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Toward Analogues of MraY Natural Inhibitors: Synthesis of 5′-Triazole-Substituted-Aminoribosyl Uridines Through a Cu-Catalyzed Azide−Alkyne Cycloaddition

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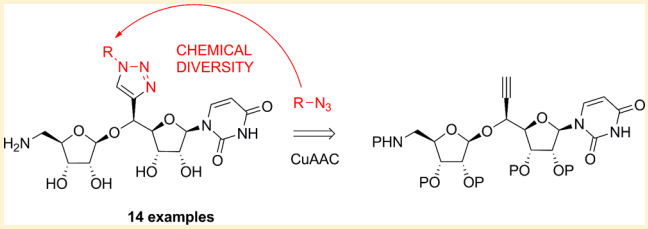
Supporting Information

ABSTRACT: A straightforward strategy for the synthesis of triazole-containing MraY inhibitors has been developed. It involves the sequential introduction of a terminal alkyne at the 5′ position of an uridine derivative and *O*-glycosylation with a protected aminoribose leading to an elaborated alkyne scaffold. An efficient Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) allowed the introduction of chemical diversity toward a small library of inhibitors.



INTRODUCTION

The worldwide emergence of multidrug resistant (MDR) bacteria has become a severe public health problem that requires the scientific community to discover novel compounds able to fight MDR strains.[1,2] One way to address antibiotic resistance is to delay this inevitable phenomenon by focusing on targets that have been little exploited so far such as the bacterial translocase MraY.[3] This transferase involved in the first membrane-associated step of peptidoglycan biosynthesis represents such a challenging target.[4] Indeed, this membrane protein, which no drug currently used in therapeutics has yet targeted, is an essential enzyme of peptidoglycan biosynthesis.[5,6] The latter is a cross-linked polymer specific to bacteria and is a major component of their cell wall, which protects the cell from osmotic stress. MraY catalyzes the transfer of the phospho-Mur-*N*-Ac-pentapeptide moiety from the cytoplasmic precursor UDP-Mur-*N*-Ac-pentapeptide to the membrane acceptor undecaprenyl phosphate (C_{55}−P) yielding undecaprenyl-pyrophosphoryl-Mur-*N*-Ac-pentapeptide (lipid I) while releasing uridine monophosphate (UMP).[7]

MraY is the target of several families of naturally occurring nucleoside antibiotics[8,9] (Figure 1), which notably include FR-900493,[10] liposidomycins,[11] caprazamycins[12] and muraymycins.[13] Several elegant synthetic approaches toward these compounds have been described.[14,15] All these natural inhibitors share a common aminoribosyl-*O*-uridine scaffold, which has been proven to be essential for biological activity.[16] However, the complexity displayed by such structures hampers rapid structure−activity relationship studies. Furthermore, the absence of crystal structure available for the MraY transferase makes the discovery of new potent inhibitors particularly challenging, not only as regards the development of new antibacterials but also in a possible contribution to MraY structural characterization.

In the context of an ongoing program[14e,i,15f,m,17] directed toward MraY inhibition, our goal was to develop a straightforward access to a new type of MraY inhibitors (Figure 2) based on the aminoribosyl-*O*-uridine skeleton displayed by known natural inhibitors. Structural diversity was planned to be introduced through a triazole linker at the 5′ position of this scaffold thanks to Cu(I)-catalyzed azide−alkyne cycloaddition[18] (CuAAC). Indeed, this robust process seemed to be particularly relevant at the ultimate key step since it is compatible with a large range of functional groups, occurs under mild conditions and is generally high yielding.[18,19] Moreover, the use of a 1,2,3-triazole to connect various fragments to the aminoribosyl-*O*-uridine skeleton appeared to be relevant because of electronic similarities with the amide bond,[20] a function present at the same position in some of the above-mentioned natural inhibitors.

RESULTS AND DISCUSSION

The retrosynthesis we designed (Scheme 1) for the preparation of the targeted inhibitors **A** relies on the CuAAC reaction between individual azides (**11a−n**, Figure 3) and 5′-alkynyl-aminoribosyl uridine **B**, which could be derived from *O*-glycosylation of the known uridine-derived propargylic alcohol **D**, by an anomerically activated and amine protected 5-amino-5-deoxy-D-ribofuranoside **C**.

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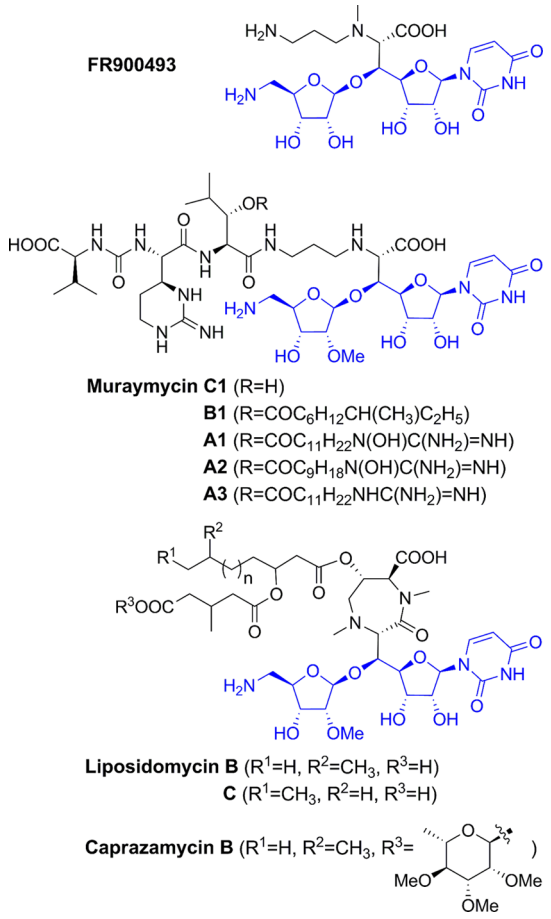


Figure 1. Natural inhibitors of MraY.

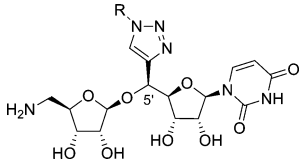


Figure 2. Structure of targeted MraY inhibitors.

In previous synthetic approaches toward caprazamycins and muraymycins, the 5-aminoribosyl moiety was introduced by glycosylation with a 5-azidoribosyl derivative as a ribosyl donor.[14d,e,g,i,15c,d,h−m] According to the proposed retrosynthetic analysis, the use of an azido group to mask the primary amine was excluded to avoid autocondensation during the CuAAC reaction step. In contrast, the easily cleavable phthalimido group could be suitable for our strategy. Accordingly, the 5-phthalimidoribosyl fluoride **8**, with pentylidene protection for the 2,3-dihydroxyl groups, was prepared in four steps (via **5**, **6** and **7**) from D-ribose in a 47% overall yield (Scheme 2).

Initially, ribose was first protected with the acid labile 3-pentylidene group, known to hinder the α-face of the ribosyl donor during the glycosylation step.[15h] Unfortunately, all attempts to introduce a phthalimide moiety as a masked primary amine on compounds exhibiting an unprotected anomeric hydroxyl, either by nucleophilic substitution from mesylate **2** or tosylate **3** or by direct Mitsunobu[21] reaction on the alcohol **1**, led exclusively to the tricyclic compound **4**.

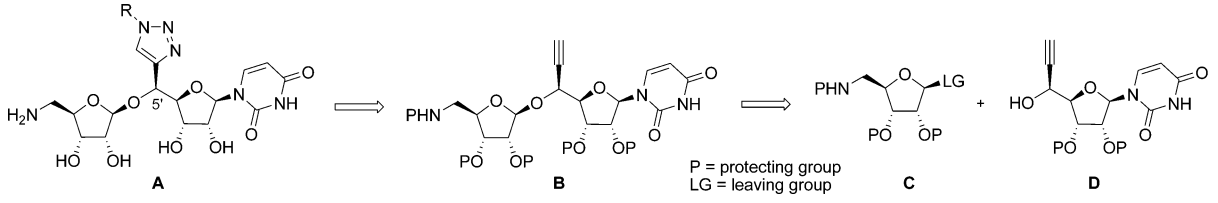
As a highly effective alternative, direct conversion of D-ribose to β-1-*O*-allyl-2,3-di-*O*-pentylidene ribofuranoside **5**,[22] with concurrent installation of the two useful protecting groups, was achieved in a single reaction in a 3-pentanone/allylic alcohol mixture in the presence of sulfuric acid to give **5** as the single β stereoisomer exhibiting a characteristic singlet for H_1 at 5.13 ppm. The configuration of the hemiketal carbon was also confirmed by the presence of a NOE between H_1 and H_4 (NOESY).

The primary alcohol **5** was then converted to the phthalimide **6** by *N*-alkylation under Mitsunobu conditions. Various attempts to deprotect the anomeric hydroxyl by using well-known deallylation conditions proved unsuccessful leading either to unchanged starting material ($Pd(PPh_3)_4$, DMBA, MeOH),[23] or to complex mixtures ($Pd(PPh_3)_4$, K_2CO_3, MeOH).[24] Treatment of compound **6** with nickel chloride and triethylaluminium[25] allowed allyl deprotection but in modest and unreproductible yields (44−63%). In contrast, removal of the allyl protecting group was successfully achieved by oxidative cleavage in the presence of 4-methylmorpholine-*N*-oxide, sodium periodate and a catalytic amount of osmium tetroxide in a 2/1 dioxane/water mixture[26] affording in 97% yield the anomeric unprotected ribose **7**. The latter was subsequently activated as its fluoride **8** using diethylaminosulfur trifluoride.

The known propargyl alcohol **9**[27] was prepared according to a literature procedure[28] from 2′,3′-*O*-isopropylidene-uridine by Dess−Martin oxidation of its primary alcohol function followed by triethylsilylethynylmagnesiumbromide condensation leading to a 2/1 mixture of the corresponding 5′*R*/5′*S* triethylsilylpropargyl alcohols. The separable major 5′*R* isomer was then converted into the desired propargyl alcohol **9** in a two step sequence allowing inversion of the configuration at $C_{5'}$ under Mitsunobu conditions (PPh_3, DIAD) leading to the 2,5′*S*-anhydro-uridine, which was subsequently hydrolyzed into the alcohol **9** under basic conditions (NaOH, MeOH/H_2O). The established *S* configuration in alcohol **9**[27] was further confirmed by differentiation from its *R* diastereoisomer, which is also known and reported.[28]

Next, the propargyl alcohol **9** was submitted to glycosylation with the ribose derivative **8** in the presence of boron trifluoride etherate[15d] at −78 °C to give the alkyne **10** with a high 13/1 β/α selectivity and in an excellent 90% yield, considering the steric hindrance of the ribosyl acceptor. Assignment of anomers for compound **10** was made according to distinguishing

Scheme 1. Retrosynthetic Analysis of Targeted Inhibitors A



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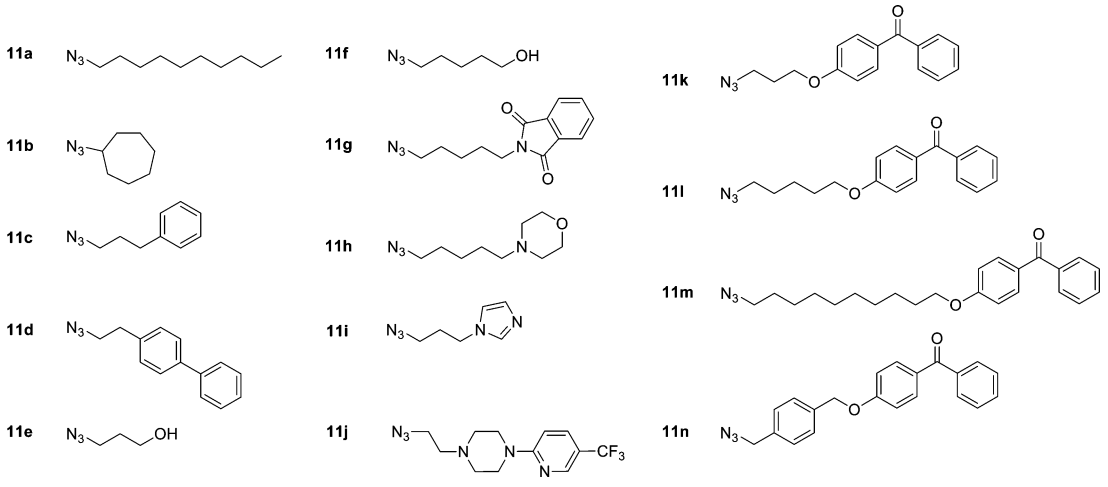
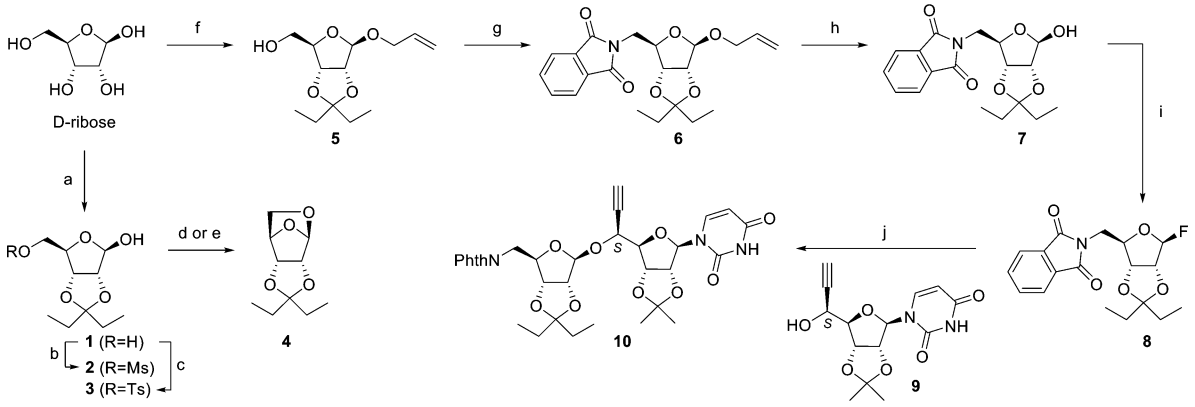


Figure 3. Structure of azide building blocks **11**.

Scheme 2. Synthesis of the Protected 5′-Ethynyl-aminoribosyl-*O*-uridine 10



Reagents and conditions: (a) pentan-3-one, H_2SO_4 cat., DMF, rt, 48 h, (77%); (b) MsCl, NEt_3, DMAP cat., CH_2Cl_2, rt, 48 h; (c) TsCl, Pyridine, 0 °C, rt, 48 h; (d) PPh_3, DIAD, PhthH, toluene, rt, 16 h, (66%); (e) **2** or **3**, PhthK, DMF, rt, 48 h (57% over two steps from **2**, 46% over two steps from **3**); (f) allylic alcohol, pentan-3-one, H_2SO_4 cat., 4 h, 60 °C, (60%); (g) PPh_3, DIAD, PhthH, toluene, rt, 18 h, (84%); (h) OsO_4 cat., NMO, $NaIO_4$, dioxane/H_2O: 2/1, 70 °C, 18 h, (97%); (i) DAST, CH_2Cl_2, −30 °C, 30 min, then rt, 1 h (97%) (β/α > 9); (j) **8**, BF_3-Et_2O, M.S. 4 Å, CH_2Cl_2, −78 °C to rt, (90%) (β/α =13/1).

characteristic ^{1}H NMR signals for $H_{1''}$, a singlet at 5.31 ppm for the major β anomer and a doublet ($^3J_{H1''-H2''}$ = 2 Hz) at 5.30 ppm for the minor α anomer.

To introduce chemical diversity in the set of final compounds, we next turned to the synthesis of second partners for CuAAC, azido building blocks displaying various structures, complexity and polarity. Thus, several apolar, aliphatic or aromatic, linear or cyclic, azides such as **11d** were selected (Figure 3). In addition, polar azido-alcohols **11e−f**, azido alkylphthalimide **11g**, morpholine **11h** and imidazole **11i** were chosen to potentially mimic the polar amine moiety present in natural MraY inhibitors. The piperazine-azide **11j**, with a more polar and complex structure,[29] was also involved in this study. Finally, in order to determine if compounds containing a benzophenone moiety could inhibit MraY, we also picked four benzophenone-derived azides **11k−n**. Indeed, inhibitors bearing such a photoactivable group[30] and exhibiting different spacers between the benzophenone and the triazole moieties could offer some original opportunities for the mapping of the yet unknown MraY active site.

The synthesis of azides **11** (**a−n**; groups **A−E**) is depicted in Scheme 3. Thus, azides **A**, **11a** and **11c−f**, were synthesized from corresponding bromide or tosyl derivatives. Azides **B**, **11b** and **11i**, were prepared by diazotransfer reaction on primary amine **13a** and **13b**, with imidazole-1-sulfonyl azide hydrochloride[31] as a diazo donor. Azides **C**, **11g** (a phthalimide) and **11h** (a morpholine) were prepared through a common intermediate **15** resulting from activation of pentane-1,5-diol as its dimesylate **14**, followed by monosubstitution with sodium azide. Further substitution by phthalimide or morpholine afforded azides **11g** and **11h**, respectively. Finally, azides **D**, **11k−m**, and azide **E**, **11n**, all containing the benzophenone group, were efficiently prepared from the corresponding dibromo reagent by successive displacement of bromides, by 4-hydroxybenzophenone and azide anion.

With azide partners **11a−n** and alkyne **10** in hand, we undertook the synthesis of the targeted triazole compounds. Accordingly, alkyne scaffold **10** and azide partners **11a−n** were submitted to CuAAC conditions, at room temperature in a 3/1 *tert*-BuOH/water mixture using catalytic $CuSO_4$ and sodium ascorbate[18] in the presence of DIPEA (Scheme 4).

The CuAAC reactions resulted in 1,4-triazoles **18a−n**, which were isolated in yields of 37−75% (Table 1), which are reasonable considering the bulkiness of the aminoribosyl

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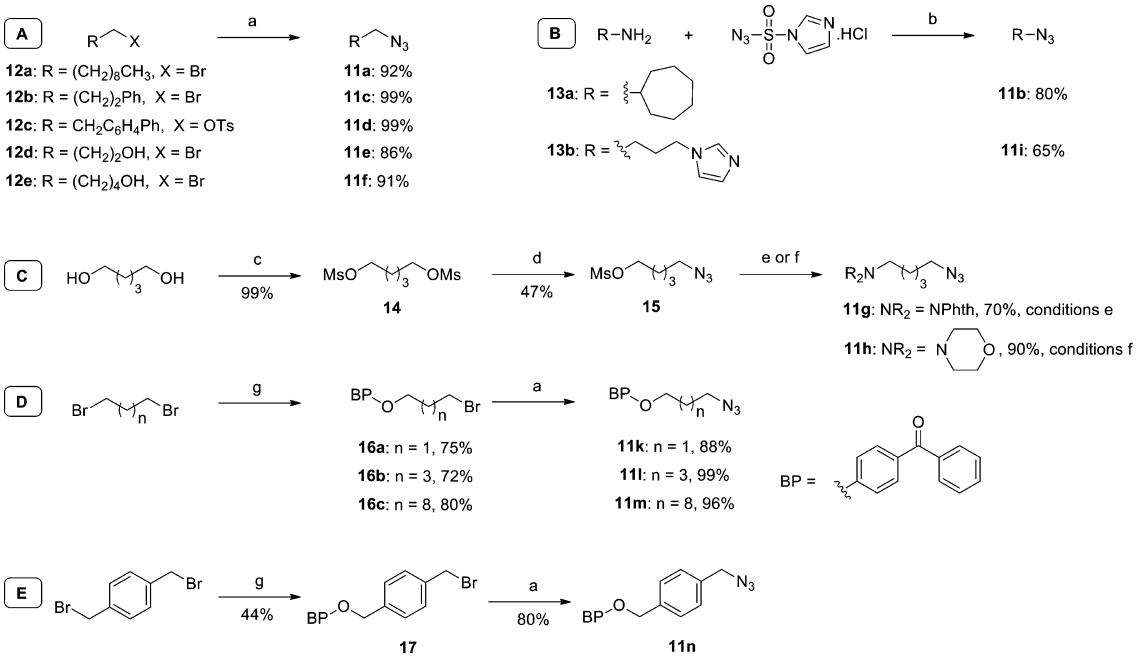
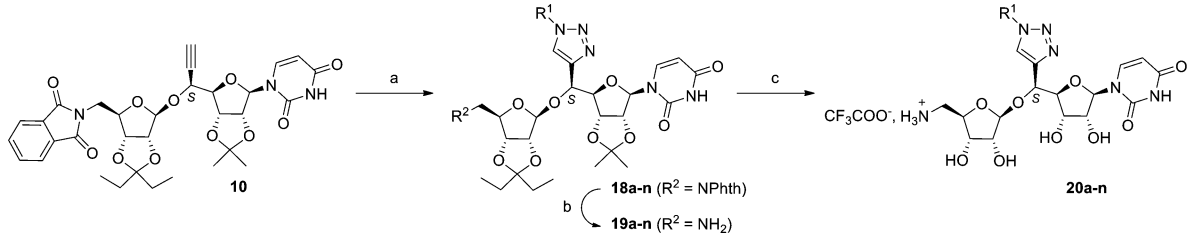
Scheme 3. Synthesis of Azides 11a−n



Reagents and conditions: (a) NaN_3, NaI, DMF, 80 °C, overnight; (b) $CuSO_4{\cdot}5H_2O$, K_2CO_3, MeOH, rt; (c) MsCl, Et_3N, CH_2Cl_2, 0 °C, 30 min, then rt, 2 h; (d) NaN_3, CH_3CN, reflux, 18 h; (e) PhthK, DMF, 80 °C, 12 h; (f) Morpholine, Et_3N, CH_3CN, reflux, 12 h; (g) 4-HO-BP, K_2CO_3, DMF, rt, 16 h.

Scheme 4. Synthesis of the Targeted Triazoles 20a−n



Reagents and conditions: (a) **11a−n** (R^1-N_3), DIPEA, $CuSO_4{\cdot}5H_2O$ (0.1 equiv), sodium ascorbate (0.3 equiv), *tert*-BuOH/H_2O; (b) CH_3NH_2, MeOH, 5 h, rt (for **18g** to **19g**, NPhth in R^1 is also cleaved); (c) TFA/H_2O 4/1 0 °C, 10 min, then rt, 90 min.

Table 1. Yields for the Synthesis of 18a−n, 19a−n, and 20a−n

R^1-N_3	**18** (yield) (%)	**19** (yield) (%)	**20** (yield) (%)
11a	**a**: 61	**a**: 65	**a**: 94
11b	**b**: 64	**b**: 63	**b**: 93
11c	**c**: 45	**c**: 58	**c**: 89
11d	**d**: 46	**d**: 55	**d**: 96
11e	**e**: 46	**e**: 47	**e**: 91
11f	**f**: 51	**f**: 71	**f**: 69
11g	**g**: 75	**g**: 60	**g**: 95[a]
11h	**h**: 56	**h**: 74	**h**: 99[a]
11i	**i**: 71	**i**: 52	**i**: 99[a]
11j	**j**: 62	**j**: 47	**j**: 86
11k	**k**: 52	**k**: 46	**k**: 99
11l	**l**: 52	**l**: 49	**l**: 96
11m	**m**: 49	**m**: 51	**m**: 99
11n	**n**: 37	**n**: 80	**n**: 99

[a]Obtained as a di-TFA salt.

moiety. The phthalimide protecting group was then removed under mild conditions by methylamine[32] to give aminoribosyltriazoles **19a−n**. Finally, acidic deprotection of the ketals in a 4/1 trifluoroacetic acid/water mixture provided the desired analogues of MraY natural inhibitors **20a−n** as their trifluoroacetate salts in nearly quantitative yield.

Preliminary in vitro biological evaluation of (Table 2) the synthesized compounds **20k−n**, which could further be exploited as molecular tools for mapping the MraY active site, was carried out on MraY purified from *Bacillus subtilis*, as described in the Experimental Section. The residual activity of the enzyme was measured in the presence of 1 mM of the tested compounds, and then the IC_{50} value was calculated. Commercially available tunicamycin from *Streptomyces sp.* was used as a positive control in the tests and resulted in an IC_{50} value equal to 0.012 μM.

Interestingly, all the compounds containing the benzophenone group revealed inhibition of the MraY enzyme. The biological evaluation of the other synthesized compounds on MraY enzymatic activity is currently in progress and will be reported elsewhere.

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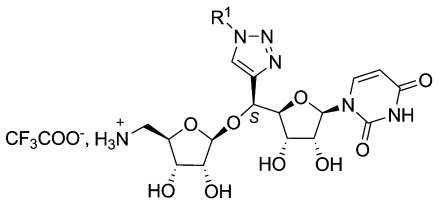
Table 2. Inhibitory Activity of Compounds 20k−n on the MraY Enzyme



			IC_{50} (μM)
R^1	BP-O-	**20k**	100
	BP-O-(CH2)3-	**20l**	100
	BP-O-(CH2)8-	**20m**	125
	BP-O-Ph-	**20n**	50

CONCLUSION

We developed a straightforward synthesis of a highly functionalized alkyne scaffold, which was easily prepared on a multigram scale from D-ribose. Subsequent introduction of chemical diversity achieved with the CuAAC reaction, at a late stage of the synthesis, allowed rapid access to variously substituted triazole-containing compounds including benzophenone derivatives. Preliminary biological evaluation of the latter showed interesting inhibition of the MraY enzyme, and these inhibitors will be further exploited as molecular tools for mapping the MraY active site.

EXPERIMENTAL SECTION

General Experimental Methods. When needed, reactions were carried out under an argon atmosphere. They were monitored by thin-layer chromatography with precoated silica on aluminum foil. Flash chromatography was performed with silica gel 60 (40−63 μm); the solvent systems were given v/v. Spectroscopic ^{1}H and ^{13}C NMR, MS and/or analytical data were obtained using chromatographically homogeneous samples. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ unless indicated. Chemical shifts (δ) are reported in ppm, and coupling constants are given in Hz. For each compound detailed peak assignments have been made according to COSY, HSQC and HMBC experiments. The numbering of molecules is indicated in the Supporting Information file. Optical rotations were measured with sodium (589 nm) or mercury (365 nm) lamp at 20 °C. Melting points were measured on a hot bench. IR spectra were recorded on a FT-IR spectrophotometer, and the wavelengths are reported in cm^{-1}. Low resolution mass spectra (LRMS) were recorded with an ion trap mass analyzer under electrospray ionization (ESI) in positive ionization mode detection or atmospheric pressure chemical ionization (APCI). High resolution mass sprectra (HRMS) were recorded with a TOF mass analyzer under electrospray ionization (ESI) in positive ionization mode detection, atmospheric pressure chemical ionization or atmospheric pressure photoionization (APPI). For MraY activity, the radioactive spots were located and quantified with a radioactivity scanner (model Multi-Tracemaster LB285).

5-Anhydro-2,3-O-isopentylidene-β-D-ribofuranose (4). Via Compound 1 by Mitsunobu Reaction. To a solution of compound **1** (350 mg, 1.6 mmol, 1 equiv), phthalimide (259 mg, 1.76 mmol, 1.1 equiv) and triphenylphosphine (839 mg, 3.2 mmol, 2 equiv) in anhydrous toluene (9 mL), diisopropylazodicarboxylate (DIAD) was added dropwise (630 μL, 3.2 mmol, 2 equiv). The resulting yellow solution was stirred at rt for 16 h and concentrated in vacuo. The crude oil was purified by flash chromatography (Cyclohexane/EtOAc 9/1, then 3/7) to give tricyclic compound **4** as a colorless oil (210 mg, 66%).

Via the Mesylate 2 by Nucleophilic Substitution. To a solution of compound **1** (350 mg, 1.6 mmol, 1 equiv) in DCM (6 mL) were successively added DMAP (10 mg, 0.08 mmol, 1 equiv), triethylamine (337 μL, 2.41 mmol, 1.5 equiv) and MsCl dropwise (190 μL, 2.41 mmol, 1.5 equiv). The mixture was stirred at rt for 48 h. After addition of EtOAc (30 mL), the mixture was washed with a 1 M HCl aqueous solution (2 × 30 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were then washed with brine (50 mL) and water (50 mL), dried (Na_2SO_4), filtrated and concentrated in vacuo to give the crude mesylate **2** as a pale yellow oil (470 mg, 99% yield). To a solution of crude mesylate **2** (470 mg, 1.6 mmol, 1 equiv) in DMF (6 mL) was added in one portion potassium phthalimide (592 mg, 3.2 mmol, 2 equiv). The mixture was stirred at rt for 48 h and then poured into Et_2O (15 mL). After addition of a saturated aqueous solution of NH_4Cl (15 mL), the aqueous phase was extracted with Et_2O (20 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was purified by flash chromatography (DCM/Acetone 99/1) to give tricyclic compound **4** as a colorless oil (181 mg, 57% yield from **1**).

Via the Tosylate 3 by Nucleophilic Substitution. At 0 °C, to a solution of compound **1** (2.36 g, 10.8 mmol, 1 equiv) in pyridine (100 mL) was added recrystallized tosyl chloride (3.16 g, 16.6 mmol, 1.53 equiv). The mixture was stirred at rt for 48 h and diluted in EtOAc (120 mL). The resulting solution was transferred into a separatory funnel and washed with a 1 M HCl aqueous solution. The organic layer was washed with brine (2 × 100 mL) and water (100 mL), dried (Na_2SO_4), filtrated and concentrated in vacuo to furnish the crude tosylate **3** as a pale yellow oil (2.89 g, 72% yield). To a solution of crude tosylate **3** (257 mg, 0.69 mmol, 1 equiv), in DMF (20 mL) was added in one portion potassium phthalimide (249 mg, 1.34 mmol, 2 equiv). The mixture was stirred at rt for 48 h, and the reaction was quenched at 0 °C by addition of a saturated aqueous solution of NH_4Cl (30 mL). The mixture was extracted with DCM (4 × 30 mL), and the combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was purified by flash chromatography (DCM to DCM/Acetone 95/5) to afford tricyclic compound **4** as a colorless oil (138 mg, 64% yield, 46% from **1**): R_f 0.73 (DCM/Acetone 97/3); $[\alpha]_D$ −51 (*c* 1.0, CH_2Cl_2); IR (film) 2976*s*, 2940*m*, 1350*m*, 1073*s*; ^{1}H NMR δ 5.43 (s, 1H, H_1), 4.69 (d, 1H, J_{H4-H5a} = 4.0 Hz, H_4), 4.31 (d, 1H, J_{H2-H3} = 5.5 Hz, H_2), 4.26 (d, 1H, J_{H3-H2} = 5.5 Hz, H_3), 3.39 (dd, 1H, $J_{H5a-H5b}$ = 7.0 Hz, J_{H5a-H4} = 4.0 Hz, H_{5a}), 3.27 (d, 1H, $J_{H5b-H5a}$ = 7.0 Hz, H_{5b}), 1.69 (q, 2H, J_{H7-H8} = 7.5 Hz, H_7), 1.54 (q, 2H, $J_{H7'-H8'}$ = 7.5 Hz, $H_{7'}$), 0.91 (t, 3H, J_{H8-H7} = 7.5 Hz, H_8), 0.86 (t, 3H, $J_{H8'-H7'}$ = 7.5 Hz, $H_{8'}$); ^{13}C NMR δ 116.5 (C_6), 99.9 (C_1), 81.7 (C_3), 79.6 (C_2), 77.8 (C_4), 63.0 (C_5), 29.5 (C_7), 29.0 ($C_{7'}$), 8.5 (C_8), 7.8 ($C_{8'}$); HRMS APCI Calcd for $C_{10}H_{17}O_4^+$ $(M + H)^+$ 201.1127, found 201.1123.

1-O-Allyl-2,3-O-isopentylidene-β-D-ribofuranose (5). To a suspension of D-ribose (10.0 g, 66.6 mmol, 1 equiv) in 3-pentanone (40 mL, 377 mmol, 5.7 equiv) was added allyl alcohol (45 mL, 662 mmol, 9.9 equiv) and concentrated sulfuric acid (0.7 mL, 13 mmol, 0.2 equiv). The suspension was vigorously stirred at 60 °C for 4 h. The resulting pale yellow solution was cooled down to rt, neutralized by a dropwise addition of Et_3N (1.88 mL, 13 mmol, 0.2 equiv) and concentrated in vacuo. After addition of water (200 mL), the residue was extracted with EtOAc (5 × 200 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The resulting pale yellow oil was purified by flash chromatography (Cyclohexane/EtOAc 8/2) to give protected ribose **5** as the single β stereoisomer and as a colorless oil (10.33 g, 60% yield): R_f 0.34 (Cyclohexane/EtOAc 8/2); $[\alpha]_D$ −73 (*c* 1.0, CH_2Cl_2); IR (film) 3469*br*, 2942*w*, 1464*w*, 1097*s*, 925*s*; ^{1}H NMR δ 5.91 (dddd, 1H, $J_{H10-H11'}$ = 17.0 Hz, $J_{H10-H11}$ = 10.0 Hz, $J_{H10-H9a}$ = 6.0 Hz, $J_{H10-H9b}$ = 6.0 Hz, H_{10}), 5.32 (dd, 1H, $J_{H11'-H10}$ = 17.0 Hz, $J_{H11'-H11}$ = 1.5 Hz, $H_{11'}$), 5.24 (br d, 1H, $J_{H11-H10}$ = 10.0 Hz, H_{11}), 5.13 (s, 1H, H_1), 4.86 (d, 1H, J_{H3-H2} = 6.0 Hz, H_3), 4.65 (d,

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1H, J_{H2-H3} = 6.0 Hz, H_2), 4.45 (dd, 1H, J_{H4-H5b} = 3.5 Hz, J_{H4-H5a} = 2.5 Hz, H_4), 4.24 (dd, 1H, $J_{H9a-H9b}$ = 12.5 Hz, $J_{H9a-H10}$ = 6.0 Hz, H_{9a}), 4.07 (dd, 1H, $J_{H9b-H9a}$ = 12.5 Hz, $J_{H9b-H10}$ = 6.0 Hz, H_{9b}), 3.70 (br d, 1H, $J_{H5a-H5b}$ = 12.0 Hz, H_{5a}), 3.63 (ddd, 1H, $J_{H5b-H5a}$ = 12.0 Hz, J_{H5b-OH} = 9.0 Hz, J_{H5b-H4} = 3.5 Hz, H_{5b}), 3.19 (br d, 1H, J_{OH-5b} = 9.0 Hz, OH), 1.71 (q, 2H, J_{H7-H8} = 7.0 Hz, H_7), 1.59 (q, 2H, $J_{H7'-H8'}$ = 7.0 Hz, $H_{7'}$), 0.93 (t, 3H, J_{H8-H7} = 7.0 Hz, H_8), 0.88 (t, 3H, $J_{H8'-H7'}$ = 7.0 Hz, $H_{8'}$); ^{13}C NMR δ 133.3 (C_{10}), 118.5 (C_{11}), 116.7 (C_6), 108.3 (C_1), 88.9 (C_4), 86.5 (C_2), 82.0 (C_3), 69.2 (C_9), 64.3 (C_5), 29.5, 29.0 (C_7, $C_{7'}$), 8.6, 7.6 (C_8, $C_{8'}$); HRMS APCI Calcd for $C_{13}H_{23}O_5^+$ $(M + H)^+$ 259.1545, found 259.1545.

*1-O-Allyl-5-deoxy-2,3-O-isopentylidene-5-phthalimido-β-D-ribofuranose (**6**).* To a solution of **5** (9.27 g, 35.9 mmol, 1 equiv), triphenylphosphine (18.8 g, 71.8 mmol, 2 equiv) and phthalimide (6.34 g, 43.1 mmol, 2 equiv), in anhydrous toluene (203 mL), DIAD was added dropwise (15.4 mL, 71.8 mmol, 2 equiv). The reaction mixture was stirred at rt for 18 h and concentrated in vacuo. The residue (55 g) was purified by flash chromatography (Cyclohexane/EtOAc 9/1 then 8/2) to give compound **6** as a colorless oil (11.64 g, 84% yield): R_f 0.44 (Cyclohexane/EtOAc 8/2); $[\alpha]_D$ −60 (*c* 1.0, CH_2Cl_2); IR (film) 2975*w*, 1774*m*, 1716*s*, 1395*s*, 1034*s*, 926*m*; ^{1}H NMR δ 7.87−7.83 (m, 2H, H_{14}), 7.72−7.70 (m, 2H, H_{15}), 5.91 (dddd, 1H, $J_{H10-H11'}$ = 17.0 Hz, $J_{H10-H11}$ = 10.0 Hz, $J_{H10-H9b}$ = 6.5 Hz, $J_{H10-H9a}$ = 5.0 Hz, H_{10}), 5.31 (dd, 1H, $J_{H11'-H10}$ = 17.0 Hz, $J_{H11'-H11}$ = 1.5 Hz, $H_{11'}$), 5.19 (br d, 1H, $J_{H11-H10}$ = 10.0 Hz, H_{11}), 5.14 (s, 1H, H_1), 4.82 (d, 1H, J_{H3-H2} = 6.5 Hz, H_3), 4.75 (d, 1H, J_{H2-H3} = 6.5 Hz, H_2), 4.48 (dd, 1H, J_{H4-H5a} = 9.0 Hz, J_{H4-H5b} = 6.0 Hz, H_4), 4.27 (dd, 1H, $J_{H9a-H9b}$ = 13.0 Hz, $J_{H9a-H10}$ = 5.0 Hz, H_{9a}), 3.98 (dd, 1H, $J_{H9b-H9a}$ = 13.0 Hz, $J_{H9b-H10}$ = 6.5 Hz, H_{9b}), 3.89 (dd, 1H, $J_{H5a-H5b}$ = 14.0 Hz, J_{H5a-H4} = 9.0 Hz, H_{5a}), 3.83 (dd, 1H, $J_{H5b-H5a}$ = 14.0 Hz, J_{H5b-H4} = 6.0 Hz, H_{5b}), 1.65 (q, 2H, J_{H7-H8} = 8.0 Hz, H_7), 1.55 (q, 2H, $J_{H7'-H8'}$ = 8.0 Hz, $H_{7'}$), 0.87 (t, 3H, J_{H8-H7} = 8.0 Hz, H_8), 0.84 (t, 3H, $J_{H8'-H7'}$ = 8.0 Hz, $H_{8'}$); ^{13}C NMR δ 168.4 (C_{12}), 134.3 (C_{15}), 133.9 (C_{10}), 132.2 (C_{13}), 123.6 (C_{14}), 117.6 (C_{11}), 116.9 (C_6), 107.9 (C_1), 86.0 (C_2), 84.8 (C_4), 82.9 (C_3), 68.6 (C_9), 41.3 (C_5), 29.7, 29.1 (C_7, $C_{7'}$), 8.5, 7.5 (C_8, $C_{8'}$); HRMS ESI$^+$ Calcd for $C_{21}H_{25}NaNO_6^+$ $(M + Na)^+$ 410.1580, found 410.1581.

*5-Deoxy-2,3-O-isopentylidene-5-phthalimido-β-D-ribofuranose (**7**).* To a solution of **6** (5.62 g, 14.5 mmol, 1 equiv), in a 2/1 dioxan/water mixture (100 mL) were successively added the *N*-methylmorpholine-*N*-oxide in one portion (7.90 g, 47.9 mmol, 3.3 equiv) and an osmium tetraoxide solution in *tert*-BuOH dropwise (2.5% w/v, 0.084 M, 985 μL, cat.). Sodium periodate was then added in one portion (10.1 g, 47.9 mmol, 3.3 equiv). The reaction mixture was stirred at 70 °C for 18 h and concentrated in vacuo. The aqueous phase was extracted with DCM (4 × 250 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The resulting oil was purified by flash chromatography (Cyclohexane/EtOAc 8/2 then 7/3) to give compound **7** as a colorless oil (4.97 g, 97% yield): R_f 0.34, (Cyclohexane/EtOAc 7/3); $[\alpha]_D$ −32 (*c* 1.0, CH_2Cl_2); IR (film) 3421*br*, 2974*w*, 2941*w*, 1773*m*, 1710*s*, 1396*s*, 1082*s*, 926*s*; ^{1}H NMR δ 7.88−7.84 (m, 2H, H_{11}), 7.74−7.71 (m, 2H, H_{12}), 5.44 (s, 1H, H_1), 4.82 (d, 1H, J_{H3-H2} = 6.0 Hz, H_3), 4.76 (d, 1H, J_{H2-H3} = 6.0 Hz, H_2), 4.51 (dd, 1H, J_{H4-H5a} = 9.0 Hz, J_{H4-H5b} = 6.5 Hz, H_4), 3.86 (dd, 1H, $J_{H5a-H5b}$ = 14.0 Hz, J_{H5a-H4} = 9.0 Hz, H_{5a}), 3.83 (dd, 1H, $J_{H5b-H5a}$ = 14.0 Hz, J_{H5b-H4} = 6.5 Hz, H_{5b}), 2.37−2.12 (br s, 1H, OH), 1.67−1.60 (m, 2H, H_7), 1.53 (q, 2H, J_{H7-H8} = 7.5 Hz, H_7), 0.86 (t, 3H, J_{H8-H7} = 7.5 Hz, H_8), 0.83 (t, 3H, J_{H8-H7} = 7.5 Hz, H_8); ^{13}C NMR δ 168.1 (C_9), 134.1 (C_{12}), 131.9 (C_{10}), 123.5 (C_{11}), 117.0 (C_6), 104.3 (C_1), 85.9 (C_2), 84.7 (C_4), 82.7 (C_3), 40.7 (C_5), 29.5, 29.0 (C_7), 8.3, 7.3 (C_8); HRMS ESI$^+$ Calcd for $C_{18}H_{22}NO_6^+$ $(M + H)^+$ 348.1461, found 348.1462.

*1,5-Dideoxy-1-fluoro-2,3-O-isopentylidene-5-phthalimido-D-ribofuranose (**8**).* At −30 °C, to a solution of compound **7** (4.94 g, 14.2 mmol, 1 equiv) in DCM (173 mL), DAST was added dropwise (2.8 mL, 21.2 mmol, 1.5 equiv). The resulting yellow solution was stirred at −30 °C for 30 min then at rt for 1 h. The reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (160 mL), and the aqueous phase was extracted with DCM (4 × 200 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The resulting oil was purified by flash chromatography (Cyclohexane/EtOAc 9/1) to give compound **8** as a β/α mixture (β/α > 9) and as a colorless oil (4.82g, 97%). Compounds **8*β*** and **8*α*** were isolated and fully characterized. **8*β***: R_f 0.44 (Cyclohexane/EtOAc 8/2); $[\alpha]_D$ + 12 (*c* 1.0, CH_2Cl_2); IR (film) 2973*w*, 1773*w*, 1712*s*, 1401*m*, 1130*m*, 724*m*; ^{1}H NMR δ 7.87−7.84 (m, 2H, H_{11}), 7.75−7.72 (m, 2H, H_{12}), 5.80 (d, 1H, J_{H1-F} = 61.5 Hz, H_1), 4.90 (dd, 1H, J_{H2-H3} = 6.0 Hz, J_{H2-F} = 5.5 Hz, H_2), 4.86 (d, 1H, J_{H3-H2} = 6.0 Hz, H_3), 4.64 (ddd, 1H, J_{H4-H5b} = 9.0 Hz, J_{H4-H5a} = 6.0 Hz, J_{H4-F} = 3.0 Hz, H_4), 3.88 (dd, 1H, $J_{H5a-H5b}$ = 14.0 Hz, J_{H5a-H4} = 6.0 Hz, H_{5a}), 3.81 (dd, 1H, $J_{H5b-H5a}$ = 14.0 Hz, J_{H5b-H4} = 9.0 Hz, H_{5b}), 1.65 (q, 2H, J_{H7-H8} = 7.5 Hz, H_7), 1.56 (q, 2H, $J_{H7'-H8'}$ = 7.5 Hz, $H_{7'}$), 0.89 (t, 3H, J_{H8-H7} = 7.5 Hz, H_8), 0.87 (t, 3H, $J_{H8'-H7'}$ = 7.5 Hz, $H_{8'}$); ^{13}C NMR δ 168.2 (C_9), 134.4 (C_{12}), 133.7 (C_{10}), 123.7 (C_{11}), 117.6 (C_6), 115.5 (d, J_{C1-F} = 221 Hz, C_1), 86.3 (C_4), 85.6 (d, J_{C2-F} = 41.5 Hz, C_2), 82.7 (C_3), 40.6 (C_5), 29.6, 27.1 (C_7, $C_{7'}$), 8.5, 7.5 (C_8, $C_{8'}$); HRMS ESI$^+$ Calcd for $C_{18}H_{20}NO_5FNa^+$ $(M + Na)^+$ 372.1223, found 372.1229. **8*α***: R_f 0.26 (Cyclohexane/EtOAc 8/2); $[\alpha]_D$ + 23 (*c* 1.0, CH_2Cl_2); IR (film) 2976*w*, 1715*s*, 1394*m*, 1105*m*, 714*m*; ^{1}H NMR δ 7.87−7.84 (m, 2H, H_{11}), 7.75−7.72 (m, 2H, H_{12}), 5.64 (dd, 1H, J_{H1-F} = 63.0 Hz, J_{H1-H2} = 3.5 Hz, H_1), 4.75 (ddd, 1H, J_{H2-F} = 14.5 Hz, J_{H2-H3} = 7.5 Hz, J_{H2-H1} = 3.5 Hz, H_2), 4.68 (dd, 1H, J_{H3-H2} = 7.5 Hz, J_{H3-H4} = 4.0 Hz, H_3), 4.62 (dt, 1H, J_{H4-H5a} = 7.0 Hz, J_{H4-H5b} = 7.0 Hz, J_{H4-H3} = 4.0 Hz, H_4), 3.93 (d, 2H, J_{H5a-H4} = J_{H5b-H4} = 7.0 Hz, H_5), 1.80 (q, 2H, J_{H7-H8} = 7.5 Hz, H_7), 1.62 (q, 2H, $J_{H7'-H8'}$ = 7.5 Hz, $H_{7'}$), 0.94 (t, 3H, J_{H8-H7} = 7.5 Hz, H_8), 0.88 (t, 3H, $J_{H8'-H7'}$ = 7.5 Hz, $H_{8'}$); ^{13}C NMR ($CDCl_3$) δ 168.2 (C_9), 134.4 (C_{12}), 133.7 (C_{10}), 123.7 (C_{11}), 121.5 (C_6), 108.0 (d, J_{C1-F} = 235 Hz, C_1), 81.5 (C_4), 81.3 (d, J_{C2-F} = 79,5 Hz, C_2), 81.1 (C_3), 39.9 (C_5), 29.9 (C_7), 29.4 ($C_{7'}$), 8.5 (C_8), 8.3 $C_{8'}$); HRMS ESI$^+$ Calcd for $C_{18}H_{20}NO_5FNa^+$ $(M + Na)^+$ 372.1223, found 372.1219.

*1″,5″-Dideoxy-2″,3″-O-isopentylidene-5″-phthalimido-1″-[2′,3′-O-isopropylidene-5′(S)-ethynyl-uridinyl]-β-D-ribofuranose (**10**).* The propargylic alcohol **9**[27] (1.1 g, 3.1 mmol, 1 equiv) and the fluoride **8** (1.62 g, 4.65 mmol, 1.5 equiv) were dried together by coevaporation with toluene (3 × 10 mL) and dissolved in DCM (86 mL). The flask was flushed with argon, and molecular sieves 4 Å (11 g) were added in one portion. The suspension was vigorously stirred at rt for 1 h and then cooled to −78 °C. At −78 °C, $BF_3{\cdot}Et_2O$ (535 μL, 4.65 mmol, 1.5 equiv) was dropwise added, and the reaction mixture was stirred at this temperature for 10 min and then at rt for 18 h. The suspension was then diluted in DCM (80 mL), and the reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution (50 mL). The aqueous phase was extracted with DCM (6 × 150 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The resulting white foam was purified by flash chromatography (Toluene/Acetone 85/15) to give alkyne **10** as a β/α mixture (β/α = 13/1) as a white foam (1.79 g, 90% combined yield). The β anomer was isolated as a white foam (69% yield): R_f 0.30, Toluene/Acetone 75/25); mp 135−137 °C; $[\alpha]_D$ −43 (*c* 1.0, CH_2Cl_2); IR (film) 3421*br*, 2974*w*, 2941*w*, 1773*m*, 1710*s*, 1396*s*, 1082*s*, 926*s*; ^{1}H NMR δ 8.82 (s, 1H, NH), 7.87−7.85 (m, 2H, $H_{11''}$), 7.74−7.73 (m, 2H, $H_{12''}$), 7.40 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.80 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.74 (d, 1H, $J_{H1'-H2'}$ = 1.5 Hz, $H_{1'}$), 5.30 (s, 1H, $H_{1''}$), 4.92−4.99 (m, 2H, $H_{2'}$, $H_{3'}$), 4.81 (d, 1H, $J_{H2''-H3''}$ = 5.5 Hz, $H_{2''}$), 4.77 (d, 1H, $J_{H3''-H2''}$ = 5.5 Hz, $H_{3''}$), 4.67 (dd, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $J_{H5'-H7'}$ = 2.0 Hz, $H_{5'}$), 4.47 (dd, 1H, $J_{H4''-H5''a}$ = 10.0 Hz, $J_{H4''-H5''b}$ = 4.5 Hz, $H_{4''}$), 4.34 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 2.5 Hz, $H_{4'}$), 3.96 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.0 Hz, $H_{5''a}$), 3.90 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 2.60 (d, 1H, $J_{H7'-H5'}$ = 2.0 Hz, $H_{7'}$), 1.65−1.61 (m, 2H, $H_{7''}$), 1.59 (s, 3H, $H_{9'}$), 1.52 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.39 (s, 3H, $H_{9'}$), 0.85 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.3 ($C_{9''}$), 162.9 (C_4), 150.1 (C_2), 142.1 (C_6), 134.3 ($C_{12''}$), 132.1 ($C_{10''}$), 123.6 ($C_{11''}$), 117.2 ($C_{6''}$), 114.7 ($C_{8'}$), 109.4 ($C_{1''}$), 102.9 (C_5), 94.8 ($C_{1'}$), 88.6 ($C_{4'}$), 85.9 ($C_{2''}$), 84.9 ($C_{4''}$), 84.2 ($C_{2'}$), 82.6 ($C_{3''}$), 81.5 ($C_{3'}$), 79.7 ($C_{6'}$), 76.5 ($C_{7'}$), 68.6 ($C_{5'}$), 40.7 ($C_{5''}$), 29.6, 28.9 ($C_{7''}$), 27.2, 25.4 ($C_{9'}$), 8.4, 7.4 ($C_{8''}$); HRMS ESI$^-$ Calcd for $C_{32}H_{34}N_3O_{11}^-$ $(M - H)^-$ 636.2193, found 636.2204.

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General Procedure for 4-Hydroxy-benzophenone Monoalkylation. To a solution of 4-hydroxy-benzophenone in DMF (0.1 M) were added dibromide derivative (2.46 equiv) and potassium carbonate (5 equiv). The solution was stirred at rt for 16 h and then diluted in Et_2O (150 mL) and water (150 mL). The aqueous phase was extracted with Et_2O (2 × 150 mL), and the combined organic layers were washed with brine (2 × 150 mL) and water (2 × 150 mL), dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was purified by flash chromatography to give the corresponding building block.

*4-O-(3-Bromo-propyl)-benzophenone (**16a**).* Compound **16a** was synthesized according to the general procedure for 4-hydroxy-benzophenone monoalkylation from 4-hydroxy-benzophenone (1.0 g, 5.0 mmol, 1 equiv) and 1,3-dibromopropane (2.5 g, 12.4 mmol, 2.46 equiv). Flash chromatography (Cyclohexane/DCM 2/1 to 1/1) afforded **16a** as a colorless oil (1.2 g, 75% yield): R_f 0.40 (Cyclohexane/DCM 1/1); IR (film) 3061*w*, 2928*s*, 1600*s*, 1250*s*; ^{1}H NMR δ 7.83 (br d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.76 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.56 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.47 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 6.97 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 4.19 (t, 2H, J_{Ha-Hb} = 5.5 Hz, H_a), 3.61 (t, 2H, J_{Hc-Hb} = 6.5 Hz, H_c), 2.35 (tt, 2H, J_{Hb-Hc} = 6.5 Hz, J_{Hb-Ha} = 5.5 Hz, H_b); ^{13}C NMR δ 195.6 (C_5), 162.4 (C_4), 138.4 (C_6), 132.7 (C_2), 132.6 (C_9), 130.1 (C_1), 129.8 (C_7), 128.3 (C_8), 114.2 (C_3), 55.7 (C_a), 32.3 (C_c), 29.8 (C_b); MS (ESI$^+$ *m*/*z* (%)) 319 ($M^{79}Br$ + H)$^+$ (100%), 321 ($M^{81}Br$ + H)$^+$ (100%); HRMS ESI$^+$ Calcd for $C_{16}H_{16}BrO_2^+$ (M + H)$^+$ 319.0334, found 319.0324.

*4-O-(5-Bromo-pentyl)-benzophenone (**16b**).* Compound **16b** was synthesized according to the general procedure for 4-hydroxy-benzophenone monoalkylation from 4-hydroxy-benzophenone (1.1 g, 5.05 mmol, 1 equiv) and 1,5-dibromopentane (2.9 g, 12.4 mmol, 2.46 equiv). Flash chromatography (Cyclohexane/DCM 1/1 to 1/3) afforded **16b** as a colorless oil (1.3 g, 72% yield): R_f 0.49 (Cyclohexane/DCM 1/2); IR (film) 2943*w*, 1650*s*, 1699*s*, 1255*s*; ^{1}H NMR δ 7.83 (br d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.76 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.57 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 6.95 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 4.06 (t, 2H, J_{Ha-Hb} = 6.5 Hz, H_a), 3.46 (t, 2H, J_{He-Hd}= 7.0 Hz, H_e), 1.96 (tt, 2H, J_{Hd-Hc} = 7.5 Hz, J_{Hd-He}= 7.0 Hz, H_d), 1.86 (tt, 2H, J_{Hb-Hc} = 7.5 Hz, J_{Hb-Ha} = 6.5 Hz, H_b), 1.69−1.63 (m, 2H, H_c); ^{13}C NMR δ 195.7 (C_5), 162.8 (C_4), 138.5 (C_6), 132.7 (C_2), 132.0 (C_9), 130.3 (C_1), 129.9 (C_7), 128.4 (C_8), 114.2 (C_3), 68.1 (C_a), 33.6 (C_e), 32.6 (C_d), 28.5 (C_b), 24.9 (C_c); MS (ESI$^+$ *m*/*z* (%)) 347 ($M^{79}Br$ + H)$^+$ (100%), 349 ($M^{81}Br$ + H)$^+$ (100%); HRMS ESI$^+$ Calcd for $C_{18}H_{20}BrO_2^+$ (M + H)$^+$ 347.0647, found 347.0651.

*4-O-(10-Bromo-decanyl)-benzophenone (**16c**).* Compound **16c** was synthesized according to the general procedure for 4-hydroxy-benzophenone monoalkylation from 4-hydroxy-benzophenone (1.0 g, 5.05 mmol, 1 equiv) and 1,10-dibromodecane (3.72 g, 12.4 mmol, 2.46 equiv). Flash chromatography (Cyclohexane/DCM 2/1 to 1/2) afforded **16c** as a white solid (1.70 g, 80% yield): R_f 0.33 Cyclohexane/DCM 1/1); mp 58−60 °C; IR (film) 2919*m*, 2850*m*, 1638*s*, 1254*s*; ^{1}H NMR δ 7.83 (br d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.77 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.57 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 6.96 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 4.05 (t, 2H, J_{Ha-Hb} = 6.5 Hz, H_a), 3.42 (t, 2H, J_{Hj-Hi} = 7.0 Hz, H_j), 1.89−1.84 (m, 2H, H_i), 1.61 (tt, 2H, J_{Hb-Hc} = 8.0 Hz, J_{Hb-Ha} = 6.5 Hz, H_b), 1.51−1.41 (m, 4H, H_c, H_h), 1.39−1.30 (m, 8H, H_d, H_e, H_f, H_g); ^{13}C NMR δ 195.7 (C_5), 163.1 (C_4), 138.6 (C_6), 132.8 (C_2), 132.0 (C_9), 130.2 (C_1), 129.9 (C_7), 128.4 (C_8), 114.2 (C_3), 68.5 (C_a), 34.2 (C_j), 33.0 (C_i), 29.7, 29.6, 29.5, 29.3 (C_b, C_d, C_e, C_f), 28.9 (C_g), 28.4 (C_h), 26.2 (C_c); MS (ESI$^+$ *m*/*z* (%)) 417 ($M^{79}Br$ + H)$^+$ (100%), 419 ($M^{81}Br$ + H)$^+$ (100%); HRMS Calcd for $C_{23}H_{29}BrO_2^+$ (M + H)$^+$ 417.1429, found 417.1434.

*α-Bromo-α′-(4-O-benzophenone)-p-xylene (**17**).* Compound **17** was synthesized according to the general procedure for 4-hydroxy-benzophenone monoalkylation from 4-hydroxy-benzophenone (1.0 g, 5.05 mmol, 1 equiv) and α,α′-dibromo-*p*-xylene (3.27 g, 12.4 mmol, 2.46 equiv). Flash chromatography (Cyclohexane/DCM 1/1 to 1/2) afforded **17** as a white solid (845 mg, 44% yield): R_f 0.16 (Cyclohexane/DCM 1/1); mp 122−124 °C; IR (film) 3062*w*, 2862*m*, 1641*s*, 1602*s*, 1250*s*; ^{1}H NMR δ 7.84 (d, 2H, J_{H2-H3} = 8.5 Hz, H_2), 7.77 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.58 (t, 1H, J_{H9-H8} = J_{H8-H7} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = 7.5 Hz, H_8), 7.46−7.42 (m, 4H, H_c, H_d), 7.04 (d, 2H, J_{H3-H2} = 8.5 Hz, H_3), 5.16 (s, 2H, H_a), 4.52 (s, 2H, H_f); ^{13}C NMR δ 195.6 (C_5), 162.4 (C_4), 138.5 (C_6), 138.0 (C_e), 136.8 (C_b), 132.7 (C_2), 132.1 (C_9), 130.8 (C_1), 129.9 (C_7), 129.6 (C_d), 128.4 (C_8), 128.0 (C_c), 114.6 (C_3), 69.9 (C_a), 33.1 (C_f); MS (ESI$^+$ *m*/*z* (%)) 381 ($M^{79}Br$ + H)$^+$ (100%), 383 ($M^{81}Br$ + H)$^+$ (100%); HRMS Calcd for $C_{21}H_{18}BrO_2^+$ (M + H)$^+$ 381.0490, found 381.0476.

General Procedure for Azides Synthesis by Nucleophilic Substitution. ***Caution!*** *The use of azide coumpounds has been shown to be hazardous.*[33] *In our case and at our scale, no troubles were noticed.* To a solution of bromine or tosyl derivative (1 equiv) in DMF (0.9 M) was added NaN_3 (2 equiv) and NaI (0.5 equiv). The mixture was stirred at 80 °C overnight and then cooled to rt. The mixture was diluted in a 1/1 Et_2O/water mixture (8 mL for 1 mL of DMF). The mixture was transferred into a separatory funnel, and the aqueous layer was extracted with Et_2O (3 × 4 mL for 1 mL of DMF). The combined organic layers were successively washed with brine and then water. The organic layer was dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was then purified by flash chromatography to give the corresponding azide.

*1-Azido-decane (**11a**).* Azide **11a** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from bromo-decane (2 g, 9 mmol). Flash chromatography (Cyclohexane/DCM 9/1) afforded **11a** as a colorless oil (1.53 g, 92% yield): R_f 0.60 (Cyclohexane/DCM 8/2); IR (film) 2926*s*, 2855*s*, 2095*s*, 1475*m*. Other spectral data were in agreement with literature.[34]

*1-Azido-3-phenyl-propane (**11c**).* Azide **11c** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from 1-bromo-3-phenyl-propane (2g, 10 mmol). Flash chromatography (Cyclohexane/DCM 8/2) afforded **11c** as a colorless oil (1.63 g, 99% yield): R_f 0.50 (Cyclohexane/DCM 8/2). Spectral data were in agreement with literature.[35]

*1-Azido-2-(4-biphenylyl)-ethane (**11d**).* Azide **11d** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from 2-(4′-biphenylyl)ethyl tosylate[36] (1.04 mmol, 368 mg). Flash chromatography (Cyclohexane/DCM 9/1) afforded **11d** as a white solid (230 mg, 99% yield): R_f 0.26, (Cyclohexane/DCM 9/1); mp 102−104 °C; IR (film) 3031*m*, 2098*s*, 1487*s*; ^{1}H NMR δ 7.62 (d, 2H, J_{H8-H9} = 8.0 Hz, H_8), 7.59 (d, 2H, J_{H5-H4} = 8.0 Hz, H_5), 7.45 (tl, 2H, J_{H9-H8} = J_{H9-H10} = 8.0 Hz, H_9), 7.39−7.36 (m, 1H, H_{10}), 7.33 (d, 2H, J_{H4-H5} = 8.1 Hz, H_4), 3.58 (t, 2H, J_{H1-H2} = 7.2 Hz, H_1), 2.97 (t, 2H, J_{H2-H1} = 7.2 Hz, H_2); ^{13}C NMR δ 141.0 (C_7), 140.0 (C_6), 137.3 (C_3), 129.3 (C_4), 128.9 (C_9), 127.6 (C_8), 127.4 (C_{10}), 127.3 (C_5), 52.6 (C_1), 35.2 (C_2); MS APCI (N_2) *m*/*z* (%) 223 (M)$^+$ (100%); HRMS APPI Calcd for $C_{14}H_{13}N_3^+$ (M)$^+$ 223.1109, found 223.1102.

*1-Azido-propan-3-ol (**11e**).* Azide **11e** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from 3-bromopropan-1-ol (1 g, 7.23 mmol). Flash chromatography (DCM) afforded **11e** as a colorless oil (650 mg, 86% yield): R_f 0.40 (DCM). Spectral data were in agreement with literature.[37]

*1-Azido-pentan-5-ol (**11f**).* Azide **11f** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from 5-bromopentan-1-ol (800 mg, 4.79 mmol). Flash chromatography (DCM) afforded **11f** as a colorless oil (561 mg, 91% yield): R_f 0.50 (DCM); IR (film) 3375*br*, 2939*m*, 2860*m*, 2096*s*, 1261*m*. Other spectral data were in agreement with literature.[38]

*4-(3-Azido-propyloxy)-benzophenone (**11k**).* Azide **11k** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from compound **16a** (1.02 g, 3.2 mmol). Flash chromatography (DCM) afforded **11k** as a colorless oil (798 mg, 88% yield): R_f 0.42 (Cyclohexane/DCM 1/1); IR (film) 2938*br*, 2098*s*, 1600*m*, 1600*s*; ^{1}H NMR δ 7.84 (br d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.77 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.58 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 6.97 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 4.15 (t, 2H, J_{Ha-Hb} = 6.0 Hz, H_a), 3.55 (t, 2H, J_{Hc-Hb} = 6.5 Hz, H_c), 2.10 (tt, 2H, J_{Hb-Hc} = 6.5 Hz, J_{Hb-Ha} = 6.0 Hz, H_b); ^{13}C NMR δ 195.7 (C_5), 162.5 (C_4), 138.5 (C_6), 132.8 (C_2), 132.1 (C_9), 130.6

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(C_1), 129.9 (C_7), 128.4 (C_8), 114.2 (C_3), 64.9 (C_a), 48.3 (C_c), 28.9 (C_b); MS (ESI$^+$ m/z (%)) 282 (M + H)$^+$ (100%); HRMS ESI$^+$ Calcd for $C_{16}H_{16}N_3O_2^+$ (M + H)$^+$ 282.1243, found 282.1245.

*4-(5-Azido-pentyloxy)-benzophenone (**11l**).* **11l** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from compound **16b** (980 mg, 2.82 mmol). Flash chromatography (DCM) afforded **11l** as a colorless oil (835 mg, 96% yield): R_f 0.37 (Cyclohexane/DCM 1/1); IR (film) 2117*s*, 1639*s*, 1602*s*, 1252*s*; ^{1}H NMR δ 7.83 (br d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.76 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.57 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 6.95 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 4.06 (t, 2H, J_{Ha-Hb} = 6.5 Hz, H_a), 3.33 (t, 2H, J_{He-Hd} = 7.0 Hz, H_e), 1.87 (tt, 2H, J_{Hb-Hc} = 7.0 Hz, J_{Hb-Ha} = 6.5 Hz, H_b), 1.61 (tt, 2H, J_{Hd-Hc} = 7.5 Hz, J_{Hd-He} = 7.0 Hz, H_d), 1.62−1.56 (m, 2H, H_c); ^{13}C NMR δ 195.7 (C_5), 162.8 (C_4), 138.5 (C_6), 132.7 (C_2), 132.0 (C_9), 130.3 (C_1), 129.9 (C_7), 128.4 (C_8), 114.2 (C_3), 68.0 (C_a), 51.5 (C_e), 28.9 (C_b), 28.8 (C_d), 23.5 (C_c); MS (ESI$^+$ m/z (%)) 310 (M + H)$^+$ (100%); HRMS ESI$^+$ Calcd for $C_{18}H_{20}N_3O_2^+$ (M + H)$^+$ 310.1556, found 310.1549.

*4-(10-Azido-decanyloxy)-benzophenone (**11m**).* Azide **11m** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from compound **16c** (1.21 g, 2.9 mmol). Flash chromatography (DCM) afforded **11m** as a white solid (980 mg, 90% yield): R_f 0.49 (Cyclohexane/DCM 1/1); mp 46−48 °C; IR (film) 2920*m*, 2851*w*, 2118*s*, 1639*s*, 1602*s*, 1252*s*; ^{1}H NMR δ 7.83 (br d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.76 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.57 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 6.96 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 4.05 (t, 2H, J_{Ha-Hb} = 6.5 Hz, H_a), 3.27 (t, 2H, J_{Hj-Hi} = 7.0 Hz, H_j), 1.83 (tt, 2H, J_{Hb-Hc} = 7.0 Hz, J_{Hb-Ha} = 6.5 Hz, H_b), 1.61 (tt, 2H, J_{Hi-Hj} = J_{Hi-Hh}= 7.0 Hz, H_i), 1.51−1.46 (m, 2H, H_c), 1.43−1.30 (m, 10H, H_d, H_e, H_f, H_g, H_h); ^{13}C NMR δ 195.7 (C_5), 163.1 (C_4), 138.6 (C_6), 132.8 (C_2), 132.0 (C_9), 130.2 (C_1), 129.9 (C_7), 126.1 (C_8), 114.2 (C_3), 68.5 (C_a), 51.7 (C_j), 29.6, 29.6, 29.5, 29.3 (C_e, C_f, C_g, C_b, C_d), 29.1 (C_i), 26.9 (C_c), 26.2 (C_h); MS (ESI$^+$ m/z (%)) 380 (M + H)$^+$ (100%), 781 (2 M + Na)$^+$ (50%); HRMS ESI$^+$ Calcd for $C_{23}H_{30}N_3O_2^+$ (M + H)$^+$ 380.2338, found 380.2332.

*4-(4-Azidoethyl-benzyloxy)-benzophenone (**11n**).* Azide **11n** was synthesized according to the general procedure for azides synthesis by nucleophilic substitution from compound **17** (840 mg, 2.20 mmol). Flash chromatography (Cyclohexane/DCM 1/1 to DCM) afforded **11n** as a white solid (601 mg, 80% yield): R_f 0.20 (Cyclohexane/DCM 1/1); mp 133−135 °C; IR (film) 3675*w*, 2988*m*, 2129*s*, 1644*s*, 1600*s*, 1252*s*; ^{1}H NMR δ 7.84 (d, 2H, J_{H2-H3} = 9.0 Hz, H_2), 7.77 (d, 2H, J_{H7-H8} = 7.5 Hz, H_7), 7.58 (t, 1H, J_{H9-H8} = 7.5 Hz, H_9), 7.48 (t, 2H, J_{H8-H9} = J_{H8-H7} = 7.5 Hz, H_8), 7.48 (d, 2H, J_{Hc-Hd} = 7.5 Hz, H_c), 7.37 (d, 2H, J_{Hd-Hc} = 7.5 Hz, H_d), 7.05 (d, 2H, J_{H3-H2} = 9.0 Hz, H_3), 5.17 (s, 2H, H_a), 4.38 (s, 2H, H_f); ^{13}C NMR δ 195.7 (C_5), 162.4 (C_4), 138.4 (C_6), 136.6 (C_e), 135.7 (C_b), 132.8 (C_2), 132.1 (C_9), 130.7 (C_1), 129.9 (C_7), 128.7 (C_d), 128.4 (C_8), 128.1 (C_c), 114.6 (C_3), 70.0 (C_a), 54.7 (C_f); HRMS ESI$^+$ Calcd for $C_{21}H_{18}N_3O_2^+$ (M + H)$^+$ 344.1399, found 344.1393.

*1,5-Dimethanesulfonyl-pentane (**14**).* To a solution of pentan-1,5-diol (2.50 g, 24 mmol, 1 equiv) in DCM (120 mL) was added triethylamine (7.68 mL, 55 mmol, 2.3 equiv). At 0 °C, was then added dropwise methanesulfonyl chloride (4.26 mL, 55 mmol, 2.3 equiv). The mixture was stirred at 0 °C for 30 min and then at rt for 2 h. The precipitate was filtrated out, and the filtrate was concentrated in vacuo. The resulting oil was purified by flash chromatography (Cyclohexane/EtOAc 4/6 then 3/7) to give compound **14** as a colorless oil (5.92 g, 99% yield): R_f 0.47 (Cyclohexane/EtOAc 4/6); IR (film) 2948*br*, 1347*s*, 1170*s*; ^{1}H NMR δ 4.25 (t, 4H, J_{Hb-Hc} = 6.5 Hz, H_b), 3.01 (s, 6H, H_a), 1.87−1.74 (m, 4H, H_c), 1.63−1.50 (m, 2H, H_d); ^{13}C NMR δ 69.6 (C_b), 37.6 (C_a), 28.7 (C_c), 21.8 (C_d); MS (ESI$^+$ m/z (%)) 283 (M + Na)$^+$ (100%); HRMS ESI$^+$ Calcd for $C_7H_{16}NaO_6S_2^+$ (M + Na)$^+$ 283.0386, found 283.0385.

*1-Azido-5-methanesulfonyl-pentane (**15**).* To a solution of compound **14** (4.75 g, 18 mmol, 1 equiv) in acetonitrile (95 mL) was added sodium azide (1.18 g, 18.2 mmol, 1 equiv). The mixture was refluxed for 18 h, cooled to rt, and the precipate was filtrated out. The filtrate was concentrated in vacuo. The resulting oil was purified by flash chromatography (Cyclohexane/EtOAc 7/3) to furnish compound **15** as a colorless oil (1.77 g, 47% yield, 60%), and starting material **14** as a colorless oil (625 mg, 13% yield). **15**: R_f 0.45 (Cyclohexane/EtOAc 7/3); IR (film) 2099*s*, 1351*s*, 1173*s*; ^{1}H NMR δ 4.22 (t, 2H, J_{Hb-Hc} = 6.5 Hz, H_b), 3.29 (t, 2H, J_{Hf-He} = 6.5 Hz, H_f), 3.00 (s, 3H, H_a), 1.80−1.66 (m, 2H, H_c), 1.69−1.57 (m, 2H, H_e), 1.54−1.46 (m, 2H, H_d); ^{13}C NMR δ 69.8 (C_b), 51.3 (C_f), 37.5 (C_a), 28.8 (C_c), 28.4 (C_e), 22.9 (C_d); MS (ESI$^+$ m/z (%)) 208 (M + H)$^+$ (100%); HRMS ESI$^+$ Calcd for $C_6H_{17}N_4O_3S^+$ (M + NH$_4$)$^+$ 225.1021, found 225.1015.

*1-Azido-5-phthalimido-pentane (**11g**).* To a solution of mesylate **15** (428 mg, 2.06 mmol, 1 equiv) in DMF (3 mL) was added potassium phthalimide (1.1 g, 6.2 mmol, 3 equiv). The suspension was stirred at 80 °C for 12 h, cooled to rt and diluted with ether (15 mL) and water (15 mL). The aqueous phase was extracted with Et_2O (3 × 15 mL), and the combined organic layers were washed with brine (2 × 20 mL) and water (20 mL), dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was purified by flash chromatography (Cyclohexane/EtOAc 8/2) to give azide **11g** as a colorless oil (370 mg, 70%): R_f 0.49 (Cyclohexane/EtOAc 8/2); IR (film) 2946*m*, 2098*s*, 1773*m*, 1713*s*, 1397*m*; ^{1}H NMR δ 7.86−7.83 (m, 2H, H_8), 7.73−7.70 (m, 2H, H_9), 3.70 (t, 2H, J_{H5-H4} = 7.5 Hz, H_5), 3.27 (t, 2H, J_{H1-H2} = 7.2 Hz, H_1), 1.75−1.62 (m, 2H, H_4), 1.68−1.62 (m, 2H, H_2), 1.46−1.40 (m, 2H, H_3); ^{13}C NMR δ 168.6 (C_6), 134.1 (C_9), 132.3 (C_7), 123.4 (C_8), 51.4 (C_1), 37.9 (C_5), 28.6 (C_2), 28.3 (C_4), 24.2 (C_3); MS (ESI$^+$ m/z (%)) 259 (M + H)$^+$ (100%) 281 (M + Na)$^+$ (50%); HRMS APCI Calcd for $C_{13}H_{15}N_2O_2^+$ (M − N$_2$ + H)$^+$ 231.1134, found 231.1133.

*1-Azido-5-morpholino-pentane (**11h**).* To a solution of mesylate **15** (315 mg, 1.51 mmol, 1 equiv) in dry acetonitrile (4 mL) were successively added morpholine (495 μL, 1.82 mmol, 1.2 equiv) and triethylamine (410 μL, 2.95 mmol, 1.95 equiv). The resulting solution was refluxed for 12 h, cooled to rt and concentrated in vacuo. The residue was purified by flash chromatography (DCM/MeOH/Et$_3$N 98/2/0.5%) to give azide **11h** as a colorless oil (268 mg, 90%): R_f 0.40 (DCM/MeOH/Et$_3$N 95/5/0.5%); IR (film) 2943*m*, 2861*m*, 2807*m*, 2095*s*, 1121*s*; ^{1}H NMR δ 3.66 (t, 4H, J_{H7-H6} = 5.0 Hz, H_7), 3.23 (t, 2H, J_{H1-H2} = 7.0 Hz, H_1), 2.40−2.38 (m, 4H, H_6), 2.31−2.26 (m, 2H, H_5), 1.51 (qt, 2H, J_{H2-H1} = J_{H2-H3} 7.0 Hz, H_2), 1.51−1.45 (m, 2H, H_4), 1.39−1.34 (m, 2H, H_3); ^{13}C NMR δ 67.0 (C_7), 58.9 (C_5), 53.9 (C_6), 51.4 (C_1), 28.8 (C_2), 26.2 (C_4), 24.7 (C_3); MS (ESI$^+$ m/z (%)) 199 (M + H)$^+$; HRMS APCI Calcd for $C_9H_{19}N_4O^+$ (M + H)$^+$ 199.1559, found 199.1556.

*Cycloheptylazide (**11b**).* ***Caution!*** *This azide is volatile.* To a solution of cycloheptylamine (292 mg, 2.58 mmol, 1 equiv), K_2CO_3 (713 mg, 5.16 mmol, 2.05 equiv) and $CuSO_4{\cdot}5H_2O$ (65 mg, 0.26 mmol, 0.1 equiv), in methanol (20 mL) was added in one portion imidazole-1-sulfonyl-azide-hydrochloride[31] (649 mg, 3.10 mmol, 1.2 equiv). The mixture was stirred at rt for 18 h. After addition of water (50 mL), the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated without heating in vacuo. The residue was purified by flash chromatography (DCM) to give azide **11b** as a colorless oil (286 mg, 80% yield): R_f 0.70 (Cyclohexane/DCM = 8/2); IR (film) 2096*s*, 1508*m*, 1231*m*, 1079*m*. Other spectral data were in agreement with literature.[35b]

*1-(3-Azido-propyl)-imidazole (**11i**).* To a solution of 1-(3-amino-propyl)-imidazole (810 mg, 6.47 mmol, 1 equiv), K_2CO_3 (1.83 g, 13.26 mmol, 2.05 equiv) and $CuSO_4{\cdot}5H_2O$ (162 mg, 0.65 mmol, 0.1 equiv), in methanol (20 mL) was added in one portion imidazole-1-sulfonyl-azide-hydrochloride[31] (1.6 g, 7.76 mmol, 1.2 equiv). The mixture was stirred at rt for 18 h. After addition of water (30 mL), the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was purified by flash chromatography (EtOAc/MeOH 98/2) to give azide **11i** as a colorless oil (636 mg, 65% yield): R_f 0.30 (EtOAc/MeOH 98/2); IR (film) 3101*w*, 2942*w*, 2900*w*, 2099*s*, 1629*s*, 1508*m*, 1231*m*, 1079*m*; ^{1}H NMR δ 7.48 (br s, 1H, H_4), 7.08 (br s, 1H, H_5), 6.91 (br s, 1H, H_6), 4.06 (t, 2H, J_{H3-H2} = 7.0 Hz, H_3),

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3.30 (t, 2H, J_{H1-H2} = 7.0 Hz, H_1), 2.02 (qt, 2H, J_{H2-H1} = J_{H2-H3} = 7.0 Hz, H_2); ^{13}C NMR δ 137.3 (C_4), 129.9 (C_5), 118.8 (C_6), 47.9 (C_3), 43.8 (C_1), 30.4 (C_2); MS (ESI$^+$ m/z (%)) 152 (M + H)$^+$ (100%), 303 (2 M + H)$^+$ (100%); HRMS APCI Calcd for $C_6H_{10}N_5^+$ (M + H)$^+$ 152.0936, found 152.0937.

General Procedure for Cu(I)-Catalyzed Azide−Alkyne Cycloaddition, Preparation of Compounds 18a−n. To a solution of alkyne **10** (1 equiv) and azide partner **11a−n** (1 to 2 equiv) in *tert*-BuOH/H_2O (1.5 mL/500 μL) were successively added $CuSO_4$ (0.1 equiv), sodium ascorbate (0.3 equiv) and *N*-ethyldiisopropylamine (2.2 equiv). The suspension was sonicated for 5 min to solubilize all reagents. The mixture was stirred at rt for 18 h and diluted with DCM (40 mL) and water (15 mL). The aqueous phase was extracted with DCM (6 × 40 mL), and the combined organic layers were dried (Na_2SO_4), filtrated and concentrated in vacuo. The residue was then purified by flash chromatography to give the corresponding triazole **18a−n**.

*Compound **18a**.* Triazole **18a** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne from alkyne **10** (230 mg, 0.36 mmol) and azido-decane **11a** (132 mg, 0.72 mmol, 2 equiv). Flash chromatography (Cyclohexane/EtOAc 1/1) afforded **18a** as a white powder (180 mg, 61% yield): R_f 0.17 (Cyclohexane/EtOAc 1/1); mp 118−120 °C; $[\alpha]_D$ −43 (*c* 1.0, CH_2Cl_2); IR (film) 2933*m*, 1714*s*, 1386*m*; ^{1}H NMR δ 7.99 (s, 1H, NH), 7.84−7.82 (m, 2H, $H_{11''}$), 7.74−7.72 (m, 2H, $H_{12''}$), 7.67 (s, 1H, $H_{7'}$), 7.39 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.88 (d, 1H, $J_{H1'-H2'}$ = 2.5 Hz, $H_{1'}$), 5.80 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.5 Hz, H_5), 5.40 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 5.5 Hz, $H_{5'}$), 5.00 (dd, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 3.0 Hz, $H_{3'}$), 4.90 (dd, 1H, $J_{H2'-H3'}$ = 6.0 Hz, $J_{H2'-H1'}$ = 2.5 Hz, $H_{2'}$), 4.79 (d, 1H, $J_{H2''-H3''}$ = 5.5 Hz, $H_{2''}$), 4.74 (d, 1H, $J_{H3''-H2''}$ = 5.5 Hz, $H_{3''}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 5.5 Hz, $J_{H4'-H3'}$ = 3.0 Hz, $H_{4'}$), 4.36−4.33 (m, 3H, $H_{8'}$, $H_{4''}$), 3.64 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.5 Hz, $H_{5''a}$), 3.33 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 3.5 Hz, $H_{5''b}$), 1.89−1.86 (m, 2H, $H_{9'}$), 1.63−1.55 (m, 2H, $H_{7''}$), 1.56 (s, 3H, $H_{19'}$), 1.52 (q, 2H, $J_{H7''-H8''}$ = 8.0 Hz, $H_{7''}$), 1.32 (s, 3H, $H_{19'}$), 1.26−1.14 (m, 14H, $H_{10'}$, $H_{11'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 0.88−0.80 (m, 9H, $H_{8''}$, $H_{17'}$); ^{13}C NMR δ 168.3 ($C_{9''}$), 162.7 (C_4), 150.2 (C_2), 144.9 ($C_{6'}$), 141.6 (C_6), 134.4 ($C_{12''}$), 131.9 ($C_{10''}$), 123.5 ($C_{11''}$, $C_{7'}$), 117.2 ($C_{6''}$), 114.8 ($C_{18'}$), 109.5 ($C_{1''}$), 103.0 (C_5), 92.9 ($C_{1'}$), 87.8 ($C_{4'}$), 85.9 ($C_{2''}$), 84.7 ($C_{4''}$), 83.9 ($C_{2'}$), 82.5 ($C_{3''}$), 80.9 ($C_{3'}$), 72.7 ($C_{5'}$), 50.6 ($C_{8'}$), 40.4 ($C_{5''}$), 31.9 ($C_{9'}$), 30.3 ($C_{7''}$), 29.6, 29.5, 29.4, 29.3, 29.0, 27.3, 26.9, 26.5, 25.4, 22.7 ($C_{7''}$, $C_{19'}$, $C_{10'}$, $C_{11'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$), 8.7, 8.4, 7.4 ($C_{8''}$, $C_{17'}$); HRMS ESI$^-$ Calcd for $C_{42}H_{55}N_6O_{11}^-$ (M − H)$^-$ 819.3929, found 819.3937.

*Compound **18b**.* Triazole **18b** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (210 mg, 0.33 mmol) and azido-cycloheptane **11b** (55 mg, 0.40 mmol, 1.2 equiv). Flash chromatography (Cyclohexane/EtOAc 4/6) afforded **18b** as a white powder (180 mg, 64% yield): R_f 0.31 (Cyclohexane/EtOAc 3/7); mp 143−145 °C; $[\alpha]_D$ −30 (*c* 1.0, CH_2Cl_2); IR (film) 2980*m*, 1717*s*, 1697*s*, 1396*m*,1086*s*; ^{1}H NMR δ 9.70−9.65 (m, 1H, NH), 7.79−7.76 (m, 2H, $H_{11''}$), 7.69 (s, 1H, $H_{7'}$), 7.69−7.67 (m, 2H, $H_{12''}$), 7.31 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.89 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.71 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 1.5 Hz, H_5), 5.36 (s, 1H, $H_{1''}$), 5.15 (d, 1H, $J_{H5'-H4'}$ = 6.0 Hz, $H_{5'}$), 5.00 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.85 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.75 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.70 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.64−4.58 (m, 1H, $H_{8'}$), 4.47 (dd, 1H, $J_{H4'-H5'}$ = 6.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.27 (dd, 1H, $J_{H4''-H5''a}$ = 10.5 Hz, $J_{H4''-H5''b}$ = 4.5 Hz, $H_{4''}$), 3.58 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.5 Hz, $H_{5''a}$), 3.33 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 2.15−2.10 (m, 2H, $H_{9'a}$), 1.99−1.89 (m, 2H, $H_{9'b}$), 1.77−1.74 (m, 2H, $H_{10'a}$), 1.64−1.53 (m, 8H, $H_{7''}$, $H_{10'b}$, $H_{11'}$), 1.52 (s, 3H, $H_{13'}$), 1.47 (q, 2H, $J_{H7''-H8''}$ = 7.0 Hz, $H_{7''}$), 1.29 (s, 3H, $H_{13'}$), 0.78 (t, 3H, $J_{H8''-H7''}$ = 7.0 Hz, $H_{8''}$), 0.76 (t, 3H, $J_{H8''-H7''}$ = 7.0 Hz, $H_{8''}$); ^{13}C NMR δ 168.1 ($C_{9''}$), 163.4 (C_4), 150.4 (C_2), 144.5 ($C_{6'}$), 141.3 (C_6), 134.2 ($C_{12''}$), 131.9 ($C_{10''}$), 123.4 ($C_{11''}$), 121.7 ($C_{7'}$), 117.1 ($C_{6''}$), 114.7 ($C_{12'}$), 109.6 ($C_{1''}$), 103.0 (C_5), 92.4 ($C_{1'}$), 87.4 ($C_{4'}$), 85.9 ($C_{2''}$), 84.7 ($C_{4''}$), 83.8 ($C_{2'}$), 82.5 ($C_{3''}$), 80.8 ($C_{3'}$), 72.2 ($C_{5'}$), 62.6 ($C_{8'}$), 40.4 ($C_{5''}$), 35.6 ($C_{9'}$), 29.5 ($C_{7''}$), 28.9 ($C_{7''}$), 27.7 ($C_{11'}$), 27.2 ($C_{13'}$), 25.4 ($C_{13'}$), 24.3 ($C_{10'}$), 8.3 ($C_{8''}$), 7.4 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{39}H_{49}N_6O_{11}^+$ (M + H)$^+$ 777.3459, found 777.3491.

*Compound **18c**.* Triazole **18c** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (200 mg, 0.31 mmol) and 1-azido-3-phenyl-propane **11c** (100 mg, 0.63 mmol, 2 equiv). Flash chromatography (Cyclohexane/EtOAc 3/7) afforded **18c** as a white powder (111 mg, 45% yield): R_f 0.54 (EtOAc); mp 125−127 °C; $[\alpha]_D$ −34 (*c* 1.0, CH_2Cl_2); IR (film) 2940*m*, 2350*m*, 1715*s*, 1390*m*; ^{1}H NMR δ 8.92 (s, 1H, NH), 7.80−7.77 (m, 2H, $H_{11''}$), 7.72−7.68 (m, 2H, $H_{12''}$), 7.72 (s, 1H, $H_{7'}$), 7.40 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.27−7.21 (m, 2H, $H_{12'}$), 7.16−7.12 (m, 3H, $H_{13'}$, $H_{14'}$), 5.86 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.77 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.40 (s, 1H, $H_{1''}$), 5.23 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 4.97 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.92 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.79 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4''-H3'}$ = 4.0 Hz, $H_{4'}$), 4.39−4.32 (m, 3H, $H_{8'}$, $H_{4''}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.0 Hz, $H_{5''a}$), 3.37 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 2.62−2.58 (m, 2H, $H_{10'}$), 2.27−2.21 (m, 2H, $H_{9'}$), 1.64−1.56 (m, 2H, $H_{7''}$), 1.55 (s, 3H, $H_{16'}$), 1.51 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.30 (s, 3H, $H_{16'}$), 0.80 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 169.2 ($C_{9''}$), 163.0 (C_4), 150.4 (C_2), 144.9 ($C_{6'}$), 141.8 (C_6), 140.2 ($C_{11'}$), 134.3 ($C_{12''}$), 132.0 ($C_{10''}$), 128.7 ($C_{13'}$), 128.5 ($C_{14'}$), 126.5 ($C_{12'}$), 123.8 ($C_{7'}$), 123.6 ($C_{11''}$), 117.3 ($C_{6''}$), 114.9 ($C_{15'}$), 109.6 ($C_{1''}$), 103.2 (C_5), 93.3 ($C_{1'}$), 88.3 ($C_{4'}$), 86.1 ($C_{2''}$), 84.9 ($C_{4''}$), 84.1 ($C_{2'}$), 82.7 ($C_{3''}$), 81.0 ($C_{3'}$), 72.9 ($C_{5'}$), 46.9 ($C_{8'}$), 40.6 ($C_{5''}$), 32.6 ($C_{10'}$), 31.8 ($C_{9'}$), 29.7, 29.1 ($C_{7''}$), 27.4, 25.6 ($C_{16'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{41}H_{47}N_6O_{11}^+$ (M + H)$^+$ 799.3303, found 799.3336.

*Compound **18d**.* Triazole **18d** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (220 mg, 0.35 mmol), and the previously described azide **11d** (107 mg, 0.44 mmol, 1.3 equiv). Flash chromatography (Cyclohexane/EtOAc = 25/75) afforded **18d** as a white powder (135 mg, 46% yield): R_f 0.35 (Cyclohexane/EtOAc 25/75); mp 167−169 °C; $[\alpha]_D$ −31 (*c* 1.0, CH_2Cl_2); IR (film) 2930*m*, 1711*s*, 1693*s*, 1393*m*, 1044*s*; ^{1}H NMR δ 9.13 (br s, 1H, NH), 7.80−7.78 (m, 2H, $H_{11''}$), 7.71−7.68 (m, 2H, $H_{12''}$), 7.58 (s, 1H, $H_{7'}$), 7.53 (d, 2H, $J_{H15'-H16'}$ = 7.5 Hz, $H_{15'}$), 7.50 (d, 2H, $J_{H12'-H11'}$ = 8.0 Hz, $H_{12'}$), 7.40 (t, 2H, $J_{H16'-H15'}$ = $J_{H16'-H17'}$ = 7.5 Hz, $H_{16'}$), 7.38 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.31 (t, 1H, $J_{H17'-H16'}$ = 7.5 Hz, $H_{17'}$), 7.18 (d, 2H, $J_{H11'-H12'}$ = 8.5 Hz, $H_{11'}$), 5.84 (d, 1H, $J_{H1'-H2'}$ = 2.5 Hz, $H_{1'}$), 5.75 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.36 (s, 1H, $H_{1''}$), 5.18 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 4.95 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.90 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.5 Hz, $H_{2'}$), 4.77 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.67 (dd, 1H, $J_{H8'a-H8'b}$ = 14.0 Hz, $J_{H8'a-H9'}$ = 7.0 Hz, $H_{8'a}$), 4.61 (dd, 1H, $J_{H8'b-H8'a}$ = 14.0 Hz, $J_{H8b'-H9'}$ = 7.0 Hz, $H_{8'b}$), 4.48 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.34 (dd, 1H, $J_{H4''-H5''a}$ = 10.0 Hz, $J_{H4''-H5''b}$ = 4.5 Hz, $H_{4''}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.0 Hz, $H_{5''a}$), 3.37 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 3.26 (t, 2H, $J_{H9'-H8'a}$ = $J_{H9'-H8'b}$ = 7.0 Hz, $H_{9'}$), 1.60 (m, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.55 (s, 3H, $H_{19'}$), 1.50 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.32 (s, 3H, $H_{19'}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.2 ($C_{9''}$), 163.2 (C_4), 150.4 (C_2), 144.9 ($C_{6'}$), 141.8 (C_6), 140.6 ($C_{14'}$), 140.1 ($C_{13'}$), 136.2 ($C_{10'}$), 134.3 ($C_{12''}$), 132.0 ($C_{10''}$), 129.3 ($C_{11'}$), 128.9 ($C_{16'}$), 127.6 ($C_{12'}$), 127.5 ($C_{17'}$), 127.1 ($C_{15'}$), 124.1 ($C_{7'}$), 123.6 ($C_{11''}$), 117.3 ($C_{6''}$), 114.8 ($C_{18'}$), 109.5 ($C_{1''}$), 103.1 (C_5), 93.5 ($C_{1'}$), 88.3 ($C_{4'}$), 86.0 ($C_{2''}$), 84.9 ($C_{4''}$), 84.1 ($C_{2'}$), 82.6 ($C_{3''}$), 81.0 ($C_{3'}$), 72.9 ($C_{5'}$), 51.8 ($C_{8'}$), 40.6 ($C_{5''}$), 36.5 ($C_{9'}$), 29.7 ($C_{7''}$), 29.1 ($C_{7''}$), 27.4 ($C_{19'}$), 25.6 ($C_{19'}$), 8.5 ($C_{8''}$), 7.5 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{46}H_{49}N_6O_{11}^+$ (M + H)$^+$ 861.3485, found 861.3459.

*Compound **18e**.* Triazole **18e** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (220 mg, 0.35 mmol) and azide **11e** (45 mg, 0.45 mmol, 1.3 equiv). Flash chromatography (EtOAc/MeOH 95/5) afforded **18e** as a white powder (115 mg, 46% yield): R_f 0.17 (EtOAc);

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mp 121−123 °C; $[\alpha]_D$ −31 (*c* 1.0, CH_2Cl_2); IR (film) 3441*br*, 2940*w*, 1715*s*, 1695*s*; ^{1}H NMR δ 9.43 (br s, 1H, NH), 7.83−7.80 (m, 2H, $H_{11''}$), 7.79 (s, 1H, $H_{7'}$), 7.71−7.35 (m, 2H, $H_{12''}$), 7.35 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.82 (d, 1H, $J_{H1'-H2'}$ = 2.5 Hz, $H_{1'}$), 5.76 (br d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.38 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 4.96 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.94 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.5 Hz, $H_{2'}$), 4.80 (d, 1H, $J_{H2''-H3''}$ = 5.5 Hz, $H_{2''}$), 4.74 (d, 1H, $J_{H3''-H2''}$ = 5.5 Hz, $H_{3''}$), 4.53 (tl, 2H, $J_{H8'-H9'}$ = 6.5 Hz, $H_{8'}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.28 (dd, 1H, $J_{H4''-H5''a}$ = 11.0 Hz, $J_{H4''-H5''b}$ = 4.0 Hz, $H_{4''}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 11.0 Hz, $H_{5''a}$), 3.61−3.54 (m, 2H, $H_{10'}$), 3.30 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.0 Hz, $H_{5''b}$), 2.42−2.28 (br s, 1H, OH), 2.16−2.11 (m, 2H, $H_{9'}$), 1.62−1.57 (m, 2H, $H_{7''}$), 1.55 (s, 3H, $H_{12'}$), 1.50 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.31 (s, 3H, $H_{12'}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.80 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.5 ($C_{9''}$), 163.4 (C_4), 150.5 (C_2), 144.8 ($C_{6'}$), 142.0 (C_6), 134.5 ($C_{12''}$), 131.2 ($C_{10''}$), 124.6 ($C_{7'}$), 123.6 ($C_{11''}$), 117.3 ($C_{6''}$), 114.9 ($C_{11'}$), 109.6 ($C_{1''}$), 103.2 (C_5), 93.3 ($C_{1'}$), 88.3 ($C_{4'}$), 86.1 ($C_{2''}$), 84.8 ($C_{4''}$), 84.0 ($C_{3'}$), 82.7 ($C_{3''}$), 81.0 ($C_{2'}$), 73.3 ($C_{5'}$), 58.6 ($C_{10'}$), 47.2 ($C_{8'}$), 40.7 ($C_{5''}$), 32.4 ($C_{9'}$), 29.6, 29.1 ($C_{7''}$), 27.4, 25.6 ($C_{12'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{35}H_{43}N_6O_{12}^+$ (M + H)$^+$ 739.2939, found 739.2925.

Compound ***18f***. Triazole **18f** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (220 mg, 0.35 mmol) and azide **11f** (57 mg, 0.45 mmol, 1.3 equiv). Flash chromatography (EtOAc to EtOAc/MeOH 95/5) afforded **18f** as a white powder (133 mg, 51% yield): R_f 0.29 (EtOAc/MeOH 95/5); mp 98−100 °C; $[\alpha]_D$ −31 (*c* 1.0, CH_2Cl_2); IR (film) 3488*br*, 2976*w*, 1714*s*, 1396*s*; ^{1}H NMR δ 9.01 (br s, 1H, NH), 7.84−7.82 (m, 2H, $H_{11''}$), 7.75−7.71 (m, 3H, $H_{7'}$, $H_{12''}$), 7.35 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 5.84 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.76 (br d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.39 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 6.0 Hz, $H_{5'}$), 5.00 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.93 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.79 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 6.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.39 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.32 (dd, 1H, $J_{H4''-H5''a}$ = 11.0 Hz, $J_{H4''-H5''b}$ = 4.5 Hz, $H_{4''}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 11.0 Hz, $H_{5''a}$), 3.59 (t, 2H, $J_{H12'-H11'}$ = 7.0 Hz, $H_{12'}$), 3.32 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 1.98−1.89 (m, 3H, $H_{9'}$, OH), 1.64−1.58 (m, 2H, $H_{7''}$), 1.58−1.54 (m, 2H, $H_{11'}$), 1.56 (s, 3H, $H_{14'}$), 1.51 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.42−1.37 (m, 2H, $H_{10'}$), 1.33 (s, 3H, $H_{14'}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.4 ($C_{9''}$), 163.1 (C_4), 150.3 (C_2), 144.8 ($C_{6'}$), 142.0 (C_6), 134.5 ($C_{12''}$), 132.0 ($C_{10''}$), 123.9 ($C_{7'}$), 123.7 ($C_{11''}$), 117.3 ($C_{6''}$), 114.9 ($C_{13'}$), 109.7 ($C_{1''}$), 103.2 (C_5), 93.4 ($C_{1'}$), 88.0 ($C_{4'}$), 86.1 ($C_{2''}$), 84.9 ($C_{4''}$), 83.9 ($C_{3'}$), 82.6 ($C_{3''}$), 80.9 ($C_{2'}$), 72.9 ($C_{5'}$), 62.3 ($C_{12'}$), 50.6 ($C_{8'}$), 40.6 ($C_{5''}$), 31.9 ($C_{11'}$), 30.0 ($C_{9'}$), 29.7, 29.1 ($C_{7''}$), 27.4, 25.6 ($C_{14'}$), 22.9 ($C_{10'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{37}H_{47}N_6O_{12}^+$ (M + H)$^+$ 767.3252, found 767.3260.

Compound ***18g***. Triazole **18g** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (110 mg, 0.18 mmol) and azide **11g** (90 mg, 0.37 mmol, 2 equiv). Flash chromatography (Cyclohexane/EtOAc 3/7 to EtOAc) afforded **18g** as a white powder (166 mg, 75% yield): R_f 0.70 (EtOAc); mp 131−133 °C; $[\alpha]_D$ −32 (*c* 1.0, CH_2Cl_2); IR (film) 2942*w*, 2976*w*, 2251*w*, 1710*s*; ^{1}H NMR δ 9.03 (br d, 1H, J_{NH-H5} = 2.0 Hz, NH), 7.82−7.79 (m, 4H, $H_{11''}$, $H_{15'}$), 7.73 (s, 1H, $H_{7'}$), 7.72−7.68 (m, 4H, $H_{12''}$, $H_{16'}$), 7.40 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.87 (d, 1H, $J_{H1'-H2'}$ = 2.5 Hz, $H_{1'}$), 5.77 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.39 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 4.97 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.90 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.5 Hz, $H_{2'}$), 4.78 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.49 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.36−4.32 (m, 3H, $H_{8'}$, $H_{4''}$), 3.67−3.62 (m, 3H, $H_{12'}$, $H_{5''a}$), 3.34 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 2.00−1.89 (m, 2H, $H_{9'}$), 1.72−1.67 (m, 2H, $H_{11'}$), 1.63−1.58 (m, 2H, $H_{7''}$), 1.56 (s, 3H, $H_{18'}$), 1.51 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.40−1.32 (m, 2H, $H_{10'}$), 1.33 (s, 3H, $H_{18'}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.5, 168.3 ($C_{9''}$, $C_{13'}$), 163.1 (C_4), 150.4 (C_2), 145.0 ($C_{6'}$), 141.7 (C_6), 134.4, 134.2 ($C_{12''}$, $C_{16'}$), 132.3, 132.1 ($C_{10''}$, $C_{14'}$), 123.8 ($C_{7'}$), 123.6, 123.4 ($C_{11''}$, $C_{15'}$), 117.3 ($C_{6''}$), 114.9 ($C_{17'}$), 109.7 ($C_{1''}$), 103.2 (C_5), 93.1 ($C_{1'}$), 87.9 ($C_{4'}$), 86.4 ($C_{2''}$), 84.9 ($C_{4''}$), 84.1 ($C_{3'}$), 82.7 ($C_{3''}$), 80.9 ($C_{2'}$), 72.9 ($C_{5'}$), 50.4 ($C_{8'}$), 40.6 ($C_{5''}$), 37.5 ($C_{12'}$), 29.8 ($C_{9'}$), 29.7, 29.1 ($C_{7''}$), 28.1 ($C_{11'}$), 27.4, 25.6 ($C_{18'}$), 23.7 ($C_{10'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{45}H_{50}N_7O_{13}^+$ (M + H)$^+$ 896.3467, found 896.3483.

Compound ***18h***. Triazole **18h** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (210 mg, 0.33 mmol) and azide **11h** (79 mg, 0.40 mmol, 1.2 equiv). Flash chromatography (EtOAc/MeOH 95/5 to 85/15) afforded **18h** as a white powder (154 mg, 56% yield): R_f 0.20 (EtOAc/MeOH 85/15); mp 130−132 °C; $[\alpha]_D$ −30 (*c* 1.0, CH_2Cl_2); IR (film) 2936*w*, 2258*w*, 1714*s*, 1458*w*, 1395*m*; ^{1}H NMR δ 9.33 (br s, 1H, NH), 7.82−7.79 (m, 2H, $H_{11''}$), 7.73−7.70 (m, 2H, $H_{12''}$), 7.68 (s, 1H, $H_{7'}$), 7.36 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 5.85 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.74 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.37 (s, 1H, $H_{1''}$), 5.18 (d, 1H, $J_{H5'-H4'}$ = 6.0 Hz, $H_{5'}$), 4.97 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.89 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.77 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.71 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.47 (dd, 1H, $J_{H4'-H5'}$ = 6.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.34 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.31 (dd, 1H, $J_{H4''-H5''a}$ = 10.0 Hz, $J_{H4''-H5''b}$ = 4.0 Hz, $H_{4''}$), 3.67 (tl, 4H, $J_{H13'-H14'}$ = 4.5 Hz, $H_{13'}$), 3.62 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.0 Hz, $H_{5''a}$), 3.30 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.0 Hz, $H_{5''b}$), 2.42−2.32 (m, 4H, $H_{14'}$), 2.27 (t, 2H, $J_{H12'-H11'}$ = 7.5 Hz, $H_{12'}$), 1.91 (qt, 2H, $J_{H9'-H8'}$ = $J_{H9'-H10'}$ =7.5 Hz, $H_{9'}$), 1.61−1.56 (m, 2H, $H_{7''}$), 1.54 (s, 3H, $H_{16'}$), 1.52−1.46 (m, 4H, $H_{7''}$,$H_{11'}$), 1.34−1.28 (m, 2H, $H_{10'}$), 1.31 (s, 3H, $H_{16'}$), 0.80 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.2 ($C_{9''}$), 163.2 (C_4), 150.3 (C_2), 144.9 ($C_{6'}$), 141.6 (C_6), 134.3 ($C_{12''}$), 131.9 ($C_{10''}$), 123.6 ($C_{11''}$, $C_{7'}$), 117.2 ($C_{6''}$), 114.8 ($C_{15'}$), 109.6 ($C_{1''}$), 103.1 (C_5), 93.1 ($C_{1'}$), 87.9 ($C_{4'}$), 85.9 ($C_{2''}$), 84.8 ($C_{4''}$), 83.9 ($C_{3'}$), 82.5 ($C_{3''}$), 80.9 ($C_{2'}$), 72.8 ($C_{5'}$), 66.9 ($C_{13'}$), 58.6 ($C_{12'}$), 53.7 ($C_{14'}$), 50.4 ($C_{8'}$), 40.5 ($C_{5''}$), 30.2 ($C_{9'}$), 29.6 ($C_{11'}$), 29.0 ($C_{7''}$), 27.3 ($C_{7''}$), 25.8, 25.5 ($C_{16'}$), 24.4 ($C_{10'}$), 8.4, 7.5 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{41}H_{54}N_7O_{12}^+$ (M + H)$^+$ 836.3830, found 836.3863.

Compound ***18i***. Triazole **18i** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (230 mg, 0.36 mmol) and azide **11i** (71 mg, 0.47 mmol, 1.3 equiv). Flash chromatography (EtOAc to EtOAc/MeOH 9/1) afforded **18i** as a white powder (200 mg, 71% yield): R_f 0.21 (EtOAc/MeOH 8/2); mp 151−153 °C; $[\alpha]_D$ −34 (*c* 1.0, CH_2Cl_2); IR (film) 2977*w*, 2937*w*, 1715*s*, 1394*m*, 1087*m*; ^{1}H NMR δ 10.52 (s, 1H, NH), 7.76 (s, 1H, $H_{7'}$), 7.74−7.71 (m, 2H, $H_{11''}$), 7.67−7.64 (m, 2H, $H_{12''}$), 7.52 (br s, 1H, $H_{11'}$), 7.33 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 6.99 (br s, 1H, $H_{12'}$), 6.91 (br s, 1H, $H_{13'}$), 5.73 (d, 1H, $J_{H1'-H2'}$ = 2.5 Hz, $H_{1'}$), 5.70 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.34 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 7.0 Hz, $H_{5'}$), 4.97 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.5 Hz, $H_{2'}$), 4.87 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.74 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.68 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.46 (dd, 1H, $J_{H4'-H5'}$ = 7.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.35−4.27 (m, 2H, $H_{8'}$), 4.23 (dd, 1H, $J_{H4''-H5''a}$ = 11.0 Hz, $J_{H4''-H5''b}$ = 4.0 Hz, $H_{4''}$), 4.02−3.87 (m, 2H, $H_{10'}$), 3.66 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 11.0 Hz, $H_{5''a}$), 3.28 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.0 Hz, $H_{5''b}$), 2.44−2.31 (m, 2H, $H_{9'}$), 1.54−1.49 (m, 2H, $H_{7''}$), 1.47 (s, 3H, $H_{12'}$), 1.43 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.22 (s, 3H, $H_{12'}$), 0.73 (t, 6H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.1 ($C_{9''}$), 163.5 (C_4), 150.6 (C_2), 145.0 ($C_{6'}$), 142.0 (C_6), 137.3 ($C_{11'}$), 134.2 ($C_{12''}$), 131.7 ($C_{10''}$), 129.6 ($C_{12'}$), 124.1 ($C_{7'}$), 123.4 ($C_{11''}$), 118.8 ($C_{13'}$), 116.9 ($C_{6''}$), 114.5 ($C_{11'}$), 109.6 ($C_{1''}$), 103.0 (C_5), 94.1 ($C_{1'}$), 88.8 ($C_{4'}$), 85.9 ($C_{2''}$), 84.6 ($C_{4''}$), 84.1 ($C_{2'}$), 82.5 ($C_{3''}$), 81.1 ($C_{3'}$), 73.2 ($C_{5'}$), 46.9 ($C_{8'}$), 43.4 ($C_{10'}$), 40.5 ($C_{5''}$), 31.3 ($C_{9'}$), 29.5, 28.9 ($C_{7''}$), 27.2, 25.4 ($C_{12'}$), 8.4, 7.4 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{38}H_{45}N_8O_{11}^+$ (M + H)$^+$ 789.3208, found 789.3244.

Compound ***18j***. Triazole **18j** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (220 mg, 0.35 mmol) and azide **11j** (111 mg, 0.37 mmol, 1.1 equiv). Flash chromatography (EtOAc/MeOH 98/2)

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afforded **18j** as a white powder (198 mg, 62% yield): R_f 0.44 (EtOAc/MeOH 95/5); mp 143−145 °C; $[\alpha]_D$ −27 (*c* 1.0, CH_2Cl_2); IR (film) 2940*m*, 1715*s*, 1695*s*, 1081*s*; ^{1}H NMR δ 9.19 (br s, 1H, NH), 8.32 (s, 1H, $H_{16'}$), 7.88 (s, 1H, $H_{7'}$), 7.78−7.76 (m, 2H, $H_{11''}$), 7.69−7.67 (m, 2H, $H_{12''}$), 7.58 (dd, 1H, $J_{H14'-13'}$ = 9.0 Hz, $J_{H14'-16'}$ = 2.5 Hz, $H_{14'}$), 7.36 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 6.56 (d, 1H, $J_{H13'-H14'}$ = 9.0 Hz, $H_{13'}$), 5.83 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.74 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.38 (s, 1H, $H_{1''}$), 5.21 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz $H_{5'}$), 4.99 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.94 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.78 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.56−4.52 (m, 2H, $H_{8'}$), 4.52 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.31 (dd, 1H, $J_{H4''-H5''a}$ = 10.5 Hz, $J_{H4''-H5''b}$ = 4.5 Hz, $H_{4''}$), 3.67 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.5 Hz, $H_{5''a}$), 3.62−3.51 (m, 4H, $H_{10'}$), 3.37 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 2.99−2.81 (m, 2H, $H_{9'}$), 2.61−2.58 (m, 4H, $H_{11'}$), 1.59−1.57 (m, 2H, $H_{7''}$), 1.56 (s, 3H, $H_{13'}$), 1.49 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.31 (s, 3H, $H_{13'}$), 0.85 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.80 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 168.2 ($C_{9''}$), 163.1 (C_4), 160.4 ($C_{12'}$), 150.4 (C_2), 145.9−145.6 (m, $C_{16'}$), 144.9 ($C_{6'}$), 141.9 (C_6), 134.6 ($C_{14'}$), 134.4 ($C_{12''}$), 132.0 ($C_{10''}$), 124.5 ($C_{7'}$), 123.7 ($C_{11''}$), 121.8 (q, $J_{C17'-F}$ = 71.5 Hz, $C_{17'}$), 117.3 ($C_{6''}$), 115.4 (q, $J_{C15'-F}$ = 33.0 Hz, $C_{15'}$), 114.8 ($C_{18'}$), 109.7 ($C_{1''}$), 105.7 ($C_{13'}$), 103.1 (C_5), 93.7 ($C_{1'}$), 88.4 ($C_{4'}$), 86.1 ($C_{2''}$), 84.9 ($C_{4''}$), 84.1 ($C_{2'}$), 82.7 ($C_{3''}$), 81.1 ($C_{3'}$), 73.0 ($C_{5'}$), 57.5 ($C_{9'}$), 52.9 ($C_{10'}$), 48.0 ($C_{8'}$), 44.8 ($C_{11'}$), 40.7 ($C_{5''}$), 29.7, 29.1 ($C_{7''}$), 27.4, 25.6 ($C_{19'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{44}H_{51}F_3N_9O_{11}^+$ $(M + H)^+$ 938.3660, found 938.3687.

Compound ***18k***. Triazole **18k** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (250 mg, 0.39 mmol) and azide **11k** (166 mg, 0.59 mmol, 1.6 equiv). Flash chromatography (Cyclohexane/EtOAc 3/7) afforded **18k** as a white powder (185 mg, 52% yield): R_f 0.15 (Cyclohexane/EtOAc 3/7); mp 127−129 °C; $[\alpha]_D$ −30 (*c* 1.0, CH_2Cl_2); IR (film) 2972*m*, 1713*s*, 1395*m*, 1074*s*; ^{1}H NMR δ 8.27 (br s, 1H, NH), 7.81−7.70 (m, 9H, $H_{7'}$, $H_{11''}$, $H_{12''}$, $H_{13'}$, $H_{17'}$), 7.58 (t, 1H, $J_{H19'-H18'}$ = 7.5 Hz, $H_{19'}$), 7.48 (t, 2H, $J_{H18'-H19'}$ = $J_{H18'-H17'}$ = 7.5 Hz, $H_{18'}$), 7.36 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 6,92 (d, 2H, $J_{H12'-H13'}$ = 7.5 Hz, $H_{12'}$), 5.82 (d, 1H, $J_{H1'-H2'}$ = 2.5 Hz, $H_{1'}$), 5.75 (br d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.39 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 5.01−4.97 (m, 1H, $H_{3'}$), 4.94−4.91 (m, 1H, $H_{2'}$), 4.78 (d, 1H, $J_{H2''-H3''}$ = 5.5 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 5.5 Hz, $H_{3''}$), 4.63 (t, 2H, $J_{H10'-H9'}$ = 6.5 Hz, $H_{10'}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 3.0 Hz, $H_{4'}$), 4.32 (dd, 1H, $J_{H4''-H5''a}$ = 10.5 Hz, $J_{H4''-H5''b}$ = 4.0 Hz, $H_{4''}$), 4.10−4.02 (m, 2H, $H_{8'}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.5 Hz, $H_{5''a}$), 3.32 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.0 Hz, $H_{5''b}$), 2.49−2.42 (m, 2H, $H_{9'}$), 1.63−1.59 (m, 2H, $H_{7''}$), 1.55 (s, 3H, $H_{21'}$), 1.51−1.49 (m, 2H, $H_{7''}$), 1.32 (s, 3H, $H_{21'}$), 0.83−0.81 (m, 6H, $H_{8''}$); ^{13}C NMR δ 195.5 ($C_{15'}$), 168.2 ($C_{9''}$), 163.1 (C_4), 162.2 ($C_{11'}$), 150.4 (C_2), 145.2 ($C_{6'}$), 141.9 (C_6), 138.3 ($C_{16'}$), 134.4 ($C_{12''}$), 132.7 ($C_{13'}$), 132.1 ($C_{10''}$), 131.9 ($C_{19'}$), 130.7 ($C_{14'}$), 129.9 ($C_{17'}$), 128.4 ($C_{18'}$), 124.3 ($C_{7'}$), 123.6 ($C_{11''}$), 117.3 ($C_{6''}$), 114.8 ($C_{20'}$), 114.2 ($C_{12'}$), 109.8 ($C_{1''}$), 103.1 (C_5), 93.7 ($C_{1'}$), 88.4 ($C_{4'}$), 86.1 ($C_{2''}$), 84.9 ($C_{4''}$), 84.1 ($C_{3'}$), 82.6 ($C_{3''}$), 81.1 ($C_{2'}$), 73.1 ($C_{5'}$), 64.6 ($C_{8'}$), 47.3 ($C_{10'}$), 40.6 ($C_{5''}$), 30.0 ($C_{9'}$), 29.7, 29.1 ($C_{7''}$), 27.4, 25.6 ($C_{21'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{48}H_{51}N_6O_{13}^+$ $(M + H)^+$ 919.3514, found 919.3549.

Compound ***18l***. Triazole **18l** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (230 mg, 0.36 mmol) and azide **11l** (223 mg, 0.72 mmol, 2 equiv). Flash chromatography (Cyclohexane/EtOAc 35/65) afforded **18l** as a white powder (177 mg, 52% yield): R_f 0.33 (Cyclohexane/EtOAc 1/9); mp 119−121 °C; $[\alpha]_D$ −30 (*c* 1.0, CH_2Cl_2); IR (film) 1715*s*, 1693*s*, 1395*m*, 1090*m*; ^{1}H NMR δ 9.12 (br s, 1H, NH), 7.79−7.67 (m, 9H, $H_{7'}$, $H_{11''}$, $H_{12''}$, $H_{15'}$, $H_{19'}$), 7.55 (tl, 1H, $J_{H21'-H20'}$ = 7.5 Hz, $H_{21'}$), 7.46 (t, 2H, $J_{H20'-H21'}$ = $J_{H20'-H19'}$ = 7.5 Hz, $H_{20'}$), 7.38 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 6,89 (d, 2H, $J_{H14'-H15'}$ = 9.0 Hz, $H_{14'}$), 5.86 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.75 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.39 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 4.99 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.92 (m, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.79 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.73 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.40 (t, 2H, $J_{H12'-H11'}$ = 7.0 Hz, $H_{12'}$), 4.32 (dd, 1H, $J_{H4''-H5''a}$ = 10.5 Hz, $J_{H4''-H5''b}$ = 4.0 Hz, $H_{4''}$), 3.99 (t, 2H, $J_{H12'-H11'}$ = 7.0 Hz, $H_{8'}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 10.5 Hz, $H_{5''a}$), 3.32 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.0 Hz, $H_{5''b}$), 2.02−1.99 (m, 2H, $H_{11'}$), 1.84−1.61 (m, 2H, $H_{9'}$) 1.60−1.55 (m, 2H, $H_{7''}$), 1.55 (s, 3H, $H_{23'}$), 1.53−1.31 (m, 4H, $H_{7''}$, $H_{10'}$), 1.31 (s, 3H, $H_{23'}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz $H_{8''}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz $H_{8''}$); ^{13}C NMR δ 195.6 ($C_{17'}$), 168.2 ($C_{9''}$), 163.1 (C_4), 162.7 ($C_{13'}$), 150.4 (C_2), 145.1 ($C_{6'}$), 141.8 (C_6), 138.5 ($C_{18'}$), 134.4 ($C_{12''}$), 132.7 ($C_{15'}$), 132.0 ($C_{10''}$, $C_{21'}$), 130.4 ($C_{16'}$), 129.9 ($C_{19'}$), 128.3 ($C_{20'}$), 123.7 ($C_{7'}$), 123.6 ($C_{11''}$), 117.3 ($C_{6''}$), 114.9 ($C_{22'}$), 114.2 ($C_{14'}$), 109.8 ($C_{1''}$), 103.1 (C_5), 93.3 ($C_{1'}$), 88.2 ($C_{4'}$), 86.1 ($C_{2''}$), 84.9 ($C_{4''}$), 84.1 ($C_{2'}$), 82.7 ($C_{3''}$), 81.1 ($C_{3'}$), 73.1 ($C_{5'}$), 67.9 ($C_{8'}$), 50.4 ($C_{12'}$), 40.6 ($C_{5''}$), 30.1 ($C_{11'}$), 29.7, 29.1 ($C_{7''}$), 28.6 ($C_{9'}$), 27.4, 25.6 ($C_{23'}$), 23.2 ($C_{10'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{50}H_{55}N_6O_{13}^+$ $(M + H)^+$ 947.3827, found 947.3859.

Compound ***18m***. Triazole **18m** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (220 mg, 0.35 mmol) and azide **11m** (266 mg, 0.70 mmol, 2 equiv). Flash chromatography (Cyclohexane/EtOAc 35/65) afforded **18m** as a white powder (174 mg, 49% yield): R_f 0.27 (Cyclohexane/EtOAc 3/7); mp 110−113 °C; $[\alpha]_D$ −28 (*c* 1.0, CH_2Cl_2); IR (film) 2935*m*, 1715*s*, 1600*m*, 1256*s*; ^{1}H NMR δ 8.37 (br s, 1H, NH), 7.85−7.72 (m, 8H, $H_{11''}$, $H_{12''}$, $H_{20'}$, $H_{24'}$), 7.68 (s, 1H, $H_{7'}$), 7.57 (t, 1H, $J_{H26'-H25'}$ = 7.5 Hz, $H_{26'}$), 7.48 (t, 2H, $J_{H25'-H26'}$ = 7.5 Hz, $J_{H25'-H24'}$ = 7.5 Hz, $H_{25'}$), 7.38 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 6,95 (d, 2H, $J_{H19'-H20'}$ = 8.0 Hz, $H_{19'}$), 5.88 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.76 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.40 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 5.00 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.90 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.79 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.74 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.50 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.37−4.34 (m, 1H, $H_{4''}$); 4,35 (t, 2H, $J_{H17'-H16'}$ = 7.5 Hz, $H_{17'}$), 4.03 (t, 2H, $J_{H8'-H9'}$ = 6.5 Hz, $H_{8'}$), 3.65 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 11.0 Hz, $H_{5''a}$), 3.35 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 1.91−1.88 (m, 2H, $H_{16'}$), 1.82−1.77 (m, 2H, $H_{9'}$), 1.66−1.59 (m, 2H, $H_{7''}$), 1.57 (s, 3H, $H_{28'}$), 1.52 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.47−1.41 (m, 2H, $H_{10'}$), 1.34 (s, 3H, $H_{28'}$), 1.32−1.22 (m, 10H, $H_{11'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$), 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 195.7 ($C_{22'}$), 168.3 ($C_{9''}$), 163.1 (C_4), 162.7 ($C_{18'}$), 150.2 (C_2), 145.0 ($C_{6'}$), 141.6 (C_6), 138.6 ($C_{23'}$), 134.4 ($C_{12''}$), 132.7 ($C_{20'}$), 132.1 ($C_{10''}$), 132.0 ($C_{26'}$), 130.2 ($C_{21'}$), 129.9 ($C_{24'}$), 128.4 ($C_{25'}$), 123.7 ($C_{11''}$), 123.6 ($C_{7'}$), 117.4 ($C_{6''}$), 114.9 ($C_{27'}$), 114.2 ($C_{19'}$), 109.7 ($C_{1''}$), 103.2 (C_5), 93.1 ($C_{1'}$), 87.9 ($C_{4'}$), 86.1 ($C_{2''}$), 84.9 ($C_{4''}$), 84.0 ($C_{2'}$), 82.7 ($C_{3''}$), 81.0 ($C_{3'}$), 72.9 ($C_{5'}$), 68.5 ($C_{8'}$), 50.7 ($C_{17'}$), 40.6 ($C_{5''}$), 30.5 ($C_{16'}$), 29.7 ($C_{7''}$), 29.6, 29.5, 29.4, 29.3 ($C_{11'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$), 29.2 (2C, $C_{9'}$, $C_{7''}$), 27.4 ($C_{28'}$), 26.7 ($C_{15'}$), 26.2 ($C_{10'}$), 25.6 ($C_{28'}$), 8.5, 7.6 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{55}H_{65}N_6O_{13}^+$ $(M + H)^+$ 1017.4610, found 1017.4644.

Compound ***18n***. Triazole **18n** was synthesized according to the general procedure for Cu(I)-catalyzed azide−alkyne cycloaddition from alkyne **10** (220 mg, 0.35 mmol) and azide **11n** (151 mg, 0.44 mmol, 1.3 equiv). Flash chromatography (Cyclohexane/EtOAc 25/75) afforded **18n** as a white powder (123 mg, 37% yield): R_f 0.26 (Cyclohexane/EtOAc 25/75); mp 141−143 °C; $[\alpha]_D$ −24 (*c* 1.0, CH_2Cl_2); IR (film) 2342*w*, 1713*m*,1396*s*, 1249*m*, 1067*s*; ^{1}H NMR δ 9.16 (br d, 1H, J_{NH-H5} = 2.0 Hz, NH), 7.91 (d, 2H, $J_{16'-15'}$ = 9.0 Hz, $H_{16'}$), 7.78−7.77 (m, 2H, $H_{11''}$), 7.75 (d, 2H, $J_{20'-21'}$ = 7.5 Hz, $H_{20'}$), 7.70 (s, 1H, $H_{7'}$), 7.69−7.67 (m, 2H, $H_{12''}$), 7.56 (t, 1H, $J_{H22'-H21'}$ = 7.5 Hz, $H_{22'}$), 7.47 (t, 2H, $J_{H21'-H20'}$ = $J_{H21'-H22'}$ = 7.5 Hz, $H_{21'}$), 7.36 (d, 2H, $J_{H11'-H10'}$ = 8.0 Hz, $H_{11'}$), 7.33 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.27 (d, 2H, $J_{H10'-H11'}$ = 8.0 Hz, $H_{10'}$), 6.96 (d, 2H, $J_{15'-16'}$ = 9.0 Hz, $H_{15'}$), 5.86 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.70 (dd, 1H, J_{H5-H6} = 8.0 Hz, J_{H5-NH} = 2.0 Hz, H_5), 5.58 (d, 1H, $J_{H8'a-H8'b}$ = 15.0 Hz, $H_{8'a}$), 5.52 (d, 1H, $J_{H8'b-H8'a}$ = 15.0 Hz, $H_{8'b}$), 5.39 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 6.5 Hz, $H_{5'}$), 4.98 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.97 (s, 2H, $H_{13'}$), 4.90 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.76 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.68 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.48 (dd, 1H, $J_{H4'-H5'}$ = 6.5 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.31

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(dd, 1H, $J_{H4''-H5''a}$ = 11.0 Hz, $J_{H4''-H5''b}$ = 4.5 Hz, $H_{4''}$), 3.54 (dd, 1H, $J_{H5''a-H5''b}$ = 14.0 Hz, $J_{H5''a-H4''}$ = 11.0 Hz, $H_{5''a}$), 3.19 (dd, 1H, $J_{H5''b-H5''a}$ = 14.0 Hz, $J_{H5''b-H4''}$ = 4.5 Hz, $H_{5''b}$), 1.60 (m, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.54 (s, 3H, $H_{24'}$), 1.49 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.31 (s, 3H, $H_{24'}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR δ 195.6 ($C_{18'}$), 168.1 ($C_{9''}$), 163.2 (C_4), 162.3 ($C_{14'}$), 150.3 (C_2), 145.6 ($C_{6'}$), 141.6 (C_6), 138.4 ($C_{19'}$), 137.1 ($C_{12'}$), 134.8 ($C_{9'}$), 134.4 ($C_{12''}$), 132.7 ($C_{16'}$), 132.1 ($C_{22'}$), 132.0 ($C_{10''}$), 130.7 ($C_{17'}$), 129.9 ($C_{20'}$), 128.4 ($C_{21'}$), 128.4 ($C_{10'}$), 128.2 ($C_{11'}$), 123.9 ($C_{7'}$), 123.6 ($C_{11''}$), 117.3 ($C_{6''}$), 114.9 ($C_{23'}$), 114.5 ($C_{15'}$), 109.9 ($C_{1''}$), 103.1 (C_5), 93.1 ($C_{1'}$), 88.0 ($C_{4'}$), 86.1 ($C_{2''}$), 84.8 ($C_{4''}$), 84.0 ($C_{2'}$), 82.6 ($C_{3''}$), 80.9 ($C_{3'}$), 73.1 ($C_{5'}$), 69.6 ($C_{13'}$), 54.0 ($C_{8'}$), 40.4 ($C_{5''}$), 29.6 ($C_{7''}$), 29.1 ($C_{7''}$), 27.4 ($C_{24'}$), 25.6 ($C_{24'}$), 8.5 ($C_{8''}$), 7.5 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{53}H_{53}N_6O_{13}^+$ (M + H)$^+$ 981.3671, found 981.3702.

General Procedure for Phthalimide Cleavage, Preparation of Compounds 19a−n. To a solution of protected triazole (1 equiv) in distilled MeOH (0.1 M) was added dropwise a solution of methylamine (8.03 M in EtOH, 400 equiv), the mixture was stirred at rt for 5 h, and volatiles were removed in vacuo. The residue was dissolved in DCM (5 mL) and filtrated on Millipore to remove the methylphthalimide byproduct. The filtrate was then concentrated in vacuo, and the residue was purified by flash chromatography and then lyophilized.

*Compound **19a**.* Amine **19a** was prepared according to the general procedure for phthalimide cleavage from triazole **18a** (152 mg, 0.19 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 97/3/0.3%) afforded **19a** as a white solid (83 mg, 65% yield): R_f 0.17 (EtOAc); mp 103−105 °C; $[\alpha]_D$ −22 (*c* 0.5, MeOH); IR (film) 2976*m*, 2940*m*, 1697*s*, 1650*m* 1383*m*, 1075*s*; ^{1}H NMR (CD_3OD) δ 7.98 (s, 1H, $H_{7'}$), 7.63 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.74 (s, 1H, $H_{1'}$), 5.67 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.28 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.10 (br d, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $H_{2'}$), 4.71 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.65 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.56 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.42−4.35 (m, 3H, $H_{8'}$, $H_{4'}$), 4.12 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 5.0 Hz, $H_{4''}$), 2.61 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.53 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 1.88 (qt, 2H, $J_{H9'-H10'}$ = $J_{H9'-H8'}$ = 7.0 Hz, $H_{9'}$), 1.59 (q, 2H, $J_{H7''-H8''}$ = 7.0 Hz, $H_{7''}$), 1.52 (q, 2H, $J_{H7''-H8''}$ = 7.0 Hz, $H_{7''}$), 1.47 (s, 3H, $H_{19'}$), 1.35−1.25 (m, 14H, $H_{10'}$, $H_{11'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 1.24 (s, 3H, $H_{19'}$), 0.86 (t, 3H, $J_{H17'-H16'}$ = 6.5 Hz, $H_{17'}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.0 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.0 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.4 (C_4), 152.3 (C_2), 145.9 ($C_{6'}$), 145.6 (C_6), 125.0 ($C_{7'}$), 117.3 ($C_{6''}$), 115.3 ($C_{18'}$), 111.4 ($C_{1''}$), 103.1 (C_5), 97.0 ($C_{1'}$), 91.7 ($C_{4'}$), 89.2 ($C_{4''}$), 87.3 ($C_{2''}$), 85.7 ($C_{2'}$), 83.9 ($C_{3''}$), 83.1 ($C_{3'}$), 74.4 ($C_{5'}$), 51.6 ($C_{8'}$), 45.3 ($C_{5''}$), 33.2 ($C_{10'}$), 31.4 ($C_{9'}$), 30.6 ($C_{7''}$), 30.0 ($C_{7''}$), 30.8, 30.2, 27.3, 23.9 (6C, $C_{11'}$, $C_{12'}$,$C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$), 27.5 ($C_{19'}$), 25.6 ($C_{19'}$), 14.6 ($C_{17'}$), 8.5, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{34}H_{55}N_6O_9^+$ (M + H)$^+$ 691.4031, found 691.4039.

*Compound **19b**.* Amine **19b** was prepared according to the general procedure for phthalimide cleavage from triazole **18b** (141 mg, 0.18 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 96/4/0.3%) afforded **19b** as a white solid (83 mg, 63% yield): R_f 0.40 (DCM/MeOH/Et_3N 95/5/0.3%); mp 125−127 °C; $[\alpha]_D$ −26 (*c* 0.5, MeOH); IR (film) 2937*m*, 1692*s*, 1460*m*, 1273*m*,1158*m*; ^{1}H NMR (CD_3OD) δ 8.03 (s, 1H, $H_{7'}$), 7.63 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.79 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.69 (br d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.32 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 8.5 Hz, $H_{5'}$), 5.11 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.76 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5, Hz, $H_{3'}$), 4.75−4.69 (m, 1H, $H_{8'}$), 4.67 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.58 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.46 (dd, 1H, $J_{H4'-H5'}$ = 8.5 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.10 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 6.0 Hz, $H_{4''}$), 2.54 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 6.0 Hz, $H_{5''a}$), 3.33 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 2.20−2.14 (m, 2H, $H_{9a'}$), 2.09−1.03 (m, 2H, $H_{9b'}$), 1.80−1.83 (m, 2H, $H_{10a'}$), 1.74−1.59 (m, 8H, $H_{7''}$, $H_{10b'}$, $H_{11'}$), 1.54 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.49 (s, 3H, $H_{13'}$), 1.27 (s, 3H, $H_{13'}$), 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.3 (C_4), 152.2 (C_2), 145.7 ($C_{6'}$), 145.2 (C_6), 123.1 ($C_{7'}$), 117.6 ($C_{6''}$), 115.2 ($C_{12'}$), 111.3 ($C_{1''}$), 103.0 (C_5), 96.6 ($C_{1'}$), 91.2 ($C_{4'}$), 89.6 ($C_{2''}$), 87.2 ($C_{4''}$), 85.4 ($C_{2'}$), 83.7 ($C_{3''}$), 82.9 ($C_{3'}$), 74.2 ($C_{5'}$), 64.1 ($C_{8'}$), 45.4 ($C_{5''}$), 36.5 ($C_{9'}$), 30.4 ($C_{7''}$), 29.8 ($C_{7''}$), 28.9 ($C_{11'}$), 27.4 ($C_{13'}$), 25.4 ($C_{13'}$), 25.3 ($C_{10'}$), 8.7 ($C_{8''}$), 7.7 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{31}H_{47}N_6O_9^+$ (M + H)$^+$ 647.3405, found 647.3387.

*Compound **19c**.* Amine **19c** was prepared according to the general procedure for phthalimide cleavage from triazole **18c** (111 mg, 0.14 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 97/3/0.3%) afforded **19c** as a white solid (83 mg, 58% yield): R_f 0.30 (DCM/MeOH/Et_3N 95/5/0.1%); mp 108−110 °C; $[\alpha]_D$ −23 (*c* 0.5, MeOH); IR (film) 2976*m*, 2976*m*, 2940*m*, 1697*s*, 1650*m* 1383*m*, 1075*s*; ^{1}H NMR (CD_3OD) δ 8.02 (s, 1H, $H_{7'}$), 7.65 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.28−7.25 (m, 2H, $H_{12'}$), 7.18−7.16 (m, 3H, $H_{13'}$, $H_{14'}$), 5.77 (d, 1H, $J_{H1'-H2'}$ = 1.5 Hz, $H_{1'}$), 5.69 (d1, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.33 (s, 1H, $H_{1''}$), 5.22 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.12 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 1.5 Hz, $H_{2'}$), 4.75 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.5 Hz, $H_{3'}$), 4.69 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.59 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.48−4.39 (m, 3H, $H_{4'}$, $H_{8'}$), 4.16 (dd, 1H, $J_{H4''-H5''a}$ = 9.5 Hz, $J_{H4''-H5''b}$ = 5.0 Hz, $H_{4''}$), 2.68−2.53 (m, 4H, $H_{5''a}$, $H_{5''b}$, $H_{10'}$), 2.26−2.20 (m, 2H, $H_{9'}$), 1.62 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.55 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.48 (s, 3H, $H_{16'}$), 1.23 (s, 3H, $H_{16'}$), 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.4 (C_4), 152.3 (C_2), 146.0 ($C_{6'}$), 145.6 (C_6), 142.1 ($C_{11'}$), 129.7 ($C_{13'}$), 129.6 ($C_{14'}$), 127.4 ($C_{12'}$), 125.2 ($C_{7'}$), 117.3 ($C_{6''}$), 114.9 ($C_{15'}$), 111.5 ($C_{1''}$), 103.2 (C_5), 97.3 ($C_{1'}$), 91.6 ($C_{4'}$), 88.9 ($C_{4''}$), 87.3 ($C_{2''}$), 85.6 ($C_{2'}$), 83.8 ($C_{3''}$), 83.1 ($C_{3'}$), 74.5 ($C_{5'}$), 50.9 ($C_{8'}$), 45.2 ($C_{5''}$), 33.5 ($C_{10'}$), 33.0 ($C_{9'}$), 30.6, 30.0 ($C_{7''}$), 27.5, 25.5 ($C_{16'}$), 8.8, 7.8 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{33}H_{45}N_6O_9^+$ (M + H)$^+$ 669.3248, found 669.3219.

*Compound **19d**.* Amine **19d** was prepared according to the general procedure for phthalimide cleavage from triazole **18d** (122 mg, 0.15 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 95/5/0.3%) afforded **19d** as a white solid (61 mg, 55% yield): R_f 0.48 (DCM/MeOH/Et_3N 95/5/0.3%); mp 128−130 °C; $[\alpha]_D$ −18 (*c* 0.5, MeOH); IR (film) 2971*w*, 2940*w*, 1696*s*, 1457*m*; ^{1}H NMR (CD_3OD) δ 7.79 (s, 1H, $H_{7'}$), 7.61 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.56 (br d, 2H, $J_{H15'-H16'}$ = 7.5 Hz, $H_{15'}$), 7.51 (d, 2H, $J_{H12'-H11'}$ = 8.0 Hz, $H_{12'}$), 7.40 (t, 2H, $J_{H16'-H15'}$ = $J_{H16'-H17'}$ = 7.5 Hz, $H_{16'}$), 7.31 (t, 1H, $J_{H17'-H16'}$ = 7.5 Hz, $H_{17'}$), 7.16 (br d, 2H, $J_{H11'-12'}$ = 8.0 Hz, $H_{11'}$), 5.74 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.67 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.26 (s, 1H, $H_{1''}$), 5.16 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.07 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.71 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.70 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.61 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.52 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.41 (dd, 1H, $J_{H4'-H5'}$ = 9.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.08 (dd, 1H, $J_{H4''-H5''b}$ = 9.5 Hz, $J_{H4''-H5''a}$ = 5.5 Hz, $H_{4''}$), 3.25 (t, 2H, $J_{H9'-H8'}$ = 7.0 Hz, $H_{9'}$), 2.51 (dd, 1H, $J_{H5''a-H5''b}$ = 13.5 Hz, $J_{H5''a-H4''}$ = 5.5 Hz, $H_{5''a}$), 2.43 (dd, 1H, $J_{H5''b-H5''a}$ = 13.5 Hz, $J_{H5''b-H4''}$ = 9.5 Hz, $H_{5''b}$), 1.60 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.52 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.47 (s, 3H, $H_{19'}$), 1.24 (s, 3H, $H_{19'}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.5 (C_4), 152.3 (C_2), 145.9 ($C_{6'}$), 145.5 (C_6), 142.1 ($C_{14'}$), 141.2 ($C_{13'}$), 137.9 ($C_{10'}$), 130.5 ($C_{11'}$), 130.0 ($C_{16'}$), 128.5 ($C_{17'}$), 128.4 ($C_{12'}$), 127.9 ($C_{15'}$), 125.4 ($C_{7'}$), 117.8 ($C_{6''}$), 115.2 ($C_{18'}$), 111.2 ($C_{1''}$), 103.1 (C_5), 97.1 ($C_{1'}$), 91.8 ($C_{4'}$), 89.7 ($C_{4''}$), 87.3 ($C_{2''}$), 85.6 ($C_{2'}$), 83.9 ($C_{3''}$), 83.1 ($C_{3'}$), 74.0 ($C_{5'}$), 52.9 ($C_{8'}$), 45.5 ($C_{5''}$), 37.2 ($C_{9'}$), 30.5, 30.0 ($C_{7''}$), 27.5, 25.6 ($C_{19'}$), 8.8, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{38}H_{47}N_6O_9^+$ (M + H)$^+$ 731.3405, found 731.3411.

*Compound **19e**.* Amine **19e** was prepared according to the general procedure for phthalimide cleavage from triazole **18e** (110 mg, 0.15 mmol). Flash chromatography (EtOAc/NEt_3 100/0.3% to EtOAc/MeOH/NEt_3 97/3/0.3%) afforded **19e** as a white solid (42 mg, 47% yield): R_f 0.20 (EtOAc/MeOH/Et_3N 8/2/0.3%); mp 120−121 °C; $[\alpha]_D$ −13 (*c* 0.3, MeOH); IR (film) 3126*br*, 2929*m*, 2852*m*, 1694*s*, 1459*m*; ^{1}H NMR (CD_3OD) δ 7.97 (s, 1H, $H_{7'}$), 7.60 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.71 (br s, 1H, $H_{1'}$), 5.64 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.27 (s, 1H, $H_{1''}$), 5.17 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.09 (br d, 1H,

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$J_{H2'-H3'}$ = 6.0 Hz, $H_{2'}$), 4.70 (dd, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.64 (d, 1H, $J_{H2''-H3''}$ = 5.5 Hz, $H_{2''}$), 4.56 (d, 1H, $J_{H3''-H2''}$ = 5.5 Hz, $H_{3''}$), 4.49 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.38 (dd, 1H, $J_{H4'-H5'}$ = 9.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.15 (dd, 1H, $J_{H4''-H5''b}$ = 10.0 Hz, $J_{H4''-H5''a}$ = 5.0 Hz, $H_{4''}$), 3.51 (t, 2H, $J_{H10'-H9'}$ = 6.0 Hz, $H_{10'}$), 2.68 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.58 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 10.0 Hz, $H_{5''b}$), 2.16–2.03 (m, 2H, $H_{9'}$), 1.57 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.50 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.46 (s, 3H, $H_{12'}$), 1.23 (s, 3H, $H_{12'}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.78 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.4 (C_4), 152.2 (C_2), 145.9 ($C_{6'}$), 145.7 (C_6), 125.7 ($C_{7'}$), 118.0 ($C_{6''}$), 115.4 ($C_{11'}$), 111.7 ($C_{1''}$), 103.1 (C_5), 97.1 ($C_{1'}$), 91.5 ($C_{4'}$), 88.1 ($C_{4''}$), 87.2 ($C_{2''}$), 85.7 ($C_{2'}$), 83.1 ($C_{3''}$), 83.1 ($C_{3'}$), 74.5 ($C_{5'}$), 51.6 ($C_{8'}$), 44.8 ($C_{5''}$), 33.2 ($C_{10'}$), 34.0 ($C_{9'}$), 30.9 ($C_{7''}$), 30.9 ($C_{7''}$), 27.5 ($C_{12'}$), 25.5 ($C_{12'}$), 14.6 ($C_{17'}$), 8.8, 7.8 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{27}H_{41}N_6O_{10}^+$ (M + H)$^+$ 609.2884, found 609.2897.

Compound ***19f***. Amine **19f** was prepared according to the general procedure for phthalimide cleavage from triazole **18f** (118 mg, 0.15 mmol). Flash chromatography (EtOAc/NEt_3 100/0.3% to EtOAc/MeOH/NEt_3 97/3/0.3%) afforded **19f** as a white solid (68 mg, 71% yield): R_f 0.50 (EtOAc/MeOH/Et_3N 8/2/0.5%); mp 115–117 °C; $[\alpha]_D$ −12 (*c* 0.4, CH_2Cl_2); IR (film) 3382*br*, 2940*m*, 1696*s*, 1457*m*, 1274*m*; ^{1}H NMR (CD_3OD) δ 8.03 (s, 1H, $H_{7'}$), 7.65 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.77 (br s, 1H, $H_{1'}$), 5.73 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.30 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.09 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.73 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.5 Hz, $H_{3'}$), 4.67 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.58 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.61–4.42 (m, 3H, $H_{4'}$, $H_{8'}$), 4.09 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 5.0 Hz, $H_{4''}$), 3.53 (t, 2H, $J_{H12'-H11'}$ = 6.5 Hz, $H_{12'}$), 2.53 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.58 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 1.96–1.90 (m, 2H, $H_{9'}$), 1.61 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.57–1.49 (m, 4H, $H_{11'}$, $H_{7''}$), 1.48 (s, 3H, $H_{14'}$), 1.57–1.49 (m, 2H, $H_{10'}$), 1.25 (s, 3H, $H_{14'}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.9 (C_4), 152.5 (C_2), 145.9 ($C_{6'}$), 145.6 (C_6), 125.2 ($C_{7'}$), 117.9 ($C_{6''}$), 115.5 ($C_{13'}$), 111.3 ($C_{1''}$), 103.2 (C_5), 96.9 ($C_{1'}$), 91.6 ($C_{4'}$), 89.7 ($C_{4''}$), 87.2 ($C_{2''}$), 85.6 ($C_{2'}$), 83.8 ($C_{3''}$), 83.0 ($C_{3'}$), 74.3 ($C_{5'}$), 62.6 ($C_{12'}$), 51.6 ($C_{8'}$), 45.4 ($C_{5''}$), 32.9 ($C_{9'}$), 31.0 ($C_{11'}$), 30.5, 29.9 ($C_{7''}$), 27.5, 25.5 ($C_{14'}$), 23.8 ($C_{10'}$), 8.9, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{29}H_{45}N_6O_{10}^+$ (M + H)$^+$ 637.3197, found 637.3206.

Compound ***19g***. Amine **19g** was prepared according to the general procedure for phthalimide cleavage from triazole **18g** (140 mg, 0.16 mmol). Flash chromatography (EtOAc/NEt_3 100/0.3% to EtOAc/MeOH/NEt_3 8/2/5%) afforded **19g** as a white solid (59 mg, 60% yield): R_f 0.10 (EtOAc/MeOH/Et_3N 8/2/5%); mp 115–117 °C; $[\alpha]_D$ + 20 (*c* 0.5, MeOH); IR (film) 2968*w*, 2934*w*, 1687*s*, 1454*m*, 1377*m*; ^{1}H NMR (CD_3OD) δ 8.03 (s, 1H, $H_{7'}$), 7.56 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.71 (d, 1H, $J_{H1'-H2'}$ = 1.5 Hz, $H_{1'}$), 5.62 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.31 (s, 1H, $H_{1''}$), 5.22 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.11 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 1.5 Hz, $H_{2'}$), 4.76 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.66 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.57 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.46–4.43 (m, 3H, $H_{4'}$, $H_{8'}$), 4.07 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 5.5 Hz, $H_{4''}$), 2.72 (t, 2H, $J_{H12'-H11'}$ = 7.0 Hz, $H_{12'}$), 2.50 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.5 Hz, $H_{5''a}$), 2.43 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 1.97–1.93 (m, 2H, $H_{9'}$), 1.61 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.59–1.52 (m, 4H, $H_{11'}$, $H_{7''}$), 1.49 (s, 3H, $H_{14'}$), 1.38–1.31 (m, 2H, $H_{10'}$), 1.26 (s, 3H, $H_{14'}$), 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 167.8 (C_4), 153.2 (C_2), 146.1 ($C_{6'}$), 145.2 (C_6), 124.9 ($C_{7'}$), 117.6 ($C_{6''}$), 115.1 ($C_{13'}$), 111.2 ($C_{1''}$), 103.1 (C_5), 96.8 ($C_{1'}$), 91.5 ($C_{4'}$), 89.9 ($C_{4''}$), 87.2 ($C_{2''}$), 85.5 ($C_{2'}$), 83.7 ($C_{3''}$), 82.9 ($C_{3'}$), 74.2 ($C_{5'}$), 51.2 ($C_{12'}$), 45.6 ($C_{8'}$), 41.6 ($C_{5''}$), 31.4 ($C_{9'}$), 30.8 ($C_{11'}$), 30.4, 29.9 ($C_{7''}$), 27.4, 25.5 ($C_{14'}$), 24.6 ($C_{10'}$), 8.7, 7.7 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{29}H_{46}N_7O_9^+$ (M + H)$^+$ 636.3357, found 636.3342.

Compound ***19h***. Amine **19h** was prepared according to the general procedure for phthalimide cleavage from triazole **18h** (145 mg, 0.17 mmol). Flash chromatography (EtOAc/NEt_3 100/0.3% to EtOAc/MeOH/NEt_3 8/2/0.3%) afforded **19h** as a white solid (88 mg, 74% yield): R_f 0.22 (EtOAc/MeOH/Et_3N 8/2/5%); mp 115–117 °C; $[\alpha]_D$ −18 (*c* 0.5, MeOH); IR (film) 2970*m*, 2940*m*, 2859*w*, 2810*w*, 1697*s*, 1634*m*; ^{1}H NMR (CD_3OD) δ 8.02 (s, 1H, $H_{7'}$), 7.65 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.79 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.70 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.31 (s, 1H, $H_{1''}$), 5.22 (d, 1H, $J_{H5'-H4'}$ = 8.0 Hz, $H_{5'}$), 5.12 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.76 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.68 (d, 1H, $J_{H2''-H3''}$ = 5.5 Hz, $H_{2''}$), 4.59 (d, 1H, $J_{H3''-H2''}$ = 5.5 Hz, $H_{3''}$), 4.46–4.42 (m, 3H, $H_{8'}$, $H_{4'}$), 4.14 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 5.0 Hz, $H_{4''}$), 3.66 (tl, 4H, $J_{H13'-H14'}$ = 4.5 Hz, $H_{13'}$), 2.62 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 3.30 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 2.47–2.43 (m, 4H, $H_{14'}$), 2.34 (t, 2H, $J_{H12'-H11'}$ = 8.0 Hz, $H_{12'}$), 1.91 (qt, 2H, $J_{H9'-H8'}$ = $J_{H9'-H10'}$ =7.5 Hz, $H_{9'}$), 1.62 (q, 2H, $J_{H7''-H8''}$ =7.0 Hz, $H_{7''}$), 1.59–1.52 (m, 4H, $H_{7''}$,$H_{11'}$), 1.50 (s, 3H, $H_{16'}$), 1.35–1.28 (m, 2H, $H_{10'}$), 1.27 (s, 3H, $H_{16'}$), 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.0 Hz, $H_{8''}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.0 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.3 (C_4), 152.1 (C_2), 145.8 ($C_{6'}$), 145.4 (C_6), 124.9 ($C_{7'}$), 117.7 ($C_{6''}$), 115.2 ($C_{15'}$), 111.3 ($C_{1''}$), 103.0 (C_5), 96.7 ($C_{1'}$), 91.4 ($C_{4'}$), 89.1 ($C_{2''}$), 87.2 ($C_{4''}$), 85.5 ($C_{3'}$), 83.7 ($C_{3''}$), 82.9 ($C_{2'}$), 74.2 ($C_{5'}$), 67.6 ($C_{13'}$), 59.8 ($C_{12'}$), 54.7 ($C_{14'}$), 51.3 ($C_{8'}$), 45.2 ($C_{5''}$), 30.9 ($C_{9'}$), 30.4 ($C_{11'}$), 29.9 ($C_{7''}$), 27.4 ($C_{7''}$), 25.8, 25.5 ($C_{16'}$), 25.2 ($C_{10'}$), 8.7, 7.7 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{33}H_{52}N_7O_{10}^+$ (M + H)$^+$ 706.3776, found 706.3805.

Compound ***19i***. Amine **19i** was prepared according to the general procedure for phthalimide cleavage from triazole **18i** (194 mg, 0.25 mmol). Flash chromatography (EtOAc to EtOAc/MeOH 8/2) afforded **19i** as a white solid (86 mg, 52% yield): R_f 0.10, EtOAc/MeOH/Et_3N 8/2/5%); mp 137–139 °C; $[\alpha]_D$ −19 (*c* 0.5, MeOH); IR (film) 2944*w*, 1695*s*, 1459*m*, 1080*s*; ^{1}H NMR (CD_3OD) δ 8.04 (s, 1H, $H_{7'}$), 7.66 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.65 (br s, 1H, $H_{11'}$), 7.15 (br s, 1H, $H_{12'}$), 6.99 (br s, 1H, $H_{13'}$), 5.77 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.70 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.32 (s, 1H, $H_{1''}$), 5.23 (d, 1H, $J_{H5'-H4'}$ = 8.5 Hz, $H_{5'}$), 5.14 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.77 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.68 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.59 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.47–4.37 (m, 3H, $H_{4'}$, $H_{8'}$), 4.14 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 5.0 Hz, $H_{4''}$), 4.09–3.99 (m, 2H, $H_{10'}$), 2.62 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.53 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 2.45 (qt, 2H, $J_{H9'-H8'}$ = $J_{H9'-H10'}$ = 7.0 Hz, $H_{9'}$), 1.62 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.55 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$) 1.49 (s, 3H, $H_{15'}$), 1.25 (s, 3H, $H_{15'}$), 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.3 (C_4), 152.1 (C_2), 146.2 ($C_{6'}$), 145.6 (C_6), 138.6 ($C_{11'}$), 129.4 ($C_{12'}$), 125.1 ($C_{7'}$), 120.6 ($C_{13'}$), 117.7 ($C_{6''}$), 115.2 ($C_{14'}$), 111.3 ($C_{1''}$), 102.9 (C_5), 97.0 ($C_{1'}$), 91.6 ($C_{4'}$), 89.7 ($C_{2''}$), 87.2 ($C_{4''}$), 85.6 ($C_{2'}$), 83.7 ($C_{3''}$), 82.9 ($C_{3'}$), 74.3 ($C_{5'}$), 48.3 ($C_{8'}$), 45.2 ($C_{10'}$), 44.7 ($C_{5''}$), 32.3 ($C_{9'}$), 30.4, 29.8 ($C_{7''}$), 27.4, 25.4 ($C_{15'}$), 8.7, 7.7 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{30}H_{43}N_8O_9^+$ (M + H)$^+$ 659.3153, found 659.3157.

Compound ***19j***. Amine **19j** was prepared according to the general procedure for phthalimide cleavage from triazole **18j** (177 mg, 0.19 mmol, 1 equiv). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 97/3/0.3%) afforded **19j** as a white solid (72 mg, 47% yield): R_f 0.54 (DCM/MeOH/Et_3N 9/1/0.3%); mp 108–110 °C; $[\alpha]_D$ −16 (*c* 0.5, MeOH); IR (film) 2978*w*, 2939*w*, 1695*s*, 1612*s*, 1328*m*, 1107*s*; ^{1}H NMR (CD_3OD) δ 8.29 (br s, 1H, $H_{16'}$), 8.07 (s, 1H, $H_{7'}$), 7.67 (dd, 1H, $J_{H14'-H13'}$ = 9.5 Hz, $J_{H14'-H16'}$ = 2.5 Hz, $H_{14'}$), 7.62 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 6.82 (d, 1H, $J_{H13'-H14'}$ = 9.5 Hz, $H_{13'}$), 5.73 (d, 1H, $J_{H1'-H2'}$ = 1.5 Hz, $H_{1'}$), 5.66 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.27 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz $H_{5'}$), 5.11 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 1.5 Hz, $H_{2'}$), 4.74 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.63 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.57 (t, 2H, $J_{H8'-H9'}$ = 6.0 Hz, $H_{8'}$), 4.54 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.44 (dd, 1H, $J_{H4'-H5'}$ = 9.0 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.07 (dd, 1H, $J_{H4''-H5''a}$ = 9.0 Hz, $J_{H4''-H5''b}$ = 5.0 Hz, $H_{4''}$), 3.60 (t, 4H, $J_{H11'-H10'}$ = 5.0 Hz, $H_{11'}$), 2.89–2.87 (m, 2H, $H_{9'}$), 2.59–2.43 (m, 6H, $H_{5''a}$, $H_{5''b}$, $H_{10'}$), 1.58 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.51 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.44 (s, 3H, $H_{19'}$), 1.21 (s, 3H, $H_{19'}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.79 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 166.5 (C_4), 162.1 ($C_{12'}$), 152.3 (C_2), 146.7–146.5

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(m, $C_{16'}$), 145.9 ($C_{6'}$), 145.9 (C_6), 135.8 ($C_{14'}$), 127.6 (q, $J_{C17'-F}$ = 71.5 Hz, $C_{17'}$), 126.0 ($C_{7'}$), 117.8 ($C_{6''}$), 116.3 (q, $J_{C15'-F}$ = 32.5 Hz, $C_{15'}$), 115.2 ($C_{18'}$), 111.4 ($C_{1''}$), 107.5 ($C_{13'}$), 103.1 (C_5), 97.3 ($C_{1'}$), 91.9 ($C_{4'}$), 89.9 ($C_{4''}$), 87.4 ($C_{2''}$), 85.7 ($C_{2'}$), 83.9 ($C_{3''}$), 83.2 ($C_{3'}$), 74.3 ($C_{5'}$), 58.3 ($C_{9'}$), 53.8 ($C_{10'}$), 48.8 ($C_{8'}$), 46.0 ($C_{11'}$), 45.6 ($C_{5''}$), 30.6, 30.0 ($C_{7''}$), 27.5, 27.6 ($C_{19'}$), 8.8, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{36}H_{49}F_3N_9O_9^+$ (M + H)$^+$ 808.3605, found 808.3607.

Compound ***19k***. Amine **19k** was prepared according to the general procedure for phthalimide cleavage from triazole **18k** (185 mg, 0.20 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 97/3/0.3%) afforded **19k** as a white solid (72 mg, 46% yield): R_f 0.16 (DCM/MeOH 95/5); mp 119−121 °C; $[\alpha]_D$ −22 (*c* 0.5, MeOH); IR (film) 2976*m*, 2940*m*, 1697*s*, 1650*m* 1383*m*, 1075*s*; ^{1}H NMR (CD_3OD) δ 8.05 (s, 1H, $H_{7'}$), 7.81 (d, 2H, $J_{H13'-H12'}$ = 9.0 Hz, $H_{13'}$), 7.73 (d, 2H, $J_{H17'-H18'}$ = 7.5 Hz, $H_{17'}$), 7.67−7.62 (m, 2H, $H_{19'}$, H_6), 7.54 (t, 2H, $J_{H18'-H19'}$ = $J_{H18'-H17'}$ = 7.5 Hz, $H_{18'}$), 7.05 (d, 2H, $J_{H12'-H13'}$ = 9.0 Hz, $H_{12'}$), 5.77 (br s, 1H, $H_{1'}$), 5.70 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.32 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.12 (d, 1H, $J_{H2'-H3'}$ = 6.0 Hz, $H_{2'}$), 4.76 (dd, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.69 (t, 2H, $J_{H10'-H9'}$ = 7.0 Hz, $H_{10'}$), 4.67 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.57 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.44 (dd, 1H, $J_{H4'-H5'}$ = 9.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.14−4.07 (m, 3H, $H_{8'}$, $H_{4''}$), 2.56 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.51−2.42 (m, 3H, $H_{5''b}$, $H_{9'}$), 1.62 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.55 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.48 (s, 3H, $H_{21'}$), 1.24 (s, 3H, $H_{21'}$) 0.84 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.81 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 197.7 ($C_{15'}$), 166.5 (C_4), 164.2 ($C_{11'}$), 152.3 (C_2), 146.2 ($C_{6'}$), 145.6 (C_6), 139.6 ($C_{16'}$), 133.8 ($C_{13'}$), 133.5 ($C_{19'}$), 131.6 ($C_{14'}$), 130.8 ($C_{17'}$), 129.6 ($C_{18'}$), 125.5 ($C_{7'}$), 117.8 ($C_{6''}$), 115.5 ($C_{12'}$), 115.3 ($C_{20'}$), 111.4 ($C_{1''}$), 103.1 (C_5), 97.1 ($C_{1'}$), 91.7 ($C_{4'}$), 89.7 ($C_{4''}$), 87.4 ($C_{2''}$), 85.7 ($C_{2'}$), 83.9 ($C_{3''}$), 83.1 ($C_{3'}$), 74.1 ($C_{5'}$), 66.2 ($C_{8'}$), 49.0 ($C_{10'}$), 45.5 ($C_{5''}$), 30.9 ($C_{9'}$), 30.6, 30.0 ($C_{7''}$), 27.5, 25.6 ($C_{21'}$), 8.8, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{40}H_{49}N_6O_{11}^+$ (M + H)$^+$ 789.3459, found 789.3463.

Compound ***19l***. Amine **19l** was prepared according to the general procedure for phthalimide cleavage from triazole **18l** (100 mg, 0.11 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 97/3/0.3%) afforded **19l** as a white solid (42 mg, 49% yield): R_f 0.19 (DCM/MeOH/Et_3N 98/2/0.3%); mp 127−129 °C; $[\alpha]_D$ −26 (*c* 0.5, MeOH); IR (film) 2895*m*, 1697*s*, 1600*s* 1257*m*; ^{1}H NMR (CD_3OD) δ 8.03 (s, 1H, $H_{7'}$), 7.78 (br d, 2H, $J_{H15'-H14'}$ = 8.0 Hz, $H_{15'}$), 7.71 (br d, 2H, $J_{H19'-H20'}$ = 7.5 Hz, $H_{19'}$), 7.63 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.60 (t, 1H, $J_{H21'-H20'}$ = 7.5 Hz, $H_{21'}$), 7.51 (t, 2H, $J_{H20'-H21'}$ = 7.5 Hz, $J_{H20'-H19'}$ = 7.5 Hz, $H_{20'}$), 7.01 (br d, 2H, $J_{H14'-H15'}$ = 8.0 Hz, $H_{14'}$), 5.76 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.68 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.31 (s, 1H, $H_{1''}$), 5.22 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.10 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.75 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.66 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.57 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.48 (tl, 2H, $J_{H12''-H11'}$ = 7.5 Hz, $H_{12'}$), 4.44 (dd, 1H, $J_{H4'-H5'}$ = 9.0 Hz, $J_{H4'-H3'}$ = 4.0 Hz, $H_{4'}$), 4.12 (dd, 1H, $J_{H4''-H5''a}$ = 9.0 Hz, $J_{H4''-H5''b}$ = 5.0 Hz, $H_{4''}$), 4.07 (t, 2H, $J_{H8'-H9'}$ = 6.0 Hz, $H_{8'}$), 2.60 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.53 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 2.04−1.98 (m, 2H, $H_{11'}$), 1.88−1.82 (m, 2H, $H_{9'}$), 1.61 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.51 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.49−1.46 (m, 2H, $H_{10'}$), 1.46 (s, 3H, $H_{23'}$), 1.23 (s, 3H, $H_{23'}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 197.7 ($C_{17'}$), 166.6 (C_4), 164.7 ($C_{13'}$), 152.5 (C_2), 146.1 ($C_{6'}$), 145.5 (C_6), 139.7 ($C_{18'}$), 133.8 ($C_{15'}$), 133.4 ($C_{21'}$), 131.2 ($C_{16'}$), 130.8 ($C_{19'}$), 129.6 ($C_{20'}$), 125.1 ($C_{7'}$), 117.9 ($C_{6''}$), 115.5 ($C_{14'}$), 115.3 ($C_{22'}$), 111.5 ($C_{1''}$), 103.1 (C_5), 97.0 ($C_{1'}$), 91.6 ($C_{4'}$), 89.2 ($C_{4''}$), 87.3 ($C_{2''}$), 85.7 ($C_{2'}$), 83.8 ($C_{3''}$), 83.1 ($C_{3'}$), 74.4 ($C_{5'}$), 69.3 ($C_{8'}$), 51.5 ($C_{12'}$), 45.3 ($C_{5''}$), 30.9 ($C_{11'}$), 30.6, 30.0 ($C_{7''}$), 29.6 ($C_{9'}$), 27.5, 25.6 ($C_{23'}$), 24.1 ($C_{10'}$), 8.8, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{42}H_{53}N_6O_{11}^+$ (M + H)$^+$ 817.3772, found 817.3808.

Compound ***19m***. Amine **19m** was prepared according to the general procedure for phthalimide cleavage from triazole **18m** (174 mg, 0.17 mmol). Flash chromatography (EtOAc to EtOAc/MeOH 9/1) afforded **19m** as a white solid (76 mg, 51% yield): R_f 0.56 (EtOAc/MeOH 9/1); mp 125−127 °C; $[\alpha]_D$ −24 (*c* 0.5, MeOH); IR (film) 2895*w*, 2840*w*, 1697*s*, 1653*m*, 1600*m*, 1257*m*; ^{1}H NMR (CD_3OD) δ 7.99 (s, 1H, $H_{7'}$), 7.78 (br d, 2H, $J_{H20'-H19'}$ = 9.0 Hz, $H_{20'}$), 7.71 (br d, 2H, $J_{H24'-H25'}$ = 7.5 Hz, $H_{24'}$), 7.63−7.60 (m, 2H, $H_{26'}$, H_6), 7.51 (t, 2H, $J_{H25'-H26'}$ = 7.5 Hz, $J_{H25'-H24'}$ = 7.5 Hz, $H_{25'}$), 7.02 (br d, 2H, $J_{H19'-H20'}$ = 9.0 Hz, $H_{19'}$), 5.76 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.67 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.30 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.10 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.73 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 4.0 Hz, $H_{3'}$), 4.66 (d, 1H, $J_{H2''-H3''}$ = 6.0 Hz, $H_{2''}$), 4.57 (d, 1H, $J_{H3''-H2''}$ = 6.0 Hz, $H_{3''}$), 4.45−4.37 (m, 3H, $H_{17'}$, $H_{4'}$), 4.10 (dd, 1H, $J_{H4''-H5''a}$ = 9.5 Hz, $J_{H4''-H5''b}$ = 5.0 Hz, $H_{4''}$), 4.08 (t, 2H, $J_{H8'-H9'}$ = 6.5 Hz, $H_{8'}$), 2.56 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 5.0 Hz, $H_{5''a}$), 2.50 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.5 Hz, $H_{5''b}$), 1.95−1.86 (m, 2H, $H_{16'}$), 1.83−1.77 (m, 2H, $H_{9'}$), 1.61 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.54 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.48 (s, 3H, $H_{19'}$), 1.41−1.27 (m, 12H, $H_{10'}$, $H_{11'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$), 1.24 (s, 3H, $H_{19'}$), 0.83 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$), 0.82 (t, 3H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 197.8 ($C_{22'}$), 166.3 (C_4), 164.9 ($C_{18'}$), 150.5 (C_2), 146.0 ($C_{6'}$), 145.5 (C_6), 136.8 ($C_{23'}$), 133.8 ($C_{20'}$), 133.4 ($C_{26'}$), 131.1 ($C_{21'}$), 130.8 ($C_{24'}$), 129.6 ($C_{25'}$), 125.1 ($C_{7'}$), 117.8 ($C_{6''}$), 115.4 ($C_{19'}$), 115.3 ($C_{27'}$), 111.4 ($C_{1''}$), 103.1 (C_5), 96.9 ($C_{1'}$), 91.7 ($C_{4'}$), 89.5 ($C_{4''}$), 87.4 ($C_{2''}$), 85.7 ($C_{2'}$), 83.9 ($C_{3''}$), 83.1 ($C_{3'}$), 74.4 ($C_{5'}$), 69.6 ($C_{8'}$), 51.6 ($C_{17'}$), 45.5 ($C_{5''}$), 31.2 ($C_{16'}$), 30.6, 30.6, 30.6, 30.5, 30.4, 30.1, 30.0, 27.5, 27.5 ($C_{9'}$, $C_{10'}$, $C_{11'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{7''}$), 27.2, 25.9 ($C_{28'}$), 8.8, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{47}H_{63}N_6O_{11}^+$ (M + H)$^+$ 887.4555, found 887.4575.

Compound ***19n***. Amine **19n** was prepared according to the general procedure for phthalimide cleavage from protected triazole **18n** (102 mg, 0.10 mmol). Flash chromatography (DCM/NEt_3 100/0.3% to DCM/MeOH/NEt_3 95/5/0.3%) afforded **19n** as a white solid (70 mg, 80% yield): R_f 0.22 (DCM/MeOH 9/1); mp 131−133 °C; $[\alpha]_D$ −20 (*c* 0.5, MeOH); IR (film) 2972*w*, 2937*w*, 1691*s*, 1651*m*, 1597*m*, 1253*m*; ^{1}H NMR (CD_3OD) δ 8.01 (s, 1H, $H_{7'}$), 7.75 (d, 2H, $J_{16'-15'}$ = 9.0 Hz, $H_{16'}$), 7.69 (d, 2H, $J_{H20'-H21'}$ = 8.0 Hz, $H_{20'}$), 7.59 (t, 1H, $J_{H22'-H21'}$ = 8.0 Hz, $H_{22'}$), 7.56 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 7.48 (t, 2H, $J_{H21'-H20'}$ = $J_{H21'-H22'}$ = 8.0 Hz, $H_{21'}$), 7.45 (d, 2H, $J_{H11'-H10'}$ = 8.5 Hz, $H_{11'}$), 7.31 (d, 2H, $J_{H10'-H11'}$ = 8.5 Hz, $H_{10'}$), 7.06 (d, 2H, $J_{H15'-16'}$ = 9.0 Hz, $H_{15'}$), 5.76 (d, 1H, $J_{H1'-H2'}$ = 2.0 Hz, $H_{1'}$), 5.62 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.61 (s, 2H, $H_{8'}$), 5.30 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 9.0 Hz, $H_{5'}$), 5.17 (s, 2H, $H_{13'}$), 5.03 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 2.0 Hz, $H_{2'}$), 4.73 (dd, 1H, $J_{H3'-H2'}$ = 6.5 Hz, $J_{H3'-H4'}$ = 3.5 Hz, $H_{3'}$), 4.63 (d, 1H, $J_{H2''-H3''}$ = 6.5 Hz, $H_{2''}$), 4.53 (d, 1H, $J_{H3''-H2''}$ = 6.5 Hz, $H_{3''}$), 4.41 (dd, 1H, $J_{H4'-H5'}$ = 9.0 Hz, $J_{H4'-H3'}$ = 3.5 Hz, $H_{4'}$), 4.05 (dd, 1H, $J_{H4''-H5''b}$ = 9.0 Hz, $J_{H4''-H5''a}$ = 5.5 Hz, $H_{4''}$), 2.45 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 11.0 Hz, $H_{5''a}$), 2.81 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''b}$), 1.59 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.51 (q, 2H, $J_{H7''-H8''}$ = 7.5 Hz, $H_{7''}$), 1.43 (s, 3H, $H_{24'}$), 1.21 (s, 3H, $H_{24'}$), 0.81 (t, 6H, $J_{H8''-H7''}$ = 7.5 Hz, $H_{8''}$); ^{13}C NMR (CD_3OD) δ 197.5 ($C_{18'}$), 166.4 (C_4), 164.1 ($C_{14'}$), 152.3 (C_2), 146.6 ($C_{6'}$), 145.2 (C_6), 139.5 ($C_{19'}$), 138.6 ($C_{12'}$), 136.6 ($C_{9'}$), 133.8 ($C_{16'}$), 133.4 ($C_{22'}$), 131.5 ($C_{17'}$), 130.8 ($C_{20'}$), 129.6 ($C_{21'}$), 129.4 ($C_{10'}$), 129.3 ($C_{11'}$), 125.4 ($C_{7'}$), 117.8 ($C_{6''}$), 115.8 ($C_{15'}$), 115.4 ($C_{23'}$), 111.3 ($C_{1''}$), 103.2 (C_5), 96.5 ($C_{1'}$), 91.2 ($C_{4'}$), 89.8 ($C_{4''}$), 87.3 ($C_{2''}$), 85.5 ($C_{2'}$), 83.8 ($C_{3''}$), 82.9 ($C_{3'}$), 74.3 ($C_{5'}$), 70.8 ($C_{13'}$), 54.8 ($C_{8'}$), 45.6 ($C_{5''}$), 30.5, 29.9 ($C_{7''}$), 27.6 ($C_{24'}$), 25.6 ($C_{24'}$), 8.9, 7.9 ($C_{8''}$); HRMS ESI$^+$ Calcd for $C_{45}H_{51}N_6O_{11}^+$ (M + H)$^+$ 851.3616, found 851.3657.

General Procedure for Ketals Hydrolysis, Preparation of Compounds 20a−n. At 0 °C, to a suspension of protected amine (1 equiv), in pure water, was dropwise added trifluoroacetic acid (1/4 v/v, final concentration: 10^{-2} M). The mixture was stirred at 0 °C for 10 min and then at rt for 90 min. Trifluoroacetic acid was then removed in vacuo without heating. The residue was dissolved in water and lyophilized. The resulting powder was recrystallized to furnish the corresponding deprotected compound as a trifluoroacetate or a bis-trifluoroacetate salt.

Compound ***20a***. Tetrol **20a** was prepared according to the general procedure for ketals hydrolysis from amine **19a** (22 mg, 0.032 mmol). Recrystallization in Et_2O afforded **20a** as a white powder (21 mg, 94% yield): mp 123−125 °C; $[\alpha]_D$ + 14 (*c* 0.6, MeOH); IR (film) 2919*br*, 2301*w*, 1714*s*, 1685*s*, 1462*m*, 1202*m*; ^{1}H NMR (CD_3OD) δ 7.96 (s,

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1H, $H_{7'}$), 7.76 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.76 (d, 1H, $J_{H1'-H2'}$ = 4.0 Hz, $H_{1'}$), 5.64 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.18 (s, 1H, $H_{1''}$), 5.06 (d, 1H, $J_{H5'-H4'}$ = 3.0 Hz, $H_{5'}$), 4.32 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.23 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 3.0 Hz, $H_{4'}$), 4.14 (dd, 1H, $J_{H2'-H3'}$ = 5.0 Hz, $J_{H2'-H1'}$ = 4.0 Hz, $H_{2'}$), 4.09 (dd, 1H, $J_{H3'-H4'}$ = 5.5 Hz, $J_{H3'-H2'}$ = 5.0 Hz, $H_{3'}$), 4.07–4.03 (m, 1H, $H_{4''}$), 4.01–3.98 (m, 2H, $H_{2''}$, $H_{3''}$), 3.13 (dd, 1H, $J_{H5''a-H5''b}$ = 12.5 Hz, $J_{H5''a-H4''}$ = 2.0 Hz, $H_{5''a}$), 2.75 (dd, 1H, $J_{H5''b-H5''a}$ = 12.5 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 1.86–1.80 (m, 2H, $J_{H9'-H8'}$ = 7.0 Hz, $H_{9'}$), 1.25–1.20 (m, 14H, $H_{10'}$, $H_{11'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$, $H_{16'}$), 0.82 (t, 3H, $J_{H17'-H16'}$ = 6.5 Hz, $H_{17'}$); ^{13}C NMR (CD_3OD) δ 166.2 (C_4, CO TFA), 152.3 (C_2), 142.5 (C_6),125.2 ($C_{7'}$), 125.1 ($C_{6'}$), 110.5 ($C_{1''}$), 102.8 (C_5), 91.9 ($C_{1'}$), 86.5 ($C_{4'}$), 80.6 ($C_{4''}$), 76.4 ($C_{2''}$), 75.3 ($C_{2'}$), 73.7 ($C_{3''}$), 73.5 ($C_{5'}$), 71.2 ($C_{3'}$), 51.7 ($C_{8'}$), 43.5 ($C_{5''}$), 31.4 ($C_{9'}$), 33.1, 30.7, 30.7, 30.5, 30.2, 27.6, 23.8 ($C_{10'}$, $C_{11'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$), 14.5 ($C_{17'}$); HRMS ESI$^+$ Calcd for $C_{26}H_{43}N_6O_9^+$ (M + H)$^+$ 583.3092, found 583.3073.

Compound ***20b***. Tetrol **20b** was prepared according to the general procedure for ketals hydrolysis from amine **19b** (62 mg, 0.096 mmol). Recrystallization in Et_2O afforded **20b** as a white powder (58 mg, 93% yield): mp 151–153 °C; $[\alpha]_D$ + 4 (*c* 0.8, MeOH); IR (film) 3230*br*, 2928*w*, 2863*w*, 1681*s*, 1204*s*, 1134*s*; ^{1}H NMR (CD_3OD) δ 8.03 (s, 1H, $H_{7'}$), 7.82 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 5.84 (d, 1H, $J_{H1'-H2'}$ = 3.5 Hz, $H_{1'}$), 5.72 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.25 (s, 1H, $H_{1''}$), 5.12 (d, 1H, $J_{H5'-H4'}$ = 3.5 Hz, $H_{5'}$), 4.73–4.67 (m, 1H, $H_{8'}$), 4.29 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 3.5 Hz, $H_{4'}$), 4.21 (dd, 1H, $J_{H2'-H3'}$ = 5.5 Hz, $J_{H2'-H1'}$ = 3.5 Hz, $H_{2'}$), 4.16 (t, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 6.0, Hz, $H_{3'}$), 4.14–4.06 (m, 3H, $H_{2''}$,$H_{3''}$, $H_{4''}$), 3.20 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 2.5 Hz, $H_{5''a}$), 2.82 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''b}$), 2.15–2.13 (m, 2H, H_{9a}), 2.06–2.04 (m, 2H, H_{9b}), 1.88–1.83 (m, 2H, H_{10a}), 1.74–1.59 (m, 6H, H_{10b}, H_{11}); ^{13}C NMR (CD_3OD) δ 166.1 (C_4), 152.2 (C_2), 146.5 ($C_{6'}$), 142.4 (C_6), 123.2 ($C_{7'}$), 110.3 ($C_{1''}$), 102.6 (C_5), 91.7 ($C_{1'}$), 86.3 ($C_{4'}$), 80.4 ($C_{4''}$), 87.2 ($C_{3''}$), 76.2 ($C_{2''}$), 75.1 ($C_{5'}$), 73.5 ($C_{2''}$), 71.0 ($C_{3'}$), 64.2 ($C_{8'}$), 43.3 ($C_{5''}$), 36.5 (C_9), 28.8 (C_{11}), 25.3 (C_{10}); HRMS ESI$^+$ Calcd for $C_{23}H_{35}N_6O_9^+$ (M + H)$^+$ 539.2480, found 539.2480.

Compound ***20c***. Tetrol **20c** Compound **20c** was prepared according to the general procedure for ketals hydrolysis from amine **19c** (15 mg, 0.023 mmol). Recrystallization in DCM/MeOH 95/5 afforded **20c** as a white powder (13.8 mg, 89% yield): mp 127–129 °C; $[\alpha]_D$ + 19 (*c* 0.7, MeOH); IR (film) 3423*br*, 2954*s*, 2927*s*, 1733*s*, 1690*m*; ^{1}H NMR (CD_3OD) δ 8.02 (s, 1H, $H_{7'}$), 7.83 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 7.28–7.25 (m, 2H, $H_{12'}$), 7.19–7.16 (m, 3H, $H_{13'}$, $H_{14'}$), 5.84 (d, 1H, $J_{H1'-H2'}$ = 4.0 Hz, $H_{1'}$), 5.71 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.26 (s, 1H, $H_{1''}$), 5.13 (d, 1H, $J_{H5'-H4'}$ = 4.5 Hz, $H_{5'}$), 4.41 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.29 (dd, 1H, $J_{H4'-H3'}$ = 6.5 Hz, $J_{H4'-H5'}$ = 4.5 Hz, $H_{4'}$), 4.22 (dd, 1H, $J_{H2'-H3'}$ = 4.5 Hz, $J_{H2'-H1'}$ = 4.0 Hz, $H_{2'}$), 4.16 (dd, 1H, $J_{H3'-H4'}$ = 6.5 Hz, $J_{H3'-H2'}$ = 4.5 Hz, $H_{3'}$), 4.13–4.10 (m, 1H, $H_{4''}$), 4.09–4.05 (m, 2H, $H_{2''}$, $H_{3''}$), 3.20 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 2.5 Hz, $H_{5''a}$), 2.82 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''b}$), 2.63 (t, 2H, $J_{H10'-H9'}$ = 7.5 Hz, $H_{10'}$), 2.23 (tt, 2H, $J_{H9'-H10'}$ = 7.5 Hz, $J_{H9'-H8'}$ = 7.0 Hz, $H_{9'}$); ^{13}C NMR (CD_3OD) δ 166.3 (C_4), 152.3 (C_2), 142.5 ($C_{6'}$, $C_{11'}$), 141.9 (C_6), 129.7 ($C_{13'}$), 129.6 ($C_{14'}$), 127.4 ($C_{12'}$), 125.5 ($C_{7'}$), 110.4 ($C_{1''}$), 102.8 (C_5), 91.8 ($C_{1'}$), 86.5 ($C_{4'}$), 80.5 ($C_{4''}$), 76.3 ($C_{2''}$), 75.2 ($C_{2'}$), 73.7 ($C_{3''}$), 73.5 ($C_{3'}$), 71.2 ($C_{5'}$), 51.0 ($C_{8'}$), 43.5 ($C_{5''}$), 33.6 ($C_{10'}$), 32.9 ($C_{9'}$); HRMS ESI$^+$ Calcd for $C_{25}H_{33}N_6O_9^+$ (M + H)$^+$ 561.2322, found 561.2322.

Compound ***20d***. Tetrol **20d** was prepared according to the general procedure for ketals hydrolysis from amine **19d** (44 mg, 0.06 mmol). Recrystallization in DCM/MeOH 95/5 afforded **20d** as a white powder (42 mg, 96% yield): mp 137–139 °C; $[\alpha]_D$ + 15 (*c* 0.5, MeOH); IR (film) 3384*br*, 2914*w*, 2067*w*, 1678*s*, 1459*m*, 1202*s*; ^{1}H NMR (CD_3OD) δ 7.79 (s, 1H, $H_{7'}$), 7.73 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.50 (d, 2H, $J_{H15'-H16'}$ = 8.0 Hz, $H_{15'}$), 7.45 (d, 2H, $J_{H12'-H11'}$ = 8.0 Hz, $H_{12'}$), 7.35 (t, 2H, $J_{H16'-H15'}$ = $J_{H16'-H17'}$ = 7.5 Hz, $H_{16'}$), 7.25 (t, 1H, $J_{H17'-H16'}$ = 7.5 Hz, $H_{17'}$), 7.11 (d, 2H, $J_{H11'-12'}$ = 8.0 Hz, $H_{11'}$), 5.73 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.62 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.17 (s, 1H, $H_{1''}$), 5.07–5.03 (m, 1H, $H_{5'}$), 4.69–4.60 (m, 2H, $H_{8'}$), 4.23–4.19 (m, 1H, $H_{4'}$), 4.16–4.12 (m, 1H, $H_{2'}$), 4.10–4.06 (m, 2H, $H_{3'}$, $H_{4''}$), 4.04–3.92 (m, 2H, $H_{2''}$, $H_{3''}$), 3.24–3.16 (m, 2H, $H_{9'}$), 3.12 (br d, 1H, $J_{H5''a-H5''b}$ = 13.5 Hz, $H_{5''a}$), 2.70 (dd, 1H, $J_{H5''b-H5''a}$ = 13.5 Hz, $J_{H5''b-H4''}$ = 8.0 Hz, $H_{5''b}$); ^{13}C NMR (CD_3OD) δ 166.4 (C_4), 152.2 (C_2), 142.2 (C_6), 141.9 ($C_{6'}$), 141.1 ($C_{14'}$, $C_{13'}$), 137.7 ($C_{10'}$), 130.4 ($C_{11'}$), 129.9 ($C_{16'}$), 128.4 ($C_{17'}$), 128.2 ($C_{12'}$), 127.7 ($C_{15'}$), 125.6 ($C_{7'}$), 110.2 ($C_{1''}$), 102.6 (C_5), 91.7 ($C_{1'}$), 86.3 ($C_{4'}$), 80.4 ($C_{4''}$), 76.2 ($C_{2''}$), 75.2 ($C_{2'}$), 73.6 ($C_{3''}$), 73.1 ($C_{3'}$), 70.9 ($C_{5'}$), 52.8 ($C_{8'}$), 43.4 ($C_{5''}$), 37.1 ($C_{9'}$); HRMS ESI$^+$ Calcd for $C_{30}H_{35}N_6O_9^+$ (M + H)$^+$ 623.2466, found 623.2448.

Compound ***20e***. Tetrol **20e** was prepared according to the general procedure for ketals hydrolysis from amine **19e** (9.2 mg, 0.015 mmol). Recrystallization in Et_2O afforded **20e** as a white powder (8.4 mg, 91% yield): mp 161–163 °C; $[\alpha]_D$ + 12 (*c* 0.4, MeOH); IR (film) 3413*br*, 2917*w*, 2897*w*, 1685*s*, 1198*s*; ^{1}H NMR (CD_3OD) δ 7.98 (s, 1H, $H_{7'}$), 7.77 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.77 (d, 1H, $J_{H1'-H2'}$ = 4.0 Hz, $H_{1'}$), 5.65 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.18 (s, 1H, $H_{1''}$), 5.07 (d, 1H, $J_{H5'-H4'}$ = 4.0 Hz, $H_{5'}$), 4.45 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.22 (dd, 1H, $J_{H4'-H3'}$ = 6.0 Hz, $J_{H4'-H5'}$ = 4.0 Hz, $H_{4'}$), 4.15 (dd, 1H, $J_{H2'-H3'}$ = 5.5 Hz, $J_{H2'-H1'}$ = 4.0 Hz, $H_{2'}$), 4.10 (dd, 1H, $J_{H3'-H4'}$ = 6.0 Hz, $J_{H3'-H2'}$ = 5.5 Hz, $H_{3'}$), 4.06–3.99 (m, 3H, $H_{4'}$, $H_{2''}$, $H_{3''}$), 3.50 (t, 2H, $J_{H10'-H9'}$ = 6.0 Hz, $H_{10'}$), 3.13 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 2.0 Hz, $H_{5''a}$), 2.72 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 8.0 Hz, $H_{5''b}$), 2.06–2.01 (m, 2H, $H_{9'}$); ^{13}C NMR (CD_3OD) δ 166.2 (C_4), 152.4 (C_2), 146.8 ($C_{6'}$), 142.5 (C_6), 125.4 ($C_{7'}$), 110.4 ($C_{1''}$), 102.7 (C_5), 91.8 ($C_{1'}$), 86.5 ($C_{4'}$), 80.4 ($C_{4''}$), 76.3 ($C_{3''}$), 75.3 ($C_{2'}$), 73.7 ($C_{5'}$), 73.5 ($C_{2''}$), 71.1 ($C_{3'}$), 59.4 ($C_{10'}$), 49.6 ($C_{8'}$), 43.5 ($C_{5''}$), 33.9 ($C_{9'}$); HRMS ESI$^+$ Calcd for $C_{19}H_{29}N_6O_{10}^+$ (M + H)$^+$ 501.1945, found 501.1943.

Compound ***20f***. Tetrol **20f** was prepared according to the general procedure for ketals hydrolysis from amine **19f** (29 mg, 0.045 mmol). Recrystallization in Et_2O afforded **20f** as a white powder (20 mg, 69% yield): mp 161–163 °C; $[\alpha]_D$ + 17 (*c* 0.5, MeOH); IR (film) 3452*br*, 2925*w*, 2895*w*, 1690*s*, 1200*s*; ^{1}H NMR (CD_3OD) δ 7.97 (s, 1H, $H_{7'}$), 7.76 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.77 (d, 1H, $J_{H1'-H2'}$ = 4.0 Hz, $H_{1'}$), 5.65 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.18 (s, 1H, $H_{1''}$), 5.07–5.05 (m, 1H, $H_{5'}$), 4.34 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.22–4.20 (m, 1H, $H_{4'}$), 4.15–4.13 (m, 1H, $H_{2'}$), 4.10–4.08 (m, 1H, $H_{3'}$), 4.04–3.92 (m, 3H, $H_{4''}$, $H_{2''}$, $H_{3''}$), 3.46 (t, 2H, $J_{H12'-H11'}$ = 6.0 Hz, $H_{12'}$), 3.12 (br d, 1H, $J_{H5''a-H5''b}$ = 12.5 Hz, $H_{5''a}$), 2.72 (dd, 1H, $J_{H5''b-H5''a}$ = 12.5 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''b}$), 1.88–1.82 (m, 2H, $H_{9'}$), 1.47–1.45 (m, 2H, $H_{11'}$), 1.32–1.27 (m, 2H, $H_{10'}$); ^{13}C NMR (CD_3OD) δ 166.2 (C_4), 152.4 (C_2), 143.1 ($C_{6'}$) 142.5 (C_6), 125.2 ($C_{7'}$), 110.4 ($C_{1''}$), 102.9 (C_5), 91.7 ($C_{1'}$), 86.6 ($C_{4'}$), 80.5 ($C_{4''}$), 76.3 ($C_{3''}$), 75.2 ($C_{2'}$), 73.7 ($C_{5'}$), 73.5 ($C_{2''}$), 71.2 ($C_{3'}$), 62.7 ($C_{12'}$), 51.6 ($C_{8'}$), 43.6 ($C_{5''}$), 32.9 ($C_{9'}$), 31.0 ($C_{11'}$), 23.8 ($C_{10'}$); HRMS ESI$^+$ Calcd for $C_{21}H_{33}N_6O_{10}^+$ (M + H)$^+$ 529.2258, found 529.2240.

Compound ***20g***. Tetrol **20g** was prepared according to the general procedure for ketals hydrolysis from amine **19g** (52 mg, 0.081 mmol). Recrystallization in Et_2O afforded **20g** as a white powder (60 mg, 95% yield as a bis-trifluoroacetate salt): mp 140–142 °C; $[\alpha]_D$ + 14 (*c* 0.5, H_2O); IR (film) 3164*br*, 2923*m*,1673*s*, 1201*s*, 1132*s*; ^{1}H NMR (CD_3OD + 50 μL of D_2O) δ 7.97 (s, 1H, $H_{7'}$), 7.84 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.89 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.85 (d, 1H, $J_{H1'-H2'}$ = 4.0 Hz, $H_{1'}$), 5.26 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 3.5 Hz, $H_{5'}$), 4.48 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.32 (m, 2H, $H_{2'}$,$H_{4'}$), 4.24 (dd, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 5.0 Hz, $H_{3'}$), 4.18–4.12 (m, 3H, $H_{2''}$, $H_{3''}$, $H_{4''}$), 3.26 (dd, 1H, $J_{H5''a-H5''b}$ = 13.5 Hz, $J_{H5''a-H4''}$ = 2.0 Hz, $H_{5''a}$), 2.97 (t, 2H, $J_{H12'-H11'}$ = 7.5 Hz, $H_{12'}$), 2.82 (dd, 1H, $J_{H5''b-H5''a}$ = 13.5 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''b}$), 2.06–1.94 (m, 2H, $H_{9'}$), 1.75–1.68 (m, 2H, $H_{11'}$), 1.43–1.36 (m, 2H, $H_{10'}$); ^{13}C NMR (CD_3OD + 50 μL of D_2O) δ 166.6 (C_4), 163.7 (q, *J* = 35.0 Hz, $\underline{C}O_{TFA}$), 152.3 (C_2), 142.7 (C_6, $C_{6'}$), 125.4 ($C_{7'}$), 109.5 ($C_{1''}$), 103.0 (C_5), 91.4 ($C_{1'}$), 86.0 ($C_{4'}$), 79.7 ($C_{4''}$), 75.6 ($C_{2''}$), 74.5 ($C_{2'}$), 73.3 ($C_{3''}$), 73.2 ($C_{3'}$), 70.7 ($C_{5'}$), 51.2 ($C_{8'}$), 43.3 ($C_{5''}$), 40.2 ($C_{12'}$), 30.2 ($C_{9'}$), 27.4 ($C_{11'}$), 23.9 ($C_{10'}$); HRMS ESI$^+$ Calcd for $C_{21}H_{34}N_7O_9^+$ (M + H)$^+$ 528.2418, found 528.2423.

Compound ***20h***. Tetrol **20h** was prepared according to the general procedure for ketals hydrolysis from amine **19h** (62 mg, 0.088 mmol). Recrystallization in Et_2O afforded **20h** as a white powder (73 mg, 99% yield as a bis-trifluoroacetate salt): mp 128–130 °C; $[\alpha]_{365}$ + 80 (*c* 0.5, H_2O); IR (film) 2922*w*, 2877*w*, 2511*w*, 1674*s*, 1200*s*; ^{1}H NMR

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(CD_3OD + 50 μL of D_2O) δ 8.05 (s, 1H, $H_{7'}$), 7.73 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 5.84 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.78 (d, 1H, $J_{H1'-H2'}$ = 3.5 Hz, $H_{1'}$), 5.20 (s, 1H, $H_{1''}$), 5.15 (d, 1H, $J_{H5'-H4'}$ = 4.5 Hz, $H_{5'}$), 4.41 (t, 2H, $J_{H8'-H9'}$ = 7.0 Hz, $H_{8'}$), 4.29 (dd, 1H, $J_{H2'-H3'}$ = 6.0 Hz, $J_{H2'-H1'}$ = 3.5 Hz, $H_{2'}$), 4.26 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 4.5 Hz, $H_{4'}$), 4.20 (dd, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 5.5 Hz, $H_{3'}$), 4.15–4.12 (m, 2H, $H_{2''}$, $H_{3''}$), 4.06–4.04 (m, 3H, $H_{4''}$, $H_{13'a}$), 3.77–3.72 (m, 2H, $H_{13'b}$), 3.46–3.43 (m, 2H, $H_{14'a}$), 3.20 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 2.5 Hz, $H_{5''a}$), 3.11–3.06 (m, 4H, $H_{12'}$, $H_{14'b}$), 2.72 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.5 Hz, $H_{5''b}$), 1.94–1.87 (m, 2H, $H_{9'}$), 1.74–1.67 (m, 2H, $H_{11'}$), 1.32–1.24 (m, 2H, $H_{10'}$); ^{13}C NMR (CD_3OD + 50 μL of D_2O) δ 166.9 (C_4), 163.7 (q, J = 39.5 Hz, $\underline{C}O_{TFA}$), 152.3 (C_2), 145.8 ($C_{6'}$), 142.8 (C_6), 125.5 ($C_{7'}$), 109.2 ($C_{1''}$), 103.0 (C_5), 91.1 ($C_{1'}$), 85.8 ($C_{4'}$), 79.5 ($C_{2''}$), 75.3 ($C_{4''}$), 74.2 ($C_{3'}$), 73.3 ($C_{3''}$), 72.9 ($C_{2'}$), 70.5 ($C_{5'}$), 64.7 ($C_{13'}$), 57.8 ($C_{12'}$), 52.6 ($C_{14'}$), 51.1 ($C_{8'}$), 43.2 ($C_{5''}$), 29.9 ($C_{9'}$), 23.6 ($C_{11'}$), 23.4 ($C_{10'}$); HRMS ESI^+ Calcd for $C_{25}H_{40}N_7O_{10}^+$ $(M + H)^+$ 598.2837, found 598.2831.

Compound ***20i***. Tetrol **20i** prepared according to the general procedure for ketals hydrolysis from amine **19i** (22 mg, 0.033 mmol). Recrystallization in Et_2O afforded **20i** as a white powder (25.4 mg, 99% yield as a bis-trifluoroacetate salt): mp 118–120 °C; $[\alpha]_D$ + 13 (*c* 0.4, H_2O); IR (film) 3146*br*, 2928*w*, 2848*w*, 2352*w*, 1676*s*, 1199*s*, 1127*s*; ^1H NMR (D_2O) δ 8.76 (br s, 1H, $H_{11'}$), 8.10 (s, 1H, $H_{7'}$), 7.86 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.53 (br s, 1H, $H_{12'}$), 7.49 (br s, 1H, $H_{13'}$), 5.95 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.77 (d, 1H, $J_{H1'-H2'}$ = 3.5 Hz, $H_{1'}$), 5.30 (s, 1H, $H_{1''}$), 5.24 (d, 1H, $J_{H5'-H4'}$ = 3.5 Hz, $H_{5'}$), 4.68–4.62 (m, 2H, $H_{8'}$), 4.44 (dd, 1H, $J_{H2'-H3'}$ = 6.5 Hz, $J_{H2'-H1'}$ = 3.5 Hz, $H_{1'}$), 4.36–4.30 (m, 4H, $H_{3'}$, $H_{4'}$, $H_{10'}$), 4.26–4.21 (m, 2H, $H_{2''}$, $H_{3''}$), 4.17–4.14 (m, 1H, $H_{4''}$), 3.30 (dd, 1H, $J_{H5''a-H5''b}$ = 13.5 Hz, $J_{H5''a-H4''}$ = 3.0 Hz, $H_{5''a}$), 2.82 (dd, 1H, $J_{H5''b-H5''a}$ = 13.5 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''b}$), 2.63–2.60 (m, 2H, $H_{9'}$); ^{13}C NMR (D_2O) δ 167.6 (C_4), 164.1 (q, J = 36.2 Hz, $\underline{C}O_{TFA}$), 152.9 (C_2), 146.6 ($C_{6'}$), 143.4 (C_6), 136.2 ($C_{11'}$), 126.1 ($C_{12'}$), 123.1 ($C_{7'}$), 121.5 ($C_{13'}$), 109.7 ($C_{1''}$), 103.6 (C_5), 91.8 ($C_{1'}$), 86.2 ($C_{4'}$), 79.9 ($C_{2''}$), 75.8 ($C_{4''}$), 74.7 ($C_{2'}$), 73.8 ($C_{3''}$), 73.5 ($C_{3'}$), 70.9 ($C_{5'}$), 48.9 ($C_{8'}$), 47.9 ($C_{10'}$), 43.8 ($C_{5''}$), 30.9 ($C_{9'}$); HRMS ESI^+ Calcd for $C_{22}H_{31}N_8O_9^+$ $(M + H)^+$ 551.2214, found 551.2209.

Compound ***20j***. Tetrol **20j** was prepared according to the general procedure for ketals hydrolysis from amine **19j** (14.7 mg, 0.018 mmol). Recrystallization in Et_2O afforded **20j** as a white powder (12.6 mg, 86% yield): mp 137–139 °C; $[\alpha]_D$ + 19 (*c* 0.5, MeOH); IR (film) 3369*br*, 2925*m*, 2847*m*, 2341*w*, 1686*s*, 1203*s*; ^1H NMR (CD_3OD) δ 8.41 (br s, 1H, $H_{16'}$), 8.18 (s, 1H, $H_{7'}$), 7.84 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 7.81 (dd, 1H, $J_{H14'-H13'}$ = 9.0 Hz, $J_{H14'-H16'}$ = 2.0 Hz, $H_{14'}$), 6.99 (d, 1H, $J_{H13'-H14'}$ = 9.0 Hz, $H_{13'}$), 5.83 (d, 1H, $J_{H1'-H2'}$ = 3.5 Hz, $H_{1'}$), 5.71 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.26 (s, 1H, $H_{1''}$), 5.20 (d, 1H, $J_{H5'-H4'}$ = 3.5 Hz $H_{5'}$), 4.91 (t, 2H, $J_{H8'-H9'}$ = 6.5 Hz, $H_{8'}$), 4.30 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 3.5 Hz, $H_{4'}$), 4.23 (dd, 1H, $J_{H2'-H3'}$ = 5.5 Hz, $J_{H2'-H1'}$ = 3.5 Hz, $H_{2'}$), 4.19 (t, 1H, $J_{H3'-H2'}$ = 5.5 Hz, $J_{H3'-H4'}$ = 5.5 Hz, $H_{3'}$), 4.14–4.10 (m, 1H, $H_{4''}$), 4.08 (d, 1H, $J_{H2''-H3''}$ = 4.5 Hz, $H_{2''}$), 4.06 (br d, 1H, $J_{H3''-H2''}$ = 4.5 Hz, $H_{3''}$), 3.99–3.89 (m, 4H, $H_{10'}$), 3.71 (t, 2H, $J_{H9'-H8'}$ = 6.5 Hz, $H_{9'}$), 3.37–3.32 (m, 4H, $H_{11'}$), 3.21 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 2.5 Hz, $H_{5''a}$), 2.87 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$); ^{13}C NMR (CD_3OD) δ 166.2 (C_4), 161.2 ($C_{12'}$), 152.3 (C_2), 147.6–146.5 (m, $C_{16'}$), 146.6 ($C_{6'}$), 142.5 (C_6), 136.3 ($C_{14'}$), 126.1 ($C_{7'}$), 126.0 (q, J_{C-F} = 270.0 Hz, $C_{17'}$), 117.9 (q, $J_{C15'-F}$ = 34.5 Hz, $C_{15'}$), 110.5 ($C_{1''}$), 108.1 ($C_{13'}$), 102.9 (C_5), 92.1 ($C_{1'}$), 86.5 ($C_{4'}$), 80.6 ($C_{4''}$), 76.4 ($C_{3''}$), 75.3 ($C_{2'}$), 73.8 ($C_{2''}$), 73.5 ($C_{5'}$), 71.2 ($C_{3'}$), 59.8 ($C_{9'}$), 53.3 ($C_{10'}$), 46.3 ($C_{8'}$), 43.7 ($C_{5''}$), 43.6 ($C_{11'}$); HRMS ESI^+ Calcd for $C_{28}H_{37}F_3N_9O_9^+$ $(M + H)^+$ 700.2626, found 700.2657.

Compound ***20k***. Tetrol **20k** was prepared according to the general procedure for ketals hydrolysis from amine **19k** (30 mg, 0.034 mmol). Recrystallization in Et_2O afforded **20k** as a white powder (26.7 mg, 99% yield): mp 157–159 °C; $[\alpha]_D$ + 21 (*c* 0.5, MeOH); IR (film) 3272*br*, 2920*m*, 1678*s*, 1600*m*, 1467*m*, 1202*s*; ^1H NMR (CD_3OD) δ 8.04 (s, 1H, $H_{7'}$), 7.78 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 7.75 (d, 2H, $J_{H13'-H12'}$ = 9.0 Hz, $H_{13'}$), 7.69 (d, 2H, $J_{H17'-H18'}$ = 7.5 Hz, $H_{17'}$), 7.59 (t, 1H, $J_{H19'-H18'}$ = 7.5 Hz, $H_{19'}$), 7.49 (t, 2H, $J_{H18'-H19'}$ = $J_{H18'-H17'}$ = 7.5 Hz, $H_{18'}$), 6.98 (d, 2H, $J_{H12'-H13'}$ = 9.0 Hz, $H_{12'}$), 5.74 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.65 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.21 (s, 1H, $H_{1''}$), 5.19 (d, 1H, $J_{H5'-H4'}$ = 4.0 Hz, $H_{5'}$), 4.63 (t, 2H, $J_{H10'-H9'}$ = 6.5 Hz, $H_{10'}$), 4.23 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 4.0 Hz, $H_{4'}$), 4.17 (dd, 1H, $J_{H2'-H3'}$ = 5.0 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.11 (dd, 1H, $J_{H3'-H4'}$ = 5.5 Hz, $J_{H3'-H2'}$ = 5.0 Hz, $H_{3'}$), 4.09–4.07 (m, 3H, $H_{8'}$, $H_{4''}$), 4.05–4.00 (m, 2H, $H_{2''}$, $H_{3''}$), 3.15 (dd, 1H, $J_{H5''a-H5''b}$ = 12.5 Hz, $J_{H5''a-H4''}$ = 2.0 Hz, $H_{5''a}$), 2.79 (dd, 1H, $J_{H5''b-H5''a}$ = 12.5 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 2.40 (tt, 2H, $J_{H9'-H10'}$= 6.5 Hz, $J_{H9'-H8'}$= 5.5 Hz, $H_{9'}$); ^{13}C NMR (CD_3OD) δ 197.7 ($C_{15'}$), 166.2 (C_4, $\underline{C}O$ TFA), 164.1 ($C_{11'}$), 152.2 (C_2), 146.9 ($C_{6'}$), 142.4 (C_6), 139.5 ($C_{16'}$), 133.8 ($C_{13'}$), 133.4 ($C_{19'}$), 131.6 ($C_{14'}$), 130.8 ($C_{17'}$), 129.5 ($C_{18'}$), 125.6 ($C_{7'}$), 115.4 ($C_{12'}$), 110.5 ($C_{1''}$), 102.7 (C_5), 92.0 ($C_{1'}$), 86.4 ($C_{4'}$), 80.5 ($C_{4''}$), 76.4 ($C_{2''}$), 75.3 ($C_{2'}$), 73.7 ($C_{3''}$), 73.4 ($C_{5'}$), 71.1 ($C_{3'}$), 66.2 ($C_{8'}$), 48.6 (with CD_3OD, $C_{10'}$), 43.5 ($C_{5''}$), 30.9 ($C_{9'}$); HRMS ESI^+ Calcd for $C_{32}H_{37}N_6O_{11}^+$ $(M + H)^+$ 681.2520, found 681.2520.

Compound ***20l***. Tetrol **20l** was prepared according to the general procedure for ketals hydrolysis from amine **19l** (27 mg, 0.033 mmol). Recrystallization in Et_2O afforded **20l** as a white powder (26 mg, 96% yield): mp 146–148 °C; $[\alpha]_D$ + 24 (*c* 0.5, MeOH); IR (film) 3270*br*, 2914*m*, 1675*s*, 1603*m*, 1452*m*, 1201*s*; ^1H NMR (CD_3OD) δ 8.06 (s, 1H, $H_{7'}$), 7.83 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.78 (d, 2H, $J_{H15'-H14'}$ = 8.5 Hz, $H_{15'}$), 7.71 (d, 2H, $J_{H19'-H20'}$ = 7.5 Hz, $H_{19'}$), 7.62 (t, 1H, $J_{H21'-H20'}$ = 7.5 Hz, $H_{21'}$), 7.51 (t, 2H, $J_{H20'-H21'}$ = 7.5 Hz, $J_{H20'-H19'}$ = 7.5 Hz, $H_{20'}$), 7.01 (d, 2H, $J_{H14'-H15'}$ = 8.5 Hz, $H_{14'}$), 5.83 (d, 1H, $J_{H1'-H2'}$ = 3.0 Hz, $H_{1'}$), 5.71 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.26 (s, 1H, $H_{1''}$), 5.14 (d, 1H, $J_{H5'-H4'}$ = 4.0 Hz, $H_{5'}$), 4.46 (t, 2H, $J_{H12'-H11'}$ = 7.0 Hz $H_{12'}$), 4.30 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 4.0 Hz, $H_{4'}$), 4.21 (dd, 1H, $J_{H2'-H3'}$ = 6.0 Hz, $J_{H2'-H1'}$ = 3.0 Hz, $H_{2'}$), 4.17 (dd, 1H, $J_{H3'-H2'}$ = 6.0 Hz, $J_{H3'-H4'}$ = 5.5 Hz, $H_{3'}$), 4.14–4.08 (m, 1H, $H_{4''}$), 4.08–4.06 (m, 4H, $H_{8'}$, $H_{2''}$, $H_{3''}$), 3.22 (dd, 1H, $J_{H5''a-H5''b}$ = 12.5 Hz, $J_{H5''a-H4''}$ = 2.5 Hz, $H_{5''a}$), 2.83 (dd, 1H, $J_{H5''b-H5''a}$ = 12.5 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 2.03–1.97 (m, 2H, $H_{11'}$), 1.87–1.82 (m, 2H, $H_{9'}$), 1.55–1.49 (m, 2H, $H_{10'}$); ^{13}C NMR (CD_3OD) δ 197.9 ($C_{17'}$), 166.2 (C_4), 164.6 ($C_{13'}$), 152.3 (C_2), 142.5 ($C_{6'}$, C_6), 139.7 ($C_{18'}$), 133.8 ($C_{15'}$), 133.4 ($C_{21'}$), 131.2 ($C_{16'}$), 130.8 ($C_{19'}$), 129.6 ($C_{20'}$), 125.2 ($C_{7'}$), 115.4 ($C_{14'}$), 110.5 ($C_{1''}$), 102.8 (C_5), 91.9 ($C_{1'}$), 86.5 ($C_{4'}$), 80.6 ($C_{4''}$), 76.4 ($C_{2''}$), 75.3 ($C_{2'}$), 73.7 ($C_{3''}$), 73.5 ($C_{5'}$), 71.2 ($C_{3'}$), 69.2 ($C_{8'}$), 51.6 ($C_{12'}$), 43.5 ($C_{5''}$), 31.0 ($C_{11'}$), 29.6 ($C_{9'}$), 24.4 ($C_{10'}$); HRMS ESI^+ Calcd for $C_{34}H_{41}N_6O_{11}^+$ $(M + H)^+$ 709.2828, found 709.2853.

Compound ***20m***. Tetrol **20m** was prepared according to the general procedure for ketals hydrolysis from amine **19m** (16 mg, 0.018 mmol). Recrystallization in Et_2O afforded **20m** as a white powder (15.9 mg, 99% yield): mp 151–153 °C; $[\alpha]_D$ + 26 (*c* 0.5, MeOH); IR (film) 3338*br*, 2930*m*, 2857*m*, 1680*s*, 1597*s*, 1257*s*, 1202*s*; ^1H NMR (CD_3OD) δ 8.02 (s, 1H, $H_{7'}$), 7.82 (d, 1H, J_{H6-H5} = 8.5 Hz, H_6), 7.77 (d, 2H, $J_{H20'-H19'}$ = 8.5 Hz, $H_{20'}$), 7.70 (d, 2H, $J_{H24'-H25'}$ = 7.5 Hz, $H_{24'}$), 7.61 (t, 1H, $J_{H26'-H25'}$ = 7.5 Hz, $H_{26'}$), 7.50 (t, 2H, $J_{H25'-H26'}$ = 7.5 Hz, $J_{H25'-H24'}$ = 7.5 Hz, $H_{25'}$), 7.01 (d, 2H, $J_{H19'-H20'}$ = 8.5 Hz, $H_{19'}$), 5.82 (d, 1H, $J_{H1'-H2'}$ = 4.0 Hz, $H_{1'}$), 5.69 (d, 1H, J_{H5-H6} = 8.5 Hz, H_5), 5.24 (s, 1H, $H_{1''}$), 5.12 (d, 1H, $J_{H5'-H4'}$ = 4.0 Hz, $H_{5'}$), 4.39 (t, 2H, $J_{H17'-H16'}$ = 7.5 Hz $H_{17'}$), 4.29 (dd, 1H, $J_{H4'-H3'}$ = 5.5 Hz, $J_{H4'-H5'}$ = 4.0 Hz, $H_{4'}$), 4.20 (dd, 1H, $J_{H2'-H3'}$ = 5.0 Hz, $J_{H2'-H1'}$ = 4.0 Hz, $H_{2'}$), 4.15 (dd, 1H, $J_{H3'-H4'}$ = 5.5 Hz, $J_{H3'-H2'}$ = 5.0 Hz, $H_{3'}$), 4.13–4.09 (m, 1H, $H_{4''}$), 4.08–4.02 (m, 4H, $H_{8'}$, $H_{2''}$, $H_{3''}$), 3.19 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''a-H4''}$ = 2.5 Hz, $H_{5''a}$), 2.83 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 9.0 Hz, $H_{5''b}$), 1.92–1.86 (m, 2H, $H_{16'}$), 1.82–1.76 (m, 2H, $H_{9'}$), 1.50–1.44 (m, 2H, $H_{10'}$), 1.38–1.27 (m, 10H, $H_{11'}$, $H_{12'}$, $H_{13'}$, $H_{14'}$, $H_{15'}$); ^{13}C NMR (CD_3OD) δ 197.8 ($C_{22'}$), 166.2 (C_4), 164.8 ($C_{18'}$), 152.3 (C_2), 146.8 ($C_{6'}$), 142.5 (C_6), 139.7 ($C_{23'}$), 133.8 ($C_{20'}$), 133.4 ($C_{26'}$), 131.0 ($C_{21'}$), 130.8 ($C_{24'}$), 129.5 ($C_{25'}$), 125.1 ($C_{7'}$), 115.4 ($C_{19'}$), 110.4 ($C_{1''}$), 102.7 (C_5), 91.8 ($C_{1'}$), 86.2 ($C_{4'}$), 80.6 ($C_{4''}$), 76.4 ($C_{2''}$), 75.3 ($C_{2'}$), 73.7 ($C_{5'}$), 73.5 ($C_{3''}$), 71.2 ($C_{3'}$), 69.5 ($C_{8'}$), 51.7 ($C_{17'}$), 43.5 ($C_{5''}$), 31.4, 30.6, 30.5, 30.5, 30.3, 30.1, 27.6, 27.2 ($C_{9'}$, $C_{10'}$, $C_{11'}$, $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{15'}$, $C_{16'}$); HRMS ESI^+ Calcd for $C_{39}H_{51}N_6O_{11}^+$ $(M + H)^+$ 779.3616, found 779.3597.

Compound ***20n***. Tetrol **20n** was prepared according to the general procedure for ketals hydrolysis from amine **19n** (15 mg, 0.017 mmol). Recrystallization in DCM/MeOH 95/5 afforded **20n** as a white powder (15 mg, 99% yield): mp 129–131 °C; $[\alpha]_D$ + 12 (*c* 0.5,

MeOH); IR (film) 3384*br*, 2914*w*, 2067*w*, 1678*s*, 1459*m*, 1202*s*; ^{1}H NMR (CD_3OD) δ 8.07 (s, 1H, $H_{7'}$), 7.78 (d, 2H, $J_{16'\text{-}15'}$ = 9.0 Hz, $H_{16'}$), 7.76 (d, 1H, J_{H6-H5} = 8.0 Hz, H_6), 7.76 (d, 2H, $J_{20'\text{-}21'}$ = 7.5 Hz, $H_{20'}$), 7.62 (t, 1H, $J_{H22'-H21'}$ = 7.5 Hz, $H_{22'}$), 7.51 (t, 2H, $J_{H21'-H20'}$ = $J_{H21'-H22'}$ = 7.5 Hz, $H_{21'}$), 7.49 (d, 2H, $J_{H11'-H10'}$ = 8.0 Hz, $H_{11'}$), 7.37 (d, 2H, $J_{H10'-H11'}$ = 8.0 Hz, $H_{10'}$), 7.10 (d, 2H, $J_{H15'\text{-}16'}$ = 9.0 Hz, $H_{15'}$), 5.81 (d, 1H, $J_{H1'-H2'}$ = 3.5 Hz, $H_{1'}$), 5.66 (d, 1H, J_{H5-H6} = 8.0 Hz, H_5), 5.62 (s, 2H, $H_{8'}$), 5.24 (s, 1H, $H_{1''}$), 5.20 (s, 2H, $H_{13'}$), 5.13 (d, 1H, $J_{H5'-H4'}$ = 3.5 Hz, $H_{5'}$), 4.28 (dd, 1H, $J_{H4'-H3'}$ = 6.0 Hz, $J_{H4'-H5'}$ = 3.5 Hz, $H_{4'}$), 4.19 (dd, 1H, $J_{H2'-H3'}$ = 6.0 Hz, $J_{H2'-H1'}$ = 3.5 Hz, $H_{2'}$), 4.15 (t, 1H, $J_{H3'-H2'}$ = $J_{H3'-H4'}$ = 6.0 Hz, $H_{3'}$), 4.12–4.09 (m, 1H, $H_{4''}$), 4.06 (d, 1H, $J_{H2''-H3''}$ = 5.0 Hz, $H_{2''}$), 4.05 (d, 1H, $J_{H3''-H2''}$ = 5.0 Hz, $H_{3''}$), 3.18 (dd, 1H, $J_{H5''b-H5''a}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 11.0 Hz, $H_{5''b}$), 2.81 (dd, 1H, $J_{H5''a-H5''b}$ = 13.0 Hz, $J_{H5''b-H4''}$ = 8.5 Hz, $H_{5''a}$); ^{13}C NMR (CD_3OD) δ 197.8 ($C_{18'}$), 164.2 ($C_{14'}$, C_4), 152.3 (C_2), 148.0 ($C_{6'}$), 142.5 (C_6), 139.6 ($C_{19'}$), 138.9 ($C_{12'}$), 136.6 ($C_{9'}$), 133.8 ($C_{16'}$), 133.5 ($C_{22'}$), 131.6 ($C_{17'}$), 130.8 ($C_{20'}$), 129.6 ($C_{21'}$), 129.5 ($C_{10'}$), 129.4 ($C_{11'}$), 125.4 ($C_{7'}$), 115.9 ($C_{15'}$), 110.5 ($C_{1''}$), 102.8 (C_5), 91.9 ($C_{1'}$), 86.4 ($C_{4'}$), 80.6 ($C_{4''}$), 76.4 ($C_{3''}$), 75.2 ($C_{2'}$), 73.7 ($C_{2''}$), 73.4 ($C_{5'}$), 71.2 ($C_{3'}$), 70.8 ($C_{13'}$), 54.9 ($C_{8'}$), 43.5 ($C_{5''}$); HRMS ESI$^+$ Calcd for $C_{37}H_{39}N_6O_{11}^+$ $(M + H)^+$ 743.2677, found 743.2672.

Enzymatic Assays. The activities of the compounds against MraY from *Bacillus subtilis* were tested as previously described.[6] The assay was performed in a reaction mixture of 10 μL containing, in final concentrations, 100 mM Tris-HCl, pH 7.5, 40 mM $MgCl_2$, 1.1 mM C_{55}–P, 250 mM NaCl, 0.25 mM UDP-Mur-*N*-Ac-[^{14}C]pentapeptide (337 Bq), and 8.4 mM *N*-lauroyl sarcosine. The reaction was initiated by the addition of MraY enzyme (50 ng), and the mixture was incubated for 30 min at 37 °C under shaking with a thermomixer (Eppendorf). The reaction was stopped by heating at 100 °C for 1 min. The radiolabeled substrate (UDP-Mur-*N*-Ac-pentapeptide) and reaction product (lipid I) were separated by TLC on silica gel plates using 2-propanol/ammonium hydroxide/water (6:3:1; v/v/v) as the mobile phase. The radioactive spots were located and quantified with a radioactivity scanner.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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