Supporting Information

A Ferrier Glycosylation / *cis*-Dihydroxylation Strategy to Synthesize *Leishmania* spp Lipophosphoglycan-Associated βGal(1,4)Man Disaccharide

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Figure S1. ¹H NMR (500 MHz, CDCl₃) spectrum of 3,6-Di-*O*-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol **3**



Figure S2. ¹³C{¹H} NMR (125 MHz, CDCl₃) spectrum of 3,6-Di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol **3**



Figure S3 ¹H NMR (500 MHz, CDCl₃) spectrum of benzyl 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside **5**



Figure S4. ¹³C{¹H} NMR (125 MHz, CDCl₃) spectrum of benzyl 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside **5**



Figure S5. ¹H NMR (400 MHz, CDCl₃) spectrum of benzyl 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-allopyranoside **6**.



Figure S6. APT $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of benzyl 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-allopyranoside **6**



Figure S7. ¹H NMR (400 MHz, CDCl₃) spectrum of benzyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside **7**



Figure S8. $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of benzyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-\beta-D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside 7



Figure S9. COSY spectrum of benzyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside 7



Figure S10. HSQC spectrum of benzyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside 7



Figure S11. ¹H NMR (400 MHz, CDCl₃) spectrum of benzyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- β -D-allopyranoside **8**



Figure S12. APT $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of benzyl 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-\beta-D-galactopyranosyl)-6-*O*-acetyl-\beta-D-allopyranoside **8**



Figure S13. COSY spectrum of benzyl 2,3-di-*O*-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- β -D-allopyranoside **8**



Figure S14. HSQC spectrum of benzyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- β -D-allopyranoside **8**



Figure S15. ¹H NMR (400 MHz, CDCl₃) spectrum of 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranose **9**



Figure S16. $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranose **9**



Figure S17. ¹H NMR (400 MHz, CDCl₃) spectrum of 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)- 1-(2,2,2-trichloroethanimidate)- α -D-mannopyranose 2,3,6-triacetate **10**



Figure S18. ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) spectrum of 4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-1-(2,2,2-trichloroethanimidate)- α -D-mannopyranose 2,3,6-triacetate **10**



Figure S19. ¹H NMR (500 MHz, CDCl₃) spectrum of 3-azidopropyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside **11**



Figure S20. APT $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl₃) spectrum of 3-azidopropyl 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranoside **11**



Figure S21. ¹H NMR (400 MHz, CD₃OD) spectrum of 3-azidopropyl 4-O- β -D-galactopyranosyl- α -D-mannopyranoside **1**



Figure S22. APT $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of 3-azidopropyl 4-O- β -D-galactopyranosyl- α -D-mannopyranoside 1



Figure S23. ¹H NMR (400 MHz, CDCl₃) spectrum of 2,3-di-*O*-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranosyl H-phosphonate **12**



Figure S24. APT $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of 2,3-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-\beta-D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranosyl H-phosphonate **12**



Figure S25. ³¹P NMR (162 MHz, CDCl₃) spectrum of 2,3-di-*O*-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-6-O-acetyl- α -D-mannopyranosyl H-phosphonate **12**



Figure S26. ¹H NMR (400 MHz, CDCl₃) spectrum of triethylammonium 3-azidopropyl 2,3-di-*O*-acetyl-4-O-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-6-*O*-acetyl- α -D-mannopyranosyl phosphate **13**



Figure S27. APT ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) spectrum of triethylammonium 3-azidopropyl 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-6-*O*-acetyl- α -D-mannopyranosyl phosphate **13**



Figure S28. ³¹P NMR (162 MHz, CDCl₃) spectrum of triethylammonium 3-azidopropyl 2,3-di-*O*-acetyl-4-O-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-6-*O*-acetyl- α -D-mannopyranosyl phosphate **13**



Figure S29. ¹H NMR (400 MHz, CD₃OD) spectrum of 3-azidopropyl 4-O- β -D-galactopyranosyl- α -D-mannopyranosyl phosphate **2**



Figure S30. APT $^{13}C\{^{1}H\}$ NMR (100 MHz, CD₃OD) spectrum of 3-azidopropyl 4-O- β -D-galactopyranosyl- α -D-mannopyranosyl phosphate **2**



Figure S31. ³¹P NMR (162 MHz, CD₃OD) spectrum of 3-azidopropyl 4-O- β -D-galactopyranosyl- α -D-mannopyranosyl phosphate **2**