5.1. Introduction

The phrase "click chemistry" was first used in 2001 by chemist K. Barry Sharpless to characterize a group of facile, potent, highly selective and modular reactions. Reactions that are dependable and selective are at the core of click chemistry and are therefore ideal for a variety of chemical and biological applications. Sharpless, Morten Meldal, Carolyn Bertozzi, and others first presented the idea of click chemistry in the early 2000 s and received the Nobel prize of 2022 in chemistry for the same discovery. The concept of click chemistry is to choose and swiftly assemble building blocks to create complex compounds by using a limited number of dependable reactions. Many disorders are treated with heterocyclic compounds, making them an important part of medicinal chemistry [1]**.** The synthesis of azido glycoside derivatives has long been a target of researchers from several fields, due to their chemical relevance as multifunctional reactive intermediates. [2]**.** Azido glycosides were utilized as building blocks in a wide variety of biochemical processes, including the production of amino sugars, glycosylamines, neoglycoconjugates (including *N*-glycopeptides, *N*-glycoproteins, heterocyclic compounds, and more), and more [3]**.** Staudinger reduction, Curtius and Schmidt rearrangements, and 1,3-dipolar cycloaddition are few examples of the chemical processes in which azido glycosides play a significant role [4]. Several methods have been developed for carbohydrate azidation at the anomeric position. These include the Mitsunobu reaction on a free anomeric hydroxyl group, addition on oxonium intermediates to facilitate Lewis acid azidation, transformation of 1,2-anhydro sugars, and nucleophilic substitution at the C1-stereocenter for carbohydrates. [5]. Nucleophilic substitution of glycosyl halides by azide ions is a commonly used method in carbohydrates [6]. As a result of the difficulty of isolating and storing glycosyl halides, a number of one-pot techniques have been developed to circumvent the need for this technology. The most direct route to azido glycosides from glycosyl acetates is to treat the

glycosyl acetates with trimethylsilyl azide (TMSA) while a Lewis acid keeps them from reacting [7]. While TMSA typically offered decent azidation yields, it is difficult to employ on a wide scale because of its instability, susceptibility to hydrolysis, and high cost. As a result, solutions that are both affordable and effective are needed to avoid these problems [8]. The tremendous potential of azido glycoside derivatives as building blocks in CuI-catalysed Huisgen cycloaddition is also contributing to their rising popularity [9].

Because glycosylation is helpful in the production of 1,2,3-triazolyl glycosides, it is of great importance to create efficient approaches towards effective glycosylation [10,11]. In recent years, the 1,2,3-triazole ring has received a great deal of interest in the field of Medicinal Chemistry [12]. This heterocycle moiety's enhanced solubility and binding to biomolecular targets is due to its capacity to participate in hydrogen bonding and dipole interactions [13]. The triazole ring is resistant to hydrolysis, oxidation, reduction, and enzyme cleavage [14]. One such heterocyclic skeleton is the 1,2,3-triazole ring, which has been linked to a wide range of biological functions. In 2018, researchers conducted a number of biological screens that ultimately led to the discovery of 1,2,3-triazole-containing hybrids with anticancer, antimicrobial, and antioxidant capabilities [15].

Considering the biological and synthetic importance, different approaches have been developed for the preparation of 1,2,3-triazole glycosides.

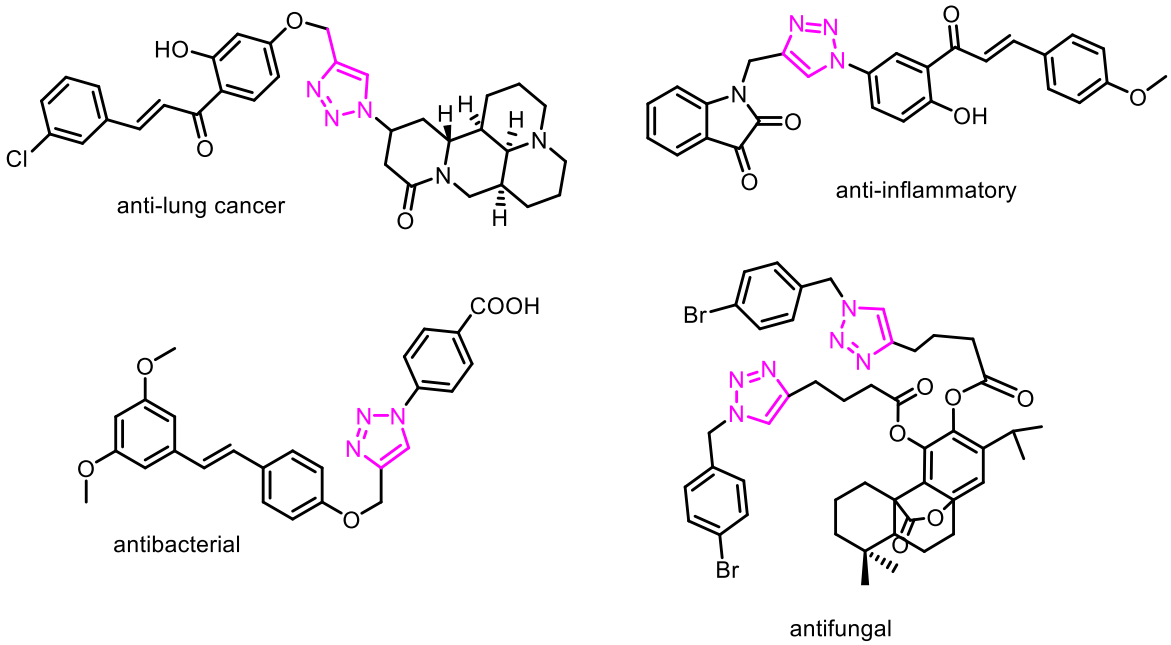


Figure 5.1 Structure of some bioactive 1,2,3-triazole rings.

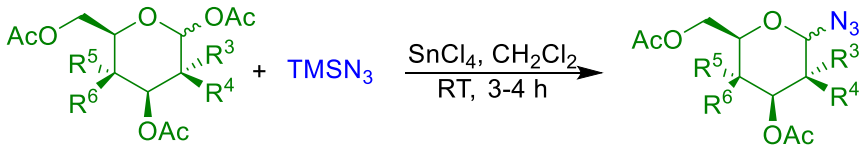
The click chemistry is standard protocol for synthesizing 1,2,3-triazoles. Since the 1,4-regioisomer of 1,2,3-triazoles are not formed in the more common Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between organic azides and alkynes [16]. The 1,2,3-triazole synthesis from azides and terminal acetylenes under copper(I) catalysis is a potent technique for joining two privileged medicinal scaffolds because of its high reliability, perfect specificity, and the biocompatibility of the reactants [17,18].

5.2 Results and Discussion

At the outset, to understand the reactivity of simple azido glycosides due to their great stability and simple chemical elaboration, azido glycosides have been used for a long time as strong and flexible synthons. Anomeric azido glycosides, in example, are crucial intermediates in the production of a wide range of useful compounds, including *N*-glycopeptides [19], Glycosamines [20], *N*-glycoproteins [21], glycosyl heterocyclic derivatives (1,2,3 triazoles) [22], *N*-glycosyl fluorides [23], solid-phase synthesis of glycopeptides [24], glycosyl amino and phosphonic acid derivatives, and enzymatic trans glycosylation are all included [25]. Since *N*-glycosylation is widely used to get access to

physiologically active templates, there has been a great deal of interest in the rational design of glycosyl azides from both the industry and academic communities [26]. There has been a lot of interest from both the industry corporate and academic worlds in the rational design of glycosyl azides since *N*-glycosylation is commonly employed to get access to physiologically active templates [27]. To get azido glycosides, anomeric acetates or halides can be treated with $TMSN_3$ in the presence of Lewis acid catalysts ($SnCl_4$). It was shown that per acetylating β-galactose results in β-azide. On the other hand, α-glycosyl azide may be obtained from per acetylated β-mannose. However, under ideal circumstances, the equivalent per acetylated α-D-glucose was resistant to azido glycosylation [28]. Thus various $SnCl_4$ catalyzed azido glycosides **4-5**, derived from per acetylated D-glucose, D-galactose and D-Mannose **1-3**, were prepared in gram scale to utilize them for click chemistry (**Table 5.1**).

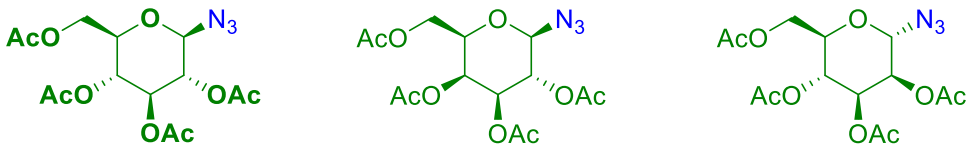
Table 5.1 $SnCl_4$ catalyzed azido glycosylation of glycoside β-peracetates.[a,b,c]



1a-1c → **2a-2c** 85-90%

1a R^5 = OAc, R^6 = H, R^3 = OAc, R^4 = H
2b R^5 = H, R^6 = OAc, R^3 = OAc, R^4 = H
3c R^5 = OAc, R^6 = H, R^3 = H, R^4 = OAc

2a R^5 = OAc, R^6 = H, R^3 = OAc, R^4 = H
2b R^5 = H, R^6 = OAc, R^3 = OAc, R^4 = H
2c R^5 = OAc, R^6 = H, R^3 = H, R^4 = OAc



2a (94%) **2b** (91%) **2c** (85%)

[a]Reaction condition: glycoside β- peracetates **1a-1c** (0.5gm, 12.82mmol), $TMSN_3$ (1.91 mL, 16.66 mmol), $SnCl_4$ (1.29 mL, 11.02 mmol) in 1 mL CH_2Cl_2, [b]Isolated yields. [C] Yield of the reaction at RT in DCM.

After having various azido glycosides in our hand, we planned to prepare designed 1,2,3-triazole-linked *N*-glycosides of the diverse pyrazolo-pyridin-7-ol substrates. The Propargyl pyrazolo-pyridine-7-ol having suitable functionalized terminal alkyne group was prepared in previous chapter 4 starting from pyrazolo-pyridin-7-ol substrates was planned to be used here as one substrate. propargyl bromide in dimethylformamide (DMF) with potassium carbonate (K_2CO_3) as the base, heated to high temperatures, affords propargyl pyrazolo-pyridine-7-ol **3a-3i** in excellent yields from a variety of pyrazolo-pyridine-7-ol. In this context, it is important to note that propargylation of pyrazolo-pyridine-7-ol results in the synthesis of a variety of propargylated compounds **3a-3i**. After having prepared propargyl pyrazolo-pyridine-7-ol **3a-3i** 1-azido-2,3,4,6-tetra-*O*-acetyl β-D-glucose **2a**, 1-azido-2,3,4,6-tetra-*O*-acetyl β-D-galactose **2b** and 1-azido-2,3,4,6-tetra-*O*-acetyl β-D mannose **2c** were prepared in excellent yields.

Under thermal conditions of 50 °C in ^{t}BuOH: H_2O (1: 1) for 6 hours with sodium ascorbate and $CuSO_4.5H_2O$, the first "click chemistry" reaction of propargyl pyrazolo-pyridine-7-ol **3a** with 1-azido-2,3,4,6-tetra-*O*-acetyl γ-D-glucose **2a** produced the desired 1,2,3-triazole linked *N*-glycosides of pyrazolo-pyridine in 95% isolated yields, with some recovered starting material. By utilizing conventional assisted click-chemistry, we aimed to expedite the reaction, reduce reaction time, and enhance yields.

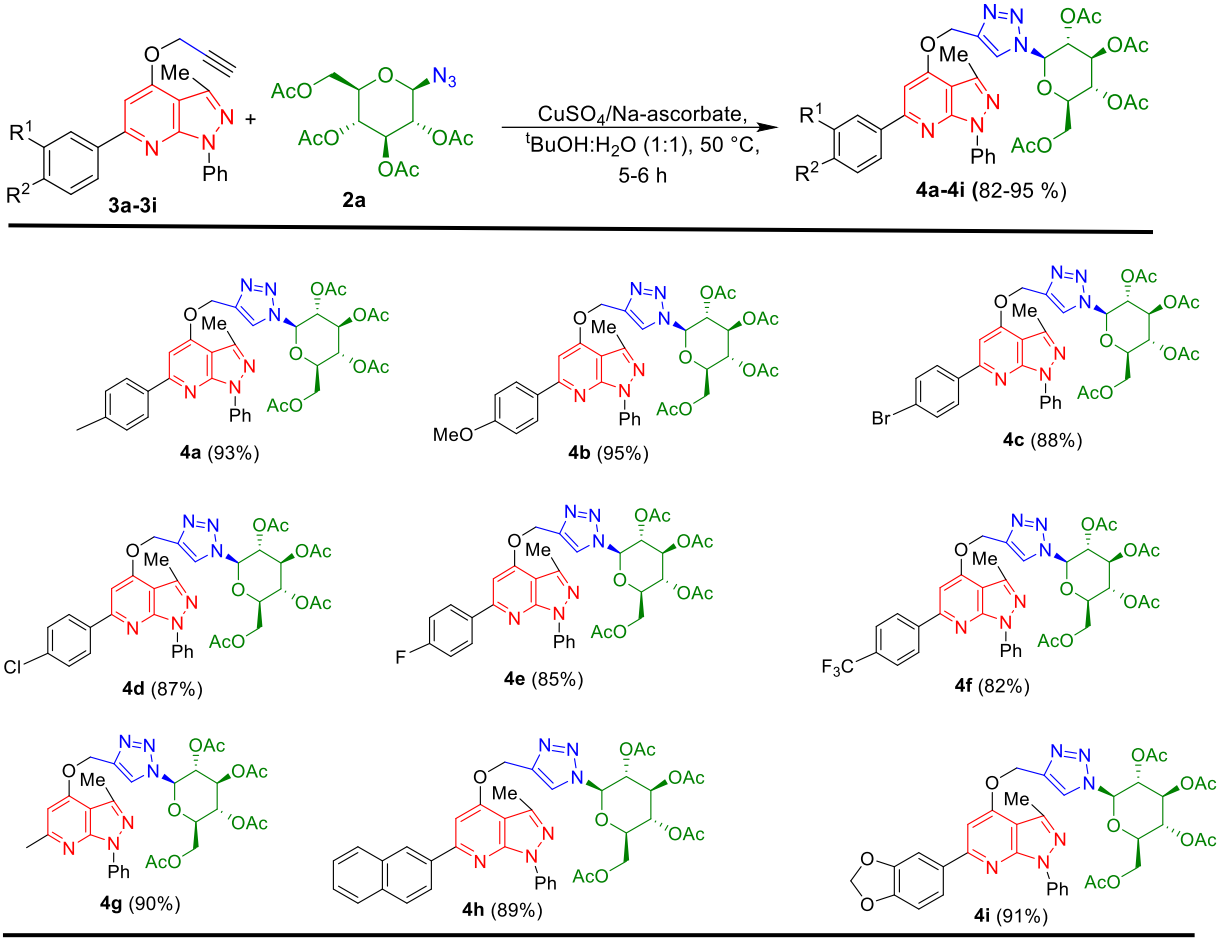
This means that in just 6 hours using a conventional method at 50 °C with $CuSO_4.5H_2O$ and sodium ascorbate in a ^{t}BuOH: H_2O (1:1) ratio, 1,2,3-triazole linked galacto-hybrids pyrazolo pyridine was produced in a very good isolated yield of 92% in a highly regioselective technique.

This process, however, will not proceed to completion without the presence of sodium ascorbate, even after 6 hours minutes. This demonstrates that both sodium ascorbate and Cu(I) are essential for this transformation, as they serve to both speed up the process and

induce the regioselectivity on these substrates. The activity profile of D-mannose-derived 1,2,3-triazole-linked glyco-hybrids pyrazolo pyridine was also of interest to us.

Therefore, 1,2,3-triazole-linked *N*-glycosides of D-mannose were synthesized using a traditional approach with excellent yields by employing an improved reaction procedure. Additionally, we were curious to see the activity profile of 1,2,3-triazole-linked *N*-glycosides generated from D-galactose. Using an azide in an alkyne cycloaddition (click chemistry). The first azide-alkyne cycloaddition which was developed by Huisgen in 1960. Since one or more of the reactants in a click reaction often have a high energy content, this is often the most challenging part of the process [29]. Thus, as seen in **Scheme 5.1**, 1,2,3-triazole-linked pyrazolo-pyridine glucosides were successfully synthesized using the traditional approach by using an improved reaction strategy.

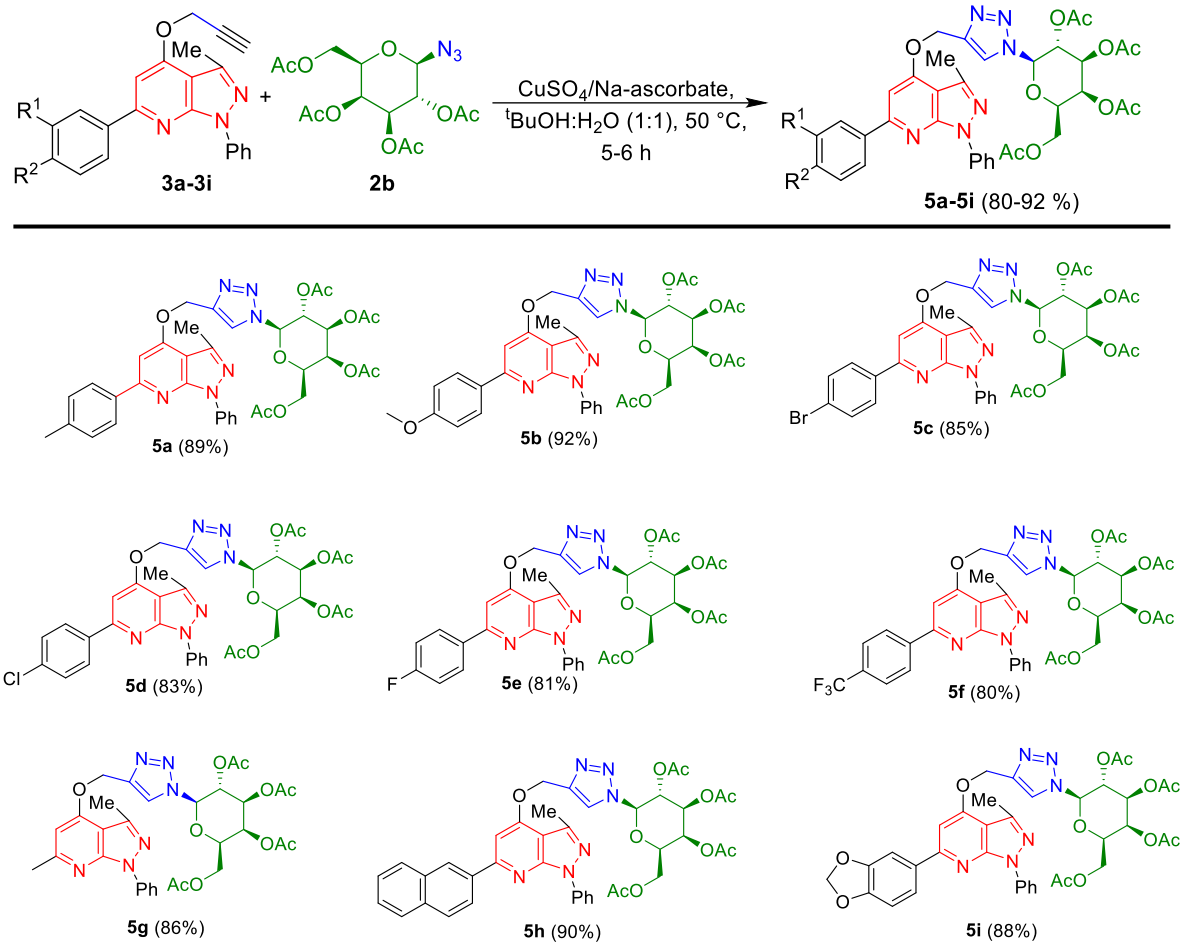
Scheme 5.1 Synthesis of triazole-linked glucohybrids of pyrazole-pyridines.[a,b,c]



[a]Reaction condition: Propargyl pyrazolo pyridine **3a-3i** (0.05 gm, 0.148 mmol, 1.0 equiv.) and 1-azido-2,3,4,6- tetra-*O*-acetyl β-D-glucose **2a** (.055 gm, 0.148 mmol, 1.0 equiv.), was taken in 3 mL (1: 1 mixture of H_2O: ^{t}BuOH) of the solvent. $CuSO_4.5H_2O$ (0.023 gm, 0.148 mmol, 1.0 equiv.), sodium ascorbate (.025 gm, 0.148 mmol, 1.0 equiv.). [b]Isolated yields. [c]Yield of the reaction at 50 °C.

Thus, 1,2,3-triazole-linked galacto-hybrids of pyrazolo-pyridine **5a-5i** were successfully made, as were propargylated pyrazolo-pyridine **3a-3i** with per-*O*-acetylated galactose **2b** as shown in **Scheme 5.2**

Scheme 5.2 Synthesis of triazole linked galactohybrids pyrazole-pyridines.[a,b,c]

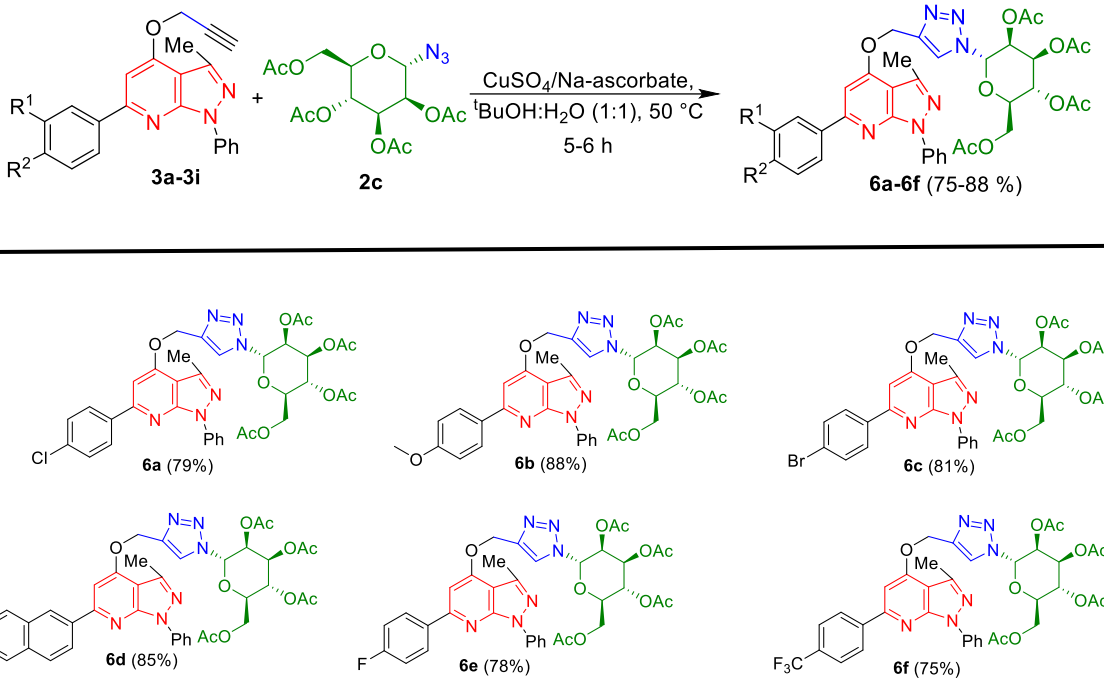


[a]Reaction condition: Propargyl pyrazolo pyridine **3a-3i** (0.05gm, 0.148 mmol, 1.0 equiv.) and 1-azido-2,3,4,6- tetra-*O*-acetyl β-D-galactohybrids **2b** 0.05gm (0.148 mmol, 1.0 equiv.), was taken in 3 mL (1: 1 mixture of H_2O: ^{t}BuOH) of the solvent. $CuSO_4.5H_2O$ (.023gm, 0.148 mmol, 1.0 equiv.), Sodium Ascorbate (2.28 mg, 0.005 mmol). [b]Isolated yields. [c]Yield of the reaction at 50 °C.

The activity profile of 1,2,3-triazole connected mannohybrids of pyrazolo-pyridine was intriguing to us as well. For this reason, as seen in **Scheme 5.3**, 1,2,3-triazole linked

mannohybrids of pyrazolo-pyridine **6a-6f** were successfully synthesized using the traditional technique by using an improved reaction strategy.

Scheme 5.3 Synthesis of triazole-linked mannohybrids of pyrazolo-pyridines.[a,b,c]



[a]Reaction condition: Propargyl pyrazolopyridine **3a-3i** (0.05gm, 0.148 mmol,1.0 equiv.) and 1-azido-2,3,4,6- tetra-*O*-acetyl β-D-mannose **2c** (0.05gm, 0.148 mmol,1.0 equiv.), was taken in 3 mL (1: 1 mixture of H_2O: ^{t}BuOH) of the solvent. $CuSO_4.5H_2O$ (0.023gm, 0.148 mmol), sodium Ascorbate (0.025gm, 0.148 mmol). [b]Isolated yields. [c]Yield of the reaction at 50 °C.

Excellent yields of glycohybrid **6a, 6b** and **6c** were achieved through the click chemistry reaction of 4-*O*-propargyl pyrazolo-pyridine and 1-azido mannoside **2c**. Thus, diversely substituted glycohybrid **6d-6f** were were prepared in good yields (**Scheme 5.3)**.

5.3 Cyclic voltammetry study of triazole linked glycohybrids of pyrazole-pyridines.

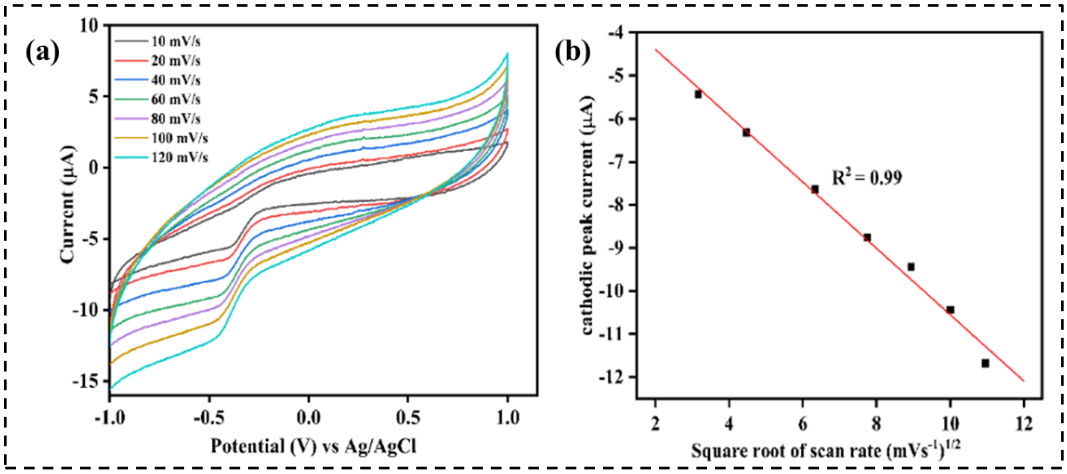


Figure.5.2 (a) Cyclic voltammogram of Triazole linked glycohybrids of pyrazolo-pyridines in pH 7 buffer solution at various scan rates **(b)** plot of cathodic peak current vs square root of scan rate.

The electrochemical technique of cyclic voltammetry (CV) is widely used to study the redox reactions of molecules. In order to conduct CV measurements, a carbon paste electrode (CPE) (d = 0.03 cm^2) working electrode, a Pt counter electrode (1cm^2), saturated KCl in Ag/AgCl as a reference electrode, and $NaClO_4$ (0.1 M) as a supporting electrolyte were utilized. There are two halves to a cyclic voltammogram: the anodic and the cathodic [30].

Under the conditions of the process, a reduction peak was seen in the cyclic voltammetry of glycohybrids. the scan rate has a direct correlation with the strength of the cathodic (reduction) peaks in the CV graphs. A quicker reaction time appears to be a side effect of a greater scan rate. Another thing that happens when you raise the scan rate is that the cathodic peak moves toward more negative potentials. Such variations in potential suggest that the rate of potential change affects the efficiency of the reduction operations [31].

Overall, these studies indicate that 1,2,3-Triazole-linked glycohybrids and galactohybrids of pyrazole-pyridines provide better results than that of 1,2,3-triazole-linked mannohybrids of pyrazolo-pyridine in terms of yields and reaction conditions.

5.4 Electrochemical impedance spectroscopy-

In summary, researchers can better understand, optimize, and control electrochemical reactions and processes with the use of electrochemical impedance spectroscopy (EIS), a versatile and powerful tool in the field of electro-organic synthesis. Techniques for electro-organic synthesis stand to gain significantly in terms of safety, selectivity, and efficiency.

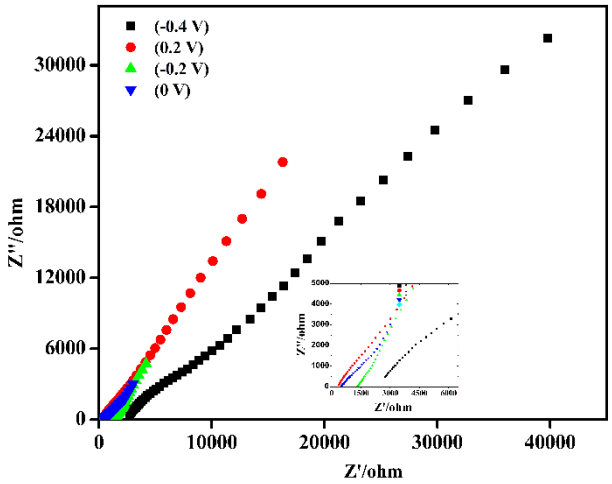


Figure 5.3 Electrochemical impedance spectroscopy EIS study of **4a** at different potential.

There are two parts to the impedance expression: the real and imaginary parts. A "Nyquist Plot" is created when the imaginary part ($Z_{imaginary}$) is plotted on the Y-axis and the real part (Z_{real}) is plotted on the X-axis. In practical terms, impedance is determined by recording the current wave that results from applying a potential wave to the working electrode. Z, Φ, Z_{real}, and $Z_{imaginary}$ are extracted and sketched from these two waves. By measuring these properties for hypothetical waves with various frequency, the spectrum is produced [32]. Consequently, the EIS might be used to study processes including mass transfer, charge transfer, and diffusion. A material's intrinsic properties or specific processes that influence the capacitance, resistance, or conductance of an electrochemical system can be studied using the EIS [33].

5.5 Conclusion

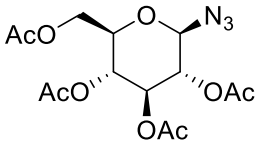
In conclusion, we have created a library of pyrazolo-pyridin-7-ol connected to 1,2,3-triazoles as carbohybrids by careful design and synthesis. The process begins with newly synthesized propargylated pyrazolo-pyridines and 1-azido glycosides obtained from their respective 2,3,4,6-tetra-*O*-acetyl β-D-glycopyranosides generated from D-glucose, D-galactose D-mannose using click-chemistry as a simple and efficient synthetic approach. The approach has a number of advantages that set it apart from others, such as its ease of use, fast reaction time, versatility in substrate, and high yields.

5.6 Experimental Procedures

5.4.1. Synthesis of Glucose, Galactose and Mannose derived azido glycosides 2a-2c:

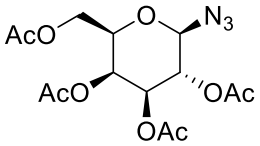
Synthesis of azido glycosides from glucose, galactose, and mannose: An experimental approach for this experiment, a round-bottom flask that had been dried in the oven was used to collect 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose **1** (0.5 g, 12.82 mmol). Afterwards, the flask was covered with a nitrogen atmosphere after being filled with anhydrous dichloromethane. After that, over an ice bath, $SnCl_4$ was added dropwise (1.29 mL, 11.02 mmol) while stirring continuously for half an hour. After that, 1.91 mL of $TMSN_3$ (16.66 mmol) was added at room temperature while stirring was maintained for another three to four hours. Using TLC, the reaction was tracked until it was finished. The mixture was cooled with ice-cold water once the reaction was finished, and then an aqueous solution of $NaHCO_3$ was added. Dichloromethane was used to extract the combination, and a brine solution was used to wash the organic layer. A crude residue was produced by drying the mixture with anhydrous Na_2SO_4 and then evaporating the solvent under vacuum. A white-colored solid 1-azido glucoside **2a** was isolated in 93% yield from the crude residue after it was purified using column chromatography. Starting with 1,2,3,4,6-penta-

O-acetyl-β-D-galactopyranose **1a** and 1,2,3,4,6-penta-*O*-acetyl-β-D- mannopyranose **2b**, each 1-azido glycoside **2b** and **2c** were synthesized using the same reaction technique.



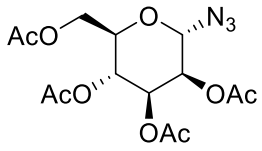
2a

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-azidotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2a): white colored solid: Rf = 0.30 (3:7 EtOAc/hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.20 (t, J = 9.5 Hz, 1H), 5.08 (t, J = 9.5 Hz, 1H), 4.93 (t, J = 9.1 Hz, 1H), 4.63 (d, J = 8.6 Hz, 1H), 4.25 (dd, J = 12.4, 4.8 Hz, 1H), 4.15 (d, J = 12.4 Hz, 1H), 3.82 – 3.75 (m, 1H), 2.07 (d, J = 12.2 Hz, 6H), 2.00 (d, J = 11.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.73, 170.23, 169.42, 169.32, 87.99, 74.09, 72.68, 70.71, 67.95, 61.74, 20.79, 20.64. HRMS (ESI-TOF), m/z calcd. $C_{14}H_{19}N_3O_9Na$ $[M+Na]^+$ 396.1014; Found: 396.1038;



2b

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-azidotetrahydro-2*H*-pyran-3,4,5- triyl triacetate (2b): white colored solid: Rf = 0.30 (3:7 EtOAc/hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.40 (d, J = 4.0 Hz, 1H), 5.14 (t, J = 10.0 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.58 (d, J = 9.3 Hz, 1H), 4.13 (dt, J = 12.0, 6.7 Hz, 2H), 4.00 (t, J = 6.7 Hz, 1H), 2.15 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.44, 170.19, 170.05, 169.44, 88.38, 72.96, 70.82, 68.18, 66.97, 61.32, 20.73, 20.67, 20.58. HRMS (ESI-TOF), m/z calcd. $C_{14}H_{19}N_3O_9Na$ $[M+Na]^+$396.1014; Found: 396.1041;

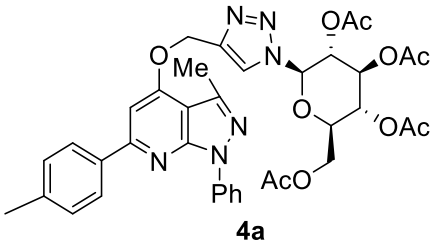


2c

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-azidotetrahydro-2*H*-pyran3,4,5-triyl triacetate (2c): white colored solid: Rf = 0.30 (3:7 EtOAc/hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.34 (s, 1H), 5.26 – 5.16 (m, 2H), 5.11 – 5.08 (m, 1H), 4.25 (dd, J = 13.3, 5.3 Hz, 1H), 4.13 – 4.07 (m, 2H), 2.11 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.54, 169.80, 169.71, 169.61, 87.46, 70.64, 69.15, 68.25, 65.61, 62.13, 20.75, 20.66, 20.62, 20.55. HRMS (ESI-TOF), m/z calcd. $C_{14}H_{19}N_3O_9Na$ $[M+Na]^+$ 396.1014; Found: 396.1030;

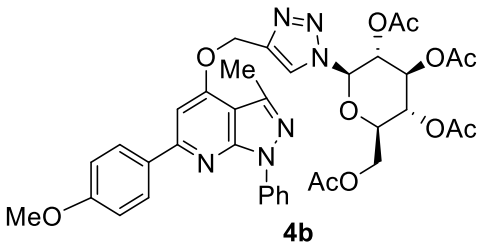
5.6.2. Synthesis of triazole linked glycohybrids of pyrazolo[1,5-a] pyrimidines 3a-3i: In an oven dried 50 mL round bottom flask taken (0.05 g, 0.148 mmol, 1.0 equiv.) of 1-azido-2,3,4,6- tetra-*O*-acetyl β-D-glucose **2a** and propargylated pyrazolo pyridines **3a** (0.05 g, 0.148 mmol, 1.0 equiv.) were taken in 3 mL (a 1: 1 mixture of H_2O: ^{t}BuOH) of the solvent. $CuSO_4.5H_2O$ (0.023 g, 0.148 mmol, 1.0 mmol) and sodium ascorbate (0.025 g, 0.148 mmol, 1.0 equiv.) were added to the above reaction mixture. The resulting reaction mixture was heated under conditions. Completion of the reaction was confirmed by TLC. After completion, 5 mL of water was added and the reaction mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with brine, then dried over Na_2SO_4 and evaporated on a rotary evaporator to get a crude product. The crude residue was purified by column chromatography and pure glycohybrid compound **4a** (138 mg) was isolated in a 90% isolated yield. Other 1,2,3-triazole linked *N*-glucosides **4b-4i** were also prepared using the above reaction protocol in good to very good yields (67–90%) using 1-azido-2,3,4,6-tetra-*O*-acetyl β-D-glucose **2a** and 4-*O*-propargylated pyrazolo-pyridines **(Table 5.2).**

Similarly, 1,2,3-triazole linked *N*-galactosides **5a-5i** were prepared in very good to excellent yields (71–94%) using 1-azido-2,3,4,6-tetra-*O*-acetyl β-D-galactose **2b** and 4-*O*-propargylated pyrazolo-pyridines **3a-3i (Table 5.3).**



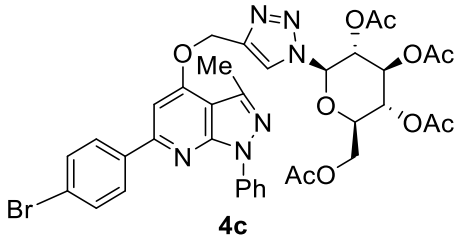
4a

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3-methyl-1-phenyl-6-(p-tolyl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4a). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), Yellow coloured sticky solid: m.p. (250 °C); Yield (83%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 7.9 Hz, 2H), 7.87 (s, 1H), 7.55 (t, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 8.5 Hz, 3H), 6.58 (s, 1H), 5.84 (d, *J* = 9.4 Hz, 1H), 5.70 – 5.57 (m, 2H), 5.38 (t, *J* = 9.5 Hz, 1H), 5.30 (t, *J* = 9.3 Hz, 1H), 5.18 (t, *J* = 9.6 Hz, 1H), 4.23 (dd, *J* = 12.7, 6.0 Hz, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 3.95 (dd, *J* = 10.7, 5.3 Hz, 1H), 2.44 (s, 3H), 2.25 (s, 3H), 2.03 (s, 9H), 1.79 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.58, 170.01, 169.48, 168.92, 162.77, 149.58, 149.08, 144.92, 143.15, 139.69, 138.84, 134.64, 129.16, 129.11, 125.69, 122.15, 121.22, 110.73, 106.95, 75.24, 72.78, 70.45, 67.82, 61.74, 59.85, 21.44, 20.76, 20.63, 20.19, 15.49 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{39}N_6O_{10}$ $[M+H]^+$ 727.2722, found 727.2999;



4b

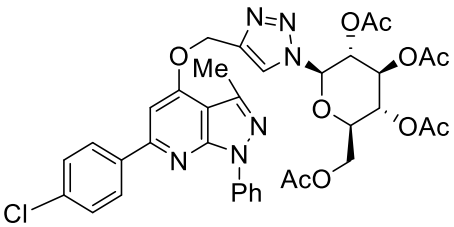
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4b). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), red coloured solid: m.p. (200 °C); Yield (95%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 7.9 Hz, 2H), 7.87 (s, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.57 (s, 1H), 5.84 (d, *J* = 9.5 Hz, 1H), 5.67 (d, *J* = 12.7 Hz, 1H), 5.59 (d, *J* = 13.2 Hz, 1H), 5.38 (t, *J* = 9.4 Hz, 1H), 5.29 (d, *J* = 9.4 Hz, 1H), 5.18 (t, *J* = 9.6 Hz, 1H), 4.22 (d, 1H), 4.11 (d, *J* = 12.9 Hz, 1H), 3.96 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H), 2.27 (s, 3H), 2.08 – 2.00 (m, 9H), 1.80 (s, 3H)); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.33, 169.76, 169.24, 168.67, 162.53, 160.03, 149.38, 148.50, 144.68, 142.86, 139.43, 130.00, 128.92, 125.44, 121.89, 120.97, 113.63, 106.63, 85.58, 75.52, 72.52, 70.19, 67.56, 61.48, 59.59, 55.24, 20.52, 20.39, 19.94, 15.35 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{39}N_6O_{11}$ $[M+H]^+$ 743.26721, found 743.2614;



4c

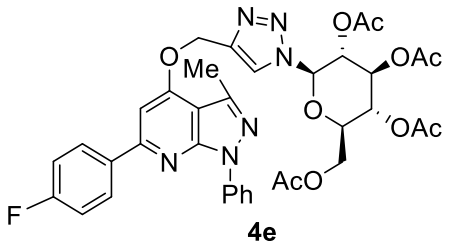
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-bromophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4c). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (170 °C); Yield (88%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.68 – 7.49 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.58 (s, 1H), 5.83 (s, 1H), 5.67 (d, *J* = 13.1 Hz, 1H), 5.61 (s, 1H), 5.38 (d, *J* = 9.5 Hz, 1H), 5.30 (t, *J* = 9.4 Hz, 1H), 5.19 (d, *J* = 10.1 Hz,

1H), 4.23 (d, *J* = 9.0 Hz, 1H), 4.11 (d, *J* = 12.2 Hz, 1H), 3.96 (d, *J* = 9.8 Hz, 1H), 2.24 (s, 3H), 2.04 – 1.57 (m, 9H), 1.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.28, 169.76, 169.26, 168.71, 147.28, 144.55, 142.55, 139.33, 131.48, 130.29, 128.98, 125.64, 123.10, 121.85, 121.05, 106.75, 85.65, 72.52, 70.23, 67.60, 61.51, 59.72, 20.54, 20.40, 19.97, 15.25 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}BrN_6O_{10}$ $[M+H]^+$ 793.1650, found 793.2006;



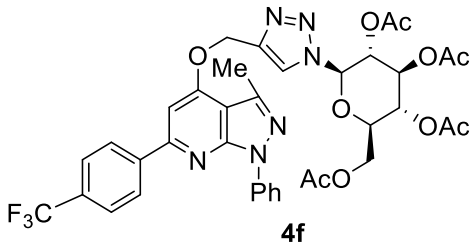
4d

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4d). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (80 °C); Yield (87%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.29 (s, 1H), 6.59 (s, 1H), 5.84 (d, *J* = 9.3 Hz, 1H), 5.68 (d, *J* = 12.8 Hz, 1H), 5.62 (d, *J* = 12.5 Hz, 1H), 5.53 (s, 2H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.21 – 4.11 (m, 2H), 2.24 (s, 3H), 2.18 – 1.99 (m, 9H), 1.84 (s, 3H)); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.46, 170.05, 169.92, 169.22, 162.75, 149.51, 147.48, 144.81, 142.74, 139.63, 135.98, 135.16, 130.25, 129.13, 128.75, 125.65, 121.63, 120.88, 110.52, 107.02, 7 4.23, 70.90, 68.02, 66.97, 61.30, 60.03, 20.74, 20.61, 20.33, 15.48 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}ClN_6O_{10}$ $[M+H]^+$ 747.2176, found 747.2165;



4e

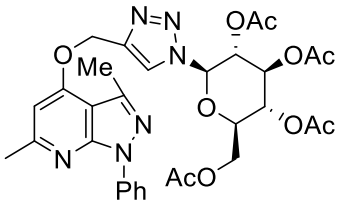
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4e). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), white coloured solid: m.p. (170 °C); Yield (85%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.29 (s, 1H), 6.59 (s, 1H), 5.84 (d, *J* = 9.3 Hz, 1H), 5.68 (d, *J* = 12.8 Hz, 1H), 5.62 (d, *J* = 12.5 Hz, 1H), 5.53 (s, 2H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.22 – 4.19 (m, 1H), 4.15 (d, *J* = 6.0 Hz, 1H), 4.11 (d, *J* = 7.1 Hz, 1H), 2.24 – 1.99 (m, 12H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.32, 169.74, 169.25, 168.69, 162.49, 149.28, 147.51, 144.56, 142.59, 139.33, 130.44, 130.38, 128.95, 125.58, 121.86, 121.01, 115.21, 106.87, 85.59, 72.50, 70.21, 67.57, 61.49, 60.97, 59.65, 20.51, 20.38, 19.94, 15.16 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}FN_6O_{10}$ $[M+H]^+$ 731.2471, found 731.2465;



4f

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3-methyl-1-phenyl-6-(4-(trifluoromethyl)phenyl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4f). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), off-white coloured solid: m.p.

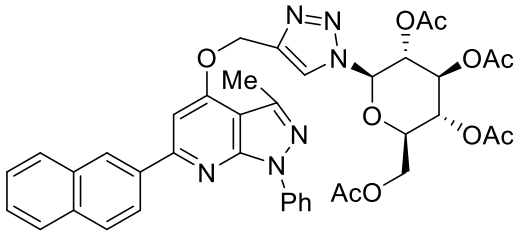
(200 °C); Yield (82%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.29 (s, 1H), 6.59 (s, 1H), 5.84 (d, *J* = 9.3 Hz, 1H), 5.68 (d, *J* = 12.8 Hz, 1H), 5.62 (d, *J* = 12.5 Hz, 1H), 5.53 (s, 2H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.21 (d, *J* = 6.5 Hz, 1H), 4.15 (d, *J* = 5.9 Hz, 1H), 4.11 (d, *J* = 6.4 Hz, 1H), 2.24 (s, 3H), 2.17 – 1.99 (m, 9H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.38, 169.80, 169.31, 168.76, 162.50, 149.29, 146.88, 144.48, 142.42, 140.94, 139.28, 129.04, 125.75, 125.28, 125.26, 121.92, 121.10, 110.06, 106.96, 72.52, 70.24, 67.58, 61.53, 59.78, 20.58, 20.01, 15.23 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{36}F_3N_6O_{10}$ $[M+H]^+$ 781.2440, found 781.2425;



4g

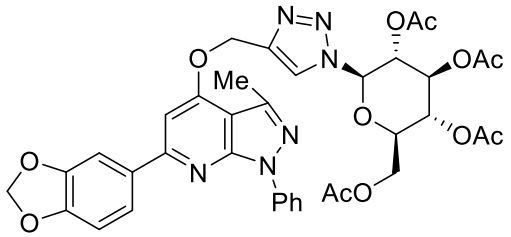
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4g). The product was purified by silica column chromatography (Ethyl acetate: Hexane 1:1), off-white coloured solid: m.p. (140 °C); Yield (90%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.1 Hz, 2H), 7.85 (s, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 5.83 (d, *J* = 8.5 Hz, 1H), 5.61 (d, *J* = 12.5 Hz, 1H), 5.52 (d, *J* = 12.9 Hz, 1H), 5.36 (t, *J* = 10.3 Hz, 1H), 5.29 (t, *J* = 9.4 Hz, 1H), 5.18 (t, *J* = 9.9 Hz, 1H), 4.22 (d, *J* = 17.2 Hz, 1H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.95 (d, *J* = 5.3 Hz, 1H), 2.67 (s, 3H), 2.60 (s, 3H), 2.04 (d, *J* = 12.0 Hz, 9H), 1.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.56, 169.98, 169.47, 168.89, 163.13, 149.37, 145.56, 144.97, 143.08, 139.71, 129.10, 125.47, 122.01, 120.91, 112.21, 107.03, 72.74, 70.40, 67.78, 61.70, 59.65, 20.74, 20.61, 20.15,

19.30, 15.28 ppm; HRMS (ESI) *m/z*: calcd for $C_{31}H_{35}N_6O_{10}$ $[M+H]^+$ 727.2722, found 727.2710;



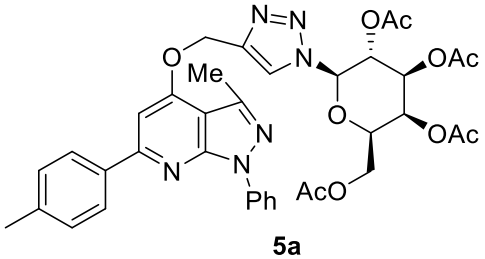
4h

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3-methyl-6-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4h). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light brown coloured solid: m.p. (120 °C); Yield (90%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.53 (t, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 6.59 (s, 1H), 5.84 (d, *J* = 9.3 Hz, 1H), 5.68 (d, *J* = 12.8 Hz, 1H), 5.62 (d, *J* = 12.5 Hz, 1H), 5.53 (s, 2H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.21 (d, *J* = 6.6 Hz, 1H), 4.15 (d, *J* = 5.5 Hz, 1H), 4.11 (s, 1H), 2.24 (s, 3H), 2.10 (s, *J* = 74.5 Hz, 9H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.36, 169.80, 168.72, 162.54, 144.67, 142.90, 139.43, 134.75, 128.97, 128.13, 127.91, 126.66, 126.49, 125.54, 121.89, 121.04, 110.57, 107.06, 72.53, 70.22, 67.58, 61.50, 59.69, 20.40, 19.96, 15.28 ppm; HRMS (ESI) *m/z*: calcd for $C_{40}H_{39}N_6O_{10}$ $[M+H]^+$ 763.2722, found 727.3029;



4i

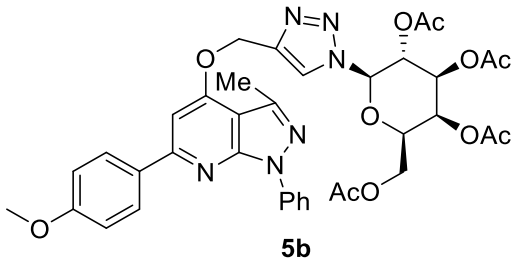
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(benzo[d][1,3]dioxol-5-yl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4i). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light brown coloured solid: m.p. (160 °C); Yield (90%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 7.9 Hz, 2H), 7.86 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.93 (s, 3H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.05 (d, *J* = 2.4 Hz, 2H), 5.83 (d, *J* = 9.1 Hz, 1H), 5.66 (d, *J* = 13.0 Hz, 1H), 5.57 (s, 1H), 5.30 (d, *J* = 9.3 Hz, 1H), 5.18 (t, *J* = 9.6 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.23 (d, *J* = 9.0 Hz, 1H), 4.11 (d, *J* = 12.6 Hz, 2H), 3.95 (s, 1H), 2.30 (s, 3H), 2.02 (d, *J* = 8.5 Hz, 9H), 1.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.42, 169.82, 169.30, 168.74, 162.54, 149.36, 147.54, 144.65, 142.81, 139.37, 131.07, 128.98, 125.57, 122.61, 121.07, 110.45, 109.22, 75.02, 72.54, 70.21, 67.58, 61.53, 59.63, 20.58, 20.45, 20.00, 15.36 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{37}N_6O_{12}$ $[M+H]^+$ 757.2464, found 757.2350;



5a

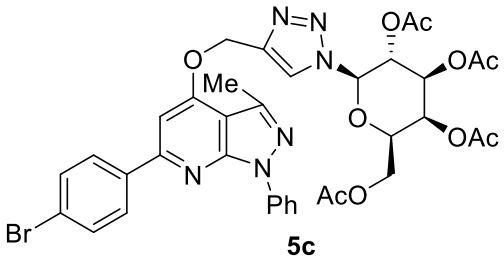
(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3-methyl-1-phenyl-6-(p-tolyl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5a). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (175 °C); Yield (89%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 7.8 Hz, 2H), 7.95 (s, 1H), 7.48 (d, *J* = 15.6 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.28 – 7.21 (m, 3H), 6.57 (s, 1H), 5.79 (s, 1H), 5.65 (d, *J* = 12.2 Hz, 1H), 5.58 (d, *J* = 12.8 Hz, 1H), 5.48 (d, *J* = 7.8 Hz, 2H), 5.20 (d, *J* = 10.2 Hz,

1H), 4.16 (d, *J* = 5.9 Hz, 1H), 4.13 – 4.10 (m, 1H), 4.08 – 4.05 (m, 1H), 2.41 (s, 3H), 2.21 (s, 3H), 2.14 – 1.96 (m, 9H), 1.54 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.45, 170.07, 169.92, 169.17, 162.80, 149.57, 149.07, 144.98, 143.13, 139.77, 138.85, 134.66, 129.11, 128.86, 125.48, 121.65, 120.85, 110.83, 106.96,73.98, 86.48, 74.23, 70.95, 68.03, 67.01, 61.32, 59.95, 21.44, 20.74, 15.24 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{39}N_6O_{10}$ $[M+H]^+$ 727.2722, found 727.3009;



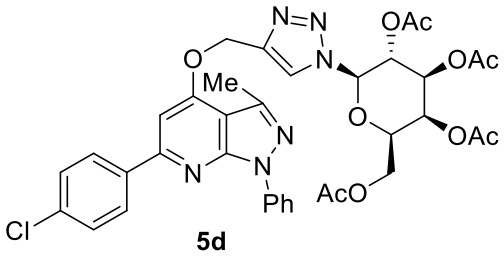
5b

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5b). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), off white coloured solid: m.p. (120 °C); Yield (92%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 3H), 6.60 (s, 1H), 5.84 (d, *J* = 9.3 Hz, 1H), 5.69 (d, *J* = 13.3 Hz, 1H), 5.63 (s, 1H), 5.53 (d, *J* = 3.7 Hz, 2H), 5.23 (d, *J* = 10.6 Hz, 1H), 4.21 – 4.18 (m, 1H), 4.16 (d, *J* = 5.5 Hz, 1H), 4.11 – 4.08 (m, 1H), 3.96 (s, 3H), 2.16 (s, 3H), 2.04 (m, *J* = 13.4 Hz, 9H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.22, 169.83, 169.69, 168.94, 162.56, 160.04, 149.37, 148.49, 144.73, 142.84, 139.52, 130.01, 128.86, 125.24, 121.39, 120.60, 113.64, 106.63, 70.69, 67.76, 66.74, 61.07, 59.69, 55.26, 20.49, 20.35, 20.07, 15.35 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{39}N_6O_{11}$ $[M+H]^+$ 743.2671, found 743.2565;



5c

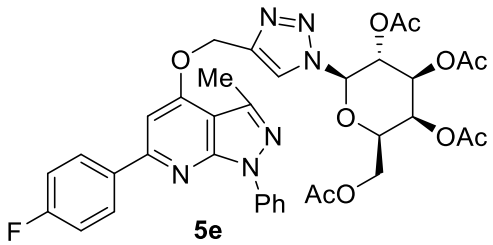
(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-bromophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5c). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), off white coloured solid: m.p. (80 °C); Yield (85%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 2H), 7.94 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 3H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.59 (s, 1H), 5.84 (d, *J* = 9.3 Hz, 1H), 5.68 (d, *J* = 14.4 Hz, 1H), 5.62 (d, *J* = 12.6 Hz, 1H), 5.53 (d, *J* = 4.1 Hz, 2H), 5.24 (d, *J* = 11.7 Hz, 1H), 4.20 (s, 1H), 4.15 (d, *J* = 6.0 Hz, 1H), 4.11 (d, *J* = 6.9 Hz, 1H), 2.17 (s, 3H), 2.01 (m, *J* = 12.1 Hz, 9H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.43, 170.03, 169.89, 169.19, 162.77, 149.53, 147.48, 144.81, 142.73, 139.63, 136.47, 131.70, 130.52, 129.12, 125.65, 121.63, 120.90, 110.44, 106.97, 70.91, 68.06, 67.00, 61.29, 60.03, 20.72, 20.57, 20.30, 15.46 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}BrN_6O_{10}$ $[M+H]^+$ 791.1671, found 791.1565;



5d

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5d). The product was purified by silica column

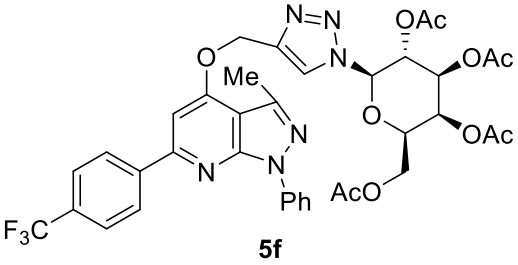
chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (200 °C); Yield (83%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 7.8 Hz, 2H), 7.87 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 6.57 (s, 1H), 5.84 (d, *J* = 9.4 Hz, 1H), 5.68 – 5.55 (m, 2H), 5.38 (t, *J* = 9.4 Hz, 1H), 5.29 (t, *J* = 9.7 Hz, 1H), 5.18 (t, *J* = 9.9 Hz, 1H), 4.22 (d, *J* = 8.2 Hz, 1H), 4.10 (d, *J* = 12.3 Hz, 2.23 (s, 3H), 2.04 (m, *J* = 15.1 Hz, 9H), 1.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.30, 169.73, 169.24, 168.68, 162.45, 149.26, 147.23, 144.49, 142.50, 139.28, 135.70, 134.87, 129.97, 128.94, 128.47, 125.59, 121.86, 120.99, 106.76, 74.97, 72.47, 70.19, 67.54, 61.47, 59.66, 20.50, 20.37, 19.92, 15.20 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}ClN_6O_{10}$ $[M+H]^+$ 747.2176, found 747.2145;



5e

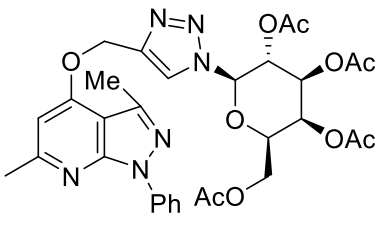
(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(4-fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5e). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (170 °C); Yield (81%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 7.5 Hz, 2H), 7.95 (s, 1H), 7.53 (s, 2H), 7.44 (d, *J* = 7.4 Hz, 3H), 7.19 (t, *J* = 8.6 Hz, 3H), 6.60 (s, 1H), 5.83 (d, 1H), 5.68 (d, 1H), 5.61 (d, 1H), 5.53 (t, 2H), 5.25 – 5.22 (m, 1H), 4.19 (d, *J* = 6.9 Hz, 1H), 4.16 (d, *J* = 5.4 Hz, 1H), 4.12 – 4.09 (m, 1H), 2.23 (s, 3H), 2.01 (m, *J* = 13.3 Hz, 9H), 1.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.21, 169.80, 169.67, 168.97, 162.51, 149.27, 147.50, 144.62, 142.56, 139.43, 130.47, 130.40, 128.89, 125.38, 121.37, 120.64, 115.40, 115.23,

106.87, 74.38, 70.67, 67.78, 66.74, 61.05, 59.77, 20.50, 20.35, 20.08, 15.19 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}FN_6O_{10}$ $[M+H]^+$ 731.2471, found 731.2445;



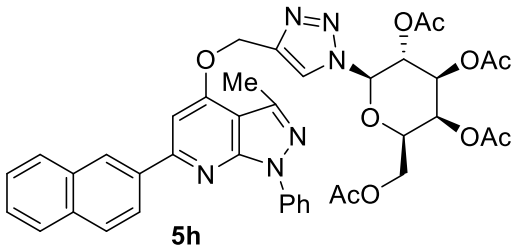
5f

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3-methyl-1-phenyl-6-(4-(trifluoromethyl)phenyl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5f). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (90 °C); Yield (80%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.0 Hz, 3H), 7.95 (s, *J* = 4.3 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 1H), 5.85 (d, *J* = 9.2 Hz, 1H), 5.69 (d, *J* = 12.7 Hz, 1H), 5.64 – 5.59 (m, 1H), 5.53 (s, 2H), 5.24 (d, *J* = 10.5 Hz, 1H), 4.21 (d, *J* = 6.9 Hz, 1H), 4.18 – 4.14 (m, 1H), 4.10 (dd, *J* = 11.0, 6.6 Hz, 1H), 2.17 (s, *J* = 4.3 Hz, 3H), 2.04 – 1.97 (m, 9H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.70, 170.28, 170.15, 169.47, 162.97, 149.73, 147.29, 144.95, 142.82, 141.40, 139.81, 129.57, 129.40, 125.98, 125.72, 121.90, 121.15, 110.59, 107.39, 74.47, 71.13, 68.29, 67.23, 61.54, 60.31, 20.97, 20.83, 20.56, 15.65 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}F_3N_6O_{10}$ $[M+H]^+$ 781.2440, found 781.2741;



5g

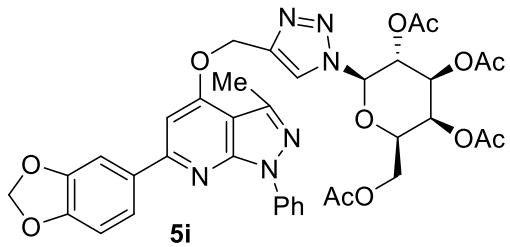
(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (31). The product was purified by silica column chromatography (Ethyl acetate: Hexane 1:1), light yellow coloured solid: m.p. (120 °C); Yield (86%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.03 (d, *J* = 7.9 Hz, 2H), 8.73 (s, 1H), 8.30 (t, *J* = 7.9 Hz, 3H), 8.05 (t, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 9.3 Hz, 1H), 6.42 (s, 1H), 6.37 (s, 1H), 6.35 – 6.32 (m, 2H), 6.04 (d, *J* = 10.8 Hz, 1H), 5.02 (t, *J* = 6.4 Hz, 1H), 4.98 – 4.94 (m, 1H), 4.90 (dd, *J* = 11.7, 6.8 Hz, 1H), 3.48 (s, 3H), 2.97 (s, 3H), 2.81 (m, *J* = 14.6 Hz, 9H), 2.63 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.45, 170.06, 169.90, 169.16, 163.13, 149.33, 145.53, 144.97, 143.06, 139.73, 129.02, 125.28, 121.58, 120.54, 112.26, 107.01, 74.11, 70.87, 67.97, 66.95, 61.29, 59.68, 20.70, 20.26, 19.30, 15.25 ppm; HRMS (ESI) *m/z*: calcd for $C_{31}H_{35}N_6O_{10}$ $[M+H]^+$ 651.2409, found 651.2361;



5h

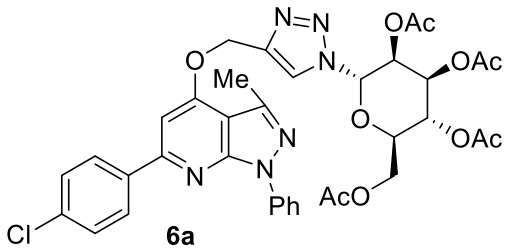
(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((3-methyl-6-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5h). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), yellow coloured solid: m.p. (135 °C); Yield (90%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 7.9 Hz, 2H), 7.97 (m, *J* = 10.0, 5.9 Hz, 5H), 7.61 – 7.49 (m, 5H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.73 (s, *J* = 3.1 Hz, 1H), 5.85 (d, *J* = 9.4, 3.0 Hz, 1H), 5.72 (d, *J* = 13.0 Hz, 1H), 5.65 (d, *J* = 12.9 Hz, 1H), 5.54 (t, *J* = 3.6 Hz, 2H), 5.26 – 5.22 (d, 1H), 4.21 (d, *J* = 6.4 Hz, 1H), 4.19 – 4.14 (d, 1H), 4.13 – 4.09 (d, 1H), 2.17 (s, *J* = 2.9 Hz, 3H), 2.01 (m, *J* = 15.6, 3.0 Hz, 9H), 1.85 (s, *J* = 3.1 Hz, 3H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ = 170.27, 169.87, 169.74, 169.01, 162.58, 149.38, 148.64, 144.72, 142.88, 139.51, 134.77, 133.13, 132.82, 128.93, 128.16, 128.03, 127.93, 127.78, 126.70, 126.52, 125.36, 121.44, 120.67, 107.07, 74.00, 70.71, 67.80, 66.77, 61.11, 59.82, 20.55, 20.41, 20.14, 15.33 ppm; HRMS (ESI) *m/z*: calcd for $C_{40}H_{39}N_6O_{10}$ $[M+H]^+$ 763.2722, found 763.2661;



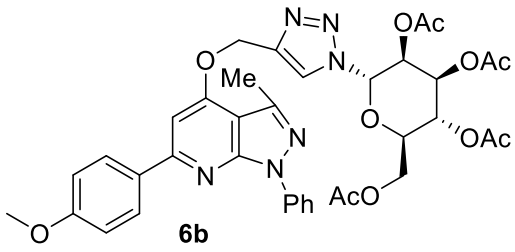
5i

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(4-(((6-(benzo[d][1,3]dioxol-5-yl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5i). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), yellow coloured solid: m.p. (110 °C); Yield (90%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 7.6 Hz, 2H), 7.94 (s, 1H), 7.52 (t, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 6.93 (s, 3H), 6.59 (s, 1H), 6.06 (s, 2H), 5.84 (d, *J* = 9.4 Hz, 1H), 5.67 (d, 1H), 5.60 (d, 1H), 5.53 (t, 2H), 5.23 (d, *J* = 12.6 Hz, 1H), 4.20 (d, *J* = 6.7 Hz, 1H), 4.16 (d, *J* = 5.4 Hz, 1H), 4.11 (d, *J* = 6.7 Hz, 1H), 2.18 (s, 3H), 2.01 (m, *J* = 13.4 Hz, 9H), 1.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.23, 169.84, 169.70, 168.96, 162.52, 149.32, 148.27, 148.07, 147.52, 144.69, 142.72, 139.46, 128.86, 125.29, 122.58, 121.39, 120.62, 110.52, 109.20, 108.11, 106.69, 101.32, 73.98, 70.68, 67.76, 66.74, 61.07, 59.71, 20.50, 20.36, 20.07, 15.32 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{37}N_6O_{12}$ $[M+H]^+$ 757.2464, found 757.2441;



6a

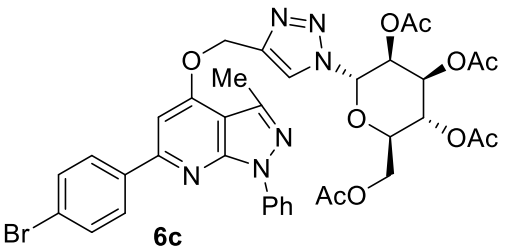
(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(4-(((6-(4-chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6a). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (85 °C); Yield (79%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 7.8 Hz, 1H),7.52 (s,1H), 7.51 (t, *J* = 7.1 Hz, 1H), 7.49 – 7.45 (d, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H),6.57 (s, 1H), 5.91 (s, *J* = 6.9 Hz, 1H), 5.71 – 5.63 (t, 1H), 5.42 (d, *J* = 10.6 Hz, 1H), 5.35 (d, 1H), 5.30 – 5.22 (d, 1H), 4.32 – 4.23 (d, 1H), 4.18 – 4.10 (d, 1H), 3.98 (d, *J* = 11.7 Hz, 1H), 2.23 (s, 3H), 2.15 (m, 9H), 2.01 (s, *J* = 16.4, 2.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.70, 170.40, 169.92, 169.28, 162.44, 149.23, 147.43, 144.53, 142.62, 139.29, 135.67, 134.98, 130.00, 128.55, 125.62, 123.64, 120.79, 110.32, 106.78, 72.11, 69.91, 68.65, 66.09, 61.34, 59.57, 20.83, 20.63, 20.59, 15.24 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}ClN_6O_{10}$ $[M+H]^+$ 747.2176, found 747.2528;



6b

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(4-(((6-(4-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6b). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), light yellow coloured solid: m.p. (100 °C);

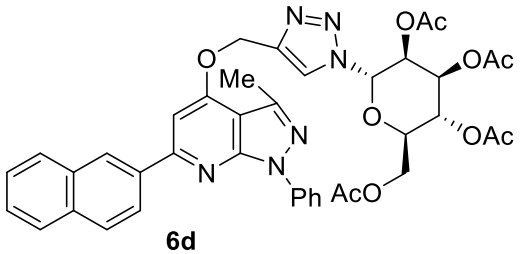
Yield (88%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.9 Hz, 2H), 7.79 (s, 1H), 7.52 – 7.49 (d, 2H), 7.40 (d, *J* = 6.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.57 (s, 1H), 5.93 (s, 2H), 5.69 (d, *J* = 10.6 Hz, 3H), 5.35 (t, *J* = 8.7 Hz, 1H), 5.26 (d, *J* = 20.0 Hz, 1H), 4.31 (d, *J* = 12.2 Hz, 1H), 4.25 (d, *J* = 10.7 Hz, 1H), 3.97 (d, *J* = 12.6 Hz, 1H), 3.88 (s, 3H), 2.27 (s, 3H), 2.15 – 2.04 (m, 9H), 2.02 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.61, 169.81, 169.78, 162.70, 160.30, 149.55, 148.89, 144.95, 143.16, 139.64, 130.24, 129.78, 129.12, 125.66, 123.82, 120.93, 113.90, 110.89, 106.83, 92.36, 83.71, 68.64, 66.31, 61.58, 59.73, 55.51, 20.85, 20.82, 20.74, 20.71, 15.59 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{39}N_6O_{11}$ $[M+H]^+$ 743.2671, found 743.2528;



6c

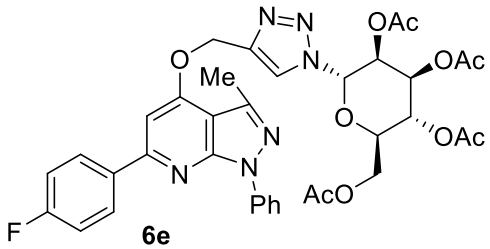
(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(4-(((6-(4-bromophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6c). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), off white coloured solid: m.p. (90 °C); Yield (81%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.33 (d, 1H), 7.52 (d, 1H), 6.57 (s, 1H), 5.92 (t, *J* = 5.9 Hz, 1H), 5.68 (d, *J* = 11.8, 2.4 Hz, 1H), 5.44 – 5.39 (d, 1H), 5.32 (d, *J* = 2.3 Hz, 1H), 5.30 – 5.27 (d, 1H), 5.24 (s, 1H), 4.24 (d, *J* = 2.3 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 4.01 – 3.96 (d, 1H), 2.14 (s, *J* = 15.0 Hz, 3H), 2.07 (m, *J* = 30.2 Hz, 9H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 171.74, 170.94, 170.32, 170.16, 169.95, 162.67, 149.45, 144.74, 142.84, 139.50, 136.36, 131.73, 130.50, 129.17, 125.85, 123.86, 123.39, 121.02, 106.94, 73.11, 70.09, 68.88, 68.66,

66.31, 62.72, 29.82, 20.86, 20.84, 15.47 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}BrN_6O_{10}$ $[M+H]^+$ 791.1671, found 791.1528;



6d

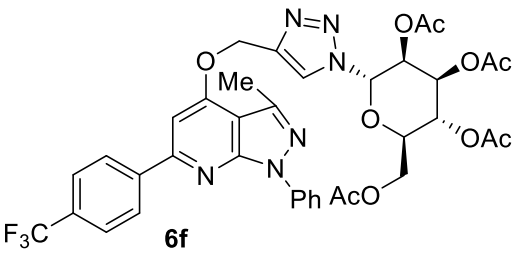
(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(4-(((3-methyl-6-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6d). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), off white coloured solid: m.p. (120 °C); Yield (85%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.4 Hz, 1H), 7.98 – 7.80 (m, 3H), 7.55 (d, *J* = 29.9 Hz, 3H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.71 (s,1H), 5.94 (s, 1H), 5.74 – 5.67 (t, 1H), 5.42 (d, *J* = 10.6 Hz, 1H), 5.29 (d, *J* = 15.3 Hz, 2H), 5.24 (s, 1H), 4.33 – 4.25 (d, 1H), 4.14 (d, 1H), 3.96 (d, *J* = 24.6 Hz, 1H), 2.16 (s, 3H), 2.07 (m, *J* = 31.4 Hz, 9H), 2.00 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 171.14, 170.51, 170.35, 170.15, 162.92, 149.74, 145.11, 139.82, 135.10, 133.56, 133.24, 129.37, 128.58, 128.20, 127.14, 126.88, 121.21, 107.47, 70.30, 69.09, 68.87, 66.52, 62.92, 60.01, 30.03, 21.26, 21.06, 15.72 ppm; HRMS (ESI) *m/z*: calcd for $C_{40}H_{39}BN_6O_{10}$ $[M+H]^+$ 791.1671, found 791.1528;



6e

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(4-(((6-(4-fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6e). The product was purified by silica column

chromatography (Ethyl acetate:Hexane 1:1), off white coloured solid: m.p. (90 °C); Yield (78%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.33 (d, 1H), 7.52 (d, 1H), 6.57 (s, 1H), 5.92 (t, *J* = 5.9 Hz, 1H), 5.68 (d, *J* = 11.8, 2.4 Hz, 1H), 5.44 – 5.39 (d, 1H), 5.32 (d, *J* = 2.3 Hz, 1H), 5.30 – 5.27 (d, 1H), 5.24 (s, 1H), 4.24 (d, *J* = 2.3 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 4.01 – 3.96 (d, 1H), 2.14 (s, *J* = 15.0 Hz, 3H), 2.07 (m, *J* = 30.2 Hz, 9H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 171.74, 170.94, 170.32, 170.16, 169.95, 162.67, 149.45, 144.74, 142.84, 139.50, 136.36, 131.73, 130.50, 129.17, 125.85, 123.86, 123.39, 121.02, 106.94, 73.11, 70.09, 68.88, 68.66, 66.31, 62.72, 29.82, 20.86, 20.84, 15.47 ppm; HRMS (ESI) *m/z*: calcd for $C_{36}H_{36}FN_6O_{10}$ $[M+H]^+$ 731.7139, found 731.7245;



6f

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(4-(((3-methyl-1-phenyl-6-(4-(trifluoromethyl)phenyl)-1*H*-pyrazolo[3,4-b]pyridin-4-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6f). The product was purified by silica column chromatography (Ethyl acetate:Hexane 1:1), off white coloured solid: m.p. (70 °C); Yield (75%), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 6.0 Hz, 1H), 7.81 – 7.73 (s, 1H), 7.55 (d, *J* = 37.2 Hz, 2H), 7.28 (d, *J* = 25.7 Hz, 1H), 6.60 (s, 1H), 5.95 – 5.87 (d, 1H), 5.71 – 5.63 (t, 1H), 5.42 (d, *J* = 10.8 Hz, 1H), 5.36 (d, 1H), 5.31 – 5.23 (s, 2H), 4.31 (d, 1H), 4.13 (d, *J* = 11.0 Hz, 2H), 3.98 (d, *J* = 11.0 Hz, 1H), 2.15 (s, 3H), 2.02 (m, *J* = 28.7 Hz, 9H), 1.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ =^{13}C NMR (151 MHz, $CDCl_3$) δ 170.72, 169.94, 169.73, 169.30, 162.43, 140.85, 142.48, 144.44, 147.02, 140.20, 139.23, 129.09, 128.97, 125.72, 125.28, 123.67, 120.84, 106.91, 69.90, 68.68, 68.42, 66.09, 62.50,

61.34, 20.83, 20.70, 20.64, 15.19 ppm; HRMS (ESI) *m/z*: calcd for $C_{37}H_{36}N_6O_{10}$ $[M+H]^+$ 781.2440, found 781.2328;

^{1}H NMR and ^{13}C NMR of pyrazolo[3,4-b]pyridine glucohybrids (4a)

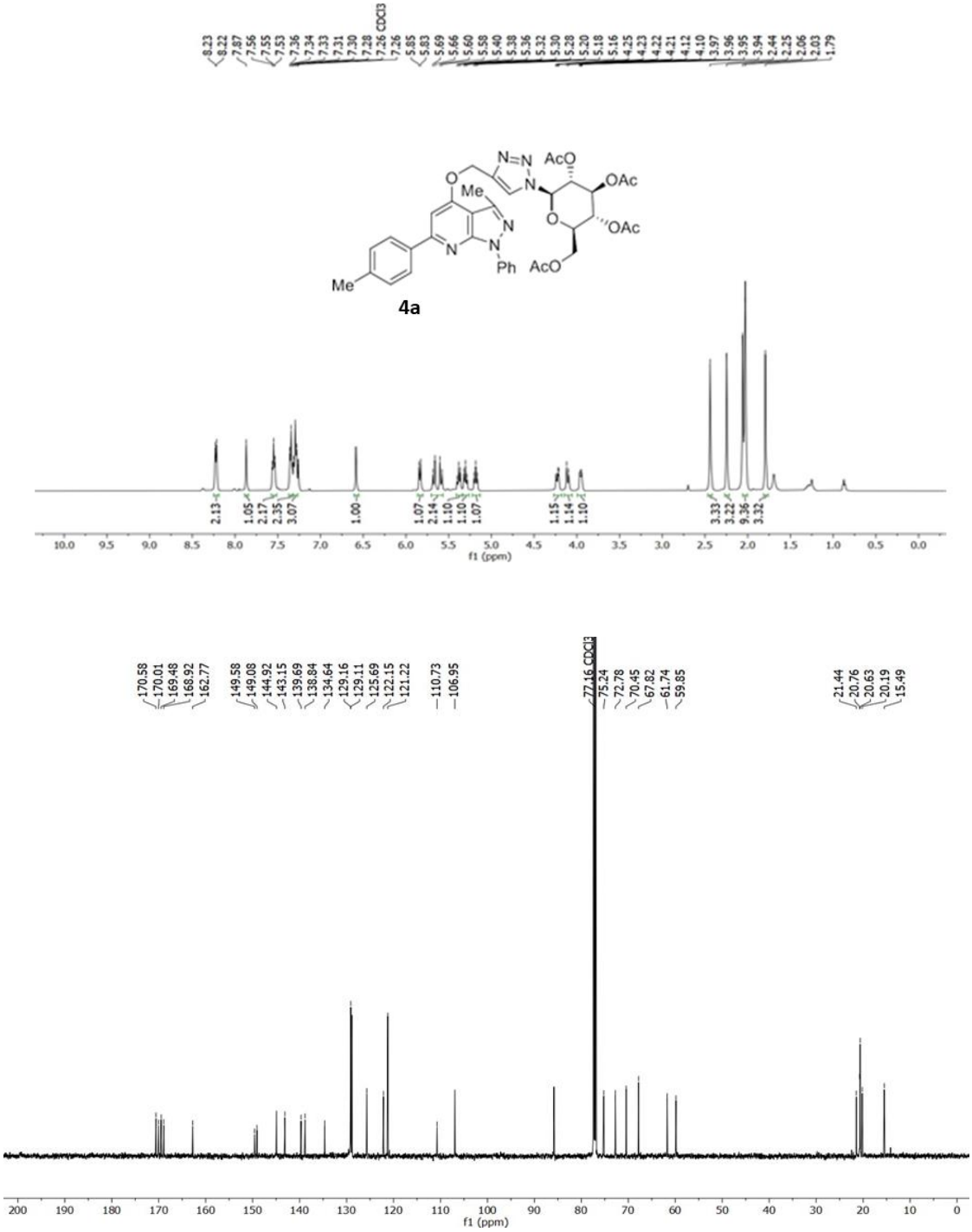


Figure 5.4 ^{1}H NMR and ^{13}C NMR spectra of compound 4a in $CDCl_3$

^{1}H NMR and ^{13}C NMR of pyrazolo[3,4-b]pyridine galactohybrids (5a)

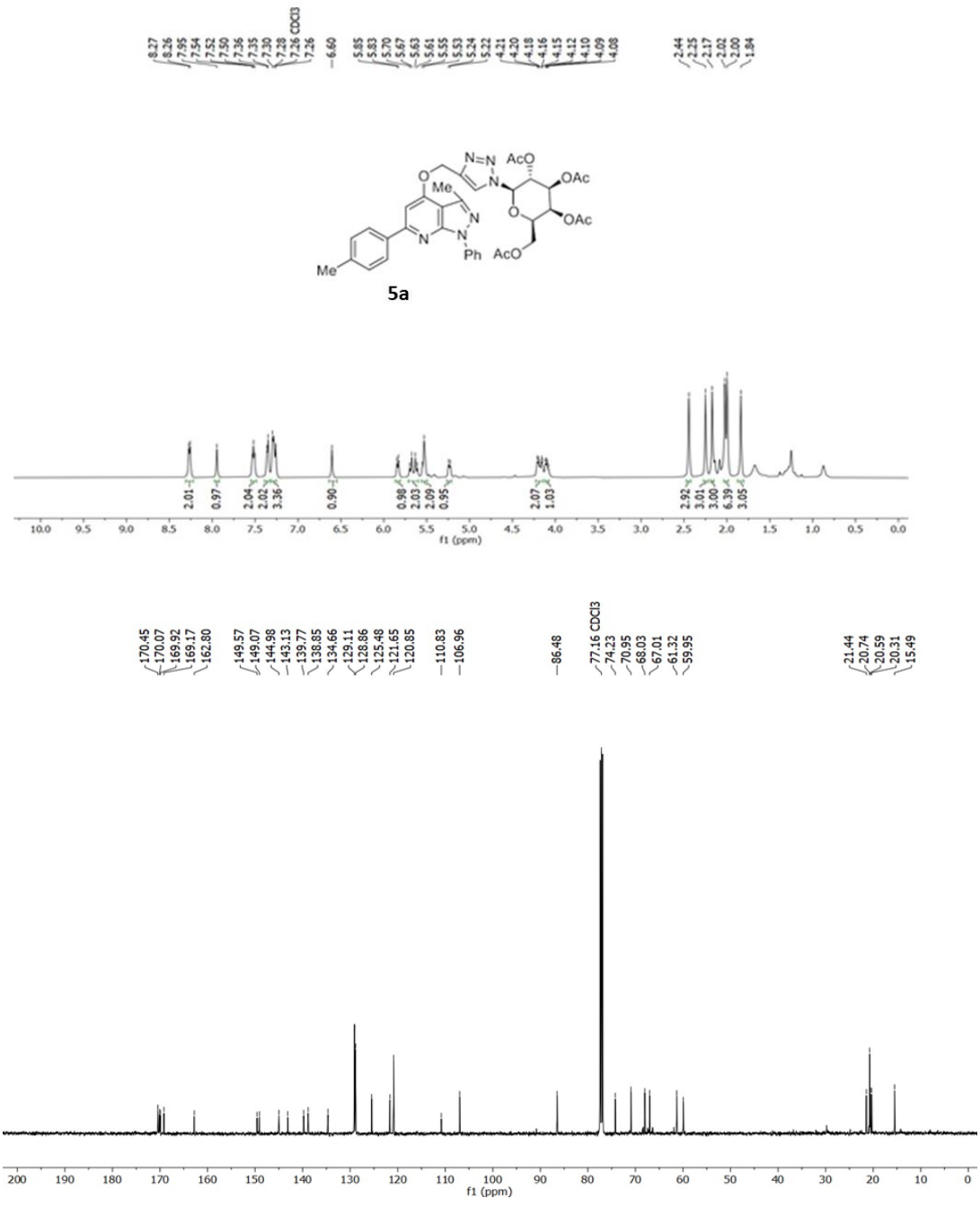


Figure 5.5 ^{1}H NMR and ^{13}C NMR spectra of compound 5a in $CDCl_3$

5.7 ^{1}H NMR and ^{13}C NMR of pyrazolo[3,4-b]pyridine mannohybrids (6a)

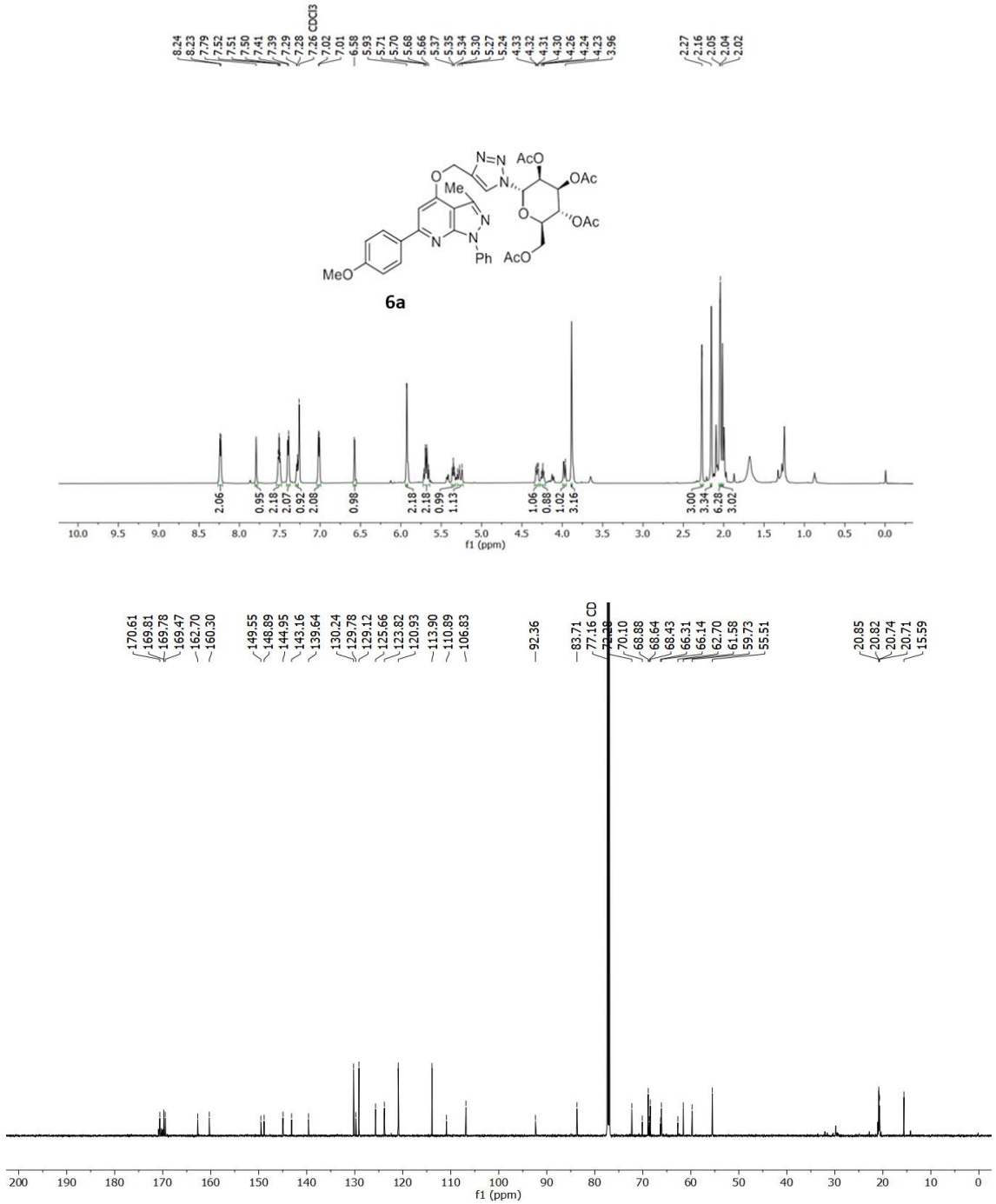


Figure 5.6 ^{1}H NMR and ^{13}C NMR spectra of compound 6a in $CDCl_3$

5.7 References

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