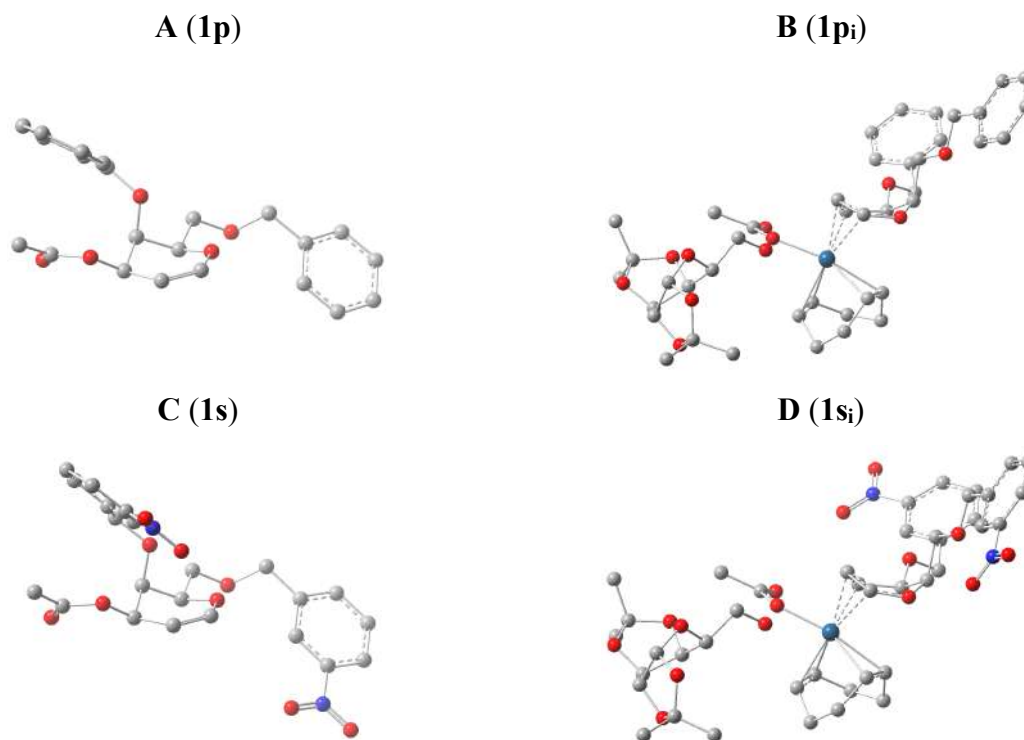
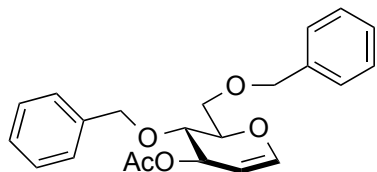


Figure S26. Optimized structures of (A) 3-*O*-acetyl-4,6-di-benzyl-D-glucal (**1p**), (B) **1p**-Ir (I)-coordinated complex (**1p_i**), (C) 3-*O*-acetyl-4,6-di-*O*-*m*-nitrobenzyl-D-glucal (**1s**) and **1s**-Ir (I)-coordinated complex (**1s_i**).

Coordinates of the species involved:

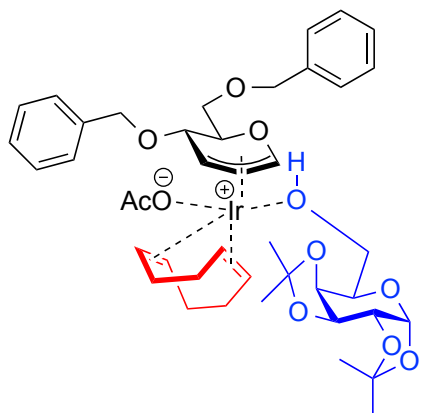
3-*O*-Acetyl-4,6-di-*O*-benzyl-D-glucal (**1p**):



O	-1.38845900	0.47558700	0.64822700
O	1.06675100	-0.70165200	-0.19439100
C	2.12593500	-1.39052400	-0.83056800
H	2.31496200	-0.97329900	-1.83425800
H	1.79887200	-2.43683400	-0.97676700
C	3.40873800	-1.38392400	-0.02790000
C	3.40210200	-1.10612300	1.34420100
C	4.62352400	-1.69018800	-0.65672800
C	4.59267000	-1.13250000	2.07534000
H	2.45848900	-0.84427700	1.82372800
C	5.81433700	-1.72184800	0.07382200
H	4.63971400	-1.89696900	-1.73074800
C	5.80243900	-1.44169000	1.44404200
H	6.75537300	-1.95516700	-0.43019200
H	6.73300700	-1.45821600	2.01634000
C	-0.72549600	1.28612000	1.50542500
H	-1.23609400	1.36285800	2.46813600
C	0.41673200	1.92838800	1.22461400
H	0.87026000	2.57866200	1.97384600
O	2.52632300	1.69775400	0.18811300
C	3.38448200	1.80308100	-0.84179400
O	3.02683800	1.84417500	-1.99855400
C	4.80632200	1.88326000	-0.36074900

H	5.00605300	1.09467600	0.37664600
H	5.49027700	1.79427400	-1.21237500
H	4.96131100	2.85375500	0.13699300
C	0.59172000	0.48389100	-0.79750100
H	0.88543500	0.52012700	-1.85714600
C	-0.93474600	0.48636800	-0.71300300
H	-1.31243700	1.41324000	-1.18160700
C	-1.55847300	-0.70857000	-1.41846400
H	-1.22669100	-0.69370300	-2.46988000
H	-1.17963600	-1.63624100	-0.95834700
O	-2.96522600	-0.64709000	-1.40091100
C	-3.60491200	-1.41018100	-0.38545000
H	-3.77583200	-2.44587700	-0.73568600
H	-2.96077700	-1.45980300	0.50810900
C	-4.91591500	-0.76221900	-0.01935200
C	-4.92889400	0.56274100	0.44653300
C	-6.12727400	-1.45529900	-0.12669500
C	-6.13052900	1.17738800	0.80021500
H	-3.98290800	1.10211100	0.52973100
C	-7.33369000	-0.84328900	0.23316600
H	-6.12757800	-2.48421400	-0.49693200
C	-7.33788900	0.47470200	0.69576500
H	-8.27191300	-1.39664900	0.14492000
H	-8.27872100	0.95608800	0.97377400
C	1.11444700	1.75144500	-0.08964000
H	0.94696300	2.60631900	-0.76686000
H	4.57704800	-0.90575200	3.14434500
H	-6.12878000	2.20853900	1.16269100

4,6-Di-*O*-benzylglucal-Ir-2a complex (**1p_i**):



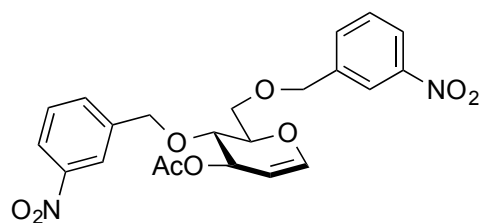
Ir	0.33891900	-0.58723600	0.91160400
C	1.38830900	-1.50103700	3.82486600
C	0.99009100	-2.78457200	3.07382700
C	-1.60534600	-0.97610600	3.38479200
C	-1.09264900	0.47640500	3.36515700
H	2.40583600	-1.62383100	4.22293600
H	0.74080400	-1.34151600	4.69832300
H	1.87093600	-3.22674000	2.58531100
H	0.62723800	-3.55059200	3.78330700
H	-2.70366700	-0.96157900	3.42882900
H	-1.26916400	-1.50254200	4.28802100
H	-1.77088400	1.10048900	2.76260200
H	-1.10658400	0.91597800	4.38028700
O	2.66739600	1.45015400	0.93746100
O	4.52170400	-1.54133400	-0.13852100
C	5.56438600	-2.13585900	0.63462400
H	5.11562600	-2.78447500	1.40960700
H	6.16236100	-1.36378200	1.14815200
C	6.44624400	-2.94994700	-0.27838000
C	5.89384000	-3.99372200	-1.02435800
C	7.81864500	-2.67898600	-0.39921200
C	6.72509800	-4.73053500	-1.86010600

H	4.83365400	-4.23868500	-0.96904500
C	8.63439000	-3.44388200	-1.24420400
H	8.25793100	-1.86023100	0.17567900
C	8.09090600	-4.48255300	-1.98916700
H	9.69968500	-3.22129800	-1.32360100
H	8.69320800	-5.09468500	-2.65851600
C	1.59866600	1.18417700	0.17280100
H	0.93216800	2.04466200	0.05683100
C	-3.40369200	1.26118400	-1.55218200
H	-3.33240500	2.33676800	-1.77976600
H	-3.33147900	0.70983600	-2.50293600
C	-4.77266900	0.99550400	-0.93388000
C	-5.01804300	-0.47665200	-0.58443400
H	-4.84984800	1.57672700	0.00191600
C	-7.04242600	1.56791400	-1.36608800
C	-6.53325600	-0.78899300	-0.44602200
H	-4.47281900	-0.72510200	0.34089700
C	-7.43947700	0.43558300	-0.38402500
H	-7.69219800	1.61474900	-2.25183300
H	-6.72500000	-1.40632200	0.45026700
H	-8.47493400	0.10735600	-0.58398300
O	-5.74285900	1.44806500	-1.87076400
O	-4.58505700	-1.32969100	-1.63869400
O	-6.84201700	-1.49298800	-1.63407900
O	-7.32494000	1.04048300	0.89187100
O	-7.19341800	2.74192500	-0.59418800
C	-5.66793900	-2.14485700	-2.09946200
C	-7.62599000	2.42387700	0.73614000
C	-9.12952400	2.67563600	0.86258500
H	-9.47532700	2.42297000	1.87588000
H	-9.35167100	3.73487000	0.66710200

H	-9.69318500	2.06906400	0.13825300
C	-6.81359400	3.22250800	1.74192400
H	-6.99513700	4.29800400	1.60470200
H	-7.10262900	2.94681900	2.76671800
H	-5.74109400	3.02338300	1.60801500
C	-5.55462700	-3.54840100	-1.50087400
H	-6.40512300	-4.16898600	-1.82046400
H	-4.62307800	-4.03155700	-1.83147400
H	-5.54910100	-3.50365000	-0.40112700
C	-5.68391100	-2.14171500	-3.61857200
H	-5.75884900	-1.10562300	-3.97669500
H	-4.76282300	-2.59602400	-4.01137500
H	-6.54461600	-2.71619300	-3.99083300
C	1.56833600	0.09091900	-0.71042500
H	0.95743500	0.08097300	-1.61206100
C	0.30380200	0.63419700	2.80560900
H	0.56348600	1.66080900	2.53061900
C	1.37021000	-0.25420200	2.95243300
H	2.34560900	0.18266700	2.74828400
C	-0.06204500	-2.56343900	2.02195400
H	-0.03972400	-3.26690900	1.18318200
C	-1.19060900	-1.74809400	2.14169100
H	-1.96921800	-1.89144100	1.38706500
O	0.28318900	-3.33531100	-1.03235600
C	2.21879200	-1.05574400	-0.14640600
H	2.11816000	-2.02560700	-0.64106000
C	-0.55015200	-2.49924300	-1.33700900
O	-0.70394200	-1.34839600	-0.70929700
C	-1.50692700	-2.65646500	-2.50175300
H	-2.51066300	-2.28053900	-2.24979300
H	-1.13143700	-2.05885400	-3.34857700

H	-1.54963600	-3.70974400	-2.80562900
C	3.53334000	-0.85669700	0.60405600
H	3.46753500	-1.29848400	1.60998100
C	3.86770500	0.66122800	0.70984200
H	4.47783200	0.86741500	1.60064000
C	4.61038100	1.20007100	-0.51117700
H	5.55901300	0.64407900	-0.61352300
H	4.03630200	1.02558800	-1.44245800
O	4.83430300	2.57146700	-0.31003300
C	5.51927300	3.20141400	-1.36654800
H	6.55536600	2.81860600	-1.45116000
H	5.02153700	2.97594600	-2.33255800
C	5.53442900	4.69764900	-1.15668000
C	4.60497300	5.30032200	-0.31249400
C	6.46430600	5.50489400	-1.83484000
C	4.62621000	6.68579800	-0.17395300
H	3.87959700	4.70393300	0.23621900
C	6.45872200	6.89564300	-1.68039000
H	7.20457900	5.04056500	-2.49204900
C	5.53223000	7.50603800	-0.84088700
H	7.18777900	7.50707200	-2.21490700
H	5.50284200	8.58437500	-0.69392300
O	-2.36344100	0.90635900	-0.66330300
H	-2.01482200	0.02570300	-0.91079700
H	3.90932800	7.14004600	0.47769000
H	6.29471500	-5.52870200	-2.42808500

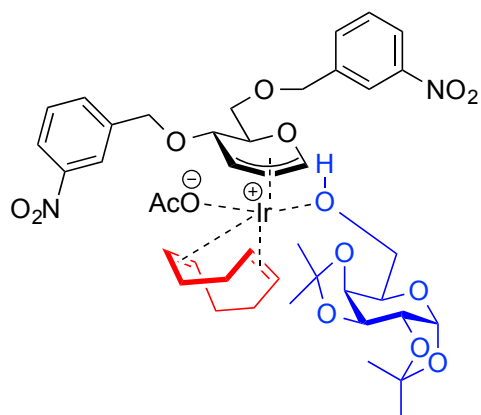
3-*O*-Acetyl-4,6-*O*-*m*-nitro-benzyl-glycal (**1s**):



O	1.20812300	-0.01447800	-0.03094900
O	-1.26606700	-1.20818900	-0.66384700
C	-2.50007800	-1.82539400	-0.95385600
H	-2.76054700	-2.57313400	-0.18431500
H	-2.39234000	-2.37944400	-1.90405100
C	-3.63018800	-0.82757600	-1.09385300
C	-3.39363000	0.54045600	-0.95653400
C	-4.93388500	-1.27406800	-1.35564600
C	-4.46558300	1.42457900	-1.06183500
H	-2.39344000	0.90870500	-0.74427000
C	-5.99500700	-0.36985500	-1.46435800
H	-5.12565300	-2.34478100	-1.46545200
C	-5.77040900	0.99876800	-1.31351700
H	-7.00471700	-0.73466700	-1.66193700
H	-6.57614100	1.72732800	-1.38461500
C	0.55863200	1.00353500	0.58336000
H	0.99394300	1.97254700	0.33043400
C	-0.48848700	0.85625900	1.40593400
H	-0.94530000	1.73329400	1.86539300
O	-2.50119400	-0.34065500	1.76812500
C	-3.21310300	-1.30795100	2.37779100
O	-2.71636900	-2.32881500	2.79681700
C	-4.67152300	-0.94712300	2.43697100
H	-5.07176900	-0.88045400	1.41402000
H	-5.22077300	-1.70789100	3.00318900
H	-4.79572100	0.04225000	2.90066400

C	-0.65131800	-1.48325900	0.57982400
H	-0.87698700	-2.51145600	0.90475100
C	0.85716800	-1.34398000	0.38008600
H	1.36053800	-1.54090200	1.34331800
C	1.40374200	-2.30448200	-0.66564200
H	1.15914600	-3.33145800	-0.34930300
H	0.89966900	-2.11582500	-1.62719600
O	2.80546700	-2.20404200	-0.77662400
C	3.29972000	-1.39458600	-1.83120100
H	3.53551800	-2.01612100	-2.71471800
H	2.53943700	-0.65554600	-2.13425700
C	4.53726000	-0.66237900	-1.37221800
C	4.48210100	0.11068000	-0.20607600
C	5.73898000	-0.72558800	-2.08842600
C	5.61955800	0.79808900	0.20547700
H	3.56048500	0.18159300	0.36739600
C	6.87275700	-0.02299400	-1.66003200
H	5.79200600	-1.33520800	-2.99380700
C	6.82450800	0.74833600	-0.50133400
H	7.80100900	-0.08504000	-2.23122700
H	7.68927100	1.30188700	-0.13931700
C	-1.07190900	-0.49495700	1.68603600
H	-0.73123800	-0.90586200	2.65051200
N	-4.20844900	2.86392800	-0.88644600
O	-3.06345100	3.21730700	-0.64520700
O	-5.15474900	3.63135900	-0.98853200
N	5.54494200	1.61363100	1.42944600
O	4.47741600	1.66178400	2.02326700
O	6.55486500	2.20175500	1.78795900

4,6-Di-*O*-*m*-nitrobenzylglucal-Ir-2a complex (**1s_i**):



Ir	-0.67839800	0.32676600	0.51513400
C	0.87997900	2.10914000	-1.66616200
C	0.36852900	3.07400700	-0.59201000
C	-2.13131800	1.75186700	-1.90741700
C	-1.59366600	0.41688700	-2.45027400
H	1.94664200	2.27378200	-1.80269100
H	0.40506400	2.30519700	-2.62636200
H	1.16284100	3.25964200	0.12878200
H	0.11367800	4.04227100	-1.03563600
H	-3.19982800	1.80909600	-2.10804300
H	-1.67285300	2.59069600	-2.42867500
H	-2.38491700	-0.32486600	-2.42031900
H	-1.30809600	0.51533500	-3.50268500
O	1.57113000	-1.80475000	0.11431000
O	2.76070600	1.30930400	0.43716500
C	3.95374800	2.01654100	0.76990700
H	4.79361900	1.32136000	0.86725700
H	3.83190700	2.54498700	1.71989600
C	0.44324100	-1.71377700	0.83917300
H	-0.24511200	-2.52973500	0.66308200
C	-3.76700000	-1.32648100	0.82994800
H	-3.60721100	-2.19015500	1.47621600

H	-3.83688700	-0.43578400	1.44017600
C	-5.04008900	-1.49746700	0.02702200
C	-5.34115500	-0.29304200	-0.85575200
H	-4.96330600	-2.37937000	-0.61762300
C	-7.29662700	-2.10792100	0.44878000
C	-6.83949200	-0.20596100	-1.22207000
H	-4.72010400	-0.33961500	-1.75167000
C	-7.64761400	-1.44841500	-0.89912000
H	-8.03039100	-1.91069100	1.22674400
H	-6.96220900	0.02127900	-2.28398900
H	-8.70969900	-1.19240600	-0.92256200
O	-2.64998700	-1.12297300	-0.04977100
H	-2.44015800	-1.95055300	-0.50244300
O	-6.07272500	-1.68473100	0.99108800
O	-5.07556200	0.91673400	-0.15755100
O	-7.32790100	0.85358300	-0.41382300
O	-7.33734500	-2.44887200	-1.85941700
O	-7.26622400	-3.49056700	0.15450700
C	-6.24567500	1.74246300	-0.15446400
C	-7.56287300	-3.71100200	-1.23553300
C	-9.01446200	-4.14280800	-1.38622100
H	-9.24854700	-4.30415200	-2.43817700
H	-9.18116200	-5.07177100	-0.84195600
H	-9.68834800	-3.38480700	-0.98781300
C	-6.58905600	-4.71709500	-1.80559300
H	-6.71445600	-5.67733800	-1.30709500
H	-6.77496300	-4.85109300	-2.87062100
H	-5.56584900	-4.37286900	-1.66305300
C	-6.13432600	2.79325400	-1.25056700
H	-7.03590200	3.40489800	-1.27500800
H	-5.27676600	3.43823600	-1.06105300

H	-6.00387500	2.32144200	-2.22472800
C	-6.42538900	2.33487000	1.22517100
H	-6.48817000	1.53529200	1.96130900
H	-5.58093100	2.98016700	1.46530800
H	-7.33789100	2.92917300	1.26010700
C	0.32939600	-0.89478000	1.97096200
H	-0.37212100	-1.10637600	2.76057900
C	-0.40431900	-0.11447900	-1.69445200
H	-0.23469100	-1.18133700	-1.78196300
C	0.68134400	0.65298000	-1.30596500
H	1.58956500	0.12289300	-1.10069400
C	-0.82511400	2.55678800	0.15383700
H	-0.92326800	2.92788900	1.16533900
C	-1.92839700	1.92626800	-0.41499300
H	-2.82453900	1.85674100	0.18897900
O	-0.82918300	2.29341200	3.31329400
C	1.02898900	0.34396300	1.81322100
H	0.85471200	1.13932400	2.52354900
C	-1.75145300	1.50701200	3.14989900
O	-1.85099600	0.64487100	2.17074100
C	-2.94229100	1.44279600	4.08089400
H	-3.83182200	1.78641600	3.55026300
H	-3.12460600	0.41545900	4.39427800
H	-2.77060400	2.07494500	4.94777400
C	2.43939500	0.23536200	1.29743300
H	3.05428900	0.29060700	2.20197000
C	2.74894500	-1.14242900	0.65647200
H	3.38338300	-0.96892100	-0.20845600
C	3.49498000	-2.11687000	1.57618500
H	3.50881600	-1.76411800	2.61369000
H	2.99709900	-3.09171200	1.55920500

O	4.81593600	-2.21462300	1.08117900
C	5.61255400	-3.11603000	1.83444700
H	5.75544500	-2.74357900	2.85412900
H	5.11523500	-4.09190900	1.89902000
C	4.20830400	3.00181900	-0.33746300
C	4.24633100	4.36076100	-0.06307700
C	4.39758100	2.55560800	-1.64311300
C	4.47000600	5.24672300	-1.10389500
H	4.09905400	4.72432700	0.94676100
C	4.62102500	3.46151000	-2.67236700
H	4.36720300	1.49412700	-1.85478000
C	4.65629400	4.82257700	-2.40777700
H	4.76864700	3.11125100	-3.68527000
H	4.82755800	5.53937800	-3.20126900
C	6.94340100	-3.27624900	1.14900200
C	8.06671400	-2.58738800	1.59892200
C	7.05020800	-4.11950100	0.05191900
C	9.29226300	-2.73793300	0.95858900
H	7.98329000	-1.93090000	2.45602400
C	8.27673500	-4.24976800	-0.57535500
H	6.18666700	-4.66517400	-0.30967700
C	9.40419000	-3.57188100	-0.14284900
H	10.16372000	-2.20370700	1.31308100
H	10.35149500	-3.69521200	-0.65302600
N	4.50636400	6.68739900	-0.81342300
O	3.53165200	7.33615300	-1.14108800
O	5.50639900	7.11054700	-0.26689100
N	8.38551400	-5.14075700	-1.73924300
O	8.52872700	-4.60972200	-2.82366500
O	8.31910100	-6.33549300	-1.52315500

Reason behind unsuccessful reaction with the phosphine ligand:

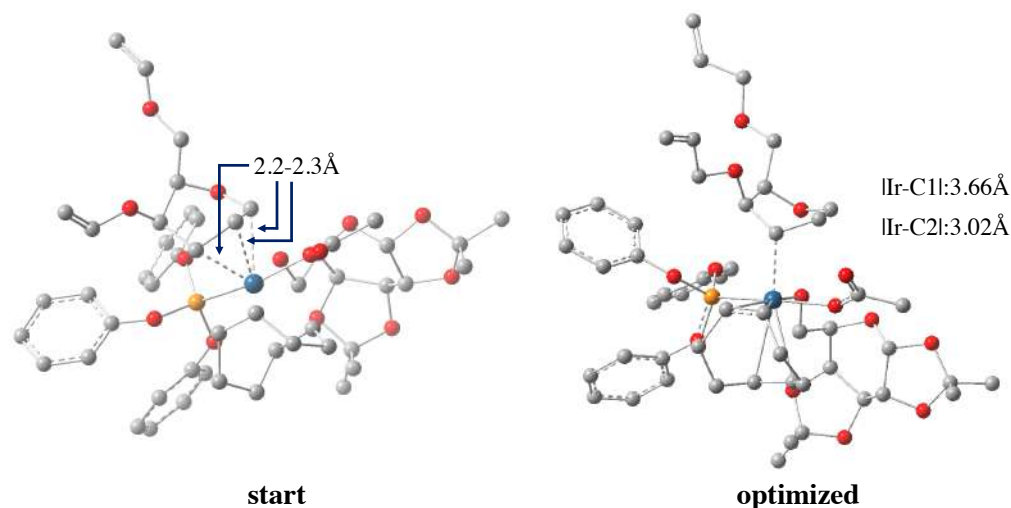


Figure S27. Schematic representation of the starting and optimized structures of glycal(**1n**)-Ir(I)-P(OPh)₃-**2a** complex.

The starting structure of glycal-Iridium π -allyl complex with P(OPh)₃ ligand, cyclohexadiene, acetate and the acceptor coordinated to the iridium metal center, which is proposed to be the reactive intermediate in the catalytic cycle of the Ir-catalyzed glycosylation with the presence of P(OPh)₃ ligand, was subjected to geometry optimization at b3lyp/gen (combination of ma-def2svp basis set for main group elements and LANL2DZ basis set for the iridium atom) level of theory. Optimized geometry indicates that with the presence of the metal coordinated phosphine ligand, the glycal does not coordinate to the metal center as a π -allyl system, with C1 and C2 dissociated from the Ir center. The result indicates that the presence of the bulky phosphine ligand suppresses coordination of the iridium to the olefinic system, making activation of the C1 anomeric carbon unfavorable, hence inhibits the glycosylation reaction.

Coordinate of the optimized glycal (**1n**)-Ir(I)-P(OPh)₃-**2a** complex:

C	-2.26964800	-1.93189100	1.92791500
C	-0.65910000	-3.46089600	0.28443400

H	-2.52191100	-0.97345500	2.38938500
O	-0.86648100	-2.13983700	2.20717300
C	-3.09949700	-2.98619400	2.66885300
H	-3.51672600	-3.73412200	1.97864500
H	-2.44577300	-3.50345200	3.39511700
O	-4.14694300	-2.29439700	3.31868100
O	-3.68770100	-2.62479000	0.10298400
H	-0.31861400	-4.35148200	-0.23735000
Ir	0.13885600	-0.95826200	-1.19791800
C	-1.00503300	-0.57443200	-3.13859300
H	-2.02795600	-0.78389600	-2.81550100
C	-0.76590100	0.79237900	-3.74626900
H	-1.52620400	1.46564400	-3.33345100
H	-0.99864700	0.70592300	-4.82201000
C	-0.18836600	-1.66688500	-3.47025200
H	-0.57105600	-2.68116300	-3.36965500
C	1.01258000	-1.53606900	-4.40414700
H	0.69327700	-0.87722000	-5.22815400
H	1.16542400	-2.53528600	-4.82632900
C	2.38270500	-1.04044300	-3.87507100
H	2.87777000	-0.47399700	-4.68413400
H	3.03552900	-1.89460100	-3.67094400
C	2.35362100	-0.15530900	-2.66286600
H	3.10612800	-0.36077100	-1.89906700
C	1.57974100	0.94948700	-2.53292000
H	1.77519400	1.61065500	-1.68719700
C	0.64741100	1.43469700	-3.61813500
H	0.50152000	2.51482300	-3.48234900
H	1.17946900	1.31211800	-4.57461700
C	-2.53539100	-1.85220500	0.39761100
H	-2.77249200	-0.81613600	0.15318400

C	-0.38804800	-3.28602600	1.58199600
H	0.27156300	-3.89769000	2.19735000
C	-1.35133800	-2.37256900	-0.45652900
H	-1.78152600	-2.71798200	-1.40426200
P	-1.10151200	0.90371100	-0.61367200
O	-1.39002900	0.99207900	0.98518400
O	-2.55813500	0.97798500	-1.29602800
O	-0.33710700	2.28823000	-0.86003500
C	-3.80448300	1.55466000	-1.02312200
C	-4.38909500	1.50153500	0.24202900
C	-4.47215500	2.10984600	-2.11476300
C	-5.66022400	2.05885100	0.41600100
H	-3.88070300	1.02890200	1.07740200
C	-5.74124900	2.66001000	-1.92445300
H	-4.00150300	2.09963600	-3.09894600
C	-6.33489100	2.64299200	-0.65817700
H	-6.12258800	2.02480100	1.40443000
H	-6.26766100	3.09985200	-2.77386400
H	-7.32680400	3.07464100	-0.51234300
C	-0.63620600	3.64652700	-0.94090400
C	-1.65288000	4.11915000	-1.76561500
C	0.16381400	4.50449200	-0.18768500
C	-1.88853100	5.49745100	-1.81321800
H	-2.25254300	3.43287900	-2.35820600
C	-0.07882800	5.87774600	-0.25224900
H	0.94647400	4.09400900	0.44933400
C	-1.10772700	6.37693600	-1.05877200
H	-2.68880400	5.87896400	-2.45050800
H	0.53649300	6.55876600	0.33937400
H	-1.29851700	7.45095500	-1.09996800
C	-1.22572800	2.05279300	1.88180700

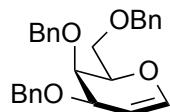
C	-1.69576200	3.33079000	1.58548600
C	-0.63589300	1.76502900	3.11365900
C	-1.51746300	4.34963400	2.52633000
H	-2.20047900	3.53825800	0.64328500
C	-0.46974200	2.79009600	4.04691000
H	-0.34090300	0.74604700	3.35067700
C	-0.89849600	4.08744700	3.75093800
H	-1.87193600	5.35514000	2.29156100
H	-0.00676200	2.56715100	5.01031000
H	-0.76238500	4.88909200	4.47923500
C	1.95804600	0.38567600	0.94863900
H	2.60323300	0.42019600	0.06729600
H	1.40146500	1.33069500	0.98245700
C	2.78371500	0.22366300	2.22846700
C	3.82642800	1.35460000	2.40384700
H	2.08315200	0.25252200	3.07062700
C	4.32945200	-1.33617600	1.27670900
C	5.23681500	0.99855800	1.88684100
H	3.90374000	1.57371200	3.47960900
C	5.30886300	-0.17361100	0.91014300
H	3.73548200	-1.66032900	0.40268800
H	5.89954500	0.73366700	2.72165900
H	5.12806100	0.17165800	-0.12159600
O	1.05508200	-0.71039200	0.72644400
H	0.41462900	-0.87928100	1.46476900
O	3.46518200	-1.02234900	2.35061500
O	3.48282100	2.55106500	1.71628300
O	5.69758500	2.22312700	1.35028900
O	6.59952900	-0.74440800	1.02077000
O	5.19016500	-2.35832600	1.69828900
C	6.46034200	-2.15355100	1.07486000

C	4.58227000	2.95597400	0.88354300
O	0.80259900	-4.18486300	-2.36595700
C	1.67644400	-3.63184100	-1.70820800
O	1.60407800	-2.43863500	-1.18834600
C	2.97300600	-4.34617700	-1.39549400
H	2.74561300	-5.37259600	-1.07270300
H	3.57285600	-4.41636500	-2.31661900
H	3.54607700	-3.83182400	-0.62302500
C	-4.52592900	-2.10185100	-0.91717600
H	-4.93283500	-1.13296300	-0.59654700
H	-3.94912900	-1.92706300	-1.83495800
C	-5.64789500	-3.08328000	-1.18739300
H	-5.77750300	-3.87163700	-0.44809000
C	-6.46449900	-3.01050400	-2.24922800
H	-6.34945800	-2.23162000	-3.00022900
H	-7.26827200	-3.72739200	-2.38754300
C	-5.09921500	-3.11725800	3.97060200
H	-4.70677500	-3.45406500	4.94035200
H	-5.29126900	-4.01592100	3.36808900
C	-6.38222200	-2.33392800	4.16602300
H	-6.46084900	-1.41256000	3.59105400
C	-7.38785400	-2.72061500	4.96356300
H	-7.36807600	-3.67966900	5.47702000
H	-8.25440900	-2.08510600	5.11984700
C	7.54421900	-2.73922900	1.96593600
H	7.44716500	-3.82503400	2.00988900
H	8.52784600	-2.48929700	1.56669900
H	7.44733300	-2.32789900	2.97062300
C	6.50315600	-2.74491300	-0.33539400
H	7.53647200	-2.81707200	-0.67888900
H	6.06589500	-3.74008000	-0.33435900

H	5.95152800	-2.11509800	-1.03519900
C	4.84879400	4.44076400	1.10580800
H	5.70399700	4.76140500	0.50878600
H	3.97656900	5.02686200	0.81331100
H	5.06237100	4.61630100	2.16021700
C	4.29072400	2.66238100	-0.59000700
H	3.54946500	3.36189100	-0.97553600
H	5.20754300	2.76961100	-1.17090300
H	3.91060600	1.65210800	-0.72911100

Reaction intermediates and transition states:

3,4,6-Tri-*O*-benzyl-D-galactal (**1a**):



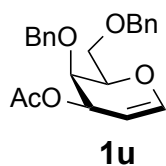
1a

C	1.64145900	-0.86997800	-0.92244900
H	2.15218000	-1.75319700	-1.34801500
O	2.01363700	-0.78471600	0.46142700
C	2.15926300	0.37967300	-1.61834300
H	1.88929400	0.31231300	-2.68523800
H	1.65159200	1.26381100	-1.19805600
O	3.56113800	0.48418800	-1.52836200
O	-0.51707600	0.07799100	-0.54230800
C	-1.58983400	0.58438800	-1.31085500
H	-2.23698600	-0.23763800	-1.65851600
H	-1.19633000	1.09648400	-2.21298300
C	-2.41429200	1.54580200	-0.49401900
C	-3.64970300	1.98290900	-0.99180100
C	-1.98188800	2.00544000	0.75531000
C	-4.44102400	2.86200200	-0.25324200

H	-4.00524200	1.61083900	-1.95630100
C	-2.77689100	2.88484100	1.49814100
H	-1.02410800	1.65868500	1.14434400
C	-4.00763900	3.31603500	0.99751400
H	-5.40827400	3.18282000	-0.64732100
H	-2.43163900	3.23220000	2.47535800
H	-4.63072100	3.99883200	1.58029300
C	4.05490400	1.31997000	-0.48947200
H	4.13622800	2.36479300	-0.84490900
H	3.35708700	1.30947400	0.36420000
C	0.13514700	-1.05547800	-1.08176000
H	-0.09108900	-1.14896700	-2.15730500
C	1.44405000	-1.69759000	1.28445700
H	1.94828000	-1.73975700	2.25317300
C	5.40293800	0.81852600	-0.03707500
C	5.53285900	-0.50102300	0.42620100
C	6.53345200	1.64360000	-0.05980300
C	6.76910000	-0.98090400	0.86013700
H	4.64991200	-1.14330200	0.44326300
C	7.77370800	1.16679300	0.38063300
H	6.44382500	2.66950700	-0.42755300
C	7.89443200	-0.14686600	0.83983000
H	6.85837800	-2.00930800	1.21943700
H	8.64782800	1.82226200	0.35754200
H	8.86236700	-0.52291800	1.18024000
C	0.39784700	-2.47096100	0.96280200
H	0.04090200	-3.20462000	1.68722100
O	-1.72860200	-2.42734700	-0.26729400
C	-0.31108300	-2.34919000	-0.35968500
H	-0.03792900	-3.19891800	-1.00944800
C	-2.35806900	-1.83583200	0.85734500

H	-1.77538100	-0.98360100	1.23529400
H	-2.42462700	-2.57380400	1.68121600
C	-3.74886100	-1.36526400	0.50553900
C	-4.38151900	-1.74936100	-0.68238400
C	-4.42984100	-0.52215800	1.39579300
C	-5.67109100	-1.29309500	-0.97779100
H	-3.84892200	-2.39944800	-1.37737400
C	-5.71692000	-0.07101600	1.10529900
H	-3.93538800	-0.19692100	2.31474200
C	-6.34343800	-0.45450400	-0.08561800
H	-6.15153900	-1.59574500	-1.91192900
H	-6.22669700	0.59851800	1.80185400
H	-7.34818300	-0.09387000	-0.31915100

3-*O*-Acetyl-4,6-di-*O*-benzyl-D-galactal (**1u**):

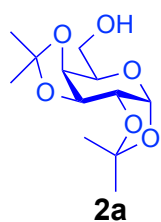


O	1.38817900	-0.47565500	0.64846400
O	-1.06671400	0.70174800	-0.19473700
C	-2.12608100	1.39035500	-0.83089700
H	-2.31523500	0.97285400	-1.83444800
H	-1.79910200	2.43664400	-0.97741700
C	-3.40877100	1.38394100	-0.02804100
C	-3.40200800	1.10615700	1.34406500
C	-4.62358500	1.69036900	-0.65673100
C	-4.59248600	1.13266400	2.07533600
H	-2.45835600	0.84420800	1.82345400
C	-5.81431200	1.72217600	0.07396200
H	-4.63988200	1.89715600	-1.73074600
C	-5.80229300	1.44199200	1.44417200

H	-4.57677600	0.90591900	3.14433600
H	-6.75537600	1.95561500	-0.42994200
H	-6.73279500	1.45862600	2.01657200
C	0.72501300	-1.28590800	1.50576000
H	1.23545300	-1.36246700	2.46856800
C	-0.41723900	-1.92812500	1.22493100
H	-0.87096800	-2.57817700	1.97423100
O	-2.52664900	-1.69768100	0.18807600
C	-3.38468100	-1.80307300	-0.84190700
O	-3.02691600	-1.84424500	-1.99863200
C	-4.80657100	-1.88322800	-0.36100200
H	-5.00646700	-1.09437900	0.37606600
H	-5.49043100	-1.79463000	-1.21274400
H	-4.96151800	-2.85354400	0.13710000
C	-0.59183000	-0.48403300	-0.79750700
H	-0.88540300	-0.52044600	-1.85718800
C	0.93462400	-0.48667700	-0.71281800
H	1.31227400	-1.41368500	-1.18118500
C	1.55860700	0.70802500	-1.41844600
H	1.22697700	0.69300100	-2.46990700
H	1.17987700	1.63585400	-0.95857100
O	2.96535900	0.64626600	-1.40062500
C	3.60497400	1.40976500	-0.38543400
H	3.77560700	2.44542500	-0.73592400
H	2.96093700	1.45943700	0.50819700
C	4.91615000	0.76214900	-0.01935300
C	4.92932300	-0.56252500	0.44734300
C	6.12744800	1.45519500	-0.12754500
C	6.13109100	-1.17693500	0.80097600
H	3.98337500	-1.10186600	0.53119400
C	7.33400700	0.84342200	0.23225300

H	6.12759700	2.48388700	-0.49839500
C	7.33839800	-0.47428200	0.69566000
H	6.12949600	-2.20785700	1.16408600
H	8.27218600	1.39674900	0.14334500
H	8.27934300	-0.95546900	0.97363200
C	-1.11473600	-1.75141000	-0.08947100
H	-0.94716100	-2.60640800	-0.76651500

1,2:3,4- di-*O*-isopropylidene- α -D-galactopyranose (**2a**):



C	0.82166700	2.88943400	0.34509500
H	1.70393900	2.84268900	-0.32013000
H	1.17791100	3.12521100	1.36087800
C	0.15325700	1.52425200	0.35147100
C	1.05292300	0.38790000	0.79849200
H	-0.72801300	1.57137500	1.01473400
C	-1.14695400	0.22809700	-1.14892800
C	0.47492000	-1.01918700	0.51488200
H	1.25974300	0.49629200	1.88123100
C	-0.63521100	-1.11488900	-0.56640100
H	-1.31624900	0.15712600	-2.23617500
H	0.04928900	-1.46329600	1.42850900
H	-0.22763600	-1.75183700	-1.36447800
O	-0.08867500	3.89007900	-0.03557100
H	-0.50554500	3.57328800	-0.85055600
O	-0.28638900	1.30392700	-0.98793700
O	2.25218500	0.40771300	0.05392800
O	1.60981600	-1.76680200	0.11831500

O	-1.80847400	-1.72292300	-0.06881800
O	-2.36601400	0.44757500	-0.47542000
C	2.74634100	-0.91606200	-0.04997000
C	-2.81312500	-0.73920300	0.17190900
C	-4.10952400	-1.21681000	-0.46546700
H	-4.42527600	-2.16891300	-0.01462200
H	-4.90424100	-0.47039200	-0.32284100
H	-3.95265100	-1.37139500	-1.54237600
C	-2.95419800	-0.46891300	1.66601200
H	-3.69066300	0.32896800	1.84037400
H	-3.28123500	-1.37965300	2.18787000
H	-1.99088900	-0.14992200	2.08925100
C	3.75460700	-1.20720900	1.05822000
H	4.07461900	-2.25824300	1.01221900
H	4.63580500	-0.55720000	0.95516500
H	3.29869300	-1.02903200	2.04345800
C	3.31627100	-1.10304400	-1.44596200
H	2.54423700	-0.84780700	-2.18532500
H	4.18319000	-0.44351800	-1.59686200
H	3.62953500	-2.14648900	-1.59242400

Catalysts:

[Ir(COD)OTf]₂:

Ir	-1.91344600	-0.31443700	0.18019600
C	-3.73569500	1.56139500	-1.38312700
C	-4.11293500	1.74025000	0.10181400
C	-4.76571500	-1.24518900	-0.50437800
C	-3.89498400	-1.56961600	-1.72895600
H	-3.52205100	2.54178500	-1.83043100

H	-4.57491700	1.13645200	-1.95516400
H	-3.63728000	2.64900400	0.49279900
H	-5.20334600	1.87500100	0.21810500
H	-5.34850300	-2.13003200	-0.21019400
H	-5.49928100	-0.45866200	-0.73768200
H	-4.44251300	-1.40263100	-2.67451300
H	-3.60978300	-2.63127400	-1.70852000
C	0.57040100	-3.22620400	1.26869100
F	0.31536300	-4.50841800	1.49248000
F	-0.16551500	-2.48363100	2.09878000
F	1.85547300	-2.98792400	1.50917800
S	0.12893800	-2.83590600	-0.52161000
O	1.22892000	-3.34150300	-1.33831300
O	0.08664400	-1.27438300	-0.50149300
O	-1.20683500	-3.40016400	-0.70169000
C	-2.60654900	-0.77351100	-1.71451400
H	-1.79303300	-1.24066500	-2.28098900
C	-2.51135200	0.66032000	-1.54924100
H	-1.64122900	1.14072900	-2.01179600
C	-3.62211800	0.58479200	0.95506800
H	-3.43899300	0.84839200	2.00418800
C	-3.89276600	-0.79825400	0.66621400
H	-3.86114300	-1.49157900	1.51810800
Ir	1.77998800	0.08457900	-0.11620200
C	4.71373600	-0.85939900	0.03073200
C	4.48882700	0.09638900	1.21482800
C	3.99808000	1.74742800	-1.43717900
C	3.55788300	0.68432100	-2.46174800
H	5.17738000	-1.79004000	0.38925000
H	5.42024200	-0.42753300	-0.69312900
H	4.27088100	-0.48875500	2.12211600

H	5.40009100	0.68230400	1.43545400
H	3.98059100	2.74141300	-1.90714300
H	5.03783900	1.57948900	-1.12010600
H	4.41198100	0.35032900	-3.07900300
H	2.82838600	1.12726200	-3.15790500
C	-0.35249000	3.45473900	-0.23525800
F	0.34025200	4.58430700	-0.15682700
F	-1.63764200	3.74433600	-0.40958500
F	0.07465600	2.76271900	-1.29281500
S	-0.11553300	2.47685500	1.38231200
O	1.09649300	3.03259500	1.98595600
O	0.08941900	1.02915200	0.87577200
O	-1.38159000	2.60168300	2.10254100
C	2.89129700	-0.50362900	-1.79805700
H	2.22865700	-1.08203200	-2.45388900
C	3.39599700	-1.19439700	-0.65874600
H	3.07031400	-2.23005800	-0.55152400
C	3.31563800	1.02341500	0.97890400
H	2.87429400	1.44711600	1.88745600
C	3.07862700	1.75797000	-0.21961500
H	2.49020000	2.67140400	-0.09988000

Ir(COD)OTf:

Ir	-0.80029300	-0.30497400	-0.55189300
C	-2.87528500	1.90448500	-0.04473200
C	-1.62913700	2.24581200	0.79625100
C	-2.67349100	-0.53912600	1.84986800
C	-3.45175000	-1.09708500	0.64113300
H	-3.18488000	2.78720000	-0.62282200
H	-3.72767200	1.65474100	0.60446500

H	-1.01770400	2.99419800	0.26890100
H	-1.91027000	2.70298600	1.76304900
H	-2.70363500	-1.26340600	2.67634100
H	-3.14557800	0.37941600	2.23057400
H	-3.38753100	-2.19604700	0.64515500
H	-4.52587200	-0.84875000	0.71623900
C	3.20488700	0.75857200	-0.12935300
F	4.25627900	0.99076500	0.64788700
F	2.36484000	1.79894700	-0.03725500
F	3.60633800	0.64854400	-1.39031000
S	2.34638000	-0.80789000	0.42688100
O	3.28329800	-1.88947200	0.17596800
O	1.17387500	-0.83635000	-0.59717100
O	1.87947100	-0.52783000	1.78779100
C	-2.87916200	-0.61425700	-0.68059900
H	-3.07896800	-1.28394600	-1.53038200
C	-2.59686400	0.74522100	-0.99789200
H	-2.58694900	1.00937700	-2.06373100
C	-0.75048900	1.03838500	1.03409800
H	0.29288600	1.26784100	1.27167200
C	-1.21831000	-0.25106300	1.49437500
H	-0.46597900	-0.85514600	2.01172700

Ir(COD):

Ir	-1.91420300	-0.31185200	0.18022300
C	-3.73394200	1.56739600	-1.38303500
C	-4.10694400	1.75132900	0.10236300
C	-4.77284900	-1.23277900	-0.49177600
C	-3.90773400	-1.56501200	-1.71820200
H	-3.51600800	2.54583200	-1.83263600

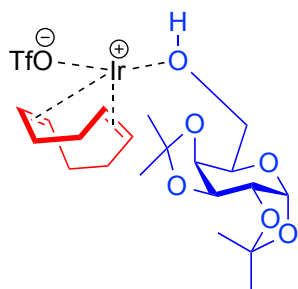
H	-4.57676900	1.14594000	-1.95240400
H	-3.62791400	2.65984300	0.48958500
H	-5.19669100	1.88922300	0.22122700
H	-5.35845700	-2.11408700	-0.19265900
H	-5.50373200	-0.44386500	-0.72545600
H	-4.45792000	-1.39850600	-2.66231200
H	-3.62709900	-2.62784600	-1.69557200
C	-2.61624400	-0.77413600	-1.71062200
H	-1.80685100	-1.24597500	-2.27892500
C	-2.51472600	0.65971600	-1.55052900
H	-1.64418400	1.13443900	-2.01793600
C	-3.61716700	0.59696900	0.95772100
H	-3.42923000	0.86378500	2.00512300
C	-3.89437100	-0.78551000	0.67453000
H	-3.86225900	-1.47637500	1.52838500

Ir(COD)OTf₂:

C	2.62012000	-2.03204100	0.85913400
F	3.81156900	-2.60830400	1.03085600
F	1.67075300	-2.90976100	1.17923000
F	2.53569900	-0.98942700	1.69191100
S	2.43927800	-1.48592800	-0.92145700
O	3.46333900	-0.44611400	-1.10007400
O	1.00996800	-0.97645200	-0.93872900
O	2.58006900	-2.72034800	-1.69677700
Ir	0.08644400	0.74536900	-0.01998000
C	1.61610100	3.23207200	0.92736300
C	0.47465600	3.00004200	1.93630100
C	-0.85593700	3.53407900	-0.87604500
C	0.21717400	3.09442600	-1.89186000

H	2.56689100	3.35798300	1.46702500
H	1.45719300	4.16676000	0.36971000
H	0.86394200	2.44872400	2.80737200
H	0.08607600	3.96007000	2.32473100
H	-1.75401500	3.87337300	-1.41314900
H	-0.50701700	4.39916600	-0.29185900
H	0.80588600	3.96133500	-2.24684900
H	-0.27599900	2.67097100	-2.78095400
C	-3.07460600	-1.55369800	-0.83343700
F	-4.36001300	-1.90077700	-0.92526900
F	-2.32429500	-2.59352000	-1.19393500
F	-2.85149500	-0.55684700	-1.67448500
S	-2.68521900	-1.03462900	0.91116600
O	-3.50878300	0.15831600	1.15821200
O	-1.19083300	-0.76854500	0.82525900
O	-2.97217000	-2.23758900	1.69566900
C	1.12648300	2.02099000	-1.32832900
H	1.63369600	1.40801600	-2.08220000
C	1.74453300	2.06080900	-0.04421100
H	2.64810800	1.45363800	0.06770500
C	-0.64633500	2.17150100	1.34198800
H	-1.27488000	1.65730800	2.07884100
C	-1.24002000	2.39253200	0.06484000
H	-2.25672000	2.00744400	-0.05493200

Ir(COD)OTf-2a:

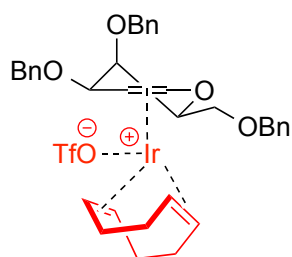


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C	3.92752000	-2.38255800	1.62549400
C	4.61231400	-1.11570600	1.07245900
C	2.98567600	-2.36463100	-1.31584900
C	1.87231800	-3.16671700	-0.61318000
H	4.34515900	-2.62536000	2.61383300
H	4.14207000	-3.25152600	0.98538000
H	4.87361100	-0.44894900	1.90907700
H	5.56425200	-1.36993600	0.57063200
H	2.86978100	-2.45530500	-2.40638000
H	3.97572400	-2.78565300	-1.08380500
H	0.95925800	-3.15456100	-1.22409900
H	2.16316000	-4.22751500	-0.49929000
C	-1.13825400	0.58920600	1.70768100
H	-1.80493100	0.63856300	2.57931800
H	-0.67357400	1.56240500	1.52547600
C	-1.87909200	0.10113800	0.48249100
C	-3.14563500	0.88507600	0.16058400
H	-1.21002500	0.17176100	-0.38483200
C	-2.54478700	-1.98039300	-0.42640500
C	-4.12509100	0.03377700	-0.67853100
H	-2.84694900	1.81270400	-0.34744700
C	-3.49102200	-1.17387200	-1.35369900
H	-2.98836100	-2.91886900	-0.06538400

H	-4.61614000	0.65261000	-1.45068200
H	-4.29624400	-1.83073700	-1.72959600
O	-0.08128400	-0.35518400	1.99394400
H	-0.51691100	-1.22751800	1.95295900
O	-2.17951300	-1.27850000	0.73336400
O	-3.89256700	1.20272100	1.32315800
O	-5.05408800	-0.44928200	0.26880700
O	-2.65005000	-0.72689700	-2.39281100
O	-1.42663500	-2.24154100	-1.23606800
C	-5.07745000	0.41028400	1.40203500
C	-1.59444900	-1.66156600	-2.54393100
C	-1.97998200	-2.76559600	-3.52533900
H	-2.14880300	-2.34123900	-4.52548600
H	-1.17691100	-3.51423800	-3.58566100
H	-2.89935500	-3.27422700	-3.19884000
C	-0.34039300	-0.91410000	-2.95061100
H	0.51640000	-1.59916300	-2.99557700
H	-0.48284100	-0.45788200	-3.94003000
H	-0.12443400	-0.11209100	-2.23757100
C	-6.28600000	1.33751400	1.33866700
H	-7.21874800	0.75639700	1.38185100
H	-6.26491400	2.04626000	2.17932200
H	-6.26730500	1.91193200	0.40074200
C	-5.04049900	-0.45465900	2.65249000
H	-4.14470600	-1.08950400	2.61777600
H	-5.00874200	0.17768000	3.55158200
H	-5.93288800	-1.09582400	2.69991100
C	1.47266500	4.00442600	-0.48956000
F	1.20849600	4.82914900	-1.49845200
F	2.77323200	4.05686000	-0.21356100
F	0.78524600	4.39495600	0.58240300

S	0.98589100	2.26937000	-0.96471000
O	-0.46739600	2.31755700	-1.17331600
O	1.35347800	1.56545100	0.34851300
O	1.83888200	1.89716800	-2.09506200
C	1.49424000	-2.57331000	0.72865200
H	0.47791300	-2.84914400	1.04484000
C	2.41691500	-2.19575500	1.74761200
H	2.03434800	-2.17237600	2.77600600
C	3.71015200	-0.33327500	0.13789400
H	3.95166500	0.73353100	0.05328800
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H	2.67432900	-0.19270800	-1.72826000

IM1 α :



IM1 α

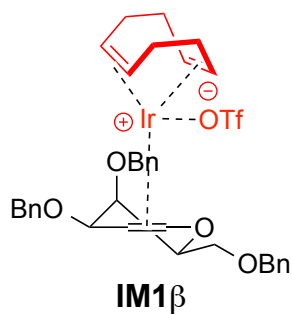
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C	4.92687269	0.04103919	-0.54013047
C	4.28983369	1.44108819	-0.56973247
H	2.43622269	-0.17741981	-3.86931947
H	3.94568969	0.24261719	-3.07539747
H	2.20907469	-2.23330681	-2.76754147
H	3.96942769	-2.14310481	-2.86448447
H	5.79926569	0.05118919	0.12944353
H	5.30543169	-0.24050681	-1.53374747

H	4.41294969	1.91644219	0.41230653
H	4.80571669	2.09973019	-1.29249847
C	-0.31626700	2.56095000	-0.95847600
H	0.48024700	2.42917900	-1.70764100
O	0.25054700	2.21311300	0.32802500
C	-0.69878400	4.03255800	-0.89473500
H	-1.13114900	4.30549800	-1.87043400
H	-1.48139900	4.15868000	-0.12721200
O	0.38910100	4.89178000	-0.66779400
O	-2.52737700	1.87755900	-0.35821400
C	-3.82470700	2.07093700	-0.89227400
H	-4.01436400	1.35217700	-1.70646700
H	-3.90231500	3.08824700	-1.32618300
C	-4.86910100	1.88513800	0.17799500
C	-6.21858000	1.80612100	-0.19302600
C	-4.52611200	1.77751200	1.53061700
C	-7.20877500	1.61881000	0.77065600
H	-6.49270500	1.86709600	-1.24950000
C	-5.51899300	1.58510300	2.49733000
H	-3.47598700	1.83404300	1.81890000
C	-6.86195800	1.50517700	2.12159800
H	-8.25524100	1.54454200	0.46563400
H	-5.23881000	1.49515000	3.54992700
H	-7.63655800	1.34972900	2.87640900
C	0.76470900	5.11006800	0.68705200
H	0.48994307	6.15267871	0.93226884
H	0.19421249	4.45409239	1.36302485
C	-1.50130300	1.66432800	-1.30625200
H	-1.84423000	1.93144500	-2.31887700
C	0.25176500	0.93782100	0.70193000
H	0.64716700	0.79863000	1.71149100

C	2.24599322	4.92874079	0.92255906
C	3.17427590	5.67134239	0.17839369
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C	4.54152586	5.56431460	0.44001966
H	2.81526330	6.33583307	-0.61055715
C	4.08295170	3.94684792	2.17765320
H	1.99971923	3.45864428	2.48520409
C	5.00015564	4.70579212	1.44554131
H	5.25483300	6.14889036	-0.14600203
H	4.43356374	3.26206483	2.95365762
H	6.07017868	4.62076807	1.64920968
C	-0.25747100	-0.09492100	-0.04642600
H	-0.42584800	-1.03373600	0.47719700
C	0.56851537	-3.97666019	0.92125729
F	0.67704397	-5.29326490	1.06255110
F	0.64803082	-3.67367546	-0.37794046
F	-0.63114838	-3.59127565	1.37003473
S	1.91848318	-3.11216509	1.88721710
O	1.65715844	-3.45298872	3.28451306
O	1.58041714	-1.65054941	1.60410685
O	3.17235055	-3.56933523	1.27512122
C	2.80308069	1.41144319	-0.86163547
H	2.29097369	2.31889719	-0.52033247
C	2.17924869	0.65740319	-1.89910047
H	1.23953869	1.05493519	-2.29385447
C	3.12640369	-1.77564681	-0.91477947
H	2.77818069	-2.73202081	-0.51545747
C	3.94053069	-1.00757981	-0.05379847
H	4.12380269	-1.43135881	0.93809253
O	-2.17196700	-0.68585100	-1.46795400
C	-1.06972300	0.18163900	-1.29905000

H	-0.45238700	0.01249700	-2.19252000
C	-2.89804400	-1.11595900	-0.32524700
H	-2.82200000	-0.38433800	0.49227900
H	-2.47482900	-2.06865000	0.04284400
C	-4.35527700	-1.32062800	-0.66097200
C	-4.82546900	-1.28704100	-1.97836900
C	-5.26449200	-1.55410700	0.38105200
C	-6.18564500	-1.47575600	-2.24892400
H	-4.11808400	-1.10307000	-2.78760100
C	-6.61889300	-1.74662900	0.11218500
H	-4.90963800	-1.56167300	1.41486700
C	-7.08597200	-1.70657700	-1.20635600
H	-6.54150900	-1.44215700	-3.28194300
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H	-8.14853600	-1.84904500	-1.41766900

IM1 β :



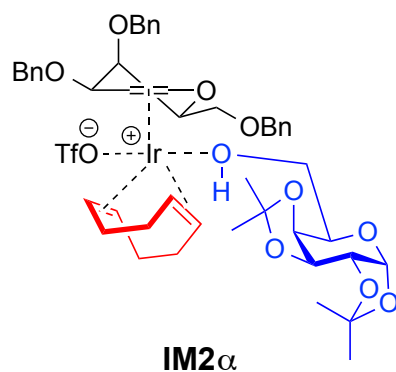
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C	-3.57770400	-1.92231700	2.04228200
C	-2.09226200	-1.63708900	2.09770900
C	-1.08103400	-2.62019700	1.99060500
C	-1.37619600	-4.10268100	1.83348200
C	-1.42090800	-4.53015900	0.35632900

C	2.07702340	-0.20209395	-2.18884527
C	3.11634807	0.54390357	-1.38350884
C	0.69977000	3.17787100	-2.09921800
C	0.57938100	4.17625600	-0.98108400
C	-0.47504800	5.09598900	-0.94836200
C	1.51681300	4.17480500	0.06154700
C	-0.59416400	6.00420500	0.10893700
C	1.39433200	5.07169000	1.12228400
C	0.33825900	5.99001000	1.14908600
C	5.04026553	0.16657603	-0.09590928
C	0.91232200	0.84836100	-2.51383500
C	6.22716055	-0.74640364	0.07765565
C	6.78897597	-0.94778752	1.34565036
C	6.80735861	-1.38085306	-1.03029780
C	7.91775255	-1.75745480	1.50425346
C	7.93024134	-2.19688403	-0.87281202
C	8.49165067	-2.38542512	0.39475734
C	-0.66473900	-1.17416000	-2.12517700
C	-0.41963800	0.13225700	-2.86508800
C	-2.08894800	1.44888200	-1.68288300
C	-3.45393400	0.83877600	-1.46111100
C	-4.14062400	0.18256200	-2.48866900
C	-4.06609400	0.96421400	-0.20474600
C	-5.41727000	-0.34376800	-2.26616800
C	-5.34688500	0.45360100	0.01382700
C	-6.02665500	-0.20703600	-1.01544600
C	-1.12826973	1.97337185	2.51191410
O	1.61587600	-1.30157500	-1.36458100
O	4.20011742	-0.31696264	-1.12015332
O	0.74523500	1.86580000	-1.55303500
O	-1.49937400	1.04037800	-2.90770700

O	0.18390328	-0.19852990	3.30673388
O	1.47311725	1.56562450	2.08354915
O	-0.14380772	0.16286513	0.83806944
F	-2.22437431	1.33285938	2.94037361
F	-1.45399227	2.64570815	1.41227911
F	-0.74619836	2.83180640	3.45335825
Ir	-1.24623900	-1.50460600	0.11364900
S	0.26180938	0.74677546	2.18470261
H	-1.59928200	-3.58180600	-1.60702300
H	-3.46473700	-2.13169800	-1.24554200
H	-1.82009200	-0.73474400	2.64616900
H	-0.10467300	-2.35510600	2.40475600
H	-4.98841900	-2.47051600	0.49064800
H	-4.03792100	-3.83005300	1.08122100
H	-4.09520400	-0.95451400	2.00357900
H	-3.90606100	-2.41335500	2.97672300
H	-0.60295500	-4.68131300	2.35913400
H	-2.32955100	-4.33668500	2.33072300
H	-0.40858600	-4.81970600	0.03234900
H	-2.05227300	-5.42807200	0.22525200
H	2.56427951	-0.68706470	-3.05156667
H	3.44559279	1.43326239	-1.95742235
H	2.64919075	0.90280034	-0.45423178
H	-0.14745500	3.27611400	-2.79855600
H	1.62843800	3.36073300	-2.67709000
H	-1.21572900	5.09588600	-1.75280400
H	2.32152000	3.43967300	0.05847800
H	-1.42372100	6.71543600	0.12478500
H	2.11843100	5.04594700	1.94000100
H	0.24081200	6.68972500	1.98288300
H	5.39401373	1.18974348	-0.34851882

H	4.48073674	0.25775243	0.85494781
H	1.26957000	1.31482300	-3.44781000
H	6.33628704	-0.46838277	2.21807831
H	6.36209332	-1.23628429	-2.01614202
H	8.34444343	-1.90529370	2.49940346
H	8.37050281	-2.68853315	-1.74412968
H	9.37019996	-3.02348809	0.51765413
H	-1.44343900	-1.78697000	-2.58504100
H	-0.31323800	-0.18287600	-3.91734500
H	-2.19456100	2.54685500	-1.72964000
H	-1.42536100	1.25006700	-0.83381300
H	-3.65756400	0.08100100	-3.46134400
H	-3.53226100	1.46383500	0.60724600
H	-5.93957300	-0.86117400	-3.07490800
H	-5.81428700	0.56149200	0.99554700
H	-7.02524000	-0.61459200	-0.84129900
C	0.42689800	-1.85281800	-1.58658000
H	0.44841300	-2.93645800	-1.45797000

IM2 α :



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C	-2.71768946	0.37594561	2.96042696
C	-2.29782046	1.75867461	2.42447296
H	0.92921554	0.96281261	4.82629796
H	-0.81425646	1.14404361	4.70727896
H	0.92086754	-1.30290039	4.22286396
H	-0.65687146	-1.22586639	5.01501996
H	-3.78811246	0.19903361	2.78452796
H	-2.59508246	0.33254461	4.05257796
H	-2.88588446	2.00621861	1.52773096
H	-2.51016346	2.55624361	3.15969496
C	2.26322374	2.67212995	0.57806796
H	1.62565774	2.72124095	1.47263596
O	1.49769974	2.00992595	-0.44749604
C	2.45752974	4.09461295	0.09255096
H	3.19434474	4.61970895	0.72417996
H	2.84634574	4.06791195	-0.93830004
O	1.20605074	4.74115895	0.16852596
O	4.31099774	1.78188995	-0.25496604
C	5.70188074	1.96182795	-0.06534304
H	6.03925474	1.43168495	0.84035696
H	5.92064074	3.03843595	0.08514496
C	6.47090274	1.43545995	-1.25013704
C	7.86777474	1.34277295	-1.17082604
C	5.82610674	1.01949995	-2.42043204
C	8.60711474	0.83901995	-2.24006504
H	8.37751274	1.64728495	-0.25289004
C	6.56735674	0.51002395	-3.49229504
H	4.73959974	1.08804695	-2.48101804
C	7.95835074	0.41751695	-3.40633504
H	9.69367674	0.75889295	-2.15834404
H	6.05170774	0.18232695	-4.39858004

H	8.53640674	0.01389195	-4.24113004
C	0.54034474	5.07341995	-1.04094004
H	0.91920289	6.04590860	-1.40936565
H	0.74120782	4.32123570	-1.82077248
C	3.52240574	1.88706695	0.91289096
H	4.07067574	2.42837195	1.70145896
C	1.35479274	0.68285695	-0.32998804
H	0.71773974	0.27296995	-1.11069204
C	-2.10618134	0.11960102	-1.93505936
H	-2.12912722	0.52234959	-2.96026411
H	-1.63660647	-0.87012590	-1.96881477
C	-3.55186695	0.01302097	-1.43018386
C	-3.93847412	-1.40862156	-1.06990005
H	-3.64553779	0.63777466	-0.52686388
C	-5.74671492	0.64712314	-2.07671849
C	-5.42920239	-1.60868460	-0.75614762
H	-3.32367602	-1.72500509	-0.21019288
C	-6.39892683	-0.59647710	-1.42019444
H	-6.27241693	0.93537811	-3.00104055
H	-5.61537096	-1.57423699	0.32740762
H	-6.98397887	-1.15632335	-2.16272835
O	-1.29148462	0.91474644	-1.09314084
H	-1.50823794	1.85511244	-1.20673587
O	-4.41682570	0.51402921	-2.44753351
O	-3.73362845	-2.25438479	-2.18461882
O	-5.67952334	-2.92678504	-1.21818217
O	-7.30102894	-0.02926268	-0.48885269
O	-5.89452659	1.65338670	-1.09447307
C	-4.60884645	-3.36741414	-2.07006421
C	-0.94467700	5.14773004	-0.77632450
C	-1.41130430	5.70653359	0.42339509

C	-1.87439964	4.62161280	-1.68418910
C	-2.77732065	5.74012678	0.71080952
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C	-3.24694197	4.66497217	-1.40288056
H	-1.52417388	4.17003627	-2.61603170
C	-3.70104445	5.22281342	-0.20381106
H	-3.12454502	6.17185166	1.65257769
H	-3.96924438	4.24744261	-2.10819356
H	-4.77003994	5.23143117	0.00675937
C	-6.86687465	1.28166086	-0.11820274
C	-8.06172786	2.21678583	-0.19530013
H	-8.83801750	1.89793315	0.51551795
H	-7.75894873	3.24474226	0.05129700
H	-8.47942658	2.19729316	-1.21171063
C	-6.19898211	1.27789932	1.25024304
H	-5.85931086	2.29163403	1.50808141
H	-6.90062100	0.93153764	2.02217291
H	-5.32275480	0.61737152	1.24376718
C	-3.91284431	-4.55137986	-1.41189472
H	-4.63282352	-5.36861136	-1.25721669
H	-3.08980421	-4.90859400	-2.04626332
H	-3.48610047	-4.25890304	-0.44388122
C	-5.15248428	-3.68319391	-3.45400966
H	-5.62756135	-2.78617910	-3.87627761
H	-4.33750402	-4.00187091	-4.12016455
H	-5.89500323	-4.49185586	-3.39421230
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H	1.93491774	-1.16170005	0.50164096
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O	-1.37420087	-3.70377725	1.30325518
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H	-0.57130246	2.57242261	1.30255096
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C	-0.70418846	-1.29242939	2.85633396
H	-0.50248646	-2.33678139	2.60615096
C	-1.91325946	-0.74121839	2.29813596
H	-2.49599346	-1.44797339	1.69851396
O	4.23186774	-0.37940205	1.56325996
C	3.11579474	0.48923395	1.44785096
H	2.77144674	0.62231595	2.48473096
C	4.58930074	-1.17225405	0.44116496
H	4.33038874	-0.66550605	-0.50019004
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C	6.06920974	-1.46824805	0.44627296
C	6.88530574	-1.15843205	1.53970696
C	6.64382774	-2.07147105	-0.68224204
C	8.25601974	-1.43892605	1.50180096
H	6.43903974	-0.68845405	2.41667696
C	8.00821674	-2.35545405	-0.71936204
H	6.01756074	-2.30062505	-1.54844104
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H	8.88327474	-1.18770005	2.36106896
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C	3.23945900	-3.27359300	-2.66749400
C	2.02909000	-4.09642100	-2.19228700
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C	0.92279700	4.21091200	1.42968200
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C	-5.45004100	-0.32040300	3.89310900
C	-7.62496900	-0.36170000	2.14529200
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C	-7.66734400	-1.10810000	3.32379200
C	1.68548300	-1.37379000	2.15464800
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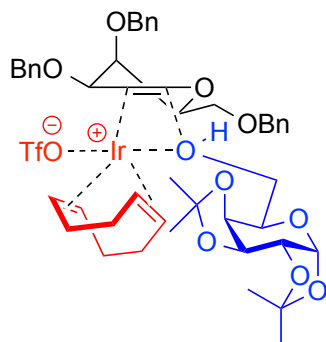
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C	-0.06155969	-1.62974425	-3.79167516
C	-1.20710102	-0.78179732	-4.32347738
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C	-3.74195021	-0.43641076	-4.39309619
C	-3.49157341	0.19733453	-5.77864020
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C	-4.80880860	-2.59194886	-2.36924127
C	-4.59392448	-3.87041610	-4.55785764
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O	-3.02997600	0.39771300	2.47331200
O	0.82386600	1.88567200	1.98156100
O	3.08775600	0.49329400	3.06025700
O	-0.02696125	-1.48119863	-2.37224114
O	-1.28433064	-0.93635342	-5.72725136
O	-2.82096051	-2.48781913	-3.76403378
O	-4.68410826	-1.48376197	-4.52481677
O	-3.70878897	1.59528047	-5.76355360
O	-1.48993120	1.33384034	-6.17015492
O	1.23880400	0.42098200	-2.98366200
O	-0.14811900	1.60789400	-1.26322500

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F	3.47099400	2.08379300	-2.41698500
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F	1.80872500	3.46923900	-2.59848100
Ir	2.00260000	-1.76871200	-0.31392600
S	1.16293300	1.08588600	-1.68032600
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H	2.17075200	-3.88649800	1.32623200
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H	3.13725500	-1.05738900	-2.63713400
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H	4.26090400	-4.73859200	-0.59974300
H	5.19685500	-2.27084500	0.90633400
H	5.80630300	-2.91239900	-0.61642900
H	3.17245600	-3.12614800	-3.75527500
H	4.17949200	-3.82039800	-2.49479800
H	1.15123500	-3.82588900	-2.79955500
H	2.18556000	-5.18132100	-2.34280300
H	-0.94917300	-0.43650300	3.58726500
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H	-1.65345000	1.45187000	1.31184000
H	1.89806300	3.27283000	3.10937100
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H	-0.77743300	3.31485700	0.44366000
H	2.57835000	6.98229700	0.31487100
H	-0.84383400	4.97951400	-1.38630700
H	0.84017500	6.81963500	-1.46499600
H	-4.05732000	2.07552400	3.11187400
H	-4.24855300	1.68928700	1.38583200
H	0.55023900	1.31576700	3.94084500

H	0.13135700	-2.73691800	1.43215100
H	-6.45260700	0.94422300	0.89302900
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H	1.74852200	-0.55710600	4.04052200
H	3.55518200	2.17535400	1.95335000
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H	5.19415800	-0.55757700	3.41865900
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H	7.56859200	-1.20849400	2.99969300
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H	8.76534100	-0.33270300	0.99565100
H	0.88506087	-1.29685078	-4.24119688
H	-0.23602950	-2.69194215	-4.00973555
H	-0.94938912	0.26459328	-4.09288444
H	-2.52531691	-0.78723414	-2.61610558
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H	-4.22161676	-0.25818945	-6.46233755
H	-0.30232611	-0.58071510	-2.13223051
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H	-5.68631035	-3.94227631	-4.66486152

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H	1.73597949	-2.48881910	3.97912479
H	0.10885312	-3.15330805	3.98995478
H	2.43075407	-3.73411072	2.11644608
H	1.28238219	-4.88019753	2.81218987
H	-2.69050272	-4.23249925	1.80930217
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H	-2.37270775	-2.22576275	3.58689154
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H	0.88238200	0.95082400	1.62041800
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C	1.48879000	2.98791700	1.92375700
H	2.06893800	2.86968300	2.85190900

H	1.94934000	3.80259200	1.33946300
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O	3.82900200	1.93649400	0.45866900
C	5.13082100	1.98357800	1.00622300
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C	7.47529800	2.55139800	0.31220100
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C	6.60277600	3.69089100	-2.07786300
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C	-0.47507400	4.12084700	1.30526300
H	-0.05449658	5.14544890	1.36893183
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C	-3.32915515	-0.59827598	-1.62885122
H	-4.06140704	0.13293736	0.25327044
C	-5.51155808	1.40975262	-1.46251878

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H	-4.74782354	-1.68329305	-2.89115359
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H	-0.97150569	-0.14460445	-1.11711405
O	-4.16881445	1.64208326	-1.16456049
O	-2.19100704	-0.34242285	-2.44963979
O	-3.98153711	0.04827635	-3.76552261
O	-6.34191507	-0.75398631	-1.15828559
O	-6.28116498	1.32660508	-0.28371570
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C	-4.77626243	4.08871692	1.66585135
H	-4.46768067	3.17669356	3.60495637
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C	-8.45525587	0.37841935	-0.74896622
H	-9.03002981	-0.55810076	-0.78524306
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H	-1.26339426	-0.26688005	2.18634013
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H	1.02586867	-0.65288361	2.72986808
C	0.60855154	-3.83868526	1.03815290
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C	-0.80297010	-3.73315247	0.90306281
H	-1.21544542	-4.10342920	-0.04011906
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C	2.84203200	-0.30515500	0.36980100

H	2.37567700	-1.02313300	1.06503300
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H	4.46500500	0.47466100	-1.45069900
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C	6.26292200	-0.57116100	-0.95861600
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C	7.06195000	-0.01460800	-1.96788600
C	8.27833400	-1.18450000	0.25065300
H	6.26007200	-1.58551400	0.93745900
C	8.45282600	-0.04408300	-1.87193800
H	6.58709000	0.46899000	-2.82543600
C	9.06789300	-0.62952000	-0.75958200
H	8.74996400	-1.64195500	1.12440200
H	9.06018100	0.40843800	-2.65925300
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C	4.39469497	-1.59537909	1.22180728
C	4.21213397	-2.03119909	-0.11950372
C	4.25224897	-3.49512409	-0.54526172
C	2.84245197	-4.11839309	-0.56313372
C	-0.89054200	1.00536300	2.86284200
C	-1.99077600	1.79946500	2.19546900
C	1.22700900	3.79672200	2.04009200
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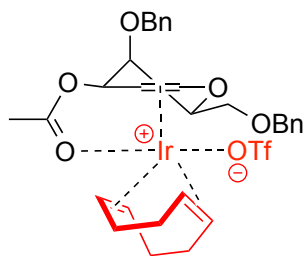
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C	1.53628500	5.79466900	-1.77192700
C	-4.34033800	1.96183300	2.14551000
C	0.37416900	1.83356100	3.07521700
C	0.34954400	-0.97527800	2.58891900
C	-5.60266500	1.14487600	2.21373800
C	-6.36974591	0.93139559	1.06073939
C	-6.01279555	0.56393005	3.42239043
C	-7.52270096	0.14313961	1.11060161
C	-7.16193270	-0.22968677	3.47241706
C	-7.91870764	-0.44559307	2.31574364
C	1.36731800	-0.50271600	3.31127400
C	1.54991400	0.95818000	3.62199900
C	3.32093598	1.85083705	1.93866345
C	4.82709513	1.83547379	1.93157363
C	5.55139320	1.36991515	3.03760516
C	5.52480655	2.20866722	0.77299954
C	6.94306006	1.25883311	2.98033609
C	6.91631065	2.09256583	0.71145852
C	7.63030329	1.61333461	1.81427627
C	-0.21399498	-2.67471291	-1.15131430
C	-1.71484471	-2.47784958	-1.10814655
C	-2.35966922	-2.86700298	0.22780616
C	-3.56222927	-3.03149478	-2.49316005
C	-3.83954055	-3.25209159	0.03319858
C	-4.44333726	-2.73821383	-1.25995172
C	-2.71346513	-5.12659968	0.73504490
C	-4.45404080	-0.86990710	-2.58242344
C	-5.86228773	-0.78946499	-3.16500849

C	-3.71348405	0.45235272	-2.64325677
C	-3.16475026	-5.43201310	2.16106579
C	-2.08905953	-6.31457724	0.02565238
C	2.81279702	1.93688958	-2.36327605
O	-0.65113500	-0.18999700	2.09290500
O	-3.21609200	1.12429500	2.34874200
O	0.69314700	2.49258900	1.87272700
O	2.82284400	1.43911600	3.20715000
O	0.39720809	-2.25192481	0.08252811
O	-2.22268290	-3.27819867	-2.17080772
O	-1.77629635	-4.04495555	0.76635100
O	-3.80698030	-4.66706137	-0.04556643
O	-4.49862110	-1.32233107	-1.23230659
O	-3.70133638	-1.87013210	-3.28032870
O	1.53564502	-0.22418942	-3.20880705
O	0.32048402	1.25210358	-1.58698205
O	2.29658002	-0.08053142	-0.82710905
F	3.94127902	1.37862758	-2.80442705
F	3.09322402	2.65510458	-1.27776005
F	2.33165002	2.74236858	-3.30633105
Ir	2.35693297	-1.45406909	0.72147128
S	1.57146602	0.59423558	-1.98714405
H	0.85367997	-3.60098109	0.23052428
H	1.38521297	-3.21642309	2.52127928
H	4.77849097	-0.57912209	1.35162128
H	4.44735397	-1.30256409	-0.90415672
H	3.39198697	-3.93719709	3.52002728
H	3.96566797	-4.54355409	1.97414728
H	4.47475697	-1.86293409	3.31729428
H	5.62620697	-2.88016309	2.45731328
H	4.70051797	-3.56885109	-1.54675672

H	4.91590197	-4.05611809	0.12916128
H	2.38769997	-3.95872709	-1.55329372
H	2.89396297	-5.21287809	-0.41657972
H	-1.24708600	0.67288800	3.85342700
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H	2.21039800	3.75201200	2.53754000
H	0.55452200	4.37494600	2.70685200
H	3.13585400	5.56100800	1.23281000
H	-0.39497000	3.51539900	-0.13092800
H	3.30138800	6.73887200	-0.95058900
H	-0.22950700	4.66948000	-2.31972900
H	1.61985100	6.29546100	-2.73952600
H	-4.34975200	2.75528000	2.92229800
H	-4.28018400	2.45681500	1.16306500
H	0.12525200	2.58773700	3.84295400
H	0.23010800	-2.02409200	2.31760300
H	-6.04135785	1.35918924	0.11096316
H	-5.40724886	0.71474830	4.31746501
H	-8.10613831	-0.02438463	0.20201299
H	-7.46467130	-0.68789035	4.41709898
H	-8.81188705	-1.07363862	2.35266392
H	2.12262000	-1.20603800	3.66670500
H	1.57067300	1.08171200	4.71697500
H	2.94683398	2.84748778	1.67009075
H	2.95373059	1.17763812	1.14723898
H	5.01162153	1.09796706	3.94641949
H	4.96949771	2.57928391	-0.09027121
H	7.49506980	0.89080295	3.84900262
H	7.44519126	2.38057223	-0.20049970
H	8.71825970	1.52237976	1.76789453

H	0.19908662	-2.10916191	-1.99628880
H	0.01647741	-3.74002709	-1.27160035
H	-1.93240116	-1.41481228	-1.30068530
H	-2.25944193	-2.04245313	0.94804005
H	-3.89216393	-3.90983518	-3.06367222
H	-4.44123728	-2.91371863	0.88689967
H	-5.44763439	-3.17573933	-1.39228141
H	0.07748422	-1.37240056	0.36993948
H	-6.44824685	-0.02382596	-2.63572995
H	-5.81351541	-0.52426167	-4.23080069
H	-6.37861468	-1.75611161	-3.07426141
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H	-3.69050576	0.81437047	-3.68104354
H	-3.88835831	-6.26065881	2.16523048
H	-2.30007464	-5.71117985	2.78052523
H	-3.64207709	-4.54618007	2.60519824
H	-1.79948438	-6.00917812	-0.98924815
H	-1.19892897	-6.65787833	0.57205605
H	-2.80751562	-7.14475856	-0.03677063

IM1 α' :



IM1 α'

Ir	-1.52019500	-0.23787500	0.80569900
C	-1.23724700	0.12953100	3.92366100
C	-1.59036800	-1.34571200	3.68802300

C	-4.02406500	0.38349900	2.65865700
C	-3.39491800	1.72015200	2.22969900
H	-0.33813900	0.18850200	4.55176800
H	-2.03553100	0.64407700	4.47593200
H	-0.66841700	-1.94251600	3.63121400
H	-2.16713900	-1.75329500	4.53692800
H	-5.09863300	0.41056400	2.43272800
H	-3.93359200	0.23591200	3.74347300
H	-3.89537200	2.08449900	1.32305700
H	-3.54427900	2.48940500	3.00767500
O	1.20425100	1.17789400	0.57893100
O	2.76563300	-2.04288700	-0.35460000
C	3.41581300	-2.70862200	0.72680200
H	2.66090000	-3.29034000	1.29084100
H	3.86651500	-1.98302700	1.42523800
C	4.47416100	-3.61748400	0.16579600
C	4.16714100	-4.48196500	-0.89562000
C	5.76884000	-3.62199500	0.69889200
C	5.14053800	-5.33904900	-1.41117900
H	3.16170400	-4.46988300	-1.32246000
C	6.74238500	-4.48724800	0.18956900
H	6.01976700	-2.94223900	1.51751500
C	6.43047000	-5.34630500	-0.86725100
H	4.89312200	-6.00599100	-2.24049700
H	7.74877900	-4.48231000	0.61463000
H	7.19151800	-6.01850500	-1.27037900
C	0.08409600	1.09013900	-0.16038500
H	-0.42844000	2.04476100	-0.27993300
C	-0.20740200	0.03450600	-1.00593500
H	-0.94749900	0.17884900	-1.79211200
C	-1.92157000	1.63401600	1.92384900

H	-1.55603000	2.47527700	1.33041300
C	-0.95986900	0.89026300	2.63516100
H	0.08288100	1.17108900	2.47197300
C	-2.36498800	-1.57283600	2.41423200
H	-2.24606000	-2.56242700	1.96223800
C	-3.42368100	-0.80450600	1.93868000
H	-4.01768600	-1.22595000	1.12514800
O	-3.00319500	0.76734200	-0.61085400
C	-4.91416500	1.41474200	-2.23878700
C	1.73227900	-1.17737300	0.01002300
H	1.20069000	-1.55819000	0.90347600
C	2.27068000	0.23858900	0.32065500
H	2.84381700	0.21445800	1.25607300
C	3.17021700	0.79708000	-0.76938300
H	3.94353900	0.04377900	-1.00780800
H	2.59034400	0.98367100	-1.69624300
O	3.71548700	1.98916700	-0.27883200
C	4.49019000	2.70853900	-1.21319800
H	5.44869000	2.19199500	-1.41531400
H	3.95044000	2.76492100	-2.18151200
C	4.73825900	4.10224400	-0.69374800
C	3.81343400	4.71642600	0.16158600
C	5.87554500	4.81628600	-1.09490200
C	4.02108000	6.02532500	0.60461700
H	2.93531000	4.15301600	0.48145800
C	6.07983800	6.12810400	-0.65841900
H	6.60891500	4.34219300	-1.75325900
C	5.15280200	6.73678400	0.19376200
H	3.29455000	6.49274200	1.27409100
H	6.97037800	6.67406500	-0.97903000
H	5.31428200	7.76049900	0.53971600

S	-3.82848900	0.01008900	-1.65361700
O	-3.02886200	-0.39135200	-2.82096000
O	-4.74672000	-0.98114800	-1.07988400
F	-4.17543100	2.35270300	-2.82395200
F	-5.80042700	0.94623100	-3.11196500
F	-5.56095300	1.95044100	-1.20511000
C	0.75772800	-1.09509800	-1.15982300
H	1.33165700	-0.94362900	-2.08626700
O	0.13327000	-2.38435500	-1.40725500
C	-1.51766100	-4.05046500	-1.57281300
H	-1.00927800	-4.28322500	-2.51585100
H	-1.25150500	-4.81937500	-0.82895600
H	-2.60763400	-4.04436800	-1.69408200
C	-1.07727500	-2.72665000	-1.04792400
O	-1.83038700	-2.06640500	-0.31521800

IM1β':

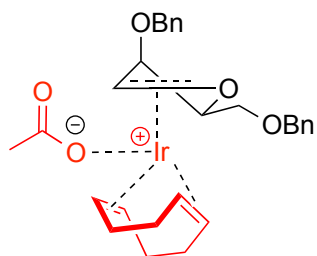
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C	-0.34980200	0.13418100	-3.48383700
C	-1.87933700	0.31512100	-3.48556900
H	-1.63148100	-3.75713400	-2.83770700
H	-1.10492900	-2.40873900	-3.84149200
H	-0.00559900	-3.39075400	-1.16156000
H	0.89667600	-3.06735300	-2.62511800
H	0.10817400	1.03555300	-3.91188100
H	-0.05441600	-0.70454600	-4.12947200
H	-2.12730700	1.35971100	-3.24613100
H	-2.28500700	0.12834500	-4.49523200

O	1.39815000	0.73314300	0.49457800
O	1.76786200	-2.10576300	1.16763900
C	1.84767900	-3.43911600	1.67085400
H	0.95622600	-3.67964400	2.27589000
H	2.73055800	-3.51740200	2.33245100
C	1.95097500	-4.37830100	0.50013900
C	2.96589200	-4.19935000	-0.45259700
C	1.01642400	-5.40496100	0.31630600
C	3.03606900	-5.02646500	-1.57446000
H	3.69586700	-3.39817900	-0.31717000
C	1.08953700	-6.23994000	-0.80382500
H	0.21917100	-5.54774900	1.05037900
C	2.09553600	-6.04791200	-1.75410900
H	3.82646200	-4.87516400	-2.31336500
H	0.35387300	-7.03641200	-0.93703100
H	2.14981400	-6.69400900	-2.63332500
C	0.06506900	0.89065900	0.63301800
H	-0.29526500	1.86227000	0.27218400
C	-0.66694400	0.11750300	1.52414800
H	-1.61608700	0.49277700	1.91137600
C	-2.60831600	-0.55291100	-2.49236800
H	-3.55552500	-0.14842700	-2.13020100
C	-2.31646000	-1.85976200	-2.16018900
H	-3.02668100	-2.36272400	-1.49318100
C	0.42516400	-1.34117200	-1.46295400
H	1.20362800	-1.37830500	-0.69960500
C	0.24935000	-0.09000400	-2.10495200
H	0.89820600	0.71218900	-1.74802700
O	-2.95291200	0.93030000	-0.22353200
C	-4.69640900	2.85358600	-0.33502400
C	1.49395900	-1.11129100	2.12302400

H	1.94712700	-1.36254600	3.09677500
C	2.09554800	0.20595400	1.65005000
H	1.98417100	0.94383100	2.46201300
C	3.55559900	0.10296800	1.26732700
H	4.10099100	-0.42853500	2.07213400
H	3.65096300	-0.50188900	0.34700200
O	4.03881800	1.40406300	1.07808500
C	5.28489300	1.49620300	0.42512700
H	6.11275000	1.21396800	1.10467800
H	5.31569800	0.78125600	-0.42341900
C	5.48346200	2.90040000	-0.09190100
C	4.37992300	3.67772800	-0.47137400
C	6.77275700	3.42992100	-0.23654800
C	4.56492800	4.96175200	-0.99051700
H	3.37725000	3.26666900	-0.34315800
C	6.95891700	4.71133400	-0.76309500
H	7.63908200	2.83630600	0.06857900
C	5.85471400	5.48176500	-1.14109800
H	3.69705100	5.56065700	-1.27809200
H	7.96956800	5.11289200	-0.86992300
H	5.99894200	6.48616600	-1.54634300
S	-3.05742100	2.34155900	0.40725500
F	-5.65921500	2.05836000	0.11145400
F	-4.95448300	4.10649100	0.01399200
F	-4.62950900	2.76638300	-1.65993600
O	-3.23834000	2.28235900	1.85792400
O	-2.05442000	3.25483100	-0.15145900
C	-0.02613300	-0.97625300	2.35161000
H	-0.51215300	-1.94157100	2.14245600
O	-0.22828100	-0.65019900	3.73166700
C	-1.44768600	-0.94900900	4.25479600

O	-2.32660400	-1.44244100	3.59042600
C	-1.52280400	-0.57167900	5.70382700
H	-0.68836300	-1.02767300	6.25637600
H	-1.42230000	0.52056000	5.79916900
H	-2.48270500	-0.89480000	6.12187600

IM2 α' :



IM2 α'

Ir	-0.24727146	-0.06420339	1.21574396
C	0.05686054	0.68842361	4.21531796
C	-0.07660946	-0.84115339	4.15617096
C	-2.71768946	0.37594561	2.96042696
C	-2.29782046	1.75867461	2.42447296
H	0.92921554	0.96281261	4.82629796
H	-0.81425646	1.14404361	4.70727896
H	0.92086754	-1.30290039	4.22286396
H	-0.65687146	-1.22586639	5.01501996
H	-3.78811246	0.19903361	2.78452796
H	-2.59508246	0.33254461	4.05257796
H	-2.88588446	2.00621861	1.52773096
H	-2.51016346	2.55624361	3.15969496
C	2.26322374	2.67212995	0.57806796
H	1.62565774	2.72124095	1.47263596
O	1.49769974	2.00992595	-0.44749604
C	2.45752974	4.09461295	0.09255096
H	3.19434474	4.61970895	0.72417996

H	2.84634574	4.06791195	-0.93830004
O	1.20605074	4.74115895	0.16852596
O	4.31099774	1.78188995	-0.25496604
C	5.70188074	1.96182795	-0.06534304
H	6.03925474	1.43168495	0.84035696
H	5.92064074	3.03843595	0.08514496
C	6.47090274	1.43545995	-1.25013704
C	7.86777474	1.34277295	-1.17082604
C	5.82610674	1.01949995	-2.42043204
C	8.60711474	0.83901995	-2.24006504
H	8.37751274	1.64728495	-0.25289004
C	6.56735674	0.51002395	-3.49229504
H	4.73959974	1.08804695	-2.48101804
C	7.95835074	0.41751695	-3.40633504
H	9.69367674	0.75889295	-2.15834404
H	6.05170774	0.18232695	-4.39858004
H	8.53640674	0.01389195	-4.24113004
C	0.54034474	5.07341995	-1.04094004
H	0.91920289	6.04590860	-1.40936565
H	0.74120782	4.32123570	-1.82077248
C	3.52240574	1.88706695	0.91289096
H	4.07067574	2.42837195	1.70145896
C	1.35479274	0.68285695	-0.32998804
H	0.71773974	0.27296995	-1.11069204
C	-2.10618134	0.11960102	-1.93505936
H	-2.12912722	0.52234959	-2.96026411
H	-1.63660647	-0.87012590	-1.96881477
C	-3.55186695	0.01302097	-1.43018386
C	-3.93847412	-1.40862156	-1.06990005
H	-3.64553779	0.63777466	-0.52686388
C	-5.74671492	0.64712314	-2.07671849

C	-5.42920239	-1.60868460	-0.75614762
H	-3.32367602	-1.72500509	-0.21019288
C	-6.39892683	-0.59647710	-1.42019444
H	-6.27241693	0.93537811	-3.00104055
H	-5.61537096	-1.57423699	0.32740762
H	-6.98397887	-1.15632335	-2.16272835
O	-1.29148462	0.91474644	-1.09314084
H	-1.50823794	1.85511244	-1.20673587
O	-4.41682570	0.51402921	-2.44753351
O	-3.73362845	-2.25438479	-2.18461882
O	-5.67952334	-2.92678504	-1.21818217
O	-7.30102894	-0.02926268	-0.48885269
O	-5.89452659	1.65338670	-1.09447307
C	-4.60884645	-3.36741414	-2.07006421
C	-0.94467700	5.14773004	-0.77632450
C	-1.41130430	5.70653359	0.42339509
C	-1.87439964	4.62161280	-1.68418910
C	-2.77732065	5.74012678	0.71080952
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H	-3.12454502	6.17185166	1.65257769
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H	-4.77003994	5.23143117	0.00675937
C	-6.86687465	1.28166086	-0.11820274
C	-8.06172786	2.21678583	-0.19530013
H	-8.83801750	1.89793315	0.51551795
H	-7.75894873	3.24474226	0.05129700
H	-8.47942658	2.19729316	-1.21171063
C	-6.19898211	1.27789932	1.25024304

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H	-5.32275480	0.61737152	1.24376718
C	-3.91284431	-4.55137986	-1.41189472
H	-4.63282352	-5.36861136	-1.25721669
H	-3.08980421	-4.90859400	-2.04626332
H	-3.48610047	-4.25890304	-0.44388122
C	-5.15248428	-3.68319391	-3.45400966
H	-5.62756135	-2.78617910	-3.87627761
H	-4.33750402	-4.00187091	-4.12016455
H	-5.89500323	-4.49185586	-3.39421230
C	2.00550974	-0.08198405	0.59355796
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C	1.27668909	-3.95100355	1.16129068
F	1.23417864	-5.25147199	1.43227400
F	1.46684365	-3.27860276	2.29973699
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O	-1.37420087	-3.70377725	1.30325518
C	-0.83270246	1.78895261	2.02606596
H	-0.57130246	2.57242261	1.30255096
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C	-0.70418846	-1.29242939	2.85633396
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C	-1.91325946	-0.74121839	2.29813596
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O	4.23186774	-0.37940205	1.56325996
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C	1.14731200	6.53836300	0.47023500
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C	2.43692700	6.99620600	0.17165700
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H	0.14602400	-2.55209900	0.94578800
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C	-3.36543400	0.61503800	2.53814900
O	-2.93173800	-0.52617700	2.03921200
C	-3.95868300	0.44997000	3.92401600

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H	1.74159100	-0.04769300	-1.79723500
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H	3.01318700	1.25278200	-0.11059700
H	2.31536600	0.28927800	1.20572700
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C	5.00746600	-3.11198000	0.02235100
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H	7.38658400	-0.91848300	1.09860400
C	7.17146600	-4.19833800	0.17865600
H	5.36026600	-5.18474000	-0.47451600
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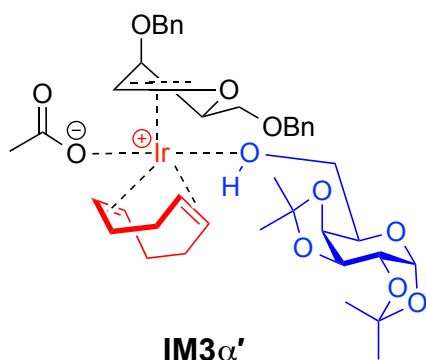
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C	-0.59200900	4.03025100	-0.75203900
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H	-1.65804300	-0.09345500	-2.34697800
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O	-3.08734000	-2.11105900	-1.19450600
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H	-1.02248500	1.08071600	4.40175700
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C	7.95885700	-4.62662100	-1.97417000
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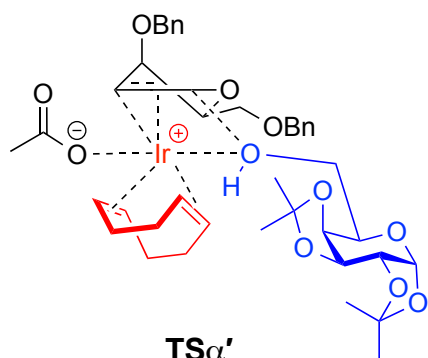
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H	-4.92480500	-2.41776900	-2.22928800
C	-5.57552900	-3.11388700	-0.29692100
C	-6.46132100	-2.27924500	0.40094500
C	-5.71336600	-4.50559200	-0.17735100
C	-7.46559500	-2.82812800	1.20498500
H	-6.35844600	-1.19535800	0.31423800
C	-6.72373700	-5.05370700	0.61799500
H	-5.02464900	-5.16774300	-0.71050900

C	-7.60250800	-4.21585600	1.31309000
H	-8.14727500	-2.16749500	1.74701300
H	-6.82048800	-6.13934100	0.69978200
H	-8.38969800	-4.64359500	1.93904300
C	-0.93535600	0.89712600	-0.81668400
H	-0.09392500	1.55012200	-0.56592700
C	3.31728800	1.38192800	-1.13511500
H	3.39910600	1.63836100	-2.20650800
H	3.05224000	2.29514900	-0.58444600
C	4.68626100	0.90670700	-0.65142500
C	4.72902200	0.50387400	0.82767300
H	4.99449700	0.02409900	-1.24407500
C	6.93921900	1.68027300	-0.79507200
C	6.17543000	0.54669900	1.39445700
H	4.28649300	-0.49822800	0.94386200
C	7.27522700	0.69113300	0.34910600
H	7.44714600	2.64972400	-0.68767200
H	6.38573400	-0.35866600	1.99165800
H	8.19841200	1.00912800	0.86536300
O	2.28363500	0.44566500	-0.89604400
H	2.43395900	-0.37342000	-1.39125200
O	5.57808200	1.99018800	-0.89344600
O	4.01761000	1.43700700	1.62928500
O	6.19098400	1.71176300	2.19791900
O	7.45411400	-0.54580400	-0.31822400
O	7.40337800	1.01766100	-1.95222600
C	4.86806500	1.97923000	2.64290300
C	7.96374600	-0.25964900	-1.61658200
C	9.49005900	-0.16273700	-1.59829800
H	9.93251800	-1.13735000	-1.34412200
H	9.85903400	0.14606000	-2.58723900

H	9.82844100	0.57946300	-0.85996400
C	7.45540600	-1.31015900	-2.58924800
H	7.81739400	-1.09289500	-3.60435600
H	7.81698500	-2.30595100	-2.29441700
H	6.35638700	-1.31713000	-2.59835800
C	4.59478100	1.28196500	3.97678400
H	5.25689400	1.68073300	4.75963100
H	3.55022300	1.44315100	4.28237900
H	4.76692800	0.19811400	3.89207500
C	4.67378800	3.48530000	2.70484000
H	4.88547000	3.91770300	1.71702300
H	3.63932800	3.72454500	2.99120200
H	5.35434100	3.92809600	3.44672400
C	-0.79606700	-0.07505700	-1.83825900
H	0.10545900	-0.15136000	-2.44030500
C	0.72395700	-2.41251000	1.47912000
H	1.56194900	-2.70364600	0.83987100
C	-0.45827900	-3.11781700	1.31586600
H	-0.49883000	-3.84022600	0.49475100
C	-2.08170000	-0.75339100	1.50780900
H	-2.83188800	-0.14399500	1.01106000
C	-0.94095100	-0.07561600	1.94864200
H	-0.90806100	0.99689000	1.74206200
O	-0.22115800	-3.88402700	-1.81980500
C	-1.81224200	-1.07741600	-1.74067400
H	-1.67820600	-2.02205400	-2.27229100
C	0.77303700	-3.17599900	-1.91595900
O	0.91416000	-1.99978800	-1.34331700
C	1.99984000	-3.62435900	-2.68957400
H	1.71714600	-3.83705300	-3.73062300
H	2.82466800	-2.90471900	-2.64640900

H	2.33258100	-4.58215000	-2.25419800
C	-3.24341400	-0.56785600	-1.60342200
H	-3.65267900	-0.66456500	-2.63188100
C	-3.23890500	0.95081600	-1.32182100
H	-3.06315000	1.44880600	-2.28923900
C	-4.53390900	1.48396700	-0.74438900
H	-5.37600000	1.03473900	-1.30570700
H	-4.64639100	1.16687600	0.31041200
O	-4.52318000	2.88264400	-0.85969000
C	-5.67471700	3.51376100	-0.33963500
H	-6.58173000	3.17990800	-0.88186800
H	-5.81917800	3.21806300	0.72161600
C	-5.53757200	5.01572800	-0.43539800
C	-4.27565300	5.62794600	-0.42253200
C	-6.68363600	5.82284600	-0.49935500
C	-4.16360200	7.02123100	-0.47032200
H	-3.38250900	5.00197400	-0.38298800
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H	-7.67356200	5.35741200	-0.52163300
C	-5.31050300	7.82005700	-0.52568400
H	-3.17376000	7.48554100	-0.46419100
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H	-5.22195400	8.90882100	-0.56287900

TS α' :



Ir	-0.11897000	-1.18114200	0.24163400
C	0.94122300	-1.84655500	3.14376700
C	1.21058400	-3.08625200	2.26493600
C	-1.88100100	-2.65372700	2.30297600
C	-2.09602400	-1.13514300	2.45057500
H	1.86857500	-1.57091100	3.66606900
H	0.21392000	-2.07943300	3.93278800
H	2.25629400	-3.09134500	1.92668200
H	1.08536500	-4.01184800	2.85421100
H	-2.86242200	-3.14082700	2.22182200
H	-1.39694600	-3.07950400	3.19128300
H	-2.90784400	-0.85427700	1.76348800
H	-2.44305500	-0.86835900	3.46459200
O	1.97790400	1.71901400	0.78770500
O	4.12523500	-1.18235700	-0.04548900
C	5.09213300	-1.62556200	0.90305200
H	4.57211500	-1.89094600	1.84428300
H	5.80797600	-0.81974300	1.14388000
C	5.81705400	-2.82842800	0.35753700
C	5.09274400	-3.86783800	-0.24762700
C	7.20749400	-2.94128600	0.47146900
C	5.75079900	-5.00353700	-0.72186000
H	4.01045000	-3.77524300	-0.36028200

C	7.86740400	-4.08264500	0.00337300
H	7.78006300	-2.13046200	0.92985100
C	7.14059200	-5.11547900	-0.59403000
H	5.17834500	-5.80543800	-1.19418700
H	8.95303900	-4.15990300	0.09876700
H	7.65539200	-6.00483700	-0.96515400
C	1.06125500	1.49880900	-0.10931800
H	0.27974300	2.25864100	-0.17044300
C	-2.47181058	2.27723935	0.47734026
H	-2.11328566	3.03958068	1.18324643
H	-3.00516765	2.79892267	-0.33519315
C	-3.48186010	1.35451968	1.17043485
C	-3.62368154	-0.00186356	0.45877356
H	-3.17108556	1.16115070	2.21062851
C	-5.74504821	1.48588739	1.89733129
C	-5.05573294	-0.56080451	0.51498035
H	-2.92720274	-0.72718346	0.90084223
C	-5.85585594	-0.04431685	1.69547752
H	-6.65316727	2.02398480	1.59200504
H	-5.03240774	-1.66399970	0.56208173
H	-6.91312754	-0.34217029	1.58948334
O	-4.70945376	2.07247796	1.16451183
O	-3.37807660	0.10143443	-0.93783613
O	-5.63118595	-0.11006988	-0.69236640
O	-5.27255923	-0.58299600	2.86910054
O	-5.53792767	1.62568703	3.28464513
C	-4.61243295	-0.01582745	-1.67793155
C	-5.49744449	0.34436929	3.92483217
C	-6.83551331	0.07297433	4.60677568
H	-6.82495319	-0.91592580	5.08758075
H	-7.03165702	0.83865526	5.37082586

H	-7.65494761	0.10012434	3.87348625
C	-4.32151672	0.29053131	4.88143854
H	-4.44953943	1.03659157	5.67802790
H	-4.25281893	-0.70642231	5.33948511
H	-3.38713139	0.49956709	4.34233189
C	-4.54245648	-1.28242802	-2.52042210
H	-5.47105615	-1.41052811	-3.09501860
H	-3.69622745	-1.22359856	-3.21983414
H	-4.39769683	-2.16182019	-1.87578499
C	-4.84476290	1.24735934	-2.48554256
H	-4.89274545	2.10650059	-1.80256614
H	-4.02897450	1.39420514	-3.20769872
H	-5.79393253	1.17527390	-3.03564601
C	1.06137100	0.36354900	-0.92262200
H	0.49312000	0.37142000	-1.85189900
C	-0.87939900	-0.30775300	2.09972100
H	-1.09530400	0.74197100	1.87230900
C	0.45674600	-0.63756600	2.35284600
H	1.14495500	0.20791700	2.33101900
C	0.32971200	-3.16743900	1.04444200
H	0.75314900	-3.70189700	0.18894000
C	-1.07007200	-2.97167800	1.05451400
H	-1.62808100	-3.38747600	0.20901700
O	1.05398900	-3.43133200	-2.00192900
C	1.85768500	-0.75935300	-0.50795200
H	2.06317400	-1.56418000	-1.21784700
C	0.04362200	-2.82529600	-2.33910500
O	-0.52324800	-1.87262700	-1.63802500
C	-0.68746600	-3.10651600	-3.63639500
H	-1.72553700	-3.40255600	-3.42155900
H	-0.73091100	-2.19088700	-4.24539400

H	-0.17819300	-3.90240100	-4.19313900
C	2.99161500	-0.54276700	0.48056000
H	2.74570200	-1.00065300	1.44675900
C	3.24363700	0.96388400	0.71648000
H	3.68699500	1.13920500	1.70347900
C	4.12375400	1.61278700	-0.33930100
H	5.07940100	1.06021900	-0.37681600
H	3.66314400	1.52447100	-1.34334600
O	4.30829600	2.95097500	0.02628500
C	5.12653200	3.68393200	-0.85952900
H	6.14447700	3.24901600	-0.89973800
H	4.71685300	3.62086000	-1.88974600
C	5.19144000	5.12635200	-0.42245600
C	4.15895900	5.69272000	0.33738200
C	6.27800500	5.92737700	-0.80125300
C	4.21217300	7.03922100	0.70947200
H	3.32024500	5.06493600	0.64137800
C	6.32790100	7.27500700	-0.43556100
H	7.09456500	5.49215300	-1.38426300
C	5.29440400	7.83531600	0.32247600
H	3.40353600	7.46882400	1.30620400
H	7.18117700	7.88769200	-0.73646000
H	5.33552000	8.88742800	0.61428500
O	-1.34044111	1.58507084	-0.01745011
H	-1.67010876	1.03376063	-0.74759204

TSβ':

Ir	-1.60787800	-1.71109400	-0.58631900
C	-2.75592600	-1.63005000	2.40350200
C	-2.27673300	-0.20876400	2.06456000

C	0.25820600	-2.01380700	1.85083900
C	-0.33046500	-3.40111900	1.51369100
H	-3.77469800	-1.57850600	2.81362100
H	-2.12458800	-2.08341500	3.18017600
H	-3.12995600	0.40158100	1.76036800
H	-1.85363200	0.28066100	2.96025000
H	1.35599400	-2.06665700	1.89609300
H	-0.06373800	-1.69950900	2.85380200
H	0.35042900	-3.92707100	0.82620000
H	-0.38739200	-4.03122600	2.41954600
O	-0.62627400	1.37206100	-1.61518400
O	-3.76594900	1.12965200	-0.23259600
C	-5.10126900	0.64670500	-0.17552100
H	-5.11784200	-0.44474500	-0.34344900
H	-5.69151800	1.11405600	-0.98875400
C	-5.70374300	0.96743500	1.16816500
C	-5.37605300	2.15315600	1.84214900
C	-6.61790600	0.08038700	1.75287500
C	-5.95298100	2.44377000	3.08076800
H	-4.65543900	2.84104800	1.39743400
C	-7.20220500	0.37547000	2.98800200
H	-6.86931100	-0.85214400	1.24031400
C	-6.86918300	1.55738000	3.65648700
H	-5.68560000	3.36743800	3.59979400
H	-7.91237600	-0.32510900	3.43352500
H	-7.31949600	1.78552200	4.62537300
C	-0.46782400	0.25392300	-2.27413000
H	0.51753500	0.03479800	-2.66951100
C	3.14360100	-0.63214600	-1.84682100
H	3.52873000	-1.14894100	-2.74096200
H	3.23113600	0.45118900	-2.00034200

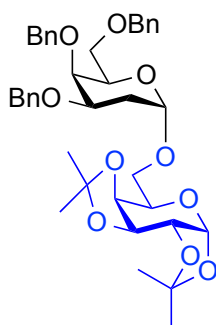
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H	3.91340900	-2.08900700	-0.44497100
C	6.30710100	-1.20100700	-0.12183300
C	4.76188700	-0.18902700	1.66359600
H	2.70802500	-0.69306900	1.07496500
C	5.90706800	-1.14249700	1.37141100
H	7.22494400	-0.63875400	-0.34245300
H	4.38665100	-0.40074100	2.68034500
H	6.77599100	-0.85187500	1.98729700
O	1.75436900	-0.90495100	-1.66280400
H	1.61861800	-1.86458500	-1.65358600
O	5.33758300	-0.67745400	-0.98570100
O	3.35419100	1.11347800	0.31970200
O	5.25060400	1.13204500	1.55474900
O	5.48264300	-2.46251500	1.65668400
O	6.50767600	-2.57723300	-0.35659900
C	4.19816200	1.96821700	1.09146700
C	6.24017400	-3.33742000	0.82968400
C	7.55753400	-3.71833100	1.50045200
H	7.36620200	-4.29716200	2.41574600
H	8.16491900	-4.32641000	0.81497200
H	8.13389000	-2.81984800	1.76533600
C	5.38586200	-4.54143000	0.48076800
H	5.93871000	-5.21725300	-0.18653100
H	5.11749400	-5.09055600	1.39455800
H	4.46581600	-4.21550000	-0.02394200
C	3.40415200	2.54197700	2.26285900
H	4.04403900	3.18638300	2.88311400
H	2.55915500	3.13681000	1.88606000
H	3.00529100	1.73097900	2.89075600

C	4.78943600	3.03045300	0.18524100
H	5.33375500	2.53752700	-0.63209300
H	3.99068400	3.65797100	-0.23265800
H	5.48147400	3.67216500	0.74916400
C	-1.52582300	-0.63444400	-2.51021600
H	-1.37635700	-1.42628600	-3.24410200
C	-1.69621100	-3.36558200	0.84735000
H	-1.91957400	-4.22625600	0.21155400
C	-2.76825500	-2.54080900	1.19790500
H	-3.73572100	-2.76068200	0.73832600
C	-1.25700900	-0.14170400	0.95455700
H	-1.20719000	0.82697700	0.46856800
C	-0.11264100	-0.93266100	0.84391200
H	0.70023000	-0.51340500	0.25229100
O	-4.50360000	-2.98904900	-1.52690400
C	-2.77844800	-0.44390600	-1.83521700
H	-3.61757500	-1.08665400	-2.10730900
C	-3.53737300	-3.50157300	-2.08379900
O	-2.30125500	-3.09723700	-1.93907300
C	-3.69326000	-4.68323000	-3.02006100
H	-4.39354700	-4.41264100	-3.82446300
H	-2.73685700	-5.00087300	-3.45265500
H	-4.14403200	-5.51738200	-2.46071700
C	-3.15077600	0.98734900	-1.48068200
H	-3.88116200	1.27528100	-2.26358900
C	-1.97270000	1.97707200	-1.65845300
H	-2.02305900	2.38484800	-2.67711900
C	-1.96051100	3.12652900	-0.67717600
H	-2.96290800	3.59347300	-0.66182400
H	-1.76584300	2.75109900	0.34559600
O	-0.95569700	4.01173900	-1.08275600

C	-0.70445900	5.06982200	-0.18421900
H	-1.55066600	5.78407100	-0.16761800
H	-0.60755700	4.66915600	0.84710500
C	0.57848500	5.76409400	-0.57023900
C	1.59356800	5.05808800	-1.23229000
C	0.78826300	7.10908800	-0.23695200
C	2.79729600	5.69045900	-1.55692100
H	1.42543700	4.01212200	-1.49310000
C	1.99659200	7.73780700	-0.55125500
H	-0.00113800	7.67078900	0.27029700
C	3.00463000	7.03038300	-1.21405800
H	3.57852700	5.13324800	-2.07977900
H	2.14761500	8.78699700	-0.28590900
H	3.94645800	7.52317400	-1.46680400

Products:

6-*O*-(2-Deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl)-1,2:3,4-Di-*O*-isopropylidene- α -D-galactopyranoside:



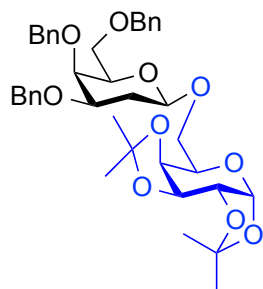
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H	-1.48594500	2.98182100	-1.48691800

H	-1.25853300	2.69450300	0.26158500
O	0.43467900	3.09162600	-0.88099500
O	-3.08301200	0.86236400	-0.07846700
C	-4.32901100	1.42610300	-0.43113100
H	-4.77768200	0.87654000	-1.27575400
H	-4.18951800	2.47462800	-0.76599400
C	-5.28650000	1.38128400	0.73231800
C	-6.64053600	1.67170000	0.51430000
C	-4.86230100	1.03860800	2.02147500
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H	-6.98418300	1.91485900	-0.49477600
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H	-3.80949600	0.80911900	2.18914300
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H	-8.61056200	1.83532700	1.37687900
H	-5.43960500	0.70647300	4.07665000
H	-7.84710500	1.22207000	3.67402500
C	1.32102600	2.93470500	0.20937100
H	0.76527900	2.99393300	1.16469400
H	1.80130900	1.94116500	0.19271900
C	-2.27090000	0.45612600	-1.17198100
H	-2.67943200	0.86387500	-2.11253100
C	-0.06269100	-1.02681600	-0.04189200
H	0.48389700	-1.36787300	0.84810600
C	1.65368300	-2.33882800	-1.12118600
H	1.34680300	-3.12632500	-0.41320500
H	1.73169000	-2.80347800	-2.11679400
C	3.02125900	-1.80708600	-0.72876100
C	4.11544900	-2.87231600	-0.84524400
H	3.27113600	-0.97976000	-1.41249600
C	4.05263400	-0.54753800	1.00779500

C	5.34492500	-2.52488500	0.02186700
H	4.38962300	-2.99334800	-1.90512500
C	5.39735500	-1.07124500	0.45803200
H	4.01007900	-0.53010000	2.10508200
H	6.28116400	-2.77935000	-0.50570100
H	6.18841200	-0.95360800	1.21947300
O	0.69252400	-1.31149900	-1.20745600
O	2.94985900	-1.31403200	0.60704400
O	3.68671300	-4.12442500	-0.33452700
O	5.17417500	-3.31058000	1.18408400
O	5.63272300	-0.25389600	-0.67218200
O	3.98936200	0.76858400	0.50675000
C	4.37427800	-4.44645300	0.87645100
C	2.38661900	4.00119500	0.17570400
C	2.53549500	4.86209600	-0.91795200
C	3.27862500	4.11223600	1.25359700
C	3.56390000	5.81149900	-0.93935900
H	1.83826500	4.77645100	-1.75198300
C	4.29938500	5.06373800	1.23699400
H	3.17805800	3.43539400	2.10617700
C	4.44959400	5.91581100	0.13593200
H	3.67160900	6.47340900	-1.80263500
H	4.98699900	5.13725800	2.08329900
H	5.25176000	6.65757300	0.12015000
C	5.08906600	1.02995400	-0.38456500
C	6.11975100	1.90381800	0.32229100
H	6.97887800	2.08200900	-0.34105900
H	5.67022000	2.86831700	0.59101600
H	6.47767200	1.41700300	1.24125000
C	4.57215200	1.64929400	-1.66825600
H	4.14684800	2.64068400	-1.46376200

H	5.39614100	1.75698400	-2.38816500
H	3.79134700	1.01321000	-2.10736200
C	5.25535200	-5.66680700	0.63239600
H	5.80346300	-5.93327600	1.54790600
H	4.63875700	-6.52427300	0.32547100
H	5.98049000	-5.45459400	-0.16734800
C	3.36940200	-4.63627300	2.00014500
H	2.77317900	-3.71918800	2.10110300
H	2.70413200	-5.48297100	1.77788900
H	3.89112500	-4.83641600	2.94742800
O	-3.54545700	-1.61614400	-1.45131400
C	-2.24126600	-1.07816200	-1.27955400
H	-1.70962100	-1.31837700	-2.21339100
C	-4.31990900	-1.90787100	-0.30259800
H	-4.05158300	-1.25620200	0.54088800
H	-4.13674900	-2.95145700	0.02204200
C	-5.79246900	-1.72307000	-0.58062200
C	-6.27349600	-1.40771500	-1.85621000
C	-6.70370100	-1.84890800	0.47806200
C	-7.64347800	-1.21426900	-2.06820300
H	-5.56247200	-1.30559100	-2.67662600
C	-8.06911500	-1.66083100	0.26768400
H	-6.33485100	-2.07197100	1.48294200
C	-8.54545300	-1.34018800	-1.00871900
H	-8.00623400	-0.96344700	-3.06843700
H	-8.76418500	-1.74829100	1.10607400
H	-9.61450800	-1.18569300	-1.17416200
C	-1.44249500	-1.68214900	-0.12429400
H	-1.94822800	-1.50568700	0.83512900
H	-1.33266500	-2.76928100	-0.25776600

6-*O*-(2-Deoxy-3,4,6-tri-*O*-benzyl-D-galactopyranosyl)-1,2:3,4-Di-*O*-isopropylidene- β -D-galactopyranoside:



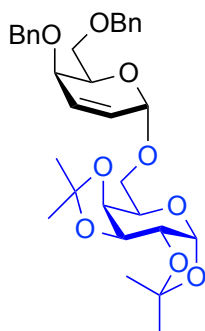
C	-1.22118800	1.32199400	-1.49567800
C	-1.10130900	2.43879200	-0.47965000
C	-3.91842500	0.97256200	0.46308300
C	-4.42194800	0.20397600	1.65798100
C	-5.56179900	0.65440000	2.33699300
C	-3.77728700	-0.95588500	2.10290400
C	-6.05620100	-0.04741100	3.43703300
C	-4.27407700	-1.66255900	3.20258500
C	-5.41554500	-1.21299900	3.87195300
C	0.34658200	4.12725600	0.27632300
C	-2.61868800	0.67195700	-1.53841000
C	-0.13307800	-0.69656200	-2.10731500
C	1.69800300	4.75430300	0.04878400
C	2.45019400	5.23266700	1.12967000
C	2.22051100	4.86862800	-1.24729700
C	3.70356100	5.81539200	0.92197400
C	3.47559700	5.44498700	-1.45604300
C	4.22160400	5.92019500	-0.37221500
C	-2.57791400	-0.50386900	-2.53056000
C	-4.36952900	-1.97153100	-1.72632000
C	-5.66405700	-1.43689400	-1.15407900
C	-6.31959600	-0.33883700	-1.72039100
C	-6.23487000	-2.06701300	-0.03837300

C	-7.51953100	0.13077700	-1.17351100
C	-7.43363000	-1.60563300	0.50414700
C	-8.08012000	-0.50030600	-0.06038500
C	2.19116300	-0.99891400	-1.82935200
C	3.06865600	-1.61244400	-0.75488000
C	2.70163200	-1.15486900	0.66504800
C	5.37702500	-1.96831900	-0.34267800
C	3.89977700	-1.27533500	1.63110700
C	5.00278800	-2.19798900	1.14123800
C	3.44741400	0.98172600	1.26951800
C	5.25572600	-4.24906200	0.16758400
C	6.56867600	-4.79925100	0.72011200
C	4.35556700	-5.33083700	-0.39863400
C	2.92568400	1.75554600	2.47329200
C	4.04434100	1.87373800	0.19271300
O	-0.24031200	0.35685800	-1.17068700
O	0.13771100	3.08316500	-0.64701400
O	-3.00116700	0.18609000	-0.26595600
O	-3.82863700	-1.13207900	-2.73171900
O	0.88346600	-1.53908000	-1.68797900
O	4.41301600	-1.25920400	-1.06618400
O	2.36988200	0.21795900	0.73449500
O	4.43311700	0.03360900	1.68313300
O	4.54329500	-3.53610600	1.17012400
O	5.53672500	-3.27614200	-0.84760800
H	-1.01392700	1.74878100	-2.49900100
H	-1.93620300	3.15457500	-0.61583800
H	-1.18066000	2.00763800	0.53599500
H	-4.77402000	1.25317600	-0.17624300
H	-3.44546800	1.91382100	0.80442900
H	-6.08058600	1.55046500	1.98577300

H	-2.89254200	-1.30627400	1.57087100
H	-6.95320600	0.30837800	3.94991800
H	-3.76694000	-2.57165400	3.53593000
H	-5.80625200	-1.76790200	4.72842200
H	-0.45237400	4.89237500	0.16879400
H	0.27663400	3.74896600	1.31524100
H	-3.35493100	1.41035800	-1.90224400
H	0.10971200	-0.25773100	-3.10202000
H	2.05806900	5.13655500	2.14561900
H	1.64342700	4.48037000	-2.08805500
H	4.28182300	6.17797600	1.77528900
H	3.87630800	5.52001500	-2.47000500
H	5.20534200	6.36669700	-0.53565800
H	-2.35082700	-0.05868500	-3.51375800
H	-3.66146900	-2.13591800	-0.90288100
H	-4.56469100	-2.95813900	-2.18731200
H	-5.87387500	0.14894900	-2.58819300
H	-5.72283100	-2.91545900	0.42290300
H	-8.01785700	0.99445100	-1.62161600
H	-7.85479900	-2.09642900	1.38428900
H	-9.01396000	-0.13075300	0.37021300
H	2.60756600	-1.25299700	-2.82029500
H	2.17327100	0.09306800	-1.70689800
H	2.95302700	-2.70828000	-0.79871200
H	1.83343600	-1.73525300	1.00730900
H	6.30861600	-1.39889700	-0.46638300
H	3.56378200	-1.61048700	2.62863300
H	5.89320200	-2.06186200	1.77977900
H	6.36975000	-5.53859800	1.50956800
H	7.14169900	-5.28276200	-0.08405600
H	7.18289300	-3.98985200	1.14123400

H	4.09432100	-6.05381400	0.38725000
H	3.43265500	-4.88424100	-0.79350600
H	4.87094200	-5.86360900	-1.21012100
H	3.72468500	2.36759300	2.91599700
H	2.10724500	2.41851600	2.16122900
H	2.54431900	1.05473900	3.23041400
H	4.41082200	1.24564000	-0.62982500
H	3.27659700	2.56232300	-0.18260300
H	4.87744600	2.46560000	0.59898600
C	-1.44032200	-1.46963400	-2.18387200
H	-1.59879700	-1.93972100	-1.20296100
H	-1.37046700	-2.25871500	-2.94713200

6-*O*-(2,3-Dideoxy-4,6-di-*O*-benzyl- α -D-threo-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranoside:



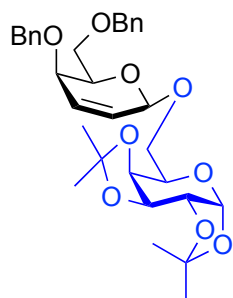
O	0.30567900	0.65885200	1.02524700
O	2.95770900	1.96480600	0.38591300
C	4.35820200	1.78579000	0.55383100
H	4.57733900	0.87775500	1.13493600
H	4.68153600	2.65540200	1.14853900
C	5.12652400	1.73490800	-0.74910300
C	4.88811200	2.68671200	-1.75300600
C	6.08383900	0.73655500	-0.97320500
C	5.59678300	2.64259100	-2.95514800

H	4.13421800	3.46000400	-1.58648300
C	6.79962500	0.69425700	-2.17441400
H	6.26424700	-0.01899000	-0.20673000
C	6.55703300	1.64569600	-3.16866900
H	5.40199200	3.38851100	-3.72989000
H	7.54040700	-0.09315200	-2.33362300
H	7.11064900	1.61071200	-4.11018900
C	-0.62006600	1.02883100	0.03567900
H	-1.30489000	1.73563600	0.53241300
C	-2.25029100	-0.65986700	0.50399700
H	-2.00561300	-1.72577800	0.63781100
H	-2.17256300	-0.16876200	1.48515800
C	-3.67346600	-0.54832300	-0.02105000
C	-4.13483200	0.89858600	-0.23879000
H	-3.72634500	-1.06426800	-0.99418200
C	-5.81322200	-1.44969800	0.46809500
C	-5.66990800	1.02846000	-0.16351500
H	-3.73961200	1.25754700	-1.19948100
C	-6.41349500	-0.28283400	-0.35258000
H	-6.39543600	-1.68316300	1.37026900
H	-6.03613000	1.76307400	-0.90240100
H	-7.47342900	-0.13559800	-0.08056900
O	-4.51196100	-1.20928200	0.92113600
O	-3.68627200	1.77681100	0.78146500
O	-5.91084900	1.46710000	1.15935400
O	-6.27470800	-0.70743500	-1.69479900
O	-5.85141600	-2.53681400	-0.42961500
C	-4.74698100	2.09908000	1.68473600
C	-6.37020700	-2.12628900	-1.70190900
C	-7.82517200	-2.57261200	-1.82487800
H	-8.24118400	-2.25269500	-2.79130700

H	-7.88941100	-3.66793000	-1.75489500
H	-8.43455300	-2.14016500	-1.01777300
C	-5.49063900	-2.67186200	-2.81075700
H	-5.51329000	-3.77064600	-2.80334100
H	-5.85182700	-2.31864900	-3.78712600
H	-4.45437000	-2.33482000	-2.67029700
C	-4.92627800	3.61170300	1.69393300
H	-5.75047200	3.89454900	2.36484200
H	-4.00437600	4.10191900	2.03953400
H	-5.15396200	3.96697700	0.67812700
C	-4.46224600	1.51199200	3.05865200
H	-4.33841300	0.42493700	2.96398200
H	-3.54522100	1.95141100	3.47713800
H	-5.29795400	1.72194700	3.74230800
C	0.03304900	1.67130900	-1.15842300
H	-0.63583500	2.16243400	-1.87043700
C	1.35681000	1.65375100	-1.33636500
H	1.82113200	2.16662400	-2.18326400
C	2.27731700	0.96007300	-0.36638700
H	3.00821800	0.35581600	-0.92812900
C	1.45903500	0.00330700	0.51028900
H	1.14787300	-0.83829600	-0.13496700
C	2.21604300	-0.55002600	1.70224900
H	2.47280700	0.28040700	2.38765200
H	1.56919300	-1.25847500	2.25406000
O	3.37533000	-1.17833500	1.21089500
C	4.23958300	-1.70073600	2.20038600
H	4.39496700	-0.96242000	3.00953400
H	3.78282700	-2.59884000	2.66473800
C	5.55759500	-2.03556700	1.54975900
C	5.58174300	-2.75941400	0.34768800

C	6.76620200	-1.58746900	2.09701700
C	6.79170600	-3.02274800	-0.29636500
H	4.64049700	-3.09352000	-0.09344400
C	7.98098800	-1.85677700	1.45741300
H	6.75658400	-1.00838700	3.02418500
C	7.99597000	-2.57102500	0.25653300
H	6.79685000	-3.57801900	-1.23743500
H	8.91577300	-1.49518200	1.89231700
H	8.94249400	-2.77311100	-0.25037300
O	-1.35486700	-0.08381600	-0.43401500

6-*O*-(2,3-Dideoxy-4,6-di-*O*-benzyl- α -D-threo-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene- β -D-galactopyranoside:



O	-0.55944600	0.73424000	-1.81722600
O	-3.32716400	1.13430300	-0.88313400
C	-4.72984500	0.99328200	-0.84512300
H	-5.06265300	0.11077800	-1.42305800
H	-5.20756100	1.87971100	-1.31424800
C	-5.19070400	0.86910600	0.58651300
C	-4.54382200	1.57891100	1.60848700
C	-6.29357200	0.06725800	0.90994900
C	-4.99564800	1.49089900	2.92758500
H	-3.67746700	2.19485400	1.36179900
C	-6.75198500	-0.01561400	2.22807600
H	-6.79657100	-0.50152100	0.12282600

C	-6.10292600	0.69562400	3.24173500
H	-4.48034600	2.04599200	3.71560500
H	-7.61285400	-0.64564800	2.46510800
H	-6.45534400	0.62665300	4.27375600
C	-0.50792000	0.03543500	-3.04135800
H	0.17361500	0.58734100	-3.73188500
C	1.31478000	-1.35702900	-2.33513000
H	1.88588700	-1.98404700	-3.03876100
H	1.80269400	-0.37504900	-2.24997900
C	1.29068200	-2.07298800	-0.99161000
C	1.03169800	-1.18002800	0.22235800
H	0.46889500	-2.80335400	-1.05080000
C	2.46441000	-3.77981500	0.13703000
C	1.38804900	-1.92439300	1.53345900
H	-0.01324500	-0.83992800	0.20133500
C	1.60412200	-3.42102800	1.37278500
H	3.50823000	-4.00981900	0.39134100
H	0.62062700	-1.74905400	2.30823600
H	2.08621100	-3.80278700	2.28996300
O	-0.02370800	-1.24366300	-2.80772300
O	2.52822100	-2.76057000	-0.81872700
O	1.89130400	-0.04861600	0.22878600
O	2.63954500	-1.38568900	1.90946300
O	0.37161700	-4.06987800	1.12850600
O	1.82845700	-4.92975600	-0.37899400
C	2.79914600	-0.09767700	1.32725100
C	0.65516100	-5.24688500	0.38191800
C	0.95745500	-6.41978700	1.31183900
H	0.07208900	-6.66490700	1.91646600
H	1.24151700	-7.30344400	0.72236900
H	1.79028200	-6.17539400	1.98758200

C	-0.50386700	-5.52377800	-0.55771400
H	-0.28637100	-6.40814900	-1.17315900
H	-1.42014100	-5.71314800	0.01957600
H	-0.67049800	-4.66208400	-1.21888700
C	2.43586600	0.97948800	2.34414800
H	3.09410300	0.90507800	3.22229800
H	2.55154700	1.97659400	1.90013800
H	1.39266300	0.85421300	2.67108400
C	4.22264000	0.01807800	0.80996100
H	4.39271200	-0.77335100	0.06720700
H	4.37450700	1.00052500	0.34299200
H	4.93933300	-0.09497700	1.63659400
C	-1.87225500	-0.09602700	-3.66633200
H	-1.95131400	-0.80099400	-4.49856100
C	-2.92036100	0.61296600	-3.23783300
H	-3.90039000	0.48842100	-3.70686400
C	-2.79120100	1.61215700	-2.10878300
H	-3.31853400	2.54579600	-2.39213300
C	-1.31577100	1.93290000	-1.87852000
H	-0.96661700	2.55208100	-2.72783200
C	-1.06211400	2.70889700	-0.60436000
H	-1.81879400	3.51231500	-0.50118200
H	-1.17363100	2.03074800	0.26103200
O	0.23703400	3.24000400	-0.67172300
C	0.68059100	3.84498600	0.51527400
H	0.11121900	4.77315200	0.72739300
H	0.50199600	3.16635200	1.37580900
C	2.15477700	4.15065300	0.41634500
C	2.96969700	3.43663300	-0.47222200
C	2.73591700	5.11769300	1.24855700
C	4.34360500	3.68829700	-0.52806800

H	2.51199100	2.67571600	-1.10418000
C	4.11095700	5.36162300	1.20074500
H	2.10675300	5.68423200	1.94114600
C	4.91976000	4.64811400	0.30971700
H	4.96875300	3.12746100	-1.22755100
H	4.55169900	6.11666400	1.85642500
H	5.99420400	4.84225800	0.26708800

Ir(COD)OAc:

Ir	-0.11897000	-1.18114200	0.24163400
C	0.94122300	-1.84655500	3.14376700
C	1.21058400	-3.08625200	2.26493600
C	-1.88100100	-2.65372700	2.30297600
C	-2.09602400	-1.13514300	2.45057500
H	1.86857500	-1.57091100	3.66606900
H	0.21392000	-2.07943300	3.93278800
H	2.25629400	-3.09134500	1.92668200
H	1.08536500	-4.01184800	2.85421100
H	-2.86242200	-3.14082700	2.22182200
H	-1.39694600	-3.07950400	3.19128300
H	-2.90784400	-0.85427700	1.76348800
H	-2.44305500	-0.86835900	3.46459200
C	-0.87939900	-0.30775300	2.09972100
H	-1.09530400	0.74197100	1.87230900
C	0.45674600	-0.63756600	2.35284600
H	1.14495500	0.20791700	2.33101900
C	0.32971200	-3.16743900	1.04444200
H	0.75314900	-3.70189700	0.18894000
C	-1.07007200	-2.97167800	1.05451400
H	-1.62808100	-3.38747600	0.20901700

O	1.05398900	-3.43133200	-2.00192900
C	0.04362200	-2.82529600	-2.33910500
O	-0.52324800	-1.87262700	-1.63802500
C	-0.68746600	-3.10651600	-3.63639500
H	-1.72553700	-3.40255600	-3.42155900
H	-0.73091100	-2.19088700	-4.24539400
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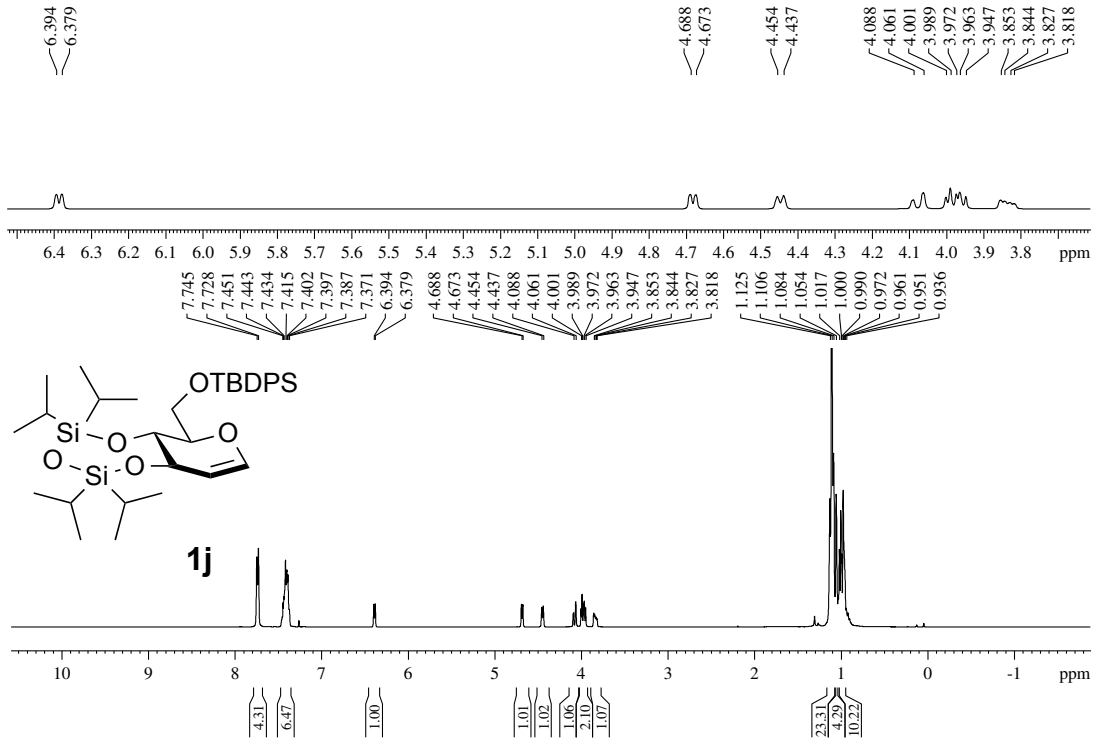
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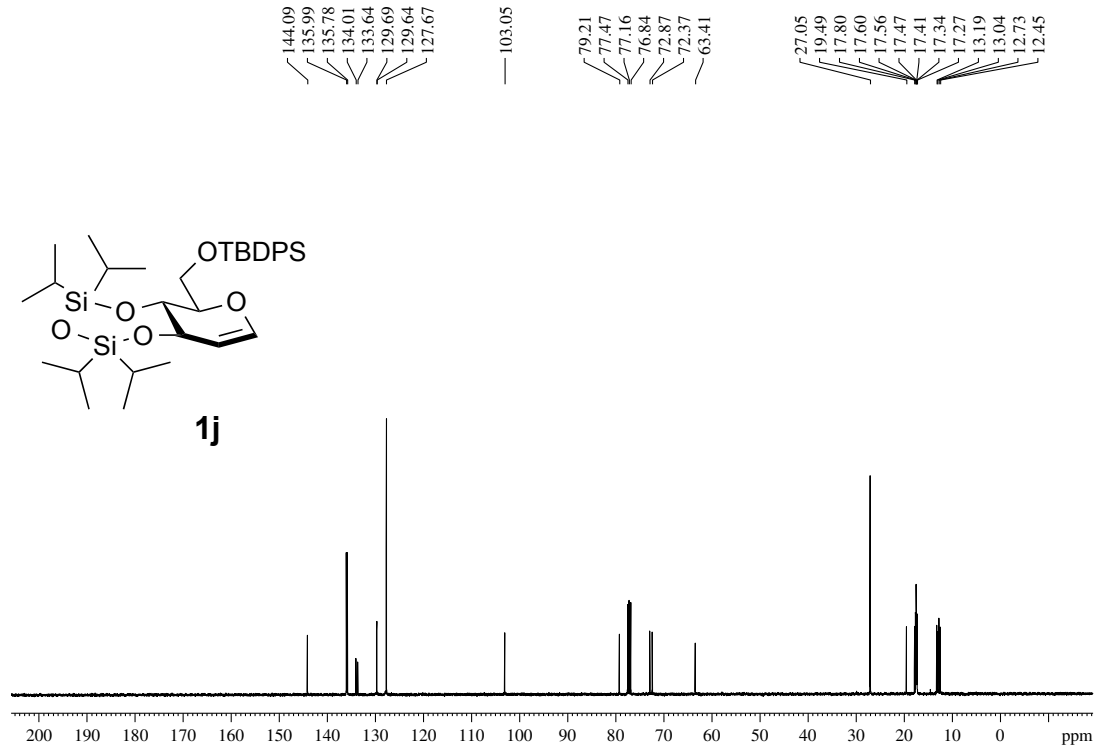
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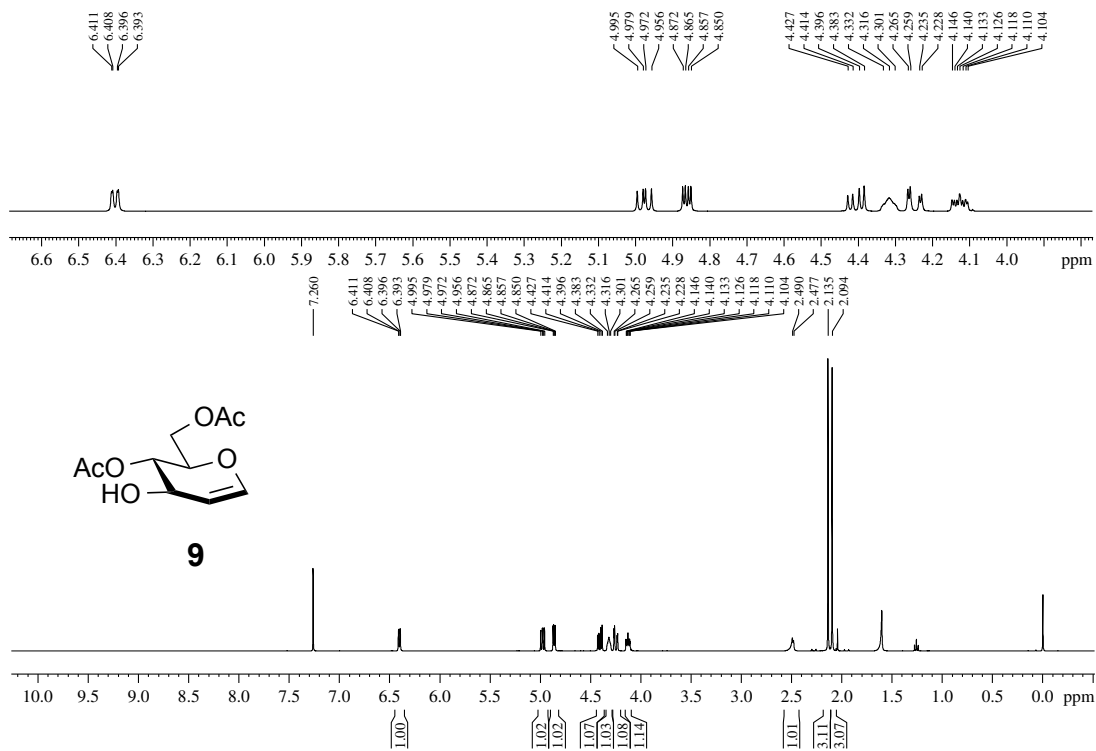
¹H NMR of **1j**, CDCl₃, 400 MHz



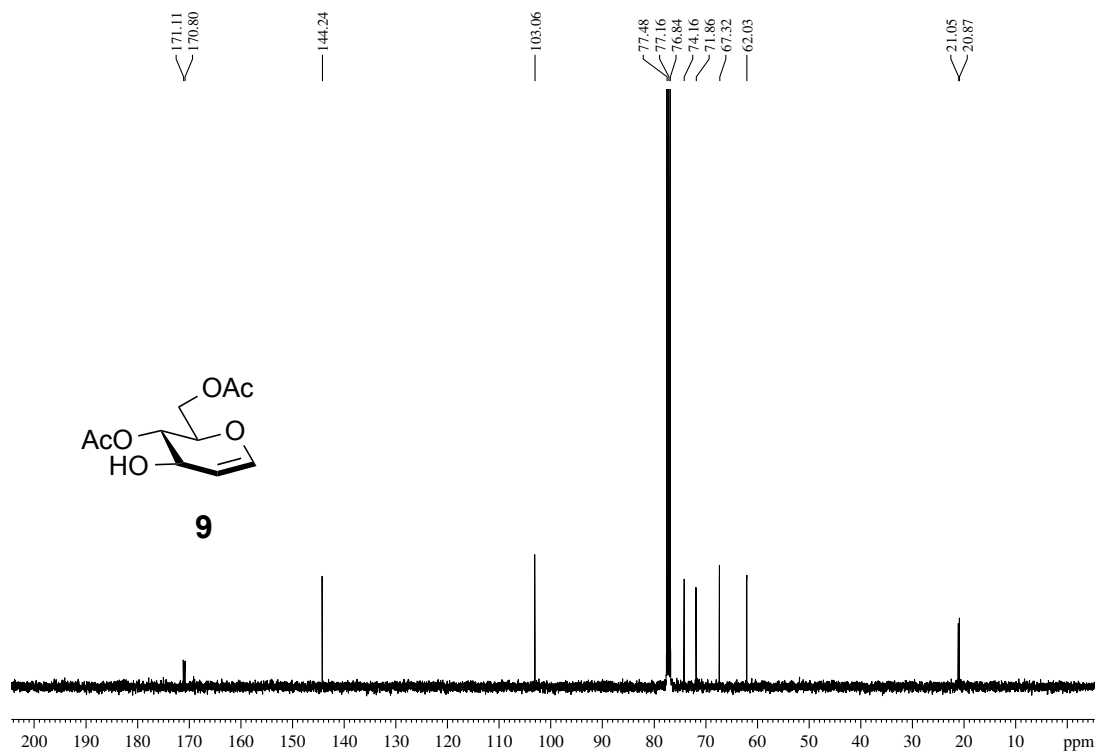
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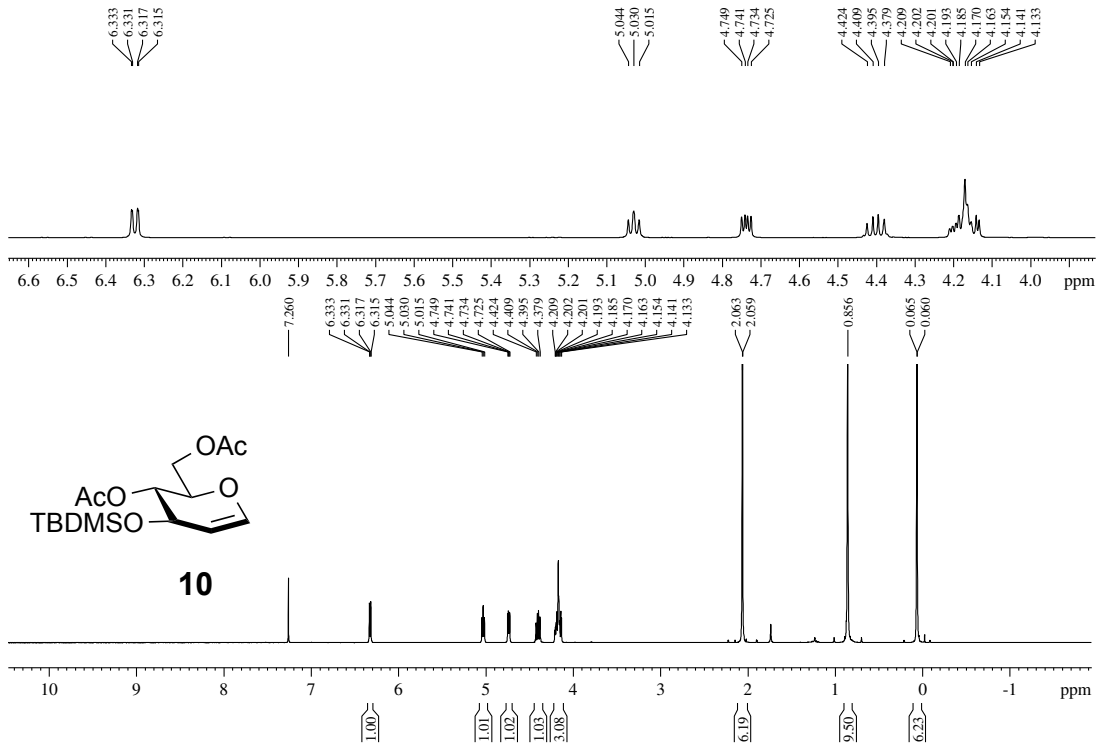
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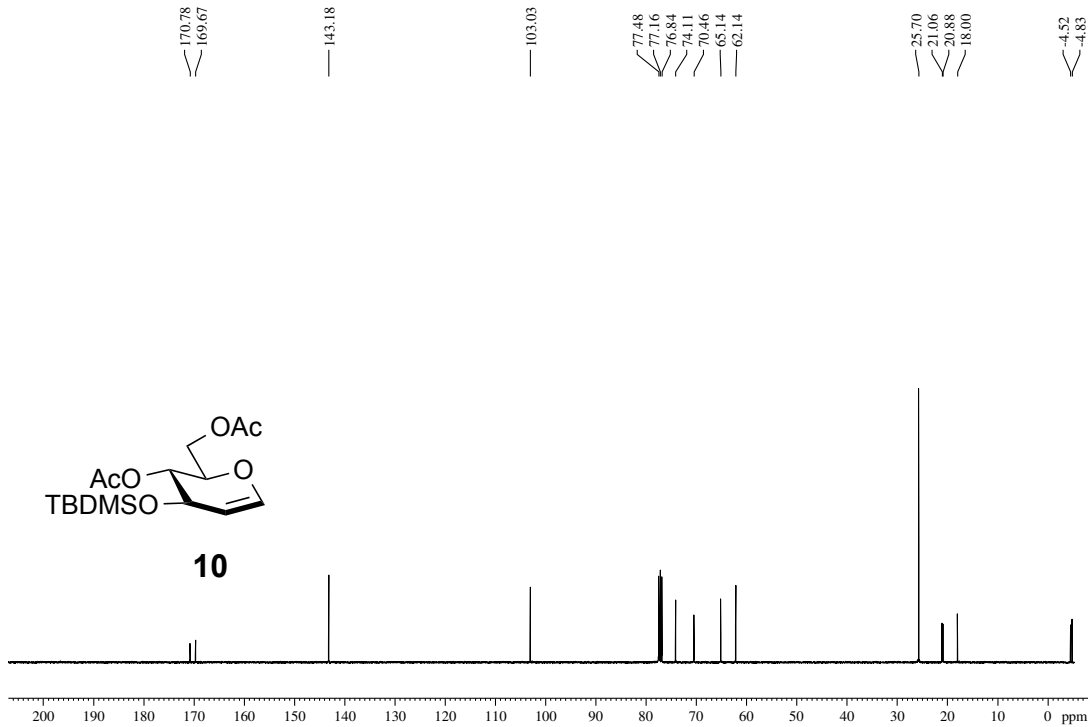
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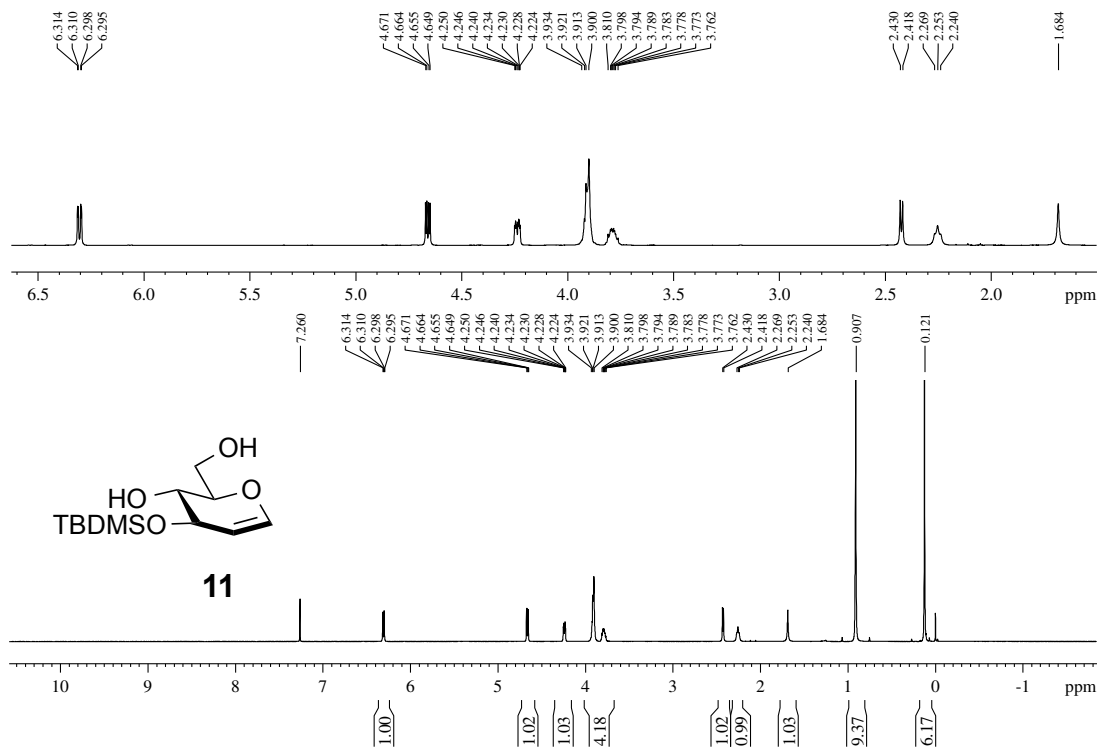
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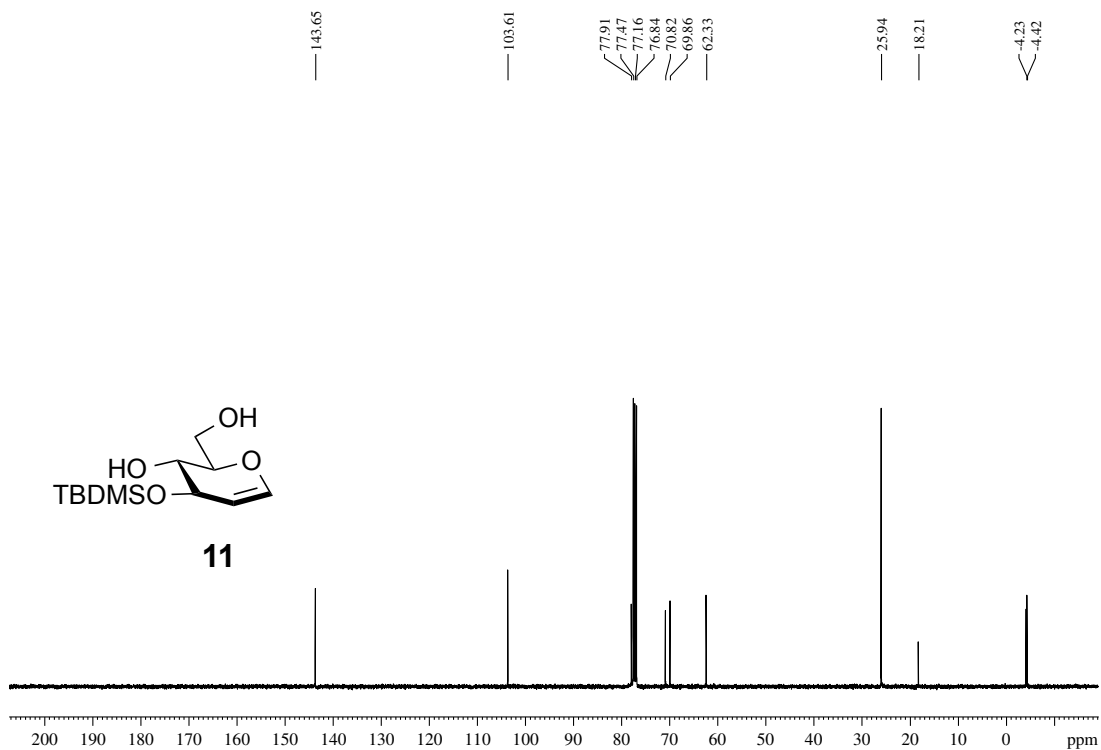
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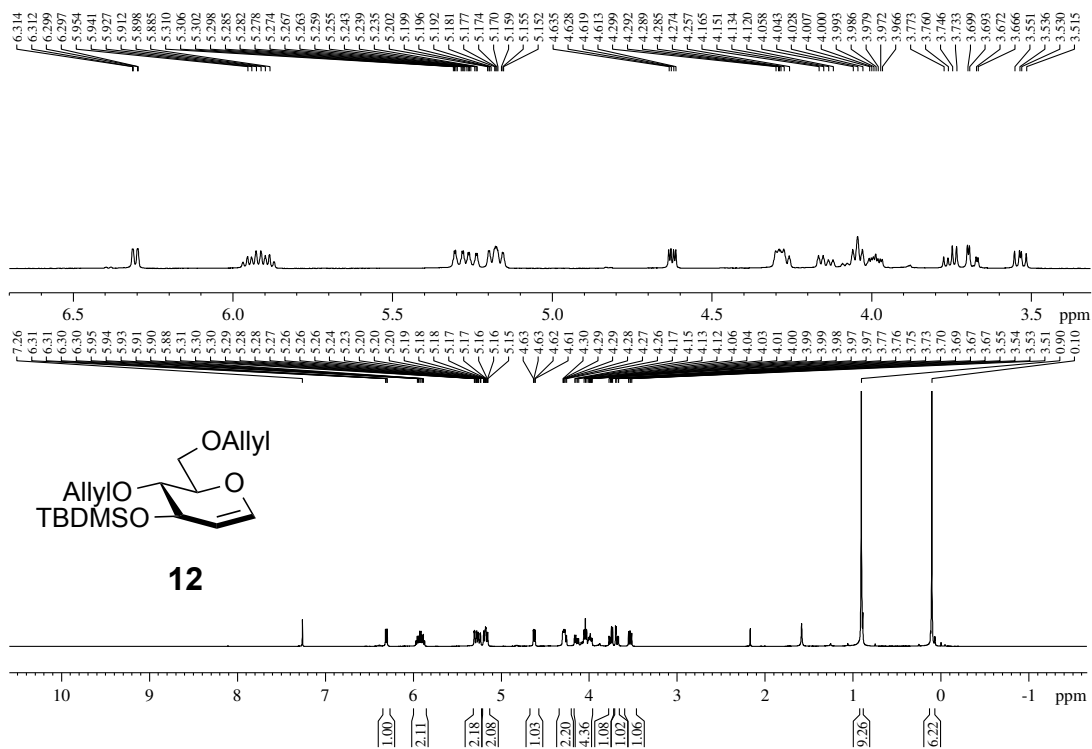
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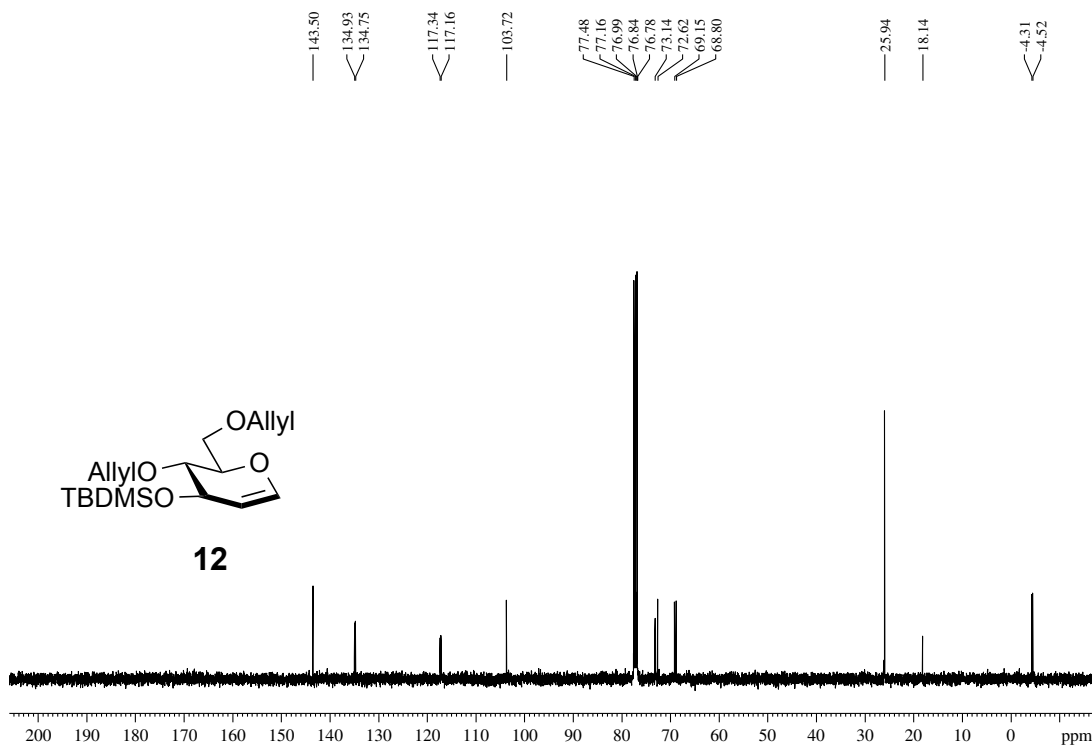
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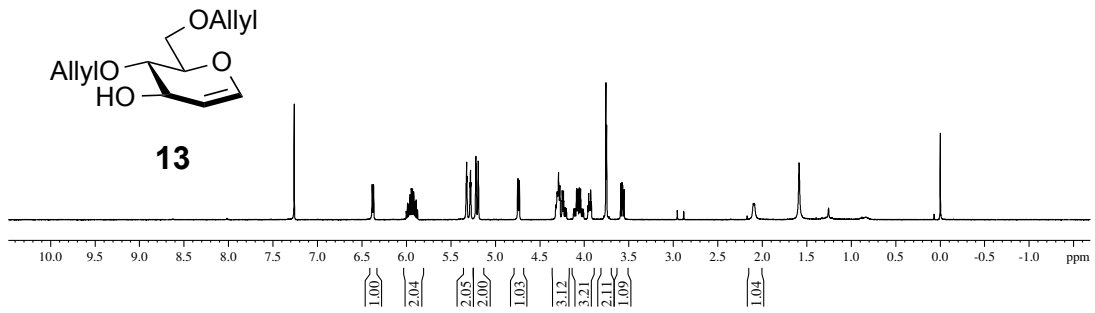
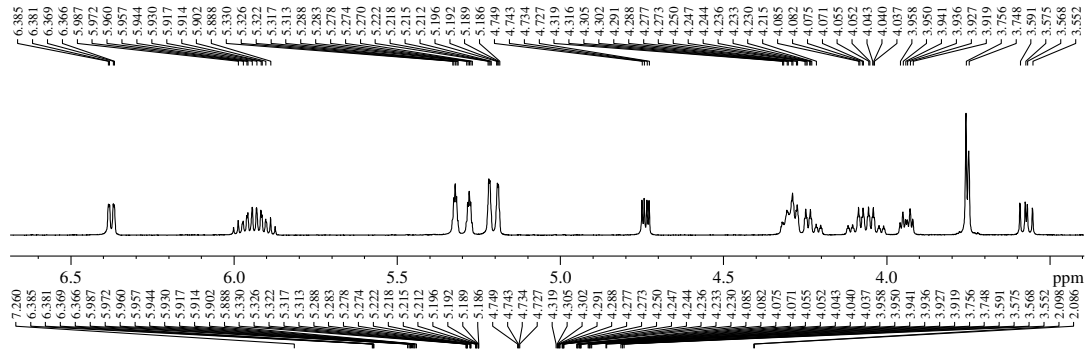
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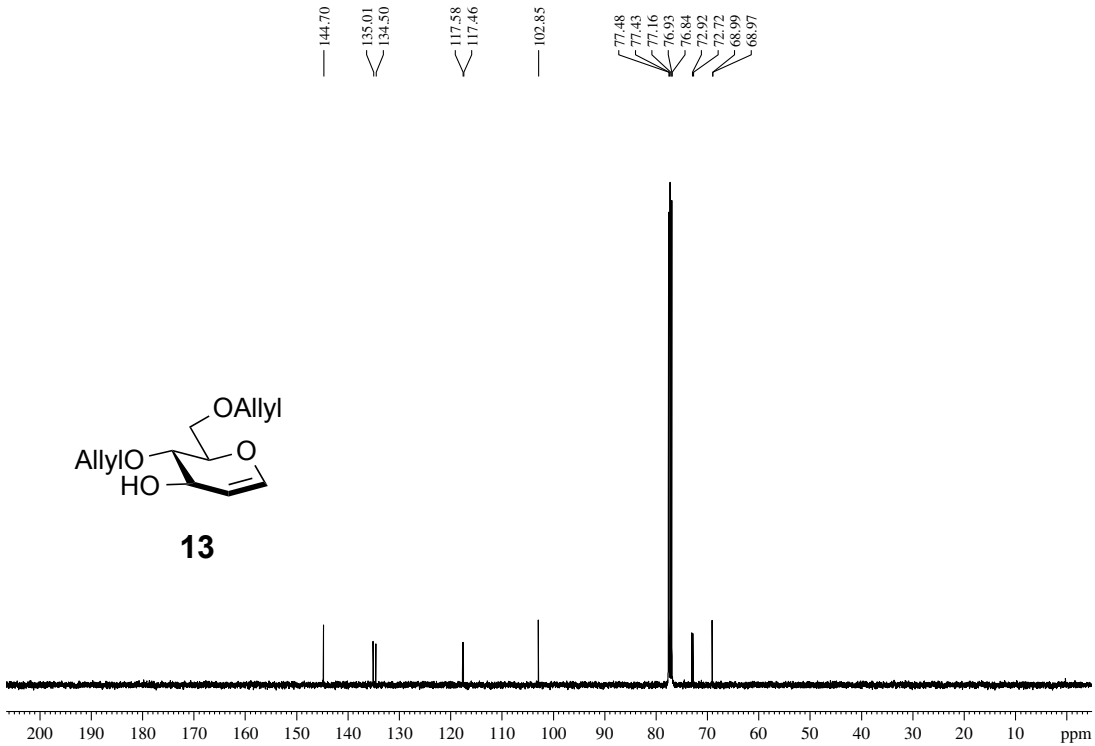
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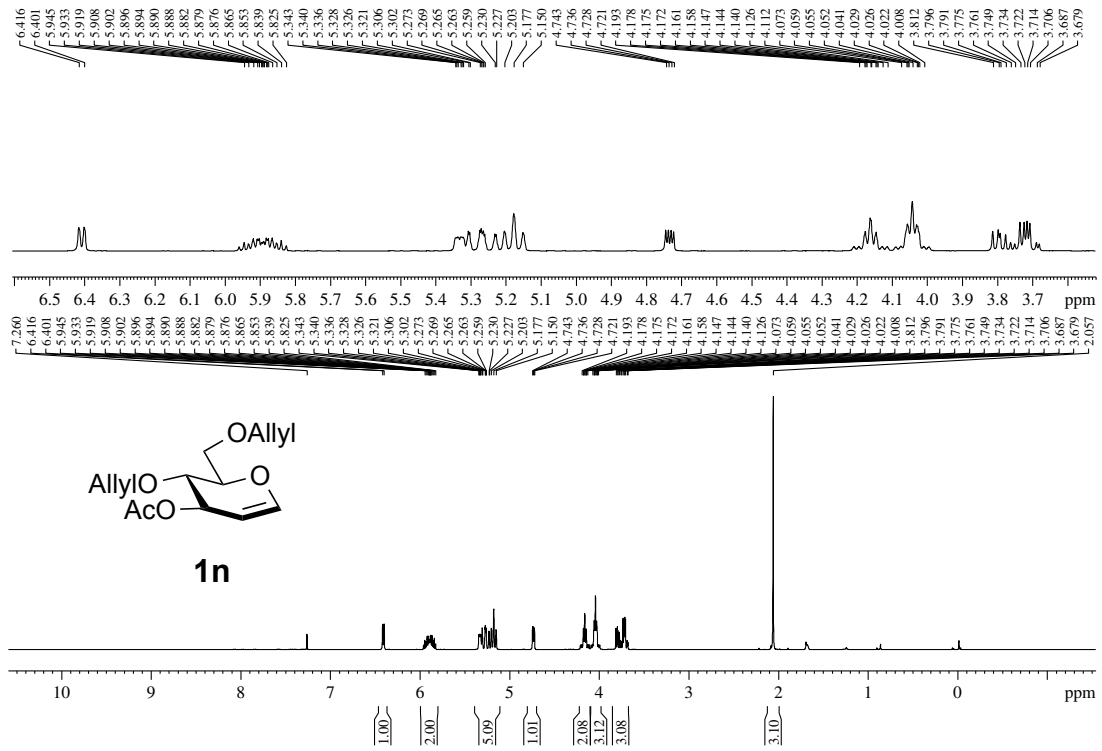
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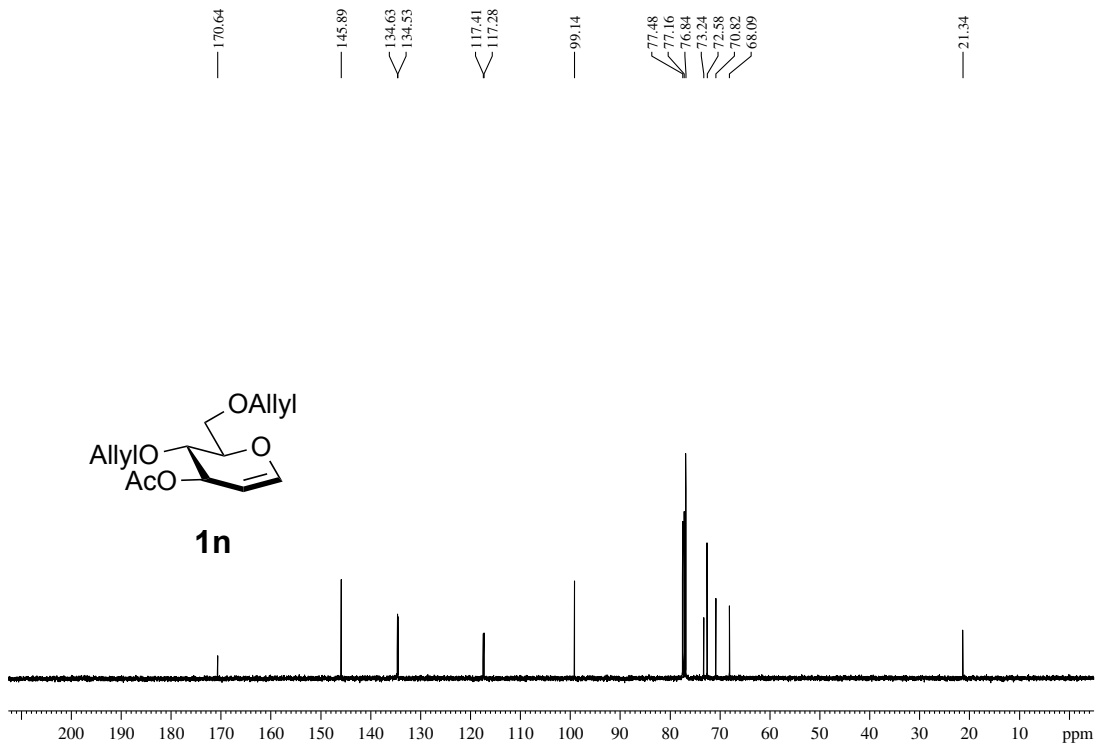
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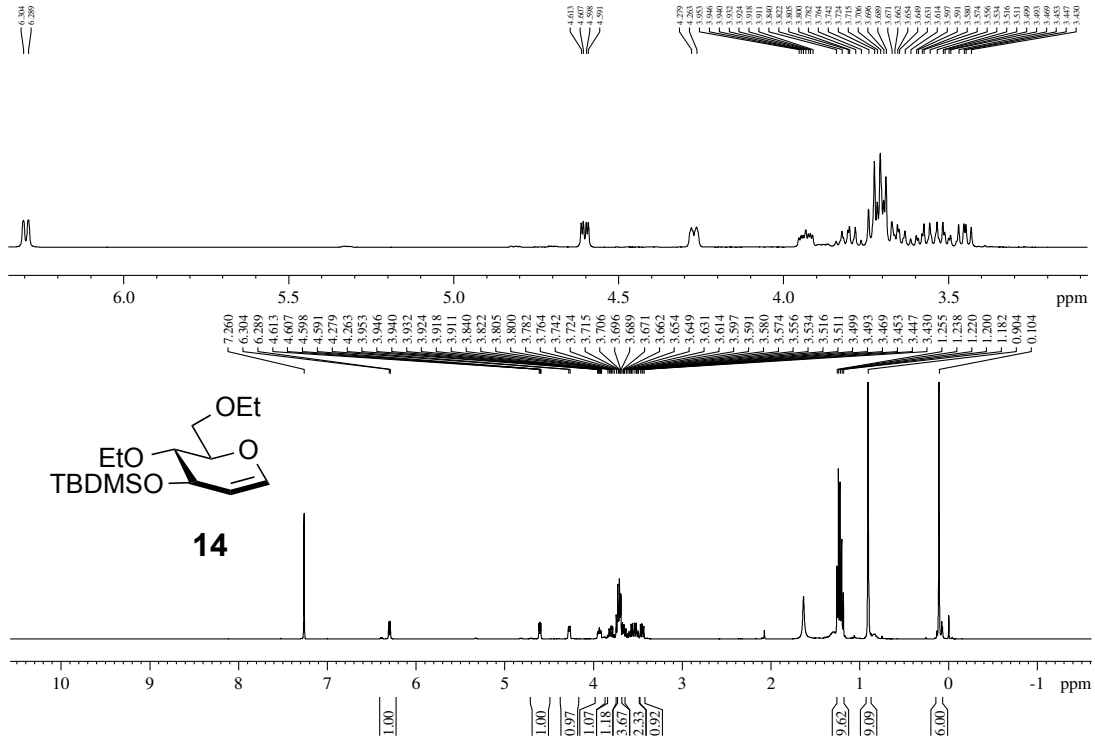
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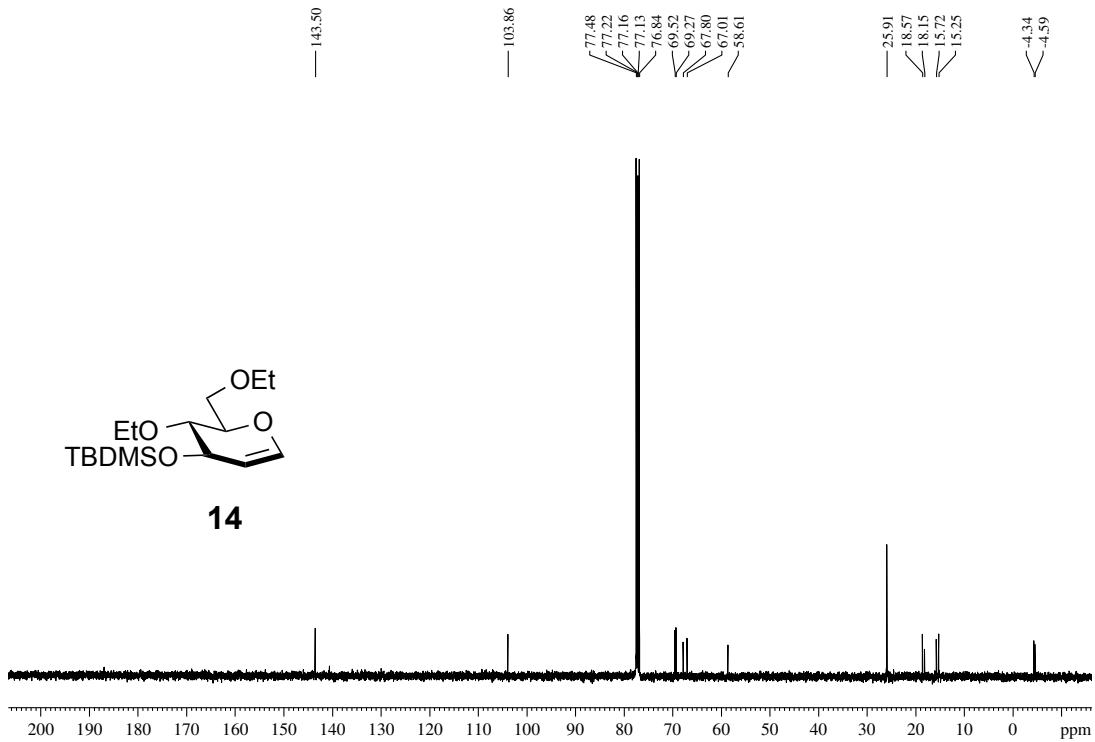
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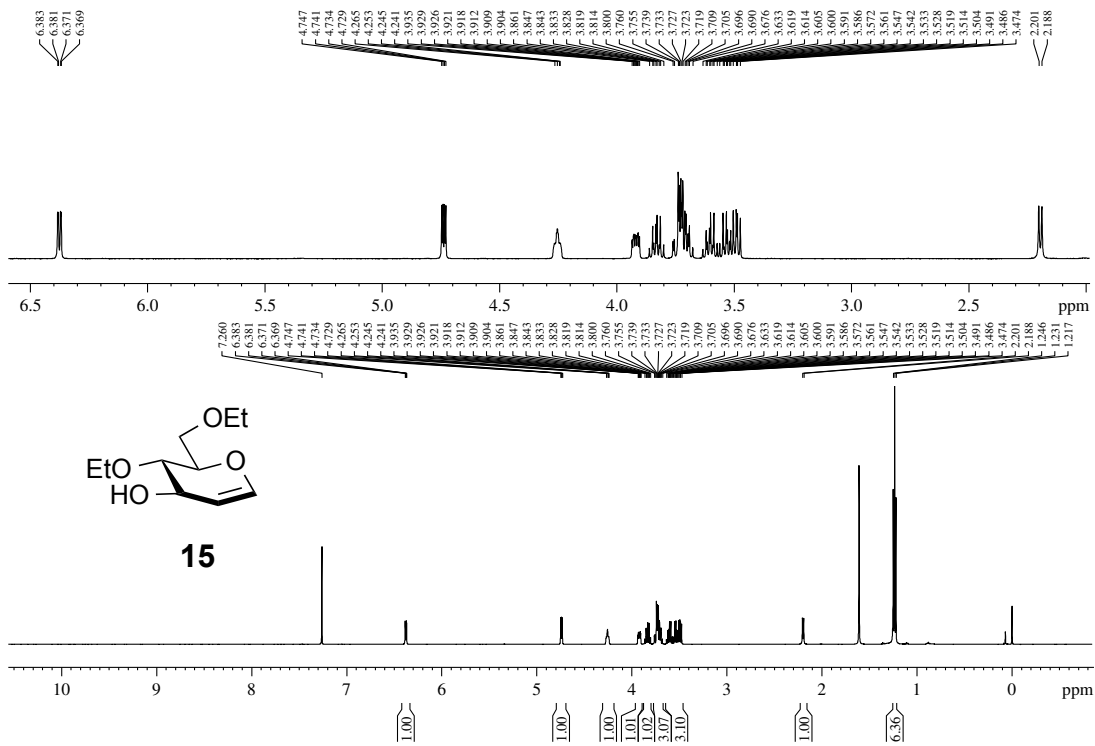
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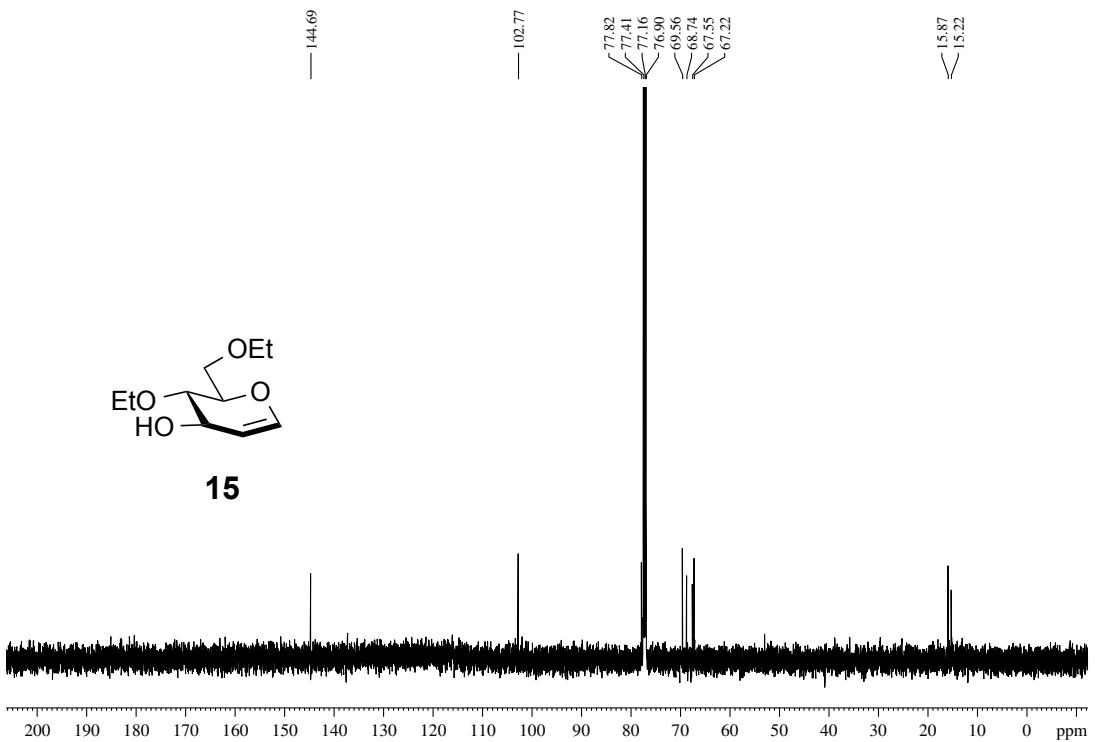
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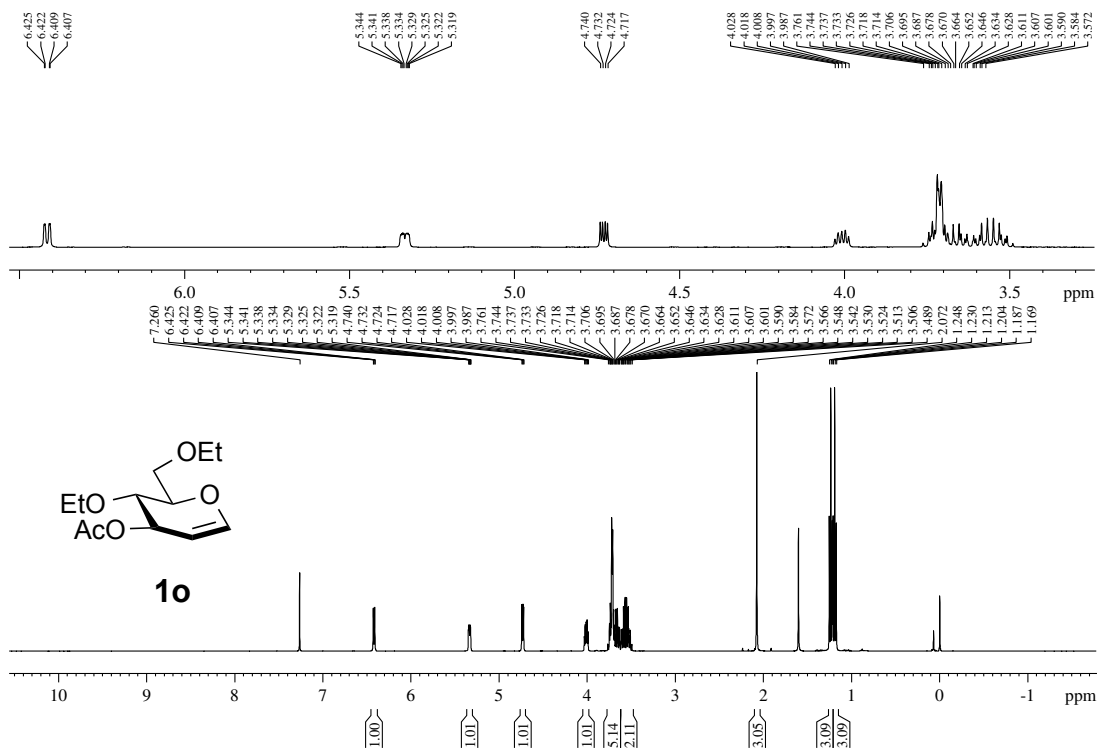
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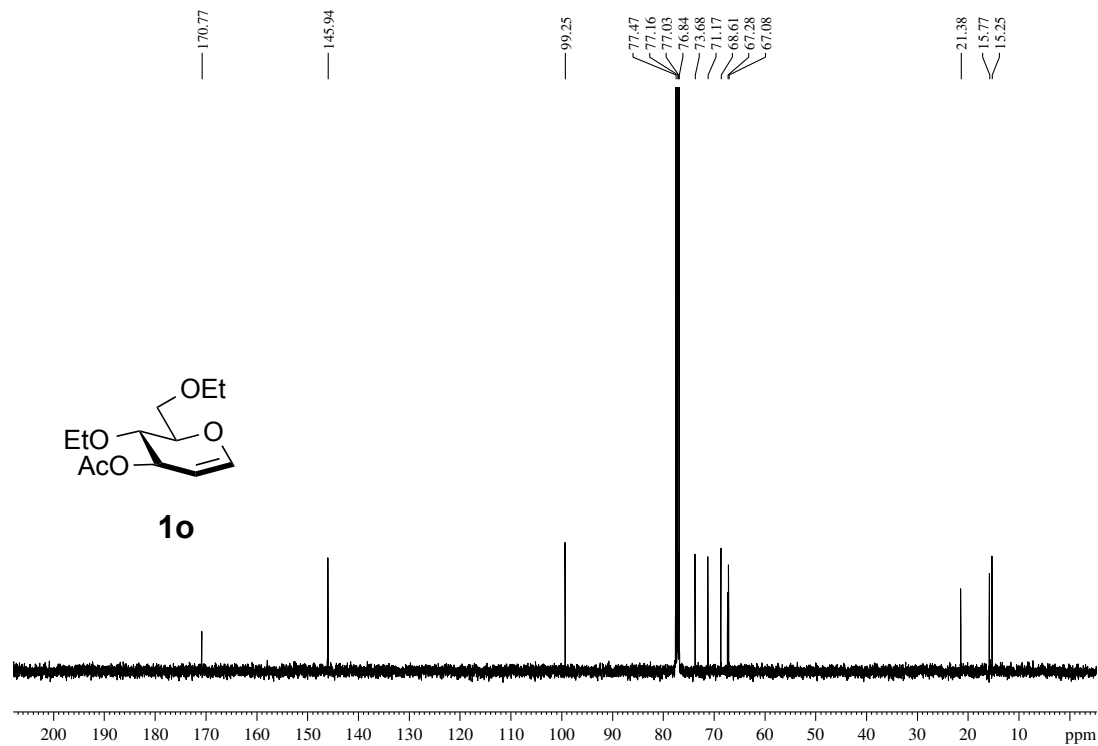
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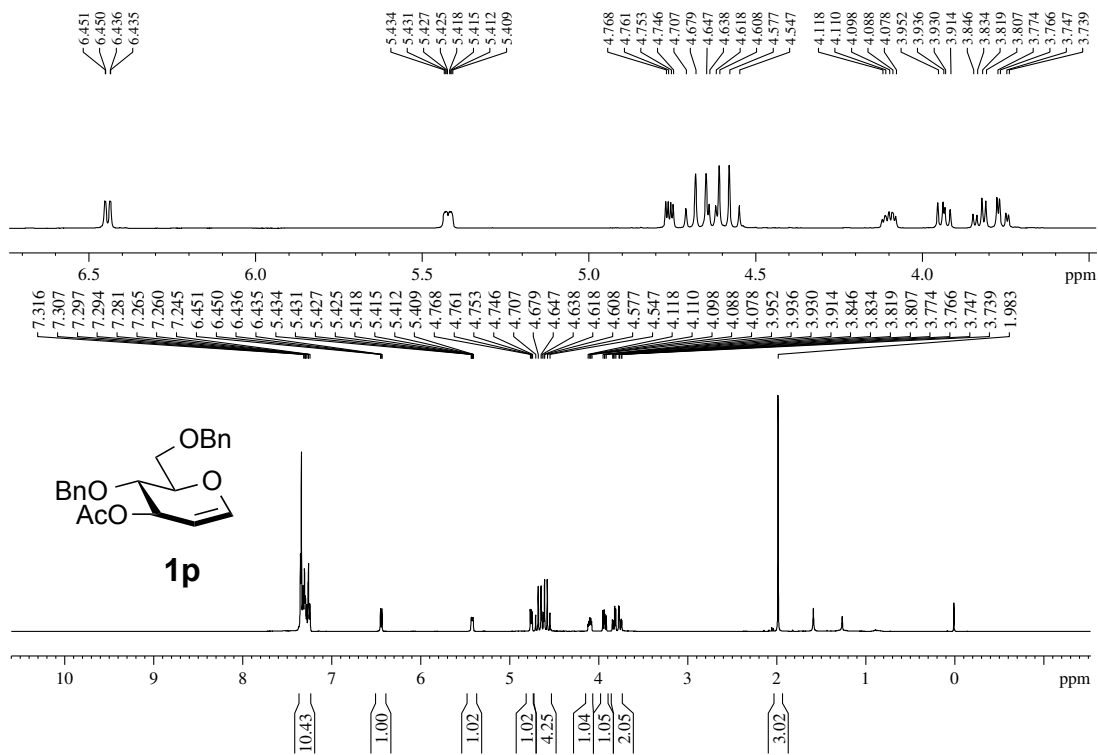
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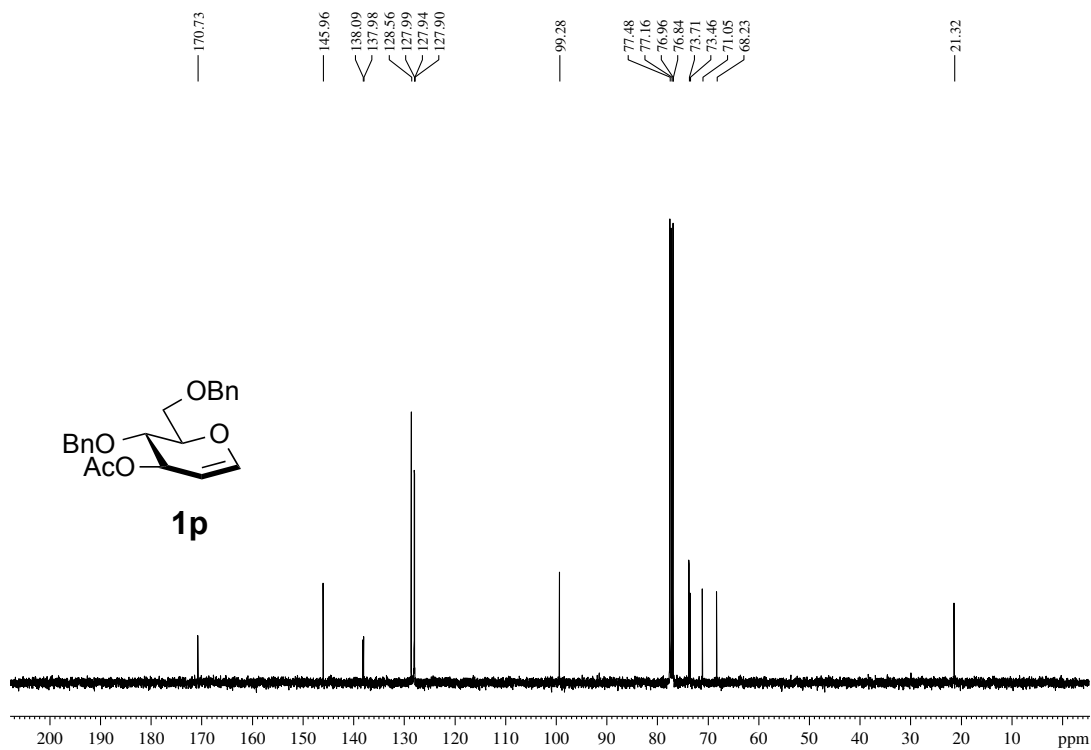
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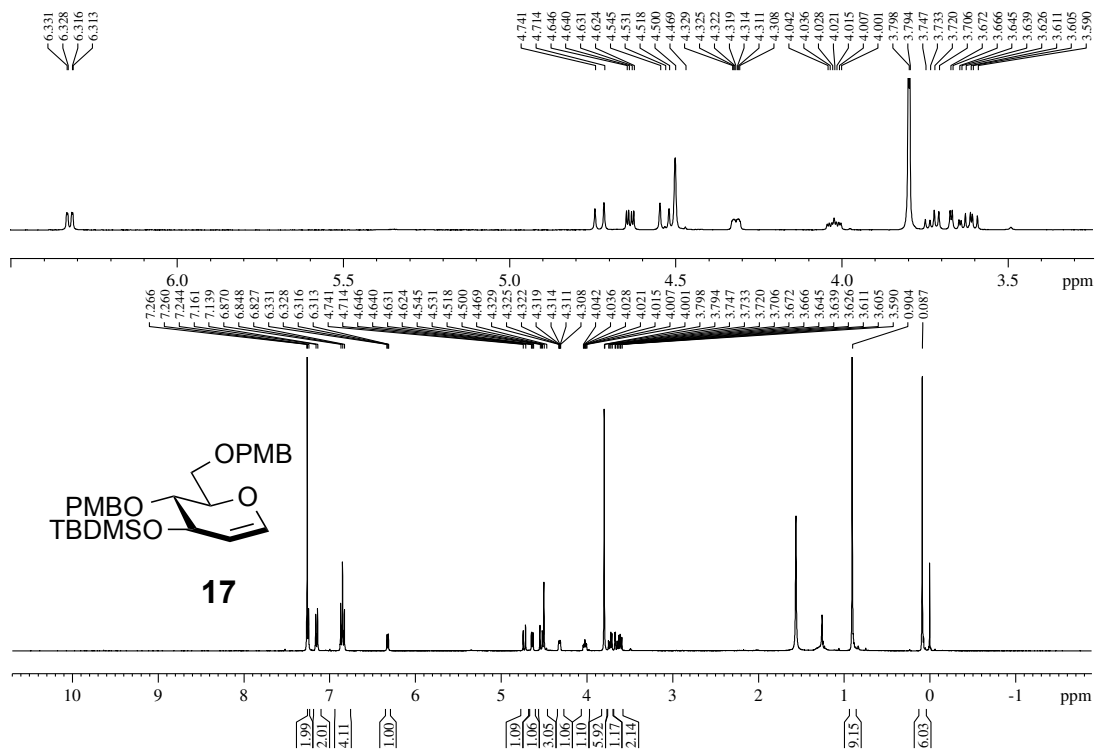
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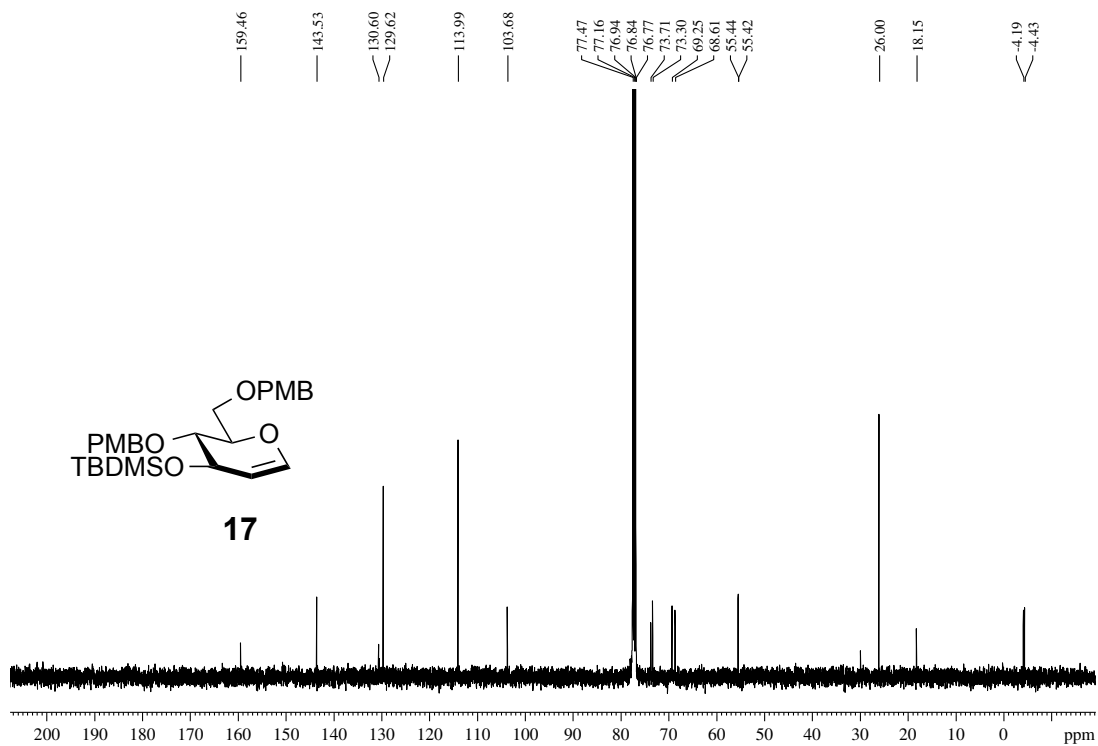
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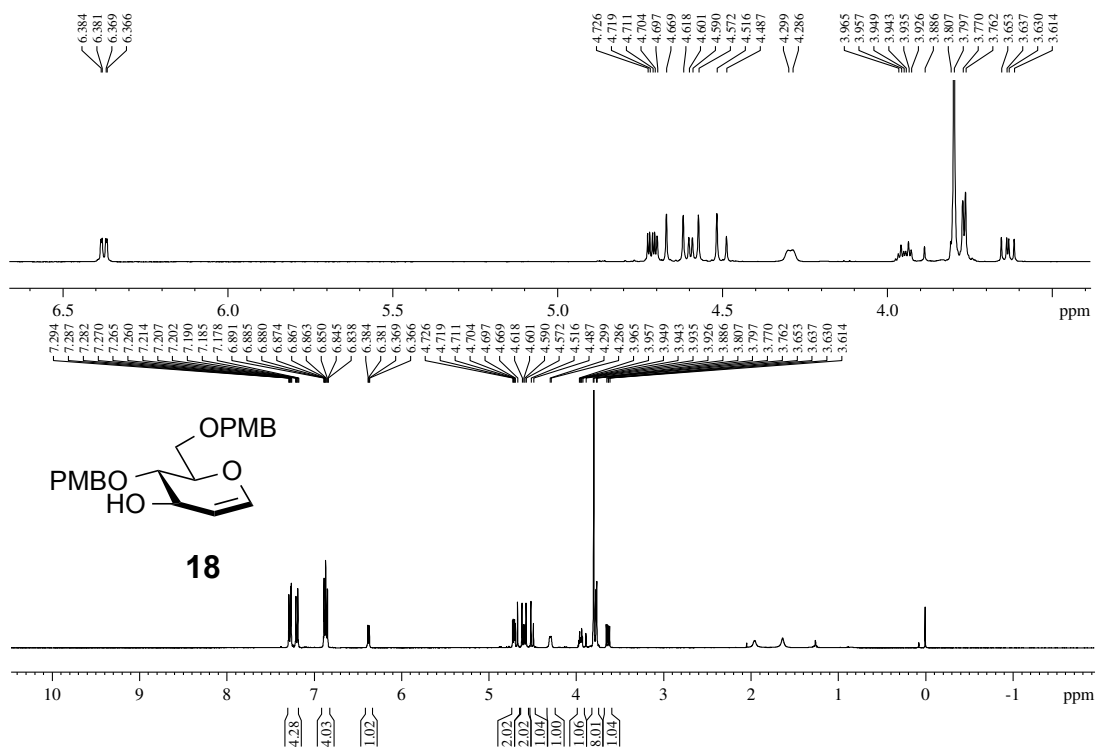
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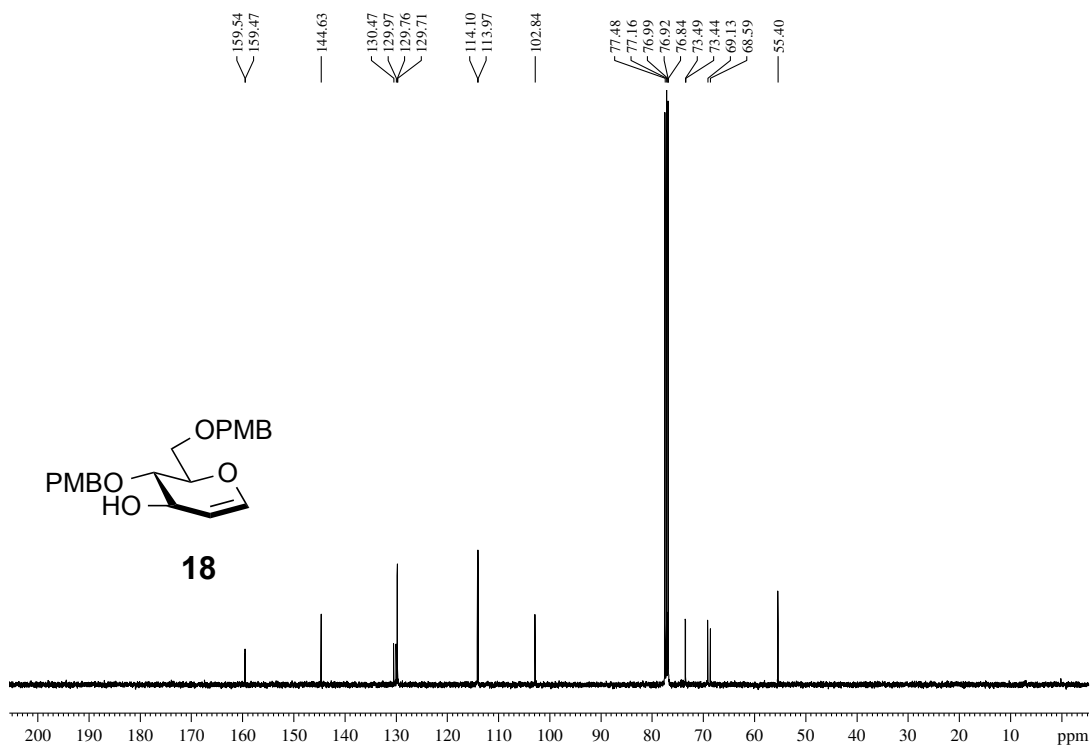
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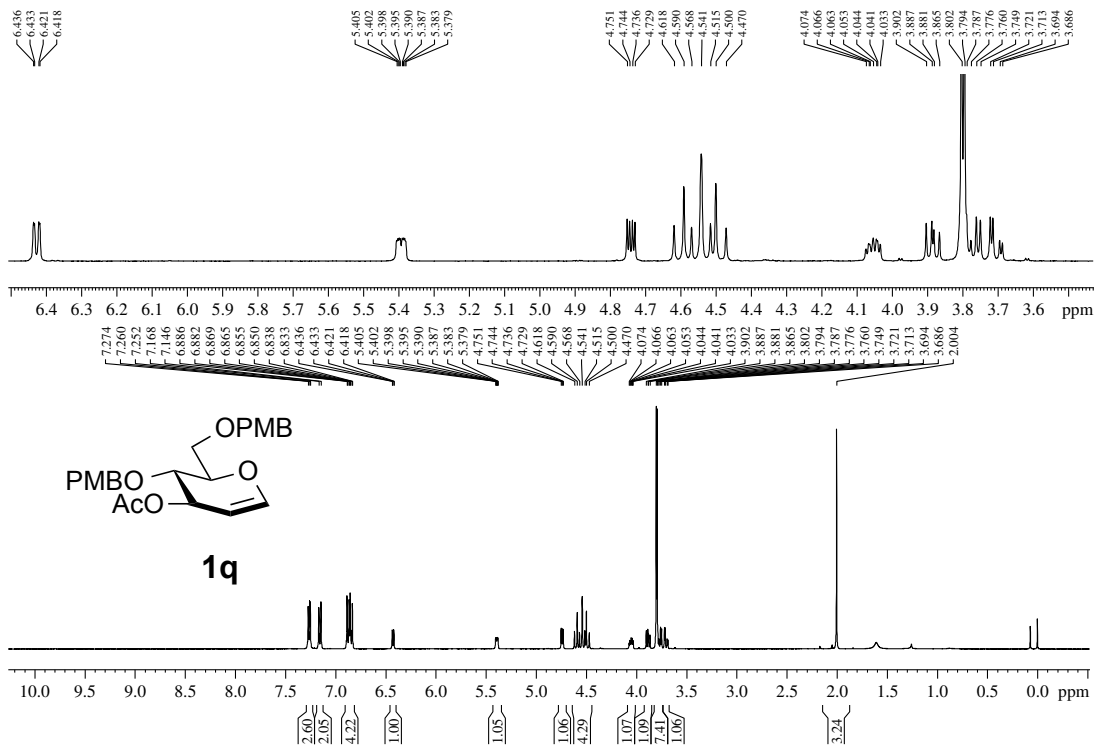
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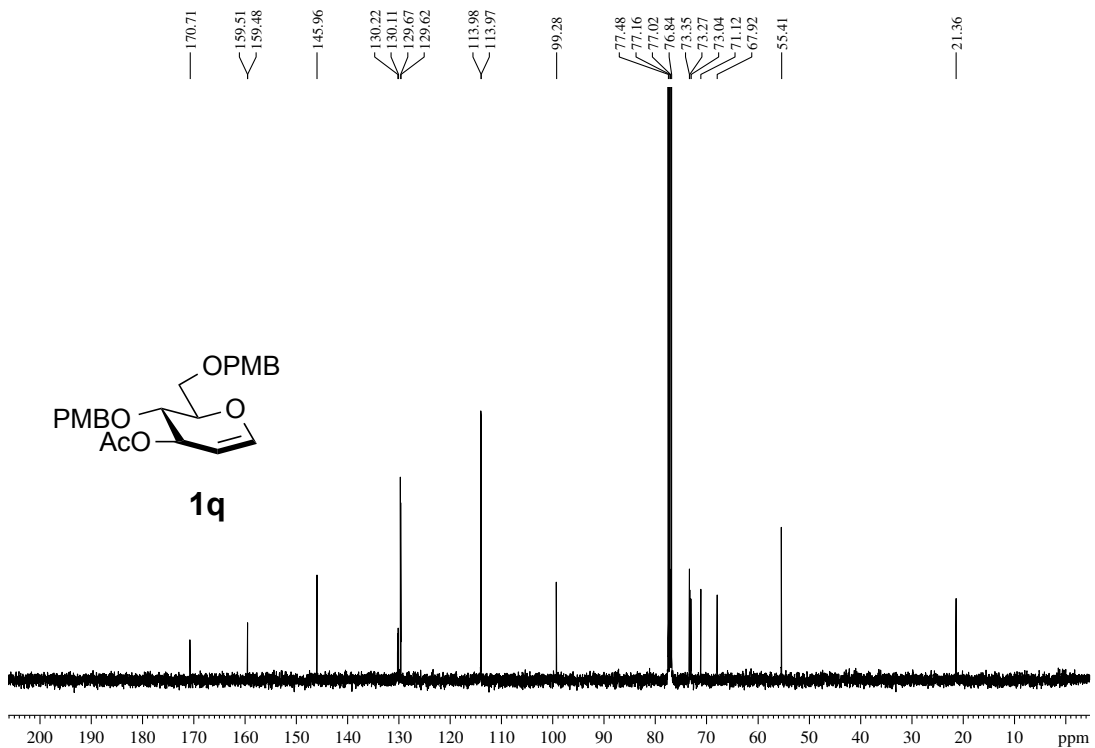
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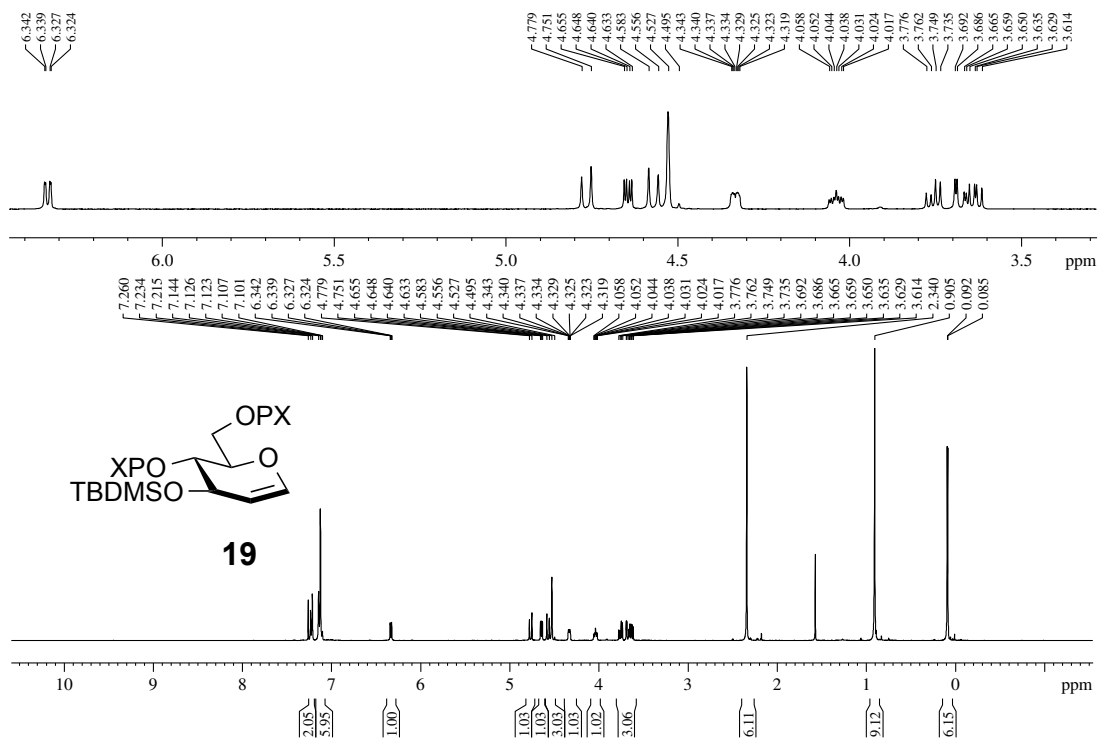
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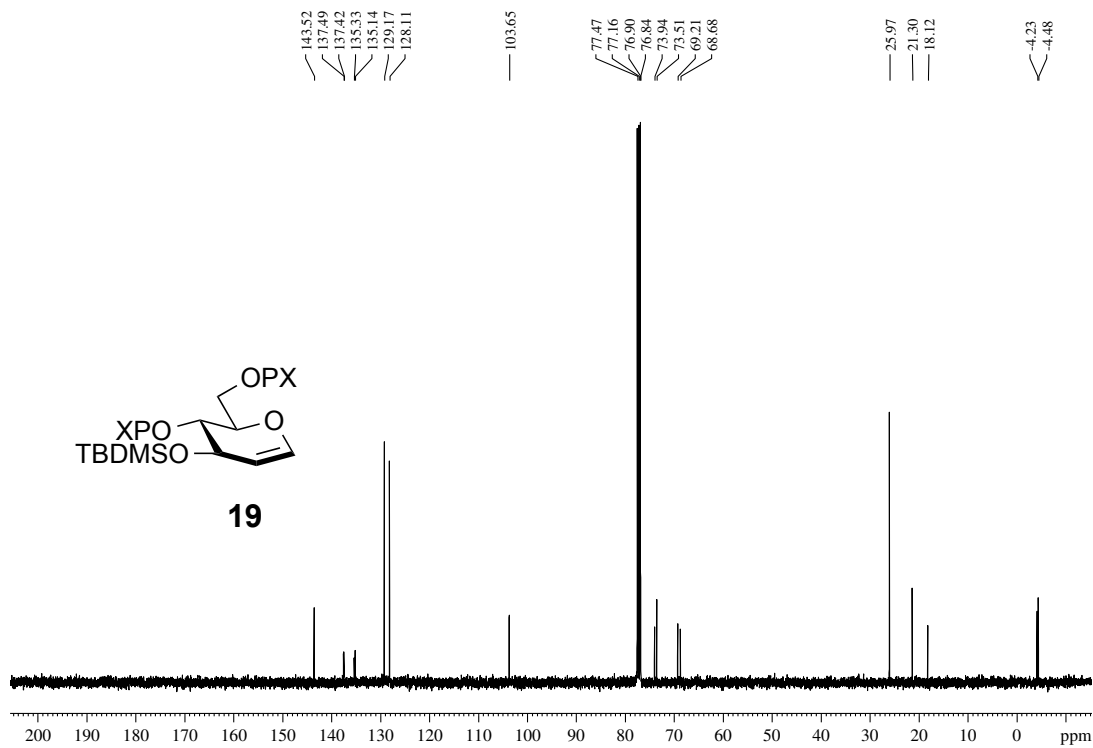
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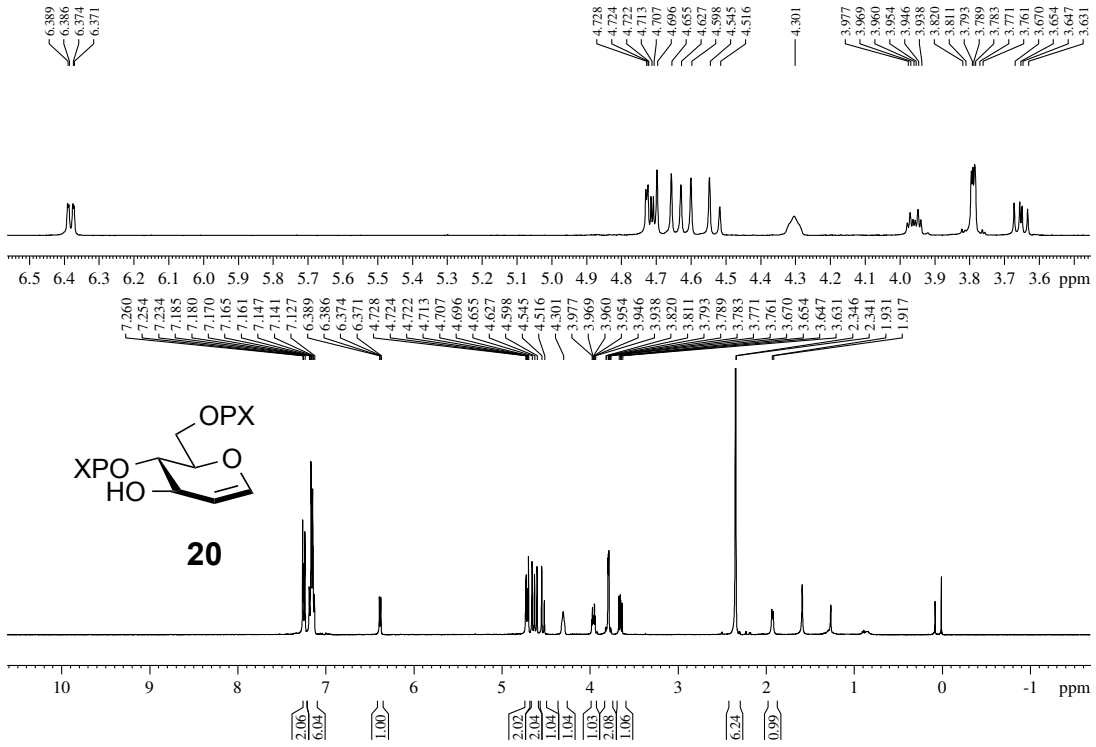
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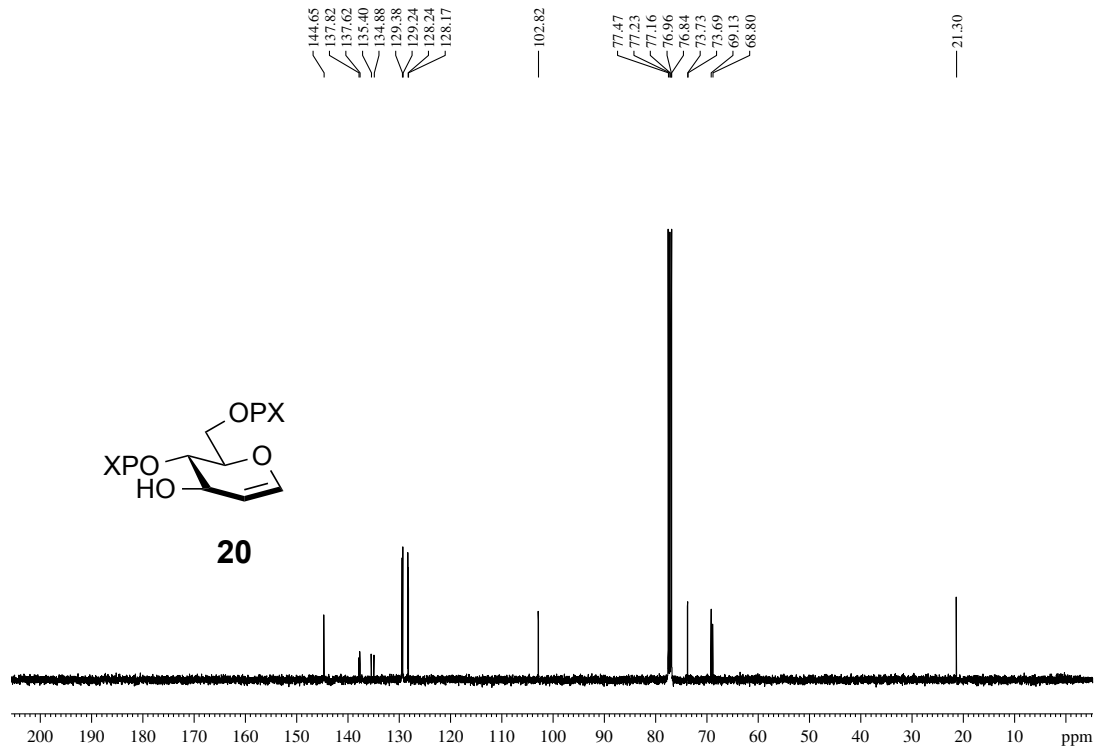
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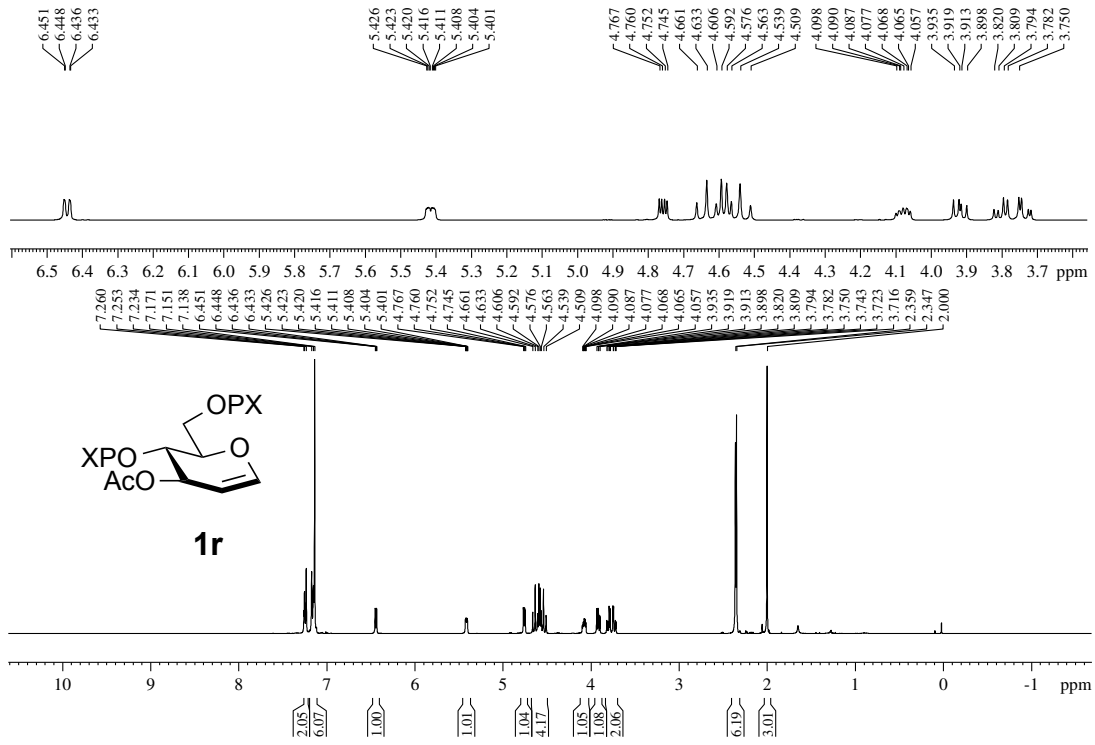
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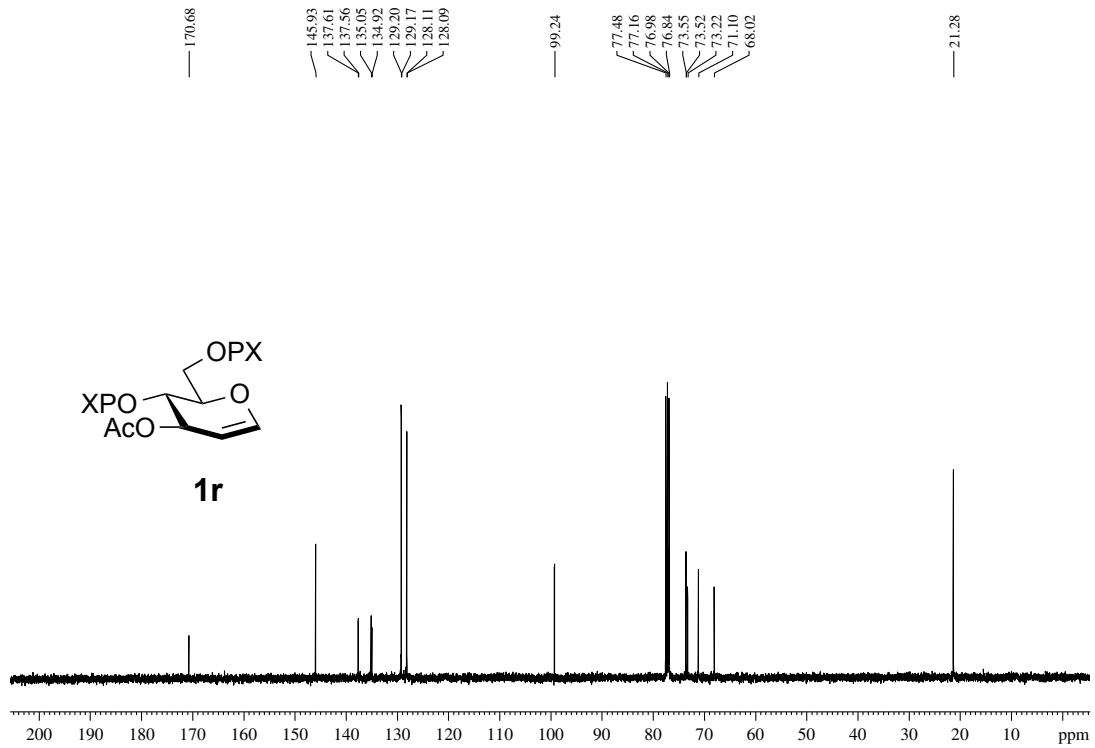
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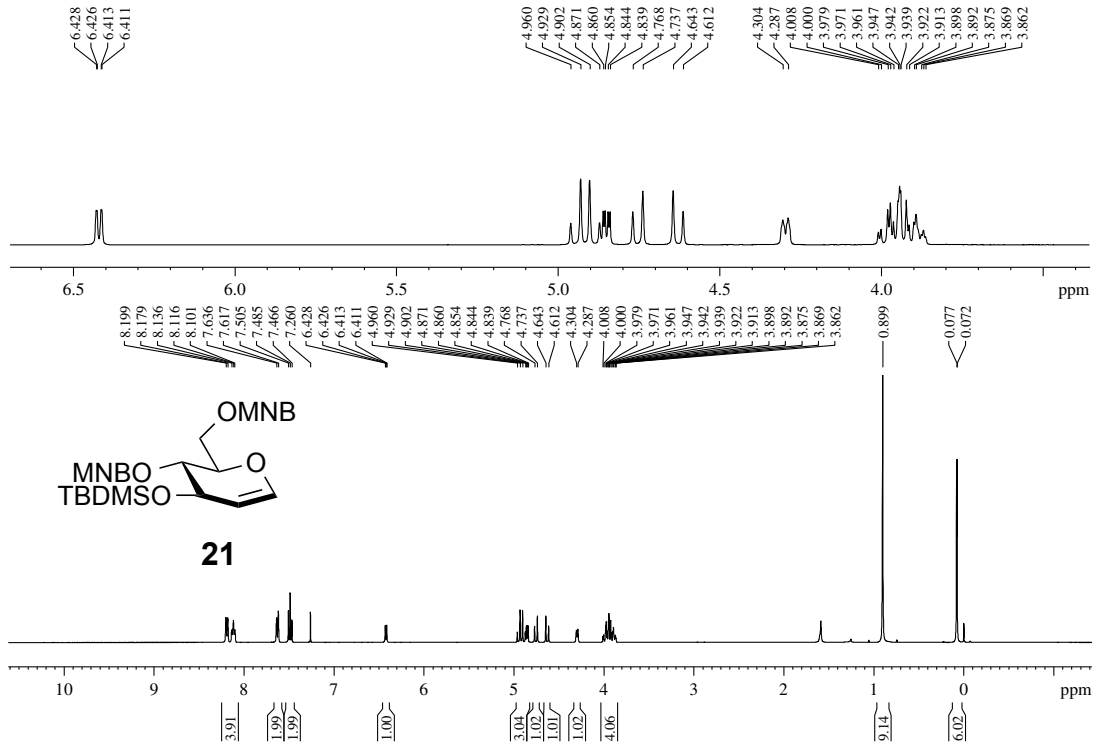
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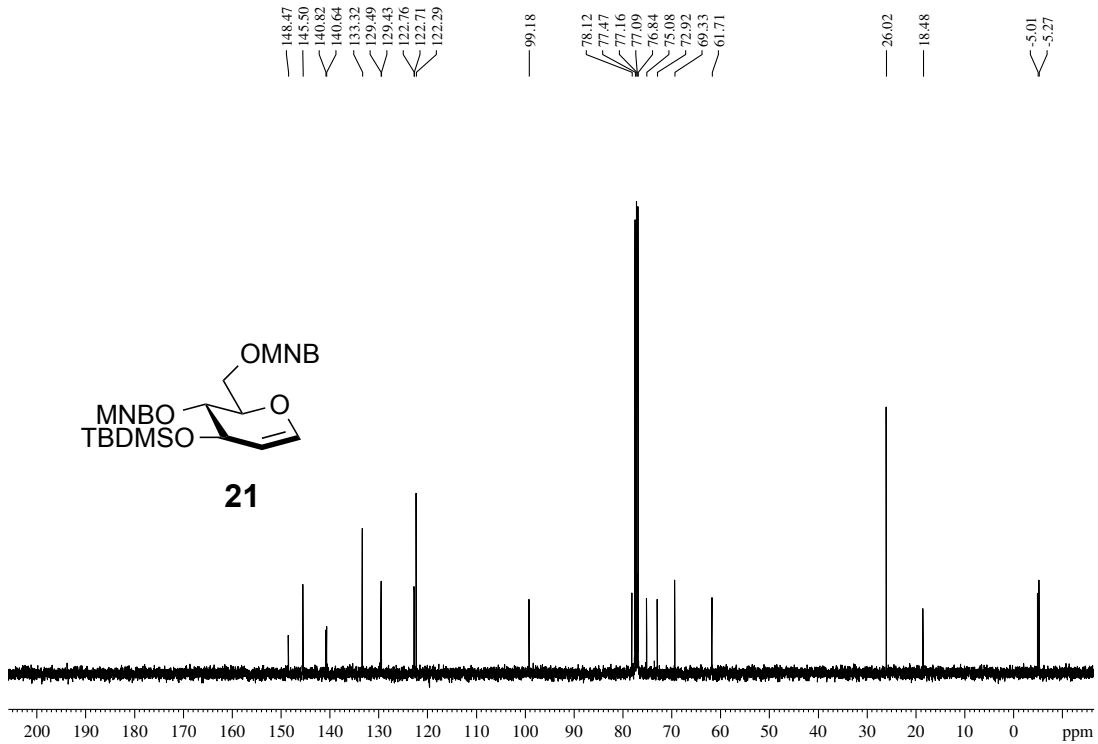
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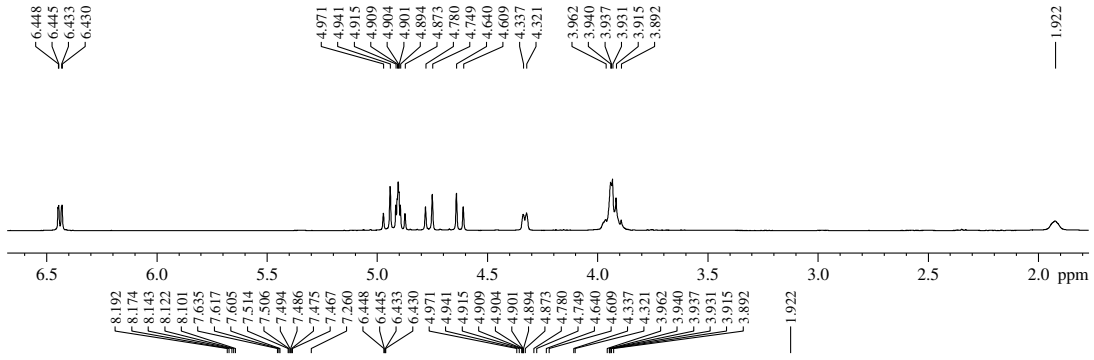
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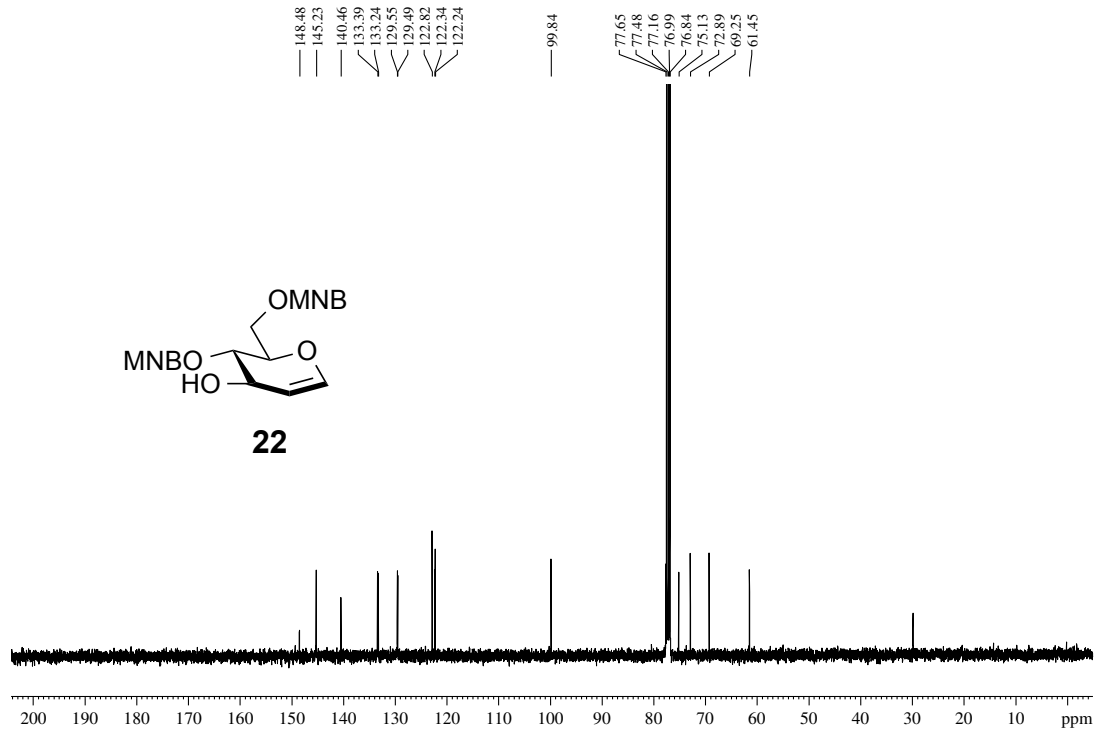
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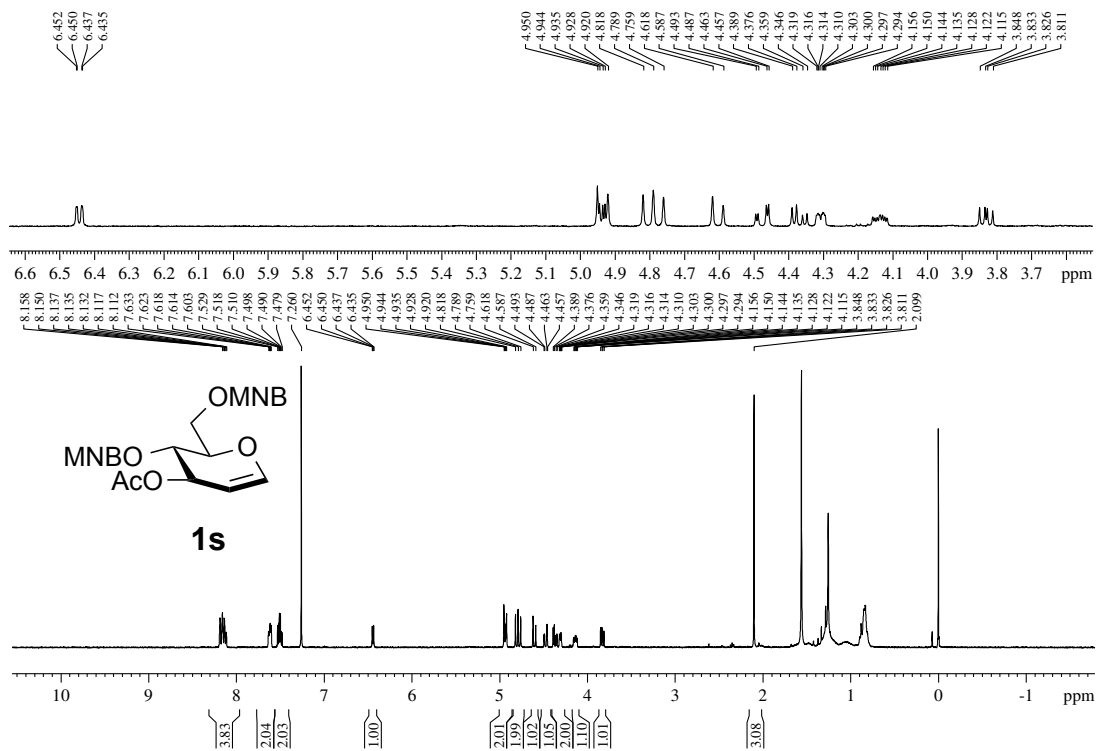
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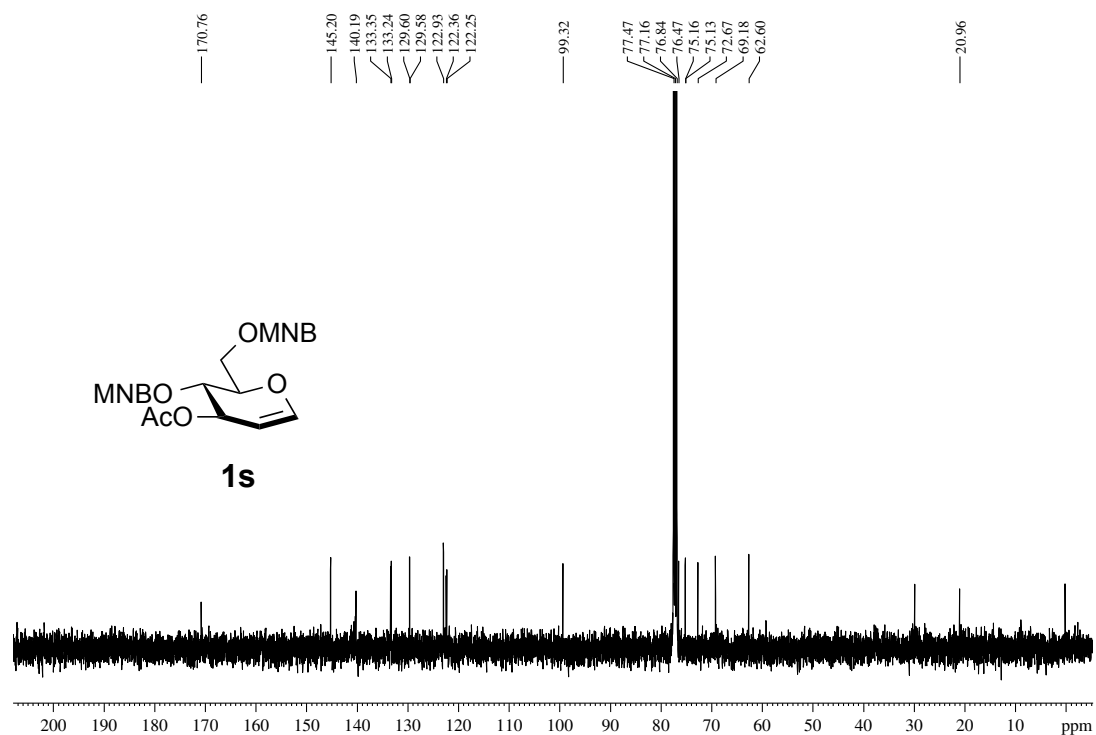
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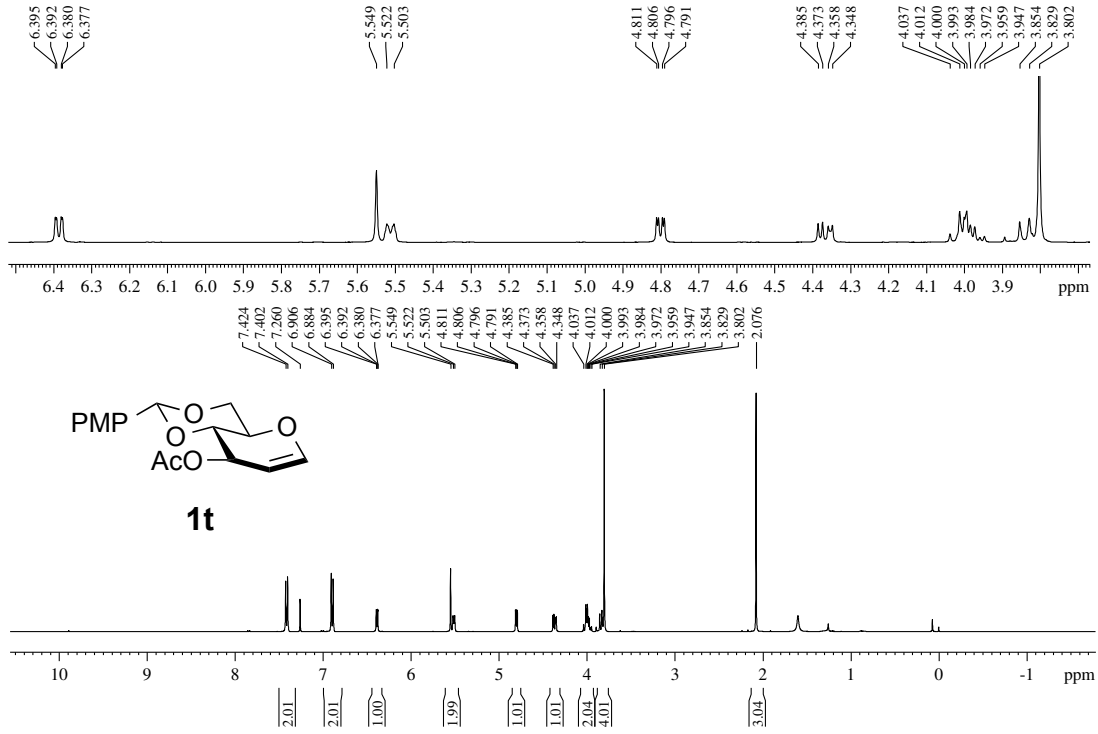
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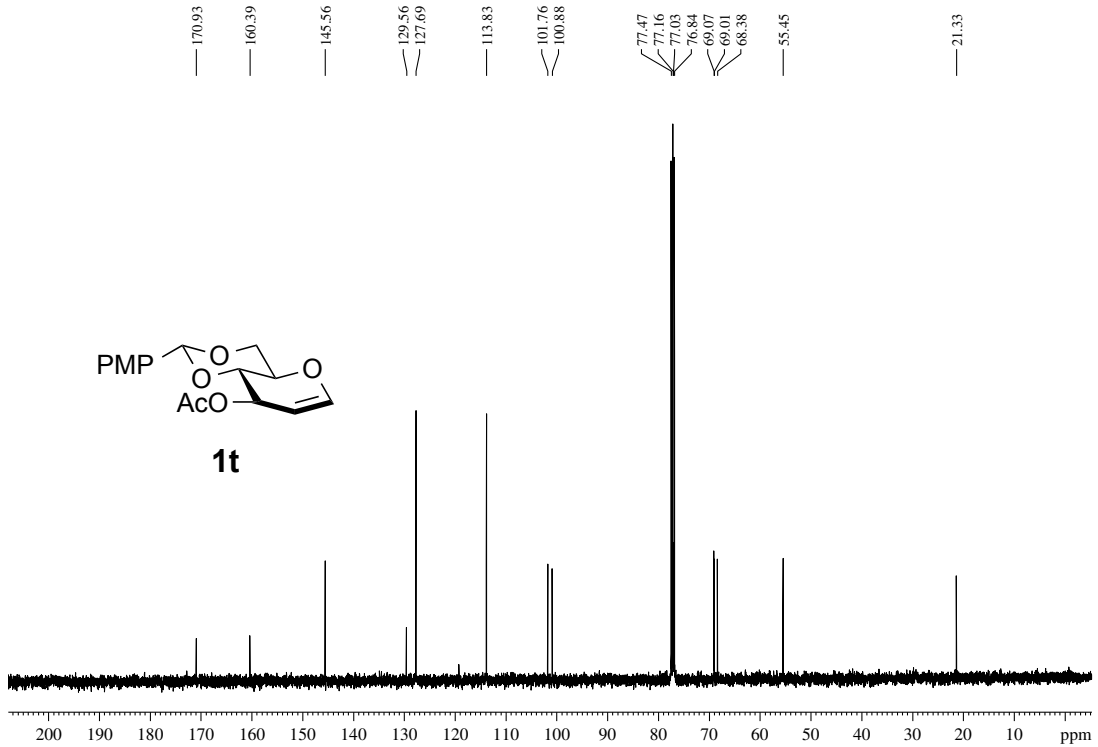
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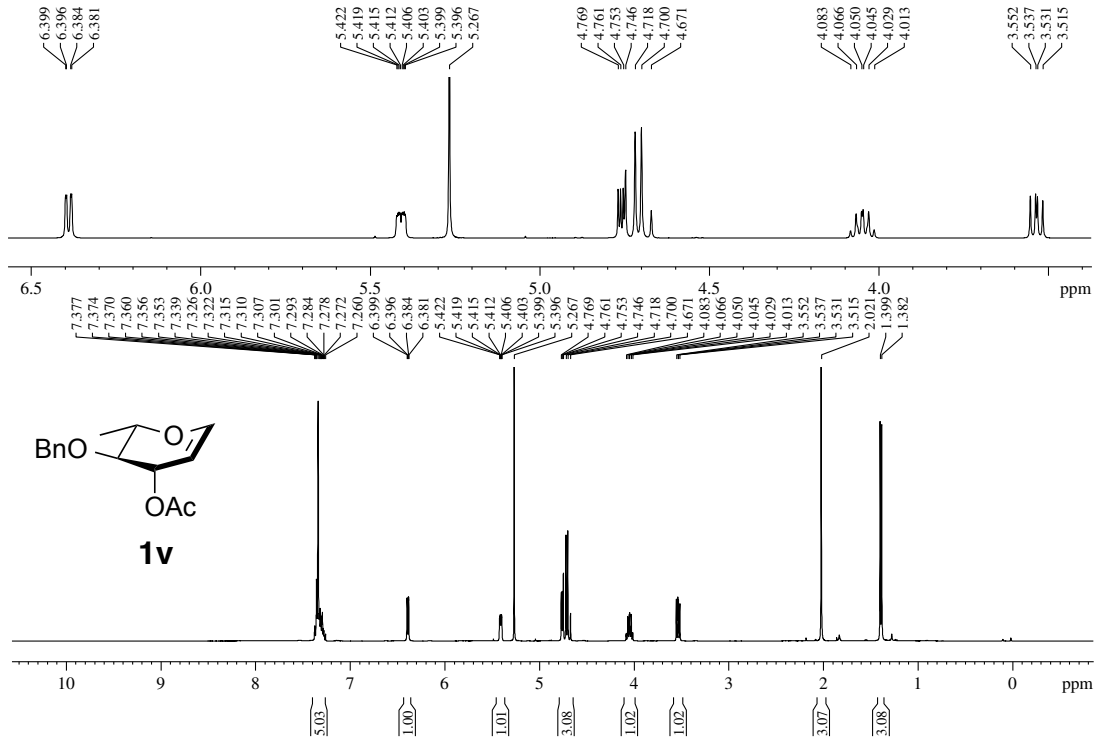
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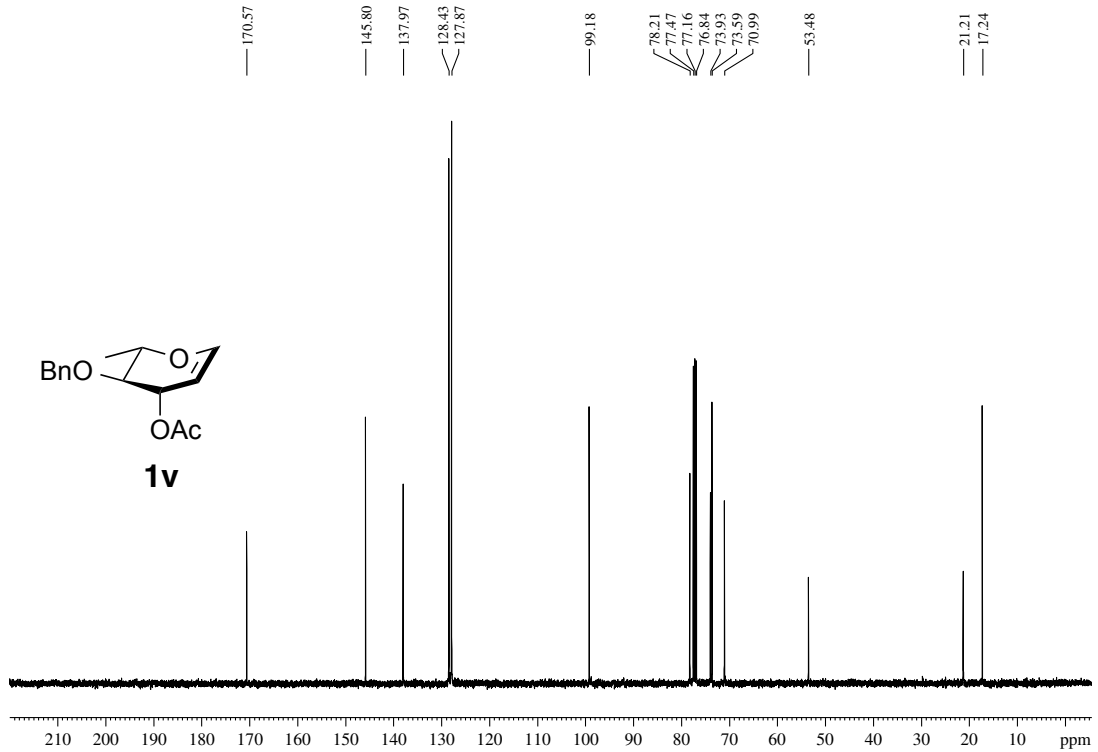
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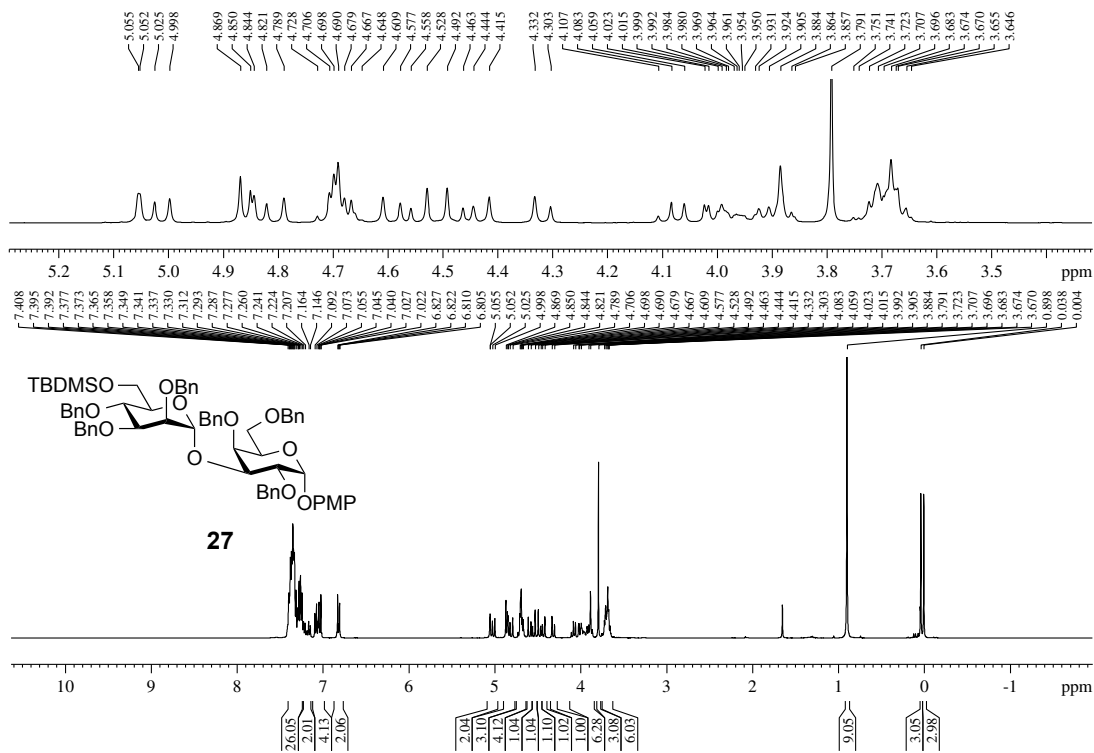
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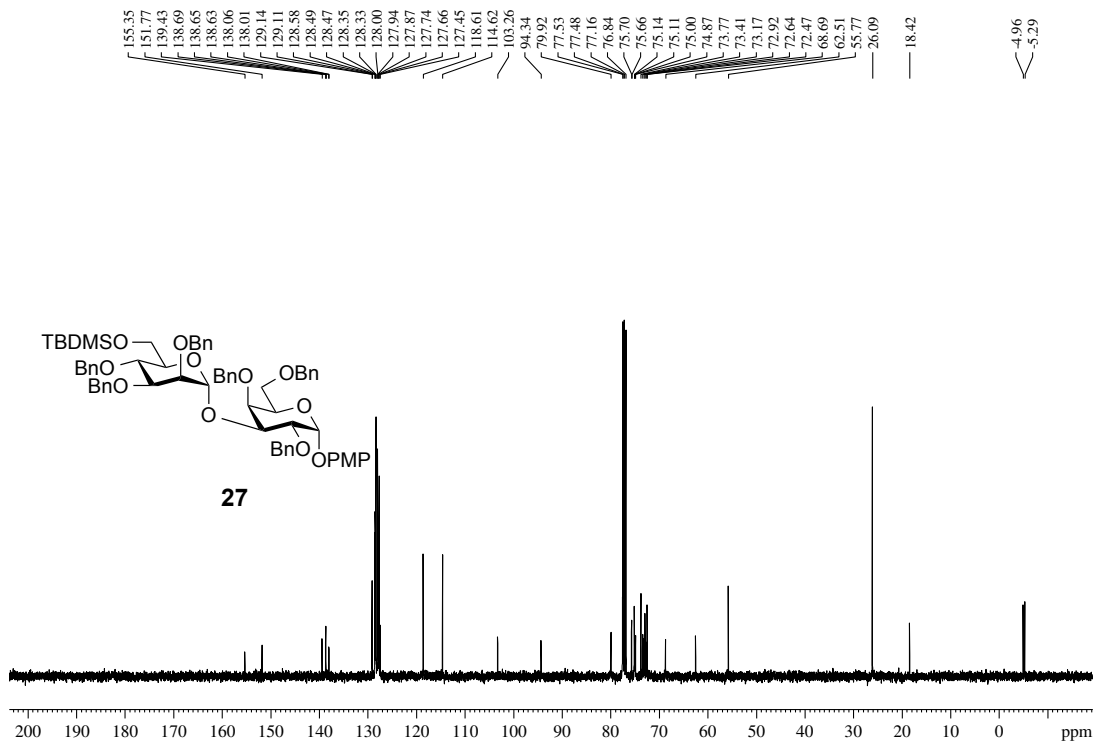
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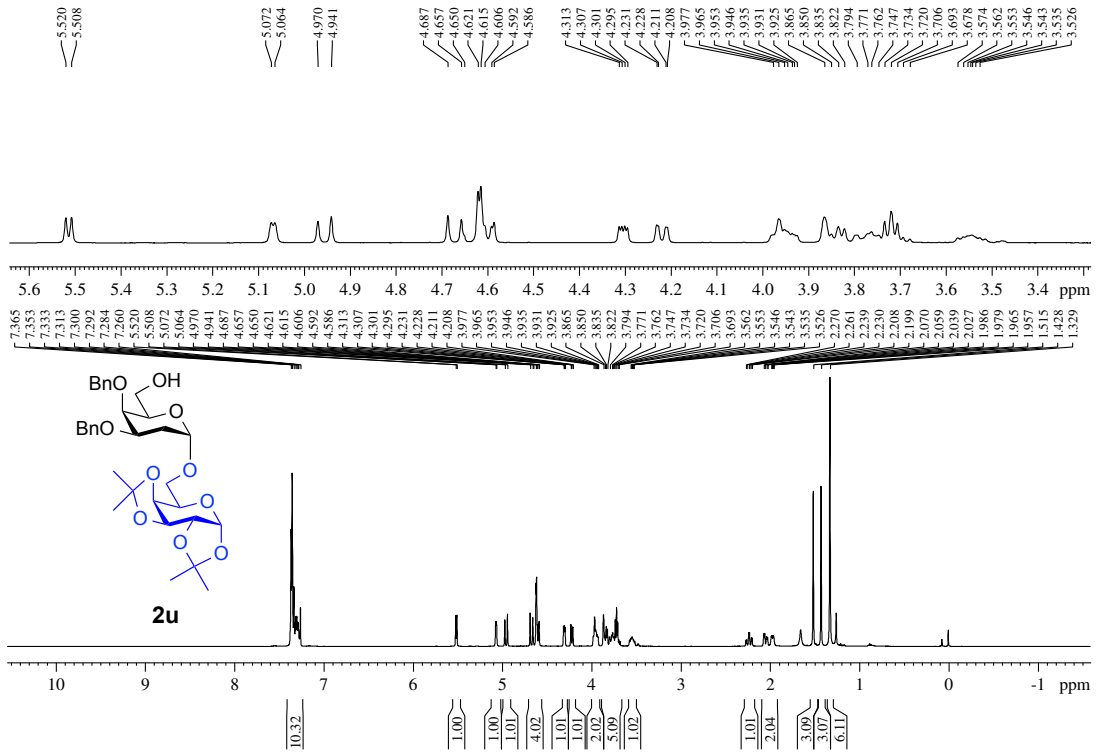
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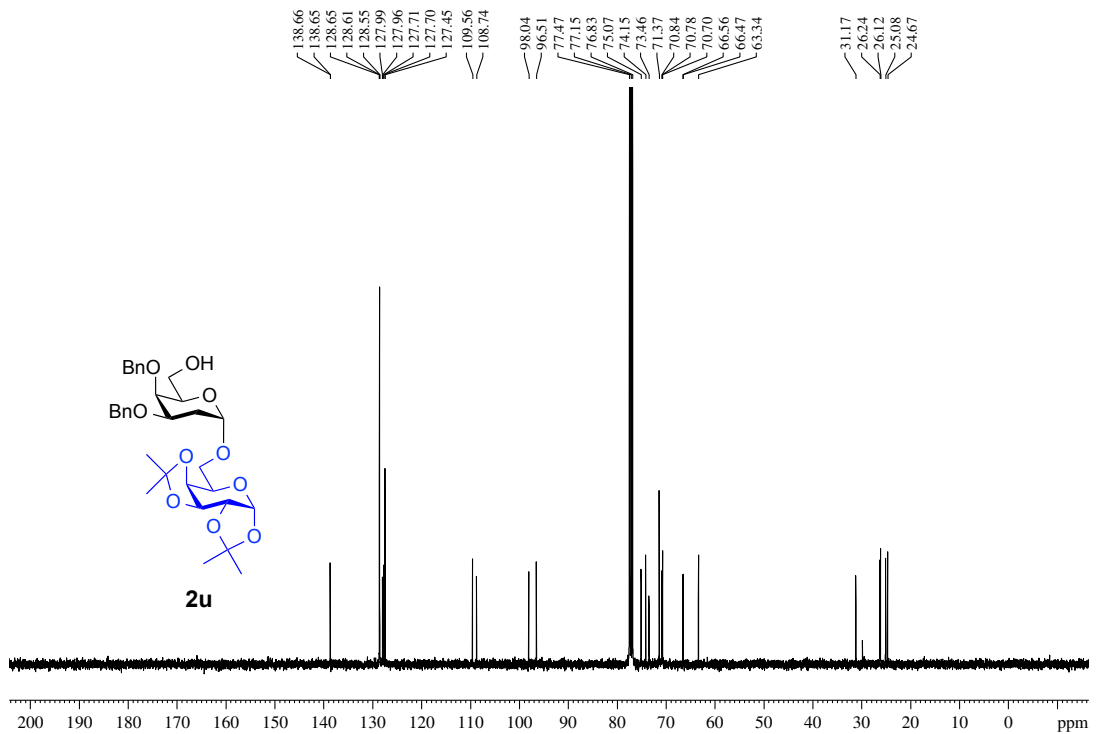
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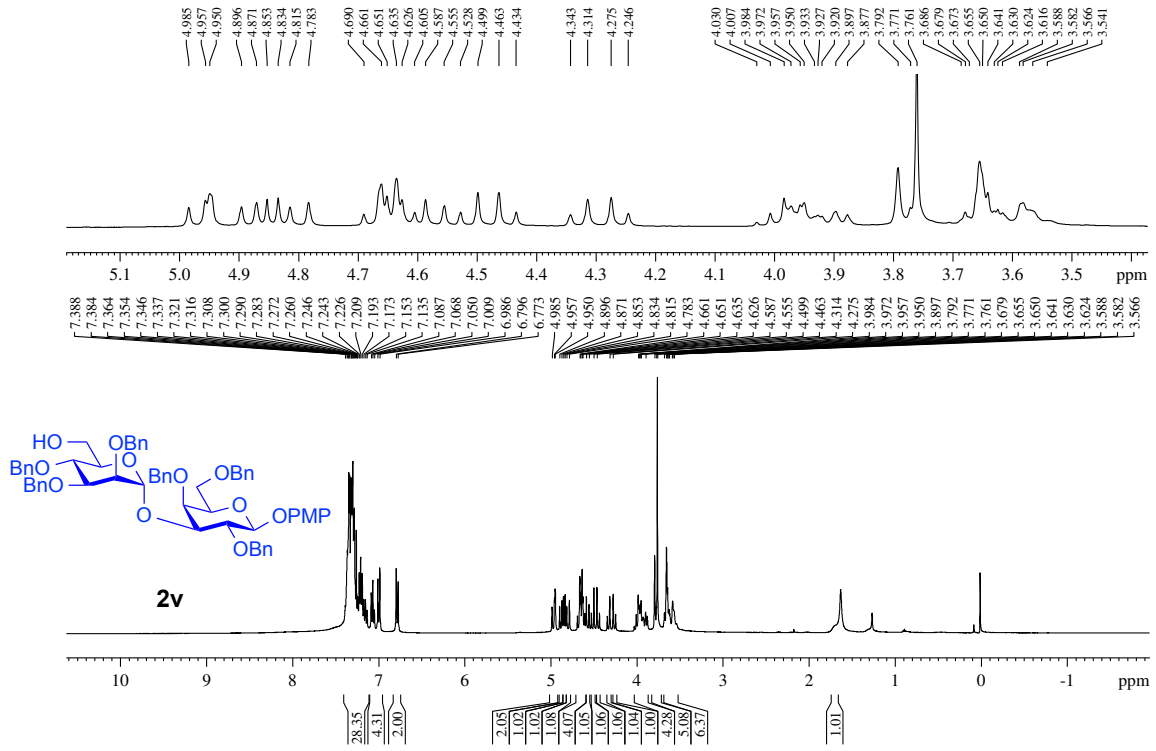
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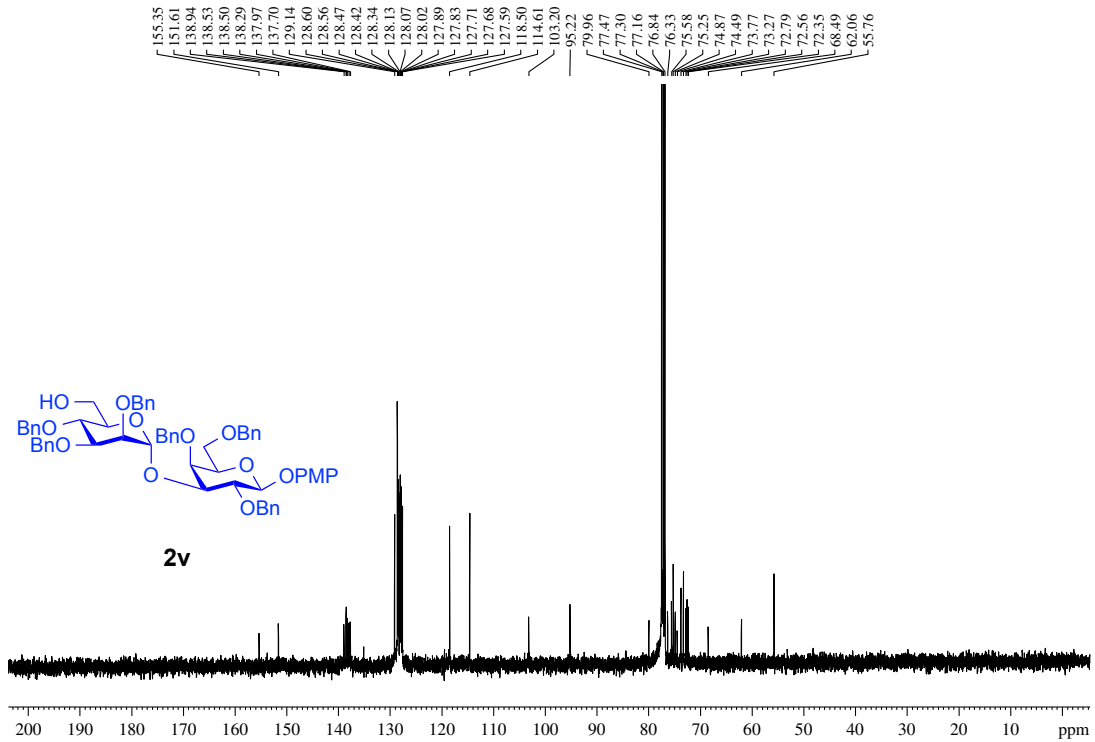
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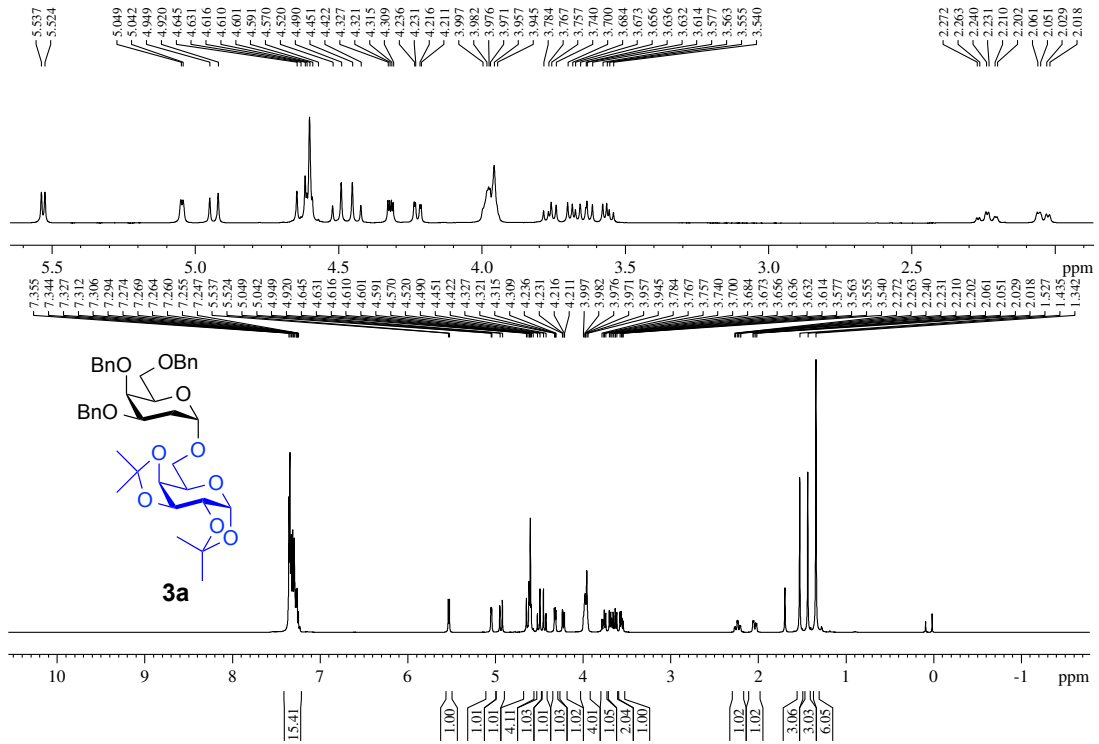
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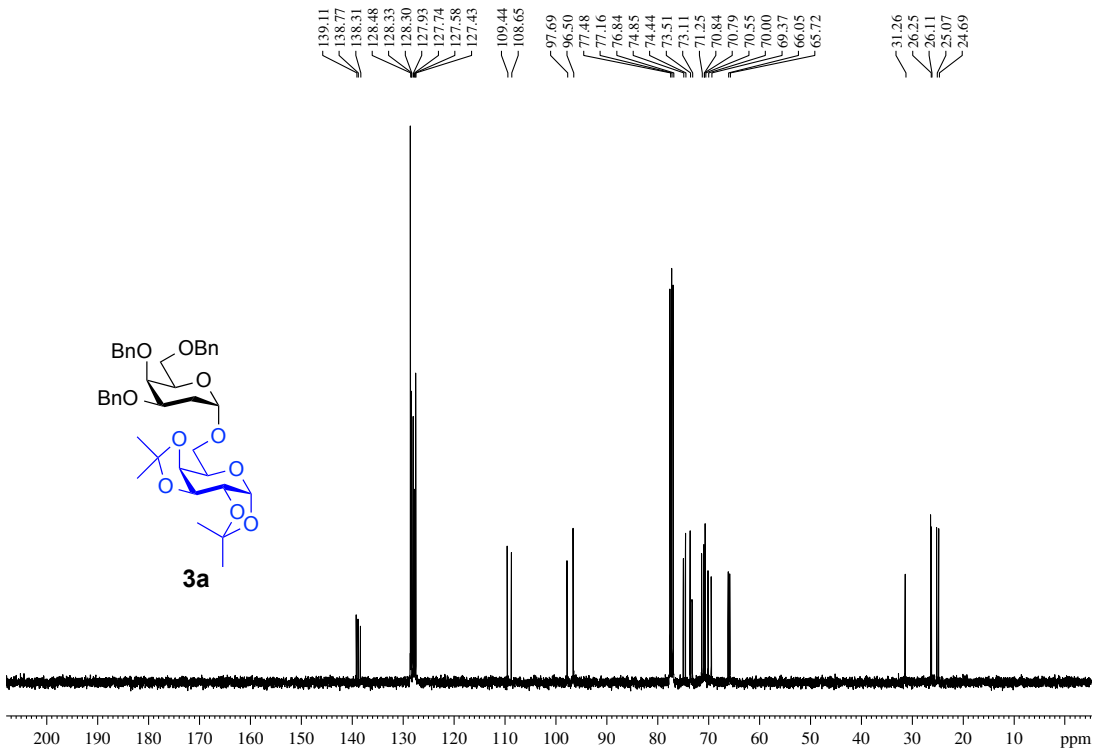
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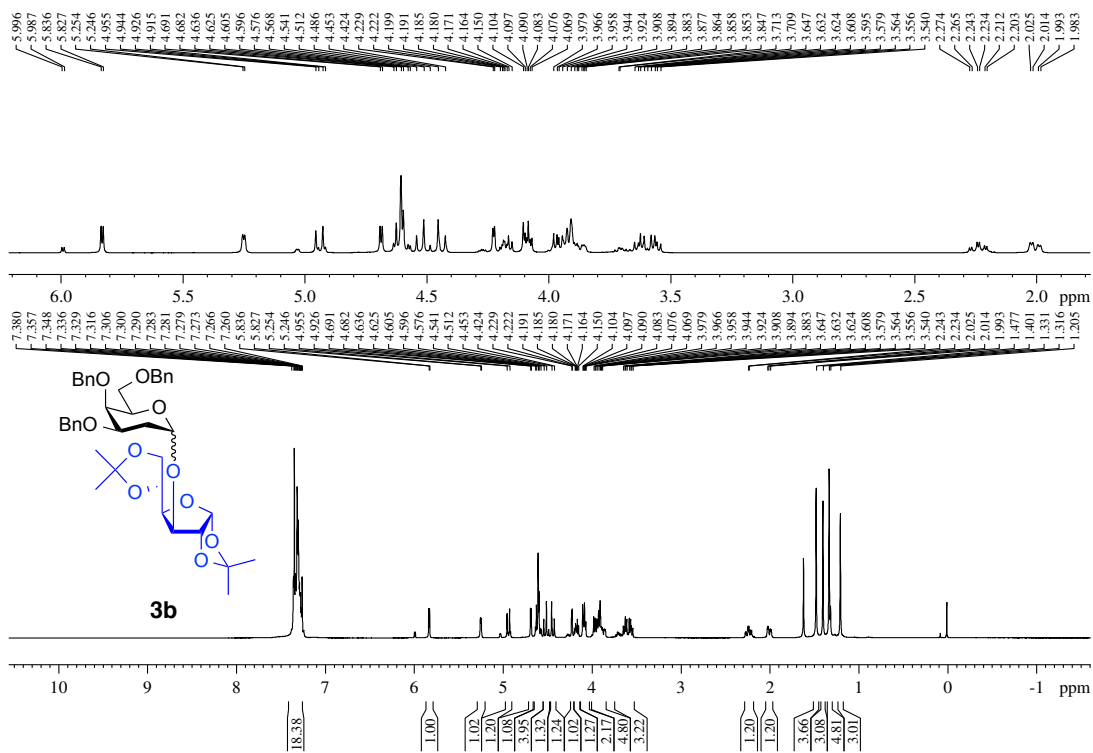
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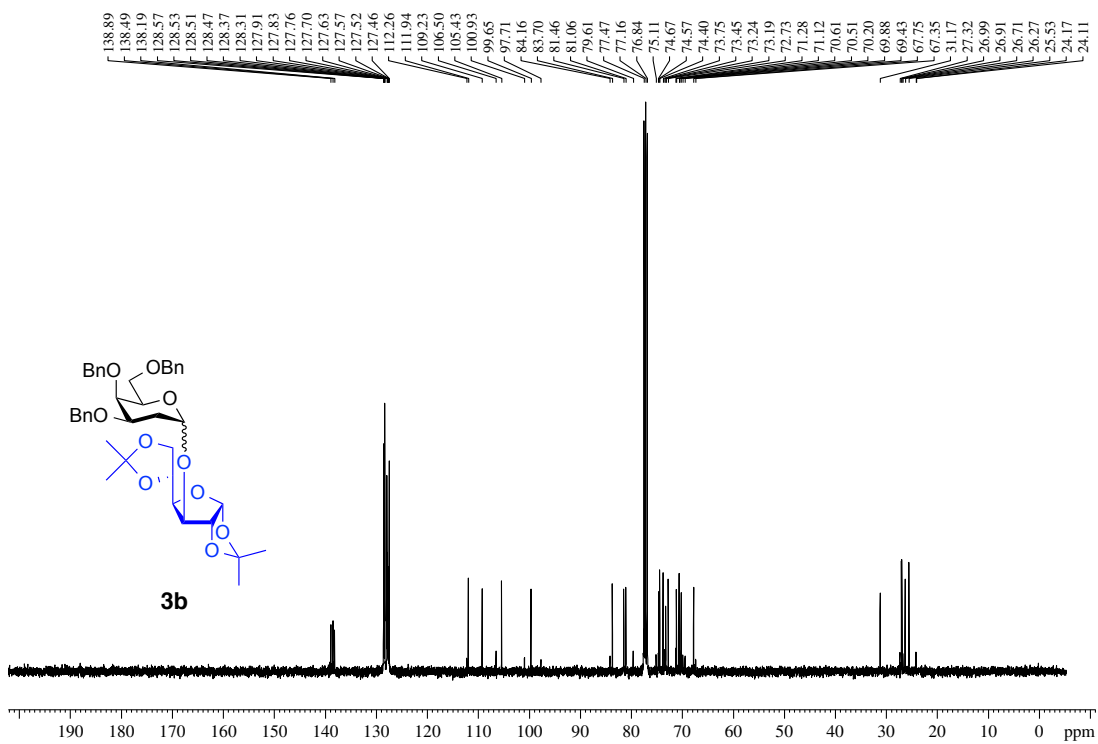
¹³C NMR of **3a**, CDCl₃, 100 MHz



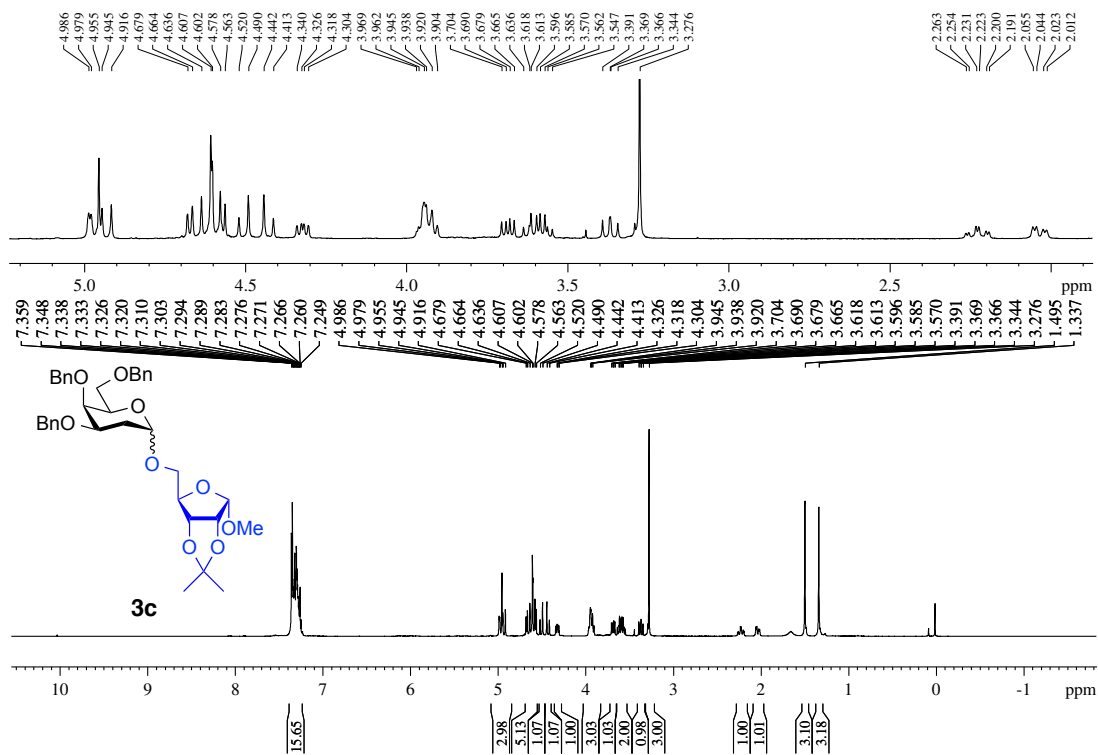
^1H NMR of **3b**, CDCl_3 , 400 MHz



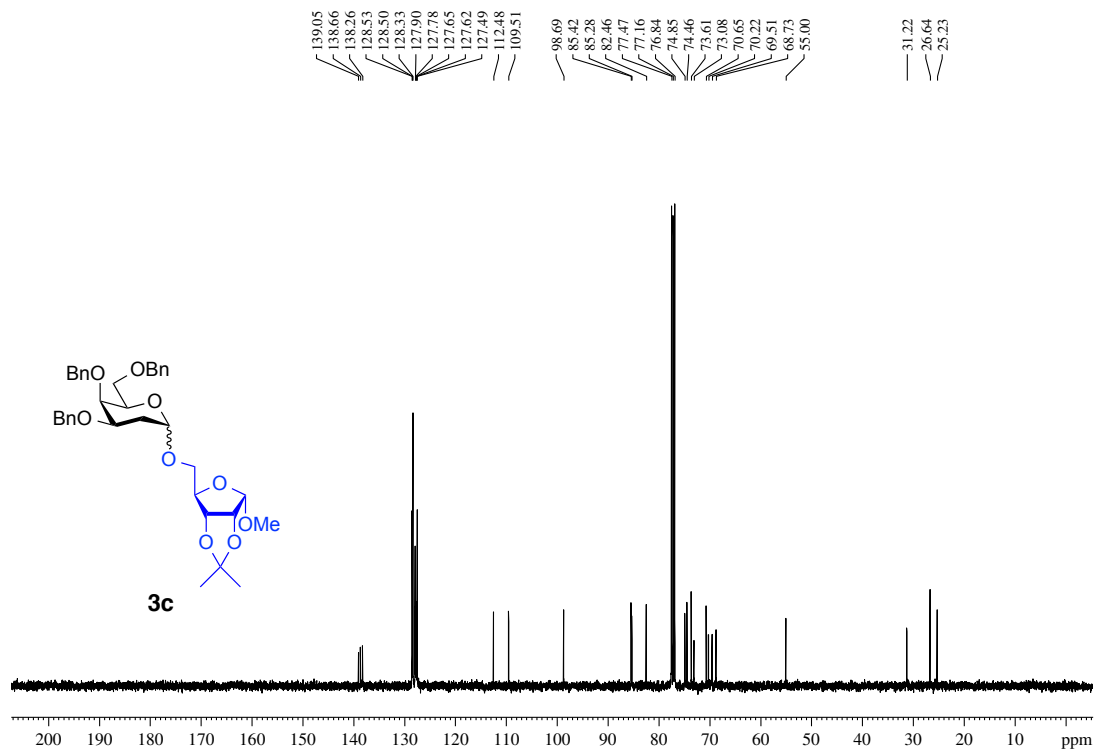
^{13}C NMR of **3b**, CDCl_3 , 100 MHz



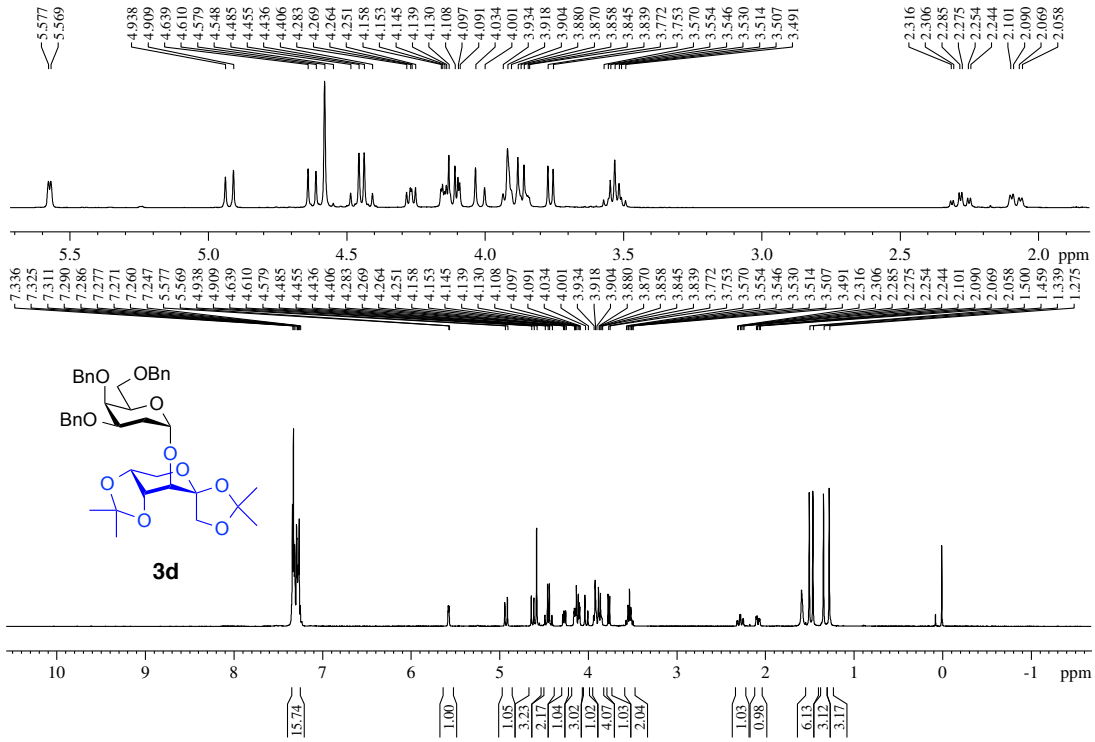
^1H NMR of **3c**, CDCl_3 , 400 MHz



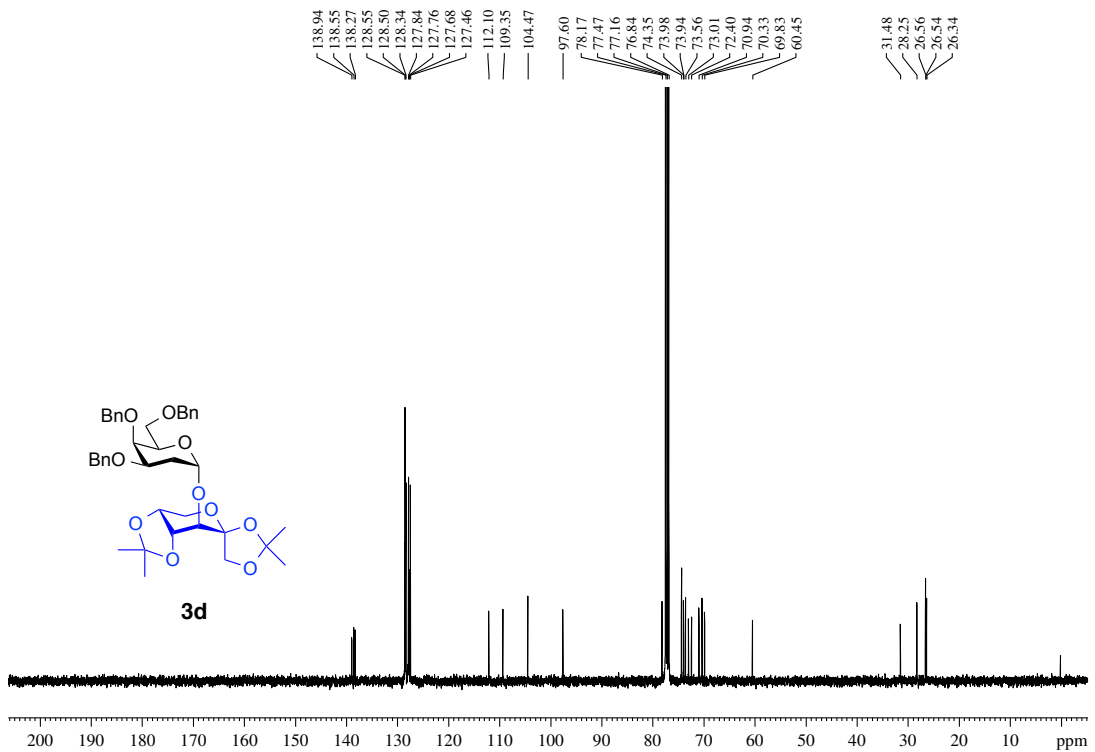
^{13}C NMR of **3c**, CDCl_3 , 100 MHz



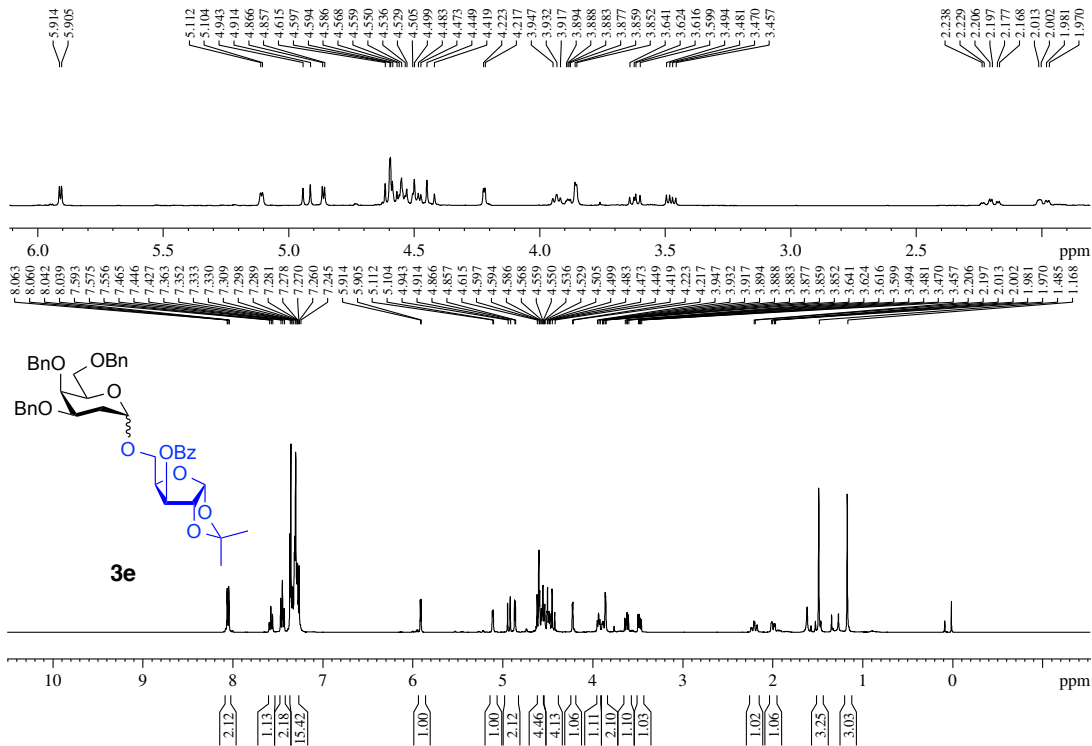
^1H NMR of **3d**, CDCl_3 , 400 MHz



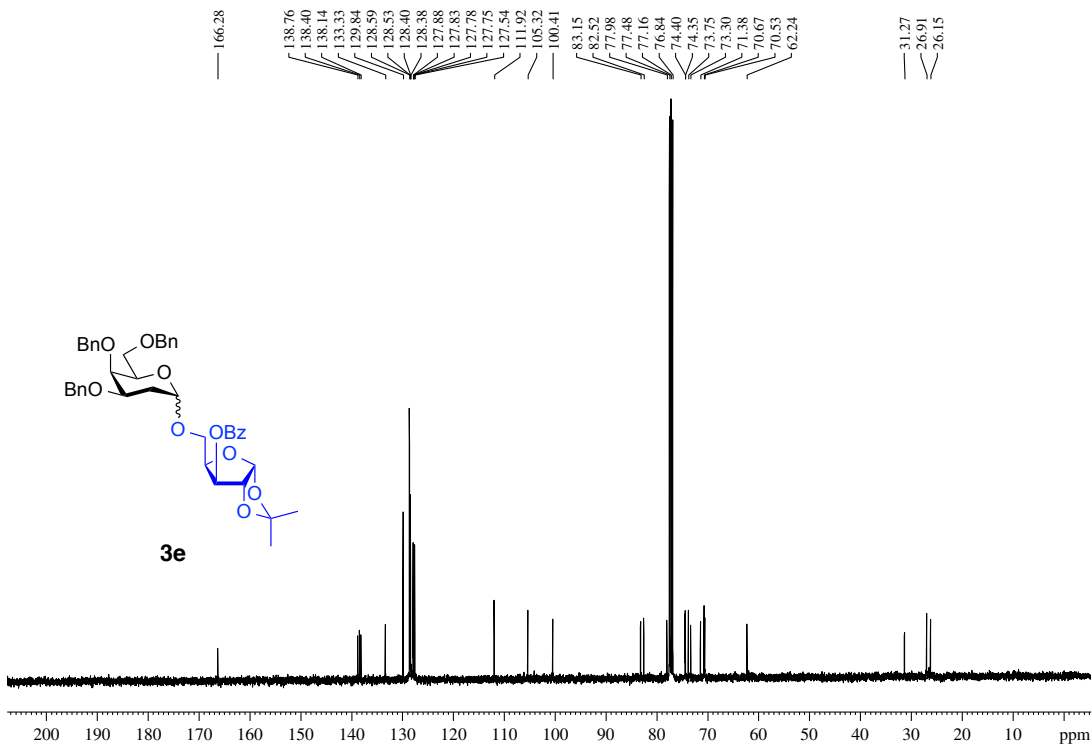
^{13}C NMR of **3d**, CDCl_3 , 100 MHz



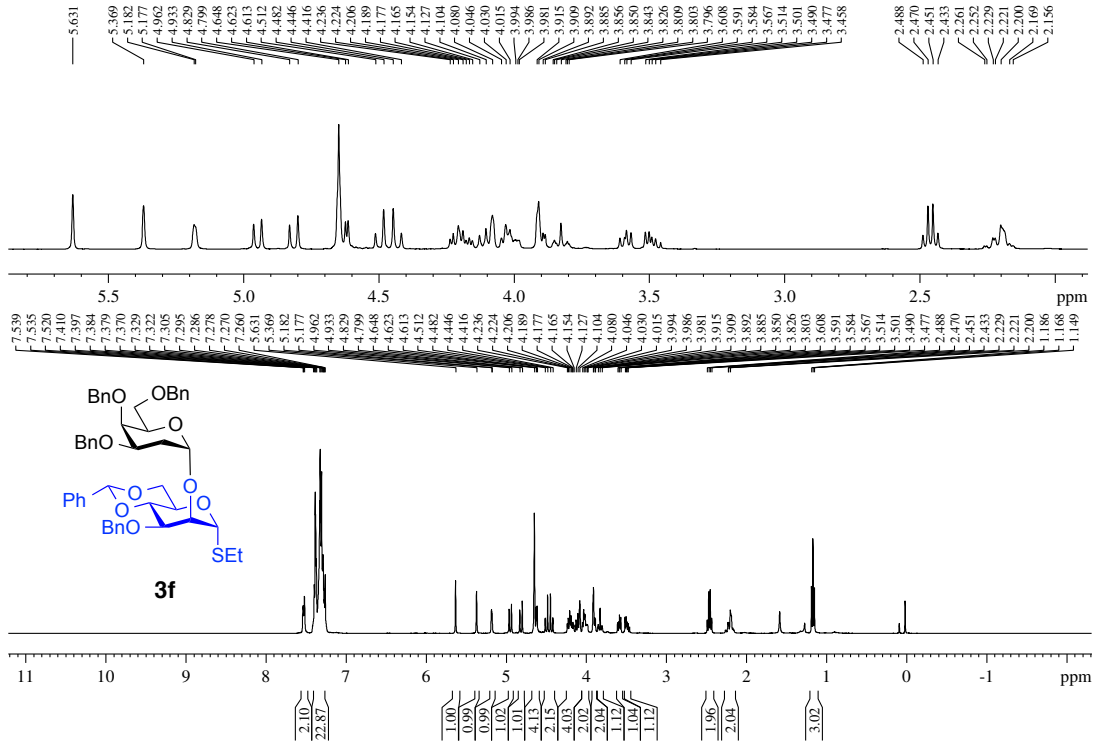
^1H NMR of **3e**, CDCl_3 , 400 MHz



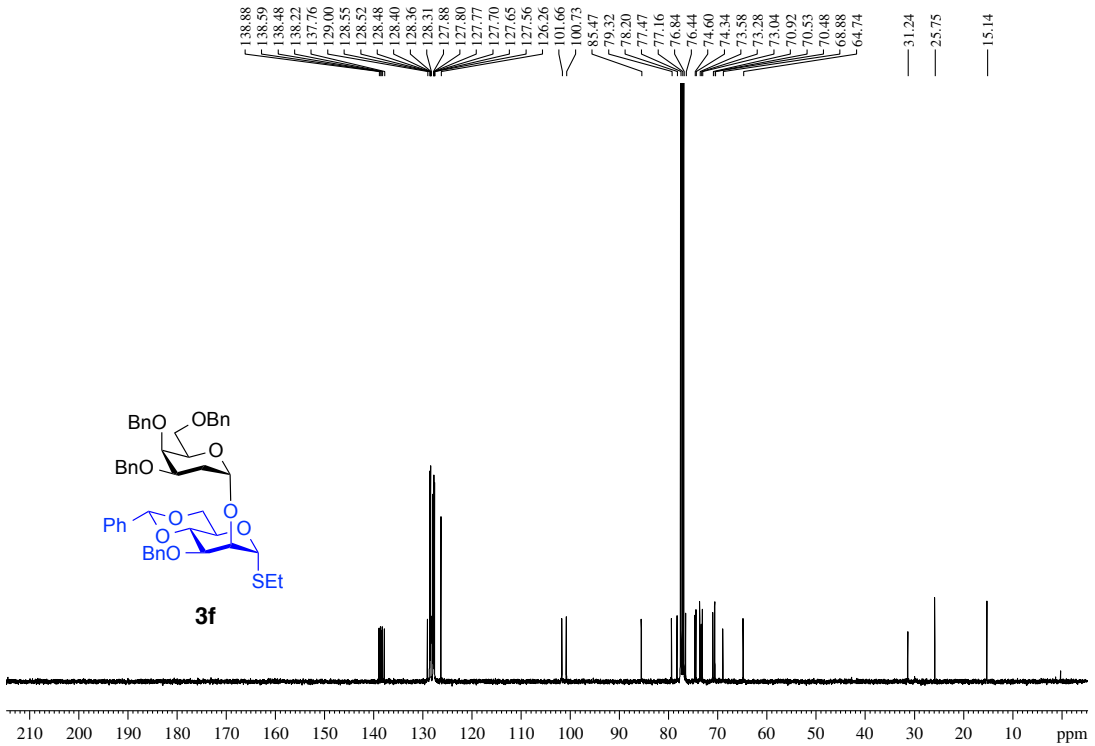
^{13}C NMR of **3e**, CDCl_3 , 100 MHz



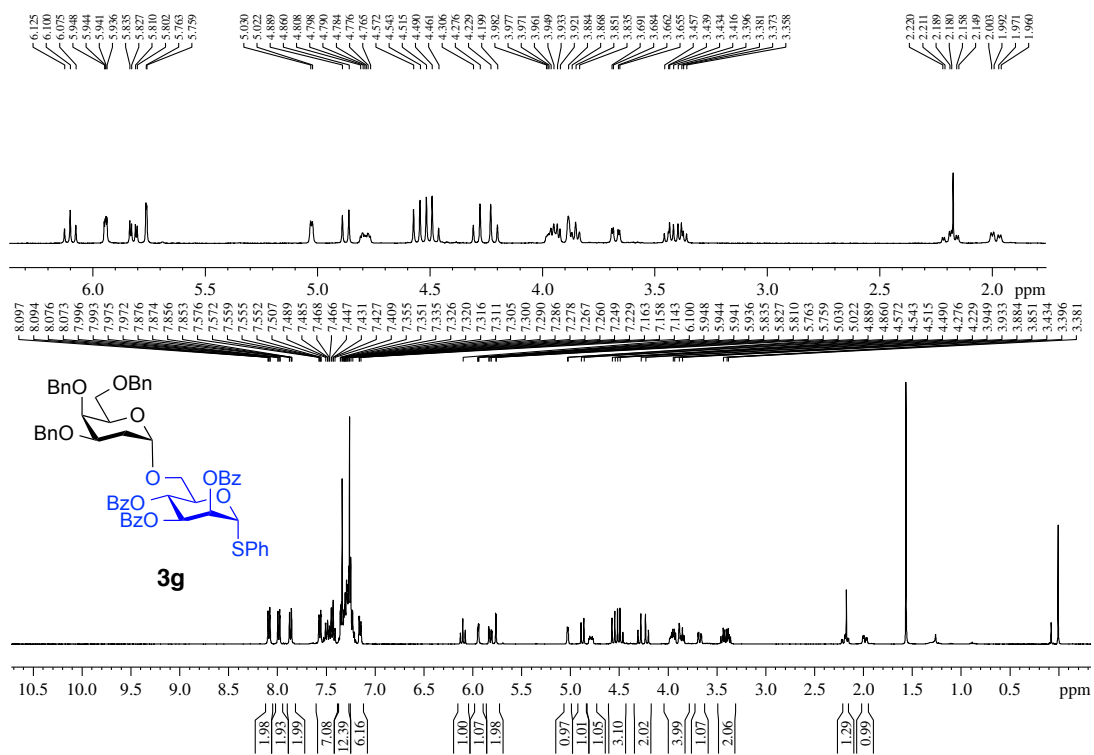
¹H NMR of **3f**, CDCl₃, 400 MHz



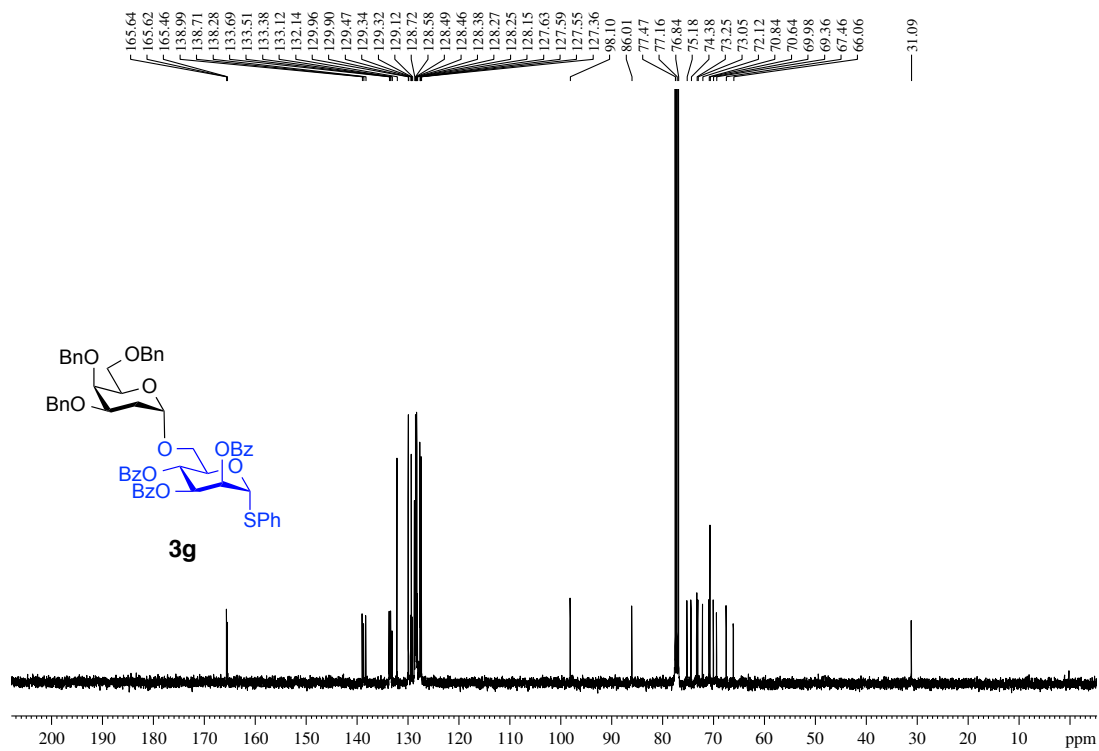
¹³C NMR of **3f**, CDCl₃, 100 MHz



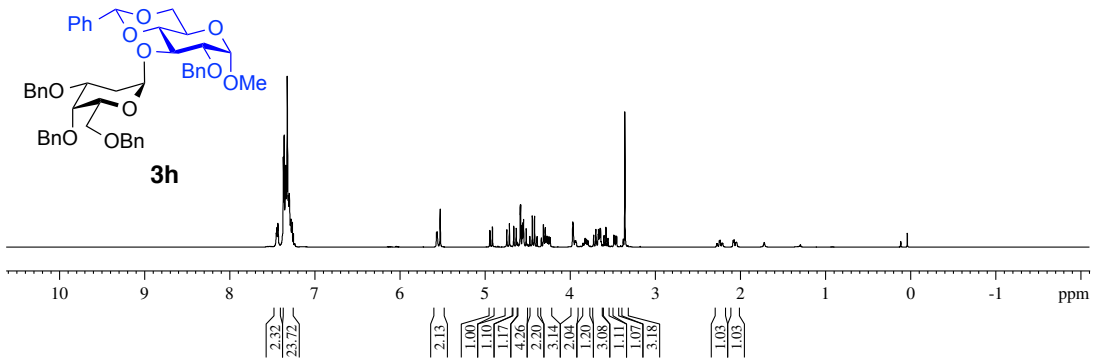
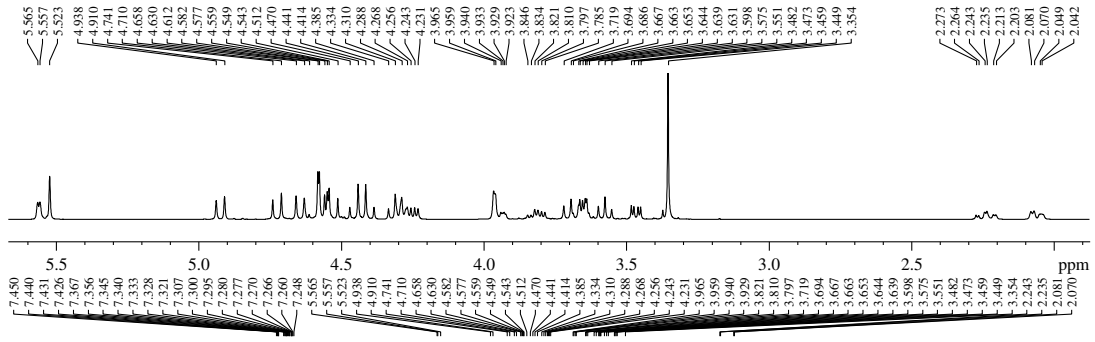
^1H NMR of **3g**, CDCl_3 , 400 MHz



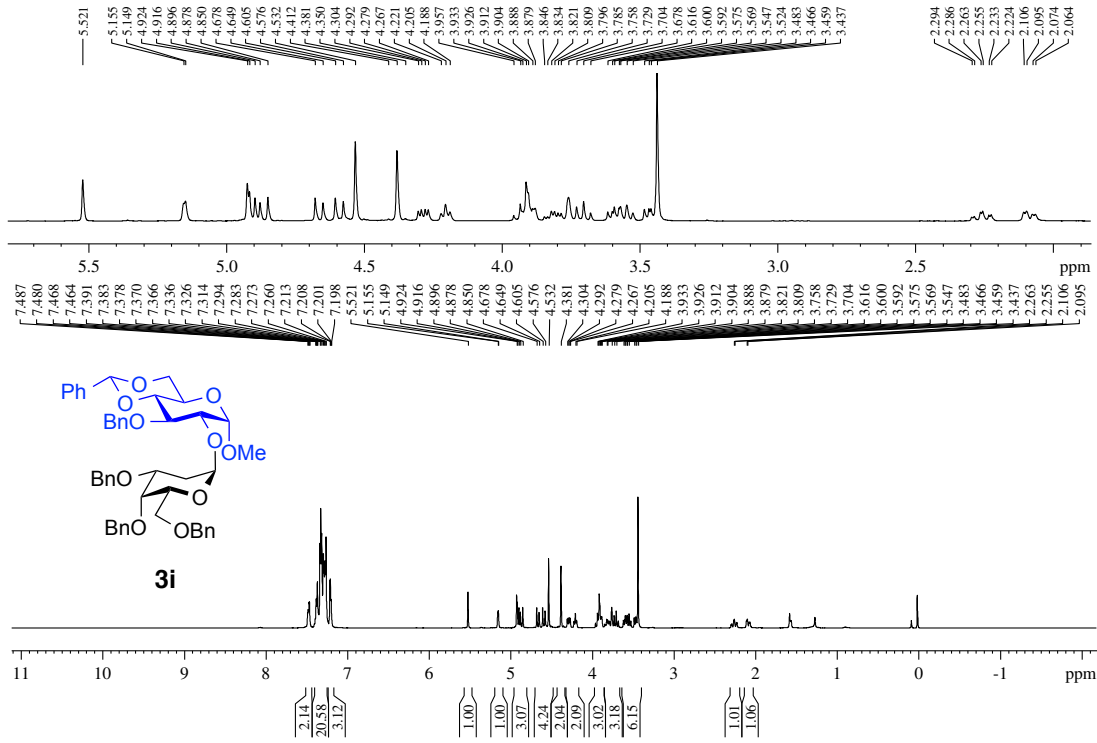
^{13}C NMR of **3g**, CDCl_3 , 100 MHz



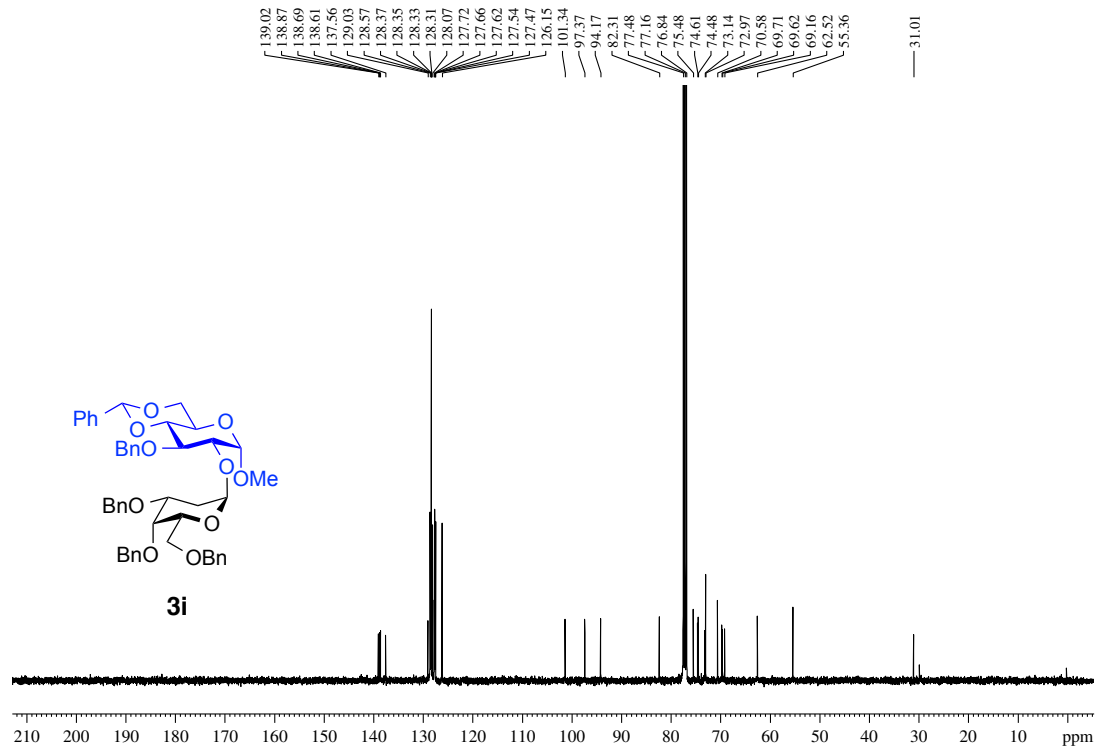
¹H NMR of **3h**, CDCl₃, 400 MHz



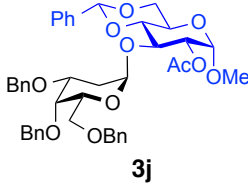
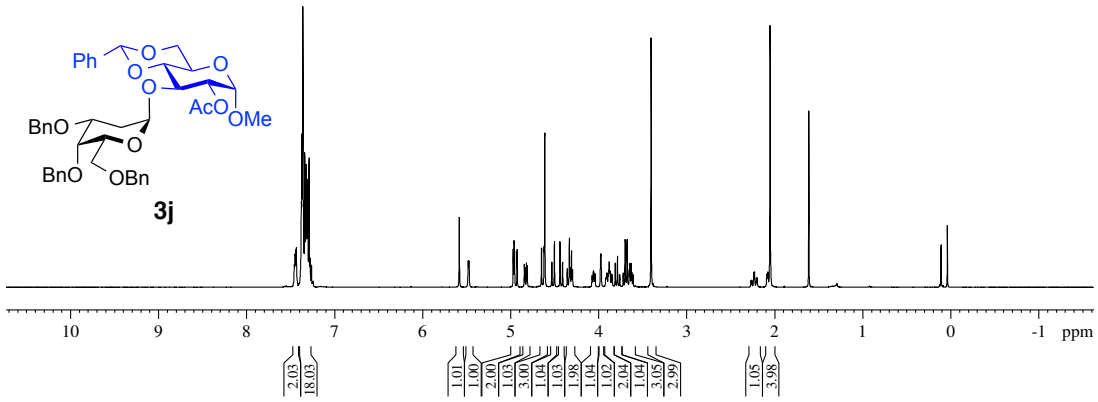
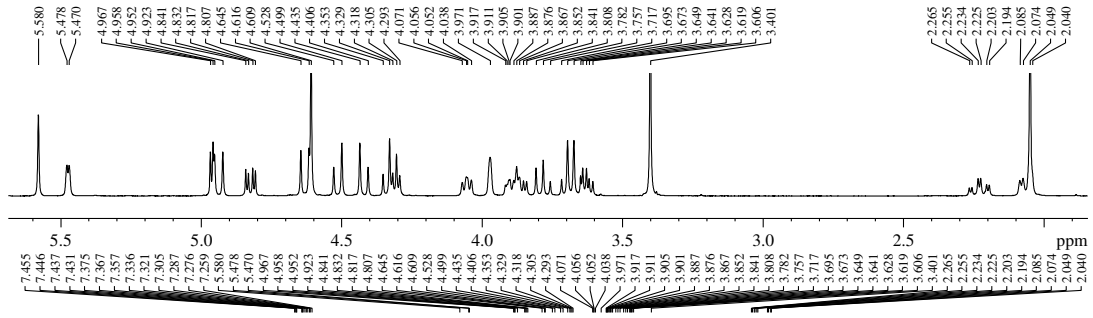
¹H NMR **3i**, CDCl₃, 400 MHz



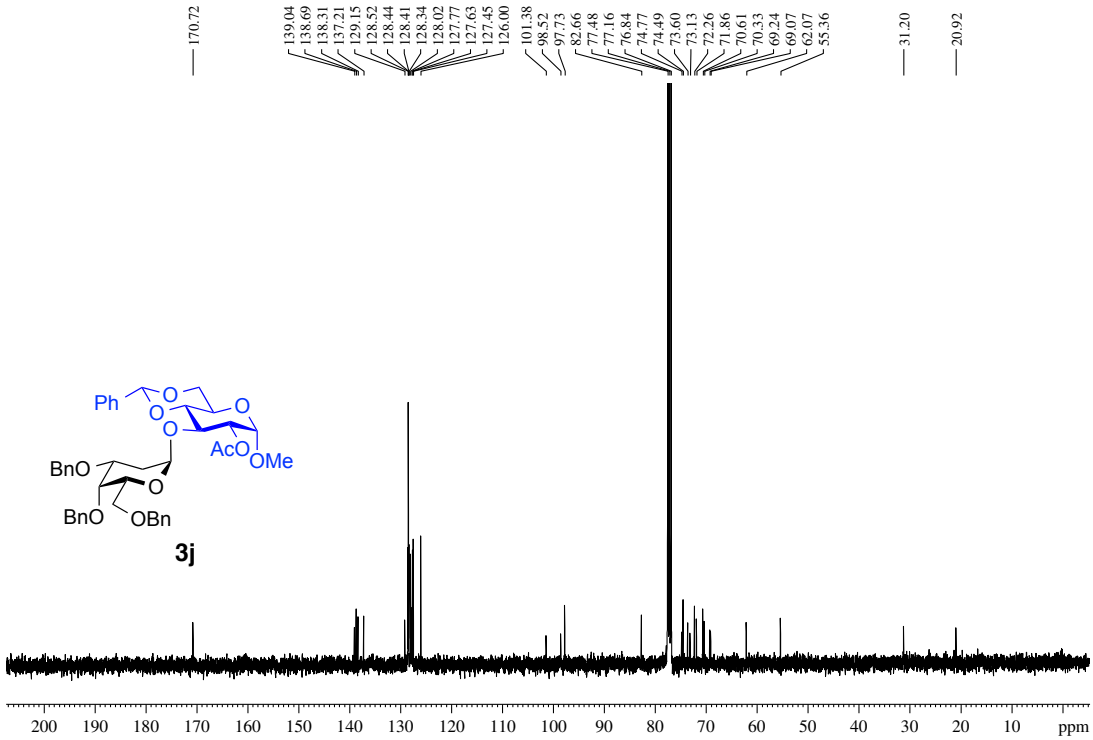
¹³C NMR of **3i**, CDCl₃, 100 MHz



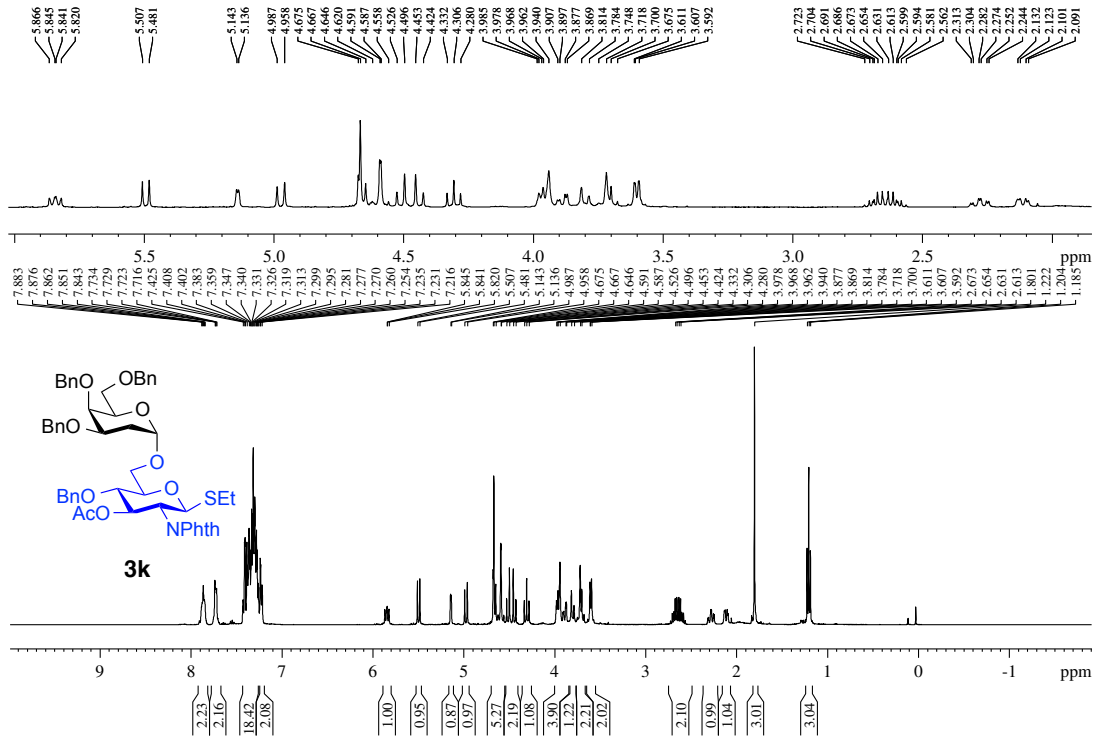
¹H NMR of **3j**, CDCl₃, 400 MHz



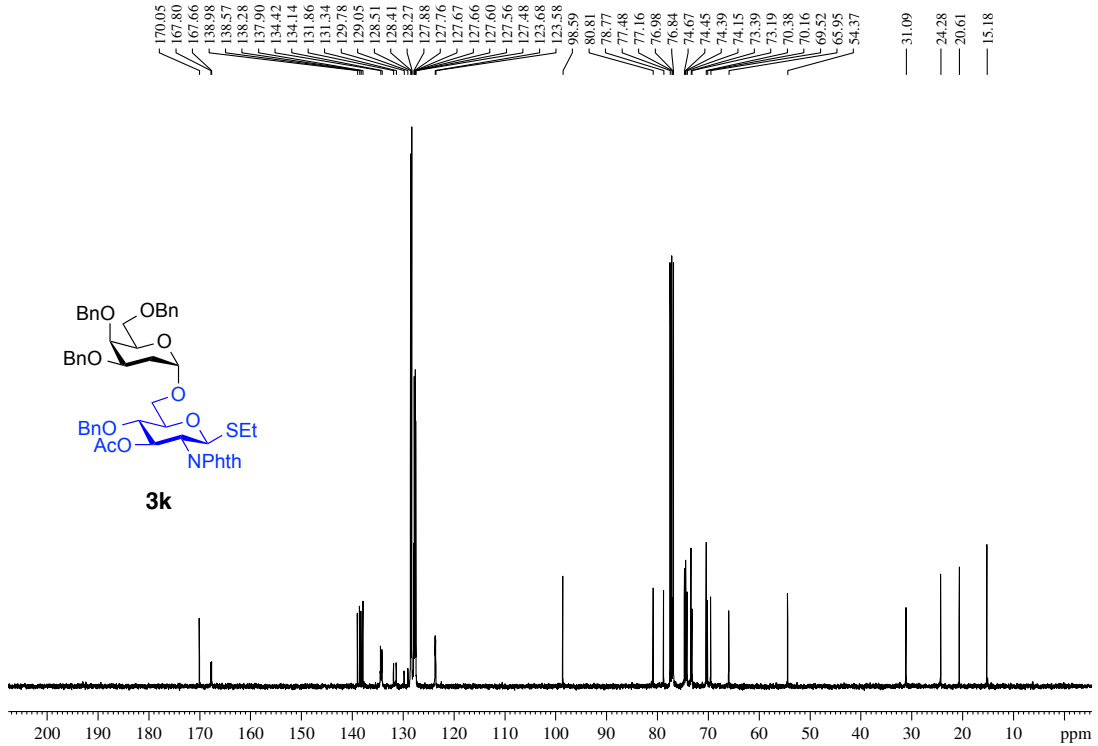
¹³C NMR of **3j**, CDCl₃, 400 MHz



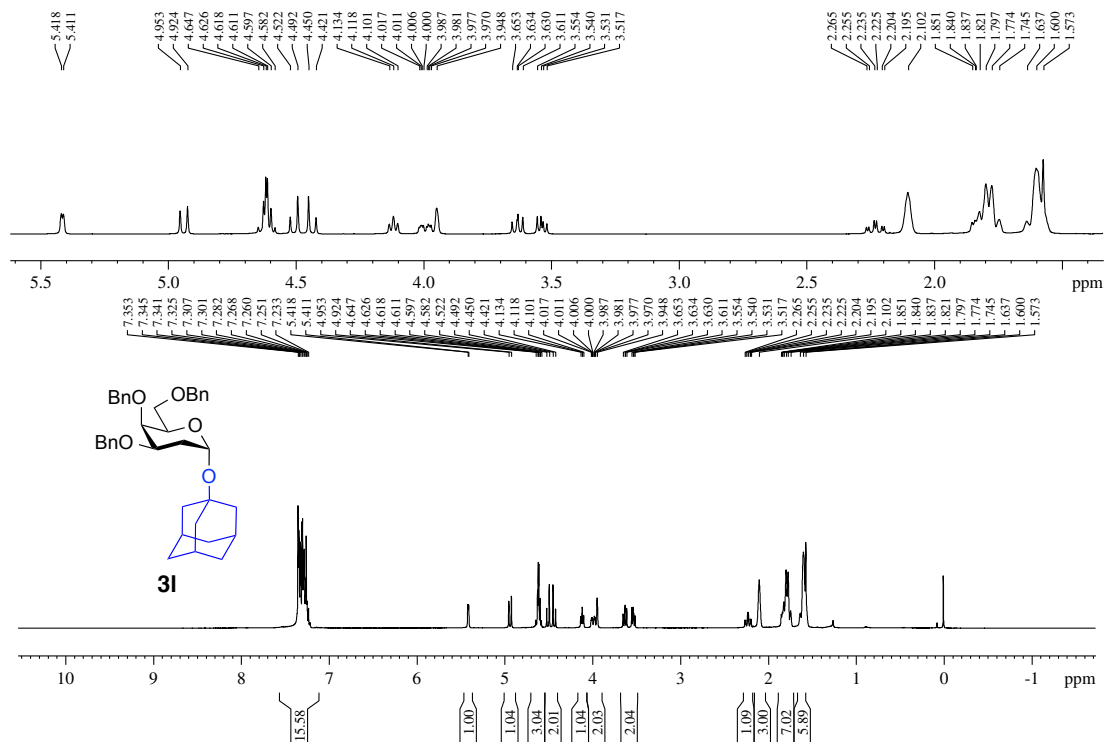
¹H NMR of **3k**, CDCl₃, 400 MHz



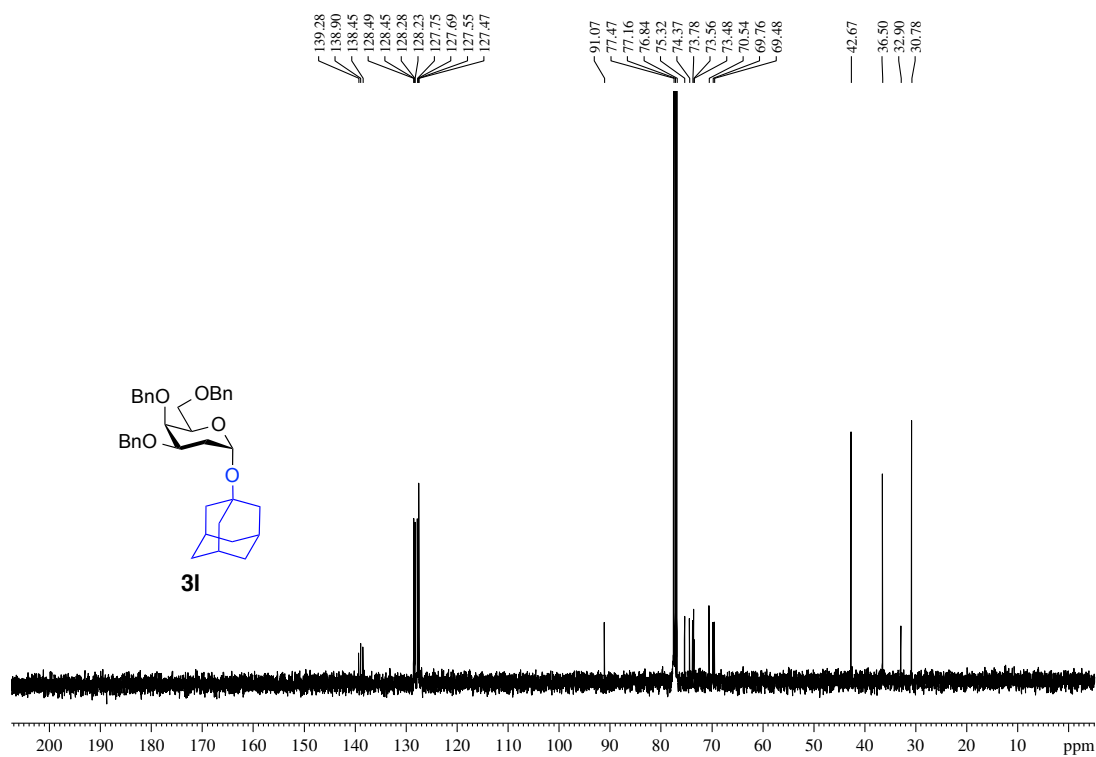
¹³C NMR of **3k**, CDCl₃, 100 MHz



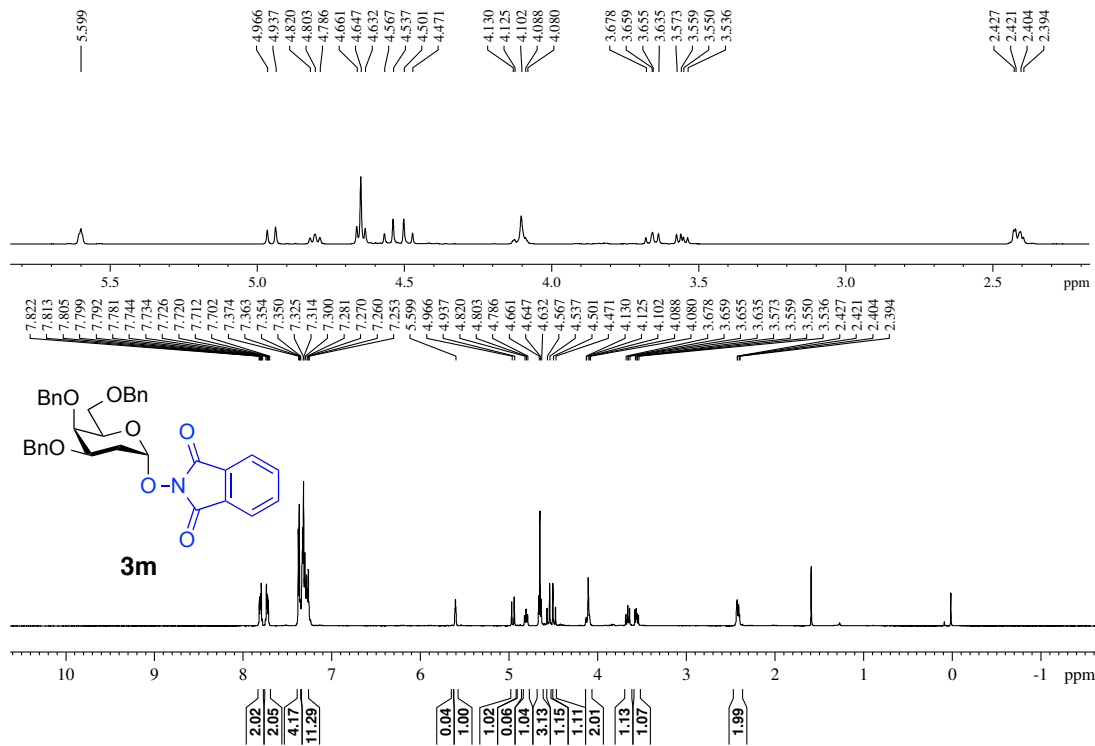
¹H NMR of **3l**, CDCl₃, 400 MHz



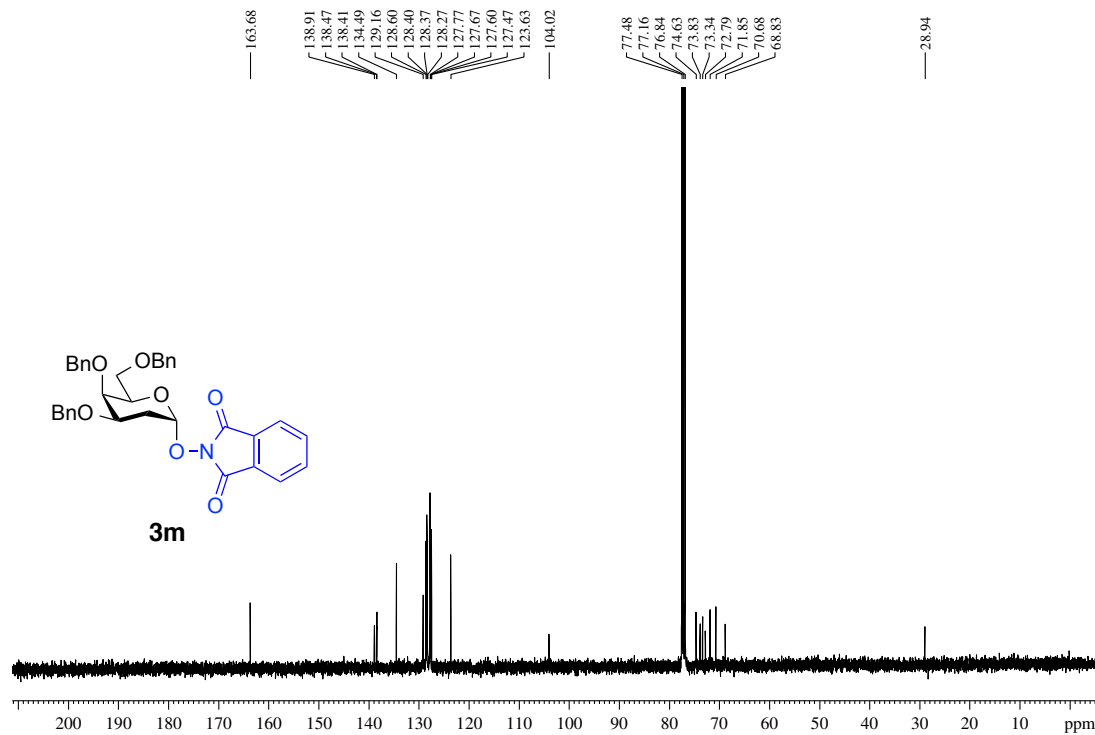
¹³C NMR of **3l**, CDCl₃, 100 MHz



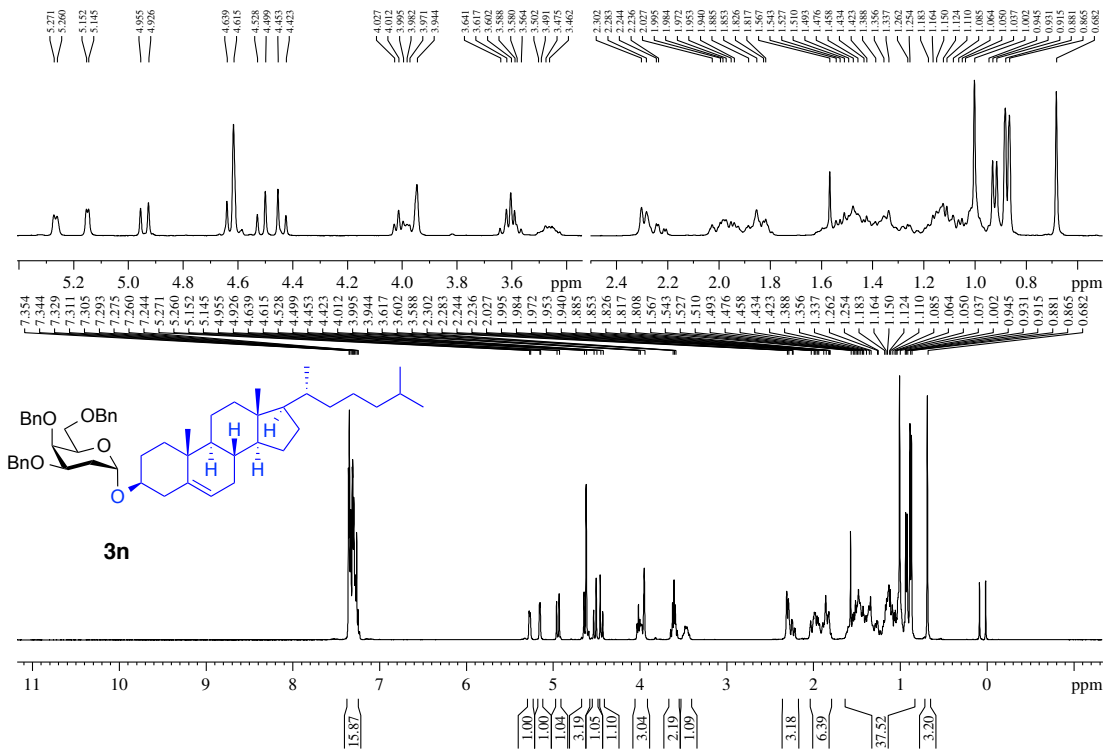
¹H NMR of **3m**, CDCl₃, 400 MHz



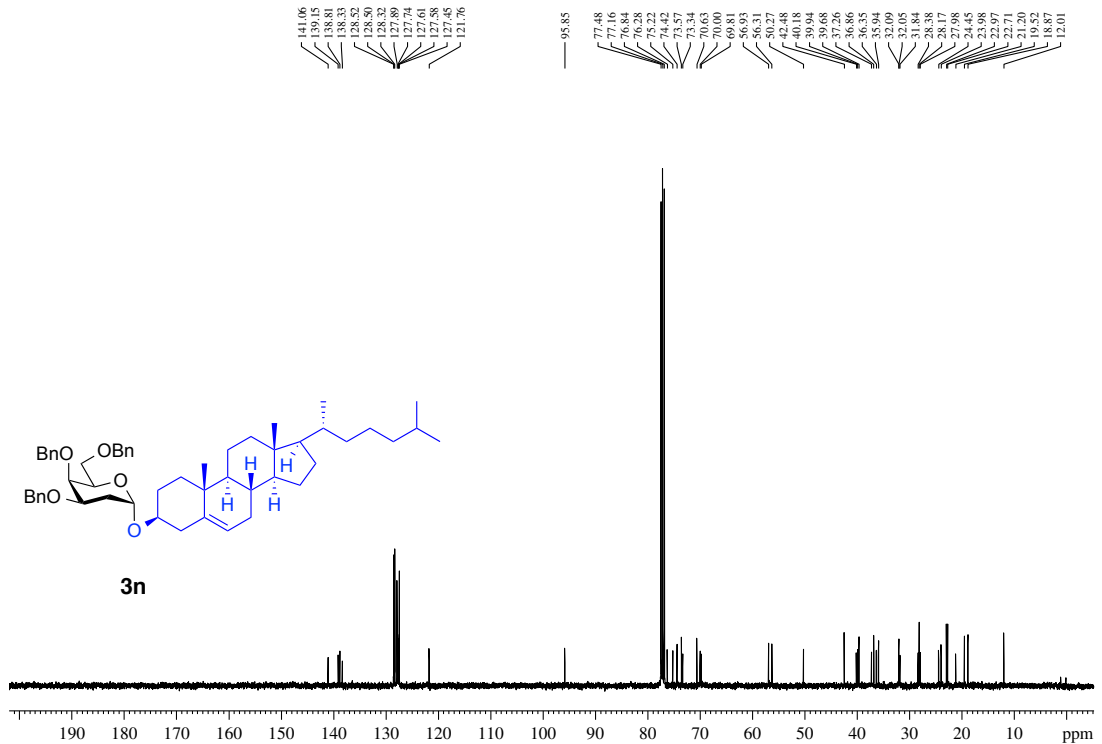
¹³C NMR of **3m**, CDCl₃, 400 MHz



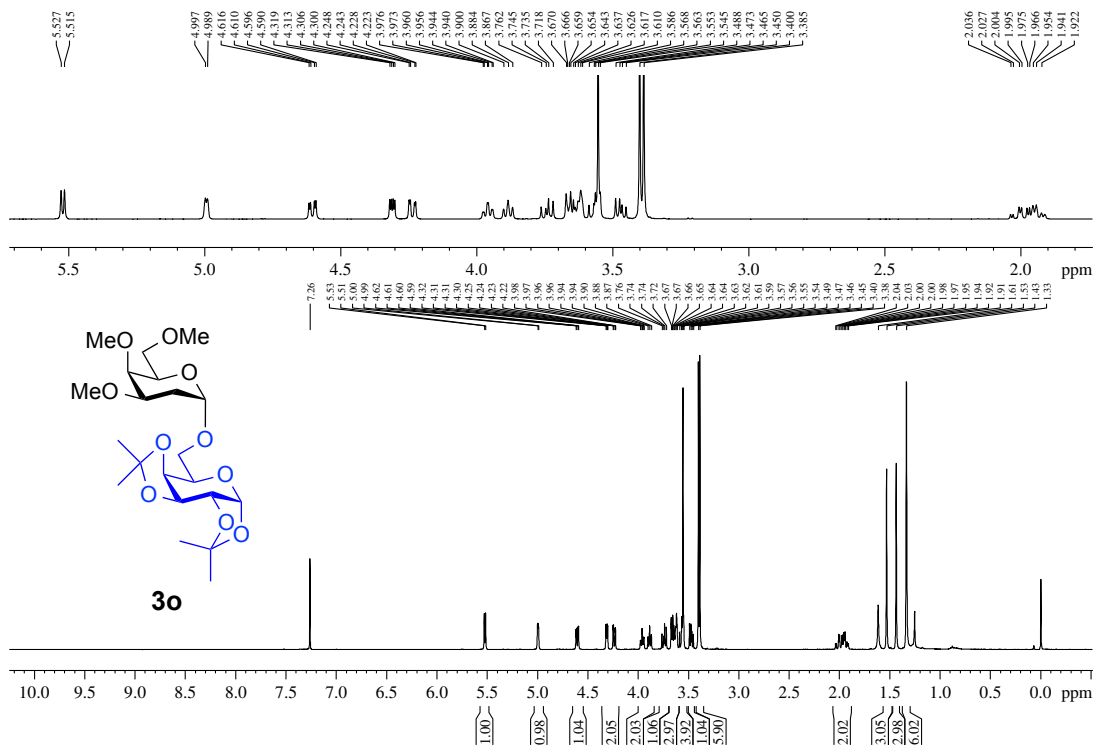
^1H NMR of **3n**, CDCl_3 , 400 MHz



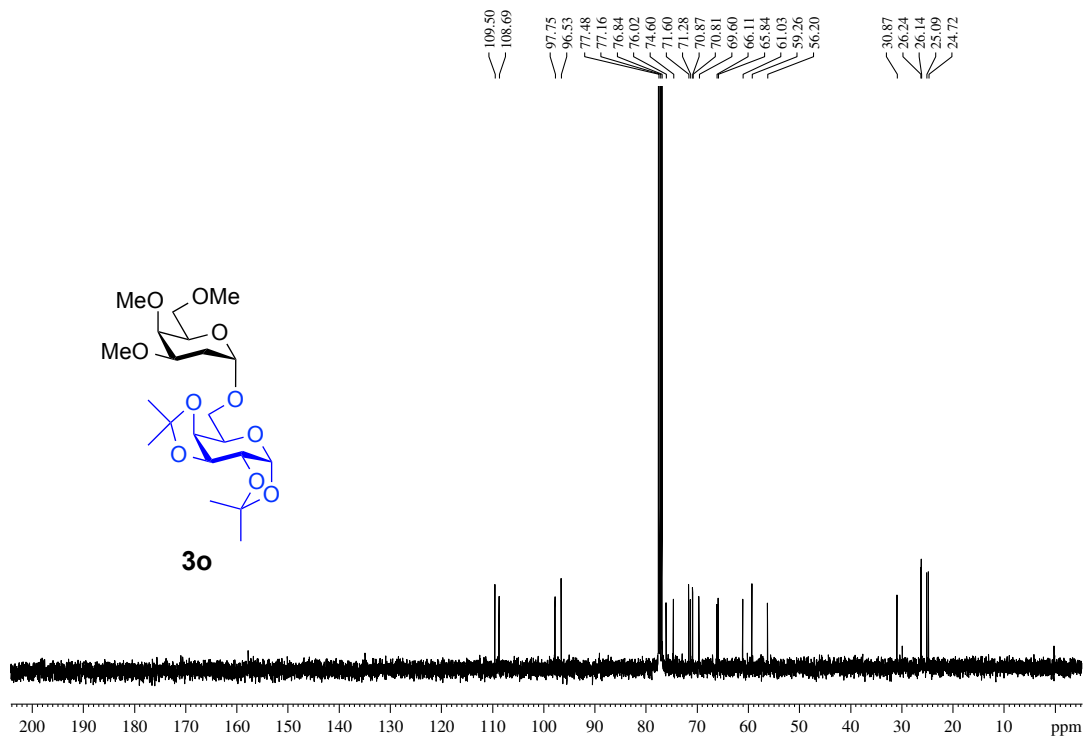
^{13}C NMR of **3n**, CDCl_3 , 100 MHz



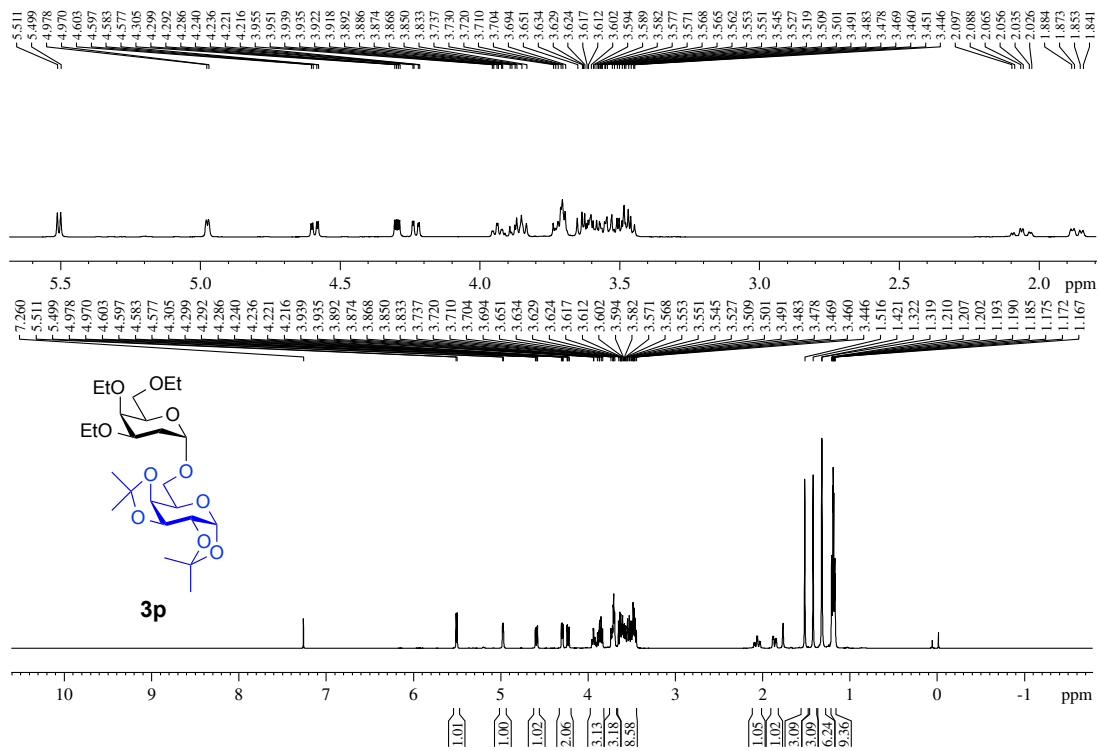
¹H NMR of **3o**, CDCl₃, 400 MHz



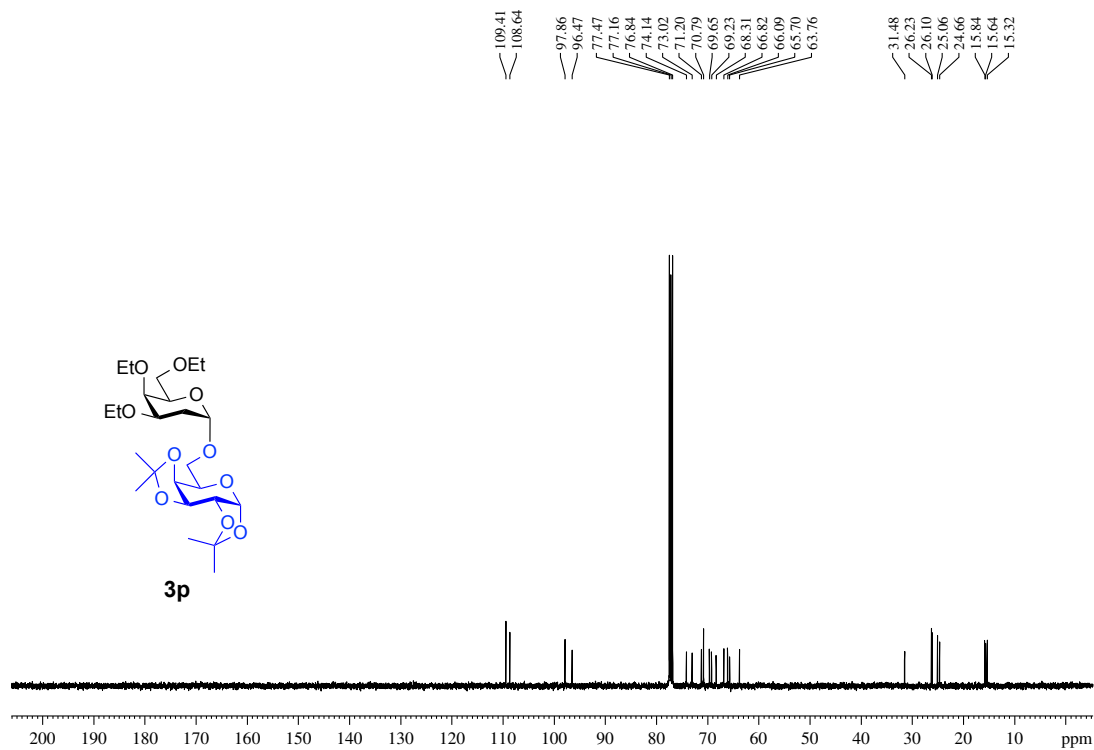
¹³C NMR of **3o**, CDCl₃, 100 MHz



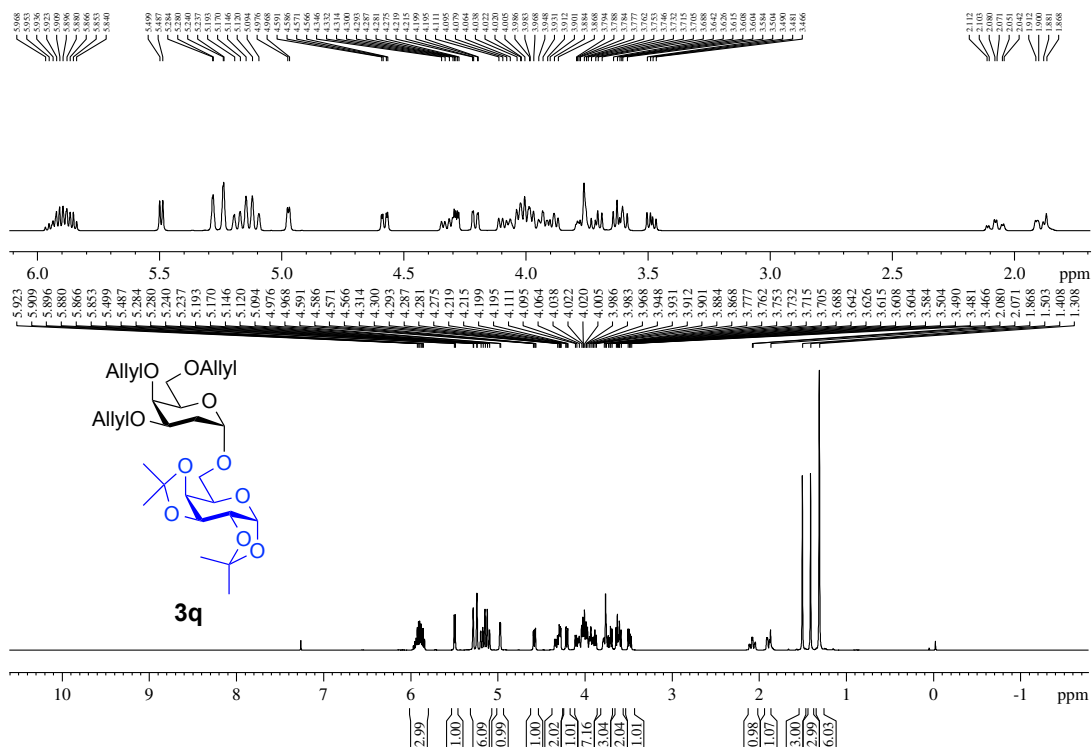
^1H NMR of **3p**, CDCl_3 , 400 MHz



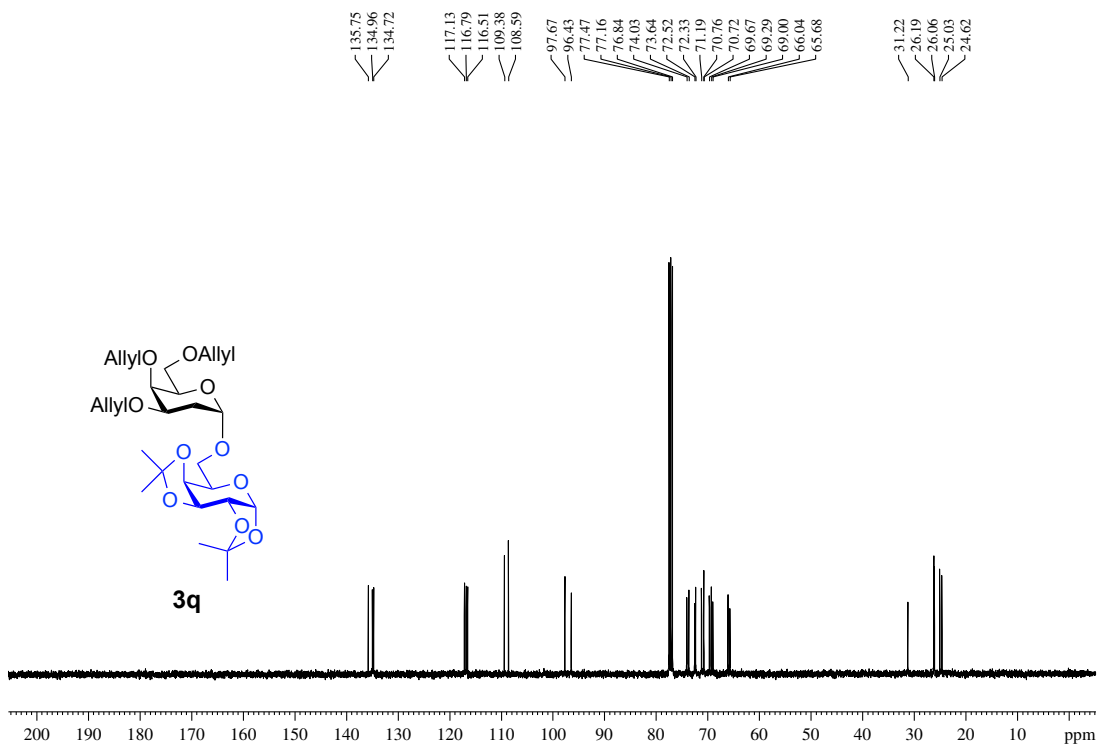
^{13}C NMR of **3p**, CDCl_3 , 100 MHz



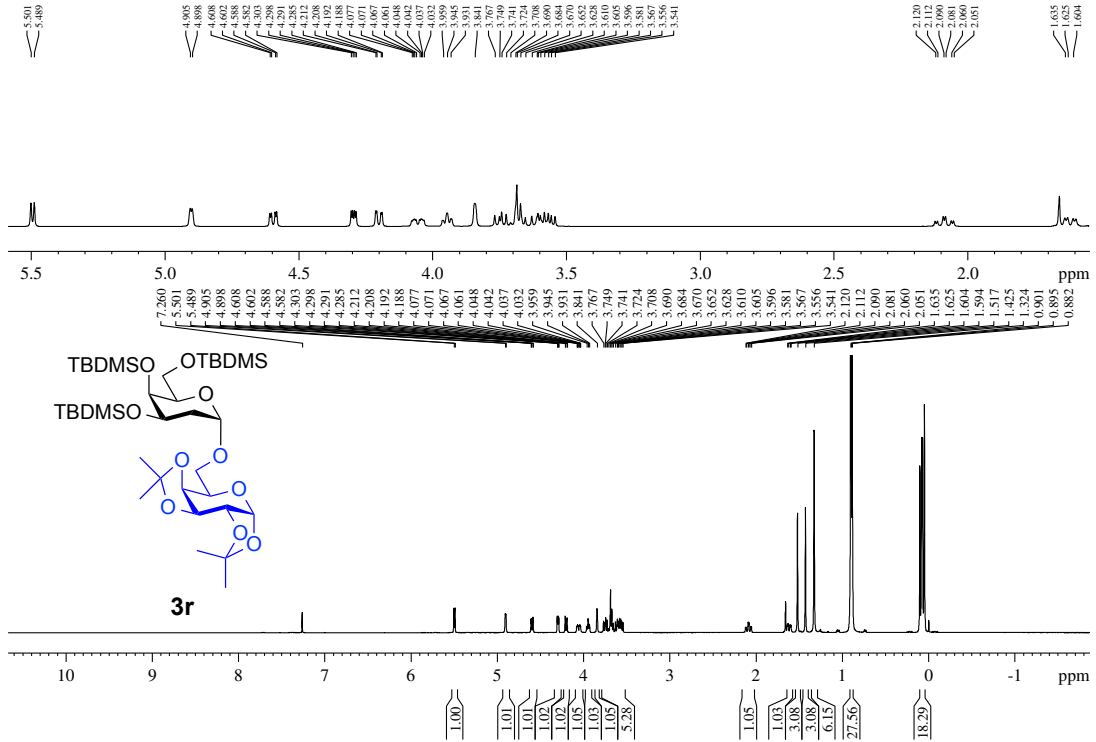
¹H NMR of **3q**, CDCl₃, 400 MHz



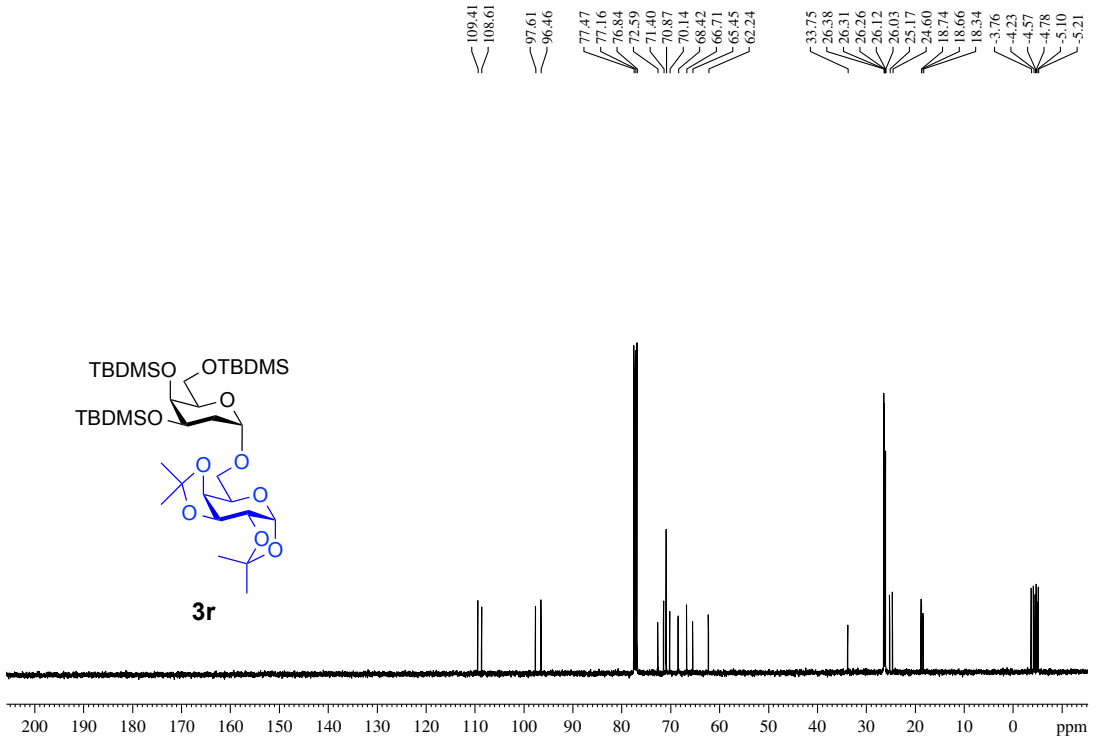
¹³C NMR of **3q**, CDCl₃, 100 MHz



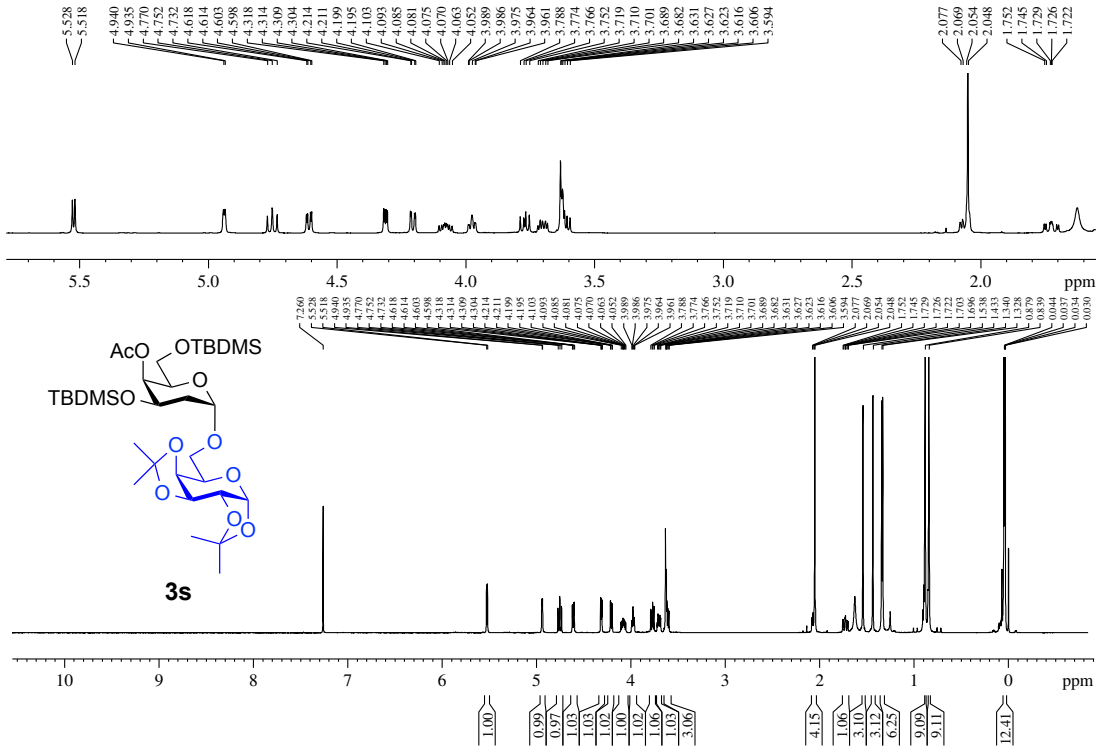
¹H NMR of **3r**, CDCl₃, 400 MHz



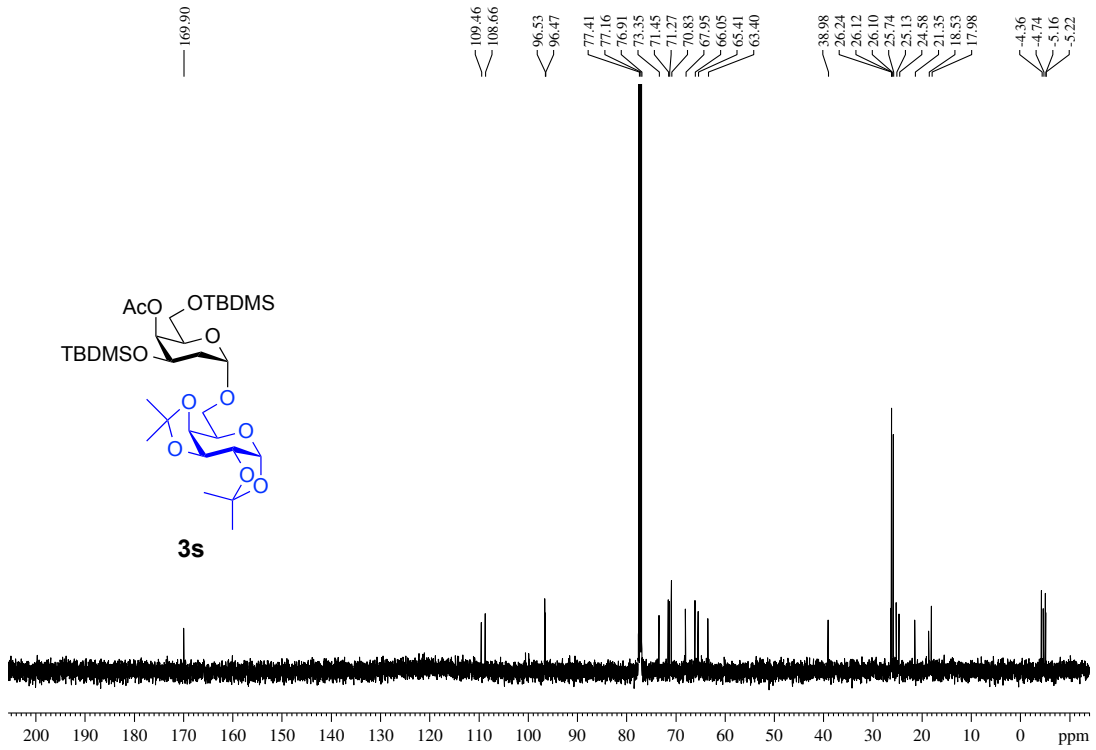
¹³C NMR of **3r**, CDCl₃, 100 MHz



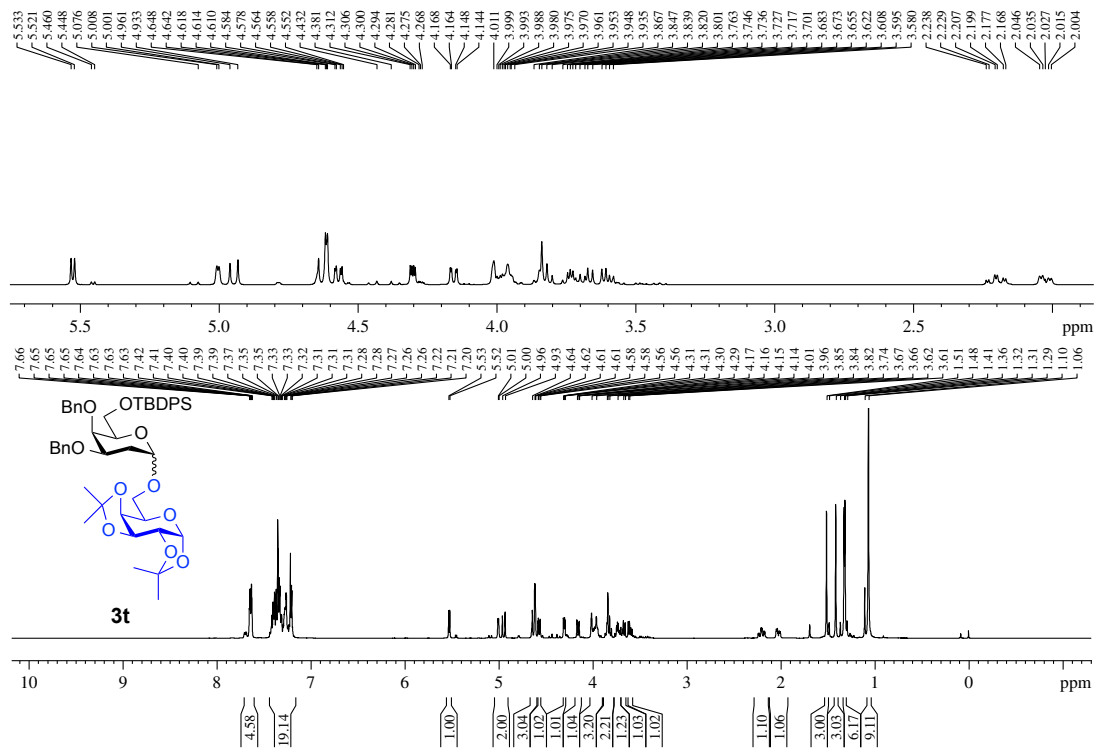
¹H NMR of **3s**, CDCl₃, 500 MHz



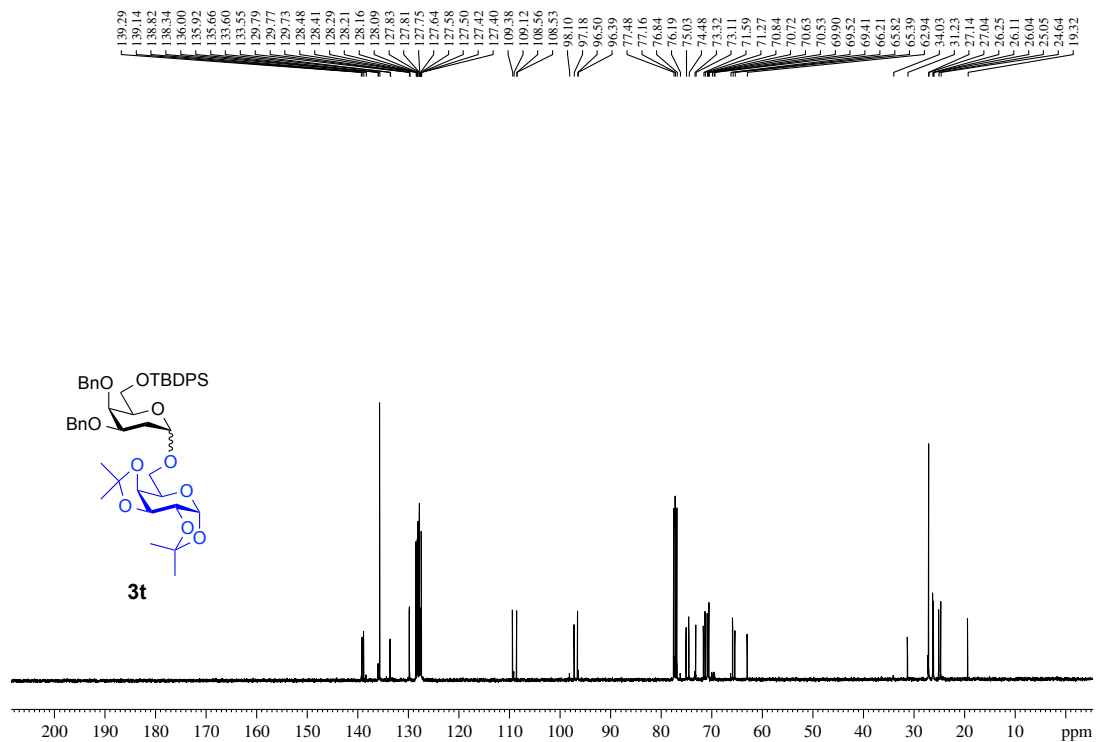
¹³C NMR of **3s**, CDCl₃, 125 MHz



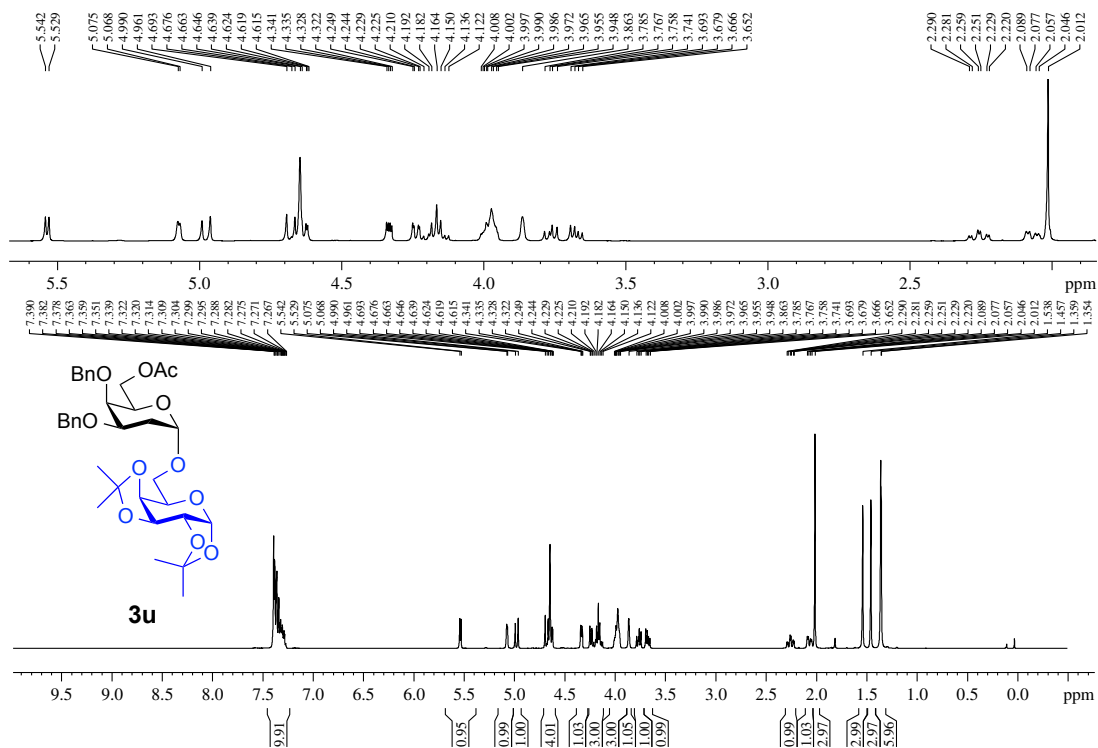
¹H NMR of **3t**, CDCl₃, 400 MHz



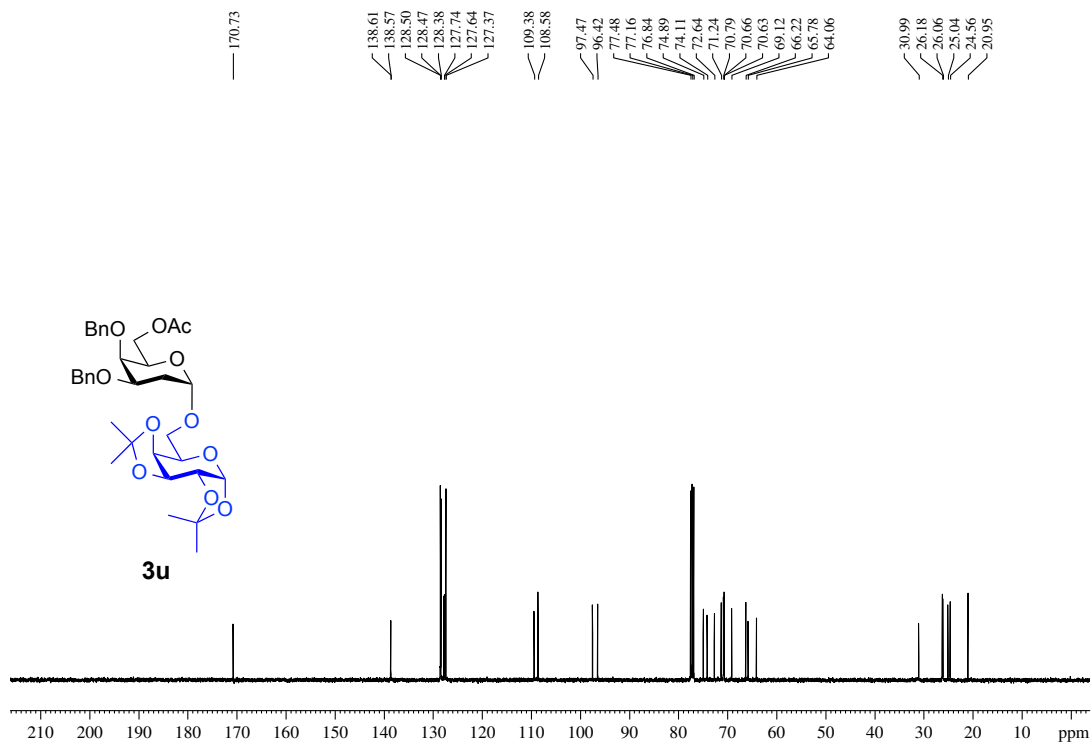
¹³C NMR of **3t**, CDCl₃, 100 MHz



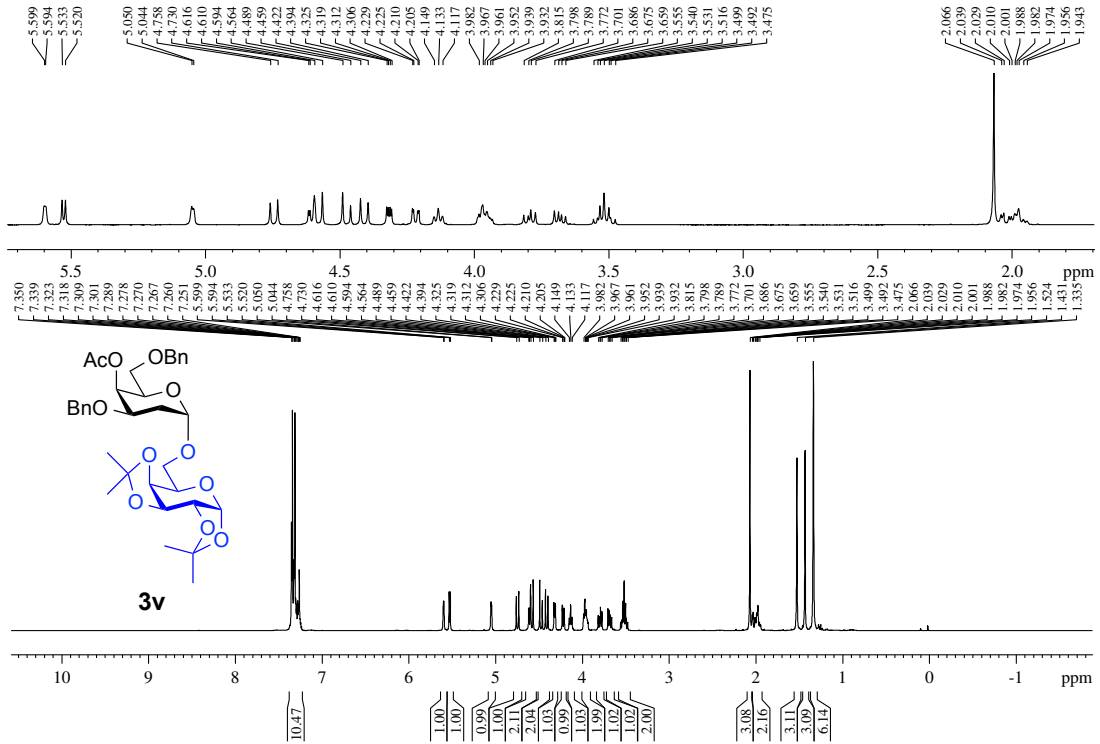
¹H NMR of **3u**, CDCl₃, 400 MHz



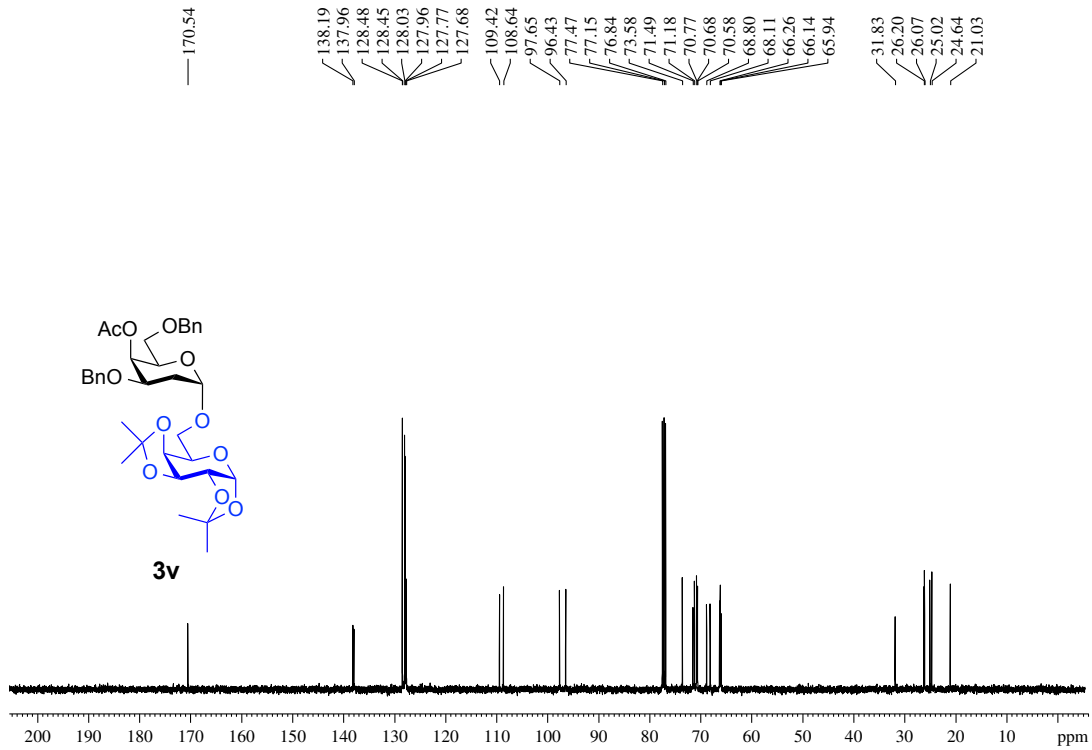
¹³C NMR of **3u**, CDCl₃, 100 MHz



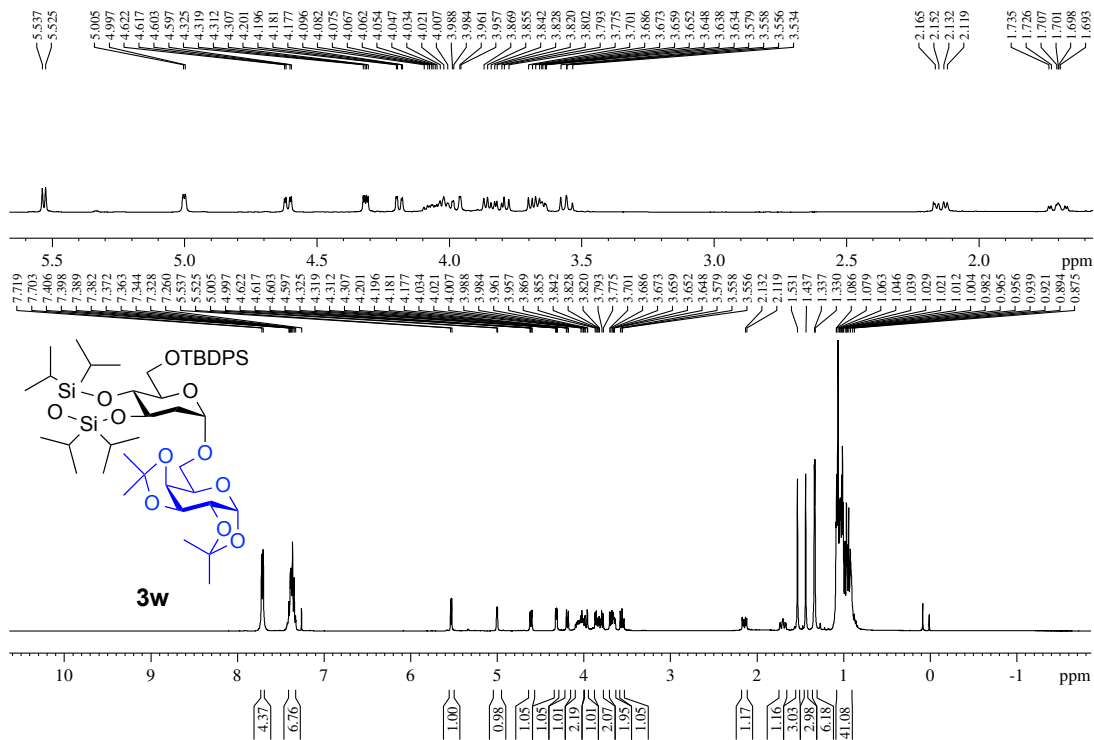
¹H NMR of **3v**, CDCl₃, 400 MHz



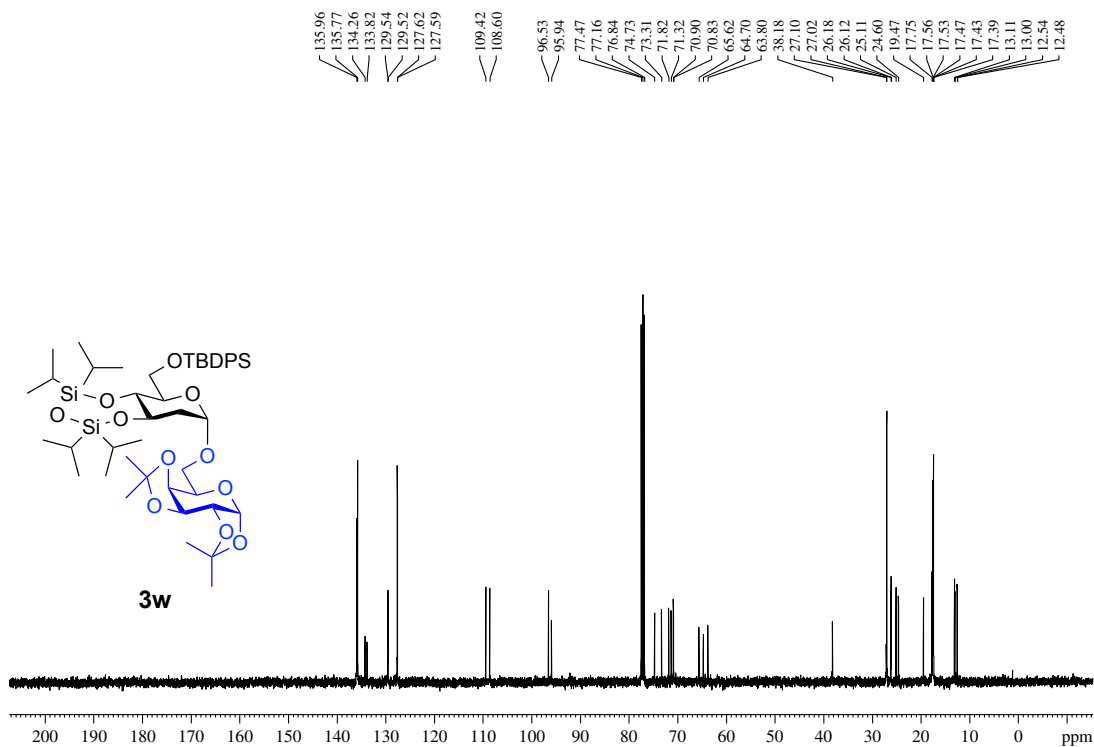
¹³C NMR of **3v**, CDCl₃, 100 MHz



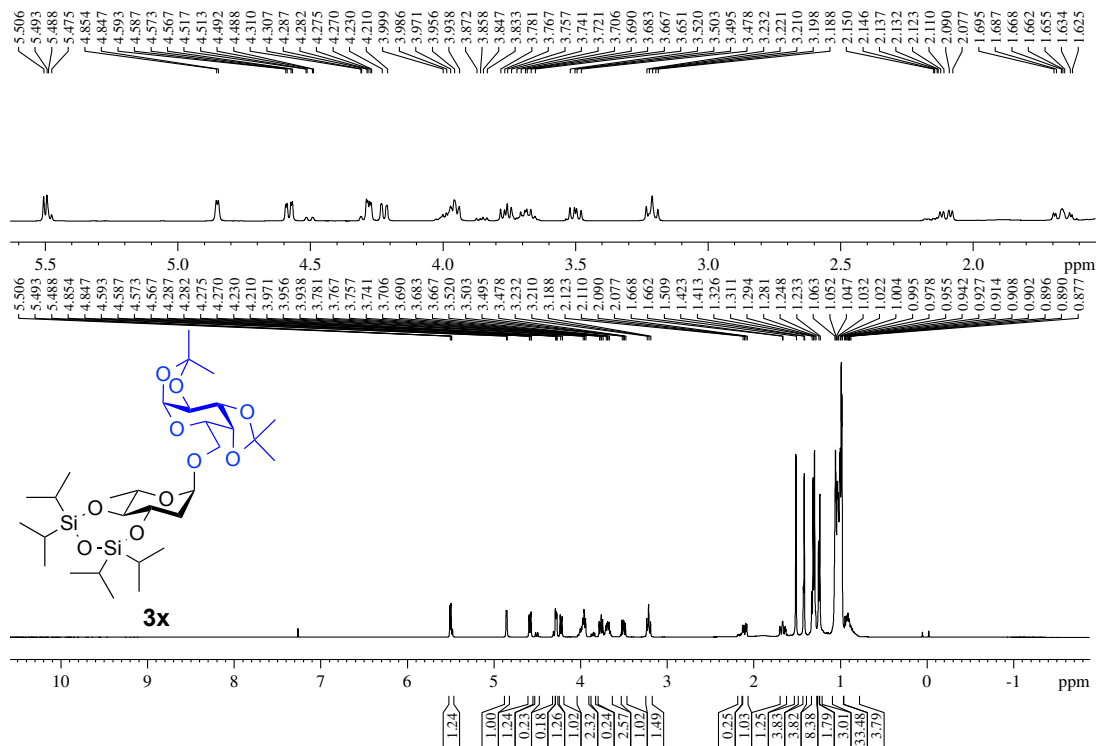
¹H NMR of **3w**, CDCl₃, 400 MHz



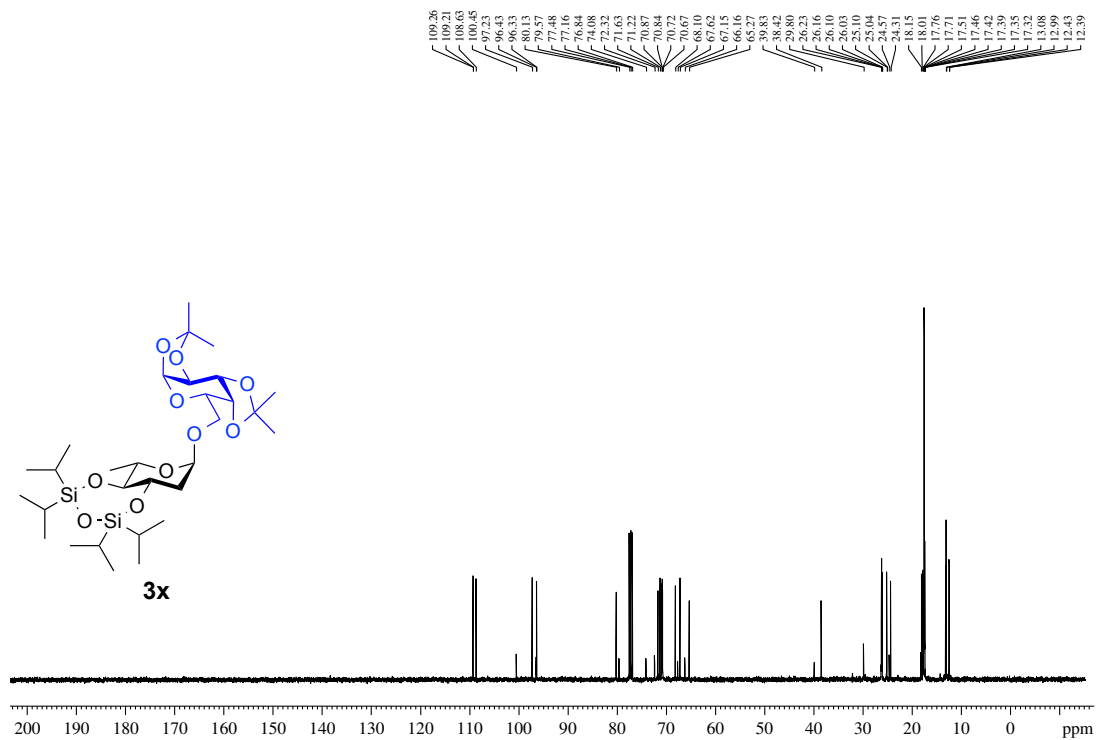
¹³C NMR of **3w**, CDCl₃, 100 MHz



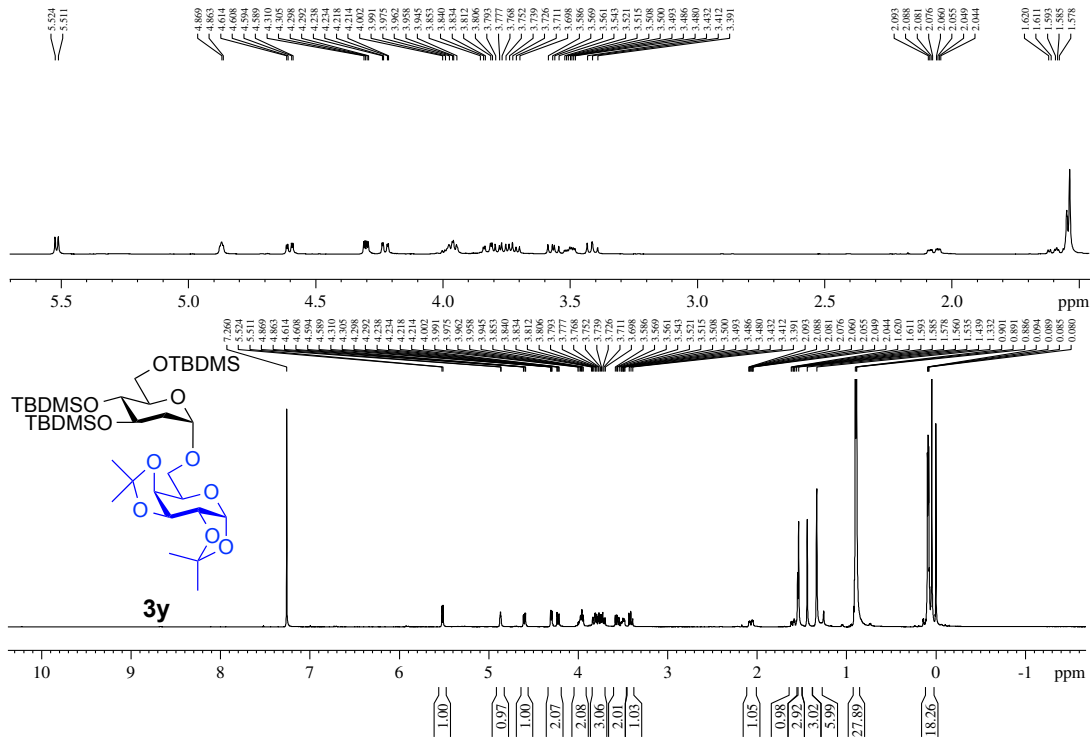
¹H NMR of **3x**, CDCl₃, 400 MHz



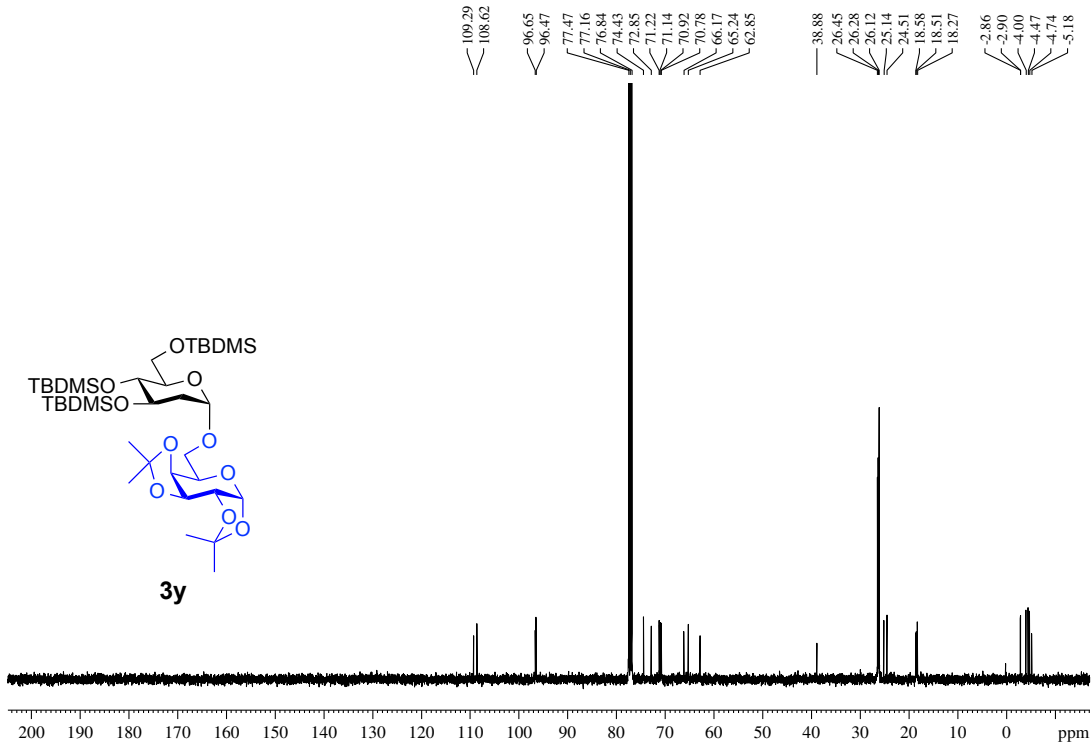
¹³C NMR of **3x**, CDCl₃, 100 MHz



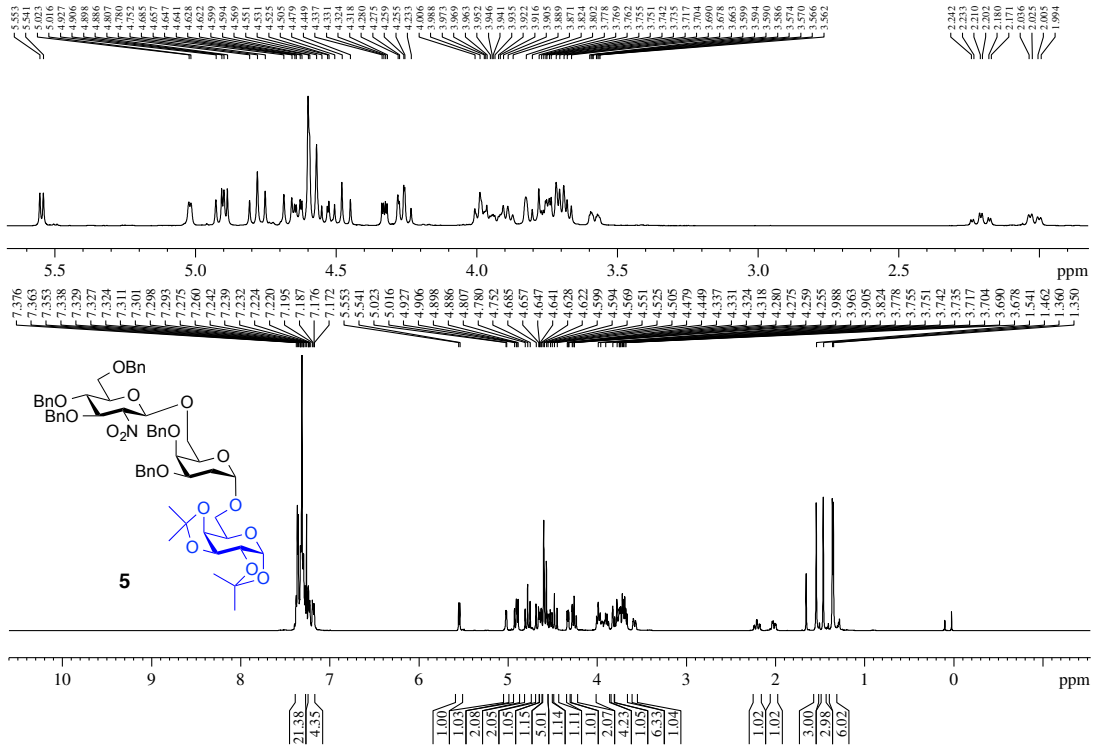
^1H NMR of **3y**, CDCl_3 , 400 MHz



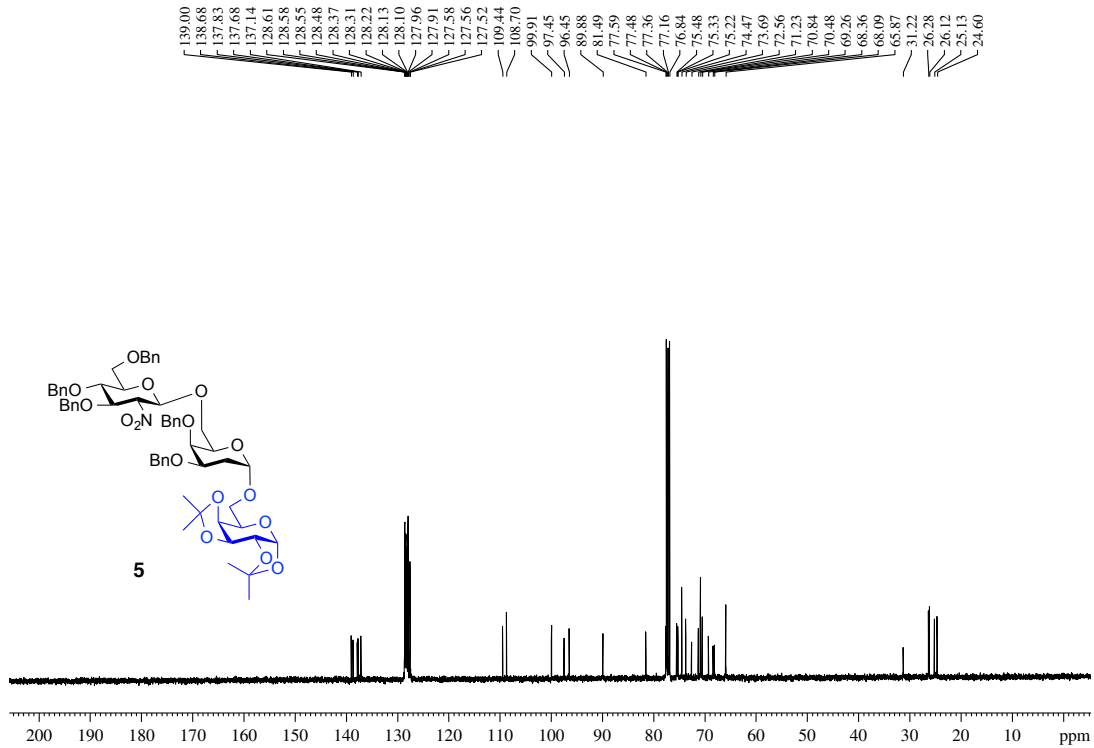
^{13}C NMR of **3y**, CDCl_3 , 100 MHz



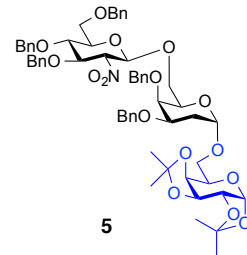
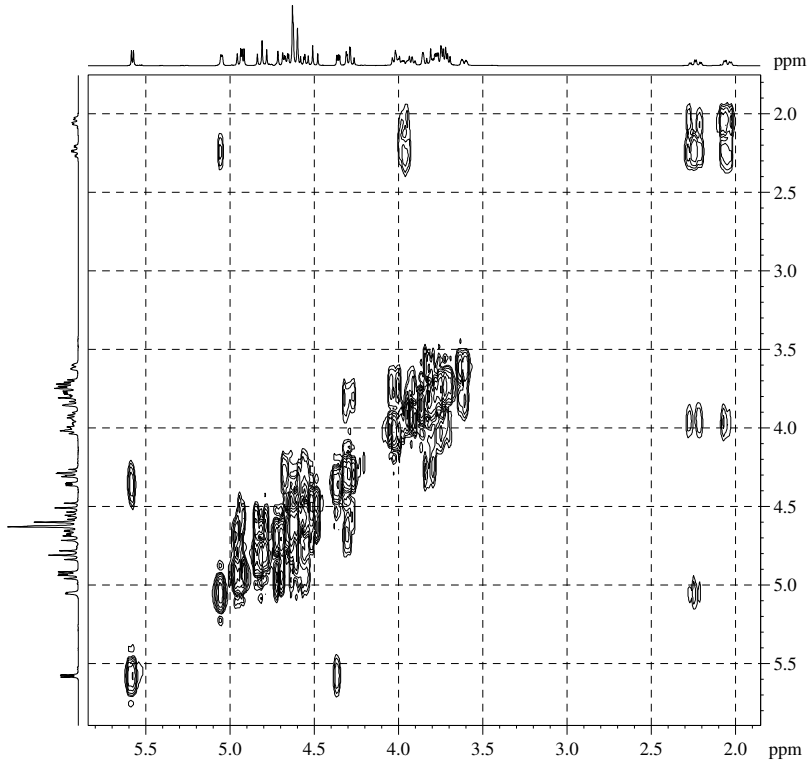
¹H NMR of **5**, CDCl₃, 400 MHz



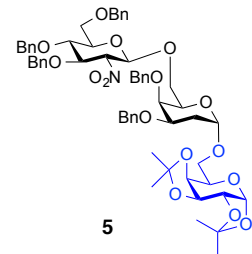
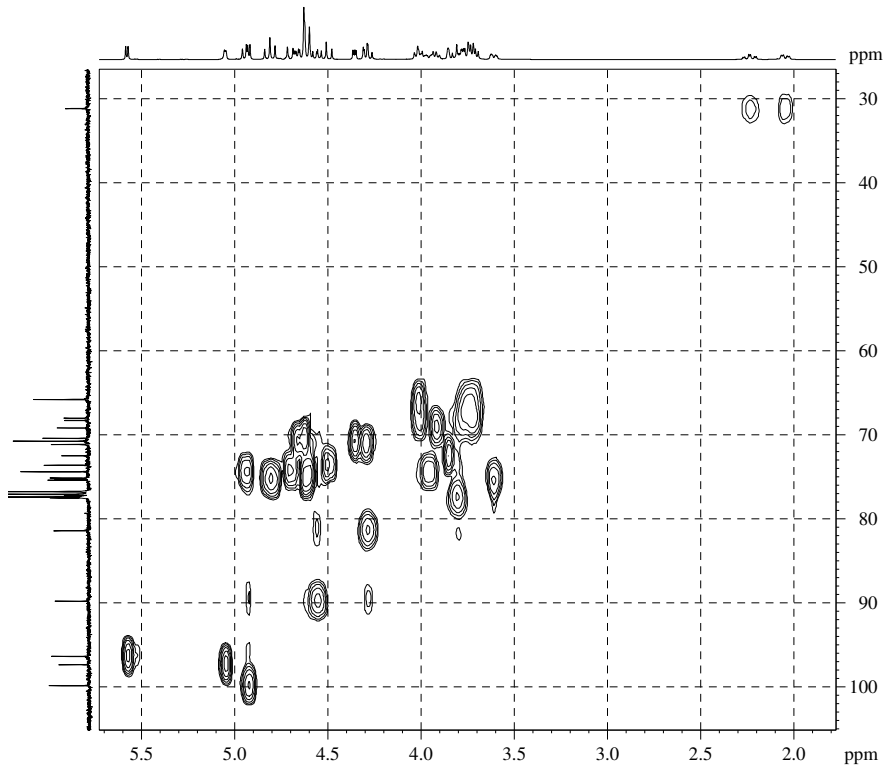
¹³C NMR of **5**, CDCl₃, 100 MHz



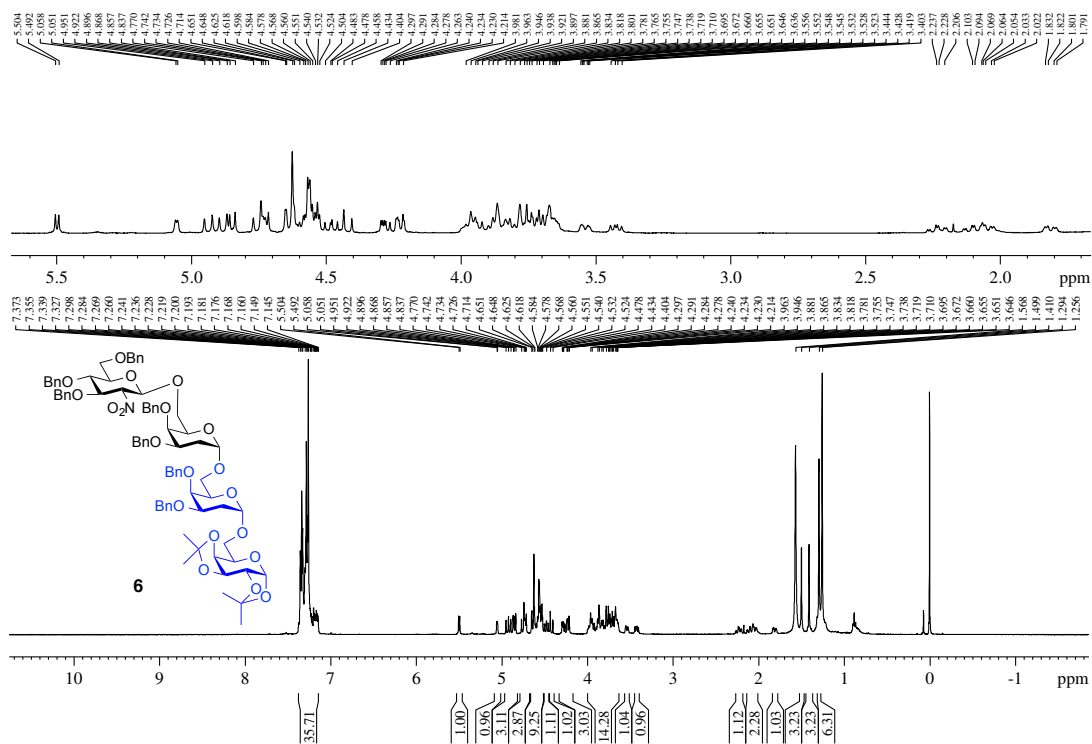
COSY of **5**, CDCl₃



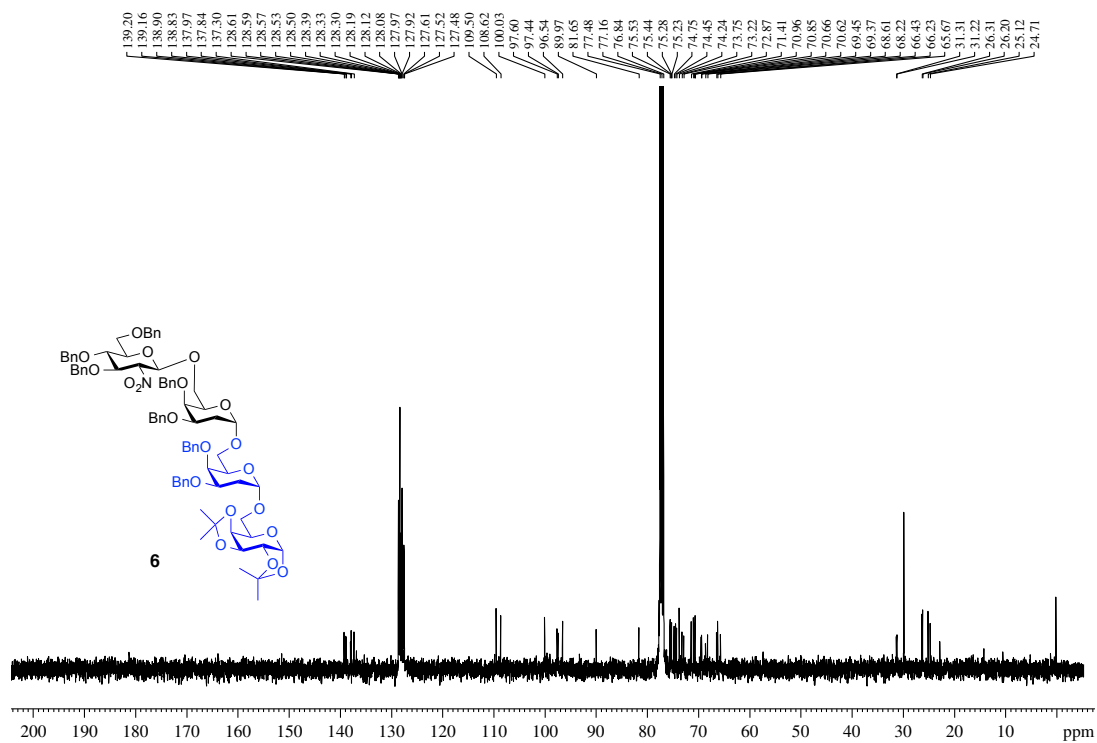
HSQC of **5**, CDCl₃



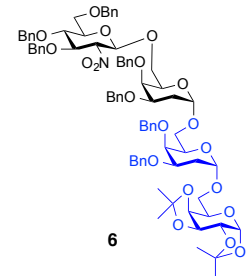
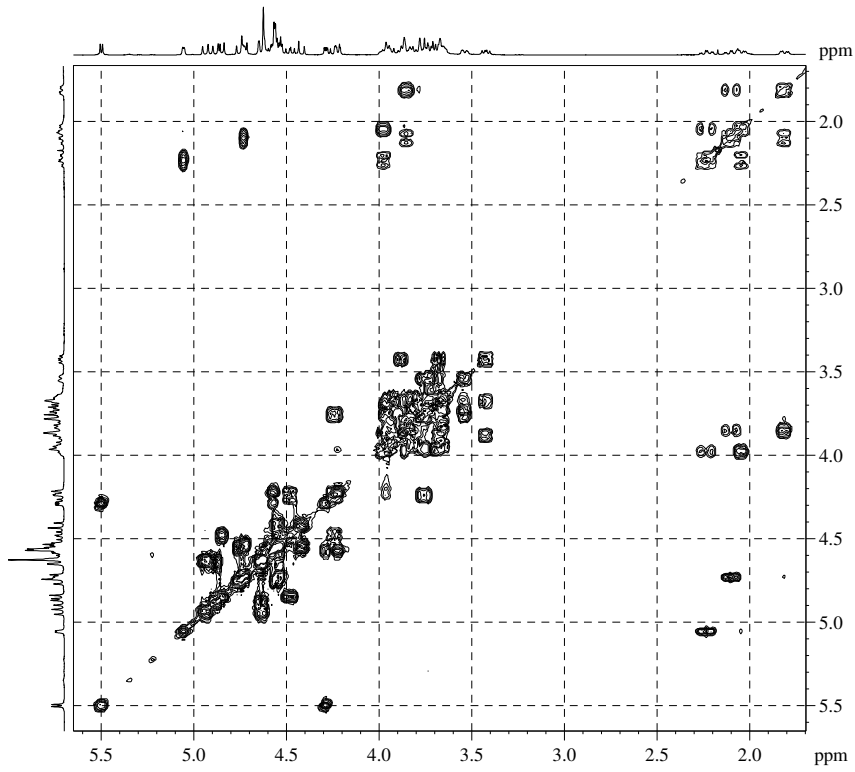
^1H NMR of **6**, CDCl_3 , 400 MHz



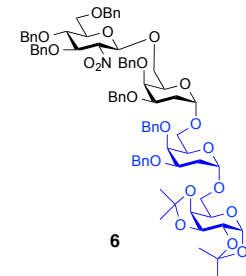
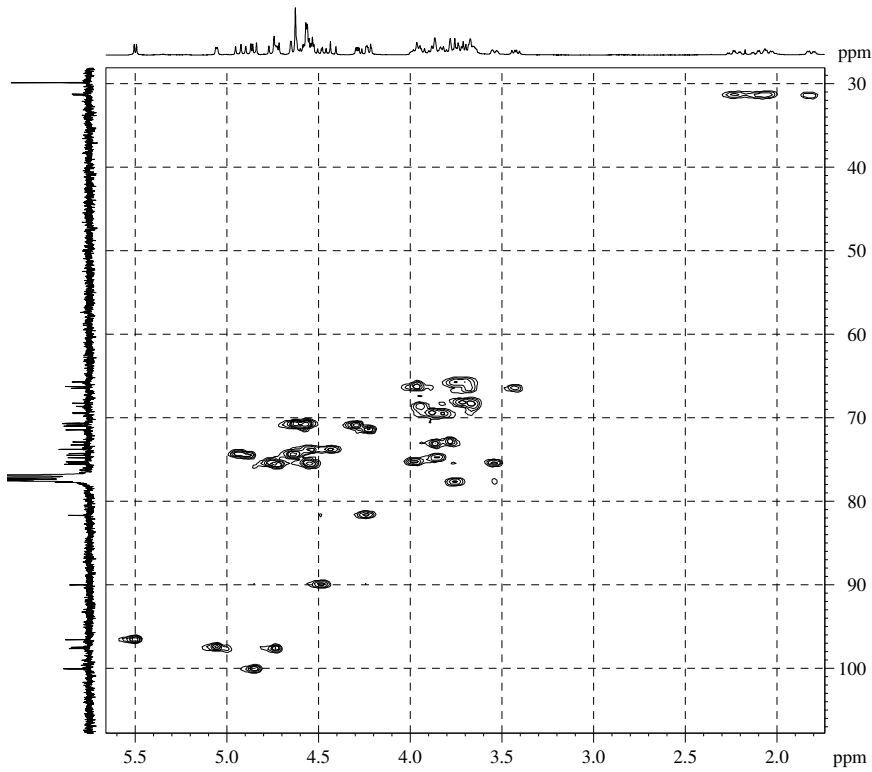
^{13}C NMR of **6**, CDCl_3 , 100 MHz



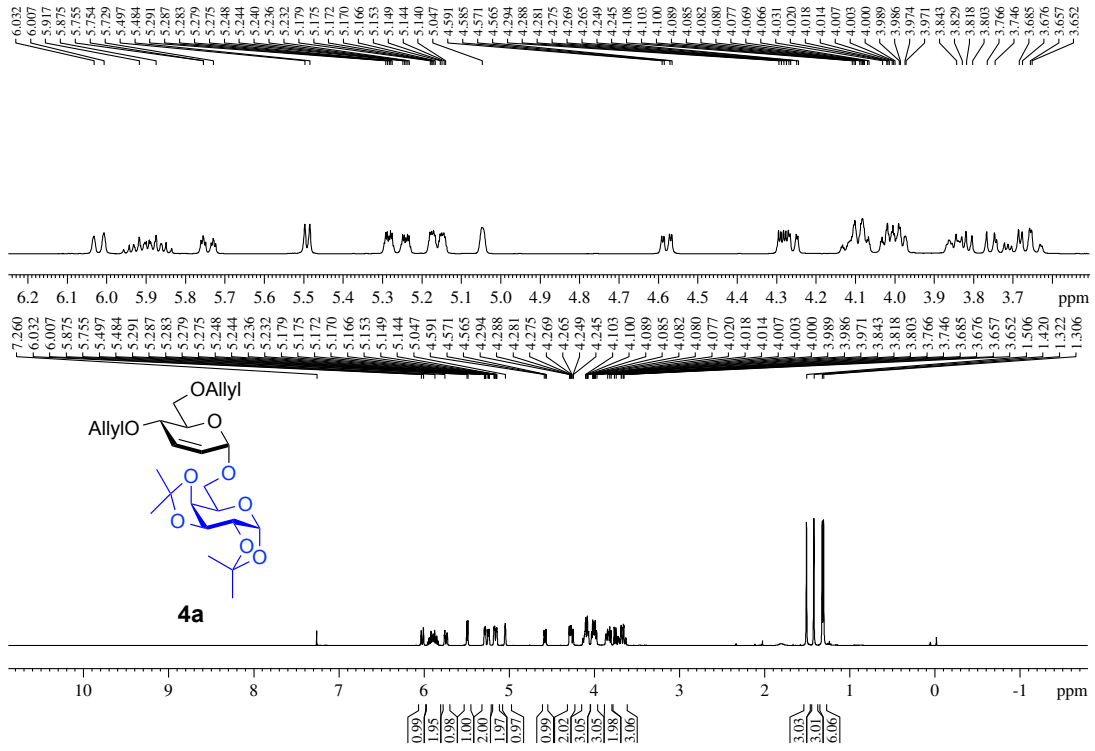
COSY of 6, CDCl₃



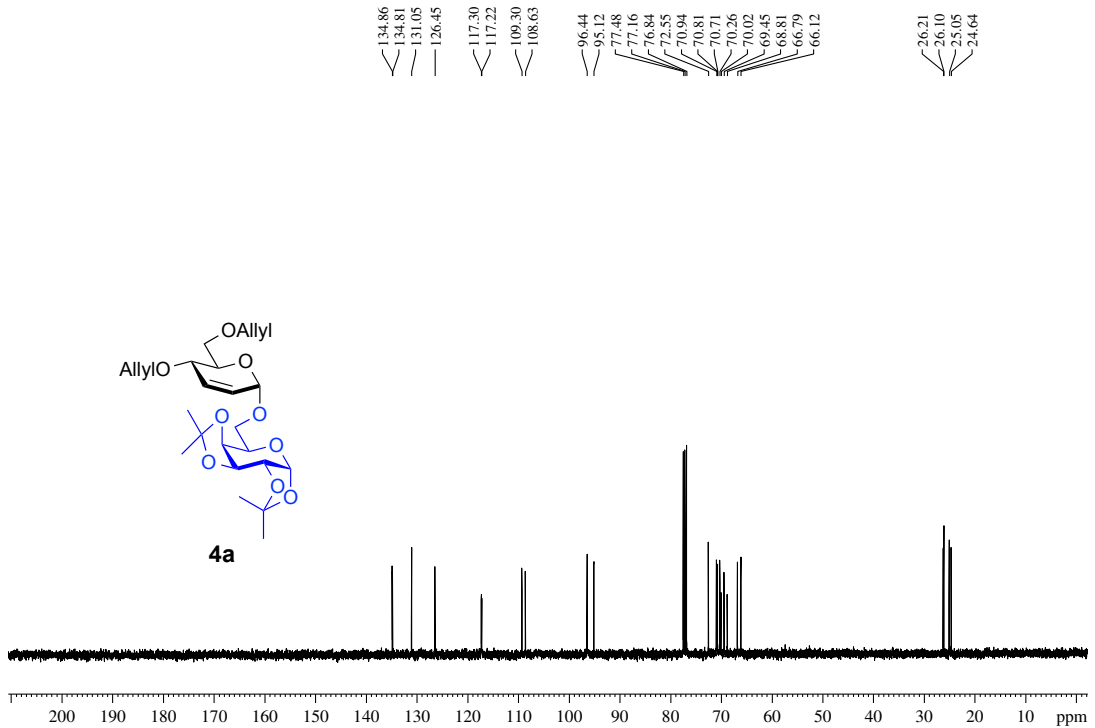
HSQC of 6, CDCl₃



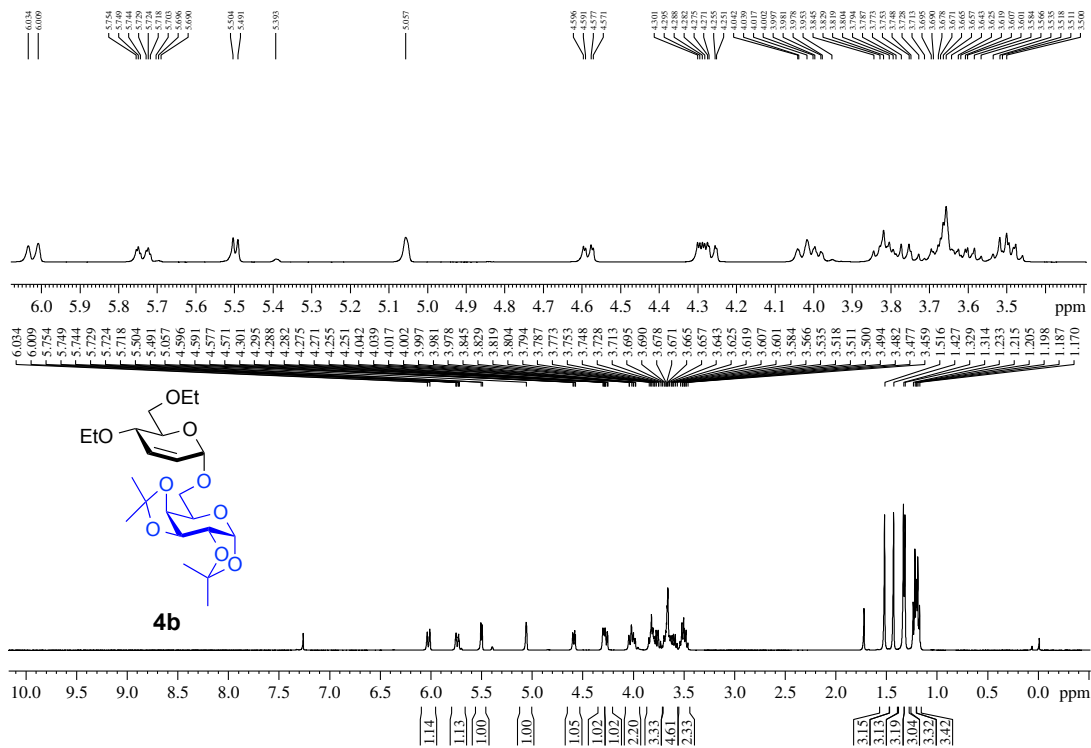
¹H NMR of **4a**, CDCl₃, 400 MHz



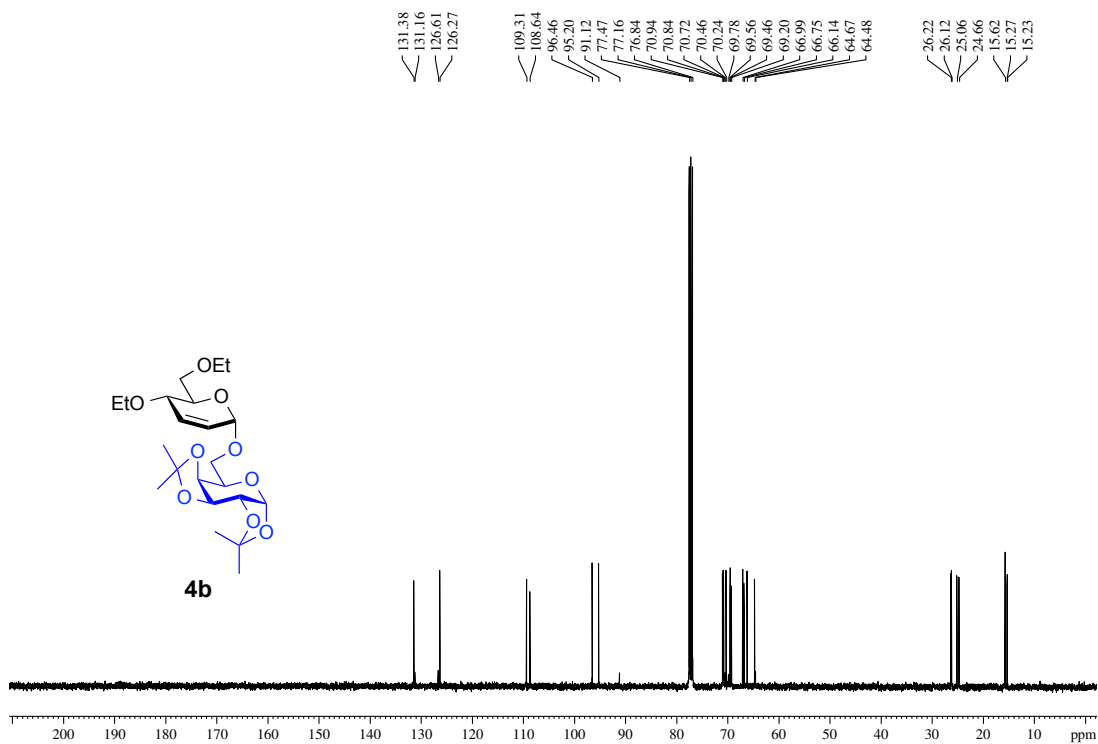
¹³C NMR of **4a**, CDCl₃, 100 MHz



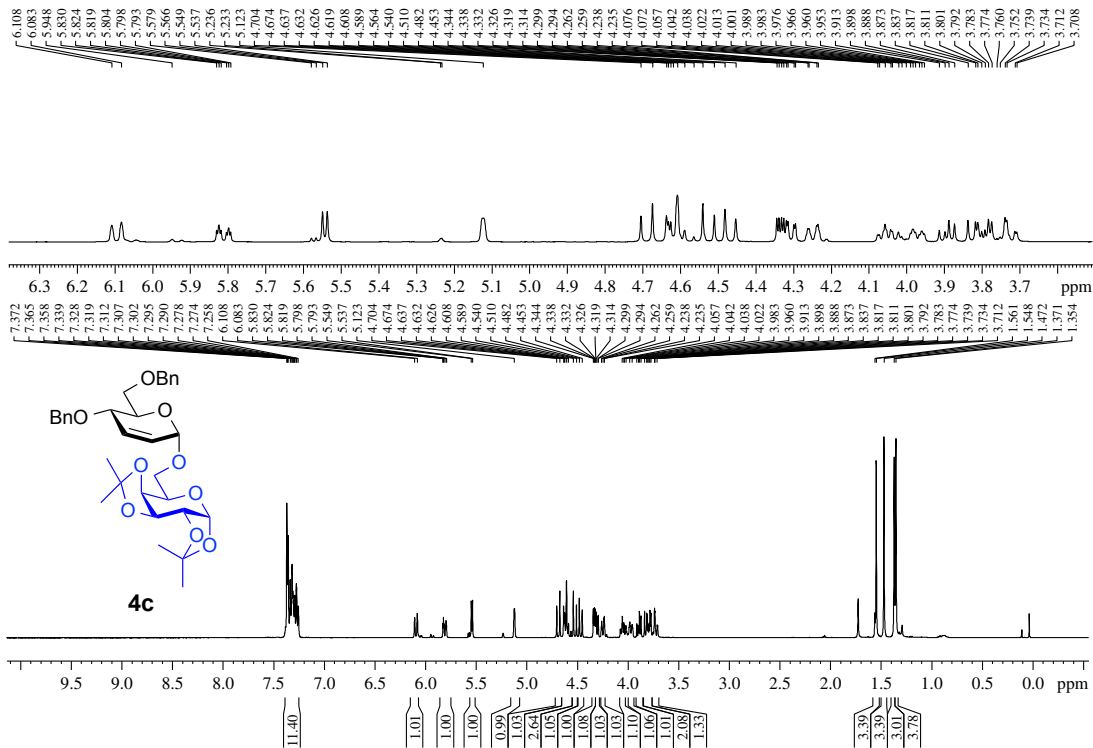
¹H NMR of **4b**, CDCl₃, 400 MHz



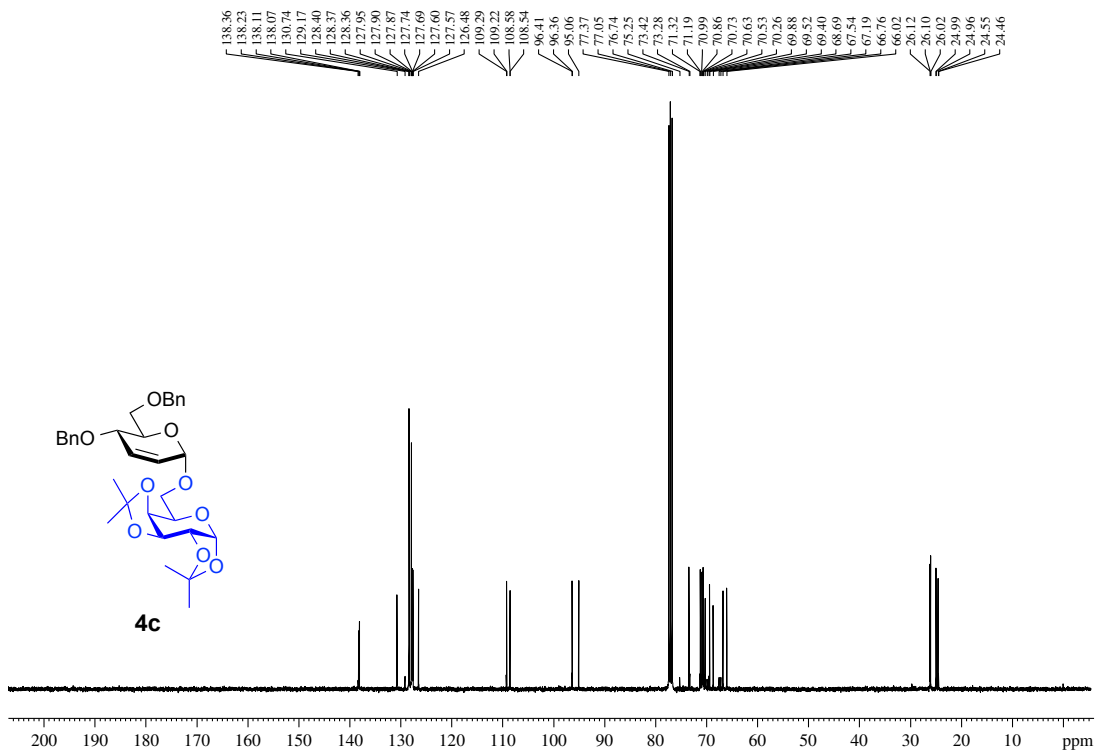
¹³C NMR of **4b**, CDCl₃, 100 MHz



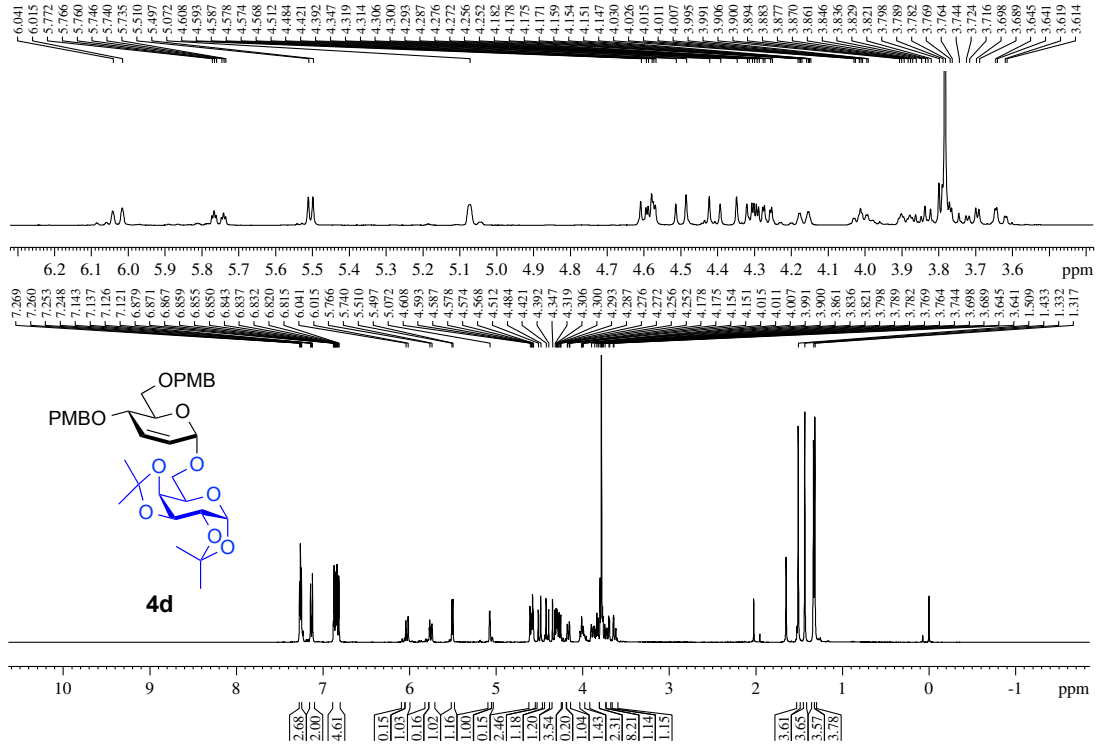
¹H NMR of **4c**, CDCl₃, 400 MHz



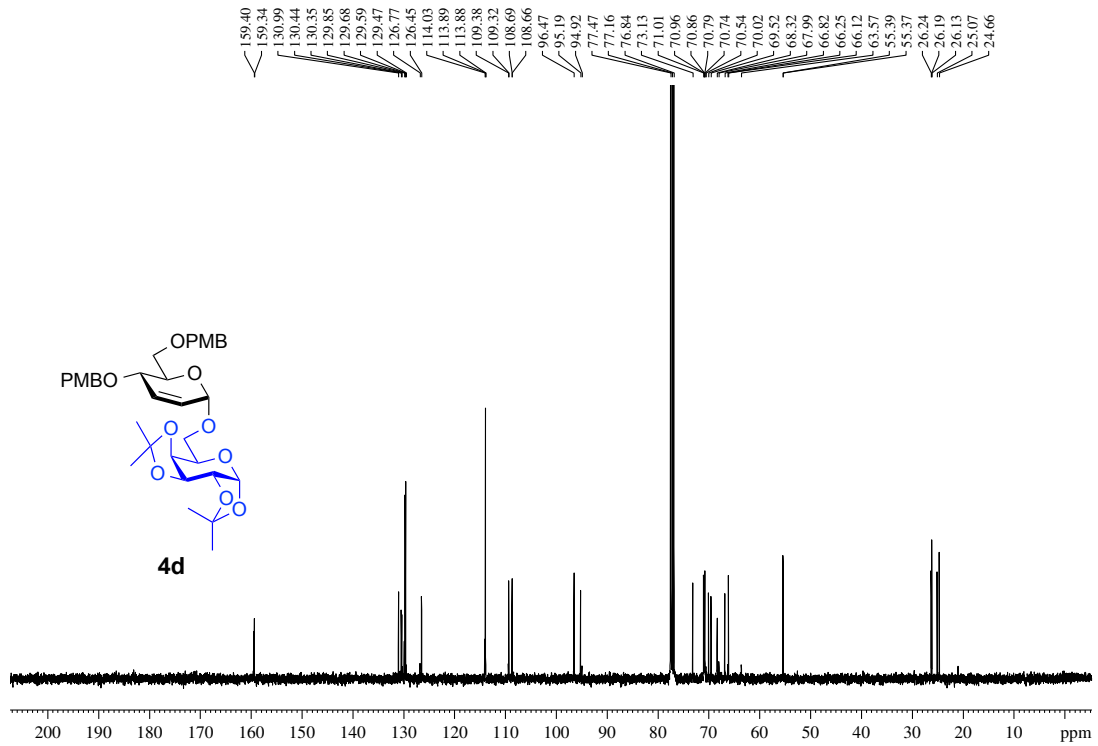
¹³C NMR of **4c**, CDCl₃, 100 MHz



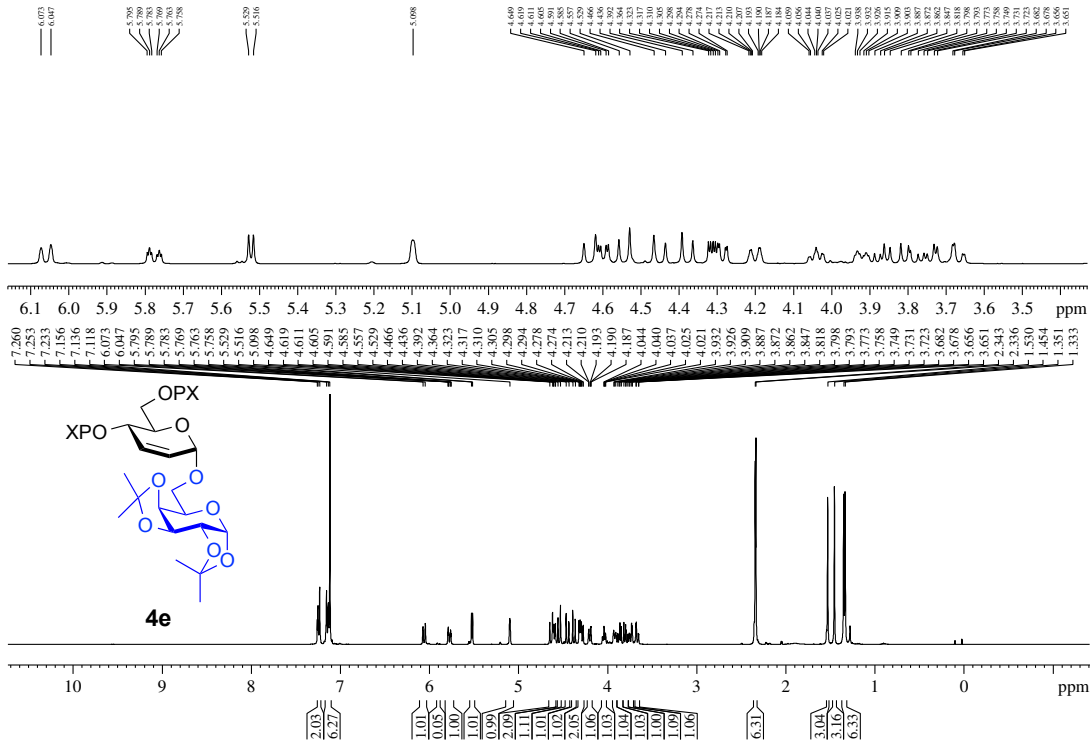
^1H NMR of 4d, CDCl_3 , 400 MHz



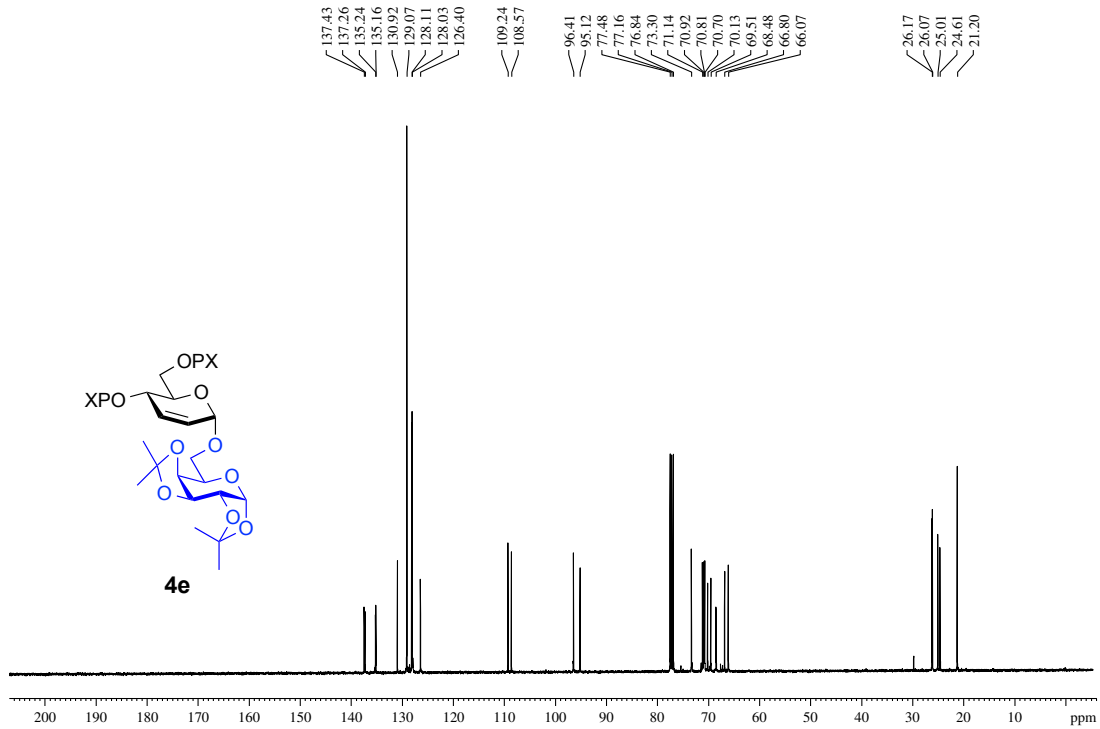
^{13}C NMR of 4d, CDCl_3 , 100 MHz



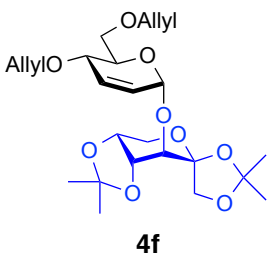
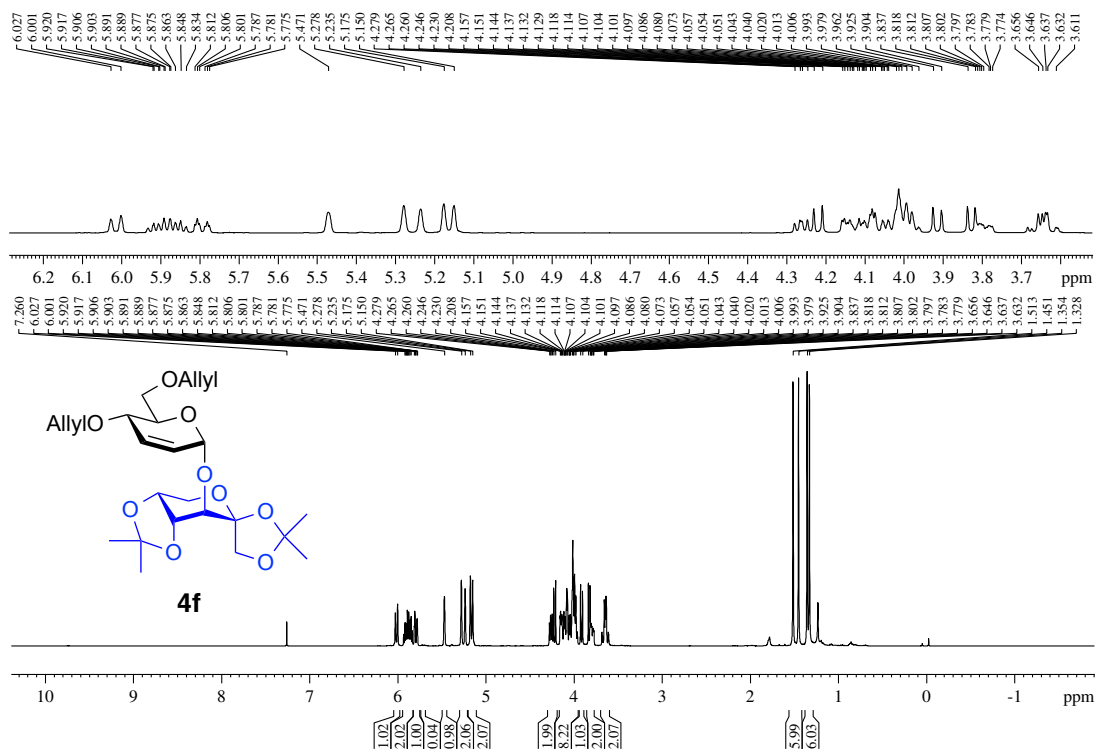
^1H NMR of **4e**, CDCl_3 , 400 MHz



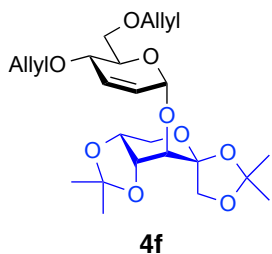
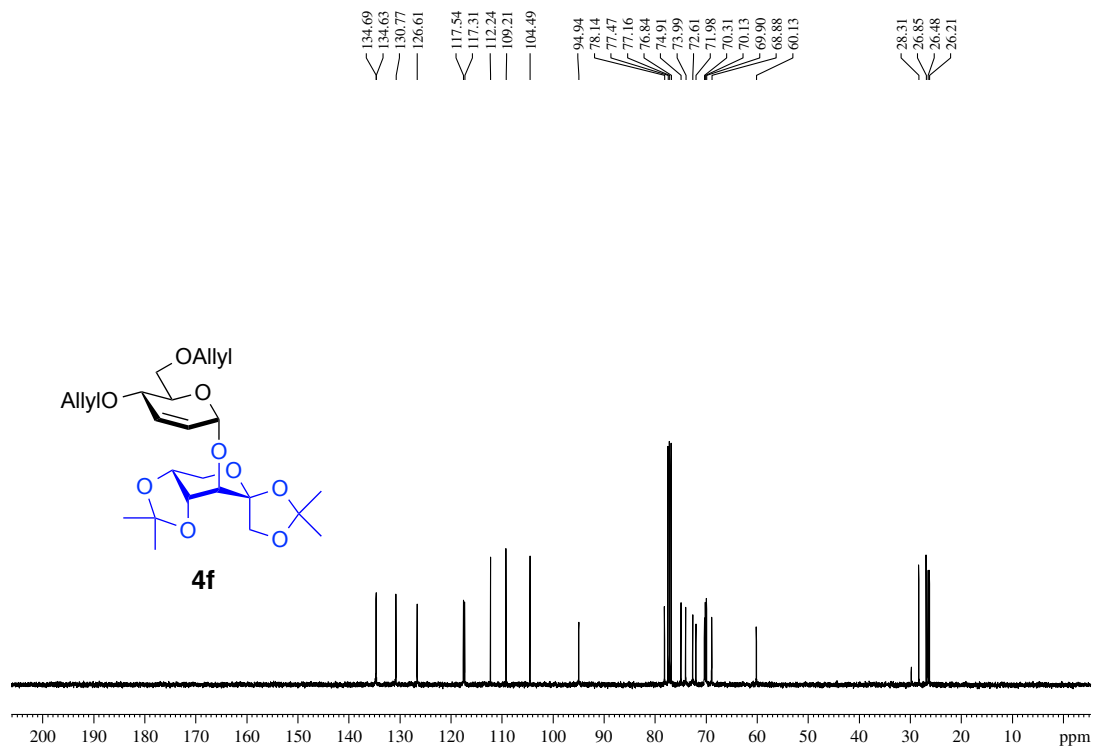
^{13}C NMR of **4e**, CDCl_3 , 100 MHz



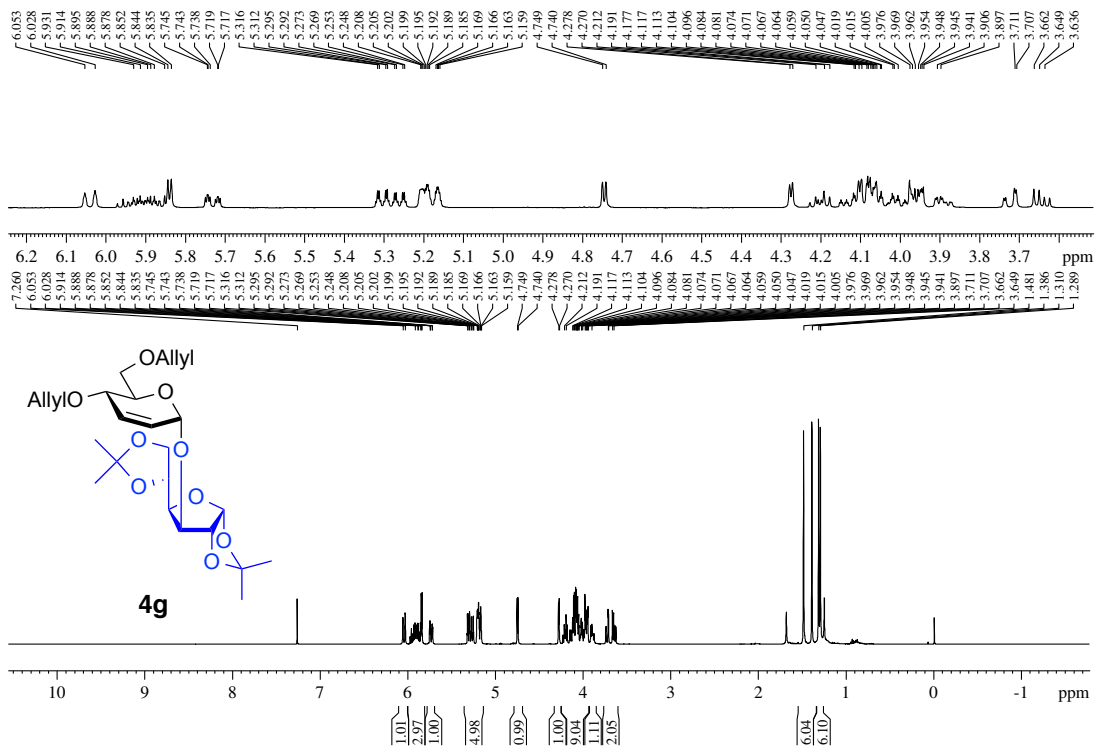
¹H NMR of **4f**, CDCl₃, 400 MHz



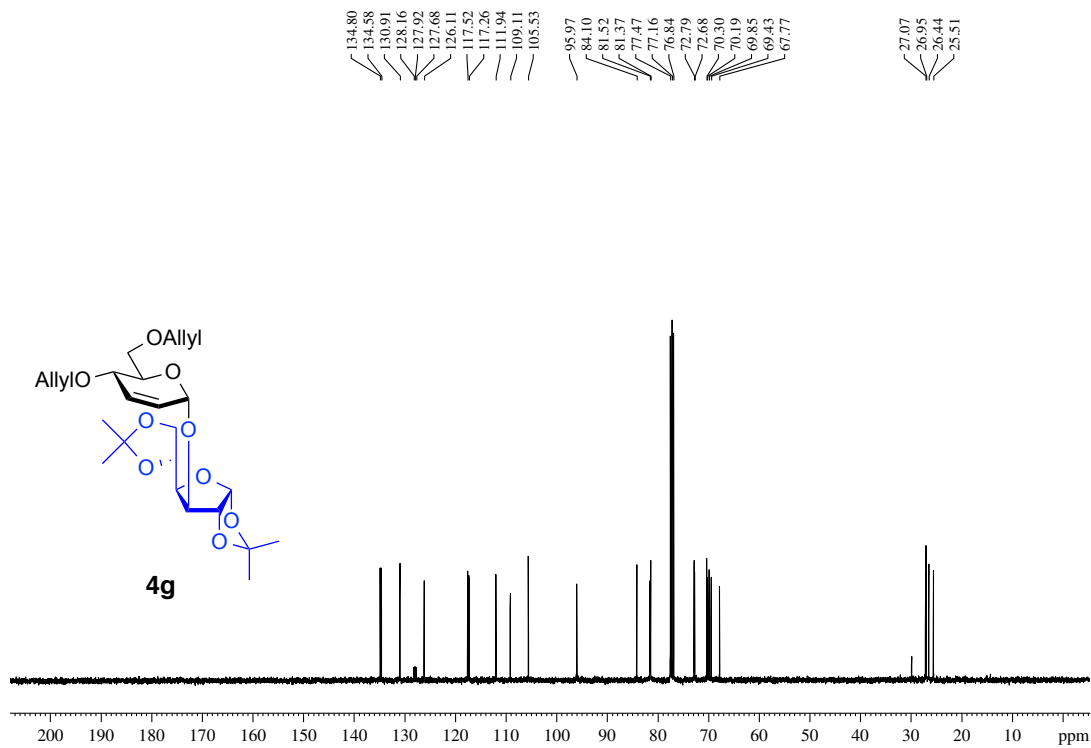
¹³C NMR **4f**, CDCl₃, 100 MHz



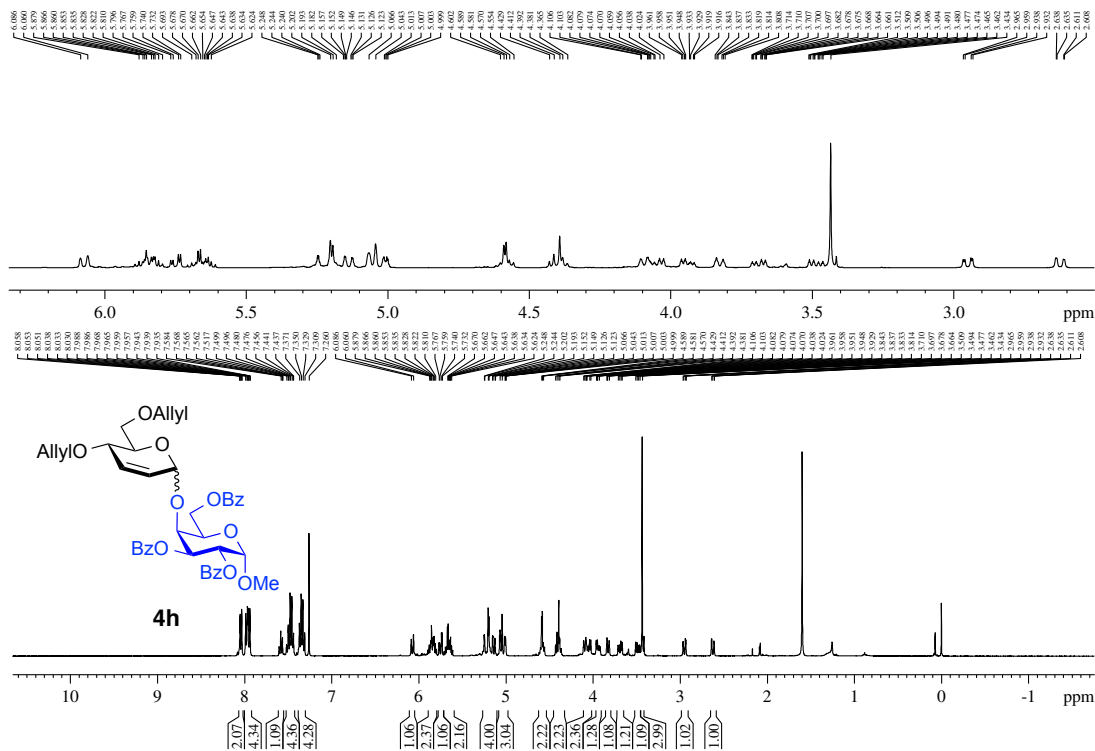
¹H NMR **4g**, CDCl₃, 400 MHz



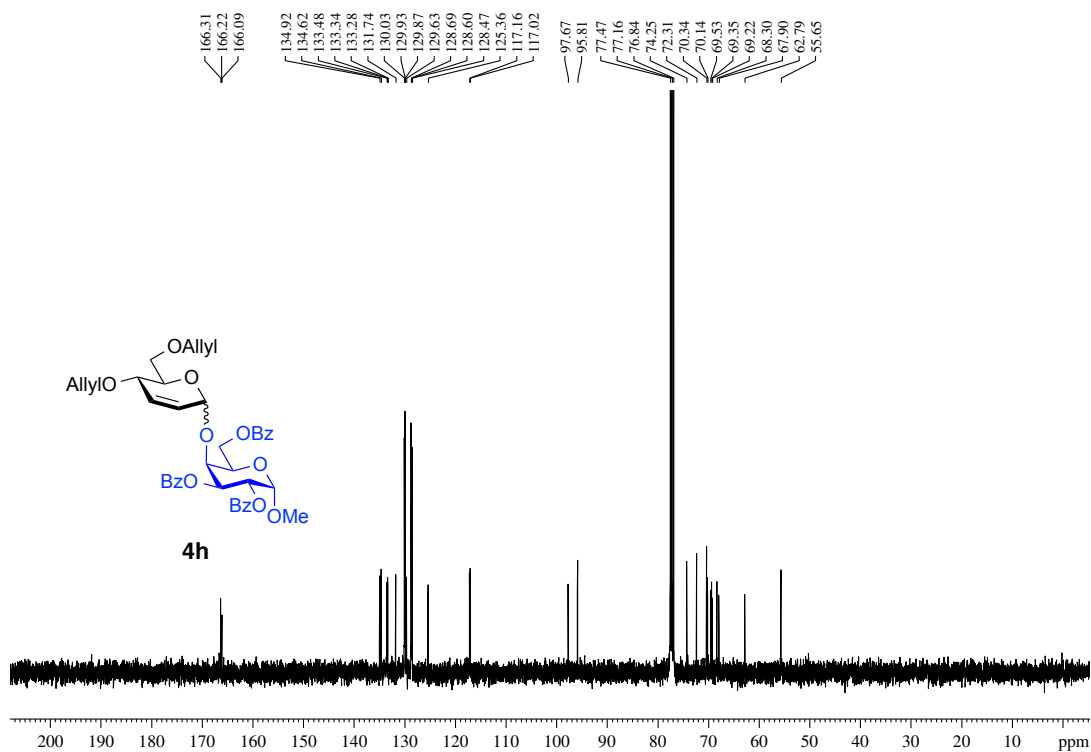
¹³C NMR **4g**, CDCl₃, 100 MHz



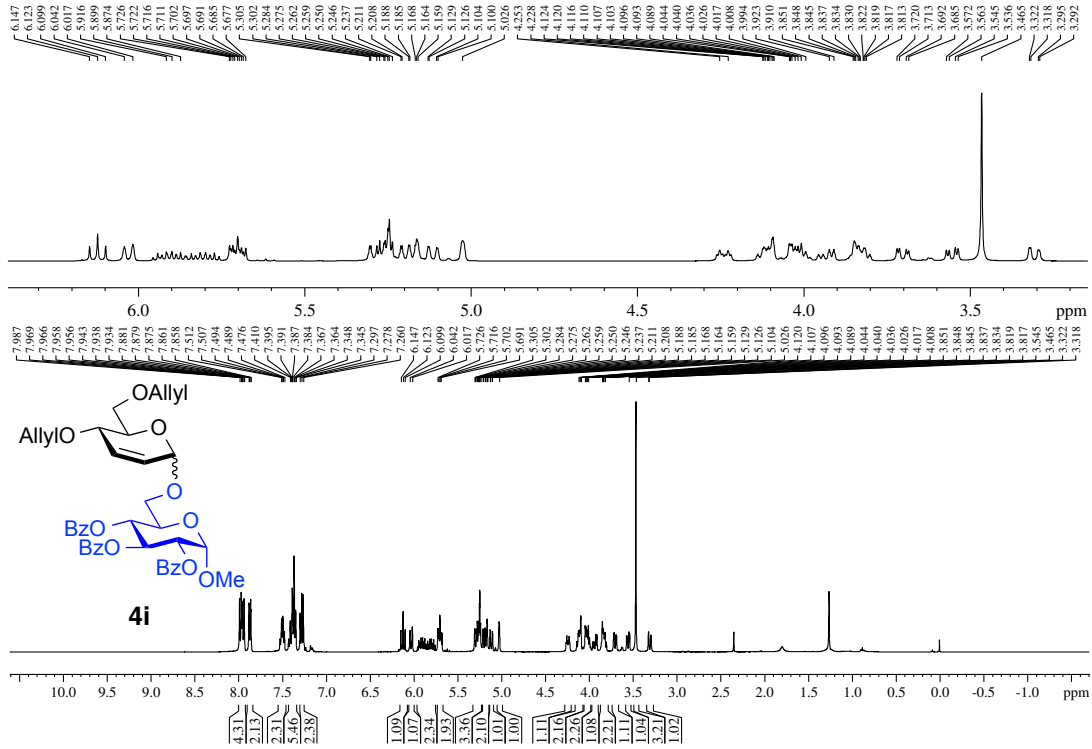
¹H NMR of **4h**, CDCl₃, 400 MHz



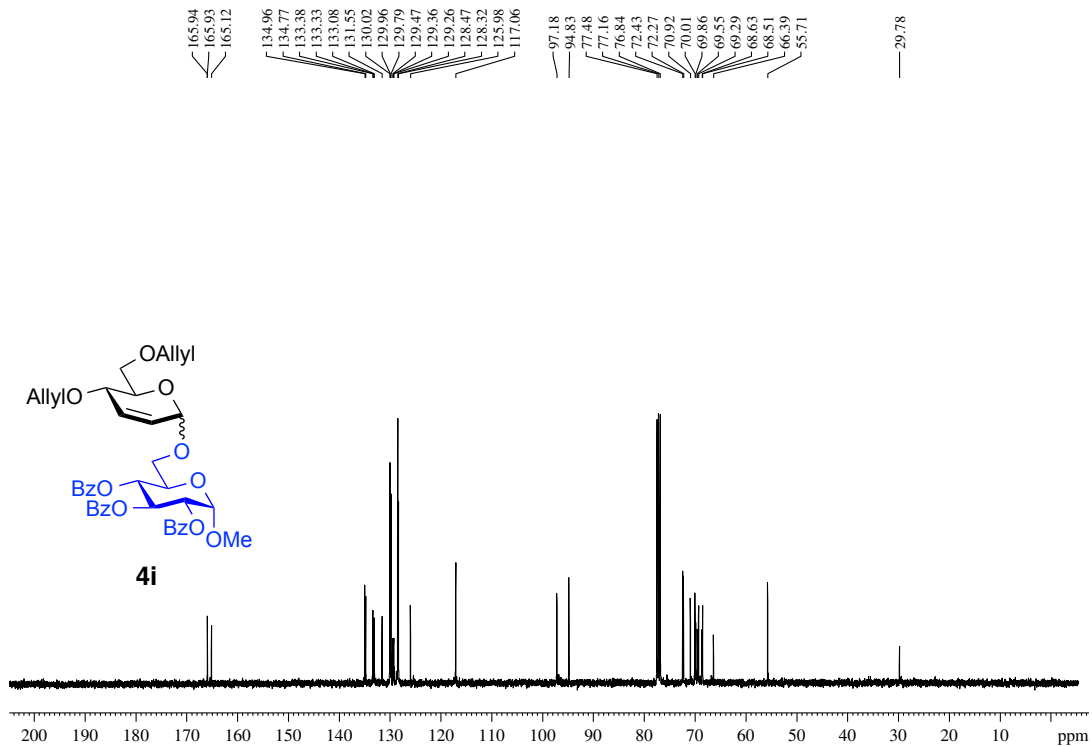
¹³C NMR of **4h**, CDCl₃, 100 MHz



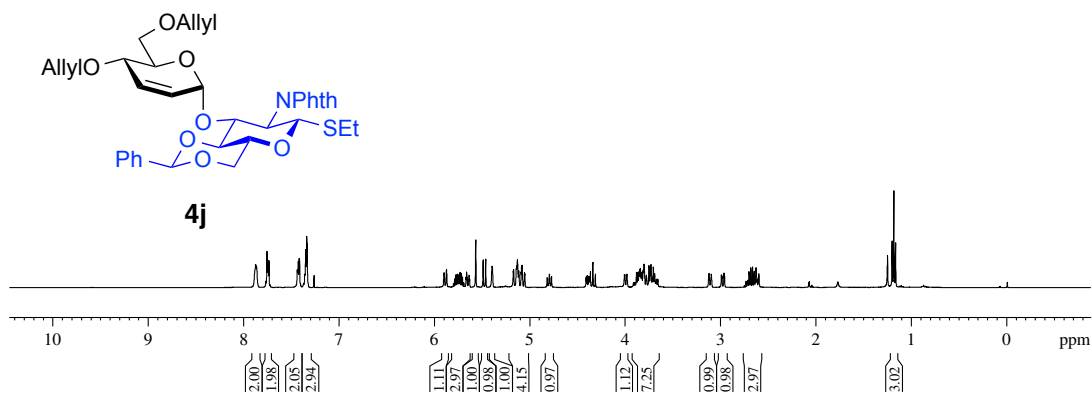
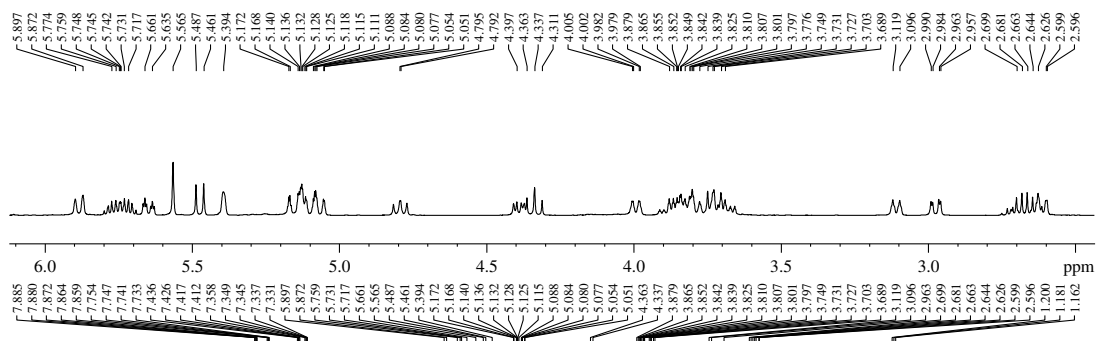
^1H NMR of **4i**, CDCl_3 , 400 MHz



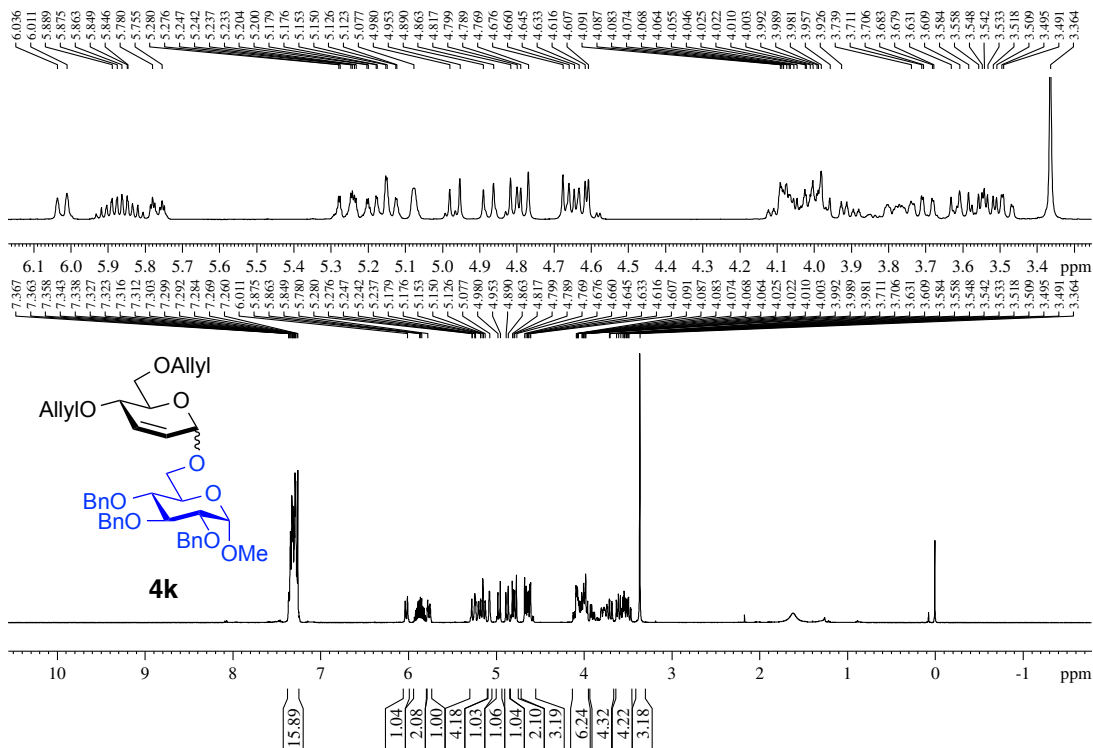
^{13}C NMR of **4i**, CDCl_3 , 100 MHz



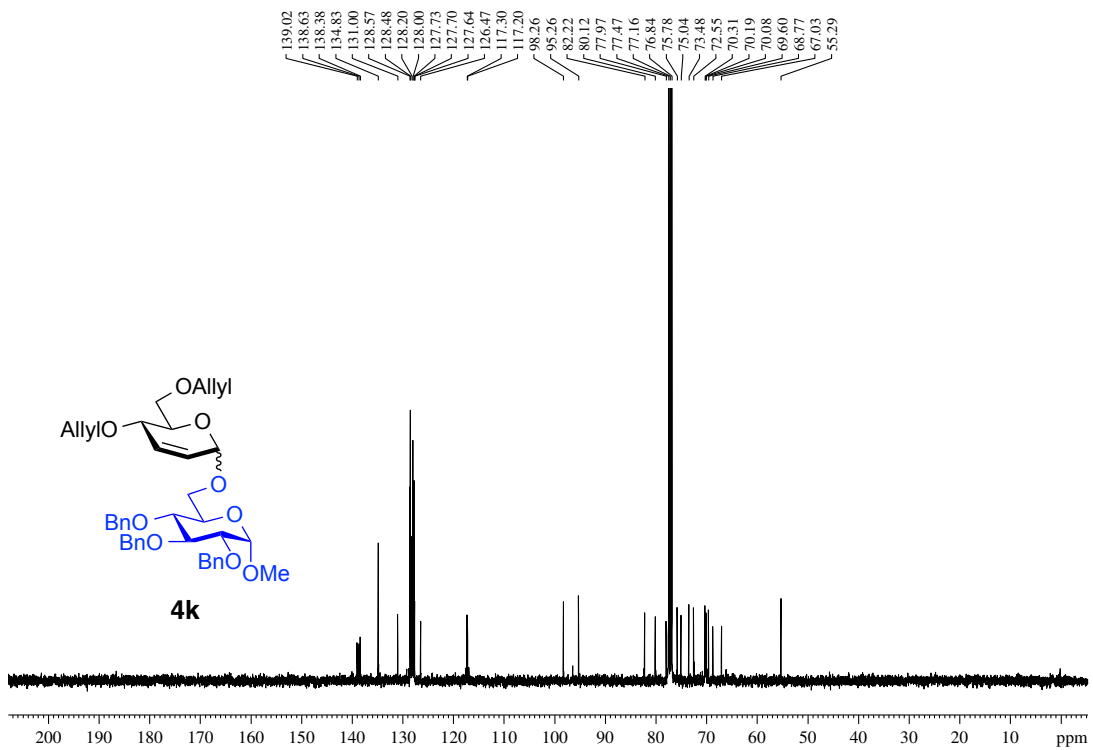
¹H NMR of **4j**, CDCl₃, 400 MHz



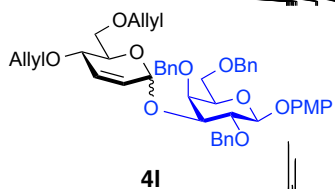
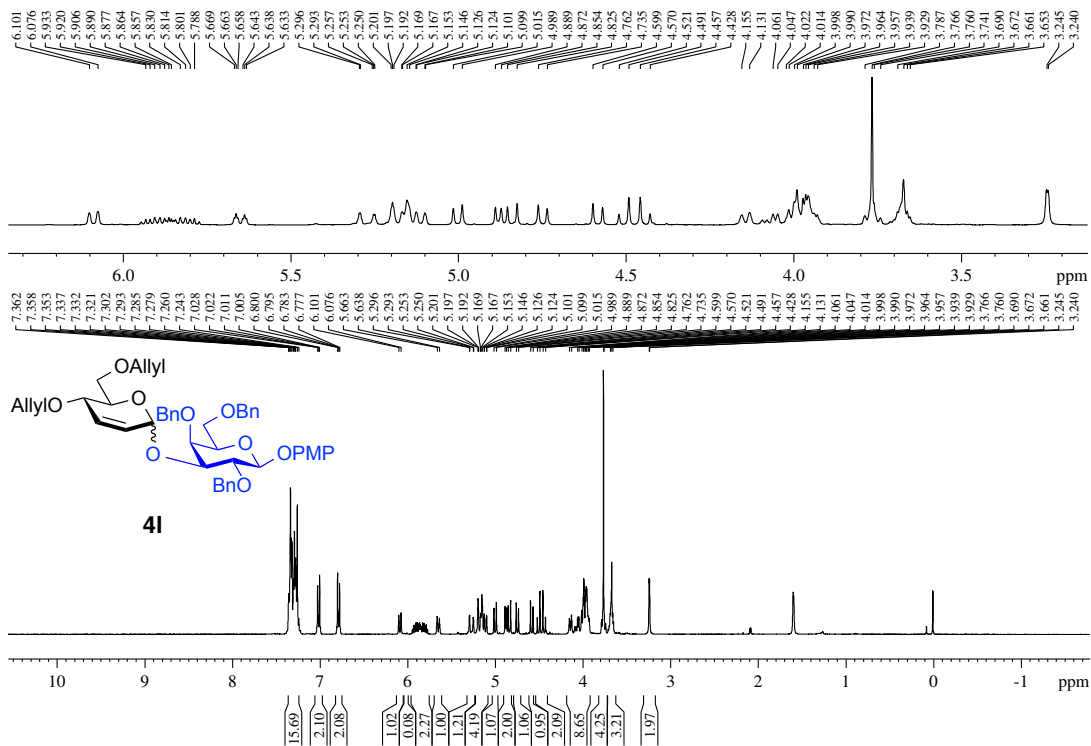
¹H NMR of **4k**, CDCl₃, 400 MHz



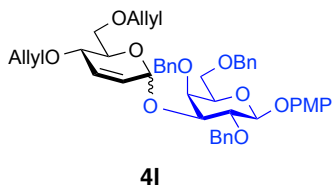
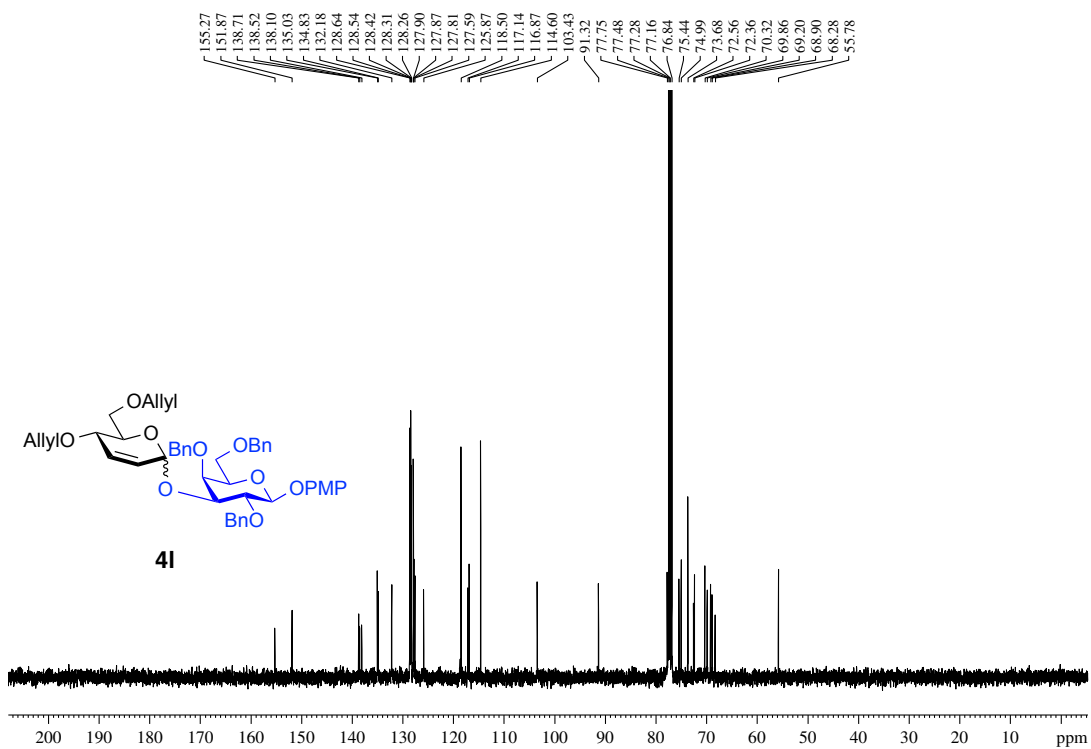
¹³C NMR of **4k**, CDCl₃, 100 MHz



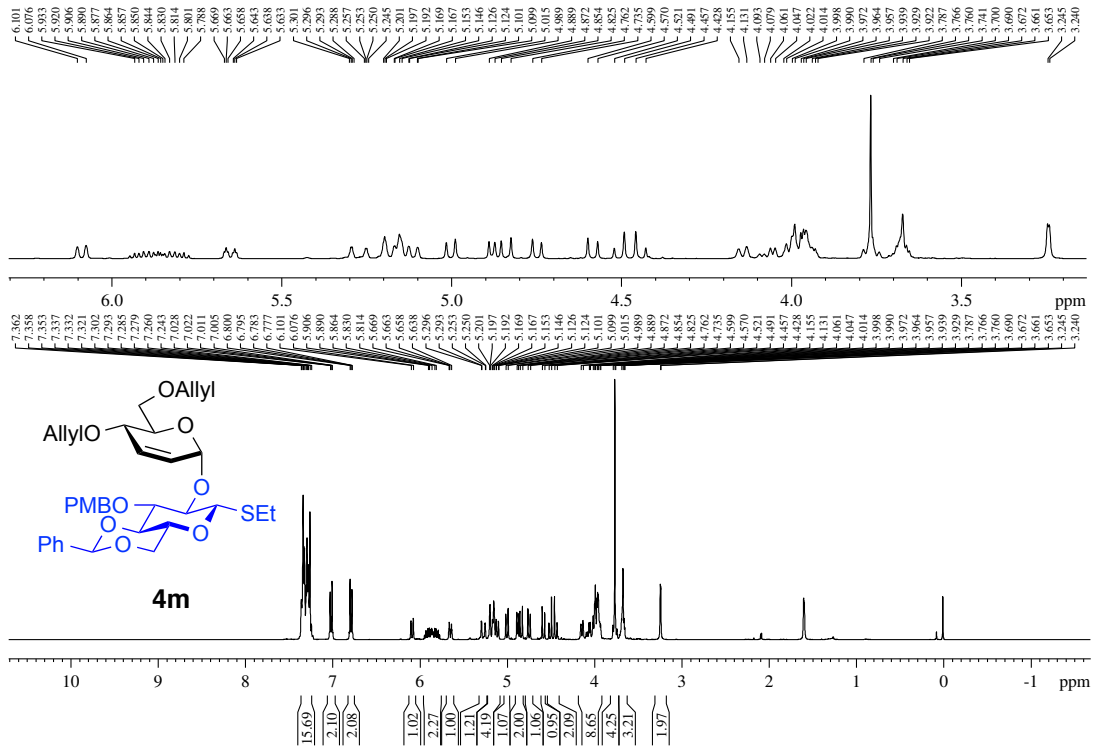
^1H NMR of **4l**, CDCl_3 , 400 MHz



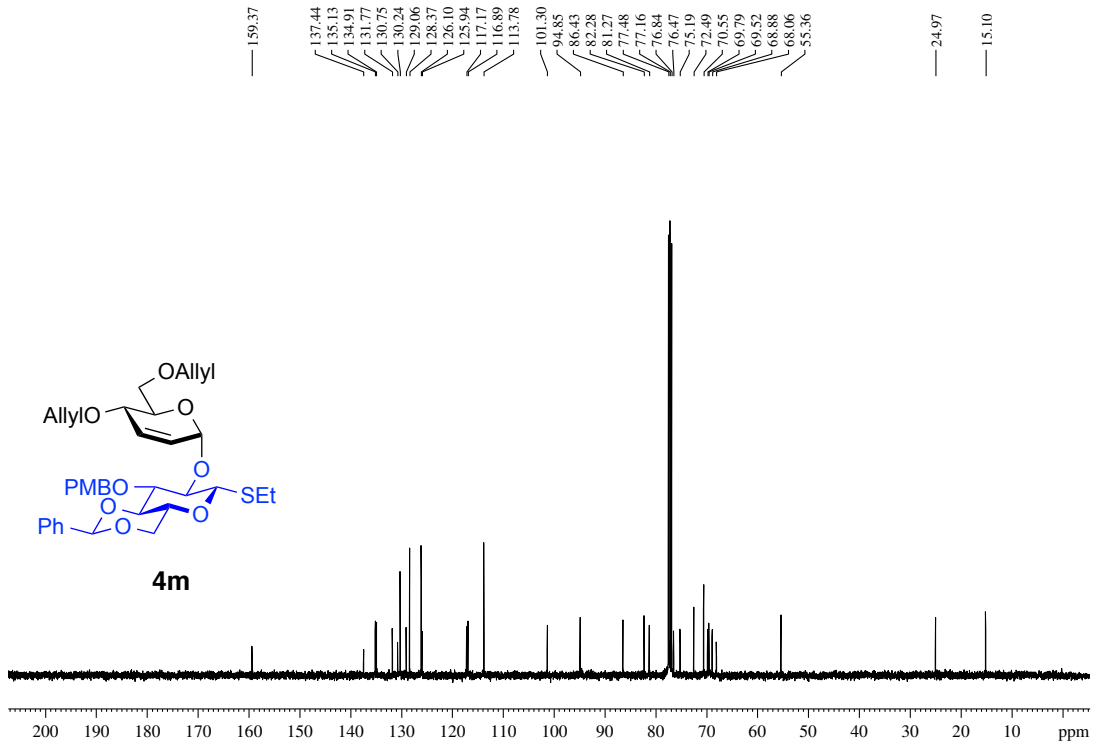
^{13}C NMR of **4l**, CDCl_3 , 100 MHz



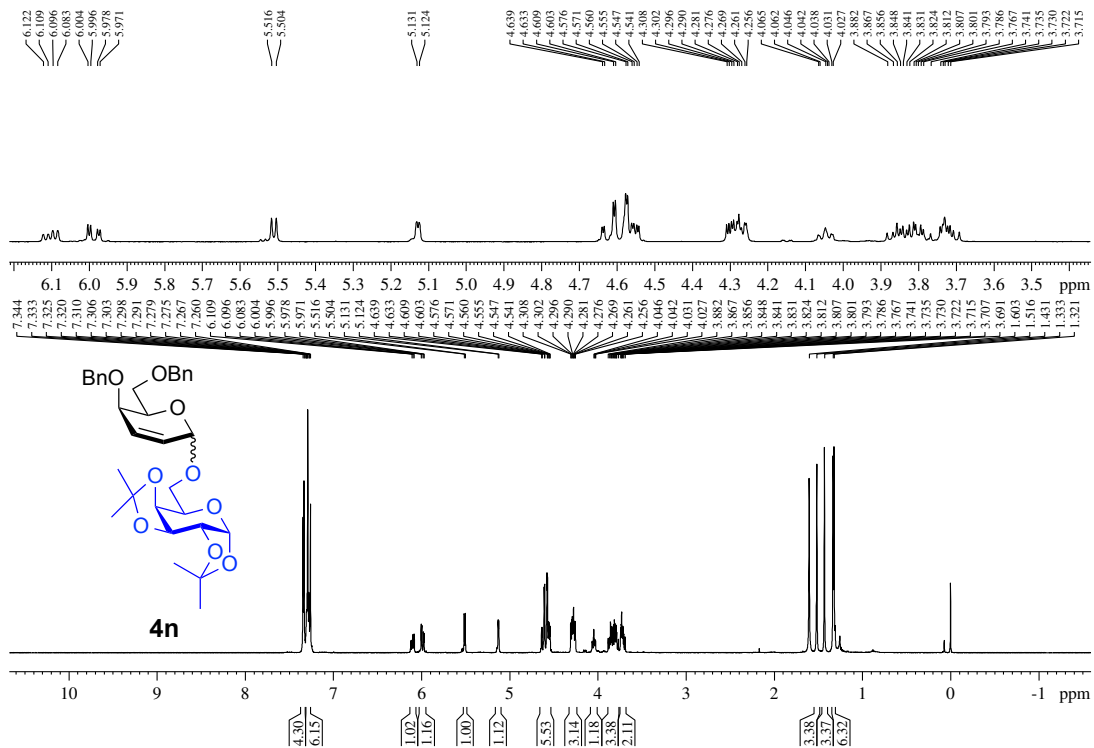
¹H NMR of **4m**, CDCl₃, 400 MHz



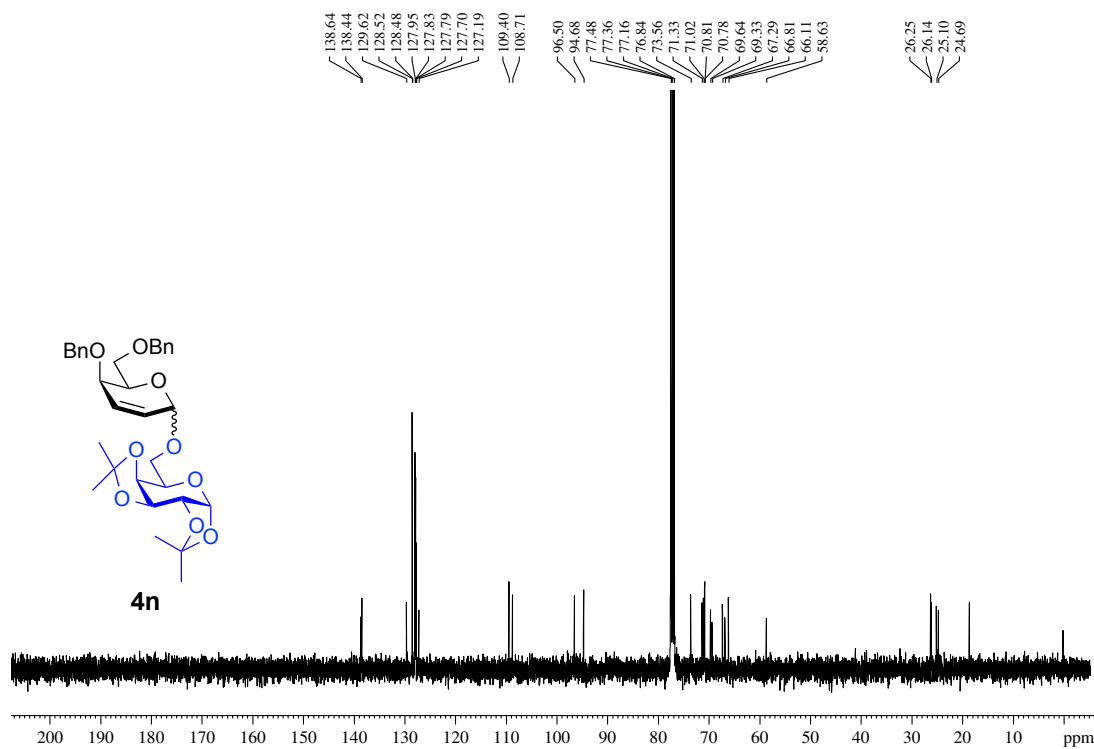
¹³C NMR of **4m**, CDCl₃, 100 MHz



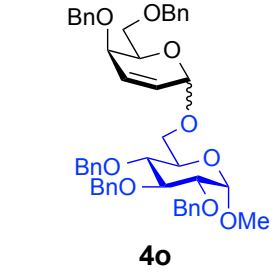
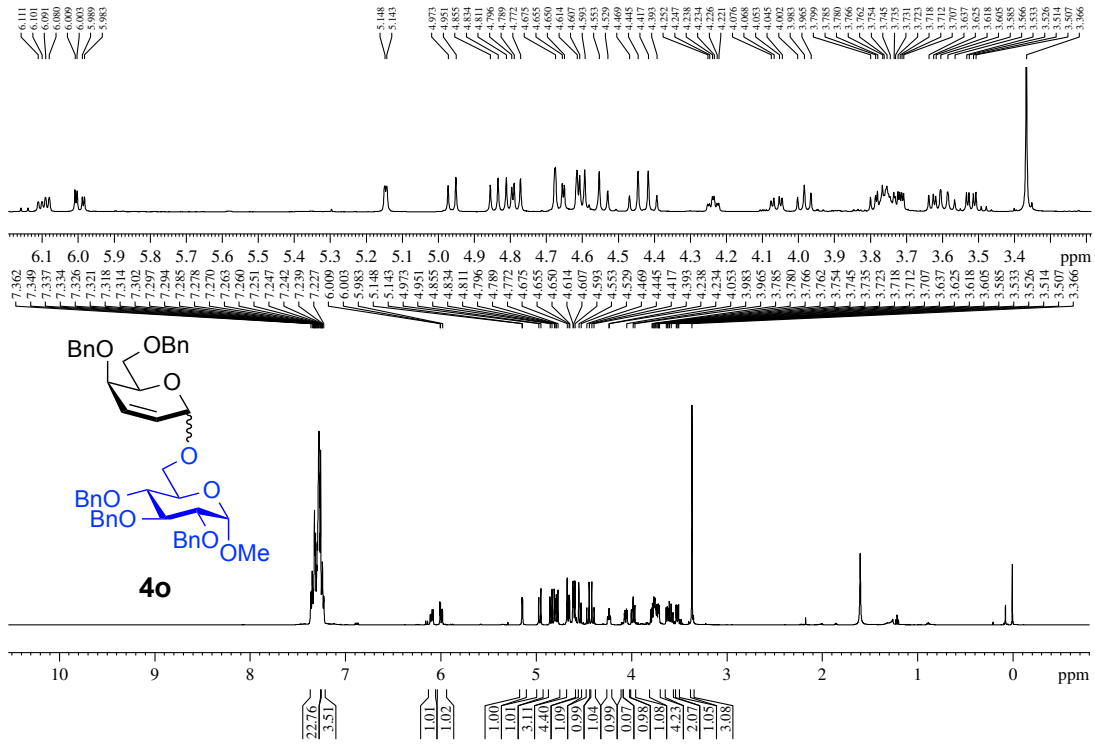
¹H NMR of **4n**, CDCl₃, 400 MHz



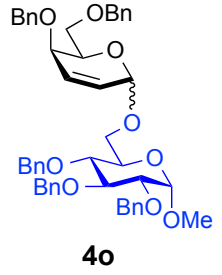
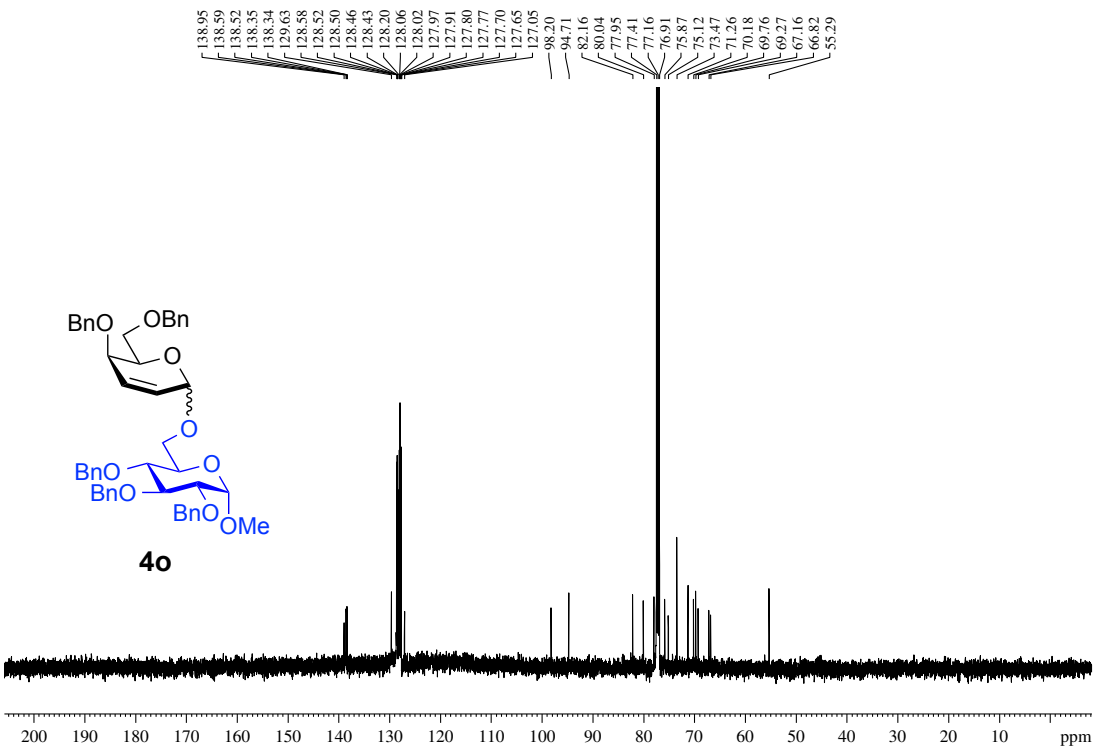
¹³C NMR of **4n**, CDCl₃, 100 MHz



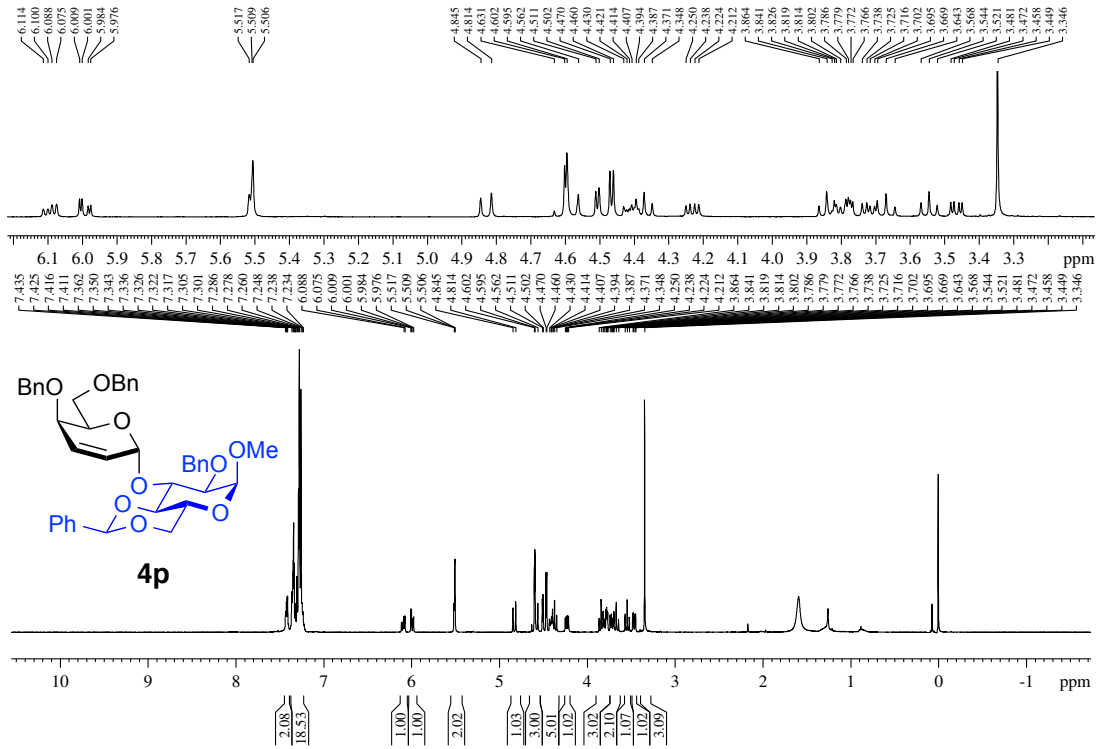
¹H NMR of **4o**, CDCl₃, 500 MHz



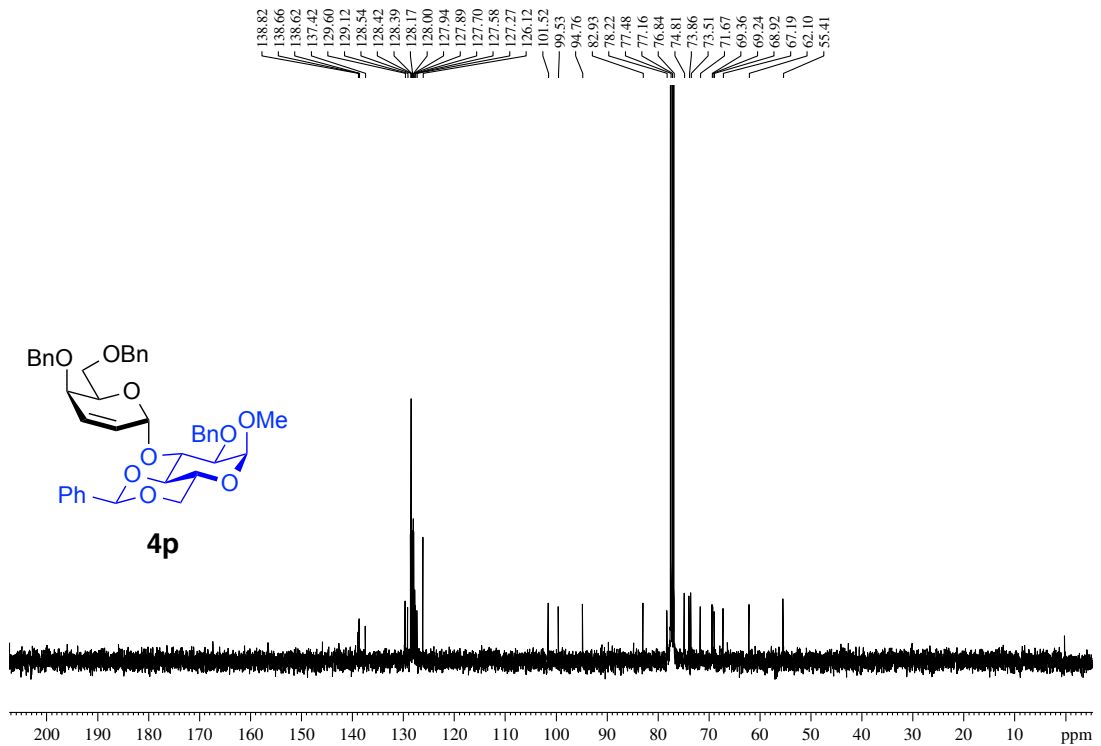
¹³C NMR of **4o**, CDCl₃, 125 MHz



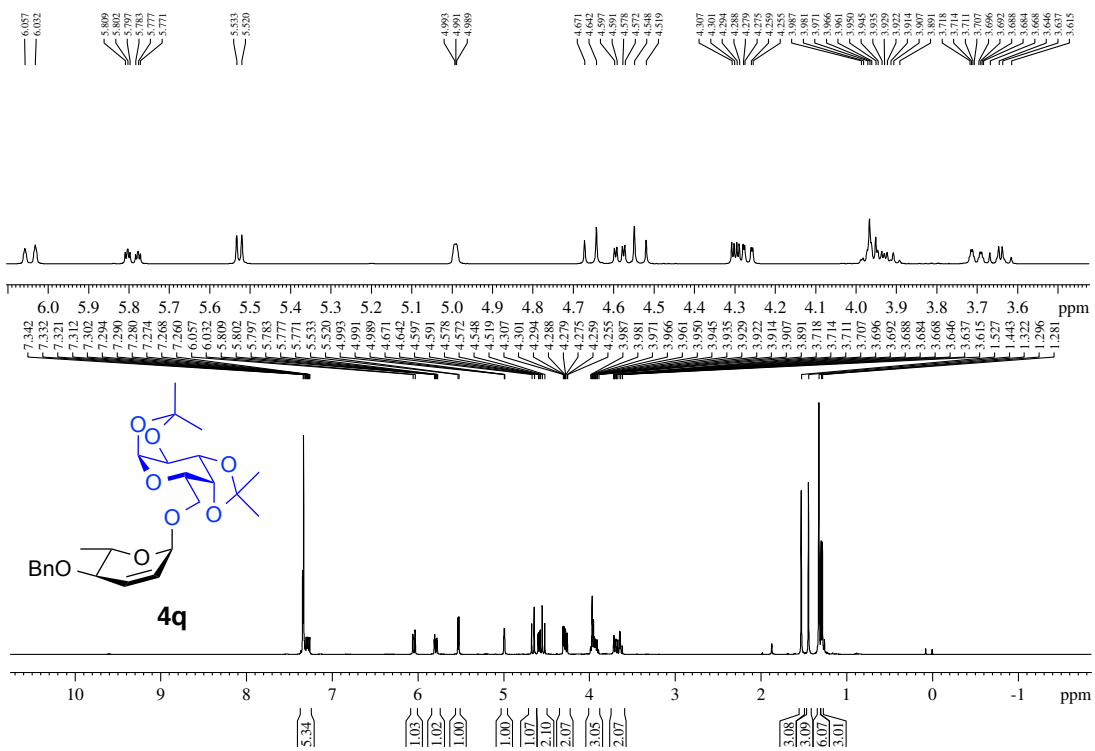
¹H NMR of **4p**, CDCl₃, 400 MHz



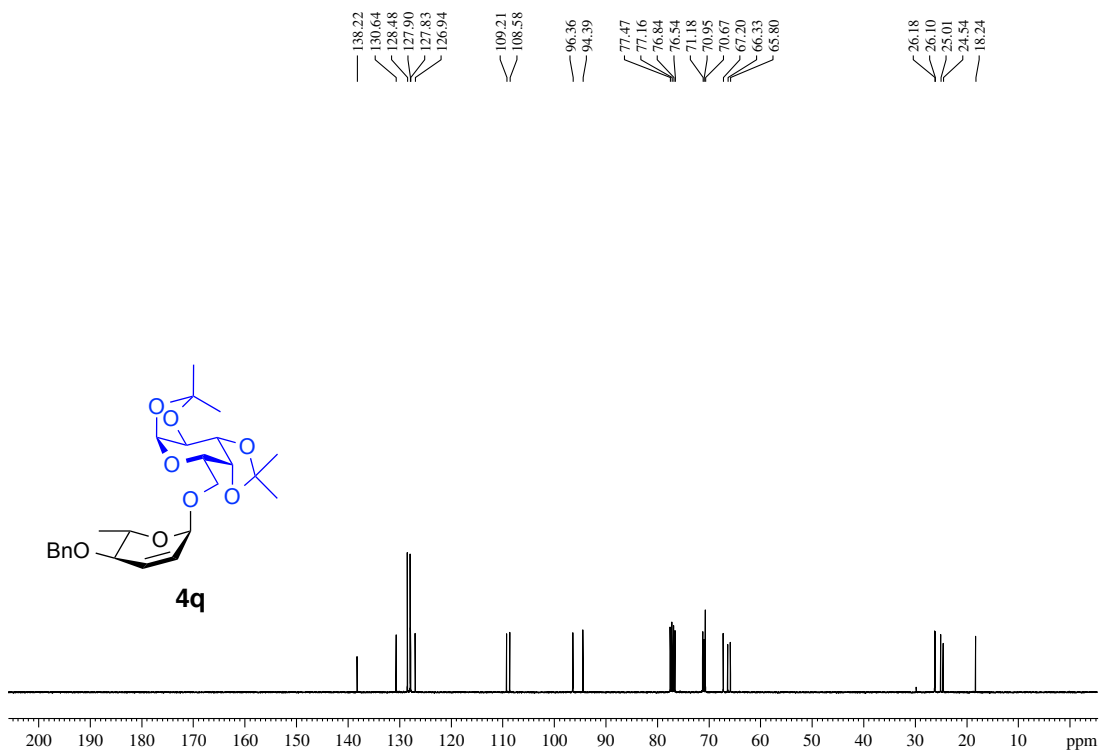
¹³C NMR of **4p**, CDCl₃, 100 MHz



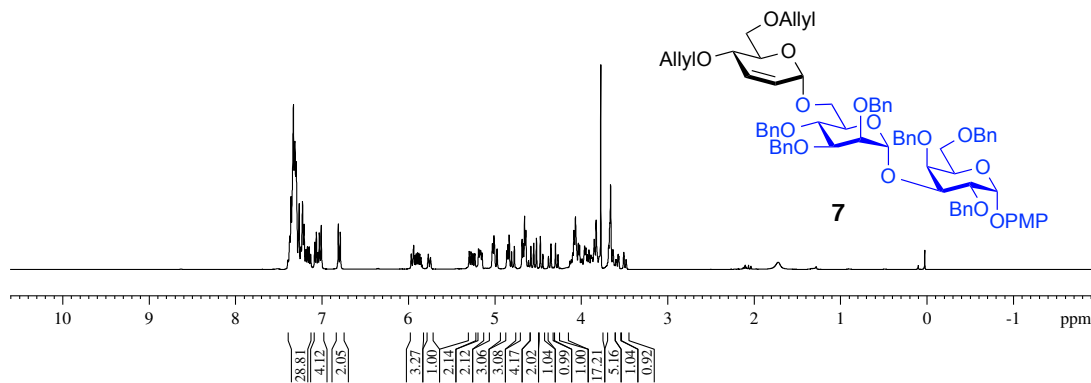
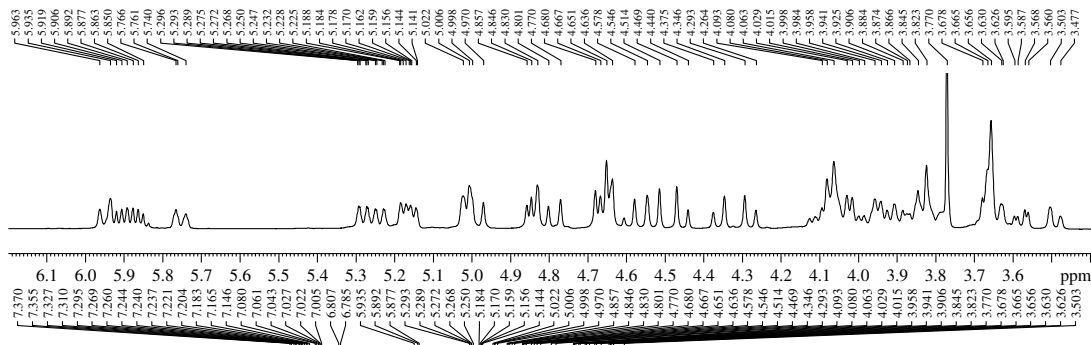
¹H NMR of **4q**, CDCl₃, 400 MHz



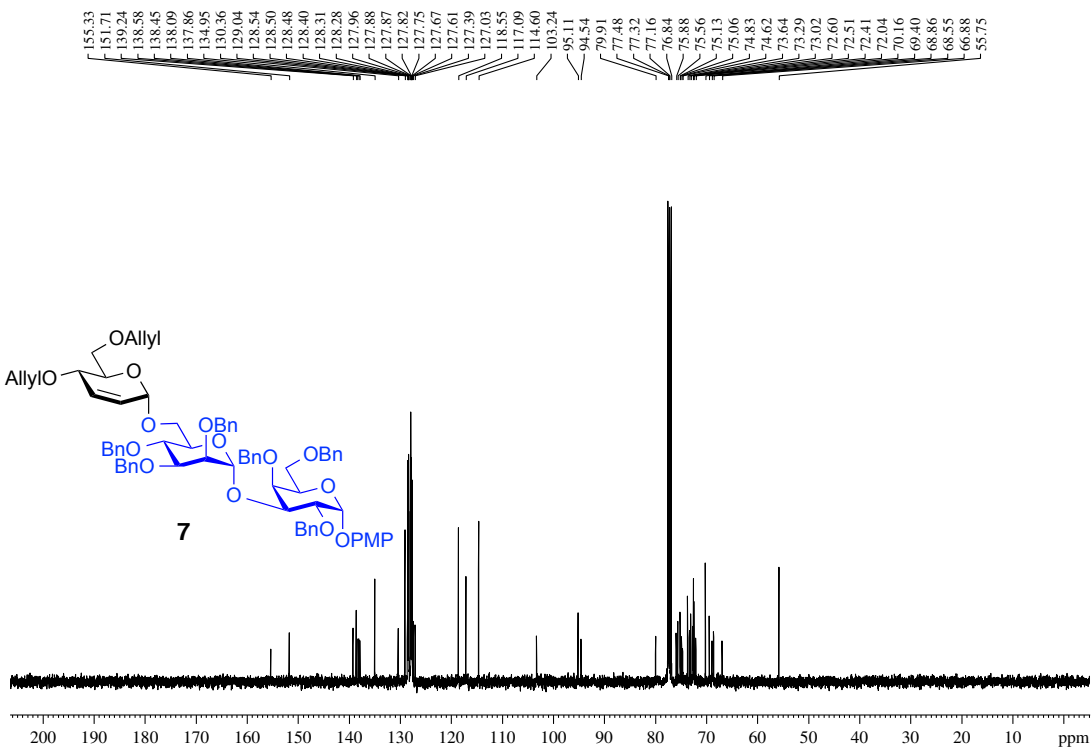
¹³C NMR of **4q**, CDCl₃, 100 MHz



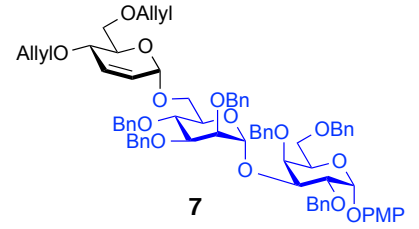
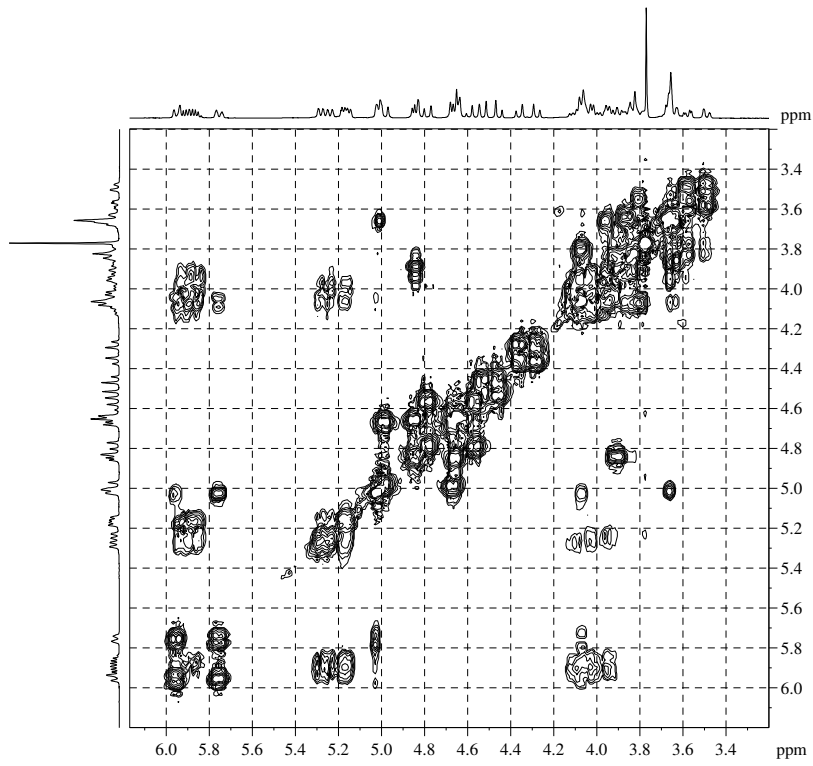
¹H NMR of 7, CDCl₃, 400 MHz



¹³C NMR of 7, CDCl₃, 100 MHz



COSY of 7, CDCl₃



HSQC of 7, CDCl₃

