Supporting Information

Copper(I)-Catalyzed Click Chemistry in Deep Eutectic Solvent for the Syntheses of β-D-Glucopyranosyltriazoles

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General experimental

The catalytic reactions were performed under nitrogen atmosphere. Chemicals were purchased from Sigma-Aldrich, TCI, Alfa-aesar, Himedia chemicals and used without further purification. Solvents, purchased from commercial suppliers were dried prior to synthesis of copper complexes. Copper catalysed azide alkyne cycloaddition reaction (CuAAC) were performed under inert condition while deep eutectic solvents were prepared inside the globe box. Deuterated solvents DMSO-d₆ and CDCl₃ were purchased from Sigma-Aldrich and used without further purification for recording NMR spectra. ¹H and ¹³C NMR spectra were recorded at Bruker AV-400 and 700 spectrometers (¹H at 400 MHz and ¹³C at 101 MHz). ¹H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane ($\delta 0.00$ ppm) and ${}^{13}C{}^{1}H$ NMR chemical shifts are referenced in ppm with respect to DMSO-d₆ (δ 39.52 ppm) and CDCl₃ (δ 77.16 ppm). The coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to describe multiplicity: bs = broad signal, s = singlet, d = doublet, t = triplet, q = quadrate, m = multiplate. High resolution mass spectra were recorded on a Bruker micrOTOF-Q II Spectrometer. Elemental analysis was carried out on a EuroEA Elemental Analyser. Crystal data were collected with Rigaku Oxford diffractometer and with INCOATEC micro source (Mo-K α radiation, $\lambda = 0.71073$ Å, multilayer optics) at 100 K.

Synthesis of ligand L₁ and copper(I) complex 1

Synthesis of ligand L₁:^[S1] Compound 3-(2-methoxyphenyl)-1H-pyrazole is a known compound and was synthesized using following procedure. A solution of 2-Methoxy acetophenone (1.50 g, 10.0 mmol) in a 1:1 mixture of DMF-DMA (15 mL) was reflux for 3 days under inert condition to give an orange brown solution. Removal of solvents under vacuum gave a brown oil. Thereafter, ethanol (20 mL) and hydrazine hydrate (1.28 g, 40.0 mmol) were added and the reaction mixture was refluxed for 2 hours. The resulting yellow solution was cooled to room temperature and cold water (15 mL) was added giving an off-white precipitate. The mixture was kept at 0-4 °C overnight to allow complete precipitation and the solid was collected after filtration. The solid was washed with cold water (3 x 20 mL) to give a white solid as pure product (1.67 g, 96%). ¹H NMR (CDCl₃): δ 12.50 (br, 1H), 7.73 (m, 1H), 7.69 (s, 1H), 7.09 (m, 2H), 6.67 (s, 1H), 4.02 (s, 3H).

In a pressure tube, 3-(2-methoxyphenyl)-1H-pyrazole (1.74 g, 10.0 mmol), 2-(chloromethyl) pyridine hydrochloride (1.64 g,10.0 mmol), NaOH solution (40%, 5 mL) and toluene (15 mL) were added and the reaction mixture was stirred at r.t. for 15 mins. Then tert-butylammonium hydroxide (4 mL) was added and the reaction mixture was stirred at 130 °C temperature for 24 h. The resulting red mixture was cooled down to r.t. and extracted with ethyl acetate (3 x 50 mL). All volatiles were removed under high vacuum to give 2-((3-(2-methoxyphenyl))-1H-pyrazol-1-yl) methyl) pyridine as pure product (2.27 g, 73%).^[S1] ¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 1H), 7.98 (dd, *J* = 7.7, 1H), 7.62–7.64 (m, *J* = 7.7, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.28–7.30 (m, *J* = 8.2, 1.7 Hz, 1H), 7.20 (dd, *J* = 7.0, Hz, 1H), 7.08–6.96 (m, 3H), 6.87 (d, *J* = 2.3 Hz, 1H), 5.53 (s, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.13, 156.87, 149.34, 149.01, 137.20, 130.53, 128.87, 122.76, 122.45, 121.83, 120.91, 111.39, 107.79, 57.73, 55.57. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₁₆H₁₆N₃O 266.1293; found 266.1285. Anal. Calcd

for C₁₆H₁₅N₃O (265.12): C, 72.43; H, 5.70; N, 15.84. Found: C, 72.25; H, 5.56; N, 15.68. FTIR v_{max} (cm⁻¹): 2800–3100 (C–H), 1505 (N–N), 1410–1600 (C=N, py; C=C, ph).

Synthesis of copper (I) complex 1

The ligand (0.066 g, 0.25 mmol) was dissolved in 5 mL CH₃CN in a Schlenk tube inside the glovebox. CuI (0.047 g, 0.25 mmol) suspension in acetonitrile was then added to the ligand solution with continuous stirring. The reaction mixture turned into whitish color solution and the stirring was continued for 24 hours. The reaction mixture was then dried in high vacuum and the NMR of the crude solid was recorded in DMSO-d₆. The crude solid was then dissolved in DMF and taken into a 5 mL vial. The crystallization was carried out by diffusing with diethyl ether. Block shape white crystals suitable for X-ray crystallography were grown at the bottom of the vial after two days. Yield: (0.093 g, 82%). ¹H NMR (700 MHz, DMSO) δ 8.51 (s, 1H), 8.03 (s, 1H), 7.95 (t, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 6.5 Hz, 1H), 7.57 (s, 1H), 7.44 (s, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.69 (s, 1H), 5.55 (s, 2H), 3.75 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 156.47, 154.19, 149.78, 148.38, 138.51, 132.36, 129.62, 129.51, 124.14, 123.97, 120.89, 120.14, 111.49, 107.21, 55.42, 54.92. Anal. Calcd. for C₃₂H₃₀Cu₂I₂N₆O₂ (911.50): C, 47.17; H, 3.32; N, 9.22; Found: C, 47.03; H, 3.37; N, 9.10. HRMS (ESI-TOF) m/z: [M]⁺ calcd for C₁₆H₁₅CuN₃O 328.0511; found 328.0517. FTIR v_{max} (cm⁻¹): 2740–3130 (C–H), 1515 (N–N), 1400–1640 (C=N, py; C=C, ph).

Characteristic spectra of ligand L₁ and copper(I) complex 1



Figure S1. ¹H NMR of 2-((3-(2-methoxyphenyl)-1H-pyrazol-1-yl) methyl)pyridine (L_1) in CDCl₃ at r.t.



Ó Figure S2. ¹³C NMR of 2-((3-(2-methoxyphenyl)-1H-pyrazol-1-yl) methyl)pyridine (L₁) in CDCl₃ at r.t.



Figure S3: ¹H NMR of complex 1 in DMSO-d₆.



Figure S4: ¹³C NMR of complex 1 in DMSO-d₆.



Figure S5: FTIR Spectrum of ligand L₁.



Figure S6: FTIR Spectrum of complex 1.

General experiments of CuAAC reactions in DESs

General procedure for CuAAC reactions (for reaction optimisation).

All the CuAAC reactions were performed under inert condition. 1-Bromo- α -D-glucose tetraacetate, 2,3,4,6-Tetra-O-acetyl- α -D-glucopyranosyl bromide (0.102 g, 0.25 mmol), phenyl acetylene (0.025 g, 0.25mmol), NaN₃ (0.040 g, 0.625 mmol), and 1.5 mol% copper complex **1** (3 mol% [Cu]), were weighed in a vial (10 mL). Thereafter, different deep eutectic solvent for different experiments was added to it. The resultant mixture was heated at appropriate temperature (r.t./ 70 °C) for an appropriate time with stirring. Formation of solid crude was observed after the desire reaction time. The crude solid product was then filtered and washed with additional 2 mL of 25 % ammonia solution to remove copper from the triazole products. The compound was then dried under vacuum and white crude solid compound was isolated as pure form. The product was dissolved in CDCl₃ and ¹H NMR spectrum was recorded. The anomeric configuration of the triazole was compared with literature reported compound and the NMR data/spectra of our products are identical with the reported β -isomer of glucopyranosyltriazoles.^[S2] The NMR signature of the corresponding α -D-Glucopyranosyltriazole is different.^[S3]

General procedure for gram-scale CuAAC reactions:

The optimised reaction conditions in TBAB/glycerol (Method **A**; 1.5 mol% of catalyst loading, ChCl/glycerol (1:2), 70 °C, 12 h) or in ChCl/glycerol (Method **B**; 1.5 mol% of catalyst loading, ChCl/glycerol (1:2), 70 °C, 12 h) was selected for gram-scale (10 mmol) CuAAC reactions as reaction medium. For this purpose, acetobromo- α -D-glucose (4.112 g, 10 mmol), phenyl acetylene (1.021 g, 10 mmol), NaN₃ (1.625 g, 25 mmol), and copper complex **1** (1.5 mol%), were added in 40 mL of TBAB/glycerol (1:4) or ChCl/glycerol (1:2). After the desired reaction time the crude solid product was filtered and washed with additional 20 mL of 25 % ammonia solution. The compound was then dried under vacuum and white crude solid compound was isolated as pure form. The product was then dissolved in CDCl₃ and ¹H NMR spectrum was recorded.

General procedure for substrate scope:

Both the optimised reaction conditions (Method A; 1.5 mol% of catalyst loading, TBAB/glycerol (1:4), 70 °C, 12 h; Method B; 1.5 mol% of catalyst loading, ChCl/glycerol (1:2), 70 °C, 12 h) were utilized for the synthesis of various β -D-glucopyranosyltriazoles. In this regard, four different glucopyran-derivatives (0.25 mmol), and alkynes (0.25 mmol) were combined with sodium azide (0.62 mmol) and copper complex **1** (1.5 mol%) in a vial (10 mL).

It is important to mention that, we did not use sodium azide when the starting glycosides had an azide functionality i.e. the substrates scope with 2-azidoethyl 2,3,4,6-tetra-O-acetyl- β -Dglucopyranoside. Thereafter, DESs ChCl/glycerol or TBAB/glycerol (1:4) (2 mL) was added to it. The reaction mixture was placed under optimized reaction conditions. After that, the reaction mixture was diluted with water followed by filtered and washed with 25 % ammonia solution to get desire β -D-glucopyranosyltriazoles product. The compound was then dried under vacuum and crude solid compound was isolated as pure form. Occasionally the crude product was purified by column chromatography using silica as stationary phase and ethyl acetate-hexane mixture (1:9) as eluent. The product was then dissolved in CDCl₃ and NMR (¹H and ¹³C) spectrum was recorded. Most of the products glucopyranosyltriazoles (β -isomer) are reported compounds and the NMR data/spectra of our products are identical with the reported compounds.^[S2] The NMR signature of the corresponding α -D-Glucopyranosyltriazole is different.^[S3]

General procedure for the recycling of the reaction medium and calculation of *E*-factor: The reaction medium was recycled as follows: For this purpose, 2 mmol reaction scale was conducted with, acetobromo-a-D-glucose (0.822 g, 2 mmol), phenyl acetylene (0.204 g, 2 mmol), NaN₃ (0.325 g, 5 mmol), and 1.5 mol% copper complex 1 (3 mol% [Cu]), using 4 mL (4.788 g) of TBAB/glycerol (1:4) or ChCl/glycerol (1:4) as reaction medium. The solid product was filtered with a Büchner funnel, washed with 25 % ammonia solution (2 mL) by portion and dried under vacuum. Thereafter, the volume of the aqueous phase was reduced to 4 mL and placed in the reaction vial equipped with a magnetic stirring bar. Acetobromo- α -D-glucose (0.102 g, 0.25 mmol), phenyl acetylene (0.025 g, 0.25 mmol), NaN₃ (0.016 g, 0.25 mmol), and 1.5 mol% copper complex 1 (3 mol% [Cu]) were added and the reaction was stirred for 12 h at 70 °C. Here it is worth to mention that only 1 eqv. amount of sodium azide is used instead of 2.5 eqv. as we assumed that recovered reaction media already contain 1.5 eqv sodium azide. The entire process was repeated four times. Thus, the reaction medium was recycled five times and no change in catalytic activity was observed. The amount of media recovered in both the methods is as follows: Method A: 1st run: 4.726 g; 2nd cycle: 4.672 g; 3rd cycle: 4.545 g; 4th cvcle: 4.320 g; 5th cvcle: 4.150 g; **Method B**: 1st run: 4.776 g; 2nd cycle: 4.650 g; 3rd cycle: 4.625 g; 4th cycle: 4.598 g; 5th cycle: 4.550 g.

The triazole product **A** was obtained in excellent isolated yield in all reaction runs: **Method A**: (1st run: 931 mg; 2nd cycle: 921 mg; 3rd cycle: 921 mg; 4th cycle: 931 mg; 5th cycle: 921 mg);

Method B: (1st run: 893 mg; 2nd cycle: 903 mg; 3rd cycle: 892 mg; 4th cycle: 897 mg; 5th cycle: 905 mg).

Overall E-factor for five consecutive reaction runs in Method A and Method B

Method A: 1.5 mol% of catalyst loading, 70 °C, 12 h in TBAB/glycerol (1:4)

Substrate:	acetobromo-α-D-glucose (2 mmol)	= 0.822 g	
	Phenyl acetylene (2 mmol)	= 0.204 g	
	Sodium azide (5 mmol)	= 0.325 g	
Catalyst:	Cu(I) iodide complex 1 (1.5 mol %)	= 0.013 g	
Solvent:	TBAB/glycerol (4 mL) x 1.1817	= 4.726 g	
	25 % ammonia solution, 2 mL (used to	wash the product) x 0.9	= 1.8 g
E-factor =	mass (waste)		
	mass (product)		
	0.195 g (sodium azide) + 0.065 g (cop (reaction medium) + 9 g (ammonia solutio	oper catalyst) + 4.726 g n used to wash the product)	
=	0.931 g + 0.921 g + 0.921 g + 0.931 g	g + 0.921 g (product)	
=	13.986 g / 4.625 g		
=	3.02 kg waste / 1 kg of product		
Method B:	1.5 mol% of catalyst loading, 70 °C, 12 h	in ChCl/glycerol (1:2),	
Substrate:	acetobromo-α-D-glucose (2 mmol)	= 0.822 g	
	Phenyl acetylene (2 mmol)	= 0.204 g	
	Sodium azide (5 mmol)	= 0.325 g	
Catalyst:	Cu(I) iodide complex 1 (1.5 mol %)	= 0.013 g	
Solvent:	ChCl/glycerol (4 mL) x 1.194	= 4.776 g	
	25 % ammonia solution, 2 mL (used to	wash the product) x 0.9	= 1.8 g
F factor -	mass (waste)		
	mass (product)		
	0.195 g (sodium azide) + 0.065 g (cop (reaction medium) + 9 g (ammonia solutio	oper catalyst) + 4.776 g n used to wash the product)	
=	0.893 g + 0.903 g + 0.892 g + 0.897 g	g + 0.905 g (product)	
=	14.036 g / 4.49 g		

= 3.12 kg waste / 1 kg of product

E-factor for a single reaction run in in Method A and Method B: Assuming that the reaction medium can be infinitely recycled.

Method A: 1.5 mol% of catalyst loading, 70 °C, 12 h in TBAB/glycerol (1:4)

mass (waste) E-factor = mass (product) 0.195 g (sodium azide) + 0.013 g (copper catalyst) + 0.054 (solvent TBAB/glycerol) + 1.8 g (ammonia solution used to wash the product) 0.931 g (product) = 2.062 g / 0.931 g= 2.21 kg waste / 1 kg of product Method B: 1.5 mol% of catalyst loading, 70 °C, 12 h in ChCl/glycerol (1:2), mass (waste) E-factor = mass (product) 0.195 g (sodium azide) + 0.013 g (copper catalyst) + 0.126 (solvent ChCl/glycerol) + 1.8 g (ammonia solution used to wash the product) 0.893 g (product) = 2.134 g / 0.893 g

= 2.38 kg waste / 1 kg of product

Synthesis and isolation of acetoazido- β -D-glucose from acetobromo- α -D-glucose followed by the reaction with phenyl acetylene to form β -D-Glucopyranosyltriazole:



In the first step, acetobromo- α -D-glucose (0.206 g, 0.5 mmol) and NaN₃ (0.040 g, 1.25 mmol) were weighed in a vial (10 mL). Thereafter, ChCl/Glycerol (1:2) or TBAB/glycerol (1:4) was added into the vial. The resultant mixture was heated at 70 °C for 12 h with stirring. Formation of solid crude was observed after the desire reaction time. The crude solid product was then filtered and washed with additional 2 mL of water. The crude was then dried under vacuum and white solid compound was isolated as pure form. The product (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-azidotetrahydro-2H-pyran-3,4,5-triyl triacetate was dissolved in CDCl₃ and

¹H NMR spectrum was recorded. Yield: 176 mg, 95%). ¹H NMR (700 MHz, CDCl₃) δ 5.21 (t, J = 9.5 Hz, 1H), 5.09 (t, J = 9.8 Hz, 1H), 4.94 (t, J = 9.2 Hz, 1H), 4.64 (d, J = 8.9 Hz, 1H), 4.26 (dd, J = 12.5, 4.8 Hz, 1H), 4.16 (dd, J = 12.4, 2.0 Hz, 1H), 3.79 (ddd, J = 10.0, 4.7, 2.2 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H). ¹³C NMR (101 MHz,) δ 170.73, 170.24, 169.43, 169.33, 88.04, 74.15, 72.73, 70.77, 68.01, 61.78, 20.81, 20.66.

In the following step, 0.25 mmol of acetoazido- β -D-glucose is treated with 0.25 mmol of phenyl acetylene in presence of catalyst **1** (1.5 mol %) in ChCl/Glycerol or TBAB/glycerol for 12 h and the resultant mixture was heated at 70 °C with stirring. Formation of solid crude was observed after the desire reaction time. The crude solid product was then filtered and washed with additional 2 mL of 25 % ammonia solution. The compound was then dried under vacuum and white crude solid compound was isolated as pure form. The product was dissolved in CDCl₃ and ¹H NMR spectrum was recorded.

NMR data of the products:



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-phenyl-1H-1,2,3-triazol-1-yl)tetrahydro-2Hpyran-3,4,5-triyl triacetate (A): Isolated as white solid (46.5 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 7.86 – 7.80 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 5.93 (d, *J* = 9.3 Hz, 1H), 5.52 (t, *J* = 9.4 Hz, 1H), 5.44 (t, *J* = 9.4 Hz, 1H), 5.27 (t, *J* = 9.7 Hz, 1H), 4.33 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.16 (dd, *J* = 12.6, 2.0 Hz, 1H), 4.03 (ddd, *J* = 10.1, 5.0, 2.1 Hz, 1H), 2.08 (d, *J* = 3.9 Hz, 6H), 2.04 (s, 3H), 1.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.65, 170.07, 169.53, 169.16, 148.65, 130.01, 129.02, 128.72, 126.05, 117.86, 85.94, 75.31, 72.87, 70.33, 67.88, 61.72, 20.82, 20.68, 20.66, 20.32.

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2Hpyran-3,4,5-triyl triacetate (B₁): Isolated as off white solid (47 mg, 96%). ¹H NMR (700 MHz, CDCl₃) δ 7.96 (d, J = 2.8 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.24 (d, J = 4.5 Hz, 2H), 5.93 (dd, J = 9.3, 2.8 Hz, 1H), 5.52 (td, J = 9.4, 2.8 Hz, 1H), 5.44 (dd, J = 9.3, 2.8 Hz, 1H), 5.27 (dd, J = 9.7, 2.7 Hz, 1H), 4.40 – 4.24 (m, 1H), 4.16 (d, J = 12.6 Hz, 1H), 4.03 (d, J = 4.8 Hz, 1H), 2.38 (d, J = 2.4 Hz, 3H), 2.08 (dd, J = 6.4, 3.0 Hz, 6H), 2.03 (d, J = 2.8 Hz, 3H), 1.88 (d, J = 2.8 Hz, 3H). ¹³C NMR (176 MHz, CDCl₃) δ 170.66, 170.07, 169.53, 169.15, 148.72, 138.63, 129.68, 127.18, 125.95, 117.47, 85.90, 75.27, 72.91, 70.30, 67.88, 61.72, 21.43, 20.82, 20.67, 20.66, 20.31.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(B2): Isolated as white solid (49 mg, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.76 (s, 1H), 7.74 (s, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 5.93 (d, *J* = 9.3 Hz, 1H), 5.52 (t, *J* = 9.4 Hz, 1H), 5.44 (t, *J* = 9.4 Hz, 1H), 5.31 – 5.22 (m, 1H), 4.40 – 4.25 (m, 1H), 4.16 (dd, *J* = 12.6, 2.1 Hz, 1H), 4.03 (ddd, *J* = 10.1, 5.0, 2.1 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.87 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.66, 170.07, 169.53, 169.13, 148.74, 145.02, 128.51, 127.43, 126.05, 117.47 (s), 85.92, 75.29, 72.91, 70.31, 67.90, 61.73, 28.82, 20.83, 20.68, 20.65, 20.31, 15.64.

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(dimethylamino)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(B₃): Isolated as white solid (50 mg, 97%).¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1H), 7.72 – 7.67 (m, 2H), 6.78 – 6.74 (m, 1H), 5.91 (d, *J* = 9.4 Hz), 5.53 (t, *J* = 9.5 Hz, 2H), 5.42 (t, *J* = 9.4 Hz, 1H), 5.32 – 5.19 (m, 1H), 4.32 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.15 (dd, *J* = 12.6, 2.1 Hz, 1H), 4.01 (ddd, *J* = 10.1, 5.0, 2.1 Hz, 1H), 2.99 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.87 (s, 3H).¹³C NMR (101 MHz,CDCl₃) δ 170.67, 170.09, 169.53, 169.13, 150.80, 149.16, 127.00, 118.11, 116.11, 112.53, 85.85, 75.22, 73.03, 70.25, 67.93, 61.76, 40.56, 20.83, 20.68, 20.67, 20.33.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (B4): Isolated as white solid (46.8 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 5.93 (d, *J* = 9.0 Hz, 1H), 5.47 (dt, *J* = 24.7, 9.5 Hz, 2H), 5.26 (t, *J* = 9.6 Hz, 1H), 4.33 (dd, *J* = 12.7, 5.0 Hz, 1H), 4.15 (d, *J* = 12.6 Hz, 1H), 4.03 (dd, *J* = 10.1, 3.2 Hz, 1H), 2.08 (d, *J* = 3.4 Hz, 6H), 2.04 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.65, 170.06, 169.53, 169.20, 147.61, 132.18, 128.93, 127.55, 122.68, 118.01, 85.95, 77.48, 77.16, 76.84, 75.32, 72.75, 70.31, 67.78, 61.67, 20.83, 20.68, 20.66, 20.33.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl) tetrahydro-2H-pyran-3,4,5-triyl triacetate (Bs): Isolated as white solid (47.8 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.83 (t, *J* = 1.6 Hz, 1H), 7.70 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.32 (ddd, *J* = 11.0, 8.4, 4.9 Hz, 2H), 5.93 (d, *J* = 9.0 Hz, 1H), 5.47 (dt, *J* = 18.5, 9.5 Hz, 2H), 5.33 – 5.19 (m, 1H), 4.32 (dd, *J* = 12.7, 5.0 Hz, 1H), 4.15 (dd, *J* = 12.6, 2.0 Hz, 1H), 4.04 (ddd, *J* = 10.1, 5.0, 2.1 Hz, 1H), 2.07 (d, *J* = 3.6 Hz, 6H), 2.03 (s, 3H), 1.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.60, 170.01, 169.49, 169.13, 147.30, 134.96, 131.75, 130.28, 128.66, 126.07, 124.08, 118.39, 85.95, 75.30, 72.73, 70.38, 67.81, 61.66, 20.78, 20.64, 20.61, 20.27.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₆): Isolated as white solid (51.43 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 5.93 (d, *J* = 9.0 Hz, 1H), 5.47 (dt, *J* = 25.0, 9.5 Hz, 2H), 5.26 (t, *J* = 9.6 Hz, 1H), 4.33 (dd, *J* = 12.7, 5.0 Hz, 1H), 4.15 (d, *J* = 12.6 Hz, 1H), 4.03 (dd, *J* = 10.1, 3.3 Hz, 1H), 2.08 (d, *J* = 3.7 Hz, 6H), 2.04 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.65, 170.06, 169.54, 169.20, 132.19, 128.97, 127.54, 122.69, 86.02, 75.34, 72.75, 70.31, 67.78, 61.67, 20.85, 20.70, 20.67, 20.35.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-nitrophenyl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₇): Isolated as yellow solid (46.8 mg, 90%). ¹H NMR (700 MHz, CDCl₃) δ 8.31 (d, J = 8.5 Hz, 2H), 8.16 (s, 1H), 8.02 (d, J = 8.5 Hz, 2H), 5.95 (d, J = 8.8 Hz, 1H), 5.48 (dq, J = 18.6, 9.5 Hz, 2H), 5.27 (t, J = 9.5 Hz, 1H), 4.35 (dd, J = 12.7, 5.0 Hz, 1H), 4.17 (d, J = 12.7 Hz, 1H), 4.05 (dd, J = 10.1, 4.9 Hz, 1H), 2.09 (d, J = 5.1 Hz, 6H), 2.05 (s, 3H), 1.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.60, 170.01, 169.52, 169.25, 147.80, 146.48, 136.23, 126.60, 124.48, 119.54, 86.13, 75.53, 72.64, 70.49, 67.81, 61.67, 20.83, 20.68, 20.66, 20.33.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(B₈): Isolated as off white solid (50 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 5.95 (d, *J* = 9.0 Hz, 1H), 5.48 (dt, *J* = 18.4, 9.5 Hz, 2H), 5.32 – 5.22 (m, 1H), 4.34 (dd, *J* = 12.7, 5.1 Hz, 1H), 4.16 (dd, *J* = 12.6, 2.0 Hz, 1H), 4.05 (ddd, *J* = 10.1, 5.0, 2.0 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.64, 170.04, 169.54, 169.22, 147.26, 133.44, 130.75, 130.42, 126.22, 126.06, 126.02, 125.50, 122.80, 118.80, 86.03, 75.42, 72.73, 70.42, 67.83, 61.69, 20.82, 20.67, 20.64, 20.31.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(trifluoromethoxy)phenyl)-1H-1,2,3triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (B9): Isolated as white solid (52.55 mg, 94%). ¹H NMR (700 MHz, CDCl₃) δ 8.01 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.93 (d, *J* = 9.3 Hz, 1H), 5.50 (t, *J* = 9.4 Hz, 1H), 5.45 (t, *J* = 9.4 Hz, 1H), 5.27 (t, *J* = 9.7 Hz, 1H), 4.33 (dd, *J* = 12.7, 4.9 Hz, 1H), 4.16 (d, *J* = 12.5 Hz, 1H), 4.04 (dd, *J* = 9.5, 4.0 Hz, 1H), 2.08 (d, *J* = 5.6 Hz, 6H), 2.04 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.68, 170.08, 169.56, 169.22, 149.36, 147.37, 128.74, 127.46, 121.55, 118.10, 85.97, 75.33, 72.71, 70.31, 67.77, 61.66, 20.85, 20.70, 20.67, 20.33. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₂₅F₃N₃O₁₀ 560.1492; Found 560.1494.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(**B**₁₀): Isolated as brown solid (45 mg, 95%). ¹H NMR (700 MHz, CDCl₃) δ 8.60 (s, 1H), 8.40 (s, 1H), 8.14 (d, *J* = 7.3 Hz, 1H), 7.77 (d, *J* = 6.8 Hz, 1H), 7.25 (s, 1H), 5.92 (d, *J* = 8.9 Hz, 1H), 5.47 (dt, *J* = 31.7, 8.3 Hz, 2H), 5.33 – 5.23 (m, 2H), 4.31 (dd, *J* = 12.5, 4.7 Hz, 1H), 4.16 (d, *J* = 12.5 Hz, 1H), 4.02 (d, *J* = 5.3 Hz, 1H), 2.08 (d, *J* = 12.7 Hz, 6H), 2.04 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.61, 170.06, 169.41, 168.93, 149.63, 149.05, 136.97, 123.27, 120.68, 120.47, 85.93, 75.18, 72.75, 70.56, 67.72, 61.58, 20.74, 20.61, 20.60, 20.26.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(thiophen-2-yl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(**B**₁₁): Isolated as off white solid (45 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.41 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.32 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.91 (d, *J* = 9.1 Hz, 1H), 5.46 (dt, *J* = 25.3, 9.5 Hz, 2H), 5.26 (t, *J* = 9.6 Hz, 1H), 4.33 (dd, *J* = 12.6, 5.1 Hz, 1H), 4.16 (dd, *J* = 12.6, 1.9 Hz, 1H), 4.02 (ddd, *J* = 10.0, 5.0, 2.0 Hz, 1H), 2.08 (d, *J* = 6.0 Hz, 6H), 2.03 (s, 3H), 1.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.65, 170.06, 169.51, 169.15, 143.77, 132.22, 127.82, 125.71, 124.96, 117.25, 85.98, 75.35, 72.83, 70.34, 67.83, 61.70, 20.83, 20.68, 20.65, 20.33.



(2S,3S,4S,5R,6R)-2-(methoxycarbonyl)-6-(4-phenyl-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(C₁): Isolated as white solid (44 mg, 95%).¹H NMR (400 MHz, DMSO) δ 9.05 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 9.1 Hz, 1H), 5.77 (t, *J* = 9.3 Hz, 1H), 5.68 (t, *J* = 9.4 Hz, 1H), 5.24 (t, *J* = 9.8 Hz, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.81 (s, 3H). ¹³C NMR (101 MHz,) δ 169.52, 169.34, 168.53, 166.58, 147.02, 129.96, 129.04, 128.36, 125.22, 120.57, 83.84, 72.88, 71.42, 69.93, 68.47, 52.68, 23.05, 20.26, 20.22, 19.89.



(2S,3S,4S,5R,6R)-2-(methoxycarbonyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(C₂): Isolated as off white solid (46.5 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.11 – 4.99 (m, 2H), 4.68 (dd, *J* = 11.3, 3.5 Hz, 1H), 4.58 – 4.48 (m, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 4.31 – 4.23 (m, 2H), 4.12 (d, *J* = 12.4 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.69 (dd, *J* = 9.9, 2.4 Hz, 1H), 2.37 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.71 (s, 3H).¹³C NMR (101 MHz, DMSO) δ 169.50, 169.31, 168.50, 166.57, 147.06, 137.71, 129.55, 127.19, 125.15, 120.09, 83.80, 72.85, 71.44, 69.90, 68.46, 52.65, 20.83, 20.25, 20.21, 19.89. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₂H₂₆N₃O₉ 476.1669; Found 476.1689.



(2R,3R,4S,5S,6S)-2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)-6-

(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(C₃): Isolated as white solid (47.4 mg, 97%). NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 2H), 5.95 (d, *J* = 8.9 Hz, 1H), 5.50 (dd, *J* = 11.8, 8.9 Hz, 2H), 5.38 (s,1H), 4.32 (d, *J* = 9.8 Hz, 1H), 3.74 (s, 3H), 2.66 (d, *J* = 7.6 Hz, 2H), 2.05 (d, *J* = 9.4 Hz, 6H), 1.86 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.91, 169.49, 169.06, 166.36, 148.85, 145.05, 128.53, 127.38, 126.06, 117.61, 85.64, 75.10, 72.16, 70.05, 69.18, 53.31, 28.84, 20.66, 20.60, 20.29, 15.64. HRMS(ESI-TOF)m/z: [M+H]⁺ calcd for C₂₃H₂₈N₃O₉490.1826; Found 490.1811



(2R,3R,4S,5S,6S)-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-6-

(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(C₄): Isolated as of white solid (45 mg, 94%).¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.84 – 7.76 (m, 2H), 7.12 (dd, J = 12.0, 5.4 Hz, 2H), 6.01 – 5.93 (m, 1H), 5.56 – 5.46 (m, 2H), 5.39 (t, J = 9.5 Hz, 1H), 4.35 (d, J = 9.8 Hz, 1H), 3.75 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.89 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 169.87, 169.48, 169.10, 166.34, 161.83, 147.87, 127.85, 126.19, 117.81, 116.15,

115.94, 85.67, 75.07, 72.06, 70.11, 69.15, 53.32, 20.65, 20.58, 20.30. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{23}N_3O_9$ 480.1418; Found 480.1389.



(2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-

yl)tetrahydro-2H-pyran-3,4-diyl diacetate(D₁): Isolated as white solid (48.8 mg, 98%). ¹H NMR (400 MHz, DMSO) δ 8.79 (s, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.13 (d, *J* = 9.9 Hz, 1H), 5.39 (t, *J* = 9.9 Hz, 1H), 5.11 (t, *J* = 9.8 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 1H), 4.28 (ddd, *J* = 10.1, 5.0, 2.2 Hz, 1H), 4.17 (dd, *J* = 12.5, 5.1 Hz, 1H), 4.08 (dd, *J* = 12.4, 2.0 Hz, 1H), 2.33 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.59 (s, 3H).¹³C NMR (101 MHz,DMSO) δ 169.50, 169.31, 168.50, 166.57, 147.06, 137.71, 129.55, 127.19, 125.15, 120.09, 83.80, 72.85, 71.44, 69.90, 68.46, 52.65, 20.83, 20.25, 20.21, 19.89. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₂₉N₄O₈ 489.1985; Found 489.1937.



(2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1yl)tetrahydro-2H-pyran-3,4-diyl diacetate(D₂): Isolated as white solid (47.3 mg, 93%). ¹H NMR (400 MHz, DMSO) δ 9.01 (s, 1H), 8.15 (d, *J* = 9.1 Hz, 1H), 7.90 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 6.16 (d, *J* = 9.9 Hz, 1H), 5.38 (d, *J* = 9.9 Hz, 1H), 5.10 (t, *J* = 9.8 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 4.32 (d, *J* = 7.3 Hz, 1H), 4.19 (dd, *J* = 12.6, 5.0 Hz, 1H), 4.09 (d, *J* = 10.7 Hz, 1H), 2.03 (s, *J* = 7.1 Hz, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.60 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 170.03, 169.58, 169.50, 169.37, 145.49, 131.99, 129.48, 127.17, 121.18, 120.65, 84.95, 73.38, 72.25, 68.02, 61.74, 52.35, 22.31, 20.52, 20.42, 20.28. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₂H₂₆ClN₄O₈ 509.1439; Found 509.1446.



(2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(3-bromophenyl)-1H-1,2,3-triazol-1yl)tetrahydro-2H-pyran-3,4-diyl diacetate(D₃): Isolated as white solid (51.4 mg, 92%).¹H NMR (400 MHz, DMSO) δ 8.92 (s, 1H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.69 – 7.66 (m, 2H), 6.15 (d, *J* = 9.9 Hz, 1H), 5.39 (t, *J* = 9.9 Hz, 1H), 5.11 (t, *J* = 9.8 Hz, 1H), 4.64 (q, *J* = 9.8 Hz, 1H), 4.29 (ddd, *J* = 10.1, 5.0, 2.2 Hz, 1H), 4.18 (dd, *J* = 12.5, 5.0 Hz, 1H), 4.09 (dd, *J* = 12.5, 2.1 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.59 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 170.03, 169.58, 169.50, 169.37, 145.49, 131.99, 129.48, 127.17, 121.18, 120.65, 84.95, 73.38, 72.25, 68.02, 61.74, 52.35, 22.31, 20.52, 20.42, 20.28. OAc

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-phenyl-1H-1,2,3-triazol-1-

yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate(**E**₁): Isolated as white solid (50.9 mg, 98%).¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.86 (s, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.12 – 4.97 (m, 2H), 4.70 (d, *J* = 14.7 Hz, 1H), 4.54 (dd, *J* = 12.1, 9.2 Hz, 1H), 4.46 (d, *J* = 7.9 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.12 (d, *J* = 11.0

Hz, 1H), 3.91 (t, *J* = 8.6 Hz, 1H), 3.75 – 3.64 (m, 1H), 2.07 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.71 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.76, 170.22, 169.65, 169.57, 130.54, 128.96, 128.30, 125.78, 121.67, 100.62, 72.49, 72.04, 70.96, 68.25, 68.00, 61.76, 50.19, 20.86, 20.71, 20.68, 20.49.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(p-tolyl)-1H-1,2,3-triazol-1-

yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate(**E**₂) : Isolated as off white solid (50.6 mg, 95%).¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.11 – 4.99 (m, 2H), 4.68 (dd, *J* = 11.3, 3.5 Hz, 1H), 4.58 – 4.48 (m, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 4.31 – 4.23 (m, 2H), 4.12 (d, *J* = 12.4 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.69 (dd, *J* = 9.9, 2.4 Hz, 1H), 2.37 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.71 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.76, 170.23, 169.65, 169.58, 130.59, 128.96, 128.28, 125.77, 121.60, 100.63, 72.50, 72.04, 70.97, 68.25, 68.01, 61.76, 50.17, 20.86, 20.71, 20.68, 20.49.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate(E₃) : Isolated as white solid (52.5 mg, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.15 (t, *J* = 9.5 Hz, 1H), 5.08 – 4.98 (m, 2H), 4.71 – 4.60 (m, 1H), 4.55 – 4.48 (m, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 4.29 – 4.20 (m, 2H), 4.11 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.90 (td, *J* = 9.7, 2.7 Hz, 1H), 3.68 (ddd, *J* = 9.8, 4.6, 2.3 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.05 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.71 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.68, 170.14, 169.58, 169.51, 147.82, 144.43, 128.39, 128.01, 125.75, 121.16, 100.62, 72.54, 72.03, 70.99, 68.31, 68.00, 61.78, 50.11, 28.73, 20.78, 20.64, 20.62, 20.46, 15.56.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-

yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (E₄)): Isolated as white solid (51.5 mg, 93%).¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.11 – 4.96 (m, 2H), 4.68 (d, *J* = 14.5 Hz, 1H), 4.59 – 4.48 (m, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.25 (dd, *J* = 12.1, 4.6 Hz, 2H), 4.12 (d, *J* = 11.2 Hz, 1H), 3.90 (t, *J* = 8.4 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.58, 170.07, 169.49, 169.43, 146.60, 131.99, 129.52, 127.22, 122.02, 121.64, 100.50, 72.37, 71.99, 70.94, 68.21, 67.76, 61.69, 50.13, 20.71, 20.56, 20.54, 20.43. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₄H₂₉ClN₃O₁₀ 554.1389; Found 554.1542.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate(E5): Isolated as white solid (54.4 mg, 91%).¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.11 - 4.96 (m, 2H), 4.68 (d, *J* = 14.5 Hz, 1H), 4.59 - 4.48 (m,

1H), 4.46 (d, J = 7.8 Hz, 1H), 4.25 (dd, J = 12.1, 4.6 Hz, 2H), 4.12 (d, J = 11.2 Hz, 1H), 3.90 (t, J = 8.4 Hz, 1H), 3.69 (d, J = 7.6 Hz, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.58, 170.07, 169.49, 169.43, 146.60, 131.99, 129.52, 127.22, 122.02, 121.64, 100.50, 72.37, 71.99, 70.94, 68.21, 67.76, 61.69, 50.13, 20.71, 20.56, 20.54, 20.43. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₄H₂₈BrN₃O₁₀ 598.1036; Found 598.1036.



(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(trifluoromethyl)phenyl)-1H-1,2,3triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate(E₆): Isolated as white solid (52.8 mg, 90%).¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.1 Hz, 2H), 7.95 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 5.17 (t, J = 9.5 Hz, 1H), 5.10 – 4.98 (m, 2H), 4.75 – 4.64 (m, 1H), 4.60 – 4.51 (m, 1H), 4.47 (d, J = 7.9 Hz, 1H), 4.31 – 4.22 (m, 2H), 4.13 (dd, J = 12.3, 2.0 Hz, 1H), 3.92 (td, J = 10.0, 2.5 Hz, 1H), 3.70 (ddd, J = 9.7, 4.4, 2.1 Hz, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.69, 170.18, 169.59, 169.55, 146.38, 134.14, 130.25, 129.92, 125.97, 125.76, 122.51, 100.62, 72.47, 72.14, 71.09, 68.34, 67.79, 61.82, 50.33, 20.81, 20.67, 20.65, 20.54. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₅H₂₉F₃N₃O₁₀ 588.1805; Found 588.2238.

NMR spectra of the products:



Figure S7. ¹H NMR of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-azidotetrahydro-2H-pyran-3,4,5-triyl triacetate in CDCl₃ at r.t.



Figure S8. ¹³C NMR of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-azidotetrahydro-2H-pyran-3,4,5-triyl triacetate in CDCl₃ at r.t.





Figure S9. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-phenyl-1H-1,2,3-triazol-1-yl) tetrahydro-2H-pyran-3,4,5-triyl triacetate (**A**) CDCl₃ at r.t.



Figure S10. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-phenyl-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**A**) in CDCl₃ at r.t.





Figure S11. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₁) CDCl₃ at r.t.



Figure S12. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₁) in CDCl₃ at



Figure S13. ¹H NMR (400 MHz) spectrum (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₂) CDCl₃ at r.t.



Figure S14. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₂) CDCl₃ at r.t.



Figure S15. ¹H NMR (400 MHz) spectrum of(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(dimethylamino)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₃) CDCl₃ at r.t.



Figure S16. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(4-(dimethylamino)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate(**B**₃) CDCl₃ at r.t.



Figure S17. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₄) CDCl₃ at r.t.



Figure S18. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₄) in CDCl₃ at r.t.



Figure S19. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**5) CDCl₃ at r.t.



Figure S20. ¹³C NMR (400 MHz) spectrum of(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**5) CDCl₃ at r.t.



Figure S21. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₆) CDCl₃ at r.t.



Figure S22. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₆) in CDCl₃ at r.t.



Figure S23. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-nitrophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**7) CDCl₃ at r.t.



Figure S24. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-nitrophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**7) in CDCl₃ at r.t.





Figure S25. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₈) CDCl₃ at r.t.



Figure S26. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₈) CDCl₃ at r.t.

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Figure S27. ¹H NMR (400 MHz) spectrum of(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(trifluoromethoxy)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**9) CDCl₃ at r.t.



Figure S28. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(4-(trifluoromethoxy)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**9) in CDCl₃ at r.t.



Figure S29. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₁₀) CDCl₃ at r.t.



Figure S30. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₁₀) in CDCl₃ at r.t.



Figure S31. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(thiophen-2-yl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₁₁) CDCl₃ at r.t.



Figure S32. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(thiophen-2-yl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**B**₁₁) CDCl₃ at r.t.



Figure S33. ¹H NMR (400 MHz) spectrum of (2S,3S,4S,5R,6R)-2-(methoxycarbonyl)-6-(4-phenyl-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C₁) DMSO at r.t.



Figure S34. ¹³C NMR (101 MHz) spectrum of (2S,3S,4S,5R,6R)-2-(methoxycarbonyl)-6-(4-phenyl-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C1) in DMSO at r.t.



Figure S35. ¹H NMR (400 MHz) spectrum of (2S,3S,4S,5R,6R)-2-(methoxycarbonyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**C**₂) DMSO at r.t.



Figure S36. ¹³C NMR (101 MHz) spectrum of (2S,3S,4S,5R,6R)-2-(methoxycarbonyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C₂) in DMSO at r.t.



Figure S37. ¹H NMR (400 MHz) spectrum of(2R,3R,4S,5S,6S)-2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C3) CDCl₃ at r.t.



Figure S38. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5S,6S)-2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C3) CDCl₃ at r.t.



Figure S39. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5S,6S)-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C4) CDCl₃ at r.t.



Figure S40. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5S,6S)-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-6-(methoxycarbonyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (C4) CDCl₃ at r.t.



Figure S41. ¹H NMR (400 MHz) spectrum of (2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (**D**₁) DMSO at r.t.



Figure S42. ¹³C NMR (101 MHz) spectrum of (2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (**D**₁) in DMSO at r.t.





Figure S43. ¹H NMR (400 MHz) spectrum of (2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (**D**₂) DMSO at r.t.



Figure S44. ¹³C NMR (101 MHz) spectrum of(2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (**D**₂) in DMSO at r.t.



Figure S45. ¹H NMR (400 MHz) spectrum of (2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(3-bromophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (**D**₃) in DMSO at r.t.



Figure S46. ¹³C NMR (400 MHz) spectrum of (2R,3S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(3-bromophenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (**D**₃) DMSO at r.t.



Figure S47. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₁) CDCl₃ at r.t.



Figure S48. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₁) in CDCl₃ at r.t.



Figure S49. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₂) CDCl₃ at r.t.



Figure S50. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₂) in CDCl₃ at r.t.



Figure S51. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (E3) CDCl₃ at r.t.



Figure S52. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(4-ethylphenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (E3) in CDCl₃ at r.t.



Figure S53. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₄) CDCl₃ at r.t.



Figure S54. ¹³C NMR (101 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (E4) in CDCl₃ at r.t.



Figure S55. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E***s*) CDCl₃ at r.t.



Figure S56. ¹³C NMR (101 MHz) spectrum (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(3-chlorophenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (E5) CDCl₃ at r.t.



Figure S57. ¹H NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₆) CDCl₃ at r.t.



Figure S58. ¹³C NMR (400 MHz) spectrum of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)ethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**E**₆) CDCl₃ at r.t.

Molecular structure determination by single crystal X-ray crystallography

A crystal of complex **1** with accession code CCDC 2240116 was mounted under crystal oil coated at ambient conditions. All measurements were made on an *Oxford Diffraction SuperNova* area-detector diffractometer using an INCOATEC micro source (Mo-K α radiation, $\lambda = 0.71073$ Å, multilayer optics) and Al filtered.

Data reduction was performed using the *CrysAlisPro*^[S4] program. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in *CrysAlisPro*^[S4] was applied. Data collection and refinement parameters are given in Table S1.

OleX^{S5} and refinement was carried out using least-square minimization implemented in ShelXL.^{S6, S7} All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were fixed geometrically in idealized positions and were refined using a riding model.

Complex	1
Empirical formula	$C_{16}H_{15}CuIN_3O$
Formula weight (g mol ⁻¹)	455.75
Temperature	100.00(10)
Radiation	MoKα ($\lambda = 0.71073$)
Crystal system	Monoclinic
Space group	$P2_{1}/c$
<i>a</i> (Å)	12.2982(5)
b (Å)	8.7867(3)
<i>c</i> (Å)	15.5899(6)
α (deg)	90
β (deg)	109.228(4)
γ (deg)	90
volume (Å ³)	1590.68(11)
Ζ	4
D_{calc} (g cm ⁻³)	1.381
$\mu (\text{mm}^{-1})$	1.903
<i>F</i> (000)	888.0
Crystal Size (mm ³)	0.2 imes 0.1 imes 0.1
2θ Range (deg)	6.92 to 60.878
Index Ranges	$-15 \le h \le 16, -11 \le k \le 11, -21 \le l \le 19$
Reflections collected	15069
Independent reflections	3809 [$R_{\text{int}} = 0.0476, R_{\text{sigma}} = 0.0397$]
Completeness to theta	99.96
Refinement method	Full-matrix least-squares on F ²
Data/Restraints/parameters	3809/0/200
Goodness-of-fit on F2	1.038
Final <i>R</i> indices $[I>2\sigma(I)]$	$R_1 = 0.0271, wR_2 = 0.0623$
<i>R</i> indices (all data)	$R_1 = 0.0322, wR_2 = 0.0644$
Largest diff. peak/hole (e Å ⁻³)	0.69/-0.69

 Table S1. Crystallographic Data and Refinement Parameters for 1.

	Bond lengths
Complexes/Bonds	1
Cu-N(pyridine)	2.091(2)
Cu–N(pyrazole)	2.118(2)
Cu–I	2.6250(4)
Cu ¹ –I	2.6271(3)
Cu–Cu ^a	2.6101(6)

Table S2. Selected bond lengths (Å) around the metal centre in copper complexes 1 and 2.

Symmetry code: ^a1-X,1-Y,1-Z

 Table S3. Selected bond angles (°) around the metal centre in copper complexes 1 and 2.

Boi	nd angles
Cu1–I1–Cu1 ^a	59.599(11)
I1–Cu1–I1 ^a	120.401(11)
Cu1 ^a –Cu1–I1	60.240(12)
Cu1 ^a –Cu1–I1 ^a	60.161(12)
N3–Cu1–I1 ^a	104.02(6)
N3–Cu1–I1	119.32(6)
N3–Cu1–Cu1 ^a	137.42(6)
N1-Cu1-I1	103.51(6)
N1–Cu1–I1 ^a	112.20(6)
N1–Cu1–Cu1 ^a	127.96(6)
N1–Cu1–N3	94.44(8)

Symmetry code: ^a 1-X,1-Y,1-Z



Figure S59. Molecular structure of complex 1.

Supp+J5+B1:S29+B1:S3	2+B1:S31	+B1:S30+B1:	:S29+B+B1:	Summary of	of Zero Pas	s Metrics Tooll	kit										
Yield, conversion, sele	ectivity, A	AE, RME									_						
Reactant (Limiting Reactant First)	Mass (g)	MW	Mol	Catalyst	Mass (g)	Reagent	Mass (g)	Reaction solvent	Volume (cm ³)	Density (g ml ⁻¹)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml ⁻¹)	Mass (g)
Glycosides	4.11	411.20	0.01	[Cu]	0.14			TBAB/glycerol	40.00	1.18	47.27		25	% ammonia solut	20.00	0.90	18.00
Phenylacetylene	1.02	102.13	0.01														
Sodium azide	1.63	65.01	0.02														
Total	6.76	578.34			0.14		0.00				47.27		0.00				18.00
								Flag									
molecular	weight	of product	× 10	0		Yield	98.0	98.0									
total molecua	lr weigh	nt of reacta	nts ^ 10	0		Conversion	100.0	100.0									
						Selectivity	98.0	98.0)				mass	mw	mol		
$RME = \frac{mass of iso}{mass of iso}$	lated pr	$\frac{oduct}{\times 10}$	0			AE	82.2					Product	4.659	475.454	0.0097991		
total mass	of react	tants 🗍				RME	69.0						mass				
												Unreacted limiting					
Solvents (Zero Pass)												reactant	0.000				
Highly hazardous solve	ents (Rec	d flag for any	y of the fol	lowing)			Li	st Highly Hazardo	us Solvents	Below							
Et ₂ O, Ber	izene, CC	l ₄ , chlorofor	rm, DCE, ni	tromethane	e, CS ₂ , HMI	PA		Noi	ne								
Health and Safety (Zer	ro Pass)																
Health & safety (Red f	lag for an	ny of the foll	lowing)			Li	st substar	ices plus the red f	lagged H-co	des below							
Highly ex	plosive		H200,	H201, H202,	H203			None									
Explosive ther	mal runav	way		H240				None									
Fatally	toxic		H30	00, H310, H3	30			None									
Mutag	enic			H350				None									
Repro-	toxic			H360				None									
Serious environme	ntal impl	ications		H420				None									

Table S4. Optimised Reaction (Method A: DES TBAB/glycerol, [Cu] 3 mol%, 70 °C, 12 h): Zero Pass CHEM21 green metrics toolkit

Supplementary Information: Appendix 2 Summ					of First Pas	s Metrics Too	lkit											
Yield, AE, RME, MI/PM	I and OE																	
Reactant (Limiting Reactant First)	Mass (g)	MW	Mol	Catalyst	Mass (g)	Reagent	Mass	(g)	Reaction solvent	Volume (cm ³)	Density (g ml ⁻¹)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml⁻¹)	Mass (g)
Glycosides	4.11	411.20	0.01	[Cu]	0.14				TBAB/glycerol	40.00	1.18	47.27		25 %	6 ammonia solu	20.00	0.90	18.00
Phenylacetylene	1.02	102.13	0.01															
Sodium azide	1.63	65.01	0.02															
Total	6.76	578.34			0.14		0.00					47.27		0.00				18.00
										Flag								
							Yield		98.0	98.0								
							Conversion	n	100.0	100.0					Mass	B.414/	Mal	
PMF - mass of isola	ted product	100							96.U 97 7	98.0			Prod	uct	1 650	175 A5A	0.01	
total mass of	reactants						RME		69.0	OF	83.0	1	FIGU		mass	473.434	0.01	-
									05.0		00.5		Unreacted	limiting	mass			
AE = molecular	weight of pr	oduct ×	100				PMI total		15.5				react	ant	0.00			
total molecua	lr weight of 1	reactants	1				PMI Reacti	ion	11.6									
							reagents,											
mass intensity = $\frac{t}{-}$	otai mass in	a process or	process si	ep			catlyst		1.5									
	ma	iss of proau	ic i				PMI reaction	on										
RME VION							solvents		10.1									
AE X 100																		
							PMI Worku	up	3.9									
							PMI Worku	ир	0.0									
							PMI worku	ID	0.0									
							solvents	γÞ	3.9									
Solvents (First Pass)							List s	olven	ts below									
Preferred solv	ents	water, EtC tBuOH, B)H, nBuOH, nOH, ethyl A d	AcOipr, Aco ene glycol, COEt, sulfola	OnBu, PhO acetone, N ane	Me, MeOH, /IEK, MIBK,	TBAB	: Glyce	erol (1: 4)									
Problematic solvents: only if substitution do advantages	(acceptable es not offer)	DMSO, cyclo AcOMe, THF MTBE, o	ohexanone F, heptane, cyclohexan py	e, DMPU, Ac Me-cyclohe e, chlorobe ridine, Me-	OH, Ac2O, exane, tolu nzene, for THF	Acetonitrile, Iene, xylene, mic acid,		non	e									
Hazardous solvents: Th have significant hea safety concer	ese solvents Ith and/or ns.	dioxane, p DMF	pentane, Tl , DMA, NM	EA, diisopro P, methoxy	pyl ether, ethanol, h	DME, DCM, exane		non	e									
Highly hazardous sol solvents which are ag be used, even in so	vents: The reed not to creening	Et ₂ O, Benze	ne, CCl ₄ , cl	nloroform, I HMPA	DCE, nitron	nethane, CS ₂ ,		non	e									
C-+	 			72.4							T i -1-	-						
Catalyst/enzyme (First	rass) used. or react	ion takes	Green	ПСК							ПСК							
place without any	catalyst/rea	gents.	Flag	x		Facile re	covery of ca	atalys	/enzyme	Green Flag								
Use of stoichiometric	quantities o	f reagents	Amber Flag			catalys	t/enzyme r	not red	overed	Amber Flag	х							
Use of reag	ents in exces	S	Red Flag															

Table S5. Optimised Reaction (Method A: DES TBAB/glycerol, [Cu] 3 mol%, 70 °C, 12 h): First Pass CHEM21 green metrics toolkit

Critical elements						1	1	1	1						
Supply remaining	Flag colour	Note element	1		Remaining years until depletion of known reserves				He						
5-50 years	Red Flag		3	4 B	(based on current rate of extraction)		° .	6 7 8 9	10 E No						
50-500 years	Amber Flag	Cu	6.941	9,012182	5-50 years 50-100 years 100-500 wears		10.811	12.0307 14.00674 15.9994 3 54 15 16 1 54 P 5	r Ne 8.99840 20.1797 7 18 Cl Δr						
+500 years	Green Flag		22.58	20. 21 Ca Sc	22 23 24 25 Ti V Cr Mn	26 27 28 2 Fe Co Ni	26 98153 9 39 31 Cu Zn Ga	28.0855 39.87376 32.066 3 32 33 34 3 Ge As Se	5.4527 39.948 5 36 Br Kr						
			39.05	83 40.078 44.9559 38 39	47.867 50.9415 51.9961 54.93804 40 41 42 43	55.845 58.93320 58.6934 6 64 45 46 4	1.546 65.39 69.723 7 48 49	72.61 74.92160 78.96 7 50 51 52 5	9.904 83.80 3 54						
			85.40	b Sr Y 78 87.62 88.9085	Zr Nb Mo Tc 91.224 92.90638 95.94 (58)	Ru Rh Pd 105.07 102.5035 106.42 1	Ag Cd In 27.8082 112.411 114.815	Sn Sb Te 118.700 121.700 127.60 1	L Xe 26.5044 131.29						
			55 C 132.5	56 57 5 Ba La* 054 137.327 138.9053	12 73 14 75 Hf Ta W Re 128.49 180.9479 181.84 186.207	75 77 78 7 Os Ir Pt 190.23 192.217 195.078 1	Au Hg Ti 80.965 200.99 201.3833	B2 B3 B4 B Pb Bi Po Bi Po 270.2 208.9804 (209) (200) (200)	At Rn (2222)						
			(223)	r Ra Ac‡	104 105 106 107 Rf Db Sg Bh (257) (260) (263) (262)	108 109 130 1 Hs Mt Ds 1 (265) (266) (271) (265)	11 112 113 Rq Uub Uut (72) (285) (284)	114 115 116 1 Uuq Uup Lv (289) (288) (292)	Uus Uuo					 	
					58 59 60 61	62 63 64	65 66	67 68 69 70	71						
				Lanthan	ides* Ce Pr Nd F 140.9077 544.24 (145) 150 90 91 93	Ym Sm Eu C 136 151.964 157.25 158 M 95 95	9253 158.9253 162.50	HO Er IM 164.9303 167.26 168.9342 13 29 103 101 10	YD Lu 13.04 174.967 12 101						
				Actini	des‡ Th Pa U I	Np Pu Am C	m Bk Cf	Es Fm Md	No Lr						
					Tornar Strong Manual St	teal teal (54	2 1 (set) 1 (seg)	front front front fr							
Energy (First Pass)			Tick					Tick							
Reaction run betwee	n 0 to 70°C	Green Flag	х		Reaction run a	at reflux	Red Flag								
Reaction run between	n -20 to 0 or	Amber Flag													
70 to 140°C	20 or above	, in the second			Reaction run 5°C or n	nore below the	Green Flag	x						 	
140°C	20 of above	Red Flag			solvent bollin	ng point									
						[
Batch/flow			Tick		Work Up			List							
Flow	Gree	n Flag			quenchi	ng									
Batch	Ambe	r Flag	X	_	filtratio	on .									
					centrifuga	ition	Green Flag	Filtration							
					Low tempe	rature									
					distillation/evaporati	on/ sublimation									
					solvent exchange, o	uenching into	Amber Flag								
					chromatography/i	on exchange									
					high tempe	rature	Red Flag							 	
					multiple recrys	tallisation									
													-	 	
Health & safety						List substances	and H-codes	List substances a	nd H-codes	List sub	ostances and H	l-codes			
	Red	Flag	Am	per Flag	Green Flag										
Highly explosive	H200, H201,	H202, H203	H205, I	1220, H224	If no red or amber					Acetobro H319, H	mo-α-D-gluco 335, Phenylac	ose: H315, etylene:			
					Hagged H codes										
Explosive thermal	H230, H2	40, H250	1	1241	present then green	Phenylacetyl	ene: H350;	Sodium azide	e: H373;	H226, H	315, H319, H33	35. H350.			
Explosive thermal runaway Toxic	H230, H2	40, H250	H301 H	1241 1311, H331	present then green flag	Phenylacetyl Sodium azide: H330, H410	ene: H350; H300, H310, Ammonia	Sodium azide Ammonia solut	e: H373; ion: H301,	H226, H Sodium a H373, H	315, H319, H33 zide: H300, H3 410: TBAB: H3	35. H350. 310, H330, 02. H315			
Explosive thermal runaway Toxic Long Term toxicity	H230, H2 H300, H3 H340, H350,	240, H250 310, H330 H360, H370,	H301, H H341, H	1241 1311, H331, 1351, H361,	flagged H codes present then green flag	Phenylacetyl Sodium azide: H330, H410. solution	ene: H350; H300, H310, Ammonia : H370.	Sodium azide Ammonia solut H311, H3	e: H373; ion: H301, 31.	H226, H Sodium a H373, H4 H319, I	315, H319, H33 izide: H300, H3 410; TBAB: H3 H335. Glycero	35. H350. 310, H330, 02, H315, I: H319.			
Explosive thermal runaway Toxic Long Term toxicity Environmental	H230, H2 H300, H3 H340, H350, H3 H400, H <u>410</u>	440, H250 110, H330 H360, H370, 372 , H411, H4 <u>20</u>	H301, F H341, F H341, F H37 H40	H241 H311, H331, H351, H361, 1, H373 1, H412	flagged H codes present then green flag	Phenylacetyl Sodium azide: H330, H410. solution	ene: H350; H300, H310, Ammonia : H370.	Sodium azida Ammonia solut H311, H3	e: H373; ion: H301, 31.	H226, H Sodium a H373, H4 H319, I Ammoni	315, H319, H33 izide: H300, H3 410; TBAB: H3 H335. Glycero a solution: H2 H314	35. H350. 310, H330, 02, H315, I: H319. 121, H225,			
Explosive thermal runaway Toxic Long Term toxicity Environmental implications	H230, H2 H300, H3 H340, H350, H3 H400, H410	440, H250 110, H330 H360, H370, 372 , H411, H420	H <u>301,</u> F H341, F H37 H40	1241 1311, H331, 1351, H361, 1, H373 1, H412	flagged H codes present then green flag	Phenylacetyl Sodium azide: H330, H410. solution	ene: H350; H300, H310, Ammonia : H370.	Sodium azide Ammonia solut H311, H3	e: H373; ion: H301, 31.	H226, H Sodium a H373, H4 H319, I Ammoni	315, H319, H33 Izide: H300, H3 410; TBAB: H3 H335. Glycero Ia solution: H2 H314	35. H350. 310, H330, 02, H315, I: H319. 21, H225,			
Explosive thermal runaway Toxic Long Term toxicity Environmental implications	H230, H2 H300, H3 H340, H350, H340, H410	440, H250 110, H330 H360, H370, 372 H411, H420	H301, F H341, F H37 H40	1241 1311, H331, 1351, H361, 13, H373 1, H412	fragged H codes present then green flag	Phenylacetyl Sodium azide: H330, H410. solution	ene: H350; H300, H310, Ammonia : H370.	Sodium azide Ammonia solut H311, H3	e: H373; ion: H301, 31.	H226, H Sodium a H373, H H319, I Ammoni	315, H319, H33 Izide: H300, H3 Itali; TBAB: H3 H335. Glycero Ia solution: H2 H314	35. H350. 310, H330, 02, H315, I: H319. 121, H225,			
Explosive thermal runaway Toxic Long Term toxicity Environmental implications Use of chemical Chemical identified a	H230, H2 H300, H3 H340, H350, H400, H410 Is of environn	40, H250 10, H330 H360, H370, 372 , H411, H420 mental conce	H301, F H341, F H341, F H37 H40	1241 1311, H331, 1351, H361, 1, H373 1, H412	flagged H codes present then green flag List substances of ve	Phenylacetyl Sodium azide: H330, H410. solution ry high concern	ene: H350; H300, H310, Ammonia :H370.	Sodium azide Ammonia solut H311, H3	e: H373; ion: H301, 31.	H226, H Sodium a H373, H H319, I Ammoni	315, H319, H33 Izide: H300, H3 H10; TBAB: H3 H335. Glycero Ia solution: H2 H314	85. H350. 310, H330, 02, H315, I: H319. 121, H225,			

Supp+J5+B1:S29+B1:S3	2+B1:S31	+B1:S30+B1:	S29+B+B1:	Summary of	of Zero Pas	ss Metrics Tool	kit										
Yield, conversion, sele	ectivity, A	E, RME															
Reactant (Limiting Reactant First)	Mass (g)	MW	Mol	Catalyst	Mass (g)	Reagent	Mass (g)	Reaction solvent	Volume (cm ³)	Density (g ml ⁻¹)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml ⁻¹)	Mass (g)
Glycosides	4.11	411.20	0.01	[Cu]	0.14			ChCl/glycerol	40.00	1.19	47.76		25	% ammonia solut	20.00	0.90	18.00
Phenylacetylene	1.02	102.13	0.01														
Sodium azide	1.63	65.01	0.02														
Total	6.76	578.34			0.14		0.00				47.76		0.00				18.00
								Flag									
AE = molecular	weight	of product	× 10	n		Yield	94.0	94.0)								
total molecua	lr weigh	t of reacta	nts î			Conversion	100.0	100.0)								
						Selectivity	94.0	94.0)				mass	mw	mol		
$RME = \frac{mass of iso}{mass of iso}$	lated pr	$\frac{oauct}{10} \times 10$	0			AE	82.2					Product	4.469	475.454	0.0093994		
total mass	of react	tants				RME	66.1						mass				
												Unreacted limiting	0.000				
Solvents (Zero Pass)												reactant	0.000				
Highly hazardous solve	ents (Rec	d flag for any	y of the fol	lowing)			LI	st Highly Hazardo	us Solvents	Below							
Et₂O, Ber	izene, CC	l ₄ , chlorofor	m, DCE, ni	tromethane	e, CS ₂ , HMI	PA		No	ne								
Health and Safety (Zer	ro Pass)																
Health & safety (Red f	lag for an	ly of the foll	owing)			L	ist substan	ices plus the red f	lagged H-co	des below							
Highly ex	plosive		H200,	H201, H202,	H203			None									
Explosive ther	mal runav	way		H240	20			None									
Fatally	toxic		H30	JU, H310, H3	30			None									
Mutag	enic			H350				None									
Repro-	toxic			H360				None									
Serious environme	ntal impl	ications		H420				None				1					

Table S6. Optimised Reaction (Method B: DES ChCl/glycerol, [Cu] 3 mol%, 70 °C, 12 h): Zero Pass CHEM21 green metrics toolkit

Supplementary Inform	ation: Appen	dix 2		Summary of	of First Pas	s Metrics Too	Metrics Toolkit											
Yield, AE, RME, MI/PM	I and OE																	
Reactant (Limiting Reactant First)	Mass (g)	MW	Mol	Catalyst	Mass (g)	Reagent	Mass	(g)	Reaction solvent	Volume (cm ³)	Density (g ml ⁻¹)	Mass (g)	Work up chemical	Mass (g)	Workup solvent	Volume (cm3)	Density (g ml⁻¹)	Mass (g)
Glycosides	4.11	411.20	0.01	[Cu]	0.14				ChCl/glycerol	40.00	1.19	47.76		25 %	% ammonia solu	20.00	0.90	18.00
Phenylacetylene	1.02	102.13	0.01															
Sodium azide	1.63	65.01	0.02															
Total	6.76	578.34			0.14		0.0	0				47.76		0.00				18.00
							NG 1.1			Flag								
							Yield		94.0	94.0								
							Soloctivit		100.0	94.0					Mass	N/1\A/	Mol	
RME = mass of isolat	ed product	100					AF	L Y	82.2	94.0			Prod	uct	4 469	475 454	0.01	
total mass of	reactants						RME		66.1	OE	80.5				mass	1101101		
													Unreacted	limiting				
$AE = \frac{molecular}{molecular}$	weight of pr	oduct × 1	100				PMI total		16.3				react	ant	0.00			
total molecua	ir weight of 1	reactants					PMI Reac	tion	12.2									
mass intensity = $\frac{t_0}{-}$	otal mass in	a process or	process st	ep			reagents, catlyst	,	1.5									
	110	iss of produ					PMI react	tion										
$OE = \frac{RME}{4E} \times 100$							solvents		10.7									
AL																		
							PIMI Work	kup	4.0									
							chemical	τup	0.0									
							PMI work	aun	0.0									
							solvents	ωp	4.0									
Solvents (First Pass)							list	solvent	s helow									
Preferred solve	ents	water, EtO tBuOH, B	H, nBuOH, nOH, ethyl Ac	AcOipr, AcO ene glycol, a OEt, sulfola	OnBu, PhO acetone, N ine	Me, MeOH, ⁄IEK, MIBK,	TBAI	B: Glyce	erol (1: 4)									
Problematic solvents: only if substitution do advantages	(acceptable es not offer)	DMSO, cyclo AcOMe, THF MTBE, o	ohexanone , heptane, : yclohexan py	, DMPU, Act Me-cyclohe e, chlorobe ridine, Me-	OH, Ac2O, exane, tolu nzene, for THF	Acetonitrile, Iene, xylene, mic acid,		non	e									
Hazardous solvents: Th have significant hea safety concer	ese solvents Ith and/or ns.	dioxane, p DMF	entane, TE , DMA, NM	A, diisopro P, methoxy	pyl ether, ethanol, h	DME, DCM, exane		non	e									
Highly hazardous sol solvents which are ag be used, even in so	vents: The reed not to creening	Et ₂ O, Benze	ne, CCl ₄ , cł	nloroform, E HMPA	DCE, nitron	nethane, CS_2 ,		non	e									

Table S7. Optimised Reaction (Method B: DES ChCl/glycerol, [Cu] 3 mol%, 70 °C, 12 h): First Pass CHEM21 green metrics toolkit

Critical elements				-			-		· · · · · ·					
Supply remaining	Flag colour	Note element	1 H		Remaining years until depletion of known reserves				2 He					
5-50 years	Red Flag		3 U	Be	(based on current rate of extraction)		В	6 7 8 9 C N O	¹⁰ F Ne					
50-500 years	Amber Flag	Cu	6.941 11 Na	9.012182 12 Mg	5-50 years 50-100 years 100-500 years		10.811 13 Al	12.0107 14.00674 15.9994 18.0 14 15 16 17 Si P S	99840 20.1797 18 Cl Ar					
+500 years	Green Flag		22.589 19 K	77 24.3050 20 21 Ca Sc	22 23 24 25 2 Ti V Cr Mn	6 27 28 29 Fe Co Ni	26.98153 20 80 83 Cu Zn Ga	28.0855 39.97376 32.066 35. 32 33 34 35 Ge As Se Se	4522 39.948 36 Br Kr					
			39.098	3 40.078 44.95593	47.667 50.9415 51.9961 52.53804 5 40 41 42 43 5	5.845 58.93320 58.0934 63 4 45 46 43	45 09.721	72.61 74.92160 78.96 79. 50 51 52 53	904 #3.80 54					
			85.467	8 87.62 88.9085 56 57	Zr ND IVIO IC 91.224 92.90638 95.94 [98] 1 72 73 78 75 7	KU Kn Pd 01.07 102.5055 106.42 10 6 77 78 79	Ag Ca in 112.411 114.818 80 80 81	SI SD IE 118.760 121.760 127.60 120 82 83 84 85	6.9044 131.29 86					
			Cs 132.90	Ba La*	Hf Ta W Re 170.9479 180.9479 180.947 1	Os Ir Pt	Au Hg Ti	Pb Bi Po A	At Rn (222)					
			87 Fr	Ra Ac‡	104 105 106 107 5 Rf Db Sg Bh 5	08 109 110 11 Hs Mt Ds	Rq Uub Uut	114 115 116 113 Uuq Uup Lv U	7 118 Jus Uuo					
			(223)	226.025 (227)	(257) (260) (263) (262) (2	165) (266) (271) (2	72) (285) (284)	(289) (288) (292)						
			_	Lanthan	ides * Ce Pr Nd P	m Sm Eu G	id Tb Dy	Ho Er Tm	Yb Lu				 	
			_	Actini	140.9077 144.24 (145) 150. 90 91 97 93 des‡ Th Pa II N	94 157.25 158.9 94 15 96 In Pu Am C	9253 158.9253 162.50 97 98 m Bk Cf	164.9203 167.26 168.9342 173 99 100 101 102 Fs Fm Md M	104 174.967 1 203				 	
				Actin	232.0391 231.0289 238.0280 (237	(244) (243) (247) (247) (251)	(252) (257) (258) (259	9) (262)					
Energy (First Pass)			Tick					Tick						
Reaction run betwee	n 0 to 70°C	Green Elog	Y		Reaction run a	t reflux	Rod Elan	THEN						
Desetting and between	201-0	Green Flag	~		Reaction run a	trenux	Red Flag							
70 to 140°C	1 -20 to 0 or	Amber Flag			Peaction run 5°C or m	ore below the								
Reaction run below -	20 or above	Ded Flee			solvent boilin	ig point	Green Flag	х						
140°C		Red Flag											 	
Batch/flow			Tick		Work Up			List						
Flow	Greer	n Flag			quenchi	าย		100						
Batch	Ambe	er Flag	x		filtratio	n								
					centrifuga	tion								
					crystallisa	tion	Green Flag	Filtration						
					Low temper	ature								
					distillation/evanoration	/								
					and children of the portacity	on/ sublimation								
					solvent exchange, q	uenching into	Amber Flag						 	
					solvent exchange, q aqueous so	on/ sublimation uenching into lvent	Amber Flag						 	
					solvent exchange, q aqueous so chromatography/id	on/ sublimation uenching into lvent on exchange rature	Amber Flag							
					solvent exchange, q aqueous so chromatography/id high tempe multiple recryst	on/ sublimation uenching into lvent on exchange rature allisation	Amber Flag Red Flag							
					solvent exchange, q aqueous so chromatography/id high tempe multiple recryst	on/ sublimation uenching into lvent on exchange rature allisation	Amber Flag Red Flag							
					solvent exchange, q aqueous so chromatography/id high tempe multiple recryst	In/ sublimation uenching into lvent on exchange rature allisation	Amber Flag Red Flag	List substances an		list sub	stances and b			
Health & safety					solvent exchange, q aqueous so chromatography/id high tempe multiple recryst	on/ sublimation uenching into lvent on exchange rature allisation List substances	Amber Flag Red Flag and H-codes	List substances ar	nd H-codes	List sul	ostances and F	l-codes		
Health & safety	Red	Flag	Amb	er Flag	solvent exchange, q aqueous so chromatography/id high tempe multiple recryst	on/ sublimation uenching into lvent on exchange arature allisation List substances	Amber Flag Red Flag and H-codes	List substances an	nd H-codes	List sub	Distances and H	l-codes		
Health & safety Highly explosive	Red H200, H201,	Flag H202, H203	Amb H205, H	er Flag 1220, H224	solvent exchange, q aqueous so chromatography/id high tempe multiple recryst Green Flag If no red or amber flagged H codes	on/ sublimation uenching into lvent on exchange rature allisation List substances	Amber Flag Red Flag and H-codes	List substances ar	nd H-codes	List sub Acetobro H319, H	postances and H mo-α-D-gluco 335, Phenylac	I-codes ose: H315, etylene:		
Health & safety Highly explosive Explosive thermal	Red H200, H201, H230, H2	Flag H202, H203 440, H250	Amb H205, H	er Flag 1220, H224 1241	solvent exchange, q aqueous so chromatography/i high tempe multiple recryst Green Flag If no red or amber flagged H codes present then green	on sublimation uenching into vent on exchange rature allisation List substances Phenylacetyl	Amber Flag Red Flag and H-codes	List substances ar	nd H-codes	List sul Acetobro H319, H H226, Soci-	ostances and H mo-α-D-gluco 335, Phenylac 315, H319, H33	I-codes ose: H315, etylene: 35. H350.		
Health & safety Highly explosive Explosive thermal runaway Tovic	Red H200, H201, H230, H2	Flag H202, H203 (40, H250	Amb H205, H H301, H	er Flag 1220, H224 1241	Solvent exchange, q aqueous so chromatography/id high tempe multiple recryst Green Flag If no red or amber flagged H codes present then green flag	on/ sublimation uenching into vent on exchange rature allisation List substances Phenylacetyl Sodium zide: H330 H410	Amber Flag Red Flag and H-codes ene: H350; H300, H310,	List substances ar Sodium azide Ammonia soluti	nd H-codes : H373; on: H301,	List sub Acetobro H319, H H226, H Sodium a H373 ut	mo-α-D-gluca 335, Phenylac 315, H319, H3 zide: H300, H3	-codes se: H315, etylene: 15. H350. 310, H330, H0ride:		
Health & safety Highly explosive Explosive thermal runaway Toxic Long Term toxicity	Red H200, H201, H230, H2 H300, H3 H340, H350.	Flag H202, H203 40, H250 10, H330 H360, H370.	Amb H205, H H301, H H301, H	er Flag 220, H224 241 311, H331, 351, H361,	Solvent exchange, q aqueous so chromatography/id high tempe multiple recryst	on/ sublimation uenching into lvent on exchange rature allisation List substances Phenylacetyl Sodium azide: H330, H410. solution:	Amber Flag Red Flag and H-codes ene: H350; H300, H310, Ammonia H370,	List substances ar Sodium azide Ammonia soluti H311, H33	nd H-codes : H373; on: H301, 31.	List sub Acetobro H319, H H226, H Sodium a H373, H3	ostances and H mo-α-D-glucc 335, Phenylac 315, H319, H33 zide: H300, H3 410; Choline C 9, H335. H303	I-codes ese: H315, etylene: 15. H350. 810, H330, hloride: Glycerol:		
Health & safety Highly explosive Explosive thermal runaway Toxic Long Term toxicity	Red H200, H201, H230, H2 H300, H3 H340, H350, H3	Flag H202, H203 440, H250 110, H330 H360, H370, 372	Amb H205, H H301, H H301, H H341, H H341, H	er Flag 2220, H224 221 311, H331, 351, H361, 1, H373	Solvent exchange, q aqueous so chromatography/iti high tempe multiple recryst Green Flag If no red or amber flagged H codes present then green flag	on sublimation uenching into lvent on exchange rature allisation List substances Phenylacetyl Sodium azide: H330, H410. solution:	Amber Flag Red Flag and H-codes ene: H350; H300, H310, Ammonia :H370.	List substances ar Sodium azide Ammonia soluti H311, H33	14 H-codes : H373; on: H301, 31.	List sub Acetobro H319, H H226, H Sodium a H373, H H315, H3 H319, An	ostances and H mo-α-D-gluco 335, Phenylac 315, H319, H33 zide: H300, H1 410; Choline C 19, H335. H303 nmonia soluti	I-codes se: H315, etylene: 55. H350. 810, H330, H310, H330, H310; H321,		
Health & safety Highly explosive Explosive thermal runaway Toxic Long Term toxicity Environmental implications	Red H200, H201, H230, H2 H300, H3 H340, H350, H340, H350, H340, H350,	Flag H202, H203 40, H250 10, H330 H360, H370, 572 H411, H420	Amb H205, H H301, H H301, H H311, H H37: H401	er Flag 2220, H224 241 311, H331, 351, H361, 1, H373 1, H412	Solvent exchange, q aqueous so chromatography/id high tempe multiple recryst If no red or amber flagged H codes present then green flag	on sublimation uenching into lvent on exchange rature allisation List substances Phenylacetyl Sodium azide: H330, H410. solution:	Amber Flag Red Flag and H-codes ene: H350; H300, H310, Ammonia :H370.	List substances ar Sodium azide Ammonia solutii H311, H33	: H373; on: H301, 31.	List sub Acetobro H319, H H226, H Sodium a H373, H H315, H3 H319, Ar	pro-α-D-gluca 335, Phenylac 315, H319, H33 izide: H300, H1 izide: H300, H1 410; Choline C 19, H335. H303 nmonia soluti H225, H314	I-codes se: H315, etylene: 5, H350, 5, H350, hloride: Glycerol: on: H221,		
Health & safety Highly explosive Explosive thermal runaway Toxic Long Term toxicity Environmental implications	Red H200, H201, H230, H3 H340, H350, H340, H350, H340, H310	Flag	Amb H205, H H301, H H301, H H341, H H377 H401	er Flag 1220, H224 1241 1241 111, H331, 351, H361, 1, H373 1, H412	Solvent exchange, q aqueous so chromatography/iu high tempe multiple recryst	on/ sublimation uenching into lvent an exchange rature allisation List substances Phenylacetyl Sodium azide: H330, H410. solution:	Amber Flag Red Flag and H-codes ene: H350; H300, H310, Ammonia :H370.	List substances ar Sodium azide Ammonia soluti H311, H33	: 	List sub Acetobro H319, H H226, H Sođium a H373, H H315, H31 H319, Ar	ostances and H mo-α-D-glucc 335, Phenylac 335, Phenylac 315, H319, H33 izide: H300, H3 410; Choline C 19, H335. H303 H225, H314			
Health & safety Highly explosive Explosive thermal runaway Toxic Long Term toxicity Environmental implications Use of chemica	Red H200, H201, H230, H2 H340, H350, H340, H350, H400, H410 Is of environm	Flag H202, H203 40, H250 10, H330 H360, H370, 172 H411, H420 Mental conce	Amb H205, H H301, H H341, H H341, H H347 H401	er Flag 220, H224 241 241 311, H331, 351, H361, 1, H373 1, H412	Solvent exchange, q aqueous so chromatography/ic high tempe multiple recryst Green Flag If no red or amber flagged H codes present then green flag	yn sublimation uenching into ivent an exchange rature allisation List substances Phenylacetyl Sodium azide: H330, H410. solution: y high concern	Amber Flag Red Flag and H-codes ene: H350; H300, H310, Ammonia :H370.	List substances ar Sodium azide Ammonia soluti H311, H33	: H373; on: H301, 31.	List sub Acetobro H319, H H226, H Sodium a H315, H31 H319, An	ostances and H mo-α-D-glucc 335, Phenylac 335, Phenylac 315, H319, H3 izide: H300, H3 410; Choline C 19, H335. H303 H225, H314	I-codes sse: H315, etylene: 15. H350. 110, H330, hloride: Glycerol: pn: H221,		

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