Electronic Supporting Information (ESI)

belonging to:

Carbohydrate-functionalized N-Heterocyclic Carbene Ru(II) Complexes: Synthesis, characterization and catalytic transfer hydrogenation activity

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S1 – Additional experimental details S2
S2 - NMR spectra of new compounds S4
S2.1 – 1,2,3-Triazole NMR spectra S4
S2.2 - Triazolium salt NMR spectra S7
S2.3 - Ruthenium complex NMR spectra S10
S2.4 Deprotection of 5Glc: ^{1}H NMR and HSQC spectra S13
S3 – Catalytic results S16
S4 – Base-promoted transfer hydrogenation of ketones S17

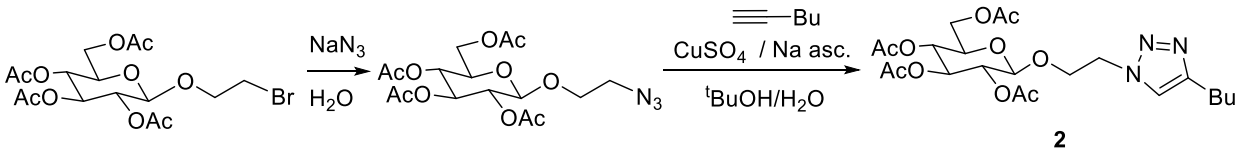
S1 – Additional experimental details

Synthesis of protected monosaccharide β-azides Azides were prepared according to a modified literature procedure.[S1] To a stirred solution of acetylated pyranose (1 equiv.) in anhydrous CH_2Cl_2, at 0 °C, was added azidotrimethylsilane (1.54 equiv.) and $SnCl_4$ (0.5 equiv.). The reaction mixture was stirred overnight, warming slowly to room temperature. The reaction mixture was diluted with CH_2Cl_2 until it formed a clear solution. This was washed with $NaHCO_{3\ (aq.,\ sat.)}$ (×3), deionised water (×1) and brine (×2), dried over $MgSO_4$ and concentrated under reduced pressure, yielding the azide as a white solid. ^{1}H NMR spectra matched literature values.[S1]

β-Glc-N_3^{OAc}. Yield: 70%. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.01, 2.04, 2.08, 2.11 (4 × s, 3H, OC(O)CH_3), 3.80 (ddd, 1H, *J* = 9.9, 4.7, 2.3 Hz, glucosyl C^{5}H), 4.14–4.33 (m, 2H, glucosyl C$^6H_2$), 4.65 (d, 1H, *J* = 9.1 Hz, glucosyl CH), 4.96 (t, 1H, *J* = 9.1 Hz, glucosyl CH), 5.11 (t, 1H, *J*= 9.9 Hz, glucosyl CH), 5.22 (t, 1H, *J* = 9.1 Hz, glucoyl C^{1}H).

β-Gal-N_3^{OAc}. Yield = 66%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.99, 2.07, 2.09, 2.17 (4 × s, 3H, OC(O)CH_3), 4.03 (td, 1H, *J* = 3.3, 1.1 Hz, galactosyl C^{5}H), 4.17 (dd, 2H, *J* = 6.5, 2.4 Hz, galactosyl C$^6H_2$), 4.60 (d, 1H, *J* = 8.7 Hz, galactosyl CH), 5.04 (dd, 1H, *J* = 10.3, 3.3 Hz, galactosyl CH), 5.17 (dd, 1H, *J* = 10.3, 8.7 Hz, galactosyl CH), 5.43 (dd, 1H, *J* = 3.3, 1.1 Hz, galactosyl C^{1}H).

Synthetic route to complex 2. The complex with an ethylene spacer was prepared from triazole **2**, which was synthesised as outlined in Scheme S1, modified from literature procedures as follows:



Scheme S1. *Synthetic route to triazole **2**, containing an ethylene spacer between carbohydrate and triazole motif (precursor to complex **2**)*

[S1] H. Paulsen, Z. Györgydeák and M. Friedmann, *Chem. Ber.* 1974, **107**, 1568–1578.

2,3,4,6-Tetra(*O*-acetyl)-1-bromoethyl-glucopyranoside. Acetylated glucose (0.200 g, 0.51 mmol) and 2-bromoethanol (0.04 mL, 0.61 mmol) were dissolved in dry CH_2Cl_2 and degassed by bubbling with nitrogen. Boron trifluoride diethyl etherate (0.19 mL, 1.5 mmol) was added dropwise, and the solution was left to stir overnight at room temperature. The organic layer was washed with saturated $NaHCO_{3(aq)}$ (×3) and water (×2), dried over Na_2SO_4, purified by flash chromatography (cyclohexane–EtOAc 60:40) and concentrated under reduced pressure to yield the title compound as a white solid (0.23 g, 0.51 mmol, quantitative yield). Spectroscopic data matched literature values.[S2]

2,3,4,6-Tetra(*O*-acetyl)-1-azidoethyl-glucopyranoside. 2,3,4,6-Tetra(*O*-acetyl)-1-bromo ethyl-glucopyranoside (0.500 g, 1.10 mmol) and sodium azide (0.179 g, 2.75 mmol) were dissolved in water and heated to reflux for 16 hours. The reaction mixture was extracted with CH_2Cl_2 and washed with water (×3), to yield 2,3,4,6-tetra(*O*-acetyl)-1-azidoethyl-glucopyranoside as a white solid in quantitative yield, which matched literature spectroscopic data and was used without further purification.[S3]

[S2] P. Quagliotto, G. Viscardi, C. Barolo, D. D'Angelo, E. Barni, C. Compari, E. Duce, and E. Fisicaro, *J. Org. Chem*., 2005, **70**, 9857–9866

[S3] S. M. Paterson, J. Clark, K. A. Stubbs, T. V. Chirila, and M. V. Baker, *J. Polym. Sci. Part A Polym. Chem.*, 2011, **49**, 4312–4315

S2 - NMR spectra of new compounds

S2.1 – 1,2,3-Triazole NMR spectra

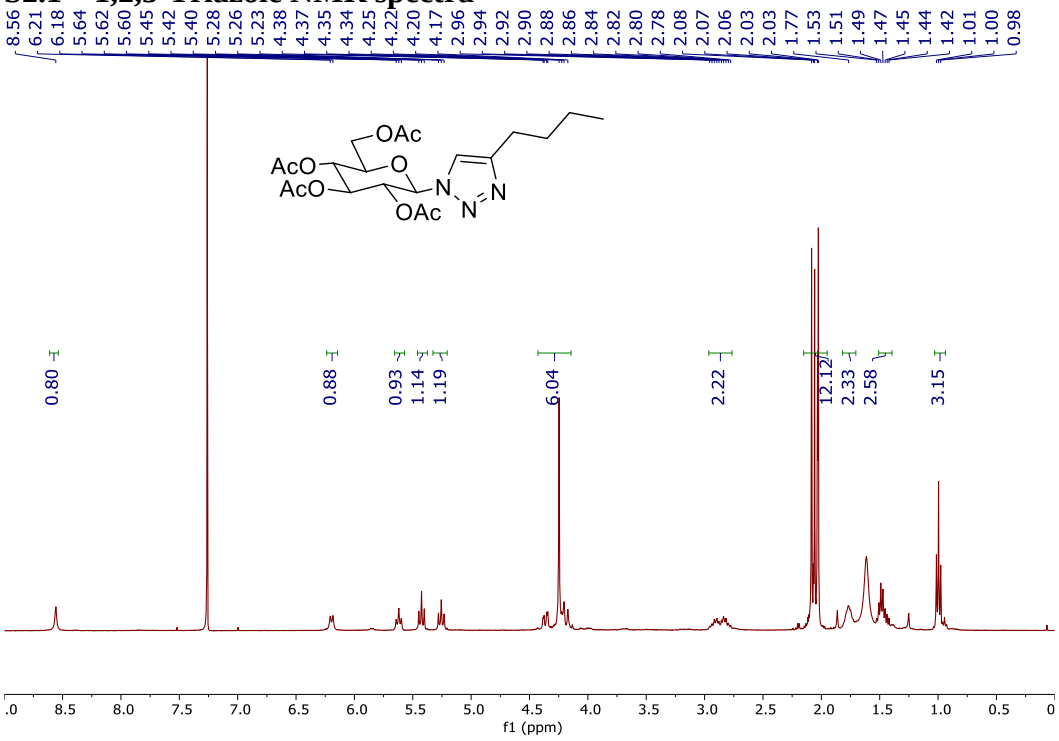


Figure S1. *^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of* ***1Glc***

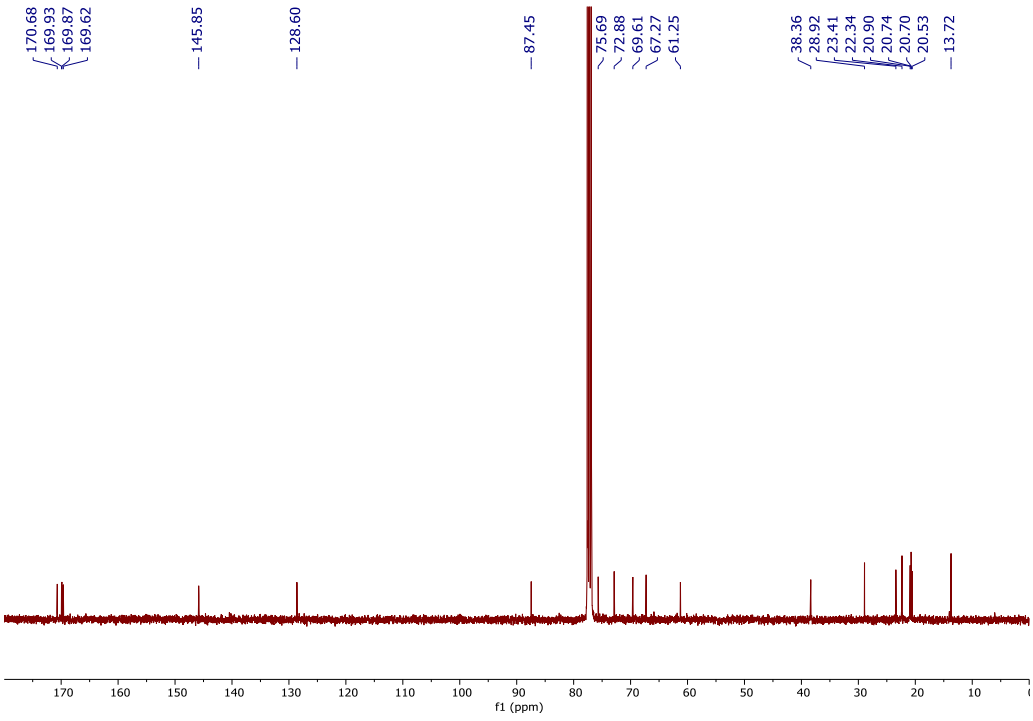


Figure S2. *^{13}C NMR ($CDCl_3$, 150 MHz) spectrum of* ***1Glc***

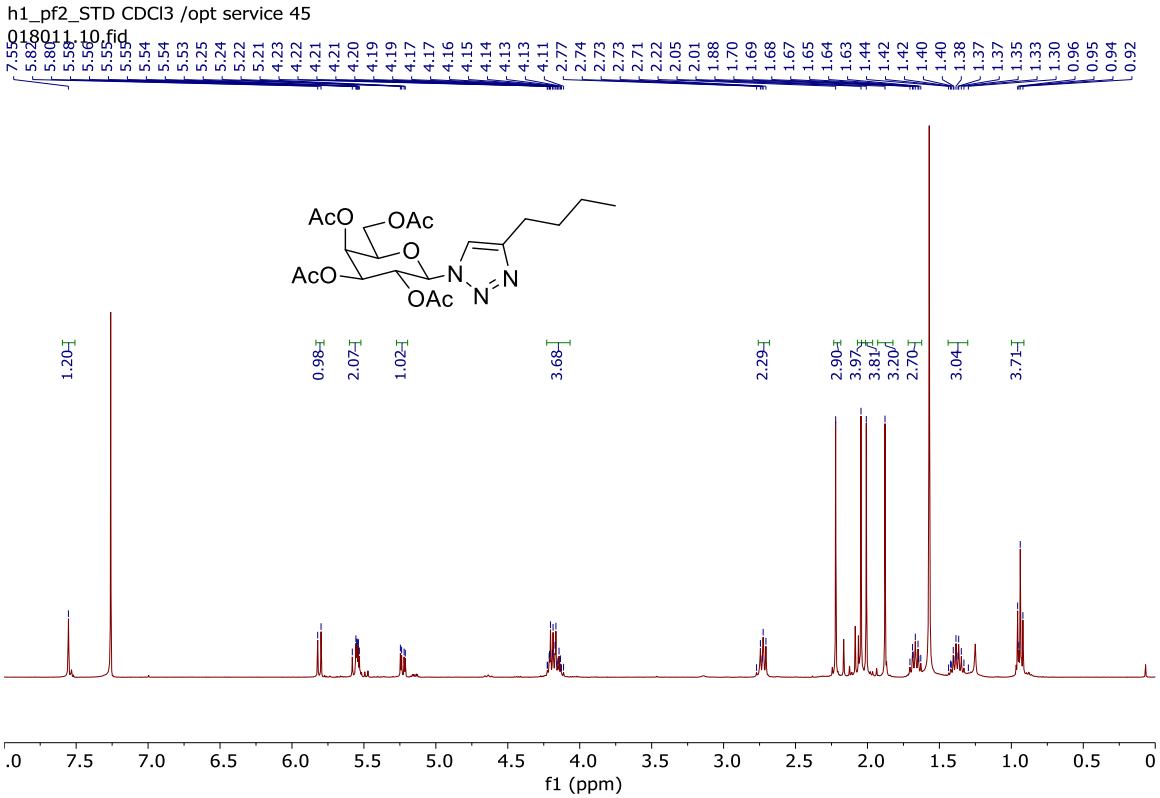


Figure S3. *^{1}H NMR (400 MHz, $CDCl_3$) spectrum of* ***1Gal***

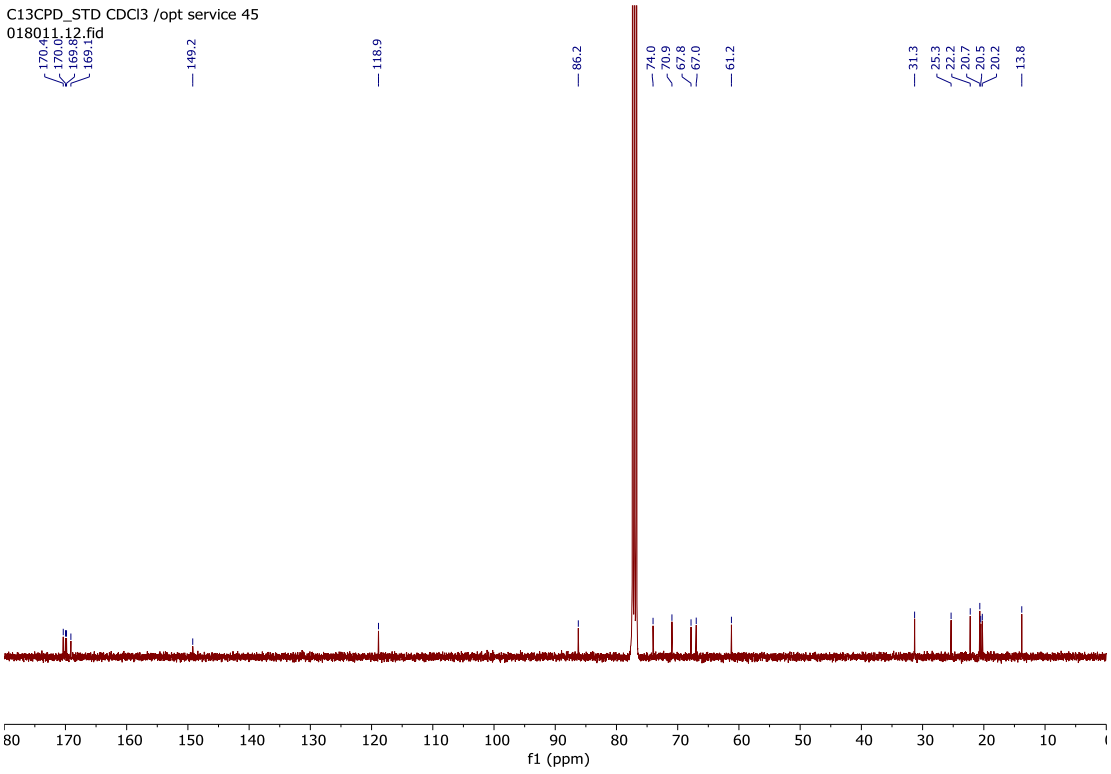


Figure S4. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of* ***1Gal***

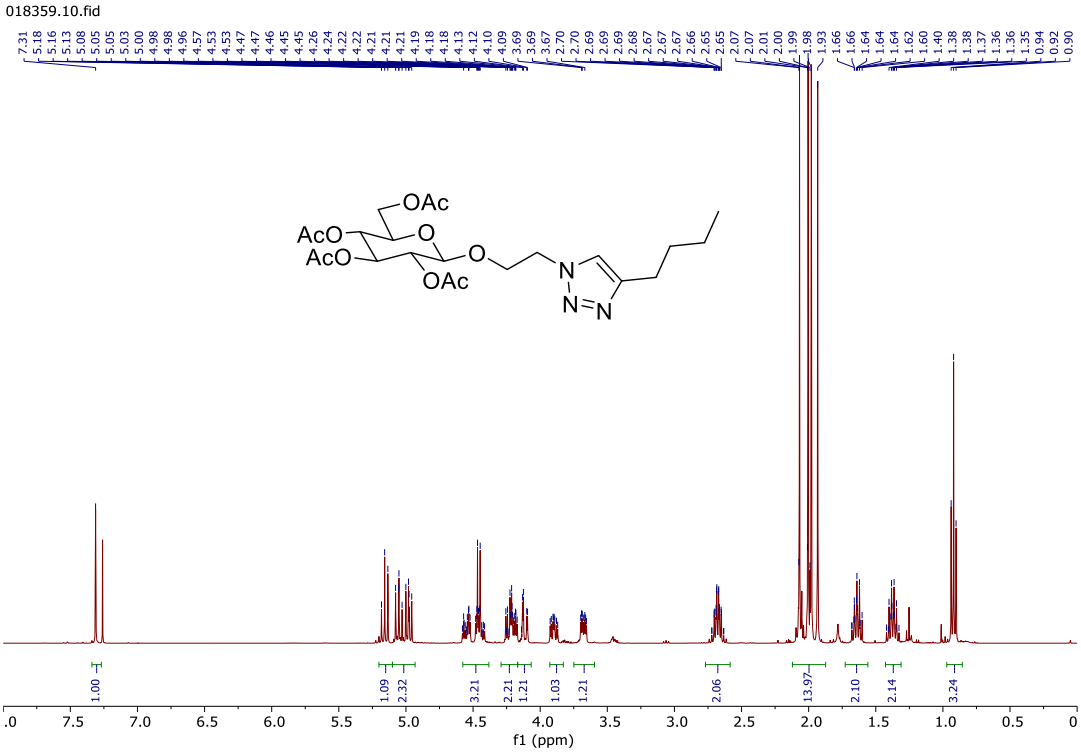


Figure S5. *^{1}H NMR (400 MHz, $CDCl_3$) spectrum of* ***2***

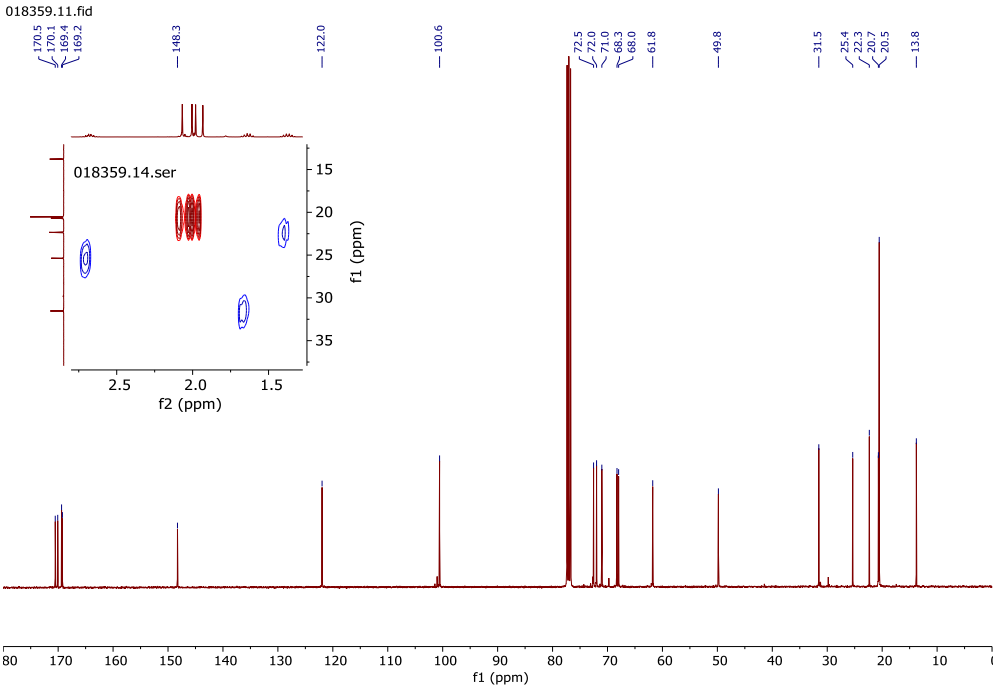


Figure S6. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of* ***2****. Inset: Detail of HSQC spectrum, showing overlap of $C(O)CH_3$ ^{13}C resonances from the four protecting groups.*

S2.2 - Triazolium salt NMR spectra

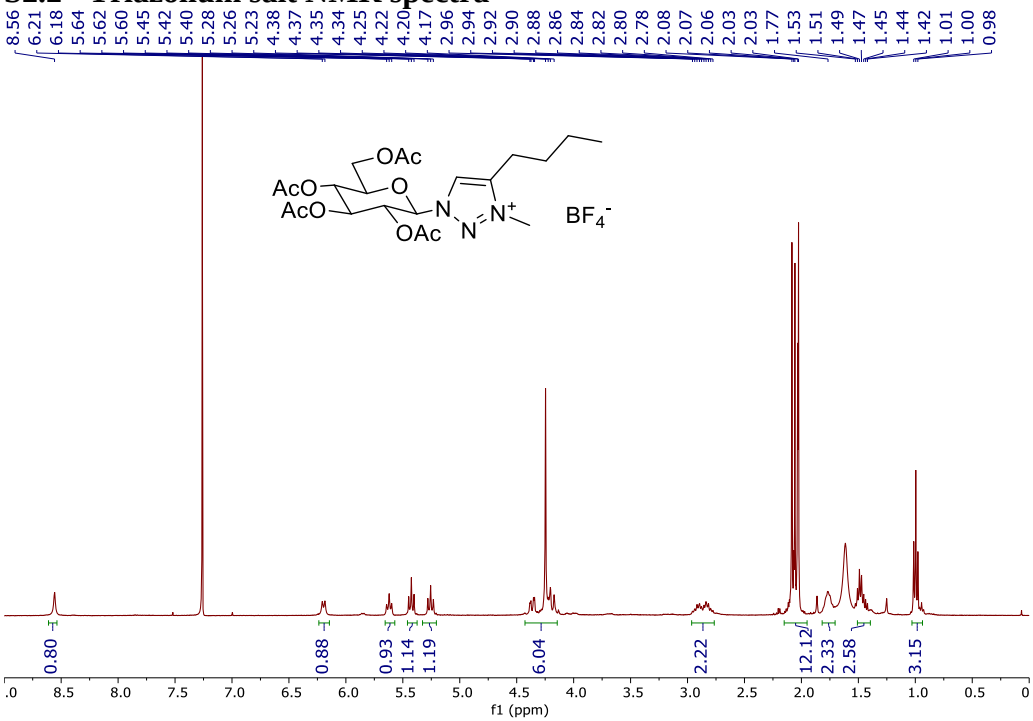


Figure S7. *[1]H NMR (400 MHz, $CDCl_3$) spectrum of triazolium salt* ***3Glc***

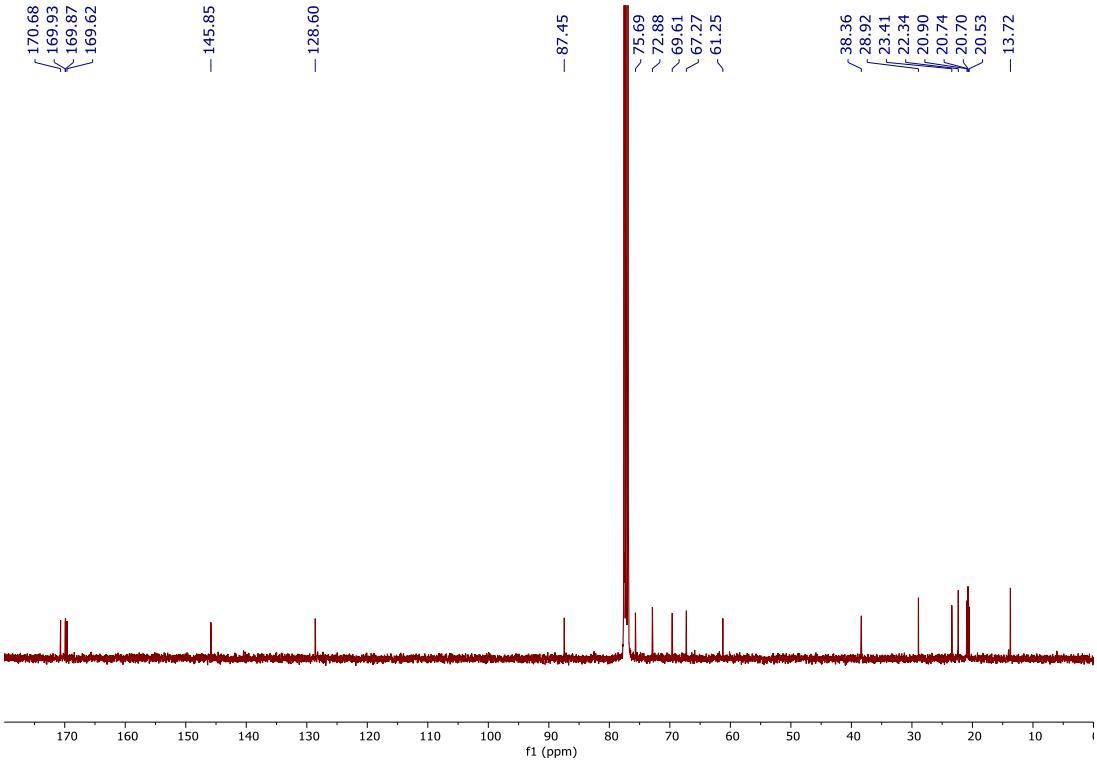


Figure S8. *[13]C NMR (100 MHz, $CDCl_3$) spectrum of triazolium salt* ***3Glc***

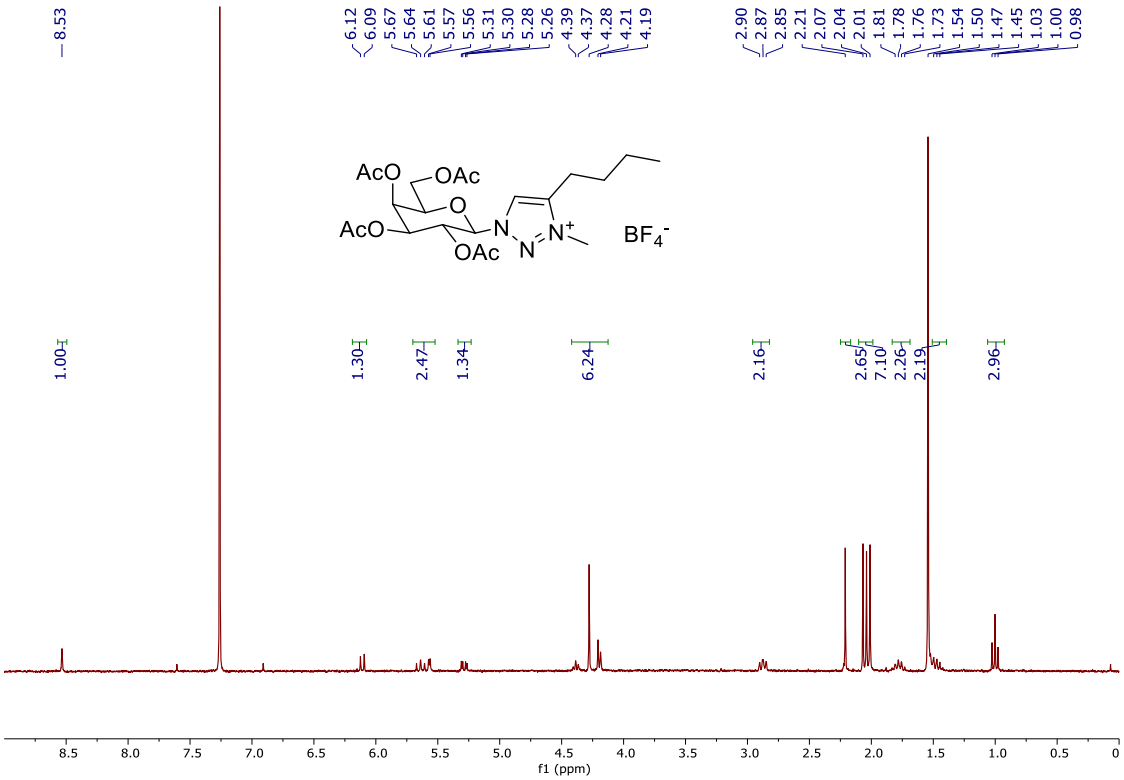


Figure S9. *^{1}H NMR (400 MHz, $CDCl_3$) spectrum of triazolium salt* ***3Gal***

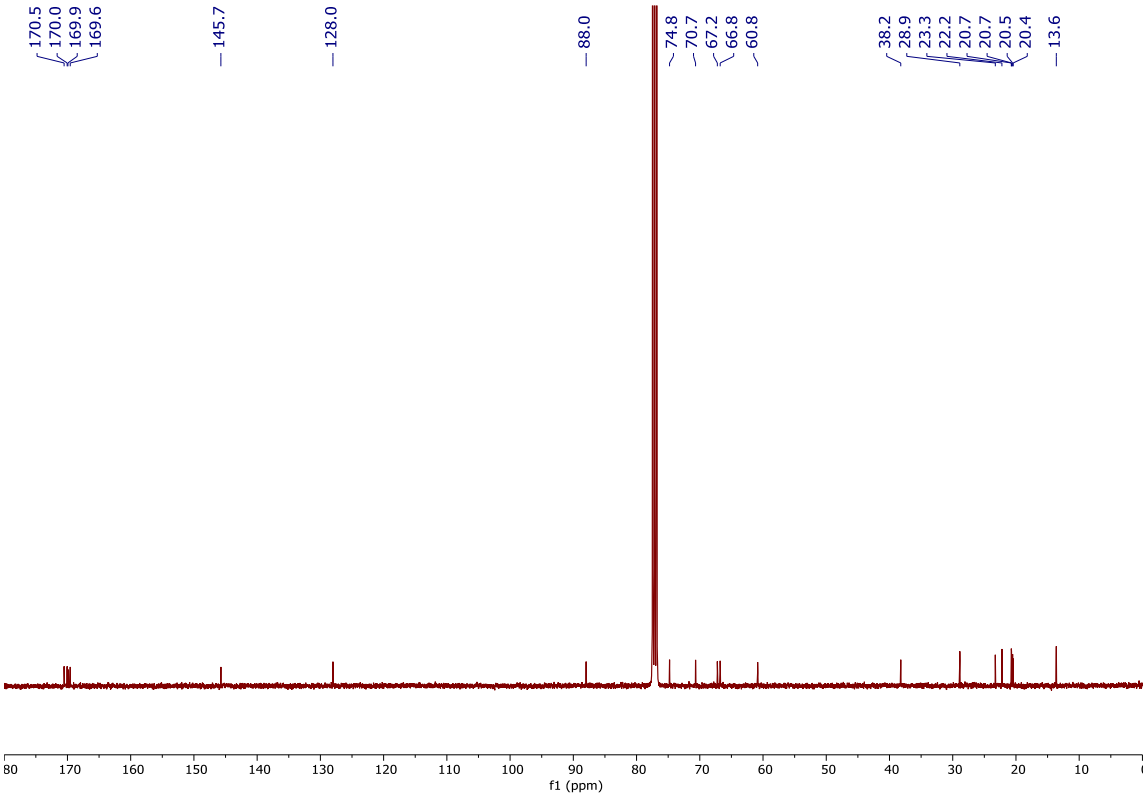


Figure S10. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of triazolium salt* ***3Gal***

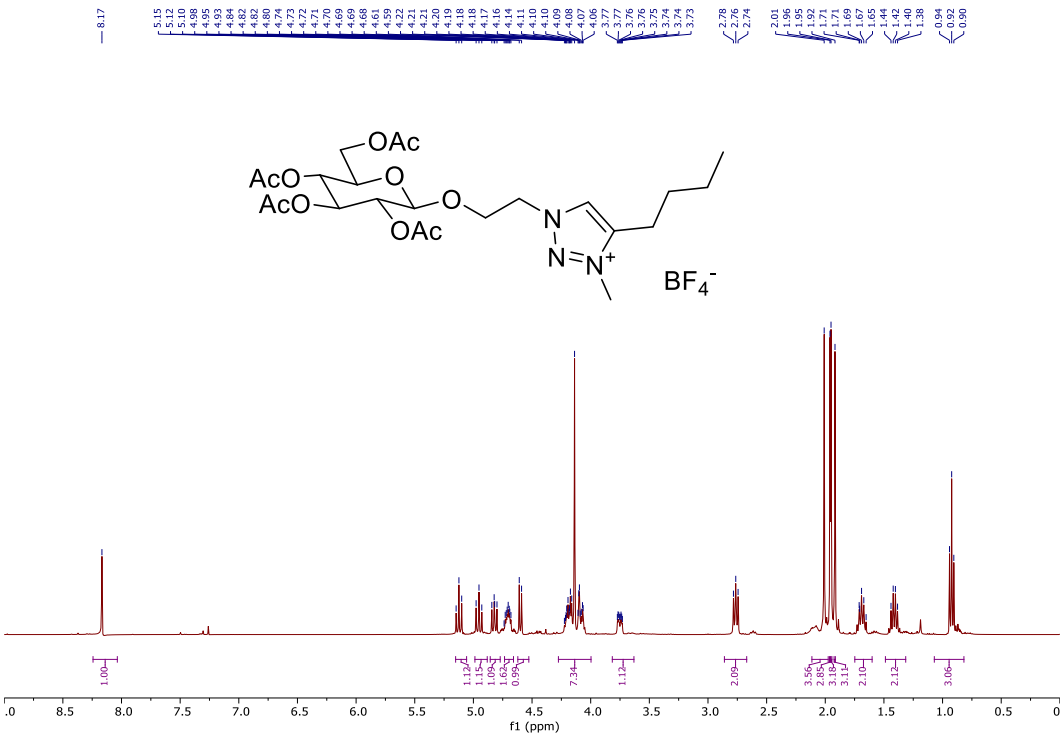


Figure S11. *^{1}H NMR (400 MHz, $CDCl_3$) of triazolium salt* ***4***

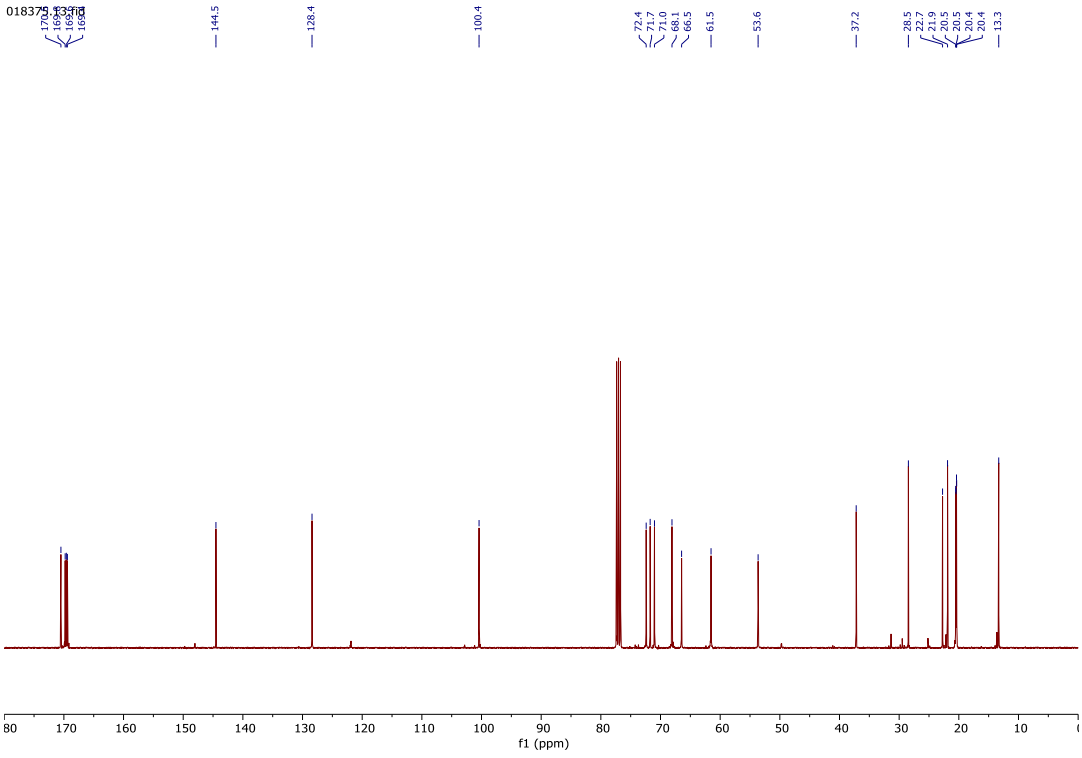


Figure S12. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of triazolium salt* ***4***

S2.3 - Ruthenium complex NMR spectra

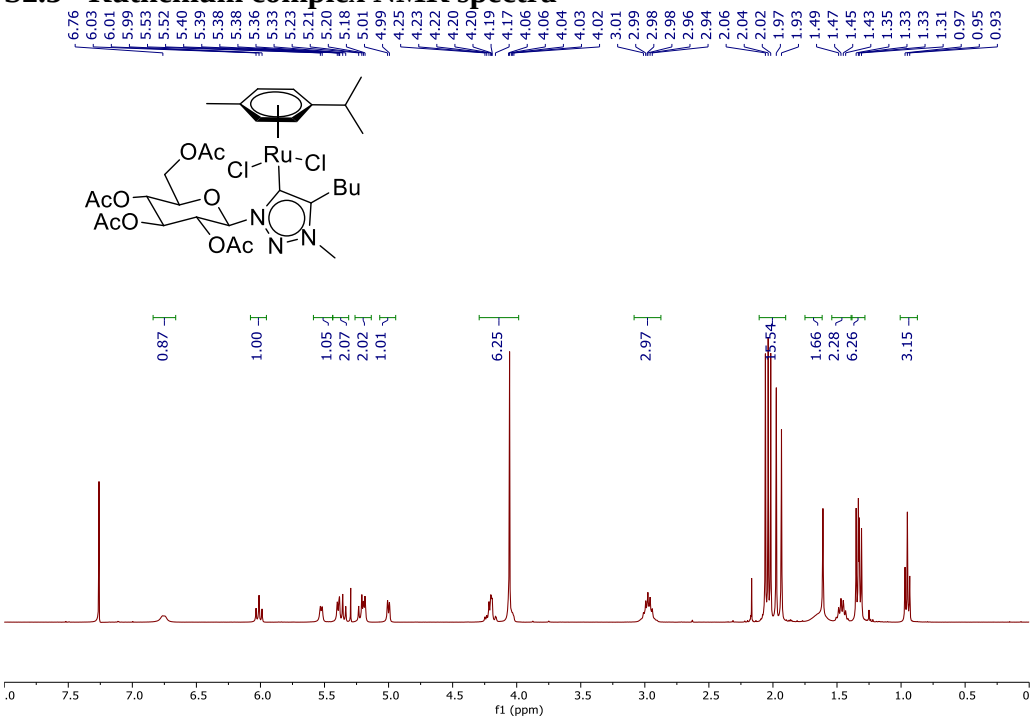


Figure S13. *^{1}H NMR (400 MHz, $CDCl_3$) spectrum of* ***5Glc***

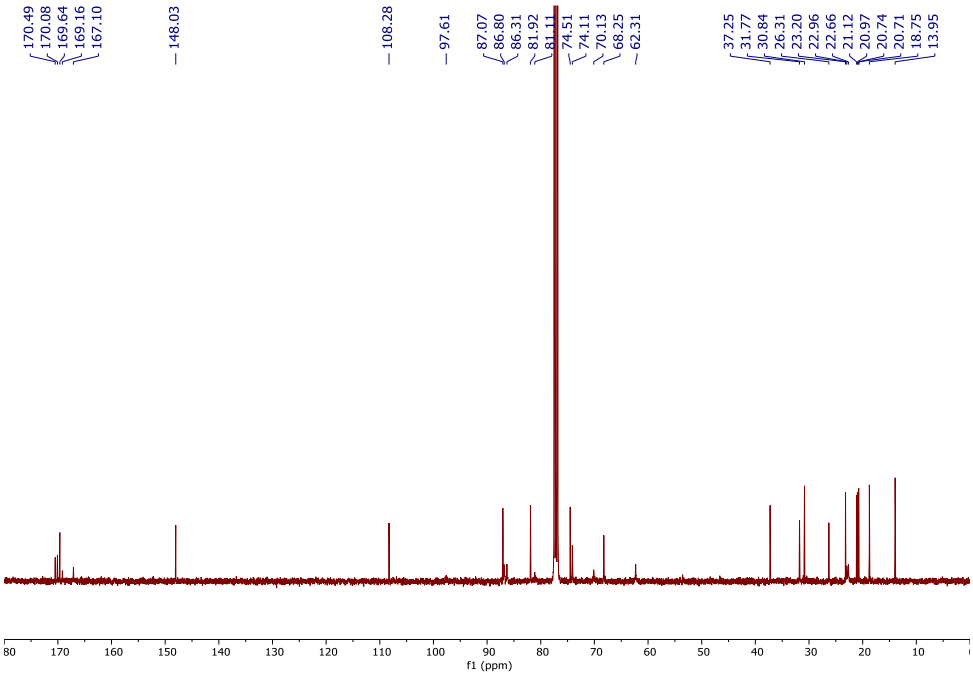


Figure S14. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of* ***5Glc***

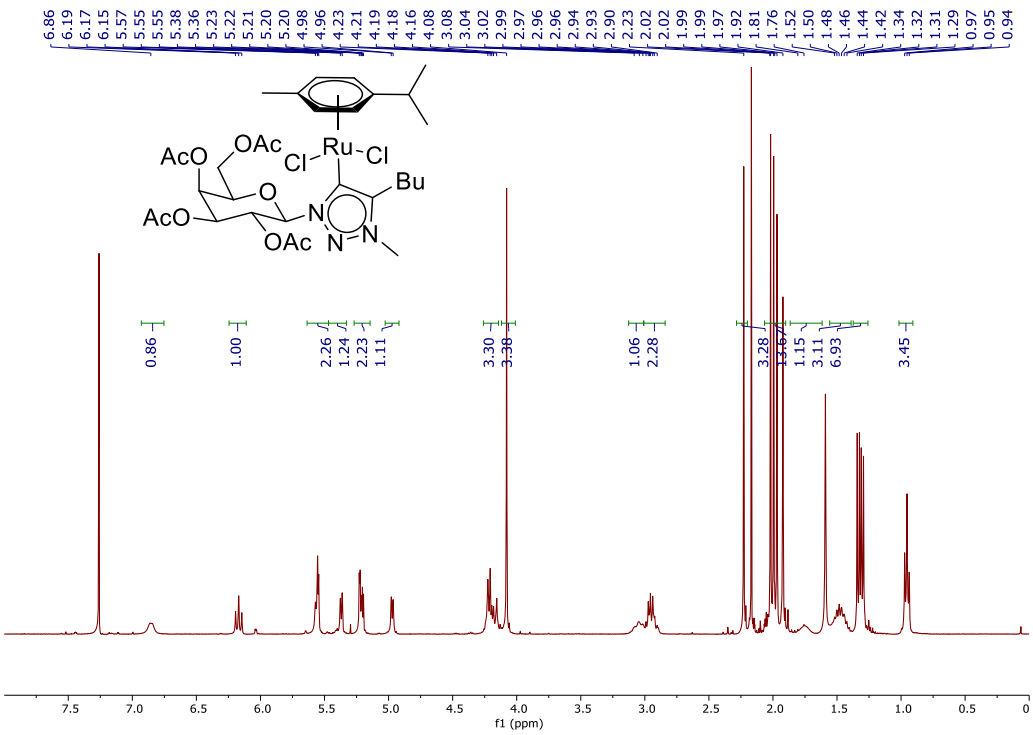


Figure S15. *^{1}H NMR (400 MHz, $CDCl_3$) spectrum of* ***5Gal***

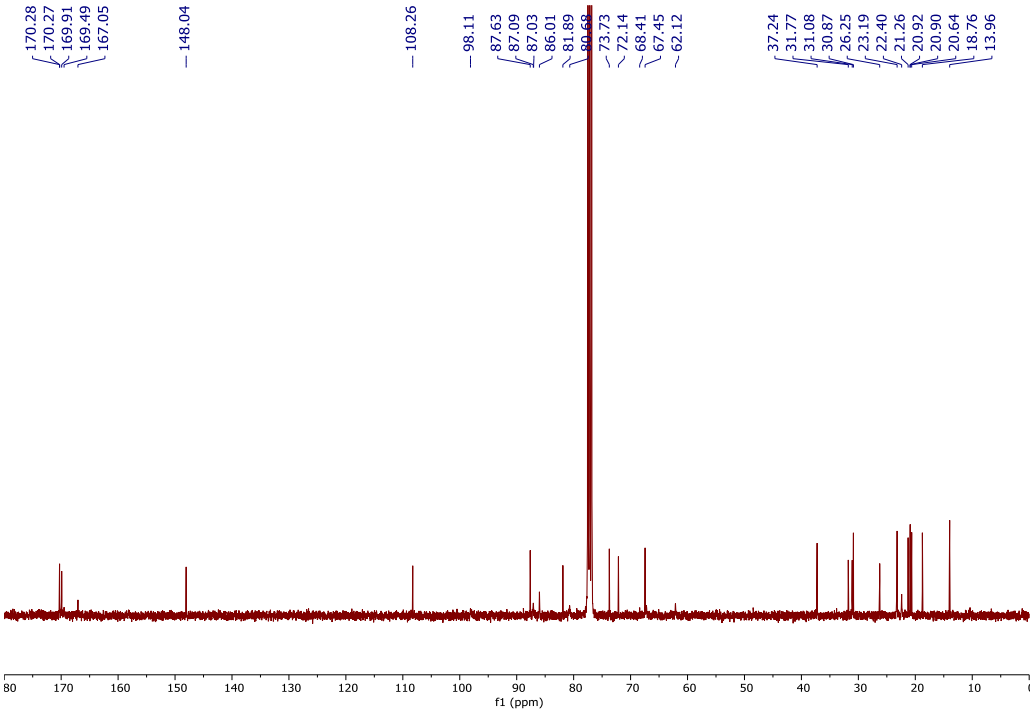


Figure S16. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of* ***5Gal***

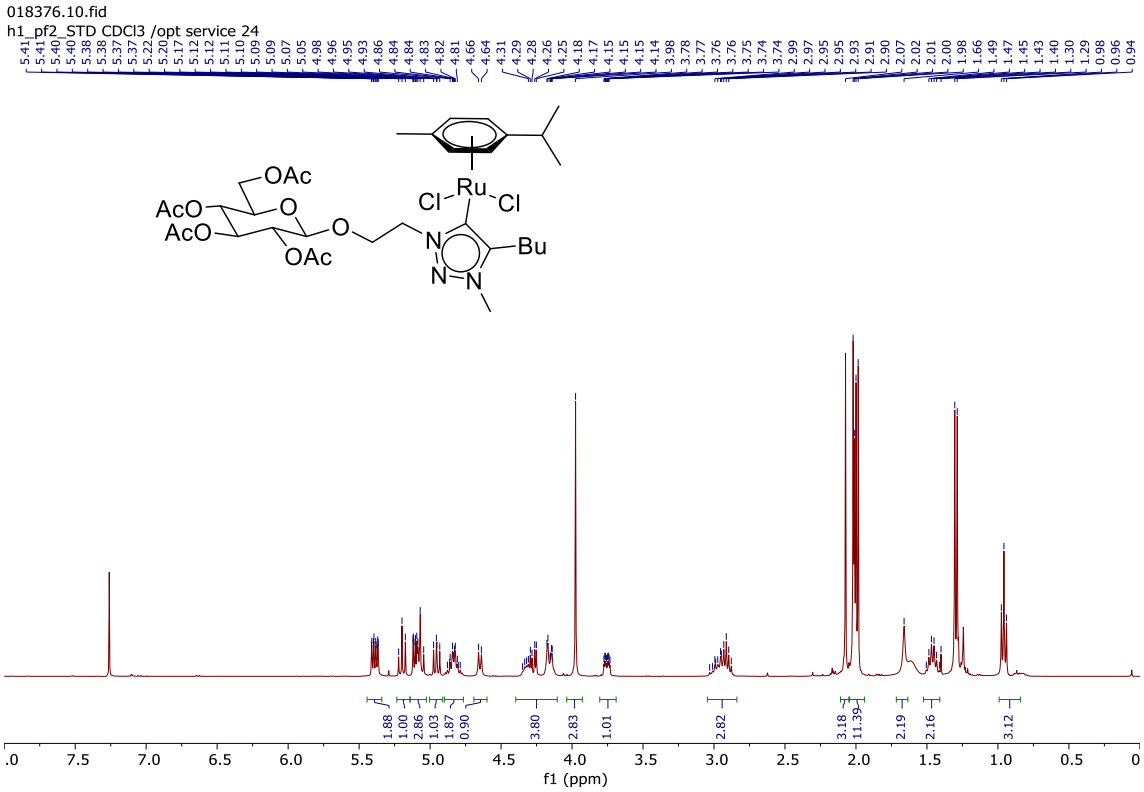


Figure S17. *^{1}H NMR (400 MHz, $CDCl_3$) spectrum of* ***6***

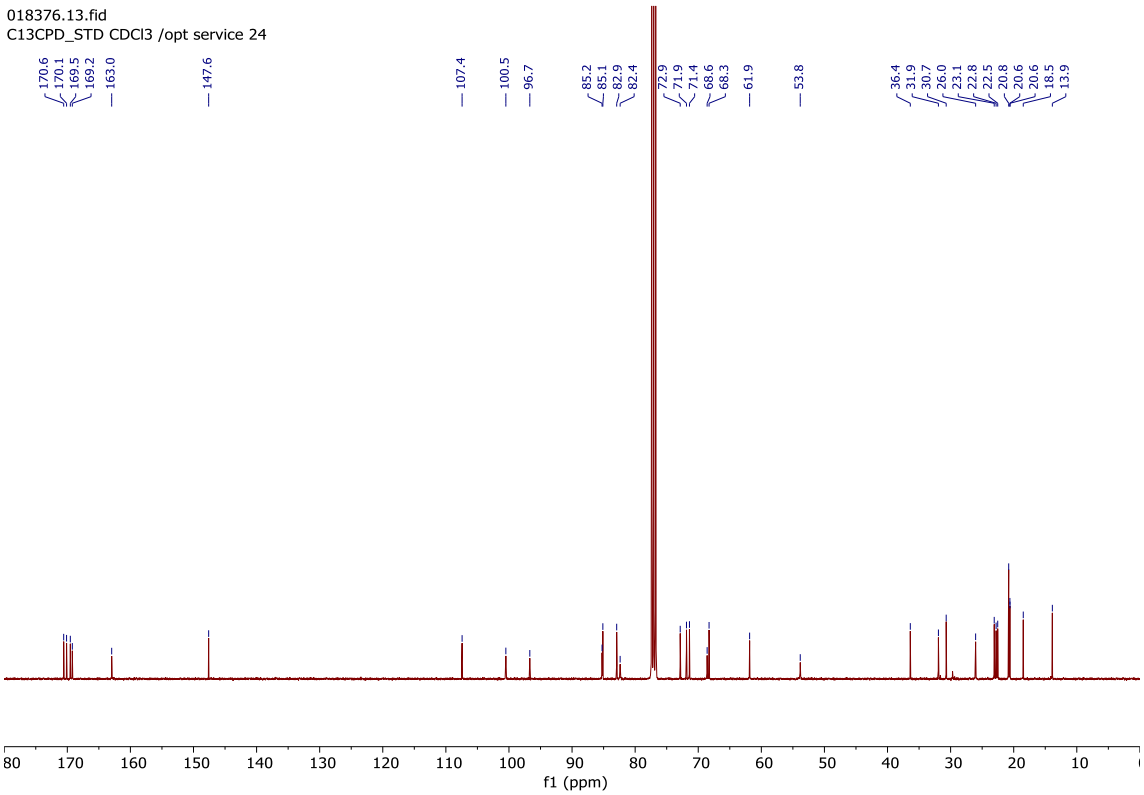


Figure S18. *^{13}C NMR (100 MHz, $CDCl_3$) spectrum of* ***6***

S3 – Deprotection of 5Glc: ^{1}H NMR and HSQC spectra

The complex **5Glc** was analyzed by ^{1}H NMR spectroscopy and use of HSQC experiments to characterize the deprotected complex formed upon treatment with KOH, mimicking the conditions of the catalytic reaction. This reaction was carried out in both D_2O and isopropanol-d_8. Both sets of spectra were analogous. The D_2O solutions gave spectra that allowed for more convenient analysis, since they do not display the isopropanol residual solvent resonances, which overlap with some key signals in the spectrum. These spectra are given in the section below:

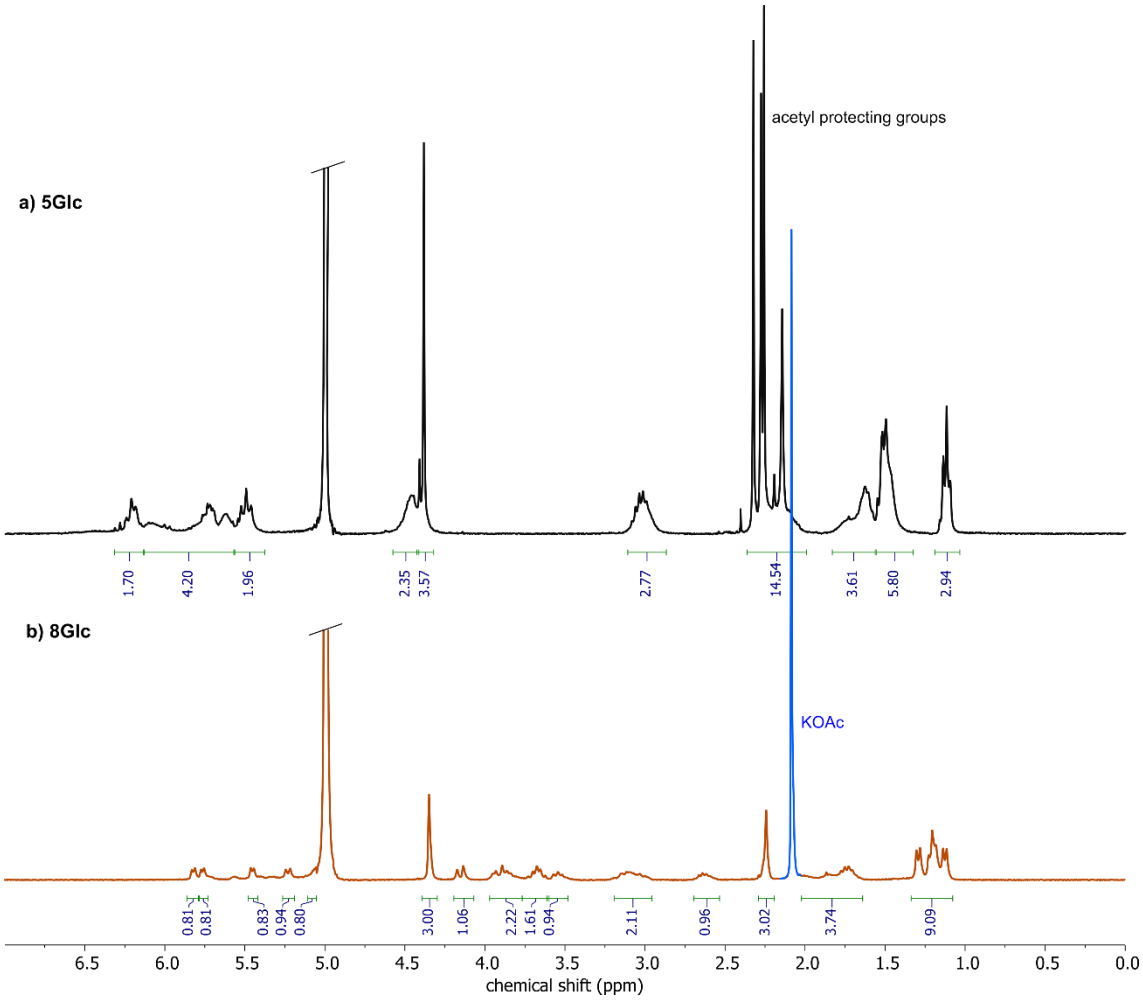


Figure S19. *^{1}H NMR (300 MHz, D_2O) spectrum of a solution of* ***(a)*** *acetyl-protected complex* ***5Glc****, and* ***(b)*** *upon treatment with $KOH_{(aq)}$, demonstrating in situ deprotection to* ***8Glc****.*

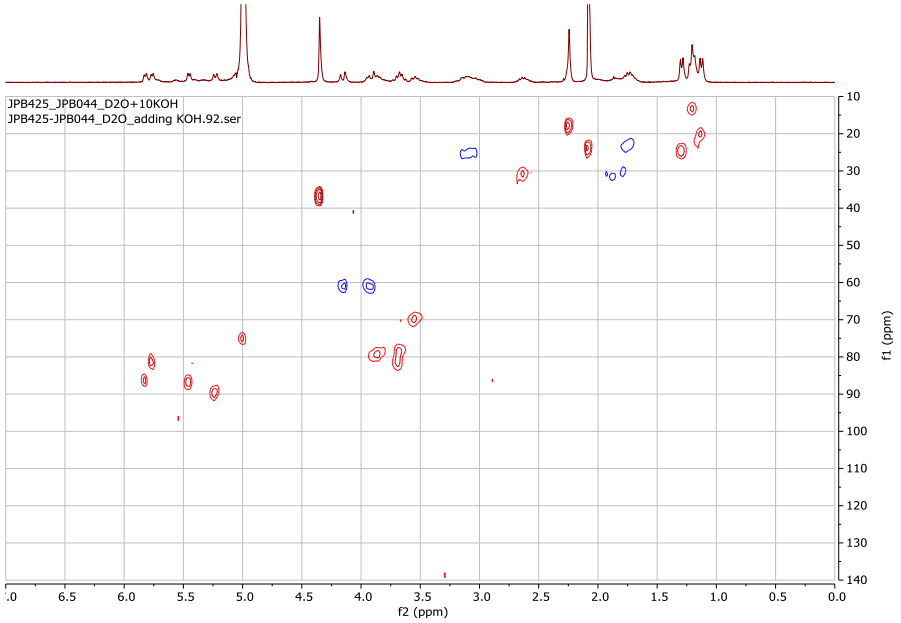


Figure S20. *HSQC of deprotected complex* ***8Glc*** *in* D_2O

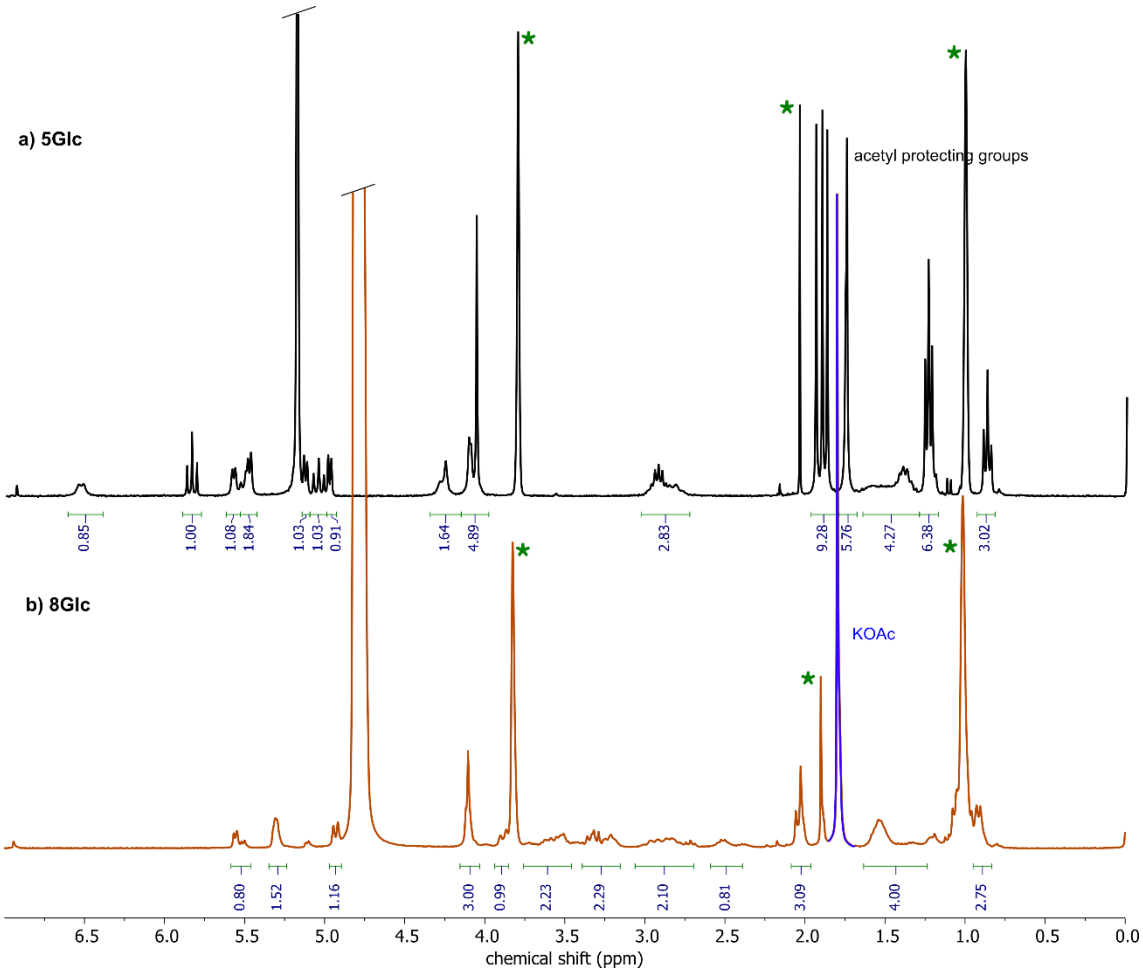


Figure S21. *^{1}H NMR (300 MHz, isopropanol-d_8) spectrum of a solution of* ***(a)*** *acetyl-protected complex* ***5Glc*** *and* ***(b)*** *upon addition of $KOH_{(aq)}$, demonstrating deprotection to* ***8Glc****. Resonances marked with an asterisk (*) arise from residual protonated solvent.*

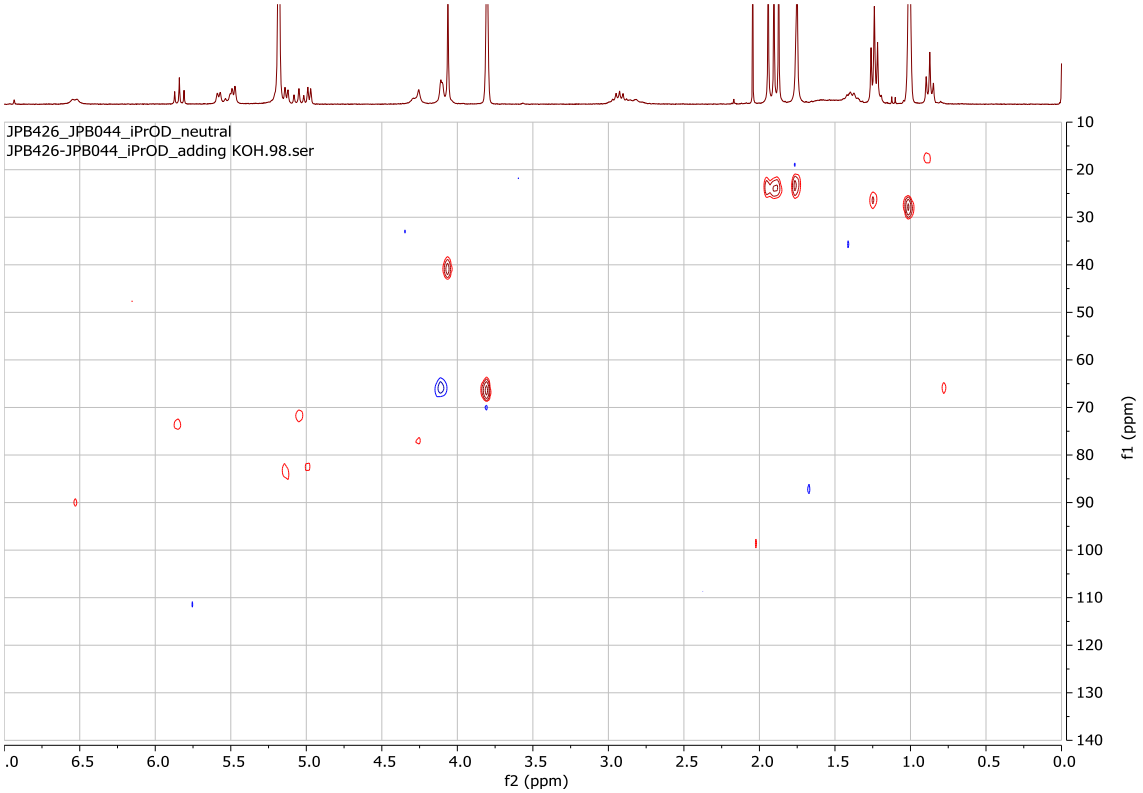


Figure S22. *HSQC of acetyl-protected complex* ***5Glc*** *in isopropanol-d_8.*

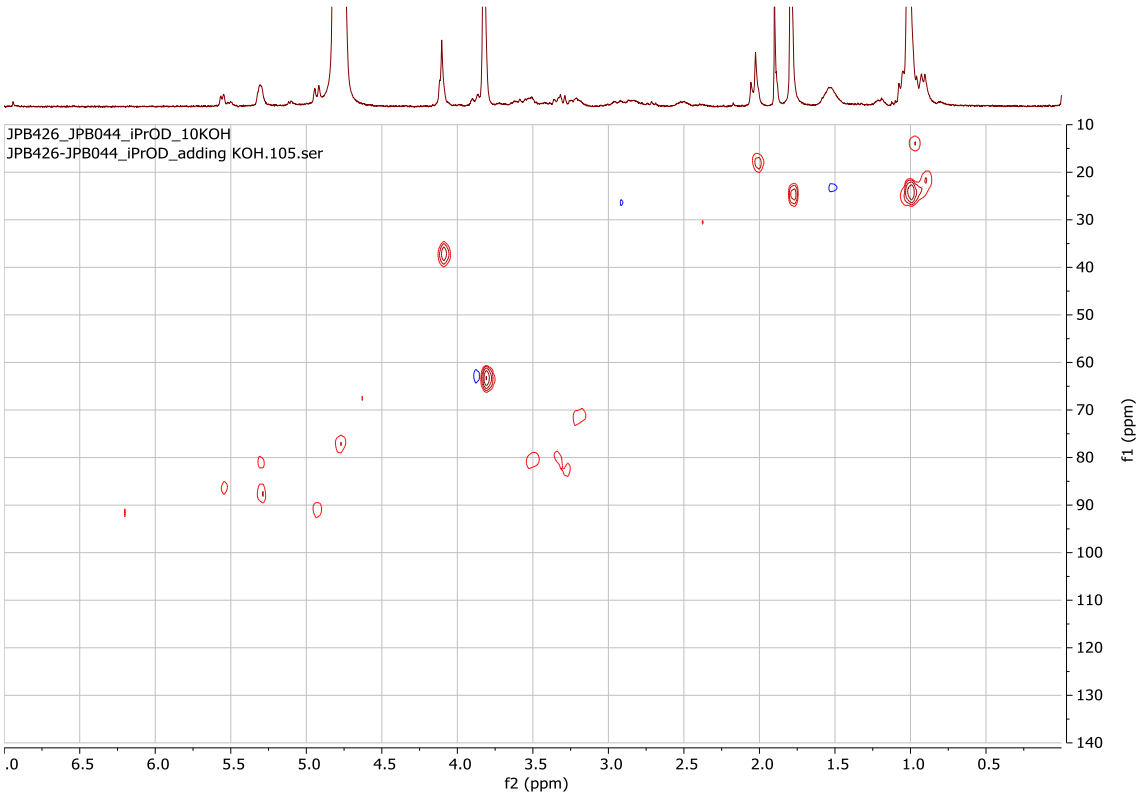
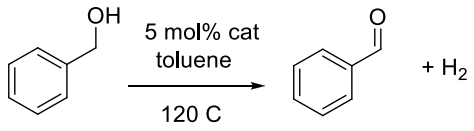


Figure S23. *HSQC of deprotected complex* ***8Glc*** *in isopropanol-d_8.*

S4 – Acceptorless alcohol oxidation catalysis

Complexes **5Glc** and **5Gal**, were evaluated as catalysts for the base- and oxidant-free oxidation of benzyl alcohol to benzaldehyde refluxing toluene[S4]. Maximum conversions of 39% were reached in both cases after 24 h, with almost 30% conversion already after 4 h (Table 2). These results are comparable to the catalytic activity of related triazolylidene ruthenium complexes, though the active species derived from **5** is less robust, as the productivity is capped at about 8 turnovers.[S5]

Table S1. *Conversion of benzyl alcohol to benzaldehyde, catalyzed by Ru complexes.*[a]



Entry	Complex	Substrate[a]	Conversion (%)[b]						
			0.5 h	*1 h*	*2 h*	*4 h*	*6 h*	*8 h*	*24 h*
1	**5Glc**	BnOH	8	16	24	29	30	33	39
2	**5Gal**	BnOH	7	15	26	32	33	33	39

[a] Reaction conditions: Benzyl alcohol (0.2 mmol), anisole (0.2 mmol) and Ru complex (0.01 mmol) were dissolved in toluene (2 mL) and heated in a sealed microwave vial at 120 °C, sampling regularly by ^{1}H NMR.

[S4] A. Prades, E. Peris, and M. Albrecht, *Organometallics*, 2011, **30**, 1162–1167

[S5] B. Bagh, A. M. McKinty, A. J. Lough and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 12842–12850; R. Pretorius, J. Olguín and M. Albrecht, *Inorg. Chem.*, 2017, **56**, 12410–12420

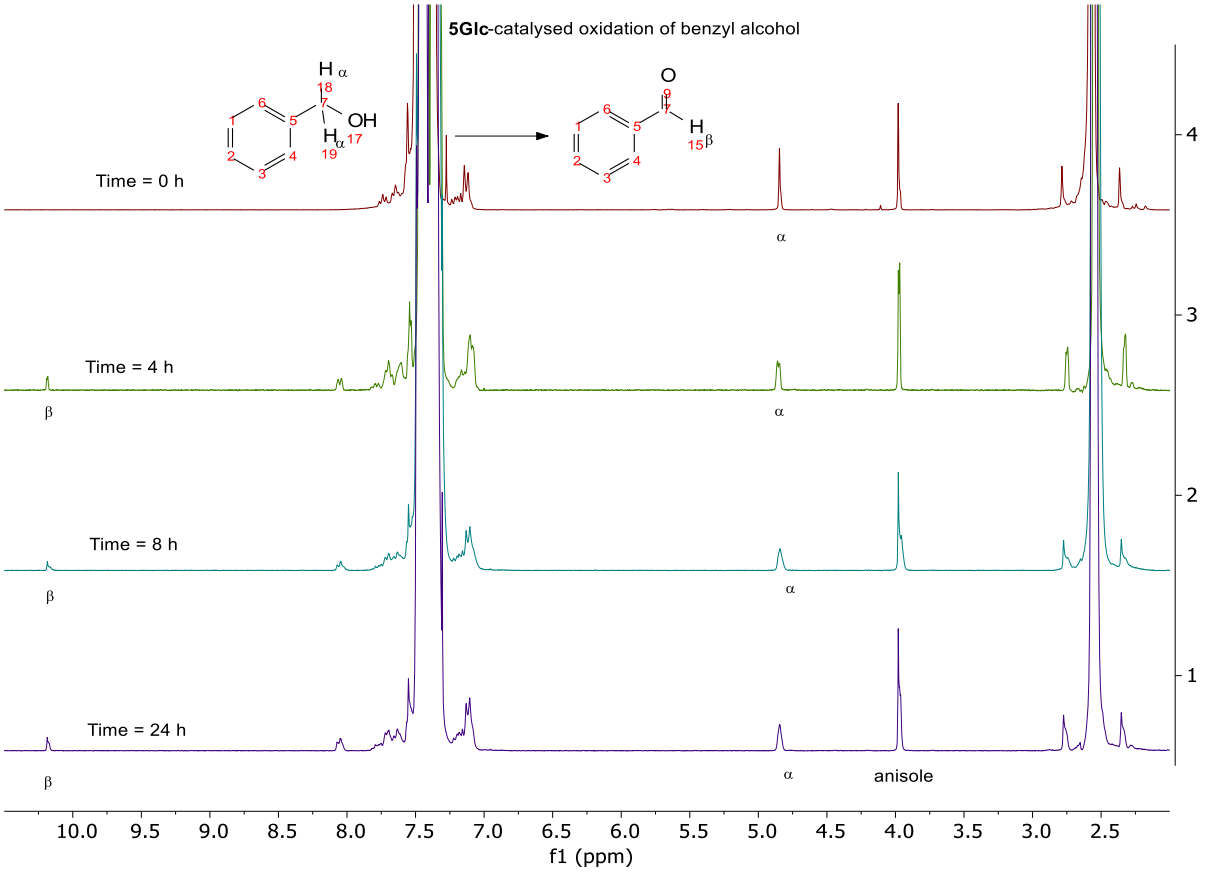


Figure S24. *Representative ^{1}H NMR spectra monitoring oxidation of benzyl alcohol by* ***5Glc***

S5 – Base-promoted transfer hydrogenation of ketones

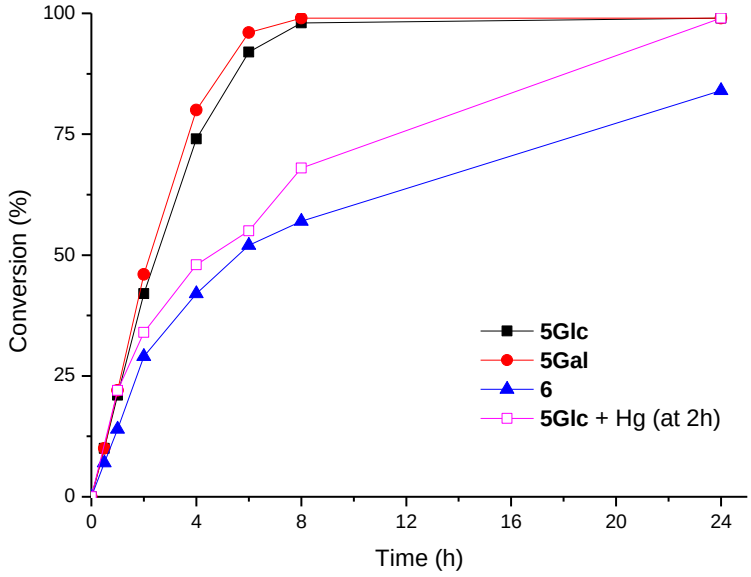


Figure S25. *Conversion profile for transfer hydrogenation of benzophenone, catalyzed by 1 mol% of,* ***5Glc****,* ***5Gal*** *and* ***6****, and by* ***5Glc*** *in the presence of mercury (added 2h after substrate).*

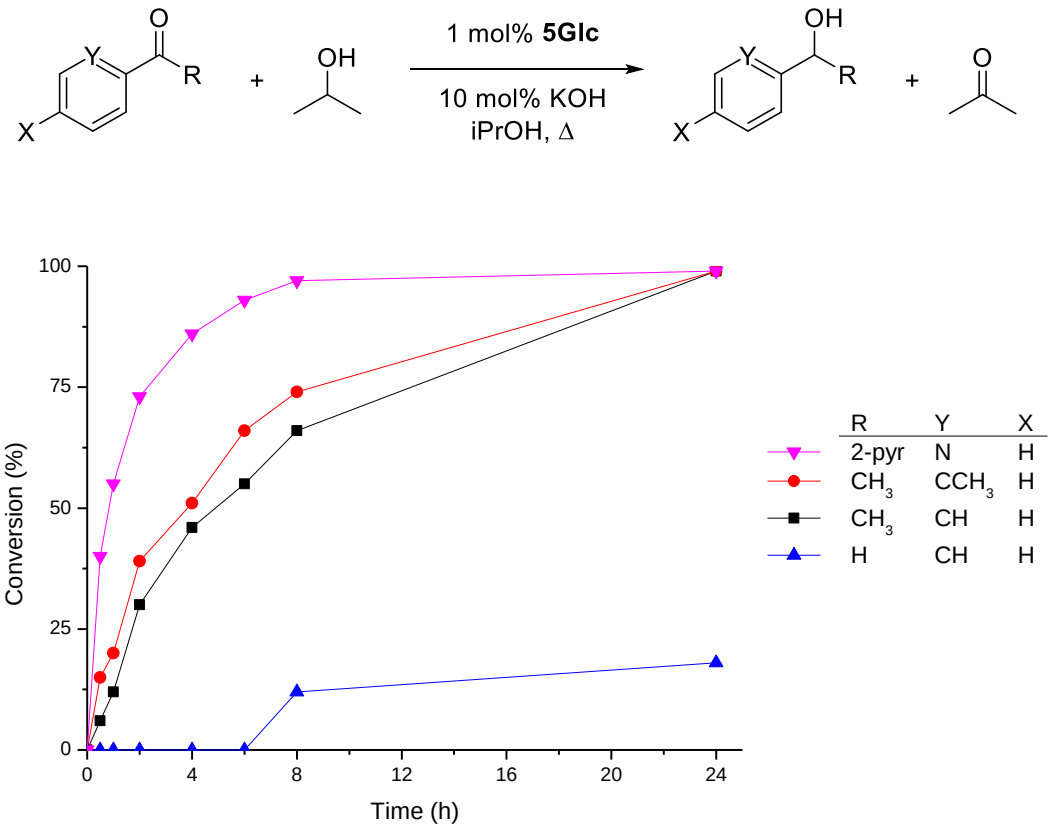


Figure S26. *Conversion profile for transfer hydrogenation of various ketone and aldehyde substrates, catalyzed by* ***5Glc****.*

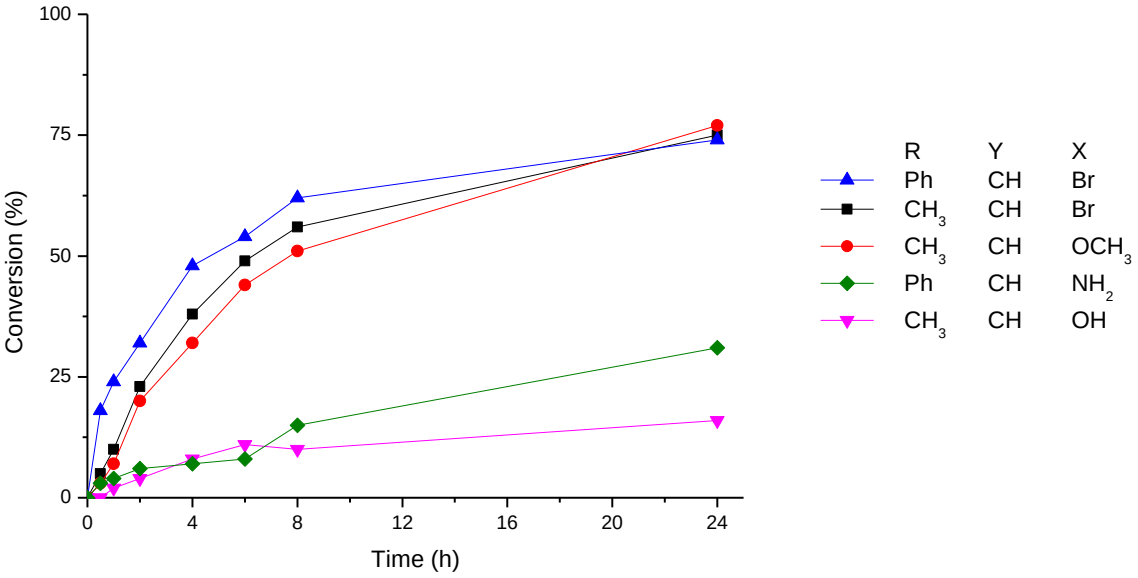


Figure S27. *Conversion profile for transfer hydrogenation of various ketone substrates, catalyzed by* ***5Glc****.*

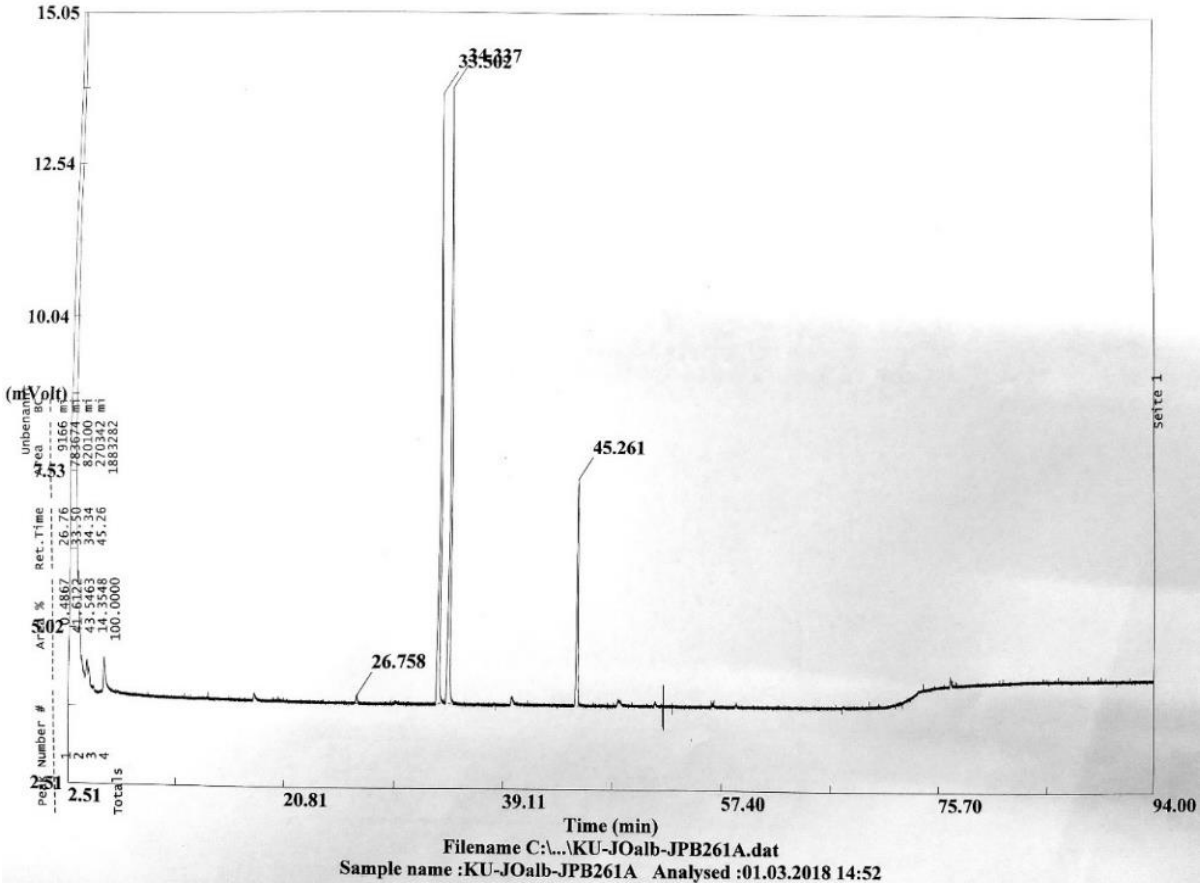


Figure S28. *Gas chromatogram of reaction mixture after transfer hydrogenation of acetophenone by* ***5Glc****, showing production of racemic mixture of (S)- and (R)-1-phenylethanol, with the signals at retention times of 33.5 and 34.3 min having areas of 784,364 and 820,100 units, respectively.*

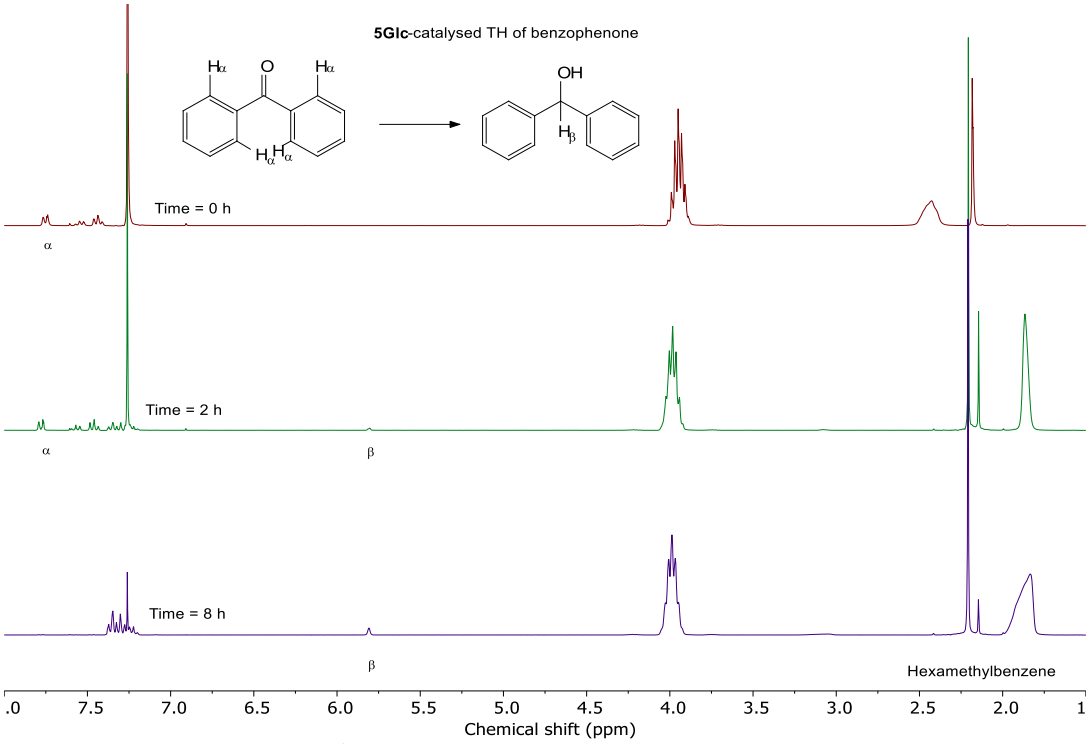


Figure S29. *Representative ^{1}H NMR spectra of the transfer hydrogenation of benzophenone by* ***5Glc****.*