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Preparation of tri- and hexasubstituted triptycene synthons *via* transition metal-catalyzed cross-coupling for post-modifications.

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Abstract: Rational building strategies and appropriate synthons have been developed for the use of triptycene as a rigid presenting scaffold. Palladium catalyzed cross-coupling reactions such as, Sonogashira and Suzuki couplings were used to install a variety of different synthetic handles around the triptycene periphery in a high yielding and controlled manner. These triptycene molecular handles were investigated for their potential in the construction of molecular arrays with defined spatial orientation *e.g.*, for host-guest interactions or drug delivery systems. Such molecular synthons afforded expansion from the triptycene core employing arm extension increasing the internal free volume characteristic of triptycene scaffolds for such applications. In addition a range of mesogenic and glycosyl triptycene derivatives were achieved as a synthetic proof of concept for future work on potential drug delivery systems.

Introduction

Rigid molecular frameworks are required as scaffolds for a variety of applications. In this regard, triptycenes are a unique family of homoconjugated aromatic compounds consisting of three separate arene units fused together through a bicyclic [2.2.2] octane framework. Their three dimensional structure offers a scaffold with a well-defined spatial arrangement and substantial internal free volume (IFV). Several reactive positions for functionalization and open electron-rich cavities exist around the periphery, all affording several prospective applications not exploited until after the 1980's. Examples include molecular machines,[1] supramolecular chemistry,[2] electron transfer,[3] anti-cancer,[4] and sensor[5] applications. Over the last two decades, advancement in the synthetic protocols and functional appendages of iptycenes coincided with the development of such applications concisely reviewed by Jiang and Chen[6a] and Zhao *et al.*[6b]

Despite their rigidity, symmetry and ability to project groups in a spatially defined manner, the use of triptycene derivatives as scaffolding material is limited particularly in the area of C-C bond forming reactions.[6b] Synthetic methods to tri- and hexahalogenated triptycenes are now well established; however, there is a general lack of manipulation of such precursors to provide versatile molecular handles.[7]

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Considering post-functionalization of triptycene scaffolds, triiodotriptycene (**1a/b**), tribromotriptycene (**2a/b**)[7b] and hexabromotriptycene (**3**)[7a] offer a good platform for transition metal (TM) catalyzed reactions affording a niche in triptycene research scarcely reported (Figure 1). Such useful modern synthetic methods have been explored for mono-, di- and trisubstituted triptycenes. Following the construction of 2,6,14- and 2,7,14-triiodotriptycenes by Zhang and Chan in 2006,[7b] two interesting examples of TM-catalyzed cross-coupling reactions were developed. The first of which was the synthesis of a 2,7,14-trialkynyltriptycene derivative from the 2,7,14-triiodo (**1b**) precursor *via* Sonogashira coupling reactions and subsequent deprotection, which was subject to Glaser coupling, thus affording a dimeric molecular cage structure with a microporous cavity.[8] These trisubstituted conjugates were a prequel to work conducted by our group, using 2,6,14-triiodotriptycene as a coupling partner for porphyrin scaffolds in both TM-catalyzed Suzuki and Sonogashira cross-coupling reactions which were investigated for their host-guest properties with the bidentate ligand, 4,4'-bipyridine (bipy).[9] Sonogashira couplings have also been recently examined by Chakraborty *et al.* for the installation of trisubstituted alkyne residues onto the triptycene scaffold from tribromotriptycenes (**2a/b**) for further conversion to carboxylic acids or phosphine residues for applications as chemosensors and DNA binding experiments.[10] While the use of Suzuki coupling reactions have predominantly focused on the preparation of π-extended triptycene platforms [11a] and metallotrispirane nano-complexes[11b] in recent times.
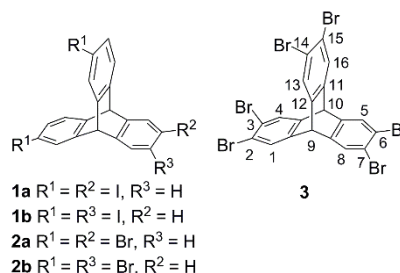

Figure 1. Tri- and hexahalogenated triptycenes.

Considering the investment in three-fold systems, only limited examples have been explored in the higher order substitutions such as hexanitro- or hexaaminotriptycene,[12] hexahydroxytriptycene[13] and hexabromotriptycene (**3**).[7a] A general lack of modern synthetic methods on higher order substituted triptycenes has provided few useful synthons for expansion from the core and has limited the scope of potential for a multitude of arrays around the periphery. In continuation of previous work within our group the aim of this research was to synthesize a number of highly functionalized triptycene scaffolds predominantly with TM-catalyzed coupling reactions affording interesting molecular synthons that can undergo a range of

substitutions. In addition, we provide select examples of potential post-modification including expanding the IFV and incorporating bioconjugates in the guise of carbohydrate units to highlight the synthetic potential of such functionalized triptycenes to expand the scope of the field.

Results and Discussion

In terms of halogenated triptycenes, there are two derivatives, triiodotriptycene (**1a**) and hexabromotriptycene (**3**) which are pivotal building blocks to this research.[7] As mentioned previously, in 2006 Zhang and Chan reported the synthesis of 2,6,14- and 2,7,14-triiodotriptycenes (**1a/b**) by nitrating the triptycene scaffold, followed by reduction to the amino groups and ultimately a Sandmeyer reaction affords the iodo derivative (**1a/b**).[7b] King *et al.* also provided significant advancement in this field through the synthesis of hexabromotriptycenes (**3**) bearing either hydrogen, or alkyl moieties at the bridgehead carbon atoms.[7a] It was conceived that these halogenated triptycene scaffolds would act as excellent coupling partners in Suzuki and Sonogashira cross-coupling reactions (Figure 2) and help update work previously established within the group *i.e.* the synthesis of triptycene-porphyrin trimers,[9] to include tri- and hexasubstituted triptycene derivatives with increased IFV and bioconjugation.
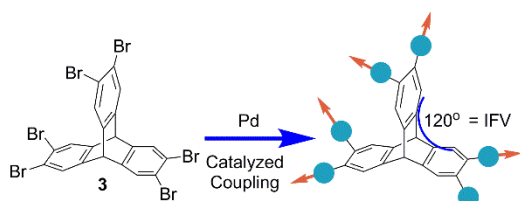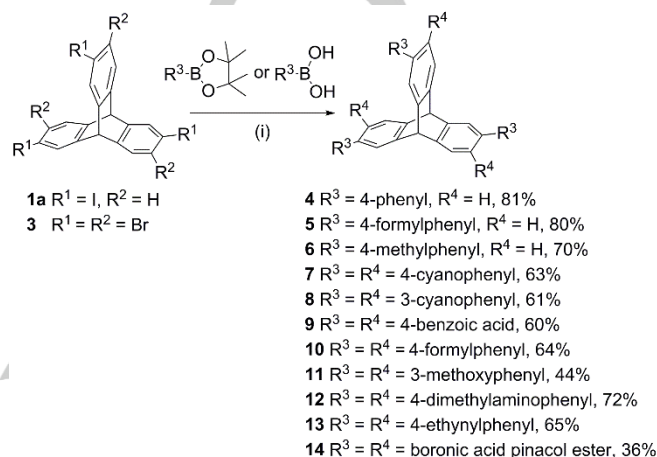

Figure 2. Potential synthetic pathway to yield functionalized triptycene scaffolds.

Suzuki Coupling Reactions

Initial investigations focused on the attainment of tri- and hexasubstitution triptycenes with functionalized arms through Suzuki coupling reactions aimed at allowing additional chemical manipulation for further functionalization, *i.e.* arm extensions (increasing the IFV) or even cylcoaddition reactions. A screen of boronic acids/esters was conducted in order to investigate the viability and robustness of this synthetic pathway with large equivalents required to promote conversion to the desired product. Starting with routine Suzuki reaction conditions *i.e.* Pd(PPh$_3$)$_4$ and K$_3$PO$_4$/Cs$_2$CO$_3$ as our base, we attempted the three- and six-fold introduction of substituted aryl moieties around the triptycene periphery.[14] We found the reaction conditions described in Scheme 1 to be quite tolerable of a variety of different functional groups and our only required optimization came in the guise of increased equivalents of the boronic acids/esters and the nature of the base and solvent used. A comprehensive report on reaction equivalents is given in Table **S1** in the supporting information (SI).

This synthetic pathway has proved itself to be extremely robust in producing tri- and hexafunctionalized triptycene scaffolds **4**-**14** in good yields whilst allowing for the presence of distal functional

groups that can be implemented in further reactions. The synthetically versatile groups present in our screen in particular **9**, **10**, **13** and **14** can be used in a wide assortment of chemical transformations and applications. For example, scaffold **9** with the six carboxylic acid functionalities shows promise as a molecular scaffold in the ever expanding field of metal-organic frameworks and due to the inherent structural rigidity of the triptycene scaffold, some unique and interesting results may prevail from this field. Also, we envisage scaffold **13** as a potentially excellent coupling partner in Glaser coupling reactions or cycloaddition chemistry.

1a R^1 = I, R^2 = H
3 R^1 = R^2 = Br

4 R^3 = 4-phenyl, R^4 = H, 81%
5 R^3 = 4-formylphenyl, R^4 = H, 80%
6 R^3 = 4-methylphenyl, R^4 = H, 70%
7 R^3 = R^4 = 4-cyanophenyl, 63%
8 R^3 = R^4 = 3-cyanophenyl, 61%
9 R^3 = R^4 = 4-benzoic acid, 60%
10 R^3 = R^4 = 4-formylphenyl, 64%
11 R^3 = R^4 = 3-methoxyphenyl, 44%
12 R^3 = R^4 = 4-dimethylaminophenyl, 72%
13 R^3 = R^4 = 4-ethynylphenyl, 65%
14 R^3 = R^4 = boronic acid pinacol ester, 36%

Scheme 1. Suzuki cross-coupling reaction of aryl boronic acids/esters with 2,6,14-triiodotriptycene (**1a**) or 2,3,6,7,14,15-hexabromotriptycene (**3**). (i) Cs$_2$CO$_3$ or K$_3$PO$_4$ or K$_2$CO$_3$, Pd(PPh$_3$)$_4$, toluene/EtOH/H$_2$O (6:4:2, v/v/v) or THF, reflux.

Following the success of the six-fold introduction of aryl moieties through optimized Suzuki methodology, we expanded such investigations to examine the possibility of applying these optimized conditions to the reaction of simple alkyl boronic acids – historically a much more challenging reaction.[15,16] Unfortunately, the reaction conditions optimized previously were unsuccessful in obtaining the target derivatives with the reaction mixture consisting of mainly debrominated starting material. Due to this we decided to investigate catalysts more tolerant of alkyl functionalities. From previous literature, dichloro[1,1'-bis(diphenylphosphino)ferrocene] palladium(II), [Pd(dppf)Cl$_2$] stood out as being widely applicable to such reactions as its large bite angle favors reductive coupling over β-hydride elimination.[15-17] This catalyst system proved quite efficient at generating hexasubstituted alkyltriptycenes in moderate yield (Scheme 2). While the yields are significantly lower than couplings with aryl substituents, we feel that this successful addition of alkyl substituents still highlights the robustness and versatility of the procedure, allowing one-pot generation of a wide variety of highly substituted systems.
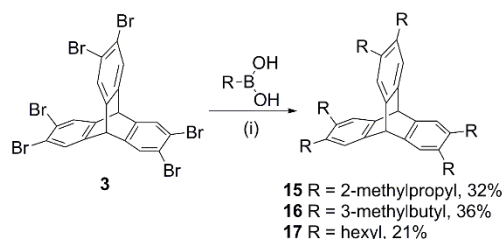
Scheme 2. Suzuki cross-coupling reaction of alkyl boronic acids with hexabromotriptycene. (i) Cs$_2$CO$_3$, Pd(dppf)Cl$_2$, THF, 80 °C.

Sonogashira Coupling Reactions

After establishing the scope of Suzuki cross-coupling reactions, other TM-catalyzed reactions were investigated to identify if the preparation of tri- and hexafunctionalized compounds was sustainable. Focusing efforts specifically on palladium catalyzed reactions, the Sonogashira reaction has its advantages, with significant applicability and further chemical manipulation, though substantially more challenging than the Suzuki reaction.[18] Sonogashira reactions install alkyne residues *via* coupling of organohalides and alkynes, for potential couplings in cycloaddition reactions, additional Sonogashira or Glaser couplings affording a dynamic methodology in organic chemistry clearly outlined by Chinchilla and Nájera.[18b,c] With regard to triptycene, induction of synthons such as alkyne groups preserve the angular projection of such distal groups as well as maintaining the rigidity inferred in the triptycene core and providing platforms for potential further functionalization with extended conjugation.

Studies with trialkyne triptycene systems have been previously reported by Chakraborty and co-workers, coupling triiodotriptycenes and TMS-acetylene *via* Sonogashira cross-coupling reactions in good yield.[10b] The advantage of using the iodo group is its facile reactivity in Sonogashira reactions. Implementing similar conditions to the reported literature afforded **18**, and the subsequent synthesis of 2,6,14-triethynyltriptycene (**20**) was achieved with immediate deprotection using a large excess of tetra-*n*-butylammonium fluoride (TBAF) in 75% yield (Scheme 3).
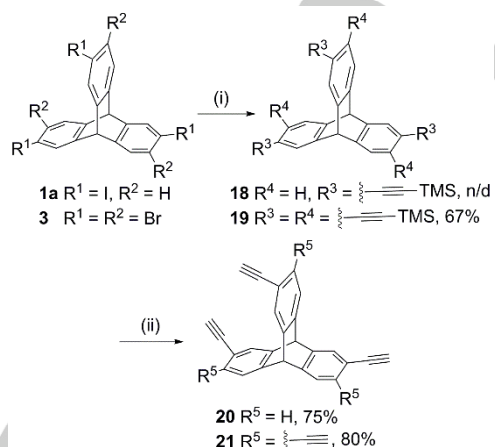
Scheme 3. Synthesis of 2,6,14-triethynyltriptycene and 2,3,6,7,14,15-hexaethynyltriptycene. (i) TMS-acetylene, Pd(PPh$_3$)$_2$Cl$_2$, PPh$_3$, CuI, TEA, 70 °C, 17/18 h; (ii) TBAF, CH$_2$Cl$_2$, 25 °C, 6/13 h.

Having optimized conditions for the installment of three-fold substitution around the periphery of the triptycene scaffold, synthesis of hexaethynyltriptycene from the hexabromo derivative (**3**) ensued. Similar reaction conditions were employed for the installation of six-fold substitution around the triptycene. Conducting the coupling reaction of **3** and TMS-acetylene in neat TEA *as per* Scheme 3 afforded **19a** in a good yield of 67%. An optimization of the reaction conditions was also conducted to increase the the yield, however, showed limited progression (Table S2 in Supporting information). Subsequent deprotection of the trimethylsilyl groups was achieved with TBAF in THF at 25 °C for 13 h affording 2,3,6,7,14,15-hexaethynyltriptycene **21** in 80% yield. These alkyne moieties grant further functionalization prospects with rigid extensions protruding from the core increasing the IFV. Further elongation of the appendage could therefore, afford elaborate IFV formed by the concave sides between the aromatic rings and may allow for further studies into host guest or molecular rector applications.[1b,2b,19]

Post-modified Prototypes

The new synthetic pathways to tri- and hexasubstituted triptycenes offer a scaffold system in which the periphery can be further manipulated to both extend from the core and/or use such systems as an anchor for multivalent arrays. Illustration of such post-functionalization were conducted *via* "arm" appendage extension and Huisgen "click" cycloaddition reactions[20a,b] discussed in detail herein.

Arm Extended Triptycenes – Potentially Increasing IFV. Increasing the extension of the triptycene periphery has previously been achieved by expanding the arene blades,[7a.12c,21] conjugation *via* alkynes[8] and crown ethers[2a] to name a few. The strength of such a feature has been exploited in host guest chemistry,[2a,22,23] molecular cage formation[8] and complex iptycene construction.[19] The primary focus was on tailoring the synthetic route to afford an alternative route to increasing the blade extension. Given that the optimized Sonogashira reaction conditions offered a high yielding method for extending the conjugation of the triptycene, a rational approach conceded to such methodology.

To investigate the original Sonogashira conditions (Scheme 3) for this application, an elongated appendage with a terminal alkyne was required. Similar extended conjugated systems have previously been employed in light harvesting and charge transfer systems.[24] Adapting the procedure developed by Weil *et al*.,[24c] the appendage **24** was synthesized *via* initial Sonogashira coupling of TIPS-acetylene and **22** in dry toluene at room temperature affording **23** in 75% yield. The TMS moiety in compound **23** was selectively deprotected in basic conditions with 1M KOH in THF, proving more labile then the TIPS group. Thus, with the arm appendage **24** readily accessible, Sonogashira coupling using similar conditions to the synthesis of **19a** were implemented. Compound **3** was coupled with **24** in the presence of Pd(PPh$_3$)$_2$Cl$_2$ (0.6 eq.), PPh$_3$ (1.2 eq.) and CuI (0.3 eq.) in TEA (7 mL) for 24 h with the addition of THF (2 mL) to improve solubility thus, affording the hexaconjugate **25**. Immediate deprotection using TBAF in THF at 25 °C for 12 h afforded **26** in 31% yield. From the success of this initial synthetic pathway, future work will be invested in the preparation

of larger arm extended triptycenes and examined for potential host-guest interactions.
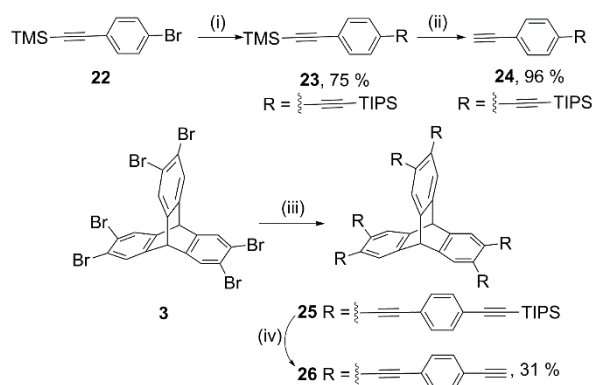

Scheme 4. Synthesis of the arm-extended triptycene **26** *via* Sonogashira coupling reactions and subsequent deprotection. (i) TIPS-acetylene, Pd(PPh₃)₂Cl₂, PPh₃, CuI, toluene/TEA, 25 °C, 24 h; (ii) NaOH, THF/EtOH, 25 °C, 1 h; (iii) **24**, Pd(PPh₃)₂Cl₂, PPh₃, CuI, TEA, 70 °C, 24 h; (iv) TBAF, THF, 25 °C, 24 h.

Mesogenic and Glycosyl Triptycenes. One of the long term goals of this triptycene research is to obtain scaffold systems with distal appendages that could be readily functionalized with a plethora of molecules from light harvesting arrays to bioconjugates. With this in mind, the second application that will be considered is the potential of triptycenes 3D structural characteristics and their advantages in drug delivery systems. Most drugs, both under development or established therapeutics distribute non-specially within the human body interacting both with healthy and pathological cells ultimately resulting in reduced efficacy. Using targeting strategies for drug delivery such as the use of a drug delivery vector encompassing a drug and multivalent targeting units has the potential to improve pharmacokinetic properties.

One such approach to glyco-therapeutics includes the use of drug delivery systems, consisting of glycosylated frameworks with a cluster of saccharide units for targeting and bioavailability, partnered with a pro-drug derivative for delivery. In nature clusters of carbohydrates are inferred on cellular structures with a bloom of potential binding sites of which distance between such substrates is paramount for cell-cell interactions and lectin active sites.[25] There is a limitation of molecular handles with 3D orientations to mimic such complex structures found in nature. One potential structure that opens avenues to these types of arrays is triptycene. Drawing from extensive work previously invested in selective microwave assisted "click" chemistry[20c] previously conducted in our group, similar success was anticipated for triptycene.

Mesogenic Triptycenes. With the alkyne substituted systems **20** and **21** to hand, attention turned to the post-functionalization potential of such conjugates. As a proof of concept the preparation of mesogenic triptycene derivatives were investigated *via* 1,3-dipolar cycloaddition of 1-azidoalkane to the trialkyne system **20** similar to those previously prepared by Suzuki coupling (Scheme 2). Implementing similar reaction conditions as previously reported for glycosylated porphyrin derivatives within our group,[20c,d] three-fold 1,3-dipolar cycloaddition of triptycene **20** was achieved in 89% yield by

microwave-assisted conditions with 1-azidononane in the presence of [Cu(CH₃CN)₄][PF₆] (0.35 eq.) in degassed DMF (8 mL) at 115 °C for 30 minutes.
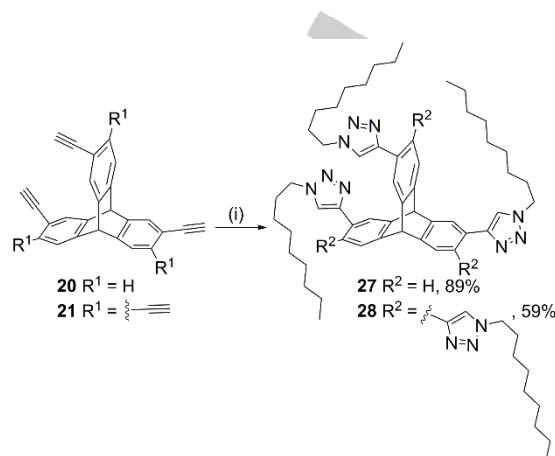
Scheme 5. Synthesis of tri- and hexamesogenic triptycenes *via* 1,3-dipolar cycloaddition chemistry. (i) 1-azidononane, [Cu(CH₃CN)₄][PF₆], DMF, 115 °C, microwave, 30/60 minutes.

With success afforded to the three-fold system, slight alterations to reaction times were investigated for conversion to hexafunctionalization. Compound **21**, 1-azidononane and [Cu(CH₃CN)₄][PF₆] (2.4 eq.) were dissolved in degassed DMF (8 mL) and subject to microwave heating conditions at 115 °C for 70 minutes affording successful preparation of the hexasubstituted derivative **28** in 59% yield.

Glycosyl Triptycenes.
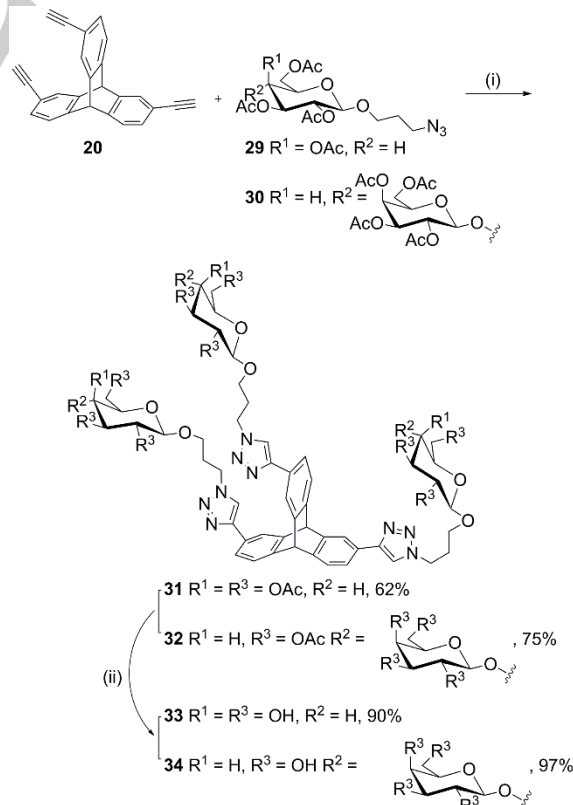
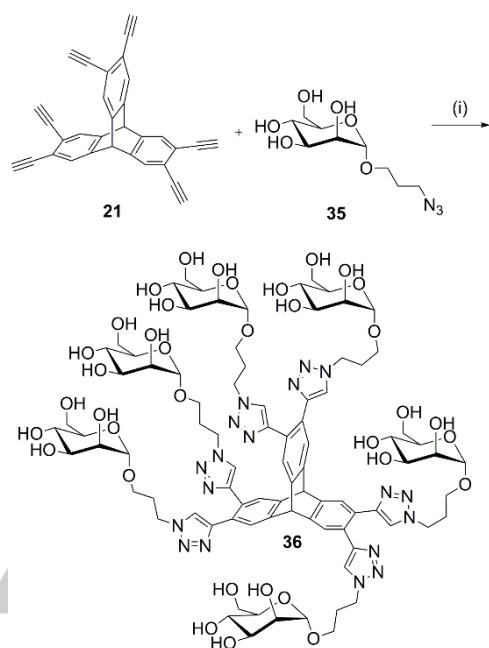**Scheme 6.** Synthesis of triglycosyltriptycenes *via* 1,3-dipolar cycloaddition reactions. (i) [Cu(CH₃CN)₄][PF₆], DMF, 115 °C, microwave, 30 minutes; (ii) NaOMe, MeOH, 25 °C, 2 h.

Scheme 7. Attempted synthesis of deprotected hexaglycosyltriptycene *via* 1,3-dipolar cycloaddition reactions. (i) [Cu(CH₃CN)₄][PF₆], MeOH/H₂O, 115 °C, microwave, 60 minutes.

Next, attention was reverted to glycosyl units as substrates for such systems. For direct binding comparisons of mono- and disaccharide units in a multivalent unit presented at fixed distances to a lectin, *D*-galactose and *D*-lactose (containing a terminal *D*-galactose moiety) were enlisted. Their similarity and binding potential to Galectins which have been proven to be over-expressed on malignant cells could afford interesting comparable results.[26]

Both azido glycosyl substrates **29** and **30** were synthesized *via* previously reported protocol from the peracetylated glycosides.[27] Using the same procedure as tailored for **27**, the successful synthesis of **31** and **32** in 62% and 75% yields, respectively, was accomplished. The reaction proceeded without complication and afforded one product which proved facile to purify by column chromatography.

The acetyl protecting groups provide improved solubility in organic solvents and ease in column chromatography during purification, however, they impede the natural binding of saccharide units to lectins. Thus, for future lectin binding studies the acetyl groups were removed *via* classic Zemplén deprotection methods,[28] affording **33** and **34** in 90% and 97% respectively. Solubility tests were conducted on the two conjugates concluding both to be soluble in CH₃OH:H₂O (4:1, v:v) while **34** proved to be more soluble than **33** in CH₃OH:H₂O (1:1, v:v). Such trisubstituted conjugates could prove ideal core molecules for coupling with drug conjugates as delivery/targeting vectors with such solubility characteristics affording [3+3]-systems. This approach would impact on drug dosage with three drug molecules introduced at the same time into a cell. They nevertheless pose a significant medicinal potential as delivery agents if the substitution can be controlled by desymmetrization with further investigations.

Hexaglycosylated triptycenes would offer an interesting comparative study with regard lectin binding as well as the potential of desymmetrization affording pentaglycosylated triptycene with one therapeutic agent. Initial work on the hexaglycosylated derivatives proved positive with the preparation of the deprotected mannosyl triptycene conjugate **36** confirmed by high resolution mass spectrometry. Unfortunately, efforts to isolate this material for characterization proved futile in agreement with findings detailed in a recent publication by Bonaccorsi and co-workers when examining similar glycosylated triptycene conjugates.[29]

Conclusions

In conclusion, we have successfully synthesized a library of tri- and hexasubstituted triptycene building blocks through the use of TM-catalyzed cross-coupling reactions *i.e.*, Suzuki and Sonogashira couplings. The first examples of one-pot hexafunctionalization *via* Suzuki cross-coupling to a triptycene scaffold with several different functionalities are reported. Through these newly developed methodology we have been successful in installing synthetic handles upon which further functionalization reactions may occur.

These highly substituted derivatives may be implemented as synthetic scaffolds in future reactions for applications such as metal-organic frameworks, light-harvesting arrays and drug-delivery vehicle. Preliminary examples of such applications have been investigated including arm extension for increased IFV in host guest applications as well as bioconjugation for potential development of drug delivery systems with positive results. These applications are currently undergoing further investigations.

Experimental Section

General Remarks: All commercial chemicals used were of analytical grade and supplied by Sigma Aldrich, Frontier Scientific and Acros chemicals and used without further purification. ¹H and ¹³C NMR spectra were recorded on an Agilent 400-NMR (400 MHz for ¹H NMR; 100 MHz for ¹³C NMR) and Bruker Advance 400 and 600 spectrometer ¹H (400 MHz for ¹H NMR; 100 & 150 MHz for ¹³C NMR). NMR was carried out at room temperature with deuterated solvent indicated in each case. Photophysical measurements were carried out in CH₂Cl₂. UV-vis absorption measurements were performed with a Specord 250 spectrophotometer. HRMS spectra were measured on MALDI-Q-Tof Premier Micromass and Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray ionization source (ESI). Melting points were acquired on a Stuart SMP-10 melting point apparatus and are uncorrected. Microwave reactions were carried out in a Biotage® Initiator microwave reactor. Specific rotation was recorded in a Rudolph research autopol IV polarimeter with a D-line sodium lamp (589 nm) at 20 °C and are quoted as deg.cm³.g⁻¹.dm⁻¹ Thin layer chromatography (TLC) was performed on silica gel 60 (fluorescence indicator F254; Merck) pre-coated aluminium sheets and visualized by either UV irradiation or molybdenum staining [solution of ammonium molybdate (7.5 g, H₂SO₄ (7.8 mL) and H₂O (150 mL)]. Flash chromatography was carried out using Fluka Silica Gel 60 (230-400 mesh). 2,6,14-Triiodotriptycene (**1a**), hexabromotriptycene (**3**),

1-azido nonane, 3'-azidopropyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranoside, 3-azidopropyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside and 3'-azidopropyl α-*D*-mannopyranoside were synthesized by known methodologies and had analytical data consistent with the literature.[7,27,30,31] Compounds **23** and **24** were prepared as reported in documented literature.[24c]

General procedure for Pd-catalyzed three-fold Suzuki coupling of 1a with aryl organoboron reagents: A 25 mL Schlenk tube equipped with a stirring bar and rubber septum was flushed for 10 minutes with argon gas and charged with 2,6,14-triiodotriptycene **1a** (50 mg, 79 μmol, 1 eq.) and K_3PO_4 or K_2CO_3 (12 eq.) and dried under vacuum. The mixture was dissolved in toluene/EtOH/H_2O (1.2:0.8:0.4 mL) and was degassed *via* three freeze-pump-thaw cycles and was placed under argon. Boronic acid (6 eq.) and Pd(PPh$_3$)$_4$ (28 mg, 24 μmol, 0.3 eq.) were added and the mixture was heated with stirring at reflux under argon atmosphere for 17 h. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (10 mL). The crude product was washed sequentially with sat. aq. $NaHCO_3$ (20 mL), deionized H_2O (20 mL) and brine (20 mL). The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the crude product was purified by column chromatography.

2,6,14-Triphenyltriptycene (**4**). This compound was prepared *via* the general procedure above using K_3PO_4 (201 mg, 0.95 mmol, 12 eq.), Pd(PPh$_3$)$_4$ (28 mg, 24 μmol, 0.3 eq.), 4-phenyl boronic acid (57 mg, 0.47 mmol, 6 eq.). The crude product was purified by column chromatography on silica gel (EtOAc:*n*-hexane = 1/49, v/v) and gave the pure product as white solid of **4** (31 mg, 64 μmol, 81%). mp = 115-116 °C; R_f = 0.22 (EtOAc:*n*-hexane = 1/49, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.70 (br s, 3H, Ar-*H*), 7.54 (m, 9H, Ar-*H*), 7.43 (t, *J* = 7.4 Hz, 3H, Ar-*H*), 7.34 (app-t, *J* = 7.3 Hz, 6H, Ar-*H*), 7.29 (m, 3H, Ar-*H*), 5.63 (s, 1H, bridgehead-*H*), 5.61 (s, 1H, bridgehead-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 145.7, 144.1, 141.3, 138.8, 128.7, 127.2, 127.1, 124.3, 123.9, 122.9, 54.1, 53.6 ppm; HRMS (APCI) *m/z* calcd. for [C$_{38}$H$_{27}$] (M$^+$): 483.2107; found 483.2097.

2,6,14-Tris(4-formylphenyl)triptycene (**5**). This compound was prepared *via* the general procedure above using K_2CO_3 (131 mg, 0.95 mmol, 12 eq.), Pd(PPh$_3$)$_4$ (28 mg, 24 μmol, 0.3 eq.), 4-formylphenyl boronic acid (71 mg, 0.47 mmol, 6 eq.). The crude product was purified by column chromatography on silica gel using 15-30% EtOAc in *n*-hexane and gave the pure product as white solid of **5** (36 mg, 63 μmol, 80%). mp decomposition at 220 °C; R_f = 0.25 (EtOAc/*n*-hexane = 3:7, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.04 (s, 3H, C*H*O), 7.92 (d, *J* = 8.2 Hz, 6H, Ar-*H*), 7.74 (br s, 3H, Ar-*H*), 7.69 (d, *J* = 8.2 Hz, 6H, Ar-*H*), 7.57 (d, *J* = 7.7 Hz, 3H, Ar-*H*), 7.33 (d, *J* = 7.7 Hz, 3H, Ar-*H*), 5.67 (s, 1H, bridgehead-*H*), 5.65 (s, 1H, bridgehead-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 191.9, 147.0, 145.6, 144.9, 137.5, 135.1, 130.3, 127.7, 124.9, 124.4, 123.0, 54.0, 53.6 ppm; HRMS (APCI) *m/z* calcd. for [C$_{41}$H$_{27}$O$_3$] (M$^+$): 567.1955; found 567.1947.

2,6,14-Tris(4-methylphenyl)triptycene (**6**). This compound was prepared *via* the general procedure above using K_2CO_3 (131 mg, 0.95 mmol, 12 eq.), Pd(PPh$_3$)$_4$ (28 mg, 24 μmol, 0.3 eq.), 4-methylphenyl boronic acid (64 mg, 0.47 mmol, 6 eq.). The crude product was purified by column chromatography on silica gel (EtOAc:*n*-hexane, 1/49, v/v) and gave the pure product as white solid of **6** (29 mg, 55 μmol, 70%). mp = 117-118 °C; R_f = 0.18 (EtOAc/*n*-hexane = 1:49, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.64 (br s, 3H, Ar-*H*), 7.47 (d, *J* = 7.7 Hz, 3H, Ar-*H*), 7.41 (d, *J* = 8.2 Hz, 6H, Ar-*H*), 7.21 (m, 9H, Ar-*H*), 5.57 (s, 1H, bridgehead-*H*), 5.55 (s, 1H, bridgehead-*H*) 2.37 (s, 9H, C*H$_3$*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 145.8, 143.9, 138.7, 138.4, 136.8, 129.4, 127.1, 124.0, 123.9, 122.6, 54.1, 53.6, 21.1 ppm; HRMS (APCI) *m/z* calcd. for [C$_{41}$H$_{33}$] (M$^+$): 525.2577; found 525.2583.

General procedure for Pd-catalyzed six-fold Suzuki coupling of 3 with aryl organoboron reagents: A 25 mL Schlenk tube equipped with

a stirring bar and rubber septum was flushed for 10 minutes with argon gas and charged with hexabromotriptycene **3** (50 mg, 69 μmol, 1 eq.) and K_3PO_4 or Cs_2CO_3 (15-30 eq.) and dried under vacuum. The mixture was dissolved in anhydrous THF (5 mL) and was degassed *via* three freeze-pump-thaw cycles and was placed under argon. Boronic acid/ester (12-30 eq.) and Pd(PPh$_3$)$_4$ (0.3-1.2 eq.) were added and the mixture was heated with stirring at 65 °C under argon atmosphere for 17-18 h. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (10 mL). The crude product was washed sequentially with sat. aq. $NaHCO_3$ (20 mL), deionized H_2O (20 mL) and brine (20 mL). The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the crude product was purified.

2,3,6,7,14,15-Hexakis(4-cyanophenyl)triptycene (**7**). This compound was prepared *via* the general procedure above using Cs_2CO_3 (336 mg, 1.03 mmol, 15 eq.), Pd(PPh$_3$)$_4$ (24 mg, 20 μmol, 0.3 eq.), 4-cyanophenyl boronic acid (131 mg, 0.89 mmol, 13 eq.). The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:2, v/v) and gave the pure product as white crystals of **7** (38 mg, 43 μmol, 63%). mp >300 °C; R_f = 0.38 (CH$_2$Cl$_2$/*n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.55 (s, 6H, Ar-*H*), 7.49 (d, *J* = 8.0 Hz, 12H, Ar-*H*), 7.12 (d, *J* = 8.0 Hz, 12H, Ar-*H*), 5.73 (s, 2H, bridgehead-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.5, 144.2, 136.1, 129.9, 125.8, 117.9, 110.7, 52.4 ppm; HRMS (ES+) *m/z* calcd. for [C$_{62}$H$_{32}$N$_6$Na] (M+Na$^+$): 883.2586; found 883.2604.

2,3,6,7,14,15-Hexakis(3-cyanophenyl)triptycene (**8**). This compound was prepared *via* the general procedure above using Cs_2CO_3 (290 mg, 0.89 mmol, 13 eq.), Pd(PPh$_3$)$_4$ (24 mg, 20 μmol, 0.3 eq.), 3-cyanophenyl boronic acid (197 mg, 1.3 mmol, 19 eq.). The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:2, v/v) and gave the pure product as white crystals of **8** (36 mg, 40 μmol, 61%). mp >300 °C; R_f = 0.40 (CH$_2$Cl$_2$/*n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.56 (s, 6H, Ar-*H*), 7.51 (d, *J* = 7.5 Hz, 6H, Ar-*H*), 7.39 (s, 6H, Ar-*H*), 7.30 (m, 6H, Ar-*H*), 7.20 (m, 6H, Ar-*H*), 5.75 (s, 2H, bridgehead-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.3, 141.2, 135.5, 133.9, 132.6, 130.4, 128.7, 125.9, 117.9, 112.2, 52.4 ppm; HRMS (ES+) *m/z* calcd. for [C$_{62}$H$_{32}$N$_6$Na] (M+Na$^+$): 883.2586; found 883.2585.

2,3,6,7,14,15-Hexakis(4-benzoic acid)triptycene (**9**). This compound was prepared *via* the general procedure above using Cs_2CO_3 (483 mg, 1.48 mmol, 21 eq.), Pd(PPh$_3$)$_4$ (24 mg, 20 μmol, 0.3 eq.), 4-methoxycarbonylphenylboronic acid (200 mg, 1.11 mmol, 16 eq.). The crude product was taken forward without further purification and isolation with subsequent hydrolysis to the free carboxylic acid. 160 mg (0.15 mmol, 1 eq.) of the crude material and KOH (1.69 g, 30 mmol, 200 eq.) dissolved in a minimal amount of H_2O was added to a flask containing a THF:MeOH (1:1) solvent mixture of 40 mL and brought to a temperature as to maintain a gentle reflux for 24 h. After the elapsed time period, a further 100 eq. of KOH was added and allowed react for a further 18 h to drive the reaction to completion. The reaction mixture was taken into ethyl acetate and washed with 0.1 M HCl solution, then sodium bicarbonate, sodium chloride and water respectively. The solvent was removed *in vacuo* and the product was purified through Büchner filtration washed with CH_2Cl_2 as a solvent and yielded a yellow/brown solid **9** (63 mg, 65 μmol, 94%). mp >300 °C; R_f = 0.24 (EtOAc/*n*-hexane = 30:90, v/v); ^{1}H NMR (400 MHz, CDCl$_3$/C$_6$D$_5$N): δ = 7.82 (d, *J* = 6.8 Hz, 12H, Ar-*H*), 7.45 (s, 6H, Ar-*H*), 7.02 (d, *J* = 6.8 Hz, 12H, Ar-*H*), 5.59 (s, 2H, bridgehead-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$/C$_6$D$_5$N): δ = 168.8, 145.1, 144.4, 137.2, 129.9, 129.7, 129.4, 126.0, 52.9 ppm; HRMS (ESI) *m/z* calcd. for [C$_{62}$H$_{38}$O$_{12}$Na] (M+Na$^+$): 997.2261; found 997.2251.

2,3,6,7,14,15-Hexakis(4-formylphenyl)triptycene (**10**). This compound was prepared *via* the general procedure above using Cs_2CO_3 (290 mg, 0.89 mmol, 13 eq.), Pd(PPh$_3$)$_4$ (24 mg, 20 μmol, 0.3 eq.), 4-formylphenyl boronic acid (133 mg, 0.89 mmol, 13 eq.). The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/methanol = 25:1, v/v) and gave the pure product **10** as white crystals (39 mg, 44 μmol, 64%). mp >300 °C; R_f = 0.55 (CH$_2$Cl$_2$/methanol = 20:1, v/v); ^{1}H NMR

(400 MHz, CDCl$_3$): δ = 9.94 (s, 6H, CHO), 7.70 (d, *J* = 8.0 Hz, 12H, Ar-*H*), 7.61 (s, 6H, Ar-*H*), 7.22 (d, *J* = 8.0 Hz, 12H, Ar-*H*), 5.75 (s, 2H, bridgehead-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 191.3, 146.5, 144.2, 136.7, 134.3, 130.1, 129.2, 125.8, 53.0 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{62}$H$_{39}$O$_6$] (M+H$^+$): 879.2747; found 879.2735.

2,3,6,7,14,15-Hexakis(3-methoxyphenyl)triptycene (**11**). This compound was prepared *via* the general procedure above using Cs$_2$CO$_3$ (336 mg, 1.03 mmol, 15 eq.), Pd(PPh$_3$)$_4$ (24 mg, 20 µmol, 0.3 eq.), 3-methoxyphenylboronic acid (125 mg, 0.82 mmol, 12 eq.).The crude product was purified by column chromatography on silica gel (EtOAc/*n*-hexane = 5:95, v/v) to afford a white solid of **11** (27 mg, 30 µmol, 44%). The isolated product had analytical data consistent with the literature.[11a] mp = 246 °C; *R$_f$* = 0.24 (EtOAc/*n*-hexane = 20:80, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.59 (s, 6H, Ar-*H*), 7.14 (t, *J* = 7.9 Hz, 6H, Ar-*H*), 6.74 (d, *J* = 7.9 Hz, 6H, Ar-*H*), 6.74 (d, *J* = 7.9 Hz, 6H, Ar-*H*), 6.65 (s, 6H, Ar-*H*), 5.68 (s, 2H, bridgehead-*H*), 3.62 (s, 18H, Ar-O*CH$_3$*) ppm.

2,3,6,7,14,15-Hexakis(4-dimethylaminophenyl)triptycene (**12**). This compound was prepared *via* the general procedure above using K$_3$PO$_4$ (438 mg, 2.06 mmol, 30 eq.), Pd(PPh$_3$)$_4$ (95 mg, 82 µmol, 1.2 eq.) and 4-(dimethylamino)phenyl boronic acid (340 mg, 2.06 mmol, 30 eq.). The crude product was purified by column chromatography on Al$_2$O$_3$ (Brockman grade III) (CH$_2$Cl$_2$/petroleum ether = 10-30/90-70, v/v) to afford a grey/brown solid of **12** (48 mg, 50 µmol, 72%). mp >300 °C; *R$_f$* = 0.2 (CH$_2$Cl$_2$/petroleum ether = 30/70, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47 (s, 6H, Ar-*H*), 7.03 (d, *J* = 8.5 Hz, 12H, Ar-*H*), 6.61 (d, *J* = 8.5 Hz, 12H, Ar-*H*), 5.54 (s, 2H, bridgehead-*H*), 2.94 (s, 36H, N-C*H$_3$*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 148.3, 143.2, 136.7, 130.2, 130.1, 125.4, 111.7, 52.8, 40.2 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{68}$H$_{68}$N$_6$] (M$^+$): 968.5505; found 968.5487.

2,3,6,7,14,15-Hexakis(4-ethynylphenyl)triptycene (**13**). This compound was prepared *via* the general procedure above using K$_3$PO$_4$ (438 mg, 2.06 mmol, 30 eq.), Pd(PPh$_3$)$_4$ (95 mg, 82 µmol, 1.2 eq.) and 4-[(trimethylsilyl)ethynyl]phenyl boronic acid pinacol ester (619 mg, 2.06 mmol, 30 eq.). The crude product was dissolved in THF (5 mL) and excess TBAF (1 M in THF, 4 mL) was added. The reaction was followed by TLC using EtOAc/petroleum ether (1:4, v/v). Upon completion, the solvent was removed *in vacuo* and dissolved in CH$_2$Cl$_2$ (20 mL). The organic layer was washed with H$_2$O (50 mL), brine (50 mL) and dried over MgSO$_4$. The solid was dry loaded onto silica gel. Purification of the product was carried out twice by column chromatography on silica gel eluted in EtOAc/petroleum ether, 2-10/98-90, v/v) to afford a cream residue of **13** (38 mg, 44 µmol, 65%). mp >300 °C; *R$_f$* = 0.24 (EtOAc/petroleum ether = 1/9, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.52 (s, 6H, Ar-*H*), 7.31 (d, *J* = 8.3 Hz, 12H, Ar-*H*), 7.01 (d, *J* = 8.3 Hz, 12H, Ar-*H*), 5.65 (s, 2H, bridgehead-*H*), 3.06 (s, 6H, C-*H*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.3, 141.5, 137.1, 131.8, 129.8, 126.0, 120.3, 77.6, 77.2, 53.0 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{68}$H$_{38}$] (M$^+$): 854.2974; found 854.2951.

2,3,6,7,14,15-Hexakis(boronic acid pinacol ester)triptycene (**14**). This compound was prepared *via* a modified version of the general procedure above, using Cs$_2$CO$_3$ (224 mg, 0.69 mmol, 10 eq.), PdCl$_2$(PPh$_3$)$_2$ (3 mg, 4 µmol, 0.06 eq.), Bis(pinacolato)diboron (837 mg, 3.3 mmol, 48 eq.) in 10 mL of dichloroethane. The reaction mixture was washed with a saturated solution of KCl and then followed the routine procedure with subsequent recrystallization from EtOAc/*n*-hexane affording a white solid **14** (25 mg, 25 µmol, 36%). mp = 128-130 °C; *R$_f$* = 0.23; (EtOAc/*n*-hexane = 1:5, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.63 (s, 6H, Ar-*H*), 5.44 (s, 2H, Ar-*H*), 1.33 (s, 72H, C*H$_3$*) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 145.7, 132.1, 128.8, 83.6, 54.0, 24.9 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{56}$H$_{80}$B$_6$O$_{12}$] (M$^+$): 1010.6208; found 1010.6243.

General procedure for Pd-catalyzed six-fold cross coupling of 3 with alkyl organoboron reagents: A 25 mL Schlenk tube equipped with a stirring bar, rubber septum and condenser was flushed for 10 minutes with argon gas and charged with hexabromotriptycene **3** (70 mg, 0.1

mmol, 1 eq.) and Cs$_2$CO$_3$ (1.3 g, 4 mmol, 40 eq.) in anhydrous THF (10 mL). The solution was degassed *via* three freeze-pump-thaw cycles and was placed under argon. Boronic acid (6 mmol, 60 eq.) and Pd(dppf)Cl$_2$ (90 mg, 0.12 mmol, 1.2 eq.) were added and a balloon filled with argon gas was then connected to the top of the condenser. The mixture was heated with stirring at 80 °C under argon atmosphere for 18 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was washed sequentially with sat. aq. NaHCO$_3$ (30 mL), deionized H$_2$O (20 mL) and brine (20 mL). The organic phase was dried over MgSO$_4$, the solvent was evaporated and the crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane).

2,3,6,7,14,15-Hexakis(2-methylpropyl)triptycene (**15**). The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:10, v/v) and gave the product as white crystals (19 mg, 30 µmol, 32%). mp >300 °C; *R$_f$* = 0.62 (CH$_2$Cl$_2$/*n*-hexane = 1:7, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.04 (s, 6H, Ar-*H*), 5.12 (s, 2H, bridgehead-*H*), 2.34 (d, *J* = 8.0 Hz, 12H, C*H$_2$*), 1.76 (m, 6H, C*H*), 0.87 (d, *J* = 8.0 Hz, 36H, C*H$_3$*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.7, 135.3, 124.4, 52.6, 41.4, 30.5, 22.4 ppm; HRMS (ES+) *m/z* calcd. for [C$_{44}$H$_{62}$] (M$^+$): 590.4852; found 590.4835.

2,3,6,7,14,15-Hexakis(3-methylbutyl)triptycene (**16**). The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:10, v/v) and gave the pure product as white crystals (24 mg, 35 µmol, 36%). mp >300 °C; *R$_f$* = 0.65 (CH$_2$Cl$_2$/*n*-hexane = 1:7, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.07 (s, 6H, Ar-*H*), 5.14 (s, 2H, bridgehead-*H*), 2.42 (m, 12H, C*H$_2$*), 1.58 (m, 6H, C*H*), 1.35 (m, 12H, C*H$_2$*), 0.90 (d, 36H, *J* = 8.0 Hz, C*H$_3$*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.9, 136.3, 123.7, 52.6, 40.5, 29.9, 27.9, 22.1 ppm; HRMS (ES+) *m/z* calcd. for [C$_{50}$H$_{74}$] (M$^+$): 674.5791; found 674.5804.

2,3,6,7,14,15-Hexahexyltriptycene (**17**). The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:10, v/v) and gave the pure product as first fraction as white crystals (16 mg, 20 µmol, 21%). mp >300 °C; *R$_f$* = 0.66 (CH$_2$Cl$_2$/*n*-hexane = 1:7, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.08 (s, 6H, Ar-*H*), 5.15 (s, 2H, bridgehead-*H*), 2.44 (t, *J* = 8.0 Hz, 12H, C*H$_2$*), 1.46 (m, 12H, C*H$_2$*), 1.30 (m, 36H, C*H$_2$*), 0.86 (t, *J* = 8.0 Hz, 18H, C*H$_3$*) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.8, 136.2, 123.6, 52.6, 32.2, 31.3, 30.9, 29.2, 22.2, 13.7 ppm; HRMS (ES+) *m/z* calcd. for [C$_{56}$H$_{86}$] (M+Na$^+$): 758.6730; found 758.6727.

Pd-Catalyzed Sonogashira Couplings

2,6,14-Triethynyltriptycene (**20**). 2,6,14-Triiodotriptycene **1a** (100 mg, 0.16 mmol, 1 eq.) was placed in a 50 mL Schlenk flask and dried under vacuum and dissolved in TEA (6 mL) under an argon atmosphere. The solvent was degassed *via* three freeze-pump-thaw cycles. Trimethylsilylacetylene (0.54 mL, 3.80 mmol, 24 eq.), CuI (9 mg, 47 µmol, 0.3 eq.), triphenylphosphine (50 mg, 0.19 mmol, 1.2 eq.) and PdCl$_2$(PPh$_3$)$_2$ (33 mg, 47 µmol, 0.3 eq.) were added and heated at 70 °C for 17 h. The progress of the reaction was monitored by TLC (EtOAc:*n*-hexane = 1:99, v/v). The solvent was removed *in vacuo* and the residue was dry loaded onto silica gel with EtOAc (20 mL). The reaction mixture was filtered through a small plug of silica eluting Glaser coupled TMS acetylene with 100% *n*-hexane and the product eluting with 100% EtOAc. The crude product was dissolved in THF (5 mL) and TBAF (1 M in THF, 0.6 mL, 0.55 mmol, 3.5 eq.) was added. The reaction was monitored by TLC using EtOAc/*n*-hexane (1:9, v/v). Upon completion, the organic layer was washed with sat. aq. NaHCO$_3$ (30 mL × 3), deionized H$_2$O (30 mL), dried with MgSO$_4$ and filtered using EtOAc as eluent. The crude product mixture was purified by flash chromatography on silica gel eluting with 0-10% EtOAc with *n*-hexane to afford a cream solid **20** (39 mg, 0.12 mmol, 75%). The isolated product had analytical data consistent with the literature.[7b] mp = 173-175 °C; *R$_f$* = 0.4 (EtOAc:*n*-hexane = 1:9, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.48 (br s, 3H, Ar-*H*), 7.31 (d, *J* = 7.5 Hz, 3H, Ar-*H*), 7.16 (m, 3H, Ar-*H*), 5.37 (s, 1H, bridgehead-*H*), 5.35 (s, 1H, bridgehead-*H*), 2.95 (s, 3H, *H*$_{C≡CH}$) ppm.

2,3,6,7,14,15-Hexakis(trimethylsilylethynyl)triptycene (**19a**). A mixture of hexabromotriptycene **3** (102 mg, 0.14 mmol, 1 eq.), CuI (17 mg, 90 µmol, 0.65 eq.) and triphenylphosphine (44 mg, 0.17 mmol, 1.2 eq.) were placed in a 50 mL Schlenk flask and dried under vacuum. The mixture was dissolved in TEA (5 mL) under an argon atmosphere and was degassed *via* three freeze-pump-thaw cycles. Trimethylsilylacetylene (0.5 mL, 3.36 mmol, 24 eq.) and PdCl$_2$(PPh$_3$)$_2$ (59 mg, 84 µmol, 0.6 eq.) were added and heated at 70 °C for 18 h. The progress of the reaction was monitored by TLC (EtOAc:*n*-hexane = 1:99, v/v). The solvent was removed under reduced pressure and the reaction mixture was filtered through a small plug of silica eluting with CH$_2$Cl$_2$ (50 mL). The crude product mixture was purified by flash chromatography on silica gel (EtOAc:*n*-hexane = 1:99, v/v) to afford a brown/orange residue of **19a** (75 mg, 90 µmol, 67%). mp >300 °C; R_f = 0.74 (EtOAc:*n*-hexane = 1:99, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.38 (s, 6H, Ar-*H*), 5.19 (s, 2H, bridgehead-*H*), 0.22 (s, 54H, C*H*$_3$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 143.2, 127.4, 123.4, 103.1, 98.2, 52.5, 0.9 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{50}$H$_{62}$Si$_6$] (M$^+$): 830.3467; found 830.3483.

2,3,6,7,14,15-Hexaethynyltriptycene (**21**). Compound **19a** (280 mg, 0.34 mmol, 1 eq.) was dissolved in THF (6 mL) and TBAF (1 M in THF, 2.2 mL, 2.19 mmol, 6.5 eq.) was added. The reaction was monitored by TLC using EtOAc/*n*-hexane (1:4, v/v). Upon completion, the solvents were removed *in vacuo* and the residue was dissolved in CH$_2$Cl$_2$ (20 mL) and dry loaded onto silica gel. The residue was filtered through a plug of silica using EtOAc/*n*-hexane (1:4, v/v). The solvent was removed *in vacuo* and the residue was recrystallized from CHCl$_3$/*n*-hexane affording a cream solid **21** (107 mg, 0.27 mmol, 80%). mp decomposed at 140 °C; R_f = 0.28 (EtOAc:*n*-hexane = 1:4, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.49 (s, 6H, Ar-*H*), 5.32 (s, 2H, bridgehead-*H*), 3.24 (s, 6H, *H*$_{C\equiv CH}$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 143.6, 127.9, 122.9, 81.6, 80.9, 52.3 ppm; HRMS (APCI) *m/z* calcd. for [C$_{32}$H$_{15}$] (M+H$^+$): calcd. 399.1168; found 399.1168.

2,3,6,7,14,15-Hexakis[(4-ethynylphenyl)ethynyl]triptycene (**26**). Hexabromotriptycene **3** (50 mg, 69 µmol, 1 eq.) was placed in a 50 mL Schlenk flask dried under vacuum and dissolved in TEA:THF (10 mL, 4:1, v/v) under an argon atmosphere. The solvent was degassed *via* three freeze-pump-thaw cycles. [(4-Ethynylphenyl)ethynyl]triisopropylsilane **24** (932 mg, 3.3 mmol, 48 eq.), CuI (4 mg, 21 µmol, 0.3 eq.), triphenylphosphine (22 mg, 82 µmol, 1.2 eq.) and PdCl$_2$(PPh$_3$)$_2$ (29 mg, 41 µmol, 0.6 eq.) were added and the reaction was heated at 70 °C for 24 h. The progress of the reaction was monitored by TLC (EtOAc:*n*-hexane = 1:99, v/v). The solvents were removed under reduced pressure and re-dissolved in CH$_2$Cl$_2$ (60 mL). The crude product was washed sequentially with deionized H$_2$O (20 mL) and brine (20 mL × 3). The organic phase was dried over MgSO$_4$ and the crude product was filtered through a small plug of silica eluting in CH$_2$Cl$_2$ (100 mL) and the solvents were removed *in vacuo*. The crude product was dissolved in THF in a 100 mL RBF and an excess of TBAF (6 mL, 1 M in THF) was added. The reaction was monitored by TLC using EtOAc/*n*-hexane (1:9, v/v) as eluent. Upon completion, the reaction mixture was filtered through a plug of silica using CH$_2$Cl$_2$ (20 mL) as eluent. The solvents were removed *in vacuo* and the residue was dry loaded onto silica gel. The crude product mixture was purified three times by flash chromatography on silica gel eluting with 0-10% EtOAc:*n*-hexane to afford a yellow residue of **26** (21 mg, 21 µmol, 31%). mp = 87-90 °C; R_f = 0.2 (EtOAc:*n*-hexane = 1:9, v/v); ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.62 (s, 6H, Ar-*H*), 7.48 (br s, 24H, Ar-*H*), 5.45 (s, 2H, bridgehead-*H*), 3.20 (s, 6H, *H*$_{C\equiv CH}$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 143.3, 132.0, 131.3, 127.0, 123.4, 123.3, 122.0, 92.8, 89.9, 83.0, 79.0, 52.6 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{80}$H$_{38}$] (M$^+$): 998.2974; found 998.2969.

Post-Functionalization Bioconjugation

2,6,14-Tris-(1'-*n*-nonyl-1*H*-1,2,3-triazol-4'-yl)triptycene (**27**). 2,6,14-Triethynyltriptycene **20** (11 mg, 35 µmol, 1 eq.), Cu(MeCN)$_4$PF$_6$ (5 mg, 12 µmol, 0.35 eq.) and 1-azidononane (107 mg, 0.63 mmol, 18 eq.) were added to a 20 mL microwave tube and dissolved in degassed DMF (8

mL). The tube was then sealed and heated to 115 °C in a microwave reactor for 30 minutes. The reaction was diluted with EtOAc (20 mL) and the organic layer was washed with deionized H$_2$O (30 mL), brine (50 mL × 5) and dried over MgSO$_4$. The solvents were removed *in vacuo* and the residue was dry loaded onto silica gel with CH$_2$Cl$_2$ (20 mL). The reaction mixture was filtered through a small plug of silica eluting excess 1-azidononane with *n*-hexane and the product eluting with EtOAc. The crude product was purified by column chromatography eluting with 10-50% EtOAc in *n*-hexane to afford **27** as a cream residue (26 mg, 31 µmol, 89%). mp = 72-74 °C; R_f = 0.3 (EtOAc:*n*-hexane = 1:1, v/v); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.96 (m, 3H, Ar-*H*), 7.68 (br s, 3H, triazole-*H*), 7.45 (m, 6H, Ar-*H*), 5.56 (s, 1H, bridgehead-*H*), 5.53 (s, 1H, bridgehead-*H*), 4.36 (t, *J* = 7.0 Hz, 6H, NC*H*$_2$), 1.92 (m, 6H, C*H*$_2$), 1.30 (m, 36H, C*H*$_2$), 0.88 (m, 9H, C*H*$_3$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 147.6, 145.5, 144.7, 127.9, 124.0, 123.9, 122.7, 121.3, 121.2, 119.2, 53.9, 53.6, 50.4, 31.8, 30.2, 29.3, 29.1, 29.0, 26.4, 22.6, 14.0 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{53}$H$_{72}$N$_9$] (M$^+$): 834.5911; found 834.5906.

2,3,6,7,14,15-Hexakis-(1'-*n*-nonyl-1*H*-1,2,3-triazol-4'-yl)triptycene (**28**). 2,3,6,7,14,15-Hexaethynyltriptycene **21** (10 mg, 25 µmol, 1 eq.), Cu(MeCN)$_4$PF$_6$ (22 mg, 60 µmol, 2.4 eq.) and 1-azidononane (204 mg, 1.2 mmol, 48 eq.) were added to a 20 mL microwave tube and dissolved in degassed DMF (10 mL). The tube was then sealed and heated to 115 °C in a microwave reactor for 60 minutes. The reaction was diluted with EtOAc (20 mL) and the organic layer was washed with deionized H$_2$O (30 mL), brine (50 mL × 5) and dried over MgSO$_4$. The solvent was removed *in vacuo* and the residue was dry loaded onto silica gel with CH$_2$Cl$_2$ (30 mL). The reaction mixture was filtered through a small plug of silica eluting 1-azidononane with *n*-hexane and the crude product eluting with CH$_2$Cl$_2$:CH$_3$OH (9:1, v/v). The crude product was purified twice by column chromatography (CH$_2$Cl$_2$:CH$_3$OH = 9:1, v/v) to afford the alkyltriptycene **28** as a cream solid (21 mg, 15 µmol, 59%). mp = 82-84 °C; R_f = 0.5 (EtOAc:*n*-hexane = 1:1, v/v); ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.82 (s, 6H, Ar-*H*), 7.36 (s, 6H, triazole-*H*), 5.66 (s, 2H, bridgehead-*H*), 4.29 (t, *J* = 6.8 Hz, 12H, NC*H*$_2$), 1.86 (m, 12H, C*H*$_2$), 1.29 (m, 72H, C*H*$_2$) 0.88 (m, 18H, C*H*$_3$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 146.3, 144.4, 126.7, 125.5, 122.4, 53.3, 50.1, 31.6, 30.2, 29.2, 29.0, 28.8, 26.3, 22.5, 13.9 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{86}$H$_{129}$N$_{18}$] (M$^+$): 1414.0648; found 1414.0620.

2,6,14-Tris-(1'-[(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)oxypropyl]-1*H*-1,2,3-triazol-4'-yl)triptycene (**31**). 2,6,14-Triethynyltriptycene **20** (60 mg, 0.18 mmol, 1 eq.), Cu(MeCN)$_4$PF$_6$ (24 mg, 64 µmol, 0.35 eq.) and 3'-azidopropyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranoside **29** (1.4 g, 3.31 mmol, 18 eq.) were added to a 20 mL microwave tube and dissolved in degassed DMF (8 mL). The tube was then sealed and heated to 115 °C in a microwave reactor for 30 minutes. The reaction was diluted with EtOAc (20 mL) and the organic layer was washed with brine (50 mL × 5) and dried over MgSO$_4$. The solvent was removed *in vacuo* and the residue was dry loaded onto silica gel with CH$_2$Cl$_2$ (20 mL). The reaction mixture was filtered through a small plug of silica eluting excess sugar **29** with EtOAc:*n*-hexane (1:1, v:v) and the product **31** eluting with CH$_2$Cl$_2$:CH$_3$OH (9:1, v:v). The crude product was purified by column chromatography (CH$_2$Cl$_2$:CH$_3$OH, 9:1, v:v) to afford the glycotriptycene **31** as a cream solid (180 mg, 0.11 mmol, 62%). mp = 122-125 °C; R_f = 0.2 (EtOAc:*n*-hexane = 7:3, v/v); [α]$_D^{20}$ = -1.2° (*c* = 0.1 g/100mL in CHCl$_3$). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.96 (m, 3H, Ar-*H*), 7.72 (br s, 3H, triazole-*H*), 7.45 (m, 6H, Ar-*H*), 5.57 (s, 1H, bridgehead-*H*), 5.53 (s, 1H, bridgehead-*H*), 5.39 (m, 3H, *H*$_4$), 5.22 (dd, *J*$_{2,3}$ = 10.2 Hz, *J*$_{2,1}$ = 8.1 Hz, 3H, *H*$_2$), 5.02 (dd, *J*$_{3,2}$ = 10.2 Hz, *J*$_{3,4}$ = 3.4 Hz, 3H, *H*$_3$), 4.52 (m, 3H, NC*H*$_2$), 4.47 (d, *J*$_{1,2}$ = 7.9 Hz, 3H, *H*$_1$), 4.42 (m, 3H, NC*H*$_2$), 4.14 (m, 6H, *H*$_6$*H*$_6$'), 3.89 (m, 6H, *H*$_5$, OC*H*$_2$), 3.49 (m, 3H, OC*H*$_2$), 2.23 (m, 6H, C*H*$_2$), 2.14 (s, 9H, C*H*$_3$), 2.09 (s, 9H, C*H*$_3$), 1.98 (m, 18H, C*H*$_3$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 170.2, 170.0, 169.9, 169.5, 147.5, 145.4, 144.6, 127.7, 123.9, 122.6, 121.1, 119.7, 101.2, 70.6, 68.7, 66.8, 65.7, 61.1, 53.7, 53.5, 46.5, 30.1, 20.7, 20.5, 20.4 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{77}$H$_{90}$N$_9$O$_{30}$] (M$^+$): 1620.5794; found 1620.5829.

2,6,14-Tris-(1'-[(4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl)oxypropyl]-1*H*-1,2,3-triazol-4'-yl)triptycene (**32**). 2,6,14-Triethynyltriptycene **20** (50 mg, 0.15 mmol, 1 eq.), Cu(MeCN)$_4$PF$_6$ (20 mg, 54 µmol, 0.35 eq.) and 3-azidopropyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside **30** (1.98 g, 2.76 mmol, 18 eq.) were added to a 20 mL microwave tube and dissolved in degassed DMF (8 mL). The tube was then sealed and heated to 115 °C in a microwave reactor for 30 minutes. The reaction was diluted with EtOAc (20 mL) and the organic layer was washed with deionized H$_2$O (30 mL), brine (50 mL × 5) and dried over MgSO$_4$. The solvent was removed *in vacuo* and the residue was dry loaded onto silica gel with CH$_2$Cl$_2$ (30 mL). The reaction mixture was filtered through a small plug of silica eluting excess sugar **30** with EtOAc:*n*-hexane (1:1, v:v) and the product eluting with CH$_2$Cl$_2$:CH$_3$OH (9:1, v/v). The crude product was purified by column chromatography (CH$_2$Cl$_2$:CH$_3$OH = 9:1, v/v) to afford the glycotriptycene **32** as a cream solid (284 mg, 0.11 mmol, 75%). mp = 143-145 °C; R_f = 0.2 (EtOAc:*n*-hexane = 7:3, v/v); [α]$_D^{20}$ = -5.6° (*c* = 0.14 g/100mL in CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.96 (br s, 3H, Ar-*H*), 7.72 (br s, 3H, triazole-*H*), 7.44 (m, 6H, Ar-*H*), 5.57 (s, 1H, bridgehead-*H*), 5.54 (s, 1H, bridgehead-*H*), 5.35 (br s, 3H, *H$_{4'}$*), 5.22 (dd, $J_{3,4}$ = 9.6 Hz, $J_{3,2}$ = 9.0 Hz, 3H, *H$_3$*), 5.13 (dd, $J_{2',3'}$ = 9.6 Hz, $J_{2',1'}$ = 8.7 Hz, 1H, *H$_{2'}$*), 4.94 (m, 6H, *H$_{3'}$*, *H$_2$*), 4.48 (m, 9H, *H$_1$*, *H$_{1'}$*, *H$_{6a}$*, NC*H$_2$*), 4.11 (m, 9H, *H$_{6b}$*, *H$_{6'}$*), 3.88 (m, 3H, *H$_4$*), 3.80 (m, 6H, *H$_{5'}$*, OC*H$_2$*), 3.59 (m, 3H, *H$_5$*), 3.49 (m, 3H, OC*H$_2$*), 2.19 (m, 6H, C*H$_2$*), 2.15 (s, 9H, C*H$_3$*), 2.05 (m, 45H, C*H$_3$*), 1.96 (s, 9H, C*H$_3$*) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 170.3, 170.3, 170.1, 170.0, 169.7, 169.7, 169.0, 147.6, 145.5, 144.8, 127.8, 124.0, 122.7, 121.2, 119.8, 101.0, 100.6, 76.1, 72.8, 72.6, 71.6, 70.9, 70.7, 69.1, 66.6, 65.9, 61.8, 60.8, 53.8, 53.6, 46.7, 30.3, 20.8, 20.7, 20.6, 20.5 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{113}$H$_{137}$N$_9$O$_{54}$Na] (M+Na$^+$): 2506.8149; found 2506.8225.

2,6,14-Tris-(1'-[(β-*D*-galactopyranosyl)oxypropyl]-1*H*-1,2,3-triazol-4'-yl)triptycene (**33**). 2,6,14-Tri-(1'-[(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)oxypropyl]-1H-1,2,3-triazol-4'-yl)triptycene (**31**) (147 mg, 91 µmol, 1 eq.) and NaOMe (2 mg, 27 µmol, 0.3 eq.) were dissolved in methanol (6 mL) and stirred at 20 °C for 2 h. The reaction mixture was neutralized with Dowex® resin and filtered with methanol (40 mL). The solvent filtrate was removed *in vacuo* to afford the deprotected glycotriptycene **33** as a cream solid (91 mg, 82 µmol, 90%). mp = 78-80 °C; R_f = 0.6 (EtOH:H$_2$O = 7:3, v/v); [α]$_D^{20}$ = -2.7° (*c* = 0.07 g/100mL in CHCl$_3$); ^{1}H NMR (600 MHz, [CD$_3$]$_2$SO): δ = 8.51 (br s, 3H, triazole-*H*), 7.99 (br s, 3H, Ar-*H*), 7.55 (m, 3H, Ar-*H*), 7.50 (m, 3H, Ar-*H*), 5.84 (s, 1H, bridgehead-*H*), 5.79 (s, 1H, bridgehead-*H*), 4.95 (br s, 3H, O*H*), 4.75 (br s, 3H, O*H*), 4.57 (br s, 3H, O*H*), 4.49 (t, *J* = 6.5 Hz, 6H, NC*H$_2$*), 4.39 (br s, 3H, O*H*), 4.08 (d, $J_{1,2}$ = 7.4 Hz, 3H, *H$_1$*), 3.76 (m, 3H, OC*H$_2$*), 3.64 (br s, 3H, *H$_4$*), 3.54 (m, 3H, *H$_6$*), 3.48 (m, 3H, *H$_{6'}$*), 3.42 (m, 3H, OC*H$_2$*), 3.33 (m, 9H, *H$_5$*, *H$_2$*, *H$_3$*), 2.09 (m, 6H, C*H$_2$*) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 146.1, 145.6, 144.4, 127.9, 124.1, 121.9, 121.4, 120.7, 103.5, 75.2, 73.3, 70.5, 68.1, 65.1, 60.4, 52.3, 52.0, 46.6, 29.9 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{50}$H$_{62}$N$_9$O$_{18}$Na] (M+Na$^+$): 1138.4345; found 1138.4357.

2,6,14-Tris-(1'-[(4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl)oxypropyl]-1*H*-1,2,3-triazol-4'-yl)triptycene (**34**). 2,6,14-Tri-(1'-[(4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl)oxypropyl]-1*H*-1,2,3-triazol-4'-yl)triptycene (**32**) (231 mg, 93 µmol, 1 eq.) and NaOMe (3 mg, 56 µmol, 0.6 eq.) were dissolved in methanol (6 mL) and stirred at 20 °C for 2 h. The reaction mixture was neutralized with Dowex® resin and filtered with methanol (40 mL). The solvent filtrate was removed *in vacuo* to afford the deprotected glycotriptycene **34** as a cream solid (145 mg, 90 µmol, 97%). mp = 96-98 °C; R_f = 0.5 (EtOH:H$_2$O = 7:3, v/v); [α]$_D^{20}$ = -7.5° (*c* = 0.11 g/100mL in CHCl$_3$); ^{1}H NMR (600 MHz, [CD$_3$]$_2$SO): δ = 8.51 (br s, 3H, triazole-*H*), 7.98 (m, 3H, Ar-*H*), 7.56 (m, 3H, Ar-*H*), 7.51 (m, 3H, Ar-*H*), 5.84 (s, 1H, bridgehead-*H*), 5.79 (s, 1H, bridgehead-*H*), 5.17 (br s, 6H, O*H*), 4.72 (br s, 16H, O*H*), 4.49 (m, 6H, NC*H$_2$*), 4.22 (m, 6H, *H$_1$*, *H$_{1'}$*), 3.76 (m, 6H, *H$_{6a}$*, OC*H$_2$*), 3.64 (m, 6H, *H$_{6b}$*, *H$_{4'}$*), 3.52 (m, 6H, *H$_{6'}$*), 3.50 (m, 6H, OC*H$_2$*, *H$_{5'}$*), 3.31 (m, 15H, *H$_3$*, *H$_4$*, *H$_5$*, *H$_{2'}$*, *H$_{3'}$*), 3.06 (m, 3H, *H$_2$*), 2.11 (m, 6H, C*H$_2$*) ppm; ^{13}C NMR (150 MHz, CDCl$_3$): δ = 146.2, 145.6, 144.4, 127.9, 124.2, 122.0, 121.4, 120.7, 103.8, 102.5, 80.5, 75.5, 74.9, 74.8, 73.2, 73.1, 70.5,

68.1, 65.4, 60.4, 60.3, 52.3, 52.1, 46.6, 29.8 ppm; HRMS (MALDI) *m/z* calcd. for [C$_{71}$H$_{95}$N$_9$O$_{33}$Na] (M+Na$^+$): 1624.5930; found 1624.5912.

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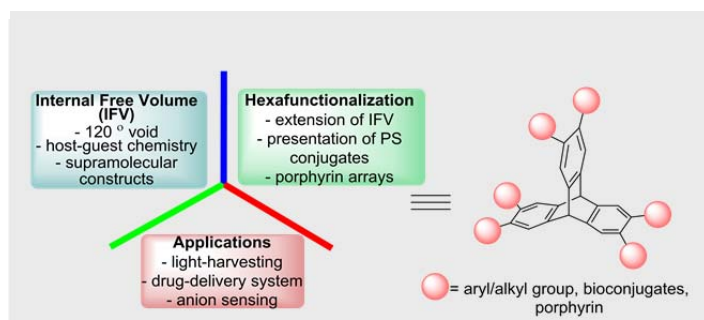
Triptycene Functionalization

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Page No. – Page No.

Preparation of tri- and hexasubstituted triptycene synthons *via* transition metal-catalyzed cross-coupling for post-modifications